DOI: 10.1002/adsc.201000825

Copper-Catalyzed Aromatic Trifluoromethylation *via* Group Transfer from Fluoral Derivatives

Hideaki Kondo,[a] Masahiro Oishi,[a] Kenichi Fujikawa,[a] and Hideki Amii[a,b,*]

[a] Department of Chemistry, Graduate School of Science, Kobe University, 1–1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan
[b] Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan
Fax: (+81)-277-30-1280; e-mail: amii@chem-bio.gunma-u.ac.jp

Received: November 3, 2010; Revised: March 13, 2011; Published online: May 17, 2011

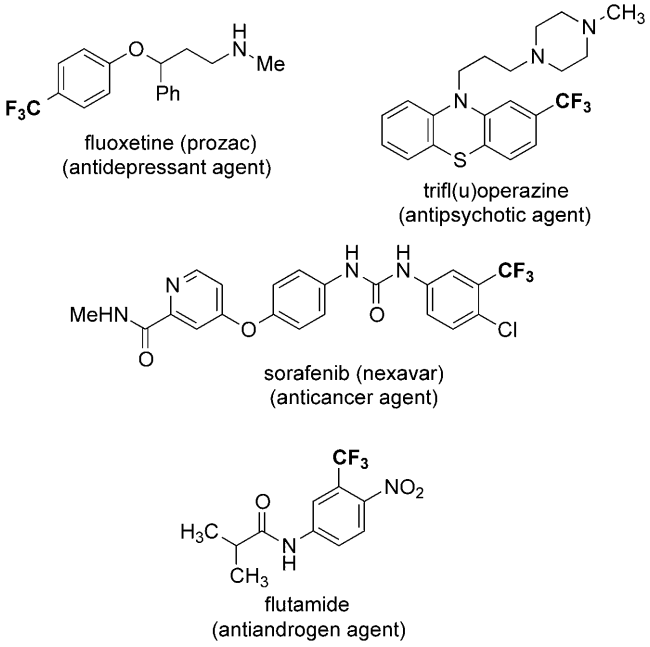
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000825.

Abstract: Starting from a readily available fluoral derivative, catalytic aromatic trifluoromethylation has been successfully achieved. A small amount of copper(I) iodide-phenanthroline complex catalyzed the cross-coupling reactions of aryl/heteroaryl iodides with the *O*-silylated hemiaminal of fluoral (trifluoroacetaldehyde) to provide trifluoromethylated arenes in moderate to high yields.

Keywords: aromatic substitution; copper; cross-coupling; retro reactions; trifluoromethylation

Trifluoromethylated aromatic compounds (Ar-CF_3) are substances of considerable interest in various industrial fields. The high lipophilicity, strong electron-withdrawing ability, and charasteristic size of the trifluoromethyl group are key influences in biologically active molecules.[1] Due to these attractive properties, Ar-CF_3 structural motifs have been widely employed in the design of pharmaceuticals, agrochemicals, dyes, liquid crystals, and polymers (Scheme 1).[2] Therefore, the development of highly efficient methodologies for aromatic trifluoromethylation is of significant importance for wide fields of science and technology.

With respect to the high regiochemical fidelity in aromatic substitution, the cross-coupling of aryl halides with organometallic reagents is one of the most powerful and versatile tools in organic synthesis.[4] Trifluoromethylcopper (CF_3Cu), which is unstable and needs to be generated *in situ*, acts as a prominent cross-coupling participant of aromatic trifluoromethylation.[5–8] In order to generate CF_3Cu species, there have been several protocols using CF_3I/Cu,[5a–d] CF_3Br/Cu-anode,[5e] $CF_3N(NO)Tf$/Cu,[5f] CF_2Br_2/Cu/DMAc,[5g,h] $(CF_3)_2Hg$/Cu,[5i] CF_3CdX/CuX,[5j,k] CF_3ZnX/CuX,[5j–l] CF_3SO_2Cl/Cu,[5m] $FSO_2CF_2CO_2Me$/CuI,[5n] $FSO_2CF_2CF_2OCF_2CO_2Me$/CuI,[5o] CF_3CO_2Na/CuI,[5p,q] CF_3CO_2Me/CsF/CuI,[5r] $ClCF_2CO_2Me$/KF/CuI,[5s] CF_3SiEt_3/KF/Cu,[5t,u] and $[CF_3SPh_2]^+OTf^-$/Cu.[5w] For most of the aromatic trifluoromethylations using CF_3Cu, stoichiometric (sometimes, excess) amounts of copper reagents are required to complete the cross-coupling reactions.[5a–m,o–v,6–8] Recently, detailed studies on transition metal-catalyzed aromatic trifluoromethylation have been described.[6–12] In order to develop a practical and environmentally benign process, it is desirable to reduce the quantity of heavy metal reagents employed in these transfor-



Scheme 1. Selected examples of trifluoromethylated phamaceuticals.

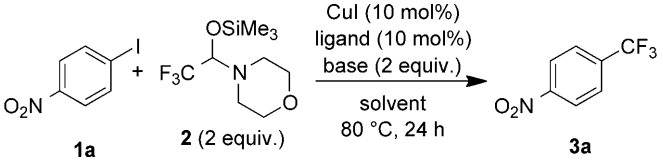
mations.[5n,12–18] Recently, Watson and Buchwald et al. have demonstrated the palladium-catalyzed cross-coupling reactions of aryl chlorides with trifluoromethyl-(triethyl)silane (CF_3SiEt_3).[14] In 2009, we reported an efficient procedure for aromatic trifluoromethylation using a diamine ligand, which makes possible a reaction using catalytic copper.[15] In the presence of a small amount of CuI and 1,10-phenanthroline (phen), the cross-coupling reactions of iodoarenes with CF_3SiEt_3 proceeded smoothly to afford trifluoromethylated aromatics in good yields. Despite its efficiency for catalytic aromatic trifluoromethylation,[14,15] CF_3SiEt_3 is a highly expensive reagent with limited availability.[7c] Therefore, more convenient CF_3 sources have been required for cross-coupling reactions.

Meanwhile, fluoral (trifluoroacetaldehyde) and its derivatives are one of the most available and common organofluorine compounds. Hemiaminals of fluoral are stable compounds and they are known to be convenient sources of trifluoromethyl anion.[19,20] *O*-Silylated hemiaminal derivative **2** was readily prepared from commercially available $CF_3CH(OH)(OEt)$ (hemiacetal of fluoral) and morpholine.[20a] Previously, Langlois and Billard reported the nucleophilic trifluoromethylation of aldehydes and ketones by the use of compound **2** as a CF_3 anion equivalent.[20b] In spite of the great synthetic utility, to the best of our knowledge, there has been no successful report of aromatic trifluoromethylation using *O*-silyl hemiaminal **2**.[21] Herein, we disclose a new catalytic procedure for aromatic trifluoromethylation by the use of trifluoroacetaldehyde hemiaminal derivative **2** as a cross-coupling partner (Scheme 2).

Our initial studies were focused on a survey of suitable reaction conditions such as ligand, base, and solvent for the Cu-catalyzed aromatic trifluoromethylation (Table 1).

When a mixture of 4-nitroiodobenzene (**1a**) and *O*-silylated hemiaminal **2** and KF in DMF was heated at 80 °C for 24 h in the presence of a copper complex (0.1 equiv. to **1a**) prepared *in situ* from CuI and 1,10-phenanthroline (phen), the cross-coupling product **3a** was obtained in 7% yield (entry 1). Several attempts to transform **1a** to the trifluoromethylarene **3a** were made by using solvents such as DMF, NMP, DMSO, and DME, which were frequently employed in the catalyzed cross-coupling reactions, but they were with a limited success (entries 2–5). In particular, when utilizing diethylene glycol dimethyl ether (diglyme) as a solvent, the CuI-phen complex showed high catalytic activity and the yield of **3a** increased upto 77% (entry 6). Diglyme could play an important role to dissolve CsF efficiently by chelation.[22] The combination of CsF as a base and diglyme as a solvent was effective for the catalytic aromatic trifluoromethylation; the use of KF as a base in place of CsF resulted in the formation of **3a** in only 3% yield (entry 7).

Table 1. Optimization of the reaction conditions.

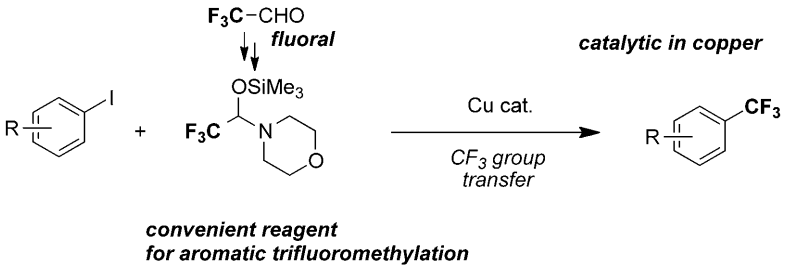


1a **2** (2 equiv.) **3a**

Entry	Base	Solvent	Yield [%][a]
1	CsF	DMF	7
2	CsF	NMP	17
4	CsF	DMSO	20
5	CsF	DME	33
6	CsF	diglyme	77
7	KF	diglyme	3

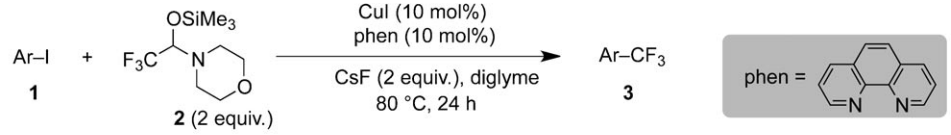
[a] NMR yield, which was calculated by ^{19}F NMR integration of product **3a** relative to the trifluoromethoxybenze internal standard.

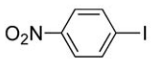
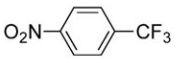
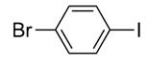
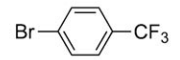
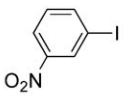
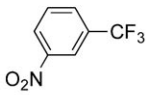
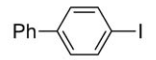
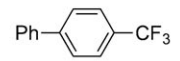
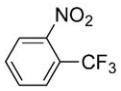
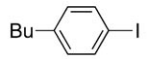
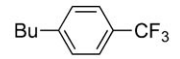
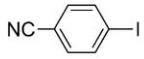
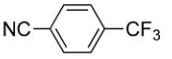
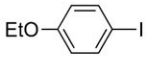
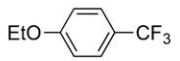
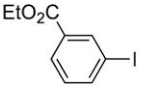
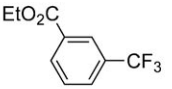
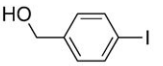
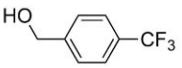
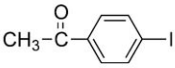
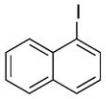
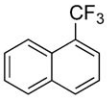
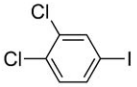
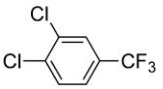
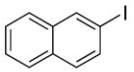
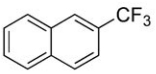
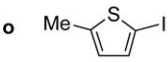
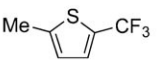
Representative examples of the formation of trifluoromethylarenes **3** are summarized in Table 2. Using 10 mol% of the copper(I) complex prepared *in situ* from CuI and phen in a molar ratio of 1:1 worked well for cross-coupling of aryl iodides **1** with *O*-silylated hemiaminal **2** to afford the corresponding trifluoromethylated arenes **3**. As a noteworthy advance, selective aromatic trifluoromethylation was accomplished; less than 1% yield of pentafluoroethylated by-product[5k] was observed in each case. Iodobenzenes **1a–g** endowed with electron-withdrawing groups on the aryl rings underwent catalytic trifluoromethylation smoothly to provide the desired cross-coupling products in good yields (entries 1–8). In the



Scheme 2.

Table 2. Scope of Cu-catalyzed aromatic trifluoromethylation.



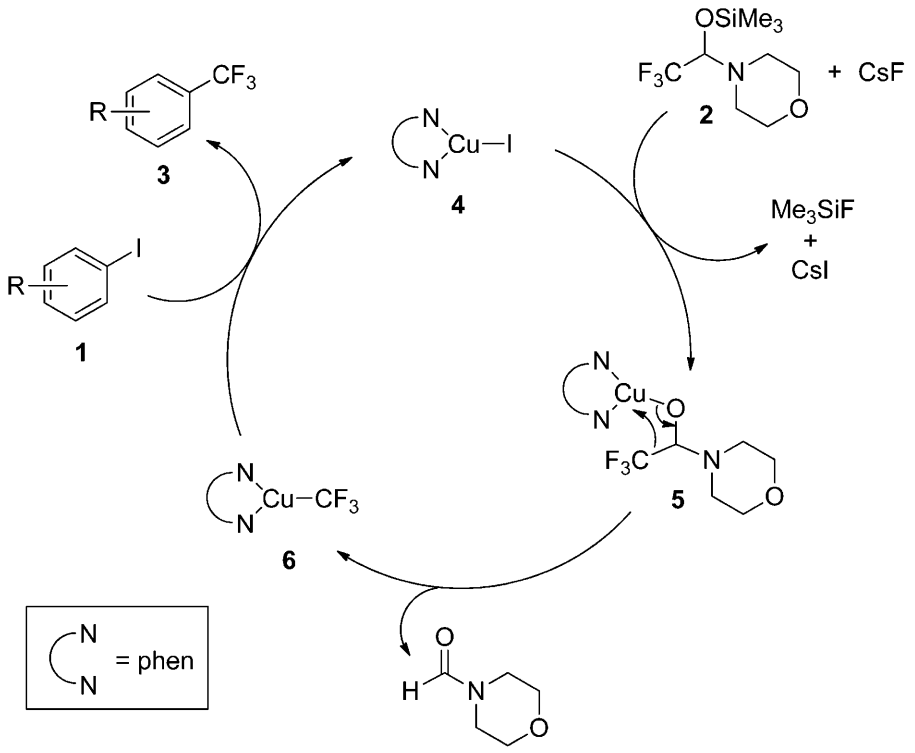
Entry	Iodoarene **1**	Product **3**	Yield [%][a]	Entry	Iodoarene **1**	Product **3**	Yield [%][a]
1	**1a** 	**3a** 	77	9	**1h** 	**3h** 	53
2 3[b]	**1b** 	**3b** 	90 90	10	**1i** 	**3i** 	53
4	**1c** 	**3c** 	47	11 12[d]	**1j** 	**3j** 	40 38
5	**1d** 	**3d** 	93	13	**1k** 	**3k** 	57
6	**1e** 	**3e** 	60	14[e]	**1l** 	**3l** 	44
7	**1f** 	–	– [c]	15	**1m** 	**3m** 	97
8	**1g** 	**3g** 	97	16	**1n** 	**3n** 	95
				17	**1o** 	**3o** 	75

[a] NMR yield, which was calculated by ^{19}F NMR integration of product **3a** relative to the trifluoromethoxybenze internal standard.[a] NMR yields, which were calculated by ^{19}F NMR integration of products **3** relative to the trifluoromethoxybenzene internal standard.
[b] The reaction was carried out in the presence of CuI (5 mol%) and phen (5 mol%).
[c] A complex mixture was obtained.
[d] The reaction was carried out in the presence of CuI (20 mol%) and phen (20 mol%).
[e] Silyl hemiaminal **2** (3 equiv.) and CsF (3 equiv.) were used.

case of 3-iodonitrobenzene (**1b**), 5 mol% catalyst loading was sufficient to complete the cross-coupling reaction (entry 3). Even *ortho*-substituted iodoarene **1c** underwent the cross-coupling reaction to produce 2-nitro(trifluoromethyl)benzene (**3c**) in 47% yield (entry 4).

Not only a nitro group, but cyano and ester groups in **1d** and **1e** were tolerable under the nucleophilic trifluoromethylating conditions (entries 5 and 6). However, the reaction of 4-iodoacetophenone (**1f**) with **2** gave a complex mixture containing 1,2-adduct of the carbonyl moiety of **1f** (entry 7). C–Cl and C–Br functionalities in **1g** and **1h** were compatible with the present reaction conditions to provide the corresponding trifluoromethyl arenes **3g** and **3h**, respectively (entries 8 and 9). Of significant interest, the present protocol worked well for both electron-deficient and electron-rich iodoarenes; employing CuI-phenanthroline complex engendered the cross-coupling reaction of iodobiphenyl **1i** with **2** to deliver trifluoromethylated biphenyl **3i** in 53% yield (entry 10). The reactions of **1j** and **1k** possessing electron-donating groups such as butyl and ethoxy groups with *O*-silylated hemiaminal **2** provided *p*-butyl(trifluoromethyl)benzene (**3j**) and *p*-ethoxy(trifluoromethyl)benzene (**3k**) in 40% and 57% yields, respectively (entries 11 and 13). Intriguingly, iodoarene **1l** bearing a hydroxy group participated in the catalytic aromatic trifluoromethylation upon treatment with excess amounts of silyl hemiaminal **2** and CsF (3 equiv. to **1l**) (entry 14). Both 1- and 2-iodonaphthalenes **1m** and **1n** underwent the group-transfer trifluoromethylation to afford the corresponding trifluoromethylnaphthalenes **3m** and **3n** in high yields (entries 15 and 16). Furthermore, heteroarene **1o** partook in the catalytic trifluoromethylation to give **3o** in 75% yield (entry 17).

One of the key features is that an aromatic trifluoromethylation that is catalytic in copper has



Scheme 3. Proposed mechanism for the Cu-catalyzed cross-coupling between aryl iodides **1** and fluoral derivative **2**.

been accomplished; a small amount of copper complex is enough to complete the cross-coupling. The catalytic formation of trifluoromethylarenes **3** can be explained by assuming the pathway pictured in Scheme 3. First, the fluoride ion-induced reaction of *O*-silyl hemiaminal **2** with CuI-diamine complex **4** gives copper alkoxide **5**. Next, the migration of the trifluoromethyl group in **5** readily takes place leading to the elimination of *N*-formylmorpholine and the generation of trifluoromethyl-copper(I) complex **6**.[23] Finally, σ-bond metathesis[24] between CF_3Cu complex (**6**) and Ar-I (**1**) allows the formation of trifluoromethylarenes **3** and the regeneration of CuI-diamine complex **4**, which is reusable in the aromatic trifluoromethylation again.

In conclusion, we have demonstrated that a small amount of CuI-phenanthroline complex catalyzes the CF_3-group transfer cross-coupling reactions of aryl/heteroaryl iodides[25,26] with *O*-silylated hemiaminal **2** to give trifluoromethylated arenes in moderate to high yields. The substrate scope of the present methodology is broad and a variety of functional groups are tolerated. Starting from a readily available CF_3 source, catalytic aromatic trifluoromethylation has been successfully achieved. Thus, the ingenious design of the catalytic reactions expands remarkably the scope of organofluorine compounds in practical synthetic applications.

Experimental Section

General Procedure for Catalytic Aromatic Trifluoromethylation

An oven-dried Schlenk tube was charged with CuI (0.030 mmol, 5.7 mg), 1,10-phenanthroline (0.030 mmol, 5.4 mg) and CsF (0.60 mmol, 67.3 mg). The tube was evacuated and backfilled with argon, and then diglyme (0.60 mL), 4-nitroiodobenzene (**1a**, 0.30 mmol, 74.7 mg), and *O*-silylated hemiaminal **2** (0.60 mmol, 154 mg) were added. The resulting reaction mixture was stirred at 80 °C for 24 h. After the reaction was complete, the mixture was cooled to room temperature, diluted with water, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and the volatiles were removed under vacuum. The residue was purified by chromatography on silica gel to yield trifluoromethyl arene **3a**. The identity and purity of the known products were confirmed by ^1H, ^{19}F NMR and GC-MS analysis. See the Supporting Information for full details.

Acknowledgements

The financial support of the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grant-in-Aid for Scientific Research), 'Japan Science and Technology Agency (Research for Promoting Technological Seeds), Ube Foundation, Asahi Glass Foundation, Naito Foundation, and Astellas

Foundation is gratefully acknowledged. We would like to thank Prof. Masahiko Hayashi (Kobe University) for his useful suggestions.

References

[1] a) R. E. Banks, B. E. Smart, J. C. Tatlow, *Organofluorine Chemistry: Principles and Commercial Applications*, Plenum Press, New York, **1994**; b) T. Hiyama, K. Kanie, T. Kusumoto, Y. Morizawa, M. Shimizu, *Organofluorine Compounds: Chemistry and Application*, Springer-Verlag, Berlin, **2000**; c) P. Kirsh, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, **2004**; d) R. D. Chambers, *Fluorine in Organic Chemistry*, Blackwell, Oxford, **2004**; e) K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, **2006**; f) J.-P. Bégué, D. Bonnet-Delpon, *Bioorganic and Medicinal Chemistry of Fluorine*, John Wiley & Sons Inc., Hoboken, **2008**.

[2] J. H. Clark, D. Wails, T. W. Bastock, in: *Aromatic Fluorination*, CRC Press, Boca Raton, **1996**, pp 89–118.

[3] M. A. McClinton, D. A. McClinton, *Tetrahedron* **1992**, *48*, 6555–6666.

[4] *Metal-Catalyzed Cross-Coupling Reactions*, (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**.

[5] For methods of generating perfluoroalkyl copper reagents for aromatic trifluoromethylation (stoichiometric in copper), see: a) Y. Kobayashi, I. Kumadaki, *Tetrahedron Lett.* **1969**, 4095–4096; b) C. C. R. McLoughlin, J. Thrower, *Tetrahedron* **1969**, *25*, 5921–5940; c) Y. Kobayashi, K. Yamamoto, I. Kumadaki, *Tetrahedron Lett.* **1979**, 4071–4072; d) J.-C. Xiao, C. Ye, J. M. Shreeve, *Org. Lett.* **2005**, *7*, 1963–1965; e) J. M. Paratian, S. Sibille, J. Périchon, *J. Chem. Soc. Chem. Commun.* **1992**, 53–54; f) T. Umemoto, A. Ando, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 447–452; g) D. J. Burton, D. M. Wiemers, J. C. Easdon, *U.S.Patent* 4,582,921, **1986**; h) J. H. Clark, M. A. McClinton, R. J. Blade *J. Chem. Soc. Chem. Commun.* **1988**, 638–639; i) N. V. Kondratenko, E. P. Vechirko, L. M. Yagupolskii, *Synthesis* **1980**, 932–933; j) D. J. Burton, D. M. Wiemers, *J. Am. Chem. Soc.* **1985**, *107*, 5014–5015; k) D. M. Wiemers, D. J. Burton, *J. Am. Chem. Soc.* **1986**, *108*, 832–834; l) M. M. Kremlev, W. Tyrra, A. I. Mushta, D. Naumann, Y. L. Yagupolskii, *J. Fluorine Chem.* **2010**, *131*, 212–216; m) C. A. Heaton, R. L. Powell, *J. Fluorine Chem.* **1989**, *45*, 86–86; n) Q.-Y. Chen, S.-W. Wu, *J. Chem. Soc. Chem. Commun.* **1989**, 705–706; o) Q.-Y. Chen, J.-X. Duan *J. Chem. Soc. Chem. Commun.* **1993**, 1389–1391; p) K. Matsui, R. Tobita, M. Ando, *Chem. Lett.* **1981**, *10*, 1719–1720; q) G. E. Carr, R. D. Chambers, T. F. Holmes, D. G. Parker, *J. Chem. Soc. Perkin Trans. 1* **1988**, 921–926; r) B. R. Langlois, N. Roques, *J. Fluorine Chem.* **2007**, *128*, 1318–1325; s) D.-B. Su, J.-X. Duan, Q.-Y. Chen, *Tetrahedron Lett.* **1991**, *32*, 7689–7690; t) H. Urata, T. Fuchikami, *Tetrahedron Lett.* **1991**, *32*, 91–94; u) F. Cottet, M. Schlosser, *Eur. J. Org. Chem.* **2002**, 327–330; v) C.-P. Zhang, Z.-L. Wang, Q.-Y. Chen, C.-T. Zhang, Y.-C. Gu, J.-C. Xiao, *Angew. Chem.* **2011**, *123*, 1936–1940; *Angew. Chem. Int. Ed.* **2011**, *50*, 1896–1900.

[6] A. Kütt, V. Movchun, T. Rodima, T. Dansauer, E. B. Rusanov, I. Leito, I. Kaljurand, J. Koppel, V. Pihl, I. Koppel, G. Ovsjannikov, L. Toom, M. Mishima, M. Medebielle, E. Lork, G. V. Röschenthaler, I. A. Koppel, A. A. Kolomeitsev, *J. Org. Chem.* **2008**, *73*, 2607–2620.

[7] a) G. G. Dubinina, H. Furutachi, D. A. Vicic, *J. Am. Chem. Soc.* **2008**, *130*, 8600–8601; b) G. G. Dubinina, J. Ogikubo, D. A. Vicic, *Organometallics* **2008**, *27*, 6233–6235; c) I. Kieltsch, G. G. Dubinina, C. Hamacher, A. Kaiser, J. Torres-Nieto, J. M. Hutchison, A. Klein, Y. Budnikova, D. A. Vicic, *J. Fluorine Chem.* **2010**, *131*, 1108–1112.

[8] For Cu-promoted oxidative trifluoromethylation; a) L. Chu, F.-L. Qing, *Org. Lett.* **2010**, *12*, 5060–5063; b) T. D. Senecal, A. T. Parsons, S. L. Buchwald, *J. Org. Chem.* **2011**, *76*, 1174–1176.

[9] a) V. V. Grushin, W. J. Marshall, *Acc. Chem. Res.* **2010**, *43*, 160–171; b) T. Ritter, *Nature* **2010**, *466*, 447–448; c) R. J. Lundgren, M. Stradiotto, *Angew. Chem.* **2010**, *122*, 9510–9512; *Angew. Chem. Int. Ed.* **2010**, *49*, 9322–9324.

[10] a) V. V. Grushin, W. J. Marshall, *J. Am. Chem. Soc.* **2006**, *128*, 4632–4641; b) V. V. Grushin, W. J. Marshall, *J. Am. Chem. Soc.* **2006**, *128*, 12644–12645.

[11] a) N. D. Ball, J. W. Kampf, M. S. Sanford, *J. Am. Chem. Soc.* **2010**, *132*, 2878–2879; b) N. D. Ball, J. W. Kampf, M. S. Sanford, *J. Am. Chem. Soc.* **2010**, *132*, 14682–14687.

[12] a) T. Kitazume, N. Ishikawa, *Chem. Lett.* **1982**, *11*, 137–140; b) T. Kitazume, N. Ishikawa, *J. Am. Chem. Soc.* **1985**, *107*, 5186–5191.

[13] For Pd(II)-catalyzed electrophilic trifluoromethylation; X. Wang, L. Truesdale, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 3648–3649.

[14] E. J. Cho, T. D. Senecal, T. Kinzel, Y. Zhang, D. A. Watson, S. L. Buchwald, *Science* **2010**, *328*, 1679–1681.

[15] M. Oishi, H. Kondo, H. Amii, *Chem. Commun.* **2009**, 1909–1911.

[16] Cu-catalyzed cross-coupling by the use of CF_3-$SiMe_3$ as a nucleophilic trifluoromethylating agent: a) K. Araki, M. Inoue, K. Kawada, *Jpn. Kokai Tokkyo Koho JP* 2009234921 A 20091015, **2009**; b) R. Kuwano, S. Soga, *Jpn. Kokai Tokkyo Koho JP* 2010222304 A 20101007, **2010**.

[17] For Fenton's reagent-catalyzed radicalic trifluoromethylation: T. Kino, Y. Nagase, Y. Ohtsuka, K. Yamamoto, D. Uraguchi, K. Tokuhisa, T. Yamakawa, *J. Fluorine Chem.* **2010**, *131*, 98–105.

[18] Very recently, the copper-catalyzed aromatic trifluoromethylation of aryl iodides employing K^+ $[CF_3B(OMe)_3]^-$ has been developed: T. Knauber, F. Arikan, G.-V. Röschenthaler, L. J. Gooβen, *Chem. Eur. J.* **2011**, *17*, 2689–2697.

[19] For reviews on nucleophilic trifluoromethylation: a) B. R. Langlois, T. Billard, *Synthesis* **2003**, 185–194; b) B. R. Langlois, T. Billard, S. Roussel, *J. Fluorine Chem.* **2005**, *126*, 173–179.

[20] a) T. Billard, B. R. Langlois, G. Blond, *Tetrahedron Lett.* **2000**, *41*, 8777–8780; b) T. Billard, S. Bruns, B. R. Langlois, *Org. Lett.* **2000**, *2*, 2101–2103.

[21] Watson and Buchwald et al. conducted the experiment on aromatic trifluoromethylation of aryl chlorides using

O-silyl hemiaminal **2** as a coupling partner, however, only a trace amount of the desired product was obtained under their reaction condition (see the Supporting Information of ref.[14]).

[22] D. A. Wynn, M. M. Roth, B. D. Pollard, *Talanta* **1984**, *31*, 1036–1040.

[23] B. Folléas, I. Marek, J.-F. Normant, L. Saint-Jalmes, *Tetrahedron* **2000**, *56*, 275–283.

[24] For reviews on Cu-catalyzed cross-coupling: a) J. Lindley, *Tetrahedron* **1984**, *40*, 1433–1456; b) I. P. Beletskaya, A. V. Cheprakov, *Coord. Chem. Rev.* **2004**, *248*, 2337–2364; c) F. Monnier, M. Taillefer, *Angew. Chem.* **2009**, *121*, 7088–7105; *Angew. Chem. Int. Ed.* **2009**, *48*, 6954–6971; d) A. Vagalok, A. K. Kaspi, *Top. Organomet. Chem.* **2010**, *31*, 19–38.

[25] Pd-catalyzed arylation of aryl halides with arylmethanols *via* retro-arylation: Y. Terao, H. Wakui, M. Nomoto, T. Satoh, M. Miura, M. Nomura *J. Org. Chem.* **2003**, *68*, 5236–5243.

[26] Pd-catalyzed allylation of aryl halides with homoallyl alcohols *via* retro-allylation: S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima *J. Am. Chem. Soc.* **2006**, *128*, 2210–2211.

