### Supporting Information

Three-Component Difluoroalkylation and Trifluoromethylthiolation/Trifluoromethylselenolation of π-Bonds

Bo-Sheng Zhang, Lu-Yao Gao, Zhe Zhang, Yu-Hua Wen, Yong-Min Liang*
State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China
E-mail: liangym@lzu.edu.cn

---

**Table of Contents**

1. General Methods .............................................. 2
2. Optimization of Reaction Conditions: ......................... 3-4
3. General Procedure ............................................ 5
4. Synthesis of bpyCuSCF$_3$ and bpyCuSeCF$_3$ .................. 6
5. Characterization Data ........................................... 7-19
6. NMR Spectroscopic Data ........................................ 20-98
7. The Noe of the Compound 5a (600 MHz) ....................... 99-102
8. GC-MS Spectrum of Trapping the Radical Intermediate. .... 103-105
1. General Methods

The starting materials were purchased and used without further purification. Unless otherwise noted, reactions were carried out under an argon atmosphere. For Column chromatography, 200-300 mesh silica gel and preparative TLC (PTLC) was employed. Analytical TLC was performed with silica gel GF254 plates. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) were recorded in CDCl$_3$ using TMS as internal standard. All products were further characterized by high resolution mass spectra (HRMS, FTMS, ESI full ms [100-2000]), copies of their $^1$H NMR and $^{13}$C NMR spectra were provided.
2. Optimization of Reaction Conditions:

**Reaction conditions:**  
4j (0.2 mmol), ICF₂COOEt (0.4 mmol), bpyCuSCF₃ (0.4 mmol), solvent (2.0 mL), under an Ar atmosphere, 18 h, 100 °C.  

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Base (equiv.)</th>
<th>Yield (%)</th>
<th>E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dioxane</td>
<td>-</td>
<td>21</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>-</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>DMSO</td>
<td>-</td>
<td>trace</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>-</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>DME</td>
<td>-</td>
<td>30</td>
<td>3:1</td>
</tr>
<tr>
<td>6</td>
<td>DCE</td>
<td>-</td>
<td>7</td>
<td>-</td>
</tr>
</tbody>
</table>

Yields of isolated products. Determined by GC (phenylate was used as internal standard).

**Reaction conditions:**  
4j (0.2 mmol), ICF₂COOEt (0.4 mmol), bpyCuSCF₃ (0.4 mmol), DME (2.0 mL), under an Ar atmosphere, 18 h.  

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Base (equiv.)</th>
<th>Yield (%)</th>
<th>E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R.t.</td>
<td>-</td>
<td>trace</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>-</td>
<td>trace</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>-</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>-</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>-</td>
<td>30</td>
<td>3:1</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>-</td>
<td>28</td>
<td>3:1</td>
</tr>
</tbody>
</table>

Yields of isolated products. Determined by GC (phenylate was used as internal standard).
<table>
<thead>
<tr>
<th>entry</th>
<th>additive</th>
<th>yield (%)</th>
<th>E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DBU</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>TMEDA</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>AgF</td>
<td>42</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>AgOAc</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Pd(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;k&lt;/sub&gt;</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>PMDTA</td>
<td>25</td>
<td>-</td>
</tr>
</tbody>
</table>

Reaction conditions: *<sup>a</sup> 4j (0.2 mmol), ICF<sub>2</sub>COOEt (0.4 mmol), LCuSCF<sub>3</sub> (0.4 mmol), CsF (0.8 mmol), additive (0.4 mmol), DME (2.0 mL), under an Ar atmosphere, 18 h, 100 °C. *<sup>b</sup> Yields of isolated products. *<sup>c</sup> Determined by GC (phenylate was used as internal standard).

---

**Diagram:**

![Diagram](image-url)
3. General Procedure

In a 10 mL tube, bpyCuSCF₃ (bpyCuSeCF₃) (0.4 mmol, 2.0 equiv.), CsF (0.8 mmol, 4.0 equiv.) were added and charged with argon more than three times. DME (2 mL), alkene (alkyne) (0.2 mmol, 1.0 equiv) and ICF₂COOEt (0.4 mmol, 2.0 equiv.) was injected into the tube. Afterwards, the reaction tube was then immersed in an oil bath, which was preheated at 100 °C for 18 h. After the reaction was completed, the residue was purified with chromatography column on silica gel or preparative TLC (PTLC) (Petroleum ether/EtOAc = 40:1 - 200:1).
4. Synthesis of bpyCuSCF$_3$ and bpyCuSeCF$_3$

The method is following Weng's work1-2. Small change is added so that the purity of bpyCuSCF$_3$ and bpyCuSeCF$_3$ can meet requirement of reaction without glovebox.

CuF$_2$ (3.03 g, 30.0 mmol), S$_8$ (0.96 g, 30.0 mmol) and 90 mL CH$_3$CN were added to an oven-dried 200 ml round flask (round flask is sealed with tipping plug and white medical adhesive plaster) and round flask was charged with argon more than three times. CF$_3$SiMe$_3$ (12.77 g, 90.0 mmol) was injected into this tube. The mixture was stirred in a preheated oil bath at 80 °C for 10 h. The reaction mixture was then allowed to cool to room temperature and filtered through Celite quickly under air. The volatiles were removed under reduced pressure and the resulting dark-brown solid was washed with Et$_2$O (3 x 15 mL). The solid was re-dissolved in 20 mL of CH$_3$CN, and solution was filtered through Celite quickly again (it is important to improve the purity), the filtrate (20 ml) was in 150 ml round flask and round flask was charged with argon more than three times. The solution was carefully added injected 2,2’-bipyridine (4.68 g, 30.0 mmol) in 80 mL of Et$_2$O. The resulting solution was then kept at -25 °C for 24 h. The resulting orange crystals (powder) were washed with Et$_2$O (5 × 15 mL) (removing the absorbed 2,2’-bipyridine).

CuI (5.71 g, 30.0 mmol), Se (4.74 g, 60.0 mmol), KF (5.22 g, 90.0 mmol) and 60 mL CH$_3$CN were added to an 150 ml round flask (round flask is sealed with tipping plug and white medical adhesive plaster) and round flask was charged with argon more than three times. CF$_3$SiMe$_3$ (12.77 g, 90.0 mmol) was added into this tube. The mixture was vigorously stirred at rt (15 °C ~ 25 °C) for 24 h (high pressure in round flask). The reaction mixture was then filtered through a layer of Celite quickly under air (cautiously, it is foul smell solution). The volatiles were removed under reduced pressure and the resulting dark-brown solid was washed with hexane (3 x 10 mL). The solid was re-dissolved in 20 mL of CH$_3$CN and solution was filtered through Celite quickly again (it is important to improve the purity). The filtrate (20 ml) was in 150 ml round flask and round flask was charged with argon more than three times. 2,2’-bipyridine (4.68 g, 30.0 mmol) in 80 mL of Et$_2$O was carefully added to this solution. The resulting solution was then kept at -25 °C for 48 h. The resulting orange crystals were washed with Et$_2$O (5 × 15 mL).

Reference

5. Characterization Data

**ethyl 2,2-difluoro-4-phenyl-4-((trifluoromethyl)thio)butanoate (2a)**

43.5 mg, yield: 66%. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.48 – 7.27 (m, 5H), 4.72 – 4.50 (m, 1H), 4.12 – 3.92 (m, 2H), 3.03 – 2.77 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-d) δ 163.04 (t, J = 31.8 Hz), 138.02, 129.82 (q, J = 306.10 Hz), 128.92, 128.66, 127.60, 114.10 (t, J = 250.40 Hz), 63.09, 42.92 (m), 41.26 (t, J = 23.9 Hz), 13.67.

$^{19}$F NMR (376 MHz, Chloroform-d) δ -40.37, -103.93 (d, d, J = 1194.9 Hz, 266.2 Hz).

HRMS (ESI) Calcd for C$_{13}$H$_{13}$F$_{5}$O$_2$S [M+Na]$^+$ 351.0449, found 351.0456.

**ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)thio)butanoate (2b)**

59.1 mg, yield: 83%. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.23 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 4.67 – 4.50 (m, 1H), 4.08 – 3.94 (m, 2H), 3.79 (s, 3H), 2.98 – 2.75 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-d) δ 163.07 (t, J = 32.0 Hz), 159.71, 129.60, 128.88, 114.22, 114.145 (t, J = 249.7 Hz), 63.07, 55.28, 42.56 (m), 41.34 (t, J = 23.8 Hz), 13.67.

$^{19}$F NMR (376 MHz, Chloroform-d) δ -40.33, -103.97 (d, d, J = 1328.9 Hz, 266.0 Hz).

HRMS (ESI) Calcd for C$_{14}$H$_{15}$F$_{5}$O$_3$S [M+Na]$^+$ 381.0554, found 381.0558.

**ethyl 2,2-difluoro-4-(2-methoxyphenyl)-4-((trifluoromethyl)thio)butanoate (2c)**

43.1 mg, yield: 60%. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.25 (m, 1H), 7.21 (d, J = 7.5 Hz, 1H), 6.98 – 6.81 (m, 2H), 4.86 – 4.60 (m, 1H), 4.12 – 3.94 (m, 2H), 3.88 (s, 3H), 3.25 – 3.04 (m, 1H), 2.93 – 2.76 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-d) δ 163.21 (t, J = 32.0 Hz), 156.85, 130.82 (q, J = 305.4 Hz), 129.87, 128.93, 126.43, 120.654, 114.45 (t, J = 250.1 Hz), 111.14, 62.91, 55.55, 40.59 (t, J = 23.6 Hz), 38.86 (m), 13.68.

$^{19}$F NMR (376 MHz, Chloroform-d) δ -41.65, -104.34 (d, d, J = 1062.5 Hz, 266.1 Hz).
ethyl 2,2-difluoro-4-((methylthio)phenyl)-4-((trifluoromethyl)thio)butanoate (2d)
56.3 mg, yield: 75 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.31 – 7.12 (m, 4H), 4.69 – 4.51 (m, 1H), 4.17 – 3.91 (m, 2H), 3.05 – 2.71 (m, 2H), 2.47 (s, 3H), 1.24 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.03 (t, $J = 32.0$ Hz), 139.54, 134.26, 129.73 (q, $J = 308.1$ Hz), 128.02, 126.29, 114.04 (t, $J = 251.8$ Hz), 63.17, 42.53 (m), 41.06 (t, $J = 23.8$ Hz), 15.32, 13.66.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.27, -103.93 (d, $d$, $J = 1102.5$ Hz, 266.5 Hz).

HRMS (ESI) Calcd for C$_{14}$H$_{15}$F$_5$O$_3$S [M+Na]$^+$ 397.0326, found 397.0332.

ethyl 2,2-difluoro-4-(4-(methylthio)phenyl)-4-((trifluoromethyl)thio)butanoate (2e)
41.9 mg, yield: 61 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.19 (d, $J = 8.1$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 4.68 – 4.49 (m, 1H), 4.11 – 3.92 (m, 2H), 2.99 – 2.74 (m, 2H), 2.33 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.09 (t, $J = 31.8$ Hz), 138.74, 137.87, 129.41, 128.80, 128.21, 124.60, 114.16 (t, $J = 251.3$ Hz), 63.05, 42.74 (m), 41.32 (t, $J = 23.8$ Hz), 21.11, 13.65.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.37, -103.93 (dd, $J = 1179.2$ Hz, 265.9 Hz).

HRMS (ESI) Calcd for C$_{14}$H$_{15}$F$_5$O$_3$S [M+Na]$^+$ 365.0605, found 365.0607.

ethyl 2,2-difluoro-4-(m-tolyl)-4-((trifluoromethyl)thio)butanoate (2f)
37.5 mg, yield: 55 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.26 – 7.21 (m, 1H), 7.16 – 7.05 (m, 3H), 4.62 – 4.49 (m, 1H), 4.09 – 3.95 (m, 2H), 3.00 – 2.78 (m, 2H), 2.35 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.08 (t, $J = 31.8$ Hz), 138.74, 137.87, 129.87 (q, $J = 306.2$ Hz), 129.41, 128.80, 128.21, 124.60, 114.14 (t, $J = 250.2$ Hz), 63.04, 42.89 (m), 41.35 (t, $J = 23.8$ Hz), 21.31, 13.65.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.42, -103.94 (dd, $J = 1206.7$ Hz, 266.1 Hz).

HRMS (ESI) Calcd for C$_{14}$H$_{15}$F$_5$O$_3$S [M+Na]$^+$ 365.0605, found 365.0604.
ethyl 2,2-difluoro-4-(o-tolyl)-4-((trifluoromethyl)thio)butanoate (2g)

41.3 mg, yield: 60 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.35 – 7.26 (m, 1H), 7.25 – 7.02 (m, 3H), 5.05 – 4.72 (m, 1H), 4.09 – 3.82 (m, 2H), 3.14 – 2.97 (m, 1H), 2.96 – 2.79 (m, 1H), 2.41 (s, 3H), 1.21 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.06 (t, $J$ = 31.8 Hz), 135.88, 135.42, 131.03, 129.99 (q, t, $J$ = 306.2 Hz), 128.51, 126.99, 126.62, 114.13 (t, $J$ = 252.0 Hz), 63.05, 41.25 (t, $J$ = 23.6 Hz), 19.07, 13.61.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.71, -104.10 (dd, $J$ = 1559.2 Hz, 264.6 Hz).

HRMS (ESI) Calcd for C$_{14}$H$_{15}$F$_5$O$_2$S [M+Na]$^+$ 365.0605, found 365.0604.

ethyl 4-(4-(tert-butyl)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2h)

40.1 mg, yield: 52 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.36 (d, $J$ = 8.3 Hz, 2H), 7.22 (d, $J$ = 8.3 Hz, 2H), 4.68 – 4.49 (m, 1H), 4.03 – 3.83 (m, 2H), 3.07 – 2.79 (m, 1H), 1.30 (s, 9H), 1.19 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.05 (t, $J$ = 32.3 Hz), 151.76, 134.56, 129.89 (q, $J$ = 306.0 Hz), 127.31, 125.83, 114.14 (t, $J$ = 249.5 Hz), 62.97, 42.63 (m), 41.436 (t, $J$ = 24.1 Hz), 34.613, 31.19, 13.65.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.40, -103.91 (dd, $J$ = 1662.4 Hz, 265.4 Hz).

HRMS (ESI) Calcd for C$_{17}$H$_{21}$F$_5$O$_2$S [M+Na]$^+$ 407.1075, found 407.1081.

ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2i)

44.8 mg, yield: 55 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.66 – 7.51 (m, 4H), 7.44 (t, $J$ = 7.5 Hz, 2H), 7.41 – 7.29 (m, 3H), 4.80 – 4.50 (m, 1H), 4.20 – 3.84 (m, 2H), 3.08 – 2.80 (m, 2H), 1.22 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.068 (t, $J$ = 31.8 Hz), 141.58, 140.11, 136.90, 129.84 (q, $J$ = 306.3 Hz), 128.85, 128.05, 127.67, 127.56, 127.01, 114.11 (t, $J$ = 251.8 Hz), 63.13, 42.68 (m), 41.26 (t, $J$ = 24.0 Hz), 13.67.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.25, -103.85 (dd, $J$ = 1202.2 Hz, 266.3 Hz).

HRMS (ESI) Calcd for C$_{19}$H$_{17}$F$_5$O$_2$S [M+Na]$^+$ 427.0762, found 427.0762.
ethyl 4-(4-chlorophenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2j)
33.6 mg, yield: 46 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.33 (d, $J = 8.5$ Hz, 2H), 7.26 (d, $J = 8.5$ Hz, 2H), 4.70 – 4.50 (m, 1H), 4.20 – 4.00 (m, 2H), 2.95 – 2.73 (m, 2H), 1.26 (t, $J = 7.2$ Hz, 3H).
$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 162.98 (t, $J = 31.7$ Hz), 136.82, 134.54, 129.66 (q, $J = 306.3$ Hz), 129.13, 128.96, 113.98 (t, $J = 251.9$ Hz), 63.26, 42.26 (m), 41.00 (t, $J = 23.8$ Hz), 13.70.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.27, -103.98 (dd, $J = 785.0$ Hz, 267.0 Hz).

HRMS (ESI) Calcd for C$_{13}$H$_{12}$ClF$_5$O$_2$S [M+Na]$^+$ 385.0059, found 385.0060.

ethyl 2,2-difluoro-4-(4-(trifluoromethyl)phenyl)-4-((trifluoromethyl)thio)butanoate (2k)
32.8 mg, yield: 41 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.63 (d, $J = 8.1$ Hz, 2H), 7.46 (d, $J = 8.1$ Hz, 2H), 4.82 – 4.54 (m, 1H), 4.11 (q, $J = 7.0$ Hz, 2H), 2.98 – 2.76 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H).
$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 162.95 (t, $J = 31.7$ Hz), 142.58, 131.13, 130.86 (q, $J = 32.6$ Hz), 129.60 (q, $J = 306.5$ Hz), 125.96 (q, $J = 3.0$ Hz), 123.72 (q, $J = 270.7$ Hz), 113.93 (t, $J = 252.0$ Hz), 63.32, 42.30 (m), 40.86 (t, $J = 24.1$ Hz), 13.68.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.27, -62.84, -103.97 (dd, $J = 596.8$ Hz, 267.7 Hz).

HRMS (ESI) Calcd for C$_{14}$H$_{12}$F$_8$O$_2$S [M+Na]$^+$ 419.0322, found 419.0330.

ethyl 4-(3,4-dimethoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2l)
56.0 mg, yield: 72 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 6.90 – 6.85 (m, 1H), 6.81 (d, $J = 9.4$ Hz, 2H), 4.68 – 4.50 (m, 1H), 4.11 – 4.00 (m, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 3.03 – 2.76 (m, 2H), 1.23 (t, $J = 7.1$ Hz, 3H).
$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.11 (t, $J = 32.0$ Hz), 149.24, 149.16, 130.02, 129.80 (q, $J = 308.2$ Hz), 120.09, 114.13 (t, $J = 252.4$ Hz). 111.07, 110.55, 63.09, 55.96, 55.89, 42.92 (m), 41.38 (t, $J = 23.7$ Hz), 13.65.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.35, -103.94 (dd, $J = 1362.9$ Hz, 266.5 Hz).

HRMS (ESI) Calcd for C$_{15}$H$_{17}$F$_5$O$_4$S [M+Na]$^+$ 411.0660, found 411.0668.
ethyl 4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2m)
54.3 mg, yield: 70 %. Light yellow liquid.
1H NMR (400 MHz, Chloroform-d) δ 6.87 – 6.79 (m, 2H), 6.79 – 6.73 (m, 1H), 4.56 – 4.48 (m, 1H), 4.24 (s, 4H), 4.14 – 4.05 (m, 2H), 2.95 – 2.75 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H).
13C NMR (100 MHz, Chloroform-d) δ 163.07 (t, J = 31.9 Hz), 143.79, 143.61, 130.90, 129.83 (q, J = 306.2 Hz), 120.64, 117.63, 116.44, 114.10 (t, J = 215.5 Hz), 64.31, 64.27, 63.08, 42.53 (m), 41.37 (t, J = 24.0 Hz), 13.68.
19F NMR (376 MHz, Chloroform-d) δ -40.40, -104.02 (dd, J = 1066.4 Hz, 266.1 Hz).

ethyl 2,2-difluoro-4-(4-methoxyphenyl)-3-methyl-4-((trifluoromethyl)thio)butanoate (2o)
31.1 mg, yield: 42 %. Light yellow liquid. (d.r. = 13:1)
1H NMR (400 MHz, Chloroform-d) δ 7.28 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 4.55 (d, J = 6.1 Hz, 1H), 4.23 – 4.04 (m, 2H), 3.80 (s, 3H), 2.97 – 2.65 (m, 1H), 1.34 – 1.20 (m, 6H).
13C NMR (101 MHz, Chloroform-d) δ 163.32 (t, J = 32.3 Hz), 159.34, 131.33, 130.26 (q, J = 307.0 Hz), 129.34, 115.86 (t, J = 256.6 Hz), 113.83, 63.03, 55.26, 48.64 (m), 44.35 (t, J = 22.0 Hz), 13.72, 10.06 (t, J = 4.7 Hz).
19F NMR (376 MHz, Chloroform-d) δ -40.19, -109.25 (dd, J = 1927.3 Hz, 262.1 Hz).

ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)selenyl)butanoate (3a)
66.7 mg, yield: 82 %. Light yellow liquid.
1H NMR (400 MHz, Chloroform-d) δ 7.24 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 4.97 – 4.66 (m, 1H), 4.09 – 3.92 (m, 2H), 3.79 (s, 3H), 3.24 – 3.04 (m, 1H), 2.99 – 2.81 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H).
13C NMR (100 MHz, Chloroform-d) δ 163.16 (t, J = 32.1 Hz), 159.64, 129.50, 128.93, 122.87 (q, J = 332.4 Hz), 114.39 (t, J = 253.9 Hz), 114.27, 63.02, 55.27, 41.74 (t, J = 23.7 Hz), 38.73 (m), 13.65.
19F NMR (376 MHz, Chloroform-d) δ -33.78, -104.08 (dd, J = 1510.9 Hz, 264.0 Hz).
ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (3b)

66.2 mg, yield: 73 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.56 (d, $J = 8.3$ Hz, 4H), 7.48 – 7.31 (m, 5H), 4.99 – 4.73 (m, 1H), 4.10 – 3.87 (m, 2H), 3.32 – 3.08 (m, 1H), 3.07 – 2.87 (m, 1H), 1.20 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.17 (t, $J = 31.8$ Hz), 141.45, 140.09, 136.81, 128.86, 128.10, 127.67, 126.98, 122.81 (q, $J = 330.5$ Hz), 114.38 (t, $J = 252.2$ Hz), 63.08, 41.60 (t, $J = 23.7$ Hz), 38.72 (m), 13.65.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -33.66, -103.98 (dd, $J = 1415.1$ Hz, 264.6 Hz).

HRMS (ESI) Calcd for C$_{14}$H$_{15}$F$_{5}$O$_{3}$Se [M+Na]$^+$ 428.9999, found 429.0005.

ethyl 2,2-difluoro-4-(p-tolyl)-4-((trifluoromethyl)selanyl)butanoate (3c)

52.4 mg, yield: 67 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.20 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 4.89 – 4.71 (m, 1H), 4.05 – 3.92 (m, 2H), 3.24 – 3.06 (m, 1H), 2.99 – 2.85 (m, 1H), 2.32 (s, 3H), 1.21 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.17 (t, $J = 31.9$ Hz), 138.49, 134.75, 129.61, 127.52, 122.85 (q, $J = 330.4$ Hz), 114.40 (t, $J = 252.4$ Hz), 63.00, 41.69 (t, $J = 23.4$ Hz), 38.87 (m), 21.10, 13.62.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -33.81, -104.06 (dd, $J = 1415.1$ Hz, 264.6 Hz).

HRMS (ESI) Calcd for C$_{16}$H$_{17}$F$_{5}$O$_{3}$Se [M+Na]$^+$ 475.0206, found 475.0211.

ethyl 2,2-difluoro-4-(pyridin-2-yl)-4-((trifluoromethyl)selanyl)butanoate (3d)

48.7 mg, yield: 65 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.55 (d, $J = 4.6$ Hz, 1H), 7.71 – 7.61 (m, 1H), 7.31 (d, $J = 7.8$ Hz, 1H), 7.24 – 7.16 (m, 1H), 4.85 – 4.71 (m, 1H), 4.21 – 4.10 (m, 2H), 3.55 – 3.41 (m, 1H), 3.07 – 2.92 (m, 1H), 1.28 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.24 (t, $J = 32.2$ Hz), 158.05, 149.81, 136.99, 123.17 (q, $J = 330.0$ Hz), 122.94, 122.28, 114.62 (t, $J = 251.0$ Hz), 63.07, 41.37 (t, $J = 23.1$ Hz), 40.11 (m), 13.74.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -34.25, -104.63 (dd, $J = 316.2$ Hz, -262.8 Hz).

HRMS (ESI) Calcd for C$_{18}$H$_{19}$F$_{5}$N$_{2}$O$_{3}$Se [M+Na]$^+$ 413.0050, found 413.0058.

ethyl 2,2-difluoro-4-((1H-pyrazol-2-yl)-4-((trifluoromethyl)selanyl)butanoate (3e)

45.3 mg, yield: 67 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.60 (d, $J = 5.2$ Hz, 1H), 7.55 – 7.38 (m, 1H), 7.25 – 7.12 (m, 1H), 4.95 – 4.78 (m, 2H), 3.71 – 3.52 (m, 1H), 3.06 – 2.92 (m, 1H), 1.28 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 163.18 (t, $J = 31.8$ Hz), 158.05, 149.81, 136.99, 123.17 (q, $J = 330.0$ Hz), 122.94, 122.28, 114.62 (t, $J = 251.0$ Hz), 63.07, 41.37 (t, $J = 23.1$ Hz), 40.11 (m), 13.74.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -34.25, -104.63 (dd, $J = 316.2$ Hz, -262.8 Hz).

HRMS (ESI) Calcd for C$_{18}$H$_{19}$F$_{5}$NO$_{3}$Se [M+Na]$^+$ 399.9846, found 399.9852.
ethyl (E)-2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)thio)but-3-enate (5a)

52.2 mg, yield: 73 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.33 (d, $J$ = 8.8 Hz, 2H), 6.88 (d, $J$ = 8.7 Hz, 2H), 6.42 (t, $J$ = 10.8 Hz, 1H), 3.96 (q, $J$ = 7.1 Hz, 2H), 3.82 (s, 3H), 1.17 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 162.41 (t, $J$ = 33.0 Hz), 161.10, 139.94 (m), 131.01, 128.59 (q, $J$ = 308.3 Hz), 127.16 (m), 126.45, 113.62, 110.91 (t, $J$ = 246.1 Hz), 63.12, 55.29, 13.62.

$^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -40.20, -92.13.

HRMS (ESI) Calcd for C$_{14}$H$_{13}$F$_{5}$O$_{3}$S [M+Na]$^+$ 379.0398, found 379.0402.

ethyl (E)-2,2-difluoro-4-(4-(pentyloxy)phenyl)-4-((trifluoromethyl)thio)but-3-enate (5b)

55.7 mg, yield: 68 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.31 (d, $J$ = 8.7 Hz, 2H), 6.86 (d, $J$ = 8.7 Hz, 2H), 6.41 (t, $J$ = 10.8 Hz, 1H), 4.02 – 3.90 (m, 4H), 1.83 – 1.75 (m, 2H), 1.46 – 1.35 (m, 4H), 1.17 (t, $J$ = 7.2 Hz, 3H), 0.94 (t, $J$ = 7.0 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 162.43 (t, $J$ = 32.8 Hz), 160.74, 140.04 (m), 130.99, 128.61 (q, $J$ = 308.3 Hz), 126.97 (m), 126.17, 114.10, 110.94 (t, $J$ = 246.0 Hz), 68.10, 63.09, 28.83, 28.14, 22.42, 13.96, 13.62.

$^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -40.23, -91.99.

HRMS (ESI) Calcd for C$_{18}$H$_{21}$F$_{5}$O$_{3}$S [M+Na]$^+$ 435.1024, found 435.1024.

ethyl (E)-4-(4-(benzyloxy)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enate (5c)

59.5 mg, yield: 69 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.46 – 7.30 (m, 7H), 6.95 (d, $J$ = 8.7 Hz, 2H), 6.42 (t, $J$ = 10.8 Hz, 1H), 5.07 (s, 2H), 3.91 (q, $J$ = 7.1 Hz, 2H), 1.14 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 162.70 (t, $J$ = 33.0 Hz), 160.24, 139.85 (m), 136.30, 131.20, 128.63, 128.58 (q, $J$ = 308.3 Hz), 128.16, 127.52, 127.21 (m), 126.68, 114.49, 110.89 (t, $J$ = 246.2 Hz), 70.03, 63.10, 13.61.

$^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -40.15, -92.03.

HRMS (ESI) Calcd for C$_{20}$H$_{17}$F$_{5}$O$_{3}$S [M+Na]$^+$ 455.0711, found 455.0707.
ethyl (E)-4-(4-acetoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5d)

22.4 mg, yield: 29 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.40 (d, $J = 8.7$ Hz, 2H), 7.12 (d, $J = 8.6$ Hz, 2H), 6.49 (t, $J = 10.9$ Hz, 1H), 3.98 (q, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 1.19 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 168.78, 162.27 (t, $J = 32.9$ Hz), 152.04, 138.98 (m), 131.74, 130.54, 129.49 (q, $J = 300.0$ Hz), 128.60 (m), 121.51, 110.67 (t, $J = 247.7$ Hz), 63.38, 21.10, 13.64.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.05, -92.75.

HRMS (ESI) Calcd for C$_{15}$H$_{13}$F$_5$O$_4$S [M+Na]$^+$ 407.0347, found 407.0347.

ethyl (E)-2,2-difluoro-4-($p$-tolyl)-4-((trifluoromethyl)thio)but-3-enoate (5e)

34.3 mg, yield: 50 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.26 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.44 (t, $J = 10.9$ Hz, 1H), 3.94 (q, $J = 7.1$ Hz, 2H), 2.37 (s, 3H), 1.17 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 162.38 (t, $J = 33.0$ Hz), 140.48, 140.14 (m), 131.43, 129.23, 128.90, 128.55 (q, $J = 308.3$ Hz), 127.60 (m), 110.82 (t, $J = 246.6$ Hz), 63.11, 21.36, 13.59.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.15, -92.60.

HRMS (ESI) Calcd for C$_{15}$H$_{13}$F$_5$O$_2$S [M+Na]$^+$ 363.0449, found 363.0451.

ethyl (E)-4-((tert-butyl)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5f)

44.1 mg, yield: 58 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.38 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H), 6.45 (t, $J = 10.7$ Hz, 1H), 3.87 (q, $J = 7.1$ Hz, 2H), 1.31 (s, 9H), 1.13 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 162.35 (t, $J = 32.8$ Hz), 153.60, 139.97 (m), 131.42, 129.11, 128.59 (q, $J = 308.7$ Hz), 127.62 (m), 126.15, 110.87 (t, $J = 246.3$ Hz), 63.02, 34.82, 31.11, 13.61.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.26, -92.00.

HRMS (ESI) Calcd for C$_{17}$H$_{19}$F$_5$O$_2$S [M+Na]$^+$ 405.0918, found 405.0919.
ethyl (E)-2,2-difluoro-4-(4-propylphenyl)-4-((trifluoromethyl)thio)but-3-enolate (5g)
30.4 mg, yield: 41 %. Light yellow liquid.
1H NMR (400 MHz, Chloroform-d) δ 7.28 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.45 (t, J = 10.8 Hz, 1H), 3.91 (q, J = 7.1 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 1.64 (q, J = 7.4 Hz, 2H), 1.16 (t, J = 7.1 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H).
13C NMR (100 MHz, Chloroform-d) δ 162.32 (t, J = 32.9 Hz), 145.22, 140.11 (m), 133.15, 129.25, 128.56 (q, J = 308.4 Hz), 128.30, 127.56 (m), 110.83 (t, J = 246.2 Hz), 63.06, 37.78, 24.22, 13.68, 13.61.
19F NMR (376 MHz, Chloroform-d) δ -40.20, -92.24.

ethyl (E)-4-(4-chlorophenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enolate (5h)
15.5 mg, yield: 21 %. Light yellow liquid.
1H NMR (400 MHz, Chloroform-d) δ 7.44–7.28 (m, 4H), 6.50 (t, J = 11.2 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H).
13C NMR (100 MHz, Chloroform-d) δ 162.31 (t, J = 33.1 Hz), 138.84 (m), 136.38, 132.89, 130.56, 128.86 (m), 128.55, 128.40 (q, J = 308.9 Hz), 110.58 (t, J = 248 Hz), 63.40, 13.68.
19F NMR (376 MHz, Chloroform-d) δ -39.87, -93.75.

ethyl (E)-2,2-difluoro-4-(4-(methylthio)phenyl)-4-((trifluoromethyl)thio)but-3-enolate (5i)
45.1 mg, yield: 61 %. Light yellow liquid.
1H NMR (400 MHz, Chloroform-d) δ 7.29 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 6.46 (t, J = 11.0 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 2.49 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H).
13C NMR (100 MHz, Chloroform-d) δ 162.37 (t, J = 32.9 Hz), 142.08, 139.59 (m), 130.51, 129.62, 128.50 (q, J = 310.8 Hz), 127.89 (m), 125.09, 110.76 (t, J = 248 Hz), 63.24, 14.93, 13.62.
19F NMR (376 MHz, Chloroform-d) δ -39.87, -93.75.

ethyl (E)-4-([1,1’-biphenyl]-4-yl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enolate (5j)
41.3 mg, yield: 51 %. Light yellow liquid.
$^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.60 (d, $J = 8.1$ Hz, 4H), 7.48 – 7.42 (m, 4H), 7.38 (d, $J = 7.2$ Hz, 1H), 6.51 (t, $J = 10.9$ Hz, 1H), 3.96 (q, $J = 7.1$ Hz, 2H), 1.16 (t, $J = 7.2$ Hz, 3H).

$^1$C NMR (100 MHz, Chloroform-\textit{d}) $\delta$ 162.38 (t, $J = 32.9$ Hz), 142.94, 139.80, 139.68 (m), 133.25, 129.79, 128.90, 128.51 (q, it coincides with peak 127.07 ppm), 128.24 (m), 127.97, 127.07, 126.79, 110.79 (t, $J = 247.0$ Hz), 63.23, 13.63.

$^{19}$F NMR (376 MHz, Chloroform-\textit{d}) $\delta$ -39.99, -92.73.

HRMS (ESI) Calcd for C$_{10}$H$_{13}$F$_3$O$_2$S [M+Na]$^+$ 425.0605, found 425.0607.

$^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.59 (d, $J = 8.3$ Hz, 2H), 7.52 (d, $J = 8.1$ Hz, 2H), 7.44 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 6.50 (t, $J = 10.9$ Hz, 1H), 3.94 (q, $J = 7.1$ Hz, 2H), 2.63 (t, $J = 7.6$ Hz, 2H), 1.73 – 1.63 (m, 2H), 1.15 (t, $J = 7.2$ Hz, 3H), 0.97 (t, $J = 7.3$ Hz, 3H).

$^1$C NMR (100 MHz, Chloroform-\textit{d}) $\delta$ 162.38 (t, $J = 32.7$ Hz), 159.04, 140.20 (m), 135.179, 130.12, 129.43, 129.32, 128.58 (q, $J = 306.4$ Hz), 128.11 (m), 126.88, 126.57, 110.81 (t, $J = 246.8$ Hz), 63.20, 37.67, 24.50, 13.82, 13.62.

$^{19}$F NMR (376 MHz, Chloroform-\textit{d}) $\delta$ -40.03, -92.51.

HRMS (ESI) Calcd for C$_{22}$H$_{21}$F$_5$O$_2$S [M+Na]$^+$ 467.1075, found 467.1077.

ethyl (\textit{E})-2,2-difluoro-4-(4'-propyl-[1,1'-biphenyl]-4-yl)-4-((trifluoromethyl)thio)but-3-enoate (5k) 42.6 mg, yield: 48%. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.83 – 7.70 (m, 3H), 7.48 – 7.40 (m, 1H), 7.21 – 7.16 (m, 1H), 7.12 (d, $J = 2.1$ Hz, 1H), 6.54 (t, $J = 10.6$ Hz, 1H), 3.93 (s, 3H), 3.71 (q, $J = 7.1$ Hz, 2H), 0.98 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-\textit{d}) $\delta$ 162.32 (t, $J = 32.7$ Hz), 159.04, 140.20 (m), 135.179, 130.12, 129.43, 129.32, 128.58 (q, $J = 309.2$ Hz, it coincides with peak 130.12 ppm), 128.24 (m), 127.75, 126.81, 126.44, 119.75, 110.95 (t, $J = 246.2$ Hz), 105.72, 63.05, 55.36, 13.38.

$^{19}$F NMR (376 MHz, Chloroform-\textit{d}) $\delta$ -40.05, -91.70.

HRMS (ESI) Calcd for C$_{18}$H$_{15}$F$_5$O$_3$S [M+Na]$^+$ 429.0554, found 429.0554.

ethyl (\textit{E})-2,2-difluoro-4-(6-methoxynaphthalen-2-yl)-4-((trifluoromethyl)thio)but-3-enoate (5l) 33.5 mg, yield: 41%. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.87 – 7.70 (m, 3H), 7.47 – 7.40 (m, 1H), 7.21 – 7.16 (m, 1H), 7.12 (d, $J = 2.1$ Hz, 1H), 6.54 (t, $J = 10.6$ Hz, 1H), 3.93 (s, 3H), 3.71 (q, $J = 7.1$ Hz, 2H), 0.98 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-\textit{d}) $\delta$ 162.32 (t, $J = 32.7$ Hz), 159.04, 140.20 (m), 135.179, 130.12, 129.43, 129.32, 128.58 (q, $J = 309.2$ Hz, it coincides with peak 130.12 ppm), 128.24 (m), 127.75, 126.81, 126.44, 119.75, 110.95 (t, $J = 246.2$ Hz), 105.72, 63.05, 55.36, 13.38.

$^{19}$F NMR (376 MHz, Chloroform-\textit{d}) $\delta$ -40.05, -91.70.

HRMS (ESI) Calcd for C$_{18}$H$_{15}$F$_5$O$_3$S [M+Na]$^+$ 429.0554, found 429.0554.
ethyl (E)-4-(3,4-dimethoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5m)

46.5 mg, yield: 60 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.03 – 6.98 (m, 1H), 6.92 (d, $J = 1.8$ Hz, 1H), 6.84 (d, $J = 8.3$ Hz, 1H), 6.42 (t, $J = 10.8$ Hz, 1H), 3.98 – 3.93 (m, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 1.16 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 162.35 (t, $J = 32.9$ Hz), 150.67, 148.18, 139.78 (m), 128.55 (q, $J = 308.4$ Hz), 127.15 (m), 126.61 (m), 122.77, 112.26, 110.93 (t, $J = 246$ Hz), 110.38, 63.11, 55.87, 13.59.

$^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -40.26, -91.78.

HRMS (ESI) Calcd for C$_{15}$H$_{15}$F$_5$O$_4$S [M+Na]$^+$ 409.0503, found 409.0505.

ethyl (E)-4-(2,3-dihydrobenzofuran-5-yl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5n)

58.3 mg, yield: 79 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.22 (s, 1H), 7.16 (d, $J = 8.3$ Hz, 1H), 6.75 (d, $J = 8.3$ Hz, 1H), 6.39 (t, $J = 10.8$ Hz, 1H), 4.61 (t, $J = 8.8$ Hz, 2H), 3.96 (q, $J = 7.1$ Hz, 2H), 3.22 (t, $J = 8.7$ Hz, 2H), 1.18 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 162.43 (t, $J = 33.0$ Hz), 161.88, 140.27 (m), 130.09, 128.56 (q, $J = 305.2$ Hz, it coincides with peak 130.09 ppm), 127.27, 127.06, 126.67 (m), 126.33, 110.95 (t, $J = 245.7$ Hz), 108.49, 71.75, 63.07, 29.21, 13.60.

$^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -40.26, -91.90.

HRMS (ESI) Calcd for C$_{15}$H$_{13}$F$_5$O$_3$S [M+Na]$^+$ 391.0398, found 391.0399.

ethyl (E)-2,2-difluoro-4-(3-fluoro-4-methoxyphenyl)-4-((trifluoromethyl)thio)but-3-enoate (5o)

40.0 mg, yield: 53 %. Light yellow liquid.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.19 – 7.09 (m, 2H), 6.93 (t, $J = 8.6$ Hz, 1H), 6.46 (t, $J = 11.1$ Hz, 1H), 4.05 (q, $J = 7.1$ Hz, 2H), 3.92 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 162.31 (t, $J = 33.1$ Hz), 151.52 (d, $J = 246.5$ Hz), 149.30 (d, $J = 10.5$ Hz), 138.63 (m), 128.46 (q, $J = 308.7$ Hz), 128.30 (m), 126.83 (d, $J = 6.8$ Hz), 126.08 (d, $J = 2.7$ Hz), 116.99 (d, $J = 19.9$ Hz), 112.49, 110.68 (t, $J = 247.1$ Hz), 63.32, 56.14, 13.65.

$^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -40.10, -93.15, -134.35.
ethyl (E)-2,2-difluoro-4-(9-phenyl-9H-carbazol-3-yl)-4-((trifluoromethyl)thio)but-3-enolate (5p)

50.2 mg, yield: 51%. Light yellow liquid

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.15 (d, $J$ = 7.9 Hz, 2H), 7.59 (d, $J$ = 7.6 Hz, 2H), 7.53 (d, $J$ = 7.2 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.39 – 7.29 (m, 3H), 6.52 (t, $J$ = 10.8 Hz, 1H), 3.82 (q, $J$ = 7.1 Hz, 2H), 1.02 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 162.50 (t, $J$ = 32.9 Hz), 141.60, 141.47, 141.03 (m), 137.02, 129.98, 128.66 (q, $J$ = 309.5 Hz), 127.91, 127.33, 127.03, 126.84 (m), 126.67, 125.74, 123.00, 122.89, 121.86, 120.63, 120.52, 111.12 (t, $J$ = 246.2 Hz), 110.11, 109.49, 63.03, 13.47.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.10, -91.66.

HRMS (ESI) Calcd for C$_{14}$H$_{12}$F$_{6}$O$_{3}$S [M+Na]$^+$ 397.0304, found 397.0303.

ethyl (E)-2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)selenyl)but-3-enolate (6a)

44.5 mg, yield: 55%. Light yellow liquid

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.32 (d, $J$ = 8.7 Hz, 2H), 6.87 (d, $J$ = 8.8 Hz, 2H), 6.49 (t, $J$ = 10.8 Hz, 1H), 3.97 (q, $J$ = 7.1 Hz, 2H), 3.82 (s, 3H), 1.18 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 162.55 (t, $J$ = 33.1 Hz), 160.85, 139.41 (m), 130.86, 127.90 (m), 127.79, 122.30 (q, $J$ = 331.6 Hz), 113.56, 110.99 (t, $J$ = 247.1 Hz), 63.09, 55.28, 13.62.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -34.12, -92.41.

HRMS (ESI) Calcd for C$_{14}$H$_{13}$F$_{5}$O$_{3}$Se [M+Na]$^+$ 514.0871, found 514.0872.

ethyl (E)-4-(2,3-dihydrobenzofuran-5-yl)-2,2-difluoro-4-((trifluoromethyl)selenyl)but-3-enolate (6b)

50.9 mg, yield: 61%. Light yellow liquid

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.21 (s, 1H), 7.15 (d, $J$ = 8.3 Hz, 1H), 6.74 (d, $J$ = 8.3 Hz, 1H), 6.45 (t, $J$ = 10.7 Hz, 1H), 4.61 (t, $J$ = 8.7 Hz, 2H), 3.98 (q, $J$ = 7.1 Hz, 2H), 3.21 (t, $J$ = 8.7 Hz, 2H), 1.19 (t, $J$ = 7.1 Hz, 3H).
$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 162.59 (t, $J = 33.0$ Hz), 161.64, 139.84 (m), 129.95, 127.66, 127.43 (m), 127.21, 126.19, 122.34 (q, $J = 333.8$ Hz), 111.03 (t, $J = 246.8$ Hz), 108.95, 71.73, 63.05, 29.23, 13.62.  

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -34.19, -92.22.  

HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{13}\text{F}_{5}\text{O}_{3}\text{Se}$ [M+Na]$^+$ 438.9842, found 438.9841.

![](image)

(3,3,4,5,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hexyl)(trifluoromethyl)sulfane (11)

41.5 mg, yield: 46 %. Light yellow liquid

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.25 (d, $J = 8.7$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 4.74 (dd, $J = 9.0, 5.2$ Hz, 1H), 3.81 (s, 3H), 2.98 – 2.73 (m, 2H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 159.80, 129.83, 129.78 (q, $J = 308.2$ Hz) 129.19, 128.41, 114.52, 55.27, 41.61 (m), 37.73 (t, $J = 20.8$ Hz).

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -40.55, -81.10, -111.33 – -115.17 (m), -124.47, -125.96.

HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{10}\text{F}_{12}\text{OS}$ [M+Na]$^+$ 477.0153, no found.  

GC-MS (EI) Calcd for $\text{C}_{14}\text{H}_{10}\text{F}_{12}\text{OS}$ [M]$^+$ 454, found 454.
6. NMR Spectroscopic Data

The examples of identifying all the peaks in $^1$H NMR, $^{13}$C NMR, and $^{19}$F NMR.
2 (dd, $J=1328.9$ Hz, 266.0 Hz)
$t, J = 247.2 \text{ Hz}$

$12$ ($t, J = 32.9 \text{ Hz}$)

$8$ ($m [tq]$)

$9$ ($q, J = 310.8 \text{ Hz}$)

$10$ ($m [tq]$)
ethyl 2,2-difluoro-4-phenyl-4-((trifluoromethyl)thio)butanoate (2a)
ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-(((trifluoromethyl)thio)butanoate (2b)
ethyl 2,2-difluoro-4-(2-methoxyphenyl)-4-(((trifluoromethyl)thio)butanoate (2c)
ethyl 2,2-difluoro-4-(4-(methylthio)phenyl)-4-((trifluoromethyl)thio)butanoate (2d)
ethyl 2,2-difluoro-4-(p-tolyl)-4-((trifluoromethyl)thio)butanoate (2e)
ethyl 2,2-difluoro-4-(m-tolyl)-4-((trifluoromethyl)thio)butanoate (2f)
ethyl 4-(4-(tert-butyl)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2h)
ethyl 4-((1,1'-biphenyl)-4-yl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2i)
ethyl 4-(4-chlorophenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2j)
ethyl 2,2-difluoro-4-(4-(trifluoromethyl)phenyl)-4-((trifluoromethyl)thio)butanoate (2k)
ethyl 4-(3,4-dimethoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2l)
ethyl 4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2,2-difluoro-4-((trifluoromethyl)thio)butanoate (2m)
ethyl 2,2-difluoro-4-(4-methoxyphenyl)-3-methyl-4-((trifluormethyl)thio)butanoate (2o)

d.r. = 13:1
ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)selanyl)butanoate (3a)
ethyl 4-((1,1'-biphenyl)-4-yl)-2,2-difluoro-4-((trifluoromethyl)selanyl)butanoate (3b)
ethyl 2,2-difluoro-4-(p-tolyl)-4-((trifluoromethyl)selanyl)butanoate (3c)
ethyl 2,2-difluoro-4-(pyridin-2-yl)-4-((trifluoromethyl)selanyl)butanoate (3d)
ethyl \((E)\)-2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)thio)but-3-enoate (5a)
ethyl (E)-2,2-difluoro-4-(4-(pentyloxy)phenyl)-4-( trifluoromethyl)thio)but-3-enoate (5b)
ethyl (E)-4-(4-(benzyloxy)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5c)
ethyl (E)-4-(4-acetoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5d)
ethyl (E)-2,2-difluoro-4-(p-tolyl)-4-((trifluoromethyl)thio)but-3-enoate (5e)
ethyl \((E)\)-4-(4-((tert-butyl)phenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5f)
ethyl \((E)\)-2,2-difluoro-4-(4-propylphenyl)-4-((trifluoromethyl)thio)but-3-enoate (5g)
ethyl \((E)\)-4-(4-chlorophenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5h)
ethyl (E)-2,2-difluoro-4-(4-(methylthio)phenyl)-4-((trifluoromethyl)thio)but-3-enoate (5i)
ethyl (E)-4-((1',1'-biphenyl)-4-yl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5j)
ethyl (E)-2,2-difluoro-4-(4'-propyl-[1,1'-biphenyl]-4-yl)-4-((trifluoromethyl)thio)but-3-enoate (5k)
ethyl (E)-2,2-difluoro-4-(6-methoxynaphthalen-2-yl)-4-((trifluoromethyl)thio)but-3-enoate (5l)
ethyl (\textit{E})-4-(3,4-dimethoxyphenyl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5m)
ethyl \((E)\)-4-(2,3-dihydrobenzofuran-5-yl)-2,2-difluoro-4-((trifluoromethyl)thio)but-3-enoate (5n)
ethyl (E)-2,2-difluoro-4-(3-fluoro-4-methoxyphenyl)-4-((trifluoromethyl)thio)but-3-enoate (5o)
ethyl (E)-2,2-difluoro-4-(9-phenyl-9H-carbazol-3-yl)-4-((trifluoromethyl)thio)but-3-enoate (5p)
ethyl (E)-2,2-difluoro-4-(4-methoxyphenyl)-4-((trifluoromethyl)selanyl)but-3-enoate (6a)
ethyl (E)-4-(2,3-dihydrobenzofuran-5-yl)-2,2-difluoro-4-((trifluoromethyl)selanyl)but-3-enoate (6b)
(3,3,4,5,6,6,6-nonafluoro-1-(4-methoxyphenyl)hexyl)(trifluoromethyl)sulfane (11)
7. The Noe of the Compound 5a (600 MHz)
Reference

8. GC-MS Spectrum of Trapping the Radical Intermediate.