Fe-mediated nucleophilic trifluoromethylselenolation of activated alkyl bromides via umpolung reactivity of trifluoromethyl tolueneselenosulfinate

Kevin Grollier, Emmanuel Chefdeville, Arnaud de Zordo-Banliat, Bruce Pegot, Guillaume Dagousset, Emmanuel Magnier, Thierry Billard

Fe-mediated nucleophilic trifluoromethylselenolation of activated alkyl bromides via umpolung reactivity of trifluoromethyl tolueneselenosulfinate.

Kevin Grollier,[a] Emmanuel Chefdeville,[b] Arnaud De Zordo-Banliat,[c] Bruce Pegot,[c] Guillaume Dagousset,[c] Emmanuel Magnier,[c] and Thierry Billard*[a, d]

[a] *Institute of Chemistry and Biochemistry (ICBMS, UMR CNRS 5246), Univ Lyon, Université Lyon 1, CNRS, CPE, INSA, 43 Bd du 11 novembre 1918, 69622 Villeurbanne (France)*
[b] *NMR Centre, Univ Lyon, Université Lyon 1, CNRS, 43 Bd du 11 novembre 1918, 69622 Lyon (France). Thierry.billard@univ-lyon1.fr*
[c] *Institut Lavoisier de Versailles (UMR CNRS 8180), Université Paris-Saclay, UVSQ, CNRS 78035 Versailles (France)*
[d] *CERMEP-In vivo imaging, 59 Bd Pinel, 69677 Lyon (France)*

Abstract: Trifluoromethyl tolueneselenosulfonate is a versatile reagent which can be reduced by iron powder to generate *in situ* trifluoromethylselenolate anion. This species can then react with alkyl bromide to perform S_N2 reaction.

Keywords: Fluorine, Selenium, Trifluoromethylselenolation, Iron

1. Introduction

Because of the intrinsic properties of fluorine atom, fluorinated molecules generally possess particular characteristics [1-4]. Consequently, fluorinated compounds played these last years important role in various fields of applications from materials to life sciences [5-19]. In the objective to propose new substrates with dedicated properties, the development of new emerging fluorinated motifs known a rising interest this last decade [20]. In particular, merging of trifluoromethyl group with heteroatoms known a certain craze. More specifically, trifluoromethylchalcogen motifs were particularly investigated, in partly due to their high Hansch-Leo lipophilicity parameters ($\pi_R(CF_3O) = 1.04$, ($\pi_R(CF_3S) = 1.44$, ($\pi_R(CF_3Se) = 1.61$) which contribute to enhance the bioavailability of molecules [3, 21-23].

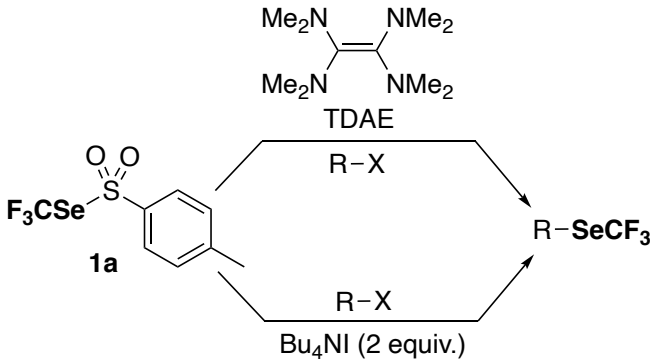
If CF_3O and CF_3S chemistry is now well described [24-31], CF_3Se group remains still less explored [31-33], maybe due to the toxicity generally associated with selenium [34, 35]. However, selenium is also an indispensable trace element playing a crucial role in human

physiology [36-38]. Furthermore, selenylated compounds find applications in various fields such as materials or life sciences [35, 39-49]. Moreover, recently, trifluoromethylselenolated derivatives of nonsteroidal anti-inflammatory have shown promising anticancer properties [50, 51].

Consequently, development of new synthetic methods to efficiently introduce CF_3Se onto organic substrates is highly required. In particular, late-stage direct trifluoromethylselenolation is particularly studied these last years [27, 31-33]. Among the various described approaches, nucleophilic reactions with CF_3Se^- anion are well investigated [27]. However, this anion suffers from various drawbacks: stability issues and tedious synthesis [32, 52]. Therefore, new strategies to *in situ* generate this anion are necessary.

2. Results and discussion

We recently described trifluoromethyl tolueneselenosulfonate (**1a**) as a versatile reagent to perform trifluoromethylselenolation following various pathways [22, 53-57]. Thus, its umpolung reactivity was described through *in situ* generation of CF_3Se^- anion to perform S_N2 reactions. This umpolung behavior is based either on the 2 electrons reduction of **1a** with TDAE (tetrakis(dimethylamino) ethylene) [56] or on the transient generation of CF_3SeI, which possesses an inverted polarity, in presence of an excess of TBAI (tetrabutylammonium iodide) [57] (Scheme 1).

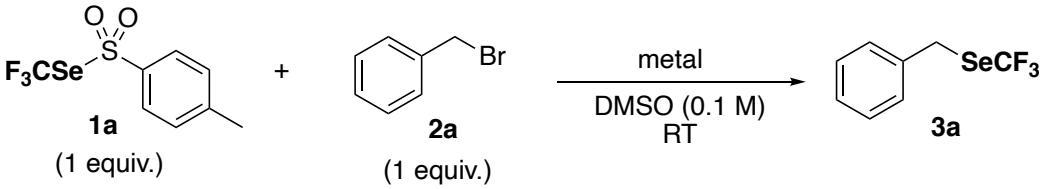


Scheme 1. Previous umpolung reactivity of **1a**.

Despite the efficiency of these methods, they require the use of sensitive TDAE or an excess of TBAI. Consequently, we decided to investigate a novel approach cheaper, cleaner and with an easier purification process. In particular, the reductive conditions, developed with TDAE, was reinvestigated by using other reducers. More specifically, a great interest was focused on inexpensive non-precious metals.

Redox potential of **1a** was previously measured in DMSO at -0.32 V (*vs* SHE) [54]. Such value led us to consider Zn ($E^0\{Zn^{2+}/Zn\}$ = -0.76 V) and Fe ($E^0\{Fe^{2+}/Fe\}$ = -0.45 V) as potential metallic reducer [58]. The conditions reaction were screened with benzyl bromide (**2a**) as model substrate (Table 1).

Table 1. Nucleophilic Trifluoromethylselenolation of **2a** with **1a**.

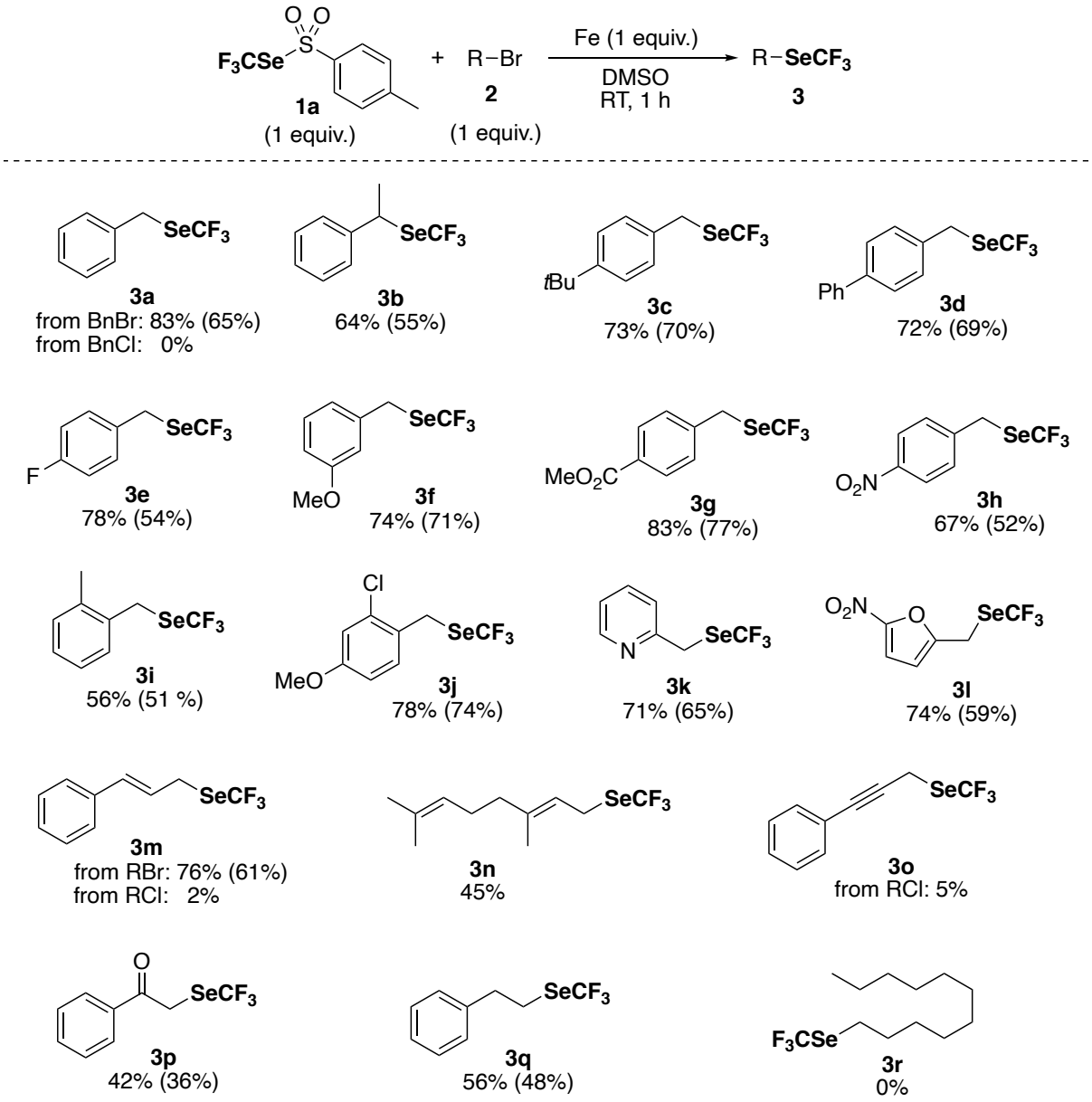


Entry	Metal (equiv.)	Solvent	t (min)	**3a** (%)[a]
1	Zn (3 equiv.)	DMSO	60	90
2	Zn (2 equiv.)	DMSO	60	93
3	Zn (1 equiv.)	DMSO	60	65
4	Zn (2 equiv.)	DMSO	15	95
5	Zn (2 equiv.)	CH_3CN	15	0
6	Zn (2 equiv.)	THF	15	11
7	Fe (2 equiv.)	DMSO	15	86
8	Fe (1 equiv.)	DMSO	60	83
9	-	DMSO	60	0

[a] Yields determined by ^{19}F NMR with $PhOCF_3$ as internal standard.

In presence of 3 equivalents of zinc powder, a good yield was obtained in 1 h at room temperature (entry 1). The same result was also obtained with 2 equivalents of Zn (entry 2) whereas with only 1 equivalent, the yield dropped (entry 3). Interestingly, good result was observed in only 15 min of reaction (entry 4). Other solvents were tested but with highly disappointing results (entries 5-6). In view of these positive results, cheaper iron was then considered as reducing metal. With 2 equivalents of Fe in DMSO, a slightly lower yield was obtained (entry 7). In contrast to Zn, the use of only 1 equivalent provided also good result (entry 8). Finally, as expected, Fe appeared essential to the reaction (entry 9).

The optimal conditions with Fe in hand (entry 8), the scope of reaction was then investigated (Scheme 2).

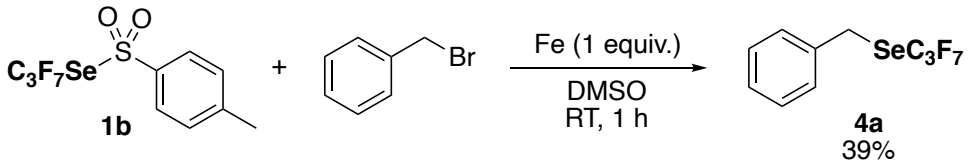


Scheme 2. Fe-mediated trifluoromethylselenolation. Yields determined by ^{19}F NMR with $PhOCF_3$ as internal standard. In parentheses, isolated yields.

Good yields were obtained with benzylic substrates, whatever the aromatic substituents (electron withdrawing or donating) (**3a-j**). The steric hindrance has only a slight influence (**3b**, **3i-j**). Heteroaromatic benzylic substrates led also to good result (**3k-l**). The reaction is compatible with functional groups such as ester (**3g**) or nitro (**3h**, **3l**) as well as aromatic chloride (**3j**). Cinnamyl bromide was efficiently trifluoromethylselenolated (**3m**) whereas geranyl bromide led only to medium yield (**3n**). Starting from bromo-acetophenone, medium result was obtained (**3p**), maybe due to an interaction between carbonyl and Fe. With non-

activated substrates, a lower reactivity was observed (**3q**-**r**), bromoundecane staying unreactive (**3r**). On contrary to bromide derivatives, chloride ones were quite unreactive (**3a**, **3m**, **3o**). Interestingly, because of the simplicity of the procedure, most of the final products can be isolated with satisfactory purity by a simple extraction.

Finally, the method was extended to a higher fluorinated homolog of **1a**. Thus, nucleophilic heptafluoropropylselenolation, scarcely described, was performed with medium yield, but satisfactory in this series (Scheme 3).



Scheme 3. Heptafluoropropylselenolation of benzyl bromide. Isolated yield.

3. Conclusion

This work contributes to demonstrate the high versatility of trifluoromethyl tolueneselenosulfinate as trifluoromethylselenolating reagent. With these results, a third method to initiate umpolung reactivity of this reagent is described. This approach is complementary of the previous ones and, in particular, allows a rapid way to obtain expected products, without further purifications, with satisfactory purity.

4. Experimental

General. Commercial reagents were used as supplied. Anhydrous solvents were used as supplied. NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz (^{1}H NMR), 376 MHz (^{19}F NMR) or on a Bruker AV 300 spectrometer at 300 MHz (^{1}H NMR), 282 MHz (^{19}F NMR). Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). All coupling constants were reported in Hz.

Typical procedure for the perfluororalkylselenolation of alkyl halides.

To a 10 mL tube equipped with a magnetic stir bar was weighted Fe (0.1 mmol, 1 equiv.). A solution of **1** (0.1 mmol, 1 equiv.) and **2** (0.1 mmol, 1 equiv.) in anhydrous DMSO (1 mL, 0.1 M) was added to the tube and the tube was rapidly sealed. The crude mixture was vigorously stirred at room temperature for 1 h. Conversion was checked by ^{19}F using $PhOCF_3$ as internal standard (filtration of the sample on PTFE 0.45 µm filter was required). The crude mixture was partitioned between pentane or Et_2O and water. The aqueous layer was extracted with pentane

or Et_2O two times, combined organic layers were washed with water and brine, dried over $MgSO_4$, filtered and concentrated to dryness under moderate vacuum affording the desired product **3** or **4**.

Synthesis of benzyl(trifluoromethyl)selane (3a).

Colorless oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37-7.27 (m, 5H), 4.24 (s, 2H)

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.46 (s, 3F).

Characterization data match that reported in the literature [59].

Synthesis of (1-phenylethyl)(trifluoromethyl)selane (3b).

Yellowish oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.23 (m, 5H), 4.79 (q, *J* = 7.1 Hz, 1H), 1.93 (qq, *J*(H,H) = 7.1, *J*(H,F) 0.7 Hz, 3H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -33.57 (s, 3F).

Characterization data match that reported in the literature [56].

Synthesis of (4-(tert-butyl)benzyl)(trifluoromethyl)selane (3c).

Colorless oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36 (m, 2H), 7.28 (m, 2H), 4.24 (s, 2H), 1.32 (s, 9H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.53 (s, 3F).

Characterization data match that reported in the literature [60].

Synthesis of ([1,1'-biphenyl]-4-ylmethyl)(trifluoromethyl)selane (3d).

White solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 4H), 7.50 – 7.33 (m, 5H), 4.31 (s, 2H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.93 (s, 3F).

Characterization data match that reported in the literature [61].

Synthesis of (4-fluorobenzyl)(trifluoromethyl)selane (3e).

Yellowish oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 (m, 2H), 7.02 (m, 2H), 4.22 (s, 2H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.38 (s, 3F), -114,11 (m, 1H).

Characterization data match that reported in the literature [60].

Synthesis of (3-methoxybenzyl)(trifluoromethyl)selane (3f).

Yellowish oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.24 (m, 1H), 6.93 (m, 1H), 6.88 (m, 1H), 6.82 (m, 1H), 4.22 (s, 2H), 3.81 (s, 3H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.52 (s, 3F).

Characterization data match that reported in the literature [62].

Synthesis of methyl 4-(((trifluoromethyl)selanyl)methyl)benzoate (3g).

Yellowish oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.00 (m, 2H), 7.40 (m, 2H), 4.25 (s, 2H), 3.91 (s, 3H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.33 (s, 3F).

Characterization data match that reported in the literature [56].

Synthesis of (4-nitrobenzyl)(trifluoromethyl)selane (3h)

Yellow oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.22 (m, 2H), 7.52 (m, 2H), 4.28 (s, 2H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.12 (s, 3F).

Characterization data match that reported in the literature [62].

Synthesis of (2-methylbenzyl)(trifluoromethyl)selane (3i).

Colorless oil.

^{1}H NMR (300 MHz, Chloroform-d) 7.27 (m, 1H), 7.23-7.13 (m, 3H), 4.28 (s, 2H), 2.40 (s, 3H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.49 (s, 3F).

Characterization data match that reported in the literature [60].

Synthesis of (2-chloro-4-methoxybenzyl)(trifluoromethyl)selane (XX)

Yellowish oil.

^{1}H NMR (500 MHz, Chloroform-d) δ 7.26 (d, J = 8.6 Hz, 1H), 6.94 (d, J = 2.6 Hz, 1H), 6.77 (dd, J = 8.5, 2.6 Hz, 1H), 4.26 (s, 2H), 3.79 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 160.03, 134.88, 131.47, 126.54, 123.06 (q, J = 331.3 Hz), 115.34, 113.38, 55.69, 26.62 (d, J = 1.8 Hz).

^{19}F NMR (376 MHz, Chloroform-d) δ -34.28.

HRMS (EI): calc. for [$C_9H_8ClF_3OSe$] 303.9376, measured 3030.9366

Synthesis of 2-(((trifluoromethyl)selanyl)methyl)pyridine (3k).

Synthetized From HBr salt.

Yellowish oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 4.8 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.19 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 4.37 (s, 2H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.59 (s, 3F).

Characterization data match that reported in the literature [56].

Synthesis of 2-nitro-5-(((trifluoromethyl)selanyl)methyl)furan (3l).

Brownish oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.26 (d, *J* = 3.7 Hz, 1H), 6.52 (d, *J* = 3.7 Hz, 1H), 4.18 (s, 2H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.45 (s, 3F).

Characterization data match that reported in the literature [56].

Synthesis of cinnamyl(trifluoromethyl)selane (3m).

Colorless oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.37-7.21 (m, 5H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.31 (dt, *J* = 15.5, 7.7 Hz, 1H), 3.82 (d, *J* = 7.7 Hz, 2H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -33.79 (s, 3F).

Characterization data match that reported in the literature [62].

Synthesis of (*E*)-(3,7-dimethylocta-2,6-dien-1-yl)(trifluoromethyl)selane (3n).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -34.06 (s, 3F).

Characterization data match that reported in the literature [63].

Synthesis of (3-phenylprop-2-yn-1-yl)(trifluoromethyl)selane (3o).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -35.41 (s, 3F).

Characterization data match that reported in the literature [62].

Synthesis of 1-phenyl-2-((trifluoromethyl)selanyl)ethan-1-one (3p).

Yellowish oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.97 (m, 2H), 7.63 (t, *J* = 7.4, 1.2 Hz, 1H), 7.51 (m, 2H), 4.63 (s, 2H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.21 (s, 3F).

Characterization data match that reported in the literature [64].

Synthesis of phenethyl(trifluoromethyl)selane (3q).

Yellowish oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.33 (m, 2H), 7.27 (m, 1H), 7.21 (m, 2H), 3.23 (m, 2H), 3.10 (m, 2H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -34.10 (s, 3F).

Characterization data match that reported in the literature [62].

Synthesis of benzyl(perfluoropropyl)selane (4a)

Yellowish oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 5H), 4.29 (s, 2H).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -79.73 (t, J = 9.2 Hz, 3F), -87.70 (m, 2F), -122.74 (t, J = 3.9 Hz, 2F).

Characterization data match that reported in the literature [59].

Acknowledgments

This work was supported by a grant from the French National Research Agency (ANR 18-CE07-0039-01). The authors are grateful to the French National Research Agency, the CNRS and the French Ministry of Research for financial support. The French Fluorine Network (GIS-FLUOR) is also acknowledged for its support.

Reference

[1] The Curious World of Fluorinated Molecules, K. Seppelt, Ed., Elsevier, Amsterdam, 2021.

[2] A. Tressaud, Fluorine A Paradoxical Element, Elsevier, Amsterdam, 2019.

[3] P. Kirsch, Modern Fluoroorganic Chemistry, Wiley-VCH, Weinheim, 2013.

[4] B.E. Smart, J. Fluorine Chem. 109 (2001) 3-11.

[5] Y. Zhou, J. Wang, Z. Gu, S. Wang, W. Zhu, J.L. Aceña, V.A. Soloshonok, K. Izawa, H. Liu, Chem. Rev. 116 (2016) 422-518.

[6] N.A. Meanwell, J. Med. Chem. 61 (2018) 5822-5880.

[7] H. Mei, J. Han, S. Fustero, M. Medio-Simon, D.M. Sedgwick, C. Santi, R. Ruzziconi, V.A. Soloshonok, Chem. Eur. J. 25 (2019) 11797-11819.

[8] J. Han, A.M. Remete, L.S. Dobson, L. Kiss, K. Izawa, H. Moriwaki, V.A. Soloshonok, D. O'Hagan, J. Fluorine Chem. 239 (2020) 109639.
[9] M. Cheng, C. Guo, M.L. Gross, Angew. Chem. Int. Ed. 59 (2020) 5880-5889.
[10] B.M. Johnson, Y.-Z. Shu, X. Zhuo, N.A. Meanwell, J. Med. Chem. 63 (2020) 6315-6386.
[11] M. Inoue, Y. Sumii, N. Shibata, ACS Omega 5 (2020) 10633-10640.
[12] P. Jeschke, Pest Manage. Sci. 66 (2010) 10-27.
[13] T. Fujiwara, D. O'Hagan, J. Fluorine Chem. 167 (2014) 16-29.
[14] Y. Ogawa, E. Tokunaga, O. Kobayashi, K. Hirai, N. Shibata, iScience 23 (2020) 101467.
[15] D. Chopra, T.N.G. Row, CrystEngComm 13 (2011) 2175-2186.
[16] M. Pagliaro, R. Ciriminna, J. Mater. Chem. 15 (2005) 4981-4991.
[17] R. Berger, G. Resnati, P. Metrangolo, E. Weber, J. Hulliger, Chem. Soc. Rev. 40 (2011) 3496-3508.
[18] Fascinating Fluoropolymers and Their Applications, B. Ameduri, S. Fomin, Eds., Elsevier, Amsterdam, Netherlands, 2020.
[19] B. Améduri, Macromol. Chem. Phys. 221 (2020) 1900573.
[20] Emerging Fluorinated Motifs: Synthesis, Properties and Applications, D. Cahard, J.A. Ma, Eds., Wiley, Weinheim, Germany, 2020.
[21] A. Leo, C. Hansch, D. Elkins, Chem. Rev. 71 (1971) 525-616.
[22] K. Grollier, A. De Zordo-Banliat, F. Bourdreux, B. Pegot, G. Dagousset, E. Magnier, T. Billard, Chem. Eur. J. 27 (2021) 6028-6033.
[23] R.J. Glyn, G. Pattison, J. Med. Chem. 64 (2021) 10246-10259.
[24] X.-H. Xu, K. Matsuzaki, N. Shibata, Chem. Rev. 115 (2015) 731-764.
[25] A.-L. Barthelemy, E. Magnier, G. Dagousset, Synthesis 50 (2018) 4765-4776.
[26] M. Hamzehloo, A. Hosseinian, S. Ebrahimiasl, A. Monfared, E. Vessally, J. Fluorine Chem. 224 (2019) 52-60.
[27] X.-H. Yang, D. Chang, R. Zhao, L. Shi, Asian J. Org. Chem. 10 (2021) 61-73.
[28] F.R. Leroux, B. Manteau, J.-P. Vors, S. Pazenok, Beilstein J. Org. Chem. 4 (2008) 13.
[29] A. Tlili, F. Toulgoat, T. Billard, Angew. Chem. Int. Ed. 55 (2016) 11726-11735.
[30] T. Besset, P. Jubault, X. Pannecoucke, T. Poisson, Org. Chem. Front. 3 (2016) 1004-1010.
[31] F. Toulgoat, F. Liger, T. Billard, Chemistry of OCF_3, SCF_3, and $SeCF_3$ Functional Groups, in: Organofluorine Chemistry: Synthesis, Modeling, and Applications, K. Szabó, N. Selander (Eds.), Wiley-VCH, Weinheim, Germany, 2021, pp. 49-97.

[32] T. Billard, F. Toulgoat, When Fluorine Meets Selenium, in: Emerging Fluorinated Motifs: Synthesis, Properties and Applications, D. Cahard, J.A. Ma (Eds.), Wiley, Weinheim, Germany, 2020, pp. 691-721.
[33] Y. Wang, Z. Ye, H. Zhang, Z. Yuan, Adv. Synth. Catal. 363 (2021) 1835-1854.
[34] M.J. Yaeger, R.D. Neiger, L. Holler, T.L. Fraser, D.J. Hurley, I.S. Palmer, J. Vet. Diagn. Invest. 10 (1998) 268-273.
[35] C.W. Nogueira, G. Zeni, J.B.T. Rocha, Chem. Rev. 104 (2004) 6255-6286.
[36] M.P. Rayman, Lancet 356 (2000) 233-241.
[37] EFSA Panel on Dietetic Products, Nutrition and Allergies, EFSA J. 12 (2014) 3846.
[38] European Food Safety Authority, EFSA Supporting Publications 14 (2017) e15121E.
[39] G. Mugesh, W.-W. du Mont, H. Sies, Chem. Rev. 101 (2001) 2125-2180.
[40] N. Singh, A.C. Halliday, J.M. Thomas, O.V. Kuznetsova, R. Baldwin, E.C.Y. Woon, P.K. Aley, I. Antoniadou, T. Sharp, S.R. Vasudevan, G.C. Churchill, Nat. Commun. 4 (2013) 1332.
[41] C.M. Weekley, H.H. Harris, Chem. Soc. Rev. 42 (2013) 8870-8894.
[42] J.B.T. Rocha, B.C. Piccoli, C.S. Oliveira, ARKIVOC (2017) 457-491.
[43] Organoselenium Compounds in Biology and Medicine: Synthesis, Biological and Therapeutic Treatments, V.K. Jain, K.I. Priyadarsini, Eds., Royal Society of Chemistry, Croydon, UK, 2018.
[44] V. Alcolea, S. Pérez-Silanes, Eur. J. Med. Chem. 206 (2020) 112673.
[45] Z. Chen, H. Lai, L. Hou, T. Chen, Chem. Commun. 56 (2020) 179-196.
[46] A.D. Landgraf, A.S. Alsegiani, S. Alaqel, S. Thanna, Z.A. Shah, S.J. Sucheck, ACS Chem. Neurosci. 11 (2020) 3008-3016.
[47] L.V. Romashov, V.P. Ananikov, Chem. Eur. J. 19 (2013) 17640-17660.
[48] W. Guo, Y. Fu, Chem. Eur. J. 26 (2020) 13322-13331.
[49] Q. Li, Y. Zhang, Z. Chen, X. Pan, Z. Zhang, J. Zhu, X. Zhu, Org. Chem. Front. 7 (2020) 2815-2841.
[50] X. He, M. Zhong, S. Li, X. Li, Y. Li, Z. Li, Y. Gao, F. Ding, D. Wen, Y. Lei, Y. Zhang, Eur. J. Med. Chem. 208 (2020) 112864.
[51] X. He, Y. Nie, M. Zhong, S. Li, X. Li, Y. Guo, Z. Liu, Y. Gao, F. Ding, D. Wen, Y. Zhang, Eur. J. Med. Chem. 218 (2021) 113384.
[52] W. Tyrra, D. Naumann, Y.L. Yagupolskii, J. Fluorine Chem. 123 (2003) 183-187.
[53] Q. Glenadel, C. Ghiazza, A. Tlili, T. Billard, Adv. Synth. Catal. 359 (2017) 3414-3420.
[54] C. Ghiazza, V. Debrauwer, C. Monnereau, L. Khrouz, M. Médebielle, T. Billard, A. Tlili, Angew. Chem. Int. Ed. 57 (2018) 11781-11785.

[55] K. Grollier, E. Chefdeville, E. Jeanneau, T. Billard, Chem. Eur. J. in press (2021), doi: 10.1002/chem.202102121.
[56] C. Ghiazza, A. Kataria, A. Tlili, F. Toulgoat, T. Billard, Asian J. Org. Chem. 8 (2019) 675-678.
[57] K. Grollier, A. Taponard, A. De Zordo-Banliat, E. Magnier, T. Billard, Beilstein J. Org. Chem. 16 (2020) 3032-3037.
[58] CRC Handbook of Chemistry and Physics, 84th Edition, D.R. Lide (Ed.),Taylor & Francis, Boca Raton, 2003, pp. 8-23 - 8-28
[59] Q. Glenadel, E. Ismalaj, T. Billard, J. Org. Chem. 81 (2016) 8268-8275.
[60] C. Ghiazza, L. Khrouz, T. Billard, C. Monnereau, A. Tlili, Eur. J. Org. Chem. 2020 (2020) 1559-1566.
[61] X.-L. Chen, S.-H. Zhou, J.-H. Lin, Q.-H. Deng, J.-C. Xiao, Chem. Commun. 55 (2019) 1410-1413.
[62] T. Dong, J. He, Z.-H. Li, C.-P. Zhang, ACS Sustainable Chem. Eng. 6 (2018) 1327-1335.
[63] M. Rong, R. Huang, Y. You, Z. Weng, Tetrahedron 70 (2014) 8872-8878.
[64] C. Ghiazza, A. Tlili, T. Billard, Eur. J. Org. Chem. 2018 (2018) 3498-3498.

Graphical abstract