Selective trifluorination of alkyl aryl sulfides using IF_5

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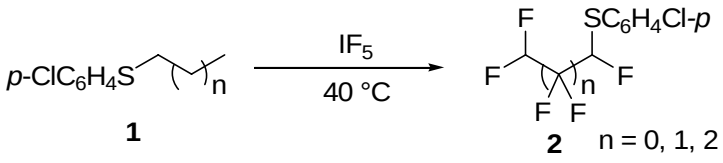
Abstract: In the reaction of IF_5 with alkyl aryl sulfides in heptane under reflux conditions, the arylthio group migrated once and three fluorine atoms were selectively introduced on the alkyl chain. In order to find the reason why the reaction stopped at the trifluorination step, we examined the oxidation potentials of the starting material, a reaction intermediate, and the product, and the time course of the reactions.

1. Introduction

Oxidative fluorination of sulfur compounds has been conveniently used to introduce one or several fluorine atoms into organic molecules under mild conditions.[1] Recently, we have found that an arylthio group of alkyl aryl sulfides migrated on the carbon chain successively to the terminal carbon by the reaction with IF_5 at 40 °C in a tight-screw capped vessel, and the fluorination took place on the carbon where the arylthio group was attached.[2] Finally, 3-7 fluorine atoms could be introduced into the alkyl chains depending on the alkyl chain length (Scheme 1). During our continuous study of fluorination using IF_5, we found that three fluorine atoms can be selectively introduced into the alkyl chain of the alkyl aryl sulfides regardless of the alkyl chain length by carrying out the reaction in heptane under reflux conditions.



1 **2** n = 0, 1, 2

Scheme 1

Keywords: Halogenation; Hypervalent elements; Migration; Sulfides.

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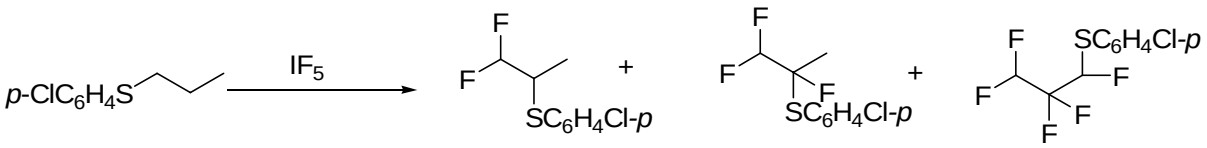
2. Results and Discussion

When *p*-chlorophenyl propyl sulfide (**1a**) was allowed to react with 1.2 eq of IF_5 in heptane under reflux condition for 1 h, the arylthio group migrated once and a mixture of 1,1-difluoro-2-(*p*-chlorophenylthio)propane (**3a**) and 1,1,2-trifluoro-2-(*p*-chlorophenylthio)propane (**4a**) was obtained. By using 2.4 eq of IF_5, **4a** could be selectively obtained and the formation of **3a** was not observed. When the reaction was carried out at 40 °C in a tight-screw capped vessel, the arylthio group migrated twice and 1,2,2,3,3-pentafluoro-1-(*p*-chlorophenylthio)propane (**2a**) was obtained as the main product. However, under reflux in heptane, the main product was **4a** even after 6 h, and **2a** was formed only as a minor product (5 %) (Table 1).

Table 1. Reaction of **1a** with IF_5 under various conditions[a]

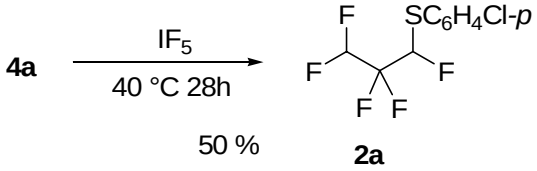


1a **3a** **4a** **2a**

Amount of IF_5 (eq to **1a**)	Reaction time (h)	Yield (%)[b] **3a**	**4a**	**2a**
1.2	1	43	17	0
2.4	1	0	74	0
2.4	6	0	72	5
2.4[c]	48	0	0	72

a) If otherwise not mentioned, the reaction was carried out in heptane under reflux. b) Isolated yield based on **1a**. c) The reaction was carried out in hexane at 40 °C in a tight-screw capped vessel.

When isolated **4a** was subjected to the reaction with IF_5 at 40 °C in the tight-screw capped vessel for 28 h, further fluorination and migration of the arylthio group took place to give **2a** as the main product (Scheme 2).

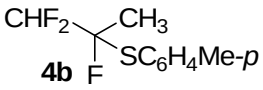
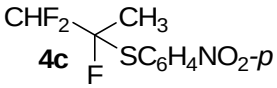
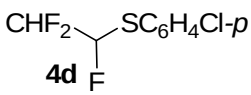
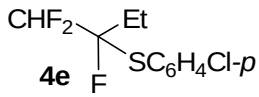
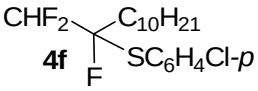
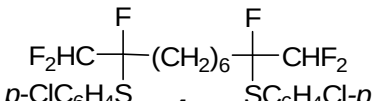
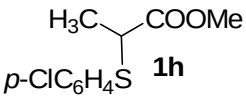
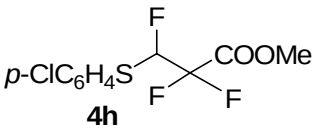
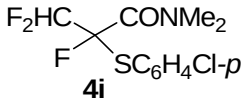
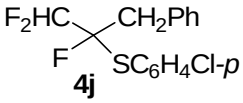


2a

Scheme 2

Various alkyl aryl sulfides were used for the reaction with IF_5 under reflux condition in heptane (Table 2). When an electron-donating group was attached at the *p*-position of a phenyl group (**1b**), 1.2 eq of IF_5 was enough to obtain the trifluorinated product (**4b**). On the other hand, the presence of a strong electron-withdrawing group (**1c**) retarded the reaction, and longer reaction time and large excess of IF_5 were required to complete the reaction. When phenyl propyl sulfide was used, a competitive iodination by *in situ*-generated IF[3] at the *p*-position of the phenyl group took place,[4] and a mixture of 1,1,2-trifluoro-2-phenylthiopropane and 1,1,2-trifluoro-2-(*p*-iodophenylthio)propane was formed. In all cases, the arylthio group migrated only once and three fluorine atoms were introduced into the sulfides regardless of the alkyl chain length. The functional groups such as ester (**1h**) or amide (**1i**), can tolerate the reaction conditions.

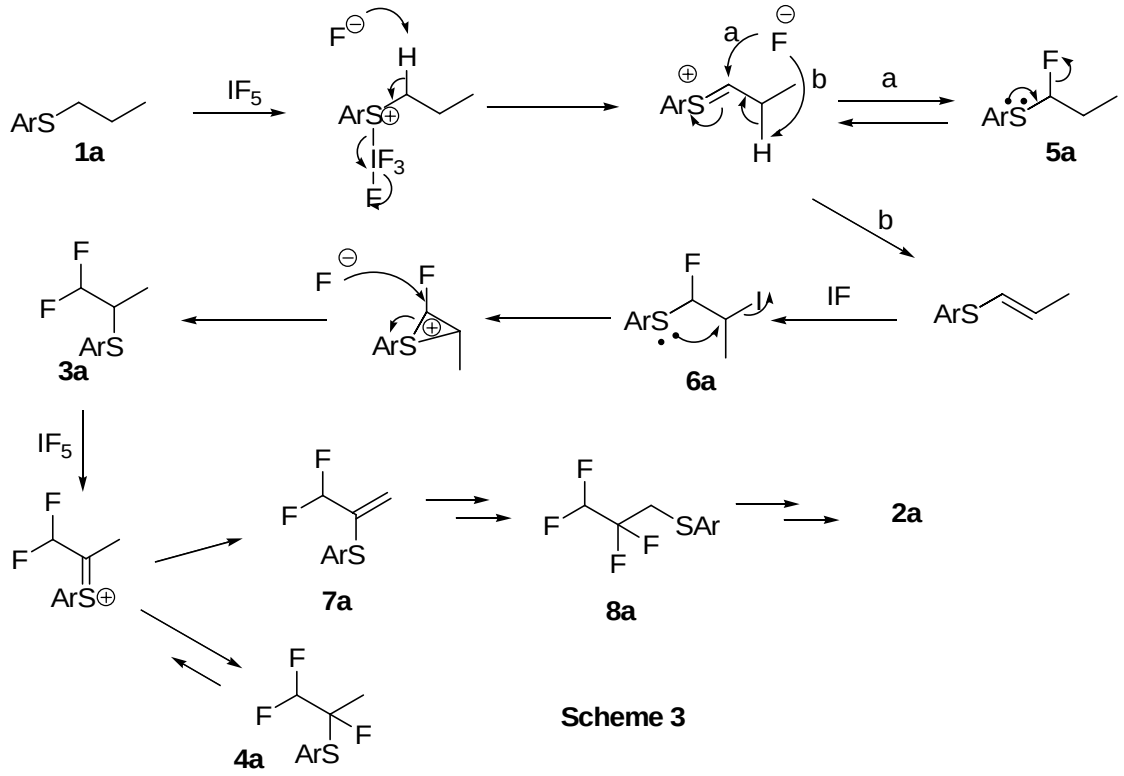
Table 2. Fluorination of Alkyl Aryl Sulfides Using IF_5[a]

Substrate	IF_5 / **1**	Product	Yield (%)[b]
p-MeC_6H_4SPr **1b**	1.2	 **4b**	51
p-$NO_2C_6H_4SPr$ **1c**	4.8	 **4c**	66[c]
p-ClC_6H_4SEt **1d**	2.4	 **4d**	66
p-ClC_6H_4SBu **1e**	2.4	 **4e**	70
p-$ClC_6H_4SC_{12}H_{25}$ **1f**	3.6	 **4f**	83
p-$ClC_6H_4S(CH_2)_{10}SC_6H_4Cl$-*p* **1g**	7.2	 **4g**	75
 **1h**	4.8	 **4h**	71[d]
p-$ClC_6H_4S(CH_2)_2CONMe_2$ **1i**	2.4	 **4i**	71
p-$ClC_6H_4S(CH_2)_3Ph$ **1j**	3.6	 **4j**	71

a) If otherwise not mentioned, the reaction was carried out in heptane under reflux for 1 h. b) Isolated yields based on substrates. c) The reaction was carried out for 24 h. d) The reaction was carried out for 6 h.

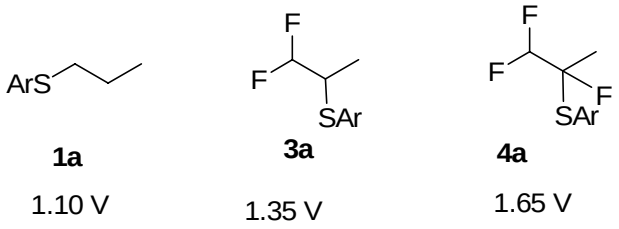
As previously proposed,[2] the fluorination and migration of the arylthio group proceed as follows. In the first step, oxidation of the sulfur in **1a** takes place to give a sulfonium intermediate which gives mono-fluorinated product **5a**,[5] or a vinylic sulfide.[6] Addition of *in situ*-generated IF to the vinylic sulfide gives 1-arylthio-1-fluoro-2-iodopropane (**6a**).[3] Then elimination of an iodide, migration of the arylthio group, and fluorination at the terminal carbon take place successively to give 1,1-difluoro-2-arylthiopropane **3a**. Finally, the oxidative fluorination of **3a** takes place at

the α-carbon of the sulfur to give **4a.** The next step, elimination of HF from **4a** to a vinylic sulfide **7a**, is slow and **4a** can be selectively obtained (Scheme 3).



Scheme 3

The oxidation potentials of **1a**, **3a**, and **4a** were measured by an electrochemical method to find the reason why the reaction stopped at **4a (**Scheme 4). As expected, the starting material **1a** has low oxidation potential (1.10 V) and, therefore, the oxidative fluorination step of **1a** proceeded fast under the reaction conditions. 1,1-Difluoro-2-arylthiopropane **3a**, which was isolated as the main product when the reaction was carried out using 1.2 eq of IF_5 to **1a**, has higher oxidation potential than **1a** due to the electron-withdrawing effect of the difluoromethyl group, and the oxidative fluorination of **3a** to **4a** proceeds relatively slowly. Trifluorinated product **4a** has the highest oxidation potential of 1.65 V which indicates that a lone-paired electron density on the sulfur is the lowest because of the strong electron-withdrawing effect of an attached trifluoropropyl group. Generally, α-fluorosulfides are unstable due to the lone-paired electrons on the sulfur and a facile elimination of fluoride takes place to cause their decomposition,[8] and isolation of 1-fluoro-1-arylthiopropane (**5a**) was unsuccessful. Though **4a** is also the α-fluorosulfide, **4a** was stable enough to isolate. As the lone-paired electron density on the sulfur is low in **4a**, the arylthio group did not destabilize **4a**. Consequently, elimination of HF from **4a** to the formation of **7a** is slow.



1a 1.10 V **3a** 1.35 V **4a** 1.65 V

Scheme 4

Then, we investigated the time courses of the reactions at 40 ºC in the tight-screw capped vessel to find the reason why the reaction does not stop at **4a** and proceeds to **2a** under the reaction conditions. The yields of **3a** increase up to 1 h and then gradually decrease with an increase in the yields of **4a**. The amount of **4a** gradually increases up to 3 h and then begins to decrease with an increase in the yields of **2a**. After 24 h, **2a** is almost the sole product and the yields of **3a** and **4a** are less than 2 %. During the reaction, the formation of 1,1,2,2-tetrafluoro-3-(*p*-chlorophenylthio)propane (**8a**) is observed but the yield is low (less than 6 %) (Fig. 1). When the reaction is carried out under reflux in heptane, **3a** and **4a** are formed as main products in 15 min and then the yields of **3a** decrease with an increase in the yields of **4a**. After 1 h, **3a** disappears and **4a** becomes the sole main product. The formation of **2a** is observed but the yield is low (less than 6 %) (Fig. 2). These results suggest that IF_5 quickly decomposes at the higher temperature (98 ºC) before **4a** changes to **2a**. However, such a possibility is ruled out because an extra addition of IF_5 to the reaction mixture after 1 h does not cause an increase of **2a**. Another possibility is the generation of a volatile material which is necessary to transform **4a** to **2a**. When the reaction is carried out in the tight-screw capped vessel, it stays in the reaction mixture and the transformation from **4a** to **2a** proceeds. On the other hand, it escapes from the reaction mixture under reflux conditions and the reaction stopps at **4a**. In order to examine the possibility, we carried out the reaction at 98 ºC in the tight-screw capped vessel. Under the reaction conditions, the generated volatile material stays in the reaction mixture and, therefore, the reaction must proceed to give **2a**. As expected, the reaction is completed in 1 h and **2a** is formed as the main product with a trace amount of **8a** (Fig. 3). The reaction proceeds more quickly than that at 40 ºC, and **3a** and **4a** disappear in 30 min. These results indicate that volatile material which is necessary to convert **4a** to **2a**, may be formed during the reaction. When the reaction is carried out under reflux without tight-screw cap, it escapes from the reaction mixture and the further conversion of **4a** does not take place. A volatile material such as HF (bp 19.5 ºC) or IF (1.0 ºC) is generated during the reaction. However, we could not identify the material which actually plays an important role to convert **4a** to **2a**.

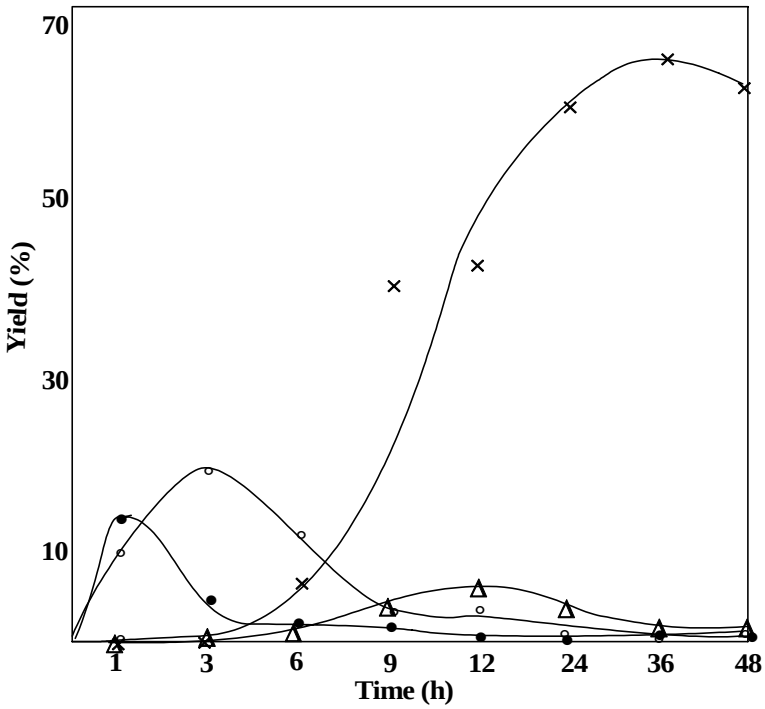


Fig 1. Time dependence of the product distributions in the reaction of IF_5 with **1a** at 40 °C in a tight-screw capped vessel (•; **3a**, o; **4a**, Δ; **8a**, ×; **2a**).

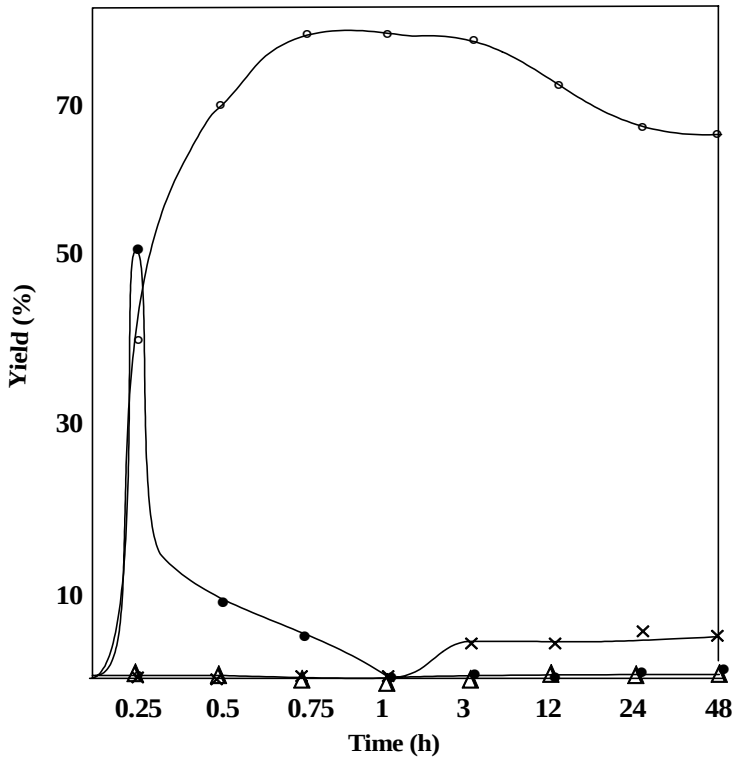


Fig 2. Time dependence of the product distributions in the reaction of IF_5 with **1a** under reflux in heptane (•; **3a**, o; **4a**, Δ; **8a**, ×; **2a**).

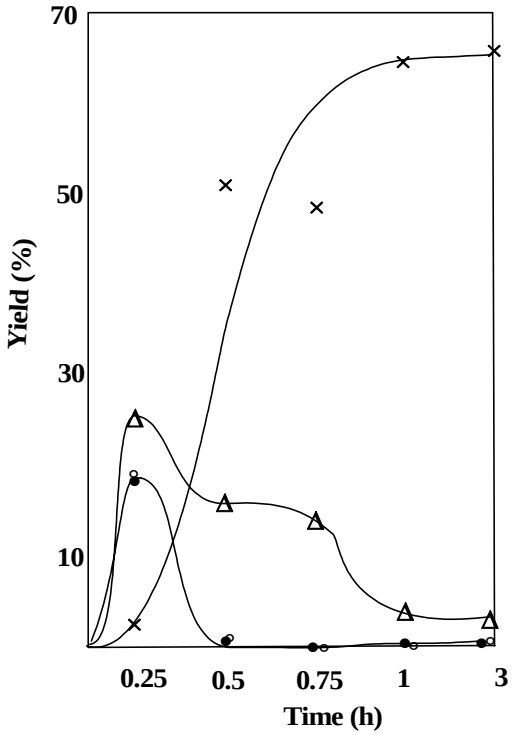


Fig 3. Time dependence of the product distributions in the reaction of IF_5 with **1a** at 98 °C in a tight-screw capped vessel (•; **3a**, o; **4a**, Δ; **8a**, ×; **2a**).

3. Conclusion

We have succeeded in introducing three fluorine atoms into sulfides selectively by the reaction with IF_5 in heptane under reflux conditions. During the reaction, the migration of the arylthio group takes place only once.

4. Experimental

4.1. General

The IR spectra were recorded using a JASCO FT/IR-410. The ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz), and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ on a JEOL JNM-A400II FT NMR and the chemical shift, δ, are referred to TMS (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F), respectively. The EI-low and high-resolution mass spectra were measured on a JEOL JMS-700TZ, JMS-FABmate or JMS-HX110. IF_5 in a stainless-steel cylinder was supplied by Daikin Industries, Ltd. IF_5

decomposes in air emitting HF fume, and, therefore, it should be carefully handled in a bench hood with rubber-gloved hands. Due to its low viscosity and high density, it is difficult to transfer IF_5 from the cylinder to a reaction vessel with a pipette; therefore, IF_5 was used as a CH_2Cl_2 solution. From the cylinder, IF_5 was transferred through a Teflon™ tube into a Teflon™ FEP bottle under an N_2 atmosphere. After measuring the amount of IF_5 in the bottle, CH_2Cl_2 was added to make a 16.7 mol% solution. IF_5 in CH_2Cl_2 was kept in the Teflon ™ FEP bottle and transferred quickly from the bottle to the reaction vessel using a Teflon™ pipette in open air. The sulfides other than **1i** were prepared from the corresponding aryl mercaptans and alkyl halides under basic conditions.[9] The sulfide **1i** was prepared from *p*-chlorophenylthiol with *N*,*N*-diethylacrylamide.[10] Et_3N-5HF was prepared by the addition of Et_3N to anhydrous HF.[11]

4.2. Fluorination of sulfides 1 using IF_5

4.2.1. General procedure. The reaction was carried out in an 8 ml- Teflon™ FEP bottle. IF_5 in CH_2Cl_2 (0.776 g of 16.7 mol% solution, 1.2 mmol), heptane (1 ml) and substrate (0.5 mmol) were introduced into a reaction vessel and a Teflon™ tube with a diameter of 10 mm and a length of 1000 mm was attached to the top of the bottle. A water-jacket was attached to the Teflon™ tube for cooling and the reaction mixture was stirred under reflux for 1 h. After consumption of the starting material was confirmed by GC, the reaction mixture was poured into ice-water and the product was extracted three times with ether. The combined ethereal phases were washed with aqueous $Na_2S_2O_3$, $NaHCO_3$, and brine, successively and dried over $MgSO_4$. After concentration under reduced pressure, the product was isolated by column chromatography (silica gel/hexane-ether as eluent).

4.2.2. 1,1-Difluoro-2-(*p*-chlorophenylthio)propane 3a. Colorless liquid: IR (neat) 1477, 1455, 1390, 1150, 1095, 1051, 1033, 1013, 823 cm^{-1}. ^1H NMR δ 1.37 (d, *J* = 7.1 Hz, 3H), 3.24 - 3.37 (m, 1H), 5.74 (dt, *J* = 56.6, 3.7 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H). ^{19}F NMR δ -124.56 (ddd, *J* = 276.0, 56.5, 16.3 Hz, 1F), -118.34 (ddd, *J* = 276.0, 56.2, 9.8 Hz, 1F). ^{13}C NMR δ 13.40 (t, *J* = 4.1 Hz), 45.76 (t, *J* = 21.9 Hz), 116.59 (t, *J* = 246.0 Hz), 129.25 (2C, s), 131.09 (s), 134.43 (s), 134.68 (2C, s). MS: 224 (M^++2, 25), 222 (M^+, 69), 173 (37), 172 (10), 171 (100), 145 (17), 144 (12), 143 (45), 136 (18), 109 (10), 108 (28), 59 (11). HRMS(EI) Calcd for $C_9H_9ClF_2S$: (M^+) 222.0081. Found: 222.0075.

4.2.3. 1,1,2-Trifluoro-2-(*p*-chlorophenylthio)propane 4a. Colorless liquid: IR (neat) 1574, 1477, 1448, 1389, 1225, 1092, 1015, 938, 852, 825 cm^{-1}. ^{1}H NMR δ 1.67 (dm, *J* = 19.0 Hz, 3H), 5.50 (ddd, *J* = 56.6, 54.4, 2.0 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H). ^{19}F NMR δ -135.96 - -135.73 (m, 1F), -135.62 (dddd, *J* = 283.5, 56.8, 14.6, 1.2 Hz, 1F), -127.88 (dddd, *J* = 283.5, 54.3, 12.2, 1.2 Hz, 1F). ^{13}C NMR δ 18.79 (dd, *J* = 23.2, 2.5 Hz), 101.83 (dm, *J* = 221.4 Hz), 112.12 (ddd, *J* = 253.5, 246.9, 40.5 Hz), 125.53 (s), 129.49 (2C, s), 136.72 (s), 137.71 (2C, s); MS: 242 (M^++2, 37), 241 (M^++1, 11), 240 (M^+, 100), 191 (28), 189 (76), 146 (32), 145 (18), 144 (87), 143 (32), 134 (11), 109 (23), 108 (33). HRMS(EI) Calcd for $C_9H_8ClF_3S$: (M^+) 239.9987. Found: 239.9980.

4.2.4. 1,1,2-Trifluoro-2-(*p*-methylphenylthio)propane 4b. Colorless liquid: IR (neat) 2993, 1494, 1386, 1096, 1072, 813 cm^{-1}. ^{1}H NMR δ 1.66 (d, *J* = 19.0 Hz, 3H), 2.38 (s, 3H), 5.34 - 5.64 (m, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H). ^{19}F NMR δ -136.58 - -135.53 (m, 2F), -128.56 - -127.60 (m, 1F). ^{13}C NMR δ 18.37 - 18.76 (m), 21.25 (s), 101.79 (ddd, *J* = 222.17, 27.9, 23.8 Hz), 112.13 (ddd, *J* = 253.5, 246.0, 41.4 Hz), 123.36 (s), 129.97 (2C, s), 136.50 (2C, s), 140.38(s). MS: 221 (M^++1, 12), 220 (M^+, 100), 200 (13), 169 (62), 149 (17), 124 (41), 123 (63), 121 (10), 92 (11), 91 (47), 79 (12), 77 (16). HRMS(EI) Calcd for $C_{10}H_{11}F_3S$: (M^+) 220.0533. Found: 220.0526.

4.2.5. 1,1,2-Trifluoro-2-(*p*-nitrophenylthio)propane 4c. Colorless liquid: IR (neat) 3104, 2996, 1600, 1523, 1347, 1093, 854 cm^{-1}. ^{1}H NMR δ 1.74 (d, *J* = 19.3 Hz, 3H), 5.58 (ddd, *J* = 56.1, 54.2, 2.4 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 9.0 Hz, 2H). ^{19}F NMR δ -135.97 - -135.74 (m, 1F), -133.53 (ddd, *J* = 285.0, 55.8, 14.3 Hz, 1F), -127.29 (ddd, *J* = 285.0, 54.3, 12.8 Hz, 1F). ^{13}C NMR δ 19.29 (d, *J* = 23.2 Hz), 102.06 (ddd, *J* = 225.8, 27.3, 24.8 Hz), 112.11 (ddd, *J* = 253.5, 248.5, 39.3 Hz), 123.93 (2C, s), 124.17 (s), 136.23 (2C, s), 148.57 (s). MS: 251 (M^+, 84), 201 (10), 200 (100), 155 (32), 154 (12), 125 (14), 109 (16), 108 (17), 97 (11), 69 (11). HRMS(EI) Calcd for $C_9H_8O_2NF_3S$: (M^+) 251.0228. Found: 251.0217.

4.2.6. 1,1,2-Trifluoro-2-(*p*-chlorophenylthio)ethane 4d. Colorless liquid: IR (neat) 1571, 1477, 1378, 1151, 1095, 1013, 826 cm^{-1}. ^{1}H NMR δ 5.67 (ddt, *J* = 25.2, 9.0, 3.9 Hz, 1H), 5.80 (tt, *J* = 54.8, 3.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H). ^{19}F NMR δ -168.00 (ddd, *J*

= 50.7, 19.2, 3.7 Hz, 1F), -128.76 (dddd, *J* = 293.0, 54.9, 18.9, 9.8 Hz, 1F), -126.85 (dddd, *J* = 292.3, 54.3, 23.8, 9.2 Hz, 1F). ^{13}C NMR δ 97.63 (dt, *J* = 226.6, 28.1 Hz), 111.48 (ddd, *J* = 248.9, 246.5, 34.7 Hz), 127.62 (s), 129.70 (2C, s), 135.32 (2C, s), 136.06 (s). MS: 228 (M^++2, 37), 226 (M^+, 100), 177 (33), 175 (90), 143 (47), 108 (29). HRMS (EI) Calcd for $C_8H_6ClF_3S$: (M^+) 225.9831. Found: 225.9829.

4.2.7. 1,1,2-Trifluoro-2-(*p*-chlorophenylthio)butane 4e. Colorless liquid: IR (neat) 1574, 1477, 1389, 1187, 1093, 1015, 891, 825 cm^{-1}. ^{1}H NMR δ 1.16 (t, *J* = 7.6 Hz, 3H), 1.88 - 2.19 (m, 2H), 5.49 (ddd, *J* = 56.4, 54.5, 2.3 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H). ^{19}F NMR δ -144.89 - -144.72 (m, 1F), -135.67 (ddd, *J* = 283.8, 56.5, 14.3 Hz, 1F), -127.94 (ddd, *J* = 283.8, 53.9, 13.0 Hz, 1F). ^{13}C NMR δ 7.49 (d, *J* = 4.1 Hz), 25.43 (dd, *J* = 22.3, 2.5 Hz), 104.35 (ddd, *J* = 226.2, 26.9, 23.2 Hz), 112.44 (ddd, *J* = 253.9, 247.3, 41.4 Hz), 125.53 (s), 129.43 (2C, s), 136.55 (s), 137.76 (2C, s). MS: 256 (M^++2, 26), 254 (M^+, 70), 205 (11), 203 (29), 146 (38), 145 (19), 144 (100), 143 (31), 109 (21), 108 (27). HRMS(EI) Calcd for $C_{10}H_{10}ClF_3S$: (M^+) 254.0144. Found: 254.0160.

4.2.8. 1,1,2-Trifluoro-2-(*p*-chlorophenylthio)dodecane 4f. Colorless liquid: IR (neat) 2925, 2855, 1574, 1476, 1093, 1015, 824 cm^{-1}. ^{1}H NMR δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.27 (bs, 14H), 1.53 - 1.63 (m, 2H), 1.83 - 2.09 (m, 2H), 5.47 (ddd, *J* = 58.3, 56.4, 2.0 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H). ^{19}F NMR δ -143.15 - -142.98 (m, 1F), -135.88 (ddd, *J* = 282.6, 55.5, 14.0 Hz, 1F), -127.76 (ddd, *J* = 283.8, 54.3, 12.2 Hz, 1F). ^{13}C NMR δ 14.11 (s), 22.69 (s), 22.93 (d, *J* = 2.5 Hz), 29.29 (s), 29.32 (s), 29.47(s), 29.56 (s), 29.65 (s), 31.86 - 31.91 (m), 32.06 (d, *J* = 1.7 Hz), 104.06 (ddd, *J* = 225.8, 27.3, 24.0 Hz), 112.30 (ddd, *J* = 253.1, 247.3, 41.0 Hz), 125.61 (s), 129.39 (2C, s), 136.52 (s), 137.69 (2C, s). MS: 368 (M^++2, 31), 367 (M^++1, 17), 366 (M^+, 81), 146 (37), 145 (13), 144 (100), 143 (12), 57 (12), 43 (18). HRMS(EI) Calcd for $C_{18}H_{26}ClF_3S$: (M^+) 366.1396. Found: 366.1404.

4.2.9. 2, 9-Bis(*p*-chlorophenylthio)-1,1,2,9,10,10-hexafluorodecane 4g. Yellow solid: mp 59 - 62 °C; IR (neat) 2938, 2858, 1745, 1573, 1475, 1092, 825 cm^{-1}. ^{1}H NMR δ 0.88 - 2.13 (m, 12H), 5.46 (ddd, *J* = 56.4, 54.2, 2.0 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 4H), 7.53 (d, *J* = 8.5 Hz, 4H). ^{19}F NMR δ -143.25 - -143.07 (m, 2F), -136.01 (ddd, *J* = 282.6, 56.2, 14.6, Hz, 2F), -127.76 (ddd, *J* = 283.2, 53.7, 12.8 Hz, 2F). ^{13}C NMR δ 22.78 (2C, s) 29.25 (2C, s), 31.80 (2C, d, J = 20.7 Hz),

101.83 (2C, dm, *J* = 221.4 Hz), 112.12 (2C, ddd, *J* = 253.5, 246.9, 40.5 Hz), 125.53 (2C, s), 129.49 (4C, s), 136.72 (2C, s), 137.71 (4C, s). MS: 538 (M^++4, 16), 537 (M^++3, 17), 536 (M^++2, 68), 535 (M^++1, 24), 534 (M^+, 91), 390 (12), 146 (37), 145 (27), 144 (100), 143 (41), 109 (13), 108 (15). HRMS(EI) Calcd for $C_{22}H_{22}Cl_2F_6S_2$: (M^+) 534.0444. Found: 534.0433.

4.2.10. Methyl 3-(*p*-chlorophenylthio)-2,2,3-trifluoropropanoate 4h. Colorless liquid: IR (neat) 2961, 1785, 1575, 1478, 1442, 1391, 1312, 1220, 1096, 1074, 1014 cm^{-1}. ^1H NMR δ 3.95 (s, 3H), 6.00 (ddd, *J* = 50.0, 12.2, 9.3 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H). ^{19}F NMR δ -167.38 (ddd, *J* = 50.0, 22.0, 20.1 Hz, 1F), -115.63 (ddd, *J* = 268.6, 20.1, 12.2 Hz, 1F), -114.27 (ddd, *J* = 268.6, 22.0, 9.3 Hz, 1F). ^{13}C NMR δ 53.91 (s), 99.23 (ddd, *J* = 230.5, 29.7, 27.3 Hz), 111.13 (ddd, *J* = 259.7, 258.9, 30.6 Hz), 128.47 (s), 129.61 (2C, s), 134.74 (2C, s), 135.85 (s), 161.78 (t, *J* = 31.0 Hz). MS: 286 (M^++2, 23), 284 (M^+, 57), 177 (37), 175 (100), 145 (20), 143 (53), 108 (46). HRMS(EI) Calcd for $C_{10}H_8F_3O_2ClS$: (M^+) 283.9885. Found: 283.9880.

4.2.11. *N*, *N*-Dimethyl 2-(*p*-chlorophenylthio)-2,3,3-trifluoropropanamide 4i. White solid: mp 37 - 39 °C; IR (KBr) 3056, 2942, 1651, 1476, 1402, 1153, 1085, 1015, 926, 825 cm^{-1}. ^1H NMR δ 2.81 (s, 3H), 2.85 (d, *J* = 7.1 Hz, 3H), 6.43 (ddd, *J* = 54.6, 53.4, 11.0 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H). ^{19}F NMR δ -152.70 - -152.54 (m, 1F), -135.99 (ddd, *J* = 223.4, 54.9, 17.7 Hz, 1F), -125.32 (ddd, *J* = 225.2, 53.1, 20.1 Hz, 1F). ^{13}C NMR δ 37.12 (d, *J* = 15.7 Hz), 37.30 (s), 103.29 (dt, *J* = 256.4, 22.3 Hz), 113.48 (ddd, *J* = 254.4, 249.8, 24.0 Hz), 124.69 (s), 129.23 (2C, s), 137.29 (s), 138.14 (2C, s), 162.24 (dd, *J* = 20.7, 4.1 Hz). MS: 299 (M^++2, 10), 297 (M^+, 27), 72 (100). HRMS(EI) Calcd for $C_{11}H_{11}F_3ONClS$: (M^+) 297.0202. Found: 297.0202.

4.2.12. 1,1,2-Trifluoro-2-(*p*-chlorophenylthio)-3-phenylpropane 4j. Colorless liquid: IR (neat) 3033, 2988, 1476, 1092, 1015, 984, 825, 700 cm^{-1}. ^1H NMR δ 3.17 (ddd, *J* = 26.8, 14.9, 2.2 Hz, 1H), 3.44 (t, *J* = 15.6 Hz, 1H), 5.45 (ddd, *J* = 55.9, 54.2, 1.5 Hz, 1H), 7.31-7.47 (m, 7H), 7.49 (d, *J* = 8.3 Hz, 2H). ^{19}F NMR δ -142.14 - -141.95 (m, 1F), -135.12 (dddd, *J* = 283.8, 56.2, 14.3, 1.2 Hz, 1F), -128.92 (dddd, *J* = 283.8, 54.3, 12.8, 2.4 Hz, 1F). ^{13}C NMR δ 38.43 (d, *J* = 20.7 Hz), 103.42 (ddd, *J* = 228.3, 26.5, 24.0 Hz), 112.11 (ddd, *J* = 258.1, 248.1, 41.4 Hz), 125.50 (s), 127.67 (s), 128.40 (2C, s), 129.39 (2C, s), 130.82 (2C, s), 132.53 (s), 136.51 (s), 137.64 (2C, s).

MS: 318 (M^++2, 38), 317 (M^++1, 18), 316 (M^+, 100), 225 (16), 173 (64), 157 (21), 153 (12), 146 (10), 144 (26), 143 (13), 133 (12), 127 (19), 122 (15), 109 (17), 108 (14), 91 (95). HRMS(EI) Calcd for $C_{15}H_{12}ClF_3S$: (M^+) 316.0301. Found: 316.0300.

4.3. Oxidation potentials of the sulfides 1a, **3a**, **and 4a**.[11] The oxidation potentials of the sulfides **1a**, **3a**, and **4a** (0.25 mmol) were measured in Et_3N-5HF (6 ml) using an undivided cell (30 ml) made of Teflon™ PFA, a smooth Pt wire (1 mm x 10 mm) as a working electrode, and a smooth Pt sheet (20 mm x 20 mm) as a counter electrode. The reference electrode was $Ag^+/AgCoO_3$ (0.01 M) in MeCN containing Et_4NBF_4 (0.1 M). The potential was scanned with a potential scanner (Nichia ES 512A) connected to a potentio/galvanostat (Nichia NP-100M).

4.3.1. Fluorination of 4a with IF_5: Hexane (2 ml), **4a** (0.118 g, 0.5 mmol), and IF_5 in CH_2Cl_2 (0.776 g of 16.7 mol% solution, 1.2 mmol) were introduced into a reaction vessel made of Teflon™ FEP with a tight screw cap and the mixture was stirred at 40 °C for 28 h. After consumption of the starting material was confirmed by GC, the reaction mixture was poured into ice-water and the product was extracted three times with ether. The combined etheral phases were washed with aqueous $Na_2S_2O_3$, $NaHCO_3$, and brine successively and dried over $MgSO_4$. After concentration under reduced pressure, the product was isolated by column chlomatography (silica gel/hexane-ether as eluent).

4.3.2. 1,2,2,3,3-Pentafluoro-1-(*p*-chlorophenylthio)propane 2a. Colorless liquid: IR (neat) 1478, 1391, 1215, 1096, 1013, 829, 744 cm^{-1}. ^1H NMR δ 5.87 (ddd, *J* = 66.8, 16.1, 6.1 Hz, 1H), 6.02 (dt, *J* = 52.7, 6.4 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H). ^{19}F NMR δ -167.19 (ddt, *J* = 50.7, 18.9, 9.2 Hz, 1F), -140,65 (dddd, *J* = 305.2, 53.1, 8.9, 5.8 Hz, 1F), -137.08 (ddt, *J* = 304.9, 52.8, 9.5 Hz, 1F), -128.50 (dm, *J* = 276.5 Hz, 1F), -125.77 (dm, *J* = 276.5 Hz, 1F). ^{13}C NMR δ 98.60 (ddd, *J* = 227.4, 33.1, 25.6 Hz), 108.70 (tm, *J* = 251.5 Hz), 112.74 (tm, *J* = 255.4 Hz), 128.35 (s), 129.79 (2C, s), 134.81 (2C, s), 136.18 (s). MS: 278 (M^++2, 37), 276 (M^+, 100), 175 (81), 143 (48), 108 (27). HRMS(EI) Calcd for $C_9H_6ClF_5S$: (M^+) 275.9799. Found: 275.9797.

4.3.3. The time course of the reaction of 1a with IF_5 at 40 °C in the tight-screw capped vessel. The reaction was carried out at 40 °C using hexane (2 ml), **1a** (0.093 g, 0.5 mmol), and IF_5 in

CH_2Cl_2 (0.776 g of 16.7 mol% solution, 1.2 mmol) in the tight-screw capped vessel as described in **4.4.1** and the yields were obtained by GC using undecane as an internal standard.

4.3.4. The time course of the reaction of 1a with IF_5 in heptane under reflux condition. The reaction was carried out using heptane (1 ml), **1a** (0.093 g, 0.5 mmol), and IF_5 in CH_2Cl_2 (0.776 g of 16.7 mol% solution, 1.2 mmol) as described in **4.2.1** and the yields were obtained by GC using undecane as an internal standard.

4.3.5. The time course of the reaction of 1a with IF_5 at 98 °C in the tight-screw capped vessel. The reaction was carried out at 98 °C using heptane (2 ml), **1a** (0.093 g, 0.5 mmol), and IF_5 in CH_2Cl_2 (0.776 g of 16.7 mol% solution, 1.2 mmol) in a tight-screw capped vessel as described in **4.4.1** and the yields were obtained by GC using undecane as an internal standard.

Acknowledgment

We are grateful to Daikin Industries, Ltd. for their donation of IF_5.

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