Electrolytic Partial Fluorination of Organic Compounds. 12.[1] Selective Anodic Monofluorination of Fluoroalkyl and Alkyl Sulfides

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Highly regioselective anodic monofluorination of various aryl and alkyl fluoroalkyl sulfides was successfully carried out, and fluorine was exclusively (aryl sulfides) or preferentially (alkyl sulfides) introduced at the position α to the fluoroalkyl group. Even simple alkyl phenyl sulfides devoid of an electron-withdrawing group could be anodically monofluorinated in satisfactory yields for the first time when etheral solvents were used as an electrolytic solution. A unique Pummerer-type mechanism *via* fluorosulfonium ions was proposed for this anodic fluorination by comparison with anodic α-methoxylation previously studied.

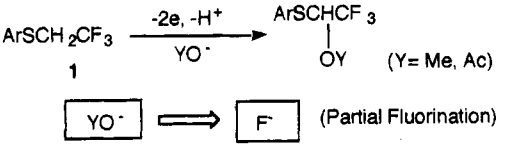
Introduction

Fluoro organic compounds have rather unique chemical and physical properties. Among them, partially fluorinated compounds are highly useful for developing novel medicines[2-4] and agricultural chemicals[5] and new functional materials such as ferroelectric liquid crystals.[6] Efficient methods for the partial fluorination of organic compounds are becoming increasingly important. So far, chemical methods using various reagents such as F_2, $FClO_3$, CF_3OF, XeF_2, Et_2NSF_3 (DAST), *N*-fluorinated triethylenediamine derivatives, and *N*-fluoropyridinium triflates have been mainly employed for partial fluorination.[7-9] However, they are dangerous, difficult to handle, or very costly.

Electrochemical partial fluorination is very attractive because fluorine atoms can be introduced into organic molecules in one step under safe conditions.[10,11] However, in contrast to well-established anodic perfluorination, anodic partial fluorination has not been developed owing to low selectivity for the fluorination and low nucleophilicity of fluoride ions.[12] In fact, only limited successful anodic partial fluorination has been reported.[10,11]

In 1970, Rozhkov and co-workers reported the first successful example of anodic monofluorination of naphthalene.[13,14] Since then, anodic partial fluorination of aromatics, heteroaromatics, olefins, and α-phenyl acetate derivatives has been performed.[10,11] However, there has so far been no report on anodic partial fluorination of organo sulfur compounds.[15]

Scheme 1



Recently, we found that a trifluoromethyl group markedly promotes anodic methoxylation and acetoxylation of aryl 2,2,2-trifluoroethyl sulfides (Scheme 1) **1**.[16-18]

This finding prompted us to attempt anodic substitution of sulfides **1** with fluorine, and we have found that the trifluoromethyl and other fluoroalkyl groups also markedly facilitate anodic α-fluorination of sulfides.[19,20] At almost the same time, Brigaud and Laurent reported successful anodic α-fluorination of sulfides having electron-withdrawing ester and benzoyl groups by use of $Et_3N{\cdot}3HF$ as a supporting electrolyte.[21] However, they failed to fluorinate a simple alkyl phenyl sulfide.

In this work, we have systematically examined the anodic fluorination of various types of aryl and alkyl fluoroalkyl sulfides together with simple nonfluoroalkyl sulfides in order to determine the full scope of this reaction.

Results and Discussion

Anodic Fluorination of Fluoroalkyl Sulfides. First, anodic monofluorination was investigated in detail using

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Table 1. Anodic Monofluorination of Aryl 2,2,2-Trifluoroethyl Sulfides 1

run	sulfide no.	X	supporting electrolyte	anodic potential, V vs SSCE	charge passed, F/mol	product yield, %
1	**1a**	H	$Py{\cdot}(HF)_n$	+2.0	4.1	0 (**2a**)
2	**1a**	H	$Bu_4NF{\cdot}3H_2O$	+2.0	1.9	0 (**2a**)
3	**1a**	H	$Et_3N{\cdot}3HF$	+1.9	3.2	62 (**2a**)
4	**1b**	Cl	$Et_3N{\cdot}3HF$	+2.0	7.2	65 (**2b**)
5	**1c**	Me	$Et_3N{\cdot}3HF$	+2.1	8.2	51 (**2c**)
6	**1d**	MeO	$Et_3N{\cdot}3HF$	+1.7	6.0	56 (**2d**)

Table 2. Anodic Monofluorination of Fluoroalkyl Phenyl Sulfides 1

run	sulfide no.	Rf	anodic potential, V vs SSCE	charge passed, F/mol	product yield, %
1	**1a**	CF_3	+1.9	3.2	62 (**2a**)
2	**1e**	C_3F_7	+2.3	3.0	67 (**2e**)
3	**1f**	CHF_2	+2.3	4.0	53 (**2f**)
4	**1g**	CH_2F	+2.1	2.7	60 (**2g**)
5	**1h**	CF_2Cl	+2.0	5.0	46 (**2h**)
6	**1i**	CH_2Cl	+1.8	3.0	30 (**2i**)

phenyl 2,2,2-trifluoroethyl sulfide (**1a**) as a model compound. Anodic oxidation of **1a** was carried out at constant potential in acetonitrile containing various fluorides as supporting electrolytes and the fluoride ion source, using an undivided cell.

Scheme 2

$$\underset{\mathbf{1}}{p\text{-}XC_6H_4SCH_2CF_3} \xrightarrow[F^-/MeCN]{-2e,-H^+} \underset{\mathbf{2}}{p\text{-}XC_6H_4SCHFCF_3}$$

As shown in Table 1, anodic monofluorination proceeded smoothly, providing tetrafluoroethyl sulfide **2a** in good yield only when $Et_3N{\cdot}3HF$ was used (run 3), whereas the other two fluorides were not effective (runs 1 and 2).

Next, the reaction was extended to various p-substituted phenyl 2,2,2-trifluoroethyl sulfides **1b-1d**. They underwent monofluorination quite well regardless of the substituent X groups on the benzene ring. Fluorine was exclusively introduced at the position α to the trifluoromethyl group. Neither aromatic fluorination nor benzylic fluorination was observed in run 5. The results are noteworthy because nucleophilic substitution at the position α to the trifluoromethyl group is usually quite difficult to achieve.[22,23] Moreover, products **2** are difficult to prepare by other methods.

Scheme 3

$$\underset{\mathbf{1}}{PhSCH_2Rf} \xrightarrow[Et_3N{\cdot}3HF]{-2e,-H^+} \underset{\mathbf{2}}{PhSCHFRf}$$

Anodic fluorination was further extended to various fluoroalkyl phenyl sulfides (**1e-1i**). The results are summarized in Table 2. As shown in Table 2, anodic fluorination proceeded to afford the corresponding α-monofluorinated products **2** regardless of the fluoroalkyl groups. A strong electron-withdrawing perfluoroalkyl group, such as a heptafluoropropyl group, promoted anodic fluorination (run 2). Interestingly, weaker electron-withdrawing groups such as difluoromethyl and monofluoromethyl groups similarly promoted fluorination (runs 3 and 4). Therefore, it was revealed that the electron-withdrawing ability of the fluoroalkyl groups does not affect the efficiency of anodic monofluorination. It was clarified previously that in the case of anodic methoxylation of halogenated sulfides, the decrease in the electron-withdrawing ability of the halogenoalkyl group resulted in a substantial decrease in the yield of the α-methoxylation process and that monofluoro sulfide **1** did not give α-methoxylated product at all.[8] Therefore, the results of anodic fluorination are quite different from those of anodic methoxylation.[18]

It is notable that the promotion effect of a fluorine atom on anodic fluorination is much more pronounced than that of a chlorine atom, although the electronegativities of these atoms are similar (runs 1, 5 and 4, 6). Therefore, the effect of a fluorine atom is quite specific.

Table 3. Anodic Monofluorination of Benzyl Fluoroalkyl Sulfides 3

run	sulfide no.	Rf	anodic potential, V vs SSCE	charge passed, F/mol	product yield, % 4	4′
1[a]	**3a**	CF_3	+2.5−+2.8	4.0	22 (**4a**)	32 (**4a′**)
2[a]	**3a**	CF_3	+2.3	11.5	26 (**4a**)	45 (**4a′**)
3[b]	**3a**	CF_3	+2.3	17.0	51 (**4a**)	30 (**4a′**)
4[a]	**3b**	CH_2F	+2.5−+2.7	3.0	13 (**4b**)	34 (**4b′**)

[a] 0.35 M $Et_3N{\cdot}3HF$/MeCN was used for the electrolytic solution. [b] 1.69 M $Et_3N{\cdot}3HF$/MeCN was used for the electrolytic solution.

As shown in Scheme 4 and Table 3, the anodic fluorination of benzyl fluoroalkyl sulfides **3** resulted in the formation of two regioisomers **4** and **4′**.

Scheme 4

$$\underset{\mathbf{3}}{PhCH_2SCH_2Rf} \xrightarrow[Et_3N{\cdot}3HF]{-2e,-H^+} \underset{\mathbf{4}}{PhCH_2SCHFRf} + \underset{\mathbf{4'}}{PhCHFSCH_2Rf}$$

Benzylic fluorination occurred preferentially in both cases of sulfides **3a** and **3b**. However, interestingly, the regioselectivity in the case of **3a** was reversed at higher concentration fluoride ions. It was expected that the fluorination should occur predominantly at the benzylic position of **3** since benzylic anodic substitution is known to easily take place. Therefore, it should be noted that the fluorination took place rather preferentially at the position α to the trifluoromethyl group under high concentration of fluoride ions. However, the reason is not clear at present.

Anodic Fluorination of Alkyl Phenyl Sulfides and a Benzyl Sulfide. It was found that even simple alkyl phenyl sulfides **5** devoid of an electron-withdrawing group underwent fluorination in acetonitrile to provide monofluoro sulfides **6**, although the yields were not satisfactory (Table 4, runs 1, 2, and 9). Since the nucleophilicity of fluoride ions is well known to be greatly affected by solvents, the electrolytic solvent was changed to achieve higher yields. Thus, the yields were approximately doubled when ethereal solvents such as THF, dimethoxyethane (DME), and dioxane instead of acetonitrile were used as the solvent (runs 3−6, 10), whereas dichloromethane and DMF were not effective (runs 7 and 8).

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Table 4. Anodic Monofluorination of Alkyl Phenyl Sulfides 5

run	sulfide no.	R	solvent	anodic potential, V vs SSCE	current density, mA/cm²	charge passed, F/mol	product yield (%) 6	7
1	**5a**	H	MeCN	+1.6		2.1	23 (**6a**)	45 (**7a**)
2	**5a**	H	MeCN		6.3[a]	2.0	20 (**6a**)	62 (**7a**)
3	**5a**	H	THF	+3.3		6.1	45 (**6a**)	*b* (**7a**)
4	**5a**	H	THF		6.3[a]	5.0	52 (**6a**)	32 (**7a**)
5	**5a**	H	DME		6.3[a]	4.5	57 (**6a**)	25 (**7a**)
6	**5a**	H	Dioxane		6.3[a]	3.0	47 (**6a**)	21 (**7a**)
7	**5a**	H	CH_2Cl_2		6.3[a]	3.0	22 (**6a**)	24 (**7a**)
8	**5a**	H	DMF	+1.6		4.0	5 (**6a**)	6 (**7a**)
9	**5b**	Me	MeCN	+1.8		4.0	18 (**6b**)	*b*
10	**5b**	Me	THF	+3.3		6.1	45 (**6b**)	*b*

[a] Constant current electrolysis. [b] Not determined.

Scheme 5

$$\underset{\mathbf{5}}{PhSCH_2R} \xrightarrow[Et_3N\cdot 3HF]{-2e,-H^+} \underset{\mathbf{6}}{PhSCHFR} + \underset{\mathbf{7}}{PhS(O)CH_2R}$$

As shown in Table 4 (runs 2, 4–7), selective anodic monofluorination could be achieved by constant current electrolysis because the fluorinated products had much higher oxidation potentials than the starting materials. For example, the peak oxidation potentials of starting sulfide **5a** and α-fluorinated **6a** measured at a platinum anode in 0.1 M Et_4NBF_4/MeCN (scan rate, 100 mV/s) were +1.51 and +1.85 V vs SSCE, respectively. Such large oxidation potential difference made the highly selective monofluorination of sulfides possible.

Thus, in a similar manner, aliphatic sulfide, heptyl methyl sulfide (**5c**), underwent fluorination rather effectively in DME as shown in Scheme 6.

Scheme 6

$$\underset{\mathbf{5c}}{C_6H_{13}CH_2SCH_3} \xrightarrow[Et_3N\cdot 3HF/DME]{-2e,-H^+} (4V \text{ vs SSCE; } 4 \text{ F/mol})$$

$$\underset{\mathbf{6c}}{C_6H_{13}CHFSCH_3} + \underset{\mathbf{6c'}}{C_6H_{13}CH_2SCH_2F}$$

22% 31%

In this case, fluorination took place at both α-positions, and it was found that fluorine was preferentially introduced into the methyl group of **5c** by ^1H and ^{19}F NMR spectral study. This preferential fluorination at the methyl group seems to be due to ease of deprotonation of the cationic intermediate (*vide infra*). However, separation of these isomers was unsuccessful.

Although the yields of the fluorination of **5** are moderate, these results are the first example of the successful anodic monofluorination of simple alkyl sulfides devoid of an electron-withdrawing substituent. Products **6** thus prepared are known to be useful building blocks for the preparation of monofluorovinyl sulfides.[24]

Reaction Mechanism. The electrochemical reaction → chemical reaction → electrochemical reaction → chemical reaction (ECEC) mechanism is well established for anodic methoxylation of amines[25,26] amides,[27] and carbamates.[28] We have recently clarified that the anodic methoxylation of fluoroalkyl sulfides proceeds with a typical ECEC mechanism, as shown in Scheme 7.[18]

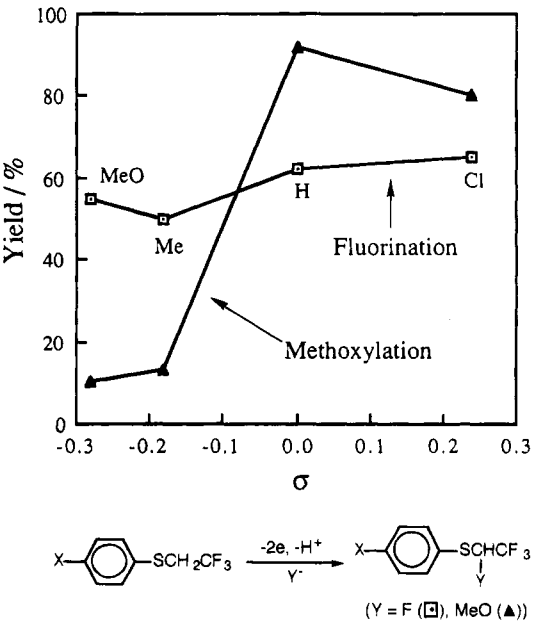
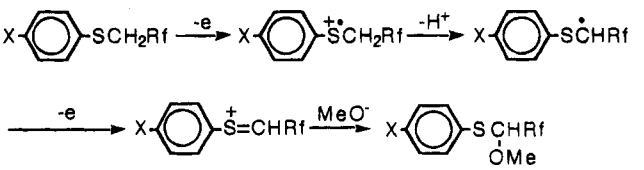


Figure 1. Relationships between substituent constants (σ) and yields of the fluorinated and methoxylated sulfides in the anodic fluorination and methoxylation[18] of trifluoroethyl sulfides.

Scheme 7



Anodic fluorination of fluoroalkyl sulfides **1** and **3** and simple sulfides **5** also appears to proceed similarly. However, the effects of both substituents (X and R_f groups in Scheme 7) on anodic fluorination are totally different from those observed for anodic methoxylation as shown in Figures 1 and 2. As reported previously by us, the anodic methoxylation was greatly affected by the substituents X at the benzene ring. An electron-withdrawing group such as a chlorine atom promoted the anodic methoxylation while electron-donating groups such as methyl and methoxy groups significantly interfered with the methoxylation, as shown in Figure 1.[18] On the other hand, the anodic fluorination did not depend on the

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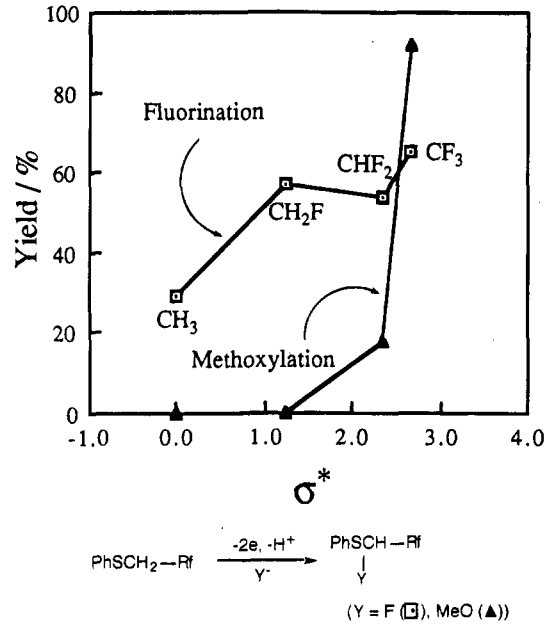
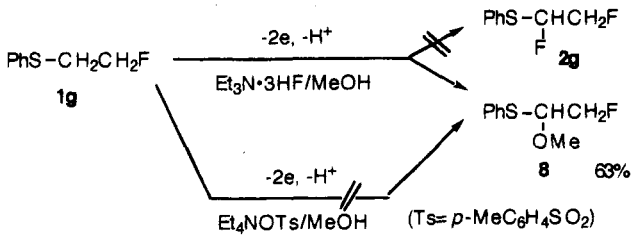


Figure 2. Relationships between substituent constants (Rf group σ^*) and yields of the fluorinated and methoxylated sulfides in the anodic fluorination and methoxylation[18] of trifluoroethyl sulfides.

Scheme 8



substituents X and always proceeded efficiently. As illustrated in Figure 2, the anodic methoxylation was significantly affected by fluoroalkyl groups. A difluoromethyl group caused a drastic decrease in the yield, and a monofluoromethyl group did not promote the methoxylation any more.[18] In contrast to this, the anodic fluorination was not affected by the fluoroalkyl groups, and the fluorination took place efficiently regardless of the electron-withdrawing ability and even an electron-donating methyl group promoted the fluorination to some extent. Considering these facts, the mechanism for anodic fluorination might be different from that for anodic methoxylation (the conventional ECEC mechanism).

We observed some very interesting phenomena. Namely, anodic fluorination of **1g** in methanol provided α-methoxylated product **8** instead of α-fluorinated product **2g** in a good yield (Scheme 8).[20] As reported previously,[18] **8** was not obtained under conventional anodic methoxylation conditions, and this is attributed to the very slow deprotonation of the cation radical intermediate due to the weak electron-withdrawing ability of the CH_2F group. This marked promotion effect of $Et_3N{\cdot}3HF$ on the α-methoxylation of **1g** cannot be explained by the conventional ECEC mechanism.

From these results, this anodic fluorination seems to proceed with a Pummerer-type mechanism[29] *via* the

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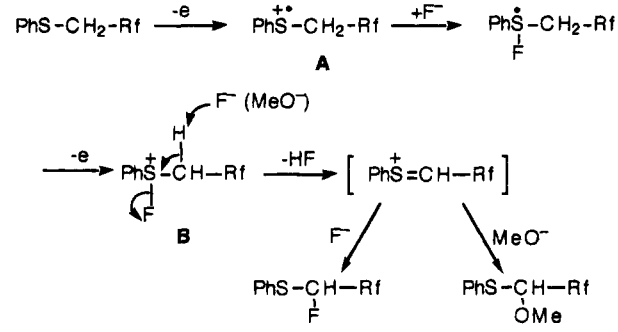
Scheme 9



fluorosulfonium cation **B**, as shown in Scheme 9. In this mechanism, the cation radical **A** of the sulfide is trapped by a fluoride ion, and this step should suppress side reactions from the cation radical **A** (such as dimerization and nucleophilic attack on an aromatic ring) even when deprotonation of **A** is slow. Since the fluoride ion is a much weaker nucleophile than the methoxide ion, it is reasonable that methoxylation predominated in methanol. Thus, efficient α-fluorination in acetonitrile and α-methoxylation in methanol of **1g** in the presence of $Et_3N{\cdot}3HF$ can both be explained by assuming the common intermediate **B**.

In summary, we have developed selective anodic fluorination of fluoroalkyl and simple alkyl sulfides and clarified interesting features of their anodic fluorination. Furthermore, a unique fluorination mechanism via fluorosulfonium ions was established. This anodic fluorination does not require any special, dangerous, or costly reagents and can be performed in normal laboratory glassware without precautions. Therefore, this fluorination should be highly useful for developing new types of various fluorinated sulfides.

Experimental Section

^1H NMR and ^{19}F NMR spectra were recorded at 60 MHz on Varian EM 360 NMR and Hitachi R-1200F NMR spectrometers, respectively. The chemical shifts for ^1H and ^{19}F NMR are given in δ ppm downfield from internal Me_4Si and upfield from external CF_3COOH, respectively. IR spectra were obtained with a Hitachi 295 infrared spectrometer. Mass spectra were obtained with a JEOL JMS-D100 GC–mass spectrometer. High-resolution mass spectra were obtained with a Hitachi M-80B GC–mass spectrometer. Cyclic voltammetric and preparative electrolysis experiments were carried out using a Hokutodenko HA-501 Potentiostat/Galvanostat equipped with a Hokutodenko HF-201 digital coulometer.

Anodic Fluorination of Sulfides. The electrolysis was performed at a platinum anode and cathode (3 × 4 cm) in 0.37 M $Et_3N{\cdot}3HF$/MeCN (50 mL) containing 5 mmol of the substrate. During the electrolysis, the temperature was maintained at ca. 20 °C. After the starting material was completely consumed (silica gel, TLC monitoring), the electrolysis solution was neutralized with 12% aqueous ammonia. The acetonitrile was then removed by evaporation below 40 °C. The residue was extracted with ether (40 mL, then 20 mL × 4). The extracts were washed with brine (200 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($CHCl_3/CCl_4$, 1:1–4:1) to provide the desired product. Some of the fluorinated products (**4a′**, **4b**, **4b′**, **6c**, and **6c′**) were very sensitive toward moisture and easily decomposed with HF gas evolution. Therefore, the yields of these products were determined by ^{19}F NMR using C_6H_5F as an internal standard after neutralization of electrolytic solution with anhydrous NH_3 gas. Their high-resolution mass spectra could not be obtained due to their instability.

Phenyl 1,2,2,2-tetrafluoroethyl sulfide (2a): ^{1}H NMR ($CDCl_3$) δ 5.77 (dq, 1 H, J = 50.0, 6.0 Hz), 7.1–7.7 (m, 5H); ^{19}F NMR δ 2.0 (dd, 3F, J = 16.0, 6.0 Hz), −84.4 (dq, 1F, J = 50.0, 16.0 Hz); IR (neat) 1270, 1240, 1200, 1180, 1030, 750, 685 cm^{-1}; MS *m/e* 210 (M^+), 141 ($M^+ - CF_3$), 109 (PhS^+); calcd for $C_8H_6F_4S$ *m/e* 210.0125, found 210.0087.

***p*-Chlorophenyl 1,2,2,2-tetrafluoroethyl sulfide (2b)**: ^{1}H NMR ($CDCl_3$) δ 5.77 (dq, 1H, J = 50.0, 6.0 Hz), 7.23–7.70 (m, 4H); ^{19}F NMR δ 1.5 (dd, 3F, J = 15.6, 6.0 Hz), −85.3 (dq, 1F, J = 50.0, 15.6 Hz); IR (neat) 1480, 1355, 1280, 1190, 1140, 1095, 1015, 820 cm^{-1}; MS *m/e* 246 ($M^+ + 2$), 244 (M^+) 175 ($M^+ - CF_3$), 143 ($ClC_6H_4S^+$); calcd for $C_8H_5ClF_4S$ *m/e* 243.9736, found 243.9725.

***p*-Tolyl 1,2,2,2-tetrafluoroethyl sulfide (2c)**: ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 5.73 (dq, 1H, J = 50.0, 6.0 Hz), 7.10–7.63 (m, 4H); ^{19}F NMR δ 1.6 (dd, 3F, J = 16.0, 6.0 Hz), −86.0 (dq, 1F, J = 50.0, 16.0 Hz); IR (neat) 1490, 1210, 805 cm^{-1}; MS *m/e* 224 (M^+), 155 ($M^+ - CF_3$), 123 ($MeC_6H_4S^+$); calcd for $C_9H_8F_4S$ *m/e* 224.0283, found 224.0311.

***p*-Methoxyphenyl 1,2,2,2-tetrafluoroethyl sulfide (2d)**: ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 3H), 5.64 (dq, 1H, J = 50.0, 6.0 Hz), 6.7–7.7 (m, 4H); ^{19}F NMR δ 1.0 (dd, 3F, J = 16.0, 6.0 Hz), −86.1 (dq, 1F, J = 50.0, 16.0 Hz); IR (neat) 1600, 1490, 1350, 1290, 1280, 1250, 1190, 1130, 1030, 870, 830 cm^{-1}; MS *m/e* 240 (M^+), 139 ($MeOC_6H_4S^+$); calcd for $C_8H_6F_4OS$ *m/e* 240.0230, found 240.0201.

Phenyl 1,2,2,3,3,4,4,4-octafluorobutyl sulfide (2e): ^{1}H NMR ($CDCl_3$) δ 6.00 (ddd, 1H, J = 50.0, 16.0, 6.0 Hz), 7.0–7.7 (m, 5H); ^{19}F NMR δ 3.0 (t, 3F, J = 1.1 Hz), −38.0 (d, 1F, J = 300 Hz), −44.0 (d, 1F, J = 300 Hz), −46.3 (m, 2F), −84.3 (m, 1F); IR (neat) 3080, 1445, 1235, 1115, 710 cm^{-1}; MS *m/e* 310 (M^+), 141 ($M^+ - CF_2CF_2CF_3$); calcd for $C_{10}H_6F_8S$ *m/e* 310.0061, found 310.0050.

Phenyl 1,2,2-trifluoroethyl sulfide (2f): ^{1}H NMR ($CDCl_3$) δ 5.67 (dtd, 1H, J = 50.4, 8.2 4.0 Hz), 5.77 (tdd, 1H, J = 54.0, 4.0, 4.0 Hz), 7.2–7.8 (m, 5H); ^{19}F NMR δ −46.7 (dddd, 1F, J = 300, 54.0, 22.5, 8.2 Hz), −48.7 (dddd, 1F, J = 300, 54.0, 19.6, 8.2 Hz), −86.7 (dddd, 1F, J = 50.4, 22.5, 19.6, 4.0 Hz); IR (neat) 3050, 2970, 1470, 1440, 1375, 1150, 1060, 1020, 740, 685 cm^{-1}; MS *m/e* 192 (M^+), 141 ($M^+ - CHF_2$), 109 (PhS^+); calcd for $C_8H_7F_3S$ *m/e* 192.0219, found 192.0209.

Phenyl 1,2-difluoroethyl sulfide (2g): ^{1}H NMR ($CDCl_3$) δ 4.51 (dddd, 1H, J = 47.5, 14.9, 10.6, 6.6 Hz), 4.60 (dddd, 1H, J = 46.5, 20.8, 10.6, 3.3 Hz), 5.89 (dddd, 1H, J = 53.4, 15.4, 6.6, 3.3 Hz), 7.3–7.6 (m, 5H); ^{19}F NMR δ −78.0 (dddd, 1F, J = 53.4, 22.3, 20.8, 14.9 Hz), −139.8 (tdd, 1F, J = 47.0, 22.3, 15.4 Hz); IR (neat) 3080, 2960, 1590, 1480, 1445, 1085, 1050, 1030, 870, 750 cm^{-1}; MS *m/e* 174 (M^+), 141 ($M^+ - CH_2F$), 109 (PhS^+); calcd for $C_8H_8F_2S$ *m/e* 174.0313, found 174.0293.

Phenyl 2-chloro-1,2,2-trifluoroethyl sulfide (2h): ^{1}H NMR ($CDCl_3$) δ 5.74 (dt, 1H, J = 51.0, 6.4 Hz), 7.2–7.8 (m, 5 H); ^{19}F NMR δ 23.9 (dd, 2F, J = 22.0, 6.4 Hz), −76.8 (dt, 1F, J = 51.0, 22.0 Hz); IR (neat) 3080, 2980, 1480, 1450, 1320, 1230, 1210, 1040, 1020, 745 cm^{-1}; MS *m/e* 228 ($M^+ + 2$), 226 (M^+) 141 ($M^+ - CClF_2$), 109 (PhS^+); calcd for $C_8H_6ClF_3S$ *m/e* 225.9831, found 225.9897.

Phenyl 2-chloro-1-fluoroethyl sulfide (2i): ^{1}H NMR ($CDCl_3$) δ 3.75 (dd, 2H, J = 15.4, 5.5 Hz), 5.78 (dt, 1H, J = 51.5, 5.5 Hz), 7.2–7.7 (m, 5 H); ^{19}F NMR δ −70.7 (dt, J = 51.5, 15.4 Hz); IR (neat) 1470, 1440, 985, 735, 685 cm^{-1}; MS *m/e* 192 ($M^+ + 2$), 190 (M^+) 141 ($M^+ - CH_2Cl$), 109 (PhS^+); calcd for C_8H_8ClFS *m/e* 190.0018, found 190.0004.

Benzyl 1,2,2,2-tetrafluoroethyl sulfide (4a): ^{1}H NMR ($CDCl_3$) δ 3.98 (s, 2H), 5.55 (dq, 1H, J = 50.5, 6.0 Hz), 7.26 (s, 5H); ^{19}F NMR δ 0.70 (dd, 3F, J = 16.0, 6.0 Hz), −90.7 (dq, 1F, J = 50.5, 16.0 Hz); IR (neat) 2940, 2870, 1495, 1460, 1360, 1190, 1135, 1015, 875 cm^{-1}; MS *m/e* 224 (M^+), 155 ($M^+ - CF_3$), 123 ($PhCH_2S^+$); calcd for $C_8H_6F_4S$ *m/e* 224.0282, found 224.0332.

α-Fluorobenzyl 2,2,2-trifluoroethyl sulfide (4a′): ^{1}H NMR ($CDCl_3$) δ 3.40 (q, 2H, J = 8.0 Hz), 6.71 (d, 1H, J = 45.6 Hz), 7.38 (s, 5H); ^{19}F NMR δ 11.0 (t, 3F, J = 8.0 Hz), −69.8 (d, 1F, J = 45.6 Hz); MS *m/e* 224 (M^+), 155 ($M^+ - CF_3$), 109 ($PhCHF^+$).

Benzyl 1,2-difluoroethyl sulfide (4b): ^{19}F NMR δ −82.5 (m, 1F), −140.5 (m, 1F); MS *m/e* 188 (M^+), 123 ($PhCH_2S^+$).

α-Fluorobenzyl 2-fluoroethyl sulfide (4b′): ^{19}F NMR δ −67.0 (d, 1F, J = 55.0 Hz), −130.0 (tt, 1F, J = 43.0, 19.0 Hz); MS *m/e* 188 (M^+), 109 ($PhCHF^+$).

Fluoromethyl phenyl sulfide (6a): ^{1}H NMR ($CDCl_3$) δ 5.67 (d, 2H, J = 53.0 Hz), 7.1–7.6 (m, 5H); ^{19}F NMR δ −100.6 (t, J = 53.0 Hz); IR (neat) 3060, 2950, 1585, 1480, 1440, 1320, 1230, 1025, 960, 735, 685 cm^{-1}; MS *m/e* 142 (M^+), 109 (PhS^+); calcd for C_7H_7FS *m/e* 142.0279, found 142.0249.

2-Fluoroethyl phenyl sulfide (6b): ^{1}H NMR ($CDCl_3$) δ 1.67 (dd, 3H, J = 22.0, 6.2 Hz), 5.90 (dq, 1H, J = 56.0, 6.2 Hz), 7.1–7.7 (m, 5H); ^{19}F NMR δ −59.2 (dq, J = 56.0, 22.0 Hz); IR (neat) 2990, 2940, 1505, 1475, 1440, 1060, 875, 745, 685 cm^{-1}; MS *m/e* 156 (M^+), 110 ($PhSH^+$), 47 (CH_3CHF^+); calcd for C_7H_7FS *m/e* 156.0409, found 156.0416.

1-Fluoroheptyl methyl sulfide (6c): ^{1}H NMR ($CDCl_3$) δ 0.7–2.0 (m, 13H), 2.24 (s, 3H), 5.55 (dt, 2H, J = 57.0, 5.9 Hz); ^{19}F NMR δ −36.0 (dt, J = 57.0, 14.0 Hz); MS *m/e* 164 (M^+), 149 ($M^+ - CH_3$).

Fluoromethyl heptyl sulfide (6c′): ^{1}H NMR ($CDCl_3$) δ 0.7–2.0 (m, 13H), 2.70 (m, 2H), 5.51 (d, 2H, J = 53.4 Hz); ^{19}F NMR δ −69.1 (t, J = 53.4 Hz); MS *m/e* 164 (M^+), 131 ($M^+ - CH_2F$).

Anodic Methoxylation of 1g in the Presence of Fluoride Ions. The electrolysis of **1g** (1.5 mmol) was carried out at platinum electrodes (2 × 2 cm) at 170 °C in 0.33 M $Et_3N{\cdot}3HF$ in methanol (15 mL). After a constant current (25 mA) was passed until **1g** was almost consumed (monitored by GC column: PEG 20M or silicone OV17), the electrolyte solution was neutralized with 12% aqueous ammonia. The solution was extracted repeatedly with ether. The extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by silica gel TLC (hexane/AcOEt, mainly 5:1) to provide α-methoxylated product **8**.

2-Fluoro-1-methoxyethyl phenyl sulfide (8):[30] ^{1}H NMR ($CDCl_3$) δ 3.40 (s, 3H), 3.9–5.0 (m, 3H), 7.2–7.6 (m, 5H); ^{19}F NMR δ −133.0 (td, J = 48.0, 14.0 Hz); IR (neat) 2960, 2840, 1585, 1475, 1440, 1195, 1130, 1080 cm^{-1}; MS *m/e* 186 (M^+), 110 ($PhSH^+$); calcd for $C_{10}H_{11}FO_2S$ *m/e* 186.0514, found 186.0514.

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Supplementary Material Available: ^{1}H NMR spectra of **2a-i**, **4a**, and **6a,b** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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