OL | Organic Letters

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

Mn-Mediated Electrochemical Trifluoromethylation/C(sp^2)−H Functionalization Cascade for the Synthesis of Azaheterocycles

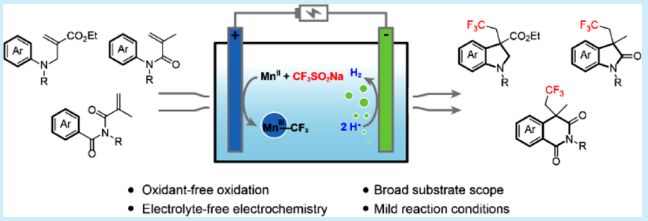
Zhenxing Zhang,[†] Lei Zhang,[†] Yang Cao,[†] Feng Li,[‡] Guangcan Bai,[‡] Guoquan Liu,[‡] Yang Yang,[§] and Fanyang Mo*[,†,⊥]

[†]Department of Energy and Resources Engineering, College of Engineering and [‡]State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Beijing 100871, China

[§]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

Supporting Information

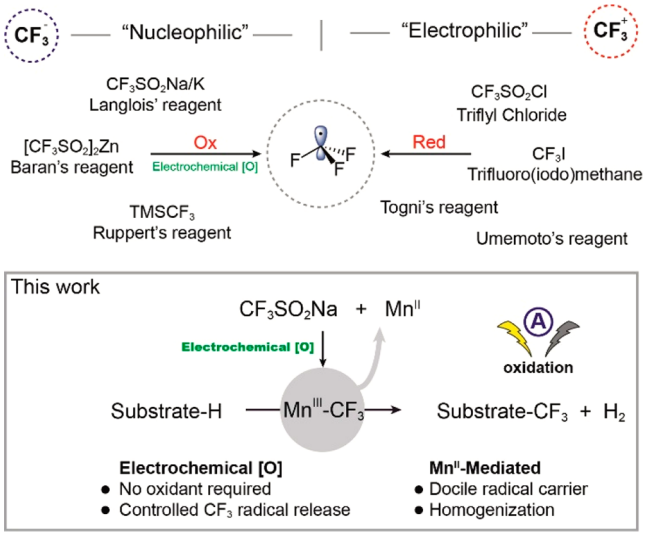
ABSTRACT: A general electrohemical strategy for the combined trifluoromethylation/C(sp^2)−H functionalization using Langlois' reagent as the CF_3 source under oxidant-free conditions was developed. Using Mn salts as the redox mediator, this method provides an efficient and sustainable means to access a variety of functionalized heterocycles bearing a CF_3 moiety. Detailed mechanistic studies are consistent with the formation of CF_3-bound high oxidation state Mn species, suggesting a transition-metal-mediated CF_3 transfer mechanism for this trifluoromethylation/C(sp^2)−H functionalization process.



Owing to the prevalence of the trifluoromethyl group in pharmaceuticals,[1] agrochemicals,[2] and functional materials,[3] the development of efficient and sustainable methods for the introduction of the trifluoromethyl group into organic molecules has attracted much attention.[4] Among various means to prepare trifluoromethylated compounds, trifluoromethylation based on a radical mechanism has been extensively studied and proven highly useful.[4d] Two strategies are commonly used to generate the trifluoromethyl radical, namely, the chemical oxidation of nucleophilic trifluoromethylation reagents (e.g., Langlois' reagent and Baran's reagent) and the single electron reduction of electrophilic trifluoromethylation reagents (e.g., triflyl chloride, CF_3I and Togni's reagent) (Scheme 1). Despite their synthetic utility, the use of stoichiometric quantities of chemical oxidants or reductants inevitably generates environmentally hazardous waste and greatly reduces the functional group compatibility of these methods.

To address these limitations, organic electrochemistry represents a very attractive alternative to conventional redox transformations, wherein the substrate or reagent can directly undergo redox processes without the use of stoichiometric chemical oxidants/reductants.[5] As a part of our program directed toward the development of novel electrochemical methods for organic synthesis,[6] we recently became interested in using the bench stable and highly inexpensive Langlois' reagent (CF_3SO_2Na) for radical trifluoromethylation under electrochemical conditions. In this approach, cathodic hydrogen evolution balances the oxidative part of the redox cycle, thus making the overall transformation oxidant-free. Addtionally, the release of reactive intermediate (CF_3·) can be easily regulated by electric current, allowing the reaction to proceed

Scheme 1. Conventional and Electrochemical Approaches to the Generation of Trifluoromethyl Radical



in a controlled maner. Moreover, the use of a transition metal redox mediator can benefit the reaction by enabling the key steps of the aimed transformation being conducted homogeneously. Despite these desirable features, electrochemical trifluoromethylation is still rare and has only been applied in a few examples, including the C−H functionalization of

Received: December 16, 2018

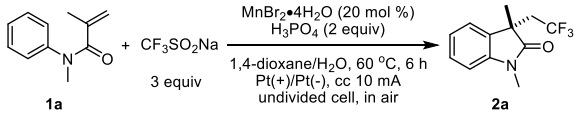
DOI: 10.1021/acs.orglett.8b04010
Org. Lett. XXXX, XXX, XXX−XXX

electron-rich arenes[7] and heterocycles[8] and olefin difunctionalization.[9]

Oxindole is an important structural motif in numerous natural products and bioactive compounds, and trifluoromethylated oxindoles and their analogs hold great promise for application in medicinal chemistry.[10] Previous synthetic routes toward these molecules all required the use of stoichiometric quantities of chemical oxidants or reductants to generate the key trifluoromethyl radical species.[11] Herein, we report a general Mn-mediated electrochemical trifluoromethylation for the construction of a variety of trifluoromethyl-containing oxindoles and related heterocycles to bypass the use of stoichiometric chemical oxidants. Notably, a variety of substrates, including those previously unexplored ones, are readily accommodated by this electrochemical process, affording a diverse range of trifluoromethylated heterocycles bearing an all-carbon quaternary center in excellent yield.[12]

Using *N*-methyl-*N*-phenylmethacrylamide (**1a**) as the model substrate, we commenced our study on the electrochemical trifluoromethylation/C(sp^2)−H functionalization using Langlois reagent as the CF_3 source. The use of a catalytic amount of redox active transition-metal species was found to be critical for this transformation, and manganese salts proved to be optimal for this process.[13] After extensive optimization, we found that using $MnBr_2$ as the mediator, H_3PO_4 as the sacrificial oxidant, and Pt meshes as the electrodes with a constant electric current of 10 mA for 6 h, the desired trifluoromethyl-substituted oxindole product **2a** formed in 67% yield (Table 1, entry 1). Control experiment in the absence of

Table 1. Reaction Development and Optimization[a]



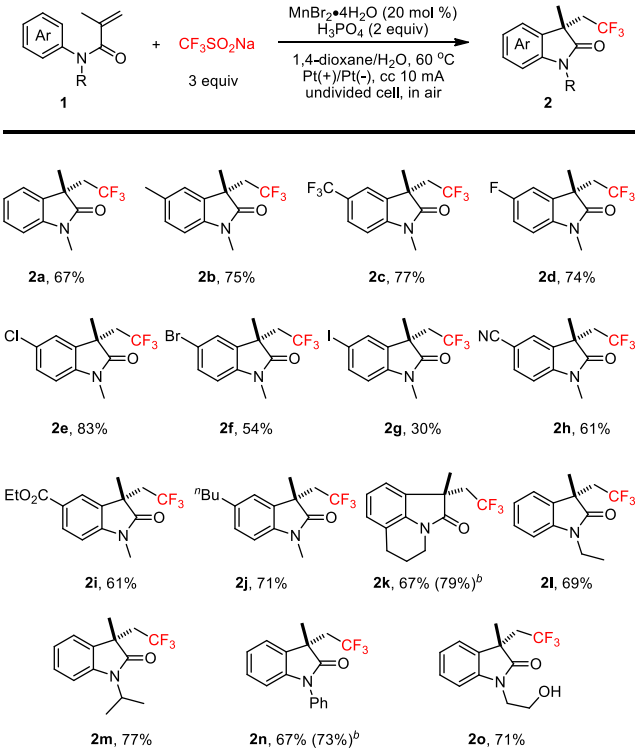
entry	deviation from the standard conditions	yield %[b]
1	none	69 (67)
2	no Mn salt	12
3	$MnSO_4$ instead of $MnBr_2·4H_2O$	54
4	$NiBr_2$ instead of $MnBr_2·4H_2O$	trace
5	room temperature	trace
6	DMA instead of 1,4-dioxane	53
7	MeCN instead of 1,4-dioxane	58
8	no H_3PO_4	27
9	AcOH instead of H_3PO_4	66
10	no electricity	0

[a]Reaction conditions: 0.3 mmol scale, 1,4-dioxane 3 mL, H_2O 0.3 mL, Pt gauze electrodes (1 cm × 1 cm, 52 meshes) were applied. cc, constant current. 1.5 equiv of CF_3SO_2Na was added at the beginning. After 3 h, another 1.5 equiv of CF_3SO_2Na was then added. [b]Yields were determined by ^1H NMR spectroscopic analysis using 1,3,5-trimethoxybenzene as the internal standard. Isolated yield are shown in parentheses.

manganese salt only provided 12% yield of **2a** (entry 2), thereby demonstrating the pivotal role of the manganase catalyst. We found that $MnSO_4$ also catalyzed this trifluoromethylation/C(sp^2)−H functionalization reaction, albeit in lower yield (entry 3). In contrast, other transition metal salts such as $NiBr_2$ were found to be ineffective (entry 4). Additionally, when the reaction was carried out at room temperature, only a trace amount of product was observed (entry 5). Other polar and water miscible solvents, such as DMA and MeCN, were less efficient (entries 6 and 7). It was found that the use of an acid additive such as H_3PO_4 can significantly improve the rate of proton reduction on the Pt electrode, and the yield of **2a** was much lower in the absence of H_3PO_4 (entry 8). Replacing H_3PO_4 with a weaker acid, HOAc, resulted in a similar yield (entry 9). No reaction occurred in the absence of externally applied potential (entry 10). Notably, we were able to avoid the use of electrolytes for this transformation, thus further fulfilling the requirement of green and sustainable chemistry.

With the optimized reaction conditions in hand, we next surveyed the substrate scope of this trifluoromethylation/C(sp^2)−H functionalization process (Scheme 2). A wide range

Scheme 2. Oxidant-Free Electrochemical Trifluoromethylation-Initiated Radical Oxidative Annulation towards Oxindoles[a]



[a]Reaction conditions: **1** (0.3 mmol), $MnBr_2$ (0.06 mmol, 0.2 equiv), 1,4-dioxane 3 mL, H_2O 0.3 mL, Pt gauze electrodes (1 cm × 1 cm, 52 meshes) were applied. cc, constant current. 1.5 equiv CF_3SO_2Na was added at the beginning. After 3 h, another 1.5 equiv was added. Isolated yields were given. [b]isolated yields from ref 11f were given. Reaction conditions of ref 11f: **1** (0.25 mmol), CF_3SO_2Na (0.75 mmol), $K_2S_2O_8$ (2 equiv), CH_3CN/H_2O (2.5 mL, 4/1), 80 °C, 12−36 h, under N_2.

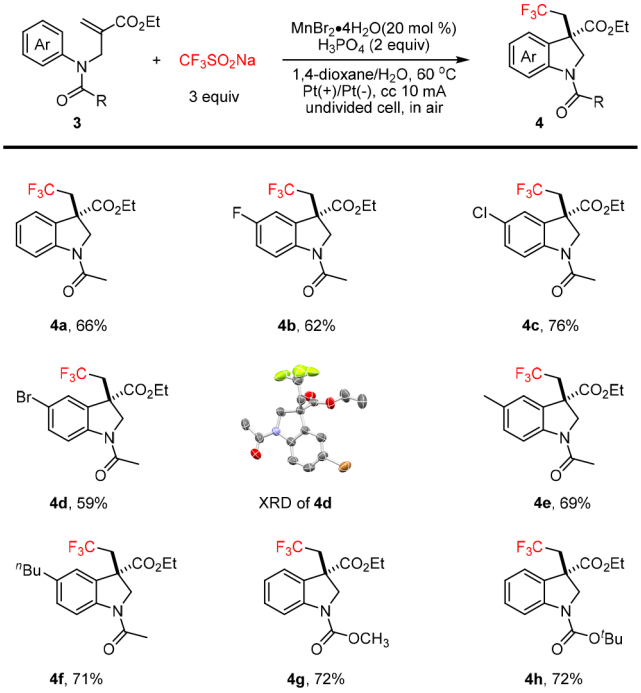
of *N*-arylmethacrylamide derivatives bearing different substituents on aryl ring was found to be excellent substrates. Substrates bearing electron-withdrawing (**2c**−**2i**) or electron-donating groups (**2b** and **2j**) afforded the desired products. Notably, this anodic oxidative process tolerated a variety of functional groups, such as an ester (**2i**), halides (**2d**−**2g**), a nitrile (**2h**), and a free alcohol (**2o**). Substrates with different protecting groups on the nitrogen atom (**1k**−**1o**) were also successfully transformed to the corresponding oxindole

DOI: 10.1021/acs.orglett.8b04010
Org. Lett. XXXX, XXX, XXX−XXX

derivatives (**2k**–**2o**) in good yields (67–77%). Finally, this reaction was also compatible with a fused ring system (**2k**).

Further investigations revealed that the current electrochemical trifluoromethylation/C(sp^2)–H functionalization is a widely applicable strategy and could be readily applied in the synthesis of CF_3-substituted indoline derivatives (Scheme 3)

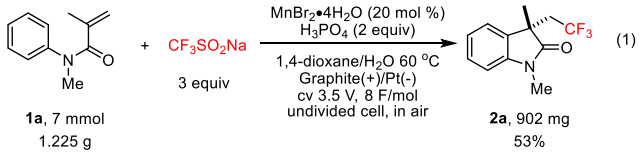
Scheme 3. Oxidant-Free Electrochemical Trifluoromethylation-Initiated Radical Oxidative Cyclization towards Indolines[a]



[a]Reaction conditions: **3** (0.3 mmol), $MnBr_2$ (0.06 mmol, 0.2 equiv), 1,4-dioxane 3 mL, H_2O 0.3 mL, Pt gauze electrodes (1 cm × 1 cm, 52 meshes) were applied. cc, constant current. 1.5 equiv CF_3SO_2Na was added at the beginning. After 3 h, another 1.5 equiv was added. Isolated yields were given.

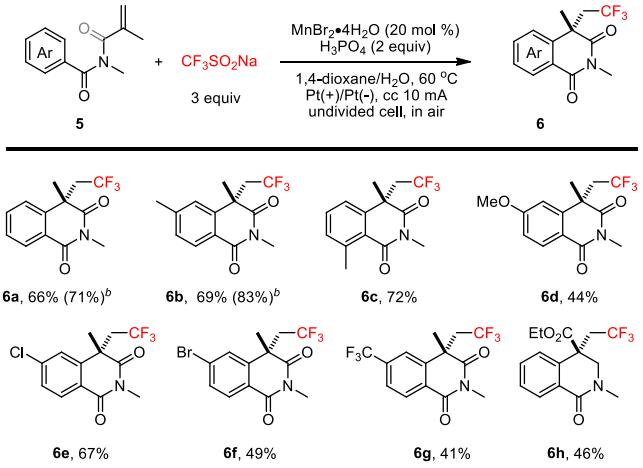
and CF_3-containing hydroisoquinoline-1,3-dione derivatives (Scheme 4). A variety of *N*-arylamide acrylates **3** and *N*-methacryloyl-*N*-methylarylamides **5** could be converted to the corresponding trifluoromethylated indoline and hydroisoquinoline-1,3-dione derivatives in good yields. Of special note, the trifluoromethylation/C(sp^2)–H functionalization of substrates **3** type of compounds has not been reported before.

To further demonstrate the utility of this electrochemical protocol, a gram-scale synthesis of oxindole **2a** was carried out under air (eq 1). This reaction was performed with graphite as the anode and platinum as the cathode, and furnished in 53% isolated yield.



To probe the mechanism of this electrochemical reaction, we performed a series of polarographic and spectroscopic analysis, including cyclic voltammetry (CV), ^{19}F NMR, and stoichiometric control experiment. First, we investigated the

Scheme 4. Oxidant-Free Electrochemical Trifluoromethylation-initiated Radical Oxidative Cyclization towards Hydroisoquinoline-1,3-diones[a]



[a]Reaction conditions: **5** (0.3 mmol), $MnBr_2$ (0.06 mmol, 0.2 equiv), 1,4-dioxane 3 mL, H_2O 0.3 mL, Pt gauze electrodes (1 cm × 1 cm, 52 meshes) were applied. cc, constant current. 1.5 equiv CF_3SO_2Na was added at the beginning. After 3 h, another 1.5 equiv was added. Isolated yields were given. [b]Isolated yields from ref 11i were given. Reaction conditions of ref 11i: **5**, CF_3SO_2Na (3.0 equiv), 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN, 2 mol %), N_2 (with 0.5 mol % of O_2), rt, *c* = 0.02 M, DCE, blue LEDs.

redox behavior of $MnBr_2$, CF_3SO_2Na, **1a** and their combination in solution by cyclic voltammetry (Figure 1).

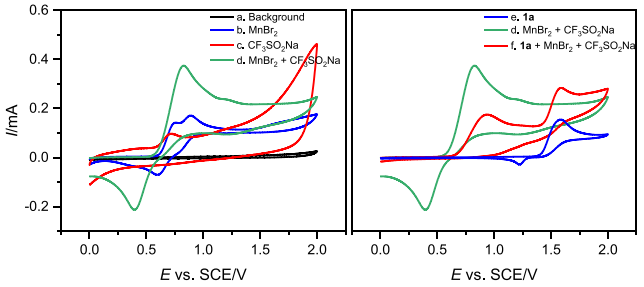


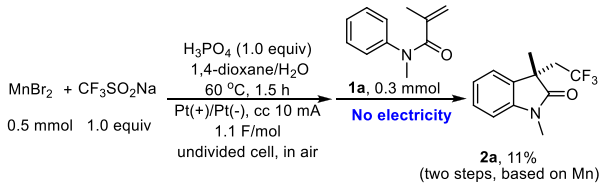
Figure 1. CVs of $MnBr_2$, CF_3SO_2Na, and substrate **1a**. Conditions: a L-type glassy carbon working electrode, a saturated calomel electrode (SCE) reference electrode, and a platinum wire counter electrode, $LiClO_4$ (0.10 M in MeCN), TFA (60 mM), 0.1 V/s with (a) Background; (b) $MnBr_2{\cdot}4H_2O$ (2 mM); (c) CF_3SO_2Na (8 mM); (d) $MnBr_2{\cdot}4H_2O$ (2 mM) and CF_3SO_2Na (8 mM); (e) **1a** (4 mM); (f) **1a** (4 mM), $MnBr_2{\cdot}4H_2O$ (2 mM) and CF_3SO_2Na (8 mM).

The TFA/MeCN solution of $MnBr_2$ displays a quasi-reversible anodic wave (line b) of 0.75 and 0.89 V and cathodic wave of 0.60 V versus saturated calomel electrode (SCE), which we attributed to the Mn^{II}/Mn^{III} redox couple of the bromide-bound complex and the direct oxidation of free Br^-. CF_3SO_2Na shows an irreversible anodic wave at 0.71 V (line c). Furthermore, the combination of $MnBr_2$ and CF_3SO_2Na exhibits a quasi-reversible anodic CV feature at 0.83 V (line d), which we attributed to the Mn^{II}/Mn^{III} redox couple of the CF_3-bound complex. The lower cathodic-to-anodic peak current ratio (I_c/I_a = 0.56) reflects the instability and high reactivity of Mn^{III}–CF_3 under these conditions. CV of **1a** shows a relatively higher oxidation wave larger than 1.5 V, indicating its unlikely interacting with electrodes directly in the

DOI: 10.1021/acs.orglett.8b04010
Org. Lett. XXXX, XXX, XXX–XXX

presence of Mn salt and Langlois' reagent. Addition of **1a** to a mixture of $MnBr_2$ and CF_3SO_2Na resulted in the appearance of two irreversible anodic waves of 0.94 and 1.59 V (line f), which corresponds to the formation of the putative $Mn^{III}-CF_3$ and the single electron oxidation leading to the formation of the final product (*vide infra*, Scheme 5).

Scheme 5. Stoichiometric Experiment

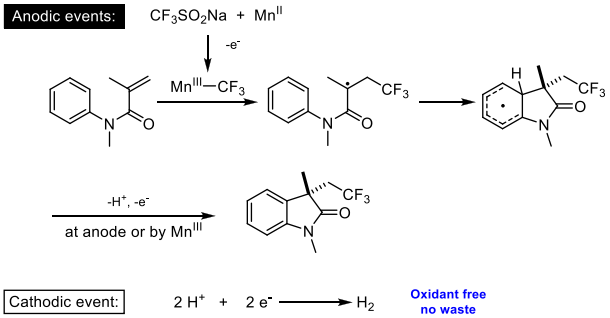


To gain more insight into the mechanism of this Mn-mediated electrochemical trifluoromethylation, the electrochemical reaction of CF_3SO_2Na and Mn^{II} was studied with ^{19}F NMR spectroscopy. In accord with literature, free CF_3SO_2Na reagent shows a singlet peak at −87.5 ppm.[14] When electric current of 1.1 F/mol was applied, the ^{19}F NMR signal of CF_3SO_2Na disappeared, indicating its complete consumption upon electrolysis. New peaks around −73.0 ppm appearance indicated new CF_3 species formation (Figure S4).

Moreover, we performed an electrically controlled stoichiometric experiment. We first applied electricity of 1.1 F/mol to the dioxane/H_2O solution of $MnBr_2$ and CF_3SO_2Na and then introduced substrate **1a**. The mixture was allowed to react in the absence of external electricity, and this two-step reaction afforded the desired product (**2a**) in 11% isolated yield. The result showed that the electrochemically generated high oxidation state Mn species can function both as a CF_3 carrier and an oxidant for the trifluoromethylation/$C(sp^2)-H$ functionalization.

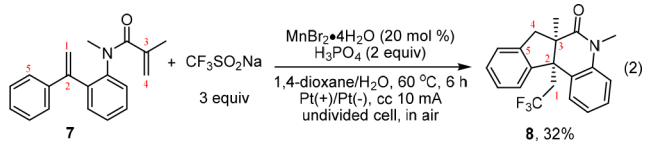
Based on these mechanistic studies, a plausible mechanism for the trifluoromethylation/$C(sp^2)-H$ functionalization is proposed in Scheme 6. At the anode, the $Mn^{III}-CF_3$ species is

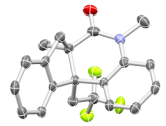
Scheme 6. Proposed Reaction Events on Both Electrodes and in Bulk Solvent



generated by anodic oxidation of Mn^{II} in the presence of Langlois reagent. Subsequently, Mn-assisted delivery of $CF_3\cdot$ to the olefin moiety provides a transient carbon centered radical. Further radical addition to the aromatic ring followed by either anode or Mn^{III}-mediated oxidation furnishes the final $C(sp^2)-H$ functionalization product. At the cathode, reduction of proton to dihydrogen takes place to balance the overall transformation.

Finally, we found that this electrochemical C−H trifluoromethylation method could be applied in the rapid construction of complex ring systems. Under the same reaction conditions as described above, trifluoromethlated product **8** featuring bicyclic ring systems could be conveniently synthesized in 32% yield (eq 2). Further extension of this electrochemical trifluoromethylation process to the preparation of other complex polycyclic compounds is currently underway in our laboratory.





X-ray structure of **8**

In summary, we have developed a general Mn-mediated electrochemical protocol for the trifluoromethylation/$C(sp^2)-H$ functionalization process. This method provides a sustainable means for the synthesis of a variety of trifluoromethylated oxindoles and related heterocycles. We expect that these efforts will guide the further development of synthetically useful electrochemical organic transformations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b04010.

Experimental procedures, additional information, and characterization data (PDF)

Accession Codes

CCDC 1885350 and 1890462 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: fmo@pku.edu.cn.

ORCID

Lei Zhang: 0000-0001-9031-4318
Guoquan Liu: 0000-0003-0680-4811
Yang Yang: 0000-0002-4956-2034
Fanyang Mo: 0000-0002-4140-3020

Present Address

⊥Jiangsu Weiming Environmental Protection S&T Co., ltd.

Notes

The authors declare no competing financial interest.

DOI: 10.1021/acs.orglett.8b04010
Org. Lett. XXXX, XXX, XXX−XXX

■ ACKNOWLEDGMENTS

The project was supported by the Natural Science Foundation of China (Grants 21772003). We also thank the "1000-Youth Talents Plan" and Peking University for start-up funds.

■ REFERENCES

(1) (a) Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881. (b) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320.

(2) Peter, J. *ChemBioChem* **2004**, *5*, 570.

(3) (a) Iacono, S. T.; Iyer, S. S., Eds. *Handbook of Fluoropolymer Science and Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, 2014. (b) Hiyama, T.; Yamamoto, H., Fluorine-Containing Materials. In *Organofluorine Compounds: Chemistry and Applications*, Yamamoto, H., Ed. Springer Berlin Heidelberg: Berlin, Heidelberg, 2000; pp 183.

(4) (a) Furuya, T.; Kamlet, A. S.; Ritter, T. *Nature* **2011**, *473*, 470. (b) Nie, J.; Guo, H.-C.; Cahard, D.; Ma, J.-A. *Chem. Rev.* **2011**, *111*, 455. (c) Tomashenko, O. A.; Grushin, V. V. *Chem. Rev.* **2011**, *111*, 4475. (d) Studer, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 8950. (e) Sebastián, B. V.; Beatriz, L.; Al, P. *Chem. - Eur. J.* **2014**, *20*, 16806. (f) Charpentier, J.; Früh, N.; Togni, A. *Chem. Rev.* **2015**, *115*, 650. (g) Liu, X.; Xu, C.; Wang, M.; Liu, Q. *Chem. Rev.* **2015**, *115*, 683. (h) Wang, L.; Studer, A. *Org. Lett.* **2017**, *19*, 5701. (i) Kautzky, J. A.; Wang, T.; Evans, R. W.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2018**, *140*, 6522. (j) Le, C.; Chen, T. Q.; Liang, T.; Zhang, P.; MacMillan, D. W. C. *Science* **2018**, *360*, 1010. (k) Lubbesmeyer, M.; Leifert, D.; Schafer, H.; Studer, A. *Chem. Commun.* **2018**, *54*, 2240.

(5) (a) Moeller, K. D. *Tetrahedron* **2000**, *56*, 9527. (b) Yoshida, J.-i.; Kataoka, K.; Horcajada, R.; Nagaki, A. *Chem. Rev.* **2008**, *108*, 2265. (c) Francke, R.; Little, R. D. *Chem. Soc. Rev.* **2014**, *43*, 2492. (d) Horn, E. J.; Rosen, B. R.; Baran, P. S. *ACS Cent. Sci.* **2016**, *2*, 302. (e) Yan, M.; Kawamata, Y.; Baran, P. S. *Chem. Rev.* **2017**, *117*, 13230. (f) Jiang, Y.; Xu, K.; Zeng, C. *Chem. Rev.* **2018**, *118*, 4485. (g) Möhle, S.; Zirbes, M.; Rodrigo, E.; Gieshoff, T.; Wiebe, A.; Waldvogel, S. R. *Angew. Chem., Int. Ed.* **2018**, *57*, 6018. (h) Tang, S.; Liu, Y.; Lei, A. *Chem.* **2018**, *4*, 27. (i) Waldvogel, S. R.; Lips, S.; Selt, M.; Riehl, B.; Kampf, C. J. *Chem. Rev.* **2018**, *118*, 6706. (j) Wiebe, A.; Gieshoff, T.; Möhle, S.; Rodrigo, E.; Zirbes, M.; Waldvogel, S. R. *Angew. Chem., Int. Ed.* **2018**, *57*, 5594.

(6) (a) Liu, Q.; Sun, B.; Liu, Z.; Kao, Y.; Dong, B.-W.; Jiang, S.-D.; Li, F.; Liu, G.; Yang, Y.; Mo, F. *Chem. Sci.* **2018**, *9*, 8731. (b) Zhang, L.; Zhang, Z.; Hong, J.; Yu, J.; Zhang, J.; Mo, F. *J. Org. Chem.* **2018**, *83*, 3200. (c) Zhang, L.; Zhang, Z.; Zhang, J.; Li, K.; Mo, F. *Green Chem.* **2018**, *20*, 3916.

(7) Tommasino, J.-B.; Brondex, A.; Médebielle, M.; Thomalla, M.; Langlois, B. R.; Billard, T. *Synlett* **2002**, *2002*, 1697.

(8) O'Brien, A. G.; Maruyama, A.; Inokuma, Y.; Fujita, M.; Baran, P. S.; Blackmond, D. G. *Angew. Chem., Int. Ed.* **2014**, *53*, 11868.

(9) (a) Ye, K.-Y.; Pombar, G.; Fu, N.; Sauer, G. S.; Keresztes, I.; Lin, S. *J. Am. Chem. Soc.* **2018**, *140*, 2438. (b) Ye, K.-Y.; Song, Z.; Sauer, G. S.; Harenberg, J. H.; Fu, N.; Lin, S. *Chem. - Eur. J.* **2018**, *24*, 12274. (c) Zhang, L.; Zhang, G.; Wang, P.; Li, Y.; Lei, A. *Org. Lett.* **2018**, *20*, 7396.

(10) (a) Marti, C.; Carreira, E. M. *Eur. J. Org. Chem.* **2003**, *2003*, 2209. (b) Galliford, C. V.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8748. (c) Zhou, F.; Liu, Y.-L.; Zhou, J. *Adv. Synth. Catal.* **2010**, *352*, 1381.

(11) (a) Mu, X.; Wu, T.; Wang, H.-y.; Guo, Y.-l.; Liu, G. *J. Am. Chem. Soc.* **2012**, *134*, 878. (b) Lin, J.-S.; Liu, X.-G.; Zhu, X.-L.; Tan, B.; Liu, X.-Y. *J. Org. Chem.* **2014**, *79*, 7084. (c) Lu, Q.; Liu, C.; Peng, P.; Liu, Z.; Fu, L.; Huang, J.; Lei, A. *Asian J. Org. Chem.* **2014**, *3*, 273. (d) Tang, X.-J.; Thomoson, C. S.; Dolbier, W. R. *Org. Lett.* **2014**, *16*, 4594. (e) Li, L.; Deng, M.; Zheng, S.-C.; Xiong, Y.-P.; Tan, B.; Liu, X.-Y. *Org. Lett.* **2014**, *16*, 504. (f) Wei, W.; Wen, J.; Yang, D.; Liu, X.; Guo, M.; Dong, R.; Wang, H. *J. Org. Chem.* **2014**, *79*, 4225. (g) An, Y.; Li, Y.; Wu, J. *Org. Chem. Front.* **2016**, *3*, 570. (h) Sakamoto, R.; Kashiwagi, H.; Selvakumar, S.; Moteki, S. A.; Maruoka, K. *Org. Biomol. Chem.* **2016**, *14*, 6417. (i) Lu, M.; Liu, Z.; Zhang, J.; Tian, Y.; Qin, H.; Huang, M.; Hu, S.; Cai, S. *Org. Biomol. Chem.* **2018**, *16*, 6564.

(12) During the preparation of this work, a similar work was reported by Zeng. Jiang, Y.-Y.; Dou, G.-Y.; Xu, K.; Zeng, C.-C. *Org. Chem. Front.* **2018**, *5*, 2573.

(13) (a) Fu, N.; Sauer, G. S.; Lin, S. *J. Am. Chem. Soc.* **2017**, *139*, 15548. (b) Fu, N.; Sauer, G. S.; Saha, A.; Loo, A.; Lin, S. *Science* **2017**, *357*, 575.

(14) Langlois, B. R.; Billard, T.; Mulatier, J.-C.; Yezeguelian, C. *J. Fluorine Chem.* **2007**, *128*, 851.

DOI: 10.1021/acs.orglett.8b04010
Org. Lett. XXXX, XXX, XXX−XXX