Transition-State Control by [5.5]-*P*-Spiro Chiral Aminophosphonium Ions: Regio- and Stereoselective Michael Reactions to Electron-Deficient Extended Conjugated Systems

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Chapter 1

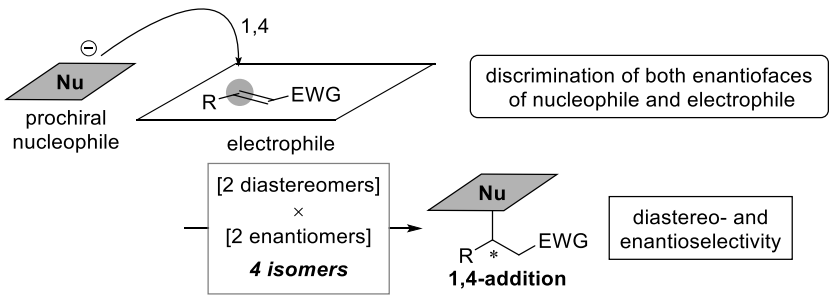
General Introduction and Summary

As compared with the much progress in the field of catalytic asymmetric Michael reactions of carbon nucleophiles to electron-deficient alkenes, study on the development of the stereoselective conjugate addition to electron-deficient extended conjugated systems, such as dienyl carbonyl compounds, has largely been scattered, despite its potential synthetic utilities. Especially the stereoselective introduction of prochiral enolates to a remote electrophilic position from a activating group on the system has been regarded as a formidable challenge, because the methodology requires the control of not only regioselectivity, but also stereoselectivity in the carbon–carbon bond-forming event.

In this context, the author is interested in the unique functionalities, such as transition-state control-capability by macrocyclic hydrogen-bonding network, of [5.5]-*P*-spiro chiral triaminoiminophosphorane as an organic base catalyst for the regio-, diastereo-, and enantioselective Michael reaction to electron-deficient extended conjugated systems from the viewpoint of transition-state control by macrocyclic hydrogen-bonding network.

1.1. Catalytic Asymmetric Michael Reaction

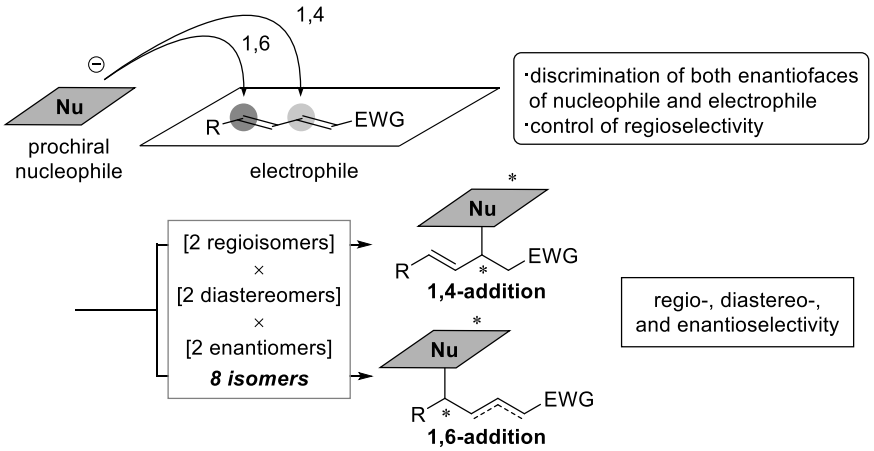
Michael reaction, the conjugate addition of carbon nucleophiles to *α,β*-unsaturated carbonyl compounds and related systems, is undoubtedly one of the most important carbon-carbon bond-forming reactions. In the case of the addition of prochiral nucleophiles to *β*-substituted electrophiles, four stereoisomers, namely two diastereomers and enantiomers, would be provided after a bond-forming step (Scheme 1), however a various type of asymmetric catalyst systems for discriminating both enantiofaces of a nucleophile and an electrophile has been developed to provide a stereoisomer in high diastereo- and enantioselectivities during these last few decades.[1]



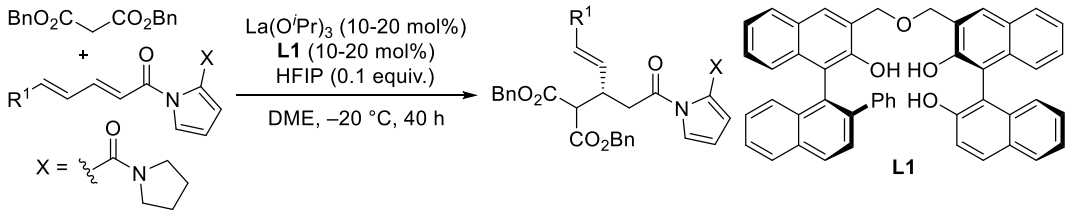
Scheme 1. Asymmetric Michael Addition to Electron-Deficient Olefins

1.2. Asymmetric Conjugate Addition to Electron-Deficient Dienes

Despite the potential synthetic utility of the optically acitive products possessing olefinic appendages, the asymmetric conjugate addition to electron-deficient, extended conjugated systems, such as dienyl carbonyl compounds, remains underdeveloped methodology.[2] This is probably because the vinylogous Michael acceptor has similarly reactive two reaction sites and therefore simultaneous control of regio- and stereoselectivities must be achieved for providing a single stereoisomer out of 8 possibly generated isomers (Scheme 2). In addition, it is well recognized that 1,4-addition is generally favored over 1,6-addition with electron-deficient dienes (Scheme 3: typical example[3a]),[3] although the principle of vinylogy, originally introduced by Fuson, states that the reactivity is, in theory, maintained by the propagation of the electronic effect of the directing functional group through a π-conjugated system.[4]



Scheme 2. Asymmetric Conjugate Addition to Electron-Deficient Dienes

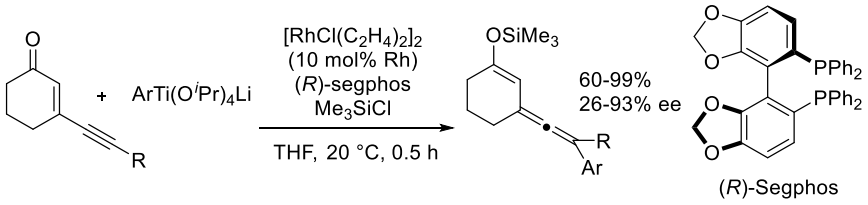


Scheme 3. Catalytic Asymmetric 1,4-Addition to Dienyl *N*-Acylpyrroles

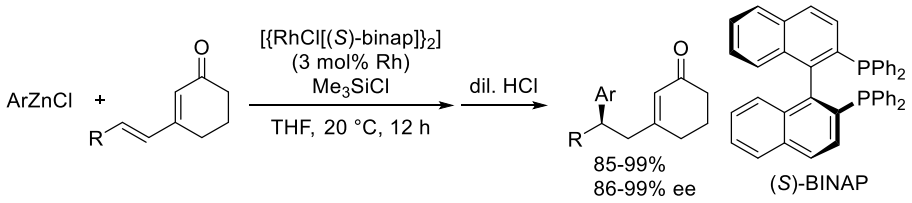
1.3. Transition-Metal Catalyzed Asymmetric 1,6-Addition of Carbon Nucleophiles

Among transition-metal catalyzed 1,6-addition giving optically unacitive compounds, Hayashi, Tokunaga and Inoue reported a chiral rhodium complex catalyzed the first asymmetric 1,6-addition of aryltitanates to cyclic enynones in the presence of chlorotrimethylsilane giving axially chiral allenylalkenyl silyl enol ethers with high enantioselectivity in 2004 (Scheme 4).[5] Next year, they also achieved a highly enantioselective 1,6-addition of aryl zinc reagents to dienones under the similar

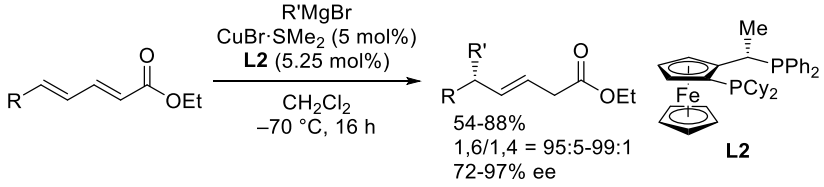
chiral rhodium catalysis (Scheme 5).[6a] Although the excellent regioselectivity had associated with specific structural features of the substrates in these methodologies, Feringa, Minnaard, and co-workers realized first cupper-catalyzed asymmetric 1,6-addition of alkyl Grignard reagents to simple linear δ-substituted 2,4-dienoates in 2008 (Scheme 6).[6d] With these reports as turning points, several transition-metal catalyses have been shown to be effective for overcoming the regioselectivity issue in the conjugate addition to extended π-conjugated systems, enabling the introduction of carbanionic nucleophiles to the δ-carbon on δ-substituted dienyl acceptors with high level of stereocontrol.[6]



Scheme 4. Rhodium-Catalyzed Asymmetric 1,6-Addition Giving Axially Chrial Allenes



Scheme 5. Rhodium-Catalyzed Asymmetric 1,6-Addition to Dienones

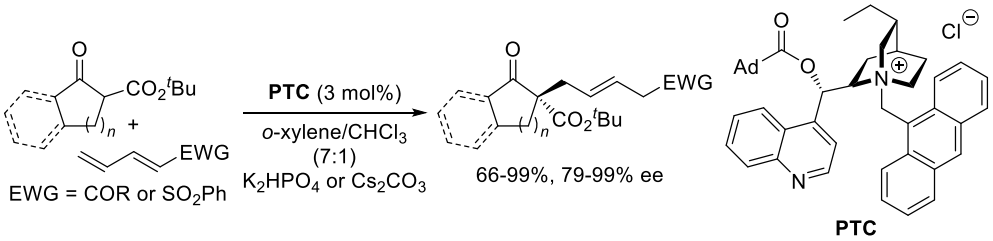


Scheme 6. Cupper-Catalyzed Asymmetric 1,6-Addition to Simple Linear Dienoates

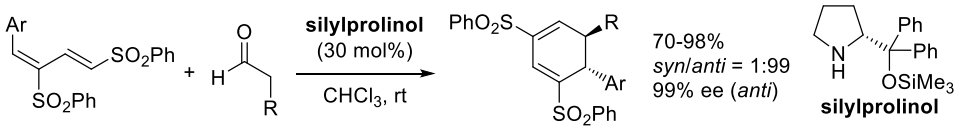
1.4. Catalytic Asymmetric 1,6-Addition of Enolates and Enolate Equivalents

While transition-metal catalyzed asymmetric 1,6-addition has came applicable to a wide range of substrates, catalytic asymmetric 1,6-addition of prochiral enolates and enolate equivalents to electron-deficient dienes has been originally limited to the examples in which regioselectivity control depend on steric or electronic factors of electrophiles.[7] In 2007, Jørgensen and co-workers firstly reported catalytic enantioselective 1,6-additions of enolates to electron-poor terminal carbon-unsubstituted dienes having ketones, esters and sulfones in the presence of cinchona alkaloid-derived phase-transfer catalyst (Scheme 7).[7a] Alexakis, Stephens and co-workers demonstrated the effectiveness of using

1,3-bis(sulfonyl)-butadiene as a *α,β,γ,δ*-diunsaturated system in a catalytic stereoselective formal [4+2] cycloaddition with aldehydes for directing the initial 1,6-addition of a chiral enamine intermediate to give optically active 1,3-bis(sulfonyl)cyclohexadienes in 2011 (scheme 8)[7b, 8]. While a few systems for overcoming the regioselectivity issue was recently reported,[9] a catalyst-controlled asymmetric 1,6-addition has still remained as a challenging process. Therefore, this fact convinced the auther that a development of a new strategy found a catalytic system for controlling those multiple selectivities simultaneously is in high demand.



Scheme 7. Enantioselective 1,6-Addition of Enolates to *δ*-Unsubstituted Electron-Deficient Dienes



Scheme 8. Asymmetric Formal [4+2] Cycloaddition with Aldehydes and 1,3-Bis(sulfonyl)-butadiene

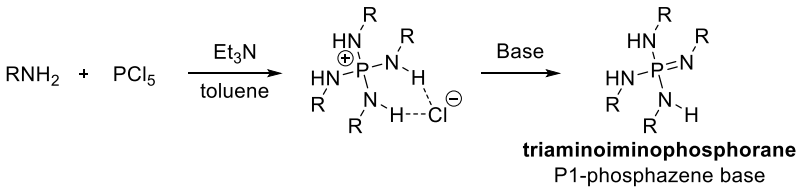
1.5. Asymmetric 1,6-Additions of Hetero Nucleophiles

As well as the asymmetric 1,6-addition of carbon nucleophiles, several methodologies for catalytic asymmetric 1,6-addition of other nucleophiles, such as silicon, phospholus, boron, sulfur, and nitrogen in the presence of the transition-metal complexes or organocatalyst has been developed.[10,11]

1.6. Catalysis of [5.5]-*P*-spiro Chiral Tetraaminophophonium Salt

1.6.1. Tetraaminophosphonium Salt

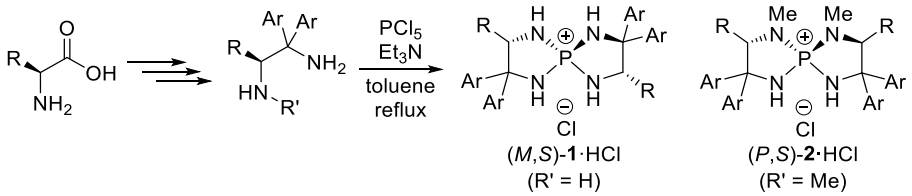
In the modern synthetic organic chemistry, the phosphonium salt has been widely used as stoichiometric reagents, such as Wittig reagents. However, the utilization of phosphinium salts as catalysts is rather limited probably because of intrinsic reactivity of them under strongly basic condition.[12] On the other hand, the tetraaminophosphonium salt has been known to be stable molecules due to the presence of PN_4 core structure, which has electronically and sterically stabilized the centred phosphorus atom.[13] Amang various aminophosphonium salts, primary amine-derived one has unique propertires. The first one is anion recognition ability via double hydrogen bonding by two N–H protons, and the second point is the formation of the triaminoiminophosphorane, P1-phosphazene base, upon treated with an appropriate base (Scheme 9).[14,15]



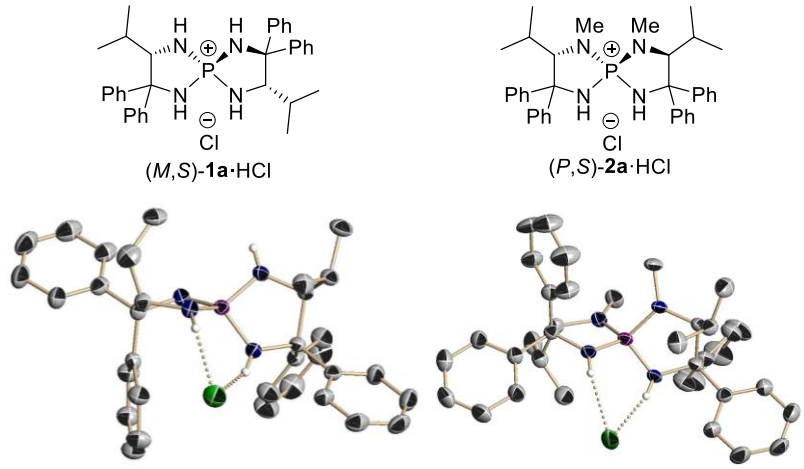
Scheme 9. Synthesis and Features of Tetraaminophosphonium Salt and Triaminoiminophosphorane

1.6.2. [5.5]-*P*-Spiro Chiral Tetraaminophosphonium Salt

In 2007, Ooi and co-workers has opened the chemistry of [5.5]-*P*-spiro chiral tetraaminophosphonium salts.[16] These molecules could be easily prepared from *α*-amino acid-derived chiral diamime and phosphorus pentachloride (Scheme 10), and the phosphonium ions have double hydrogen-bonding ability to a counter ion (Figure 1). Ooi et al. also demonstrated the unique catalytic activity of chiral triaminoiminophosphoranes, in situ generated from tetraaminophosphonium salts and potassium *tert*-butoxide, in the development of a highly *anti*- and enantioselective Henry reaction (Scheme 11).[17]

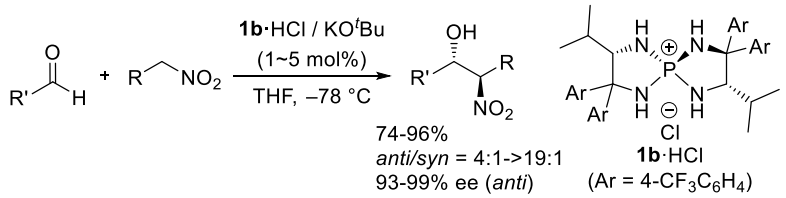


Scheme 10. Synthesis of the [5.5]-*P*-Spiro Chiral Tetraaminophosphonium Salt



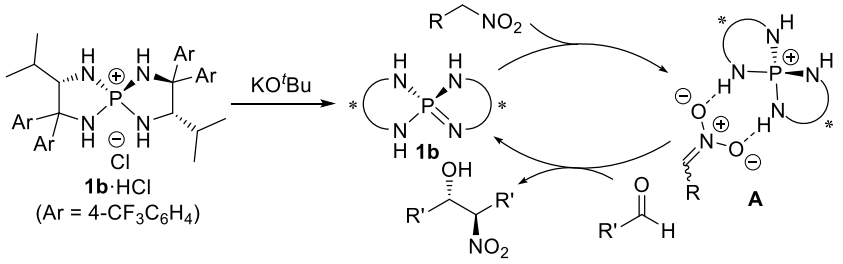
ORTEP diagram of (*M*,*S*)-**1a**·HCl ORTEP diagram of (*P*,*S*)-**2a**·HCl

Figure 1. ORTEP Diagrams of the [5.5]-*P*-Spiro Chiral Tetraaminophosphonium Salts



Scheme 11. Chiral Iminophosphorane Catalyzed *anti*-Selective Asymmetric Henry Reaction

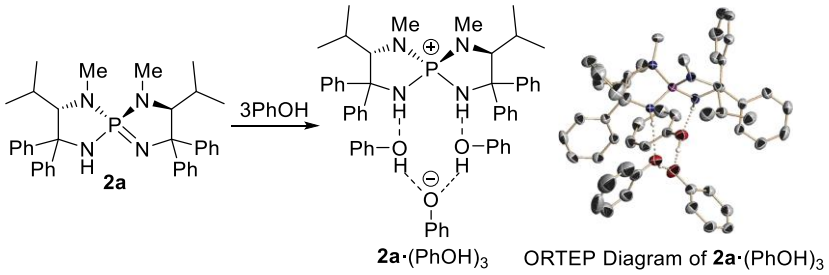
In this reaction, a nitroalkane is initially deprotonated by chiral iminophosphorane **1b**. Since resulting nitronate is a bidentate hydrogen-bonding acceptor, the chiral phosphonium ion and the nitronate could form a structural ion pair **A** via double hydrogen-bonding interaction. Subsequent stereoselective addition of the nitronate to an aldehyde under the guidance of the chiral phosphonium ion would afford the ionic product precursor, which could be protonated by either the phosphonium ion or a nitroalkane.



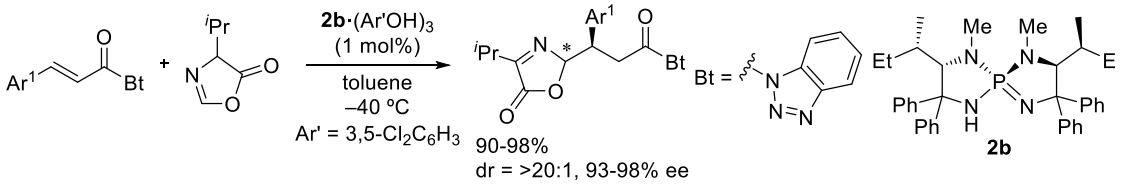
Scheme 12. Plausible Mechanism of Chiral Iminophosphorane Catalyzed Henry Reaction

1.6.3. Chiral Aminophosphonium Salts as A Supramolecular Catalyst

In 2009, Ooi and co-workers found that a tetraaminophosphonium ion, two phenols, and a phenoxide spontaneously assemble into a supramolecular architecture through a hydrogen-bonding interaction (Scheme 13).[18] The solid-state structure of the molecular assembly was unambiguously determined by X-ray crystallographic analysis, which revealed a 10-membered antidromic circular hydrogen-bonding network. Furthermore, a catalyst complex which was assembled from L-isoleucine-derived iminophosphorane and three equivalents of 3,5-dichlorophenol effectively promoted a highly stereoselective conjugate addition of 2-unsubstituted azlactone – an acyl anion equivalent – to α,β-unsaturated acylbenzotriazoles with a broad substrate scope[18a] (Scheme 14). It should be described that all structural components of the catalyst assembly, i.e., the phosphonium ion, aryloxide, and aryl hydroxide, cooperatively participate in the stereocontrolling event in this system.

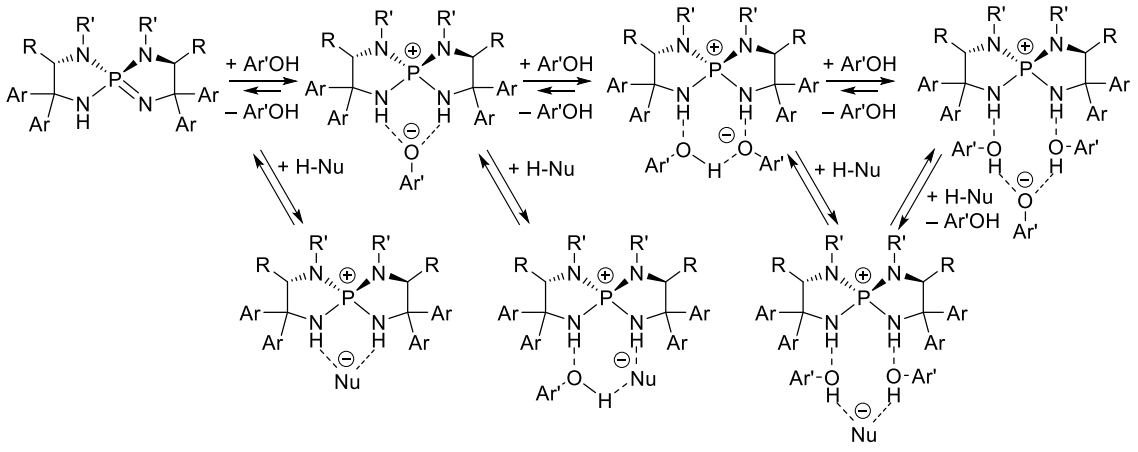


Scheme 13. Structure of a Supramolecular Chiral Aminophosphonium Salt

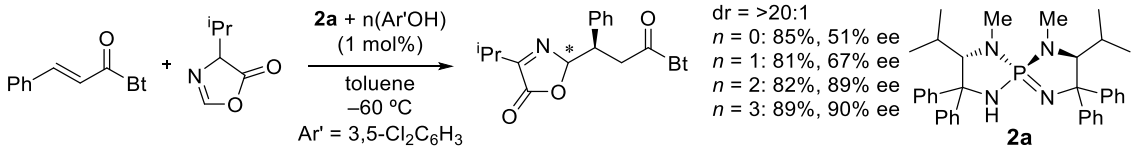


Scheme 14. Supramolecular Chiral Aminophosphonium Salt Catalyzed Asymmetric Conjugate Addition

This molecular assembly is characterized as not only **2**·(Ar'OH)$_3$, but also the related modes of assembly, **2**·(Ar'OH)$_1$ and **2**·(Ar'OH)$_2$ by simply treating **2** with Ar'OH in an appropriate stoichiometry.[18b] Each state of assembly was detected by low-temperature ^{31}P NMR spectroscopy in solution and determined by X-ray crystallographic analysis in solid state (Scheme 15), and each catalytic ability of the three assembling modes is reflected in the stereoselectivity in the following conjugate addition (Scheme 16). Participation of the plausible molecular assemblies of **2**, Ar'OH, and pronucleophile (H–Nu), such as azlactone, to the transition state was proposed on the basis of the reaction results. Furthermore, Ooi et al. discovered that solvent polarity could regulate the catalyst assembly, and demonstrated the utility of this phenomena in highly stereoselective conjugate addition of the 2-unsubstituted azlactone to nitroolefins.[18c]



Scheme 15. Plausible Molecular Assemblies of **2**, Ar'OH, and Prenucleophile (H–Nu)



Scheme 16. Relationship between the Equivalent of Ar'OH and Selectivity in the Reaction

1.6.4. Investigation of Transition State in the Catalysis of [5.5]-*P*-Spiro Chiral Tetraaminophosphonium Salt

While origin of selectivities and transition-state structute in this catalysis was unclear, Simón and Paton clalified details of this catalysis, through optimizing transition-state structures by using computational method, density functional theory (DFT) calculation.[19] They try to generate many types of structures of transition-state models, such as two catalyst molecules-containing one, they finally realized a single-catalyst molecule-containing structure as a most reliable transition-state model for explaining the origin of *anti*-selectivity in the Henry reaction. In this macrocyclic transition-state structure, one of the two N–H proton of phosphonium ion interacts to an oxygen atom of a nitronate, and the other interacts to a carbonyl oxygen of an aldehyde (Figure 2).

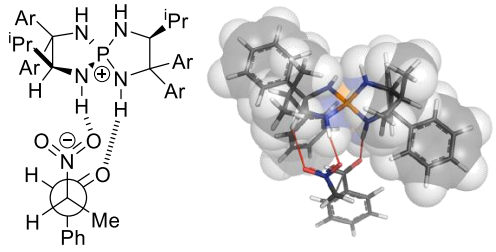


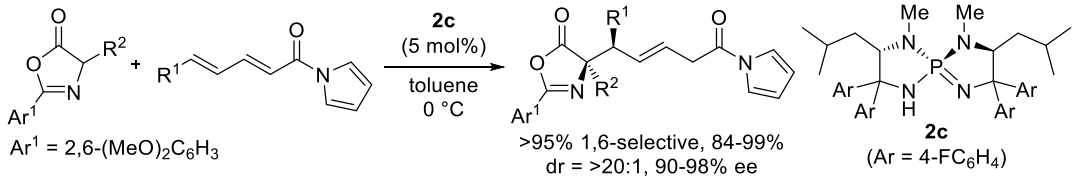
Figure 2. Transition-State Structure of Carbon-Carbon Bond Formimg Step in Chiral Imino-phosphorane Catalyzed Henry Reaction

1.7. Highly Regio-, Diastereo-, and Enantioselective 1,6- and 1,8-Additions of Azlactones to Di- and Trienyl *N*-Acylpyrroles (Chapter 2)

1.7.1. Highly Regio-, Diastereo-, and Enantioselective 1,6-Addition

The auther focused on these unique catalytic features of [5.5]-*P*-spiro chiral triaminoimino-phosphorane for accomplishing the simultaneous control of regio-, diastereo-, and enantioselectivities in a conjugate addition of prochiral enolates to *δ*-substituted dienyl carbonyl compounds. As the model substrates for a 1,6-addition, a phenylalanine-derived azlactone[20] as a precurser of an enolate and *δ*-methyl dienyl *N*-acylpyrroles[21] as vinylogous Michael acceptors were selected in consideration of their synthetic utility. While employing catalytic amount of diazabicyclo[5.4.0]undec-7-ene (DBU), a representative organic base, to the model reaction gave a complex mixture of regio- and

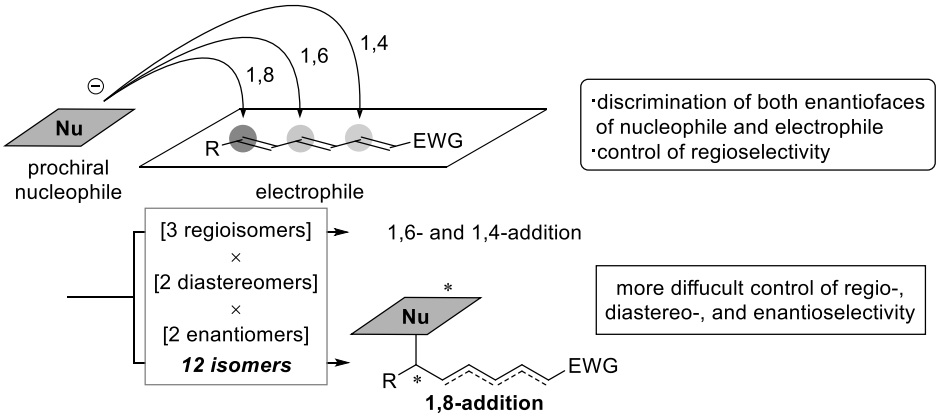
stereoisomers, namely diastereomers of 1,4- and 1,6-adducts , L-leucine-derived iminophosphorane **2c** predominantly provided the 1,6-adduct with nearly perfect diastereo- and enantioselectivities (Scheme 17). This this catalytic system enabled to accomplish broad substrate scope in a highly diastereo- and enantioselective 1,6-addition of azlactones to *δ*-alkyl dienyl *N*-acylpyrrole.



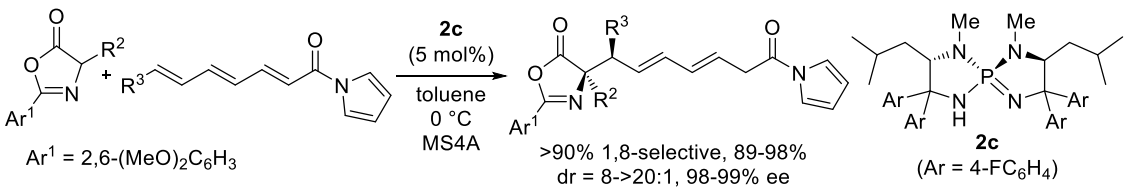
Scheme 17. Chiral Iminophosphorane Catalyzed Highly Stereoselective 1,6-Addition

1.7.2. Highly Regio-, Diastereo-, and Enantioselective 1,8-Addition

For futher demonstration of salient feature of *P*-spiro chiral iminophosphorane catalysis, the auther challenged hithert unknown bis-vinylog of Michael reaction (1,8-addition). Although obtaining a product as a single isomer in a conjugate addition to electron-deficient trienes is certainly more difficult than the 1,6-addition because 12 isomers would be possibly generated due to the existence of three similarly reactive sites on the trienes (Scheme 17), to our surprise, chiral iminophosphorane **2c** was revealed to be equally effective to this transformation, and 1,8-adducts were isolated in virtually complete diastereo- and enantioselectivities under the same conditions as those for 1,6-addition, except for the use of powdered 4A molecular sieves (MS4A) (Scheme 18). This system showed fair substantial generality in alkyl substitutents on azlactones and *ζ*-alkyl trienyl *N*-acylpyrroles.



Scheme 17. Asymmetric Michael Reaction to Electron-Deficient Trienes



Scheme 18. Chiral Iminophosphorane Catalyzed Highly Stereoselective 1,8-Addition

1.8. Origin of High Regio-, Diastereo-, and Enantioselectivities in 1,6- and 1,8-Addition of Azlactones to Dienyl *N*-Acylpyrroles: Experimental and Computational Mechanistic Studies (Chapter 3)

For understanding the origin of high regio-, diastereo-, and enentioselectivities in the 1,6- and 1,8-addtion, the auther attempted to conduct mechanistic study from both of experimental and computational approaches. As experimental studies, investigation of relationship between enantiomeric purity of the catalyst and product and a control experiment, a conjugate addition to electron-deficient tetraenes, were carried out. Observed linear relationship in 1,6-addition suggested the participation of a single chiral aminophosphonium ion to the stereodetermining C–C bond-forming step, and a mixture of 1,8-, 1,6-, and 1,4-adducts except for 1,10-adducts were obtained in the reaction with the tetraene under optimized conditions for 1,6- or 1,8-addition, which implied importance of distance from carbonyl moiety for determining the regioselectivity.

For further exploration of the reaction mechanism, quantum approach was pursued by employing DFT calculation. In a preliminary study on the reaction mechanism by using a simplified chemical model, C–C bond-formation via 14-membered cyclic transition state followed by C^{α}-protonation from one of the N–H proton of phosphonium ion, was revealed to be the most energetically favorable process. The validity of this cyclic transition-state model was demonstrated by the consistency of major isomer in experiment and DFT calculation using realistic chemical model (Figure 3).

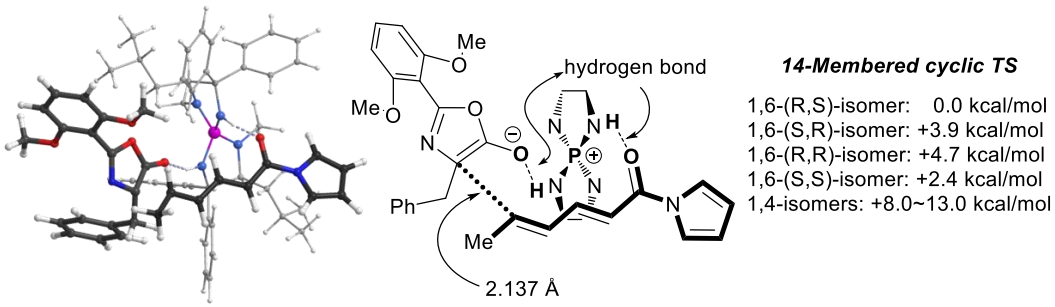
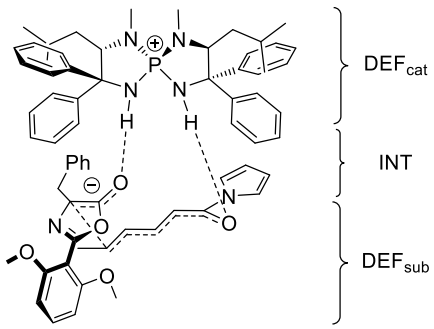


Figure 3. Cyclic Transition-State Model for the 1,6-Addition

From distortion/interaction analysis[22], the auther found that stereoselectivity was origined from difference of interaction energy between the phosphonium ion and substrates. On the other hand, regioselectivity was origined from distortion energy, and the distortion energy of substrate gave particularly larger effect to destabilize the transition-state structure of 1,4-addition. The auther interprets this result as those derived from that disruption of π-conjugation in 1,4-addition gave this unstabilizaion effect (Figure 4). Almost same tendency of energy profile was obtained in the case of the addition to the electron-deficient trienes. Distortion energies of substrate were large in the calculations of 1,4- and 1,6-additions.



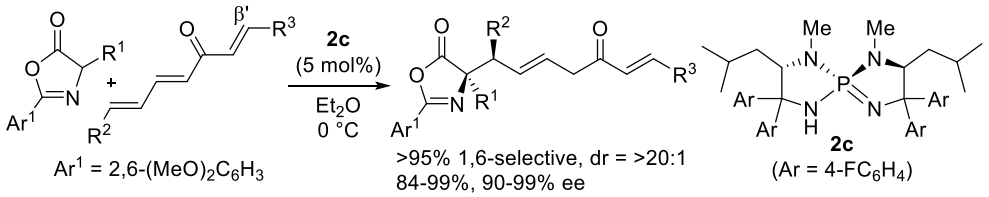
TS	ΔDEF$_{cat}$	ΔDEF$_{sub}$	ΔINT
TS1,6$_{rs}$	0.0	0.0	0.0
TS1,6$_{sr}$	0.1	0.1	3.9
TS1,6$_{ss}$	0.5	0.1	3.5
TS1,6$_{rr}$	0.0	0.0	3.8
TS1,4$_{ss}$	2.2	**4.2**	1.1

ΔDEF = DEF(**TS**) - DEF(**TS3rs**) /kcal mol^{-1}
ΔINT = INT(**TS**) - INT(**TS3rs**) /kcal mol^{-1}

Figure 4. Distortion/Interaction Analysis

1.9. Asymmetric 1,6-Addition of Azlactone to Alkenyl Dienyl Ketones

From the above computational study, the auther realized that origin of regioselectivity in the conjugate addition to dienyl *N*-acylpyrroles was derived from the energetical disadvantage of TS for 1,4-addition including disruption process of π-conjugation of dienes. Then the auther were interested in the addition to alkenyl dienyl ketones because 1,4'-addition, the addition of *β*'-position, potentially would not include disruption process of π-conjugation of substrate. In fact, 1,6-addition was successfully proceeded in high diastereo- and enantioselectivities under the catalysis of L-leucine derived chiral iminophosphorane **2c** (Scheme 19). This result implies the presence of additional factors for promoting 1,6-addition as well as the disruption of π-conjugation in this system.



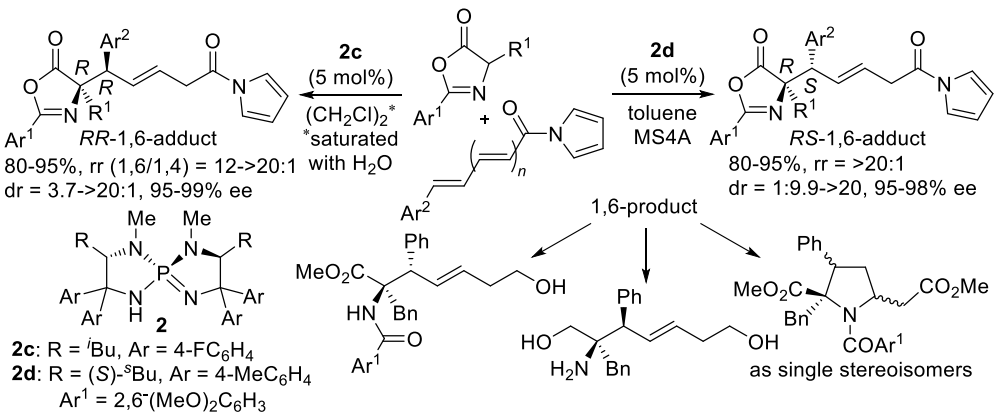
Scheme 19. Asymmetric 1,6-Addition of Azlactone to Alkenyl Dienyl Ketone

1.10. Complete Diastereodivegence in Asymmetric 1,6-Addition Reactions to *δ*-Aryl Dienyl *N*-Acylpyrroles Enabled by Minimal Modification of a Chiral Catalyst (Chapter 4)

1.10.1. Diastereodivergent Asymmetric 1,6-Addition to *δ*-Aryl Dienyl *N*-Acylpyrroles

As already described in 1.7-9, the auther achieved asymmetric 1,6-addition to *δ*-alkyl dienes, but this catalytic system was not applicable to *δ*-aryl electron deficient dienes probably due to the extention of *π*-conjugation in the substrate. Indeed, even under the optimal conditions in the previous reaction, the product of the conjugate addition to *δ*-aryl dienyl *N*-acylpyrrole was obtained in low diastereoselectivity with low reproducibility problem. After pursuing many control experiments, the auther found that the selectivities were very sensitive to contamination of water, and good

stereoselectivities and reproducibility can be secured by conducting reaction in a wet solvent at low temperature. After optimization of catalyst structure and reaction conditions for the 1,6-addition of azlactones to *δ*-aryl dienyl *N*-acylpyrroles, the auther found that leucine-derived iminophosphorane **2c** was the best catalyst for providing *RR*-1,6-adduct and isoleucine-derived one **2d** gave opposite diastereomer, *RS*-1,6-adduct, as a major isomer with high enantioselectivity. By using these two systems, the auther succeeded to realize complete diastereodivergence in the asymmetric 1,6-addition (Scheme 20). Both catalytic systems represented broad substrate generality with respect to azlactones and δ-aryl *N*-acylpyrroles and both diastereomers were obtained in almost stereochemically pure form. The synthetic utility of this methodologies was clearly demonstrated through the derivatization to non-natural amino-acid derivatives, such as dencely substituted proline-derivatives, and a chiral amino diol. The origin of diastereodivergence in the 1,6-addition is elucidated by the experimental and computatianl analysis of the catalyst behavior and transition-state structures.

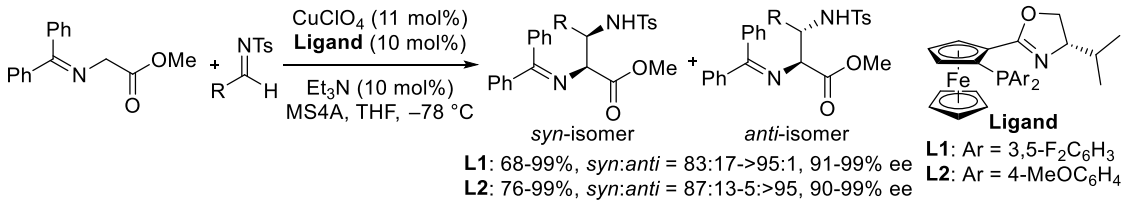


Scheme 20. Diastereodivergent Asymmetric 1,6-Addition to *δ*-Aryl Dienyl *N*-Acylpyrroles

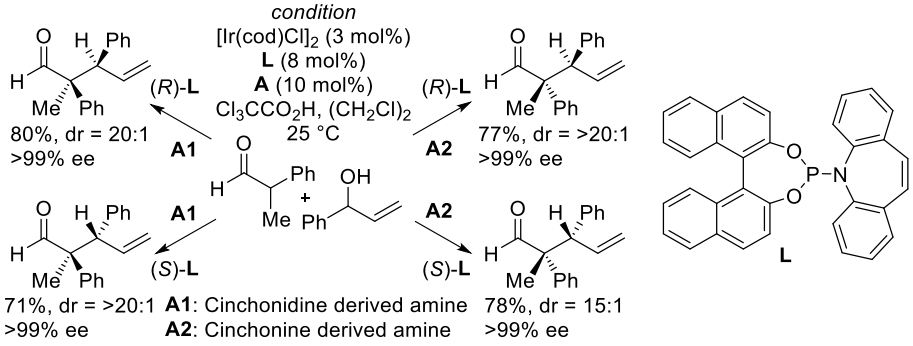
1.10.2. Diastereodivergenct Asymmetric Catalysis

Despite numerous advances in the field of asymmetric synthesis, arbitrary access to all the possible product diastereomers is incredibly difficult because diastereochemical preference is largely governed by the inherent structural and stereoelectronic nature of substrates. As a powerful strategy for addressing this intrinsic problem, catalyst-directed diastereodivergence would be much sought after. Impressive progress has been made in the development of diastereodivergent asymmetric catalysis for carbon-carbon and carbon-heteroatom bond-forming reactions.[23] However, except for one example (Scheme 21),[23c] the processes currently available rely on using two catalytic systems having different structures or proceeding in variant reaction mechanisms, or the appropriate combination of two different catalysts, such as the report by Carreira and coworkers, which is recognized as the most reliable system (Scheme 22),[23j] to access complementary diastereomers selectively. This situation demonstrates the formidable challenge and scientific value of the diastereodivergent asymmetric 1,6-

additions in achieving rigorous diastereodivergence by overriding substrate bias through minimal modification of a single catalyst scaffold.



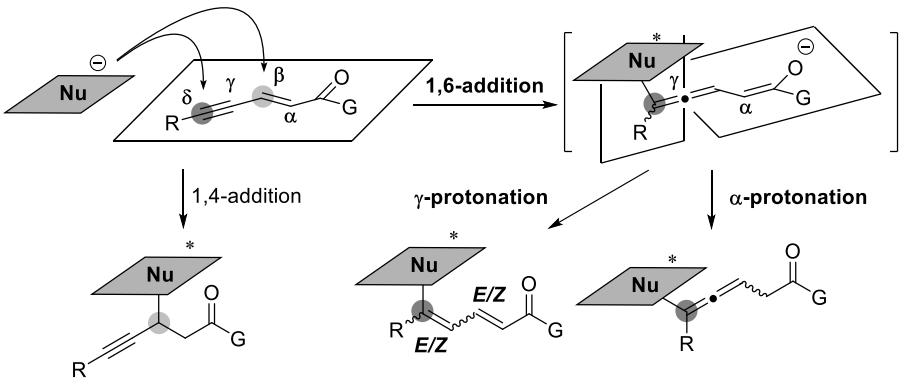
Scheme 21. Diastereodivergent Asymmetric Dual Catalysis



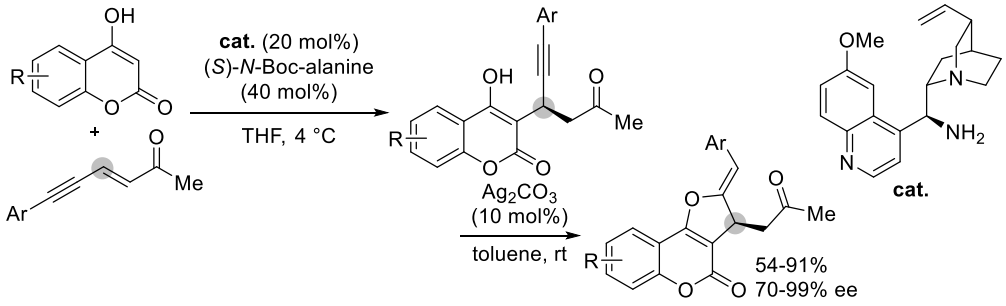
Scheme 22. Enantio- and Diastereodivergent Dual Catalysis

1.11. Asymmetric 1,6-Addition of Azlactones to Ynenyl *N*-Acylpyrazoles

Based on the establishment of catalytic asymmetric 1,6-addition to electron-deficient dienes, the auther was interested in asymmetric 1,6-addition to ynenyl carbonyl compounds (Scheme 23). In the transition-metal, such as copper, mediated 1,6-addition, it is recognized that the use of this class of acceptor could facilitate the bond formation at δ-position. Indeed, an asymmetric version of the transision-metal catalyzed 1,6-additon to electron deficient enynes was reported by Hayashi and co-workers in 2004 (Scheme 4). However, the conjugate addition of enolates or enolate equivalents to electron deficient enynes has been known to be generally proceeded at β-position as reported by Enders and co-workers (Scheme 24).[24] It should be noted that not only control of regiochemistry and facial discrimination of a prochiral enolate in C–C bond-forming step but also regio- and facial control (γ-protonation) in protonation step of intermediary allenic enolate are required for affording a single isomer in the 1,6-addition to ynenyl carbonyl compounds. The above facts realized the development of a new strategy is crucial for controlling regio- and stereoselectivity in both step of the C–C bond formation and the protonation in this reaction.

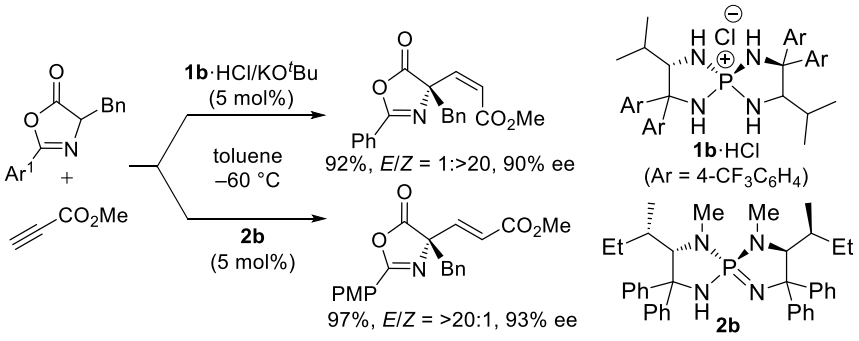


Scheme 23 Asymmetric Conjugate Addition to Electron-Deficient Enynes

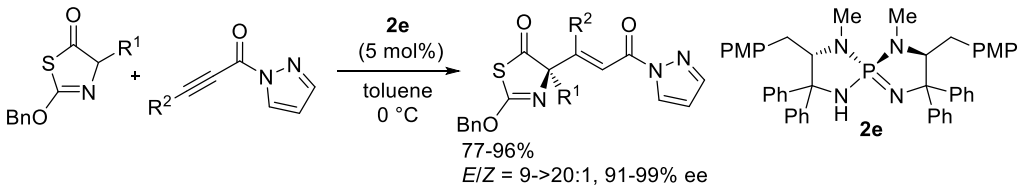


Scheme 24. Asymmetric Conjugate Addition of Enolates to Electron-Deficient Enynes

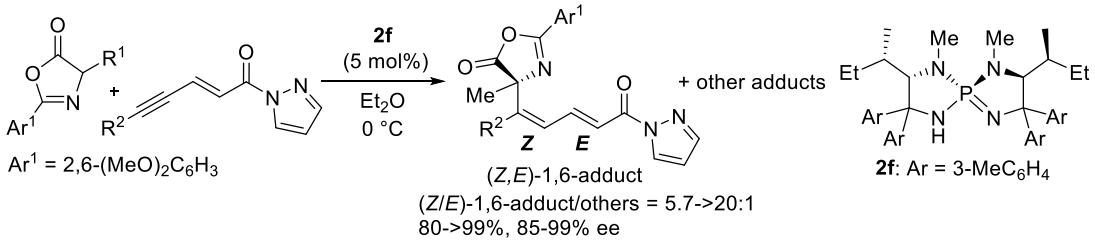
Ooi and co-workers reported highly enantio-, and *E*- or *Z*-selsective conjugate addition of enolates to electron-deficient triple bonds (Scheme 25, 26).[16d,i] These reports indicate that chiral iminophosphorane catalysis is effective for stereocontrol in not only C–C bond-forming step but also protonation step of allenic enolate intermediates. After the considerable optimization of the catalyst structure and reaction conditions for the conjugate addition of azlactones to ynenyl *N*-acylpyrazoles[25-27], (*Z*/*E*)-1,6-adduct was obtained as almost single isomer by using chiral iminophosphorane catalyst **2f** (Scheme 27). Synthesic utility of this system was demonstrated through derivatization of the product to non-natural aminosugar derivatives.



Scheme 25. Asymmetric Conjugate Addition to Methyl Propiolate



Scheme 26. Asymmetric Conjugate Addition to Electron-Deficient Internal Alkynes



Scheme 27. Asymmetric Conjugate Addition of Enolates to Electron-Deficient Enynes

1.12. Summary

In these studies, the author achieved unprecedented highly regio-, diastereo- and enantioselective 1,6- and 1,8-addition of azlactones to various type of electron-deficient extended conjugated systems under the catalysis of chiral [5.5]-*P*-spiro triaminoiminophosphorane. Furthermore, complete diastereodivergence in asymmetric 1,6-addition to *δ*-aryl dienyl carbonyl compounds was accomplished by minimal modification of the chiral iminophosphorane. The origin of regio- and stereoselectivity in these results were also elucidated by analysis of transition-state structures by DFT calculation. The auther anticipates that the reported salient features of the iminophosphorane catalysis in multiple selectivity control will find fruitful applications.

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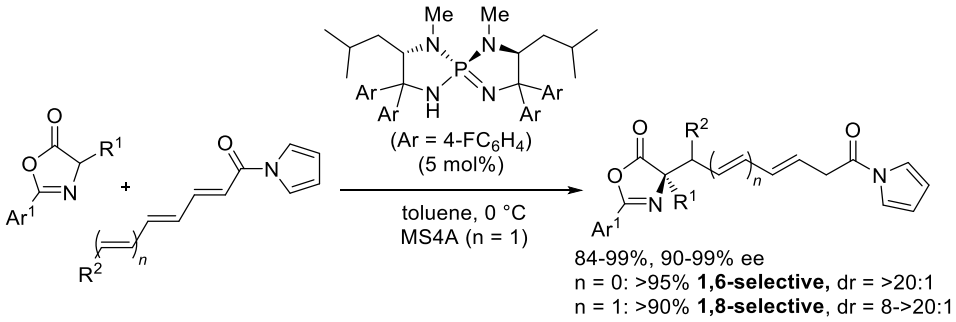
Chapter 2

Highly Regio-, Diastereo-, and Enantioselective 1,6- and 1,8-Additions of Azlactones to Di- and Trienyl *N*-Acylpyrroles



Abstract:

A vinylog of Michael reaction (1,6-addition) of azlactones to *δ*-substituted dienyl *N*-acylpyrroles has been developed with virtually complete 1,6-, diastereo, and enantioselectivities by means of chiral *P*-spiro triaminoiminophosphorane as a catalyst. This system has been successfully extended to an unprecedented bis-vinylog of Michael reaction (1,8-addition) of azlactones to *ζ*-substituted trienyl N-acylpyrroles with high levels of regio-, and stereocontrol.

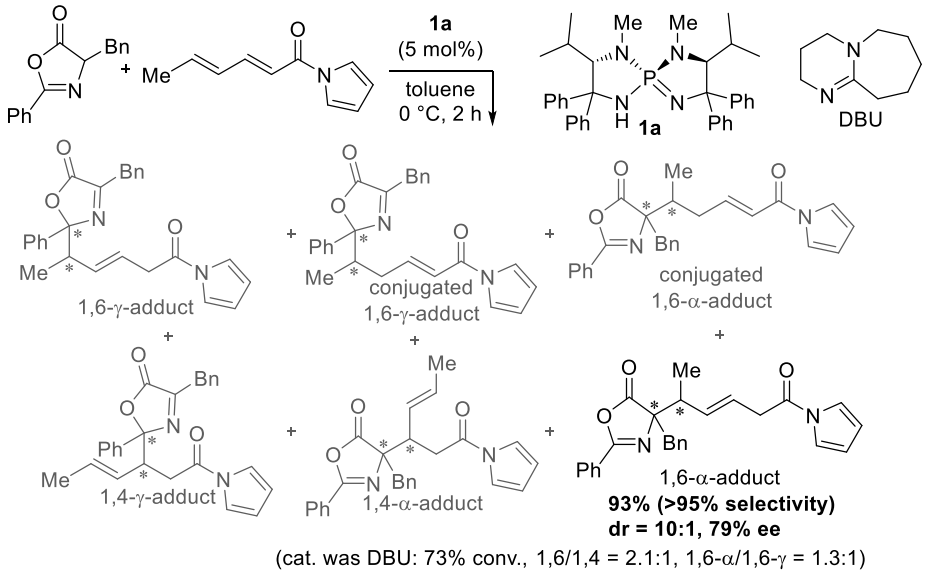
2.1. Introduction

In contrast to the considerable progress in the field of catalytic asymmetric Michael reaction (1,4-addition) of carbon nucleophiles to electron-deficient alkenes, research on the development of the vinylog of Michael reaction (1,6-addition) to extended conjugated systems, such as dienyl carbonyl compounds and related systems, has largely been sporadic, despite the potential synthetic utility of the reaction.[1] While the principle of vinylogy states that the reactivity is, in theory, maintained by the propagation of the electronic effect of the directing functional group through a conjugated π-system,[2] it is well recognized that 1,4-addition is usually preferred over 1,6-addition even with electron-deficient dienes.[3] Several transition-metal catalysts have been shown to be effective for overcoming this regioselectivity issue, enabling the introduction of carbanionic nucleophiles to the δ-carbon of δ-substituted dienyl acceptors with high levels of enantiocontrol.[4] On the other hand,, there are only a few examples of the catalytic asymmetric 1,6-addition of enolates or enamines, in which δ-unsubstituted or β-disubstituted dienyl carbonyl and sulfonyl compounds were employed to appreciate the spatial accessibility of the terminal double bond for governing the regioselectivity,[5] except for the recent excellent reports.[6] This methodological deficiency poses a formidable challenge associated with control of not only the regiochemistry but also the stereochemistry in the addition of prochiral enolates to δ-substituted, electron-deficient dienes, where simultaneous discrimination of both enantiofaces of the enolate and the vinylogous Michael acceptor should be realized. In conjunction with continuous efforts by Ooi and co-workers to explore the potential of *P*-spiro chiral triaminoiminophosphorane[7] of type **1** (see Table 1) as a strong organic base catalyst,[8,9] the auther disclose herein the solution to this problem: the development of a highly diastereo- and enantioselective 1,6-addition of azlactones[10] to simple δ-monosubstituted dienyl *N*-acylpyrroles **2**[3a,d,h] by the utilization of chiral iminophosphorane **1f** as a requisite catalyst for total yet rigorous selectivity control. Furthermore, this system can be successfully extended to the hitherto unknown bis-vinylog of Michael addition (1,8-addition) to ζ-substituted trienyl acceptors with high levels of regio- and stereocontrol.

2.2. Result and Discussion

As a vinylogous Michael acceptor, the auther employed dienyl *N*-acylpyrrole **2** in consideration of its synthetic utility, i.e., the *N*-acylpyrrole moiety can be easily converted into various carbonyl functionalities with different oxidation states.[11] The initial attempt was made by treating *N*-(2*E*,4*E*)-hexadienoylpyrrole **2a** with azlactone **3a** in the presence of 5 mol% of L-valine-derived iminophosphorane **1a** in toluene at 0 °C. Although catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), a general organic base catalyst, gave complex mixture of regio- and stereoisomer and isomeric, α,β-unsaturated analog of 1,6-adducts in moderate conversion, the reaction in the presence of the iminophosphorane **1a** proceeded to completion in 2 h, and

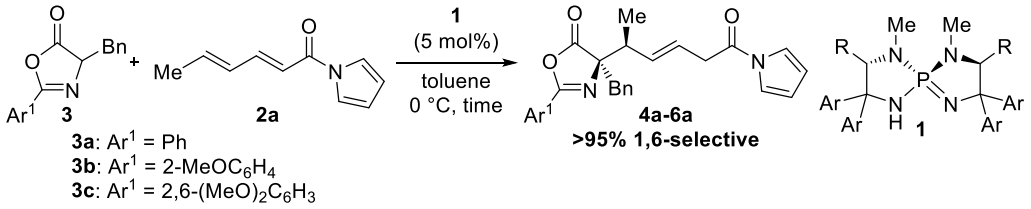
interestingly, ^{1}H NMR (400 MHz) analysis of the crude aliquot revealed the exclusive formation of the 1,6-*α*-adduct, *β,γ*-unsaturated *N*-acylpyrrole **4a**, with a diastereomeric ratio of 10:1 (Scheme 1 and Table 1, entry 1). Since no evidence for the concomitant production of the isomeric, *α,β*-unsaturated analog of **4a** was detected, the intermediary generated vinylogous enolate was thought to be protonated predominantly at the *α*-position of the carbonyl group. After purification by standard silica gel column chromatography, the diastereomeric mixture of **4a** was isolated in 93% yield with promising enantioselectivity for the major diastereomer (79% ee).



Scheme 1. First Attempt

Encouraged by this prime finding of the extraordinarily regioselective 1,6-addition, the auther next investigated the effect of the catalyst structure on the stereochemical outcome. In accordance with the anticipation from the previous studies on this catalysis, appropriate choice of the alkyl group (R) originating from the parent *α*-amino acid and the geminal aromatic substitutents (Ar) on the diazaphosphacycles of **1** turned out to be crucial for improving the stereoselectivity. This scrutiny led to the identification of L-leucine-derived iminophosphorane **1f** bearing 4-fluorophenyl substituents as an optimal catalyst, and **4a** was isolated with good diastereoselectivity (dr = 12:1) and high enantiomeric excess of 94% (entries 1–6), It should be noted that the diastereo- and enantioselectivities were further enhanced by the modification of the aromatic substituent at the 2-position of azlactone **3**. Introduction of a 2,6-dimethoxyphenyl group (**3c**) allowed for the addition of **2a** to proceed with virtually complete selectivity control in the presence of **1f** to afford almost stereochemically pure **6a** in 97% yield (entries 7 and 8).

Table 1. Effect of the Structure of Catalyst **1** and Ar^1 of Azlactone **3** on the Stereoselectivity[a]



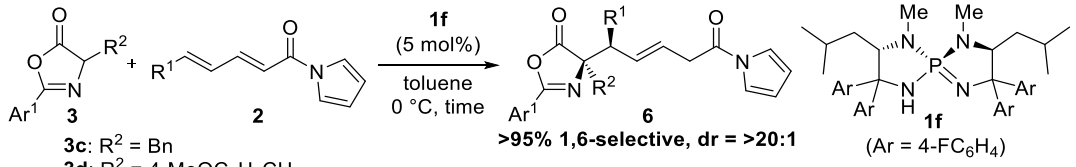
3a: Ar^1 = Ph
3b: Ar^1 = 2-$MeOC_6H_4$
3c: Ar^1 = 2,6-$(MeO)_2C_6H_3$

entry	catalyst R, Ar (**1**)	**3**	time (h)	yield[b] (%)	dr[c,d]	ee[d,e] (%)	prod
1	^{i}Pr, Ph (**1a**)	**3a**	2	93	10:1	79	**4a**
2	Me, Ph (**1b**)	**3a**	2	96	12:1	84	**4a**
3	Bn, Ph (**1c**)	**3a**	2	91	2:1	38	**4a**
4	^{i}Bu, Ph (**1d**)	**3a**	2	95	13:1	92	**4a**
5	^{i}Bu, 4-MeC_6H_4 (**1e**)	**3a**	1	93	11:1	86	**4a**
6	^{i}Bu, 4-FC_6H_4 (**1f**)	**3a**	1	99	12:1	94	**4a**
7	**1f**	**3b**	2	96	14:1	91	**5a**
8	**1f**	**3c**	2	97	>20:1	98	**6a**

[a]Reaction were performed with 0.11 mmol of **2a** and 0.1 mmol of **3** in toluene (1.0 mL) in the presence of **1** (5 mol%) at 0 °C for 1-2 h. [b]Isolated yield. [c]Diastereomeric ratios of 1,6-adducts were indicated, which were determined by ^{1}H NMR (400MHz) analysis of crude aliquot. [d]Absolute configuration of **4a**-**6a** were assigned by analogy to that of **6d**. [e]Enantiomeric excesses of the major diastereomer were indicated, which were analyzed by chiral stationary phase HPLC.

Having established the optimized conditions, the auther studied the scope of this new catalytic, highly stereoselective 1,6-addition protocol. The representative results are listed in Table 2. Generally, the reaction reached completion within 3 h using 5 mol% of **1f** to give **6** in nearly quantitative yield, and neither the isomeric *α,β*-unsaturated 1,6-adducts nor the 1,4-adducts were formed to a detectable extent. With respect to the vinylogous Michael acceptor, the present system tolerated the incorporation of various linear and branched terminal substituents (R^1, **2b**–**e**), and excellent stereoselectivities were uniformly observed (entries 2–5). Dienyl *N*-acylpyrroles **2f**–**h** bearing a functional group, such as olefin, ether, and ester, also appeared to be good candidates for the reaction (entries 6–8). In addition to the benzyl-substituted **3c**, other azlactones with different alkyl appendages at the 4-position (R^2, **3d**–**f**) could be employed as donor substrates, and high levels of stereochemical control were achieved regardless of their structural features (entries 9–11).

Table 2. Substrare Scope of the 1,6-Addition[a]

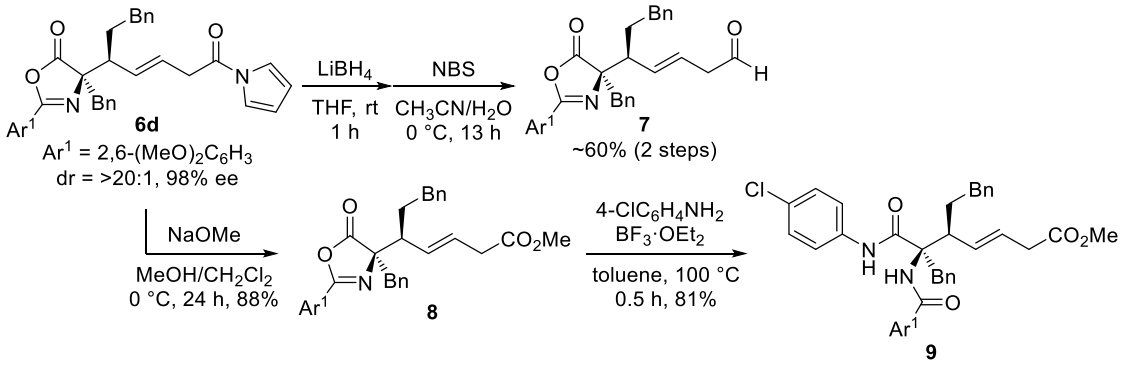


3c: R^2 = Bn
3d: R^2 = 4-$MeOC_6H_4CH_2$
3e: R^2 = ^{i}Bu
3f: R^2 = $MeS(CH_2)_2$

entry	R^1	**3**	time (h)	yield[b] (%)	ee[c,d] (%)	prod. (**6**)
1	Me (**2a**)	**3c**	2	97	98	**6a**
2	$Me(CH_2)_2$ (**2b**)	**3c**	2	94	98	**6b**
3	$Me(CH_2)_6$ (**2c**)	**3c**	2	84	98	**6c**
4	$Ph(CH_2)_2$ (**2d**)	**3c**	3	99	98	**6d**
5	^{i}Bu (**2e**)	**3c**	2	95	98	**6e**
6	CH_2=$CH(CH_2)_3$ (**2f**)	**3c**	2	98	98	**6f**
7	$BnOCH_2$ (**2g**)	**3c**	2	93	97	**6g**
8	$BzOCH_2$ (**2h**)	**3c**	2	96	94	**6h**
9	Me (**2a**)	**3d**	2	98	98	**6i**
10	Me (**2a**)	**3e**	3	97	94	**6j**
11	Me (**2a**)	**3f**	1	95	90	**6k**

[a]Reaction were performed with 0.11 mmol of **2** and 0.1 mmol of **3** in toluene (1.0 mL) in the presence of **1f** (5 mol%) at 0 °C. Diastereomeric ratios of **6** were >20:1 as indicated, which were determined by ^{1}H NMR (400 MHz) analysis of crude aliquot. [b]Isolated yield. [c]Absolute configuration of **6d** was determined by X-ray crystallographic analysis of its derivative **9**, see Scheme 2 and experimental section for details. Absolute configurations of **6b**,**c**, and **6e-k** were assigned by analogy to that of **6d**. [d]Enantiomeric excesses of the major diastereomer of **6** were indicated, which were analyzed by chiral stationary phase HPLC.

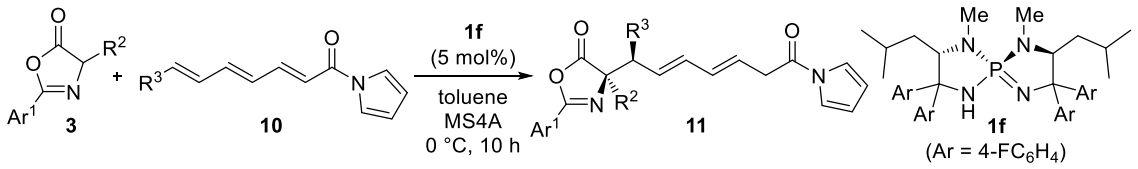
The *N*-acylpyrrole and azlactone moieties of the 1,6-adducts **6** could be separately derivatized into various carbonyl functionalities (Scheme 2).[10,11] For example, selective reduction of the *N*-acylpyrrole moiety by lithium borohydride and subsequent treatment with *N*-bromosuccinimide in aqueous acetonitrile afforded aldehyde **7**. In addition, the *N*-acylpyrrole moiety could be readily converted into the corresponding esters by treatment with sodium methoxide, as shown by the illustrative transformation from **6d** to **8**. Subsequent ring opening of the azlactone component[12] with 4-chloroaniline provided secondary amide **9**, and the absolute configuration of **6d** was determined by single-crystal X-ray diffraction analysis of **9**.



Scheme 2. Derivatization of 1,6-Adduct **6d** (Ar^1 = 2,6-$(MeO)_2C_6H_3$)

The significant potential of this approach based on the catalysis of *P*-spiro chiral triaminoiminophosphorane **1f** was amply demonstrated by applying it to the development of the bis-vinylog of Michael reaction (1,8-addition) of **3** to trienyl *N*-acylpyrroles **10** (Table 3).[13] Reaction of **3c** with (2*E*,4*E*,6*E*)-octatrienoylpyrrole **10a** under the same conditions as those for 1,6-addition, except for the use of powdered 4A molecular sieves (MS4A) for ensuring reproducibility on the regioselectivity, resulted in carbon–carbon bond formation at the *ζ*-position of **10a** to afford the 1,8-adduct, *β,γ,δ,ε*-unsaturated *N*-acylpyrrole **11a**, almost exclusively in 89% yield (1,8-/1,6-/1,4-adducts = >20:<1:1) (entry 1). Further, ^{1}H NMR (400 MHz) analysis indicated that **11a** was obtained virtually as a single diastereomer (dr = >20:1), and the enantiomeric excess was determined to be 99% by chiral HPLC measurement. A brief survey of the possible variation in the structures of the pronucleophile **3** and the bis-vinylogous Michael acceptor **10** showed the promising generality of this unprecedented, regioselective 1,8-addition of enolates to electron-deficient trienes efficiently catalyzed by **1f** with remarkably high relative and absolute stereocontrol (entries 2–5, Table 3).

Table 3. Catalytic, Regio- and Stereoselective 1,8-Addition to ζ-Alkyl Trienyl *N*-Acylpyrroles **10**[a]



entry	R^3 (**10**)	**3**	yield[b] (%)	rr[c] (1,8:1,6:1,4)	dr[d,e]	ee[e,f] (%)	prod. (**11**)
1	Me (**10a**)	**3c**	89	>20:<1:1	>20:1	99	**11a**
2	$Me(CH_2)_6$ (**10b**)	**3c**	94	>20:<1:1	18:1	99	**11b**
3	$BnOCH_2$ (**10c**)	**3c**	98	14:1:<1	>20:1	98	**11c**
4	**10a**	**3d**	90	>20:<1:1	>20:1	99	**11d**
5	**10a**	**3e**	90	>20:<1:1	8:1	99	**11e**

[a]Reaction were performed with **1f** (5 mol%), 0.11 mmol of **10**, and 0.1 mmol of **3** in toluene (1.0 mL) containing 100 mg of MS4A at 0 °C for 10 h. [b]Isolated yield. [c]Regioisomeric ratios (rr) were determined by ^{1}H NMR (400 MHz for entries 1, 3, and 4, 700 MHz for entries 2 and 5) analysis of crude aliquot. [d]Diastereomeric ratios of 1,8-adduct **11** were indicated, which were determined by ^{1}H NMR (400 MHz for entries 1, 3, and 4, 700 MHz for entries 2 and 5) analysis of crude aliquot. [e]Absolute configuration of **11a-e** were assigned by analogy to that of **6d**. [f]Enantiomeric excesses of the major diastereomer of **11** were indicated, which were analyzed by chiral stationary phase HPLC.

2.3. Conclusion

In conclusion, the auther have developed the 1,6-addition of azlactones to *δ*-monosubstituted dienyl *N*-acylpyrroles, with essentially complete control of regio-, diastereo-, and enantioselectivities by virtue of chiral *P*-spiro triaminoiminophosphorane as a strong organic base catalyst. This methodology has further been evolved into the highly regio-, and stereoselevtive 1,8-addition to ζ-substituted trienyl acceptors. The auther believe that the present study would provide a new perspective of coping with the selectivity issues associated with the conjugate addition of prochiral enolates to prochiral electron-deficient polyenes and of exploiting rich chemistry involved in this type of selective carbon–carbon bond-forming reactions.

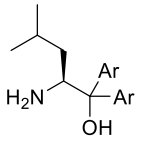
2.4. Experimental Section

General Information: Infrared spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) or Varian INOVA-700 (700 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance (CD_3OD; 3.31 ppm) or tetramethylsilane (0.0 ppm) resonance as the internal standard [$(CD_3)_2CO$, $CDCl_3$]. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, br = broad) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard [$(CD_3)_2CO$; 29.84 ppm, CD_3OD; 49.0 ppm, $CDCl_3$; 77.16 ppm]. ^{19}F NMR spectra were recorded on a JEOL JNM-ECS400 (376 MHz) spectrometer. Chemical shifts are reported in ppm from benzotrifluoride (–64.0 ppm) resonance as the external standard. ^{31}P NMR spectra were recorded on a JEOL JNM-ECS400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 (0.0 ppm) resonance as the external standard. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) and Chromatorex® TLC plates NH (0.2 mm; Fuji Silysia Chemical ltd.). Flash column chromatography was performed on PSQ60AB (spherical, av. 55 μm; Fuji Silysia Chemical ltd.), Silica gel 60 (Merck 1.09385.9929, 230-400 mesh), and Chromatorex® NH DM2035 (spherical, 45-75 μm; Fuji Silysia Chemical ltd.). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK AD-3 (AD3), CHIRALCEL OD-3 (OD3), CHIRALCEL OZ-3 (OZ3), CHIRALPAK IC-3 (IC3), CHIRALPAK IA (IA), CHIRALPAK IC (IC)] with hexane (H), 2-propanol (IPA), and ethanol (EtOH) as eluent.

Toluene, dichloromethane (CH_2Cl_2), and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Dienylacylpyrroles **2**[14], azlactones **3**[15], trienylacylpyrroles **10**[14] were prepared by following the literature procedure. Powdered 4A molecular sieves (MS4A) was supplied from Merck. Trifluoroacetic acid (TFA) and trifluoromethanesulfonic acid (TfOH) were kindly supplied from Asahi Glass Co., Ltd. and Central Glass Co., Ltd., respectively. Other simple chemicals were purchased and used as such.

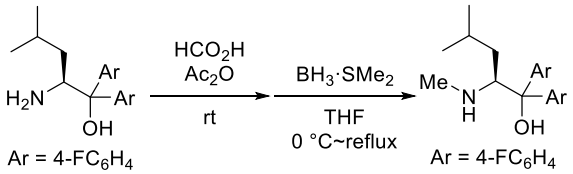
Synthesis and Characterization of Iminophosphorane 1:

Characterization of Amino Alcohol S1:

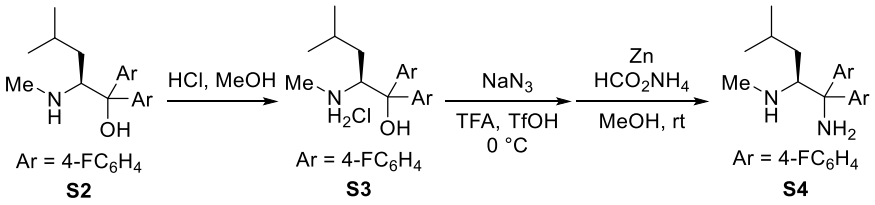


Ar = 4-FC_6H_4

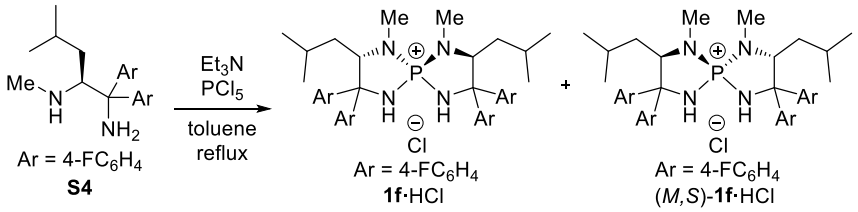
S1: The title compound was prepared from *N*-Boc L-leucine methyl ester by following the literature procedure.[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (2H, dd, $J_{H\text{-}H}$ = 8.9, $J_{F\text{-}H}$ = 5.3 Hz), 7.40 (2H, dd, $J_{H\text{-}H}$ = 8.9, $J_{F\text{-}H}$ = 5.5 Hz), 7.00 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.9 Hz), 6.96 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.9 Hz), 3.89 (1H, dd, J = 10.3, 2.0 Hz), 1.56 (1H, d-sept-d, J = 10.4, 6.6, 4.0 Hz), 1.23 (1H, ddd, J = 14.2, 10.3, 4.0 Hz), 1.01 (1H, ddd, J = 14.2, 10.4, 2.0 Hz), 0.87$_4$ (3H, d, J = 6.6 Hz), 0.86$_5$ (3H, d, J = 6.6 Hz), N-H and O-H protons were not found due to broading; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (d, $J_{F\text{-}C}$ = 249.6 Hz), 161.5 (d, $J_{F\text{-}C}$ = 248.7 Hz), 142.9 (d, $J_{F\text{-}C}$ = 2.9 Hz), 140.3 (d, $J_{F\text{-}C}$ = 2.9 Hz), 127.7 (d, $J_{F\text{-}C}$ = 8.8 Hz), 127.3 (d, $J_{F\text{-}C}$ = 7.7 Hz), 115.4 (d, $J_{F\text{-}C}$ = 21.3 Hz), 115.0 (d, $J_{F\text{-}C}$ = 21.3 Hz), 78.6, 54.6, 39.5, 25.4, 24.1, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –116.2, –116.5; IR (liq. film): 3406, 2955, 2870, 1601, 1504, 1468, 1366, 1223, 1157, 1015, 827 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{22}NOF_2$ ([M+H]$^+$) 306.1669. Found 306.1661.; $[\alpha]^{22}{}_D$ –99.8 (*c* = 1.06, $CHCl_3$).



Preparation of S2: A mixture of formic acid (5.0 mL) and acetic anhydride (11.7 mL) was warmed to 60 °C and stirred for 5 h. To the solution was added amino alcohol **S1** (5.37 g, 17.6 mmol) and the reaction mixture was stirred for 0.5 h at room temperature. The resulting solution was diluted with chloroform and the organic phase was sequentially washed with water (x 2), a saturated aqueous solution of $NaHCO_3$, 1 N hydrochloric acid, and brine. The white solid was obtained on evaporation of all volatiles. This crude solid was dissolved into THF (176.0 mL) and $BH_3{\cdot}SMe_2$ (3.3 mL, 35.2 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 2 h under reflux and then cooled to 0 °C. To the mixture were added ice and a 1 *N* aqueous solution of NaOH. The aqueous phase was extracted with ethyl acetate (EA) twice. The combined organic phases were washed with brine, and dried over $NaSO_4$. Filtration and concentration of the organic phase gave crude residue, which was purified by silica gel chromatography (H/EA = 2/1) to afford *N*-methyl amino alcohol **S2** (3.65 g, 11.4 mmol, 65%). **S2:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (2H, dd, $J_{H\text{-}H}$ = 8.8 Hz, $J_{F\text{-}H}$ = 5.3 Hz), 7.42 (2H, dd, $J_{H\text{-}H}$ = 8.8 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 6.98 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.8 Hz), 6.96 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.8 Hz), 3.40 (1H, dd, J = 9.3, 2.7 Hz), 2.14 (3H, s), 1.51 (1H, d-sept-d, J = 10.1, 6.7, 4.6 Hz), 1.24 (1H, ddd, J = 14.8, 10.1, 2.7 Hz), 1.10 (1H, ddd, J = 14.8, 9.3, 4.6 Hz), 0.89 (3H, d, J = 6.7 Hz), 0.85 (3H, d, J = 6.7 Hz), N-H and O-H protons were not found due to broading; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (d, $J_{F\text{-}C}$ = 248.7 Hz), 161.5 (d, $J_{F\text{-}C}$ = 248.7 Hz), 143.5 (d, $J_{F\text{-}C}$ = 2.9 Hz), 141.0 (d, $J_{F\text{-}C}$ = 2.9 Hz), 127.9 (d, $J_{F\text{-}C}$ = 7.7 Hz), 127.6 (d, $J_{F\text{-}C}$ = 7.7 Hz), 115.0 (d, $J_{F\text{-}C}$ = 21.3 Hz), 114.9 (d, $J_{F\text{-}C}$ = 21.3 Hz), 78.1, 65.1, 40.7, 36.9, 26.0, 23.9, 22.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ –116.6; IR (liq. film): 3370, 2957, 2870, 1601, 1504, 1366, 1221, 1157, 1069, 1015, 908, 827 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{24}NOF_2$ ([M+H]$^+$) 320.1820. Found 320.1818.; $[\alpha]^{22}{}_D$ –40.8 (*c* = 4.47, $CHCl_3$).

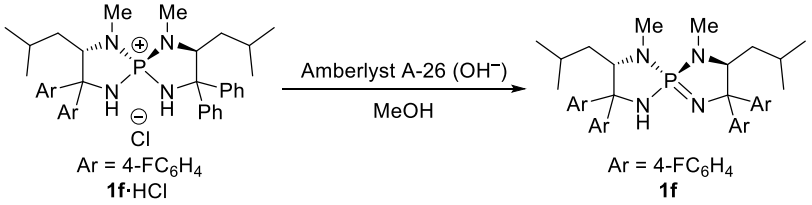


Preparation of S4: The *N*-methyl amino alcohol hydrochloride **S3** (4.08 g, 11.4 mmol) was simply prepared by treatment of the amino alcohol **S2** with a 1 *N* methanolic solution of HCl followed by concentration. To a solution of NaN_3 (2.10 g, 32.5 mmol) in trifluoroacetic acid (32.0 mL) was slowly added **S3** (2.30 g, 6.5 mmol) at 0 °C, followed by the addition of TfOH (4.8 mL) dropwise. After being stirred for 2 h, the resulting solution was poured onto ice and the aqueous solution thus obtained was neutralized by solid NaOH. The aqueous phase was extracted with EA and the organic phase was dried over $NaSO_4$. Filtration and concentration of the organic phase gave crude amino azide. The crude material was dissolved into MeOH (6.5 mL) and ammonium formate (0.81 g, 13.0 mmol) and zinc powder (0.84 g, 13.0 mmol) were introduced to the solution at room temperature. After being stirred for 1 h, resulting suspension was filtered through a pad of Celite and the filtrate was concentrated. EA was added to the residue and the organic phase was washed with a 4:1 mixture of 1 *N* aqueous solution of NaOH and 2 *N* aqueous solution of EDTA·2Na and then brine. Purification of the concentrated crude residue by silica gel column chromatography (H/EtOH = 1/2) was performed to obtain diamine **S4** (1.3 g, 4.23 mmol, 65%) as a pale-yellow viscous oil. **S4:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (2H, dd, $J_{H\text{-}H}$ = 8.8 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 7.42 (2H, dd, $J_{H\text{-}H}$ = 8.8 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 6.97 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.8 Hz), 6.95 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.8 Hz), 3.30 (1H, dd, J = 9.3, 2.2 Hz), 2.13 (3H, s), 1.82-1.41 (4H, m), 1.35 (1H, ddd, J = 14.4, 9.8, 2.2 Hz), 1.06 (1H, ddd, J = 14.4, 9.3, 4.6 Hz), 0.95 (3H, d, J = 6.4 Hz), 0.88 (3H, d, J = 6.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, $J_{F\text{-}C}$ = 249.6 Hz), 161.3 (d, $J_{F\text{-}C}$ = 248.7 Hz), 143.4 (d, $J_{F\text{-}C}$ = 2.9 Hz), 142.4 (d, $J_{F\text{-}C}$ = 3.9 Hz), 128.6 (d, $J_{F\text{-}C}$ = 7.7 Hz), 114.8 (d, $J_{F\text{-}C}$ = 21.3 Hz), 114.7 (d, $J_{F\text{-}C}$ = 21.3 Hz), 65.3, 64.0, 42.1, 37.5, 26.2, 24.1, 22.4 one carbon was not found probably due to overlapping; ^{19}F NMR (376 MHz, $CDCl_3$) δ –116.6, –117.1; IR (liq. film): 2955, 2868, 1599, 1504, 1368, 1223, 1159, 1015, 826 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{25}N_2F_2$ ($[M+H]^+$) 319.1980. Found 319.1977.; $[\alpha]^{22}{}_D$ +37.9 (c = 4.61, $CHCl_3$).



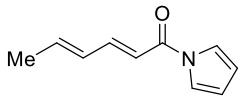
Preparation of Phosphonium Salt 1f·HCl: To a solution of Et_3N (0.42 mL, 3.0 mmol) and the diamine **S4** (0.39 g, 1.2 mmol) in toluene (3.0 mL) was introduced a solution of PCl_5 (0.13 g, 0.61 mmol) in toluene (3.0 mL) and the reaction mixture was stirred for 16 h under reflux. The mixture was cooled to room temperature and concentrated. The residual solid thus obtained was dissolved into chloroform. This solution was washed with 1 *N* hydrochloric acid and the organic phase was dried over $NaSO_4$. After filtration and concentration, purification of the crude material by silica gel chromatography (EA/MeOH = 10/1) furnished the phosphonium salt **1f**·HCl as a white solid (0.19 g, 0.27 mmol, 45%) along with its diastereomer (*M*,*S*)-**1f**·HCl (0.034 g, 0.049 mmol, 8%). The salt was purified by recrystallization from H/EtOH solvent system. **1f·HCl:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.57 (4H, dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{F\text{-}H}$ = 5.0 Hz), 7.33 (4H, dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 7.20 (4H, t,

$J_{H\text{-}H} = J_{F\text{-}H} = 8.7$ Hz), 7.09 (4H, t, $J_{H\text{-}H} = J_{F\text{-}H} = 8.7$ Hz), 4.10 (2H, ddd, $J_{P\text{-}H} = 22.4$ Hz, $J_{H\text{-}H} = 7.3$, 4.6 Hz), 1.99 (6H, d, $J_{P\text{-}H} = 10.5$ Hz), 1.42 (2H, ddd, $J = 14.1$, 7.3, 4.6 Hz), 1.26 (2H, ddd, $J = 14.1$, 7.3, 5.0 Hz), 0.81 (6H, d, $J = 6.2$ Hz), 0.64 (2H, m), 0.62 (6H, brs), N-H protons were not found due to deuterium exchange; ^{13}C NMR (101 MHz, CD_3OD) δ 163.7 (d, $J_{F\text{-}C} = 250.6$ Hz), 163.6 (d, $J_{F\text{-}C} = 250.6$ Hz), 143.8, 137.6 (dd, $J_{P\text{-}C} = 12.6$ Hz, $J_{F\text{-}C} = 2.9$ Hz), 130.6 (d, $J_{F\text{-}C} = 7.7$ Hz), 130.0 (d, $J_{F\text{-}C} = 7.7$ Hz), 116.8 (d, $J_{F\text{-}C} = 22.3$ Hz), 116.1 (d, $J_{F\text{-}C} = 21.3$ Hz), 70.2 (d, $J_{P\text{-}C} = 9.7$ Hz), 64.8 (d, $J_{P\text{-}C} = 12.6$ Hz), 40.4, 29.6 (d, $J_{P\text{-}C} = 5.8$ Hz), 26.0, 23.2, 22.3; ^{19}F NMR (376 MHz, CD_3OD) δ –117.6, –117.8; ^{31}P NMR (162 MHz, CD_3OD) δ 34.4; IR (film): 3051, 2959, 1603, 1508, 1383, 1227, 1177, 1163, 1042, 1015, 953, 826 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{44}N_4F_4P^+$ ([M-Cl]$^+$) 663.3234. Found 663.3228.; $[\alpha]^{20}{}_D$ –184.1 ($c = 1.00$, CH_3OH).

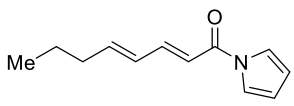


Preparation of Iminophosphorane 1f: Iminophosphorane **1f** was prepared by passage of a methanolic solution of the corresponding phosphonium salt **1f**·HCl through a column of ion exchange resin Amberlyst A-26 OH form. The solution was concentrated by evaporation to give a solid material. The residual solid was suspended into water and then collected by filtration with the aid of water. The solid thus obtained was dried under reduced pressure to afford the iminophosphorane **1f** as a white solid. **1f:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.55 (4H, dd, $J_{H\text{-}H} = 8.8$ Hz, $J_{F\text{-}H} = 5.0$ Hz), 7.34 (4H, dd, $J_{H\text{-}H} = 8.8$ Hz, $J_{F\text{-}H} = 5.5$ Hz), 7.16 (4H, t, $J_{H\text{-}H} = J_{F\text{-}H} = 8.8$ Hz), 7.06 (4H, t, $J_{H\text{-}H} = J_{F\text{-}H} = 8.8$ Hz), 4.04 (2H, ddd, $J_{P\text{-}H} = 22.4$ Hz, $J_{H\text{-}H} = 7.4$, 4.9 Hz), 1.96 (6H, d, $J_{P\text{-}H} = 10.6$ Hz), 1.39 (2H, ddd, $J = 14.2$, 7.4, 4.9 Hz), 1.24 (2H, ddd, $J = 14.2$, 7.4, 4.9 Hz), 0.80 (6H, d, $J = 6.0$ Hz), 0.63 (2H, m), 0.61 (6H, brs), N-H proton was not found due to deuterium exchange; ^{13}C NMR (101 MHz, CD_3OD) δ 163.4 (d, $J_{F\text{-}C} = 249.6$ Hz), 163.3 (d, $J_{F\text{-}C} = 249.6$ Hz), 145.4, 139.3, 130.8 (d, $J_{F\text{-}C} = 7.7$ Hz), 130.0 (d, $J_{F\text{-}C} = 7.7$ Hz), 116.2 (d, $J_{F\text{-}C} = 22.3$ Hz), 115.6 (d, $J_{F\text{-}C} = 21.3$ Hz), 70.5 (d, $J_{P\text{-}C} = 8.7$ Hz), 65.1 (d, $J_{P\text{-}C} = 14.5$ Hz), 40.5, 29.5 (d, $J_{P\text{-}C} = 4.8$ Hz), 26.1, 23.2, 22.4; ^{19}F NMR (376 MHz, CD_3OD) δ –116.6, –116.7; ^{31}P NMR (162 MHz, CD_3OD) δ 36.2; IR (film): 2955, 1601, 1504, 1466, 1331, 1225, 1161, 1125, 1103, 1045, 1013, 827 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{44}N_4F_4P^+$ ([M+H]$^+$) 663.3234. Found 663.3228.; $[\alpha]^{20}{}_D$ –193.5 ($c = 1.00$, CH_3OH).

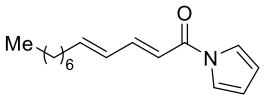
Characterization of Dienyl *N*-Acylpyrroles 2:



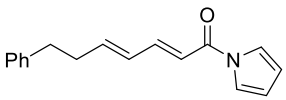
2a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (1H, dd, $J = 15.1$, 9.9 Hz), 7.38 (2H, t, $J = 2.3$ Hz), 6.50 (1H, d, $J = 15.1$ Hz), 6.35 (1H, dd, $J = 15.1$, 9.9 Hz), 6.32 (2H, t, $J = 2.3$ Hz), 6.30 (1H, dq, $J = 15.1$, 5.8 Hz), 1.91 (3H, d, $J = 5.8$ Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 148.0, 142.1, 130.1, 119.3, 116.7, 113.2, 19.0; IR (film): 3142, 1678, 1634, 1605, 1466, 1406, 1346, 1277, 1121, 1061, 999, 941, 924 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_{12}NO$ ([M+H]$^+$) 162.0913. Found 162.0914.



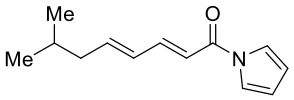
2b:[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, dd, $J = 15.1$, 10.0 Hz), 7.39 (2H, t, $J = 2.3$ Hz), 6.52 (1H, d, $J = 15.1$ Hz), 6.38-6.23 (4H, m), 2.21 (2H, td, $J = 7.3$, 6.0 Hz), 1.50 (2H, sext, $J = 7.3$ Hz), 0.95 (3H, t, $J = 7.3$ Hz).



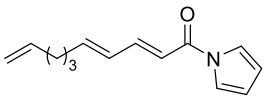
2c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, dd, J = 14.7, 8.2 Hz), 7.39 (2H, t, J = 2.3 Hz), 6.52 (1H, d, J = 14.7 Hz), 6.37-6.24 (2H, m), 6.32 (2H, t, J = 2.3 Hz), 2.21 (2H, td, J = 7.3, 5.5 Hz), 1.52-1.39 (2H, m), 1.37-1.20 (8H, m), 0.89 (3H, t, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 148.3, 147.7, 128.6, 119.3, 116.8, 113.2, 33.3, 31.9, 29.3, 29.2, 28.7, 22.8, 14.2; IR (liq. film): 2922, 2851, 1738, 1682, 1630, 1607, 1468, 1358, 1285, 1217, 1126, 1070, 991, 939 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{23}NONa$ ([M+Na]$^+$) 268.1672. Found 268.1671.



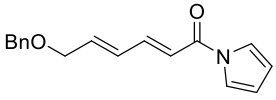
2d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (1H, dd, J = 15.1, 7.8 Hz), 7.38 (2H, t, J = 1.8 Hz), 7.30 (2H, t, J = 7.4 Hz), 7.21 (1H, t, J = 7.4 Hz), 7.19 (2H, d, J = 7.4 Hz), 6.51 (1H, d, J = 15.1 Hz), 6.38-6.25 (4H, m), 2.79 (2H, t, J = 7.8 Hz), 2.55 (2H, td, J = 7.8, 5.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 147.9, 145.9, 141.1, 129.2, 128.6, 128.5, 126.3, 119.3, 117.3, 113.2, 35.1, 35.0; IR (film): 3154, 2941, 1676, 1630, 1599, 1468, 1404, 1362, 1335, 1283, 1121, 1072, 997, 937 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}NO$ ([M+H]$^+$) 252.1383. Found 252.1383.



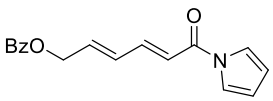
2e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, dd, J = 15.1, 10.1 Hz), 7.39 (1H, t, J = 2.3 Hz), 6.52 (1H, d, J = 15.1 Hz), 6.32$_1$ (1H, dd, J = 15.1, 10.1 Hz), 6.31$_9$ (2H, t, J = 2.3 Hz), 6.26 (1H, dt, J = 15.1, 6.9 Hz), 2.11 (2H, t, J = 6.9 Hz), 1.75 (1H, nonet, J = 6.9 Hz), 0.93 (6H, d, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 148.1, 146.3, 129.7, 119.3, 116.9, 113.2, 42.6, 28.4, 22.5; IR (liq. film): 2957, 2870, 1690, 1634, 1607, 1466, 1358, 1339, 1285, 1126, 1070, 999, 937 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{18}NO$ ([M+H]$^+$) 204.1383. Found 204.1384.



2f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (1H, dd, J = 14.9, 10.1 Hz), 7.38 (2H, t, J = 2.3 Hz), 6.52 (1H, d, J = 14.9 Hz), 6.32 (1H, dd, J = 14.6, 10.1 Hz), 6.31 (2H, t, J = 2.3 Hz), 6.26 (1H, dt, J = 14.6, 6.9 Hz), 5.80 (1H, ddt, J = 17.4, 10.7, 7.1 Hz), 5.03 (1H, dq, J = 17.4, 1.8 Hz), 4.99 (1H, brd, J = 10.7 Hz), 2.23 (2H, q, J = 7.1 Hz), 2.09 (2H, q, J = 7.1 Hz), 1.56 (2H, quin, J = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 148.0, 146.8, 138.2, 128.8, 119.2, 117.0, 115.1, 113.2, 33.2, 32.6, 27.8; IR (liq. film): 2928, 1690, 1634, 1605, 1466, 1348, 1281, 1119, 1070, 997, 937 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{18}NO$ ([M+H]$^+$) 216.1383. Found 216.1384.



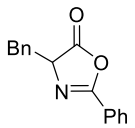
2g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (1H, dd, J = 14.8, 11.3 Hz), 7.41-7.28 (7H, m), 6.61 (1H, d, J = 14.8 Hz), 6.59 (1H, dd, J = 15.3, 11.3 Hz), 6.33$_2$ (1H, dt, J = 15.3, 5.0 Hz), 6.33$_0$ (2H, t, J = 2.3 Hz), 4.58 (2H, s), 4.20 (2H, dd, J = 5.0, 0.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 146.8, 141.1, 137.9, 128.8, 128.6, 128.0, 127.9, 119.3, 119.1, 113.4, 72.9, 69.6; IR (film): 3150, 2868, 1686, 1638, 1603, 1468, 1404, 1341, 1277, 1103, 1061, 1003, 937 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}NO_2$ ([M+H]$^+$) 268.1332. Found 268.1332.



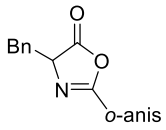
2h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (2H, dd, J = 7.8, 1.4 Hz), 7.61 (1H, dd, J = 15.1, 10.9 Hz), 7.60 (1H, t, J = 7.8 Hz), 7.48 (2H, t, J = 7.8 Hz), 7.39 (2H, t, J = 2.3 Hz), 6.67 (1H, d, J = 15.1 Hz), 6.61 (1H, dd, J = 15.6, 10.9 Hz), 6.40 (1H, dt, J = 15.6, 5.5 Hz), 6.34 (2H, t, J = 2.3 Hz), 5.00 (2H, dd, J = 5.5, 1.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 162.9, 146.0, 137.7, 133.5, 130.2, 129.9, 128.7, 120.2, 119.3, 113.5, 64.1, one carbon was not found probably due to overlapping; IR (film): 3146, 1711, 1686, 1645, 1612, 1456, 1379, 1348, 1271, 1180, 1109, 1070, 995, 928 cm^{-1}; HRMS (ESI)

Calcd for $C_{17}H_{15}NO_3Na$ ([M+Na]$^+$) 304.0944. Found 304.0944.

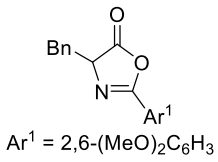
Characterization of Azlactones:



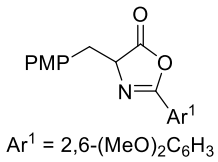
3a:[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 7.8 Hz), 7.55 (1H, t, J = 7.8 Hz), 7.45 (2H, t, J = 7.8 Hz), 7.31-7.18 (5H, m), 4.69 (1H, dd, J = 6.4, 5.0 Hz), 3.37 (1H, dd, J = 14.2, 5.0 Hz), 3.19 (1H, dd, J = 14.2, 6.4 Hz).



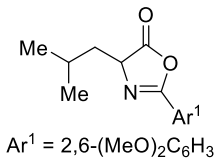
3b:[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (1H, dd, J = 8.2, 1.4 Hz), 7.47 (1H, td, J = 8.2, 1.4 Hz), 7.31-7.18 (5H, m), 6.99 (1H, d, J = 8.2 Hz), 6.98 (1H, t, J = 8.2 Hz), 4.71 (1H, t, J = 5.6 Hz), 3.90 (3H, s), 3.39 (1H, dd, J = 14.2, 5.5 Hz), 3.24 (1H, dd, J = 14.2, 5.6 Hz).



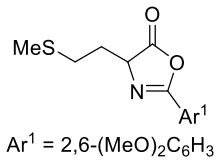
3c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (1H, t, J = 8.5 Hz), 7.32-7.21 (5H, m), 6.52 (2H, d, J = 8.5 Hz), 4.70 (1H, dd, J = 6.4, 5.1 Hz), 3.72 (6H, s), 3.39 (1H, dd, J = 14.2, 5.1 Hz), 3.24 (1H, dd, J = 14.2, 6.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 159.3, 158.9, 135.6, 132.9, 130.0, 128.4, 127.0, 105.9, 103.8, 66.7, 56.1, 37.0; IR (film): 2974, 1827, 1668, 1585, 1476, 1433, 1300, 1233, 1109, 1022, 982, 901, 874 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{18}NO_4$ ([M+H]$^+$) 312.1230. Found 312.1229.



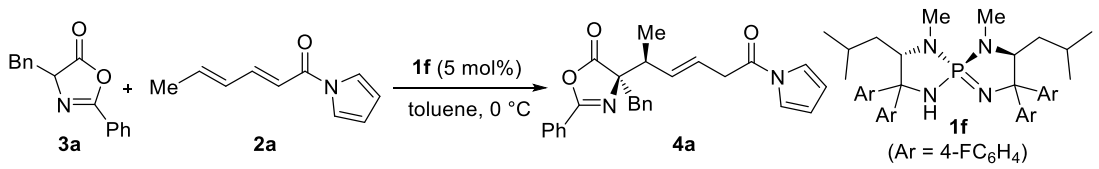
3d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (1H, t, J = 8.7 Hz), 7.21 (2H, d, J = 8.9 Hz), 6.82 (2H, d, J = 8.9 Hz), 6.52 (2H, d, J = 8.7 Hz), 4.67 (1H, dd, J = 6.0, 5.0 Hz), 3.78 (3H, s), 3.72 (6H, s), 3.33 (1H, dd, J = 14.2, 5.0 Hz), 3.21 (1H, dd, J = 14.2, 6.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 159.3, 158.9, 158.7, 132.9, 131.1, 127.5, 113.7, 105.8, 103.7, 66.9, 56.1, 55.3, 36.1; IR (liq. film): 2938, 2839, 1809, 1674, 1593, 1512, 1476, 1433, 1304, 1246, 1179, 1109, 1022, 962, 883 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{20}NO_5$ ([M+H]$^+$) 342.1336. Found 342.1336.



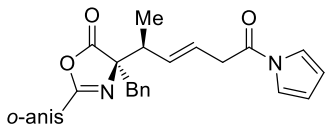
3e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (1H, t, J = 8.4 Hz), 6.58 (2H, d, J = 8.4 Hz), 4.43 (1H, dd, J = 8.1, 6.0 Hz), 3.82 (6H, s), 2.06 (1H, nonet, J = 7.0 Hz), 1.89 (1H, ddd, J = 13.9, 7.0, 6.0 Hz), 1.74 (1H, ddd, J = 13.9, 8.1, 7.0 Hz), 1.03 (3H, d, J = 7.0 Hz), 1.00 (3H, d, J = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.9, 159.3, 158.7, 132.9, 106.1, 103.8, 64.0, 56.2, 40.6, 25.1, 22.8, 22.3; IR (film): 2936, 1823, 1678, 1591, 1477, 1433, 1304, 1261, 1111, 1015, 899 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{20}NO_4$ ([M+H]$^+$) 278.1387. Found 278.1386.



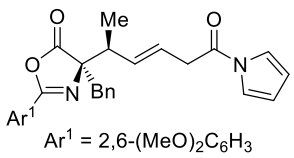
3f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (1H, t, J = 8.2 Hz), 6.59 (2H, d, J = 8.2 Hz), 4.59 (1H, t, J = 6.3 Hz), 3.83 (6H, s), 2.73 (1H, ddd, J = 13.7, 7.5, 6.3 Hz), 2.71 (1H, ddd, J = 13.7, 7.5, 6.3 Hz), 2.34 (1H, ddt, J = 14.2, 7.5, 6.3 Hz), 2.21 (1H, ddt, J = 14.2, 7.5, 6.3 Hz), 2.12 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2, 159.4, 159.2, 133.0, 105.9, 103.8, 63.9, 56.2, 30.3, 29.7, 15.1; IR (liq. film): 2918, 2841, 1809, 1674, 1593, 1476, 1433, 1306, 1258, 1109, 1007, 874 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{18}NO_4S$ ([M+H]$^+$) 296.0951. Found 296.0951.



Representative Procedure for Asymmetric 1,6-Addition of Azlactone 3 to Dienyl *N*-Acylpyrrole 2 with Chiral Iminophosphorane 1f as a catalyst: Azlactone **3a** (25.13 mg, 0.10 mmol) and dienyl *N*-acylpyrrole **2a** (17.73 mg, 0.11 mmol) was dissolved into toluene (1.0 mL) under Ar atmosphere. A solid of chiral iminophosphorane **1f** (3.40 mg, 5.0 μmol) was added slowly at 0 °C and the resulting reaction mixture was stirred for 2 h. The reaction was quenched by the addition of a solution of trifluoroacetic acid in toluene (0.5 M, 50.0 μL) and all volatiles were removed by evaporation to give crude residue. The diastereomeric ratio of **4a** was determined by ^{1}H NMR analysis (400 MHz) of it. Subsequent purification by column chromatography on silica gel (H/EA = 1:1 as eluent) gave the adduct in 99% yield as a mixture of isomers (40.8 mg, 0.099 mmol). The enantiomeric excess of 1,6-adduct **4a** was determined by HPLC analysis. **4a:** HPLC OD3, H/IPA/EtOH = 45:4:1, flow rate = 0.5 mL/min, λ = 254 nm, 19.2 min (minor diastereomer), 20.2 min (major isomer of major diastereomer), 28.6 min (minor isomer of major diastereomer), 32.4 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.82 (2H, d, J = 7.8 Hz), 7.52 (1H, t, J = 7.8 Hz), 7.41 (2H, t, J = 7.8 Hz), 7.32 (2H, brs), 7.16-7.04 (5H, m), 6.30 (2H, t, J = 2.3 Hz), 5.94 (1H, dt, J = 15.6, 6.4 Hz), 5.83 (1H, dd, J = 15.6, 9.2 Hz), 3.67 (2H, d, J = 6.4 Hz), 3.26 (1H, d, J = 13.3 Hz), 3.05 (1H, d, J = 13.3 Hz), 2.88 (1H, dq, J = 9.2, 6.9 Hz), 1.02 (3H, d, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 179.5, 168.6, 160.3, 134.9, 134.6, 132.6, 130.2, 128.8, 128.2, 127.9, 127.2, 125.7, 124.5, 119.2, 113.5, 77.7, 44.4, 42.4, 38.5, 16.0; IR (liq. film): 2968, 1811, 1717, 1653, 1468, 1333, 1290, 1254, 1113, 1072, 966, 918, 891 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{25}N_2O_3$ ([M+H]$^+$) 413.1860. Found 413.1859.

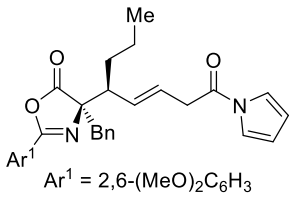


5a: HPLC IC3, H/IPA/EtOH = 94:3:3, flow rate = 0.5 mL/min, λ = 210 nm, 24.7 min (major isomer of major diastereomer), 27.1 min (minor diastereomer), 28.4 min (minor diastereomer), 30.2 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.43 (1H, ddd, J = 8.5, 7.3, 1.7 Hz), 7.32 (2H, brs), 7.30 (1H, dd, J = 7.3, 1.7 Hz), 7.23-7.12 (5H, m), 6.93 (1H, t, J = 7.3 Hz), 6.92 (1H, d, J = 8.5 Hz), 6.29 (2H, t, J = 2.3 Hz), 5.94 (1H, dt, J = 15.6, 6.4 Hz), 5.83, (1H, dd, J = 15.6, 8.9 Hz), 3.80 (3H, s), 3.66 (2H, d, J = 6.4 Hz), 3.27 (1H, d, J = 13.3 Hz), 3.06 (1H, d, J = 13.3 Hz), 2.89 (1H, dq, J = 8.9, 6.9 Hz), 1.08 (3H, d, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 179.9, 168.6, 159.8, 158.5, 135.0, 134.8, 133.3, 130.7, 130.4, 128.1, 127.2, 124.5, 120.4, 119.2, 115.9, 113.4, 111.8, 77.4, 56.1, 44.1, 42.2, 38.5, 15.9; IR (liq. film): 2967, 1809, 1717, 1653, 1601, 1493, 1468, 1333, 1310, 1263, 1113, 1022, 966 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{27}N_2O_4$ ([M+H]$^+$) 443.1965. Found 443.1965.

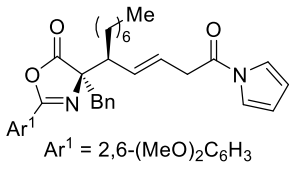


6a: HPLC IC3, H/IPA/EtOH = 18:1:1, flow rate = 1.0 mL/min, λ = 210 nm, 14.0 min (major isomer of major diastereomer), 15.6 min (minor diastereomer), 16.7 min (minor diastereomer), 19.6 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.32 (2H, brs), 7.31 (1H, t, J = 8.5 Hz), 7.25-7.15 (5H, m), 6.48 (2H, d, J = 8.5 Hz), 6.29 (2H, t, J = 2.3 Hz), 5.93 (1H, dt, J = 15.6, 6.0 Hz), 5.88 (1H, dd, J = 15.6, 7.5 Hz), 3.66 (2H, d, J = 6.0 Hz), 3.64 (3H, s), 3.29 (1H, d, J = 13.8 Hz), 3.08 (1H, d, J = 13.8 Hz), 2.86 (1H, quin, J = 7.5 Hz), 1.13 (3H, d, J = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 180.3,

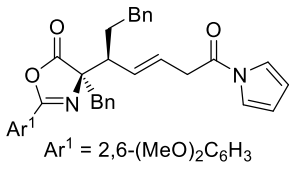
168.6, 159.2, 157.7, 135.4, 134.9, 132.8, 130.7, 128.0, 126.8, 124.2, 119.2, 113.4, 105.7, 103.6, 77.6, 55.9, 44.7, 42.0, 38.5, 15.7; IR (liq. film): 2967, 1805, 1717, 1674, 1595, 1476, 1333, 1304, 1256, 1113, 961 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{29}N_2O_5$ ([M+H]$^+$) 473.2071. Found 473.2073.



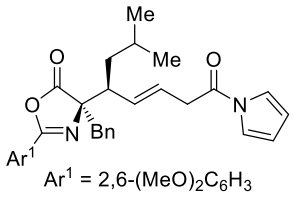
6b: HPLC IC, H/IPA/EtOH = 93:5:2, flow rate = 1.0 mL/min, λ = 254 nm, 13.0 min (major isomer of major diastereomer), 14.0 min (minor diastereomer), 15.0 min (minor diastereomer), 17.2 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.33 (2H, brs), 7.31 (1H, t, J = 8.7 Hz), 7.26-7.14 (5H, m), 6.48 (2H, d, J = 8.7 Hz), 6.29 (2H, t, J = 2.3 Hz), 5.90 (1H, dt, J = 15.6, 6.7 Hz), 5.74 (1H, dd, J = 15.6, 9.6 Hz), 3.71 (1H, ddd, J = 17.1, 6.7, 1.4 Hz), 3.67 (1H, ddd, J = 17.1, 6.7, 1.6 Hz), 3.63 (6H, s), 3.30 (1H, d, J = 13.7 Hz), 3.03 (1H, d, J = 13.7 Hz), 2.66 (1H, ddd, J = 11.9, 9.6, 2.8 Hz), 1.55-1.32 (2H, m), 1.32-1.12 (2H, m), 0.89 (3H, t, J = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 180.6, 168.6, 159.1, 157.6, 134.8, 134.0, 132.8, 130.8, 128.0, 126.8, 125.8, 119.2, 113.4, 105.7, 103.6, 77.8, 55.8, 50.7, 42.2, 38.5, 31.8, 20.5, 14.1; IR (liq. film): 2957, 1805, 1717, 1674, 1595, 1476, 1337, 1298, 1256, 1113, 1032, 961, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{33}N_2O_5$ ([M+H]$^+$) 501.2384. Found 501.2382.



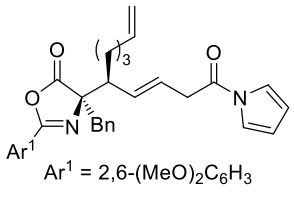
6c: HPLC AD3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 254 nm, 5.1 min (minor isomer of major diastereomer), 5.3 min (minor diastereomer), 6.1 min (major isomer of major diastereomer), 6.8 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.33 (2H, brs), 7.30 (1H, t, J = 8.5 Hz), 7.25-7.14 (5H, m), 6.47 (2H, d, J = 8.5 Hz), 6.29 (2H, t, J = 2.3 Hz), 5.90 (1H, dt, J = 15.7, 6.6 Hz), 5.74 (1H, dd, J = 15.7, 10.1 Hz), 3.69 (2H, dd, J = 6.6, 0.9 Hz), 3.63 (6H, s), 3.30 (1H, d, J = 13.7 Hz), 3.03 (1H, d, J = 13.7 Hz), 2.63 (1H, t, J = 10.1 Hz), 1.57-1.40 (1H, m), 1.39-1.12 (11H, m), 0.87 (3H, t, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 180.6, 168.6, 159.1, 157.6, 134.8, 134.1, 132.8, 130.8, 128.0, 126.8, 125.9, 119.2, 113.3, 105.7, 103.6, 77.8, 55.8, 50.9, 42.2, 38.6, 32.0, 29.7, 29.6, 29.3, 27.4, 22.8, 14.2; IR (liq. film): 2926, 2855, 1805, 1717, 1674, 1595, 1476, 1337, 1298, 1256, 1113, 1072, 961, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{41}N_2O_5$ ([M+H]$^+$) 557.3010. Found 557.3011.



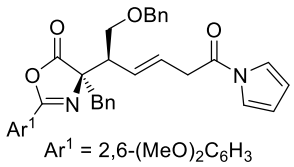
6d: The structure of **6d** was determined by X-ray crystallographic analysis (see page 43).HPLC OZ3, H/EtOH = 10:1, flow rate = 1.0 mL/min, λ = 254 nm, 14.8 min (minor diastereomer), 16.8 min (minor isomer of major diastereomer), 19.1 min (minor diastereomer), 24.4 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.35 (2H, brs), 7.27 (1H, t, J = 8.7 Hz), 7.27-7.10 (10H, m), 6.42 (2H, d, J = 8.7 Hz), 6.31 (2H, t, J = 2.3 Hz), 5.95 (1H, dt, J = 15.6, 6.6 Hz), 5.83 (1H, dd, J = 15.6, 10.1 Hz), 3.73 (2H, dd, J = 6.6, 0.9 Hz), 3.45 (6H, s), 3.31 (1H, d, J = 13.7 Hz), 3.03 (1H, d, J = 13.7 Hz), 2.73 (1H, ddd, J = 11.2, 10.1, 2.9 Hz), 2.67 (1H, ddd, J = 13.7, 10.8, 4.6 Hz), 2.50 (1H, ddd, J = 13.7, 11.2, 6.5 Hz), 1.77 (1H, dtd, J = 13.7, 11.2, 4.6 Hz), 1.64 (2H, dddd, J = 13.7, 10.8, 6.5, 2.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 180.5, 168.5, 159.1, 157.9, 142.0, 134.7, 133.7, 132.8, 130.8, 128.6, 128.4, 128.0, 126.8, 126.7, 125.9, 119.2, 113.5, 105.6, 103.5, 77.7, 55.6, 50.6, 42.2, 38.6, 33.6, 32.0; IR (liq. film): 2938, 1805, 1717, 1676, 1595, 1476, 1339, 1298, 1258, 1113, 961, 916 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{35}N_2O_5$ ([M+H]$^+$) 563.2540. Found 563.2542.



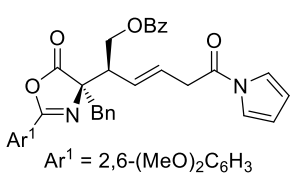
6e: HPLC AD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 7.4 min (minor isomer of major diastereomer), 10.3 min (minor diastereomer), 11.3 min (major isomer of major diastereomer), 13.3 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.32 (2H, brs), 7.30 (1H, t, J = 8.5 Hz), 7.26-7.14 (5H, m), 6.47 (2H, d, J = 8.5 Hz), 6.29 (2H, t, J = 2.3 Hz), 5.92 (1H, dt, J = 15.6, 6.8 Hz), 5.73 (1H, dd, J = 15.6, 9.6 Hz), 3.71 (1H, ddd, J = 17.2, 6.8, 1.2 Hz), 3.67 (1H, dd, J = 17.2, 6.8 Hz), 3.63 (6H, s), 3.32 (1H, d, J = 13.7 Hz), 3.04 (1H, d, J = 13.7 Hz), 2.76 (1H, ddd, J = 12.1, 9.6, 2.7 Hz), 1.63-1.48 (2H, m), 0.97 (1H, ddd, J = 14.1, 11.3, 2.7 Hz), 0.90 (3H, d, J = 6.4 Hz), 0.88 (3H, d, J = 6.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 180.5, 168.6, 159.2, 157.7, 134.9, 134.0, 132.8, 130.8, 128.0, 126.8, 125.7, 119.2, 113.4, 105.7, 103.6, 77.8, 55.8, 48.7, 42.3, 38.6, 38.5, 25.0, 24.4, 20.7; IR (liq. film): 2955, 1805, 1717, 1674, 1595, 1476, 1333, 1298, 1256, 1113, 961, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{35}N_2O_5$ ([M+H]$^+$) 515.2540. Found 515.2542.



6f: HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 254 nm, 21.1 min (minor isomer of major diastereomer), 24.0 min (minor diastereomer), 43.8 min (major isomer of major diastereomer), 55.5 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.32 (2H, brs), 7.30 (1H, t, J = 8.4 Hz), 7.26-7.14 (5H, m), 6.47 (2H, d, J = 8.4 Hz), 6.29 (2H, t, J = 2.3 Hz), 5.91 (1H, dt, J = 15.6, 6.8 Hz), 5.77 (1H, ddt, J = 17.2, 10.1, 6.6 Hz), 5.75 (1H, dd, J = 15.6, 9.4 Hz), 4.99 (1H, dq, J = 17.2, 1.4 Hz), 4.93 (1H, dd, J = 10.1, 1.4 Hz), 3.69 (2H, d, J = 6.8 Hz), 3.63 (6H, s), 3.30 (1H, d, J = 13.7 Hz), 3.03 (1H, d, J = 13.7 Hz), 2.65 (1H, ddd, J = 11.7, 9.4, 2.3 Hz), 2.15-1.90 (2H, m), 1.58-1.38 (2H, m), 1.38-1.23 (2H, m); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 180.5, 168.6, 159.2, 157.7, 138.5, 134.8, 133.9, 132.9, 130.8, 128.0, 126.8, 126.1, 119.2, 114.8, 113.4, 105.7, 103.6, 77.7, 55.9, 50.8, 42.3, 38.5, 33.7, 29.2, 26.8; IR (liq. film): 2936, 1805, 1717, 1674, 1595, 1476, 1433, 1337, 1300, 1256, 1113, 961, 916 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{35}N_2O_5$ ([M+H]$^+$) 527.2540. Found 527.2541.

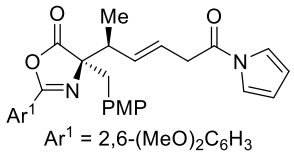


6g: HPLC OZ3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 210 nm, 12.1 min (minor diastereomer), 13.4 min (minor diastereomer), 15.8 min (minor isomer of major diastereomer), 21.5 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.32 (2H, brs), 7.30 (1H, t, J = 8.7 Hz), 7.27-7.14 (10H, m), 6.46 (2H, d, J = 8.7 Hz), 6.29 (2H, t, J = 2.3 Hz), 6.05 (1H, dt, J = 15.6, 6.8 Hz), 5.86 (1H, dd, J = 15.6, 9.8 Hz), 4.50 (1H, d, J = 12.4 Hz), 4.39 (1H, d, J = 12.4 Hz), 3.70 (1H, dd, J = 17.4, 6.8 Hz), 3.66 (1H, dd, J = 17.4, 6.8 Hz), 3.66 (1H, t, J = 9.8 Hz), 3.58 (6H, s), 3.47 (1H, dd, J = 9.8, 5.7 Hz), 3.29 (1H, d, J = 13.3 Hz), 3.27 (1H, td, J = 9.8, 5.7 Hz), 3.02 (1H, d, J = 13.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 179.8, 168.4, 159.2, 158.4, 138.1, 134.2, 132.9, 131.1, 130.7, 128.3, 127.9, 127.4, 127.3, 127.2, 126.8, 119.2, 113.5, 105.6, 103.6, 74.2, 72.8, 70.2, 55.8, 50.5, 42.3, 38.5; IR (liq. film): 2934, 1809, 1717, 1668, 1595, 1476, 1335, 1300, 1256, 1111, 961, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{35}N_2O_6$ ([M+H]$^+$) 579.2490. Found 579.2488.

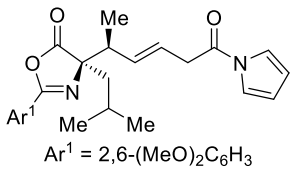


6h: HPLC IC, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 210 nm, 17.7 min (minor diastereomer), 22.5 min (minor isomer of major diastereomer), 34.9 min (minor diastereomer), 43.2 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.98 (2H, d, J = 7.8 Hz), 7.49 (1H, t, J = 7.8 Hz), 7.37 (2H, t, J = 7.8 Hz), 7.31 (2H, brs), 7.27 (1H, t, J = 8.5 Hz), 7.27-7.17 (5H, m), 6.43 (2H, d, J = 8.5 Hz), 6.29 (2H, t, J = 2.3

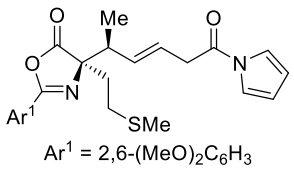
Hz), 6.17 (1H, dt, *J* = 15.6, 6.7 Hz), 5.93 (1H, dd, *J* = 15.6, 9.9 Hz), 4.41 (1H, dd, *J* = 11.4, 6.0 Hz), 4.28 (1H, dd, *J* = 11.4, 9.9 Hz), 3.71 (2H, d, *J* = 6.7 Hz), 3.59 (6H, s), 3.40 (1H, td, *J* = 9.9, 6.0 Hz), 3.33 (1H, d, *J* = 13.7 Hz), 3.08 (1H, d, *J* = 13.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 180.1, 168.1, 166.4, 159.2, 158.9, 134.0, 133.1, 132.9, 131.1, 129.8, 129.6$_9$, 129.6$_6$, 128.5, 128.3, 128.1, 127.0, 119.2, 113.6, 105.4, 103.5, 74.3, 64.6, 55.9, 49.7, 42.4, 38.5; IR (liq. film): 2938, 1809, 1717, 1670, 1595, 1476, 1341, 1298, 1256, 1111, 1072, 959, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{33}N_2O_7$ ([M+H]$^+$) 593.2282. Found 593.2281.



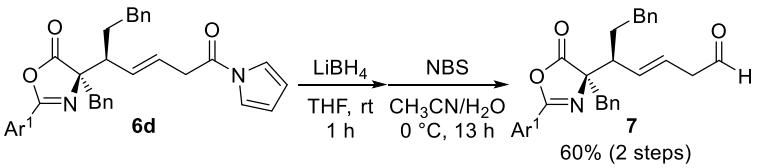
6i: HPLC OZ3, H/IPA/EtOH = 90:7:3, flow rate = 1.0 mL/min, λ = 254 nm, 20.2 min (minor diastereomer), 21.7 min (minor isomer of major diastereomer), 22.9 min (minor diastereomer), 25.3 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.32 (2H, brs), 7.31 (1H, t, *J* = 8.4 Hz), 7.10 (2H, d, *J* = 8.7 Hz), 6.77 (2H, d, *J* = 8.7 Hz), 6.49 (2H, d, *J* = 8.4 Hz), 6.29 (2H, t, *J* = 2.3 Hz), 5.92 (1H, dt, *J* = 15.6, 6.0 Hz), 5.86 (1H, dd, *J* = 15.6, 7.8 Hz), 3.77 (3H, s), 3.65$_4$ (2H, d, *J* = 6.0 Hz), 3.64$_7$ (6H, s), 3.23 (1H, d, *J* = 14.0 Hz), 3.02 (1H, d, *J* = 14.0 Hz), 2.85 (1H, dq, *J* = 7.8, 6.9 Hz), 1.12 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 180.4, 168.7, 159.2, 158.5, 157.7, 135.4, 132.9, 131.7, 127.0, 124.1, 119.2, 113.4, 105.7, 103.6, 77.8, 55.8, 55.2, 44.5, 41.2, 38.5, 15.8, one carbon was not found probably due to overlapping; IR (liq. film): 2936, 2839, 1805, 1717, 1674, 1595, 1512, 1476, 1333, 1300, 1254, 1179, 1113, 1034, 962 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{31}N_2O_6$ ([M+H]$^+$) 503.2177. Found 503.2175.



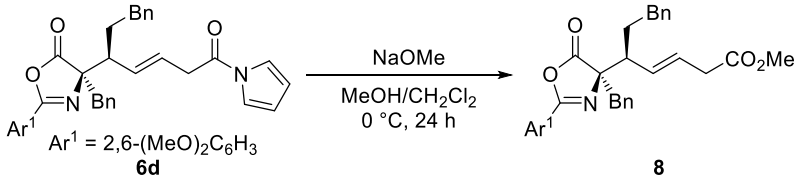
6j: HPLC OD3, H/IPA/EtOH = 18:1:1, flow rate = 1.0 mL/min, λ = 254 nm, 13.3 min (major isomer of major diastereomer), 15.1 min (minor diastereomer), 20.0 min (minor isomer of major diastereomer), 21.3 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.38 (1H, t, *J* = 8.5 Hz), 7.30 (2H, brs), 6.59 (2H, d, *J* = 8.5 Hz), 6.28 (2H, t, *J* = 2.3 Hz), 5.81 (1H, dt, *J* = 15.8, 6.0 Hz), 5.74 (1H, dd, *J* = 15.8, 8.2 Hz), 3.81 (6H, s), 3.63 (1H, dd, *J* = 16.7, 6.0 Hz), 3.58 (1H, dd, *J* = 16.7, 6.0 Hz), 2.64 (1H, dq, *J* = 8.2, 6.9 Hz), 2.05 (1H, q, *J* = 7.4 Hz), 1.77-1.62 (2H, m), 1.07 (3H, d, *J* = 6.9 Hz), 0.91 (3H, d, *J* = 7.4 Hz), 0.90 (3H, d, *J* = 7.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 181.7, 168.7, 159.2, 157.5, 135.6, 132.9, 124.0, 119.2, 113.3, 106.2, 103.8, 75.5, 55.9, 45.0, 44.7, 38.6, 24.7, 24.5, 22.9, 15.1; IR (liq. film): 2957, 1803, 1717, 1680, 1595, 1476, 1331, 1256, 1111, 1022, 945, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{31}N_2O_5$ ([M+H]$^+$) 439.2227. Found 439.2226.



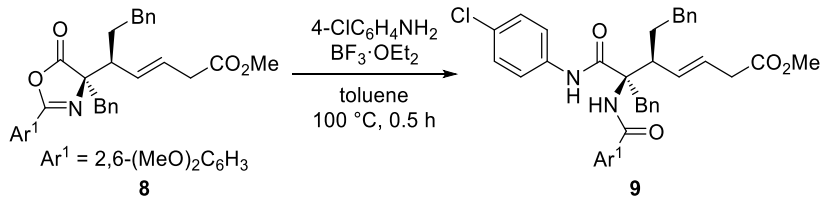
6k: HPLC AD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 17.1 min (major isomer of major diastereomer), 21.4 min (minor isomer of major diastereomer), 25.6 min (minor diastereomer), 26.8 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.40 (1H, t, *J* = 8.7 Hz), 7.30 (2H, brs), 6.60 (2H, d, *J* = 8.7 Hz), 6.29 (2H, t, *J* = 2.3 Hz), 5.85 (1H, dt, *J* = 16.0, 6.5 Hz), 5.74 (1H, dd, *J* = 16.0, 9.2 Hz), 3.83 (6H, s), 3.63 (1H, ddd, *J* = 16.9, 6.5, 1.4 Hz), 3.58 (1H, ddd, *J* = 16.9, 6.5, 1.4 Hz), 2.72 (1H, dq, *J* = 9.2, 6.9 Hz), 2.57 (1H, ddd, *J* = 13.0, 11.0, 3.9 Hz), 2.37 (1H, ddd, *J* = 13.0, 11.0, 6.2 Hz), 2.27 (1H, ddd, *J* = 13.4, 11.0, 3.9 Hz), 2.13 (1H, ddd, *J* = 13.4, 11.0, 6.2 Hz), 2.07 (3H, s), 1.08 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 180.7, 168.6, 159.1, 158.5, 135.1, 133.0, 124.2, 119.2, 113.4, 106.0, 103.8, 75.5, 56.1, 44.1, 38.4, 35.1, 28.3, 15.2$_9$, 15.2$_6$; IR (liq. film): 2968, 1805, 1717, 1678, 1595, 1476, 1333, 1258, 1111, 989 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{29}N_2O_5S$ ([M+H]$^+$) 457.1792. Found 457.1789.



Site Selective Reduction of *N*-Acylpyrrole Moiety of 6d and Subsequent Transformation to Aldehyde 7: The 1,6-adduct **6d** (54.0 mg, 0.096 mmol) was placed in a test tube and suspended in THF (0.096 mL) under Ar atmosphere. $LiBH_4$ (5.9 mg, 0.11 mmol) was introduced to the solution and the reaction mixture was stirred for 1 h. After quenching by water, the aqueous phase was extracted with EA twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4 and filtered. All volatiles were removed under reduced pressure and the resulting crude residue was transferred to a test tube with acetonitrile (0.50 mL) and water (0.10 mL). After cooling to 0 °C, *N*-bromosuccinimide (5.9 mg, 0.11 mmol) was introduced to the solution and the reaction mixture was stirred for 13 h. After quenching with water, the aqueous phase was extracted with EA twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4 and filtered. All volatiles were removed by evaporation to give the crude residue. Purification of the residue by column chromatography on silica gel (H/EA = 1:1 as eluent) afforded **7** in 60% yield (44.6 mg, 0.084 mmol). **7:** ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 9.78 (1H, t, J = 1.4 Hz), 7.37 (1H, t, J = 8.5 Hz), 7.32-7.11 (10H, m), 6.61 (2H, d, J = 8.5 Hz), 5.92 (1H, dt, J = 15.7, 6.86 Hz), 5.72 (1H, ddt, J = 15.7, 9.8, 1.4 Hz), 3.51 (6H, s), 3.40 (2H, dt, J = 6.9, 1.4 Hz), 3.34 (1H, d, J = 13.7 Hz), 2.99 (1H, d, J = 13.7 Hz), 2.75 (1H, ddd, J = 13.7, 11.2, 4.7 Hz), 2.69 (1H, ddd, J = 11.2, 9.8, 2.7 Hz), 2.52 (1H, ddd, J = 13.7, 11.2, 4.7 Hz), 1.80 (1H, dtd, J = 13.7, 11.2, 4.7 Hz), 1.59 (1H, dddd, J = 13.7, 11.2, 6.6, 2.7 Hz).

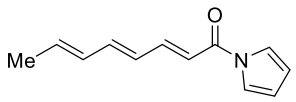


Methanolysis of *N*-Acylpyrrole Moiety of 6d: The 1,6-adduct **6d** (54.0 mg, 0.096 mmol) was placed in a test tube and dissolved into MeOH (0.096 mL) and CH_2Cl_2 (0.096 mL) under Ar atmosphere. After cooling to 0 °C, NaOMe (5.9 mg, 0.11 mmol) was introduced slowly to the solution and the reaction mixture was stirred for 24 h. The whole mixture was poured into an ice-cooled, saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with chloroform twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4 and filtered. All volatiles were removed by evaporation and the diastereomeric ratio of **8** was determined to be >20:1 by ^{1}H NMR analysis (400 MHz) of the crude residue. Purification of the residue by column chromatography on silica gel (H/EA = 1:1 as eluent) afforded **8** in 88% yield (44.6 mg, 0.084 mmol). **8:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.11 (11H, m), 6.42 (2H, d, J = 8.2 Hz), 5.84 (1H, dt, J = 15.6, 6.9 Hz), 5.72 (1H, dd, J = 15.6, 10.1 Hz), 3.70 (3H, s), 3.45 (6H, s), 3.32 (1H, d, J = 14.0 Hz), 3.22 (2H, d, J = 6.9 Hz), 3.02 (1H, d, J = 14.0 Hz), 2.74-2.62 (2H, m), 2.49 (1H, ddd, J = 13.7, 10.8, 6.4 Hz), 1.77 (1H, tdd, J = 13.7, 10.8, 4.6 Hz), 1.63 (1H, dddd, J = 13.7, 10.8, 6.9, 3.0 Hz); ^{13}C NMR (101 MHz, CDCl3) δ 180.6, 172.1, 159.1, 157.8, 142.1, 134.9, 132.8, 132.7, 130.8, 128.6, 128.4, 128.0, 127.4, 126.8, 125.9, 105.7, 103.5, 77.8, 55.6, 52.0, 50.7, 42.2, 37.9, 33.7, 32.0; IR (film): 2938, 2841, 1805, 1736, 1674, 1595, 1476, 1433, 1258, 1173, 1113, 1032, 961, 887 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{34}NO_6$ ($[M+H]^+$) 528.2381. Found 528.2381.

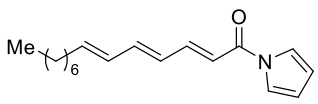


Ring-opening Reaction of 8: The methyl ester **8** (39.6 mg, 0.075 mmol) and 4-chloroaniline (22.7 mg, 0.18 mmol) were placed into an oven-dried test tube and dissolved into toluene (0.25 mL). $BF_3{\cdot}OEt_2$ (0.0112 mL, 0.089 mmol) was added to the solution and the reaction mixture was stirred for 0.5 h at 100 °C under Ar. After cooling to room temperature, the mixture was poured into water and extracted with EA twice. The combined organic phases were dried over Na_2SO_4, filtrated, and concentrated, giving the crude residue. Subsequent purification of the crude material by column chromatography on silica gel (H/acetone = 2/1~1/2 as eluent) afforded **9** in 81% yield (39.9 mg, 0.061 mmol). The absolute configuration of **9** was determined to be 5*S*,6*R* by X-ray crystallographic analysis (see page 44). **9:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (1H, brs), 7.44 (2H, d, J = 9.2 Hz), 7.35-7.27 (3H, m), 7.29 (2H, d, J = 9.2 Hz), 7.25-7.12 (8H, m), 6.59 (2H, d, J = 8.2 Hz), 6.00 (1H, brs), 5.57 (1H, dd, J = 15.6, 8.7 Hz), 5.51 (1H, dt, J = 15.6, 5.8 Hz), 3.95 (1H, d, J = 14.6 Hz), 3.84 (6H, s), 3.56 (3H, s), 3.46 (1H, d, J = 14.6 Hz), 3.12 (1H, dd, J = 16.7, 5.8 Hz), 3.03 (1H, dd, J = 16.7, 5.8 Hz), 2.74 (1H, m), 2.45-2.28 (3H, m), 1.72-1.60 (1H, m); ^{13}C NMR (101 MHz, CDCl3) δ 171.5, 169.8, 165.2, 157.5, 141.7, 136.7, 136.5, 133.1, 131.5, 131.4, 129.7, 129.1, 128.8, 128.6, 128.5, 128.1, 126.7, 126.2, 122.8, 115.4, 104.3, 65.9, 56.1, 52.1, 46.9, 37.8, 35.6, 33.7, 30.9; IR (film): 3364, 2949, 2839, 1734, 1682, 1595, 1491, 1304, 1250, 1109, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{40}N_2O_6Cl$ ([M+H]$^+$) 655.2569. Found 655.2569.

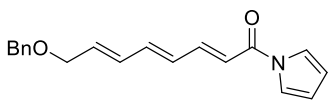
Characterization of Trienyl *N*-Acylpyrroles 10:



10a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, dd, J = 14.7, 11.2 Hz), 7.39 (2H, t, J = 2.4 Hz), 6.67 (1H, dd, J = 14.9, 11.0 Hz), 6.57 (1H, d, J = 14.9 Hz), 6.34 (1H, dd, J = 14.7, 11.0 Hz), 6.32 (2H, t, J = 2.4 Hz), 6.21 (1H, ddq, J = 15.1, 11.2, 1.4 Hz), 6.03 (1H, dq, J = 15.1, 7.0 Hz), 1.87 (3H, d, J = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 148.0, 143.4, 136.9, 131.3, 127.7, 119.3, 117.5, 113.2, 18.9; IR (film): 3148, 3022, 1682, 1599, 1587, 1466, 1406, 1356, 1281, 1113, 1070, 1003, 937 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{14}NO$ ([M+H]$^+$) 188.1070. Found 188.1071.

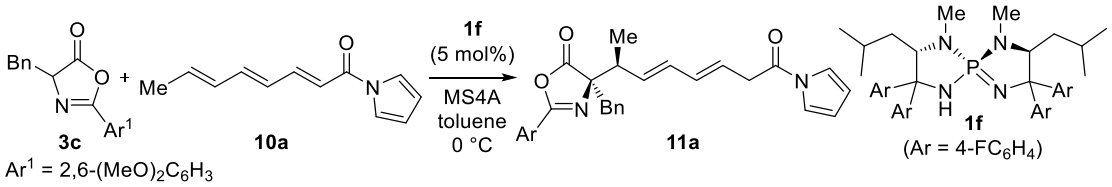


10b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, dd, J = 14.8, 11.1 Hz), 7.39 (2H, t, J = 2.4 Hz), 6.67 (1H, dd, J = 14.8, 11.0 Hz), 6.56 (1H, d, J = 14.8 Hz), 6.35 (1H, dd, J = 14.8, 11.0 Hz), 6.32 (2H, t, J = 2.4 Hz), 6.18 (1H, dd, J = 15.4, 11.1 Hz), 6.02 (1H, dt, J = 15.4, 7.0 Hz), 2.17 (2H, q, J = 7.0 Hz), 1.49-1.36 (2H, m), 1.36-1.19 (8H, m), 0.89 (3H, t, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 148.0, 143.6, 142.5, 129.9, 127.8, 119.3, 117.5, 113.2, 33.3, 31.9, 29.3$_2$, 29.2$_6$, 29.1, 22.8, 14.2; IR (film): 2916, 2847, 1678, 1612, 1587, 1472, 1463, 1410, 1368, 1296, 1128, 1070, 995, 941 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{26}NO$ ([M+H]$^+$) 272.2009. Found 272.2009.

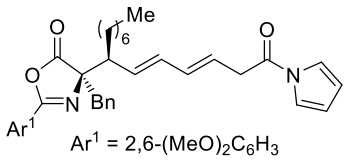


10c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, dd, J = 15.1, 11.1 Hz), 7.39 (2H, t, J = 2.3 Hz), 7.37-7.27 (5H, m), 6.72 (1H, dd, J = 14.9, 11.1 Hz), 6.60 (1H, d, J = 14.9 Hz), 6.49-6.38 (2H, m), 6.32 (2H, t, J = 2.3 Hz), 6.08 (1H, dt, J = 15.6, 5.8 Hz), 4.55 (2H, s), 4.14 (2H, d, J

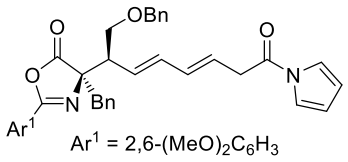
= 5.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 147.3, 142.0, 138.1, 136.0, 131.0, 130.0, 128.6, 127.9, 119.3, 118.7, 113.3, 72.7, 70.0, one carbon was not found probably due to overlapping; IR (film): 3150, 2868, 1682, 1599, 1582, 1470, 1350, 1283, 1105, 1061, 1001, 937 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{20}NO_2$ ([M+H]$^+$) 294.1489. Found 294.148.



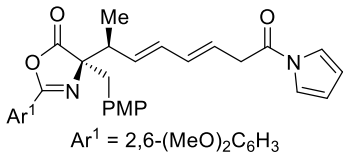
Representative Procedure for Asymmetric 1,8-Addition of Azlactone 3 to Trienyl *N*-Acylpyrrole 10 with Chiral Iminophosphorane 1f as a Catalyst: A test tube was charged with a magnetic stirrer bar and MS4A (100.0 mg) under argon atmosphere. MS4A was then dried with heat gun under reduced pressure for 5 min and the test tube was refilled with argon. Azlactone **3c** (31.13 mg, 0.10 mmol) and trienyl *N*-acylpyrrole **10a** (20.60 mg, 0.11 mmol) were added to the test tube, and dissolved in toluene (1.0 mL). After cooling to 0 °C, a solid of chiral iminophosphorane **1f** was added slowly. After being stirred for 10 h, a solution of trifluoroacetic acid in toluene (0.5 M, 50 μL) was then introduced to the reaction mixture to quench the reaction. The whole mixture was passed through a pad of Celite with the aid of toluene to remove MS4A and the filtrate was concentrated. The regio- and diastereomeric ratio of adducts were determined by ^{1}H NMR analysis in $(CD_3)_2CO$. Subsequent purification by colomn chromatography on silica gel (H/EA = 1:1 as eluent) gave the adduct in 89% yield as a mixture of isomers. The enantiomeric excess of 1,8-adduct **11a** was determined by HPLC analysis. **11a:** HPLC IC, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 254 nm, 28.2 min (major isomer of major diastereomer), 33.5 min (minor isomer of major diastereomer); ^{1}H NMR [400 MHz, $(CD_3)_2CO$] major diastereomer δ 7.43 (2H, t, J = 2.4 Hz), 7.40 (1H, t, J = 8.5 Hz), 7.30-7.21 (3H, m), 7.21-7.12 (2H, m), 6.65 (2H, d, J = 8.5 Hz), 6.43-6.31 (2H, m), 6.29 (2H, t, J = 2.4 Hz), 5.93 (1H, dt, J = 14.8, 7.0 Hz), 5.84 (1H, dd, J = 14.5, 9.4 Hz), 3.81 (2H, d, J = 7.0 Hz), 3.68 (6H, s), 3.23 (1H, d, J = 13.7 Hz), 3.05 (1H, d, J = 13.7 Hz), 2.82 (1H, dq, J = 9.4, 6.9 Hz), 1.11 (3H, d, J = 6.9 Hz); ^{13}C NMR [101 MHz, $(CD_3)_2CO$] major diastereomer δ 180.8, 169.5, 159.9, 157.7, 136.0, 134.7, 134.4, 133.7, 133.0, 131.4, 128.7, 127.6, 125.5, 120.0, 113.6, 107.0, 104.6, 78.3, 56.3, 45.5, 42.6, 38.6, 16.0; IR (liq. film): 2934, 2841, 1805, 1715, 1674, 1595, 1476, 1331, 1304, 1258, 1113, 961 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{31}N_2O_5$ ([M+H]$^+$) 499.2227. Found 499.2229.



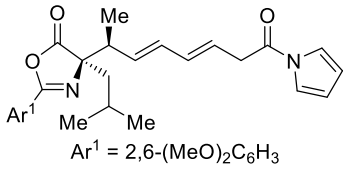
11b: HPLC IA, H/IPA/EtOH = 48:1:1, flow rate = 0.5 mL/min, λ = 210 nm, 44.2 min (minor isomer of major diastereomer), 56.7 min (major isomer of major diastereomer); ^{1}H NMR [400 MHz, $(CD_3)_2CO$] major diastereomer δ 7.43 (2H, t, J = 2.5 Hz), 7.40 (1H, t, J = 8.4 Hz), 7.30-7.20 (3H, m), 7.20-7.08 (2H, m), 6.66 (2H, d, J = 8.4 Hz), 6.41 (1H, dd, J = 14.4, 10.1 Hz), 6.39 (1H, dd, J = 14.4, 10.1 Hz), 6.29 (2H, t, J = 2.5 Hz), 5.95 (1H, dt, J = 14.4, 6.7 Hz), 5.70 (1H, dd, J = 14.4, 10.4 Hz), 3.82 (2H, d, J = 6.7 Hz), 3.69 (6H, s), 3.24 (1H, d, J = 13.7 Hz), 3.00 (1H, d, J = 13.7 Hz), 2.62 (1H, ddd, J = 12.4, 10.4, 2.0 Hz), 1.62-1.46 (1H, m), 1.46-1.16 (11H, m), 0.87 (3H, t, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 180.7, 168.6, 159.2, 157.6, 134.9, 134.3, 133.7, 133.0, 132.8, 130.8, 128.0, 126.8, 123.4, 119.2, 113.4, 105.7, 103.6, 78.0, 55.8, 51.2, 42.4, 38.5, 32.0, 29.9, 29.7, 29.3, 27.6, 22.7, 14.2; IR (liq. film): 2926, 2855, 1805, 1717, 1674, 1595, 1476, 1341, 1300, 1258, 1115, 961, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{36}H_{43}N_2O_5$ ([M+H]$^+$) 583.3166. Found 583.3165.



11c: HPLC AD3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 254 nm, 22.4 min (major isomer of major diastereomer), 35.6 min (minor isomer of major diastereomer); ^{1}H NMR [400 MHz, $(CD_3)_2CO$] major diastereomer δ 7.43 (2H, t, J = 2.4 Hz), 7.37 (1H, t, J = 8.6 Hz), 7.34-7.17 (8H, m), 7.17-7.09 (2H, m), 6.63 (2H, d, J = 8.6 Hz), 6.52 (1H, dd, J = 15.3, 10.5 Hz), 6.39 (1H, dd, J = 15.3, 10.5 Hz), 6.29 (2H, t, J = 2.4 Hz), 5.97 (1H, dt, J = 15.3, 7.0 Hz), 5.82 (1H, dd, J = 15.3, 9.6 Hz), 4.52 (1H, d, J = 12.2 Hz), 4.44 (1H, d, J = 12.2 Hz), 3.82 (2H, d, J = 7.0 Hz), 3.72 (1H, t, J = 9.6 Hz), 3.64 (6H, s), 3.44 (1H, dd, J = 9.6, 5.8 Hz), 3.25 (1H, d, J = 13.7 Hz), 3.21 (1H, td, J = 9.6, 5.8 Hz), 2.99 (1H, d, J = 13.7 Hz); ^{13}C NMR [101 MHz, $(CD_3)_2CO$] major diastereomer δ 180.3, 169.4, 160.0, 158.3, 139.5, 135.6, 135.5, 134.5, 133.6, 131.7, 129.8, 128.9, 128.5, 127.9$_3$, 127.8$_8$, 127.5, 126.2, 120.0, 113.6, 107.0, 104.6, 75.0, 73.1, 71.1, 56.2, 51.4, 42.9, 38.6; IR (liq. film): 2934, 2839, 1809, 1715, 1668, 1595, 1476, 1335, 1298, 1256, 1111, 959, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{37}H_{37}N_2O_6$ ([M+H]$^+$) 605.2646. Found 605.2645.



11d: HPLC AD3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 254 nm, 62.3 min (minor isomer of major diastereomer), 76.7 min (major isomer of major diastereomer); ^{1}H NMR [400 MHz, $(CD_3)_2CO$] major diastereomer δ 7.43 (2H, t, J = 2.3 Hz), 7.40 (1H, t, J = 8.2 Hz), 7.06 (2H, d, J = 9.0 Hz), 6.81 (2H, d, J = 9.0 Hz), 6.66 (2H, d, J = 8.2 Hz), 6.43-6.30 (2H, m), 6.29 (2H, t, J = 2.3 Hz), 5.93 (1H, dt, J = 14.3, 6.7 Hz), 5.83 (1H, dd, J = 14.1, 9.2 Hz), 3.81 (2H, d, J = 6.7 Hz), 3.77 (3H, s), 3.70 (6H, s), 3.16 (1H, d, J = 13.8 Hz), 2.98 (1H, d, J = 13.8 Hz), 2.79 (1H, dq, J = 9.2, 6.9 Hz), 1.10 (3H, d, J = 6.9 Hz); ^{13}C NMR [101 MHz, $(CD_3)_2CO$] major diastereomer δ 180.9, 169.5, 159.9, 159.5, 157.6, 134.7, 134.5, 133.6, 132.9, 132.4, 127.8, 125.5, 120.0, 114.0, 113.6, 107.0, 104.6, 78.5, 56.2, 55.3, 45.3, 41.8, 38.6, 16.1; IR (liq. film): 2938, 2839, 1805, 1678, 1595, 1512, 1476, 1329, 1250, 1113, 1030, 962 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{33}N_2O_6$ ([M+H]$^+$) 529.2333. Found 529.2335.



11e: HPLC AD3, H/IPA/EtOH = 93:5:2, flow rate = 1.0 mL/min, λ = 195 nm, 14.5 min (minor isomer of major diastereomer), 16.9 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.38 (1H, t, J = 8.4 Hz), 7.31 (1H, brs), 6.59 (2H, d, J = 8.4 Hz), 6.30 (2H, t, J = 2.3 Hz), 6.19 (1H, dd, J = 15.2, 10.6 Hz), 6.16 (1H, dd, J = 15.4, 10.6 Hz), 5.84 (1H, dt, J = 15.2, 6.7 Hz), 5.74 (1H, dd, J = 15.4, 9.3 Hz), 3.81 (6H, s), 3.63 (2H, d, J = 6.7 Hz), 2.62 (1H, dq, J = 9.3, 7.0 Hz), 2.01 (1H, dd, J = 17.2, 8.0 Hz), 1.80-1.60 (2H, m), 1.06 (3H, d, J = 7.0 Hz), 0.92 (3H, d, J = 6.2 Hz), 0.90 (3H, d, J = 6.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) major diastereomer δ 181.8, 168.6, 159.3, 157.5, 134.6, 134.5, 132.9, 131.7, 123.2, 119.3, 113.4, 106.3, 103.8, 75.8, 56.0, 45.3, 44.9, 38.6, 24.7, 24.5, 23.0, 15.3; IR (liq. film): 2959, 2841, 1803, 1717, 1678, 1595, 1476, 1337, 1306, 1258, 1113, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{33}N_2O_5$ ([M+H]$^+$) 465.2384. Found 465.2381.

Crystallographic Structure Determination: The single crystal, which was obtained by the procedure exemplified below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 93 K on a Rigaku VariMax with Saturn diffractometer with fine-focus sealed tube Mo/Kα radiation (λ = 0.71075 Å). An absorption correction was made using Crystal Structure. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[20] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen and oxygen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed

in calculated positions and isotropic thermal parameters refined.

Recrystallization of 6d: Recrystallization from a solution of **6d** in THF at room temperature afforded single crystals of **6d**. The crystallographic data were summarized in Table S1 and ORTEP diagram was shown in Figure S1.

Recrystallization of 9: Recrystallization from a solution of **9** in H/THF solvent system at room temperature afforded single crystals of **9**. The crystallographic data were summarized in Table S2 and ORTEP diagram was shown in Figure S2.

Table S1. Crystal data and structure refinement for **6d**.

Empirical formula	$C_{35}\ H_{34}\ N_2\ O_5,\ C_4\ H_8\ O$	
Formula weight	634.74	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.907(5) Å	α = 90°.
	b = 13.767(7) Å	β = 90°.
	c = 22.431(12) Å	γ = 90°.
Volume	3368(3) $Å^3$	
Z	4	
Density (calculated)	1.252 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	1352	
Crystal size	0.10 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.736 to 25.496°.	
Index ranges	–13<=h<=13, –14<=k<=16, –17<=l<=27	
Reflections collected	18170	
Independent reflections	5846 [R(int) = 0.0297]	
Completeness to theta = 25.242°	94.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.5129	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5846 / 0 / 426	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.1365	
R indices (all data)	R1 = 0.0562, wR2 = 0.1907	
Absolute structure parameter	-0.2(3)	
Extinction coefficient	0	
Largest diff. peak and hole 0	0.479 and –0.481 $e.Å^{-3}$	

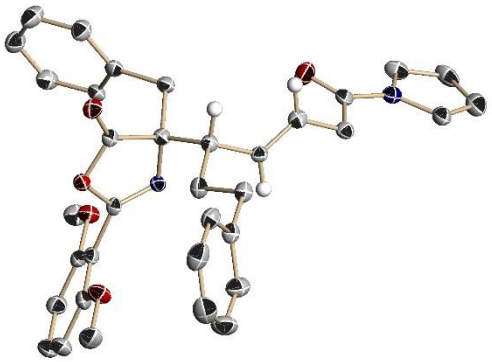


Figure S1. ORTEP diagram of **6d**. All calculated hydrogen atoms are omitted for clarity except for hydrogen atoms attached to the stereogenic center and olefinic carbons. Blue = nitrogen, red = oxygen, gray = carbon.

Table S2. Crystal data and structure refinement for **9**.

Empirical formula	$C_{38}\ H_{39}\ Cl_1\ N_2\ O_6$	
Formula weight	655.16	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.008(3) Å	α = 90°.
	b = 10.996(3) Å	β = 90°.
	c = 30.926(10) Å	γ = 90°.
Volume	3403.3(18) $Å^3$	
Z	4	
Density (calculated)	1.279 Mg/m^3	
Absorption coefficient	0.161 mm^{-1}	
F(000)	1384	
Crystal size	0.15 x 0.05 x 0.01 mm^3	
Theta range for data collection	3.051 to 25.496°.	
Index ranges	–12<=h<=12, –14<=k<=13, –36<=l<=40	
Reflections collected	24638	
Independent reflections	6308 [R(int) = 0.0526]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.8913	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6308 / 0 / 435	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0605, wR2 = 0.1519	
R indices (all data)	R1 = 0.0789, wR2 = 0.1739	
Absolute structure parameter	0.05(5)	
Extinction coefficient	0	
Largest diff. peak and hole 0	0.324 and –0.336 $e.Å^{-3}$	

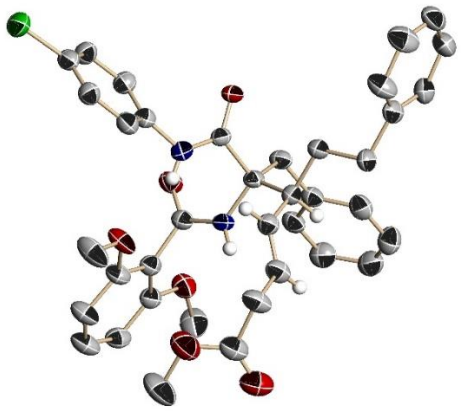


Figure S2. ORTEP diagram of **9**. All calculated hydrogen atoms are omitted for clarity except for hydrogen atoms attached to the stereogenic center and olefinic carbons. Blue = nitrogen, red = oxygen, light green = chlorine, gray = carbon.

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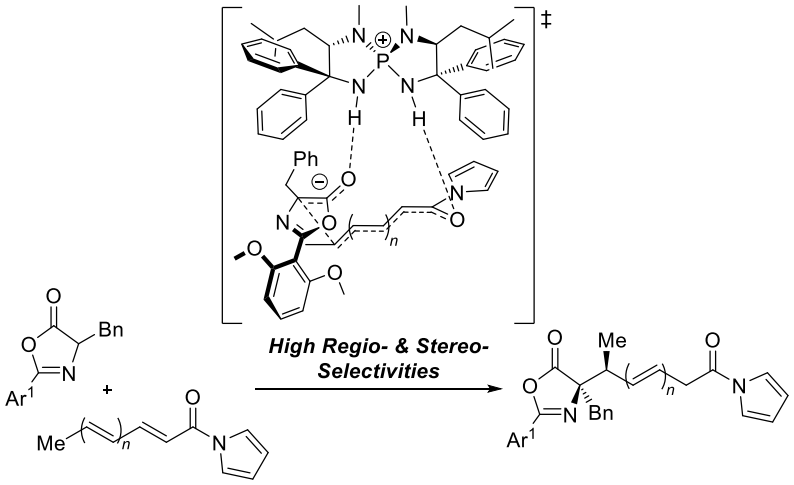
Chapter 3

Origin of High Regio-, Diastereo-, and Enantioselectivities in 1,6- and 1,8-Addition of Azlactones to Dienyl *N*-Acylpyrroles: Experimental and Computational Mechanistic Studies

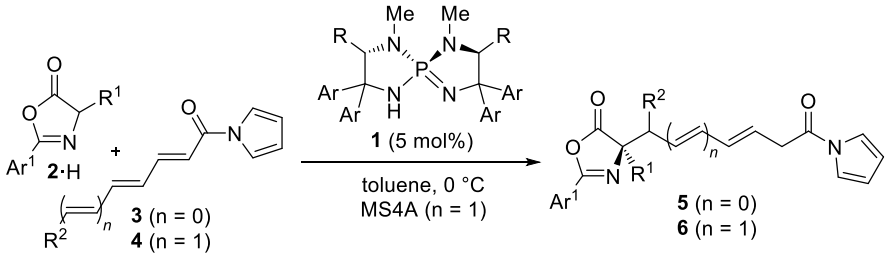


Abstract:

Chiral *P*-spiro triaminoiminophosphorane has been developed to promote the highly regio-, diastereo-, and enantioselective 1,6- and 1,8-additions of azlactones to di- and trienyl *N*-acylpyrroles. DFT calculations have enabled the auther to gain deep insight into the whole reaction mechanism as well as the origin of the high regio- and stereoselectivities. The C–C bond formation is irreversible and the rate- and stereodetermining step. The C^{α}-protonation of the resulting enolate anion preferentially proceeds rather than the thermodynamically and kinetically disfavored *O*- and C^{γ}-protonation. The hydrogen bonds (NH–O and CH–O) and the attractive CH–π interaction between catalyst and substrates play a key role in achieving high stereocontrol. The high regioselectivity is mainly controlled by the structural distortion of the catalyst and the disruption of the π-conjugated system of diene (1,4-system) and triene (1,4- and 1,6-systems).

3.1. Introduction

As described in chapter 2, the auther developed highly regio-, diastereo-, and enantioselective 1,6-addition controlled by a catalytic amount of chiral *P*-spiro triaminoiminophosphorane **1**, in which oxazol-5-(4H)-one **2**·H, i.e., azlactone, and *δ*-alkyl dienyl *N*-acylpyrroles **3** were used as the nucleophile and the electrophile, respectively (Scheme 1).[1] Furthermore, the same catalyst system was found to be highly effective for stereoselective 1,8-addition of **2**·H to trienyl *N*-acylpyrroles **4**. As the reactive sites of extended Michael acceptors **3** and **4** have similar stereoelectronic properties, the observed complete regioselectivity is facilitated by the core structure and the hydrogen-bonding ability of aminophosphonium ion **1**·H. On the other hand, the structures of α-amino acid-derived alkyl substituents (R) on the diazaphosphacycles of **1**·H were found to have a considerable impact on the diastereo- and enantioselectivities in the 1,6-selective reaction, and the isobutyl group was identified to be an optimal substituent. The aromatic substituent (Ar^1) at the 2-position of **2**·H also affects the stereochemical outcome of product **5**. Introduction of the 2,6-dimethoxyphenyl group was finally singled out to afford nearly ideal stereoselectivity. These experimental results have qualitatively indicated the importance of the entire structure of **1**·H. However, quantitative evaluation of the effect of each parameter on the selectivities has not been carried out so far. The auther describe herein him efforts to gain deep insight into the origin of the high selectivities in the **1**-catalyzed 1,6- and 1,8-additions of **2**·H to **3** and **4** through several control experiments and DFT calculations.



Scheme 1. Regio-, Diastereo-, and Enantioselective 1,6- and 1,8-Addition

3.2. Results and Discussion

From the initial experimental investigation, checking nonlinear effect, linear relationship between enantiomeric purity of the iminophosphorane catalysts and 1,6-adduct was showed, and this result suggested the participation of a single chiral aminophosphonium salt to the stereodetermining C–C bond-forming step (Figure 1 and Figure S1 in Experimental Section). For further experimental investigation, the auther employed the conjugate addition of azlactone **2** to electron-deficient tetraene **7** under the optimal condition in 1,8-addition. If this catalyst facilitates the addition from conjugate end, 1,10-addition (the addition from *θ*-position of **7**) would be occured. However, contrary to the expectation, the auther observed the mixture of 1,8-, 1,6-, and 1,4-adducts except for 1,10-adducts.

This result inspired the participation of carbonyl moiety of electrophile in the stereodetermining transition-state structure (Scheme 2).

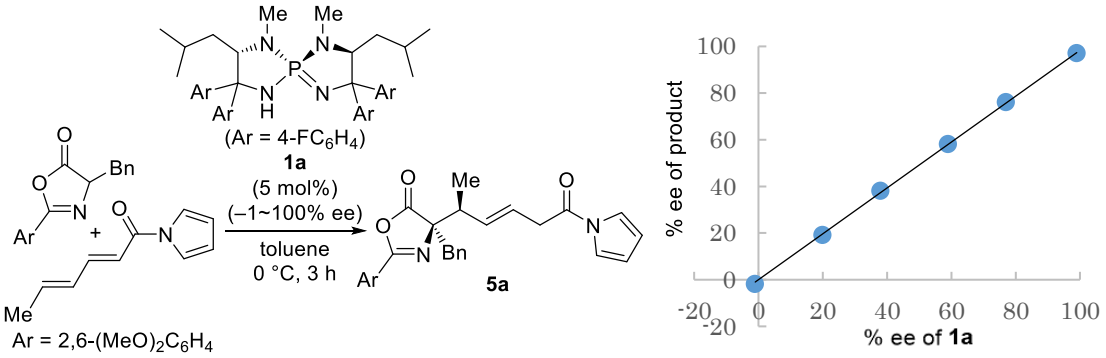
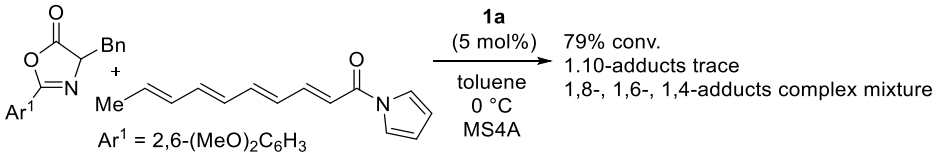
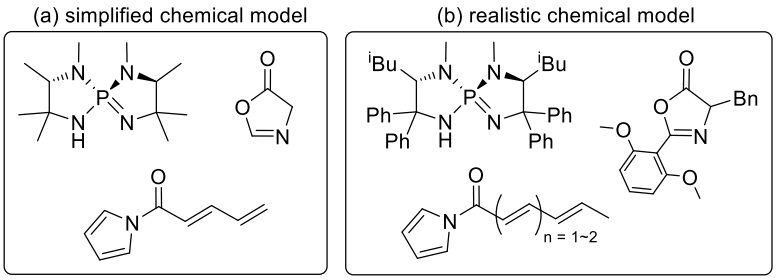


Figure 1. Linear Relationship between Enantiomeric Purity of **1a** and **5a**



Scheme 2. Conjugate Addition to Electron-Deficient Tetraene

For further exploration of reaction mechanism, quantum approach was employed through DFT calculation. All calculations were performed with the Gaussian 09 package.[2] Geometries were fully optimized and characterized by frequency calculation at the B3LYP/6-31G* level.[3] The molecular structures were depicted using the CYLview v1.0.561 *β*.[4] To elucidate the catalytic function of **1**, the reaction mechanism was investigated in detail using a simplified chemical model (Scheme 3a). In the simplified chemical model, the R and Ar substituents in **1** were exchanged with Me groups, and the R^1 and Ar^1 substituents in **2**·H and R^2 substituent in **3** were removed (by exchanging with H atoms) to reduce computational cost. Focusing on the regio- and stereodetermining C−C bond formation in the 1,6-addition system, diastereomeric transition state (TS) models were compared using a realistic chemical model to clarify the major factor contributing to the asymmetric induction (Scheme 3b).



Scheme 3. Chemical Models

As a preliminary study, the reaction mechanism in the 1,6-addition system was explored using the simplified chemical model (Figures 2 and 3). At the first step of the present reaction, phosphonium-enolate ion-pair complexes would be formed in equilibrium. *P*-Spiro iminophosphorane **Cat** abstracts the proton at the C^4-position in azlactone **AZ**·H to form ion-pair complex **CP1** through two-point hydrogen-bonding interaction between the two NH residues in protonated iminophosphorane **Cat**·H and the oxygen atom in enolate anion **AZ**. The introduction of *N*-acylpyrrole **AC** results in loss of the enolate coordination with one of the NH residues in **Cat**·H to further form complex **CP2**. In **CP2**, the phosphonium moiety (e.g., HN-P-NH) enables bridging between **AC** and **AZ**. At the next step, the C−C bond formation proceeds through **TS1**, which is the highest in energy and thus regarded as the rate- and stereodetermining step. Recently, Simón and Paton elucidated a related reaction mechanism for the asymmetric nucleophilic addition of nitroalkanes and phosphites to aldehydes catalyzed by *P*-spiro iminophosphorane **1** in their ONIOM QM/MM study.[5] At the final protonation step, there are three possible pathways, namely, *O*-protonation and *C*-protonation at the C^{α} and C^{γ} positions of the resulting enolate anion in **CP3**. The *O*-protonation is kinetically favored because of the lowest **TS2a** but affords the thermodynamically less stable *O*-protonated product **CP4a**. In contrast, the thermodynamically more stable *C*-protonated products are obtained, albeit with their higher energy barriers. Whereas the C^{γ}-protonated products **CP4d** and **CP4e** are thermodynamically more stable than the C^{α}-protonated products **CP4b** and **CP4c**, the C^{γ}-protonation **TS2d** and **TS2e** is energetically less favored than the C^{α}-protonation **TS2b** and **TS2c**. Both **TS2d** and **TS2e** are, in particular, located at the higher energy level of **TS1**. Two scenarios (shown in red and blue) are observed in C^{α}- and C^{γ}-protonation, depending on which of the two NH residues of the phosphonium moiety protonate the resulting enolate anion. In the most facile C^{α}-protonation, **TS2b** connects from **CP3'** generated through the rotation of the azlactone fragment of **CP3** (e.g., C^{γ}−C^{δ} bond rotation) with a small energy loss (ca. 5 kcal/mol activation barrier, **TS3−3'**). For C^{α}- and C^{γ}-protonation in **TS2b** and **TS2d** to occur, the hydrogen bond between the positively charged NH residue of **Cat**·H and **AZ** needs to dissociate. Therefore, C^{α}- and C^{γ}-protonation in **TS2b** and **TS2d** proceeds after breaking the hydrogen bond through the C^{γ}-C^{δ} bond rotation (**TS3−3'**) followed by generating **CP3'** as the directly connected complex to **TS2b** and **TS2d**. **TS2c** directly connected from **CP3** is less stable than **TS2b** due to loss of the strong hydrogen bond between the positively charged NH residue of **Cat**·H and the negatively charged oxygen atom of the resulting enolate anion. In the energetically unfavorable C^{γ}-protonation, both **TS2d** and **TS2e** are considerably destabilized by the mismatched position between C^{γ} and the carbonyl oxygen atoms on the two NH residues of **Cat**·H. These computational results using the simplified model indicate that (1) the C−C bond formation (**TS1**) is irreversible at the rate- and stereodetermining step and (2) C^{α}-protonation (**TS2b** and **TS2c**) is thermodynamically and kinetically more favorable than *O*-protonation (**TS2a**) and C^{γ}-protonation (**TS2d** and **TS2e**), respectively. Solvation exerts little influence on the energy profile because of the

intramolecular chemical transformations (C−C bond formation and protonation) in the unimolecular ion-pair system. The energy profile in solution using polarizable continuum model (PCM) is shown in the Experimental Section.

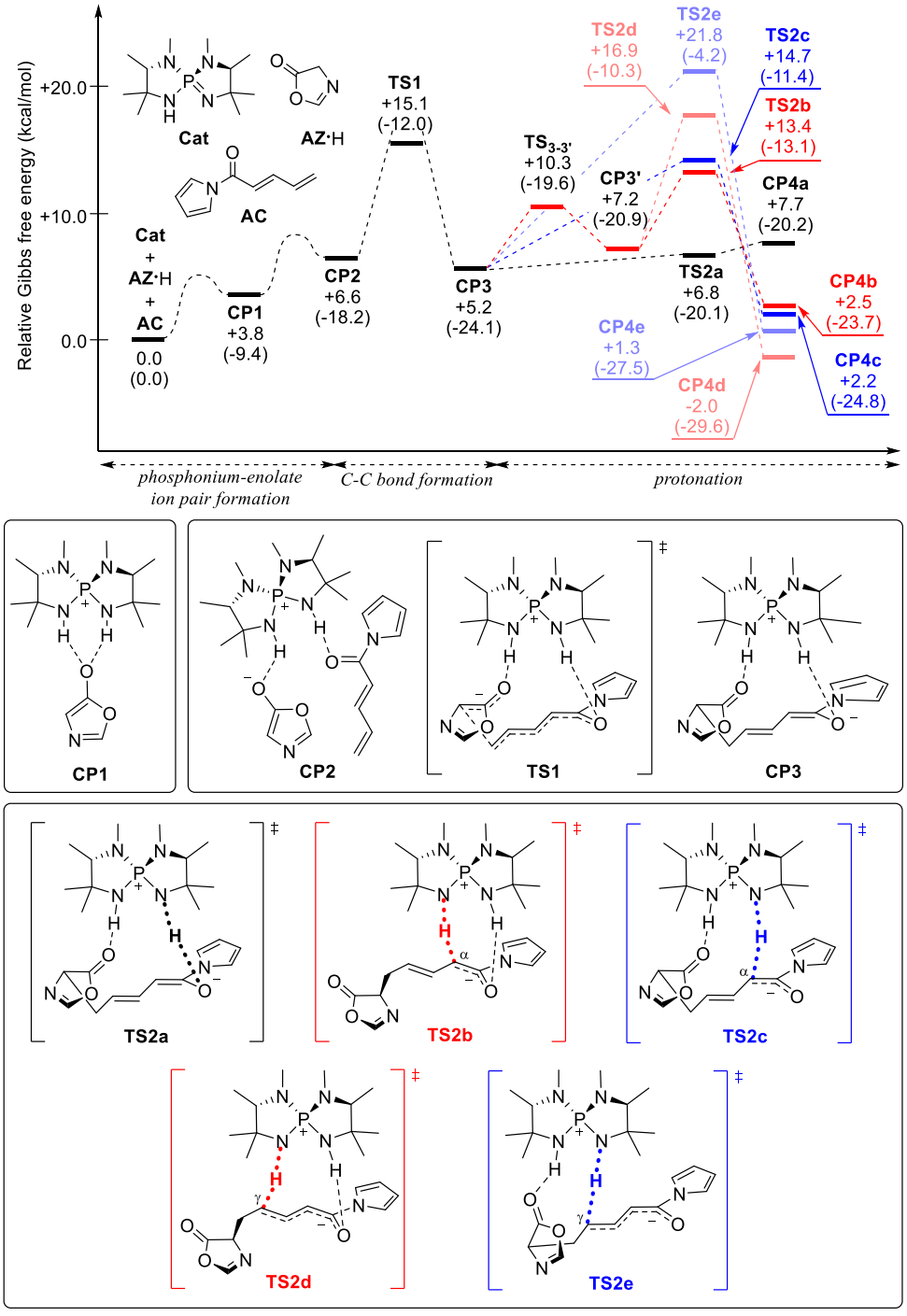


Figure 2. Gibbs Energy Profile of 1,6-Addition of **AZ**·H to **AC** Catalyzed by **Cat**. Relative electronic energies are in parentheses (kcal/mol).

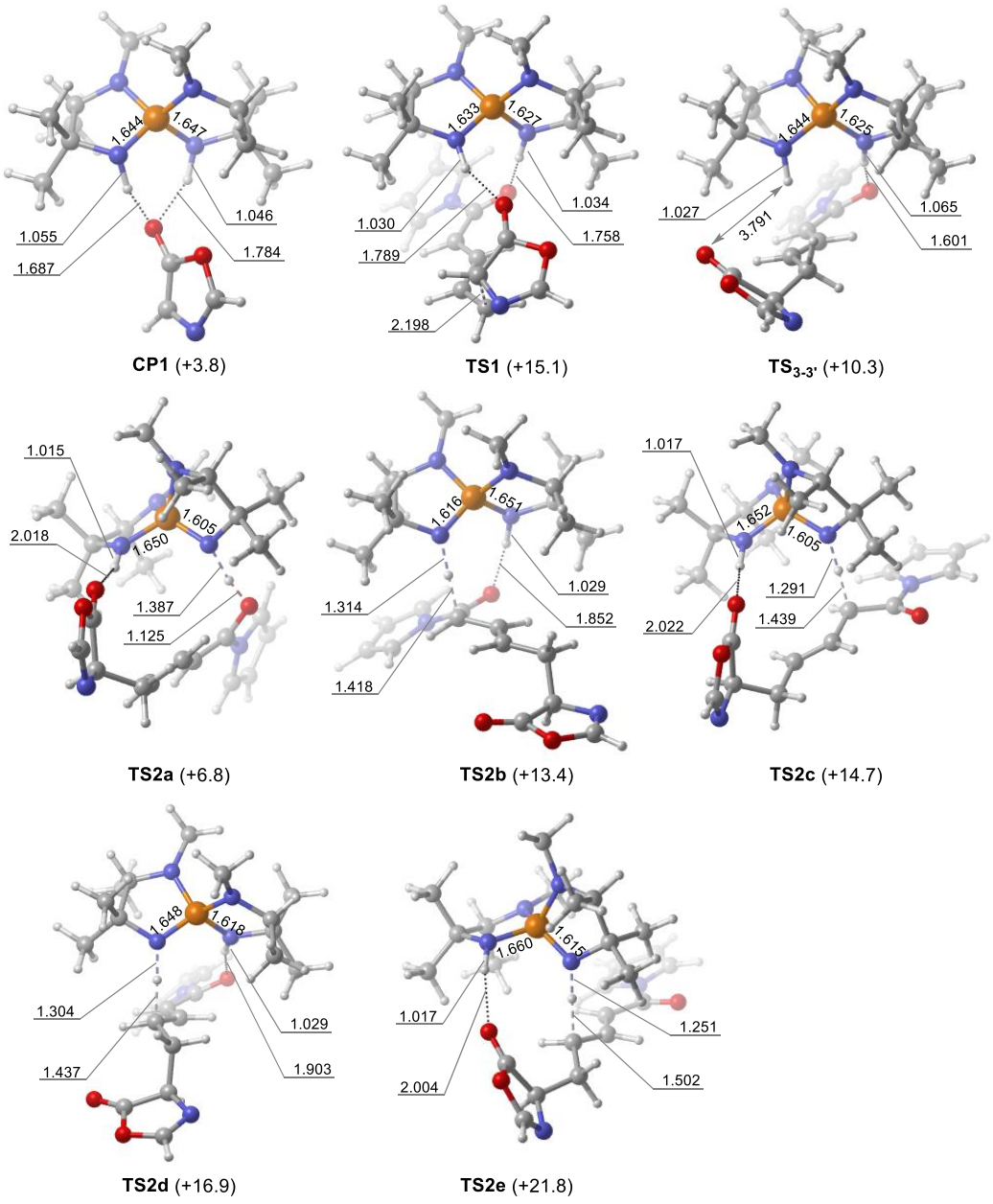


Figure 3. 3D Structures of the Ion-Pair Complex (**CP1**), the C−C Bond Formation (**TS1**), the C^{γ}-C^{δ} Bond Rotation (**TS3−3'**), and the *O*-/*C*-Protonation (**TS2a**, **TS2b**, **TS2c**, **TS2d**, and **TS2e**). Relative Gibbs free energies are shown in parentheses (kcal/mol). Bond lengths are shown in Å

To gain deep insight into the high regio- and stereoselectivities, therefore, the diastereomeric TS structures were investigated using the realistic model based on **TS1**. To identify the notable features of phosphonium ion **1**·H as the stereocontroller, the electrostatic potentials were computed (Figure 4). Four Ph groups (A and B rings) create a considerably narrow and rigid chiral space (shown by dotted purple circle). The two NH residues are not in plane (H−N−N−H dihedral angle: 103°) and are most positively charged to act as acidic sites. Therefore, **1**·H is predicted to tightly capture both substrates

on the NH residues and precisely control the regio- and stereochemical outcome through the steric interaction with four Ph groups.

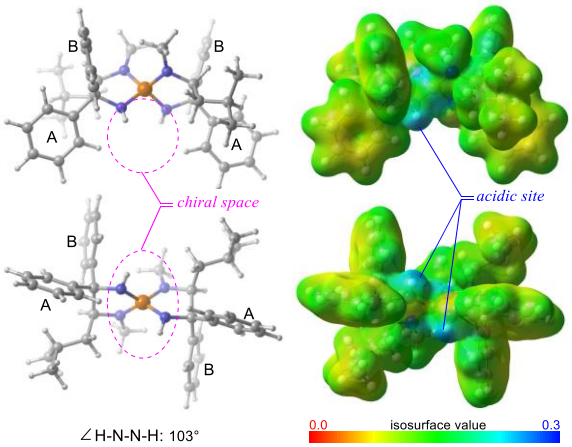


Figure 4. Front and Bottom Views of 3D Structure and Electrostatic Potentials of Protonated *P*-Spiro Iminophosphorene **1**·H

To identify the major factor contributing to the asymmetric induction in the 1,6-addition of **2**·H to **3** catalyzed by **1**, four diastereomeric TS structures corresponding to the facial selection of **2** and **3** [leading to major and minor enantiomers of major diastereomers (**TS3rs** and **TS3sr**) and minor diastereomers (**TS3ss** and **TS3rr**)] were compared (Figure 5). For the inclusion of dispersion correction in the realistic chemical model, single-point energy calculations of the optimized structures were conducted at the B3LYP-D3/6-31+G** level.[6] To evaluate more reliable relative Gibbs energies including dispersion corrections, zero-point energy corrections and thermal and entropic corrections calculated at the B3LYP/6-31G* level were added to the electronic energy calculated at the B3LYP-D3/6-31+G** level. Whereas **TS3rs** leading to the major enantiomer is the most stable among the four diastereomeric TSs, **TS3sr** leading to the minor enantiomer is 3.9 kcal/mol less stable than **TS3rs**. Diastereomeric **TS3ss** and **TS3rr** are 2.4 and 4.7 kcal/mol less stable than **TS3rs**.[7] These computational results are qualitatively consistent with the experimental results. In all the diastereomeric TSs, both enolate anion **2** and **3** are oriented almost perpendicular to the two Ph groups of **1**·H (A rings in Figure 4) due to the spatial requirement of the narrow space. The dihedral angles of H−N−N−H in the phosphonium center of **1**·H range from 76 ° to 85 ° to readily incorporate **2** and **3** in a manner suitable for facilitating 1,6-fashion. Both **2** and **3** fit the chiral space well in the most stable **TS3rs** (Figure 5a). Therefore, two main NH−O hydrogen bonds are formed between the NH residues of **1**·H and the negatively charged oxygen atoms of **2** and **3** (1.845 and 1.740 Å, respectively) in **TS3rs**. It should be noted that a CH−π interaction (3.033 Å) (see Experimental Section, for details) and a CH−O hydrogen bond (2.354 Å) exist on the A and B rings of **1**·H in addition to the main NH−O hydrogen bonds (shown in red, Figure 5a). The introduction of electron-withdrawing F

atom on the Ph group of **1** increases the acidity of the CH group to strengthen the CH−O hydrogen bonds and further stabilize **TS3rs**. This is consistent with the experimentally observed substituent effects of **1**. These rational hydrogen-bonding networks and the additional attractive dispersion interaction result in the stability of **TS3rs** being higher than those of the other diastereomeric TSs. In contrast, unfavorable steric interactions of the 2,6-$(MeO)_2C_6H_3$ group of **2** and the pyrrole ring of **3** with the B rings of **1**·H weaken the main NH−O hydrogen bonds (1.872 and 1.776 Å), thereby destabilizing **TS3sr** (shown by curved purple line, Figure 5b). The significant steric repulsion between the B ring and the ^{i}Bu group of **1**·H and the Bn and 2,6-$(MeO)_2C_6H_3$ groups of **2** reduces the main NH−O hydrogen bonding interactions (1.852 and 1.745 Å) and thus destabilizes **TS3rr** (shown by curved purple line, Figure 5d). Computational results suggest that **TS3sr** and **TS3rr** become more destabilized with increasing bulkiness of the alkyl substituent (R) in **1** and the aryl substituent (Ar^1) in **2**. This is qualitatively consistent with the experimentally observed tendency of the substituent effects of **1** and **2**. In a manner similar to that of **TS3rs**, both **2** and **3** are well-oriented in the chiral space in **TS3ss** without any significant unfavorable steric interactions (Figure 5c). Although the main NH−O hydrogen bonds efficiently form, there are no additional and notable CH−π and CH−O interactions in **TS3ss**. Whereas the CH−O hydrogen bonds on the A and B rings are in the range of ca. 2.5−2.8 Å, there is geometrically no possibility of the CH−π and π−π interactions in **TS2ss**. These computational results indicate that the attractive interactions between **1**·H and **2** and **3** are the fundamental factors that determine the stability of the diastereomeric TSs.

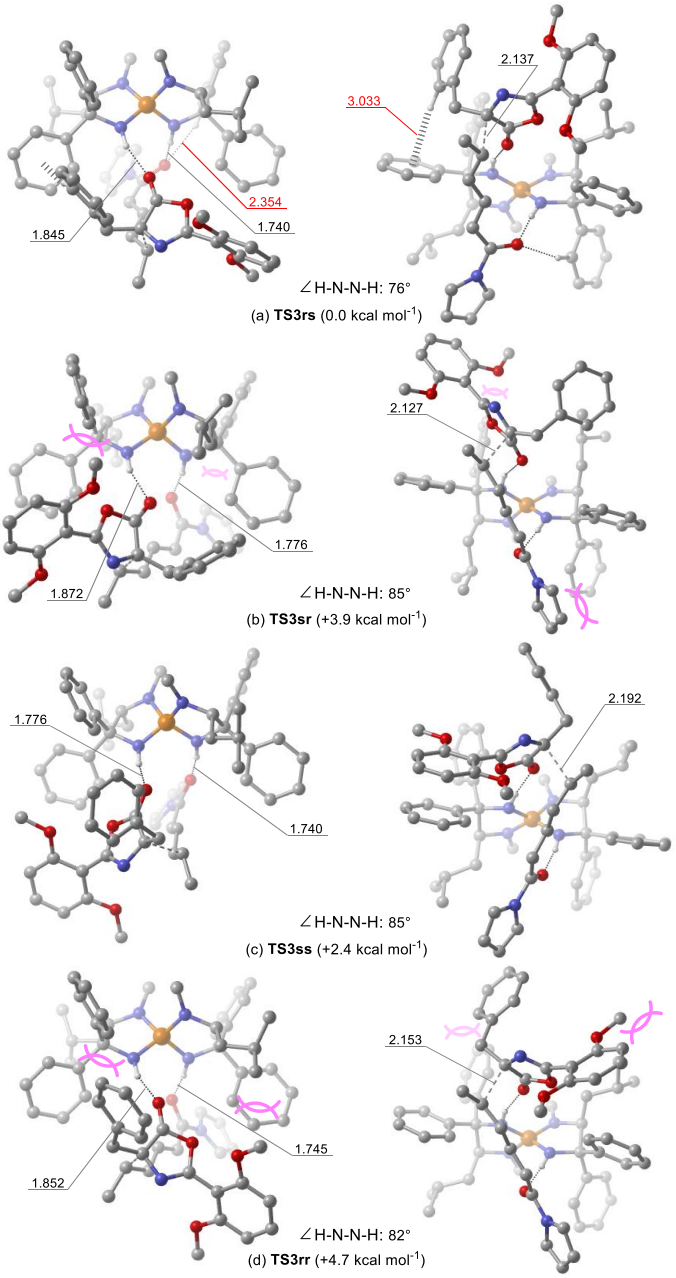


Figure 5. Front and Bottom Views of 3D Structures and the Relative Gibbs Free Energies of (a) **TS3rs**, (b) **TS3sr**, (c) **TS3ss**, and (d) **TS3rr**

To elucidate the origin of the high 1,6-selectivity, diastereomeric TSs in the 1,4-addition of **2**·H to **3** (**TS4**) were explored and compared with those of **TS3**. Four diastereomeric TSs in the 1,4-addition (**TS4rs**, **TS4sr**, **TS4rr**, and **TS4ss**) are located at energy levels higher than that of **TS3** in agreement with the experimentally observed high 1,6-selectivity. In contrast to **TS3**, the most stable TS among the four diastereomeric TSs is **TS4ss**, in which the facial selectivity of **2** is reversed relative to that of the most stable **TS3rs** (Figure 6). The difference in the electrophilic carbon center of **3** (e.g., C^{β}) induces significant structural changes, in particular, the relative orientation of **3**, in the diastereomeric

TSs albeit retaining the strong main NH−O hydrogen bonds whose lengths range from ca. 1.7−1.9 Å (Figure S4 in the Experimental Section). No steric repulsion is noted between **1**·H and **2** and **3** in **TS4ss**. In comparison with **TS3ss**, the *N*-acyl group is close to the phosphonium center of **1**·H to form the CH−O hydrogen bond (2.171 Å), thereby stabilizing **TS4ss**. The two NH residues of **1**·H forming the NH−O hydrogen bonds are considerably distorted in **TS4ss** (H−N−N−H dihedral angle: 55 °) relative to the optimized **1**·H structure (H−N−N−H dihedral angle: 103 °).

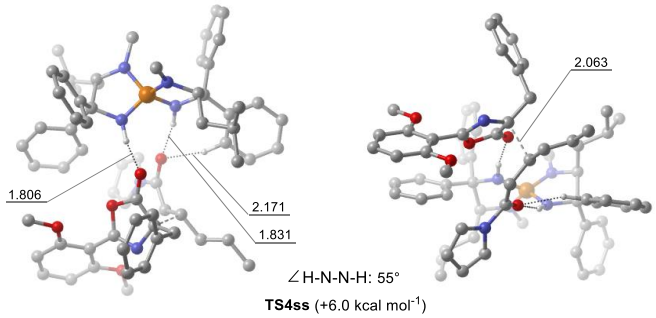
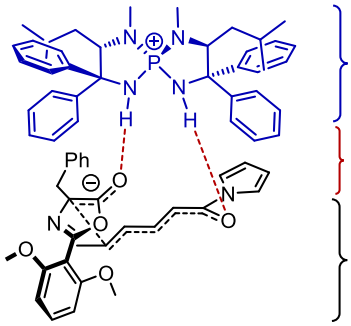


Figure 6. Front and Bottom Views of 3D Structure of **TS4ss**. The relative Gibbs free energy of **TS4ss** to **TS3rs** is shown in parentheses.

To identify the main factor in controlling regio- and stereoselectivities, the distortion/interaction analysis[8] of diastereomeric TSs was carried out (Table 1). The high stereoselectivity (**TS3rs** vs **TS3sr**, **TS3ss**, and **TS3rr**) is mainly due to the interaction energy difference between **1**·H and **2** and **3** (ΔINT). Whereas ΔINT has a large impact on the relative stability of diastereomeric **TS3** structures, the distortion energy difference (ΔDEF_{cat} and ΔDEF_{sub}) exerts little influence. This is attributed to the notable structural features that **1**·H has the rigid chiral space (Figure 4) and **2** and **3** have highly conjugated structures. In contrast to stereoselectivity control, ΔDEF_{sub} preferentially contributes to the high 1,6-selectivity (**TS3rs** vs **TS4ss**). The 1,4-addition disrupts the π-conjugated system between C=C and C=O bonds in **3**, inducing significantly large ΔDEF_{sub} in **TS4ss**.

Table 1. Distortion/Interaction Analysis of **TS3rs**, **TS3sr**, **TS3ss**, **TS3rr**, and **TS4ss**.



TS	ΔDEF_{cat}	ΔDEF_{sub}	ΔINT
TS1,6$_{rs}$	0.0	0.0	0.0
TS1,6$_{sr}$	0.1	0.1	3.9
TS1,6$_{ss}$	0.5	0.1	3.5
TS1,6$_{rr}$	0.0	0.0	3.8
TS1,4$_{ss}$	2.2	**4.2**	1.1

ΔDEF = DEF(**TS**) - DEF(**TS3rs**) /kcal mol^{-1}

ΔINT = INT(**TS**) - INT(**TS3rs**) /kcal mol^{-1}

The auther further addressed the high regioselectivity in the 1,8-addition of **2**·H to **4** catalyzed by **1**. Diastereomeric TS structures related to the 1,8- (**TS5**), 1,6- (**TS6**), and 1,4-addition (**TS7**) were explored based on the realistic model study of the 1,6-addition system (Figure 7). As a preliminary study, the diastereomeric TSs, including all s-trans, s-trans/s-cis, and all s-cis conformers of **4**, were explored using the simplified chemical model (Figure S5 in the Experimental Section). On the basis of the most stable TS, including all s-trans conformer of **4**, the relative energies of the most stable diastereomeric TSs for 1,8- (**TS5rs**), 1,6- (**TS6rs**), and 1,4-addition (**TS7ss**) were compared. **TS5rs** is the most stable TS, in good agreement with the preference for the 1,8-addition observed in the experimental results. As expected from the experimental results leading to the same absolute structure of the major enantiomer in both 1,8- and 1,6-addition systems, a similar structural tendency is found in both **TS5** and **TS6**. Both **2** and **4** fit the chiral space well with additional CH−π and CH−O interactions in **TS5rs** and **TS6rs**, respectively (Figures 7a and b). Diastereomeric **TS7** structures have structural properties similar to that of **TS4**, and **TS7ss** is the most stable (Figure 7c).

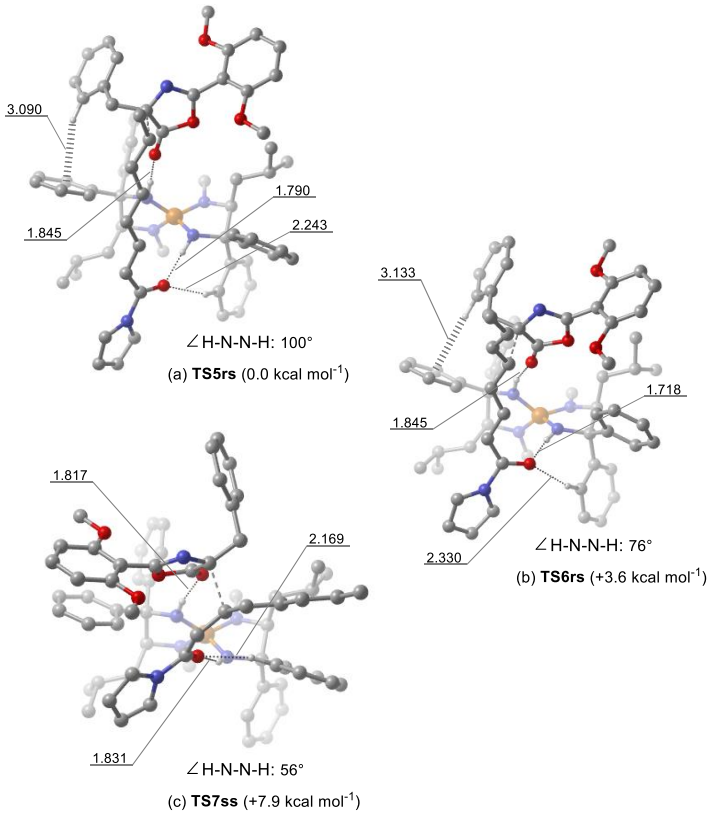


Figure 7. Front Views of 3D Structures and the Relative Gibbs Free Energies of (a) **TS5rs**, (b) **TS6rs**, and (c) **TS7ss**.

The distortion/interaction analysis indicates that distortion energy differences (ΔDEF_{cat}, ΔDEF_{sub}) significantly contribute to the relative stability of the diastereomeric TSs (Figure 8). The large

ΔDEF_{sub} of **TS6rs** and **TS7ss** in particular are attributed to distortion destabilization through the disruption of the π-conjugated system between C=C and C=O bonds. On the other hand, ΔDEF_{cat} of **TS6rs** and **TS7ss** makes a non-negligible contribution to the relative stability of the diastereomeric TSs. The two NH residues of **1**·H forming the NH−O hydrogen bonds are considerably distorted from the optimized **1**·H structure (H−N−N−H dihedral angle: 103 °) in the order of TS7ss (56 °) > TS6rs (76 °) > TS5rs (100 °). The dihedral angle between the two NH residues depends on the distance between the two oxygen atoms of **2** and **4**. In **TS5rs**, the relative orientation of **2** and **4** is suitable for the optimized location of the two NH residues of **1**·H.

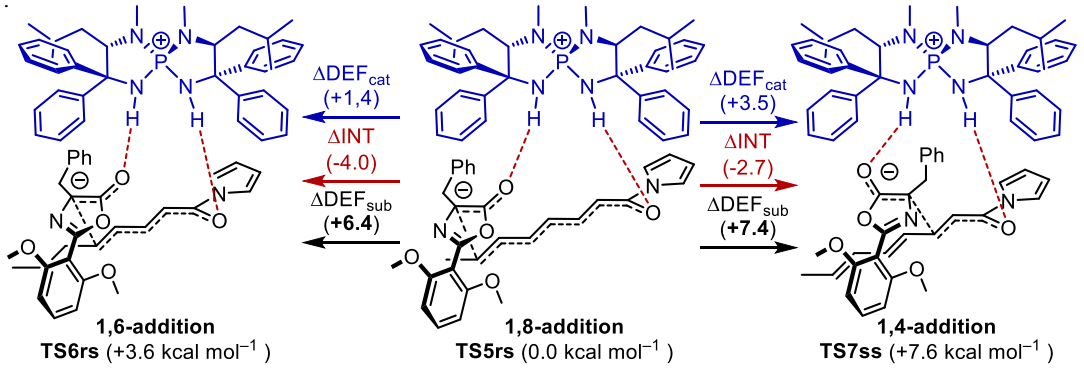


Figure 8. Distortion/Interaction Analysis of **TS5rs**, **TS6rs**, and **TS7ss**

3.3. Conclusion

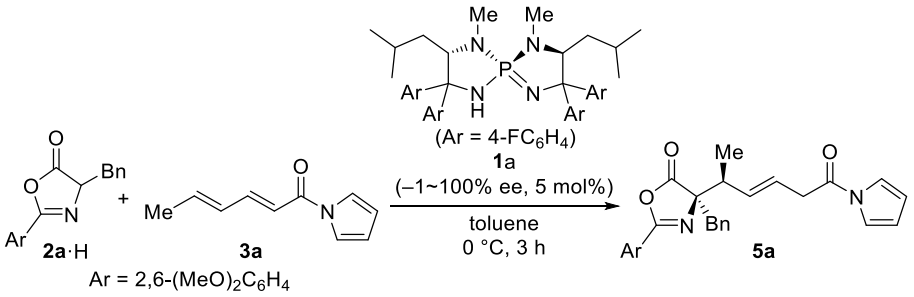
DFT calculations of the asymmetric 1,6- and 1,8-additions of **2**·H to **3** and **4** catalyzed by **1** were carried out to elucidate the whole reaction mechanism as well as the origin of the high regio- and stereocontrolling ability of **1**. The rate- and stereodetermining C−C bond formation (**TS1**) proceeds through the formation of phosphonium-enolate ion-pair complexes (**CP1**, and **CP2**). The C^{α}-protonation of the resulting enolate anion (**TS2b** and **TS2c**) is energetically favored over the C^{γ}-protonation (**TS2d** and **TS2e**) involving a high energy barrier and the reversible *O*-protonation (**TS2a**). The C^{α}-protonated product is eventually obtained along with the regeneration of **1**. The high regio- and enantioselectivities in the 1,6-addition system are attributed to the notable steric and electronic features of **1**·H and **3**. The hydrogen bonds (NH−O and CH−O) and the attractive CH−π interaction between **1**·H and **2** and **3** play a crucial role in achieving high stereocontrol. There exist rational catalyst−substrate interaction networks with no unfavorable steric interactions in **TS3rs**, leading to the major enantiomer. Steric repulsion together with the narrow and rigid chiral space constructed by the four Ph groups of **1**·H decreases the NH−O hydrogenbonding interaction and destabilizes other diastereomeric TSs, leading to the minor enantiomer and diastereomer. On the other hand, the distortion energy difference of **3** mainly contributes to the high regiocontrol. The large distortion of **3** in **TS4ss** (1,4-addition) originates in the disruption of the π-conjugated system. In a manner similar to that of the 1,6-addition system, the catalyst-substrate interaction networks are a fundamental factor

in controlling stereoselectivity in the 1,8-addition system. The high 1,8-selectivity is achieved by the destabilization of **TS6rs** (1,6-addition) and **TS7ss** (1,4-addition), consisting of the structurally and electronically distorted **1**·H and **4**, respectively. These computational results provide deep insight into the high regio- and stereocontrolling ability of the precisely designed **1**.

3.4. Experimental Section

General Information: ^{1}H NMR spectra were recorded on a JEOL JNM-ECZ400S (400 MHz). Chemical shifts are reported in ppm from tetramethylsilane (0.0 ppm) resonance as the internal standard ($CDCl_3$). ^{31}P NMR spectra were recorded on a JEOL JNM-ECS400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 (0.0 ppm) resonance as the external standard. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on PSQ60AB (spherical, av. 55 μm; Fuji Silysia Chemical ltd.), Silica gel 60 (Merck 1.09385.9929, 230-400 mesh). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK IC-3 (IC3)] with hexane (H), 2-propanol (IPA), and ethanol (EtOH) as eluent.

Toluene, dichloromethane (CH_2Cl_2), and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Triaminoiminophosphorane **1**,[1] azlactones **2**·H,[9] dienylacylpyrroles **3**,[10] tetraenylacylpyrroles **7**[10] were prepared by following the literature procedure. Powdered 4A molecular sieves (MS4A) was supplied from Merck. Trifluoroacetic acid (TFA) and trifluoromethanesulfonic acid (TfOH) were kindly supplied from Asahi Glass Co., Ltd. and Central Glass Co., Ltd., respectively. Other simple chemicals were purchased and used as such.



Experimental Procedure for Investigating Correlation between the Enantiomeric Excess of Catalyst 1a and that of the 1,6-Adduct 5a: Azlactone **2a**·H (25.13 mg, 0.10 mmol) and dienylacylpyrrole **3a** (17.73 mg, 0.11 mmol) was dissolved into toluene (1.0 mL) under Ar atmosphere. Chiral iminophosphorane **1a** (3.40 mg, 5.0 μmol) was added portionwise at 0 °C, and the resulting reaction mixture was stirred for 3 h. The reaction was quenched by the addition of a solution of trifluoroacetic acid in toluene (0.5 M, 50.0 μL), and all volatiles were removed under reduced pressure to give a crude residue. The diastereomeric ratio of **5a** was determined by 1H NMR analysis (400 MHz). Subsequent purification by column chromatography on silica gel (H/EA = 1/1 as eluent) gave the adducts in >99% yield as a mixture of isomers. The enantiomeric excess of 1,6-adduct **5a** was determined by HPLC analysis.

%ee of **1a**	%yield of **5a**	dr of **5a**	%ee of **5a**
-1	>99	17:1	-2
20	>99	17:1	19
38	>99	20:1	38
59	>99	18:1	58
77	98	20:1	76
>99	>99	>20:1	97

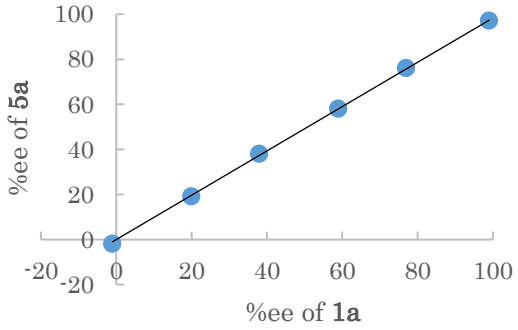
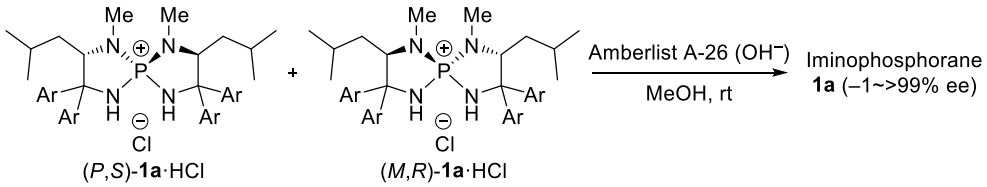
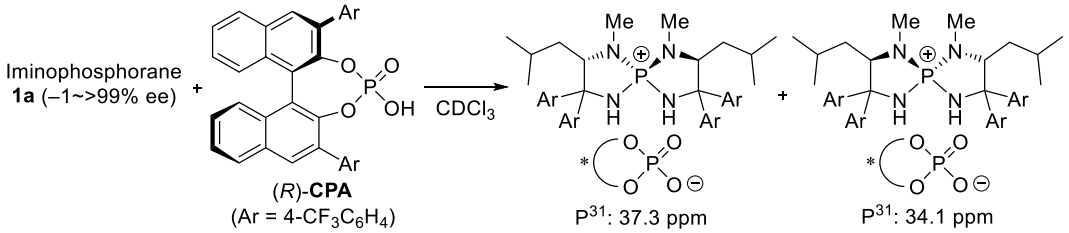


Figure S1. Correlation between % ee of **1a** and **5a**



Procedure for Preparation of Iminophosphorane 1a (−1~>99% ee): An appropriate ratio mixture of chiral tetraaminophosphonium chlorides (*P*,*S*)-**1a**·HCl and (*M*,*R*)-**1a**·HCl was placed into a sample tube, and the mixture was dissolved into methanol. The methanolic solution was passed through a column of ion-exchange resin (Amberlyst A-26 OH form) to afford a solution of iminophosphorane **1a** (−1~>99% ee). The resulting solution was concentrated by rotary evaporation, and residual solid was washed with deionized water on a funnel. The solid thus obtained was dried under reduced pressure to afford the iminophosphorane **1a** as a white solid. Enantiomeric excess of iminophosphorane **1a** was checked as follows.



A mixture of iminophosphorane **1a** (−1~>99% ee) and chiral phosphoric acid (*R*)-**CPA** was dissolved into $CDCl_3$. Enantiomeric excess of **1a** was determined by the integration ratio of diastereomeric phosphonium salts in ^{31}P NMR.

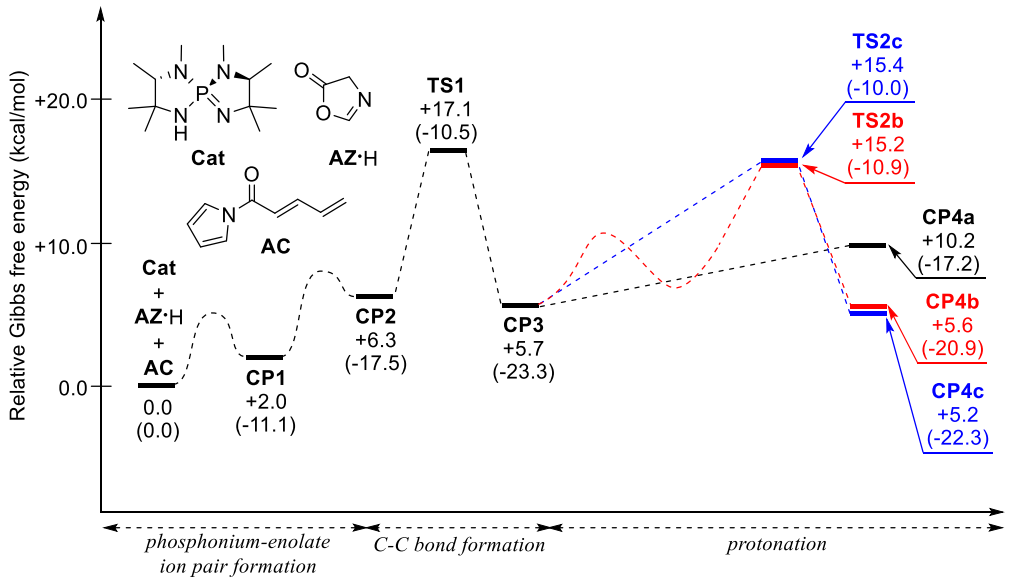
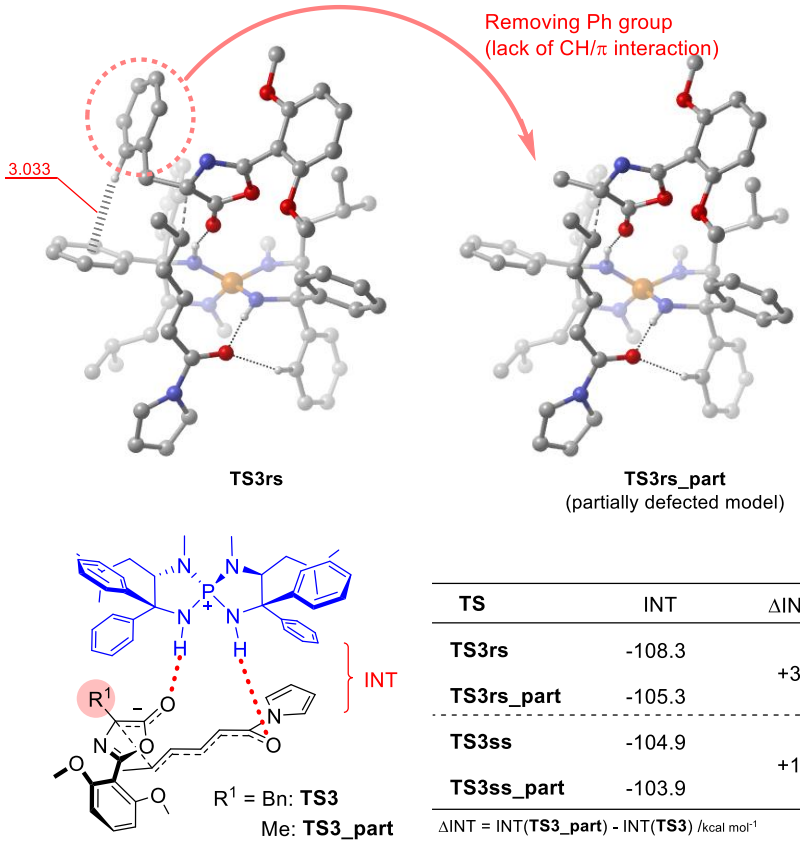


Figure S2. Gibbs Energy Profile in Solution of 1,6-Addition of **AZ**·H to **AC** Catalyzed by **Cat**. Relative electronic energies are in parentheses (kcal/mol)

All calculations were performed with the Gaussian 09 package.[2] Based on the gas phase calculation (Figure 2), typical local minima and TS structures were re-optimized at B3LYP/6-31G* with the polarized continuum model (PCM, toluene). Frequency with the polarized continuum model (PCM, toluene). Frequency calculation were carried out to characterize the stationary points and to estimate Gibbs free energies.



TS	INT	ΔINT
TS3rs	-108.3	+3.0
TS3rs_part	-105.3	
TS3ss	-104.9	+1.0
TS3ss_part	-103.9	

ΔINT = INT(**TS3_part**) - INT(**TS3**) /kcal mol^{-1}

Figure S3. The Catalyst/Substrate Interaction Energies (counterpoise method) of **TS3rs**, **TS3rs_part**, **TS3ss**, and **TS3ss_part**

To identify the contribution of the attractive CH/π interaction between Ph groups of **1**·H and **2** in **TS3rs**, the catalyst/substrate interaction energies in the full and the partially defected (removing Ph group of **2**) TS model **TS3rs_part** were calculated by the counterpoise method at the B3LYP-D3/6-31+G** level and compared. In the defected TS model, the H atom exchanged with the Ph group of **2** was partially optimized and all the other atoms were frozen at the same position as the optimized TS structure. The catalyst/substrate interaction energy of **TS3rs** is 2.0 kcal/mol larger than that of **TS3rs_part.** This energy difference is enough large to identify the non-covalent interaction (e.g., CH/π interaction) in comparison with the 1.0 kcal/mol energy difference between **TS3ss** and **TS3ss_part** as a reference value without notable CH/π and CH/O interactions.

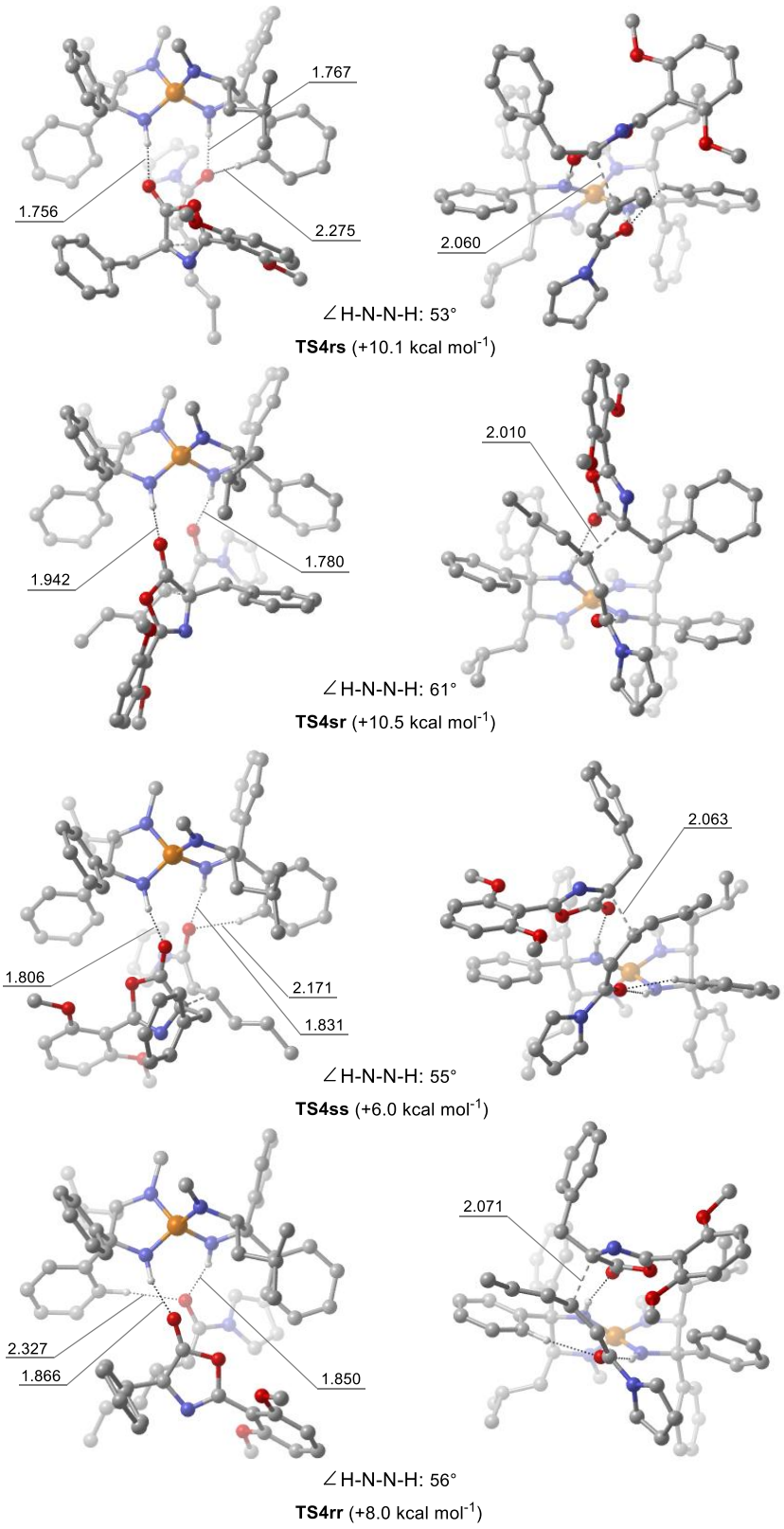


Figure S4. Front and Bottom View of 3D Structure of **TS4** Series. The relative Gibbs free energies of **TS4** series to **TS3rs** is shown in parentheses.

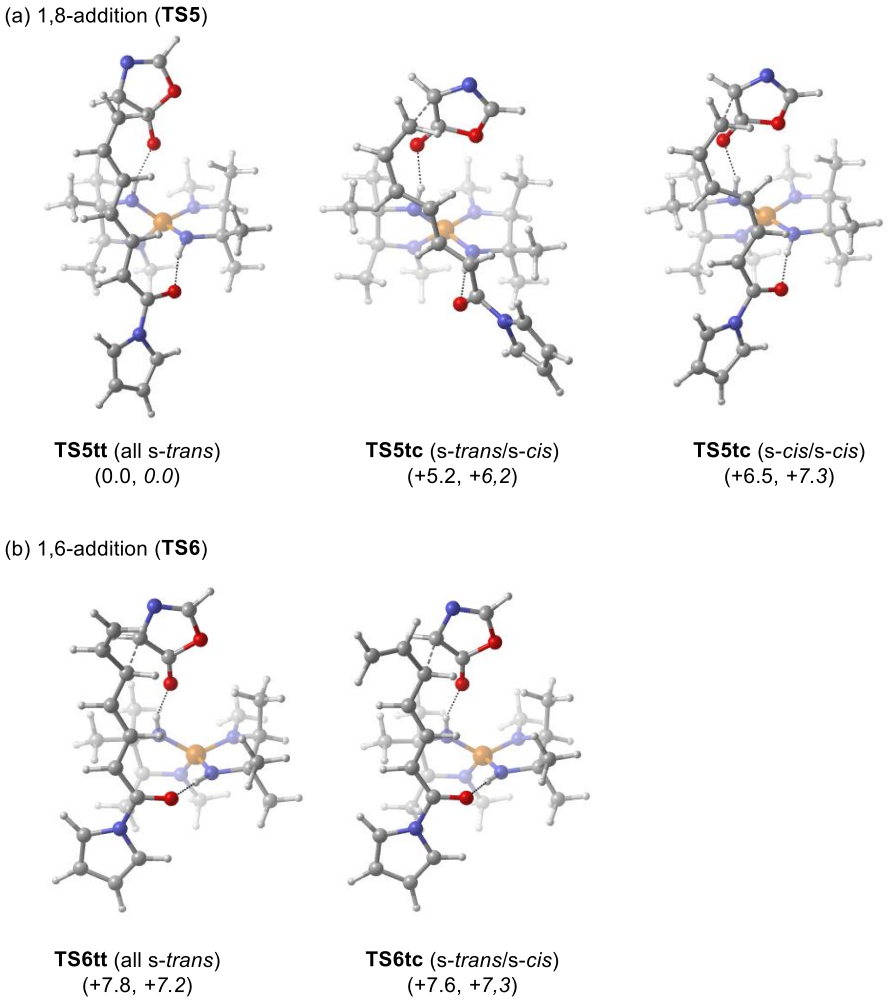


Figure S5. 3D Structures of (a) **TS5** (1,8-Addition) and (b) **TS6** (1,6-Addition) Including All s-trans (**tt**), s-trans/s-cis (**tc**), and all s-cis (**cc**) Conformers of **AC**. The relative energies to **TS5tt** are shown in parentheses (kcal/mol). The relative Gibbs free energies are in *italics*.

The 1,8-addition TS (**TS5tt**) including all s-trans conformer of **AC** is ca. 6~7 kcal/mol more stable than other TS including s-cis conformers (**TS5tc**, **TS5cc**) as well as 1,6-addition TSs (**TS6tt**, **TS6tc**).

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(7) Diasteromers of product should be stereoselectively obtained; however, it was not supplied with sufficient quantities for determining the enantiomeric excess.

(8) The energies of **TS-S** and **TS-R** were dissected into the distortion (DEF) and interaction energies (INT) for the two distorted fragments (catalyst and substrates) constructing TS. The differences for each energy (ΔDEF and ΔINT) between diastereomeric TSs were calculated by the counterpoise method at the B3LYP-D3/6-31+G** level. For the original distortion/interaction analysis, see: (a) Morokuma, K.; Kitaura, K. *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1981. (b) Ess, D. N.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 10646. (c) Ess, D. H.; Houk, K. N. *J. Am. Chem. Soc.* **2008**, *130*, 10187. (d) Lam, Y.-H.; Cheong, P. H.-Y.; Blasco Mata, J. M.; Stanway, S. J.; Gouverneur, V. R.; Houk, K. N. *J. Am. Chem. Soc.* **2009**, *131*, 1947. (e) Paton, R. S.; Kim, S.; Ross, A. G.; Danishefsky, S. J.; Houk, K. N. *Angew. Chem., Int. Ed.* **2011**, *50*, 10366. (f) Green, A. G.; Liu, P.; Merlic, C. A.; Houk, K. N. *J. Am. Chem. Soc.* **2014**, *136*, 4575. (g) Yang, Y.-F.; Liang, Y.; Liu, F.; Houk, K. N. *J. Am. Chem. Soc.* **2016**, *138*, 1660.

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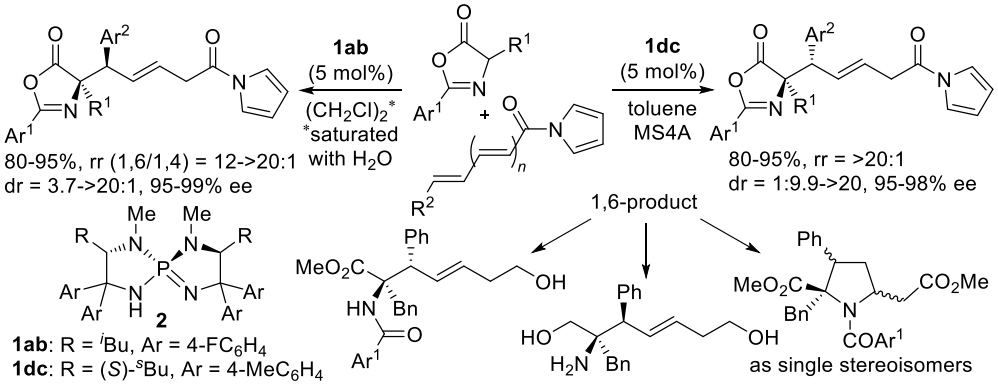
Chapter 4

Complete Diastereodivergence in Asymmetric 1,6-Addition Reactions enabled by Minimal Modification of a Chiral Catalyst



Abstract:

Catalytic systems that allow selective generation of any diastereomer of a reaction product bearing multiple stereocentres through minimal modification of a single catalyst scaffold remain elusive, particularly for carbon-carbon bond formations requiring simultaneous control of multiple selectivity factors. Here, the auther describes a catalyst-directed pinpoint inversion of diastereochemical preference in the 1,6-addition of azlactones to *δ*-aryl dienyl carbonyl compounds with full control over other selectivities preserved. This rigorous diastereodivergence is enabled by the slight structural adjustment of a chiral iminophosphorane catalyst, providing access to all the stereoisomers with high regio-, distereo-, and enantioselectivity. The utility of this method is demonstrated in the facile stereodivergent preparation of densely functionalized proline derivatives. The experimental and computational elucidation of the origin of the diastereodivergence is also described.

4.1. Introduction

As already described in Chapter 2-3, the auther established asymmetric 1,6-addition to δ-alkyl dienes,[1] but the catalytic system was not applicable to δ-aryl electron deficient dienes probably due to the transition of reactivity originated from the extention of π-conjugation of substrate. Indeed, even under the optimal conditions in the previous reaction, the product was obtained in low diastereoselectivity. In addition, the auther faced reproducibility problem. After many control experiments, the auther found that the selectivities were very sensitive to contamination of water and good stereoselectivities and reproducibility could be secured by conducting reaction in a wet solvent at low temperature. From the viewpoint of transition state models, this water effect was comprehensible by the intervention of new transition state incorporating a water molecule which is related to the previous finding, supramolecular phosphonium salts,[2] which means this transition state seems to be better for attaining high selectivities. Interestingly, after considerable optimization of catalyst structure and reaction conditions, the auther found that diastereoselectivity was switched by changing alkyl substituents originated from amino acid (^{i}Bu group from leucine or (*S*)-^{s}Bu group from isoleucine). Although numerous advances in the field of asymmetric synthesis have led to the establishment of reliable stereoselective methods for assembling enantiomerically enriched organic compounds in the last few decades,[3] in reactions involving the creation of multiple stereogenic centres in a single bond-forming event, arbitrary access to all the possible product diastereomers is incredibly difficult because diastereochemical preference is largely governed by the inherent structural and stereoelectronic nature of substrates, while absolute stereochemistry can be dictated by the choice of enantiomeric chiral catalyst. This is particularly true in diastereo- and enantioselective bond formation between two prochiral intermediates. Precise stereochemical control becomes even more complicated when additional selectivity factors, such as chemo- and regioselectivity, are associated with this type of bond construction, despite offering an unparalleled synthetic tool for rapidly increasing molecular complexity in a highly predictable and controlled manner. As a powerful strategy for addressing this intrinsic problem, catalyst-directed diastereodivergence would be much sought after. Impressive progress has been made in the development of diastereodivergent asymmetric catalysis for carbon-carbon and carbon-heteroatom bond-forming reactions.[4] However, the processes currently available rely on using each elaborated catalyst, or the appropriate combination of two different catalysts, to access complementary diastereomers selectively. This situation demonstrates the formidable challenge faced in achieving rigorous diastereodivergence by overriding substrate bias through minimal modification of a single catalyst scaffold. The auther herein describe a complete inversion of diastereoselectivity in the 1,6-addition of azlactones (oxazol-5(4*H*)-ones) to δ-aryl dienyl carbonyl compounds enabled by the slight structural alteration of iminophosphorane catalyst **1** (Figure 1). Since the minimal change in catalyst structure allows the preservation of other selectivity values in this bond connection between two prochiral reactants with two reaction sites, the

present diastereodivergent catalysis provides access to two distinct isomers out of 2^3 possibly generated isomers, even without considering the newly generated olefin geometry, with almost perfect fidelity. The synthetic utility of this protocol is also demonstrated by the facile derivatization of diastereomeric 1,6-adducts to various α-tetrasubstituted α-amino acids, such as multiply functionalized proline derivatives. In addition, the origin of the unique diastereodivergence is discussed based on the structural elucidation of aminophosphonium ions, conjugate acids of the iminophosphorane catalysts, and computational analysis of the transition-state structures.

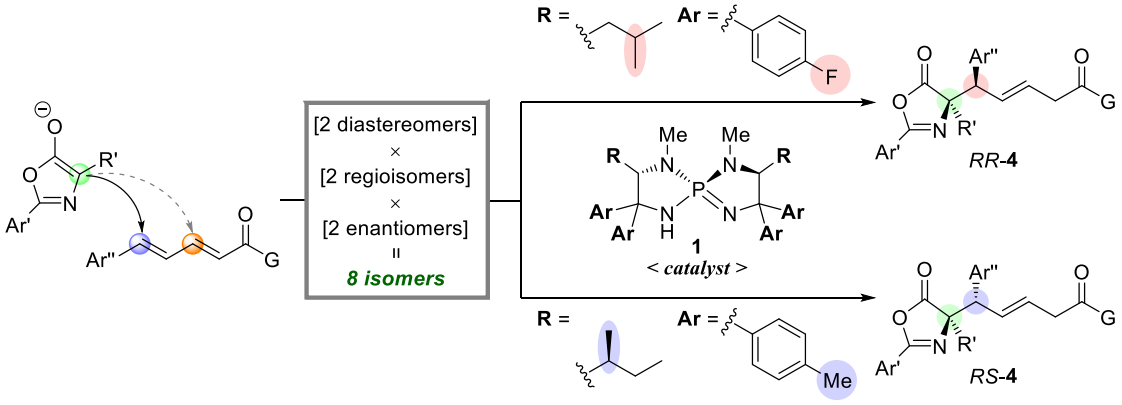


Figure 1. Diastereodivergent 1,6-Addition of Azlactones to *δ*-Aryl Dienyl *N*-Acylpyrroles (G = 1-Pyrrolyl)

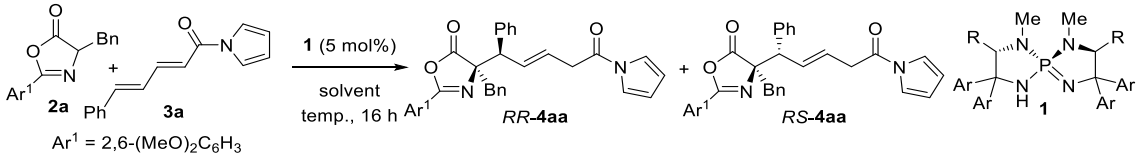
4.2. Result and Discussion

This study originated from observing that the regio- and stereoselectivity of the **1**-catalyzed conjugate addition of azlactones **2** to *δ*-aryl dienyl *N*-acylpyrroles **3** were sensitive to water content in the reaction medium. For instance, the treatment of azlactone **2a** with **3a** in the presence of L-leucine-derived iminophosphorane **1aa** (5 mol%) in dehydrated toluene under an argon atmosphere at 0 °C afforded a mixture of addition products, including desired 1,6-adduct **4aa**, with variable selectivities (a representative result is shown in Table 1, entry 1). On the other hand, attempting the reaction in the presence of powdered molecular sieves 4A (MS4A) under otherwise identical conditions led to a substantial decrease in regio- and enantioselectivity (entry 2). These results prompted the auther to employ wet toluene (w-toluene; saturated with water)[5] as a solvent to exploit the potentially positive effect of water on the selectivity profile without experimental inconsistency. As expected, a notable enhancement in both regio- and enantioselectivity was attained in a reproducible manner (entry 3). Moreover, lowering the reaction temperature to –30 °C delivered a significant improvement in diastereoselectivity with complete regio- and enantiocontrol (entry 5). The interest in gaining an insight into the role of the water prompted the auther to examine the 1,6-addition with other protic additives in a defined molar ratio to L-leucine-derived iminophosphorane **1aa**. Specifically, the auther attempted the reactions in the presence of 3,5-dichlorophenol (1 equivalents to **1aa**) in

dehydrated toluene with MS4A for figuring out the selectivity profile induced by the *in-situ* generated, supramolecularly assembled aminophosphonium catalyst[2] in comparison with that observed with **1aa** as a sole catalyst in w-toluene. Although the selectivity was only slightly improved upon addition of the phenol at 0 °C (entry 4), all the selectivities were markedly enhanced to the identical level with those obtained with **1aa** in w-toluene at –30 °C (entries 5 and 6). Since structural perturbation of the dynamic ion-pair assembly would decrease at lower temperature, these observations imply that water molecules participate in the formation of a structurally defined ion-pair assembly relevant to the transition state (Figure 2). The auther then evaluated the impact of alkyl substituents (R) of **1** on the selectivities in w-toluene at –30 °C with a series of α-amino acid-derived iminophosphoranes **1ba**–**fa** as catalysts (entries 8–12). Interestingly, while **1aa** turned out to be the most selective catalyst in providing *RR*-**4aa** ((4*R*,1'*R*)-oxazol-5(4*H*)-one) (entry 5), the totally opposite diastereochemical preference was observed with comparable degree of other selectivity values, when L-phenylalanine-derived **1ca** was applied (entries 10). In addition, L-isoleucine-derived **1da** showed a similar tendency, affording major diastereomer *RS*-**4aa** ((4*R*,1'*S*)-oxazol-5(4*H*)-one) with a higher enantiomeric excess (entry 11). Noteworthy is that D-*allo*-isoleucine-derived iminophosphorane *ent*-**1ea**, which is a diastereomer of **1da**, behaved almost as an enantiomer of the valine-derived **1ba**, revealing the critical importance of central chirality at the branching carbon in the aliphatic side chain of **1da** for inducing the inversion of diastereoselectivity (entry 9 vs 12). This surprising finding clearly indicated the possibility of establishing an efficient diastereodivergent catalysis in this conjugate addition reaction that entails multiple selectivity control. Therefore, the auther first undertook modification of geminal aromatic substituents of **1aa** and found that introducing 4-fluorophenyl groups further enhanced the diastereoselectivity (entries 15–18). The subsequent solvent screening revealed that chlorinated solvents were beneficial, and stereochemically pure *RR*-**4aa** was isolated in 88% yield by performing the reaction in wet 1,2-dichloroethane (w-DCE) under similar conditions (entries 19–21). To achieve complete diastereodivergence with the present single catalyst scaffold, the auther next adopted L-isoleucine-derived iminophosphorane **1da** as a lead catalyst due to its high enantiofacial discriminating capability. Importantly, exclusion of water was crucial in shaping each selectivity value in this case (entry 25), and slight structural manipulation of the aromatic substituents allowed him to identify **1dc**, possessing 4-tolyl groups, as the optimal catalyst for obtaining *RS*-**4aa** with immaculate stereochemical integrity (entries 26–29). It should be added that the auther examined the reactions with **1ba** and *ent*-**1ea** as catalysts in dehydrated toluene with MS4A because the auther conducted DFT calculations for elucidating the transition-state structures of the reactions with these catalysts under dry conditions (entries 13 and 14). Likewise, the auther checked the profile of the reactions with **1aa** in w-DCE and dehydrated DCE with MS4A and, to the surprise, a comparable yet high level of stereoselectivity was attained regardless of the presence and absence of water (entries 23 vs. 24), unlike the cases with toluene as solvent, where a

considerable difference in diastereoselectivity was observed (entry 5 vs. 7). Furthermore, similar tendency was observed in the reactions with the optimal catalyst **1ab**, confirming that the effect of water was marginal when the reaction was performed with catalysts bearing α-branched aliphatic substituents or in DCE at –30 °C, while slightly improving diastereoselectivity (entry 21 vs. 22).

Table 1. Optimization of Reaction Parameters[a]



entry	R, Ar (**1**)	additive	solvent	temp (°C)	yield (%)[b]	rr (1,6:1,4)[c]	dr (*RR*:*RS*)[c]	ee (%)[d]
1	^{i}Bu, Ph (**1aa**)	-	toluene	0	78	16:1	1:1.2	85/17
2	^{i}Bu, Ph (**1aa**)	MS4A	toluene	0	89	4.2:1	1:3.4	22/14
3	^{i}Bu, Ph (**1aa**)	-	w-toluene[e]	0	79	19:1	1.9:1	94/18
4	^{i}Bu, Ph (**1aa**)	MS4A, 3,5-$Cl_2C_6H_3OH$	toluene	0	94	12:1	1:2.3	69/14
5	^{i}Bu, Ph (**1aa**)	-	w-toluene[e]	–30	82	>20:1	7.2:1	99/31
6	^{i}Bu, Ph (**1aa**)	MS4A, 3,5-$Cl_2C_6H_3OH$	toluene	–30	96	>20:1	7.2:1	99/33
7	^{i}Bu, Ph (**1aa**)	MS4A	toluene	–30	95	>20:1	2.7:1	97/34
8	Me, Ph (**1fa**)	-	w-toluene[e]	–30	97	>20:1	4.7:1	94/61
9	^{i}Pr, Ph (**1ba**)	-	w-toluene[e]	–30	52	11:1	3.5:1	93/59
10	Bn, Ph (**1ca**)	-	w-toluene[e]	–30	95	>20:1	1:8.3	72/81
11	(*S*)-^{s}Bu, Ph (**1da**)	-	w-toluene[e]	–30	49	12:1	1:6.9	32/93
12	(*S*)-^{s}Bu, Ph (*ent*-**1ea**)[f]	-	w-toluene[e]	–30	41	15:1	5.0:1	–97/–46
13	^{i}Pr, Ph (**1ba**)	MS4A	toluene	–30	93	14:1	3.4:1	95/64
14	(*S*)-^{s}Bu, Ph (*ent*-**1ea**)[f]	MS4A	toluene	–30	97	>20:1	4.5:1	–98/–50
15	^{i}Bu, 4-FC_6H_4 (**1ab**)	-	w-toluene[e]	–30	91	>20:1	12:1	>99/28
16	^{i}Bu, 4-MeC_6H_4 (**1ac**)	-	w-toluene[e]	–30	94	>20:1	3.2:1	98/61
17	^{i}Bu, 3-FC_6H_4 (**1ad**)	-	w-toluene[e]	–30	65	>20:1	7.7:1	99/7
18	^{i}Bu, 3-MeC_6H_4 (**1ae**)	-	w-toluene[e]	–30	32	12:1	1:1.2	95/–31
19	^{i}Bu, 4-FC_6H_4 (**1ab**)	-	w-Et_2O[e]	–30	9	-	7.1:1	97/27
20	^{i}Bu, 4-FC_6H_4 (**1ab**)	-	w-CH_2Cl_2[e]	–30	76	>20:1	17:1	99/50
21	^{i}Bu, 4-FC_6H_4 (**1ab**)	-	w-DCE[e]	–30	88	>20:1	>20:1	99/-
22	^{i}Bu, 4-FC_6H_4 (**1ab**)	MS4A	DCE	–30	95	>20:1	18:1	99/41
23	^{i}Bu, Ph (**1aa**)	-	w-DCE[e]	–30	76	>20:1	11:1	96/53
24	^{i}Bu, Ph (**1aa**)	MS4A	DCE	–30	93	>20:1	10:1	98/61
25	(*S*)-^{s}Bu, Ph (**1da**)	MS4A	toluene	–30	96	>20:1	1:8.1	43/95
26	(*S*)-^{s}Bu, 4-FC_6H_4 (**1db**)	MS4A	toluene	–30	89	>20:1	1:7.0	74/97
27	(*S*)-^{s}Bu, 4-MeC_6H_4 (**1dc**)	MS4A	toluene	–30	89	>20:1	1:>20	-/98
28	(*S*)-^{s}Bu, 3-FC_6H_4 (**1dd**)	MS4A	toluene	–30	85	>20:1	1:5.8	56/94
29	(*S*)-^{s}Bu, 3-MeC_6H_4 (**1de**)	MS4A	toluene	–30	96	>20:1	1:6.0	10/84

MS4A = molecular sieves 4A, DCE = 1,2-dichloroethane [a]Reactions were performed with 0.50 mmol of **2a** and 0.25 mmol of **3a** in 1.25 mL of solvent in the presence of **1** (5 mol%) for 16 h. [b]Isolated yield is indicated. [c]Ratios of regioisomers and diastereomers were determined by ^{1}H NMR (700 MHz) analysis of crude aliquot. [d]Enantiomeric excess was analyzed by chiral stationary phase HPLC. Absolute configurations of *RR*- and *RS*-**4aa** were assigned according to the results of X-ray crystallographic analysis of *RR*-**4ad** and *RS*-**4ac**-derived **10** (See 112-113). [e]Organic solvent was saturated with water.[5] [f]D-*Allo*-isoleucine-derived iminophosphorane was used.

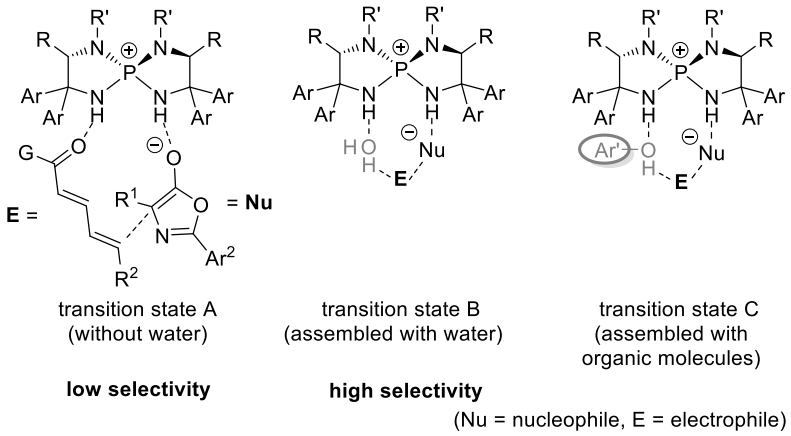
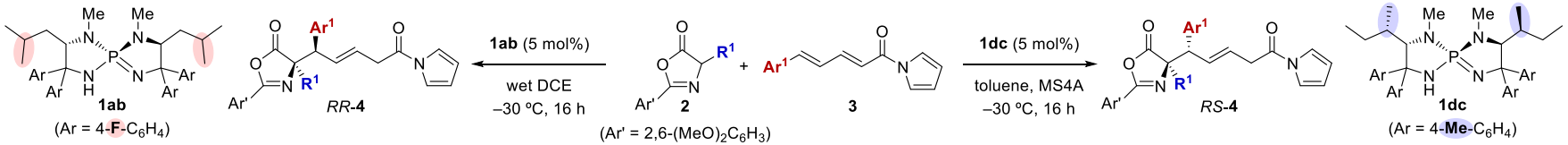


Figure 2. Plausible Model of Transition State

Having established the strictly diastereodivergent asymmetric 1,6-addition of azlactones **2** to *δ*-aryl dienyl *N*-acylpyrroles **3** through minimal adjustment of the structure of chiral iminophosphorane **1** and the reaction solvent, the scope of each optimal catalytic system was surveyed independently (Table 2). Under catalysis of **1ab** in w-DCE, the reaction of azlactone **2a** tolerated a wide variety of **3**, containing terminal aromatic substituents of different electronic properties, as an acceptor, giving 1,6-adduct *RR*-**4** in high chemical yield with excellent regio-, diastereo-, and enantioselectivity (entries 1–10), whereas the *ortho*-substituted aryl appendage appeared to cause an erosion in regio- and diastereoselectivity (entry 11). Heteroaryl-substituted dienyl *N*-acylpyrroles were also amenable to this conjugate addition protocol (entries 12 and 13). Not only *δ*-aromatic but also *δ*-alkynyl dienyl acylpyrrole **3n** were well accommodated to this system to afford desired 1,6-adduct *RR*-**4an** in 92% yield with high stereoselectivity (entry 14). An array of azlactones **2**, bearing different *α*-side chains of amino acid origin, were employed as enolate precursors, although a certain decrease in diastereoselectivity was detected for those derived from aliphatic amino acids (entries 15 and 18). On the other hand, subjecting the same series of substrate combinations to catalysis of **1dc** with MS4A in toluene revealed the efficiency and robustness of the diastereodivergent asymmetric catalysis, providing *RS*-**4** with high stereochemical purity (entries 19–36). It should be noted that the permutations of either dienes with *δ*-heteroaryl or alkynyl substituents (**3l**–**3n**) as an acceptor, or leucine-derived azlactone **2b** as an enolate precursor, caused a slight loss in diastereoselectivity (entries 30–32). The absolute configurations of both diastereomers were unambiguously determined as *RR* and *RS* by single crystal X-ray diffraction analysis (see Experimental Section), and the stereochemistry of other examples was assumed by analogy.

Table 2. Substrate Scope[a]



	catalyst = **1ab**								catalyst = **1dc**				
entry	yield (%)	rr (1,6/1,4)	dr (***RR***/*RS*)	ee (%)	R^1 (**2**)	Ar^1 (**3**)	product (**4**)	entry	yield (%)	rr (1,6/1,4)	dr (*RR*/***RS***)	ee (%)
1	88	>20:1	>20:1	99	Bn (**2a**)	Ph (**3a**)	**4aa**	19	89	>20:1	1:>20	98
2	77	>20:1	>20:1	99	Bn (**2a**)	4-FC_6H_4 (**3b**)	**4ab**	20	96	>20:1	1:14	98
3[b]	80	>20:1	18:1	98	Bn (**2a**)	4-ClC_6H_4 (**3c**)	**4ac**	21	86	>20:1	1:17	98
4[c,d]	87	>20:1	20:1	99	Bn (**2a**)	4-$MeSC_6H_4$ (**3d**)	**4ad**	22	92	>20:1	1:17	98
5[c]	95	>20:1	19:1	99	Bn (**2a**)	4-$MsOC_6H_4$ (**3e**)	**4ae**	23[c]	94	>20:1	1:16	96
6	95	>20:1	20:1	99	Bn (**2a**)	4-$^tBuO_2CC_6H_4$ (**3f**)	**4af**	24	90	>20:1	1:13	98
7	90	>20:1	>20:1	99	Bn (**2a**)	4-$VinylC_6H_4$ (**3g**)	**4ag**	25	90	>20:1	1:17	98
8	85	>20:1	17:1	97	Bn (**2a**)	3-BrC_6H_4 (**3h**)	**4ah**	26	92	>20:1	1:18	99
9	90	>20:1	>20:1	99	Bn (**2a**)	3-$MeOC_6H_4$ (**3i**)	**4ai**	27	95	>20:1	1:16	98
10	82	>20:1	18:1	99	Bn (**2a**)	3-MeC_6H_4 (**3j**)	**4aij**	28	91	>20:1	1:>20	99
11	81	12:1	3.7:1	98	Bn (**2a**)	2-FC_6H_4 (**3k**)	**4ak**	29	89	>20:1	1:>20	95
12	90	>20:1	>20:1	99	Bn (**2a**)	3-Thienyl (**3l**)	**4al**	30	94	>20:1	1:11	98
13	85	>20:1	>20:1	98	Bn (**2a**)	3-Pyridyl (**3m**)	**4am**	31	87	>20:1	1:10	98
14	92	>20:1	20:1	98	Bn (**2a**)	PhC≡C (**3n**)	**4an**	32	91	>20:1	1:4.6	96
15	92	>20:1	8.6:1	95	^{i}Bu (**2b**)	Ph (**3a**)	**4ba**	33	89	>20:1	1:9.9	95
16	88	>20:1	>20:1	99	PMB (**2c**)	Ph (**3a**)	**4ca**	34	95	>20:1	1:19	98
17[c,d]	80	>20:1	13:1	99	*N*-Ts-3-indolyl-CH_2 (**2d**)	Ph (**3a**)	**4da**	35[c,d]	84	>20:1	1:19	97
18[d]	86	18:1	5.9:1	97	allyl (**2e**)	Ph (**3a**)	**4ea**	36[d]	88	>20:1	1:>20	98

Ts = 4-$MeC_6H_4SO_2$ [a]Reactions were performed with 0.50 mmol of **2** and 0.25 mmol of **3** in 1.25 mL of solvent in the presence of **1** (5 mol%) at –30 °C for 16 h. Isolated yields are indicated. Ratios of regioisomers and diastereomers were determined by ^{1}H NMR (800 MHz) analysis of crude aliquot. Enantiomeric excesses of the major diastereomer were indicated. Enantiomeric excesses were analyzed by chiral stationary phase HPLC. Absolute configurations of *RR*- and *RS*-**4** were assigned by analogy to *RR*-**4ad** and *RS*-**4ac**. [b]Reaction was conducted at –20 °C due to less solubility of **3c**. [c]Reaction was stirred for 40 h. [d]10 mol% of catalyst was used.

The auther then prepared enantiomeric catalysts, *ent*-**1ab** and *ent*-**1dc**, from the parent D-amino acids in order to demonstrate the accessibility of the full array of stereoisomers of 1,6-adduct **4aa**. Using each iminophosphorane catalyst system, all four stereoisomers of **4aa** were obtained from the same set of starting materials, **2a** and **3a**, in high yields with virtually complete regio-, enantio-, and diastereoselectivity as illustrated in Figure 2.

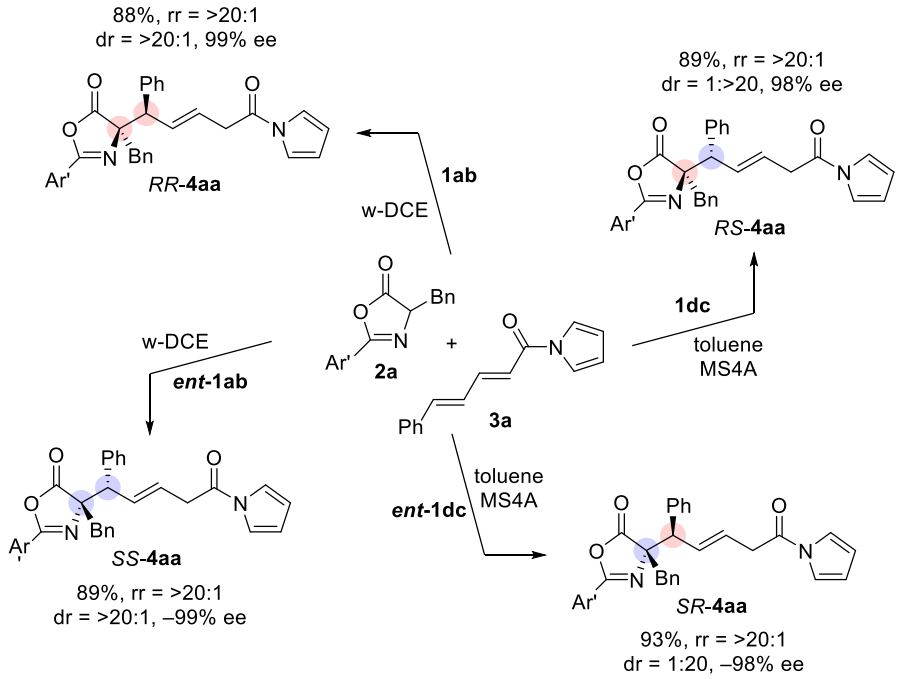


Figure 3. Stereodivergent Synthesis of All Stereoisomers of **4aa** (Ar' = 2,6-$(MeO)_2C_6H_3$)

All reactions were performed with 5 mol% of **1** in the indicated solvent at –30 °C for 16 h.

The efficient diastereodivergent catalysis of iminophosphoranes **1ab** and **1dc** could further be extended to the reactions with other *δ*-aryl dienyl carbonyl compounds (Figure 4). For example, in the conjugate addition of **2a** to vinylogous chalcone derivative **5a**, near complete inversion of diastereoselectivity was accomplished with full preservation of other selectivity values by the proper use of **1ab** or **1dc** as a catalyst, giving rise to 1,6-adducts *RR*-**6aa** and *RS*-**6aa** of high stereochemical purity, respectively. It was of interest that dehydrated condition was beneficial in both catalytic systems for this substrate combination, which clearly demonstrates that the slight structural difference between iminophosphoranes **1ab** and **1dc** plays a pivotal role in inducing the rigorous diastereodivergence. Similar reactivity and selectivity were attained in the reactions of **2a** with **5**, bearing different aromatic substituents at the *δ*-position, implying general applicability of this unique stereodivergent protocol. Moreover, vinylidene malonate **7** also appeared to be a good candidate as an acceptor for the addition of **2a** under the catalysis of either **1ab** or **1dc**.

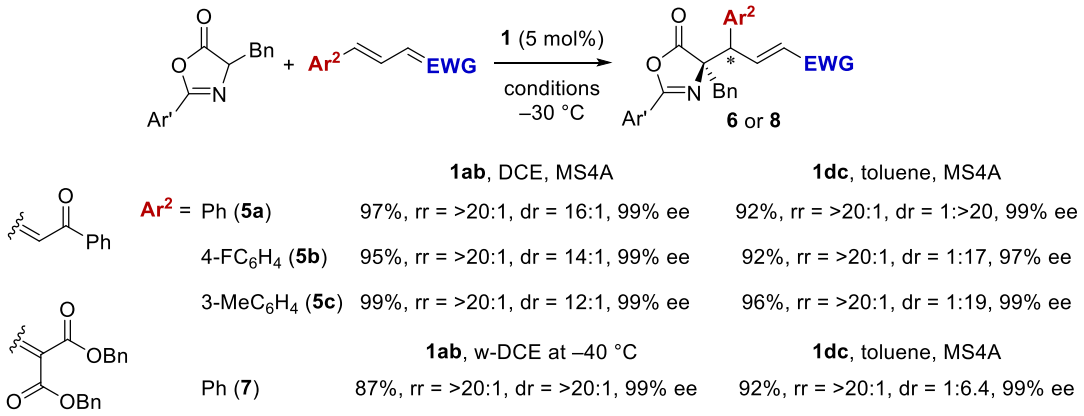


Figure 4. Diastereodivergence of 1,6-Selective Conjugate Addition of δ-Aryl Dienyl Carbonyl Compounds (Ar' = 2,6-$(MeO)_2C_6H_3$)

Conjugate adduct **4** can be converted into a series of functionalized α-amino acid derivatives (Figure 5). Harnessing the structural feature of **4**, possessing two differentiated functionalities of carboxylic acid oxidation state, the acyl pyrrole unit was selectively transformed into methyl ester by treatment with sodium methoxide in methanol. The azlactone ring of resultant ester **9** was cleaved by reaction with either 4-chloroaniline in the presence of Lewis acid, to give amide **10**, or with thionyl chloride in methanol, to furnish diester **11**. Selective reduction of the sterically more accessible ester group in **11** was feasible, and thus protected α-allylic α-amino acid **12** was isolated in 95% yield. The complete reduction of the two terminal ester moieties and subsequent removal of the nitrogen protecting group by methanolic potassium hydroxide under microwave irradiation afforded corresponding amino diol **13** in 78% yield (two steps). Moreover, the olefin component of diester **11** was utilized as a functional handle to increase the molecular complexity in a stereodivergent manner by taking advantage of the availability of two diastereomers, *RR*- and *RS*-**11**, in an essentially pure form. For example, aza-platination of *RR*-**11**, followed by protodeplatination, resulted in the diastereoselective production of functionalized proline derivative **14** via 5-*endo* cyclization. In contrast, diastereomeric **15** was preferably formed by treating *RR*-**11** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in methanol, presumably through an olefin isomerization-aza-conjugate addition sequence.[6] Upon exposure of *RS*-**11** to similar basic conditions, another diastereomer **16** was obtained in 88% yield with a diastereomeric ratio of 14:1.

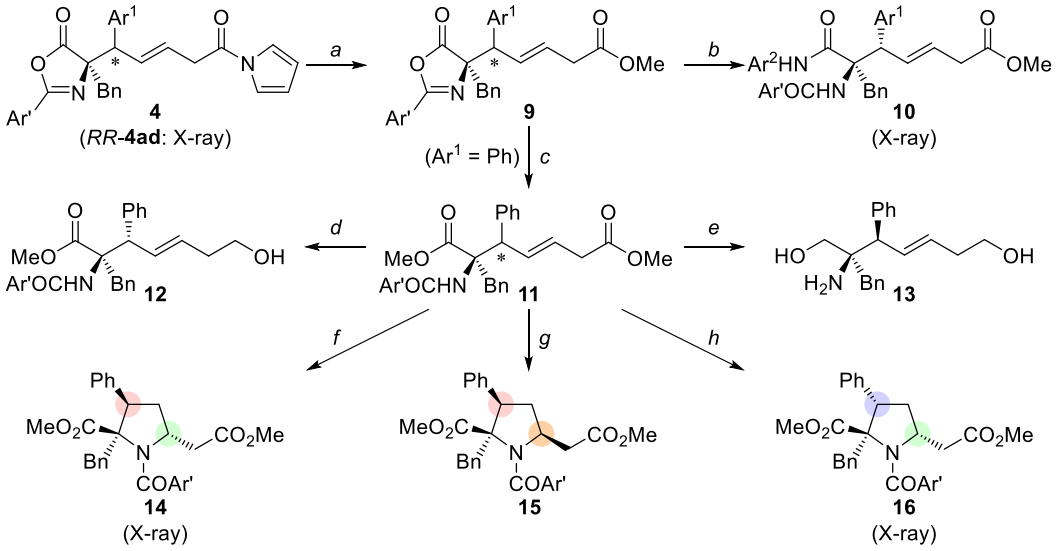


Figure 5. Conversion to Various α-Tetrasubstituted α-Amino Acid Derivatives

Conditions (Ar′ = 2,6-$(MeO)_2C_6H_3$)**:** a) NaOMe, MeOH/CH_2Cl_2, 0 °C, 81% (from *RS*-**4ac**); 91% (from *RR*-**4aa**); 83% (from *RS*-**4aa**), b) $BF_3{\cdot}OEt_2$, 4-$ClC_6H_4NH_2$ (Ar^2NH_2), toluene, 100 °C, 56% (from *RS*-**9ac**), c) $SOCl_2$, MeOH, 5 °C, 83% (from *RR*-**9aa**); 69% (from *RS*-**9aa**), d) $LiBH_4$, THF, rt, 95% (from *RS*-**11**), e) (i) $LiAlH_4$, Et_2O, reflux, (ii) KOH, aqueous MeOH, 150 °C (MW), 78% (2 steps from *RR*-**11**), f) $PtCl_2$, Cs_2CO_3, DMF, 140 °C, 76% (pure diastereomer) (from *RR*-**11**), g) DBU, MeOH, 40 °C, 54% (pure diastereomer) (from *RR*-**11**), h) DBU, MeOH, 60 °C, 88% (diastereomeric mixture, dr = 14:1) (from *RS*-**11**).

The observed complete inversion of diastereoselectivity most likely stems from the unique structural feature of L-isoleucine(Ile)-derived iminophosphorane catalyst **1da**, compared to L-valine(Val)- and D-*allo*-isoleucine(Allo)-derived **1ba** and *ent*-**1ea**, as judged from the data of entries 13, 14, and 25 in Table 1. Therefore, in order to clarify the difference in the structures of the conjugate acids of these iminophosphoranes that possess α-branched aliphatic side chains, namely, aminophosphonium ions **1ba**·H, **1da**·H, and *ent*-**1ea**·H, their molecular architectures were visualized using a single crystal X-ray diffraction analysis (Figure 6a). While three-dimensional structures created by [5.5]-spirocyclic core and aromatic substituents are nearly identical, α-amino acid-derived aliphatic substituents cause notable structural difference in each aminophosphonium ion. Dihedral angles (ϕ) between C-H bond on the stereogenic center of the diazaphosphacycles and C-H bond on the branching carbons of the aliphatic substituents were determined to be –59.3, –82.2° for **1ba**·H, –73.6, –156.0° for **1da**·H, and 67.9, 147.2° for *ent*-**1ea**·H, respectively. Because it was uncertain whether the unsymmetrical disposition of two aliphatic substituents of **1da** and *ent*-**1ea** reflected the most stable structures of these aminophosphonium ions or it was induced by different effects, such as a crystal packing, energy profile associated with the rotation around the axis of the C-C bond was analyzed by the density functional theory (DFT) calculation at B3LYP/6-31G* level (signs of dihedral angles for *ent*-**1ea**·H were inverted for comparison with the others).[7] As shown in Figure 6b, the most preferable ϕ is around –75° and the second stable conformer is formed around –150° in all three cations as a consequence of minimizing steric repulsion between α-branched aliphatic substituent and

anchimeric phenyl group. These results indicate that the aminophosphonium ions adopt one of the possible energetically favorable conformers in the solid state. In solution state, ϕ of the H-C-C-H component is expected to totter between ca. –75~–150° and one of the two alkyl groups attached on the branching carbon of the aliphatic substituent would be directed toward the chiral cavity constructed by the aromatic substituents. While methyl groups of Val- and Allo-derived aminophosphonium ions **1ba**·H and *ent*-**1ea**·H overhang the cavity, the bulkier ethyl group is dangling in the case of Ile-derived cation **1da**·H due to the (*S*)-configuration at the branching carbon of *sec*-butyl substituent, which may induce different diastereochemical outcome. To gain insight into the transition state (TS) structures, further analysis was pursued *in silico*. Experimentally observed linear relationship between enantiomeric purity of the iminophosphorane catalysts and 1,6-addition products (See Experimental Section), and the quantum mechanistic study on the related iminophosphorane catalysis suggested the participation of a single chiral aminophosphonium ion to the stereodetermining C-C bond-forming step of the conjugate addition reaction.[8,9] Most likely, the aminophosphonium ion featuring two N-H protons accommodates the two nucleophilic and electrophilic substrates in a way that one N-H proton makes hydrogen bond with the azlactone enolate and the other with the carbonyl of the *N*-acylpyrrole to organize a macrocyclic transition state structure, thereby enabling rigorous control of multiple selectivity factors. Based on this presupposition, we designed and generated the macrocyclic transition state models of the reaction between **2a** and **3a** with Ile-derived **1da** as a catalyst for DFT calculation. Initially, relatively stable TSs that afforded each diastereomer were selected from 32 possible TSs (B3LYP/6-31G*) and the energy of the TS was estimated by calculation at B3LYP-D3/6-311++G** level with solvent and temperature parameters (PCM, toluene at –30 °C) (Figure 6c and see Computational Details).[10] The resulting energy profile qualitatively reproduced experimental selectivities in the **1da**-catalyzed reaction (Table 1, entry 7). From structural viewpoint, entire form of aminophosphonium residues in all TSs is very similar, but positions of ethyl groups are variable depending on the orientations of the two substrates captured via hydrogen-bonding interactions, while ϕ of the H-C-C-H component fall within –80.7~–152.0°. In the most stable TS giving the major *RS*-isomer, the steric demand imposed by one ethyl group regulates the placement of **3a** that lies down into the chiral cavity and expose the *si* face to the enolate of **2a**. The other ethyl group is situated as to avoid inducing steric repulsion with the substituent of **2a** and is directed toward phenyl group across the aminophosphonium core of **1da**·H. The steric effect caused by the position of the ethyl group appears crucial for attaining high diastereoselectivity because it contributes to destabilize the TS leading to the minor *RR*-isomer, which is 3.3 kcal/mol higher in energy. Importantly, the steric constraint between the ethyl group and the *N*-acylpyrrole moiety of **3a** is relieved in the reaction with Val-derived catalyst **1ba** to an extent enough for the TS giving *RR*-isomer to be stabilized to constitute a major stereochemical pathway, as evident from the side view of the TS structure in comparison to that of the TS with Ile-derived catalyst **1da** (90° clockwise rotation from

1da-*RR* around the vertical axis). These results are consistent with the analysis based on the solid state structures of the aminophosphonium ions obtained from the X-ray diffraction measurements and account for the reversal of diastereochemical preference between the reactions with **1ba** and **1da** as catalysts, respectively. With Leu-derived catalyst **1aa**, lack of *α*-branching in the isobutyl substituents allows for the accommodation of **3a** without obvious steric congestion. Instead, steric collision of one of the isobutyl groups with the substituent of **2a** contributes to make the TS affording *RS*-isomer 1.8 kcal/mol higher in energy than the most stable, stereodetermining TS, in which **3a** is tilted toward the isobutyl group, having the *re* face available for the attack of the enolate of **2a**. The auther assume that this TS structure leading to *RR*-isomer could be slightly modified by the intervention of water molecules, which would be critical to form even more stable, well-defined macrocyclic TS depending on the reaction solvent employed. The overall elucidation reveals that the ability of the aminophosphonium ion with two hydrogen-bonding donor sites embedded in the rigid structural core to simultaneously accommodate the two reacting substrates is essential for organizing the macrocyclic TS, wherein small difference in the catalyst substituents, aliphatic substituents, in particular, plays a key role in altering the orientation of the substrates, especially the dienyl carbonyl electrophile, for achieving the strict diastereodivergence without affecting the prominent regio- and enantioselectivity.

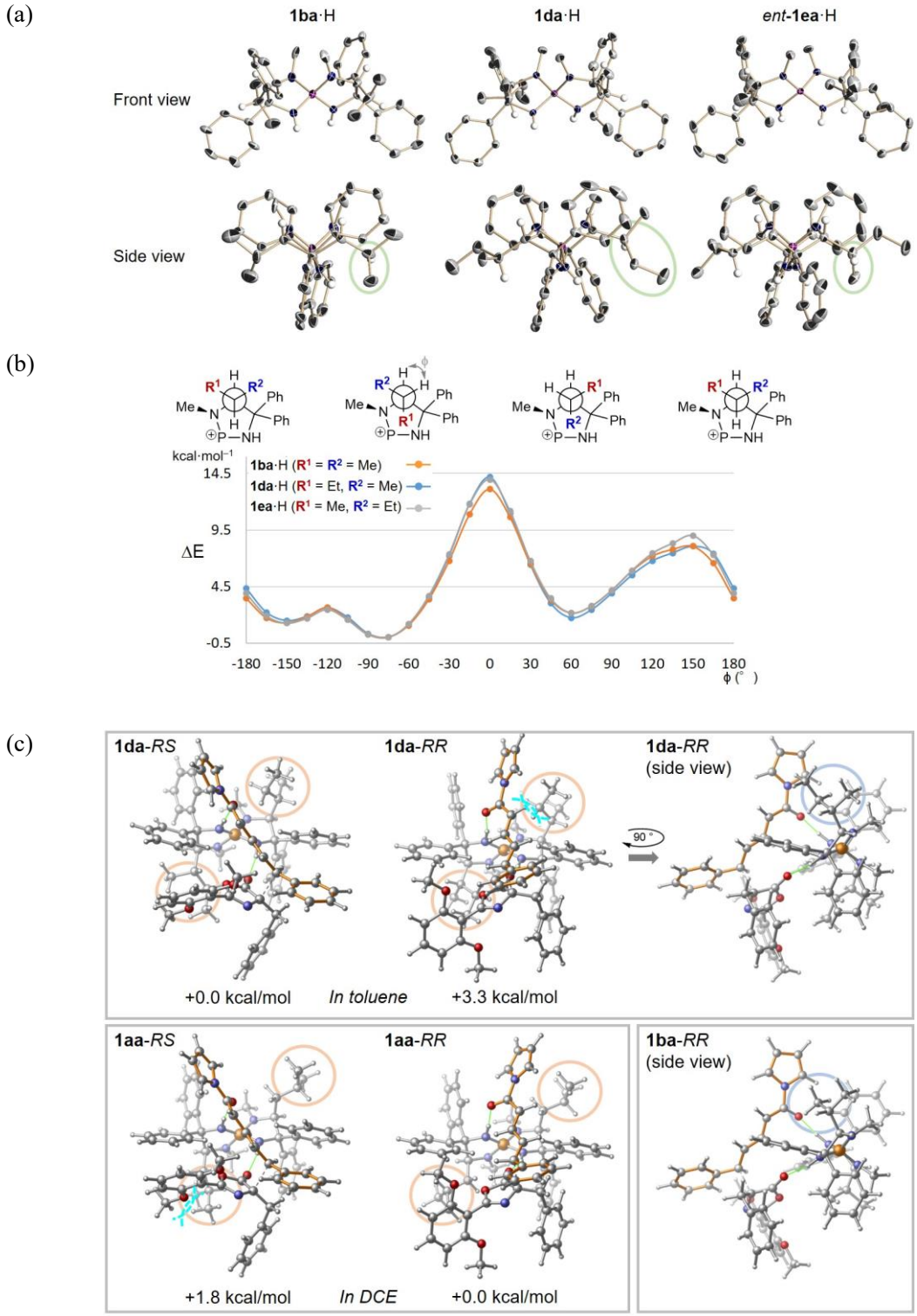


Figure 6. (a) ORTEP Diagrams of Aminophosphonium Ions **1**, (b) Energy Profile on Rotation Around C-C Axis of the Stereogenic Carbon of **1** and the Branching Carbon of Alkyl Side Chain, (c) Transition Structure Models for the C-C Bond-Forming Step from DFT Calculation and Relative Gibbs Free Energies at PCM-B3LYP-D3/6-311++G**//B3LYP/6-31G* level

4.3 Conclusion

In summary, the auther achieved near perfect diastereodivergence in asymmetric 1,6-addition reactions of azlactones to δ-aryl dienyl *N*-acylpyrroles with consistently excellent levels of regio- and enantiocontrol, primarily through minimal modification of chiral iminophosphorane catalysts. Using each optimal iminophosphorane catalyst and its enantiomer under appropriate conditions enabled access to the full complement of stereoisomers of the structurally diverse 1,6-adduct. The synthetic utility of the method was highlighted by the facile preparation of various α-tetrasubstituted α-amino acids, including densely functionalized proline derivatives. Furthermore, the origin of the diastereodivergence was elucidated by the experimental and computational analysis of the catalyst behavior and transition-state structures. The auther anticipate that the reported salient feature of the iminophosphorane catalysis in multiple selectivity control will find fruitful applications, and further studies in this line are currently underway.

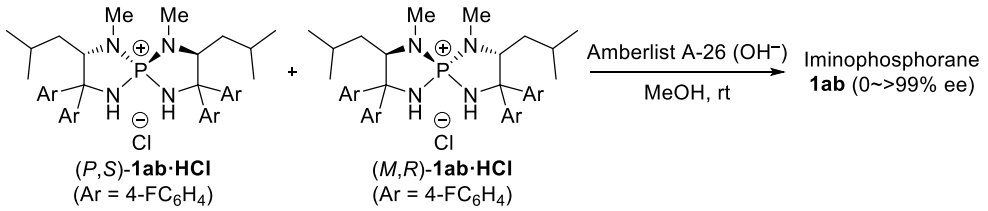
4.4 Experimental Session

General Information: Infrared spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz), JEOL JNM-ECZ400S (400 MHz), JEOL JNM-ECA600II (600 MHz), JEOL JNM-ECA800 (800 MHz), and Varian INOVA-700 (700 MHz) spectrometers. Chemical shifts are reported in ppm from the solvent resonance (CD_3OD; 3.31 ppm) or tetramethylsilane (0.0 ppm) resonance as the internal standard [$(CD_3)_2CO$, $CDCl_3$]. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz), JEOL JNM-ECZ400S (101 MHz), and JEOL JNM-ECA600II (151 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard [$(CD_3)_2CO$; 29.84 ppm, CD_3OD; 49.0 ppm, $CDCl_3$; 77.16 ppm]. ^{19}F NMR spectra were recorded on a JEOL JNM-ECS400 (376 MHz) spectrometer. Chemical shifts are reported in ppm from benzotrifluoride (–64.0 ppm) resonance as the external standard. ^{31}P NMR spectra were recorded on a JEOL JNM-ECS400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 (0.0 ppm) resonance as the external standard. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive. Microwave experiment was performed by using Anton-Paar Monowave 300. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) and Chromatorex® TLC plates NH (0.2 mm; Fuji Silysia Chemical ltd.). TLC Plate-*WAKO* (silica gel 70 GF_{254}, 0.25 mm) was used for the preparative thin layer chromatography (PLC). Flash column chromatography was conducted on silica gel 60 (spherical, 40–50 μm; Kanto Chemical Co., Inc.), silica gel 60N (spherical, 40–50 μm; Kanto Chemical Co., Inc.), PSQ60AB (spherical, av. 55 μm; Fuji Silysia Chemical ltd.), Silica gel 60 (Merck 1.09385.9929, 230–400 mesh), and Chromatorex® NH DM2035 (spherical, 45–75 μm; Fuji Silysia Chemical ltd.). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK AD-3 (AD3), CHIRALCEL OD-3 (OD3), CHIRALCEL OZ-3 (OZ3), CHIRALCEL OX-3 (OX3), CHIRALPAK IA-3 (IA3), CHIRALPAK IC-3 (IC3)] with hexane (H), 2-propanol (IPA), and ethanol (EtOH) as eluent.

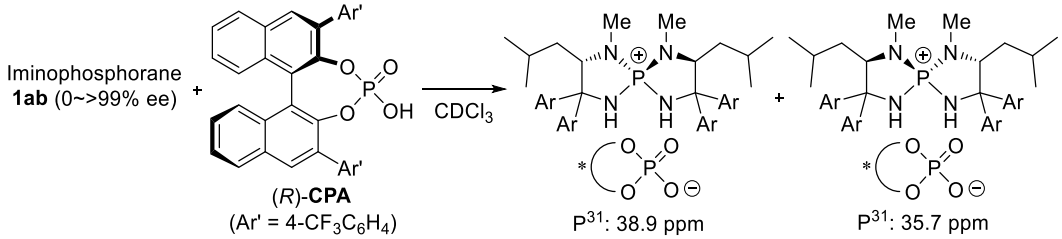
Toluene, dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Chiral tetraaminophosphonium salts **1**·HCl,[1] chiral triaminoiminophosphorane **1**,[1] azlactones **2**,[11] dienyl *N*-acylpyrroles **3**,[12] dienyl ketones **5**,[13] and dienylidene malonate **7**[14] were prepared by following the literature procedure. Powdered molecular sieves 4A (MS4A) was supplied from Sigma-Aldrich. Other simple chemicals were purchased and used as such.

Nonlinear Effect

Procedure for Preparation of Iminophosphorane 1ab (0~>99% ee)



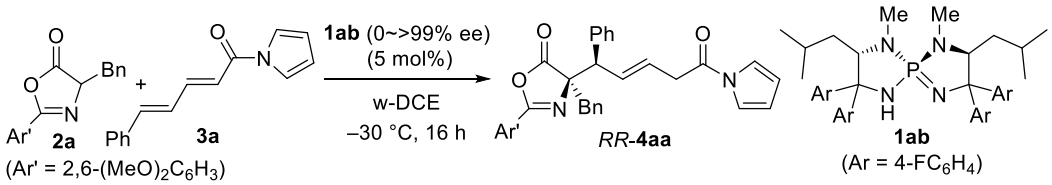
A mixture of chiral tetraaminophosphonium chlorides (*P*,*S*)-**1ab**·HCl and (*M*,*R*)-**1ab**·HCl in an appropriate ratio was placed in a sample tube, and the mixture was dissolved into methanol. The methanolic solution was passed through a column of ion exchange resin (Amberlyst A-26 OH form) to afford a solution of iminophosphorane **1ab** (0~>99% ee). The resulting solution was concentrated by rotary evaporation and residual solid was washed with deionized water on a funnel. The solid thus obtained was dried under reduced pressure to afford the iminophosphorane **1ab** as a white solid. Enantiomeric excess of iminophosphorane **1ab** was determined as shown below.



A mixture of iminophosphorane **1ab** (0~>99% ee) and chiral phosphoric acid (*R*)-**CPA** was dissolved into $CDCl_3$. Enantiomeric excess of **1ab** was determined by the ratio of the integration of diastereomeric phosphonium salts in ^{31}P NMR.

Experiments for investigating correlation between the enantiomeric excess of catalyst **1ab** or **1dc** and that of the 1,6-adduct *RR*-**4aa** or *RS*-**4aa** followed the representative procedure.

Experimental Result using Catalyst 1ab (0~>99% ee)



%ee of **1ab**	%yield of **4aa**	dr of **4aa**	%ee of *RR*-**4aa**
0	75	>20:1	0
20	83	>20:1	21
40	81	>20:1	38
59	95	>20:1	56
79	89	>20:1	77
100	88	>20:1	99

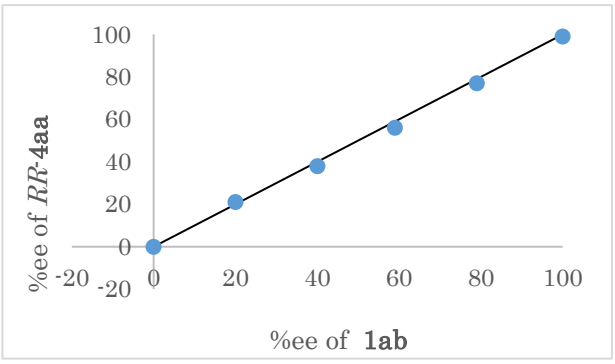
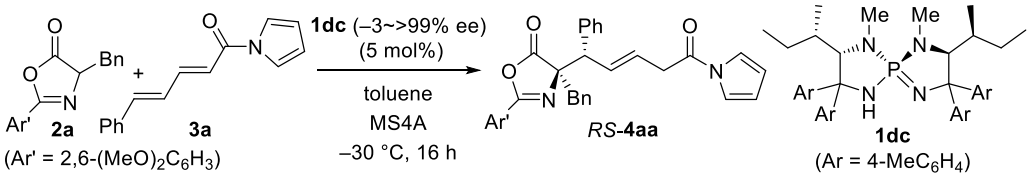


Table S1. and Figure S1. Correlation between % ee of **1ab** and *RR*-**4aa**

The data of Table S1 and the graph of Figure S1 show a linear relationship between the enantiomeric excess (ee) of **1ab** and that of *RR*-**4aa**, which suggests that a single catalyst molecule is involved in the stereo-determining step.

Experimental Result using Catalyst 1dc (–3~>99% ee)



%ee of **1dc**	%yield of **4aa**	dr of **4aa**	%ee of *RS*-**4aa**
–3	96	1:20	–2
18	94	1:>20	14
38	94	1:20	31
66	96	1:20	62
85	90	1:20	81
100	89	1:>20	98

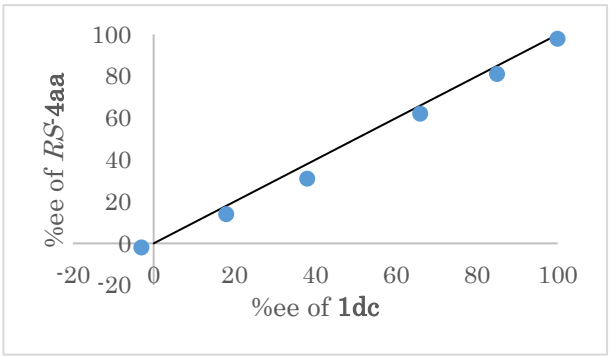
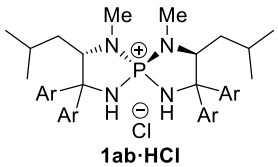


Table S2. and Figure S2. Correlation between % ee of **1dc** and *RS*-**4aa**

The linear relationship is also observed, suggesting that the same mechanism is operative during the carbon-carbon bond-forming event.

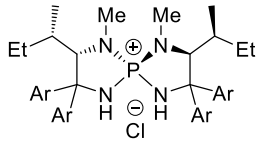
Experimental Section:

Characterization of Tetraaminophosphonium Salts 1·HCl:



1ab·HCl
(Ar = 4-FC$_6$H$_4$)

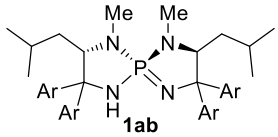
1ab·HCl[1]**:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.57 (4H, dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{F\text{-}H}$ = 5.0 Hz), 7.33 (4H, dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 7.20 (4H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.7 Hz), 7.09 (4H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.7 Hz), 4.10 (2H, ddd, $J_{P\text{-}H}$ = 22.4 Hz, $J_{H\text{-}H}$ = 7.3, 4.6 Hz), 1.99 (6H, d, $J_{P\text{-}H}$ = 10.5 Hz), 1.42 (2H, ddd, J = 14.1, 7.3, 4.6 Hz), 1.26 (2H, ddd, J = 14.1, 7.3, 5.0 Hz), 0.81 (6H, d, J = 6.2 Hz), 0.64 (2H, m), 0.62 (6H, brs), N-H protons were not found due to deuterium exchange.



1dc·HCl
(Ar = 4-MeC_6H_4)

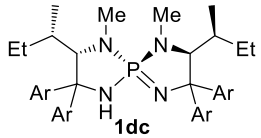
1dc·HCl: ^{1}H NMR (400 MHz, CD_3OD) δ 7.47 (4H, d, J = 8.2 Hz), 7.25 (4H, d, J = 8.2 Hz), 7.20 (4H, br), 7.13 (4H, d, J = 8.2 Hz), 4.00 (2H, dd, $J_{P\text{-}H}$ = 19.5 Hz, $J_{H\text{-}H}$ = 4.2 Hz), 2.34 (6H, s), 2.31 (6H, s), 1.90 (6H, d, $J_{P\text{-}H}$ = 10.1 Hz), 1.78 (2H, dqd, J = 13.3, 7.3, 2.6 Hz), 1.42 (2H, dqdd, J = 11.3, 6.9, 4.2, 2.6 Hz), 0.92 (2H, ddq, J = 13.3, 11.3, 7.3 Hz), 0.77 (6H, t, J = 7.3 Hz), 0.62 (6H, d, J = 6.9 Hz), N-H protons were not found due to deuterium exchange.; ^{13}C NMR (101 MHz, CD_3OD) δ 146.2, 139.0 (d, $J_{P\text{-}C}$ = 13.5 Hz), 138.9, 138.7, 130.4, 129.6, 128.7, 127.8, 72.9 (d, $J_{P\text{-}C}$ = 10.6 Hz), 71.1 (d, $J_{P\text{-}C}$ = 10.6 Hz), 37.7, 32.6 (d, $J_{P\text{-}C}$ = 6.8 Hz), 26.1, 21.0, 20.9, 18.9, 12.3; ^{31}P NMR (162 MHz, CD_3OD) δ 35.9; IR (film): 2972, 1508, 1456, 1362, 1348, 1175, 1022, 1011, 808 cm^{-1}; HRMS (ESI) Calcd for $C_{42}H_{56}N_4P^+$ ([M–Cl]$^+$) 647.4237. Found 647.4219.; $[\alpha]^{27}_D$ –223.6 (c = 1.00, CH_3OH).

Characterization of Triaminoiminophosphoranes 1:



1ab
(Ar = 4-FC_6H_4)

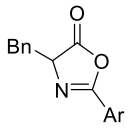
1ab[1]**:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.55 (4H, dd, $J_{H\text{-}H}$ = 8.8 Hz, $J_{F\text{-}H}$ = 5.0 Hz), 7.34 (4H, dd, $J_{H\text{-}H}$ = 8.8 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 7.16 (4H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.8 Hz), 7.06 (4H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.8 Hz), 4.04 (2H, ddd, $J_{P\text{-}H}$= 22.4 Hz, $J_{H\text{-}H}$ = 7.4, 4.9 Hz), 1.96 (6H, d, $J_{P\text{-}H}$ = 10.6 Hz), 1.39 (2H, ddd, J = 14.2, 7.4, 4.9 Hz), 1.24 (2H, ddd, J = 14.2, 7.4, 4.9 Hz), 0.80 (6H, d, J = 6.0 Hz), 0.63 (2H, m), 0.61 (6H, brs), N-H proton was not found due to deuterium exchange.



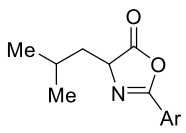
1dc
(Ar = 4-MeC_6H_4)

1dc: ^{1}H NMR (400 MHz, CD_3OD) δ 7.47 (4H, d, J = 8.3 Hz), 7.25 (4H, d, J = 8.3 Hz), 7.20 (4H, br), 7.13 (4H, d, J = 8.3 Hz), 4.00 (2H, dd, $J_{P\text{-}H}$ = 19.6 Hz, $J_{H\text{-}H}$ = 4.0 Hz), 2.34 (6H, s), 2.31 (6H, s), 1.89 (6H, d, $J_{P\text{-}H}$ = 10.4 Hz), 1.78 (2H, dqd, J = 13.2, 7.1, 2.7 Hz), 1.42 (2H, dqdd, J = 10.8, 6.9, 4.0, 2.7 Hz), 0.92 (2H, ddq, J = 13.2, 10.8, 7.1 Hz), 0.76 (6H, t, J = 7.1 Hz), 0.62 (6H, d, J = 6.9 Hz), N-H proton was not found due to deuterium exchange.; ^{13}C NMR (151 MHz, CD_3OD) δ 146.2, 139.1 (d, $J_{P\text{-}C}$ = 13.1 Hz), 138.9, 138.7, 130.4, 129.6, 128.7, 127.8, 73.0 (d, $J_{P\text{-}C}$ = 11.6 Hz), 71.2 (d, $J_{P\text{-}C}$ = 10.2 Hz), 37.7, 32.6 (d, $J_{P\text{-}C}$ = 7.2 Hz), 26.1, 21.0, 20.9, 18.9, 12.2; ^{31}P NMR (162 MHz, CD_3OD) δ 35.9; IR (film): 2918, 1609, 1508, 1456, 1375, 1327, 1190, 1099, 1018, cm^{-1}; HRMS (ESI) Calcd for $C_{42}H_{56}N_4P^+$ ([M+H]$^+$) 647.4237. Found 647.4229; $[\alpha]^{27}_D$ –228.3 (c = 1.00, CH_3OH).

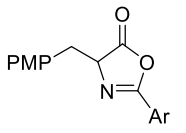
Characterization of Azlactones 2 (Ar = 2,6-$(MeO)_2C_6H_3$):



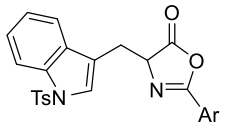
2a[1]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (1H, t, J = 8.5 Hz), 7.32-7.21 (5H, m), 6.52 (2H, d, J = 8.5 Hz), 4.70 (1H, dd, J = 6.4, 5.1 Hz), 3.72 (6H, s), 3.39 (1H, dd, J = 14.2, 5.1 Hz), 3.24 (1H, dd, J = 14.2, 6.4 Hz).



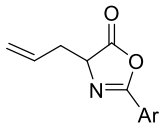
2b[1]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (1H, t, J = 8.4 Hz), 6.58 (2H, d, J = 8.4 Hz), 4.43 (1H, dd, J = 8.1, 6.0 Hz), 3.82 (6H, s), 2.06 (1H, nonet, J = 7.0 Hz), 1.89 (1H, ddd, J = 13.9, 7.0, 6.0 Hz), 1.74 (1H, ddd, J = 13.9, 8.1, 7.0 Hz), 1.03 (3H, d, J = 7.0 Hz), 1.00 (3H, d, J = 7.0 Hz).



2c[1]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (1H, t, J = 8.7 Hz), 7.21 (2H, d, J = 8.9 Hz), 6.82 (2H, d, J = 8.9 Hz), 6.52 (2H, d, J = 8.7 Hz), 4.67 (1H, dd, J = 6.0, 5.0 Hz), 3.78 (3H, s), 3.72 (6H, s), 3.33 (1H, dd, J = 14.2, 5.0 Hz), 3.21 (1H, dd, J = 14.2, 6.0 Hz).

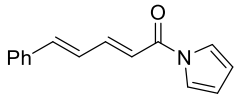


2d: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (1H, d, J = 7.7 Hz), 7.66 (2H, d, J = 8.2 Hz), 7.58 (1H, d, J = 7.7 Hz), 7.57 (1H, s), 7.31 (1H, t, J = 8.5 Hz), 7.26 (1H, t, J = 7.7 Hz), 7.19 (1H, t, J = 7.7 Hz), 7.06 (2H, d, J = 8.2 Hz), 6.46 (2H, d, J = 8.5 Hz), 4.73 (1H, t, J = 5.1 Hz), 3.50 (6H, s), 3.44 (1H, dd, J = 14.8, 5.1 Hz), 3.37 (1H, dd, J = 14.8, 5.1 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 159.4, 159.2, 144.7, 135.2, 135.0, 132.9, 131.2, 129.8, 126.7, 125.5, 124.6, 123.3, 120.1, 116.7, 113.5, 105.5, 103.6, 65.7, 55.9, 26.0, 21.5; IR (film): 2938, 2841, 1809, 1674, 1595, 1476, 1447, 1433, 1364, 1304, 1258, 1171, 1111, 1020, 907 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{25}N_2O_6S$ ([M+H]$^+$) 505.1428. Found 505.1418.

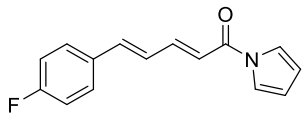


2e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (1H, t, J = 8.6 Hz), 6.58 (2H, d, J = 8.6 Hz), 5.87 (1H, ddt, J = 16.9, 10.2, 6.6 Hz), 5.25 (1H, dq, J = 16.9, 1.2 Hz), 5.18 (1H, d, J = 10.2 Hz), 4.50 (1H, t, J = 6.6 Hz), 3.82 (6H, s), 2.84 (1H, dt, J = 14.2, 6.6 Hz), 2.66 (1H, dt, J = 14.2, 6.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 159.2, 159.1, 133.0, 131.7, 119.3, 106.0, 103.8, 65.4, 56.1, 35.2; IR (film): 2940, 2841, 1813, 1674, 1593, 1476, 1433, 1304, 1256, 1109, 1015, 883 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{15}NO_4Na$ ([M+Na]$^+$) 284.0893. Found 284.0887.

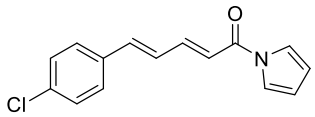
Characterization of δ-Aryl Dienyl *N*-Acylpyrroles 3:



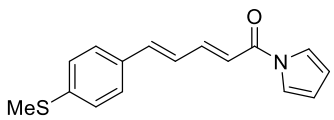
3a[15]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (1H, ddd, J = 15.0, 8.0, 2.6 Hz), 7.51 (2H, d, J = 7.8, Hz), 7.42 (2H, t, J = 2.3 Hz), 7.39 (2H, t, J = 7.8 Hz), 7.34 (1H, t, J = 7.8 Hz), 7.09-6.96 (2H, m), 6.72 (1H, d, J = 15.0 Hz), 6.34 (2H, t, J = 2.3 Hz).



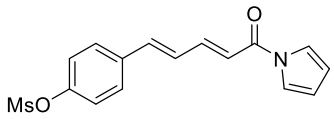
3b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (1H, dd, J = 14.9, 10.3 Hz), 7.48 (2H, dd, $J_{H\text{-}H}$ = 8.9 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 7.42 (2H, t, J = 2.3 Hz), 7.07 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.9 Hz), 7.00 (1H, d, J = 15.7 Hz), 6.93 (1H, dd, J = 15.7, 10.3 Hz), 6.71 (1H, d, J = 14.9 Hz), 6.34 (2H, t, J = 2.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (d, $J_{F\text{-}C}$ = 254.5 Hz), 163.1, 147.4, 141.3, 132.2 (d, $J_{F\text{-}C}$ = 2.9 Hz), 129.3 (d, $J_{F\text{-}C}$ = 8.7 Hz), 126.0 (d, $J_{F\text{-}C}$ = 2.9 Hz), 119.3, 118.8, 116.2 (d, $J_{F\text{-}C}$ = 22.3 Hz), 113.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –110.6; IR (film): 3142, 1672, 1591, 1506, 1464, 1402, 1354, 1290, 1227, 1123, 991, 935 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{13}NOF$ ([M+H]$^+$) 242.0976. Found 242.0976.



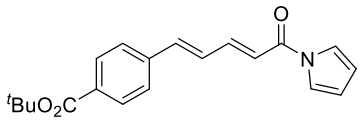
3c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (1H, ddd, J = 14.8, 6.3, 4.2 Hz), 7.46-7.38 (4H, m), 7.35 (2H, d, J = 8.7 Hz), 7.04-6.92 (2H, m), 6.73 (1H, d, J = 14.8 Hz), 6.35 (2H, t, J = 2.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 147.2, 141.1, 135.4, 134.4, 129.3, 128.7, 126.7, 119.3, 113.5, one carbon atom was not found propably due to overlapping.; IR (film): 3146, 1672, 1601, 1470, 1402, 1356, 1292, 1125, 1092, 1065, 991, 939 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{13}NOCl$ ([M+H]$^+$) 258.0680. Found 258.0682.



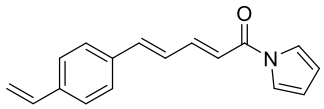
3d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (1H, ddd, J = 14.7, 6.5, 3.9 Hz), 7.42_0 (2H, d, J = 8.2 Hz), 7.41_6 (2H, t, J = 2.4 Hz), 7.23 (2H, d, J = 8.2 Hz), 7.00 (1H, dd, J = 15.6, 3.9 Hz), 6.96 (1H, dd, J = 15.6, 6.5 Hz), 6.70 (1H, d, J = 14.7 Hz), 6.34 (2H, t, J = 2.4 Hz), 2.51 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 147.7, 142.1, 141.0, 132.5, 127.9, 126.3, 125.4, 119.3, 118.3, 113.3, 15.4; IR (film): 3140, 2918, 1692, 1582, 1466, 1406, 1356, 1287, 1115, 1059, 989, 935, 829 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}NOS$ ([M+H]$^+$) 270.0947. Found 270.0948.



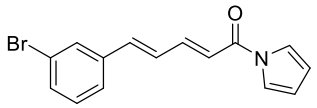
3e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (1H, ddd, J = 14.9, 6.9, 3.7 Hz), 7.54 (2H, d, J = 8.7 Hz), 7.42 (2H, t, J = 2.4 Hz), 7.30 (2H, d, J = 8.7 Hz), 7.05-6.93 (2H, m), 6.75 (1H, d, J = 14.9 Hz), 6.35 (2H, t, J = 2.4 Hz), 3.17 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 149.6, 146.9, 140.5, 135.2, 129.0, 127.3, 122.6, 119.7, 119.3, 113.5, 37.7; IR (film): 3146, 3022, 2941, 1674, 1591, 1470, 1348, 1296, 1157, 1125, 991, 941, 839 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}NO_4S$ ($[M+H]^+$) 318.0795. Found 318.0794.



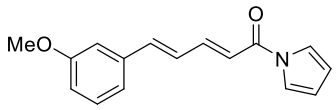
3f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (2H, d, J = 8.5 Hz), 7.76 (1H, dd, J = 14.9, 9.6 Hz), 7.53 (2H, d, J = 8.5 Hz), 7.42 (2H, t, J = 2.3 Hz), 7.10 (1H, dd, J = 15.9, 9.6 Hz), 7.04 (1H, d, J = 15.9 Hz), 6.78 (1H, d, J = 14.9 Hz), 6.35 (2H, t, J = 2.3 Hz), 1.61 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 163.0, 146.9, 141.3, 139.6, 132.6, 130.1, 128.2, 127.2, 120.0, 119.3, 113.5, 81.5, 28.3; IR (film): 3142, 2992, 1703, 1674, 1597, 1472, 1414, 1360, 1292, 1163, 1128, 988, 937 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{22}NO_3$ ($[M+H]^+$) 324.1594. Found 324.1594.



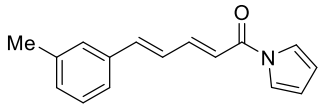
3g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (1H, ddd, J = 14.8, 5.6, 5.0 Hz), 7.47 (2H, d, J = 8.7 Hz), 7.42_3 (2H, d, J = 8.7 Hz), 7.42_2 (2H, t, J = 2.3 Hz), 7.04 (1H, dd, J = 15.8, 5.0 Hz), 7.00 (1H, dd, J = 15.8, 5.6 Hz), 6.72_1 (1H, d, J = 14.8 Hz), 6.72_0 (1H, dd, J = 17.7, 11.1 Hz), 6.35 (2H, t, J = 2.3 Hz), 5.81 (1H, d, J = 17.7 Hz), 5.31 (1H, d, J = 11.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 147.7, 142.2, 138.9, 136.3, 135.4, 127.8, 126.9, 126.1, 119.3, 118.7, 115.1, 113.4; IR (film): 3140, 1674, 1593, 1468, 1400, 1360, 1283, 1121, 1069, 995, 939, 843 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{16}NO$ ($[M+H]^+$) 250.1226. Found 250.1227.



3h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (1H, dd, J = 15.0, 10.4 Hz), 7.65 (1H, s), 7.45 (1H, d, J = 7.8 Hz), 7.41 (2H, t, J = 2.4 Hz), 7.40 (1H, d, J = 7.8 Hz), 7.25 (1H, t, J = 7.8 Hz), 7.01 (1H, dd, J = 15.9, 10.4 Hz), 6.93 (1H, d, J = 15.9 Hz), 6.75 (1H, d, J = 15.0 Hz), 6.35 (2H, t, J = 2.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 146.8, 140.6, 138.0, 132.3, 130.5, 130.1, 127.5, 126.2, 123.2, 119.8, 119.3, 113.5; IR (film): 3146, 1682, 1601, 1464, 1354, 1287, 1121, 1070, 995, 868 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{13}NO^{79}Br$ ($[M+H]^+$) 302.0175. Found 302.0175.

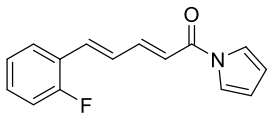


3i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (1H, dt, J = 14.9, 5.4 Hz), 7.42 (2H, t, J = 2.4 Hz), 7.30 (1H, t, J = 8.0 Hz), 7.10 (1H, d, J = 8.0 Hz), 7.02_{26} (1H, dd, J = 16.3, 5.4 Hz), 7.02_{21} (1H, t, J = 1.8 Hz), 6.98 (1H, dd, J = 16.3, 5.4 Hz), 6.90 (1H, dd, J = 8.0, 1.8 Hz), 6.72 (1H, d, J = 14.9 Hz), 6.34 (2H, t, J = 2.4 Hz), 3.84 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 160.0, 147.5, 142.5, 137.3, 130.0, 126.5, 120.3, 119.3, 118.9, 115.4, 113.4, 112.5, 55.4; IR (film): 3142, 2963, 1672, 1605, 1576, 1470, 1433, 1360, 1267, 1125, 1042, 993, 941 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}NO_2$ ($[M+H]^+$) 254.1176. Found 254.1176.

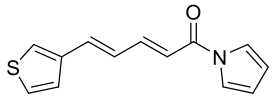


3j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (1H, ddd, J = 15.0, 5.9, 4.9 Hz), 7.42 (2H, t, J = 2.3 Hz), 7.32_3 (1H, s), 7.31_6 (1H, d, J = 7.3 Hz), 7.27 (1H, t, J = 7.3 Hz), 7.16 (1H, d, J = 7.3 Hz), 7.03 (1H, dd, J = 15.9, 5.9 Hz), 6.99 (1H, dd, J = 15.9, 4.9 Hz), 6.71 (1H, d, J = 15.0 Hz), 6.34 (2H, t, J = 2.3 Hz), 2.38 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 147.8, 142.9, 138.7, 135.9, 130.5, 128.9, 128.3, 126.1, 124.8, 119.3, 118.6, 113.3, 21.5; IR (film): 3146, 2916, 1674, 1593, 1464, 1404, 1350, 1285, 1128, 1070,

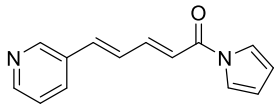
991, 939 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}NO$ ($[M+H]^+$) 238.1226. Found 238.1228.



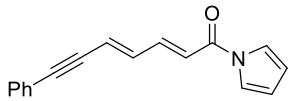
3k: ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (1H, dd, J = 14.9, 9.8 Hz), 7.53 (1H, td, J = 7.8, 1.4 Hz), 7.42 (2H, t, J = 2.3 Hz), 7.31 (1H, tdd, J_{H-H} = 7.8, 1.6 Hz, J_{F-H} = 5.8 Hz), 7.16$_0$ (1H, d, J = 15.6 Hz), 7.15$_8$ (1H, td, J_{H-H} = 7.8, 1.6 Hz, J_{F-H} = 7.8 Hz), 7.09$_9$ (1H, dd, J = 15.6, 9.8 Hz), 7.09$_2$ (1H, ddd, J_{H-H} = 7.8, 1.4 Hz, J_{F-H} = 11.0 Hz), 6.74 (1H, d, J = 14.9 Hz), 6.34 (2H, t, J = 2.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 161.0 (d, J_{F-C} = 256.4 Hz), 147.6, 135.0 (d, J_{F-C} = 1.9 Hz), 130.9 (d, J_{F-C} = 8.7 Hz), 128.7 (d, J_{F-C} = 6.8 Hz), 128.4 (d, J_{F-C} = 2.9 Hz), 124.5 (d, J_{F-C} = 2.9 Hz), 123.9 (d, J_{F-C} = 1.5 Hz), 119.4 (d, J_{F-C} = 25.2 Hz), 119.3, 116.3 (d, J_{F-C} = 22.3 Hz), 113.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.3; IR (film): 3142, 1670, 1595, 1456, 1406, 1358, 1281, 1229, 1123, 993, 937 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{13}NOF$ ($[M+H]^+$) 242.0976. Found 242.0975.



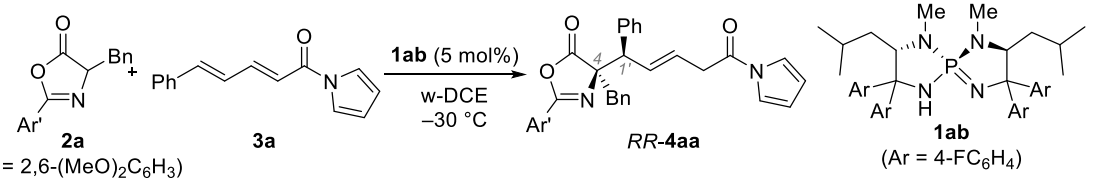
3l: ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (1H, dd, J = 15.0, 11.4 Hz), 7.41 (2H, t, J = 2.3 Hz), 7.40 (1H, dd, J = 3.0, 1.1 Hz), 7.34 (1H, dd, J = 5.3, 3.0 Hz), 7.31 (1H, dd, J = 5.3, 1.1 Hz), 7.04 (1H, d, J = 15.5 Hz), 6.84 (1H, dd, J = 15.5, 11.4 Hz), 6.69 (1H, d, J = 15.0 Hz), 6.34 (2H, t, J = 2.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 147.8, 139.1, 136.3, 127.0, 126.3, 126.2, 125.0, 119.3, 118.3, 113.3; IR (film): 3140, 1672, 1597, 1510, 1466, 1418, 1354, 1281, 1123, 993, 932 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{12}NOS$ ($[M+H]^+$) 230.0634. Found 230.0635.



3m: ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (1H, d, J = 1.1 Hz), 8.56 (1H, dd, J = 4.8, 1.1 Hz), 7.81 (1H, d, J = 8.1 Hz), 7.75 (1H, dd, J = 15.0, 10.3 Hz), 7.42 (2H, t, J = 2.2 Hz), 7.32 (1H, dd, J = 8.1, 4.8 Hz), 7.08 (1H, dd, J = 15.9, 10.3 Hz), 7.01 (1H, d, J = 15.9 Hz), 6.78 (1H, d, J = 15.0 Hz), 6.36 (2H, t, J = 2.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 150.2, 149.2, 146.6, 138.4, 133.7, 131.6, 128.1, 123.8, 120.2, 119.3, 113.6; IR (film): 3134, 1682, 1603, 1470, 1427, 1362, 1281, 1128, 1067, 993, 937 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{13}N_2O$ ($[M+H]^+$) 225.1022. Found 225.1021.

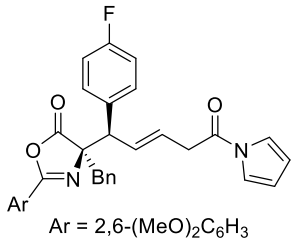


3n: ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (1H, dd, J = 14.8, 11.5 Hz), 7.51-7.44 (2H, m), 7.39 (2H, t, J = 2.3 Hz), 7.37-7.33 (3H, m), 6.87 (1H, dd, J = 15.2, 11.5 Hz), 6.69 (1H, d, J = 14.8 Hz), 6.34 (2H, t, J = 2.3 Hz), 6.33 (1H, d, J = 15.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 146.0, 138.4, 131.9, 129.2, 128.6, 122.7, 121.6, 120.4, 119.3, 113.6, 97.6, 88.4; IR (film): 3146, 3067, 3032, 2191, 1678, 1599, 1470, 1358, 1288, 1125, 989 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{13}NONa$ ($[M+Na]^+$) 270.0889. Found 270.0891.

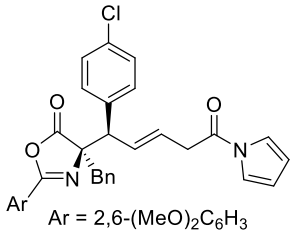


Representative Procedure for Asymmetric 1,6-Addition of Azlactone 2 to δ-Aryl Dienyl *N*-Acylpyrrole 3 with Chiral Iminophosphorane 1ab as a Catalyst: To a solution of azlactone **2a** (155.67 mg, 0.50 mmol) and dienyl *N*-acylpyrrole **3a** (55.82 mg, 0.25 mmol) in 1,2-dichloroethane saturated with water (w-DCE, 1.05 mL) was added a solution of chiral iminophosphorane **1ab** (8.50 mg, 12.5 μmol) in DCE (0.20 mL) at –30 °C under Ar atmosphere. The resulting mixture was stirred for 16 h and the reaction was then quenched by the addition of a solution of trifluoroacetic acid in toluene (0.5 M, 125.0 μL). All volatiles were removed by evaporation to give crude residue, which

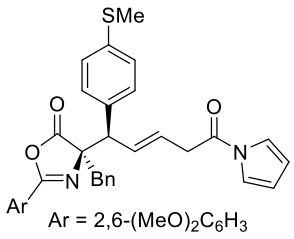
was analyzed by ^{1}H NMR (800 MHz) to determine the regioisomeric and diastereomeric ratio of adducts. The subsequent purification by column chromatography on silica gel (H/ethyl acetate (EA) = 1:1 as eluent) gave adducts in 88% yield as a mixture of isomers (117.6 mg, 0.22 mmol). The enantiomeric excess of 1,6-adduct **4aa** was determined by HPLC analysis. *RR*-**4aa** (4*R*,1'*R*)**:** HPLC OZ3, H/EtOH = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 16.5 min (minor diastereomer), 18.9 min (minor diastereomer), 20.5 min (minor isomer of major diastereomer), 30.1 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (2H, dd, J = 8.2, 1.4 Hz), 7.32-7.14 (11H, m), 6.42 (2H, d, J = 8.4 Hz), 6.39 (1H, ddt, J = 15.5, 9.8, 1.3 Hz), 6.27 (2H, t, J = 2.3 Hz), 6.02 (1H, dt, J = 15.5, 7.0 Hz), 3.98 (1H, d, J = 9.8 Hz), 3.72 (1H, ddd, J = 17.4, 7.0, 1.3 Hz), 3.65 (1H, ddd, J = 17.4, 7.0, 1.3 Hz), 3.58 (6H, s), 3.44 (1H, d, J = 13.7 Hz), 3.17 (1H, d, J = 13.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 168.4, 159.4, 158.1, 138.0, 134.6, 132.9, 132.8, 130.9, 129.6, 128.3, 128.0, 127.4, 126.9, 125.8, 119.2, 113.4, 105.1, 103.5, 78.2, 56.0, 55.9, 42.9, 38.4; IR (film): 3030, 2936, 2839, 1805, 1717, 1663, 1595, 1476, 1331, 1300, 1256, 1115, 964, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{31}N_2O_5$ ([M+H]$^+$) 535.2227. Found 535.2226.



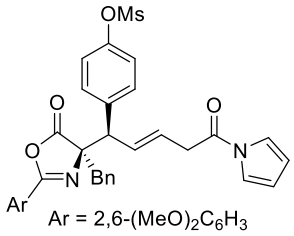
RR-**4ab:** HPLC OZ3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 254 nm, 12.6 min (minor diastereomer), 14.1 min (minor diastereomer), 16.0 min (minor isomer of major diastereomer), 53.9 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (2H, dd, $J_{H\text{-}H}$ = 8.9 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 7.32-7.27 (2H, brs), 7.28 (1H, t, J = 8.7 Hz), 7.24-7.15 (5H, m), 6.94 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.9 Hz), 6.43 (2H, d, J = 8.7 Hz), 6.36 (1H, dd, J = 15.5, 10.1 Hz), 6.28 (2H, t, J = 2.5 Hz), 6.02 (1H, dt, J = 15.5, 6.7 Hz), 3.98 (1H, d, J = 10.1 Hz), 3.72 (1H, ddd, J = 17.2, 6.7, 1.3 Hz), 3.66 (1H, ddd, J = 17.2, 6.7, 1.3 Hz), 3.59 (6H, s), 3.42 (1H, d, J = 13.7 Hz), 3.16 (1H, d, J = 13.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 168.4, 162.2 (d, $J_{F\text{-}C}$ = 248.7 Hz), 159.4, 158.2, 134.5, 133.8 (d, $J_{F\text{-}C}$ = 2.9 Hz), 133.0, 132.5, 131.2 (d, $J_{F\text{-}C}$ = 7.7 Hz), 130.9, 128.0, 127.0, 126.1, 119.2, 115.1 (d, $J_{F\text{-}C}$ = 22.3 Hz), 113.5, 104.9, 103.5, 78.2, 55.9, 55.2, 42.7, 38.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.4; IR (film): 3148, 2936, 2839, 1805, 1717, 1661, 1595, 1508, 1476, 1433, 1333, 1300, 1256, 1223, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}N_2O_5F$ ([M+H]$^+$) 553.2133. Found 553.2131.



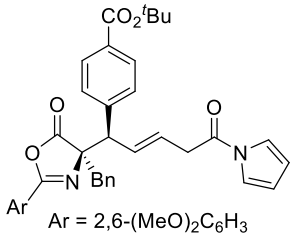
RR-**4ac:** HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 20.7 min (minor diastereomer), 22.8 min (major isomer of major diastereomer), 36.7 min (minor isomer of major diastereomer), 41.7 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (5H, m), 7.24-7.16 (7H, m), 6.43 (2H, d, J = 8.5 Hz), 6.35 (1H, ddt, J = 15.4, 10.1, 1.1 Hz), 6.28 (2H, t, J = 2.3 Hz), 6.02 (1H, dt, J = 15.4, 6.8 Hz), 3.96 (1H, d, J = 10.1 Hz), 3.72 (1H, ddd, J = 17.2, 6.8, 1.1 Hz), 3.66 (1H, ddd, J = 17.2, 6.8, 1.1 Hz), 3.59 (6H, s), 3.43 (1H, d, J = 13.8 Hz), 3.17 (1H, d, J = 13.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 168.3, 159.4, 158.3, 136.5, 134.4, 133.3, 133.1, 132.2, 130.9$_1$, 130.8$_7$, 128.4, 128.0, 127.1, 126.3, 119.2, 113.5, 104.8, 103.5, 78.1, 55.9, 55.3, 42.7, 38.4; IR (film): 3030, 2936, 2839, 1805, 1715, 1659, 1595, 1476, 1332, 1302, 1256, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}N_2O_5Cl$ ([M+H]$^+$) 569.1838. Found 569.1835.



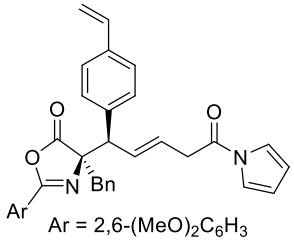
RR-**4ad:** The absolute configuration of *RR*-**4ad** was determined by X-ray crystallographic analysis (see page 112). HPLC OX3, H/IPA/EtOH = 18:1:1, flow rate = 1.0 mL/min, λ = 254 nm, 30.6 min (minor diastereomer), 33.8 min (*SS*-isomer), 36.5 min (minor diastereomer), 45.6 min (*RR*-isomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (2H, brs), 7.28 (2H, d, J = 8.2 Hz), 7.27 (1H, t, J = 8.1 Hz), 7.24-7.16 (5H, m), 7.13 (2H, d, J = 8.2 Hz), 6.43 (2H, d, J = 8.1 Hz), 6.36 (1H, ddt, J = 15.5, 10.1, 1.3 Hz), 6.27 (2H, t, J = 2.3 Hz), 6.00 (1H, dt, J = 15.5, 6.9 Hz), 3.94 (1H, d, J = 10.1 Hz), 3.71 (1H, ddd, J = 17.2, 6.9, 1.3 Hz), 3.65 (1H, ddd, J = 17.2, 6.9, 1.3 Hz), 3.59 (6H, s), 3.42 (1H, d, J = 13.7 Hz), 3.17 (1H, d, J = 13.7 Hz), 2.43 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 168.4, 159.4, 158.1, 137.4, 134.7, 134.5, 133.0, 132.6, 130.9, 129.9, 127.9, 126.9, 126.2, 125.9, 119.2, 113.4, 104.9, 103.5, 78.2, 55.9, 55.5, 42.8, 38.4, 15.6; IR (film): 3030, 2924, 2837, 1805, 1715, 1661, 1595, 1476, 1333, 1300, 1254, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{33}N_2O_5S$ ([M+H]$^+$) 581.2105. Found 581.2101.



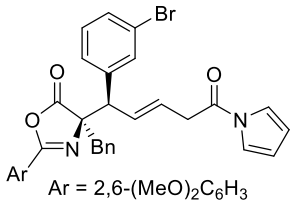
RR-**4ae:** HPLC OX3, H/EtOH = 4:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 25.6 min (minor isomer of major diastereomer), 27.8 min (major isomer of major diastereomer), 33.1 min (minor diastereomer), 36.7 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (2H, d, J = 8.7 Hz), 7.30 (2H, brs), 7.29 (1H, t, J = 8.5 Hz), 7.24-7.18 (5H, m), 7.18 (2H, d, J = 8.7 Hz), 6.44 (2H, d, J = 8.5 Hz), 6.35 (1H, dd, J = 15.3, 10.1 Hz), 6.29 (2H, t, J = 2.1 Hz), 6.03 (1H, dt, J = 15.3, 6.8 Hz), 4.01 (1H, d, J = 10.1 Hz), 3.73 (1H, dd, J = 17.3, 6.8 Hz), 3.67 (1H, dd, J = 17.3, 6.8 Hz), 3.60 (6H, s), 3.43 (1H, d, J = 13.5 Hz), 3.17 (1H, d, J = 13.5 Hz), 3.09 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 168.3, 159.4, 158.4, 148.6, 137.5, 134.3, 133.1, 132.1, 131.2, 130.9, 128.0, 127.1, 126.5, 121.7, 119.2, 113.5, 104.8, 103.6, 78.0, 56.0, 55.2, 42.8, 38.3, 37.3; IR (film): 3030, 2936, 2841, 1805, 1717, 1661, 1595, 1476, 1366, 1256, 1113, 964, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{33}N_2O_8S$ ([M+H]$^+$) 629.1952. Found 629.1949.



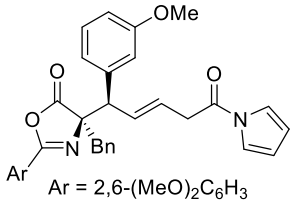
RR-**4af:** HPLC IC3, H/EtOH = 19:1, flow rate = 1.0 mL/min, λ = 250 nm, 26.6 min (major isomer of major diastereomer), 30.7 min (minor diastereomer), 36.4 min (minor isomer of minor diastereomer), 58.5 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (2H, d, J = 8.5 Hz), 7.41 (2H, d, J = 8.5 Hz), 7.30 (2H, brs), 7.28 (1H, t, J = 8.7 Hz), 7.24-7.16 (5H, m), 6.43 (2H, d, J = 8.7 Hz), 6.40 (1H, ddt, J = 15.5, 10.1, 1.4 Hz), 6.28 (2H, t, J = 2.5 Hz), 6.04 (1H, dt, J = 15.5, 6.8 Hz), 4.04 (1H, d, J = 10.1 Hz), 3.73 (1H, ddd, J = 17.2, 6.8, 1.4 Hz), 3.67 (1H, ddd, J = 17.2, 6.8, 1.4 Hz), 3.58 (6H, s), 3.45 (1H, d, J = 13.7 Hz), 3.19 (1H, d, J = 13.7 Hz), 1.56 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 168.3, 165.8, 159.4, 158.3, 142.6, 134.4, 133.1, 132.1, 131.1, 130.9, 129.4$_4$, 129.4$_0$, 128.0, 127.1, 126.5, 119.2, 113.5, 104.8, 103.5, 81.0, 78.1, 55.9, 42.8, 38.4, 28.3, one carbon atom was not found probably due to overlapping; IR (film): 2974, 2839, 1807, 1707, 1659, 1595, 1476, 1294, 1256, 1165, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{39}N_2O_7$ ([M+H]$^+$) 635.2752. Found 635.2749.



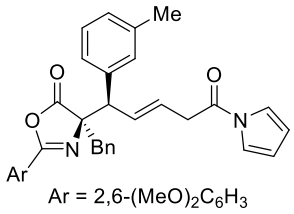
RR-**4ag:** HPLC OD3, H/EtOH = 10:1, flow rate = 1.0 mL/min, λ = 240 nm, 15.4 min (minor diastereomer), 18.7 min (major isomer of major diastereomer), 28.5 min (minor isomer of major diastereomer), 41.7 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (6H, m), 7.27 (1H, t, *J* = 8.7 Hz), 7.24-7.15 (5H, m), 6.66 (1H, dd, *J* = 17.7, 11.3 Hz), 6.42 (2H, d, *J* = 8.7 Hz), 6.39 (1H, dd, *J* = 15.6, 10.1 Hz), 6.28 (2H, t, *J* = 2.5 Hz), 6.02 (1H, dt, *J* = 15.6, 6.6 Hz), 5.70 (1H, d, *J* = 17.7 Hz), 5.20 (1H, d, *J* = 11.3 Hz), 3.98 (1H, d, *J* = 10.1 Hz), 3.72 (1H, dd, *J* = 16.9, 6.6 Hz), 3.66 (1H, dd, *J* = 16.9, 6.6 Hz), 3.57 (6H, s), 3.43 (1H, d, *J* = 17.7 Hz), 3.18 (1H, d, *J* = 17.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 168.4, 159.4, 158.1, 137.6, 136.6, 134.6, 133.0, 132.6, 130.9, 129.7, 128.0, 127.0, 126.2, 125.9, 119.2, 113.9, 113.4, 105.0, 103.5, 78.2, 55.9, 55.8, 42.8, 38.4, one carbon atom was not found probably due to overlapping.; IR (film): 3030, 2930, 2839, 1805, 1717, 1663, 1595, 1476, 1339, 1300, 1256, 1115, 964, 916 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{33}N_2O_5$ ($[M+H]^+$) 561.2384. Found 561.2383.



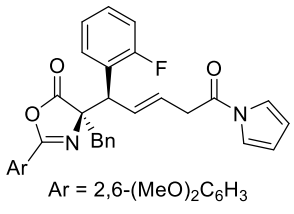
RR-**4ah:** HPLC OD3, H/IPA/EtOH = 15:1:4, flow rate = 0.5 mL/min, λ = 254 nm, 24.8 min (minor diastereomer), 28.7 min (minor isomer of major diastereomer), 32.6 min (major isomer of major diastereomer), 44.5 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (1H, t, *J* = 1.7 Hz), 7.35 (1H, dt, *J* = 7.9, 1.7 Hz), 7.33-7.26 (3H, m), 7.29 (1H, t, *J* = 8.5 Hz), 7.24-7.17 (5H, m), 7.13 (1H, t, *J* = 7.9 Hz), 6.44 (2H, d, *J* = 8.5 Hz), 6.33 (1H, ddt, *J* = 15.4, 10.1, 1.4 Hz), 6.29 (2H, t, *J* = 2.5 Hz), 6.03 (1H, dt, *J* = 15.4, 6.5 Hz), 3.94 (1H, d, *J* = 10.1 Hz), 3.73 (1H, ddd, *J* = 17.2, 6.5, 1.4 Hz), 3.67 (1H, ddd, *J* = 17.2, 6.5, 1.4 Hz), 3.61 (6H, s), 3.43 (1H, d, *J* = 13.7 Hz), 3.17 (1H, d, *J* = 13.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 168.3, 159.5, 158.4, 140.4, 134.3, 133.1, 132.2, 132.1, 130.9, 130.6, 129.9, 128.4, 128.0, 127.1, 126.5, 122.5, 119.2, 113.5, 104.8, 103.5, 77.9, 56.1, 55.6, 42.7, 38.4; IR (film): 2936, 2839, 1805, 1715, 1659, 1593, 1474, 1333, 1300, 1254, 1111, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}N_2O_5{}^{79}Br$ ($[M+H]^+$) 613.1333. Found 613.1330.



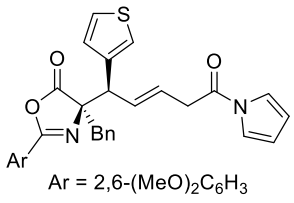
RR-**4ai:** HPLC AD3, H/IPA/EtOH = 85.9:9.1:5, flow rate = 1.0 mL/min, λ = 210 nm, 19.9 min (minor isomer of major diastereomer), 22.0 min (minor diastereomer), 25.2 min (major isomer of major diastereomer), 29.4 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (2H, brs), 7.27 (1H, t, *J* = 8.6 Hz), 7.25-7.18 (5H, m), 7.18 (1H, t, *J* = 8.1 Hz), 6.96 (1H, d, *J* = 8.1 Hz), 6.91 (1H, t, *J* = 2.3 Hz), 6.77 (1H, dd, *J* = 8.1, 2.3 Hz), 6.43 (2H, d, *J* = 8.6 Hz), 6.37 (1H, ddt, *J* = 15.3, 10.1, 1.2 Hz), 6.28 (2H, t, *J* = 2.3 Hz), 6.02 (1H, dt, *J* = 15.3, 6.9 Hz), 3.96 (1H, d, *J* = 10.1 Hz), 3.72 (1H, ddd, *J* = 16.9, 6.9, 1.2 Hz), 3.70 (3H, s), 3.66 (1H, ddd, *J* = 16.9, 6.9, 1.2 Hz), 3.59 (6H, s), 3.44 (1H, d, *J* = 13.7 Hz), 3.18 (1H, d, *J* = 13.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 168.5, 159.4, 159.3, 158.2, 139.5, 134.6, 133.0, 132.7, 130.9, 129.3, 128.0, 127.0, 125.9, 121.9, 119.2, 114.8, 113.4, 113.2, 105.0, 103.5, 78.1, 56.1, 55.9, 55.1, 42.9, 38.4; IR (film): 3030, 2936, 2837, 1805, 1717, 1661, 1595, 1476, 1335, 1300, 1258, 1113, 966, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{33}N_2O_6$ ($[M+H]^+$) 565.2333. Found 565.2333.



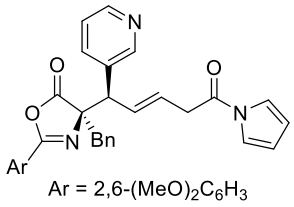
RR-**4aj:** HPLC AD3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 210 nm, 29.1 min (minor isomer of major diastereomer), 31.8 min (minor diastereomer), 34.7 min (major isomer of major diastereomer), 55.0 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (2H, brs), 7.27 (1H, t, J = 8.4 Hz), 7.24-7.17 (6H, m), 7.15 (1H, t, J = 7.5 Hz), 7.14 (1H, s), 7.02 (1H, d, J = 7.5 Hz), 6.43 (2H, d, J = 8.4 Hz), 6.36 (1H, ddt, J = 15.5, 9.8, 1.3 Hz), 6.27 (2H, t, J = 2.5 Hz), 6.00 (1H, dt, J = 15.5, 6.9 Hz), 3.93 (1H, d, J = 9.8 Hz), 3.71 (1H, ddd, J = 17.4, 6.9, 1.3 Hz), 3.65 (1H, ddd, J = 17.4, 6.9, 1.3 Hz), 3.59 (6H, s), 3.42 (1H, d, J = 13.7 Hz), 3.17 (1H, d, J = 13.7 Hz), 2.28 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 168.5, 159.5, 158.0, 138.0, 137.9, 134.7, 133.0, 130.9, 130.3, 128.2$_1$, 128.1$_5$, 128.0, 126.9, 126.5, 125.6, 119.2, 113.4, 105.1, 103.5, 78.1, 56.1, 55.9, 42.9, 38.5, 21.6, one carbon atom was not found probably due to overlapping.; IR (film): 3030, 2926, 2839, 1805, 1717, 1661, 1595, 1474, 1333, 1300, 1254, 1113, 964, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{33}N_2O_5$ ([M+H]$^+$) 549.2384. Found 549.2384.



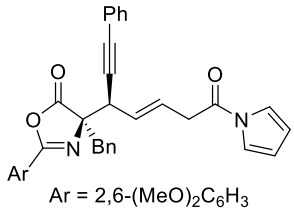
RR-**4ak:** HPLC OZ3, H/EtOH = 19:1, flow rate = 1.0 mL/min, λ = 210 nm, 20.1 min (minor diastereomer), 22.2 min (minor diastereomer), 34.0 min (minor isomer of major diastereomer), 46.2 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, td, J = 7.8 Hz, $J_{F\text{-}H}$ = 1.8 Hz), 7.29$_3$ (1H, t, J = 8.7 Hz), 7.28$_6$ (2H, brs), 7.24-7.16 (6H, m), 7.08-7.00 (2H, m), 6.45 (2H, d, J = 8.7 Hz), 6.30 (1H, ddq, $J_{H\text{-}H}$ = 15.6, 9.7, 1.3 Hz, $J_{F\text{-}H}$ = 1.3 Hz), 6.27 (2H, t, J = 2.3 Hz), 6.04 (1H, dt, J = 15.6, 6.5 Hz), 4.50 (1H, d, J = 9.7 Hz), 3.71 (1H, ddd, J = 16.8, 6.5, 1.3 Hz), 3.65 (1H, ddd, J = 16.8, 6.5, 1.3 Hz), 3.61 (6H, s), 3.46 (1H, d, J = 13.7 Hz), 3.20 (1H, d, J = 13.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 168.3, 160.3 (d, $J_{F\text{-}C}$ = 251.6 Hz), 159.4, 158.3, 134.4, 133.0, 131.9, 131.0, 130.7 (d, $J_{F\text{-}C}$ = 3.9 Hz), 128.9 (d, $J_{F\text{-}C}$ = 8.7 Hz), 128.0, 127.0, 126.5, 125.4 (d, $J_{F\text{-}C}$ = 14.5 Hz), 123.9 (d, $J_{F\text{-}C}$ = 3.9 Hz), 119.2, 115.8 (d, $J_{F\text{-}C}$ = 24.2 Hz), 113.4, 105.0, 103.6, 77.8, 55.9, 46.9, 42.7, 38.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.5; IR (film): 3030, 2936, 2839, 1807, 1715, 1661, 1595, 1476, 1333, 1300, 1256, 1111, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}N_2O_5F$ ([M+H]$^+$) 553.2133. Found 553.2135.



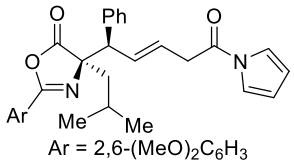
RR-**4al:** HPLC OZ3, H/IPA = 4:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 8.4 min (minor diastereomer), 9.0 min (minor isomer of major diastereomer), 11.1 min (minor diastereomer), 12.5 min (major isomer of major diastereomer); ^{1}H NMR [400 MHz, $(CD_3)_2CO$] δ 7.45 (2H, t, J = 2.3 Hz), 7.37 (1H, t, J = 8.5 Hz), 7.36 (1H, dd, J = 5.0, 3.0 Hz), 7.33 (1H, dd, J = 3.0, 1.4 Hz), 7.28-7.20 (3H, m), 7.20-7.15 (2H, m), 7.12 (1H, dd, J = 5.0, 1.4 Hz), 6.61 (2H, d, J = 8.5 Hz), 6.30 (1H, ddt, J = 15.4, 9.6, 1.4 Hz), 6.28 (2H, t, J = 2.3 Hz), 6.05 (1H, dt, J = 15.4, 6.4 Hz), 4.19 (1H, d, J = 9.6 Hz), 3.90 (1H, ddd, J = 16.7, 6.4, 1.4 Hz), 3.84 (1H, ddd, J = 16.7, 6.4, 1.4 Hz), 3.66 (6H, s), 3.41 (1H, d, J = 13.7 Hz), 3.13 (1H, d, J = 13.7 Hz; ^{13}C NMR [101 MHz, $(CD_3)_2CO$] δ 179.8, 169.6, 160.2, 158.0, 139.8, 135.8, 133.8, 133.3, 131.6, 129.4, 128.6, 127.7, 126.8, 125.4, 124.0, 120.1, 113.6, 106.2, 104.5, 78.6, 56.3, 52.1, 43.2, 38.6; IR (film): 3011, 2934, 2839, 1805, 1715, 1661, 1595, 1476, 1329, 1302, 1254, 1113, 964, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{29}N_2O_5S$ ([M+H]$^+$) 541.1792. Found 541.1792.



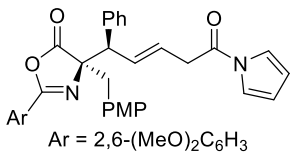
RR-**4am:** HPLC OX3, H/IPA/EtOH = 8:1:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 24.4 min (minor isomer of major diastereomer), 25.9 min (major isomer of major diastereomer), 46.0 min (minor diastereomer), 52.4 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (1H, brs), 8.47 (1H, brd, J = 3.7 Hz), 7.67 (1H, d, J = 7.8 Hz), 7.29 (2H, brs), 7.26 (1H, t, J = 8.5 Hz), 7.24-7.14 (6H, m), 6.42 (2H, d, J = 8.5 Hz), 6.41 (1H, dd, J = 15.5, 9.8 Hz), 6.28 (2H, t, J = 2.3 Hz), 6.06 (1H, dt, J = 15.5, 6.7 Hz), 4.00 (1H, d, J = 9.8 Hz), 3.73 (1H, dd, J = 17.4, 6.7 Hz), 3.67 (1H, dd, J = 17.4, 6.7 Hz), 3.59 (6H, s), 3.45 (1H, d, J = 13.8 Hz), 3.19 (1H, d, J = 13.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 168.1, 159.3, 158.5, 150.7, 148.6, 137.1, 134.2, 133.7, 133.0, 131.6, 130.8, 128.0, 127.1, 126.9, 123.2, 119.1, 113.5, 104.8, 103.5, 77.9, 55.9, 53.6, 42.7, 38.2; IR (film): 3030, 2930, 2841, 1805, 1713, 1661, 1593, 1470, 1327, 1302, 1256, 1113, 962, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{30}N_3O_5$ ([M+H]$^+$) 536.2180. Found 536.2175.



RR-**4an:** HPLC OD3, H/EtOH = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 210 nm, 16.5 min (major isomer of major diastereomer), 18.3 min (minor diastereomer), 20.3 min (minor isomer of major diastereomer), 22.9 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.41 (2H, m), 7.33-7.18 (11H, m), 6.46 (2H, d, J = 8.4 Hz), 6.25$_0$ (2H, t, J = 2.4 Hz), 6.24$_8$ (1H, dt, J = 15.3, 7.3 Hz), 5.98 (1H, dd, J = 15.3, 7.1 Hz), 3.94 (1H, d, J = 7.1 Hz), 3.70 (1H, dd, J = 18.1, 7.3 Hz), 3.63 (1H, dd, J = 18.1, 7.3 Hz), 3.54 (6H, s), 3.41 (1H, d, J = 13.7 Hz), 3.37 (1H, d, J = 13.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 168.1, 159.4, 158.5, 134.4, 133.0, 131.9, 130.8, 128.8, 128.3, 128.2, 128.1, 126.9$_9$, 126.9$_5$, 123.0, 119.1, 113.4, 105.4, 103.6, 86.7, 84.5, 76.7, 55.9, 42.5, 41.4, 38.3; IR (film): 3032, 2936, 2839, 2251, 1809, 1717, 1668, 1595, 1476, 1433, 1329, 1302, 1256, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{31}N_2O_5$ ([M+H]$^+$) 559.2227. Found 559.2224.

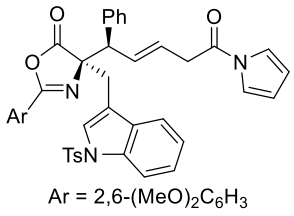


RR-**4ba:** HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 19.9 min (major isomer of major diastereomer), 26.1 min (minor diastereomer), 32.5 min (minor diastereomer), 36.6 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (1H, t, J = 8.5 Hz), 7.32-7.18 (7H, m), 6.53 (2H, d, J = 8.5 Hz), 6.26 (2H, t, J = 2.5 Hz), 6.25 (1H, dd, J = 15.5, 9.8 Hz), 5.90 (1H, dt, J = 15.5, 6.8 Hz), 3.74 (1H, d, J = 9.8 Hz), 3.73 (6H, s), 3.67 (1H, dd, J = 17.3, 6.8 Hz), 3.59 (1H, dd, J = 17.3, 6.8 Hz), 2.28-2.16 (1H, m), 1.83-1.62 (2H, m), 0.93 (3H, d, J = 6.4 Hz), 0.89 (3H, d, J = 6.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.5, 168.4, 159.4, 157.9, 138.0, 133.1, 133.0, 129.5, 128.3, 127.3, 125.6, 119.2, 113.3, 105.7, 103.8, 76.3, 56.3, 55.9, 45.6, 38.5, 24.8, 24.4, 23.0; IR (film): 2957, 2839, 1805, 1715, 1667, 1595, 1470, 1346, 1331, 1256, 1111, 957, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{33}N_2O_5$ ([M+H]$^+$) 501.2384. Found 501.2382.

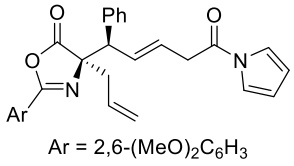


RR-**4ca:** HPLC OZ3, H/IPA/EtOH = 18:1:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 15.1 min (minor diastereomer), 17.1 min (major isomer of major diastereomer), 18.6 min (minor isomer of major diastereomer), 20.2 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (2H, d, J = 7.4 Hz), 7.30 (2H, brs), 7.33-7.17 (4H, m), 7.13 (2H, d, J = 8.7 Hz), 6.74 (2H, d, J = 8.7 Hz), 6.43 (2H, d, J = 8.7 Hz), 6.38 (1H, dd, J = 15.6, 10.2 Hz), 6.27 (2H, t, J = 2.5 Hz), 6.01 (1H, dt, J = 15.6, 6.6 Hz), 3.96 (1H, d, J = 10.2 Hz), 3.74 (3H, s), 3.71 (1H, dd, J = 18.5, 6.6 Hz), 3.65 (1H, dd, J = 18.5, 6.6 Hz), 3.60 (6H, s), 3.38 (1H, d, J = 14.0 Hz), 3.12 (1H, d, J = 14.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 168.4, 159.4, 158.6, 158.0, 138.1, 132.9, 132.8, 132.0, 129.5, 128.3, 127.4, 126.6, 125.7, 119.2, 113.4, 113.3, 105.1, 103.5, 78.3, 55.8,

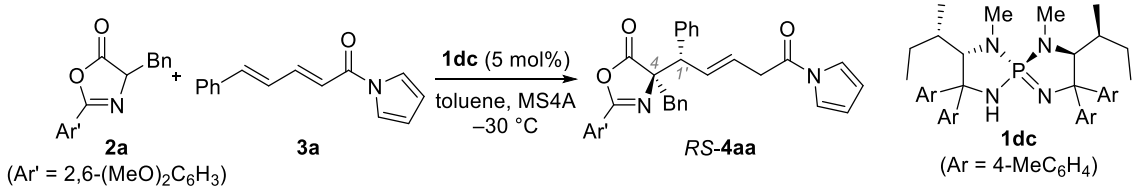
55.2, 42.1, 38.4; IR (film): 3113, 2936, 2835, 1807, 1730, 1665, 1595, 1512, 1470, 1348, 1298, 1254, 1117, 962, 920 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{33}N_2O_6$ ([M+H]$^+$) 565.2333. Found 565.2329.



RR-**4da:** HPLC IA3, H/IPA = 3:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 9.9 min (minor isomer of major diastereomer), 10.9 min (major isomer of major diastereomer), 12.3 min (minor diastereomer), 13.9 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (1H, d, J = 7.8 Hz), 7.57 (1H, d, J = 7.8 Hz), 7.57 (2H, d, J = 8.2 Hz), 7.51 (1H, s), 7.35 (2H, d, J = 8.0 Hz), 7.29 (2H, brs), 7.27-7.20 (5H, m), 7.18 (1H, t, J = 7.8 Hz), 6.91 (2H, d, J = 8.2 Hz), 6.39 (1H, ddt, J = 15.5, 10.2, 1.4 Hz), 6.32 (2H, d, J = 8.7 Hz), 6.28 (2H, t, J = 2.3 Hz), 6.03 (1H, dt, J = 15.5, 6.9 Hz), 4.02 (1H, d, J = 10.2 Hz), 3.69 (1H, ddd, J = 17.1, 6.9, 1.4 Hz), 3.64 (1H, ddd, J = 17.1, 6.9, 1.4 Hz), 3.55 (1H, d, J = 14.6 Hz), 3.29 (1H, d, J = 14.6 Hz), 3.21 (6H, s), 2.14 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 168.4, 159.3, 158.5, 144.6, 137.8, 135.1, 134.8, 132.9, 132.7, 131.7, 129.7, 129.5, 128.3, 127.5, 126.7, 126.0, 125.8, 124.5, 123.3, 120.3, 119.2, 116.3, 113.5, 113.4, 104.7, 103.3, 77.8, 55.9, 55.6, 38.3, 31.7, 21.5.; IR (film): 3053, 2932, 2837, 1807, 1715, 1659, 1593, 1470, 1352, 1329, 1300, 1256, 1171, 1115, 966, 907 cm^{-1}; HRMS (ESI) Calcd for $C_{42}H_{38}N_3O_7S$ ([M+H]$^+$) 728.2425. Found 728.2418.

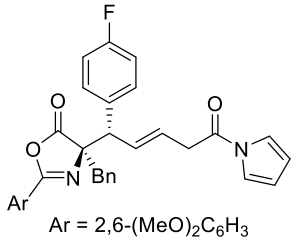


RR-**4ea:** HPLC OD3, H/IPA = 4:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 10.4 min (major isomer of major diastereomer), 13.5 min (minor diastereomer), 20.8 min (minor isomer of major diastereomer), 23.0 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (1H, t, J = 8.6 Hz), 7.32-7.19 (7H, m), 6.52 (2H, d, J = 8.6 Hz), 6.29 (1H, ddt, J = 15.5, 10.4, 1.3 Hz), 6.27 (2H, d, J = 2.4 Hz), 5.95 (1H, dt, J = 15.5, 6.7 Hz), 5.80 (1H, dtd, J = 16.6, 9.7, 6.3 Hz), 5.20 (1H, d, J = 16.6 Hz), 5.14 (1H, d, J = 9.7 Hz), 3.86 (1H, d, J = 10.4 Hz), 3.71 (6H, s), 3.67 (1H, ddd, J = 16.8, 6.7, 1.3 Hz), 3.61 (1H, ddd, J = 16.8, 6.7, 1.3 Hz), 2.88 (1H, dd, J = 13.8, 6.3 Hz), 2.61 (1H, dd, J = 13.8, 9.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 168.4, 159.3, 158.2, 138.1, 133.0, 132.7, 131.2, 129.4, 128.3, 127.3, 125.6, 120.1, 119.2, 113.4, 105.8, 103.8, 55.9, 54.8, 41.1, 38.4, one carbon atom was not found probably due to overlapping.; IR (film): 2940, 2907, 1807, 1715, 1668, 1593, 1476, 1346, 1327, 1256, 1113, 962, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{29}N_2O_5$ ([M+H]$^+$) 485.2071. Found 485.2063.

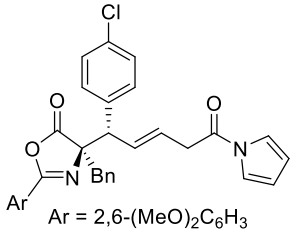


Representative Procedure for Asymmetric 1,6-Addition of Azlactone 2 to δ-Aryl Dienyl *N*-Acylpyrrole 3 with Chiral Iminophosphorane 1dc as a Catalyst: A test tube was charged with a magnetic stirrer bar and MS4A (100.0 mg) under argon atmosphere. MS4A was then dried with a heat gun under reduced pressure for 5 min and the test tube was refilled with Ar. Azlactone **2a** (155.67 mg, 0.50 mmol) and dienyl *N*-acylpyrrole **3a** (55.82 mg, 0.25 mmol) were added, and dissolved in toluene (1.05 mL). A solution of chiral iminophosphorane **1dc** (8.31 mg, 12.5 μmol) in toluene (0.20 mL) was added dropwise at –30 °C. After being stirred for 16 h, a solution of trifluoroacetic acid in toluene (0.5 M, 125 μL) was introduced to the reaction mixture to quench the reaction. The whole mixture was passed through a pad of Celite with the aid of toluene to remove MS4A and the filtrate was concentrated. The regioisomeric and diastereomeric ratios of adducts

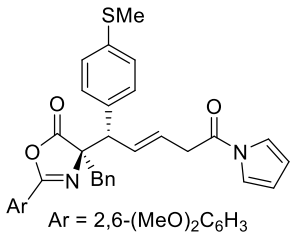
were determined by ^{1}H NMR analysis (800 MHz) of the crude residue. The subsequent purification by column chromatography on silica gel (H/EA = 1:1 as eluent) gave the adducts in 89% yield as a mixture of isomers (119.0 mg, 0.22 mmol). The enantiomeric excess of 1,6-adduct *RS*-**4aa** was determined by HPLC analysis. *RS*-**4aa** (4*R*,1'*S*)**:** HPLC OZ3, H/EtOH = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 17.0 min (minor isomer of major diastereomer), 19.3 min (major isomer of major diastereomer), 21.1 min (minor diastereomer), 31.3 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (2H, d, J = 7.4 Hz), 7.36 (2H, t, J = 7.4 Hz), 7.32 (1H, t, J = 8.6 Hz), 7.28 (1H, t, J = 7.4 Hz), 7.22 (2H, brs), 7.21-7.15 (3H, m), 7.14-7.07 (2H, m), 6.48 (2H, d, J = 8.6 Hz), 6.20 (1H, ddt, J = 15.3, 9.9, 1.4 Hz), 6.17 (2H, t, J = 2.3 Hz), 5.90 (1H, dt, J = 15.3, 6.8 Hz), 3.88 (1H, d, J = 9.9 Hz), 3.63 (6H, s), 3.61 (1H, ddd, J = 16.8, 6.8, 1.4 Hz), 3.50 (1H, ddd, J = 16.8, 6.8, 1.4 Hz), 3.12 (1H, d, J = 13.7 Hz), 2.89 (1H, d, J = 13.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 168.2, 159.4, 157.5, 138.5, 134.5, 132.9, 132.8, 130.8, 129.4, 128.8, 128.0, 127.5, 126.8, 125.4, 119.2, 113.3, 105.6, 103.7, 78.5, 56.6, 56.0, 41.6, 38.8; IR (film): 3030, 2938, 2839, 1805, 1717, 1670, 1595, 1476, 1333, 1302, 1256, 1113, 964, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{31}N_2O_5$ ([M+H]$^+$) 535.2227. Found 535.2228.



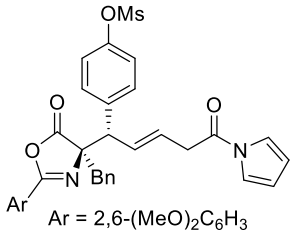
RS-**4ab:** HPLC OZ3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 254 nm, 12.6 min (minor isomer of major diastereomer), 14.1 min (major isomer of major diastereomer), 16.2 min (minor diastereomer), 54.2 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (2H, dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 7.32 (1H, t, J = 8.7 Hz), 7.23-7.16 (3H, m), 7.15-7.08 (2H, m), 7.04 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.7 Hz), 6.48 (2H, d, J = 8.7 Hz), 6.20 (2H, t, J = 2.3 Hz), 6.19 (1H, dd, J = 15.5, 10.1 Hz), 5.90 (1H, dt, J = 15.5, 7.1 Hz), 3.88 (1H, d, J = 10.1 Hz), 3.62$_9$ (6H, s), 3.62$_6$ (1H, dd, J = 16.8, 7.1 Hz), 3.52 (1H, dd, J = 16.8, 7.1 Hz), 3.13 (1H, d, J = 13.5 Hz), 2.89 (1H, d, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.8, 168.2, 162.3 (d, $J_{F\text{-}C}$ = 249.7 Hz), 159.3, 157.6, 134.4, 134.3 (d, $J_{F\text{-}C}$ = 2.9 Hz), 133.0, 132.4, 131.0 (d, $J_{F\text{-}C}$ = 7.7 Hz), 130.7, 128.1, 126.9, 125.7, 119.2, 115.6 (d, $J_{F\text{-}C}$ = 21.3 Hz), 113.4, 105.4, 103.7, 78.4, 56.0, 55.6, 41.7, 38.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.2; IR (film): 3148, 2938, 2841, 1805, 1717, 1670, 1595, 1508, 1476, 1337, 1302, 1258, 1223, 1113, 966 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}N_2O_5F$ ([M+H]$^+$) 553.2133. Found 553.2131.



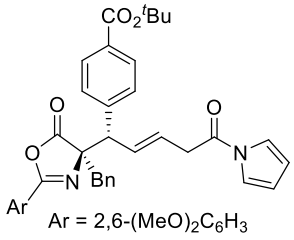
RS-**4ac:** The absolute configuration of *RS*-**4ac** was determined by X-ray crystallographic analysis after derivertization (see page S18 and S25). HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 20.7 min (minor isomer of major diastereomer), 23.1 min (minor diastereomer), 36.7 min (minor diastereomer), 41.5 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (2H, d, J = 8.5 Hz), 7.31$_{51}$ (1H, t, J = 8.7 Hz), 7.31$_{50}$ (1H, t, J = 8.5 Hz), 7.23 (2H, brs), 7.23-7.16 (3H, m), 7.15-7.08 (2H, m), 6.47 (2H, d, J = 8.7 Hz), 6.20 (2H, t, J = 2.3 Hz), 6.19 (1H, ddt, J = 15.6, 9.8, 1.4 Hz), 5.91 (1H, dt, J = 15.6, 6.8 Hz), 3.87 (1H, d, J = 9.8 Hz), 3.63 (1H, ddd, J = 16.9, 6.8, 1.4 Hz), 3.62 (6H, s), 3.52 (1H, ddd, J = 16.9, 6.8, 1.4 Hz), 3.14 (1H, d, J = 13.5 Hz), 2.91 (1H, d, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 168.1, 159.3, 157.6, 137.1, 134.3, 133.3, 133.0, 132.1, 130.8, 128.9, 128.1, 126.9, 125.9, 119.2, 113.4, 105.3, 103.7, 78.2, 56.0, 55.7, 41.7, 38.7; IR (film): 3030, 2936, 2839, 1805, 1717, 1668, 1595, 1476, 1335, 1300, 1256, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}N_2O_5Cl$ ([M+H]$^+$) 569.1838. Found 569.1838.



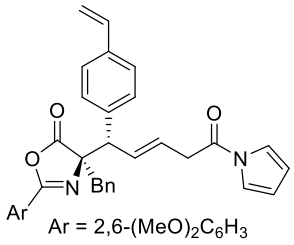
RS-**4ad:** HPLC OX3, H/IPA/EtOH = 18:1:1, flow rate = 1.0 mL/min, λ = 254 nm, 30.4 min (minor isomer of major diastereomer), 33.6 min (minor diastereomer), 36.1 min (major isomer of major diastereomer), 45.8 min (minor diastereomer); ^{1}H NMR [400 MHz, $(CD_3)_2CO$] δ 7.56 (2H, d, J = 8.5 Hz), 7.42 (1H, t, J = 8.5 Hz), 7.36 (2H, t, J = 2.3 Hz), 7.28 (2H, d, J = 8.5 Hz), 7.25-7.16 (3H, m), 7.12-7.02 (2H, m), 6.68 (2H, d, J = 8.5 Hz), 6.20 (2H, t, J = 2.3 Hz), 6.17 (1H, ddt, J = 15.5, 10.1, 1.4 Hz), 5.88 (1H, dt, J = 15.5, 6.7 Hz), 3.91 (1H, d, J = 10.1 Hz), 3.77 (1H, ddd, J = 17.5, 6.7, 1.4 Hz), 3.73 (6H, s), 3.68 (1H, ddd, J = 17.5, 6.7, 1.4 Hz), 3.09 (1H, d, J = 13.7 Hz), 2.84 (1H, d, J = 13.7 Hz), 2.49 (3H, s); ^{13}C NMR [101 MHz, $(CD_3)_2CO$] δ 180.2, 169.2, 160.1, 157.7, 138.3, 136.7, 135.6, 133.7, 133.3, 131.3, 131.0, 128.6, 127.5, 126.9, 126.4, 119.9, 113.5, 106.7, 104.6, 79.0, 56.7, 56.4, 42.0, 38.7, 15.3; IR (film): 3030, 2922, 2839, 1805, 1715, 1670, 1595, 1476, 1337, 1300, 1256, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{33}N_2O_5S$ ($[M+H]^+$) 581.2105. Found 581.2101.



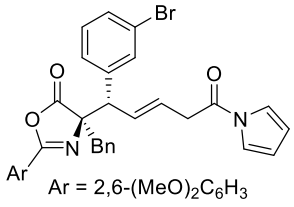
RS-**4ae:** HPLC OX3, H/EtOH = 4:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 25.6 min (minor diastereomer), 27.9 min (minor diastereomer), 33.0 min (minor isomer of major diastereomer), 36.6 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (2H, d, J = 8.7 Hz), 7.33 (1H, t, J = 8.5 Hz), 7.28 (2H, d, J = 8.7 Hz), 7.23-7.15 (3H, m), 7.22 (2H, brs), 7.14-7.07 (2H, m), 6.49 (2H, d, J = 8.5 Hz), 6.19 (2H, t, J = 2.5 Hz), 6.15 (1H, ddt, J = 15.5, 9.9, 1.2 Hz), 5.92 (1H, dt, J = 15.5, 6.7 Hz), 3.91 (1H, d, J = 9.9 Hz), 3.64 (6H, s), 3.62 (1H, ddd, J = 16.9, 6.7, 1.2 Hz), 3.51 (1H, ddd, J = 16.9, 6.7, 1.2 Hz), 3.13 (1H, d, J = 13.7 Hz), 3.12 (3H, s), 2.88 (1H, d, J = 13.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 168.1, 159.3, 157.8, 148.6, 138.0, 134.2, 133.1, 132.0, 131.1, 130.7, 128.1, 127.0, 126.1, 122.2, 119.1, 113.4, 105.3, 103.7, 78.2, 56.0, 55.7, 41.6, 38.6, 37.4; IR (film): 3032, 2938, 2841, 1805, 1715, 1668, 1595, 1476, 1366, 1256, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{33}N_2O_8S$ ($[M+H]^+$) 629.1952. Found 629.1947.



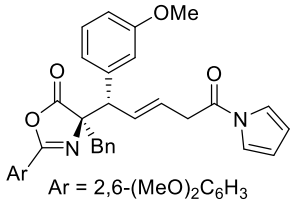
RS-**4af:** HPLC IC3, H/EtOH = 19:1, flow rate = 1.0 mL/min, λ = 250 nm, 27.2 min (minor diastereomer), 30.6 min (major isomer of major diastereomer), 36.6 min (minor diastereomer), 58.7 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 8.7 Hz), 7.54 (2H, d, J = 8.7 Hz), 7.31 (1H, t, J = 8.5 Hz), 7.23 (2H, brs), 7.22-7.15 (3H, m), 7.15-7.06 (2H, m), 6.47 (2H, d, J = 8.5 Hz), 6.22 (1H, ddt, J = 15.6, 9.6, 1.3 Hz), 6.19 (2H, d, J = 2.3 Hz), 5.92 (1H, dt, J = 15.6, 6.7 Hz), 3.95 (1H, d, J = 9.6 Hz), 3.62 (1H, ddd, J = 16.9, 6.7, 1.3 Hz), 3.61 (6H, s), 3.52 (1H, ddd, J = 16.9, 6.7, 1.3 Hz), 3.15 (1H, d, J = 13.5 Hz), 2.90 (1H, d, J = 13.5 Hz), 1.58 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 168.0, 165.7, 159.3, 157.5, 143.3, 134.3, 133.0, 132.0, 131.2, 130.7, 129.9, 129.3, 128.1, 126.9, 126.1, 119.1, 113.4, 105.4, 103.7, 81.2, 78.2, 56.3, 55.9, 41.7, 38.6, 28.3; IR (film): 2974, 2839, 1807, 1709, 1670, 1595, 1476, 1294, 1256, 1111, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{39}N_2O_7$ ($[M+H]^+$) 635.2752. Found 635.2749.



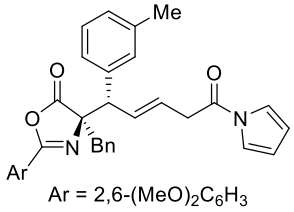
RS-**4ag:** HPLC OD3, H/EtOH = 10:1, flow rate = 1.0 mL/min, λ = 240 nm, 15.3 min (minor isomer of major diastereomer), 18.6 min (minor diastereomer), 28.3 min (minor diastereomer), 40.5 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (2H, d, J = 8.5 Hz), 7.39 (2H, d, J = 8.5 Hz), 7.30 (1H, t, J = 8.5 Hz), 7.22 (2H, brs), 7.22-7.15 (3H, m), 7.15-7.07 (2H, m), 6.70 (1H, dd, J = 17.9, 11.1 Hz), 6.46 (2H, d, J = 8.5 Hz), 6.21 (1H, ddt, J = 15.5, 9.8, 1.2 Hz), 6.18 (2H, t, J = 2.5 Hz), 5.90 (1H, dt, J = 15.5, 6.8 Hz), 5.74 (1H, d, J = 17.9 Hz), 5.23 (1H, d, J = 11.1 Hz), 3.88 (1H, d, J = 9.8 Hz), 3.61 (1H, ddd, J = 16.7, 6.8, 1.2 Hz), 3.60 (6H, s), 3.50 (1H, ddd, J = 16.7, 6.8, 1.2 Hz), 3.14 (1H, d, J = 13.5 Hz), 2.92 (1H, d, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.9, 168.1, 159.3, 157.4, 138.1, 136.7, 136.5, 134.5, 132.9, 132.5, 130.7, 129.5, 128.0, 126.8, 126.6, 125.5, 119.1, 113.9, 113.3, 105.5, 103.6, 78.4, 56.2, 55.9, 41.6, 38.7; IR (film): 3032, 2936, 2839, 1805, 1717, 1670, 1595, 1476, 1339, 1300, 1256, 1113, 964, 907cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{33}N_2O_5$ ([M+H]$^+$) 561.2384. Found 561.2383.



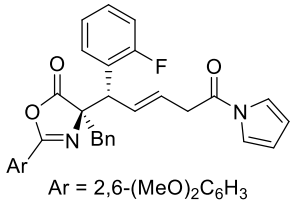
RS-**4ah:** HPLC OD3, H/IPA/EtOH = 15:1:4, flow rate = 0.5 mL/min, λ = 254 nm, 24.3 min (minor isomer of major diastereomer), 28.3 min (minor diastereomer), 32.1 min (minor diastereomer), 43.2 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (1H, t, J = 1.8 Hz), 7.43 (1H, d, J = 8.0 Hz), 7.41 (1H, d, J = 8.0 Hz), 7.32 (1H, t, J = 8.7 Hz), 7.26-7.15 (6H, m), 7.15-7.07 (2H, m), 6.48 (2H, d, J = 8.7 Hz), 6.19 (2H, t, J = 2.5 Hz), 6.15 (1H, ddt, J = 15.5, 10.1, 1.1 Hz), 5.91 (1H, dt, J = 15.5, 6.6 Hz), 3.84 (1H, d, J = 10.1 Hz), 3.64 (6H, s), 3.61 (1H, ddd, J = 16.9, 6.6, 1.1 Hz), 3.51 (1H, ddd, J = 16.9, 6.6, 1.1 Hz), 3.13 (1H, d, J = 13.5 Hz), 2.91 (1H, t, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 168.1, 159.4, 157.6, 140.9, 134.3, 133.0, 132.5, 131.9, 130.7, 130.6, 130.3, 128.1, 128.0, 126.9, 126.1, 122.7, 119.1, 113.4, 105.4, 103.7, 78.1, 56.0, 41.6, 38.6, one carbon was not found probably due to overlapping.; IR (film): 3030, 2938, 2839, 1805, 1717, 1670, 1593, 1476, 1335, 1294, 1256, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}N_2O_5{}^{79}Br$ ([M+H]$^+$) 613.1333. Found 613.1331.



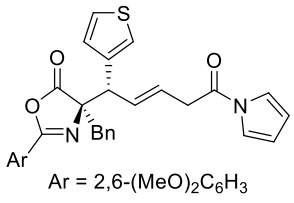
RS-**4ai:** HPLC AD3, H/IPA/EtOH = 85.9:9.1:5, flow rate = 1.0 mL/min, λ = 210 nm, 19.7 min (minor diastereomer), 21.8 min (major isomer of major diastereomer), 24.9 min (minor diastereomer), 29.0 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (1H, t, J = 8.4 Hz), 7.27 (1H, t, J = 7.9 Hz), 7.22 (2H, brs), 7.21-7.15 (3H, m), 7.15-7.10 (2H, m), 7.10 (1H, d, J = 7.9 Hz), 7.03 (1H, t, J = 2.8 Hz), 6.82 (1H, dd, J = 7.9, 2.8 Hz), 6.47 (2H, d, J = 8.4 Hz), 6.20 (1H, ddt, J = 15.6, 10.1, 1.4 Hz), 6.17 (2H, t, J = 2.5 Hz), 5.90 (1H, dt, J = 15.6, 6.7 Hz), 3.85 (1H, d, J = 10.1 Hz), 3.80 (3H, s), 3.62 (6H, s), 3.60 (1H, ddd, J = 16.8, 6.7, 1.4 Hz), 3.50 (1H, ddd, J = 16.8, 6.7, 1.4 Hz), 3.14 (1H, d, J = 13.5 Hz), 2.94 (1H, d, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 168.1, 159.7, 159.4, 157.3, 140.1, 134.6, 132.9, 132.6, 130.8, 129.7, 128.0, 126.8, 125.4, 121.6, 119.2, 115.4, 113.3, 112.8, 105.7, 103.7, 78.4, 56.6, 56.0, 55.3, 41.7, 38.8; IR (film): 2936, 2837, 1805, 1715, 1667, 1593, 1470, 1335, 1298, 1254, 1111, 966, 905 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{33}N_2O_6$ ([M+H]$^+$) 565.2333. Found 565.2337.



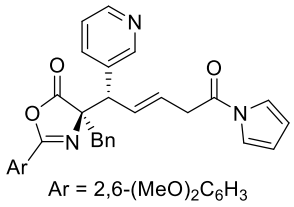
RS-**4aj:** HPLC AD3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 210 nm, 29.0 min (minor diastereomer), 31.5 min (major isomer of major diastereomer), 34.7 min (minor diastereomer), 54.9 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (1H, d, J = 7.8 Hz), 7.31 (1H, t, J = 8.6 Hz), 7.28-7.21 (2H, m), 7.22 (2H, brs), 7.21-7.15 (3H, m), 7.15-7.09 (2H, m), 7.09 (1H, d, J = 7.8 Hz), 6.48 (2H, d, J = 8.6 Hz), 6.19 (1H, ddt, J = 15.5, 10.1, 1.4 Hz), 6.17 (2H, t, J = 2.3 Hz), 5.89 (1H, dt, J = 15.5, 6.7 Hz), 3.83 (1H, d, J = 10.1 Hz), 3.63 (6H, s), 3.59 (1H, ddd, J = 16.6, 6.7, 1.4 Hz), 3.49 (1H, ddd, J = 16.6, 6.7, 1.4 Hz), 3.12 (1H, d, J = 13.5 Hz), 2.91 (1H, d, J = 13.5 Hz), 2.36 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 168.2, 159.4, 157.3, 138.4, 138.2, 134.6, 132.9, 130.8, 130.3, 128.7, 128.3, 128.0, 126.8, 126.3, 125.2, 119.2, 113.3, 105.7, 103.7, 78.5, 56.6, 56.0, 41.6, 38.8, 21.7, one carbon atom was not found probably due to overlapping.; IR (film): 3030, 2936, 2839, 1805, 1717, 1670, 1595, 1476, 1335, 1298, 1256, 1113, 964, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{33}N_2O_5$ ($[M+H]^+$) 549.2384. Found 549.2384.



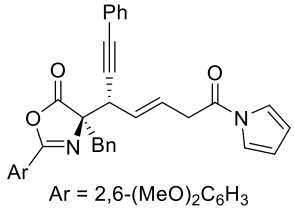
RS-**4ak:** HPLC OZ3, H/EtOH = 19:1, flow rate = 1.0 mL/min, λ = 210 nm, 20.7 min (minor isomer of major diastereomer), 22.8 min (major isomer of major diastereomer), 35.4 min (minor diastereomer), 49.0 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (1H, td, J = 7.6, 1.7 Hz), 7.32 (1H, t, J = 8.5 Hz), 7.30-7.14 (7H, m), 7.14-7.06 (3H, m), 6.48 (2H, d, J = 8.5 Hz), 6.17 (2H, t, J = 2.3 Hz), 6.14 (1H, dd, J = 15.3, 9.8 Hz), 5.96 (1H, dt, J = 15.3, 6.7 Hz), 4.44 (1H, d, J = 9.8 Hz), 3.64 (6H, s), 3.60 (1H, ddd, J = 16.9, 6.7, 1.2 Hz), 3.49 (1H, ddd, J = 16.9, 6.7, 1.2 Hz), 3.23 (1H, d, J = 13.6 Hz), 2.89 (1H, d, J = 13.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 168.1, 160.7 (d, $J_{F\text{-}C}$ = 249.7 Hz), 159.3, 157.7, 134.3, 133.0, 131.5, 130.8, 130.6 (d, $J_{F\text{-}C}$ = 2.9 Hz), 128.9 (d, $J_{F\text{-}C}$ = 8.7 Hz), 128.0, 126.8, 126.4, 125.5 (d, $J_{F\text{-}C}$ = 14.5 Hz), 124.7 (d, $J_{F\text{-}C}$ = 3.9 Hz), 119.2, 115.6 (d, $J_{F\text{-}C}$ = 23.2 Hz), 113.4, 105.5, 103.7, 78.6, 56.0, 47.0, 40.9, 38.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –117.0; IR (film): 3032, 2938, 2839, 1807, 1717, 1670, 1595, 1476, 1339, 1300, 1258, 1113, 966, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{30}N_2O_5F$ ($[M+H]^+$) 553.2133. Found 553.2135.



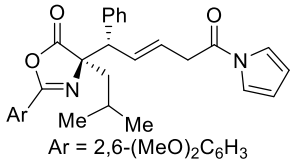
RS-**4al:** HPLC OZ3, H/IPA = 4:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 8.4 min (minor isomer of major diastereomer), 9.0 min (minor diastereomer), 11.0 min (major isomer of major diastereomer), 12.5 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (1H, t, J = 8.7 Hz), 7.32-7.27 (2H, m), 7.27-7.21 (3H, m), 7.21-7.16 (3H, m), 7.16-7.08 (2H, m), 6.48 (2H, d, J = 8.7 Hz), 6.19 (2H, t, J = 2.3 Hz), 6.14 (1H, ddt, J = 15.6, 9.8, 1.2 Hz), 5.89 (1H, dt, J = 15.6, 6.6 Hz), 4.06 (1H, d, J = 9.8 Hz), 3.63 (6H, s), 3.61 (1H, ddd, J = 16.8, 6.6, 1.2 Hz), 3.51 (1H, ddd, J = 16.8, 6.6, 1.2 Hz), 3.15 (1H, d, J = 13.8 Hz), 2.97 (1H, d, J = 13.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.8, 168.2, 159.4, 157.5, 138.5, 134.5, 132.9, 132.3, 130.8, 128.3, 128.0, 126.8, 125.7, 125.3, 123.3, 119.2, 113.4, 105.5, 103.7, 78.3, 56.0, 51.7, 41.6, 38.7; IR (film): 3030, 2936, 2839, 1805, 1717, 1670, 1595, 1476, 1331, 1304, 1258, 1113, 966, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{29}N_2O_5S$ ($[M+H]^+$) 541.1792. Found 541.1791.



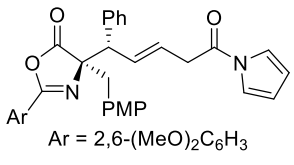
RS-**4am:** HPLC OX3, H/IPA/EtOH = 8:1:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 24.4 min (minor diastereomer), 26.0 min (minor diastereomer), 45.7 min (major isomer of major diastereomer), 52.4 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (1H, brd, J = 1.8 Hz), 8.54 (1H, dd, J = 4.3, 1.8 Hz), 7.86 (1H, dt, J = 8.3, 1.8 Hz), 7.31 (1H, t, J = 8.7 Hz), 7.28 (1H, dd, J = 8.3, 4.3 Hz), 7.23 (2H, brs), 7.25-7.15 (3H, m), 7.15-7.05 (2H, m), 6.47 (2H, d, J = 8.7 Hz), 6.20$_4$ (1H, dd, J = 15.3, 10.1 Hz), 6.19$_7$ (2H, t, J = 1.8 Hz), 5.95 (1H, dt, J = 15.3, 6.8 Hz), 3.93 (1H, d, J = 10.1 Hz), 3.63 (1H, dd, J = 16.9, 6.8 Hz), 3.62 (6H, s), 3.53 (1H, dd, J = 16.9, 6.8 Hz), 3.17 (1H, d, J = 13.5 Hz), 2.90 (1H, d, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 167.9, 159.3, 157.8, 150.8, 148.9, 136.5, 134.3, 134.0, 133.0, 131.5, 130.7, 128.1, 126.9, 126.6, 123.7, 119.1, 113.4, 105.2, 103.6, 77.9, 56.0, 53.6, 41.7, 38.5; IR (film): 3028, 2839, 1805, 1713, 1667, 1591, 1470, 1329, 1302, 1256, 1109, 962, 905 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{30}N_3O_5$ ([M+H]$^+$) 536.2180. Found 536.2174.



RS-**4an:** HPLC OD3, H/EtOH = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 210 nm, 16.5 min (minor diastereomer), 18.3 min (minor isomer of major diastereomer), 20.2 min (minor diastereomer), 22.9 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.41 (2H, m), 7.34-7.19 (11H, m), 6.46 (2H, d, J = 8.6 Hz), 6.25 (2H, t, J = 2.3 Hz), 6.10 (1H, dt, J = 15.4, 6.2 Hz), 5.96 (1H, dd, J = 15.4, 8.3 Hz), 3.92 (1H, d, J = 8.3 Hz), 3.69 (1H, dd, J = 16.8, 6.2 Hz), 3.63 (1H, dd, J = 16.8, 6.2 Hz), 3.56 (6H, s), 3.49 (1H, d, J = 13.5 Hz), 3.32 (1H, d, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 168.1, 159.4, 158.2, 134.3, 133.0, 132.0, 130.9, 129.0, 128.3, 128.2, 128.1, 127.0, 126.8, 123.1, 119.2, 113.4, 105.5, 103.7, 86.3, 85.0, 77.0, 55.9, 43.3, 41.3, 38.4; IR (film): 3032, 2938, 2839, 2247, 1807, 1717, 1668, 1595, 1476, 1456, 1433, 1331, 1301, 1256, 1113, 966, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{31}N_2O_5$ ([M+H]$^+$) 559.2233. Found 559.2227.

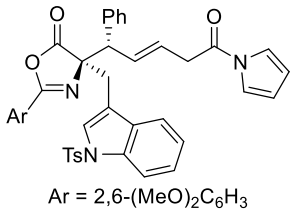


RS-**4ba:** HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 20.0 min (minor diastereomer), 25.5 min (major isomer of major diastereomer), 32.6 min (minor isomer of major diastereomer), 36.7 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38$_1$ (1H, t, J = 8.5 Hz), 7.37$_9$ (2H, d, J = 7.4 Hz), 7.30 (2H, t, J = 7.4 Hz), 7.24 (1H, t, J = 7.4 Hz), 7.24 (2H, brs), 6.58 (2H, d, J = 8.5 Hz), 6.20 (2H, t, J = 2.3 Hz), 6.15 (1H, ddt, J = 15.6, 10.1, 1.3 Hz), 5.85 (1H, dt, J = 15.6, 6.6 Hz), 3.79 (6H, s), 3.67 (1H, d, J = 10.1 Hz), 3.61 (1H, ddd, J = 16.7, 6.6, 1.3 Hz), 3.50 (1H, ddd, J = 16.7, 6.6, 1.3 Hz), 1.79-1.58 (3H, m), 0.87 (3H, d, J = 6.2 Hz), 0.80 (3H, d, J = 6.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.3, 168.2, 159.4, 157.3, 138.7, 133.0, 132.5, 129.4, 128.6, 127.3, 125.2, 119.2, 113.3, 106.1, 103.9, 76.7, 57.2, 56.0, 44.5, 38.7, 24.6, 24.4, 22.8; IR (film): 3148, 2951, 2866, 1805, 1713, 1680, 1593, 1454, 1323, 1302, 1254, 1107, 955, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{33}N_2O_5$ ([M+H]$^+$) 501.2384. Found 501.2377.



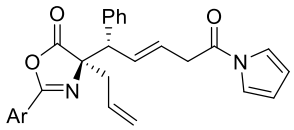
RS-**4ca:** HPLC OZ3, H/IPA/EtOH = 18:1:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 15.1 min (minor isomer of major diastereomer), 17.2 min (minor diastereomer), 18.6 min (minor diastereomer), 20.1 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (2H, d, J = 7.7 Hz), 7.35 (2H, t, J = 7.7 Hz), 7.31 (1H, t, J = 8.5 Hz), 7.27 (1H, t, J = 7.7 Hz), 7.22 (2H, brs), 7.02 (2H, d, J = 8.7 Hz), 6.71 (2H, d, J = 8.7 Hz), 6.48 (2H, d, J = 8.5 Hz), 6.19 (1H, ddt, J = 15.6, 9.8, 1.2 Hz), 6.17 (2H, t, J = 2.3 Hz), 5.89 (1H, dt, J = 15.6, 6.7 Hz), 3.87 (1H, d, J = 9.8 Hz), 3.73 (3H, s), 3.63 (6H, s), 3.59 (1H, ddd, J = 16.6, 6.7, 1.2 Hz), 3.49 (1H,

ddd, *J* = 16.6, 6.7, 1.2 Hz), 3.07 (1H, d, *J* = 13.9 Hz), 2.83 (1H, d, *J* = 13.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 168.1, 159.3, 158.5, 157.3, 138.5, 132.9, 132.8, 131.7, 129.4, 128.7, 127.4, 126.5, 125.3, 119.1, 113.3$_1$, 113.2$_6$, 105.5, 103.6, 78.6, 56.4, 55.9, 55.1, 40.8, 38.7; IR (film): 3022, 2934, 2835, 1807, 1715, 1667, 1593, 1512, 1470, 1335, 1296, 1248, 1111, 964, 903 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{33}N_2O_6$ ([M+H]$^+$) 565.2333. Found 565.2330.



Ar = 2,6-$(MeO)_2C_6H_3$

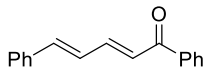
RS-**4da:** HPLC IA3, H/IPA = 3:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 9.9 min (minor diastereomer), 10.9 min (minor diastereomer), 12.3 min (major isomer of major diastereomer), 13.9 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (1H, d, *J* = 7.4 Hz), 7.60 (2H, d, *J* = 8.5 Hz), 7.50 (2H, d, *J* = 8.0 Hz), 7.43 (1H, s), 7.42 (1H, d, *J* = 7.4 Hz), 7.36 (2H, t, *J* = 8.0 Hz), 7.28$_1$ (1H, t, *J* = 7.4 Hz), 7.27$_8$ (1H, t, *J* = 8.7 Hz), 7.23 (2H, brs), 7.20 (1H, t, *J* = 8.0 Hz), 7.11 (1H, t, *J* = 7.4 Hz), 7.02 (2H, d, *J* = 8.5 Hz), 6.40 (2H, d, *J* = 8.7 Hz), 6.23 (1H, ddt, *J* = 15.3, 10.1, 1.0 Hz), 6.19 (2H, t, *J* = 2.3 Hz), 5.92 (1H, dt, *J* = 15.3, 6.8 Hz), 3.93 (1H, d, *J* = 10.1 Hz), 3.62 (1H, ddd, *J* = 16.9, 6.8, 1.0 Hz), 3.52 (1H, ddd, *J* = 16.9, 6.8, 1.0 Hz), 3.37 (6H, s), 3.24 (1H, d, *J* = 14.6 Hz), 2.97 (1H, d, *J* = 14.6 Hz), 2.20 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 168.1, 159.2, 158.1, 144.7, 138.4, 135.1, 134.8, 132.9, 132.6, 131.5, 129.7, 129.3, 128.8, 127.5, 126.7, 126.0, 125.5, 124.4, 123.2, 120.4, 119.1, 116.0, 113.4, 113.3, 105.2, 103.4, 78.0, 56.5, 55.8, 38.7, 30.9, 21.5; IR (film): 3026, 2940, 2839, 1805, 1713, 1667, 1593, 1470, 1360, 1335, 1256, 1171, 1111, 968, 905 cm^{-1}; HRMS (ESI) Calcd for $C_{42}H_{38}N_3O_7S$ ([M+H]$^+$) 728.2425. Found 728.2422.



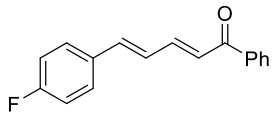
Ar = 2,6-$(MeO)_2C_6H_3$

RS-**4ea:** HPLC OD3, H/IPA = 4:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 10.5 min (minor diastereomer), 13.4 min (major isomer of major diastereomer), 20.9 min (minor diastereomer), 23.0 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, d, *J* = 7.5 Hz), 7.37 (1H, t, *J* = 8.3 Hz), 7.31 (2H, t, *J* = 7.5 Hz), 7.28-7.21 (3H, m), 6.57 (2H, d, *J* = 8.3 Hz), 6.22 (2H, t, *J* = 2.1 Hz), 6.16 (1H, ddt, *J* = 15.2, 9.2, 1.2 Hz), 5.88 (1H, dt, *J* = 15.2, 6.7 Hz), 5.69 (1H, dddd, *J* = 17.1, 10.5, 8.6, 6.2 Hz), 5.10 (1H, d, *J* = 17.1 Hz), 5.09 (1H, d, *J* = 10.5 Hz), 3.80 (1H, d, *J* = 9.2 Hz), 3.79 (6H, s), 3.63 (1H, ddd, *J* = 16.6, 6.7, 1.2 Hz), 3.53 (1H, ddd, *J* = 16.6, 6.7, 1.2 Hz), 2.52 (1H, dd, *J* = 13.9, 8.6 Hz), 2.41 (1H, dd, *J* = 13.9, 6.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.9, 168.2, 159.4, 157.7, 138.4, 133.0, 132.7, 131.1, 129.3, 128.7, 127.4, 125.3, 120.0, 119.2, 113.4, 106.2, 104.0, 77.4, 56.1, 55.7, 40.1, 38.7; IR (film): 2940, 2839, 1807, 1715, 1674, 1595, 1476, 1331, 1304, 1256, 1113, 964, 918 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{29}N_2O_5$ ([M+H]$^+$) 485.2071. Found 485.2068.

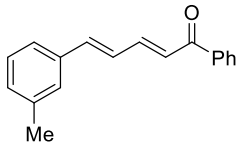
Characterization of δ-Aryl Dienyl Phenylketone 5:



5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (2H, d, *J* = 7.5 Hz), 7.60 (1H, ddd, *J* = 15.0, 7.1, 3.3 Hz), 7.56 (1H, tt, *J* = 7.5, 1.6 Hz), 7.49 (2H, d, *J* = 6.5 Hz), 7.48 (2H, tt, *J* = 7.5, 1.6 Hz), 7.37 (2H, tt, *J* = 6.5, 1.8 Hz), 7.31 (1H, tt, *J* = 6.5, 1.8 Hz), 7.09 (1H, d, *J* = 15.0 Hz), 7.04 (1H, dd, *J* = 15.6, 7.1 Hz), 6.99 (1H, dd, *J* = 15.6, 3.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 144.9, 142.0, 138.4, 136.2, 132.8, 129.3, 129.0, 128.7, 128.5, 127.4, 127.1, 125.6; IR (film): 3057, 3028, 1655, 1599, 1572, 1447, 1350, 1287, 1250, 1150, 1016, 997 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{14}ONa$ ([M+Na]$^+$) 257.0937. Found 257.0935.

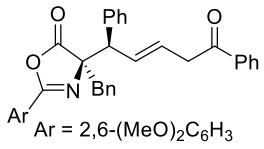


5b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 7.8 Hz), 7.58 (1H, ddd, J = 14.9, 8.7, 1.4 Hz), 7.56 (1H, t, J = 7.8 Hz), 7.48 (2H, t, J = 7.8 Hz), 7.47 (2H, dd, $J_{H\text{-}H}$ = 8.6 Hz, $J_{F\text{-}H}$ = 5.4 Hz), 7.08 (1H, d, J = 14.9 Hz), 7.06 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.6 Hz), 6.97 (1H, dd, J = 15.6, 1.4 Hz), 6.92 (1H, dd, J = 15.6, 8.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 163.4 (d, $J_{F\text{-}C}$ = 250.7 Hz), 144.7, 140.6, 138.3, 132.8, 132.5 (d, $J_{F\text{-}C}$ = 2.9 Hz), 129.1 (d, $J_{F\text{-}C}$ = 7.7 Hz), 128.7, 128.5, 126.9 (d, $J_{F\text{-}C}$ = 2.9 Hz), 125.6, 116.1 (d, $J_{F\text{-}C}$ = 22.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –111.1; IR (film): 3067, 1651, 1574, 1504, 1356, 1327, 1288, 1252, 1223, 1148, 1011 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{13}OFNa$ ([M+Na]$^{+}$) 275.0843. Found 275.0844.

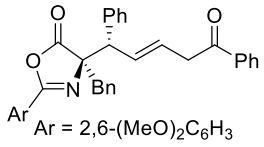


5c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (2H, dt, J = 7.3, 1.5 Hz), 7.60 (1H, ddd, J = 14.9, 8.6, 1.7 Hz), 7.57 (1H, tt, J = 7.3, 1.5 Hz), 7.49 (2H, tt, J = 7.3, 1.5 Hz), 7.32 (1H, s), 7.31 (1H, d, J = 7.3 Hz), 7.26 (1H, t, J = 7.3 Hz), 7.14 (1H, d, J = 7.3 Hz), 7.08 (1H, d, J = 14.9 Hz), 7.03 (1H, dd, J = 15.6, 8.6 Hz), 6.98 (1H, dd, J = 15.6, 1.7 Hz), 2.37 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 145.1, 142.3, 138.6, 138.4, 136.2, 132.8, 130.2, 128.9, 128.7, 128.5, 128.2, 126.9, 125.4, 124.6, 21.5; IR (film): 3026, 2920, 1655, 1599, 1584, 1447, 1348, 1285, 1258, 1016 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{16}ONa$ ([M+Na]$^{+}$) 271.1093. Found 271.1091.

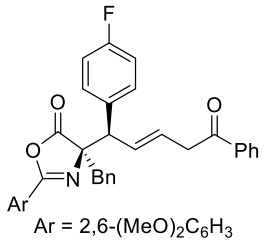
Characterization of 1,6-Adduct 6:



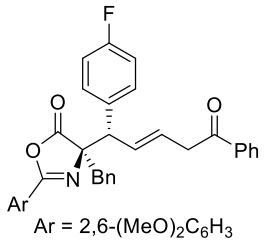
RR-**6aa:** HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 230 nm, 23.1 min (minor diastereomer), 31.5 min (minor diastereomer), 34.9 min (major isomer of major diastereomer), 39.0 min (minor isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 7.4 Hz), 7.51 (1H, tt, J = 7.4, 1.5 Hz), 7.41 (2H, t, J = 7.4 Hz), 7.38 (2H, d, J = 7.6 Hz), 7.28-7.14 (9H, m), 6.40 (2H, d, J = 8.4 Hz), 6.35 (1H, dd, J = 15.4, 9.9 Hz), 6.06 (1H, dt, J = 15.4, 6.8 Hz), 3.97 (1H, d, J = 9.9 Hz), 3.85 (1H, ddd, J = 17.1, 6.8, 1.2 Hz), 3.78 (1H, ddd, J = 17.1, 6.8, 1.2 Hz), 3.55 (6H, s), 3.45 (1H, d, J = 13.6 Hz), 3.16 (1H, d, J = 13.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 179.0, 159.4, 157.9, 138.3, 136.6, 134.7, 133.2, 132.8, 131.7, 130.9, 129.5, 128.7, 128.3, 128.2, 127.9, 127.5, 127.2, 126.8, 105.1, 103.5, 78.2, 56.2, 55.8, 42.9, 42.4; IR (film): 3030, 2936, 2839, 1805, 1661, 1595, 1476, 1454, 1431, 1300, 1256, 1113, 962, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{32}NO_5$ ([M+H]$^{+}$) 546.2275. Found 545.2271.



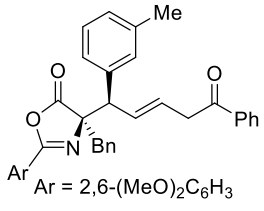
RS-**6aa:** HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 230 nm, 23.1 min (minor isomer of major diastereomer), 31.5 min (major isomer of major diastereomer), 35.0 min (minor diastereomer), 38.8 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (2H, d, J = 7.7 Hz), 7.49 (2H, d, J = 7.0 Hz), 7.42 (1H, tt, J = 7.7, 1.4 Hz), 7.38-7.23 (6H, m), 7.19-7.13 (3H, m), 7.13-7.06 (2H, m), 6.46 (2H, d, J = 8.6 Hz), 6.15 (1H, dd, J = 15.4, 9.8 Hz), 5.94 (1H, dt, J = 15.4, 6.5 Hz), 3.86 (1H, d, J = 9.8 Hz), 3.73 (1H, ddd, J = 16.4, 6.5, 1.4 Hz), 3.61 (6H, s), 3.60 (1H, ddd, J = 16.4, 6.5, 1.4 Hz), 3.10 (1H, d, J = 13.5 Hz), 2.87 (1H, d, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 179.9, 159.3, 157.3, 138.8, 136.4, 134.6, 133.0, 132.8, 131.8, 130.7, 129.4, 128.7, 128.6, 128.4, 127.9, 127.3, 127.1, 126.7, 105.7, 103.6, 78.5, 56.8, 55.9, 42.8, 41.6; IR (film): 3030, 2938, 2839, 1805, 1674, 1595, 1476, 1454, 1433, 1300, 1256, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{32}NO_5$ ([M+H]$^{+}$) 546.2275. Found 546.2270.



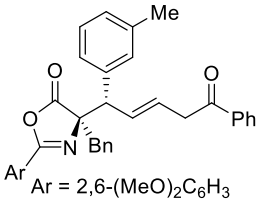
RR-**6ab:** HPLC OX3, H/EtOH = 19:1, flow rate = 1.0 mL/min, λ = 254 nm, 23.1 min (minor diastereomer), 25.2 min (minor isomer of major diastereomer), 29.2 min (minor diastereomer), 34.5 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 7.4 Hz), 7.52 (1H, tt, J = 7.4, 1.5 Hz), 7.42 (2H, t, J = 7.4 Hz), 7.32 (2H, dd, $J_{H\text{-}H}$ = 8.5 Hz, $J_{F\text{-}H}$ = 5.6 Hz), 7.25 (1H, t, J = 8.5 Hz), 7.24-7.16 (5H, m), 6.92 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.5 Hz), 6.41 (2H, d, J = 8.5 Hz), 6.31 (1H, dd, J = 15.4, 9.8 Hz), 6.06 (1H, dt, J = 15.4, 6.8 Hz), 3.97 (1H, d, J = 9.8 Hz), 3.86 (1H, ddd, J = 17.6, 6.8, 1.0 Hz), 3.80 (1H, ddd, J = 17.6, 6.8, 1.0 Hz), 3.57 (6H, s), 3.43 (1H, d, J = 13.6 Hz), 3.16 (1H, d, J = 13.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 179.0, 162.1 (d, $J_{F\text{-}C}$ = 245.9 Hz), 159.3, 158.0, 136.6, 134.6, 134.1 (d, $J_{F\text{-}C}$ = 2.9 Hz), 133.2, 132.9, 131.5, 131.1 (d, $J_{F\text{-}C}$ = 7.7 Hz), 130.8, 128.7, 128.3, 127.9, 127.7, 126.9, 114.9 (d, $J_{F\text{-}C}$ = 21.3 Hz), 105.0, 103.5, 78.2, 55.8, 55.3, 42.7, 42.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.6; IR (film): 3030, 2938, 2839, 1805, 1661, 1595, 1508, 1476, 1433, 1300, 1256, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{31}NO_5F$ ([M+H]$^+$) 564.2186. Found 564.2183.



RS-**6ab:** HPLC OX3, H/EtOH = 19:1, flow rate = 1.0 mL/min, λ = 254 nm, 22.9 min (minor isomer of major diastereomer), 25.3 min (minor diastereomer), 28.8 min (major isomer of major diastereomer), 34.7 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (2H, d, J = 7.8 Hz), 7.443$_7$ (2H, dd, $J_{H\text{-}H}$ = 8.9 Hz, $J_{F\text{-}H}$ = 5.5 Hz), 7.443$_6$ (1H, t, J = 7.8 Hz), 7.33 (2H, t, J = 7.8 Hz), 7.30 (1H, t, J = 8.5 Hz), 7.22-7.14 (3H, m), 7.14-7.07 (2H, m), 7.02 (2H, t, $J_{H\text{-}H}$ = $J_{F\text{-}H}$ = 8.9 Hz), 6.46 (2H, d, J = 8.5 Hz), 6.13 (1H, dd, J = 15.4, 9.7 Hz), 5.94 (1H, dt, J = 15.4, 6.4 Hz), 3.86 (1H, d, J = 9.7 Hz), 3.75 (1H, ddd, J = 16.6, 6.4, 1.3 Hz), 3.63 (1H, ddd, J = 16.6, 6.4, 1.3 Hz), 3.61 (6H, s), 3.11 (1H, d, J = 13.5 Hz), 2.88 (1H, d, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 179.8, 162.2 (d, $J_{F\text{-}C}$ = 246.8 Hz), 159.3, 157.4, 136.4, 134.7 (d, $J_{F\text{-}C}$ = 2.9 Hz), 134.5, 133.1, 132.9, 131.5, 131.0 (d, $J_{F\text{-}C}$ = 7.7 Hz), 130.7, 128.6, 128.4, 128.0, 127.4, 126.8, 115.4 (d, $J_{F\text{-}C}$ = 21.3 Hz), 105.5, 103.6, 78.4, 55.9, 55.8, 42.7, 41.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.4; IR (film): 3032, 2938, 2839, 1805, 1674, 1595, 1508, 1476, 1433, 1300, 1256, 1223, 1111, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{31}NO_5F$ ([M+H]$^+$) 564.2186. Found 565.2182.

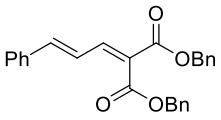


RR-**6ac:** The absolute configuration of *RR*-**6ac** was determined by X-ray crystallographic analysis (see page 116). HPLC OX3, H/EtOH = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 12.7 min (minor diastereomer), 15.8 min (minor isomer of major diastereomer), 17.7 min (minor diastereomer), 20.0 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 7.6 Hz), 7.52 (1H, tt, J = 7.6, 1.6 Hz), 7.42 (2H, t, J = 7.6 Hz), 7.26 (1H, t, J = 8.4 Hz), 7.23-7.10 (8H, m), 7.01 (1H, d, J = 7.6 Hz), 6.41 (2H, d, J = 8.4 Hz), 6.32 (1H, dd, J = 15.4, 9.9 Hz), 6.04 (1H, dt, J = 15.4, 6.7 Hz), 3.92 (1H, d, J = 9.9 Hz), 3.85 (1H, ddd, J = 17.1, 6.7, 1.4 Hz), 3.78 (1H, ddd, J = 17.1, 6.7, 1.4 Hz), 3.57 (6H, s), 3.42 (1H, d, J = 13.6 Hz), 3.15 (1H, d, J = 13.6 Hz), 2.27 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 179.1, 159.5, 157.8, 138.3, 137.8, 136.7, 134.8, 133.2, 132.8, 131.9, 130.9, 130.3, 128.7, 128.3, 128.1, 127.9, 127.3, 126.8, 126.5, 105.2, 103.5, 78.2, 56.3, 55.9, 42.9, 42.5, 21.5, one carbon atom was not found probably due to overlapping; IR (film): 3030, 2936, 2839, 1805, 1661, 1595, 1476, 1449, 1431, 1300, 1256, 1111, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{36}H_{34}NO_5$ ([M+H]$^+$) 560.2437. Found 560.2430.



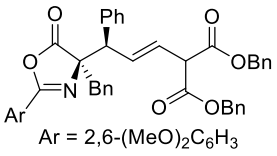
RS-**6ac:** HPLC OX3, H/EtOH = 10:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 12.7 min (minor isomer of major diastereomer), 15.8 min (minor diastereomer), 17.6 min (major isomer of major diastereomer), 20.0 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (2H, d, J = 7.6 Hz), 7.43 (1H, tt, J = 7.6, 1.1 Hz), 7.36-7.21 (6H, m), 7.20-7.14 (3H, m), 7.14-7.05 (3H, m), 6.47 (2H, d, J = 8.6 Hz), 6.15 (1H, dd, J = 15.3, 9.8 Hz), 5.94 (1H, dt, J = 15.3, 6.5 Hz), 3.83 (1H, d, J = 9.8 Hz), 3.73 (1H, ddd, J = 16.4, 6.5, 1.4 Hz), 3.62 (6H, s), 3.61 (1H, ddd, J = 16.4, 6.5, 1.4 Hz), 3.11 (1H, d, J = 13.6 Hz), 2.90 (1H, d, J = 13.6 Hz), 2.36 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 180.0, 159.4, 157.2, 138.7, 138.1, 136.5, 134.7, 133.0, 132.8, 131.9, 130.7, 130.2, 128.6, 128.4, 128.1, 127.9, 126.9, 126.7, 126.3, 105.8, 103.6, 78.5, 56.8, 55.9, 42.8, 41.6, 21.7, one carbon atom was not found probably due to overlapping; IR (film): 3030, 2938, 2839, 1805, 1674, 1595, 1476, 1449, 1433, 1298, 1256, 1111, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{36}H_{34}NO_5$ ([M+H]$^+$) 560.2437. Found 560.2430.

Characterization of δ-Aryl Dienylidene Maronate 7:

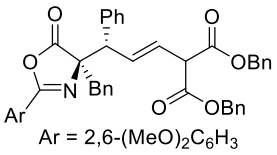


7: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, d, J = 11.6 Hz), 7.45-7.39 (2H, m), 7.39-7.30 (13H, m), 7.18 (1H, dd, J = 15.4, 11.6 Hz), 7.01 (1H, d, J = 15.4 Hz), 5.34 (2H, s), 5.26 (2H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 164.7, 146.5, 145.3, 135.9, 135.8, 135.7, 130.1, 129.0, 128.8, 128.7$_4$, 128.7$_1$, 128.5, 128.4, 128.3, 128.0, 124.2, 123.4, 67.3, 67.2; IR (film): 3032, 2953, 1717, 1616, 1589, 1450, 1283, 1231, 1150, 1155, 980 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{22}O_4Na$ ([M+Na]$^+$) 421.1410. Found 421.1417.

Characterization of 1,6-Adduct 8:

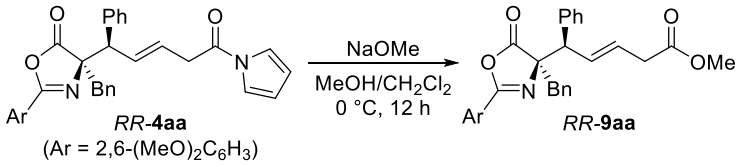


RR-**8:** HPLC OZ3, H/EtOH = 19:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 22.9 min (minor diastereomer), 37.0 min (minor isomer of major diastereomer), 50.7 min (major isomer of major diastereomer), 54.6 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (2H, d, J = 8.0 Hz), 7.27-7.15 (20H, m), 6.44 (1H, dd, J = 15.4, 10.0 Hz), 6.40 (2H, d, J = 8.4 Hz), 6.05 (1H, dd, J = 15.4, 9.2 Hz), 5.13 (1H, d, J = 12.2 Hz), 5.10 (1H, d, J = 12.3 Hz), 5.09 (1H, d, J = 12.2 Hz), 5.06 (1H, d, J = 12.3 Hz), 4.25 (1H, d, J = 9.2 Hz), 3.95 (1H, d, J = 10.0 Hz), 3.55 (6H, s), 3.35 (1H, d, J = 13.5 Hz), 3.08 (1H, d, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 167.6, 167.5, 159.4, 158.1, 137.5, 135.2, 135.1, 134.5, 134.3, 132.9, 131.0, 129.6, 128.6$_0$, 128.5$_7$, 128.4$_3$, 128.3$_7$, 128.3, 128.2, 128.1, 128.0, 127.9, 127.4, 126.9, 125.8, 105.0, 103.5, 78.1, 67.6, 67.4, 55.9, 55.8, 42.8; IR (film): 3032, 2938, 2839, 1807, 1732, 1661, 1595, 1476, 1454, 1433, 1300, 1256, 1146, 1113, 962, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{44}H_{40}NO_8$ ([M+H]$^+$) 710.2748. Found 710.2749.

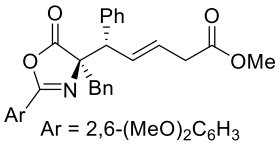


RS-**8:** HPLC OZ3, H/EtOH = 19:1, flow rate = 1.0 mL/min, 40 °C, λ = 254 nm, 22.9 min (minor isomer of major diastereomer), 36.9 min (minor diastereomer), 50.7 min (minor diastereomer), 54.5 min (major isomer of major diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (2H, d, J = 7.3 Hz), 7.35 (2H, t, J = 7.3 Hz), 7.27 (1H, t, J = 8.4 Hz), 7.27-7.13 (15H, m), 7.13-7.07 (2H, m), 6.43 (2H, d, J = 8.4 Hz), 6.27 (1H, dd, J = 15.3, 9.9 Hz), 6.00 (1H, dd, J = 15.3, 8.9 Hz), 5.08 (1H, d, J = 12.2 Hz), 5.05 (1H, d, J = 12.1 Hz), 5.02 (1H, d, J = 12.1 Hz), 4.97 (1H, d, J = 12.2 Hz), 4.07 (1H, dd, J = 8.9, 0.7 Hz), 3.89 (1H, d, J = 9.9 Hz), 3.54 (6H, s), 3.11 (1H, d, J = 13.5 Hz), 2.86 (1H, d, J = 13.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 167.4, 167.3, 159.3, 157.6, 138.3, 135.3, 135.2, 134.5, 134.3, 132.8, 130.7, 129.4, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.5,

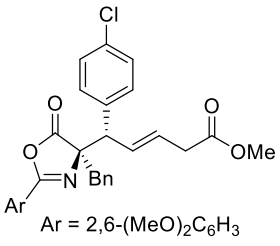
126.7, 125.3, 105.6, 103.6, 78.3, 67.4, 67.3, 55.9, 55.7, 41.6, two carbon atoms were not found probably due to overlapping; IR (film): 3032, 2940, 2839, 1807, 1732, 1670, 1595, 1476, 1454, 1298, 1256, 1113, 964, 907 cm^{-1}; HRMS (ESI) Calcd for $C_{44}H_{40}NO_8$ ($[M+H]^+$) 710.2748. Found 710.2747.



Methanolysis of *N*-Acylpyrrole Moiety of *RR*-4aa: A solution of *RR*-**4aa** (96.2 mg, 0.18 mmol) in CH_2Cl_2 (1.8 mL) was treated with a solution of NaOMe (10.8 mg, 0.20 mmol) in methanol (1.8 mL) at 0 °C for 12 h under Ar atmosphere. The whole mixture was poured into an ice-cooled, saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with CH_2Cl_2 twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4 and filtered. All volatiles were removed by evaporation to give crude material, which was purified by column chromatography on silica gel (H/EA = 1:1 as eluent) afforded *RR*-**9aa** in 91% yield (81.8 mg, 0.16 mmol). *RR*-**9aa:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (2H, d, J = 6.8 Hz), 7.29-7.14 (9H, m), 6.41 (2H, d, J = 8.4 Hz), 6.28 (1H, dd, J = 15.0, 9.6 Hz), 5.88 (1H, dt, J = 15.0, 7.2 Hz), 3.93 (1H, d, J = 9.6 Hz), 3.63 (3H, s), 3.57 (6H, s), 3.43 (1H, d, J = 13.2 Hz), 3.20 (1H, dd, J = 16.9, 7.2 Hz), 3.15 (1H, d, J = 13.2 Hz), 3.13 (1H, dd, J = 16.9, 7.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 171.8, 159.4, 157.9, 138.1, 134.6, 132.8, 131.7, 130.9, 129.5, 128.2, 127.9, 127.3, 126.8, 126.6, 105.1, 103.5, 78.1, 56.0, 55.8, 51.8, 42.8, 37.8; IR (film): 3030, 2951, 2839, 1807, 1734, 1661, 1595, 1476, 1454, 1433, 1256, 1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{30}NO_6$ ($[M+H]^+$) 500.2068. Found 500.2065.

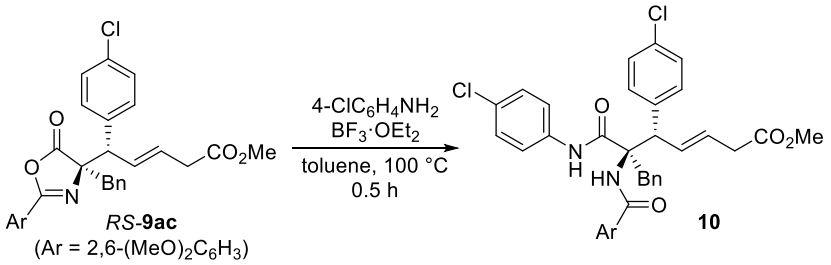


RS-**9aa** was obtained in 83% yield (194.7 mg, 0.39 mmol) by following the above procedure using *RS*-**4aa** as a starting material. *RS*-**9aa:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (2H, d, J = 7.4 Hz), 7.36 (2H, t, J = 7.4 Hz), 7.30 (1H, t, J = 8.3 Hz), 7.27 (1H, t, J = 7.4 Hz), 7.22-7.14 (3H, m), 7.14-7.07 (2H, m), 6.47 (2H, d, J = 8.3 Hz), 6.07 (1H, dd, J = 15.0, 9.6 Hz), 5.80 (1H, dt, J = 15.0, 7.3 Hz), 3.84 (1H, d, J = 9.6 Hz), 3.63 (6H, s), 3.57 (3H, s), 3.10 (1H, d, J = 13.6 Hz), 3.07 (1H, ddd, J = 16.5, 7.3, 1.2 Hz), 3.00 (1H, dd, J = 16.5, 7.3 Hz), 2.86 (1H, d, J = 13.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 171.6, 159.4, 157.4, 138.9, 134.7, 132.8, 132.0, 130.7, 129.5, 128.7, 128.0, 127.4, 126.7, 126.0, 105.8, 103.7, 78.7, 56.6, 55.9, 51.8, 41.6, 38.0; IR (film): 3028, 2949, 2839, 1805, 1736, 1672, 1595, 1476, 1454, 1433, 1300, 1256, 1169, 1113, 964, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{30}NO_6$ ($[M+H]^+$) 500.2068. Found 500.2063.

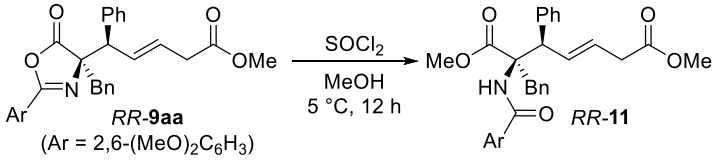


RS-**9ac** was obtained in 81% yield (104.4 mg, 0.20 mmol) by following the above procedure using *RS*-**4ac** as a starting material. *RS*-**9ac:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (2H, d, J = 8.8 Hz), 7.32 (2H, d, J = 8.8 Hz), 7.31 (1H, t, J = 8.5 Hz), 7.22-7.16 (3H, m), 7.16-7.08 (2H, m), 6.48 (2H, d, J = 8.5 Hz), 6.05 (1H, ddt, J = 15.2, 9.9, 1.2 Hz), 5.79 (1H, dt, J = 15.2, 7.2 Hz), 3.82 (1H, d, J = 9.9 Hz), 3.63 (6H, s), 3.60 (3H, s), 3.11 (1H, d, J = 13.6 Hz), 3.09 (1H, ddd, J = 16.4, 7.2, 1.2 Hz), 3.01 (1H, ddd, J = 16.4, 7.2, 1.2 Hz), 2.88 (1H, d, J = 13.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 171.6, 159.4, 157.6, 137.5, 134.5, 133.3, 133.0, 131.4, 130.8$_2$, 130.7$_6$, 128.9, 128.1, 126.9, 126.6, 105.6, 103.7, 78.4, 56.0, 55.8, 51.9, 41.7, 38.0; IR (film): 2951, 2839, 1805, 1736, 1670, 1595, 1476, 1433, 1300, 1256, 1165,

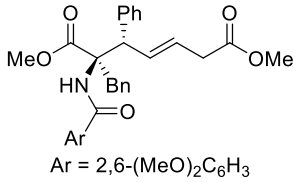
1113, 964, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{29}NO_6Cl$ ($[M+H]^+$) 534.1678. Found 534.1678.



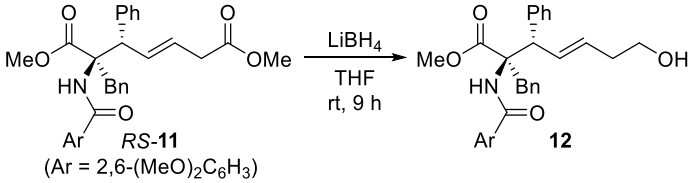
Azlactone Ring-Opening Reaction of *RS*-9ac: The monoester *RS*-**9ac** (25.7 mg, 0.048 mmol) and 4-chloroaniline (13.5 mg, 0.11 mmol) were placed in an oven-dried test tube and dissolved into toluene (0.48 mL). $BF_3{\cdot}OEt_2$ (0.0067 mL, 0.053 mmol) was added to the solution and the reaction mixture was then stirred for 0.5 h at 100 °C under Ar atmosphere. After cooling to room temperature, the mixture was poured into water and the aqueous phase was extracted with EA twice. The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated. The subsequent purification of the crude material by column chromatography on silica gel (H/acetone = 2:1~1:2 as eluent) afforded **10** in 56% yield (16.9 mg, 0.027 mmol). The absolute configuration of **10** was determined by X-ray crystallographic analysis (see page 113). **10:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (1H, brs), 7.46 (2H, d, J = 7.8 Hz), 7.44 (2H, d, J = 8.9 Hz), 7.30 (2H, d, J = 8.9 Hz), 7.28-7.20 (4H, m), 7.19 (2H, d, J = 8.2 Hz), 7.08 (2H, d, J = 8.2 Hz), 6.51 (2H, d, J = 8.7 Hz), 6.35 (1H, dd, J = 15.4, 9.0 Hz), 6.25 (1H, brs), 5.76 (1H, dt, J = 15.4, 7.0 Hz), 4.14 (1H, brd, J = 5.0 Hz), 3.88 (1H, d, J = 14.4 Hz), 3.77 (1H, d, J = 14.4 Hz), 3.71 (3H, s), 3.61 (6H, s), 3.22 (1H, dd, J = 16.8, 7.0 Hz), 3.16 (1H, dd, J = 16.8, 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 168.8, 164.8, 157.6, 138.0, 136.2, 136.0, 133.4, 132.9, 131.5, 131.4, 131.0, 129.7, 129.1, 128.5, 128.0, 127.4, 126.9, 122.0, 114.8, 104.1, 67.5, 55.8, 52.2$_0$, 52.1$_7$, 37.5; IR (film): 3366, 2949, 2839, 1732, 1680, 1593, 1489, 1472, 1435, 1398, 1250, 1107, 978, 907 cm^{-1}; HRMS (ESI) Calcd for $C_{36}H_{35}N_2O_6Cl_2$ ($[M+H]^+$) 661.1867. Found 661.1864.



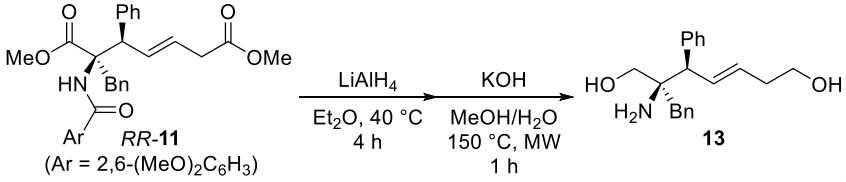
Methanolysis of Azlactone Moiety of *RR*-9aa: To a solution of *RR*-**9aa** (57.0 mg, 0.11 mmol) in methanol (1.1 mL) was introduced $SOCl_2$ (0.29 mL, 4.0 mmol) dropwise at 5 °C and the reaction mixture was stirred for 12 h at the same temperature. Then, a saturated aqueous solution of $NaHCO_3$ was added to quench the reaction. The aqueous phase was extracted with EA twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4 and filtered. After concentration, the residue was purified by column chromatography on silica gel (H/EA = 1:1 as eluent) to afford *RR*-**11** in 83% yield (48.4 mg, 0.091 mmol). *RR*-**11:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 6.8 Hz), 7.33-7.11 (9H, m), 6.74 (1H, brs), 6.53 (2H, d, J = 8.0 Hz), 6.31 (1H, dd, J = 14.7, 9.7 Hz), 5.81 (1H, dt, J = 14.7, 7.0 Hz), 4.43 (1H, d, J = 9.7 Hz), 4.38 (1H, d, J = 14.0 Hz), 3.76 (6H, s), 3.66 (3H, s), 3.60 (3H, s), 3.19 (1H, dd, J = 16.7, 7.0 Hz), 3.11 (1H, dd, J = 16.7, 7.0 Hz), 3.00 (1H, d, J = 14.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 172.1, 165.2, 157.7, 139.6, 136.8, 132.7, 130.7, 130.6, 129.6, 128.1, 127.8, 127.1, 126.4, 125.2, 116.4, 104.0, 70.0, 56.8, 55.7, 52.2, 51.7, 38.6, 38.0; IR (film): 3397, 2951, 2839, 1734, 1668, 1595, 1495, 1472, 1435, 1252, 1206, 1161, 1111, 968, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{34}NO_7$ ($[M+H]^+$) 532.2330. Found 532.2324.



RS-**11** was obtained in 69% yield (50.6 mg, 0.095 mmol) by following the above procedure using *RS*-**9aa** as a starting material. *RS*-**11:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (4H, m), 7.24-7.12 (7H, m), 6.65 (1H, brs), 6.48 (2H, d, J = 8.8 Hz), 6.36 (1H, dd, J = 14.9, 10.4 Hz), 5.95 (1H, dt, J = 14.9, 7.1 Hz), 4.99 (1H, d, J = 10.4 Hz), 4.12 (1H, d, J = 13.4 Hz), 3.78 (3H, s), 3.68 (3H, s), 3.63 (6H, s), 3.40 (1H, d, J = 13.4 Hz), 3.20 (1H, dd, J = 16.5, 7.1 Hz), 3.15 (1H, dd, J = 16.5, 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 172.0, 164.5, 158.2, 140.2, 137.0, 133.2, 130.9, 130.6, 129.0, 128.2, 127.9, 126.9, 126.5, 126.1, 115.6, 104.1, 70.5, 55.6, 52.7, 52.4, 51.9, 39.4, 38.3; IR (film): 3404, 3030, 2949, 2839, 1734, 1661, 1595, 1495, 1472, 1433, 1250, 1227, 1206, 1111, 972, 912 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{34}NO_7$ ([M+H]$^+$) 532.2330. Found 532.2325.

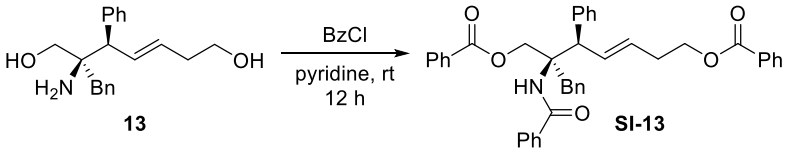


Site-Selective Reduction of *RS*-11: To a solution of *RS*-**11** (24.8 mg, 0.047 mmol) in THF (1.0 mL) was added $LiBH_4$ (20.3 mg, 0.93 mmol) at room temperature under Ar atmosphere. After 9 h of stirring, the reaction was quenched by adding water and the aqueous phase was extracted with EA twice. The organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4 and filtered. All volatiles were removed by evaporation and purification of the residue by column chromatography on silica gel (H/EA = 1:4 as eluent) afforded **12** in 95% yield (22.7 mg, 0.045 mmol). **12:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.24 (3H, m), 7.24-7.13 (8H, m), 6.66 (1H, brs), 6.49 (2H, d, J = 8.4 Hz), 6.34 (1H, dd, J = 15.0, 10.2 Hz), 5.81 (1H, dt, J = 15.0, 6.9 Hz), 4.95 (1H, d, J = 10.2 Hz), 4.12 (1H, d, J = 14.1 Hz), 3.78 (3H, s), 3.69 (2H, t, J = 6.9 Hz), 3.64 (6H, s), 3.40 (1H, d, J = 14.1 Hz), 2.43 (1H, dq, J = 13.6, 6.9 Hz), 2.39 (1H, dq, J = 13.6, 6.9 Hz), 1.60 (1H, brs); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5, 164.5, 158.2, 140.6, 136.9, 132.7, 131.0, 130.6, 130.5, 129.0, 128.2, 128.0, 126.9, 126.5, 115.6, 104.0, 70.4, 62.0, 55.7, 53.0, 52.5, 39.5, 36.3; IR (film): 3399, 3030, 2941, 2837, 1732, 1647, 1595, 1497, 1474, 1433, 1358, 1304, 1252, 1111, 1032, 972, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{34}NO_6$ ([M+H]$^+$) 504.2381. Found 504.2387.

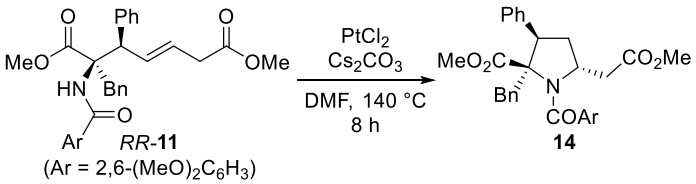


Reduction of Ester Moieties of *RR*-11 and Subsequent Deprotection on Nitrogen: $LiAlH_4$ (17.5 mg, 0.46 mmol) was placed in a test tube and suspended into dry Et_2O (0.50 mL) under Ar atmosphere. A solution of *RR*-**11** (12.2 mg, 0.023 mmol) in Et_2O (0.50 mL) was introduced slowly to the suspension at 0 °C and the reaction mixture was stirred for 4 h at 40 °C. The reaction was quenched by water and 1 N aqueous solution of NaOH at 0 °C. The aqueous phase was extracted with EA twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4 and filtered. All volatiles were removed under reduced pressure and the resulting crude residue was transferred to a test tube for a microwave apparatus with methanol (1.0 mL). Water (1.0 mL) and potassium hydroxide (0.17 g, 3.0 mmol) were added to the tube and the reaction mixture was stirred for 1 h at 150 °C under microwave irradiation. After addition of water, the aqueous phase was extracted with EA twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by column

chromatography on silica gel (EA/MeOH = 10:1 as eluent) afforded **13** in 78% yield (5.6 mg, 0.018 mmol). **13:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.19 (8H, m), 7.17 (2H, d, J = 7.2 Hz), 6.21 (1H, dd, J = 14.6, 10.3 Hz), 5.61 (1H, dt, J = 14.6, 6.5 Hz), 3.68 (1H, dt, J = 12.2, 6.5 Hz), 3.66 (1H, dt, J = 12.2, 6.5 Hz), 3.60 (1H, d, J = 10.3 Hz), 3.27 (1H, d, J = 10.6 Hz), 3.14 (1H, d, J = 10.6 Hz), 2.89 (1H, d, J = 9.2 Hz), 2.74 (1H, d, J = 9.2 Hz), 2.39 (1H, dq, J = 13.2, 6.5 Hz), 2.34 (1H, dq, J = 13.2, 6.5 Hz), 1.68 (4H, brs); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 137.2, 132.6, 130.9, 130.0, 129.5, 128.7, 128.4, 126.9, 126.7, 65.9, 62.0, 57.8, 55.6, 41.3, 36.3; IR (film): 3341, 3028, 2924, 1734, 1647, 1599, 1582, 1495, 1452, 1252, 1113, 1032, 974, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{26}NO_2$ ([M+H]$^+$) 312.1958. Found 312.1954.

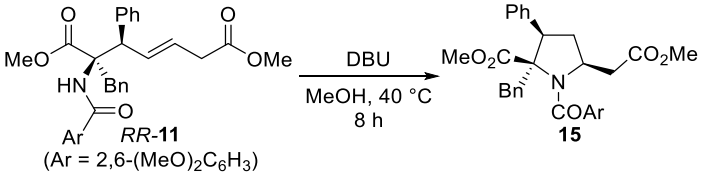


Benzoylation of Amino and Hydroxy Moieties of 13: To a solution of **13** (12.5 mg, 0.040 mmol) in pyridine (0.40 mL) was introduced benzoyl chloride (28.0 μL, 0.24 mmol) at room temperature under Ar atmosphere. After 12 h of stirring, the reaction mixture was poured into an ice-cooled, 1 N hydrochloric acid. The aqueous phase was extracted with EA twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4 and filtered. All volatiles were removed by evaporation and the resulting residue was purified by column chromatography on silica gel (H/EA = 10:1 as eluent) to give SI-**13** in 73% yield (18.1 mg, 0.029 mmol). The enantiomeric excess of SI-**13** was determined by HPLC analysis. SI-**13:** HPLC 99% ee, OZ3, H/IPA = 97:3, flow rate = 1.0 mL/min, 40 °C, λ = 220 nm, 18.7 min (minor isomer of major diastereomer), 26.3 min (major isomer of major diastereomer), 38.6 min (minor diastereomer), 41.8 min (minor diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (2H, d, J = 7.4 Hz), 7.83 (2H, d, J = 7.4 Hz), 7.64 (2H, d, J = 7.4 Hz), 7.57 (1H, t, J = 7.4 Hz), 7.52-7.40 (6H, m), 7.40-7.27 (7H, m), 7.20-7.10 (3H, m), 7.10-7.02 (2H, m), 6.70 (1H, brs), 6.26 (1H, dd, J = 14.7, 9.6 Hz), 5.69 (1H, dt, J = 14.7, 6.9 Hz), 4.87 (1H, d, J = 9.6 Hz), 4.53 (1H, d, J = 12.0 Hz), 4.41 (1H, d, J = 12.0 Hz), 4.09 (1H, dt, J = 11.2, 6.9 Hz), 4.02$_0$ (1H, d, J = 13.8 Hz), 4.01$_8$ (1H, dt, J = 11.2, 6.9 Hz), 2.70 (1H, d, J = 13.8 Hz), 2.32 (1H, dq, J = 13.8, 6.9 Hz), 2.25 (1H, dq, J = 13.8, 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 167.1, 166.4, 140.1, 136.7, 135.8, 133.8, 132.8, 132.3, 131.5, 130.6, 130.3, 130.1, 129.8, 129.6, 129.4, 128.9, 128.8, 128.4, 127.3, 126.8, 126.7, 67.7, 64.1, 62.8, 54.4, 39.0, 32.3; IR (film): 3370, 3061, 2957, 1717, 1663, 1531, 1489, 1450, 1314, 1269, 1111, 1070, 1026, 972, 908 cm^{-1}; HRMS (ESI) Calcd for $C_{41}H_{38}NO_5$ ([M+H]$^+$) 624.2744. Found 624.2733.

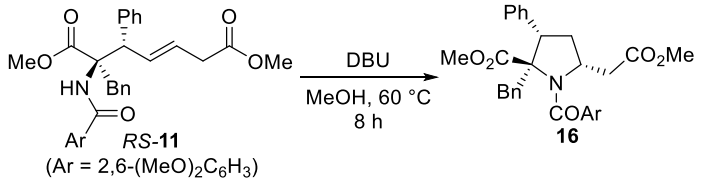


Cyclization Reaction of *RR*-11 Mediated by Platinum Chloride: *RR*-**11** (12.2 mg, 0.023 mmol), platinum chloride (6.12 mg, 0.023 mmol), and cesium carbonate (14.99 mg, 0.046 mmol) were suspended into DMF (0.23 mL) under Ar atmosphere. After 8 h of stirring at 140 °C, the reaction mixture was diluted with water. The aqueous phase was extracted with EA twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated. The resulting crude residue was analyzed by ^{1}H NMR (400 MHz) to determine

diastereoselectivity (>20:1) and was purified by column chromatography on silica gel (H/EA = 1:4 as eluent) to afford **14** as a single diastereomer in 76% yield (9.3 mg, 0.017 mmol). The absolute configuration of **14** was determined by X-ray crystallographic analysis (see page 113). **14:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (2H, d, J = 6.8 Hz), 7.45-7.27 (9H, m), 6.59 (2H, d, J = 8.4 Hz), 4.20 (1H, ddd, J = 11.5, 7.7, 3.0 Hz), 4.06 (1H, d, J = 14.4 Hz), 3.95 (3H, s), 3.92 (3H, s), 3.65 (1H, dd, J = 13.1, 6.1 Hz), 3.51 (3H, s), 3.37 (3H, s), 3.25 (1H, d, J = 14.4 Hz), 2.81 (1H, td, J = 13.1, 7.7 Hz), 1.85 (1H, dd, J = 16.3, 3.0 Hz), 1.66 (1H, dd, J = 13.1, 6.1 Hz), 1.10 (1H, dd, J = 16.3, 11.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 171.3, 167.2, 157.0$_3$, 156.9$_9$, 136.9, 136.3, 132.8, 130.8, 128.7, 128.6, 128.0, 127.9, 127.0, 115.8, 104.5, 104.3, 74.9, 56.2, 56.1, 55.9, 51.8, 51.4, 46.7, 38.5, 36.2, 33.6; IR (film): 2949, 2839, 1736, 1638, 1595, 1474, 1393, 1254, 1111, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{34}NO_7$ ([M+H]$^+$) 532.2330. Found 532.2324.



Cyclization Reaction of *RR*-11 under the Influence of DBU: *RR*-**11** (14.2 mg, 0.027 mmol) was placed in a test tube and dissolved into methanol (0.53 mL) under Ar atmosphere. DBU (80.0 μL, 0.53 mmol) was introduced to the solution and the reaction mixture was stirred for 8 h at 40 °C. After cooling to room temperature, the reaction was quenched by adding water. The aqueous phase was extracted with EA twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4 and filtered. All volatiles were removed by evaporation and the diastereomeric ratio of cyclization products was determined to be 4.4:1 by ^{1}H NMR (400 MHz) analysis of the crude residue. Purification of the residue was then performed by using preparative thin layer chromatography on silica gel (H/EA = 1:1 as eluent) to give **15** as a single diastereomer in 64% yield (9.2 mg, 0.017 mmol). **15:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (2H, d, J = 7.2 Hz), 7.42-7.22 (9H, m), 6.58 (1H, d, J = 8.0 Hz), 6.52 (1H, d, J = 8.0 Hz), 4.33 (1H, d, J = 15.0 Hz), 4.07 (1H, tdd, J = 9.0, 7.1, 4.9 Hz), 3.87 (3H, s), 3.72 (3H, s), 3.63 (1H, dd, J = 12.1, 7.1 Hz), 3.51 (3H, s), 3.46 (3H, s), 3.28 (1H, d, J = 15.0 Hz), 2.59 (1H, dd, J = 15.2, 9.0 Hz), 2.49 (1H, dd, J = 15.2, 4.9 Hz), 2.22 (1H, td, J = 12.1, 9.0 Hz), 2.15 (1H, dt, J = 12.1, 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 171.9, 165.8, 158.7, 156.6, 137.4, 137.3, 132.2, 131.3, 128.7, 128.5, 128.2, 127.7, 126.5, 116.2, 104.8, 103.8, 77.2, 56.5, 55.6, 52.0, 51.5, 47.2, 39.8, 37.1, 36.9, one carbon atom was not found probably due to overlapping.; IR (film): 2947, 2837, 1734, 1628, 1593, 1474, 1433, 1398, 1254, 1111, 912 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{34}NO_7$ ([M+H]$^+$) 532.2330. Found 532.2326.



Cyclization Reaction of *RS*-11 under the Influence of DBU: A methanolic solution (1.0 mL) of *RS*-**11** (12.9 mg, 0.024 mmol) was treated with DBU (73.0 μL, 0.49 mmol) at 60 °C for 8 h under Ar atmosphere. The reaction mixture was diluted with water at room temperature. The aqueous phase was extracted with EA twice and the organic phases were washed with brine. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated. The diastereomeric ratio of cyclization products was determined to be 14:1 by ^{1}H NMR (400 MHz) analysis of the crude residue. The

residue was purified by column chromatography on silica gel (H/EA = 1:4 as eluent) to afford **16** as a mixture of diastereomers in 88% yield (11.2 mg, 0.021 mmol). The absolute configuration of **16** was determined by X-ray crystallographic analysis (see page 114). **16:** ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.40 (2H, t, J = 7.3 Hz), 7.33 (1H, t, J = 7.3 Hz), 7.28 (1H, t, J = 8.2 Hz), 7.22-7.11 (5H, m), 7.09-6.99 (2H, m), 6.58 (1H, d, J = 8.2 Hz), 6.56 (1H, d, J = 8.2 Hz), 4.32 (1H, tdd, J = 9.8, 6.3, 3.4 Hz), 4.00 (1H, dd, J = 13.4, 6.3 Hz), 3.95 (3H, s), 3.90 (3H, s), 3.89 (3H, s), 3.69 (1H, d, J = 14.4 Hz), 3.40 (3H, s), 2.93 (1H, d, J = 14.4 Hz), 2.36 (1H, dt, J = 12.2, 6.3 Hz), 2.19 (1H, dd, J = 16.6, 3.4 Hz), 1.43 (1H, ddd, J = 13.4, 12.2, 9.8 Hz) 1.40 (1H, dd, J = 16.6, 9.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) *major diastereomer* δ 174.6, 171.6, 166.9, 157.7, 156.8, 137.8, 136.7, 132.3, 131.2, 128.5_7, 128.5_5, 127.5, 127.4, 126.6, 115.3, 104.6, 104.4, 73.9, 56.1_1, 56.0_5, 54.3, 52.6, 51.4, 49.3, 39.5, 36.2, 34.8; IR (film): 2947, 2839, 1734, 1632, 1595, 1474, 1400, 1362, 1302, 1254, 1171, 1111, 1032, 912 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{34}NO_7$ ($[M+H]^+$) 532.2330. Found 532.2329.

Crystallographic Structure Determination of *RR*-4ad: The single crystal, which was obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 93 K on a Bruker D8 QUEST with CCD diffractometer with graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined.

Recrystallization of *RR*-4ad: Recrystallization was performed by using a H/$CHCl_3$ solvent system at room temperature to afford single crystals of *RR*-**4ad**. The crystallographic data are summarized in Table S3 and ORTEP diagram is shown in Figure S3.

Crystallographic Structure Determination of 10: The single crystal, which was obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a Rigaku FR-X with Pilatus diffractometer with fine-focus sealed tube Mo/Kα radiation (λ = 0.71075 Å). An absorption correction was made using Crystal Clear. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined.

Recrystallization of 10: Recrystallization was performed by using a H/CH_2Cl_2 solvent system at room temperature to afford single crystals of **10**. The crystallographic data are summarized in Table S4 and the ORTEP diagram is shown in Figure S4.

Crystallographic Structure Determination of 14: The single crystal, which was obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a Rigaku FR-X with Pilatus diffractometer with fine-focus sealed tube Mo/Kα radiation (λ = 0.71075 Å). An absorption correction was made using Crystal Clear. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their

coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined.

Recrystallization of 14: Recrystallization was performed by using a H/EA solvent system at room temperature to afford single crystals of **14**. The crystallographic data are summarized in Table S5 and the ORTEP diagram is shown in Figure S5.

Crystallographic Structure Determination of 16: The single crystal, which was obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a Rigaku FR-X with Pilatus diffractometer with fine-focus sealed tube Mo/Kα radiation (λ = 0.71075 Å). An absorption correction was made using Crystal Clear. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined.

Recrystallization of 16: Recrystallization was performed by using a H/benzene solvent system at room temperature to afford single crystals of **16**. The crystallographic data are summarized in Table S6 and the ORTEP diagram is shown in Figure S6.

Crystallographic Structure Determination of *RR*-6ac: The single crystal, which was obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a Rigaku MicroMax-007HF with R-AXIS RAPID II with fine-focus sealed tube Cu/Kα radiation (λ = 1.54187 Å). An absorption correction was made using RAPID-AUTO. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined.

Recrystallization of *RR*-6ac: Recrystallization was performed by using a H/$CHCl_3$ solvent system at room temperature to afford single crystals of *RR*-**6ac**. The crystallographic data are summarized in Table S7 and the ORTEP diagram is shown in Figure S7.

Crystallographic Structure Determination of 1aa·HCl: The single crystal, which was obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a Rigaku FR-X with Pilatus diffractometer with fine-focus sealed tube Mo/Kα radiation (λ = 0.71075 Å). An absorption correction was made using Crystal Clear. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen and oxygen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined. SQUEEZE/PLATON was used in structural refinement.

Recrystallization of 1aa·HCl: Recrystallization was performed by using a H/EA solvent system at room temperature to afford single crystals of **1aa**·HCl. The crystallographic data are summarized in Table S8 and the ORTEP diagram is shown in Figure S8.

Crystallographic Structure Determination of 1ba·HCl: The single crystal, which was obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 93 K on a Bruker D8 QUEST with CCD diffractometer with graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined.

Recrystallization of 1ba·HCl: Recrystallization was performed by using a H/acetone solvent system at room temperature to afford single crystals of **1ba**·HCl. The crystallographic data are summarized in Table S9 and the ORTEP diagram is shown in Figure S9.

Crystallographic Structure Determination of 1da·HCl: The single crystal, which was obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a Rigaku FR-X with Pilatus diffractometer with fine-focus sealed tube Mo/Kα radiation (λ = 0.71075 Å). An absorption correction was made using Crystal Clear. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined. Hydrogen atoms bonded to O4 and O5 which are likely H_2O molecules could not be assigned.

Recrystallization of 1da·HCl: Recrystallization was performed by using a H/acetone solvent system at room temperature to afford single crystals of **1da**·HCl. The crystallographic data are summarized in Table S10 and the ORTEP diagram is shown in Figure S10.

Crystallographic Structure Determination of *ent*-1ea·HCl: The single crystal, which was obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a Rigaku FR-X with Pilatus diffractometer with fine-focus sealed tube Mo/Kα radiation (λ = 0.71075 Å). An absorption correction was made using Crystal Clear. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined.

Recrystallization of *ent*-1ea·HCl: Recrystallization was performed by using a H/acetone solvent system at room temperature to afford single crystals of *ent*-**1ea**·HCl. The crystallographic data are summarized in Table S11 and the ORTEP diagram is shown in Figure S11.

Table S3. Crystal data and structure refinement for *RR*-**4ad** (CCDC 1494061).

Empirical formula	$C_{34}H_{32}N_2O_5S_1 \cdot C_1H_1Cl_3$	
Formula weight	700.04	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.2529(5) Å	α = 90°.
	b = 14.0909(6) Å	β = 90°.
	c = 21.3929(11) Å	γ = 90°.
Volume	3392.1(3) $Å^3$	
Z	4	
Density (calculated)	1.371 Mg/m^3	
Absorption coefficient	0.376 mm^{-1}	
F(000)	1456	
Crystal size	0.30 x 0.30 x 0.30 mm^3	
Theta range for data collection	2.316 to 25.499°.	
Index ranges	–13<=h<=12, –16<=k<=17, –25<=l<=24	
Reflections collected	24918	
Independent reflections	6278 [R(int) = 0.0329]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.90 and 0.83	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6278 / 0 / 418	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R_1 = 0.0235, wR_2 = 0.0592	
R indices (all data)	R_1 = 0.0247, wR_2 = 0.0601	
Absolute structure parameter	0.009(12)	
Extinction coefficient	0	
Largest diff. peak and hole	0.210 and –0.164 e.$Å^{-3}$	

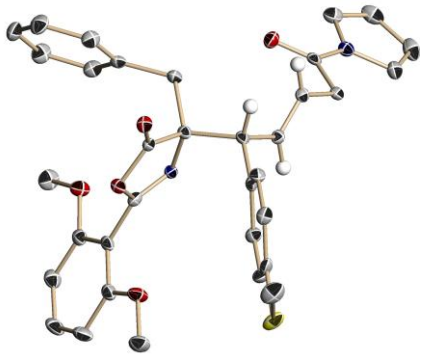


Figure S3. Molecular structure of *RR*-**4ad**. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms except them attached to olefinic and stereogenic carbons are omitted for clarity. Blue = nitrogen, red = oxygen, gray = carbon, yellow = sulfur.

Table S4. Crystal data and structure refinement for **10** (CCDC 1494060).

Empirical formula	$C_{36}H_{34}Cl_2N_2O_6$	
Formula weight	661.55	
Temperature	123.0(2) K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.2557(9) Å	α = 90°.
	b = 11.4883(15) Å	β = 90°.
	c = 34.369(4) Å	γ = 90°.
Volume	3259.7(7) $Å^3$	
Z	4	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	0.249 mm^{-1}	
F(000)	1384	
Crystal size	0.010 x 0.010 x 0.020 mm^3	
Theta range for data collection	3.039 to 25.495°.	
Index ranges	–9<=h<=9, –13<=k<=13, –41<=l<=41	
Reflections collected	18848	
Independent reflections	5813 [R(int) = 0.0264]	
Completeness to theta = 25.242°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.913	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5813 / 0 / 426	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R_1 = 0.0281, wR_2 = 0.0605	
R indices (all data)	R_1 = 0.0374, wR_2 = 0.0646	
Absolute structure parameter	0.020(17)	
Extinction coefficient	0	
Largest diff. peak and hole	0.193 and –0.228 e.$Å^{-3}$	

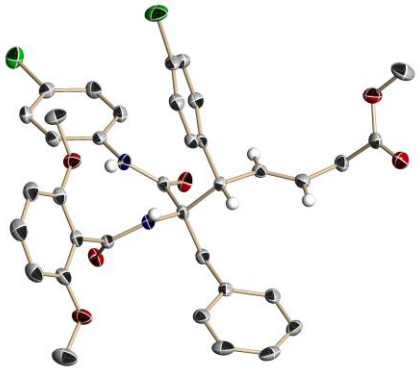


Figure S4. Molecular structure of **10**. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms except them attached to olefinic and stereogenic carbons are omitted for clarity. Blue = nitrogen, red = oxygen, gray = carbon, green = chlorine.

Table S5. Crystal data and structure refinement for **14** (CCDC 1494058).

Empirical formula	$C_{31}H_{33}N_1O_7$	
Formula weight	531.58	
Temperature	123.0(2) K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 9.8460(15) Å	α = 73.576(8)°.
	b = 10.1027(13) Å	β = 81.882(9)°.
	c = 15.545(2) Å	γ = 67.752(6)°.
Volume	1371.8(3) $Å^3$	
Z	2	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	564	
Crystal size	0.010 x 0.020 x 0.050 mm^3	
Theta range for data collection	3.076 to 25.499°.	
Index ranges	–11<=h<=11, –12<=k<=12, –18<=l<=15	
Reflections collected	9504	
Independent reflections	6980 [R(int) = 0.0164]	
Completeness to theta = 25.242°	95.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.933	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6980 / 3 / 711	
Goodness-of-fit on F^2	0.975	
Final R indices [I>2sigma(I)]	R_1 = 0.0286, wR_2 = 0.0596	
R indices (all data)	R_1 = 0.0378, wR_2 = 0.0625	
Absolute structure parameter	0.3(4)	
Extinction coefficient	0	
Largest diff. peak and hole	0.155 and –0.185 e.$Å^{-3}$	

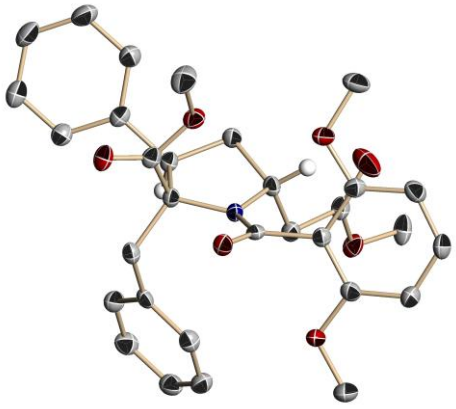


Figure S5. Molecular structure of **14**. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms except them attached to stereogenic carbons are omitted for clarity. Blue = nitrogen, red = oxygen, gray = carbon.

Table S6. Crystal data and structure refinement for **16** (CCDC 1494059).

Empirical formula	$C_{31}H_{33}N_1O_7$	
Formula weight	531.58	
Temperature	123.0(2) K	
Wavelength	0.71075 Å	
Crystal system	Trigonal	
Space group	P3(2)	
Unit cell dimensions	a = 10.7136(11) Å	α = 90°.
	b = 10.7136(11) Å	β = 90°.
	c = 21.153(2) Å	γ = 120°.
Volume	2102.7(5) $Å^3$	
Z	3	
Density (calculated)	1.259 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	846	
Crystal size	0.60 x 0.60 x 0.60 mm^3	
Theta range for data collection	3.629 to 25.500°.	
Index ranges	–12<=h<=12, –12<=k<=11, –25<=l<=25	
Reflections collected	14477	
Independent reflections	5108 [R(int) = 0.0204]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.917	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5108 / 1 / 356	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R_1 = 0.0320, wR_2 = 0.0850	
R indices (all data)	R_1 = 0.0340, wR_2 = 0.0860	
Absolute structure parameter	0.1(2)	
Extinction coefficient	0	
Largest diff. peak and hole	0.245 and –0.191 e.$Å^{-3}$	

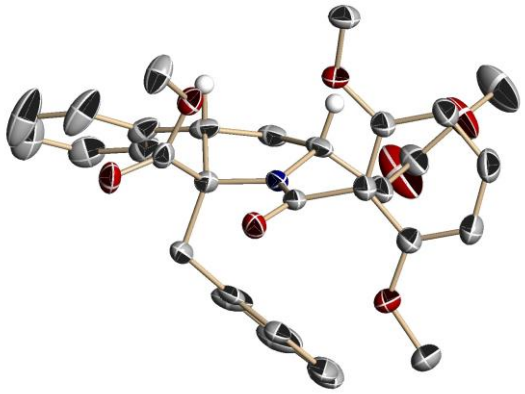


Figure S6. Molecular structure of **16**. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms except them attached to stereogenic carbons are omitted for clarity. Blue = nitrogen, red = oxygen, gray = carbon.

Table S7. Crystal data and structure refinement for *RR*-**6ac** (CCDC 1520998).

Empirical formula	$C_{36}H_{33}NO_5 \cdot CHCl_3$	
Formula weight	679.00	
Temperature	123.0(2) K	
Wavelength	1.54187 Å	
Crystal system	Orthothombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.4072(2) Å	α = 90°.
	b = 14.4661(3) Å	β = 90°.
	c = 21.9250(4) Å	γ = 90°.
Volume	3300.84(11) $Å^3$	
Z	4	
Density (calculated)	1.366 Mg/m^3	
Absorption coefficient	2.879 mm^{-1}	
F(000)	1416	
Crystal size	0.250 x 0.250 x 0.250 mm^3	
Theta range for data collection	3.661 to 68.249°.	
Index ranges	–12<=h<=12, –17<=k<=17, –26<=l<=26	
Reflections collected	60946	
Independent reflections	6057 [R(int) = 0.0342]	
Completeness to theta = 67.678°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.916	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6057 / 0 / 419	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R_1 = 0.0276, wR_2 = 0.0703	
R indices (all data)	R_1 = 0.0284, wR_2 = 0.0707	
Absolute structure parameter	–0.002(2)	
Extinction coefficient	0.00232(16)	
Largest diff. peak and hole	0.272 and –0.295 e.$Å^{-3}$	

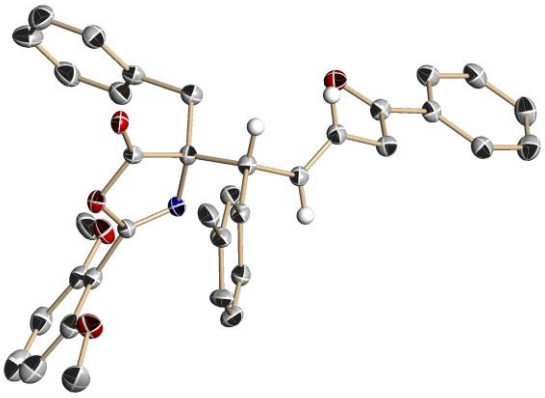
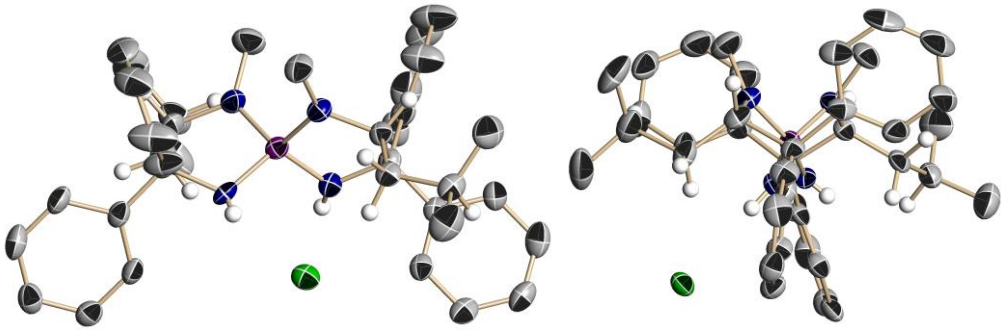


Figure S7. Molecular structure of *RR*-**6ac**. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms except them attached to olefinic and stereogenic carbons are omitted for clarity. Blue = nitrogen, red = oxygen, gray = carbon.

Table S8. Crystal data and structure refinement for **1aa**·HCl (CCDC 1520999).

Empirical formula	$2(C_{38}H_{48}N_4P)\cdot 2(Cl)\cdot H_2O$	
Formula weight	1272.46	
Temperature	123.0(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 13.167(2) Å	α = 90°.
	b = 18.308(3) Å	β = 98.277(3) °.
	c = 18.269(3) Å	γ = 90°.
Volume	4358.1(12) $Å^3$	
Z	2	
Density (calculated)	0.970 Mg/m^3	
Absorption coefficient	0.151 mm^{-1}	
F(000)	1364	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Theta range for data collection	3.029 to 25.500°.	
Index ranges	–15<=h<=15, –21<=k<=19, –15<=l<=22	
Reflections collected	30253	
Independent reflections	15180 [R(int) = 0.0432]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.829	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15180 / 4 / 838	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R_1 = 0.0425, wR_2 = 0.1012	
R indices (all data)	R_1 = 0.0536, wR_2 = 0.1063	
Absolute structure parameter	0.03(3)	
Extinction coefficient	0	
Largest diff. peak and hole	0.363 and –0.254 e.$Å^{-3}$	

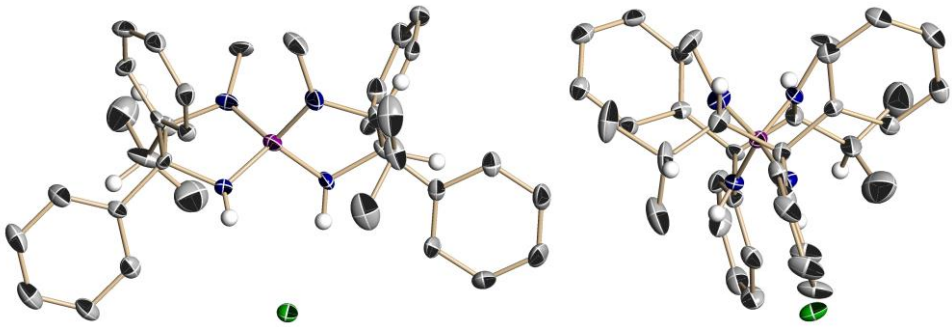


(a) Front view (b) Side view

Figure S8. Molecular structure of **1aa**·HCl. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms except them attached, α-position, and β-position to stereogenic carbons are omitted for clarity. Blue = nitrogen, gray = carbon, green = chlorine, purple = phosphorus.

Table S9. Crystal data and structure refinement for **1ba**·HCl (CCDC 1520995).

Empirical formula	$C_{36}H_{44}N_4P \cdot C_3H_6O \cdot Cl \cdot H_2O$	
Formula weight	675.27	
Temperature	93.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.3872(5) Å	α = 90°.
	b = 16.9120(7) Å	β = 90°.
	c = 17.8208(7) Å	γ = 90°.
Volume	3733.3(3) $Å^3$	
Z	4	
Density (calculated)	1.201 Mg/m^3	
Absorption coefficient	0.183 mm^{-1}	
F(000)	1448	
Crystal size	0.2 x 0.1 x 0.1 mm^3	
Theta range for data collection	2.286 to 25.495°.	
Index ranges	–15<=h<=14, –19<=k<=20, –19<=l<=21	
Reflections collected	26371	
Independent reflections	6900 [R(int) = 0.0572]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.982 and 0.978	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6900 / 5 / 449	
Goodness-of-fit on F^2	1.165	
Final R indices [I>2sigma(I)]	R_1 = 0.0732, wR_2 = 0.1721	
R indices (all data)	R_1 = 0.0816, wR_2 = 0.1763	
Absolute structure parameter	0.11(3)	
Extinction coefficient	0	
Largest diff. peak and hole	1.281 and –0.476 e.$Å^{-3}$	

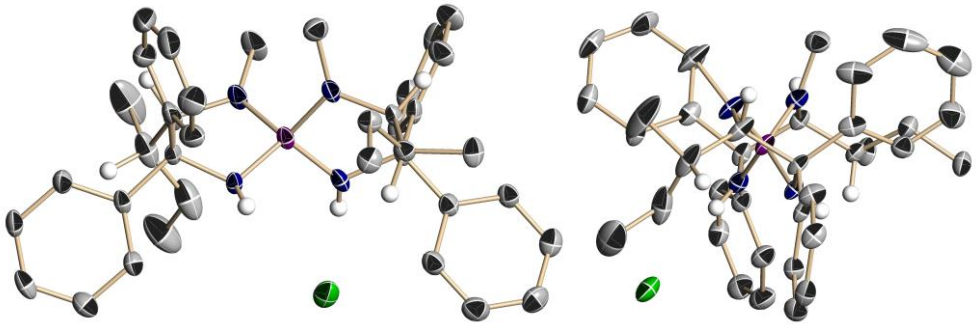


(a) Front view (b) Side view

Figure S9. Molecular structure of **1ba**·HCl. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms except them attached and α-position to stereogenic carbons are omitted for clarity. Blue = nitrogen, gray = carbon, green = chlorine, purple = phosphorus.

Table S10. Crystal data and structure refinement for **1da**·HCl (CCDC 1520997).

Empirical formula	$2(C_{38}H_{48}N_4P)\cdot C_3H_6O\cdot 2(Cl)\cdot H_2O\cdot 2(O)$	
Formula weight	1362.54	
Temperature	123.0(2) K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 17.8512(18) Å	α = 90°.
	b = 17.9844(17) Å	β = 90°.
	c = 23.459(2) Å	γ = 90°.
Volume	7531.3(12) $Å^3$	
Z	4	
Density (calculated)	1.202 Mg/m^3	
Absorption coefficient	0.183 mm^{-1}	
F(000)	2920	
Crystal size	0.50 x 0.30 x 0.20 mm^3	
Theta range for data collection	3.061 to 25.497°.	
Index ranges	–21<=h<=21, –19<=k<=21, –28<=l<=28	
Reflections collected	49497	
Independent reflections	13884 [R(int) = 0.1359]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.690	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13884 / 3 / 896	
Goodness-of-fit on F^2	0.994	
Final R indices [I>2sigma(I)]	R_1 = 0.0599, wR_2 = 0.1486	
R indices (all data)	R_1 = 0.0690, wR_2 = 0.1522	
Absolute structure parameter	0.08(5)	
Extinction coefficient	0	
Largest diff. peak and hole	1.127 and –0.792 e.$Å^{-3}$	

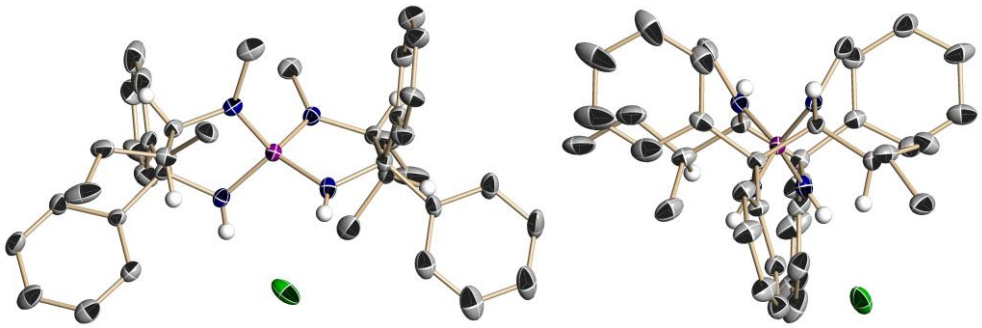


(a) Front view (b) Side view

Figure S10. Molecular structure of **1da**·HCl. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms except them attached to stereogenic carbons are omitted for clarity. Blue = nitrogen, gray = carbon, green = chlorine, purple = phosphorus.

Table S11. Crystal data and structure refinement for *ent*-**1ea**·HCl (CCDC 1520996).

Empirical formula	$C_{38}H_{48}N_4P\cdot Cl\cdot H_2O$	
Formula weight	645.24	
Temperature	123.0(2) K	
Wavelength	0.71075 Å	
Crystal system	Tetragonal	
Space group	P4(3)2(1)2	
Unit cell dimensions	a = 22.8786(18) Å	α = 90°.
	b = 22.8786(18) Å	β = 90°.
	c = 13.6070(11) Å	γ = 90°.
Volume	7122.3(13) Å^3	
Z	8	
Density (calculated)	1.203 Mg/m^3	
Absorption coefficient	0.187 mm^{-1}	
F(000)	2768	
Crystal size	0.100 x 0.100 x 0.100 mm^3	
Theta range for data collection	3.062 to 25.499°.	
Index ranges	–27<=h<=22, –27<=k<=27, –16<=l<=16	
Reflections collected	47836	
Independent reflections	6635 [R(int) = 0.0307]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.845	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6635 / 2 / 440	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R_1 = 0.0269, wR_2 = 0.0672	
R indices (all data)	R_1 = 0.0294, wR_2 = 0.0688	
Absolute structure parameter	–0.003(11)	
Extinction coefficient	0	
Largest diff. peak and hole	0.291 and –0.261 e.Å^{-3}	



(a) Front view (b) Side view

Figure S11. Molecular structure of *ent*-**1ea**·HCl. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms except them attached to stereogenic carbons are omitted for clarity. Blue = nitrogen, gray = carbon, green = chlorine, purple = phosphorus.

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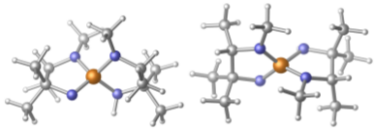
Computational Details:

Computational Details for Chapter 3:

All calculations were performed with the Gaussian 09 package.[1] Typical local minima and TS structures were optimized at B3LYP/6-31G* and frequency calculation were carried out to characterize the stationary points and to estimate Gibbs free energies. Single point calculations were performed at B3LYP-D3/6-31+G**. To evaluate more reliable relative Gibbs energies including dispersion corrections, zero-point energy, thermal, and entropic corrections calculated at B3LYP/6-31G* at 25 °C and 1 atm were added to the electronic energy calculated at B3LYP-D3/6-31+G**. The energy profile in solution was performed by using polarizable continuum model (PCM). The molecular structures were depicted by using the CYLview v1.0.561 β.[2]

Data for DFT Calculations:

- **Cat**



B3LYP/6-31G*

E = -1033.90262371

Zero-point correction = 0.394908 (Hartree/Particle)

Thermal correction to Energy = 0.415125

Thermal correction to Enthalpy = 0.416069

Thermal correction to Gibbs Free Energy = 0.349094

Sum of electronic and zero-point Energies = -1033.507716

Sum of electronic and thermal Energies = -1033.487499

Sum of electronic and thermal Enthalpies = -1033.486555

Sum of electronic and thermal Free Energies = -1033.553530

0 1			
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N	-1.10774900	-0.77574800	-0.98666600
P	0.06133500	0.03778800	-0.08108400
N	-1.11870500	0.58871400	1.01315900
C	-2.44787200	0.69296200	0.39234600
C	-2.50910900	-0.56249400	-0.54966500
C	-0.79915300	1.44178600	2.14581400
H	0.15681700	1.12445700	2.56989400
H	-0.72114200	2.50725400	1.88514900
H	-1.56974300	1.33261400	2.91973000
H	-3.20001300	0.57252100	1.18526400
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C	2.49288900	-0.69568700	0.30107300
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C	0.82784100	-1.87864200	1.81856700
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H	3.21462700	-0.60804100	1.12667000
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H	3.88083100	1.78036400	0.75168700
H	2.63154800	2.78842900	-0.01797700
H	2.22296300	1.78722900	1.38564400
C	2.86405400	-1.92737700	-0.53671000
H	3.89419300	-1.86149100	-0.90132200
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H	-3.69605100	2.12654000	-0.69322800
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H	-3.07550500	0.44955900	-2.40997300
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H	-4.03450400	-1.67695800	0.55266500
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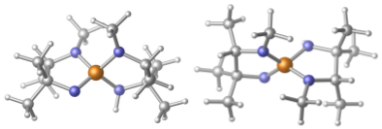
- **Cat** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -1033.90657162

Zero-point correction = 0.394782 (Hartree/Particle)

Thermal correction to Energy = 0.414975

Thermal correction to Enthalpy = 0.415919

Thermal correction to Gibbs Free Energy = 0.349062

Sum of electronic and zero-point Energies = -1033.511790

Sum of electronic and thermal Energies = -1033.491596

Sum of electronic and thermal Enthalpies = -1033.490652

Sum of electronic and thermal Free Energies = -1033.557509

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C	2.50619800	0.57875400	-0.53741000
C	0.80268500	-1.49835200	2.10907800
H	-0.15807800	-1.19797800	2.53454800
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H	-4.45095000	-0.51039900	-1.38459200
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H	-2.22919300	-1.81437200	1.34976800
C	-2.85299700	1.94498000	-0.49684000
H	-3.88556900	1.89719100	-0.85754200
H	-2.76368200	2.84610900	0.12036700
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C	2.71499100	-2.03454000	-0.33167200
H	3.73989700	-2.08967400	-0.71344600
H	2.58034300	-2.86536700	0.36891100
H	2.02134500	-2.18707800	-1.16579100
C	3.40881200	0.42807500	-1.76697000
H	4.44540100	0.23749500	-1.46860300
H	3.08326000	-0.38949300	-2.41717200
H	3.39841700	1.35525100	-2.35177200
C	2.97128200	1.78903400	0.29277100
H	4.02029000	1.67757700	0.59322700
H	2.87342400	2.70894800	-0.29309800
H	2.36389900	1.89364700	1.19704300

- **AZ**·H

B3LYP/6-31G*

E = -321.310520302

Zero-point correction = 0.063036 (Hartree/Particle)

Thermal correction to Energy = 0.067576

Thermal correction to Enthalpy = 0.068520

Thermal correction to Gibbs Free Energy = 0.035121

Sum of electronic and zero-point Energies = -321.247485

Sum of electronic and thermal Energies = -321.242945

Sum of electronic and thermal Enthalpies = -321.242000

Sum of electronic and thermal Free Energies = -321.275400

0 1			
O	-2.01432700	-0.05241000	0.00018200
C	-0.82073100	0.00453700	-0.00058000
C	0.14884000	1.18274900	0.00002900
O	-0.00502500	-1.13445000	0.00000900
N	1.48641900	0.59234100	0.00003200
C	1.29057600	-0.66134800	0.00008500
H	-0.00616500	1.81447200	-0.88207700
H	2.05122400	-1.43419300	0.00002200
H	-0.00727600	1.81258100	0.88311000

- **AZ**·H (PCM)

PCM(toluene)-B3LYP/6-31G*

E = -321.314541603

Zero-point correction = 0.063021 (Hartree/Particle)

Thermal correction to Energy = 0.067554

Thermal correction to Enthalpy = 0.068499

Thermal correction to Gibbs Free Energy = 0.035117

Sum of electronic and zero-point Energies = -321.251521

Sum of electronic and thermal Energies = -321.246987

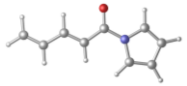
Sum of electronic and thermal Enthalpies = -321.246043

Sum of electronic and thermal Free Energies = -321.279425

0 1

O	-2.01403600	-0.05449000	-0.00011200
C	-0.81832000	0.00718100	0.00022700
C	0.14900600	1.18378900	0.00001300
O	-0.00725200	-1.13171100	0.00001000
N	1.48606300	0.59071700	-0.00008000
C	1.29131800	-0.66335600	0.00000700
H	-0.00689200	1.81350000	-0.88314400
H	2.04932700	-1.43830100	-0.00009600
H	-0.00658100	1.81369800	0.88313800

- **AC**



B3LYP/6-31G*

E = -478.307562018

Zero-point correction = 0.159317 (Hartree/Particle)

Thermal correction to Energy = 0.169451

Thermal correction to Enthalpy = 0.170395

Thermal correction to Gibbs Free Energy = 0.122350

Sum of electronic and zero-point Energies = -478.148245

Sum of electronic and thermal Energies = -478.138111

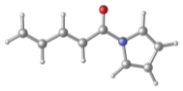
Sum of electronic and thermal Enthalpies = -478.137167

Sum of electronic and thermal Free Energies = -478.185212

0 1

C	-4.76217800	-0.21162900	-0.00012500
C	-3.51039900	-0.69726100	-0.00022100
H	-4.95530400	0.85846600	0.00038500
H	-3.35017500	-1.77510500	-0.00071100
C	-2.33168500	0.14605400	0.00026100
H	-2.47885600	1.22482100	0.00110600
C	-1.06379900	-0.31427100	-0.00029200
H	-0.87211100	-1.38162000	-0.00118300
C	0.06348300	0.64039300	0.00011900
O	-0.08665800	1.85290000	0.00065700
N	1.36920800	0.09677600	-0.00006500
C	2.50581900	0.90052100	-0.00066800
C	1.77604800	-1.24051000	0.00008900
C	3.60519600	0.08929700	-0.00052200
C	3.14213700	-1.26958700	0.00074200
H	2.39333600	1.97250100	-0.00118300
H	1.06553300	-2.05053100	0.00042600
H	4.63490400	0.42059700	-0.00090700
H	3.75289600	-2.16261500	0.00151800
H	-5.62913900	-0.86518800	-0.00055400

- **AC** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -478.310985107

Zero-point correction = 0.159380 (Hartree/Particle)

Thermal correction to Energy = 0.169458

Thermal correction to Enthalpy = 0.170403

Thermal correction to Gibbs Free Energy = 0.122733

Sum of electronic and zero-point Energies = -478.151605

Sum of electronic and thermal Energies = -478.141527

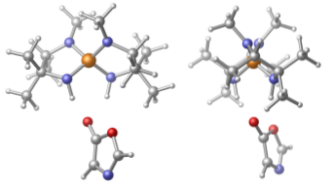
Sum of electronic and thermal Enthalpies = -478.140583

Sum of electronic and thermal Free Energies = -478.188252

0 1

C	4.76090900	-0.21315100	-0.00029000
C	3.50872100	-0.69914200	0.00004800
H	4.95413400	0.85696500	-0.00059200
H	3.34642800	-1.77640700	0.00034400
C	2.33266100	0.14749000	0.00004200
H	2.48615500	1.22527300	-0.00023900
C	1.06307500	-0.31079300	0.00036100
H	0.87099000	-1.37769700	0.00064800
C	-0.06288400	0.64148500	0.00037700
O	0.08297800	1.85688800	0.00024400
N	-1.36836800	0.09790400	0.00012600
C	-2.50727900	0.89956500	0.00017100
C	-1.77245900	-1.24073600	-0.00054300
C	-3.60510700	0.08581600	-0.00034600
C	-3.13873800	-1.27254300	-0.00010000
H	-2.40017800	1.97207500	0.00045700
H	-1.06023000	-2.04918900	-0.00091500
H	-4.63560000	0.41503200	-0.00046700
H	-3.74760300	-2.16692600	-0.00011400
H	5.62726400	-0.86750600	-0.00027500

- **CP1**



B3LYP/6-31G*

E = -1355.22808086

Zero-point correction = 0.460377 (Hartree/Particle)

Thermal correction to Energy = 0.486276

Thermal correction to Enthalpy = 0.487220

Thermal correction to Gibbs Free Energy = 0.405256

Sum of electronic and zero-point Energies = -1354.767704

Sum of electronic and thermal Energies = -1354.741805

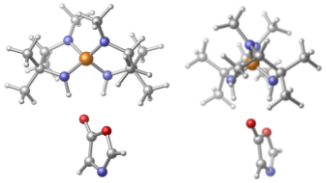
Sum of electronic and thermal Enthalpies = -1354.740861

Sum of electronic and thermal Free Energies = -1354.822825

0 1

H	0.45564000	-1.34251500	0.23778200
N	-0.50380100	-1.13137800	0.62166600
P	-1.07393800	0.29797500	0.04282400
N	-2.59222800	-0.26912800	-0.33243700
C	-2.58440700	-1.74694700	-0.48026500
C	-1.51806900	-2.22075100	0.57467200
C	-3.66523800	0.51506000	-0.92751400
H	-3.56130700	1.55961700	-0.62411800
H	-3.66303700	0.47262400	-2.02435100
H	-4.63371200	0.14790900	-0.56773900
H	-3.57470200	-2.10829100	-0.17345300
C	0.27685600	2.37081900	-0.80757000
C	-0.13849900	2.63725900	0.68614400
N	-1.26969100	1.69939000	0.91194400
C	-2.11208400	1.84566800	2.09096800
H	-2.95042000	1.14780900	2.02600100
H	-1.56941700	1.64656500	3.02364400
H	-2.51536700	2.86432800	2.13273900
H	-0.54733300	3.65325300	0.76495400
C	1.75302400	2.65649400	-1.10233200
H	1.98920900	3.70657500	-0.89670500
H	2.41922500	2.01921900	-0.51623200
H	1.95559300	2.47202300	-2.16287700
C	-0.61071200	3.20356300	-1.74966600
H	-0.38987700	4.27272700	-1.64686500
H	-0.43104700	2.91057400	-2.78849000
H	-1.67405000	3.05367200	-1.53238400
C	0.97699100	2.46029300	1.72229000
H	1.73300200	3.24434900	1.61224000
H	0.57350100	2.53759500	2.73770900
H	1.47627200	1.49115600	1.61972200
C	-2.31843100	-2.17644100	-1.92769300
H	-2.40583200	-3.26173900	-2.03708600
H	-3.04848600	-1.71963700	-2.60437400
H	-1.31703900	-1.87668600	-2.25541800
C	-0.81128400	-3.52805500	0.20055000
H	-1.53499600	-4.34181300	0.08109500
H	-0.22946700	-3.42511400	-0.71855500
H	-0.11845700	-3.80983300	1.00019200
C	-2.18249700	-2.36267700	1.95488100
H	-2.88734400	-3.20286100	1.96345300
H	-1.42041000	-2.54073300	2.71945200
H	-2.73206200	-1.45453200	2.22620600
O	1.71111300	-1.23321500	-0.88395800
C	2.91483500	-1.17511900	-0.44389500
C	4.08587000	-1.87071200	-0.63407300
O	3.23680200	-0.16249700	0.49958700
N	5.11112300	-1.33791400	0.14658100
C	4.56412400	-0.35507300	0.77871100
H	5.01681400	0.32241100	1.48995800
H	4.24432300	-2.71850700	-1.28412900
N	0.00788900	0.92217800	-1.03031200
H	0.81061400	0.27360500	-1.20311900

- **CP1** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -1355.23876327

Zero-point correction = 0.460447 (Hartree/Particle)

Thermal correction to Energy = 0.486409

Thermal correction to Enthalpy = 0.487353

Thermal correction to Gibbs Free Energy = 0.405085

Sum of electronic and zero-point Energies = -1354.778316

Sum of electronic and thermal Energies = -1354.752354

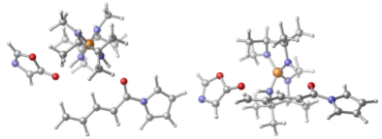
Sum of electronic and thermal Enthalpies = -1354.751410

Sum of electronic and thermal Free Energies = -1354.833679

0 1

H	0.45017300	-1.35778000	0.23317900
N	-0.50451000	-1.14336600	0.59979700
P	-1.08431400	0.29160400	0.03548700
N	-2.59692600	-0.27969000	-0.33491000
C	-2.60521200	-1.75858200	-0.46453300
C	-1.52180900	-2.23250100	0.57254600
C	-3.69184300	0.50415300	-0.89321400
H	-3.57197900	1.55140700	-0.60683000
H	-3.73148900	0.44713800	-1.98796500
H	-4.64528600	0.14433300	-0.48994400
H	-3.59084900	-2.10585100	-0.12958100
C	0.25719200	2.37622300	-0.81106800
C	-0.16561300	2.64069800	0.68040700
N	-1.28050500	1.68581300	0.90875000
C	-2.15317200	1.84913200	2.06500600
H	-2.96247200	1.11723700	2.01588100
H	-1.61878700	1.70918000	3.01242900
H	-2.59443000	2.85241800	2.05668100
H	-0.59034200	3.64985500	0.75449400
C	1.73070700	2.67716700	-1.10203100
H	1.95301400	3.73070500	-0.90054600
H	2.40195800	2.05320300	-0.50724800
H	1.94063000	2.48924000	-2.16052900
C	-0.63597500	3.19698600	-1.75785300
H	-0.42971300	4.26843900	-1.65150100
H	-0.44619300	2.90828800	-2.79618000
H	-1.69829900	3.03254800	-1.54691900
C	0.94758200	2.48658400	1.72229600
H	1.69447400	3.27890500	1.61006200
H	0.53713500	2.56540100	2.73448700
H	1.45692500	1.52173600	1.63033200
C	-2.38388300	-2.20686200	-1.91330100
H	-2.48270700	-3.29256700	-2.00739400
H	-3.13060700	-1.75127700	-2.57196100
H	-1.39145100	-1.91741600	-2.27521300
C	-0.82642300	-3.54306800	0.19119100
H	-1.55480100	-4.35570700	0.09920300
H	-0.27430300	-3.45138000	-0.74739100
H	-0.11212900	-3.81969900	0.97366600
C	-2.16291900	-2.36802300	1.96426900
H	-2.87406700	-3.20232100	1.98388000
H	-1.38998000	-2.55230100	2.71657200
H	-2.70068700	-1.45527000	2.24343400
O	1.78363700	-1.23082700	-0.89537800
C	2.97790300	-1.16366700	-0.44920600
C	4.16547700	-1.83374400	-0.65343300
O	3.28464100	-0.17212400	0.52500600
N	5.17930300	-1.30350400	0.14567100
C	4.61147500	-0.34688000	0.80348600
H	5.05065800	0.31882800	1.53422300
H	4.34088600	-2.66097300	-1.32592100
N	0.00395400	0.92285600	-1.03166200
H	0.81305300	0.29275300	-1.20361700

- **CP2**



B3LYP/6-31G*

E = -1833.54979746

Zero-point correction = 0.620641 (Hartree/Particle)

Thermal correction to Energy = 0.658741

Thermal correction to Enthalpy = 0.659685

Thermal correction to Gibbs Free Energy = 0.546185

Sum of electronic and zero-point Energies = -1832.929157

Sum of electronic and thermal Energies = -1832.891056

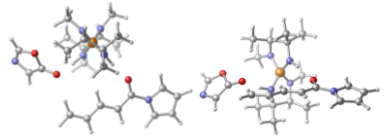
Sum of electronic and thermal Enthalpies = -1832.890112

Sum of electronic and thermal Free Energies = -1833.003612

0 1

O	-2.01161100	1.92795700	-0.45855100
C	-3.20139000	2.17259300	-0.05573600
C	-3.80736200	3.05411400	0.81605300
O	-4.26190900	1.37036600	-0.55606100
N	-5.18528300	2.84113000	0.86166900
C	-5.38687700	1.85786900	0.04971300
C	0.10863700	4.17093700	-1.22313000
C	1.41045000	3.83411300	-1.15870000
H	-0.68721200	3.46120200	-0.98433800
H	2.18324400	4.56582700	-1.39579700
C	1.85402100	2.51135900	-0.77852600
H	1.08360300	1.77560500	-0.55502800
C	3.15692800	2.15342000	-0.67390000
H	3.93069900	2.88539900	-0.87901600
C	3.55264800	0.79722000	-0.29663300
O	2.78688100	-0.16885800	-0.25097100
N	4.90982000	0.58915600	0.02360700
C	5.44320200	-0.67641100	0.25947900
C	5.92691400	1.53386800	0.19451500
C	6.76707700	-0.53384300	0.56277400
C	7.07288800	0.86905400	0.52609500
H	4.80851800	-1.54307700	0.17449500
H	5.73697200	2.58998700	0.09707000
H	7.45446000	-1.33852600	0.78646800
H	8.03140500	1.32840800	0.72731800
H	-1.30545700	0.85314300	0.51178600
N	-0.91914200	-0.01383100	0.98944200
P	-0.88997500	-1.39696100	0.12141700
N	-0.78821100	-2.39336300	1.45407500
C	-0.43857100	-1.63640900	2.67961500
C	-1.07446800	-0.21863200	2.44842700
C	-0.58181600	-3.83192900	1.39954800
H	-1.05767200	-4.23013400	0.49968400
H	0.47938000	-4.11542000	1.38659300
H	-1.05531000	-4.30099100	2.27007400
H	-0.95656400	-2.11912300	3.51893400
N	0.23575900	-1.31469500	-1.06843800
C	-0.18243000	-1.83027100	-2.38790100
C	-1.75321000	-1.77097300	-2.32212700
N	-2.06532800	-2.00783600	-0.88770100
H	1.13632100	-0.85642600	-0.92219400
C	-3.46189100	-2.16154700	-0.48038400
H	-3.49618400	-2.55771900	0.53807600
H	-4.01424000	-1.21579500	-0.51479900
H	-3.94535300	-2.88873600	-1.14217500
H	-2.14915600	-2.63316900	-2.87565500
H	-6.32481900	1.38441600	-0.20815500
H	-3.33438300	3.84446800	1.38147600
H	-0.18542600	5.17641300	-1.51439900
C	0.42737200	-0.94973500	-3.48460100
H	0.09449100	-1.27521200	-4.47602300
H	0.15942500	0.10109100	-3.35276000
H	1.52017900	-1.03136900	-3.45840200
C	-2.40192900	-0.49196300	-2.86023500
H	-2.18622800	-0.37122200	-3.92701000
H	-3.48928000	-0.54760100	-2.75146900
H	-2.07498200	0.39881600	-2.31298100
C	0.28567500	-3.28667000	-2.57153200
H	0.01690300	-3.66061900	-3.56671000
H	1.37347400	-3.35392200	-2.46228200
H	-0.17419700	-3.94244100	-1.82496500
C	-2.55791800	-0.22026700	2.86306900
H	-3.04485400	0.70381000	2.53337400
H	-3.09334100	-1.06652700	2.42034500
H	-2.65306800	-0.29154400	3.95340800
C	-0.34517900	0.91509600	3.18022500
H	-0.84613700	1.86460200	2.96413500
H	-0.37103700	0.76210600	4.26532700
H	0.69534500	0.99998800	2.85771000
C	1.07109300	-1.65220600	2.95421800
H	1.30149100	-1.15005400	3.89896100
H	1.43202200	-2.68320700	3.03893500
H	1.63319900	-1.16038800	2.15286300

- **CP2** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -1833.56000455

Zero-point correction = 0.620293 (Hartree/Particle)

Thermal correction to Energy = 0.658654

Thermal correction to Enthalpy = 0.659598

Thermal correction to Gibbs Free Energy = 0.544788

Sum of electronic and zero-point Energies = -1832.939712

Sum of electronic and thermal Energies = -1832.901351

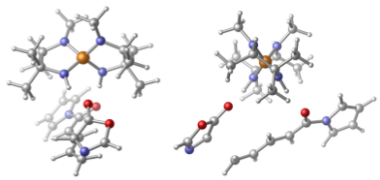
Sum of electronic and thermal Enthalpies = -1832.900407

Sum of electronic and thermal Free Energies = -1833.015217

0 1

O	-2.20530800	1.85526200	-0.71993000
C	-3.40758800	2.09136600	-0.37115700
C	-4.08971800	3.09314500	0.29327100
O	-4.40868300	1.12799800	-0.68903300
N	-5.45049300	2.79592400	0.38430700
C	-5.57173900	1.64893700	-0.20015100
C	0.07962700	4.11003600	-1.26392900
C	1.38769000	3.80572600	-1.17539400
H	-0.70687600	3.37923400	-1.06704200
H	2.14283000	4.56493300	-1.37904100
C	1.86407900	2.48787800	-0.81530500
H	1.11446000	1.72409300	-0.61622700
C	3.17548200	2.16693100	-0.70455700
H	3.92839200	2.92441700	-0.89157600
C	3.60435400	0.81449600	-0.34694600
O	2.85220000	-0.16089800	-0.27478600
N	4.97406100	0.62301800	-0.07661000
C	5.52547800	-0.63519000	0.16197700
C	5.99204100	1.57718300	0.03154400
C	6.85992200	-0.47876400	0.40701300
C	7.15500300	0.92535100	0.32814600
H	4.89478900	-1.50803900	0.12199800
H	5.79500000	2.62988900	-0.08595800
H	7.56099700	-1.27481700	0.61917800
H	8.11848100	1.39401400	0.47793000
H	-1.41833600	0.88164800	0.37023100
N	-0.97256100	0.11533200	0.93995900
P	-0.84763300	-1.36794500	0.25662600
N	-0.68543600	-2.16955200	1.70583900
C	-0.39977500	-1.24073000	2.82540200
C	-1.12298500	0.09115500	2.41425700
C	-0.39977900	-3.59049300	1.84587300
H	-0.84081400	-4.13171900	1.00519600
H	0.67518800	-3.81063000	1.87788200
H	-0.85876500	-3.96290000	2.76867600
H	-0.89509500	-1.64535900	3.71741100
N	0.26355900	-1.34707100	-0.94911300
C	-0.10492000	-2.08382900	-2.17596800
C	-1.67564400	-2.12031900	-2.11167200
N	-1.98011900	-2.17264300	-0.65791600
H	1.16769900	-0.88531600	-0.84447200
C	-3.35896600	-2.38810500	-0.22199300
H	-3.36430700	-2.64462400	0.84069200
H	-3.98931100	-1.50535500	-0.37731300
H	-3.77840300	-3.23408900	-0.77698300
H	-2.01254700	-3.07355500	-2.53949500
H	-6.47062200	1.06485500	-0.34686700
H	-3.67912100	4.01245900	0.68646900
H	-0.23404800	5.11367800	-1.54006800
C	0.44997500	-1.33460500	-3.39288600
H	0.14906200	-1.82763300	-4.32343200
H	0.10785300	-0.29737200	-3.41815900
H	1.54544100	-1.33374700	-3.35672900
C	-2.40497600	-0.97383000	-2.81983500
H	-2.19786400	-0.99148800	-3.89464400
H	-3.48647800	-1.08414800	-2.69324500
H	-2.13161600	0.00404900	-2.40998600
C	0.46162000	-3.51610300	-2.14591000
H	0.22975800	-4.04524300	-3.07772000
H	1.55028300	-3.49256700	-2.02746400
H	0.03825100	-4.08883800	-1.31436300
C	-2.60614600	0.04500200	2.82735200
H	-3.14608200	0.89547000	2.39790600
H	-3.08648300	-0.87593000	2.48164100
H	-2.70334300	0.09168100	3.91854200
C	-0.47428400	1.35370400	2.99553400
H	-1.03049200	2.23488000	2.65857500
H	-0.50265800	1.33848800	4.09098700
H	0.56279900	1.46302200	2.66916800
C	1.10415800	-1.12600200	3.10391300
H	1.29379200	-0.48778700	3.97227900
H	1.52331000	-2.11307600	3.32649800
H	1.64317300	-0.71499800	2.24339300

- **TS1**



B3LYP/6-31G*

E = -1833.53987428

Zero-point correction = 0.621048 (Hartree/Particle)

Thermal correction to Energy = 0.657977

Thermal correction to Enthalpy = 0.658922

Thermal correction to Gibbs Free Energy = 0.549717

Sum of electronic and zero-point Energies = -1832.918826

Sum of electronic and thermal Energies = -1832.881897

Sum of electronic and thermal Enthalpies = -1832.880953

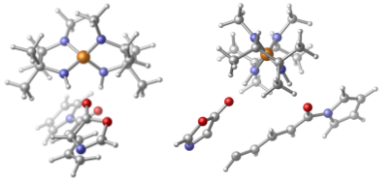
Sum of electronic and thermal Free Energies = -1832.990157

0 1

O	-2.51866900	0.53657100	0.22880700
C	-3.46665600	1.32912400	0.29230200
C	-3.75099700	2.51621300	1.02734700
O	-4.54291500	1.20067500	-0.60845700
N	-5.03959700	2.97022600	0.69633300
C	-5.41380200	2.20393800	-0.26607200
C	-2.45099900	3.85008500	-0.14024700
C	-1.09827400	3.76814700	0.18551700
H	-2.79513200	3.43927700	-1.08617500
H	-0.72880900	4.37163100	1.01503100
C	-0.18898300	2.93095800	-0.47496200
H	-0.57396400	2.30196700	-1.27621400
C	1.17586200	2.86485600	-0.22735800
H	1.60438000	3.50584000	0.53571400
C	2.02729200	2.00896300	-0.98069100
O	1.66174400	1.12944300	-1.79162400
N	3.44073500	2.14357600	-0.78570500
C	4.35560200	1.23458700	-1.29609900
C	4.14057900	3.13636300	-0.10908000
C	5.61572400	1.63872500	-0.93824300
C	5.47906200	2.84980100	-0.18678200
H	3.99933400	0.39557900	-1.87104800
H	3.63086900	3.97550000	0.33589900
H	6.53832600	1.13209300	-1.18942500
H	6.27699000	3.44558900	0.23702500
H	-1.11264000	-0.07106300	1.15317000
N	-0.34861200	-0.73278700	1.35379700
P	0.07726200	-1.86387100	0.25557500
N	1.27301100	-2.50889400	1.22464200
C	1.63521900	-1.61668900	2.35168600
C	0.30722000	-0.83598600	2.67126300
C	2.20120700	-3.54445400	0.79382900
H	1.70138800	-4.19943200	0.07571700
H	3.10583200	-3.13955200	0.32204100
H	2.50037600	-4.14984300	1.65764700
H	1.87045900	-2.26138200	3.20926200
N	0.26837300	-1.20929200	-1.22136700
C	-0.32983200	-1.96125800	-2.34581200
C	-1.37997000	-2.91164600	-1.65559800
N	-0.83041900	-3.14513900	-0.29663300
H	0.69856500	-0.28283200	-1.38322500
C	-1.41345000	-4.17544200	0.54986400
H	-0.78808400	-4.31252700	1.43554600
H	-2.43269000	-3.93313900	0.87698800
H	-1.44202100	-5.12502600	0.00197600
H	-1.35701000	-3.87905100	-2.17527300
H	-6.33656700	2.24772300	-0.82962600
H	-3.31678900	2.75776400	1.98639400
H	-3.04349800	4.68139200	0.22663500
C	-0.94830100	-0.95464500	-3.32377900
H	-1.42179500	-1.46857500	-4.16759800
H	-1.69069100	-0.32571000	-2.82691400
H	-0.16242300	-0.30322000	-3.72009500
C	-2.82633500	-2.40645000	-1.61596400
H	-3.22585800	-2.29968900	-2.62946500
H	-3.46234000	-3.13075200	-1.09464600
H	-2.90725800	-1.44340100	-1.10177700
C	0.74929400	-2.79605100	-3.05890200
H	0.32871000	-3.32116400	-3.92498500
H	1.55830500	-2.14677000	-3.40907700
H	1.17833300	-3.54254800	-2.38104400
C	-0.55762100	-1.64688900	3.65538700
H	-1.54889800	-1.19213500	3.75293700
H	-0.68777000	-2.67771200	3.30914800
H	-0.09430900	-1.67574200	4.64887200
C	0.53493700	0.57596900	3.22431800
H	-0.43151400	1.04844700	3.43242500

H	1.09706200	0.54193200	4.16418700
H	1.06774600	1.20619600	2.50849600
C	2.86151900	-0.75154400	2.03956300
H	3.14800000	-0.15120700	2.90829900
H	3.71911000	-1.38276300	1.78473900
H	2.68183800	-0.07500600	1.19862900

● **TS1** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -1833.54876813

Zero-point correction = 0.621104 (Hartree/Particle)

Thermal correction to Energy = 0.657907

Thermal correction to Enthalpy = 0.658851

Thermal correction to Gibbs Free Energy = 0.550903

Sum of electronic and zero-point Energies = -1832.927664

Sum of electronic and thermal Energies = -1832.890861

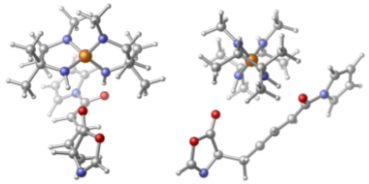
Sum of electronic and thermal Enthalpies = -1832.889917

Sum of electronic and thermal Free Energies = -1832.997865

0 1

O	2.56633300	-0.41945600	0.21064300
C	3.56585900	-1.14213700	0.28015800
C	3.92164400	-2.32045400	0.99962200
O	4.65119900	-0.91969200	-0.59641000
N	5.24819900	-2.67146700	0.68801400
C	5.58545200	-1.86168100	-0.25365600
C	2.73387700	-3.72464000	-0.19398500
C	1.37620800	-3.73512300	0.12438600
H	3.05503400	-3.28512300	-1.13521200
H	1.04482300	-4.36372800	0.95137700
C	0.41665100	-2.95284000	-0.53248700
H	0.76020000	-2.30043400	-1.33408200
C	-0.94842100	-2.96590200	-0.27735000
H	-1.33397400	-3.62291700	0.49480100
C	-1.84993600	-2.15622000	-1.02301300
O	-1.53741400	-1.27361400	-1.85191200
N	-3.25372800	-2.35106200	-0.79844600
C	-4.21809500	-1.49120800	-1.30302400
C	-3.89528800	-3.36716500	-0.09891900
C	-5.45272800	-1.94954900	-0.92011300
C	-5.24741600	-3.14431900	-0.15762900
H	-3.91293700	-0.64006200	-1.88967400
H	-3.34061200	-4.17540300	0.34969400
H	-6.40169400	-1.48776100	-1.15972000
H	-6.00950100	-3.77126700	0.28701000
H	1.07384600	0.11960000	1.09758300
N	0.25758600	0.70678500	1.30994000
P	-0.23929400	1.86338700	0.26447300
N	-1.44017000	2.41466900	1.27645300
C	-1.71860100	1.48719600	2.39909900
C	-0.34691400	0.76333600	2.65646300
C	-2.42017100	3.43209300	0.91911500
H	-1.97761800	4.12551500	0.19990700
H	-3.33097300	3.00889100	0.47732700
H	-2.69831600	3.99986800	1.81435300
H	-1.95167600	2.10532700	3.27589300
N	-0.41786000	1.23748800	-1.23086300
C	0.11946000	2.05619500	-2.34147700
C	1.13315100	3.03384600	-1.63722000
N	0.59163000	3.20148500	-0.26631100
H	-0.75835100	0.28062900	-1.40675300
C	1.11348900	4.25690800	0.59156500
H	0.48032600	4.35120200	1.47683900
H	2.14401900	4.06843800	0.91758600
H	1.08836500	5.20988600	0.05068100
H	1.06034800	4.01297600	-2.12829000
H	6.52038600	-1.82813100	-0.79769700
H	3.49164700	-2.60380100	1.94915500
H	3.37562000	-4.52065800	0.16873300
C	0.77004600	1.12085900	-3.36721900
H	1.20522300	1.69400700	-4.19289800
H	1.55073500	0.50916500	-2.90898600
H	0.01222600	0.44876000	-3.78294900
C	2.60159500	2.59575800	-1.62732900
H	2.99533000	2.53946600	-2.64709000
H	3.20681100	3.33198700	-1.08697000
H	2.73304100	1.62234200	-1.14370000
C	-1.01280400	2.85987500	-3.00621900
H	-0.63326200	3.43398800	-3.85976200
H	-1.79503600	2.18385200	-3.36683200
H	-1.46595300	3.56035400	-2.29611200
C	0.51989100	1.59715700	3.61948200
H	1.53494400	1.18892200	3.66568900
H	0.58596200	2.64020200	3.29248200
H	0.09819300	1.58264100	4.63139100
C	-0.48879800	-0.66465500	3.19689800
H	0.50550300	-1.09426900	3.36173000
H	-1.01567300	-0.66794300	4.15735600
H	-1.02002700	-1.30987600	2.49338300
C	-2.91528700	0.57305100	2.11423800
H	-3.14368500	-0.05247400	2.98232800
H	-3.80727800	1.17064100	1.90023000
H	-2.73434600	-0.08108700	1.25572200

● **CP3**



B3LYP/6-31G*

E = -1833.55919010

Zero-point correction = 0.623090 (Hartree/Particle)

Thermal correction to Energy = 0.659811

Thermal correction to Enthalpy = 0.660755

Thermal correction to Gibbs Free Energy = 0.553289

Sum of electronic and zero-point Energies = -1832.936100

Sum of electronic and thermal Energies = -1832.899379

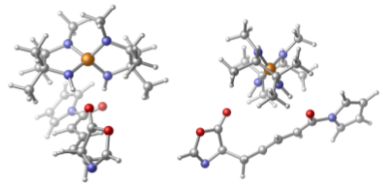
Sum of electronic and thermal Enthalpies = -1832.898435

Sum of electronic and thermal Free Energies = -1833.005901

0 1

O	3.03007200	0.05526400	0.48860400
C	3.95868000	-0.68653500	0.28724900
C	4.15288600	-2.17863700	0.49491100
O	5.14182800	-0.21599800	-0.27220000
N	5.55575000	-2.41732300	0.13452600
C	5.99325900	-1.30889900	-0.29317600
C	3.18964900	-3.04174300	-0.39840800
H	3.24557400	-2.66000000	-1.42545300
C	1.77043500	-3.10296100	0.06773600
H	1.58737400	-3.65475600	0.99203900
C	0.72416800	-2.59537800	-0.63321400
H	0.94980100	-2.04681400	-1.54942800
C	-0.67111500	-2.71914000	-0.34011500
H	-0.97887800	-3.36044400	0.47974800
C	-1.62786400	-2.10222200	-1.13954100
O	-1.41794500	-1.24964100	-2.06292100
N	-3.02232500	-2.39717200	-0.88788000
C	-4.04894500	-1.58718400	-1.33303700
C	-3.56911200	-3.43066400	-0.14814600
C	-5.24110100	-2.09578500	-0.87052700
C	-4.93540800	-3.27093300	-0.11865700
H	-3.81741000	-0.73528200	-1.95147200
H	-2.94531900	-4.21127700	0.25823400
H	-6.22353400	-1.68404800	-1.06323700
H	-5.63834900	-3.93389000	0.36959100
H	-0.65676300	0.03300400	-1.44397200
H	1.21203500	0.32772400	1.19794100
N	0.37461400	0.84927400	1.45193900
P	-0.48411700	1.65075400	0.30813800
N	-1.85873700	1.72977900	1.24366700
C	-1.84124300	0.80505400	2.40424200
C	-0.31208600	0.62085800	2.74154600
C	-3.12574300	2.29508600	0.79661000
H	-2.93002200	3.10163400	0.08556100
H	-3.65774200	2.71996000	1.65605300
H	-3.77312100	1.55124000	0.31604000
H	-2.30934200	1.34501500	3.23882900
N	-0.28396000	0.98530500	-1.16393800
C	-0.10510100	1.96609000	-2.25975100
C	0.49029000	3.22465000	-1.53598000
N	-0.14929700	3.20478500	-0.19981500
C	-0.00538000	4.34670000	0.69001800
H	-0.29052400	5.26136200	0.15689100
H	1.01708900	4.47128600	1.07117100
H	-0.67962600	4.22758000	1.54207600
H	0.13538400	4.12608100	-2.05354200
H	3.98459600	-2.44834500	1.54297500
H	3.65880400	-4.03515800	-0.40888300
H	6.98326500	-1.09769400	-0.68151100
C	2.02115400	3.27760300	-1.44461500
H	2.46687700	3.35276100	-2.44135800
H	2.33842400	4.16120900	-0.87991500
H	2.42995200	2.39138500	-0.94746900
C	0.82628900	1.34551500	-3.30878000
H	1.02549900	2.05134100	-4.12350000
H	1.77603300	1.03523500	-2.86673200
H	0.34593800	0.45798000	-3.73269800
C	-1.45868300	2.30209500	-2.91404900
H	-1.31994700	2.94223500	-3.79360900
H	-1.95185400	1.37733300	-3.22906400
H	-2.11966800	2.82479500	-2.21422200
C	0.12712100	1.68058100	3.76935400
H	1.21401500	1.65637600	3.90071100
H	-0.15324800	2.68707500	3.44055900
H	-0.34232500	1.49622900	4.74315800
C	0.05050800	-0.77860200	3.25211800
H	1.12392100	-0.82135800	3.47001600
H	-0.48390200	-1.00721600	4.18022700
H	-0.17669500	-1.54679200	2.50930500
C	-2.63063800	-0.48082300	2.14873400
H	-2.69382100	-1.08006700	3.06297000
H	-3.65546500	-0.25397100	1.83897100
H	-2.17136500	-1.09092900	1.36643400

● **CP3** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -1833.56919717

Zero-point correction = 0.622977 (Hartree/Particle)

Thermal correction to Energy = 0.659812

Thermal correction to Enthalpy = 0.660757

Thermal correction to Gibbs Free Energy = 0.553070

Sum of electronic and zero-point Energies = -1832.946220

Sum of electronic and thermal Energies = -1832.909385

Sum of electronic and thermal Enthalpies = -1832.908441

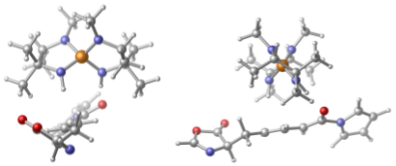
Sum of electronic and thermal Free Energies = -1833.016127

0 1

O	3.05482400	-0.10770800	0.50681900
C	3.93655700	-0.90464500	0.30313000
C	4.02779300	-2.41001400	0.48286100
O	5.15386300	-0.50210100	-0.23115600
N	5.41072800	-2.73665400	0.11110000
C	5.92875100	-1.64980100	-0.28205600
C	3.00162300	-3.18681400	-0.41393100
H	3.05588900	-2.77936300	-1.43102000
C	1.59071900	-3.18529000	0.08485100
H	1.40639100	-3.73608600	1.00968000
C	0.54773000	-2.63291500	-0.58647500
H	0.77116800	-2.08189900	-1.50194100
C	-0.84463400	-2.72124600	-0.26414800
H	-1.15085100	-3.35742300	0.56036000
C	-1.80660000	-2.08418600	-1.04009800
O	-1.61546900	-1.22317500	-1.95824000
N	-3.19934600	-2.40000800	-0.77988300
C	-4.24208600	-1.59585600	-1.19505700
C	-3.72625300	-3.48757900	-0.10585800
C	-5.42599500	-2.16048700	-0.77776500
C	-5.09737600	-3.36670600	-0.08651300
H	-4.02755800	-0.69977300	-1.75482800
H	-3.08539600	-4.27182100	0.26573500
H	-6.41641600	-1.76063800	-0.95487300
H	-5.78759100	-4.07308500	0.35750200
H	-0.79360300	0.12213300	-1.41659600
H	1.20553800	0.23967100	1.12799700
N	0.39283800	0.80080400	1.37490000
P	-0.36841100	1.75014700	0.27890200
N	-1.65912600	2.04838100	1.28509300
C	-1.73477100	1.11663800	2.43661700
C	-0.24077200	0.70206600	2.70772500
C	-2.82620700	2.84286400	0.92323000
H	-2.53470000	3.60621500	0.19797100
H	-3.21216100	3.34900400	1.81547900
H	-3.63123200	2.23769000	0.48843600

H	-2.08751100	1.70431400	3.29430200
N	-0.35943500	1.05463200	-1.19571500
C	-0.11359900	1.99020000	-2.31703300
C	0.70592000	3.15215400	-1.65098800
N	0.16895500	3.22711400	-0.27144500
C	0.52766600	4.34815700	0.58662000
H	0.34381100	5.28707400	0.05223500
H	1.57889200	4.32635000	0.90153200
H	-0.10141700	4.33732500	1.48030000
H	0.44494200	4.09357300	-2.15184500
H	3.85057300	-2.68282700	1.52888900
H	3.40983000	-4.20590700	-0.46377700
H	6.93259100	-1.49633900	-0.66117100
C	2.23109800	2.99231500	-1.66782400
H	2.61259700	3.00212800	-2.69340600
H	2.70360700	3.82570100	-1.13696300
H	2.54699200	2.06131000	-1.18535600
C	0.64529100	1.23880600	-3.41759800
H	0.87641400	1.90402800	-4.25712400
H	1.57574300	0.80684700	-3.04142600
H	0.02195700	0.42008000	-3.79055700
C	-1.44237100	2.52596300	-2.88232800
H	-1.26651400	3.15907900	-3.76006600
H	-2.08363300	1.69083700	-3.18149000
H	-1.97775300	3.12030000	-2.13442300
C	0.41213200	1.69318200	3.68899200
H	1.48764600	1.50100900	3.76375400
H	0.27240200	2.72709500	3.35616300
H	-0.02558100	1.59363500	4.68933500
C	-0.07739300	-0.73007900	3.23009700
H	0.98520800	-0.93973200	3.39769000
H	-0.59481400	-0.85624700	4.18696900
H	-0.46012400	-1.46337800	2.51624800
C	-2.71519100	-0.03439600	2.19565800
H	-2.83024300	-0.63811100	3.10138300
H	-3.70467400	0.35503400	1.93614300
H	-2.38448500	-0.69000800	1.38484100

● **TS3-3'**



B3LYP/6-31G*

E = -1833.55194453

Zero-point correction = 0.622609 (Hartree/Particle)

Thermal correction to Energy = 0.658571

Thermal correction to Enthalpy = 0.659515

Thermal correction to Gibbs Free Energy = 0.554281

Sum of electronic and zero-point Energies = -1832.929336

Sum of electronic and thermal Energies = -1832.893374

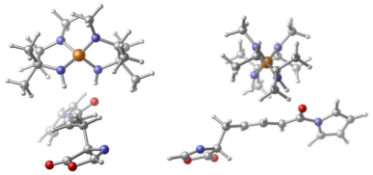
Sum of electronic and thermal Enthalpies = -1832.892429

Sum of electronic and thermal Free Energies = -1832.997664

0 1

O	-4.05640100	1.82747900	1.60290500
C	-4.61534200	1.73726100	0.54591300
C	-4.19753900	2.10472800	-0.87971200
O	-5.89820700	1.18872000	0.43636100
N	-5.34620000	1.72112500	-1.71053100
C	-6.20097600	1.23729200	-0.91035800
C	-2.89184800	1.40893800	-1.32026800
H	-3.01875600	0.32867500	-1.12967000
C	-1.66914200	1.98805800	-0.64049400
H	-1.84267300	2.58554800	0.25295000
C	-0.40160300	1.84495100	-1.11635200
H	-0.26238100	1.22111700	-2.00236300
C	0.80412500	2.40547200	-0.58871200
H	0.73800100	3.19114400	0.15697400
C	2.05018500	1.98135200	-1.04559100
O	2.28790600	0.96488000	-1.77690600
N	3.21385200	2.72298100	-0.63329800
C	4.49728300	2.21388000	-0.70365000
C	3.27714300	4.00385900	-0.11010900
C	5.36891900	3.15858400	-0.21749500
C	4.59274100	4.29859000	0.15756400
H	4.64989100	1.22448400	-1.10325800
H	2.38720900	4.60578400	-0.01407200
H	6.44355800	3.05150900	-0.14505000
H	4.96089700	5.23319600	0.56118900
H	1.50527600	-0.33499100	-1.26716600
H	-0.86244500	0.11991500	0.48196300
N	-0.54209000	-0.66429300	1.06256100
P	0.49969800	-1.75958500	0.40503500
N	1.35275800	-1.97876300	1.81851900
C	1.14133400	-0.87742000	2.78837200
C	-0.33637400	-0.41606600	2.51890700
C	2.49010700	-2.87420800	1.97643700
H	2.40126300	-3.70062200	1.26743600
H	2.49251900	-3.29091000	2.99073300
H	3.45019100	-2.37143000	1.80447600
H	1.19011500	-1.32263700	3.79107600
N	1.04402400	-1.26950500	-1.04581100
C	1.11694100	-2.33418100	-2.07254800
C	0.04626100	-3.38087900	-1.59879200
N	0.07279500	-3.28322400	-0.12111700
C	-0.60546400	-4.28667600	0.68514400
H	-0.28100000	-5.28677100	0.37362100
H	-1.69912600	-4.23546900	0.60299800
H	-0.33385800	-4.15316800	1.73517300
H	0.39906600	-4.38659600	-1.86379000
H	-4.05350800	3.19116600	-0.94441400
H	-2.83544700	1.51526100	-2.41055300
H	-7.17886500	0.84217500	-1.16376900
C	-1.36712900	-3.19249300	-2.16330500
H	-1.38041600	-3.34268800	-3.24705600
H	-2.05519800	-3.92212600	-1.72315300
H	-1.75277000	-2.19012100	-1.94873100
C	0.82425500	-1.70974900	-3.44282200
H	0.85805600	-2.46920700	-4.23237300
H	-0.15348100	-1.22258900	-3.46448900
H	1.57829500	-0.94763500	-3.66062700
C	2.51962700	-2.97085300	-2.09177100
H	2.60478000	-3.70762300	-2.89956700
H	3.27528800	-2.19506400	-2.25009100
H	2.73929700	-3.47596400	-1.14495200
C	-1.31679800	-1.28347500	3.32761700
H	-2.34630400	-1.05581200	3.03493500
H	-1.13815100	-2.35088700	3.15800000
H	-1.21149000	-1.08660400	4.40105500
C	-0.58869000	1.06336200	2.82378000
H	-1.63498600	1.31361100	2.62222900
H	-0.39045900	1.26968700	3.88132200
H	0.04318600	1.71391800	2.21409400
C	2.21352000	0.21094800	2.67288100
H	2.10192200	0.95477600	3.46783000
H	3.21348300	-0.22422900	2.77225500
H	2.16198600	0.73042600	1.71034700

● **CP3'**



B3LYP/6-31G*

E = -1833.55405658

Zero-point correction = 0.622710 (Hartree/Particle)

Thermal correction to Energy = 0.659560

Thermal correction to Enthalpy = 0.660504

Thermal correction to Gibbs Free Energy = 0.551446

Sum of electronic and zero-point Energies = -1832.931346

Sum of electronic and thermal Energies = -1832.894496

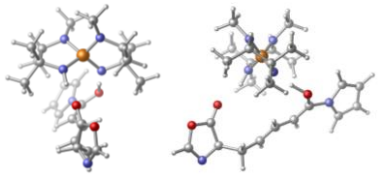
Sum of electronic and thermal Enthalpies = -1832.893552

Sum of electronic and thermal Free Energies = -1833.002611

0 1

O	-5.36293500	1.63117400	1.38327500
C	-5.57048100	0.79619600	0.55095700
C	-4.74304100	0.27991100	-0.62479900
O	-6.75347900	0.03688600	0.54227500
N	-5.57976200	-0.75738000	-1.24269800
C	-6.62982100	-0.81417900	-0.53388300
C	-3.35214900	-0.27240400	-0.18968900
H	-3.53365900	-1.03563000	0.58230600
C	-2.39264200	0.78954500	0.26950400
H	-2.65105500	1.31920800	1.18579900
C	-1.33806900	1.21302400	-0.48548900
H	-1.13421100	0.66302500	-1.40705000
C	-0.43873500	2.29169900	-0.22585600
H	-0.67965600	3.00051900	0.55937800
C	0.70713700	2.47151800	-0.99941000
O	1.19746400	1.65268000	-1.84362300
N	1.45884400	3.68724900	-0.82526800
C	2.76961700	3.83093800	-1.24214800
C	1.05241100	4.87346300	-0.23644500
C	3.19724100	5.09381600	-0.90971000
C	2.10363300	5.75803000	-0.27280900
H	3.25645000	3.00981200	-1.74272200
H	0.04094000	4.99688400	0.11725000
H	4.17984500	5.50249900	-1.10722200
H	2.08664700	6.77412900	0.10012900
H	1.22259400	0.13141500	-1.37753400
H	-0.47879900	-0.49057300	0.98790000
N	0.33012500	-1.00043500	1.36092500
P	1.47411400	-1.55894800	0.31508800
N	2.72788600	-1.35230700	1.39292900
C	2.39017400	-0.40399300	2.48143200
C	0.84994200	-0.62176100	2.70476300
C	4.12340000	-1.66275100	1.11390700
H	4.17553500	-2.49017700	0.40231200
H	4.62085500	-1.97519200	2.03962100
H	4.67133300	-0.80937700	0.69501000
H	2.92203400	-0.74661400	3.37898100
N	1.29296300	-0.91158600	-1.16314900
C	1.49054600	-1.86090500	-2.28224100
C	1.15137200	-3.25769100	-1.64691000
N	1.58328600	-3.12830400	-0.23459600
C	1.64844000	-4.30655400	0.61718900
H	2.22292300	-5.09125600	0.11104100
H	0.65856500	-4.70868300	0.86977200
H	2.16449300	-4.05451600	1.54710600
H	1.79251900	-4.01820400	-2.11232700
H	-4.57598600	1.09261900	-1.34093700
H	-2.95235900	-0.79792900	-1.06571900
H	-7.47570000	-1.47767300	-0.68045700
C	-0.30901100	-3.70926600	-1.76388900
H	-0.58739500	-3.87121300	-2.80954800
H	-0.46010500	-4.65690400	-1.23591900
H	-0.99390200	-2.97018100	-1.33489300
C	0.56743400	-1.45299000	-3.43712300
H	0.67278600	-2.14202400	-4.28281300
H	-0.48096400	-1.43052500	-3.13034900
H	0.83475200	-0.44712700	-3.77500500
C	2.95355600	-1.83264000	-2.76353200
H	3.09080500	-2.47875600	-3.63886900
H	3.23297600	-0.81129600	-3.04040100
H	3.63555200	-2.17412300	-1.97740800
C	0.62335000	-1.78244400	3.68975000
H	-0.44026300	-2.03692000	3.73447100
H	1.17589000	-2.67702800	3.38296600
H	0.95492000	-1.50545000	4.69750500
C	0.11422100	0.62798900	3.19640900
H	-0.94593100	0.39887100	3.34755500
H	0.52329900	0.96058100	4.15644300
H	0.18449200	1.44690600	2.47636700
C	2.82719600	1.02961000	2.16198800
H	2.65542400	1.69023000	3.01726600
H	3.89859800	1.06074600	1.93780900
H	2.28793100	1.43860600	1.30165900

● **TS2a**



B3LYP/6-31G*

E = -1833.55280428

Zero-point correction = 0.619103 (Hartree/Particle)

Thermal correction to Energy = 0.655424

Thermal correction to Enthalpy = 0.656368

Thermal correction to Gibbs Free Energy = 0.549514

Sum of electronic and zero-point Energies = -1832.933702

Sum of electronic and thermal Energies = -1832.897380

Sum of electronic and thermal Enthalpies = -1832.896436

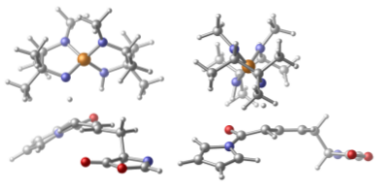
Sum of electronic and thermal Free Energies = -1833.003290

0 1

O	-3.12494000	0.21729500	0.83562100
C	-3.96823100	1.01544300	0.52388700
C	-3.98154200	2.53785100	0.47771800
O	-5.22196500	0.60599500	0.07773500
N	-5.34621100	2.87944500	0.05677300
C	-5.92791000	1.77429200	-0.14997000
C	-2.91916300	3.12878900	-0.49969400
H	-2.97149100	2.58536100	-1.45103900

C	-1.51732900	3.14007500	0.02960700
H	-1.34598400	3.74919800	0.91949300
C	-0.46987400	2.53409200	-0.57143100
H	-0.66208500	1.92579100	-1.45463900
C	0.91200500	2.66382700	-0.18562300
H	1.15681700	3.35036100	0.61887200
C	1.93407800	2.03911500	-0.84962800
O	1.81452100	1.08889700	-1.75433200
N	3.28538900	2.39756900	-0.59677200
C	4.36858900	1.57752300	-0.86983200
C	3.75429000	3.57253700	-0.02917200
C	5.51192900	2.22257700	-0.46665900
C	5.12191100	3.49066400	0.06500500
H	4.20570300	0.61824200	-1.33309300
H	3.07629200	4.37511800	0.21516200
H	6.51913300	1.83650500	-0.55265100
H	5.77432700	4.26216000	0.45264000
H	1.11039700	0.26166600	-1.46018300
H	-1.22159100	-0.35265500	1.18879300
N	-0.43310400	-0.96821200	1.36291500
P	0.33687300	-1.74875000	0.12977400
N	1.61316100	-2.19575100	1.13228600
C	1.69169600	-1.39858300	2.37360700
C	0.19522200	-1.03707300	2.69390300
C	2.78904100	-2.91323400	0.66750400
H	2.49801600	-3.60013300	-0.13135900
H	3.20574900	-3.50652200	1.49090900
H	3.57809300	-2.25169400	0.28456800
H	2.06156500	-2.06669000	3.16423100
N	0.36940000	-0.88673900	-1.22333900
C	0.08057700	-1.72627500	-2.41172800
C	-0.77689000	-2.93719600	-1.88313800
N	-0.22737900	-3.18535200	-0.53471500
C	-0.64812400	-4.35031500	0.22343200
H	-0.54930400	-5.24855300	-0.39850300
H	-1.68683900	-4.28943600	0.57856600
H	0.00516500	-4.46795000	1.09221200
H	-0.56263900	-3.82215500	-2.49933400
H	-3.79678900	2.94265700	1.47995300
H	-3.27112600	4.14975100	-0.70318100
H	-6.94562900	1.62310300	-0.49217900
C	-2.29562400	-2.71559600	-1.85755100
H	-2.69135000	-2.58535900	-2.86977500
H	-2.80168200	-3.58265300	-1.41850700
H	-2.56185700	-1.83476600	-1.26308200
C	-0.65728600	-0.86490700	-3.44627800
H	-0.92689600	-1.45009400	-4.33404300
H	-1.56591900	-0.42511000	-3.02647200
H	-0.00479800	-0.04534100	-3.76496100
C	1.38749500	-2.25028900	-3.04271400
H	1.19077900	-2.78393600	-3.98139200
H	2.05856100	-1.41193400	-3.25540900
H	1.90366600	-2.93743100	-2.36355300
C	-0.44526400	-2.15426000	3.54087300
H	-1.52551100	-1.99432300	3.62469600
H	-0.28063500	-3.13489800	3.08296000
H	-0.01966400	-2.17248600	4.55179000
C	0.01707100	0.31025400	3.40514600
H	-1.04842300	0.48825700	3.59123700
H	0.52798900	0.31276600	4.37418600
H	0.39783600	1.13721400	2.80104200
C	2.64998700	-0.20767300	2.25567100
H	2.77219900	0.29404500	3.22132100
H	3.64205000	-0.54212000	1.93592500
H	2.29315900	0.52773000	1.52837800

● **TS2b**



B3LYP/6-31G*

E = -1833.54165313

Zero-point correction = 0.618736 (Hartree/Particle)

Thermal correction to Energy = 0.655025

Thermal correction to Enthalpy = 0.655970

Thermal correction to Gibbs Free Energy = 0.548880

Sum of electronic and zero-point Energies = -1832.922917

Sum of electronic and thermal Energies = -1832.886628

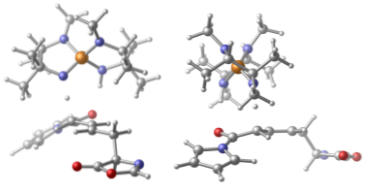
Sum of electronic and thermal Enthalpies = -1832.885684

Sum of electronic and thermal Free Energies = -1832.992773

0 1

O	-5.35777800	1.24804300	1.95627800
C	-5.78139400	0.56141600	1.07192200
O	-7.02296600	-0.08661700	1.16435800
C	-5.21035400	0.16329700	-0.28940200
C	-7.16207600	-0.77569800	-0.02136100
N	-6.23735700	-0.70085800	-0.88555500
C	-3.83535800	-0.55225700	-0.19322900
H	-3.95668000	-1.41596500	0.47711700
C	-2.71891000	0.34760900	0.26005900
H	-2.80153400	0.75464100	1.26691800
C	-1.68027700	0.69515700	-0.52001800
H	-1.62011700	0.28199900	-1.52786500
C	-0.57291300	1.59106100	-0.14329900
H	-0.83000100	2.32066700	0.62377900
C	0.26694700	2.06117300	-1.22336300
O	0.59188800	1.37309100	-2.20740700
N	0.87555300	3.34526200	-1.10714100
C	1.93625900	3.74886800	-1.90895800
C	0.54601900	4.39497800	-0.25397100
C	2.28007500	5.02756000	-1.55910100
C	1.39497200	5.43948800	-0.51060400
H	2.32489900	3.07055200	-2.65102000
H	-0.28099900	4.31709800	0.43296100
H	3.07370200	5.61328400	-2.00398300
H	1.38071000	6.40003100	-0.01239900
H	1.19996200	-0.30903800	-1.72755300
N	1.51383100	-1.19867300	-1.31720200
P	1.87489000	-1.28073000	0.29150700
N	1.51159600	-2.91993100	0.37692500
C	0.65308900	-3.37219400	-0.73620800
C	1.10362200	-2.47568300	-1.94467000
C	1.58232800	-3.71655500	1.59131400
H	1.78541200	-4.76281800	1.33174500
H	2.40499900	-3.35612400	2.21374400
H	0.65909900	-3.68114800	2.18571500
H	0.92509000	-4.41391900	-0.95573500
N	1.21785400	-0.04950800	1.10647500
C	2.13970800	0.45865700	2.15517900
C	3.59267300	0.11992400	1.64778100
N	3.41886800	-1.15947500	0.92869700
C	4.57724500	-1.93823000	0.52650400
H	4.24681800	-2.91367700	0.16025500
H	5.23442000	-2.10263300	1.38976600
H	5.16466900	-1.45448900	-0.26614300
H	4.23683700	-0.07494000	2.51702700
H	0.35163800	0.74988100	0.52665000
C	1.91549200	1.96181400	2.36465400
H	2.62044100	2.35455300	3.10667800
H	2.02954700	2.53571000	1.44270000
H	0.90348900	2.13413000	2.74603300
C	1.87511600	-0.26485900	3.49171800
H	2.48887500	0.15644100	4.29798900
H	0.82111200	-0.15905400	3.76713900
H	2.10021000	-1.33396100	3.41868400
C	4.25652800	1.19093900	0.77356400
H	4.46636800	2.09687100	1.35054900
H	5.21102100	0.82624800	0.37830600
H	3.62165400	1.46667900	-0.07529300
C	-0.83761000	-3.32212700	-0.37791000
H	-1.45418900	-3.71672300	-1.19186700
H	-1.03253400	-3.93911100	0.50612400
H	-1.16254400	-2.30038900	-0.15311600
C	-0.00247200	-2.20785100	-2.97107100
H	-0.33402500	-3.14360200	-3.43472300
H	-0.86729300	-1.71449300	-2.52249100
H	0.37930700	-1.55698700	-3.76475600
C	2.30825100	-3.12468600	-2.65342900
H	2.72406500	-2.43543500	-3.39532200
H	3.09868500	-3.37215200	-1.93732600
H	2.01000100	-4.04712400	-3.16647500
H	-8.08580400	-1.33803600	-0.10748900
H	-5.08740200	1.06241800	-0.90520200
H	-3.62659800	-0.95309900	-1.19157400

● **TS2b** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -1833.54949180

Zero-point correction = 0.618360 (Hartree/Particle)

Thermal correction to Energy = 0.654713

Thermal correction to Enthalpy = 0.655657

Thermal correction to Gibbs Free Energy = 0.548461

Sum of electronic and zero-point Energies = -1832.931132

Sum of electronic and thermal Energies = -1832.894778

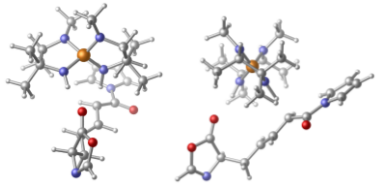
Sum of electronic and thermal Enthalpies = -1832.893834

Sum of electronic and thermal Free Energies = -1833.001030

0 1

O	-5.37565700	1.25904800	1.91677800
C	-5.78925500	0.53460900	1.05533600
O	-7.01462700	-0.12997500	1.17627500
C	-5.21635800	0.10622500	-0.29435600
C	-7.15292900	-0.85818100	0.01173800
N	-6.23331800	-0.79115300	-0.85869900
C	-3.83071300	-0.58730800	-0.18408500
H	-3.94000200	-1.44035900	0.50112100
C	-2.72711000	0.33493700	0.25574900
H	-2.81466900	0.75544600	1.25669300
C	-1.68709200	0.67774700	-0.52390600
H	-1.61835400	0.24939600	-1.52462200
C	-0.58499100	1.58306100	-0.14808400
H	-0.84761700	2.30636600	0.62322700
C	0.23901500	2.07541500	-1.23239300
O	0.56509600	1.40203900	-2.22542900
N	0.82760100	3.36869600	-1.10862500
C	1.88297500	3.79466700	-1.90632600
C	0.47435000	4.41029900	-0.25462600
C	2.19969300	5.07999200	-1.55389300
C	1.30249800	5.47265500	-0.50759500
H	2.29312400	3.12521100	-2.64490600
H	-0.35181100	4.31447200	0.43113100
H	2.98448700	5.68127500	-1.99395300
H	1.26745800	6.43186900	-0.00767200
H	1.20686900	-0.31162300	-1.72818600
N	1.53568100	-1.19322700	-1.31937500
P	1.89316300	-1.27210500	0.29341800
N	1.54505700	-2.91230200	0.37633500
C	0.70174000	-3.37848000	-0.74235300
C	1.14687900	-2.47739900	-1.94893500
C	1.63462800	-3.71683700	1.58533200
H	1.86673300	-4.75477500	1.31809400
H	2.44498300	-3.33918900	2.21337300
H	0.70846900	-3.71049800	2.17560600
H	0.99021800	-4.41599200	-0.95852000
N	1.21790100	-0.04504100	1.10163400
C	2.13135100	0.47180500	2.15449000
C	3.59038600	0.14597800	1.65616400
N	3.43249200	-1.13230700	0.93266900
C	4.60051100	-1.90933800	0.55240500
H	4.27986900	-2.88514900	0.17917100
H	5.24096900	-2.07228400	1.42803500
H	5.20097100	-1.42264200	-0.22816800
H	4.23043700	-0.04504600	2.52887100
H	0.33800000	0.76212400	0.50525700
C	1.89317700	1.97316400	2.36165300
H	2.59089200	2.37296600	3.10656700
H	2.00866900	2.54573900	1.43888800
H	0.87736300	2.13784400	2.73657600
C	1.86770000	-0.25177300	3.49134100
H	2.47751600	0.17440500	4.29799600
H	0.81246900	-0.15188700	3.76526700
H	2.09947200	-1.31951200	3.41972200
C	4.25238100	1.22342300	0.78845100
H	4.45295300	2.12944300	1.36871800
H	5.21101400	0.86467000	0.39825800
H	3.62033400	1.49514400	-0.06401100
C	-0.79181000	-3.35073000	-0.39402200
H	-1.39649600	-3.75974500	-1.20973200
H	-0.98133600	-3.96517500	0.49272200
H	-1.13428900	-2.33297000	-0.17731100
C	0.04324600	-2.22838000	-2.98240700
H	-0.27457500	-3.17108000	-3.44106600
H	-0.83075000	-1.74396400	-2.54122100
H	0.42186500	-1.57965500	-3.77953300
C	2.36496800	-3.10992500	-2.64905300
H	2.77416300	-2.41740300	-3.39176400
H	3.15501000	-3.34313900	-1.92785300
H	2.08270100	-4.03843400	-3.15977900
H	-8.06796500	-1.43692600	-0.04958000
H	-5.11144800	0.98907800	-0.93623300
H	-3.61298600	-1.00174800	-1.17476700

● **TS2c**



B3LYP/6-31G*

E = -1833.53881929

Zero-point correction = 0.618072 (Hartree/Particle)

Thermal correction to Energy = 0.654657

Thermal correction to Enthalpy = 0.655601

Thermal correction to Gibbs Free Energy = 0.548045

Sum of electronic and zero-point Energies = -1832.920747

Sum of electronic and thermal Energies = -1832.884163

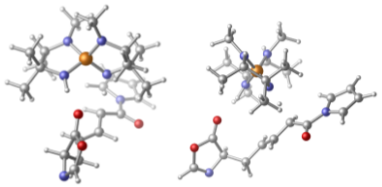
Sum of electronic and thermal Enthalpies = -1832.883219

Sum of electronic and thermal Free Energies = -1832.990774

0 1

O	-3.18469500	0.15983600	0.34636200
C	-4.03464500	-0.66863500	0.14564600
C	-4.22685400	-1.69543800	-0.96219800
O	-5.11591300	-0.82259500	1.00461000
N	-5.54306200	-2.28508300	-0.69015700
C	-5.92585300	-1.77251700	0.40284700
C	-3.12531100	-2.79983800	-0.99772500
C	-1.74040700	-2.29401200	-1.27109100
H	-3.15007700	-3.34242800	-0.04506500
H	-1.60050000	-1.72464600	-2.19279100
C	-0.68533500	-2.54560900	-0.47350500
H	-0.84377400	-3.14032000	0.42685900
C	0.68415200	-2.06372700	-0.65490100
H	0.89804900	-1.67220700	-1.65018900
C	1.74282100	-2.83594200	-0.03143700
O	1.60368200	-3.58812500	0.93343900
N	3.08922500	-2.58825600	-0.48546100
C	4.19601600	-3.07206400	0.19414700
C	3.53330000	-1.86374000	-1.58382300
C	5.32666200	-2.65580500	-0.46114500
C	4.90551300	-1.88904500	-1.59355000
H	4.04795300	-3.67042900	1.07857500
H	2.84150900	-1.41288200	-2.27619900
H	6.34502100	-2.87714700	-0.16963600
H	5.54062800	-1.42118600	-2.33506000
H	-1.63307100	1.11485900	-0.52968900
N	-0.81947700	1.70006300	-0.70499600
P	0.48352900	1.66828600	0.30944500
N	1.41854500	2.57393600	-0.75702400
C	0.87252400	2.59616800	-2.12921300
C	-0.68451300	2.51170900	-1.92633400
C	2.84181200	2.80934900	-0.54931200
H	3.02418500	2.98084300	0.51452900
H	3.47090000	1.97020000	-0.87516300
H	3.14539500	3.70983700	-1.09622200
H	1.11208900	3.57761200	-2.56133700
N	0.75865800	0.19363900	0.87919800
C	1.05932500	0.18957100	2.33515700
C	0.42187100	1.52125400	2.89122300
N	0.55863100	2.47860800	1.77089400
H	0.73839000	-0.87921000	0.16095100
C	0.28729900	3.89108300	1.97537900
H	0.63345400	4.45364500	1.10416000
H	-0.77836500	4.11154600	2.12975300
H	0.84225000	4.24718900	2.85180500
H	1.04589800	1.89092400	3.71661100
C	0.45839900	-1.07089800	2.97247400
H	0.60800900	-1.06164600	4.05905900
H	-0.61266400	-1.14850900	2.76749700
H	0.94222100	-1.96585800	2.56944200
C	2.58150600	0.20446400	2.57511500
H	2.81037400	0.12417300	3.64525900
H	3.05369700	-0.63748300	2.05976700
H	3.03147500	1.13047200	2.19999500
C	-1.02873000	1.41707700	3.38163800
H	-1.10150600	0.76341700	4.25616300
H	-1.40158300	2.40330500	3.68096900
H	-1.69257100	1.02675600	2.60259600
C	1.48306700	1.51113000	-3.02521300
H	1.11895500	1.59517700	-4.05406200
H	2.57282900	1.61107300	-3.05436100
H	1.24768300	0.50933300	-2.65182700
C	-1.42781100	1.82762200	-3.08024200
H	-1.28915100	2.37776100	-4.01738700
H	-1.09414900	0.79713000	-3.22579600
H	-2.50277500	1.80969800	-2.86581900
C	-1.26424000	3.92474100	-1.71494200
H	-1.20716000	4.51378600	-2.63836400
H	-2.31491600	3.86174800	-1.41220000
H	-0.71650800	4.45999000	-0.93325100
H	-4.24054100	-1.18489800	-1.93276000
H	-3.46895200	-3.50471400	-1.76803100
H	-6.84129400	-1.98586800	0.94307900

● **TS2c** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -1833.54810853

Zero-point correction = 0.617727 (Hartree/Particle)

Thermal correction to Energy = 0.654357

Thermal correction to Enthalpy = 0.655301

Thermal correction to Gibbs Free Energy = 0.547412

Sum of electronic and zero-point Energies = -1832.930382

Sum of electronic and thermal Energies = -1832.893752

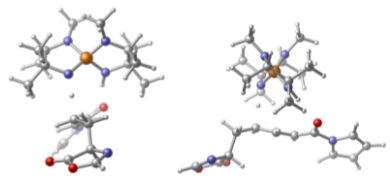
Sum of electronic and thermal Enthalpies = -1832.892808

Sum of electronic and thermal Free Energies = -1833.000697

0 1

O	-3.18822000	0.01540700	0.51881800
C	-4.01411100	-0.82576000	0.27084000
C	-4.15688000	-1.81665400	-0.87569800
O	-5.10601200	-1.03533100	1.10100500
N	-5.45568700	-2.46021100	-0.64072200
C	-5.87602900	-1.99262900	0.45915000
C	-3.01773500	-2.87799100	-0.93730200
C	-1.65261300	-2.32037000	-1.21657000
H	-3.01422500	-3.43948600	0.00446700
H	-1.54078900	-1.73876900	-2.13397500
C	-0.58190800	-2.54757500	-0.43421300
H	-0.71508700	-3.15248300	0.46322000
C	0.77887600	-2.03700800	-0.63471900
H	0.96714300	-1.64115300	-1.63415600
C	1.85252900	-2.83357100	-0.06855700
O	1.73018600	-3.66590500	0.83276600
N	3.19121000	-2.54113900	-0.51469700
C	4.30367400	-3.18204000	0.00958100
C	3.62097200	-1.63484200	-1.47596000
C	5.42302800	-2.69016700	-0.61161800
C	4.98905500	-1.70500400	-1.55596000
H	4.16936800	-3.92929900	0.77477800
H	2.92329000	-1.01320400	-2.01266400
H	6.44200000	-2.99904400	-0.41762800
H	5.61377800	-1.11815100	-2.21733700
H	-1.67588400	0.95229800	-0.44478900
N	-0.89442000	1.55261800	-0.69788400
P	0.42983200	1.69477400	0.27919500
N	1.20746200	2.70149900	-0.81727200
C	0.59291900	2.69646900	-2.16004300
C	-0.93011100	2.41862500	-1.88889500
C	2.57183000	3.18181000	-0.65291000
H	2.79151800	3.28336900	0.41265800
H	3.32024200	2.51156500	-1.09586000
H	2.67201400	4.17041900	-1.11697800
H	0.69250300	3.71052800	-2.57038200
N	0.87939600	0.25670200	0.84110000
C	1.25046900	0.29760700	2.27831200
C	0.51059000	1.56071800	2.86700500
N	0.47797200	2.51375600	1.73727000
H	0.84809900	-0.85608000	0.14892400
C	0.09998000	3.89950600	1.96087000
H	0.31199400	4.48147600	1.06043000
H	-0.96300300	4.02232500	2.21087200
H	0.69617000	4.31491600	2.78235800
H	1.13981400	2.00159400	3.65237800
C	0.81552900	-1.01040800	2.95437400
H	1.02586800	-0.97582400	4.03004800
H	-0.25240100	-1.19798800	2.81383400
H	1.36053100	-1.85886500	2.53058200
C	2.77413400	0.46747200	2.43854500
H	3.06649400	0.42753800	3.49540700
H	3.29932800	-0.33196000	1.90633700
H	3.10900700	1.42628700	2.02775600
C	-0.88916500	1.31198800	3.44485200
H	-0.84252300	0.66090200	4.32307500
H	-1.34068200	2.25837700	3.76267300
H	-1.55465400	0.85166900	2.70635200
C	1.28439400	1.71730600	-3.11732600
H	0.87383800	1.79486500	-4.12895100
H	2.35425900	1.94103300	-3.17977100
H	1.17321100	0.68272100	-2.77600400
C	-1.64203300	1.68630600	-3.03300200
H	-1.61991400	2.28180000	-3.95210100
H	-1.19083300	0.71179400	-3.23535100
H	-2.69416700	1.52674600	-2.76932500
C	-1.66597000	3.74092100	-1.59563800
H	-1.72965700	4.36143000	-2.49753700
H	-2.68425200	3.53852000	-1.24637800
H	-1.14793800	4.31465700	-0.82117900
H	-4.17938400	-1.27036900	-1.82642400
H	-3.33749400	-3.57988900	-1.72024900
H	-6.79276900	-2.25007800	0.97697000

● **TS2d**



B3LYP/6-31G*

E = -1833.53727038

Zero-point correction = 0.619093 (Hartree/Particle)

Thermal correction to Energy = 0.655218

Thermal correction to Enthalpy = 0.656162

Thermal correction to Gibbs Free Energy = 0.550008

Sum of electronic and zero-point Energies = -1832.918178

Sum of electronic and thermal Energies = -1832.882053

Sum of electronic and thermal Enthalpies = -1832.881109

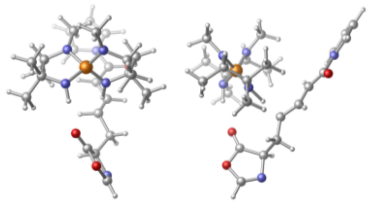
Sum of electronic and thermal Free Energies = -1832.987263

0 1

O	4.97474500	-0.99309800	1.47745800
C	5.15103500	-0.35875400	0.47724700
O	6.34101500	0.35156000	0.24992300
C	4.27185800	-0.08931700	-0.74277600
C	6.17797500	0.94737200	-0.98209700
N	5.09377900	0.76191200	-1.61310000
C	2.91920100	0.58362300	-0.37694300
H	3.13670600	1.48997800	0.20398700
C	1.94489500	-0.31453900	0.36174900
H	2.31994600	-0.69022400	1.31701200
C	1.13413900	-1.21216000	-0.38041100
H	0.87852300	-0.89432700	-1.39307400
C	0.47878900	-2.34268200	0.06250400
H	0.75507900	-2.80905700	1.00256500
C	-0.62704100	-2.85880000	-0.69427100
O	-1.25156900	-2.22189700	-1.56599100
N	-1.07240200	-4.17636000	-0.40249300
C	-2.27291700	-4.69690500	-0.86601000
C	-0.42377600	-5.15629700	0.34295600
C	-2.38780100	-5.98358600	-0.41158700
C	-1.21120500	-6.27688300	0.35327300
H	-2.91740500	-4.08148300	-1.47247300
H	0.55313100	-4.97676500	0.76258700
H	-3.21888100	-6.64985900	-0.60174000
H	-0.97270300	-7.21103100	0.84467900
H	-1.35476700	-0.37589600	-1.11746300
N	-1.43611100	0.64960400	-1.10949800
P	-1.40316700	1.59603100	0.23913100
N	-1.71039300	2.99248000	-0.64725200
C	-1.48001100	2.82401600	-2.09544500
C	-1.83300400	1.31992800	-2.36537100
C	-1.72016900	4.33000200	-0.07694600
H	-2.36538700	4.97778100	-0.68270900
H	-2.13530400	4.29015000	0.93321300
H	-0.72332300	4.78883900	-0.02244200
H	-2.21450300	3.45155400	-2.61919400
N	-0.12258900	1.28651500	1.17919100
C	-0.47825700	1.32058900	2.62267300
C	-2.01828300	0.99851100	2.69339600
N	-2.55513400	1.59985100	1.45646300
C	-3.98774000	1.77478300	1.28901600

H	-4.17588100	2.39661300	0.41009600
H	-4.40262500	2.28931900	2.16488300
H	-4.52548200	0.82512500	1.16190300
H	-2.45559600	1.54396000	3.54169700
H	0.86983200	0.54705700	0.76986300
C	0.37606400	0.30593000	3.39411600
H	0.07599900	0.27463000	4.44796600
H	0.29160900	-0.70053400	2.97782000
H	1.43015000	0.59867500	3.35714400
C	-0.21775800	2.72557300	3.20260500
H	-0.38936700	2.74480500	4.28628400
H	0.81905700	3.02017500	3.01170000
H	-0.87289000	3.47269100	2.74249800
C	-2.38505000	-0.48566000	2.82129800
H	-2.06829400	-0.88985400	3.78788100
H	-3.47020000	-0.61932100	2.75196700
H	-1.91828100	-1.08201800	2.03014000
C	-0.07412300	3.26982200	-2.51831600
H	0.05204100	3.20932500	-3.60372400
H	0.09527100	4.31204200	-2.22743300
H	0.70060100	2.65867700	-2.04357500
C	-1.06107000	0.69493400	-3.53481500
H	-1.31552300	1.19167700	-4.47809200
H	0.01988500	0.75844000	-3.38744600
H	-1.32362300	-0.36383100	-3.62238800
C	-3.34565000	1.16233900	-2.61444300
H	-3.61248500	0.10061000	-2.63393700
H	-3.92783600	1.64848700	-1.82508800
H	-3.63288800	1.60666100	-3.57510400
H	7.02556700	1.54043700	-1.30903300
H	4.05836600	-1.03608400	-1.25358400
H	2.48480500	0.92054400	-1.32706900

● **TS2e**



B3LYP/6-31G*

E = -1833.52740538

Zero-point correction = 0.618354 (Hartree/Particle)

Thermal correction to Energy = 0.654916

Thermal correction to Enthalpy = 0.655861

Thermal correction to Gibbs Free Energy = 0.548055

Sum of electronic and zero-point Energies = -1832.909051

Sum of electronic and thermal Energies = -1832.872489

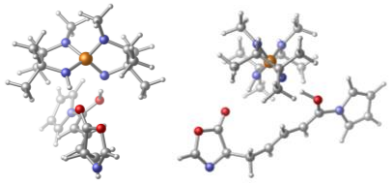
Sum of electronic and thermal Enthalpies = -1832.871545

Sum of electronic and thermal Free Energies = -1832.979351

0 1

O	3.20925800	0.76863300	-1.29824000
C	3.46434000	1.91328400	-1.03192500
C	2.62085100	3.18594100	-1.05201200
O	4.73945600	2.29959400	-0.63766800
N	3.57587000	4.25688400	-0.73430400
C	4.67879900	3.67915500	-0.50918400
C	1.43106100	3.19004700	-0.06537500
C	0.34868900	2.16294300	-0.40128000
H	1.83735400	3.04502300	0.94687500
H	0.40487300	1.77534500	-1.42493200
C	-0.96683300	2.38642600	0.08497700
H	-1.06442900	2.97313500	1.00212700
C	-2.13851400	1.82521100	-0.36880700
H	-2.14470500	1.26632000	-1.29780900
C	-3.34011300	1.92102800	0.41886600
O	-3.42662600	2.39924500	1.55090200
N	-4.53790400	1.36714900	-0.16319800
C	-5.70185100	1.19171500	0.56402300
C	-4.75692300	0.91514800	-1.45893000
C	-6.64723200	0.62790000	-0.25500800
C	-6.04793100	0.45592700	-1.54296700
H	-5.72264600	1.48853100	1.60030700
H	-3.99902200	1.00889300	-2.22008700
H	-7.65799500	0.36706400	0.03025400
H	-6.51847900	0.05374500	-2.43113600
H	2.42701100	-1.05095700	-0.99165300
N	1.76634800	-1.81526500	-0.87387900
P	0.65409200	-1.64806900	0.34756900
N	-0.57351100	-2.36241800	-0.54095100
C	-0.30596000	-2.38470600	-1.99338700
C	1.26044200	-2.49292700	-2.09353400
C	-1.94267000	-2.52662700	-0.06221800
H	-1.92702100	-2.72945600	1.01118600
H	-2.56585700	-1.64118400	-0.23796200
H	-2.40209400	-3.38594200	-0.56446200
H	-0.74159700	-3.31287800	-2.38798100
N	0.73618200	-0.17367100	1.00103200
C	0.58692600	-0.21444400	2.48168100
C	1.14327000	-1.62757400	2.89369100
N	0.73277100	-2.50586700	1.77733100
H	0.58705400	0.89564700	0.36942500
C	0.82354700	-3.95032500	1.90681600
H	0.32099500	-4.42107800	1.05807100
H	1.85947100	-4.31525800	1.94057400
H	0.31475000	-4.27137500	2.82398200
H	0.61059800	-1.96625400	3.79268800
C	1.38372700	0.94287900	3.09830200
H	1.38425200	0.87651200	4.19251400
H	2.41919000	0.95431500	2.74703200
H	0.91962600	1.89645200	2.82796700
C	-0.88921300	-0.09669500	2.91365500
H	-0.96712300	-0.06053000	4.00763500
H	-1.35506500	0.80601000	2.50902100
H	-1.47049100	-0.95668800	2.56531600
C	2.65296400	-1.69998000	3.15649400
H	2.92874500	-1.11648300	4.04040400
H	2.96186400	-2.73503600	3.33917100
H	3.22273100	-1.32227600	2.30076600
C	-0.94463800	-1.20246700	-2.73069700
H	-0.80541000	-1.29186000	-3.81293500
H	-2.02198700	-1.17195100	-2.53794300
H	-0.51926500	-0.24910200	-2.40185000
C	1.85582000	-1.81244400	-3.33103400
H	1.46786700	-2.26732800	-4.24857700
H	1.64022900	-0.74125300	-3.35173300
H	2.94433600	-1.93642200	-3.33264600
C	1.67907200	-3.97429700	-2.07014800
H	1.35687700	-4.48541600	-2.98533700
H	2.76758500	-4.05817600	-1.99041500
H	1.23422800	-4.49396200	-1.21530700
H	2.23200900	3.33383400	-2.06784100
H	1.05281900	4.22073700	-0.08940500
H	5.61658600	4.14215300	-0.22299000

● **CP4a**



B3LYP/6-31G*

E = -1833.55295093

Zero-point correction = 0.621419 (Hartree/Particle)

Thermal correction to Energy = 0.658263

Thermal correction to Enthalpy = 0.659207

Thermal correction to Gibbs Free Energy = 0.551043

Sum of electronic and zero-point Energies = -1832.931532

Sum of electronic and thermal Energies = -1832.894688

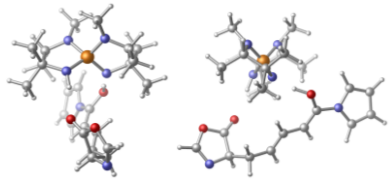
Sum of electronic and thermal Enthalpies = -1832.893744

Sum of electronic and thermal Free Energies = -1833.001908

0 1

O	3.09793400	-0.37314800	0.95733700
C	3.91479200	-1.18284100	0.60977800
C	3.87347800	-2.70080500	0.48231300
O	5.18826800	-0.79733500	0.19769500
N	5.22586400	-3.06945200	0.04463400
C	5.85037000	-1.97646800	-0.09421300
C	2.79219000	-3.20325300	-0.52071500
H	2.85929500	-2.61350000	-1.44301100
C	1.39183000	-3.19830900	0.01380400
H	1.20885300	-3.83539500	0.88151400
C	0.35758300	-2.54547500	-0.55806600
H	0.55912500	-1.90799300	-1.41771200
C	-1.02367800	-2.66327500	-0.16027100
H	-1.26717300	-3.36113800	0.63483000
C	-2.04969600	-2.01895200	-0.79101300
O	-1.94117200	-1.04873800	-1.68975100
N	-3.39807900	-2.36695100	-0.53512000
C	-4.47709200	-1.52463700	-0.75693200
C	-3.87103000	-3.56159400	-0.01260100
C	-5.62035000	-2.17634300	-0.36607900
C	-5.23586900	-3.47031300	0.10416900
H	-4.31184400	-0.54679900	-1.17865500
H	-3.19719500	-4.38012700	0.18611600
H	-6.62462000	-1.77729000	-0.42016700
H	-5.89087000	-4.25156900	0.46683000
H	-1.20744900	-0.31459600	-1.44280000
H	1.23316500	0.36589100	1.20538700
N	0.47916000	1.02850600	1.35470800
P	-0.25261700	1.79678900	0.08795100
N	-1.50764200	2.33997400	1.07621500
C	-1.63038800	1.57936500	2.33565900
C	-0.15378800	1.16272600	2.67787100
C	-2.65107000	3.08769500	0.58095700
H	-2.32814900	3.73571500	-0.23782000
H	-3.04898800	3.72380700	1.38154400
H	-3.46455600	2.44693800	0.21321100
H	-1.97913700	2.28071100	3.10693900
N	-0.32642100	0.89091000	-1.22942800
C	0.00254100	1.68155100	-2.44005900
C	0.91552200	2.87076700	-1.95329200
N	0.37918200	3.18852400	-0.61497200
C	0.84922500	4.35843800	0.10406200
H	0.77769200	5.24225800	-0.54226700
H	1.88850100	4.27070400	0.45268500
H	0.20900400	4.52471300	0.97467800
H	0.74308900	3.74318100	-2.59995100
H	3.67492200	-3.14876300	1.46362200
H	3.10797300	-4.22379900	-0.77855600
H	6.87537500	-1.84520800	-0.42267900
C	2.42260100	2.57931200	-1.91825800
H	2.81404900	2.40181700	-2.92505000
H	2.96890000	3.43294700	-1.50165200
H	2.64532000	1.70379300	-1.29840700
C	0.69949500	0.75637200	-3.44805700
H	0.99886600	1.29973600	-4.35291500
H	1.58497600	0.28468100	-3.01317900
H	0.00787300	-0.03934000	-3.74457000
C	-1.27664100	2.24765100	-3.09272300
H	-1.05350700	2.73987500	-4.04819600
H	-1.98824400	1.43695500	-3.27984900
H	-1.75972600	2.98153700	-2.43860500
C	0.52903200	2.27499000	3.49815100
H	1.60073600	2.07077000	3.59435800
H	0.41011600	3.24821700	3.01138300
H	0.09830200	2.34018400	4.50500300
C	-0.03804400	-0.16948300	3.42960200
H	1.01781500	-0.38819300	3.62670200
H	-0.55291200	-0.12209700	4.39556600
H	-0.45148300	-0.99737600	2.84855700
C	-2.63630300	0.42557100	2.23845900
H	-2.78451800	-0.04993500	3.21366400
H	-3.61196300	0.79339700	1.90486400
H	-2.30532400	-0.33948500	1.52952800

● **CP4a** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -1833.55947008

Zero-point correction = 0.620998 (Hartree/Particle)

Thermal correction to Energy = 0.657875

Thermal correction to Enthalpy = 0.658819

Thermal correction to Gibbs Free Energy = 0.550526

Sum of electronic and zero-point Energies = -1832.938472

Sum of electronic and thermal Energies = -1832.901595

Sum of electronic and thermal Enthalpies = -1832.900651

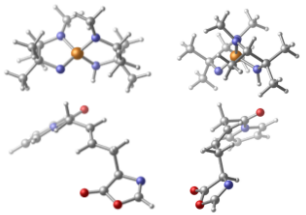
Sum of electronic and thermal Free Energies = -1833.008944

0 1

O	2.55248500	-1.09269500	1.56744800
C	3.43753100	-1.69675700	1.02314700
C	3.55151900	-3.14602900	0.57770100
O	4.63188000	-1.08427200	0.65375600
N	4.91738900	-3.26290100	0.05223800
C	5.40985000	-2.09689500	0.11713400
C	2.49717800	-3.52140700	-0.50819700
H	2.61053200	-2.83157900	-1.35317300

C	1.08034200	-3.52505300	-0.01978300
H	0.83158800	-4.25652700	0.75092100
C	0.12051800	-2.70689800	-0.50037200
H	0.40046300	-1.97798100	-1.25874700
C	-1.26986600	-2.73391800	-0.11783500
H	-1.58160400	-3.47288500	0.61356400
C	-2.22548500	-1.92576400	-0.66036400
O	-2.04090900	-0.89361000	-1.47700400
N	-3.60161000	-2.15074000	-0.39839500
C	-4.58768800	-1.18241800	-0.50481900
C	-4.19006400	-3.33595900	0.01591100
C	-5.78846200	-1.74735300	-0.14903900
C	-5.53618700	-3.11519000	0.17983700
H	-4.32824600	-0.18750200	-0.82752600
H	-3.60420600	-4.23613000	0.11644300
H	-6.74460800	-1.24080200	-0.13339100
H	-6.26376900	-3.85672700	0.48306400
H	-1.17998400	-0.29397600	-1.28394300
H	1.29420900	0.47089700	1.34534200
N	0.66855600	1.27040700	1.36304500
P	0.01231100	1.86667000	-0.03718400
N	-1.23427200	2.62663200	0.80249800
C	-1.46582500	2.04651800	2.14023700
C	-0.03361200	1.61367400	2.61864600
C	-2.29820500	3.37802300	0.15492100
H	-1.88807800	3.91346500	-0.70512400
H	-2.70079100	4.11891800	0.85599000
H	-3.12677200	2.74653300	-0.19455500
H	-1.81976700	2.85745500	2.79127200
N	-0.09765600	0.77070100	-1.20403900
C	0.31306000	1.35121200	-2.50923000
C	1.29970600	2.53399000	-2.17645300
N	0.76521900	3.08381300	-0.91517800
C	1.31036200	4.31079200	-0.36018500
H	1.32034000	5.09079200	-1.13122400
H	2.33224900	4.19748000	0.02885700
H	0.66878300	4.65148200	0.45679400
H	1.20162800	3.30983000	-2.94898300
H	3.42467900	-3.81087300	1.43985500
H	2.80100600	-4.51408500	-0.86724800
H	6.39728500	-1.78241400	-0.20110700
C	2.78197800	2.15071500	-2.06164400
H	3.17852700	1.81679100	-3.02575500
H	3.37767500	3.01378400	-1.74472000
H	2.93300700	1.35006700	-1.32900800
C	0.96144100	0.24755800	-3.35700800
H	1.32084100	0.63958300	-4.31637900
H	1.79994400	-0.22216600	-2.83544400
H	0.21841100	-0.52902200	-3.56765100
C	-0.90777600	1.90204000	-3.27743400
H	-0.62614900	2.23252900	-4.28550300
H	-1.67231000	1.12389300	-3.37002900
H	-1.35213000	2.75484100	-2.75352900
C	0.66486100	2.79777200	3.31409900
H	1.71508900	2.55602600	3.50894800
H	0.63133800	3.69440400	2.68710500
H	0.18042000	3.02954400	4.27048200
C	-0.02844300	0.39799800	3.55333600
H	1.00086400	0.15823300	3.84131200
H	-0.59187300	0.60975800	4.46851400
H	-0.45636000	-0.48540500	3.07319300
C	-2.52312700	0.93540400	2.12857900
H	-2.74499400	0.59129700	3.14392700
H	-3.45938200	1.30289400	1.69626300
H	-2.19518900	0.07445300	1.53707000

- **CP4b**



B3LYP/6-31G*

E = -1833.55848611

Zero-point correction = 0.623041 (Hartree/Particle)

Thermal correction to Energy = 0.660343

Thermal correction to Enthalpy = 0.661287

Thermal correction to Gibbs Free Energy = 0.548385

Sum of electronic and zero-point Energies = -1832.935445

Sum of electronic and thermal Energies = -1832.898143

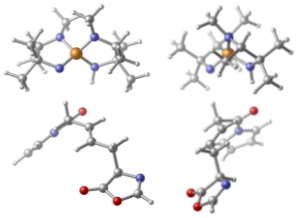
Sum of electronic and thermal Enthalpies = -1832.897199

Sum of electronic and thermal Free Energies = -1833.010101

0 1

O	-6.24165700	0.73508400	1.51877600
C	-6.44129200	-0.24802500	0.86508800
O	-7.62093400	-0.99349900	0.97817900
C	-5.59411000	-0.97447500	-0.18188900
C	-7.47601700	-2.04211200	0.09382100
N	-6.41178800	-2.12276200	-0.59071600
C	-4.20568800	-1.41345300	0.34665200
H	-4.36206100	-2.02562500	1.24604000
C	-3.28861000	-0.25740500	0.64294700
H	-3.63067300	0.44821700	1.39902900
C	-2.11389700	-0.06662000	0.03780000
H	-1.77702700	-0.76251500	-0.72935700
C	-1.16780200	1.06330500	0.35224800
H	-1.63549400	1.76766500	1.04174100
C	-0.65534900	1.72148600	-0.91329700
O	-0.19429100	1.06567400	-1.83874300
N	-0.68348100	3.12095700	-1.01408800
C	-0.18823000	3.80232300	-2.12872700
C	-1.16865400	4.06624200	-0.10218500
C	-0.35849900	5.13996000	-1.92206100
C	-0.97974500	5.30762600	-0.63707300
H	0.23046200	3.24113900	-2.94796800
H	-1.60136500	3.77181000	0.83923400
H	-0.07425800	5.92623200	-2.60849800
H	-1.25344300	6.24288000	-0.16735200
H	1.20558500	-0.35882300	-1.48843900
N	1.93538700	-1.01598900	-1.21979400
P	2.69236700	-0.79585000	0.25120800
N	3.04750500	-2.45482200	0.35976400
C	2.13260200	-3.28206000	-0.44181100
C	1.86397100	-2.40542100	-1.71633300
C	3.73535200	-3.05130700	1.49113600
H	4.24514200	-3.96959900	1.17179600
H	4.49217200	-2.35239200	1.85630300
H	3.06891600	-3.30313200	2.32914800
H	2.67856600	-4.18623600	-0.74726100
N	1.86235500	0.13201900	1.23668600
C	2.78194000	1.04552700	1.95153000
C	4.05458200	1.24675100	1.03157000
N	4.20851400	-0.06449000	0.37301500
C	5.36410500	-0.34022400	-0.45828500
H	5.39076700	-1.40837000	-0.69193000
H	6.28414600	-0.08997900	0.08584700
H	5.36591400	0.21750200	-1.40683400
H	4.93871700	1.41215400	1.66502200
H	-0.25223100	0.66776700	0.83937600
C	2.04628500	2.36305900	2.23722300
H	2.69862700	3.09146400	2.73562300
H	1.65692100	2.81613000	1.32134600
H	1.19760300	2.16336200	2.90085000
C	3.22319900	0.43771600	3.30093000
H	3.81039300	1.15155400	3.89431800
H	2.33967600	0.14940600	3.87988200
H	3.83431400	-0.45831800	3.14844200
C	3.95946000	2.39744400	0.01998500
H	3.92945400	3.36830700	0.52502100
H	4.83105300	2.40115600	-0.64436200
H	3.06175200	2.30466000	-0.60110400
C	0.88529000	-3.71414600	0.34425400
H	0.25583600	-4.39191700	-0.24214500
H	1.17996800	-4.24754600	1.25432500
H	0.28527500	-2.84876200	0.64640300
C	0.49833600	-2.65260400	-2.36756900
H	0.41767700	-3.68504200	-2.72574200
H	-0.32541900	-2.46206100	-1.67464900
H	0.37306800	-1.98924400	-3.23052100
C	2.97298800	-2.65189500	-2.75797700
H	2.88246500	-1.93509700	-3.58079400
H	3.96225000	-2.52943300	-2.30643700
H	2.90679800	-3.66584200	-3.17210100
H	-8.31820200	-2.72503100	0.06607100
H	-5.44613400	-0.31104500	-1.04331700
H	-3.76839600	-2.07025600	-0.41276400

- **CP4b** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -1833.56536248

Zero-point correction = 0.622944 (Hartree/Particle)

Thermal correction to Energy = 0.660168

Thermal correction to Enthalpy = 0.661112

Thermal correction to Gibbs Free Energy = 0.549031

Sum of electronic and zero-point Energies = -1832.942419

Sum of electronic and thermal Energies = -1832.905195

Sum of electronic and thermal Enthalpies = -1832.904251

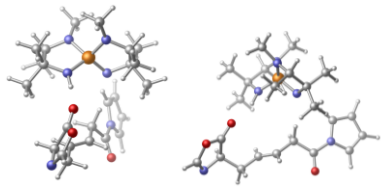
Sum of electronic and thermal Free Energies = -1833.016332

0 1

O	-6.22492300	0.57416500	1.51959500
C	-6.39295900	-0.42351900	0.87564000
O	-7.55457400	-1.19016000	0.98570200
C	-5.51733100	-1.14155300	-0.15136300
C	-7.38055300	-2.24868700	0.11568600
N	-6.30607500	-2.31240800	-0.55465300
C	-4.12476000	-1.54466600	0.39595600
H	-4.27567900	-2.15388600	1.29786800
C	-3.23774200	-0.36552300	0.69337800
H	-3.59379600	0.32836500	1.45371200
C	-2.07049700	-0.14124000	0.08496800
H	-1.71854300	-0.82667400	-0.68507900
C	-1.15352000	1.01477500	0.39707200
H	-1.61736300	1.68195200	1.12466100
C	-0.72419000	1.72406800	-0.87211200
O	-0.17465300	1.12412600	-1.78807700
N	-0.94701100	3.10359100	-0.99407300
C	-0.52747100	3.83807000	-2.10683500
C	-1.59248900	3.97690800	-0.10945400
C	-0.89791700	5.13839100	-1.92426700
C	-1.57410800	5.22641700	-0.65844000
H	-0.00589500	3.33822000	-2.90660100
H	-2.01093700	3.63084200	0.82092500
H	-0.71119700	5.95094900	-2.61367200
H	-1.99731300	6.11592600	-0.21116900
H	1.22924600	-0.31483400	-1.45549500
N	1.98751700	-0.94981500	-1.21317200
P	2.76768600	-0.72689000	0.24527000
N	3.18242900	-2.37031800	0.32240800
C	2.29993800	-3.22268100	-0.49036600
C	1.96611500	-2.33052800	-1.73881000
C	3.91575000	-2.96007500	1.42937400
H	4.46631700	-3.84292800	1.08010600
H	4.64151800	-2.23376900	1.80393200
H	3.27302700	-3.26629800	2.26732600
H	2.88870900	-4.08736600	-0.82762800
N	1.92486900	0.15369600	1.26560700
C	2.82029700	1.11025900	1.95537600
C	4.06087300	1.36639900	1.00703400
N	4.25427300	0.06456300	0.34160900
C	5.40696300	-0.16407200	-0.50890900
H	5.46969900	-1.22919300	-0.74880000
H	6.32489500	0.11766100	0.02285500
H	5.37369600	0.39830600	-1.45398900
H	4.95138000	1.56805200	1.62051300
H	-0.20591700	0.64207000	0.83589700
C	2.03359600	2.39443000	2.25875000
H	2.66553300	3.15159600	2.74032700
H	1.60166300	2.82907800	1.35280000
H	1.21054000	2.15900600	2.94275400
C	3.32217100	0.52661400	3.29456000
H	3.89398300	1.26722500	3.86993100
H	2.46776500	0.20350200	3.89881100
H	3.96627600	-0.34359100	3.12794000
C	3.89644100	2.51449300	0.00085800
H	3.83648600	3.48217900	0.50952100
H	4.75392400	2.55513600	-0.68020400
H	2.99144000	2.38525900	-0.60302500
C	1.09025500	-3.74340700	0.30035700
H	0.49130600	-4.43890800	-0.29694800
H	1.42773000	-4.28375400	1.19114300
H	0.44635500	-2.92191400	0.63336200
C	0.59926800	-2.62301100	-2.36849000
H	0.55587300	-3.64974600	-2.74832200
H	-0.21775000	-2.48433600	-1.65531100
H	0.42891600	-1.94761100	-3.21435600
C	3.06243700	-2.50549500	-2.80810400
H	2.91970400	-1.78064900	-3.61658900
H	4.05473600	-2.34332100	-2.37590300

H	3.03502400	-3.51443700	-3.23804600
H	-8.20866600	-2.94806300	0.08859900
H	-5.37651500	-0.48462000	-1.01874300
H	-3.66366500	-2.19448300	-0.35514500

- **CP4c**



B3LYP/6-31G*

E = -1833.56023710

Zero-point correction = 0.622726 (Hartree/Particle)

Thermal correction to Energy = 0.660137

Thermal correction to Enthalpy = 0.661081

Thermal correction to Gibbs Free Energy = 0.549523

Sum of electronic and zero-point Energies = -1832.937511

Sum of electronic and thermal Energies = -1832.900100

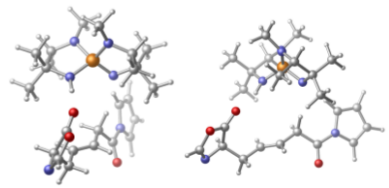
Sum of electronic and thermal Enthalpies = -1832.899156

Sum of electronic and thermal Free Energies = -1833.010714

0 1

O	-3.17099500	0.30504700	0.58320300
C	-4.13797000	-0.40431200	0.51804600
C	-4.49268400	-1.57916500	-0.39169500
O	-5.22858000	-0.23743700	1.36610600
N	-5.86110900	-1.94314500	-0.00726400
C	-6.15876500	-1.17624100	0.95623500
C	-3.53331800	-2.79057200	-0.25353300
C	-2.13062400	-2.51141300	-0.71364000
H	-3.53514300	-3.12899000	0.78897500
H	-2.01842300	-2.16753600	-1.74372600
C	-1.04579700	-2.67971800	0.04529500
H	-1.16290400	-3.04017700	1.06688400
C	0.36061700	-2.38147700	-0.38184600
H	0.40109900	-2.13720200	-1.45246300
C	1.29253800	-3.55637200	-0.13143700
O	0.90579800	-4.66217000	0.19847000
N	2.66559900	-3.31469900	-0.33814100
C	3.61820700	-4.33150100	-0.37153500
C	3.30372800	-2.09091900	-0.56393300
C	4.83508300	-3.76352400	-0.62236700
C	4.63695900	-2.34541400	-0.73757700
H	3.30837800	-5.35364600	-0.22387700
H	2.76132900	-1.15654900	-0.50108600
H	5.77292200	-4.29523100	-0.71507400
H	5.40005900	-1.59922100	-0.91665000
H	-1.35524400	0.91550100	-0.28883600
N	-0.62295500	1.46319500	-0.72890500
P	0.79523600	1.83530800	0.06182900
N	1.30212800	2.79053400	-1.24989700
C	0.56918100	2.50617000	-2.49341000
C	-0.87750400	2.14554000	-2.00463500
C	2.63472400	3.36393600	-1.32608600
H	2.93877000	3.69085000	-0.32821700
H	3.39526100	2.66517900	-1.70369000
H	2.62003100	4.24397200	-1.98160400
H	0.51737100	3.43880300	-3.07385100
N	1.48336800	0.55731600	0.70485200
C	2.01286000	0.88475600	2.04845700
C	1.18417100	2.11727000	2.59525900
N	0.87693200	2.89000600	1.37757900
H	0.72938200	-1.47879200	0.13615600
C	0.29945800	4.21595200	1.47208700
H	0.34996800	4.69926800	0.49241600
H	-0.74993100	4.21805400	1.80356700
H	0.87916700	4.82414800	2.17868400
H	1.83435900	2.73537800	3.23185100
C	1.88202500	-0.35927400	2.93956200
H	2.22564000	-0.16221600	3.96310200
H	0.84910000	-0.71616900	2.98030300
H	2.49929800	-1.16412900	2.52670800
C	3.50546100	1.27222800	1.97347100
H	3.93436500	1.41512800	2.97434000
H	4.06686500	0.47937100	1.46849100
H	3.64475700	2.20144700	1.41004800
C	-0.08348100	1.77030800	3.38969500
H	0.15984000	1.25474800	4.32434600
H	-0.63213100	2.68188000	3.65327100
H	-0.75669700	1.13126200	2.80709800
C	1.25827300	1.43863600	-3.35708800
H	0.73855000	1.29753700	-4.31052900
H	2.28418000	1.74456500	-3.58743600
H	1.30524900	0.47617200	-2.83659700
C	-1.63355400	1.20203400	-2.94988400
H	-1.77046700	1.65757600	-3.93727600
H	-1.11202600	0.24944400	-3.07164800
H	-2.62943600	0.99438300	-2.54075600
C	-1.70905300	3.42906000	-1.80437800
H	-1.94526900	3.90119300	-2.76620200
H	-2.65132100	3.19189500	-1.29800400
H	-1.16628500	4.15366800	-1.19084200
H	-4.48403900	-1.23823500	-1.43490300
H	-3.98941400	-3.59333300	-0.84775400
H	-7.08649000	-1.16151900	1.51719000

- **CP4c** (PCM)



PCM(toluene)-B3LYP/6-31G*

E = -1833.56767715

Zero-point correction = 0.622498 (Hartree/Particle)

Thermal correction to Energy = 0.659819

Thermal correction to Enthalpy = 0.660763

Thermal correction to Gibbs Free Energy = 0.550737

Sum of electronic and zero-point Energies = -1832.945179

Sum of electronic and thermal Energies = -1832.907858

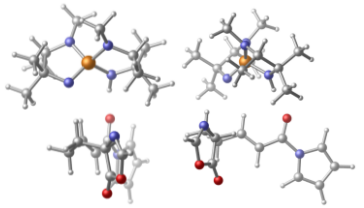
Sum of electronic and thermal Enthalpies = -1832.906914

Sum of electronic and thermal Free Energies = -1833.016940

0 1

O	-3.12711200	0.24049400	0.55391000
C	-4.08645600	-0.48037700	0.47752200
C	-4.41036700	-1.66716700	-0.42625500
O	-5.19136700	-0.31586400	1.30301800
N	-5.78006400	-2.04477600	-0.05830500
C	-6.10539600	-1.27090000	0.89104600
C	-3.43726700	-2.86386000	-0.26027700
C	-2.03359800	-2.56641600	-0.70572200
H	-3.44895900	-3.19118500	0.78544700
H	-1.91523700	-2.22905300	-1.73708600
C	-0.95487200	-2.70377000	0.06833200
H	-1.07693900	-3.05238800	1.09370900
C	0.44814100	-2.37120100	-0.34692100
H	0.48481900	-2.10028300	-1.41131100
C	1.40411200	-3.53188800	-0.13274200
O	1.03948300	-4.66893800	0.11153500
N	2.77594800	-3.24352200	-0.27358000
C	3.75814100	-4.23137800	-0.33661900
C	3.38713400	-1.99094900	-0.39707900
C	4.96666600	-3.61678600	-0.50597700
C	4.73232600	-2.19929300	-0.53758900
H	3.47512600	-5.26951400	-0.26684300
H	2.81648000	-1.07531900	-0.30262800
H	5.92188900	-4.11694600	-0.59813300
H	5.47979100	-1.42348200	-0.64118300
H	-1.34929200	0.83232900	-0.40629400
N	-0.59028000	1.35146400	-0.83733100
P	0.73358900	1.84273600	0.05162500
N	1.27410300	2.80758100	-1.23535500
C	0.64592400	2.46720300	-2.52315700
C	-0.80458600	2.01874400	-2.13007600
C	2.57305600	3.46017900	-1.23102300
H	2.79242100	3.81351900	-0.21994500
H	3.39589900	2.80532100	-1.55184600
H	2.54779400	4.33218800	-1.89632900
H	0.57525900	3.39019900	-3.11622900
N	1.46644300	0.62583000	0.76645200
C	1.85530800	1.00449800	2.14445100
C	0.89315000	2.17324800	2.60396800
N	0.63235600	2.91073600	1.35422600
H	0.79737600	-1.47388700	0.19121800
C	-0.03892000	4.19584400	1.38460000
H	0.05260400	4.67141100	0.40426900
H	-1.10772900	4.12884800	1.63711200
H	0.44370100	4.84872300	2.12324800
H	1.43906700	2.84362900	3.28384900
C	1.74664400	-0.23810500	3.04062500
H	1.98835100	-0.00622700	4.08574400
H	0.74358900	-0.67226700	3.00222400
H	2.45445000	-0.99761900	2.69126200
C	3.31441000	1.50807300	2.18771100
H	3.64581400	1.69342100	3.21827000
H	3.97772000	0.75895600	1.74233700
H	3.42618800	2.44024300	1.62311600
C	-0.40677200	1.73800700	3.29642600
H	-0.20380100	1.25222900	4.25642700
H	-1.04078600	2.60885300	3.49840800
H	-0.98053000	1.04478700	2.67086100
C	1.45762600	1.43922700	-3.32481900
H	1.00884400	1.25559900	-4.30644500
H	2.47396000	1.80977200	-3.49434800
H	1.53221400	0.48682400	-2.78924700
C	-1.43833700	1.03031400	-3.11890800
H	-1.53043100	1.47471800	-4.11644400
H	-0.85789300	0.10766600	-3.19758500
H	-2.44792000	0.76853700	-2.77988200
C	-1.72504000	3.24867200	-1.99252900
H	-1.93159000	3.69661700	-2.97230200
H	-2.68031300	2.95651200	-1.54198900
H	-1.26755700	4.01149300	-1.35658900
H	-4.38943800	-1.33519300	-1.47200100
H	-3.87088800	-3.67855000	-0.85476000
H	-7.04162300	-1.25977400	1.43715700

- **CP4d**



B3LYP/6-31G*

E = -1833.56781887

Zero-point correction = 0.623665 (Hartree/Particle)

Thermal correction to Energy = 0.660903

Thermal correction to Enthalpy = 0.661847

Thermal correction to Gibbs Free Energy = 0.550520

Sum of electronic and zero-point Energies = -1832.944154

Sum of electronic and thermal Energies = -1832.906916

Sum of electronic and thermal Enthalpies = -1832.905971

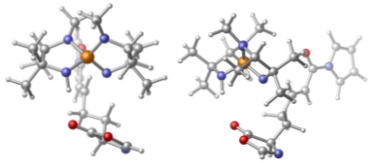
Sum of electronic and thermal Free Energies = -1833.017299

0 1

O	-4.13567600	-3.10001900	0.58152600
C	-3.14055700	-3.52204300	0.06248200
O	-3.11076100	-4.75352500	-0.60024400
C	-1.72593600	-2.95534100	-0.05079800
C	-1.81856600	-4.88248700	-1.06937700
N	-0.98770400	-3.95529600	-0.83083500
C	-1.05373900	-2.67438300	1.30903000
H	-1.03864400	-3.59946600	1.89781300
C	-1.75288900	-1.55826400	2.11605500
H	-2.79547200	-1.82110500	2.32047400
C	-1.65453800	-0.23172700	1.42657200
H	-0.63925400	0.12572600	1.24868500
C	-2.71113800	0.48859600	1.01356600
H	-3.71742600	0.11803800	1.17896600
C	-2.52512000	1.77757100	0.32044800
O	-1.44515600	2.18623200	-0.09854200
N	-3.67165500	2.57394500	0.12903300
C	-3.64152700	3.77689000	-0.57475100
C	-4.97695400	2.36503200	0.58778900
C	-4.89849100	4.30981400	-0.56550600
C	-5.74510800	3.41535300	0.17413000
H	-2.71316200	4.11522900	-1.00492700
H	-5.23701900	1.50248400	1.17855200
H	-5.19422200	5.23895600	-1.03383100
H	-6.80055500	3.54063700	0.37570300
H	0.33520800	1.43760800	-0.64182800
N	1.19748100	1.08924200	-1.05508000
P	2.35670900	0.34590200	-0.12587600
N	3.11005200	-0.28546000	-1.51253600
C	2.21290600	-0.35409600	-2.67697100
C	1.28276800	0.90226600	-2.51339900
C	4.26531300	-1.16356400	-1.45941100
H	4.83371500	-1.08131800	-2.39501600
H	4.91610300	-0.84902300	-0.63944600
H	4.00791400	-2.22176900	-1.30647200
H	2.82693300	-0.21201300	-3.57835000
N	1.74586000	-0.40203200	1.13795500
C	2.62634700	-0.19762800	2.30962600

C	3.39908000	1.16588900	2.08813900
N	3.59813700	1.20747500	0.62909200
C	4.43572900	2.22455100	0.02580000
H	4.58668900	1.98175500	-1.02971300
H	5.41933900	2.24005100	0.51406300
H	4.01005200	3.23754500	0.08629200
H	4.38911000	1.10347800	2.56432500
H	-1.23044000	-1.48561600	3.07978900
C	1.76297500	-0.18458200	3.57968800
H	2.36389500	0.01039700	4.47714800
H	0.97177300	0.56789100	3.51943900
H	1.28792100	-1.16447600	3.70206000
C	3.65445800	-1.34333400	2.43555600
H	4.23220900	-1.26924200	3.36680900
H	3.13495200	-2.30722800	2.42477100
H	4.36019400	-1.33138600	1.59820700
C	2.68673000	2.42075200	2.61335300
H	2.61916700	2.41130200	3.70621300
H	3.23612600	3.32505200	2.32805900
H	1.67313300	2.49925700	2.20500000
C	1.49951100	-1.70836900	-2.79561600
H	0.88141300	-1.75665600	-3.69838500
H	2.23595900	-2.51627900	-2.86322300
H	0.86744200	-1.91580700	-1.92636000
C	-0.12698500	0.71430600	-3.08917300
H	-0.08961300	0.54329200	-4.17088000
H	-0.64679800	-0.12683000	-2.62232400
H	-0.72169400	1.61681500	-2.91094100
C	1.94144900	2.12832000	-3.17699000
H	1.38020400	3.03688300	-2.93355800
H	2.96808000	2.25636700	-2.82030400
H	1.96733900	2.02056200	-4.26871000
H	-1.63056700	-5.79844100	-1.61886200
H	-1.77105100	-2.01752000	-0.62004200
H	-0.01634100	-2.38143400	1.11219700

● **CP4e**



B3LYP/6-31G*

E = -1833.56459712

Zero-point correction = 0.623985 (Hartree/Particle)

Thermal correction to Energy = 0.661092

Thermal correction to Enthalpy = 0.662036

Thermal correction to Gibbs Free Energy = 0.552601

Sum of electronic and zero-point Energies = -1832.940612

Sum of electronic and thermal Energies = -1832.903506

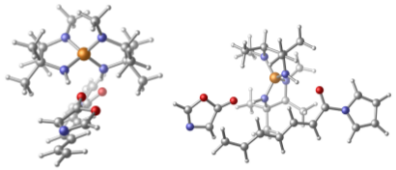
Sum of electronic and thermal Enthalpies = -1832.902561

Sum of electronic and thermal Free Energies = -1833.011996

0 1

O	-1.85308900	-1.96277500	-2.20718700
C	-1.83458700	-2.87224600	-1.42071800
C	-0.69710100	-3.76430800	-0.91940200
O	-2.98142300	-3.31465600	-0.77354500
N	-1.35258600	-4.71938400	-0.01771600
C	-2.57383000	-4.38457200	0.00353600
C	0.40358500	-2.96099600	-0.19365200
C	1.29943000	-2.16675900	-1.16358000
H	-0.07790700	-2.25932900	0.49528700
H	1.96292200	-2.83680600	-1.72587400
C	2.07840000	-1.10549100	-0.45008000
H	1.48909800	-0.40719200	0.14331700
C	3.40936000	-0.94649000	-0.49841100
H	4.02664200	-1.63239900	-1.07005100
C	4.04659000	0.19510400	0.19410000
O	3.42705100	1.14426100	0.65281300
N	5.45657500	0.17068300	0.30149100
C	6.18577700	1.23601400	0.82212600
C	6.34822300	-0.85174800	-0.03336200
C	7.50927900	0.89671600	0.80929900
C	7.61225300	-0.42975100	0.26989000
H	5.66648800	2.12466100	1.14226200
H	6.00420600	-1.79323000	-0.42899600
H	8.32536500	1.52214300	1.14545000
H	8.51878100	-1.00295900	0.12785200
H	-2.49669000	0.05949000	-1.58642000
N	-2.38851500	1.01977300	-1.27057900
P	-1.73144800	1.18088400	0.26838000
N	-0.74786400	2.46787000	-0.21668200
C	-0.54978900	2.55243600	-1.67149200
C	-1.89501300	1.99788000	-2.26972400
C	0.20912300	3.11562300	0.67187700
H	-0.21344600	3.15574500	1.67949400
H	1.17506400	2.59677800	0.72041900
H	0.38021900	4.14659200	0.33645600
H	-0.46844700	3.61805600	-1.93173200
N	-1.32583800	-0.21464600	0.91264700
C	-1.77913800	-0.25890800	2.32438800
C	-2.99043300	0.74902600	2.47120200
N	-2.65147100	1.82533400	1.52532700
H	0.64990700	-1.66695700	-1.89620100
C	-3.42303400	3.05168400	1.49780400
H	-2.89883100	3.79098400	0.88591400
H	-4.43723400	2.92530500	1.08951200
H	-3.51324900	3.45746600	2.51393000
H	-2.98529300	1.17459300	3.48565200
C	-2.18028200	-1.70050900	2.66989000
H	-2.57652400	-1.77748200	3.69051000
H	-2.93270400	-2.07771900	1.97177800
H	-1.30273500	-2.35256900	2.60364500
C	-0.64670400	0.17625300	3.27860900
H	-0.92967300	0.04104200	4.33130300
H	0.25249900	-0.41738800	3.08376300
H	-0.39167100	1.23027300	3.12766700
C	-4.38224700	0.15900500	2.19973500
H	-4.65592600	-0.58245200	2.95749200
H	-5.14462000	0.94595500	2.22269300
H	-4.42174600	-0.31986700	1.21525900
C	0.72795800	1.84923600	-2.14686400
H	0.91375400	2.04232400	-3.20905100
H	1.59615100	2.20579000	-1.58403900
H	0.66286300	0.76717400	-1.99966100
C	-1.73750300	1.30580000	-3.62850800
H	-1.34112900	2.00164900	-4.37605400
H	-1.07613200	0.43767200	-3.57247700
H	-2.71545500	0.95990000	-3.98189200
C	-2.90953000	3.14899700	-2.40483700
H	-2.58991200	3.86268500	-3.17433500
H	-3.89259400	2.75476900	-2.68224800
H	-3.01453000	3.69064600	-1.45994100
H	-0.26365800	-4.31028200	-1.76817800
H	0.99975800	-3.67100300	0.38921700
H	-3.36905800	-4.85135500	0.57357400

● **TS5tt**



B3LYP/6-31G*

E = -1910.94710838

Zero-point correction = 0.654945 (Hartree/Particle)

Thermal correction to Energy = 0.693922

Thermal correction to Enthalpy = 0.694866

Thermal correction to Gibbs Free Energy = 0.581739

Sum of electronic and zero-point Energies = -1910.292163

Sum of electronic and thermal Energies = -1910.253186

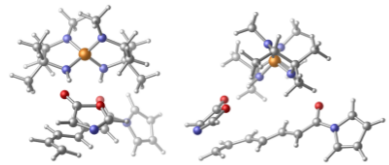
Sum of electronic and thermal Enthalpies = -1910.252242

Sum of electronic and thermal Free Energies = -1910.365369

0 1

O	3.02337500	-0.31215700	-0.29177200
C	4.14386400	-0.83743600	-0.29752100
C	4.78854400	-1.87153800	0.44403200
O	5.06713100	-0.49637500	-1.30601200
N	6.11175500	-2.01002900	-0.00313700
C	6.19056200	-1.22999400	-1.02338600
C	3.75247700	-3.56646500	-0.55961000
C	2.46442700	-3.78688700	-0.07658500
H	3.88629400	-3.10015000	-1.53183200
H	2.33289600	-4.46007800	0.77058300
C	1.34083000	-3.10641200	-0.56234000
H	1.51400400	-2.39265400	-1.36824800
C	0.03118300	-3.22959600	-0.10298000
H	-0.18817600	-3.94697100	0.68844600
C	-0.99942300	-2.42156100	-0.59974300
H	-0.71304200	-1.69501800	-1.35937600
C	-2.33549300	-2.42342100	-0.22981600
H	-2.70150500	-3.16618900	0.47073600
C	-3.23473700	-1.44819700	-0.75966600
O	-2.90211600	-0.42166200	-1.39446700
N	-4.62761700	-1.63478500	-0.52750300
C	-5.57449700	-0.65076500	-0.77367700
C	-5.28340500	-2.76745800	-0.05489500
C	-6.80951800	-1.14803500	-0.45089200
C	-6.62480400	-2.49457300	0.00218900
H	-5.25619600	0.30532900	-1.15558200
H	-4.74331000	-3.67532000	0.16012500
H	-7.74726800	-0.61414400	-0.53046000
H	-7.39529900	-3.18373700	0.32218300
H	1.60582500	0.04714900	0.72807900
N	0.81875100	0.53684000	1.17958300
P	0.00566000	1.72904100	0.40963500
N	-0.82166800	2.19914600	1.77908200
C	-0.73799500	1.19474000	2.86655500
C	0.65561400	0.50495600	2.64796000
C	-1.87392000	3.20521500	1.80020100
H	-1.65822600	3.96935300	1.04917300
H	-1.89020700	3.69037300	2.78304600
H	-2.87033700	2.79045800	1.59979800
H	-0.70534700	1.74943100	3.81391100
N	-0.66601100	1.21106200	-0.98854100
C	-0.55183000	2.15340500	-2.12538500
C	0.71192800	3.01114100	-1.76197600
N	0.68217800	3.08832700	-0.27900400
H	-1.40909400	0.49154700	-1.03822400
C	1.62656100	3.95635500	0.41278400
H	2.65596000	3.57675400	0.38888200
H	1.60810600	4.94788900	-0.05318600
H	1.31907700	4.06785400	1.45581400
H	0.55272600	4.03072000	-2.13804700
C	-1.80397200	3.04575100	-2.21777500
H	-2.70056600	2.42079800	-2.28003800
H	-1.89391700	3.69331100	-1.33903600
H	-1.76338200	3.68399200	-3.10838200
C	-0.40645500	1.33974800	-3.41734100
H	-1.31200500	0.74410700	-3.57244400
H	-0.28008500	1.99980400	-4.28299600
H	0.44484500	0.65678500	-3.36721300
C	2.05669800	2.49503400	-2.28798000
H	2.06144800	2.47361100	-3.38211500
H	2.86306800	3.16829200	-1.97688200
H	2.29521100	1.49525000	-1.90982200
C	1.76653100	1.31233600	3.34699200
H	2.75090200	0.94314500	3.04097800
H	1.70614600	2.37545400	3.09244600
H	1.68845300	1.21780900	4.43663300
C	0.71032500	-0.95392300	3.11848400
H	1.70853800	-1.36156300	2.92575400
H	0.52207200	-1.02511800	4.19577800
H	-0.00965800	-1.57626400	2.58352600
C	-1.94987700	0.25617000	2.88710400
H	-1.90717100	-0.41410700	3.75127600
H	-2.87725400	0.83286300	2.96855500
H	-2.00704600	-0.35562000	1.98069100
H	4.56518400	-4.21905200	-0.25902200
H	4.51354000	-2.17092300	1.44453400
H	7.03935100	-1.07468600	-1.67632200

● **TS5tc**



B3LYP/6-31G*

E = -1910.93880848

Zero-point correction = 0.655191 (Hartree/Particle)

Thermal correction to Energy= 0.693863

Thermal correction to Enthalpy= 0.694807

Thermal correction to Gibbs Free Energy= 0.583317

Sum of electronic and zero-point Energies= -1910.283618

Sum of electronic and thermal Energies= -1910.244945

Sum of electronic and thermal Enthalpies= -1910.244001

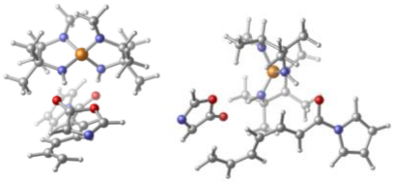
Sum of electronic and thermal Free Energies= -1910.355491

0 1

O	-3.11443100	1.00473300	-0.08128300
C	-3.13231900	1.96530300	-0.85389300
C	-3.91805800	3.15290500	-0.94469000
O	-2.14752800	2.11003700	-1.85975600

N	-3.52145900	3.88615600	-2.07606000
C	-2.49138600	3.25961900	-2.52483600
C	-3.07655900	4.25414700	0.78179600
C	-2.76807000	3.40587800	1.84409100
H	-2.28782700	4.66342000	0.15783200
H	-3.56664600	3.14574400	2.53561900
C	-1.54574600	2.72913100	1.99969900
H	-1.51684900	1.96762900	2.77939200
C	-0.35599900	2.92010100	1.29740900
H	-0.27704100	3.73900200	0.58409500
C	0.74359100	2.06897200	1.45258600
H	0.60571800	1.19419700	2.08861700
C	1.99784800	2.20888600	0.87699400
H	2.23785800	3.10697000	0.31782100
C	2.97035700	1.17638200	1.00453200
O	2.73510300	-0.00538700	1.35168200
N	4.32143100	1.49061100	0.66880400
C	5.31033400	0.52773300	0.52338300
C	4.88946200	2.74052500	0.44955500
C	6.48479200	1.15864500	0.20428700
C	6.21771200	2.56495600	0.16026300
H	5.06478900	-0.50980900	0.68123200
H	4.30636900	3.64153200	0.55260900
H	7.43565700	0.67381700	0.02636400
H	6.92680800	3.35457400	-0.05126000
H	-1.86328500	-0.24793500	0.28847900
N	-1.46027900	-1.12294700	0.66438400
P	-0.41201700	-2.05784300	-0.17811200
N	-0.61930500	-3.38472700	0.81202300
C	-1.31195300	-3.04137500	2.07615000
C	-2.25578900	-1.85355500	1.68096200
C	0.17933900	-4.59940400	0.73024700
H	0.43553200	-4.79476500	-0.31401600
H	-0.41175600	-5.44566400	1.09876900
H	1.10896400	-4.54388800	1.31173100
H	-1.93363700	-3.90403600	2.35063700
N	0.99117500	-1.27358200	-0.46323700
C	1.56841000	-1.47859900	-1.81268400
C	0.31894500	-1.85642700	-2.68476500
N	-0.56690800	-2.59063100	-1.75016600
H	1.53561500	-0.78281500	0.26914500
C	-1.70762600	-3.33242600	-2.26807100
H	-2.51211700	-2.68257200	-2.63608000
H	-1.37578600	-3.97523200	-3.09173900
H	-2.11115200	-3.97328900	-1.48046900
H	0.63999200	-2.57414900	-3.45154700
C	2.58252500	-2.63798600	-1.80149200
H	3.35872200	-2.44840700	-1.05321400
H	2.09759600	-3.58964400	-1.55997900
H	3.06673600	-2.74049600	-2.77988400
C	2.26811400	-0.19377700	-2.27142700
H	3.15917800	-0.01619200	-1.66186500
H	2.59369500	-0.28689500	-3.31365100
H	1.61457300	0.67646100	-2.17872900
C	-0.40268600	-0.69146200	-3.37137900
H	0.24601400	-0.21606200	-4.11355900
H	-1.28761600	-1.05869300	-3.90229900
H	-0.73145000	0.07188300	-2.65911600
C	-3.57262900	-2.37719200	1.07624300
H	-4.12894000	-1.54493300	0.63407500
H	-3.38580800	-3.12298500	0.29672600
H	-4.19658700	-2.84211500	1.84875100
C	-2.58001300	-0.90061000	2.83668700
H	-3.19498500	-0.07805800	2.45975700
H	-3.14073000	-1.42102500	3.62166500
H	-1.67543400	-0.47331400	3.27527000
C	-0.32415100	-2.75907200	3.21524200
H	-0.85270800	-2.56855500	4.15410100
H	0.32626200	-3.62502200	3.37812700
H	0.31287700	-1.89626600	2.99260100
H	-3.96499100	4.87508000	0.83577700
H	-4.93574400	3.21688600	-0.58698400
H	-1.87001000	3.52629000	-3.36982600

- **TS5cc**



B3LYP/6-31G*

E = -1910.93670366

Zero-point correction = 0.655158 (Hartree/Particle)

Thermal correction to Energy = 0.693919

Thermal correction to Enthalpy = 0.694863

Thermal correction to Gibbs Free Energy = 0.583013

Sum of electronic and zero-point Energies = -1910.281546

Sum of electronic and thermal Energies = -1910.242784

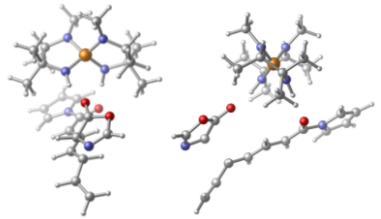
Sum of electronic and thermal Enthalpies = -1910.241840

Sum of electronic and thermal Free Energies = -1910.353691

0 1

O	-2.83843100	0.86106500	1.26286700
C	-3.75489700	1.06601300	0.46307000
C	-4.87296500	1.94366500	0.42179400
O	-3.78962800	0.39461300	-0.78955900
N	-5.63728500	1.68479000	-0.72282000
C	-4.94954300	0.82081800	-1.38508800
C	-3.72319100	3.82984900	-0.16172600
C	-2.52010900	3.99746500	0.51125400
H	-3.74074800	3.49633000	-1.19452600
H	-2.53938000	4.52501700	1.46267100
C	-1.27492400	3.47899200	0.10097700
H	-0.43232300	3.71286800	0.75185900
C	-1.00387400	2.70024600	-1.01969400
H	-1.83349800	2.40868100	-1.65805500
C	0.24896100	2.15012700	-1.34705900
H	0.24425100	1.43157400	-2.16524800
C	1.49593500	2.37469500	-0.78088200
H	1.64059500	3.15710700	-0.04499600
C	2.60723100	1.56472000	-1.16204600
O	2.53975600	0.48596300	-1.79554300
N	3.90728700	1.99140700	-0.76111400
C	5.02759200	1.17586700	-0.83298200
C	4.29660300	3.23144900	-0.26531800
C	6.10838800	1.88483000	-0.37811400
C	5.64445300	3.19235400	-0.02110400
H	4.92546700	0.17049200	-1.20770300
H	3.58917100	4.03955300	-0.17024700
H	7.12350600	1.51659200	-0.30924200
H	6.24014200	4.01119700	0.36059400
H	-1.31109700	-0.07317800	0.97669300
N	-0.46712900	-0.60533100	1.24687500
P	0.15641700	-1.85672000	0.40455300
N	1.18270700	-2.32267100	1.63376300
C	1.31632400	-1.29090600	2.68944000
C	-0.06068300	-0.53646500	2.67058100
C	2.18407400	-3.37237800	1.51655600
H	1.81565100	-4.15092200	0.84379500
H	2.35028700	-3.82493400	2.50107500
H	3.14673300	-3.00842100	1.13433600
H	1.40793600	-1.82152000	3.64668400
N	0.58357700	-1.40520900	-1.10832800
C	0.29867000	-2.39479700	-2.16970900
C	-0.88484100	-3.23744300	-1.57238700
N	-0.63665400	-3.23051500	-0.11182500
H	1.24257600	-0.63140600	-1.31339500
C	-1.39511000	-4.12085200	0.75525700
H	-2.45171100	-3.83699400	0.84299100
H	-1.34097700	-5.14304400	0.36224800
H	-0.95144000	-4.11770500	1.75400700
H	-0.77281800	-4.27609900	-1.91178200
C	1.52448800	-3.29273000	-2.42548300
H	2.39640100	-2.67509900	-2.66413200
H	1.76428300	-3.89945200	-1.54585600
H	1.34138100	-3.97134700	-3.26707300
C	-0.05671000	-1.64140700	-3.45767900
H	0.80666700	-1.05093900	-3.78150100
H	-0.31062600	-2.34075600	-4.26222200
H	-0.89572600	-0.95842200	-3.30541400
C	-2.29839700	-2.75847200	-1.92266100
H	-2.47678800	-2.83068900	-3.00022100
H	-3.04308300	-3.39172700	-1.42846300
H	-2.47544200	-1.72529100	-1.60701700
C	-1.08860700	-1.25751000	3.56176200
H	-2.08164600	-0.82881400	3.39616200
H	-1.12965600	-2.32802200	3.33244400
H	-0.83169100	-1.14580800	4.62193800
C	0.02763200	0.93899700	3.07954800
H	-0.96299500	1.39481500	2.99223600
H	0.36586400	1.03440200	4.11778100
H	0.70982100	1.49245300	2.43001900
C	2.56057400	-0.41784700	2.49145400
H	2.68465600	0.27925000	3.32559600
H	3.46165700	-1.03879500	2.44947000
H	2.50557300	0.16238600	1.56499300
H	-4.58761400	4.41332300	0.13596200
H	-5.31970500	2.39344000	1.29612700
H	-5.18344400	0.38459600	-2.34742300

- **TS6tt**



B3LYP/6-31G*

E = -1910.93469643

Zero-point correction = 0.654106 (Hartree/Particle)

Thermal correction to Energy = 0.693269

Thermal correction to Enthalpy = 0.694214

Thermal correction to Gibbs Free Energy = 0.580768

Sum of electronic and zero-point Energies = -1910.280590

Sum of electronic and thermal Energies = -1910.241427

Sum of electronic and thermal Enthalpies = -1910.240483

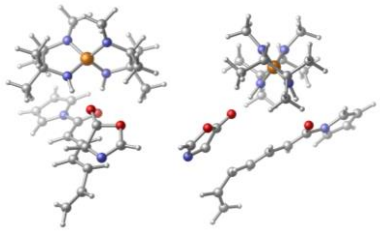
Sum of electronic and thermal Free Energies = -1910.353928

0 1

O	-2.01648100	-0.89245100	0.56043000
C	-3.23997200	-0.96985900	0.55969400
C	-4.31148800	-0.16292900	1.09914900
O	-3.88034000	-1.96277300	-0.20551200
N	-5.53344200	-0.83041000	0.83771900
C	-5.21924800	-1.79890700	0.06011500
C	-4.22351400	1.47547900	-0.13216600
C	-3.02492100	2.21224200	0.10095700
H	-4.25883700	0.89766000	-1.05660500
H	-3.06082300	2.98417100	0.87131600
C	-1.83572700	2.02424800	-0.58355700
H	-1.79724900	1.24805000	-1.34586400
C	-0.66622300	2.77728900	-0.41198000
H	-0.67171100	3.59019400	0.30581100
C	0.48979000	2.51393600	-1.17224300
O	0.62885600	1.60087000	-2.02629100
N	1.64764800	3.34716700	-0.95107800
C	2.83602700	3.15893700	-1.63641800
C	1.81646900	4.40577200	-0.06845800
C	3.74923700	4.08325500	-1.19246600
C	3.10058700	4.87569600	-0.19450500
H	2.89401600	2.38504000	-2.38403400
H	1.01293000	4.74317900	0.56583900
H	4.76612100	4.18987900	-1.54707800
H	3.52676400	5.70193800	0.35997400
H	-0.32313800	-0.45521200	1.16180200
N	0.68610800	-0.56134400	1.30058600
P	1.60370700	-1.42740000	0.25906300
N	2.99363900	-1.23460500	1.15995900
C	2.87150200	-0.16678000	2.18215700
C	1.34562100	-0.16710000	2.56203900
C	4.31434300	-1.66524200	0.72315000
H	4.21712700	-2.56566800	0.11138700
H	4.84108600	-0.90193100	0.13617400
H	4.92470100	-1.91243100	1.59968200
H	3.44267600	-0.49805800	3.06001600
N	1.35997200	-0.94316400	-1.27525500
C	1.21427300	-2.02695500	-2.27346600
C	0.85822100	-3.30017900	-1.41685600
N	1.49862200	-3.04970000	-0.10175300
H	1.09179700	0.03135600	-1.52271600
C	1.59425200	-4.12876500	0.86996600
H	2.22798400	-3.81204600	1.70194800
H	0.61701600	-4.42765400	1.27043100
H	2.05872400	-5.00425800	0.40043900
H	1.37211700	-4.16436000	-1.85914200
H	-5.88290800	-2.51780600	-0.40361400
H	-4.20339400	0.35688400	2.04222400
C	0.12499300	-1.62293400	-3.27443500
H	-0.02233400	-2.40616400	-4.02634500
H	-0.82636300	-1.42802600	-2.77441800
H	0.42328400	-0.70473600	-3.78980900
C	-0.63177400	-3.62868700	-1.28071000
H	-1.06875800	-3.85604600	-2.25802100
H	-0.76611900	-4.51629900	-0.65248700
H	-1.19190400	-2.80469100	-0.82822000
C	2.54755700	-2.24762500	-3.01154700
H	2.44201500	-3.01508600	-3.78781400
H	2.87335700	-1.31776500	-3.48856000
H	3.33263600	-2.56895500	-2.31797100
C	1.07480500	-1.20509400	3.66798100
H	-0.00310200	-1.32872000	3.81608500
H	1.49672800	-2.18085700	3.40470600
H	1.51716900	-0.88631400	4.61928000
C	0.81452800	1.20364000	2.99689300
H	-0.24971300	1.12342200	3.24461600
H	1.33996500	1.55691200	3.89111900

H	0.91726800	1.94596200	2.20272400
C	3.44421900	1.17002500	1.69980300
H	3.39584400	1.92493700	2.49001000
H	4.49867400	1.05510700	1.42776000
H	2.91314900	1.55604800	0.82484100
C	-5.49654100	2.14131300	0.20560500
H	-5.46121100	2.82052800	1.05818800
C	-6.64232900	1.99203900	-0.46635100
H	-6.72121000	1.32423100	-1.32042400
H	-7.54220000	2.53089000	-0.18355200

- **TS6tc**



B3LYP/6-31G*

E = -1910.93491799

Zero-point correction = 0.654613 (Hartree/Particle)

Thermal correction to Energy = 0.693640

Thermal correction to Enthalpy = 0.694585

Thermal correction to Gibbs Free Energy = 0.581220

Sum of electronic and zero-point Energies = -1910.280304

Sum of electronic and thermal Energies = -1910.241278

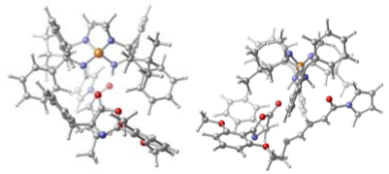
Sum of electronic and thermal Enthalpies = -1910.240333

Sum of electronic and thermal Free Energies = -1910.353698

0 1

O	-2.00992300	-1.05111600	0.54153800
C	-3.22561400	-1.18676300	0.46006900
C	-4.36725500	-0.44182700	0.93476500
O	-3.76543600	-2.19849400	-0.35909100
N	-5.53644700	-1.15525200	0.57128600
C	-5.12428000	-2.09723400	-0.19538900
C	-4.29136000	1.23976200	-0.27743600
C	-3.13498400	2.01912300	-0.01639800
H	-4.26078200	0.64086100	-1.18997800
H	-3.19555200	2.75758400	0.78277800
C	-1.93213700	1.88450600	-0.69427000
H	-1.86051100	1.12310900	-1.46956400
C	-0.79410400	2.67638000	-0.50238700
H	-0.83622100	3.48114900	0.22330000
C	0.38012600	2.46364100	-1.25338000
O	0.57130000	1.54866100	-2.09396300
N	1.49134600	3.35710700	-1.03463300
C	2.70716000	3.19679600	-1.67835000
C	1.58497800	4.45839800	-0.19372800
C	3.56354000	4.17961600	-1.24792800
C	2.84947000	4.98190900	-0.30355200
H	2.82257100	2.39590600	-2.39000600
H	0.74591800	4.78794700	0.39727600
H	4.58496600	4.31862200	-1.57733800
H	3.22034500	5.85040500	0.22546300
H	-0.36224600	-0.49774000	1.16410800
N	0.64959000	-0.53084600	1.31882500
P	1.63682800	-1.36322000	0.31434700
N	2.99816400	-1.05199000	1.22517000
C	2.78953100	0.01747700	2.23117800
C	1.25942000	-0.07268100	2.58341300
C	4.35072400	-1.39964500	0.81294400
H	4.32033400	-2.30524600	0.20181200
H	4.83724300	-0.60521100	0.23264000
H	4.96111500	-1.60604000	1.70010700
H	3.36253000	-0.26779200	3.12401800
N	1.37908900	-0.94511900	-1.23691900
C	1.31332300	-2.06584200	-2.20259400
C	1.04254800	-3.33511200	-1.30859300
N	1.64859600	-2.99926400	0.00261700
H	1.06868400	0.00487000	-1.52336700
C	1.81281000	-4.03788400	1.00847900
H	2.43244400	-3.65725900	1.82419500
H	0.85761300	-4.38032300	1.42681800
H	2.32522600	-4.89936300	0.56377900
H	1.62306700	-4.17200900	-1.71991800
H	-5.72093000	-2.83380100	-0.71827100
H	-4.35382800	0.07911000	1.88266900
C	0.20175100	-1.76905700	-3.21622700
H	0.10996400	-2.58492500	-3.94160700
H	-0.76152100	-1.62361100	-2.72212800
H	0.43860000	-0.85036800	-3.76189400
C	-0.42074400	-3.76963700	-1.17685200
H	-0.82833900	-4.05525700	-2.15161500
H	-0.49638300	-4.64790100	-0.52581200
H	-1.04660000	-2.97767600	-0.75423500
C	2.66169500	-2.21467800	-2.93071600
H	2.61192600	-3.00778200	-3.68650900
H	2.92589400	-1.27770600	-3.43131900
H	3.46341600	-2.46379400	-2.22645900
C	1.03343400	-1.10531800	3.70443400
H	-0.03735500	-1.29214700	3.83733600
H	1.51860100	-2.05783200	3.46628400
H	1.43907200	-0.74324400	4.65659300
C	0.63286400	1.26878200	2.98159400
H	-0.42991000	1.12493100	3.20578700
H	1.11217300	1.67032800	3.88142100
H	0.70724400	2.00295100	2.17664200
C	3.28890200	1.38174000	1.74478400
H	3.17529400	2.13986700	2.52510800
H	4.35444400	1.32986700	1.49787300
H	2.75550700	1.72432500	0.85354600
C	-5.64447000	1.76885000	0.02963000
H	-6.44854600	1.03794900	-0.00897700
C	-5.92882900	3.04220700	0.32596500
H	-5.16909800	3.81801800	0.35112600
H	-6.94967400	3.35164000	0.53408300

- **TS3rs**



B3LYP/6-31G*

E = -3606.12498938

Zero-point correction = 1.287895 (Hartree/Particle)

Thermal correction to Energy = 1.363400

Thermal correction to Enthalpy = 1.364344

Thermal correction to Gibbs Free Energy = 1.169123

Sum of electronic and zero-point Energies = -3604.837095

Sum of electronic and thermal Energies = -3604.761590

Sum of electronic and thermal Enthalpies = -3604.760646

Sum of electronic and thermal Free Energies = -3604.955867

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

E = -3606.58239161

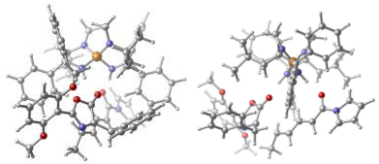
G = -3605.413269

0 1

O	1.08142700	0.64786200	0.31156500
C	2.23227700	0.81633900	0.71107300
C	2.86050100	1.78155300	1.57841800
O	3.22370700	-0.13178000	0.42563300
N	4.24804800	1.50182700	1.58681800
C	4.38960000	0.38483000	0.96619700
C	5.63311800	-0.38268300	0.75507600
C	5.93219800	-1.49743300	1.55774800
C	6.54857000	0.01069500	-0.23871000
C	7.12872200	-2.20437800	1.38272500
C	7.74748300	-0.69177500	-0.42133600
C	8.01831300	-1.78801400	0.39434600
O	4.99106200	-1.81670700	2.49515100
C	5.28868500	-2.84327900	3.43187200
H	6.19519500	-2.60981300	4.00423800
H	5.41031400	-3.81643800	2.93913100
H	4.43232800	-2.88561500	4.10660800
O	6.17740200	1.09012600	-0.97960300
C	7.04513800	1.54305900	-2.00620100
H	8.01561600	1.86075700	-1.60325300
H	7.20508800	0.77057800	-2.76977800
H	6.54247000	2.39990000	-2.45803100
H	7.36812900	-3.06151100	1.99971300
H	8.45875900	-0.39537900	-1.18243300
H	8.94747900	-2.33435100	0.25532800
C	2.38679900	3.21200900	1.66593000
H	1.32068900	3.20834300	1.91734700
H	2.91300400	3.69479000	2.49899600
C	2.60345000	4.03140600	0.39963500
C	1.52724900	4.67403700	-0.22507400
C	3.88381100	4.17766900	-0.15792700
C	1.71875100	5.44409900	-1.37598600
C	4.07650800	4.94701900	-1.30505700
C	2.99530000	5.58409300	-1.92043000
H	0.52966000	4.57689400	0.19606800
H	4.72453100	3.67097000	0.30696500
H	0.86728100	5.93285300	-1.84304800
H	5.07700000	5.05478100	-1.71850100
H	3.14873100	6.18672000	-2.81241400
C	2.25665600	0.87597100	3.41766000
C	0.85959400	0.92500500	3.63989000
H	2.66158100	-0.08641600	3.10452700
H	0.47451500	1.77055100	4.21306400
C	-0.04370200	-0.05459600	3.23588300
H	0.34076800	-0.89301000	2.65756500
C	-1.40275600	-0.09808200	3.56427900
H	-1.81525100	0.68013300	4.19820600
C	-2.24836500	-1.14214200	3.12253700
O	-1.97847100	-2.01088400	2.25741000
N	-3.55995400	-1.21741500	3.70484300
C	-4.59342700	-1.95552700	3.15321700
C	-4.01911100	-0.62528900	4.87296100
C	-5.70054100	-1.82181900	3.95472000
C	-5.33303300	-0.98019800	5.05173900
H	-4.42957100	-2.49961100	2.23730900
H	-3.35926600	-0.04232800	5.49530300
H	-6.66558400	-2.28093000	3.78368500
H	-5.95974100	-0.68290500	5.88245900
C	3.15579700	1.62434600	4.37881300
H	4.16674800	1.74149100	3.98224700
H	2.75046300	2.61387200	4.61998400
H	3.21737100	1.06336600	5.32199200
H	-0.60995100	1.04366300	-0.31062600
N	-1.55583300	0.89289500	-0.67317300
P	-1.98488700	-0.54958700	-1.33535100
N	-3.56354200	-0.08715100	-1.55291600
C	-3.88502000	1.20473600	-0.90191300
C	-2.50820800	1.98638200	-0.95712700
C	-4.63554000	-0.92779100	-2.06555700
H	-4.21341800	-1.83303900	-2.50634900
H	-5.33226900	-1.22642200	-1.27273600
H	-5.19842800	-0.39003400	-2.83919800
H	-4.61579000	1.70580400	-1.54092800
C	-4.49950400	1.02094400	0.50434000
H	-4.96087800	0.02617300	0.55259400
H	-3.70221600	1.00946900	1.25372500
C	-5.57209800	2.06561800	0.88953600
H	-5.19878100	3.06235000	0.61959700
C	-6.89089200	1.83061600	0.13446400
C	-5.81042500	2.05091700	2.40617400
C	-2.40157900	3.09840600	0.09854300
C	-1.83301400	2.86241400	1.35721400
C	-2.90054800	4.38097700	-0.17962800
C	-1.77770700	3.88039500	2.31375400
C	-2.84876900	5.39349500	0.77770400
C	-2.28568400	5.14755700	2.03132500
H	-1.43206900	1.88644700	1.60624300
H	-3.32570000	4.59628700	-1.15471200
H	-1.32891400	3.67270300	3.28116200
H	-3.24223800	6.37783500	0.53815100
H	-2.23832200	5.93753300	2.77591300
C	-2.20708100	2.57845500	-2.36108100
C	-0.86396000	2.81363800	-2.69878300
C	-3.18924600	2.93421800	-3.29452900
C	-0.51508300	3.37279400	-3.92642100
C	-2.84169800	3.48755600	-4.53176900
C	-1.50445600	3.70782300	-4.85421100
H	-0.07862300	2.56321900	-1.99240800
H	-4.24284500	2.79373300	-3.07548200
H	0.53283700	3.55232700	-4.15022200
H	-3.62511400	3.74787000	-5.23890600
H	-1.23505000	4.14054700	-5.81389400
N	-1.34789200	-1.74637800	-0.42237400
C	-0.96796400	-2.95530500	-1.19363800
C	-0.51940100	-2.32172100	-2.57207100
N	-1.50583000	-1.23183200	-2.77031600
H	-1.47563400	-1.78664400	0.60632400
C	-1.71374000	-0.66875000	-4.09619900
H	-2.50628900	0.08035000	-4.05446800
H	-0.81136900	-0.18436800	-4.48874500
H	-2.01600300	-1.46208900	-4.79103200
H	-0.67560600	-3.04563400	-3.37415500
C	0.92594900	-1.78133800	-2.66260800
H	0.91657400	-0.97437000	-3.40878500
H	1.19562100	-1.30243800	-1.71625700
C	2.03039700	-2.77554400	-3.08603300
H	2.00617400	-3.64178700	-2.41541900
C	1.84163300	-3.28274000	-4.52508600
C	3.40355100	-2.10366800	-2.93069000
C	0.17405500	-3.69709300	-0.48381900
C	1.08328000	-3.00766100	0.32928700
C	0.35934100	-5.07291900	-0.68293300
C	2.16327000	-3.67308900	0.91156800
C	1.43535400	-5.73895700	-0.09572300
C	2.34326800	-5.04058000	0.70166400
H	0.96159000	-1.94301100	0.49290400

H	-0.34103000	-5.63167400	-1.29546700
H	2.86787900	-3.10717400	1.51396700
H	1.55971500	-6.80605800	-0.26146100
H	3.18280900	-5.56064900	1.15620700
C	-2.20632700	-3.88145200	-1.32562300
C	-2.64137400	-4.46052400	-2.52392600
C	-2.92634400	-4.17301700	-0.15246000
C	-3.76806800	-5.29086100	-2.55786700
C	-4.04433800	-5.00363700	-0.18531600
C	-4.47534300	-5.56516000	-1.39040900
H	-2.11323800	-4.28219400	-3.45471900
H	-2.61253400	-3.74243400	0.79441900
H	-4.08402800	-5.72277500	-3.50413000
H	-4.57853700	-5.21514000	0.73742800
H	-5.34850800	-6.21165600	-1.41567900
H	4.21183000	-2.79684400	-3.19318500
H	3.48834000	-1.22896500	-3.59011600
H	3.56507500	-1.76280100	-1.90291500
H	2.64979800	-3.96983900	-4.80219800
H	0.89816700	-3.82506200	-4.66267200
H	1.85559900	-2.45034300	-5.24184000
H	-7.62423900	2.60870500	0.37666600
H	-6.76031300	1.83533000	-0.95542800
H	-7.32975900	0.86336300	0.41192700
H	-6.58332300	2.77598100	2.68923800
H	-6.13333400	1.06021800	2.74812600
H	-4.89429200	2.30479400	2.95017000

- **TS3sr**



B3LYP/6-31G*

E = -3606.12079434

Zero-point correction = 1.287643 (Hartree/Particle)

Thermal correction to Energy = 1.363154

Thermal correction to Enthalpy = 1.364098

Thermal correction to Gibbs Free Energy = 1.168678

Sum of electronic and zero-point Energies = -3604.833151

Sum of electronic and thermal Energies = -3604.757641

Sum of electronic and thermal Enthalpies = -3604.756697

Sum of electronic and thermal Free Energies = -3604.952117

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

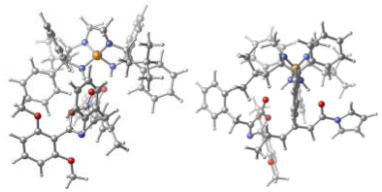
E = -3606.57577799

G = -3605.407100

0 1

O	-0.94506500	0.89118900	0.16630600
C	-2.12029000	1.08558200	0.48498300
C	-2.78405300	2.07251600	1.31149800
O	-3.09709500	0.14926900	0.15180700
N	-4.16790500	1.78545500	1.26542700
C	-4.29180200	0.67209300	0.63125300
C	-5.51975900	-0.08165700	0.33500900
C	-6.38262500	-0.50480100	1.36800200
C	-5.87204700	-0.36989800	-1.00089900
C	-7.56883500	-1.18954400	1.07071800
C	-7.05374500	-1.05790500	-1.30071100
C	-7.88682600	-1.45697800	-0.25811300
O	-5.97854100	-0.22516000	2.63716600
C	-6.81598600	-0.60245200	3.71808900
H	-7.79797900	-0.11634400	3.65535800
H	-6.30310300	-0.26379100	4.61975700
H	-6.95236100	-1.69094600	3.76409700
O	-5.00357100	0.08581500	-1.94751100
C	-5.37135800	-0.01556600	-3.31317300
H	-6.32247100	0.49439300	-3.51344800
H	-5.44984300	-1.06240400	-3.63700100
H	-4.57193000	0.47598900	-3.87052400
H	-8.23377600	-1.51798100	1.85967100
H	-7.32816200	-1.27497200	-2.32560000
H	-8.80627500	-1.98928500	-0.48681300
C	-2.33935000	3.51612300	1.37044400
H	-1.26296400	3.52648700	1.56857700
H	-2.82865600	3.98528800	2.23373700
C	-2.64033200	4.33436200	0.12423400
C	-1.60287500	4.81440500	-0.68461400
C	-3.96196100	4.64886200	-0.22846100
C	-1.87332900	5.59354700	-1.81261800
C	-4.23479300	5.42228300	-1.35631400
C	-3.19096800	5.90067100	-2.15271800
H	-0.57243900	4.57860000	-0.42946100
H	-4.77536300	4.27194000	0.38519100
H	-1.05132100	5.96410000	-2.42069500
H	-5.26548900	5.65680100	-1.61193700
H	-3.40390400	6.50968300	-3.02784000
C	-2.11842200	1.30497600	3.18051800
C	-0.82915000	1.80055500	3.50350800
H	-2.16784200	0.27054100	2.84251600
H	-0.78931500	2.70351300	4.11526800
C	0.38065400	1.23802500	3.10866300
H	0.35511100	0.36249500	2.46494200
C	1.64943600	1.68414500	3.49185100
H	1.72015500	2.51848100	4.18124200
C	2.83055800	1.03354800	3.07468400
O	2.90846200	0.04262600	2.29681100
N	4.07611700	1.52827100	3.58861700
C	4.33904000	2.74355900	4.20612600
C	5.25641200	0.80465800	3.53167000
C	5.67078700	2.78461300	4.53411900
C	6.25298000	1.54861800	4.11212400
H	3.56988300	3.49077000	4.31592600
H	5.25262700	-0.18562200	3.10639800
H	6.17674300	3.61235000	5.01385500
H	7.28452200	1.24329500	4.22957200
C	-3.26975000	1.70095500	4.08097300
H	-3.24188900	2.77218600	4.31257200
H	-3.17954800	1.16273600	5.03564400
H	-4.23707000	1.46497400	3.63495500
H	-0.32384400	-0.85252500	-0.11127300
N	0.36993900	-1.59974900	-0.25089700
P	1.75263000	-1.25582200	-1.06988700
N	2.34844200	-2.79691300	-0.93651600
C	1.54882800	-3.61498900	0.01271100
C	0.08284600	-3.05052100	-0.17677500
C	3.52980500	-3.32738900	-1.60596500
H	3.94537100	-2.56778700	-2.27099900
H	4.31061600	-3.60918800	-0.89485500
H	3.26527500	-4.20908900	-2.20491300
H	1.60156700	-4.65516500	-0.31836800
C	2.03634500	-3.50677400	1.47253800
H	1.88323500	-2.47560800	1.81067800
H	1.38654300	-4.13927700	2.08980000
C	3.49963900	-3.89408200	1.76780900
C	3.82180300	-3.53934200	3.22834500
C	3.79482900	-5.37624600	1.49063100
H	4.15808600	-3.27802300	1.14116300
C	-0.82964400	-3.39845600	1.00649700
C	-1.06490700	-2.50043700	2.05276500
C	-1.41787800	-4.67075500	1.07265300
C	-1.86514400	-2.86220000	3.13828900
C	-2.21055800	-5.03554800	2.15970100
C	-2.44008900	-4.13064100	3.19781400
H	-0.61205100	-1.51714900	2.03107200
H	-1.26543500	-5.37968600	0.26422900
H	-2.03173800	-2.14598400	3.93817700
H	-2.65555700	-6.02667600	2.18973600
H	-3.06264100	-4.41221000	4.04277300
C	-0.59539600	-3.50815500	-1.49412300
C	-1.70278500	-2.76912100	-1.94540000
C	-0.19020900	-4.61473800	-2.25012500
C	-2.36859400	-3.11903400	-3.11729400
C	-0.85804900	-4.96625000	-3.42917100
C	-1.94753600	-4.21901300	-3.86949700
H	-2.05756300	-1.91586500	-1.37373400
H	0.65117500	-5.22423900	-1.93682900
H	-3.22290400	-2.52967700	-3.43911700
H	-0.51969700	-5.82867600	-3.99782900
H	-2.46664400	-4.49187800	-4.78437600
N	2.39187700	0.11930700	-0.45665800
C	3.11689300	0.92879600	-1.46309300
C	2.21901800	0.68301200	-2.74272600
N	1.88126100	-0.76216300	-2.64614100
H	2.57062400	0.20126400	0.56014900
C	1.73424300	-1.59474700	-3.83305000
H	0.90155400	-1.26786800	-4.46142900
H	1.53862100	-2.62604600	-3.53486400
H	2.65520600	-1.57121000	-4.43074400
H	2.81245800	0.81841900	-3.64931400
C	0.97638000	1.59289200	-2.80304500
H	1.32461800	2.63114300	-2.86742600
H	0.43220700	1.50580700	-1.85624300
C	-0.01052800	1.34224000	-3.96301500
H	-0.33872000	0.29470300	-3.92036900
C	-1.26462700	2.20788200	-3.76394500
C	0.61236200	1.60858900	-5.34246200
C	4.56079900	0.38489600	-1.62371900
C	5.20637100	0.21794100	-2.85588200
C	5.27886000	0.07424600	-0.45608300
C	6.51987900	-0.26024100	-2.92403000
C	6.58894400	-0.39489200	-0.52245900
C	7.21654500	-0.56980900	-1.75844100
H	4.70276600	0.46194100	-3.78591100
H	4.80856700	0.19771000	0.51515200
H	6.99343400	-0.38413600	-3.89466900
H	7.12163400	-0.61802200	0.39814000
H	8.23787800	-0.93743400	-1.80996400
C	3.16184300	2.40550400	-1.04125300
C	4.07085800	3.28052400	-1.65456700
C	2.29372000	2.91463000	-0.06673100
C	4.10940800	4.63013700	-1.30621700
C	2.34687300	4.26316700	0.29334500
C	3.25008700	5.12706300	-0.32495100
H	4.76668300	2.90518200	-2.39881800
H	1.56533900	2.26785700	0.40842200
H	4.82333400	5.28921800	-1.79333000
H	1.67852000	4.63090300	1.06716700
H	3.29005400	6.17528900	-0.04108100
H	-0.11750000	1.43726300	-6.14279300
H	0.94771800	2.65110500	-5.41961300
H	1.47818700	0.96783900	-5.54889200
H	-1.99205700	2.03403800	-4.56715000
H	-1.75136400	1.98827400	-2.80796300
H	-1.01693300	3.27629600	-3.76650200
H	4.83650000	-5.61991100	1.73098900
H	3.15470800	-6.02058600	2.10760700
H	3.62951800	-5.65447300	0.44248200
H	4.86433600	-3.77790200	3.47136500
H	3.66098300	-2.47133300	3.40920000
H	3.18187500	-4.10255600	3.92037000

- **TS3ss**



B3LYP/6-31G*

E = -3606.11970801

Zero-point correction = 1.287123 (Hartree/Particle)

Thermal correction to Energy = 1.362932

Thermal correction to Enthalpy = 1.363877

Thermal correction to Gibbs Free Energy = 1.166580

Sum of electronic and zero-point Energies = -3604.832585

Sum of electronic and thermal Energies = -3604.756776

Sum of electronic and thermal Enthalpies = -3604.755831

Sum of electronic and thermal Free Energies = -3604.953128

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

E = -3606.57597854

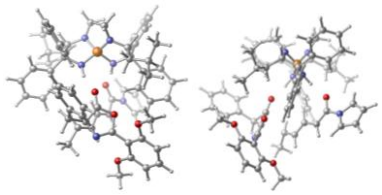
G = –3605.409399

0 1

O	-0.95621300	-1.49484800	0.09338200
C	-2.10051400	-1.46017900	-0.38399100
C	-2.83069300	-2.37687100	-1.21635200
O	-2.89269000	-0.34164100	-0.26617200
N	-4.11849200	-1.84451700	-1.41575300
C	-4.08909600	-0.66122500	-0.90789400
C	-5.15215200	0.35389600	-0.87660200
C	-5.60098800	0.86471500	0.36120300
C	-5.75616300	0.82354600	-2.06185800
C	-6.61080600	1.83378900	0.41564700
C	-6.77438000	1.78615000	-2.00917600
C	-7.18399000	2.27954500	-0.77287300
O	-5.01026800	0.32610900	1.45986500
C	-5.39569400	0.79005500	2.74343500
H	-6.46013200	0.60146400	2.93698800
H	-5.18205100	1.85897300	2.86273800
H	-4.79205600	0.22260800	3.45371100
O	-5.27707800	0.30738800	-3.22837500
C	-5.86526800	0.72924900	-4.44804500
H	-5.73593800	1.80767500	-4.61002900
H	-5.34156000	0.18170500	-5.23349500
H	-6.93451800	0.48408900	-4.48620500
H	-6.95633800	2.22413800	1.36487000
H	-7.23948000	2.15362700	-2.91526300
H	-7.97241000	3.02681400	-0.73532800
C	-2.64417000	-3.87329800	-1.09646200
H	-1.59872000	-4.12831800	-1.30953900
H	-3.26405900	-4.36263400	-1.85427100
C	-3.02037800	-4.40393900	0.27855100
C	-2.04482800	-4.60777100	1.26356000
C	-4.35911500	-4.66882300	0.59940400
C	-2.39488300	-5.07213000	2.53331600

C	-4.71239100	-5.13095400	1.86729600
C	-3.73091300	-5.33708200	2.83961000
H	-1.00573300	-4.38730000	1.03261500
H	-5.12689400	-4.49898200	-0.15123400
H	-1.62146900	-5.23511300	3.28076800
H	-5.75598100	-5.33309500	2.09599200
H	-4.00521900	-5.70349800	3.82570200
C	-1.78832400	-1.80138900	-3.05679800
C	-1.69869600	-0.40411900	-3.23923300
H	-0.88380200	-2.29569800	-2.70090900
H	-2.49820500	0.08916200	-3.79026000
C	-0.62345900	0.36087600	-2.79025800
H	0.13787100	-0.16021900	-2.21296400
C	-0.40724600	1.71834800	-3.02985200
H	-1.15404500	2.27332500	-3.58709400
C	0.79895400	2.37085300	-2.67015100
O	1.81792400	1.85415700	-2.14980400
N	0.88952500	3.77589000	-2.94967700
C	2.08824900	4.46955500	-2.94686100
C	-0.13292700	4.67002500	-3.24187900
C	1.83211100	5.78447800	-3.24358800
C	0.41879000	5.91306800	-3.42457500
H	3.00557000	3.94081800	-2.74703300
H	-1.16330100	4.35316300	-3.25716400
H	2.57143500	6.57008300	-3.32854500
H	-0.12814000	6.81804200	-3.65515700
C	-2.63557800	-2.58412200	-4.03508000
H	-3.65598700	-2.18944900	-4.05628800
H	-2.21054800	-2.49102300	-5.04453600
H	-2.68298200	-3.64918800	-3.79629800
H	-0.01922400	-0.14470400	0.76671000
N	0.70437400	0.46865000	1.18239100
P	2.28845700	0.04179700	1.09724000
N	2.78058400	1.23020600	2.14514100
C	1.71540300	2.22956400	2.39238400
C	0.39820900	1.35833000	2.32852400
C	4.15097500	1.52374100	2.53675300
H	4.18912600	1.72640200	3.61425700
H	4.55751500	2.39140700	2.00268400
H	4.78675600	0.66388600	2.32001800
H	1.86020700	2.60710500	3.40712800
C	1.79652900	3.41003200	1.39576900
H	2.84326200	3.50420500	1.07641000
H	1.23873600	3.15603700	0.48958300
C	1.34492000	4.78546000	1.93596700
H	0.38659700	4.66063800	2.45471000
C	1.12218900	5.76139800	0.77136300
C	2.35679200	5.36404000	2.93866800
C	-0.85365800	2.20572800	2.04942700
C	-1.51432500	2.84544500	3.11009700
C	-1.34142600	2.38970600	0.75053400
C	-2.61829600	3.66419700	2.87486400
C	-2.45664000	3.19717200	0.51752600
C	-3.09588100	3.84315000	1.57420600
H	-1.16934300	2.70127400	4.12923900
H	-0.86338500	1.89901200	-0.08872800
H	-3.10724100	4.15774200	3.71124100
H	-2.82469100	3.30848500	-0.49802300
H	-3.96209500	4.47252600	1.38840500
C	0.17536100	0.50215400	3.60429700
C	-0.59400100	-0.66884100	3.48855100
C	0.66166600	0.84329800	4.87341700
C	-0.85619300	-1.47168400	4.59735200
C	0.40305000	0.03638500	5.98675800
C	-0.35547400	-1.12481900	5.85451100
H	-0.98873200	-0.96634400	2.52187800
H	1.24665300	1.74548500	5.02164900
H	-1.45430600	-2.37044100	4.47035100
H	0.79851700	0.32427500	6.95760100
H	-0.55644400	-1.75080800	6.71987400
N	2.68031400	-0.17829500	-0.48472000
C	3.79113200	-1.13543400	-0.67793300
C	3.44958100	-2.20122800	0.43720700
N	3.04449300	-1.35331100	1.58346600
H	2.38487200	0.51732900	-1.19036300
C	3.05217200	-1.89840200	2.93269900
H	2.35261100	-2.73655600	3.04212500
H	2.76455600	-1.12079100	3.64293500
H	4.06042700	-2.24890400	3.18623700
H	4.35570300	-2.73202000	0.73872800
C	2.35348900	-3.22789000	0.06189900
H	1.68514400	-2.78316200	-0.68227000
H	1.72869200	-3.38931700	0.95034000
C	2.85460900	-4.60625000	-0.42324500
H	3.62031200	-4.44894000	-1.19292800
C	3.48316500	-5.42399500	0.71690700
C	1.70208500	-5.38848400	-1.06978000
C	3.80730600	-1.72908700	-2.09476700
C	4.89052100	-2.53186000	-2.48977000
C	2.78720000	-1.49097200	-3.02112100
C	4.93735200	-3.09880700	-3.76160800
C	2.83742900	-2.05294800	-4.30025900
C	3.90682800	-2.86295900	-4.67468400
H	5.71385900	-2.70639500	-1.80348300
H	1.95602300	-0.84778600	-2.76670500
H	5.78573800	-3.71769500	-4.04171300
H	2.03396400	-1.84428300	-5.00122200
H	3.94557200	-3.29794500	-5.66967900
C	5.14538300	-0.41415000	-0.43709100
C	6.22190700	-0.97664500	0.26035900
C	5.31462400	0.86622400	-0.99082200
C	7.42450500	-0.27904200	0.41491800
C	6.51379900	1.56017700	-0.84218700
C	7.57599600	0.99208600	-0.13445700
H	6.14477000	-1.96766100	0.69649300
H	4.49715300	1.32655600	-1.53860400
H	8.24102000	-0.73754900	0.96682600
H	6.61817600	2.54809700	-1.28301700
H	8.51039900	1.53394200	-0.01630100
H	2.03811500	-6.37180300	-1.41968200
H	0.88536600	-5.55254300	-0.35443200
H	1.29183300	-4.84720600	-1.92978200
H	3.85814100	-6.38569200	0.34770500
H	4.32734200	-4.90752000	1.19084000
H	2.74271700	-5.63567800	1.49968000
H	2.00151800	6.31789700	3.34590500
H	2.53709900	4.69513000	3.78982000
H	3.32400600	5.55091600	2.45321800
H	0.82554900	6.75122700	1.13923900
H	2.03517200	5.88498800	0.17559800
H	0.33869200	5.40315400	0.09568300

● **TS3rr**



B3LYP/6-31G*

E = -3606.11856516

Zero-point correction = 1.288149 (Hartree/Particle)

Thermal correction to Energy = 1.363716

Thermal correction to Enthalpy = 1.364660

Thermal correction to Gibbs Free Energy = 1.167428

Sum of electronic and zero-point Energies = -3604.830416

Sum of electronic and thermal Energies = -3604.754850

Sum of electronic and thermal Enthalpies = -3604.753905

Sum of electronic and thermal Free Energies = -3604.951137

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

E = -3606.57313772

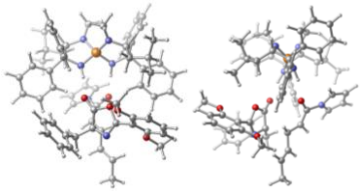
G = -3605.405710

0 1

O	-0.86350000	-1.25935400	-0.13758400
C	-2.01968400	-1.35398000	0.28559600
C	-2.68696000	-2.29794500	1.15040100
O	-2.94009800	-0.34532600	0.05011400
N	-4.04065000	-1.90603500	1.24747200
C	-4.11982100	-0.76453100	0.66037400
C	-5.30440400	0.10022700	0.50929400
C	-5.91472600	0.71078700	1.62426200
C	-5.87698700	0.29145500	-0.76494100
C	-7.05777200	1.50696800	1.46302800
C	-7.01608800	1.08866200	-0.93122000
C	-7.58903700	1.68668000	0.18872300
O	-5.32539600	0.48426900	2.83031300
C	-5.90620800	1.06141600	3.98919100
H	-6.93134100	0.70247600	4.14723100
H	-5.90985300	2.15808200	3.93741200
H	-5.27931600	0.74258100	4.82353300
O	-5.26185300	-0.37064200	-1.78517500
C	-5.86885300	-0.35047000	-3.06818900
H	-6.89100400	-0.74911300	-3.03219700
H	-5.88779400	0.66166400	-3.49167100
H	-5.24856600	-0.98975800	-3.69781600
H	-7.52823600	1.98325800	2.31396500
H	-7.45631600	1.23709800	-1.90938100
H	-8.47413600	2.30530700	0.06585600
C	-2.34190900	-3.77087100	1.13583000
H	-1.30943600	-3.91372600	1.47885500
H	-2.98982400	-4.27079800	1.86521900
C	-2.50677600	-4.46698700	-0.20995800
C	-1.49920900	-5.30708700	-0.70045300
C	-3.67974800	-4.32211500	-0.96608300
C	-1.65527400	-5.98959000	-1.90990100
C	-3.83570500	-4.99817100	-2.17614600
C	-2.82546800	-5.83658800	-2.65391400
H	-0.58267000	-5.43146200	-0.12747800
H	-4.46853300	-3.67091400	-0.60041300
H	-0.86315800	-6.64492400	-2.26508700
H	-4.75306000	-4.87332600	-2.74658500
H	-2.95118400	-6.36685800	-3.59458000
C	-1.86100600	-1.56802400	2.99948900
C	-1.88354400	-0.15950800	3.13619200
H	-0.89554100	-2.00477200	2.74589800
H	-2.74754000	0.28784700	3.62440500
C	-0.84224300	0.67087000	2.73144200
H	-0.00851900	0.20661100	2.20910200
C	-0.72297000	2.04118300	2.96461800
H	-1.50600500	2.55508200	3.51112800
C	0.44402800	2.74939800	2.59677200
O	1.45817400	2.27133000	2.02083600
N	0.50723500	4.14080200	2.93558800
C	1.69470600	4.85219500	2.98518300
C	-0.53180900	4.99869200	3.26850300
C	1.41344000	6.14390000	3.35307400
C	-0.00340200	6.23881400	3.52524500
H	2.62394800	4.34546400	2.78152600
H	-1.55695900	4.66571500	3.24196600
H	2.13841000	6.93560300	3.48990700
H	-0.56834400	7.12184800	3.79445400
C	-2.70743100	-2.36475000	3.97007600
H	-2.34305300	-2.19619300	4.99313700
H	-2.67293400	-3.44036700	3.78310900
H	-3.75124800	-2.04022400	3.92227800
H	0.96672700	-1.28536800	0.14199600
N	1.96190000	-1.05177600	0.05133200
P	2.42413400	0.14893700	-0.97759000
N	4.04071600	-0.13556800	-0.73781700
C	4.30782100	-1.07988100	0.37092600
C	3.03216800	-2.02643400	0.34892000
C	5.13343600	0.62623800	-1.32504200
H	4.75191800	1.24113100	-2.14234900
H	5.61075100	1.29233200	-0.59601900
H	5.89334800	-0.05713700	-1.72459800
H	5.18945500	-1.65775100	0.08662600
C	4.60371000	-0.33214100	1.68914800
H	3.66152000	-0.02371300	2.15280000
H	5.11705700	0.60233900	1.42476100
C	5.49147700	-1.07257000	2.71472800
H	5.08846300	-2.08062000	2.86935000
C	5.44680800	-0.34021700	4.06416200
C	6.94403700	-1.21009600	2.22889400
C	3.11588500	-3.08067100	-0.78749300
C	4.31642300	-3.67795600	-1.19822800
C	1.92831000	-3.49991500	-1.41009900
C	4.33562600	-4.64078500	-2.21152100
C	1.94477200	-4.46448400	-2.41768900
C	3.15022300	-5.03610900	-2.82886700
H	5.25778800	-3.41228200	-0.72712600
H	0.97507900	-3.07210200	-1.11430200
H	5.28299400	-5.08063800	-2.51239300
H	1.00649600	-4.76738500	-2.87388800
H	3.16463800	-5.78415400	-3.61695600
C	2.75821300	-2.71250000	1.69978900
C	2.04763100	-2.04734800	2.70964800
C	3.23591600	-4.00404400	1.96694500
C	1.83056500	-2.64966500	3.95038300
C	3.02386500	-4.60427400	3.20907100
C	2.32041600	-3.93028500	4.20749100
H	1.66460700	-1.04975700	2.53102000
H	3.77141300	-4.55423800	1.20118100
H	1.27198400	-2.11106100	4.71089400
H	3.40422400	-5.60626400	3.38959900
H	2.14969500	-4.40037500	5.17215700
N	1.52332300	1.46564300	-0.63286000
C	1.24876600	2.33997200	-1.79512900
C	1.18087200	1.28383200	-2.98028100
N	2.22558800	0.29516200	-2.61429700
H	1.40096800	1.78877500	0.34479200
C	2.79386700	-0.57571300	-3.63259600
H	3.22888000	0.02976500	-4.43771500
H	2.04428000	-1.24830800	-4.06628900
H	3.58134500	-1.18872100	-3.19054700
H	1.51752400	1.75813300	-3.90350700
C	-0.17100600	0.58811800	-3.24136400
H	-0.64774200	0.34164000	-2.28768500
H	0.05419400	-0.37829200	-3.71442200
C	-1.16689700	1.32470100	-4.16390800
H	-1.32555600	2.33777400	-3.77805000
C	-2.51880900	0.59658800	-4.13435900
C	-0.65351500	1.44006200	-5.60877800
C	-0.07549500	3.09115700	-1.56887800
C	-1.09887800	2.51125000	-0.80555000

C	-0.30129600	4.35036400	-2.14447800
C	-2.32087000	3.16392600	-0.63816600
C	-1.52342500	5.00202100	-1.97590800
C	-2.53944300	4.41071500	-1.22377800
H	-0.95403800	1.54220800	-0.34363600
H	0.47983300	4.83440500	-2.72090100
H	-3.09605100	2.68270800	-0.04947700
H	-1.67473500	5.97904400	-2.42779600
H	-3.48984400	4.92106000	-1.09050800
C	2.42070000	3.33993400	-1.97838000
C	3.02876100	3.87323100	-0.82929200
C	2.87673900	3.78429400	-3.22727700
C	4.06565100	4.79971000	-0.92924800
C	3.92137900	4.70838300	-3.32878300
C	4.52375700	5.21771700	-2.18033200
H	2.68255400	3.56800100	0.15360700
H	2.41743600	3.43082500	-4.14514800
H	4.51139000	5.20022300	-0.02255100
H	4.25672400	5.02968500	-4.31163100
H	5.33431200	5.93741200	-2.25804400
H	6.07387800	-0.84517500	4.80842800
H	5.81157500	0.69071000	3.96521800
H	4.42520500	-0.29653500	4.45687700
H	7.55165600	-1.74628200	2.96708200
H	7.02328700	-1.76171300	1.28399000
H	7.40193300	-0.22366300	2.07656900
H	-1.39005800	1.94787800	-6.24260000
H	0.28026500	2.01094100	-5.68238800
H	-0.47199200	0.44747400	-6.04294600
H	-3.25460900	1.11302300	-4.76338100
H	-2.41787300	-0.42941200	-4.51465800
H	-2.91791400	0.53686000	-3.11632700

- **TS4rs**



B3LYP/6-31G*

E = -3606.10803320

Zero-point correction = 1.286869 (Hartree/Particle)

Thermal correction to Energy = 1.362748

Thermal correction to Enthalpy = 1.363692

Thermal correction to Gibbs Free Energy = 1.166750

Sum of electronic and zero-point Energies = -3604.821164

Sum of electronic and thermal Energies = -3604.745285

Sum of electronic and thermal Enthalpies = -3604.744341

Sum of electronic and thermal Free Energies = -3604.941283

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

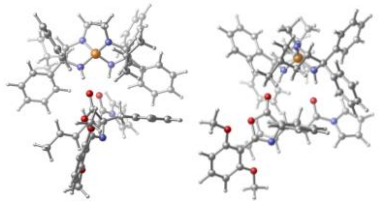
E = -3606.56386634

G = -3605.397116

0 1

O	0.69264600	-1.57057800	0.17878700
C	1.86471600	-1.32639600	-0.09025700
C	2.82484300	-2.00039700	-0.94135400
O	2.51613700	-0.20303400	0.41761900
N	4.08061400	-1.38368900	-0.70496400
C	3.84434900	-0.35404600	0.02428300
C	4.81580400	0.63310400	0.53299300
C	5.52575200	1.48703400	-0.33314100
C	5.08978100	0.69081700	1.91558800
C	6.49145700	2.37086200	0.16756300
C	6.05041400	1.57543400	2.42190800
C	6.73945900	2.40170900	1.53741400
O	5.19592500	1.41167900	-1.65659300
C	5.93560300	2.19184200	-2.58580300
H	7.00401600	1.94432200	-2.55439700
H	5.80589900	3.26664900	-2.40443000
H	5.53250500	1.94008600	-3.56786900
O	4.37826400	-0.17709300	2.68388200
C	4.64888600	-0.23678400	4.07450000
H	5.69495300	-0.50594400	4.27032200
H	4.42074100	0.71560200	4.57114600
H	3.99560100	-1.01699600	4.46848300
H	7.03819200	3.03196800	-0.49294300
H	6.26717600	1.61692200	3.48212700
H	7.48755100	3.08800900	1.92527500
C	2.77121900	-3.50807400	-1.08650500
H	1.77683300	-3.77566800	-1.46233200
H	3.50263500	-3.79814500	-1.84837600
C	3.05298100	-4.25818000	0.20333500
C	2.00622700	-4.74720400	0.99659600
C	4.37128100	-4.46274800	0.63561600
C	2.26925400	-5.42817200	2.18701800
C	4.63676100	-5.14250700	1.82439600
C	3.58563800	-5.63028600	2.60464400
H	0.97902000	-4.58905000	0.67817500
H	5.19017600	-4.07428900	0.03558000
H	1.44309200	-5.80518400	2.78546400
H	5.66618900	-5.29499300	2.14041100
H	3.79173400	-6.16584400	3.52829200
C	2.30605800	-1.27712300	-2.79886800
C	0.95513400	-1.52247300	-3.18889000
H	2.52756700	-0.25082100	-2.51218200
H	0.75733000	-2.38209900	-3.81934300
C	-0.06319100	-0.57830100	-2.99972800
O	0.02534000	0.51389000	-2.38204400
N	-1.32797900	-0.83122000	-3.66275700
C	-1.83062600	-2.02403500	-4.15252300
C	-2.19863400	0.18452800	-4.01042400
C	-3.01580100	-1.76466400	-4.80116600
C	-3.24733300	-0.35802200	-4.71574800
H	-1.32113400	-2.95695800	-3.97057800
H	-1.94578400	1.20422900	-3.76786000
H	-3.64875500	-2.50162900	-5.27803300
H	-4.07945800	0.19078200	-5.13741600
C	3.33076900	-1.91453400	-3.65362500
H	3.00542200	-2.79962700	-4.20337000
C	4.58421500	-1.47249900	-3.82588400
H	4.91229600	-0.60474900	-3.25682000
C	5.59519400	-2.10760600	-4.73468900
H	5.18279200	-2.98051000	-5.25296500
H	6.48202500	-2.43342300	-4.17307000
H	5.95235300	-1.40053800	-5.49713600
H	-0.89135200	-0.90737600	0.54335100
N	-1.88036500	-0.63232900	0.63172600
P	-2.33987300	0.94212500	0.70457200
N	-3.95611700	0.57189100	0.75100200
C	-4.23470000	-0.86626900	0.54369100
C	-2.93011200	-1.57197300	1.09224700
C	-5.06087000	1.51736500	0.79075100
H	-4.68151900	2.52421500	0.97296100
H	-5.75557900	1.25136700	1.59808500
H	-5.61593500	1.53011100	-0.15528000
H	-5.07854700	-1.11742900	1.19045600
C	-4.62259100	-1.19070100	-0.91868800
H	-3.73646400	-1.50639200	-1.47678400
H	-4.95596600	-0.26114500	-1.39842900
C	-5.74605200	-2.24247800	-1.06851100
H	-5.49985800	-3.10087700	-0.42933600
C	-5.82042500	-2.74856200	-2.51546000
C	-7.11199000	-1.69295000	-0.62510000
C	-2.73726600	-2.98524600	0.51918400
C	-3.45329600	-4.05577200	1.08000900
C	-1.88198100	-3.24642400	-0.55729300
C	-3.32936300	-5.34746200	0.57136900
C	-1.75014200	-4.54504000	-1.05796600
C	-2.47271900	-5.59904900	-0.50200300
H	-4.10445100	-3.88421200	1.93180200
H	-1.29218300	-2.45290200	-0.99703300
H	-3.89474300	-6.15838400	1.02306400
H	-1.06954200	-4.72551900	-1.88568800
H	-2.36481900	-6.60692700	-0.89366500
C	-2.88356300	-1.65347800	2.64298400
C	-1.62423100	-1.81025100	3.24783200
C	-4.01014900	-1.61934100	3.47426800
C	-1.49822600	-1.91493000	4.63092300
C	-3.88509500	-1.72001400	4.86467200
C	-2.62976600	-1.86567200	5.44940000
H	-0.73304300	-1.85557200	2.62814700
H	-5.00744100	-1.51887900	3.05814800
H	-0.51166100	-2.03951000	5.06938300
H	-4.77733100	-1.68588300	5.48465300
H	-2.53211800	-1.94548300	6.52871500
N	-1.47603600	1.78739300	-0.40462000
C	-1.26372500	3.20784200	-0.02402200
C	-1.12554700	3.10509700	1.55135000
N	-2.12431500	2.07109000	1.90068400
C	-2.68137100	2.03907500	3.24428200
H	-3.19672400	2.98337000	3.46340500
H	-1.90067000	1.88550500	3.99924200
H	-3.39660000	1.21993400	3.32997100
H	-1.46826300	4.03624200	2.00659700
C	0.26977300	2.76127300	2.11413700
H	0.11673100	2.19052800	3.04080600
H	0.78549900	2.07825100	1.43099800
C	1.17996800	3.96488300	2.44857900
H	1.20795200	4.63520100	1.58102500
C	0.66098700	4.76515400	3.65477300
C	2.61240700	3.47804400	2.70678900
C	-0.01248200	3.80048800	-0.69495800
C	1.08351600	2.99627600	-1.03606500
C	0.07984700	5.18265100	-0.92681700
C	2.23827700	3.55935600	-1.58277000
C	1.23636300	5.74447700	-1.46729800
C	2.32349800	4.93424600	-1.79615000
H	1.04233300	1.92237300	-0.91362000
H	-0.75643900	5.83222800	-0.69395800
H	3.06623600	2.90490000	-1.83879100
H	1.27978300	6.81722000	-1.63760500
H	3.22264700	5.37147500	-2.22308200
C	-2.52598000	4.01983000	-0.42754800
C	-3.19702400	3.67881700	-1.61229800
C	-3.01163300	5.11370900	0.30350600
C	-4.31499300	4.39193200	-2.04307400
C	-4.13714400	5.82647900	-0.12070300
C	-4.79615000	5.46823900	-1.29521600
H	-2.84477400	2.83496700	-2.19590200
H	-2.51258500	5.44031200	1.21039200
H	-4.81032800	4.10331400	-2.96642700
H	-4.49229300	6.66567700	0.47183700
H	-5.67042100	6.02208700	-1.62625300
H	-1.03016000	1.33657600	-1.22860800
H	-7.88606200	-2.46600500	-0.69682900
H	-7.10923800	-1.33308600	0.41154700
H	-7.42045700	-0.85539900	-1.26494400
H	1.31452900	5.62026300	3.86346100
H	-0.34954600	5.16265900	3.49828300
H	0.63500200	4.14033500	4.55778600
H	-6.61040100	-3.50110800	-2.62837900
H	-6.03796400	-1.92579400	-3.20834400
H	-4.87128600	-3.19534400	-2.82670500
H	3.27727100	4.31501500	2.95127700
H	2.64022100	2.77248000	3.54832000
H	3.02100800	2.96636100	1.83016300

- **TS4sr**



B3LYP/6-31G*

E = -3606.10422936

Zero-point correction = 1.287295 (Hartree/Particle)

Thermal correction to Energy = 1.362962

Thermal correction to Enthalpy = 1.363907

Thermal correction to Gibbs Free Energy = 1.167399

Sum of electronic and zero-point Energies = -3604.816935

Sum of electronic and thermal Energies = -3604.741267

Sum of electronic and thermal Enthalpies = -3604.740323

Sum of electronic and thermal Free Energies = -3604.936831

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

E = -3606.56385438

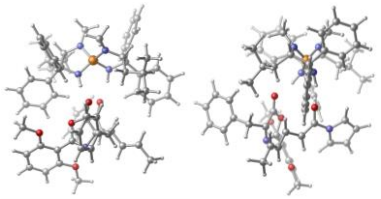
G = -3605.396455

0 1

O	1.29371400	0.59542000	-1.01227600
C	2.33759300	0.19338700	-0.49553900
C	2.60383300	-0.75136100	0.59191300
O	3.55747000	0.73498900	-0.84164700
N	4.01900000	-0.84531000	0.70829100
C	4.50680600	0.03097400	-0.09037400
C	5.91920500	0.34453700	-0.35794000
C	6.39324300	0.43727000	-1.68726200
C	6.84605600	0.51340800	0.69682700
C	7.73454300	0.73446900	-1.95657200
C	8.19118200	0.80194900	0.42599200
C	8.61593300	0.91502600	-0.89412400
O	5.47673100	0.18243600	-2.66208400
C	5.87357000	0.28878600	-4.01864600
H	6.66005200	-0.43539700	-4.26933900
H	6.22435400	1.30102700	-4.25819400
H	4.97971600	0.06861600	-4.60490200
O	6.35451600	0.40030300	1.95780700
C	7.25595000	0.46871100	3.05001400
H	8.03032000	-0.30587400	2.98108100
H	7.73448500	1.45450900	3.12317100
H	6.65106300	0.29518500	3.94163900
H	8.09402100	0.80650600	-2.97527600
H	8.89926700	0.94267800	1.23273800

H	9.65879200	1.14128600	-1.09997700
C	1.82689500	-2.04312800	0.67731800
H	0.78320000	-1.82162400	0.41885100
H	1.79971500	-2.35764200	1.72782600
C	2.32508200	-3.20937300	-0.16777200
C	3.09421800	-3.05813000	-1.32913300
C	1.97355700	-4.51144900	0.21945300
C	3.49482800	-4.16896600	-2.07616800
C	2.36414900	-5.62259100	-0.52690400
C	3.13102500	-5.45645800	-1.68158800
H	3.40219600	-2.07049700	-1.65605800
H	1.37828500	-4.65272400	1.11795500
H	4.10044900	-4.02280000	-2.96753700
H	2.07454400	-6.61894400	-0.20135800
H	3.44651000	-6.31976300	-2.26229300
C	1.91730100	0.38391600	2.10209400
C	1.30935800	-0.41904100	3.12612100
H	1.18740600	0.92081800	1.50209400
H	1.92124100	-0.77754100	3.94673400
C	-0.05954100	-0.68223100	3.12508900
O	-0.92557600	-0.24079400	2.30944500
N	-0.57308800	-1.51849700	4.18896700
C	-1.88478200	-1.47736500	4.62221000
C	0.10170900	-2.47967800	4.92126700
C	-2.04226100	-2.40066600	5.62921100
C	-0.78008300	-3.04311500	5.81542000
H	-2.56812400	-0.77224200	4.17634900
H	1.13789600	-2.70072100	4.71758700
H	-2.95689000	-2.59428000	6.17439300
H	-0.54821500	-3.83180300	6.51964300
C	3.07888100	1.20552600	2.49671300
H	3.74472300	0.77333000	3.24269600
C	3.34842600	2.42384400	2.00625800
H	2.68686900	2.84514800	1.24994800
C	4.50333000	3.28618200	2.42381500
H	5.08985400	2.81552100	3.21937100
H	4.15792200	4.26505500	2.78490800
H	5.17620800	3.48342000	1.57794400
H	-0.46730400	1.24275900	-0.51150100
N	-1.44640300	1.54572800	-0.49416300
P	-2.65915400	0.50320000	-0.85781800
N	-3.83624600	1.66638200	-0.77341700
C	-3.35138900	2.91815400	-0.14648200
C	-1.82508300	2.97516000	-0.57806900
C	-5.26601700	1.46433800	-0.96154200
H	-5.44830800	0.48662800	-1.40984800
H	-5.66631900	2.23914900	-1.62753800
H	-5.81397000	1.50152200	-0.01256800
H	-3.89065900	3.73880400	-0.62244200
C	-3.65422000	2.93341700	1.36896800
H	-4.58800200	2.37443300	1.51929300
H	-2.88204600	2.36638800	1.89804300
C	-3.83921000	4.32087500	2.02333600
H	-2.98899000	4.95673300	1.75082400
C	-5.12699500	5.01523000	1.55027100
C	-3.84083300	4.17629000	3.55249900
C	-1.64505400	3.47764300	-2.03500300
C	-2.51079000	4.39002100	-2.65382100
C	-0.52701900	3.03403100	-2.76251500
C	-2.28554700	4.82807800	-3.96252600
C	-0.30002700	3.47431000	-4.06584300
C	-1.18072900	4.36951600	-4.67639400
H	-3.37087400	4.78767500	-2.12424000
H	0.17916800	2.34214100	-2.31274500
H	-2.97812700	5.53201700	-4.41686800
H	0.57372700	3.11508700	-4.60304600
H	-1.00400800	4.70928100	-5.69340800
C	-0.97163100	3.80521600	0.39550900
C	-0.71943800	5.16324900	0.15094700
C	-0.47539300	3.23231100	1.57633500
C	-0.01201500	5.93529900	1.07343700
C	0.23504800	4.00703500	2.49619900
C	0.46458700	5.36156500	2.25266800
H	-1.07023200	5.62512400	-0.76578400
H	-0.64167400	2.17898500	1.78424500
H	0.17098500	6.98584000	0.86278600
H	0.62033100	3.53717700	3.39618100
H	1.01831300	5.96187000	2.96976000
N	-2.48249600	-0.83435300	0.07240600
C	-2.98205200	-2.06245600	-0.59098800
C	-2.58278500	-1.78542800	-2.09151700
N	-2.92167500	-0.34498200	-2.25582900
H	-1.92282900	-0.79335000	0.94244200
C	-3.50961900	0.16464800	-3.48884600
H	-2.84659300	0.00777600	-4.34393900
H	-4.46822200	-0.33093500	-3.69327000
H	-3.68403600	1.23755800	-3.38998600
H	-3.23097200	-2.34364200	-2.76964400
C	-1.10513600	-2.07072500	-2.42218200
H	-0.47922600	-1.47451900	-1.74761800
H	-0.88442000	-3.12110000	-2.20067600
C	-0.67935100	-1.77609900	-3.87757100
C	0.84705500	-1.88232300	-4.00765500
H	-0.94253600	-0.73587200	-4.11149800
C	-1.37356300	-2.69729800	-4.89351900
C	-4.52721300	-2.14828700	-0.41072500
C	-5.37903700	-2.72995500	-1.35980600
C	-5.09414500	-1.69575600	0.79019000
C	-6.75377700	-2.82883400	-1.12946900
C	-6.46398500	-1.80279100	1.02735100
C	-7.30424900	-2.36386300	0.06393000
H	-4.98638200	-3.12757300	-2.29036700
H	-4.45043000	-1.25703500	1.54575100
H	-7.39118300	-3.27731500	-1.88714600
H	-6.87375900	-1.44853700	1.96972200
H	-8.37266200	-2.44453500	0.24444800
C	-2.41157600	-3.35008100	0.01419100
C	-2.51823200	-4.55203300	-0.70376000
C	-1.91523200	-3.39729700	1.32134300
C	-2.12533000	-5.76228300	-0.13733500
C	-1.52930400	-4.61279500	1.89424500
C	-1.63112100	-5.79818400	1.16854800
H	-2.91992900	-4.55003200	-1.71347600
H	-1.82981400	-2.49878500	1.92061900
H	-2.21089800	-6.67813000	-0.71614000
H	-1.15597000	-4.61639000	2.91467300
H	-1.33308700	-6.74310600	1.61489200
H	1.16539700	-1.66566600	-5.03512900
H	1.34305200	-1.17122500	-3.33888300
H	1.20122800	-2.88705900	-3.74888300
H	-1.04574200	-2.46962200	-5.91476700
H	-1.12665400	-3.74833600	-4.69461000
H	-2.46667100	-2.60420400	-4.87533700
H	-3.97299800	5.14892000	4.04090700
H	-4.65798700	3.52279900	3.88641000
H	-2.89874600	3.74551200	3.90826900
H	-5.23040100	6.00203700	2.01627800
H	-5.15099900	5.16772400	0.46417600
H	-6.01313800	4.42616900	1.82258000

- **TS4ss**



B3LYP/6-31G*

E = -3606.11226899

Zero-point correction = 1.286672 (Hartree/Particle)

Thermal correction to Energy = 1.362657

Thermal correction to Enthalpy = 1.363602

Thermal correction to Gibbs Free Energy = 1.166593

Sum of electronic and zero-point Energies = -3604.825597

Sum of electronic and thermal Energies = -3604.749612

Sum of electronic and thermal Enthalpies = -3604.748667

Sum of electronic and thermal Free Energies = -3604.945676

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

E = -3606.57037764

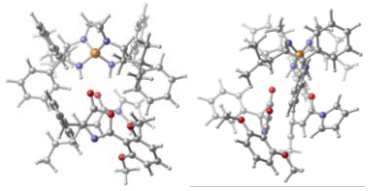
G = -3605.403785

0 1

O	0.67411300	0.84199000	1.18987200
C	1.79094300	1.05200300	0.70709300
C	2.49081300	2.28055200	0.36234500
O	2.60856800	0.02829600	0.30077700
N	3.80550100	1.92000800	-0.00649800
C	3.80430500	0.63776200	-0.10072300
C	4.91534100	-0.25386600	-0.46915900
C	5.28393100	-1.32044300	0.38375800
C	5.67143200	-0.04336200	-1.64335900
C	6.35002400	-2.16832300	0.05665300
C	6.74696200	-0.88235000	-1.96391600
C	7.06855100	-1.93594400	-1.11271200
O	4.56768200	-1.42831800	1.53223700
C	4.84948900	-2.49738800	2.42033600
H	5.87513100	-2.44019400	2.80877900
H	4.69051200	-3.46921200	1.93779300
H	4.14357300	-2.38648700	3.24499000
O	5.27220000	0.98595500	-2.44419500
C	6.06222700	1.31339900	-3.57705800
H	7.09205800	1.55941500	-3.28902400
H	5.59008400	2.19146300	-4.02092500
H	6.07539700	0.50015100	-4.31452600
H	6.62922400	-2.98444100	0.71110800
H	7.32134500	-0.72739900	-2.86854800
H	7.90048800	-2.58816800	-1.36526300
C	2.28156500	3.52322200	1.20179100
H	1.21402300	3.77337200	1.19699000
H	2.80804900	4.35354300	0.72344500
C	2.75740600	3.36643000	2.63608400
C	1.86503500	3.00888100	3.65578900
C	4.10629600	3.55843400	2.96650000
C	2.30466800	2.85740600	4.97213100
C	4.54894600	3.40679200	4.28061800
C	3.64874300	3.05840700	5.29023900
H	0.82086200	2.83640000	3.40742500
H	4.81096400	3.81854600	2.18084800
H	1.59537400	2.58570300	5.75077700
H	5.59869500	3.56292800	4.51746300
H	3.99253500	2.94526700	6.31542900
C	1.58462500	2.61382000	-1.46118100
C	1.81125300	1.53715600	-2.37074000
H	0.58024000	2.68166800	-1.04550200
H	2.70027700	1.57172500	-2.98598000
C	0.90106500	0.48839800	-2.55387700
O	-0.22367500	0.34465500	-2.00456000
N	1.26784200	-0.54103200	-3.50061400
C	0.34868500	-1.37674100	-4.10554300
C	2.53478100	-0.88487000	-3.94269400
C	1.02341600	-2.24072200	-4.93602400
C	2.41448700	-1.93126200	-4.82769100
H	-0.70139400	-1.25394600	-3.89496400
H	3.40538500	-0.37742600	-3.55854500
H	0.57277000	-3.00230400	-5.55914400
H	3.23261500	-2.42743500	-5.33401100
C	2.18765400	3.90767300	-1.83665600
H	3.18389700	3.85109600	-2.27646800
C	1.59821900	5.10569400	-1.70677800
H	0.60086200	5.15723300	-1.26684700
C	2.20223300	6.41164600	-2.13812800
H	3.20046900	6.26884100	-2.56598300
H	1.57960700	6.91404100	-2.89172400
H	2.29269900	7.10940800	-1.29392100
H	-0.31188000	-0.62074500	0.80292600
N	-1.07300200	-1.31348100	0.70226500
P	-2.62857800	-0.83207000	0.53142800
N	-3.23911900	-2.37053500	0.62267200
C	-2.17795300	-3.39253200	0.45831700
C	-0.92883800	-2.71712600	1.15704200
C	-4.63845100	-2.74886300	0.49016600
H	-4.87681500	-3.53315600	1.21886500
H	-4.87685100	-3.11989200	-0.51452100
H	-5.27305600	-1.88328800	0.68850200
H	-2.48946200	-4.27139400	1.02598400
C	-2.00484000	-3.77942200	-1.02886800
H	-1.35750500	-3.04189100	-1.51442300
H	-2.98885600	-3.67683400	-1.50763600
C	-1.48965800	-5.20325700	-1.33365800
H	-0.56206100	-5.37016400	-0.77450900
C	-1.15933300	-5.31944800	-2.82978000
C	-2.49837900	-6.28785600	-0.92188700
C	0.40300100	-3.30977800	0.67078200
C	0.95696200	-4.42978000	1.30977600
C	1.05618500	-2.78471600	-0.45126800
C	2.11973800	-5.02505100	0.82003800
C	2.22349600	-3.37697800	-0.93752800
C	2.75548600	-4.50245300	-0.30884900
H	0.48213200	-4.84156700	2.19460600
H	0.65608400	-1.91055500	-0.95166300
H	2.52751000	-5.89780800	1.32445900
H	2.70816400	-2.95041300	-1.81070000
H	3.66193200	-4.96484600	-0.69097900
C	-1.00964400	-2.76983800	2.70540500
C	-1.67217000	-3.77695000	3.41980500
C	-0.34406200	-1.77208700	3.43874000
C	-1.68786300	-3.78025100	4.81850900
C	-0.35479000	-1.77732300	4.83261800
C	-1.03129600	-2.77969100	5.53160400
H	-2.18219000	-4.58264700	2.90145100
H	0.18538200	-0.97930600	2.91833900
H	-2.21527100	-4.57176000	5.34488000
H	0.17059300	-0.99330000	5.37167900
H	-1.04238700	-2.78196700	6.61829100
N	-2.74210700	0.20581900	-0.74072500
C	-3.80144700	1.23021100	-0.55872700
C	-3.75644500	1.47351000	1.00274800

N	-3.56304800	0.10262000	1.53345600
H	-1.94362900	0.29770400	-1.37955000
C	-3.92025400	-0.20537400	2.91053900
H	-3.35132100	0.40347000	3.62403100
H	-3.70933700	-1.25644000	3.11671100
H	-4.99045500	-0.02418100	3.07125100
H	-4.73143800	1.81884000	1.35384600
C	-2.66421600	2.44569900	1.50251400
H	-1.80430800	2.40119600	0.82561100
H	-2.29243400	2.06671600	2.46404400
C	-3.11318200	3.90950200	1.71102900
C	-1.88845600	4.82332700	1.86112200
H	-3.66390200	4.23753200	0.82083100
C	-4.04171600	4.05643600	2.92766700
C	-3.54514900	2.50358500	-1.37985800
C	-4.59788900	3.41400000	-1.57411100
C	-2.29570800	2.80345500	-1.93570900
C	-4.40419700	4.59366500	-2.29015200
C	-2.10681700	3.98212700	-2.66496600
C	-3.15441800	4.88329100	-2.84200300
H	-5.58329900	3.19641800	-1.17405800
H	-1.45763500	2.12230400	-1.82960900
H	-5.23563300	5.28059500	-2.42507300
H	-1.12803700	4.18390300	-3.09135900
H	-3.00430200	5.79732500	-3.41036400
C	-5.14913700	0.60422000	-1.01709500
C	-6.36374800	0.75263300	-0.33554300
C	-5.15670600	-0.12529600	-2.21688600
C	-7.54212500	0.17977100	-0.82668400
C	-6.32887000	-0.69123900	-2.71284100
C	-7.53104700	-0.54507100	-2.01597200
H	-6.41895000	1.31778400	0.58923300
H	-4.22660400	-0.25160000	-2.76190100
H	-8.46831800	0.30700100	-0.27220200
H	-6.30292900	-1.24675500	-3.64666400
H	-8.44643100	-0.98840500	-2.39825700
H	-2.18940100	5.86568300	2.02006500
H	-1.27063500	4.52209500	2.71741200
H	-1.25812300	4.78846900	0.96555000
H	-4.37760400	5.09393000	3.03932100
H	-4.94040800	3.43156800	2.85026500
H	-3.52126000	3.77530200	3.85281200
H	-2.10989500	-7.28641600	-1.15359500
H	-2.72298800	-6.27129300	0.15165800
H	-3.44723200	-6.16882200	-1.46237700
H	-0.77214600	-6.31676300	-3.07004500
H	-2.05559100	-5.15547900	-3.44391000
H	-0.40681100	-4.58205400	-3.13004700

- **TS4rr**



B3LYP/6-31G*

E = -3606.11078904

Zero-point correction = 1.287555 (Hartree/Particle)

Thermal correction to Energy = 1.363222

Thermal correction to Enthalpy = 1.364166

Thermal correction to Gibbs Free Energy = 1.168849

Sum of electronic and zero-point Energies = -3604.823234

Sum of electronic and thermal Energies = -3604.747567

Sum of electronic and thermal Enthalpies = -3604.746623

Sum of electronic and thermal Free Energies = -3604.941940

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

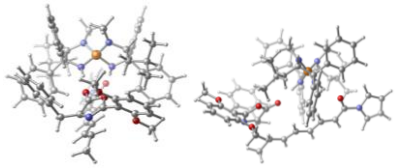
E = -3606.56942018

G = -3605.400571

0 1

O	0.54062800	-1.00630300	0.86530200
C	1.67772700	-1.18650100	0.43253200
C	2.32663500	-2.30864900	-0.22587800
O	2.61817000	-0.16981100	0.45133100
N	3.69705300	-1.97985200	-0.36013000
C	3.79761800	-0.74290600	-0.03214200
C	5.01347200	0.09189400	-0.01481300
C	5.75815000	0.33947800	-1.18784100
C	5.49822500	0.60099600	1.21022600
C	6.94480200	1.08450200	-1.13679300
C	6.67901400	1.35202400	1.26259000
C	7.38660700	1.58234200	0.08564100
O	5.24850700	-0.16584200	-2.34684300
C	6.01769100	-0.04971900	-3.53540600
H	6.99830400	-0.52943900	-3.42475400
H	6.15609300	0.99866100	-3.82972300
H	5.44534500	-0.56553400	-4.30800900
O	4.76133400	0.28122500	2.30929300
C	5.27107100	0.61769800	3.59054000
H	6.26015600	0.17143500	3.75625300
H	5.33413500	1.70461100	3.72837300
H	4.55955800	0.20604100	4.30753400
H	7.51567000	1.28164100	-2.03540000
H	7.04988100	1.74189400	2.20226800
H	8.30507800	2.16218700	0.12207900
C	1.94218900	-3.72288700	0.15679400
H	0.87431500	-3.86551200	-0.04771500
H	2.48663000	-4.40793900	-0.50076800
C	2.21819100	-4.07492800	1.61004300
C	1.16726100	-4.36950700	2.48762400
C	3.53145700	-4.12403700	2.10236800
C	1.41546500	-4.70701200	3.82015900
C	3.78204200	-4.45818100	3.43280300
C	2.72504500	-4.75226900	4.29839200
H	0.14360500	-4.33961100	2.12071900
H	4.35436100	-3.88671600	1.43371500
H	0.58424900	-4.93872800	4.48246600
H	4.80690900	-4.49314200	3.79501200
H	2.92212800	-5.01680600	5.33437700
C	1.63059900	-2.03752000	-2.15763100
C	1.84184800	-0.72129300	-2.66483500
H	0.60611500	-2.28900700	-1.89437300
H	2.75482100	-0.53701300	-3.21484600
C	0.87335300	0.29120400	-2.62621800
O	-0.27966600	0.24161500	-2.11307600
N	1.20556100	1.52729700	-3.29663900
C	0.25070700	2.39420100	-3.79456200
C	2.45842700	2.04595400	-3.57220700
C	0.89319100	3.45405000	-4.39114600
C	2.29664400	3.23620900	-4.24196300
H	-0.79396300	2.13894200	-3.71129600
H	3.34675300	1.54573300	-3.21901700
H	0.41397700	4.28873400	-4.88619100
H	3.09434300	3.88831100	-4.57384300
C	2.38470300	-3.10279500	-2.84879900
H	3.39964600	-2.83612800	-3.14368900
C	1.91710100	-4.32234500	-3.15361300
H	0.90431400	-4.59118700	-2.85233200
C	2.68792200	-5.37088300	-3.90373900
H	2.78783900	-6.29304900	-3.31431800
H	2.18113700	-5.65175500	-4.83786600
H	3.69494800	-5.02270000	-4.15761500
H	-1.23426000	-0.98418800	0.28917000
N	-2.21403500	-0.68391900	0.23555200
P	-2.63119300	0.86574100	0.56463900
N	-4.23250700	0.61651200	0.20996300
C	-4.48972600	-0.68943800	-0.43703100
C	-3.34784600	-1.62429900	0.15556100
C	-5.29572200	1.60788200	0.27514300
H	-4.92534800	2.51484000	0.75536300
H	-5.65974300	1.88013200	-0.72306300
H	-6.14076300	1.21853200	0.85779200
H	-5.46009800	-1.03420100	-0.07396200
C	-4.55176900	-0.54270000	-1.97345900
H	-3.53331000	-0.52983000	-2.37410700
H	-4.96682500	0.45165600	-2.18797800
C	-5.41273200	-1.57502500	-2.73509000
H	-5.11780900	-2.58254100	-2.41984400
C	-6.91295700	-1.40491800	-2.44462600
C	-5.14537700	-1.46109600	-4.24342200
C	-3.69080600	-2.13790300	1.57900100
C	-4.99260100	-2.43306300	2.00641100
C	-2.63611800	-2.36911700	2.47874000
C	-5.23802300	-2.91953000	3.29438800
C	-2.87864300	-2.85955800	3.76130200
C	-4.18288800	-3.13244400	4.17908600
H	-5.83921500	-2.30203100	1.33951600
H	-1.61324600	-2.16002300	2.17980700
H	-6.25937100	-3.13297400	3.59905000
H	-2.04137200	-3.02757500	4.43356300
H	-4.37296300	-3.51035000	5.18001000
C	-3.00410500	-2.79774300	-0.77738600
C	-2.11378700	-2.61838900	-1.84716500
C	-3.61503500	-4.05024200	-0.61550900
C	-1.87384000	-3.65925700	-2.74798800
C	-3.36675900	-5.08940300	-1.51340100
C	-2.49995800	-4.89613100	-2.58925000
H	-1.60135600	-1.66856300	-1.98081900
H	-4.28765800	-4.22318700	0.21754400
H	-1.18651600	-3.49614000	-3.57338900
H	-3.85132200	-6.05106100	-1.36604200
H	-2.30846900	-5.70305600	-3.29163600
N	-1.53406600	1.84579300	-0.15095900
C	-1.27671600	3.10507500	0.59737200
C	-1.49262900	2.64698000	2.09684900
N	-2.63580500	1.70779500	1.99463500
C	-3.42467800	1.38844200	3.17508900
H	-2.81549100	0.93042600	3.96369100
H	-3.88687700	2.29957400	3.57603600
H	-4.21455400	0.68405700	2.90813800
H	-1.82311300	3.50199700	2.69164700
C	-0.29238800	1.97839800	2.80299100
H	-0.70566000	1.27252600	3.53710600
H	0.25476900	1.35815600	2.08619000
C	0.68069600	2.90734500	3.56139500
C	1.91957100	2.10617100	3.98891400
C	0.02192800	3.56770700	4.78368200
H	1.01600300	3.70156800	2.88513600
C	0.13849500	3.64346500	0.36006100
C	0.40141800	5.00947400	0.55202700
C	1.20045700	2.79732400	0.02436200
C	1.69529700	5.51166900	0.42121800
C	2.49579300	3.30150400	-0.10811100
C	2.74905600	4.65765600	0.09050100
H	-0.40881200	5.68693500	0.80249400
H	1.03486400	1.73747700	-0.11965800
H	1.87610300	6.57278900	0.57308300
H	3.30136600	2.62114700	-0.36436400
H	3.75776900	5.04779000	-0.01653800
C	-2.31972300	4.15204900	0.12408100
C	-3.22456700	4.81754500	0.95827500
C	-2.35303400	4.44526800	-1.25044900
C	-4.14290300	5.73832900	0.43786000
C	-3.26224400	5.36185700	-1.77008200
C	-4.16752800	6.01303100	-0.92648400
H	-3.23546100	4.63507600	2.02752700
H	-1.64598700	3.95566900	-1.91494400
H	-4.83506200	6.23951200	1.10978900
H	-3.26185500	5.57198700	-2.83642600
H	-4.87806200	6.72918300	-1.33046000
H	-0.99192400	1.50603900	-0.96514700
H	-7.50067700	-2.15411500	-2.98770600
H	-7.15282400	-1.51661500	-1.38009400
H	-7.26561200	-0.41433900	-2.76193000
H	-5.74790200	-2.18333400	-4.80684500
H	-5.39652500	-0.45803200	-4.61355300
H	-4.09115700	-1.65003300	-4.47296000
H	2.63846200	2.74824400	4.51308000
H	1.64257000	1.29118800	4.67173600
H	2.42215300	1.66091100	3.12392200
H	0.73369000	4.21922600	5.30436200
H	-0.84337600	4.18676100	4.51607200
H	-0.31943500	2.81009000	5.50211800

- **TS5rs**



B3LYP/6-31G*

E = -3683.53070275

Zero-point correction = 1.321027 (Hartree/Particle)

Thermal correction to Energy = 1.398958

Thermal correction to Enthalpy = 1.399902

Thermal correction to Gibbs Free Energy = 1.197663

Sum of electronic and zero-point Energies = -3682.209676

Sum of electronic and thermal Energies = -3682.131745

Sum of electronic and thermal Enthalpies = -3682.130800

Sum of electronic and thermal Free Energies = -3682.333040

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

E = -3683.99962655

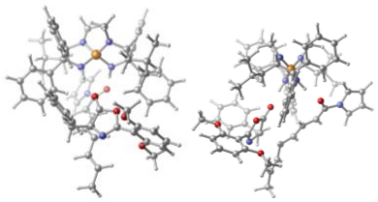
G = -3682.801964

0 1

O	-1.49927600	-0.76171500	0.65939000
C	-2.69131800	-0.58980400	0.90704700
C	-3.65066200	-1.31656900	1.70102700
O	-3.35998200	0.56235900	0.47422200
N	-4.90426700	-0.69453800	1.52765300
C	-4.67572300	0.39034100	0.87155600
C	-5.64265200	1.44391300	0.51200000
C	-5.57153200	2.71053000	1.12287000
C	-6.67169200	1.19097900	-0.41578000
C	-6.50537000	3.70824300	0.81616700
C	-7.61267400	2.18362200	-0.72331500
C	-7.51409100	3.42665100	-0.10280200

O	-4.55802600	2.86972800	2.02232000
C	-4.46774600	4.09655700	2.73177800
H	-5.37565200	4.28866400	3.31761700
H	-4.28466200	4.94015100	2.05456600
H	-3.61751700	3.98563100	3.40675700
O	-6.66667400	-0.04760000	-0.98010800
C	-7.68039400	-0.37193500	-1.91750600
H	-7.64906600	0.28929600	-2.79364400
H	-7.47336500	-1.39653600	-2.23119700
H	-8.67907200	-0.32494600	-1.46431800
H	-6.45755000	4.68330400	1.28475300
H	-8.40756100	1.99739500	-1.43473500
H	-8.24265200	4.19690000	-0.34176100
C	-3.56175500	-2.80713200	1.91145700
H	-2.55473500	-3.04261000	2.27251700
H	-4.26432500	-3.08390100	2.70788400
C	-3.86076600	-3.64576600	0.67533200
C	-2.93309000	-4.58933300	0.21616100
C	-5.07701600	-3.51273200	-0.01346800
C	-3.20910900	-5.38486700	-0.89899300
C	-5.35399900	-4.30732800	-1.12592400
C	-4.42238200	-5.24854600	-1.57380400
H	-1.98478700	-4.70379400	0.73582100
H	-5.79703900	-2.77153600	0.32154400
H	-2.47126200	-6.10724800	-1.23878100
H	-6.30458700	-4.19641300	-1.64345100
H	-4.64207900	-5.86975500	-2.43874100
C	-3.05746300	-0.47301200	3.61205100
C	-1.75836100	-0.88680700	3.98357500
H	-3.15092000	0.53260000	3.20252000
H	-1.66820200	-1.75982700	4.63158600
C	-0.59409000	-0.27104000	3.54178500
H	-0.71338100	0.58102500	2.87195200
C	0.72571000	-0.62579500	3.86339800
H	0.89624700	-1.44857000	4.55869800
C	1.81575100	0.00379600	3.26795200
H	1.58234500	0.79563100	2.55753700
C	3.17026900	-0.27173300	3.43734500
H	3.48199800	-1.01950200	4.15814300
C	4.14270500	0.37068900	2.63064500
O	3.91762000	1.11271700	1.64266100
N	5.52006800	0.13054200	2.93523400
C	6.55242400	0.42191700	2.05794500
C	6.06571800	-0.41827300	4.08816700
C	7.73722900	0.05129100	2.64292100
C	7.42771700	-0.47780900	3.93604800
H	6.32676500	0.86209200	1.10038600
H	5.44173600	-0.68074000	4.92730400
H	8.72002300	0.14981000	2.20079900
H	8.12912700	-0.84853000	4.67202900
C	-4.23008500	-0.89567200	4.46644700
H	-5.17748300	-0.79193200	3.93247100
H	-4.27062800	-0.26081500	5.36319800
H	-4.12511800	-1.93125400	4.80953400
H	0.12058100	-0.89154200	-0.21481400
N	1.03568500	-1.00568300	-0.66491100
P	1.76918900	0.25971200	-1.42373800
N	2.94728500	-0.68781500	-2.10267200
C	2.98304900	-2.04265500	-1.49705900
C	1.46225400	-2.32629800	-1.19835800
C	4.08568800	-0.20472400	-2.87200000
H	3.86546400	0.78759200	-3.26986800
H	4.27349300	-0.88404200	-3.71220800
H	4.99743700	-0.13722100	-2.26584200
C	1.25889600	-3.44230400	-0.16456400
C	1.00609400	-3.17308100	1.18462800
C	1.34070400	-4.78138500	-0.57997100
C	0.84885300	-4.22019700	2.09763100
C	1.19056000	-5.82408100	0.33251600
C	0.94305300	-5.54681300	1.67947400
H	0.92152900	-2.15272300	1.53783000
H	1.51251600	-5.01153800	-1.62747300
H	0.65042000	-3.98536500	3.13971000
H	1.26081700	-6.85290900	-0.01086600
H	0.81965300	-6.35812600	2.39194800
C	0.63919300	-2.66308800	-2.46963700
C	-0.76138900	-2.63730900	-2.35836800
C	1.19506000	-3.00753100	-3.70803000
C	-1.57596900	-2.93758000	-3.44766600
C	0.37864500	-3.30482600	-4.80529100
C	-1.00832600	-3.27018000	-4.68053300
H	-1.22183900	-2.38911500	-1.40657500
H	2.27055500	-3.04805000	-3.84524000
H	-2.65494700	-2.92544500	-3.32360500
H	0.83676500	-3.56650800	-5.75581000
H	-1.64170600	-3.50630500	-5.53151000
H	3.34154800	-2.73090400	-2.26600400
C	3.92766600	-2.10975100	-0.27231900
H	4.66151100	-1.29817400	-0.36057000
H	3.35710600	-1.88910000	0.63511000
C	4.70327900	-3.43416500	-0.09456500
H	3.99275000	-4.26695600	-0.17525300
C	5.33272100	-3.48985300	1.30552200
H	4.56508700	-3.42818500	2.08454400
H	6.03325500	-2.65955300	1.45978700
H	5.88584000	-4.42585400	1.44976300
C	5.78203300	-3.61797200	-1.17440300
H	5.36983900	-3.60340300	-2.19143200
H	6.53668400	-2.82311500	-1.10910000
H	6.29950300	-4.57626400	-1.04913100
N	1.98150300	1.50324100	-0.36355000
C	1.88184600	2.83774900	-1.01273700
C	0.75968900	2.56752600	-2.08970800
N	1.11886900	1.22382900	-2.60519100
H	2.60452600	1.36718000	0.45372000
C	0.57851700	0.76090300	-3.87644300
H	-0.51284100	0.65389200	-3.85239400
H	0.84446500	1.47391900	-4.66607500
H	1.00941700	-0.21057900	-4.12410600
C	1.48016200	3.90514400	0.01775900
C	1.72639000	5.26192200	-0.24256100
C	0.84744600	3.56256300	1.21882400
C	1.34031600	6.24634900	0.66649200
C	0.46891900	4.54696500	2.13390500
C	0.71096900	5.89270700	1.86138300
H	2.23453300	5.55275300	-1.15665400
H	0.65206100	2.52038400	1.44215700
H	1.54341100	7.29052000	0.44365300
H	-0.00821900	4.25358900	3.06513700
H	0.42185200	6.65855800	2.57611600
C	3.24562000	3.22155600	-1.65030500
C	4.39715000	3.11876700	-0.84938900
C	3.39915400	3.69182600	-2.96112200
C	5.65181500	3.46200800	-1.34985700
C	4.65942500	4.03391700	-3.46430800
C	5.79209100	3.91952700	-2.66224700
H	4.32143400	2.75615300	0.17115800
H	2.54453500	3.80414000	-3.61972500
H	6.52296200	3.37417900	-0.70574200
H	4.74574500	4.39247300	-4.48687100
H	6.77086700	4.18706600	-3.05125900
H	0.87174200	3.27020400	-2.91727400
C	-0.70295200	2.61594200	-1.59301300
H	-0.75509900	2.24631100	-0.56384900
H	-1.27857000	1.89427800	-2.18771500
C	-1.41678700	3.98193300	-1.70194900
H	-0.79296300	4.74459100	-1.22004400
C	-1.64343100	4.40498600	-3.16291900
H	-0.70851400	4.50443600	-3.72790200
H	-2.15213900	5.37501500	-3.20969300
H	-2.27441100	3.67547200	-3.68789900
C	-2.75651600	3.92689300	-0.95450800
H	-3.27263100	4.89349400	-1.00520000
H	-2.61725500	3.66468200	0.09911400
H	-3.42114100	3.17029700	-1.38907900

- **TS6rs**



B3LYP/6-31G*

E = -3683.52497056

Zero-point correction = 1.320359 (Hartree/Particle)

Thermal correction to Energy = 1.398483

Thermal correction to Enthalpy = 1.399427

Thermal correction to Gibbs Free Energy = 1.197212

Sum of electronic and zero-point Energies = -3682.204612

Sum of electronic and thermal Energies = -3682.126487

Sum of electronic and thermal Enthalpies = -3682.125543

Sum of electronic and thermal Free Energies = -3682.327759

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

E = -3683.99347769

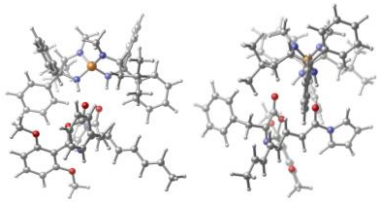
G = -3682.796266

0 1

O	-0.97865700	-0.71813100	0.06032400
C	-2.16125700	-0.81567000	0.36243400
C	-2.92159200	-1.78841200	1.12786700
O	-3.05751200	0.21483500	0.06120300
N	-4.28811600	-1.40776300	1.03010800
C	-4.29842700	-0.25442500	0.47012400
C	-5.46075800	0.61475800	0.19389800
C	-5.89397100	1.56208900	1.13654600
C	-6.15164800	0.49353900	-1.02514500
C	-7.01023200	2.36757800	0.87644700
C	-7.26787800	1.29613700	-1.29513500
C	-7.67948300	2.22005300	-0.33702700
O	-5.15595800	1.63035000	2.28519100
C	-5.56895800	2.53180300	3.30470100
H	-5.53532100	3.57254900	2.95835700
H	-4.85875900	2.39882400	4.12198900
H	-6.58111700	2.29849200	3.65795700
O	-5.65430200	-0.44129500	-1.87934300
C	-6.30176000	-0.64228100	-3.12566400
H	-6.27262000	0.26319000	-3.74557800
H	-5.74382900	-1.43924400	-3.61999100
H	-7.34474400	-0.95710400	-2.99116400
H	-7.35419500	3.09820900	1.59779600
H	-7.80817200	1.20702900	-2.22963600
H	-8.54515300	2.84438400	-0.54177300
C	-2.57317700	-3.26047700	1.06416300
H	-1.53710200	-3.38412000	1.39840200
H	-3.21489300	-3.78278800	1.78408300
C	-2.73489500	-3.88476200	-0.31350400
C	-1.63254900	-4.43325000	-0.98173400
C	-3.98935400	-3.93492800	-0.94178700
C	-1.77428400	-5.01803800	-2.24345700
C	-4.13262900	-4.51773900	-2.20075200
C	-3.02590800	-5.06259300	-2.85796900
H	-0.65466500	-4.40952700	-0.50671400
H	-4.84972100	-3.50207200	-0.43967500
H	-0.90422300	-5.43959900	-2.74088600
H	-5.11420700	-4.55340900	-2.66816000
H	-3.14074600	-5.52198400	-3.83679900
C	-2.43116400	-1.18532700	3.01620400
C	-1.03051800	-1.29990700	3.30599500
H	-2.79947500	-0.17244800	2.85146600
H	-0.70075900	-2.22330000	3.78487600
C	-0.09453400	-0.30081700	3.10388200
H	-0.42617900	0.62111300	2.62812100
C	1.24708500	-0.32780800	3.52287600
H	1.60674300	-1.18589800	4.08165300
C	2.12644700	0.74382600	3.27319300
O	1.92567200	1.72194500	2.50634000
N	3.39895400	0.72452900	3.94603500
C	3.76052100	0.01018100	5.07794300
C	4.48406000	1.48090400	3.54044000
C	5.06737700	0.30680900	5.37972300
C	5.52999200	1.23824200	4.39799000
H	3.04329500	-0.60886100	5.59311700
H	4.39690500	2.11637400	2.67411600
H	5.62663700	-0.08652000	6.21871800
H	6.51468200	1.68358200	4.33842400
C	-3.32619000	-2.01085900	3.85288800
H	-2.89503400	-2.93400600	4.24411800
C	-4.58599800	-1.69247400	4.18159600
H	-5.01253100	-0.77397600	3.78044000
C	-5.47688100	-2.51936800	5.06041300
H	-6.38389600	-2.82794500	4.52211200
H	-5.81374900	-1.95222100	5.93969400
H	-4.96970400	-3.42324800	5.41543200
H	0.75412400	-0.99718600	-0.50940000
N	1.72659800	-0.83162000	-0.77783900
P	2.24311100	0.66688000	-1.21292300
N	3.82409700	0.18367200	-1.34847800
C	2.67739700	-1.91335500	-1.10668900
C	4.05893300	-1.18824100	-0.83636400
C	4.95549700	1.04150900	-1.66956700
H	4.59477300	2.01374500	-2.01134300
H	5.55724300	0.58942400	-2.46850200
H	5.60143600	1.20431500	-0.79827400
H	4.83312800	-1.63197300	-1.46646000
C	4.54767900	-1.19215800	0.62903400
H	5.03718400	-0.23078900	0.83093500
H	3.68511300	-1.22725500	1.30140400
C	5.54400900	-2.31921600	0.98504900
H	5.16020300	-3.26382800	0.57739600
C	6.93145100	-2.06512500	0.37311400
H	6.89676200	-1.94799200	-0.71768200
H	7.37897700	-1.15354800	0.79037600
H	7.61226900	-2.89692300	0.58859000
C	5.64781600	-2.47495200	2.50896200
H	5.97435700	-1.54145600	2.98282200
H	6.36583500	-3.26028800	2.77530100
H	4.67842700	-2.74238900	2.94289800
C	2.49169500	-2.32272200	-2.59327200
C	3.54493000	-2.57036600	-3.48275900
C	1.17952300	-2.49592500	-3.06519000
C	3.29766500	-2.95744600	-4.80462100
C	0.93017000	-2.88797100	-4.37860500
C	1.99066500	-3.11556100	-5.25947000
H	4.57773500	-2.47247400	-3.16432800
H	0.33998600	-2.32774700	-2.39748000

H	4.13546000	-3.13667300	-5.47357700
H	-0.09671000	-3.02066600	-4.70819300
H	1.79877800	-3.41826800	-6.28531500
C	2.44702600	-3.13996000	-0.20864600
C	1.77309700	-3.03745900	1.01597800
C	2.93233800	-4.39765100	-0.60121500
C	1.59927900	-4.16315000	1.82649000
C	2.76388200	-5.51736600	0.21236500
C	2.09422600	-5.40537400	1.43219700
H	1.38048400	-2.08477300	1.35311000
H	3.43810000	-4.50908300	-1.55508300
H	1.07035100	-4.05768400	2.76963500
H	3.14946300	-6.47958400	-0.11414600
H	1.95489500	-6.27856500	2.06375300
N	1.54553600	1.75749700	-0.21504800
C	1.24909900	3.06003000	-0.86088000
C	0.91261600	2.60856900	-2.33848600
N	1.90369900	1.53317000	-2.58715600
H	1.59554700	1.67606100	0.82111400
C	2.23144900	1.14864900	-3.95195100
H	2.60443700	2.02210000	-4.50124200
H	1.36620400	0.74143800	-4.48938500
H	3.01092800	0.38482100	-3.94118100
H	1.13957200	3.42123300	-3.03052000
C	-0.52202800	2.10294500	-2.61358600
H	-0.86680100	1.51036800	-1.75988300
H	-0.45024400	1.39743200	-3.45365100
C	-1.59409100	3.14822100	-2.99461000
H	-1.67022600	3.88962600	-2.19179400
C	-2.95696100	2.44785300	-3.11472300
H	-3.75047200	3.17031400	-3.34080700
H	-3.22087000	1.92864800	-2.18787500
H	-2.94366800	1.70370900	-3.92317200
C	-1.25862500	3.88994300	-4.29874600
H	-2.06209400	4.58749400	-4.56308400
H	-0.33557200	4.47776100	-4.22712900
H	-1.14369800	3.18675600	-5.13505200
C	0.05928700	3.73742100	-0.16524800
C	-0.91286100	2.98045000	0.50121300
C	-0.10235800	5.12887600	-0.23360900
C	-2.02837400	3.59713500	1.06996700
C	-1.21524600	5.74564100	0.33849700
C	-2.18377400	4.98123200	0.99103900
H	-0.80964200	1.90346500	0.56117100
H	0.64612500	5.73730400	-0.73142100
H	-2.77770900	2.98435900	1.56329900
H	-1.32071400	6.82570100	0.27572700
H	-3.05092000	5.46290500	1.43580200
C	2.50551700	3.96625000	-0.77485600
C	3.05637600	4.66532800	-1.85587400
C	3.11735400	4.10913900	0.48433700
C	4.19122800	5.46907300	-1.69384800
C	4.24351000	4.91328000	0.64633000
C	4.79056800	5.59595600	-0.44364000
H	2.61511800	4.60370200	-2.84511100
H	2.71339300	3.58163100	1.34425000
H	4.59840100	5.99648200	-2.55284600
H	4.69272700	5.00819900	1.63157100
H	5.66993900	6.22173000	-0.31654100

● **TS7ss**



B3LYP/6-31G*

E = -3683.51858525

Zero-point correction = 1.320318 (Hartree/Particle)

Thermal correction to Energy = 1.398508

Thermal correction to Enthalpy = 1.399452

Thermal correction to Gibbs Free Energy = 1.197321

Sum of electronic and zero-point Energies = -3682.198267

Sum of electronic and thermal Energies = -3682.120077

Sum of electronic and thermal Enthalpies = -3682.119133

Sum of electronic and thermal Free Energies = -3682.321264

B3LYP-D3/6-31+G**//B3LYP/6-31G*@25 °C

E = -3683.98665363

G = -3682.789333

0 1

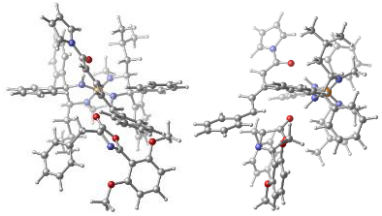
O	0.67883200	0.43800800	1.29849700
C	1.82428700	0.50740000	0.84561400
C	2.71787200	1.63527500	0.61171900
O	2.47816900	-0.59639600	0.36164100
N	3.96624600	1.09898500	0.22347200
C	3.76407700	-0.15457200	0.02331900
C	4.72820700	-1.18097300	-0.40274100
C	4.89255600	-2.36136700	0.35974900
C	5.54552800	-0.99857200	-1.53984700
C	5.81958500	-3.34031500	-0.02012900
C	6.48211000	-1.97195800	-1.91302300
C	6.60327600	-3.13091100	-1.15141000
O	4.13007700	-2.44758000	1.47968800
C	4.21561900	-3.61300200	2.28331200
H	5.22576100	-3.74778400	2.69257900
H	3.92159700	-4.50817200	1.72219200
H	3.51146300	-3.45575700	3.10195300
O	5.34390200	0.14578500	-2.25341400
C	6.21103500	0.43165200	-3.34049800
H	7.25790300	0.47871700	-3.01514300
H	5.90256500	1.40975000	-3.71340400
H	6.11340800	-0.30811400	-4.14587900
H	5.94305900	-4.24260200	0.56561600
H	7.10174100	-1.83665600	-2.79041900
H	7.32773600	-3.88613000	-1.44481500
C	2.69966800	2.81092700	1.56770300
H	1.68666500	3.22951200	1.58954000
H	3.35914500	3.58805800	1.17182000
C	3.12677200	2.44016900	2.97780300
C	2.17791400	2.13192500	3.96195300
C	4.48537500	2.37804600	3.31764500
C	2.57427700	1.78061400	5.25375300
C	4.88469300	2.02650200	4.60711900
C	3.92983400	1.72890900	5.58219100
H	1.12197600	2.15637100	3.70461800
H	5.23030400	2.59799300	2.55736500
H	1.82254200	1.55087800	6.00565300
H	5.94345600	1.98664600	4.85173400
H	4.24021100	1.45965700	6.58876200
C	1.91179700	2.26781600	-1.16123800
C	1.99343800	1.25888300	-2.17275800
H	0.91871700	2.44533100	-0.75021200
H	2.89072900	1.21653900	-2.77542700
C	0.93529400	0.39212000	-2.46853200
O	-0.21213100	0.37489200	-1.94659500
N	1.16049000	-0.58678100	-3.50904900
C	0.13762700	-1.20340400	-4.20343600
C	2.36883000	-1.08142500	-3.97144600
C	0.68969200	-2.07753500	-5.11057700
C	2.10880200	-2.00363900	-4.95879700
H	-0.88527100	-0.93879300	-3.98948200
H	3.29823100	-0.75817500	-3.52989800
H	0.14130300	-2.69418500	-5.81082700
H	2.85173500	-2.57037300	-5.50541400
C	2.69757400	3.48574100	-1.41315900
H	3.67730500	3.33166500	-1.86578800
C	2.28782300	4.74659700	-1.15521100
H	1.30719300	4.90444800	-0.70382500
H	-0.50041800	-0.83207000	0.75337700
N	-1.35042000	-1.39163800	0.57391300
P	-2.81405600	-0.66792600	0.44910100
N	-3.64685400	-2.09945600	0.37680300
C	-2.74539700	-3.24769800	0.11934400
C	-1.42479400	-2.83844900	0.88782300
C	-5.08449700	-2.25284400	0.21026300
H	-5.45051900	-3.04160200	0.87903700
H	-5.35761800	-2.51372100	-0.81978000
H	-5.58501100	-1.31749900	0.46612000
H	-3.19453200	-4.12210900	0.59464200
C	-2.60002700	-3.51003300	-1.39819600
H	-1.83208900	-2.84265600	-1.80276100
H	-3.54347300	-3.20513000	-1.87228700
C	-2.31040700	-4.96235000	-1.83716100
H	-1.44085200	-5.33091900	-1.28152700
C	-1.95402600	-4.98495600	-3.33151000
C	-3.49370000	-5.90175700	-1.55343300
C	-0.18840800	-3.57776700	0.35377600
C	0.16151000	-4.83251000	0.87614800
C	0.57255900	-3.04988100	-0.69643200
C	1.23111700	-5.55150700	0.34274800
C	1.64682200	-3.76785900	-1.22675000
C	1.97632000	-5.02217700	-0.71383800
H	-0.40155000	-5.25293500	1.70350100
H	0.32868700	-2.07625100	-1.10551500
H	1.48070500	-6.52588800	0.75591500
H	2.21810200	-3.33724100	-2.04375700
H	2.81088200	-5.58056900	-1.12986300
C	-1.53702800	-3.02463600	2.42368100
C	-2.39442100	-3.94207300	3.04469000
C	-0.69821200	-2.24852900	3.24301700
C	-2.42783200	-4.07108600	4.43756800
C	-0.72747300	-2.37942900	4.63002100
C	-1.59624100	-3.28986200	5.23664400
H	-3.04809400	-4.57874700	2.45717200
H	-0.01824800	-1.52957100	2.79520700
H	-3.10739500	-4.78809400	4.89120900
H	-0.06621400	-1.76612800	5.23656700
H	-1.62121300	-3.39029000	6.31844800
N	-2.74128200	0.50369000	-0.70331000
C	-3.63328300	1.65545500	-0.41651500
C	-3.58675100	1.71925800	1.16170100
N	-3.62047100	0.28588000	1.54056500
H	-1.92801100	0.53399000	-1.32906100
C	-4.04151100	-0.10495300	2.87794500
H	-3.40212700	0.33978100	3.65053800
H	-3.98739000	-1.19075500	2.97628500
H	-5.07667300	0.21315700	3.05466900
H	-4.50385400	2.17425400	1.54276700
C	-2.36665200	2.44637500	1.77252800
H	-1.51297900	2.35364500	1.09278100
H	-2.07178500	1.90098100	2.67905000
C	-2.59047400	3.92529200	2.16032900
C	-1.24327800	4.61416000	2.42135800
H	-3.06821600	4.43997300	1.31761800
C	-3.50723000	4.06317000	3.38695600
C	-3.16580200	2.95659600	-1.08713000
C	-4.05294100	4.04486800	-1.14891600
C	-1.88557300	3.11027400	-1.63171700
C	-3.66637400	5.25461800	-1.72206600
C	-1.50391500	4.32182400	-2.21837000
C	-2.38646000	5.39878100	-2.26204800
H	-5.06042100	3.94577900	-0.75663100
H	-1.17129400	2.29307100	-1.62515600
H	-4.37173400	6.08091700	-1.75542600
H	-0.50627700	4.41033400	-2.63936200
H	-2.08601700	6.33804100	-2.71861800
C	-5.04956700	1.30189500	-0.95173600
C	-6.24333600	1.55626800	-0.26477700
C	-5.13939300	0.72592300	-2.22931300
C	-7.48322000	1.23281200	-0.82718800
C	-6.37181700	0.40906300	-2.79557200
C	-7.55403900	0.65726100	-2.09348000
H	-6.23356200	2.01116200	0.72038600
H	-4.22691400	0.52190400	-2.78058400
H	-8.39222600	1.43622700	-0.26700600
H	-6.40856900	-0.03167200	-3.78838800
H	-8.51682100	0.40778800	-2.53101000
H	-1.38355500	5.66414800	2.70446700
H	-0.69707300	4.12092600	3.23610500
H	-0.60746900	4.58854200	1.52929900
H	-3.68852000	5.11809400	3.62339900
H	-4.48660800	3.59176900	3.23639700
H	-3.04887900	3.59958100	4.27062200
H	-3.26256200	-6.92458900	-1.87301000
H	-3.75125300	-5.94768500	-0.48810900
H	-4.39097300	-5.57973000	-2.09906600
H	-1.72939500	-6.00449700	-3.66683000
H	-2.79005300	-4.61302400	-3.93975100
H	-1.08063700	-4.35803500	-3.54184600
C	3.06536900	5.93555700	-1.45479200
H	4.04456700	5.77362900	-1.90953600
C	2.66316700	7.19537500	-1.20905400
H	1.68372200	7.35027700	-0.75287200
C	3.45990600	8.42981700	-1.50825500
H	3.65367400	9.01270200	-0.59665000
H	4.42575400	8.18465200	-1.96319900
H	2.92208200	9.09858300	-2.19528800

Computational Details for Chapter 4:

All calculations were performed with the Gaussian 09 package.[1] Typical local minima and TS structures were optimized at B3LYP/6-31G* and frequency calculation were carried out to characterize the stationary points and to estimate Gibbs free energies. Single point calculations with the polarized continuum model (PCM, toluene and DCE) were performed at B3LYP-D3/6-311++G**. To evaluate more reliable relative Gibbs energies including dispersion corrections, zero-point energy, thermal, and entropic corrections calculated at B3LYP/6-31G* at –30 °C and 1 atm were added to the electronic energy calculated at B3LYP-D3/6-311++G**. The molecular structures were depicted by using the CYLview v1.0.561 β.[2]

Data for DFT Calculations:

- **1aa**-*SS*



B3LYP/6-31G*

E = –3797.857997

Zero-point correction = 1.340415 (Hartree/Particle)

Thermal correction to Energy = 1.419315

Thermal correction to Enthalpy = 1.420259

Thermal correction to Gibbs Free Energy = 1.216443

Sum of electronic and zero-point Energies = –3796.517581

Sum of electronic and thermal Energies = –3796.438681

Sum of electronic and thermal Enthalpies = –3796.437737

Sum of electronic and thermal Free Energies = –3796.641554

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.05151024

G = –3797.799957

PCM(DCE)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

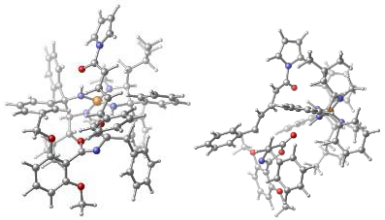
E = –3799.06559931

G = –3797.814046

0 1

O	0.79071100	-0.67978200	-0.23356600
C	2.00424500	-0.74667600	-0.05296900
C	2.84849800	-1.61214400	0.76919800
O	2.84423100	0.23031700	-0.57055900
N	4.18848800	-1.21062300	0.52780600
C	4.13431700	-0.15548100	-0.19830000
C	5.23914700	0.66310100	-0.72316900
C	5.29375200	2.04678300	-0.45941600
C	6.25219400	0.07936100	-1.51368100
C	6.33198700	2.83458500	-0.97180000
C	7.29830800	0.86413200	-2.01969400
C	7.32131000	2.22837800	-1.74298600
O	4.29473700	2.53365800	0.32954100
C	4.25770600	3.92974800	0.59612600
H	5.15675800	4.25887600	1.13313900
H	3.38014800	4.08830600	1.22253700
H	4.15473300	4.50868600	-0.33035700
O	6.12131400	-1.24845800	-1.76130000
C	7.06910100	-1.88528700	-2.60258900
H	8.07525700	-1.86566800	-2.16389900
H	7.09894100	-1.42473400	-3.59885800
H	6.72950800	-2.91817000	-2.69138400
H	6.37991200	3.89663900	-0.76707100
H	8.08013300	0.42286400	-2.62517100
H	8.13217300	2.83536600	-2.13713300
C	2.58381100	-3.09826700	0.89554100
H	1.53732200	-3.23113200	1.18595700
H	3.20201300	-3.47029400	1.72168800
C	2.88484800	-3.90713100	-0.35478600
C	4.20784300	-4.21359600	-0.70810500
C	1.84908800	-4.38558500	-1.16717700
C	4.48313500	-4.98654200	-1.83614700
C	2.12324700	-5.15669200	-2.29970700
C	3.44179200	-5.46201100	-2.63756800
H	5.01929100	-3.83329400	-0.09444100
H	0.81752700	-4.15890800	-0.90860000
H	5.51396900	-5.23081100	-2.08407300
H	1.30302000	-5.52671000	-2.91020700
H	3.65699900	-6.06994700	-3.51282200
C	2.30582800	-0.86020400	2.58477000
C	1.15070700	-1.54395100	3.10275500
H	2.10583000	0.14436900	2.21537900
H	1.32082100	-2.36340800	3.79855400
C	-0.16402700	-1.23836600	2.79713700
H	-0.35668800	-0.44227000	2.08318300
C	-1.30026400	-1.86392600	3.33802000
H	-1.15812000	-2.64907600	4.07276700
C	-2.60712300	-1.45090200	3.02223200
O	-2.93946200	-0.51162400	2.24158700
N	-3.69247600	-2.14469300	3.66022700
C	-3.67479500	-3.37374600	4.30380200
C	-4.98191300	-1.64328000	3.71562200
C	-4.94059200	-3.64301000	4.76179200
C	-5.77092200	-2.53923700	4.39373400
H	-2.77707500	-3.96958000	4.34121600
H	-5.19680300	-0.67952100	3.28389400
H	-5.24247500	-4.53679200	5.29228500
H	-6.82477300	-2.41910300	4.60859400
H	-0.09238700	1.03265100	-0.24344200
N	-0.91277600	1.64814000	-0.26526300
P	-2.25665200	1.12869400	-1.06399500
N	-3.07768700	2.55065100	-0.82968000
C	-2.39952400	3.42375300	0.16015700
C	-0.86465900	3.11703300	-0.08041700
C	-4.34071000	2.92867200	-1.45180200
H	-4.63453300	2.16198500	-2.17054900
H	-5.14739400	3.02563800	-0.72094400
H	-4.23062100	3.88336600	-1.98310300
H	-2.61836900	4.46070000	-0.10568500
C	-2.84217900	3.15857900	1.61459800
O	-2.53087400	2.14593900	1.89631000
H	-2.29062700	3.84892700	2.26431400
C	-4.34392200	3.30233000	1.93421900
C	-4.58942700	2.84749700	3.38198600
C	-4.86874200	4.73006200	1.71668900
H	-4.90534100	2.61498400	1.28747900
C	-0.01578900	3.52105100	1.13330300
C	0.35689800	2.60123000	2.11874400
C	0.34303300	4.86707700	1.30599400
C	1.07072700	3.00962000	3.24802300
C	1.04125600	5.28005000	2.44069700
C	1.41198300	4.35133700	3.41681900
H	0.06551100	1.56328500	2.02439400
H	0.07754600	5.59947400	0.54923200
H	1.34826900	2.27212500	3.99589900
H	1.29937500	6.32942900	2.55856100
H	1.95934400	4.67165100	4.29918200
C	-0.28461900	3.78309000	-1.35433000
C	0.92933100	3.28359300	-1.85881700
C	-0.87740500	4.86369100	-2.01852300
C	1.51916800	3.83961200	-2.99184300
C	-0.28684200	5.42212800	-3.15818800
C	0.91173400	4.91224100	-3.65057700
H	1.42804500	2.45469600	-1.36348600
H	-1.80831600	5.29267200	-1.66206100
H	2.45704800	3.43143200	-3.35887900
H	-0.77149400	6.25847700	-3.65541400
H	1.37067000	5.34520500	-4.53528800
N	-2.64509700	-0.35716300	-0.50660300
C	-3.31916600	-1.20047700	-1.51843200
C	-2.55301600	-0.76430000	-2.83386000
N	-2.38013100	0.70393500	-2.66010000
H	-2.73479600	-0.52256300	0.51518500
C	-2.37659100	1.61612300	-3.79754600
H	-1.53219400	1.43110000	-4.46651400
H	-2.29898800	2.64439600	-3.43965800
H	-3.30729500	1.51411600	-4.37144000
H	-3.19536400	-0.91190000	-3.70464500
C	-1.22443200	-1.51567800	-3.04644900
H	-1.45951800	-2.58225300	-3.15058000
H	-0.61868100	-1.41630300	-2.13928100
C	-0.36880700	-1.09361200	-4.25934900
H	-0.12695500	-0.02660900	-4.16064100
C	0.96646100	-1.85372600	-4.23135600
C	-1.08309600	-1.31532000	-5.60199900
C	-4.83192700	-0.85622900	-1.55413400
C	-5.58246600	-0.72340000	-2.72947600
C	-5.49801900	-0.70635900	-0.32528000
C	-6.95099000	-0.43418500	-2.68301500
C	-6.86169200	-0.42489200	-0.27818900
C	-7.59643000	-0.28246600	-1.45825500
H	-5.12002400	-0.84977800	-3.70338600
H	-4.94418400	-0.81011300	0.60360500
H	-7.50717400	-0.33281200	-3.61152200
H	-7.35157400	-0.32299600	0.68653200
H	-8.65976100	-0.06139800	-1.42130700
C	-3.14089000	-2.69109700	-1.19010800
C	-3.94235400	-3.64719800	-1.83172600
C	-2.17728800	-3.13073700	-0.27359600
C	-3.78112500	-5.00713000	-1.56985100
C	-2.03058800	-4.49252100	0.00153100
C	-2.82659400	-5.43635400	-0.64631800
H	-4.71119800	-3.32993800	-2.52986600
H	-1.52932800	-2.41865300	0.22389200
H	-4.41412800	-5.72956500	-2.07855500
H	-1.29067800	-4.80807900	0.73192100
H	-2.71063500	-6.49475100	-0.42913800
H	-0.43805300	-1.02727700	-6.44058400
H	-1.34043200	-2.37462600	-5.73266200
H	-2.01062400	-0.73708400	-5.69011900
H	1.60839900	-1.55032600	-5.06724400
H	1.51042800	-1.66645400	-3.29989900
H	0.80876000	-2.93683900	-4.30768000
H	-5.93305200	4.79940800	1.97110600
H	-4.33005100	5.44221100	2.35566500
H	-4.75823000	5.06907400	0.67935900
H	-5.65450500	2.90216600	3.63756700
H	-4.25244500	1.81517500	3.52556800
H	-4.04406200	3.48317400	4.09191900
C	3.57210400	-0.90313400	3.37289800
C	3.96357600	-2.02693000	4.12090500
C	4.41169500	0.22359200	3.39069400
C	5.14414200	-2.02059500	4.86163600
H	3.34276000	-2.91759400	4.12771700
C	5.58940800	0.23358800	4.13590700
H	4.13851300	1.09678900	2.80406300
C	5.96190500	-0.88903900	4.87659000
H	5.42435300	-2.90269800	5.43200400
H	6.21938900	1.11970400	4.13483700
H	6.88016800	-0.88382200	5.45815000

- **1aa**-*RR*



B3LYP/6-31G*

E = –3797.861773

Zero-point correction = 1.340230 (Hartree/Particle)

Thermal correction to Energy = 1.419195

Thermal correction to Enthalpy = 1.420139

Thermal correction to Gibbs Free Energy = 1.215217

Sum of electronic and zero-point Energies = –3796.521543

Sum of electronic and thermal Energies = –3796.442578

Sum of electronic and thermal Enthalpies = –3796.441634

Sum of electronic and thermal Free Energies = –3796.646556

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.05592746

G = –3797.805396

PCM(DCE)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

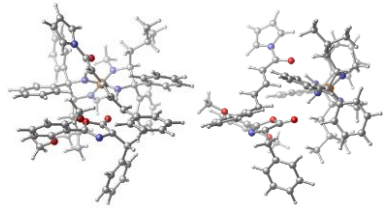
E = –3799.069885

G = –3797.819354

0 1

O	0.89790500	-0.46198400	0.24866200
C	2.10742900	-0.51048800	0.06295400
C	3.01107800	-1.56132200	-0.37787500
O	2.88815700	0.64417600	0.16199500
N	4.32747000	-1.03576700	-0.27874800
C	4.19632900	0.21420700	-0.02365300
C	5.25985000	1.22848000	0.12907900
C	5.62293700	2.06344900	-0.94107400
C	5.93050400	1.35980300	1.35922800
C	6.64605000	3.00866900	-0.79459800
C	6.95515800	2.30309100	1.51479800
C	7.29634400	3.11214400	0.43358300
O	4.91970300	1.87769900	-2.09931400
C	5.27420600	2.65121300	-3.23932900
H	6.31605500	2.47387900	-3.53358000
H	5.12398900	3.72291100	-3.05832500
H	4.60895500	2.32146900	-4.03849000
O	5.50663100	0.52275900	2.34333500
C	6.14035600	0.58054600	3.61145100
H	7.21059200	0.34790000	3.53749400
H	6.01444600	1.56491200	4.08095400
H	5.64498900	-0.17829700	4.21932300
H	6.93511300	3.65390000	-1.61478900
H	7.47810900	2.40973100	2.45724100
H	8.09059500	3.84464000	0.55061700
C	2.76980700	-2.99822200	0.02835600
H	1.77516300	-3.29125200	-0.32587200
H	3.50219900	-3.62257800	-0.49584600
C	2.86549700	-3.24929200	1.52613600
C	1.75366300	-3.70408800	2.24649400
C	4.07045800	-3.04331100	2.21657500
C	1.83765600	-3.94896600	3.62020000
C	4.15618500	-3.28820200	3.58703100
C	3.04031400	-3.74186300	4.29598200
H	0.81546700	-3.87873100	1.72555800
H	4.93618100	-2.67808900	1.67192500
H	0.96168300	-4.30493500	4.15695000
H	5.10135000	-3.13306300	4.10285300
H	3.11111900	-3.93789500	5.36316600
C	2.64015100	-1.46494300	-2.40305300
C	1.28946400	-1.78465500	-2.75535000
H	2.87810700	-0.40201700	-2.44088800
H	1.06601000	-2.80640800	-3.05678800
C	0.26229800	-0.85776700	-2.83141900
H	0.47720900	0.17052700	-2.54412500
C	-1.03098800	-1.10516500	-3.32074200
H	-1.26900600	-2.09487400	-3.69698600
C	-2.01501200	-0.09767500	-3.37687100
O	-1.96241800	1.03913800	-2.83983100
N	-3.21759300	-0.39118000	-4.11151200
C	-4.39112700	0.32784900	-3.96619000
C	-3.42031000	-1.37211000	-5.07044100
C	-5.33451300	-0.20113600	-4.81352300
C	-4.71465000	-1.27886600	-5.52043100
H	-4.43215300	1.14647300	-3.26619100
H	-2.61422500	-2.01822200	-5.37992300
H	-6.35289800	0.14802000	-4.92506400
H	-5.16459100	-1.90212200	-6.28231200
H	-0.84345700	-0.81442600	0.79418400
N	-1.84643700	-0.70136400	0.95621500
P	-2.54142200	0.78838200	0.99274700
N	-4.07638600	0.17201900	1.11511900
C	-4.13001600	-1.29594900	0.91053400
C	-2.72334900	-1.78278100	1.45180700
C	-5.30664200	0.95033000	1.12955300
H	-5.07098300	2.00563200	1.28148300
H	-5.85796800	0.85641500	0.18614500
H	-5.95588200	0.61373500	1.94788400
H	-4.92350600	-1.67526000	1.55849700
C	-4.45642700	-1.67480700	-0.55100100
H	-5.01105400	-0.84450400	-1.00641800
H	-3.52710500	-1.75210200	-1.12375500
C	-5.29561600	-2.96157100	-0.72351800
H	-4.87162400	-3.74253800	-0.07861300
C	-6.76017300	-2.74506100	-0.30857700
C	-5.21491100	-3.45897600	-2.17387300
C	-2.29149500	-3.14500700	0.88573500
C	-1.51272900	-3.24309400	-0.27522900
C	-2.69546200	-4.32951400	1.52237500
C	-1.15902800	-4.49448400	-0.78818700
C	-2.34542000	-5.57635800	1.00573700
C	-1.57378700	-5.66477600	-0.15422600
H	-1.17683200	-2.35118800	-0.79188400
H	-3.28100300	-4.28056200	2.43483500
H	-0.55259700	-4.54372900	-1.68828300
H	-2.67049300	-6.47855300	1.51703900
H	-1.29412500	-6.63557300	-0.55426400
C	-2.65767100	-1.82382300	3.00309800
C	-1.39510100	-1.71710000	3.60984900
C	-3.77076900	-1.99977200	3.83495600
C	-1.25224200	-1.77037600	4.99483000
C	-3.63174400	-2.04593000	5.22646800
C	-2.37364700	-1.92911000	5.81310200
H	-0.50932300	-1.59654500	2.99372500
H	-4.76604600	-2.10966300	3.41676000
H	-0.25996500	-1.69219600	5.43069000
H	-4.51466900	-2.17672600	5.84680600
H	-2.26570800	-1.96673800	6.89369400
N	-1.86295200	1.70865600	-0.17493200
C	-1.75684100	3.14618300	0.17956400
C	-1.51784700	3.06768200	1.74022400
N	-2.41946900	1.96585900	2.15595600
H	-1.80687000	1.39920400	-1.16652000
C	-2.82244800	1.84132400	3.54883300
H	-3.51634000	1.00577900	3.65531100
H	-1.96951900	1.66009500	4.21436300
H	-3.32768400	2.76065200	3.87011000
H	-1.88449500	3.98105700	2.21253400
C	-0.07049500	2.80396600	2.21468600
H	-0.14200500	2.27613000	3.17629000
H	0.41300200	2.10106600	1.52865800
C	0.83781400	4.03370800	2.43840500
H	0.84966000	4.63877400	1.52478400
C	0.34450800	4.92242800	3.59188500
C	2.27597100	3.56216300	2.70317000
C	-0.57956000	3.79103600	-0.56600100
C	0.51893800	3.02691500	-0.97963000
C	-0.56281400	5.17402500	-0.79949100
C	1.61527400	3.63278000	-1.59556200
C	0.53077100	5.77873400	-1.41919500
C	1.62532200	5.00980700	-1.81806700
H	0.52804200	1.95718700	-0.80660100
H	-1.40985300	5.78381700	-0.50150400
H	2.46311000	3.01886800	-1.88519400
H	0.52273600	6.85175700	-1.59274800
H	2.47710500	5.48252700	-2.30067500
C	-3.08052000	3.86190800	-0.19889200
C	-3.80610000	4.69730400	0.65902800
C	-3.56916200	3.67148300	-1.50471800
C	-4.98994300	5.31361400	0.23606300
C	-4.74459200	4.28863500	-1.92689500
C	-5.46497400	5.11199200	-1.05700900
H	-3.46675800	4.88958300	1.67147500
H	-3.02841300	3.02912800	-2.19454800
H	-5.53349600	5.95451200	0.92570700
H	-5.09619300	4.12680800	-2.94259300
H	-6.38222300	5.59260200	-1.38667300
H	2.95067900	4.41653600	2.83565500
H	2.32738800	2.95309600	3.61611100
H	2.65313900	2.95392500	1.87470900
H	1.01802600	5.77504900	3.73783600
H	-0.65748100	5.33159500	3.41349400
H	0.31265500	4.36114000	4.53566400
H	-7.33080500	-3.67748600	-0.39131100
H	-6.85868100	-2.39483800	0.72701600
H	-7.24244700	-2.00244400	-0.95753900
H	-5.82256300	-4.36148300	-2.31320000
H	-5.57275300	-2.69723200	-2.87686600
H	-4.18262200	-3.70131800	-2.44835600
C	3.74391900	-2.30186600	-2.95866900
C	4.97374300	-1.70027600	-3.27661200
C	3.60214000	-3.67813500	-3.21076000
C	6.01385300	-2.43846300	-3.83786800
H	5.10832000	-0.64261400	-3.07283400
C	4.64455900	-4.41954100	-3.76536300
H	2.66937500	-4.17935700	-2.97163200
C	5.85530000	-3.80299600	-4.08586800
H	6.95281300	-1.94649700	-4.07947800
H	4.50785800	-5.48205900	-3.95058800
H	6.66588200	-4.38026100	-4.52302200

- **1aa**-*RS*



B3LYP/6-31G*

E = –3797.860355

Zero-point correction = 1.341186 (Hartree/Particle)

Thermal correction to Energy = 1.419764

Thermal correction to Enthalpy = 1.420708

Thermal correction to Gibbs Free Energy = 1.218293

Sum of electronic and zero-point Energies = –3796.519169

Sum of electronic and thermal Energies = –3796.440591

Sum of electronic and thermal Enthalpies = –3796.439647

Sum of electronic and thermal Free Energies = –3796.642062

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.055861

G = –3797.802712

PCM(DCE)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.069649

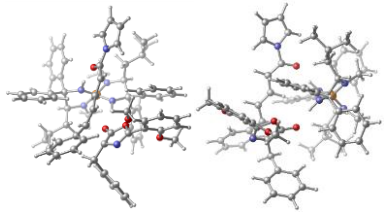
G = –3797.8165

0 1

O	0.89339200	-1.03301600	0.99063600
C	2.02835100	-0.64719700	0.69647400
C	3.22447100	-1.35276000	0.27195000
O	2.32713300	0.69362700	0.59429900
N	4.25094000	-0.39609800	0.13796300
C	3.68305000	0.75292000	0.25371800
C	4.29530300	2.08553600	0.13364900
C	5.05499800	2.44389200	-1.00391300
C	4.16052400	3.03243700	1.17536200
C	5.63803300	3.71506200	-1.10252100
C	4.73619700	4.30546700	1.07205500
C	5.46745400	4.62907500	-0.06722500
O	5.16480600	1.50684200	-1.98471800
C	5.87405400	1.83941700	-3.16858000
H	6.92793000	2.06216600	-2.95819200
H	5.41866700	2.69357700	-3.68598900
H	5.81251900	0.95589300	-3.80613300
O	3.47259800	2.61066800	2.26862400
C	3.26549100	3.52406000	3.33502000
H	4.21631600	3.85809600	3.77064700
H	2.68313000	4.39389600	3.00715300
H	2.69999600	2.97224100	4.08684000
H	6.21347200	3.99486500	-1.97556400
H	4.63017500	5.02940300	1.86984500
H	5.91911800	5.61423900	-0.14822500
C	3.55613800	-2.72002200	0.83055400
H	2.73377000	-3.40842900	0.60411900
H	4.44058900	-3.09442800	0.30553900
C	3.80856200	-2.72045000	2.33029400

C	2.92806000	-3.36668700	3.20661200
C	4.93190800	-2.07440500	2.86836000
C	3.16091800	-3.37382500	4.58408000
C	5.16614500	-2.07849700	4.24284500
C	4.28185900	-2.72923300	5.10742100
H	2.05432600	-3.87414800	2.80309700
H	5.61460300	-1.55897200	2.19849500
H	2.46795300	-3.88690800	5.24706300
H	6.04333700	-1.57404400	4.64085600
H	4.46736700	-2.73495700	6.17858000
C	2.59755500	-1.66928800	-1.69183100
C	2.36964900	-0.44338600	-2.39296000
H	1.69638800	-2.19279600	-1.37179400
H	3.17369200	-0.05184300	-3.00949400
C	1.15457900	0.22670700	-2.37741400
H	0.37112900	-0.17610300	-1.73789200
C	0.79746400	1.35798900	-3.11992700
H	1.52622000	1.80450300	-3.78755000
C	-0.51856400	1.86802900	-3.09396100
O	-1.49902700	1.39212500	-2.45845100
N	-0.79341300	3.02584800	-3.89618600
C	-2.07477000	3.40909100	-4.25423400
C	0.10313700	3.93742900	-4.43499800
C	-1.99216000	4.54584000	-5.01910400
C	-0.60730700	4.88577600	-5.12789600
H	-2.91280300	2.80516000	-3.94648300
H	1.16021200	3.85893200	-4.23737600
H	-2.82712500	5.07605500	-5.45824600
H	-0.18497800	5.73682700	-5.64632900
H	-0.81555500	-1.38420800	0.29315300
N	-1.82178000	-1.38066800	0.09596600
P	-2.75293800	-0.16573300	0.70431700
N	-4.17360500	-0.87719000	0.22575700
C	-3.96113500	-2.04186300	-0.66563200
C	-2.57598400	-2.62787000	-0.16102500
C	-5.50078700	-0.29072700	0.35085100
H	-5.47575900	0.52521000	1.07512600
H	-5.86389200	0.11778400	-0.59966900
H	-6.21064300	-1.05034500	0.70105600
H	-4.75698500	-2.75693400	-0.44692500
C	-4.04869700	-1.63374600	-2.15289200
H	-3.09919100	-1.18871300	-2.46613700
H	-4.78476500	-0.82154800	-2.22372000
C	-4.48483400	-2.73612800	-3.14426900
H	-3.87040000	-3.62837100	-2.97551300
C	-4.23798600	-2.26555200	-4.58533700
C	-5.95898200	-3.13113700	-2.95601200
C	-2.72790300	-3.42909400	1.16017600
C	-3.86969300	-4.17342500	1.48817900
C	-1.64949100	-3.45105700	2.06145800
C	-3.94408800	-4.89661200	2.68265500
C	-1.72150800	-4.17421900	3.25167300
C	-2.87172400	-4.89779500	3.57217800
H	-4.71969100	-4.21278000	0.81421900
H	-0.74102300	-2.89871100	1.84021000
H	-4.84542600	-5.45963400	2.91074400
H	-0.87161500	-4.16999200	3.92906500
H	-2.92858900	-5.45882200	4.50099700
C	-1.85748000	-3.47615500	-1.22453400
C	-1.05949900	-2.87058300	-2.20573000
C	-2.01127900	-4.87014000	-1.26012000
C	-0.44263200	-3.63341000	-3.19915300
C	-1.40032000	-5.63226300	-2.25671400
C	-0.61339900	-5.01795300	-3.23174700
H	-0.92148100	-1.79614300	-2.20202000
H	-2.60443600	-5.37106100	-0.50286600
H	0.17877500	-3.13702800	-3.93903900
H	-1.53553100	-6.71066000	-2.26270800
H	-0.13310800	-5.61191600	-4.00459800
N	-2.09233200	1.25476100	0.23506100
C	-2.35379500	2.36171600	1.18270100
C	-2.27420300	1.59585600	2.56579000
N	-2.95112400	0.30274300	2.28063800
H	-1.80902100	1.40326100	-0.75185400
C	-3.76861000	-0.37074800	3.28221900
H	-4.55197000	0.30478100	3.65102700
H	-3.17307200	-0.71259500	4.13288300
H	-4.24494000	-1.24389800	2.83278800
H	-2.87464200	2.11528700	3.31574400
C	-0.83665900	1.42141100	3.09125500
H	-0.42115800	2.42120400	3.26955200
H	-0.22717900	0.96559800	2.30342000
C	-0.67589400	0.58640300	4.37928000
H	-1.10643100	-0.40814700	4.20055000
C	-1.37672200	1.21779300	5.59300000
C	0.81633900	0.37273200	4.67558400
C	-1.29640100	3.46789700	1.05034700
C	-0.08673400	3.25752100	0.37859800
C	-1.53188100	4.72299700	1.63366700
C	0.85678600	4.28246000	0.27905600
C	-0.58270400	5.73980900	1.54820500
C	0.61508500	5.52557600	0.86238200
H	0.14074000	2.29419200	-0.06047800
H	-2.47037200	4.91610700	2.14449200
H	1.78213900	4.09783000	-0.25724300
H	-0.78855400	6.70507600	2.00383100
H	1.34863300	6.32305400	0.77631900
C	-3.75641500	2.95975400	0.89445000
C	-4.10320600	3.19424000	-0.44747600
C	-4.68213500	3.31286100	1.88456600
C	-5.33484800	3.75155800	-0.78372600
C	-5.92266700	3.86626000	1.54750900
C	-6.25511000	4.08676400	0.21310000
H	-3.40160700	2.93602200	-1.23588700
H	-4.45436400	3.17034200	2.93629600
H	-5.57365900	3.92779000	-1.82919000
H	-6.62378900	4.12627400	2.33649600
H	-7.21691800	4.51922700	-0.04907000
H	-4.54671700	-3.02991300	-5.30827600
H	-4.80528100	-1.35126900	-4.80438200
H	-3.17777900	-2.04903300	-4.75477700
H	-6.24104900	-3.92612300	-3.65603600
H	-6.17150100	-3.50051700	-1.94515300
H	-6.62138700	-2.27528400	-3.14264100
H	0.95592300	-0.26563600	5.55607400
H	1.32539300	-0.10108200	3.83083800
H	1.31493300	1.32927500	4.87966000
H	-1.22540800	0.60962500	6.49278200
H	-0.96913800	2.21664500	5.79794000
H	-2.45866200	1.32688200	5.45189000
C	3.65682600	-2.58017900	-2.20463500
C	3.36705600	-3.93820300	-2.41657500
C	4.95029600	-2.11822500	-2.50956600
C	4.32768600	-4.80482600	-2.93983300
C	2.37277700	-4.31208700	-2.18477100
C	5.90999600	-2.98693500	-3.02532900
H	5.20423400	-1.08515600	-2.29585300
C	5.60337100	-4.33237100	-3.24926000
H	4.07801900	-5.85040300	-3.10324300
H	6.90755500	-2.61460300	-3.24611700
H	6.35479600	-5.00602400	-3.65308100

● **1aa**-*SR*



B3LYP/6-31G*

E = –3797.86084

Zero-point correction = 1.340082 (Hartree/Particle)

Thermal correction to Energy = 1.419075

Thermal correction to Enthalpy = 1.420019

Thermal correction to Gibbs Free Energy = 1.214593

Sum of electronic and zero-point Energies = –3796.520758

Sum of electronic and thermal Energies = –3796.441765

Sum of electronic and thermal Enthalpies = –3796.440821

Sum of electronic and thermal Free Energies = –3796.646248

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.054043

G = –3797.804042

PCM(DCE)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.067722

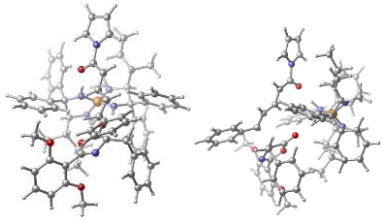
G = –3797.817721

0 1

O	0.98022800	0.75679900	1.17071700
C	2.12240100	0.62383100	0.71209800
C	3.14586900	1.58222900	0.35517600
O	2.59047700	-0.60069300	0.29982200
N	4.26924100	0.85542500	-0.08528100
C	3.88851400	-0.37153900	-0.15989500
C	4.66084700	-1.55144200	-0.57946900
C	4.84593900	-2.62107200	0.32489900
C	5.24924800	-1.63801100	-1.85865900
C	5.57568400	-3.75769400	-0.04523200
C	5.98671900	-2.77184000	-2.22819800
C	6.13595700	-3.81571500	-1.31886100
O	4.30030700	-2.44133400	1.55553300
C	4.42493600	-3.47452800	2.51947100
H	5.47717000	-3.67435700	2.76169500
H	3.94162000	-4.39804900	2.17910600
H	3.91181600	-3.10778500	3.40988000
O	5.03992600	-0.58273000	-2.69566000
C	5.59657300	-0.62997800	-4.00047100
H	5.20175100	-1.47571400	-4.57833500
H	5.30184100	0.30457600	-4.48083300
H	6.69190900	-0.69214000	-3.96944300
H	5.71988700	-4.57667500	0.64847500
H	6.43576000	-2.84712200	-3.21041300
H	6.70748000	-4.69353200	-1.60885000
C	3.34659700	2.85128500	1.15303800
H	2.40961000	3.42082300	1.16166000
H	4.09413700	3.46405200	0.64041400
C	3.78434500	2.58645400	2.58462200
C	2.85671900	2.60453300	3.63449000
C	5.12307800	2.29345200	2.88021200
C	3.25545200	2.34561700	4.94748200
C	5.52429700	2.03332600	4.19056200
C	4.59209200	2.06043100	5.23061500
H	1.81279100	2.81634100	3.41543200
H	5.84808200	2.26037500	2.07114600
H	2.52209200	2.37355500	5.75042900
H	6.56776900	1.81128300	4.40080100
H	4.90591200	1.86299700	6.25261500
C	2.20396600	2.20896200	-1.45518800
C	1.96534100	1.13058900	-2.35363700
H	1.32814600	2.55600700	-0.90619900
H	2.71160300	0.91643400	-3.11377400
C	0.77540000	0.41181100	-2.35876500
H	0.05598300	0.65300400	-1.57811100
C	0.37686600	-0.56311600	-3.27693800
H	1.06827400	-0.86451800	-4.05602000
C	-0.94023500	-1.08211100	-3.28831700
O	-1.90242700	-0.73006700	-2.55864000
N	-1.23056000	-2.11166600	-4.24479400
C	-2.51985900	-2.48671900	-4.58359100
C	-0.34201000	-2.89644900	-4.96858100
C	-2.45134600	-3.48962400	-5.51770100
C	-1.06605500	-3.75421300	-5.75775500
H	-3.35527800	-1.98335000	-4.12584900
H	0.72309600	-2.80261200	-4.83031900
H	-3.29604000	-3.98012800	-5.98341800
H	-0.65184500	-4.49605600	-6.42814400
H	-0.36254900	-0.45928400	1.04688000
N	-1.26111800	-0.96940600	1.05021400
P	-2.67988800	-0.14861400	0.95968500
N	-3.60516000	-1.49056300	1.26414100
C	-2.82454400	-2.74686300	1.17205400
C	-1.38802800	-2.30895300	1.67272200
C	-5.05966500	-1.54340400	1.29580600
H	-5.38737800	-2.14877400	2.15004500
H	-5.47726500	-1.97618700	0.37873400
H	-5.46160500	-0.53484000	1.40661800
H	-3.26174500	-3.44689700	1.88748500
C	-2.90528200	-3.36498000	-0.24265000
H	-3.87155500	-3.07258300	-0.67521000
H	-2.15178500	-2.90362400	-0.88708100
C	-2.81215800	-4.90610500	-0.31199300
H	-1.97170300	-5.23721700	0.30994100
C	-2.52792600	-5.35257400	-1.75366500
C	-4.08937600	-5.57823900	0.21855300
C	-0.28192300	-3.25025600	1.17020400
C	0.04879100	-4.40120000	1.90256600
C	0.38305600	-3.01434000	-0.03905300
C	0.99941200	-5.30320000	1.42521000
C	1.34326100	-3.91132800	-0.51058400
C	1.65106800	-5.06227900	0.21348900
H	-0.43623400	-4.59739900	2.85371700
H	0.16266300	-2.12667800	-0.61987300
H	1.23122200	-6.19333800	2.00494200
H	1.85253900	-3.69687300	-1.44525700
H	2.39671200	-5.76000300	-0.15825000
C	-1.30159400	-2.16848700	3.21648900
C	-0.30485600	-1.33003900	3.74669200
C	-2.12897800	-2.85144100	4.11757900
C	-0.15098700	-1.17470500	5.12287700
C	-1.97892200	-2.69275200	5.49972700
C	-0.99062600	-1.85367500	6.00914700
H	0.35633500	-0.78377500	3.08066000
H	-2.90342100	-3.52386000	3.76313000
H	0.63079500	-0.51983500	5.49889100
H	-2.63974200	-3.23233800	6.17342700
H	-0.87309500	-1.73166500	7.08259800
N	-2.62507700	0.81499600	-0.37447400

C	-3.48252900	2.01506900	-0.25277800
C	-3.25115000	2.38183600	1.26786900
N	-3.27801600	1.05663400	1.93143000
H	-2.33846600	0.40081500	-1.27875500
C	-3.51804600	0.96190500	3.36363200
H	-2.74862900	1.48604700	3.94419900
H	-3.51468300	-0.08689400	3.66623100
H	-4.49608200	1.39518700	3.60770500
H	-4.10514800	2.94730300	1.64734800
C	-1.94632100	3.14850000	1.58479700
H	-1.17254200	2.84801800	0.87078400
H	-1.58728400	2.80061400	2.56275500
C	-2.05185000	4.68848200	1.64674300
H	-2.54808000	5.04551300	0.73630100
C	-2.87407800	5.16285600	2.85642100
C	-0.64651500	5.30696600	1.68359000
C	-3.04205500	3.13065000	-1.21488900
C	-3.89849000	4.21385200	-1.47032800
C	-1.79371400	3.11232200	-1.84603600
C	-3.50859800	5.25140400	-2.31588700
C	-1.40470100	4.14641600	-2.70151500
C	-2.25785400	5.22294100	-2.93646400
H	-4.88386900	4.24529700	-1.01651700
H	-1.11869800	2.28304400	-1.68661700
H	-4.19020200	6.07836900	-2.49710700
H	-0.43216500	4.09688900	-3.18346700
H	-1.95795500	6.02665000	-3.60341000
C	-4.95612200	1.63492400	-0.56280600
C	-6.05929000	2.14117000	0.13699100
C	-5.20120600	0.76365300	-1.63765400
C	-7.36425700	1.78008800	-0.21376600
C	-6.50141800	0.40777900	-1.99210300
C	-7.59176200	0.91178900	-1.27935000
H	-5.92422000	2.82919700	0.96576300
H	-4.36726700	0.35143900	-2.19833300
H	-8.20041200	2.18414700	0.35111300
H	-6.66126000	-0.26559200	-2.83007200
H	-8.60533900	0.63243300	-1.55374000
H	-0.69637400	6.40121600	1.73038700
H	-0.08546100	4.96202500	2.56231200
H	-0.07094400	5.03456900	0.79168500
H	-2.95432300	6.25602500	2.86869800
H	-3.89604600	4.76384800	2.85477200
H	-2.39928900	4.85505000	3.79761500
H	-3.99178300	-6.67010100	0.20392700
H	-4.32210000	-5.28754700	1.25115100
H	-4.95577900	-5.31494300	-0.40284600
H	-2.48280000	-6.44615100	-1.82502900
H	-3.30931300	-5.00382000	-2.44058900
H	-1.57482400	-4.95034200	-2.11203300
C	3.11548100	3.30213200	-1.88027800
C	2.69628400	4.63878300	-1.77177700
C	4.38638000	3.04358400	-2.42543800
C	3.50700200	5.68564500	-2.21251000
H	1.71618200	4.85659900	-1.35266200
C	5.19739800	4.09065700	-2.85764900
H	4.74537400	2.02043400	-2.46310300
C	4.76146600	5.41543100	-2.75995800
H	3.15767700	6.71150200	-2.12547600
H	6.18109500	3.87311700	-3.26676500
H	5.39765500	6.22836000	-3.10026400

● **1da**-*RR* (HH)



B3LYP/6-31G*

E = –3797.844244

Zero-point correction = 1.342046 (Hartree/Particle)

Thermal correction to Energy = 1.420406

Thermal correction to Enthalpy = 1.421350

Thermal correction to Gibbs Free Energy = 1.221185

Sum of electronic and zero-point Energies = –3796.502198

Sum of electronic and thermal Energies = –3796.423839

Sum of electronic and thermal Enthalpies = –3796.422894

Sum of electronic and thermal Free Energies = –3796.623059

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

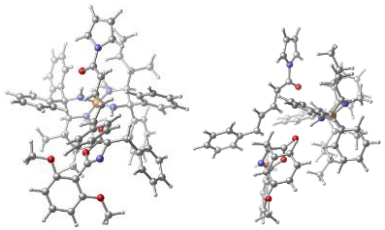
E = –3799.041782

G = –3797.786157

0 1

O	-0.91309700	-0.59385400	-0.07886400
C	-2.11204200	-0.41845800	0.09360400
C	-3.12838800	-1.13453100	0.84528100
O	-2.73865100	0.72905600	-0.39772900
N	-4.36974400	-0.50610700	0.55314100
C	-4.08662400	0.55910900	-0.10188900
C	-5.00960200	1.58848200	-0.62265600
C	-5.31476100	2.74042700	0.12101700
C	-5.59554400	1.41490800	-1.88989700
C	-6.20606700	3.69749800	-0.38137300
C	-6.48873000	2.36603600	-2.39999100
C	-6.78003000	3.49299800	-1.63459200
O	-4.69277800	2.84449000	1.33421300
C	-5.00204200	3.96056300	2.15990100
H	-6.07069300	3.99165300	2.40605400
H	-4.71040000	4.90457100	1.68261300
H	-4.42284200	3.82137000	3.07389000
O	-5.22369500	0.28348700	-2.54763600
C	-5.82016700	-0.00799200	-3.80191900
H	-6.91141900	-0.08957000	-3.71717700
H	-5.56965200	0.75108400	-4.55429800
H	-5.40621700	-0.97120500	-4.10415600
H	-6.45085500	4.58721000	0.18506400
H	-6.94700300	2.23787100	-3.37299200
H	-7.47165600	4.23439900	-2.02583700
C	-3.07892100	-2.64469400	0.93325800
H	-2.10815600	-2.92907900	1.35516500
H	-3.85402500	-2.97008100	1.63572400
C	-3.27459900	-3.33799300	-0.40580000
C	-2.21651800	-4.01567000	-1.02479300
C	-4.51891800	-3.30619500	-1.05435600
C	-2.39270600	-4.64775100	-2.25883200
C	-4.69728600	-3.93716700	-2.28542400
C	-3.63446900	-4.61105600	-2.89380900
H	-1.24757100	-4.05473600	-0.53283400
H	-5.34276700	-2.77148000	-0.59040200
H	-1.55754500	-5.17034500	-2.71872300
H	-5.67187600	-3.91011900	-2.76781800
H	-3.77628500	-5.10816300	-3.85046100
C	-2.69086500	-0.42397900	2.72121100
C	-1.37648200	-0.75900200	3.17970500
H	-2.80904500	0.61091500	2.40036900
H	-1.26560900	-1.62452300	3.82992200
C	-0.24885000	0.01329800	2.94863200
H	-0.34333100	0.87718200	2.29322000
C	0.99871300	-0.15602900	3.57065800
H	1.08657600	-0.91486600	4.34042300
C	2.06503400	0.74220600	3.35615500
O	2.13894600	1.61847400	2.45657300
N	3.17527100	0.69590900	4.27469100
C	4.17396000	1.65499000	4.28460600
C	3.41952400	-0.19612800	5.31115600
C	5.04180300	1.37495300	5.31079800
C	4.56480700	0.19437100	5.96014500
H	4.13860200	2.46247200	3.57233200
H	2.76792100	-1.03417500	5.49763000
H	5.91707700	1.95355800	5.57573500
H	5.01232300	-0.31013100	6.80676900
H	0.77882200	-1.14940000	-0.41260300
N	1.77325700	-1.15828700	-0.65025500
P	2.52074900	0.19510700	-1.19396200
N	4.01505200	-0.52737500	-1.21524100
C	4.02247900	-1.91816200	-0.68653500
C	2.51742100	-2.40496700	-0.91918100
C	5.20957900	0.03244100	-1.84056000
H	4.98225400	1.01999600	-2.24511100
H	6.02200800	0.15035900	-1.12150700
H	5.55446500	-0.61346600	-2.65933400
H	4.69089500	-2.47850700	-1.34555300
C	4.56621700	-2.08776900	0.76755500
H	3.72523400	-1.98083600	1.46236300
C	5.60887000	-1.02491600	1.17578900
H	6.48947700	-1.10079500	0.52120400
C	6.07114400	-1.14061100	2.63364300
C	2.01292000	-3.50370900	0.03786100
C	1.44944000	-3.17288400	1.27960000
C	2.08858800	-4.86042100	-0.31626800
C	0.99540200	-4.17124300	2.14460400
C	1.63818700	-5.85579800	0.55096300
C	1.08888400	-5.51575900	1.78785500
H	1.35410900	-2.13592100	1.58363700
H	2.49588100	-5.14820400	-1.27960000
H	0.56218600	-3.88534900	3.09909000
H	1.70875800	-6.89801800	0.25117400
H	0.72982900	-6.28993800	2.46052500
C	2.27811800	-2.85211800	-2.38817300
C	0.99437800	-2.69164100	-2.93568000
C	3.25381600	-3.47083000	-3.18228200
C	0.70281700	-3.11518000	-4.23169800
C	2.96669900	-3.88873400	-4.48593800
C	1.69158000	-3.71033500	-5.01826700
H	0.20729800	-2.23755700	-2.34207200
H	4.25125000	-3.65391500	-2.79525600
H	-0.30322400	-2.98301100	-4.62009400
H	3.74622700	-4.36006700	-5.07896500
H	1.46800700	-4.03695000	-6.03021600
N	2.00240400	1.46640000	-0.31037800
C	2.01471900	2.75156300	-1.05134600
C	1.61226400	2.27458600	-2.52346200
N	2.29976900	0.96393500	-2.64656300
H	1.95827700	1.45631500	0.72752900
C	2.83866000	0.53848600	-3.93386200
H	3.33181000	-0.42841700	-3.82559500
H	2.04870000	0.42523500	-4.67881600
H	3.56966400	1.26957200	-4.30509900
H	2.08785600	2.93117600	-3.25670300
C	0.08269700	2.25344400	-2.84686200
H	-0.46101600	2.00809800	-1.92964400
C	-0.32072600	1.18104400	-3.88328900
H	0.12987200	1.41653400	-4.85921400
C	-1.83821700	1.03407100	-4.06115800
C	1.01673700	3.71545700	-0.38324600
C	-0.14346800	3.22219600	0.23119100
C	1.23036400	5.10146800	-0.38380100
C	-1.07667600	4.08887000	0.79961700
C	0.30125500	5.96859100	0.19313400
C	-0.85842800	5.46653000	0.78357600
H	-0.32415000	2.15433700	0.26197100
H	2.12905200	5.51310300	-0.83011100
H	-1.97666600	3.67505500	1.24568500
H	0.49136100	7.03874400	0.18295400
H	-1.58076400	6.14360300	1.23245700
C	3.44601400	3.35298200	-1.01948900
C	4.00758200	4.08254400	-2.07685200
C	4.20508100	3.20575800	0.15420600
C	5.29612800	4.61840600	-1.98087400
C	5.48815400	3.74262800	0.25163000
C	6.04506500	4.44582100	-0.81879100
H	3.44637900	4.26148900	-2.98875900
H	3.78280200	2.67422000	1.00183300
H	5.70707500	5.17436300	-2.81973900
H	6.05212600	3.61175400	1.17150700
H	7.04670900	4.86060400	-0.74397300
H	-2.06044300	0.20421700	-4.74268800
H	-2.33143900	0.82442000	-3.10650100
H	-2.29416100	1.93504600	-4.48602900
H	6.70280000	-0.28767700	2.90172900
H	5.22345800	-1.14158200	3.32670500
H	6.65535800	-2.05059200	2.80877200
C	-3.86584000	-0.89609400	3.51237800
C	-5.01569500	-0.09148700	3.58948400
C	-3.86939400	-2.11414000	4.21537200
C	-6.11725800	-0.47874300	4.35007800
H	-5.04054600	0.84258400	3.03714700
C	-4.97366100	-2.50604400	4.97110100
H	-3.00263700	-2.76651800	4.17374300
C	-6.10277200	-1.68856100	5.04611600
H	-6.99172300	0.16571300	4.39637800
H	-4.94925200	-3.45255400	5.50544400
H	-6.96146600	-1.99233000	5.63925900
C	-0.35482300	3.64979300	-3.32589300
H	0.07997200	3.86840400	-4.31166700
H	-1.44267400	3.70902000	-3.42214000
H	-0.04805000	4.44086300	-2.63846800
H	0.08128100	0.21128500	-3.57122400
H	5.17988700	-0.02794300	1.02374600
C	5.15686600	-3.50196700	0.92096800
H	6.08551200	-3.59123400	0.33972200
H	5.39799200	-3.71627800	1.96572800
H	4.47054000	-4.28057300	0.58129500

- **1da**-*RR* (HH-2)



B3LYP/6-31G*

E = –3797.843126

Zero-point correction = 1.342173 (Hartree/Particle)

Thermal correction to Energy = 1.420456

Thermal correction to Enthalpy = 1.421400

Thermal correction to Gibbs Free Energy = 1.220799

Sum of electronic and zero-point Energies = –3796.500952

Sum of electronic and thermal Energies = –3796.422669

Sum of electronic and thermal Enthalpies = –3796.421725

Sum of electronic and thermal Free Energies = –3796.622327

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

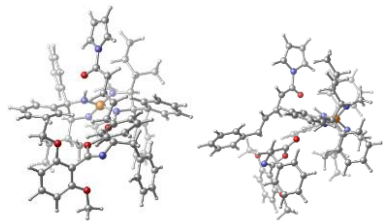
E = –3799.039651

G = –3797.78433

0 1

O	0.99085800	0.35727500	-0.17951500
C	2.19074800	0.23998100	0.05270200
C	3.10197800	0.87847700	0.99024800
O	2.93450000	-0.75251000	-0.58070100
N	4.39799800	0.38952500	0.69843400
C	4.24674000	-0.55354600	-0.15881000
C	5.28106600	-1.40900900	-0.76531800
C	5.24396000	-2.80768100	-0.60520500
C	6.32779900	-0.83634500	-1.51806100
C	6.22882700	-3.62206600	-1.17784300
C	7.31871000	-1.64742400	-2.08866800
C	7.25371800	-3.02689200	-1.91030100
O	4.21424400	-3.28501600	0.15259600
C	4.05027800	-4.69221500	0.25949100
H	4.88068800	-5.15431600	0.80900400
H	3.96363400	-5.16026000	-0.72895300
H	3.11978500	-4.84191900	0.80819400
O	6.28165100	0.51263700	-1.66201800
C	7.28143600	1.15486300	-2.43567700
H	8.27939100	1.01833900	-1.99893300
H	7.28709700	0.79142900	-3.47191800
H	7.02018600	2.21412800	-2.42400300
H	6.21065400	-4.69686100	-1.04762300
H	8.12505700	-1.21490700	-2.66792700
H	8.02256600	-3.65518300	-2.35228900
C	2.95502000	2.33699300	1.36353400
H	1.91473600	2.51039600	1.65815900
H	3.58492100	2.52515700	2.24093200
C	3.34572100	3.29398300	0.24894600
C	2.36945300	3.95364600	-0.50810200
C	4.69625300	3.53330100	-0.04670000
C	2.72846300	4.82944500	-1.53564100
C	5.05707300	4.41316200	-1.06724800
C	4.07433100	5.06447200	-1.81790300
H	1.31890600	3.78645000	-0.28672600
H	5.46168700	3.01455100	0.52321000
H	1.95234800	5.33092000	-2.10862900
H	6.10943600	4.59935700	-1.27137100
H	4.35666300	5.75248700	-2.61113000
C	2.52438400	-0.16285200	2.69859100
C	1.30097700	0.34173100	3.24137600
H	2.43018700	-1.11195300	2.17160900
H	1.36176800	1.11106000	4.00885700
C	0.04372800	-0.14618400	2.92730600
H	-0.02612300	-0.92498600	2.17171800
C	-1.15408300	0.21405900	3.56697000
H	-1.09993300	0.90717900	4.39979400
C	-2.37950800	-0.42876800	3.29670400
O	-2.60956400	-1.28805300	2.40645600
N	-3.49126600	-0.11179400	4.15755500
C	-4.60316000	-0.92698100	4.27506200
C	-3.64362500	0.96313500	5.02199300
C	-5.44998600	-0.37999500	5.20781700
C	-4.84365500	0.82622200	5.67694900
H	-4.65776900	-1.83484400	3.69679800
H	-2.90592700	1.74796800	5.07166100
H	-6.39644000	-0.79743900	5.52560400
H	-5.24656100	1.51720500	6.40614500
H	-0.67805800	1.05210600	-0.43759200
N	-1.65717200	1.15182200	-0.72026300
P	-2.49662700	-0.13426200	-1.29442300
N	-3.89339600	0.74079800	-1.48849600
C	-3.80268400	2.14149400	-0.99795600
C	-2.23752800	2.45963800	-1.09246600
C	-5.08392600	0.27846000	-2.19646500
H	-4.89167600	-0.70072100	-2.63754200
H	-5.94180800	0.17590500	-1.52923100
H	-5.34242000	0.98148300	-2.99931100
H	-4.33677100	2.74458700	-1.73699200
C	-4.46774500	2.42489900	0.38669700
H	-3.71974000	2.25866200	1.16991800
C	-5.65520800	1.49446100	0.71575700
H	-6.44649600	1.62447400	-0.03673000
C	-6.25625000	1.72978400	2.10754600
C	-1.72029800	3.53047400	-0.11099900
C	-1.34649300	3.18297700	1.19634700
C	-1.60521600	4.87527500	-0.49809200
C	-0.89369900	4.15487300	2.09121000
C	-1.15478500	5.84481500	0.39848800
C	-0.79800200	5.48952600	1.69965700
H	-1.39906200	2.15170400	1.52894600
H	-1.86203500	5.17344500	-1.50882800
H	-0.60987600	3.85541100	3.09629900
H	-1.07423900	6.87819300	0.07197600
H	-0.43888200	6.24292400	2.39533200
C	-1.81658200	2.83098000	-2.54099700
C	-0.52550300	2.48859200	-2.97690000
C	-2.63457300	3.55201000	-3.42270300
C	-0.07902200	2.83565000	-4.25157000
C	-2.19135800	3.89524200	-4.70385100
C	-0.91300800	3.53556600	-5.12583600
H	0.14343400	1.94778500	-2.31494200
H	-3.62648300	3.87415200	-3.12143600
H	0.92673300	2.56009000	-4.55667600
H	-2.85106400	4.44952000	-5.36641200
H	-0.56713800	3.80282700	-6.12064400
N	-2.21564400	-1.40963100	-0.31479200
C	-2.36036200	-2.71757100	-0.99544100
C	-1.76410100	-2.38843300	-2.44173600
N	-2.23254500	-0.99747900	-2.68605400
H	-2.27462000	-1.33676600	0.72040000
C	-2.56862000	-0.55403700	-4.03538400
H	-3.01742100	0.43947400	-3.99294700
H	-1.68522900	-0.48973700	-4.67343000
H	-3.28638500	-1.24606900	-4.49584400
H	-2.26824800	-3.00548900	-3.19048700
C	-0.22990800	-2.61770200	-2.61945300
H	0.26792700	-2.37665300	-1.67437500
C	0.40580600	-1.70561800	-3.69196300
H	-0.05041800	-1.91528600	-4.67104000
C	1.92843300	-1.85119600	-3.81334600
C	-1.59429900	-3.77728600	-0.17888300
C	-0.46886400	-3.41646200	0.57512400
C	-2.01602400	-5.11485300	-0.14028800
C	0.20964300	-4.36069400	1.34622300
C	-1.32851400	-6.06261000	0.61872900
C	-0.21504100	-5.68903000	1.37149500
H	-0.12624600	-2.38843000	0.56839100
H	-2.89625500	-5.42327500	-0.69386500
H	1.05998300	-4.00456400	1.94468400
H	-1.67872700	-7.09137300	0.63323300
H	0.30613500	-6.42217100	1.98149000
C	-3.86452200	-3.09920900	-1.07203900
C	-4.43245100	-3.80311600	-2.14310500
C	-4.69495300	-2.77056900	0.01368200
C	-5.79024600	-4.13870500	-2.14906100
C	-6.04796200	-3.10832200	0.00964400
C	-6.60601400	-3.78770600	-1.07546800
H	-3.82504500	-4.11742600	-2.98614500
H	-4.27905700	-2.25286400	0.87323900
H	-6.20314800	-4.67922800	-2.99696500
H	-6.66592000	-2.84085500	0.86277400
H	-7.66128900	-4.04703500	-1.07937600
H	2.32228900	-1.11606200	-4.52509000
H	2.41737300	-1.67744700	-2.84982300
H	2.22294600	-2.84193900	-4.17581000
H	-6.99488100	0.95508700	2.33870000
H	-5.49101900	1.69013900	2.88977300
H	-6.76449900	2.69765400	2.17769200
C	3.76183500	-0.11061900	3.52600300
C	4.70824000	-1.14392600	3.41417200
C	4.01996600	0.91930800	4.44773800
C	5.86165800	-1.15353500	4.19531400
H	4.53258000	-1.94499900	2.70145600
C	5.17727200	0.91480000	5.22480400
H	3.31066200	1.73264300	4.56613000
C	6.10347800	-0.12283700	5.10507300
H	6.57486900	-1.96739500	4.09105700
H	5.35267000	1.72327000	5.93018500
H	7.00300000	-0.12813700	5.71517700
C	0.02406900	-4.09725600	-2.96339300
H	-0.33802000	-4.31979400	-3.97719000
H	1.09260300	-4.32857700	-2.93577900
H	-0.47356600	-4.77945300	-2.27144600
H	0.18012100	-0.66186800	-3.44866900
H	-5.31939200	0.45319600	0.65389100
C	-4.91360500	3.89827100	0.43721200
H	-5.76656700	4.06125300	-0.23665900
H	-5.22964500	4.17843200	1.44565500
H	-4.11692500	4.58589300	0.14543600

- **1da**-*RR* (HMe)



B3LYP/6-31G*

E = –3797.84022

Zero-point correction = 1.341429 (Hartree/Particle)

Thermal correction to Energy = 1.420011

Thermal correction to Enthalpy = 1.420955

Thermal correction to Gibbs Free Energy = 1.219630

Sum of electronic and zero-point Energies = –3796.498791

Sum of electronic and thermal Energies = –3796.420210

Sum of electronic and thermal Enthalpies = –3796.419266

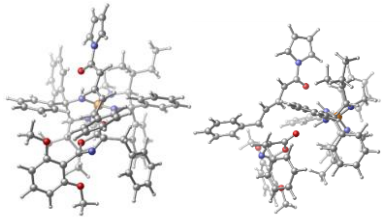
Sum of electronic and thermal Free Energies = –3796.620590

0 1

O	-0.95473000	-0.65405200	-0.05688000
C	-2.14763900	-0.41829300	0.07637800
C	-3.23898200	-1.15034600	0.69635000
O	-2.68506500	0.81567400	-0.30077200
N	-4.42739900	-0.41856000	0.42930700
C	-4.05218900	0.69494500	-0.08450800
C	-4.89605000	1.83233100	-0.50602600
C	-5.11420400	2.92835700	0.34484600
C	-5.50375000	1.81674700	-1.77485700
C	-5.93577100	3.99022700	-0.05476300
C	-6.32679900	2.87466000	-2.18357500
C	-6.52956700	3.94464600	-1.31481400
O	-4.48091400	2.86976100	1.55569800
C	-4.71858700	3.90980200	2.49627200
H	-5.78311700	3.98083100	2.75173100
H	-4.36921500	4.87911400	2.11874500
H	-4.14758000	3.64018600	3.38578100
O	-5.22602300	0.72454600	-2.53506000
C	-5.85073400	0.59160700	-3.80155300
H	-6.94478600	0.58707600	-3.71188900
H	-5.54719400	1.39244900	-4.48888400
H	-5.51471400	-0.37044300	-4.19182400
H	-6.11291900	4.83764700	0.59579300
H	-6.80017700	2.86996000	-3.15777600
H	-7.16718600	4.76710600	-1.62809400
C	-3.28327100	-2.66042800	0.60992500
H	-2.34769600	-3.05333300	1.02270100
H	-4.10147000	-3.01419900	1.24640800
C	-3.47247500	-3.17800400	-0.80738300
C	-2.42363700	-3.80972000	-1.48806900
C	-4.70151300	-3.02491100	-1.46742800
C	-2.59475400	-4.27954500	-2.79306600
C	-4.87520000	-3.49549900	-2.76900800
C	-3.82205500	-4.12502800	-3.43850200
H	-1.46683600	-3.94153000	-0.98975200
H	-5.51728200	-2.52289000	-0.95514000
H	-1.76714800	-4.77017000	-3.29976100

H	-5.83905900	-3.37849900	-3.25961900
H	-3.96049000	-4.49672400	-4.45100400
C	-2.84584300	-0.66202200	2.65020400
C	-1.54741000	-1.05866500	3.10818500
H	-2.94234700	0.40289600	2.43925600
H	-1.45926300	-1.98601300	3.67107500
C	-0.41147700	-0.27655600	2.97151900
H	-0.49567200	0.64839100	2.40311800
C	0.83423700	-0.50606300	3.57843500
H	0.94439300	-1.35110300	4.25039200
C	1.90404500	0.40033600	3.42520900
O	1.99891500	1.31035400	2.56127300
N	3.00062200	0.29816200	4.35180900
C	4.19376200	0.98182600	4.19351700
C	3.04675600	-0.38661600	5.55896500
C	4.99264100	0.72480600	5.28034900
C	4.26222800	-0.14411500	6.14964400
H	4.35358400	1.57620200	3.30930800
H	2.19523000	-0.94470000	5.91352800
H	5.98981400	1.11429000	5.43978500
H	4.58804500	-0.53419300	7.10524100
H	0.72835300	-1.06664800	-0.63389900
N	1.71936400	-1.15932500	-0.87178300
P	2.66711400	0.14552300	-1.16201500
N	4.06841500	-0.74361400	-1.11194700
C	3.87296100	-2.16858500	-0.73104800
C	2.35915800	-2.46188300	-1.15652100
C	5.37378800	-0.27424500	-1.56751600
H	5.27127600	0.72571500	-1.99202900
H	6.09482300	-0.22013500	-0.74898700
H	5.76957700	-0.94648300	-2.34044100
H	4.54618700	-2.73739100	-1.37763500
C	4.24641900	-2.53798800	0.73882900
H	3.36082700	-2.39366900	1.36793100
C	5.35875200	-1.65607500	1.34600500
H	6.27891400	-1.75917900	0.75249100
C	5.67622500	-1.99332500	2.80855400
C	1.65363100	-3.56766300	-0.34753300
C	1.03845200	-3.28630500	0.88120800
C	1.61462100	-4.88866700	-0.82295700
C	0.42776400	-4.30223900	1.62023400
C	1.00417600	-5.90142900	-0.08314300
C	0.40938700	-5.61315400	1.14585600
H	1.01798700	-2.27568800	1.27319100
H	2.06100800	-5.13367500	-1.78087500
H	-0.04127700	-4.05376700	2.56790800
H	0.98878000	-6.91496200	-0.47496700
H	-0.07172000	-6.39974800	1.72074300
C	2.22270900	-2.77078800	-2.67346900
C	0.98671200	-2.50596100	-3.28798500
C	3.23016800	-3.34896000	-3.45618500
C	0.77498300	-2.78431500	-4.63673900
C	3.02339500	-3.62305300	-4.81296900
C	1.79822000	-3.33790600	-5.41088600
H	0.17451100	-2.08770200	-2.70141300
H	4.19072800	-3.60976800	-3.02392000
H	-0.19496000	-2.57281600	-5.07852000
H	3.82685900	-4.06584300	-5.39591500
H	1.63743100	-3.55234900	-6.46390300
N	2.15495300	1.36479700	-0.20593000
C	2.31482700	2.71503800	-0.80027500
C	2.17516000	2.44548300	-2.35873100
N	2.75439600	1.09056300	-2.52771400
H	2.04164600	1.26238500	0.82284700
C	3.07765300	0.60000900	-3.86212500
H	3.67383600	-0.31094700	-3.78617100
H	2.18484700	0.36605600	-4.45279900
H	3.66536900	1.35647600	-4.39650200
H	2.84581100	3.14468700	-2.86672200
C	0.83018200	2.58628000	-3.14317100
H	1.14373400	2.31774800	-4.16471600
C	0.32508500	4.04310800	-3.25951700
H	-0.25042500	4.31559600	-2.37087800
C	-0.53002900	4.28543300	-4.51049200
C	1.24082500	3.66154000	-0.24135600
C	0.04339200	3.16905400	0.29013300
C	1.44127500	5.04918900	-0.27309300
C	-0.94379700	4.04230000	0.75084300
C	0.45746800	5.92230300	0.18873600
C	-0.74191300	5.42152500	0.69918400
H	-0.12755900	2.10052500	0.33877100
H	2.37222500	5.45225400	-0.65991400
H	-1.87010000	3.63084200	1.14159300
H	0.63209600	6.99456000	0.15317000
H	-1.50809500	6.10313600	1.06002700
C	3.72506800	3.25143000	-0.41296900
C	4.74045800	3.58762300	-1.31589100
C	3.99635300	3.38815900	0.96162300
C	5.98527900	4.04678200	-0.86694400
C	5.23300600	3.84625000	1.40813800
C	6.23718100	4.18051100	0.49476600
H	4.59218700	3.50266300	-2.38701700
H	3.23525200	3.11883500	1.68813700
H	6.75235200	4.30181400	-1.59385200
H	5.41009200	3.94558500	2.47592100
H	7.20124000	4.54103000	0.84343900
H	-0.84698200	5.33307800	-4.56573900
H	0.02777500	4.05794800	-5.42822500
H	-1.43646700	3.67013600	-4.51070700
H	6.36697400	-1.25649800	3.22894000
H	4.77319200	-1.97368000	3.42838400
H	6.13979300	-2.98037800	2.91097900
C	-4.04993200	-1.19716200	3.35109900
C	-5.18946600	-0.38501300	3.48270400
C	-4.09250600	-2.48474700	3.91483800
C	-6.31922600	-0.83299600	4.16451400
H	-5.18123700	0.60495600	3.03738000
C	-5.22477300	-2.93686500	4.59142900
H	-3.23453400	-3.14382200	3.82361500
C	-6.34319500	-2.11186700	4.72382100
H	-7.18501300	-0.18185000	4.25676200
H	-5.23113600	-3.93655800	5.01876200
H	-7.22379600	-2.46306100	5.25547300
C	-0.28122000	1.60023100	-2.76375000
H	-0.74069100	1.82950200	-1.80250400
H	-1.07455600	1.62178800	-3.51873400
H	0.08865500	0.57115900	-2.72097500
H	1.18505400	4.72708700	-3.28821400
H	5.05477900	-0.60448400	1.28865900
C	4.65693200	-4.02195000	0.79425100
H	5.63322300	-4.16429000	0.30959700
H	4.74700300	-4.36644400	1.82794000
H	3.93638200	-4.67486100	0.29787600

- **1da**-*RR* (MeH)



B3LYP/6-31G*

E = –3797.843528

Zero-point correction = 1.341814 (Hartree/Particle)

Thermal correction to Energy = 1.420404

Thermal correction to Enthalpy = 1.421348

Thermal correction to Gibbs Free Energy = 1.219660

Sum of electronic and zero-point Energies = –3796.501714

Sum of electronic and thermal Energies = –3796.423124

Sum of electronic and thermal Enthalpies = –3796.422179

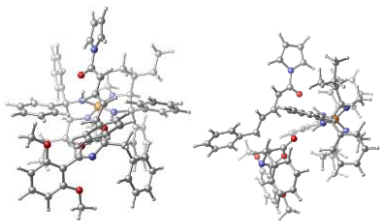
Sum of electronic and thermal Free Energies = –3796.623868

0 1

O	-0.86825200	-0.73415200	0.02234800
C	-2.06931100	-0.52901400	0.13295300
C	-3.12326500	-1.19979600	0.87632800
O	-2.65919400	0.60679300	-0.42684800
N	-4.34312900	-0.56223800	0.51774400
C	-4.01990200	0.47045300	-0.16919200
C	-4.91233800	1.49185600	-0.75490700
C	-5.26811700	2.64792100	-0.04045400
C	-5.43090900	1.29815100	-2.04825800
C	-6.13846100	3.59204200	-0.60097700
C	-6.30164300	2.23664200	-2.61687200
C	-6.64190600	3.36967900	-1.88113800
O	-4.71572900	2.76925400	1.20421900
C	-5.08138000	3.88958700	2.00034100
H	-6.16238200	3.91203300	2.18593600
H	-4.77239900	4.83191300	1.53067200
H	-4.55320400	3.76465500	2.94673700
O	-5.02173400	0.15848400	-2.66876600
C	-5.56843800	-0.16602700	-3.93775400
H	-6.66201400	-0.24747300	-3.89282200
H	-5.28963300	0.57410000	-4.69893000
H	-5.14221600	-1.13586000	-4.19896700
H	-6.42162800	4.48527200	-0.05837600
H	-6.70652900	2.09319100	-3.61115600
H	-7.31677500	4.10128900	-2.31746000
C	-3.10795500	-2.70897100	1.00219200
H	-2.15717000	-3.00269500	1.46114400
H	-3.91103800	-3.00168500	1.68705000
C	-3.27579100	-3.42893800	-0.32661000
C	-2.20695000	-4.12403800	-0.90699300
C	-4.50411100	-3.40363100	-1.00507000
C	-2.35722700	-4.77869400	-2.13275300
C	-4.65665800	-4.05684300	-2.22804400
C	-3.58337200	-4.74751400	-2.79808200
H	-1.25075400	-4.15907500	-0.39055200
H	-5.33605800	-2.85678400	-0.57068600
H	-1.51488700	-5.31592600	-2.56168700
H	-5.61943500	-4.03424600	-2.73373500
H	-3.70530900	-5.26283800	-3.74779600
C	-2.74130300	-0.44401800	2.73151600
C	-1.43157200	-0.74267700	3.22920800
H	-2.86739600	0.58309700	2.38855900
H	-1.31452300	-1.59967300	3.88957800
C	-0.31937600	0.05905600	3.02147000
H	-0.42403400	0.91804700	2.36047400
C	0.91737800	-0.07449100	3.67015500
H	1.02778700	-0.85146700	4.41936800
C	1.98760300	0.81869600	3.45236800
O	2.11353700	1.63458900	2.50187600
N	3.05953900	0.79976500	4.41190900
C	4.28620900	1.40615700	4.20190900
C	3.06701200	0.23069700	5.67825800
C	5.06817500	1.21046700	5.31297000
C	4.29020800	0.46579400	6.25407300
H	4.47787800	1.91391500	3.27140400
H	2.18847900	-0.25209200	6.07451700
H	6.08230000	1.56494100	5.44446100
H	4.59183800	0.15211600	7.24505500
H	0.84215600	-1.06416300	-0.50484600
N	1.84453500	-1.05621200	-0.70576400
P	2.57783800	0.32308500	-1.20177300
N	4.07719900	-0.38630000	-1.27609600
C	4.10896600	-1.79570100	-0.80507300
C	2.60868100	-2.28250300	-1.00287300
C	5.31836300	0.32392900	-1.55892200
H	5.09304600	1.27689500	-2.04192900
H	5.89068900	0.53948100	-0.64978300
H	5.94365300	-0.27210700	-2.23549700
H	4.73684700	-2.34077600	-1.51518700
C	4.85109600	-1.92310900	0.55968900
H	5.79892500	-1.40004900	0.35640700
C	5.26635900	-3.37174200	0.90574600
H	4.42653900	-3.90730700	1.35739400
C	6.47510700	-3.44170600	1.84863400
C	2.16893900	-3.43042300	-0.07697500
C	1.41303000	-3.19779400	1.07974500
C	2.50118100	-4.75448100	-0.40345900
C	1.02516500	-4.26202900	1.89913800
C	2.11942400	-5.81349000	0.41802500
C	1.37897800	-5.57150000	1.57698000
H	1.11583600	-2.19265500	1.35499400
H	3.05904900	-4.96378100	-1.31091600
H	0.44076800	-4.05509900	2.79141900
H	2.39335600	-6.82930700	0.14556500
H	1.07352900	-6.39627800	2.21510000
C	2.31722300	-2.71034200	-2.47490300
C	0.97396500	-2.71374300	-2.89088500
C	3.28362400	-3.13664300	-3.39427300
C	0.61422600	-3.11153600	-4.17629600
C	2.92611000	-3.53153700	-4.68883000
C	1.59232700	-3.51904500	-5.08739500
H	0.19257200	-2.41152500	-2.20019800
H	4.33367400	-3.17967600	-3.12460700
H	-0.43517500	-3.10999100	-4.45774700
H	3.70098800	-3.85260900	-5.38027600
H	1.31542800	-3.82831700	-6.09158300
N	2.02463100	1.54910700	-0.27452600
C	1.97907600	2.85950400	-0.97397700
C	1.61041300	2.41378700	-2.46209600
N	2.37251900	1.15119500	-2.62387100
H	1.95602900	1.49628900	0.76106200
C	2.96536400	0.80469600	-3.91060600
H	3.59144000	-0.08146500	-3.79665500
H	2.20457300	0.58345800	-4.66308200
H	3.58877600	1.63275400	-4.27339900
H	2.04444600	3.12330600	-3.17104400
C	0.08668900	2.30929300	-2.79854300
H	-0.44792500	1.99322400	-1.89721700
C	-0.23142600	1.25424400	-3.88210700

H	0.22799400	1.55202000	-4.83663000
C	-1.73279600	1.02549300	-4.10292000
C	0.93015200	3.75678100	-0.29554500
C	-0.20943500	3.20171400	0.30265100
C	1.07653800	5.15174300	-0.28325500
C	-1.18709000	4.01765100	0.87201300
C	0.10302200	5.96797800	0.29377900
C	-1.03501500	5.40414400	0.87093600
H	-0.34113300	2.12637900	0.32051800
H	1.95712800	5.60868900	-0.72210300
H	-2.07025600	3.55782000	1.30586500
H	0.24064400	7.04614500	0.29407800
H	-1.79217400	6.04102000	1.32130900
C	3.37901500	3.52568300	-0.88787000
C	4.00960200	4.18667300	-1.94980100
C	4.03685200	3.49810700	0.35525700
C	5.26965500	4.77464000	-1.78835000
C	5.28824800	4.08886000	0.51763500
C	5.91681400	4.72445600	-0.55641500
H	3.53118000	4.26821700	-2.92034200
H	3.55766400	3.01822100	1.20436000
H	5.73663600	5.27581100	-2.63243200
H	5.77141200	4.05690000	1.49079300
H	6.89414800	5.18247500	-0.42993400
H	-1.88798400	0.21171800	-4.82143600
H	-2.23437500	0.74814100	-3.16998500
H	-2.23324900	1.91384300	-4.50362200
H	6.75084000	-4.48324500	2.04916000
H	7.35119000	-2.94334000	1.41402000
H	6.26654000	-2.96628200	2.81292700
C	-3.92730000	-0.91347500	3.50978900
C	-5.09420900	-0.13032400	3.53014000
C	-3.92543800	-2.10643300	4.25432000
C	-6.20748700	-0.51370600	4.27569100
H	-5.12310900	0.78352500	2.94509600
C	-5.04104900	-2.49463000	4.99528600
H	-3.04533200	-2.74209900	4.25799600
C	-6.18754000	-1.69840700	5.01350100
H	-7.09514600	0.11418600	4.27751900
H	-5.01173200	-3.42152200	5.56275900
H	-7.05511900	-1.99911400	5.59515500
C	-0.43960400	3.69027700	-3.23103700
H	-0.01790300	3.96957100	-4.20709600
H	-1.52866200	3.68150100	-3.32980700
H	-0.18556100	4.47589900	-2.51686900
H	0.21800200	0.29677500	-3.59798400
H	5.51338000	-3.91330100	-0.01932400
C	4.19681300	-1.19919600	1.74024900
H	3.29808300	-1.71151900	2.08901500
H	4.89132700	-1.13648300	2.58334300
H	3.91642100	-0.17247200	1.49044500

- **1da**-*RR* (McMe)



B3LYP/6-31G*

E = –3797.83938

Zero-point correction = 1.341142 (Hartree/Particle)

Thermal correction to Energy = 1.420091

Thermal correction to Enthalpy = 1.421035

Thermal correction to Gibbs Free Energy = 1.216828

Sum of electronic and zero-point Energies = –3796.498238

Sum of electronic and thermal Energies = –3796.419289

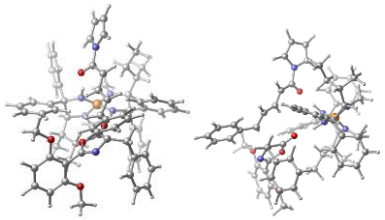
Sum of electronic and thermal Enthalpies = –3796.418345

Sum of electronic and thermal Free Energies = –3796.622552

0 1

O	-0.93493700	-0.79738000	-0.06492500
C	-2.12453300	-0.53951100	0.05798500
C	-3.22939500	-1.25530100	0.67524000
O	-2.64314900	0.69779500	-0.32983700
N	-4.40768300	-0.51129100	0.38944900
C	-4.01435700	0.59504800	-0.12534000
C	-4.83718700	1.74376700	-0.55762800
C	-5.10709600	2.81304300	0.31239400
C	-5.37022300	1.76695500	-1.85936700
C	-5.90613600	3.88625800	-0.10265900
C	-6.16970500	2.83645100	-2.28368000
C	-6.42481500	3.87952300	-1.39605000
O	-4.54496300	2.72011000	1.55553700
C	-4.84402300	3.72927600	2.51229200
H	-5.92236200	3.78917400	2.70466900
H	-4.47680300	4.71106000	2.18763200
H	-4.32695900	3.43271700	3.42590700
O	-5.04954000	0.69549100	-2.63288800
C	-5.59237700	0.60577600	-3.94045500
H	-6.68992200	0.60263800	-3.92130100
H	-5.24380700	1.42732900	-4.58022100
H	-5.23401100	-0.34433100	-4.34006400
H	-6.12201600	4.71375100	0.56163500
H	-6.58618400	2.86087600	-3.28321600
H	-7.04437100	4.71122800	-1.72085800
C	-3.28544100	-2.76562300	0.58968100
H	-2.36398400	-3.16508400	1.02794900
H	-4.12164500	-3.11043000	1.20755200
C	-3.44181800	-3.29264000	-0.82857800
C	-2.41265400	-4.01818100	-1.44219700
C	-4.62152500	-3.06201400	-1.55373300
C	-2.55446600	-4.50456800	-2.74507000
C	-4.76521100	-3.54704800	-2.85347900
C	-3.73202100	-4.27062800	-3.45594200
H	-1.49468500	-4.21103900	-0.89259100
H	-5.42138300	-2.48951100	-1.09315900
H	-1.74350800	-5.06890400	-3.19888400
H	-5.69114900	-3.36747000	-3.39546200
H	-3.84845200	-4.65436800	-4.46670600
C	-2.86775300	-0.76651600	2.61940700
C	-1.57190000	-1.14745700	3.10058800
H	-2.97246100	0.29840000	2.41147000
H	-1.48236000	-2.07357900	3.66510400
C	-0.44264700	-0.35104100	2.99263300
H	-0.52131900	0.57329800	2.42175600
C	0.78513300	-0.57298000	3.63589200
H	0.87795000	-1.42202500	4.30527300
C	1.87427000	0.31227500	3.50207400
O	2.01526200	1.21362500	2.63423900
N	2.94771700	0.17476500	4.45065200
C	4.20280100	0.73181000	4.27534700
C	2.92864600	-0.48095800	5.67351100
C	4.97639500	0.41907100	5.36589200
C	4.16354400	-0.34817500	6.25793400
H	4.42086100	1.28568700	3.37726600
H	2.02582400	-0.94340600	6.03885600
H	6.00842300	0.70937200	5.51464000
H	4.45072400	-0.74361800	7.22364800
H	0.78688800	-0.97242400	-0.69413100
N	1.78773100	-1.03017400	-0.90064600
P	2.67465000	0.31740200	-1.19161700
N	4.09766900	-0.53160500	-1.31350600
C	3.97937400	-1.97598700	-0.99098300
C	2.45135600	-2.29447100	-1.28298000
C	5.40897100	0.06937000	-1.52057300
H	5.28761000	1.07565400	-1.92646100
H	5.98322600	0.14958900	-0.59052000
H	5.98412000	-0.53087900	-2.23671200
H	4.57990800	-2.50902800	-1.73356600
C	4.66098400	-2.30701500	0.37264900
H	5.66442700	-1.87334300	0.23628300
C	4.90960700	-3.81698100	0.59263900
H	4.00393000	-4.29760800	0.97280600
C	6.07352700	-4.10270900	1.55102300
C	1.88516100	-3.47984300	-0.48278200
C	1.14411300	-3.29807800	0.69138000
C	2.10012000	-4.78851000	-0.94368800
C	0.65777100	-4.40096100	1.39956400
C	1.61981700	-5.88689300	-0.23332600
C	0.89651100	-5.69770000	0.94634900
H	0.92868700	-2.30441500	1.06430400
H	2.64546300	-4.95300400	-1.86793800
H	0.08654600	-4.23237400	2.30816500
H	1.80417900	-6.89041100	-0.60766200
H	0.51510000	-6.55217600	1.49883300
C	2.17238900	-2.55260600	-2.79526800
C	0.83136500	-2.48138800	-3.21363200
C	3.13844900	-2.87338900	-3.75607000
C	0.47366600	-2.70563700	-4.54015600
C	2.78260700	-3.09467600	-5.09247600
C	1.45186500	-3.00930900	-5.49156700
H	0.05198600	-2.26035200	-2.49020900
H	4.18668900	-2.96286000	-3.49064400
H	-0.57382900	-2.65258900	-4.82372300
H	3.55666800	-3.33772000	-5.81592700
H	1.17636600	-3.18436200	-6.52804500
N	2.16795200	1.45739300	-0.13754500
C	2.26530700	2.84927900	-0.64013400
C	2.08249200	2.68150100	-2.21053300
N	2.67813900	1.35414400	-2.49014100
H	2.04698900	1.27360800	0.87780900
C	2.99852900	0.97475800	-3.86046400
H	3.61220100	0.07235200	-3.85638100
H	2.10338300	0.76923000	-4.45885500
H	3.56468400	1.78198100	-4.34132200
H	2.72858700	3.42138500	-2.69004300
C	0.71588600	2.85108200	-2.95084300
H	1.01263100	2.67341500	-3.99715400
C	0.17497700	4.29915000	-2.93652500
H	-0.38533000	4.48351900	-2.01611200
C	-0.71592400	4.62125300	-4.14380100
C	1.18153400	3.71779300	0.01931000
C	0.00257000	3.15148300	0.51836900
C	1.35086600	5.10639300	0.11490300
C	-0.99759800	3.95502600	1.06784700
C	0.35441500	5.91017300	0.66752000
C	-0.82696600	5.33755600	1.14180900
H	-0.14366700	2.07918800	0.47379100
H	2.26754500	5.56590000	-0.24137300
H	-1.90999600	3.48850800	1.42826900
H	0.50604300	6.98461500	0.73074600
H	-1.60267800	5.96495400	1.57359600
C	3.67051000	3.40544700	-0.25972500
C	4.58956400	3.97251900	-1.15047300
C	4.03216900	3.33271900	1.09917300
C	5.83316500	4.44057700	-0.70696500
C	5.26691300	3.80117200	1.54048700
C	6.17869000	4.35685600	0.63820000
H	4.36508300	4.07073500	-2.20732900
H	3.34218300	2.89955900	1.81830700
H	6.52495700	4.87425400	-1.42472800
H	5.51379300	3.73478400	2.59696300
H	7.14209200	4.72293300	0.98291100
H	-1.06118600	5.66062200	-4.10431900
H	-0.17477700	4.48617800	-5.08932000
H	-1.60555300	3.98272600	-4.17516800
H	6.23289800	-5.18194200	1.65554200
H	7.01028600	-3.66201400	1.18637000
H	5.88475800	-3.70123500	2.55223000
C	-4.07420500	-1.31253400	3.31109400
C	-5.22437700	-0.51331900	3.42731400
C	-4.10732800	-2.59758900	3.88109100
C	-6.35540600	-0.97109600	4.10073600
H	-5.22398500	0.47380700	2.97593200
C	-5.24072000	-3.05959100	4.54910000
H	-3.24090500	-3.24705500	3.80217700
C	-6.36993000	-2.24715000	4.66658000
H	-7.22960700	-0.32966100	4.18123400
H	-5.23930800	-4.05705500	4.98162300
H	-7.25140100	-2.60587300	5.19172200
C	-0.36112900	1.80775600	-2.63068500
H	-0.81420000	1.95272400	-1.86793800
H	-1.16659000	1.86100400	-3.37103700
H	0.03726600	0.78870300	-2.66967400
H	1.01825900	5.00419500	-2.92743400
H	5.12736000	-4.29568100	-0.37336200
C	4.05373200	-1.62081600	1.59989700
H	3.09582300	-2.05928600	1.88617700
H	4.72678900	-1.70477100	2.45835200
H	3.89405600	-0.55191900	1.43345100

- **1da**-*RR* (EtEt)



B3LYP/6-31G*

E = –3797.845811

Zero-point correction = 1.341656 (Hartree/Particle)

Thermal correction to Energy = 1.420221

Thermal correction to Enthalpy = 1.421165

Thermal correction to Gibbs Free Energy = 1.220963

Sum of electronic and zero-point Energies = –3796.504154

Sum of electronic and thermal Energies = –3796.425590

Sum of electronic and thermal Enthalpies = –3796.424646

Sum of electronic and thermal Free Energies = –3796.624848

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

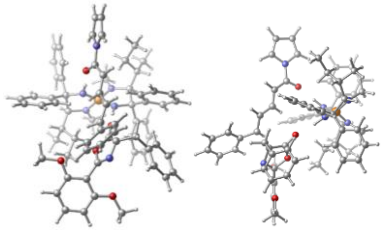
E = –3799.044961

G = –3797.789553

0 1

O	0.94722000	0.66533400	0.05815800
C	2.13269500	0.37262800	0.14876400
C	3.24472700	0.96148600	0.87721200
O	2.63066400	-0.79735000	-0.42629700
N	4.41008600	0.24485400	0.48872200
C	4.00104600	-0.75692400	-0.19897000
C	4.80849400	-1.83356000	-0.80842100
C	5.04928400	-3.03653300	-0.12454100
C	5.36014600	-1.65039400	-2.08932800
C	5.84316700	-4.03749900	-0.69887800
C	6.15403600	-2.64651700	-2.67289900
C	6.38416300	-3.82436000	-1.96537500
O	4.46274900	-3.14248900	1.10597200
C	4.71875900	-4.30645900	1.88247900
H	5.79013800	-4.42050400	2.08881000
H	4.34521900	-5.21041700	1.38515200
H	4.18063600	-4.16005800	2.81999100
O	5.05979200	-0.46389600	-2.68478700
C	5.63916700	-0.16460800	-3.94559300
H	6.73546600	-0.17968600	-3.89611500
H	5.30057800	-0.86354600	-4.72135300
H	5.30044300	0.84347400	-4.18974800
H	6.03834100	-4.96628100	-0.17749600
H	6.58402200	-2.51303500	-3.65797800
H	6.99974900	-4.59948500	-2.41400900
C	3.33969400	2.46490800	1.02736800
H	2.41852900	2.82006400	1.50238600
H	4.16894600	2.68593800	1.70826300
C	3.54812800	3.19967900	-0.28848400
C	2.55573100	4.04318300	-0.80383200
C	4.74058000	3.04900900	-1.01381700
C	2.74508600	4.72071600	-2.01180900
C	4.93174400	3.72508100	-2.21872800
C	3.93450200	4.56428600	-2.72401200
H	1.62860300	4.17563100	-0.25178400
H	5.51187300	2.38736200	-0.63059300
H	1.96134700	5.37207400	-2.39046700
H	5.86688600	3.60371900	-2.76107000
H	4.08775200	5.09642800	-3.65983600
C	2.84613600	0.19279700	2.72898600
C	1.55705500	0.54385700	3.24706900
H	2.91703500	-0.83117300	2.36215800
H	1.48573800	1.38612600	3.93240900
C	0.40967600	-0.19729500	3.01543600
H	0.47708900	-1.03797500	2.32609800
C	-0.82804300	-0.03335600	3.65756300
H	-0.92581400	0.72032500	4.43219900
C	-1.92167500	-0.87751200	3.37841000
O	-2.04180900	-1.65504100	2.39595300
N	-3.02347700	-0.85635500	4.30313800
C	-4.28261200	-1.34418400	4.00019200
C	-3.03462300	-0.39602300	5.61177100
C	-5.08939100	-1.18214500	5.09993600
C	-4.29428100	-0.58412100	6.12675900
H	-4.47783900	-1.74367200	3.01856100
H	-2.13459600	-0.02256200	6.07368500
H	-6.13325000	-1.46014300	5.16628900
H	-4.60884600	-0.33517400	7.13200800
H	-0.74494600	1.07178300	-0.54597600
N	-1.74144400	1.22142600	-0.72178200
P	-2.71731600	-0.01378900	-1.17906200
N	-4.09309600	0.91103400	-1.08969500
C	-3.87322300	2.32491500	-0.70132900
C	-2.31080500	2.56532900	-0.93109900
C	-5.43374700	0.41856400	-1.37975600
H	-5.36644300	-0.53870900	-1.90105700
H	-6.01917500	0.26364400	-0.46753500
H	-5.96618200	1.13161800	-2.02128400
H	-4.40828500	2.92478100	-1.44167400
C	-4.46677500	2.74464000	0.67686700
H	-3.95692900	3.68001900	0.93394100
C	-4.20409100	1.74799500	1.82100200
H	-4.79222700	0.83442800	1.66005400
C	-1.70423600	3.57520700	0.05892600
C	-1.02702300	3.16318100	1.21350400
C	-1.84650800	4.95183800	-0.17947300
C	-0.51552300	4.10675500	2.10932900
C	-1.34228600	5.89057200	0.71915300
C	-0.67236200	5.47125300	1.87049200
H	-0.88222700	2.11092300	1.42604500
H	-2.34841400	5.29561900	-1.07904600
H	0.00971700	3.76044500	2.99503800
H	-1.46621800	6.95050900	0.51330100
H	-0.27215000	6.20154900	2.56853100
C	-1.97455900	3.02862800	-2.38061100
C	-0.64610100	2.86721600	-2.81334100
C	-2.87866000	3.62693800	-3.26680400
C	-0.24485300	3.26662800	-4.08559900
C	-2.48022500	4.02366500	-4.54909200
C	-1.16482700	3.84202100	-4.96648100
H	0.09141300	2.43496300	-2.14410800
H	-3.90989300	3.80680800	-2.98083500
H	0.79264100	3.13613100	-4.38021600
H	-3.20811000	4.47983800	-5.21517000
H	-0.85547800	4.15206600	-5.96094100
N	-2.26264900	-1.33953200	-0.34328600
C	-2.42725100	-2.61932000	-1.07566600
C	-2.27828600	-2.19331400	-2.60253500
N	-2.79819800	-0.81037900	-2.63606300
H	-2.13296900	-1.34960200	0.68873900
C	-3.19359300	-0.19562300	-3.89644500
H	-3.77606100	0.70558500	-3.69595600
H	-2.33349800	0.09081700	-4.51142500
H	-3.81603800	-0.89511000	-4.46731800
H	-2.97706100	-2.80693700	-3.17631700
C	-0.89172600	-2.39348000	-3.29713900
H	-0.46863700	-3.30559400	-2.86402200
C	0.11626400	-1.25479700	-3.04622900
H	-0.24606600	-0.32931100	-3.51480200
C	1.53055600	-1.55866100	-3.55767400
C	-1.34086800	-3.62031200	-0.65292700
C	-0.13391400	-3.19554900	-0.08495800
C	-1.52382800	-4.98915000	-0.89924700
C	0.87110100	-4.11570100	0.21926500
C	-0.52097900	-5.90859800	-0.59350200
C	0.68155000	-5.47434600	-0.03300700
H	0.03184700	-2.14338900	0.11225200
H	-2.45854000	-5.34103300	-1.32591800
H	1.80376100	-3.75677600	0.64516100
H	-0.68376200	-6.96520300	-0.79004000
H	1.46256100	-6.19180600	0.20582400
C	-3.83077700	-3.19898300	-0.73895900
C	-4.84484000	-3.45621000	-1.66906700
C	-4.09738300	-3.47046500	0.61644500
C	-6.08551500	-3.96540900	-1.26457700
C	-5.33032700	-3.97730000	1.01858100
C	-6.33412300	-4.22932700	0.07869100
H	-4.69900500	-3.26993100	-2.72782800
H	-3.33659800	-3.26705700	1.36470600
H	-6.85190500	-4.15599200	-2.01169500
H	-5.50423200	-4.17801500	2.07251900
H	-7.29532600	-4.62757500	0.39251000
H	2.22654600	-0.76912700	-3.25927600
H	1.90652700	-2.49664400	-3.13207800
H	1.56625800	-1.64420800	-4.64998700
C	4.06238500	0.58668700	3.50042800
C	5.18572500	-0.25801900	3.49610800
C	4.13144500	1.76642600	4.26266400
C	6.32556500	0.05408500	4.23464800
H	5.15788800	-1.16401200	2.89882900
C	5.27377500	2.08318700	4.99683100
H	3.28642700	2.44784800	4.28510300
C	6.37623200	1.22689000	4.99003800
H	7.17829800	-0.62020100	4.21766900
H	5.30006800	3.00136700	5.57841700
H	7.26466500	1.47196600	5.56627000
C	-1.07707700	-2.68630800	-4.80082000
H	-1.41516600	-1.80862100	-5.36331800
H	-0.13514600	-3.01600900	-5.24922700
H	-1.80807900	-3.48861300	-4.96164300
H	0.18245000	-1.04954800	-1.97377600
H	-3.15384300	1.43946300	1.80589200
C	-5.96233800	3.10417200	0.55198500
H	-6.59902700	2.22375000	0.41165500
H	-6.31075400	3.61289300	1.45565000
H	-6.14097100	3.78549500	-0.28969900
C	-4.52117000	2.32007200	3.20882700
H	-4.26833400	1.60055600	3.99180000
H	-3.94506600	3.23613400	3.39168900
H	-5.58324400	2.56483200	3.32142100

- **1da**-*RR* (EtEt-2)



B3LYP/6-31G*

E = –3797.843424

Zero-point correction = 1.340920 (Hartree/Particle)

Thermal correction to Energy = 1.420005

Thermal correction to Enthalpy = 1.420949

Thermal correction to Gibbs Free Energy = 1.215465

Sum of electronic and zero-point Energies = –3796.502504

Sum of electronic and thermal Energies = –3796.423419

Sum of electronic and thermal Enthalpies = –3796.422475

Sum of electronic and thermal Free Energies = –3796.627959

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.039127

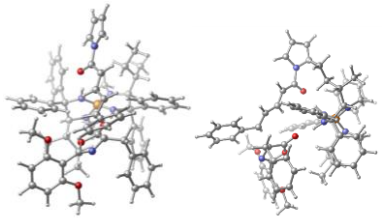
G = –3797.788245

0 1

O	1.06260400	0.56539500	0.09875000
C	2.24127300	0.23209900	0.18389400
C	3.29399600	0.55371300	1.13238400
O	2.78601700	-0.71384500	-0.68101500
N	4.47957800	-0.05031200	0.65276600
C	4.13464600	-0.78631500	-0.34032300
C	4.98965500	-1.65576100	-1.16683100
C	4.76633500	-3.04475200	-1.21810300
C	6.05623200	-1.10721200	-1.90871700
C	5.58570000	-3.87506000	-1.99291700
C	6.88374000	-1.93494200	-2.68060600
C	6.63485700	-3.30489200	-2.71140300
O	3.73268200	-3.49894200	-0.45128700
C	3.39579700	-4.87716900	-0.51589900
H	4.20347800	-5.50895900	-0.12400800
H	3.16007200	-5.18339100	-1.54274200
H	2.50622300	-4.99432300	0.10472700
O	6.19094400	0.24096600	-1.83460000
C	7.24336700	0.86859100	-2.54769900
H	8.22601700	0.51318600	-2.21105200
H	7.15188300	0.70760600	-3.63032500
H	7.14589800	1.93305500	-2.32873000
H	5.42298400	-4.94505000	-2.02949200
H	7.70415600	-1.52113200	-3.25394600
H	7.27618700	-3.94635600	-3.31017000
C	3.39433700	1.92786500	1.75614500
H	2.40636200	2.20000300	2.14225600
H	4.08346400	1.86818200	2.60607400
C	3.88448200	2.98671200	0.78196600
C	2.97849600	3.78183600	0.06789600
C	5.25655700	3.17371600	0.56226300
C	3.43017200	4.74225100	-0.83969300
C	5.71066600	4.13669800	-0.33991000
C	4.79837000	4.92570900	-1.04531100
H	1.91225700	3.64682300	0.22501600

H	5.96785500	2.55180500	1.09894200
H	2.70873200	5.35008200	-1.38023400
H	6.77958300	4.27803500	-0.48518100
H	5.15174400	5.67964900	-1.74468800
C	2.66518800	-0.70563500	2.67821400
C	1.51153200	-0.19495200	3.34770600
H	2.46883400	-1.53556500	1.99984600
H	1.66232100	0.41790300	4.23438600
C	0.20555000	-0.50282500	3.00169600
H	0.04662900	-1.11790900	2.11819300
C	-0.93646300	-0.15800200	3.74109500
H	-0.80624800	0.40632900	4.65865000
C	-2.23064800	-0.59184200	3.38916500
O	-2.58886800	-1.11172700	2.30013400
N	-3.26734500	-0.43077400	4.37299700
C	-4.61608600	-0.54066300	4.07990400
C	-3.13454800	-0.19212000	5.73347900
C	-5.33131000	-0.35783200	5.23825000
C	-4.38795100	-0.14070100	6.29056000
H	-4.92671300	-0.72650600	3.06495600
H	-2.16164000	-0.12258400	6.19267500
H	-6.40973200	-0.37926500	5.32699600
H	-4.60681300	0.02112100	7.33801900
H	-0.58968000	0.95845300	-0.56637200
N	-1.52341300	1.27197500	-0.85010600
P	-2.66282400	0.23134400	-1.39434800
N	-3.83080700	1.40228000	-1.50900200
C	-3.40862900	2.75716900	-1.08996400
C	-1.80740700	2.70045800	-1.08279100
C	-5.18433000	1.17255900	-1.99806700
H	-5.23920600	0.19056700	-2.47159200
H	-5.92029900	1.19589700	-1.18795200
H	-5.45188900	1.93724400	-2.73806800
H	-3.70220700	3.42035500	-1.90696500
C	-4.11922300	3.30893100	0.18412300
H	-3.45545300	4.08463900	0.57989000
C	-4.32726400	2.26780700	1.30196500
H	-5.13237000	1.57673100	1.01575900
C	-1.18742300	3.55128300	0.04320700
C	-0.87837000	2.99224800	1.29090400
C	-0.96712600	4.92475800	-0.14557800
C	-0.37630500	3.78902700	2.32247400
C	-0.47015800	5.71959100	0.88757800
C	-0.17323200	5.15500800	2.12885300
H	-1.01519800	1.93342400	1.47185600
H	-1.17852900	5.38100000	-1.10713900
H	-0.14363100	3.32608500	3.27720500
H	-0.30758200	6.78035900	0.71592700
H	0.22080000	5.77191800	2.93175400
C	-1.20322200	3.12543800	-2.45277200
C	0.03726000	2.58356300	-2.83106000
C	-1.79110500	4.06540300	-3.31107700
C	0.64912500	2.94629900	-4.02981000
C	-1.18108400	4.42793400	-4.51623800
C	0.03888600	3.86625600	-4.88494400
H	0.54086900	1.87718500	-2.17943700
H	-2.72876300	4.54760200	-3.05246500
H	1.61015000	2.51080900	-4.28939700
H	-1.66662100	5.15548900	-5.16154000
H	0.51326900	4.14712100	-5.82129700
N	-2.57928400	-1.10747600	-0.46048600
C	-3.01238700	-2.34992500	-1.13876500
C	-2.60900600	-2.08866200	-2.65668200
N	-2.74407900	-0.62421900	-2.81583400
H	-2.54414400	-1.04770500	0.57393800
C	-2.81155900	-0.01605700	-4.13852200
H	-3.13902300	1.02199100	-4.04616900
H	-1.84071300	-0.01738800	-4.64524200
H	-3.53386100	-0.55705300	-4.76167100
H	-3.38177000	-2.54146400	-3.28269000
C	-1.25934600	-2.68539800	-3.16629700
H	-1.15185500	-3.65158300	-2.66096900
C	-0.01933200	-1.84211600	-2.81455200
H	-0.08323900	-0.86400700	-3.31114800
C	1.30842400	-2.50905500	-3.19402900
C	-2.30223100	-3.57495500	-0.54022900
C	-1.18382300	-3.45118000	0.29018300
C	-2.77784900	-4.86233000	-0.83682800
C	-0.56068000	-4.58499200	0.81777400
C	-2.14497100	-5.99374700	-0.32574000
C	-1.03398800	-5.85945500	0.51015900
H	-0.80350900	-2.46927600	0.54091100
H	-3.65935100	-4.98155100	-1.46046000
H	0.28806100	-4.46115400	1.48531900
C	-2.53112200	-6.98030300	-0.56818400
H	-0.55247100	-6.74022500	0.92668100
C	-4.54572700	-2.52017400	-0.92881900
C	-5.48640800	-2.71802800	-1.94616000
C	-5.00925200	-2.48515600	0.39985200
C	-6.84824500	-2.86360600	-1.65210500
C	-6.36232700	-2.63254400	0.69221500
C	-7.29261700	-2.82080300	-0.33424400
H	-5.18767300	-2.76717800	-2.98817300
H	-4.30318900	-2.33622700	1.21248200
H	-7.55506100	-3.01436200	-2.46414800
H	-6.68895900	-2.60539600	1.72849800
H	-8.34863600	-2.93707400	-0.10588100
H	2.14574800	-1.91857300	-2.81597700
H	1.38301400	-3.51060900	-2.75174100
H	1.42575800	-2.61200200	-4.27860600
C	3.92790900	-0.89938000	3.44282900
C	4.77666600	-1.96927700	3.10958400
C	4.30465000	-0.07246400	4.51610100
C	5.94880000	-2.21004600	3.82279800
H	4.50855000	-2.61501700	2.27819600
C	5.48113900	-0.30788300	5.22616000
H	3.67352200	0.76211700	4.80548900
C	6.30853200	-1.37944700	4.88552800
H	6.58441000	-3.04739700	3.54576500
H	5.74892300	0.34644600	6.05208500
H	7.22295300	-1.56493000	5.44307800
C	-1.34096400	-3.00596800	-4.67375500
H	-1.33936900	-2.10526500	-5.29761800
H	-0.48931800	-3.61750500	-4.98560600
H	-2.24921500	-3.57454600	-4.90979100
H	-0.00596200	-1.63486000	-1.73932500
H	-3.42854200	1.65204600	1.41067300
C	-5.43277700	4.02773600	-0.18809400
H	-6.20618100	3.33643500	-0.54077700
H	-5.84200200	4.55730900	0.67753900
H	-5.26860800	4.77518200	-0.97460600
C	-4.65366300	2.89725600	2.66255700
H	-4.79041200	2.12298300	3.42324400
H	-3.83874100	3.55338000	2.99133400
H	-5.57225000	3.49433100	2.63066200

● **1da**-*RR* (EtH)



B3LYP/6-31G*

E = –3797.845098

Zero-point correction = 1.341503 (Hartree/Particle)

Thermal correction to Energy = 1.420145

Thermal correction to Enthalpy = 1.421089

Thermal correction to Gibbs Free Energy = 1.219545

Sum of electronic and zero-point Energies = –3796.503595

Sum of electronic and thermal Energies = –3796.424952

Sum of electronic and thermal Enthalpies = –3796.424008

Sum of electronic and thermal Free Energies = –3796.625553

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.043533

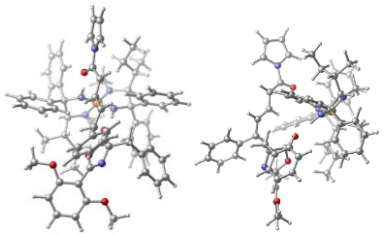
G = –3797.789296

0 1

O	0.91128900	0.74917700	0.05292800
C	2.09730900	0.46490800	0.14603600
C	3.18844300	1.02686600	0.92470800
O	2.61831200	-0.66845900	-0.48257400
N	4.36788600	0.33768800	0.52816300
C	3.98374800	-0.63163200	-0.21784200
C	4.81289000	-1.67618300	-0.85356000
C	5.11862100	-2.87219900	-0.18280100
C	5.32138000	-1.46698300	-2.14836300
C	5.93228500	-3.83987500	-0.78639700
C	6.13424600	-2.42961400	-2.76064300
C	6.42761100	-3.60157400	-2.06680300
O	4.57356200	-3.00860400	1.06351200
C	4.89646900	-4.16830000	1.82112200
H	5.97718900	-4.24403800	1.99361100
H	4.54128700	-5.08134200	1.32695500
H	4.38327800	-4.04924300	2.77641100
O	4.96392700	-0.28714600	-2.72495600
C	5.50386900	0.04553600	-3.99487700
H	6.60084900	0.06899800	-3.96926600
H	5.17293200	-0.65674100	-4.77082800
H	5.12423000	1.04305400	-4.22124500
H	6.17669700	-4.76361500	-0.27704000
H	6.53146400	-2.27464100	-3.75626100
H	7.05793600	-4.35150300	-2.53725900
C	3.26159800	2.52377800	1.14123100
H	2.33418000	2.84252300	1.63049900
H	4.08617600	2.72641100	1.83326200
C	3.45726500	3.32152500	-0.13889100
C	2.45330200	4.17746700	-0.60940300
C	4.64859000	3.22046800	-0.87438200
C	2.63058700	4.91616600	-1.78283300
C	4.82762100	3.95672300	-2.04534600
C	3.81930000	4.80845700	-2.50551900
H	1.52663300	4.27151400	-0.04819600
H	5.42945200	2.55086600	-0.52558800
H	1.83895400	5.57757000	-2.12609200
H	5.76158400	3.87206800	-2.59643300
H	3.96328400	5.38797200	-3.41423900
C	2.76156400	0.18813500	2.73584900
C	1.45914700	0.50608200	3.24196800
H	2.85262500	-0.82271900	2.33810000
H	1.36497600	1.33271500	3.94335300
C	0.32635800	-0.25199200	2.99018900
H	0.41219300	-1.07900700	2.28646600
C	-0.91204800	-0.12443000	3.63878200
H	-1.01530600	0.61140200	4.42958700
C	-1.99398200	-0.98675500	3.36391300
O	-2.12524300	-1.74380000	2.36726800
N	-3.07035900	-1.01331700	4.31799700
C	-4.31882800	-1.54551100	4.04722800
C	-3.06246500	-0.56357300	5.63079200
C	-5.10030300	-1.42135100	5.16935100
C	-4.29945200	-0.80110600	6.17834300
H	-4.52668500	-1.94552000	3.06872100
H	-2.16478200	-0.16108400	6.07202400
H	-6.13034200	-1.73999700	5.26278000
H	-4.59485800	-0.57090600	7.19378800
H	-0.77168400	1.14894900	-0.49139300
N	-1.77826400	1.21883500	-0.65799800
P	-2.61937400	-0.08203900	-1.19063700
N	-4.07530500	0.71113000	-1.14619600
C	-3.99641400	2.13022200	-0.72003700
C	-2.45318300	2.50931900	-0.88340500
C	-5.35722800	0.08304200	-1.44574000
H	-5.18992000	-0.85640800	-1.97736900
H	-5.92415900	-0.14462200	-0.53733900
H	-5.96067800	0.74227300	-2.08158000
H	-4.55630100	2.70082300	-1.46539600
C	-4.66834400	2.46841900	0.64339200
H	-4.27237500	3.45435900	0.91312700
C	-4.32136600	1.50578000	1.79405700
H	-4.81482900	0.53813600	1.63015200
C	-1.97246400	3.55839100	0.13446000
C	-1.25199500	3.20196400	1.28142000
C	-2.26676500	4.91480500	-0.07878900
C	-0.84844600	4.18003600	2.19568400
C	-1.87131700	5.88647500	0.83851000
C	-1.15798800	5.52243000	1.98276900
H	-0.99296400	2.16733400	1.47353600
H	-2.80242800	5.21682700	-0.97414300
H	-0.28866800	3.87926600	3.07701000
H	-2.11347000	6.92967000	0.65326500
H	-0.84235200	6.27917600	2.69584200
C	-2.09887800	3.02123900	-2.31234100
C	-0.73881300	3.02249300	-2.67197800
C	-3.01753900	3.52004900	-3.24349500
C	-0.31799800	3.48866500	-3.91466900
C	-2.59838800	3.98413000	-4.49635000
C	-1.24968700	3.96897800	-4.83927500
H	0.00786600	2.66590800	-1.96851200
H	-4.07751200	3.56885900	-3.01675000
H	0.74249300	3.48514500	-4.15065900
H	-3.33764800	4.36146300	-5.19831800
H	-0.92492000	4.33256000	-5.81040900
N	-2.10930200	-1.39640200	-0.36637300
C	-2.15035100	-2.65601400	-1.15671600
C	-1.79892800	-2.12481800	-2.61786300
N	-2.51306600	-0.82665700	-2.67012200
H	-2.02344700	-1.42836100	0.67024500
C	-3.11506000	-0.36168400	-3.91316800
H	-3.70207300	0.53740200	-3.71972600
H	-2.36183400	-0.11473500	-4.66586200
H	-3.78039700	-1.13427200	-4.32081300
H	-2.27347200	-2.76734500	-3.36376300

C	-0.27731000	-2.05375600	-2.97668000
H	0.28514900	-1.84961400	-2.05978800
C	0.07236200	-0.91325000	-3.95851700
H	-0.40834400	-1.09767100	-4.93085900
C	1.58023400	-0.72761300	-4.17619500
C	-1.12846600	-3.65043700	-0.58001400
C	0.04505000	-3.19899600	0.03901800
C	-1.33438200	-5.03355800	-0.68997100
C	0.99712900	-4.10253800	0.51163200
C	-0.38609200	-5.93787300	-0.21080700
C	0.78556800	-5.47580100	0.38932900
H	0.22267400	-2.13584800	0.14899100
H	-2.24219900	-5.41205000	-1.14808400
H	1.90693900	-3.72064000	0.96580700
H	-0.56940100	-7.00511900	-0.30470100
H	1.52315400	-6.18156000	0.76296300
C	-3.57816300	-3.25923800	-1.07204000
C	-4.29335700	-3.76717000	-2.16384700
C	-4.17517800	-3.33353200	0.19957700
C	-5.57539600	-4.30551700	-2.00014000
C	-5.44784300	-3.87597100	0.36358500
C	-6.15993000	-4.35935000	-0.73759800
H	-3.86727500	-3.76453200	-3.16176400
H	-3.63158600	-2.97000000	1.06748400
H	-6.10839900	-4.68697200	-2.86740100
H	-5.88236200	-3.92625200	1.35869500
H	-7.15375700	-4.77986800	-0.60939000
H	1.76523600	0.15403700	-4.80131300
H	2.10469100	-0.58093300	-3.22601400
H	2.03399700	-1.58722300	-4.68175200
C	3.95819700	0.57151000	3.54425300
C	5.09943700	-0.24855600	3.52000300
C	3.99112300	1.71708000	4.35917700
C	6.22129200	0.05377000	4.28962600
H	5.10108600	-1.12537500	2.88041500
C	5.11535700	2.02414100	5.12473600
H	3.13183500	2.37940400	4.39923800
C	6.23579700	1.19201600	5.09751700
H	7.08863200	-0.60100900	4.25556100
H	5.11322000	2.91572700	5.74688100
H	7.11009600	1.42925600	5.69814000
C	0.18089800	-3.40895900	-3.54535600
H	-0.26715400	-3.57887000	-4.53486200
H	1.26782900	-3.43766100	-3.66333000
H	-0.09722900	-4.24579700	-2.90146600
H	-0.33447700	0.02954000	-3.57724800
H	-3.24605200	1.30229800	1.79239700
C	-6.19120800	2.66202900	0.48696800
H	-6.72475000	1.71645300	0.34572100
H	-6.60951000	3.13763200	1.37899400
H	-6.42726000	3.31214000	-0.36522600
C	-4.71004500	2.05091600	3.17459800
H	-4.40234100	1.36192700	3.96522300
H	-4.22345400	3.01710100	3.35944400
H	-5.79171200	2.19684400	3.27180900

● **1da**-*RR* (EtH-2)



B3LYP/6-31G*

E = –3797.843499

Zero-point correction = 1.341846 (Hartree/Particle)

Thermal correction to Energy = 1.420409

Thermal correction to Enthalpy = 1.421354

Thermal correction to Gibbs Free Energy = 1.218632

Sum of electronic and zero-point Energies = –3796.501653

Sum of electronic and thermal Energies = –3796.423090

Sum of electronic and thermal Enthalpies = –3796.422145

Sum of electronic and thermal Free Energies = –3796.624867

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*(@–30 °C

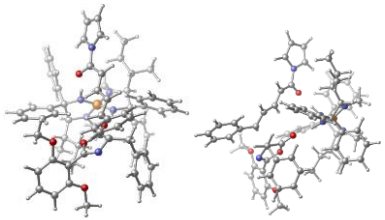
E = –3799.039126

G = –3797.785582

0 1

O	0.94909800	0.45434700	0.02304100
C	2.15080900	0.25635900	0.17300300
C	3.11168200	0.66864800	1.18528100
O	2.83641500	-0.61113700	-0.67217400
N	4.37985200	0.20566700	0.75541400
C	4.16801000	-0.54232000	-0.26546900
C	5.14882900	-1.29037500	-1.06953900
C	5.04366600	-2.68741800	-1.21594100
C	6.21027400	-0.61567200	-1.70923000
C	5.97468900	-3.40094900	-1.98093000
C	7.14825700	-1.32744700	-2.47017200
C	7.01568700	-2.70791300	-2.59500700
O	4.00540500	-3.27091400	-0.55023200
C	3.76865600	-4.65767100	-0.74952400
H	4.58756900	-5.26860300	-0.34777300
H	3.63192800	-4.88989100	-1.81321100
H	2.84610800	-4.88174700	-0.21257400
O	6.22990100	0.73271300	-1.55688900
C	7.23614900	1.48465400	-2.21448000
H	8.23872500	1.22250000	-1.85193100
H	7.19748500	1.34733400	-3.30334000
H	7.02227200	2.52685900	-1.97264500
H	5.90344000	-4.47611000	-2.08779000
H	7.96562400	-0.81644900	-2.96347900
H	7.74338700	-3.25907400	-3.18485000
C	3.03208600	2.03926900	1.82256300
H	2.01136400	2.18276800	2.19269100
H	3.70579000	2.04896700	2.68722000
C	3.40771100	3.16700000	0.87592200
C	2.42153400	3.93001600	0.23766000
C	4.75429500	3.45686700	0.61089200
C	2.76832700	4.95706200	-0.64333400
C	5.10306600	4.48758800	-0.26212300
C	4.11097900	5.24159000	-0.89480100
H	1.37377900	3.72098000	0.43573600
H	5.52684700	2.86000000	1.08737900
H	1.98535400	5.53602800	-1.12660700
H	6.15287500	4.70968800	-0.44218900
H	4.38340500	6.04683900	-1.57279300
C	2.54019100	-0.64251300	2.67401900
C	1.34765300	-0.21141600	3.33792300
H	2.39700600	-1.47783200	1.98849000
H	1.45252100	0.39973400	4.23233300
C	0.06768200	-0.59645400	2.97390900
H	-0.04250900	-1.21455300	2.08661200
C	-1.10470800	-0.34149800	3.70192900
H	-1.02365900	0.20177200	4.63746200
C	-2.36034300	-0.86369000	3.32434000
O	-2.67647500	-1.36009600	2.21172300
N	-3.40619500	-0.83516700	4.31133800
C	-4.73340100	-1.10214800	4.02074000
C	-3.29828700	-0.60021700	5.67531400
C	-5.46103600	-1.02148500	5.18250900
C	-4.54666200	-0.70474500	6.23527500
H	-5.02201000	-1.32179700	3.00630500
H	-2.34017000	-0.41962700	6.13477500
H	-6.52816900	-1.17697300	5.27378200
H	-4.77952000	-0.58172000	7.28499700
H	-0.68121000	1.09871800	-0.41843400
N	-1.64067000	1.28683600	-0.72098400
P	-2.55094300	0.10469400	-1.39034600
N	-3.89553000	1.06488500	-1.52242000
C	-3.72223800	2.45770300	-1.04522300
C	-2.13331500	2.65597000	-0.93091500
C	-5.17735500	0.62239500	-2.05813900
H	-5.05670200	-0.34495800	-2.54966100
H	-5.92755200	0.50320500	-1.27015000
H	-5.55014200	1.34624200	-2.79376400
H	-4.06319600	3.09141800	-1.86780600
C	-4.58521700	2.85291800	0.19089300
H	-4.07499200	3.71222900	0.64010100
C	-4.69011000	1.76357700	1.27669100
H	-5.37529300	0.97362100	0.93887100
C	-1.70652900	3.53578100	0.26381500
C	-1.37772500	2.95817200	1.49945400
C	-1.65980200	4.93420900	0.15160700
C	-1.02726400	3.75720600	2.59010000
C	-1.31421000	5.73068900	1.24369300
C	-0.99629500	5.14604100	2.46999400
H	-1.38676700	1.88195300	1.62616800
H	-1.88472200	5.41254200	-0.79553900
H	-0.77719600	3.27887500	3.53282600
H	-1.28495300	6.81101600	1.12880700
H	-0.71982800	5.76593800	3.31841900
C	-1.54496900	3.23305700	-2.25046300
C	-0.26303600	2.83143900	-2.65999900
C	-2.20661200	4.19311900	-3.03108900
C	0.32377800	3.35396500	-3.81267000
C	-1.62255600	4.71534600	-4.18827100
C	-0.35543100	4.29504100	-4.58780200
H	0.29284800	2.10701500	-2.07431400
H	-3.18597500	4.56365500	-2.74293200
H	1.31897800	3.02444200	-4.09808700
H	-2.16431500	5.45450300	-4.77270700
H	0.09994700	4.69956900	-5.48759900
N	-2.31240300	-1.25677100	-0.52068100
C	-2.45837100	-2.50564000	-1.30797000
C	-1.87112700	-2.05837200	-2.72355800
N	-2.34891900	-0.65736300	-2.85049600
H	-2.34105700	-1.26497000	0.51735400
C	-2.73383000	-0.11628100	-4.14938300
H	-3.17059400	0.87501900	-4.01459300
H	-1.87663000	-0.01724100	-4.81900900
H	-3.47978900	-0.76589200	-4.62644000
H	-2.36931800	-2.62021100	-3.51789800
C	-0.33345300	-2.24788800	-2.92521700
H	0.16644500	-2.07399200	-1.96598400
C	0.27363900	-1.23865600	-3.92543900
H	-0.17935700	-1.38714300	-4.91723000
C	1.79960100	-1.32686800	-4.05609600
C	-1.68351000	-3.63115000	-0.59693100
C	-0.55112200	-3.34228000	0.17653600
C	-2.09945400	-4.96789700	-0.69093100
C	0.13894900	-4.35639300	0.84227000
C	-1.40075900	-5.98399300	-0.03853200
C	-0.28095100	-5.68256800	0.73741200
H	-0.20964000	-2.31788300	0.26762400
H	-2.98233300	-5.22172600	-1.26768300
H	0.99568300	-4.09899700	1.45942600
H	-1.74618700	-7.01081300	-0.12498200
H	0.24904600	-6.47079300	1.26557100
C	-3.96257200	-2.88324200	-1.39417400
C	-4.57448700	-3.41672600	-2.53644400
C	-4.74704100	-2.72757000	-0.23759500
C	-5.93257100	-3.75394400	-2.53714000
C	-6.09821800	-3.06933500	-0.23643400
C	-6.70173400	-3.57728300	-1.38943300
H	-4.00512700	-3.59274900	-3.44368400
H	-4.29192300	-2.34377800	0.67111400
H	-6.38141000	-4.15988200	-3.44012000
H	-6.68000600	-2.94269300	0.67287500
H	-7.75611200	-3.84024300	-1.38887900
H	2.16886200	-0.53006900	-4.71247400
H	2.28429800	-1.20893100	-3.08180700
H	2.12560200	-2.27879800	-4.48876400
C	3.79650100	-0.79039300	3.46286300
C	4.69866900	-1.81663500	3.13394800
C	4.11453300	0.03929800	4.55232000
C	5.86703500	-2.01315400	3.86688600
H	4.47721800	-2.46323800	2.28914500
C	5.28691900	-0.15135800	5.28221300
H	3.44022400	0.84050000	4.83848800
C	6.16851500	-1.18017500	4.94560600
H	6.54510000	-2.81744700	3.59257500
H	5.50914100	0.50417300	6.12060500
H	7.07968600	-1.33096400	5.51869900
C	-0.04864500	-3.68882000	-3.38690600
H	-0.41758700	-3.84104800	-4.41116600
H	1.02586300	-3.89295000	-3.38947000
H	-0.52014300	-4.43526900	-2.74502700
H	0.01700900	-0.22272900	-3.60631500
H	-3.72008400	1.27600400	1.41521800
C	-5.97136500	3.36968800	-0.24655500
H	-6.59986400	2.58058800	-0.67358200
H	-6.51340800	3.79060600	0.60575600
H	-5.88071700	4.16615900	-0.99599600
C	-5.16375400	2.30585700	2.63157300
H	-5.21913200	1.50211200	3.37165700
H	-4.46841800	3.06513700	3.00954300
H	-6.15711700	2.76490100	2.56717200

● **1da**-*RR* (HEt)



B3LYP/6-31G*

E = –3797.844594

Zero-point correction = 1.341977 (Hartree/Particle)

Thermal correction to Energy = 1.420299

Thermal correction to Enthalpy = 1.421244

Thermal correction to Gibbs Free Energy = 1.222278

Sum of electronic and zero-point Energies = –3796.502617

Sum of electronic and thermal Energies = –3796.424294

Sum of electronic and thermal Enthalpies = –3796.423350

Sum of electronic and thermal Free Energies = –3796.622316

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

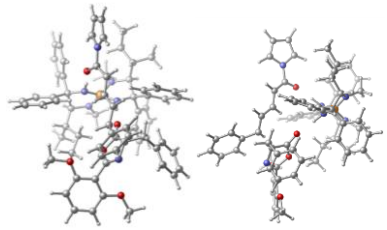
E = –3799.043217

G = –3797.786721

0 1

O	0.94247300	0.59916800	0.04108300
C	2.13728000	0.35190500	0.14112200
C	3.22645200	0.99160300	0.85931900
O	2.67577800	-0.81435000	-0.40582900
N	4.41595600	0.30488100	0.49377900
C	4.04264800	-0.72432300	-0.17359500
C	4.88725600	-1.78577200	-0.75875200
C	5.13613700	-2.98117700	-0.06483100
C	5.46539800	-1.59530100	-2.02693100
C	5.96502200	-3.96701900	-0.61530200
C	6.29510600	-2.57615600	-2.58642700
C	6.53289100	-3.74629500	-1.86878900
O	4.52117000	-3.09500300	1.15126900
C	4.78111200	-4.25086100	1.93836800
H	5.84908600	-4.34264300	2.17182900
H	4.43838000	-5.16395200	1.43557200
H	4.21681200	-4.11234500	2.86159000
O	5.15217600	-0.41933000	-2.63531000
C	5.75798400	-0.10918000	-3.88075700
H	6.85265000	-0.09866100	-3.80190400
H	5.45689000	-0.81750800	-4.66355300
H	5.40256400	0.89028800	-4.13619900
H	6.16690000	-4.88966000	-0.08559000
H	6.74609200	-2.43696100	-3.56130100
H	7.17605700	-4.50945100	-2.29892400
C	3.27500600	2.50011300	0.97665800
H	2.33632300	2.84014500	1.42716900
H	4.08782000	2.76326600	1.66198600
C	3.48312200	3.19479800	-0.36006100
C	2.43089700	3.86974000	-0.99265800
C	4.73252400	3.15743700	-0.99763400
C	2.61869100	4.49249600	-2.22946100
C	4.92290400	3.78040000	-2.23123500
C	3.86605900	4.45079300	-2.85343300
H	1.45827400	3.91368000	-0.50989700
H	5.55169500	2.62445600	-0.52342800
H	1.78798200	5.01361800	-2.69946800
H	5.90191200	3.74967500	-2.70439300
H	4.01680200	4.94152500	-3.81204400
C	2.82700400	0.24117500	2.72731700
C	1.52748200	0.57538900	3.22789600
H	2.92206100	-0.78533300	2.37356700
H	1.43748600	1.42043800	3.90779100
C	0.39209700	-0.18197800	2.98682500
H	0.47859000	-1.02588100	2.30403600
C	-0.85493900	-0.03198000	3.61449100
H	-0.96645700	0.71977900	4.38908400
C	-1.92261000	-0.91399200	3.34542200
O	-2.01513000	-1.70264900	2.36921100
N	-3.01833800	-0.93689300	4.27773400
C	-4.20703200	-1.60341500	4.03505700
C	-3.06918300	-0.40632500	5.56015800
C	-5.00783900	-1.48733100	5.14437500
C	-4.28326900	-0.72746500	6.11492900
H	-4.36245200	-2.08547700	3.08422400
H	-2.22157900	0.10912200	5.98208200
H	-6.00225100	-1.90044900	5.25359500
H	-4.61224600	-0.45997700	7.11076600
H	-0.73331900	1.11506200	-0.48485300
N	-1.72503900	1.23600300	-0.70462900
P	-2.67227500	-0.01927800	-1.16556900
N	-4.07394800	0.85316000	-0.98816700
C	-3.87720000	2.21632500	-0.42367100
C	-2.36605400	2.56360000	-0.81619300
C	-5.38063100	0.44868000	-1.49806900
H	-5.29058100	-0.51554300	-2.00101000
H	-6.11217800	0.34029600	-0.69449700
H	-5.75632100	1.18856100	-2.21777400
H	-4.55491600	2.86475200	-0.98519400
C	-4.23699200	2.38785600	1.08535300
H	-3.34378200	2.16500700	1.67992200
C	-5.34073200	1.42988500	1.58143700
H	-6.26950800	1.61368400	1.02176000
C	-5.63627700	1.55920700	3.08111200
C	-1.65180200	3.55363800	0.12538900
C	-1.03141800	3.11018900	1.30270200
C	-1.60646500	4.92513900	-0.17336400
C	-0.40682600	4.01622800	2.16284400
C	-0.98337900	5.82828800	0.68808400
C	-0.38133700	5.37775000	1.86346700
H	-1.01921200	2.05698700	1.55917800
H	-2.05698600	5.29601100	-1.08766900
H	0.06669100	3.64258800	3.06610100
H	-0.96284000	6.88423900	0.43205600
H	0.11043600	6.07912200	2.53197300
C	-2.24393500	3.06809000	-2.28068100
C	-1.02865600	2.85520400	-2.95343400
C	-3.24594600	3.78058400	-2.95250500
C	-0.83191000	3.31552500	-4.25414000
C	-3.05470500	4.23690000	-4.26136900
C	-1.84979800	4.00298600	-4.92001600
H	-0.22231400	2.33051600	-2.45094700
H	-4.18891600	4.00812700	-2.46598400
H	0.12231700	3.13950200	-4.74335800
H	-3.85339500	4.78118700	-4.75861500
H	-1.70054100	4.35882800	-5.93578300
N	-2.17371800	-1.35986700	-0.37962900
C	-2.33724500	-2.61665800	-1.15018900
C	-2.20762800	-2.13999600	-2.66358500
N	-2.74588300	-0.76147800	-2.64990100
H	-2.06069100	-1.39927500	0.65354000
C	-3.13059100	-0.10301300	-3.89211100
H	-3.67976900	0.81344200	-3.66918300
H	-2.26456600	0.17098600	-4.50319200
H	-3.77877000	-0.76706600	-4.47701200
H	-2.90264000	-2.74463900	-3.25158700
C	-0.82270800	-2.30303800	-3.37093800
H	-0.38897600	-3.22294500	-2.96605200
C	0.17618100	-1.16394900	-3.08824000
H	-0.19105600	-0.23075500	-3.53788000
C	1.59502700	-1.44711600	-3.59924600
C	-1.23955800	-3.62114300	-0.76670600
C	-0.03753200	-3.20255100	-0.18399700
C	-1.40794800	-4.98280400	-1.05945800
C	0.97712400	-4.12164300	0.09060600
C	-0.39504100	-5.90086500	-0.78445500
C	0.80229800	-5.47282500	-0.20778100
H	0.11748600	-2.15516400	0.04518700
H	-2.33890200	-5.33016900	-1.49803900
H	1.90499400	-3.76672300	0.53012900
H	-0.54580100	-6.95189300	-1.01721900
H	1.59094600	-6.18948900	0.00712800
C	-3.73280700	-3.21957500	-0.82122100
C	-4.75824900	-3.43887800	-1.74859500
C	-3.97918100	-3.55808500	0.52276200
C	-5.98929000	-3.97726200	-1.35290200
C	-5.20202900	-4.09532300	0.91610200
C	-6.21686400	-4.30950700	-0.02119500
H	-4.62820200	-3.20035700	-2.79881000
H	-3.21016600	-3.38411600	1.26959700
H	-6.76457400	-4.13719200	-2.09801500
H	-5.35977800	-4.35129000	1.96061000
H	-7.17013600	-4.73144300	0.28567600
H	2.28588200	-0.66262300	-3.27621200
H	1.97281700	-2.39409000	-3.19585300
H	1.63834000	-1.50422900	-4.69322600
H	-6.32482400	0.77269400	3.40353700
H	-4.72490700	1.44903200	3.67890300
H	-6.09300300	2.52355000	3.32836400
C	4.02940100	0.67289000	3.49865800
C	5.16811800	-0.15078900	3.51963900
C	4.07152900	1.86937100	4.23633300
C	6.29658900	0.19736100	4.25942500
H	5.16119200	-1.06977900	2.94175200
C	5.20237200	2.22210000	4.97187300
H	3.21415500	2.53560800	4.23777700
C	6.32028700	1.38617700	4.99071900
H	7.16154800	-0.46137400	4.26240500
H	5.20773400	3.15252900	5.53429300
H	7.19977900	1.65939000	5.56802000
C	-1.00826600	-2.55559700	-4.88198300
H	-1.35513300	-1.66655200	-5.42078600
H	-0.06357900	-2.86397700	-5.33982700
H	-1.73161200	-3.36026200	-5.06415200
H	0.23459600	-0.98250900	-2.01137500
H	-5.03864600	0.39701100	1.37378000
C	-4.64798300	3.85071900	1.34003900
H	-5.62761900	4.05503400	0.88527300
H	-4.73100900	4.05494100	2.41083400
H	-3.93082700	4.56478400	0.93012800

● **1da**-*RR* (HEt-2)



B3LYP/6-31G*

E = –3797.842054

Zero-point correction = 1.341586 (Hartree/Particle)

Thermal correction to Energy = 1.420183

Thermal correction to Enthalpy = 1.421128

Thermal correction to Gibbs Free Energy = 1.218103

Sum of electronic and zero-point Energies = –3796.500469

Sum of electronic and thermal Energies = –3796.421871

Sum of electronic and thermal Enthalpies = –3796.420927

Sum of electronic and thermal Free Energies = –3796.623951

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.036733

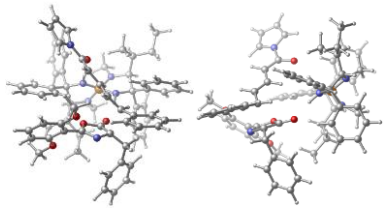
G = –3797.783664

0 1

O	1.15781800	0.63130300	-0.01639400
C	2.32347400	0.26641400	0.10043500
C	3.40116500	0.67139600	0.98390000
O	2.82451000	-0.80398000	-0.63923400
N	4.56122400	-0.02215700	0.56952900
C	4.17534500	-0.87283700	-0.31063800
C	4.98593500	-1.88232200	-1.01441500
C	4.74292000	-3.25509400	-0.82200800
C	6.02662200	-1.48581900	-1.87820300
C	5.51764100	-4.21951800	-1.47832000
C	6.80957500	-2.44674700	-2.53344800
C	6.54159300	-3.79751300	-2.32435400
O	3.73616600	-3.55212300	0.05104700
C	3.37303800	-4.91321800	0.23040200
H	4.18648600	-5.49074600	0.68843200
H	3.08657400	-5.37877700	-0.72078500
H	2.51144300	-4.90433900	0.89987700
O	6.18177000	-0.14637700	-2.03208800
C	7.21973300	0.33576400	-2.86882400
H	8.20708100	0.01531400	-2.51149500
H	7.08737500	0.00782400	-3.90867600
H	7.14994200	1.42353500	-2.81848100
H	5.33974500	-5.27723600	-1.32858000
H	7.60990400	-2.15125400	-3.20068500
H	7.14816800	-4.54235500	-2.83286400
C	3.53938500	2.10570700	1.43962200
H	2.56136900	2.44437600	1.79795500
H	4.23749300	2.13471600	2.28360200
C	4.03970600	3.02291600	0.33583000
C	3.14141700	3.71665300	-0.48605300
C	5.41345200	3.16687600	0.09658300
C	3.60308200	4.53487300	-1.51896300
C	5.87765700	3.98816100	-0.93184000
C	4.97331200	4.67581100	-1.74498300
H	2.07381000	3.61322700	-0.31469100

H	6.11870800	2.62128700	0.71775000
H	2.88835200	5.06597800	-2.14315900
H	6.94789800	4.09702300	-1.09371700
H	5.33413600	5.31905500	-2.54403200
C	2.77234500	-0.40768200	2.67516400
C	1.60221000	0.14779100	3.27420600
H	2.60571700	-1.31299000	2.09239600
H	1.73301400	0.85729200	4.08917500
C	0.30408900	-0.22651600	2.96461000
H	0.15762600	-0.93578100	2.15131900
C	-0.83797000	0.17722800	3.67458100
H	-0.70370500	0.84634300	4.51819300
C	-2.13140900	-0.31598800	3.40991500
O	-2.50792300	-0.97779300	2.40718600
N	-3.14427200	-0.04113100	4.39414400
C	-4.49937700	-0.18008200	4.14982800
C	-2.97705900	0.34591300	5.71653400
C	-5.18546900	0.13172600	5.29804600
C	-4.21616500	0.46119800	6.29580200
H	-4.83592500	-0.47785200	3.17052900
H	-1.99291100	0.46089200	6.14128300
H	-6.26129800	0.12347800	5.41514500
H	-4.40859000	0.73729800	7.32441200
H	-0.55927000	0.93170700	-0.54594500
N	-1.50522300	1.21391100	-0.82310200
P	-2.63337100	0.14353800	-1.33744100
N	-3.80872400	1.30586700	-1.49709200
C	-3.41163000	2.63931400	-0.97751900
C	-1.82122200	2.62980200	-1.12996900
C	-5.05492900	1.14740200	-2.24047000
H	-5.09942500	0.14337600	-2.66398700
H	-5.92997500	1.27824500	-1.60071900
H	-5.10470000	1.87903600	-3.05810400
H	-3.83451600	3.36759700	-1.67397800
C	-3.97221200	2.99464300	0.43799100
H	-3.27008300	2.62140800	1.19247900
C	-5.33770500	2.33476600	0.73035300
H	-6.07699300	2.68543200	-0.00451300
C	-5.88133700	2.61211700	2.13780100
C	-1.07802700	3.54782100	-0.14187600
C	-0.75442000	3.10954300	1.14996900
C	-0.73031200	4.85864100	-0.50638800
C	-0.12616200	3.96655700	2.05590900
C	-0.10389100	5.71372600	0.40066300
C	0.19849400	5.27218400	1.68936800
H	-0.97621500	2.09551200	1.46204200
H	-0.94820600	5.22037700	-1.50578900
H	0.11173600	3.59766900	3.04951700
H	0.15453500	6.72346900	0.09312200
H	0.69267100	5.93494200	2.39437300
C	-1.37036500	2.94755700	-2.58208300
C	-0.13723500	2.43271000	-3.01891000
C	-2.08905200	3.76195800	-3.46733400
C	0.34391800	2.70149500	-4.29901700
C	-1.61076400	4.02819600	-4.75501100
C	-0.39550100	3.49571800	-5.17887500
H	0.45842000	1.82135600	-2.34793300
H	-3.02758800	4.21733200	-3.16839600
H	1.30298600	2.29225300	-4.60471900
H	-2.19398000	4.65915400	-5.42080500
H	-0.02315800	3.70347400	-6.17834000
N	-2.56829400	-1.15452800	-0.34319200
C	-3.07504700	-2.39614400	-0.96743300
C	-2.62752200	-2.23248600	-2.48582600
N	-2.68807700	-0.77136400	-2.72183900
H	-2.53773700	-1.03574600	0.68647100
C	-2.68418800	-0.22781500	-4.07444400
H	-2.98346000	0.82176900	-4.04954400
H	-1.69353500	-0.27965400	-4.53766400
H	-3.39551300	-0.78029200	-4.70002900
H	-3.40633900	-2.67978700	-3.10933200
C	-1.29784800	-2.92046600	-2.92303100
H	-1.28021600	-3.88156600	-2.39811900
C	-0.02194200	-2.15859200	-2.52084300
H	0.01560900	-1.19399100	-3.04567700
C	1.26850200	-2.93654300	-2.80605000
C	-2.47833200	-3.64663700	-0.30369900
C	-1.45987300	-3.57661300	0.65155500
C	-2.97616100	-4.91016100	-0.66311200
C	-0.94802400	-4.74253300	1.22898300
C	-2.45455100	-6.07193700	-0.09931800
C	-1.43536100	-5.99251600	0.85326200
H	-1.08225400	-2.61540600	0.97551200
H	-3.78772000	-4.98529300	-1.38191500
H	-0.17371000	-4.66170100	1.98747700
H	-2.85421600	-7.03866900	-0.39413300
H	-1.03794000	-6.89680300	1.30645000
C	-4.62097000	-2.45114100	-0.78113100
C	-5.55266300	-2.66562800	-1.80304700
C	-5.10617300	-2.29602300	0.53118000
C	-6.92582700	-2.71098000	-1.53062300
C	-6.47082100	-2.34371300	0.80262300
C	-7.39132200	-2.54922500	-0.22946000
H	-5.23700500	-2.80536900	-2.83174600
H	-4.40654900	-2.13671300	1.34753700
H	-7.62531100	-2.87714600	-2.34599000
H	-6.81530800	-2.22639100	1.82674200
H	-8.45639200	-2.58726000	-0.01752300
H	2.12740100	-2.39719900	-2.40209900
H	1.23977800	-3.92674000	-2.33273600
H	1.43436800	-3.08506300	-3.87899500
H	-6.80645500	2.04802100	2.30278800
H	-5.17118600	2.30314200	2.91196300
H	-6.11494100	3.67096700	2.29014100
C	4.03222300	-0.47442100	3.46490800
C	4.90635600	-1.55929200	3.27695000
C	4.38254100	0.49284200	4.42414300
C	6.07714100	-1.67970900	4.02231700
H	4.65781800	-2.31188500	2.53422200
C	5.55775100	0.37743200	5.16507000
H	3.73248000	1.34488900	4.59749900
C	6.41030800	-0.71080800	4.97063900
H	6.73268100	-2.53159200	3.85964400
H	5.80524700	1.13914100	5.90030800
H	7.32378700	-0.80250600	5.55251700
C	-1.32366500	-3.26648200	-4.42703500
H	-1.19688600	-2.38614800	-5.06673200
H	-0.51766000	-3.96334100	-4.67490600
H	-2.26645900	-3.75229800	-4.70859100
H	-0.05763300	-1.92055200	-1.45247800
H	-5.24748200	1.25036100	0.59915800
C	-4.08363100	4.52431800	0.57840600
H	-4.88552600	4.90812700	-0.06822000
H	-4.32455100	4.80645100	1.60695800
H	-3.15921800	5.03831400	0.31021000

- **1da**-*RS* (MeH)



B3LYP/6-31G*

E = –3797.845138

Zero-point correction = 1.342135 (Hartree/Particle)

Thermal correction to Energy = 1.420477

Thermal correction to Enthalpy = 1.421421

Thermal correction to Gibbs Free Energy = 1.221153

Sum of electronic and zero-point Energies = –3796.503003

Sum of electronic and thermal Energies = –3796.424661

Sum of electronic and thermal Enthalpies = –3796.423717

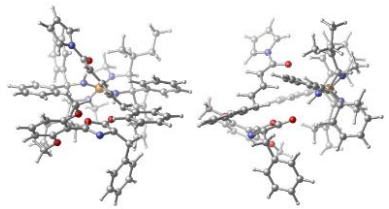
Sum of electronic and thermal Free Energies = –3796.623985

0 1

O	-0.84291800	-1.15342500	-0.83791700
C	-1.98464900	-0.74402300	-0.62308200
C	-3.18378000	-1.39764700	-0.12466300
O	-2.29368300	0.59583600	-0.71109600
N	-4.21919400	-0.43711100	-0.14153200
C	-3.65615400	0.68920000	-0.40315000
C	-4.27188200	2.02402100	-0.47366100
C	-5.00952200	2.54925100	0.61208500
C	-4.15610700	2.80386100	-1.64657700
C	-5.58563100	3.82494500	0.53298000
C	-4.72430700	4.08177400	-1.72238500
C	-5.43065900	4.57507000	-0.62882400
O	-5.10595400	1.76361700	1.71823900
C	-5.79554300	2.26415700	2.85405100
H	-6.85230000	2.45866500	2.63059700
H	-5.33044100	3.18125200	3.23780500
H	-5.72504400	1.47985700	3.60944500
O	-3.49391500	2.21794900	-2.68036100
C	-3.34996600	2.94461300	-3.89110000
H	-4.32523800	3.20305400	-4.32363800
H	-2.76187300	3.85866100	-3.74085600
H	-2.81897800	2.27779600	-4.57107400
H	-6.14414100	4.23305400	1.36562000
H	-4.62970600	4.68046200	-2.61928600
H	-5.87602000	5.56474700	-0.68551300
C	-3.49963200	-2.82734000	-0.51459100
H	-2.72585100	-3.49099400	-0.11211200
H	-4.43965100	-3.10431300	-0.02594500
C	-3.60864800	-3.05364600	-2.01494800
C	-2.76134800	-3.96141000	-2.66262000
C	-4.56365100	-2.36895700	-2.78187600
C	-2.86088400	-4.18314600	-4.03860300
C	-4.66264500	-2.58499500	-4.15608600
C	-3.81145400	-3.49284900	-4.79164800
H	-2.01982600	-4.50524800	-2.08112600
H	-5.22354600	-1.65843900	-2.29174600
H	-2.20062500	-4.90140800	-4.51975300
H	-5.40996400	-2.04543900	-4.73287400
H	-3.89310100	-3.66408000	-5.86204400
C	-2.60318600	-1.47114900	1.85054600
C	-2.36995100	-0.17280900	2.40775000
H	-1.70444000	-2.04405400	1.61978500
H	-3.18700800	0.29853900	2.94651100
C	-1.15099700	0.48858600	2.35467200
H	-0.33928800	0.01337000	1.80443300
C	-0.83708600	1.70575300	2.97125200
H	-1.60083900	2.20257400	3.55932100
C	0.46169000	2.25633400	2.92860800
O	1.47279600	1.76342100	2.36021500
N	0.67662900	3.48939600	3.63265900
C	1.93468500	3.95044600	3.98017100
C	-0.26385100	4.40744000	4.07827600
C	1.79471000	5.14244600	4.64604000
C	0.39642900	5.43660600	4.70180600
H	2.80159200	3.35784600	3.73805000
H	-1.31336000	4.27300400	3.87111800
H	2.60062800	5.73885600	5.05336700
H	-0.06797200	6.31054500	5.14007600
H	0.84386200	-1.43148700	-0.14871100
N	1.84986500	-1.42391100	0.04846700
P	2.76942200	-0.25129400	-0.65349700
N	4.19834800	-0.94690600	-0.17460700
C	4.03644900	-2.14968400	0.67560700
C	2.59020500	-2.68316200	0.28470600
C	5.51851600	-0.36236900	-0.37446400
H	5.47871700	0.36443900	-1.18801000
H	5.88507300	0.15755800	0.51780000
H	6.23311200	-1.14993600	-0.64386400
H	4.76579300	-2.87968700	0.31455000
C	4.46940200	-1.86969000	2.15006600
H	5.48491000	-1.46536400	2.01143900
C	4.66834500	-3.15686100	2.98345400
H	3.70898900	-3.50482700	3.37662200
C	5.65508700	-2.97902800	4.14533600
C	2.62042800	-3.52055200	-1.03130300
C	3.72239800	-4.27265100	-1.46182400
C	1.45188600	-3.56995500	-1.81245600
C	3.67291500	-5.02223200	-2.64184800
C	1.40149400	-4.31583000	-2.98917900
C	2.51466800	-5.04337200	-3.41488100
H	4.64028400	-4.30100100	-0.88356400
H	0.56471500	-3.02174500	-1.51085400
H	4.54748400	-5.58967700	-2.94953200
H	0.48365100	-4.32257800	-3.57105700
H	2.47665500	-5.62276900	-4.33336400
C	1.90102200	-3.51007100	1.38555400
C	1.03343500	-2.91281600	2.30863600
C	2.13320700	-4.88988000	1.49009900
C	0.43916700	-3.66434400	3.32533800
C	1.54375600	-5.64102000	2.50628100
C	0.69578500	-5.03131100	3.43245300
H	0.82529900	-1.85178500	2.24431700
H	2.77615600	-5.38807700	0.77225700
H	-0.22769000	-3.17274700	4.02804900
H	1.74406200	-6.70745100	2.56779700
H	0.23450400	-5.61637000	4.22344300
N	2.13212500	1.20014200	-0.25808400
C	2.40400900	2.25804700	-1.26275800
C	2.31245000	1.42717500	-2.61993300
N	2.93339700	0.12851500	-2.25744600
H	1.82096900	1.42450800	0.70709200
C	3.69252300	-0.63509800	-3.24080800
H	4.42737800	0.01505600	-3.73329600
H	3.04558900	-1.07618300	-4.00338700
H	4.22387100	-1.44619300	-2.73974400
H	2.97470700	1.87471300	-3.36570100
C	0.88771800	1.34064600	-3.26217200
C	0.58268600	-0.00987200	-3.94523600
H	1.25443300	-0.15853100	-4.80339600

C	-0.87036700	-0.13826400	-4.42274900
C	1.36761200	3.38750800	-1.12918800
C	0.10048100	3.15209700	-0.58021400
C	1.67437300	4.68612600	-1.56604700
C	-0.83573500	4.18306300	-0.47872700
C	0.73599900	5.71335100	-1.47270900
C	-0.52454400	5.46602300	-0.92661800
H	-0.17150600	2.16448500	-0.22851600
H	2.65643300	4.90354500	-1.97355600
H	-1.80723800	3.97203600	-0.04300200
H	0.99870800	6.71070800	-1.81597400
H	-1.25307100	6.26799900	-0.84150600
C	3.82310500	2.83644900	-1.01026700
C	4.18263900	3.11635700	0.31990400
C	4.74847700	3.13659800	-2.01775500
C	5.42967300	3.65505800	0.62879400
C	6.00403200	3.67241000	-1.70811800
C	6.35202700	3.93015200	-0.38447000
H	3.47295900	2.91732400	1.11817100
H	4.50864400	2.96941400	-3.06288900
H	5.67865500	3.86606700	1.66546300
H	6.70416500	3.89008600	-2.51067700
H	7.32583700	4.34800900	-0.14370100
H	5.79005500	-3.92180600	4.68745200
H	6.64141900	-2.65669500	3.78733800
H	5.30396200	-2.23421300	4.86760400
H	-1.08198000	-1.16316800	-4.74639700
H	-1.57197900	0.10300400	-3.61697500
H	-1.08384900	0.52205100	-5.27150600
C	-3.68467300	-2.29618400	2.46083800
C	-3.41989700	-3.61767700	2.85570800
C	-4.97563500	-1.78085700	2.67769700
C	-4.40250600	-4.39436300	3.47174700
H	-2.42948900	-4.03438300	2.68991200
C	-5.95716800	-2.56024700	3.28653700
H	-5.20966000	-0.78243000	2.32345300
C	-5.67531800	-3.86790800	3.69247300
H	-4.17222900	-5.41246400	3.77617900
H	-6.95218200	-2.14853300	3.43786700
H	-6.44363600	-4.47185800	4.16834700
H	0.77983600	-0.81892300	-3.23555100
C	0.72353700	2.50527400	-4.25557300
H	1.38448500	2.36500900	-5.12276100
H	-0.30221600	2.56582300	-4.62938500
H	0.96133800	3.47098800	-3.80224900
H	0.14412600	1.45019900	-2.46644700
H	5.04045100	-3.95988500	2.33058700
C	3.67636700	-0.79197600	2.90058500
H	2.69137700	-1.14398800	3.21119600
H	4.21772800	-0.49285100	3.80461700
H	3.52715900	0.11207100	2.30583300

● **1da**-*RS* (MeMe)



B3LYP/6-31G*

E = –3797.840828

Zero-point correction = 1.341320 (Hartree/Particle)

Thermal correction to Energy = 1.420063

Thermal correction to Enthalpy = 1.421007

Thermal correction to Gibbs Free Energy = 1.217883

Sum of electronic and zero-point Energies = –3796.499508

Sum of electronic and thermal Energie s= –3796.420765

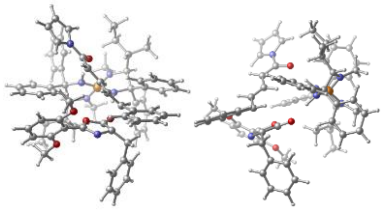
Sum of electronic and thermal Enthalpies = –3796.419821

Sum of electronic and thermal Free Energies = –3796.622945

0 1

O	-1.13039200	1.21130200	0.80261100
C	-2.15635300	0.54677000	0.64988700
C	-3.50780000	0.92427000	0.26909500
O	-2.14469400	-0.83065700	0.67675500
N	-4.29377900	-0.24606500	0.29780900
C	-3.47081200	-1.22228800	0.45314900
C	-3.76847500	-2.66342300	0.48406900
C	-4.47545300	-3.28762900	-0.56986800
C	-3.38459800	-3.45171400	1.59261700
C	-4.76320000	-4.65912300	-0.52279000
C	-3.66817400	-4.82270700	1.63718600
C	-4.35341000	-5.40788100	0.57608400
O	-4.83511800	-2.49602700	-1.61557500
C	-5.49601900	-3.08721800	-2.72422400
H	-6.46422700	-3.51583000	-2.43531800
H	-4.88008500	-3.86452300	-3.19444700
H	-5.65904500	-2.27610600	-3.43581100
O	-2.75917200	-2.78525600	2.60016800
C	-2.37208200	-3.51245500	3.75519300
H	-3.23763900	-3.97143200	4.25051500
H	-1.63502700	-4.28799400	3.51162800
H	-1.91902400	-2.78035100	4.42463900
H	-5.29694900	-5.14141300	-1.33159800
H	-3.37213200	-5.42485100	2.48656700
H	-4.57794300	-6.47070200	0.60866600
C	-4.10595200	2.23123500	0.74487900
H	-3.48357100	3.05875000	0.38592700
H	-5.08909700	2.34277800	0.27661700
C	-4.24019700	2.33143600	2.25614800
C	-3.47401500	3.25076600	2.98357300
C	-5.13858700	1.51073300	2.95449300
C	-3.60076600	3.35379400	4.37084800
C	-5.26498300	1.60931800	4.33979900
C	-4.49700400	2.53219100	5.05475500
H	-2.77598500	3.89677300	2.45534800
H	-5.73121200	0.78657000	2.40204500
H	-3.00334800	4.08144700	4.91581300
H	-5.96853600	0.96614000	4.86304500
H	-4.60005600	2.61163400	6.13409000
C	-3.08425000	1.18551200	-1.73541100
C	-2.63623800	-0.02290200	-2.36131200
H	-2.30415500	1.91600200	-1.52189100
H	-3.37028100	-0.61332300	-2.90194600
C	-1.31729300	-0.45156300	-2.36072400
H	-0.59503700	0.13572600	-1.79542900
C	-0.79298500	-1.55851700	-3.03951900
H	-1.45510400	-2.16549100	-3.64761000
C	0.58737900	-1.84610500	-3.03535000
O	1.49691700	-1.18575800	-2.46458700
N	1.01827800	-2.98849400	-3.79478300
C	2.31007000	-3.14261900	-4.26605500
C	0.27440600	-4.09078100	-4.18640300
C	2.38389800	-4.32710300	-4.95732800
C	1.09113900	-4.93416900	-4.89915400
H	3.03555500	-2.36501300	-4.08922100
H	-0.75322800	-4.20134500	-3.87831900
H	3.26209100	-4.71598200	-5.45607500
H	0.80007000	-5.88720700	-5.32158500
H	0.62613700	1.51606700	0.32689700
N	1.60839800	1.73056800	0.11582500
P	2.80513700	0.71699200	0.60878200
N	4.01426400	1.72590700	0.08133800
C	3.53683000	2.91626600	-0.65824400
C	2.06240200	3.12409400	-0.10194300
C	5.43760200	1.41538000	0.12987800
H	5.62034800	0.65875900	0.89542000
H	5.81412100	1.02659700	-0.82318900
H	6.00209700	2.31944800	0.38919900
H	4.13942100	3.75929100	-0.30949800
C	3.87108200	2.80821500	-2.18067300
H	4.96036400	2.64273800	-2.15599900
C	3.69346000	4.13690700	-2.95121700
H	2.65066800	4.26232700	-3.25526700
C	4.59598700	4.24293900	-4.18796700
C	2.04797200	3.87253200	1.26618900
C	3.05565800	4.73541400	1.71637700
C	0.92041700	3.69695100	2.08934200
C	2.95711900	5.37943200	2.95511300
C	0.82123900	4.33790600	3.32253700
C	1.84320600	5.18064500	3.76646700
H	3.93601900	4.93242700	1.11321900
H	0.10527100	3.05561400	1.76754800
H	3.75893000	6.03874300	3.27760900
H	-0.06199600	4.17546200	3.93474600
H	1.76753700	5.67984200	4.72868300
C	1.12926900	3.85784100	-1.07945600
C	0.32265300	3.15864700	-1.98453800
C	1.08541100	5.26003800	-1.09428400
C	-0.47981200	3.83968800	-2.90283300
C	0.28568400	5.94188500	-2.01052600
C	-0.49799800	5.23452500	-2.92387900
H	0.32609900	2.07595000	-1.98499200
H	1.67735900	5.82828900	-0.38432200
H	-1.09056400	3.27076600	-3.59819800
H	0.27267600	7.02858700	-2.00496800
H	-1.12121800	5.76450000	-3.63913100
N	2.38085900	-0.79176200	0.14470100
C	2.95908000	-1.86362300	0.98717800
C	3.00773900	-1.18904500	2.42508600
N	3.26974300	0.23946300	2.12839300
H	2.02083200	-0.98268500	-0.80892200
C	3.74501800	1.13167900	3.17810300
H	4.56863400	0.65321200	3.72220000
H	2.95619500	1.39400000	3.89240400
H	4.11298000	2.05723300	2.73111600
H	3.90006700	-1.56147800	2.93470700
C	1.87103800	-1.34914100	3.48103300
C	1.82183700	-2.75703900	4.11891000
H	1.22965600	-3.43170600	3.49339600
C	1.25835900	-2.75032700	5.54633300
C	2.09538000	-3.13407900	0.90330700
C	0.77595100	-3.09724800	0.43702000
C	2.63854800	-4.37328500	1.27670600
C	0.01590400	-4.26680000	0.35832000
C	1.87539700	-5.53764000	1.21329600
C	0.55833700	-5.48939800	0.75205100
H	0.32494900	-2.16160600	0.13022500
H	3.66923700	-4.43370300	1.61204900
H	-1.00051300	-4.21127600	-0.01809800
H	2.31798100	-6.48505400	1.51003200
H	-0.03413200	-6.39807700	0.68592100
C	4.38369600	-2.20028700	0.44955000
C	4.52155200	-2.36218200	-0.94097700
C	5.52019000	-2.39282400	1.24521900
C	5.75141700	-2.68350700	-1.50995600
C	6.75790400	-2.71108300	0.67382500
C	6.88104800	-2.85433600	-0.70535300
H	3.65530000	-2.24222200	-1.58551200
H	5.47106100	-2.31000800	2.32612000
H	5.82305600	-2.80878700	-2.58707300
H	7.62224400	-2.84943400	1.31840900
H	7.84109300	-3.10399800	-1.14903400
H	4.45653600	5.20817300	-4.68784100
H	5.65671600	4.15796700	-3.91870100
H	4.37597900	3.46044800	-4.92240500
H	1.23344300	-3.76404500	5.96236200
H	1.87171200	-2.13217800	6.21427800
H	0.23714100	-2.35486300	5.57995800
C	-4.34101200	1.80017800	-2.24639500
C	-4.37159900	3.16617200	-2.57169000
C	-5.51243600	1.04389600	-2.43383000
C	-5.52414200	3.75586500	-3.09290700
H	-3.47763400	3.76752700	-2.42447500
C	-6.66444900	1.63594600	-2.94753000
H	-5.51997500	0.00150600	-2.13213000
C	-6.67557000	2.99221000	-3.28601100
H	-5.52168300	4.81350600	-3.34511000
H	-7.56332700	1.03785300	-3.07707300
H	-7.57597900	3.44956700	-3.68797600
H	2.83464000	-3.18380800	4.14960500
C	0.48673500	-0.83600600	3.06837200
H	-0.15518000	-0.73745500	3.95096200
H	0.53085300	0.15307300	2.60511000
H	-0.01930300	-1.50425800	2.36969800
H	2.22150000	-0.68564100	4.28767300
H	3.92005400	4.97946500	-2.28237800
C	3.27226900	1.60301500	-2.91640300
H	2.19495800	1.69074700	-3.06023100
H	3.72970600	1.50493500	-3.90688900
H	3.45243800	0.66288900	-2.38891600

- **1da**-*RS* (HMe)



B3LYP/6-31G*

E = –3797.844091

Zero-point correction = 1.342174 (Hartree/Particle)

Thermal correction to Energy = 1.420524

Thermal correction to Enthalpy = 1.421468

Thermal correction to Gibbs Free Energy = 1.220961

Sum of electronic and zero-point Energies = –3796.501918

Sum of electronic and thermal Energies = –3796.423567

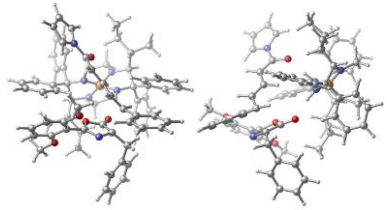
Sum of electronic and thermal Enthalpies = –3796.422623

Sum of electronic and thermal Free Energies = –3796.623131

0 1

O	-1.28379200	1.27675700	0.74729900
C	-2.24123200	0.51505900	0.59716600
C	-3.61026400	0.74666200	0.17363500
O	-2.10531000	-0.85666300	0.68524000
N	-4.28586700	-0.48797700	0.22714600
C	-3.38298000	-1.37587000	0.45100500
C	-3.55460400	-2.83409500	0.56745800
C	-4.10619600	-3.59797300	-0.48511600
C	-3.20876900	-3.49398700	1.76744200
C	-4.27812600	-4.98307400	-0.34728400
C	-3.37744700	-4.87746900	1.90554500
C	-3.90869200	-5.60337600	0.84267100
O	-4.43899300	-2.92081300	-1.61696600
C	-4.95549600	-3.64909400	-2.72046800
H	-5.90512000	-4.13983900	-2.47139600
H	-4.24078700	-4.40152000	-3.07819800
H	-5.12653900	-2.91123200	-3.50603400
O	-2.73849700	-2.69248900	2.76107800
C	-2.44647600	-3.27452800	4.02115100
H	-3.32995100	-3.76252600	4.45281500
H	-1.62661400	-4.00052900	3.94928200
H	-2.14112100	-2.44712600	4.66313900
H	-4.69355800	-5.57314800	-1.15424300
H	-3.10931200	-5.38224300	2.82498000
H	-4.04354600	-6.67681100	0.94606400
C	-4.34284300	2.01018600	0.56991200
H	-3.77891100	2.87773200	0.20863300
H	-5.30978800	2.01752200	0.05761800
C	-4.55218500	2.13941800	2.07016500
C	-3.81433200	3.06302200	2.82095700
C	-5.48475800	1.33014400	2.73582100
C	-4.00329900	3.18175000	4.19963400
C	-5.67480500	1.44560900	4.11249800
C	-4.93540700	2.37344700	4.85081800
H	-3.08636300	3.69524200	2.31748000
H	-6.05310600	0.60050600	2.16526700
H	-3.42465900	3.90979000	4.76377200
H	-6.40479500	0.81182800	4.61043700
H	-5.08746800	2.46631900	5.92331200
C	-3.14751600	0.96508800	-1.86114000
C	-2.57478400	-0.22018000	-2.41753800
H	-2.44558200	1.77087900	-1.64948900
H	-3.23385700	-0.90107800	-2.94824600
C	-1.21953500	-0.51342600	-2.37750600
H	-0.57388100	0.16448400	-1.82265500
C	-0.57330600	-1.58416100	-3.00613500
H	-1.16114300	-2.28571400	-3.58804000
C	0.83019100	-1.71655700	-2.98777200
O	1.65769100	-0.92433800	-2.45530300
N	1.38779700	-2.84794500	-3.67547600
C	2.69610300	-2.89844400	-4.12537800
C	0.76305500	-4.03947200	-4.01242400
C	2.89648200	-4.10514200	-4.74946200
C	1.66936300	-4.83399200	-4.67008700
H	3.34152600	-2.04691700	-3.98336800
H	-0.25238900	-4.23614500	-3.70740800
H	3.81638400	-4.43126600	-5.21698500
H	1.48048400	-5.83278400	-5.04172100
H	0.45816400	1.63937400	0.28316500
N	1.43891000	1.89082700	0.10525300
P	2.67604900	0.95307400	0.64392900
N	3.84082600	1.97067300	0.04684200
C	3.29765300	3.02015800	-0.84534900
C	1.84725100	3.27780800	-0.23252900
C	5.26130500	1.94369200	0.37356500
H	5.45905900	1.13052800	1.07362500
H	5.87616000	1.78018000	-0.51528300
H	5.56110400	2.89221300	0.83919000
H	3.92107400	3.90568300	-0.69740600
C	3.33583800	2.66528000	-2.36880300
H	2.40443500	2.14610500	-2.61449800
C	4.47118000	1.69412000	-2.76445000
H	5.44217600	2.20824000	-2.70373100
C	4.29142800	1.10067900	-4.16785300
C	1.89511000	4.12384300	1.06799100
C	2.89793500	5.05668900	1.36231600
C	0.84283500	3.97639200	1.98918800
C	2.86987800	5.79763400	2.54897100
C	0.81146200	4.71710200	3.16926600
C	1.82956200	5.62873700	3.45968900
H	3.71474400	5.23252200	0.66974900
H	0.03652100	3.27828900	1.78230100
H	3.66557200	6.50961100	2.75261200
H	-0.01458100	4.58066100	3.86222800
H	1.80695100	6.20405000	4.38122300
C	0.84657600	3.90137600	-1.22051000
C	0.14992300	3.10854100	-2.14235300
C	0.63675500	5.28889000	-1.24782200
C	-0.70957600	3.68460300	-3.07947600
C	-0.22401700	5.86559400	-2.18222200
C	-0.89922200	5.06654200	-3.10564200
H	0.28557600	2.03390300	-2.14115600
H	1.14592000	5.92878800	-0.53524700
H	-1.23145900	3.04372900	-3.78446300
H	-0.36770900	6.94286700	-2.18255100
H	-1.56832700	5.51530400	-3.83488800
N	2.33148400	-0.59530200	0.24109000
C	2.98419900	-1.59071600	1.12007800
C	2.96364400	-0.86377400	2.53388700
N	3.13448900	0.57030300	2.18959800
H	2.05404700	-0.82271600	-0.73118500
C	3.52259300	1.53035000	3.21489300
H	4.40414400	1.16134000	3.75410400
H	2.71989100	1.71496500	3.93764800
H	3.77361700	2.48467200	2.74851800
H	3.87045800	-1.15508000	3.07013400
C	1.82117600	-1.06440800	3.57589000
C	1.85417900	-2.45354500	4.25476500
H	1.32973500	-3.18640600	3.63444100
C	1.25096800	-2.44846100	5.66578800
C	2.21924200	-2.92544300	1.06357200
C	0.90762400	-2.99521600	0.57777800
C	2.84190900	-4.11293500	1.47768000
C	0.23188400	-4.21662800	0.52238000
C	2.16292500	-5.32937900	1.43555300
C	0.85264800	-5.38684100	0.95680800
H	0.39809500	-2.10069700	0.24052900
H	3.86908100	-4.09396500	1.82762500
H	-0.78141400	-4.24234300	0.13430100
H	2.66652500	-6.23498200	1.76397700
H	0.32560900	-6.33612100	0.91096100
C	4.44188300	-1.83488300	0.62061700
C	4.64345600	-1.95755600	-0.76556200
C	5.55402400	-1.99774400	1.45776400
C	5.90883100	-2.21374200	-1.28966400
C	6.82644400	-2.24830500	0.93199300
C	7.01137100	-2.35441300	-0.44387300
H	3.80305300	-1.85911100	-1.44600400
H	5.45581000	-1.94805900	2.53744600
H	6.02834000	-2.31174600	-2.36530200
H	7.66905100	-2.36472900	1.60886100
H	7.99845300	-2.55227300	-0.85294300
H	5.10594900	0.40247600	-4.39430600
H	3.34791100	0.54665500	-4.22460700
H	4.29167100	1.86438800	-4.95305700
H	1.29645700	-3.44761400	6.11413700
H	1.79266100	-1.76191400	6.32894500
H	0.20043000	-2.13804500	5.65861700
C	-4.44454400	1.43609400	-2.41479900
C	-4.60143100	2.78334000	-2.78034100
C	-5.53036600	0.56217500	-2.60712200
C	-5.79273000	3.24145400	-3.34449200
H	-3.77432200	3.47328300	-2.63077000
C	-6.72134900	1.02275300	-3.16440200
H	-5.44306200	-0.46789600	-2.27673400
C	-6.85766100	2.36194500	-3.54189600
H	-5.88827100	4.28693700	-3.62733800
H	-7.55289300	0.33489300	-3.29773400
H	-7.78817600	2.71653700	-3.97763700
H	2.89380500	-2.80482800	4.32513500
C	0.41353000	-0.65770700	3.12488100
H	-0.24855100	-0.57342200	3.99385200
H	0.39966500	0.31595800	2.62767600
H	-0.03552600	-1.38088600	2.44238500
H	2.11252100	-0.35650500	4.36814100
H	4.50482100	0.86019000	-2.05651600
C	3.42487500	3.95825300	-3.19899600
H	4.39687200	4.44634700	-3.04079600
H	3.33250900	3.74652900	-4.26820300
H	2.64268700	4.67553900	-2.94144900

- **1da**-*RS* (HH)



B3LYP/6-31G*

E = –3797.847583

Zero-point correction = 1.341927 (Hartree/Particle)

Thermal correction to Energy = 1.420269

Thermal correction to Enthalpy = 1.421213

Thermal correction to Gibbs Free Energy = 1.220496

Sum of electronic and zero-point Energies = –3796.505655

Sum of electronic and thermal Energies = –3796.427314

Sum of electronic and thermal Enthalpies = –3796.426369

Sum of electronic and thermal Free Energies = –3796.627087

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.048862

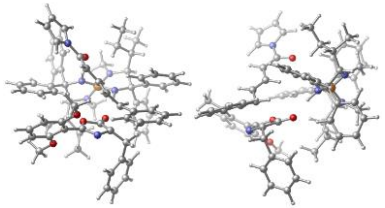
G = –3797.793823

0 1

O	1.04005500	1.17514100	-0.83324700
C	2.09741700	0.57749000	-0.62379200
C	3.38405700	1.01121100	-0.10838700
O	2.18393200	-0.79414800	-0.74274200
N	4.24686900	-0.10421700	-0.13820800
C	3.50914200	-1.11673500	-0.42978500
C	3.89855700	-2.53292400	-0.52629600
C	4.53222700	-3.19395800	0.55097600
C	3.67009600	-3.25855900	-1.71758400
C	4.89569700	-4.54398900	0.44648400
C	4.02794900	-4.60891600	-1.81965100
C	4.63461400	-5.23363300	-0.73358400
O	4.74653800	-2.45862400	1.67533100
C	5.32807800	-3.09267400	2.80474100
H	6.34024500	-3.45646400	2.58643000
H	4.71082400	-3.92715300	3.16140900
H	5.38001800	-2.32488200	3.57840500
O	3.11895900	-2.55322300	-2.74174500
C	2.89581700	-3.21544000	-3.97722100
H	3.83100600	-3.60717400	-4.39787200
H	2.17238900	-4.03320200	-3.86787900
H	2.48889400	-2.45674400	-4.64621900
H	5.37281100	-5.05539300	1.27264400
H	3.84799200	-5.16501500	-2.73075100
H	4.91581300	-6.28053800	-0.81070000
C	3.93355400	2.37888500	-0.45536100
H	3.23883700	3.14694400	-0.09650700
H	4.87126500	2.51417700	0.09266100
C	4.17120900	2.57811700	-1.94388200
C	3.38702500	3.47282900	-2.68227700
C	5.18131800	1.86831900	-2.61032100
C	3.60381400	3.65919600	-4.04985000
C	5.39849200	2.04998600	-3.97572200
C	4.61108100	2.94723700	-4.70212600
H	2.60231800	4.03279400	-2.17811300

H	5.78872600	1.16325700	-2.04929200
H	2.98940000	4.36567900	-4.60350000
H	6.18736700	1.49192100	-4.47430200
H	4.78426800	3.09199800	-5.76552900
C	2.79380100	1.12129300	1.88618600
C	2.36333400	-0.14272700	2.39840500
H	1.99449900	1.82782300	1.66197800
H	3.09362400	-0.75052000	2.92462600
C	1.05658700	-0.60406400	2.32197900
H	0.33506000	0.00702000	1.78188200
C	0.54940200	-1.77455500	2.89849400
H	1.22261400	-2.41389900	3.45893300
C	-0.82315500	-2.09837600	2.85085500
O	-1.74481500	-1.40511700	2.33703500
N	-1.23008200	-3.32410300	3.47741600
C	-2.54229300	-3.60198300	3.82159600
C	-0.44480300	-4.41059900	3.83708200
C	-2.58752700	-4.84500800	4.40191300
C	-1.25436000	-5.36213300	4.40509000
H	-3.30780600	-2.86541200	3.64055200
H	0.60950600	-4.43145500	3.61275300
H	-3.47396200	-5.33220600	4.78659100
H	-0.93158900	-6.32784700	4.77204900
H	-0.59275100	1.61162000	-0.09265300
N	-1.59466800	1.71896100	0.09760500
P	-2.66375500	0.71286100	-0.65034500
N	-3.98554800	1.54437300	-0.09213500
C	-3.64107100	2.56561400	0.92453000
C	-2.18452900	3.02733000	0.46843700
C	-5.36785100	1.37519000	-0.52435500
H	-5.42367100	0.59725200	-1.28734700
H	-6.01395100	1.07630600	0.30488700
H	-5.74977200	2.31387100	-0.94769600
H	-4.34778300	3.38797900	0.78698500
C	-3.75186500	2.08044900	2.40830600
H	-2.77939800	1.66932200	2.69659700
C	-4.77012000	0.94025500	2.63559200
H	-5.79534800	1.32959900	2.54516000
C	-4.60120700	0.24636700	3.99359200
C	-2.23160400	3.95452900	-0.77589500
C	-3.27330700	4.85733600	-1.03151500
C	-1.15001900	3.92955800	-1.67350800
C	-3.25100800	5.68835700	-2.15624900
C	-1.12505300	4.76048800	-2.79312200
C	-2.17868600	5.64146800	-3.04475400
H	-4.11609000	4.93914400	-0.35239300
H	-0.31464100	3.25645700	-1.50357600
H	-4.07656400	6.37371700	-2.33002800
H	-0.27576900	4.71572300	-3.46976500
H	-2.16084600	6.28614300	-3.91924800
C	-1.34578500	3.68731200	1.57771500
C	-0.60595600	2.91293300	2.48240400
C	-1.32240100	5.08271300	1.72823900
C	0.11657900	3.51089600	3.51685800
C	-0.60173700	5.68116400	2.76218200
C	0.11972400	4.89802500	3.66411300
H	-0.59561700	1.83383100	2.38818200
H	-1.86544200	5.71280000	1.03242700
H	0.68086700	2.88329500	4.20071900
H	-0.60183400	6.76392800	2.85605000
H	0.68239800	5.36358800	4.46874200
N	-2.22634700	-0.83058900	-0.33303500
C	-2.67247100	-1.78572000	-1.37650800
C	-2.45374600	-0.91687800	-2.69549700
N	-2.86895900	0.44546500	-2.27063500
H	-2.00717000	-1.12737900	0.63691800
C	-3.47318200	1.37128000	-3.22182600
H	-4.32642200	0.89490200	-3.72263300
H	-2.75752400	1.69749700	-3.97986400
H	-3.82767100	2.25896800	-2.69533700
H	-3.17555800	-1.22208900	-3.45754600
C	-1.03031900	-1.02562300	-3.33510200
C	-0.50254400	0.28938800	-3.94795700
H	-1.12488100	0.58444500	-4.80561700
C	0.96045200	0.20370500	-4.40412300
C	-1.83093700	-3.07209700	-1.29887300
C	-0.54920800	-3.06851700	-0.73270700
C	-2.33798400	-4.28449400	-1.79321500
C	0.20507600	-4.24207000	-0.66709100
C	-1.58066700	-5.45400200	-1.73599900
C	-0.30485400	-5.43807900	-1.16992700
H	-0.12529100	-2.15228700	-0.33954100
H	-3.33691700	-4.32280300	-2.21569200
H	1.19160400	-4.21111300	-0.21532500
H	-1.99729300	-6.38047600	-2.12278600
H	0.28128000	-6.35142300	-1.11181100
C	-4.16583400	-2.14150800	-1.13996000
C	-4.56783800	-2.42777800	0.17690300
C	-5.12537400	-2.24411700	-2.15526300
C	-5.88360800	-2.78339500	0.46573900
C	-6.44885100	-2.59577200	-1.86550300
C	-6.83489900	-2.86363900	-0.55459200
H	-3.84080300	-2.37550000	0.98267600
H	-4.86127000	-2.06447800	-3.19246300
H	-6.16381400	-3.00405900	1.49229400
H	-7.17238400	-2.66316900	-2.67398300
H	-7.86158500	-3.13931300	-0.32931300
H	-5.34126600	-0.55461500	4.10783300
H	-3.60565300	-0.20519500	4.06475600
H	-4.73299200	0.93220100	4.83760600
H	1.34430600	1.19640500	-4.66251300
H	1.59681200	-0.19726800	-3.60814100
H	1.07815100	-0.43176900	-5.28980200
C	3.98461000	1.75678600	2.51477800
C	3.92514500	3.09771400	2.92882600
C	5.17900600	1.04496300	2.72959200
C	5.01201500	3.70410700	3.56050100
H	3.01165400	3.66456800	2.76657800
C	6.26532500	1.65445300	3.35389000
H	5.25908700	0.02733400	2.36187600
C	6.18683300	2.98407200	3.77842000
H	4.93981400	4.74114700	3.87918800
H	7.18368600	1.09150800	3.50279900
H	7.03644300	3.45492400	4.26621600
H	-0.57922900	1.08497800	-3.20083000
C	-1.04521400	-2.15039000	-4.38592100
H	-1.67625300	-1.86924200	-5.24114700
H	-0.04003800	-2.34682400	-4.76901700
H	-1.42723300	-3.09008000	-3.97877600
H	-0.32162100	-1.29407000	-2.54532000
H	-4.64653900	0.17874300	1.85964600
C	-4.07765500	3.27911200	3.31753400
H	-5.08705600	3.65684200	3.10253300
H	-4.05072300	2.99237900	4.37294000
H	-3.37454600	4.10496800	3.18748300

- **1da**-*RS* (EtH)



B3LYP/6-31G*

E = –3797.848941

Zero-point correction = 1.342010 (Hartree/Particle)

Thermal correction to Energy = 1.420365

Thermal correction to Enthalpy = 1.421309

Thermal correction to Gibbs Free Energy = 1.220626

Sum of electronic and zero-point Energies = –3796.506931

Sum of electronic and thermal Energies = –3796.428576

Sum of electronic and thermal Enthalpies = –3796.427632

Sum of electronic and thermal Free Energies = –3796.628314

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.049946

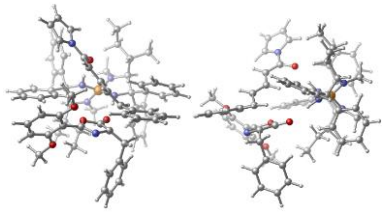
G = –3797.794783

0 1

O	-0.95215200	-1.13366700	-0.82100400
C	-2.04677900	-0.60211800	-0.62476900
C	-3.30323700	-1.10402100	-0.09404600
O	-2.21891200	0.75588100	-0.77937700
N	-4.23478900	-0.04544600	-0.15544900
C	-3.56210600	1.00341000	-0.47440900
C	-4.03743700	2.38922900	-0.61047900
C	-4.73202400	3.03274800	0.43967500
C	-3.82723200	3.10265600	-1.81287100
C	-5.17670300	4.35457900	0.29689300
C	-4.26400000	4.42612800	-1.95161000
C	-4.93250000	5.03413800	-0.89261400
O	-4.92002500	2.31125200	1.57764100
C	-5.56033000	2.93279700	2.68206800
H	-6.59041400	3.22387800	2.43979900
H	-5.00507700	3.81446900	3.02690600
H	-5.57460900	2.18188800	3.47369400
O	-3.21283000	2.41054700	-2.80956800
C	-2.97731300	3.06676800	-4.04575600
H	-3.91458600	3.40262900	-4.50809600
H	-2.30240300	3.92293000	-3.92143100
H	-2.50565500	2.32160700	-4.68716300
H	-5.70179800	4.85301000	1.10156200
H	-4.09867200	4.97337800	-2.87089000
H	-5.27585600	6.05973600	-0.99882600
C	-3.76718300	-2.51203000	-0.40433400
H	-3.03272200	-3.22634600	-0.01487500
H	-4.69979800	-2.68462100	0.14234800
C	-3.98084300	-2.77894000	-1.88619100
C	-3.19184300	-3.71515200	-2.56587400
C	-4.97772500	-2.10019200	-2.60343400
C	-3.38829300	-3.96961700	-3.92563100
C	-5.17390200	-2.34946600	-3.96135300
C	-4.37981600	-3.28523400	-4.62946600
H	-2.42044800	-4.25558300	-2.02129000
H	-5.59258600	-1.36725700	-2.08826700
H	-2.77130300	-4.70831600	-4.43254600
H	-5.95222900	-1.81396400	-4.49966000
H	-4.53676500	-3.48207300	-5.68698600
C	-2.71647000	-1.12583900	1.89129500
C	-2.36291000	0.17551200	2.37012300
H	-1.87357600	-1.78900100	1.69448500
H	-3.13190200	0.75645500	2.87112000
C	-1.08328300	0.70638300	2.29044300
H	-0.32251500	0.11781700	1.77881600
C	-0.64821800	1.92029400	2.83512700
H	-1.36092100	2.53252500	3.37641300
C	0.70311100	2.32268100	2.78232300
O	1.66265000	1.68180100	2.27260000
N	1.04289300	3.57171500	3.40253100
C	2.34027100	3.92302500	3.73481800
C	0.20056900	4.61067800	3.77313600
C	2.32080600	5.16532200	4.31784800
C	0.96041900	5.60561600	4.33552800
H	3.14409000	3.23196200	3.54093800
H	-0.85579900	4.57202700	3.56141300
H	3.18209200	5.70173300	4.69404600
H	0.58680100	6.55038800	4.70874000
H	0.67653300	-1.57114400	-0.08387900
N	1.67609600	-1.66986400	0.12184800
P	2.73531700	-0.65193100	-0.62197900
N	4.07048200	-1.47534200	-0.08011900
C	3.76294200	-2.58858200	0.84518400
C	2.26146200	-2.98060500	0.47506100
C	5.45078300	-1.08010600	-0.33513300
H	5.49216100	-0.43207300	-1.21264800
H	5.88758200	-0.53081700	0.50538200
H	6.05825300	-1.97208500	-0.52905800
H	4.40380200	-3.41991600	0.54268000
C	4.09061300	-2.31015400	2.34697200
H	3.47230700	-3.00777500	2.92248600
C	3.73898300	-0.88262000	2.80963400
H	4.43840500	-0.16708700	2.35590700
C	3.75001800	-0.69598800	4.33170400
C	2.19703800	-3.93392100	-0.75403500
C	3.18033900	-4.88945400	-1.04902400
C	1.06839500	-3.88013000	-1.59079600
C	3.05790300	-5.74116300	-2.15117200
C	0.94496000	-4.72967100	-2.69000800
C	1.94168000	-5.66281300	-2.98080800
H	4.05762800	-4.99907200	-0.41924500
H	0.26982700	-3.17162000	-1.39338700
H	3.84154300	-6.46658000	-2.35403300
H	0.06205900	-4.65512100	-3.31936800
H	1.84656000	-6.32212300	-3.83925900
C	1.49933700	-3.60515800	1.65821400
C	0.76497000	-2.80738100	2.54644400
C	1.56205000	-4.98512500	1.90267600
C	0.11679900	-3.36981500	3.64807200
C	0.91938700	-5.54718000	3.00628700
C	0.19244400	-4.74282000	3.88455300
H	0.70626000	-1.73750400	2.38870600
H	2.10613400	-5.63300500	1.22367800
H	-0.45022500	-2.72669200	4.31516500
H	0.98279600	-6.61940400	3.17228000
H	-0.31175700	-5.18094700	4.74160600
N	2.26441600	0.88352700	-0.31795400
C	2.66845600	1.84436700	-1.37482200
C	2.49094800	0.95401800	-2.68580800
N	2.95234800	-0.38574200	-2.24221600
H	1.98937200	1.20080100	0.63068600
C	3.61133200	-1.29762300	-3.16987800
H	4.40853700	-0.77061600	-3.71007400
H	2.91300400	-1.71915200	-3.89736200
H	4.05506600	-2.12368500	-2.61109200

H	3.20656000	1.27839200	-3.44583000
C	1.07052600	0.99748000	-3.33878600
C	0.61760100	-0.34070300	-3.96138500
H	1.26939700	-0.60454000	-4.80739400
C	-0.84005100	-0.32525200	-4.44218700
C	1.76904800	3.09146000	-1.31375300
C	0.47614900	3.02806300	-0.77774900
C	2.22925300	4.32520900	-1.80055600
C	-0.33541700	4.16338400	-0.73528000
C	1.41573800	5.45738300	-1.76486800
C	0.12878800	5.38146700	-1.22985100
H	0.08837300	2.09461400	-0.38872800
H	3.23447800	4.40960500	-2.20067700
H	-1.32970900	4.08459500	-0.30689100
H	1.79674400	6.40193000	-2.14460300
H	-0.50167500	6.26578400	-1.18900200
C	4.14392500	2.26548700	-1.13490900
C	4.52444200	2.57989000	0.18192400
C	5.10602700	2.39309900	-2.14456200
C	5.82461200	2.98489600	0.47638600
C	6.41396000	2.79461400	-1.84898100
C	6.78045400	3.08800600	-0.53789300
H	3.79127200	2.51241600	0.98105600
H	4.85631300	2.19289700	-3.18156300
H	6.08940700	3.22675300	1.50236200
H	7.14079000	2.87976100	-2.65280800
H	7.79516000	3.40168400	-0.30797300
H	3.40769900	0.31273900	4.58432100
H	3.07305300	-1.40812100	4.81977700
H	4.74763000	-0.83112600	4.76505700
H	-1.16891300	-1.33421600	-4.71370700
H	-1.50915900	0.03726800	-3.65449300
H	-0.97512100	0.31017500	-5.32528500
C	-3.86568300	-1.81448200	2.54344700
C	-3.71707800	-3.13029600	3.01142700
C	-5.10524700	-1.17591700	2.73027800
C	-4.76243100	-3.78229600	3.66737400
H	-2.76676300	-3.64013300	2.87325700
C	-6.14985300	-1.83142900	3.37886000
H	-5.25217600	-0.18088900	2.32322500
C	-5.98349300	-3.13463200	3.85639000
H	-4.62140000	-4.79835900	4.02786400
H	-7.10406100	-1.32556200	3.50567300
H	-6.80075100	-3.64148000	4.36303300
H	0.72045400	-1.13325300	-3.21404200
C	1.03956500	2.12461000	-4.38658100
H	1.68783900	1.87483500	-5.23868700
H	0.02870700	2.27559700	-4.77528300
H	1.37537900	3.07996200	-3.97587200
H	0.34127900	1.22525700	-2.55508400
H	2.74838600	-0.59878500	2.44676300
C	5.55321000	-2.68123900	2.66633800
H	6.27206700	-1.99732500	2.20143400
H	5.73079100	-2.65344700	3.74586200
H	5.78954900	-3.69756100	2.32660300

● **1da**-*RS* (HEt)



B3LYP/6-31G*

E = –3797.845308

Zero-point correction = 1.341405 (Hartree/Particle)

Thermal correction to Energy = 1.420093

Thermal correction to Enthalpy = 1.421038

Thermal correction to Gibbs Free Energy = 1.217914

Sum of electronic and zero-point Energies = –3796.503904

Sum of electronic and thermal Energies = –3796.425215

Sum of electronic and thermal Enthalpies = –3796.424271

Sum of electronic and thermal Free Energies = –3796.627394

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

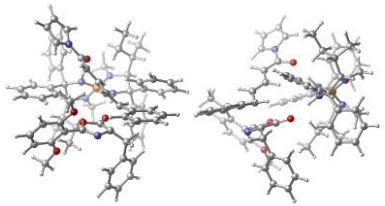
E = –3799.04514

G = –3797.792242

0 1

O	-1.06921300	1.18321700	0.66353800
C	-2.14952500	0.60163800	0.54522300
C	-3.45460600	1.05045400	0.09695600
O	-2.25953600	-0.76830100	0.70481900
N	-4.33459600	-0.04661700	0.18244900
C	-3.60421900	-1.06649400	0.46425100
C	-4.02971200	-2.47072800	0.61434400
C	-4.62585600	-3.17235400	-0.45728000
C	-3.88936600	-3.13325600	1.85413700
C	-5.03931800	-4.50289300	-0.29986700
C	-4.29721700	-4.46442900	2.01101500
C	-4.86523500	-5.13150500	0.92903700
O	-4.75875700	-2.49277400	-1.62860100
C	-5.30397800	-3.16963200	-2.75107800
H	-6.33669300	-3.49150200	-2.56553000
H	-4.69673000	-4.03986000	-3.03157800
H	-5.29377900	-2.44403100	-3.56606800
O	-3.36678000	-2.38854400	2.86615900
C	-3.28636300	-2.97007400	4.15951500
H	-4.27393100	-3.28802400	4.51722700
H	-2.59919900	-3.82574800	4.17177900
H	-2.89876300	-2.18699300	4.81179900
H	-5.48887600	-5.04530900	-1.12173400
H	-4.18636800	-4.97253200	2.96050800
H	-5.18489400	-6.16331500	1.04843100
C	-3.96240700	2.43312200	0.44343100
H	-3.23682300	3.17618600	0.09316900
H	-4.89263600	2.60446400	-0.10687100
C	-4.20305600	2.62637500	1.93186700
C	-3.32216000	3.38564700	2.71258000
C	-5.31129000	2.03623400	2.55738700
C	-3.54112600	3.55562500	4.08190800
C	-5.53265300	2.20443800	3.92385800
C	-4.64864300	2.96600200	4.69245900
H	-2.45997500	3.85073000	2.23979000
H	-5.99225900	1.43256100	1.96360100
H	-2.84919900	4.15435500	4.66987800
H	-6.39918000	1.74180400	4.39024300
H	-4.82361200	3.10030100	5.75698800
C	-2.93977900	1.13497700	-1.94496100
C	-2.50559400	-0.12801000	-2.44969100
H	-2.14673500	1.85274100	-1.73853700
H	-3.23228800	-0.74685800	-2.96768400
C	-1.19654900	-0.57994300	-2.35976200
H	-0.48658300	0.04343500	-1.81972600
C	-0.67236800	-1.75410800	-2.91061500
H	-1.32751300	-2.41498800	-3.46778900
C	0.70274000	-2.05720700	-2.83442400
O	1.60834800	-1.33934500	-2.32563800
N	1.13178900	-3.29375000	-3.42727200
C	2.43475300	-3.53611200	-3.82812300
C	0.37239600	-4.42099200	-3.70267800
C	2.49875100	-4.80015300	-4.36129200
C	1.18891500	-5.36578100	-4.27358400
H	3.17721200	-2.76157700	-3.72388100
H	-0.66669900	-4.46934900	-3.41828000
H	3.38205400	-5.26897500	-4.77503700
H	0.88660600	-6.35812200	-4.58211000
H	0.73014300	1.56701400	0.16390300
N	1.73166400	1.70197700	-0.00595400
P	2.85354500	0.66928500	0.61301300
N	4.12352800	1.47963800	-0.07800600
C	3.69870400	2.52161200	-1.04167200
C	2.29971600	3.00021500	-0.44224100
C	5.53635100	1.28970300	0.22908100
H	5.64834800	0.47839100	0.95047100
H	6.10630400	1.02559300	-0.66491500
H	5.96166400	2.20697200	0.65837200
H	4.42786700	3.33244500	-0.96394200
C	3.66286900	2.05298700	-2.53421000
H	2.66576200	1.64668900	-2.73017200
C	4.64959400	0.91128200	-2.86755800
H	5.68220200	1.29105500	-2.85296800
C	4.36677400	0.24891600	-4.22215900
C	2.47051400	3.92136600	0.79614600
C	3.57033200	4.76449500	1.00205100
C	1.43861000	3.94171700	1.75036200
C	3.65206200	5.58080500	2.13553100
C	1.51608700	4.75777900	2.87748200
C	2.62819400	5.57853100	3.08010800
H	4.37923400	4.80874900	0.27992700
H	0.56445800	3.31221400	1.61213000
H	4.52067800	6.21989200	2.27151300
H	0.70265300	4.75195300	3.59811000
H	2.69136500	6.21230300	3.96042000
C	1.37018000	3.67443900	-1.46544800
C	0.55319800	2.91493600	-2.31397500
C	1.34609600	5.07158100	-1.59818000
C	-0.24326300	3.52940100	-3.28217100
C	0.54933000	5.68665400	-2.56402700
C	-0.24724000	4.91815800	-3.41385500
H	0.54364200	1.83477900	-2.23203600
H	1.95128400	5.68911700	-0.94339200
H	-0.86186500	2.91328900	-3.92845700
H	0.55051900	6.77030800	-2.64658300
H	-0.86703300	5.39627500	-4.16754900
N	2.31089400	-0.85007500	0.34249300
C	2.80817600	-1.83837200	1.32446200
C	2.89221400	-0.97857100	2.66043700
N	3.28360600	0.36901400	2.18565000
H	2.00309200	-1.12702200	-0.60735500
C	3.87446700	1.33292300	3.10468400
H	4.71637400	0.87111800	3.63535600
H	3.15055000	1.69580800	3.84154300
H	4.24379800	2.19613700	2.54827100
H	3.73856000	-1.35241500	3.24035300
C	1.65995300	-0.99955300	3.62562300
C	0.62289400	0.10261400	3.33461100
H	1.03572900	1.08094500	3.61677600
C	-0.72375400	-0.09633500	4.03861300
C	1.83599600	-3.02318500	1.43385600
C	0.51925900	-2.93397400	0.96559100
C	2.25419000	-4.21742700	2.04101400
C	-0.35390800	-4.01656400	1.09337100
C	1.37718800	-5.29192600	2.18079600
C	0.06913400	-5.19759500	1.70159700
H	0.15667800	-2.02001800	0.51056200
H	3.27587000	-4.31702600	2.39474400
H	-1.36582800	-3.92530600	0.71205500
H	1.72372100	-6.20838000	2.65166900
H	-0.61216100	-6.03916700	1.79575300
C	4.20011700	-2.36191800	0.86504900
C	4.35393600	-2.69412900	-0.49269000
C	5.29242100	-2.57503200	1.71654200
C	5.55534000	-3.20596800	-0.97767000
C	6.50233200	-3.08192500	1.22886300
C	6.64091400	-3.39840400	-0.11988800
H	3.52613700	-2.55528600	-1.18162300
H	5.22542000	-2.36386900	2.77905000
H	5.63594700	-3.46325400	-2.03035100
H	7.33227300	-3.23156800	1.91482500
H	7.57879300	-3.79613900	-0.49812400
H	5.07866700	-0.56472100	-4.40438500
H	3.35865300	-0.17953200	-4.22899800
H	4.45218400	0.94843700	-5.06073000
H	-1.39367800	0.74033700	3.81541400
H	-1.21219500	-1.00633800	3.67647300
H	-0.62486800	-0.15982500	5.12906600
C	-4.16112300	1.74537400	-2.53227900
C	-4.14775100	3.09192400	-2.93328100
C	-5.34305200	1.00566700	-2.72104600
C	-5.26634900	3.67641600	-3.52870600
H	-3.24562700	3.68099000	-2.78631400
C	-6.46104500	1.59291900	-3.30934200
H	-5.38761600	-0.01744000	-2.36257000
C	-6.42777400	2.92807400	-3.72236500
H	-5.22979200	4.71807500	-3.83822300
H	-7.36857200	1.00814300	-3.43905500
H	-7.30204600	3.38152100	-4.18227200
H	0.41923400	0.14879900	2.26213900
C	2.13722600	-0.97910400	5.09154900
H	2.64528800	-0.04199100	5.35061100
H	1.29428500	-1.09324600	5.77989000
H	2.83350600	-1.80267300	5.29368200
H	1.16260300	-1.96300000	3.47558500
H	4.58048600	0.13433400	-2.10023000
C	3.90565800	3.25815800	-3.46078400
H	4.93627000	3.62302800	-3.34851500
H	3.76646400	2.98200800	-4.51005700
H	3.22976900	4.09047500	-3.25227600

- **1da**-*RS* (EtEt)



B3LYP/6-31G*

E = –3797.846449

Zero-point correction = 1.341103 (Hartree/Particle)

Thermal correction to Energy = 1.420027

Thermal correction to Enthalpy = 1.420971

Thermal correction to Gibbs Free Energy = 1.216481

Sum of electronic and zero-point Energies = –3796.505346

Sum of electronic and thermal Energies = –3796.426422

Sum of electronic and thermal Enthalpies = –3796.425478

Sum of electronic and thermal Free Energies = –3796.629969

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

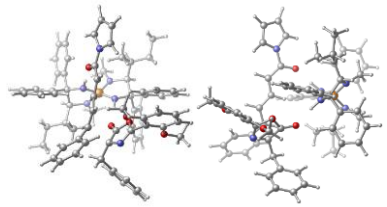
E = –3799.045815

G = –3797.794099

0 1

O	1.02777100	1.07650800	-0.60420800
C	2.13304400	0.54370000	-0.49896300
C	3.40409200	1.02173200	0.01404900
O	2.31228300	-0.80107900	-0.76121600
N	4.34117200	-0.02293000	-0.14887100
C	3.66629300	-1.05043400	-0.52361300
C	4.16318800	-2.41050200	-0.80609600
C	4.71057600	-3.22114700	0.21102800
C	4.14188300	-2.90728100	-2.12708700
C	5.19226500	-4.50499500	-0.08248300
C	4.61957300	-4.19022900	-2.42253100
C	5.13534600	-4.97241400	-1.39226400
O	4.73170800	-2.68795800	1.46296500
C	5.24673100	-3.47195200	2.52901600
H	6.30286200	-3.72424600	2.36954200
H	4.66924300	-4.39503700	2.66661400
H	5.15467600	-2.85171500	3.42203400
O	3.65983400	-2.04853900	-3.06712100
C	3.74717700	-2.42289600	-4.43394500
H	4.78486800	-2.63041500	-4.72530300
H	3.12567200	-3.30060600	-4.65312400
H	3.37295700	-1.56782100	-4.99798800
H	5.60567300	-5.13438100	0.69528800
H	4.60049000	-4.57282500	-3.43525100
H	5.50794100	-5.96836800	-1.61668100
C	3.84454900	2.45176500	-0.21330500
H	3.15133100	3.12980500	0.29772800
H	4.82117100	2.57822600	0.26649400
C	3.93265700	2.85967100	-1.67691100
C	3.21663000	3.96674700	-2.14996500
C	4.74253300	2.15449200	-2.58032800
C	3.30717400	4.36631000	-3.48574600
C	4.83074500	2.54827500	-3.91561700
C	4.11452900	3.65663400	-4.37502900
H	2.58513400	4.52557400	-1.46252100
H	5.29874200	1.29028700	-2.22808200
H	2.75123300	5.23647800	-3.82787400
H	5.46626200	1.99060100	-4.59949000
H	4.18870400	3.96498500	-5.41485200
C	2.88125000	0.93233700	2.02959900
C	2.45868100	-0.37006800	2.43926800
H	2.07671600	1.65319000	1.88470000
H	3.19342100	-1.02338700	2.90045000
C	1.14885900	-0.81505800	2.33471900
H	0.42928600	-0.15099800	1.85882500
C	0.63296100	-2.02654800	2.80790600
H	1.29680300	-2.72207900	3.30968800
C	-0.74382500	-2.32259000	2.73806700
O	-1.65473700	-1.57823100	2.28111100
N	-1.17009100	-3.58271800	3.27903400
C	-2.46814200	-3.83564500	3.68794900
C	-0.41291200	-4.72438000	3.49475200
C	-2.53191500	-5.12077300	4.16729900
C	-1.22655100	-5.68868700	4.03627800
H	-3.20758100	-3.05375800	3.62502400
H	0.62180800	-4.76578200	3.19389300
H	-3.41225300	-5.60290100	4.57189100
H	-0.92546800	-6.69484400	4.29776100
H	-0.71801700	1.49509700	-0.12541600
N	-1.70986000	1.67245500	0.06084000
P	-2.86879300	0.70596400	-0.59345600
N	-4.11632000	1.60739600	0.02738200
C	-3.69115900	2.71751100	0.90763100
C	-2.19307300	3.01539600	0.44480500
C	-5.52870900	1.29367800	-0.15113800
H	-5.64655000	0.60997500	-0.99459100
H	-5.96187400	0.81419900	0.73309900
H	-6.08935900	2.21213000	-0.36334600
H	-4.29921000	3.58092500	0.62720400
C	-3.95104800	2.48164800	2.43034100
H	-3.25533700	3.14001700	2.96115000
C	-3.67408800	1.03797700	2.89514400
H	-4.44810600	0.36814000	2.49565400
C	-3.60573400	0.87341300	4.41831700
C	-2.12674700	3.95287600	-0.79548000
C	-3.09635000	4.91401900	-1.11157700
C	-0.99752600	3.86391600	-1.62957600
C	-2.96106000	5.73717300	-2.23477900
C	-0.85954000	4.68564300	-2.74692300
C	-1.84530600	5.62430600	-3.06055100
H	-3.97207900	5.05131700	-0.48527200
H	-0.20959300	3.14936100	-1.41079800
H	-3.73436400	6.46840600	-2.45579000
H	0.02648000	4.58733500	-3.36852600
H	-1.74061200	6.26277300	-3.93359400
C	-1.33265300	3.59708200	1.57967300
C	-0.61895600	2.76157600	2.44923900
C	-1.29266300	4.98101800	1.80410500
C	0.10682900	3.29260500	3.51733700
C	-0.57063300	5.51222800	2.87343000
C	0.13293700	4.67067800	3.73581700
H	-0.64115700	1.68812700	2.30614100
H	-1.82062900	5.65380400	1.13633600
H	0.65204800	2.62092700	4.17451500
H	-0.55513500	6.58818100	3.02597800
H	0.69636600	5.08373500	4.56811800
N	-2.42243500	-0.83816400	-0.30552300
C	-2.90527100	-1.81290600	-1.30741800
C	-2.96757600	-0.94738700	-2.64801100
N	-3.26945900	0.42286600	-2.17669000
H	-2.08688800	-1.14398300	0.62587200
C	-3.80142200	1.42172900	-3.09447700
H	-4.63657400	0.99522300	-3.66351300
H	-3.04301600	1.78035800	-3.79833000
H	-4.16596000	2.28066300	-2.52748800
H	-3.84956800	-1.27091100	-3.20453200
C	-1.76790600	-1.04808500	-3.64250900
C	-0.60954500	-0.08783300	-3.31420800
H	-0.91499300	0.94665700	-3.52382100
C	0.68628800	-0.39320500	-4.07264400
C	-1.92405000	-2.99526700	-1.40204900
C	-0.59141900	-2.86660200	-0.98797200
C	-2.33978200	-4.21845900	-1.94905200
C	0.30068800	-3.93273100	-1.11683900
C	-1.44587300	-5.28040200	-2.08426800
C	-0.12144400	-5.14291400	-1.66604100
H	-0.23297600	-1.93502700	-0.56781400
H	-3.37071000	-4.35146300	-2.26132400
H	1.32620100	-3.80349800	-0.78430600
H	-1.79200100	-6.22019400	-2.50693900
H	0.57335400	-5.97303000	-1.76276700
C	-4.30899300	-2.33034800	-0.87913100
C	-4.52015400	-2.60127800	0.48427200
C	-5.35991300	-2.59596500	-1.76769500
C	-5.74150600	-3.09431900	0.93910000
C	-6.58839000	-3.08540300	-1.31109500
C	-6.78745200	-3.33259300	0.04475300
H	-3.71889400	-2.43472800	1.19787900
H	-5.24313100	-2.44251200	-2.83587600
H	-5.87025000	-3.30129400	1.99819900
H	-7.38518300	-3.27568300	-2.02565800
H	-7.74073300	-3.71448700	0.40019700
H	-3.31630300	-0.15228700	4.66900400
H	-2.85407000	1.54454000	4.85202600
H	-4.56369900	1.08150400	4.90848900
H	1.47645500	0.30005300	-3.76733600
H	1.03570900	-1.40535500	-3.84302500
H	0.56518600	-0.30551600	-5.15918300
C	4.08749100	1.51207700	2.68093700
C	4.04243500	2.81649200	3.20047100
C	5.28019600	0.77922700	2.82127100
C	5.14267500	3.36674100	3.85949900
H	3.12950500	3.39827700	3.09771000
C	6.37953100	1.33245400	3.47423400
H	5.34745200	-0.20960900	2.37978700
C	6.31601600	2.62565900	4.00151700
H	5.08183600	4.37570500	4.26011100
H	7.29586200	0.75429800	3.56594300
H	7.17595100	3.05245000	4.51129400
H	-0.38362900	-0.12739800	-2.24576800
C	-2.25553700	-0.90106100	-5.09833700
H	-2.61999400	0.10893500	-5.31965700
H	-1.44489600	-1.11452500	-5.80178300
H	-3.06765800	-1.60538200	-5.31878300
H	-1.38427300	-2.06982300	-5.55251900
H	-2.72900800	0.67858200	2.48087200
C	-5.36479800	2.95808600	2.82057000
H	-6.15333000	2.33455400	2.38479400
H	-5.49419200	2.93379900	3.90696600
H	-5.53938300	3.99217800	2.49759700

- **1da**-*SR* (MeMe)



B3LYP/6-31G*

E = –3797.8409

Zero-point correction = 1.341047 (Hartree/Particle)

Thermal correction to Energy = 1.419926

Thermal correction to Enthalpy = 1.420870

Thermal correction to Gibbs Free Energy = 1.216860

Sum of electronic and zero-point Energies = –3796.499853

Sum of electronic and thermal Energies = –3796.420974

Sum of electronic and thermal Enthalpies = –3796.420030

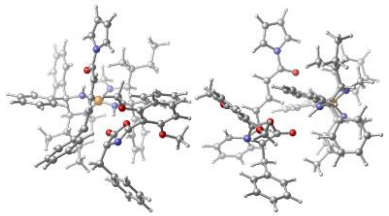
Sum of electronic and thermal Free Energies = –3796.624040

0 1

O	-1.09354300	0.31315400	-1.20223900
C	-2.23254200	0.42216200	-0.73480000
C	-3.17393900	1.52238200	-0.71770000
O	-2.78563700	-0.56271400	0.05014700
N	-4.34428700	1.06238700	-0.07698100
C	-4.05614000	-0.09927000	0.39226400
C	-4.91417800	-1.02816200	1.14779900
C	-5.27253100	-2.26281300	0.56426100
C	-5.41025200	-0.71323900	2.42834800
C	-6.08321100	-3.17452400	1.25187100
C	-6.22905800	-1.62024200	3.11648300
C	-6.54918200	-2.83749800	2.52081500
O	-4.79800300	-2.46537500	-0.69259700
C	-5.13677800	-3.66427200	-1.37053100
H	-6.22363800	-3.76628500	-1.48786700
H	-4.73798900	-4.54463300	-0.85197600
H	-4.67069700	-3.58669500	-2.35393400
O	-5.03469100	0.49201200	2.94192800
C	-5.47561300	0.84339800	4.24502200
H	-5.11648700	0.13010700	4.99796400
H	-5.04789900	1.82705300	4.44561500
H	-6.57008800	0.90622400	4.29711900
H	-6.35955800	-4.12186500	0.80555200
H	-6.60980300	-1.38798800	4.10301800
H	-7.18214900	-3.53922300	3.05764300
C	-3.29793700	2.46850400	-1.89184700
H	-2.32692700	2.94387700	-2.07325700
H	-3.99881300	3.26230500	-1.61477800
C	-3.76503700	1.78844500	-3.16895900
C	-2.87973800	1.56881800	-4.23180600
C	-5.09305700	1.35847800	-3.30595900
C	-3.30765600	0.94290200	-5.40525900
C	-5.52261700	0.73100100	-4.47502600
C	-4.63202500	0.52160000	-5.53112900
H	-1.84612800	1.89407200	-4.13795500
H	-5.78458100	1.51100600	-2.48167600
H	-2.60771000	0.79449900	-6.22477700
H	-6.55702400	0.40772100	-4.56380100
H	-4.96916600	0.03798500	-6.44454300

C	-2.17566300	2.64727900	0.77836100
C	-1.93440700	1.89449000	1.96301400
H	-1.30270700	2.78222100	0.13907100
H	-2.67616800	1.92399300	2.75637200
C	-0.75065100	1.19862500	2.17440000
H	-0.02865500	1.20697600	1.35875600
C	-0.36822300	0.52053400	3.33553400
H	-1.07753700	0.44396400	4.15218300
C	0.94512900	0.03297800	3.52714300
O	1.93413300	0.19253200	2.76619400
N	1.19879900	-0.69836100	4.73570200
C	2.47087100	-0.94479000	5.22399100
C	0.27936900	-1.28807300	5.59300300
C	2.36027400	-1.67233900	6.38236200
C	0.96645200	-1.89579100	6.61350900
H	3.32688600	-0.55453700	4.69878400
H	-0.77653600	-1.26278400	5.37660400
H	3.18282500	-2.00588300	7.00145100
H	0.52277800	-2.44906200	7.43109100
H	0.37830400	-0.72719700	-0.91746200
N	1.25137700	-1.27280900	-0.85904100
P	2.72885200	-0.55563200	-0.93548100
N	3.54277800	-2.00301000	-0.96273200
C	2.68001600	-3.19084000	-0.76584100
C	1.26657000	-2.69625500	-1.28403700
C	4.99149900	-2.15660400	-0.99915700
H	5.25424100	-2.98211700	-1.67221100
H	5.41504900	-2.36012200	-0.00929900
H	5.44937400	-1.24019600	-1.37474100
H	3.04304200	-3.95209400	-1.46174100
C	2.89201100	-3.82476600	0.64613900
H	3.98861600	-3.92199000	0.68746900
C	2.36013100	-5.27271000	0.75688900
H	2.47471300	-5.78108500	-0.21171200
C	3.08306100	-6.10161100	1.82707800
C	0.08204100	-3.47002100	-0.68140300
C	-0.26786500	-4.72060600	-1.21531200
C	-0.66170100	-2.97215900	0.39333400
C	-1.29930400	-5.47283200	-0.65772900
C	-1.70578700	-3.71923400	0.94367800
C	-2.01944400	-4.97711500	0.43206700
H	0.27100500	-5.11339300	-2.07182900
H	-0.43991800	-1.99659400	0.80770400
H	-1.54229400	-6.44494600	-1.07930900
H	-2.27682300	-3.30271400	1.76771100
H	-2.82371700	-5.56205900	0.87100400
C	1.15185200	-2.75499500	-2.83895200
C	0.16758800	-1.95348100	-3.44531300
C	1.92622800	-3.57604900	-3.66922700
C	-0.02165400	-1.96294400	-4.82542100
C	1.74120900	-3.58238000	-5.05670100
C	0.76906900	-2.77544600	-5.64196300
H	-0.46306300	-1.31306400	-2.83602600
H	2.68493900	-4.23400200	-3.25834700
H	-0.79676800	-1.33498600	-5.25703400
H	2.36192700	-4.22727400	-5.67363200
H	0.62375200	-2.78297600	-6.71893000
N	2.77270800	0.66381900	0.16570300
C	3.78234400	1.69945200	-0.16484400
C	3.66454200	1.77890600	-1.74371400
N	3.41152600	0.37037200	-2.13291000
H	2.42589200	0.52301800	1.13163300
C	3.67924000	-0.07491700	-3.49358700
H	2.95153600	0.32133500	-4.21115600
H	3.63054900	-1.16448800	-3.53678000
H	4.68384000	0.24393400	-3.79953700
H	4.64873200	2.03235300	-2.14750000
C	2.67831900	2.75750400	-2.45393700
H	2.72184500	2.41482300	-3.49981200
C	3.18680000	4.21814100	-2.48858300
H	4.28295200	4.22037300	-2.57851300
C	2.60596600	5.03682900	-3.64927200
C	3.51070300	3.02499600	0.56916700
C	4.49008200	4.03137600	0.55730700
C	2.33488400	3.25629800	1.29026700
C	4.28354600	5.24224600	1.21458400
C	2.12859800	4.46762300	1.95583500
C	3.09713900	5.46825600	1.91621100
H	5.42830100	3.86878700	0.03612300
H	1.57531900	2.49054900	1.35762800
H	5.05644500	6.00584900	1.18563200
H	1.20593400	4.61478100	2.51017500
H	2.93780300	6.40893200	2.43634600
C	5.18688200	1.19975100	0.29634700
C	6.36788000	1.34700900	-0.44267400
C	5.27801400	0.60810000	1.56865200
C	7.59489700	0.89713100	0.05740600
C	6.50001000	0.16334200	2.06912100
C	7.66708400	0.29984500	1.31322200
H	6.36179100	1.81810900	-1.42052400
H	4.38478400	0.49730300	2.17678100
H	8.49267600	1.02036000	-0.54294200
H	6.53928300	-0.28846000	3.05681300
H	8.61969400	-0.04865800	1.70279900
H	3.01829100	6.05216700	-3.65151800
H	2.84171900	4.57993900	-4.61894300
H	1.51653400	5.12764400	-3.58143100
H	2.69549100	-7.12649000	1.85082500
H	4.16126400	-6.15825100	1.62886700
H	2.95074700	-5.67868400	2.82854100
C	-3.04696100	3.84849200	0.85740800
C	-2.60269800	5.06336200	0.30933400
C	-4.29849600	3.82456800	1.49976100
C	-3.36936100	6.22444000	0.41484200
H	-1.63719700	5.09893700	-0.19031600
C	-5.06559000	4.98326200	1.59808000
H	-4.67904200	2.88315700	1.88170200
C	-4.60469500	6.18941400	1.06220300
H	-3.00036800	7.15478800	-0.00975400
H	-6.03455700	4.94453900	2.08998900
H	-5.20671300	7.09076600	1.14356700
H	1.28779600	-5.26372600	0.97086000
C	2.48496800	-2.95917400	1.84331000
H	2.87270900	-3.38915200	2.77266700
H	2.87674600	-1.94154200	1.78349000
H	1.40015200	-2.88909400	1.94395600
C	1.21068700	2.66037600	-2.02266000
H	0.58327700	3.24887500	-2.70170800
H	0.82692400	1.63852700	-2.04633600
H	1.06148100	3.05136500	-1.01290900
H	2.95983900	4.71894300	-1.54290500

- **1da**-*SR* (MeH)



B3LYP/6-31G*

E = –3797.841961

Zero-point correction = 1.342118 (Hartree/Particle)

Thermal correction to Energy = 1.420544

Thermal correction to Enthalpy = 1.421488

Thermal correction to Gibbs Free Energy = 1.219985

Sum of electronic and zero-point Energies = –3796.499844

Sum of electronic and thermal Energies = –3796.421418

Sum of electronic and thermal Enthalpies = –3796.420473

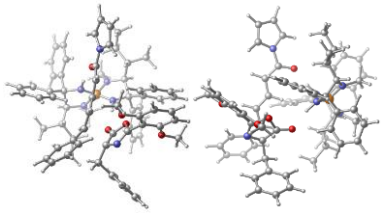
Sum of electronic and thermal Free Energies = –3796.621976

0 1

O	-1.08544200	0.30184900	-1.33242800
C	-2.18889800	0.34187200	-0.77332500
C	-3.23068800	1.35106400	-0.72897500
O	-2.56973300	-0.62637600	0.13038000
N	-4.27632000	0.84463600	0.06990300
C	-3.83488600	-0.24864300	0.57995400
C	-4.53992900	-1.19769100	1.46010100
C	-4.88487100	-2.47017900	0.95605000
C	-4.92248500	-0.86078800	2.77328800
C	-5.56150000	-3.40053600	1.75499800
C	-5.60458900	-1.78806200	3.57480000
C	-5.90907300	-3.04386200	3.05628900
O	-4.53538200	-2.69121200	-0.33814000
C	-4.91274700	-3.91267600	-0.95303900
H	-6.00123800	-4.05325600	-0.93054000
H	-4.42001200	-4.76963900	-0.47792300
H	-4.57776000	-3.83528500	-1.98846600
O	-4.58341700	0.38797400	3.19861500
C	-4.91897300	0.76858600	4.52434900
H	-4.43800200	0.11705100	5.26533800
H	-4.54544400	1.78705100	4.64277300
H	-6.00481300	0.75962100	4.68422600
H	-5.82558800	-4.37794600	1.37032600
H	-5.89472800	-1.54025500	4.58801900
H	-6.43640800	-3.76063600	3.68032000
C	-3.59110800	2.18436500	-1.93962200
H	-2.68360200	2.65091500	-2.33938700
H	-4.25005800	2.99458500	-1.61188700
C	-4.27803200	1.38541600	-3.03818400
C	-3.61640300	1.08298000	-4.23451500
C	-5.59540400	0.93230400	-2.87147900
C	-4.25030900	0.35109700	-5.24144900
C	-6.23039700	0.20074100	-3.87442200
C	-5.56087200	-0.09277100	-5.06529600
H	-2.59572000	1.42739000	-4.37961300
H	-6.11340100	1.14775200	-1.94129900
H	-3.71999700	0.13259100	-6.16565700
H	-7.25289800	-0.13898400	-3.72733300
H	-6.05820200	-0.65936500	-5.84866600
C	-2.18969000	2.64386500	0.59491100
C	-1.89182900	2.01466200	1.83791500
H	-1.34838400	2.73551700	-0.09325800
H	-2.59948200	2.12936500	2.65350300
C	-0.69545100	1.35358500	2.08454400
H	-0.00469000	1.26096600	1.24833400
C	-0.26272000	0.82732200	3.30446500
H	-0.94254400	0.83833500	4.14925200
C	1.06732600	0.39311700	3.50662400
O	2.03048100	0.49387800	2.70338600
N	1.37342100	-0.20098200	4.77601400
C	2.66379400	-0.36692300	5.24982700
C	0.49226500	-0.72091600	5.71457500
C	2.60233900	-0.97446400	6.47881500
C	1.22121500	-1.20475500	6.77163700
H	3.49536300	-0.01475000	4.66215200
H	-0.56889900	-0.74265400	5.52534900
H	3.44916500	-1.22425500	7.10459900
H	0.81369400	-1.68151700	7.65369400
H	0.43913500	-0.75217300	-0.94317400
N	1.33249100	-1.25054600	-0.81407400
P	2.76930000	-0.45396000	-0.92659200
N	3.67015900	-1.84117900	-0.80252000
C	2.87265800	-3.06777300	-0.56748000
C	1.44459300	-2.69257000	-1.15008500
C	5.12599800	-1.90485400	-0.75840200
H	5.47722400	-2.72949000	-1.39144500
H	5.50387600	-2.05652700	0.25858900
H	5.55020000	-0.97213000	-1.13219400
H	3.30235200	-3.83847900	-1.21319100
C	3.08398400	-3.61634400	0.88067500
H	4.18295900	-3.65471700	0.94598800
C	2.62855400	-5.08320000	1.05781900
H	2.79527200	-5.63451100	0.12088400
C	3.36863400	-5.81131300	2.18798800
C	0.29962000	-3.50512300	-0.52360900
C	0.02487200	-4.79756400	-0.99854900
C	-0.47050700	-3.00472200	0.53081900
C	-0.95432900	-5.58645600	-0.39870100
C	-1.46006800	-3.79046800	1.12564900
C	-1.69531300	-5.08871600	0.67578000
H	0.58294000	-5.19655000	-1.83940100
H	-0.30962600	-1.99792500	0.89451400
H	-1.13834900	-6.58998100	-0.77395000
H	-2.04972200	-3.37513100	1.93691600
H	-2.45595700	-5.70331000	1.15051600
C	1.37898900	-2.85664500	-2.70033400
C	0.39760400	-2.12494700	-3.39394400
C	2.19362000	-3.72010800	-3.44514100
C	0.25458500	-2.23940100	-4.77537200
C	2.05293800	-3.83336400	-4.83289200
C	1.08579600	-3.09174600	-5.50587700
H	-0.26917900	-1.45789100	-2.85515500
H	2.94887500	-4.33260700	-2.96350100
H	-0.51679100	-1.66216800	-5.27814100
H	2.70447300	-4.50956300	-5.38055800
H	0.97514100	-3.18030000	-6.58324300
N	2.70989100	0.86328600	0.05528800
C	3.62452400	1.95004400	-0.38708800
C	3.43718800	1.86326900	-1.96339000
N	3.40257400	0.40027300	-2.20116300
H	2.38564300	0.79024800	1.03911100
C	3.99740300	-0.16608500	-3.40583100
H	3.46532900	0.15172400	-4.30657300
H	3.95415600	-1.25519800	-3.35673700
H	5.04815000	0.14206500	-3.49055200
H	4.33210100	2.23806600	-2.46731200
C	2.20955200	2.64433400	-2.53727000
H	1.43450900	2.66096700	-1.76194100
C	1.57795900	1.97244100	-3.77678100

H	1.45070700	0.90199500	-3.58946800
C	0.20371400	2.54235700	-4.14636800
C	3.21620500	3.29702300	0.23451500
C	4.15246700	4.33771500	0.34804100
C	1.91347600	3.53121900	0.68784400
C	3.78738500	5.57519800	0.87700100
C	1.54725800	4.76622100	1.22620500
C	2.48155400	5.79628100	1.31873300
H	5.17714000	4.18361000	0.02653300
H	1.17566100	2.74350400	0.63583900
H	4.53105100	6.36427300	0.95217300
H	0.52930300	4.90903400	1.57796000
H	2.20013600	6.75757700	1.74000300
C	5.07384000	1.61396400	0.05713100
C	6.20792200	1.81631400	-0.74028300
C	5.26329100	1.12082100	1.36005500
C	7.48842000	1.51238100	-0.26492500
C	6.53896200	0.82268300	1.83585600
C	7.65983600	1.01088000	1.02336200
H	6.11870300	2.22285600	-1.74262000
H	4.40506900	0.96938300	2.00891300
H	8.34931200	1.67466400	-0.90842700
H	6.65620100	0.44425100	2.84791000
H	8.65399600	0.77608000	1.39381100
H	-0.19144200	2.03740300	-5.03555400
H	-0.50344700	2.37419900	-3.32694100
H	0.23323500	3.61464400	-4.36719200
H	3.03692200	-6.85335400	2.26041400
H	4.45296200	-5.81848900	2.01710800
H	3.18850100	-5.34212200	3.16107800
C	-3.08764000	3.82733100	0.60379300
C	-2.70882000	4.99526400	-0.07889500
C	-4.30645200	3.83099800	1.30679000
C	-3.50696900	6.13947200	-0.04578800
H	-1.77072600	5.00795800	-0.62944300
C	-5.10550300	4.97171900	1.33262400
H	-4.63592800	2.92089500	1.79731500
C	-4.70911100	6.13283700	0.66217800
H	-3.18887400	7.03428000	-0.57501500
H	-6.04823000	4.95391300	1.87408500
H	-5.33559100	7.02068600	0.68698700
H	1.55245500	-5.12359500	1.24728600
C	2.61370800	-2.71101900	2.02436700
H	3.03460600	-3.05303600	2.97576900
H	2.92634200	-1.67205800	1.89900100
H	1.52693300	-2.71670300	2.12863100
C	2.61572500	4.09176500	-2.86891900
H	3.34272100	4.10286900	-3.69300100
H	1.74960400	4.67942200	-3.18737800
H	3.06307300	4.60793700	-2.01764600
H	2.25821600	2.07006400	-4.63603100

● **1da**-*SR* (HH)



B3LYP/6-31G*

E = –3797.844291

Zero-point correction = 1.342160 (Hartree/Particle)

Thermal correction to Energy = 1.420517

Thermal correction to Enthalpy = 1.421461

Thermal correction to Gibbs Free Energy = 1.220179

Sum of electronic and zero-point Energies = –3796.502130

Sum of electronic and thermal Energies = –3796.423774

Sum of electronic and thermal Enthalpies = –3796.422830

Sum of electronic and thermal Free Energies = –3796.624112

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

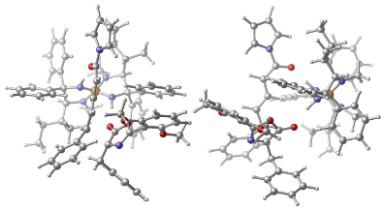
E = –3799.041975

G = –3797.787147

0 1

O	-1.16028000	0.35359200	-1.38721600
C	-2.24198300	0.36681600	-0.78398700
C	-3.24448800	1.39668600	-0.60511500
O	-2.62155600	-0.67177300	0.03400900
N	-4.27759900	0.85222300	0.18175900
C	-3.85492600	-0.29841200	0.56975900
C	-4.54810400	-1.29710100	1.40127800
C	-4.91395900	-2.53464700	0.82915000
C	-4.89713100	-1.03966100	2.74212300
C	-5.57923100	-3.50764300	1.58569300
C	-5.56667700	-2.01043800	3.50131500
C	-5.89326100	-3.23002100	2.91418800
O	-4.60072900	-2.67896600	-0.48482900
C	-4.99892200	-3.86127000	-1.15917100
H	-6.08810400	-3.99509700	-1.12507500
H	-4.50556500	-4.74700800	-0.74088900
H	-4.68137700	-3.72941800	-2.19468100
O	-4.53797100	0.17776600	3.23696800
C	-4.84424200	0.47861300	4.58963800
H	-4.35325700	-0.21918300	5.28038900
H	-4.46140800	1.48592100	4.76213900
H	-5.92672700	0.46621900	4.77096100
H	-5.86070400	-4.45743500	1.14793300
H	-5.83076000	-1.82370900	4.53455300
H	-6.41187700	-3.98025800	3.50537500
C	-3.60254400	2.36353100	-1.71080100
H	-2.68978600	2.85361600	-2.06710200
H	-4.24611900	3.14251000	-1.29159500
C	-4.30611500	1.69246400	-2.87982400
C	-3.59328000	1.29543900	-4.01865400
C	-5.68436300	1.44084500	-2.83261700
C	-4.23979300	0.67119000	-5.08707700
C	-6.33308600	0.81653900	-3.89799600
C	-5.61358700	0.43125800	-5.03157900
H	-2.52151900	1.47343300	-4.06102200
H	-6.24448500	1.73026700	-1.94739600
H	-3.67063000	0.37655700	-5.96594200
H	-7.40350700	0.63298500	-3.84429100
H	-6.11996900	-0.05026200	-5.86443300
C	-2.08007600	2.51216500	0.79265400
C	-1.78380400	1.75994000	1.96449800
H	-1.26082500	2.60815400	0.07899500
H	-2.44698800	1.86289700	2.81848900
C	-0.64340600	0.97773400	2.10353500
H	0.00447500	0.88772200	1.23260400
C	-0.21941700	0.33066400	3.26723900
H	-0.85600800	0.37149400	4.14441600
C	1.05656600	-0.26502200	3.39039400
O	1.99167300	-0.26628500	2.54733600
N	1.33522600	-0.92040500	4.63763000
C	2.61529700	-1.14962100	5.11126700
C	0.42952900	-1.42509700	5.55967100
C	2.52348200	-1.78431600	6.32565100
C	1.13351600	-1.96626700	6.60673000
H	3.46300400	-0.80923800	4.53969300
H	-0.63048500	-1.39928200	5.36289400
H	3.35663200	-2.08196700	6.94870900
H	0.70309100	-2.45067500	7.47355700
H	0.30013600	-0.70661700	-1.03320900
N	1.21112300	-1.19100400	-0.99243200
P	2.62618100	-0.36610100	-1.08839000
N	3.55254800	-1.73874100	-1.15927200
C	2.78595600	-2.97908900	-0.88087900
C	1.32362100	-2.61313600	-1.40639300
C	4.95672100	-1.80764500	-1.55079900
H	5.07261500	-2.47029600	-2.41870500
H	5.58742600	-2.17645500	-0.73959800
H	5.31275700	-0.81238400	-1.81848500
H	3.21926700	-3.75088600	-1.52180700
C	2.88140900	-3.49977800	0.58999900
H	2.10974900	-2.99648200	1.18295500
C	4.23162000	-3.17471900	1.26612000
H	4.41481800	-2.09778500	1.19940700
C	4.30112700	-3.58290100	2.74297800
C	0.19275200	-3.42493200	-0.74925700
C	-0.28406700	-4.60334000	-1.34405600
C	-0.35956700	-3.02637200	0.47577400
C	-1.25230300	-5.38270000	-0.71112400
C	-1.33494900	-3.80122400	1.10388700
C	-1.77680100	-4.98799300	0.52100900
H	0.10532000	-4.92175800	-2.30519800
H	-0.03501600	-2.10420500	0.94369300
H	-1.59636400	-6.29804000	-1.18622000
H	-1.75357100	-3.46443000	2.04739700
H	-2.53062800	-5.59327800	1.01779400
C	1.22261800	-2.71622000	-2.95333500
C	0.29463900	-1.89737000	-3.62037000
C	1.96680300	-3.62127500	-3.72334200
C	0.13802400	-1.96711000	-5.00405300
C	1.81440500	-3.68778400	-5.11214200
C	0.90254000	-2.85799200	-5.76039400
H	-0.31977900	-1.20138400	-3.05695400
H	2.66955700	-4.30335100	-3.25557300
H	-0.59107800	-1.32350800	-5.48922000
H	2.41070200	-4.39669500	-5.68092600
H	0.78237600	-2.90953400	-6.83919600
N	2.64869100	0.80163600	0.06819100
C	3.56879200	1.91539500	-0.26913400
C	3.28037100	2.07157100	-1.82974800
N	3.13589900	0.66443600	-2.28471800
H	2.39594800	0.55389200	1.04354800
C	3.53167300	0.26711200	-3.63170100
H	2.85831000	0.67156500	-4.39110800
H	3.50874200	-0.82108800	-3.71342500
H	4.55183500	0.61312200	-3.84413700
H	4.17138700	2.45863800	-2.33137600
C	2.09421800	3.02447300	-2.18930000
H	1.39173200	3.01873500	-1.34796700
C	1.28839400	2.58435200	-3.42968300
H	0.96099100	1.54821900	-3.29500700
C	0.05015600	3.44966700	-3.69251000
C	3.24064600	3.15509500	0.58448200
C	4.21032800	4.14463000	0.81500700
C	1.97488800	3.32906200	1.15731500
C	3.91345400	5.27634300	1.57399600
C	1.67731900	4.45769100	1.92340200
C	2.64427900	5.43937800	2.13210600
H	5.21038900	4.03088800	0.41008100
H	1.21225000	2.57461600	1.02209200
H	4.68288900	6.02651000	1.73697100
H	0.68596000	4.55473700	2.35707900
H	2.41691300	6.31689900	2.73130300
C	5.03564400	1.49014000	0.01586000
C	6.12402900	1.84531400	-0.79259100
C	5.29768300	0.75652100	1.18550800
C	7.42731200	1.46060400	-0.46007100
C	6.59643300	0.37643200	1.52047300
C	7.66947200	0.72133600	0.69544500
H	5.97982200	2.43709000	-1.69113600
H	4.47761300	0.47822900	1.84136800
H	8.25056600	1.74643900	-1.10973200
H	6.76849500	-0.19006900	2.43176500
H	8.68141300	0.42259600	0.95498000
H	-0.54101900	3.03457500	-4.51628400
H	-0.59634600	3.48397600	-2.80823400
H	0.30811900	4.47904900	-3.96251100
H	5.24899200	-3.25030900	3.18296900
H	3.49112200	-3.12389000	3.31908900
H	4.24517700	-4.66790800	2.87897300
C	-2.90364200	3.73962300	0.93554300
C	-2.46394700	4.94571700	0.36527100
C	-4.11103800	3.74331100	1.65829200
C	-3.19087700	6.12559600	0.52839600
H	-1.53328700	4.95942400	-0.19769200
C	-4.83933500	4.92071200	1.81333200
H	-4.48911400	2.80750200	2.05756600
C	-4.38162600	6.11830700	1.25548900
H	-2.82629900	7.04914000	0.08555400
H	-5.77474200	4.90379200	2.36736800
H	-4.95260600	7.03458900	1.38110500
H	5.04608500	-3.67609400	0.72215600
C	2.63613700	-5.02004500	0.61819900
H	2.53675800	-5.38122400	1.64555200
H	1.73021000	-5.31215300	0.08537400
H	3.48404000	-5.54969800	0.16065900
C	2.63214800	4.45566400	-2.37287200
H	3.23594300	4.52162100	-3.28891600
H	1.81577200	5.17808300	-2.46176900
H	3.25527200	4.77504600	-1.53467600
H	1.93152500	2.61139400	-4.32097000

- **1da**-*SR* (HMe)



B3LYP/6-31G*

E = –3797.843512

Zero-point correction = 1.341498 (Hartree/Particle)

Thermal correction to Energy = 1.420139

Thermal correction to Enthalpy = 1.421083

Thermal correction to Gibbs Free Energy = 1.218081

Sum of electronic and zero-point Energies = –3796.502015

Sum of electronic and thermal Energies = –3796.423373

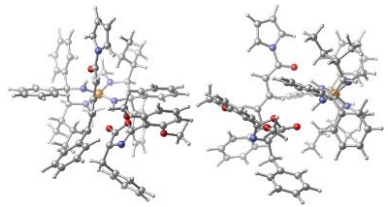
Sum of electronic and thermal Enthalpies = –3796.422429

Sum of electronic and thermal Free Energies = –3796.625431

0 1

O	1.17575100	0.35667700	1.31638000
C	2.28439400	0.43003400	0.77171600
C	3.20894300	1.53015200	0.60154500
O	2.79842900	-0.61422600	0.04197300
N	4.33909400	1.02942800	-0.07524100
C	4.03606500	-0.17085300	-0.42526800
C	4.85423500	-1.14844500	-1.16181200
C	5.23722200	-2.34925300	-0.52523800
C	5.29315800	-0.91034900	-2.47991900
C	6.01335100	-3.30287400	-1.19572500
C	6.07543000	-1.86067700	-3.15179100
C	6.41979900	-3.04331700	-2.50253800
O	4.82461900	-2.47784200	0.76277800
C	5.20026100	-3.63480900	1.49113200
H	6.29193300	-3.72678300	1.56493200
H	4.78429800	-4.54447300	1.04109700
H	4.77839200	-3.50344400	2.48873100
O	4.90145300	0.26652100	-3.04489600
C	5.28467500	0.53822900	-4.38435200
H	4.88873400	-0.21454100	-5.07825200
H	4.85320600	1.51180400	-4.62289100
H	6.37601100	0.58977800	-4.48941600
H	6.30905100	-4.22359800	-0.70807700
H	6.41042800	-1.68777400	-4.16668300
H	7.02508500	-3.77832100	-3.02662500
C	3.39086400	2.58204000	1.67302700
H	2.42542600	3.06094100	1.87391100
H	4.05956900	3.35492100	1.28180400
C	3.95038600	2.02128600	2.97076900
C	3.12474700	1.82799700	4.08554200
C	5.30432200	1.67027000	3.07262700
C	3.63640500	1.30480900	5.27513200
C	5.81773900	1.14573000	4.25847600
C	4.98605600	0.96230100	5.36611800
H	2.07139600	2.08976100	4.01713400
H	5.94976600	1.80081600	2.20806700
H	2.98120600	1.17182800	6.13330500
H	6.87087600	0.88196600	4.31948400
H	5.38795000	0.55839100	6.29200000
C	2.08237600	2.49703000	-0.93065500
C	1.84231500	1.64971800	-2.04886200
H	1.23352600	2.62763600	-0.25974700
H	2.53719900	1.68877900	-2.88307300
C	0.71279500	0.84753900	-2.15851900
H	0.03663500	0.82912400	-1.30442900
C	0.33101700	0.09436000	-3.27247800
H	0.98934300	0.07183600	-4.13406000
C	-0.92865700	-0.53950400	-3.37061900
O	-1.87657800	-0.50064700	-2.54274300
N	-1.17242900	-1.29522700	-4.56745600
C	-2.44014000	-1.60371200	-5.02939900
C	-0.24287400	-1.83686700	-5.44392000
C	-2.31727600	-2.32482400	-6.19166500
C	-0.91979500	-2.47956100	-6.45058300
H	-3.30364500	-1.24965100	-4.49078500
H	0.81440400	-1.75951200	-5.24602800
H	-3.13487500	-2.69708100	-6.79488600
H	-0.46612800	-3.01246900	-7.27609700
H	-0.28601700	-0.67473400	1.03046400
N	-1.17827700	-1.19226800	1.05110600
P	-2.63626800	-0.44718500	1.08267300
N	-3.48183700	-1.86544800	1.23475700
C	-2.64672900	-3.07422100	1.02132300
C	-1.20791200	-2.60088400	1.52271700
C	-4.86455600	-1.99044900	1.68324100
H	-4.91113100	-2.61659800	2.58411400
H	-5.50447400	-2.43111700	0.91522900
H	-5.26124700	-1.00276100	1.92221500
H	-3.03590100	-3.83529800	1.70207200
C	-2.72241000	-3.67476600	-0.41975300
H	-1.99795700	-3.14973600	-1.05233900
C	-4.10555500	-3.47594500	-1.07758900
H	-4.36368200	-2.41267900	-1.05396200
C	-4.17923200	-3.95445300	-2.53281700
C	-0.03131400	-3.36751100	0.89305300
C	0.52660800	-4.48153900	1.53904000
C	0.48785200	-2.99038300	-0.35282200
C	1.54734100	-5.21853000	0.93870300
C	1.51586000	-3.72162100	-0.94805400
C	2.04359400	-4.84382300	-0.31135800
H	0.16024800	-4.78194600	2.51513400
H	0.09675900	-2.11807600	-0.86355100
H	1.95511100	-6.08488100	1.45366400
H	1.90615000	-3.39970800	-1.90878500
H	2.84030000	-5.41485900	-0.78102800
C	-1.08926200	-2.62654000	3.07154000
C	-0.16538100	-1.75793700	3.67985400
C	-1.80979400	-3.49851600	3.89930600
C	0.01189500	-1.74956800	5.06224200
C	-1.63747600	-3.48594000	5.28788900
C	-0.72916100	-2.60928900	5.87654800
H	0.42830200	-1.08327800	3.07029000
H	-2.50917200	-4.21447900	3.48028000
H	0.73950900	-1.07059700	5.49928600
H	-2.21549100	-4.17068300	5.90328000
H	-0.59338000	-2.60085400	6.95475400
N	-2.69499900	0.65111300	-0.13971800
C	-3.69368800	1.71576400	0.10358400
C	-3.53225900	1.96717400	1.66564300
N	-3.24778200	0.61236000	2.20254800
H	-2.40545400	0.35712200	-1.08955500
C	-3.39494700	0.33332500	3.62495800
H	-2.61981300	0.82255100	4.22556400
H	-3.31669700	-0.74208700	3.79714300
H	-4.37828500	0.67274500	3.97472100
H	-4.50984500	2.25131900	2.06509400
C	-2.54468800	3.02973500	2.23855800
H	-2.56758000	2.81398300	3.31819200
C	-3.07052400	4.47934200	2.11035400
H	-4.16563700	4.48012300	2.21269900
C	-2.48595500	5.43196800	3.16172200
C	-3.42664400	2.94454200	-0.78587200
C	-4.40331500	3.94517500	-0.91248400
C	-2.24108400	3.08439400	-1.51582500
C	-4.18407700	5.06491100	-1.71251800
C	-2.02252800	4.20187200	-2.32535800
C	-2.98914200	5.20078400	-2.42255400
H	-5.34879100	3.85057300	-0.38826800
H	-1.47670400	2.32071900	-1.46718100
H	-4.95508200	5.82724200	-1.78812300
H	-1.09130000	4.27811900	-2.87959800
H	-2.82102000	6.06962700	-3.05307600
C	-5.11667000	1.18080900	-0.24977200
C	-6.27965900	1.49668000	0.46611000
C	-5.25236700	0.38369000	-1.39947300
C	-7.53026700	1.01554500	0.06496000
C	-6.49864100	-0.09300800	-1.80283700
C	-7.64620400	0.21562300	-1.06913500
H	-6.23982000	2.13251900	1.34489600
H	-4.37579000	0.13114100	-1.98869400
H	-8.41223100	1.27407800	0.64533600
H	-6.57062200	-0.70681600	-2.69674400
H	-8.61727200	-0.15818000	-1.38202500
H	-2.90891000	6.43699900	3.05253000
H	-2.70613100	5.08720900	4.18019300
H	-1.39827900	5.52415000	3.07059900
H	-5.15491900	-3.70123000	-2.96487800
H	-3.41003900	-3.47444700	-3.14731300
H	-4.05835100	-5.03901600	-2.62246600
C	2.88430600	3.73103700	-1.13218100
C	2.39187200	4.96274000	-0.66969400
C	4.11982500	3.71590200	-1.80541300
C	3.09588700	6.14731800	-0.88918600
H	1.43839700	4.99164300	-0.14708400
C	4.82474300	4.89878600	-2.01669900
H	4.53868800	2.76508300	-2.11857000
C	4.31572600	6.12038300	-1.56589500
H	2.69071400	7.08993700	-0.52956500
H	5.78287100	4.86760500	-2.52987800
H	4.86919700	7.04047600	-1.73487700
H	-4.87129300	-4.00535200	-0.49062500
C	-2.37183600	-5.17411400	-0.38008000
H	-2.26537200	-5.57790600	-1.39085600
H	-1.43839300	-5.37625300	0.14694700
H	-3.17236900	-5.73772000	0.12019600
C	-1.08305400	2.89831100	1.79631200
H	-0.44990400	3.55545200	2.40336100
H	-0.68995200	1.88565000	1.91170800
H	-0.95645500	3.19071100	0.75086400
H	-2.85898500	4.86944500	1.11061500

- **1da**-*SR* (EtEt)



B3LYP/6-31G*

E = –3797.846402

Zero-point correction = 1.341305 (Hartree/Particle)

Thermal correction to Energy = 1.420096

Thermal correction to Enthalpy = 1.421040

Thermal correction to Gibbs Free Energy = 1.217907

Sum of electronic and zero-point Energies = –3796.505098

Sum of electronic and thermal Energies = –3796.426306

Sum of electronic and thermal Enthalpies = –3796.425362

Sum of electronic and thermal Free Energies = –3796.628495

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.043497

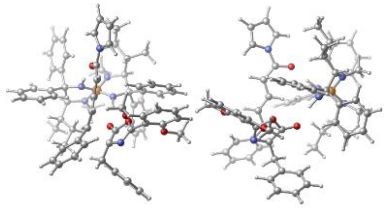
G = –3797.790604

0 1

O	-1.10809100	0.07735600	-1.32757700
C	-2.22601700	0.21451900	-0.81604200
C	-3.28325200	1.18285300	-1.03202400
O	-2.61809900	-0.53554200	0.26818500
N	-4.35000700	0.83880400	-0.17569300
C	-3.90590700	-0.09980800	0.58180100
C	-4.61777300	-0.83577100	1.64088400
C	-4.90227300	-2.20520400	1.45127900
C	-5.06002000	-0.20688000	2.82138300
C	-5.58404100	-2.93957300	2.42966600
C	-5.74657900	-0.93838200	3.80160200
C	-5.99418600	-2.29275800	3.59337000
O	-4.49458300	-2.71919000	0.26168400
C	-4.79681300	-4.07169900	-0.04181300
H	-5.88000200	-4.25141400	-0.03644600
H	-4.30537100	-4.75903700	0.65703300
H	-4.40504000	-4.24113300	-1.04591500
O	-4.77109300	1.11903900	2.94446800
C	-5.16974600	1.79326100	4.12817800
H	-4.69891400	1.35725500	5.01879600
H	-4.83214300	2.82414200	4.00906900
H	-6.26027700	1.78093400	4.25171900
H	-5.80430200	-3.99011000	2.28557600
H	-6.08279500	-0.46461300	4.71523300
H	-6.52606500	-2.85680600	4.35512200
C	-3.60639300	1.71320600	-2.41166800
H	-2.73105900	2.23026800	-2.81989800
H	-4.39795900	2.46177400	-2.30524200
C	-4.04481400	0.63118400	-3.38670100
C	-3.21542300	0.23910700	-4.44496200
C	-5.28841600	-0.00197800	-3.24288300
C	-3.61717800	-0.75290900	-5.34325200
C	-5.69034600	-0.99538700	-4.13533600
C	-4.85732300	-1.37448500	-5.19118100
H	-2.24770100	0.71972400	-4.56828200

H	-5.93409900	0.28413800	-2.41708300
H	-2.96454100	-1.03107500	-6.16799000
H	-6.65941700	-1.47224300	-4.00922600
H	-5.17439800	-2.14399600	-5.89058300
C	-2.30724600	2.76476100	-0.02323400
C	-1.99267000	2.43578200	1.32719000
H	-1.46618300	2.72890800	-0.71622600
H	-2.69320100	2.73111100	2.10317000
C	-0.80165100	1.82799500	1.70291900
H	-0.12470300	1.53079800	0.90262500
C	-0.36432900	1.58889100	3.00916700
H	-1.01777700	1.85692600	3.83206800
C	0.93309300	1.11330900	3.30188400
O	1.86282400	0.87289300	2.48869100
N	1.24753700	0.90570400	4.68861100
C	2.54228300	0.83473400	5.17283900
C	0.37262600	0.73665200	5.75225200
C	2.48991100	0.63309200	6.53035700
C	1.10977000	0.56341600	6.89717800
H	3.37138000	0.96419500	4.49673600
H	-0.69335500	0.70556800	5.59303300
H	3.34263100	0.55037800	7.19145600
H	0.70743800	0.39399800	7.88748500
H	0.38782900	-0.89347500	-0.80971100
N	1.26014700	-1.41787700	-0.64258400
P	2.73450300	-0.75072300	-0.90974900
N	3.55752400	-2.15614600	-0.59437000
C	2.71314700	-3.27286900	-0.12452200
C	1.25240000	-2.90110600	-0.64774000
C	5.00431100	-2.30982000	-0.68828400
H	5.24013200	-3.28461900	-1.13128900
H	5.49537500	-2.23747200	0.28790400
H	5.41528700	-1.52649200	-1.32785900
H	3.04313900	-4.15380200	-0.67921800
C	2.88064400	-3.63892100	1.38367100
H	1.97961400	-4.19853700	1.65533700
C	2.97279100	-2.42336100	2.32517600
H	2.20502700	-1.68832000	2.06826200
C	2.81156700	-2.78231300	3.80782100
C	0.15973000	-3.44224900	0.28986800
C	-0.23055400	-4.78771800	0.19819400
C	-0.40756900	-2.64865100	1.29300700
C	-1.13692800	-5.33188600	1.10690800
C	-1.32860300	-3.18960600	2.19227800
C	-1.68789100	-4.53402200	2.11250400
H	0.17802100	-5.41797100	-0.58574900
H	-0.13782000	-1.60354500	1.38174600
H	-1.41373400	-6.38008000	1.02499800
H	-1.76641700	-2.54827000	2.95114400
H	-2.39652500	-4.95383400	2.82166200
C	0.98780000	-3.40599900	-2.09714300
C	-0.01698400	-2.76253200	-2.84249700
C	1.64368200	-4.49200300	-2.69322700
C	-0.33766900	-3.17811900	-4.13313400
C	1.32736000	-4.90643900	-3.99189100
C	0.33759200	-4.25090500	-4.71947800
H	-0.56383700	-1.92692000	-2.41694900
H	2.40605700	-5.04995300	-2.15936700
H	-1.12698700	-2.66119800	-4.67261200
H	1.85958200	-5.74917700	-4.42580300
H	0.08999700	-4.57474600	-5.72689700
N	2.79399300	0.69465500	-0.13302800
C	3.80405700	1.61406400	-0.69969800
C	3.71932700	1.29586000	-2.25850600
N	3.39661000	-0.14757200	-2.30768000
H	2.43352600	0.79729600	0.83072200
C	3.61448100	-0.93284400	-3.51580100
H	2.84965500	-0.74133000	-4.27595700
H	3.58080800	-1.99635600	-3.26852000
H	4.59877000	-0.70205900	-3.94069400
H	4.72572700	1.39724200	-2.67340600
C	2.80267500	2.20952800	-3.12626300
H	2.94664600	3.22382600	-2.73760900
C	1.30363400	1.88093900	-3.01161800
H	1.02701400	1.79654700	-1.95670500
C	0.39626800	2.92630100	-3.67037900
C	3.48812400	3.08243700	-0.37019800
C	4.42640100	4.07871400	-0.68703700
C	2.28691900	3.47073800	0.23084600
C	4.15936800	5.42185800	-0.43076700
C	2.02255200	4.81684600	0.49800300
C	2.95284300	5.79847700	0.16409200
H	5.37936000	3.80546300	-1.13012500
H	1.55158500	2.73044600	0.51325400
H	4.90076600	6.17379500	-0.68818200
H	1.08288700	5.08545600	0.97247600
H	2.74694800	6.84498900	0.37182500
C	5.20050600	1.27342300	-0.09667000
C	6.40363700	1.32023100	-0.81364100
C	5.26378400	0.95111000	1.27036900
C	7.62536500	1.03127900	-0.19669500
C	6.48105200	0.66650300	1.88686700
C	7.67045700	0.69955300	1.15512600
H	6.41801200	1.58786500	-1.86563900
H	4.35270200	0.92282800	1.86062700
H	8.54062100	1.06982300	-0.78181000
H	6.49814100	0.42190700	2.94567400
H	8.61908100	0.47542100	1.63526700
H	-0.65500600	2.67611800	-3.49724800
H	0.57625300	3.92496600	-3.25229100
H	0.54427000	2.98703600	-4.75435200
H	2.83115400	-1.87907700	4.42558400
H	1.85187700	-3.28397100	3.98354100
H	3.60691600	-3.44711400	4.16453000
C	-3.24560200	3.88809400	-0.27793000
C	-2.90662200	4.88356000	-1.20924000
C	-4.46739300	4.00635000	0.40998100
C	-3.74690000	5.97451700	-1.43450300
H	-1.96650600	4.80659500	-1.75099500
C	-5.30838400	5.09246600	0.17860200
H	-4.76673700	3.21902400	1.09426900
C	-4.95167100	6.08461200	-0.73957700
H	-3.45927600	6.73690700	-2.15425700
H	-6.25284600	5.16266600	0.71274800
H	-5.61053600	6.93099300	-0.91551500
H	3.93574000	-1.91520500	2.17542700
C	4.05828400	-4.61575600	1.58192100
H	5.03216200	-4.13967700	1.42282800
H	4.05727100	-5.01782100	2.59955100
H	3.98704600	-5.47090500	0.89782800
C	3.28598700	2.24568600	-4.59080600
H	3.08819900	1.30919900	-5.12373600
H	2.78417300	3.04523500	-5.14411300
H	4.36386800	2.44268300	-4.64963700
H	1.10144300	0.89562400	-3.45240700

- **1da**-*SR* (HEt)



B3LYP/6-31G*

E = –3797.844646

Zero-point correction = 1.341398 (Hartree/Particle)

Thermal correction to Energy = 1.420057

Thermal correction to Enthalpy = 1.421001

Thermal correction to Gibbs Free Energy = 1.218045

Sum of electronic and zero-point Energies = –3796.503248

Sum of electronic and thermal Energies = –3796.424589

Sum of electronic and thermal Enthalpies = –-3796.423645

Sum of electronic and thermal Free Energies = –3796.626601

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.042251

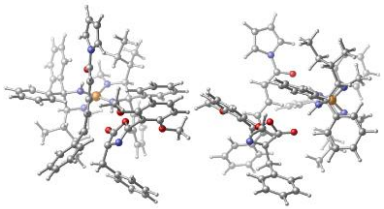
G = –3797.789251

0 1

O	-1.15336300	0.45976300	-1.30659900
C	-2.25802200	0.44132500	-0.74810800
C	-3.26627800	1.46232400	-0.55255400
O	-2.67527700	-0.64404700	-0.01244600
N	-4.33257200	0.87573800	0.15597900
C	-3.92889200	-0.29854100	0.49057800
C	-4.65727400	-1.33828800	1.23736100
C	-5.00679200	-2.53975200	0.58409600
C	-5.05250100	-1.15491600	2.57745800
C	-5.70493400	-3.54871600	1.25957800
C	-5.75529000	-2.16155900	3.25561500
C	-6.06683700	-3.34367400	2.58905400
O	-4.64367000	-2.61318700	-0.72298300
C	-5.01492900	-3.75682300	-1.47445400
H	-6.10501700	-3.88653300	-1.49630900
H	-4.54416500	-4.66571300	-1.08053900
H	-4.65059800	-3.57400100	-2.48655700
O	-4.70211600	0.02886800	3.15461100
C	-5.05594400	0.25398300	4.51051700
H	-4.59482500	-0.48643500	5.17706400
H	-4.67381700	1.24661400	4.75465600
H	-6.14440300	0.23965200	4.65122000
H	-5.97570700	-4.47024800	0.75915800
H	-6.05564100	-2.03162100	4.28763600
H	-6.61125900	-4.12189400	3.11753700
C	-3.57547700	2.49493700	-1.61233000
H	-2.66341400	3.05314000	-1.85049100
H	-4.28872900	3.21005900	-1.19141800
C	-4.14253700	1.88966800	-2.88668000
C	-3.33487000	1.69955400	-4.01535700
C	-5.48592000	1.49317900	-2.95158900
C	-3.85478300	1.13540600	-5.18219600
C	-6.00764000	0.92792100	-4.11499500
C	-5.19437400	0.74826800	-5.23664000
H	-2.28903800	1.99506800	-3.97609500
H	-6.11736400	1.62177500	-2.07645700
H	-3.21412000	1.00501800	-6.05160900
H	-7.05286300	0.62982300	-4.14746800
H	-5.60269000	0.31290000	-6.14530600
C	-2.16256900	2.51061800	0.95097700
C	-1.85987800	1.68823300	2.07208900
H	-1.33745500	2.67819900	0.25848800
H	-2.53543300	1.71398200	2.92256400
C	-0.70446700	0.92212300	2.16724400
H	-0.04622600	0.90765200	1.29938400
C	-0.28104500	0.19643400	3.28406900
H	-0.92117900	0.17185600	4.15912200
C	0.99346700	-0.40822200	3.36498500
O	1.92185000	-0.36445400	2.51506300
N	1.27811500	-1.13870600	4.56871900
C	2.56065100	-1.41009100	5.01239900
C	0.37752800	-1.68765600	5.47051900
C	2.47571600	-2.11466900	6.18816800
C	1.08720500	-2.29783700	6.47485700
H	3.40637000	-1.04506100	4.45332400
H	-0.68457000	-1.63874400	5.29030000
H	3.31254700	-2.45768300	6.78227400
H	0.66110200	-2.82787000	7.31674000
H	0.33080000	-0.60093700	-1.05412000
N	1.22973600	-1.10799200	-1.06970200
P	2.67563400	-0.33965100	-1.11450200
N	3.54668800	-1.74494900	-1.23834700
C	2.73663900	-2.96544700	-1.00655900
C	1.28328300	-2.52752600	-1.50623500
C	4.93258300	-1.84999700	-1.68244200
H	4.99308400	-2.47901800	-2.58055300
H	5.57672400	-2.27715400	-0.91070200
H	5.31506400	-0.85725000	-1.92430900
H	3.13581200	-3.72566500	-1.68255200
C	2.83482200	-3.54966200	0.44022600
H	2.10105900	-3.03651100	1.07150300
C	4.21470600	-3.31223900	1.09284100
H	4.44837300	-2.24342100	1.05890300
C	4.30078900	-3.77511200	2.55254500
C	0.13176800	-3.30513400	-0.84465100
C	-0.41606200	-4.44039000	-1.46146300
C	-0.36585100	-2.92212100	0.40821300
C	-1.40302900	-5.19308600	-0.82493900
C	-1.35881700	-3.67031300	1.04031900
C	-1.87493900	-4.81398000	0.43301400
H	-0.06751000	-4.74678700	-2.44207000
H	0.01569400	-2.03264700	0.89611700
H	-1.80244300	-6.07612300	-1.31775300
H	-1.73246200	-3.34442000	2.00623900
H	-2.64627000	-5.39588400	0.93056200
C	1.15184200	-2.59408500	-3.05241300
C	0.22936800	-1.73761500	-3.67942500
C	1.85846600	-3.49683800	-3.85911200
C	0.04087200	-1.77019600	-5.06013000
C	1.67522800	-3.52523400	-5.24580300
C	0.76894700	-2.65963600	-5.85373100
H	-0.35494100	-1.04062900	-3.08609200
H	2.55434200	-4.20627400	-3.42309100
H	-0.68514200	-1.09975700	-5.51260800
H	2.24284300	-4.23302300	-5.84453800
H	0.62458000	-2.68259600	-6.93058300
N	2.71218300	0.77517700	0.09151400
C	3.69877500	1.84847400	-0.14801800
C	3.61239700	2.05188300	-1.73029200
N	3.27626000	0.70685100	-2.25221000
H	2.41872400	0.48919300	1.04253000
C	3.45203400	0.37896800	-3.66154900
H	2.68644800	0.84651700	-4.28938300
H	3.37766700	-0.70199800	-3.79832600
H	4.44004600	0.70842600	-4.00629300

H	4.62164800	2.27006900	-2.08823200
C	2.71378700	3.21169600	-2.25443500
H	2.84883200	4.03112100	-1.53971200
C	1.21189500	2.87767700	-2.29022900
H	0.91577100	2.41512500	-1.34425600
C	0.32388500	4.10290700	-2.53694800
C	3.33656300	3.11734200	0.64524700
C	4.26151300	4.16866000	0.75298500
C	2.09010900	3.26765600	1.26262200
C	3.93915700	5.33848500	1.43869400
C	1.76950500	4.43525900	1.95967700
C	2.68977100	5.47793900	2.04700800
H	5.24701600	4.07347200	0.30782200
H	1.35904300	2.47229900	1.21260000
H	4.67220300	6.13818300	1.50570800
H	0.79503400	4.51684400	2.43326700
H	2.44194000	6.38639700	2.58921700
C	5.11213500	1.37304800	0.30511400
C	6.30360800	1.72167100	-0.34657000
C	5.20904700	0.60074600	1.47562100
C	7.54540600	1.29729300	0.13672100
C	6.44676000	0.18002900	1.96015900
C	7.62360300	0.52147100	1.29061600
H	6.29241600	2.34097000	-1.23815700
H	4.31058200	0.32195900	2.01791500
H	8.44988800	1.58068900	-0.39533000
H	6.48847600	-0.41632600	2.86773400
H	8.58767800	0.19091300	1.66733500
H	-0.73343800	3.82444000	-2.49163800
H	0.49935900	4.87534500	-1.77729600
H	0.49842800	4.55619900	-3.51910300
H	5.27092700	-3.49542600	2.98068200
H	3.52166900	-3.30694100	3.16355600
H	4.20475900	-4.86123100	2.65248400
C	-3.02840900	3.69889500	1.15820800
C	-2.62100900	4.95205100	0.67118900
C	-4.24491900	3.61880800	1.86102500
C	-3.38867100	6.09532900	0.89635700
H	-1.68470300	5.03105900	0.12327300
C	-5.01354300	4.76018800	2.07802500
H	-4.59868100	2.64849200	2.19463200
C	-4.58818100	6.00451600	1.60315500
H	-3.04896900	7.05598100	0.51717700
H	-5.95540700	4.67826400	2.61508600
H	-5.19072100	6.89237100	1.77655100
H	4.99153300	-3.83060900	0.51071300
C	2.52046400	-5.05724000	0.41540500
H	2.42950500	-5.45533200	1.42990200
H	1.58924200	-5.28667000	-0.10433100
H	3.33172700	-5.60529200	-0.08492600
C	3.22881100	3.74534900	-3.60743900
H	3.04906300	3.04809900	-4.43297900
H	2.73333600	4.68634300	-3.86470900
H	4.30623400	3.94968500	-3.57045500
H	1.01431500	2.12361600	-3.06351600

● **1da**-*SR* (EtH)



B3LYP/6-31G*

E = –3797.845507

Zero-point correction = 1.341377 (Hartree/Particle)

Thermal correction to Energy = 1.420045

Thermal correction to Enthalpy = 1.420989

Thermal correction to Gibbs Free Energy = 1.217709

Sum of electronic and zero-point Energies = –3796.504130

Sum of electronic and thermal Energies = –3796.425462

Sum of electronic and thermal Enthalpies = –3796.424518

Sum of electronic and thermal Free Energies = –3796.627798

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

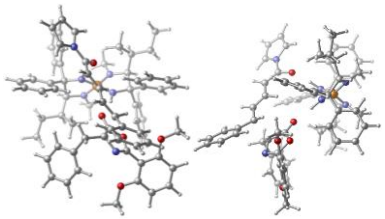
E = –3799.041914

G = –3797.78919

0 1

O	-1.12412900	-0.15791400	-1.36336900
C	-2.21700600	0.06452300	-0.82772400
C	-3.27482500	1.01054400	-1.12782600
O	-2.56459800	-0.52108100	0.36798100
N	-4.30089000	0.80937100	-0.18209100
C	-3.83179000	-0.02324800	0.67723200
C	-4.50308700	-0.59649900	1.85599400
C	-4.79277700	-1.97792300	1.87897500
C	-4.91305500	0.20167300	2.94238100
C	-5.44169600	-2.55767100	2.97636600
C	-5.56720400	-0.37511400	4.04073600
C	-5.81672600	-1.74495600	4.04389200
O	-4.42570200	-2.66412500	0.76504600
C	-4.78081300	-4.03327900	0.65481800
H	-5.86728200	-4.17188400	0.72997500
H	-4.27769400	-4.64153500	1.41594300
H	-4.44126600	-4.34533500	-0.33398900
O	-4.62870200	1.53023300	2.85461800
C	-5.00746600	2.37848100	3.92748000
H	-4.51389500	2.09064000	4.86486900
H	-4.68172200	3.37996800	3.64140400
H	-6.09497200	2.37954700	4.07633700
H	-5.66422600	-3.61741600	2.99599300
H	-5.87779100	0.22938100	4.88347400
H	-6.32279400	-2.18901100	4.89711100
C	-3.66338000	1.33859500	-2.55325500
H	-2.78672000	1.71249000	-3.09329800
H	-4.39383800	2.15337600	-2.52539000
C	-4.24725700	0.15008700	-3.30347000
C	-3.53486800	-0.47066900	-4.33724500
C	-5.51369500	-0.35301000	-2.96992600
C	-4.07115800	-1.56215800	-5.02513100
C	-6.05032200	-1.44393300	-3.65300200
C	-5.33193900	-2.05351900	-4.68488100
H	-2.55240000	-0.09187900	-4.60745800
H	-6.06894300	0.11179200	-2.16005500
H	-3.50617000	-2.02167000	-5.83328300
H	-7.03475200	-1.81759800	-3.38145600
H	-5.75342600	-2.90046400	-5.22055700
C	-2.22796200	2.69022700	-0.39708400
C	-1.91830300	2.57728000	0.99044900
H	-1.39455100	2.50838500	-1.07724200
H	-2.59052900	3.04688400	1.70310900
C	-0.76080100	1.97680100	1.46989700
H	-0.11395500	1.49419000	0.73829400
C	-0.31993700	1.95873900	2.79562700
H	-0.94847600	2.40609500	3.55766600
C	0.95788100	1.48156900	3.16419400
O	1.87018900	1.06752400	2.40340200
N	1.27167100	1.49282900	4.56625700
C	2.56431600	1.43009200	5.05740300
C	0.39730400	1.55214500	5.64217200
C	2.51175500	1.45970400	6.42930800
C	1.13288500	1.53065800	6.80086200
H	3.39331900	1.39540000	4.36985300
H	-0.66998700	1.55451600	5.48908300
H	3.36383500	1.43862900	7.09605100
H	0.72974700	1.55130700	7.80504400
H	0.39509500	-1.04188000	-0.72006800
N	1.27839200	-1.51184600	-0.46830600
P	2.73163000	-0.83399600	-0.82224500
N	3.60093900	-2.17174900	-0.36701000
C	2.78757800	-3.25604900	0.22297500
C	1.32301800	-2.98922600	-0.34137800
C	5.05426300	-2.28176600	-0.41091800
H	5.33535400	-3.27473400	-0.78196900
H	5.51040100	-2.13066000	0.57237700
H	5.46306000	-1.52762100	-1.08495100
H	3.14291000	-4.18604300	-0.22642000
C	2.95496600	-3.44854900	1.76379100
H	2.06262200	-3.99049100	2.09267300
C	3.01794500	-2.13495400	2.56527800
H	2.22551100	-1.45509100	2.24025200
C	2.88333300	-2.33040600	4.08078300
C	0.24557500	-3.49243500	0.63042300
C	-0.06726200	-4.86088100	0.66164700
C	-0.37996600	-2.63962200	1.54579600
C	-0.95439200	-5.36799600	1.60930000
C	-1.28183100	-3.14578500	2.48457500
C	-1.56161900	-4.51078600	2.53045400
H	0.39001900	-5.53594300	-0.05590900
H	-0.16896700	-1.57729900	1.53434700
H	-1.17200800	-6.43299000	1.62506700
H	-1.76548400	-2.46340900	3.17685700
H	-2.25080900	-4.90324100	3.27384400
C	1.08476700	-3.62242200	-1.74408400
C	-0.03811300	-3.17952300	-2.46738200
C	1.88602300	-4.61201000	-2.32806100
C	-0.33936100	-3.69861100	-3.72387400
C	1.58628400	-5.13295400	-3.59269400
C	0.47444200	-4.67964200	-4.29666200
H	-0.68566800	-2.41446000	-2.05046300
H	2.75704000	-5.00650000	-1.81502100
H	-1.21798300	-3.33404000	-4.24959200
H	2.22950500	-5.89893000	-4.01854300
H	0.24094800	-5.08646300	-5.27695800
N	2.74736300	0.68927200	-0.20760900
C	3.68418400	1.59031800	-0.92554500
C	3.44477800	1.11964200	-2.42609000
N	3.34071700	-0.35377600	-2.28971300
H	2.39101600	0.89846400	0.74303300
C	3.84134700	-1.22990100	-3.34185100
H	3.28778400	-1.09382800	-4.27463700
H	3.73015100	-2.27113100	-3.03404900
H	4.90437000	-1.03019500	-3.53284900
H	4.33931500	1.31135600	-3.02498200
C	2.23386600	1.79732000	-3.14554300
H	1.50040800	2.06409500	-2.37553500
C	1.50211000	0.87281500	-4.14486500
H	1.31876700	-0.10042500	-3.67851700
C	0.14903900	1.42526300	-4.60669800
C	3.34745500	3.06603300	-0.64699200
C	4.32427200	4.06137800	-0.81491700
C	2.07170400	3.46040600	-0.22787000
C	4.02494400	5.40455500	-0.58988900
C	1.77207300	4.80362300	0.00687200
C	2.74606100	5.78310300	-0.17705800
H	5.33068600	3.79038400	-1.11626000
H	1.30087500	2.72028800	-0.06659500
H	4.79948300	6.15448100	-0.72789600
H	0.77316500	5.07010700	0.34059400
H	2.51639600	6.82888900	0.00832500
C	5.13276500	1.31223200	-0.44010700
C	6.25255100	1.28570400	-1.28142800
C	5.33882300	1.12931600	0.93806500
C	7.53443600	1.05695000	-0.76917500
C	6.61580500	0.90788200	1.45046900
C	7.72164900	0.86354300	0.59762400
H	6.14994700	1.45161600	-2.34924300
H	4.48909700	1.16104200	1.61400700
H	8.38440600	1.03541100	-1.44637700
H	6.74650600	0.77278300	2.52091400
H	8.71704000	0.68784200	0.99638000
H	-0.31485100	0.74260100	-5.32788800
H	-0.53025800	1.51557900	-3.75235000
H	0.23225900	2.40375500	-5.09150400
H	2.86858500	-1.36164900	4.58983500
H	1.94739800	-2.84771700	4.32578000
H	3.70916500	-2.91571500	4.50170900
C	-3.11906500	3.80004000	-0.82474400
C	-2.74097800	4.62911500	-1.89344100
C	-4.33511200	4.06793100	-0.16971700
C	-3.53735400	5.70577300	-2.28537500
H	-1.80430100	4.43491500	-2.41108500
C	-5.13250700	5.13916100	-0.56663400
H	-4.66441500	3.40440100	0.62368600
C	-4.73666900	5.96649500	-1.62184300
H	-3.21994600	6.33925900	-3.10996000
H	-6.07347500	5.32608500	-0.05492000
H	-5.36151900	6.80177100	-1.92725200
H	3.96287400	-1.61635200	2.34953800
C	4.14580800	-4.37946300	2.07437000
H	5.11508800	-3.91107300	1.86999300
H	4.14217200	-4.66707800	3.13002700
H	4.09136800	-5.30597200	1.48863500
C	2.70284400	3.08189200	-3.85261400
H	3.38170700	2.83398100	-4.68052600
H	1.85665600	3.63205300	-4.27451800
H	3.22715700	3.76187000	-3.17833300
H	2.14228200	0.69635400	-5.02191900

- **1da**-*SS* (MeMe)



B3LYP/6-31G*

E = –3797.837525

Zero-point correction = 1.341470 (Hartree/Particle)

Thermal correction to Energy = 1.420033

Thermal correction to Enthalpy = 1.420978

Thermal correction to Gibbs Free Energy = 1.219512

Sum of electronic and zero-point Energies = –3796.496055

Sum of electronic and thermal Energies = –3796.417492

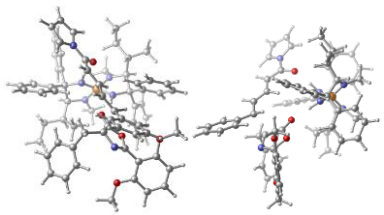
Sum of electronic and thermal Enthalpies = –3796.416548

Sum of electronic and thermal Free Energies = –3796.618013

0 1

O	0.87752400	-0.52699700	-0.05926000
C	2.09383300	-0.66883200	0.00190900
C	2.96003700	-1.67248700	0.62495300
O	2.94688200	0.32037100	-0.48116100
N	4.29194600	-1.32301800	0.27642800
C	4.23485500	-0.18221900	-0.30506400
C	5.34209600	0.63735300	-0.83016800
C	5.59895700	1.91401600	-0.29313300
C	6.16183700	0.15862700	-1.87231800
C	6.65156300	2.69921200	-0.77977100
C	7.22105600	0.93831800	-2.35833400
C	7.44907600	2.19571500	-1.80515800
O	4.77474600	2.29636400	0.72263500
C	4.95078100	3.58669700	1.29115300
H	5.93648900	3.68495700	1.76409800
H	4.16819800	3.68517900	2.04350000
H	4.82785100	4.37424200	0.53709000
O	5.83842300	-1.06510800	-2.36659700
C	6.59237400	-1.58518800	-3.45007100
H	7.64162000	-1.74653200	-3.17084800
H	6.54762000	-0.92587500	-4.32692000
H	6.12932500	-2.54240800	-3.69403400
H	6.85737500	3.67769300	-0.36424200
H	7.85693400	0.57637900	-3.15644100
H	8.27058100	2.79917900	-2.18223500
C	2.59713300	-3.14233000	0.63256200
H	1.59018700	-3.23527300	1.05140600
H	3.28436300	-3.64086100	1.32806500
C	2.66136800	-3.85007500	-0.71202200
C	1.51770700	-4.44714500	-1.25666100
C	3.87332600	-3.97069400	-1.41079800
C	1.57490200	-5.14649200	-2.46535800
C	3.93226600	-4.66894700	-2.61671600
C	2.78428400	-5.26016400	-3.15094800
H	0.57113000	-4.37087600	-0.72655500
H	4.76505900	-3.50339100	-1.00451900
H	0.67498300	-5.60902700	-2.86356700
H	4.88290000	-4.76497600	-3.13721800
H	2.83466200	-5.80934500	-4.08791000
C	2.72174700	-1.09949200	2.56756400
C	1.52643300	-1.67195700	3.12756300
H	2.64651900	-0.03837600	2.33267200
H	1.62568900	-2.56795700	3.73700900
C	0.25794800	-1.16308700	2.92606600
H	0.16520600	-0.29207800	2.28549400
C	-0.94296200	-1.65295600	3.46952700
H	-0.90867000	-2.47443400	4.17761700
C	-2.17729200	-1.05820700	3.15905200
O	-2.36979300	-0.08365500	2.37720000
N	-3.35429900	-1.59323400	3.79523700
C	-3.53019800	-2.82937700	4.39517500
C	-4.53568300	-0.88102000	3.90756700
C	-4.81317600	-2.89850800	4.88201400
C	-5.45096200	-1.65667800	4.57864300
H	-2.74540200	-3.56881800	4.38222900
H	-4.58315700	0.12790400	3.53047100
H	-5.25088600	-3.74885300	5.38869400
H	-6.46125000	-1.36561400	4.83567900
H	-0.27534700	0.99888800	-0.36253200
N	-1.03829100	1.66986300	-0.51899100
P	-2.46397900	1.20376900	-1.17281600
N	-3.08715100	2.74645000	-1.18214100
C	-2.28895600	3.72861000	-0.41308900
C	-0.81381100	3.13196800	-0.45749500
C	-4.43848400	3.08428600	-1.61377500
H	-4.79315100	2.32986600	-2.31813400
H	-5.14955700	3.12833700	-0.78065600
H	-4.42848100	4.05826200	-2.11827000
H	-2.27146600	4.65428500	-0.99591900
C	-3.02678800	4.13894400	0.90578600
C	-2.38831400	5.33973100	1.64104800
C	-3.40426300	6.16092000	2.44674300
H	-1.90715800	6.00356900	0.90933000
C	0.01573800	3.48363900	0.78721500
C	0.03029300	2.64696500	1.91043000
C	0.75241800	4.67621300	0.82742200
C	0.74734700	3.00597500	3.05449100
C	1.45547900	5.04194300	1.97478500
C	1.45480700	4.20815900	3.09590700
H	-0.53665900	1.72190900	1.90933500
H	0.77171400	5.32901700	-0.03993900
H	0.74323800	2.33979300	3.91274200
H	2.00453400	5.98015700	1.99066900
H	2.00078100	4.49260400	3.99187700
C	-0.03750400	3.54560300	-1.74178700
C	1.23256300	2.96950100	-1.92851000
C	-0.51888700	4.40061300	-2.74016600
C	1.98761500	3.23861700	-3.06628700
C	0.23987200	4.67386600	-3.88511400
C	1.49463300	4.09586900	-4.05401900
H	1.64435100	2.30100700	-1.17877800
H	-1.49244900	4.87129900	-2.65664000
H	2.96387500	2.77434800	-3.17592800
H	-0.16100200	5.34386000	-4.64156000
H	2.08324900	4.30904400	-4.94233000
N	-2.94372600	-0.13463900	-0.37197700
C	-3.76132700	-1.07149700	-1.17095900
C	-3.20872800	-0.85548000	-2.64739800
N	-2.83043400	0.58026700	-2.66803100
H	-2.83862300	-0.20512900	0.65823300
C	-2.55852000	1.24828900	-3.93438100
H	-1.62170800	0.91067600	-4.39271300
H	-2.48310000	2.32467700	-3.76763600
H	-3.38022900	1.05870000	-4.63585900
H	-4.05447000	-0.96466900	-3.33182300
C	-2.08926800	-1.74114800	-3.27892800
H	-1.98511500	-1.29479100	-4.28116200
C	-2.52240200	-3.20138100	-3.54425300
H	-3.59666900	-3.22846300	-3.77564700
C	-1.75752500	-3.85363600	-4.70390900
C	-5.25556100	-0.64932700	-1.02932400
C	-6.14189400	-0.41933600	-2.08772500
C	-5.74736200	-0.50171500	0.28033300
C	-7.46924000	-0.04056300	-1.84974400
C	-7.06677800	-0.12982600	0.51954300
C	-7.93779100	0.10744100	-0.54776500
H	-5.82810100	-0.53153500	-3.11994000
H	-5.09360100	-0.68951000	1.12700300
H	-8.13229900	0.13313400	-2.69349800
H	-7.41429000	-0.03551700	1.54476500
H	-8.96880000	0.39720700	-0.36355200
C	-3.60113200	-2.50388700	-0.63437000
C	-4.56907100	-3.47457600	-0.93272000
C	-2.51236300	-2.86955500	0.16694900
C	-4.43570300	-4.78299800	-0.47197500
C	-2.38730900	-4.17793400	0.64101200
C	-3.34109800	-5.14185700	0.31707200
H	-5.43822100	-3.20679100	-1.52579200
H	-1.75952700	-2.13919800	0.43941000
H	-5.19626300	-5.51880800	-0.71961500
H	-1.54372500	-4.42957000	1.27773200
H	-3.24293100	-6.15840500	0.68834600
H	-2.11365000	-4.87597200	-4.87560700
H	-1.89297100	-3.29387600	-5.63841300
H	-0.68240700	-3.91053100	-4.50214000
H	-2.91357200	7.00696200	2.94119500
H	-4.19467000	6.56569300	1.80159600
H	-3.88666900	5.56247900	3.22739400
C	4.03320900	-1.42770400	3.19839400
C	4.30307600	-2.67890500	3.77983200
C	5.04437300	-0.45289700	3.23951100
C	5.53225000	-2.94089700	4.38320500
H	3.54753700	-3.45836700	3.76454300
C	6.27151500	-0.71122200	3.84702500
H	4.86301000	0.51480000	2.78016900
C	6.52229400	-1.95756300	4.42327600
H	5.71527600	-3.91675400	4.82615400
H	7.03518500	0.06243300	3.86777500
H	7.47891200	-2.16149200	4.89742200
C	-3.40639100	2.99117300	1.85001600
H	-3.96153100	2.20434000	1.32998000
H	-2.54551500	2.51856800	2.32272900
H	-4.05864600	3.36713500	2.64601300
H	-3.97602300	4.53192000	0.50756200
H	-1.59342400	4.99535400	2.30828200
C	-0.71445000	-1.63602700	-2.61255500
H	-0.36857600	-0.59960100	-2.55457800
H	-0.70810200	-2.03953800	-1.59994700
H	0.03323500	-2.18841300	-3.19015800
H	-2.39162300	-3.80323400	-2.64086800

- **1da**-*SS* (HMe)



B3LYP/6-31G*

E = –3797.840213

Zero-point correction = 1.341502 (Hartree/Particle)

Thermal correction to Energy = 1.419984

Thermal correction to Enthalpy = 1.420929

Thermal correction to Gibbs Free Energy = 1.219235

Sum of electronic and zero-point Energies = –3796.498711

Sum of electronic and thermal Energies = –3796.420229

Sum of electronic and thermal Enthalpies = –3796.419285

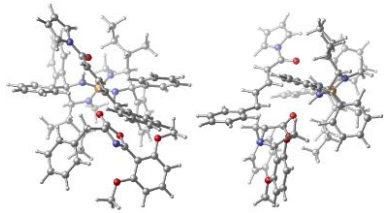
Sum of electronic and thermal Free Energies = –3796.620978

0 1

O	0.89364000	-0.45749900	-0.06493900
C	2.10822400	-0.62243200	-0.00460500
C	2.94979800	-1.65484600	0.60085300
O	2.97927100	0.35855100	-0.46929400
N	4.29027000	-1.32027600	0.27317900
C	4.25668900	-0.17176300	-0.29471800
C	5.38403300	0.61889600	-0.82453600
C	5.73285000	1.85163100	-0.24231500
C	6.12605500	0.15087100	-1.92725200
C	6.80449900	2.60295300	-0.74145400
C	7.20285400	0.89600700	-2.42828000
C	7.52490900	2.11022400	-1.82732100
O	4.97357700	2.22920100	0.82435200
C	5.24532200	3.47966100	1.44073000
H	6.25391800	3.50319900	1.87355900
H	4.50155200	3.58470400	2.23046100
H	5.13507400	4.30747900	0.72889500
O	5.71100900	-1.02844000	-2.45992600
C	6.37484800	-1.53261900	-3.60766100
H	7.42788900	-1.76088900	-3.39738400
H	6.31787800	-0.82885700	-4.44859900
H	5.84725800	-2.45152000	-3.86712600
H	7.08229400	3.54777400	-0.29137700
H	7.77912400	0.54079300	-3.27344400
H	8.36011000	2.68790200	-2.21462200
C	2.56636400	-3.11950700	0.56518600
H	1.54862700	-3.20925500	0.95773900
H	3.23057800	-3.64499000	1.26315000
C	2.65329200	-3.79212600	-0.79620300
C	1.50609700	-4.31182700	-1.40841500
C	3.88714600	-3.95483900	-1.44617900
C	1.58080400	-4.97639600	-2.63558400
C	3.96450600	-4.62192600	-2.66878000
C	2.81239500	-5.13571100	-3.27052800
H	0.54200500	-4.20242400	-0.91748300
H	4.78230700	-3.54514100	-0.98859900
H	0.67642200	-5.37753200	-3.08676800
H	4.93203300	-4.75571100	-3.14812000
H	2.87669000	-5.66105000	-4.22025200

C	2.67746200	-1.13520700	2.56630900
C	1.47233700	-1.72367400	3.08419600
H	2.60888100	-0.06830000	2.35824700
H	1.56066600	-2.64297000	3.65970400
C	0.20396700	-1.21220700	2.88219100
H	0.11489700	-0.31671000	2.27694300
C	-1.00004300	-1.73981400	3.37941400
H	-0.96349300	-2.60550100	4.03222200
C	-2.24100400	-1.14745600	3.08819600
O	-2.44371200	-0.11973800	2.37961600
N	-3.41702700	-1.76473900	3.65122400
C	-3.55673900	-3.03407200	4.19080400
C	-4.63630600	-1.11586000	3.74549900
C	-4.85225800	-3.18548500	4.62107200
C	-5.53804900	-1.96325000	4.34406600
H	-2.73781500	-3.73529800	4.18307200
H	-4.72512500	-0.09848500	3.40194300
H	-5.26637500	-4.07669500	5.07454400
H	-6.57072000	-1.73177200	4.57121300
H	-0.20260600	1.07768800	-0.25442500
N	-0.96298000	1.75248400	-0.40632500
P	-2.39499400	1.30310100	-1.06244500
N	-3.08070300	2.79699800	-0.84923800
C	-2.30316800	3.66751000	0.06207500
C	-0.79674100	3.21384800	-0.21447900
C	-4.29458700	3.29247800	-1.48662800
H	-4.70527700	2.51880900	-2.13677300
H	-5.05871900	3.55474700	-0.75053000
H	-4.06961600	4.18135600	-2.09148900
H	-2.44607700	4.69171800	-0.29056200
C	-2.76191500	3.62329900	1.55828900
C	-4.25140300	3.26334400	1.75536900
C	-4.60536300	2.96193400	3.21755600
H	-4.49319100	2.37497500	1.16297600
C	0.15647300	3.47901900	0.96245900
C	0.24878700	2.57816000	2.03291600
C	0.91879000	4.65550100	1.01322600
C	1.06712300	2.85296600	3.13000700
C	1.72664000	4.93680800	2.11560200
C	1.80362300	4.03695800	3.18047800
H	-0.34094300	1.66807100	2.02830400
H	0.87912800	5.36291500	0.19125700
H	1.11711800	2.13725600	3.94590900
H	2.29599500	5.86261600	2.13864800
H	2.42800300	4.25785200	4.04254400
C	-0.21272300	3.82488400	-1.51612900
C	0.90991400	3.19576100	-2.08443700
C	-0.70982900	4.97127700	-2.14789500
C	1.49717500	3.68561600	-3.24848900
C	-0.12392700	5.46205800	-3.32077200
C	0.97867200	4.82054600	-3.87825900
H	1.33938600	2.31868400	-1.60832200
H	-1.55712200	5.51143900	-1.73891100
H	2.36573200	3.17922900	-3.66081400
H	-0.53588100	6.35137600	-3.79090300
H	1.43481100	5.20168400	-4.78795200
N	-2.82216200	-0.12873400	-0.40359200
C	-3.64167500	-0.97865500	-1.29456600
C	-3.09506900	-0.60634400	-2.73999900
N	-2.74849100	0.83447300	-2.61634100
H	-2.80264600	-0.24541600	0.62749900
C	-2.42743800	1.62138600	-3.80130400
H	-1.45950200	1.34834400	-4.23722300
H	-2.38825500	2.68032100	-3.53716000
H	-3.20745400	1.48095500	-4.55919100
H	-3.93864500	-0.67118900	-3.43346100
C	-1.95408200	-1.40236600	-3.44820300
H	-1.84045300	-0.84648900	-4.39296300
C	-2.36349200	-2.82871900	-3.88211000
H	-3.42945500	-2.83699900	-4.15073700
C	-1.55506000	-3.34934700	-5.07831800
C	-5.13803000	-0.58262100	-1.10782300
C	-5.99211300	-0.12461200	-2.11789100
C	-5.66132400	-0.68914900	0.19318700
C	-7.32071900	0.22045500	-1.83885300
C	-6.98095300	-0.34811700	0.47307000
C	-7.82148100	0.11133400	-0.54500000
H	-5.64946300	-0.02358100	-3.14205100
H	-5.03232900	-1.04925100	1.00171900
H	-7.95942800	0.57190900	-2.64531600
H	-7.35021800	-0.45241200	1.48960500
H	-8.85348000	0.37563900	-0.33052800
C	-3.47652000	-2.45812700	-0.91282500
C	-4.42480300	-3.39764300	-1.34495300
C	-2.41410500	-2.89668500	-0.11330300
C	-4.29736900	-4.74544500	-1.01533700
C	-2.29670000	-4.24621700	0.23094000
C	-3.22991800	-5.17653100	-0.22471100
H	-5.27372000	-3.07259800	-1.93910200
H	-1.67732100	-2.19114200	0.25372200
H	-5.04131400	-5.45642100	-1.36493900
H	-1.47562900	-4.55972300	0.86973300
H	-3.13723000	-6.22476400	0.04630000
H	-1.90265200	-4.34542600	-5.37570000
H	-1.65650800	-2.68888800	-5.94925800
H	-0.48813700	-3.43142500	-4.84423200
H	-5.64944700	2.63823300	3.29951800
H	-3.97071900	2.15658900	3.60386900
H	-4.48348800	3.83462400	3.86798500
C	3.97847000	-1.48855000	3.20353800
C	4.23046700	-2.75300100	3.76440300
C	4.99908500	-0.52503800	3.27231400
C	5.45037800	-3.03792000	4.37600600
H	3.46825300	-3.52510300	3.72724500
C	6.21704100	-0.80664400	3.88784300
H	4.83364100	0.45173500	2.82675300
C	6.44938600	-2.06531200	4.44466600
H	5.61898400	-4.02337900	4.80314000
H	6.98824500	-0.04136500	3.92993900
H	7.39866900	-2.28711900	4.92547000
C	-2.44232700	4.96965300	2.23324600
H	-1.40310500	5.27293200	2.08933000
H	-3.08551600	5.76234800	1.82565800
H	-2.61905100	4.92220700	3.31154400
H	-2.19988300	2.83034700	2.06017000
H	-4.89009900	4.08037600	1.38805900
C	-0.59259200	-1.35890100	-2.74903300
H	-0.26047100	-0.33278500	-2.56699200
H	-0.60079800	-1.87265400	-1.78760100
H	0.17173700	-1.83660400	-3.37005400
H	-2.25615000	-3.52399500	-3.04512200

● **1da**-*SS* (HH)



B3LYP/6-31G*

E = –3797.844356

Zero-point correction = 1.341466 (Hartree/Particle)

Thermal correction to Energy = 1.419924

Thermal correction to Enthalpy = 1.420868

Thermal correction to Gibbs Free Energy = 1.220206

Sum of electronic and zero-point Energies = –3796.502890

Sum of electronic and thermal Energies = –3796.424433

Sum of electronic and thermal Enthalpies = –3796.423488

Sum of electronic and thermal Free Energies = –3796.624151

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.043499

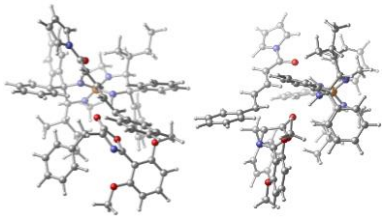
G = –3797.788763

0 1

O	0.73152800	-0.64610800	-0.27385600
C	1.94083700	-0.78096800	-0.10768300
C	2.74563500	-1.69667500	0.70327800
O	2.82849200	0.14927200	-0.63240600
N	4.10408300	-1.36961900	0.44317500
C	4.09951000	-0.31268500	-0.28136900
C	5.24367100	0.43489800	-0.82942100
C	5.40391400	1.80724400	-0.55194600
C	6.18975300	-0.20762900	-1.65638800
C	6.48290200	2.52570200	-1.08195300
C	7.27604200	0.50703500	-2.18117100
C	7.40563600	1.86149400	-1.88701600
O	4.46152500	2.35481300	0.26641900
C	4.54032000	3.74423400	0.55582300
H	5.47512800	3.99279900	1.07482900
H	3.69245500	3.95962100	1.20588000
H	4.46077200	4.34607500	-0.35845700
O	5.95649900	-1.51860800	-1.91870300
C	6.82365000	-2.20413200	-2.80764200
H	7.84336200	-2.27000300	-2.40632600
H	6.85264300	-1.72347200	-3.79434500
H	6.40427100	-3.20628000	-2.90569200
H	6.61279300	3.57847000	-0.86544500
H	8.00741800	0.01948200	-2.81337800
H	8.24783500	2.41435800	-2.29480400
C	2.40417100	-3.16915300	0.81647400
H	1.35698400	-3.24887200	1.12224200
H	3.01295000	-3.58090200	1.63088200
C	2.64095100	-3.98571900	-0.44256700
C	1.56407300	-4.43851500	-1.21587500
C	3.94108900	-4.33451500	-0.83904900
C	1.77497700	-5.22114600	-2.35422900
C	4.15312300	-5.12155100	-1.97100400
C	3.07128700	-5.56782000	-2.73487900
H	0.54889500	-4.18483800	-0.92043500
H	4.78423700	-3.97663400	-0.25565400
H	0.92323500	-5.56840000	-2.93424100
H	5.16669300	-5.40051500	-2.25133700
H	3.23822200	-6.18556900	-3.61376200
C	2.26303800	-0.94220200	2.51918100
C	1.09661500	-1.59865400	3.05171300
H	2.08006900	0.07227500	2.16744900
H	1.25368400	-2.42967600	3.73683200
C	-0.21146500	-1.26698600	2.74727100
H	-0.38461600	-0.45846500	2.04220500
C	-1.36174000	-1.88807800	3.26290800
H	-1.23883100	-2.69817200	3.97367500
C	-2.65929000	-1.45278600	2.93799700
O	-2.96767700	-0.47432300	2.19746900
N	-3.76081300	-2.17369100	3.51673300
C	-3.75663600	-3.43024400	4.10555600
C	-5.05292600	-1.67864300	3.55869700
C	-5.03341100	-3.72246900	4.51648000
C	-5.85714100	-2.60548800	4.17457500
H	-2.85825900	-4.02505400	4.14137600
H	-5.26003500	-0.69715200	3.16545500
H	-5.34634700	-4.63930300	4.99915000
H	-6.91700200	-2.49736700	4.36495300
H	-0.10850200	1.09363400	-0.14444100
N	-0.90571600	1.73803800	-0.16143300
P	-2.23622000	1.30537300	-1.03110700
N	-2.98903400	2.76288200	-0.78918800
C	-2.31577300	3.58846700	0.24219600
C	-0.78421600	3.20161200	0.04142200
C	-4.20590300	3.22923300	-1.44294100
H	-4.52138500	2.50120000	-2.19213700
H	-5.02691500	3.35519500	-0.73296700
H	-4.02091200	4.18950700	-1.94249700
H	-2.47451400	4.63309700	-0.03862600
C	-2.85913500	3.39913100	1.70067500
C	-4.33266800	2.93918500	1.77566700
C	-4.74888300	2.46844000	3.17517600
H	-4.49015300	2.10331100	1.08772200
C	0.10195800	3.51082300	1.25849200
C	0.29901100	2.57287800	2.27964100
C	0.71219500	4.76884800	1.38489700
C	1.07898400	2.88039900	3.39715000
C	1.47763000	5.08374300	2.50824100
C	1.66792000	4.13847600	3.51929700
H	-0.16795500	1.59782700	2.21507800
H	0.58856900	5.51097100	0.60249000
H	1.21870900	2.12913500	4.16921800
H	1.92880900	6.06953600	2.58922900
H	2.26953300	4.38053800	4.39119100
C	-0.15786800	3.84948100	-1.22281600
C	1.01416400	3.27326900	-1.74500000
C	-0.66561600	4.98981000	-1.85775500
C	1.63965900	3.80806200	-2.86961000
C	-0.03980500	5.52706200	-2.98852900
C	1.11278100	4.93763800	-3.50153800
H	1.45503200	2.40090200	-1.27064700
H	-1.55573700	5.48483100	-1.48386200
H	2.54271100	3.33793200	-3.24951500
H	-0.46084400	6.41012500	-3.46235600
H	1.59875200	5.35357400	-4.37995000
N	-2.71680000	-0.17327900	-0.53697500
C	-3.39827600	-0.95366500	-1.59532400
C	-2.56025700	-0.51974200	-2.87994800
N	-2.32354500	0.93013100	-2.64031500
H	-2.80600500	-0.39507700	0.47457200
C	-2.24452500	1.87156700	-3.75143400
H	-1.36836800	1.68790100	-4.37756400
H	-2.17050300	2.88959000	-3.36493900
H	-3.14562500	1.79640500	-4.37446500
H	-3.19084000	-0.57868600	-3.77125500

C	-1.27660900	-1.36967200	-3.15560800
H	-0.90670800	-1.74260400	-2.19511200
C	-0.11531100	-0.56503300	-3.77973200
H	0.09600200	0.30528100	-3.14989700
C	1.18203800	-1.36958100	-3.93229800
C	-4.88423000	-0.50941000	-1.67890100
C	-5.58411900	-0.30736300	-2.87504200
C	-5.58400600	-0.34484200	-0.47053900
C	-6.93123200	0.07263500	-2.86794300
C	-6.92651800	0.02722200	-0.46212800
C	-7.60751600	0.24505400	-1.66277100
H	-5.09975500	-0.45161200	-3.83535500
H	-5.07233900	-0.51649300	0.47229900
H	-7.44706500	0.22723500	-3.81225400
H	-7.44264800	0.14140500	0.48736600
H	-8.65400100	0.53773100	-1.65673700
C	-3.33801800	-2.45099400	-1.24427200
C	-4.29014600	-3.34229500	-1.76262200
C	-2.35048000	-2.95547700	-0.38679800
C	-4.24733600	-4.70003400	-1.44748400
C	-2.31957500	-4.31297400	-0.05875700
C	-3.26228600	-5.19194500	-0.59025900
H	-5.08103100	-2.97499000	-2.40880500
H	-1.60414400	-2.29225200	0.03608400
H	-4.99684100	-5.36935800	-1.86156800
H	-1.55831200	-4.67446100	0.62692600
H	-3.23862800	-6.24647500	-0.32928300
H	1.99980400	-0.71421800	-4.25296300
H	1.47662900	-1.82907400	-2.98339300
H	1.09187000	-2.16817500	-4.67601600
H	-5.79374300	2.13596900	3.16854200
H	-4.13026200	1.62045100	3.48675000
H	-4.66596200	3.25842000	3.92934600
C	3.53880000	-1.02251700	3.29043000
C	3.91143300	-2.16115700	4.02519200
C	4.40752200	0.08167600	3.30351200
C	5.10236700	-2.19095000	4.74864100
H	3.26762000	-3.03533100	4.03523700
C	5.59606700	0.05561000	4.03108400
H	4.14856000	0.96591200	2.72718000
C	5.94982300	-1.08142700	4.75881900
H	5.36752700	-3.08403700	5.30903800
H	6.24903300	0.92497000	4.02669300
H	6.87637500	-1.10430800	5.32666800
C	-2.67246600	4.70318900	2.49731500
H	-1.64251200	5.06494800	2.47779000
H	-3.31677100	5.49434900	2.08869700
H	-2.94729100	4.56411800	3.54680800
H	-2.27359300	2.60319600	2.17291500
H	-4.99536300	3.75554800	1.45136900
C	-1.64262100	-2.56806700	-4.04993000
H	-2.49895700	-3.12561000	-3.66458500
H	-1.88842100	-2.22794000	-5.06605300
H	-0.80641000	-3.26887000	-4.12725800
H	-0.41320700	-0.18527200	-4.76827000

● **1da**-*SS* (MeH)



B3LYP/6-31G*

E = –3797.841891

Zero-point correction = 1.340835 (Hartree/Particle)

Thermal correction to Energy = 1.419647

Thermal correction to Enthalpy = 1.420591

Thermal correction to Gibbs Free Energy = 1.218302

Sum of electronic and zero-point Energies = –3796.501056

Sum of electronic and thermal Energies = –3796.422244

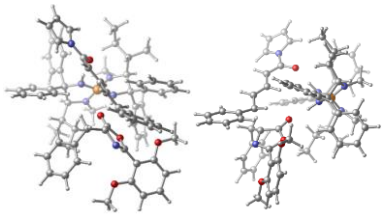
Sum of electronic and thermal Enthalpies = –3796.421300

Sum of electronic and thermal Free Energies = –3796.623589

0 1

O	0.67612400	-0.70839400	-0.26191000
C	1.88415800	-0.83862000	-0.08474300
C	2.68634900	-1.73540800	0.75236300
O	2.77377000	0.08255200	-0.62200000
N	4.04672800	-1.41041000	0.49164100
C	4.04361900	-0.36840200	-0.25310100
C	5.18741000	0.37562900	-0.80776800
C	5.34773600	1.75017200	-0.54090500
C	6.13258000	-0.27324700	-1.63053400
C	6.42616300	2.46449300	-1.07796500
C	7.21849300	0.43713300	-2.16193800
C	7.34820300	1.79382900	-1.87867100
O	4.40525800	2.30547600	0.27343000
C	4.50627900	3.69046800	0.58072800
H	5.44924000	3.91707600	1.09465000
H	3.66720100	3.90956100	1.24080000
H	4.42673400	4.30566200	-0.32436800
O	5.89902000	-1.58635800	-1.88095100
C	6.76563100	-2.28022200	-2.76412500
H	7.78567800	-2.34187000	-2.36306000
H	6.79338000	-1.80904700	-3.75540000
H	6.34642500	-3.28335400	-2.85206900
H	6.55613800	3.51904400	-0.87047500
H	7.94934400	-0.05546100	-2.79084100
H	8.18977800	2.34365300	-2.29177000
C	2.35037000	-3.20802200	0.88429200
H	1.30518300	-3.28799800	1.19693600
H	2.96487900	-3.60714100	1.70059200
C	2.58437500	-4.03785000	-0.36643300
C	1.50580200	-4.50126500	-1.13112600
C	3.88393800	-4.38768000	-0.76396300
C	1.71479500	-5.29516500	-2.26199600
C	4.09398800	-5.18570300	-1.88858900
C	3.01057800	-5.64246200	-2.64391300
H	0.49101600	-4.24735600	-0.83468400
H	4.72834500	-4.02202200	-0.18721100
H	0.86189300	-5.65086500	-2.83516600
H	5.10725300	-5.46513900	-2.16957700
H	3.17587300	-6.26881500	-3.51699600
C	2.20225700	-0.95244200	2.54104500
C	1.03869600	-1.60063900	3.09203500
H	2.01630800	0.05574900	2.17220800
H	1.20309400	-2.40998500	3.80093100
C	-0.27329500	-1.28875400	2.78265500
H	-0.45690500	-0.50336800	2.05311800
C	-1.41340900	-1.89845800	3.33324500
H	-1.27630100	-2.66300100	4.09051200
C	-2.71936900	-1.49774200	2.99515100
O	-3.04810000	-0.58830200	2.18421700
N	-3.80738300	-2.16688700	3.65662500
C	-3.79821100	-3.38117700	4.32662500
C	-5.08934900	-1.64902600	3.71046000
C	-5.06373500	-3.62554300	4.80018700
C	-5.88380500	-2.52007200	4.41451000
H	-2.90659200	-3.98594400	4.36959800
H	-5.29277400	-0.69021300	3.26223200
H	-5.37200300	-4.50397800	5.35233300
H	-6.93437200	-2.38237500	4.63502400
H	-0.14870100	1.06076800	-0.25715300
N	-0.93812600	1.71611900	-0.26489000
P	-2.28134800	1.27442700	-1.11005600
N	-2.97973500	2.77834700	-0.98693000
C	-2.24859700	3.70720200	-0.08990800
C	-0.75209800	3.18140000	-0.16400500
C	-4.33832700	3.09069000	-1.41770000
H	-4.63328200	2.41079300	-2.21926000
H	-5.07165100	2.99068300	-0.60968500
H	-4.37307700	4.11768800	-1.80091700
H	-2.27460200	4.69374300	-0.56271100
C	-3.09090900	3.90443700	1.26107100
C	-2.51699000	5.11550600	2.08862100
C	-3.61130100	5.71711000	2.98062500
H	-2.15112000	5.90102400	1.41201100
C	0.08483600	3.55006200	1.07043500
C	0.30842700	2.64429700	2.11316100
C	0.64234300	4.83399300	1.17000800
C	1.05106300	3.01553500	3.23767800
C	1.36853400	5.21275200	2.29830200
C	1.57644800	4.30356300	3.33946700
H	-0.10733900	1.64541400	2.05983000
H	0.50436000	5.54573800	0.36151400
H	1.21193600	2.29083800	4.03082300
H	1.77640500	6.21845900	2.36108300
H	2.14647600	4.59547100	4.21736300
C	0.00098400	3.67959800	-1.43385400
C	1.25389400	3.09787000	-1.70209600
C	-0.47082000	4.65181700	-2.32343500
C	1.99734600	3.46797300	-2.81995800
C	0.27682900	5.02802700	-3.44614600
C	1.51158400	4.43843100	-3.70083400
H	1.66734400	2.34902100	-1.03317500
H	-1.42858800	5.13605300	-2.16805000
H	2.95860000	2.99376800	-2.99840900
H	-0.11723500	5.78612200	-4.11821400
H	2.09072500	4.72987600	-4.57290400
N	-2.78781800	-0.16196900	-0.52704100
C	-3.46645300	-1.01227700	-1.53497900
C	-2.64425400	-0.65121800	-2.84988900
N	-2.40553000	0.80867400	-2.69454000
H	-2.82630300	-0.37217600	0.49071400
C	-2.39079600	1.68676400	-3.85837000
H	-1.53031900	1.49230200	-4.50332200
H	-2.33851700	2.72586800	-3.53001900
H	-3.30893700	1.54790000	-4.44428700
H	-3.28544000	-0.76151800	-3.72853300
C	-1.35971900	-1.50738100	-3.09997000
H	-0.96015700	-1.81227400	-2.12727800
C	-0.22729500	-0.72979400	-3.80679900
H	-0.01017500	0.18206300	-3.24064500
C	1.07705900	-1.52539800	-3.94603400
C	-4.95629200	-0.58428600	-1.62369600
C	-5.66558800	-0.41316200	-2.81860000
C	-5.64598100	-0.39276900	-0.41313900
C	-7.01354900	-0.03509700	-2.80934400
C	-6.98869000	-0.02273600	-0.40269600
C	-7.67973100	0.16574500	-1.60308900
H	-5.18848700	-0.57864400	-3.77916800
H	-5.12407500	-0.54475100	0.52780300
H	-7.53764100	0.09572300	-3.75270500
H	-7.49817800	0.11210800	0.54777100
H	-8.72670900	0.45675400	-1.59546300
C	-3.38817100	-2.48649300	-1.10087300
C	-4.35108700	-3.40679600	-1.54336300
C	-2.37149900	-2.94191000	-0.25048100
C	-4.29195000	-4.74625500	-1.15991500
C	-2.32454900	-4.28011100	0.14693200
C	-3.27876200	-5.18890100	-0.30884200
H	-5.16190200	-3.07593400	-2.18435100
H	-1.61473000	-2.25662800	0.11396700
H	-5.05015900	-5.43895300	-1.51557400
H	-1.54204100	-4.60205800	0.82817100
H	-3.24191000	-6.22816600	0.00629800
H	1.87313600	-0.88294100	-4.33920000
H	1.40896700	-1.91246700	-2.97725300
H	0.97573500	-2.37610000	-4.62794900
H	-3.22568900	6.57555700	3.54216600
H	-4.46554000	6.06521300	2.38589300
H	-3.98786000	4.99194400	3.71006300
C	3.47571700	-1.01060400	3.32069000
C	3.85587100	-2.13774600	4.06896800
C	4.33242600	0.10263000	3.32819200
C	5.04212200	-2.14739200	4.80059300
H	3.22156400	-3.01880400	4.08289600
C	5.51628400	0.09703800	4.06402200
H	4.06830500	0.97764200	2.74026200
C	5.87740800	-1.02862100	4.80554400
H	5.31326600	-3.03205400	5.37140200
H	6.15981400	0.97340900	4.05514000
H	6.80028300	-1.03574900	5.37976300
C	-3.19727600	2.64419700	2.11242500
H	-3.63343400	1.81739300	1.54810500
H	-2.26040300	2.28403300	2.53941500
H	-3.87914000	2.85173500	2.94417500
H	-4.01205800	4.19602800	0.91133400
H	-1.66457200	4.82651500	2.71016900
C	-1.73077200	-2.76572700	-3.90580700
H	-2.57067500	-3.30788800	-3.46645300
H	-2.00299400	-2.49535200	-4.93609600
H	-0.88658200	-3.45931700	-3.95693000
H	-0.55949000	-0.41673500	-4.80787600

- **1da**-*SS* (HEt)



B3LYP/6-31G*

E = –3797.842438

Zero-point correction = 1.341957 (Hartree/Particle)

Thermal correction to Energy = 1.420464

Thermal correction to Enthalpy = 1.421408

Thermal correction to Gibbs Free Energy = 1.219077

Sum of electronic and zero-point Energies = –3796.500481

Sum of electronic and thermal Energies = –3796.421975

Sum of electronic and thermal Enthalpies = –3796.421031

Sum of electronic and thermal Free Energies = –3796.623361

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

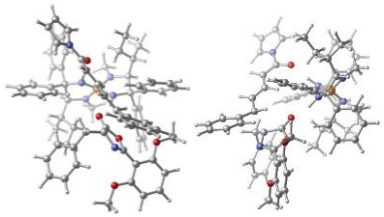
E = –3799.038823

G = –3797.784906

0 1

O	0.82802700	-0.53449600	-0.19224300
C	2.04378200	-0.67681500	-0.08932800
C	2.88273100	-1.62255800	0.65108300
O	2.90883200	0.27046500	-0.62073100
N	4.22814400	-1.27926000	0.35305000
C	4.19282900	-0.19964100	-0.33643100
C	5.31577100	0.56101700	-0.91136200
C	5.51042600	1.91640100	-0.58098100
C	6.20564100	-0.05402000	-1.81749600
C	6.57067200	2.64533000	-1.13418900
C	7.27261100	0.67060900	-2.36769400
C	7.43857700	2.00792900	-2.01807500
O	4.61918200	2.43589500	0.30898700
C	4.72271100	3.81195400	0.64672700
H	5.67903000	4.03386900	1.13821900
H	3.90136200	4.00821900	1.33590500
H	4.61409000	4.44929100	-0.24019500
O	5.93742900	-1.34800100	-2.12583700
C	6.74513800	-2.00600700	-3.08852800
H	7.78544600	-2.09524700	-2.74922000
H	6.72295800	-1.48741900	-4.05612300
H	6.31020400	-3.00017800	-3.19880000
H	6.72794300	3.68504500	-0.87641000
H	7.96056300	0.20422900	-3.06169500
H	8.26598200	2.56868800	-2.44499700
C	2.55353400	-3.10090200	0.73272000
H	1.49433600	-3.19428500	0.98808500
H	3.12462900	-3.51565300	1.57268100
C	2.86232500	-3.91477200	-0.51294800
C	1.83154100	-4.40651500	-1.32310900
C	4.18623000	-4.23621600	-0.85013500
C	2.10863800	-5.20211700	-2.43794000
C	4.46517100	-5.03534000	-1.95899100
C	3.42753300	-5.52215200	-2.75886600
H	0.79920500	-4.16989600	-1.07704200
H	4.99504500	-3.84835900	-0.23842900
H	1.29089500	-5.57832100	-3.04792400
H	5.49648000	-5.29236000	-2.19142500
H	3.64598400	-6.15029400	-3.61893300
C	2.45745200	-0.94835500	2.52227300
C	1.31482600	-1.64393900	3.05635100
H	2.25199200	0.07604800	2.21613200
H	1.49658800	-2.49593700	3.70859600
C	0.00007800	-1.32799200	2.76931300
H	-0.18516400	-0.50170600	2.09062600
C	-1.14334900	-1.98329900	3.25688700
H	-1.02096600	-2.81747100	3.93977800
C	-2.44136600	-1.54960400	2.93595500
O	-2.75712900	-0.54051900	2.23925000
N	-3.53579700	-2.31566900	3.47172800
C	-3.52555300	-3.62963700	3.91388600
C	-4.81525900	-1.81254000	3.63009100
C	-4.78789800	-3.95245400	4.34827200
C	-5.60660400	-2.79423300	4.17541900
H	-2.63567100	-4.23321500	3.83232900
H	-5.02059700	-0.78710300	3.36959100
H	-5.09524900	-4.91558600	4.73465500
H	-6.65394200	-2.69525300	4.42955100
H	-0.21870300	1.07616400	-0.21123000
N	-1.01083100	1.72976800	-0.23726000
P	-2.40548500	1.32156400	-1.00524400
N	-3.13995200	2.76585600	-0.65157200
C	-2.39949700	3.56395300	0.35063500
C	-0.88161600	3.18073500	0.04626400
C	-4.38461700	3.26070600	-1.22677300
H	-4.74258300	2.55701900	-1.98051300
H	-5.16639600	3.37085300	-0.47107800
H	-4.21835800	4.23459800	-1.70618800
H	-2.56776100	4.61500800	0.10110500
C	-2.86156200	3.35105800	1.83357500
C	-4.32583000	2.88058000	1.98384500
C	-4.64903200	2.36724700	3.39296600
H	-4.52066900	2.06335900	1.28269000
C	0.06107100	3.42142200	1.23586700
C	0.24280400	2.45057700	2.22893100
C	0.72484200	4.64967000	1.37690800
C	1.05834000	2.69797700	3.33508100
C	1.52757800	4.90482700	2.48982400
C	1.70059800	3.92838800	3.47365400
H	-0.27086200	1.50020500	2.15302100
H	0.61219300	5.41634200	0.61705300
H	1.18179900	1.92304600	4.08625200
H	2.01842900	5.87026100	2.58515900
H	2.32890500	4.12489900	4.33818000
C	-0.31567300	3.88961300	-1.21268800
C	0.82436600	3.32937600	-1.81739600
C	-0.84219600	5.06196800	-1.76862300
C	1.40058800	3.91081700	-2.94448200
C	-0.26681600	5.64521400	-2.90380800
C	0.85386300	5.07155000	-3.49847300
H	1.27587400	2.43145100	-1.40446900
H	-1.70664100	5.54845500	-1.32888000
H	2.28121000	3.45407900	-3.38803200
H	-0.70176900	6.55216400	-3.31590300
H	1.30087700	5.52410600	-4.37948100
N	-2.81395300	-0.18440300	-0.52780400
C	-3.60729500	-0.93683300	-1.51893500
C	-3.06856400	-0.37284100	-2.91280500
N	-2.68112300	1.02644000	-2.61132700
H	-2.80684800	-0.42774400	0.48153200
C	-2.48655800	1.99315900	-3.68461400
H	-1.57170800	1.79744300	-4.25333400
H	-2.40953700	2.99836800	-3.26549100
H	-3.34020900	1.96356500	-4.37291600
H	-3.92255100	-0.30357100	-3.58962100
C	-1.98844300	-1.20705000	-3.67027700
H	-2.23541500	-2.25726400	-3.47661200
C	-0.55622600	-0.96786400	-3.16103100
H	-0.52368200	-1.13144200	-2.08067900
C	0.50441500	-1.85895000	-3.81784900
C	-5.12048200	-0.63071600	-1.31127200
C	-6.04986600	-0.49019000	-2.35101200
C	-5.59819700	-0.55093300	0.00835800
C	-7.40258300	-0.25164100	-2.08592100
C	-6.94663200	-0.32081400	0.27359700
C	-7.85758400	-0.16207500	-0.77293500
H	-5.74673000	-0.57693500	-3.38976900
H	-4.91279900	-0.67846000	0.84045700
H	-8.09681400	-0.14187900	-2.91517500
H	-7.28448700	-0.27613200	1.30541200
H	-8.90875400	0.01983900	-0.56613400
C	-3.37631700	-2.44819200	-1.33803600
C	-4.24069200	-3.36872100	-1.95087400
C	-2.31598800	-2.93980400	-0.56544500
C	-4.04569000	-4.74115600	-1.80518500
C	-2.13525400	-4.31608600	-0.40370900
C	-2.99312500	-5.22229100	-1.02485500
H	-5.08438400	-3.01410200	-2.53498600
H	-1.62520500	-2.25781300	-0.08292000
H	-4.72884800	-5.43372500	-2.28988600
H	-1.32117500	-4.67291300	0.22106900
H	-2.85019800	-6.29162600	-0.89527000
H	1.47249400	-1.72158000	-3.32593400
H	0.24425900	-2.92040400	-3.73071000
H	0.63873800	-1.63233900	-4.88177000
H	-5.69017800	2.02738800	3.44518000
H	-4.00463600	1.51689400	3.64035700
H	-4.52063100	3.13599600	4.16259900
C	3.76046800	-1.04936800	3.24078800
C	4.15962100	-2.20624000	3.93223600
C	4.63216100	0.05297600	3.24616800
C	5.37940300	-2.25613300	4.60502600
H	3.51382800	-3.07872400	3.94963500
C	5.84938900	0.00663300	3.92307300
H	4.35195300	0.95176600	2.70342400
C	6.22975300	-1.14896000	4.60720600
H	5.66446600	-3.16305000	5.13246100
H	6.50401900	0.87469300	3.91357300
H	7.17888000	-1.18749500	5.13557500
C	-2.63190000	4.64382000	2.63689200
H	-1.60307800	5.00364100	2.56617800
H	-3.29509000	5.44130000	2.27328800
H	-2.85026900	4.49169100	3.69788100
H	-2.25033600	2.55204500	2.26444400
H	-5.01268100	3.70045600	1.72583900
C	-2.11747000	-1.01809500	-5.19600000
H	-1.50455100	-1.75184800	-5.72789000
H	-3.15328500	-1.16248000	-5.52839000
H	-1.79613500	-0.02478400	-5.52894800
H	-0.27943200	0.08409500	-3.31438200

- **1da**-*SS* (EtEt)



B3LYP/6-31G*

E = –3797.843973

Zero-point correction = 1.341576 (Hartree/Particle)

Thermal correction to Energy = 1.420239

Thermal correction to Enthalpy = 1.421184

Thermal correction to Gibbs Free Energy = 1.218851

Sum of electronic and zero-point Energies = –3796.502397

Sum of electronic and thermal Energies = –3796.423733

Sum of electronic and thermal Enthalpies = –3796.422789

Sum of electronic and thermal Free Energies = –3796.625121

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.041826

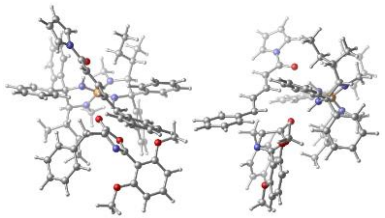
G = –3797.788136

0 1

O	0.77880200	-0.59460200	-0.25254100
C	1.99354500	-0.73681200	-0.13904800
C	2.82897000	-1.71835500	0.55849900
O	2.85967100	0.24694100	-0.59748700
N	4.17665800	-1.34755700	0.30259400
C	4.14344600	-0.22797300	-0.31951500
C	5.26473300	0.58168900	-0.82566600
C	5.41749200	1.92585700	-0.43035300
C	6.19574000	0.02800400	-1.73060400
C	6.47314400	2.70365900	-0.92256500
C	7.25918400	0.80160700	-2.21753600
C	7.38099500	2.12626600	-1.80764800
O	4.49200000	2.38562100	0.45860200
C	4.58539900	3.73461000	0.89766800
H	5.53754100	3.92279400	1.41031200
H	3.75947900	3.87585200	1.59452500
H	4.47777900	4.43478900	0.05961400
O	5.97111700	-1.25738200	-2.10142900
C	6.82804600	-1.85452200	-3.06154800
H	7.85754600	-1.93435700	-2.68878300
H	6.82711900	-1.29584200	-4.00677500
H	6.42162700	-2.85263200	-3.22955700
H	6.59662200	3.73490600	-0.61720300
H	7.97851900	0.38235900	-2.90975200
H	8.20502800	2.72491900	-2.18693600
C	2.51082400	-3.20192300	0.53809100
H	1.45121400	-3.32064000	0.78125000
H	3.08115100	-3.66770000	1.35127000
C	2.83098400	-3.92646700	-0.75832100
C	1.80763400	-4.35784400	-1.61127900
C	4.15791100	-4.22536300	-1.10409100
C	2.09563000	-5.07202000	-2.77725200
C	4.44751100	-4.94346400	-2.26435900
C	3.41748000	-5.37002800	-3.10717600
H	0.77300700	-4.13793800	-1.35857900

H	4.96075900	-3.88406100	-0.45757300
H	1.28418900	-5.40269900	-3.42104000
H	5.48078900	-5.18525700	-2.50430100
H	3.64390900	-5.93528900	-4.00782400
C	2.37389900	-1.16706100	2.45172700
C	1.23230100	-1.90463900	2.92874200
H	2.16150700	-0.12665100	2.21060300
H	1.41653300	-2.79740600	3.52327400
C	-0.08421000	-1.57695500	2.66203400
H	-0.27709900	-0.70517000	2.04345400
C	-1.22102100	-2.26752000	3.11383200
H	-1.08828600	-3.13334300	3.75390100
C	-2.52422900	-1.82343800	2.82863400
O	-2.85023000	-0.79461400	2.17013200
N	-3.61198200	-2.59668400	3.36557200
C	-3.60070200	-3.91623100	3.79093300
C	-4.88660100	-2.09045000	3.54875500
C	-4.85810500	-4.23916400	4.23909300
C	-5.67437400	-3.07529500	4.09279500
H	-2.71461900	-4.52259800	3.69098600
H	-5.09088100	-1.06184500	3.29986000
H	-5.16391800	-5.20569800	4.61819100
H	-6.71796700	-2.97567500	4.36148700
H	-0.18931800	1.07655300	-0.27602400
N	-0.95908800	1.75556100	-0.21625900
P	-2.38773900	1.43913000	-0.96493000
N	-3.04320500	2.91673100	-0.57880500
C	-2.21639400	3.72877700	0.33854700
C	-0.73764600	3.18512600	0.10057500
C	-4.39751400	3.32471800	-0.93553200
H	-4.73415000	2.74957600	-1.80106200
H	-5.11316200	3.15846100	-0.12347800
H	-4.40322500	4.38911300	-1.19804900
H	-2.24506100	4.75728400	-0.03136100
C	-2.73766000	3.79624400	1.81090300
C	-3.23869200	2.44745400	2.36065100
C	-3.45696900	2.43148400	3.87834800
H	-2.52949900	1.65176500	2.12179700
C	0.12777700	3.35428600	1.35758600
C	0.31883700	2.31294500	2.27084000
C	0.68799200	4.60882100	1.64529000
C	1.05056400	2.51416000	3.44430800
C	1.40216500	4.81711800	2.82512600
C	1.59031200	3.76809800	3.72962600
H	-0.12035700	1.34235100	2.08007400
H	0.56271400	5.42933000	0.94446100
H	1.18732600	1.68489300	4.13258200
H	1.81488200	5.80067000	3.03546500
H	2.15056400	3.92845900	4.64674600
C	-0.01736400	3.85260800	-1.10551400
C	1.22995900	3.31862700	-1.47833000
C	-0.51707800	4.92796900	-1.84926200
C	1.94235900	3.83621300	-2.55680500
C	0.19910200	5.45102100	-2.93321600
C	1.42938100	4.90837600	-3.29274100
H	1.66008800	2.49112100	-0.92153800
H	-1.47111600	5.38379800	-1.60571000
H	2.90140200	3.39753900	-2.81887600
H	-0.21508400	6.28687900	-3.49128400
H	1.98463000	5.31445300	-4.13396000
N	-2.85431100	-0.06229800	-0.52744100
C	-3.68102100	-0.76296900	-1.53024100
C	-3.15001400	-0.16998500	-2.91423500
N	-2.71366200	1.20385100	-2.57290200
H	-2.81825800	-0.37900500	0.45964500
C	-2.53889000	2.20540200	-3.61628200
H	-1.64098500	2.02285200	-4.21608500
H	-2.44377700	3.19359800	-3.16222900
H	-3.41073100	2.20517500	-4.28197000
H	-4.01438500	-0.05068000	-3.57073800
C	-2.11073800	-1.00830400	-3.72275600
H	-2.37663500	-2.05779000	-3.55233400
C	-0.65962300	-0.81605700	-3.24768800
H	-0.60257100	-0.99668700	-2.17102600
C	0.35607400	-1.72932700	-3.94385400
C	-5.18013800	-0.41839400	-1.28776900
C	-6.12379700	-0.23599300	-2.30790900
C	-5.62855600	-0.33675100	0.04201900
C	-7.46163500	0.04805500	-2.01455600
C	-6.96251500	-0.05901700	0.33502500
C	-7.88705900	0.14341400	-0.69198100
H	-5.84333000	-0.32384600	-3.35301000
H	-4.93115300	-0.50506700	0.85697900
H	-8.16756100	0.18982100	-2.82893400
H	-7.28013100	-0.01084300	1.37325700
H	-8.92648100	0.36248000	-0.46288700
C	-3.48277200	-2.28441900	-1.40229200
C	-4.39398600	-3.16470800	-2.00575400
C	-2.39917800	-2.82511600	-0.69719600
C	-4.22213500	-4.54539000	-1.91736900
C	-2.24034600	-4.20927000	-0.59326700
C	-3.14506700	-5.07535800	-1.20542600
H	-5.25585200	-2.77300400	-2.53709500
H	-1.67328200	-2.17698800	-0.22008400
H	-4.94222600	-5.20609600	-2.39301300
H	-1.40682700	-4.60353800	-0.01860200
H	-3.01933800	-6.15133600	-1.12066300
H	1.34041100	-1.62954600	-3.47594600
H	0.06397200	-2.78313200	-3.86417800
H	0.46981800	-1.49199500	-5.00774000
H	-3.72130900	1.42029100	4.20348900
H	-2.54154700	2.72126200	4.40921100
H	-4.25822900	3.10845400	4.19658300
C	3.66877900	-1.29737600	3.18196300
C	4.07770100	-2.49255100	3.79805100
C	4.52179000	-0.18468500	3.27530000
C	5.28949100	-2.56946100	4.48276100
H	3.44610800	-3.37405700	3.74586200
C	5.73085800	-0.25815600	3.96444600
H	4.23382800	0.74473500	2.79118500
C	6.12145300	-1.45198800	4.57280000
H	5.58278500	-3.50601500	4.95050500
H	6.37091300	0.61875300	4.02384000
H	7.06417800	-1.51205800	5.11051500
C	-3.78468900	4.91714600	1.97326700
H	-3.42084600	5.86769600	1.56282100
H	-4.73455400	4.68121300	1.48136100
H	-4.00237000	5.08621700	3.03226900
H	-1.87914200	4.10212400	2.41762000
H	-4.17680800	2.17155200	1.86002200
C	-2.27430900	-0.77079200	-5.23829200
H	-1.68889100	-1.49884200	-5.80779300
H	-3.32067800	-0.88564100	-5.54848600
H	-1.94208600	0.22645400	-5.54863100
H	-0.35649700	0.22954100	-3.39551800

- **1da**-*SS* (EtH)



B3LYP/6-31G*

E = –3797.846039

Zero-point correction = 1.340972 (Hartree/Particle)

Thermal correction to Energy = 1.419679

Thermal correction to Enthalpy = 1.420623

Thermal correction to Gibbs Free Energy = 1.218482

Sum of electronic and zero-point Energies = –3796.505067

Sum of electronic and thermal Energies = –3796.426360

Sum of electronic and thermal Enthalpies = –3796.425416

Sum of electronic and thermal Free Energies = –3796.627557

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3799.045637

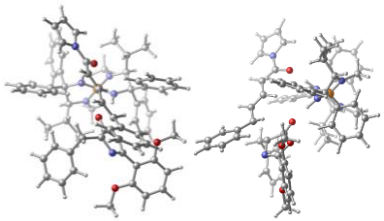
G = –3797.792354

0 1

O	0.70274000	-0.65420300	-0.31882800
C	1.90968600	-0.79958000	-0.14396400
C	2.70673100	-1.77666700	0.60066300
O	2.80252800	0.17191100	-0.57800300
N	4.06799800	-1.42899000	0.38315700
C	4.06984700	-0.31515600	-0.24982000
C	5.21703400	0.48005800	-0.71929900
C	5.37305200	1.82224700	-0.31862600
C	6.17025800	-0.08528900	-1.59293800
C	6.45418600	2.58672500	-0.77495500
C	7.25916400	0.67468100	-2.04362400
C	7.38380700	1.99776400	-1.62939800
O	4.42302800	2.29423600	0.53828000
C	4.52527400	3.63844400	0.99159600
H	5.46369100	3.80511500	1.53581500
H	3.68040300	3.78914000	1.66333100
H	4.45652700	4.34687800	0.15658200
O	5.94169700	-1.36814100	-1.97118000
C	6.82162800	-1.97479100	-2.90409500
H	7.83664500	-2.07157600	-2.49728400
H	6.86070200	-1.41330500	-3.84677700
H	6.40657500	-2.96613000	-3.09041500
H	6.58017300	3.61648300	-0.46554100
H	7.99631500	0.24639700	-2.71116900
H	8.22753600	2.58595200	-1.98065900
C	2.36296700	-3.25343000	0.58428100
H	1.31047000	-3.35615000	0.86462300
H	2.95689300	-3.73448800	1.37112300
C	2.62014200	-3.96078900	-0.73527400
C	1.55654900	-4.34698300	-1.56136400
C	3.92713700	-4.27488800	-1.13836900
C	1.78741600	-5.03073000	-2.75802100
C	4.15893800	-4.96340300	-2.32905300
C	3.09028400	-5.34374200	-3.14542400
H	0.53626400	-4.11980600	-1.26134300
H	4.76009500	-3.96792800	-0.51276800
H	0.94597700	-5.32813300	-3.37932500
H	5.17736800	-5.21765900	-2.61520300
H	3.27236000	-5.88519300	-4.07040600
C	2.21411100	-1.17722400	2.46783100
C	1.04480300	-1.87313000	2.93842300
H	2.03452500	-0.13624700	2.20160800
H	1.19735200	-2.75904800	3.55190200
C	-0.26154900	-1.50716100	2.66751600
H	-0.43000400	-0.63982300	2.03348000
C	-1.41237200	-2.15395400	3.14818900
H	-1.28825800	-3.00171400	3.81332600
C	-2.71025100	-1.69319000	2.86165200
O	-3.02191500	-0.69386800	2.15428800
N	-3.81108900	-2.40728700	3.44978600
C	-3.81901500	-3.67239600	4.01927800
C	-5.08985100	-1.88441600	3.53416900
C	-5.09109800	-3.94335600	4.45876200
C	-5.89840500	-2.80311500	4.15652600
H	-2.93322400	-4.28688200	4.02393800
H	-5.28308300	-0.89223100	3.16060000
H	-5.41167800	-4.86079800	4.93523600
H	-6.95032300	-2.67511900	4.37628200
H	-0.11157000	1.09931100	-0.21592300
N	-0.88973000	1.76703800	-0.15832700
P	-2.26103100	1.41313000	-0.99749600
N	-2.94709800	2.90124700	-0.72164100
C	-2.17265600	3.75740900	0.20501100
C	-0.68242100	3.21404500	0.06661500
C	-4.29467300	3.27259200	-1.14007800
H	-4.59726200	2.65792800	-1.99033000
H	-5.03359100	3.12911000	-0.34520300
H	-4.30615300	4.32495200	-1.44704900
H	-2.18920600	4.77029800	-0.20729900
C	-2.76415600	3.87890400	1.64670200
C	-3.27838700	2.54896500	2.22962400
C	-3.57952000	2.59701900	3.73227500
H	-2.54860300	1.75327400	2.06367600
C	0.13429200	3.46987600	1.34105900
C	0.32916200	2.47901800	2.30910100
C	0.65703100	4.75094200	1.57841200
C	1.02738200	2.75803200	3.48736600
C	1.33776500	5.03600300	2.76159100
C	1.52916200	4.03808900	3.72165200
H	-0.08068200	1.48810200	2.15699600
H	0.52984600	5.53159300	0.83353900
H	1.16871000	1.96882400	4.22043500
H	1.72298400	6.03835700	2.93086700
H	2.06327000	4.25791000	4.64207800
C	0.08123800	3.80771900	-1.15126700
C	1.34278200	3.25781500	-1.44417000
C	-0.39373300	4.83138300	-1.97943500
C	2.09227200	3.70868200	-2.52765000
C	0.36040700	5.28902400	-3.06694800
C	1.60401000	4.73030800	-3.34725900
H	1.75577700	2.46940800	-0.82206900
H	-1.35828400	5.29435100	-1.80125300
H	3.06035900	3.25753800	-2.72762400
H	-0.03529800	6.08608600	-3.69126500
H	2.18818800	5.08497300	-4.19212100
N	-2.76895200	-0.06657300	-0.53296700
C	-3.47587500	-0.81706500	-1.59866200
C	-2.67023400	-0.35041700	-2.89056400
N	-2.41894800	1.08811500	-2.61407300
H	-2.81445600	-0.35342500	0.46432800
C	-2.41199400	2.06421900	-3.69665500
H	-1.56031900	1.92449600	-4.36740900
H	-2.34886800	3.07026700	-3.27908800
H	-3.33798300	1.98284400	-4.28115800
H	-3.32535100	-0.38111700	-3.76522300

C	-1.39475100	-1.18958400	-3.23037300
H	-0.99261400	-1.59000000	-2.29398700
C	-0.25951600	-0.35779800	-3.86775900
H	-0.04003400	0.50164700	-3.22572700
C	1.04260400	-1.14185000	-4.07384800
C	-4.96097200	-0.36542100	-1.62658600
C	-5.69026200	-0.10308700	-2.79286400
C	-5.62606800	-0.25202900	-0.39281000
C	-7.03351500	0.28614000	-2.73116100
C	-6.96453600	0.12896600	-0.33069400
C	-7.67549600	0.40733000	-1.50132600
H	-5.23311300	-0.20491700	-3.77188600
H	-5.08861700	-0.47226100	0.52552900
H	-7.57344300	0.48845700	-3.65272400
H	-7.45482500	0.20167000	0.63650300
H	-8.71904300	0.70670000	-1.45352400
C	-3.40771400	-2.32460000	-1.29913300
C	-4.38023600	-3.19455300	-1.81585700
C	-2.38707500	-2.86257900	-0.50313300
C	-4.32533100	-4.56427200	-1.55953400
C	-2.34330200	-4.23254100	-0.23402900
C	-3.30653400	-5.08998600	-0.76411700
H	-5.19539900	-2.80144100	-2.41503300
H	-1.62491700	-2.21783700	-0.08013400
H	-5.09094700	-5.21683100	-1.97089200
H	-1.55575500	-4.62082500	0.40567800
H	-3.27229000	-6.15457000	-0.54911600
H	1.83877000	-0.47112700	-4.41646100
H	1.37632100	-1.60496900	-3.13971400
H	0.93875000	-1.93505900	-4.82150200
H	-3.85438300	1.59805100	4.08512300
H	-2.69764800	2.91927100	4.30008900
H	-4.40249900	3.27892700	3.97562400
C	3.48590400	-1.32390100	3.23633600
C	3.85575000	-2.52147500	3.87197300
C	4.35351900	-0.22484900	3.34970200
C	5.04355400	-2.61316900	4.59553500
H	3.21255700	-3.39349000	3.80353700
C	5.53881700	-0.31294200	4.07766800
H	4.09647400	0.70562500	2.85050700
C	5.89025800	-1.50852200	4.70581000
H	5.30675900	-3.55135600	5.07770200
H	6.19073900	0.55405300	4.15182500
H	6.81411400	-1.58022900	5.27395500
C	-3.82618300	4.99580500	1.71454600
H	-3.45339700	5.92960600	1.27463700
H	-4.75363100	4.72842700	1.19648100
H	-4.08813900	5.21226700	2.75481200
H	-1.93613100	4.21815600	2.27808800
H	-4.18508400	2.23749200	1.69352500
C	-1.78380500	-2.36213800	-4.14851900
H	-2.61938500	-2.94090900	-3.74934000
H	-2.07158700	-1.99127300	-5.14258900
H	-0.94467500	-3.05106100	-4.28173800
H	-0.59076500	0.04148600	-4.83793400

● **1ba**-*SS* (HH)



B3LYP/6-31G*

E = –3719.221269

Zero-point correction = 1.284239 (Hartree/Particle)

Thermal correction to Energy = 1.359952

Thermal correction to Enthalpy = 1.360896

Thermal correction to Gibbs Free Energy = 1.164995

Sum of electronic and zero-point Energies = –3717.937030

Sum of electronic and thermal Energies = –3717.861317

Sum of electronic and thermal Enthalpies = –3717.860373

Sum of electronic and thermal Free Energies = –3718.056274

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

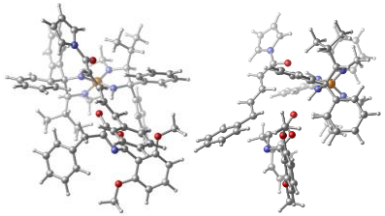
E = –3720.386288

G = –3719.187561

0 1

O	0.68837200	-0.59212600	-0.18805900
C	1.90837500	-0.71726500	-0.13773000
C	2.79378300	-1.73932600	0.42231900
O	2.73833100	0.31646200	-0.56032600
N	4.11831200	-1.34250200	0.09554800
C	4.03760800	-0.16998800	-0.41585400
C	5.12529900	0.70235800	-0.89218200
C	5.33617600	1.96322300	-0.30041200
C	5.96714800	0.29408500	-1.94688900
C	6.36399200	2.80294600	-0.74744400
C	7.00296900	1.12793200	-2.39153700
C	7.18432600	2.36882000	-1.78637300
O	4.49510900	2.27477400	0.72538200
C	4.60814600	3.55538100	1.33156500
H	5.58654800	3.68635600	1.81174600
H	3.82051600	3.59650800	2.08409600
H	4.45136600	4.35695900	0.59883800
O	5.68681500	-0.91687500	-2.49559700
C	6.46099800	-1.36281200	-3.59750500
H	7.51344000	-1.50528700	-3.31999300
H	6.39997600	-0.66489800	-4.44288600
H	6.02839300	-2.32117100	-3.88832800
H	6.53386700	3.77026600	-0.29150200
H	7.65648800	0.82126300	-3.19860100
H	7.98727100	3.01439400	-2.13247000
C	2.46047200	-3.21380800	0.32924800
H	1.45145600	-3.35582100	0.72904600
H	3.15166600	-3.74537800	0.99550900
C	2.55279200	-3.82282900	-1.06118100
C	1.41511300	-4.34958100	-1.68580600
C	3.78480900	-3.91848900	-1.72753900
C	1.50071900	-4.96158500	-2.93969000
C	3.87121000	-4.52851200	-2.97901100
C	2.73051900	-5.05406800	-3.59151600
H	0.45254900	-4.29112500	-1.18291300
H	4.67114400	-3.50117500	-1.25949300
H	0.60613700	-5.37602400	-3.39820000
H	4.83707900	-4.60806000	-3.47351200
H	2.80168900	-5.53647500	-4.56319700
C	2.54326200	-1.30016300	2.39276600
C	1.35627400	-1.92398500	2.91496500
H	2.45147900	-0.22652700	2.23081700
H	1.46571400	-2.86375300	3.45240200
C	0.08452700	-1.40337500	2.76957200
H	-0.01426700	-0.48323800	2.20325500
C	-1.11358800	-1.93354800	3.27951300
H	-1.07749600	-2.82207200	3.90087600
C	-2.34649600	-1.30507100	3.03077400
O	-2.52975400	-0.25748300	2.34555500
N	-3.53092000	-1.89344600	3.59730200
C	-3.69892500	-3.15152800	4.15537000
C	-4.74189300	-1.22469300	3.65779100
C	-5.00389600	-3.27528300	4.56451600
C	-5.66642600	-2.04766600	4.25329900
H	-2.89000900	-3.86392700	4.17845000
H	-4.80404500	-0.21078600	3.29725900
H	-5.43941800	-4.15137800	5.02739500
H	-6.70063000	-1.79899500	4.45305100
H	-0.25054400	1.10976500	0.00194800
N	-1.03979900	1.75660500	-0.09057300
P	-2.36398600	1.29880200	-0.93968500
N	-3.13845600	2.74675800	-0.71680700
C	-2.50260200	3.57471200	0.33841800
C	-0.95665100	3.20817400	0.18604600
C	-4.32753800	3.21047900	-1.42167300
H	-4.61587100	2.47485200	-2.17439200
H	-5.17647300	3.34490300	-0.74751500
H	-4.12107100	4.16517200	-1.92362300
H	-2.66562600	4.61808500	0.05655300
C	-3.10626700	3.37166700	1.76554000
C	-4.60290300	3.01747600	1.76917000
H	-4.82081300	2.11884100	1.18610500
C	-0.12355100	3.43887400	1.45869200
C	-0.07491900	2.46636000	2.46830900
C	0.58230600	4.63603600	1.64824200
C	0.65556300	2.68809800	3.63721500
C	1.29865900	4.86369100	2.82447200
C	1.34137700	3.88901000	3.82375300
H	-0.62978200	1.54084400	2.35548000
H	0.57328200	5.39869900	0.87641300
H	0.67980300	1.91596300	4.40102600
H	1.82679200	5.80498200	2.95546700
H	1.90243500	4.06446000	4.73794300
C	-0.29402700	3.92532800	-1.02041800
C	0.85560400	3.34318900	-1.58346600
C	-0.74382900	5.13718300	-1.56051200
C	1.51389100	3.94009100	-2.65674000
C	-0.08740100	5.73529300	-2.64209800
C	1.04155700	5.13856600	-3.19761800
H	1.25293800	2.41652500	-1.18032700
H	-1.60869000	5.64533700	-1.14672700
H	2.40064100	3.46448600	-3.06695100
H	-0.46530500	6.67227300	-3.04323300
H	1.55176700	5.60246500	-4.03748800
N	-2.83486300	-0.17151000	-0.41325300
C	-3.49497800	-0.99233300	-1.45126200
C	-2.66134700	-0.57075900	-2.74269000
N	-2.45684800	0.88943100	-2.53975900
H	-2.83453100	-0.37929200	0.60227000
C	-2.35228900	1.80228700	-3.67162800
H	-1.47858600	1.58406700	-4.29010800
H	-2.25547700	2.82697900	-3.30680300
H	-3.25226300	1.73655900	-4.29757900
H	-3.28101100	-0.67292900	-3.63787300
C	-1.35222400	-1.38991900	-2.97382700
H	-0.98923700	-1.72595900	-1.99813400
C	-0.19781900	-0.59347000	-3.60285900
H	0.06631100	0.29147100	-3.01802900
C	-4.99024800	-0.58283400	-1.54461000
C	-5.68258100	-0.36852000	-2.74250700
C	-5.70557100	-0.45720000	-0.34092400
C	-7.03742300	-0.01586300	-2.74045000
C	-7.05484000	-0.11205700	-0.33628300
C	-7.72860800	0.11750800	-1.53907700
H	-5.18622500	-0.48018200	-3.70083300
H	-5.20280100	-0.64170500	0.60421800
H	-7.54712400	0.14871400	-3.68639300
H	-7.58125300	-0.02890600	0.61070600
H	-8.78075700	0.38908100	-1.53724400
C	-3.40077100	-2.48091300	-1.07574900
C	-4.32182900	-3.40252200	-1.59742500
C	-2.40919800	-2.94984600	-0.20315300
C	-4.24465900	-4.75577300	-1.27037400
C	-2.34281400	-4.30367100	0.13535000
C	-3.25456700	-5.21296800	-0.39923100
H	-5.11361600	-3.06191500	-2.25711400
H	-1.68353700	-2.26575500	0.22235400
H	-4.96985100	-5.44962000	-1.68740400
H	-1.57789600	-4.63635900	0.83150800
H	-3.20307900	-6.26479000	-0.13121200
C	3.86023600	-1.64745000	3.00238000
C	4.14969900	-2.92785300	3.50520600
C	4.85585000	-0.66112700	3.10479800
C	5.38369200	-3.20794100	4.09047200
H	3.40553600	-3.71595500	3.44365100
C	6.08757600	-0.93778000	3.69461500
H	4.65867400	0.33125000	2.70866800
C	6.35860900	-2.21390500	4.19102300
H	5.58204400	-4.20637300	4.47226800
H	6.83889700	-0.15495200	3.76382900
H	7.31893700	-2.43221500	4.65103500
C	-2.89852200	4.62898700	2.62850900
H	-1.85134900	4.92745100	2.70548900
H	-3.46331300	5.47583100	2.21380400
H	-3.26927500	4.45426000	3.64465400
H	-2.59698300	2.52476800	2.23471600
H	-5.22388800	3.84138800	1.39452400
C	-1.64150300	-2.62136900	-3.84963300
H	-2.42508300	-3.25996400	-3.43511500
H	-1.95229900	-2.31262200	-4.85787000
H	-0.73558800	-3.22740600	-3.95396600
H	-0.41906200	-0.28781600	-4.63371700
H	-4.91644900	2.82313100	2.80095400
H	0.68996900	-1.23358700	-3.63934900

● **1ba**-*SS* (MeH)



B3LYP/6-31G*

E = –3719.222543

Zero-point correction = 1.284083 (Hartree/Particle)

Thermal correction to Energy = 1.359878

Thermal correction to Enthalpy = 1.360822

Thermal correction to Gibbs Free Energy = 1.164880

Sum of electronic and zero-point Energies = –3717.938460

Sum of electronic and thermal Energies = –3717.862665

Sum of electronic and thermal Enthalpies = –3717.861721

Sum of electronic and thermal Free Energies = –3718.057663

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

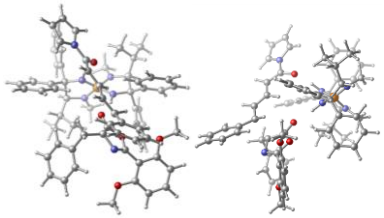
E = –3720.3882

G = –3719.189581

0 1

O	0.68817800	-0.62159000	-0.22449300
C	1.90815500	-0.74520200	-0.17569400
C	2.79768000	-1.80177100	0.31141400
O	2.73685900	0.31918300	-0.51514900
N	4.12127400	-1.37995000	0.01337000
C	4.03728600	-0.17097200	-0.40404700
C	5.11797200	0.74698700	-0.80235000
C	5.28039400	1.98329100	-0.14474100
C	5.99934500	0.41186900	-1.85129300
C	6.29512000	2.87069500	-0.52513200
C	7.02305600	1.29310300	-2.22756500
C	7.15369700	2.50858800	-1.56109400
O	4.40587300	2.22416200	0.87358400
C	4.48214600	3.46898400	1.55778200
H	5.45176500	3.59196800	2.05711100
H	3.68577800	3.44663700	2.30197000
H	4.31371000	4.30926100	0.87292500
O	5.76676800	-0.77754400	-2.46415400
C	6.57457000	-1.14591200	-3.57041600
H	7.62492100	-1.27407700	-3.27850800
H	6.51009200	-0.40807200	-4.38085200
H	6.17492500	-2.09964700	-3.91818800
H	6.42574500	3.81926100	-0.01978800
H	7.70509500	1.04240400	-3.03046600
H	7.94650500	3.19144500	-1.85490000
C	2.46311500	-3.26516900	0.11382000
H	1.46231300	-3.43823900	0.52179200
H	3.16824900	-3.84506900	0.72230600
C	2.52494500	-3.75971500	-1.32253900
C	1.36956700	-4.21456400	-1.97082900
C	3.74462100	-3.81244100	-2.01556100
C	1.42659600	-4.71441400	-3.27501400
C	3.80225000	-4.30938600	-3.31763400
C	2.64421400	-4.76339500	-3.95408900
H	0.41654800	-4.18784200	-1.44712600
H	4.64447700	-3.45071400	-1.52719000
H	0.51946300	-5.07631800	-3.75300200
H	4.75825300	-4.35498100	-3.83507400
H	2.69241500	-5.15746100	-4.96616700
C	2.56387700	-1.49516900	2.30460400
C	1.38595200	-2.16038400	2.79464900
H	2.46541800	-0.41345800	2.21603300
H	1.50854900	-3.12963100	3.27399300
C	0.10838400	-1.64638700	2.68373600
H	-0.00563000	-0.69456200	2.17387000
C	-1.07871500	-2.22607500	3.16388900
H	-1.02542700	-3.14731500	3.73426100
C	-2.32185000	-1.60496200	2.95510300
O	-2.51976500	-0.51986300	2.33664300
N	-3.49325400	-2.24585400	3.48892700
C	-3.64087600	-3.54858000	3.94048300
C	-4.70729100	-1.59586700	3.62930200
C	-4.93652800	-3.71845200	4.36245500
C	-5.61366100	-2.47449700	4.17048800
H	-2.82646500	-4.25293900	3.88482600
H	-4.78564800	-0.55539100	3.35880500
H	-5.35679100	-4.63502100	4.75589600
H	-6.64544600	-2.25286000	4.41047100
H	-0.24747600	1.09685400	-0.02189100
N	-1.02751200	1.76434300	-0.00302000
P	-2.38402000	1.41407400	-0.85422500
N	-3.06448900	2.91039800	-0.60958900
C	-2.32435700	3.75748900	0.35178200
C	-0.83201300	3.20149400	0.28519100
C	-4.38465600	3.30275000	-1.08946800
H	-4.67593000	2.66464600	-1.92615700
H	-5.15475500	3.21109000	-0.31684200
H	-4.35623500	4.34299700	-1.43572400
H	-2.30737300	4.76971100	-0.06110100
C	-2.99267600	3.89665200	1.75823900
C	-3.64872800	2.61787500	2.29469100
H	-2.96254200	1.77083700	2.35986900
C	-0.09169200	3.37985700	1.61895600
C	-0.07412100	2.36290900	2.58242700
C	0.53481000	4.59973500	1.91492000
C	0.56743000	2.55768200	3.80797300
C	1.15889300	4.79969200	3.14658900
C	1.18388200	3.77558300	4.09692400
H	-0.58716500	1.42635100	2.39164900
H	0.53860000	5.39729100	1.17749000
H	0.57462300	1.75164600	4.53635500
H	1.62968000	5.75599900	3.36066100
H	1.67490100	3.92842400	5.05439800
C	-0.00035000	3.83023300	-0.86812000
C	1.29523200	3.32213900	-1.07192000
C	-0.45247200	4.83121000	-1.73633600
C	2.10282400	3.79326400	-2.10368700
C	0.35944900	5.31033500	-2.77162400
C	1.63860300	4.79509100	-2.96053200
H	1.68664100	2.54614700	-0.42204900
H	-1.44324200	5.25974500	-1.63193800
H	3.09559500	3.37182600	-2.23507400
H	-0.01942900	6.09017200	-3.42743400
H	2.26768800	5.16684000	-3.76489800
N	-2.92458600	-0.04848900	-0.37215900
C	-3.60756900	-0.82026100	-1.43580700
C	-2.77825300	-0.37623300	-2.72149000
N	-2.52638600	1.06550000	-2.46627700
H	-2.87022300	-0.34444400	0.62104800
C	-2.45324800	2.01629700	-3.56820000
H	-1.60887400	1.80586800	-4.22917300
H	-2.32498200	3.02444100	-3.17027600
H	-3.37905600	1.98497600	-4.15834200
H	-3.41496600	-0.42359600	-3.60917500
C	-1.49677600	-1.22033400	-3.01047500
H	-1.12351500	-1.60589100	-2.05726000
C	-0.33365400	-0.42868500	-3.63030200
H	-0.02976700	0.42146700	-3.01386400
C	-5.09219600	-0.37047300	-1.49733100
C	-5.79744900	-0.11308600	-2.67916500
C	-5.78349300	-0.24810200	-0.27941500
C	-7.14076600	0.27969300	-2.64696200
C	-7.12178200	0.13577000	-0.24494100
C	-7.80773500	0.40962100	-1.43152400
H	-5.32059100	-0.22074700	-3.64788900
H	-5.26739500	-0.46520500	0.65127900
H	-7.66101400	0.47829400	-3.58054100
H	-7.63088000	0.21507600	0.71188300
H	-8.85110500	0.71220700	-1.40672400
C	-3.54022700	-2.32357800	-1.11909700
C	-4.49987700	-3.20187900	-1.64563000
C	-2.52612200	-2.85220500	-0.30852800
C	-4.43824700	-4.57038900	-1.38437800
C	-2.47448000	-4.22112000	-0.03603800
C	-3.42466300	-5.08688700	-0.57602500
H	-5.30870300	-2.81663900	-2.25831400
H	-1.77233400	-2.20385800	0.12348000
H	-5.19349700	-5.22981600	-1.80390500
H	-1.69065300	-4.59914300	0.61421300
H	-3.38457200	-6.15099200	-0.35953400
C	3.88636500	-1.87460300	2.88269800
C	4.19487400	-3.19066100	3.26827300
C	4.86681900	-0.88681400	3.07480300
C	5.43291400	-3.50400100	3.82718900
H	3.46246900	-3.98070700	3.13306300
C	6.10247400	-1.19685100	3.63960700
H	4.65453200	0.13422600	2.76935900
C	6.39259300	-2.50839100	4.01896900
H	5.64667000	-4.52983500	4.11693200
H	6.84180500	-0.41224200	3.78063200
H	7.35608500	-2.75291800	4.45871100
C	-3.98534000	5.07665700	1.78173200
H	-3.51061100	6.00969800	1.45259700
H	-4.86185600	4.90538600	1.14719800
H	-4.35129000	5.23636500	2.80224600
H	-2.18843800	4.17016300	2.44763500
H	-4.50046300	2.30889700	1.67672700
C	-1.83673000	-2.40712600	-3.92852200
H	-2.62434200	-3.04515400	-3.52082500
H	-2.16537600	-2.04849000	-4.91427600
H	-0.94783700	-3.02746000	-4.08267500
H	-0.56845100	-0.07075700	-4.64108100
H	0.53392400	-1.09149800	-3.71548700
H	-4.03446600	2.80351400	3.30413300

● **1ba**-*SS* (MeMe)



B3LYP/6-31G*

E = –3719.221138

Zero-point correction = 1.283904 (Hartree/Particle)

Thermal correction to Energy = 1.359739

Thermal correction to Enthalpy = 1.360683

Thermal correction to Gibbs Free Energy = 1.164759

Sum of electronic and zero-point Energies = –3717.937234

Sum of electronic and thermal Energies = –3717.861399

Sum of electronic and thermal Enthalpies = –3717.860455

Sum of electronic and thermal Free Energies = –3718.056378

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3720.385301

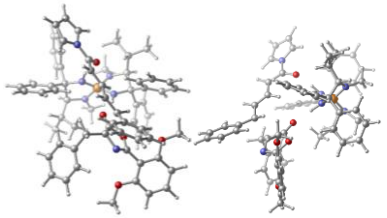
G = –3719.186807

0 1

O	0.80040000	-0.49400500	-0.15767000
C	2.01798800	-0.64791600	-0.14668000
C	2.88434400	-1.77417300	0.20371400
O	2.86865800	0.42571500	-0.38537700
N	4.21359300	-1.35532800	-0.06368600
C	4.15721500	-0.10747400	-0.35117500
C	5.25946200	0.81139300	-0.68387200
C	5.49952000	1.95351200	0.10517400
C	6.08776400	0.56527200	-1.79840400
C	6.54267000	2.83471600	-0.20630500
C	7.13754900	1.44106000	-2.10974400
C	7.34812500	2.56146300	-1.30992300
O	4.66921700	2.10803300	1.17454700
C	4.81237500	3.26553000	1.98663600
H	5.79243300	3.28985800	2.48066300
H	4.02275700	3.19875800	2.73534300
H	4.67715000	4.18282500	1.40003200
O	5.77887800	-0.53369700	-2.53367800
C	6.53148500	-0.80873700	-3.70397700
H	7.58425000	-1.01213300	-3.46855300
H	6.47426800	0.01762300	-4.42473700
H	6.07645400	-1.69989600	-4.13858000
H	6.73480800	3.70929700	0.40241700
H	7.77908900	1.25823500	-2.96280500
H	8.16240700	3.23941800	-1.55195200
C	2.51167700	-3.19907300	-0.15039300
H	1.49873200	-3.38254700	0.22084100
H	3.18751700	-3.86125900	0.40476400
C	2.59107700	-3.54011600	-1.62959300
C	1.43188500	-3.81827400	-2.36466700
C	3.83095500	-3.61944700	-2.28269000
C	1.50335800	-4.16639900	-3.71637000
C	3.90438100	-3.97049300	-3.63060300
C	2.74112700	-4.24483600	-4.35473300
H	0.46274200	-3.76761000	-1.87394500

H	4.73544900	-3.39271700	-1.72634900
H	0.59048200	-4.38599900	-4.26507700
H	4.87537300	-4.04402300	-4.11596200
H	2.80070900	-4.52387400	-5.40384900
C	2.66523400	-1.69717700	2.23676400
C	1.47805600	-2.39801400	2.64633700
H	2.58331400	-0.61137600	2.26833400
H	1.58579100	-3.41453900	3.01957300
C	0.20668800	-1.86304400	2.57076600
H	0.11096100	-0.86402600	2.15894500
C	-0.99462800	-2.47542700	2.96892800
H	-0.96368100	-3.44738900	3.45029400
C	-2.22780600	-1.82475000	2.80062800
O	-2.41381200	-0.68332200	2.28962600
N	-3.41098800	-2.50978400	3.25539000
C	-3.59199800	-3.86381000	3.48489000
C	-4.59523700	-1.85457700	3.54492300
C	-4.88110500	-4.06362500	3.91614200
C	-5.51746300	-2.78521300	3.96190800
H	-2.80536700	-4.57082000	3.27424300
H	-4.64197600	-0.78076100	3.45945400
H	-5.32391000	-5.02059600	4.15994500
H	-6.53096300	-2.57528300	4.27865100
H	-0.32172800	1.06651100	-0.08414300
N	-1.08278500	1.75695900	-0.04468400
P	-2.51795000	1.48264700	-0.78272100
N	-3.14238100	2.96712200	-0.36916700
C	-2.31412100	3.72948600	0.58814900
C	-0.84301600	3.15637900	0.37054600
C	-4.47226600	3.43582600	-0.73906200
H	-4.82893200	2.87295100	-1.60371100
H	-5.20112100	3.30918700	0.06844600
H	-4.42687800	4.49875900	-1.00575500
H	-2.30500200	4.76735100	0.24535500
C	-2.87916000	3.77933100	2.04546000
C	-3.53304200	2.47903500	2.53264300
H	-2.86784700	1.61361400	2.49242800
C	-0.02192300	3.19717800	1.66788400
C	0.01481700	2.10201500	2.54034800
C	0.64682400	4.37465800	2.03409000
C	0.71068600	2.18173900	3.74890700
C	1.32651000	4.45897300	3.24942500
C	1.36521000	3.35964600	4.11095100
H	-0.52637200	1.19415400	2.29650000
H	0.63538000	5.23182500	1.36709600
H	0.72823400	1.31825000	4.40806400
H	1.82756600	5.38488300	3.52075300
H	1.89500000	3.42360800	5.05792900
C	-0.06722300	3.87339300	-0.76957600
C	1.19967200	3.35791600	-1.09837300
C	-0.54357900	4.95973800	-1.51305300
C	1.95576700	3.90512800	-2.13094100
C	0.21662800	5.51331400	-2.55081100
C	1.46750300	4.98982300	-2.86498800
H	1.60768700	2.51861300	-0.54380900
H	-1.51304100	5.40102300	-1.30671000
H	2.92943600	3.47934700	-2.35764100
H	-0.17958900	6.35809700	-3.10860700
H	2.05718900	5.42023600	-3.66997600
N	-3.00896800	-0.01516200	-0.36232900
C	-3.82457900	-0.70812000	-1.38034400
C	-3.28466800	-0.09894600	-2.75043100
N	-2.87316800	1.27836300	-2.39253500
H	-2.91861100	-0.35001500	0.61587800
C	-2.65270400	2.28522100	-3.42268200
H	-1.73511000	2.10360600	-3.99218500
H	-2.56888300	3.26936400	-2.95694400
H	-3.50012800	2.29600400	-4.11887400
H	-4.13748900	-0.00575200	-3.42785000
C	-2.21171400	-0.91789300	-3.53406800
H	-2.46929400	-1.97056000	-3.38137300
C	-0.77553900	-0.71250100	-3.04162100
H	-0.65721500	-0.94297500	-1.98147300
C	-5.32132800	-0.38110100	-1.11067800
C	-6.19909400	0.21974500	-2.01986400
C	-5.82087400	-0.71417600	0.16119200
C	-7.52940900	0.48592400	-1.67103700
C	-7.14233700	-0.45338600	0.50943400
C	-8.00715600	0.15154300	-0.40750100
H	-5.87419300	0.49420300	-3.01772000
H	-5.17094600	-1.18946200	0.89013100
H	-8.18736500	0.95335900	-2.39931300
H	-7.49469800	-0.73279500	1.49860100
H	-9.04052000	0.35403500	-0.13898400
C	-3.62064100	-2.22798500	-1.29314700
C	-4.52598100	-3.08304800	-1.94091000
C	-2.54068700	-2.79219200	-0.60361900
C	-4.34883500	-4.46514000	-1.91224200
C	-2.37551800	-4.17947200	-0.56065500
C	-3.27201500	-5.02059700	-1.21786800
H	-5.38310600	-2.66589900	-2.46224500
H	-1.82368800	-2.16216700	-0.09004700
H	-5.06168400	-5.10822600	-2.42171300
H	-1.54264800	-4.59389300	0.00048800
H	-3.14052600	-6.09865800	-1.18248900
C	3.98549900	-2.16286100	2.74897600
C	4.26797800	-3.51815200	2.99351000
C	4.99423100	-1.22252300	3.01910500
C	5.50752900	-3.91517300	3.49252700
H	3.51370300	-4.27315800	2.79430800
C	6.23170000	-1.61701700	3.52368700
H	4.80304400	-0.17134300	2.82110100
C	6.49524600	-2.96661900	3.76364700
H	5.70054800	-4.96974500	3.67307000
H	6.99341300	-0.86836900	3.72714400
H	7.46013000	-3.27667400	4.15654900
C	-3.83653200	4.97472800	2.22629600
H	-3.36468200	5.91894100	1.92618500
H	-4.76343600	4.86591800	1.65254600
H	-4.11917200	5.06954200	3.28082100
H	-2.02386100	3.98370600	2.69574100
H	-4.43248300	2.23408200	1.95489000
C	-2.31859600	-0.67605100	-5.05292500
H	-1.64456000	-1.35623500	-5.58569200
H	-3.33499100	-0.86431700	-5.42155500
H	-2.04097700	0.34351500	-5.34180300
H	-0.43394100	0.31764900	-3.19810800
H	-3.84530200	2.59985500	3.57673400
H	-0.09245000	-1.36871700	-3.59177900

1ba-*SS* (HMe)



B3LYP/6-31G*

E = –3719.220135

Zero-point correction = 1.284550 (Hartree/Particle)

Thermal correction to Energy = 1.360151

Thermal correction to Enthalpy = 1.361095

Thermal correction to Gibbs Free Energy = 1.166366

Sum of electronic and zero-point Energies = –3717.935585

Sum of electronic and thermal Energies = –3717.859984

Sum of electronic and thermal Enthalpies = –3717.859040

Sum of electronic and thermal Free Energies = –3718.053768

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3720.384062

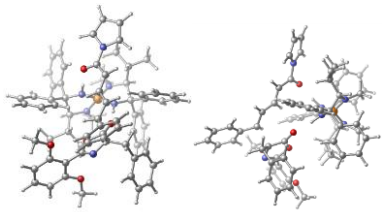
G = –3719.184179

0 1

O	0.80449700	-0.46969800	-0.12950400
C	2.02266800	-0.62448800	-0.12175500
C	2.88750500	-1.73062400	0.28744000
O	2.87188800	0.42957500	-0.43866700
N	4.21543300	-1.33281200	-0.01515200
C	4.15840300	-0.10643000	-0.38381600
C	5.26472500	0.77762800	-0.79310700
C	5.57529900	1.92898900	-0.04518100
C	6.02703700	0.48285600	-1.94155600
C	6.62712300	2.77091500	-0.42833200
C	7.08413900	1.31957100	-2.32646800
C	7.36720900	2.45005800	-1.56417900
O	4.80259300	2.13451600	1.05816600
C	5.01990200	3.30699200	1.83032700
H	6.02003900	3.30977600	2.28305600
H	4.26020800	3.28831000	2.61191500
H	4.89231600	4.21301600	1.22464900
O	5.64999600	-0.62393400	-2.63298800
C	6.34266900	-0.95511900	-3.82547800
H	7.39970100	-1.17775900	-3.62979900
H	6.27392500	-0.15054100	-4.56958800
H	5.84736100	-1.84789600	-4.20981300
H	6.87575100	3.65301800	0.14824700
H	7.67611500	1.10007700	-3.20632100
H	8.18721300	3.09814400	-1.86234600
C	2.50990300	-3.17356700	0.02408000
H	1.49415900	-3.32849500	0.40075400
H	3.18004000	-3.80116200	0.62447900
C	2.59550300	-3.61064000	-1.42960400
C	1.43901100	-3.93041600	-2.15171200
C	3.83825400	-3.73941100	-2.06925300
C	1.51559400	-4.36753800	-3.47701500
C	3.91712700	-4.18004400	-3.39042000
C	2.75620000	-4.49527400	-4.10168600
H	0.46732900	-3.84276100	-1.67167100
H	4.74099100	-3.48113100	-1.52407600
H	0.60416800	-4.61783600	-4.01488800
H	4.89061400	-4.29117500	-3.86338400
H	2.81976500	-4.84388500	-5.12956100
C	2.67587900	-1.53610700	2.32077800
C	1.47922300	-2.19323600	2.77298300
H	2.61305500	-0.44924200	2.28734900
H	1.57303700	-3.18632100	3.20789300
C	0.21467100	-1.64604900	2.66700100
H	0.13417600	-0.67483500	2.19214600
C	-0.99478700	-2.21517500	3.10343600
H	-0.97530000	-3.15846800	3.63924100
C	-2.22099100	-1.56041800	2.90010900
O	-2.40015700	-0.44733200	2.32647600
N	-3.41192500	-2.20944800	3.39011300
C	-3.60436600	-3.54410200	3.70812900
C	-4.59493800	-1.52951200	3.62201100
C	-4.89886100	-3.70675600	4.13864800
C	-5.52761200	-2.42439800	4.09091000
H	-2.82015200	-4.26860100	3.55629000
H	-4.63393200	-0.46451700	3.45891200
H	-5.34994400	-4.64228300	4.44302700
H	-6.54255200	-2.18731000	4.38307200
H	-0.31203900	1.07028900	-0.05307000
N	-1.08312100	1.74729400	-0.10681100
P	-2.49553100	1.38194300	-0.84927200
N	-3.20830700	2.82093100	-0.43515100
C	-2.46958800	3.53864700	0.63032100
C	-0.95096700	3.16148000	0.31746900
C	-4.41841000	3.38931200	-1.01592300
H	-4.76156800	2.75525100	-1.83476400
H	-5.22897100	3.46131500	-0.28660400
H	-4.20934400	4.39235000	-1.41086600
H	-2.62619000	4.60633800	0.45628800
C	-2.97127500	3.21986000	2.07606400
C	-4.47209400	2.89190800	2.15650800
H	-4.74975500	2.04677700	1.52085300
C	-0.02539200	3.25154700	1.54248700
C	0.05388900	2.19340300	2.45944100
C	0.72206600	4.41160700	1.79257700
C	0.84803800	2.29904200	3.60258800
C	1.50570600	4.52128700	2.94236400
C	1.57184200	3.46539400	3.85366000
H	-0.52956300	1.29256100	2.30058000
H	0.69079700	5.23906100	1.09136400
H	0.89023600	1.46438500	4.29683000
H	2.06480400	5.43607900	3.12284000
H	2.17918700	3.55174100	4.75109500
C	-0.36038500	3.98107600	-0.86016900
C	0.74445100	3.43938100	-1.54104500
C	-0.82949500	5.23596100	-1.26791300
C	1.34110000	4.11871600	-2.60059400
C	-0.23521100	5.91730300	-2.33664800
C	0.84923500	5.36101900	-3.00994100
H	1.15262900	2.48034900	-1.23581400
H	-1.66008600	5.71311400	-0.75843200
H	2.19587700	3.67511300	-3.10400300
H	-0.62607700	6.88698100	-2.63423900
H	1.31151900	5.88996900	-3.83904100
N	-2.92025900	-0.12903300	-0.40223800
C	-3.73463800	-0.84775200	-1.40119900
C	-3.19726400	-0.26300700	-2.78405300
N	-2.80892800	1.13142500	-2.45901300
H	-2.88006400	-0.38831800	0.60132200
C	-2.56028900	2.11185600	-3.50897000
H	-1.63701200	1.90473000	-4.05965700
H	-2.46781800	3.10608000	-3.06602300
H	-3.39693800	2.12055300	-4.21822900
H	-4.04777000	-0.20103100	-3.46809800
C	-2.10807800	-1.08752000	-3.53764900

H	-2.35641300	-2.13865700	-3.35984600
C	-0.67889300	-0.85617300	-3.03721700
H	-0.57086400	-1.05210900	-1.96914100
C	-5.23490100	-0.52541800	-1.14213400
C	-6.11506100	0.04737400	-2.06718700
C	-5.73586000	-0.83310100	0.13561500
C	-7.44903700	0.30826100	-1.72859200
C	-7.06047700	-0.57564900	0.47464500
C	-7.92793700	-0.00119400	-0.45909800
H	-5.78879000	0.30327600	-3.06955800
H	-5.08614800	-1.28589200	0.87873400
H	-8.10885600	0.75298700	-2.46930400
H	-7.41068200	-0.83402000	1.47018600
H	-8.96394100	0.19813100	-0.19857400
C	-3.52468300	-2.36386800	-1.27465200
C	-4.41177900	-3.24002900	-1.91948600
C	-2.46421700	-2.90415600	-0.53729100
C	-4.23551000	-4.62021200	-1.84159500
C	-2.30044600	-4.28945300	-0.44528500
C	-3.17853800	-5.15198500	-1.09959000
H	-5.25511000	-2.84026600	-2.47601400
H	-1.76106600	-2.25498900	-0.02757200
H	-4.93366300	-5.28017500	-2.34982200
H	-1.48295800	-4.68627300	0.15031000
H	-3.04796400	-6.22820500	-1.02587000
C	3.99132900	-1.99565700	2.84960000
C	4.24985100	-3.33882000	3.17513900
C	5.02153700	-1.06118400	3.05105400
C	5.48644300	-3.72934300	3.68665900
H	3.47935100	-4.08970700	3.02989700
C	6.25599400	-1.44895900	3.56793200
H	4.85006100	-0.02109000	2.78801900
C	6.49541400	-2.78614200	3.88920800
H	5.66035100	-4.77442600	3.93065500
H	7.03469900	-0.70493500	3.71676700
H	7.45808400	-3.09075500	4.29168500
C	-2.67064700	4.38963500	3.02956300
H	-1.61294400	4.65824900	3.05628800
H	-3.24027100	5.28184000	2.73367000
H	-2.97358500	4.13149700	4.05037600
H	-2.45134700	2.32526400	2.43061100
H	-5.09999300	3.75331400	1.89476300
C	-2.20495700	-0.88733700	-5.06325200
H	-1.51860100	-1.57340000	-5.57222100
H	-3.21599300	-1.09761700	-5.43471400
H	-1.93757600	0.12744200	-5.37744400
H	-0.34415200	0.17174400	-3.22084300
H	-4.71782400	2.61866100	3.18877200
H	0.01430000	-1.52324600	-3.56095800

● **1ba**-*RR* (HH)



B3LYP/6-31G*

E = –3719.223806

Zero-point correction = 1.284255 (Hartree/Particle)

Thermal correction to Energy = 1.359867

Thermal correction to Enthalpy = 1.360811

Thermal correction to Gibbs Free Energy = 1.165651

Sum of electronic and zero-point Energies = –3717.939550

Sum of electronic and thermal Energies = –3717.863938

Sum of electronic and thermal Enthalpies = –3717.862994

Sum of electronic and thermal Free Energies = –3718.058154

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

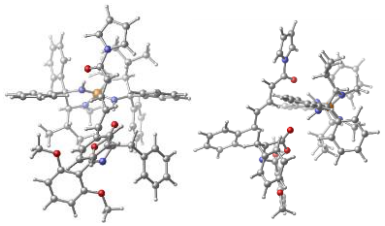
E = –3720.393004

G = –3719.193756

0 1

O	-0.92670200	-1.20608200	-0.08544100
C	-2.06259700	-0.75369300	-0.04075700
C	-3.28141000	-1.25442300	0.56643100
O	-2.37130700	0.51129200	-0.54050900
N	-4.32161900	-0.36375300	0.18868900
C	-3.74984900	0.63220800	-0.38417300
C	-4.37002500	1.85894800	-0.92352600
C	-4.80766800	2.89376800	-0.07740800
C	-4.54779800	1.99362700	-2.31393700
C	-5.42495900	4.03448700	-0.60834800
C	-5.16017300	3.13227200	-2.85216700
C	-5.59161900	4.13590400	-1.98728900
O	-4.58221600	2.71128000	1.25709200
C	-5.06561700	3.69246700	2.16598300
H	-6.15279400	3.81302600	2.08270500
H	-4.57766000	4.66221900	2.00573500
H	-4.81740900	3.32049500	3.16119800
O	-4.09529900	0.94729900	-3.06001100
C	-4.39708800	0.91821900	-4.44753700
H	-5.47854200	0.98227600	-4.62144000
H	-3.89239400	1.72944600	-4.98799500
H	-4.02669100	-0.04268200	-4.80790400
H	-5.76500200	4.83596700	0.03509300
H	-5.30407000	3.23764700	-3.92045000
H	-6.06846700	5.02143800	-2.39881500
C	-3.55110000	-2.74529200	0.55955600
H	-2.74251600	-3.24031200	1.10975600
H	-4.48311400	-2.92799300	1.10334300
C	-3.63708100	-3.32432000	-0.84242300
C	-2.55132600	-4.01302400	-1.40028000
C	-4.79340400	-3.15676400	-1.61784900
C	-2.61849100	-4.52436300	-2.69846900
C	-4.86347300	-3.66758900	-2.91417400
C	-3.77590900	-4.35427000	-3.46008300
H	-1.64704600	-4.14590300	-0.81167200
H	-5.63696500	-2.61370900	-1.19975100
H	-1.76635200	-5.06008900	-3.11012000
H	-5.77154500	-3.53416300	-3.49764300
H	-3.83333100	-4.75819300	-4.46801100
C	-2.90958100	-0.73341800	2.52646900
C	-1.65643200	-1.21472500	3.02249500
H	-2.91840000	0.32871900	2.28160400
H	-1.63586700	-2.16218800	3.55698400
C	-0.47006600	-0.50698500	2.92717500
H	-0.48560300	0.44288200	2.39462700
C	0.75254800	-0.84861600	3.52818400
H	0.79183900	-1.72536800	4.16598200
C	1.88470300	-0.01440200	3.44439600
O	1.99066600	1.06486400	2.80486500
N	3.04709600	-0.41292600	4.20211000
C	4.03500900	0.47434900	4.58644000
C	3.38000900	-1.67318500	4.67472800
C	4.98465700	-0.21259700	5.30413700
C	4.57298800	-1.58069200	5.35211400
H	3.94175300	1.51646800	4.32670400
H	2.76373300	-2.53026400	4.45365700
H	5.87208900	0.21502800	5.75219700
H	5.09406000	-2.40169200	5.82758800
H	0.79871300	-1.09946600	-0.52696800
N	1.80966600	-1.04293000	-0.69400000
P	2.54085400	0.39207400	-0.99650600
N	4.05240200	-0.28322900	-1.08198700
C	4.07616000	-1.71127400	-0.66419500
C	2.62585000	-2.21838100	-1.07641700
C	5.26532600	0.37896100	-1.54829900
H	5.02728800	1.39381200	-1.87104800
H	6.01801900	0.44824300	-0.75985900
H	5.69355400	-0.16888600	-2.39839800
H	4.83640200	-2.20074500	-1.27966700
C	4.45280800	-1.94191400	0.83278100
H	3.52778400	-1.90965600	1.41827000
C	5.38356400	-0.86875900	1.41903300
H	6.37755800	-0.89543700	0.95329200
C	2.14153800	-3.47199700	-0.32713500
C	1.39833100	-3.37949700	0.85680400
C	2.44024400	-4.74878200	-0.83025300
C	0.97619600	-4.53391000	1.52182200
C	2.02553600	-5.89890600	-0.16065700
C	1.28839200	-5.79658700	1.02077400
H	1.13290300	-2.41370400	1.27020800
H	2.99735500	-4.84889900	-1.75647500
H	0.39487700	-4.43386400	2.43443100
H	2.27130700	-6.87532300	-0.56989400
H	0.95551400	-6.69204800	1.53877400
C	2.47926800	-2.46368900	-2.60310600
C	1.17862800	-2.46965800	-3.13771500
C	3.54596400	-2.72137200	-3.47238100
C	0.95634300	-2.70910600	-4.49164700
C	3.32554300	-2.95700900	-4.83484200
C	2.03221400	-2.94980700	-5.35087400
H	0.32809500	-2.29397100	-2.48496200
H	4.56718100	-2.75324900	-3.10688800
H	-0.06179500	-2.71328300	-4.87149300
H	4.17364900	-3.15068600	-5.48665300
H	1.86140300	-3.13620900	-6.40770600
N	1.94201200	1.49306400	0.06057600
C	1.97011200	2.87822900	-0.46912200
C	1.58645800	2.61806200	-1.99210000
N	2.35561600	1.38774100	-2.30798300
H	1.89588100	1.30891900	1.08174600
C	2.87737600	1.16494900	-3.65072600
H	3.41423800	0.21562200	-3.68502600
H	2.07466000	1.11907300	-4.39058900
H	3.56814400	1.97194600	-3.92993700
H	1.99829200	3.41095000	-2.62254400
C	0.05573100	2.51698300	-2.28170500
H	-0.43344400	2.12870200	-1.38450500
C	-0.31890800	1.54712500	-3.41468000
H	0.00215600	1.91575100	-4.39787500
C	0.96911400	3.75216000	0.30580000
C	-0.15970800	3.18949800	0.91627300
C	1.15388600	5.13975900	0.40267800
C	-1.08508100	3.98966200	1.58687200
C	0.23039400	5.94028400	1.07496700
C	-0.89471800	5.36841700	1.66998900
H	-0.32416700	2.12032800	0.86463700
H	2.02855100	5.60291800	-0.04135100
H	-1.95609100	3.52352300	2.03804800
H	0.39804800	7.01232600	1.13818200
H	-1.61032700	5.99216500	2.19958700
C	3.40024700	3.46140700	-0.31779200
C	4.01161400	4.28671000	-1.27121700
C	4.10678900	3.18517500	0.86577800
C	5.29648500	4.79996200	-1.06452500
C	5.38593400	3.69928800	1.07354000
C	5.99117900	4.50547700	0.10663500
H	3.49500600	4.55500400	-2.18733900
H	3.65126100	2.56447700	1.63251400
H	5.74755300	5.43303300	-1.82442000
H	5.90945300	3.46814500	1.99743400
H	6.98949300	4.90321800	0.26807300
C	-4.17506700	-1.16245700	3.19166700
C	-5.29026800	-0.30632400	3.16921600
C	-4.30350100	-2.38896200	3.86762300
C	-6.47846800	-0.65328400	3.80931100
H	-5.21907000	0.63063700	2.62687300
C	-5.49404000	-2.73946100	4.50324700
H	-3.46782900	-3.08061100	3.90243900
C	-6.58738500	-1.87192800	4.48165900
H	-7.32406700	0.02960700	3.77960200
H	-5.56478500	-3.69315800	5.02035400
H	-7.51346000	-2.14376300	4.98158000
C	-0.53011500	3.90462400	-2.59509800
H	-0.11222200	4.29703800	-3.53318200
H	-1.61641700	3.83582500	-2.71981400
H	-0.33284900	4.63417300	-1.80649200
H	0.09834700	0.54766100	-3.26333300
H	4.97396700	0.13935100	1.31681800
C	5.10932700	-3.31971400	1.03068600
H	6.07385500	-3.36317200	0.50572800
H	5.30524300	-3.48573100	2.09543500
H	4.49090000	-4.14463600	0.67162700
H	5.51686100	-1.05610200	2.48862400
H	-1.40810900	1.43990500	-3.43759100

● **1ba**-*RR* (HH-2)



B3LYP/6-31G*

E = –3719.223197

Zero-point correction = 1.283914 (Hartree/Particle)

Thermal correction to Energy = 1.359692

Thermal correction to Enthalpy = 1.360637

Thermal correction to Gibbs Free Energy = 1.164711

Sum of electronic and zero-point Energies = –3717.939284

Sum of electronic and thermal Energies = –3717.863505

Sum of electronic and thermal Enthalpies = –3717.862561

Sum of electronic and thermal Free Energies = –3718.058486

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

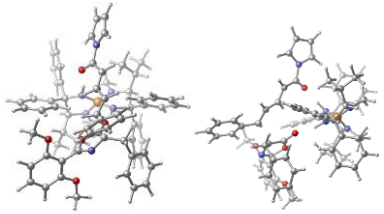
E = –3720.390173

G = –3719.191725

0 1

O	-1.05852600	-1.08949200	0.05733700
C	-2.17634200	-0.58591000	0.10157500
C	-3.34123100	-0.87552600	0.91217500
O	-2.50412200	0.54036600	-0.65205800
N	-4.39116500	-0.05691500	0.43355400
C	-3.85910400	0.75016100	-0.41126600
C	-4.51550900	1.82983900	-1.17229000
C	-4.24415100	3.17983000	-0.88386200
C	-5.43760800	1.51767300	-2.19045400
C	-4.88379700	4.20511900	-1.59286000
C	-6.08304600	2.53899600	-2.90194500
C	-5.79537100	3.86589300	-2.59118000
O	-3.34886600	3.39362800	0.12348900
C	-3.04585800	4.73435700	0.48898100
H	-3.93521700	5.25615600	0.86480800
H	-2.62286700	5.29380300	-0.35419600
H	-2.29661100	4.66445300	1.27786100
O	-5.62482100	0.19293600	-2.42318700
C	-6.54915100	-0.20605500	-3.42192900
H	-7.56438500	0.14384700	-3.19409900
H	-6.25451800	0.15881400	-4.41490300
H	-6.53014400	-1.29705600	-3.41500100
H	-4.68835700	5.24647200	-1.36951800
H	-6.79334800	2.30850200	-3.68648200
H	-6.29560100	4.65859400	-3.14134000
C	-3.64991900	-2.29147000	1.34063700
H	-2.76499100	-2.69291100	1.84694200
H	-4.46692600	-2.25739100	2.06967200
C	-4.03103600	-3.19718800	0.18116300
C	-3.10150500	-4.09218700	-0.36467600
C	-5.31643000	-3.14163900	-0.37754200
C	-3.44710600	-4.91607000	-1.43841200
C	-5.66441600	-3.96624800	-1.44774800
C	-4.73073400	-4.85793400	-1.98268600
H	-2.09963700	-4.14177800	0.05452200
H	-6.03953000	-2.43889300	0.02743600
H	-2.71162200	-5.60650500	-1.84427100
H	-6.67048700	-3.92004100	-1.85918600
H	-5.00377000	-5.50426500	-2.81335400
C	-2.69791400	0.10112700	2.65521700
C	-1.56895100	-0.54514900	3.24377900
H	-2.46818900	1.01786500	2.11255000
H	-1.74364900	-1.30077200	4.00716400
C	-0.25482500	-0.21817900	2.95283400
H	-0.08593800	0.54850700	2.19893700
C	0.88582600	-0.74623900	3.57983900
H	0.75280300	-1.50565500	4.34346700
C	2.18156400	-0.24300800	3.35074500
O	2.50919800	0.73229500	2.62396300
N	3.26068100	-0.88710000	4.05595100
C	4.47199600	-0.27276100	4.31544600
C	3.30365100	-2.17681100	4.56412100
C	5.27516900	-1.15999000	4.99107200
C	4.53512400	-2.37426700	5.14099200
H	4.62612700	0.74901100	4.00828900
H	2.47397900	-2.85240700	4.42843000
H	6.27756000	-0.96182000	5.34769800
H	4.87154400	-3.28782300	5.61388500
H	0.63693900	-1.05576300	-0.50823100
N	1.63082800	-1.13612800	-0.75781500
P	2.52602700	0.17261300	-1.17567600
N	3.89235400	-0.72232100	-1.45624900
C	3.76271100	-2.12910700	-0.98937600
C	2.21783400	-2.42176500	-1.21307100
C	5.11928800	-0.25630000	-2.09122400
H	4.99103500	0.77457600	-2.42428600
H	5.96760600	-0.28179000	-1.40340000
H	5.35295900	-0.88101600	-2.96366500
H	4.36487300	-2.74031800	-1.66778800
C	4.27768300	-2.37953200	0.46368100
H	3.44366800	-2.19866700	1.14990100
C	5.41564700	-1.44161400	0.89778800
H	6.33330800	-1.62244100	0.32265000
C	1.66101400	-3.59076700	-0.38368300
C	1.10673900	-3.39375200	0.88737200
C	1.70771400	-4.89700300	-0.89712700
C	0.62622600	-4.47674300	1.62791900
C	1.23269800	-5.97716200	-0.15452100
C	0.68850900	-5.77155700	1.11487300
H	1.03120400	-2.39925300	1.31007100
H	2.11286600	-5.07485900	-1.88838400
H	0.19609700	-4.29533700	2.60921400
H	1.28173500	-6.97876500	-0.57364800
H	0.31019700	-6.61099100	1.69205500
C	1.85422000	-2.64501300	-2.70581800
C	0.50511700	-2.49769800	-3.07440600
C	2.76977200	-3.01071800	-3.69976200
C	0.09328000	-2.69245000	-4.39054900
C	2.35826400	-3.20480300	-5.02380800
C	1.02061500	-3.04383000	-5.37557100
H	-0.23172900	-2.23521200	-2.32022300
H	3.81852400	-3.15733400	-3.46373100
H	-0.95669200	-2.57449600	-4.64433200
H	3.09205700	-3.48568500	-5.77501400
H	0.70042300	-3.19600200	-6.40277500
N	2.27940400	1.34446200	-0.05234200
C	2.47623700	2.70717500	-0.60139800
C	1.80054300	2.53543900	-2.02590600
N	2.30807900	1.20561800	-2.45349000
H	2.35331700	1.12894100	0.95953200
C	2.55754200	0.91565200	-3.85979000
H	2.98330700	-0.08412000	-3.95783900
H	1.63797400	0.94656500	-4.44948800
H	3.26840000	1.64227400	-4.27510400
H	2.20622200	3.26537900	-2.73240300
C	0.24130700	2.66523900	-2.03259200
H	-0.12511400	2.38363100	-1.03866000
C	-0.46055400	1.73826300	-3.03916900
H	-0.23854400	2.02227700	-4.07597000
C	1.83589300	3.77583800	0.30021700
C	1.02282700	3.44762400	1.38982900
C	2.10956800	5.13346200	0.06020100
C	0.49207000	4.44705600	2.21174400
C	1.56737900	6.13017900	0.86793700
C	0.75430100	5.79066900	1.95245200
H	0.83233300	2.41238200	1.63787300
H	2.76366200	5.41631500	-0.75919100
H	-0.11432100	4.16076600	3.06703900
H	1.79458800	7.17232900	0.65913800
H	0.34721400	6.56566100	2.59651100
C	3.99704200	3.01585300	-0.68979000
C	4.60924500	3.65124500	-1.77758500
C	4.79890400	2.67741300	0.41396500
C	5.98181900	3.92336200	-1.77451200
C	6.16522600	2.95137600	0.41955300
C	6.76613800	3.57333200	-0.67788400
H	4.03019200	3.94920500	-2.64594600
H	4.34860000	2.19318600	1.27627400
H	6.43124600	4.41242400	-2.63502900
H	6.76097000	2.67862900	1.28651500
H	7.83181800	3.78544300	-0.67447700
C	-3.97213700	0.20581300	3.41693200
C	-4.79644400	1.32860500	3.22599900
C	-4.38476600	-0.76140000	4.35103800
C	-5.97940100	1.48540900	3.94483400
H	-4.49952600	2.08060500	2.50089900
C	-5.57186800	-0.60873600	5.06593800
H	-3.77471500	-1.64241800	4.52453200
C	-6.37444500	0.51654700	4.86911200
H	-6.59579500	2.36573600	3.78059400
H	-5.86793500	-1.37070800	5.78263200
H	-7.29718000	0.63668900	5.43081200
C	-0.19124700	4.11357600	-2.32183600
H	0.13506300	4.42170100	-3.32518900
H	-1.28422600	4.18661700	-2.29787800
H	0.20982100	4.82922400	-1.60138900
H	-0.19421600	0.68741400	-2.89920700
H	5.14549000	-0.38644400	0.80549100
C	4.74759400	-3.83444200	0.63990200
H	5.63162400	-4.02998700	0.01684300
H	5.03308500	-4.00686200	1.68314600
H	3.98100200	-4.56649000	0.37850600
H	5.64543800	-1.62372000	1.95217700
H	-1.54225200	1.81502400	-2.89876100

● **1ba**-*RR* (MeMe)



B3LYP/6-31G*

E = –3719.221152

Zero-point correction = 1.283776 (Hartree/Particle)

Thermal correction to Energy = 1.359805

Thermal correction to Enthalpy = 1.360750

Thermal correction to Gibbs Free Energy = 1.164227

Sum of electronic and zero-point Energies = –3717.937376

Sum of electronic and thermal Energies = –3717.861347

Sum of electronic and thermal Enthalpies = –3717.860402

Sum of electronic and thermal Free Energies = –3718.056925

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3720.3874

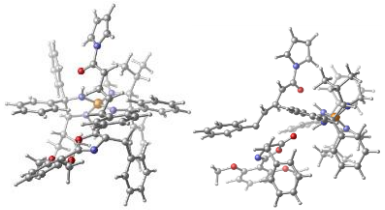
G = –3719.189329

0 1

O	0.93886000	0.81634000	0.14331200
C	2.10148200	0.43605800	0.09998700
C	3.29983300	0.85315300	0.81202900
O	2.47100000	-0.67546900	-0.65420000
N	4.38093400	0.11688300	0.24918100
C	3.85217900	-0.75794300	-0.52553600
C	4.52324200	-1.80756900	-1.31900400
C	4.91119600	-3.02669000	-0.73776800
C	4.78176200	-1.58682500	-2.68435800
C	5.57439100	-3.99919200	-1.49780200
C	5.44251000	-2.55394600	-3.45228800
C	5.83148800	-3.74524300	-2.84339000
O	4.58486800	-3.18633200	0.57983500
C	4.98804000	-4.38011300	1.23965400
H	6.07875700	-4.49627500	1.22375000
H	4.52066500	-5.26460000	0.78869800
H	4.64833300	-4.27617900	2.27105100
O	4.35017600	-0.38934500	-3.16634200
C	4.65132900	-0.04444800	-4.50947900
H	5.73391000	-0.04108000	-4.69032500
H	4.16733200	-0.72725800	-5.22004600
H	4.25759200	0.96360700	-4.64877100
H	5.88091700	-4.93995900	-1.05791400
H	5.65216000	-2.38778100	-4.50182100
H	6.34548000	-4.49862900	-3.43437400
C	3.50728100	2.32073800	1.12557700
H	2.66626600	2.65771600	1.74246000
H	4.41593700	2.41309500	1.72981300
C	3.61556100	3.20371900	-0.10733400
C	2.61873900	4.14111500	-0.40715200
C	4.71775400	3.10111900	-0.97047700
C	2.71713600	4.95794600	-1.53714400
C	4.81724700	3.91381300	-2.09953600
C	3.81739000	4.84692300	-2.38825100
H	1.76060500	4.23714500	0.25351800

H	5.49246000	2.37101300	-0.75364500
H	1.93394200	5.68254100	-1.74617500
H	5.68262700	3.82420400	-2.75224300
H	3.90077200	5.48650800	-3.26370300
C	2.98213800	-0.09067500	2.57750100
C	1.73372300	0.23303400	3.20577500
H	3.00114200	-1.07361000	2.10624300
H	1.72379500	1.00333200	3.97412500
C	0.55230800	-0.45031600	2.96834500
H	0.55383700	-1.21922900	2.19673200
C	-0.64057200	-0.31885700	3.69686300
H	-0.66319100	0.35566800	4.54653700
C	-1.77991400	-1.09749300	3.40826200
O	-1.98956200	-1.76863700	2.36343100
N	-2.82076000	-1.13154900	4.40047000
C	-4.10254900	-1.58908600	4.14730600
C	-2.74418600	-0.76453000	5.73653900
C	-4.83568300	-1.49822600	5.30461800
C	-3.96977700	-0.97794600	6.31688400
H	-4.36289500	-1.92379300	3.15682800
H	-1.81440000	-0.42687400	6.16533700
H	-5.87531400	-1.77652300	5.41946100
H	-4.21676100	-0.79613800	7.35489100
H	-0.78127400	1.19268000	-0.40863000
N	-1.78733400	1.33669000	-0.53058700
P	-2.75757300	0.13437000	-1.07744000
N	-4.14228700	1.03831100	-0.90710600
C	-3.93189100	2.36918900	-0.28944600
C	-2.39560800	2.68158000	-0.56310100
C	-5.48537700	0.54093200	-1.18140400
H	-5.42519800	-0.32020500	-1.85033400
H	-6.00486100	0.22381500	-0.27089000
H	-6.07905600	1.32383700	-1.66831200
H	-4.52648300	3.08054700	-0.86919400
C	-4.43097800	2.49967900	1.18152100
H	-3.92416200	3.38074400	1.58788400
C	-4.08036800	1.30550800	2.07362100
H	-4.53917100	0.37866500	1.71199300
C	-1.77943400	3.59988800	0.50408100
C	-0.99790400	3.10516300	1.55486000
C	-2.02575400	4.98127300	0.44120600
C	-0.48134300	3.97423600	2.52076500
C	-1.51742400	5.84378900	1.41041800
C	-0.73935600	5.34244700	2.45663800
H	-0.77297100	2.04866100	1.63165700
H	-2.61240500	5.38793400	-0.37775600
H	0.12579200	3.56669100	3.32433500
H	-1.72257700	6.90891900	1.34229400
H	-0.33574200	6.01392200	3.20967800
C	-2.13099000	3.30648800	-1.96400200
C	-0.79302800	3.35130300	-2.39650900
C	-3.10965900	3.83350000	-2.81389400
C	-0.45033100	3.89219800	-3.63234900
C	-2.76846700	4.37513500	-4.05962300
C	-1.44061800	4.40549900	-4.47538000
H	-0.00516500	2.96670600	-1.75502500
H	-4.15663500	3.83823500	-2.52940600
H	0.59485900	3.91962800	-3.92786500
H	-3.55152100	4.77514700	-4.69875900
H	-1.17643200	4.82897700	-5.44065000
N	-2.27214700	-1.24726800	-0.35325800
C	-2.44846400	-2.46756600	-1.17779600
C	-2.30464400	-1.91933900	-2.66393700
N	-2.86056900	-0.55136300	-2.58881800
H	-2.11999100	-1.33110700	0.67203900
C	-3.27816100	0.14769200	-3.79682800
H	-3.88155500	1.01601200	-3.52647800
H	-2.42941700	0.50099600	-4.39270600
H	-3.88643500	-0.52269200	-4.41578200
H	-2.97971000	-2.50306200	-3.29460200
C	-0.90252100	-2.01096800	-3.34818700
H	-0.43437200	-2.92259800	-2.96673800
C	0.03455000	-0.83831100	-3.03213200
H	-0.33671200	0.10424500	-3.45228800
C	-1.36631100	-3.50448700	-0.84172000
C	-0.14978400	-3.12908600	-0.25948400
C	-1.56079700	-4.85043800	-1.18505600
C	0.85287400	-4.07383900	-0.03508700
C	-0.55999900	-5.79501000	-0.95904500
C	0.65156000	-5.40948900	-0.38286800
H	0.02378300	-2.09460600	0.00943800
H	-2.50289000	-5.16569600	-1.62374700
H	1.79422100	-3.75382900	0.40295900
H	-0.73168000	-6.83361100	-1.22986400
H	1.43079800	-6.14649800	-0.20617800
C	-3.85251800	-3.06381600	-0.87842700
C	-4.85325900	-3.29322400	-1.82967000
C	-4.12949500	-3.39268500	0.46216100
C	-6.09401900	-3.82735200	-1.45914500
C	-5.36234100	-3.92517500	0.83008900
C	-6.35458600	-4.14575000	-0.12988000
H	-4.69572800	-3.06538800	-2.87861600
H	-3.37540200	-3.21934300	1.22512500
H	-6.85103100	-3.99433300	-2.22132300
H	-5.54519500	-4.17262500	1.87256100
H	-7.31585300	-4.56335400	0.15747900
C	4.25137900	0.18789700	3.31761800
C	5.36260900	-0.65062900	3.12265700
C	4.38362700	1.25040900	4.22912500
C	6.55109700	-0.44678800	3.82153500
H	5.28781800	-1.46059000	2.40440200
C	5.57397100	1.45853900	4.92496100
H	3.55068400	1.92504900	4.40050100
C	6.66361600	0.60841800	4.72833000
H	7.39358000	-1.11367000	3.65496200
H	5.64789200	2.28680700	5.62532600
H	7.58975100	0.76830000	5.27440100
C	-1.03870000	-2.20899300	-4.87090900
H	-1.46730000	-1.33517900	-5.37486700
H	-0.05180600	-2.38554500	-5.31378700
H	-1.66641700	-3.07645300	-5.11078900
H	0.18251500	-0.69617600	-1.96073900
H	-3.00193300	1.14428700	2.13959800
C	-5.93803000	2.81741700	1.24473300
H	-6.56362900	1.97388800	0.93530700
H	-6.22058400	3.06612100	2.27371000
H	-6.19722600	3.67814100	0.61492400
H	-4.44935900	1.46988500	3.09116900
H	1.02520500	-1.02160300	-3.46226500

- **1ba**-*RR* (MeMe-2)



B3LYP/6-31G*

E = –3719.215704

Zero-point correction = 1.284403 (Hartree/Particle)

Thermal correction to Energy = 1.359861

Thermal correction to Enthalpy = 1.360805

Thermal correction to Gibbs Free Energy = 1.168187

Sum of electronic and zero-point Energies = –3717.931301

Sum of electronic and thermal Energies = –3717.855843

Sum of electronic and thermal Enthalpies = –3717.854899

Sum of electronic and thermal Free Energies = –3718.047516

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3720.383522

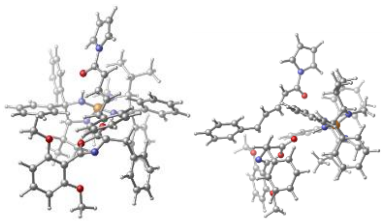
G = –3719.182208

0 1

O	-0.93197000	-0.39629800	-0.24562500
C	-2.13274000	-0.16438000	-0.18420600
C	-3.27535000	-0.95214700	0.26723300
O	-2.63383600	1.09806000	-0.46665300
N	-4.43069600	-0.19614400	-0.04493100
C	-4.02461600	0.97710600	-0.40472300
C	-4.83387800	2.15761000	-0.73758000
C	-4.34864000	3.21585700	-1.55629800
C	-6.16744000	2.27404900	-0.24821500
C	-5.14328100	4.33445600	-1.84013400
C	-6.95567200	3.39241100	-0.54692300
C	-6.43548000	4.41200400	-1.33476300
O	-3.09582700	3.07967300	-2.06519400
C	-2.55608200	4.14000600	-2.83813800
H	-2.49527200	5.06972900	-2.25940600
H	-3.13998800	4.31312900	-3.75176700
H	-1.54889600	3.82221400	-3.10739900
O	-6.62131900	1.26349600	0.53103100
C	-7.96618100	1.28199300	0.98112300
H	-8.16260100	2.13427300	1.64553000
H	-8.67072900	1.30946000	0.14010600
H	-8.09508800	0.35141200	1.53515800
H	-4.76300000	5.13457000	-2.46114000
H	-7.96411400	3.47079700	-0.16207800
H	-7.04849900	5.27992000	-1.56234900
C	-3.31154300	-2.44736000	0.02521600
H	-2.42278600	-2.88932300	0.48854500
H	-4.18746300	-2.84747800	0.54744100
C	-3.37053200	-2.85380900	-1.43913100
C	-2.34577800	-3.61994100	-2.00901000
C	-4.46449300	-2.49735400	-2.24361100
C	-2.40755200	-4.02144800	-3.34650800
C	-4.52552900	-2.89264900	-3.57949700
C	-3.49760100	-3.65757400	-4.13747500
H	-1.49606900	-3.91392100	-1.39756400
H	-5.26241400	-1.89950000	-1.81281100
H	-1.60245900	-4.62021600	-3.76512300
H	-5.38146000	-2.60676900	-4.18631000
H	-3.55043500	-3.97118900	-5.17723700
C	-3.05929200	-0.67518200	2.24606400
C	-1.79224900	-1.09323200	2.78491500
H	-3.16594200	0.40691000	2.15966500
H	-1.74451300	-2.06305700	3.27686500
C	-0.66838300	-0.28718600	2.84308100
H	-0.70641100	0.68265300	2.34888500
C	0.50539900	-0.56149900	3.56483600
H	0.54777300	-1.45740600	4.17565000
C	1.59726000	0.32941500	3.57675400
O	1.79633900	1.28460200	2.77967600
N	2.59899600	0.12700700	4.58832400
C	3.86329200	0.68818300	4.53611100
C	2.49809700	-0.61526300	5.75629900
C	4.56225200	0.29458400	5.65043300
C	3.69193600	-0.53095000	6.42907200
H	4.14000200	1.30320400	3.69583800
H	1.57246000	-1.09765500	6.02662500
H	5.58222500	0.56816500	5.88765900
H	3.91392000	-0.99483600	7.38147100
H	0.83226300	-1.02859000	-0.64916700
N	1.83986400	-1.18470300	-0.71379500
P	2.88882400	0.06869700	-0.86946900
N	4.22643700	-0.90397200	-0.72430900
C	3.92745900	-2.33711500	-0.49465800
C	2.42804100	-2.50627700	-1.00821400
C	5.60149800	-0.41882000	-0.74204900
H	5.63207700	0.57692200	-1.18955800
H	6.02730300	-0.34890200	0.26446100
H	6.22621800	-1.09241300	-1.34085100
H	4.57531200	-2.89505800	-1.17517900
C	4.25787000	-2.86410900	0.93357900
H	3.69243700	-3.79578300	1.04169900
C	3.83789700	-1.92295700	2.06518300
H	4.36256800	-0.96310000	2.01097300
C	1.66862600	-3.62643700	-0.27943600
C	0.79144000	-3.36081500	0.77952900
C	1.87578700	-4.96273500	-0.65929700
C	0.14829900	-4.40878800	1.44498500
C	1.23849900	-6.00537400	0.01074900
C	0.36907100	-5.73238900	1.06879200
H	0.59689700	-2.34413400	1.10010900
H	2.53477700	-5.19303000	-1.49090100
H	-0.52724200	-4.17560600	2.26308900
H	1.41612000	-7.03112100	-0.30138100
H	-0.13336200	-6.54334300	1.58896200
C	2.34787200	-2.76448600	-2.54292500
C	1.13791900	-2.45930100	-3.19023600
C	3.37631500	-3.31922100	-3.31561600
C	0.97080400	-2.67856900	-4.55589800
C	3.21380200	-3.53650400	-4.68867300
C	2.01377500	-3.21348200	-5.31653700
H	0.30718600	-2.05368900	-2.62140100
H	4.32347700	-3.60230700	-2.86781200
H	0.01755600	-2.43919100	-5.01872700
H	4.03359400	-3.96327300	-5.26077000
H	1.88721300	-3.38355800	-6.38224400
N	2.34875000	1.29577400	0.06101900
C	2.61557000	2.64888300	-0.48890900
C	2.64503500	2.40381800	-2.05966800
N	3.18421900	1.03527900	-2.19038500
H	2.08759700	1.18872000	1.06365800
C	3.73571800	0.57065700	-3.45705600
H	4.30991000	-0.34321000	-3.29374500
H	2.96066300	0.35083100	-4.19940200
H	4.40611400	1.33638200	-3.86501900
H	3.39000300	3.08320300	-2.48107300

C	1.33552600	2.66377500	-2.87215700
H	0.83589400	3.50288200	-2.37884100
C	0.35795600	1.48189700	-2.89628100
H	0.78644300	0.61321000	-3.40956600
C	1.49906100	3.62280900	-0.08246000
C	0.23134200	3.16626400	0.29688900
C	1.72492900	5.00595200	-0.15260900
C	-0.78842000	4.07239600	0.59474400
C	0.70598900	5.91008500	0.14559500
C	-0.55620400	5.44587200	0.52269300
H	0.02927800	2.10339500	0.34916000
H	2.70579200	5.37978100	-0.43157100
H	-1.76558800	3.69187400	0.87571000
H	0.90303700	6.97770800	0.09092600
H	-1.34850400	6.14963200	0.76469000
C	3.97556200	3.14821500	0.07434200
C	5.09473300	3.48200000	-0.69741200
C	4.08420900	3.25759500	1.47347700
C	6.28547500	3.91052200	-0.09714100
C	5.26759000	3.68513200	2.07019600
C	6.37763200	4.01563600	1.28723600
H	5.07101500	3.41912600	-1.78015500
H	3.23860600	2.98992300	2.10089900
H	7.13665300	4.16419700	-0.72403600
H	5.31946200	3.76284000	3.15306100
H	7.29988400	4.35200500	1.75332800
C	-4.28386400	-1.29840100	2.83722600
C	-5.40495500	-0.49969700	3.11412100
C	-4.34703100	-2.65949500	3.18643800
C	-6.53569300	-1.03293000	3.73244600
H	-5.38413700	0.54991800	2.84079100
C	-5.48244200	-3.19773600	3.79045300
H	-3.49981400	-3.30819200	2.98546800
C	-6.58257300	-2.38589100	4.07200100
H	-7.38021600	-0.38611000	3.95854200
H	-5.50378400	-4.25370300	4.04806600
H	-7.46327700	-2.80243700	4.55384800
C	1.65965900	3.13911100	-4.30251000
H	2.13895600	2.36097600	-4.90666900
H	0.73799900	3.42631200	-4.82214200
H	2.32056300	4.01496500	-4.29692800
H	0.04685000	1.17000400	-1.89726100
H	2.76438600	-1.72063600	2.05853800
C	5.74259700	-3.25799700	1.06315000
H	6.41365900	-2.39301800	1.04760600
H	5.90644400	-3.77383700	2.01575700
H	6.05338300	-3.94035500	0.26147900
H	4.08070800	-2.36504700	3.03723100
H	-0.55284400	1.75756500	-3.43925700

● **1ba**-*RR* (HMe)



B3LYP/6-31G*

E = –3719.221859

Zero-point correction = 1.284445 (Hartree/Particle)

Thermal correction to Energy = 1.360165

Thermal correction to Enthalpy = 1.361109

Thermal correction to Gibbs Free Energy = 1.165363

Sum of electronic and zero-point Energies = –3717.937414

Sum of electronic and thermal Energies = –3717.861694

Sum of electronic and thermal Enthalpies = –3717.860749

Sum of electronic and thermal Free Energies = –3718.056496

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

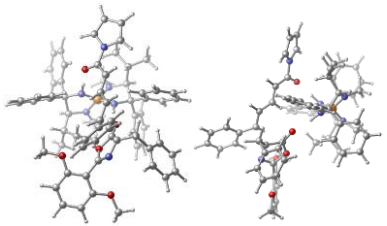
E = –3720.388279

G = –3719.189212

0 1

O	0.90457300	0.55463100	-0.00805200
C	2.10534400	0.31735800	0.03435300
C	3.21959400	0.96081600	0.70969200
O	2.62857800	-0.83839700	-0.54744200
N	4.39729800	0.28769800	0.28624700
C	4.00327500	-0.73926500	-0.37320300
C	4.83063900	-1.79222100	-0.99753900
C	5.07751400	-3.00740800	-0.33766300
C	5.39202900	-1.57618300	-2.26943900
C	5.88318500	-3.98984600	-0.92733000
C	6.19863500	-2.55367900	-2.86761400
C	6.43158600	-3.74539000	-2.18493500
O	4.48841900	-3.14262500	0.88923900
C	4.76276200	-4.31406300	1.64775300
H	5.83599000	-4.41502100	1.85144800
H	4.40264700	-5.21622300	1.13735600
H	4.22355700	-4.19016600	2.58794900
O	5.08851500	-0.38033000	-2.84112000
C	5.65147600	-0.06110700	-4.10337500
H	6.74853000	-0.05902200	-4.06561400
H	5.31734300	-0.75850800	-4.88296000
H	5.29416700	0.94344000	-4.33571400
H	6.08272800	-4.92777900	-0.42430200
H	6.63666300	-2.39474100	-3.84536600
H	7.05676200	-4.50574500	-2.64549200
C	3.25769100	2.46727200	0.84803000
H	2.34459000	2.78697500	1.36210100
H	4.10776000	2.72791200	1.48804200
C	3.37330600	3.19521900	-0.48242200
C	2.29917100	3.93772700	-0.98974500
C	4.55716400	3.13276300	-1.23357100
C	2.40167300	4.60336300	-2.21436100
C	4.66217400	3.79820600	-2.45501600
C	3.58447600	4.53703100	-2.95143700
H	1.37657000	4.00014500	-0.41828900
H	5.39088300	2.54692000	-0.85730100
H	1.55568400	5.17632400	-2.58635700
H	5.59206500	3.74740500	-3.01727600
H	3.66962600	5.06069100	-3.90064000
C	2.90336300	0.19462600	2.58490000
C	1.63882600	0.56125300	3.14744300
H	2.95577200	-0.83155400	2.22108700
H	1.60456400	1.41197900	3.82546400
C	0.46664800	-0.15354800	2.95893200
H	0.48947800	-1.00755600	2.28390100
C	-0.74597100	0.06955600	3.63044400
H	-0.78691400	0.84645200	4.38682500
C	-1.88056500	-0.73994900	3.41647500
O	-2.06269200	-1.55013200	2.47090600
N	-2.94974500	-0.63883100	4.37548900
C	-4.20768100	-1.17862800	4.17111600
C	-2.92569800	-0.05324100	5.63391700
C	-4.97860300	-0.92416000	5.27878600
C	-4.16099800	-0.21122700	6.21080700
H	-4.42482000	-1.68605100	3.24596900
H	-2.02263200	0.38669800	6.02499700
H	-6.01070900	-1.22063600	5.41392700
H	-4.44536600	0.13227400	7.19701700
H	-0.79831200	1.10697200	-0.44238600
N	-1.79523400	1.21452700	-0.64352600
P	-2.72888100	-0.05002300	-1.10955900
N	-4.13850600	0.80956400	-0.94655300
C	-3.95490000	2.13032900	-0.28938200
C	-2.46984100	2.52994100	-0.70855800
C	-5.44104700	0.42312600	-1.47778800
H	-5.36622300	-0.56050000	-1.94467700
H	-6.19355700	0.36288100	-0.68869300
H	-5.77923600	1.14794900	-2.23083400
H	-4.66967900	2.80909500	-0.76255700
C	-4.25054500	2.13112500	1.24189900
H	-3.33678700	1.82692100	1.76491000
C	-5.35064200	1.14054900	1.65624900
H	-6.32861600	1.42714000	1.24757600
C	-1.77061200	3.52087400	0.23954800
C	-1.08045700	3.07411800	1.37543700
C	-1.82058900	4.90208900	-0.00935200
C	-0.47892700	3.98607700	2.24592000
C	-1.22002700	5.81057200	0.86211500
C	-0.54704600	5.35622100	1.99732600
H	-0.99911900	2.01608700	1.59631800
H	-2.32927300	5.27618800	-0.89146800
H	0.04863300	3.61068100	3.11802400
H	-1.27361000	6.87437700	0.64638200
H	-0.07379200	6.06254300	2.67398600
C	-2.39560500	3.06632600	-2.16435100
C	-1.18542300	2.91291900	-2.86199200
C	-3.43962400	3.74396200	-2.80743400
C	-1.03163700	3.40179800	-4.15786200
C	-3.29124900	4.22820000	-4.11197800
C	-2.08904500	4.05677800	-4.79433300
H	-0.34975300	2.41173900	-2.38369900
H	-4.38398400	3.91908600	-2.30223000
H	-0.07970600	3.27394200	-4.66611600
H	-4.12140700	4.74453400	-4.58704200
H	-1.97288800	4.43492300	-5.80637700
N	-2.21070300	-1.37554600	-0.30897200
C	-2.40192400	-2.64277500	-1.05131800
C	-2.26158800	-2.18930700	-2.57150500
N	-2.80356900	-0.81201500	-2.58236400
H	-2.08398900	-1.38328900	0.72215600
C	-3.19036300	-0.17480300	-3.83509700
H	-3.70831600	0.76303900	-3.62693700
H	-2.32671100	0.05742400	-4.46648300
H	-3.86693000	-0.83366900	-4.39344300
H	-2.94695500	-2.80279500	-3.16125900
C	-0.86416800	-2.34451500	-3.25261900
H	-0.40535100	-3.23072000	-2.80528600
C	0.08940500	-1.16440200	-3.02638600
H	-0.27388000	-0.25083800	-3.51215800
C	-1.32454100	-3.66089400	-0.64808600
C	-0.10368400	-3.24735500	-0.10052700
C	-1.52753200	-5.02804000	-0.88578300
C	0.89479500	-4.17745300	0.19271300
C	-0.53085200	-5.95763800	-0.58962100
C	0.68486400	-5.53514400	-0.04915400
H	0.07839600	-2.19497700	0.08197800
H	-2.47241600	-5.37125200	-1.29657200
H	1.83970400	-3.82589100	0.59708700
H	-0.70889300	-7.01324200	-0.77817100
H	1.46078100	-6.26084100	0.18130800
C	-3.80972400	-3.21043500	-0.71163300
C	-4.79257300	-3.54796700	-1.64965200
C	-4.10711800	-3.40301000	0.65103100
C	-6.03464300	-4.05419000	-1.24606100
C	-5.34101600	-3.90882000	1.05189700
C	-6.31484000	-4.23752300	0.10435500
H	-4.61877500	-3.43133100	-2.71414100
H	-3.37011300	-3.14451900	1.40621300
H	-6.77694700	-4.30663600	-1.99910100
H	-5.53946900	-4.05024500	2.11115900
H	-7.27705100	-4.63343600	0.41795000
C	4.15227100	0.59077900	3.30003500
C	5.26863200	-0.26220200	3.26289500
C	4.26092400	1.78199400	4.03948200
C	6.44024900	0.05290700	3.94841000
H	5.20969700	-1.17744900	2.68211500
C	5.43509500	2.10207300	4.71994500
H	3.42215000	2.46981500	4.08544000
C	6.53041000	1.23752100	4.68140600
H	7.28700500	-0.62781800	3.90692700
H	5.49205000	3.02936800	5.28465100
H	7.44386800	1.48531700	5.21584600
C	-1.00764500	-2.65743400	-4.75538100
H	-1.43263800	-1.82251600	-5.32385700
H	-0.02397800	-2.87516700	-5.18672300
H	-1.64269400	-3.53598800	-4.92527800
H	0.24580500	-0.94352900	-1.96915900
H	-5.12598200	0.11659300	1.34648500
C	-4.65082100	3.53702200	1.72423000
H	-5.59271900	3.84897800	1.25175200
H	-4.81529800	3.52724100	2.80709600
H	-3.89648700	4.29568200	1.50849200
H	1.07165800	-1.39360700	-3.45407900
H	-5.44035300	1.13288500	2.74676900

● **1ba**-*RR* (HMe-2)



B3LYP/6-31G*

E = –3719.223318

Zero-point correction = 1.283707 (Hartree/Particle)

Thermal correction to Energy = 1.359706

Thermal correction to Enthalpy = 1.360650

Thermal correction to Gibbs Free Energy = 1.164139

Sum of electronic and zero-point Energies = –3717.939610

Sum of electronic and thermal Energies = –3717.863611

Sum of electronic and thermal Enthalpies = –3717.862667

Sum of electronic and thermal Free Energies = –3718.059178

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

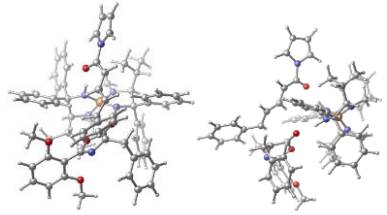
E = –3720.389364

G = –3719.191382

0 1

O	-1.17384400	-0.91007900	-0.05758700
C	-2.29699100	-0.42049800	0.02931100
C	-3.42917500	-0.71301500	0.88525700
O	-2.66607100	0.69341300	-0.72033100
N	-4.49772900	0.10402000	0.45698800
C	-4.00469700	0.90964800	-0.41460000
C	-4.68191900	2.01060800	-1.12124200
C	-4.25905400	3.34154000	-0.94119500
C	-5.77198000	1.74929800	-1.97565700
C	-4.90649400	4.39493200	-1.59869900
C	-6.42769600	2.80071600	-2.63188300
C	-5.98422500	4.10599600	-2.43390400
O	-3.21422300	3.51071300	-0.07873300
C	-2.70102600	4.82063300	0.12141300
H	-3.44789600	5.47781000	0.58545100
H	-2.36276000	5.26648500	-0.82246000
H	-1.84627100	4.70709800	0.78981100
O	-6.10330600	0.44096800	-2.12134300
C	-7.19752300	0.09699300	-2.95458200
H	-8.13412300	0.54195400	-2.59404400
H	-7.02757100	0.40466400	-3.99511200
H	-7.26881700	-0.99073700	-2.90504200
H	-4.59133400	5.42118200	-1.45651200
H	-7.26572200	2.60832600	-3.29043500
H	-6.49290700	4.92092100	-2.94230000
C	-3.71816100	-2.12133400	1.34855800
H	-2.79173900	-2.53912900	1.75744100
H	-4.45299400	-2.07329500	2.16012300
C	-4.24328700	-3.01676300	0.23822800
C	-3.38495000	-3.87750500	-0.45831300
C	-5.59738400	-2.98243300	-0.12454600
C	-3.86727100	-4.68835000	-1.48815300
C	-6.08156900	-3.79373000	-1.15113900
C	-5.21794300	-4.65142800	-1.83730100
H	-2.33192300	-3.91074400	-0.19159900
H	-6.26812200	-2.30641900	0.39878500
H	-3.18499400	-5.35308500	-2.01258700
H	-7.13769800	-3.76295400	-1.41041200
H	-5.59619200	-5.28752300	-2.63392000
C	-2.70015900	0.28461100	2.61967500
C	-1.60402600	-0.41888800	3.19898300
H	-2.42563600	1.17261800	2.05132800
H	-1.81410900	-1.17129500	3.95686200
C	-0.27547400	-0.15496000	2.91129800
H	-0.06203100	0.61907000	2.17556100
C	0.83072200	-0.76153800	3.53126200
H	0.65074100	-1.53373400	4.27231900
C	2.15235200	-0.32684800	3.32311400
O	2.53452800	0.65525300	2.62980100
N	3.19147200	-1.05290600	4.00640400
C	4.42747400	-0.51025100	4.30663200
C	3.16488300	-2.36410000	4.45687700
C	5.17748400	-1.46429000	4.95150900
C	4.37787200	-2.64648200	5.03849400
H	4.63341700	0.51679500	4.05145600
H	2.30427800	-2.99062900	4.28273300
H	6.18340000	-1.33146100	5.32787900
H	4.66326200	-3.59497200	5.47474000
H	0.57243500	-0.92872100	-0.59197500
N	1.55393200	-1.12524300	-0.82253700
P	2.63576600	0.05368500	-1.18990200
N	3.87652800	-1.01805600	-1.43290400
C	3.54455600	-2.39822500	-0.99822400
C	1.98164600	-2.47658300	-1.27373500
C	5.17011300	-0.71204100	-2.03271200
H	5.16584800	0.31411300	-2.40489400
H	5.98727700	-0.80544300	-1.31300800
H	5.36129400	-1.39042500	-2.87451500
H	4.07682900	-3.07532400	-1.67213600
C	3.98424900	-2.73892500	0.46140000
H	3.16935400	-2.45205900	1.13421700
C	5.23205800	-1.97376900	0.93230600
H	6.12706100	-2.27073200	0.36986200
C	1.25894800	-3.57401300	-0.47595700
C	0.73842000	-3.33556100	0.80223800
C	1.13802500	-4.86466100	-1.01587600
C	0.13517300	-4.36614700	1.52690400
C	0.53793700	-5.89308100	-0.29002100
C	0.03519800	-5.64885400	0.98919900
H	0.78644700	-2.34767900	1.24306300
H	1.51366300	-5.07225700	-2.01263700
H	-0.26368800	-4.15292100	2.51500000
H	0.45920200	-6.88393800	-0.72961100
H	-0.43883300	-6.44688800	1.55419000
C	1.64249300	-2.63436900	-2.78024800
C	0.35363100	-2.26013900	-3.19947300
C	2.51809800	-3.15753200	-3.73948300
C	-0.03578700	-2.38745400	-4.53105800
C	2.13048900	-3.28194000	-5.07861700
C	0.85465500	-2.89479800	-5.48127500
H	-0.35571100	-1.87336600	-2.47308500
H	3.51533700	-3.48465900	-3.46377000
H	-1.04033300	-2.09414400	-4.82391700
H	2.83323400	-3.68735200	-5.80209900
H	0.55280300	-2.99365400	-6.52045800
N	2.51076600	1.24252200	-0.06634300
C	2.95628400	2.55887300	-0.57183500
C	2.44492900	2.52326800	-2.07474700
N	2.63986500	1.10881000	-2.47186900
H	2.52048000	1.00769800	0.94306600
C	2.68287400	0.71510100	-3.87565000
H	3.15461200	-0.26492600	-3.96932100
H	1.68544800	0.64846900	-4.32239500
H	3.27501400	1.44351600	-4.44118500
H	3.13178800	3.11242500	-2.68871600
C	1.02172200	3.09463200	-2.34032200
H	0.97830900	4.03081200	-1.77382200
C	-0.12267400	2.20010800	-1.85620300
H	-0.13067600	1.23411800	-2.37368600
C	2.36294900	3.71915200	0.24447600
C	1.55043300	3.51658200	1.36496500
C	2.67598100	5.03865800	-0.12436000
C	1.05120700	4.60733100	2.08551500
C	2.16738800	6.12362700	0.58491000
C	1.34744600	5.91203500	1.69652500
H	1.33408700	2.51578300	1.71763600
H	3.33110600	5.22218100	-0.97165500
H	0.43825800	4.42360600	2.96400500
H	2.42121600	7.13419100	0.27568200
H	0.95973800	6.75621500	2.26052400
C	4.50787700	2.66123500	-0.46701000
C	5.32505200	3.26852300	-1.42943600
C	5.12070100	2.16507800	0.69690400
C	6.70910600	3.35962400	-1.24916600
C	6.49948500	2.25827600	0.87842700
C	7.30385700	2.85314600	-0.09622500
H	4.90382700	3.68850700	-2.33732600
H	4.51598800	1.70164300	1.47124200
H	7.31695600	3.83099000	-2.01726100
H	6.94439000	1.86435000	1.78829200
H	8.37894300	2.92388600	0.04471600
C	-3.95881100	0.47129300	3.38654700
C	-4.72315200	1.63293300	3.17723500
C	-4.41451800	-0.45132400	4.34571300
C	-5.88981200	1.86878500	3.90052900
H	-4.39087100	2.35379900	2.43591600
C	-5.58592100	-0.21952000	5.06505400
H	-3.84968800	-1.35838500	4.53744900
C	-6.32881400	0.94251200	4.84840400
H	-6.45904900	2.77752200	3.72168900
H	-5.91603700	-0.94809800	5.80132800
H	-7.23903800	1.12442800	5.41390600
C	0.82575600	3.48617900	-3.81824600
H	0.73248600	2.61639900	-4.47682000
H	-0.09664700	4.06796200	-3.92656400
H	1.65141000	4.10591800	-4.19136200
H	-0.06988200	2.00265300	-0.78378600
C	5.11295900	-0.88998100	0.85321700
C	4.24334200	-4.24689100	0.62636500
H	5.09750600	-4.55959100	0.00945100
H	4.49226800	-4.46584900	1.67023100
H	3.38426400	-4.86166200	0.35162200
H	-1.08917800	2.67455900	-2.05028100
H	5.41429800	-2.20219500	1.98701000

● **1ba**-*RR* (MeH)



B3LYP/6-31G*

E = –3719.222454

Zero-point correction = 1.283531 (Hartree/Particle)

Thermal correction to Energy = 1.359585

Thermal correction to Enthalpy = 1.360529

Thermal correction to Gibbs Free Energy = 1.163853

Sum of electronic and zero-point Energies = –3717.938923

Sum of electronic and thermal Energies = –3717.862869

Sum of electronic and thermal Enthalpies = –3717.861925

Sum of electronic and thermal Free Energies = –3718.058601

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3720.389858

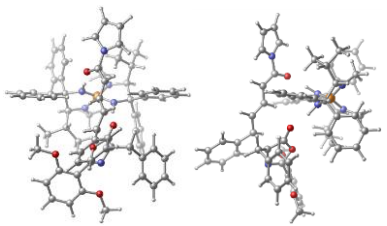
G = –3719.192132

0 1

O	0.95537300	1.20301800	0.19663600
C	2.06460400	0.69137100	0.12354500
C	3.30614600	0.96909900	0.82642400
O	2.30446500	-0.43499000	-0.65897800
N	4.29807200	0.13471100	0.23771600
C	3.67421700	-0.66706700	-0.54498900
C	4.22122800	-1.77724400	-1.34980700
C	4.58703600	-2.99920500	-0.75644600
C	4.39331600	-1.61391100	-2.73756200
C	5.12795000	-4.03325300	-1.53274400
C	4.93015900	-2.64362200	-3.52030000
C	5.29123500	-3.83917100	-2.90218000
O	4.37074700	-3.09963400	0.58761300
C	4.74865700	-4.30182100	1.24633400
H	5.82198500	-4.49923900	1.13482700
H	4.17792600	-5.15970400	0.86916300
H	4.51758300	-4.14528600	2.30111600
O	4.01043300	-0.40246800	-3.22909400
C	4.29287100	-0.09628400	-4.58683900
H	5.36561200	-0.18332700	-4.80070600
H	3.73084900	-0.74370400	-5.27223700
H	3.97688400	0.93869500	-4.72575300
H	5.41123800	-4.97760700	-1.08535400
H	5.06949800	-2.52043300	-4.58724300
H	5.70923500	-4.64171400	-3.50394100
C	3.66062900	2.40815200	1.14667900
H	2.88169500	2.81018000	1.80474300
H	4.60063200	2.41137200	1.70710500
C	3.78335200	3.28542700	-0.08710900
C	2.76823500	4.18929200	-0.42758500
C	4.90679600	3.19526400	-0.92238400
C	2.87220000	4.98693800	-1.57009300
C	5.01299700	3.98985200	-2.06388400
C	3.99601500	4.89020700	-2.39260600
H	1.89012900	4.26820600	0.20872700

H	5.69483700	2.48929900	-0.67404200
H	2.07607000	5.68698900	-1.81164500
H	5.89510500	3.91082400	-2.69507600
H	4.08343200	5.51617800	-3.27740800
C	2.91376500	0.05801700	2.59206300
C	1.68596300	0.47067000	3.20806200
H	2.86646000	-0.92823500	2.12917700
H	1.71240400	1.27826200	3.93636500
C	0.47417300	-0.16958700	3.00483800
H	0.44680800	-0.97801700	2.27554600
C	-0.71119400	0.04571000	3.72443400
H	-0.70366300	0.77523100	4.52719400
C	-1.87481000	-0.72458400	3.51218200
O	-2.11934600	-1.47841100	2.53384700
N	-2.90118600	-0.64889800	4.51813300
C	-4.18191000	-1.14254600	4.33832000
C	-2.81257900	-0.12741100	5.80177600
C	-4.90203600	-0.92304300	5.48604600
C	-4.02891900	-0.28021500	6.41858300
H	-4.44828400	-1.59985900	3.40027800
H	-1.88353100	0.26871700	6.17835200
H	-5.93673700	-1.19666500	5.64695800
H	-4.26550200	0.02239600	7.43048400
H	-0.74323500	1.24579900	-0.37742300
N	-1.75450700	1.29887100	-0.54964400
P	-2.57439000	-0.00291900	-1.11156600
N	-4.02744600	0.80101700	-1.16894600
C	-3.97325000	2.18561800	-0.64124200
C	-2.44078300	2.58646600	-0.78025300
C	-5.29622300	0.18359200	-1.53852300
H	-5.10990600	-0.70523500	-2.14436300
H	-5.87946800	-0.12654700	-0.66537500
H	-5.89249600	0.89046600	-2.12732100
H	-4.54782400	2.80791300	-1.33337000
C	-4.63037200	2.38679200	0.75693500
H	-4.24942400	3.34611800	1.12255700
C	-4.26287000	1.31426900	1.78573900
H	-4.59055600	0.31809100	1.46875800
C	-2.00904500	3.64442500	0.24770300
C	-1.27574800	3.31958800	1.39485400
C	-2.37251500	4.98479700	0.03765000
C	-0.92015400	4.31514600	2.31011600
C	-2.02688700	5.97260300	0.95722400
C	-1.29508900	5.64082100	2.09995400
H	-0.96546500	2.29924300	1.58422900
H	-2.92254700	5.26053500	-0.85789500
H	-0.34694100	4.04083200	3.19140300
H	-2.32142300	7.00288700	0.77536600
H	-1.01681500	6.41050800	2.81484700
C	-2.06282300	3.10370200	-2.19908600
C	-0.69080500	3.21768000	-2.48944300
C	-2.97408800	3.47751500	-3.19326000
C	-0.24999700	3.68200200	-3.72543700
C	-2.53321000	3.94185200	-4.43892900
C	-1.17233800	4.04642200	-4.71091500
H	0.04467400	2.94704500	-1.73695500
H	-4.04419300	3.42046900	-3.02326000
H	0.81748300	3.76664500	-3.90989800
H	-3.26518000	4.22400300	-5.19150400
H	-0.83135100	4.41104300	-5.67617000
N	-2.10383500	-1.30426500	-0.23449200
C	-2.17475200	-2.58236300	-0.99021000
C	-1.73598400	-2.10160100	-2.44192000
N	-2.41117700	-0.78744500	-2.56446100
H	-2.04267900	-1.29669000	0.80384300
C	-2.91402200	-0.33561900	-3.85507200
H	-3.42216700	0.62184400	-3.73337700
H	-2.10557300	-0.19710900	-4.57742400
H	-3.62708900	-1.06544000	-4.26199300
H	-2.18158100	-2.75284800	-3.19889000
C	-0.19547300	-2.05777600	-2.69798400
H	0.30215200	-1.85895600	-1.74519400
C	0.25493500	-0.93838500	-3.65148100
H	-0.07403000	-1.11912900	-4.68338500
C	-1.23505000	-3.62200400	-0.35752900
C	-0.09359200	-3.23051300	0.35296500
C	-1.49034000	-4.99431700	-0.50121300
C	0.77633000	-4.17939200	0.89056300
C	-0.62213900	-5.94413800	0.03718500
C	0.51653700	-5.54050500	0.73559300
H	0.12105800	-2.17789500	0.48727700
H	-2.37735000	-5.32873600	-1.02911700
H	1.65666000	-3.84285100	1.43020500
H	-0.84372200	-7.00121600	-0.08451200
H	1.18758000	-6.28130600	1.16282600
C	-3.63311200	-3.11057900	-0.94862400
C	-4.31951200	-3.63213800	-2.05208700
C	-4.29219600	-3.09642300	0.29383100
C	-5.63360000	-4.09890700	-1.92943700
C	-5.59814100	-3.56606400	0.41736800
C	-6.28000100	-4.06408600	-0.69644000
H	-3.84479900	-3.69239000	-3.02616300
H	-3.77168800	-2.72070400	1.17092200
H	-6.14415400	-4.49290200	-2.80452700
H	-6.08291100	-3.54765500	1.39001900
H	-7.29945900	-4.42779600	-0.60000300
C	4.19837100	0.25462900	3.33321900
C	5.26632700	-0.63197100	3.10931000
C	4.38725400	1.28374700	4.27244000
C	6.46695400	-0.50550100	3.80577500
H	5.14974800	-1.41572900	2.36801800
C	5.59020000	1.41455400	4.96558600
H	3.58928000	1.99209100	4.47116000
C	6.63606800	0.51814200	4.73964300
H	7.27471900	-1.20816100	3.61575100
H	5.70754200	2.21864200	5.68787200
H	7.57155500	0.61772000	5.28409100
C	0.30536200	-3.40874200	-3.23736400
H	-0.12440600	-3.60961700	-4.22901800
H	1.39536100	-3.39091200	-3.34649200
H	0.05043800	-4.24542700	-2.58306900
H	-0.10357300	0.04615000	-3.33844200
H	-3.18672400	1.26996000	1.96553800
C	-6.15915700	2.55573700	0.65288200
H	-6.67109900	1.62817500	0.37712000
H	-6.56217200	2.86891200	1.62244100
H	-6.43425700	3.32383600	-0.08132200
H	-4.74915700	1.52370700	2.74413100
H	1.34855900	-0.89485000	-3.65242500

● **1ba**-*RR* (MeH-2)



B3LYP/6-31G*

E = –3719.222716

Zero-point correction = 1.283823 (Hartree/Particle)

Thermal correction to Energy = 1.359725

Thermal correction to Enthalpy = 1.360669

Thermal correction to Gibbs Free Energy = 1.164092

Sum of electronic and zero-point Energies = –3717.938893

Sum of electronic and thermal Energies = –3717.862991

Sum of electronic and thermal Enthalpies = –3717.862047

Sum of electronic and thermal Free Energies = –3718.058624

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3720.389102

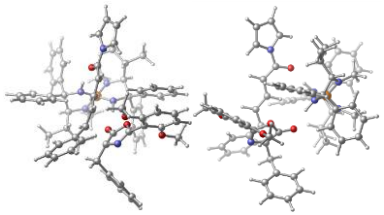
G = –3719.191155

0 1

O	1.03821900	1.05885200	0.23998300
C	2.14946400	0.54028500	0.20666500
C	3.35113700	0.76836500	0.98657500
O	2.42844300	-0.54318900	-0.62238400
N	4.37076500	-0.02814200	0.40800100
C	3.79111600	-0.78076500	-0.45453000
C	4.39564200	-1.83183900	-1.29469200
C	4.11966600	-3.18982300	-1.05041100
C	5.27346900	-1.48740200	-2.34085700
C	4.71120300	-4.19138200	-1.83132800
C	5.87076200	-2.48506300	-3.12435800
C	5.57973000	-3.82053600	-2.85643900
O	3.26947700	-3.43552000	-0.01182500
C	2.96645200	-4.78667600	0.31297600
H	3.86509200	-5.33199000	0.62828600
H	2.50009000	-5.30746300	-0.53197100
H	2.25345300	-4.74027200	1.13646700
O	5.46905100	-0.15605300	-2.52547100
C	6.34809900	0.27298700	-3.55233200
H	7.36897900	-0.09607800	-3.38917400
H	6.00057300	-0.04851700	-4.54315000
H	6.34313700	1.36300600	-3.50178100
H	4.51251400	-5.23898500	-1.64260200
H	6.54712300	-2.23002700	-3.93087800
H	6.04292500	-4.59483400	-3.46236700
C	3.69491800	2.16172900	1.46433200
H	2.85025400	2.53699000	2.05306700
H	4.56174800	2.08921600	2.13006000
C	3.99361000	3.12160100	0.32490400
C	3.03447600	4.04973100	-0.10197500
C	5.22761400	3.07927600	-0.34086600
C	3.29885500	4.91481700	-1.16703700
C	5.49560100	3.94558200	-1.40097400
C	4.53156600	4.86663500	-1.82004600
H	2.07329700	4.09400900	0.40443300
H	5.97232200	2.35254100	-0.02810800
H	2.54141700	5.62945900	-1.47952600
H	6.46349700	3.90808500	-1.89629200
H	4.74294400	5.54511800	-2.64297400
C	2.79851600	-0.29302400	2.67129100
C	1.68947100	0.30044500	3.35218900
H	2.55078500	-1.18131900	2.09008700
H	1.89060200	0.98114200	4.17696400
C	0.36738700	0.00412200	3.06573600
H	0.17710200	-0.67634700	2.23797900
C	-0.75819900	0.45052000	3.77580500
H	-0.60852400	1.09367000	4.63666600
C	-2.05917400	-0.00580200	3.48527500
O	-2.39663400	-0.82924300	2.59372900
N	-3.12870700	0.49666900	4.30854800
C	-4.36357200	-0.11972000	4.40222800
C	-3.14808800	1.63842200	5.09548400
C	-5.15671100	0.61726700	5.24751200
C	-4.38562100	1.74006800	5.68241200
H	-4.53815700	-1.04096300	3.87085400
H	-2.29873600	2.30169600	5.13280000
H	-6.17306400	0.37774900	5.53200700
H	-4.70679400	2.53396100	6.34431100
H	-0.62273300	1.08717500	-0.45485400
N	-1.60612400	1.22867700	-0.72246500
P	-2.53247200	-0.01509000	-1.24793600
N	-3.83286700	0.95426400	-1.60981100
C	-3.66666800	2.36298400	-1.17949900
C	-2.09107700	2.56307300	-1.14158900
C	-5.11813500	0.47354700	-2.10414400
H	-4.98890900	-0.49725500	-2.58587500
H	-5.85369700	0.35217200	-1.30253200
H	-5.51435200	1.18105700	-2.84216400
H	-4.05967700	2.98950800	-1.98530000
C	-4.47036700	2.75399400	0.09971200
H	-3.97106800	3.63713800	0.50962500
C	-4.47937300	1.67785500	1.19033600
H	-5.01081700	0.77532200	0.86645900
C	-1.66283500	3.64670700	-0.14118200
C	-1.16986600	3.33492700	1.13069400
C	-1.79232300	4.99773700	-0.50166400
C	-0.81745400	4.35358600	2.02072100
C	-1.45062100	6.01145400	0.39131200
C	-0.95830600	5.69247400	1.65917800
H	-1.04410200	2.30396500	1.43799000
H	-2.15353200	5.25933000	-1.49250800
H	-0.43133300	4.08608000	3.00045300
H	-1.56020200	7.05059900	0.09213200
H	-0.68323200	6.48134700	2.35413400
C	-1.47790000	2.89692500	-2.53182700
C	-0.07392300	2.92695700	-2.61710500
C	-2.21008600	3.15856900	-3.69539000
C	0.57027400	3.20771300	-3.81857600
C	-1.56420500	3.43952400	-4.90588700
C	-0.17423500	3.46614500	-4.97336500
H	0.52348100	2.73410600	-1.73063700
H	-3.29489000	3.15079900	-3.68847000
H	1.65618900	3.23304800	-3.84525600
H	-2.15939700	3.64061500	-5.79311100
H	0.32598800	3.68865500	-5.91210700
N	-2.38514800	-1.23557500	-0.15958900
C	-2.59319400	-2.57558500	-0.76077500
C	-1.86808800	-2.37811600	-2.15824300
N	-2.30799000	-1.01561200	-2.55137000
H	-2.40336900	-1.06485000	0.86153300
C	-2.52737200	-0.67805700	-3.95192300
H	-2.92538200	0.33522400	-4.02357800
H	-1.59976700	-0.71668400	-4.52879300
H	-3.25016400	-1.37302400	-4.39971600
H	-2.28124900	-3.06603700	-2.90162000

C	-0.31603300	-2.56846800	-2.13284500
H	0.04016300	-2.31918900	-1.12668300
C	0.43878400	-1.64919900	-3.10779100
H	0.21983400	-1.90053000	-4.15368300
C	-2.00053300	-3.69112700	0.11667900
C	-1.13329000	-3.42609300	1.18164000
C	-2.35471300	-5.02765100	-0.13586700
C	-0.63082300	-4.46672500	1.96880700
C	-1.84065700	-6.06609100	0.63737000
C	-0.97444300	-5.78964800	1.69804800
H	-0.87894500	-2.40726200	1.43905200
H	-3.04816400	-5.26138600	-0.93788200
H	0.01744900	-4.22802100	2.80782300
H	-2.13082900	-7.09069500	0.41991100
H	-0.58864600	-6.59640400	2.31570000
C	-4.11877700	-2.83381500	-0.90205300
C	-4.72138800	-3.41171500	-2.02625300
C	-4.93902800	-2.50474800	0.19094000
C	-6.10210700	-3.63580000	-2.06874800
C	-6.31313200	-2.73228100	0.15236800
C	-6.90409200	-3.29558700	-0.98187400
H	-4.12842000	-3.70252800	-2.88753000
H	-4.49384200	-2.06522000	1.07924300
H	-6.54401200	-4.08048600	-2.95677100
H	-6.92294500	-2.47074900	1.01307400
H	-7.97590600	-3.47128600	-1.01371900
C	4.09951300	-0.44218000	3.38303100
C	4.90876300	-1.55816100	3.10886400
C	4.55103100	0.47647800	4.34708800
C	6.11477900	-1.75630300	3.77768300
H	4.58147300	-2.27206800	2.35873900
C	5.76096100	0.28285500	5.01246500
H	3.95378100	1.35204100	4.58249400
C	6.54812000	-0.83600100	4.73376000
H	6.71896200	-2.63094500	3.54976700
H	6.08707300	1.00769600	5.75421600
H	7.48881800	-0.98837500	5.25654300
C	0.06624700	-4.02675300	-2.44175400
H	-0.25480700	-4.30335000	-3.45590000
H	1.15513600	-4.14128900	-2.40256400
H	-0.37411600	-4.73950100	-1.74177900
H	0.21497600	-0.59130800	-2.94683900
H	-3.47247500	1.37944200	1.48571600
C	-5.90262600	3.20388700	-0.24908800
H	-6.52183000	2.38665900	-0.63454400
H	-6.39934200	3.58966400	0.64818000
H	-5.90303300	4.00708000	-0.99689100
H	-4.98509900	2.04829200	2.08801200
H	1.51437700	-1.77544000	-2.95583600

● **1ba**-*SR* (HH)



B3LYP/6-31G*

E = –3719.223401

Zero-point correction = 1.284334 (Hartree/Particle)

Thermal correction to Energy = 1.359988

Thermal correction to Enthalpy = 1.360933

Thermal correction to Gibbs Free Energy = 1.165995

Sum of electronic and zero-point Energies = –3717.939067

Sum of electronic and thermal Energies = –3717.863413

Sum of electronic and thermal Enthalpies = –3717.862468

Sum of electronic and thermal Free Energies = –3718.057406

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

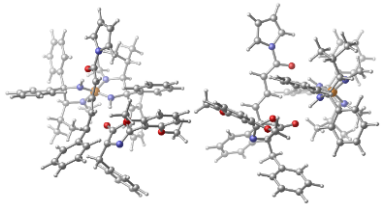
E = –3720.390595

G = –3719.191043

0 1

O	-0.95792400	0.32705600	-1.38554800
C	-2.08418800	0.40644100	-0.87822300
C	-3.03942600	1.49089700	-0.79427000
O	-2.59454200	-0.60736800	-0.10328200
N	-4.17578600	1.00095800	-0.12097300
C	-3.85520500	-0.16971400	0.30569800
C	-4.66871800	-1.12104700	1.07942000
C	-4.96447000	-2.38915700	0.53142400
C	-5.19119500	-0.79319600	2.34770400
C	-5.73518400	-3.31763600	1.24224400
C	-5.97026300	-1.71817300	3.05741100
C	-6.22663600	-2.96695000	2.49738600
O	-4.47900200	-2.60748600	-0.71804500
C	-4.74946000	-3.84636400	-1.35353500
H	-5.82851900	-4.00881900	-1.47548200
H	-4.31023000	-4.68491000	-0.79981300
H	-4.27965500	-3.78025900	-2.33609400
O	-4.87909500	0.44231200	2.83104600
C	-5.36588000	0.81462900	4.11138600
H	-4.98728800	0.14836300	4.89733000
H	-4.99424000	1.82586200	4.28528200
H	-6.46303600	0.82160400	4.13919000
H	-5.96297200	-4.28953900	0.82233600
H	-6.36917300	-1.47524900	4.03409900
H	-6.82938300	-3.68217100	3.05094500
C	-3.21646400	2.47481300	-1.92884700
H	-2.24155400	2.91319100	-2.17306300
H	-3.86007700	3.28908100	-1.58244900
C	-3.81204600	1.84346400	-3.17740500
C	-3.00359300	1.50580200	-4.27010000
C	-5.18559900	1.57107100	-3.25271000
C	-3.55075700	0.91883100	-5.41301000
C	-5.73490900	0.98383800	-4.39220700
C	-4.91980400	0.65713800	-5.47888400
H	-1.93502700	1.70150500	-4.22048400
H	-5.81940800	1.81319000	-2.40386500
H	-2.90704400	0.67094600	-6.25403500
H	-6.80275800	0.78288300	-4.43330100
H	-5.34917400	0.20410400	-6.36902500
C	-1.98213700	2.55949300	0.71809800
C	-1.77375300	1.78116200	1.89247900
H	-1.10833300	2.66679800	0.07444900
H	-2.50805300	1.84501000	2.69060900
C	-0.62459100	1.02613900	2.09587400
H	0.08879500	0.99297400	1.27395700
C	-0.26053800	0.33501500	3.25469000
H	-0.95791400	0.29832900	4.08442200
C	1.03104700	-0.21861800	3.42387200
O	2.01396000	-0.11439300	2.64548400
N	1.26620400	-0.96585000	4.62610500
C	2.53339100	-1.26690900	5.09674300
C	0.33389100	-1.52000300	5.49270800
C	2.40692700	-1.99476800	6.25359600
C	1.00801800	-2.16080000	6.50172900
H	3.39694100	-0.90958200	4.56058400
H	-0.72275700	-1.44797600	5.29042200
H	3.22242200	-2.36456000	6.86127300
H	0.55208200	-2.69839000	7.32297600
H	0.38798600	-0.79508100	-0.89258000
N	1.28266200	-1.29098200	-0.75213700
P	2.70883900	-0.49158800	-0.89631000
N	3.62103900	-1.87039500	-0.79022000
C	2.82402200	-3.05505400	-0.38060700
C	1.39906600	-2.74757500	-1.01715500
C	5.04439700	-1.99438100	-1.08090500
H	5.20441100	-2.78034500	-1.83070800
H	5.62548200	-2.23659500	-0.18786700
H	5.42226300	-1.05134600	-1.47826200
H	3.27499100	-3.91743900	-0.87888700
C	2.82822800	-3.33892700	1.15566600
H	2.01477900	-2.76318000	1.60709700
C	4.11436900	-2.89422800	1.86989500
H	4.32404700	-1.83279700	1.72082500
C	0.23774900	-3.49975300	-0.34579300
C	-0.14515600	-4.76904900	-0.80777300
C	-0.43912500	-2.95859500	0.75445400
C	-1.15281700	-5.48922900	-0.16697700
C	-1.45427900	-3.67569000	1.38955100
C	-1.80984200	-4.94609900	0.93935500
H	0.34816200	-5.20310300	-1.67141500
H	-0.18366900	-1.97162900	1.12131300
H	-1.42387400	-6.47513400	-0.53644600
H	-1.96885000	-3.22856800	2.23467700
H	-2.59633700	-5.50427600	1.44062300
C	1.36553200	-3.00076100	-2.54946800
C	0.41578900	-2.30093600	-3.31518000
C	2.19087600	-3.91900600	-3.21232600
C	0.31114100	-2.50039900	-4.69055600
C	2.08979200	-4.11690500	-4.59396400
C	1.15206400	-3.40701100	-5.34024500
H	-0.25182700	-1.59068900	-2.83598200
H	2.92161000	-4.50638400	-2.66588800
H	-0.43537100	-1.94542100	-5.25260800
H	2.74758400	-4.83321900	-5.07967600
H	1.07229700	-3.56146300	-6.41294700
N	2.70205900	0.79811500	0.12515800
C	3.60341100	1.88416900	-0.32982500
C	3.30828500	1.85667100	-1.89243500
N	3.25301900	0.40028900	-2.18383600
H	2.44220800	0.64555400	1.11644600
C	3.68722000	-0.12766900	-3.47194300
H	3.03804700	0.20104800	-4.28714800
H	3.66255800	-1.21870000	-3.44712600
H	4.71445500	0.19552800	-3.68653800
H	4.16400000	2.25272100	-2.44703000
C	2.03968100	2.65589100	-2.33075100
H	1.33243200	2.63761600	-1.49419200
C	1.30269900	2.05194900	-3.53705700
H	0.98238200	1.02317200	-3.35877800
C	3.25933500	3.21212200	0.36664700
C	4.19630200	4.25821600	0.39442100
C	2.02116000	3.41990500	0.98533400
C	3.89271500	5.47685600	0.99947100
C	1.71776000	4.63760800	1.59910200
C	2.64979500	5.67350300	1.60490900
H	5.17506000	4.12168000	-0.05388500
H	1.28511900	2.62810400	1.00540100
H	4.63540300	6.27038800	1.00513600
H	0.74857600	4.76343200	2.07362500
H	2.41649100	6.62048600	2.08399000
C	5.07558500	1.51913000	0.00533100
C	6.15703600	1.75516900	-0.85334700
C	5.34656900	0.96751700	1.26913600
C	7.46441100	1.43295800	-0.47326800
C	6.64889800	0.65027800	1.65120500
C	7.71641200	0.87741900	0.77912000
H	6.00389800	2.20320200	-1.82988600
H	4.53052600	0.78310000	1.96197000
H	8.28320200	1.62303000	-1.16245300
H	6.82852500	0.22607100	2.63542700
H	8.73163000	0.62858000	1.07583600
C	-2.80528300	3.79202700	0.81868400
C	-2.30822900	5.00267700	0.30757500
C	-4.06575600	3.79810900	1.44388900
C	-3.03254200	6.18873400	0.43489900
H	-1.33552400	5.01456400	-0.17927500
C	-4.79044300	4.98200200	1.56288600
H	-4.48615400	2.86023500	1.79190400
C	-4.27705400	6.18355900	1.06550800
H	-2.62385800	7.11514100	0.03898800
H	-5.76747700	4.96704100	2.03990200
H	-4.84617800	7.10448200	1.16248500
H	4.98612600	-3.47951200	1.54901300
C	2.60316800	-4.83480000	1.43873000
H	2.55798100	-5.00768400	2.51950800
H	1.67996700	-5.21962000	1.00220200
H	3.43946500	-5.42969600	1.04487700
C	2.39633500	4.11837700	-2.65231000
H	3.06797200	4.16676100	-3.52081200
H	1.49061100	4.67902300	-2.90954300
H	2.88091400	4.63393600	-1.82109300
H	1.91292300	2.08764000	-4.44847500
H	0.40034100	2.64203500	-3.73257300
H	3.99050000	-3.05221700	2.94638500

● **1ba**-*SR* (MeMe)



B3LYP/6-31G*

E = –3719.223026

Zero-point correction = 1.283438 (Hartree/Particle)

Thermal correction to Energy = 1.359566

Thermal correction to Enthalpy = 1.360510

Thermal correction to Gibbs Free Energy = 1.163052

Sum of electronic and zero-point Energies = –3717.939588

Sum of electronic and thermal Energies = –3717.863460

Sum of electronic and thermal Enthalpies = –3717.862516

Sum of electronic and thermal Free Energies = –3718.059974

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

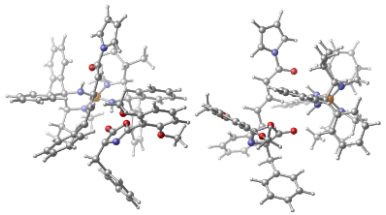
E = –3720.387469

G = –3719.190401

0 1

O	-0.97715000	0.02719800	-1.25931700
C	-2.13383200	0.19671300	-0.85751800
C	-3.14456600	1.17734500	-1.19664800
O	-2.64120400	-0.52417700	0.19607400
N	-4.29787800	0.86515300	-0.44579000
C	-3.94639300	-0.06403600	0.37124400
C	-4.75786400	-0.75457600	1.38714500
C	-4.98448800	-2.14309200	1.26458000
C	-5.33830900	-0.06619800	2.47152300
C	-5.75128300	-2.83252600	2.21220500
C	-6.11173400	-0.75289200	3.41843700
C	-6.30351600	-2.12479400	3.27717700
O	-4.43626500	-2.72349600	0.16569100
C	-4.63225400	-4.11235900	-0.04723200
H	-5.69785300	-4.35652800	-0.15043300
H	-4.19429900	-4.70748600	0.76307300
H	-4.11499600	-4.34152400	-0.98015100
O	-5.08663600	1.27155200	2.54424100
C	-5.62299100	2.00523100	3.63480700
H	-5.24584100	1.63300400	4.59611000
H	-5.29019900	3.03437300	3.48990100
H	-6.72013800	1.97600600	3.63997400
H	-5.92767500	-3.89685700	2.11797700
H	-6.55575400	-0.23166600	4.25702400
H	-6.90257000	-2.65443800	4.01331700
C	-3.30019200	1.68671600	-2.61296200
H	-2.36558200	2.16501200	-2.92842500
H	-4.07333900	2.46155800	-2.60985600
C	-3.66056000	0.59768200	-3.61118600
C	-2.73095700	0.15992000	-4.56287700
C	-4.93048600	0.00169400	-3.59488700
C	-3.05924700	-0.84150100	-5.48050800
C	-5.25981800	-1.00073800	-4.50667800
C	-4.32607000	-1.42646100	-5.45503500
H	-1.74196500	0.61197600	-4.58711200
H	-5.65509800	0.32382800	-2.85188100
H	-2.32742800	-1.15586800	-6.22151200
H	-6.25021800	-1.44876100	-4.47969400
H	-4.58605200	-2.20312400	-6.16992400
C	-2.25326500	2.78228900	-0.14033000
C	-2.00690000	2.46422700	1.22640400
H	-1.37097000	2.75360600	-0.78067400
H	-2.76472600	2.71722100	1.96294600
C	-0.81111400	1.90233700	1.65378400
H	-0.07845100	1.66703600	0.88279900
C	-0.42672400	1.62943900	2.96989100
H	-1.12991900	1.82358800	3.77194600
C	0.87708400	1.18712400	3.28884100
O	1.84062100	1.03520000	2.49316300
N	1.15294200	0.89170400	4.66627200
C	2.43478800	0.73412000	5.16589600
C	0.25235100	0.69765000	5.70559000
C	2.34987300	0.45299100	6.50634500
C	0.96126800	0.42459500	6.84816300
H	3.27958700	0.85663300	4.50874900
H	-0.81147600	0.73055500	5.53436700
H	3.18629900	0.28940300	7.17320000
H	0.53438300	0.21796000	7.82104000
H	0.46327700	-0.91174800	-0.63747100
N	1.33310200	-1.42653000	-0.43006400
P	2.80825100	-0.79154600	-0.75149200
N	3.62424900	-2.17244000	-0.32598000
C	2.77240000	-3.22683200	0.26260800
C	1.31506300	-2.90137300	-0.29620500
C	5.07014600	-2.34427500	-0.39804600
H	5.29989200	-3.35697100	-0.74988300
H	5.55882300	-2.18802800	0.56955700
H	5.49051900	-1.62547700	-1.10378700
H	3.09621600	-4.16491700	-0.19318000
C	2.93533400	-3.41545100	1.80326300
H	2.01426400	-3.89457600	2.14802100
C	3.10582300	-2.10929100	2.58704800
H	2.30140500	-1.39322500	2.40825900
C	0.20793300	-3.33680300	0.67997400
C	-0.19609200	-4.68049200	0.72600800
C	-0.37496800	-2.43316400	1.57583600
C	-1.13769000	-5.11131600	1.65958400
C	-1.33039800	-2.86177800	2.49893300
C	-1.70983800	-4.20170300	2.55233700
H	0.22399200	-5.39774100	0.02774400
H	-0.09198300	-1.38790100	1.56044300
H	-1.42631100	-6.15930300	1.68435800
H	-1.77600400	-2.13554300	3.17189900
H	-2.44812400	-4.53337900	3.27765800
C	1.05662000	-3.54517900	-1.69068200
C	0.10436100	-2.94330200	-2.53249900
C	1.67078100	-4.72241500	-2.14106600
C	-0.20493800	-3.48651900	-3.77836600
C	1.36520300	-5.26635400	-3.39314400
C	0.42866900	-4.65026100	-4.21953900
H	-0.40976800	-2.04068800	-2.21799200
H	2.39135200	-5.25025600	-1.52425300
H	-0.95180400	-2.99565400	-4.39701400
H	1.86390100	-6.17753100	-3.71382600
H	0.19003200	-5.07389200	-5.19149000
N	2.87478900	0.70779700	-0.08698300
C	3.86451300	1.59076600	-0.73938800
C	3.74750300	1.15522500	-2.26501900
N	3.46640300	-0.29731600	-2.19352700
H	2.50471700	0.87940300	0.86116400
C	3.70028500	-1.17777600	-3.33197400
H	2.90273900	-1.11457700	-4.07994400
H	3.75259800	-2.21287700	-2.98618000
H	4.65258800	-0.92043400	-3.81018900
H	4.73495300	1.25435700	-2.72423500
C	2.77204300	1.97583700	-3.15869600
H	2.95296400	3.02413500	-2.89803500
C	1.28998700	1.67855900	-2.91359400
H	0.99578800	1.86145400	-1.87882900
C	3.55096000	3.07821000	-0.50812800
C	4.44450500	4.04842000	-0.99272800
C	2.41238900	3.50842900	0.17999000
C	4.19208700	5.40665000	-0.81630600
C	2.16406400	4.87169400	0.36587200
C	3.04636100	5.82569700	-0.13502800
H	5.35141800	3.74144000	-1.50589200
H	1.71915100	2.79197400	0.59949100
H	4.89655400	6.13788600	-1.20402400
H	1.27392700	5.17622700	0.90917500
H	2.85147700	6.88483900	0.00977100
C	5.27521700	1.30860800	-0.14095900
C	6.46123600	1.28244600	-0.88584200
C	5.36916200	1.12504200	1.24971500
C	7.69692300	1.05730400	-0.26990400
C	6.59984000	0.90549300	1.86537700
C	7.77257200	0.86441400	1.10723600
H	6.45117900	1.44262400	-1.95948400
H	4.47014500	1.15690800	1.85821600
H	8.59903800	1.03624700	-0.87594200
H	6.64114800	0.77028800	2.94292900
H	8.73219100	0.69090400	1.58645900
C	-3.18602700	3.89326000	-0.46207100
C	-2.78999600	4.89112200	-1.36813700
C	-4.45372100	4.00253600	0.13812500
C	-3.62000200	5.97593400	-1.65303300
H	-1.81269700	4.82219100	-1.84069000
C	-5.28414200	5.08251600	-0.15313500
H	-4.79468300	3.21283800	0.79920700
C	-4.87140200	6.07716500	-1.04460500
H	-3.28787000	6.74029500	-2.35121700
H	-6.26465600	5.14571800	0.31268000
H	-5.52265500	6.91855100	-1.26688900
H	4.05058200	-1.61098600	2.33807800
C	4.07363300	-4.40277300	2.12773400
H	5.06190600	-4.00757400	1.86752400
H	4.08517400	-4.61880300	3.20202500
H	3.94419800	-5.35746800	1.60201500
C	3.11880400	1.84367800	-4.65444700
H	2.87186200	0.85606200	-5.05765200
H	2.54798700	2.57842100	-5.23346700
H	4.18334500	2.03060900	-4.84507100
H	1.03624400	0.63853300	-3.14406700
H	3.12117300	-2.31700500	3.66271600
H	0.67016100	2.31646100	-3.55499700

● **1ba**-*SR* (HMe)



B3LYP/6-31G*

E = –3719.229538

Zero-point correction = 1.283668 (Hartree/Particle)

Thermal correction to Energy = 1.359715

Thermal correction to Enthalpy = 1.360659

Thermal correction to Gibbs Free Energy = 1.163838

Sum of electronic and zero-point Energies = –3717.939698

Sum of electronic and thermal Energies = –3717.863651

Sum of electronic and thermal Enthalpies = –3717.862707

Sum of electronic and thermal Free Energies = –3718.059528

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3720.38958

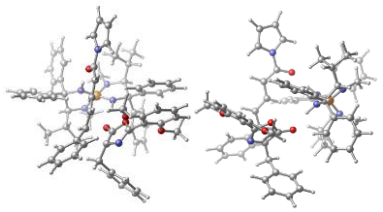
G = –3719.191841

0 1

O	-1.02958000	0.21975000	-1.34562900
C	-2.15836000	0.35259000	-0.85824000
C	-3.08445000	1.46472800	-0.84216100
O	-2.71097300	-0.61040000	-0.04601900
N	-4.24395100	1.03930700	-0.16510500
C	-3.96394700	-0.12008200	0.31843600
C	-4.81699300	-1.01239600	1.12029700
C	-5.15619400	-2.28778300	0.61669100
C	-5.33319900	-0.62027600	2.37240100
C	-5.96600900	-3.16020800	1.35453400
C	-6.15225700	-1.48801200	3.10881500
C	-6.45276000	-2.74548300	2.59197200
O	-4.66923100	-2.57024500	-0.61953300
C	-4.98105400	-3.82024800	-1.21208100
H	-6.06447000	-3.94739200	-1.33713100
H	-4.57803300	-4.65433000	-0.62465900
H	-4.50158800	-3.80777400	-2.19207400
O	-4.97423000	0.61833500	2.81396000
C	-5.45430000	1.05578800	4.07616600
H	-5.10901100	0.40318000	4.88843500
H	-5.04271300	2.05661800	4.21727200
H	-6.55040400	1.10852200	4.09430100
H	-6.22730200	-4.13766000	0.96835200
H	-6.54808900	-1.19504700	4.07300400
H	-7.08617000	-3.41675000	3.16594200
C	-3.21260800	2.40400400	-2.01993700
H	-2.22726600	2.82766200	-2.24681500
H	-3.86249200	3.23448200	-1.72710800
C	-3.76564900	1.73075900	-3.26607400
C	-2.92466900	1.39077600	-4.33319300
C	-5.13048200	1.42429100	-3.36663600
C	-3.43151300	0.76768900	-5.47572200
C	-5.63938200	0.80106400	-4.50573000
C	-4.79207600	0.47176700	-5.56680700
H	-1.86289100	1.61614400	-4.26478200

H	-5.78902500	1.66880200	-2.53749300
H	-2.76309800	0.51857900	-6.29694900
H	-6.70106800	0.57409800	-4.56684400
H	-5.19013800	-0.00956200	-6.45666200
C	-2.01451300	2.59429500	0.63958000
C	-1.80349900	1.85656300	1.83738500
H	-1.14455100	2.67349900	-0.01260700
H	-2.53783500	1.94047500	2.63385400
C	-0.65540100	1.10493600	2.05878700
H	0.06052200	1.05386800	1.23973900
C	-0.29852600	0.43458400	3.23185900
H	-0.99841200	0.41877400	4.06004900
C	0.98421700	-0.13423300	3.41064600
O	1.96577700	-0.06177900	2.62586200
N	1.21076500	-0.86122100	4.62651800
C	2.47357700	-1.17524700	5.10068800
C	0.27100100	-1.38316300	5.50530400
C	2.33714200	-1.87864100	6.27141500
C	0.93615800	-2.01599400	6.52508700
H	3.34279300	-0.84429300	4.55692300
H	-0.78468100	-1.29774700	5.30342300
H	3.14748300	-2.25070900	6.88456000
H	0.47277100	-2.53024200	7.35701400
H	0.43547000	-0.77413600	-0.91195300
N	1.32849300	-1.27691900	-0.79311300
P	2.78429000	-0.52792700	-0.89070000
N	3.64177300	-1.93657600	-0.72298000
C	2.79576500	-3.08663200	-0.31777700
C	1.40131000	-2.74700800	-1.00399100
C	5.06259000	-2.11621600	-0.99494700
H	5.20436400	-2.89254800	-1.75867300
H	5.61623800	-2.40216100	-0.09737100
H	5.48417500	-1.18033000	-1.36511100
H	3.23154400	-3.97380100	-0.78536600
C	2.75194400	-3.33965300	1.22302000
H	1.96038300	-2.71388100	1.64611600
C	4.04604700	-2.94552100	1.95311600
H	4.31668400	-1.90100700	1.78413800
C	0.19835400	-3.43715700	-0.34155900
C	-0.22653700	-4.69783500	-0.79070500
C	-0.47145500	-2.85451700	0.74125700
C	-1.26907600	-5.36966200	-0.15349400
C	-1.52133700	-3.52293500	1.37244400
C	-1.91884400	-4.78542200	0.93603500
H	0.26223400	-5.16337000	-1.64055700
H	-0.18498900	-1.87250800	1.09844200
H	-1.57293300	-6.34976500	-0.51266500
H	-2.03029600	-3.04245600	2.20237900
H	-2.73221800	-5.30576800	1.43522300
C	1.39251900	-3.03899100	-2.52906300
C	0.44109200	-2.36675800	-3.31769100
C	2.24255300	-3.95278600	-3.16496100
C	0.35826900	-2.58930500	-4.69049000
C	2.16355300	-4.17345200	-4.54504900
C	1.22410800	-3.49141800	-5.31438000
H	-0.24415000	-1.66181300	-2.85519800
H	2.97702300	-4.51707400	-2.59983100
H	-0.39037100	-2.05698800	-5.27138400
H	2.83986300	-4.88563500	-5.01099800
H	1.16132800	-3.66409100	-6.38545000
N	2.76509400	0.78120600	0.10400900
C	3.74560400	1.81523600	-0.29062400
C	3.68281200	1.74413200	-1.87973300
N	3.45728500	0.30693600	-2.15850200
H	2.46150700	0.64236800	1.08400600
C	3.69826600	-0.25201400	-3.48331800
H	2.92241000	0.03513800	-4.20126500
H	3.70910900	-1.34248600	-3.42514200
H	4.67044500	0.08895200	-3.85915200
H	4.67724400	1.98017200	-2.26704700
C	2.69739900	2.71833400	-2.59486200
H	2.73544000	3.65167600	-2.02396700
C	1.24198000	2.24097700	-2.61372000
H	0.85430400	2.03650900	-1.61465000
C	3.35589900	3.19573500	0.26512000
C	4.26184800	4.26530700	0.17813100
C	2.10770500	3.43137500	0.85115700
C	3.92024800	5.53247000	0.64714600
C	1.76767300	4.69872800	1.33142700
C	2.66974900	5.75567400	1.22790300
H	5.24799000	4.10851800	-0.24807800
H	1.39112400	2.62692900	0.94577500
H	4.63860200	6.34421100	0.56724900
H	0.79256200	4.84775200	1.78694600
H	2.40684300	6.74150700	1.60169200
C	5.15285300	1.44477300	0.26474100
C	6.35322000	1.65276100	-0.42845500
C	5.23258800	0.92737100	1.56961600
C	7.58760200	1.33614400	0.14834800
C	6.46240900	0.61518100	2.14683300
C	7.64888000	0.81331500	1.43752900
H	6.35543400	2.07343600	-1.42917100
H	4.32653500	0.76021900	2.14459800
H	8.49966200	1.50441700	-0.41853200
H	6.49053100	0.21716500	3.15765700
H	8.60713400	0.56772100	1.88700100
C	-2.83688300	3.82922900	0.69077300
C	-2.34213800	5.01518500	0.12211500
C	-4.09224800	3.86572400	1.32502800
C	-3.06315000	6.20723400	0.20295000
H	-1.37401700	5.00289300	-0.37379200
C	-4.81353800	5.05533500	1.39795900
H	-4.51191000	2.94521900	1.71681100
C	-4.30205500	6.23271800	0.84397300
H	-2.65635400	7.11432500	-0.23718300
H	-5.78664600	5.06355500	1.88308400
H	-4.86853800	7.15834200	0.90512600
H	4.89112300	-3.58399700	1.66354500
C	2.44784100	-4.81592400	1.53393700
H	2.37793700	-4.96164500	2.61741200
H	1.51381900	-5.16460300	1.09096100
H	3.25952400	-5.46021000	1.16715600
C	3.18354000	3.07109100	-4.01426100
H	3.14251900	2.21789700	-4.69999400
H	2.55163100	3.85851500	-4.44049000
H	4.21480800	3.44613500	-4.00627200
H	1.11875500	1.32444600	-3.20109300
H	0.60434000	3.00808900	-3.06895100
H	3.89351200	-3.07189000	3.03013200

- **1ba**-*SR* (MeH)



B3LYP/6-31G*

E = –3719.222645

Zero-point correction = 1.283761 (Hartree/Particle)

Thermal correction to Energy = 1.358758

Thermal correction to Enthalpy = 1.359702

Thermal correction to Gibbs Free Energy = 1.166085

Sum of electronic and zero-point Energies = –3717.938884

Sum of electronic and thermal Energies = –3717.863887

Sum of electronic and thermal Enthalpies = –3717.862943

Sum of electronic and thermal Free Energies = –3718.056560

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3720.387746

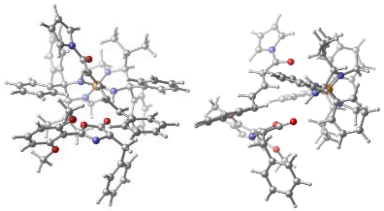
G = –3719.188334

0 1

O	-0.89976300	0.12382200	-1.31773700
C	-2.04938700	0.24154600	-0.87464200
C	-3.08592100	1.22696800	-1.11052100
O	-2.51208300	-0.56272600	0.13644700
N	-4.21124900	0.83859800	-0.35315600
C	-3.82054500	-0.13939500	0.38445700
C	-4.59099000	-0.91585300	1.36872700
C	-4.77411600	-2.30200700	1.16859500
C	-5.18099600	-0.30972900	2.49689000
C	-5.50284600	-3.07006800	2.08524400
C	-5.91595300	-1.07596100	3.41277400
C	-6.06231500	-2.44365600	3.19626100
O	-4.22710500	-2.80011500	0.02950600
C	-4.39859300	-4.17664500	-0.26949000
H	-5.46103300	-4.43674400	-0.36559600
H	-3.92923200	-4.81282100	0.49017100
H	-3.89832800	-4.33285200	-1.22649500
O	-4.97820500	1.02996000	2.63974200
C	-5.52630800	1.68302700	3.77450100
H	-5.12351700	1.27397200	4.71016000
H	-5.23296000	2.73009700	3.68228800
H	-6.62157400	1.61304600	3.79030400
H	-5.64435000	-4.13277600	1.93252900
H	-6.36642100	-0.61888500	4.28460500
H	-6.63181400	-3.03468800	3.90876600
C	-3.29604600	1.82464300	-2.48530000
H	-2.36605300	2.30391400	-2.81303100
H	-4.05244500	2.61137800	-2.40301200
C	-3.72498400	0.80075600	-3.52455600
C	-2.83538100	0.36219200	-4.51339400
C	-5.02104700	0.26446100	-3.50720800
C	-3.22794400	-0.58187100	-5.46571800
C	-5.41513400	-0.68018000	-4.45443600
C	-4.52064600	-1.10706100	-5.43928200
H	-1.82608200	0.76618800	-4.53762500
H	-5.71490000	0.58616800	-2.73532400
H	-2.52552000	-0.89800200	-6.23388200
H	-6.42503500	-1.08216600	-4.42594800
H	-4.83066300	-1.83860100	-6.18130300
C	-2.19500400	2.74213000	0.03594300
C	-1.97671500	2.34899300	1.39011900
H	-1.30191600	2.74137000	-0.59083800
H	-2.72869800	2.60791800	2.13025600
C	-0.80786100	1.72427900	1.80536300
H	-0.08908100	1.46974400	1.02795700
C	-0.42721900	1.40621100	3.11112600
H	-1.11652000	1.60378600	3.92435900
C	0.87086600	0.92807000	3.40682300
O	1.82664200	0.78403300	2.60253600
N	1.14869100	0.58419100	4.77252200
C	2.43079300	0.39094700	5.25836800
C	0.25096400	0.37145300	5.81036600
C	2.34916500	0.06901300	6.58982300
C	0.96217800	0.05147100	6.93937500
H	3.27231600	0.51959500	4.59805800
H	-0.81310800	0.42621200	5.64597900
H	3.18668200	-0.12922300	7.24584800
H	0.53784700	-0.17905500	7.90802400
H	0.43575400	-0.93744300	-0.64934900
N	1.31754500	-1.43454800	-0.44692600
P	2.75046800	-0.71160900	-0.78232200
N	3.64488000	-2.07754200	-0.49110500
C	2.85778100	-3.21181700	0.03999400
C	1.37174700	-2.91326400	-0.45358100
C	5.09484700	-2.17802800	-0.60392200
H	5.35972100	-3.13231000	-1.07505900
H	5.59263000	-2.11572900	0.36921900
H	5.47613700	-1.36503000	-1.22382900
H	3.20956700	-4.09765600	-0.49310300
C	3.07355300	-3.50854300	1.55748200
H	2.17921800	-4.04449600	1.88896200
C	3.22256400	-2.26232700	2.43714900
H	2.39074600	-1.56207100	2.33869500
C	0.31137500	-3.48890800	0.50194100
C	-0.02144000	-4.85127200	0.44343700
C	-0.29923800	-2.69293200	1.47847300
C	-0.92049500	-5.40626000	1.35321100
C	-1.21247800	-3.24567500	2.37832500
C	-1.52091100	-4.60420200	2.32683700
H	0.42181400	-5.48613200	-0.31757600
H	-0.06538800	-1.63746800	1.54573700
H	-1.15383700	-6.46666700	1.29649200
H	-1.68007900	-2.60303100	3.11824100
H	-2.22495700	-5.03359500	3.03477800
C	1.11236600	-3.44321300	-1.89533200
C	0.12134700	-2.81182200	-2.66786900
C	1.76260500	-4.55247100	-2.45511500
C	-0.19180700	-3.25994800	-3.95012900
C	1.45321200	-5.00082900	-3.74365500
C	0.47684400	-4.35595300	-4.49905400
H	-0.41973100	-1.95844000	-2.27261700
H	2.51537200	-5.10127400	-1.89821900
H	-0.96793300	-2.74772300	-4.51292100
H	1.98070400	-5.86063700	-4.14890300
H	0.23569500	-4.70524800	-5.49949300
N	2.79107300	0.74025000	-0.01643800
C	3.67320600	1.72512700	-0.69052700
C	3.35386800	1.40279800	-2.21477400
N	3.28445500	-0.08038300	-2.22070400
H	2.43588800	0.85416800	0.94801700
C	3.71486800	-0.85168400	-3.38031600
H	3.07190800	-0.67691300	-4.24671700
H	3.67307300	-1.91608000	-3.14096100
H	4.74754400	-0.59193700	-3.64894900
H	4.20444600	1.67741100	-2.84541400

C	2.08440300	2.11147000	-2.78652600
H	1.37939400	2.24990800	-1.95932700
C	1.34313400	1.29465400	-3.85728000
H	1.01774200	0.31949600	-3.48803000
C	3.33979500	3.16195300	-0.25538700
C	4.28607900	4.18643400	-0.42378400
C	2.10199700	3.49371700	0.30621400
C	3.99105700	5.50069400	-0.06447200
C	1.80663600	4.80859000	0.67274400
C	2.74732100	5.81927500	0.48478500
H	5.26503300	3.95944300	-0.83313200
H	1.36025900	2.72697300	0.47862000
H	4.74081200	6.27467600	-0.20636400
H	0.83775200	5.02890600	1.11199000
H	2.52051600	6.84218700	0.77283900
C	5.14884800	1.42492600	-0.31307700
C	6.21998800	1.47434000	-1.21397200
C	5.43169600	1.13362500	1.03230300
C	7.52932800	1.21751300	-0.79199300
C	6.73559300	0.88462200	1.45595600
C	7.79287200	0.91913900	0.54287300
H	6.05674200	1.71985700	-2.25858000
H	4.61924600	1.10067900	1.75259300
H	8.34064600	1.25656100	-1.51431100
H	6.92562000	0.66545700	2.50331600
H	8.80970400	0.72197100	0.87123600
C	-3.10249300	3.89027600	-0.22702400
C	-2.67110000	4.94479400	-1.04835200
C	-4.38295200	3.97397800	0.34956700
C	-3.48015600	6.05921300	-1.27327700
H	-1.68311400	4.89596900	-1.50087800
C	-5.19235000	5.08414200	0.11806100
H	-4.74875000	3.14318100	0.94412900
C	-4.74492700	6.13430900	-0.68902900
H	-3.12131200	6.86728500	-1.90595200
H	-6.18295700	5.12799200	0.56428800
H	-5.37963900	6.99889200	-0.86528200
H	4.14333600	-1.71217400	2.20705700
C	4.25136200	-4.47947400	1.77337900
H	5.21860100	-4.03565500	1.51226400
H	4.30472600	-4.77302700	2.82784100
H	4.13257300	-5.39673500	1.18253400
C	2.44167500	3.48820200	-3.37449700
H	3.10764700	3.37335400	-4.24107200
H	1.53555500	3.99514800	-3.72498600
H	2.93264700	4.14565300	-2.65487000
H	1.95273200	1.15379400	-4.75897900
H	0.44447300	1.84329100	-4.16042000
H	3.27565600	-2.55536600	3.49174400

● **1ba**-*RS* (HH)



B3LYP/6-31G*

E = –3719.222719

Zero-point correction = 1.284169 (Hartree/Particle)

Thermal correction to Energy = 1.359892

Thermal correction to Enthalpy = 1.360837

Thermal correction to Gibbs Free Energy = 1.164424

Sum of electronic and zero-point Energies = –3717.938550

Sum of electronic and thermal Energies = –3717.862826

Sum of electronic and thermal Enthalpies = –3717.861882

Sum of electronic and thermal Free Energies = –3718.058294

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*(@–30 °C

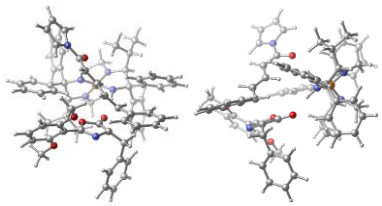
E = –3720.391378

G = –3719.193125

0 1

O	1.05037600	1.27055900	-0.80846500
C	2.06447600	0.58891900	-0.64674500
C	3.38578800	0.90592900	-0.13788500
O	2.05100300	-0.77882600	-0.83253700
N	4.16680900	-0.26457800	-0.23489400
C	3.35541200	-1.20524800	-0.56568700
C	3.65024700	-2.63270000	-0.77662100
C	4.17265400	-3.43959800	0.25760100
C	3.45454800	-3.21086200	-2.04975700
C	4.45487100	-4.79453900	0.03032800
C	3.73617400	-4.56329200	-2.27847900
C	4.22880800	-5.33771400	-1.23142300
O	4.37025400	-2.83205200	1.45879900
C	4.85764900	-3.60755400	2.54320100
H	5.85443000	-4.01546100	2.33178900
H	4.17398400	-4.42975800	2.79126200
H	4.92079800	-2.92256800	3.39031500
O	3.01117000	-2.36195900	-3.01733900
C	2.96694300	-2.82916700	-4.35642600
H	3.94887600	-3.19141700	-4.68733000
H	2.22421300	-3.62718800	-4.48287400
H	2.67711800	-1.96756800	-4.96030800
H	4.84729400	-5.41975900	0.82217600
H	3.58083200	-5.00707400	-3.25371000
H	4.44880300	-6.38786500	-1.40427600
C	4.02425100	2.24669600	-0.43414500
H	3.37771000	3.04319700	-0.04836000
H	4.96764500	2.30303400	0.11750500
C	4.27681800	2.48307400	-1.91488400
C	3.53726700	3.43576100	-2.62641100
C	5.25628700	1.74960700	-2.60105600
C	3.76888600	3.65637100	-3.98605700
C	5.48864800	1.96634300	-3.95881400
C	4.74635900	2.92197400	-4.65780000
H	2.77526500	4.01305800	-2.10729300
H	5.82775100	0.99909000	-2.06172100
H	3.18761100	4.40565600	-4.51872500
H	6.25468800	1.39029500	-4.47253400
H	4.93134000	3.09381700	-5.71524400
C	2.83617900	0.97136600	1.88209700
C	2.34175300	-0.27945300	2.36449900
H	2.07794200	1.73192900	1.69580200
H	3.04472100	-0.94364400	2.85863000
C	1.00503600	-0.65022000	2.32441800
H	0.31146700	0.01502100	1.81254600
C	0.43340700	-1.78208900	2.91765400
H	1.07323800	-2.46635200	3.46418100
C	-0.96208100	-1.99317600	2.92367600
O	-1.84029400	-1.23962100	2.42083600
N	-1.44959000	-3.16372900	3.59608500
C	-2.76776900	-3.31078600	3.99366800
C	-0.75243600	-4.30678300	3.96024300
C	-2.90371100	-4.52918900	4.61104600
C	-1.62335600	-5.16565500	4.58296500
H	-3.46593500	-2.50850200	3.81845800
H	0.28690300	-4.42907300	3.70087200
H	-3.81536700	-4.92339400	5.04068000
H	-1.37593600	-6.14719900	4.96612500
H	-0.58574300	1.63959500	-0.08550400
N	-1.58284300	1.77088200	0.11931800
P	-2.68517200	0.78104300	-0.59743900
N	-3.98008800	1.65457800	-0.04176000
C	-3.59731600	2.67976100	0.96106500
C	-2.13418400	3.09664000	0.48557300
C	-5.36845000	1.50362200	-0.46206500
H	-5.43044000	0.76692300	-1.26437600
H	-6.00747500	1.15947100	0.35459200
H	-5.75434800	2.46209600	-0.83362000
H	-4.28542700	3.51837600	0.82451400
C	-3.70973700	2.20780200	2.44501700
H	-2.77307900	1.70915800	2.71301700
C	-4.82376900	1.17805100	2.69451500
H	-5.82195600	1.59962400	2.51950200
C	-2.16885200	4.01678500	-0.76429700
C	-3.19680300	4.93317100	-1.02610000
C	-1.08721900	3.96997600	-1.66130100
C	-3.16220900	5.75616000	-2.15652900
C	-1.05006300	4.79279400	-2.78646100
C	-2.09071800	5.68745100	-3.04444900
H	-4.03835800	5.03282800	-0.34796200
H	-0.26052000	3.28794800	-1.48481000
H	-3.97746600	6.45263300	-2.33482900
H	-0.20091000	4.73140400	-3.46197600
H	-2.06316900	6.32605200	-3.92316700
C	-1.26123200	3.73706700	1.58004500
C	-0.53953800	2.94356000	2.48291300
C	-1.18358600	5.13177300	1.71537700
C	0.21965500	3.52385900	3.50089400
C	-0.42673900	5.71257300	2.73353000
C	0.27767100	4.91143900	3.63315900
H	-0.57416100	1.86402900	2.40029500
H	-1.71326300	5.77451800	1.02071300
H	0.76751300	2.88241800	4.18543900
H	-0.38471700	6.79541500	2.81657400
H	0.86869400	5.36343000	4.42514200
N	-2.28901600	-0.76882900	-0.25554700
C	-2.75691900	-1.72521700	-1.28764900
C	-2.49060100	-0.88211300	-2.61054600
N	-2.90292200	0.49047100	-2.21268000
H	-2.08706200	-1.05138400	0.72303900
C	-3.47209900	1.41442000	-3.18653100
H	-4.33479400	0.95296200	-3.68518800
H	-2.74184800	1.70576900	-3.94506700
H	-3.80616700	2.32176100	-2.67985200
H	-3.18450600	-1.19179900	-3.39699900
C	-1.04302300	-0.99514200	-3.18343500
C	-0.52673700	0.28105500	-3.86657700
H	-1.08298500	0.51448700	-4.78389600
C	-1.96375400	-3.03991300	-1.18664600
C	-0.68878100	-3.08079000	-0.60694200
C	-2.51001500	-4.23523900	-1.68130600
C	0.02268300	-4.28040000	-0.53255200
C	-1.79604000	-5.43089400	-1.61307500
C	-0.52507500	-5.45869100	-1.03656200
H	-0.23624700	-2.18023700	-0.20985600
H	-3.50463800	-4.23858400	-2.11536300
H	1.00816000	-4.28337800	-0.07677200
H	-2.24190900	-6.34311000	-2.00122800
H	0.02902500	-6.39147000	-0.97438900
C	-4.26426700	-2.02401800	-1.06506700
C	-4.69173900	-2.28239100	0.24940400
C	-5.21479900	-2.10022400	-2.09090800
C	-6.02290800	-2.58717700	0.52581700
C	-6.55351700	-2.40032300	-1.81394500
C	-6.96436000	-2.64216300	-0.50537600
H	-3.97293300	-2.24794400	1.06352100
H	-4.93147700	-1.93806800	-3.12591600
H	-6.32275100	-2.78805100	1.55086800
H	-7.26983700	-2.44812500	-2.63022600
H	-8.00297600	-2.87837800	-0.29015000
C	4.07663400	1.50858000	2.50374600
C	4.11339400	2.83796500	2.95586800
C	5.22330900	0.71213700	2.67844800
C	5.24857100	3.35223500	3.58402200
H	3.23674800	3.46801600	2.82520900
C	6.35785700	1.22945900	3.29984300
H	5.22821400	-0.29953900	2.28546600
C	6.37555500	2.54914200	3.76106700
H	5.25158200	4.38207600	3.93271200
H	7.23801500	0.60207800	3.41839100
H	7.26248200	2.94812900	4.24648300
H	-0.55359600	1.14669000	-3.20087000
C	-0.96084900	-2.16514700	-4.17917000
H	-1.60667200	-1.97757800	-5.04873100
H	0.06402300	-2.27220700	-4.54897700
H	-1.25644100	-3.11908300	-3.73689700
H	-0.36013500	-1.19219100	-2.35170100
H	-4.70508300	0.28047600	2.08254000
C	-3.92853300	3.40900400	3.38224600
H	-4.90048100	3.88041700	3.17977000
H	-3.93778800	3.07613500	4.42605900
H	-3.15597100	4.17435800	3.28567200
H	-4.78581700	0.86357800	3.74329300
H	0.52033500	0.13007400	-4.15044700

● **1ba**-*RS* (MeH)



B3LYP/6-31G*

E = –3719.223894

Zero-point correction = 1.283967 (Hartree/Particle)

Thermal correction to Energy = 1.359819

Thermal correction to Enthalpy = 1.360763

Thermal correction to Gibbs Free Energy = 1.164371

Sum of electronic and zero-point Energies = –3717.939928

Sum of electronic and thermal Energies = –3717.864076

Sum of electronic and thermal Enthalpies = –3717.863131

Sum of electronic and thermal Free Energies = –3718.059523

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

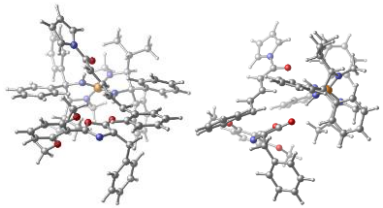
E = –3720.391948

G = –3719.193754

0 1

O	0.92027800	1.17013700	-0.81019400
C	2.00085200	0.59434400	-0.66807500
C	3.29000600	1.03250500	-0.16030900
O	2.11894100	-0.76222200	-0.87598600
N	4.18018500	-0.05595900	-0.28703000
C	3.46038900	-1.06635200	-0.62488000
C	3.88137000	-2.45900500	-0.84825900
C	4.53057000	-3.20495600	0.16035000
C	3.66521900	-3.06919900	-2.10415600
C	4.92303200	-4.53045500	-0.07491400
C	4.05219100	-4.39436400	-2.33828600
C	4.67453100	-5.10750500	-1.31691700
O	4.73098400	-2.57365900	1.34891100
C	5.33528700	-3.29590700	2.41135400
H	6.35417000	-3.61324100	2.15500600
H	4.74059400	-4.17497800	2.69134000
H	5.37445900	-2.60282100	3.25327800
O	3.09584500	-2.27442800	-3.05006500
C	2.91738900	-2.79597500	-4.35701000
H	3.87241200	-3.10676900	-4.80035900
H	2.22050700	-3.64376300	-4.36174600
H	2.49646700	-1.97871800	-4.94511500
H	5.41384400	-5.10854900	0.69761800
H	3.88234100	-4.86225000	-3.29965100
H	4.97873600	-6.13552900	-1.49491100
C	3.79521200	2.43359600	-0.43432300
H	3.08767500	3.15748200	-0.01391600
H	4.73893500	2.56098900	0.10555600
C	4.00237400	2.74204900	-1.90915600
C	3.24650800	3.73360500	-2.54674000
C	4.96542500	2.05086800	-2.66003800
C	3.44308500	4.03067000	-3.89758400
C	5.16141500	2.34300300	-4.00937200
C	4.40107000	3.33451000	-4.63490800
H	2.50166000	4.28418400	-1.97586000
H	5.55428000	1.27566700	-2.17751600
H	2.85109300	4.81046800	-4.37161000
H	5.91404000	1.79782200	-4.57401600
H	4.55799100	3.56452700	-5.68577600
C	2.76722400	1.00853800	1.84875900
C	2.38162200	-0.29260400	2.30012400
H	1.94420600	1.70799400	1.69903700
H	3.14516300	-0.91815400	2.75313500
C	1.07991300	-0.77098200	2.25997800
H	0.32230000	-0.13970500	1.79653900
C	0.62205900	-1.98113600	2.79446400
H	1.33249100	-2.63197300	3.29220300
C	-0.74461600	-2.33104900	2.79211500
O	-1.69939000	-1.64288000	2.33920900
N	-1.10516500	-3.58053500	3.39884200
C	-2.39540000	-3.88199000	3.80013000
C	-0.29228600	-4.66792600	3.68586100
C	-2.39979900	-5.14193900	4.34460600
C	-1.06341200	-5.64464500	4.26482800
H	-3.17355600	-3.14586900	3.68081600
H	0.74976500	-4.67009000	3.40905500
H	-3.26097500	-5.64968300	4.75893900
H	-0.71367600	-6.61729400	4.58595200
H	-0.68423700	1.59375500	-0.02582600
N	-1.67273800	1.71935600	0.21782200
P	-2.78288900	0.73948100	-0.50330900
N	-4.07736100	1.60515800	0.07234500
C	-3.70569100	2.70320900	0.99221800
C	-2.20715400	3.05032700	0.57680800
C	-5.47704000	1.25655600	-0.14232100
H	-5.56563400	0.60350300	-1.01256300
H	-5.91132200	0.73024000	0.71422700
H	-6.05820700	2.16773400	-0.32834100
H	-4.33099500	3.55622500	0.71882600
C	-3.99209000	2.42161200	2.50125700
H	-3.32061400	3.07781200	3.06377900
C	-3.72178600	0.97849600	2.94826100
H	-4.41443400	0.27215600	2.47602700
C	-2.14881000	3.99316100	-0.66069900
C	-3.12552400	4.95528400	-0.95502600
C	-1.02975200	3.91897900	-1.50914500
C	-3.00663500	5.79379800	-2.06788800
C	-0.90987500	4.75529300	-2.61872800
C	-1.90064000	5.69528000	-2.90876400
H	-3.99505500	5.08104800	-0.31772300
H	-0.23584600	3.20490100	-1.31258900
H	-3.78514800	6.52498400	-2.26989400
H	-0.03436100	4.66514100	-3.25631100
H	-1.80839400	6.34452100	-3.77518500
C	-1.39311800	3.65912200	1.73248700
C	-0.65307700	2.84618400	2.60205800
C	-1.41208300	5.04157700	1.96970100
C	0.04456800	3.39745000	3.67865300
C	-0.71986500	5.59235800	3.04863600
C	0.01345300	4.77335400	3.90806500
H	-0.63007900	1.77391900	2.44931300
H	-1.96043600	5.69908400	1.30326500
H	0.61314200	2.74318300	4.33354400
H	-0.74936800	6.66674100	3.21008600
H	0.55619800	5.20259900	4.74587700
N	-2.35226000	-0.80983100	-0.21421000
C	-2.79607200	-1.75200400	-1.27223500
C	-2.60649300	-0.85763600	-2.57601300
N	-3.04657100	0.48570400	-2.11901700
H	-2.06178100	-1.14030100	0.72619700
C	-3.70661000	1.41321700	-3.03008600
H	-4.52860400	0.90504000	-3.55084200
H	-3.01744200	1.82055000	-3.77416000
H	-4.11770700	2.24857500	-2.46019000
H	-3.32028500	-1.16726200	-3.34462300
C	-1.18386600	-0.89529900	-3.21594000
C	-0.77829100	0.41203500	-3.91513100
H	-1.40808900	0.62463300	-4.78891300
C	-1.93261800	-3.02419600	-1.23644400
C	-0.62317400	-3.00024500	-0.73894600
C	-2.44074100	-4.24046800	-1.71955600
C	0.15995000	-4.15603300	-0.73553500
C	-1.65625100	-5.39342400	-1.72074000
C	-0.35082000	-5.35596700	-1.22823900
H	-0.19950000	-2.08267800	-0.34963500
H	-3.45858200	-4.29385100	-2.09197800
H	1.17036700	-4.10702200	-0.34160100
H	-2.07339800	-6.32378500	-2.09756600
H	0.25840900	-6.25586300	-1.21974800
C	-4.27982500	-2.12987900	-1.01604800
C	-4.64588400	-2.46220300	0.30053600
C	-5.26458800	-2.19771400	-2.00913900
C	-5.95339700	-2.82930700	0.61107500
C	-6.58009400	-2.56050600	-1.69710800
C	-6.93127200	-2.87424800	-0.38654100
H	-3.89518600	-2.43773800	1.08595400
H	-5.02746400	-1.97892800	-3.04529200
H	-6.20707100	-3.08699500	1.63598900
H	-7.32499200	-2.59985600	-2.48785000
H	-7.95172400	-3.15863900	-0.14424300
C	3.96291400	1.63215100	2.48114400
C	3.88490200	2.94220400	2.98153300
C	5.17770400	0.93609800	2.62031200
C	4.97486000	3.53345500	3.62204600
H	2.95449400	3.49572900	2.88015200
C	6.26675000	1.53071300	3.25415600
H	5.26971300	-0.05611100	2.19056100
C	6.17063700	2.82907000	3.76357700
H	4.88830400	4.54620700	4.00810600
H	7.20045300	0.98081300	3.34482100
H	7.02256400	3.28814200	4.25850400
H	-0.80638700	1.26930900	-3.23845800
C	-1.08561900	-2.05271300	-4.22510100
H	-1.77619000	-1.89082200	-5.06488300
H	-0.07323600	-2.10533800	-4.63972500
H	-1.31413400	-3.02365500	-3.78069600
H	-0.45151100	-1.05683700	-2.41958000
H	-2.70900900	0.63479700	2.72865100
C	-5.42214000	2.85282300	2.88228600
H	-6.18966100	2.23822400	2.39907400
H	-5.56585700	2.75867600	3.96457200
H	-5.61252000	3.89984400	2.61456800
H	-3.86619200	0.89575000	4.03164200
H	0.25304500	0.31906000	-4.27242500

● **1ba**-*RS* (HMe)



B3LYP/6-31G*

E = –3719.222486

Zero-point correction = 1.284479 (Hartree/Particle)

Thermal correction to Energy = 1.360212

Thermal correction to Enthalpy = 1.361156

Thermal correction to Gibbs Free Energy = 1.164447

Sum of electronic and zero-point Energies = –3717.938007

Sum of electronic and thermal Energies = –3717.862274

Sum of electronic and thermal Enthalpies = –3717.861330

Sum of electronic and thermal Free Energies = –3718.058038

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3720.390774

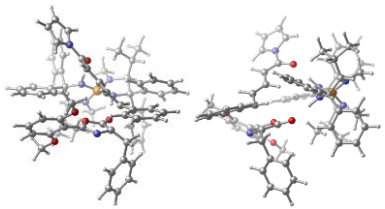
G = –3719.192443

0 1

O	-1.20082400	1.29523500	0.60827900
C	-2.16265700	0.52527000	0.60155800
C	-3.55523100	0.71199900	0.23819500
O	-2.01436100	-0.82766500	0.83384100
N	-4.22035200	-0.50697100	0.47321700
C	-3.30115100	-1.36798500	0.73740600
C	-3.46015000	-2.80619900	1.00762200
C	-4.12979800	-3.65209500	0.09344800
C	-2.97876500	-3.36810300	2.21198100
C	-4.29027300	-5.01748600	0.36899100
C	-3.13607800	-4.73307900	2.48535500
C	-3.78989100	-5.53956100	1.55798000
O	-4.58255800	-3.07422500	-1.05199300
C	-5.22541800	-3.88962100	-2.01967900
H	-6.14183200	-4.34278600	-1.62035800
H	-4.55976300	-4.68068000	-2.38845600
H	-5.48267200	-3.22115100	-2.84293700
O	-2.39276900	-2.49603700	3.07606600
C	-1.88293700	-2.99781300	4.30123400
H	-2.67293100	-3.45666100	4.90998300
H	-1.08050300	-3.72695300	4.13168200
H	-1.48078800	-2.13242400	4.83019200
H	-4.79651500	-5.66869200	-0.33203300
H	-2.76618000	-5.16199500	3.40784400
H	-3.91677600	-6.59816700	1.76865500
C	-4.26672200	2.01642800	0.52548500
H	-3.74913300	2.82881300	0.00275200
H	-5.27362900	1.95173200	0.10119000
C	-4.34980200	2.35166900	2.00623200
C	-3.61763900	3.41879600	2.54128500
C	-5.16077000	1.59872100	2.86839400
C	-3.69430500	3.73232100	3.90022200
C	-5.23743600	1.90790700	4.22604900
C	-4.50519700	2.97750200	4.74815000
H	-2.98442000	4.01063300	1.88405600

H	-5.72487200	0.76163100	2.46585200
H	-3.12379400	4.57032300	4.29466300
H	-5.87377000	1.31463000	4.87841100
H	-4.56941800	3.22103600	5.80577000
C	-3.21455000	0.70162800	-1.82916400
C	-2.65487300	-0.53195500	-2.28685900
H	-2.51070400	1.52980000	-1.75022100
H	-3.32806700	-1.27402000	-2.70642100
C	-1.29151000	-0.78752500	-2.28604200
H	-0.64736900	-0.03843500	-1.83057400
C	-0.62739500	-1.88846400	-2.83907300
H	-1.20120400	-2.66236600	-3.33752100
C	0.78138000	-1.95381400	-2.85939900
O	1.58466900	-1.08798300	-2.41468500
N	1.37708000	-3.10511800	-3.48050000
C	2.67128000	-3.11317300	-3.97215600
C	0.81408800	-4.35138700	-3.70608900
C	2.92400800	-4.35085400	-4.51195900
C	1.74572000	-5.14061500	-4.33503700
H	3.26297500	-2.21339100	-3.91877400
H	-0.17860300	-4.58102700	-3.35252600
H	3.84550400	-4.65796100	-4.98921900
H	1.60540700	-6.17383200	-4.62507200
H	0.54406600	1.58395700	0.10935600
N	1.51883300	1.82635300	-0.10914500
P	2.77505700	0.94369000	0.46890400
N	3.91792800	1.91511300	-0.23766700
C	3.34428900	2.89035200	-1.19554600
C	1.90132800	3.17999200	-0.57965600
C	5.34589100	1.91114700	0.05724600
H	5.55298300	1.17338300	0.83399700
H	5.94198900	1.64906800	-0.82009200
H	5.66130900	2.90027800	0.41541400
H	3.96042800	3.79096100	-1.12760300
C	3.36566500	2.41649500	-2.68360500
H	2.45600600	1.83859200	-2.86958900
C	4.53687800	1.48076100	-3.02654800
H	5.50698800	1.98871000	-2.95266400
C	1.95774800	4.14202700	0.63653400
C	2.94288300	5.12040100	0.82226800
C	0.92844600	4.05573700	1.59112300
C	2.92008700	5.96637600	1.93692400
C	0.90210100	4.90069200	2.69903600
C	1.90289800	5.85812900	2.88229700
H	3.74100700	5.25246800	0.09879300
H	0.13402900	3.32536100	1.46683900
H	3.70178600	6.71213800	2.05663400
H	0.09276500	4.80927400	3.41867800
H	1.88476800	6.51517500	3.74758900
C	0.86933500	3.68678000	-1.60192400
C	0.17995700	2.79157100	-2.43151300
C	0.61744500	5.05905400	-1.75065400
C	-0.71697300	3.25439500	-3.39578400
C	-0.27995200	5.52236900	-2.71366700
C	-0.94964900	4.62228900	-3.54335100
H	0.35172300	1.72590000	-2.33731500
H	1.12108100	5.77585400	-1.11100500
H	-1.23387700	2.53685100	-4.02684200
H	-0.45655600	6.59045100	-2.80955600
H	-1.64745100	4.98260700	-4.29451000
N	2.44172700	-0.63322500	0.19009900
C	3.10527800	-1.55107000	1.13934300
C	3.09812800	-0.71004100	2.48935300
N	3.26868500	0.68897600	2.03286400
H	2.13837900	-0.93166200	-0.75584100
C	3.67311800	1.73829300	2.96047200
H	4.55978800	1.41781100	3.52105100
H	2.88017600	1.99076000	3.67216400
H	3.91976200	2.64472000	2.40396500
H	4.00101400	-0.96681100	3.04886900
C	1.90555200	-0.93664900	3.46995600
C	0.64531700	-0.13575500	3.12529500
H	0.81594200	0.94448900	3.19489200
C	2.32876400	-2.87197200	1.25316200
C	1.01632400	-2.99965400	0.78286600
C	2.93575100	-3.98090600	1.86397800
C	0.33068800	-4.20984900	0.91556800
C	2.24508700	-5.18246300	2.00997800
C	0.93833500	-5.30279400	1.53185000
H	0.51299000	-2.16101700	0.31684200
H	3.96057100	-3.91044200	2.21659800
H	-0.68260000	-4.28758900	0.53470300
H	2.73513100	-6.02864200	2.48479500
H	0.40154100	-6.24241900	1.63194900
C	4.54322800	-1.85930300	0.62859700
C	4.68160500	-2.21943900	-0.72379900
C	5.69725800	-1.84664500	1.42182300
C	5.92494500	-2.54341900	-1.26067000
C	6.94901400	-2.16622600	0.88238600
C	7.06981600	-2.51458100	-0.45995600
H	3.80789900	-2.25100400	-1.36786300
H	5.65076100	-1.59733500	2.47693300
H	5.99306700	-2.82791200	-2.30713900
H	7.82662000	-2.14405700	1.52353100
H	8.04074900	-2.76702200	-0.87751700
C	-4.54558800	1.10163500	-2.35845700
C	-4.72677300	2.38685100	-2.89519500
C	-5.63921900	0.21676200	-2.36049500
C	-5.95206000	2.77141000	-3.44132700
H	-3.89259800	3.08472100	-2.89496100
C	-6.86409800	0.60519300	-2.89936500
H	-5.52768400	-0.75745300	-1.89555900
C	-7.02592700	1.88067600	-3.44830300
H	-6.06710100	3.76874400	-3.85878300
H	-7.70173900	-0.08806800	-2.88364000
H	-7.98277100	2.17886400	-3.86905100
H	0.27064500	-0.35290600	2.12456500
C	2.33242700	-0.70228300	4.93260600
H	2.56974700	0.34665200	5.14093400
H	1.52014500	-0.98900300	5.61038900
H	3.21075000	-1.30388800	5.19913600
H	1.65578100	-1.99980900	3.39541800
H	4.55551700	0.58855800	-2.39513000
C	3.39873200	3.62404000	-3.63680300
H	4.34031500	4.17831400	-3.51880100
H	3.34569400	3.28599900	-4.67757300
H	2.57422900	4.32064500	-3.47164100
H	4.42852700	1.14460300	-4.06371500
H	-0.15969300	-0.38011200	3.82667500

- **1ba**-*RS* (MeMe)



B3LYP/6-31G*

E = –3719.223609

Zero-point correction = 1.284095 (Hartree/Particle)

Thermal correction to Energy = 1.360001

Thermal correction to Enthalpy = 1.360945

Thermal correction to Gibbs Free Energy = 1.164096

Sum of electronic and zero-point Energies = –3717.939514

Sum of electronic and thermal Energies = –3717.863608

Sum of electronic and thermal Enthalpies = –3717.862664

Sum of electronic and thermal Free Energies = –3718.059513

PCM(toluene)-B3LYP-D3/6-311++G**//B3LYP/6-31G*@–30 °C

E = –3720.391858

G = –3719.193855

0 1

O	-1.15720700	1.28400800	0.58871800
C	-2.13710400	0.53793200	0.60213300
C	-3.52170400	0.74595700	0.21540700
O	-2.02264000	-0.80518500	0.88533900
N	-4.21836800	-0.44703500	0.49643200
C	-3.32155000	-1.31988600	0.79694400
C	-3.51086900	-2.74468400	1.11031200
C	-4.23311400	-3.59434200	0.23966700
C	-2.99983900	-3.29259800	2.30970300
C	-4.41672600	-4.94855900	0.55259400
C	-3.17790200	-4.64749800	2.61771300
C	-3.88470000	-5.45741900	1.73337000
O	-4.71010100	-3.03323000	-0.90397600
C	-5.40503500	-3.85537000	-1.82932700
H	-6.32094100	-4.27096500	-1.39004600
H	-4.77374500	-4.67485500	-2.19628200
H	-5.66854700	-3.20174900	-2.66244800
O	-2.36461200	-2.41752500	3.13466200
C	-1.79836800	-2.91026400	4.33879300
H	-2.56271100	-3.34219100	4.99800400
H	-1.02119000	-3.65827700	4.13785100
H	-1.35025200	-2.04471200	4.82909300
H	-4.96364200	-5.60214800	-0.11480700
H	-2.78508700	-5.06499700	3.53588400
H	-4.02848800	-6.50787800	1.97197000
C	-4.20102700	2.07817200	0.45181700
H	-3.66801800	2.85531700	-0.10753500
H	-5.21036400	2.01858300	0.03209300
C	-4.27287000	2.48256000	1.91602800
C	-3.57940400	3.60616200	2.38299100
C	-5.04100600	1.74480200	2.82923700
C	-3.65140300	3.98877500	3.72461200
C	-5.11202000	2.12254000	4.16981600
C	-4.41792000	3.24710200	4.62389800
H	-2.98164500	4.18985800	1.68627300
H	-5.57652700	0.86615300	2.47996300
H	-3.11422300	4.87163900	4.06434700
H	-5.71462500	1.53937500	4.86207000
H	-4.47809800	3.54359500	5.66810400
C	-3.16891100	0.64622600	-1.82543100
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H	-2.43505400	1.45141200	-1.78616400
H	-3.35570200	-1.36412900	-2.60543200
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H	-0.61571100	-0.20044300	-1.81281600
C	-0.70644700	-2.11438700	-2.69944000
H	-1.33237200	-2.88032600	-3.14437400
C	0.69366500	-2.27619700	-2.72050500
O	1.55879800	-1.44332100	-2.33394900
N	1.20267900	-3.49966600	-3.27671000
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C	5.37855500	1.81043300	-0.24541900
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H	5.78963900	1.32974400	-1.13971600
H	5.86522900	2.78430800	-0.11417000
H	3.89574800	3.94632700	-1.01204800
C	3.51298600	2.74430600	-2.73800600
H	2.71732200	3.30562400	-3.23712100
C	3.37212900	1.27000100	-3.14060000
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C	0.72346700	4.04658100	1.45941800
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C	0.59521200	4.88140100	2.56790200
C	1.54833100	5.87039900	2.82368400
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H	-0.24565500	6.55397900	-3.17491100
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H	-5.53805000	-0.72400700	-1.84841200
C	-6.91779000	1.89031800	-3.54432100
H	-5.88199800	3.71736400	-4.03566600
H	-7.67472600	-0.02091500	-2.89184200
H	-7.85831300	2.20405600	-3.98981100
H	0.34529400	-0.26412500	2.12932800
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H	1.66755100	-0.78797000	5.60811600
H	3.35244200	-1.10185200	5.17357100
H	1.76256000	-1.87118500	3.42664400
H	2.42338500	0.82254500	-2.83779600
C	4.83786100	3.33012000	-3.26642400
H	5.71754300	2.81716400	-2.86184900
H	4.88062500	3.23309200	-4.35710500
H	4.93154100	4.39697300	-3.02710500
H	-0.05131700	-0.24612900	3.84007900
H	3.44084000	1.17893000	-4.23079300

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List of Publications

Chapter 2.

(1) Highly Regio-, Diastereo-, and Enantioselective 1,6- and 1,8-Additions of Azlactones to Di- and Trienyl *N*-Acylpyrroles
Uraguchi, D.; Yoshioka, K.; Ueki, Y.; Ooi, T. *J. Am. Chem. Soc.* **2012**, *134*, 19370-19373.

Chapter 3.

(2) Origin of High Regio-, Diastereo-, and Enantioselectivities in 1,6-Addition of Azlactones to Dienyl *N*-Acylpyrroles: A Computational Study
Yamanaka, M.; Sakata, K.; Yoshioka, K.; Uraguchi, D.; Ooi, T. *J. Org. Chem.* **2017**, *82*, 541-548.

Chapter 4.

(3) Complete diastereodivergence in asymmetric 1,6-addition reactions enabled by minimal modification of a chiral catalyst
Uraguchi, D.; Yoshioka, K.; Ooi, T. *Nat. Commun.* **2017**, accepted.

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