A Facile Synthesis of Trifluoromethyl- and 3,3,3-Trifluoropropenyl-Substituted Aromatic Compounds by the Oxidative Desulfurization-Fluorination of the Corresponding Carbodithioates

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Trifluoromethyl-substituted aromatic compounds were easily synthesized by the oxidative desulfurization-fluorination reaction of readily accessible methyl arenecarbodithioates using $[n\text{-Bu}_4\text{N}]\text{H}_2\text{F}_3$ and 1,3-dibromo-5,5-dimethylhydantoin (DBH) under extremely mild conditions. Use of *N*-bromosuccinimide or *N*-iodosuccinimide instead of DBH afforded difluoro(methylthio)methyl-substituted aromatics. In a similar way, 3,3,3-trifluoropropenyl-substituted aromatic compounds were readily prepared from the corresponding α,β-unsaturated carbodithioates.

In view of increasing interest in fluorine-containing organic chemicals, the exploratory research on new fluorination methods has been attracting much attention.[1] Aromatic compounds upon functionalization by a trifluoromethyl group show higher lipophilicity and lower viscosity; these changes often induce remarkable biological activities and/or physical properties. Accordingly,[2] a variety of synthetic drugs, agrochemicals and liquid crystalline materials have been developed that contain a trifluoromethyl-substituted aromatic moiety. To facilitate the synthesis of trifluoromethyl-substituted aromatics, a regio- and chemoselective method for the introduction of a trifluoromethyl group should be established. Compounds of type Ar–CF_3 have been accessible by a transformation of Ar–C(O)OH with SF_4,[3] a halogen-exchange of Ar–CCl_3 with SbF_3[4] or HF,[5] a treatment of Ar–H with CCl_4/HF,[6] a trifluoromethylation of Ar–$C(SEt)_3$ with HF/Py and 1,3-dibromo-5,5-dimethylhydantoin (DBH),[7] or a transformation of Ar–CS_2H with XeF_2.[8] An alternative approach is a trifluoromethylation of Ar–H with an electrophilic species such as $CF_3\cdot$ or CF_3^+. This transformation is often carried out using *N*-trifluoromethyl-*N*-nitrosotrifluoromethanesulfonamide,[9] a combination of CF_3CO_2H and XeF_2,[10] bis(trifluoroacetyl)peroxide,[11] bistrifluoromethyl telluride,[12] trifluoromethanesulfonyl chloride in the presence of a ruthenium phosphine complex,[13] or *S*-(trifluoromethyl)dibenzothiophenium triflate.[14] A third method for the synthesis of Ar–CF_3 is a coupling reaction of aryl halides with a CF_3–metal reagent.[15] This method, however, suffers severe limitations such as harmful reaction conditions and use of a highly toxic and/or unstable reagent in addition to low yields and poor regioselectivities.

In addition to Ar–CF_3 type compounds, there are many agents containing a trifluoropropenyl group and exhibiting remarkable antibacterial,[16] antiviral,[17] insecticidal[18] or acaricidal[18] activity. Synthetic intermediates for the inhibitors of angiotensin converting enzyme[19] also possess such a fluorine functionality. In general, substituted 3,3,3-trifluoropropenes are prepared starting with a fluorinated building block. For instance, 1-trifluoromethylethenyllithium derived from 2-bromo-3,3,3-trifluoropropene is a versatile nucleophilic reagent for this purpose.[20] Allylic alcohols containing a *gem*-difluorovinyl moiety, prepared through a carbonyl addition of trifluorodichloroethylzinc[21] or 2,2-difluorovinyllithium,[22] gives trifluoromethyl-substituted ethenes upon treatment with diethylaminosulfur trifluoride (DAST). The cross-coupling reaction of trifluoromethylzinc iodide with vinylic halides is a straightforward method.[23] Likewise, the Wittig reaction of trifluoroacetate derivatives is a convenient procedure in some cases.[24]

From a viewpoint of synthetic economy, in general, it is desired to introduce a fluorine functionality at a late stage of a synthetic scheme. Moreover, the fluorination reaction should be performed with safety and selectivity using less toxic reagents under very mild reaction conditions.

We have recently demonstrated that the oxidative desulfurization-fluorination reaction using tetrabutylammonium dihydrogentrifluoride ($[n\text{-Bu}_4\text{N}]\text{H}_2\text{F}_3$)[25] and an *N*-halo imide oxidant is a convenient entry to the synthesis of organofluorine compounds.[26] This reaction allows us to replace C–S bond(s) with C–F bond(s) under extremely mild conditions with many functional groups intact. For example, a trifluoromethyl functional group can readily be derived from the corresponding –C(S)SR moiety. Advantages of the present method are as follows: the fluorinating agent $[n\text{-Bu}_4\text{N}]\text{H}_2\text{F}_3$ is safe, stable, and easy-to-handle and can be stored at room

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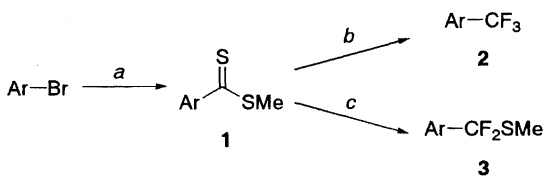
temperature for a long period. In addition, conventional glassware can be used without any special care. We have applied this reaction to methyl arenecarbodithioates Ar–C(S)-SMe and α,β-unsaturated carbodithioates (*E*)-ArCH=CRC-(S)SR′; we found that trifluoromethyl aromatic compounds Ar–CF_3 or 3,3,3-trifluoropropenyl aromatic compounds (*E*)-ArCH=CRCF_3 can readily be prepared in moderate to good yields.[27,28] In this paper we report the experimental details in addition to the scope, and the limitations of the trifluorination reaction.

Results and Discussion

Synthesis of Trifluoromethylated Aromatic Compounds by the Oxidative Desulfurization-Fluorination of Methyl Arenecarbodithioates. Aryl bromides Ar–Br were first converted into Grignard reagents Ar–MgBr. These were then treated with CS_2 and MeI to give arenecarbodithioates Ar–C(S)SMe **1** in high yields.[29] The carbodithioates **1** were readily accessible through an alternative method involving a reaction of $ArCH_2X$ and sulfur in the presence of sodium methoxide followed by a treatment with MeI.[30] When **1** were allowed to react with [*n*-Bu_4N]H_2F_3 and 1,3-dibromo-5,5-dimethylhydantoin (DBH), a trifluorination reaction took place smoothly. Trifluoromethyl aromatic compounds Ar–CF_3 **2** could be isolated in yields of synthetic use. DBH could be replaced by *N*-bromosuccinimide (NBS) or *N*-iodosuccinimide (NIS) but gave difluorination products Ar–CF_2SMe **3** (Scheme 1).

Results are summarized in Table 1. Unsubstituted starting materials or those substituted by an electron-donating group gave trifluorinated products in good yields (Runs 1, 6, 8, 11, and 14), whereas those bearing such an electron-withdrawing group as bromine gave only a complex mixture of products. In this case, the target trifluorination product was obtained by use of HF/pyridine (HF/Py, 70/30 wt%) as a fluoride ion source (Run 15). This fluoride agent was effective also for the trifluorination of **1a**; in combination with DBH, NBS, or NIS, it gave **2a** in yields of 79%, 43%, or 63%, respectively (Runs 2, 3, or 4). On the other hand, substrates containing an electron-rich aromatic ring suffered a ring bromination during the trifluoromethylation (Run 12). The starting material for Run 14 was prepared through a selective *ortho*-lithiation[31] of methoxymethyl ether of *p*-cresol, followed by the treatment with CS_2 and MeI. The example of Run 14 demonstrates that a regioselective electrophilic introduction of a trifluoromethyl group into an aromatic nucleus is readily attained by the dithiocarboxylation and the subsequent oxidative desulfurization-fluorination.

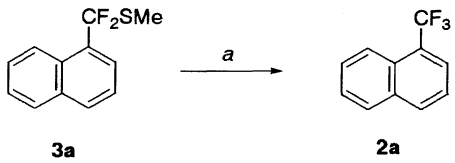


a : Mg, CS_2, MeI
b : [*n*-Bu_4N]H_2F_3 (5 mol), DBH (4 mol), CH_2Cl_2, 0 °C to rt, 1 h
c : [*n*-Bu_4N]H_2F_3 (5 mol), NBS or NIS (3 mol), CH_2Cl_2, 0 °C to rt, 1 h

Scheme 1.

Please note that difluorination products of type Ar–CF_2SMe were obtained upon treatment of the same substrates with [*n*-Bu_4N]H_2F_3 and NBS (Run 9) or NIS (Runs 5, 7, and 10). The ring bromination occurred again upon use of electron-rich substrate **1e** (Run 13).

The difluorination products, Ar–CF_2SMe, are assumed to be the precursors of Ar–CF_3. Indeed, Ar–CF_2SMe could be converted into Ar–CF_3 by DBH and [*n*-Bu_4N]H_2F_3 at higher temperatures. For example, **2a** was obtained from **3a** in 84% yield at the refluxing temperature of dichloromethane (Eq. 1).



a : [*n*-Bu_4N]H_2F_3 (2 mol), DBH (2 mol), CH_2Cl_2, 0 °C to reflux, 2 h, 84 %. (1)

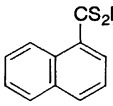
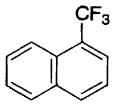
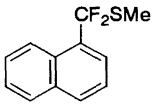
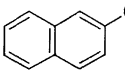
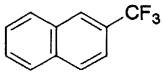
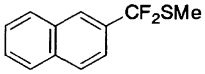
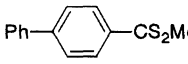
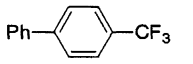
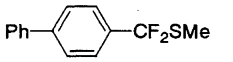
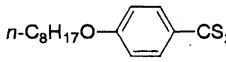
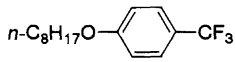
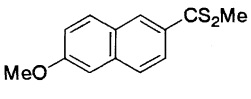
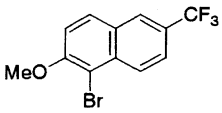
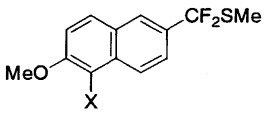
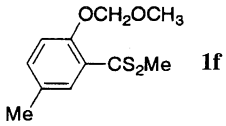
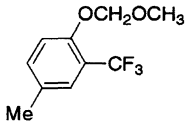
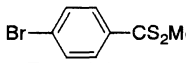
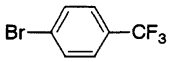
The reaction is considered to be initiated by an electrophilic reaction of positive halogen X^+ with Ar–C(S)SMe to generate Ar–C(=S^+X)SMe. Subsequent nucleophilic attack by a fluoride ion to the electrophilic carbon makes a C–F bond to give Ar–CF(SX)SMe, which is again attacked by X^+ and substituted by a fluoride ion to give a difluorination product Ar–CF_2SMe. Repeated oxidation and substitution of the sulfide bond gives trifluorination product Ar–CF_3.

Synthesis of 3,3,3-Trifluoropropenyl-Substituted Aromatic Compounds. We envisaged that when the fluorination would be applied to α,β-unsaturated carbodithioates, trifluoromethyl-substituted olefins should be produced. Thus, we studied first the preparation of various propenedithioates, requisite substrates for the fluorination reaction.

Preparation of Various Ar-Substituted Propenedithioates. Arenecarbaldehydes ArCHO were allowed to react with $LiCH_2CS_2Et$ prepared by treatment of CH_3CS_2Et with LiN(*i*-Pr)$_2$ at −78 °C,[32] affording β-hydroxy carbodithioates **4**, which were then treated with MsCl and Py (excess). Mesylation followed by elimination took place to give α,β-unsaturated carbodithioates **5** in good yields. Stereochemistry of the olefinic moiety was proved to be exclusively *E* by ^{1}H NMR (Scheme 2). Starting with terephthalaldehyde, ethyl 4-formyldithiocinnamate (**5g**) and diethyl 3,3′-(1,4-benzenediyl)bis(propenedithioate) (**5h**) were prepared. Yields and structures of **4** and **5** are summarized in Table 2. Dehydration of β-hydroxy carbodithioate **4j** derived from 3-phenylpropanal gave a complex mixture of products. All attempts to isolate **5j** failed.

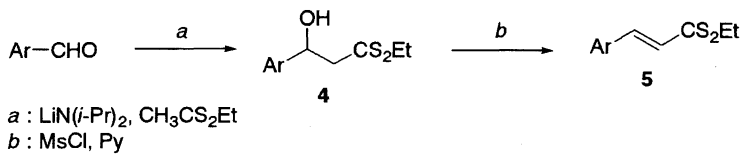
In place of CH_3CS_2Et, $PhCH_2CH_2CS_2Me$ could be employed for the aldol reaction; hereby diastereoisomeric mixtures of β-hydroxy carbodithioates were obtained in relatively lower yields (Scheme 3 and Table 3). We presume that either the lithium enolate of methyl 3-phenylpropane-

Table 1. Oxidative Desulfurination-Fluorination of Methyl Arenecarbodithioates **1**[a)]

Run	Methyl arenecarbodithioates	Oxidant	Product	Yield[b)] / %
1	 **1a**	DBH	 **2a**	63
2[c)]	**1a**	DBH	**2a**	79
3[c)]	**1a**	NBS	**2a**	43
4[c)]	**1a**	NIS	**2a**	63
5	**1a**	NIS	 **3a**	61
6	 **1b**	DBH	 **2b**	59
7	**1b**	NIS	 **3b**	52
8	 **1c**	DBH	 **2c**	52
9	**1c**	NBS	 **3c**	69
10	**1c**	NIS	**3c**	86
11	 **1d**	DBH	 **2d**	62
12	 **1e**	DBH	 **2e**	78
13	**1e**	NBS	 **3e** X=Br **3e′** (X=H)	62 19
14	 **1f**	DBH	 **2f**	71
15[d)]	 **1g**	DBH	 **2g**	82

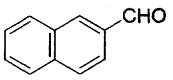
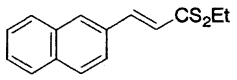
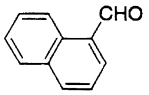
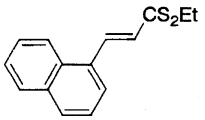
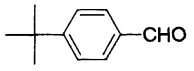
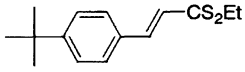
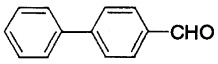
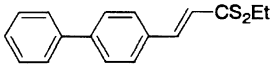
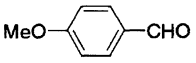
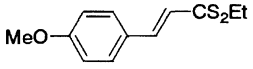
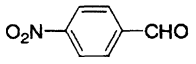
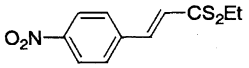
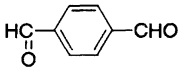
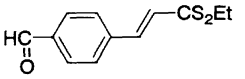
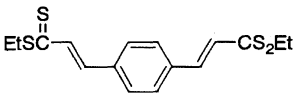
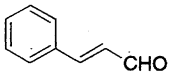
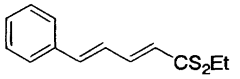
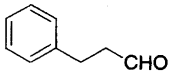
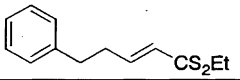
a) Substrate **1** was allowed to react with [*n*-Bu_4N]H_2F_3 (5 mol) and DBH (4 mol) or NBS (3 mol) or NIS (3 mol) in CH_2Cl_2. b) Isolated yields are given. c) HF/Py (2.3 mol, F^-: 20.8 mol) was used as a fluorinating agent. d) In place of [*n*-Bu_4N]H_2F_3, HF/Py (8.8 mol, F^-: 80 mol) was employed.

dithioate is not stable enough to undergo the aldol addition effectively or the aldol adducts are not stable under the reaction conditions. In any event, separation of erythro product **6** and threo product **7** could be carried out by the normal pressure silica-gel column chromatography. The configurations of **6** and **7** were assigned on the base of their ^{1}H NMR and ^{13}C NMR spectra. Typical NMR data also are collected in Table 3. In particular, the vicinal coupling constants be-



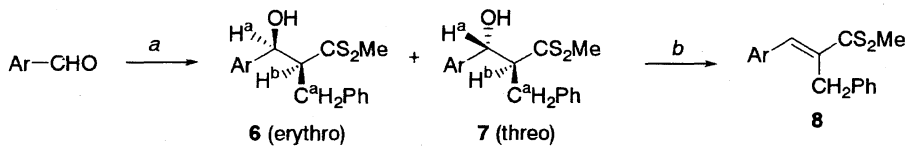
Scheme 2.

Table 2. Synthesis of Aryl-Substituted Carbodithioates **5**

Run	Ar-CHO	**4**, Yield/%	**5**	Yield/%
1		**4a**, 88		**5a**, 80
2		**4b**, 77		**5b**, 77
3		**4c**, 91		**5c**, 94
4		**4d**, 76		**5d**, 83
5		**4e**, 66		**5e**, 85
6		**4f**, 75		**5f**, 60
7		**4g**, 19		**5g**, 71
8		**4h**, 79		**5h**, 93
9		**4i**, 62		**5i**, 72
10		**4j**, 71		**5j**, —

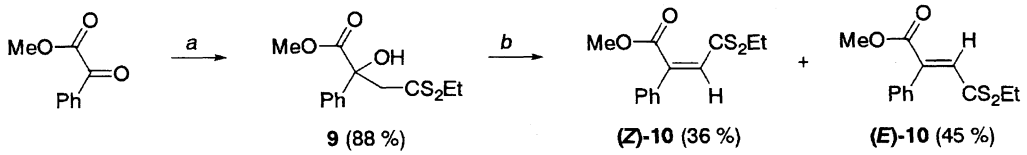
tween H^a and H^b and chemical shifts of C^a carbon were in accord with the literature values.[33] Each diastereomer was treated with MsCl and Py to give identical (*E*)-α,β-unsaturated carbodithioates **8**. The stereochemistry of the olefinic moiety in **8** was determined by ^{1}H NMR. For example, we observed 15% NOE between the benzylic methylene protons and H(2) protons of the 4-methoxyphenyl ring in **8a**.

A substrate having an electron-withdrawing group on the propenedithioate moiety was prepared as above by the aldol reaction of CH_3CS_2Et with methyl phenylglyoxylate followed by dehydration. The sequence of reactions is illustrated in Scheme 4. The resulting propenedithioate **10**



a : LiN(*i*-Pr)$_2$, $PhCH_2CH_2CS_2Me$
b : MsCl, Py

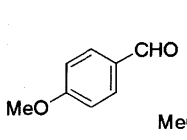
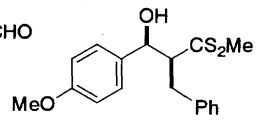
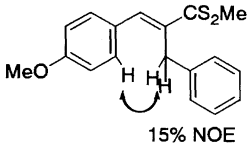
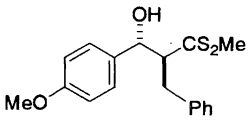
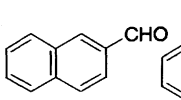
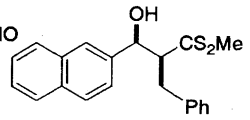
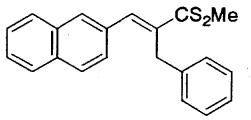
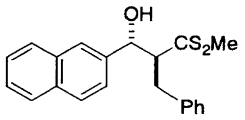
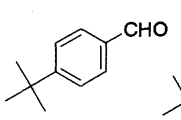
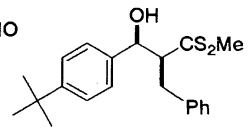
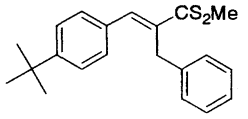
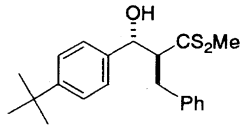
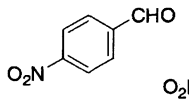
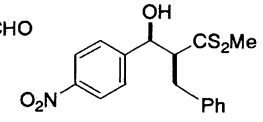
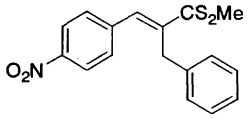
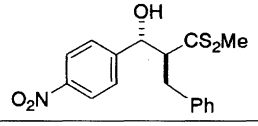
Scheme 3.



a : LiN(*i*-Pr)$_2$ (1 mol), CH_3CS_2Et (1 mol), THF, -78 °C, 11 h
b : MsCl (3 mol), Py, 0 °C to rt, 3 h

Scheme 4.

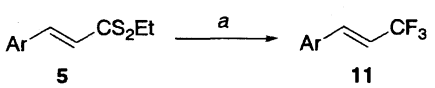
Table 3. Synthesis and NMR Data of β-Hydroxy Carbodithioates **6** and **7** and Carbodithioates **8**

Run	Ar-CHO	**6** and **7**, Yield/%	$^3J_{H^a-H^b}$/Hz	δ (C^a)	**8**, Yiled/%
1					 15% NOE
		 **6a**, 9	4.4	36.87	**8a**, 54
		7a, 14	7.2	40.54	**8a**, 49
2					
		 **6b**, 31	3.9	36.53	**8b**, 48
		7b, 24	6.4	40.69	**8b**, 15
3					
		 **6c**, 12	3.8	36.39	**8c**, 53
		7c, 27	7.2	40.49	**8c**, 37
4					
		 **6d**, 44	4.0	36.64	**8d**, 4
		7d, 12	8.3	40.57	**8d**, 12

turned out to be a 1.2 : 1 mixture of *E* and *Z* isomers.

Oxidative Desulfurization-Fluorination of Ar-Substituted Propenedithioates. When **5** were treated with [*n*-Bu_4N]H_2F_3 and NIS, trifluorination took place smoothly to give 3,3,3-trifluoropropenyl aromatic compounds **11** as shown in Scheme 5. This reaction coupled with the condensation of aldehydes Ar–CH=O with ethyl dithioacetate allows us to construct a structural moiety of Ar–CH=$CHCF_3$ readily from Ar–CH=O.

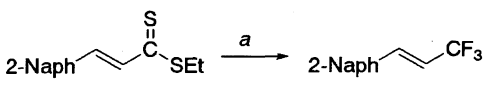
With **5a** as a model substrate (Eq. 2), we optimized the reaction time and the amounts of the two reagents as summarized in Table 4. The best chemical yield was attained when the reaction was carried out for 4 h using 6 mol of [*n*-Bu_4N]-H_2F_3 and 12 mol of NIS (Run 1). Use of greater amounts of the two reagents decreased the yield probably due to the decomposition of product **11a** (Runs 2, 3, and 4). Use of smaller amounts of the two reagents also reduced the yield of **11a**. Hereby, a sulfonium ion intermediate produced by an electrophilic attack of I^+ to **5a** might have fewer chances to be attacked by a fluoride ion (Run 5). Instead, hydrolysis of the thiocarbonyl group occurred to give *S*–alkyl thioate **12a** (see footnote of Table 4). In lieu of NIS, NBS or DBH could be employed for the fluorination, but in these cases the yields of **11a** were 14 or 7% yield, respectively, probably due to side reactions and/or tar formation. Use of HF/Py produced intractable products with no **11a**.



5 **11**

a : [*n*-Bu_4N]H_2F_3 (6 mol), NIS (12 mol), CH_2Cl_2, 0 °C to rt

Scheme 5.



5a **11a**

a : [*n*-Bu_4N]H_2F_3, NIS, CH_2Cl_2, 0 °C to rt (2)

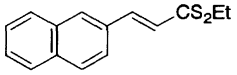
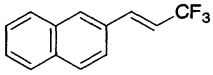
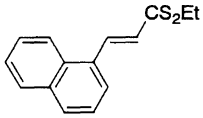
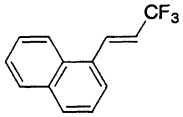
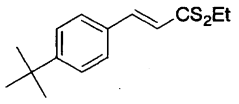
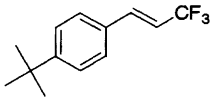
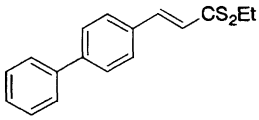
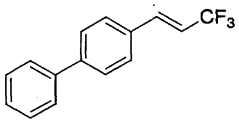
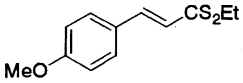
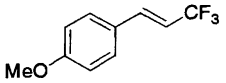
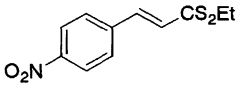
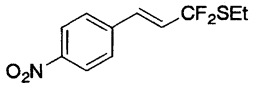
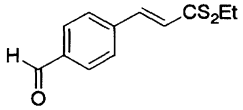
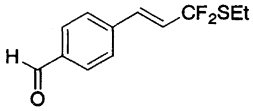
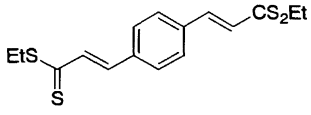
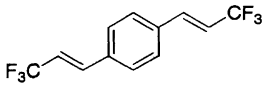
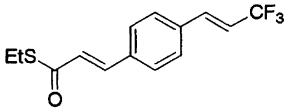
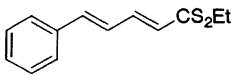
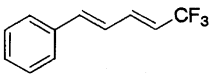
Table 4. Optimization of the Fluorination of **5a**

Run	$[n\text{-Bu}_4\text{N}]H_2F_3$	NIS	Time	Yield of **11a**
	mol	mol	h	%
1	6	12	4	72
2	5	16	3	56
3	10	10	4	48
4	10	16	2	63
5[a)]	4	5	3	12

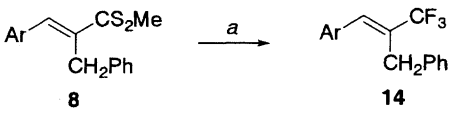
a) Major product was 2-Naphthyl–CH=CHCOSEt (**12a**) (50% yield).

The best conditions (Run 1, Table 4) were applied to various α,β-unsaturated dithiocarboxylates **5**; the results are summarized in Table 5. The substrates **5** with an *E*-configuration were converted into **11** with retention of the configuration. Please note that such side reactions as halogenation of an aromatic ring and halofluorination of the C=C bond[34)] did not take place during this transformation. With substrates whose aryl group is unsubstituted (Runs 1 and 2) or is substituted by an electron-donating group (Runs 4 and 5), the trifluorination occurred smoothly and rapidly. In contrast, substrates **5f** and **5g** substituted by an electron-withdrawing group gave difluorination products with the unprotected functional group being intact (Runs 6 and 7). Trifluorination did not take place even after prolonged reaction time or in use of the reagents in excess, due probably to the reduced electron density at the reaction center. Bifunctional substrate **5h** gave double trifluorinated product **11h** in 18% yield along with trifluorinated *S*-ethyl carbothioate **11h′** even upon use of excess amounts of the reagents (Run 8). Once one of the $-CS_2Et$ groups is trifluorinated, the remaining group is apparently deactivated to be converted into a sulfonium ion

Table 5. Oxidative Desulfurination-Fluorination of Propenedithioates **5**[a)]

Run	Propenedithioates		Time	Product		Yield[b)]
			h			%
1		**5a**	4		**11a**	72
2		**5b**	4		**11b**	40
3		**5c**	4		**11c**	55
4		**5d**	1.5		**11d**	60
5		**5e**	1		**11e**	50
6		**5f**	2		**13f**	57
7		**5g**	2		**13g**	36
8[c)]		**5h**	7		**11h**	18
					**11h′**	23
9		**5i**	1.5		**11i**	32

a) Substrate **5** was allowed to react with $[n\text{-Bu}_4\text{N}]H_2F_3$ (6 mol) and NIS (12 mol) in CH_2Cl_2. b) Isolated yields are given. c) $[n\text{-Bu}_4\text{N}]H_2F_3$ (24 mol) and NIS (48 mol) were used.



8 **14**

a : [*n*-Bu_4N]H_2F_3, NIS or NBS or DBH, CH_2Cl_2, 0 °C to rt

Scheme 6.

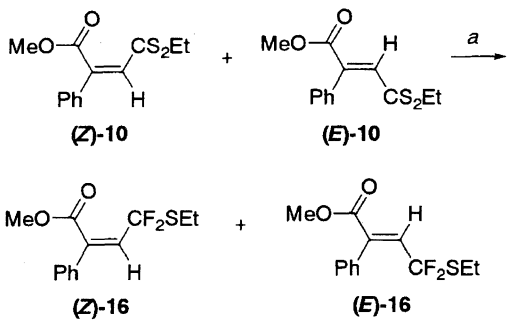
intermediate, which probably remains as such until aqueous workup. (1*E*,3*E*)-5,5,5-Trifluoro-1-phenyl-1,3-pentadiene (**11i**) was obtained in 32% yield from the corresponding 2,4-pentadienedithioate **5i** (Run 9) with the two olefinic bonds remaining unaffected.

When 2,3-disubstituted propenedithioates **8** were treated with [*n*-Bu_4N]H_2F_3 and NIS or NBS or DBH, trifluorination products **14** were isolated in good yields (Scheme 6).

The optimized reaction conditions were applied to various types of **8**; the results are summarized in Table 6. The effect of a substituent on an aromatic ring was again obvious. For substrate **8a** having an electron-donating group on Ar, NIS was found to be the best oxidant (Run 1). For substrates with a less electron-donating group, NBS, a stronger oxidant than NIS, proved to be the reagent of choice (Runs 2, 3, and 4). In contrast, it is probable that substrates substituted by an electron-withdrawing group underwent difluorination only (Runs 5, 6 and 7).

The configuration of trifluorination products **14** was assigned on the basis of their ^{1}H NMR and ^{13}C NMR spectra. Values of vicinal coupling constant ^4J(HF) = 1.6 Hz and chemical shift δ (CF_3) = −66.51 ppm are consistent with the literature data[35] for *E*-olefins.

An *E*/*Z* mixture of substrate **10** having a methoxycarbonyl group on the olefinic part was next subjected to the oxidative desulfurization-fluorination. When **10** was treated with [*n*-Bu_4N]H_2F_3 and NIS or NBS or DBH, an *E*/*Z* mixture of difluorination product **16** was isolated (Scheme 7). The results are shown in Table 7. Please note that, although substrate **10** was *E*-rich, a (*Z*)-isomer of **16** was preferentially formed. Trifluorination did not take place, probably because the es-



(*Z*)-10 **(*E*)-10**

(*Z*)-16 **(*E*)-16**

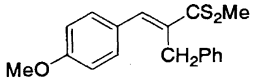
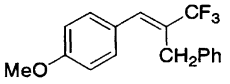
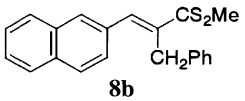
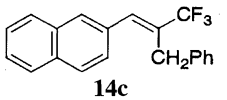
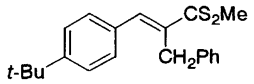
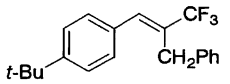
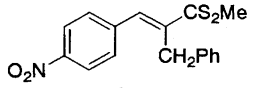
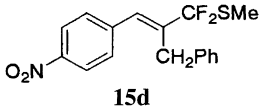
a : [*n*-Bu_4N]H_2F_3, NIS or NBS or DBH, CH_2Cl_2, 0 °C to rt

Scheme 7.

Table 7. Fluorination of **10**

Run	*Z*:*E* of **10**	Reagent (mol)	Time	Yield of (*Z*)-**16**	Yield of (*E*)-**16**
			h	%	%
1	1:1.2	[*n*-Bu_4N]H_2F_3 (6) NIS (12)	3	34	2
2	1:1.2	[*n*-Bu_4N]H_2F_3 (6) NBS (12)	1.5	30	3
3	1:1.3	[*n*-Bu_4N]H_2F_3 (5) DBH (4)	1	17	—

Table 6. Oxidative Desulfurination-Fluorination of Propenedithioates **8**[a]

Run	Propenedithioates	Reagent (mol)	Time	Product	Yield[b]
			h		%
1	 **8a**	[*n*-Bu_4N]H_2F_3 (6) NIS (12)	2.5	 **14a**	76
2	 **8b**	[*n*-Bu_4N]H_2F_3 (6) NBS (12)	1.5	 **14c**	53
3		[*n*-Bu_4N]H_2F_3 (5) DBH (4)	0.5		43
4	 **8c**	[*n*-Bu_4N]H_2F_3 (6) NBS (12)	1.2	 **14c**	65
5	 **8d**	[*n*-Bu_4N]H_2F_3 (6) NIS (12)	3	 **15d**	64
6		[*n*-Bu_4N]H_2F_3 (5) NBS (4)	3.5		61
7		[*n*-Bu_4N]H_2F_3 (5) DBH (4)	1		41

a) Substrate **8** was allowed to react with [*n*-Bu_4N]H_2F_3 and NIS or NBS or DBH in CH_2Cl_2. b) Isolated yields are given.

ter functionality reduced the reactivity of the carbodithioate moiety.

Conclusion

We have demonstrated here that the oxidative desulfurization-fluorination of methyl arenecarbodithioates Ar–CS_2Me **1** gives trifluoromethyl-substituted aromatic compounds Ar–CF_3 **2** or difluoromethyl compounds Ar–CF_2SMe **3**, depending on the kind of a positive halogen oxidant. Taking advantage of the oxidative desulfurization-fluorination disclosed here in combination with a regioselective metalation strategy for the functionalization of aromatic compounds, a trifluoromethyl group can be introduced at a designed position of aromatic substrates. In addition, substrates **5** or **8** of type α,β-unsaturated carbodithioates (*E*)-ArCH=$CRCS_2R'$ are shown to give 3,3,3-trifluoropropenyl aromatic compounds **11** or **14** of type (*E*)-ArCH=$CRCF_3$. Under similar conditions, disubstituted propenedithioates **10** of type Ar$C(CO_2Me)$=$CHCS_2Et$ give difluorination products **16** of type Ar$C(CO_2Me)$=$CHCF_2SEt$. Thus, the methodology reported in this article may find applications particularly in the synthetic studies of new drugs, agrochemicals, and electro-optical materials.

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, ^{19}F or ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker AC-200 spectrometer operating at 200, 188 or 50.3 MHz, with Me_4Si, $CFCl_3$ or $CDCl_3$ as an internal standard, respectively. Mass spectra were recorded with a Shimadzu QP-5000 GC-MS system or a VG Autospec mass spectrometer. High resolution mass spectra were obtained with a VG Autospec mass spectrometer.

Wakogel C-200 or Merck Kieselgel 60 PF_{254} was used for 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_4N]H_2F_3 was prepared as reported.[36] HF/pyridine was purchased and used without further purification

A General Procedure for the Preparation of Methyl Arenecarbodithioates. Methyl 1-Naphthalenecarbodithioate (1a): To a vigorously stirred suspension of magnesium turnings (0.27 g, 11 mmol) in tetrahydrofuran (2 ml) was added one drop of 1,2-dibromoethane under an argon atmosphere. A small portion of 1-bromonaphthalene was added to initiate the reaction. After the reaction mixture turned turbid, the remaining solution of 1-bromonaphthalene (totally, 1.4 ml, 10 mmol) in tetrahydrofuran (14 ml) was added. The reaction mixture was further heated under reflux for 1 h; then carbon disulfide (1.8 ml, 30 mmol) was added dropwise to this mixture at 0 °C. The mixture was stirred for 12 h at room temperature before methyl iodide (1.9 ml, 30 mmol) was added dropwise to the reaction mixture at 0 °C. The resulting mixture was stirred at room temperature for 5 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 **1a**[37] (2.1 g, 96% yield). R_f = 0.16 (hexane). Mp 52—54 °C (hexane) (lit,[37] mp 54 °C). IR (KBr) 3056, 2986, 1244, 1183, 1117, 1061, 1026, 1006, 894, 796, 776, 648, 633, 560 cm^{-1}; ^1H NMR δ = 8.17—8.11 (m, 1H), 7.89—7.81 (m, 2H), 7.52—7.42 (m, 4H), 2.83 (s, 3H); MS *m/z* (rel intensity) 218 (M^+; 84), 203 (52), 171 (100), 155 (22), 127 (90), 101 (68), 77 (64), 63 (54).

Methyl 2-Naphthalenecarbodithioate (1b):[38] This product (0.71 g) was obtained in 82% yield from 2-bromonaphthalene (0.83 g, 4.0 mmol). R_f = 0.21 (hexane). Mp 90—92 °C (hexane) (lit,[38] mp 91—92 °C). ^1H NMR δ = 8.53 (s, 1H), 8.16—8.10 (m, 1H), 8.00—7.80 (m, 3H), 7.61—7.51 (m, 2H), 2.84 (s, 3H);

Methyl 4-Phenyldithiobenzoate (1c): This compound (2.2 g) was isolated in 89% yield from 4-bromobiphenyl (2.3 g, 10.0 mmol). R_f = 0.17 (hexane). Mp 98—100 °C (hexane). IR (KBr) 3040, 1595, 1482, 1396, 1235, 1180, 1119, 1049, 1000, 955, 881, 839, 826, 760, 740, 723, 695 cm^{-1}; ^1H NMR δ = 8.11 (d, *J* = 8.7 Hz, 2H), 7.65—7.56 (m, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.50—7.37 (m, 3H), 2.79 (s, 3H); MS *m/z* (rel intensity) 244 (M^+; 30), 197 (100), 152 (27). Found: *m/z* 244.0382. Calcd for $C_{14}H_{12}S_2$: M, 244.0380.

Methyl 4-Octyloxydithiobenzoate (1d): This substrate (1.3 g) was generated in 84% yield from 4-bromophenyl octyl ether (1.4 g, 5.0 mmol). R_f = 0.58 (hexane). IR (neat) 2925, 2854, 1598, 1567, 1501, 1467, 1422, 1306, 1261, 1241, 1171, 1048, 961, 886, 833, 622 cm^{-1}; ^1H NMR δ = 8.08 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 2.76 (s, 3H), 1.87—1.71 (m, 2H), 1.52—1.20 (m, 10H), 0.89 (t, *J* = 6.6 Hz, 3H); MS *m/z* (rel intensity) 296 (M^+; 31), 249 (93), 233 (28), 137 (100), 121 (61), 108 (28). Found: *m/z* 296.1269. Calcd for $C_{16}H_{24}OS_2$: M, 296.1269.

Methyl 6-Methoxydithio-2-naphthoate (1e): Similarly, **1e** (2.3 g) was obtained in 91% yield from 2-bromo-6-methoxynaphthalene (2.4 g, 10.0 mmol). R_f = 0.34 (hexane). Mp 94—96 °C (hexane). IR (KBr) 2970, 2910, 1619, 1480, 1384, 1262, 1240, 1191, 1180, 1163, 1059, 1020, 960, 925, 894, 854 cm^{-1}; ^1H NMR δ = 8.52 (d, *J* = 1.9 Hz, 1H), 8.15 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.22—7.12 (m, 2H), 3.95 (s, 3H), 2.83 (s, 3H); MS *m/z* (rel intensity) 248 (M^+; 24), 232 (3), 201 (100), 185 (31), 158 (46), 114 (28). Found: *m/z* 248.0329. Calcd for $C_{13}H_{12}OS_2$: M, 248.0330.

Methyl 2-Methoxymethoxy-5-methyldithiobenzoate (1f): A solution of *n*-BuLi in hexane (1.7 ml, 1.43 M, 2.5 mmol, 1 M = 1 mol dm^{-3}) was slowly added dropwise to a stirred solution of 4-(methoxymethoxy)toluene (0.31 g, 2.0 mmol) in tetrahydrofuran (4 ml) at −10 °C under an argon atmosphere. After the solution was allowed to warm to 0 °C in 1 h, carbon disulfide (0.37 ml, 6.2 mmol) was added dropwise to this mixture at 0 °C. The mixture was stirred for 12 h at room temperature; then methyl iodide (0.19 ml, 3.1 mmol) was added dropwise to the reaction mixture at 0 °C. The mixture was stirred at room temperature for 3 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 **1f** (0.31 g, 62% yield). IR (KBr) 3070, 3000, 2952, 2930, 1722, 1620, 1593, 1561, 1500, 1458, 1381, 1361, 1339, 1261, 1220, 1182, 1158, 1108, 1082, 1047, 1020, 928, 860, 812, 781, 743 cm^{-1}; ^1H NMR δ = 7.43—7.21 (m, 3H), 5.17 (s, 2H), 3.50 (s, 3H), 2.78 (s, 3H), 2.33 (s, 3H); MS *m/z* (rel intensity) 242 (M^+; 59), 227 (85), 195 (100), 165 (75), 150 (19), 134 (16), 121 (28). Found: *m/z* 242.0436. Calcd for $C_{11}H_{14}O_2S_2$: M, 242.0435.

Methyl 4-Bromodithiobenzoate (1g):[30,39] Synthesis was car-

ried out according to the literature;[30] **1g** (47 mg) was obtained in 40% yield from 4-bromo-1-(bromomethyl)benzene (0.12 g, 0.48 mmol). Mp 51—53 °C (hexane) (lit,[39] mp 53—54 °C). ^{1}H NMR δ = 7.90 (d, J = 9 Hz, 2H), 7.56 (d, J = 9 Hz, 2H), 2.77 (s, 3H).

A Typical Procedure for Oxidative Desulfurization-Fluorination of Methyl Arenecarbodithioates. Preparation of 1-Trifluoromethylnaphthalene (2a): To a dichloromethane (3 ml) solution of **1a** (0.22 g, 1.01 mmol) and [n-Bu$_4$N]H$_2$F$_3$ (1.5 g, 5.0 mmol) was added DBH (1.2 g, 4.0 mmol) in one portion at 0 °C under an argon atmosphere; the resulting mixture was stirred at room temperature for 1 h before dilution with a 10 : 1 mixture (110 ml) of hexane and diethyl ether. The resulting insoluble materials were removed through a short silica-gel column. The effluent 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**[40] (0.12 g, 63% yield). R_f = 0.59 (hexane). IR (neat) 2950, 2830, 1724, 1583, 1516, 1380, 1357, 1316, 1260, 1207, 1180, 1120, 1064, 1021, 978, 802, 767, 734, 642 cm^{-1}; ^{1}H NMR δ = 8.42—8.16 (m, 1H), 8.00—7.76 (m, 3H), 7.67—7.41 (m, 3H); ^{19}F NMR δ = −60.22 (d, J = 1.8 Hz, 3F); MS m/z (rel intensity) 196 (M$^+$; 100), 146 (32).

1-[Difluoro(methylthio)methyl]naphthalene (3a): This product (78 mg) was synthesized in 61% yield from **1a** (0.13 g, 0.57 mmol). R_f = 0.42 (hexane). IR (neat) 3052, 2940, 1808, 1730, 1718, 1672, 1660, 1593, 1508, 1460, 1430, 1382, 1264, 1224, 1171, 1078, 1060, 900, 803, 792, 779, 620 cm^{-1}; ^{1}H NMR δ = 8.53—8.47 (m, 1H), 8.04—7.94 (m, 2H), 7.87—7.82 (m, 1H), 7.59—7.41 (m, 3H), 2.53 (s, 3H); ^{19}F NMR δ = −72.72 (s, 2F); MS m/z (rel intensity) 177 (M$^+$ − SMe; 100), 127 (20), 77 (3). Found: m/z 177.0517. Calcd for $C_{11}H_7F_2$: M − SMe, 177.0516.

2-Trifluoromethylnaphthalene (2b):[40b,41] This compound (0.12 g) was produced in 59% yield from **1b** (0.22 g, 1.0 mmol). R_f = 0.42 (hexane). Mp 63—65 °C (hexane) (lit,[40b] mp 64—66 °C). ^{1}H NMR δ = 8.11 (s, 1H), 8.06—7.81 (m, 3H), 7.63—7.46 (m, 3H); ^{19}F NMR δ = −62.72 (s, 3F).

2-[Difluoro(methylthio)methyl]naphthalene (3b): This product (58 mg) was isolated in 52% yield from **1b** (0.11 g, 0.50 mmol). R_f = 0.33 (hexane). IR (neat) 3059, 2922, 2856, 1511, 1278, 1225, 1192, 1078, 1044, 967, 922, 894, 861, 807, 744 cm^{-1}; ^{1}H NMR δ = 8.09 (s, 1H), 7.93—7.89 (m, 3H), 7.65—7.54 (m, 3H), 2.51 (s, 3H); ^{19}F NMR δ = −76.49 (s, 2F); MS m/z (rel intensity) 177 (M$^+$ − SMe; 100), 127 (18), 77 (3). Found: m/z 177.0514. Calcd for $C_{11}H_7F_2$: M − SMe, 177.0516.

4-Trifluoromethylbiphenyl (2c):[42] In a similar way, **2c** (0.12 g) was obtained in 52% yield from **1c** (0.25 g, 1.0 mmol). R_f = 0.41 (hexane). Mp 65—67 °C (hexane) (lit,[42] mp 66.0—66.5 °C). IR (KBr) 3096, 3040, 1613, 1568, 1489, 1403, 1326, 1271, 1170, 1158, 1113, 1070, 1018, 1002, 880, 841, 764, 724, 691 cm^{-1}; ^{1}H NMR δ = 7.67—7.55 (m, 6H), 7.50—7.37 (m, 3H); ^{19}F NMR δ = −62.93 (s, 3F); MS m/z (rel intensity) 222 (M$^+$; 100), 203 (16), 172 (26).

4-[Difluoro(methylthio)methyl]biphenyl (3c): This product (0.22 g) was obtained in 86% yield from **1c** (0.25 g, 1.0 mmol). R_f = 0.27 (hexane). Mp 45—47 °C (hexane). IR (KBr) 3080, 3050, 2930, 1648, 1600, 1580, 1484, 1401, 1220, 1192, 1178, 1162, 1120, 1000, 968, 912, 844, 772, 750, 728, 692 cm^{-1}; ^{1}H NMR δ = 7.66—7.57 (m, 6H), 7.50—7.41 (m, 3H), 2.52 (s, 3H); ^{19}F NMR δ = −76.56 (s, 2F); MS m/z (rel intensity) 203 (M$^+$ − SMe; 100), 183 (7), 152 (18). Found: m/z 203.0671. Calcd for $C_{13}H_9F_2$: M − SMe, 203.0672.

1-Octyloxy-4-trifluoromethylbenzene (2d): Similarly, **2d** (85 mg) was obtained in 62% yield from **1d** (0.15 g, 0.50 mmol). R_f = 0.60 (hexane). IR (neat) 2940, 2860, 1615, 1585, 1519, 1468, 1380, 1330, 1255, 1175, 1160, 1118, 1065, 831, 720. 632 cm^{-1}; ^{1}H NMR δ = 7.53 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 1,86—1.72 (m, 2H), 1.50—1.25 (m, 10H), 0.89 (t, J = 6.6 Hz, 3H); ^{19}F NMR δ = −62.00 (s); MS m/z (rel intensity) 274 (M$^+$; 88), 255 (23), 175 (18), 162 (100), 145 (46), 112 (65), 83 (54), 71 (80). Found: m/z 274.1544. Calcd for $C_{15}H_{21}F_3O$: M, 274.1545.

1- Bromo- 2- methoxy- 6- trifluoromethylnaphthalene (2e): This product (0.12 g) was formed in 78% yield from **1e** (0.12 g, 0.50 mmol). R_f = 0.19 (hexane). Mp 81—83 °C (hexane). IR (KBr) 2990, 2950, 2853, 1630, 1602, 1500, 1488, 1451, 1440, 1340, 1308, 1272, 1248, 1200, 1182, 1154, 1141, 1127, 1072, 1059, 972, 903, 855, 819, 802, 760 cm^{-1}; ^{1}H NMR δ = 8.33 (d, J = 9.2 Hz, 1H), 8.09 (s, 1H), 7.91 (d, J = 9.2 Hz, 1H), 7.71 (dd, J = 9.0, 1.5 Hz, 1H), 7.37 (d, J = 9.0 Hz, 1H), 4.07 (s, 3H); MS m/z (rel intensity) 306 (M$^+$+2; 98), 304 (M$^+$; 100), 287 (8), 285 (9), 263 (69), 261 (70), 182 (34), 175 (10), 162 (11), 132 (9). Found: m/z 303.9710. Calcd for $C_{12}H_8BrF_3O$: M, 303.9711.

1- Bromo- 6- [difluoro(methylthio)methyl]- 2- methoxynaphthalene (3e): This compound (0.10 g) was prepared in 62% yield from **1e** (0.12 g, 0.50 mmol) along with **3e′** (24 mg, 19% yield). R_f = 0.17 (hexane). Mp 98—100 °C (hexane). IR (KBr) 2970, 2950, 1624, 1600, 1492, 1438, 1274, 1240, 1180, 1061, 1030, 980, 960, 880, 818, 803 cm^{-1}; ^{1}H NMR δ = 8.29 (d, J = 8.9 Hz, 1H), 8.04 (s, 1H), 7.91 (d, J = 9.1 Hz, 1H), 7.69 (dd, J = 8.9, 1.9 Hz, 1H), 7.36 (d, J = 9.1 Hz, 1H), 4.07 (s, 3H), 2.51 (s, 3H); MS m/z (rel intensity) 287 (M$^+$+2 − SMe; 98), 285 (M$^+$ − SMe; 100), 272 (7), 270 (8), 244 (12), 242 (13), 175 (9). Found: m/z 284.9726. Calcd for $C_{12}H_8BrF_2O$: M − SMe, 284.9727.

2-[Difluoro(methylthio)methyl]-6-methoxynaphthalene (3e′): R_f = 0.21 (hexane). Mp 59—61 °C (hexane). IR (KBr) 3052, 3000, 2950, 2920, 1650, 1620, 1602, 1482, 1452, 1424, 1408, 962, 938, 900, 878, 846, 812; 783, 723 cm^{-1}; ^{1}H NMR δ = 8.01 (s, 1H), 7.84—7.77 (m, 2H), 7.58 (dd, J = 8.6, 1.7 Hz, 1H), 7.25—7.15 (m, 2H), 3.95 (s, 3H), 2.52 (s, 3H); MS m/z (rel intensity) 239 (M$^+$ − Me; 4), 220 (6), 207 (M$^+$ − SMe; 100), 189 (4), 164 (25). Found: m/z 207.0622. Calcd for $C_{12}H_9F_2O$: M − SMe, 207.0621.

1-Methoxymethoxy-4-methyl-2-trifluoromethylbenzene (2f): This product (66 mg) was synthesized in 71% yield from **1f** (0.10 g, 0.42 mmol). IR (neat) 2965, 2930, 1728, 1620, 1596, 1503, 1420, 1403, 1381, 1323, 1270, 1241, 1205, 1132, 1082, 1052, 984, 920, 884, 818, 729 cm^{-1}; ^{1}H NMR δ = 7.45—7.15 (m, 3H), 5.24 (s, 2H), 3.52 (s, 3H), 2.33 (s, 3H); MS m/z (rel intensity) 220 (M$^+$; 32), 201 (16), 188 (39), 159 (100), 119 (59), 109 (32). Found: m/z 220.0711. Calcd for $C_{10}H_{11}F_3O_2$: M, 220.0712.

Alternative Synthesis of 1-Trifluoromethylnaphthalene (2a) Using HF/Py: To a dichloromethane (1.5 ml) solution of **1a** (0.11 g, 0.50 mmol) and DBH (0.57 g, 2.0 mmol) was added dropwise HF/Py (70/30 wt%, 0.26 ml, F$^-$: 10.4 mmol) at 0 °C under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 h, 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 **2a** (78 mg, 79% yield).

4-Bromo-1-trifluoromethylbenzene (2g):[43] Using HF/Py, **2g** (92 mg) was obtained in 82% yield from **1g** (0.12 g, 0.50 mmol). IR (neat) 2928, 1920, 1721, 1658, 1650, 1490, 1400, 1322, 1168, 1130,

1101, 1072, 1060, 1012, 830, 773, 720 cm^{-1}; ^1H NMR δ = 7.64 (d, J = 8 Hz, 2H), 7.50 (d, J = 8 Hz, 2H); ^{19}F NMR δ = −63.3 (s); MS m/z (rel intensity) 226 (M^++2; 83), 224 (M^+; 85), 207 (13), 205 (13), 145 (100).

Synthesis of 1-Trifluoromethylnaphthalene (2a) from 3a: To a dichloromethane (1.5 ml) solution of **3a** (0.11 g, 0.50 mmol) and [n-Bu_4N]H_2F_3 (0.30 g, 1.0 mmol) was added DBH (0.29 g, 1.0 mmol) in one portion at 0 °C under an argon atmosphere; the resulting mixture was heated under reflux for 2 h before dilution with a 10 : 1 mixture (110 ml) of hexane and diethyl ether. The resulting insoluble materials were removed through a short silica-gel column. The effluent 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 **2a** (82 mg, 84% yield).

A General Procedure for the Preparation of β-Hydroxy Propanedithioates.[32] **Ethyl 3-Hydroxy-3-(2-naphthyl)propanedithioate (4a):** To a solution of diisopropylamine (0.56 ml, 4.0 mmol) in tetrahydrofuran (5 ml) was added a solution of n-BuLi in hexane (2.5 ml, 1.63 M, 4.0 mmol) at 0 °C under an argon atmosphere. After 10 min of stirring at 0 °C, the solution was cooled (−78 °C) and ethyl dithioacetate (0.46 ml, 4.0 mmol) was added. The mixture was stirred for 30 min at −78 °C, and 2-naphthaldehyde (0.63 g, 4.0 mmol) in tetrahydrofuran (7 ml) was added dropwise to the reaction mixture at −78 °C. The reaction mixture was stirred at −78 °C for 5 min, 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 **4a** (0.98 g, 88% yield). R_f = 0.25 (EtOAc–hexane 1 : 10). IR (neat) 3480, 2969, 2929, 1682, 1603, 1508, 1261, 1068, 976, 832, 802, 747 cm^{-1}; ^1H NMR δ = 7.83—7.78 (m, 4H), 7.51—7.43 (m, 3H), 5.44—5.36 (m, 1H), 3.44—3.37 (m, 3H), 3.21 (q, J = 7.5 Hz, 2H), 1.28 (t, J = 7.5 Hz, 3H); MS m/z (rel intensity) 276 (M^+; 17), 259 (6), 214 (35), 201 (16), 155 (100), 127 (38). Found: m/z 276.0642. Calcd for $C_{15}H_{16}OS_2$: M, 276.0643.

Ethyl 3-Hydroxy-3-(1-naphthyl)propanedithioate (4b): This product (1.3 g) was obtained in 77% yield from 1-naphthaldehyde (0.83 ml, 6.1 mmol). R_f = 0.23 (EtOAc–hexane 1 : 10). IR (neat) 3432, 3056, 2970, 2931, 1736, 1512, 1372, 1267, 1220, 1169, 1144, 1076, 1000, 927, 781 cm^{-1}; ^1H NMR δ = 8.15—8.09 (m, 1H), 7.90—7.73 (m, 3H), 7.59—7.43 (m, 3H), 6.05 (dd, J = 8.4, 2.9 Hz, 1H), 3.53—3.31 (m, 2H), 3.28 (q, J = 7.5 Hz, 2H), 1.34 (t, J = 7.5 Hz, 3H); MS m/z (rel intensity) 276 (M^+; 7), 258 (34), 214 (23), 197 (55), 165 (28), 155 (100), 128 (93), 120 (36). Found: m/z 276.0642. Calcd for $C_{15}H_{16}OS_2$: M, 276.0643.

Ethyl 3-(4-*t*-Butylphenyl)-3-hydroxypropanedithioate (4c): In a similar way, **4c** (0.56 g) was isolated in 91% yield from 4-(*t*-butyl)benzaldehyde (0.36 ml, 2.2 mmol). R_f = 0.17 (EtOAc–hexane 1 : 10). IR (neat) 3446, 2963, 2875, 1632, 1486, 1432, 1317, 1263, 1198, 1086, 1061, 942, 839 cm^{-1}; ^1H NMR δ = 7.36 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 5.26—5.18 (m, 1H), 3.35—3.19 (m, 2H), 3.24 (q, J = 7.5 Hz, 2H), 1.31 (s, 9H), 1.31 (t, J = 7.5 Hz, 3H); MS m/z (rel intensity) 282 (M^+; 18), 264 (11), 220 (48), 207 (8), 161 (100), 147 (74), 133 (17), 91 (42), 57 (57). Found: m/z 282.1112. Calcd for $C_{15}H_{22}OS_2$: M, 282.1112.

Ethyl 3-(4-Biphenylyl)-3-hydroxypropanedithioate (4d): This compound (0.70 g) was generated in 76% yield from 4-biphenylcarbaldehyde (0.56 g, 3.1 mmol). R_f = 0.10 (EtOAc–hexane 1 : 10). Mp 47—49 °C (hexane). IR (KBr) 3402, 3021, 2986, 1716, 1504, 1389, 1225, 1096, 1053, 945, 821, 768, 683 cm^{-1}; ^1H NMR δ = 7.62—7.33 (m, 9H), 5.31 (dd, J = 7.2, 4.9 Hz, 1H), 3.40—3.35 (m, 2H), 3.26 (q, J = 7.5 Hz, 2H), 1.33 (t, J = 7.5 Hz, 3H); MS m/z (rel intensity) 302 (M^+; 4), 284 (13), 240 (43), 223 (28), 181 (100), 152 (44), 120 (31), 59 (46). Found: m/z 302.0800. Calcd for $C_{17}H_{18}OS_2$: M, 302.0799.

Ethyl 3-Hydroxy-3-(4-methoxyphenyl)propanedithioate (4e): This product (0.51 g) was formed in 66% yield from 4-methoxybenzaldehyde (0.37 ml, 3.1 mmol). R_f = 0.09 (EtOAc–hexane 1 : 10). IR (neat) 3424, 2967, 2930, 2876, 1611, 1513, 1455, 1400, 1300, 1248, 1172, 1033, 833, 561 cm^{-1}; ^1H NMR δ = 7.29 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.18 (dd, J = 8.1, 4.2 Hz, 1H), 3.78 (s, 3H), 3.33—3.26 (m, 3H), 3.21 (q, J = 7.5 Hz, 2H), 1.29 (t, J = 7.5 Hz, 3H); MS m/z (rel intensity) 256 (M^+; 20), 238 (19), 194 (40), 177 (35), 135 (100), 120 (37), 77 (40), 59 (64). Found: m/z 256.0591. Calcd for $C_{12}H_{16}O_2S_2$: M, 256.0592.

Ethyl 3-Hydroxy-3-(4-nitrophenyl)propanedithioate (4f):[44] This compound (0.62 g) was produced in 75% yield from 4-nitrobenzaldehyde (0.46 g, 3.1 mmol). R_f = 0.05 (EtOAc–hexane 1 : 10). ^1H NMR δ = 8.20 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 5.37 (t, J = 6.0 Hz, 1H), 3.31 (d, J = 6.0 Hz, 2H), 3.24 (q, J = 7.5 Hz, 2H), 1.32 (t, J = 7.5 Hz, 3H).

Ethyl 3-(4-Formylphenyl)-3-hydroxypropanedithioate (4g): To a solution of diisopropylamine (0.31 ml, 2.2 mmol) in tetrahydrofuran (2 ml) was added a solution of n-BuLi in hexane (1.4 ml, 1.57 M, 2.2 mmol) (1 M = 1 mol dm^{-3}) at 0 °C under an argon atmosphere. After 10 min of stirring at 0 °C, the solution was cooled (−78 °C) and ethyl dithioacetate (0.25 ml, 2.2 mmol) was added. The mixture was stirred for 30 min at −78 °C, and terephthalaldehyde (0.15 g, 1.1 mmol) in tetrahydrofuran (7 ml) was added dropwise to the reaction mixture at −78 °C. The reaction mixture was stirred at −78 °C for 10 min, 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 **4g** (53 mg, 19% yield) along with **4h** (0.30 g, 79% yield). R_f = 0.26 (EtOAc–hexane 1 : 3). IR (neat) 3430, 2967, 2922, 2833, 1698, 1608, 1578, 1389, 1306, 1211, 1168, 1067, 1035, 928, 831 cm^{-1}; ^1H NMR δ = 9.99 (s, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 5.37—5.30 (m, 1H), 3.61 (d, J = 3.1 Hz, 1H), 3.34—3.30 (m, 2H), 3.23 (q, J = 7.5 Hz, 2H), 1.31 (t, J = 7.5 Hz, 3H); MS m/z (rel intensity) 254 (M^+; 47), 236 (82), 221 (13), 208 (34), 192 (79), 147 (95), 133 (98), 120 (81), 77 (83), 59 (100). Found: m/z 254.0436. Calcd for $C_{12}H_{14}O_2S_2$: M, 254.0435.

Diethyl 3,3′-(1,4-Phenylene)bis(3-hydroxypropanedithioate) (4h): R_f = 0.17 (EtOAc–hexane 1 : 3). Mp 73—75 °C (hexane). IR (KBr) 3268, 3222, 2974, 2947, 1453, 1217, 1202, 1134, 1068, 1019, 968, 837, 575 cm^{-1}; ^1H NMR δ = 7.38 (s, 4H), 5.24 (dd, J = 7.4, 4.7 Hz, 2H), 3.33—3.23 (m, 6H), 3.24 (q, J = 7.4 Hz, 4H), 1.32 (t, J = 7.4 Hz, 6H); MS m/z (rel intensity) 374 (M^+; 2), 356 (4), 338 (12), 254 (44), 236 (64), 192 (73), 147 (84), 133 (97), 120 (85), 59 (100). Found: m/z 374.0504. Calcd for $C_{16}H_{22}O_2S_4$: M, 374. 0503.

Ethyl (*E*)-3-Hydroxy-5-phenyl-4-pentenedithioate (4i): This substance (0.34 g) was synthesized in 62% yield from *trans*-cinnamaldehyde (0.28 ml, 2.2 mmol). R_f = 0.16 (EtOAc–hexane 1 : 10). IR (neat) 3422, 2967, 2922, 1672, 1494, 1450, 1407, 1261, 1217, 1150, 1050, 967, 928, 850, 750, 694, 667 cm^{-1}; ^1H NMR δ = 7.40—7.22 (m, 5H), 6.66 (d, J = 15.9 Hz, 1H), 6.23 (dd, J = 15.9, 6.0 Hz, 1H), 4.85 (dd, J = 11.7, 6.0 Hz, 1H), 3.28—3.24 (m, 2H), 3.23 (q, J = 7.5 Hz, 2H), 1.31 (t, J = 7.5 Hz, 3H); MS m/z (rel intensity) 252 (M^+;

15), 234 (13), 219 (14), 190 (47), 173 (16), 131 (100), 103 (34), 59 (42). Found: *m/z* 252.0642. Calcd for $C_{13}H_{16}OS_2$: M, 252.0643.

Ethyl 3-Hydroxy-5-phenylpentanedithioate (4j): This carbodithioate (0.55 g) was prepared in 71% yield from 3-phenylpropanal (0.27 ml, 3.1 mmol). R_f = 0.22 (EtOAc–hexane 1 : 10). IR (neat) 3444, 3025, 2927, 2831, 1674, 1496, 1454, 1183, 1052, 942, 821, 749, 700 cm^{-1}; ^1H NMR δ = 7.33—7.12 (m, 5H), 4.21—4.06 (m, 1H), 3.23 (q, J = 7.5 Hz, 2H), 3.22—3.00 (m, 3H), 2.92—2.63 (m, 2H), 1.90—1.77 (m, 2H), 1.32 (t, J = 7.5 Hz, 3H); MS *m/z* (rel intensity) 254 (M^+; 27), 192 (19), 133 (34), 105 (43), 91 (100). Found: *m/z* 254.0799. Calcd for $C_{13}H_{18}OS_2$: M, 254.0799.

A General Procedure for the Preparation of Propenedithioates. Ethyl (*E*)-3-(2-Naphthyl)propenedithioate (5a): Methanesulfonyl chloride (0.09 ml, 1.2 mmol) was added to a solution of **4a** (0.11 g, 0.40 mmol) in pyridine (0.3 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred at room temperature for 20 min, poured into sat. NH_4Cl aq solution, 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 **5a** (84 mg, 80% yield). R_f = 0.56 (EtOAc–hexane 1 : 10). IR (neat) 3054, 2968, 2925, 1668, 1599, 1508, 1448, 1373, 1264, 962, 938, 859, 818, 747 cm^{-1}; ^1H NMR δ = 8.01—7.68 (m, 6H), 7.53—7.45 (m, 3H), 3.38 (q, J = 7.4 Hz, 2H), 1.39 (t, J = 7.4 Hz, 3H); MS *m/z* (rel intensity) 258 (M^+; 50), 229 (9), 197 (100), 165 (20), 152 (22), 127 (4). Found: *m/z* 258.0536. Calcd for $C_{15}H_{14}S_2$: M, 258.0537.

Ethyl (*E*)-3-(1-Naphthyl)propenedithioate (5b): This product (0.13 g) was obtained in 77% yield from **4b** (0.18 g, 0.65 mmol). R_f = 0.63 (EtOAc–hexane 1 : 10). Mp 27—29 °C (hexane). IR (KBr) 3042, 2965, 2920, 1670, 1595, 1511, 1445, 1395, 1373, 1251, 1184, 982, 940, 775 cm^{-1}; ^1H NMR δ = 8.64 (d, J = 15.3 Hz, 1H), 8.26—8.21 (m, 1H), 7.92—7.80 (m, 3H), 7.63—7.40 (m, 4H), 3.39 (q, J = 7.4 Hz, 2H), 1.43 (t, J = 7.4 Hz, 3H); MS *m/z* (rel intensity) 258 (M^+; 63), 229 (13), 197 (100), 165 (54), 152 (45). Found: *m/z* 258.0538. Calcd for $C_{15}H_{14}S_2$: M, 258.0537.

Ethyl (*E*)-3-(4-*t*-Butylphenyl)propenedithioate (5c): This compound (0.22 g) was isolated in 94% yield from **4c** (0.25 g, 0.89 mmol). R_f = 0.67 (EtOAc–hexane 1 : 10). Mp 40—42 °C (hexane). IR (KBr) 2963, 2886, 1670, 1583, 1522, 1483, 1338, 1246, 1116, 1034, 978, 863 cm^{-1}; ^1H NMR δ = 7.77 (d, J = 15.5 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 15.5 Hz, 1H), 3.35 (q, J = 7.4 Hz, 2H), 1.38 (t, J = 7.4 Hz, 3H), 1.33 (s, 9H); MS *m/z* (rel intensity) 264 (M^+; 52), 231 (7), 207 (54), 187 (16), 179 (28), 147 (76), 57 (100). Found: *m/z* 264.1005. Calcd for $C_{15}H_{20}S_2$: M, 264.1006.

Ethyl (*E*)-3-(4-Biphenylyl)propenedithioate (5d): Similarly, **5d** (61 mg) was generated in 83% yield from **4d** (78 mg, 0.26 mmol). R_f = 0.49 (EtOAc–hexane 1 : 10). Mp 55—57 °C (hexane). IR (KBr) 3019, 2994, 2983, 1658, 1492, 1472, 1231, 1016, 968, 848, 752, 721 cm^{-1}; ^1H NMR δ = 7.82 (d, J = 15.5 Hz, 1H), 7.70—7.60 (m, 6H), 7.50—7.37 (m, 4H), 3.37 (q, J = 7.4 Hz, 2H), 1.39 (t, J = 7.4 Hz, 3H); MS *m/z* (rel intensity) 284 (M^+; 72), 251 (13), 223 (100), 189 (17), 178 (24), 165 (26). Found: *m/z* 284.0695. Calcd for $C_{17}H_{16}S_2$: M, 284.0693.

Ethyl (*E*)-3-(4-Methoxyphenyl)propenedithioate (5e): This product (0.16 g) was synthesized in 85% yield from **4e** (0.20 g, 0.79 mmol). R_f = 0.43 (EtOAc–hexane 1 : 10). IR (neat) 2963, 2931, 2831, 1670, 1611, 1506, 1456, 1306, 1256, 1173, 1112, 1034, 940, 829, 785 cm^{-1}; ^1H NMR δ = 7.77 (d, J = 15.4 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 15.4 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 3.35 (q, J = 7.4 Hz, 2H), 1.37 (t, J = 7.4 Hz, 3H); MS *m/z* (rel intensity) 238 (M^+; 43), 210 (13), 177 (100), 162 (12), 145 (7), 134 (27). Found: *m/z* 238.0487. Calcd for $C_{12}H_{14}OS_2$: M, 238.0486.

Ethyl (*E*)-3-(4-Nitrophenyl)propenedithioate (5f):[44] This compound (0.14 g) was obtained in 60% yield from **4f** (0.24 g, 0.90 mmol). R_f = 0.42 (EtOAc–hexane 1 : 10). Mp 110—111 °C (hexane) (lit,[44] mp 110 °C). ^1H NMR δ = 8.24 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 15.5 Hz, 1H), 7.73 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 15.5 Hz, 1H), 3.37 (q, J = 7.4 Hz, 2H), 1.40 (t, J = 7.4 Hz, 3H); MS *m/z* (rel intensity) 253 (M^+; 23), 192 (25), 162 (41), 146 (100), 102 (64), 62 (81).

Ethyl (*E*)-3-(4-Formylphenyl)propenedithioate (5g): This propenedithioate (0.16 g) was produced in 71% yield from **4g** (0.23 g, 0.92 mmol). R_f = 0.30 (EtOAc–hexane 1 : 10). Mp 45—47 °C (hexane). IR (KBr) 2973, 2929, 2829, 1708, 1698, 1605, 1573, 1427, 1388, 1305, 1211, 1166, 939, 906, 833 cm^{-1}; ^1H NMR δ = 10.03 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 15.6 Hz, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 15.6 Hz, 1H), 3.36 (q, J = 7.4 Hz, 2H), 1.39 (t, J = 7.4 Hz, 3H); MS *m/z* (rel intensity) 236 (M^+; 22), 208 (8), 189 (51), 174 (22), 161 (100), 147 (41), 105 (57), 77 (49). Found: *m/z* 236.0331. Calcd for $C_{12}H_{12}OS_2$: M, 236.0330.

Diethyl (2*E*,2′*E*)-3,3′-(1,4-Phenylene)bis(propenedithioate) (5h): Methanesulfonyl chloride (0.10 ml, 1.3 mmol) was added to a solution of **4h** (0.12 g, 0.31 mmol) in pyridine (0.4 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred at room temperature for 10 min, poured into sat. NH_4Cl aq solution, 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 **5h** (98 mg, 93% yield). R_f = 0.33 (EtOAc–hexane 1 : 10). Mp 96—98 °C (hexane). IR (KBr) 2978, 2922, 1606, 1414, 1394, 1322, 1271, 1225, 1172, 958, 947, 821 cm^{-1}; ^1H NMR δ = 7.74 (d, J = 15.5 Hz, 2H), 7.61 (s, 4H), 7.39 (d, J = 15.5 Hz, 2H), 3.36 (q, J = 7.4 Hz, 4H), 1.39 (t, J = 7.4 Hz, 6H); MS *m/z* (rel intensity) 338 (M^+; 54), 309 (21), 277 (20), 236 (58), 215 (38), 171 (31), 147 (100). Found: *m/z* 338.0293. Calcd for $C_{16}H_{18}S_4$: M, 338.0291.

Ethyl (2*E*,4*E*)-5-Phenyl-2,4-pentadienedithioate (5i): This substance (79 mg) was produced in 72% yield from **4i** (0.12 g, 0.47 mmol). R_f = 0.63 (EtOAc–hexane 1 : 10). IR (neat) 3026, 2976, 2925, 1678, 1582, 1494, 1448, 1373, 1262, 1179, 963, 934, 749, 696 cm^{-1}; ^1H NMR δ = 7.65—7.32 (m, 6H), 7.10—6.80 (m, 3H), 3.33 (q, J = 7.4 Hz, 2H), 1.36 (t, J = 7.4 Hz, 3H); MS *m/z* (rel intensity) 234 (M^+; 88), 205 (14), 173 (100), 157 (12), 128 (36), 115 (27). Found: *m/z* 234.0538. Calcd for $C_{13}H_{14}S_2$: M, 234.0537.

Methyl *erythro*-2-Benzyl-3-hydroxy-3-(4-methoxyphenyl)-propanedithioate (6a): To a solution of diisopropylamine (0.42 ml, 3.0 mmol) in tetrahydrofuran (4 ml) was added a solution of *n*-BuLi in hexane (1.9 ml, 1.60 M, 3.0 mmol) at 0 °C under an argon atmosphere. After 10 min of stirring at 0 °C, the solution was cooled (−78 °C); then methyl 3-phenylpropanedithioate (0.59 g, 3.0 mmol) in tetrahydrofuran (4 ml) was added. The mixture was stirred for 30 min at −78 °C; 4-methoxybenzaldehyde (0.37 ml, 3.0 mmol) in tetrahydrofuran (4 ml) was added dropwise to the reaction mixture at −78 °C. The resulting mixture was stirred at −78 °C for 10 min, 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 **6a** (93 mg, 9% yield) along with **7a** (0.14 g, 14% yield). R_f = 0.10 (EtOAc–hexane 1 : 10). IR (neat) 3444, 3006, 2956, 2933, 1738, 1614, 1515, 1456, 1261, 1178,

1044, 933, 833, 750, 701 cm^{-1}; ^1H NMR δ = 7.34 (d, J = 8.8 Hz, 2H), 7.18—7.10 (m, 3H), 7.01—6.96 (m, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.03 (d, J = 4.4 Hz, 1H), 3.80 (s, 3H), 3.74 (dt, J = 10.0, 4.4 Hz, 1H), 3.35—3.13 (m, 2H), 2.39 (s, 3H); ^{13}C NMR δ = 206.65, 159.00, 139.20, 133.58, 128.95, 128.07, 127.61, 126.06, 113.65, 76.18, 69.58, 55.22, 36.87, 19.58; MS *m/z* (rel intensity) 332 (M^+; 1), 314 (1), 267 (12), 196 (76), 149 (31), 135 (84), 115 (50), 91 (100). Found: *m/z* 332.0906. Calcd for $C_{18}H_{20}O_2S_2$: M, 332.0905.

Methyl *threo*-2-Benzyl-3-hydroxy-3-(4-methoxyphenyl)propanedithioate (7a): R_f = 0.05 (EtOAc–hexane 1 : 10). IR (neat) 3434, 2956, 2911, 2833, 1736, 1610, 1513, 1456, 1249, 1178, 1036, 928, 834, 750, 700 cm^{-1}; ^1H NMR δ = 7.28 (d, J = 8.7 Hz, 2H), 7.24—7.01 (m, 5H), 6.87 (d, J = 8.7 Hz, 2H), 4.99 (d, J = 7.2 Hz, 1H), 3.87—3.73 (m, 1H), 3.79 (s, 3H), 3.18—2.81 (m, 2H), 2.44 (s, 3H); ^{13}C NMR δ = 207.04, 159.18, 138.52, 134.05, 128.92, 128.15, 127.65, 126.27, 113.77, 76.84, 69.00, 55.20, 40.54, 19.72; MS *m/z* (rel intensity) 332 (M^+; 2), 314 (63), 267 (66), 196 (91), 149 (64), 135 (96), 115 (82), 91 (100). Found: *m/z* 332.0904. Calcd for $C_{18}H_{20}O_2S_2$: M, 332.0905.

Methyl *erythro*-2-Benzyl-3-hydroxy-3-(2-naphthyl)propanedithioate (6b): This product (64 mg) was prepared in 31% yield from 2-naphthaldehyde (0.11 g, 0.58 mmol) along with **7b** (50 mg, 24% yield). R_f = 0.27 (EtOAc–hexane 1 : 10). IR (neat) 3436, 3056, 3027, 2911, 1732, 1602, 1494, 1456, 1372, 1239, 1158, 1045, 922, 820, 751, 700 cm^{-1}; ^1H NMR δ = 7.93 (s, 1H), 7.88—7.80 (m, 3H), 7.55—7.45 (m, 3H), 7.17—7.08 (m, 3H), 6.97—6.92 (m, 2H), 5.25 (d, J = 3.9 Hz, 1H), 3.89 (dt, J = 10.8, 3.7 Hz, 1H), 3.64 (br. s, 1H), 3.41—3.11 (m, 2H), 2.39 (s, 3H); ^{13}C NMR δ = 207.23, 139.00, 138.68, 133.19, 132.91, 128.93, 128.16, 128.12, 128.06, 127.63, 126.11, 126.08, 125.91, 125.56, 124.21, 76.42, 69.04, 36.53, 19.62; MS *m/z* (rel intensity) 352 (M^+; 1), 334 (2), 234 (16), 196 (81), 156 (89), 127 (87), 115 (66), 91 (100). Found: *m/z* 352.0956. Calcd for $C_{21}H_{20}OS_2$: M, 352.0956.

Methyl *threo*-2-Benzyl-3-hydroxy-3-(2-naphthyl)propanedithioate (7b): R_f = 0.19 (EtOAc–hexane 1 : 10). IR (neat) 3444, 3056, 3028, 2922, 1730, 1606, 1511, 1456, 1370, 1256, 1156, 1033, 939, 822, 750, 700 cm^{-1}; ^1H NMR δ = 7.84—7.79 (m, 4H), 7.50—7.43 (m, 3H), 7.26—7.06 (m, 5H), 5.18 (d, J = 6.4 Hz, 1H), 3.95 (dt, J = 9.0, 6.1 Hz, 1H), 3.21—2.93 (m, 2H), 2.39 (s, 3H); ^{13}C NMR δ = 207.66, 139.37, 138.41, 133.13, 132.99, 129.00, 128.23, 128.17, 128.02, 127.63, 126.38, 126.14, 125.93, 125.64, 124.06, 76.94, 68.42, 40.69, 19.70; MS *m/z* (rel intensity) 352 (M^+; 2), 334 (4), 293 (7), 196 (55), 156 (81), 127 (83), 115 (64), 91 (100). Found: *m/z* 352.0955. Calcd for $C_{21}H_{20}OS_2$: M, 352.0956.

Methyl *erythro*-2-Benzyl-3-(4-*t*-butylphenyl)-3-hydroxypropanedithioate (6c): This compound (74 mg) was obtained in 12% yield from 4-(*t*-butyl)benzaldehyde (0.34 g, 1.7 mmol) along with **7c** (0.17 g, 27% yield). R_f = 0.23 (EtOAc–hexane 1 : 10). Mp 85—87 °C (hexane). IR (KBr) 3493, 2966, 1468, 1263, 1235, 1121, 1024, 913, 883, 836, 752, 702 cm^{-1}; ^1H NMR δ = 7.40—7.31 (m, 5H), 7.19—7.08 (m, 2H), 6.99—6.94 (m, 2H), 5.05 (d, J = 3.8 Hz, 1H), 3.86—3.74 (m, 1H), 3.47 (br. s, 1H), 3.36—3.10 (m, 2H), 2.39 (s, 3H), 1.32 (s, 9H); ^{13}C NMR δ = 207.32, 150.42, 139.17, 138.26, 128.92, 128.01, 126.03, 125.99, 125.12, 76.12, 69.14, 36.39, 34.46, 31.31, 19.52; MS *m/z* (rel intensity) 358 (M^+; 11), 310 (8), 293 (12), 267 (41), 196 (63), 163 (57), 147 (100), 115 (59), 91 (68). Found: *m/z* 358.1424. Calcd for $C_{21}H_{26}OS_2$: M, 358.1425.

Methyl *threo*-2-Benzyl-3-(4-*t*-butylphenyl)-3-hydroxypropanedithioate (7c): R_f = 0.11 (EtOAc–hexane 1 : 10). Mp 92—94 °C (hexane). IR (KBr) 3508, 2981, 1471, 1273, 1248, 1117, 1026, 921, 893, 831, 748, 707 cm^{-1}; ^1H NMR δ = 7.40—7.27 (m, 5H), 7.23—7.11 (m, 2H), 7.05—7.00 (m, 2H), 5.03 (dd, J = 7.2, 5.0 Hz, 1H), 3.90—3.78 (m, 1H), 3.11—2.77 (m, 2H), 2.45 (s, 3H), 1.31 (s, 9H); ^{13}C NMR δ = 207.78, 150, 89, 138.76, 138.52, 128.91, 128.11, 126.35, 126.21, 125.33, 77.40, 68.82, 40.49, 34.50, 31.30, 19.70; MS *m/z* (rel intensity) 358 (M^+; 1), 340 (1), 267 (11), 196 (54), 162 (30), 147 (100), 115 (42), 91 (92). Found: *m/z* 358.1425. Calcd for $C_{21}H_{26}OS_2$: M, 358.1425.

Methyl *erythro*-2-Benzyl-3-hydroxy-3-(4-nitrophenyl)propanedithioate (6d): This substance (0.25 g) was synthesized in 44% yield from 4-nitrobenzaldehyde (0.32 g, 1.6 mmol) along with **7d** (0.12 g, 21% yield). R_f = 0.27 (EtOAc–hexane 1 : 5). IR (neat) 3437, 3011, 2974, 1728, 1605, 1520, 1347, 1158, 1075, 863, 742, 701 cm^{-1}; ^1H NMR δ = 8.20 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 8.9 Hz, 2H), 7.22—7.12 (m, 3H), 6.97—6.92 (m, 2H), 5.18 (d, J = 4.0 Hz, 1H), 3.76 (dt, J = 10.5, 3.9 Hz, 1H), 3.35—3.01 (m, 2H), 2.43 (s, 3H); ^{13}C NMR δ = 207.98, 148.67, 138.25, 130.42, 128.85, 128.18, 127.32, 126.34, 123.43, 75.47, 68.56, 36.64, 19.66; MS *m/z* (rel intensity) 347 (M^+; 2), 329 (4), 293 (12), 196 (60), 151 (49), 115 (55), 91 (100). Found: *m/z* 347.0651. Calcd for $C_{17}H_{17}NO_3S_2$: M, 347.0650.

Methyl *threo*-2-Benzyl-3-hydroxy-3-(4-nitrophenyl)propanedithioate (7d): R_f = 0.22 (EtOAc–hexane 1 : 5). IR (neat) 3420, 3014, 2987, 1716, 1612, 1523, 1327, 1156, 1085, 883, 764, 717 cm^{-1}; ^1H NMR δ = 8.14 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 8.9 Hz, 2H), 7.33—7.17 (m, 5H), 5.02 (dd, J = 8.3, 4.9 Hz, 1H), 4.22 (d, J = 8.5 Hz, 1H), 3.83 (dt, J = 4.9, 7.4 Hz, 1H), 3.21—3.15 (m, 2H), 2.39 (s, 3H); ^{13}C NMR δ = 208.52, 149.63, 137.75, 129.04, 128.48, 127.31, 126.83, 126.75, 123.28, 74.61, 67.27, 40.57, 19.63; MS *m/z* (rel intensity) 347 (M^+; 2), 329 (6), 256 (17), 196 (48), 147 (47), 115 (68), 91 (100). Found: *m/z* 347.0651. Calcd for $C_{17}H_{17}NO_3S_2$: M, 347.0650.

Methyl (*E*)-2-Benzyl-3-(4-methoxyphenyl)propenedithioate (8a): Methanesulfonyl chloride (0.07 ml, 0.84 mmol) was added to a solution of **6a** (93 mg, 0.28 mmol) in pyridine (0.4 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred at room temperature for 1.5 h, poured into sat. NH_4Cl aq solution, 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 **8a** (47 mg, 54% yield). R_f = 0.39 (EtOAc–hexane 1 : 10). IR (neat) 3022, 2911, 2833, 1606, 1511, 1453, 1306, 1257, 1178, 1157, 1067, 1033, 950, 894, 828, 733, 700 cm^{-1}; ^1H NMR δ = 7.84 (s, 1H), 7.36 (d, J = 8.9 Hz, 2H), 7.29—7.18 (m, 5H), 6.86 (d, J = 8.9 Hz, 2H), 4.45 (s, 2H), 3.80 (s, 3H), 2.65 (s, 3H); MS *m/z* (rel intensity) 314 (M^+; 80), 299 (9), 283 (10), 267 (98), 234 (27), 189 (32), 121 (50), 91 (100). Found: *m/z* 314.0798. Calcd for $C_{18}H_{18}OS_2$: M, 314.0799.

Methyl (*E*)-2-Benzyl-3-(2-naphthyl)propenedithioate (8b): In a similar way, **8b** (19 mg) was obtained in 48% yield from **6b** (42 mg, 0.12 mmol). R_f = 0.41 (EtOAc–hexane 1 : 10). Mp 37—39 °C (hexane). IR (KBr) 3068, 3033, 2986, 1670, 1499, 1483, 1175, 1098, 970, 735, 716 cm^{-1}; ^1H NMR δ = 7.93 (s, 1H), 7.87—7.67 (m, 5H), 7.51—7.41 (m, 3H), 7.33—7.13 (m, 4H), 4.47 (s, 2H), 2.64 (s, 3H); MS *m/z* (rel intensity) 334 (M^+; 34), 318 (25), 302 (23), 287 (24), 271 (100), 254 (35), 211 (36), 155 (36), 91 (97). Found: *m/z* 334.0849. Calcd for $C_{21}H_{18}S_2$: M, 334.0850.

Methyl (*E*)-2-Benzyl-3-(4-*t*-butylphenyl)propenedithioate (8c): This product (37 mg) was obtained in 53% yield from **6c** (73 mg, 0.20 mmol). R_f = 0.64 (EtOAc–hexane 1 : 10). Mp 67—69 °C (hexane). IR (KBr) 2974, 1661, 1587, 1512, 1499, 1471, 1183, 1072, 964, 935, 884 cm^{-1}; ^1H NMR δ = 7.82 (s, 1H), 7.35 (s, 4H), 7.32—7.18 (m, 5H), 4.44 (s, 2H), 2.64 (s, 3H), 1.30 (s, 9H); MS *m/z* (rel intensity) 340 (M^+; 48), 325 (5), 283 (98), 235

(64), 149 (46), 91 (58), 57 (100). Found: *m/z* 340.1321. Calcd for $C_{21}H_{24}S_2$: M, 340.1319.

Methyl (*E*)-2-Benzyl-3-(4-nitrophenyl)propenedithioate (8d): This product (10 mg) was isolated in 12% yield from **7d** (83 mg, 0.24 mmol). R_f = 0.36 (EtOAc–hexane 1 : 10). Mp 93—95 °C (hexane). IR (KBr) 3033, 1691, 1617, 1561, 1519, 1492, 1389, 1347, 1183, 1142, 1066, 887, 703 cm^{-1}; ^1H NMR δ = 8.19 (d, J = 8.8 Hz, 2H), 7.67 (s, 1H), 7.52 (d, J = 8.8 Hz, 2H), 7.30—7.15 (m, 5H), 4.34 (s, 2H), 2.67 (s, 3H); MS *m/z* (rel intensity) 329 (M^+; 96), 314 (4), 282 (83), 235 (37), 202 (24), 91 (100). Found: *m/z* 329.0546. Calcd for $C_{17}H_{15}NO_2S_2$: M, 329.0544.

Ethyl 3-Hydroxy-3-methoxycarbonyl-3-phenylpropanedithioate (9): To a solution of diisopropylamine (0.43 ml, 3.1 mmol) in tetrahydrofuran (2 ml) was added a solution of *n*-BuLi in hexane (1.9 ml, 1.60 M, 3.1 mmol) at 0 °C under an argon atmosphere. After 10 min of stirring at 0 °C, the solution was cooled (−78 °C); then ethyl dithioacetate (0.35 ml, 3.1 mmol) was added. The mixture was stirred for 30 min at −78 °C; methyl phenylglyoxylate (0.44 ml, 3.1 mmol) in tetrahydrofuran (5 ml) was added dropwise to the reaction mixture at −78 °C. The reaction mixture was stirred at −78 °C for 11 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 **9** (0.76 g, 88% yield). R_f = 0.46 (EtOAc–hexane 1 : 5). IR (neat) 3495, 2984, 2961, 1732, 1448, 1231, 1198, 1167, 1145, 1085, 963, 700 cm^{-1}; ^1H NMR δ = 7.66—7.61 (m, 2H), 7.36—7.28 (m, 3H), 4.76 (s, 1H), 4.00 (d, J = 15.3 Hz, 1H), 3.73 (s, 3H), 3.53 (d, J = 15.3 Hz, 1H), 3.20 (q, J = 7.5 Hz, 2H), 1.29 (t, J = 7.5 Hz, 3H); MS *m/z* (rel intensity) 284 (M^+; 19), 225 (9), 120 (18), 105 (100), 77 (37), 59 (21). Found: *m/z* 284.0541. Calcd for $C_{13}H_{16}O_3S_2$: M, 284.0541.

Ethyl (*Z*)-3-Methoxycarbonyl-3-phenylpropenedithioate ((*Z*)-10): Methanesulfonyl chloride (0.29 ml, 3.8 mmol) was added to a solution of **9** (0.36 g, 1.3 mmol) in pyridine (1.4 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred at room temperature for 3 h, poured into sat. NH_4Cl aq solution, 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 (*Z*)-**10** (0.12 g, 36% yield) along with its (*E*)-isomer (0.15 g, 45% yield). R_f = 0.38 (EtOAc–hexane 1 : 10). IR (neat) 2978, 2947, 1732, 1597, 1440, 1433, 1372, 1250, 1202, 1178, 1067, 1006, 960, 922, 696 cm^{-1}; ^1H NMR δ = 7.55—7.26 (m, 6H), 3.80 (s, 3H), 3.10 (q, J = 7.4 Hz, 2H), 1.12 (t, J = 7.4 Hz, 3H); MS *m/z* (rel intensity) 266 (M^+; 100), 251 (93), 235 (10), 205 (85), 177 (58), 145 (54), 102 (51), 75 (67). Found: *m/z* 266.0437. Calcd for $C_{13}H_{14}O_2S_2$: M, 266.0435.

Ethyl (*E*)-3-Methoxycarbonyl-3-phenylpropenedithioate ((*E*)-10): R_f = 0.38 (EtOAc–hexane 1 : 10). IR (neat) 2969, 2947, 1731, 1597, 1438, 1433, 1373, 1248, 1202, 1177, 1065, 1003, 960, 925, 696 cm^{-1}; ^1H NMR δ = 7.54—7.28 (m, 5H), 7.05 (s, 1H), 3.83 (s, 3H), 3.28 (q, J = 7.4 Hz, 2H), 1.35 (t, J = 7.4 Hz, 3H); MS *m/z* (rel intensity) 266 (M^+; 100), 251 (98), 235 (14), 223 (21), 205 (95), 191 (32), 177 (69), 145 (63), 102 (58). Found: *m/z* 266.0436. Calcd for $C_{13}H_{14}O_2S_2$: M, 266.0435.

A Typical Procedure for the Oxidative Desulfurization-Fluorination of Propenedithioates. Preparation of (*E*)-3,3,3-Trifluoro-1-(2-naphthyl)propene (11a): To a dichloromethane (4 ml) solution of **5a** (0.15 g, 0.58 mmol) and $[n\text{-}Bu_4N]H_2F_3$ (1.1 g, 3.5 mmol) was added NIS (1.6 g, 7.0 mmol) in one portion at 0 °C under an argon atmosphere; the resulting mixture was stirred at room temperature for 4 h before dilution with a 10 : 1 mixture (110 ml) of hexane and diethyl ether. The resulting insoluble materials were removed through a short silica-gel column. The effluent 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 **11a**[45] (93 mg, 72% yield). R_f = 0.64 (EtOAc–hexane 1 : 10). Mp 108—110 °C (hexane) (lit,[45] mp 108—108.5 °C). IR (KBr) 3080, 1665, 1299, 1281, 1133, 1108, 965, 961, 833, 716 cm^{-1}; ^1H NMR δ = 7.88—7.82 (m, 4H), 7.62—7.48 (m, 3H), 7.32 (dq, J = 16.1, 2.1 Hz, 1H), 6.32 (dq, J = 16.1, 6.6 Hz, 1H); ^{19}F NMR δ = −63.69 (dd, J = 6.6, 2.1 Hz, 3F); MS *m/z* (rel intensity) 222 (M^+; 100), 201 (79), 183 (32), 172 (43), 152 (90), 111 (30), 101 (36), 76 (73). Found: *m/z* 222.0655. Calcd for $C_{13}H_9F_3$: M, 222.0656.

***S*-Ethyl (*E*)-3-(2-Naphthyl)propenethioate (12a):** R_f = 0.30 (EtOAc–hexane 1 : 10). Mp 61—63 °C (hexane). IR (KBr) 3006, 2981, 1668, 1607, 1248, 1096, 1083, 1068, 970, 824, 796, 737 cm^{-1}; ^1H NMR δ = 7.96 (s, 1H), 7.89—7.63 (m, 5H), 7.54—7.48 (m, 2H), 6.82 (d, J = 15.8 Hz, 1H), 3.04 (q, J = 7.4 Hz, 2H), 1.34 (t, J = 7.4 Hz, 3H); MS *m/z* (rel intensity) 242 (M^+; 33), 181 (100), 176 (8), 152 (46), 127 (14), 76 (7). Found: *m/z* 242.0764. Calcd for $C_{15}H_{14}OS$: M, 242.0765.

(*E*)-3,3,3-Trifluoro-1-(1-naphthyl)propene (11b):[45] This product (17 mg) was synthesized as an oil in 40% yield from **5b** (51 mg, 0.20 mmol). R_f = 0.66 (EtOAc–hexane 1 : 10). IR (neat) 3064, 2983, 1662, 1510, 1397, 1352, 1307, 1276, 1128, 969, 869, 795, 774, 674, 592 cm^{-1}; ^1H NMR δ = 8.07—7.82 (m, 4H), 7.65—7.44 (m, 4H), 6.27 (dq, J = 15.9, 6.5 Hz, 1H); ^{19}F NMR δ = −63.94 (dd, J = 6.5, 2.3 Hz, 3F); MS *m/z* (rel intensity) 222 (M^+; 100), 201 (23), 183 (15), 170 (6), 153 (98). Found: *m/z* 222.0658. Calcd for $C_{13}H_9F_3$: M, 222.0656.

(*E*)-1-(4-*t*-Butylphenyl)-3,3,3-trifluoropropene (11c): In a similar way, **6c** (55 mg) was prepared in 55% yield from **5c** (0.12 g, 0.44 mmol). R_f = 0.56 (hexane). Mp 28—30 °C (hexane). IR (KBr) 2970, 2929, 1666, 1514, 1386, 1335, 1314, 1274, 1216, 1132, 1107, 977, 850, 816, 650 cm^{-1}; ^1H NMR δ = 7.40 (s, 4H), 7.12 (dq, J = 16.1, 2.2 Hz, 1H), 6.16 (dq, J = 16.1, 6.6 Hz, 1H), 1.32 (s, 9H); ^{19}F NMR δ = −63.66 (dd, J = 6.6, 2.2 Hz, 3F); MS *m/z* (rel intensity) 228 (M^+; 22), 213 (100), 185 (68), 151 (10), 128 (18), 115 (23). Found: *m/z* 228.1127. Calcd for $C_{13}H_{15}F_3$: M, 228.1126.

(*E*)-1-(4-Biphenylyl)-3,3,3-trifluoropropene (11d): This product (32 mg) was obtained in 60% yield from **5d** (60 mg, 0.21 mmol). R_f = 0.51 (EtOAc–hexane 1 : 10). Mp 109—111 °C (hexane). IR (KBr) 3083, 2961, 1664, 1362, 1334, 1315, 1283, 1184, 1107, 968, 764, 625 cm^{-1}; ^1H NMR δ = 7.64—7.36 (m, 9H), 7.19 (dq, J = 16.1, 2.1 Hz, 1H), 6.23 (dq, J = 16.1, 6.5 Hz, 1H); ^{19}F NMR δ = −63.73 (dd, J = 6.5, 2.1 Hz, 3F); MS *m/z* (rel intensity) 248 (M^+; 100), 227 (14), 198 (13), 178 (58), 152 (27). Found: *m/z* 248.0814. Calcd for $C_{15}H_{11}F_3$: M, 248.0813.

(*E*)-3,3,3-Trifluoro-1-(4-methoxyphenyl)propene (11e):[45] This substance (35 mg) was isolated in 50% yield from **5e** (82 mg, 0.34 mmol). R_f = 0.46 (EtOAc–hexane 1 : 10). Mp 37—39 °C (hexane) (lit,[45] mp 37—37.5 °C). IR (KBr) 3018, 2882, 1665, 1607, 1515, 1283, 1258, 1188, 1137, 1101, 975, 811 cm^{-1}; ^1H NMR δ = 7.39 (d, J = 8.7 Hz, 2H), 7.08 (dq, J = 16.1, 2.0 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.06 (dq, J = 16.1, 6.6 Hz, 1H), 3.83 (s, 3H); ^{19}F NMR δ = −63.36 (dd, J = 6.6, 2.0 Hz, 3F); MS *m/z* (rel intensity) 202 (M^+; 100), 187 (10), 151 (7), 139 (7), 109 (23). Found: *m/z* 202.0606. Calcd for $C_{10}H_9F_3O$: M, 202.0606.

(*E*)-3-Ethylthio-3,3-difluoro-1-(4-nitrophenyl)propene (13f): Similarly, **13f** (38 mg) was generated in 57% yield from **5f** (65 mg, 0.26 mmol). R_f = 0.42 (EtOAc–hexane 1 : 10). IR (neat) 2978, 2933, 1655, 1599, 1522, 1347, 1272, 1179, 1111, 1028, 989, 970, 866, 764, 688 cm^{-1}; ^1H NMR δ = 8.23 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.04 (dt, J = 16.1, 2.3 Hz, 1H), 6.46 (dt, J = 16.1, 9.3 Hz, 1H), 2.92 (q, J = 7.5 Hz, 2H), 1.35 (t, J = 7.5 Hz, 3H); ^{19}F NMR δ = −72.78 (dd, J = 9.3, 2.3 Hz, 2F); MS *m/z* (rel intensity) 259 (M^+; 20), 198 (98), 181 (15), 176 (18), 152 (100), 102 (14). Found: *m/z* 259.0479. Calcd for $C_{11}H_{11}F_2NO_2S$: M, 259.0479.

This difluorination product (12 mg) was isolated in 36% yield from **5g** (31 mg, 0.13 mmol). R_f = 0.31 (EtOAc–hexane 1 : 10). IR (neat) 2965, 2931, 1702, 1664, 1606, 1511, 1323, 1306, 1256, 1156, 1112, 1051, 1029, 829, 701 cm^{-1}; ^1H NMR δ = 10.02 (s, 1H), 7.89 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.03 (dt, J = 16.1, 2.3 Hz, 1H), 6.45 (dt, J = 16.1, 9.4 Hz, 1H), 2.91 (q, J = 7.5 Hz, 2H), 1.38 (t, J = 7.5 Hz, 3H); ^{19}F NMR δ = −72.47 (dd, J = 9.4, 2.3 Hz, 2F); MS *m/z* (rel intensity) 242 (M^+; 17), 181 (100), 159 (40), 153 (83), 133 (97), 103 (19). Found: *m/z* 242.0575. Calcd for $C_{12}H_{12}F_2OS$: M, 242.0577.

1,4-Bis[(*E*)-3,3,3-trifluoropropenyl]benzene (11h): To a dichloromethane (4 ml) solution of **5h** (70 mg, 0.21 mmol) and [*n*-$Bu_4N]H_2F_3$ (1.5 g, 5.0 mmol) was added NIS (2.2 g, 9.9 mmol) in one portion at 0 °C under an argon atmosphere; the resulting mixture was stirred at room temperature for 7 h before dilution with a 10 : 1 mixture (110 ml) of hexane and diethyl ether. Workup and purification by preparative TLC gave **11h** (10 mg, 18% yield) along with **11h′** (13 mg, 23% yield). R_f = 0.34 (EtOAc–hexane 1 : 10). Mp 61—63 °C (hexane). IR (KBr) 2958, 2922, 1669, 1302, 1276, 1198, 1125, 970, 763, 662 cm^{-1}; ^1H NMR δ = 7.48 (s, 4H), 7.15 (dq, J = 16.2, 2.1 Hz, 2H), 6.25 (dq, J = 16.2, 6.4 Hz, 2H); ^{19}F NMR δ = −64.00 (dd, J = 6.4, 2.1 Hz, 6F); MS *m/z* (rel intensity) 266 (M^+; 100), 247 (43), 228 (2), 197 (50), 177 (78), 151 (53). Found: *m/z* 266.0532. Calcd for $C_{12}H_{18}F_6$: M, 266.0532.

***S*-Ethyl 3-{4-[(*E*)-3,3,3-Trifluoropropen-1-yl]phenyl}-(*E*)-propenethioate (11h′):** R_f = 0.43 (EtOAc–hexane 1 : 10). Mp 74—76 °C (hexane). IR (KBr) 2996, 2972, 1667, 1615, 1421, 1313, 1281, 1118, 1109, 1023, 968, 803, 762, 685 cm^{-1}; ^1H NMR δ = 7.58 (d, J = 15.8 Hz, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.15 (dq, J = 16.2, 2.2 Hz, 1H), 6.73 (d, J = 15.8 Hz, 1H), 6.25 (dq, J = 16.2, 6.5 Hz, 1H), 3.03 (q, J = 7.4 Hz, 2H), 1.33 (t, J = 7.4 Hz, 3H); ^{19}F NMR δ = −63.97 (dd, J = 6.5, 2.2 Hz, 3F); MS *m/z* (rel intensity) 286 (M^+; 9), 225 (100), 197 (13), 177 (11), 151 (8), 128 (12). Found: *m/z* 286.0638. Calcd for $C_{14}H_{13}F_3OS$: M, 286.0639.

(1*E*,3*E*)-5,5,5-Trifluoro-1-phenyl-1,3-pentadiene (11i):[22,45,46] This product (13 mg) was synthesized in 32% yield from **5i** (48 mg, 0.21 mmol). R_f = 0.68 (EtOAc–hexane 1 : 10). Mp 34—35 °C (hexane) (lit,[45] mp 34—35 °C). IR (KBr) 3138, 2963, 1727, 1650, 1441, 1365, 1278, 1246, 1114, 990, 956, 740 cm^{-1}; ^1H NMR δ = 7.47—7.27 (m, 5H), 7.00—6.75 (m, 3H), 5.80 (dq, J = 15.1, 7.2 Hz, 1H); ^{19}F NMR δ = −62.73 (dd, J = 7.2, 1.3 Hz, 3F); MS *m/z* (rel intensity) 198 (M^+; 23), 177 (9), 164 (4), 129 (100), 115 (6), 77 (14), 63 (17). Found: *m/z* 198.0657. Calcd for $C_{11}H_9F_3$: M, 198.0656.

(*E*)-2-Benzyl-3,3,3-trifluoro-1-(4-methoxyphenyl)propene (14a): This trifluoropropene (19 mg) was synthesized in 76% yield from **8a** (27 mg, 0.09 mmol). R_f = 0.49 (EtOAc–hexane 1 : 10). IR (neat) 2968, 2935, 1657, 1607, 1514, 1454, 1303, 1259, 1183, 1157, 1102, 1051, 978, 911, 829, 732, 698 cm^{-1}; ^1H NMR δ = 7.30—7.20 (m, 8H), 6.85 (d, J = 8.9 Hz, 2H), 3.85 (s, 2H), 3.79 (s, 3H); ^{19}F NMR δ = −66.51 (d, J = 1.6 Hz, 3F); ^{13}C NMR δ = 160.01, 137.63, 134.12 (q, J = 6.1 Hz), 130.55, 128.57, 127.94, 127.58, 126.45, 126.25, 125.69, 122.14, 55.24, 32.13; MS *m/z* (rel intensity) 292 (M^+; 100), 279 (16), 273 (16), 223 (33), 167 (23), 149 (44), 115 (24). Found: *m/z* 292.1074. Calcd for $C_{17}H_{15}F_3O$: M, 292.1075.

(*E*)-2-Benzyl-3,3,3-trifluoro-1-(2-naphthyl)propene (14b): This product (24 mg) was obtained in 53% yield from **8b** (48 mg, 0.14 mmol). R_f = 0.46 (EtOAc–hexane 1 : 10). IR (neat) 3018, 2930, 1672, 1622, 1581, 1496, 1454, 1308, 1291, 1183, 1147, 1117, 1048, 920, 819, 751, 730, 698 cm^{-1}; ^1H NMR δ = 7.83—7.68 (m, 4H), 7.50—7.39 (m, 4H), 7.31—7.21 (m, 5H), 3.91 (s, 2H); ^{19}F NMR δ = −66.43 (d, J = 1.6 Hz, 3F); MS *m/z* (rel intensity) 312 (M^+; 97), 297 (14), 271 (14), 234 (80), 184 (50), 165 (100), 128 (69), 115 (99), 91 (89). Found: *m/z* 312.1125. Calcd for $C_{20}H_{15}F_3$: M, 312.1126.

(*E*)-2-Benzyl-1-(4-*t*-butylphenyl)-3,3,3-trifluoropropene (14c): This compound (11 mg) was prepared in 65% yield from **8c** (18 mg, 0.05 mmol). R_f = 0.72 (EtOAc–hexane 1 : 10). Mp 51—53 °C (hexane). IR (KBr) 2964, 1668, 1347, 1326, 1306, 1273, 1228, 1211, 1154, 1110, 1051, 966, 910, 731, 696 cm^{-1}; ^1H NMR δ = 7.38—7.19 (m, 10H), 3.86 (s, 2H), 1.30 (s, 9H); ^{19}F NMR δ = −66.52 (d, J = 1.7 Hz, 3F); MS *m/z* (rel intensity) 318 (M^+; 92), 303 (98), 262 (23), 225 (65), 197 (65), 183 (83), 165 (61), 103 (100). Found: *m/z* 318.1595. Calcd for $C_{20}H_{21}F_3$: M, 318.1595.

(*E*)-2-Benzyl-3-ethylthio-3,3-difluoro-1-(4-nitrophenyl)-propene (15d): This product (22 mg) was generated in 64% yield from **8d** (34 mg, 0.10 mmol). R_f = 0.36 (EtOAc–hexane 1 : 10). IR (neat) 3031, 2931, 2854, 1728, 1600, 1517, 1501, 1346, 1167, 1040, 968, 796, 746, 697 cm^{-1}; ^1H NMR δ = 8.14 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.34—7.15 (m, 6H), 3.85 (s, 2H), 2.33 (s, 3H); ^{19}F NMR δ = −77.31 (d, J = 1.5 Hz, 2F); MS *m/z* (rel intensity) 335 (M^+; 11), 287 (100), 242 (47), 221 (46), 165 (47), 149 (45), 127 (85), 91 (70). Found: *m/z* 335.0792. Calcd for $C_{17}H_{15}F_2NO_2S$: M, 335.0792.

Methyl (*Z*)-4-Ethylthio-4,4-difluoro-2-phenyl-2-propenoate ((*Z*)-16): To a dichloromethane (1.5 ml) solution of (*Z*)-**10** (25 mg, 0.10 mmol) and (*E*)-**10** (31 mg, 0.12 mmol) and *n*-$Bu_4NH_2F_3$ (0.38 g, 1.3 mmol) was added NIS (0.57 g, 2.5 mmol) in one portion at 0 °C under an argon atmosphere; the resulting mixture was stirred at room temperature for 3 h before dilution with a 10 : 1 mixture (110 ml) of hexane and diethyl ether. Workup followed by preparative TLC gave (*Z*)-**16** (19 mg, 34% yield) along with (*E*)-**16** (2 mg, 2% yield). R_f = 0.36 (EtOAc–hexane 1 : 10). IR (neat) 2958, 2934, 1728, 1643, 1497, 1435, 1357, 1253, 1200, 1059, 991, 936, 756, 706 cm^{-1}; ^1H NMR δ = 7.41—7.23 (m, 5H), 6.99 (t, J = 11.5 Hz, 1H), 3.77 (s, 3H), 2.78 (q, J = 7.5 Hz, 2H), 1.25 (t, J = 7.5 Hz, 3H); ^{19}F NMR δ = −68.73 (d, J = 11.5 Hz, 2F); MS *m/z* (rel intensity) 272 (M^+; 22), 241 (8), 211 (100), 183 (74), 151 (47), 102 (30), 81 (50). Found: *m/z* 272.0683. Calcd for $C_{13}H_{14}F_2O_2S$: M, 272.0683.

Methyl (*E*)-4-Ethylthio-4,4-difluoro-2-phenyl-2-propenoate ((*E*)-16): R_f = 0.36 (EtOAc–hexane 1 : 10). IR (neat) 2958, 2935, 1727, 1646, 1497, 1438, 1357, 1252, 1200, 1059, 993, 936, 758, 707 cm^{-1}; ^1H NMR δ = 7.38—7.24 (m, 5H), 6.08 (t, J = 11.6 Hz, 1H), 3.87 (s, 3H), 2.91 (q, J = 7.5 Hz, 2H), 1.35 (t, J = 7.5 Hz, 3H); ^{19}F NMR δ = −71.24 (d, J = 11.6 Hz, 2F); MS *m/z* (rel intensity) 272 (M^+; 13), 241 (7), 211 (100), 183 (75), 151 (43), 102 (26), 81 (46). Found: *m/z* 272.0683. Calcd for $C_{13}H_{14}F_2O_2S$: M, 272.0683.

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