A Convenient Synthesis of Trifluoromethyl Ethers by Oxidative Desulfurization–Fluorination of Dithiocarbonates

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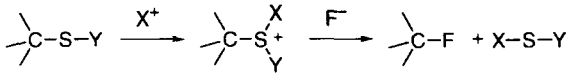
Trifluoromethyl ethers R-OCF_3 are easily synthesized from the corresponding dithiocarbonates R–OCS_2Me (R = aryl or primary alkyl) by a reagent system consisting of 70% HF/pyridine and an *N*-halo imide. When the reaction is applied to R–OCS_2Me wherein R = secondary alkyl, tertiary alkyl, or benzylic group, fluorination leading to the corresponding alkyl fluorides R–F is achieved, whereas a combination of 50% HF/pyridine and *N*-bromosuccinimide affords the corresponding trifluoromethyl ethers R–OCF_3 (R = secondary).

Introduction of a fluorine functional group to pharmaceuticals or agrochemicals often brings enhancement of activity due to increase of lipophilicity and/or dipole moment.[1] In addition, physical properties of materials are improved by fluorine functionality.[2] Accordingly, organofluorine compounds have attracted much attention in the pharmaceutical and material science fields. Since organofluorine compounds are extremely rare in nature, fluorination is the only accessible way to obtain these compounds.[3] For the synthesis of fluorine-containing target molecules, introduction of fluorine atom(s) at the desired position of a molecule is preferably carried out at a late stage of synthesis, because the anomalous reactivity of organofluorine compounds often inhibits conventional synthetic transformations.[4] Moreover, fluorination reagents and fluorinated starting materials are generally expensive. Therefore, exploitation of mild, efficient, and selective fluorination reactions with common reagents has been one of research topics in synthetic organofluorine chemistry.[3]

The oxidative desulfurization–fluorination reaction recently disclosed by us transforms organosulfur compounds to the corresponding organofluorine compounds through replacement of C–S bond(s) with C–F bond(s).[5] The reaction using an *N*-halo imide and a fluoride source provides with organofluorine compounds under extremely mild conditions with many functional groups being intact (Fig. 1). According to the present method, trifluoromethyl-substituted aromatics[6] and trifluoromethylamines[7] are readily accessible. Due to high chemical stability, high lipophilicity, high oxygen solubility, and low toxicity, trifluoromethyl ethers[8] have found many applications in liquid crystalline materials,[9] biologically active compounds,[1a,1b] and artificial blood substitutes.[10]



X^+: halonium ion from an *N*-halo imide

F^-: from $TBAH_2F_3$, $Et_3N/3HF$, 50-70% HF/Py, or 80% HF/melamine

Fig. 1. Schematic illustration of *oxidative desulfurization–fluorination*.

Aryl trifluoromethyl ethers have been prepared by i) fluorination of aryl trichloromethyl ethers with $SbF_3/SbCl_5$[11] or HF,[12] ii) trifluoromethylation of phenols with CCl_4/HF,[13] or iii) fluorination of aryl fluoroformate or -thioformate with SF_4[14] or MoF_6,[15] respectively. Alkyl trifluoromethyl ethers, though relatively ineffectively, have also been synthesized by i) the reaction of alkenes with CF_3OF,[16] ii) electrophilic trifluoromethylation of alcohols by treatment with *O*-(trifluoromethyl)dibenzofuranium salts,[17] or iii) fluorination of alkyl fluoroformates with SF_4.[18] All of these methods employ toxic and/or explosive reagents such as hydrogen fluoride, SF_4, and/or CF_3OF under special conditions. The methods thus suffer from problems including difficult accessibility of starting materials and low chemoselectivity. These drawbacks have hampered the flexibility in design of trifluoromethoxy-substituted agents and materials.

We have recently demonstrated that the oxidative desulfurization-fluorination of dithiocarbonates using *N*-halo imides and 70% HF/pyridine (HF/Py)[19] or 80% HF/melamine complexes[20] is a convenient entry to trifluoromethyl ethers. For example, it is extremely effective that the transformation can be performed by a readily available reagent system consisting of HF/Py and an *N*-halo imide. Furthermore,

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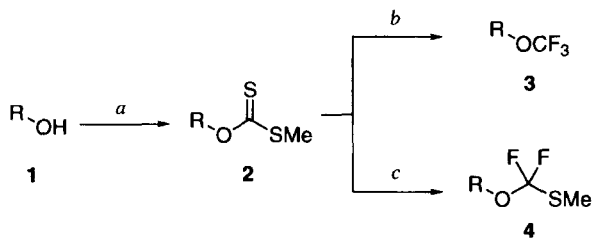
according to the method, we can prepare primary- and secondary-aliphatic and aryl trifluoromethyl ethers with many functional groups being intact.[8,9b] In this paper we report the experimental details of the trifluoromethyl ether synthesis.

Results and Discussion

Oxidative Desulfurization–Fluorination of Dithiocarbonates Derived from Aromatic and Primary Aliphatic Alcohols: Synthesis of Trifluoromethyl Ethers and Difluoro(methylthio)methyl Ethers. Dithiocarbonates, the substrates of the oxidative desulfurization-fluorination, were easily obtained in high yields by treatment of the corresponding phenols or alcohols **1** with sodium hydride (NaH), CS_2, and then with MeI.[21] Oxidative desulfurization–fluorination of dithiocarbonates **2** was carried out using 70% HF/Py[19] or tetrabutylammonium dihydrogentrifluoride ($TBAH_2F_3$)[22] with an *N*-halo imide as shown in Scheme 1. When the reaction was performed with 70% HF/Py as a fluoride source, the fluorination proceeded effectively to give trifluoromethyl ethers **3**, whereas use of $TBAH_2F_3$ afforded difluoro(methylthio)methyl ethers **4** as a sole product. Fluorinated ethers **4** have no precedents. The results are summarized in Table 1.

We first studied the optimization of the fluorination conditions using *S*-methyl *O*-4-propylphenyl dithiocarbonate (**2a**) as a substrate. For an *N*-halo imide, we first tested 1,3-dibromo-5,5-dimethylhydantoin (DBH) or *N*-bromosuccinimide (NBS), that was already shown to be effective oxidants for the transformation.[7] Substrate **2a** was treated with NBS (3 mol) and 70% HF/Py (80 mol) in dichloromethane to give **3a** in 16% yield (Entry 1). Use of DBH improved the yield to 58%. The reaction performed with DBH (5 mol) achieved the trifluoromethylation, but was accompanied by mono- and dibromination of the phenyl ring in **3a**; these products could not be separated (Entry 3). The reaction carried out with HF/Py (40 mol) was not accompanied by bromination and gave **3a** in 81% yield as a sole product. Use of HF/Py (20 mol) also promoted the reaction without ring bromination, though less efficiently.

The conditions in Entry 2 for the trifluoromethyl ether synthesis were applied to various kinds of dithiocarbonates derived from phenols, and the corresponding aryl trifluoromethyl ethers **3** were readily obtained in moderate-to-high yields (Entries 10, 14, 17, 19, 21, 24, and 25). For this transformation, exactly theoretical amounts of DBH (3 mol) should be used to avoid aromatic bromination by excess of the reagent particularly with a substrate lacking an electron-withdrawing group on an aromatic ring.[23] Indeed, this side reaction occurred readily with substrates containing an alkoxy group. For example, *O*-4-benzyloxyphenyl *S*-methyl dithiocarbonate (**2e**) was converted into 1-benzyloxy-2-bromo-4-trifluoromethoxybenzene (**3e′**) with 70% HF/Py (80 mol) and DBH (4 mol) (Entry 14), whereas a complex mixture resulted with DBH (3 mol). Compound **2d** having a methoxy group gave similar results (Entry 12).



a: i) NaH (1.2 mol), ii) CS_2 (5.0 mol), iii) MeI (2.0 mol)
b: 70% HF/Py, *N*-halo imide, CH_2Cl_2, -78; 0 °C, 1 h
c: $TBAH_2F_3$, *N*-halo imide, CH_2Cl_2, rt, 1 h

Scheme 1. Synthesis of trifluoromethyl ethers **3** and difluoro(methylthio)methyl ethers **4**.

For the synthesis of alkyl trifluoromethyl ethers, we again optimized the conditions using *O*-2-(4-bromophenyl)ethyl *S*-methyl dithiocarbonate (**2l**) as the substrate. The reaction performed with 70% HF/Py (60—80 mol) induced the trifluoromethylation effectively along with aromatic bromination (Entries 27 and 28). When the reaction was performed with HF/Py (40 mol), the trifluoromethylation proceeded with little ring bromination (< 2%) to give desired product **3l** in 81% yield (Entry 29). Use of HF/Py (20 mol) gave **3l** in only 20% yield (Entry 30). The trifluoromethylation–bromination is applicable to **2m**, and 1-bromo-4-[3-(trifluoromethoxy)propyl]benzene (**3m′**) was obtained in 75% as a sole product (Entry 32). Substrates without an aromatic ring effectively underwent the reaction with HF/Py (80 mol) (Entries 34 and 35). In summary, alkyl trifluoromethyl ethers of primary alcohols could be obtained in excellent yields by the oxidative desulfurization–fluorination procedure.[24]

In the meantime, Motherwell and his co-workers reported that the dithiocarbonates derived from primary and secondary alkanols were converted into the corresponding fluorides by means of 4-(difluoroiodo)toluene ($TolIF_2$).[25] For example, *O*-hexadecyl *S*-methyl dithiocarbonate (**2o**) was reportedly converted into the corresponding 1-fluorohexadecane in 48% yield by $TolIF_2$. In contrast, under the oxidative desulfurization reaction conditions, compound **2o** was converted into trifluoromethyl ether **3o** in 95% yield (Entry 35) as a sole product, no trace of other products being detected. To compare the two reagents, we used [bis(trifluoroacetoxy)-iodo]benzene (3 mol) in place of DBH and found that only trifluoromethyl ether **3o** was obtained again in 67% yield (Entry 36). Thus, the reagent system consisting of 70% HF/Py and an oxidant exhibited unique reactivity in sharp contrast to $TolIF_2$. The formation of different products may be attributed to different reaction pathways (vide infra).

We next studied the fluorination using $TBAH_2F_3$ as a fluorination reagent to find that novel products difluoro(methylthio)methyl ethers **4** were produced. In particular, the use of $TBAH_2F_3$ (5 mol) and NBS (4 mol) was the most effective for the difluorination (Entry 6). Under these reaction conditions, no trace of trifluoromethyl ethers were produced. The difluorination reaction was applied to various kinds of dithiocarbonates, and a variety of aryl difluoro(methylthio)methyl ethers were obtained in fair yields from the corresponding *O*-aryl dithiocarbonates (Entries 9, 11, 13, 16, 18, 20, 22,

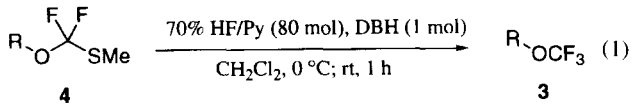
Table 1. Synthesis of Trifluoromethyl Ethers **3** or Difluoro(methylthio)methyl Ethers **4** from **2**

Entry	R	Yields of **2** (%)		Fluoride source (mol)[a]	*N*-Halo imide (mol)	Yields of **3** or **4** (%)[b]	
1	4-*n*-Pr–C_6H_4–	**2a**	80	70% HF/Py (80)	NBS (3)	**3a**	16[c]
2				(80)	DBH (3)		58
3				(80)	(5)		—[d]
4				(40)	(3)		81[c]
5				(20)	(3)		60[c]
6				$TBAH_2F_3$ (5)	NBS (4)	**4a**	58
7				(4)	(3)		30
8				(6)	(5)		35
9	4-Me–C_6H_4–	**2b**	82	(5)	(4)	**4b**	64
10	4-*n*-Hex–C_6H_4–	**2c**	82	70% HF/Py (80)	DBH (3)	**3c**	50
11				$TBAH_2F_3$ (5)	NBS (4)	**4c**	36
12	4-MeO–C_6H_4–	**2d**	56	70% HF/Py (80)	DBH (3)	**3d**	—
13				$TBAH_2F_3$ (5)	NBS (4)	**4d**	33
14	4-$PhCH_2O$–C_6H_4–	**2e**	85	70% HF/Py (80)	DBH (4)	**3e′**[e]	56
15					(3)		—
16				$TBAH_2F_3$ (5)	NBS (4)	**4e**	43
17	4-Br–C_6H_4–	**2f**	67	70% HF/Py (80)	DBH (3)	**3f**	62
18				$TBAH_2F_3$ (5)	NBS (4)	**4f**	43
19	4-*n*-PrOC(O)–C_6H_4–	**2g**	33	70% HF/Py (80)	DBH (3)	**3g**	30
20				$TBAH_2F_3$ (5)	NBS (4)	**4g**	42
21	3-MeOC(O)–C_6H_4–	**2h**	77	70% HF/Py (80)	DBH (3)	**3h**	76
22				$TBAH_2F_3$ (5)	NBS (4)	**4h**	32
23	4-Ph–C_6H_4–	**2i**	84			**4i**	23
24	4-(4-AcO–C_6H_4)–C_6H_4–	**2j**	34[f]	70% HF/Py (80)	DBH (3)	**3j**	80
25	4-(4-Br–C_6H_4)–C_6H_4–	**2k**	74			**3k**	52 (78)[g]
26				$TBAH_2F_3$ (5)	NBS (4)	**4k**	28
27	4-Br–C_6H_4–CH_2CH_2–	**2l**	99	70% HF/Py (80)	DBH (3)	**3l**[d]	—
28				(60)			43 (47)[h]
29				(40)			81
30				(20)			20
31				$TBAH_2F_3$ (5)	NBS (4)	**4l**	19
32	Ph–$CH_2CH_2CH_2$–	**2m**	95	70% HF/Py (80)	DBH (3)	**3m′**[i]	75
33				$TBAH_2F_3$ (5)	NBS (4)	**4m**	15
34	*n*-$C_{10}H_{21}$–	**2n**	66	70% HF/Py (80)	DBH (3)	**3n**	80
35	*n*-$C_{16}H_{33}$–	**2o**	88			**3o**	95
36					$PhI(OCOCF_3)_2$ (3)		67
37				$TBAH_2F_3$ (5)	NBS (4)	**4o**	9

a) Mol amounts of F^- and $H_2F_3^-$ are indicated in parentheses for 70% HF/Py and $TBAH_2F_3$, respectively. b) Isolated yields. c) Yields estimated by ^{19}F NMR using 1,3-$(CF_3)_2C_6H_4$ as internal standard. d) Accompanied by aromatic bromination. e) The product was 2-Br-4-CF_3O–C_6H_3–$OCH_2C_6H_5$ (**3e′**). f) Yields for 2 steps. See experimental. g) HF/Py (40 mol) was used for the reaction. h) Brominated product 2,4-Br_2–C_6H_3–CH_2CH_2–OCF_3 (**3l′**) is produced. i) The product was 4-Br–C_6H_4–$CH_2CH_2CH_2$–OCF_3 (**3m′**).

23, and 26), whereas the alkyl difluoro(methylthio)methyl ethers were isolated in relatively low yields (Entries 31, 33, and 37). In contrast to the trifluorination, aromatic rings having an alkoxy group remained intact under the difluorination conditions (Entries 13 and 16).

Conversion to Trifluoromethyl Ethers of Difluoro(methylthio)methyl Ethers. To examine the reactivity of difluoro(methylthio)methyl ethers **4**, these were treated with HF/Py (80 mol) and DBH (1.0 mol) at 0 °C to room temperature (Eq. 1). The results summarized in Table 2 clearly show that **4a**, **4h**, and **4m** smoothly gave trifluoromethyl ethers **3a**, **3h**, and **3m**, respectively, without ring bromination. However, substrate **4e** having a benzyloxyphenyl moiety was brominated to give **3e′**. Thus, DBH (2 mol) was necessary for the effective transformation. The



4 **3** (1)

results shown in Table 2 demonstrate that difluoro(methylthio)methyl ethers **4** are precursors of trifluoromethyl ethers **3**.

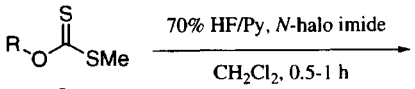
Oxidative Desulfurization-Fluorination of Dithiocarbonates Derived from Secondary, Tertiary, or Benzylic Alcohols. To compare the reactivity of dithiocarbonates towards $TolIF_2$[25] with that towards 70% HF/Py and an *N*-halo imide in more detail, we next examined the oxidative desulfurization–fluorination of dithiocarbonates derived from secondary, tertiary, or benzylic alcohols. In contrast to the di-

Table 2. Conversion of R–OCF_2SMe into R–OCF_3 [a]

Entry	R		DBH (mol)	Yields of **3** (%)[b]	
1	4-*n*-Pr–C_6H_4–	**4a**	1	**3a**	42
2	4-$PhCH_2O$–C_6H_4–	**4e**	2	**3e′** [c]	62
3	3-MeOC(O)–C_6H_4–	**4h**	1	**3h**	51
4	Ph–$CH_2CH_2CH_2$–	**4m**	1	**3m**	41

a) All the reaction were performed with 70% HF/Py (80 mol of F^-) and DBH. b) Isolated yields. c) The product was 2-Br–4-CF_3O–C_6H_3–$OCH_2C_6H_5$ (**3e′**).

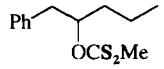
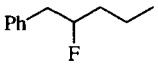
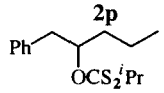
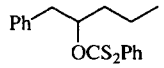
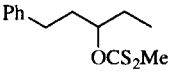
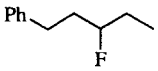
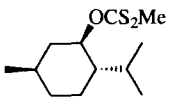
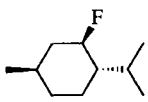
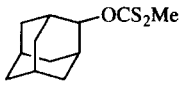
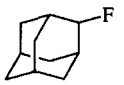
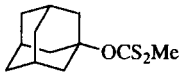
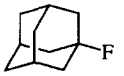
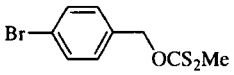
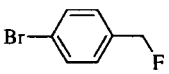
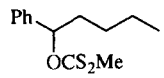
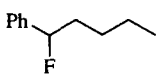
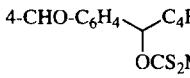
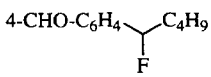
thiocarbonates of primary alcohols, these dithiocarbonates were converted into the corresponding fluorides **5** (Eq. 2).



2 **5** (2)

We first optimized the reaction conditions using *O*-1-benzylbutyl *S*-methyl dithiocarbonate (**2p**) as a substrate. Initially, we applied the standard reaction conditions for primary dithiocarbonates using HF/Py (80 mol) and DBH (3.0 mol). ^{19}F NMR and GC-MS of the crude inseparable mixture of products revealed the formation of **5p** in addition to its monobromo, dibromo, and tribromo derivatives. The results are summarized in Entry 1 of Table 3. We next used *N*-iodosuccinimide (NIS) as an oxidant to prevent the aromatic halogenation (Entries 2—5). Upon use of HF/Py (40 mol) and NIS (3 mol) (Entry 2), the fluorination gave **5p** with a small amount of its iodination product. Use of HF/Py (20 mol) was highly effective to produce **5p** in 70% yield without any ring halogenation (Entry 3). Reduction of the amount of either HF/Py (Entry 4) or NIS (Entry 5) decreased the yield of fluorination product **5p**. We next examined the influence of a substituent on sulfur using *S*-isopropyl or

Table 3. Synthesis of Alkyl Fluorides **5** by Oxidative Desulfurization–Fluorination[a]

Entry	Dithiocarbonates **2**		70% HF/Py (mol)	*N*-Halo imide (mol)	Products **5**		Yields of **5** (%)
1		**2p**	80	DBH (3)		**5p**	—[b,c]
2		**2p**	40	NIS (3)		**5p**	48
3		**2p**	20	NIS (3)		**5p**	70
4		**2p**	5	NIS (3)		**5p**	No reaction
5		**2p**	40	NIS (1)		**5p**	45
6		**2q**	40	NIS (3)		**5p**	78
7		**2r**	40	NIS (3)		**5p**	42
8		**2s**	40	NIS (3)		**5s**	65
9		**2t**	40	NIS (3)		**5t**	48[d]
10		**2u**	40	NIS (3)		**5u**	82[c]
11		**2v**	40	NIS (3)		**5v**	78[c]
12		**2w**	40	DBH (3)		**5w**	43[c]
13		**2x**	40	DBH (3)		**5x**	94[c] (76)[c,e]
14		**2y**	40	NIS (3)		**5y**	91[c]
15	**2y**		40	DBH (3)	**5y**		60 (23)[c,f]

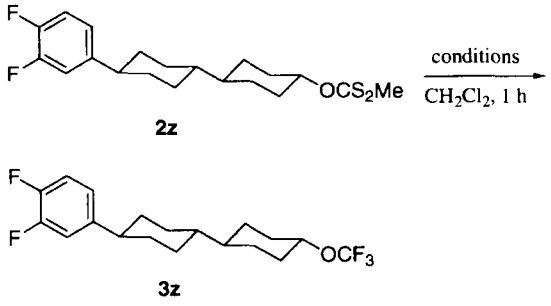
a) Unless otherwise noted, all the reaction was performed in CH_2Cl_2 at −42 °C for 1 h. b) Accompanied by aromatic bromination. c) The reaction was carried out at −78 °C then 0 °C for 1 h. d) The reaction was carried out at −78 °C then 0 °C for 0.5 h. e) NIS (3.0 mol) was used. f) Yield of 4-F_2CH–C_6H_4–CHF–C_4H_9 (**6**) is given in parentheses.

S-phenyl dithiocarbonates (**2q** or **2r**). Both of these were fluorinated to give **5p**; no trace of trifluoromethyl ether **3** was detected. We applied the optimized fluorination conditions to dithiocarbonates derived from various secondary, tertiary, and benzylic alcohols. The conditions and yields of products are summarized in Table 3. As readily seen, both secondary (Entries 8—10) and tertiary (Entry 11) alkyl fluorides are readily available in high yields. Dithiocarbonate **2t** derived from menthol afforded **5t** as a single isolable product (Entry 9). Although the reaction appears to have proceeded with retention of configuration, we consider that **5t** was produced through a carbocationic intermediate. Similar stereochemical results are reported with other fluorination reagents.[25,26] Primary benzylic dithiocarbonate **2w** and secondary ones **2x** and **2y** gave the corresponding benzylic fluorides **5w**, **5x**, and **5y**, respectively. For **2w** and **2x**, DBH was the most effective oxidant (see, Entry 13); bromination of aromatic ring was not observed. Substrate **2y** having a formyl functionality, caused difluorination of the CHO group when DBH (3 mol) was used as an oxidant (Entry 15). For this substrate, NIS was the best oxidant to produce fluorination product **5y** in 91% yield.

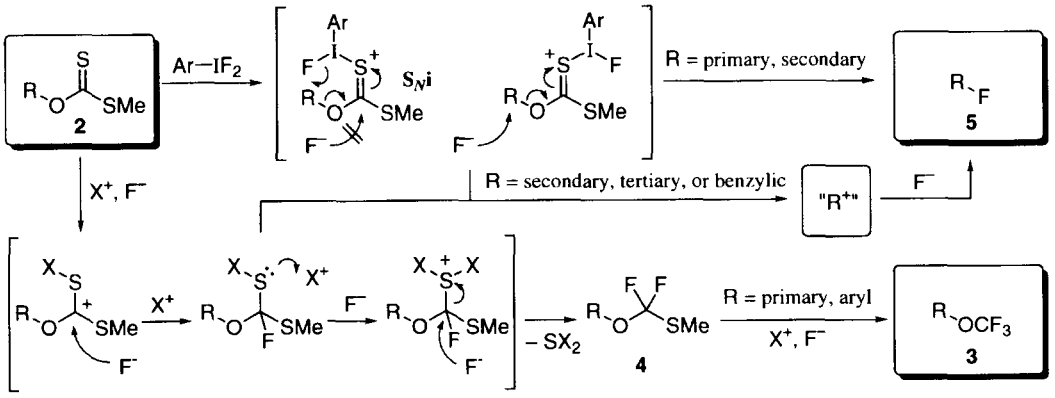
Reaction Mechanism. A plausible reaction mechanism for the fluorination of dithiocarbonates is summarized in Scheme 2. As we demonstrated above, the reagent system consisting of 70% HF/Py and an *N*-halo imide converts R–OCS_2R' **2** into trifluoromethyl ethers R–OCF_3 **3** (R = primary and aryl) or alkyl fluorides R–F **5** (R = secondary, tertiary, and benzylic), depending on the cation stabilizing nature of R. In particular, the dithiocarbonates derived from primary alcohols gave trifluoromethyl ethers in striking contrast to the reaction with $TolIF_2$.[25] The reactivity difference may be attributed to an involvement of an S_Ni pathway with $TolIF_2$ as shown in Scheme 2. The oxidative desulfurization–fluorination appears to be initiated by an electrophilic reaction of a positive halogen (X^+) with a thiocarbonyl group of R–OC(S)SMe to generate a cationic species R–OC^+(SX)-SMe; a subsequent nucleophilic attack by a fluoride ion at the electrophilic carbon forms a C–F bond. The resulting R–OCF(SX)SMe is again oxidized by X^+ and then fluorinated to yield difluorination product **4** as an isolable product. Further oxidation–fluorination affords trifluorination product R–OCF_3. The reagent combination clearly demonstrates that the fluorination proceeds via an intermolecular nucleophilic reaction three times to finally give trifluoromethyl ether **3**. Therefore, the fluorination of secondary, tertiary, and benzylic aliphatic dithiocarbonates leading to fluoride **5** may be attributed to elimination of a –OCS_2Me, –OCF(SX)SMe, or –OCF_2SMe group to generate carbocationic spicies "R^+" under the weakly acidic conditions, followed by a fluoride attack.

Synthesis of Secondary Alkyl Trifluoromethyl Ethers Through the Oxidative Desulfurization–Fluorination. To the best of our knowledge, no synthetic method has been available for the synthesis of trifluoromethyl ethers from secondary aliphatic alcohols.[27] An already reported alternative approach involves addition of CF_3OF to alkenes to give *vic*-fluoro(trifluoromethoxy)alkanes.[16] As CF_3OF is highly explosive and toxic, special equipments and techniques should be employed with great care. Furthermore, the reaction is often accompanied by the formation of regio-isomers and formal F_2 adducts β-fluorination, and thus the desired trifluoromethyl ethers are produced generally in low yields.

Based on the mechanism suggested in Scheme 2, it is essential to prevent the elimination of a –OCS_2Me, –OCF(SX)SMe, or –OCF_2SMe group for the synthesis of trifluoromethyl ethers derived from secondary alcohols. We thus envisaged that, if the acidity of the reaction conditions might be controlled by a proper choice of the reagent system, we would be able to switch the reaction pathway to the trifluoromethyl ether formation. To this end, we initially used HF/Py complex with HF content lower than the Olah reagent. The results using **2z** as a model substrate are summarized in Table 4.



(3)



Scheme 2. A proposed mechanism for the fluorination of dithiocarbonates.

Table 4. Synthesis of Substituted Cyclohexyl Trifluoromethyl Ether **3z**

Entry	Conditions (mol)	Temp (°C)	Isolated yield of **3z** (%)
1	55% HF/Py (40), NBS (5)	0	37
2	50% HF/Py (40), NBS (5)	0	42
3	50% HF/Py (80), NBS (5)	0	38
4	50% HF/Py (40), NBS (5)	−42	29
5	45% HF/Py (40), NBS (5)	0	Trace
6	70% HF/Py (40), NBS (5), KHF_2 (40)	−42	Trace
7	70% HF/Py (40), NBS (5), KHF_2 (20)	−42	30
8	70% HF/Py (40), DBH (5), KHF_2 (15)	−42	31
9	70% HF/Py (40), DBH (5), KHF_2 (10)	−78	27

Dilution of 70% HF/Py with appropriate amounts of dry pyridine gave reagents 45—55% HF/Py (40—80 mol of F^-). When a reaction was performed using 50% HF/Py (40 mol) and NBS (5 mol) in dichloromethane at 0 °C, compound **2z** was converted into the corresponding cyclohexyl trifluoromethyl ether derivative **3z** in 42% yield without any fluorination product being detected (Entry 2). DBH (5 mol) was not effective for this transformation. Use of 55% HF/Py (40 mol) (Run 1) or 50% HF/Py (80 mol) (Run 3) at −42 °C also gave **3z** but in lower yields. When 45% HF/Py (40 mol) was employed for the reaction, the fluorination did not complete, and the formation of a difluoro(methylthio)methyl ether (R–OCF_2SMe) was detected by ^{19}F NMR (Entry 5). A combined use of 70% HF/Py and KHF_2 was also effective for this transformation; when the reaction was performed with 70% HF/Py and KHF_2 (20, 15, or 10 mol), **3z** was obtained in 30, 31, or 27% yield, respectively. Potassium hydrogendifluoride is known to enhance the fluoride nucleophilicity and reduce the acidity of 70% HF/Py.[28]

The trifluoromethyl ether synthesis was applied to the dithiocarbonates derived from several secondary aliphatic alcohols. The products and isolated yields are shown in Fig. 2. As one can readily see, the corresponding secondary aliphatic trifluoromethyl ethers were prepared under the oxidative desulfurization–fluorination conditions, though the yields are not striking. It is worthy to emphasize that either alkyl fluorides **5p** and **5s** or trifluoromethyl ethers **3p** and **3s** are available from dithiocarbonates **2p** and **2s**, respectively, only by tuning the HF content of the Olah reagents.

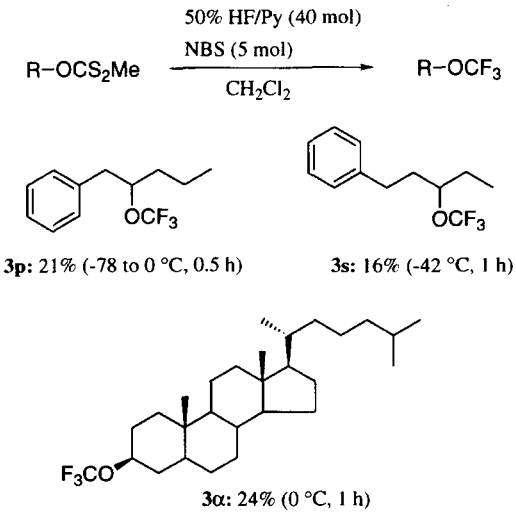


Fig. 2. Synthesis of secondary aliphatic trifluoromethyl ethers.

Conclusions

We have demonstrated that a convenient synthesis of trifluoromethyl ethers is achieved by the oxidative desulfurization–fluorination of dithiocarbonates that are readily accessible from the corresponding alcohols or phenols. When the reaction is carried out using a reagent system consisting of 70% HF/Py and an *N*-halo imide, R–OCS_2Me (R = aryl or primary alkyl) is transformed selectively to trifluoromethyl ethers R–OCF_3. When the similar conditions are applied to R–OCS_2Me (R = secondary and tertiary alkyl or benzylic), fluorination leading to alkyl fluorides R–F proceeds without any formation of R–OCF_3. Furthermore, a combination of 50% HF/Py and NBS converts R–OCS_2Me (R = secondary) to afford trifluoromethyl ethers R–OCF_3 (R = secondary). Thus, the reaction pathway towards secondary alkyl fluorides or trifluoromethyl ethers can be controlled simply by an appropriate choice of the fluorination reagent starting with the same substrate.

The convenient transformations disclosed herein should find further applications particularly in liquid crystalline materials, pharmaceuticals, and agrochemicals.

Experimental

General. All of the temperatures are uncorrected. Unless otherwise noted, reagents and solvents were purchased from Aldrich Chemical Co., Kanto Chemicals, Tokyo Kasei, or Wako Chemicals, Inc. and used as received. Each reaction was carried out entirely under an argon atmosphere in a dry, freshly distilled solvent unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Dichloromethane (CH_2Cl_2) was predried with P_2O_5 and distilled from calcium hydride. Pyridine was distilled from KOH and kept over solid KOH at room temperature. *N*,*N*-Dimethylformamide (DMF) was distilled 2 times from calcium hydride under reduced pressure. NBS and NIS were purified by recrystallization from hot water and dioxane/CCl_4, respectively. Unless otherwise stated, yields refer to materials purified by column chromatography, recrystallization, or distillation under reduced pressure. Reactions were monitored by thin-layer chromatography using 0.25 mm E. Merck silica-gel plates (Silica Gel F_{254}) with a visualizing device of UV light and/or by dipping the

plates in an ethanolic phosphomolybdic acid or *p*-anisaldehyde solution by heating the plates. Silica gel from E. Merck (Kieselgel 60, 230—400 mesh) or Nacalai Tesque (silica gel 60, 150—325 mesh) was used for flash column chromatography. Silica gel purchased from E. Merck (Kieselgel 60, 70—230 mesh) or Wako (Wakogel C-200) was used for column chromatography under an atmospheric or slightly positive pressure. Unless otherwise noted, NMR spectra were measured in a $CDCl_3$ solution. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a JEOL FX-100 spectrometer operating at 100 (^{1}H) or 93.6 (^{19}F) MHz, on a Bruker AC-200 spectrometer at 200 (^{1}H), 50.3 (^{13}C), or 188 (^{19}F) MHz, or on a Varian Mercury-300 spectrometer at 300 (^{1}H), 75.5 (^{13}C), or 282 (^{19}F) MHz, respectively. Chemical shifts of ^{1}H NMR, ^{13}C NMR, or ^{19}F NMR signals are quoted relative to internal standard Me_4Si (δ = 0.00), $CDCl_3$ (δ = 77.00), or $CFCl_3$ (δ = 0.00), respectively. IR spectra were recorded on a Shimadzu FTIR-8100A in neat unless otherwise noted. Mass spectra were recorded on a Shimadzu GC/MS QP-5000 or on a Hitachi H-80 double-focusing tandem GC-MS (70 eV) spectrometer. Melting points were measured with an Olympus BH-2 optical polarizing microscope equipped with a Mettler FP-900 hot-stage. Elemental analyses were carried out by Elemental Analysis Center, Tokyo Institute of Technology, using Yanako MT2 CHN Corder. High-resolution mass spectra were obtained on a JEOL MStation. $TBAH_2F_3$ was prepared according to the literature procedure[22] and dried in vacuo at room temperature overnight right before use.

General Procedure for the Preparation of Dithiocarbonates 2. To a stirred solution of alcohol **1** (80 mmol) in THF (or DMF) (160 mL), sodium hydride (NaH, 60% in oil, 96 mmol) was slowly added portionwise at 0 °C. After the resulting mixture was stirred for 1 h at room temperature, carbon disulfide (160 mmol) was added dropwise at 0 °C. The resulting mixture was stirred for 10 h at room temperature before MeI (96 mmol) was added dropwise to the reaction mixture at 0 °C. The resulting mixture was stirred for 1 h at room temperature, treated with aqueous NH_4Cl solution, and extracted with Et_2O. The organic phase was separated; the aqueous phase was extracted with Et_2O three times. The combined organic phase was washed with sat. NaCl solution containing small portions of sodium hydrogen sulfite, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography or recrystallization from EtOH to give dithiocarbonates **2**. Yields and spectral properties of **2** are as follows.

***S*-Methyl *O*-4-Propylphenyl Dithiocarbonate (2a).** Prepared in 80% yield upon use of DMF in lieu of THF. A pale yellow oil; R_f = 0.83 (hexane–Et_2O = 2 : 1). IR 2960, 2930, 2870, 1500, 1175, 1040, 965, 819 cm^{-1}; ^{1}H NMR (300 MHz) δ = 0.94 (t, J = 8 Hz, 3 H), 1.05—1.64 (m, 2 H), 2.59 (t, J = 8 Hz, 2 H), 2.65 (s), 6.99 (d, J = 9 Hz, 2 H), 7.20 (d, J = 9 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 13.8 (s), 19.9 (s), 24.4 (s), 37.4 (s), 121.5 (s), 129.3 (s), 141.0 (s), 152.6 (s), 215.9 (s); MS *m/z* (rel intensity) 226 (M^+; 6), 200 (2), 198 (20), 121 (5), 93 (9), 91 (100), 65 (5). Found: *m/z* 226.0485. Calcd for $C_{11}H_{14}OS_2$: M, 226.0486.

***S*-Methyl *O*-4-Methylphenyl Dithiocarbonate (2b).** Yield, 82% with DMF as a reaction solvent. A pale yellow oil; R_f = 0.57 (hexane–EtOAc = 10 : 1). IR 3042, 2924, 1884, 1720, 1597, 1503, 1420, 1413, 1382, 1213, 1192, 1180, 1103, 1041, 1020, 962, 821 cm^{-1}; ^{1}H NMR (200 MHz) δ = 2.36 (s, 3 H), 2.70 (s, 3 H), 7.02 (d, J = 9 Hz, 2 H), 7.24 (d, J = 9 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 19.9 (s), 20.9 (s), 121.6 (s), 130.0 (s), 136.2 (s), 152.4 (s), 216.0 (s); MS *m/z* (rel intensity) 199 (M^++1; 0.5), 198 (M^+; 3), 170 (28), 138 (2), 107 (5), 91 (100), 77 (13), 65 (10). Found: *m/z* 198.0177. Calcd for $C_9H_{10}OS_2$: M, 198.0173.

***O*-4-Hexylphenyl *S*-Methyl Dithiocarbonate (2c).** Yield, 82% with DMF as a reaction solvent. A pale yellow oil; R_f = 0.50 (hexane). IR 2926, 2857, 1505, 1460, 1415, 1383, 1179, 1042, 965, 831 cm^{-1}; ^{1}H NMR (100 MHz) δ = 0.89 (t, J = 6 Hz, 3 H), 1.15—1.80 (m, 8 H), 2.65 (t, J = 7 Hz, 2 H), 2.67 (s, 3 H), 7.03 (d, J = 6 Hz, 2 H), 7.25 (d, J = 6 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 19.9 (s), 22.6 (s), 29.0 (s), 31.3 (s), 31.7 (s), 35.4 (s), 121.6 (s), 129.3 (s), 141.3 (s), 152.6 (s), 216.0 (s); MS *m/z* (rel intensity) 270 (M^++2; 1), 269 (M^++1; 2), 268 (M^+; 13), 240 (47), 169 (18), 121 (14), 107 (11), 93 (26), 91 (100), 75 (14), 65 (10). Found: *m/z* 268.0961. Calcd for $C_{14}H_{20}OS_2$: M, 268.0956.

***O*-4-Methoxyphenyl *S*-Methyl Dithiocarbonate (2d).** Yield, 56% with DMF as a reaction solvent. A pale yellow oil; R_f = 0.44 (hexane–EtOAc = 10 : 1). IR 3000, 2875, 2820, 1500, 1250, 1185, 1170, 1040, 830 cm^{-1}; ^{1}H NMR (100 MHz) δ = 2.64 (s, 3 H), 3.80 (s, 3 H), 6.87 (d, J = 7 Hz, 2 H), 7.05 (d, J = 7 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 19.9 (s), 55.5 (s), 114.4 (s), 122.7 (s), 148.2 (s), 157.7 (s), 216.4 (s); MS *m/z* (rel intensity) 214 (M^+; 7), 186 (23), 149 (20), 123 (22), 111 (12), 109 (11), 105 (18), 97 (26), 95 (34), 91 (100), 83 (38), 71 (52). Found: *m/z* 214.0119. Calcd for $C_9H_{10}O_2S_2$: M, 214.0122.

***O*-4-Benzyloxyphenyl *S*-Methyl Dithiocarbonate (2e).** Yield, 85% with DMF as a reaction medium. A pale yellow oil; R_f = 0.66 (hexane–Et_2O = 2 : 1). IR 3010, 2860, 1500, 1383, 1242, 1185, 1150, 1055, 1019, 838, 742, 695 cm^{-1}; ^{1}H NMR (100 MHz) δ = 2.67 (s, 3 H), 5.08 (s, 2 H), 7.03 (s, 4 H), 7.30—7.60 (m, 5 H); ^{13}C NMR (75.5 MHz) δ = 19.9 (s), 70.4 (s), 115.4 (s), 122.8 (s), 127.5 (s), 128.1 (s), 128.6 (s), 136.7 (s), 148.4 (s), 157.0 (s), 216.3 (s); MS *m/z* (rel intensity) 292 (M^++2; 1), 291 (M^++1; 2), 290 (M^+; 9), 262 (11), 151 (2), 93 (10), 92 (198), 91 (100), 65 (35). Found: *m/z* 290.0435. Calcd for $C_{15}H_{14}O_2S_2$: M, 290.0435.

***O*-4-Bromophenyl *S*-Methyl Dithiocarbonate (2f).** Yield, 67% with DMF as a reaction medium. A pale yellow oil; R_f = 0.43 (hexane). IR 3120, 2950, 1883, 1724, 1582, 1482, 1420, 1400, 1190, 1172, 1100, 1037, 1015, 965, 832, 806, 715 cm^{-1}; ^{1}H NMR (200 MHz) δ = 2.66 (s, 3 H), 7.01 (d, J = 9 Hz, 2 H), 7.55 (d, J = 9 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 20.1 (s), 119.8 (s), 123.9 (s), 132.6 (s), 153.5 (s), 215.5 (s); MS *m/z* (rel intensity) 264 (M^++2; 2), 262 (M^+; 1), 236 (10), 234 (8), 145 (4), 143 (3), 119 (4), 93 (10), 91 (100), 75 (16), 64 (9). Found: *m/z* 261.9115. Calcd for $C_8H_7{}^{79}BrOS_2$: M, 261.9122.

***S*-Methyl *O*-4-(Propoxycarbonyl)phenyl Dithiocarbonate (2g).** Obtained in 33% yield by the reaction in DMF. A pale yellow oil; R_f = 0.53 (hexane–Et_2O = 5 : 1). IR 2969, 2922, 1721, 1601, 1501, 1412, 1275, 1194, 1159, 1113, 1040, 1015, 776, 702 cm^{-1}; ^{1}H NMR (100 MHz) δ = 1.05 (t, J = 6 Hz, 3 H), 1.79 (tq, J = 6, 6 Hz, 2 H), 2.66 (s, 3 H), 4.30 (t, J = 6 Hz, 2 H), 7.18 (d, J = 9 Hz, 2 H), 8.12 (d, J = 9 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 10.5 (s), 20.0 (s), 22.1 (s), 66.7 (s), 122.2 (s), 128.7 (s), 131.1 (s), 157.8 (s), 165.6 (s), 215.0 (s); MS *m/z* (rel intensity) 271 (M^++1; 1), 270 (M^+; 1), 242 (12), 194 (9), 152 (52), 135 (88), 107 (10), 93 (10), 82 (19), 91 (100), 77 (21), 75 (25), 64 (14). Found: *m/z* 270.0380. Calcd for $C_{12}H_{14}O_3S_2$: M, 270.0384.

***O*-3-(Methoxycarbonyl)phenyl *S*-Methyl Dithiocarbonate (2h).** Isolated in 77% yield by the reaction carried out in DMF. A pale yellow oil; R_f = 0.46 (hexane–Et_2O = 5 : 1). IR 2950, 1725, 1580, 1440, 1295, 1265, 1175, 1100, 1040, 1000, 760, 695 cm^{-1}; ^{1}H NMR (100 MHz) δ = 2.69 (s, 3 H), 3.93 (s, 3 H), 7.22—7.64 (m, 2 H), 7.72—8.04 (m, 2 H); ^{13}C NMR (75.5 MHz) δ = 20.0 (s), 52.4 (s), 123.4 (s), 126.8 (s), 127.7 (s), 129.5 (s), 131.8 (s), 154.4 (s), 165.9 (s), 215.5 (s); MS *m/z* (rel intensity) 242 (M^+; 1), 214

(26), 135 (4), 121 (2), 119 (3), 105 (4), 97 (3), 93 (10), 91 (100), 75 (9). Found: *m/z* 242.0071. Calcd for $C_{10}H_{10}O_3S_2$: M, 242.0071.

***O*-4-Biphenyl *S*-Methyl Dithiocarbonate (2i).** Yield, 84% (DMF as a reaction solvent). Pale yellow crystals, mp 80.2—80.9 °C; R_f = 0.23 (hexane). IR (KBr) 3057, 2924, 1888, 1510, 1481, 1184, 1036, 1005, 839, 766, 725 cm^{-1}; ^1H NMR (100 MHz) δ = 2.70 (s, 3 H), 7.21 (d, J = 6 Hz, 2 H), 7.35—7.81 (m, 7 H); ^{13}C NMR (75.5 MHz) δ = 20.0 (s), 122.3 (s), 127.1 (s), 127.4 (s), 128.2 (s), 128.7 (s), 139.6 (s) 140.0 (s), 154.0 (s), 215.7 (s); MS *m/z* (rel intensity) 262 (M^++2; 1), 261 (M^++1; 2), 260 (M^+; 12), 232 (36), 185 (9), 152 (13), 141 (11), 115 (23), 93 (16), 91 (100), 76 (15), 75 (16). Found: *m/z* 260.0331. Calcd for $C_{14}H_{12}OS_2$: M, 260.0330.

***O*-4′-Bromo-4-biphenyl *S*-Methyl Dithiocarbonate (2k).** Yield, 74% (in DMF). Pale yellow crystals, mp 109.8—110.6 °C; R_f = 0.26 (hexane). IR (KBr) 3040, 2925, 1584, 1478, 1387, 1182, 1051, 1001, 961, 822 cm^{-1}; ^1H NMR (200 MHz) δ = 2.71 (s, 3 H), 7.19 (d, J = 9 Hz, 2 H), 7.46 (d, J = 9 Hz, 2 H), 7.42—7.67 (m, 4 H); ^{13}C NMR (75.5 MHz) δ = 20.0 (s), 121.8 (s), 122.5 (s), 128.0 (s), 128.7 (s), 131.9 (s), 138.3 (s), 139.0 (s), 154.2 (s), 215.7 (s); MS *m/z* (rel intensity) 340 (M^++2; 5), 338 (M^+; 4), 312 (11), 310 (10), 152 (7), 139 (10), 91 (100), 75 (8). Found: *m/z* 337.9435. Calcd for $C_{14}H_{11}{}^{79}BrOS_2$: M, 337.9435.

***O*-2-(4-Bromophenyl)ethyl *S*-Methyl Dithiocarbonate (2l).** Obtained in 99% yield, a pale yellow oil; R_f = 0.26 (hexane). IR 2941, 2921, 1489, 1406, 1219, 1175, 1071, 1049, 1013, 812 cm^{-1}; ^1H NMR (300 MHz) δ = 2.52 (s, 3 H), 3.05 (t, J = 7 Hz, 2 H), 4.76 (t, J = 7 Hz, 2 H), 7.11 (d, J = 9 Hz, 2 H), 7.58 (d, J = 9 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 18.9 (s), 34.0 (s), 73.4 (s), 120.6 (s), 130.6 (s), 131.6 (s), 136.2 (s), 215.6 (s); MS *m/z* (rel intensity) 292 (M^++2; 0.01), 290 (M^+; 0.01), 185 (20), 184 (96), 183 (21), 182 (100), 104 (98), 103 (41), 102 (11), 91 (18), 89 (12), 78 (26), 77 (41), 76 (14), 75 (14), 63 (13). Found: *m/z* 289.9434. Calcd for $C_{10}H_{11}{}^{79}BrOS_2$: M, 289.9435.

***S*-Methyl *O*-3-Phenylpropyl Dithiocarbonate (2m).** Yield, 95%. A pale yellow oil; R_f = 0.19 (hexane). IR 3025, 2950, 2920, 1718, 1495, 1455, 1380, 1220, 1175, 1060, 740, 700 cm^{-1}; ^1H NMR (200 MHz) δ = 1.90—2.38 (m, 2 H), 2.55 (s, 3 H), 2.76 (t, J = 7 Hz, 2 H), 4.61 (t, J = 7 Hz, 2 H), 7.10—7.48 (m, 5 H); ^{13}C NMR (75.5 MHz) δ = 18.9 (s), 29.8 (s), 32.0 (s), 73.1 (s), 126.0 (s), 128.3 (s), 128.4 (s), 140.8 (s), 215.7 (s); MS *m/z* (rel intensity) 226 (M^+; 11), 205 (21), 153 (12), 123 (12), 119 (25), 118 (86), 92 (13), 91 (100), 71 (24). Found: *m/z* 226.0487. Calcd for $C_{11}H_{14}OS_2$: M, 226.0486.

***O*-Decyl *S*-Methyl Dithiocarbonate (2n).** Yield, 66%. A pale yellow oil; R_f = 0.50 (hexane). IR 2924, 2855, 1725, 1464, 1383, 1223, 1063, 966, 725 cm^{-1}; ^1H NMR (100 MHz) δ = 0.88 (t, J = 6 Hz, 3 H), 1.04—1.62 (m, 14 H), 1.68—2.05 (m, 2 H), 2.56 (s, 3 H), 4.62 (t, J = 6 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 18.9 (s), 22.7 (s), 25.9 (s), 28.2 (s), 29.2 (s), 29.3 (s), 29.46 (s), 29.48 (s), 31.9 (s), 74.3 (s), 215.9 (s); MS *m/z* (rel intensity) 248 (M^+; 3), 215 (11), 141 (11), 140 (75), 109 (27), 91 (23), 75 (61), 71 (100), 69 (92). Found: *m/z* 248.1235. Calcd for $C_{12}H_{24}OS_2$: M, 248.1269.

***O*-Hexadecyl *S*-Methyl Dithiocarbonate (2o).** Yield, 88%. A pale yellow oil; R_f = 0.79 (hexane–EtOAc = 10 : 1). IR 2924, 2853, 1466, 1223, 1063, 967 cm^{-1}; ^1H NMR (200 MHz) δ = 0.88 (t, J = 7 Hz, 3 H), 1.20—1.50 (m, 26 H), 1.72—1.87 (m, 2 H), 2.56 (s, 3 H), 4.59 (t, J = 7 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 14.1 (s), 18.9 (s), 22.7 (s), 25.9 (s), 28.2 (s), 29.2 (s), 29.4 (s), 29.47 (s), 29.54 (s), 29.62 (s), 29.65 (s), 29.68 (br), 31.9 (s), 74.2 (s), 215.9 (s); MS *m/z* (rel intensity) 333 (M^++1; 0.2), 332 (M^+; 0.4), 299 (7), 285 (5), 224 (24), 125 (11), 111 (35), 109 (77), 108 (13), 98 (12), 97 (53), 91 (29), 85 (39), 83 (57), 71 (100), 69 (89). Found: *m/z* 332.2209. Calcd for $C_{18}H_{36}OS_2$: M, 332.2208.

***O*-1-Benzylbutyl *S*-Methyl Dithiocarbonate (2p).** Yield, 90%. A pale yellow oil; R_f = 0.63 (hexane–EtOAc = 10 : 1). IR 3029, 2959, 2872, 1456, 1219, 1129, 1051, 964, 741, 700 cm^{-1}; ^1H NMR (200 MHz) δ = 0.88 (t, J = 7 Hz, 3 H), 1.24—1.84 (m, 4 H), 2.52 (s, 3 H), 2.91 (dd, J = 7, 14 Hz, 1 H), 3.12 (dd, J = 6, 14 Hz, 1 H), 5.82—5.96 (m, 1 H), 7.20—7.30 (m, 5 H); ^{13}C NMR (75.5 MHz) δ = 13.8 (s), 18.5 (s), 18.7 (s), 34.8 (s), 39.6 (s), 84.4 (s), 126.5 (s), 128.3 (s), 129.4 (s), 136.8 (s), 215.4 (s); MS *m/z* (rel intensity) 254 (M^+; 0.13), 147 (12), 146 (84), 117 (47), 115 (11), 105 (13), 104 (24), 92 (17), 91 (100), 77 (8), 69 (4), 65 (21). Found: *m/z* 254.0797. Calcd for $C_{13}H_{18}OS_2$: M, 254.0799.

***O*-1-Benzylbutyl *S*-1-Methylethyl Dithiocarbonate (2q).** Prepared by treatment with 2-iodopropane in lieu of MeI and isolated in 84% yield as a pale yellow oil; R_f = 0.61 (hexane–EtOAc = 10 : 1). IR 2961, 2930, 2872, 1497, 1455, 1246, 1217, 1069, 1038, 787, 700 cm^{-1}; ^1H NMR (300 MHz) δ = 0.84 (t, J = 6 Hz, 3 H), 1.25—1.80 (m, 10 H), 2.90 (dd, J = 7, 14 Hz, 1 H), 3.12 (dd, J = 6, 14 Hz, 1 H), 3.78 (heptet, J = 7 Hz, 1 H), 5.86—5.95 (m, 1 H), 7.19—7.32 (m, 5 H); ^{13}C NMR (75.5 MHz) δ = 13.9 (s), 18.6 (s), 22.2 (s), 22.4 (s), 34.8 (s), 39.7 (s), 40.5 (s), 83.9 (s), 126.5 (s), 128.4 (s), 129.5 (s), 136.9 (s), 214.1 (s); MS *m/z* (rel intensity) 282 (M^+; 0.2), 147 (6), 146 (33), 117 (16), 105 (8), 104 (8), 92 (9), 91 (100), 65 (7). Found: *m/z* 282.1111. Calcd for $C_{15}H_{22}OS_2$: M, 282.1112.

***O*-(1-Ethyl-2-phenylethyl) *S*-Methyl Dithiocarbonate (2s).** Isolated in 80% yield as a pale yellow oil, R_f = 0.69 (hexane–EtOAc = 10 : 1). IR 3027, 2969, 1456, 1223, 1132, 1048, 965, 747, 698 cm^{-1}; ^1H NMR (200 MHz) δ = 0.94 (t, J = 7 Hz, 3 H), 1.78 (dq, J = 7, 7 Hz, 2 H), 1.90—2.20 (m, 2 H), 2.54 (s, 3 H), 2.58—2.76 (m, 2 H), 5.64—5.76 (m, 1 H), 7.13—7.35 (m, 5 H); ^{13}C NMR (75.5 MHz) δ = 9.2 (s), 18.7 (s), 26.4 (s), 31.4 (s), 34.8 (s), 84.9 (s), 125.8 (s), 128.1 (s), 128.2 (s), 141.2 (s), 215.6 (s); MS *m/z* (rel intensity) 254 (M^+; 0.2), 221 (0.6), 146 (27), 131 (5), 116 (15), 104 (10), 92 (10), 91 (100), 65 (5). Found: *m/z* 254.0790. Calcd for $C_{13}H_{18}OS_2$: M, 254.0799.

***O*-(−)-Menthyl *S*-Methyl Dithiocarbonate (2t).** Yield, 97%. A pale yellow oil; R_f = 0.72 (hexane–Et_2O = 10 : 1). IR 2957, 2924, 2870, 1456, 1370, 1246, 1219, 1148, 1051, 943, 901 cm^{-1}; ^1H NMR (200 MHz) δ = 0.80 (d, J = 7 Hz, 3 H), 0.88—1.19 (m, 9 H), 1.42—1.78 (m, 4 H), 1.84—1.94 (m, 1 H), 2.18—2.26 (m, 1 H), 2.55 (s, 3 H), 5.52 (ddd, J = 5, 11, 11 Hz, 1 H); ^{13}C NMR (75.5 MHz) δ = 17.0 (s), 18.8 (s), 20.6 (s), 22.0 (s), 23.8 (s), 26.6 (s), 31.3 (s), 34.1 (s), 39.6 (s), 47.2 (s), 84.4 (s), 215.4 (s); MS *m/z* (rel intensity) 246 (M^+; 0.6), 171 (2), 140 (3), 139 (9), 138 (42), 97 (17), 95 (29), 91 (21), 83 (100), 81 (32), 71 (19), 69 (52), 67 (30). Found: *m/z* 246.1105. Calcd for $C_{12}H_{22}OS_2$: M, 246.1112.

***O*-2-Adamantyl *S*-Methyl Dithiocarbonate (2u).** Yield, 91%. Pale yellow needles, mp 106.4—107.6 °C; R_f = 0.70 (hexane–EtOAc = 10 : 1). IR (KBr) 2905, 2855, 1703, 1451, 1426, 1406, 1356, 1340, 1225, 1211, 1177, 1049, 963, 914 cm^{-1}; ^1H NMR (200 MHz) δ = 1.60—1.68 (m, 2 H), 1.72—1.96 (m, 8 H), 1.98—2.08 (m, 2 H), 2.20—2.28 (m, 2 H), 2.56 (s, 3 H), 5.62—5.78 (m, 2 H); MS *m/z* (rel intensity) 244 (M^++2; 2), 243 (M^++1; 3), 242 (M^+; 17), 182 (34), 136 (37), 135 (100), 107 (34), 93 (62), 91 (54), 81 (42), 79 (59), 77 (38), 67 (34). Found: *m/z* 242.0804. Calcd for $C_{12}H_{18}OS_2$: M, 242.0799.

***O*-1-Adamantyl *S*-Methyl Dithiocarbonate (2v).** Yield, 78%. Pale yellow needles, mp 110.6—111.2 °C; R_f = 0.76 (hexane–EtOAc = 10 : 1). IR (KBr) 2912, 2849, 1456, 1354, 1186, 1105, 1048, 1024, 954, 860, 714 cm^{-1}; ^1H NMR (200 MHz) δ = 1.69 (s, 6 H), 2.24 (brs, 3 H), 2.43 (s, 3 H), 2.45 (s, 6 H); ^{13}C NMR (75.5

MHz) δ = 19.1 (s), 31.4 (s), 36.0 (s), 41.1 (s), 91.2 (s), 212.5 (s); MS *m/z* (rel intensity) 242 (M^+; 0.8), 167 (1), 149 (2), 107 (9), 93 (19), 91 (13), 79 (25), 67(8). Found: *m/z* 242.0793. Calcd for $C_{12}H_{18}OS_2$: M, 242.0799.

***O*-4-Bromophenylmethyl *S*-Methyl Dithiocarbonate (2w).** Obtained in 99% yield as a pale yellow oil; R_f = 0.62 (hexane–EtOAc = 10 : 1). IR 2921, 1900, 1595, 1489, 1406, 1368, 1223, 1197, 1177, 1071, 1013, 967, 851, 803, 731 cm^{-1}; ^1H NMR (200 MHz) δ = 2.56 (s, 3 H), 5.57 (s, 2 H), 7.26 (d, *J* = 8 Hz, 2 H), 7.50 (d, *J* = 8 Hz, 2 H); ^{13}C NMR (75.5 MHz) δ = 19.1 (s), 73.8 (s), 122.5 (s), 129.9 (s), 131.5 (s), 133.5 (s), 215.2 (s); MS *m/z* (rel intensity) 278 (M^++2; 3), 276 (M^+; 2), 218 (3), 216 (3), 171 (81), 169 (100), 90 (33), 89 (28), 63 (20). Found: *m/z* 275.9280. Calcd for $C_9H_9{}^{79}BrOS_2$: M, 275.9279.

***S*-Methyl *O*-1-Phenyl-1-pentyl Dithiocarbonate (2x).** Yield, 95%. A pale yellow oil; R_f = 0.61 (hexane–EtOAc = 10 : 1). IR 3033, 2957, 2930, 1456, 1244, 1211, 1055, 964, 758, 698 cm^{-1}; ^1H NMR (200 MHz) δ = 0.88 (t, *J* = 7 Hz, 3 H), 1.23—1.45 (m, 4 H), 1.80—2.01 (m, 1 H), 2.04—2.34 (m, 1 H), 2.53 (s, 3 H), 6.51 (dd, *J* = 6, 8 Hz, 1 H) 7.23—7.36 (m, 5 H); ^{13}C NMR (75.5 MHz) δ = 13.9 (s), 18.9 (s), 22.5 (s), 27.5 (s), 35.9 (s), 85.3 (s), 125.8 (s), 126.8 (s), 128.0 (s), 128.4 (s), 215.0 (s); MS *m/z* (rel intensity) 254 (M^+; 3), 147 (71), 146 (15), 137 (8), 117 (44), 115 (23), 105 (32), 104 (27), 92 (26), 91 (100), 78 (11), 77 (18), 75 (11), 65 (16). Found: *m/z* 254.0792. Calcd for $C_{13}H_{18}OS_2$: M, 254.0799.

***O*-1-(4-Formylphenyl)pentyl *S*-Methyl Dithiocarbonate (2y).** Yield, 25%. A pale yellow oil; R_f = 0.48 (hexane–EtOAc = 10 : 1). IR 2957, 2924, 2870, 1713, 1456, 1370, 1246, 1219, 1159, 1051, 1005, 943, 901 cm^{-1}; ^1H NMR (200 MHz) δ = 0.89 (t, *J* = 7 Hz, 3 H), 1.22—1.50 (m, 4 H), 1.85—2.25 (m, 2 H), 2.56 (s, 3 H), 6.52 (dd, *J* = 6, 8 Hz, 1 H), 7.49 (d, *J* = 8 Hz, 2 H), 7.87 (d, *J* = 8 Hz, 2 H), 10.00 (s, 1 H); ^{13}C NMR (75.5 MHz) δ = 13.9 (s), 19.1 (s), 22.4 (s), 27.4 (s), 36.0 (s), 84.3 (s), 127.2 (s), 129.9 (s), 135.9 (s), 146.5 (s), 191.7 (s), 215.1 (s); MS *m/z* (rel intensity) 283 (M^++1; 1), 282 (M^+; 13), 207 (12), 197 (17), 178 (22), 149 (24), 147 (40), 135 (40), 121 (21), 117 (24), 111 (29), 105 (35), 97 (100), 83 (61). Found: *m/z* 282.0740. Calcd for $C_{14}H_{18}O_2S_2$: M, 282.0748.

***O*-{*trans*-4-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]cyclohexyl} *S*-Methyl Dithiocarbonate (2z).** Yield, 86%. Pale yellow needles, phase transition temperature/°C: Cr 95 N 148 Iso; R_f = 0.71 (hexane–EtOAc = 10 : 1) IR (KBr) 2961, 2921, 2857, 1605, 1516, 1497, 1449, 1429, 1356, 1285, 1271, 1190, 1161, 1051, 1021, 968, 870, 824, 777, 749 cm^{-1} ; ^1H NMR (200 MHz) δ = 1.00—1.30 (m, 6 H), 1.31—1.61 (m, 4 H), 1.76—1.98 (m, 6 H), 2.14—2.30 (m, 2 H), 2.41 (tt, *J* = 3, 12 Hz, 1 H), 2.55 (s, 3 H), 5.45 (tt, *J* = 4, 11 Hz, 1 H), 6.84—7.07 (m, 3 H); ^{19}F NMR (188 MHz) δ = −139.1 (ddd, *J* = 8, 12, 21 Hz, 1 F), −143.0 (dddd, *J* = 5, 8, 10, 21 Hz, 1 F); ^{13}C NMR (75.5 MHz) δ = 18.6 (s), 27.7 (s), 30.1 (s), 31.0 (s), 34.3 (s), 41.82 (s), 41.84 (s), 43.5 (d, *J* = 1 Hz), 115.2 (d, *J* = 17 Hz), 116.6 (d, *J* = 16 Hz), 122.4 (dd, *J* = 3, 6 Hz), 144.5 (dd, *J* = 4, 5 Hz), 148.4 (dd, *J* = 13, 245 Hz), 150.0 (dd, *J* = 13, 247 Hz), 215.0 (s); MS *m/z* (rel intensity) 384 (M^+; 0.17), 277 (15), 276 (47), 195 (17), 179 (19), 153 (22), 140 (37), 127 (100), 109 (18), 95 (20), 83 (50), 81 (58), 79 (31), 67 (51). Found: C, 62.27; H, 6.92%. Calcd for $C_{20}H_{26}F_2OS_2$: C, 62.47; H, 6.82%.

***O*-3β-Cholestanyl *S*-Methyl Dithiocarbonate (2α).** Yield, 93%. A colorless powder, mp 98.8—100.0 °C; R_f = 0.66 (hexane). IR (KBr) 2868, 2851, 1468, 1447, 1383, 1367, 1331, 1258, 1246, 1221, 1194, 1154, 1129, 1059, 1030, 995, 963, 922 cm^{-1}; ^1H NMR (200 MHz) δ = 0.60—2.15 (m, 47 H), 2.53 (s, 3 H), 5.38—5.60 (m, 1 H); ^{13}C NMR (50.3 MHz) δ = 12.1 (s), 12.2 (s), 18.7 (s), 18.8 (s), 21.2 (s), 22.5 (s), 22.8 (s), 23.8 (s), 24.2 (s), 26.8 (s), 28.0 (s), 28.2 (s), 28.6 (s), 32.0 (s), 33.3 (s), 35.5 (s), 35.8 (s), 36.2 (s), 36.7 (s), 39.5 (s), 40.0 (s), 42.6 (s), 44.6 (s), 54.2 (s), 56.3 (s), 56.4 (s), 83.6 (s), 215.2 (s); MS *m/z* (rel intensity) 478 (M^+; 0.2), 371 (29), 370 (40), 355 (13), 316 (13), 215 (34), 163 (16), 161 (21), 111 (20), 109 (43), 107 (43), 95 (79), 91 (53), 83 (44), 81 (100), 67 (73). Found: *m/z* 478.3264 (M^+). Calcd for $C_{29}H_{50}OS_2$: M, 478.3303. Found: C, 72.28; H, 10.46%. Calcd for $C_{29}H_{50}OS_2$: C, 72.74; H, 10.53%.

Synthesis of *O*-4-(4′-Acetoxy)biphenyl *S*-Methyl Dithiocarbonate (2j). According to the general procedure for the preparation of dithiocarbonates described above, *O*-4′-hydroxy-4-biphenyl *S*-methyl dithiocarbonate was prepared in 42% yield with DMF as the reaction media. A mixture of the dithiocarbonate (1.5 mmol), pyridine (2.5 mL), and 4-dimethylaminopyridine (DMAP, 10 mg) was treated with Ac_2O (1.8 mL, 0.17 mmol) overnight. Workup and purification gave **2j** in 82% as a pale yellow powder, mp 112.8—113.4 °C; R_f = 0.23 (hexane–EtOAc = 10 : 1). IR (KBr) 3059, 2924, 1905, 1751, 1599, 1491, 1431, 1367, 1317, 1213, 1062, 1003, 914, 839, 800, 721 cm^{-1}; ^1H NMR (200 MHz) δ = 2.32 (s, 3 H), 2.70 (s, 3 H), 7.06—7.20 (m, 4 H), 7.52—7.71 (m, 4 H); ^{13}C NMR (75.5 MHz) δ = 20.0 (s), 21.1 (s), 115.7 (s), 121.9 (s), 122.4 (s), 128.2 (s), 137.9 (s), 138.8 (s), 150.3 (s), 154.1 (s), 169.4 (s), 215.7 (s); MS *m/z* (rel intensity) 319 (M^++1; 1), 318 (M^+; 4), 312 (11), 310 (10), 152 (7), 139 (10), 91 (100), 75 (8). Found: *m/z* 318.0377. Calcd for $C_{16}H_{14}O_3S_2$: M, 318.0384.

***O*-1-Benzylbutyl *S*-Phenyl Dithiocarbonate (2r).** This substrate was prepared from 1-phenyl-2-pentanol (0.53 g, 3.2 mmol) by treatment with phenyl chlorodithioformate (0.55 mL, 3.9 mmol), pyridine (0.5 mL, 9.4 mmol), and DMAP (61 mg, 0.50 mmol) in dichloromethane (2.0 mL) at room temperature for 1 h. Workup and purification afforded **2r** (0.31 g, 30% yield) as a pale yellow oil; R_f = 0.50 (hexane–EtOAc = 10 : 1). IR 3061, 3028, 2959, 2872, 1497, 1473, 1456, 1233, 1129, 1078, 1040, 1021, 999, 746, 700 cm^{-1}; ^1H NMR (300 MHz) δ = 0.83 (t, *J* = 7 Hz, 3 H), 1.14—1.39 (m, 2 H), 1.43—1.60 (m, 2 H), 2.83 (dd, *J* = 7, 14 Hz, 1 H), 2.99 (dd, *J* = 6, 14 Hz, 1 H), 5.75—5.84 (m, 1 H), 7.02—7.10 (m, 2 H), 7.16—7.28 (m, 3 H), 7.38—7.49 (m, 5 H); ^{13}C NMR (75.5 MHz) δ = 13.8 (s), 18.3 (s), 34.6 (s), 39.4 (s), 84.9 (s), 126.5 (s), 128.3 (s), 129.1 (s), 129.4 (s), 129.8 (s), 129.9 (s), 135.1 (s), 136.7 (s), 212.3 (s); MS *m/z* (rel intensity) 316 (M^+; 1), 268 (2), 240 (8), 167 (4), 146 (8), 91 (100), 77 (10). Found: *m/z* 316.0956. Calcd for $C_{18}H_{20}OS_2$: M, 316.0956.

A General Procedure for the Preparation of Trifluoromethyl Ethers of Primary Alcohols and Phenols. An oven-dried polypropylene round bottom tube equipped with a rubber septum, a Teflon®-coated magnetic stirring bar, and an argon inlet, was flushed with argon and charged with DBH (3.0 mmol) and dry CH_2Cl_2 (30 mL). The suspension was cooled to −78 °C using an external acetone-dry ice bath and stirred at −78 °C for 10 min. To the mixture was slowly added over 5 min 70% HF/Py (2.0 mL, 40 mmol of HF/mL) using a polypropylene/polyethylene syringe under an argon atmosphere. The resulting suspension was stirred vigorously. To this mixture was added dropwise a solution of **2** (1.0 mmol) in CH_2Cl_2 (3.0 mL) at −78 °C via a cannula by positive argon pressure. After the addition was completed, the acetone–dry ice bath was replaced by an ice-cold NaCl solution bath. The resulting red-brown reaction mixture was stirred at the same temperature for 30 min, diluted with diethyl ether at 0 °C, carefully (*caution!! during this operation, vigorous evaporation of hydrogen fluoride often occurs*), and quenched by careful addition of an ice-cold aqueous $NaHSO_3$/$NaHCO_3$/NaOH (pH 10) solution until a red-brownish color of the mixture disappeared at 0 °C. The pH value was readjusted to 10 at 0 °C by slow addition of ice-

cooled 30% NaOH aq solution and diluted with diethyl ether. The contents were transferred to a separatory funnel; the organic phase was separated. The aqueous phase was extracted four times with portions of diethyl ether; the combined organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Pyridine of the residue was removed by double toluene azeotrope under reduced pressure. The residue was purified by flash column chromatography or bulb-to-bulb distillation to give trifluoromethyl ethers **3**. Yields and spectral properties of products are as follows.

4-Propyl-1-trifluoromethoxybenzene (3a). Isolated in 58% yield as a colorless oil; $R_f = 0.68$ (hexane). IR 2962, 2934, 2874, 1728, 1599, 1508, 1487, 1464, 1387, 1262, 1221, 1169, 1073, 846, 743 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.95$ (t, $J = 7$ Hz, 3 H), 1.64 (tq, $J = 7$, 7 Hz, 2 H), 2.59 (t, $J = 7$ Hz, 2 H), 7.12 (d, $J = 9$ Hz, 2 H), 7.19 (d, $J = 9$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -58.46$ (s); MS *m/z* (rel intensity) 205 (M^++1; 4), 204 (M^+; 6), 189 (11), 187 (13), 175 (38), 117 (12), 115 (18), 107 (16), 105 (15), 91 (15), 89 (19), 88 (14), 84 (100), 77 (44), 74 (20), 69 (85). Found: *m/z* 204.0755. Calcd for $C_{10}H_{11}F_3O$: M, 204.0762.

4-Hexyl-1-trifluoromethoxybenzene (3c). Yield, 50%. A colorless oil; $R_f = 0.70$ (hexane). IR 2932, 2861, 1510, 1262, 1223, 1165, 1020, 842, 808 cm^{-1}; ^1H NMR (100 MHz) $\delta = 0.90$ (t, $J = 6$ Hz, 3 H), 1.10—1.87 (m, 8 H), 2.63 (t, $J = 7$ Hz, 2 H), 7.03 (d, $J = 6$ Hz, 2 H), 7.22 (d, $J = 6$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -58.50$ (s); MS *m/z* (rel intensity) 247 (M^++1; 3), 246 (M^+; 22), 176 (22), 175 (100), 109 (5), 78 (3). Found: C, 63.72; H, 6.97%. Calcd for $C_{13}H_{17}F_3O$: C, 63.40; H, 6.96%.

2- Benzyloxy- 1- bromo- 3- trifluoromethoxybenzene (3e′). Yield, 56%. A colorless oil; $R_f = 0.41$ (hexane). IR 2928, 1595, 1582, 1491, 1252, 1219, 1169, 1073, 1049, 1011, 808, 719 cm^{-1}; ^1H NMR (200 MHz) $\delta = 5.15$ (s, 2 H), 6.91 (d, $J = 9$ Hz, 2 H), 7.14 (dd, $J = 3$, 9 Hz, 1 H), 7.4—7.6 (m, 6 H); ^{19}F NMR (188 MHz) $\delta = -58.94$ (s); MS *m/z* (rel intensity) 348 (M^++2; 1), 346 (M^+; 1), 257 (2), 171 (58), 170 (9), 169 (100), 149 (6), 90 (18), 89 (12), 79 (3), 69 (11), 63 (9), 58 (8). Found: *m/z* 345.9810. Calcd for $C_{14}H_{10}{}^{79}BrF_3O_2$: M, 345.9816.

4-Bromo-1-trifluoromethoxybenzene (3f).[29] Obtained in 62% yield. ^1H NMR (200 MHz) $\delta = 7.06$ (d, $J = 8$ Hz, 2 H), 7.51 (d, $J = 8$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -58.63$ (s).

Propyl 4-Trifluoromethoxybenzoate (3g). Yield, 30%. A colorless oil; $R_f = 0.46$ (hexane–Et_2O = 10 : 1). IR 2973, 2884, 1725, 1609, 1507, 1416, 1307, 1260, 1221, 1169, 1103, 1019, 770, 710 cm^{-1}; ^1H NMR (300 MHz) $\delta = 1.03$ (t, $J = 7$ Hz, 3 H), 1.80 (tq, $J = 7$, 7 Hz, 2 H), 4.29 (t, $J = 7$ Hz, 2 H), 7.27 (d, $J = 7$ Hz, 2 H), 8.10 (t, $J = 7$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -58.14$ (s); ^{13}C NMR (75.5 MHz) $\delta = 10.5$ (s), 22.1 (s), 66.8 (s), 120.2 (s), 120.3 (q, $J = 259$ Hz), 128.9 (s), 131.5 (s), 152.5 (s), 165.4 (s); MS *m/z* (rel intensity) 249 (M^++1; 0.1), 248 (M^+; 0.7), 207 (20), 206 (58), 190 (10), 189 (100), 161 (12), 95 (37), 75 (8), 69 (8), 64 (13). Found: *m/z* 248.0663. Calcd for $C_{11}H_{11}F_3O_3$: M, 248.0660.

Methyl 3-Trifluoromethoxybenzoate (3h). Yield, 76%. A colorless oil; $R_f = 0.24$ (hexane) IR 2959, 1732, 1592, 1449, 1302, 1256, 1171, 1102, 1078, 997, 760, 708 cm^{-1}; ^1H NMR (200 MHz) $\delta = 3.94$ (s, 3 H), 7.42 (d, $J = 8$ Hz, 1 H), 7.48 (dd, $J = 8$, 8 Hz, 1 H), 7.90 (s, 1 H), 7.98 (d, $J = 8$ Hz, 1 H); ^{19}F NMR (188 MHz) $\delta = -58.45$ (s); ^{13}C NMR (75.5 MHz) $\delta = 52.4$ (s), 120.4 (q, $J = 258$ Hz), 122.0 (s), 125.3 (s), 127.9 (s), 129.9 (s), 132.2 (s), 149.2 (q, $J = 2$ Hz), 165.7 (s); MS *m/z* (rel intensity) 222 (M^++2; 1), 221 (M^++1; 4), 220 (M^+; 33), 190 (10), 189 (100) 161 (31), 135 (9), 111 (3), 95 (43), 92 (11), 75 (12), 69 (19), 63 (21). Found: *m/z* 220.0348. Calcd for $C_9H_7F_3O_3$: M, 220.0347.

4-Acetoxy-4′-trifluoromethoxybiphenyl (3j). Isolated in 80% yield as colorless crystals, mp 126 °C; $R_f = 0.68$ (hexane–CH_2Cl_2 = 1 : 1). IR (KBr) 3072, 2930, 1911, 1761, 1604, 1496, 1373, 1292, 1215, 1167, 1006, 914, 842, 798 cm^{-1}; ^1H NMR (200 MHz) $\delta = 2.33$ (s, 3 H), 7.21 (d, $J = 9$ Hz, 2 H), 7.34 (d, $J = 9$ Hz, 2 H), 7.55 (d, $J = 9$ Hz, 2 H), 7.57 (d, $J = 9$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -58.34$ (s); ^{13}C NMR (75.5 MHz) $\delta = 21.1$ (s), 120.5 (q, $J = 258$ Hz), 121.2 (s), 122.0 (s), 128.1 (s), 128.4 (s), 137.5 (s), 139.1 (s), 148.7 (s), 150.4 (s), 169.4 (s); MS *m/z* (rel intensity) 297 (M^++1; 2), 296 (M^+; 10), 255 (14), 254 (100), 185 (13), 157 (7), 128 (6), 69 (3). Found: C, 60.69; H, 3.86%. Calcd for $C_{15}H_{11}F_3O_3$: C, 60.82; H, 3.74%.

4-Bromo-4′-trifluoromethoxybiphenyl (3k). Obtained in 52% yield with HF/Py (80 molar amounts) or in 78% yield with HF/Py (40 molar amounts) as colorless needles, mp 59.9—61.2 °C; $R_f = 0.70$ (hexane). IR (KBr) 3060, 3030, 1906, 1589, 1514, 1481, 1389, 1260, 1163, 1003, 834, 808 cm^{-1}; ^1H NMR (200 MHz) $\delta = 7.29$ (d, $J = 9$ Hz, 2 H), 7.42 (d, $J = 9$ Hz, 2 H), 7.54 (t, $J = 8$ Hz, 2 H), 7.58 (d, $J = 8$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -58.33$ (s); MS *m/z* (rel intensity) 320 (M^++4; 1), 319 (M^++3; 13), 318 (M^++2; 96), 317 (M^++1; 14), 316 (M^+; 100), 249 (27), 247 (27), 221 (25), 219 (26), 152 (18), 140 (26), 139 (49), 69 (25). Found: C, 48.96; H, 2.47%. Calcd for $C_{13}H_8BrF_3O$: C, 49.24; H, 2.54%.

1-Bromo-4-(2-trifluoromethoxyethyl)benzene (3l). Yield, 81%. A colorless oil, bp 120 °C/6 mmHg (1 mmHg = 133.322 Pa); $R_f = 0.47$ (hexane). IR 2975, 2915, 1595, 1491, 1404, 1267, 1144, 1075, 1013, 826, 804 cm^{-1}; ^1H NMR (300 MHz) $\delta = 2.95$ (t, $J = 7$ Hz, 2 H), 4.13 (t, $J = 7$ Hz, 2 H), 7.10 (d, $J = 8$ Hz, 2 H), 7.44 (d, $J = 8$ Hz, 2 H); ^{19}F NMR (282 MHz) $\delta = -61.23$ (s); ^{13}C NMR (75.5 MHz) $\delta = 34.6$ (s), 67.3 (q, $J = 4$ Hz), 120.8 (s), 121.5 (q, $J = 255$ Hz), 130.6 (s), 131.7 (s), 135.6 (s); MS *m/z* (rel intensity) 271 (M^++3; 3), 270 (M^++2; 24), 269 (M^++1; 3), 268 (M^+; 24), 251 (10), 249 (22), 247 (11), 171 (80), 170 (12), 169 (100), 90 (36), 89 (36), 86 (37), 84 (61), 77 (23), 75 (15), 74 (24), 69 (54), 63 (54). Found: *m/z* 267.9714. Calcd for $C_9H_8{}^{79}BrF_3O$: M, 267.9711.

1- Bromo- 4- [3- (trifluoromethoxy)propyl]benzene (3m′). Yield, 75%. A colorless oil, $R_f = 0.33$ (hexane). IR 2973, 1489, 1408, 1271, 1140, 1073, 1013, 855, 835, 797 cm^{-1}; ^1H NMR (300 MHz) $\delta = 1.97$ (tt, $J = 6$, 8 Hz, 2 H), 2.68 (t, $J = 8$ Hz, 2 H), 3.94 (t, $J = 6$ Hz, 2 H), 7.05 (d, $J = 8$ Hz, 2 H), 7.41 (d, $J = 8$ Hz, 2 H); ^{19}F NMR (282 MHz) $\delta = -61.17$ (s); ^{13}C NMR (75.5 MHz) $\delta = 30.1$ (s), 31.0 (s), 66.2 (q, $J = 3$ Hz), 120.0 (s), 121.7 (q, $J = 254$ Hz), 130.2 (s), 131.6 (s), 139.5 (s); MS *m/z* (rel intensity) 285 (M^++3; 2), 284 (M^++2; 23), 283 (M^++1; 2), 282 (M^+; 19), 172 (15), 171 (55), 169 (100), 117 (14), 115 (13), 104 (11), 91 (41), 90 (33), 89 (29), 77 (25), 69 (47), 65 (13). Found: *m/z* 281.9866. Calcd for $C_{10}H_{10}{}^{79}BrF_3O$: M, 281.9868.

1-Trifluoromethoxydecane (3n). Yield, 80%. A colorless oil; $R_f = 0.75$ (hexane). IR 2928, 2857, 1728, 1466, 1408, 1383, 1273, 1142, 1044, 725 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.88$ (t, $J = 6$ Hz, 3 H), 1.15—1.48 (m, 14 H), 1.60—1.79 (m, 2 H), 3.94 ($J = 6$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -61.14$ (s); MS *m/z* (rel intensity) 227 (M^++1; 0.7), 226 (M^+; 57), 141 (1), 112 (5), 97 (13), 83 (14), 69 (26), 57 (57), 43 (100). Found: *m/z* 226.1540. Calcd for $C_{11}H_{21}F_3O$: M, 226.1544.

1-Trifluoromethoxyhexadecane (3o). Isolated in 95% yield with DBH or in 67% yield using [bis(trifluoroacetoxy)iodo]benzene as an oxidant, respectively. A colorless oil; $R_f = 0.78$ (hexane). IR 2926, 2855, 1468, 1408, 1273, 1223, 1142, 860, 722 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.88$ (t, $J = 6$ Hz, 3 H), 1.18—1.48 (m, 26 H), 1.60—1.79 (m, 2 H), 3.94 ($J = 7$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -61.18$ (s); ^{13}C NMR (75.5 MHz) $\delta = 14.1$ (s), 22.7 (s),

25.4 (s), 28.7 (s), 29.1 (s), 29.37 (s), 29.45 (s), 29.54 (s), 29.63 (s), 29.67 (s), 29.69 (s), 29.71 (s), 31.9 (s), 67.5 (q, J = 3 Hz), 121.7 (q, J = 254 Hz); MS m/z (rel intensity) 312 (M^++2; 0.2), 311 (M^++1; 0.9), 310 (M^+; 5), 224 (3), 211(4), 169 (7), 155 (8), 141 (5), 140 (4), 126 (13), 111 (33), 99 (36), 98 (68), 97 (68), 96 (12), 85 (94), 84 (39), 83 (72), 75 (15), 71 (100), 70 (74), 69 (93). Found: m/z 310.2484. Calcd for $C_{17}H_{33}F_3O$: M, 310.2483.

Oxidative Desulfurization–Fluorination of Difluoro(methylthio)methyl Methyl Ethers. Difluoro(methylthio)methyl methyl ethers **4** were fluorinated under the conditions for the fluorination of dithiocarbonates **2**. Yields (amounts and reagent) and spectral properties of products are as follows:

Compound **3a**: 42% yield, (70%, HF/Py 80 mol; DBH, 1 mol).

Compound **3e′**: 62% yield, (70%, HF/Py 80 mol; DBH, 2 mol).

Compound **3h**: 51% yield, (70%, HF/Py 80 mol; DBH, 1 mol).

3-(Trifluoromethoxy)propylbenzene (3m): Obtained in 41% yield as a colorless oil using 70% HF/Py (80 mol) and DBH (1 mol); R_f = 0.32 (hexane). IR 2928, 2862, 1456, 1408, 1270, 1141, 1033, 852 cm^{-1}; ^1H NMR (200 MHz) δ = 2.00 (tq, J = 7, 7 Hz, 2 H), 2.71 (t, J = 7 Hz, 2 H), 3.96 (t, J = 7 Hz, 2 H), 7.0—7.4 (m, 5 H); ^{19}F NMR (188 MHz) δ = −61.09 (s); MS m/z (rel intensity) 205 (M^++1; 3), 204 (M^+; 6), 167 (2), 150 (8), 149 (100), 117 (3), 107 (6), 92 (10), 91 (33), 85 (12), 83 (10), 71 (26), 69 (27). Found: m/z 204.0758. Calcd for $C_{10}H_{11}F_3O$: M, 204.0762.

A General Procedure for the Difluorination of Dithiocarbonate. Method A. To a stirred solution of $TBAH_2F_3$ (5.0 mmol) and dithiocarbonate **2** (1.0 mmol) in CH_2Cl_2 (2.0 mL) was added NBS (4.0 mmol) in one portion at room temperature. The resulting mixture was stirred for 1 h at room temperature, then poured into an aq solution of $NaHCO_3$, NaOH, and $NaHSO_3$, and extracted three times with dichloromethane. The combined organic phase was dried over anhydrous sodium sulfate, filtered through a pad of Celite/silica gel (Wako Gel C-100), and concentrated. The residue was purified by flash column or preparative thin layer chromatography to give difluoro(methylthio)methyl ether **4**.

Method B. The reaction was carried out by a procedure similar to that described in Method A. Work-up was effected as follows. The reaction mixture was diluted with a mixture of pentane and diethyl ether (5 : 1). The resulting insoluble material was filtered through a short silica gel (Wako gel C-100) column. The filtrate was concentrated under reduced pressure. The residue was purified by flash column or preparative thin layer chromatography to give **4**.

Method, yield, and spectroscopic properties of products follow:

1-Difluoro(methylthio)methoxy-4-propylbenzene (4a). Method A, 58% yield. A colorless oil; R_f = 0.35 (hexane–CH_2Cl_2 = 40 : 1). IR 2955, 2930, 1720, 1502, 1205, 1198, 1138, 1108, 1050, 1028, 963, 838, 796 cm^{-1}; ^1H NMR (200 MHz) δ = 0.93 (t, J = 7 Hz, 3 H), 1.60 (qt, J = 7, 8 Hz, 2 H), 2.36 (s, 3 H), 2.60 (t, J = 8 Hz, 2 H), 7.10 (d, J = 7 Hz, 2 H), 7.16 (d, J = 7 Hz, 2 H); ^{19}F NMR (188 MHz) δ = −46.55 (s); MS m/z (rel intensity) 276 (M^++2; 1), 275 (M^++1; 4), 274 (M^+; 22), 203 (9), 161 (9), 97 (100), 91 (11). Found: C, 56.79; H, 6.05%. Calcd for $C_{11}H_{14}F_2OS$: C, 56.88; H, 6.08%.

4-[Difluoro(methylthio)methoxy]toluene (4b). Method A, 64% yield. A colorless oil; R_f = 0.69 (hexane–Et_2O = 5 : 1). IR 3048, 2942, 1724, 1508, 1440, 1382, 1218, 1200, 1171, 1142, 1113, 1053, 1034, 973, 872, 721 cm^{-1}; ^1H NMR (200 MHz) δ = 2.35 (s, 3 H), 2.37 (s, 3 H), 7.10 (d, J = 9 Hz, 2 H), 7.16 (d, J = 9 Hz, 2 H); ^{19}F NMR (188 MHz) δ = −46.49 (s); ^{13}C NMR (75.5 MHz) δ = 12.4 (t, J = 3 Hz), 20.8 (s), 121.3 (s), 129.8 (t, J = 292 Hz), 129.9 (s), 135.8 (s), 148.4 (s); MS m/z (rel intensity) 205 (M^++1; 6), 204 (M^+; 33), 154 (13), 107 (8), 97 (100), 95 (11), 91 (32), 71 (18). Found: m/z 204.0425. Calcd for $C_9H_{10}F_2OS_2$: M, 204.0420.

1-Difluoro(methylthio)methoxy-4-hexylbenzene (4c). Method A, 36% yield. A colorless oil; R_f = 0.33 (hexane–CH_2Cl_2 = 40 : 1). IR 2930, 2859, 1726, 1507, 1466, 1383, 1200, 1144, 1055, 972 cm^{-1}; ^1H NMR (200 MHz) δ = 0.89 (t, J = 7 Hz, 3 H), 1.05—1.85 (m, 8 H), 2.36 (s, 3 H), 2.61 (t, J = 7 Hz, 2 H), 6.81—7.49 (m, 4 H); ^{19}F NMR (188 MHz) δ = −46.40 (s); MS m/z (rel intensity) 276 (M^++2; 1), 275 (M^++1; 4), 274 (M^+; 22), 203 (9), 161 (9), 97 (100), 91 (11). Found: C, 61.26; H, 7.17%. Calcd for $C_{14}H_{20}F_2OS$: C, 61.29; H, 7.35%.

1- Difluoro(methylthio)methoxy- 4- methoxybenzene (4d). Method A, 33% yield. R_f = 0.56 (hexane–Et_2O = 5 : 1). IR 2946, 2840, 1720, 1600, 1500, 1250, 1190, 1140, 1110, 1030, 830 cm^{-1}; ^1H NMR (200 MHz) δ = 2.36 (s, 3 H), 3.80 (s, 3 H), 6.83 (d, J = 8 Hz, 2 H), 7.21 (d, J = 8 Hz, 2 H); ^{19}F NMR (188 MHz) δ = −46.84 (s); MS m/z (rel intensity) 222 (M^++2; 2), 221 (M^++1; 3), 220 (M^+; 31), 123 (26), 107 (13), 97 (100), 92 (10), 77 (13). Found: C, 49.25; H, 4.63%. Calcd for $C_9H_{10}F_2O_2S$: C, 49.08; H, 4.58%.

1- Benzyloxy- 4- difluoro(methylthio)methoxybenzene (4e). Method A, 43% yield. A colorless oil; R_f = 0.64 (hexane–Et_2O = 5 : 1). IR 3030, 2940, 1500, 1455, 1245, 1196, 1140, 1110, 1025, 830, 740, 690 cm^{-1}; ^1H NMR (200 MHz) δ = 2.39 (s, 3 H), 5.06 (s, 2 H), 6.94 (d, J = 8 Hz, 2 H), 7.16 (d, J = 8 Hz, 2 H), 7.28—7.60 (m, 5 H); ^{19}F NMR (188 MHz) δ = −46.82 (s); MS m/z (rel intensity) 298 (M^++2; 0.5), 297 (M^++1; 1), 296 (M^+; 8), 97 (13), 92 (10), 91 (100), 65 (11). Found: C, 60.78; H, 4.68%. Calcd for $C_{15}H_{14}F_2O_2S$: C, 60.80; H, 4.76%.

1-Bromo-4-[difluoro(methylthio)methoxy]benene (4f). Method A, 43% yield. A colorless oil; R_f = 0.68 (hexane–Et_2O = 5 : 1). IR 3125, 2950, 2880, 1890, 1730, 1584, 1489, 1440, 1383, 1201, 1168, 1140, 1100, 1068, 1011, 973, 863, 830, 780, 724 cm^{-1}; ^1H NMR (200 MHz) δ = 2.38 (s, 3 H), 7.11 (d, J = 10 Hz, 2 H), 7.49 (d, J = 10 Hz, 2 H); ^{19}F NMR (188 MHz) δ = −46.96 (s); ^{13}C NMR (75.5 MHz) δ = 12.3 (t, J = 3 Hz), 123.2 (s), 129.7 (t, J = 294 Hz), 132.5 (s), 132.6 (s), 149.6 (s); MS m/z (rel intensity) 271 (M^++3; 0.7), 270 (M^++2; 7), 269 (M^++1; 0.7), 268 (M^+; 7), 223 (0.6), 221 (0.6), 157 (6), 155 (6), 145 (2), 143 (2), 119 (1), 117 (1), 97 (100). Found: m/z 267.9371. Calcd for $C_8H_7{}^{79}BrF_2OS_2$: M, 267.9369.

Propyl 4-[Difluoro(methylthio)methoxy]benzoate (4g). Method A, 25% yield. A colorless oil; R_f = 0.46 (hexane–Et_2O = 5 : 1). IR 2961, 2930, 1728, 1601, 1466, 1273, 1123, 1073, 1042, 743 cm^{-1}; ^1H NMR (200 MHz) δ = 1.03 (t, J = 6 Hz, 3 H), 1.80 (tq, J = 6, 6 Hz, 2 H), 2.44 (s, 3 H), 4.30 (t, J = 6 Hz, 2 H), 7.25 (d, J = 9 Hz, 2 H), 8.10 (d, J = 9 Hz, 2 H); ^{19}F NMR (188 MHz) δ = −46.87 (s); ^{13}C NMR (75.5 MHz) δ = 10.5 (s), 12.4 (t, J = 3 Hz), 22.1 (s), 66.7 (s), 120.6 (s), 122.2 (s), 129.7 (t, J = 294 Hz), 131.2 (s), 154.0 (s), 165.7 (s); MS m/z (rel intensity) 276 (M^+; 9), 167 (36), 149 (100), 104 (6), 83 (8), 71 (29), 70 (25). Found: m/z 276.0630. Calcd for $C_{12}H_{14}F_2O_3S$: M, 276.0632.

Methyl 3-[Difluoro(methylthio)methoxy]benzoate (4h). Method A, 32% yield. A colorless oil; R_f = 0.38 (hexane–Et_2O = 5 : 1). IR 2950, 1727, 1585, 1442, 1382, 1296, 1285, 1272, 1203, 1130, 1103, 1058, 748 cm^{-1}; ^1H NMR (100 MHz) δ = 2.32 (s, 3 H), 3.86 (s, 3 H), 7.27—7.49 (m, 2 H), 7.72—7.95 (m, 2 H); ^{19}F NMR (188 MHz) δ = −46.98 (s); MS m/z (rel intensity) 249 (M^++1; 2), 248 (M^+; 13), 217 (6), 135 (12), 97 (100), 76 (6), 63 (5). Found: C, 48.56; H, 4.13%. Calcd for $C_{10}H_{10}F_2O_3S$: C, 48.38; H, 4.06%.

4-[Difluoro(methylthio)methoxy]biphenyl (4i). Method A, 23% yield. A colorless oil; R_f = 0.58 (hexane–EtOAc = 10 : 1). IR

3034, 2934, 1726, 1605, 1514, 1485, 1207, 1142, 1057, 1008, 972, 841, 760, 698 cm^{-1}; ^1H NMR (200 MHz) δ = 2.59 (s, 3 H), 7.29—7.61 (m, 9 H); ^{19}F NMR (188 MHz) δ = −47.91 (s); ^{13}C NMR (75.5 MHz) δ = 12.4 (s), 121.7 (s), 127.0 (s), 127.1 (s), 127.4 (s), 128.1 (s), 128.8 (s), 129.6 (t, J = 290 Hz), 139.1 (s), 140.1 (s); MS *m/z* (rel intensity) 268 (M^++2; 2), 267 (M^++1; 7), 266 (M^+; 41), 169 (6), 153 (17), 152 (15), 141 (8), 115 (11), 97 (100). Found: C, 62.99; H, 4.38%. Calcd for $C_{14}H_{12}F_2OS$: C, 63.14; H, 4.54%.

4- Bromo- 4′- [difluoro(methylthio)methoxy]biphenyl (4k). Method A, 28% yield. Colorless crystals, mp 37.5—38.3 °C; R_f = 0.60 (hexane–EtOAc = 10 : 1). IR (KBr) 3042, 2942, 1902, 1586, 1512, 1480, 1387, 1213, 1090, 1028, 818, 785, 720 cm^{-1}; ^1H NMR (200 MHz) δ = 2.40 (s, 3 H), 7.27 (d, J = 9 Hz, 2 H), 7.42 (d, J = 9 Hz, 2 H), 7.52 (d, J = 8 Hz, 2 H), 7.56 (d, J = 8 Hz, 2 H); ^{19}F NMR (188 MHz) δ = −46.64 (s); MS *m/z* (rel intensity) 347 (M^++3; 2), 346 (M^++2; 14), 345 (M^++1; 2), 344 (M^+; 14), 152 (15), 139 (8), 97 (100). Found: C, 48.57; H, 3.19%. Calcd for $C_{14}H_{11}BrF_2OS$: C, 48.71; H, 3.21%.

1-Bromo-4-{2-[difluoro(methylthio)methoxy]ethyl}benzene (4l). Method B, 19% yield. A colorless oil; R_f = 0.69 (hexane–Et_2O = 5 : 1). IR 2934, 1709, 1489, 1406, 1266, 1152, 1073, 1048, 1013, 972, 814, 723 cm^{-1}; ^1H NMR (300 MHz) δ = 2.21 (s, 3 H), 2.92 (t, J = 7 Hz, 2 H), 4.09 (t, J = 7 Hz, 2 H), 7.10 (d, J = 8 Hz, 2 H), 7.42 (d, J = 8 Hz, 2 H); ^{19}F NMR (188 MHz) δ = −50.70 (s); ^{13}C NMR (75.5 MHz) δ = 12.1 (t, J = 3 Hz), 34.9 (s), 66.3 (t, J = 4 Hz), 120.5 (s), 130.2 (t, J = 290 Hz), 130.6 (s), 131.6 (s), 136.3 (s); MS *m/z* (rel intensity) 298 (M^++2; 3), 296 (M^+; 3), 204 (2), 202 (2), 185 (39), 184 (100), 183 (42), 182 (99), 171 (16), 169 (15), 104 (77), 103 (26), 97 (18), 90 (13), 89 (13), 77 (30). Found: *m/z* 295.9717. Calcd for $C_{10}H_{11}{}^{79}BrF_2OS$: M, 232.0733.

{3-[Difluoro(methylthio)methoxy]propyl}benzene (4m). Method B, 15% yield. A colorless oil; R_f = 0.60 (hexane–Et_2O = 5 : 1). IR 3028, 2932, 2855, 1712, 1454, 1313, 1147, 1030, 746, 700 cm^{-1}; ^1H NMR (300 MHz) δ = 1.98 (tt, J = 7, 8 Hz, 2 H), 2.31 (s, 3 H), 2.72 (t, J = 8 Hz, 2 H), 3.93 (t, J = 7 Hz, 2 H), 7.17—7.32 (m, 5 H); ^{19}F NMR (188 MHz) δ = −50.51 (s); ^{13}C NMR (75.5 MHz) δ = 12.2 (t, J = 3 Hz), 30.6 (s), 31.8 (s), 65.4 (t, J = 5 Hz), 126.0 (s), 128.38 (s), 128.43 (s), 130.2 (t, J = 290 Hz), 141.0 (s); MS *m/z* (rel intensity) 232 (M^+; 0.4), 207 (2), 186 (2), 161 (40), 159 (100), 131 (12), 113 (14), 111 (41), 76 (10), 75 (55), 73 (12). Found: *m/z* 232.0734. Calcd for $C_{11}H_{14}F_2OS$: M, 232.0733.

1-[Difluoro(methylthio)methoxy]hexadecane (4o). Method B, 9% yield. A colorless oil; R_f = 0.78 (hexane–EtOAc = 10 : 1). IR 2924, 2855, 1715, 1468, 1352, 1150, 740 cm^{-1}; ^1H NMR (200 MHz) δ = 0.88 (t, J = 7 Hz, 3 H), 1.20—1.40 (m, 28 H), 1.62—1.71 (m, 2 H), 2.33 (s, 3 H), 4.21 (t, J = 7 Hz, 2 H); ^{19}F NMR (282 MHz) δ = −50.96 (s); ^{13}C NMR (75.5 MHz) δ = 13.4 (s), 14.1 (s), 22.7 (s), 25.8 (s), 28.7 (s), 29.0 (s), 29.2 (s), 29.4 (s), 29.5 (s), 29.55 (s), 29.62 (s), 29.66 (s), 29.7 (s), 31.9 (s), 67.7 (s), 128.7 (t, J = 290 Hz); MS *m/z* (rel intensity) 338 (M^+; 3), 270 (6), 229 (4), 167 (10), 149 (6), 99 (14), 97 (16), 85 (45), 75 (16), 71 (100), 69 (32). Found: *m/z* 338.2452. Calcd for $C_{18}H_{36}F_2OS$: M, 338.2455.

A General Procedure for the Fluorination of Dithiocarbonates Derived from Secondary, Tertiary, and Benzylic Alcohols. To a suspension of NIS (1.5 mmol) in dichloromethane (2.0 mL) in an oven-dried polypropylene round-bottom tube was added dropwise 70% HF/Py (0.5 mL, 20 mmol of HF) at −42 °C (carbon tetrachloride–dry ice bath) under stirring with a Teflon®-coated magnetic bar under an argon atmosphere. A dichloromethane solution (0.5 mL) of dithiocarbonate **2p** to **2y** (0.5 mmol) was added dropwise to the mixture at −42 °C via a cannula by an argon positive pressure. The resulting mixture was stirred at −42 °C for 1 h, poured into an ice-cold pH = 10 buffer solution ($NaHCO_3$, $NaHSO_3$, and NaOH) carefully, and extracted with diethyl ether three times. The combined ethereal layer was washed with sat. aqueous NaCl solution, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give fluorinated products **5**. Yields and spectral properties of **5** follow.

(2-Fluoropentyl)benzene (5p). Isolated in 70% yield as a colorless oil; R_f = 0.79 (hexane–EtOAc = 10 : 1). IR 3065, 2961, 2936, 1605, 1417, 1466, 1381, 1192, 1129, 1082, 1009, 961, 829, 747, 739, 700 cm^{-1}; ^1H NMR (200 MHz) δ = 0.92 (t, J = 7 Hz, 3 H), 1.25—1.70 (m, 4 H), 2.70—3.05 (m, 2 H), 4.70 (dm, J = 51 Hz, 1 H), 7.15—7.40 (m, 5 H); ^{19}F NMR (188 MHz) δ = −179.32 (dm, J = 51 Hz); ^{13}C NMR (75.5 MHz) δ = 13.9 (s), 18.4 (d, J = 5 Hz), 36.8 (d, J = 21 Hz), 41.7 (d, J = 22 Hz), 94.3 (d, J = 171 Hz), 126.5 (s), 128.4 (s), 129.3 (s), 137.4 (s); MS *m/z* (rel intensity) 167 (M^++1; 2), 166 (M^+; 15), 151 (2), 117 (2), 109 (1), 105 (2), 104 (2), 103 (2), 92 (22), 91 (100), 65 (11). Found: *m/z* 166.1165. Calcd for $C_{11}H_{15}F$: M, 166.1158.

(3-Fluoropentyl)benzene (5s). Yield, 65%. A colorless oil; R_f = 0.30 (hexane). IR 2969, 2941, 1605, 1497, 1455, 1385, 1362, 1115, 1059, 945, 745, 700 cm^{-1}; ^1H NMR (300 MHz) δ = 0.96 (t, J = 8 Hz, 3 H), 1.51—2.04 (m, 4 H), 2.62—2.86 (m, 2 H), 4.41 (dm, J = 49 Hz, 1 H), 7.16—7.31 (m, 5 H); ^{19}F NMR (282 MHz) δ = −183.21——183.72 (m); ^{13}C NMR (75.5 MHz) δ = 9.3 (d, J = 6 Hz), 28.1 (d, J = 21 Hz), 31.4 (d, J = 5 Hz), 36.5 (d, J = 21 Hz), 94.6 (d, J = 168 Hz), 125.9 (s), 128.40 (s), 128.43 (s), 141.6 (s); MS *m/z* (rel intensity) 167 (M^++1; 8), 166 (M^+; 45), 117 (27), 115 (17), 109 (14), 104 (13), 103 (13), 92 (100), 78 (22), 77 (25), 65 (37). Found: *m/z* 166.1156. Calcd for $C_{11}H_{15}F$: M, 166.1158.

(−)-Menthyl Fluoride (5t).[25] Yield, 48%; A colorless oil. IR 2957, 2930, 2872, 1458, 1385, 1371, 1183, 1013, 992, 976, 845 cm^{-1}; ^1H NMR (200 MHz) δ = 0.80—0.98 (m, 9 H), 0.99—1.50 (m, 5 H), 1.54—1.74 (m, 2 H), 1.98—2.18 (m, 2 H), 4.31 (ddt, J = 5, 11, 50 Hz); ^{19}F NMR (188 MHz) δ = −175.40 (dm, J = 50 Hz); ^{13}C NMR (75.5 MHz) δ = 17.0 (s), 20.4 (s), 22.0 (s), 23.6 (d, J = 9 Hz), 26.5 (d, J = 2 Hz), 31.2 (d, J = 11 Hz), 34.1 (d, J = 2 Hz), 41.5 (d, J = 17 Hz), 48.3 (d, J = 17 Hz), 93.2 (d, J = 173 Hz); MS *m/z* (rel intensity) 158 (M^+; 17), 138 (25), 123 (35), 99 (11), 97 (29), 96 (69), 95 (90), 81 (100), 73 (38), 72 (20), 67 (69), 59 (47), 55 (80), 53 (59), 41 (93). Found: *m/z* 158.1467. Calcd for $C_{10}H_{19}F$: M, 158.1471.

2-Fluoroadamantane (5u).[25] Yield, 82%. Colorless crystals, mp 84.2—84.7 °C. IR (KBr) 2909, 2857, 1453, 1383, 1363, 1102, 1048, 1007, 934, 816 cm^{-1}; ^1H NMR (300 MHz) δ = 1.50—1.95 (m, 10 H), 2.04—2.20 (m, 4 H), 4.68 (dm, J = 50 Hz, 1 H); ^{19}F NMR (188 MHz) δ = −174.42 (dm, J = 50 Hz); ^{13}C NMR (75.5 MHz) δ = 14.9 (s), 26.8 (d, J = 2 Hz), 27.2 (s), 27.6 (d, J = 14 Hz), 31.4 (s), 31.9 (s), 32.5 (s), 32.6 (s), 32.9 (s), 35.6 (s), 35.7 (s), 37.2 (s), 37.8 (s), 38.7 (s), 94.6 (d, J = 178 Hz); MS *m/z* (rel intensity) 155 (M^++1; 5), 154 (M^+; 32), 111 (16), 109 (12), 99 (11), 98 (42), 97 (100), 93 (43), 71 (42), 69 (49), 67 (40). Found: *m/z* 154.1155. Calcd for $C_{10}H_{15}F$: M, 154.1158.

1-Fluoroadamantane (5v). Yield, 78%. Colorless crystals, mp 108 °C (sublimation). IR (KBr) 2915, 2853, 1456, 1352, 1318, 1300, 1111, 1103, 1088, 968, 918, 812 cm^{-1}; ^1H NMR (200 MHz) δ = 1.55—1.76 (m, 6 H), 1.80—1.90 (m, 6 H), 2.15—2.35 (m, 3 H); ^{19}F NMR (188 MHz) δ = −128.95——129.01 (m); ^{13}C NMR (75.5 MHz) δ = 31.5 (d, J = 10 Hz), 35.9 (d, J = 2 Hz), 42.7 (d, J = 17 Hz), 92.5 (d, J = 184 Hz); MS *m/z* (rel intensity) 155 (M^++1; 2), 154 (M^+; 17), 136 (13), 135 (100), 111 (6), 107 (8), 97 (4), 93 (25), 92 (12), 91 (20), 79 (64), 77 (26), 67 (69), 34 (64). Found:

m/z 154.1160. Calcd for $C_{10}H_{15}F$: M, 154.1158.

4-Bromobenzyl Fluoride (5w). Yield, 43%. A colorless oil; $R_f = 0.42$ (hexane). IR 2961, 2897, 1902, 1595, 1489, 1468, 1408, 1373, 1213, 1071, 1013, 988, 837, 799 cm^{-1}; ^1H NMR (200 MHz) $\delta = 5.33$ (d, $J = 48$ Hz, 2 H), 7.26 (d, $J = 8$ Hz, 2 H), 7.52 (d, $J = 8$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -208.71$ (t, $J = 48$ Hz); ^{13}C NMR (75.5 MHz) $\delta = 83.7$ (d, $J = 167$ Hz), 122.7 (d, $J = 4$ Hz), 129.0 (d, $J = 6$ Hz), 131.7 (s), 135.1 (d, $J = 17$ Hz); MS *m/z* (rel intensity) 191 (M^++3; 3), 190 (M^++2; 3), 189 (M^++1; 10), 188 (M^+; 24), 187 (7), 110 (8), 109 (100), 108 (11), 107 (12), 83 (24), 63 (18). Found: *m/z* 187.9641. Calcd for C_7H_6BrF: M, 187.9637.

(1-Fluoropentyl)benzene (5x). Yield, 94% (DBH). A colorless oil; $R_f = 0.48$ (hexane). IR 2959, 2934, 1489, 1458, 1073, 1013, 822, 718 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.90$ (t, $J = 7$ Hz, 3 H), 1.25—1.55 (m, 4 H), 1.60—2.10 (m, 2 H), 5.41 (ddd, $J = 5$, 8, 48 Hz, 1 H), 7.20—7.50 (m, 5 H); ^{19}F NMR (188 MHz) $\delta = -174.69$ (ddd, $J = 17$, 27, 48 Hz); ^{13}C NMR (75.5 MHz) $\delta = 13.9$ (s), 22.5 (s), 27.2 (d, $J = 4$ Hz), 36.9 (d, $J = 24$ Hz), 94.7 (d, $J = 171$ Hz), 125.5 (d, $J = 7$ Hz), 128.1 (d, $J = 2$ Hz), 128.3 (s), 140.6 (d, $J = 20$ Hz); MS *m/z* (rel intensity) 167 (M^++1; 2), 166 (M^+; 15), 146 (32), 118 (10), 117 (74), 115 (42), 110 (21), 109 (100), 104 (29), 91 (32), 77 (10), 65 (11). Found: *m/z* 166.1164. Calcd for $C_{11}H_{15}F$: M, 166.1158.

4-(1-Fluoropentyl)benzaldehyde (5y). Yield, 91% (NIS), 60% (DBH). A colorless oil; $R_f = 0.50$ (hexane–Et_2O = 5 : 1). IR 2959, 2934, 2735, 1705, 1611, 1306, 1210, 1169, 1048, 831 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.91$ (t, $J = 7$ Hz, 3 H), 1.14—1.55 (m, 4 H), 1.63—2.05 (m, 2 H), 5.50 (ddd, $J = 5$, 8, 48 Hz, 1 H), 7.48 (d, $J = 8$ Hz, 2 H), 7.90 (d, $J = 8$ Hz, 2 H), 10.02 (s, 1 H); ^{19}F NMR (188 MHz) $\delta = -179.69$ (ddd, $J = 20$, 27, 48 Hz); ^{13}C NMR (75.5 MHz) $\delta = 13.9$ (s), 22.4 (s), 28.5 (d, $J = 4$ Hz), 37.0 (d, $J = 23$ Hz), 93.8 (d, $J = 173$ Hz), 125.8 (d, $J = 8$ Hz), 129.9 (s), 136.0 (s), 147.4 (d, $J = 20$ Hz), 191.8 (s); MS *m/z* (rel intensity) 195 (M^++1; 7), 194 (M^+; 39), 193 (6), 165 (19), 151 (7), 147 (11), 138 (62), 137 (100), 133 (13), 132 (15), 131 (12), 110 (24), 109 (96), 108 (15), 107 (11), 105 (15), 91 (60), 77 (21). Found: *m/z* 194.1110. Calcd for $C_{12}H_{15}FO$: M, 194.1107.

1-Difluoromethyl-4-(1-fluoropentyl)benzene (6). Yield, 23% (DBH). A colorless oil; $R_f = 0.38$ (hexane). IR 2961, 1773, 1684, 1559, 1541, 1375, 1221,1075, 1032 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.91$ (t, $J = 7$ Hz, 3 H), 1.20—1.45 (m, 4 H), 1.70—2.10 (m, 2 H), 5.46 (ddd, $J = 5$, 8, 48 Hz, 1 H), 6.65 (t, $J = 56$ Hz, 1 H), 7.40 (d, $J = 8$ Hz, 2 H), 7.52 (d, $J = 8$ Hz, 2 H); ^{19}F NMR (188 MHz) $\delta = -111.19$ (d, $J = 56$ Hz, 2 F), -177.50 (ddd, $J = 18$, 28, 52 Hz, 1 F); MS *m/z* (rel intensity) 216 (M^+; 12), 198 (3), 197 (20), 160 (14), 159 (80), 155 (30), 154 (12), 141 (100), 140 (9), 109 (15), 63 (6). Found: *m/z* 216.1123. Calcd for $C_{12}H_{15}F_3$: M, 216.1126.

A General Procedure for the Preparation Trifluoromethyl Ethers of Secondary Alcohols. To a suspension of NBS (5.0 mmol) and dichloromethane (2.5 mL) placed in an oven-dried polypropylene round-bottom tube equipped with a rubber septum and Teflon®-coated magnetic stirring bar were added dropwise distilled pyridine (0.46 mL) and subsequently 70% HF/Py (1.0 mL, 40 mmol of HF) at -42 °C (cooled by a CCl_4/dry ice bath) under an argon atmosphere. The resulting mixture was stirred at room temperature for 5 min and then cooled to 0 °C using an ice-water bath. A dichloromethane (1.5 mL) solution of dithiocarbonate **2p**, **2s**, **2α**, or **2z** (1.0 mmol) was added dropwise to the suspension at 0 °C. The dark-red reaction mixture was stirred at 0 °C for 1 h, diluted carefully with Et_2O (5 mL), and poured into an ice-cold buffer solution (pH = 10, $NaHCO_3$, $NaHSO_3$, and NaOH). The pH of the mixture was adjusted to 10 by careful addition of ice-cold 10% NaOH aqueous solution. The whole was diluted with Et_2O, and the organic phase was separated. The aqueous phase was extracted with diethyl ether three times. The combined organic phase was washed with sat. NaCl aq solution, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography (cyclohexane) afforded the corresponding trifluoromethyl ether.

***trans*-1-[*trans*-4-(3,4-Difluorophenyl)cyclohexyl]-4-trifluoromethoxycyclohexane (3z).** Yield, 42%. A colorless powder, mp 43 °C; $R_f = 0.41$ (hexane). IR (KBr) 2928, 2861, 1607, 1520, 1455, 1270, 1208, 1129, 1032, 860, 773 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.96$—1.26 (m, 6 H), 1.30—1.62 (m, 4 H), 2.06—2.20 (m, 2 H), 2.41 (tt, $J = 3$, 12 Hz, 1 H), 4.09 (tt, $J = 5$, 11 Hz, 1 H), 6.82—7.18 (m, 3 H); ^{19}F NMR (188 MHz) $\delta = -58.1$ (s, 3 F), -139.1 (dddd, $J = 1$, 8, 12, 21 Hz, 1 F), -142.9 (dddd, $J = 3$, 7, 12, 21 Hz, 1 F); ^{13}C NMR (75.5 MHz) $\delta = 27.8$ (s), 30.2 (s), 32.6 (s), 34.4 (s), 41.6 (s), 41.9 (s), 43.7 (s), 78.4 (q, $J = 2$ Hz), 115.3 (d, $J = 17$ Hz), 116.7 (d, $J = 17$ Hz), 121.7 (q, $J = 254$ Hz), 122.5 (dd, $J = 3$, 6 Hz), 144.5 (dd, $J = 4$, 5 Hz), 148.5 (dd, $J = 13$, 245 Hz), 150.1 (dd, $J = 12$, 247 Hz); MS *m/z* (rel intensity) 363 (M^++1; 6), 362 (M^+; 30), 153 (23), 140 (93), 128 (10), 127 (100), 97 (21), 95 (20), 85 (18), 83 (27), 81 (87), 79 (27), 67 (47). Found: *m/z* 362.1668 (M^+). Calcd for $C_{19}H_{23}F_5O$: M, 362.1669.

1-Phenyl-2-trifluoromethoxypentane (3p). Yield, 21%. A colorless oil. $R_f = 0.45$ (hexane). IR 3032, 2963, 2876, 1456, 1284, 1217, 1136, 1009, 747, 700 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.88$ (t, $J = 7$ Hz, 3 H), 1.25—1.66 (m, 4 H), 2.82—3.10 (m, 2 H), 4.30—4.50 (m, 1 H), 7.13—7.38 (m, 5 H); ^{19}F NMR (188 MHz) $\delta = -58.14$ (s); MS *m/z* (rel intensity) 232 (M^+; 12), 123 (2), 117 (3), 115 (3), 104 (2), 103 (4), 92 (36), 91 (100), 89 (2), 77 (9), 75 (26), 69 (10), 65 (24). Found: *m/z* 232.1077. Calcd for $C_{12}H_{15}F_3O$: M, 232.1075.

(3-Trifluoromethoxypentyl)benzene (3s). Yield, 16%. A colorless oil. $R_f = 0.48$ (hexane). IR 2957, 2925, 2855, 1464, 1378, 1366, 1261, 1123, 771, 721 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.95$ (t, $J = 7$ Hz, 3 H), 1.64—1.80 (m, 2 H), 1.82—1.98 (m, 2 H), 2.56—2.84 (m, 2 H), 4.12—4.25 (m, 1 H), 7.15—7.35 (m, 5 H); ^{19}F NMR (188 MHz) $\delta = -57.74$ (s); MS *m/z* (rel intensity) 232 (M^+; 23), 146 (8), 118 (9), 117 (56), 115 (6), 105 (19), 104 (35), 92 (37), 91 (100), 78 (13), 77 (11), 69 (35), 65 (24), 61 (12). Found: *m/z* 232.1073. Calcd for $C_{12}H_{15}F_3O$: M, 232.1075.

3β-Trifluoromethoxycholestane (3α). Yield, 24%. Colorless needles, mp = 92—94°C (EtOH); $R_f = 0.79$ (hexane). IR (KBr) 2930, 2870, 1468, 1447, 1385, 1283, 1219, 1134, 1021, 853 cm^{-1}; ^1H NMR (200 MHz) $\delta = 0.60$—2.15 (m, 46 H), 4.05—4.20 (m, 1 H); ^{19}F NMR (188 MHz) $\delta = -58.02$ (s); ^{13}C NMR (50.3 MHz) $\delta = 12.1$ (s), 12.2 (s), 18.7 (s), 21.2 (s), 22.6 (s), 22.8 (s), 23.8 (s), 24.2 (s), 28.0 (s), 28.2 (s), 28.4 (s), 28.5 (s), 31.9 (s), 34.8 (s), 35.2 (s), 35.4 (s), 35.8 (s), 36.2 (s), 36.6 (s), 39.5 (s), 39.9 (s), 42.6 (s), 44.6 (s), 54.2 (s), 56.2 (s), 56.4 (s), 78.6 (q, $J = 2.2$ Hz), 121.6 (q, $J = 254.1$ Hz); MS *m/z* (rel intensity) 457 (M^++1; 7), 456 (M^+; 23), 302 (54), 301 (100), 287 (28), 233 (23), 149 (11), 147 (11), 135 (13), 123 (27), 121 (25), 109 (33), 108 (37), 107 (47), 95 (60), 93 (45), 81 (67), 67 (78). Found: C, 73.59; H, 10.52%. Calcd for $C_{28}H_{47}F_3O$: C, 73.64; H, 10.37%.

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