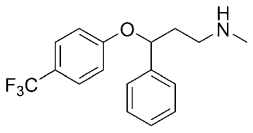
Synthetic Methods

DOI: 10.1002/ange.201006823

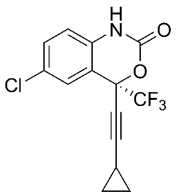
Copper-Mediated Trifluoromethylation of Heteroaromatic Compounds by Trifluoromethyl Sulfonium Salts**

*Cheng-Pan Zhang, Zong-Ling Wang, Qing-Yun Chen, Chun-Tao Zhang, Yu-Cheng Gu, and Ji-Chang Xiao**

Trifluoromethylated organic compounds are becoming increasingly important in organic chemistry.[1] Such compounds often behave in a unique manner because of the special inductive and resonance effects caused by fluorine, and the resilience of the trifluoromethyl group to metabolism. Drug candidates and crop protection agents containing trifluoromethyl groups usually possess improved physical and chemical properties.[1,2] For example, the strategic introduction of a trifluoromethyl group into fluoxetine (an antidepressant) and efavirenz (an antiviral) was critical to their applications in medicinal chemistry.[1c]



fluoxetine (Prozac)



efavirenz

To the best of our knowledge, no naturally occurring trifluoromethylated compounds are reported in the literature, and all the known trifluoromethylated compounds are synthetic.[1–3] The introduction of the trifluoromethyl group into common organic molecular frameworks under mild and selective reaction conditions is among one of the most challenging synthetic problems. Although there are various approaches, the direct transfer of a CF_3 synthon is the most appealing.[4] Conversion of a functional group into the CF_3 group using SF_4, SbF_3, BrF_3, or HF requires harsh conditions, which are often incompatible with other functionalities in the target molecule. The building block strategy can be employed when direct and mild CF_3 transfer reagents cannot be used, but this approach can be arduous and time consuming, which limits its use.

Methods for the direct introduction of the trifluoromethyl group are available through radical, nucleophilic, or electrophilic approaches.[5] Trifluoromethyl radicals generated under oxidative, reductive, photochemical, thermal, or electrochemical conditions can react with electron-rich aromatic and heteroaromatic compounds to give the desired trifluoromethylated products,[6] but poor regioselectivity is often encountered in this kind of reaction. Over the last few decades, nucleophilic trifluoromethylation has become the most successful approach through the use of the convenient and easy-to-handle Me_3SiCF_3, environmentally friendly CF_3H, and other compounds which lead to the formation of $CuCF_3$ as an intermediate.[7] However, such reactions still suffer from low yields and the formation of numerous fluorinated side-products when heteroaromatic compounds are employed as the substrates.[8] (*S*)-(Trifluoromethyl)diarylsulfonium salts, first prepared by Yagupolskii and co-workers[9a] and then developed by Umemoto and Ishihara,[9b–d] have been used for the electrophilic trifluoromethylation of nucleophiles, but their reactivity with heteroaromatic compounds has proved to be unsatisfactory so far. Togni and co-workers have recently reported the electrophilic trifluoromethylation of carbon- and heteroatom-centered nucleophiles using a hypervalent iodine(III) trifluoromethyl compound as the reagent.[4,10] Although this approach was suitable for a range of nucleophiles, the trifluoromethylation of heteroaromatic compounds was still barely studied. Clearly, the development of an effective and mild approach for the preparation of trifluoromethylated heteroaromatic compounds is still urgently required.

Herein, we report that iodo-substituted heteroaromatic compounds can be smoothly trifluoromethylated by (*S*)-(trifluoromethyl)diphenylsulfonium salts in the presence of copper. To our knowledge, this is the first time that trifluoromethyl sulfonium salts, reduced by copper, have been used to convert iodo-substituted aromatics and heteroaromatics into the corresponding trifluoromethylated compounds in high yield.

[*] C.-P. Zhang, Prof. Dr. Q.-Y. Chen, Prof. Dr. J.-C. Xiao
Key Laboratory of Organofluorine Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
345 Lingling Road, Shanghai 200032 (China)
Fax: (+86) 21-6416-6128
E-mail: jchxiao@mail.sioc.ac.cn
Z.-L. Wang, C.-T. Zhang
Hunan University of Chinese Medicine
Changsha, Hunan Province 410208 (China)
Dr. Y.-C. Gu
Syngenta, Jealott's Hill International Research Centre
Bracknell, Berkshire, RG42 6EY (UK)

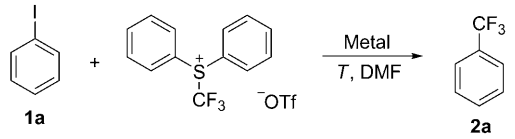
[**] We thank the Chinese Academy of Sciences (Hundreds of Talents Program), the National Natural Science Foundation (20972179, 21032006), Merck Research Laboratories, and the Syngenta PhD Studentship Award for financial support. We thank Dr. John Clough of Syngenta at Jealott's Hill International Research Centre and Dr. Shubin Liu of University of North Carolina for proofreading of the manuscript.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201006823.

Although a series of electrophilic trifluoromethylating reagents have been extensively designed and synthesized, they are still limited to electrophilic and radical reactions.[9,11] In our previous study, we reported that fluoroalkyl radicals are formed when (*S*)-(fluoroalkyl)diphenylsulfonium salts react with nucleophiles at low temperature.[12] It seems that a redox process cannot be excluded in the generation of these radicals. Based on this result, we have continued to investigate the reaction of sulfonium salts with metals. Owing to the straightforward one-pot process discovered by Magnier and co-workers, the preparation of (*S*)-(trifluoromethyl)diphenylsulfonium salts is most convenient.[13] For this reason, (*S*)-(trifluoromethyl)diphenylsulfonium triflate was employed as the prototype.

As shown in Table 1, (*S*)-(trifluoromethyl)diphenylsulfonium triflate can be successfully reduced by metals. For example, after the treatment of $[Ph_2SCF_3]^+[OTf]^-$ with iodobenzene **1a** in the presence of Fe at 110 °C for 10 hours,

Table 1: Trifluoromethylation of iodobenzene **1a** by $[Ph_2SCF_3]^+[OTf]^-$ in the presence of metals.



1a **2a**

Entry	M	**1a**/$[Ph_2SCF_3]^+[OTf]^-$/M[a]	T [°C]	t [h]	**2a**/$[Ph_2SCF_3]^+$/$[OTf]^-$[b] (conv. [%][c])
1	Fe	1:1:1.5	110	10	0:0.17:1 (83)
2	$[Pd(PPh_3)_4]$	1:1:1.5	110	10	0:0.3:1 (70)
3	Zn	1:1:2	60	9	0:0:1 (quant.)
4	Ag	1:1:2	60	9	0:0.92:1 (8)
5	CuI	1:1:2	60	9	0:0.85:1 (15)
6	Cu	1:1:2	60	9	0.5:0:1 (quant.)
7	Cu	1:1:2	60	4	0.34:0:1 (quant.)
8	Cu	1:1:1	60	9	0.1:0:1 (quant.)
9	Cu	1:1:0.5	60	9	0:0.3:1 (70)
10	Cu	1:1:2	RT	9	0:1:1 (0)

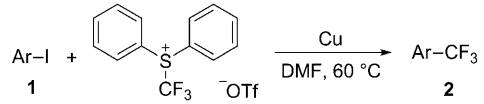
[a] Molar ratio. [b] Molar ratio, determined by ^{19}F NMR spectroscopy. [c] Conversion of $[Ph_2SCF_3]^+[OTf]^-$ determined by ^{19}F NMR spectroscopy. DMF = *N*,*N*-dimethylformamide, Tf = triflate.

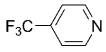
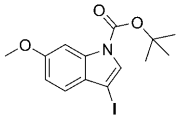
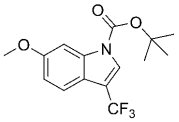
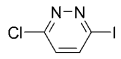
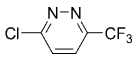
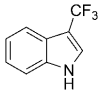
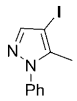
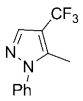
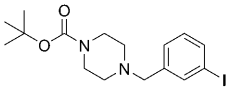
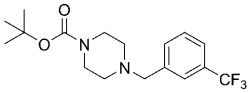
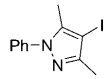
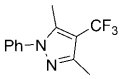
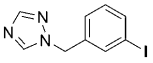
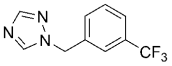
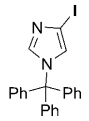
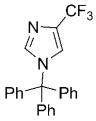
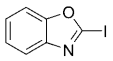
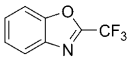
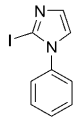
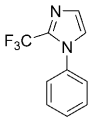
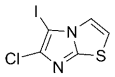
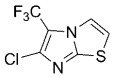
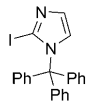
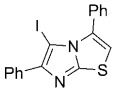
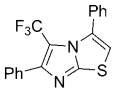
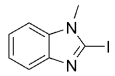
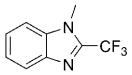
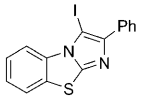
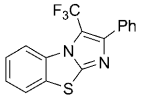
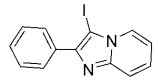
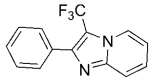
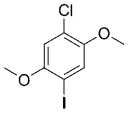
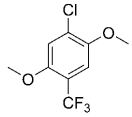
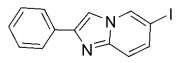
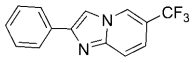
only 17% of $[Ph_2SCF_3]^+$ remained (Table 1, entry 1). Upon replacement of Fe by $[Pd(PPh_3)_4]$, 70% of the cation was converted under the same conditions (Table 1, entry 2). Zinc was a good reductant for the reaction compared to Ag, Fe, and CuI (Table 1, entries 1, 3–5) and, with this metal, the $[Ph_2SCF_3]^+$ cation was completely transformed even when the reaction was conducted at 60 °C for 9 hours (Table 1, entry 3). Although zinc was effective in reducing the sulfonium salt, serious defluorination of the CF_3 synthon invariably took place, and none of the desired trifluoromethylbenzene **2a** was formed. Using Cu instead of Zn, however, we found that defluorination was somewhat alleviated and **2a** was detected (Table 1, entry 6). When the reaction time was shortened, **2a** was obtained in a lower yield (Table 1, entry 7). The $[Ph_2SCF_3]^+[OTf]^-$ was completely reduced but the active intermediate $CuCF_3$ still remained in the reaction, as determined by ^{19}F NMR spectroscopy (see the Supporting Information), according to the literature ($\delta = -35.5$ ppm).[14] Therefore, sufficient reaction time should be provided to ensure the complete transformation of $CuCF_3$ into the trifluoromethylated product. Increasing the reaction time to more than 9 hours, however, always gave yields of **2a** that were less than 50%, if the sulfonium salt was used as the standard. It appears that only one half of the salt was effective in the trifluoromethylation step. Moreover, the amount of copper added was shown to have an important influence on the reaction yield. When the amount of copper was reduced from two to one equivalents of $[Ph_2SCF_3]^+[OTf]^-$, a yield of only 10% of **2a** was obtained (Table 1, entry 8), and no **2a** at all was obtained when half an equivalent of copper was used (Table 1, entry 9). Finally, thermal energy was necessary to initiate the reaction. Treating $[Ph_2SCF_3]^+[OTf]^-$ with **1a** and Cu at room temperature did not yield any of the product **2a** (Table 1, entry 10).

It is well known that the synthesis of trifluoromethylated heteroaromatic compounds under mild conditions is challenging. Encouraged by the results described above, we turned our attention to the copper-mediated trifluoromethylation of iodo-substituted heteroaromatic compounds. As shown in Table 2, 4-iodopyridine **1b** (1 equiv) was treated with $[Ph_2SCF_3]^+[OTf]^-$ (2 equiv) in the presence of Cu (3 equiv) and gave 4-(trifluoromethyl)pyridine **2b** in 91% yield (Table 2, entry 1). Under the same reaction conditions, the iodopyridazine **1c** was converted into the corresponding trifluoromethylpyridazine **2c** in almost quantitative yield (Table 2, entry 2). These yields are much higher than those obtained using the previously reported reagent mixtures $TMSCF_3$/CuI/KF or $ClCF_2CO_2CH_3$/KF/CuI.[14a,15a,b] Similar results were found when **1d, 1e**, and **1f** were treated with $[Ph_2SCF_3]^+[OTf]^-$ (Table 2, entries 3–5).

The steric hindrance around the iodo-substituent in the substrates had a marked impact on the trifluoromethylation reaction. When iodine is flanked by two methyl groups on a pyrazole ring, higher reaction temperatures were needed to ensure complete trifluoromethylation (compare Table 2, entries 3 and 4). The 2-iodoimidazoles **1g** and **1i** were also trifluoromethylated in high yield (Table 2, entries 6 and 8). Changing the *N*-phenyl group to the much more bulky trityl group, however, yielded none of the desired product, even when the reaction was run at 80 °C for 11 hours (compare Table 2, entries 6 and 7). Trifluoromethylation of **1j** by $[Ph_2SCF_3]^+[OTf]^-$ in the presence of Cu gave **2j** in a 92% yield (Table 2, entry 9), which is much higher than the 65% yield previously reported for the same transformation using $TMSCF_3$/CuI/KF as the reagent mixture.[15c] 6-Trifluoromethyl-2-phenylimidazo[1,2-a]pyridine (**2k**) could also be prepared under our reaction conditions when **1k** was employed as the substrate (Table 2, entry 10). Upon Treatment of **1l** with $[Ph_2SCF_3]^+[OTf]^-$/Cu, **2l** was successfully generated, without loss of the *N*-*tert*-butoxycarbonyl group (Table 2, entry 11). Moreover, our method was suitable for the trifluoromethylation of 3-iodo-1*H*-indole (**1m**) and produced **2m** (Table 2, entry 12). This result is particularly significant because reactions previously employed to prepare

Table 2: Trifluoromethylation of **1b–t** by $[Ph_2SCF_3]^+[OTf]^-$ in the presence of copper.



Entry	Substrate[a]	Product	Yield [%][b]	Entry	Substrate[a]	Product	Yield [%][b]
1	**1b** 	**2b** 	91[c] (70,[d] 48[e])	11	**1l** 	**2l** 	96
2	**1c** 	**2c** 	98 (25[f])	12	**1m** 	**2m** 	90
3	**1d** 	**2d** 	95	13	**1n** 	**2n** 	98
4[g]	**1e** 	**2e** 	96	14[g]	**1o** 	**2o** 	93
5	**1f** 	**2f** 	95	15	**1p** 	**2p** 	85[c]
6	**1g** 	**2g** 	90	16	**1q** 	**2q** 	92
7[g]	**1h** 	–	–[h]	17	**1r** 	**2r** 	98
8	**1i** 	**2i** 	85	18	**1s** 	**2s** 	91
9	**1j** 	**2j** 	92 (65[f])	19	**1t** 	**2t** 	92
10	**1k** 	**2k** 	90				

[a] The molar ratio of **1**/$[Ph_2SCF_3]^+[OTf]^-$/Cu was 1:2:3. These reactions were conducted at 60 °C for 9–11 h. [b] Yield of isolated products. [c] Determined by ^{19}F NMR spectroscopy. [d] This yield is reported to have been obtained using $TMSCF_3$/CuI/KF as the reagent.[14a] [e] This yield is reported to have been obtained using $TMSCF_3$/CuI/KF as the reagent.[15a] [f] Methyl chlorodifluoroacetate/KF/CuI was used as the trifluoromethylation reagent.[15b] [g] The reaction was conducted at 80 °C for 9–11 h. [h] No desired product was formed. [i] This yield is reported to have been obtained using $TMSCF_3$/CuI/KF as the reagent.[15c] TMS = trimethylsilyl.

2m through the direct introduction of a trifluoromethyl group into 1*H*-indole have often suffered from poor chemical selectivity and low productivity.[15d–g]

Heterocycles with iodo-substituents located on benzene rings also performed well in the trifluoromethylation reaction. As a result of the effectiveness of the $[Ph_2SCF_3]^+[OTf]^-$/Cu system, the desired trifluoromethylated products **2n** and **2o** were obtained in high yields (Table 2, entries 13 and 14). In addition, oxygen- or sulfur-containing heteroaromatic compounds were investigated (Table 2, entries 15–18), for which products **2p**, **2q**, **2r**, and **2s** were successfully generated, thus indicating that the $[Ph_2SCF_3]^+[OTf]^-$/Cu system has excellent functional group compatibility. Furthermore, this $[Ph_2SCF_3]^+[OTf]^-$/Cu system was very efficient for more simple iodobenzene derivatives as well. For example, a 92% yield of **2t** was formed when **1t** reacted with $[Ph_2SCF_3]^+[OTf]^-$ in the presence of copper (Table 2, entry 19).

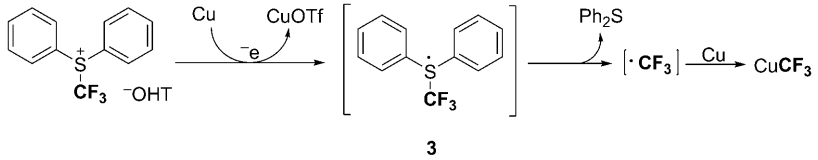
In fact, copper is the most promising metal in trifluoromethylation reactions thus far. These copper-mediated reactions have been assumed to involve the generation of $CuCF_3$ in situ.[16] Recently, Vicic and co-workers reported the first thermally stable LCu^ICF_3 complexes which could tri-

fluoromethylate organic halides under mild conditions ($\delta = -33.7$ ppm).[14a] This report provided further evidence that the $CuCF_3$ intermediate is the actual trifluoromethylating reagent. Furthermore, ^{19}F NMR analysis of the reaction mixture showed that $CuCF_3$ is generated under our reaction conditions ($\delta = -33.9$ ppm). As the reaction proceeded, $CuCF_3$ was consumed and the concentration of the trifluoromethylated product gradually increased. Analysis of the reaction mixture by using ESI-MS methods also indicated that $CuCF_3$ was formed in our reaction (*m*/*z* 131.9; see the Supporting Information). Taking all the evidence together, we consider it likely that $CuCF_3$ is the intermediate involved in the trifluoromethylation of heteroaromatic compounds that we describe here.

On the basis of these analyses, we propose that $CuCF_3$ is generated by the mechanism shown in Scheme 1. The (*S*)-(trifluoromethyl)diphenylsulfonium triflate is first reduced by copper via single electron transfer (SET). Intermediate **3** then decomposes rapidly to produce the CF_3 radical, which further generates $CuCF_3$. The Ph_2S was formed correspondingly and could be isolated by column chromatography after workup. No TMSF, SO_2, or CO_2 were formed in this reaction. It has been suggested that these three compounds disrupt trifluoromethylation, thereby leading to low yields or a complete failure to produce trifluoromethylated heteroaromatic compounds.[15–17] Effort was once focused on using $FSO_2CF_2CO_2Me$/CuI as the reagent to trifluoromethylate heteroaromatics. Although this reagent was very effective in trifluoromethylation of simple iodo-substituted aromatic compounds,[15d,16] there were no desired products (**2f**, **2n**, and **2o)** formed when **1f**, **1n**, and **1o** were employed as the substrate.

Temperature also has an influence on this reaction. Increasing the temperature causes decomposition of the CF_3 radical or $CuCF_3$, thus leading to the formation of the pentafluoroethylated by-product, to compete with product formation. A similar fluorocarbon chain elongation reaction has been discovered by the research groups of Burton[14b] and Yagupolskii.[17]

In summary, we report a convenient method for the synthesis of trifluoromethylated heteroaromatic compounds under mild conditions that is based on the observation that (*S*)-(trifluoromethyl)diphenylsulfonium triflate can be reduced by certain metals. Heteroaromatic systems containing nitrogen, oxygen, and/or sulfur and substituted with iodine were employed to investigate the effectiveness of the trifluoromethylation reaction using (*S*)-(trifluoromethyl)diphenylsulfonium salt and copper as the reagent mixture. Trifluoromethylated products were obtained in high yields. We propose that the (*S*)-(trifluoromethyl) diphenylsulfonium salt is reduced by copper via a SET mechanism, and that $CuCF_3$ is the most probable intermediate in this reaction. Investigations on the application of the trifluoromethylation method to the synthesis of pharmaceuticals and agrochemicals are currently underway.



3

Scheme 1. Proposed mechanism for generation of $CuCF_3$ from (*S*)-(trifluoromethyl)diphenylsulfonium salt.

Experimental Section

General procedure for the trifluoromethylation of iodo-substituted heteroaromatic compounds: In a sealed tube (2 mL), the heteroaromatic compound (1 equiv) and $[Ph_2SCF_3]^+[OTf]^-$ (2 equiv) were dissolved in DMF, then Cu (3 equiv) was added. The reaction mixture was stirred at 60 °C for 11 h. After cooling to room temperature, the mixture was diluted with diethyl ether, washed with H_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate (15:1)) to give the desired product.

Received: October 30, 2010
Published online: January 18, 2011

Keywords: copper · fluorine · heterocycles · sulfonium salts · trifluoromethylation

[1] a) P. Kirsch, *Modern Fluoroorganic Chemistry: Synthesis Reactivity, Applications*, Wiley-VCH, Weinheim, **2004**; b) M. Schlosser, *Angew. Chem.* **2006**, *118*, 5558–5572; *Angew. Chem. Int. Ed.* **2006**, *45*, 5432–5446; c) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320–330; d) C. Isanbor, D. O'Hagan, *J. Fluorine Chem.* **2006**, *127*, 303–319.

[2] a) R. Koller, K. Stanek, D. Stolz, R. Aardoom, K. Niedermann, A. Togni, *Angew. Chem.* **2009**, *121*, 4396–4400; *Angew. Chem. Int. Ed.* **2009**, *48*, 4332–4336; b) F. R. Leroux, B. Manteau, J.-P. Vors, S. Pazenok, *Beilstein J. Org. Chem.* **2008**, *4*, 13, DOI: 10.3762/bjoc.4.13; c) *The Pesticide Manual: A World Compendium (13th)*, Version 3.2 (Ed.: C. D. S. Tomlin), British Crop Production Council, Surrey, UK, **2005**; d) A. Kleemann, J. Engel, B. Kutscher, D. Reichert, *Pharmaceutical Substances*, Thieme, Stuttgart, **2006**.

[3] M. Shimizu, T. Hiyama, *Angew. Chem.* **2005**, *117*, 218–234; *Angew. Chem. Int. Ed.* **2005**, *44*, 214–231.

[4] P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, *12*, 2579–2586.

[5] a) J. T. Welch, S. Eswarakrishnan, *Fluorine in Bioorganic Chemistry*, Wiley, New York, **1991**; b) T. Hiyama, *Organofluorine Compounds, Chemistry and Applications*, Springer, Berlin, **2000**.

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

[7] a) J.-A. Ma, D. Cahard, *J. Fluorine Chem.* **2007**, *128*, 975–996; b) I. Ruppert, K. Schlich, W. Volbach, *Tetrahedron Lett.* **1984**, *25*, 2195–2198; c) Y. Kobayashi, I. Kumadaki, *Tetrahedron Lett.* **1969**, *10*, 4095–4096; d) Y. Kobayashi, K. Yamamoto, I. Kumadaki, *Tetrahedron Lett.* **1979**, *20*, 4071–4072; e) M. Oishi, H. Kondo, H. Amii, *Chem. Commun.* **2009**, 1909–1911.

[8] a) M. Adamczewski, C. Arnold, A. Becker, L. Carles, P. Dahmen, R. Dunkel, E. –M. Franken, U. Görgens, M. –C. Grosjean-Cournoyer, H. Helmke, S. Hillebrand, H. Hiroyuki, J. Kluth, T. Knobloch, P. Lösel, D. Nennstiel, H. Rieck, R. Rama,

R. Suelmann, A. Voerste, U. Wachendorff-Neumann, WO2010012793A1, **2010**.

[9] a) L. M. Yagupolskii, N. V. Kondratenko, G. N. Timofeeva, *J. Org. Chem.* **1984**, *20*, 103 – 106; b) T. Umemoto, S. Ishihara, *Tetrahedron Lett.* **1990**, *31*, 3579 – 3582; c) T. Umemoto, S. Ishihara, *J. Am. Chem. Soc.* **1993**, *115*, 2156 – 2164; d) T. Umemoto, *Chem. Rev.* **1996**, *96*, 1757 – 1777.

[10] a) I. Kieltsch, P. Eisenberger, A. Togni, *Angew. Chem.* **2007**, *119*, 768 – 771; *Angew. Chem. Int. Ed.* **2007**, *46*, 754 – 757; b) P. Eisenberger, I. Kieltsch, N. Armanino, A. Togni, *Chem. Commun.* **2008**, *13*, 1575 – 1577; c) I. Kieltsch, P. Eisenberger, K. Stanek, A. Togni, *Chimia* **2008**, *62*, 260 – 263; d) K. Stanek, R. Koller, A. Togni, *J. Org. Chem.* **2008**, *73*, 7678 – 7685; e) R. Koller, Q. Huchet, P. Battaglia, J. M. Welch, A. Togni, *Chem. Commun.* **2009**, 5993 – 5995.

[11] a) J.-J. Yang, R. L. Kirchmeier, J. M. Shreeve, *J. Org. Chem.* **1998**, *63*, 2656 – 2660; b) L. M. Yagupolskii, V. A. Matsnev, R. K. Orlova, B. G. Deryabkin, Y. L. Yagupolskii, *J. Fluorine Chem.* **2008**, *129*, 131 – 136; c) L. M. Yagupolskii, I. I. Maletina, N. V. Kondratenko, V. V. Orda, *Synthesis* **1978**, 835 – 837; d) A. Matsnev, S. Noritake, Y. Nomura, E. Tokunaga, S. Nakamura, N. Shibata, *Angew. Chem.* **2010**, *122*, 582 – 586; *Angew. Chem. Int. Ed.* **2010**, *49*, 572 – 576; e) S. Noritake, N. Shibata, S. Nakamura, T. Toru, M. Shiro, *Eur. J. Org. Chem.* **2008**, 3465 – 3468.

[12] C.-P. Zhang, H.-P. Cao, Z.-L. Wang, C.-T. Zhang, Q.-Y. Chen, J.-C. Xiao, *Synlett* **2010**, 1089 – 1092.

[13] a) E. Magnier, J.-C. Blazejewski, M. Tordeux, C. Wakselman, *Angew. Chem.* **2006**, *118*, 1301 – 1304; *Angew. Chem. Int. Ed.* **2006**, *45*, 1279 – 1282; b) Y. Mace, B. Raymondeau, C. Pradet, J.-C. Blazejewski, E. Magnier, *Eur. J. Org. Chem.* **2009**, 1390 – 1397.

[14] a) G. G. Dubinina, H. Furutachi, D. A. Vicic, *J. Am. Chem. Soc.* **2008**, *130*, 8600 – 8601; b) D. M. Wiemers, D. J. Burton, *J. Am. Chem. Soc.* **1986**, *108*, 832 – 834.

[15] a) F. Cottet, M. Schlosser, *Eur. J. Org. Chem.* **2002**, 327 – 330; b) A. J. Goodman, S. P. Stanforth, B. Tarbit, *Tetrahedron* **1999**, *55*, 15067 – 15070; c) S. Takizawa, J. Nishida, T. Tsuzuki, S. Tokito, Y. Yamashita, *Inorg. Chem.* **2007**, *46*, 4308 – 4319; d) Q.-Y. Chen, Z.-T. Li, *J. Chem. Soc. Perkin Trans. 1* **1993**, *6*, 645 – 648; e) Y. Girard, J. G. Atkinson, P. C. Belanger, J. J. Fuentes, J. Rokach, C. S. Rooney, D. C. Remy, C. A. Hunt, *J. Org. Chem.* **1983**, *48*, 3220 – 3234; f) M. Yoshida, T. Yoshida, M. Kobayashi, N. Kamigata, *J. Chem. Soc. Perkin Trans. 1* **1989**, 909 – 914; g) T. Kino, Y. Nagase, Y. Ohtsuka, K. Yamamoto, D. Uraguchi, K. Tokuhisa, T. Yamakawa, *J. Fluorine Chem.* **2010**, *131*, 98 – 105.

[16] a) B. R. Langlois, N. Roques, *J. Fluorine Chem.* **2007**, *128*, 1318 – 1325; b) Y. Chang, C. Cai, *Tetrahedron Lett.* **2005**, *46*, 3161 – 3164; c) Q.-Y. Chen, J.-X. Duan, *Tetrahedron Lett.* **1993**, *34*, 4241 – 4244; d) Y. Kobayashi, I. Kumadaki, S. Sato, N. Hara, E. Chikami, *Chem. Pharm. Bull.* **1970**, *18*, 2334 – 2339; e) Q.-Y. Chen, S.-W. Wu, *J. Chem. Soc. Perkin Trans. 1* **1989**, 2385 – 2387; f) Y. Kobayashi, K. Yamamoto, I. Kumadaki, *Tetrahedron Lett.* **1979**, *20*, 4071 – 4072; g) C. Liu, Q.-Y. Chen, *Eur. J. Org. Chem.* **2005**, 3680 – 3686; h) F.-L. Qing, X. Zhang, Y. Peng, *J. Fluorine Chem.* **2001**, *111*, 185 – 187; i) D. E. Young, L. R. Anderson, D. E. Gould, W. B. Fox, *Tetrahedron Lett.* **1969**, *10*, 723 – 726.

[17] M. M. Kremlev, W. Tyrra, A. I. Mushta, D. Naumann, Y. L. Yagupolskii, *J. Fluorine Chem.* **2010**, *131*, 212 – 216.

