Synthesis of Benzo-Fused Cyclic Ketones via Metal-Free Ring Expansion of Cyclopropanols Enabled by Proton-Coupled Electron Transfer

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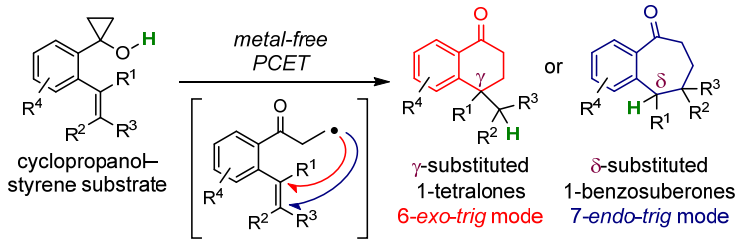
Supporting Information Placeholder



ABSTRACT: The metal-free ring expansion of cyclopropanols containing a pendant styrene moiety was successfully achieved using a proton-coupled electron transfer enabled by an organic photoredox catalyst. Through this, variants on 1-tetralone and 1-benzosuberone bearing a substituent at the benzylic position were selectively obtained through the regioselective ring closure of alkyl radical intermediates depending on the substitution pattern of the alkene moiety.

1-Tetralones and 1-benzosuberones are broadly found in natural products such as Hamigeran A, Merochlorin B, and Parviflorol (Figure 1a).[1] In addition, they have been used as versatile building blocks in the synthesis of complex molecules.[2] Accordingly, considerable effort has been devoted to achieve efficient constructions of these benzo-fused ketone frameworks.[3–5] However, metal-free catalytic methods for the synthesis of 1-tetralones and 1-benzosuberones bearing substituents at the benzylic position have been underdeveloped.[6]

The radical-mediated ring enlargements, such as the Beckwith–Dowd ring-expansion reaction, are powerful tools in organic synthesis as they provide efficient access to cyclic ketones via alkoxy radical intermediates.[7] In particular, readily available cycloalkanols can be used as convenient precursors for the synthesis of cyclic ketones because the single-electron oxidation of cycloalkanols generates reactive carbon-centered radicals via β-scission of cycloalkoxy radical intermediates. For example, both Zhu et al. and Gong et al. independently reported the radical ring-expansion of 1-arylcyclobutanols mediated by Ag^{I} or Ce^{IV} to prepare 1-tetralone derivatives (Figure 1b).[8,9] However, these transformations require a noble-metal-based catalyst or a transition-metal oxidant, leading to metal waste after reaction completion. In addition, the products obtained from these reactions are limited to variations on 1-tetralone which have unsubstituted γ-positions.

Recently, increased attention has been paid to proton-coupled electron transfer (PCET) as it enables redox-neutral and highly atom-economical transformations.[10] In their pioneering work, Knowles et al. developed the PCET-initiated ring-expansion of 5–7-membered cyclic alcohols using an Ir-based photoredox catalyst to selectively afford 6–9-membered cyclic ketones bearing substituents at the α- and/or β-positions (Figure 1c).[11] Although transition-metal oxidants were unnecessary in this method, the cyclic alcohol substrates were limited to heterocycles or carbocycles with a tertiary center that produces stabilized α-amino, α-alkoxy, or tertiary-alkyl radical intermediates after ring opening. Therefore, a new strategy is required to synthesize benzo-fused ketones using PCET-initiated ring expansion: we designed a novel cyclopropanol substrate **1** with a pendant styrene moiety with the expectation that the strained cyclopropanol obviates the need for radical stabilizing groups (Figure 1d).[12] The required substrate **1** was readily prepared from commercially available 2'-iodoacetophenone using Simmons–Smith cyclopropanation and well-established cross-coupling reactions (see Supporting Information for details). Herein, we report our study along this line to establish the efficient synthesis of γ-substituted 1-tetralones and δ-substituted 1-benzosuberones. To the best of our knowledge, this is the first example of using PCET for the ring expansion of cyclopropanols.[10,11]

We began a preliminary study using **1a** as the model substrate (Table 1). Several photoredox catalysts were first

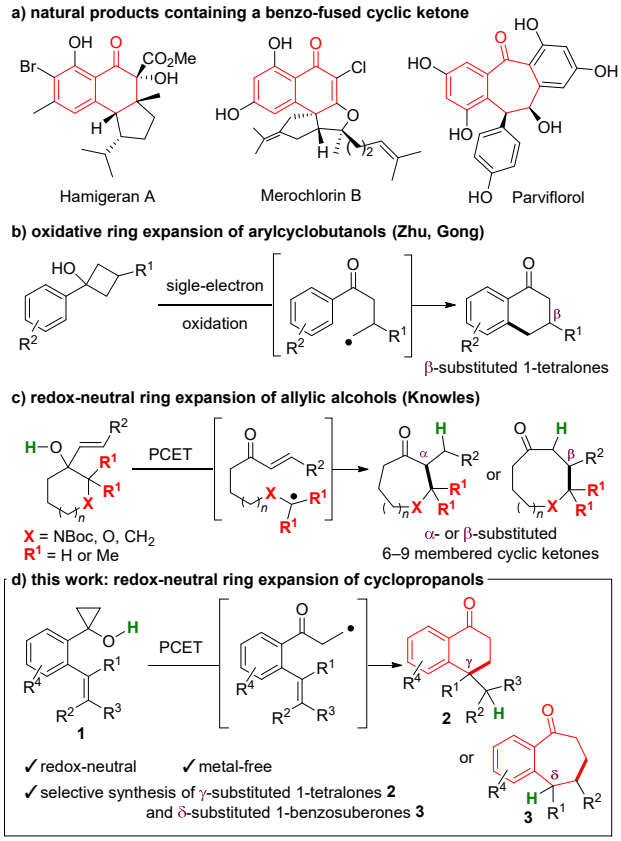
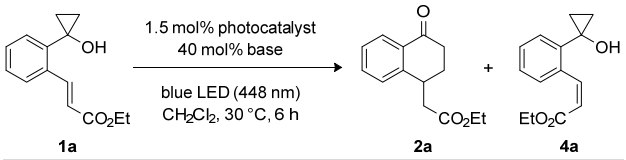


Figure 1. Natural products containing a benzo-fused cyclic ketone and ring expansion of cyclic alcohols leading to cyclic ketones.

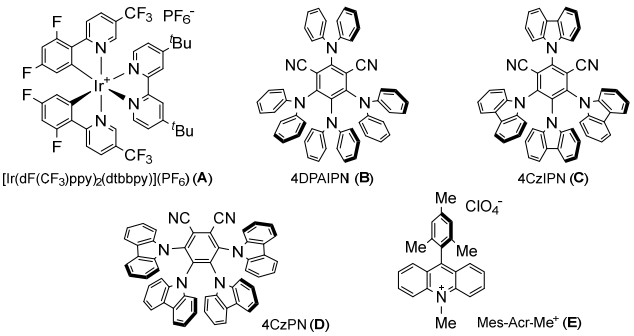
assessed under blue-light irradiation in the presence of a commercially available base $P^nBu_3Et^+(EtO)_2POO^-$. The reaction of **1a** in the presence of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (**A**) [$E_{1/2}(*P/P^-)$ = 1.21 V vs SCE in MeCN][13] yielded 33% of the desired 1-tetralone **2a**, although **4a**, the stereoisomer of **1a**, was obtained in 8% yield (entry 1). The use of 4DPAIPN (**B**) [$E_{1/2}(*P/P^-)$ = 1.10 V vs SCE in MeCN][14] increased the yield of **4a**, while the yield of **2a** decreased (entry 2). These results suggest that photocatalysts with relatively high oxidation potentials are required to promote the PCET process of **1a**. Therefore, we tested 4CzIPN (**C**) [$E_{1/2}(*P/P^-)$ = 1.35 V vs SCE in MeCN].[15] This photocatalyst exhibited better catalytic activity, yielding 54% of **2a** (entry 3), while 4CzPN (**D**) [$E_{1/2}(*P/P^-)$ = 1.40 V vs SCE in MeCN][15] was not as effective as **C** (entry 4). The use of Mes-Acr-Me$^+$ [$E_{1/2}(*P/P^-)$ = 2.06 V vs SCE in MeCN][16] gave a complex mixture, resulting in a lower yield of **2a** (entry 5). Subsequently, we investigated various bases previously reported to be effective for the ring-opening reaction of cyclic alcohols via a PCET process (entries 6–9).[12a–c] We found that the use of $P^nBu_4^+(PhO)_2POO^-$ slightly improved the reaction outcome (entry 8). When the reaction was performed at 0 °C, the yield increased to 72% (entry 10). The yield of **2a** was improved further by increasing the amount of photocatalyst **C** (entry 11). In addition, control reactions without a photocatalyst, base, or blue-light irradiation resulted in no conversion of **1a**, indicating the essential role each component plays in this reaction (see Supporting Information for details).

With the optimal reaction conditions determined, we examined the scope of the substrates (Scheme 1). First, we performed the reaction of **1a** using 1.5 mol% 4CzIPN at 1 mmol scale. The reaction proceeded smoothly to yield 72% of **2a**. Substrates possessing methyl (**1b**), *n*-butyl (**1c**), and benzyl (**1d**) esters at the olefin terminus gave the desired products **2b–d** in good yields. Dimethylaminocarbonyl (**1e**) and benzenesulfonyl (**1f**) groups were tolerated, and the yields of **2e** and **2f** were 81% and 68%, respectively. When substrates bearing cyano (**1g**) and 2-pyridyl (**1h**) groups were used, the corresponding products **2g** and **2h** were obtained in moderate yields. Incorporating a methyl group at the α-position of the ester moiety did not affect the catalytic efficiency, yielding 79% of **2i**. Remarkably, 1-tetralone **2j** bearing a quaternary carbon at the benzylic position was obtained in 49% yield from substrate **1j**, which possessed a 2-methylcyclopenet-2-ene-1-one moiety. The reaction of substrates with 4-bromo (**1k**), 5-chloro (**1l**), or 4,5-dimethoxy (**1m**) groups on the aromatic ring afforded the corresponding 1-tetralones **2k–m** in good yields. Notably, a high yield of 1-tetralone **2m**, bearing a 1,2-dimethoxybenzene moiety which could be easily oxidized, was obtained,

Table 1. Optimization study[a]

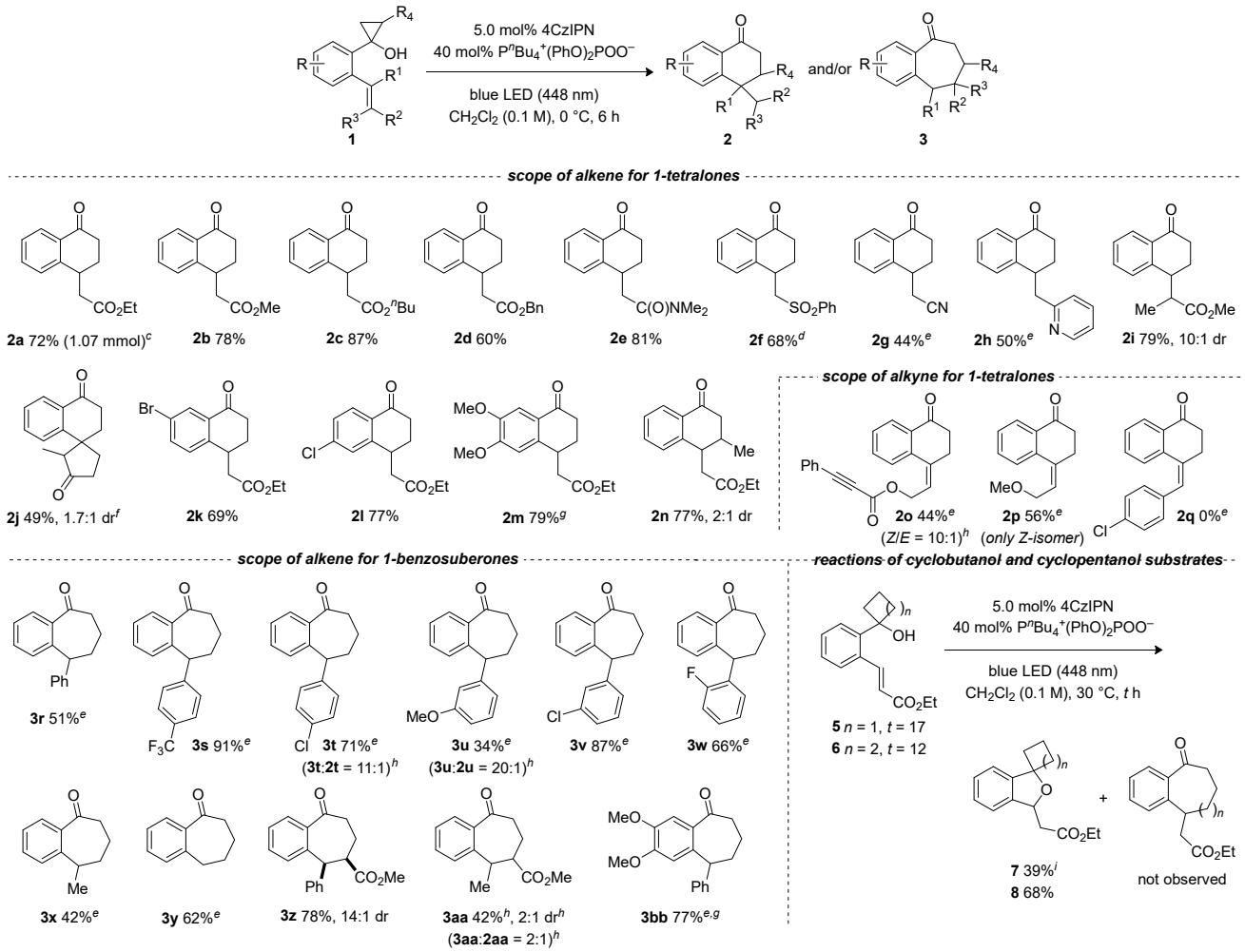


entry	photo-catalyst	base	**2a** (%)[c,d]	**4a** (%)[c,e]
1[b]	**A**	$P^nBu_3Et^+(EtO)_2POO^-$	33	8
2	**B**	$P^nBu_3Et^+(EtO)_2POO^-$	12	31
3	**C**	$P^nBu_3Et^+(EtO)_2POO^-$	54	10
4	**D**	$P^nBu_3Et^+(EtO)_2POO^-$	33	37
5	**E**	$P^nBu_3Et^+(EtO)_2POO^-$	22	15
6	**C**	collidine	15	16
7	**C**	$P^nBu_4^+CF_3COO^-$	39	N.D.
8	**C**	$P^nBu_4^+(PhO)_2POO^-$	57	1
9	**C**	$N^nBu_4^+(PhO)_2POO^-$	51	N.D.
10[f]	**C**	$P^nBu_4^+(PhO)_2POO^-$	72	N.D.
11[f,g]	**C**	$P^nBu_4^+(PhO)_2POO^-$	86 (85)	N.D.



[a]Reactions were performed on a 0.1 mmol scale at a concentration of 0.1 M. [b]Blue LED (385 nm) was used as a light source. [c]Determined by ^{1}HNMR using 2-methoxynaphthalene as an internal standard. [d]Isolated yield is shown in parenthesis. [e]N.D. = Not detected. [f]The reaction was performed at 0 °C. [g]5.0 mol% 4CzIPN was used.

Scheme 1. Substrate scope[a,b]



[a]All reactions were performed on a 0.1 mmol scale. [b]Isolated yields are shown. [c]1.5 mol% 4CzIPN was used. [d]The reaction was performed for 3 h. [e]The reaction was performed at 30 °C. [f]The reaction was performed at –20 °C. [g]The reaction was performed for 2 h. [h]Determined by ^{1}H NMR analysis of the crude product mixture. [i]P^{n}Bu$_3$Et$^+$(EtO)$_2$POO$^-$ was used as a base.

indicating that the reaction conditions were mild. The introduction of a methyl group into the cyclopropane ring was allowed to obtain di-substituted 1-tetralone **2n** in 77% yield with 2:1 dr.

We previously reported the rhodium-catalyzed cycloisomerization of ester-tethered 1,6-diynes with a cyclopropanol moiety, such as **1o**, which leads to tetralone/exocyclic diene hybrid molecules.[3d] We found that the reaction starts with oxidative coupling of the diyne moiety leading to a rhodacyclopentadiene intermediate and as such substrate **1p**, which had no diyne moiety, failed to undergo ring expansion. In contrast to these earlier findings, the reaction of **1o** under the modified PCET conditions afforded a yield of 44% for 4-alkylidene-1-tetralone **2o** (Z/E = 10:1) with the propiolate moiety intact. Moreover, 1-(2-alkynylphenyl)cyclopropanol **1p** was converted to the corresponding 1-tetralone **2p** in 56% yield as the *Z*-isomer, while the *E*-isomer of **2p** was not observed. Unfortunately, the reaction of aryl-substituted alkyne **1q** did not proceed.

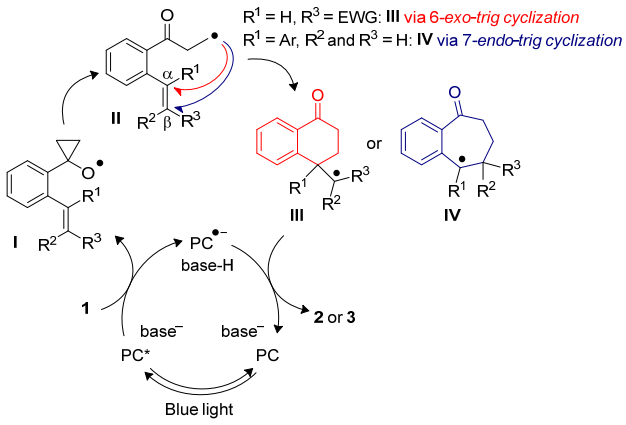
In contrast, the reaction of 1,1-diarylethene-type substrate **1r** was performed at 30 °C and afforded δ-phenyl 1-benzosuberone (**3r**) in 51% yield, rather than the corresponding 1-tetralone (**2r**). The reactions of substrates bearing 4-(trifluoromethyl)phenyl (**1s**) and 4-chlorophenyl (**1t**) groups resulted in the formation of **3s** and **3t** in 91% and 71% yields, respectively. The introduction of the 3-methoxyphenyl group resulted in a low yield of **3u** and most of **1u** remained unreacted, although the 3-chlorophenyl group was successfully incorporated to afford **3v** in 87% yield. Notably, a little amount of 1-tetralones **2t** and **2u** were observed when using **1t** and **1u**. The substrate possessing a 2-fluorophenyl group (**1w**) was converted to the corresponding 1-benzosuberone **3w** in 66% yield. When we used the cyclopropanol substrate **1x**, which contained a methyl group instead of an aryl group at the benzylic position, **3x** was obtained in moderate yield. Unsubstituted 1-benzosuberone (**3y**) was also selectively obtained when **1y**, which contained an unsubstituted styrene moiety, was used as the substrate. The reaction of substrate **1z**, possessing a β-phenylacrylate moiety, selectively afforded γ,δ-disubstituted 1-benzosuberone **3z** in 78% yield.[17] The major isomer of **3z** was determined to be the cis isomer by X-ray crystallographic analysis.[18] In contrast, the reaction of **1aa**, bearing

a β-methylacrylate moiety, provided 1-benzosuberone **3aa** (2:1 dr) in 42% NMR yield along with **2aa** in 21 % NMR yield. Finally, the reaction of a substrate bearing a 4,5-dimethoxy group (**1bb**) proceeded smoothly to afford **3bb** in 77% yield.

Subsequently, the PCET-induced ring-expansion conditions were applied to cyclobutanol **5** and cyclopentanol **6**; however, phthalan-type products **7** and **8** were obtained instead of the expected benzo-fused cyclic ketones. In the reaction of **6**, the intramolecular Michael addition of the alkoxy radical intermediate might occur rather than the ring-opening of the cyclic alcohol moiety.[19] In contrast, in the reaction of **5**, the alkoxy radical intermediate should be immediately transformed into the primary alkyl radical species via β-scission, which is indicated by the DFT calculation, although several control experiments indicate that **7** was not formed via the ionic reaction process (see Supporting Information for details). The reason of the formation of **7** is not clear at the present stage.

A plausible reaction mechanism for the ring expansion of **1** is shown in Scheme 2. First, alkoxy radical **I** is generated via PCET of the alcohol moiety. The ring-opening through β-scission of **I** with the aid of ring-strain relief generates the primary alkyl radical intermediate **II**, which then undergoes cyclization with the pendant alkene moiety. The regioselectivity of nucleophilic radical addition depends on the alkene substituents. The radical cyclization of intermediate **I** bearing an electron-withdrawing group (EWG) at the β-position of the styrene moiety (R^1 = H, R^3 = EWG) preferentially proceeds in a 6-*exo-trig* mode, giving radical intermediate **III**. In contrast, 7-*endo-trig* cyclization is favored for 1,1-diarylethene-type substrates (R^1 = Ar, R^2, and R^3 = H) because of the steric hindrance imposed by the α-aryl substituent and generation of a stable dibenzylic radical intermediate **IV**. In fact, the 6-*exo-trig* cyclization was allowed when using **1aa**, while the 7-*endo-trig* cyclization exclusively proceeds when using **1x** and **1z**. Finally, a single-electron reduction of radical intermediates **III**/**IV** and subsequent protonation of the resultant carbanions afforded the final products **2** and **3**, respectively, completing the photoredox cycle.

Scheme 2. Plausible mechanism for the ring expansion of 1.



In summary, we have established a metal-free radical ring-expansion of 1-(2-alkenylaryl)cyclopropanols invoked by PCET activation using an organic photoredox catalyst. The reaction of substrates bearing an electron-withdrawing group at the β-position of the styrene moiety selectively afforded γ-substituted 1-tetralones via 6-*exo-trig* cyclization, while δ-substituted 1-benzosuberones were selectively obtained from 1,1-diarylethene-type substrates via 7-*endo-trig* cyclization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and full spectroscopic data for all new compounds (PDF)

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) (a) Wellington, K. D.; Cambie, R. C.; Rutledge, P. S.; Bergquist, P. R.; Chemistry of Sponges. 19. Novel Bioactive Metabolites from *Hamigera tarangaensis*. *J. Nat. Prod.* **2000,** *63,* 79-85. (b) Kaysser, L.; Bernhardt, P.; Nam, S.-J.; Loesgen, S.; Ruby, J. G.; Skewes-Cox, P.; Jensen, P. R.; Fenical, W.; Moore, B. S. Merochlorins A–D, Cyclic Meroterpenoid Antibiotics Biosynthesized in Divergent Pathways with Vanadium-Dependent Chloroperoxidases. *J. Am. Chem. Soc.* **2012**, *134*, 11988–11991. (c) Tanaka, T.; Ito, T.; Ido, Y.; Son, T.-K.; Nakaya, K.; Iinuma, M.; Ohyama, M.; Chelladurai, V. Stilbenoids in the stem bark of *Hopea parviflora*. *Phytochemistry* **2000**, *53*, 1015–1019.

(2) (a) Poon, P. S.; Banerjee, A. K.; Vera, W. J.; Mora, H. D.; Laya, M. S.; Cabrera, E. V.; Melean, C. E. Use of 5-methoxy, 6-methoxy and 7-methoxy-α-tetralones in the synthesis of diterpenes,

sesquiterpenes and other natural products. *J. Chem. Res.* **2008**, 181–187. (b) Farghaly, T. A.; Gomha, S. M.; Dawoodac, K. M.; Shaaban, M. R. Synthetic routes to benzosuberone-based fused and spiro-heterocyclic ring systems. *RSC Adv.* **2016**, *6*, 17955–17979.
(3) Selected reports using a transition metal catalyst: (a) Nishimura, T.; Ohe, K.; Uemura, S. Oxidative Transformation of *tert*-Cyclobutanols by Palladium Catalysis under Oxygen Atmosphere. *J. Org. Chem.* **2001**, *66*, 1455–1465. (b) Ishida, N.; Sawano, S.; Murakami, M. Synthesis of 3,3-disubstituted α-tetralones by rhodium-catalysed reaction of 1-(2-haloaryl)cyclobutanols. *Chem. Commun.* **2012**, *48*, 1973–1975. (c) Hoshimoto, Y.; Hayashi, Y.; Suzuki, H.; Ohashi, M.; Ogoshi, S. Synthesis of Five- and Six-Membered Benzocyclic Ketones through Intramolecular Alkene Hydroacylation Catalyzed by Nickel(0)/N-Heterocyclic Carbenes. *Angew. Chem. Int. Ed.* **2012**, *51*, 10812–10815. (d) Yasui, T.; Kikuchi, T.; Yamamoto, Y. Rhodium-catalyzed cycloisomerization of ester-tethered 1,6-diynes with cyclopropanol moiety leading to tetralone/exocyclic diene hybrid molecules. *Chem. Commun.* **2020**, *56*, 12865–12868.
(4) Selected reports of visible-light-mediated synthesis of 1-tetralones: (a) Shu, W.; Nevado, C. Visible-Light-Mediated Remote Aliphatic C–H Functionalizations through a 1,5-Hydrogen Transfer Cascade. *Angew. Chem. Int. Ed.* **2017**, *56*, 1881–1884. (b) Dange,N. S.; Jatoi, A. H.; Robert, F.; Landais, Y. Visible-Light-Mediated Addition of Phenacyl Bromides onto Cyclopropenes. *Org. Lett.* **2017**, *19*, 3652–3655.
(5) Selected reports of the synthesis of 1-benzosuberones using intramolecular Friedel-Crafts acylation: (a) Yamada, R.; Adachi, Y.; Yokoshima, S.; Fukuyama, T. Total Synthesis of (−)-Daphenylline. *Angew. Chem. Int. Ed.* **2016**, *55*, 6067–6070. (b) Xu, B.; Wang, B.; Xun, W.; Qiu, F. G. Total Synthesis of (−)-Daphenylline. *Angew. Chem. Int. Ed.* **2019**, *58*, 5754–5757.
(6) (a) Wang, K.; Meng, L.-G.; Zhang, Q.; Wang, L. Direct construction of 4-aryl tetralones *via* visible-light-induced cyclization of styrene with molecular oxygen. *Green Chem*. **2016**, *18*, 2864–2870; (b) Xia, Z.-L.; Zheng, C.; Xu, R.-Q.; You, S.-L. Chiral phosphoric acid catalyzed aminative dearomatization of α-naphthols/Michael addition sequence. *Nat. Commun.* **2019**, *10*, #3150.
(7) A review of radical-mediated ring expansions: Dowd, P.; Zhang, W. Free Radical-Mediated Ring Expansion and Related Annulations. *Chem. Rev.* **1993**, *93*, 2091–2115.
(8) Yu, J.; Zhao, H.; Liang, S.; Bao, X.; Zhu, C. A facile and regioselective synthesis of 1-tetralones via silver-catalyzed ring expansion. *Org. Biomol. Chem.* **2015**, *13*, 7924–7927.
(9) Fang, J.; Li, L.; Yang, C.; Chen, J.; Deng, G.-J.; Gong, H. Tandem Oxidative Ring-Opening/Cyclization Reaction in Seconds in Open Atmosphere for the Synthesis of 1-Tetralones in Water–Acetonitrile. *Org. Lett.* **2018**, *20*, 7308–7311.
(10) Reviews of synthetic application of PCET: (a) Gentry, E. C.; Knowles, R. R. Synthetic Applications of Proton-Coupled Electron Transfer. *Acc. Chem. Res.* **2016**, *49*, 1546–1556. (b) Miller, D. C.; Tarantino, K. T.; Knowles, R. R. Proton-Coupled Electron Transfer in Organic Synthesis: Fundamentals, Applications, and Opportunities. *Top. Curr. Chem.* **2016**, *374*, #30. (c) Hoffmann, N. Proton-Coupled Electron Transfer in Photoredox Catalytic Reactions. *Eur. J. Org. Chem.* **2017**, *2017*, 1982–1992.
(11) (a) Zhao, K.; Yamashita, K.; Carpenter, J. E.; Sherwood, T. C.; Ewing, W. R.; Cheng, P. T. W.; Knowles, R. R. Catalytic Ring Expansions of Cyclic Alcohols Enabled by Proton-Coupled Electron Transfer. *J. Am. Chem. Soc.* **2019**, *141*, 8752–8757. Pioneering applications of PCET process to the transformation of alcohols, see also: (b) Yayla, H. G.; Wang, H.; Tarantino, K. T.; Orbe, H. S.; Knowles, R. R. Catalytic Ring-Opening of Cyclic Alcohols Enabled by PCET Activation of Strong O−H Bonds. *J. Am. Chem. Soc.* **2016**, *138*, 10794–10797. (c) Ota, E.; Wang, H.; Frye, N. L.; Knowles, R. R. A Redox Strategy for Light-Driven, Out-of-Equilibrium Isomerizations and Application to Catalytic C−C Bond Cleavage Reactions. *J. Am. Chem. Soc.* **2019**, *141*, 1457–1462. (d) Nguyen, S. T.; Murray, P. R. D.; Knowles, R. R. Light-Driven Depolymerization of Native Lignin Enabled by Proton-Coupled Electron Transfer. *ACS Catal.* **2020**, *10*, 800–805. (e) Huang, L.; Ji, T.; Rueping, M. Remote Nickel-Catalyzed Cross-Coupling Arylation via Proton-Coupled Electron Transfer-Enabled C–C Bond Cleavage. *J. Am. Chem. Soc.* **2020**, *142*, 3532–3539.
(12) (a) Nikolaev, A.; Orellana, A. Transition-Metal- Catalyzed C–C and C–X Bond-Forming Reactions Using Cyclopropanols. *Synthesis* **2016**, *48*, 1741–1768. (b) McDonald, T. R.; Mills, L. R.; West, M. S.; Rousseaux, S. A. L. Selective Carbon–Carbon Bond Cleavage of Cyclopropanols. *Chem. Rev.* **2021**, *121*, 3–79; (c) Morcillo, S. P. Radical-Promoted C–C Bond Cleavage: A Deconstructive Approach for Selective Functionalization. *Angew. Chem. Int. Ed*. **2019**, *58*, 14044–14054; (d) Murakami, M.; Ishida, N. Cleavage of Carbon–Carbon σ-Bonds of Four-Membered Rings. *Chem. Rev*. **2021**, *121*, 264–299; (e) Yu, X.-Y.; Chen, J.-R.; Xiao, W.-J. Visible Light-Driven Radical-Mediated C–C Bond Cleavage/Functionalization in Organic Synthesis. *Chem. Rev*. **2021**, *121*, 506–561.
(13) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. Single-Layer Electroluminescent Devices and Photoinduced Hydrogen Production from an Ionic Iridium(III) Complex. *Chem. Mater.* **2005**, *17*, 5712–5719.
(14) Ishimatsu, R.; Matsunami, S.; Kasahara, T.; Mizuno, J.; Edura, T.; Adachi, C.; Nakano, K.; Imato, T. Electrogenerated Chemiluminescence of Donor–Acceptor Molecules with Thermally Activated Delayed Fluorescence. *Angew. Chem. Int. Ed.* **2014**, *53*, 6993–6996.
(15) Luo, J.; Zhang, J. Donor–Acceptor Fluorophores for Visible-Light-Promoted Organic Synthesis: Photoredox/Ni Dual Catalytic C(sp^3)–C(sp^2) Cross-Coupling. *ACS Catal.* **2016**, *6*, 873−877.
(16) (a) Fukuzumi, S.; Kotani, H.; Ohkubo, K.; Ogo, S.; Tkachenko, N. V.; Lemmetyinen, H. Electron-Transfer State of 9-Mesityl-10-methylacridinium Ion with a Much Longer Lifetime and Higher Energy Than That of the Natural Photosynthetic Reaction Center. *J. Am. Chem. Soc.* **2004**, *126*, 1600–1601. (b) Ohkubo, K.; Mizushima, K.; Iwata, R.; Souma, K.; Suzuki, N.; Fukuzumi, S. Simultaneous production of *p*-tolualdehyde and hydrogen peroxide in photocatalytic oxygenation of *p*-xylene and reduction of oxygen with 9-mesityl-10-methylacridinium ion derivatives. *Chem. Commun.* **2010**, *46*, 601–603.
(17) Lovett, G. H.; Sparling, B. A. Decarboxylative Anti-Michael Addition to Olefins Mediated by Photoredox Catalysis. *Org. Lett.* **2016**, *18*, 3494–3497.
(18) The relative configuration of **3z** was determined by X-ray crystallographic analysis of the corresponding hydrazone derivative. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre database (http://www.ccdc.cam.ac.uk/) under code CCDC 2084574. For details, see Supporting Information.
(19) Intramolecular hydroetherification of alkenols was reported by Knowles and co-workers: Tsui, E.; Metrano, A. J.; Tsuchiya, Y.; Knowles, R. R. Catalytic Hydroetherification of Unactivated Alkenes Enabled by Proton-Coupled Electron Transfer. *Angew. Chem. Int. Ed.* **2020**, *59*, 11845–11849.