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An Efficient Preparation of New Sulfonyl Fluorides and Lithium Sulfonates

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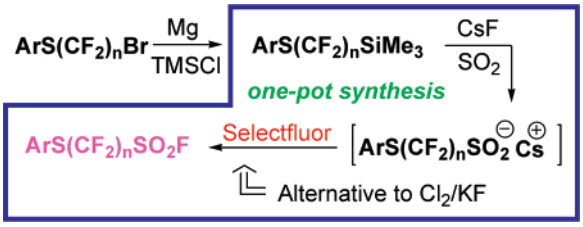

An efficient preparation of several polyfluoroalkanesulfonyl fluorides is reported. This method, based on the synthesis of polyfluoroalkyl trimethyl silanes (precursors of polyfluoroalkylsulfinates) as intermediates, allows the successive transformations to be carried out in one pot. Moreover, these sulfonyl fluorides can be obtained from the corresponding sulfinates by electrophilic fluorination. This original approach avoids isolation and purification of some thermally or hydrolytically unstable intermediates. A series of new sulfonyl fluorides have been thus prepared from halogenodifluoromethylated precursors RCF_2X (X = F, Br; R = ArC(O), $ArS(O)_n(CF_2)_m$; n = 0, 1, 2; m = 1, 2) and have been transformed into the corresponding lithium sulfonates, which have potential applications as electrolytes for lithium batteries.

Introduction

Technological improvements in lithium batteries are driven by an ever-increasing demand for portable electronic devices. To obtain more and more breakthroughs, not only new electrodes but also new electrolytes have to be designed. Lithium salts, such as $LiPF_6$, lithium triflate, and especially $(CF_3SO_2)_2$-NLi (LiTFSI), are promising electrolyte salts,[1] but there is a growing interest to provide new organic salts with improved physicochemical properties. Furthermore, other salts from sulfonic acids and sulfonimides have received considerable attention in recent years as ionic liquids,[2] electrolytes for fuel cells,[3] or acid catalysts.[4] Concerning all these applications, it must be mentioned that fluorinated compounds exhibit the most interesting properties: the strong electron-withdrawing effect of fluorinated moieties enhances the acidity of the sulfonic proton (or sulfonimide proton) while, by enhancing the delocalization of the negative charge, it stabilizes their conjugated bases and increases their ionic conductivity. As sulfonyl fluorides are key precursors of fluorinated sulfonamides, sulfonimides, sulfonic acids, and their derivatives, several methods have been developed for their preparation.[5] The preferred one is the electrochemical fluorination (ECF) of alkanesulfonyl halides in anhydrous HF. Although ECF has been successfully developed for the large-scale production of various sulfonyl fluorides, from CF_3SO_2F to $C_8F_{17}SO_2F$,[6] the yields of the perfluoroalkanesulfonyl fluorides fall dramatically when in-

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creasing the chain length of the starting material.[5] On the other hand, sultone rearrangements provide certain types of sulfonyl fluorides,[7] but with a limited diversity. Alternatively, a large variety of sulfonyl fluorides can be obtained from the reaction of potassium fluoride with the corresponding sulfonyl chlorides,[8] which can be prepared by oxidative chlorination of benzyl thioethers[9] or direct chlorination of sulfinates.[10] Finally, sulfinatodehalogenation of halogenodifluoromethyl compounds,[11] followed by chlorination of the resulting sulfinates, then halide exchange, has become a popular method.[12] However, several drawbacks remain. For example, sulfinates have to be isolated and purified because of their contamination by inorganic salts generated as side products. Such purification is particularly tedious. Thus, in some cases, only crude products were available, as reported for sodium phenyl difluoromethanesulfinate ($PhCF_2SO_3Na$) or sodium 2-phenyl-1,1,2,2-tetrafluoroethanesulfinate ($PhCF_2CF_2SO_3Na$).[13] In addition, organic salts are often hygroscopic; therefore, some water could be incorporated during sulfinate isolation, which is harmful for further transformations. To overcome some of these drawbacks, we wish to report an improved synthesis of a series of new sulfonyl fluorides, as well as that of their corresponding lithium sulfonates. These sulfonyl fluorides may also be transformed into lithium sulfonimides.

A number of perfluoroalkanesulfonic acids,[14] such as triflic acid or polymeric perfluorosulfonic acid (Nafion-H), have been known for decades,[15] but few aromatic compounds with pendant fluoroalkylsulfonate groups have been reported. The same trend is observed for sulfonimides. Furthermore, as most of these products are claimed in patents, few synthetic details are available. Concerning their structure, two types of compounds are known (Figure 1): those in which the fluorinated moiety is directly linked to the aromatic group,[16−20] and those in which the fluorinated group is separated from the aromatic ring by a linker.[21−23]

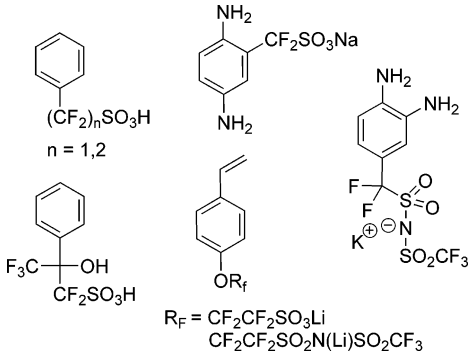

FIGURE 1. Known aromatic-containing polyfluoroalkyl sulfonates and sulfonimides.

New properties could be expected depending on the nature of the linker. For example, an oxygen as well as a sulfur atom could bring some flexibility to the molecules, whereas a sulfoxide or sulfone linker could enhance the electron-withdrawing properties and the polarity. To provide electrolyte salts with better conductivity and stability, we wish to report the synthesis of new sulfonyl fluorides as precursors of original organic salts, in which an aryl group is separated from a fluorinated moiety by a linker that could be a carbonyl, a sulfide, a sulfoxide, or a sulfone.

Results and Discussion

It has been reported that trifluoromethanesulfinate (CF_3SO_2Cs) and pentafluoroethanesulfinate ($C_2F_5SO_2Cs$) can be prepared from the corresponding silanes (CF_3SiMe_3 and $C_2F_5SiMe_3$) in the presence of CsF and SO_2.[24] Nevertheless, a similar reaction, used to prepare higher perfluoroalkyl analogues ($R_F = C_6F_{13}$, C_7F_{15}, C_8F_{17}), was found to proceed with lower yields (<20%).[24b] In this approach, Me_3SiF (TMSF, bp 16.4 °C)[25] is the only byproduct and is volatile enough to make this method quite attractive, compared to the sulfinatodehalogenation process. Moreover, as sulfinates are considered as intermediates for sulfonyl fluorides and as TMSF would be inert for further transformations, this "clean" reaction allows the possibility of

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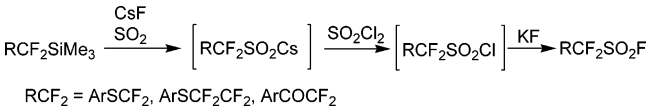
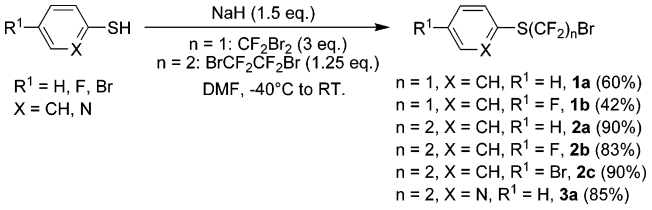
a one-pot strategy for the synthesis of such products (Scheme 1). The fluoride ion desilylation methodology for the transformation of perfluoroalkylsilanes (R_FSiMe_3) to the corresponding perfluoroalkyl anions is a well-known process. The methodology was extensively developed for the introduction of a trifluoromethyl moiety into organic molecules of synthetic and biological interests.[26]

SCHEME 1. Proposed Route to Polyfluoroalkanesulfonyl Fluorides



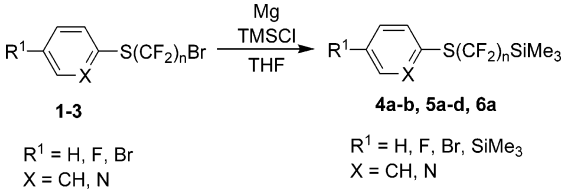
In this strategy, silanes are the key starting materials. They can be prepared from the corresponding bromodifluoromethyl compounds **1a**,**b**, **2a**−**c**, and **3a**. The method described by Suda and Hino[27] for the synthesis of **1a** (using NaH in DMF in the presence of CF_2Br_2) was repeated and adapted to the preparation of **1b**. **2a**−**c** and **3a** (Scheme 2) were prepared in a similar way, from the corresponding thiols and 1,2-dibromotetrafluoroethane. This reaction was found to proceed equally well and constitutes significant progress over the phase-transfer technique reported by Wakselman et al., since $BrCF_2CF_2Br$ was used only in a slight excess and no tetrafluoroethyl sulfide was by-produced.[28] All these compounds were obtained as liquids in moderate to good yields.

SCHEME 2. Synthesis of the Bromodifluoromethyl Starting Materials



While silane **4a**[29] and (1-phenyl-2,2-difluoroenoxy)trimethylsilane (**9**)[13,30] were known from the work of Prakash et al. and Uneyama et al., silanes with two CF_2 groups were unknown. Using a similar procedure, we easily obtained not only silanes **4b** but also **5a**−**d**, bearing a tetrafluoroethylene chain, from the corresponding bromodifluoromethyl compounds (Table 1). As already demonstrated in the literature,[13,30] difluoroenoxysilane **9** is preferably used as a crude (containing a little amount of $PhCOCF_2H$ **12** that is easily removed at the final stage) because of its instability. The latter result was not obviously predictable since the cleaved CF_2−Br bond was not in the vicinity of an electron scavenger such as C═O or S. **5c** and **5d** were obtained as a mixture (Table 1, entries 5 and 6), along with some unreacted **2c**, but in a rather low isolated yield since they were partially decomposed over silica gel. In fact, **5d** resulted from the reduction of both C−Br and CF_2−Br bonds, since we demonstrated that **5d** could be prepared by reduction of **5c** with magnesium, in the presence of trimethylchlorosilane. The best yields were obtained with a large excess of magnesium (6 equiv) and TMSCl (12 equiv) at −78 °C for **5c** and after warming to +50 °C for **5d**. It can be noticed that THF was preferred, as solvent, to DMF (used by Prakash et al. and Uneyama et al.) to facilitate the workup.

TABLE 1. Synthesis of [Arylthio(perfluoroalkyl)]silanes

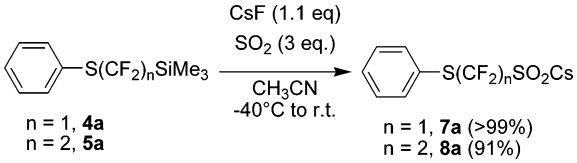


entry	R^1	n	X	product	isolated yield (%)[a]
1	H	1	CH	**4a**	92
2	F	1	CH	**4b**	95
3	H	2	CH	**5a**	90
4	F	2	CH	**5b**	88
5	Br	2	CH	**5c**	25[b] (55)[c]
6	$SiMe_3$	2	CH	**5d**	28[d] (52)[c]
7	H	2	N	**6a**	76

[a] Mg (2 equiv), TMSCl (4 equiv), −78 °C to room temperature. [b] Mg (6 equiv), TMSCl (12 equiv), −78 °C. [c] In situ yield (determined by ^{19}F NMR with $PhOCF_3$ as internal standard). [d] Mg (6 equiv), TMSCl (12 equiv), −78 to +50 °C.

Since silanes were thus available, their condensation onto SO_2, in the presence of a fluoride source, was examined. It should also be noted that, for this purpose, 1,2-dimethoxyethane (glyme), previously used as solvent for the preparation of cesium trifluoromethanesulfinate,[24b] was advantageously replaced by acetonitrile, which is more volatile. Thus, the new sulfinates **7a** and **8a** were easily isolated (Scheme 3).

SCHEME 3. Polyfluorosulfinates from Polyfluorosilanes



Nevertheless, problems occurred during the synthesis of sulfinate **10** from difluoroenoxysilane **9**. Actually, **10** was observed in solution [δ_F (DMSO-d_6) = −112.2 ppm/$CFCl_3$] but was readily transformed into α,α-difluoroacetophenone **12**. To prove that **10** was indeed generated, benzyl bromide was added to the reaction mixture, and sulfone **11** was isolated in 14% yield (Scheme 4).

The instability of sulfinate **10** can be explained by the formation of the corresponding enolate, which was further protonated to provide α,α-difluoroacetophenone **12** (Scheme 5).

Consequently, sulfinatodehalogenation could not be used to prepare **10**, because, as we observed, a high temperature was

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(28) As our work was under completion, a patent from DuPont (WO, 113491, 2005) appeared in the literature that presented the synthesis of compound **2c**; however, the reported synthesis is less efficient than ours because the potassium salt of the thiolate was isolated and needed to be carefully dried, and because **2c** was apparently obtained in a crude 88.5% yield. Our approach does not need to isolate the thiolate, and our isolated yield is higher.

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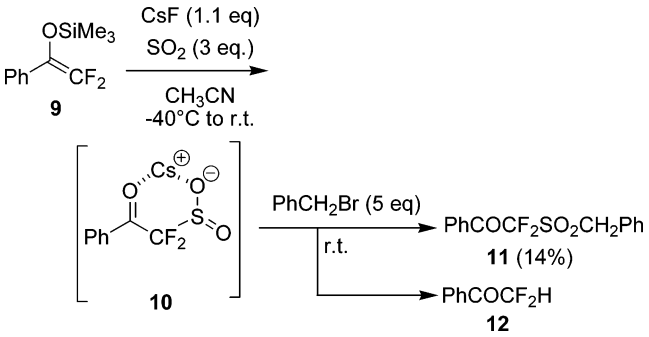
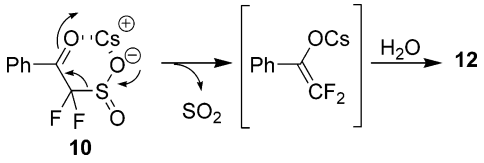
SCHEME 4. Sulfonylation of Difluoroenoxysilane 9



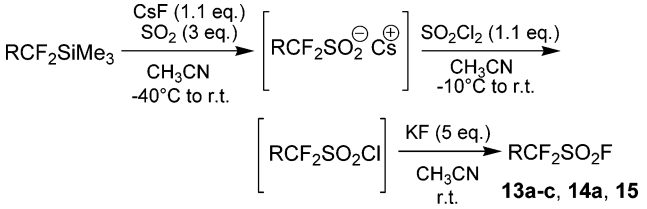
SCHEME 5. Decomposition of Sulfinate 10



required in this case that obviously accelerated the sulfinate degradation. Considering this result, the use of silanes as sulfinate precursors proved its efficiency. To avoid such problems, we decided to carry out further transformations in the same pot.

As reported in the literature for similar compounds,[22] sulfinates react with chlorine to provide sulfonyl chlorides, then sulfonyl fluorides after halogen exchange. However, we preferred to use another electrophilic chlorinating reagent, such as sulfuryl chloride (SO_2Cl_2) or *N*-chlorosuccinimide (NCS), which would be easier to handle on the laboratory scale. Sulfuryl chloride was chosen since the byproducts were expected to be inert toward our compounds. As sulfonyl fluorides could be formed from sulfonyl chlorides and KF in acetonitrile, which is the solvent used in the first step, the one-pot transformation of silanes into sulfonyl fluorides was carried out with success, and several sulfonyl fluorides were isolated with quite good yields (Table 2).

TABLE 2. Synthesis of Sulfonyl Fluorides via Sulfonyl Chlorides



entry	R	sulfonyl fluorides	isolated yield (%)[a]
1	$C_6H_5SCF_2$	**13a**	64
2	*p*-$FC_6H_4SCF_2$	**13b**	67
3	*p*-$Me_3SiC_6H_4SCF_2$	**13c**	48
4	$C_5H_4NSCF_2$	**14a**	70
5	C_6H_5CO	**15**	45

[a] From polyfluoroalkyl silanes.

Unfortunately, attempts to prepare sulfonyl halides from sulfinate **7a** failed, because a chlorodifluoromethyl sulfide was only obtained (Scheme 6).

To circumvent this problem, a new strategy was considered. As sulfonyl chlorides can be obtained by electrophilic chlorination of sulfinates, we assumed that sulfinates should react with an electrophilic fluorinating agent to provide the corresponding sulfonyl fluorides in one step. This second pathway was comforted by a previous work where benzenesulfonyl fluoride was detected by ^{19}F NMR during the reaction of sodium benzenesulfinate with Selectfluor.[31] Therefore, sulfinates were formed *in situ* by condensation of silanes onto SO_2, and then Selectfluor was added to the reaction mixture. When performed without any precaution, this procedure led to a mixture of sulfonyl fluorides and sulfonates. Indeed, sulfonyl halides were readily hydrolyzed by humidity in the presence of a base. In the reaction mixture, several species could act as base, for example, the Selectfluor residue or the remaining fluoride from step 1. Nevertheless, moderate to good yields (32−79%) of sulfonyl fluorides were obtained when solvents, fluoride source, and Selectfluor were rigorously dried and the reaction conducted under anhydrous conditions (Table 3).

SCHEME 6. Chlorination of 7a

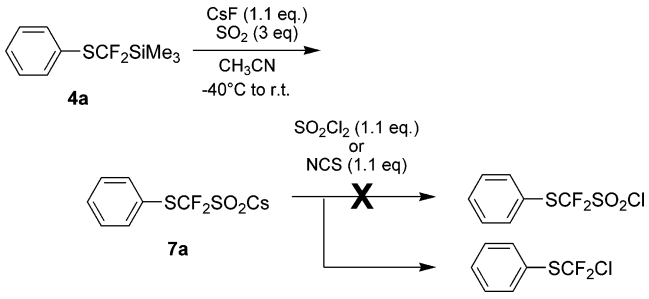
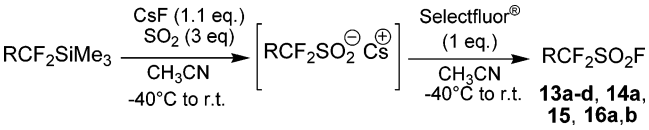


TABLE 3. Synthesis of Sulfonyl Fluorides by Electrophilic Fluorination

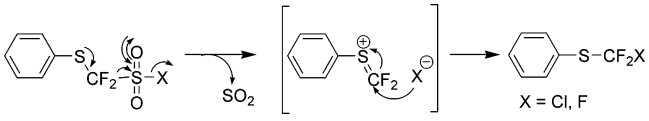


entry	R	sulfonyl fluorides	isolated yield (%)[a]
1	$C_6H_5SCF_2$	**13a**	79
2	*p*-$FC_6H_4SCF_2$	**13b**	64
3	*p*-$Me_3SiC_6H_4SCF_2$	**13c**	77
4	*p*-$BrC_6H_4SCF_2$	**13d**	62
5	$C_5H_4NSCF_2$	**14a**	72
6	C_6H_5CO	**15**	67
7	C_6H_5S	**16a**	57
8	*p*-FC_6H_4S	**16b**	32

[a] From polyfluoroalkyl silanes.

Using this procedure, we were now able to isolate sulfonyl fluorides **16a** and **16b**. As its corresponding sulfonyl chloride,[32] but to a far less extent, **16a** was found to produce trifluoromethylsulfanyl-benzene when heated. This instability may be explained by a push−pull reaction where SO_2 was expulsed, though the attempts to trap the putative ylide intermediate were unsuccessful (Scheme 7).

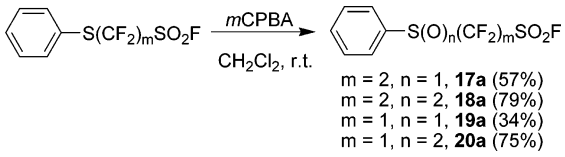
SCHEME 7. Decomposition of *β*-(Phenylthio)difluoromethansesulfonyl Halides



Nevertheless, as the sulfur−fluorine bond is stronger than the sulfur−chlorine one, sulfonyl fluorides $RSCF_2SO_2F$ can be isolated more easily than the corresponding sulfonyl chlorides. On the other hand, such instability problems are not observed with the CF_2-CF_2 analogues **13a**−**d** as the cleavage of a carbon−carbon bond would be a disfavored process. Thus, electrophilic fluorination of sulfinates was an efficient method to provide new sulfonyl fluorides and avoid the formation of unstable sulfonyl chlorides.[33]

With such a series of sulfur(II)-containing sulfonyl fluorides in hand, it was interesting to prepare their corresponding sulfoxides or sulfones by oxidation with *m*CPBA (Scheme 8). Such compounds are of interest because of their increased polarity that may be useful to enhance the conductivity of their corresponding lithium sulfonates as well as lithium sulfonimides as potential electrolytes for lithium batteries. The sulfoxides were obtained in moderate yields when using 2 equiv of *m*CPBA in dichloromethane at room temperature for 24 h; the reaction was not selective since sulfones were already formed before complete conversion of the starting material. However, sulfoxides could be easily separated from the starting materials and sulfones by silica gel chromatography. No attempts were made to improve their yields. In contrast, sulfones were easily accessible using an excess of *m*CPBA (8 equiv) and were isolated in good yields (Scheme 8).

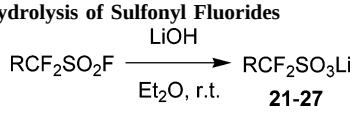
SCHEME 8. Oxidation of (Phenylthio)perfluoroalkanesulfonyl Fluorides



To illustrate the utility of such sulfonyl fluorides, they were hydrolyzed with LiOH to provide lithium sulfonates. The latter compounds were isolated in good yields using Et_2O as solvent (Table 4). On the contrary, hydrolysis of the sulfonyl chlorides was found to give inseparable mixtures of lithium sulfinates and sulfonates.

These sulfonyl fluorides were found to be contaminated by a small amount of the corresponding $-CF_2H$ (purity > 95% as determined by ^1H and ^{19}F NMR), but no additional purification was required, as it was easily removed in the next step (hydrolysis to the lithium sulfonates). To the best of our knowledge, all these sulfonyl fluorides and lithium sulfonates have not been described previously. Nevertheless, it should be noticed that triethylammonium sulfonates containing the same anion as **24**, **25**, and **26** are claimed in a Japanese patent,[23] published when our work was in progress. In contrast to our methods, the reported synthesis is not so general as ours and is based on the use of IF_5.

TABLE 4. Hydrolysis of Sulfonyl Fluorides



entry	R	lithium sulfonate	isolated yield (%)
1	$C_6H_5SCF_2$	**21**	98
2	$C_6H_5S(O)CF_2$	**22**	71
3	$C_6H_5SO_2CF_2$	**23**	92
4	C_6H_5S	**24**	83
5	$C_6H_5S(O)$	**25**	51
6	$C_6H_5SO_2$	**26**	72
7	C_6H_5CO	**27**	77

Conclusion

In conclusion, we have developed two efficient one-pot approaches to new sulfonyl fluorides.[34] These two methods are based on the use of silanes as precursors of sulfinates. Our proposed synthesis allowed us to carry out further transformations in the same pot to avoid isolation of unstable intermediates such as some sulfinates and sulfonyl chlorides. Sulfuryl chloride was preferred as chlorinating agent since it was easier to handle at the laboratory scale than chlorine, a toxic and corrosive gas. On the other hand, we have demonstrated that electrophilic fluorinating agents, such as Selectfluor, react with sulfinates to provide sulfonyl fluorides in one step with good yields, making the synthesis shorter. In this case, sulfonyl fluorides were obtained in a "one-pot two-step" procedure from the corresponding silanes. Furthermore, it avoided the formation of sulfonyl chlorides, some of them being unstable. These two methods were applied to the synthesis of several sulfonyl fluorides, which were transformed into lithium sulfonates, as potential electrolytes for lithium batteries. Data about the physical and electrochemical properties of these lithium salts will be published as soon as they are available. As an example, the electrochemical investigation of polymer electrolytes based on $PhSCF_2CF_2SO_3Li$ **21** is in press.[35] In addition, these sulfonyl fluorides are good precursors of sulfonates or lithium sulfonimides, the synthesis of which will be published in due course.[36]

Experimental Section

Synthesis of 1-(Bromodifluoromethylsulfanyl)-4-fluorobenzene (1b). To a suspension of sodium hydride (1.2 g, 30 mmol) in anhydrous DMF (30 mL) was slowly added *p*-fluorothiophenol (2.2 mL, 20 mmol) at 0 °C within 30 min. The reaction mixture was cooled to −50 °C for 15 min before bromodifluoromethane (5.5 mL, 60 mmol) was added. The resulting mixture was maintained at −50 °C for 3 h and then warmed to room temperature within 1 h. The crude mixture was cooled in an ice−water bath, and excess sodium hydride was quenched by dropwise addition of water (50 mL). The aqueous phase was extracted with Et_2O (3 × 50 mL),

(31) (a) Banks, R. E.; Sharif, I. *J. Fluorine Chem.* **1991**, *55*, 207−214. (b) Banks, R. E.; Besheesh, M. K.; Mohialdin-Khaffaf, S. N.; Sharif, I. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2069−2076.

(32) Similar sulfonyl chlorides are claimed in a patent from Daikin Industries, Ltd. (see ref 23). However, no $ArSCF_2SO_2Cl$ was exemplified.

(33) The synthesis of sulfonyl fluoride **13d** was recently published in a patent from DuPont (WO, 113491, 2005) as our work was under completion; their synthesis differs from ours as they used the classical sodium sulfinate (from dithionite reduction of the corresponding $-SCF_2CF_2Br$) as precursor which has to be isolated, transformed into the sulfonyl chloride, and then transformed into the corresponding sulfonyl fluoride through an halogene exchange reaction. Our approach is more general, much simpler and is carried out in the same pot.

(34) Sanchez, J.-Y.; Langlois, B.; Médebielle, M.; Toulgoat, F. FR 0606466, 2006.

(35) Paillard, E.; Toulgoat, F.; Sanchez, J.-Y.; Médebielle, M.; Iojoiu, C.; Alloin, F.; Langlois, B. *Electrochim. Acta* [Online early access]. DOI: 10.1016/j.electacta.2007.05.027. Published Online: May 24, 2007.

(36) (a) Sanchez, J.-Y.; Paillard, E.; Iojoiu, C.; Alloin, F.; Toulgoat, F.; Médebielle, M.; Langlois, B. FR 0606471, 2006. (b) Sanchez, J.-Y.; Paillard, E.; Iojoiu, C.; Alloin, F.; Toulgoat, F.; Médebielle, M.; Langlois, B. FR 0606469, 2006.

the combined organic layers were washed with water (3 × 50 mL) and brine (50 mL) and dried over $MgSO_4$. Filtration and solvent evaporation left a crude product that was purified by chromatography on silica gel (pentane). **1b** was obtained as a colorless liquid (2.15 g, 42%). $R_f = 0.7$ (pentane). ^{1}H NMR: δ 7.65 (m, 2H), 7.12 (m, 2H); ^{13}C NMR: δ 164.8 (d, $^1J_{F-C} = 253.0$ Hz), 138.9 (d, $^3J_{F-C} = 8.8$ Hz), 122.9 (m), 119.5 (td, $^1J_{F-C} = 338.4$ Hz, $^6J_{F-C} = 2.8$ Hz), 116.9 (d, $^2J_{F-C} = 22.0$ Hz); ^{19}F NMR: δ −23.32 (s, 2F), −108.54 (m, 1F). Anal. Calcd for $C_7H_4BrF_3S$: C, 32.70; H, 1.57. Found: C, 32.82; H, 1.68.

General Procedure for the Synthesis of 2a−c and 3a. (2-Bromo-1,1,2,2-tetrafluoroethylsulfanyl)-benzene (2a).[30] To a suspension of sodium hydride (6 g, 150 mmol) in anhydrous DMF (100 mL) was slowly added thiophenol (10.2 mL, 100 mmol) at 0 °C within 30 min. The reaction mixture was cooled to −50 °C for 15 min before 1,2-dibromotetrafluoroethane (15 mL, 125 mmol) was added. The resulting mixture was maintained at −50 °C for 3 h then warmed to room temperature within 1 h. The crude mixture was cooled in an ice−water bath, and excess sodium hydride was quenched by dropwise addition of water (150 mL). The aqueous phase was extracted with Et_2O (3 × 100 mL), the combined organic layers were washed with water (3 × 100 mL) and brine (100 mL) and dried over $MgSO_4$. Filtration and solvent evaporation left a crude product that was purified by chromatography on silica gel (pentane). **2a** was obtained as a colorless liquid (26.07 g, 90%). $R_f = 0.8$ (pentane). ^{1}H NMR: δ 7.65 (d, 2H, $^3J_{H-H} = 7.1$ Hz), 7.50 (m, 1H), 7.41 (m, 2H); ^{13}C NMR: δ 137.4, 131.1, 129.5, 123.6 (t, $^3J_{F-C} = 2.7$ Hz), 122.8 (tt, $^1J_{F-C} = 290.7$ Hz, $^2J_{F-C} = 33.8$ Hz), 116.93 (tt, $^1J_{F-C} = 312.9$ Hz, $^2J_{F-C} = 40.6$ Hz); ^{19}F NMR: δ −62.61 (t, 2F, $^3J_{F-F} = 8.0$ Hz), −85.57 (t, 2F, $^3J_{F-F} = 8.0$ Hz).

General Procedure for the Synthesis of 4a,b, 5a,b, 6a. (Difluorophenylsulfanylmethyl)-trimethylsilane (4a).[29,30] **1a** (4.8 g, 20 mmol) was added dropwise, at −78 °C, to a mixture of Mg turnings (0.96 g, 40 mmol), TMSCl (10.2 mL, 80 mmol), and anhydrous THF (50 mL). The reaction mixture was stirred for 1 h at −78 °C, then warmed to room temperature over 3 h. After the reaction was completed (monitored by TLC or ^{19}F NMR), most of the THF was evaporated, and pentane was added to the residue. The resulting salt was filtered and the filtrate concentrated to give **4a** as a yellow liquid (4.3 g, 92%). $R_f = 0.5$ (pentane). ^{1}H NMR: δ 7.60 (m, 2H), 7.40−7.35 (m, 3H), 0.25 (m, 9H); ^{13}C NMR: δ 136.3 (t, $^4J_{F-C} = 1.1$ Hz), 134.1 (t, $^1J_{F-C} = 300.2$ Hz), 129.4, 128.9, 126.4 (t, $^3J_{F-C} = 4.1$ Hz), −4.1 (t, $^3J_{F-C} = 1.3$ Hz); ^{19}F NMR: δ −88.01 (s, 2F).

Synthesis of [2-(4-Bromophenylsulfanyl)-1,1,2,2-tetrafluoroethyl]-trimethylsilane (5c). 2c (0.37 g, 1 mmol) was added dropwise, at −78 °C, to a mixture of Mg turnings (0.155 g, 6.4 mmol), TMSCl (1.5 mL, 11.8 mmol), and anhydrous THF (5 mL). The reaction mixture was stirred for 8 h at −78 °C. At this temperature, the reaction was quenched by dropwise addition of water (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic layers were washed with water (3 × 20 mL) and dried over $MgSO_4$. Filtration and solvent evaporation left a crude product that was purified by chromatography on silica gel (pentane) to give **5c** as a colorless liquid (0.09 g, 25%). $R_f = 0.5$ (pentane). ^{1}H NMR: δ 7.54−7.48 (m, 4H), 0.27 (s, 9H); ^{13}C NMR: δ 138.7, 132.5, 127.0 (tt, $^1J_{F-C} = 282.1$ Hz, $^2J_{F-C} = 32.8$ Hz), 125.4, 123.8 (m), 122.7 (tt, $^1J_{F-C} = 272.6$ Hz, $^2J_{F-C} = 45.4$ Hz), −4.0 (m); ^{19}F NMR: δ −82.81 (t, 2F, $^3J_{F-F} = 5.2$ Hz), −122.40 (t, 2F, $^3J_{F-F} = 5.2$ Hz). Anal. Calcd for $C_{11}H_{13}BrF_4SSi$: C, 36.57; H, 3.63. Found: C, 36.75; H, 3.82.

Synthesis of 1-(1,1,2,2-Tetrafluoro-2-trimethylsilanylethylsulfanyl]-4-trimethylsilanylbenzene (5d). 2c (0.74 g, 2 mmol) was added dropwise, at −78 °C, to a mixture of Mg turnings (0.06 g, 2.1 mmol), TMSCl (0.6 mL, 4.8 mmol), and anhydrous THF (5 mL). The reaction mixture was stirred for 1 day from −78 °C to room temperature. Solution was cooled to −78 °C, Mg turnings (0.1 g, 4.1 mmol) and TMSCl (0.6 mL, 4.8 mmol) were added, and the reaction was stirred from −78 to +50 °C over 1 day. The solution was then cooled to 0 °C and quenched by dropwise addition of water (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic layers were washed with water (3 × 10 mL) and dried over $MgSO_4$. Filtration and solvent evaporation left a crude product that was purified by chromatography on silica gel (pentane) to give **5d** as a colorless liquid (0.2 g, 28%). $R_f = 0.5$ (pentane). ^{1}H NMR: δ 7.54−7.48 (m, 4H), 0.27 (s, 9H); ^{13}C NMR: δ 143.3, 136.3, 134.1, 127.6 (tt, $^1J_{F-C} = 281.8$ Hz, $^2J_{F-C} = 32.5$ Hz), 125.1, 123.0 (tt, $^1J_{F-C} = 272.3$ Hz, $^2J_{F-C} = 45.2$ Hz), −1.1, −4.0 (m); ^{19}F NMR: δ −82.63 (t, 2F, $^3J_{F-F} = 5.2$ Hz), −122.51 (t, 2F, $^3J_{F-F} = 5.2$ Hz). Anal. Calcd for $C_{14}H_{22}F_4SSi_2$: C, 47.43; H, 6.25. Found: C, 47.62; H, 6.55.

General Procedure for the Synthesis of 7a and 8a. Cesium Difluorophenylsulfanylmethanesulfinate (7a). A solution of sulfur dioxide (0.16 g, 2.5 mmol) was prepared by bubbling sulfur dioxide into anhydrous acetonitrile (2 mL). Into that solution were added, at −40 °C, **4a** (0.12 g, 0.5 mmol) and CsF (0.09 g, 0.6 mmol). After warming slowly to room temperature, the reaction mixture was stirred again for 24 h (reaction monitored by TLC or ^{19}F NMR). After filtration of the reaction mixture and removal of volatile materials, the resulting solid was washed with pentane to give **7a** as a white solid (0.18 g, >99%). Mp 127 °C. ^{1}H NMR (acetone-d_6): δ 7.60 (m, 2H), 7.38−7.35 (m, 3H); ^{13}C NMR (DMSO-d_6): δ 136.7 (t, $^1J_{F-C} = 334.0$ Hz), 135.7, 129.1, 129.0, 127.8 (t, $^3J_{F-C} = 1.9$ Hz); ^{19}F NMR (acetone-d_6): δ −85.62 (s, 2F).

Cesium 1,1,2,2-Tetrafluoro-2-phenylsulfanylethanesulfinate (8a): White solid (91% yield); ^{1}H NMR (DMSO-d_6): δ 7.60 (d, 2H, $^3J_{H-H} = 6.8$ Hz), 7.51−7.44 (m, 3H); ^{13}C NMR (DMSO-d_6): δ 136.6, 130.5, 129.4, 128.8 (tt, $^1J_{F-C} = 292.8$ Hz, $^2J_{F-C} = 32.1$ Hz), 124.2 (t, 2F, $^3J_{F-F} = 2.2$ Hz), 123.0 (tt, $^1J_{F-C} = 288.7$ Hz, $^2J_{F-C} = 32.1$ Hz); ^{19}F NMR (DMSO-d_6): δ −85.23 (t, 2F, $^3J_{F-F} = 6.3$ Hz), −127.30 (t, 2F, $^3J_{F-F} = 6.3$ Hz).

*HRMS or combustion of new sulfinates **7a** and **8a** is precluded by their thermal stability.*

Synthesis of 2,2-Difluoro-1-phenyl-2-phenylmethanesulfonylethanone (11). A solution of sulfur dioxide was prepared by bubbling sulfur dioxide (1.2 g, 18 mmol) into anhydrous THF (4 mL). Into that solution were added, at −40 °C, **9** (0.9 g, 4 mmol) and *n*-Bu_4NF (4 mL, 1 M in THF). After warming slowly to room temperature, the reaction mixture was stirred again for 1 h, and volatile materials were removed. The residue was dissolved in THF (4 mL), and benzyl bromide (2.3 mL, 19.5 mmol) was added at −78 °C. The reaction mixture was warmed to room temperature overnight. After volatile materials were removed, the residue was purified by chromatography on silica gel (petroleum ether/CH_2Cl_2, 7:3) to give **11** as a white solid (0.15 g, 14%). Mp 72−74 °C. $R_f = 0.4$ (petroleum ether/CH_2Cl_2, 7:3). ^{1}H NMR: δ 8.13 (d, 2H, $^3J_{H-H} = 7.5$ Hz), 7.69 (m), 7.53 (m, 2H), 7.52−7.43 (m, 5H), 4.59 (s, 2H); ^{13}C NMR: δ 184.7 (t, $^2J_{C-F} = 22.7$ Hz), 135.7, 131.7 (t, $^3J_{C-F} = 1.4$ Hz), 131.68, 130.8 (t, $^4J_{C-F} = 3.0$ Hz), 129.8, 129.1, 129.0, 123.8, 117.0 (t, $^1J_{F-C} = 302.0$ Hz), 56.4; ^{19}F NMR: δ −103.03 (s); MS (IC): $m/z = 311$ [(M + H)$^+$], 247. Anal. Calcd for $C_{15}H_{12}F_2O_3S$: C, 58.06; H, 3.90. Found: C, 58.26; H, 4.22.

General Procedure for the Synthesis of 13a−d, 14a, 15, and 16a,b. 1,1,2,2-Tetrafluoro-2-phenylsulfanylethanesulfonyl Fluoride (13a). Method A. A solution of sulfur dioxide was prepared by bubbling sulfur dioxide (4.0 g, 63 mmol) into anhydrous acetonitrile (30 mL). **5a** (5.87 g, 20.3 mmol) and CsF (3.2 g, 21 mmol) were added at −40 °C to this solution. After warming slowly to room temperature, the reaction mixture was stirred for 24 h (reaction monitored by TLC or ^{19}F NMR). Then sulfuryl chloride (2.0 mL, 25.2 mmol) was added to the reaction mixture at −20 °C. The mixture was warmed to room temperature within 4 h, before KF (6.0 g, 105 mmol) was added. The suspension was further stirred for 3 days more at room temperature. Volatile materials were removed, and the residue was purified by chromatography on silica gel (pentane) to give **13a** as a colorless liquid (3.76 g, 64%).

Method B. A solution of sulfur dioxide was prepared by bubbling sulfur dioxide (1.02 g, 16 mmol) into anhydrous acetonitrile (20 mL). Then **5a** (2.25 g, 8 mmol) and CsF (1.4 g, 9 mmol) were added at −40 °C to this solution. After warming slowly to room temperature, the reaction mixture was stirred for 24 h (reaction monitored by TLC or ^{19}F NMR). Selectfluor (2.9 g, 8.2 mmol) was then added to the reaction mixture at −40 °C. The mixture was warmed to room temperature within 4 h. Volatile materials were removed, and Et_2O was added. The resulting solid was filtered, and the filtrate was concentrated to give a crude product that was purified by chromatography on silica gel (pentane) to yield **13a** as a colorless liquid (1.86 g, 79%).

1,1,2,2-Tetrafluoro-2-phenylsulfanylethanesulfonyl Fluoride (13a): R_f = 0.7 (pentane). ^{1}H NMR: δ 7.67 (d, 2H, $^3J_{H-H}$ = 7.4 Hz), 7.54 (t, 1H, $^3J_{H-H}$ = 7.4 Hz), 7.44 (dd, 2H, $^3J_{H-H}$ = $^3J_{H-H}$ = 7.4 Hz); ^{13}C NMR: δ 137.5, 131.7, 129.8, 122.0 (t, $^3J_{F-C}$ = 3.6 Hz), 121.8 (ttd, $^1J_{F-C}$ = 290.9 Hz, $^2J_{F-C}$ = 31.7 Hz, $^3J_{F-C}$ = 1.2 Hz), 116.2 (ttd, $^1J_{F-C}$ = 300.6 Hz, $^2J_{F-C}$ = 40.8 Hz, $^2J_{F-C}$ = 32.6 Hz); ^{19}F NMR: δ 45.98 (m, 1F), −86.57 (m, 2F), −105.56 (m, 2F); MS (EI): *m*/*z* = 77, 109, 159, 292 (M^+); HRMS: calcd for $C_8H_5F_5O_2S_2$: 291.9651; found: 291.9654.

General Procedure for the Synthesis of 17a and 19a. 2-Benzenesulfinyl-1,1,2,2-tetrafluoroethanesulfonyl Fluoride (17a). 14a (1.15 g, 4 mmol) was added dropwise, at 0 °C, to a suspension of *m*CPBA (1.4 g, 8 mmol) in CH_2Cl_2. The mixture was warmed to room temperature over 24 h. After the solvent was removed, the residue was purified by chromatography on silica gel (pentane → pentane/CH_2Cl_2, 3:2) to give **17a** as a colorless liquid (0.70 g, 57%). R_f = 0.6 (pentane/CH_2Cl_2, 1:1). ^{1}H NMR: δ 7.82 (d, 2H, $^3J_{H-H}$ = 7.4 Hz), 7.74−7.61 (m, 3H); ^{13}C NMR: δ 134.7 (dd, $^3J_{F-C}$ = $^3J_{F-C}$ = 2.5 Hz), 134.4, 129.9, 126.8 (m), 121.7−111.8 (m, 2C); ^{19}F NMR: δ 46.33 (m, 1F), −106.79 (m, 2F), −110.16 (m, 1/2 AB system, 1F), −121.60 (m, 1/2 AB system, 1F); MS (EI): *m*/*z* = 125, 308 (M^+); HRMS: calcd for $C_8H_5F_5O_3S_2$: 307.9600; found: 307.9599.

General Procedure for the Synthesis of 18a and 20a. 2-Benzenesulfonyl-1,1,2,2-tetrafluoroethanesulfonyl Fluoride (18a). 14a (1.32 g, 4.5 mmol) was added dropwise, at 0 °C, to a suspension of *m*CPBA (6.25 g, 36 mmol) in CH_2Cl_2. The reaction mixture was warmed to room temperature over 24 h. After the solvent was removed, the residue was purified by chromatography on silica gel chromatography (pentane → pentane/CH_2Cl_2, 4:1) to give **18a** as a colorless liquid (1.15 g, 79%). R_f = 0.7 (pentane/CH_2Cl_2, 1:1). ^{1}H NMR: δ 8.06 (d, 2H, $^3J_{H-H}$ = 7.5 Hz), 7.89 (t, 1H, $^3J_{H-H}$ = 7.5 Hz), 7.71 (dd, 2H, $^3J_{H-H}$ = $^3J_{H-H}$ = 7.5 Hz); ^{13}C NMR: δ 137.2, 131.8, 131.4, 130.1, 115.4 (ttd, $^1J_{F-C}$ = 302.0 Hz, $^2J_{F-C}$ = 35.0 Hz, $^3J_{F-C}$ = 35.0 Hz), 113.6 (tt, $^1J_{F-C}$ = 302.0 Hz, $^2J_{F-C}$ = 35.0 Hz); ^{19}F NMR: δ 46.25 (m, 1F), −106.32 (m, 2F), −110.77 (m, 2F); MS (EI): *m*/*z* = 77, 141, 324 (M^+); HRMS calcd for $C_8H_5F_5O_4S_2$: 323.9549; found: 323.9554.

General Procedure for the Synthesis of 21−27. Lithium 1,1,2,2-Tetrafluoro-2-phenylsulfanylethanesulfonate (21). LiOH·H_2O (0.67 g, 16 mmol) was added to a solution of sulfonyl fluoride **13a** (1.15 g, 4 mmol) in diethyl ether (20 mL). The reaction mixture was stirred at room temperature for 1 day (reaction monitored by TLC or ^{19}F NMR). After filtration of the reaction mixture and concentration of the filtrate, the resulting solid was washed with pentane (3 × 40 mL) to give **21** as a white solid (1.15 g, 98%). Mp 160 °C. ^{1}H NMR (acetone-d_6): δ 7.65 (m, 2H), 7.56−7.43 (m, 3H), 3.11 (br s, H_2O linked); ^{13}C NMR (acetone-d_6): δ 137.8, 131.3, 130.1, 125.7 (t, $^3J_{F-C}$ = 2.5 Hz), 124.4 (tt, $^1J_{F-C}$ = 289.6 Hz, $^2J_{F-C}$ = 32.2 Hz), 115.1 (tt, $^1J_{F-C}$ = 288.2 Hz, $^2J_{F-C}$ = 32.2 Hz); ^{19}F NMR (acetone-d_6): δ −85.48 (t, 2F, $^3J_{F-F}$ = 6.8 Hz), −113.82 (t, 2F, $^3J_{F-F}$ = 6.8 Hz); MS (ESI-MeOH): *m*/*z* = 289.1 (M^-), 290, 291, 584.9

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Supporting Information Available: General methods, experimental procedures, compound characterization, and copies of the NMR spectra data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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