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<td>Tahara, Ryuhei; Fukuhara, Tadahito; Hara, Shoji</td>
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A novel method for introducing a polyfluoroalkyl group into aromatic compounds

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Keywords: polyfluoroalkylation, fluoro-Pummerer rearrangement, desulfurizing-difluorination, IF₅, 5-(perfluoroethyl)uracil

Abstract

Introduction of a polyfluoroalkyl group into aromatic compounds was achieved by Friedel-Crafts reaction using (1-chloro-1-hydroperfluoroalkyl) sulfides 1, and the subsequent desulfurizing-difluorination of the resulting product using IF₅/ Et₃N-nHF. Perfluoroethyl, 1,1,2,2,3,3-hexafluoropropyl, and 1,1,2,2,3,3,4,4,5,5-decafluoropentyl groups were introduced to various aromatic compounds by this method. Selective perfluoroethylation of uracil at the 5-position was also performed.

1. Introduction

Introduction of a polyfluoroalkyl group into an aromatic compound has been well studied [1] because the resulting compounds exhibit remarkably different physical, chemical, and biological properties [2]. Among the many methods available for the polyfluoroalkylation of aromatic compounds, the electrophilic method has an advantage
over other methods: in a nucleophilic method, an aromatic halide is required as a substrate, and in a free radical method, regioselectivity is low. On the other hand, in an electrophilic polyfluoroalkylation, the polyfluoroalkyl group can be introduced by substitution with a hydrogen atom under mild conditions [3]. However, the electrophilic polyfluoroalkylation method requires a special reagent, which is unstable and difficult to prepare [2a, 4]. Therefore, a more convenient method for the introduction of a polyfluoroalkyl group into an aromatic compound has been desired. Previously, Uneyama et al. reported that a 1-(phenylsulfanyl)-2,2,2-trifluoroethyl group can be introduced to aromatic compounds by Friedel-Crafts reaction using (1-chloro-2,2,2-trifluoroethyl) phenyl sulfide (1b, R = Ph, Rf = CF₃) [5]. Various (1-chloro-1-hydroperfluoroalkyl) sulfides 1 can be prepared from commercially available 1,1-dihydroperfluoroalkanols [6], and they can be used for the reaction with aromatic compound to synthesize (1-aryl-1-hydroperfluoroalkyl) sulfides 2. Recently, we reported a desulfurizing-difluorination reaction of benzyl sulfides having an electron-withdrawing group using IF₅, where two fluorine atoms were introduced to the benzyl position by substitution with a hydrogen atom and an alkylsulfanyl group [7]. As the perfluoroalkyl group in 2 is a strong electron-withdrawing group, the desulfurizing-difluorination reaction can be applied to 2, and the polyfluoroalkyl group substituted aromatic compound 3 must be prepared from 2 (Scheme 1) [8].
2. Result and discussion

1-Chloro-2,2,2-trifluoroethyl hexyl sulfide 1a, 1-chloro-2,2,2-trifluoroethyl phenyl sulfide 1b, 1-chloro-2,2,3,3-tetrafluoropropyl hexyl sulfide 1c, and 1-chloro-2,2,3,3,4,4,5,5-octafluoropentyl hexyl sulfide 1d were prepared from the corresponding polyfluoroalcohols [6], and used for the Friedel-Crafts reaction with naphthalene in the presence of a Lewis acid (TiCl₄ or SnCl₄). The alkylation occurred selectively at 1-position and 1-(1-hexylsulfanyl-2,2,2-trifluoroethyl)naphthalene 2a, 1-(1-phenylsulfanyl-2,2,2-trifluoroethyl)naphthalene 2b, 1-(1-hexylsulfanyl-2,2,3,3-tetrafluoropropyl)naphthalene 2g, and 1-(1-hexylsulfanyl-2,2,3,3,4,4,5,5-octafluoropentyl)naphthalene 2h were obtained in good yield as shown in Table 1 [9]. Similarly, in the reaction of 1a with p-xylene, p-dimethoxybenzene, octahydroanthracene, and benzothiophene, the corresponding 1-(hexylsulfanyl)-2,2,2-trifluoroethylated products 2c-f were obtained in good yields (Table 1).
### Table 1

Friedel-Crafts reaction of aromatic compounds with sulfide 1

<table>
<thead>
<tr>
<th>Aromatic compound</th>
<th>Reagent</th>
<th>Reaction time (h)</th>
<th>Product</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<tbody>
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<td><img src="image1" alt="benzene" /></td>
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<td><img src="image3" alt="Cl" /></td>
<td>10</td>
<td><img src="image4" alt="benzene" /> <img src="image5" alt="HexS" /> <img src="image6" alt="Cl" /></td>
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<td><img src="image7" alt="naphthalene" /></td>
<td><img src="image8" alt="PhS" /></td>
<td><img src="image9" alt="Cl" /></td>
<td>20</td>
<td><img src="image10" alt="naphthalene" /> <img src="image11" alt="PhS" /> <img src="image12" alt="Cl" /></td>
</tr>
<tr>
<td><img src="image13" alt="toluene" /></td>
<td><img src="image14" alt="1a" /></td>
<td><img src="image15" alt="OMe" /></td>
<td>15</td>
<td><img src="image16" alt="toluene" /> <img src="image17" alt="1a" /></td>
</tr>
<tr>
<td><img src="image18" alt="anisole" /></td>
<td><img src="image14" alt="1a" /></td>
<td><img src="image15" alt="OMe" /></td>
<td>12</td>
<td><img src="image19" alt="anisole" /> <img src="image17" alt="1a" /></td>
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<tr>
<td><img src="image20" alt="fluorene" /></td>
<td><img src="image14" alt="1a" /></td>
<td><img src="image15" alt="OMe" /></td>
<td>15</td>
<td><img src="image21" alt="fluorene" /> <img src="image17" alt="1a" /></td>
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<tr>
<td><img src="image22" alt="benzo[b]thiophene" /></td>
<td><img src="image14" alt="1a" /></td>
<td><img src="image15" alt="OMe" /></td>
<td>15</td>
<td><img src="image23" alt="benzo[b]thiophene" /> <img src="image17" alt="1a" /></td>
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<tr>
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<td><img src="image3" alt="Cl" /></td>
<td><img src="image19" alt="CF&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;" /></td>
<td>15</td>
</tr>
<tr>
<td><img src="image7" alt="naphthalene" /></td>
<td><img src="image2" alt="HexS" /></td>
<td><img src="image3" alt="Cl" /></td>
<td><img src="image19" alt="CF&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;" /></td>
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</tbody>
</table>

<sup>a</sup>If otherwise not mentioned, the reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub>, using 1.5 eq of TiCl<sub>4</sub> and 2 eq of ArH.<br>
<sup>b</sup>Isolated yield based on 1 used. In parenthesis, isomer ratio.<br>
<sup>c</sup>1.2 eq of SnCl<sub>4</sub> was used as Lewis-acid.<br>
<sup>d</sup>1.0 eq of SnCl<sub>4</sub> was used.<br>
<sup>e</sup>5.0 eq of naphthalene was used.
Next, the desulfurizing-difluorination of 1-(1-hexylsulfanyl-2,2,2-trifluoroethyl)naphthalene \(2a\) and 1-(1-phenylsulfanyl-2,2,2-trifluoroethyl)naphthalene \(2b\) was investigated for the synthesis of 1-(perfluoroethyl)naphthalene \(3a\). When \(2a\) was subjected to the reaction with IF\(_5\), the expected \(3a\) was obtained in 77% yield. However, 1-(1,2,2,2-tetrafluoroethyl)naphthalene \(4a\) was also formed in 14% yield (Entry 1 in Table 2). When IF\(_5\)/Et\(_3\)N-3HF was used instead of IF\(_5\) to prevent the formation of \(4a\) [10], the yield of \(4a\) was reduced to 8% (Entry 2). Finally, \(3a\) was selectively obtained using IF\(_5\)/Et\(_3\)N-2HF (Entry 3). On the other hand, in the reaction of \(2b\) with IF\(_5\), the decomposition of \(2b\) took place under the same conditions, and neither \(3a\) nor \(4a\) was obtained in reasonable yield (Entry 4). In the reaction of \(2b\) with IF\(_5\)/Et\(_3\)N-3HF, \(4a\) was selectively obtained in good yield without the formation of \(3a\) (Entries 5 and 6). Consequently, the perfluoroethyl or the 1,2,2,2-tetrafluoroethyl group can be selectively introduced to 1-position of naphthalene using \(1a\) or \(1b\).
Table 2
Desulfurizing-difluorination reaction of 2a and 2b

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Reagent</th>
<th>Condition</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2a (R = Hex)</td>
<td>IF&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0 °C, 13 h</td>
<td>77 14</td>
</tr>
<tr>
<td>2</td>
<td>2a</td>
<td>IF&lt;sub&gt;5&lt;/sub&gt; / Et&lt;sub&gt;3&lt;/sub&gt;N-3HF</td>
<td>0 °C, 8 h</td>
<td>86 8</td>
</tr>
<tr>
<td>3</td>
<td>2a</td>
<td>IF&lt;sub&gt;5&lt;/sub&gt; / Et&lt;sub&gt;3&lt;/sub&gt;N-2HF</td>
<td>rt, 65 h</td>
<td>98(80) 0</td>
</tr>
<tr>
<td>4</td>
<td>2b (R = Ph)</td>
<td>IF&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0 °C, 13 h</td>
<td>0 3</td>
</tr>
<tr>
<td>5</td>
<td>2b</td>
<td>IF&lt;sub&gt;5&lt;/sub&gt; / Et&lt;sub&gt;3&lt;/sub&gt;N-3HF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0 °C, 60 h</td>
<td>0 68</td>
</tr>
<tr>
<td>6</td>
<td>2b</td>
<td>IF&lt;sub&gt;5&lt;/sub&gt; / Et&lt;sub&gt;3&lt;/sub&gt;N-3HF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>rt, 18 h</td>
<td>0 92(80)</td>
</tr>
</tbody>
</table>

<sup>a</sup> If otherwise not mentioned, the reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub> using 1.5 eq of IF<sub>5</sub> reagent.
<sup>b</sup> <sup>19</sup>F NMR yield based on 2 used. In parentheses, isolated yield.
<sup>c</sup> 0.75 eq of IF<sub>5</sub> / Et<sub>3</sub>N-3HF was used.

The difference in the reactivities of 2a and 2b can be explained from leaving ability of the alkylsulfanyl group (Scheme 2): In path 1, substitution of hydrogen with a fluoride (fluoro-Pummerer reaction) initially took place to afford tetrafluoro-sulfide 5. In the next step, 5 was converted to 3a by the substitution of the alkylsulfanyl group with a fluoride (desulfurizing-fluorination reaction). In path 2, the desulfurizing-fluorination reaction initially took place to afford 4a. The reaction of 2a mainly proceeded though path 1 and 3a was formed as a main product. When a less reactive IF<sub>5</sub> / Et<sub>3</sub>N-nHF was used as a fluorination reagent, the reaction predominantly proceeded through path 1 and 3a was formed selectively (Entries 1-3 in Table 2). On the other hand, in the reaction of 2b, because of the higher leaving ability of the phenylsulfanyl group, the reaction...
proceeded through path 2 to afford 4a selectively (Entries 5 and 6).

![Scheme 2](image)

From various (1-aryl-2,2,2-trifluoroethyl) hexyl sulfides 2a and 2c-f, the corresponding perfluoroethylated aromatic compounds 3a and 3c-f were obtained with good selectivity (100-90%) by desulfurizing-difluorination reaction using IF₅ / Et₃N-nHF, as shown in Table 3. Similarly, 1-(1,1,2,2,3,3-hexafluoropropyl) and 1-(1,1,2,2,3,3,4,4,5,5-decafluoropentyl)naphthalene 3g-h were selectively formed by the reaction of the corresponding sulfides 2g-h with IF₅ / Et₃N-HF.
Table 3
The desulfurizing-fluorination reaction of 2

<table>
<thead>
<tr>
<th>Substrate</th>
<th>reagent</th>
<th>condition</th>
<th>Product (ratio)</th>
<th>Yield (%)[^b][^c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>IF$_5$/Et$_3$N-2HF</td>
<td>rt, 65 h</td>
<td><img src="image" alt="3a" /></td>
<td>80 (99)</td>
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<tr>
<td>2b</td>
<td>IF$_5$/Et$_3$N-3HF</td>
<td>rt, 18 h</td>
<td><img src="image" alt="4a" /></td>
<td>80 (92)[^c]</td>
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<tr>
<td>2c</td>
<td>IF$_5$/Et$_3$N-3HF</td>
<td>rt, 60 h</td>
<td><img src="image" alt="3c" /></td>
<td>80</td>
</tr>
<tr>
<td>2d</td>
<td>IF$_5$/Et$_3$N-HF</td>
<td>rt, 37 h</td>
<td><img src="image" alt="3d" /> : <img src="image" alt="4d" /></td>
<td>86</td>
</tr>
<tr>
<td>2e</td>
<td>IF$_5$/Et$_3$N-2HF</td>
<td>rt, 70 h</td>
<td><img src="image" alt="3e" /> : <img src="image" alt="4e" /></td>
<td>75</td>
</tr>
<tr>
<td>2f</td>
<td>IF$_5$/Et$_3$N-HF</td>
<td>rt, 50 h</td>
<td><img src="image" alt="3f" /> : <img src="image" alt="4f" /></td>
<td>79</td>
</tr>
<tr>
<td>2g</td>
<td>IF$_5$/Et$_3$N-HF</td>
<td>rt, 32 h</td>
<td><img src="image" alt="3g" /></td>
<td>86</td>
</tr>
<tr>
<td>2h</td>
<td>IF$_5$/Et$_3$N-HF</td>
<td>rt, 24 h</td>
<td><img src="image" alt="3h" /></td>
<td>83</td>
</tr>
</tbody>
</table>

[^a]: If otherwise not mentioned, the reaction was carried out in CH$_2$Cl$_2$ using 1.5 eq of IF$_5$ reagent.

[^b]: Isolated yield based on 2 used. In parentheses, $^{19}$F NMR yield.

[^c]: 0.75 eq of IF$_5$/Et$_3$N-3HF was used.
Fluorine-containing pyrimidine derivatives including uracils and nucleosides are potent antitumor and antiviral agents [11], and much effort has gone into the synthesis of 5-(trifluoromethyl)uracil derivatives [12]. However, there are few reports on the synthesis of their perfluoroethyl derivatives. Therefore, we used our method for the synthesis of a 5-(perfluoroethyl)uracil derivative. The Friedel-Crafts reaction of 1a with uracil or N-protected uracil was unsuccessful, and the expected 5-(2,2,2-trifluoro-1-(hexylsulfanyl)ethyl)uracil 7 was not obtained. Therefore, 7 was prepared by the reaction of uracil with trifluoroacetaldehyde ethyl hemiacetal [13], and the subsequent reaction of the resulting product with hexanethiol (Scheme 3) [14]. The nitrogen atom at 1-position in 7 was protected with a tosyl group to afford 1-tosyl-5-{2,2,2-trifluoro-1-(hexylsulfanyl)ethyl}uracil 2i. In the reaction of 2i with IF₅, the expected 5-(perfluoroethyl)uracil 3i was obtained in 54% yield with 3% of 5-(1,2,2,2-tetrafluoroethyl)uracil. On the other hand, when IF₅ / Et₃N-3HF was used for the reaction with 2i, the formation of 3i, and 5-{1,2,2,2-tetrafluoro-1-(hexylsulfanyl)ethyl}uracil (the fluoro-Pummerer rearrangement product), and the absence of 5-(tetrafluoroethyl)uracil were confirmed from ¹⁹F-NMR analysis of the reaction mixture after 24 h at room temperature. Under these conditions, the desulfurizing-fluorination reaction is slow and is the rate-determining step. The desulfurizing-fluorination step was accelerated by the addition of IF₃ to the reaction mixture, and 3i was obtained in 61% yield in 48 h (Scheme 3).
3. Conclusion

Perfluoroethyl, hexafluoropropyl, and decafluoropentyl groups can be introduced to various aromatic compounds by Friedel-Crafts reaction with (1-chloro-1-hydroperfluoro)alkyl sulfides 1, and the subsequent desulfurizing-difluorination of the resulting product with IF₅/Et₃N-nHF. As the starting sulfides 1 can be prepared from commercially available polyfluoro-alcohols, our method is useful for introducing various polyfluoro-alkyl groups into aromatic compounds. In order to demonstrate the usefulness of our method, 5-(perfluoroethyl)uracil was synthesized.

4. Experimental

4.1. General

The melting points were measured with a Yanagimoto micro melting-point apparatus.
The IR spectra were recorded using a JASCO FT/IR-410. The $^1$H NMR (400 MHz) spectra, $^{19}$F NMR (376 MHz) spectra, and $^{13}$C NMR (100 MHz) were recorded in CDCl$_3$ on a JEOL JNM-A400II FT NMR and the chemical shift, $\delta$, is referred to TMS ($^1$H, $^{13}$C) and CFCl$_3$ ($^{19}$F), respectively. The EI-high-resolution mass spectra were measured on a JEOL JMS-700TZ. IF$_5$ in a stainless-steel cylinder was supplied by Asahi Glass Co., Ltd. IF$_5$ was transferred through a Teflon$^\text{TM}$ tube into a Teflon$^\text{TM}$FEP bottle from the cylinder under an N$_2$ atmosphere. IF$_5$ was transferred quickly from the bottle to the reaction vessel made of Teflon$^\text{TM}$FEP in open air. IF$_5$/5CH$_2$Cl$_2$ and IF$_5$/Et$_3$N-3HF were prepared as described previously [10]. IF$_5$ decomposes in air emitting HF fume, and, therefore, it should be carefully handled in a bench hood with rubber-gloved hands. 2,2,3,3-Tetrafluoropropanol and 2,2,3,3,4,4,5,5-octafluoropentanol were donated from Daikin Industries, Ltd. (1-Chloro-2,2,2-trifluoroethyl) hexyl sulfide 1a, (1-chloro-2,2,2-trifluoroethyl) phenyl sulfide 1b, (1-chloro-2,2,3,3-tetrafluoropropyl) hexyl sulfide 1c, and (1-chloro-2,2,3,3,4,4,5,5-octafluoropentyl) hexyl sulfide 1d were prepared from 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol, and 2,2,3,3,4,4,5,5-octafluoropentanol, respectively, according to the reported procedure [6].

4.2. Friedel-Crafts reaction of aromatic compounds with I

4.2.1. 1-{2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl}naphthalene (2a)

To a CH$_2$Cl$_2$ solution (20 mL) of naphthalene (1.28 g, 10 mmol) and 1a (1.18 g, 5 mmol) was added TiCl$_4$ (1.44 g, 7.5 mmol) under N$_2$ atmosphere at 0 °C. The mixture was stirred at room temperature for 10 h and then 3 M aqueous HCl (10 mL) was added. After stirring for 30 min, the mixture was extracted with CH$_2$Cl$_2$ (30 mL X 3). The
combined organic phase was dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane:benzene = 50:1) gave 2a (1.37 g) in 84% yield (containing ca 2% of 2-substituted isomer). Pure 2a is obtainable by careful column chromatography. Oil: IR (neat) 2929, 1251, 1149, 1105 cm⁻¹. ¹H NMR δ 0.84 (3H, t, J = 7.0 Hz), 1.18-1.35 (6H, m), 1.48-1.61 (2H, m), 2.64-2.76 (2H, m), 5.19 (1H, brs), 7.48-7.60 (3H, m), 7.62-8.05 (4H, m). ¹³C NMR δ 13.9, 22.4, 28.3, 28.9, 31.2, 33.1, 46.3 (q, J_C,F = 29.3 Hz), 122.2, 125.2, 125.9 (2C), 126.5 (q, J_C,F = 279.4 Hz), 126.8, 129.2, 129.3, 129.5, 131.1, 133.8. ¹⁹F NMR δ -67.54 (3F, s). HRMS (EI) calcd for C₁₈H₂₁F₃S (M⁺) 326.13161, found 326.13105.

4.2.2. 1-{2,2,2-Trifluoro-1-(phenylsulfanyl)ethyl}naphthalene (2b)
Oil: IR (neat) 3062, 1248, 1105 cm⁻¹. ¹H NMR δ 5.45 (1H, q, J = 7.8 Hz), 7.24-7.32 (3H, m), 7.41-7.65 (6H, m), 7.85-8.00 (3H, m). ¹³C NMR δ 50.8 (q, J_C,F = 29.2 Hz), 122.2, 125.2, 125.9, 126.1 (q, J_C,F = 280.4 Hz), 126.8, 127.0, 128.8 (2C), 129.1 (2C), 129.2 (2C), 129.4, 130.9, 132.7, 133.8, 134.0. ¹⁹F NMR δ -67.16 (3F, d, J = 6.2 Hz). HRMS (EI) calcd for C₁₈H₁₃F₃S (M⁺) 318.06901, found 318.06848.

4.2.3. 2-{2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl}-1,4-dimethylbenzene (2c)
Oil: IR (neat) 2928, 1255, 1147, 1111 cm⁻¹. ¹H NMR δ 0.87 (3H, t, J = 6.9 Hz), 1.20-1.39 (6H, m), 1.50-1.63 (2H, m), 2.32 (3H, s), 2.35 (3H, s), 2.60-2.72 (2H, m), 4.50 (1H, q, J = 8.5 Hz), 7.02-7.08 (2H, m), 7.26-7.27 (1H, m). ¹³C NMR δ 14.0, 19.2, 21.0, 22.5, 28.3, 29.1, 31.3, 33.1, 47.2 (q, J_C,F = 31.5 Hz), 126.5 (q, J_C,F = 279.6 Hz), 128.8, 129.3, 130.4, 131.9, 132.9, 136.1. ¹⁹F NMR δ -68.11 (3F, d, J = 7.1 Hz). HRMS (EI) calcd for C₁₆H₂₃F₃S (M⁺) 304.14726, found 304.14684.

4.2.4. 2-{2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl}-1,4-dimethoxybenzene (2d)
Oil: IR (neat) 2931, 1503, 1236 cm⁻¹. ¹H NMR δ 0.87 (3H, t, J = 7.0 Hz), 1.23-1.39 (6H,
m), 1.54-1.62 (2H, m), 2.59-2.72 (2H, m), 3.77 (3H, s), 3.82 (3H, s), 4.92-4.98 (1H, q, J = 8.8 Hz), 6.844 (2H, brs), 7.03 (1H, s). $^{13}$C NMR $\delta$ 14.0, 22.4, 28.3, 29.0, 31.3, 33.1, 43.3 (q, $^{2}$J$_{CF}$ = 30.5 Hz), 55.7, 56.3, 111.9, 114.8, 114.9, 123.4, 126.3 (q, $^{1}$J$_{CF}$ = 279.4 Hz), 150.8, 153.6. $^{19}$F NMR $\delta$ -68.48 (3F, d, J = 8.9 Hz). HRMS (EI) calcd for C$_{16}$H$_{23}$F$_{3}$O$_{2}$S (M$^+$) 336.13708, found 336.13645.

4.2.5. 9-{2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl}-1,2,3,4,5,6,7,8-octahydroanthracene (2e)

Oil: IR (neat) 2930, 1250, 1146, 1102 cm$^{-1}$. $^1$H NMR $\delta$ 0.88 (3H, t, J = 6.7 Hz), 1.25-1.43 (6H, m), 1.54-1.89 (10H, m), 2.68-2.94 (10H, m), 4.77 (1H, q, J = 10.0 Hz), 6.84 (1H, s). $^{13}$C NMR $\delta$ 14.0, 21.9, 22.3, 22.5 (2C), 23.9, 27.7, 27.8 (q, $^{2}$J$_{CF}$ = 3.5 Hz), 28.4, 29.3, 29.4, 30.2, 31.3, 35.8, 47.2 (q, $^{2}$J$_{CF}$ = 30.7 Hz), 127.0 (q, $^{1}$J$_{CF}$ = 281.4 Hz), 130.6 (2C), 132.6, 134.9, 136.5, 136.7. $^{19}$F NMR $\delta$ -65.70 (3F, d, J = 9.0 Hz). HRMS (EI) calcd for C$_{22}$H$_{32}$F$_{3}$S (M$^+$+1) 385.21768, found 385.21366.

4.2.6. 3-(2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl)benzo[b]thiophene (2f)

Oil. IR (neat) 2928, 1253, 1150, 1108 cm$^{-1}$. $^1$H NMR $\delta$ 0.84 (3H, t, J = 6.6 Hz), 1.18-1.34 (6H, m), 1.44-1.59 (2H, m), 2.53-2.60 (1H, m), 2.67-2.74 (1H, m), 4.73 (1H, q, J = 8.4 Hz), 7.39-7.47 (2H, m), 7.56 (1H, s), 7.87 (2H, dd, J = 15.1, 8.5 Hz). $^{13}$C NMR $\delta$ 13.9, 22.4, 28.3, 28.9, 31.2, 32.5, 45.5 (q, $^{2}$J$_{CF}$ = 30.8 Hz), 121.6, 122.9, 124.4, 124.8, 126.0, 126.1 (q, $^{1}$J$_{CF}$ = 279.7 Hz), 127.1, 137.3, 139.9. $^{19}$F NMR $\delta$ -68.27 (3F, d, J = 9.0 Hz). HRMS (EI) calcd for C$_{16}$H$_{19}$F$_{3}$S$_{2}$ (M$^+$) 332.08803, found 332.08739.

4.2.7. 1-{2,2,3,3-Tetrafluoro-1-(hexylsulfanyl)propyl}naphthalene (2g)

Oil: IR (neat) 2929, 1227, 1115, 1041 cm$^{-1}$. $^1$H NMR $\delta$ 0.82 (3H, t, J = 6.7 Hz), 1.14-1.26 (6H, m), 1.45-1.54 (2H, m), 2.50-2.63 (2H, m), 5.17 (1H, t, J = 15.2 Hz), 5.97 (1H, tt, J = 54.4, 5.2 Hz), 7.51-7.61 (3H, m), 7.86-7.92 (3H, m), 8.00 (1H, d, J = 8.9 Hz).
13C NMR δ 13.9, 22.4, 28.2, 29.0, 31.2, 32.8, 44.2 (t, J$_{C,F}$ = 22.9 Hz), 109.5 (tt, J$_{C,F}$ = 251.8 Hz, J$_{C,F}$ = 33.7 Hz), 116.9 (tt, J$_{C,F}$ = 254.1 Hz, J$_{C,F}$ = 25.3 Hz), 122.1, 125.4, 125.9, 126.9, 128.0, 129.2, 129.3, 129.9, 131.5, 133.7. 19F NMR δ -119.58 to -119.64 (2F, m), -138.30 (2F, ddt, J = 297.3, 53.7, 7.2 Hz). HRMS (EI) calcd for C$_{10}$H$_{22}$F$_{4}$S (M$^+$) 358.13732.

4.2.8. 1-{2,2,3,3,4,4,5,5-Octafluoro-1-(hexylsulfanyl)pentyl}naphthalene (2h)

Oil: IR (neat) 2930, 1172, 1130 cm$^{-1}$. 1H NMR δ 0.82 (3H, t, J = 6.8 Hz), 1.16-1.32 (6H, m), 1.46-1.57 (2H, m), 2.55-2.67 (2H, m), 5.36 (1H, dd, J = 17.9, 12.9 Hz), 5.97 (1H, tt, J = 52.1, 5.5 Hz), 7.49-7.61 (3H, m), 7.82-7.99 (4H, m). 13C NMR δ 13.8, 22.4, 28.2, 29.0, 31.2, 33.4, 44.2 (t, J$_{C,F}$ = 23.2 Hz), 104.8-120.3 (4C, m), 121.7, 125.3, 125.8, 127.0, 128.0, 129.2, 129.3, 129.7, 131.1, 133.7. 19F NMR δ -108.60 (1F, dt, J = 276.7, 13.8 Hz), -120.84 (1F, d, J = 274.9 Hz), -122.67 to -121.64 (2F, m), -130.49 to -130.62 (2F, m), -136.83 to -138.73 (2F, m). HRMS (EI) calcd for C$_{21}$H$_{22}$F$_{8}$S (M$^+$) 458.13145, found 458.13161.

4.3.1. 1-(Perfluoroethyl)naphthalene (3a)

IF$_5$/Et$_3$N-2HF (0.75 mmol) was prepared in situ by the addition of Et$_3$N (25.3 mg, 0.25 mmol) to a mixture of IF$_5$/5CH$_2$Cl$_2$ (0.16 g, 0.25 mmol), IF$_5$/Et$_3$N-3HF (190 mg, 0.5 mmol), and CH$_2$Cl$_2$ (0.5 mL) at 0 °C in Teflon PFA bottle. To the resulting CH$_2$Cl$_2$ solution of IF$_5$/Et$_3$N-2HF (0.75 mmol), a CH$_2$Cl$_2$ solution (2.5 mL) of 2a (164 mg, 0.5 mmol) was added at 0 °C and the mixture was stirred at room temperature for 65 h. The mixture was poured into saturated aqueous NaHCO$_3$ (30 mL) and extracted with ether (30 mL X 3). The combined organic phase was washed with aqueous Na$_2$S$_2$O$_3$, dried over MgSO$_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel / hexane:CH$_2$Cl$_2$ = 50:1) gave 3a (100 mg) in 80% yield.
Oil: IR (neat) 3059, 1133 cm⁻¹. ¹H NMR δ 7.52-7.62 (3H, m), 7.83 (1H, d, J = 7.3 Hz), 7.92 (1H, d, J = 8.3 Hz), 8.04 (1H, J = 8.2 Hz), 8.24 (1H, d, J = 8.3 Hz). ¹³C NMR δ 115.3 (tq, ¹J_{CF} = 255.3 Hz, ²J_{CF} = 39.4 Hz), 119.7 (tq, ²J_{CF} = 39.3 Hz, ¹J_{CF} = 287.0 Hz), 124.2 (t, ²J_{CF} = 21.7 Hz), 124.3, 124.7-124.8 (m), 126.4, 127.4 (t, ³J_{CF} = 9.5 Hz), 127.6 129.0, 129.9, 133.3, 134.1. ¹⁹F NMR δ -83.97 (3F, s), -108.90 (2F, s) (lit. [15] -83.8 (3F, s), -108.9 (2F, s)).

1-(1,2,2,2-Tetrafluoroethyl)naphthalene (4a)

Oil: IR (neat) 3059, 1359, 1274, 1185, 1140 cm⁻¹. ¹H NMR δ 6.42 (1H, dq, J = 43.5, 5.8 Hz ), 7.26-7.62 (3H, m), 7.77 (1H, d, J = 7.2 Hz), 7.92-7.98 (3H, m). ¹³C NMR δ 85.8 (dq, ¹J_{CF} = 185.7 Hz, ²J_{CF} = 35.0 Hz), 122.5, 122.9 (dq, ¹J_{CF} = 282.3 Hz, ²J_{CF} = 29.5 Hz), 125.0, 126.0 (d, ²J_{CF} = 18.3 Hz), 126.1, 126.3 (d, ³J_{CF} = 10.5 Hz), 127.2, 129.1, 130.6 (d, ³J_{CF} = 3.8 Hz), 131.1 (d, ⁴J_{CF} = 1.9 Hz), 133.6. ¹⁹F NMR δ -78.09 (3F, dd, J = 12.5, 5.4 Hz), -195.1 (1F, dq, J = 43.0, 12.6 Hz) (lit. [16] -77.9 (3F, dd, J = 13, 6 Hz), -194.9 (1F, dq, J = 44, 13 Hz)).

2-(Perfluoroethyl)-1,4-dimethylbenzene (3c)

Oil: IR (neat) 2931, 1207, 1187 cm⁻¹. ¹H NMR δ 2.36 (3H, s), 2.43 (3H, t, J = 3.0 Hz), 7.14-7.31 (3H, m). ¹³C NMR δ 19.7-19.8 (m), 20.7, 115.0 (tq, ¹J_{CF} = 254.2 Hz, ²J_{CF} = 38.2 Hz), 119.7 (tq, ²J_{CF} = 40.1 Hz, ¹J_{CF} = 286.1), 126.6 (t, ²J_{CF} = 21.7 Hz), 128.5 (t, ³J_{CF} = 8.6 Hz), 132.4, 132.5, 134.7 (t, ²J_{CF} = 2.2 Hz), 135.8. ¹⁹F NMR δ -84.86 (3F, s), -110.94 (2F, s), (lit. [17] -84.72 (3F, s), -110.78 (2F, s)).

2-(Perfluoroethyl)-1,4-dimethoxybenzene (3d)

Oil: IR (neat) 2958, 2842, 1057, 1200 cm⁻¹. ¹H NMR δ 3.79 (3H, s), 3.82 (3H, s), 6.94-6.97 (1H, m), 7.04-7.05 (2H, m). ¹³C NMR δ 55.8, 56.6, 113.4 (tq, ¹J_{CF} = 255.6 Hz, ²J_{CF} = 39.3 Hz), 114.1 (t, ²J_{CF} = 9.0 Hz), 114.2, 117.4(t, ²J_{CF} = 16.1 Hz), 118.5,
119.4 (qt, $J_{C,F} = 296.6$, $J_{C,F} = 39.1$ Hz), 152.4 (t, $J_{C,F} = 2.9$ Hz), 153.2. $^19$F NMR $\delta$ -84.4 (3F, s), -112.5 (2F, s). HRMS (EI) calcd for C$_{10}$H$_9$F$_5$O$_2$ (M$^+$) 256.05227, found 256.05179.

2-(1,2,2,2-Tetrafluoroethyl)-1,4-dimethoxybenzene (4d)

Oil: IR (neat) 2958, 2842, 1506, 1226, 1184 cm$^{-1}$. $^1$H NMR $\delta$ 3.79 (3H, s), 3.82 (3H, s), 6.14 (1H, dt, $J = 43.8, 6.1$ Hz), 6.87 (1H, d, $J = 9.0$ Hz), 6.96 (1H, dd, $J = 9.1, 3.2$ Hz), 7.07 (1H, d, $J = 2.8$ Hz). $^{13}$C NMR $\delta$ 55.6, 56.0, 82.9 (dq, $J_{C,F} = 182.1$ Hz, $J_{C,F} = 35.6$ Hz), 122.6 (dq, $J_{C,F} = 30.6$ Hz, $J_{C,F} = 281.3$ Hz), 112.0, 113.3 (d, $J = 7.6$ Hz), 116.7 (d, $J_{C,F} = 1.9$ Hz), 119.5 (d, $J_{C,F} = 20.0$ Hz), 151.4 (d, $J_{C,F} = 5.5$ Hz), 153.7. $^{19}$F NMR $\delta$ -79.31 (3F, dd, $J = 13.4, 6.3$ Hz), -198.77 (1F, dq, $J = 43.8, 12.4$ Hz). HRMS (EI) calcd for C$_{10}$H$_{10}$F$_4$O$_2$ (M$^+$) 238.06169, found 238.06115.

9-(Perfluoroethyl)-1,2,3,4,5,6,7,8-octahydroanthracene (3e)

Oil: IR (neat) 2937, 1200, 1146, 1033 cm$^{-1}$. $^1$H NMR $\delta$ 1.71-1.72 (8H, m), 2.73-2.83 (8H, m), 6.98 (1H, s). $^{13}$C NMR $\delta$ 21.87 (2C), 23.1 (2C, t, $J_{C,F} = 1.9$ Hz), 27.3-27.5 (2C), 30.0 (2C), 117.0 (tq, $J_{C,F} = 256.5$ Hz, $J_{C,F} = 39.1$ Hz), 121.6 (qt, $J_{C,F} = 288.0$ Hz, $J_{C,F} = 39.1$ Hz), 124.8 (t, $J_{C,F} = 19.8$ Hz), 133.9, 136.4 (2C), 137.0 (2C, t, $J_{C,F} = 2.6$ Hz). $^{19}$F NMR $\delta$ -83.61 (3F, t, $J = 3.5$ Hz), -99.65 (2F, s). HRMS (EI) calcd for C$_{16}$H$_{17}$F$_5$ (M$^+$) 304.12504, found 304.12414.

9-(1,2,2,2-Tetrafluoroethyl)-1,2,3,4,5,6,7,8-octahydroanthracene (4e)

Oil: IR (neat) 2935, 1274, 1180, 1138 cm$^{-1}$. $^1$H NMR $\delta$ 1.68-1.83 (8H, m), 2.74 (8H, brs), 6.16 (1H, dt, $J = 36.5, 7.5$ Hz), 6.92 (1H, s). $^{13}$C NMR $\delta$ 22.3 (2C), 23.2 (2C), 26.5-26.6 (2C), 29.8 (2C), 87.2 (dq, $J_{C,F} = 187.2$ Hz, $J_{C,F} = 35.3$ Hz), 123.5 (dq, $J_{C,F} = 28.7$ Hz, 283.4 Hz), 125.5 (2C, d, $J_{C,F} = 16.5$ Hz), 129.6, 132.5 (2C), 135.6. $^{19}$F NMR $\delta$ -75.39 (3F, dd, $J = 13.4, 7.2$ Hz), -196.47 (1F, dq, $J = 43.9, 13.4$ Hz). HRMS (EI) calcd
for C₁₆H₁₈F₄ (M⁺) 286.13446, found 286.13371.

3-(Perfluoroethyl)benzo[b]thiophene (3f)

Oil: IR (neat) 3112, 1332, 1202 cm⁻¹. ¹H NMR δ 7.42-7.49 (2H, m), 7.90-7.98 (3H, m). ¹³C NMR δ 112.9 (tq, ¹J_C-F = 252.7 Hz, ²J_C-F = 40.1 Hz), 119.2 (qt, ¹J_C-F = 286.4, ²J_C-F = 39.1 Hz), 122.7, 123.2 (t, ³J_C-F = 2.6 Hz), 124.1 (t, ²J_C-F = 26.4 Hz), 125.2, 125.3, 130.8 (t, ³J_C-F = 17.6 Hz), 135.1, 140.4. ¹⁹F NMR δ -84.80 (3F, s), -110.83 (2F, s). HRMS (EI) calcd for C₁₀H₅F₅S (M⁺) 252.00321, found 252.00271.

3-(1,2,2,2-Tetrafluoroethyl)benzo[b]thiophene (4f)

Oil: IR (neat) 3086, 1278, 1187, 1147 cm⁻¹. ¹H NMR δ 6.00 (1H, dq, J = 44.0 Hz, J = 6.1 Hz), 7.40-7.48 (2H, m), 7.74 (1H, d, J = 1.7 Hz), 7.85 (1H, d, J = 7.8 Hz), 7.90-7.92 (1H, m). ¹³C NMR δ 85.0 (dq, ¹J_C-F =185.0 Hz, ²J_C-F =36.2 Hz), 122.0, 122.3 (dq, ²J_C-F = 29.4 Hz, ¹J_C-F = 281.3 Hz), 122.9, 124.9, 125.1, 125.2 (d, ³J_C-F = 21.2 Hz), 128.6 (d, ³J_C-F = 7.9 Hz), 136.6 (d, ³J_C-F = 6.0 Hz), 140.2. ¹⁹F NMR δ -78.21 (3F, dd, J = 13.4 Hz, 6.2 Hz), -192.95 (1F, dq, J = 43.8 Hz, J = 13.5 Hz). HRMS (EI) calcd for C₁₀H₆F₄S (M⁺) 234.01263, found 234.01224.

1-(1,1,2,2,3,3-Hexafluoropropyl)naphthalene (3g)

Oil: IR (neat) 3059, 1516, 1133 cm⁻¹. ¹H NMR δ 6.15 (1H, tt, J = 52.2, 5.5 Hz), 7.26-7.62 (3H, m), 7.80 (1H, d, J = 7.3 Hz), 7.91 (1H, d, J = 6.8 Hz), 8.05 (1H, J = 8.2 Hz), 8.24 (1H, d, J = 8.0 Hz). ¹³C NMR δ 105.8 (tt, ¹J_C-F = 252.9 Hz, ²J_C-F = 15.8 Hz), 110.7-114.1 (m), 117.8 (tt, ¹J_C-F=254.1 Hz, ²J_C-F = 33.0 Hz), 124.2, 124.8 (t, ²J_C-F = 21.7 Hz), 124.9-125.1 (m), 126.3, 127.5, 127.6 (t, ³J_C-F = 9.8 Hz), 129.0, 130.2, 133.2, 134.1. ¹⁹F NMR δ -106.09 (2F, t, J = 7.5 Hz), -129.34 to -129.38 (2F, m), -137.00 to -137.21 (2F, m). HRMS (EI) calcd for C₁₃H₈F₆ (M⁺) 278.05302, found 278.05256.

1-(1,1,2,2,3,3,4,4,5,5-Decafluoropentyl)naphthalene (3h)
Oil: IR (neat) 1516, 1188, 1132 cm⁻¹. ¹H NMR δ 6.06 (1H, tt, J = 52.6, 5.3 Hz), 7.54-7.63 (3H, m), 7.83 (1H, d, J = 7.5 Hz), 7.93 (1H, d, J = 9.5 Hz), 8.06 (1H, d, J = 8.2 Hz), 8.23 (1H, d, J = 8.5 Hz). ¹³C NMR δ 104.9-120.9 (5C, m), 124.2, 124.7(t, J_{C,F} = 21.9 Hz), 124.8-125.0 (m), 126.4, 127.6, 128.0 (t, J_{C,F} = 9.9 Hz), 129.0, 130.3, 133.4, 134.1. ¹⁹F NMR δ -105.12 (2F, t, J = 6.6 Hz), -120.99 (2F, s), -123.64 (2F, s), -130.38 (2F, s), -137.66 (2F, dm, J = 51.9 Hz). HRMS (EI) calcd for C_{15}H_{8}F_{10} (M⁺) 378.04663, found 378.04593.

5-(2,2,2-Trifluoro-1-hydroxyethyl)uracil (6)

5-(2,2,2-Trifluoro-1-hydroxyethyl)uracil 6 was prepared by the modification of the reported procedure [13]. A mixture of uracil (3.37 g, 30 mmol) and trifluoroacetaldehyde ethyl hemiacetal (containing 10% EtOH) in DMF (18 mL) was stirred at 120 °C for 15 h. After cooling to room temperature, the mixture was poured into saturated aqueous NH₄Cl (30 mL) and extracted with AcOEt (20 mL X 3). The combined organic phase was dried over MgSO₄ and concentrated under reduced pressure. The remained solid was washed with acetone to give 6 (5.23 g, 83%) which was used for the next step without further purification.

5-(2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl)uracil (7)

A mixture of crude 6 (5.23 g, 25 mmol) and hexanethiol (10 mL) in DMF (8 mL) was stirred under reflux for 48 h. After cooling to room temperature, volatile part was removed under reduced pressure. Purification by column chromatography (silica gel/hexane:acetone = 3:1) gave 7 (3.22 g) in 54% yield.

5-(2,2,2-Trifluoro-1-(hexylsulfanyl)ethyl)-1-tosyluracil (2i)

To a CH₃CN solution (5 mL) of 7 (467 mg, 1.5 mmol) was added N,O-bis(trimethylsilyl)acetamide (610 mg, 3 mmol) at room temperature under N₂.
atmosphere. The mixture was stirred under reflux for 1 h, and then cooled to 0 °C. To the mixture, TsCl (574 mg, 3 mmol) was added and the mixture was stirred under reflux for 24 h. After cooling to room temperature, a volatile part was removed under reduced pressure. Purification by column chromatography (silica gel / hexane:acetone = 3:1) gave 2i (390 mg, 0.84 mmol) in 56% yield. White solid. Mp 120-121 °C. IR (KBr) 3060, 2931, 2857, 1738, 1685, 1261, 1194 cm⁻¹. ¹H NMR δ 0.89 (3H, t, J = 6.7 Hz), 1.28-1.42 (6H, m), 1.58-1.66 (2H, m), 2.48 (3H, s), 2.68-2.80 (2H, m), 4.56 (1H, q, J = 8.4 Hz), 7.40 (2H, d, J = 8.2 Hz), 7.96 (2H, d, J = 8.5 Hz), 8.27 (1H, s), 8.47 (1H, s). ¹³C NMR δ 13.9, 21.8, 22.4, 28.2, 28.9, 31.2, 33.8, 41.5 (q, ²J_{C,F} = 31.7 Hz), 110.4, 125.4 (q, ¹J_{C,F} = 279.2 Hz), 129.8 (2C), 129.9 (2C), 132.4, 137.3, 146.5, 147.2, 161.7. ¹⁹F NMR δ -69.31 (3F, d, J = 8.1 Hz). HRMS (El) calcd for C₁₉H₂₃F₃N₂O₄S₂ (M⁺) 464.10513, found 464.10639.

5-(Perfluoroethyl)-1-tosyluracil (3i)

To IF₅ / Et₃N-3HF (250 mg, 0.65 mmol) in Teflon PFA bottle was added a CH₂Cl₂ solution (3 mL) of 2i (198.5 mg, 0.43 mmol) at 0 °C and the mixture was stirred at room temperature for 24 h (complete consumption of 3 was confirmed from NMR analysis). To the reaction mixture, IF₅ / 5CH₂Cl₂ (280 mg, 0.43 mmol) was added and the mixture was stirred at room temperature for another 24 h. Then, the mixture was poured into saturated aqueous NaHCO₃ (20 mL) and extracted with ether (30 mL X 3). The combined organic layer was washed with saturated aqueous Na₂S₂O₃ (20 mL), dried over MgSO₄, and concentrated under reduced pressure. Purification by column chromatography (silica gel / hexane:acetone = 3:1) gave 3i (101 mg) in 61% yield. White solid. Mp 211-212 °C. IR (KBr) 3437, 1709, 1205, 1179 cm⁻¹. ¹H NMR (acetone-d₆) δ 2.47 (3H, s), 7.51 (2H, d, J = 8.4 Hz), 8.04 (2H, d, J = 8.5 Hz), 8.54 (1H,
s), 10.82 (1H, brs). $^{13}$C NMR (acetone-d$_6$) $\delta$ 21.6, 104.8 (t, $^2J_{C,F}$ = 23.8 Hz), 112.8 (tq, $^1J_{C,F}$ = 255.6 Hz, $^2J_{C,F}$ = 41.0 Hz), 119.7 (qt, $^1J_{C,F}$ = 286.1, $^2J_{C,F}$ = 39.1 Hz), 130.6 (2C), 130.8 (2C), 133.6, 142.2 (t, $^2J_{C,F}$ = 10.4 Hz), 147.1, 148.1, 158.8 (t, $^3J_{C,F}$ = 1.8 Hz). $^{19}$F NMR (acetone-d$_6$) $\delta$ -81.91 (3F, s), -111.94 (2F, s). HRMS (EI) calcd for C$_{13}$H$_8$F$_5$N$_2$O$_4$S (M$^+$-1) 383.01304, found 383.01329.

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