Regioselective Electrochemical Monofluorination of α-Sulfonyl Sulfides

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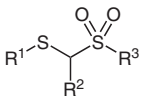
Abstract: Highly regioselective monofluorination of α-sulfonyl sulfides was successfully carried out using anodic oxidation to provide the corresponding α-fluorinated products in moderate yields. The fluorinated products would be versatile fluorine-containing building blocks.

Key words: sulfones, fluorine, electron transfer, oxidation, cations

The development of efficient methodology for fluorination of organic molecules has been increasingly important since a number of organofluorine compounds are known to show unique chemical, physical, and biological properties.[1] Particularly, α-fluoro sulfides have attracted much interest since they can be readily converted to various useful organofluorine compounds.[2] α-Fluorination of sulfides has been carried out using various reagents such as (diethylamino)sulfurtrifluoride (DAST),[3] 1-(chloromethyl)-4-fluoro-1,4-diazabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor),[4] and IF_5-Et_3N-3HF.[5] However, they are still hazardous, difficult to handle, or very costly. On the contrary, electrochemical fluorination is an ideal method because it can be done in one step under safe conditions. Previously, we successfully conducted highly regioselective anodic α-monofluorination of sulfides having various electron-withdrawing groups such as carbonyl, ester, cyano, phosphonate, and amide groups at the α-position to the sulfur atom.[6] We proposed a Pummerer-type mechanism via fluorosulfonium ions as a key intermediate, and electron-withdrawing groups markedly promoted the anodic fluorination.[7] Considering further molecular conversion, a sulfonyl group is a very useful electron-withdrawing group because it can be easily substituted after the fluorination.[8] With these facts in mind, we studied electrochemical fluorination of α-sulfonyl sulfides in this work.

First, the oxidation potentials of the sulfides having sulfonyl groups, **1a–i**,[9] and **2a**,**d** were measured by cyclic voltammetry in anhydrous acetonitrile.[10] The oxidation potentials (decomposition potential, E_d^{ox}) are summarized in Table 1. Except for **1d**, the sulfides having a sulfonyl group were found to be oxidized at more positive potentials than methyl phenyl sulfide (E_d^{ox}: 1.25 V vs. SCE), owing to the electron-withdrawing sulfonyl group. Aromatic sulfides **1d–i** and **2d** were more easily oxidized compared with aliphatic sulfides **1a–c** and **2a**. On the other hand, the oxidation potential of the α-chloro sulfide **1c** was higher than 2 V vs. SCE. Moreover, α-fluoro sulfide **2a** has a much higher oxidation potential than **1c** due to a stronger electron-withdrawing fluorine atom compared with a chlorine atom.

Table 1 Oxidation Potentials (E_d^{ox}) of α-Sulfonyl Sulfides[a]



Compd	R^1	R^2	R^3	E_d^{ox} (vs. SCE)
1a	Me	H	*p*-Tol	1.88
2a	Me	F	*p*-Tol	>2.30
1b	Me	Me	*p*-Tol	1.84
1c	Me	Cl	*p*-Tol	2.06
1d	*p*-Tol	H	Me	1.15
2d	*p*-Tol	F	Me	1.44
1e	Ph	H	Ph	1.45
1f	Ph	SPh	Ph	1.47
1g	*p*-Tol	H	Ph	1.54
1h	*p*-Tol	Me	Ph	1.51
1i	2-Py	H	Ph	1.80

[a] 5 mM of sulfide in 0.1 M $NaClO_4$/MeCN, sweep rate: 100 mV/S.

In contrast, an electron-donating methyl group decreased slightly the oxidation potential as shown in the cases of **1b** and **1h**. However, introduction of an easily oxidizable phenylthio group to the α-position of sulfide **1e** did not decrease the oxidation potential as observed in the case of **1f**.

Next, we investigated anodic monofluorination of methylthiomethyl *p*-tolyl sulfone (**1a**),[11] which is a well-known useful synthetic reagent,[12] under various electrolytic conditions as shown in Table 2.

Desired monofluorinated product **2a** was formed in moderate yield at 3 F/mol of electricity under conventional anodic fluorination conditions (0.37 M Et_3N-3HF/acetonitrile) as reported previously (entry 1).[7] In this case, 15% of starting **1a** still remained although the desired fluorinated product was obtained in moderate yield. Then, 4 F/mol of electricity was passed under the same conditions. However, **1a** was not consumed completely and the yield

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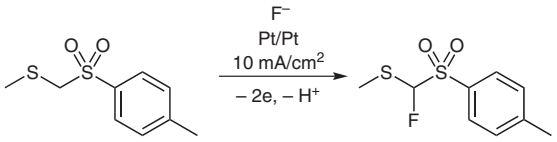
Table 2 Fluorination of Methylthiomethyl *p*-Tolyl Sulfone (**1a**)



1a (0.1 M) **2a**

Entry	Solvent	Supporting electrolyte	Charge passed (F/mol)	Yield (%)[a]
1	MeCN	Et_3N-3HF (0.37 M)	3	55
2	MeCN	Et_4NF-4HF (0.15 M)	4	64
3	CH_2Cl_2	Et_3N-3HF	2	30
4	CH_2Cl_2	Et_4NF-4HF	2	0
5	DME	Et_3N-3HF	2	23
6	DME	Et_4NF-4HF	2	66 (58)

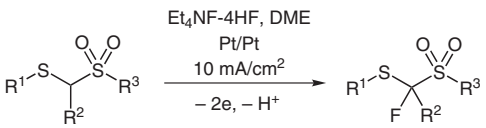
[a] Determined by ^{19}F NMR. Isolated yield is shown in parentheses.

of **2a** did not increase. Since Et_3N-3HF is rather easily oxidized, Et_3N-3HF seems to be oxidized simultaneously during the anodic oxidation of **1a**. Therefore, anodically more stable Et_4NF-4HF was employed instead of Et_3N-3HF for the anodic fluorination (entry 2). When 4 F/mol of electricity was passed, the stating **1a** was completely consumed and the yield of **2a** was increased to 64%.

In our previous reports, anodic difluorination of sulfides having an electron-withdrawing group such as ester, phosphonate, and cyano groups at α to the sulfur atom was successfully carried out with high current efficiencies using a Et_4NF-4HF as a fluorine source in acetonitrile.[13] However, difluorinated product was not obtained at all under the similar conditions (entry 2). This is as due to the high oxidation potential of monofluorinated product **2a** (E_d^{ox} > 2.30 V vs. SCE), which prevented the further oxidation of **2a**.

Dichloromethane was not suitable as a solvent for the fluorination reaction (entries 3 and 4). Particularly, when Et_4NF-4HF was used, unidentified insoluble product was formed on the surface of the anode resulting in no formation of **2a**. Next, we used dimethoxyethane (DME) as a solvent (entries 5 and 6). When Et_3N-3HF was used, fluorination did not proceed efficiently. However, when Et_4NF-4HF was employed, **1a** was mostly consumed at theoretical amount of electricity (2 F/mol) for monofluorination, and **2a** was formed in good yield. Previously, we demonstrated that DME enhances the nucleophilicity of a fluoride ion,[14] which resulted in increase of the yield. In all cases except for entry 4, byproducts such as MeSSMe were obtained. This suggests that the oxidative degradation of **1a** occurred simultaneously during anodic fluorination, which resulted in the moderate yield of **2a**. Thus, we found that Et_4NF-4HF/DME is the best system for the fluorination. In contrast, fluorination of **1a** using NaH and Selectfluor provided **2a** in extremely low yield (9%) along

Table 3 Fluorination of α-Sulfonyl Sulfides



1a–i **2a–i**

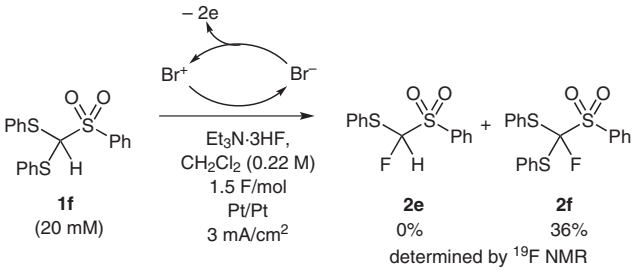
Compd	R^1	R^2	R^3	Product	Charge passed (F/mol)	Yield (%)[a]
1a	Me	H	*p*-Tol	**2a**	2	58
1b	Me	Me	*p*-Tol	**2b**	2	42[b]
1c	Me	Cl	*p*-Tol	**2c**	2	12[c]
1d	*p*-Tol	H	Me	**2d**	2	44
1e	Ph	H	Ph	**2e**	2	52
1f	Ph	SPh	Ph	**2f**	2	51
1g	*p*-Tol	H	Ph	**2g**	2	52
1h	*p*-Tol	Me	Ph	**2h**	2	45
1i	2-Py	H	Ph	**2i**	4	55

[a] Isolated yield.
[b] α-(Fluoromethylthio)ethyl *p*-tolyl sulfone: *p*-$TolSO_2CHMeSCH_2F$ (**4**) was formed in 26% yield.
[c] Starting material (65%) was recovered.

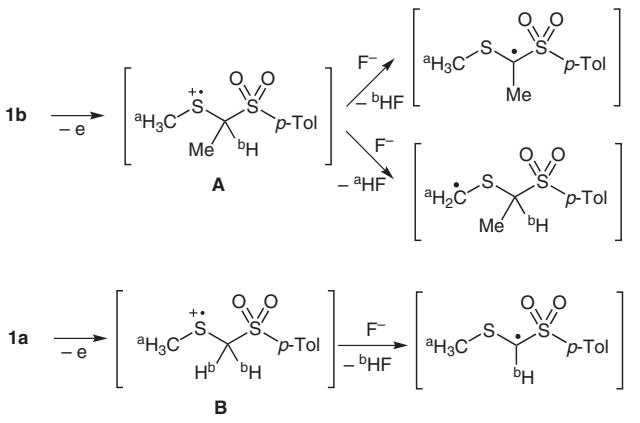
with the recovered starting material (13%) and many byproducts. Therefore, electrochemical fluorination is much more efficient for the preparation of α-fluoro-α-sulfonyl sulfides compared with a chemical method.

We extended this fluorination system to other sulfides **1b–i**.[11] The results are summarized in Table 3. The desired monofluorinated products were obtained exclusively in moderate yields in the cases of **1d–i**. Since the oxidation potential of α-fluoro-α-(*p*-tolylthio)methyl methyl sulfone (**2d**) is more positive by ca. 0.3 V compared with **1d**, difluorinated product was not obtained in the anodic fluorination of **1d**. It seems that the oxidation of **1d** proceeded efficiently in Et_4NF-4HF/DME system and **1d** was completely consumed at the theoretical amounts of electricity. Consequently, oxidation of **2d** did not occur. We also tried difluorination of **1d** in Et_4NF-4HF/MeCN system which is suitable for anodic difluorination.[13] After 4 F/mol of charge was passed, difluorination product **3** was obtained in 11% yield along with monofluorinated product **2d** (7%) and byproducts such as $(p\text{-TolS})_2$ (43%). Therefore, the oxidation of **1d** is possible, however, not efficient.

Previously, we reported the fluorination of dithioacetals of aldehydes.[15] In these cases, fluorodesulfurization took place selectively and no α-fluorination occured. In contrast, fluorodesulfurization did not take place at all in the case of α,α-di(phenylthio)methyl phenyl sulfone (**1f**). We also disclosed that the use of a bromide ion was effective for fluorodesulfurization.[16] Therefore, we tried indirect



Scheme 1 Indirect electrolysis of α,α-di(phenylthio)methyl phenyl sulfone (**1f**) using Br^- mediator



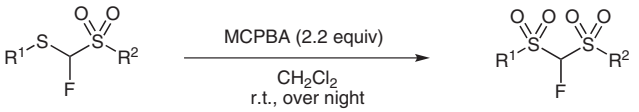
Scheme 2 Regioselectivity of deprotonation of anodically formed cation radical intermediates of **1b** and **1a**

electrolysis of **1f** by using Et_4NBr (1 mM) as a bromide ion mediator (Scheme 1). However, the fluorodesulfurization product **2e** was not detected at all and **2f** was formed in 36% yield (determined by ^{19}F NMR). Deprotonation of the cation radical intermediate of **1f** seems to be enhanced by the strong electron-withdrawing effect of the sulfone group, which provides **2f** predominantly.

On the other hand, anodic fluorination of 1-(methylthio)ethyl *p*-tolyl sulfone (**1b**) provided two monofluorinated products, α-fluoro-α-methylthioethyl *p*-tolyl sulfone (**2b**) and (α-fluoromethylthio)ethyl *p*-tolyl sulfone (**4**) in 42% and 26% yields, respectively. It is well known that the regioselectivity of anodic substitutions of heteroatom compounds like amines and sulfides is generally controlled by kinetic acidity of an α-proton of their cation radicals.[17] In the case of anodic fluorination of **1b**, the introduction of an electron-donating methyl group to the α-position to the sulfur atom of **1a** decreases the kinetic acidity of the α-methyne proton (^bH, Scheme 2). Therefore, the elimination of ^bH of cation radical intermediate **A** becomes much slower compared with that of cation radical intermediate **B** (Scheme 2). Consequently, elimination of ^aH of cation radical intermediate **A** also takes place simultaneously.

The fluorination of 1-chloro-1-methylthiomethyl *p*-tolyl sulfone (**1c**) did not proceed well and 65% of **1c** was recovered. Even when 3 F/mol of electricity was passed, the yield of **2c** did not increase and 57% of **1c** was recovered.

Table 4 Oxidation of Monofluorinated α-Sulfonyl Sulfides



Compd	R^1	R^2	Product	Yield (%)[a]
2a	Me	*p*-Tol	**5a**	90
2e	Ph	Ph	**5e**	85
2g	*p*-Tol	Ph	**5g**	Quant.
2i	2-Py	Ph	**5i**	30

[a] Isolated yield.

This seems to be as due to its high oxidation potential (E_d: 2.06 V vs. SCE).

In order to demonstrate further molecular conversion of the fluorinated products, the oxidation of monofluorinated products **2a**, **2e**, **2g**, and **2i** was demonstrated by using *m*-chloroperbenzoic acid (MCPBA, Table 4).[18] Desired sulfones (**5a**, **5e**, and **5g**) were formed in excellent yields. However, **4i** was obtained in low yield since other oxidation products such as sulfoxide and *N*-oxide were formed as byproducts. Thus prepared α-fluoro disulfones **4** are known to be useful synthetic equivalents for the monofluoromethide species since Shibata et al. successfully used α-fluoro disulfone for asymmetric monofluoromethylation.[19] α-Fluoro disulfones have been prepared by the reaction of disulfones with hazardous fluorine gas or a costly reagent, Selectfluor.[19] In contrast, our new synthetic method is quite safe and can be applied to large-scale experiments.

In conclusion, we successfully carried out selective monofluorination of α-sulfonyl sulfides by using an electrochemical methodology. This electrochemical method is more efficient for the preparation of α-fluoro-α-sulfonyl sulfides compared with the chemical method using NaH and Selectfluor. The fluorinated products are expected to be useful fluorine-containing building blocks as exemplified by the oxidative conversion of α-fluoro-α-sulfonyl sulfides to the corresponding α-fluorinated disulfones, which are useful as a monofluoromethylation regent. Their other synthetic application is also currently under way.

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(9) **Preparation of α,α-Di(phenylthio)methyl Phenyl Sulfone (1f)**

A solution of methyl phenyl sulfone (1.58 g, 10.1 mmol) in dry THF (40 mL) was treated with *n*-BuLi (6.25 mL, 1.6 M hexane solution) at –78 °C under a nitrogen atmosphere. After stirring of the solution for 10 min at –78 °C, a solution of diphenyl disulfide (1.08 g, 5.0 mmol) in dry THF (10 mL) was added slowly at –78 °C. After additional 3 h of stirring, the solution was treated with 1 M aq HCl (50 mL) and extracted with EtOAc (2 × 100 mL). The combined extracts were washed with brine and dried over anhyd Na_2SO_4. After the removal of the solvent by evaporation, the residue was purified by column chromatography on SiO_2 (hexane–EtOAc, 6:1) to yield 0.93 g (50%) of α,α-di(phenylthio)methyl phenyl sulfone (**1f**). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.00–7.96 (m, 2 H), 7.69–7.63 (m, 1 H), 7.56–7.50 (m, 2 H), 7.40–7.23 (m, 10 H) 5.12 (s, 1 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 136.70, 134.05, 134.02, 131.74, 129.90, 129.16, 129.08, 128.75, 80.78. HRMS (EI): *m/z* [M$^+$] calcd for $C_{19}H_{16}O_2S_3$: 372.0312; found: 372.0314.

Preparation of Phenyl 2-Pyridylthiomethyl Sulfone (1i)

A solution of 0.61 g (5.5 mmol) of 2-mercaptpyridine in dry MeCN (10 mL) under a nitrogen atmosphere and cooled to 0 °C was treated with NaH (0.20 g, 5.0 mmol; 60% in liquid paraffin) in dry MeCN (10 mL). The solution was stirred for 0.5 h at 0 °C, after which time chloromethyl phenyl sulfone (0.87 g, 4.6 mmol) in dry MeCN (10 mL) was added. After additional 5 h under reflux, the solution was treated with H_2O (30 mL) and extracted with EtOAc (2 × 30 mL). The combined extracts were washed with brine and dried over anhyd Na_2SO_4. After removal of the solvent by evaporation, the residue was purified by column chromatography on SiO_2 (hexane–EtOAc, 4:1) to yield 0.87 g (71%) of phenyl 2-pyridylthiomethyl sulfone (**1i**). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.20–8.18 (m, 1 H), 7.93–7.90 (m, 2 H), 7.49–7.36 (m, 4 H), 7.09–7.05 (m, 1 H), 6.95–6.91 (m, 1 H), 4.99 (s, 2 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 152.78, 148.80, 137.37, 136.22, 133.50, 128.94, 128.31, 122.12, 120.44, 52.39. HRMS–FAB: *m/z* [M + H$^+$] calcd for $C_{12}H_{12}NO_2S_2$: 266.0309; found: 266.0313.

(10) Cyclic voltammetry was carried out at a Pt electrode (0.5 × 0.5 cm^2) using a Hokutodenko HA-501 Potentiostat/Galvanostat.

(11) **Anodic Fluorination of Sulfides**

Typical anodic fluorination conditions are as follows: Electrolysis was conducted with a platinum anode and cathode [4 cm^2 (2 × 2 cm)] in 0.15 M Et_4NF-4HF/DME (10 mL) containing 1.0 mmol of sulfides using an undivided cell at ambient temperature. After the starting sulfide was mostly consumed (monitored by SiO_2 TLC), the electrolysis solution was passed through a short column of SiO_2 ($CHCl_3$). The solvent was then removed by evaporation and residue was purified by column chromatography on SiO_2 (hexane–EtOAc, 10:1 to 5:1 or $CHCl_3$) to provide the desired fluorinated product.

α-Fluoro-α-methylthiomethyl *p*-Tolyl Sulfone (2a)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.2 Hz, 2 H), 7.40 (d, *J* = 8.2 Hz, 2 H), 5.99 (d, *J* = 47.6 Hz, 1 H), 2.47 (s, 3 H), 2.43 (d, *J* = 2.1 Hz, 3 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 145.98, 132.23, 129.84, 129.41, 106.12 (d, *J* = 262.7 Hz), 21.79, 12.45 (d, *J* = 2.2 Hz). ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –82.0 (d, *J* = 47.6 Hz). HRMS–FAB: *m/z* [M + Na$^+$] calcd for $C_9H_{11}FO_2S_2Na$: 257.0082; found: 257.0086.

α-Fluoro-α-methylthioethyl *p*-Tolyl Sulfone (2b)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.1 Hz, 2 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 2.47 (s, 3 H), 2.38 (s, 3 H), 1.80 (d, *J* = 19.6 Hz, 3 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 145.63, 130.94, 130.26 (d, *J* = 1.1 Hz), 129.59, 112.88 (d, *J* = 261.0 Hz), 22.51 (d, *J* = 20.1 Hz), 21.73, 12.87 (d, *J* = 5.6 Hz). ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –56.9 (q, *J* = 19.6 Hz). HRMS–FAB: *m/z* [M + Na$^+$] calcd for $C_{10}H_{13}FO_2S_2Na$: 271.0239; found: 271.0247.

α-Chloro-α-Fluoro-α-methylthiomethyl *p*-Tolyl Sulfone (2c)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.6 Hz, 2 H), 7.41 (d, *J* = 8.6 Hz, 2 H), 2.57 (d, *J* = 1.3 Hz, 3 H), 2.49 (s, 3 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 146.73, 131.25 (d, *J* = 1.1 Hz), 129.68, 128.94, 122.31 (d, *J* = 322.5Hz), 21.94, 15.84 (d, *J* = 3.4 Hz). ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –15.8 (s). HRMS–FAB: *m/z* [M + Na$^+$] calcd for $C_9H_{10}ClFO_2S_2Na$: 290.9692; found: 290.9689.

α-Fluoro-α-(*p*-tolylthio)methyl Methyl Sulfone (2d)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.9 Hz, 2 H), 7.21 (d, *J* = 7.9 Hz, 2 H), 6.13 (d, *J* = 51.1 Hz, 1 H), 2.97 (d, *J* = 1.5 Hz, 3 H), 2.38 (s, 3 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 140.53, 134.54, 134.52, 130.38, 110.26 (d, *J* = 262.7 Hz), 37.48, 21.37. ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –71.7 (d, *J* = 51.1 Hz). HRMS (EI): *m/z* [M$^+$] calcd for $C_9H_{11}FO_2S_2$: 234.0184; found: 234.0185.

α-Fluoro-α-phenylthiomethyl Phenyl Sulfone (2e)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.01–7.98 (m, 2 H), 7.76–7.71 (m, 1 H), 7.63–7.56 (m, 4 H), 7.41–7.35 (m, 3 H), 6.20 (d, *J* = 50.9 Hz, 1 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 136.74 (d, *J* = 1.7 Hz), 134.86, 133.94, 133.91, 129.83 (d, *J* = 1.1 Hz), 129.68, 129.52, 129.20, 110.66 (d, *J* = 264.9 Hz). ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –69.0 (d, *J* = 50.9, 7.4 Hz). HRMS (EI): *m/z* [M$^+$] calcd for $C_{13}H_{11}FO_2S_2$: 282.0184; found: 282.0179.

α-Fluoro-α,α-di(phenylthio)methyl Phenyl Sulfone (2f)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.96–7.93 (m, 2 H), 7.69–7.64 (m, 1 H), 7.54–7.45 (m, 2 H), 7.42–7.24 (m, 10 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 136.70 (d, *J* = 1.1 Hz), 134.59, 134.49, 130.82 (d, *J* = 1.1Hz), 130.16, 129.19, 128.69, 127.16, 120.26 (d, *J* = 314.7 Hz). ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –28.6 (s). HRMS–FAB: *m/z* [M + Na$^+$] calcd for $C_{19}H_{15}FO_2S_3Na$: 413.0116; found: 413.0122.

α-Fluoro-α-(*p*-tolylthio)methyl Phenyl Sulfone (2g)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.99 (m, 2 H), 7.76–7.70 (m, 1 H), 7.60 (m, 2 H), 7.47 (d, *J* = 8.1 Hz, 2 H), 7.17 (d,

J = 8.1 Hz, 2 H), 6.15 (d, *J* = 50.8 Hz, 1 H), 2.36 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 140.19, 134.82, 134.23, 134.20, 130.27, 129.81 (d, *J* = 1.1 Hz), 129.19, 125.54 (d, *J* = 1.1 Hz), 110.79 (d, *J* = 264.4 Hz), 21.36. ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –69.6 (d, *J* = 50.8 Hz). HRMS–FAB): *m/z* [M + Na^+] calcd for $C_{14}H_{13}FO_2S_2Na$: 319.0239; found: 319.0237.

α-Fluoro-α-(*p*-tolylthio)ethyl Phenyl Sulfone (2h)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.00–7.97 (m, 2 H), 7.71–7.43 (m, 5 H), 7.16–7.12 (m, 2 H), 2.35 (s, 3 H), 1.72 (d, *J* = 19.3 Hz, 3 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 140.62, 136.67 (d, *J* = 2.2 Hz), 134.48, 130.62, 130.60, 129.91, 129.49, 128.83, 123.37, 115.78 (d, *J* = 260.5 Hz), 21.22 (d, *J* = 21.8 Hz). ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –40.52 (q, *J* = 19.3 Hz). HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{15}FO_2S_2$: 310.0497; found: 310.0490.

α-Fluoro-α-(2-pyridylthio)methyl Phenyl Sulfone (2i)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.45–8.43 (m, 1 H), 8.06v8.03 (m, 2 H), 7.77–7.12 (m, 1 H), 7.71 (d, *J* = 48.1 Hz, 1 H), 7.64–7.56 (m, 3 H), 7.23 (m, 1 H), 7.16–7.12 (m, 1 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 151.57 (d, *J* = 2.2 Hz), 149.58, 137.22, 134.84, 129.59, 129.18, 123.06, 123.02, 121.79, 106.01 (d, *J* = 259.9 Hz). ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –77.3 (d, *J* = 48.1 Hz). HRMS–FAB): *m/z* [M + H^+] calcd for $C_{12}H_{11}FNO_2S_2$: 284.0215; found: 284.0219.

α,α-Difluoro-α-(*p*-tolylthio)methyl Methyl Sulfone (3)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.59–7.56 (m, 2 H), 7.23–7.21 (m, 2 H), 3.03 (s, 3 H), 2.39 (s, 3 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 141.69, 137.21 (t, *J* = 1.1 Hz), 130.14, 127.81 (t, *J* = 323.1 Hz), 119.06, 35.72, 21.51. ^{19} F NMR (254 MHz, $CDCl_3$, TFA): δ = –5.14. HRMS (EI): *m/z* [M^+] calcd for $C_9H_{10}F_2O_2S_2$: 252.0090; found: 252.0083.

α-(Fluoromethylthio)ethyl *p*-Tolyl Sulfone (4)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.1 Hz, 2 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 5.84 (dd, *J* = 54.4, 10.6 Hz, 1 H), 5.59 (dd, *J* = 54.4, 10.6 Hz, 1 H), 4.20 (qd, *J* = 7.3, 1.5 Hz, 1 H), 2.47 (s, 3 H), 1.59 (d, *J* = 7.3 Hz, 3 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 145.27, 132.29, 129.68, 129.61, 85.43 (d, *J* = 216.3 Hz), 61.33 (d, *J* = 2.2 Hz), 21.75, 16.15. ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –111.6 (t, *J* = 54.4 Hz). HRMS–FAB: *m/z* [M + Na^+] calcd for $C_{10}H_{13}FO_2S_2Na$: 271.0239; found: 271.0241.

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(18) **Typical Procedure for Oxidation of Sulfides 2a,e,g,i**

m-Chloroperbenzoic acid (2.2 equiv) was added to a solution of sulfide in CH_2Cl_2 at 0 °C. The solution was stirred over night at r.t., treated with sat. aq $NaHCO_3$ and extracted with two portions of CH_2Cl_2. The combined extracts were washed with brine and dried over anhyd Na_2SO_4. After the removal of the solvent by evaporation, the residue was purified by column chromatography on SiO_2 ($CHCl_3$) to provide a pure disulfone.

α-Fluoro-α-methylsulfonylmethyl *p*-Tolyl Sulfone (5a)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.1 Hz, 2 H), 7.45 (d, *J* = 8.1 Hz, 2 H), 5.59 (d, *J* = 45.3 Hz, 1 H), 3.24 (d, *J* = 1.0 Hz, 3 H), 2.51 (s, 3 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 147.59, 131.57, 130.30, 130.00 (d, *J* = 1.1 Hz), 105.07 (d, *J* = 263.3 Hz), 39.47, 22.02. ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –96.8 (d, *J* = 45.3 Hz). HRMS (EI): *m/z* [M^+] calcd for $C_9H_{11}FO_4S_2$: 266.0083; found: 266.0077.

α-Fluoro-α-(*p*-tolyl sulfonyl)methyl Phenyl Sulfone (5g)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.99 (m, 2 H), 7.86 (d, *J* = 8.1 Hz, 2 H), 7.80–7.74 (m, 1 H), 7.62 (m, 2 H), 7.40 (d, *J* = 8.1 Hz, 2 H), 5.70 (d, *J* = 45.7 Hz, 1 H), 2.49 (s, 3 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 147.18, 135.56, 135.17, 132.06, 130.10, 130.08, 130.06, 129.36, 105.59 (d, *J* = 265.5 Hz), 22.0. ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –92.9 (d, *J* = 45.7 Hz). HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{13}FO_4S_2$: 328.0239; found: 328.0240.

α-Fluoro-α-(2-pyridylsulfonyl)methyl Phenyl Sulfone (5i)

^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.80 (m, 1 H), 8.10–7.62 (m, 8 H), 6.50 (d, *J* = 45.3 Hz, 1 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 154.47, 150.60, 138.50, 135.71, 134.84, 130.29, 129.31, 128.64, 124.14, 103.05 (d, *J* = 264.9 Hz). ^{19}F NMR (254 MHz, $CDCl_3$, TFA): δ = –96.5 (d, *J* = 45.3 Hz). HRMS (EI): *m/z* [M + H^+] calcd for $C_{12}H_{11}FNO_4S_2$: 316.0114; found: 316.0096.

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