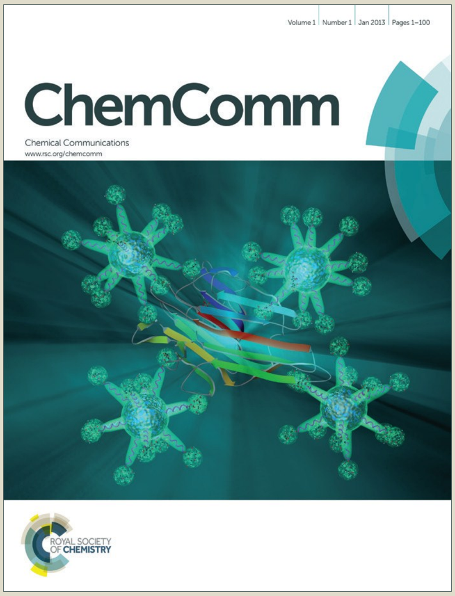
ChemComm

This article can be cited before page numbers have been issued, to do this please use: J. Dai, W. Zhang, Y. Su, Y. Sun, J. Xu, Y. Feng and H. Xu, *Chem. Commun.*, 2016, DOI: 10.1039/C6CC01530A.



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY
View Article Online
DOI: 10.1039/C6CC01530A

ChemComm

COMMUNICATION

Deboronative cyanation of potassium alkyltrifluoroborates *via* photoredox catalysis†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Jian-Jun Dai,[a] Wen-Man Zhang,[a] Yong-Jin Shu,[b] Yu-Yang Sun,[a] Jun Xu,[a] Yi-Si Feng,[b] and Hua-Jian Xu*[a,b,c]

A photoredox catalytic method was developed for the direct cyanation of alkyltrifluoroborates. This reaction provides a new and useful transformation of the easily available alkyltrifluoroborates. The photocatalytic reaction can tolerate a variety of functional groups with mild reaction conditions. Mechanistic investigations are consistent with the present reaction following a radical pathway.

Alkylboron reagents are powerful and useful building blocks in organic synthesis.[1] By comparison with other C(sp^3) organometallics (e.g., alkylmagnesium, alkylzinc, alkytin, and alkylindium reagents), alkylboron reagents are easy to purify, less toxic, and typically air and moisture stable.[2] Numerous examples of the transformations of alkylboron reagents into other functional groups have been reported, including -OH,[3] halides (-F, -Cl, and -I),[4] -CF_3,[5] -SCF_3,[6] and -NH_2.[7]

Alternatively, visible light-induced single-electron transfer (SET) by photocatalysts has received much attention and has been demonstrated as a key step in organic synthesis.[8] In this context, effort has been made to develop new transformations of alkyltrifluoroborates (alkyl-BF_3K) by means of photocatalysts via the SET processes. In a pioneering study, Akita and Koike demonstrated the generation of alkyl radicals from alkyltrifluoroborates promoted by photocatalysts to form C–O and C–C bonds.[9] Chen and coworkers described the photocatalytic alkynylation and alkenylation reactions of alkyltrifluoroborates.[10] Importantly, Molander et al. further achieved the arylation of alkyltrifluoroborates with the combination of an iridium photocatalyst and a nickel catalyst.[11] However, to our knowledge, there has been no report on *the direct photocatalytic cyanation reactions of alkyltrifluoroborates to alkyl nitriles*. Considering that the alkyltrifluoroborates have been widely used as alkyl precursors,[12] we envisioned that the photocatalytic deboronative cyanation of alkyltrifluoroborates could result in facile formation of alkyl nitriles (Fig. 1). The significance of the present study is twofold: (1) the reaction provides the first example of the transformation from alkyltrifluoroborates to alkyl nitriles by photocatalysts; and (2) nitrile-containing molecules not only constitute many medicinally and biologically important compounds, but also can be utilized as synthetic intermediates for generating other useful functional groups such as carboxylic acids, esters, amines, and amides.[13] Consequently, considerable attention has been paid to the synthesis of such compounds.[14] Our new reaction offers a general, convenient, and efficient protocol for rapid access to primary (1º), secondary (2º), and even tertiary (3º) alkyl nitriles from easily prepared alkyltrifluoroborates using the readily available cyanation reagent *p*-toluenesulfonyl cyanide (TsCN).[15] It further confirms the good functional group tolerance, broad substrate scope, and mild conditions of the reaction.

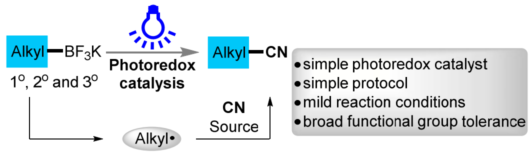


Fig. 1 Deboronative cyanation by photoredox catalysis.

We commenced our study by examining the photocatalytic cyanation of alkyltrifluoroborate **1a** with various CN sources in the presence of 2 mol % photoredox catalyst $[Ru(bpy)_3](PF_6)_2$ (**I**) in CH_2Cl_2/H_2O under visible-light irradiation from blue LEDs (λ_{max} = 425 ± 15 nm) for 24 h (Table 1). Although the desired product 3-phenylpropanenitrile **3a** could be detected with the use of a hypervalent iodine CN reagent **2a**, the yield was very low (11% yield for entry 1).[16] It was also found that a distinct amount of oxidative by-product (i.e., 2-phenylethan-1-ol) could be detected by GC-MS analysis, which was tentatively attributed to the oxidative effect of the hypervalent iodine reagent (for details see ESI† Fig. S1). To suppress the formation of this by-product, the reaction was conducted using a combination of a nonoxidative CN reagent (TsCN, **2b**) and different oxidants. Indeed, reactions conducted

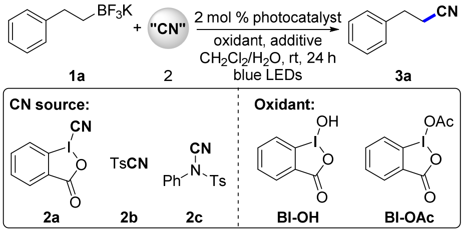
---

[a] *School of Medical Engineering, Hefei University of Technology, Hefei 230009 China. E-mail: hjxu@hfut.edu.cn*
[b] *School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009 China.*
[c] *Key Laboratory of Advanced Functional Materials and Devices of Anhui Province, Hefei 230009 China.*

†Electronic Supplementary Information (ESI) available: Experimental procedures, NMR spectra. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C6CC01530A

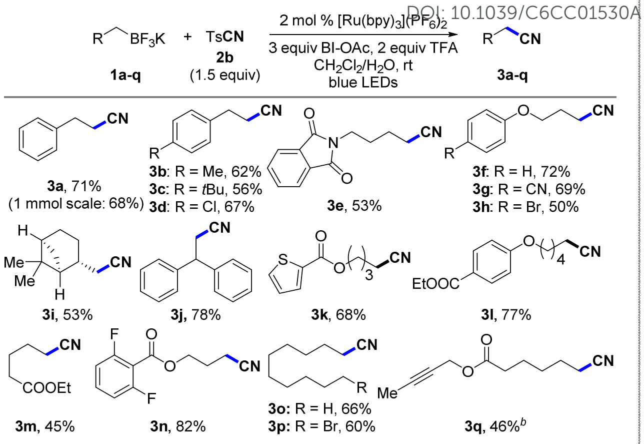
Table 1 Optimization of the reaction conditions[a]



Entry	Photocatalyst	"CN" source	Oxidant	Additive	Yield (%)[b]
1	$[Ru(bpy)_3](PF_6)_2$	**2a**	—	—	11
2	$[Ru(bpy)_3](PF_6)_2$	**2b**	$K_2S_2O_8$	—	14
3	$[Ru(bpy)_3](PF_6)_2$	**2b**	$PhI(OAc)_2$	—	trace
4	$[Ru(bpy)_3](PF_6)_2$	**2b**	PhIO	—	17
5	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OH	—	29
6	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	—	36
7	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	Na_2CO_3	5
8	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	$NaHCO_3$	6
9	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	DBU	trace
10	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	NaOAc	37
11	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	Na_2HPO_4	22
12	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	HOAc	57
13	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	H_3PO_4	65
14	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	TFA	70
15[c]	**$[Ru(bpy)_3](PF_6)_2$**	**2b**	**BI-OAc**	**TFA**	**75(71)**
16	*fac*-$Ir(ppy)_3$	**2b**	BI-OAc	TFA	71
17[c, d]	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	TFA	trace
18[c, e]	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	TFA	30
19[c]	$[Ru(bpy)_3](PF_6)_2$	**2c**	BI-OAc	TFA	15
20[c, f]	$[Ru(bpy)_3](PF_6)_2$	**2b**	BI-OAc	TFA	trace
21	—	**2b**	BI-OAc	TFA	trace

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2** (0.3 mmol, 1.5 equiv), photocatalyst (0.004 mmol, 2 mol %), oxidant (0.4 mmol, 2 equiv), additive (2 equiv), CH_2Cl_2/H_2O (2 mL, v:v = 1:1), under an atmosphere of air, 24 h at room temperature with 2 × 9 W blue LEDs irradiation, unless otherwise stated. [b] GC yields with 2-phenylacetonitrile as an internal standard added after the reaction, isolated yield in parentheses. [c] 3 equiv BI-OAc was used. [d] $PhCH_2CH_2B(OH)_2$ was used as the substrate. [e] $PhCH_2CH_2Bpin$ was used as the substrate. [f] The reaction was performed in the dark.

Table 2 Deboronative cyanation of primary alkyltrifluoroborates[a]



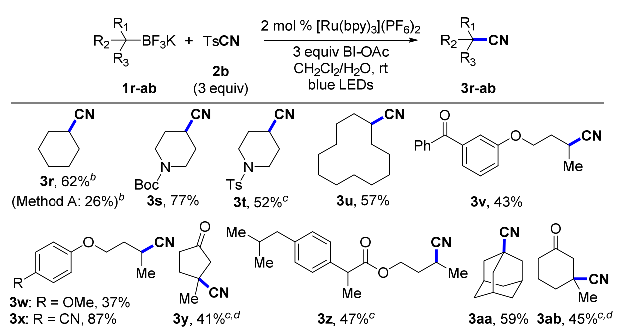
[a] Method A: The reactions were conducted for 24 h on a 0.2 mmol scale. For details see ESI†. [b] The reaction time was 48 h.

with strong oxidants such as $K_2S_2O_8$, $PhI(OAc)_2$ provided **3a** in low yields (entries 2 and 3). Pleasingly, the reaction was remarkably increased by employing mild oxidants such as iodosobenzene (PhIO), 1-hydroxy-1,2-benziodoxol-3-(1H)-one (BI-OH) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (BI-OAc) (entries 4-6). To improve the reaction, basic and acidic additives were then examined intensively. Unfortunately, bases (e.g., Na_2CO_3, $NaHCO_3$, DBU, NaOAc, and Na_2HPO_4) were found to be ineffective in promoting the reaction (entries 7–11). Contrary to these results, the reaction with acidic additives including HOAc, H_3PO_4, and TFA gave **3a** in 57%–70% yield (entries 12–14). While the role of TFA as an additive is not clear at this point, it may help to protonate the carboxylate anion formed from BI-OAc during the reaction process, which may competitively quench excited photoredox catalyst with 1º alkyl-BF_3K. The observed effect of TFA on increasing the yield of **3a** maybe ascribed to protonate carboxylate anion ($E_{1/2}$ = + 1.21 V vs. saturated calomel electrode (SCE) in CH_3CN for CH_3COO^-, $E_{1/2}$ = + 2.4 V vs. SCE for CF_3COO^-) formed during the reaction process, thus to prevent its competitive quenching of excited photoredox catalyst with 1º alkyl-BF_3K.[17] To improve the yield further, we increased the amount of oxidant to three equivalents and obtained a 71% isolated yield of **3a** (entry 15). Note that the Ir(III) photocatalyst $Ir(ppy)_3$ also promoted the present reaction, providing the product **3a** in a reasonable 71% yield (entry 16). Interestingly, when boronic acid and pinacol boronate were used instead of the trifluoroborate, only a trace or 30% yield of **3a** was detected, respectively (entries 17 and 18). We also tested a popular cyanation reagent N-cyano-N-phenyl-*p*-toluenesulfonamide (NCTS, **2c**),[18] but only a 15% yield of **3a** could be obtained (entry 19). Finally, only trace amounts of **3a** were detected from the reaction either in the dark or in the absence of the photocatalyst (entries 20 and 21). These control experiments confirm the role of photoexcited species derived from the photocatalyst in the reaction.

With the optimized conditions in hand, we investigated the scope of the photocatalytic deboronative cyanation with diverse alkyltrifluoroborates (Table 2). We found that a variety of 1º alkyltrifluoroborates with different chain lengths could be successfully transformed to the desired product in modest to good yields (45%–82%). The reaction could well tolerate a wide range of synthetic useful functional groups, including ether (**3f, 3g**, **3l**), amide (**3e**), cyano (**3g**), ester (**3k–n**, **3q**, **3r**), and even alkyne (**3q**). More importantly, not only aryl halides (**3d**, **3h**, **3n**) but also alkyl bromides (**3p**) could undergo the cyanation reaction. This feature could be useful for further transformation using crosscoupling techniques. It is notable that the substrates containing heterocyclic groups such as thiophene (**3k**) could also be used in the reaction. To demonstrate the further synthetic utility of the present reaction, we performed a reaction on a 1 mmol scale with **1a** and the corresponding product **3a** was isolated in 68% yield.

The cyanation reaction conditions indicated above were extended to 2º and 3º alkyltrifluoroborates (Method A). However, the yield of the cyanation product **3r** was only 26%.

Table 3 Deboronative cyanation of secondary and tertiary alkyltrifluoroborates[a]



[a] Method B: The reactions were conducted for 24 h on a 0.2 mmol scale. For details see ESI†. [b] GC yield. [c] The reaction time was 48 h. [d] 1 mmol scale.

By increasing the amount of **2b** to three equivalents and without the use of TFA, the yield of **3r** was improved to 62% (Method B; see ESI†).[19] With regard to the scope of this method (Table 3), both cyclic (**3r–u**, **3y**, **3aa**, **3ab**) and acyclic (**3v–x**, **3z**) alkyltrifluoroborates are good substrates. Boc- and Ts-protected piperidine-containing compounds (**3s**, **3t**) could be used in the cyanation reaction. Moreover, functional groups such as ether (**3v–x**), cyano (**3x**), ketone (**3v**, **3y**, **3ab**), and ester (**3z**) could be tolerated in the transformation.

We found that in a competitive reaction between aryl and alkyl trifluoroborates (**4**:**2a** = 1:1), the deboronative cyanation event occurred chemoselectively to deliver the alkyl nitrile product (**3a**) in good yield, whereas only tiny amounts of the aryl nitrile product (**5**) could be detected (Fig. 2). Notably, Beller and coworkers have reported the transformation of aryl boronic acid to the corresponding aryl nitriles using rhodium catalyst.[20] Thus, the present result highlights the complementarity of the two methods for deboronative cyanation.

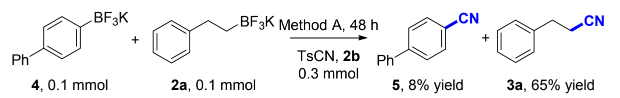
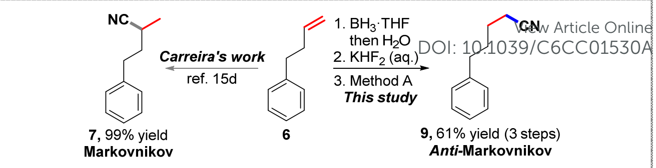


Fig. 2 Competitive reactions between aryl and alkyl trifluoroborates.

Selective functionalization of alkenes has become an important reaction in organic synthesis.[21] Carreira and coworkers presented a very simple yet elegant method for efficient Markovnikov hydrocyanation of alkenes (Fig. 3, left). Note that the combination of alkene hydroboration and our current study is complementary to the work mentioned above. As shown in Figure 3, *anti*-Markovnikov hydrocyanation of alkene could be smoothly realized in three steps (Fig. 3, right).[22] Treatment of alkene (**6**) with BH_3 at 0 °C followed by hydrolysis and addition of an aqueous solution of KHF_2 leads to the corresponding alkyltrifluoroborate **8**. A subsequent photocatalyzed deboronative cyanation reaction delivered the final product **9** in 61% yield.

To understand the mechanism of the photocatalytic reaction, we conducted free-radical trapping experiments. We conducted a radical trapping experiment using 2,2,6,6-tetramethylpiperidinoxyl (TEMPO) as a radical scavenger. The deboronative cyanation reaction was completely halted. Meanwhile, the alkyl-TEMPO adduct **10** could be isolated in 19% yield (see ESI†). In addition, the model reaction mixture, irradiated in the presence of a radical trapping agent *N*-benzylidene-*tert*-butylamine *N*-oxide (PBN), exhibited the ESR spectrum character of an alkyl spin adduct, and further, no cyanation product **3a** was detected in a GC-MS analysis (see ESI†). These observations indicated that the reaction should proceed with the intermediacy of an alkyl radical.



View Article Online
DOI: 10.1039/C6CC01530A

Fig. 3 Regioselective hydrocyanation of the alkene.

To summarize, we have developed an example of a photocatalytic deboronative cyanation of alkyltrifluoroborates.[23] This transformation not only extends the concept of the photocatalytic organic reactions, but also provides a new alternative access to 1º, 2º, and 3º alkyl nitriles. The present reaction can tolerate a number of synthetically relevant functional groups, including esters, amides, ethers, cyano, ketones, alkynes, and halides. The use of a mild oxidant BI-OAc is crucial. Preliminary mechanistic studies suggest that the current reaction involves radical species. Further investigations are ongoing in our laboratory with regard to the new transformations of alkyl boron reagents by photoredox catalysis.

We gratefully acknowledge financial support from the National Natural Science Foundation of China (21472033, 21402036 and 21272050) and the China Postdoctoral Science Foundation (2014M551793, 2015T80645).

Notes and references

1 Reviews: (a) A. C. Frisch and M. Beller, *Angew. Chem., Int. Ed.*, 2005, **44**, 674; (b) A. Rudolph and M. Lautens, *Angew. Chem., Int. Ed.*, 2009, **48**, 2656; (c) R. Jana, T. P. Pathak and M. S. Sigman, *Chem. Rev.*, 2011, **111**, 1417; (d) C.-T. Yang, Z.-Q. Zhang, H. Tajuddin, C.-C. Wu, J. Liang, J.-H. Liu, Y. Fu, M. Czyzewska, P. G. Steel, T. B. Marder and L. Liu, *Angew. Chem., Int. Ed.*, 2012, **51**, 528; (e) D. Leonori and V. K. Aggarwal, *Angew. Chem., Int. Ed.*, 2015, **54**, 1082.

2 *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2011.

3 *Oxidation of Carbon-Boron Bonds Comprehensive Organic Synthesis*, (Eds: A. Pelter and K. Smith) Elsevier, p. 593.

4 (a) C. Sandford, R. Rasappan and V. K. Aggarwal, *J. Am. Chem. Soc.*, 2015, **137**, 10100; (b) Z. Li, Z. Wang, L. Zhu, X. Tan and C. Li, *J. Am. Chem. Soc.*, 2014, **136**, 16439; (c) G. A. Molander and L. N. Cavalcanti, *J. Org. Chem.*, 2011, **76**, 7195.

5 J. Xu, B. Xiao, C.-Q. Xie, D.-F. Luo, L. Liu and Y. Fu, *Angew. Chem., Int. Ed.*, 2012, **51**, 12551.

6 X. Shao, T. Liu, L. Lu and Q. Shen, *Org. Lett.*, 2014, **16**, 4738.

7 (a) R. Larouche-Gauthier, T. G. Elford and V. K. Aggarwal, *J. Am. Chem. Soc.*, 2011, **133**, 16794; (b) S. N. Mlynarski, A. S. Karns and J. P. Morken, *J. Am. Chem. Soc.*, 2012, **134**, 16449.

8 Recent reviews: (a) J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102; (b) J. Xuan and W.-J. Xiao, *Angew. Chem., Int. Ed.*, 2012, **51**, 6828; (c) J. W. Tucker and C. R. J. Stephenson, *J. Org. Chem.*, 2012, **77**, 1617;

View Article Online
DOI: 10.1039/C6CC01550A

(d) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.,* 2013, **113**, 5322; (e) Y. Xi, H. Yi and A. Lei, *Org. Biomol. Chem.,* 2013, **11**, 2387; (f) M. Reckenthäer and A. G. Griesbeck, *Adv. Synth. Catal.,* 2013, **355**, 2727; (g) R. A. Angnes, Z. Li, C. R. D. Correia and G. B. Hammond, *Org. Biomol. Chem.,* 2015, **13**, 9152.

9 (a) Y. Yasu, T. Koike and M. Akita, *Adv. Synth. Catal.,* 2012, **354**, 3414; (b) K. Miyazawa, Y. Yasu, T. Koike and M. Akita, *Chem. Commun.,* 2013, **49**, 7249.

10 (a) H. Huang, G. Zhang, L. Gong, S. Zhang and Y. Chen, *J. Am. Chem. Soc.,* 2014, **136**, 2280; (b) H. Huang, K. Jia and Y. Chen, *Angew. Chem., Int. Ed.,* 2015, **54**, 1881.

11 (a) J. C. Tellis, D. N. Primer and G. A. Molander, *Science*, 2014, **345**, 433; (b) D. N. Primer, I. Karakaya, J. C. Tellis and G. A. Molander, *J. Am. Chem. Soc.,* 2015, **137**, 2195; (c) O. Gutierrez, J. C. Tellis, D. N. Primer, G. A. Molander and M. C. Kozlowski, *J. Am. Chem. Soc.,* 2015, **137**, 4896; (d) I. Karakaya, D. N. Primer and G. A. Molander, *Org. Lett.,* 2015, **17**, 3294; (e) Y. Yamashita, J. C. Tellisa and G. A. Molander, *Proc. Natl. Acad. Sci. U.S.A.,* 2015, **112**, 12026.

12 (a) G. A. Molander, *J. Org. Chem.,* 2015, **80**, 7837; (b) L. Li, S. Zhao, A. Joshi-Pangu, M. Diane and M. R. Biscoe, *J. Am. Chem. Soc.,* 2014, **136**, 14027; (c) S. D. Dreher, P. G. Dormer, D. L. Sandrock and G. A. Molander, *J. Am. Chem. Soc.,* 2008, **130**, 9257; (d) S. D. Dreher, S.-E. Lim, D. L. Sandrock and G. A. Molander, *J. Org. Chem.,* 2009, **74**, 3626, (e) G. A. Molander and S. R. Wisniewski, *J. Am. Chem. Soc.,* 2012, **134**, 16856; (f) P. S. Thuy-Boun, G. Villa, D. Dang, P. Richardson, S. Su and J.-Q. Yu, *J. Am. Chem. Soc.,* 2013, **135**, 17508; (g) G. A. Molander and T. Ito, *Org. Lett.,* 2001, **3**, 393; (h) N. Fleury-Brégeot, M. Presset, F. Beaumard, V. Colombel, D. Oehlrich, F. Rombouts and G. A. Molander, *J. Org. Chem.,* 2012, **77**, 10399; (i) S. R. Neufeldt, C. K. Seigerman and M. S. Sanford, *Org. Lett.,* 2013, **15**, 2302.

13 (a) F. F. Fleming, L. Yao, P. C. Ravikumar, L. Funk and B. C. Shook, *J. Med. Chem.,* 2010, **53**, 7902; (b) *Lead Optimization for Medicinal Chemists: Pharmacokinetic Properties of Functional Groups and Organic Compounds*, (Ed: F. Z. Dörwald) Wiley-VCH: Weinheim, Germany, 2012.

14 For selected examples on the synthesis of alkyl nitriles, see: (a) R. Shang, D.-S. Ji, L. Chu, Y. Fu, L. Liu, *Angew. Chem., Int. Ed.,* 2011, **50**, 4470; (b) W. Yin, C. Wang and Y. Huang, *Org. Lett.,* 2013, **15**, 1850; (c) J. Kim and S. S. Stahl, *ACS Catal.* 2013, **3**, 1652; (d) T. Shen, T. Wang, C. Qin and N. Jiao, *Angew. Chem., Int. Ed.,* 2013, **52**, 6677; (e) T. Wang and N. Jiao, *Acc. Chem. Res.,* 2014, **47**, 1137; (f) R. V. Jagadeesh, H. Junge and M. Beller, *Nat. Commun.,* 2014, **5**, 4123.

15 For representative examples of radical reactions using TsCN **2b** as a cyano source, see: (a) D. H. R. Barton, J. C. Jaszberenyl and E. A. Theodorakis, *Tetrahedron,* 1992, **48**, 2613; (b) S. Kim and H.-J. Song, *Synlett,* 2002, 2110; (c) S. Kim, C. H. Cho, S. Kim, Y. Uenoyama and I. Ryu, *Synlett,* 2005, 3160; (d) B. Gaspar and E. M. Carreira, *Angew. Chem., Int. Ed.,* 2007, **46**, 4519; (e) S. Kamijo, T. Hoshikawa and M. Inoue, *Org. Lett.,* 2011, **13**, 5928; (f) T. Hoshikawa, S. Yoshioka, S. Kamijo and M. Inoue, *Synthesis,* 2013, **45**, 874.

16 For the use of hypervalent iodine CN reagent **2a** in organic synthesis, see: (a) V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, J. T. Bolz, B. Mismash, J. K. Woodward and A. J. Simonsen, *Tetrahedron Lett.,* 1995, **36**, 7975; (b) R. Frei, T. Courant, M. D. Wodrich and J. Waser, *Chem. E. J.,* 2015, **21**, 2662.

17 (a) M. Galicia and F. J. Gonzalez, *J. Electrochem. Soc.* 2002, **149**, D46; (b) C. Depecker, H. Marzouk, S. Trevin and J. Devynck, *New J. Chem.* 1999, **23**, 739.

18 For recent examples of cyanation reactions using NCTS, see: (a) P. Anbarasan, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.,* 2011, **50**, 519; (b) P. Anbarasan, H. Neumann and M. Beller, *Chem. Eur. J.,* 2011, **17**, 4271; (c) T.-J. Gong, B. Xiao, W.-M. Cheng, W. Su, J. Xu, Z.-J. Liu, L. Liu and Y. Fu, *J. Am. Chem. Soc.,* 2013, **135**, 10630; (d) W. Liu and L. Ackermann, *Chem. Commun.,* 2014, **50**, 1878; (e) Y. Yang and S. L. Buchwald, *Angew. Chem., Int. Ed.,* 2014, **53**, 8677; (f) J. Li and L. Ackermann, *Angew. Chem., Int. Ed.,* 2015, **54**, 8551.

19 The oxidation potentials of **1a** (1º) and **1r** (2º) are +1.41 and +1.1 V vs. Cp_2Fe, respectively (See: Ref. 9a). These indicate that the reductive quenching ability of 2º alkyl-BF_3K is higher than 1º alkyl-BF_3K. Carboxylate may not be able to compete quenching the photoredox catalyst when 2º and 3º alkyl-BF_3K are used, thus the TFA additive is not necessary.

20 P. Anbarasan, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.,* 2011, **50**, 519.

21 Reviews: (a) M. Beller, J. Seavad, A. Tillack and H. Jiao, *Angew. Chem., Int. Ed.,* 2004, **43**, 3368; (b) K. Muniz, *Chem. Soc. Rev.,* 2004, **33**, 166; (c) K. H. Jensen and M. S. Sigman, *Org. Biomol. Chem.,* 2008, **6**, 4083; (d) T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo and M. Tada, *Chem. Rev.,* 2008, **108**, 3795; (e) L. Hintermann, *Top. Organomet. Chem.,* 2010, **31**, 123; (f) F. Cardona and A. Goti, *Nat. Chem.,* 2009, **1**, 269; (g) R. I. McDonald, G. Liu and S. S. Stahl, *Chem. Rev.,* 2011, **111**, 2981; (h) J. P. Wolfe, *Angew. Chem., Int. Ed.,* 2012, **51**, 10224.

22 Renaud and co-workers once reported an *anit*-Markovnikov hydrocyanation of alkene via B-alkylcatecholboranes. (see: A.-P. Schaffner, V. Darmency and P. Renaud, *Angew. Chem., Int.* Ed., 2006, **45**, 5847.)

23 During the course for the preparation of this manuscript, Peters and Fu reported a related photoinduced radical cyanation reaction using unactivated alkyl chcloride as the radical precursor. (see: T. S. Ratani, S. Bachman, G. C. Fu and J. C. Peters, *J. Am. Chem. Soc.,* 2015, **137**, 13902.)