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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.\textsuperscript{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.\textsuperscript{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.

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).

\[ \text{SC}_6\text{H}_4\text{Cl} \rightarrow \text{IF}_5 \]

1a

\[ \begin{align*}
3a & \quad + \\
4a & \quad + \\
2a & \quad \text{Yield (%)}
\end{align*} \]

<table>
<thead>
<tr>
<th>Amount of IF$_5$ (eq to 1a)</th>
<th>Reaction time (h)</th>
<th>Yield (%)$^b$</th>
<th>3a</th>
<th>4a</th>
<th>2a</th>
</tr>
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<tbody>
<tr>
<td>1.2</td>
<td>1</td>
<td>43</td>
<td>17</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>1</td>
<td>0</td>
<td>74</td>
<td>0</td>
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</tr>
<tr>
<td>2.4</td>
<td>6</td>
<td>0</td>
<td>72</td>
<td>5</td>
<td></td>
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<tr>
<td>2.4$^c$</td>
<td>48</td>
<td>0</td>
<td>0</td>
<td>72</td>
<td></td>
</tr>
</tbody>
</table>

$^a$) 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).

\[ 4a \rightarrow \text{IF}_5 \]

\[ \begin{align*}
40 \degree \text{C} & \quad 28h \\
50 \% & \quad \\
\end{align*} \]

2a

\[ \text{SC}_6\text{H}_4\text{Cl} \quad \text{IF}_5 \]
Various alkyl aryl sulfides were used for the reaction with IF$_3$ 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$_3$ 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$_3$ 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.
As previously proposed,\textsuperscript{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,\textsuperscript{5} or a vinylic sulfide.\textsuperscript{6} Addition of \textit{in situ}-generated IF to the vinylic sulfide gives 1-arylthio-1-fluoro-2-iodopropane (6a).\textsuperscript{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

<table>
<thead>
<tr>
<th>Substrate</th>
<th>IF$_5$ / 1</th>
<th>Product</th>
<th>Yield (%)$^b$</th>
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<tr>
<td>$p$-MeC$_6$H$_4$SPr</td>
<td>1.2</td>
<td>CHF$_2$CH$_3$</td>
<td>51</td>
</tr>
<tr>
<td>1b</td>
<td></td>
<td>CHF$_2$CH$_3$</td>
<td></td>
</tr>
<tr>
<td>$p$-NO$_2$C$_6$H$_4$SPr</td>
<td>4.8</td>
<td>CHF$_2$CH$_3$</td>
<td>66$^c$</td>
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<tr>
<td>1c</td>
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<td>CHF$_2$CH$_3$</td>
<td></td>
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<tr>
<td>$p$-ClC$_6$H$_4$SEt</td>
<td>2.4</td>
<td>CHF$_2$SC$_6$H$_4$Cl-p</td>
<td>66</td>
</tr>
<tr>
<td>1d</td>
<td></td>
<td>CHF$_2$SC$_6$H$_4$Cl-p</td>
<td></td>
</tr>
<tr>
<td>$p$-ClC$_6$H$_4$SBU</td>
<td>2.4</td>
<td>CHF$_2$Et</td>
<td>70</td>
</tr>
<tr>
<td>1e</td>
<td></td>
<td>CHF$_2$Et</td>
<td></td>
</tr>
<tr>
<td>$p$-ClC$<em>6$H$<em>4$SC$</em>{12}$H$</em>{25}$</td>
<td>3.6</td>
<td>CHF$<em>2$C$</em>{10}$H$_{21}$</td>
<td>83</td>
</tr>
<tr>
<td>1f</td>
<td></td>
<td>CHF$<em>2$C$</em>{10}$H$_{21}$</td>
<td></td>
</tr>
<tr>
<td>$p$-ClC$_6$H$_4$S(CH$<em>2$)$</em>{10}$SC$_6$H$_4$Cl-p</td>
<td>7.2</td>
<td>F$_2$HC$(CH_2)_6$CHF$_2$</td>
<td>75</td>
</tr>
<tr>
<td>1g</td>
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<td>F$_2$HC$(CH_2)_6$CHF$_2$</td>
<td></td>
</tr>
<tr>
<td>$p$-ClC$_6$H$_4$S</td>
<td>4.8</td>
<td>F$_2$HCSC$_6$H$_4$Cl-p</td>
<td>71$^d$</td>
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<tr>
<td>1h</td>
<td></td>
<td>F$_2$HCSC$_6$H$_4$Cl-p</td>
<td></td>
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<tr>
<td>$p$-ClC$_6$H$_4$S(CH$_2$)$_2$CONMe$_2$</td>
<td>2.4</td>
<td>F$_2$HCSC$_6$H$_4$Cl-p</td>
<td>71</td>
</tr>
<tr>
<td>1i</td>
<td></td>
<td>F$_2$HCSC$_6$H$_4$Cl-p</td>
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<tr>
<td>$p$-ClC$_6$H$_4$S(CH$_2$)$_3$Ph</td>
<td>3.6</td>
<td>F$_2$HCSC$_6$H$_4$Cl-p</td>
<td>71</td>
</tr>
<tr>
<td>1j</td>
<td></td>
<td>F$_2$HCSC$_6$H$_4$Cl-p</td>
<td></td>
</tr>
</tbody>
</table>
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).

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 IF₅ 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, 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.
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 IF₅ 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 IF₅ 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 stops 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, ○; 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, ○; 4a, Δ; 8a, ×; 2a).
3. Conclusion

We have succeeded in introducing three fluorine atoms into sulfides selectively by the reaction with IF₅ 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 ¹H NMR (400 MHz), ¹⁹F NMR (376 MHz), and ¹³C NMR (100 MHz) spectra were recorded in CDCl₃ on a JEOL JNM-A400II FT NMR and the chemical shift, δ, are referred to TMS (¹H, ¹³C) and CFCl₃ (¹⁹F), respectively. The EI-low and high-resolution mass spectra were measured on a JEOL JMS-700TZ, JMS-FABmate or JMS-HX110. IF₅ in a stainless-steel cylinder was supplied by Daikin Industries, Ltd. IF₅
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$_2$Cl$_2$ 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$_2$Cl$_2$ was added to make a 16.7 mol% solution. IF$_5$ in CH$_2$Cl$_2$ 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. The sulfide 1i was prepared from $p$-chlorophenylthiol with N,N-diethylacrylamide. Et$_3$N-5HF was prepared by the addition of Et$_3$N to anhydrous HF.

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$_2$Cl$_2$ (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$_2$S$_2$O$_3$, 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$^{-1}$. $^1$H NMR $\delta$ 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 $\delta$ -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 $\delta$ 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$_9$H$_9$ClF$_2$S: (M$^+$) 222.0081. Found: 222.0075.
4.2.3. 1,1,2-Trifluoro-2-(p-chlorophenylthio)propane 4a. Colorless liquid: IR (neat) 1574, 1477, 1389, 1225, 1092, 1015, 938, 852, 825 cm⁻¹. ¹H 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). ¹⁹F NMR δ -135.96 - -135.73 (m, 1F), -135.62 (dddd, J = 283.5, 56.8, 14.6, 1.2 Hz, 1F), -127.88 (ddddd, J = 283.5, 54.3, 12.2, 1.2 Hz, 1F). ¹³C NMR δ 18.79 (dd, J = 23.2, 2.5 Hz), 101.83 (dm, J = 221.4 Hz), 112.12 (dd, 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 C₁₀H₁₄ClF₃S: (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. ¹H 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). ¹⁹F NMR δ -136.58 - -135.53 (m, 2F), -128.56 - -127.60 (m, 1F). ¹³C NMR δ 18.37 - 18.76 (m), 21.25 (s), 101.79 (ddd, J = 222.17, 27.9, 23.8 Hz), 112.13 (dd, 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 C₁₀H₁₁F₃S: (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. ¹H 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). ¹⁹F NMR δ -135.97 - -135.74 (m, 1F), -133.53 (ddddd, J = 285.0, 55.8, 14.3 Hz, 1F), -127.29 (ddddd, J = 285.0, 54.3, 12.8 Hz, 1F). ¹³C NMR δ 19.29 (d, J = 23.2 Hz), 102.06 (dd, J = 225.8, 27.3, 24.8 Hz), 112.11 (dd, J = 253.5, 248.5, 39.3 Hz), 123.93 (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 C₁₀H₁₀O₂NF₃S: (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. ¹H 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). ¹⁹F NMR δ -168.00 (ddd, J
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 \(\delta\) 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). \(^1\)F NMR \(\delta\) -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 \(\delta\) 7.49 (d, \(J = 4.1\) Hz), 25.43 (ddd, \(J = 283.8, 53.9, 12.2\) Hz, 1F), 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\(_3\)S: (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 \(\delta\) 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). \(^1\)F NMR \(\delta\) -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 \(\delta\) 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\(_3\)S: (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 \(\delta\) 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). \(^1\)F NMR \(\delta\) -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 \(\delta\) 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\(_2\)F\(_6\)S\(_2\): (M\(^+\)) 534.0444. Found: 534.0433.

4.2.10. Methyl 3-(\( p \)-chlorophenylthio)-2,2,3-trifluoropropanoate 4h. Colorless liquid: IR (neat) 2961, 1785, 1478, 1442, 1391, 1312, 1220, 1096, 1074, 1014 cm\(^{-1}\). \(^1\)H NMR \( \delta \) 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 \( \delta \) -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 \( \delta \) 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\(_{8}\)F\(_3\)O\(_2\)ClS: (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 \(^\circ\)C; IR (KBr) 3056, 2942, 1651, 1476, 1402, 1153, 1085, 1015, 926, 825 cm\(^{-1}\). \(^1\)H NMR \( \delta \) 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 \( \delta \) -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 \( \delta \) 37.12 (d, \( J = 20.7 \) 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\(_3\)ONClS: (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\(^{-1}\). \(^1\)H NMR \( \delta \) 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 \( \delta \) -142.14 - -141.95 (m, 1F), -135.12 (ddd, \( J = 283.8, 56.2, 14.3, 1.2 \) Hz, 1F), -128.92 (ddd, \( J = 283.8, 54.3, 12.8, 2.4 \) Hz, 1F). \(^{13}\)C NMR \( \delta \) 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).
4.3. Oxidation potentials of the sulfides 1a, 3a, and 4a. The oxidation potentials of the sulfides 1a, 3a, and 4a (0.25 mmol) were measured in Et3N-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+/AgCoO3 (0.01 M) in MeCN containing Et4NBF4 (0.1 M). The potential was scanned with a potential scanner (Nichia ES 512A) connected to a potentiogalvanostat (Nichia NP-100M).

4.3.1. Fluorination of 4a with IF5: Hexane (2 ml), 4a (0.118 g, 0.5 mmol), and IF5 in CH2Cl2 (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 Na2S2O3, NaHCO3, and brine successively and dried over MgSO4. After concentration under reduced pressure, the product was isolated by column chromatography (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). ¹⁹F 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). ¹³C 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 C₉H₆ClF₅S: (M⁺) 275.9799. Found: 275.9797.

4.3.3. The time course of the reaction of 1a with IF5 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 IF5 in
CH₂Cl₂ (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 IF₅ in heptane under reflux condition. The reaction was carried out using heptane (1 ml), 1a (0.093 g, 0.5 mmol), and IF₅ in CH₂Cl₂ (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 IF₅ 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 IF₅ in CH₂Cl₂ (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.

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References and Notes


6. Motherwell also found the formation of vinylic sulfides in the reaction of difluoriodotoluene with phenylsulfanylated lactams or amides.7


