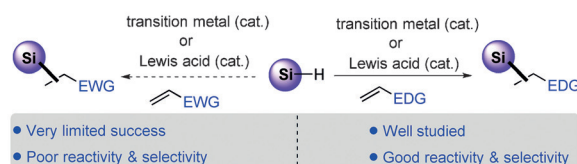**Photocatalysis**

Visible-Light-Mediated Metal-Free Hydrosilylation of Alkenes through Selective Hydrogen Atom Transfer for Si−H Activation

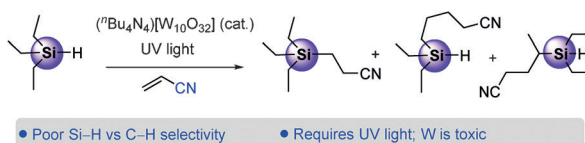*Rong Zhou, Yi Yiing Goh, Haiwang Liu, Hairong Tao, Lihua Li, and Jie Wu**

Abstract: Although there has been significant progress in the development of transition-metal-catalyzed hydrosilylations of alkenes over the past several decades, metal-free hydrosilylation is still rare and highly desirable. Herein, we report a convenient visible-light-driven metal-free hydrosilylation of both electron-deficient and electron-rich alkenes that proceeds through selective hydrogen atom transfer for Si−H activation. The synergistic combination of the organophotoredox catalyst 4CzIPN with quinuclidin-3-yl acetate enabled the hydrosilylation of electron-deficient alkenes by selective Si−H activation while the hydrosilylation of electron-rich alkenes was achieved by merging photoredox and polarity-reversal catalysis.

Organosilanes are versatile intermediates and products in medicinal chemistry and materials science. The hydrosilylation of alkenes, a 100 % atom-efficient transformation, represents one of the most important reactions in the silicone industry.[1] The direct activation of Si−H bonds for subsequent hydrosilylation has been effectively accomplished through the use of the platinum catalysts developed by Speier and Karstedt in industrial-scale manufacturing.[2] Intensive efforts in this research field have led to the discovery of complexes based on earth-abundant metals, such as iron, nickel, and cobalt, as effective hydrosilylation catalysts.[3,4] In addition, recent advances have shown that Lewis acid catalysts, especially electron-deficient boranes, can also catalyze hydrosilylations in a rare-metal-free manner (Scheme 1 A).[5] Nevertheless, successful examples have been mostly limited to electron-rich alkenes as these catalysts generally show poor reactivity and selectivity toward electron-deficient alkenes (α- vs. β-adducts, 1,2- vs. 1,4-addition).[6] To the best of our knowledge, a practical method for the effective catalytic hydrosilylation of both electron-deficient and electron-rich alkenes has not been realized, particularly in a metal-free manner.
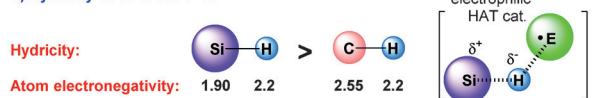
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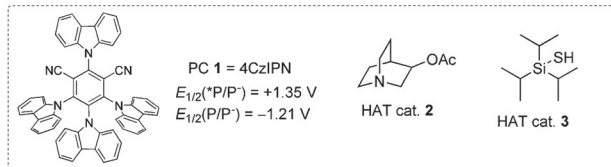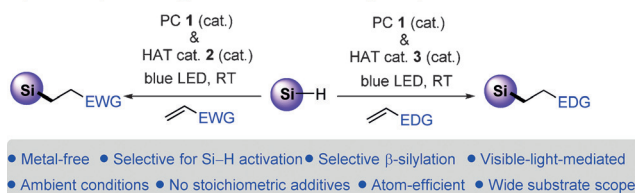
Scheme 1. Hydrosilylation of alkenes.

Significant developments have occurred in photocatalysis over the past decade, which have enabled previously impossible transformations.[7] Aside from single electron transfer (SET) and energy transfer, hydrogen atom transfer (HAT) is frequently involved in photocatalysis, offering enormous opportunities for C−H activation.[8] In the context of HAT, polarity plays a vital role to enable selective hydrogen atom abstraction beyond the control of the relative bond dissociation energies (BDEs).[9]

Fagnoni, Ravelli, and co-workers recently disclosed an elegant hydrosilylation of electron-poor alkenes through the use of tetrabutylammonium decatungstate as a direct HAT catalyst under UV light (310 nm) irradiation.[10] Notably, mixtures of the Si−H and C−H activation products were obtained with trialkylsilanes (Scheme 1B), likely owing to the similar BDEs of the Si−H and C−H bonds in these

compounds.[11] As silicon is more electropositive than carbon (electronegativity 1.90 vs. 2.55 on the Pauling scale), Si−H bonds are generally more hydridic than C−H bonds. We speculated that by incorporating a highly electrophilic HAT catalyst, such as the quinuclidinium radical cation used by the MacMillan group,[12] the Si−H bond should be selectively activated in the presence of multiple C−H bonds with similar bond strengths, therefore enabling selective hydrosilylation (Scheme 1C). Herein, we report the first visible-light-driven hydrosilylation of both electron-deficient and electron-rich alkenes in a metal-free manner (Scheme 1D).

We commenced our study by evaluating the light-promoted hydrosilylation of benzyl acrylate with triethylsilane under blue LED irradiation ($\lambda_{max} = 470$ nm). After a careful investigation of various photocatalysts and solvents (see the Supporting Information, Table S1), the combination of a catalytic amount of the organophotoredox catalyst 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN, **1**)[13] and quinuclidin-3-yl acetate (**2**) in acetonitrile (MeCN) was found to provide the best result, and the hydrosilylation product **4** was isolated in 81% yield. Remarkably, unlike in the study by Fagnoni and Ravelli,[10] only the hydrosilylation product was obtained, and C−H activation side products were not detected, highlighting the effectiveness of the electrophilic quinuclidinium radical cation HAT catalyst for selective Si−H activation. Replacing the photocatalyst with Ir[dF-(CF$_3$)ppy]$_2$(dtbpy)PF$_6$, which has a similar redox potential as 4CzIPN, delivered a comparable result. Other photocatalysts, including Ir(ppy)$_2$(dtbpy)$_3$PF$_6$, Ir(ppy)$_3$, Ru(bpy)$_3$Cl$_2$, and eosin Y, failed to afford the desired product. Among the range of solvents examined, the use of MeCN resulted in the best reactivity. Finally, no hydrosilylation product was detected in the absence of either photocatalyst **1**, quinuclidinium catalyst **2**, or light, demonstrating the need for all of these components.
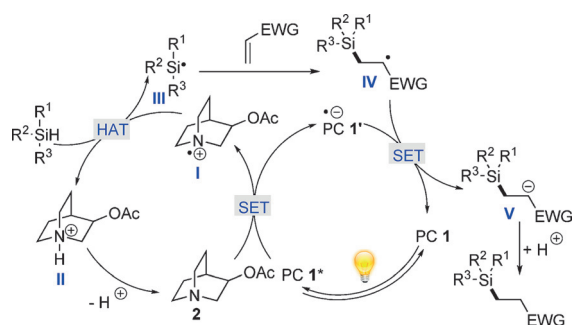
Adopting the optimized metal-free conditions, we sought to investigate the generality of this hydrosilylation. Our recently developed "stop-flow" micro-tubing (SFMT) reactor, with its enhanced light penetration efficiency, was applied when the conversions were low in batch reactors.[14] Employing Et$_3$SiH and Me$_2$PhSiH as two representative silane reagents, a diverse range of electron-deficient alkenes were examined. As depicted in Scheme 2a, acrylates with different steric and electronic properties were suitable substrates (**4**–**12**), and functional groups such as silane (**10**), ether (**11**), and epoxide (**12**) moieties were tolerated. Dimethyl maleate and a lactone were also viable substrates, readily affording the corresponding hydrosilylation products in 84% and 37% yield, respectively (**13** and **14**). Cyclic enones with different ring sizes (**15**–**17**) and acyclic enones with either alkyl or aryl substituents (**18**–**20**) were all hydrosilylated. Furthermore, the hydrosilylation was successfully applied to other types of electron-deficient alkenes such as acrylamides (**21** and **22**), a vinyl sulfone (**23**), acrylonitrile (**24**), and methylene malonates (**25**–**27**). Notably, activated C−H bonds adjacent to heteroatoms, such as α-oxy (**11** and **12**), α-nitro (**21** and **22**), and α-silyl (**10**) C−H bonds, were well tolerated in this selective Si−H activation protocol. Experiments probing the silane scope with benzyl acrylate (Scheme 2b) illustrated that
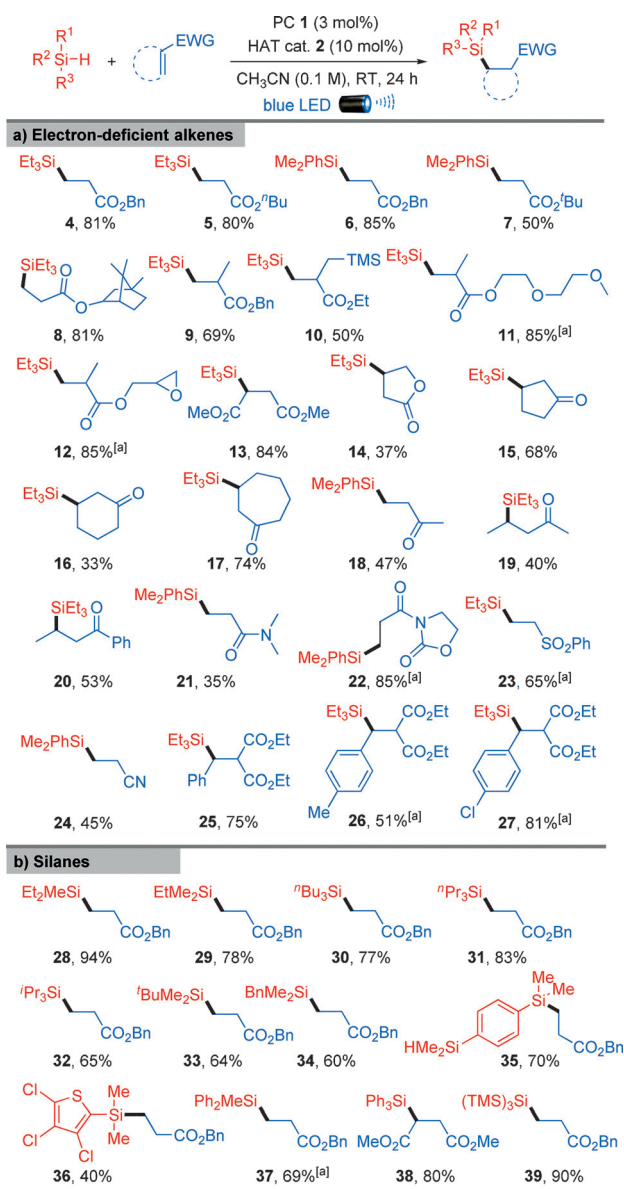
Scheme 2. Scope of the metal-free hydrosilylation of electron-deficient alkenes. For details on the reaction conditions, see the Supporting Information. Yields of isolated products for reactions conducted in batch reactors are given. [a] Reaction conducted in an SFMT reactor.

a series of trialkylsilanes with different sizes underwent the hydrosilylation to deliver products **28**–**34** in moderate to excellent yields. Notably, only the monohydrosilylation product **35** was obtained with *para*-phenylenebis(dimethylsilane). The incorporation of heteroaryl (**36**) or phenyl (**37** and **38**) substituents in the silane was also feasible. Tris(trimethylsilyl)silane gave product **39** in excellent yield, likely owing to the enhanced stability of the supersilyl radical intermediate.

As shown in Scheme 3, a plausible mechanism for the hydrosilylation of electron-deficient alkenes was proposed based on several control experiments. No reaction was detected when the radical scavengers TEMPO or hydroquinone were added, suggesting a radical-based process.[15] Stern–Volmer quenching studies supported the occurrence of
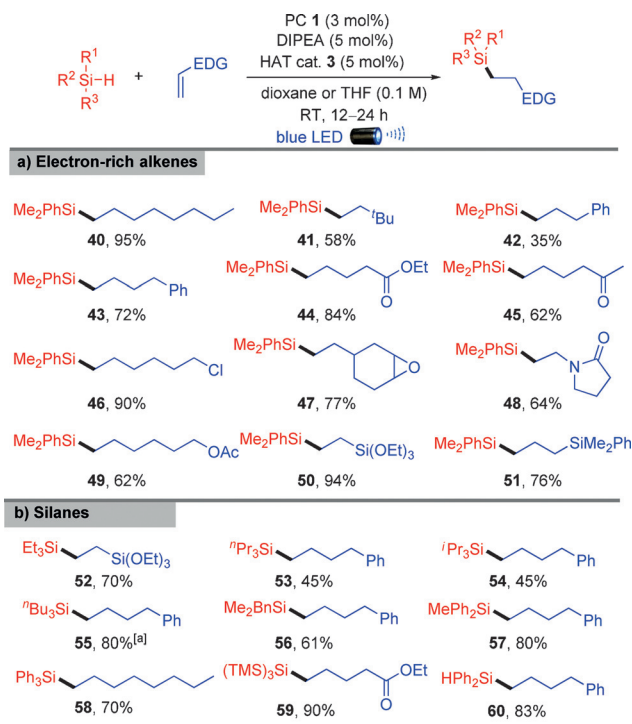
Scheme 3. Plausible mechanism for the hydrosilylation of electron-poor alkenes.

K_2CO_3 also resulted in an efficient transformation (85% yield).

With optimized reaction conditions in hand, the scope was investigated with respect to electron-rich alkenes (Scheme 4a). A broad range of aliphatic terminal alkenes were found to be good substrates, delivering the corresponding silane products in moderate to excellent yields (**40–49**).


Scheme 4. Scope of the metal-free hydrosilylation of electron-rich alkenes. For details on the reaction conditions, see the Supporting Information. Yields of isolated products for reactions conducted in batch reactors are given. [a] Reaction conducted in an SFMT reactor.

a SET from 3-acetoxyquinuclidine ($E_p = +1.22$ V vs. SCE in MeCN)[12b] to the light-activated photocatalyst **1*** [$E_{1/2}$(*P/P$^-$) $= +1.35$ V vs. SCE in MeCN][13] to afford the reduced photocatalyst **1′** and amine radical cation **I**. No obvious quenching of **1*** by the silane or benzyl acrylate was observed.[15] Owing to its high electrophilicity, radical cation **I** should selectively abstract a hydrogen atom from the more hydridic Si−H bond to deliver silyl radical **III**, along with quinuclidinium cation **II**. Nucleophilic addition of silane radical **III** to an electron-deficient alkene forms a transient radical adduct **IV**. Single-electron reduction of radical adduct **IV** by **1′** [$E_{1/2}$(P/P$^-$) $= -1.21$ V vs. SCE in MeCN][13] affords the hydrosilylation product after protonation[14b] while regenerating photocatalyst **1**. Deuterium labeling experiments indicated that anion **V** would most likely abstract a free proton from the solvent.[15] The BDE difference between the N−H bond of the quinuclidinium cation (BDE(N$^+$−H) = 100 kcal mol^{-1})[12b] and the C−H bond α to the electron-withdrawing group of the hydrosilylation product (BDE(C−H) = 85.2 kcal mol^{-1} for **4**)[11] indicates that a radical chain process between radical **IV** and cation **II** is unlikely. Furthermore, both a light on/off experiment and the calculated quantum yield ($\Phi = 0.048$) excluded the possibility of a chain mechanism.[15,16]

We next attempted to extend this visible-light-promoted metal-free hydrosilylation protocol to electron-rich alkenes. However, no product was formed with 1-octene under the reaction conditions optimized for electron-deficient alkenes (Table S2, entry 1). This might be due to the fact that the radical adduct generated from the addition of silyl radical **III** to an electron-rich alkene is not oxidizing enough to oxidize **1′** to turn over the catalytic cycle. We envisioned that combining the photoredox catalyst with a polarity-reversal catalyst for hydrogen atom abstraction might solve this problem.[9b] Employing dimethylphenylsilane and 1-octene as the model substrates, a series of thiol catalysts,[17] additives, and solvents were examined under the photoredox conditions (Table S2). It was found that the combination of PC **1** (3 mol%), *N,N*-diisopropylethylamine (DIPEA, 5 mol%), and triisopropylsilanethiol (5 mol%) in dioxane under blue LED irradiation delivered the hydrosilylation product **40** in excellent yield. Control experiments showed that the reaction proceeded smoothly even without DIPEA, albeit with lower efficiency (60% yield). Replacing DIPEA with a catalytic amount of

Functional groups such as ester (**44** and **49**), ketone (**45**), chloride (**46**), epoxide (**47**), and amide (**48**) moieties were well tolerated. Both vinyl silanes and allyl silanes could be applied to generate disilane products (**50** and **51**). Different silane reagents were examined as well (Scheme 4b). Trialkylsilanes such as triethylsilane, tripropylsilane, triisopropylsilane, tributylsilane, and benzyldimethylsilane all afforded the corresponding hydrosilylation products in good yields (**52–56**). Moreover, the hydrosilylations proceeded smoothly with aryl-substituted silanes such as diphenylmethylsilane and triphenylsilane (**57** and **58**). Tris(trimethylsilyl)silane gave the hydrosilylation product **59** in excellent yield. Notably, this protocol could be expanded to secondary silanes to give product **60** with one Si−H bond.

Mechanistically, as shown in Scheme 5, the hydrosilylation of electron-rich alkenes is initiated by the formation of thiyl radical **VI** via SET between excited photocatalyst **1*** and triisopropylsilanethiol **3** ($E_{1/2}^{ox} = +0.28$ V vs. SCE in MeCN)[15] followed by deprotonation. Stern–Volmer quenching studies illustrated that **3** can quench the excited catalyst **1*** whereas both the silane and electron-rich alkenes cannot. The
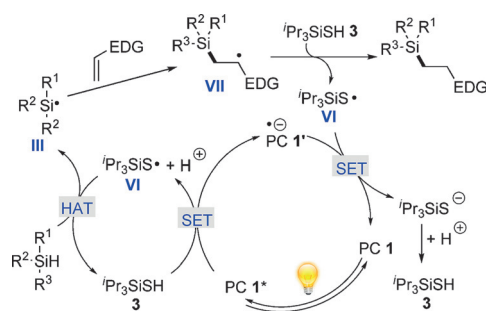
Scheme 5. Plausible mechanism for the hydrosilylation of electron-rich alkenes.

presence of a catalytic amount of base (DIPEA or K_2CO_3) presumably promotes the deprotonation to facilitate the formation of thiyl radical **VI**.[15] The electrophilic thiyl radical **VI** then abstracts the hydrogen atom of the hydridic Si−H bond to deliver silyl radical **III** while regenerating thiol **3**. Regioselective addition of the silyl radical **III** to the sterically less hindered site of the electron-rich alkene affords radical adduct **VII**. The nucleophilic radical **VII** then undergoes another polarity-matched HAT process to generate the hydrosilylation product, along with the formation of thiyl radical **VI**. The BDE difference between the S−H bond of **3** (BDE(S−H) = 88.2 kcal mol^{-1}) and the C−H bond α to the electron-donating group of the hydrosilylation product (BDE(C−H) = 93.2 kcal mol^{-1} for **40**) indicates that HAT is indeed feasible.[11] Thus thiol **3** behaves as a polarity-reversal catalyst to enable the efficient transformation. However, both a light on/off study and quantum yield measurements ($\Phi = 0.02$)[15] did not support a chain process.[17] The ineffectiveness of several photoredox catalysts with higher oxidation potentials also indicated that catalyst **1** plays other roles aside from being a simple radical initiator.[15] Therefore, in addition to abstracting a hydrogen atom from the silane, the thiyl radical **VI** ($E_{1/2}^{red} = -0.82$ V vs. SCE in MeCN)[15] may preferentially oxidize **1′** [$E_{1/2}(P/P^-) = -1.21$ V vs. SCE in MeCN] to regenerate the photocatalyst **1** to close the catalytic cycle. However, we are currently unable to exclude the possibility of a chain process with quick termination triggered by HAT between radical **VI** and the silane.[16]

To further demonstrate the synthetic utility of this method, we conducted hydrosilylations of both electron-rich and electron-poor alkenes on gram scale in flow reactors (Scheme S1). Notably, the reaction efficiency was improved in the continuous microflow system compared to the batch reactor, enabling effective reactions at a lower catalyst loading (1 mol% **1** and 5 mol% HAT catalyst).[18]

In summary, we have developed the first visible-light-mediated metal-free hydrosilylation of both electron-deficient and electron-rich alkenes through the synergistic combination of photoredox and HAT catalysis. By combining the organophotoredox catalyst 4CzIPN with the HAT catalyst quinuclidin-3-yl acetate, Si−H activation exclusively occurred over C−H activation to achieve the hydrosilylation of electron-deficient alkenes. On the other hand, the hydrosilylation of electron-rich alkenes was realized by dual organophotoredox and polarity-reversal catalysis. Both pro-

cesses benefit from their superior atom and redox economy, mild conditions, and broad substrate scopes, and are easily scaled up by using continuous-flow technology. Our study also provides convenient approaches for the generation of silicon radicals under visible-light conditions, which will likely find further application for the synthesis of functionalized silicon-containing molecules.

Conflict of interest

The authors declare no conflict of interest.

[1] L. N. Lewis, J. Stein, Y. Gao, R. E. Colborn, G. Hutchins, *Platinum Met. Rev.* **1997**, *41*, 66.

[2] a) J. L. Speier, J. A. Webster, G. H. Barnes, *J. Am. Chem. Soc.* **1957**, *79*, 974; b) B. D. Karstedt (General Electric Company), US3775452A, **1973**.

[3] For selected recent reviews, see: a) X.-Y. Du, Z. Huang, *ACS Catal.* **2017**, *7*, 1227; b) J. Sun, L. Deng, *ACS Catal.* **2016**, *6*, 290; c) Y. Nakajima, S. Shimada, *RSC Adv.* **2015**, *5*, 20603.

[4] For selected examples, see: a) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, *Science* **2012**, *335*, 567; b) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, *J. Am. Chem. Soc.* **2015**, *137*, 13244; c) D. Noda, A. Tahara, Y. Sunada, H. Nagashima, *J. Am. Chem. Soc.* **2016**, *138*, 2480; d) X. Du, Y. Zhang, D. Peng, Z. Huang, *Angew. Chem. Int. Ed.* **2016**, *55*, 6671; *Angew. Chem.* **2016**, *128*, 6783; e) B. Cheng, P. Lu, H. Zhang, X. Cheng, Z. Lu, *J. Am. Chem. Soc.* **2017**, *139*, 9439.

[5] M. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* **2015**, *44*, 2202.

[6] a) T. J. Steiman, C. Uyeda, *J. Am. Chem. Soc.* **2015**, *137*, 6104; b) N. Komine, M. Abe, R. Suda, M. Hirano, *Organometallics* **2015**, *34*, 432; c) K. Takeshita, Y. Seki, K. Kawamoto, S. Murai, N. Sonoda, *J. Org. Chem.* **1987**, *52*, 4864.

[7] For selected reviews, see: a) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075; b) D. Ravelli, S. Protti, M. Fagnoni, *Chem. Rev.* **2016**, *116*, 9850; c) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* **2016**, *116*, 10035; d) R. Brimioulle, D. Lenhart, M. M. Maturi, T. Bach, *Angew. Chem. Int. Ed.* **2015**, *54*, 3872; *Angew. Chem.* **2015**, *127*, 3944; e) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322; f) J. Xuan, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 6828; *Angew. Chem.* **2012**, *124*, 6934; g) J. M. R. Narayanam, C. R. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102.

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Angew. Chem. Int. Ed. **2017**, *56*, 16621–16625

[8] For selected reviews, see: a) L. Capaldo, D. Ravelli, *Eur. J. Org. Chem.* **2017**, 2056; b) S. Protti, M. Fagnoni, D. Ravelli, *ChemCatChem* **2015**, *7*, 1516; c) D. Ravelli, D. Dondi, M. Fagnoni, A. Albini, *Chem. Soc. Rev.* **2009**, *38*, 1999; d) M. Fagnoni, D. Dondi, D. Ravelli, A. Albini, *Chem. Rev.* **2007**, *107*, 2725.

[9] a) M. Salamone, M. Bietti, *Acc. Chem. Res.* **2015**, *48*, 2895; b) B. P. Roberts, *Chem. Soc. Rev.* **1999**, *28*, 25.

[10] H. Qrareya, D. Dondi, D. Ravelli, M. Fagnoni, *ChemCatChem* **2015**, *7*, 3350.

[11] See the Supporting Information for the calculated bond energies.

[12] a) C. Le, Y. Liang, R. W. Evans, X. Li, D. W. C. MacMillan, *Nature* **2017**, *547*, 79; b) M. H. Shaw, V. W. Shurtleff, J. A. Terrett, J. D. Cuthbertson, D. W. C. MacMillan, *Science* **2016**, *352*, 1304; c) J. L. Jeffrey, J. A. Terrett, D. W. C. MacMillan, *Science* **2015**, *349*, 1532.

[13] J. Luo, J. Zhang, *ACS Catal.* **2016**, *6*, 873.

[14] a) F. Xue, H. Deng, C. Xue, D. K. B. Mohamed, K. Y. Tang, J. Wu, *Chem. Sci.* **2017**, *8*, 3623; b) R. Zhou, H. Liu, H. Tao, X. Yu, J. Wu, *Chem. Sci.* **2017**, *8*, 4654.

[15] See the Supporting Information for details on the control experiments, luminescence quenching studies, and CV tests.

[16] M. A. Cismesia, T. P. Yoon, *Chem. Sci.* **2015**, *6*, 5426.

[17] a) M. B. Haque, B. P. Roberts, *Tetrahedron Lett.* **1996**, *37*, 9123; b) H.-S. Dang, B. P. Roberts, *Tetrahedron Lett.* **1995**, *36*, 2875.

[18] D. Cambié, C. Bottecchia, N. J. W. Straathof, V. Hessel, T. Noël, *Chem. Rev.* **2016**, *116*, 10276.