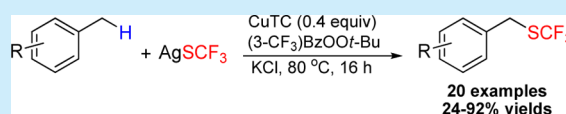


Copper-Catalyzed Direct Trifluoromethylthiolation of Benzylic C–H Bonds via Nondirected Oxidative C(sp³)–H ActivationChao Chen,[†] Xiu-Hua Xu,[†] Bin Yang,[†] and Feng-Ling Qing^{*,†,‡}[†]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China[‡]College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China

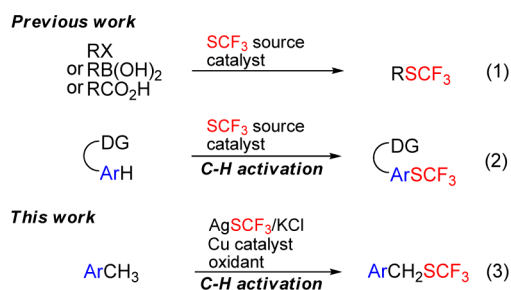
S Supporting Information

ABSTRACT: A copper-catalyzed trifluoromethylthiolation of benzylic sp³ C–H bonds was developed via nondirected oxidative C–H activation using readily prepared and stable AgSCF₃. This reaction provides a novel and straightforward method for the preparation of various benzyl trifluoromethyl sulfides.



The incorporation of fluorine-containing groups into an organic molecule can substantially change the chemical, physical, and biological properties of the parent compound.¹ Among various fluorine-containing groups, the trifluoromethylthio group (CF₃S–) has attracted special interest because of its remarkable properties, in particular the strong electron-withdrawing effect and extremely high lipophilicity.² Thus, CF₃S-containing compounds have shown unique biological activities.³ There are mainly two approaches for the formation of trifluoromethylthiolated compounds: trifluoromethylation of sulfur-containing compounds (the formation of the RS–CF₃ bond)⁴ and trifluoromethylthiolation of different substrates (the formation of the R–SCF₃ bond).^{5,6} Recently, impressive progress has been made in transition-metal-catalyzed trifluoromethylthiolation reactions [Scheme 1, eq 1].⁶ These methods

Scheme 1. Transition-Metal-Catalyzed Trifluoromethylthiolation



mentioned above require prefunctionalized starting materials. Consequently, the direct C–H trifluoromethylthiolation represents an attractive alternative on account of its high atom and step economy; however, this approach has been rarely explored. In 2012, Daugulis reported the first example of a copper-catalyzed trifluoromethylthiolation of sp² aromatic C–H bonds using CF₃SSCF₃ as the electrophilic reagent [Scheme 1, eq 2].^{7a} Very recently, Shen developed a Pd-catalyzed

trifluoromethylthiolation of aryl C–H bonds [Scheme 1, eq 2].^{7b} In both reaction systems, directing groups (DGs) were needed to assist the transformations and only sp² C–H bond activation was accomplished. Thus, it is highly desirable to develop other methods for direct trifluoromethylthiolation of C–H bonds, especially sp³ C–H bonds.

Recently, various methods have been developed for direct transformations of benzylic C–H bonds into C–C,⁸ C–N,⁹ C–O,¹⁰ and C–F bonds.¹¹ No examples, however, have been reported for the C–S bond formation by direct benzylic C–H activation. Inspired by these intriguing studies and in continuation of our research interest in the development of new methods for trifluoromethylthiolation reaction,^{5c,6b,12} we hypothesized that the direct transformation of the benzylic C–H bond into the C–SCF₃ bond would be possible in the presence of a suitable catalyst, oxidant, and trifluoromethylthio (CF₃S–) source. Herein, we describe the Cu-catalyzed trifluoromethylthiolation of benzylic sp³ C–H bonds from toluene analogues via nondirected oxidative activation with readily prepared and stable AgSCF₃ [Scheme 1, eq 3]. This work is the first example of transition-metal-catalyzed direct formation of C(sp³)–SCF₃ bonds, and it is the most straightforward method for the preparation of benzyl trifluoromethyl sulfides, compared to other methods.¹³

The main challenges in our reaction system are the activation of C(sp³)–H bonds without using directing groups and using a catalytic amount of metal reagent for the formation of C(sp³)–SCF₃ bonds. In 2007, Li's group reported FeCl₂-catalyzed oxidative activation of benzylic C–H bonds with *tert*-butyl peroxide for the formation of C–C bonds.¹⁴ Inspired by their work, we started optimizing the reaction conditions with excess toluene as the substrate and AgSCF₃ as the trifluoromethylthiolation reagent. The desired compound was obtained in only 2% yield detected by ¹⁹F NMR (Table 1, entry 1). We surmised

Received: May 15, 2014

Table 1. Optimization of Reaction Conditions^a

entry	catalyst	oxidant	additive	yield of 3a ^b
1	FeCl ₂	<i>t</i> -BuOO <i>t</i> -Bu	—	2%
2	FeCl ₂	<i>t</i> -BuOO <i>t</i> -Bu	<i>n</i> -Bu ₄ NI	5%
3	FeCl ₂	<i>t</i> -BuOOH	<i>n</i> -Bu ₄ NI	0%
4	FeCl ₂	PhOO <i>t</i> -Bu	<i>n</i> -Bu ₄ NI	7%
5	FeCl ₂	a	<i>n</i> -Bu ₄ NI	11%
6	FeCl ₂	b	<i>n</i> -Bu ₄ NI	8%
7	Pd(OAc) ₂	a	<i>n</i> -Bu ₄ NI	0%
8	CuCl	a	<i>n</i> -Bu ₄ NI	41%
9	CuBr	a	<i>n</i> -Bu ₄ NI	36%
10	CuTC	a	<i>n</i> -Bu ₄ NI	45%
11	CuSCN	a	<i>n</i> -Bu ₄ NI	26%
12	[MeCN] ₄ CuPF ₆	a	<i>n</i> -Bu ₄ NI	35%
13	[MeCN] ₄ CuBF ₆	a	<i>n</i> -Bu ₄ NI	30%
14	(CuOTf) ₂ C ₆ H ₆	a	<i>n</i> -Bu ₄ NI	22%
15	CuTC	a	<i>n</i> -Bu ₄ NBr	49%
16	CuTC	a	<i>n</i> -Bu ₄ NCl	52%
17	CuTC	a	Me ₄ NCl	17%
18	CuTC	a	Et ₄ NCl	18%
19	CuTC	a	(<i>n</i> -C ₆ H ₁₄) ₄ NCl	65%
20	CuTC	a	LiCl	81%
21	CuTC	a	NaCl	84%
22	CuTC	a	KCl	92%
23 ^c	CuTC	a	KCl	75%
24	—	a	KCl	0%
25 ^d	CuTC	a	KCl	14%
26 ^d	—	a	KCl	12%

^aReaction conditions: AgSCF₃ (0.2 mmol), **1a** (60 equiv, 12.0 mmol), additive (0.2 mmol), catalyst (0.08 mmol), oxidant (0.4 mmol), 80 °C, 16 h, under Ar. ^bYields determined by ¹⁹F NMR spectroscopy using fluorobenzene as an internal standard. ^cCatalyst (0.04 mmol). ^dCuSCF₃ (0.2 mmol) instead of AgSCF₃ (0.2 mmol).

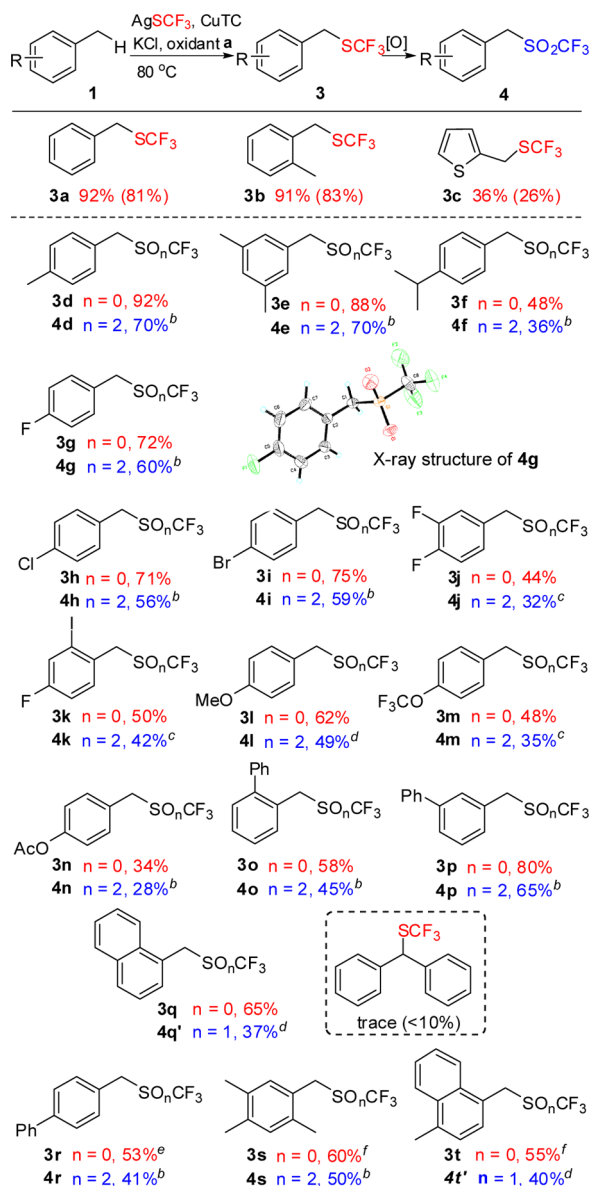
that AgSCF₃ was not active enough for this reaction. In 2000, Clark reported that the addition of *n*-Bu₄NI to AgSCF₃ in acetonitrile resulted in the formation of a reactive source of [SCF₃][−].¹⁵ Based on this work, *n*-Bu₄NI was added to the reaction system, and the yield was slightly improved to 5% (Table 1, entry 2). Having seen these initial results in hand, the optimization of reaction conditions was continued from screening the oxidants, which should lead to the generation of a benzyl radical. Among several oxidants, (3-CF₃)BzOO*t*-Bu (**a**) was proven to be optimal, increasing the yield to 11% (Table 1, entries 2–6). This unique oxidant **a** was developed by Powell and Fan and used in their reaction system for the amination of benzylic C–H bonds in 2010.¹⁶ Then, we focused on the metal catalyst, which was vital to the catalytic cycle. Two of the other metals Pd(OAc)₂ and CuCl gave totally different results (Table 1, entries 7 and 8). No desired product was obtained when Pd(OAc)₂ was used, and the yield was sharply increased to 41% with CuCl as the catalyst. Encouraged by the result caused by CuCl, different Cu salts were then screened (Table 1, entries 9–14), and CuTC was selected. To further improve the yield, different additives were investigated. This

was carried out from two aspects. In the case of anions, *n*-Bu₄NCl showed higher activity than *n*-Bu₄NI and *n*-Bu₄NBr (Table 1, entries 15 and 16). In the case of cations, the yields were found to increase when the alkyl chain became longer (Table 1, entries 17–19). To our delight, all the alkali metal chlorides gave good yields (Table 1, entries 20–22). Particularly, the yield reached as high as 92% when KCl was added. It was noteworthy that the yield dropped to 75% when the amount of CuTC decreased to 0.2 equiv and no desired product was obtained in the absence of CuTC (Table 1, entries 23 and 24). These results showed the important role of a metal catalyst in our reaction system. When CuSCF₃ was used as the trifluoromethylthio source, low yields were obtained whether CuTC was added or not (Table 1, entries 25 and 26).

Under the optimized reaction conditions, various toluene analogues were tested as the substrates for the direct benzylic C–H trifluoromethylthiolation reaction. As shown in Scheme 2, different electron-donating or -withdrawing substituents, such as alkyl, alkoxy, halogen, and aryl groups, at different positions of the aromatic ring were all well tolerated and the desired products were obtained in moderate to excellent yields. It was noteworthy that halogens, such as F, Cl, and Br, were stable in our reaction system. No C–X (F, Cl, and Br) functionalized product was obtained. For the heteroaromatic compound **1c**, the yield of product **3c** was lower than that of the aromatic analogue, probably because the coordination of the heteroatom to copper affected the catalytic cycle. In the case of substrate **1f** bearing two different benzylic H-atoms, a trace of byproduct was detected in the crude reaction mixture. Unfortunately, the activation of secondary benzylic C–H bonds was not successful, giving the desired products in low yields (<10%). To our delight, moderate yields of products **3r–t** were obtained when the amount of substrates was decreased to 6 or 10 equiv. Moreover, this method can also be applied in the synthesis of benzyl trifluoromethyl sulfide derivatives. Benzyl trifluoromethanesulfones **4** and trifluoromethanesulfoxides **4'** were prepared from compounds **1** in two steps by trifluoromethylthiolation and subsequent oxidation, without purification of intermediates **3**.

Based on the well-established Kharasch–Sosnovsky reaction,¹⁷ a plausible mechanism for the Cu-catalyzed oxidative trifluoromethylthiolation of benzylic C–H bonds is proposed in Scheme 3. First, in the presence of a Cu(I) catalyst, the homolytic cleavage of oxidant **a** gives Cu(II) carboxylate **A** and *tert*-butoxy radical **B**. Sequentially the intermediate **B** abstracts a benzylic H-atom from the substrate to afford the benzyl radical **C**, which then reacted with intermediate **A** giving the Cu(III) complex **D**.¹⁸ Complex **D** was converted to Cu(III) complex **E** by reacting with trifluoromethanethiolate, prepared from the reaction of AgSCF₃ and KCl,¹⁵ through an anion-exchange process. The last step is reductive elimination of complex **E** to afford the final product along with regeneration of the active Cu(I) species for the next catalytic cycle. Alternatively, complex **D** undergoes reductive elimination to give intermediate **F**.¹⁹ However, when **F** reacted with AgSCF₃/KCl, no desired product was obtained (see the Supporting Information); thus, **F** was the byproduct of this reaction system.

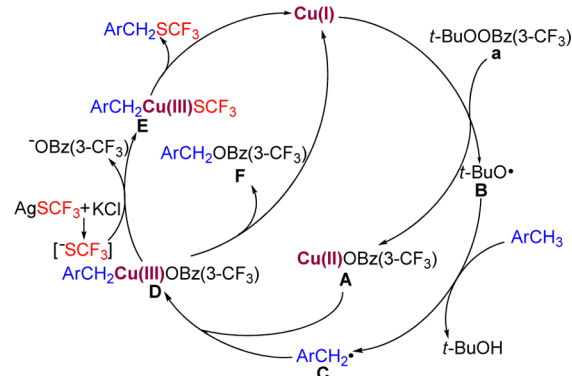
The influence of the catalyst, oxidant, and additive to the yield (Table 1) can be well explained according to the above mechanism. First, it is very clear that the Cu catalyst is crucial in the catalytic cycle. Second, the oxidant plays an important role in this reaction system. Its oxidative ability affects the formation of intermediate **A**, and its coordination property to copper is

Scheme 2. Screening Scope of Substrates^a

^aReaction conditions: AgSCF_3 (0.2 mmol), KCl (0.2 mmol), **1** (12.0 mmol), CuTC (0.08 mmol), Oxidant **a** (0.4 mmol), 80 °C, 16 h, under Ar, yields determined by ^{19}F NMR using fluorobenzene as an internal standard (isolated yields in parentheses). ^b 30 wt % H_2O_2 (1.6 mmol), AcOH (3.0 mL), 90 °C, under Ar, isolated yields for two steps. ^c CrO_3 (0.01 mmol), H_5IO_6 (0.8 mmol), MeCN (4.0 mL), rt, isolated yields for two steps. ^d Condition **a**, temperature = 40 °C. ^e **1** (2.0 mmol, 10 equiv), DCE (1.6 mL) was used as the solvent. ^f **1** (1.2 mmol, 6 equiv), DCE (1.6 mL) was used as the solvent.

necessary to stabilize Cu(II) complex **A** and Cu(III) complex **D**. Moreover, as mentioned above, there are two competing reactions from intermediate **D**: anion exchange to intermediate **E** and reductive elimination to compound **F**. The good leaving ability of the $\text{OBz(3-CF}_3\text{)}$ group makes the anion-exchange step much easier, which probably is the major reason for choosing oxidant **a**. Last, the combination of the additive and AgSCF_3 produces a new source of $[\text{SCF}_3]^-$, whose nucleophilic ability is also important in the anion-exchange step, thus affecting the yield of the desired compound.

Scheme 3. Proposed Mechanism for Benzylic C–H Trifluoromethylthiolation



In conclusion, the first Cu-catalyzed direct trifluoromethylthiolation of benzylic sp^3 C–H bonds has been developed. In this reaction system, $t\text{-BuOOBz(3-CF}_3\text{)}$ was used as the oxidant and $\text{AgSCF}_3/\text{KCl}$ was used as the active trifluoromethylthio source. Various benzyl trifluoromethyl sulfides were conveniently prepared in moderate to excellent yields. Further studies to probe the mechanism of this current reaction and to evaluate the direct trifluoromethylthiolation of other types of sp^3 C–H bonds are in progress.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and spectral data for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: flq@mail.sioc.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (21072028, 20832008) and the National Basic Research Program of China (2012CB21600) for funding this work.

■ REFERENCES

- (1) For selected reviews, see: (a) Tomashenko, O. A.; Grushin, V. V. *Chem. Rev.* **2011**, *111*, 4475. (b) Meanwell, N. A. *J. Med. Chem.* **2011**, *54*, 2529. (c) Liang, T.; Neumann, C. N.; Ritter, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 8214. (d) Wang, J.; Sánchez-Roselló, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, H. *Chem. Rev.* **2014**, *114*, 2432.
- (2) (a) Leo, A.; Hansch, C.; Elkins, D. *Chem. Rev.* **1971**, *71*, 525. (b) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. (c) Leroux, F.; Jeschke, P.; Schlosser, M. *Chem. Rev.* **2005**, *105*, 827. (d) Manteau, B.; Pazenok, S.; Vors, J. P.; Leroux, F. R. *J. Fluorine Chem.* **2010**, *131*, 140.
- (3) For selected examples, see: (a) Sharpe, T. R.; Cherkofsky, S. C.; Hewes, W. E.; Smith, D. H.; Gregory, W. A.; Haber, S. B.; Leadbetter, M. R.; Whitney, J. G. *J. Med. Chem.* **1985**, *28*, 1188. (b) Houston, M. E., Jr.; Jagt, D. L. V.; Honek, J. F. *Bioorg. Med. Chem. Lett.* **1991**, *1*, 623. (c) Chen, J.; Dixon, B. R.; Dumas, J.; Brittelli, D. *Tetrahedron Lett.* **1999**, *40*, 9195. (d) Beeler, A. B.; Schlenk, D. K.; Rimoldi, J. M. *Tetrahedron Lett.* **2001**, *42*, 5371. (e) Lesuisse, D.; Mauger, J.; Nemecek, C.; Maignan, S.; Boiziau, J.; Harlow, G.; Hittinger, A.; Ruf,

S.; Strobel, H.; Nair, A.; Ritter, K.; Malleron, J.-L.; Dagallier, A.; El-Ahmad, Y.; Guilloteau, J.-P.; Guizani, H.; Bouchard, H.; Venot, C. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 2224.

(4) For selected examples, see: (a) Kieltisch, I.; Eisenberger, P.; Togni, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 754. (b) Cherkupally, P.; Beier, P. *Tetrahedron Lett.* **2010**, *51*, 252. (c) Gouault-Bironneau, S.; Timoshenko, V. M.; Grellepois, F.; Portella, C. *J. Fluorine Chem.* **2012**, *134*, 164. (d) Kawai, H.; Yuan, Z.; Tokunaga, E.; Shibata, N. *Org. Biomol. Chem.* **2013**, *11*, 1446. (e) Riofski, M. V.; Hart, A. D.; Colby, D. A. *Org. Lett.* **2013**, *15*, 208. (f) Danoun, G.; Bayarmagnai, B.; Grünberg, M. F.; Gooßen, L. J. *Chem. Sci.* **2014**, *5*, 1312.

(5) For selected examples, see: (a) Ferry, A.; Billard, T.; Langlois, B. R.; Bacque, E. *Angew. Chem., Int. Ed.* **2009**, *48*, 8551. (b) Baert, F.; Colomb, J.; Billard, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 10382. (c) Chen, C.; Chu, L.; Qing, F.-L. *J. Am. Chem. Soc.* **2012**, *134*, 12454. (d) Weng, Z.; He, W.; Chen, C.; Lee, R.; Tan, D.; Lai, Z.; Kong, D.; Yuan, Y.; Huang, K.-W. *Angew. Chem., Int. Ed.* **2013**, *52*, 1548. (e) Alazet, S.; Zimmer, L.; Billard, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 10814. (f) Bootwicha, T.; Liu, X.; Pluta, R.; Atodiresoi, I.; Rueping, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 12856. (g) Wang, X.; Yang, T.; Cheng, X.; Shen, Q. *Angew. Chem., Int. Ed.* **2013**, *52*, 12860. (h) Xiao, Q.; Sheng, J.; Chen, Z.; Wu, J. *Chem. Commun.* **2013**, *49*, 8647. (i) Li, S.-G.; Zard, S. *Org. Lett.* **2013**, *15*, 5898. (j) Vinogradova, E. V.; Müller, P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2014**, *53*, 3125. (k) Sheng, J.; Li, S.; Wu, J. *Chem. Commun.* **2014**, *50*, 578. (l) Rueping, M.; Liu, X.; Bootwicha, T.; Pluta, R.; Merckens, C. *Chem. Commun.* **2014**, *50*, 2508. (m) Deng, Q.-H.; Rettenmeier, C.; Wadepohl, H.; Gade, L. H. *Chem.—Eur. J.* **2014**, *20*, 93. (n) Wang, X.; Zhou, Y.; Ji, G.; Wu, G.; Li, M.; Zhang, Y.; Wang, J. *Eur. J. Org. Chem.* **2014**, 3093. (o) Hu, M.; Rong, J.; Miao, W.; Ni, C.; Han, Y.; Hu, J. *Org. Lett.* **2014**, *16*, 2030. (p) Zhu, X.-L.; Xu, J.-H.; Cheng, D.-J.; Zhao, L.-J.; Liu, X.-Y.; Tan, B. *Org. Lett.* **2014**, *16*, 2192. (q) Zhu, P.; He, X.; Chen, X.; You, Y.; Yuan, Y.; Weng, Z. *Tetrahedron* **2014**, *70*, 672.

(6) (a) Teverovskiy, G.; Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 7312. (b) Chen, C.; Xie, Y.; Chu, L.; Wang, R.-W.; Zhang, X.; Qing, F.-L. *Angew. Chem., Int. Ed.* **2012**, *51*, 2492. (c) Zhang, C.-P.; Vicić, D. A. *Chem.—Asian J.* **2012**, *7*, 1756. (d) Zhang, C.-P.; Vicić, D. A. *J. Am. Chem. Soc.* **2012**, *134*, 183. (e) Shao, X.; Wang, X. Q.; Yang, T.; Lu, L.; Shen, Q. *Angew. Chem., Int. Ed.* **2013**, *52*, 3457. (f) Rueping, M.; Tolstoluzhsky, N.; Nikolaenko, P. *Chem.—Eur. J.* **2013**, *19*, 14043. (g) Yang, Y.-D.; Azuma, A.; Tokunaga, E.; Yamasaki, M.; Shiro, M.; Shibata, N. *J. Am. Chem. Soc.* **2013**, *135*, 8782. (h) Pluta, R.; Nikolaenko, P.; Rueping, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 1650. (i) Hu, F.; Shao, X.; Zhu, D.; Lu, L.; Shen, Q. *Angew. Chem., Int. Ed.* **2014**, DOI: 10.1002/anie.201402573. (j) Kang, K.; Xu, C.-F.; Shen, Q. *Org. Chem. Front.* **2014**, *1*, 294.

(7) (a) Tran, L. D.; Popov, I.; Daugulis, O. *J. Am. Chem. Soc.* **2012**, *134*, 18237. (b) Xu, C.; Shen, Q. *Org. Lett.* **2014**, *16*, 2046.

(8) For selected examples, see: (a) Zhang, B.; Xiang, S.-K.; Zhang, L.-H.; Cui, Y.; Jiao, N. *Org. Lett.* **2011**, *13*, 5212. (b) Xie, P.; Xie, Y.; Qian, B.; Zhou, H.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2012**, *134*, 9902. (c) Dastbaravardeh, N.; Schnürch, M.; Mihovilovic, M. D. *Org. Lett.* **2012**, *14*, 1930. (d) Nanjo, T.; Tsukano, C.; Takemoto, Y. *Org. Lett.* **2012**, *14*, 4270. (e) Schweitzer-Chaput, B.; Sud, A.; Pintér, S.; Dehn, S.; Schulze, P.; Klusmann, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 13228.

(9) For selected examples, see: (a) Kim, H. J.; Kim, J.; Cho, S. H.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 16382. (b) Ni, Z.; Zhang, Q.; Xiong, T.; Zheng, Y.; Li, Y.; Zhang, H.; Zhang, J.; Liu, Q. *Angew. Chem., Int. Ed.* **2012**, *51*, 1244. (c) Iglesias, Á.; Álvarez, R.; Lera, Á. R.; Muñiz, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 2225. (d) Nörder, A.; Warren, S. A.; Herdtweck, E.; Huber, S. M.; Bach, T. *J. Am. Chem. Soc.* **2012**, *134*, 13524. (e) Xue, Q.; Xie, J.; Li, H.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2013**, *49*, 3700.

(10) For selected examples, see: (a) Churakova, E.; Kluge, M.; Ullrich, R.; Arends, I.; Hofrichter, M.; Hollmann, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 10716. (b) Novák, P.; Correa, A.; Gallardo-Donaire, J.; Martin, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 12236. (c) Xie, Y.; Yang, Y.; Huang, L.; Zhang, X.; Zhang, Y. *Org. Lett.* **2012**, *14*, 1238. (d) Li, Y.;

Li, Z.; Xiong, T.; Zhang, Q.; Zhang, X. *Org. Lett.* **2012**, *14*, 3522. (e) Pandey, G.; Pal, S.; Laha, R. *Angew. Chem., Int. Ed.* **2013**, *52*, 5146.

(11) For selected examples, see: (a) Bloom, S.; Pitts, C. R.; Miller, D. C.; Haselton, N.; Holl, M. G.; Urheim, E.; Lectka, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 10580. (b) McMurtrey, K. B.; Racowski, J. M.; Sanford, M. S. *Org. Lett.* **2012**, *14*, 4094. (c) Liu, W.; Groves, J. T. *Angew. Chem., Int. Ed.* **2013**, *52*, 6024. (d) Bloom, S.; Pitts, C. R.; Woltornist, R.; Griswold, A.; Holl, M. G.; Lectka, T. *Org. Lett.* **2013**, *15*, 1722. (e) Amaoka, Y.; Nagatomo, M.; Inoue, M. *Org. Lett.* **2013**, *15*, 2160.

(12) (a) Yang, Y.; Jiang, X.; Qing, F.-L. *J. Org. Chem.* **2012**, *77*, 7538. (b) Liu, J.; Chu, L.; Qing, F.-L. *Org. Lett.* **2013**, *15*, 894.

(13) (a) Haas, A.; Krächtler, H.-U. *Chem. Ber.* **1988**, *121*, 1833. (b) Tordeux, M.; Francese, C.; Wakselman, C. *J. Fluorine Chem.* **1989**, *43*, 27. (c) Kolomeitsev, A. A.; Chababenko, K. Y.; Röschenhaler, G.-V.; Yagupolskii, Y. L. *Synthesis* **1994**, 145. (d) Billard, T.; Large, S.; Langlois, B. R. *Tetrahedron Lett.* **1997**, *38*, 65. (e) Kolomeitsev, A.; Médebielle, M.; Kirsch, P.; Lork, E.; Röschenhaler, G.-V. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2183. (f) Młostoń, G.; Prakash, G. K. S.; Olah, G. A. *Helv. Chim. Acta* **2002**, *85*, 1644. (g) Tyrre, W.; Naumann, D.; Hoge, B.; Yagupolskii, Y. L. *J. Fluorine Chem.* **2003**, *119*, 101. (h) Large-Radix, S.; Billard, T.; Langlois, B. R. *J. Fluorine Chem.* **2003**, *124*, 147. (i) Saint-Jalmes, L. *J. Fluorine Chem.* **2006**, *127*, 85. (j) Kong, D.; Jiang, Z.; Xin, S.; Bai, Z.; Yuan, Y.; Weng, Z. *Tetrahedron* **2013**, *69*, 6046.

(14) Li, Z.; Cao, L.; Li, C.-J. *Angew. Chem., Int. Ed.* **2007**, *46*, 6505.

(15) Adams, D. J.; Clark, J. H. *J. Org. Chem.* **2000**, *65*, 1456.

(16) Powell, D. A.; Fan, H. *J. Org. Chem.* **2010**, *75*, 2726.

(17) (a) Kharasch, M. S.; Sosnovsky, G. *J. Am. Chem. Soc.* **1958**, *80*, 756. (b) Kharasch, M. S.; Sosnovsky, G.; Yang, N. C. *J. Am. Chem. Soc.* **1959**, *81*, 5819.

(18) Eames, J.; Watkinson, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3567.

(19) Borduas, N.; Powell, D. A. *J. Org. Chem.* **2008**, *73*, 7822.