ChemPubSoc Europe

DOI: 10.1002/ejoc.201501623

EurJOC European Journal of Organic Chemistry

Communication

Trifluoromethylthiolation

Trifluoromethylthiolation of Unsymmetrical λ^3-Iodane Derivatives: Additive-Free, Selective and Scalable Introduction of the SCF_3 Group

Pavlo Nikolaienko,[a] Tülay Yildiz,[a] and Magnus Rueping*[a]

Abstract: The reaction of copper trifluoromethyl sulfide with diaryliodonium salts provides a straightforward pathway for the synthesis of aryl trifluoromethyl thioethers under mild reaction conditions and within short reaction times. High chemoselectivity was achieved by using mesityl as a leaving group. A large range of novel [(het)aryl](mesityl)iodonium salts underwent this reaction under the optimized conditions to give the desired products in moderate to good yields.

Introduction

In recent years fluorinated compounds received increased attention due to their widespread biological and therapeutic properties.[1] Among the vast array of fluorinated substances known to date, those containing perfluoroalkylthio groups (e.g. F_3CS, C_2F_5S) anchored to aromatic rings emerged as a valuable class of compounds[2a–2d] for the pharmaceutical and agrochemical industries.[2e] Compared with the parent alkylthio and perfluoroalkyl derivatives, the perfluoroalkylthio-containing compounds possess unique physical, chemical and biological properties.[3] In particular, the unusual high lipophilicity combined with the high electron-withdrawing ability of the perfluoroalkylthio groups raised more and more the interest of researchers for exploring new biologically active compounds containing such units. For example, tiflorex (flutiorex) is used in the treatment of nervous anorexia,[4a,4b] *N*-alkyl-4-(5*H*-dibenzo[*a*,*d*]-[7]annulen-5-ylidene)piperidines are being tested as dopamine antagonists,[4c,4d] toltrazuril is used as an antiprotozoal agent,[4e] and the thio analogue of riluzole has been tested for its potential biological activities[4f] (Figure 1).

Such aromatic derivatives containing one or more SCF_3 substituents are usually prepared according to two main synthetic strategies. One route toward aryl trifluoromethyl sulfides (Ar–SCF_3) is based on reactions of substrates that already contain sulfur. This route includes the fluorine/chlorine exchange of Ar–SCl_3 compounds[5] and trifluoromethylation of Ar–SX (X = H, Cl, CN, SR) with either CF_3X (X = I, Br), nucleophilic $CuCF_3$ or $TMSCF_3/F^-$.[6] The second route consists of the direct transfer of the SCF_3 group from special reagents to the aromatic substrates.[7]

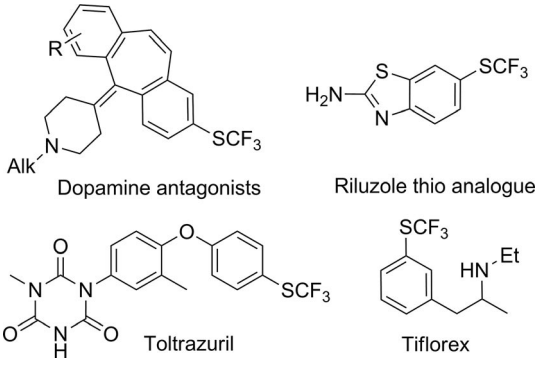


Figure 1. Biologically active compounds containing an SCF_3 group.

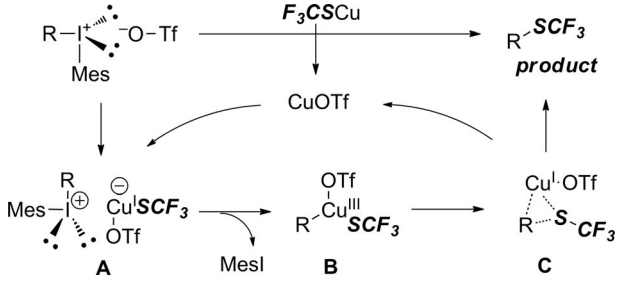
However, more recently more convenient nucleophilic and electrophilic reagents have been introduced for the trifluoromethylthiolation.[8–12] Typical nucleophilic reagents are $M(SCF_3)_n$ where M = Hg, Cu, Ag, K, Cs, $[Alk_4N]^+$.[8] On the other hand, various electrophilic reagents containing SCF_3 groups[9] as well as trifluoromethylsulfonyl hypervalent iodonium ylide[10] were applied for the synthesis of aryl trifluoromethyl sulfides.

Due to the steadily increasing usefulness and importance of this class of compounds, we were interested in devising a convenient, direct method for their synthesis under mild reaction conditions. For this purpose, our attention was drawn to diaryliodonium salts as electrophilic reagents.[13] Whereas symmetrical diaryliodonium salts were successfully applied as electrophilic arylating reagents either under transition-metal catalysis or metal-free reactions,[13] unsymmetrical diaryliodonium salts are less common as the presence of two different aromatic rings can potentially lead to the formation of a mixture of products. However, regiocontrol can be attained by discrimination of electronic and steric properties of the aromatic units.[13a] Despite significant developments in the reactions of diaryliodonium salts with various nucleophiles, there are no reports on their reaction with $CuSCF_3$.

[a] *Institute of Organic Chemistry, RWTH Aachen University*
Landoltweg 1, 52074 Aachen, Germany
E-mail: Magnus.Rueping@rwth-aachen.de
www.oc3.rwth-aachen.de/rueping/

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201501623.

It has been postulated that diaryliodonium salts react with Cu^{I} salts by oxidative insertion to form highly electrophilic Cu^{III} species.[13a] Under these circumstances, we anticipated that $CuSCF_3$ reacts with diaryliodonium salts by ligand exchange to form ion pair **A**, which undergoes oxidative insertion to give the $ArCu^{III}SCF_3$ species **B** (Scheme 1). The latter undergoes reductive elimination (**C**) to result in the formation of $ArSCF_3$ products. We also presume that the reaction can be mediated by the resulting CuOTf, which undergoes oxidative insertion more easily and then, by triflate counterion exchange with F_3CS^-, the $ArCu^{III}SCF_3$ species **B** forms much faster.

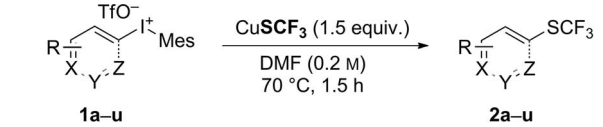


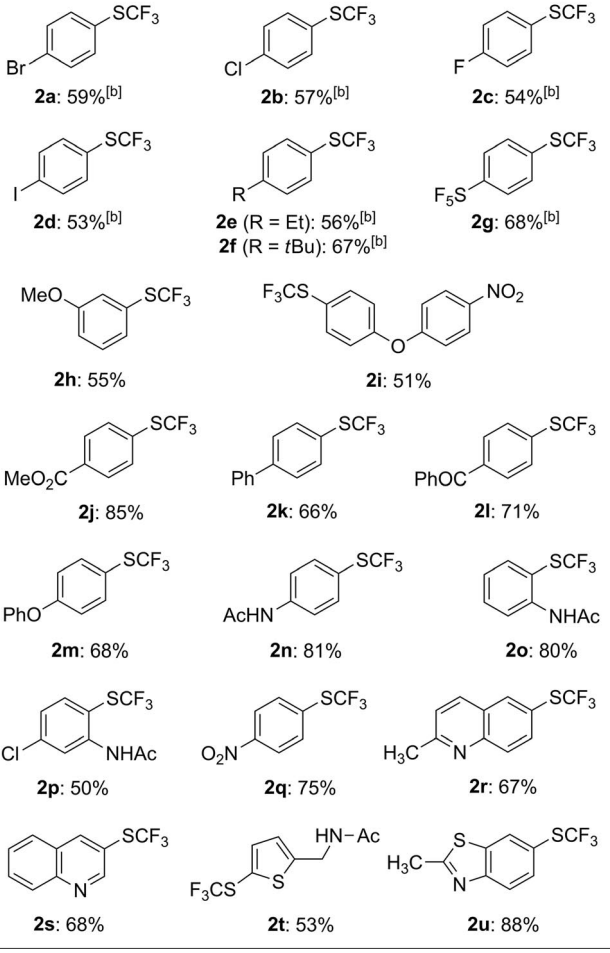
Scheme 1. Proposed mechanism for the formation of Ar–SCF_3 by oxidative addition of $Cu^{I}SCF_3$ and reductive elimination of the resulting Cu^{III} complex.

Results and Discussion

The reaction of $CuSCF_3$ with (*p*-bromophenyl)(mesityl)iodonium triflate (**1a**) was chosen as model and was performed in different solvents at room temperature for 1 h (see Table SI1 in the Supporting Information). Due to the low solubility of the starting materials, poor or no reactivity was observed in acetone, Et_2O, EtOAc, DCM, DCE and 1,4-dioxane. In CH_3CN and pyridine no reaction was observed, probably due to the copper ability to coordinate to the solvent. DMF and DMSO allowed the reaction to take place, and the desired product was formed in 65 and 60 % yield, respectively, although side products were also detected by TLC (Table SI1, Entries 1 and 2). ^{19}F NMR spectra show the formation of products with high regioselectivity (> 98:2) and unreacted $CuSCF_3$. Unfortunately, additional stirring and/or heating of the reaction mixture did not increase the yield. Solvents structurally similar to DMF, such as DMA, NMP, DMPU, TMU and others (Table SI1, Entries 12–17) were also tested; however, no improvement of the yield was observed. Given these findings, we decided to evaluate the influence of additives on the outcome of the reaction. It was found that additives such as phosphines, diketones and azines (Table SI2, Entries 1–10) almost inhibit the reaction. Additives such as tetraalkylammonium halides and tetrafluoroborates (Table SI2, Entries 11–15) did not improve the yield either. An ^{19}F NMR experiment performed in [D_7]DMF (Table SI5) showed no reaction with $AgSCF_3$, poor yield with the addition of 20 mol-% of CuBr, and good yield when 1.5 equiv. of $CuSCF_3$ was used. After extensive evaluation of different temperatures, stoichiometries, concentrations and counterions (see Supporting Information, Tables SI3–6) the optimal conditions were found as follows: 1 equiv. of diaryliodonium salt, 1.5 equiv. of $CuSCF_3$ in DMF (0.2 M), 70 °C, 1.5 h. With the optimal reaction conditions in hand, we applied various (aryl)(mesityl)iodonium triflates as starting materials in this transformation (Table 1).

Table 1. Trifluoromethylthiolation of unsymmetrical diaryliodonium salts under the optimized reaction conditions.[a]



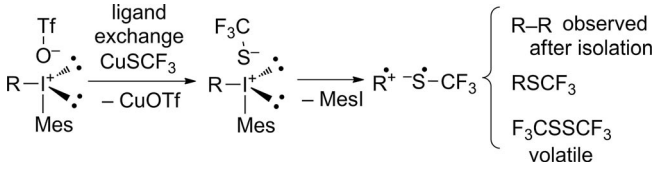


[a] Reaction conditions: **1** (0.5 mmol), $CuSCF_3$ (0.75 mmol), DMF (2.5 mL), see Supporting Information for details; yields for isolated compounds. [b] ^{19}F NMR yields ($PhCF_3$ was used as internal standard).

A wide range of electron-rich as well as electron-deficient diaryliodonium triflates **1a**–**u** was converted into the corresponding aryl trifluoromethyl sulfides **2a**–**u** under simple reaction conditions. The transformation tolerates many functional groups, and products containing groups such as halogens (**2a**–**d**), electron-donating alkyl, alkoxy, phenoxy, and aryl groups (**2e**, **2f**, **2h**, **2m**, **2k**), as well as electron-withdrawing methoxycarbonyl, benzoyl and nitro groups (**2j**, **2l**, **2q**) were obtained in good yields. It should be noted, that we faced some difficulties during the preparation of the iodonium salt starting materials containing a nitrogen atom in the molecule. Normally, we used a procedure, which requires iodoarene, mesitylene and *m*-CBPA mixed at room temperature in DCM, and slow addition of

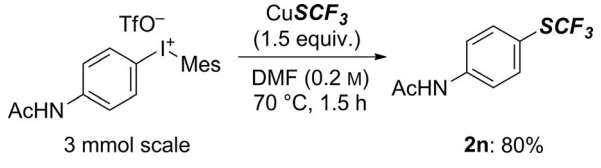
TfOH at 0 °C or –15 °C. When a nitro group is present, the ability of iodine to be oxidized to (*p*-nitro)iodosobenzene dramatically decreases.[14] In order to prepare such an iodonium salt, the mixture of iodoarene and *m*-CPBA had to be heated at reflux in DCM prior to the addition of mesitylene and TfOH. Moreover, under such conditions iodoanilines or iodobenzylamines react with *m*-CPBA to form *N*-oxides rather than iodoso derivatives. However recently, Olofsson et al.[15] reported an important advancement for the synthesis of a (mesityl)(pyridyl)iodonium salt, where it was postulated that basic N-atom is not prone to be oxidized when protonated by a strong acid (TfOH). The reaction requires elevated temperatures due to the electron-withdrawing effect of the quaternary nitrogen atom. Utilizing this approach offered us the possibility to synthesize various N-heterocycle- and amine-containing mesityliodonium salts in good yields (see Supporting Information). The results of reactions between the above-mentioned iodonium salts with $CuSCF_3$ are also presented in Table 1. Aniline derivatives **1n**–**p**, nitrogen-containing heterocycles **1r**, **1s**, **1u** as well as thiophene derivative **1t** were prepared and reacted smoothly under the typical reaction conditions. To isolate the products without copper contamination, the reaction mixture was treated with methanolic ammonia prior to the typical workup procedure without any loss in yield. It should be noted that – except for 4-(trifluoromethylthio)-1-iodobenzene (**2d**), which was obtained with 2:1 regioselectivity – all trifluoromethylthiolated products were obtained with very good regioselectivity (> 97:3).

In order to confirm the mechanism, the influence of a radical scavenger (TEMPO) and light was also carried out (Table SI2, Entries 16–20). Light did not affect the yield, and TEMPO did not suppress the reaction completely, although the yield decreased. This indicates that the reaction might also undergo a radical pathway (Scheme 2), which indirectly explains the biaryl formation in some cases.



Scheme 2. Proposed alternative mechanism for the formation of $Ar–SCF_3$.

Finally, to emphasize the applicability of our trifluoromethylthiolation protocol we performed the reaction between iodonium salt **1n** and $CuSCF_3$ on a 3 mmol scale (Scheme 3). The corresponding trifluoromethylthiolated aniline **2n** was obtained in 80 % yield. Noteworthy, the second product – mesityl iodide – was successfully recovered in 91 % yield, and was used again for the preparation of the iodonium salt.



Scheme 3. Scale-up of the trifluoromethylthiolation of diaryliodonium salts.

Conclusions

We have developed a novel method for the Cu-mediated $C_{sp^2}–SCF_3$ bond-forming reaction.[16] Extensive investigations showed that no ligand and additives are necessary. By applying this mild and rapid protocol, a variety of diaryliodonium salts were converted into their corresponding aryl trifluoromethyl thioethers in good yields Moreover, the scope was widened by utilizing heteroaromatic iodonium salts, and many of the presented (heteroaryl)(mesityl)iodonium salts were unknown prior this work. Due to the wide spectrum of biological activities exhibited by $Ar–SCF_3$ compounds, mild reaction conditions and the simplicity of our protocol, we expect this method to be added to the range of synthetic approaches affording aryl trifluoromethyl sulfides.

Acknowledgments

T. Y. thanks the Republic of Turkey Council of Higher Education (CoHE) for a fellowship.

Keywords: Fluorine · Diaryliodonium salts · Cross-coupling · Trifluoromethyl thioethers · Copper catalysis

[1] a) R. Filler, Y. Kobayashi, L. M. Yagupolskii, *Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications*, Elsevier, Amsterdam, **1993**; b) K. Muller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; c) S. Purser, P. R. Morre, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320–330; d) W. K. Hagmann, *J. Med. Chem.* **2008**, *51*, 4359–4369; e) T. Yamazaki, T. Taguchi, I. Ojima, *Fluorine in Medicinal Chemistry and Chemical Biology* (Ed.: I. Ojima), Wiley-Blackwell, Chichester, **2009**; f) V. A. Petrov, *Fluorinated Heterocyclic Compounds: Synthesis, Chemistry, and Applications*, Wiley, Hoboken, New Jersey, **2009**; g) B. Manteau, S. Pazenok, J. P. Vors, F. R. Leroux, *J. Fluorine Chem.* **2010**, *131*, 140–158; h) T. Furuya, A. S. Kamlet, T. Ritter, *Nature* **2011**, *473*, 470–477.

[2] For recent reviews summarizing methods of the synthesis of aryl trifluoromethyl sulfides, see: a) V. N. Boiko, *Beilstein J. Org. Chem.* **2010**, *6*, 880–921; b) F. Toulgoat, S. Alazet, T. Billard, *Eur. J. Org. Chem.* **2014**, 2415; c) X.-H. Xu, K. Matsuzaki, N. Shibata, *Chem. Rev.* **2015**, *115*, 731–764; d) A. Tlili, T. Billard, *Angew. Chem. Int. Ed.* **2013**, *52*, 6818–6819; *Angew. Chem.* **2013**, *125*, 6952–6954; e) A. Becker, *Inventory of Industrial Fluoro-Biochemicals*, Eyrolles, Paris, **1996**.

[3] a) C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195; b) A. Leo, C. Hansch, D. Elkins, *Chem. Rev.* **1971**, *71*, 525–616; c) L. M. Yagupolskii, A. Y. Ilchenko, N. V. Kondratenko, *Russ. Chem. Rev.* **1974**, *43*, 32–47; d) F. Leroux, P. Jeschke, M. Schlosser, *Chem. Rev.* **2005**, *105*, 827–856.

[4] a) M. J. Kirby, H. Carageorgiou-Markomihalakis, P. Turner, *Br. J. Clin. Pharmacol.* **1975**, *2*, 541–542; b) T. Silverstone, J. Fincham, J. Plumley, *Br. J. Clin. Pharmacol.* **1979**, *7*, 353–356; c) D. C. Remy, S. F. Britcher, S. W. King, P. S. Anderson, C. A. Hunt, W. C. Randall, P. Bélanger, J. G. Atkinson, Y. Girard, C. S. Rooney, J. J. Fuentes, J. A. Totaro, J. L. Robinson, E. A. Risley, M. Williams, *J. Med. Chem.* **1983**, *26*, 974–980; d) K. J. Watling, *J. Pharm. Pharmacol.* **1980**, *32*, 778–779; e) A. Günther, K.-H. Mohrmann, M. Stubbe, H. Ziemann (Bayer AG), DE3516630, **1986**; f) P. Jimonet, F. Audiau, M. Barreau, J. C. Blanchard, A. Boireau, Y. Bour, M. A. Coléno, A. Doble, G. Doerflinger, C. D. Hu, M. H. Donat, J. M. Duchesne, P. Ganil, C. Guérémy, E. Honoré, B. Just, R. Kerphirique, S. Gontier, P. Hubert, P. M. Laduron, J. Le Blevec, M. Meunier, J. M. Miquet, C. Nemecek, M. Pasquet, O. Piot, J. Pratt, J. Rataud, M. Reibaud, J. M. Stutzmann, S. Mignani, *J. Med. Chem.* **1999**, *42*, 2828–2843.

[5] a) E. A. Nodiff, S. Lipschutz, P. N. Craig, M. Gordon, *J. Org. Chem.* **1960**, *25*, 60–65; b) T. Umemoto, S. Ishihara, *J. Fluorine Chem.* **1999**, *98*, 75–81; c) J. M. Kremsner, M. Rack, C. Pilger, C. O. Kappe, *Tetrahedron Lett.* **2009**, *50*, 3665–3668.

[6] a) C. Wakselman, M. Tordeux, *J. Org. Chem.* **1985**, *50*, 4047–4051; b) T. Billard, B. R. Langlois, *Tetrahedron Lett.* **1996**, *37*, 6865–6868; c) T. Billard, S. Large, B. R. Langlois, *Tetrahedron Lett.* **1997**, *38*, 65–68; d) V. N. Movchun, A. A. Kolomeitsev, Y. L. Yagupolskii, *J. Fluorine Chem.* **1995**, *70*, 255–257; e) A. Harsanyi, E. Dorko, A. Csapo, T. Bako, C. Peltz, J. Rabai, *J. Fluorine Chem.* **2011**, *132*, 1241–1246; f) C. Pooput, M. Medebielle, W. R. Dolbier Jr., *Org. Lett.* **2004**, *6*, 301–303; g) I. Kieltsch, P. Eisenberger, A. Togni, *Angew. Chem. Int. Ed.* **2007**, *46*, 754–757; *Angew. Chem.* **2007**, *119*, 768–771.

[7] a) L. M. Yagupolskii, A. V. Bezdudnui, Y. L. Yagupolskii, *Russ. J. Org. Chem.* **2006**, *42*, 1275–1279; b) S. Munavalli, *Phosphorus Sulfur Silicon Relat. Elem.* **2006**, *181*, 305–324; c) S. Munavalli, R. K. Rohrbaugh, G. W. Wagner, H. D. Durst, F. R. Longo, *Phosphorus, Sulfur, Silicon Relat. Elem.* **2004**, *179*, 1635–1643; d) S. Munavalli, D. K. Rohrbaugh, D. I. Rossman, F. J. Berg, H. D. Durst, *Phosphorus, Sulfur, Silicon Relat. Elem.* **2004**, *179*, 1645–1655; e) S. Munavali, D. I. Rossman, D. K. Rohrbaugh, C. P. Ferguson, *J. Fluorine Chem.* **1993**, *61*, 147–153; f) L. D. Tran, I. Popov, O. Daugulis, *J. Am. Chem. Soc.* **2012**, *134*, 18237–18240.

[8] a) E. H. Man, D. D. Coffman, E. L. Muetterties, *J. Am. Chem. Soc.* **1959**, *81*, 3575–3577; b) J. Emeleus, D. E. MacDuffie, *J. Chem. Soc.* **1961**, 2597–2599; c) J. H. Clark, C. W. Jones, A. P. Kybett, M. A. McClinton, *J. Fluorine Chem.* **1990**, *48*, 249–255; d) W. Tyrra, D. Naumann, B. Hoge, Yu. Yagupolskii, *J. Fluorine Chem.* **2003**, *119*, 101–107; e) D. J. Adams, J. H. Clark, *J. Org. Chem.* **2000**, *65*, 1456–1460; f) L. M. Yagupolskii, N. V. Kondratenko, V. P. Sanbur, *Synthesis* **1975**, 721–723; g) D. J. Adams, A. Goddard, J. H. Clark, D. J. Macquarrie, *Chem. Commun.* **2000**, 987–988; h) G. Teverovskiy, D. S. Surry, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2011**, *50*, 7312–7314; *Angew. Chem.* **2011**, *123*, 7450–7452; i) C.-P. Zhang, D. A. Vicic, *J. Am. Chem. Soc.* **2012**, *134*, 183–185; j) C.-P. Zhang, D. A. Vicic, *Chem. Asian J.* **2012**, *7*, 1756–1758; k) Z. Weng, W. He, C. Chen, R. Lee, D. Tan, Z. Lai, D. Kong, Y. Yuan, K.-W. Huang, *Angew. Chem. Int. Ed.* **2013**, *52*, 1548–1552; *Angew. Chem.* **2013**, *125*, 1588–1592; l) J. Xu, X. Mu, P. Chen, J. Ye, G. Liu, *Org. Lett.* **2014**, *16*, 3942–3945; m) W. Yin, Z. Wang, Y. Huang, *Adv. Synth. Catal.* **2014**, *356*, 2998–3006; n) Q. Xiao, J. Sheng, Q. Ding, J. Wu, *Eur. J. Org. Chem.* **2014**, 217–221; o) G. Yin, I. Kalvet, U. Englert, F. Schoenebeck, *J. Am. Chem. Soc.* **2015**, *137*, 4164–4172; p) G. Yin, I. Kalvet, F. Schoenebeck, *Angew. Chem. Int. Ed.* **2015**, *54*, 6809–6813; *Angew. Chem.* **2015**, *127*, 6913–6917; q) A. B. Dürr, G. Yin, I. Kalvet, F. Napoly, F. Schoenebeck, *Chem. Sci.* **2015**, DOI: 10.1039/c5sc03359d; r) C. Matheis, V. Wagner, L. J. Goossen, *Chem. Eur. J.* **2016**, *22*, 79–82.

[9] a) A. Ferry, T. Billard, E. Bacque, B. R. Langlois, *J. Fluorine Chem.* **2012**, *134*, 160–163; b) Y. Yang, X. Jiang, F.-L. Qing, *J. Org. Chem.* **2012**, *77*, 7538–7547; c) F. Baert, J. Colomb, T. Billard, *Angew. Chem. Int. Ed.* **2012**, *51*, 10382–10385; *Angew. Chem.* **2012**, *124*, 10528–10531; d) Q. Xiao, J. Sheng, Z. Chen, J. Wu, *Chem. Commun.* **2013**, *49*, 8647–8649; e) J. Sheng, S. Li, J. Wu, *Chem. Commun.* **2014**, *50*, 578–580; f) J. Sheng, C. Fan, J. Wu, *Chem. Commun.* **2014**, *50*, 5494–5496; g) S. Alazet, L. Zimmer, T. Billard, *J. Fluorine Chem.* **2014**, *136*, 160–163; h) S. Alazet, T. Billard, *Synlett* **2015**, *26*, 76–78; i) M. Jereb, K. Gosak, *Org. Biomol. Chem.* **2015**, *13*, 3103–3115; j) Q. Glenadel, S. Alazet, A. Tlili, T. Billard, *Chem. Eur. J.* **2015**, *21*, 14694–14698; k) X. Shao, X. Wang, T. Yang, L. Lu, Q. Shen, *Angew. Chem. Int. Ed.* **2013**, *52*, 3457–3460; *Angew. Chem.* **2013**, *125*, 3541–3544; l) B. Ma, X. Shen, Q. Shen, *J. Fluorine Chem.* **2015**, *171*, 73–77; m) X. Shao, C. Xu, L. Lu, Q. Shen, *J. Org. Chem.* **2015**, *80*, 3012–3021; n) S. Munavalli, D. K. Rohrbaugh, D. I. Rossman, F. J. Berg, G. W. Wagnefi, H. D. Dud, *Synth. Commun.* **2000**, *30*, 2847–2854; o) K. Kang, C. Xu, Q. Shen, *Org. Chem. Front.* **2014**, *1*, 294–297; p) R. Honeker, J. B. Ernst, F. Glorius, *Chem. Eur. J.* **2015**, *21*, 8047–8051; q) C. Xu, Q. Shen, *Org. Lett.* **2014**, *16*, 2046–2049; for saccharine-SCF_3, see: r) C. Xu, B. Ma, Q. Shen, *Angew. Chem. Int. Ed.* **2014**, *53*, 9316–9320; *Angew. Chem.* **2014**, *126*, 9470–9474; s) Q. Wang, Z. Qi, F. Xie, X. Li, *Adv. Synth. Catal.* **2015**, *357*, 355–360; t) Q. Wang, F. Xie, X. Li, *J. Org. Chem.* **2015**, *80*, 8361–8366.

[10] For in situ generation of the SCF_3 group, see: a) Q.-Y. Chen, J.-X. Duan, *J. Chem. Soc., Chem. Commun.* **1993**, 918–919; b) C. Chen, Y. Xie, L. Chu, R. W. Wang, X. Zhang, F.-L. Qing, *Angew. Chem. Int. Ed.* **2012**, *51*, 2492–2495; *Angew. Chem.* **2012**, *124*, 2542–2545; c) L. Zhai, Y. Li, J. Yin, K. Jin, R. Zhang, X. Fu, C. Duan, *Tetrahedron* **2013**, *69*, 10262–10266; d) W. Zhong, X. Liu, *Tetrahedron Lett.* **2014**, *55*, 4909–4911; e) G. Danoun, B. Bayarmagnai, M. F. Gruenberg, L. J. Goossen, *Chem. Sci.* **2014**, *5*, 1312–1316; f) B. Bayarmagnai, C. Matheis, E. Risto, L. J. Goossen, *Adv. Synth. Catal.* **2014**, *356*, 2343–2348; g) B. Exner, B. Bayarmagnai, F. Jia, L. J. Goossen, *Chem. Eur. J.* **2015**, *21*, 17220–17223; h) L. Jiang, J. Qian, W. Yi, G. Lu, C. Cai, W. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54*, 14965–14969; *Angew. Chem.* **2015**, *127*, 15178–15182.

[11] For the use of trifluoromethylsulfonyl hypervalent iodonium ylides, see: a) Y.-D. Yang, A. Azuma, E. Tokunaga, M. Yamasaki, M. Shiro, N. Shibata, *J. Am. Chem. Soc.* **2013**, *135*, 8782–8785; b) Z. Huang, Y.-D. Yang, E. Tokunaga, N. Shibata, *Org. Lett.* **2015**, *17*, 1094–1097; c) S. Arimori, M. Takada, N. Shibata, *Dalton Trans.* **2015**, *44*, 19456–19459.

[12] Examples of our contributions: a) T. Bootwicha, X. Liu, R. Pluta, I. Atodiresei, M. Rueping, *Angew. Chem. Int. Ed.* **2013**, *52*, 12856–12859; *Angew. Chem.* **2013**, *125*, 13093–13097; b) M. Rueping, N. Tolstoluzhsky, P. Nikolaienko, *Chem. Eur. J.* **2013**, *19*, 14043–14046; c) R. Pluta, P. Nikolaienko, M. Rueping, *Angew. Chem. Int. Ed.* **2014**, *53*, 1650–1653; *Angew. Chem.* **2014**, *126*, 1676–1679; d) P. Nikolaienko, R. Pluta, M. Rueping, *Chem. Eur. J.* **2014**, *20*, 9867–9970; e) M. Rueping, X. Liu, T. Bootwicha, R. Pluta, C. Merkens, *Chem. Commun.* **2014**, *50*, 2508–2511; f) R. Pluta, M. Rueping, *Chem. Eur. J.* **2014**, *20*, 17315–17318; g) Q. Lefebvre, E. Fava, P. Nikolaienko, M. Rueping, *Chem. Commun.* **2014**, *50*, 6617–6619; h) R. Husmann, E. Sugiono, S. Mersmann, G. Raabe, M. Rueping, C. Bolm, *Org. Lett.* **2011**, *13*, 1044–1047; i) M. Rueping, M. S. Maji, H. Başpınar Küçük, I. Atodiresei, *Angew. Chem. Int. Ed.* **2012**, *51*, 12864–12868; *Angew. Chem.* **2012**, *124*, 13036–13040; j) M. Rueping, T. Bootwicha, S. Kambutong, E. Sugiono, *Chem. Asian J.* **2012**, *7*, 1195–1198; k) X. Hong, H. Başpınar Küçük, M. S. Maji, M. Rueping, K. N. Houk, *J. Am. Chem. Soc.* **2014**, *136*, 13769–13780; l) D. Parmar, M. S. Maji, M. Rueping, *Chem. Eur. J.* **2014**, *20*, 83–86; m) C. M. R. Volla, A. Das, I. Atodiresei, M. Rueping, *Chem. Commun.* **2014**, *50*, 7889–7892; n) D. Parmar, M. Rueping, *Chem. Commun.* **2014**, *50*, 13928–13931; o) Q. Lefebvre, R. Pluta, M. Rueping, *Chem. Commun.* **2015**, *51*, 4394–4397; p) Q. Lefebvre, N. Hoffmann, M. Rueping, *Chem. Commun.* **2016**, *52*, DOI: 10.1039/c5cc09881e; q) P. Nikolaienko, M. Rueping, *Chem. Eur. J.* **2016**, DOI: 10.1002/chem.201504601.

[13] For recent reviews, see: a) A. Merritt, B. Olofsson, *Angew. Chem. Int. Ed.* **2009**, *48*, 9052–9070; *Angew. Chem.* **2009**, *121*, 9214–9234; b) M. S. Yusubov, A. V. Maskaev, V. V. Zhdankin, *ARKIVOC (Gainesville, FL, U.S.)* **2011**, 370–409; c) V. V. Zhdankin, *Hypervalent Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine* Compounds, John Wiley and Sons, Inc., Chichester, West Sussex, **2014**, pp. 260–278.

[14] M. Bielawski, B. Olofsson, *Chem. Commun.* **2007**, 2521–2523.

[15] a) M. Bielawski, J. Malmgren, L. M. Pardo, Y. Wikmark, B. Olofsson, *ChemistryOpen* **2014**, *3*, 19–22; b) R. Ghosh, E. Stridfeldt, B. Olofsson, *Chem. Eur. J.* **2014**, *20*, 8888–8892.

[16] During the preparation of this manuscript, a similar study was reported: P. Saravanan, P. Anbarasan, *Adv. Synth. Catal.* **2015**, *357*, 3435–3440.

Received: December 30, 2015
Published Online: February 1, 2016

