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Copper-Mediated Trifluoromethylation Using Phenyl Trifluoromethyl Sulfoxide

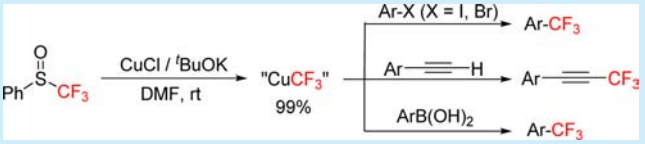
Xinjin Li,[†,‡] Jingwei Zhao,[‡] Liang Zhang,[‡] Mingyou Hu,[‡] Limin Wang,*[,†] and Jinbo Hu*[,‡]

[†]Key Laboratory of Advanced Materials, Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

[‡]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

Supporting Information

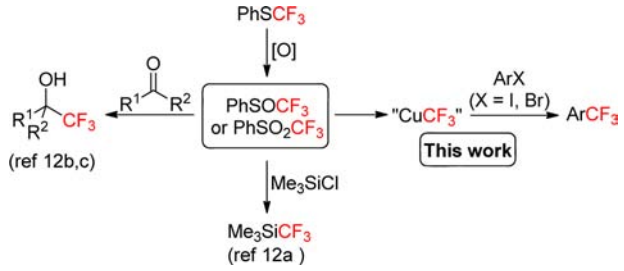
ABSTRACT: A new method for the generation of trifluoromethylcopper ("$CuCF_3$") species from readily available phenyl trifluoromethyl sulfoxide has been developed. The "$CuCF_3$" reagent can be applied in efficient trifluoromethylations of aryl iodides and activated aryl bromides in the absence of additional ligands. Furthermore, the "$CuCF_3$" species can also undergo oxidative cross-coupling with terminal alkynes and arylboronic acids.



Organofluorine compounds have been the subject of increasing research activity in recent years, since the incorporation of fluorine into bioactive compounds could enhance their lipophilicity and metabolic stability, among others.[1,2] In this context, aromatic compounds bearing CF_3 group(s) are frequently used in medicinal and agricultural chemistry. Hence, it is of great interest to develop new methods for the selective introduction of trifluoromethyl groups onto aromatic rings. As a result, various synthetic methods of aromatic trifluoromethylation have been reported, including transition-metal-mediated or -catalyzed trifluoromethylation[3] as well as radical[4] and electrophilic trifluoromethylation.[5] Among various transition-metal-assisted methods for incorporating CF_3 into arenes, copper-mediated trifluoromethylation has been most extensively studied due to its high efficiency and the relatively low cost of copper.[6] Trifluoromethylcopper ("$CuCF_3$"), which is often generated prior to the desired reaction, is a relatively stable and highly useful trifluoromethylating agent.[6f,j,l]

Me_3SiCF_3 (Ruppert–Prakash reagent),[7] a useful nulceophilic trifluoromethylating agent, can be used to generate "$CuCF_3$" utilizing a copper(I) salt.[8] A new method for the efficient generation of "$CuCF_3$" from CF_3H has been developed by Grushin et al. via treatment of CuCl and 2 equiv of ^{t}BuOK.[6l,9] More recently, Mikami et al. have also found that $PhCOCF_3$ can be used to generate "$CuCF_3$" with a similar protocol.[10] Previously, we were interested in the exploration of the synthetic application of fluorinated sulfones, sulfoxides, and sulfoximines.[11] Phenyl trifluoromethyl sulfone ($PhSO_2CF_3$) and phenyl trifluoromethyl sulfoxide ($PhSOCF_3$) as good nucleophilic trifluoromethylation reagents have been investigated.[12] Both $PhSO_2CF_3$ and $PhSOCF_3$ are commercially available and can be easily prepared from $PhSCF_3$ through oxidation (Scheme 1).[13] However, transition-metal-mediated trifluoromethylation with $PhSO_2CF_3$ or $PhSOCF_3$ is rare. It was found that CuI-mediated trifluoromethylation of iodobenzene with $PhSO_2CF_3$ was inefficient, and a 26% yield of benzotrifluoride was obtained.[12b] Herein, we report an efficient method to generate "$CuCF_3$" from $PhSOCF_3$ and its trifluoromethylation of aryl halides, terminal alkynes, and arylboronic acids.

Scheme 1. Preparation and Application of Phenyl Trifluoromethyl Sulfone or Sulfoxide



At the onset of our investigation, we employed phenyl trifluoromethyl sulfone ($PhSO_2CF_3$, **1a**) as the CF_3 source. Into the mixture of CuCl (0.3 mmol) and ^{t}BuOK (2 equiv) in DMF at rt for 30 min, **1a** was added dropwise at the same temperature for 30 min under an argon atmosphere. As expected, a 17% yield of "$CuCF_3$" (δ = −24.1 ppm) was detected by ^{19}F NMR spectroscopy (Table 1, entry 1), which matched well with the previous reported results.[6f,l,8e,9,10] The results obtained under various reaction conditions are listed in Table 1. The use of another nucleophilic base ^{t}BuONa gave a lower yield (Table 1, entry 2), while the addition of ^{t}BuOLi and MeONa did not give the "$CuCF_3$" species at all (Table 1, entries 3–4). There are two possible reasons. First of all, the formed dialkoxycuprate $[K(DMF)][(^tBuO)_2Cu]$ (as reported by Grushin[6l]) has a high nucleophilicity to activate **1a**. Second, the potassium ion plays a

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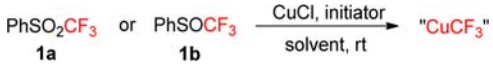
Table 1. Screening of Formation of "$CuCF_3$"[a]



entry	CF_3 source	initiator (equiv)	solvent	"$CuCF_3$"[b] (%)
1	**1a**	^{t}BuOK (2)	DMF	17
2	**1a**	^{t}BuONa (2)	DMF	7
3	**1a**	^{t}BuOLi (3)	DMF	0
4	**1a**	MeONa (2)	DMF	0
5	**1a**	^{t}BuOK (3)	DMF	72
6	**1a**	^{t}BuOK (3.5)	DMF	56
7	**1a**	^{t}BuOK (4)	DMF	48
8[c]	**1a**	^{t}BuOK (3)	DMF	52
9	**1a**	^{t}BuOK (3)	NMP	39
10	**1a**	^{t}BuOK (3)	DMPU	49
11	**1a**	^{t}BuOK (2)	DMSO	13
12	**1b**	^{t}BuOK (3)	DMF	50
13	**1b**	^{t}BuOK (2)	DMF	93
14[d]	**1b**	^{t}BuOK (2)	DMF	96
15[e]	**1b**	**^{t}BuOK (2)**	**DMF**	**99**

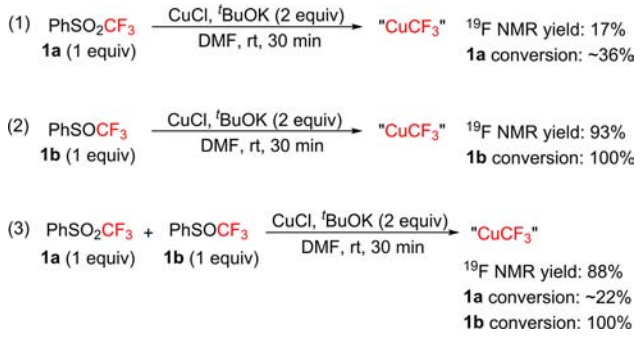
[a]Unless otherwise noted, the reactions were performed by adding CuCl (0.3 mmol) and initiator into solvent (1 mL) at rt, and then **1a** (entries 1−11) or **1b** (entries 12−15) was added into the solution at the same temperature for 30 min under argon atmosphere. [b]Yields were determined by ^{19}F NMR spectroscopy using $PhOCF_3$ as an internal standard. [c]CuI (0.3 mmol) was used. [d]$PhSOCF_3$ (0.33 mmol) was used. [e]$PhSOCF_3$ (0.39 mmol) was used. "$[Cu(CF_3)_2]^-$" (10%, ^{19}F NMR) was produced.

key role in the cupration reaction.[15] When the amount of ^{t}BuOK was increased to 3 equiv, the formation of "$CuCF_3$" was enhanced to a 72% yield (Table 1, entry 5). However, a greater excess of ^{t}BuOK led to a lower yield because of some side reactions (Table 1, entries 6−7). Furthermore, the employment of CuI failed to improve the yield of "$CuCF_3$" (Table 1, entry 8). Other aprotic polar solvents were also tested, but with less success (Table 1, entries 9−11). It is worth noting that the formation of a small amount of CF_3H was always observed in these reactions,[14] which may be caused by the moisture from solvent and/or reagent. This result indicates that CF_3^- is produced in the process of generating "$CuCF_3$".

To improve the yield of "$CuCF_3$", phenyl trifluoromethyl sulfoxide ($PhSOCF_3$, **1b**) was employed as the trifluoromethyl precursor. Disappointedly, only a 50% yield of "$CuCF_3$" was obtained under the optimized conditions on the basis of **1a** (Table 1, entry 12). However, when 2 equiv of ^{t}BuOK were used, to our delight, the yield of "$CuCF_3$" was improved to 93% (Table 1, entry 13). As a result, the generation of CF_3H was also dramatically reduced. A higher yield of "$CuCF_3$" was obtained when the loading of **1b** was increased to 1.1 equiv (Table 1, entry 14). It is noteworthy that a little excess of **1b** results in a new species (−30.6 ppm in ^{19}F NMR spectroscopy), which is assigned as "$[Cu(CF_3)_2]^-$" on the basis of the literature data.[16] Consequently, when 1.3 equiv of **1b** was used, the total yield of "$CuCF_3$" species was increased to 99% (Table 1, entry 15), with 89% contribution from L·$CuCF_3$ (−24.3 ppm in ^{19}F NMR spectroscopy) and 10% from $[Cu(CF_3)_2]^-$ (−30.6 ppm in ^{19}F NMR spectroscopy).

These results indicate that $PhSOCF_3$ is an efficient precursor to generate the "$CuCF_3$" species, and the competing reaction to produce CF_3H can be inhibited. Furthermore, we also compared

Scheme 2. Comparison of $PhSO_2CF_3$ and $PhSOCF_3$ in the Generation of "$CuCF_3$"



the reactivity of $PhSOCF_3$ and $PhSO_2CF_3$ in generating "$CuCF_3$" under the optimal conditions (Scheme 2). The results indicate that $PhSOCF_3$ is much more reactive than $PhSO_2CF_3$ to generate "$CuCF_3$", and that the formation of "$CuCF_3$" generated from $PhSOCF_3$ is less than 30 min (see Supporting Information (SI), section 3 for details). It should be noted that *this is the first report that $PhSOCF_3$ is more efficient than $PhSO_2CF_3$ in the generation of the "$CuCF_3$" species*, which is in sharp contrast to the magnesium-mediated reductive trifluoromethylation of chlorosilanes.[12a] The low reactivity of $PhSO_2CF_3$ for generating the "$CuCF_3$" species could be attributed to the steric hindrance of sulfone (compared to sulfoxide) during the nucleophilic attack of an alkoxide. Indeed, when we used $PhSOCF_3$ as the precursor to generate the "$CuCF_3$" species in the presence of ^{t}BuOK, benzenesulfinate ($PhSO_2{}^tBu$) was produced quantitatively.

Next, we examined the stability of "$CuCF_3$" under various conditions. The "$CuCF_3$" species generated from $PhSOCF_3$ was gradually decomposed under air. Furthermore, the yield of "$CuCF_3$" decreased from 93% to 72% after 24 h under an argon atomsphere at rt. Similar to Grushin's report,[9] we found that the addition of $Et_3N{\cdot}3HF$ could stabilize the "$CuCF_3$" species generated from $PhSOCF_3$ (see SI, section 4.1), but the ^{19}F NMR spectroscopy signal of the stabilized "$CuCF_3$" species shifted slightly from −24.5 to −26.5 ppm, and the signal of $[Cu(CF_3)_2]^-$ at −30.6 ppm was increased.

With an efficient method for generating "$CuCF_3$" in hand (Table 1, entry 15), we further employed the "$CuCF_3$" species for the trifluoromethylation of various aryl halides. Initially, we attempted the reaction of iodobenzene with the stabilized trifluoromethylcopper at rt for 24 h. However, only a trace amount of trifluoromethylated product was detected by ^{19}F NMR spectroscopy. When the reaction was carried out at 50 °C, to our delight, the product benzotrifluoride was formed in 50% yield after 28 h, but no obvious improvement was found when we prolonged the reaction time. Finally, the trifluoromethylation of iodobenzene proceeded smoothly at 80 °C under the standard conditions. Furthermore, it was found that the trifluoromethylation of aryl iodides proceeded well in the absence of any ligands, which is different from the previous reports.[16b−d,17] The representative results are summarized in Scheme 3. Generally, both electron-rich and -deficient aryl iodides reacted well under the optimal conditions. For electron-deficient iodoarenes, nearly quantitative conversions (monitored by GC-MS) were achieved even within 16 h (Scheme 3, **2b**, **2c**, **2f**, **2j**, **2l**). Ether, acetyl, halide, ester, and nitrile were tolerated under the standard reaction conditions. In addition, trifluoromethylated heteroarenes were also obtained in good yields (Scheme 3, **2m**−**2n**). It is noted that thiophene was not observed by GC-MS in the

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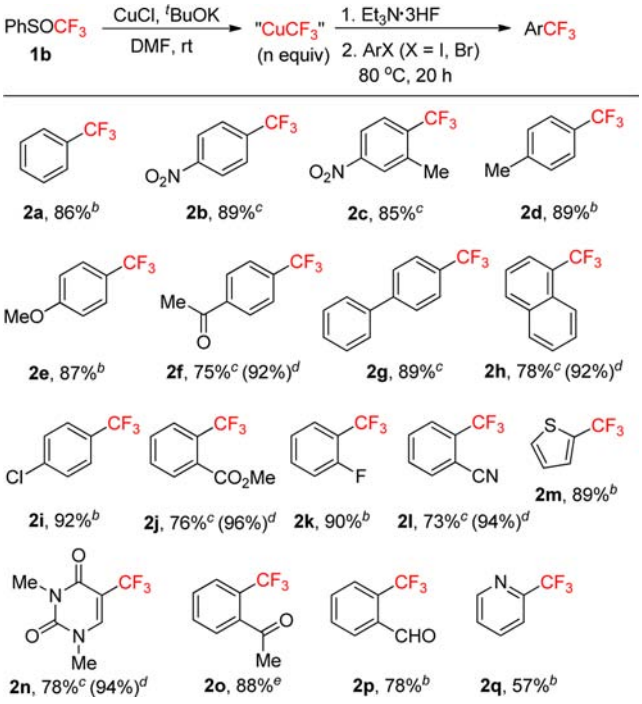
Scheme 3. Trifluoromethylation of Aryl Halides with "$CuCF_3$" Generated from $PhSOCF_3$[a]



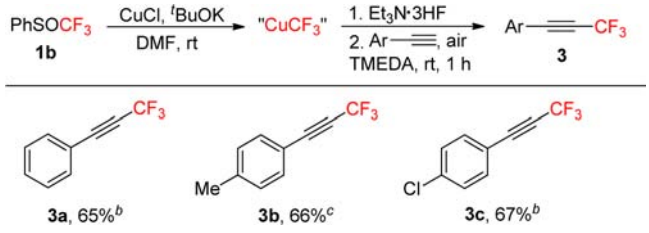
[a]All reactions were performed by adding ArX (X = I, Br) into the pregenerated "$CuCF_3$" species stabilized by $Et_3N{\cdot}3HF$. For **2a−2n**, the substrates were ArI; for **2o−2q**, the substrates were ArBr. [b] Reactions were performed on 0.1 mmol scale (n = 2) in DMF (1 mL) under an argon atmosphere. Yields were determined by ^{19}F NMR spectroscopy using $PhOCF_3$ as an internal standard. [c] Reactions were performed on 0.5 mmol scale (n = 1.5) in DMF (2.5 mL) under an argon atmosphere. Yields were of isolated products. [d] The yields were determined by ^{19}F NMR spectroscopy using $PhOCF_3$ as an internal standard. [e] The reaction was performed on 0.1 mmol scale (n = 2) in DMF (1 mL) under an argon atmosphere, and the yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

trifluoromethylation of 2-iodothiophene, which was shown as a side product reported by Grushin.[9] Compared to iodoarenes, trifluoromethylation of bromoarenes with the copper reagent is known to be more challenging. In our case, only some electron-deficient bromoarenes reacted smoothly with the "$CuCF_3$" species to afford the trifluoromethylated products in moderate to good yields (Scheme 3, **2o−2q**).

The copper-mediated oxidative cross-coupling of trifluoromethylcopper with nucleophilic substrates have proven to be powerful trifluoromethylation strategies.[18] We envisioned that the "$CuCF_3$" species generated from $PhSOCF_3$ may also work well under the standard conditions. Initially, we attempted the oxidative trifluoromethylation of terminal alkynes. We were delighted to find that the corresponding products were obtained in moderate yields when a 2-fold excess of the "$CuCF_3$" reagent was used (Scheme 4). It should be noted that, to inhibit the homocoulping of alkynes, alkynes were added slowly by a syringe pump to the "$CuCF_3$" species in DMF under an air atmosphere. Furthermore, the addition of tetramethylethylenediamine (TMEDA) as a ligand was also the key to enhancing product yields.

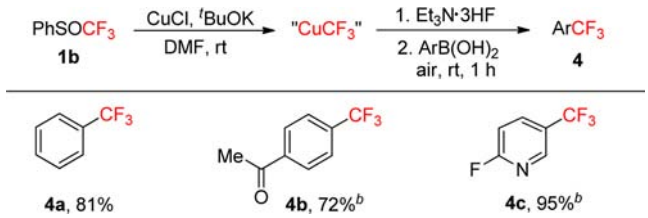
It was also encouraging to find that the trifluoromethylcopper reagent also reacted with arylboronic acids under an air

Scheme 4. Trifluoromethylation of Terminal Alkynes with "$CuCF_3$" Generated from $PhSOCF_3$[a]



[a]All reactions were performed by adding akyne (0.1 mmol) and TMEDA (2 equiv) into the pregenerated "$CuCF_3$" species (2 equiv) stabilized by $Et_3N{\cdot}3HF$. [b] Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. [c] The yield was determined by ^{19}F NMR spectroscopy using $PhOCF_3$ as an internal standard.

Scheme 5. Trifluoromethylation of Arylboronic Acids with "$CuCF_3$" Generated from $PhSOCF_3$[a]



[a]All reactions were performed by adding arylboronic acid (0.1 mmol) into the pregenerated "$CuCF_3$" species (2 equiv) stabilized by $Et_3N{\cdot}3HF$. Yields were determined by ^{19}F NMR spectroscopy using $PhOCF_3$ as an internal standard. [b] TMEDA (0.2 mmol) was used.

atmosphere at rt to give the trifluoromethylated products in up to 95% yield. Some representative results are summarized in Scheme 5.

In summary, we have shown the synthetic applications of phenyl trifluoromethyl sulfones and sulfoxides in copper-mediated trifluoromethylation and developed a new method for the synthesis of the "$CuCF_3$" species from $PhSOCF_3$. It is worth noting that $PhSOCF_3$ is more reactive than $PhSO_2CF_3$ in the formation of the "$CuCF_3$" species (up to 99% yield). The formed "$CuCF_3$" reagent has been found to be remarkably efficient in the trifluoromethylation of aryl iodides in the absence of additional ligands. Some activated aryl bromides can also be trifluoromethylated in moderate to good yields. Furthermore, the oxidative cross-coupling of terminal alkynes or arylboronic acids with the "$CuCF_3$" species has afforded the corresponding products in good yields.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data for products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: wanglimin@ecust.edu.cn.
*E-mail: jinbohu@sioc.ac.cn.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Nagib, D. A.; MacMillan, D. W. C. *Nature* **2011**, *480*, 224. (b) Furuya, T.; Kamlet, A. S.; Ritter, T. *Nature* **2011**, *473*, 470. (c) Prakash, G. K. S.; Jog, P. V.; Batamack, P. T. D.; Olah, G. A. *Science* **2012**, *338*, 1324. (d) Schlosser, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 5432. (e) Ma, J.-A.; Cahard, D. *Chem. Rev.* **2004**, *104*, 6119. (f) Shibata, N.; Mizuta, S.; Kawai, H. *Tetrahedron: Asymmetry* **2008**, *19*, 2633. (f) Qing, F.-L. *Chin. J. Org. Chem.* **2012**, *32*, 815.

(2) (a) Bégué, J.-P.; Bonnet-Delpon, D. *Bioorganic and Medicinal Chemistry of Fluorine*; Wiley: Hoboken, NJ, 2008. (b) Uneyama, K. *Organofluorine Chemistry*; Blackwell: Oxford, U.K., 2006. (c) O'Hagan, D. *Chem. Soc. Rev.* **2008**, *37*, 308. (d) Liang, T.; Neumann, C. N.; Ritter, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 8214. (e) Wu, X.-F; Neumann, H.; Beller, M. *Chem.—Asian J.* **2012**, *7*, 1744.

(3) (a) Burton, D. J.; Yang, Z. *Tetrahedron* **1992**, *48*, 189. (b) McClinton, M. A.; McClinton, D. A. *Tetrahedron* **1992**, *32*, 6555. (c) Tomashenko, O. A.; Grushin, V. V. *Chem. Rev.* **2011**, *111*, 4475.

(4) For selected examples, see: (a) Langlois, B. R.; Laurent, E.; Roidot, N. *Tetrahedron Lett.* **1991**, *32*, 7525. (b) Ji, Y.; Brueckl, T.; Baxter, R. D.; Fujiwara, Y.; Seiple, I. B.; Su, S.; Blackmond, D. G.; Baran, P. S. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 14411. (c) Wakselman, C.; Tordeux, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1701. (d) Sawada, H.; Nakayama, M. *J. Fluorine Chem.* **1990**, *46*, 423. (e) Kamigata, N.; Fukushima, T.; Yoshida, M. *Chem. Lett.* **1990**, *4*, 649. (f) Kino, T.; Nagase, Y.; Ohtsuka, Y.; Yamamoto, K.; Uraguchi, D.; Tokuhisa, K.; Yamakawa, T. *J. Fluorine Chem.* **2010**, *131*, 98. (g) Ye, Y.; Sanford, M. S. *J. Am. Chem. Soc.* **2012**, *134*, 9034.

(5) (a) Umemoto, T. *Chem. Rev.* **1996**, *96*, 1757. (b) Liu, T.; Shen, Q. *Org. Lett.* **2011**, *13*, 2342. (c) Wiehn, M. S.; Vinogradova, E. V.; Togni, A. *J. Fluorine Chem.* **2010**, *131*, 951.

(6) For selected examples, see: (a) McLoughlin, V. C. R.; Thrower, J. *Tetrahedron* **1969**, *25*, 5921. (b) Kobayashi, Y.; Kumadaki, I. *Tetrahedron Lett.* **1969**, *10*, 4095. (c) Kobayashi, Y.; Kumadaki, I. *J. Chem. Soc., Perkin Trans. 1* **1980**, 661. (d) Matsui, K.; Tobita, E.; Ando, M.; Kondo, K. *Chem. Lett.* **1981**, *10*, 1719. (e) Suzuki, H.; Yoshida, Y.; Osuka, A. *Chem. Lett.* **1982**, *11*, 135. (f) Wiemers, D. M.; Burton, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 832. (g) Umemoto, T.; Ando, A. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 447. (h) Chen, Q.-Y.; Wu, S.-W. *J. Chem. Soc., Chem. Comm.* **1989**, 705. (i) Oishi, M.; Kondo, H.; Amii, H. *Chem. Commun.* **2009**, 1909. (j) Morimoto, H.; Tsubogo, T.; Litvinas, N. D.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2011**, *50*, 3793. (k) Knauber, T.; Arikan, F.; Röschenthaler, G.-V.; Gooβen, L. J. *Chem.—Eur. J.* **2011**, *17*, 2689. (l) Zanardi, A.; Novikov, M. A.; Martin, E.; Benet-Buchholz, J.; Grushin, V. V. *J. Am. Chem. Soc.* **2011**, *133*, 20901.

(7) (a) Ruppert, I.; Schlich, K.; Volbach, W. *Tetrahedron Lett.* **1984**, *25*, 2195. (b) Prakash, G. K. S.; Krishnamuti, R.; Olah, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 393.

(8) For selected examples, see: (a) Urata, H.; Fuchikami, T. *Tetrahedron Lett.* **1991**, *32*, 91. (b) Chu, L.; Qing, F.-L. *J. Am. Chem. Soc.* **2010**, *132*, 7262. (c) Chu, L.; Qing, F.-L. *Org. Lett.* **2010**, *12*, 5060. (d) Senecal, T. D.; Parsons, A. T.; Buchwald, S. L. *J. Org. Chem.* **2011**, *76*, 1174. (e) Hu, M.; Ni, C.; Hu, J. *J. Am. Chem. Soc.* **2012**, *134*, 15257. (f) Hu, M.; He, Z.; Gao, B.; Li, L.; Ni, C.; Hu, J. *J. Am. Chem. Soc.* **2013**, *135*, 17302.

(9) Lishchynskyi, A.; Novikov, M. A.; Martin, E.; Escudero-Adán, E. C.; Novák, P.; Grushin, V. V. *J. Org. Chem.* **2013**, *78*, 11126.

(10) Serizawa, H.; Aikawa, K.; Mikami, K. *Chem.—Eur. J.* **2013**, *19*, 17692.

(11) (a) Hu, J. *J. Fluorine Chem.* **2009**, *130*, 1130. (b) Hu, J.; Zhang, W.; Wang, F. *Chem. Commun.* **2009**, 7465. (c) Prakash, G. K. S.; Hu, J. *Acc. Chem. Res.* **2007**, *40*, 921. (d) Ni, C.; Hu, M.; Hu, J. *Chem. Rev.* **2015**, DOI: 10.1021/cr5002386.

(12) (a) Prakash, G. K. S.; Hu, J.; Olah, G. A. *J. Org. Chem.* **2003**, *68*, 4457. (b) Prakash, G. K. S.; Hu, J.; Olah, G. A. *Org. Lett.* **2003**, *5*, 3253. (c) Zhao, Y.; Zhu, J.; Ni, C.; Hu, J. *Synthesis* **2010**, *11*, 1899.

(13) (a) Large, S.; Roques, N.; Langlois, B. R. *J. Org. Chem.* **2000**, *65*, 8848. (b) Russell, J.; Roques, N. *Tetrahedron* **1998**, *54*, 13771.

(14) Barrera, M. D.; Cheburkov, Y.; Lamanna, W. M. *J. Fluorine Chem.* **2002**, *117*, 13.

(15) Konovalov, A. I.; Benet-Buchholz, J.; Martin, E.; Grushin, V. V. *Angew. Chem., Int. Ed.* **2013**, *52*, 11637.

(16) (a) Willert-Porada, M. A.; Burton, D. J.; Baenziger, N. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1633. (b) Dubinina, G. G.; Ogikubo, J.; Vicic, D. A. *Organometallics* **2008**, *27*, 6233. (c) Tomashenko, O. A.; Escudero-Adan, E. C.; Belmonte, M. M.; Grushin, V. V. *Angew. Chem., Int. Ed.* **2011**, *50*, 7655.

(17) Dubinina, G. G.; Furutachi, H.; Vicic, D. A. *J. Am. Chem. Soc.* **2008**, *130*, 8600.

(18) For a recent review, see: Chu, L.; Qing, F.-L. *Acc. Chem. Res.* **2014**, *47*, 1513.

■ NOTE ADDED AFTER ASAP PUBLICATION

In Table 1, the initiators in entries 1 and 2 were corrected on December 29, 2014; this was due to a production error.

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