COMMUNICATION

Reusable Silica-Supported Ammonium BINSate Catalysts for Enantio- and Diastereoselective Friedel–Crafts-Type Double Aminoalkylation of *N*-Alkylpyrroles with Aldimines

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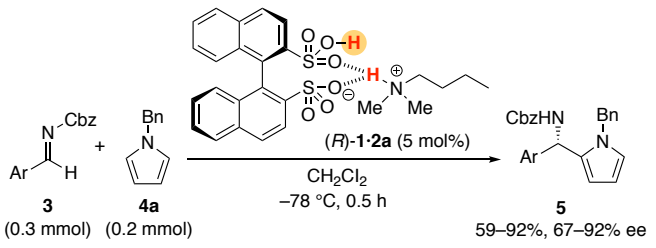
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/ajoc2020.

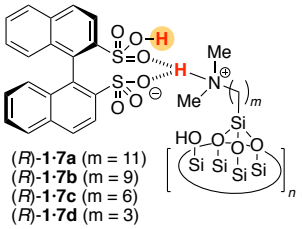
Abstract: Silica-supported ammonium (*R*)-BINSate catalysts for the enantio- and diastereoselective Friedel–Crafts-type *double* aminoalkylation of *N*-benzyl- or *N*-methylpyrrole with aldimines were developed. The present heterogeneous catalysts showed high catalytic activity compared to our previous homogeneous (*R*)-BINSA ammonium catalysts, which were effective for *single* aminoalkylation. Simple aldimines could be used, and the corresponding pyrrole-derived chiral C_2-symmetric triamines were obtained in the *dl*-form with good to extremely high enantioselectivities. The heterogeneous catalyst could be easily recovered and reused three times without any loss of catalytic activity or enantiocontrol. An XPS analysis supported precise preparation of the catalysts *in situ* and with good quality after recycling three times. From the perspective of modern green chemistry with fine asymmetric organocatalysis, the development of such chiral strong Brønsted acid catalysts might be useful for both laboratory and industrial applications.

From the perspective of modern green chemistry, considerable attention has been paid to fine asymmetric organocatalysis that does not require relatively harmful and expensive metal species over the past two decades. In particular, chiral strong Brønsted acid catalysts have played a pivotal role in this field for both laboratory and industry use.[1] Moreover, due to the high utility of heterogeneous organocatalysts in terms of their ease of recovery and reusability, some immobilized chiral strong Brønsted acid catalysts have also been developed.[2] However, immobilization of conformationally flexible molecular catalysts often reduces the original catalytic activity and selectivity, since relatively rigid structures should be used for the immobilization of molecular catalysts. To avoid reducing the conformational flexibility of immobilized chiral Brønsted acid catalysts, simple absorption of an acid molecule to an immobilized base by attractive acid–base interactions (i.e., formation of coordination bonds by neutralization) without the formation of covalent bonds should be suitable. In particular, immobilized ammonium sulfonates, which can be prepared *in situ* from highly acidic sulfonic acids and highly basic immobilized tertiary amines *via* simple protonation, are attractive. Of course, a 1:1 ratio of acid and base moieties would be easily neutralized and the catalytic functions would be significantly reduced. In contrast, we envisioned that (*R*)-BINSA **1** (1,1'-binaphthalene-2,2'-disulfonic acid)[3–6] ammonium salts could be used to solve this problem, since one of the SO_3H moieties would still remain after preparation of the catalysts (e.g., (*R*)-**1•2a** in Scheme 1). Notably, chiral ammonium BINSates act as tightly hydrogen bond-coordinating salts by taking advantage of two adjacent SO_3 moieties, and completely separated ion-pair salts are unlikely.[7a] We have already developed such homogeneous chiral ammonium BINSate catalysts for use in the enantioselective direct Mannich-type reaction,[3c] Friedel–Crafts-type aminoalkylation (aza-Friedel–Crafts reaction, Scheme 1),[7a] and



Scheme 1. Our previous study on the enantioselective Friedel–Crafts-type *single* aminoalkylation of *N*-benzylpyrrole with aldimines by using homogeneous (*R*)-BINSA ammonium salt catalysts.

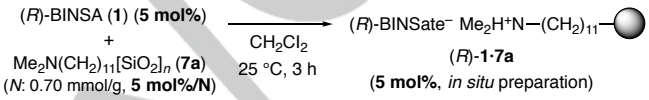
aminal synthesis[7b] by using aldimines as substrates. In the present study, we collaborated on the outstanding designs of such *chiral ammonium BINSates* by Ishihara and *silica (AEROSIL® 300)-supported tertiary amines* by Motokura.[8–10] In particular, we selected the enantioselective Friedel–Crafts-type aminoalkylation[11] of *N*-benzylpyrrole **4a** with aldimines **3**, in which we previously used (*R*)-**1** and a tertiary amine,[12] such as Me_2N*n*-Bu **2a**, for the ammonium catalysts (Scheme 1).[7a] In this reaction, biologically and pharmaceutically useful aryl(1*H*-pyrrol-2-yl)methanamines,[13] such as **5**, were obtained with good to high enantioselectivities. In the present study, in place of homogeneous catalyst (*R*)-**1•2a**, we developed heterogeneous silica-supported catalysts, such as (*R*)-**1•7**, which were easily prepared *in situ* from (*R*)-**1** and $Me_2N(CH_2)_m[SiO_2]_n$ (**7**) (Figure 1). Proper spacing among the active ammonium BINSate moieties on the SiO_2-surface might avoid acid–base neutralization and oligomerization, and thus high catalytic activity along with chemical stability would be expected. In general, since silica-supported tertiary amines have both acidic siloxy moieties and a basic amino moiety, they work alone as acid–base bifunctional catalysts to activate substrates and reagents, respectively.[8,9] In the present study, however, the much stronger Brønsted acid moiety SO_3H, compared to siloxy moieties, might work as a practical active acid center. Particularly with the use of basic substrates such as aldimines, siloxy moieties might still be useful as weak Brønsted acids to collect aldimines effectively. As a result, reactions would occur smoothly with a shift of aldimines to the SO_3H moiety over a short distance.



✓ ***Easy preparation of the catalysts in situ***
✓ ***Proper spacing among the active BINSate moieties***
✓ ***Avoidance of neutralization and oligomerization***
✓ ***High catalytic activity and chemical stability***
✓ ***Recovery and reuse as heterogeneous catalysts***

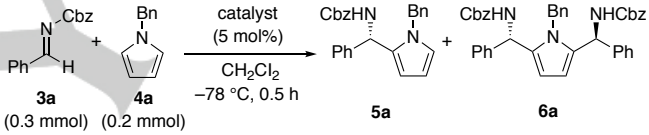
Figure 1. Design of heterogeneous silica-supported (*R*)-BINSA ammonium catalysts (*R*)-**1•7**.

Based on our previous reaction conditions using (*R*)-**1•2a**,[7a] we initially reproduced a reaction of *N*-benzylpyrrole **4a** (1 equiv) with aldimine **3a** (1.5 equiv) in dichloromethane at –78 °C for 0.5 h as a probe reaction (Table 1, entry 1). As a result, *single* aminoalkylation product **5a** was obtained in 86% yield with 87% ee along with *double* aminoalkylation product **6a** in 12% yield (*dl:meso* = 60:40) with 85% ee (*dl*), without serious problems with reproducing the previous results.[7a] A promising heterogeneous catalyst (*R*)-**1•7a**, which was prepared *in situ* from (*R*)-**1** and $Me_2N(CH_2)_{11}[SiO_2]_n$ **7a** (Scheme 2), showed higher catalytic activity than homogeneous catalyst (*R*)-**1•2a**, and the yield of *double* aminoalkylation product **6a** was unexpectedly increased to 36% (*dl:meso* = 63:37) with 88% ee (*dl*), whereas *single* aminoalkylation product **5a** was obtained in 63% yield with 91% ee (entry 2). The ratio of (*R*)-**1** to **7a** for the corresponding heterogeneous catalysts (*R*)-**1•[7]**$_x$ was important for inducing enantioselectivities of **5a** and **6a**. When (*R*)-**1•[7a]**$_{0.6}$ was used, **5a** and **6a** were obtained with lower enantioselectivities than with (*R*)-**1•7a**, although higher conversion of **4** was observed (entry 3 vs. entry 2). Moreover, (*R*)-**1•[7a]**$_2$, which was prepared with a 1:2 ratio of (*R*)-**1** and **7a**, dramatically decreased the catalytic activity, probably due to the neutralization of two SO_3H moieties by equimolar amounts of the amino moieties (entry 4). Additionally, when we used (*R*)-**1** alone, the catalytic activity was lower than that of (*R*)-**1•7a** (entry 5 vs. entry 2). **7a** alone or SiO_2 alone did not promote the reaction (entries 6 and 7). Moreover, (*R*)-**1•2b**, which was prepared *in situ* from (*R*)-**1** and tertiary amine Me_2N*n*-$C_{10}H_{21}$ **2b**, also showed similar catalytic activity as (*R*)-**1•2a** (entry 8 vs. entry 1). Therefore, the long alkyl chain of **2b** alone did not further facilitate the reaction among homogeneous catalysts.



Scheme 2. Catalyst preparation *in situ*.

Table 1. Optimization of catalysts for the enantioselective Friedel–Crafts-type aminoalkylation of **4a** with **3a**.[a]



3a (0.3 mmol) **4a** (0.2 mmol) **5a** **6a**

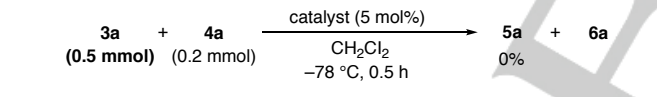
Entry	Catalyst	5a		6a	
		Yield (%)	Ee (%)	Yield (%) (*dl:meso*)	Ee (%)
1	(*R*)-**1•2a**	86	87	12 (60:40)	85
2	(*R*)-**1•7a**	**63**	**91**	**36 (63:37)**	**88**
3[b]	(*R*)-**1•[7a]**$_{0.6}$	50	63	43 (73:27)	73
4[c]	(*R*)-**1•[7a]**$_2$	0	–	0	–
5	(*R*)-**1**	88	45	13	–
6	**7a**	0	–	0	–
7[d]	SiO_2	0	–	0	–
8	(*R*)-**1•2b**	83	80	9 (65:35)	–

[a] The reaction was carried out with **3a** (0.30 mmol), **4a** (0.20 mmol), and catalyst (5 mol%) in dichloromethane at –78 °C for 0.5 h unless noted otherwise. Me_2N*n*-Bu (**2a**), Me_2N*n*-$C_{10}H_{21}$ (**2b**), and $Me_2N(CH_2)_{11}[SiO_2]_n$ (**7a**) were used. [b] 5 mol% of (*R*)-**1** and 3 mol% of **7a** were used. [c] 5 mol% of (*R*)-**1** and 10 mol% of **7a** were used. [d] 14 mg of SiO_2 (AEROSIL® 300) was used.

Since *double* aminoalkylation preferentially occurred with the use of highly active heterogeneous catalyst (*R*)-**1•7a** unlike relatively less active homogeneous catalyst (*R*)-**1•2a** (entry 2 vs. entries 1 and 8 in Table 1), we next used 2.5 molar equivalents of **3a** to effectively obtain *double* adduct **6a** (Table 2). As a result, when we used (*R*)-**1•7a**, **6a** was exclusively obtained in 85% yield (*dl:meso* = 83:17) with 99% ee (*dl*) (entry 1). At that time, **5a** was not obtained. Heterogeneous catalyst (*R*)-**1•7a** was more effective than homogeneous catalyst (*R*)-**1•2a** with regard to the

dl:meso ratio and the enantioselectivity of **6a**, since **6a** was obtained in 82% yield (*dl:meso* = 81:19) with 95% ee (*dl*) with the use of (*R*)-**1•2a** (entry 8). Since the immobilized ammonium BINSate moieties were placed away from each other, undesired association of the active sites and/or neutralization leading to deactivation of the catalysts would be effectively prevented. Next, we investigated the effect of the alkyl chain of the immobilized amines **7**. (*R*)-**1•7b** with a $(CH_2)_9$ moiety gave slightly worse results than (*R*)-**1•7a** with a $(CH_2)_{11}$ moiety, and **6a** was obtained in 85% yield (*dl:meso* = 70:30) with 95% ee (*dl*) (entry 2). Moreover, (*R*)-**1•7c** and (*R*)-**1•7d** with $(CH_2)_6$ and $(CH_2)_3$ moieties, respectively, showed a lower *dl:meso* ratio and enantioselectivity of **6a** (entries 3 and 4). These results suggest that the reasonably long alkyl chain of **7a** might prevent undesired contact of the BINSate moieties with the silica surface. In addition, in contrast to the less flexible BINSate moiety with short alkyl chains, the conformationally more flexible BINSate moiety connected with the reasonably long alkyl chain would induce inherently high catalytic activity. Interestingly, the remaining siloxy (SiO*H*) moieties in (*R*)-**1•7a** were important for promoting the reaction, since SiO-*SiMe(OMe)*$_2$-protected silica-supported catalyst (*R*)-**1•7a'** showed a lower *dl:meso* ratio and enantioselectivity of **6a** than (*R*)-**1•7a** (entry 5 vs. entry 1). Moreover, the addition of extra SiO_2 to (*R*)-**1•7a** or (*R*)-**1•7a'** had a negative effect on the *dl:meso* ratio and the enantioselectivity of **6a** (entries 6 and 7 vs. entry 1). At the present preliminary stage, the role of the remaining siloxy moieties of (*R*)-**1•7a** is not clear, although tertiary amine-connected unprotected silica (e.g., **7a**) might be essential in this reaction, as seen in our previous reactions.[14]

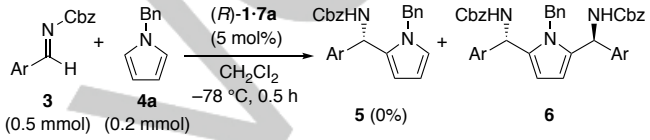
Table 2. Effect of the alkyl chain in the amino moiety of the catalysts in the enantioselective FC-type aminoalkylation of **4a** with **3a**.[a]



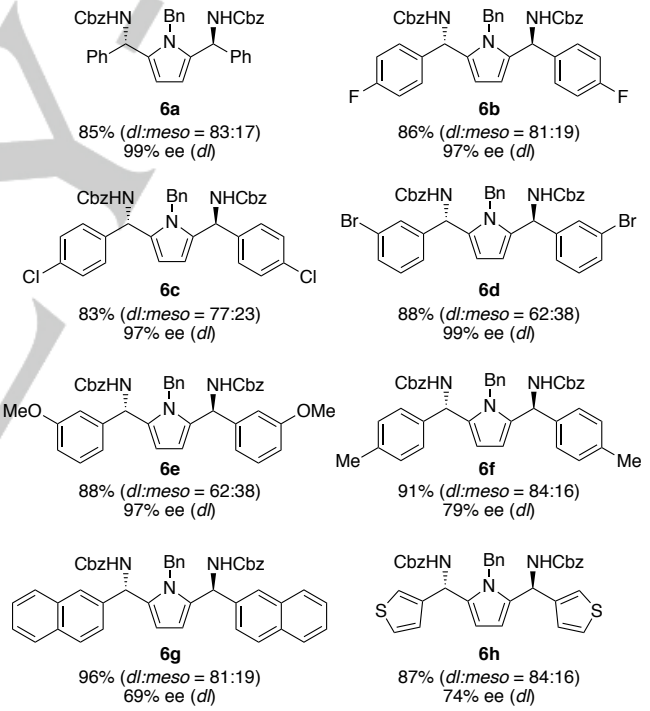
Entry	Catalyst	Yield of **6a** (*dl:meso*)	Ee of **6a** (*dl*)
1	(*R*)-**1•7a** (m = 11)	85 (83:17)	99
2	(*R*)-**1•7b** (m = 9)	85 (70:30)	95
3	(*R*)-**1•7c** (m = 6)	81 (58:42)	84
4	(*R*)-**1•7d** (m = 3)	80 (54:46)	89
5[b]	(*R*)-**1•7a'**	86 (71:29)	93
6[c]	(*R*)-**1•7a** + SiO_2	87 (65:35)	96
7[b,c]	(*R*)-**1•7a'** + SiO_2	82 (64:36)	86
8	(*R*)-**1•2a**	82 (81:19)	95

[a] The reaction was carried out with **3a** (0.50 mmol), **4a** (0.20 mmol), and catalyst (5 mol%) in dichloromethane at –78 °C for 0.5 h. Me_2N*n*-Bu (**2a**), $Me_2N(CH_2)_{11}[SiO_2]_n$ (**7a**), $Me_2N(CH_2)_9[SiO_2]_n$ (**7b**), $Me_2N(CH_2)_6[SiO_2]_n$ (**7c**), and $Me_2N(CH_2)_3[SiO_2]_n$ (**7d**) were used. *Single* aminoalkylation product **5a** was not obtained in any of theentries. [b] **7a'** was prepared from **7a** after treatment with $MeSi(OMe)_3$ (see the SI for details). [c] 14 mg of SiO_2 (AEROSIL® 300) was used.

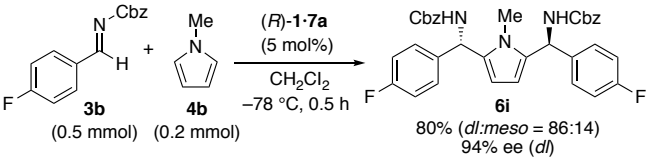
With the optimized reaction conditions in hand, we next examined the scope of aldimines **3** (Scheme 3). The obtained *double* aminoalkylation products **6** should be useful optically active C_2-symmetric triamines as chiral auxiliaries in asymmetric catalyses.[15,16] As a result, electron-withdrawing halo- substituted substrates **3b**, **3c**, and **3d** with the respective *p*-F, *p*-Cl, and *m*-Br moieties were used, and the corresponding *double* adducts **6b**, **6c**, and **6d** were obtained with extremely high enantioselectivities (97–99% ee). Moreover, **6e** with a *m*-MeO moiety, which would act as an inductive electron-withdrawing moiety, also showed extremely high enantioselectivity (97% ee). Unfortunately, electron-donating *p*-Me substituted compound **6f** showed relatively low enantioselectivity (79% ee), although the yield and the *dl:meso* ratio were good. As other aromatic groups, 2-naphthyl and 3-thienyl substrates (**3g** and **3h**, respectively) were used, and the corresponding *double* aminoalkyl adducts **6g** and **6h** were obtained with 69% ee and 74% ee, respectively. In this catalysis, *N*-unprotected pyrrole could not be used due to low



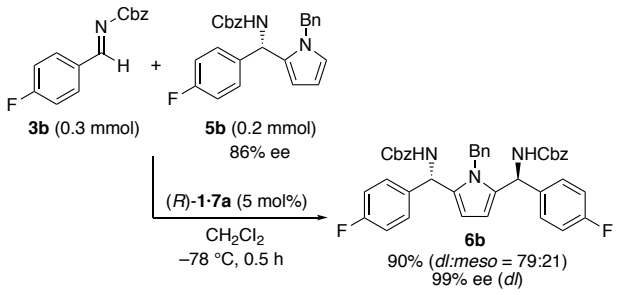
Product **6**, yield, ratio of *dl:meso*, and enantioselectivity



Scheme 3. Substrate scope of aldimines **3**. The reaction was carried out with **3** (0.50 mmol), **4a** (0.20 mmol), and (*R*)-**1•7a** (5 mol%) in dichloromethane at –78 °C for 0.5 h. *Single* aminoalkylation products **5** were not obtained in any of the cases.



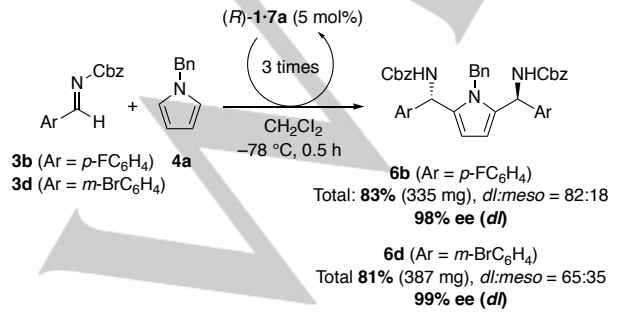
Scheme 4. Reaction with *N*-methylpyrrole **4b**.



Scheme 5. Kinetic resolution of *single* adduct **5b** in the second FC-type aminoalkylation.

enantioinduction (<10% ee).[7a] However, synthetically useful *N*-methylpyrrole **4b** also could be used, and the corresponding double aminoalkyl adducts **6i** was obtained with 94% ee (Scheme 4). In all cases in Schemes 3 and 4, *single* aminoalkylation products **5** were not obtained. In a few cases, the ratio of *dl:meso* was less than 80:20, but the enantioselectivity was relatively high at that time (see **6c**, **6d**, and **6e** in Scheme 3). We next examined whether or not kinetic resolution would occur in the second aminoalkylation (i.e., the further addition of **3** to **5**). When we used **3b** and **5b** with 86% ee, which was separately prepared in advance, **6b** was obtained in 90% yield (*dl:meso* = 79:21) with 99% ee (*dl*) (Scheme 5). This result strongly supported kinetic resolution in the second aminoalkylation, which resulted in amplification of the enantiomeric excess of *dl*-**6b** by preferentially providing *meso*-**6b**.

Finally, with regard to the synthetic utility of the present catalysis, we demonstrated recovery and reuse of the catalyst (Scheme 6). By taking advantage of the insolubility of (*R*)-**1•7a**, we could easily separate the catalyst from a resultant reaction mixture. To separate the catalyst effectively, *n*-hexane was added to the reaction mixture at –78 °C (see the Supporting Information for details). The resultant supernatant was then collected at room temperature, and the remaining catalyst was recovered after washing with diethyl ether and drying *in vacuo*. A subsequent reaction could start with the recovered catalyst after the addition of **3b** or **3d**, **4a**, and dichloromethane at –78 °C. This recovery/reuse procedure could be performed three times, and the combined organic layer was condensed and purified. As a result, **6b** was obtained in 83% yield (*dl:meso* = 82:18) with 98% ee (*dl*), and **6d** was obtained in 81% yield (*dl:meso* = 65:35) with 99% ee (*dl*). These results were comparable to that with the standard reaction procedure (see Scheme 3).



Scheme 6. Recovery and reuse of the catalyst.

To examine the conditions of the recycled catalyst in Scheme 6, an XPS analysis was performed, and the results confirmed the acid–base interaction between (*R*)-BINSA and tertiary amine on the SiO_2 surface (Figure 2, also see the Supporting Information for details). First, the N 1s signal of **7a** was shifted from 399.3 eV to 402.0 eV after the adsorption of (*R*)-**1**, which indicated formation of the protonated *N,N*-dimethylamino group in (*R*)-**1•7a**, as shown in Figure 1 (Figures 2A-(a) and (b)). In addition, the S 2p signal position of (*R*)-**1•7a** was almost the same as that of (*R*)-**1** (Figures 2B-(a) and (b)). This result suggests that the SO_3H and SO_3^- moieties were intact without decomposition after the adsorption of (*R*)-**1**. Moreover, XPS signals of N 1s and S 2p in the recovered (*R*)-**1•7a** appeared at 402.1 eV and 168.1 eV, respectively (Figures 2A-(c) and 2B-(c)), and these peaks were not essentially changed from those of fresh (*R*)-**1•7a** (Figures 2A-(b) and 2B-(b)). Although an XPS analysis cannot perfectly calibrate the amounts of elements, the nitrogen:sulfur signal ratio determined by XPS was ca. 1:1.5. These results would strongly support the presence of acid–base interaction between (*R*)-**1** and silica-supported *N,N*-dimethylamino groups without serious leaching of (*R*)-**1** after the 3rd recycling reaction.

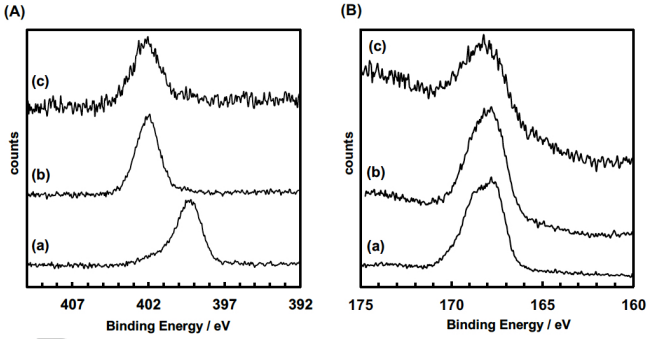


Figure 2. XPS spectra of (**A**) N 1s of (a) **7a**, (b) (*R*)-**1•7a**, and (c) recovered (*R*)-**1•7a** after the 3rd recycling catalytic reaction, and (**B**) S 2p of (a) (*R*)-**1**, (b) (*R*)-**1•7a**, and (c) recovered (*R*)-**1•7a** after the 3rd recycling catalytic reaction.

At this preliminary stage, we cannot draw any firm conclusions regarding the mechanism of the present catalysis, particularly regarding the role of the silica surface. Compared to the optimized catalyst (*R*)-**1•7a**, $SiMe(OMe)_2$-capped silica-supported catalyst (*R*)-**1•7a'** was less effective (Table 2, entries 1 vs. 5). Although a possible active site might be the highly Brønsted acidic SO_3H moiety, relatively basic aldimines would coordinate to the weakly acidic siloxy moieties nearby. As a result, the reactions would occur smoothly with a shift of aldimines over a short distance to the SO_3H moiety in a partially stereocontrollable manner (Figure 3). The adjusted distance from the silica surface to the SO_3H moiety might be important, since the addition of extra SiO_2 to (*R*)-**1•7a** or (*R*)-**1•7a'** did not further improve the *dl:meso* ratio or enantioselectivity (see Table 2, entries 6 and 7). Therefore, the design of highly active and reusable silica-supported ammonium BINSate catalysts should be reasonable in the present catalysis.

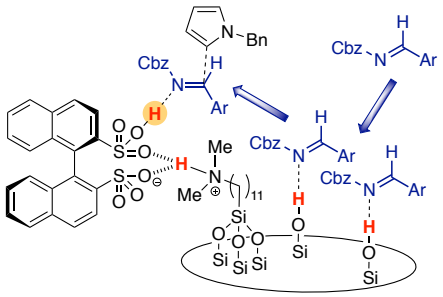


Figure 3. Possible attractive interactions between aldimines and the siloxy moieties on the silica surface.

In summary, we have developed a silica-supported ammonium BINSate catalysts for the enantioselective Friedel–Crafts-type *double* aminoalkylation of *N*-benzyl- or *N*-methylpyrrole with aldimines. The present heterogeneous catalysts showed high catalytic activity compared to our previous homogeneous (*R*)-BINSA ammonium catalysts, which were effective for *single* aminoalkylation. Some simple aldimines could be used, and the corresponding doubly functionalized pyrrole-derived optically active C_2-symmetric triamines were obtained with good to extremely high enantioselectivities. The heterogeneous catalyst could be easily recovered and reused three times without reducing catalytic activity or enantiocontrol. An XPS analysis supported the precise preparation of the catalysts *in situ* and with good quality after recycling. From the perspective of modern green chemistry regarding fine asymmetric organocatalysis, the development of such chiral strong Brønsted acid catalysts might be useful for both laboratory and industrial applications.

Experimental Section

General procedure for the catalytic enantioselective Friedel–Crafts-type *double* aminoalkylation of *N*-benzylpyrrole 4a with aldimines 3: A well-dried pyrex Schlenk tube was charged with (*R*)-BINSA **1** (4.1 mg, 0.010 mmol) and $Me_2N(CH_2)_{11}[SiO_2]_n$ **7a** (N: 0.70 mmol/g, 14.3 mg, 0.010 mmol/*N*) under a nitrogen atmosphere. Dichloromethane (1.5 mL) was added, and the solution was stirred at 25 °C for 3 h. The mixture was cooled to –78 °C and stirred at that temperature for 10 min. *n*-Benzylpyrrole **4a** (30.8 μL, 0.20 mmol) was added, and aldimine **3** (0.50 mmol) in dichloromethane (0.5 mL) was then added *via* a cannula. The resultant mixture was then stirred at –78 °C for 30 min. Triethylamine (0.2 mL) was added to the reaction mixture, and the product was extracted with ethyl acetate (15 mL × 2). The combined extracts were washed with brine (10 mL) and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: *n*-hexane:EtOAc = 2:1) to give the desired product as a mixture of *dl*- and *meso*-isomers. The ratio of *dl*- and *meso*-isomers and the enantiomeric purity of the *dl*-isomer were determined by chiral HPLC analysis.

General procedure for the recovery and reuse of the catalyst: A well-dried pyrex Schlenk tube was charged with (*R*)-BINSA **1** (4.1 mg, 0.010 mmol) and $Me_2N(CH_2)_{11}[SiO_2]_n$ **7a** (*N*: 0.70 mmol/g, 14.3 mg, 0.010 mmol/*N*) under a nitrogen atmosphere. Dichloromethane (1.5 mL) was added, and the solution was stirred at 25 °C for 3 h. The mixture was cooled to –78 °C and stirred at that temperature for 10 min. *n*-Benzylpyrrole **4a** (30.8 μL, 0.20 mmol) was added, and aldimine **3** (0.50 mmol) in dichloromethane (0.5 mL) was then added *via* a cannula. The resultant mixture was then stirred at –78 °C for 30 min. *n*-Hexane (2 mL) was then added to the mixture at –78 °C. Pale yellow precipitate was quickly generated, and the resultant supernatant was collected by a syringe at 25 °C. The remaining catalyst was recovered after washing with diethyl ether (2 mL × 2) and drying under reduced pressure (ca. 30–45 Torr) at 25 °C for 1 h. A subsequent reaction could start with the recovered catalyst after the addition of **3** (0.50 mmol), **4a** (30.8 μL, 0.20 mmol), and dichloromethane at –78 °C. This recovery/reuse procedure was performed three times, and the combined organic layer was condensed and purified by flash silica gel column chromatography (eluent: *n*-hexane:EtOAc = 2:1) to give the desired product as a mixture of *dl*- and *meso*-isomers. The ratio of *dl*- and *meso*-isomers and the enantiomeric purity of the *dl*-isomer were determined by chiral HPLC analysis.

Acknowledgements

This work was financially supported by JSPS KAKENHI Grant Numbers JP17H03054 (MH), JP20H02735 (MH), JP15H05755 (KI), Precisely Designed Catalysts with Customized Scaffolding (JP15H05810 (KI) and JP18H04242 (KM)), and the Iketani Science and Technology Foundation (MH).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: ammonium salt • chiral Brønsted acid catalyst • Friedel–Crafts reaction • organocatalyst • silica-supported catalyst

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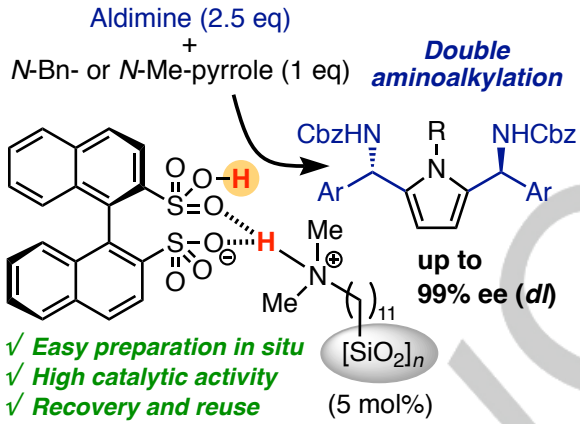

Heterogeneous chiral strong H⁺: Reusable silica-supported ammonium (*R*)-BINSate catalysts were developed for the enantioselective Friedel–Crafts-type *double* aminoalkylation of *N*-benzyl- or *N*-methylpyrrole with aldimines. Unlike homogeneous ammonium (*R*)-BINSate catalysts, the present catalysts showed high catalytic activity, and the chiral C_2-symmetric triamines were obtained successfully. From the perspective of green chemistry, the present heterogeneous chiral strong Brønsted acid catalysts might be attractive.