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# Catalyst-Free Deaminative Functionalizations of Primary Amines via Photoinduced Single-Electron Transfer

Jingjing Wu,<sup>†</sup> Phillip S. Grant,<sup>†</sup> Xiabing Li, Adam Noble, and Varinder K. Aggarwal<sup>\*[a]</sup>

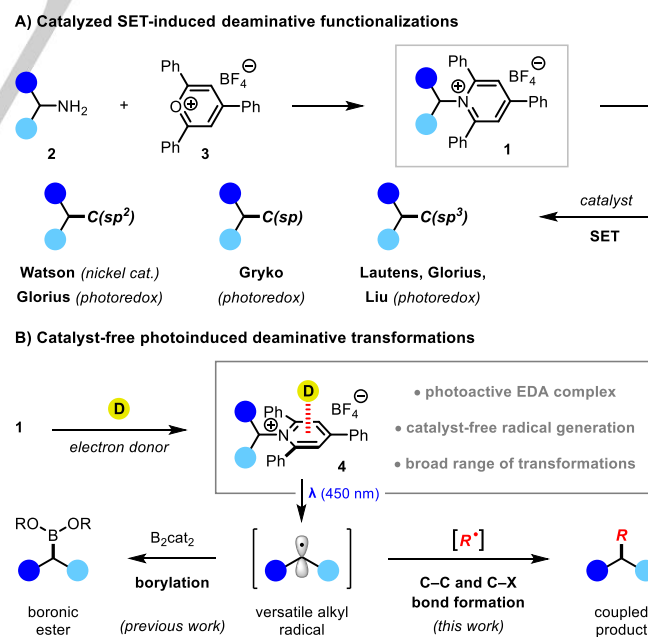
**Abstract:** The use of pyridinium-activated primary amines as photoactive functional groups for deaminative generation of alkyl radicals under catalyst-free conditions is described. By taking advantage of the visible-light absorptivity of electron donor–acceptor complexes between Katritzky pyridinium salts and either Hantzsch ester or Et<sub>3</sub>N, photoinduced single-electron transfer could be initiated in the absence of a photocatalyst. This general reactivity platform has been applied to deaminative alkylations (Giese), allylations, vinylations, alkynylations, and thioetherifications. The mild conditions are amenable to a diverse range of primary and secondary alkyl pyridiniums and demonstrate broad functional group tolerance.

Visible-light photochemistry in organic synthesis has witnessed a resurgence in research activity over the last decade.<sup>[1]</sup> This is largely due to a growing appreciation of the synthetic utility of photoredox catalysts, which, upon photoexcitation, function as single-electron or energy transfer catalysts to provide access to free-radical intermediates.<sup>[2]</sup> An alternative strategy, that circumvents the need for catalysis, is direct photoexcitation of a substrate, which has classically been performed using UV-light.<sup>[3]</sup> However, recent developments have taken advantage of the visible-light absorptivity of specific functional groups that act as photoactive handles to enable photoinduced electron transfer (PET).<sup>[4]</sup> Although direct photoexcitation is possible with a number of different functional groups,<sup>[5]</sup> such reactions more commonly take advantage of electron donor–acceptor (EDA) complexes, whose absorption spectra display a bathochromic shift relative to their constituent parts, thus enabling photoexcitation with visible-light.<sup>[6]</sup>

These strategies have enabled the development of a broad range of radical transformations that proceed via visible-light-mediated PET under catalyst-free conditions. However, such reactions are typically limited to the generation of perfluoroalkyl or stabilized alkyl radicals.<sup>[5,7,8]</sup> Access to non-stabilized alkyl radicals under such conditions is considerably more challenging,<sup>[9,10]</sup> with only a single report by Melchiorre and co-workers that generates secondary alkyl radicals via direct photoexcitation of 4-alkyl-1,4-dihydropyridine derivatives.<sup>[11]</sup> We sought an alternative functional group that could act as a versatile

photoactive handle for catalyst-free generation of non-stabilized carbon-centered radicals. One possibility was Katritzky *N*-alkylpyridinium salts **1**, which are easily prepared from primary amines **2** by reaction with 2,4,6-triphenylpyrylium **3**, are air and moisture stable, and allow selective deaminative transformations of abundant amino groups (Scheme 1A).<sup>[12]</sup> While these redox active amines have recently been applied to a number of radical-mediated transformations, they usually rely on catalysis to promote single-electron transfer (SET)-induced deamination.<sup>[13,14]</sup>

We recently reported a catalyst-free deaminative borylation reaction that proceeds via EDA complex formation between **1** and bis(catecholato)diboron (B<sub>2</sub>cat<sub>2</sub>) (Scheme 1B).<sup>[15]</sup> Subsequent PET and fragmentation provided efficient access to non-stabilized alkyl radicals that were intercepted by the diboron reagent. We reasoned that the 2,4,6-triphenylpyridinium moiety in **1** could be complexed with other electron-donors to generate EDA complex **4**,<sup>[16]</sup> thus providing a photoactive handle capable of generating non-stabilized alkyl radicals for application in a diverse range of C–C or C–X bond forming reactions (Scheme 1B). Herein, we report that Katritzky pyridinium salts are versatile substrates for photoinduced deaminative functionalizations of primary amines under catalyst-free conditions.



**Scheme 1.** Radical-mediated transformations of Katritzky pyridinium salts.

[a] Dr. J. Wu, Mr. P. S. Grant, Dr. X. Li, Dr. A. Noble, Prof. Dr. V. K. Aggarwal  
School of Chemistry, University of Bristol  
Cantock's Close, Bristol, BS8 1TS (UK)  
E-mail: [v.aggarwal@bristol.ac.uk](mailto:v.aggarwal@bristol.ac.uk)

[†] These authors contributed equally to this work.

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Our investigations began by studying the use of pyridiniums **1** in Giese reactions with electron-deficient alkenes (Table 1). Such reactions are well-developed using photocatalysis, but there are few reports of photoinduced reactions under catalyst-free conditions.<sup>[17]</sup> Given the overall transformation is reductive, a stoichiometric reductant was required. We selected Hantzsch ester (**5**) as this would act as a reductant but could also function as an electron-donor to form the key EDA complex with **1**.<sup>[10c,d]</sup> Gratifyingly, irradiation ( $\lambda_{\text{max}} = 450 \text{ nm}$ ) of a mixture of 4-aminopiperidine-derived pyridinium **1a**, Hantzsch ester, and methyl acrylate in DMA yielded the desired Giese adduct **6** in 77% yield (Table 1). Control experiments confirmed the necessity of light and **5** for successful reaction, and alternative reductants, such as  $\text{Et}_3\text{N}$ , gave no desired product.<sup>[18]</sup>

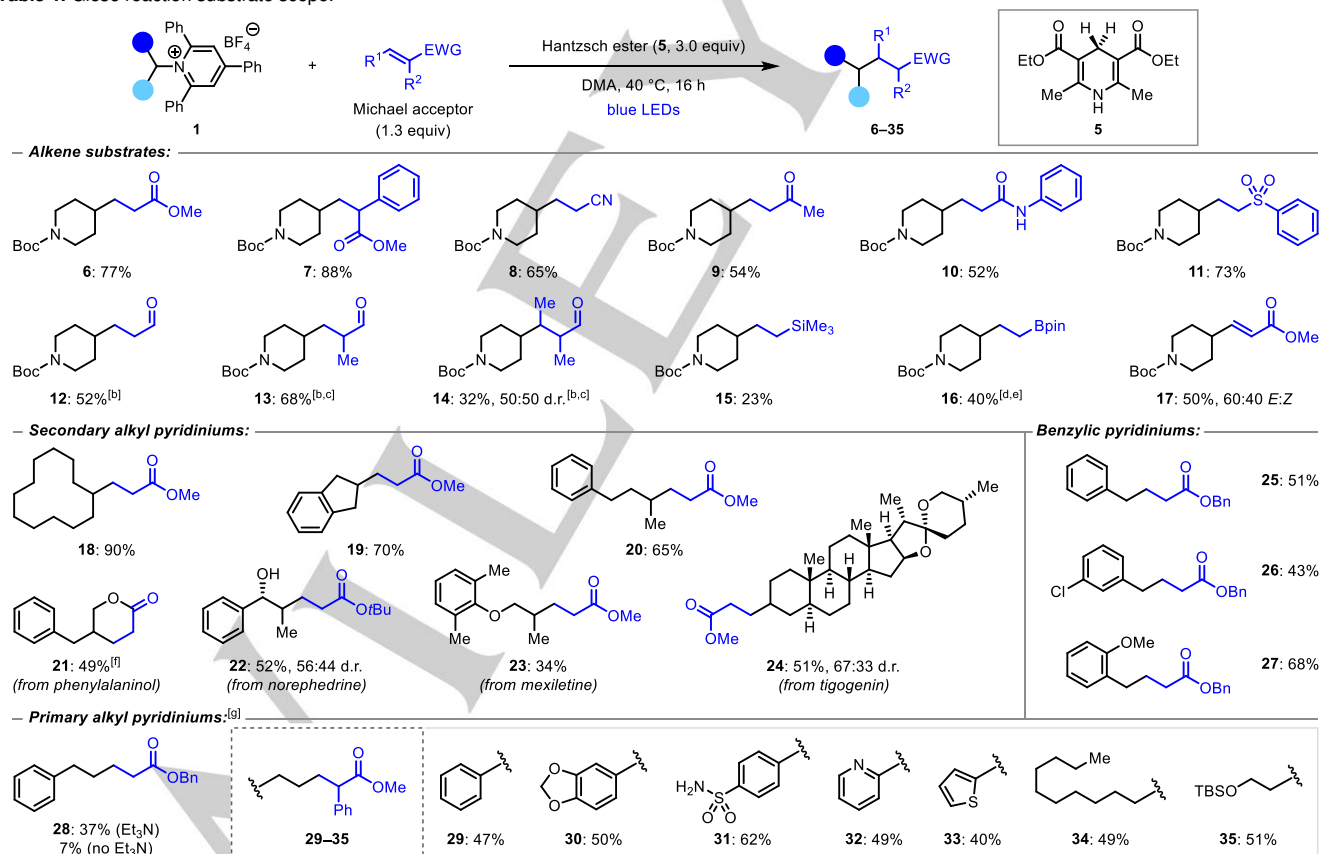
These optimized conditions were subsequently applied to a broad range of Michael acceptors (Table 1). Giese products from reactions with substituted acrylates (**7**), acrylonitrile (**8**), methyl vinyl ketone (**9**), *N*-phenylacrylamide (**10**), and phenyl vinyl sulfone (**11**) were formed in good to excellent yields. Aldehydes were tolerated (**12–14**), although the substituted enals methacrolein (**13**) and tiglic aldehyde (**14**) required higher temperatures for successful reaction. Interestingly, vinyl silanes

and boronic esters were also suitable substrates, providing products **15** and **16**, respectively, albeit in low yield. Finally, methyl propiolate underwent the Giese reaction to give alkene product **17** as a mixture of *E* and *Z* isomers.

With respect to the pyridinium salts, a variety of cyclic (**18** and **19**) and acyclic (**20**) secondary alkyl substrates reacted efficiently. The Giese product from a  $\gamma$ -amino alcohol-derived pyridinium could be cyclized by treatment with acid to generate lactone **21**. Alternatively, *t*-butyl acrylate could be used in place of methyl acrylate to inhibit lactonization, allowing isolation of norephedrine-derived alcohol **22**. Pharmaceutical and natural product derivatives were also readily accessed, as exemplified by the formation of product **23**, from the anti-arrhythmic drug mexiletine, and **24**, from the steroid tigogenin.

While primary benzylic pyridiniums yielded products **25–27** in good yields, primary non-benzylic substrates failed to undergo the deaminative Giese reaction. However, we found that adding  $\text{Et}_3\text{N}$  to the reaction mixture and increasing the reaction temperature to  $60 \text{ }^\circ\text{C}$  had a dramatic effect on the outcome of the reaction and enabled the isolation of adduct **28**, albeit in low yield. Switching from benzyl acrylate to the more activated alkene

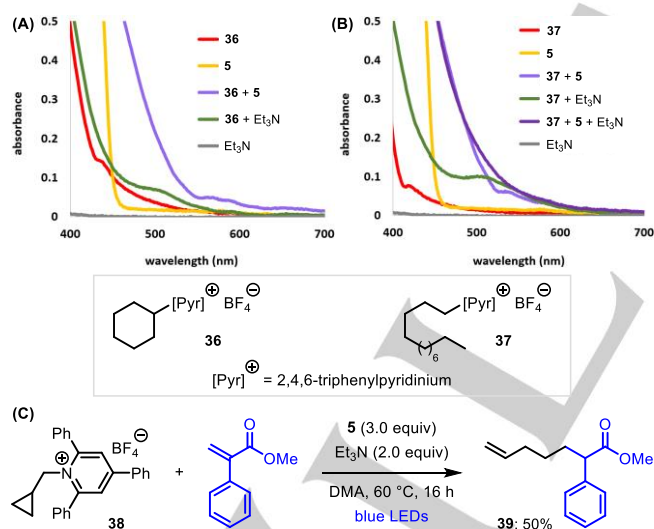
**Table 1.** Giese reaction substrate scope.<sup>[a]</sup>



[a] General conditions: Pyridinium (0.2 mmol, 1.0 equiv), Michael acceptor (1.3 equiv) and **5** (3.0 equiv) in DMA (0.5 M) at  $40 \text{ }^\circ\text{C}$  for 16 h. Yields are of isolated products after flash column chromatography. [b] Isolated as the alcohol after reduction with  $\text{NaBH}_4$ . [c] Reaction performed at  $60 \text{ }^\circ\text{C}$  for 40 h. [d] Isolated as the alcohol after oxidation with  $\text{NaBO}_3$ . [e] Using 1.8 equiv of vinylboronic acid pinacol ester. [f] Lactonization was promoted by treatment with Amberlyst®. [g] Reactions performed at  $60 \text{ }^\circ\text{C}$  in DMA (0.25 M) with the addition of  $\text{Et}_3\text{N}$  (3.0 equiv). DMA = *N,N*-dimethylacetamide. TBS = *tert*-butyldimethylsilyl.

methyl 2-phenylacrylate provided further improvements and enabled isolation of product **29** in 47% yield. Despite the yield being moderate, this result is notable as it is a rare example of a photoinduced Giese reaction of a non-stabilized primary alkyl radical under mild and catalyst-free conditions. With these new conditions, a range of non-benzylic primary alkyl pyridiniums reacted to give the Giese products (**29–35**) in moderate to good yields. Furthermore, the functional group tolerance of the methodology was highlighted by generating products bearing primary sulphonamide (**31**), pyridine (**32**), thiophene (**33**), and silyl ether (**35**) moieties.

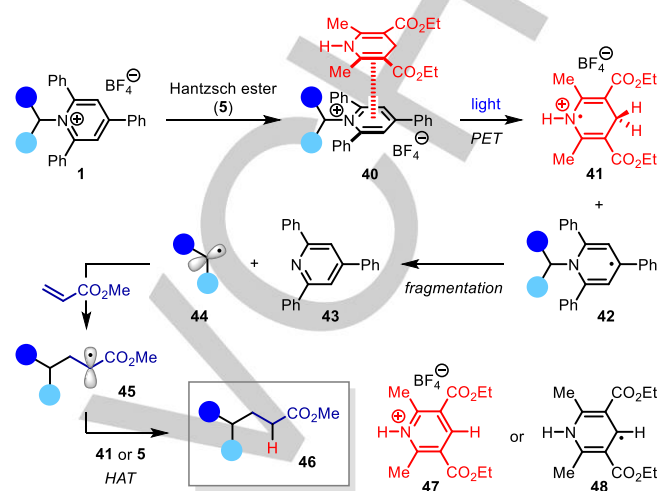
To shed light on the mechanism of this catalyst-free Giese reaction, we analyzed the reaction components by UV/Vis absorption spectroscopy. DMA solutions of secondary alkyl pyridinium **36** and Hantzsch ester (**5**) were both found to absorb in the visible region (>400 nm) (Figure 1A). However, a mixture of **36** and **5** displayed a significant red-shift in absorbance, confirming formation of the postulated EDA complex. A similar shift was observed with a mixture of primary alkyl pyridinium **37** and **5** (Figure 1B). Interestingly, a mixture of **37**, **5** and Et<sub>3</sub>N showed a further bathochromic shift, suggesting the formation of a ternary EDA complex, which could contribute to the enhanced reactivity observed with primary alkyl pyridiniums upon addition of Et<sub>3</sub>N. The formation of alkyl radical intermediates was confirmed by a radical clock experiment with cyclopropylmethyl pyridinium **38**, during which ring-opening occurred to give alkene **39** as the only observable product (Figure 1C).



**Figure 1.** Mechanistic studies. (A) Spectrophotometry of pyridinium **36**. (B) Spectrophotometry of pyridinium **37**. (C) Radical clock experiment.

These results suggest a mechanism comprised of initial formation of an EDA complex **40** between the electron-deficient pyridinium **1** and electron-rich Hantzsch ester (**5**) (Figure 2). Subsequent PET leads to dihydropyridine radical cation **41** and radical **42**, the latter of which fragments to triphenylpyridine **43** and alkyl radical **44**. Addition of **44** to methyl acrylate generates radical **45**, which undergoes hydrogen atom transfer (HAT) with dihydropyridine radical cation **41** (BDFE = 31 kcal mol<sup>-1</sup>)<sup>[19]</sup> or **5**

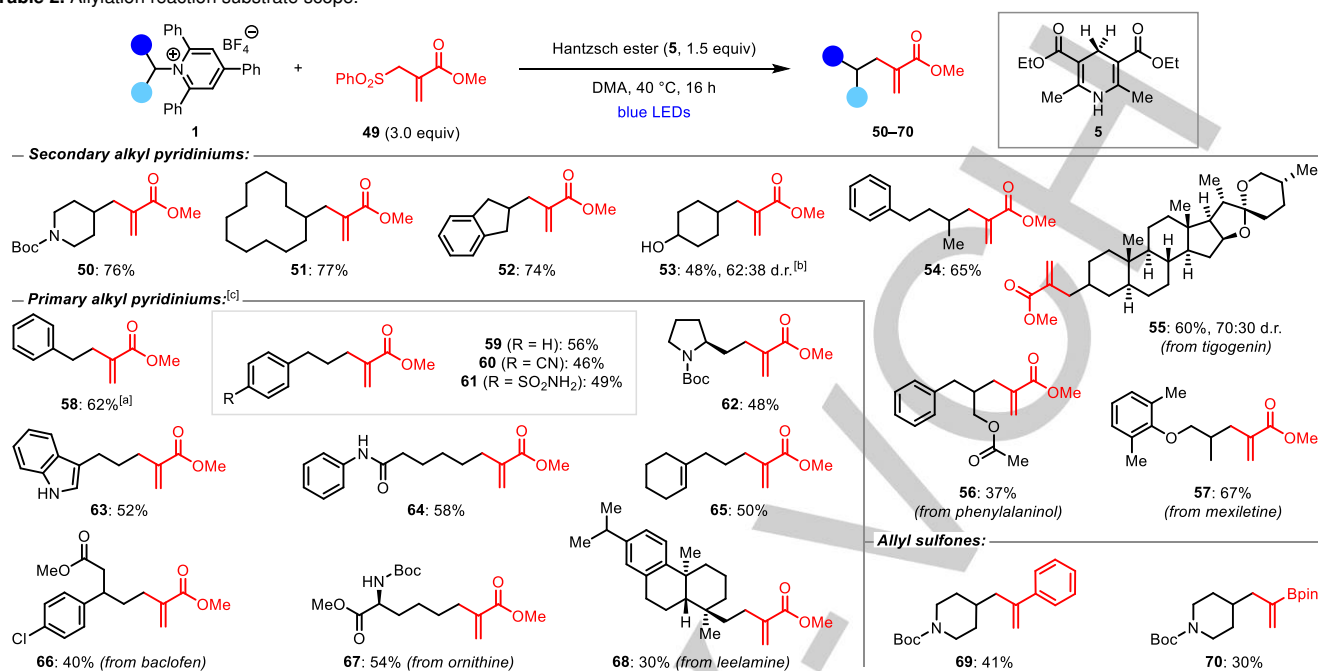
(BDFE = 69 kcal mol<sup>-1</sup>)<sup>[19]</sup> to form Giese product **46** (BDFE ≈ 96 kcal mol<sup>-1</sup>)<sup>[20]</sup> and pyridinium **47** or dihydropyridine radical **48**, respectively.<sup>[21]</sup>



**Figure 2.** Proposed mechanism.

Encouraged by the results of the Giese reaction, we proceeded to investigate other catalyst-free transformations. Pleasingly, with only slight modification to the reaction conditions,<sup>[18]</sup> allylation reactions with allyl sulfone **49** were also found to be efficient (Table 2).<sup>[14c]</sup> A range of secondary alkyl pyridiniums underwent the catalyst-free deaminative allylation to give products **50–57** in moderate to good yields. As with the Giese reaction, although benzylic pyridiniums yielded the allylation product (**58**) under these conditions, primary alkyl pyridiniums (**59–68**) required the addition of Et<sub>3</sub>N for successful reaction. The allylation reaction was found to tolerate a diverse range of functional groups, including alcohols (**53**), nitriles (**60**), sulphonamides (**61**), unprotected indoles (**63**), olefins (**65**), and secondary carbamates (**67**), and was also applied to various pharmaceuticals (**57** and **66**) and natural product derivatives (**55**, **56**, **67** and **68**). Furthermore, the use of other allyl sulfone reagents enabled the preparation of styrene derivative **69** and alkenylboronic ester **70**.

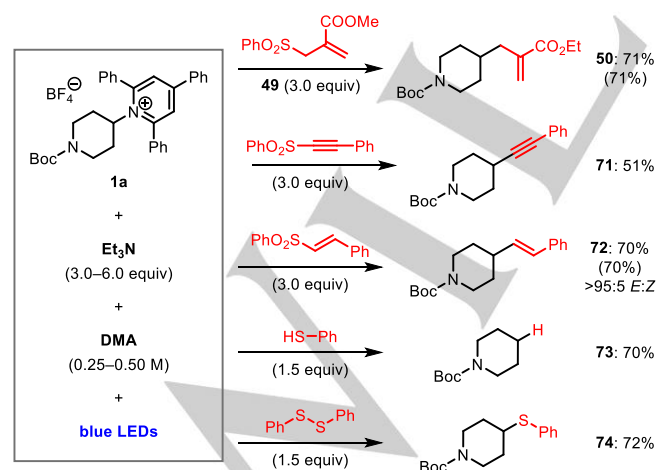
During our UV/Vis absorbance studies of pyridinium **36** we found that it also forms an EDA complex with Et<sub>3</sub>N (Figure 1A). Thus, we were curious as to whether these photoinduced reactions could be performed with Et<sub>3</sub>N in place of Hantzsch ester. While the Giese reaction proceeded with low yield, the allylation reaction proceeded smoothly to generate **50** in 71% when using 6.0 equiv of Et<sub>3</sub>N in place of Hantzsch ester (Scheme 2).<sup>[18]</sup> An identical result was also obtained when Et<sub>3</sub>N was replaced by *i*Pr<sub>2</sub>NEt. This result is intriguing given that these conditions are very similar to the photoredox-catalyzed conditions recently reported by Liu and co-workers, which differ only by the use of an iridium photocatalyst.<sup>[14c]</sup> We also investigated other addition–elimination reactions with unsaturated sulfone reagents and found that alkylation and vinylation reactions also proceeded under our catalyst-free conditions, generating alkyne **71** and alkene **72**

**Table 2.** Allylation reaction substrate scope.<sup>[a]</sup>

[a] General conditions: Pyridinium (1.0 equiv), allyl sulfone (3.0 equiv) and **5** (1.5 equiv) in DMA (0.4 M) at 40 °C for 16 h. Yields are of isolated products after flash column chromatography. [b] Isolated after acetyl protection of the alcohol. [c] Reactions performed at 60 °C with **5** (2.5 equiv) and Et<sub>3</sub>N (3.0 equiv).

in good yields. Again, these conditions are similar to previously reported photoredox-catalyzed protocols by Gryko and co-workers but proceed efficiently in the absence of a photocatalyst.<sup>[14b]</sup> Finally, we found that by replacing the unsaturated sulfones with other sulfur-based reagents, under otherwise identical conditions, high yielding hydrodeamination and deaminative thioetherification reactions were also possible, providing good yields of *N*-Boc-piperidine **73** and thioether **74**, respectively.

In conclusion, we have described the development of a general catalyst-free deaminative protocol for the generation of non-stabilized alkyl radicals, proceeding via visible-light photoexcitation of EDA complexes of *N*-alkylpyridinium salts. The radicals were shown to undergo a range of transformations, including Giese, allylation, vinylation, alkynylation, HAT, and thioetherification reactions. The mild conditions, high functional group tolerance and ease of synthesis of the pyridinium substrates make this a useful catalyst-free approach to alkyl radical formation.

**Scheme 2.** Deaminative transformations promoted by Et<sub>3</sub>N. Yields in parentheses are for reactions performed using *i*Pr<sub>2</sub>NET in place of Et<sub>3</sub>N.

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**Keywords:** Deamination • Photochemistry • Radical Reactions • Electron Donor–Acceptor Complexes • Giese Reactions

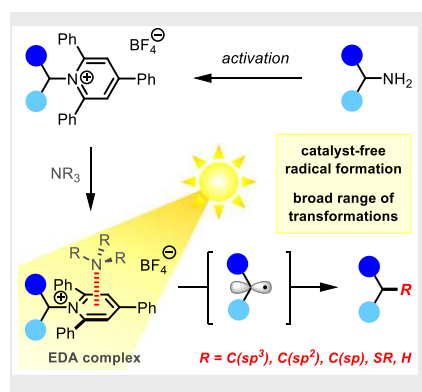
[1] a) S. Protti, M. Fagnoni, *Photochem. Photobiol. Sci.* **2009**, *8*, 1499; b) T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.* **2010**, *2*, 527; c) L. Buzzetti, G. E. M. Crisenza, P. Melchiorre, *Angew. Chem. Int. Ed.* **2018**, DOI: 10.1002/anie.201809984.

[2] a) *Visible Light Photocatalysis in Organic Chemistry* (Eds.: C. R. J. Stephenson, T. P. Yoon, D. W. C. MacMillan), Wiley-VCH, Weinheim,

- 2018; b) J. W. Tucker, C. R. J. Stephenson, *J. Org. Chem.* **2012**, *77*, 1617; c) M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898; d) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* **2016**, *116*, 10035; e) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075.
- [3] a) N. Hoffmann, *Chem. Rev.* **2008**, *108*, 1052; b) T. Bach, J. P. Hehn, *Angew. Chem. Int. Ed.* **2011**, *50*, 1000; *Angew. Chem.* **2011**, *123*, 1032.
- [4] M. Silvi, P. Melchiorre, *Nature* **2018**, *554*, 41.
- [5] For selected examples, see: a) G. Cecere, C. M. König, J. L. Alleva, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2013**, *135*, 11521; b) M. Silvi, E. Arceo, I. D. Jurberg, C. Cassani, P. Melchiorre, *J. Am. Chem. Soc.* **2015**, *137*, 6120; c) M. Silvi, C. Sandford, V. K. Aggarwal, *J. Am. Chem. Soc.* **2017**, *139*, 5736; d) A. Bahamonde, P. Melchiorre, *J. Am. Chem. Soc.* **2016**, *138*, 8019; e) G. Filippini, M. Silvi, P. Melchiorre, *Angew. Chem. Int. Ed.* **2017**, *56*, 4447; *Angew. Chem.* **2017**, *129*, 4518; f) M. Silvi, C. Verrier, Y. P. Rey, L. Buzzetti, P. Melchiorre, *Nat. Chem.* **2017**, *9*, 868; g) P. Bonilla, Y. P. Rey, C. M. Holden, P. Melchiorre, *Angew. Chem. Int. Ed.* **2018**, *57*, 12819; *Angew. Chem.* **2018**, *130*, 13001; h) G. Goti, B. Bieszczad, A. Vega-Peñaloza, P. Melchiorre, *Angew. Chem. Int. Ed.* **2019**, *58*, 1213; *Angew. Chem.* **2019**, *131*, 1226.
- [6] a) S. V. Rosokha, J. K. Kochi, *Acc. Chem. Res.* **2008**, *41*, 641; b) C. G. S. Lima, T. de M. Lima, M. Duarte, I. D. Jurberg, M. W. Paixão, *ACS Catal.* **2016**, *6*, 1389; c) A. Postigo, *Eur. J. Org. Chem.* **2018**, *2018*, 6391.
- [7] For selected examples of perfluoroalkyl radical generation, see: a) P. V. Pham, D. A. Nagib, D. W. C. MacMillan, *Angew. Chem. Int. Ed.* **2011**, *50*, 6119; *Angew. Chem.* **2011**, *123*, 6243; b) M. Nappi, G. Bergonzini, P. Melchiorre, *Angew. Chem. Int. Ed.* **2014**, *53*, 4921; *Angew. Chem.* **2014**, *126*, 5021; c) Ł. Woźniak, J. J. Murphy, P. Melchiorre, *J. Am. Chem. Soc.* **2015**, *137*, 5678; d) J. W. Beatty, J. J. Douglas, R. Miller, R. C. McAtee, K. P. Cole, C. R. J. Stephenson, *Chem* **2016**, *1*, 456; e) M. L. Spell, K. Deveaux, C. G. Bresnahan, B. L. Bernard, W. Sheffield, R. Kumar, J. R. Ragains, *Angew. Chem. Int. Ed.* **2016**, *55*, 6515; *Angew. Chem.* **2016**, *128*, 6625; f) Y. Cheng, S. Yu, *Org. Lett.* **2016**, *18*, 2962; g) Y.-Y. Liu, X.-Y. Yu, J.-R. Chen, M.-M. Qiao, X. Qi, D.-Q. Shi, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2017**, *56*, 9527; *Angew. Chem.* **2017**, *129*, 9655; h) H.-Y. Tu, S. Zhu, F.-L. Qing, L. Chu, *Chem. Commun.* **2018**, *54*, 12710; i) Q. Guo, M. Wang, H. Liu, R. Wang, Z. Xu, *Angew. Chem. Int. Ed.* **2018**, *57*, 4747; *Angew. Chem.* **2018**, *130*, 4837.
- [8] For stabilized alkyl radical generation, see: a) E. Arceo, I. D. Jurberg, A. Álvarez-Fernández, P. Melchiorre, *Nat. Chem.* **2013**, *5*, 750; b) E. Arceo, A. Bahamonde, G. Bergonzini, P. Melchiorre, *Chem. Sci.* **2014**, *5*, 2438; c) S. R. Kandukuri, A. Bahamonde, I. Chatterjee, I. D. Jurberg, E. C. Escudero-Adán, P. Melchiorre, *Angew. Chem. Int. Ed.* **2015**, *54*, 1485; *Angew. Chem.* **2015**, *127*, 1505; d) Z.-Y. Cao, T. Ghosh, P. Melchiorre, *Nat. Commun.* **2018**, *9*, 3274; e) C.-W. Hsu, H. Sundén, *Org. Lett.* **2018**, *20*, 2051.
- [9] For aryl radical generation, see: a) M. A. Fox, J. Younathan, G. E. Fryxell, *J. Org. Chem.* **1983**, *48*, 3109; b) M. Tobisu, T. Furukawa, N. Chatani, *Chem. Lett.* **2013**, *42*, 1203; c) L. Marzo, S. Wang, B. König, *Org. Lett.* **2017**, *19*, 5976; d) B. Liu, C.-H. Lim, G. M. Miyake, *J. Am. Chem. Soc.* **2017**, *139*, 13616.
- [10] For heteroatom-centered radical generation, see: a) J. Davies, S. G. Booth, S. Essafi, R. A. W. Dryfe, D. Leonori, *Angew. Chem. Int. Ed.* **2015**, *54*, 14017; *Angew. Chem.* **2015**, *127*, 14223; b) D. F. Reina, E. M. Dauncey, S. P. Morcillo, T. D. Svejstrup, M. V. Popescu, J. J. Douglas, N. S. Sheikh, D. Leonori, *Eur. J. Org. Chem.* **2016**, *2017*, 2108; c) J. Zhang, Y. Li, R. Xu, Y. Chen, *Angew. Chem. Int. Ed.* **2017**, *56*, 12619; *Angew. Chem.* **2017**, *129*, 12793; d) Y. Li, J. Zhang, D. Li, Y. Chen, *Org. Lett.* **2018**, *20*, 3296.
- [11] L. Buzzetti, A. Prieto, S. R. Roy, P. Melchiorre, *Angew. Chem. Int. Ed.* **2017**, *56*, 15039; *Angew. Chem.* **2017**, *129*, 15235.
- [12] J. B. Bapat, R. J. Blade, A. J. Boulton, J. Epszstajn, A. R. Katritzky, J. Lewis, P. Molina-Buendia, P.-L. Nie, C. A. Ramsden, *Tetrahedron Lett.* **1976**, *17*, 2691.
- [13] For nickel-catalyzed reactions, see: a) C. H. Basch, J. Liao, J. Xu, J. J. Piane, M. P. Watson, *J. Am. Chem. Soc.* **2017**, *139*, 5313; b) J. Liao, W. Guan, B. P. Boscoe, J. W. Tucker, J. W. Tomlin, M. R. Garnsey, M. P. Watson, *Org. Lett.* **2018**, *20*, 3030; c) W. Guan, J. Liao, M. P. Watson, *Synthesis* **2018**, *50*, 3231.
- [14] For photoredox-catalyzed reactions, see: a) F. J. R. Klauck, M. J. James, F. Glorius, *Angew. Chem. Int. Ed.* **2017**, *56*, 12336; *Angew. Chem.* **2017**, *129*, 12505; b) M. Ociepa, J. Turkowska, D. Gryko, *ACS Catal.* **2018**, *8*, 11362; c) M.-M. Zhang, F. Liu, *Org. Chem. Front.* **2018**, *5*, 3443; d) F. J. R. Klauck, H. Yoon, M. J. James, M. Lautens, F. Glorius, *ACS Catal.* **2019**, *9*, 236.
- [15] a) J. Wu, L. He, A. Noble, V. K. Aggarwal, *J. Am. Chem. Soc.* **2018**, *140*, 10700; b) J. Hu, G. Wang, S. Li, Z. Shi, *Angew. Chem. Int. Ed.* **2018**, *57*, 15227; *Angew. Chem.* **2018**, *130*, 15447; c) F. Sandfort, F. Strieth-Kalthoff, F. J. R. Klauck, M. J. James, F. Glorius, *Chem. Eur. J.* **2018**, *24*, 17210; For a mechanistically related decarboxylative borylation, see: d) A. Fawcett, J. Pradeilles, Y. Wang, T. Mutsuga, E. L. Myers, V. K. Aggarwal, *Science* **2017**, *357*, 283.
- [16] For EDA complexes of Katritzky pyridiniums, see: a) A. R. Katritzky, G. Z. de Ville, R. C. Patel, *Tetrahedron Lett.* **1980**, *21*, 1723; b) A. R. Katritzky, G. De Ville, R. C. Patel, *Tetrahedron* **1981**, *37*, 25.
- [17] a) K. Okada, K. Okamoto, N. Morita, K. Okubo, M. Oda, *J. Am. Chem. Soc.* **1991**, *113*, 9401; b) G. L. Lackner, K. W. Quasdorf, G. Pratsch, L. E. Overman, *J. Org. Chem.* **2015**, *80*, 6012; c) G. Pratsch, G. L. Lackner, L. E. Overman, *J. Org. Chem.* **2015**, *80*, 6025.
- [18] See Supporting Information for details.
- [19] X.-Q. Zhu, H.-R. Li, Q. Li, T. Ai, J.-Y. Lu, Y. Yang, J.-P. Cheng, *Chem. Eur. J.* **2003**, *9*, 871.
- [20] J. J. Brocks, H.-D. Beckhaus, A. L. J. Beckwith, C. Rüchardt, *J. Org. Chem.* **1998**, *63*, 1935.
- [21] See Supporting Information for further mechanistic discussions and evidence for the formation of radicals **42** and **48**.

## COMMUNICATION

Electron donor–acceptor complexes between pyridinium-activated primary amines and Hantzsch ester or triethylamine undergo catalyst-free photoinduced single-electron transfer with visible-light. Fragmentation leads to alkyl radicals that could be intercepted with a variety of acceptors. This deaminative radical generation was applied to catalyst-free Giese, allylation, vinylation, alkynylation, thioetherification, and hydrodeamination reactions.



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