A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Visible-Light Photoredox-Catalyzed and Copper-Promoted Trifluoromethoxylation of Arenediazonium Tetrafluoroborates

Authors: Shaoqiang Yang, Miao Chen, and pingping tang

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201901447
Angew. Chem. 10.1002/ange.201901447

Link to VoR: http://dx.doi.org/10.1002/anie.201901447
http://dx.doi.org/10.1002/ange.201901447

WILEY-VCH

Trifluoromethoxylation

DOI: 10.1002/anie.201((will be filled in by the editorial staff))

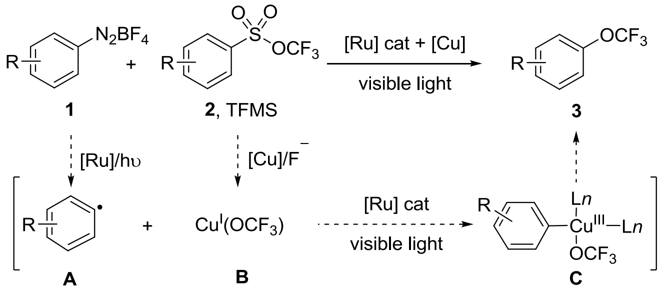
Visible-Light Photoredox-Catalyzed and Copper-Promoted Trifluoromethoxylation of Arenediazonium Tetrafluoroborates

*Shaoqiang Yang,[+] Miao Chen[+] and Pingping Tang**

Dedicated to Professor Qingyun Chen on the occasion of his 90th birthday

***Abstract**: A photoredox-catalyzed and copper-promoted trifluoromethoxylation of arenediazonium tetrafluoroborates have been developed for the first time. Trifluoromethyl arylsulfonate (TFMS) was used as the trifluoromethoxylation reagent. This reaction is scalable and proceeds regioselectively under mild reaction conditions. Furthermore, mechanistic studies suggested that Cs[Cu(OCF$_3$)$_2$] intermediate might be generated during the reaction.*

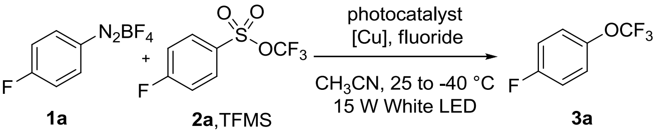
Trifluoromethyl ethers are increasingly being investigated for pharmaceutical, agrochemical, and materials science, because trifluoromethoxy group (OCF$_3$) has strongly electron-withdrawing nature and high lipophilicity.[1] Therefore, the development of new methods for the synthesis of trifluoromethyl ethers has received much attention.[2] However, due to the reversible decomposition of trifluoromethoxide anion and limited trifluoromethoxylation reagents, methods for the synthesis of trifluoromethyl aryl ethers remain extremely rare.[3] Herein, we reported the first example of a photoredox-catalyzed and copper-promoted trifluoromethoxylation of arenediazonium tetrafluoroborates under mild reaction conditions, with trifluoromethyl arylsulfonate (TFMS, **2**)[4] as the trifluoromethoxylation reagent (Scheme 1).



Scheme 1. Photoredox-catalyzed and copper-promoted trifluoromethoxylation of arenediazonium tetrafluoroborates.

The traditional synthesis of trifluoromethyl aryl ethers had been achieved by nucleophilic substitution of the corresponding trichloromethyl aryl ethers with fluoride,[5] deoxyfluorination of fluoroformates,[6] and fluorodesulfurization of sulfonate esters.[7] However, harsh reaction conditions were required. Recently, several new strategies had been developed to synthesis trifluoromethyl aryl ethers.[8] For examples, Ritter and coworkers reported a silver-mediated trifluoromethoxylation of aryl stannanes and aryl boronic acids with tris(dimethylamino)sulfonium trifluoro-methoxide (TASOCF$_3$) as the trifluoromethoxylation reagent.[9] Qing and coworkers reported a silver-mediated trifluoromethylation of phenols to prepare trifluoromethyl aryl ethers.[10] The fluorodecarboxylation for the synthesis of trifluoromethyl aryl ethers were reported by Hartwig, Hu, Sammis, and Prakash, respectively.[11] Hu and coworkers developed trifluoromethyl benzoate (TFBz) as a new trifluoromethoxylation reagent for the synthesis of trifluoromethyl aryl ethers.[12] The catalytic C(sp^2)-H trifluoromethoxylation of arenes with the new *N*-OCF$_3$ reagents under photocatalytic conditions were reported by Ngai and Togni, respectively.[13] Although the progress has been made, strong oxidants or regioisomers were observed with few exceptions. Therefore, the development of a selective trifluoromethoxylation method for the synthesis of trifluoromethyl aryl ethers without strong oxidants is highly desirable.

Table 1. Optimization of the reaction conditions.[a]



Entry	Photocatalyst	Copper salts	Fluoride	Yield (%)[f]
1	*fac*-Ir(ppy)$_3$	CuOTf	CsF	32
2	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	CuOTf	CsF	76
3	Eosin Y	CuOTf	CsF	0
4	Fluorescein	CuOTf	CsF	0
5	[Ru(bpz)$_3$](PF$_6$)$_2$	CuOTf	CsF	3
6	[Ru(phen)$_3$](PF$_6$)$_2$	CuOTf	CsF	68
7	[Ru(bpy)$_3$](PF$_6$)$_2$	CuOTf	CsF	78
8[b]	[Ru(bpy)$_3$](PF$_6$)$_2$	CuOTf	CsF	28
9	[Ru(bpy)$_3$](PF$_6$)$_2$	CuOAc	CsF	11
10	[Ru(bpy)$_3$](PF$_6$)$_2$	CuI	CsF	0
11	[Ru(bpy)$_3$](PF$_6$)$_2$	Cu$_2$O	CsF	38
12	[Ru(bpy)$_3$](PF$_6$)$_2$	Cu(OTf)$_2$	CsF	0
13	[Ru(bpy)$_3$](PF$_6$)$_2$	CuOTf	KF	0
14	[Ru(bpy)$_3$](PF$_6$)$_2$	CuOTf	AgF	32
15	[Ru(bpy)$_3$](PF$_6$)$_2$	CuOTf	none	0
16[c]	[Ru(bpy)$_3$](PF$_6$)$_2$	CuOTf	CsF	61
17[d]	[Ru(bpy)$_3$](PF$_6$)$_2$	CuOTf	CsF	67
18	[Ru(bpy)$_3$](PF$_6$)$_2$	none	CsF	0
19	none	CuOTf	CsF	3
20[e]	[Ru(bpy)$_3$](PF$_6$)$_2$	CuOTf	CsF	0

[a] General conditions: **1a** (0.05 mmol), **2a** (0.25 mmol), photocatalyst (1 to 2 mol%) , copper salts (1.0 equiv), fluoride (2.0 equiv), degassed CH$_3$CN, 25 to -40 °C, 12 h, 15 W white LED. [b] 1.0 equiv

---

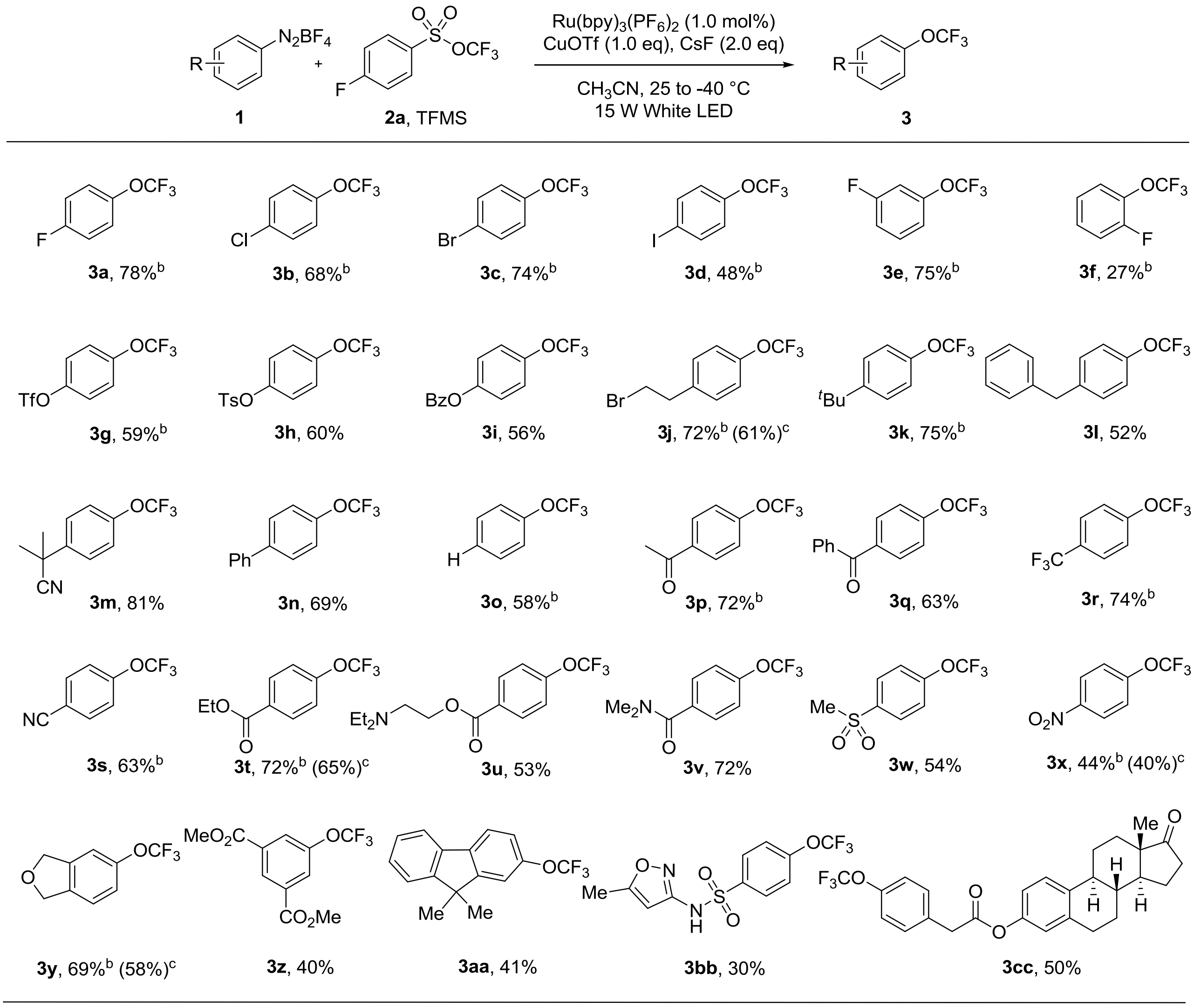
[*] S. Yang,[+] M. Chen,[+] Prof. P. Tang
State Key Laboratory and Institute of Elemento-Organic
Chemistry, College of Chemistry, Nankai University
Tianjin 300071, China
E-mail: ptang@nankai.edu.cn

[+] These authors contributed equally.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201xxxxxx.

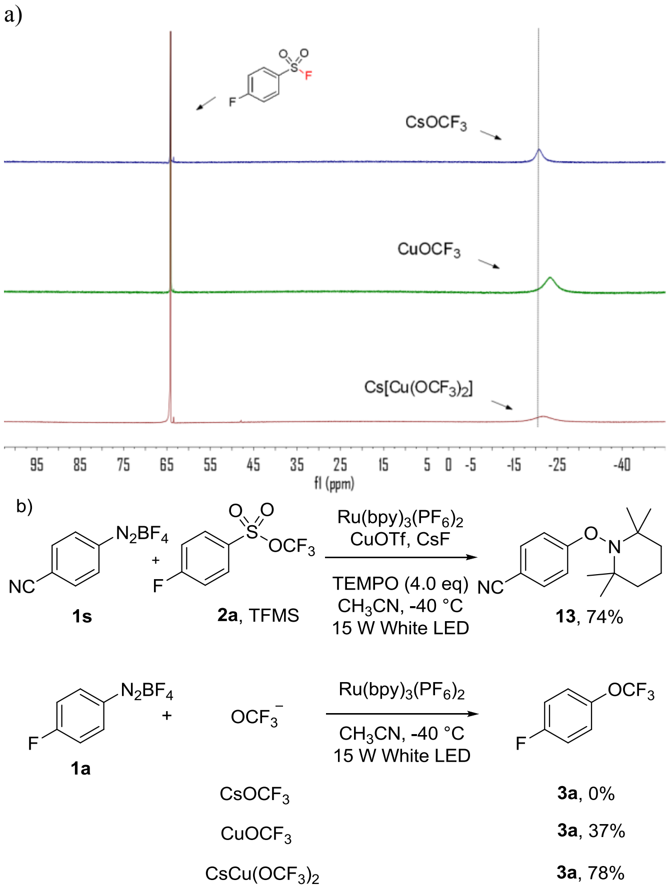
of Cu(OTf) and 1.0 equiv of CsF were used. [c] copper salts (0.4 equiv). [d] copper salts (0.6 equiv). [e] no light. [f] Yields were determined by ^{19}F NMR with benzotrifluoride as a standard.

Inspired by Kolomeitsev and Vicic reports that $CuOCF_3$ could be generated from trifluoromethane sulfonate (TFMT),[14] but no copper-catalyzed/mediated trifluoromethoxylation reaction was reported to date, we were wondering whether synthesis of trifluoromethyl aryl ethers was achieved from aryldiazonium salts via the combination of photocatalysis and copper salts (Scheme 1).[15] We envisioned that aryl radical (**A**) could be generated by photoredox reaction of aryldiazonium salts (**1**),[16] and $CuOCF_3$ (**B**) was prepared in situ with TFMS in the presence of copper salts and fluorides, we hypothesized the merger of visible-light photocatalysis with copper salts might provide a mild method for the synthesis of trifluoromethyl aryl ethers (**3**), effectively taking advantage of Cu^{III}'s propensity (**C**) to undergo facile reductive elimination from its high valency oxidation state.[17] Our initial investigations focused on the trifluoromethoxylation of 4-fluorobenzenediazonium tetrafluoroborate **1a** in the presence of a photoredox catalyst and copper salts with TFMS (**2a**). The desired product **3a** was obtained when a Cu(OTf) solution in acetonitrile was stirred with TFMS (**2a**) and cesium fluoride for 1 hour at room temperature, followed by addition of the diazonium salts and photoredox catalyst continued stirring at -40 °C for 12 hours under irradiation of white LED, as briefly illustrated in Table 1. It was crucial to use a photoredox catalyst for achieving an efficient transformation in the presence of Cu(OTf) and CsF, and $[Ru(bpy)_3](PF_6)_2$ was found to give the highest yield comparing to other photocatalysts fac-$Ir(ppy)_3$, $[Ir(ppy)_2(dtbbpy)]PF_6$ or organic photocatalysts (entries 1-7). Next, different copper salts were evaluated. Cu(OTf) was found to give the highest yield while no desired product was observed with $Cu(OTf)_2$ (entries 7-12). The yield was also sensitive to fluoride sources, and CsF was most effective (entries 7, 13, 14). Interestingly, the ratio of the amount of Cu(OTf) and CsF significantly influenced the reaction yield, and the highest yield was obtained when 1.0 equiv of Cu(OTf) and 2 equiv of CsF were used (entries 7, 8). In addition, substoichiometric amount of Cu(OTf) (0.4 or 0.6 eq) could be applied in the reaction, while it led to slightly lower yields (entries 16, 17), which might be due to the decomposition of active copper species in the reaction. Importantly, photoredox catalyst, copper salts, CsF, and visible light were all critical for this transformation. Significantly reduced yields of **3a** (<3%) were observed in the absence of these components (entries 18-20). Finally, extensive optimization with various TFMS (**2**), solvents and temperatures (See more details in the supporting information), revealed that product **3a** could be obtained in the highest yield when the reaction of **1a** was conducted with 1.0 mol% $[Ru(bpy)_3](PF_6)_2$, 1.0 equiv of Cu(OTf), 2.0 equiv of CsF and 5.5 equiv of TFMS (**2a**) in MeCN under N_2 atmosphere using 15W White LED light irradiation for 12 hours.



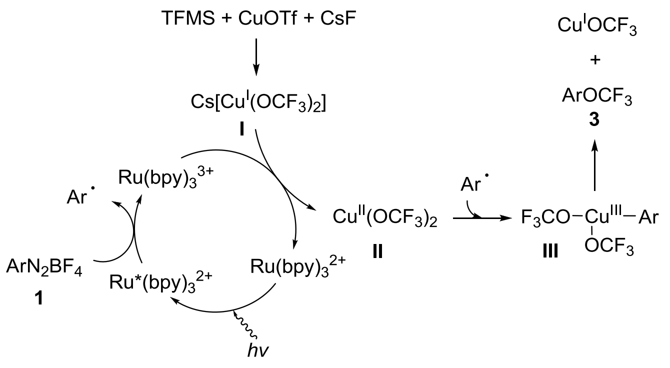
Scheme 2. Substrate scope for trifluoromethoxylation of aryldiazonium salts[a]. [a] Reaction conditions: **1a** (1.0 equiv), **2a** (5.5 equiv), $[Ru(bpy)_3](PF_6)_2$ (1 mol%) , CuOTf (1.0 equiv), CsF (2.0 equiv), CH_3CN, N_2 atmosphere, 25 to -40 °C, 12 h, 15 W White LED. Yields of isolated products are given, unless otherwise noted. [b] Yields were determined by ^{19}F NMR with benzotrifluoride as a standard. [c] The isolated yield was shown in parentheses.

Having optimized the reaction conditions, we next investigated the substrate scope of the transformation (Scheme 2). Various arenediazonium tetrafluoroborates derivatives **1a**-**1aa** bearing electron-donating to electron-withdrawing substituents were successfully converted to the desired products (**3a**-**3aa**) with yields ranging from 27% to 81%. Only for the low-boiling substrates, the products could not be isolated in good yields observed by in situ spectroscopic analysis due to their volatility. Moreover, a good range of functional groups, such as nitro, cyano, ketone, ester, amide, amine, sulfone groups was tolerated in this photoreaction. Notably, halogen-substituted aryl diazonium salts (**1a** to **1f**, **1j**) successfully underwent trifluoromethoxylation leaving the C-X bond intact, which is useful for further synthetic elaboration. However, the efficacy of the reaction was hindered by ortho substitution (**1f**, 27% yield). The yield of fluorination byproducts were less than 6% in all cases. It was worth mentioning that trifluoromethoxylation always occurred regioselectively, no other regioisomers were obtained. To further investigate the synthetic utility and generality of this reaction, we tested the sulfamethoxazole derivative (**1bb**), which is an antibiotic, and estrone derivative (**1cc**) under the reaction conditions, the desired products (**3bb**, **3cc**) were achieved with moderate yields, which highlighted the good potential of this reaction for complex molecular synthesis. A limitation of this method is that no desired products were observed with heteroaryl diazonium salts. Furthermore, in order to demonstrate the scalability of this method, we prepared **3m** on a gram scale under the standard reaction conditions in 76% isolated yield.



Scheme 3. Mechanistic investigations.

To get some insight into the mechanism, some preliminary studies were conducted (Scheme 3). When 4.0 equiv of TEMPO was added, no trifluoromethoxylated product was obtained, and the TEMPO-trapped intermediate (**13**) was isolated in 74% yield. These results indicated that an aryl radical was generated in the reaction. To verify the effect of photoirradiation, the value of *Φ* was estimated to be 0.38, which indicated that a radical chain process was unlikely in the reaction. To probe the electron transfer among the catalyst and substrates, a series of luminescence quenching experiments were investigated (See more details in the supporting information). The aryl diazonium salt (**1**) and CuOTf could quench the excited photocatalyst, respectively.[18] Furthermore, monitoring of the reaction between TFMS (**2a**) and CuOTf in the presence of CsF by ^{19}F NMR spectroscopy showed that a new intermediate (-21.9 ppm) was generated compared to the $CsOCF_3$ (-20.9 ppm) and $CuOCF_3$ (-23.5 ppm) (Scheme 3a). Based on the ratio of amount of Cu(OTf) (1.0 equiv) and CsF (2.0 equiv), the new intermediate could be postulated to be $Cs[Cu(OCF_3)_2]$.[19] In addition, the highest yield of product **3a** was observed with $Cs[Cu(OCF_3)_2]$ compared to $CsOCF_3$ or $CuOCF_3$, which suggested that the proposed $Cs[Cu(OCF_3)_2]$ was the reactive species for this reaction (Scheme 3b).



Scheme 4. Proposed mechanism.

Based on these mechanistic studies, our proposed mechanism was outlined in Scheme 4.[20] Under exposure to visible light, the photocatalyst $[Ru(bpy)_3]^{2+}$ should produce excited triplet state species $[Ru^*(bpy)_3]^{2+}$, which was oxidatively quenched by the arenediazonium tetrafluoroborates (**1**) to deliver an oxidizing $[Ru(bpy)_3]^{3+}$ and the aryl radical (Ar•) via single-electron transfer. Concurrently, the anionic Cu(I) trifluoromethoxide (**I**), which was generated in situ via Cu(I) and TFMS (**2**) in the presence of CsF, was oxidized to Cu(II) species (**II**) by the $[Ru(bpy)_3]^{3+}$ through single electron transfer. Aryl radical should quickly undergo radical trapping by Cu(II) species (**II**) to yield the key aryl-Cu(III)-OCF_3 adduct **III**. Subsequently, reductive elimination from this high-valent Cu (III) intermediate (**III**) would yield the desired product **3** and generate the Cu(I) species.

In conclusion, we had developed the first example of a photoredox-catalyzed and copper-promoted trifluoromethoxylation of arenediazonium tetrafluoroborates with trifluoromethyl arylsulfonate (TFMS) as the trifluoromethoxylation reagent. This new method took advantage of visible-light photoredox catalysis to generate the aryl radical under mild conditions and merged it with copper-promoted selective trifluoromethoxylation reaction. This method tolerated a wide range of functional groups and was applicable to late-stage trifluoromethoxylation of complex small molecules. Furthermore, mechanistic studies indicated that proposed $Cs[Cu(OCF_3)_2]$ intermediate might be generated, which could lead to the development of a new trifluoromethoxylation reaction in the future.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2016YFA0602900), NFSC (21522205, 21672110), the Natural Science Foundation of Tianjin (Grant No. 18JCJQJC47000), and the Fundamental Research Funds for the Central Universities.

Conflict of interest

The authors declare no conflict of interest.

Keywords: trifluoromethoxylation · trifluoromethyl arylsulfonate · photoredox · copper · synthetic methods

---

[1] a) F. Leroux, P. Jeschke, M. Schlosser, *Chem. Rev.* **2005**, *105*, 827; b) M. Shimizu, T. Hiyama, *Angew. Chem.* **2005**, *117*, 218; *Angew. Chem. Int. Ed.* **2005**, *44*, 214; c) B. Menteau, S. Pazenok, J. P. Vors, F. R. Leroux, *J. Fluorine Chem.* **2010**, *131*, 140; d) G. Landelle, A. Panossian, F. R. Leroux, *Curr. Top. Med. Chem.* **2014**, *14*, 941.

[2] For selected examples for the synthesis of trifluoromethoxylated compounds, see a) K. Stanek, R. Koller, A. Togni, *J. Org. Chem.* **2008**, *73*, 7678; b) O. Marrec, T. Billard, J. Vors, S. Pazenok, B. R. Langlois, *Adv. Synth. Catal*. **2010**, *352*, 2831; c) O. Marrec, T. Billard, J. Vors, S. Pazenok, B. R. Langlois, *J. Fluorine Chem.* **2010**, *131*, 200; d) J. Liu, X. Xu, F. Qing, *Org. Lett.* **2015**, *17*, 5048; e) C. Chen, P. Chen, G. Liu, *J. Am. Chem. Soc.* **2015**, *137*, 15648; f) S. Chen, Y. Huang, X. Fang, H. Li, Z. Zhang, T. S. Andy Hor, Z. Weng, *Dalton Trans*. **2015**, *44*, 19682; g) G. Zha, J. Han, X. Hu, H. Qin, W. Fang, C. Zhang, *Chem. Commun.* **2016**, *52*, 7458; (h) J. N. Brantley, A. V. Samant, F. D.Toste, *ACS Cent. Sci*. **2016**, *2*, 341; (i) X. Qi, P. Chen, G. Liu, *Angew. Chem.* **2017**, *129*, 9620; *Angew. Chem. Int. Ed.* **2017**, *56*, 9517; j) W. Huang, X. Wan, Q. Shen, *Angew. Chem.* **2017**, *129*, 12148; *Angew. Chem. Int. Ed.* **2017**, *56*, 11986; (k) C. Chen, Y. Luo, L. Fu, P. Chen, Y. Lan, G. Liu, *J. Am. Chem. Soc.* **2018**, *140*, 1207; (l) W. Zhang, J. Chen, J. Lin, J. Xiao, Y. Gu, *iScience* **2018**, *5*, 110; (m) H. Kondo, M. Maeno, K. Hirano, N. Shibata, *Chem. Commun.* **2018**, *54*, 5522; (n) C. Chen, P. M. Pflüger, P. Chen, G. Liu, *Angew. Chem.* **2019**, *131*, 2414; *Angew. Chem. Int. Ed.* **2019**, *58*, 2392.

[3] For recent reviews on trifluoromthoxylation reactions, see a) A. Tlili, F. Toulgoat, T. Billard, *Angew. Chem.* **2016**, *128*, 11900; *Angew. Chem. Int. Ed.* **2016**, *55*, 11726; b) T. Besset, P. Jubault, X. Pannecoucke, T. Poisson, *Org. Chem. Front.* **2016**, *3*, 1004; c) K. N. Lee, J. W. Lee, M. Ngai, *Tetrahedron* **2018**, *74*, 7127; d) X. Zhang, P. Tang, *Sci. Chi. Chem.* **2018**, DOI: 10.1007/s11426-018-9402-x.

[4] a) S. Guo, F. Cong, R. Guo, L. Wang, P. Tang, *Nat. Chem.* **2017**, *9*, 546; b) X. Jiang, Z. Deng, P. Tang, *Angew. Chem.* **2018**, *130*, 298; *Angew. Chem. Int. Ed.* **2018**, *57*, 292; c) F. Cong, Y. Wei, P. Tang, *Chem. Commun.* **2018**, *54*, 4473; d) H. Yang, F. Wang, X. Jiang, Y. Zhou, X. Xu, P. Tang, *Angew. Chem.* **2018**, *130*, 13450; *Angew. Chem. Int. Ed.* **2018**, 57, 13266; e) F. Wang, P. Xu, F. Cong, P. Tang, *Chem. Sci.* **2018**, *9*, 8836; f) J. Liu, Y. Wei, P. Tang, *J. Am. Chem. Soc.* **2018**, *140*, 15194.

[5] a) A. E. Feiring, *J. Org. Chem.* **1979**, *44*, 2907; b) J. Salomé, C. Mauger, S. Brunet, V. Schanen, *J. Fluorine Chem.* **2004**, *125*, 1947.

[6] W. A. Sheppard, *J. Org. Chem.* **1964**, *29*, 1.

[7] a) M. Kuroboshi, K. Suzuki, T. Hiyama, *Tetrahedron Lett.* **1992**, *33*, 4173; b) K. Kiyoshi, T. Yoichiro, S. Kazundo, K. Manabu, H. Tamejiro, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 471; c) M. Kuroboshi, K. Kanie, T. Hiyama, *Adv. Synth. Catal.* **2001**, *343*, 235.

[8] a) T. Umemoto, K. Adachi, S. Ishihara, *J. Org. Chem.* **2007**, *72*, 6905; b) R. Koller, K. Stanek, D. Stolz, R. Aardoom, K. Niedermann, A. Togni, *Angew. Chem.* **2009**, *121*, 4396; *Angew. Chem. Int. Ed.* **2009**, *48*, 4332; c) K. N. Hojczyk, P. Feng, C. Zhan, M. Y. Ngai, *Angew. Chem.* **2014**, *126*, 14787; *Angew. Chem. Int. Ed.* **2014**, *53*, 14559; d) A. Liang, S. Han, Z. Liu, L. Wang, J. Li, D. Zou, Y. Wu, Y. Wu, *Chem. Eur. J.* **2016**, *22*, 5102; e) P. Feng, K. N. Lee, J. W. Lee, C. Zhan, M. Y. Ngai, *Chem. Sci.* **2016**, *7*, 424; f) Q. Zhang, J. Hartwig, *Chem. Commun.* **2018**, *54*, 10124.

[9] C. Huang, T. Liang, S. Harada, E. Lee, T. Ritter, *J. Am. Chem. Soc.* **2011**, *133*, 13308.

[10] J. Liu, C. Chen, L. Chu, Z. Chen, X. Xu, F. Qing, *Angew. Chem.* **2015**, *127*, 12005; *Angew. Chem. Int. Ed.* **2015**, *54*, 11839.

[11] a) Q. Zhang, A. T. Brusoe, V. Mascitti, K. D. Hesp, D. C. Blakemore, J. T. Kohrt, J. F. Hartwig, *Angew. Chem.* **2016**, *128*, 9910; *Angew. Chem. Int. Ed.* **2016**, *55*, 9758; b) M. Zhou, C. Ni, Z. He, J. Hu, *Org. Lett.* **2016**, *18*, 3754; c) C. Chatalova-Sazepin, M. Binayeva, M. Epifanov, W. Zhang, P. Foth, C. Amador, M. Jagdeo, B. R. Boswell, G. M. Sammis, *Org. Lett.* **2016**, *18*, 4570; d) S. Krishanmoorthy, S. D. Schnell, H. Dang, F. Fu, G. K. S. Prakash, *J. Fluorine Chem.* **2017**, *203*, 130.

[12] M. Zhou, C. Ni, Y. Zeng, J. Hu, *J. Am. Chem. Soc.* **2018**, *140*, 6801.

[13] a) W. Zheng, C. A. Morales-Rivera, J. W. Lee, P. Liu, M. Ngai, *Angew. Chem.* **2018**, *130*, 9793; *Angew. Chem. Int. Ed.* **2018**, *57*, 9645; b) B. J. Jelier, P. F. Tripet, E. Pietrasiak, I. Franzoni, G. Jeschke, A. Togni, *Angew. Chem.* **2018**, *130*, 13980; *Angew. Chem. Int. Ed.* **2018**, *57*, 13784; c) W. Zheng, J. W. Lee, C. A. Morales-Rivera, P. Liu, M. Ngai, *Angew. Chem.* **2018**, *130*, 13991; *Angew. Chem. Int. Ed.* **2018**, *57*, 13795.

[14] a) A. A. Kolomeitsev, M. Vorobyev, H. Gillandt, *Tetrahedron Lett.* **2008**, *49*, 449; b) C. Zhang, D. A. Vicic, *Organometallics*, **2012**, *31*, 7812.

[15] For selected reviews on metallaphotocatalysis, see a) J. Xuan, W. J. Xiao, *Angew. Chem.* **2012**, *124*, 6934; *Angew. Chem. Int. Ed.* **2012**, *51*, 6828; b) X. Lang, J. Zhao, X. Chen, *Chem. Soc. Rev.* **2016**, *45*, 3026; c) D. C. Fabry, M. Rueping, *Acc. Chem. Res.* **2016**, *49*, 1969; d) M. N. Hopkinson, A. Tlahuext-Aca, F. Glorius, *Acc. Chem. Res.* **2016**, *49*, 2261; e) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* **2016**, *116*, 10035; f) J. Twilton, C. Le, P. Zhang, M. H. Shaw, R. W. Evan, D. W. C. MacMillan, *Nat. Rev. Chem.* **2017**, *1*, 0052; g) E. B. McLean,; A. Lee, *Tetrahedron* **2018**, *74*, 4881.

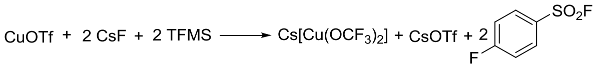
[16] a) F. Mo, G. Dong, Y. Zhang, J. Wang, *Org. Biomol. Chem.* **2013**, *11*, 1582; b) D. P. Hari, B. König, *Angew. Chem.* **2013**, *125*, 4832; *Angew. Chem. Int. Ed.* **2013**, *52*, 4734.

[17] a) Y. Ye, M. S. Sanford, *J. Am. Chem. Soc.* **2012**, *134*, 9034; b) A. Casitas, X. Ribas, *Chem. Sci.* **2013**, *4*, 2301; c) P. S. Fier, J. Luo, J. F. Hartwig, *J. Am. Chem. Soc.* **2013**, *135*, 2552; d) H. Zhang, B. Yao, L. Zhao, D. Wang, B. Xu, M. Wang, *J. Am. Chem. Soc.* **2014**, *136*, 6326; e) X. Tan, Z. Liu, H. Shen, P. Zhang, Z. Zhang, C. Li, *J. Am. Chem. Soc.* **2017**, *139*, 12430; f) Guo, S.; AbuSalim, D. I.; Cook, S. P. *J. Am. Chem. Soc.* **2018**, *140*, 12378. g) C. Le, T. Q. Chen, T. Liang, P. Zhang, D. W. C. MacMillan, *Science* **2018**, *360*, 1010; h) R. Mao, A. Frey, J. Balon, X. Hu, *Nat. Cat.* **2018**, *1*, 120; i) Y. Liang, X. Zhang, D. W. C. MacMillan, *Nature* **2018**, *559*, 83; j) L. Liu, Z. Xi, *Chin. J. Chem.* **2018**, *36*, 1213.

[18] Interestingly, the possible $Cs[Cu(OCF_3)_2]$ generated by mixing CsF, CuOTf and TFMS could not quench the excited photocatalyst.

[19] We took a lot of effort to get the x-ray crystal structure or ESI-MS of proposed structure $Cs[Cu(OCF_3)_2]$, but we failed due to the easily decomposition of this intermediate. For selected examples for other anionic Cu intermediates, see: a) S. Okamoto, S. Tominaga, N. Saino, K. Kase, K. Shimoda, *J. Organomet. Chem.* **2005**, *690*, 6001; b) R.

Giri, A. Brusoe, K. Troshin, J. Y. Wang, M. Font, J. F. Hartwig, *J. Am. Chem. Soc.* **2018**, *140*, 793. Proposed equation to generate $Cs[Cu(OCF_3)_2]$ was shown below:



[20] We tried to prepared $Cu(OCF_3)_2$ intermediate but we failed due to the decomposition of this intermediate (See more details in the supporting information) .

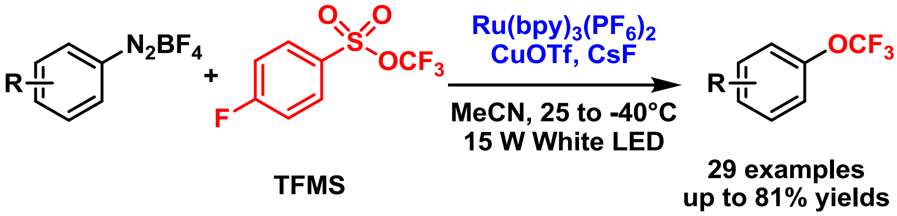
10.1002/anie.201901447

Entry for the Table of Contents

Trifluoromethoxylation

Shaoqiang Yang,[+] Miao Chen[+] and Pingping Tang* ___________ **Page – Page**

Visible-Light Photoredox-Catalyzed and Copper-Promoted Trifluoromethoxylation of Arenediazonium Tetrafluoroborates



With trifluoromethyl arylsulfonate (TFMS) as the trifluoromethoxylation reagent, a photoredox-catalyzed and copper-promoted trifluoromethoxylation of arenediazonium tetrafluoroborates has been reported for the first time. The reaction tolerates a wide range of functional groups and is applicable to late-stage trifluoromethoxylation of complex small molecules. Preliminary mechanistic studies suggest that proposed $Cs[Cu(OCF_3)_2]$ intermediate might be generated during the reaction.