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Fluorination of Orthothioesters through Oxidative Desulfurization–Fluorination

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The oxidative desulfurization-fluorination of orthothioesters of type $RCH_2C(SMe)_3$ using *n*-$Bu_4NH_2F_3$ and 1,3-dibromo-5,5-dimethylhydantoin gave bromodifluorination products $RCHBrCF_2SMe$ in good yields. The products were converted into bromodifluoro olefins $RCBr{=}CF_2$ via oxidation and thermolysis. In a similar way, the orthothioesters of type $RCH(OH)C(SMe)_3$ or $RCH(OAc)C(SMe)_3$ were fluorinated to afford difluoro ketones $RCOCF_2SMe$ or difluoro acetates $RCH(OAc)CF_2SMe$, respectively. The difluoro acetates were reduced to $RCH(OAc)CF_2H$ by radical reduction. The mechanisms are discussed for difluorination accompanied by bromination or oxidation.

Organofluorine compounds often exhibit unique biological activities.[1] For example, difluoromethylene compounds have been widely seen in various areas of bioorganic and medicinal chemistry.[2] In particular, difluoro alcohols of type $R^1CF_2CH(OH)R^2$ or difluoro ketones of type $R^3CF_2COR^4$ are remarkable. An example is 24,24-difluoro-25-hydroxyvitamin D_3, which is shown to be five-to-ten times more active than the natural type.[3] A fluorine atom is introduced to the ribose moiety of nucleosides to stabilize the glycosyl bond, and thus the nucleosides exhibit superior antitumor activity.[4] Artificial peptide derivatives having a $-CF_2CO-$ group have attracted attention as HIV-1 protease inhibitors.[5] Peptides that contain a difluorostatine or difluorostatone residue have been shown to be potent inhibitors of an aspartyl protease renin. Fluoro ketones are readily hydrated to form tetrahedral intermediates that mimic the transition states of the enzyme-catalyzed hydrolysis of peptidic bonds.[6] Anthracycline derivatives having a $-CF_2CO-$ group exhibit potent in vitro cytotoxicity and in vivo antitumor activity against P388 murine leukemia.[7] Prostaglandin derivatives with a $-CF_2CO-$ group show selective antitumor activity.[8] In addition, oxacephem derivatives having a $-CF_2S-$ side chain have potent antibacterial activity against both Gram-positive and Gram-negative bacteria.[9] Furthermore, fluoro olefins[10] are finding unique applications as peptide isosteres,[11] like enzyme inhibitors,[12] as well as materials, like liquid crystals.[13]

As we disclosed recently,[14] the oxidative desulfurization-fluorination reaction converts C–S bond(s) of dithioesters or dithio acetals into C–F bond(s), and thus provides us with a convenient synthetic entry to organofluorine compounds. Being inspired by the paper by McCarthy,[15] who reported on the trifluorination of aromatic orthothioesters, we became interested in the use of orthothioesters as substrates, because various types of orthothioesters are readily available. So far we have shown that $RCH(OH)C(SMe)_3$ and $RCH_2C(SMe)_3$ are fluorinated to $RCOCF_2SMe$[16] and $RCHBrCF_2SMe$, respectively, and that the bromodifluorination products are readily converted into $R(Br)C{=}CF_2$.[17] Herein, we describe a whole view of these transformations.

Results and Discussion

Fluorination of 2-Substituted 1,1,1-Tris(methylthio)-ethanes. Substrates **1** of type $RCH_2C(SMe)_3$ were prepared by the alkylation of $LiC(SMe)_3$ with various alkyl halides RCH_2Y in good yields.[18] When we treated **1** with tetrabutylammonium dihydrogentrifluoride (*n*-$Bu_4NH_2F_3$)[19] and 1,3-dibromo-5,5-dimethylhydantoin (DBH), difluorination took place smoothly along with bromination or dibromination, and we obtained **2** (R = alkyl) or **3** (R = aryl), depending on the kind of R (Scheme 1). Trifluorination did not take place even after prolonged reaction times. Instead of DBH, *N*-bromosuccinimide (NBS) or *N*-iodosuccinimide (NIS) could be employed for the fluorination, but complex mixtures of products often resulted. The use of $(HF)_9$-Py in lieu of *n*-$Bu_4NH_2F_3$ produced intractable products, even at −78 °C.

With **1a** as a substrate, we optimized the reaction time and amounts of the two reagents, as summarized in Table 1. The best chemical yield of bromodifluorination product **2a** was attained, when the reaction was carried out with 3 molar amounts of each reagent, and the reaction was quenched after 20 min (Run 1). A longer reaction time or the use of a more or less amount of the reagents resulted in lower yields. The optimized conditions were applied to various types of **1**; the results are summarized in Table 2. As cab be readily seen,

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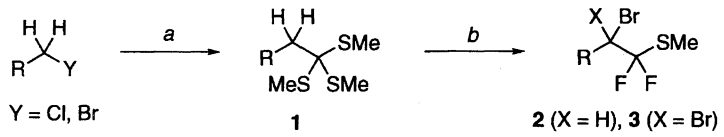
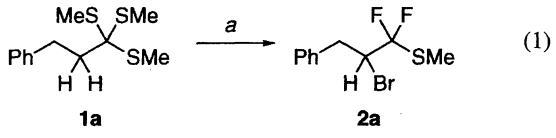


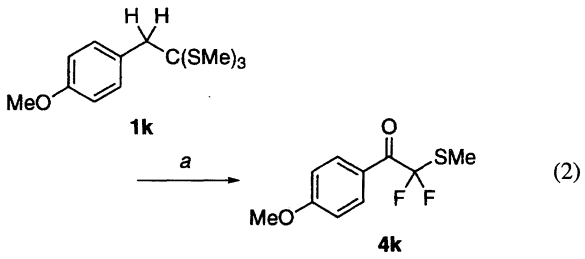
a: $LiC(SMe)_3$
b: n-$Bu_4NH_2F_3$ (3 mol), DBH (3 mol), CH_2Cl_2

Scheme 1.



(1)

a: n-$Bu_4NH_2F_3$, DBH, CH_2Cl_2, 0 °C to rt



(2)

a: i) n-$Bu_4NH_2F_3$ (3 mol), NBS (6 mol), CH_2Cl_2, -10 °C
ii) H_2O, 34 %

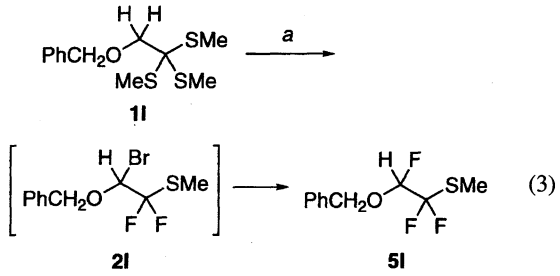
Table 1. Optimization of Oxidative Desulfurization–Fluorination of **1a**

Run	n-$Bu_4NH_2F_3$	DBH	Time	Yield of **2a**
	mol	mol	h	%
1	3	3	0.3	79
2	4	4	0.3	66
3	4	4	1	47
4	5	4	1	32
5	2	2	1	32

the reaction is applicable to a variety of substrates having an aromatic or aliphatic substituent. Olefinic substrate **1f** (Run 6) also afforded bromodifluorination product **2f**, without any trace of bromofluorination of the C=C bond.[20] Bifunctional substrate **1g** gave a double bromodifluorination product **2g** in high yield using twofold amounts of the reagents (Run 7).

When **1h** (Run 8), substrate **1** whose R is aryl, was subjected to the reaction, dibromodifluorination product **3h** was produced in 65% yield. The reaction was temperature independent: At −10 °C or at room temperature, **3h** was isolated in 55% or 56% yield, respectively. Substrate **1i** (Run 9) also gave dibromodifluorination product **3i** in 87% yield after 1 h; the yield after 20 min was 74%. In addition to **1h** having a weak electron-donating ethyl group (Run 8), substrate **1j** bearing an electron-withdrawing nitro group on phenyl (Run 10) underwent the dibromodifluorination reaction cleanly. However substrate **1k**, having a methoxy group, gave a complex mixture of products under the same conditions. At −10 °C with NBS (6 mol), **1k** gave **4k** in 34% yield after the usual workup and purification. A precursor of **4k** appears to be dibromodifluorination product **3k**, which apparently was extremely sensitive to hydrolysis during a workup and/or chromatographic purification.

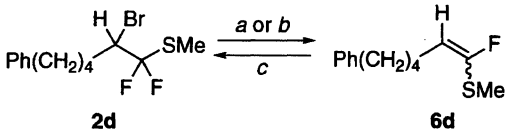
Orthothioester $PhCH_2OCH_2C(SMe)_3$ **1l**, having a benzyloxy group, afforded trifluorinated product **5l**. Probably an initially formed bromodifluorination product **2l** underwent substitution by a fluoride ion.



(3)

a: n-$Bu_4NH_2F_3$ (4 mol), DBH (3 mol), CH_2Cl_2, 0 °C to rt, 20 min, 62 %

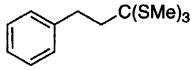
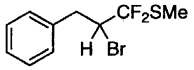
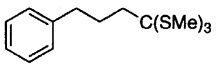
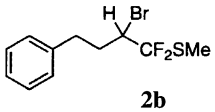
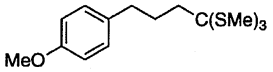
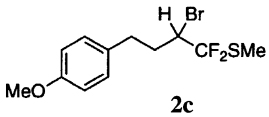
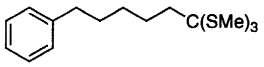
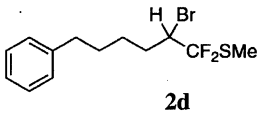
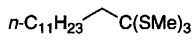
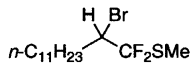
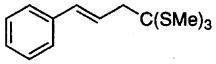
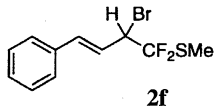
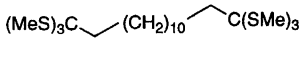
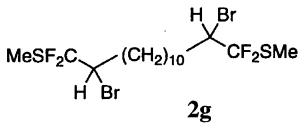
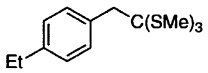
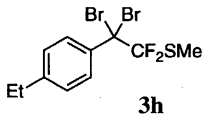
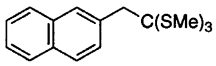
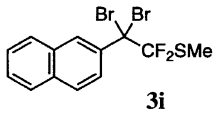
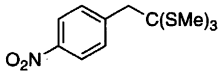
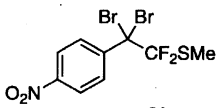
Reductive Elimination. The bromine and fluorine functional groups in **2** are removed reductively. For example, the treatment of **2d** with zinc powder in acetic acid gave a mixture of (*Z*)- and (*E*)-1-fluoroethenyl sulfide **6d** in 67% yield (*Z* : *E*=3 : 4). The *Z*/*E* ratio and the stereochemistry of **6d** were determined by ^{1}H NMR. The coupling constant, J_{HF}=15.6 Hz, was assigned for (*Z*)-**6d**; 32.2 Hz for (*E*)-**6d**. A reductive elimination was also achieved with butyllithium, and **6d** was isolated in 60% yield (*Z* : *E*=1 : 1). We assumed that **6d** might be an intermediate of the oxidative desulfurization–fluorination of **1d**, leading to **2d**. Indeed, when we treated a *Z*/*E* mixture of **6d** with n-$Bu_4NH_2F_3$ and DBH, we could isolated **2d** in 64% yield.



(4)

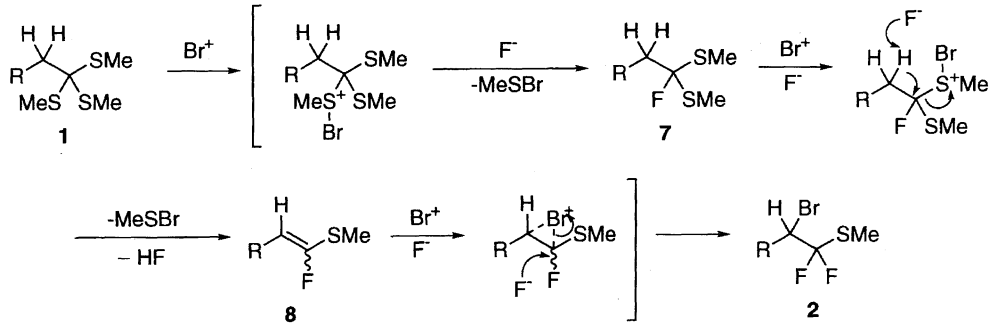
a: Zn (3 mol), AcOH–H_2O, 0 °C to r.t., 30 min, 67%, (*Z* : *E* = 3 : 4), *b*: n-BuLi (1 mol), THF, −78 °C, 5 min, 60%, (*Z* : *E* = 1 : 1), *c*: n-$Bu_4NH_2F_3$ (1.5 mol), DBH (1.5 mol), CH_2Cl_2, 0 °C to r.t., 20 min, 64%.

Table 2. Oxidative Desulfurization–Fluorination of Orthothioesters **1**[a]

Run	Orthothioester	Conditions	Product	Yield[b] / %
1	 **1a**	0 °C to r.t. 20 min	 **2a**	79
2	 **1b**	0 °C to r.t. 20 min	 **2b**	84
3	 **1c**	−10 °C 10 min	 **2c**	52
4	 **1d**	0 °C to r.t. 20 min	 **2d**	79
5	 **1e**	0 °C to r.t. 20 min	 **2e**	84
6	 **1f**	−10 °C 5 min	 **2f**	56
7	 **1g**	0 °C to r.t. 20 min[c]	 **2g**	83
8	 **1h**	0 °C to r.t. 1 h	 **3h**	65
9	 **1i**	0 °C to r.t. 1 h	 **3i**	87
10	 **1j**	0 °C to r.t. 1 h[d]	 **3j**	64

a) Substrate **1** was allowed to react with n-$Bu_4NH_2F_3$ (3 mol) and DBH (3 mol) in CH_2Cl_2. b) Isolated yield. c) Six mol of the fluorinating reagent and the oxidant were used. d) Five mol of the fluorinating reagent and the oxidant were used.

Mechanistic Aspects. With the above observations in hand, we consider that the transformation of **1** to **2** should involve (1) a first electrophilic attack of Br^+ at the sulfur atom of $RCH_2(SMe)_3$ (**1**), (2) substitution of Me–S–Br by a fluoride ion to give $RCH_2CF(SMe)_2$ (**7**), (3) a second electrophilic attack of Br^+ at the sulfur of **7**, followed by elimination of Me–S–Br and H^+ by a fluoride ion[21] to produce RCH=CFSMe (**8**), and (4) bromofluorination of the C=C bond of **8** in a manner as illustrated in Scheme 2. Fluorination of the remaining methylthio group turned out to be difficult, even under the forcing conditions which we described above. To complete trifluorination, a strongly cation-stabi-

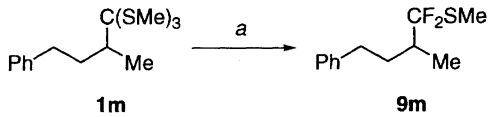


Scheme 2.

lizing group, like a heteroatom, aryl, or vinyl group, appears to be required, as we previously observed.[22]

The formation of dibromodifluoro product **3** (R = Ar) from **1** (R = Ar) may be understood in terms of a sequence of reactions involving (1) an electrophilic attack of Br^+ at –SMe followed by the elimination of Me–S–Br and H^+ by a fluoride ion to give $ArCH{=}C(SMe)_2$, (2) bromofluorination of $ArCH{=}C(SMe)_2$ to give $ArCHBr{-}CF(SMe)_2$, (3) another electrophilic attack of Br^+ at –SMe, followed by the elimination of Me–S–Br to produce $ArCBr{=}CF(SMe)$, and (4) bromofluorination of $ArCBr{=}CF(SMe)$ to give **3**.

Orthothioester **1m**, having a secondary alkyl group connected to the ester carbon, gave difluorination product **9m** without any bromination. Probably because of a steric hindrance, olefin formation induced by a fluoride ion did not take place, and oxidative desulfurization–fluorination only proceeded. The best chemical yield was attained when the reaction was carried out at −10 °C using 3 molar amounts of the respective reagents. The reactions at higher temperatures or with a double amount of DBH or NBS lowered the yield of **9m** without any trace of bromination.



(5)

a: n-$Bu_4NH_2F_3$ (3 mol), DBH (3 mol), CH_2Cl_2, -10 °C, 20 min, 64 %

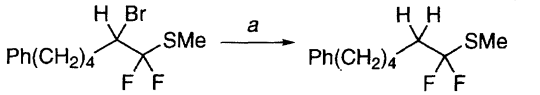
Synthetic Transformations of 2. The oxidation of bromodifluorination products **2** with a stoichiometric amount of *m*-chloroperbenzoic acid (mCPBA) at room temperature yielded sulfoxides **10**, which, upon thermolysis[23] at 160—170 °C in *o*-xylene placed in a sealed tube, afforded 2-substituted 2-bromo-1,1-difluoroethenes **11**. Examples of **2d** and **2e** are given in Scheme 3. When the thermolysis of **10d** was carried out in a neat liquid at 170 °C, the yield of **11d** was only 36%. Thus, the reaction at 160—170 °C in an *o*-xylene solvent was essential for the success of the olefin formation.

The treatment of **2d** with Raney Ni at room temperature gave hydrodebromination product **12d** with fluorine, and the methylthio group being unaffected.

2d : R = $Ph(CH_2)_4$ **10d** (99 %) **11d** (85 %)
2e : R = n-$C_{11}H_{23}$ **10e** (78 %) **11e** (75%)

a: mCPBA (1 mol), CH_2Cl_2, rt, 10 min
b: *o*-xylene, 160-170 °C, 8 h

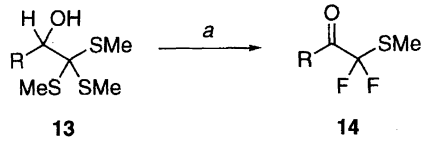
Scheme 3.



(6)

a: Raney Ni, EtOH, rt, 5 h, 34 %

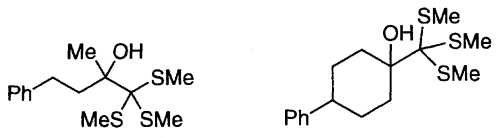
Fluorination of Tris(methylthio)ethanols (13). Reaction of $LiC(SMe)_3$ with aldehydes gave substrates of type $RCH(OH)C(SMe)_3$ **13** in good yields.[24] When **13** was treated with n-$Bu_4NH_2F_3$ and DBH, difluorination took place accompanied by oxidation of the hydroxy group, and α,α-difluoro ketones **14** were produced. Even after a prolonged reaction time, trifluorination did not take place. The use of an NIS oxidant or an $(HF)_9$-Py fluoride source resulted in the formation of a complex mixture of products.



(7)

a: n-$Bu_4NH_2F_3$ (5 mol), DBH (4 mol), CH_2Cl_2, rt, 10 min

The order of the addition of the reagents was also critical: the addition of DBH to a solution of **13a** or **13e** and n-$Bu_4NH_2F_3$ in dichloromethane at room temperature gave the highest yield of **14a** or **14e**. The reaction at room temperature was rapid enough to complete in 10 min; that at 0 °C produced a complex mixture of products. The optimized reaction conditions were applied to various types of **13**; the results are summarized in Table 3. Substrates **13** derived from both aromatic and aliphatic aldehydes were successfully converted into difluoro ketones **14** in moderate-to-good yields. Such a side reaction as the bromination of an aromatic ring or the bromofluorination of a C=C bond,[19] did not take place, even after a prolonged reaction time (Runs 1, 2, 3, 4,



17 18

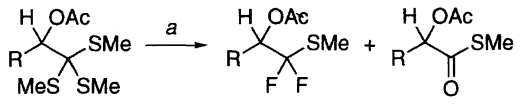
Chart 1.

and 7). However, **13h**, having a triple bond, gave a complex mixture of products. 2,2,2-Tris(methylthio)-1-(2-pyridyl)-ethanol (**13i**) underwent difluorination without oxidation to give **16i**, probably because of the electron-accepting nature of the pyridine ring.

The conversion of **13** to **14** may be attributed to difluorination as was the case in the formation of **9m**, followed by oxidation of the remaining hydroxy group.

Substrates **17** and **18**, derived from the corresponding ketones and $HC(SMe)_3$, gave complex mixtures of products; none of the difluorinated compounds could be isolated (Chart 1).

When the hydroxy group of **13** was protected by an acetoxy group and the resulting α-acetoxy orthothioesters **19** were treated with n-$Bu_4NH_2F_3$ and DBH, only difluorination proceeded, and we obtained **20** as a major product. The reaction conditions, including the temperature and addition order of the reagents, were optimized with **19a** as a substrate, and the procedure that DBH was added to a solution of **19a** and n-$Bu_4NH_2F_3$ in dichloromethane at 0 °C was found to give **20a** in a good yield along with a small amount of **21a**. Since **20a** was found to be fairly stable during the workup and purification, thiol ester **21a** should be derived from a reaction intermediate that is not well-characterized yet; however, its formation could not be suppressed. When substrate **19a** or n-$Bu_4NH_2F_3$ was added to the other two at room temperature, a fair amount of **14a** was produced. The best conditions were applied to **19b** and **19e**, and **20b** and **20e** were isolated in moderate yields along with by-products **21b** and **21e**, respectively, which were easily removed by silica-gel column chromatography. The reaction at the reflux temperature of dichloromethane for a longer time did not induce trifluorination, nor did a treatment of difluorination product **20a** with n-$Bu_4NH_2F_3$ and DBH.



(8)

19 **20** **21**

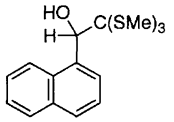
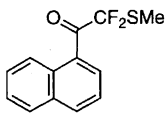
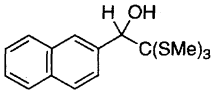
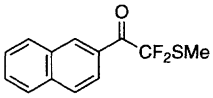
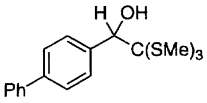
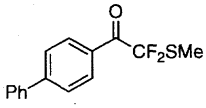
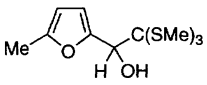
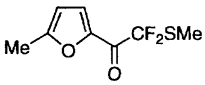
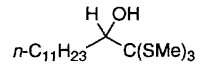
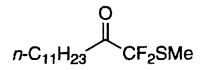
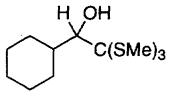
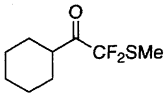
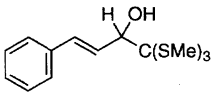
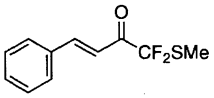
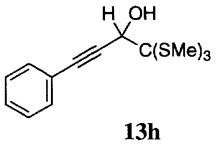
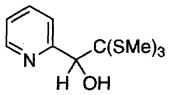
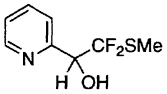
a: R = 1-Naph, **b**: R = 2-Naph, **e**: R = n-$C_{11}H_{23}$

a: n-$Bu_4NH_2F_3$ (5 mol), DBH (4 mol), CH_2Cl_2, 0 °C, 10 min

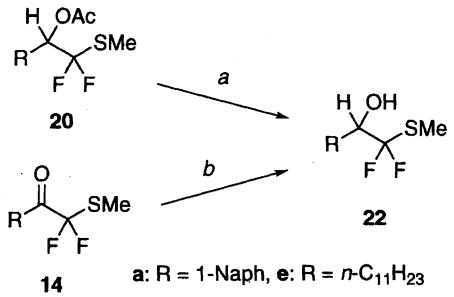
20a: 70%, **21a**: 17%; **20b**: 52%, **21b**: 22%; **20e**: 53%, **21e**: 35%

Synthetic Transformations of 20 and 14. Products **20** and **14** were corrected in the following way. The alkaline hydrolysis of difluoro acetoxy compounds **20a** and **20e** gave difluoro alcohols **22a** and **22e**, respectively, with the difluoromethylene group intact. The reduction of difluoro ketones **14a** and **14e** with sodium borohydride gave the difluoro alcohols **22a** and **22e**, respectively, as shown in Scheme 4.

Table 3. Oxidative Desulfurization–Fluorination of Orthothioesters **13**[a)]

Run	Orthothioester	Product (yield/%)
1	 **13a**	 **14a** (95)
2	 **13b**	 **14b** (80)
3	 **13c**	 **14c** (61)
4	 **13d**	 **14d** (66)
5	 **13e**	 **14e** (54)
6	 **13f**	 **14f** (51)
7[c)]	 **13g**	 **14j** (51)
8	 **13h**	Complex mixture
9[d)]	 **13i**	 **16i** (36)

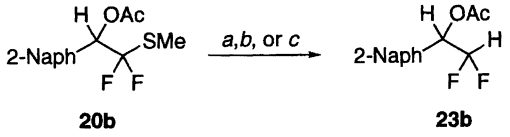
a) Unless otherwise noted, **13** was allowed to react with n-$Bu_4NH_2F_3$ (5 mol) and DBH (4 mol) in CH_2Cl_2 at room temperature for 10 min. b) Isolated yield. c) Compound **15g** possibly produced by bromination of **14g** was isolated as a by-product in 8% yield. d) The reaction was carried out at 0 °C for 10 min.



a: NaOH (1.2 mol), EtOH-H_2O, rt, 2 h, **22a**: 99%, **22e**: 80%
b: $NaBH_4$ (1.1 mol), MeOH, 0 °C, 20 min, **22a**: 93%, **22e**: 93%

Scheme 4.

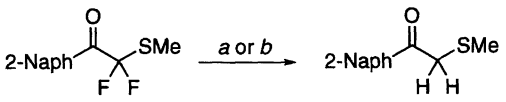
The sulfur functionality of **20b** could be reduced with *n*-Bu_3SnH or $(TMS)_3SiH$ in the presence of AIBN to give **23b**, albeit in low yields. Noteworthy is that the difluoromethylene moiety tolerated the radical conditions.



(9)

a: *n*-Bu_3SnH (1.2 mol), AIBN (0.1 mol), toluene, 80 °C, 3 h, 23%, *b*: *n*-Bu_3SnH (2.4 mol), AIBN (0.2 mol), toluene, 80 °C, 4 h to reflux, 24 h, 13%, *c*: $(TMS)_3SiH$ (2.4 mol), AIBN (0.2 mol), toluene, 80 °C, 24 h to reflux, 3 h, 55%.

In contrast, under similar conditions difluoro methylthio ketone **14b** lost fluorine atoms and gave methylthio ketone **24b**.



(10)

a: *n*-Bu_3SnH (1.2 mol), AIBN (0.1 mol), toluene, 80 °C, 6.5 h, 25 %
b: $(Me_3Si)_3SiH$ (1.2 mol), AIBN (0.1 mol), toluene, reflux, 20 h, 42 %

Conclusion

We have demonstrated here that the oxidative desulfurization–fluorination of $RCH_2C(SMe)_3$ **1** gives $RCHBrCF_2SMe$ **2** (R=alkyl) or $RCBr_2CF_2SMe$ **3** (R=aryl), depending on the kind of substituent R. The bromodifluorination products have been demonstrated to be versatile precursors of substituted bromodifluoroethenes $RCBr{=}CF_2$ **11**. Substrates of type $RCH(OH)C(SMe)_3$ **13** have been shown to give difluoro ketones $RCOCF_2SMe$ **14**. Under similar conditions, acetates $RCH(OAc)C(SMe)_3$ **19** give difluorination products $RCH(OAc)CF_2SMe$ **20**, whose methylthio group is readily reduced under radical conditions to afford $RCH(OAc)CF_2H$ **23**.

Experimental

The 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 trichlorofluoromethane as an internal standard, respectively. 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.

A Wakogel C-200 or a Merck Kieselgel 60 PF_{254} was used for the silica-gel column chromatography or silica-gel preparative thin-layer chromatography (TLC), respectively. 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.[19,25]

Alkylation of Alkyl Halides with Tris(methylthio)methyllithium.[18] **Preparation of 1,1,1-Tris(methylthio)tridecane (1e):** To a stirred solution of tris(methylthio)methane (0.27 ml, 2.0 mmol) in tetrahydrofuran (THF, 2 ml) was added dropwise a 1.56 M hexane solution (1 M = 1 mol dm^{-3}) of *n*-BuLi (1.4 ml, 2.2 mmol) at −78 °C under an argon atmosphere, and the mixture was stirred for 2 h to generate $LiC(SMe)_3$. A solution of 1-bromododecane (0.48 ml, 2.0 mmol) in THF (3 ml) was added to the $LiC(SMe)_3$ reagent, and the reaction mixture was stirred at −78 °C for 2 h. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature over 1 h; it was then poured into sat. NH_4Cl aq solution, and extracted with diethyl ether (3 times). The combined organic layer was washed with brine and then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give **1e** (0.64 g, 98% yield). R_f = 0.23 (hexane). IR (neat) 2923, 2853, 1541, 1509, 1466, 1458, 1435, 1418, 1314, 1125, 959, 764 cm^{-1}; ^1H NMR δ = 2.10 (s, 9H), 1.92—1.84 (m, 2H), 1.66—1.55 (m, 2H), 1.30—1.26 (m, 16H), 0.88 (t, J = 6.0 Hz, 3H); MS *m/z* (rel intensity) 275 (M^+ − SMe; 27), 259 (51), 227 (83), 211 (7), 197 (9), 133 (100), 61 (35). Found: *m/z* 275.1869. Calcd for $C_{15}H_{31}S_2$: M − SMe, 275.1867.

1,1,1-Tris(methylthio)-3-phenylpropane (1a): This compound (0.73 g, 94% yield) was prepared from (2-bromoethyl)benzene (0.41 ml, 3.0 mmol). R_f = 0.52 (EtOAc–hexane 1 : 10). IR (neat) 3061, 3025, 2980, 2917, 1601, 1497, 1453, 1433, 1418, 1312, 1262, 1030, 1007, 905, 795, 762, 700 cm^{-1}; ^1H NMR δ = 7.33—7.18 (m, 5H), 3.56 (t, J = 7.9 Hz, 1H), 3.15 (t, J = 7.6 Hz, 1H), 2.99—2.91 (m, 2H), 2.14 (s, 9H); MS *m/z* (rel intensity) 211 (M^+ − SMe; 100), 196 (10), 180 (47), 163 (64), 147 (53), 115 (62), 105 (67), 91 (84), 73 (67). Found: C, 56.00; H, 7.00%. Calcd for $C_{12}H_{28}S_3$: C, 55.77; H, 7.02%.

1,1,1-Tris-(methylthio)-4-phenylbutane (1b): This (0.38 g) was prepared in 91% yield from (3-bromopropyl)benzene (0.23 ml, 1.5 mmol). R_f = 0.15 (hexane). IR (neat) 3025, 2946, 2917, 1717, 1684, 1647, 1603, 1559, 1541, 1509, 1497, 1474, 1456, 1418, 1084, 747, 700 cm^{-1}; ^1H NMR δ = 7.31—7.16 (m, 5H), 2.65 (t, J = 6.7 Hz, 2H), 2.08—1.81 (m, 4H), 2.01 (s, 9H); MS *m/z* (rel intensity) 225 (M^+ − SMe; 100), 177 (65), 153 (54), 129 (93), 107 (91), 91 (71), 61 (71). Found: C, 57.28; H, 7.41%. Calcd for $C_{13}H_{20}S_3$: C, 57.30; H, 7.40%.

4- (4- Methoxyphenyl)- 1, 1, 1- tris(methylthio)butane (1c): This (0.91 g) was prepared in 98% yield from 1-(3-bromopropyl)-4-methoxybenzene (0.70 g, 3.1 mmol). R_f = 0.48 (EtOAc–hexane 1 : 10). IR (neat) 2992, 2946, 2917, 2834, 1613, 1584, 1512, 1464, 1439, 1418, 1300, 1246, 1177, 1109, 1036, 949, 831, 818, 700 cm^{-1}; ^1H NMR δ = 7.11 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.7 Hz,

2H), 3.78 (s, 3H), 2.60 (t, J = 6.8 Hz, 2H), 2.03 (s, 9H), 2.01—1.80 (m, 4H); MS m/z (rel intensity) 302 (M^+; 1), 255 (M^+ − SMe; 100), 207 (79), 159 (95), 134 (91), 121 (89), 91 (61). Found: m/z 255.0874. Calcd for $C_{13}H_{19}OS_2$: M − SMe, 255.0877.

1,1,1-Tris(methylthio)-6-phenylhexane (1d): This substrate (2.82 g) was prepared in 98% yield from (5-bromopentyl)benzene (2.17 g, 9.6 mmol). IR (neat) 3027, 2917, 2855, 1717, 1684, 1603, 1559, 1541, 1509, 1497, 1456, 1435, 1418, 1030, 959, 747, 698 cm^{-1}; ^1H NMR δ = 7.31—7.15 (m, 5H), 2.62 (t, J = 7.6 Hz, 2H), 2.09 (s, 9H), 1.91—1.80 (m, 2H), 1.74—1.55 (m, 4H), 1.43—1.27 (m, 2H); MS m/z (rel intensity) 253 (M^+ − SMe; 2), 209 (2), 205 (9), 155 (9), 130 (9), 91 (47), 61 (46), 47 (100). Found: C, 59.91; H, 7.97%. Calcd for $C_{15}H_{24}S_3$: C, 59.95; H, 8.05%.

***trans*-1,1,1-Tris(methylthio)-4-phenyl-3-butene (1f):** This (0.37 g, 67% yield) was obtained in a similar way from cinnamyl chloride (0.28 ml, 2.0 mmol). IR (neat) 3081, 3058, 3027, 2982, 2917, 2361, 1597, 1541, 1509, 1495, 1447, 1431, 1312, 1028, 963, 938, 779, 741, 693 cm^{-1}; ^1H NMR δ = 7.46—7.17 (m, 5H), 6.61—6.35 (m, 2H), 2.87 (d, J = 5.5 Hz, 2H), 2.16 (s, 9H); MS m/z (rel intensity) 223 (M^+ − SMe; 41), 207 (34), 175 (28), 160 (50), 150 (100), 128 (72), 115 (40), 91 (21). Found: m/z 223.0613. Calcd for $C_{12}H_{15}S_2$: M − SMe, 223.0615.

1,1,1,14,14,14-Hexakis(methylthio)tetradecane (1g): This substrate (0.90 g) was prepared in 94% yield from 1,12-dibromododecane (0.66 g, 2.0 mmol). IR (neat) 2980, 2919, 2851, 1561, 1541, 1509, 1466, 1433, 1418, 1312, 1119, 959, 764, 720 cm^{-1}; ^1H NMR δ = 2.10 (s, 18H), 1.92—1.84 (m, 4H), 1.66—1.55 (m, 4H), 1.34—1.25 (m, 16H); MS m/z (rel intensity) 427 (M^+ − SMe; 3), 378 (62), 363 (92), 331 (95), 315 (37), 283 (34), 187 (30), 133 (100), 87 (89), 61 (85). Found: m/z 427.1656. Calcd for $C_{19}H_{39}S_5$: M − SMe, 427.1655.

2-(4-Ethylphenyl)-1,1,1-tris(methylthio)ethane (1h): This compound (0.24 g) was isolated in 63% yield from 1-chloromethyl-4-ethylbenzene (0.21 ml, 1.4 mmol). R_f = 0.22 (hexane). IR (neat) 3022, 2964, 2916, 2871, 1511, 1491, 1432, 1418, 1313, 1116, 1054, 959, 930, 866, 816, 756 cm^{-1}; ^1H NMR δ = 7.29 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 3.23 (s, 2H), 2.64 (q, J = 7.6 Hz, 2H), 2.09 (s, 9H), 1.23 (t, J = 7.6 Hz, 3H); MS m/z (rel intensity) 225 (M^+ − SMe; 100), 178 (43), 153 (34), 147 (20), 129 (49). Found: m/z 225.0771. Calcd for $C_{12}H_{17}S_2$: M − SMe, 225.0772.

1,1,1-Tris(methylthio)-2-(2-naphthyl)ethane (1i): This (0.60 g) was prepared in 99% yield from 2-(bromomethyl)naphthalene (0.45 g, 2.0 mmol). R_f = 0.10 (hexane). IR (neat) 3054, 2982, 2915, 1601, 1509, 1431, 1366, 1314, 1271, 1019, 959, 897, 857, 824, 801, 745 cm^{-1}; ^1H NMR δ = 7.84—7.75 (m, 4H), 7.58—7.53 (m, 1H), 7.47—7.42 (m, 2H), 3.44 (s, 2H), 2.11 (s, 9H); MS m/z (rel intensity) 294 (M^+; 3), 247 (M^+ − SMe; 93), 200 (85), 184 (81), 153 (100), 141 (81), 115 (55). Found: m/z 247.0614. Calcd for $C_{14}H_{15}S_2$: M − SMe, 247.0615.

1,1,1-Tris(methylthio)-2-(4-nitrophenyl)ethane (1j): This (0.33 g) was prepared in 56% yield from 1-bromo-4-nitrobenzene (0.44 g, 2.0 mmol). R_f = 0.35 (EtOAc–hexane 1 : 10). IR (neat) 3110, 3079, 2918, 2856, 1606, 1522, 1432, 1347, 1268, 1180, 1110, 856, 802, 709 cm^{-1}; ^1H NMR δ = 8.26 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 3.35 (s, 2H), 2.13 (s, 9H); MS m/z (rel intensity) 242 (M^+ − SMe; 100), 195 (72), 179(51), 153 (27), 149 (28), 134 (35), 89(42). Found: m/z 242.0310. Calcd for $C_{10}H_{12}NO_2S_2$: M − SMe, 242.0309.

2-(4-Methoxyphenyl)-1,1,1-tris(methylthio)ethane (1k): This substrate (0.84 g) was prepared in 51% yield from 1-chloromethyl-4-methoxybenzene (0.82 ml, 6.1 mmol). R_f = 0.43 (EtOAc–hexane 1 : 10). IR (neat) 2996, 2917, 2834, 1609, 1584, 1561, 1510, 1302, 1250, 1179, 1111, 1036, 961, 907, 864, 820, 793 cm^{-1}; ^1H NMR δ = 7.29 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 3.21 (s, 2H), 2.09 (s, 9H); MS m/z (rel intensity) 274 (M^+; 6), 227 (M^+ − SMe; 97), 180 (100), 164 (47), 153 (98), 121 (99), 91 (30), 77 (22). Found: m/z 227.0565. Calcd for $C_{11}H_{15}OS_2$: M − SMe, 227.0564.

2-Benzyloxy-1,1,1-tris(methylthio)ethane (1l): This (0.52 g) was prepared in 94% yield from chloromethoxymethylbenzene (0.28 ml, 2.0 mmol). R_f = 0.42 (EtOAc–hexane 1 : 10). IR (neat) 3031, 2919, 2857, 1686, 1599, 1559, 1541, 1509, 1497, 1455, 1420, 1312, 1260, 1206, 1105, 1028, 965, 804, 737, 698 cm^{-1}; ^1H NMR δ = 7.42—7.23 (m, 5H), 4.64 (s, 2H), 3.70 (s, 2H), 2.17 (s, 9H); MS m/z (rel intensity) 274 (M^+; 1), 277 (M^+ − SMe; 100), 153 (90), 135 (43), 121 (49), 105 (58), 89 (99). Found: m/z 227.0566. Calcd for $C_{11}H_{15}OS_2$: M − SMe, 227.0564.

2-Methyl-1,1,1-tris(methylthio)-4-phenylbutane (1m): This substrate (0.45 g) was prepared in 83% yield from (3-bromobutyl)benzene (0.40 g, 1.9 mmol). R_f = 0.17 (hexane). IR (neat) 3085, 3061, 3025, 2977, 2917, 2361, 1684, 1603, 1497, 1455, 1435, 1420, 1374, 1312, 1030, 957, 791, 741, 700 cm^{-1}; ^1H NMR δ = 7.31—7.17 (m, 5H), 2.89—2.74 (m, 1H), 2.56—2.30 (m, 2H), 2.06 (s, 9H), 1.99—1.82 (m, 1H), 1.75—1.55 (m, 1H), 1.27 (d, J = 6.7 Hz, 3H); MS m/z (rel intensity) 239 (M^+ − SMe; 2), 210 (2), 161 (2), 147 (31), 101 (15), 91 (47), 61 (79), 45 (100). Found: C, 58.77; H, 7.81%. Calcd for $C_{14}H_{22}S_3$: C, 58.72; H, 7.75%.

A Typical Procedure for Oxidative Desulfurization–Fluorination of Tris(methylthio)ethanes 1. Preparation of 2-Bromo-1,1-difluoro-1-methylthio-6-phenylhexane (2d): To a dichloromethane (36 ml) solution of **1d** (2.56 g, 8.5 mmol) and n-$Bu_4NH_2F_3$ (7.70 g, 26 mmol) was added DBH (7.31 g, 26 mmol) in one portion at 0 °C under an argon atmosphere; the resulting mixture was stirred at room temperature for 20 min. The reaction mixture was diluted with a 10 : 1 mixture (330 ml) of hexane and diethyl ether, and 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 **2d** (2.17 g, 79% yield). R_f = 0.62 (EtOAc–hexane 1 : 10). IR (neat) 3027, 2936, 2861, 1717, 1603, 1559, 1541, 1509, 1497, 1455, 1437, 1163, 1090, 1030, 976, 747, 700 cm^{-1}; ^1H NMR δ = 7.33—7.15 (m, 5H), 4.22—4.05 (m, 1H), 2.64 (t, J = 6.9 Hz, 2H), 2.33 (s, 3H), 2.16—1.45 (m, 6H); ^{19}F NMR δ = −78.38 (dd, J = 204.5, 8.4 Hz, 1F), −80.69 (dd, J = 204.5, 11.2 Hz, 1F); MS m/z (rel intensity) 324 (M^++2; 29), 322 (M^+; 30), 233 (10), 231 (10), 195 (100), 175 (20), 127 (63), 91 (97). Found: m/z 322.0204. Calcd for $C_{13}H_{17}BrF_2S$: M, 322.0202.

2-Bromo-1,1-difluoro-1-methylthio-3-phenylpropane (2a): This (0.29 g) was prepared in 79% yield from **1a** (0.33 g, 1.3 mmol). R_f = 0.49 (EtOAc–hexane 1 : 10). IR (neat) 3033, 2936, 1717, 1605, 1559, 1541, 1509, 1497, 1456, 1437, 1323, 1275, 1242, 1161, 1055, 1022, 978, 930, 774, 698 cm^{-1}; ^1H NMR δ = 7.39—7.21 (m, 5H), 4.42—4.25 (m, 1H), 3.58 (dd, J = 2.8, 14.8 Hz, 1H), 3.04 (dd, J = 11.2, 14.8 Hz, 1H), 2.38 (s, 3H); ^{19}F NMR δ = −79.52 (dd, J = 204.7, 8.9 Hz, 1F), −80.34 (dd, J = 204.7, 10.1 Hz, 1F); MS m/z (rel intensity) 282 (M^++2; 4), 280 (M^+; 4), 262 (5), 260 (4), 213 (5), 201 (15), 182 (12), 165 (11), 153 (100), 135 (27), 134 (90). Found: C, 42.43; H, 3.85%. Calcd for $C_{10}H_{11}BrF_2S$: C, 42.72; H, 3.94%.

2-Bromo-1,1-difluoro-1-methylthio-4-phenylbutane (2b): This compound (69 mg) was prepared in 84% yield from **1b** (76 mg, 0.28 mmol). R_f = 0.33 (hexane). IR (neat) 3029, 2936, 1717, 1684,

1603, 1559, 1541, 1509, 1497, 1474, 1456, 1437, 1252, 1163, 1082, 976, 752, 700 cm^{-1}; ^1H NMR δ = 7.35—7.18 (m, 5H), 4.14—3.98 (m, 1H), 3.08—2.94 (m, 1H), 2.81—2.66 (m, 1H), 2.49—2.07 (m, 2H), 2.28 (s, 3H); ^{19}F NMR δ = −78.42 (dd, J = 205.3, 8.2 Hz, 1F), −80.58 (dd, J = 205.3, 11.5 Hz, 1F); MS *m/z* (rel intensity) 296 (M^++2; 9), 294 (M^+; 8), 215 (1), 195 (22), 167 (19), 147 (72), 91 (100). Found: C, 44.65; H, 4.47%. Calcd for $C_{11}H_{13}BrF_2S$: C, 44.76; H, 4.44%.

2-Bromo-1,1-difluoro-4-(4-methoxyphenyl)-1-methylthiobutane (2c): This (28 mg) was prepared in 52% yield from **1c** (50 mg, 0.17 mmol). R_f = 0.54 (EtOAc–hexane 1 : 10). IR (neat) 3006, 2936, 2836, 1613, 1584, 1541, 1514, 1466, 1441, 1302, 1250, 1179, 1107, 1036, 976, 860, 824, 756, 698 cm^{-1}; ^1H NMR δ = 7.13 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 4.13—3.96 (m, 1H), 3.79 (s, 3H), 3.01—2.88 (m, 1H), 2.76—2.61 (m, 1H), 2.44—2.04 (m, 2H), 2.29 (s, 3H); ^{19}F NMR δ = −78.21 (dd, J = 205.1, 8.3 Hz, 1F), −80.82 (dd, J = 205.1, 11.6 Hz, 1F); MS *m/z* (rel intensity) 326 (M^++2; 13), 324 (M^+; 15), 197 (3), 177(4), 121 (100), 97 (4). Found: *m/z* 323.9996. Calcd for $C_{12}H_{15}BrF_2OS$: M, 323.9995.

2-Bromo-1,1-difluoro-1-methylthiotridecane (2e): This (0.15 g) was prepared in 84% yield from **1e** (0.17 g, 0.53 mmol). R_f = 0.52 (hexane). IR (neat) 2926, 2855, 1717, 1684, 1559, 1541, 1509, 1489, 1458, 1165, 1017, 976 cm^{-1}; ^1H NMR δ = 4.22—4.06 (m, 1H), 2.33 (s, 3H), 2.17—1.58 (m, 2H), 1.49—1.18 (m, 18H), 0.88 (t, J = 6.4 Hz, 3H); ^{19}F NMR δ = −78.37 (dd, J = 204.2, 8.4 Hz, 1F), −80.66 (dd, J = 204.2, 11.2 Hz, 1F); MS *m/z* (rel intensity) 346 (M^++2; 24), 344 (M^+; 24), 265 (20), 217 (63), 161 (38), 147 (71), 85 (92), 71 (82), 57 (100). Found: *m/z* 344.0984. Calcd for $C_{14}H_{27}BrF_2S$: M, 344.0985.

***trans*-2-Bromo-1,1-difluoro-1-methylthio-4-phenyl-3-butene (2f):** This (31 mg) was prepared in 56% yield from **1f** (51 mg, 0.19 mmol). R_f = 0.22 (hexane). IR (neat) 3030, 2840, 1717, 1684, 1647, 1559, 1541, 1509, 1474, 1458, 1049, 963, 693 cm^{-1}; ^1H NMR δ = 7.45—7.29 (m, 5H), 6.72 (d, J = 15.6 Hz, 1H), 6.30 (dd, J = 15.6, 10.1 Hz, 1H), 5.01—4.86 (m, 1H), 2.35 (s. 3H); ^{19}F NMR δ = −77.41 (dd, J = 201.0, 5.3 Hz, 1F), −82.91 (dd, J = 201.0, 14.3 Hz, 1F); MS *m/z* (rel intensity) 293 (M^++1; 1), 291 (M^+−1; 1), 213 (M^+−Br; 66), 185 (13), 165 (100), 123 (32), 115 (33). Found: *m/z* 213.0550. Calcd for $C_{11}H_{11}F_2S$: M−Br, 213.0550.

2,13-Dibromo-1,1,14,14,-tetrafluoro-1,14-bis(methylthio)-tetradecane (2g): This product (0.17 g, 83% yield) was isolated from **1g** (0.19 g, 0.39 mmol). R_f = 0.26 (hexane). IR (neat) 2928, 2855, 2361, 1655, 1647, 1561, 1541, 1509, 1458, 1437, 1167, 1013, 976 cm^{-1}; ^1H NMR δ = 4.42—4.06 (m, 2H), 2.34 (s, 6H), 2.16—1.58 (m, 4H), 1.49—1.22 (m, 16H); ^{19}F NMR δ = −78.37 (dd, J = 204.3, 8.4 Hz, 1F), −80.62 (dd, J = 204.3, 11.2 Hz, 1F); MS *m/z* (rel intensity) 521 (M^++3; 3), 519 (M^++1; 5), 517 (M^+−1; 3), 441 (M^++2−Br; 85), 439 (M^+−Br; 79), 421 (18), 419 (17), 393 (63), 391 (60), 97 (72), 77 (100). Found: C, 37.19; H, 5.46%. Calcd for $C_{16}H_{28}Br_2F_4S_2$: C, 36.93; H, 5.42%.

2,2-Dibromo-2-(4-ethylphenyl)-1,1-difluoro-1-methylthioethane (3h): This (25 mg) was prepared in 65% yield from **1h** (28 mg, 0.10 mmol). R_f = 0.64 (EtOAc–hexane 1 : 10). IR (neat) 2967, 2934, 1717, 1559, 1541, 1507, 1458, 1125, 1063, 1015, 968, 878, 841, 810, 739, 691 cm^{-1}; ^1H NMR δ = 7.87 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 2.20 (s, 3H), 1.25 (t, J = 7.6 Hz, 3H); ^{19}F NMR δ = −76.41 (s, 2F); MS *m/z* (rel intensity) 295 (M^++2−Br; 98), 293 (M^+−Br; 100), 248 (40), 246 (40), 233 (46), 231 (47), 214 (93), 151 (47). HR-MS: Found: *m/z* 292.9810. Calcd for $C_{11}H_{12}BrF_2S$: M−Br, 292.9811.

2,2-Dibromo-1,1-difluoro-1-methylthio-2-(2-naphthyl)ethane (3i): This product (54 mg) was obtained in 87% yield from **1i** (46 mg, 0.16 mmol). R_f = 0.20 (hexane), mp 51—53 °C (hexane). IR (KBr) 3092, 3060, 2819, 1522, 1434, 1358, 1136, 1116, 1049, 1012, 968, 813, 782, 756, 695 cm^{-1}; ^1H NMR δ = 8.47 (s, 1H), 8.02—7.80 (m, 4H), 7.60—7.50 (m, 2H), 2.21 (s, 3H); ^{19}F NMR δ = −75.67 (s, 2F); MS *m/z* (rel intensity) 398 (M^++4; 7), 396 (M^++2; 12), 394 (M^+; 7), 317 (100), 315 (M^+−79; Br; 98), 270 (38), 268 (39), 236 (65), 189 (71), 139 (28). Found: *m/z* 393.8837. Calcd for $C_{13}H_{10}Br_2F_2S$: M, 393.8838.

2,2-Dibromo-1,1-difluoro-1-methylthio-2-(4-nitrophenyl)ethane (3j): This (26 mg) was prepared in 64% yield from **1j** (30 mg, 0.10 mmol). R_f = 0.45 (EtOAc–hexane 1 : 10), mp 69—71 °C (hexane). IR (KBr) 3104, 3082, 2357, 1603, 1521, 1349, 1130, 1062, 1012, 843, 812, 759, 725 cm^{-1}; ^1H NMR δ = 8.26—8.14 (m, 4H), 2.29 (s, 3H); ^{19}F NMR δ = −76.62 (s, 2F); MS *m/z* (rel intensity) 393 (M^++4; 3), 391 (M^++2; 6), 389 (M^+; 3), 312 (98), 310 (M^+−Br; 96), 265 (27), 263 (27), 231 (93), 138 (100), 97 (90). Found: C, 27.64; H, 1.84%. Calcd for $C_9H_7Br_2F_2O_2NS$: C, 27.65; H, 1.80%.

2,2-Difluoro-1-(4-methoxyphenyl)-2-methylthio-1-ethanone (4k): To a dichloromethane (7 ml) solution of **1k** (0.23 g, 0.84 mmol) and n-$Bu_4NH_2F_3$ (0.76 g, 2.5 mmol) was added NBS (0.90 g, 5.1 mmol) in one portion at −10 °C under an argon atmosphere; the resulting mixture was stirred at −10 °C for 30 min. The reaction mixture was diluted with a 10 : 1 mixture (110 ml) of hexane and diethyl ether, and 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 preparative TLC to give **4k** (66 mg, 34% yield). R_f = 0.43 (EtOAc–hexane 1: 10). IR (neat) 3011, 2938, 2843, 1694, 1601, 1574, 1512, 1458, 1426, 1318, 1267, 1181, 1132, 1063, 1026, 995, 972, 891, 847, 795, 781, 764, 747, 693, 644, 623, 602 cm^{-1}; ^1H NMR δ = 8.13 (d, J = 9.2 Hz, 2H), 6.96 (d, J = 9.2 Hz, 2H), 3.90 (s, 3H), 2.36 (t, J = 1.0 Hz, 3H); ^{19}F NMR δ = −81.43 (q, J = 1.0 Hz, 2F); MS *m/z* (rel intensity) 232 (M^+; 1), 162 (2), 135 (89), 97 (29), 92 (72), 77 (73), 63 (100). Found: C, 51.91; H, 4.24%. Calcd for $C_{10}H_{10}F_2O_2S$: C, 51.72; H, 4.34%.

2-Benzyloxy-1,1,2-trifluoro-1-methylthioethane (5l): To a dichloromethane (1.5 ml) solution of **1l** (49 mg, 0.18 mmol) and n-$Bu_4NH_2F_3$ (0.22 g, 0.71 mmol) was added DBH (0.15 g, 0.54 mmol) in one portion at 0 °C under an argon atmosphere; the resulting mixture was stirred at room temperature for 20 min. The reaction mixture was diluted with a 10 : 1 mixture (55 ml) of hexane and diethyl ether, and 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 preparative TLC to give **5l** (26 mg, 62% yield). R_f = 0.46 (EtOAc–hexane 1 : 10). IR (neat) 3036, 2940, 1499, 1456, 1366, 1325, 1262, 1208, 1156, 1132, 1088, 988, 957, 914, 741, 698 cm^{-1}; ^1H NMR δ = 7.46—7.28 (m, 5H), 5.90—4.60 (m, 3H), 2.31 (s, 3H); ^{19}F NMR δ = −90.22——91.49 (m, 1F), −92.41——93.69 (m, 1F), −139.52——139.98 (m, 1F); MS *m/z* (rel intensity) 236 (M^+; 9), 140 (4), 109 (4), 97 (15), 91 (100), 77 (5), 65 (12). Found: C, 51.10; H, 4.69%. Calcd for $C_{10}H_{11}F_3OS$: C, 50.84; H, 4.69%.

1-Fluoro-1-methylthio-6-phenyl-1-hexene (6d) (a mixture of *Z*- and *E*-isomers)**:** To a solution of **2d** (58 mg, 0.18 mmol) in acetic acid (0.8 ml) and water (0.08 ml) was added zinc powder (35

mg, 0.54 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 30 min. The reaction mixture was diluted with diethyl ether (20 ml); the resulting insoluble material was removed by filtration. The filtrate was washed with an aqueous solution of sodium hydrogencarbonate, and then with brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC to give **6d** (27 mg, 67% yield). R_f = 0.69 (EtOAc–hexane 1 : 10). IR (neat) 3062, 3026, 2930, 2857, 1651, 1496, 1454, 1440, 1081, 1016, 973, 746, 699 cm^{-1}; ^1H NMR δ = 7.32—7.12 (m, 5H), 5.42 and 5.09 (dt, J = 15.6, 7.8 Hz and dt, J = 32.2, 7.6 Hz, totally 1H), 2.61 (t, J = 7.6 Hz, 2H), 2.27 (s, 3H), 2.21—2.09 (m, 2H), 1.71—1.33 (m, 4H); ^{19}F NMR δ = −92.07 and −96.72 (d, J = 15.6 Hz and d, J = 32.2 Hz, totally 1F); MS m/z (rel intensity) 224 (M^+; 27), 177 (32), 157 (14), 130 (30), 105 (45), 91 (100). Found: m/z 224.1036. Calcd for $C_{13}H_{17}FS$: M, 224.1035.

1-Fluoro-1-methylthio-6-phenyl-1-hexene (6d) (a mixture of *Z*- and *E*-isomers): To a stirred solution of **2d** (52 mg, 0.16 mmol) in THF (1 ml) was added dropwise a 1.43 M hexane solution of *n*-BuLi (0.12 ml, 0.17 mmol) at −78 °C under an argon atmosphere. The reaction mixture was stirred at −78 °C for 5 min, poured into sat. NH_4Cl aq solution, and then extracted with diethyl ether (3 times). The combined organic layer was washed with brine, then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC to give **6d** (22 mg, 60% yield).

1,1-Difluoro-2-methyl-1-methylthio-4-phenylbutane (9m): To a dichloromethane (1.5 ml) solution of **1m** (49 mg, 0.17 mmol) and *n*-$Bu_4NH_2F_3$ (0.16 g, 0.51 mmol) was added DBH (0.15 g, 0.51 mmol) in one portion at −10 °C under an argon atmosphere; the resulting mixture was stirred at −10 °C for 20 min. The reaction mixture was diluted with a 10 : 1 mixture (55 ml) of hexane and diethyl ether, and 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 preparative TLC chromatography to give **9m** (25 mg, 64% yield). R_f = 0.42 (hexane). IR (neat) 3065, 3029, 2980, 2936, 2867, 1605, 1497, 1455, 1385, 1260, 1208, 1171, 1119, 1075, 968, 957, 941, 912, 749, 698 cm^{-1}; ^1H NMR δ = 7.33—7.15 (m, 5H), 2.85—2.51 (m, 2H), 2.26 (s, 3H), 2.22—1.98 (m, 2H), 1.68—1.48 (m, 1H), 1.15 (d, J = 6.9 Hz, 3H); ^{19}F NMR δ = −81.52 (d, J = 11.9 Hz, 2F); MS m/z (rel intensity) 230 (M^+; 6), 161 (3), 143 (9), 130 (7), 115 (12), 104 (74), 91 (100), 51 (82). Found: C, 62.83; H, 7.05%. Calcd for $C_{12}H_{16}F_2S$: C, 62.58; H, 7.00%.

2-Bromo-1, 1-difluoro-1-methylsulfinyl-6-phenylhexane (10d): To a dichloromethane (3 ml) solution of **2d** (0.33 g, 1.0 mmol) was added mCPBA (purity 80%, 0.22 g, 1.0 mmol) portionwise at room temperature, and the resulting mixture was stirred at room temperature for 10 min before dilution with dichloromethane (30 ml). The dichloromethane solution was washed with an aqueous solution of sodium hydrogencarbonate, 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 **10d** (0.34 g, 99% yield). R_f = 0.47 (EtOAc–hexane 1 : 3). IR (neat) 3027, 2938, 2861, 1559, 1541, 1509, 1497, 1456, 1198, 1103, 1084, 963, 749, 700 cm^{-1}; ^1H NMR δ = 7.32—7.15 (m, 5H), 4.56—4.35 (m, 1H), 2.74—2.61 (m, 5H), 2.21—1.51 (m, 6H); ^{19}F NMR δ = −107.72——110.31 (m, 1F), −113.43——116.16 (m, 1F); MS m/z (rel intensity) 340 (M^++2; 10), 338 (M^+; 10), 323 (10), 321 (10), 195 (32), 131 (31), 117 (44), 91 (100). Found: m/z 338.0153. Calcd for $C_{13}H_{17}BrF_2OS$: M, 338.0152.

2-Bromo-1,1-difluoro-1-methylsulfinyltridecane (10e): This compound (0.16 g) was prepared in 78% yield from **2e** (0.19 g, 0.55 mmol). R_f = 0.58 (EtOAc–hexane 1 : 3). IR (neat) 2925, 2854, 1466, 1438, 1407, 1196, 1122, 1097, 961, 941, 768, 734, 682 cm^{-1}; ^1H NMR δ = 4.57—4.36 (m, 1H), 2.72 (dt, J = 11.9, 1.4 Hz, 3H), 2.28—1.83 (m, 2H), 1.56—1.19 (m, 18H), 0.88 (t, J = 6.5 Hz, 3H); ^{19}F NMR δ = −107.73——110.33 (m, 1F), −113.52——116.13 (m, 1F); MS m/z (rel intensity) 362 (M^++2; 1), 360 (M^+; 1), 345 (2), 343 (2), 215 (3), 213 (3), 201 (25), 85 (32), 77 (23), 57 (100). Found: m/z 360.0933. Calcd for $C_{14}H_{27}BrF_2OS$: M, 360.0934.

2-Bromo-1,1-difluoro-6-phenyl-1-hexene (11d): An *o*-xylene (0.3 ml) solution of **10d** (0.12 g, 0.34 mmol) was heated in a sealed tube at 170 °C for 8 h. The reaction mixture was cooled and dissolved in hexane (20 ml). The resulting solution was filtered through a short silica-gel column. The filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give **11d** (79 mg, 0.29 mmol, 85% yield). R_f = 0.53 (hexane). IR (neat) 3029, 2936, 2861, 1744, 1603, 1541, 1509, 1497, 1455, 1269, 1134, 1049, 953, 747, 698 cm^{-1}; ^1H NMR δ = 7.32—7.15 (m, 5H), 2.63 (t, J = 7.1 Hz, 2H), 2.43—2.33 (m, 2H), 1.64—1.54 (m, 4H); ^{19}F NMR δ = −84.86 (dt, J = 45.2, 2.1 Hz, 1F), −91.09 (dt, J = 45.2, 3.0 Hz, 1F); MS m/z (rel intensity) 276 (M^++2; 16), 274 (M^+; 16), 196 (61), 127 (68), 117 (77), 91 (100), 77 (32). Found: m/z 274.0167. Calcd for $C_{12}H_{13}BrF_2$: M, 274.0169.

2-Bromo-1,1-difluoro-1-tridecene (11e): This (75 mg) was prepared in 75% yield from **10e** (0.12 g, 0.34 mmol). R_f = 0.82 (hexane). IR (neat) 2926, 2857, 1744, 1717, 1559, 1541, 1509, 1458, 1271, 1136, 953 cm^{-1}; ^1H NMR δ = 2.39—2.29 (m, 2H), 1.59—1.44 (m, 2H), 1.36—1.20 (m, 16H), 0.88 (t, J = 6.5 Hz, 3H); ^{19}F NMR δ = −85.17 (dt, J = 45.7, 2.2 Hz, 1F), −91.43 (dt, J = 45.7, 3.0 Hz, 1F); MS m/z (rel intensity) 298 (M^++2; 25), 296 (M^+; 25), 157 (38), 155 (39), 85 (42), 71 (47), 57 (100). Found: m/z 296.0952. Calcd for $C_{13}H_{23}BrF_2$: M, 296.0951.

1,1-Difluoro-1-methylthio-6-phenylhexane (12d): To an ethanol (0.5 ml) suspension of Raney Ni (ca. 0.2 g) was added **2d** (43 mg, 0.13 mmol) in ethanol (1 ml) at room temperature; the resulting mixture was stirred at room temperature for 5 h. The reaction mixture was diluted with ethanol (20 ml), and the resulting insoluble materials were removed by filtration. The filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC to give **12d** (11 mg, 34% yield). R_f = 0.70 (EtOAc–hexane 1 : 10). IR (neat) 3027, 2936, 2859, 1717, 1684, 1559, 1541, 1509, 1497, 1456, 1173, 1088, 1013, 747, 698 cm^{-1}; ^1H NMR δ = 7.31—7.15 (m, 5H), 2.61 (t, J = 7.6 Hz, 2H), 2.28 (s, 3H), 2.19—1.97 (m, 2H), 1.72—1.50 (m, 4H), 1.45—1.33 (m, 2H); ^{19}F NMR δ = −76.82 (t, J = 14.7 Hz, 2F); MS m/z (rel intensity) 244 (M^+; 48), 224 (36), 195 (60), 175 (43), 117 (61), 105 (66), 91 (100). Found: m/z 244.1098. Calcd for $C_{13}H_{18}F_2S$: M, 244.1097.

A Typical Procedure for the Preparation of Substrates 13.[24] **Preparation of 1,1,1-Tris(methylthio)-2-tridecanol (13e):** To a stirred solution of tris(methylthio)methane (1.4 ml, 10.5 mmol) in THF (15 ml) was added dropwise a 1.63 M hexane solution of *n*-BuLi (6.7 ml, 10.9 mmol) at −78 °C under an argon atmosphere; the mixture was stirred for 2 h. A solution of dodecanal (2.2 ml, 10.0 mmol) in THF (7 ml) was added, and the reaction mixture was stirred at −78 °C for 2 h. The cooling bath was removed. The reaction mixture was allowed to warm to room temperature for over 1 h, poured into a 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 **13e** (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}; ^1H 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-(1-naphthyl)ethanol (13a): This substrate (3.0 g, 97% yield) was prepared from 1-naphthaldehyde (1.4 ml, 10.0 mmol). $R_f = 0.29$ (EtOAc–hexane 1 : 10), mp 103—105 °C (Et_2O). IR (KBr) 3474, 3052, 2912, 2360, 1428, 1402, 1352, 1265, 1207, 1170, 1066, 806, 797, 778 cm^{-1}; ^1H NMR $\delta = 8.37$—8.32 (m, 1H), 8.10 (dd, $J = 7.3$, 1.0 Hz, 1H), 7.86—7.81 (m, 2H), 7.56—7.45 (m, 5H), 5.92 (d, $J = 2.3$ Hz, 1H), 3.59 (d, $J = 2.3$ Hz, 1H), 2.01 (s, 9H); MS *m/z* (rel intensity) 310 (M^+; 1), 263 ($M^+ - SMe$; 15), 187 (34), 167 (67), 153 (100), 128 (74), 107 (54), 91 (68). Found: C, 57.77; H, 5.78%. Calcd for $C_{15}H_{18}OS_3$: C, 58.03; H, 5.84%.

2,2,2-Tris(methylthio)-1-(2-naphthyl)ethanol (13b): This compound (3.1 g) was obtained in 99% yield 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}; ^1H 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 (13c): 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}; ^1H 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.

1-(5-Methyl-2-furyl)-2,2,2-tris(methylthio)ethanol (13d): This substrate (1.41 g) was isolated in 89% yield starting with 5-methyl-2-furfural (0.60 ml, 6.0 mmol). $R_f = 0.21$ (EtOAc–hexane 1 : 10). IR (neat) 3463, 2983, 2918, 1557, 1434, 1382, 1220, 1058, 1022, 953, 788, 731 cm^{-1}; ^1H NMR $\delta = 6.35$ (d, $J = 3.1$ Hz, 1H), 5.97 (dd, $J = 3.1$, 0.9 Hz, 1H), 4.83 (d, $J = 5.7$ Hz, 1H), 3.37 (d, $J = 5.7$ Hz, 1H), 2.31 (d, $J = 0.9$ Hz, 3H), 2.10 (s, 9H); MS *m/z* (rel intensity) 246 ($M^+ - H_2O$; 98), 231 (69), 184 (27), 169 (25), 153 (69), 141 (100), 109 (58). Found: *m/z* 246.0207. Calcd for $C_{10}H_{14}OS_3$: M−H_2O, 246.0207.

1-Cyclohexyl-2,2,2-tris(methylthio)ethanol (13f): This compound (0.61 g) was obtained in 74% yield from cyclohexanecarbaldehyde (0.37 ml, 3.1 mmol). $R_f = 0.30$ (EtOAc–hexane 1 : 10). IR (neat) 3490, 2921, 2851, 1448, 1419, 1385, 1254, 1102, 909, 815, 734 cm^{-1}; ^1H NMR $\delta = 3.54$ (dd, $J = 4.3$, 2.4 Hz, 1H), 2.73 (d, $J = 4.3$ Hz, 1H), 2.21 (s, 9H) 2.05—1.83 (m, 1H), 1.77—1.64 (m, 4H), 1.38—1.25 (m, 6H); MS *m/z* (rel intensity) 219 ($M^+ - SMe$; 92), 189 (8), 171 (23), 153 (61), 107 (100), 91 (52). Found: *m/z* 219.0876. Calcd for $C_{10}H_{19}OS_2$: M−SMe, 219.0877.

***trans*-2,2,2-Tris(methylthio)-1-styrylethanol (13g):** This (0.84 g) was prepared 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%.

1,1,1-Tris(methylthio)-4-phenyl-3-butyn-2-ol (13h): This substrate (0.60 g) was prepared in 65% yield from phenylpropynal (0.40 ml, 3.3 mmol). $R_f = 0.37$ (EtOAc–hexane 1 : 6). IR (neat) 3466, 3054, 2985, 2918, 1490, 1434, 1417, 1385, 1234, 1058, 911, 757, 732, 691 cm^{-1}; ^1H NMR $\delta = 7.48$—7.43 (m, 2H), 7.43—7.30 (m, 3H), 4.76 (d, $J = 8.5$ Hz, 1H), 3.31 (d, $J = 8.5$ Hz, 1H), 2.30 (s, 9H); MS *m/z* (rel intensity) 269 ($M^+ - Me$; 41), 237 ($M^+ - SMe$; 31), 221 (9), 189 (36), 161 (48), 153 (100), 91 (43), 77 (25). Found: *m/z* 237.0407. Calcd for $C_{12}H_{13}OS_2$: M−SMe, 237.0408.

2,2,2-Tris(methylthio)-1-(2-pyridyl)ethanol (13i): This (0.39 g) was prepared in 24% yield 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}; ^1H 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 ($M^+ - 47$, 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.

2-Methyl-1,1,1-tris(methylthio)-4-phenyl-2-butanol (17): This alcohol (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 (18): This substrate (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). 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 Oxidative Desulfurization–Fluorination of 13. Preparation of 2,2-Difluoro-2-methylthio-1-(1-naphthyl)ethanone (14a): To a dichloromethane (2 ml) solution of **13a** (0.16 g, 0.51 mmol) and *n*-$Bu_4NH_2F_3$ (0.77 g, 2.5 mmol) was added DBH (0.58 g, 2.0 mmol) in one portion at room temperature under an argon atmosphere. The resulting mixture was stirred at room temperature 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 **14a** (0.12 g, 95% yield). $R_f = 0.51$ (EtOAc–hexane 1 : 10). IR (neat) 3035, 2910, 1680, 1582, 1561, 1498, 1427, 1270, 1237, 1133, 1044, 1009, 971, 876, 859, 760 cm^{-1}; ^1H NMR $\delta = 8.51$ (dd, $J = 8.3$, 0.9 Hz, 1H), 8.27—8.21 (m, 1H), 8.04 (d, $J = 8.3$ Hz, 1H), 7.90—7.85 (m, 1H), 7.64—7.48 (m, 3H), 2.39 (t, $J = 1.2$ Hz, 3H); ^{19}F NMR

δ = −81.71 (dq, J = 1.4, 1.2 Hz, 2F); MS m/z (rel intensity) 252 (M^+; 10), 155 (100), 127 (94), 101 (20), 97 (23), 77 (29). Found; C, 61.84; H, 3.94%. Calcd for $C_{13}H_{10}F_2OS$: C, 61.89; H, 4.00%.

2,2-Difluoro-2-methylthio-1-(2-naphthyl)ethanone (14b): This product (0.40 g) was isolated in 80% yield from **13b** (0.61 g, 2.0 mmol). R_f = 0.55 (EtOAc–hexane 1 : 10). IR (neat) 3061, 2935, 1698, 1627, 1597, 1437, 1357, 1284, 1234, 1141, 1112, 1060, 1012, 973, 910, 834, 797, 754 cm^{-1}; ^1H NMR δ = 8.73 (s, 1H), 8.13—8.08 (m, 1H), 8.01—7.85 (m, 3H), 7.68—7.52 (m, 2H), 2.40 (t, J = 1.0 Hz, 3H); ^{19}F NMR δ = −81.45 (q, J = 1.0 Hz, 2F); MS m/z (rel intensity) 252 (M^+; 14), 237 (4), 190 (7), 155 (100), 127 (88), 101 (8), 77 (12). Found: m/z 252.0421. Calcd for $C_{13}H_{10}F_2OS$: M, 252.0420.

1-(4-Biphenylyl)-2,2-difluoro-2-methylthioethanone (14c): This product (87 mg) was prepared in 61% yield from **13c** (0.17 g, 0.51 mmol). R_f = 0.50 (EtOAc–hexane 1 : 10). IR (neat) 3059, 3032, 2935, 1698, 1603, 1558, 1488, 1449, 1408, 1275, 1132, 1064, 1006, 891, 838, 737, 696 cm^{-1}; ^1H NMR δ = 8.24—8.18 (m, 2H), 7.74—7.59 (m, 4H), 7.52—7.41 (m, 3H), 2.38 (t, J = 1.1 Hz, 3H); ^{19}F NMR δ = −82.10 (q, J = 1.1 Hz, 2F); MS m/z (rel intensity) 278 (M^+; 12), 181 (100), 152 (68), 127 (10), 76 (8). Found: m/z 278.0577. Calcd for $C_{15}H_{12}F_2OS$: M, 278.0577.

2,2-Difluoro-1-(5-methyl-2-furyl)-2-methylthio-1-ethanone (14d): This (96 mg) was prepared in 66% yield from **13d** (0.19 g, 0.71 mmol). R_f = 0.42 (EtOAc–hexane 1 : 5), mp 68—69 °C (hexane). IR (KBr) 1682, 1652, 1507, 1203, 1112, 1037, 986, 947, 822, 786 cm^{-1}; ^1H NMR δ = 7.45—7.41 (m, 1H), 6.27 (ddd, J = 3.6, 1.7, 0.8 Hz, 1H), 2.45 (s, 3H), 2.36 (t, J = 1.1 Hz, 3H); ^{19}F NMR δ = −84.25 (br s, 2F); MS m/z (rel intensity) 206 (M^+; 1), 184 (10), 156 (15), 109 (100), 53 (29). Found: m/z 206.0212. Calcd for $C_8H_8F_2O_2S$: M, 206.0213.

1,1-Difluoro-1-methylthio-2-tridecanone (14e): This product (0.37 g) was obtained in 54% yield from **13e** (0.82 g, 2.4 mmol). R_f = 0.76 (EtOAc–hexane 1 : 10). IR (neat) 2926, 2855, 1742, 1466, 1439, 1404, 1377, 1192, 1118, 1090, 1019, 976, 903, 723 cm^{-1}; ^1H NMR δ = 2.71 (tt, J = 7.2, 1.0 Hz, 2H), 2.26 (t, J = 1.0 Hz, 3H), 1.72—1.58 (m, 2H), 1.40—1.16 (m, 16H), 0.88 (t, J = 6.5 Hz, 3H); ^{19}F NMR δ = −90.30 (br d, J = 0.7 Hz, 2F); MS m/z (rel intensity) 280 (M^+; 7), 183 (100), 109 (18), 97 (31), 85 (52), 71 (63), 57 (78). Found: C, 59.90; H, 9.45%. Calcd for $C_{14}H_{26}F_2OS$: C, 59.97; H, 9.35%.

1-Cyclohexyl-2,2-difluoro-2-methylthio-1-ethanone (14f): This product (44 mg) was prepared in 51% yield from **13f** (0.11 g, 0.41 mmol). R_f = 0.64 (EtOAc–hexane 1 : 10). IR (neat) 2935, 2858, 1732, 1451, 1374, 1331, 1247, 1198, 1143, 1122, 1098, 1056, 1002, 932, 918, 801 cm^{-1}; ^1H NMR δ = 2.95—2.83 (m, 1H), 2.25 (t, J = 1.2 Hz, 3H), 1.92—1.22 (m, 10H); ^{19}F NMR δ = −90.23 (br s, 2F); MS m/z (rel intensity) 208 (M^+; 27), 111 (100), 97 (17), 83 (67), 55 (87). Found: m/z 208.0734. Calcd for $C_9H_{14}F_2OS$: M, 208.0733.

***trans*-1, 1-Difluoro-1-methylthio-4-phenyl-3-buten-2-one (14g):** To a dichloromethane (2 ml) solution of **13g** (0.17 g, 0.58 mmol) and n-$Bu_4NH_2F_3$ (0.87 g, 2.9 mmol) was added DBH (0.66 g, 2.3 mmol) in one portion at room temperature under an argon atmosphere. The resulting mixture was stirred at room temperature 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 **14g** (68 mg, 51% yield) along with **15g** (18 mg, 8% yield). R_f = 0.56 (EtOAc–hexane 1 : 10). IR (neat) 3062, 3029, 2935, 1704, 1609, 1576, 1450, 1337, 1205, 1052, 985, 948, 778, 752, 681 cm^{-1}; ^1H NMR δ = 7.93 (d, J = 15.9 Hz, 1H), 7.68—7.59 (m, 2H), 7.49—7.37 (m, 3H), 7.09 (dt, J = 15.9, 1.2 Hz, 1H), 2.30 (t, J = 1.1 Hz, 3H); ^{19}F NMR δ = −90.68 (br s, 2F); MS m/z (rel intensity) 228 (M^+; 62), 182 (15), 131 (100), 103 (88), 77 (75). Found: m/z 228.0421. Calcd for $C_{11}H_{10}F_2OS$: M, 228.0420.

3,4-Dibromo-1,1-difluoro-1-methylthio-4-phenyl-2-butanone (15g): R_f = 0.65 (EtOAc–hexane 1 : 10). IR (neat) 2998, 2927, 1738, 1457, 1160, 1130, 1116, 1059, 1030, 1008, 982, 943, 691 cm^{-1}; ^1H NMR δ = 7.44—7.37 (m, 5H), 5.45—5.31 (m, 2H), 2.31 (t, J = 1.1 Hz, 3H); ^{19}F NMR δ = −88.47 (dd, J = 220.2, 1.1 Hz, 1F), −91.55 (d, J = 220.2 Hz, 1F); MS m/z (rel intensity) 390 (M^++4; 1), 388 (M^++2; 2), 386 (M^+; 1), 375 (M^++4−Me; 2), 373 (M^++2−Me; 3), 371 (M^+−Me; 2), 309 (M^++2−Br; 60), 307 (M^+−Br; 58), 289 (7), 227 (8), 211 (14), 209 (13), 184 (8), 182 (9), 131 (69), 103 (58), 97 (100), 77 (43). Found: m/z 306.9605. Calcd for $C_{11}H_{10}BrF_2OS$: M−Br, 306.9604.

2,2-Difluoro-2-methylthio-1-(2-pyridyl)ethanol (16i): To a dichloromethane (2 ml) solution of **13i** (0.11 g, 0.40 mmol) and n-$Bu_4NH_2F_3$ (0.61 g, 2.0 mmol) was added DBH (0.46 g, 1.6 mmol) in one portion at 0 °C under an argon atmosphere. The resulting 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 **16i** (30 mg, 36% yield). R_f = 0.16 (EtOAc–hexane 1 : 5), mp 71—72 °C (hexane). IR (KBr) 3074, 2920, 2850, 2693, 1599, 1480, 1438, 1163, 1115, 1078, 1045, 999, 967, 767, 645, 616 cm^{-1}; ^1H NMR δ = 8.61 (dt, J = 4.8, 1.2 Hz, 1H), 7.75 (dt, J = 1.7, 7.6 Hz, 1H), 7.46—7.31 (m, 2H), 5.44 (br s, 1H), 5.03 (dd, J = 10.9, 6.3 Hz, 1H), 2.26 (t, J = 0.8 Hz, 3H); ^{19}F NMR δ = −83.69 (dd, J = 213.0, 6.3 Hz, 1F), −87.62 (dd, J = 213.0, 10.9 Hz, 1F); MS m/z (rel intensity) 190 (M^+−Me; 4), 142 (7), 108 (100), 78 (20). Found: m/z 190.0140. Calcd for $C_7H_6F_2NOS$: M−Me, 190.0138.

2,2,2-Tris(methylthio)-1-(1-naphthyl)ethyl Acetate (19a): Acetic anhydride (1.0 ml, 10.7 mmol) was added to a solution of **13a** (2.2 g, 7.1 mmol) and 4-(dimethylamino)pyridine (87 mg, 0.71 mmol) in pyridine (2.5 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred at room temperature for 2.5 h, poured into an aqueous solution of ammonium chloride, and extracted with ethyl acetate (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 **19a** (2.2 g, 87% yield). R_f = 0.44 (EtOAc–hexane 1 : 10), mp 95—97 °C (hexane). IR (KBr) 3068, 3000, 2919, 2360, 1742, 1511, 1435, 1368, 1240, 1226, 1050, 1032, 782 cm^{-1}; ^1H NMR δ = 8.41 (d, J = 8.6 Hz, 1H), 8.07 (dd, J = 7.4, 1.0 Hz, 1H), 7.87—7.80 (m, 2H), 7.59—7.42 (m, 3H), 7.18 (s, 1H), 2.13 (s, 3H), 2.11 (s, 9H); MS m/z (rel intensity) 352 (M^+; 1), 305 (M^+−SMe; 8), 246 (5), 187 (58), 153 (100), 127 (16), 91 (20). Found: C, 57.81; H, 5.79%. Calcd for $C_{17}H_{20}O_2S_3$: C, 57.92; H, 5.72%.

2,2,2-Tris(methylthio)-1-(2-naphthyl)ethyl Acetate (19b): This acetate (1.2 g) was prepared in 98% yield from **13b** (1.1 g, 3.4 mmol). R_f = 0.31 (EtOAc–hexane 1 : 10). IR (neat) 3057, 2984, 2919, 1746, 1509, 1432, 1369, 1226, 1126, 1032, 956, 860, 812, 749 cm^{-1}; ^1H NMR δ = 8.02 (s, 1H), 7.89—7.79 (m, 4H), 7.52—7.45 (m, 2H), 6.26 (s, 1H), 2.16 (s, 3H), 2.15 (s, 9H); MS m/z (rel intensity) 305 (M^+−47, SMe; 66), 292 (96), 262 (37), 230 (98), 198 (67), 187 (98), 171 (80), 153 (100), 139 (75), 127 (56). Found: m/z 305.0669. Calcd for $C_{16}H_{17}O_2S_2$: M−SMe, 305.0670.

1-[Tris(methylthio)methyl]dodecyl Acetate (19e): This ac-

etate (0.88 g) was prepared in 93% yield from **13e** (0.84 g, 2.5 mmol) as a viscous oil. $R_f = 0.61$ (EtOAc–hexane 1 : 10). IR (neat) 2955, 2924, 2855, 1748, 1466, 1437, 1370, 1229, 1022, 959, 795, 760, 720 cm^{-1}; ^1H NMR $\delta = 5.19$ (dd, $J = 7.5$, 5.1 Hz, 1H), 2.19 (s, 9H), 2.11 (s, 3H), 2.03—1.89 (m, 2H), 1.35—1.20 (m, 18H), 0.88 (t, $J = 6.5$ Hz, 3H); MS *m/z* (rel intensity) 333 ($M^+ - SMe$; 100), 320 (45), 225 (57), 215 (96), 153 (78), 91 (43), 61 (66). Found: *m/z* 333.1922. Calcd for $C_{17}H_{33}O_2S_2$: M−SMe, 333.1922.

A Typical Procedure for the Oxidative Desulfurization–Fluorination of 19: Preparation of 2,2-Difluoro-2-methylthio-1-(1-naphthyl)ethyl Acetate (20a): To a dichloromethane (2 ml) solution of **19a** (93 mg, 0.26 mmol) and *n*-$Bu_4NH_2F_3$ (0.40 g, 1.3 mmol) was added DBH (0.30 g, 1.1 mmol) in one portion at 0 °C under an argon atmosphere. The resulting 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 **20a** (55 mg, 70% yield) along with **21a** (12 mg, 17% yield). $R_f = 0.46$ (EtOAc–hexane 1 : 10). IR (neat) 3056, 2936, 1757, 1599, 1514, 1439, 1370, 1300, 1242, 1223, 1167, 1059, 1001, 916, 876, 862, 824, 791, 774, 745 cm^{-1}; ^1H NMR $\delta = 8.22$ (d, $J = 8.4$ Hz, 1H), 7.90—7.83 (m, 2H), 7.76 (d, $J = 7.2$ Hz, 1H), 7.62—7.45 (m, 3H), 7.02 (t, $J = 9.8$ Hz, 1H), 2.22 (t, $J = 0.8$ Hz, 3H), 2.19 (s, 3H); ^{19}F NMR $\delta = -84.96$ (dd, $J = 211.5$, 9.8 Hz, 1F), −85.12 (dd, $J = 211.5$, 9.8 Hz, 1F); MS *m/z* (rel intensity) 296 (M^+; 48), 199 (45), 189 (20), 170 (25), 157 (100), 139 (10), 129 (58). Found: C, 60.63; H, 5.01%. Calcd for $C_{15}H_{14}F_2O_2S$: C, 60.80; H, 4.76%.

***S*-Methyl 2-Acetoxy-2-(1-naphthyl)thioacetate (21a):** $R_f = 0.32$ (EtOAc–hexane 1 : 10). IR (neat) 3052, 2920, 1752, 1700, 1647, 1559, 1541, 1509, 1489, 1474, 1458, 1370, 1223, 1050, 916, 777 cm^{-1}; ^1H NMR $\delta = 8.20$—8.15 (m, 1H), 7.91—7.85 (m, 2H), 7.67—7.44 (m, 4H), 6.90 (s, 1H), 2.28 (s, 3H), 2.23 (s, 3H); MS *m/z* (rel intensity) 247 (M^+; 68), 199 (81), 187 (24), 174 (26), 157 (100), 139 (47), 129 (74), 75 (29). Found: *m/z* 274.0663. Calcd for $C_{15}H_{14}O_3S$: M, 274.0664.

2,2-Difluoro-2-methylthio-1-(2-naphthyl)ethyl Acetate (20b): This product (0.62 g) was prepared in 62% yield from **19b** (1.2 g, 3.4 mmol) along with **21b** (0.21 g, 22% yield). $R_f = 0.30$ (EtOAc–hexane 1 : 10), mp 33—34 °C (hexane). IR (KBr) 3062, 2358, 1755, 1434, 1372, 1224, 1180, 1168, 1047, 998, 920, 806, 801, 753 cm^{-1}; ^1H NMR $\delta = 7.94$ (s, 1H), 7.87—7.79 (m, 3H), 7.60—7.45 (m, 3H), 6.30 (t, $J = 10.1$ Hz, 1H), 2.24 (s, 3H), 2.20 (s, 3H); ^{19}F NMR $\delta = -86.10$ (d, $J = 10.1$ Hz, 2F); MS *m/z* (rel intensity) 296 (M^+; 13), 251 (5), 199 (7), 179 (29), 157 (50), 127 (20), 85 (100), 67 (48). Found: *m/z* 296.0682. Calcd for $C_{15}H_{14}F_2O_2S$: M, 296.0683.

***S*-Methyl 2-Acetoxy-2-(2-naphthyl)thioacetate (21b):** $R_f = 0.22$ (EtOAc–hexane 1 : 10), mp 72—74 °C (hexane). IR (KBr) 3056, 2358, 1753, 1682, 1372, 1220, 1127, 1095, 1048, 925, 830, 790, 749 cm^{-1}; ^1H NMR $\delta = 7.95$ (s, 1H), 7.90—7.78 (m, 3H), 7.60—7.42 (m, 3H), 6.34 (s, 1H), 2.29 (s, 3H), 2.25 (s, 3H); MS *m/z* (rel intensity) 274 (M^+; 12), 199 (36), 157 (100), 139 (10), 129 (31). Found: *m/z* 274.0663. Calcd for $C_{15}H_{14}O_3S$: M, 274.0664.

1-[Difluoro(methylthio)methyl]dodecyl Acetate (20e): This product (0.28 g) was isolated in 53% yield from **19e** (0.61 g, 1.6 mmol) along with **21e** (0.17 g, 35% yield). $R_f = 0.63$ (EtOAc–hexane 1 : 10). IR (neat) 2926, 2855, 1760, 1467, 1441, 1372, 1224, 1188, 1122, 1052, 983, 790, 721 cm^{-1}; ^1H NMR $\delta = 5.26$ (ddd, $J = 13.0$, 9.4, 4.0 Hz, 1H), 2.29 (t, $J = 0.8$ Hz, 3H), 2.13 (s, 3H), 1.83—1.64 (m, 2H), 1.40—1.15 (m, 18H), 0.88 (t, $J = 6.5$ Hz, 3H); ^{19}F NMR $\delta = -86.38$ (dd, $J = 213.9$, 9.4 Hz, 1F), −87.83 (dd, $J = 213.9$, 13.0 Hz, 1F); MS *m/z* (rel intensity) 324 (M^+; 84), 289 (34), 262 (66), 216 (43), 147 (42), 111 (59), 97 (86), 55 (100). Found: *m/z* 324.1935. Calcd for $C_{16}H_{30}F_2O_2S$: M, 324.1935.

***S*-Methyl 2-Acetoxy-1-tridecanethioate (21e):** $R_f = 0.45$ (EtOAc–hexane 1 : 10). IR (neat) 2926, 2855, 1756, 1692, 1466, 1438, 1372, 1223, 1047, 929, 722, 606 cm^{-1}; ^1H NMR $\delta = 5.22$ (dd, J=7.5, 5.3 Hz, 1H), 2.29 (s, 3H), 2.17 (s, 3H), 1.91—1.72 (m, 2H), 1.45—1.16 (m, 18H), 0.88 (t, $J = 6.5$ Hz, 3H); MS *m/z* (rel intensity) 255 ($M^+ - SMe$; 100), 227 (33), 167 (45), 111 (66), 97 (84), 55 (69). Found: *m/z* 255.1962. Calcd for $C_{15}H_{27}O_3$: M−SMe, 255.1960.

Hydrolysis of 20a. A solution of sodium hydroxide (27 mg, 0.68 mmol) in a 10 : 1 mixture (6.6 ml) of ethanol-water was mixed with **20a** (0.17 g, 0.57 mmol), and the resulting mixture was stirred at room temperature for 2 h before acidification with dil hydrochloric acid and extraction 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 **22a** (0.14 g, 99% yield). $R_f = 0.38$ (EtOAc–hexane 1 : 3). IR (neat) 3419, 3054, 2935, 2360, 1599, 1515, 1436, 1398, 1355, 1233, 1155, 1048, 986, 870, 789, 741 cm^{-1}; ^1H NMR $\delta = 8.07$ (d, $J = 7.9$ Hz, 1H), 7.88—7.82 (m, 3H), 7.57—7.44 (m, 3H), 5.85 (t, $J = 8.9$ Hz, 1H), 2.89 (br s, 1H), 2.21 (t, $J = 0.8$ Hz, 3H); ^{19}F NMR $\delta = -84.90$ (dd, $J = 209.4$, 8.9 Hz, 1F), −86.06 (dd, $J = 209.4$, 8.9 Hz, 1F); MS *m/z* (rel intensity) 254 (M^+; 72), 189 (13), 170 (12), 157 (100), 139 (13), 129 (96), 77 (17). Found: *m/z* 254.0576. Calcd for $C_{13}H_{12}F_2OS$: M, 254.0577.

1,1-Difluoro-1-methylthio-2-tridecanol (22e): This alcohol (0.11 g) was obtained in 80% yield starting with **20e** (0.11 g, 0.41 mmol). $R_f = 0.30$ (EtOAc–hexane 1 : 10). IR (neat) 3405, 2926, 2855, 1466, 1458, 1441, 1377, 1321, 1179, 1127, 1046, 984, 722, 669 cm^{-1}; ^1H NMR $\delta = 3.91$—3.82 (m, 1H), 2.31 (s, 3H), 2.02 (d, $J = 5.9$ Hz, 1H), 1.73—1.48 (m, 2H), 1.46—1.18 (m, 18H), 0.88 (t, $J = 6.4$ Hz, 3H); ^{19}F NMR $\delta = -87.22$ (dd, $J = 210.6$, 9.1 Hz, 1F), −89.12 (dd, $J = 210.6$, 9.1 Hz, 1F); MS *m/z* (rel intensity) 282 (M^+; 7), 264 ($M^+ - H_2O$; 14), 216 (8), 185 (93), 111 (66), 97 (100), 83 (96), 69 (96), 55 (86). Found: *m/z* 282.1830. Calcd for $C_{14}H_{28}F_2OS$: M, 282.1829.

Reduction of 14a. Sodium borohydride (16 mg, 0.42 mmol) was added to a methanol (2 ml) solution of **14a** (96 mg, 0.38 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 20 min, poured into an aqueous solution of sodium chloride, and extracted with ethyl acetate (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 **22a** (90 mg, 93% yield).

1,1-Difluoro-1-methylthio-2-tridecanol (22e): Similarly, this alcohol (37 mg) was prepared in 93% yield from **14e** (40 mg, 0.14 mmol).

Radical Reduction of 20b. Tris(trimethylsilyl)silane (0.26 ml, 0.84 mmol) and AIBN (12 mg, 0.070 mmol) were added to a toluene (2 ml) solution of **20b** (0.11 g, 0.35 mmol) at room temperature under an argon atmosphere. The resulting mixture was stirred at 80 °C for 24 h, further heated under reflux for 3 h, and then diluted with toluene (20 ml). The resulting insoluble materials were filtered through a short silica-gel column. The filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC to give 2,2-difluoro-1-(2-naphthyl)ethyl acetate (**23b**, 49 mg, 55% yield) along with **20b** (19 mg, 18% yield). $R_f = 0.26$ (EtOAc–hexane 1 : 10), mp 44—46 °C (hexane). IR (KBr) 3063, 3002, 2359, 1740, 1374, 1233, 1124, 1091, 1078,

1034, 829, 788, 747 cm^{-1}; ^1H NMR δ = 7.89—7.82 (m, 4H), 7.55—7.49 (m, 3H), 6.28—5.71 (m, 2H), 2.19 (m, 3H); ^{19}F NMR δ = −126.91 (ddd, J = 287.8, 55.4, 11.0 Hz, 1F), −127.98 (ddd, J = 287.8, 55.4, 11.3 Hz, 1F); MS m/z (rel intensity) 250 (M^+; 47), 280 (13), 188 (71), 171 (15), 157 (100), 141 (14), 129 (48). Found: m/z 250.0804. Calcd for $C_{14}H_{12}F_2O_2$: M, 250.0805.

Radical Reduction of 14b. Tris(trimethylsilyl)silane (0.15 ml, 0.49 mmol) and AIBN (6.6 mg, 0.040 mmol) were added to a toluene (1.5 ml) solution of **14b** (0.10 g, 0.40 mmol) at room temperature under an argon atmosphere. The resulting mixture was heated under reflux for 20 h before dilution with toluene (20 ml). Insoluble materials were filtered through a short silica-gel column. The filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC to give 2-methylthio-1-(2-naphthyl)ethanone (**24b**,[26] 37 mg, 42% yield). R_f = 0.33 (EtOAc–hexane 1 : 10). IR (neat) 3046, 2904, 1668, 1660, 1618, 1590, 1462, 1285, 1277, 1118, 780 cm^{-1}; ^1H NMR δ = 8.50 (s, 1H), 8.05—7.85 (m, 4H), 7.64—7.51 (m, 2H), 3.88 (s, 2H), 2.18 (s, 3H).

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