Facile Synthesis of α-Fluoroalkyl Sulfides under the Oxidative Desulfurization–Fluorination Conditions

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(Received June 12, 1998)

Upon treatment with n-$Bu_4NH_2F_3$ and 1,3-dibromo-5,5-dimethylhydantoin, various organic sulfides underwent a Pummerer-type rearrangement, followed by fluorination, to give α-fluoro sulfides. The fluoro-Pummerer rearrangement, when applied to $RCH(SMe)CF_2SMe$, gave trifluoro sulfides $RCF(SMe)CF_2SMe$. When an HF-pyridine reagent was used as the fluorinating agent, an oxidative desulfurization–fluorination reaction occurred depending on the structure of the substrates.

Organofluorine compounds often contribute to remarkable enhancement and/or modification of biological activities of agrochemicals and pharmaceuticals.[1] Physical properties of materials[2] also are improved by introduction of a fluorine functionality. Since fluorinated organic compounds do not exist in nature, they have to be prepared by organic synthesis. Accordingly, the exploitation of convenient and highly selective fluorination reactions has been a major research interest. Of various fluorinated molecules, the amino acids[3] and nucleic acids[4] containing an α-fluoroalkylthio moiety exhibit remarkable biological activities. In addition, α-fluoro sulfides are useful synthetic intermediates.[5] These fluorinated sulfides are readily available via the fluoro-Pummerer rearrangement. This reaction has been achieved by (1) direct fluorination of sulfides with XeF_2,[6] (2) treatment of sulfoxides[7] or sulfides[8] with Et_2NSF_3, (3) fluorination of sulfides with *N*-fluoropyridinium salts,[9] or (4) electrolytic partial fluorination with $Et_3N{\cdot}3HF$.[10] An alternative route is the fluorination of α-fluoro sulfones or α-chloro sulfides with molecular fluorine[11] or potassium fluoride,[12] respectively. From the viewpoint of organic synthesis, however, most of these methods may sometimes be inconvenient. To enhance the synthetic utility of the oxidative desulfurization-fluorination conditions,[13] we applied the reaction to various sulfides. We found that the reagent system consisting of tetrabutylammonium dihydrogentrifluoride (n-$Bu_4NH_2F_3$)[14] and 1,3-dibromo-5,5-dimethylhydantoin (DBH) mediated the fluoro-Pummerer rearrangement.[15] Herein we report the details of the Pummerer-type fluorination as applied to the synthesis of oligofluorinated compounds.

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Results and Discussion

Fluoro-Pummerer Rearrangement of Sulfides. The oxidative desulfurization-fluorination,[13] in general, converts C–S bond(s) of dithioesters or dithioacetals into C–F bond(s), and thus provides us with a convenient synthetic method for organofluorine compounds. To test the feasibility of the transformation, we applied the oxidative desulfurization–fluorination conditions to the basic substrates, sulfides **1**, and studied the scope and limitation of the substrates.

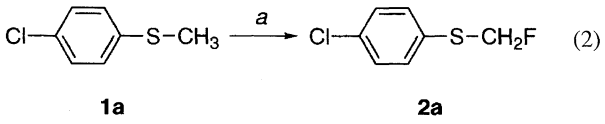
When we treated **1** with n-$Bu_4NH_2F_3$ and DBH, monofluorination took place smoothly, and we obtained α-fluoro sulfides **2**. Upon treatment with n-$Bu_4NH_2F_3$ only, the sulfides were recovered unchanged. However, addition of DBH to the mixture induced the fluorination. Advantages of the present method are that the fluorinating agent n-$Bu_4NH_2F_3$ is safe, stable, and easy-to-handle and can be stored at room temperature for a long period. In addition, conventional glasswares can be used without any special care.

$$R^1\text{–}S\text{–}CH_2R^2 \xrightarrow{a} R^1\text{–}S\text{–}CHFR^2 \quad (1)$$

1 **2**

a: n-$Bu_4NH_2F_3$, DBH, CH_2Cl_2

With **1a** as a substrate, we optimized the reaction temperature and reaction time as summarized in Table 1. The best chemical yield of α-fluoro sulfide **2a** was attained when the reaction was carried out at room temperature and quenched after 20 min (Run 3). The reaction at 0 °C resulted in lower yields even after a prolonged reaction time (Runs 1 and 2).



(2)

1a **2a**

a: *n*-$Bu_4NH_2F_3$ (1.1 mol), DBH (1.1 mol), CH_2Cl_2

Table 1. Optimization of the Fluoro-Pummerer Rearrangement of **1a**

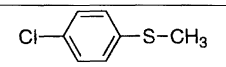
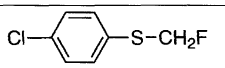
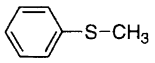
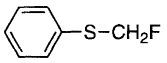
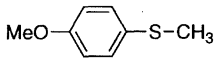
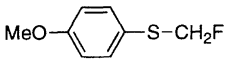
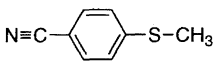
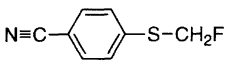
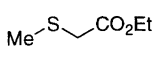
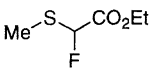
Run	Conditions	Yield of **2a**	Recovery of **1a**
		%	%
1	0 °C, 10 min	30	14
2	0 °C, 2 h	38	11
3	r.t., 20 min	66	12
4[a)]	r.t., 1.5 h	63	12

a) Instead of DBH, NBS (2.2 mol) was used.

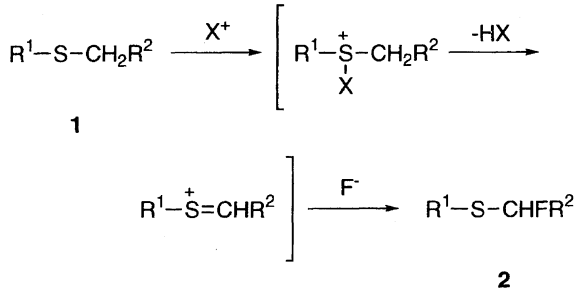
The optimized conditions were applied to various sulfides **1**; the results are summarized in Table 2. To consume all of the substrate, the amounts of the two reagents were occasionally increased. Monofluorination thus took place in moderate-to-good yields (Runs 1—4). Sulfide **1e**, in particular, gave a product resulting from the fluorination only at the carbon having an active hydrogen (Run 5). α-Fluoroalkyl sulfides are easily oxidized by an oxidizing agent to give α-fluoroalkyl sulfoxides or α-fluoroalkyl sulfones.[7a,8,9a,12)]

Such substrates as diphenyl sulfide, dibenzyl sulfide, and isopropyl phenyl sulfide gave complex mixtures of products; none of the fluorinated products could be isolated.

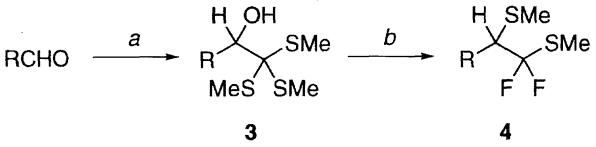
Table 2. Fluoro-Pummerer Rearrangement of Sulfide **1**[a)]

Run	Sulfide	Product[b)] (Yield/%)
1	 **1a**	 **2a** (90)
2	 **1b**	 **2b** (52)
3	 **1c**	 **2c** (59)
4	 **1d**	 **2d** (75)
5	 **1e**	 **2e** (65)

a) Substrate **1** was allowed to react with *n*-$Bu_4NH_2F_3$ (1.4 mol) and DBH (1.4 mol) in CH_2Cl_2 at room temperature for 20 min.
b) Isolated yield.



Scheme 1.



a: $LiC(SMe)_3$
b: Et_2NSF_3 (1.05 mol), CH_2Cl_2, 0 °C, 10 min

Scheme 2.

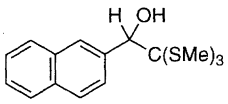
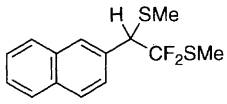
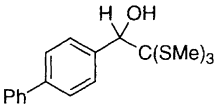
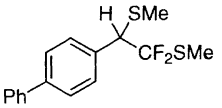
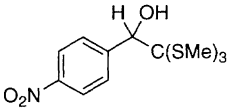
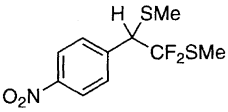
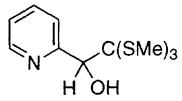
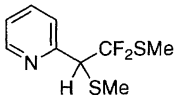
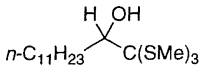
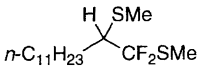
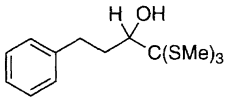
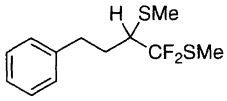
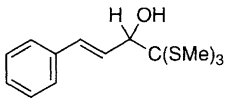
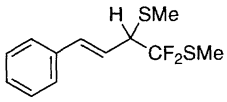
Mechanistic Aspects. The formation of product **2** can be explained by the mechanism shown in Scheme 1. An electrophilic attack of a positive halogen species X^+ (X = Br or I) to R^1–S–CH_2R^2 **1** produces sulfonium ion R^1–S^+(X)–CH_2R^2. Elimination of HX from the sulfonium ion affords R^1–S^+=CHR^2, which is attacked by a fluoride ion to give finally R^1S–CHF–R^2 **2**.

Fluorination of 1-Substituted 2,2,2-Tris(methylthio)-ethanols. Previously we disclosed that the oxidative desulfurization–fluorination converted RCH(OH)$C(SMe)_3$ **3**, which were derived from $LiC(SMe)_3$ and aldehydes,[16)] into $RCOCF_2SMe$.[17)] When hydroxy orthothioesters **3** were treated with Et_2NSF_3, rearrangement–difluorination products RCH(SMe)CF_2SMe **4**[18)] resulted as illustrated in Scheme 2.[15)] The products will be shown later to be converted into trifluorination compounds RCF(SMe)CF_2SMe via the fluoro-Pummerer rearrangement.

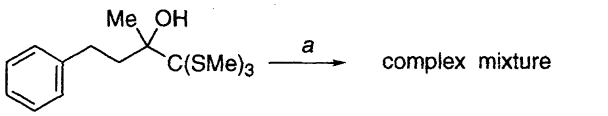
The results of the transformation of **3** to **4** are summarized in Table 3. As readily seen, the fluorination reaction is applicable to a variety of **3**. However, hydroxy orthothioesters **3d** or **3g** gave **4d** or **4g**, respectively, in a low yield. These instead underwent dehydroxylation, rearrangement of a methylthio group without fluorination to give 1,2,2-tris(methylthio)ethenes **5d** or **5g**, due probably to an electron-accepting nature of a pyridine ring or to the stabilization of an electrophilic intermediate by the conjugated system, respectively (see Run 4 or 7, respectively) (Chart 1). Trifluorination did not take place in this reaction, nor did fluorine substitution of the hydroxy group ocurr. In a similar manner, a fair amount of by-product **5c** formed during the transformation of **3c** to **4c**.

Substrates **6h** or **6i**, derived from the corresponding ketone and $HC(SMe)_3$, gave a complex mixture of products or *S*-ester of α,β-unsaturated thiocarboxylic acid **7i**, respectively; none of fluorinated products could be isolated.

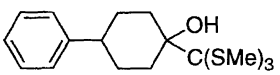
Table 3. Synthesis of Difluoro Sulfides **4**[a]

Run	Orthothioester	Product[b] (Yield/%)
1	 **3a**	 **4a** (50)
2	 **3b**	 **4b** (55)
3[c]	 **3c**	 **4c** (56)
4[d]	 **3d**	 **4d** (15)
5	 **3e**	 **4e** (71)
6	 **3f**	 **4f** (70)
7[e]	 **3g**	 **4g** (13)

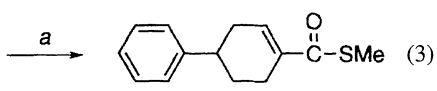
a) Substrate **3** was allowed to react with Et_2NSF_3 (1.05 mol) in CH_2Cl_2 at 0 °C for 10 min. b) Isolated yield. c) By-product **5c** was isolated in 20 % yield. d) Major product **5d** was isolated in 55% yield. e) Main product **5g** was isolated in 48% yield.



6h



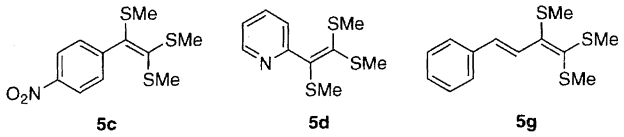
6i



(3)

7i

a: Et_2NSF_3 (1.05 mol), CH_2Cl_2, 0 °C, 10 min, 92 %



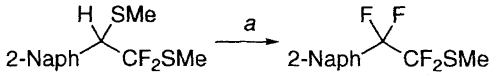
5c **5d** **5g**

Chart 1.

Fluoro-Pummerer Rearrangement of Difluoro Sulfides 4. The fluoro-Pummerer rearrangement discussed above was next applied to difluoro sulfides **4**; it gave rise selectively to trifluoro sulfides **8**, as summarized in Runs 1, 2, 3, 5, and 7 of Table 4. The methylthio group always remained intact.

When an HF-Pyridine reagent (HF-Py) was employed for the fluorination in place of *n*-$Bu_4NH_2F_3$, an alternative reaction pathway resulted depending on the kind of substituent R^1. Difluoro sulfides **4c** and **4e** underwent the fluoro-Pummerer rearrangement to give **8c** and **8e**, respectively (Runs 4 and 6), whereas **4f** afforded the Pummerer rearrangement product **8f**, in addition to a brominated product **8f′** (Run 8).

Oxidative Desulfurization Fluorination of Difluoro Sulfide 4a. When HF-Py was employed for the fluoro-Pummerer rearrangement, **4a** underwent further the oxidative desulfurization–fluorination reaction.[19] For example, upon treatment with HF-Py (5 mol) and DBH (3 mol), **4a** gave tetrafluoro sulfide **9a** in place of **8a**.

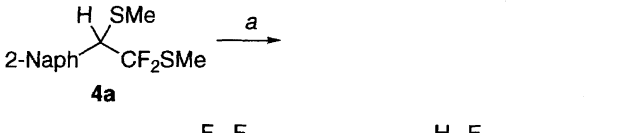


(4)

4a **9a**

a: HF-Py (5 mol), DBH (3 mol), CH_2Cl_2, 0 °C, 10 min, 41 %

Replacing DBH by *N*-iodosuccinimide (NIS) resulted in the formation of monofluorination product **10a** in addition to **9a**. These products were easily separated by silica-gel column chromatography.

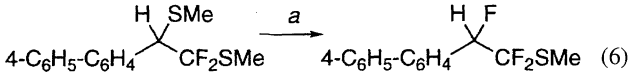


(5)

4a **9a** (20 %) **10a** (33 %)

a: HF-Py (5 mol), NIS (3 mol), CH_2Cl_2, 0 °C, 10 min

Sulfide **4b** was fluorinated with HF-Py (5 mol) and DBH (4 mol) to give **10b**, with the biphenyl moiety remaining unbrominated.

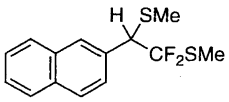
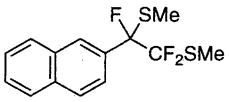
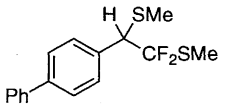
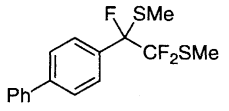
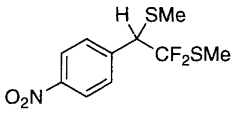
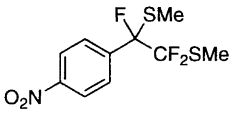
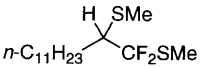
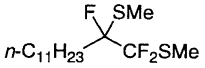
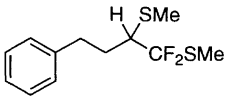
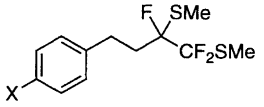


(6)

4b **10b**

a: HF-Py (5 mol), DBH (4 mol), CH_2Cl_2, 0 °C, 10 min, 38 %

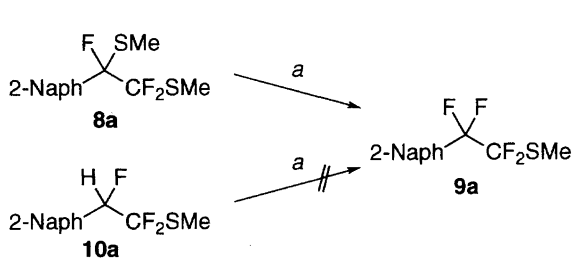
Table 4. Fluoro-Pummerer Rearrangement of Difluoro Sulfide **4**[a)]

Run	Sulfide		Reagent (mol) /Conditions	Product		Yield[b)] %
1		**4a**	*n*-$Bu_4NH_2F_3$ (3.5) DBH (2.5) r.t., 20 min		**8a**	68
2		**4b**			**8b**	58
3		**4c**			**8c**	83
4	**4c**		HF-Py (5.0) NIS (3.0) 0 °C, 10 min	**8c**		77
5		**4e**	*n*-$Bu_4NH_2F_3$ (3.5) DBH (2.5) r.t., 20 min		**8e**	80
6	**4e**		HF-Py (5.0) NIS (3.0) 0 °C, 10 min	**8e**		62
7		**4f**	*n*-$Bu_4NH_2F_3$ (3.5) DBH (2.5) r.t., 20 min		**8f** (X=H)	84
8	**4f**		HF-Py (5.0) NBS (3.0) 0 °C, 10 min	**8f** (X=H) **8f'** (X=Br)		27 13

a) Substrate **4** was allowed to react with *n*-$Bu_4NH_2F_3$ or HF-Py and DBH in CH_2Cl_2. b) Isolated yield.

Fluorination leading to tetrafluoro sulfide **9a** was alternatively achieved by treatment of **8a** with HF-Py (5 mol) and DBH (3 mol), whereas oxidative desulfurization–fluorination product **10a** did not afford **9a** under the same conditions (Scheme 3). Thus, we may conclude that the transformation of **4a** to **9a** proceeded through **8a**.

Conclusion. We have demonstrated here that the fluoro-Pummerer rearrangement of sulfides is readily carried out using *n*-$Bu_4NH_2F_3$ and a positive halogen oxidant to afford α-fluoro sulfides in moderate-to-good yields. On the other hand, 2-substituted 1,1-difluoro-1,2-bis(methylthio)ethanes (**4**) are readily prepared from 1-substituted 2,2,2-tris(methylthio)ethanols (**3**) via oxidative desulfurization–fluorination. The fluoro-Pummerer rearrangement, coupled with oxidative desulfurization–fluorination reaction, allows us to selectively introduce two, three, or four fluorine atoms into an organosulfur compound, depending on the employed fluorinating agent and the structure of the substrates.



a: HF-Py (5 mol), DBH (3 mol), CH_2Cl_2, 0 °C, 10 min, 21 %

Scheme 3.

Experimental

Melting points were measured with a Yanagimoto micro melting point apparatus. All temperatures are uncorrected. IR spectra were recorded on a Shimadzu FT-IR-8000A spectrometer or a Perkin–Elmer 1600 Series FT·IR spectrometer. ^1H or ^{19}F NMR spectra were obtained in $CDCl_3$ on a Bruker AC-200 spectrometer operating at 200 or 188 MHz, with tetramethylsilane or trichloro-

fluoromethane as an internal standard. Mass spectra were recorded with a Shimadzu QP-5000 GC-MS system or a VG Autospec mass spectrometer. Elemental analyses were carried out by Elemental Analysis Center, Tokyo Institute of Technology, using Yanako MT2 CHN Corder. High-resolution mass spectra were obtained with a VG Autospec mass spectrometer.

Wakogel C-200 was used for silica-gel column chromatography and Merck Kieselgel 60 PF_{254} was used for silica-gel preparative thin-layer chromatography (TLC). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck Kieselgel 60 F_{254}. n-$Bu_4NH_2F_3$ was prepared as reported.[20] HF-pyridine was purchased and used without further purification.

A Typical Procedure for the Fluoro-Pummerer Rearrangement of Sulfides 1. Preparation of 4-Chlorophenyl Fluoromethyl Sulfide (2a): To a dichloromethane (2 ml) solution of 4-chlorophenyl methyl sulfide (**1a**) (0.08 ml, 0.62 mmol) and n-$Bu_4NH_2F_3$ (0.26 g, 0.86 mmol) was added DBH (0.25 g, 0.86 mmol) in one portion at room temperature under an argon atmosphere; the resulting mixture was stirred at room temperature for 20 min before dilution with a 10 : 1 mixture (110 ml) of hexane and diethyl ether. The resulting insoluble materials were filtered through a short silica-gel column. The filtrate was washed with an aqueous solution of sodium hydrogencarbonate and sodium hydrogensulfite, and then with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give **2a**[12] (0.10 g, 90% yield). $R_f = 0.41$ (hexane). ^{1}H NMR $\delta = 7.45$—7.26 (m, 4H), 5.69 (d, $J = 52.7$ Hz, 2H); ^{19}F NMR $\delta = -182.77$ (t, $J = 52.7$ Hz, 1F).

Fluoromethyl Phenyl Sulfide (2b):[7a,21] This product (76 mg) was obtained in 52% yield from methyl phenyl sulfide (**1b**) (0.12 ml, 1.0 mmol). $R_f = 0.37$ (hexane). ^{1}H NMR $\delta = 7.52$—7.45 (m, 2H), 7.37—7.24 (m, 3H), 5.70 (d, $J = 52.8$ Hz, 2H); ^{19}F NMR $\delta = -182.19$ (t, $J = 52.8$ Hz, 1F).

Fluoromethyl 4-Methoxyphenyl Sulfide (2c):[7a,8] This compound (0.10 g) was prepared in 59% yield from 4-methoxyphenyl methyl sulfide (**1c**) (0.14 ml, 1.0 mmol). $R_f = 0.38$ (EtOAc–hexane 1 : 10). ^{1}H NMR $\delta = 7.45$ (d, $J = 8.9$ Hz, 2H), 6.87 (d, $J = 8.9$ Hz, 2H), 5.60 (d, $J = 53.0$ Hz, 2H), 3.80 (s, 3H); ^{19}F NMR $\delta = -182.11$ (t, $J = 53.0$ Hz, 1F).

4-Cyanophenyl Fluoromethyl Sulfide (2d): This compound (0.13 g) was prepared in 75% yield from 4-cyanophenyl methyl sulfide (**1d**) (0.15 g, 1.0 mmol). $R_f = 0.43$ (EtOAc–hexane 1 : 6). IR (neat) 3069, 3023, 2949, 2229, 1594, 1488, 1447, 1402, 1325, 1183, 1090, 1018, 966, 824, 736, 546 cm^{-1}; ^{1}H NMR $\delta = 7.64$—7.51 (m, 4H), 5.80 (d, $J = 52.3$ Hz, 2H); ^{19}F NMR $\delta = -184.69$ (t, $J = 52.3$ Hz, 1F); MS m/z (rel intensity) 167 (M^+; 94), 148 (67), 134 (100), 107 (28), 103 (57), 90 (53), 75 (41). Found: m/z 167.0206. Calcd for C_8H_6FNS: M, 167.0205.

Ethyl Fluoro(methylthio)acetate (2e):[9a] This (0.10 g) was prepared in 65% yield from ethyl (methylthio)acetate (**1e**) (0.13 ml, 1.0 mmol). $R_f = 0.34$ (EtOAc–hexane 1 : 10). ^{1}H NMR $\delta = 5.87$ (d, $J = 50.7$ Hz, 1H), 4.38 (q, $J = 7.2$ Hz, 2H), 2.41 (t, $J = 2.4$ Hz, 3H), 1.40 (t, $J = 7.2$ Hz, 3H); ^{19}F NMR $\delta = -167.84$ (dq, $J = 50.7$, 2.4 Hz, 1F); MS m/z (rel intensity) 152 (M^+; 53), 134 (11), 106 (59), 88 (16), 79 (100), 61 (55).

A Typical Procedure for the Preparation of 1,1,1-Tris(methylthio)-2-alkanols.[18] **1,1,1-Tris(methylthio)-2-tridecanol (3e):** To a stirred solution of tris(methylthio)methane (1.4 ml, 10.5 mmol) in tetrahydrofuran (THF, 15 ml) was added dropwise a 1.63 M hexane solution (1 M = 1 mol dm^{-3}) of n-BuLi (6.7 ml, 10.9 mmol) at −78 °C under an argon atmosphere; the mixture was stirred for 2 h to generate $LiC(SMe)_3$. A solution of dodecanal (2.2 ml, 10.0 mmol) in THF (7 ml) was added to the $LiC(SMe)_3$ reagent; the reaction mixture was stirred at −78 °C for 2 h. The Dry Ice cooling bath was removed; the reaction mixture was allowed to warm to room temperature over 1 h, then poured into sat. NH_4Cl aq solution and extracted with diethyl ether (3 times). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give **3e** (3.3 g, 97% yield). $R_f = 0.39$ (EtOAc–hexane 1 : 10). IR (neat) 3250, 2923, 2853, 1559, 1541, 1509, 1458, 1075, 959 cm^{-1}; ^{1}H NMR $\delta = 3.70$ (ddd, $J = 9.4$, 4.1, 2.2 Hz, 1H), 2.75 (dd, $J = 4.1$, 1.2 Hz, 1H), 2.20 (s, 9H), 1.89—1.60 (m, 2H), 1.39—1.21 (m, 18H), 0.88 (t, $J = 6.5$ Hz, 3H); MS m/z (rel intensity) 291 ($M^+ -$SMe; 100), 279 (15), 153 (36), 107 (47), 91 (12), 61 (26). Found: m/z 291.1818. Calcd for $C_{15}H_{31}OS_2$: M−SMe, 291.1816.

2,2,2-Tris(methylthio)-1-(2-naphthyl)ethanol (3a): This compound (3.1 g, 99% yield) was prepared from 2-naphthaldehyde (1.6 g, 10.1 mmol). $R_f = 0.33$ (EtOAc–hexane 1 : 10). IR (neat) 3460, 3054, 2982, 2917, 1434, 1424, 1372, 1360, 1241, 1123, 1048, 859, 810, 747 cm^{-1}; ^{1}H NMR $\delta = 8.00$ (s, 1H), 7.87—7.76 (m, 4H), 7.50—7.43 (m, 2H), 5.00 (d, $J = 2.5$ Hz, 1H), 3.61 (d, $J = 2.5$ Hz, 1H), 2.03 (s, 9H); MS m/z (rel intensity) 263 ($M^+ -$SMe; 5), 230 (6), 215 (12), 187 (21), 153 (100), 127 (32), 107 (25), 91 (18). Found: m/z 263.0563. Calcd for $C_{14}H_{15}OS_2$: M−SMe, 263.0564.

1-(4-Biphenylyl)-2,2,2-tris(methylthio)ethanol (3b): This (0.88 g) was prepared in 86% yield from 4-biphenylcarbaldehyde (0.56 g, 3.1 mmol). $R_f = 0.33$ (EtOAc–hexane 1 : 6), mp 86—88 °C (Et_2O). IR (KBr) 3462, 3030, 2918, 1486, 1411, 1382, 1316, 1232, 1199, 1184, 1060, 1008, 833, 760, 730, 698 cm^{-1}; ^{1}H NMR $\delta = 7.68$—7.55 (m, 6H), 7.47—7.33 (m, 3H), 4.90 (d, $J = 2.6$ Hz, 1H), 3.50 (d, $J = 2.6$ Hz, 1H), 2.07 (s, 9H); MS m/z (rel intensity) 289 ($M^+ -$SMe; 17), 241 (36), 213 (52), 181 (54), 153 (100), 107 (51), 91 (49), 77 (38). Found: m/z 289.0719. Calcd for $C_{16}H_{17}OS_2$: M−SMe, 289.0721.

2,2,2-Tris(methylthio)-1-(4-nitrophenyl)ethanol (3c): This product (1.10 g) was prepared in 54% yield from 4-nitrobenzaldehyde (1.01 g, 6.7 mmol). $R_f = 0.41$ (EtOAc–hexane 1 : 3), mp 46—48 °C (Et_2O). IR (KBr) 3480, 3042, 3018, 1647, 1593, 1520, 1417, 1342, 1172, 1062, 831, 673 cm^{-1}; ^{1}H NMR $\delta = 8.19$ (d, $J = 8.9$ Hz, 2H), 7.78 (d, $J = 8.9$ Hz, 2H), 4.92 (d, $J = 2.1$ Hz, 1H), 3.62 (d, $J = 2.1$ Hz, 1H), 2.09 (s, 9H); MS m/z (rel intensity) 258 ($M^+ -$SMe; 25), 210 (11), 182 (16), 153 (77), 120 (52), 107 (100), 91 (33), 76 (21). Found: m/z 258.0259. Calcd for $C_{10}H_{12}NO_3S_2$: M−SMe, 258.0259.

2,2,2-Tris(methylthio)-1-(2-pyridyl)ethanol (3d): This (0.39 g, 24% yield) was obtained in a similar way from 2-pyridinecarbaldehyde (0.60 ml, 6.3 mmol). $R_f = 0.44$ (EtOAc–hexane 1 : 1), mp 147—149 °C (Et_2O). IR (KBr) 3422, 3140, 2920, 2820, 2359, 1592, 1567, 1440, 1065, 1001, 817, 769, 606 cm^{-1}; ^{1}H NMR $\delta = 8.59$ (dt, $J = 4.9$, 1.4 Hz, 1H), 7.73—7.66 (m, 2H), 7.31—7.24 (m, 1H), 4.97 (d, $J = 6.4$ Hz, 1H), 4.91 (d, $J = 6.4$ Hz, 1H), 2.09 (s, 9H); MS m/z (rel intensity) 214 ($M^+ -$SMe; 64), 166 (18), 153 (100), 138 (21), 109 (92), 107 (93), 91 (60), 78 (58). Found: m/z 214.0359. Calcd for $C_9H_{12}NOS_2$: M−SMe, 214.0360.

1,1,1-Tris(methylthio)-4-phenyl-2-butanol (3f): This product (0.41 g) was prepared in 84% yield from hydrocinnamaldehyde (0.15 ml, 1.7 mmol). $R_f = 0.22$ (Et_2O–hexane 1 : 5). IR (neat) 3484, 3032, 2956, 2918, 2878, 1736, 1496, 1448, 1433, 1403, 1244, 1083, 1049, 735, 700 cm^{-1}; ^{1}H NMR $\delta = 7.33$—7.13 (m, 5H), 3.70 (ddd, $J = 9.9$, 4.4, 2.0 Hz, 1H), 3.06—2.92 (m, 1H), 2.78—2.62 (m, 2H), 2.28—1.95 (m, 2H), 2.14 (s, 3H); MS m/z (rel

intensity) 270 ($M^+ - H_2O$; 4), 241 ($M^+ - SMe$; 94), 179 (7), 153 (65), 145 (93), 117 (82), 107 (100), 91 (90), 77 (49). Found: *m/z* 241.0720. Calcd for $C_{12}H_{17}OS_2$: M−SMe, 241.0721.

***trans*-1,1,1-Tris(methylthio)-4-phenyl-3-buten-2-ol (3g):** This compound (0.84 g) was isolated in 92% yield from *trans*-cinnamaldehyde (0.40 ml, 3.2 mmol). $R_f = 0.29$ (EtOAc–hexane 1 : 6). IR (neat) 3466, 3025, 2983, 2917, 1495, 1434, 1417, 1242, 1112, 1072, 1043, 966, 743, 693 cm^{-1}; ^1H NMR $\delta = 7.44$—7.19 (m, 5H), 6.77 (d, $J = 16.0$ Hz, 1H), 6.49 (dd, $J = 16.0$, 5.8 Hz, 1H), 4.43 (dd, $J = 5.8$, 5.0 Hz, 1H), 3.11 (d, $J = 5.0$ Hz, 1H), 2.21 (s, 9H); MS *m/z* (rel intensity) 239 ($M^+ - SMe$; 5), 191 (20), 153 (100), 115 (72), 91 (50), 77 (22). Found: C, 54.62; H, 6.48%. Calcd for $C_{13}H_{18}OS_3$: C, 54.51; H, 6.33%.

2-Methyl-1,1,1-tris(methylthio)-4-phenyl-2-butanol (6h): This (0.66 g) was prepared in 72% yield from 4-phenyl-2-butanone (0.45 ml, 3.0 mmol). $R_f = 0.48$ (Et_2O–benzene 1 : 10). IR (neat) 3482, 3018, 2984, 2917, 1495, 1451, 1432, 1410, 1368, 1112, 960, 737, 693 cm^{-1}; ^1H NMR $\delta = 7.32$—7.13 (m, 5H), 2.93—2.62 (m, 2H), 2.42—2.11 (m, 2H), 2.27 (s, 9H), 1.55 (d, $J = 0.5$ Hz, 3H); MS *m/z* (rel intensity) 255 ($M^+ - SMe$; 26), 159 (15), 153 (18), 107 (48), 105 (47), 91 (100). Found: *m/z* 255.0876. Calcd for $C_{13}H_{19}OS_2$: M−SMe, 255.0877.

1-Tris(methylthio)methyl-4-phenylcyclohexanol (6i): This product (0.52 g) was prepared in 52% yield from 4-phenylcyclohexanone (0.53 g, 3.0 mmol). $R_f = 0.40$ (EtOAc–hexane 1 : 10). IR (neat) 3501, 3025, 2920, 2859, 1494, 1452, 1435, 1368, 1311, 1215, 1131, 966, 754, 700 cm^{-1}; ^1H NMR $\delta = 7.30$—7.17 (m, 5H), 2.60—2.38 (m, 1H), 2.31 (s, 9H), 2.12—1.79 (m, 8H); MS *m/z* (rel intensity) 281 ($M^+ - SMe$; 54), 233 (24), 185 (25), 157 (29), 107 (100), 91 (57). Anal. Found: C, 58.41; H, 7.60%. Calcd for $C_{16}H_{24}OS_3$: C, 58.49; H, 7.36%. Found: *m/z* 281.1035. Calcd for $C_{15}H_{21}OS_2$: M−SMe, 281.1034.

A Typical Procedure for the Oxidative Desulfurization-Fluorination of 3. Preparation of 1,1-Difluoro-1,2-bis(methylthio)tridecane (4e): To a dichloromethane (1.5 ml) solution of Et_2NSF_3 (0.12 ml, 0.89 mmol) was added dropwise a dichloromethane (1.5 ml) solution of **3e** (0.29 g, 0.84 mmol) at 0 °C under an argon atmosphere; the reaction mixture was stirred at 0 °C for 10 min, poured into sat. $NaHCO_3$ aq solution, and then extracted with diethyl ether (3 times). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give **4e** (0.19 g, 71% yield). $R_f = 0.45$ (CH_2Cl_2–hexane 1 : 5). IR (neat) 2926, 2855, 1559, 1541, 1509, 1489, 1458, 1368, 1183, 1104, 1018, 976, 731 cm^{-1}; ^1H NMR $\delta = 3.02$—2.83 (m, 1H), 2.30 (t, $J = 0.7$ Hz, 3H), 2.17 (t, $J = 1.2$ Hz, 3H), 1.87—1.52 (m, 2H), 1.40—1.18 (m, 18H), 0.88 (t, $J = 6.5$ Hz, 3H); ^{19}F NMR $\delta = -75.49$ (dd, $J = 203.9$, 10.7 Hz, 1F), −77.04 (dd, $J = 203.9$, 11.3 Hz, 1F); MS *m/z* (rel intensity) 312 (M^+; 27); 292 (31), 265 (14), 215 (100), 199 (35), 167 (56). Found: C, 57.49; H, 9.79%. Calcd for $C_{15}H_{30}F_2S_2$: C, 57.65; H, 9.68%.

2,2-Difluoro-1,2-bis(methylthio)-1-(2-naphthyl)ethane (4a): This (61 mg) was prepared in 50% yield from **3a** (0.13 g, 0.43 mmol). $R_f = 0.45$ (Et_2O–hexane 1 : 20), mp 45—47 °C (hexane). IR (KBr) 3038, 2902, 1142, 1044, 1019, 978, 964, 893, 809, 785, 742 cm^{-1}; ^1H NMR $\delta = 7.84$—7.80 (m, 4H), 7.59 (d, $J = 8.6$ Hz, 1H), 7.51—7.42 (m, 2H), 4.42 (dd, $J = 13.1$, 10.4 Hz, 1H), 2.25 (s, 3H), 2.09 (s, 3H); ^{19}F NMR $\delta = -75.99$ (dd, $J = 203.6$, 10.4 Hz, 1F), −76.65 (dd, $J = 203.6$, 13.1 Hz, 1F); MS *m/z* (rel intensity) 284 (M^+; 48), 264 (44), 202 (64), 190 (96), 187 (100), 171 (46), 139 (24). Found: *m/z* 284.0506. Calcd for $C_{14}H_{14}F_2S_2$: M, 284.0505.

1-(4-Biphenylyl)-2,2-difluoro-1,2-bis(methylthio)ethane (4b): This product (54 mg) was prepared in 55% yield from **3b** (0.11 g, 0.31 mmol). $R_f = 0.33$ (Et_2O–hexane 1 : 20), mp 92—94 °C (hexane). IR (KBr) 2947, 2922, 1982, 1429, 1143, 1050, 989, 961, 883, 867, 708, 695, 582 cm^{-1}; ^1H NMR $\delta = 7.65$—7.29 (m, 9H), 4.30 (dd, $J = 12.9$, 10.4 Hz, 1H), 2.28 (s, 3H), 2.15 (t, $J = 0.7$ Hz, 3H); ^{19}F NMR $\delta = -76.16$ (dd, $J = 203.6$, 10.4 Hz, 1F), −76.72 (dd, $J = 203.6$, 12.9 Hz, 1F); MS *m/z* (rel intensity) 310 (M^+; 25), 290 (18), 263 (27), 216 (78), 213 (100), 197 (28), 165 (19). Found: *m/z* 310.0622. Calcd for $C_{16}H_{16}F_2S_2$: M, 310.0622.

2,2-Difluoro-1,2-bis(methylthio)-1-(4-nitrophenyl)ethane (4c): This compound (0.30 g) was prepared in 56% yield from **3c** (0.59 g, 1.9 mmol) along with **5c** (0.11 g, 20% yield). $R_f = 0.39$ (EtOAc–hexane 1 : 6). IR (neat) 3183, 3167, 3022, 1624, 1581, 1523, 1349, 1331, 1186, 1023, 968, 840, 786 cm^{-1}; ^1H NMR $\delta = 8.22$ (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 8.8$ Hz, 2H), 4.36 (dd, $J = 11.6$, 11.1 Hz, 1H), 2.29 (s, 3H), 2.14 (s, 3H); ^{19}F NMR $\delta = -76.07$ (dd, $J = 205.6$, 11.6 Hz, 1F), −76.36 (dd, $J = 205.6$, 11.1 Hz, 1F); MS *m/z* (rel intensity) 279 (M^+; 47), 232 (4), 200 (11), 182 (100), 166 (24), 150 (11), 136 (39). Found: *m/z* 279.0200. Calcd for $C_{10}H_{11}F_2NO_2S_2$: M, 279.0199.

1,2,2-Tris(methylthio)-1-(4-nitrophenyl)ethene (5c): $R_f = 0.51$ (EtOAc–hexane 1 : 6), mp 98—100 °C (hexane). IR (KBr) 3084, 2925, 2894, 1602, 1528, 1408, 1348, 1320, 1110, 852, 842, 738 cm^{-1}; ^1H NMR $\delta = 8.25$ (d, $J = 8.9$ Hz, 2H), 7.41 (d, $J = 8.9$ Hz, 2H), 2.47 (s, 3H), 2.16 (s, 3H), 1.88 (s, 3H); MS *m/z* (rel intensity) 287 (M^+; 100), 257 (33), 225 (47), 195 (34), 163 (20), 148 (22), 120 (20). Found: *m/z* 287.0107. Calcd for $C_{11}H_{13}NO_2S_3$: M, 287.0108.

2,2-Difluoro-1,2-bis(methylthio)-1-(2-pyridyl)ethane (4d): This product (11 mg) was obtained in 15% yield from **3d** (81 mg, 0.31 mmol) along with **5d** (42 mg, 55% yield). $R_f = 0.62$ (EtOAc–hexane 1 : 2). IR (neat) 3082, 3054, 3017, 2998, 1585, 1511, 1498, 1420, 1245, 1183, 1030, 998, 729 cm^{-1}; ^1H NMR $\delta = 8.59$—8.56 (m, 1H), 7.72—7.67 (m, 1H), 7.57—7.53 (m, 1H), 7.28—7.22 (m, 1H), 4.48 (dd, $J = 13.0$, 10.7 Hz, 1H), 2.29 (s, 3H), 2.19 (s, 3H); ^{19}F NMR $\delta = -76.21$ (dd, $J = 205.9$, 10.7 Hz, 1F), −76.97 (dd, $J = 205.9$, 13.0 Hz, 1F); MS *m/z* (rel intensity) 235 (M^+; 2), 215 (45), 200 (30), 189 (48), 180 (26), 142 (100), 136 (35), 122 (33), 78 (34). Found: *m/z* 235.0300. Calcd for $C_9H_{11}F_2NS_2$: M, 235.0301.

1,2,2-Tris(methylthio)-1-(2-pyridyl)ethene (5d): $R_f = 0.50$ (EtOAc–hexane 1 : 2). IR (neat) 3036, 2988, 2919, 2843, 1582, 1563, 1531, 1460, 1425, 1311, 1152, 990, 963, 861, 753 cm^{-1}; ^1H NMR $\delta = 8.68$—8.64 (m, 1H), 7.77—7.69 (m, 1H), 7.32—7.20 (m, 2H), 2.45 (s, 3H), 2.16 (s, 3H), 1.88 (s, 3H); MS *m/z* (rel intensity) 243 (M^+; 56), 228 (100), 196 (38), 180 (25), 150 (56), 135 (77), 122 (31), 117 (23), 78 (29). Found: *m/z* 243.0211. Calcd for $C_{10}H_{13}NS_3$: M, 243.0210.

1,1-Difluoro-1,2-bis(methylthio)-4-phenylbutane (4f): This compound (0.52 g) was isolated in 70% yield from **3f** (0.82 g, 2.9 mmol). $R_f = 0.43$ (Et_2O–hexane 1 : 20). IR (neat) 3027, 2924, 2886, 1603, 1496, 1454, 1444, 1322, 1286, 1141, 1102, 1042, 970, 751, 700 cm^{-1}; ^1H NMR $\delta = 7.37$—7.16 (m, 5H), 3.06—2.66 (m, 3H), 2.34—2.16 (m, 1H), 2.27 (t, $J = 0.8$ Hz, 3H), 2.19 (t, $J = 1.2$ Hz, 3H), 1.92—1.73 (m, 1H); ^{19}F NMR $\delta = -75.78$ (dd, $J = 204.5$, 10.7 Hz, 1F), −77.10 (dd, $J = 204.5$, 11.2 Hz, 1F); MS *m/z* (rel intensity) 262 (M^+; 32), 242 (15), 165 (4), 151 (29), 117 (80), 91 (100). Found: *m/z* 262.0662. Calcd for $C_{12}H_{16}F_2S_2$: M, 262.0662.

***trans*-4,4-Difluoro-3,4-bis(methylthio)-1-phenyl-1-butene (4g):** This (43 mg) was isolated in 13% yield from **3g** (0.36 g, 1.3 mmol) along with **5g** (0.16 g, 48% yield). $R_f = 0.29$ (CH_2Cl_2–hexane 1 : 3). IR (neat) 3122, 3022, 3005, 2918, 1596,

1467, 1418, 1311, 1262, 964, 902, 756, 692, 522 cm^{-1}; ^1H NMR δ = 7.41—7.28 (m, 5H), 6.59 (d, J = 15.7 Hz, 1H), 6.13 (dd, J = 15.7, 9.7 Hz, 1H), 3.83 (dt, J = 9.7, 10.5 Hz, 1H), 2.32 (t, J = 0.7 Hz, 3H), 2.18 (t, J = 0.9 Hz, 3H); ^{19}F NMR δ = −77.50 (d, J = 10.5 Hz, 2F); MS m/z (rel intensity) 260 (M^+; 9), 213 (11), 165 (89), 163 (68), 146 (33), 115 (100). Found: m/z 260.0503. Calcd for $C_{12}H_{14}F_2S_2$: M, 260.0505.

***trans*-1,1,2-Tris(methylthio)-4-phenyl-1,3-butadiene (5g):** R_f = 0.35 (CH_2Cl_2–hexane 1 : 3). IR (neat) 3050, 2977, 2918, 2848, 1590, 1462, 1440, 1423, 1308, 1146, 1023, 958, 897, 722 cm^{-1}; ^1H NMR δ = 7.64 (d, J = 15.6 Hz, 1H), 7.58—7.19 (m, 5H), 7.13 (d, J = 15.6 Hz, 1H), 2.47 (s, 3H), 2.32 (s, 3H), 2.29 (s, 3H); MS m/z (rel intensity) 268 (M^+; 32), 253 (39), 206 (100), 159 (19), 115 (57). Found: m/z 268.0413. Calcd for $C_{13}H_{16}S_3$: M, 268.0414.

***S*-Methyl 4-Phenyl-1-cyclohexene-1-carbothioate (7i):** This product (0.10 mg) was isolated in 92% yield from **6i** (0.16 g, 0.47 mmol). R_f = 0.27 (EtOAc–hexane 1 : 3). Mp 70—72 °C (Et_2O). IR (KBr) 3050, 3017, 2928, 1638, 1492, 1383, 1212, 1167, 950, 832, 742, 691 cm^{-1}; ^1H NMR δ = 7.35—7.17 (m, 5H), 7.05—7.03 (m, 1H), 2.90—2.73 (m, 1H), 2.68—2.21 (m, 4H), 2.33 (s, 3H), 2.16—1.94 (m, 1H), 1.89—1.62 (m, 1H); MS m/z (rel intensity) 232 (M^+; 4), 185 (100), 129 (10), 115 (10), 104 (12), 91 (16), 81 (59). Found: m/z 232.0923. Calcd for $C_{14}H_{16}OS$: M, 232.0922.

A Typical Procedure for the Fluoro-Pummerer Rearrangement of 4. 1,2,2-Trifluoro-1,2-bis(methylthio)-1-(2-naphthyl)ethane (8a): To a dichloromethane (2 ml) solution of **4a** (71 mg, 0.25 mmol) and n-$Bu_4NH_2F_3$ (0.26 g, 0.87 mmol) was added DBH (0.18 g, 0.62 mmol) in one portion at room temperature under an argon atmosphere; the resulting mixture was stirred at room temperature for 20 min before dilution with a 10 : 1 mixture (110 ml) of hexane and diethyl ether. The resulting insoluble materials were filtered through a short silica-gel column; the filtrate was washed with an aqueous solution of sodium hydrogencarbonate and sodium hydrogensulfite, and then with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give **8a** (51 mg, 68% yield). R_f = 0.46 (EtOAc–hexane 1 : 10). IR (neat) 3026, 2989, 1563, 1506, 1434, 1412, 1405, 1381, 1122, 1108, 1020, 973, 764, 758 cm^{-1}; ^1H NMR δ = 8.13 (d, J = 1.0 Hz, 1H), 7.93—7.83 (m, 3H), 7.73—7.68 (m, 1H), 7.58—7.48 (m, 2H), 2.26 (dt, J = 0.9, 0.9 Hz, 3H), 2.01 (dt, J = 1.7, 0.9 Hz, 3H); ^{19}F NMR δ = −82.64 (dd, J = 212.9, 19.0 Hz, 1F), −83.91 (dd, J = 212.9, 19.5 Hz, 1F), −141.41 (dd, J = 19.5, 19.0 Hz, 1F); MS m/z (rel intensity) 302 (M^+; 11), 255 (22), 208 (39), 205 (100), 177 (23), 157 (11). Found: m/z 302.0410. Calcd for $C_{14}H_{13}F_3S_2$: M, 302.0411.

1-(4-Biphenylyl)-1,2,2-trifluoro-1,2-bis(methylthio)ethane (8b): This (79 mg) was prepared in 58% yield from **4b** (0.13 g, 0.42 mmol). R_f = 0.34 (CH_2Cl_2–hexane 1 : 5), mp 52—54 °C (hexane). IR (KBr) 2922, 2859, 1709, 1604, 1488, 1433, 1062, 1051, 1032, 1115, 924, 817, 759, 742, 690 cm^{-1}; ^1H NMR δ = 7.81—7.58 (m, 6H), 7.54—7.36 (m, 3H), 2.29 (dt, J = 1.0, 0.9 Hz, 3H), 2.06 (dt, J = 1.7, 1.1 Hz, 3H); ^{19}F NMR δ = −83.06 (dd, J = 212.6, 19.4 Hz, 1F), −84.01 (dd, J = 212.6, 19.5 Hz, 1F), −141.98 (dd, J = 19.5, 19.4 Hz, 1F); MS m/z (rel intensity) 328 (M^+; 16), 290 (7), 281 (42), 231 (100), 203 (26), 181 (21), 152 (10). Found: m/z 328.0567. Calcd for $C_{16}H_{15}F_3S_2$: M, 328.0567.

1,2,2-Trifluoro-1,2-bis(methylthio)-1-(4-nitrophenyl)ethane (8c): In a similar way, **8c** (0.27 g) was prepared in 83% yield from **4c** (0.31 g, 1.1 mmol). R_f = 0.35 (EtOAc–hexane 1 : 10). IR (neat) 3112, 2957, 2846, 1608, 1527, 1351, 1158, 1054, 1018, 929, 851, 815, 742 cm^{-1}; ^1H NMR δ = 8.28 (d, J = 9.1 Hz, 2H), 7.84 (d, J = 9.1 Hz, 2H), 2.31 (dt, J = 1.0, 1.0 Hz, 3H), 2.04 (dt, J = 1.7, 1.0 Hz, 3H); ^{19}F NMR δ = −82.56 (dd, J = 214.5, 18.9 Hz, 1F), −83.61 (ddt, J = 214.5, 19.0, 1.0 Hz, 1F), −142.15 (dd, J = 19.0, 18.9 Hz, 1F); MS m/z (rel intensity) 297 (M^+; 50), 250 (14), 200 (100), 184 (29), 154 (43), 139 (19), 97 (20). Found: m/z 297.0106. Calcd for $C_{10}H_{10}F_3NO_2S_2$: M, 297.0105.

1,1,2-Trifluoro-1,2-bis(methylthio)tridecane (8e): This compound (0.16 g) was obtained in 80% yield from **4e** (0.19 g, 0.61 mmol). R_f = 0.57 (CH_2Cl_2–hexane 1 : 8). IR (neat) 2953, 2926, 2854, 1738, 1467, 1433, 1152, 1032, 1018, 963, 876 cm^{-1}; ^1H NMR δ = 2.33 (dt, J = 1.0, 1.0 Hz, 3H), 2.25 (dt, J = 1.9, 1.9 Hz, 3H), 1.64—1.52 (m, 2H), 1.38—1.22 (m, 18H), 0.88 (t, J = 6.5 Hz, 3H); ^{19}F NMR δ = −83.81 (d, J = 17.7 Hz, 2F), −151.23 (ddt, J = 27.1, 10.1, 17.7 Hz, 1F); MS m/z (rel intensity) 330 (M^+; 10), 290 (8), 262 (13), 233 (100), 183 (50), 109 (19), 95 (32). Found: m/z 330.1663. Calcd for $C_{15}H_{29}F_3S_2$: M, 330.1663.

1,1,2-Trifluoro-1,2-bis(methylthio)-4-phenylbutane (8f): This (0.13 g) was isolated in 84% yield from **4f** (0.14 g, 0.54 mmol). R_f = 0.38 (Et_2O–hexane 1 : 20). IR (neat) 3047, 3028, 2936, 1497, 1455, 1166, 1086, 1041, 999, 902, 870, 752, 700 cm^{-1}; ^1H NMR δ = 7.33—7.15 (m, 5H), 3.06—2.78 (m, 2H), 2.58—2.07 (m, 2H), 2.32 (dt, J = 1.0, 1.0 Hz, 3H), 2.30 (dt, J = 1.9, 1.9 Hz, 3H); ^{19}F NMR δ = −83.72 (d, J = 17.7 Hz, 2F), −152.00 (ddt, J = 26.6, 9.6, 17.7 Hz, 1F); MS m/z (rel intensity) 280 (M^+; 96), 183 (79), 165 (58), 137 (92), 135 (100), 97 (41), 91 (76), 65 (68). Found: m/z 280.0568. Calcd for $C_{12}H_{15}F_3S_2$: M, 280.0567.

Alternative Synthesis of 8c Using HF-Py. To a dichloromethane (2 ml) solution of NIS (0.87 g, 3.0 mmol) and HF-Py (70/30 wt%, 0.13 ml, F^-: 5.1 mmol) was added dropwise a dichloromethane (2 ml) solution of **4c** (0.28 g, 1.01 mmol) at 0 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C for 10 min, poured into an aqueous solution of sodium hydrogencarbonate and sodium hydrogensulfite, and extracted with diethyl ether (3 times). The combined extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give **8c** (0.23 g, 77% yield).

1,1,2-Trifluoro-1,2-bis(methylthio)tridecane (8e): Using HF/Py, **8e** (61 mg) was obtained in 62% yield from **4e** (93 mg, 0.30 mmol).

1,1,2-Trifluoro-1,2-bis(methylthio)-4-phenylbutane (8f): Similarly, **8f** (92 mg) was isolated in 27% yield from **4f** (0.20 g, 0.75 mmol) along with **8f′** (29 mg, 13% yield).

4-(4-Bromophenyl)-1,1,2-trifluoro-1,2-bis(methylthio)butane (8f′): R_f = 0.39 (CH_2Cl_2–hexane 1 : 5). IR (neat) 3022, 2919, 2869, 1669, 1501, 1463, 1096, 1053, 975, 801, 738, 700 cm^{-1}; ^1H NMR δ = 7.40 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 3.18—2.73 (m, 2H), 2.60—1.99 (m, 2H), 2.33 (dt, J = 1.0, 1.0 Hz, 3H), 2.30 (dt, J = 1.9, 1.9 Hz, 3H); ^{19}F NMR δ = −83.74 (d, J = 17.6 Hz, 2F), −152.24 (ddt, J = 26.7, 9.5, 17.6 Hz, 1F); MS m/z (rel intensity) 358 (M^++2; 1), 356 (M^+; 1), 310 (13), 308 (13), 240 (39), 211 (100), 190 (84), 163 (77), 147 (70), 115 (87), 91 (93). Found: m/z 357.9669. Calcd for $C_{12}H_{14}BrF_3S_2$: M, 357.9672.

1,1,2,2-Tetrafluoro-1-methylthio-2-(2-naphthyl)ethane (9a): To a dichloromethane (1 ml) solution of DBH (0.36 g, 1.3 mmol) and HF-Py (70/30 wt%, 0.052 ml, F^-: 2.1 mmol) was added dropwise a dichloromethane (1 ml) solution of **4a** (0.12 g, 0.42 mmol) at 0 °C under an argon atmosphere; the reaction mixture was stirred at 0 °C for 10 min, poured into an aqueous solution of sodium hydrogencarbonate and sodium hydrogensulfite, and extracted with diethyl ether (3 times). The combined extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC to give **9a** (47 mg, 41%

yield). R_f = 0.53 (CH_2Cl_2–hexane 1 : 5). IR (neat) 3064, 3008, 1510, 1439, 1361, 1288, 1225, 1138, 1082, 1032, 952, 920, 861, 816, 797, 747 cm^{-1}; ^1H NMR δ = 8.12 (s, 1H), 7.93—7.80 (m, 3H), 7.65—7.45 (m, 3H), 2.31 (t, J = 0.7 Hz, 3H); ^{19}F NMR δ = −92.11 (t, J = 6.7 Hz, 2F), −109.34 (t, J = 6.7 Hz, 2F); MS *m/z* (rel intensity) 274 (M^+; 46), 177 (100), 157 (6), 127 (14), 97 (5). Found: *m/z* 274.0440. Calcd for $C_{13}H_{10}F_4S$: M, 274.0439.

1,1,2-Trifluoro-1-methylthio-2-(2-naphthyl)ethane (10a): To a dichloromethane (1 ml) solution of NIS (0.30 g, 1.4 mmol) and HF-Py (70/30 wt%, 0.056 ml, F^-: 2.3 mmol) was added dropwise a dichloromethane (1 ml) solution of **4a** (0.13 g, 0.45 mmol) at 0 °C under an argon atmosphere; the reaction mixture was stirred at 0 °C for 10 min. Workup and purification by preparative TLC gave **10a** (38 mg, 33% yield) along with **9a** (25 mg, 20% yield). R_f = 0.38 (CH_2Cl_2–hexane 1 : 5), mp 27—29 °C (Et_2O). IR (KBr) 3048, 2946, 1335, 1165, 1121, 1068, 1041, 998, 973, 826, 802, 794, 753, 668 cm^{-1}; ^1H NMR δ = 7.94—7.79 (m, 4H), 7.57—7.43 (m, 3H), 5.74 (ddd, J = 44.8, 8.9, 8.9 Hz, 1H), 2.24 (t, J = 0.9 Hz, 3H); ^{19}F NMR δ = −87.91 (ddd, J = 216.9, 18.6, 8.9 Hz, 1F), −88.04 (ddd, J = 216.9, 18.6, 8.9 Hz, 1F), −186.88 (ddd, J = 44.8, 18.6, 18.6 Hz, 1F); MS *m/z* (rel intensity) 256 (M^+; 53), 159 (100), 139 (9), 133 (13), 97 (6). Found: *m/z* 256.0535. Calcd for $C_{13}H_{11}F_3S$: M, 256.0534.

2-(4-Biphenylyl)-1,1,2-trifluoro-1-methylthioethane (10b): To a dichloromethane (0.5 ml) solution of DBH (74 mg, 0.26 mmol) and HF-Py (70/30 wt%, 0.008 ml, F^-: 0.32 mmol) was added dropwise a dichloromethane (0.5 ml) solution of **4b** (20 mg, 0.064 mmol) at 0 °C under an argon atmosphere; the reaction mixture was stirred at 0 °C for 10 min. Workup and purification by preparative TLC gave **4b** (7 mg, 38% yield). R_f = 0.44 (Et_2O–hexane 1 : 20), mp 75—77 °C (Et_2O). IR (KBr) 3018, 2924, 1483, 1410, 1172, 1059, 984, 967, 761, 747, 735, 690 cm^{-1}; ^1H NMR δ = 7.77 (s, 1H), 7.61—7.43 (m, 4H), 7.36—7.22 (m, 4H), 5.59 (ddd, J = 44.2, 8.6, 8.1 Hz, 1H), 2.33 (dd, J = 0.8, 0.8 Hz, 3H); ^{19}F NMR δ = −87.47 (ddd, J = 218.2, 19.1, 8.1 Hz, 1F), −88.68 (ddd, J = 218.2, 18.6, 8.6 Hz, 1F), −188.14 (ddd, J = 44.2, 19.1, 18.6 Hz, 1F); MS *m/z* (rel intensity) 282 (M^+; 39), 263 (8), 216 (13), 185 (100), 165 (9), 97 (4). Found: *m/z* 282.0689. Calcd for $C_{15}H_{13}F_3S$: M, 282.0690.

This work was financially supported by Grant-in-Aids for Scientific Research (A) No. 07405042 and for Scientific Research on Priority Area No. 284-09239102 both from the Ministry of Education, Science, Sports and Culture and by a Grant-in Aid for Research for the Future (JSPS-RFTF 96R11601) from the Japan Society for the Promotion of Science.

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