

# Supporting Information

## Catalyst-Free *gem*-Chlorosulfurization of Difluoromethyl-Substituted Diazo Compound with Disulfide and PhICl<sub>2</sub>

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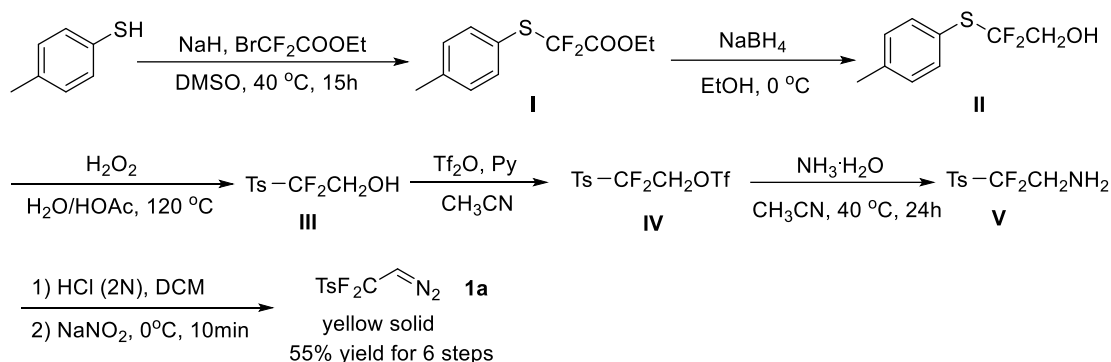
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## 1. General information

Nuclear magnetic resonance spectra ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR) were recorded with Bruker Avance III 400 (400 MHz,  $^1\text{H}$  NMR at 400 MHz,  $^{13}\text{C}$  NMR at 100 MHz,  $^{19}\text{F}$  NMR at 376MHz) or Bruker Ascend TM 500 (500 MHz,  $^1\text{H}$  NMR at 500 MHz,  $^{13}\text{C}$  NMR at 125 MHz,  $^{19}\text{F}$  NMR at 470MHz) respectively, using  $\text{CDCl}_3$  as reference standard ( $\delta$  7.26 ppm) for  $^1\text{H}$  NMR and ( $\delta$  77.0 ppm) for  $^{13}\text{C}$  NMR. HRMS (ion trap) were recorded using ESI (SHIMADZU LCMS-IT-TOF). Melting points were uncorrected (METTLER TOLEDO MP50). Precoated silica gel plates GF-254 were used for analytical thin-layer chromatography. Column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification. Starting materials (diaz compounds **1**, disulfides **2**) were prepared according to literature procedures <sup>1-3</sup>.

## 2. General experimental procedure

### Procedure for the synthesis of *p*-toluenesulfonyl difluorodiazethane **1a**:



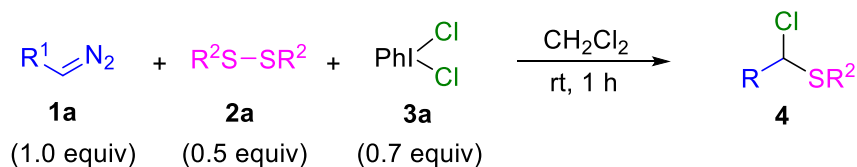
*p*-Methylthiophenol (1.24 g, 10 mmol, 1.0 equiv.) and DMSO (50 mL) were added to a 100 mL round-bottom flask and stirred at 40 °C. Then NaH (60 wt.%, 0.6 g, 15 mmol, 1.5 equiv.) was slowly added to the above mixture and stirred for 1h. Ethyl bromodifluoroacetate (1.6 mL, 12 mmol, 1.2 equiv.) was added to the reaction mixture and stirred over night at 40 °C. Then the colorless oil product **I** (2.1 g, 85% yield) was obtained by flash column chromatography.

The product **I** (2.46 g, 10 mmol, 1.0 equiv.) was dissolved in ethanol (50 mL) and stirred in an ice bath for 10 min, and then NaBH<sub>4</sub> (0.76 g, 20 mmol, 2.0 equiv.) was added to the above mixture and stirred for additional 30 min. After that, water (100 mL) was added for quenching and extraction was performed with ethyl acetate (60 mL  $\times$  3), and the crude product **II** was obtained by concentrating the solvent. Without further purification, the crude product **II** and hydrogen peroxide

(30% concentration, 10 mL, 9.0 equiv.) were transferred to a 100 mL round-bottom flask, and then a mixed solution of water-glacial acetic acid (volume ratio 1:1, 20 mL) was added to the above mixture and stirred for 2 h at 120 °C. After being cooled to room temperature, the mixture was purified by flash column chromatography to give the colorless oil pure product **III** (2.1 g, 90% yield).

The product **III** (2.36 g, 10 mmol, 1.0 equiv.) was dissolved in acetonitrile (20 mL) at 0 °C, and then pyridine (2 mL, 25 mmol, 2.5 equiv.) and trifluoromethanesulfonic anhydride (2.3 mL, 15 mmol, 1.5 equiv.) were added to the above mixture successively and stirred for 4 h at room temperature to give the crude product **IV** in the reaction solution. Without further purification, ammonium hydroxide solution (25% concentration, 8 mL, 3.5 equiv.) was added to the above reaction solution and stirred for 24 h at 40 °C, then the crude product **IV** gradually transformed into product **V**. Without further purification, the mixture of crude product **V** was stirred for 30 min in an ice-water bath, then 2N hydrochloric acid was added to adjust the pH to weak acidity. And then dichloromethane (20 mL) and sodium nitrite (1.04 g, 15 mmol, 1.5 equiv.) were added, and continued stirred in an ice water bath for 10 min. After purification by column chromatography, the yellow solid product **1a** was obtained (1.76 g, 72% yield). In summary, the preparation process of *p*-toluenesulfonyl difluorodiazooethane (TsCF<sub>2</sub>CHN<sub>2</sub>) is easier to obtain than that of phenylsulfone difluorodiazooethane (PhSO<sub>2</sub>CF<sub>2</sub>CHN<sub>2</sub>)<sup>4</sup>, whose total reaction is yield of about 55%.

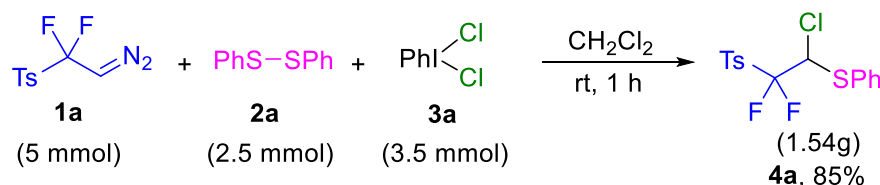
### General procedure for the *gem*-chlorosulfurization of diazo compound with disulfide and PhICl<sub>2</sub>.



A mixture of disulfide **2** (0.1 mmol, 0.5 equiv.), PhICl<sub>2</sub> **3a** (0.14 mmol, 0.7 equiv.) was stirred in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at room temperature, then a solution of diazo compound **1** (0.2 mmol, 1.0 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added slowly to the above mixture. The progress of the reaction was monitored by TLC. After the reaction was complete, the solvent was evaporated under reduced pressure. The

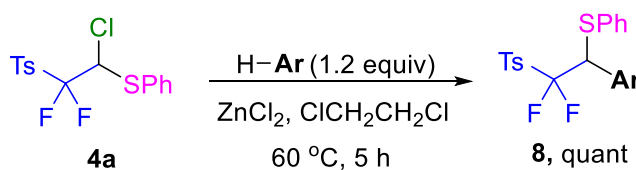
residue was purified by flash column chromatography (petroleum ether/ethyl acetate 20:1 to 10:1) to give the pure product **4**.

#### Procedure for the gram-scale synthesis of **4a**:



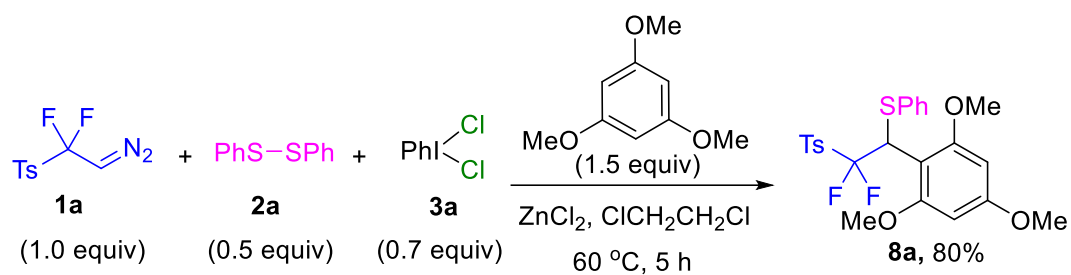
A mixture of diphenyl disulfide **2a** (0.55 g, 2.5 mmol, 0.5 equiv.),  $\text{PhICl}_2$  **3a** (0.96 g, 3.5 mmol, 0.7 equiv.) was stirred in  $\text{CH}_2\text{Cl}_2$  (20 mL) at room temperature, then a solution of  $\text{TsCF}_2\text{CHN}_2$  **1a** (1.23 g, 5 mmol, 1.0 equiv.) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added slowly to the above mixture. The progress of the reaction was monitored by TLC. After the reaction was complete, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 20:1 to 10:1) to give 1.54g of the pure product **4a** (85% yield).

#### Procedure for the derivatives **8**:



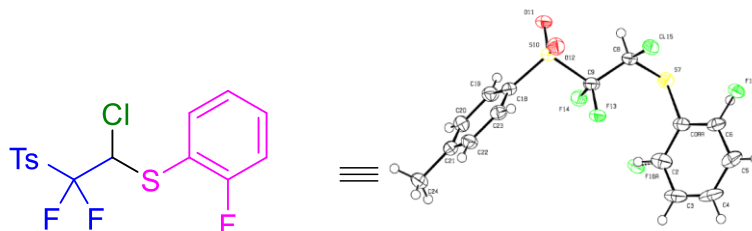
A mixture of three-component product **4a** (73 mg, 0.2 mmol, 1.0 equiv.), electron-rich aromatic hydrocarbons (0.24 mmol, 1.2 equiv.),  $\text{ZnCl}_2$  (41 mg, 0.3 mmol, 1.5 equiv.) was stirred in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (3 mL) at 60 °C. After 5 h, the reaction was complete by TLC monitoring and then the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1) to give the pure derivatives **8** in quantitative yields.

### Procedure for the derivative **8a** by multi-component operation:



A mixture of diphenyl disulfide **2a** (22 mg, 0.1 mmol, 0.5 equiv.),  $\text{PhICl}_2$  **3a** (39 mg, 0.14 mmol, 0.7 equiv.), 1,3,5-trimethoxybenzene (50 mg, 0.3 mmol, 1.5 equiv.),  $\text{TsCF}_2\text{CHN}_2$  **1a** (50 mg, 0.2 mmol, 1.0 equiv.) and  $\text{ZnCl}_2$  (41 mg, 0.3 mmol, 1.5 equiv.) was stirred in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (3 mL) at  $60\text{ }^\circ\text{C}$  for 5 h. The progress of the reaction was monitored by TLC. After the reaction was complete, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1) to give 79 mg the product **8a** in 80% yield.

### 3. X-Ray structure of product 4c (CCDC 1996733):



Bond precision: C-C = 0.0057 Å

Wavelength=1.54184

Cell: a=8.7553 (2) b=6.4721 (3) c=28.2921 (10)  
alpha=90 beta=97.357 (3) gamma=90  
Temperature: 100 K

|                | Calculated          | Reported            |
|----------------|---------------------|---------------------|
| Volume         | 1589.98 (10)        | 1589.98 (10)        |
| Space group    | P 21/c              | P 1 21/c 1          |
| Hall group     | -P 2ybc             | -P 2ybc             |
| Moiety formula | C15 H12 Cl F3 O2 S2 | C15 H12 Cl F3 O2 S2 |
| Sum formula    | C15 H12 Cl F3 O2 S2 | C15 H12 Cl F3 O2 S2 |
| Mr             | 380.82              | 380.82              |
| Dx, g cm-3     | 1.591               | 1.591               |
| Z              | 4                   | 4                   |
| Mu (mm-1)      | 4.941               | 4.941               |
| F000           | 776.0               | 776.0               |
| F000'          | 782.46              |                     |
| h,k,lmax       | 11,8,35             | 10,7,35             |
| Nref           | 3314                | 3122                |
| Tmin,Tmax      | 0.580,0.781         | 0.409,1.000         |
| Tmin'          | 0.355               |                     |

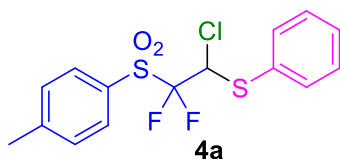
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AbsCorr = MULTI-SCAN
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Data completeness= 0.942                      Theta(max)= 75.864

R(reflections) = 0.0565 ( 2406)      wR2(reflections) = 0.1449 ( 3122)

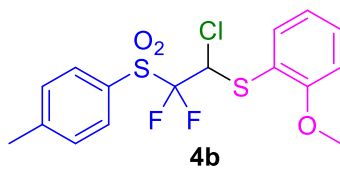
S = 1.052                      Npar= 213

#### 4. Characterization data of new compounds:



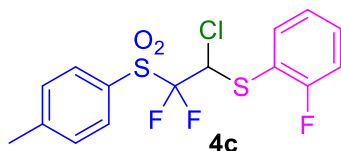
##### (1-Chloro-2,2-difluoro-2-tosylethyl)(phenyl)sulfane **4a**:

Yield: 90%, 65 mg. Colorless oil.  $R_f$  = 0.3 (PE:EtOAc = 10:1).  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J$  = 8.3 Hz, 2H), 7.73 – 7.64 (m, 2H), 7.46 – 7.37 (m, 5H), 5.78 (dd,  $J$  = 14.1, 10.6 Hz, 1H), 2.49 (s, 3H) ppm;  **$^{13}\text{C NMR}$**  (100 Hz,  $\text{CDCl}_3$ ):  $\delta$  147.31, 134.93, 130.79, 130.22, 130.13, 130.05, 129.66, 129.48, 119.47 (dd,  $J_{\text{CF}}$  = 296.1, 293.8 Hz), 64.90 (dd,  $J_{\text{CF}}$  = 25.3, 22.9 Hz), 21.92 ppm;  **$^{19}\text{F NMR}$**  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -97.92 (dd,  $J$  = 230.0, 10.6 Hz), -102.80 (dd,  $J$  = 230.0, 14.1 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{F}_2\text{S}_2\text{ClNa}$  384.9906  $[\text{M}+\text{Na}]^+$ ; found 384.9903.



##### (1-Chloro-2,2-difluoro-2-tosylethyl)(2-methoxyphenyl)sulfane **4b**:

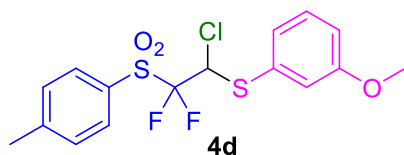
Yield: 85%, 67 mg. Colorless solid, m.p. = 80-82 °C.  $R_f$  = 0.3 (PE:EtOAc = 5:1).  **$^1\text{H NMR}$**  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J$  = 7.7 Hz, 2H), 7.53 (d,  $J$  = 7.8 Hz, 1H), 7.41 (d,  $J$  = 7.3 Hz, 3H), 6.96 (t,  $J$  = 6.9 Hz, 2H), 6.07 (t,  $J$  = 12.2 Hz, 1H), 3.94 (s, 3H), 2.48 (s, 3H) ppm;  **$^{13}\text{C NMR}$**  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.38, 147.19, 135.85, 131.71, 130.87, 130.29, 130.06, 121.18, 119.75 (dd,  $J_{\text{CF}}$  = 292.5, 290.0 Hz), 117.63, 111.38, 62.12 (dd,  $J_{\text{CF}}$  = 25.0, 22.5 Hz), 55.98, 21.91 ppm;  **$^{19}\text{F NMR}$**  (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -101.33 (d,  $J$  = 231.7 Hz), -102.39 (d,  $J$  = 231.6 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{16}\text{H}_{15}\text{O}_3\text{F}_2\text{S}_2\text{ClNa}$  415.0011  $[\text{M}+\text{Na}]^+$ ; found 415.0012.



##### (1-Chloro-2,2-difluoro-2-tosylethyl)(2-fluorophenyl)sulfane **4c**:

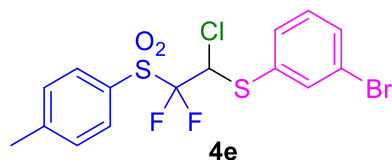
Yield: 88%, 67 mg. Colorless solid, m.p. = 72-74 °C.  $R_f$  = 0.4 (PE:EtOAc = 10:1).  **$^1\text{H NMR}$**  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J$  = 7.9 Hz, 2H), 7.65 (t,  $J$  = 7.4 Hz, 1H), 7.49 – 7.38 (m, 3H), 7.22 – 7.13

(m, 2H), 5.81 (t,  $J = 11.9$  Hz, 1H), 2.48 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.90 (d,  $J_{\text{CF}} = 248.8$  Hz), 147.40, 137.21, 132.66 (d,  $J_{\text{CF}} = 8.8$  Hz), 130.82, 130.10 (d,  $J_{\text{CF}} = 12.5$  Hz), 124.98 (d,  $J_{\text{CF}} = 3.8$  Hz), 119.41 (dd,  $J_{\text{CF}} = 296.2, 292.8$  Hz), 116.56 (d,  $J_{\text{CF}} = 17.5$  Hz), 116.47 (d,  $J_{\text{CF}} = 22.5$  Hz), 62.70 (dd,  $J_{\text{CF}} = 27.4, 22.3$  Hz), 21.90 ppm;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -101.26 (d,  $J = 231.3$  Hz), -102.26 (d,  $J = 231.6$  Hz), -105.46 (s) ppm; HRMS ( $m/z$ ) (ESI): calc. for  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{F}_3\text{S}_2\text{ClNa}$  402.9812  $[\text{M}+\text{Na}]^+$ ; found 402.9813.



**(1-Chloro-2,2-difluoro-2-tosylethyl)(3-methoxyphenyl)sulfane 4d:**

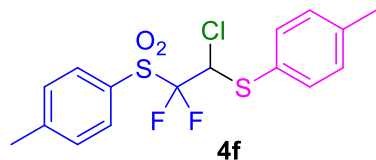
Yield: 91%, 72 mg. Colorless solid, m.p.= 86-88 °C.  $R_f = 0.3$  (PE:EtOAc = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 (d,  $J = 7.8$  Hz, 2H), 7.44 (d,  $J = 7.9$  Hz, 2H), 7.33 (t,  $J = 7.9$  Hz, 1H), 7.27 (d,  $J = 9.2$  Hz, 1H), 7.23 (s, 1H), 6.99 (d,  $J = 8.0$  Hz, 1H), 5.82 (dd,  $J = 14.2, 10.5$  Hz, 1H), 3.85 (s, 3H), 2.51 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.98, 147.30, 130.83, 130.79, 130.25, 130.12, 126.68, 119.53, 119.44 (dd,  $J_{\text{CF}} = 295.0, 292.5$  Hz), 116.07, 65.07 (dd,  $J_{\text{CF}} = 25.2, 23.0$  Hz), 55.47, 21.91 ppm;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -97.79 (d,  $J = 230.0$  Hz), -102.98 (d,  $J = 229.9$  Hz) ppm; HRMS ( $m/z$ ) (ESI): calc. for  $\text{C}_{16}\text{H}_{15}\text{O}_3\text{F}_2\text{S}_2\text{ClNa}$  415.0011  $[\text{M}+\text{Na}]^+$ ; found 415.0005.



**(3-Bromophenyl)(1-chloro-2,2-difluoro-2-tosylethyl)sulfane 4e:**

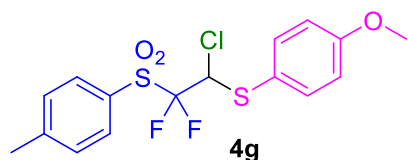
Yield: 85%, 75 mg. Colorless solid, m.p.= 95-97 °C.  $R_f = 0.3$  (PE:EtOAc = 10:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 (d,  $J = 7.8$  Hz, 2H), 7.80 (s, 1H), 7.62 (d,  $J = 7.7$  Hz, 1H), 7.57 (d,  $J = 8.0$  Hz, 1H), 7.43 (d,  $J = 7.9$  Hz, 2H), 7.29 (d,  $J = 7.9$  Hz, 1H), 5.76 (dd,  $J = 13.8, 10.5$  Hz, 1H), 2.49 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.44, 137.30, 133.47, 133.21, 131.42, 130.81, 130.73, 130.18, 130.03, 122.87, 119.32 (dd,  $J_{\text{CF}} = 296.4, 294.1$  Hz), 64.18 (dd,  $J_{\text{CF}} = 25.4, 23.2$  Hz), 21.94 ppm;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -97.73 (d,  $J = 230.0$  Hz), -103.02 (d,  $J = 230.2$  Hz) ppm; HRMS ( $m/z$ ) (ESI): calc. for  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{F}_2\text{S}_2\text{ClBrNa}$  462.9011, 464.8988  $[\text{M}+\text{Na}]^+$ ; found 462.9009, 464.8974.





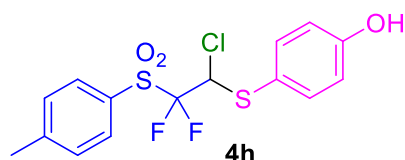
**(1-Chloro-2,2-difluoro-2-tosylethyl)(p-tolyl)sulfane 4f:**

Yield: 86%, 65 mg. Colorless oil.  $R_f = 0.2$  (PE:EtOAc = 10:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J = 8.0$  Hz, 2H), 7.56 (d,  $J = 7.8$  Hz, 2H), 7.41 (d,  $J = 8.0$  Hz, 2H), 7.21 (d,  $J = 7.8$  Hz, 2H), 5.72 (dd,  $J = 13.8, 10.9$  Hz, 1H), 2.49 (s, 3H), 2.38 (s, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.25, 140.56, 135.24, 130.78, 130.30, 130.23, 130.10, 125.98, 119.52 (dd,  $J_{CF} = 296.2, 293.6$  Hz), 65.06 (dd,  $J_{CF} = 25.4, 22.6$  Hz), 21.90, 21.34 ppm;  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -97.94 (d,  $J = 229.8$  Hz), -102.72 (d,  $J = 229.8$  Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{F}_2\text{S}_2\text{ClNa}$  399.0062  $[\text{M}+\text{Na}]^+$ ; found 399.0064.



**(1-Chloro-2,2-difluoro-2-tosylethyl)(4-methoxyphenyl)sulfane 4g:**

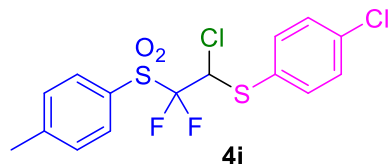
Yield: 89%, 70 mg. Colorless solid, m.p. = 105-107 °C.  $R_f = 0.2$  (PE:EtOAc = 5:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 (d,  $J = 7.9$  Hz, 2H), 7.61 (d,  $J = 8.2$  Hz, 2H), 7.41 (d,  $J = 7.9$  Hz, 2H), 6.91 (d,  $J = 8.2$  Hz, 2H), 5.65 (dd,  $J = 13.2, 11.5$  Hz, 1H), 3.82 (s, 3H), 2.48 (s, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.43, 147.24, 137.56, 130.77, 130.10, 119.63, 119.56 (dd,  $J_{CF} = 295.0, 292.5$  Hz), 114.92, 64.97 (dd,  $J_{CF} = 25.4, 22.3$  Hz), 55.42, 21.90 ppm;  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -97.81 (d,  $J = 229.7$  Hz), -102.67 (d,  $J = 229.6$  Hz); **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{16}\text{H}_{15}\text{O}_3\text{F}_2\text{S}_2\text{ClNa}$  415.0011  $[\text{M}+\text{Na}]^+$ ; found 415.0009.



**4-((1-Chloro-2,2-difluoro-2-tosylethyl)thio)phenol 4h:**

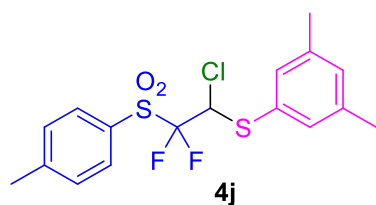
Yield: 85%, 64 mg. Colorless oil.  $R_f = 0.2$  (PE:EtOAc = 5:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 (d,  $J = 7.9$  Hz, 2H), 7.54 (d,  $J = 8.1$  Hz, 2H), 7.42 (d,  $J = 7.9$  Hz, 2H), 6.85 (d,  $J = 8.1$  Hz, 2H), 5.89

(s, 1H), 5.68 – 5.59 (m, 1H), 2.48 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.88, 147.36, 137.77, 130.76, 130.15, 130.11, 119.59, 119.58 (dd,  $J_{\text{CF}}$  = 293.8, 291.2 Hz), 116.50, 64.96 (dd,  $J_{\text{CF}}$  = 25.5, 22.3 Hz), 21.91 ppm;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -97.91 (d,  $J$  = 229.7 Hz), -102.45 (d,  $J$  = 229.7 Hz) ppm; HRMS ( $m/z$ ) (ESI): calc. for  $\text{C}_{15}\text{H}_{13}\text{O}_3\text{F}_2\text{S}_2\text{ClNa}$  400.9855  $[\text{M}+\text{Na}]^+$ ; found 400.9853.



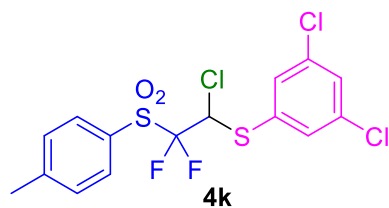
**(1-Chloro-2,2-difluoro-2-tosylethyl)(4-chlorophenyl)sulfane 4i:**

Yield: 80%, 63 mg. Colorless solid, m.p.= 106-108 °C.  $R_f$  = 0.2 (PE:EtOAc = 10:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 (d,  $J$  = 7.9 Hz, 2H), 7.62 (d,  $J$  = 8.0 Hz, 2H), 7.42 (d,  $J$  = 7.9 Hz, 2H), 7.37 (d,  $J$  = 8.0 Hz, 2H), 5.73 (dd,  $J$  = 14.2, 10.2 Hz, 1H), 2.48 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.40, 136.79, 136.62, 130.77, 130.16, 130.08, 129.66, 127.63, 119.38 (dd,  $J_{\text{CF}}$  = 296.3, 294.3 Hz), 64.16 (dd,  $J_{\text{CF}}$  = 25.3, 22.9 Hz), 21.91 ppm;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -97.13 (d,  $J$  = 229.7 Hz), -103.22 (d,  $J$  = 229.7 Hz) ppm; HRMS ( $m/z$ ) (ESI): calc. for  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{F}_2\text{S}_2\text{Cl}_2\text{Na}$  418.9516  $[\text{M}+\text{Na}]^+$ ; found 418.9522.



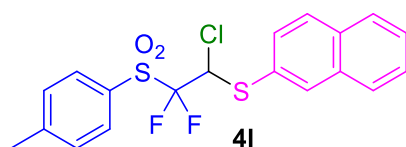
**(1-Chloro-2,2-difluoro-2-tosylethyl)(3,5-dimethylphenyl)sulfane 4j:**

Yield: 88%, 68 mg. Colorless oil.  $R_f$  = 0.3 (PE:EtOAc = 10:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 (d,  $J$  = 7.8 Hz, 2H), 7.42 (d,  $J$  = 7.8 Hz, 2H), 7.26 (s, 2H), 7.05 (s, 1H), 5.86 – 5.73 (m, 1H), 2.49 (s, 3H), 2.33 (s, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.24, 139.24, 132.01, 131.73, 130.81, 130.33, 130.10, 129.37, 119.51 (dd,  $J_{\text{CF}}$  = 295.9, 293.5 Hz), 65.41 (dd,  $J_{\text{CF}}$  = 25.4, 22.9 Hz), 21.91, 21.18 ppm;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -98.48 (d,  $J$  = 230.3 Hz), -102.57 (d,  $J$  = 230.1 Hz) ppm; HRMS ( $m/z$ ) (ESI): calc. for  $\text{C}_{17}\text{H}_{17}\text{O}_2\text{F}_2\text{S}_2\text{ClNa}$  413.0219  $[\text{M}+\text{Na}]^+$ ; found 413.0221.



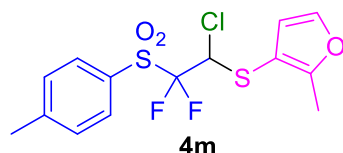
**(1-Chloro-2,2-difluoro-2-tosylethyl)(3,5-dichlorophenyl)sulfane 4k:**

Yield: 78%, 67 mg. Colorless solid, m.p.= 122-124 °C.  $R_f$  = 0.3 (PE:EtOAc = 10:1).  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J$  = 7.9 Hz, 2H), 7.55 (s, 2H), 7.44 (s, 1H), 7.43 (s, 2H), 5.77 (dd,  $J$  = 14.1, 10.0 Hz, 1H), 2.50 (s, 3H) ppm;  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.55, 135.52, 132.64, 132.31, 130.82, 130.32, 130.21, 129.90, 119.20 (dd,  $J_{CF}$  = 295.0, 292.5 Hz), 63.57 (dd,  $J_{CF}$  = 25.0, 23.8 Hz), 21.94 ppm;  **$^{19}\text{F}$  NMR** (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -97.48 (d,  $J$  = 230.4 Hz), -103.22 (d,  $J$  = 230.3 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{15}\text{H}_{11}\text{O}_2\text{F}_2\text{S}_2\text{Cl}_3\text{Na}$  452.9126  $[\text{M}+\text{Na}]^+$ ; found 452.9120.



**(1-Chloro-2,2-difluoro-2-tosylethyl)(naphthalen-2-yl)sulfane 4l:**

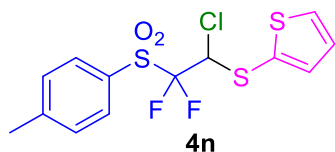
Yield: 85%, 70 mg. Colorless solid, m.p.= 68-70 °C.  $R_f$  = 0.4 (PE:EtOAc = 10:1).  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (s, 1H), 7.88 (dd,  $J$  = 13.4, 6.1 Hz, 5H), 7.71 (d,  $J$  = 8.5 Hz, 1H), 7.55 (p,  $J$  = 7.7 Hz, 2H), 7.42 (d,  $J$  = 7.9 Hz, 2H), 5.87 (dd,  $J$  = 13.9, 10.7 Hz, 1H), 2.49 (s, 3H) ppm;  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.30, 135.14, 133.57, 133.47, 130.82, 130.75, 130.24, 130.13, 129.28, 128.11, 127.81, 127.53, 126.91, 126.77, 119.52 (dd,  $J_{CF}$  = 296.0, 293.9 Hz), 64.85 (dd,  $J_{CF}$  = 25.4, 22.9 Hz), 21.91 ppm;  **$^{19}\text{F}$  NMR** (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -97.91 (d,  $J$  = 229.9 Hz), -102.76 (d,  $J$  = 229.9 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{19}\text{H}_{15}\text{O}_2\text{F}_2\text{S}_2\text{ClNa}$  435.0062  $[\text{M}+\text{Na}]^+$ ; found 435.0065.



**3-((1-chloro-2,2-difluoro-2-tosylethyl)thio)-2-methylfuran 4m:**

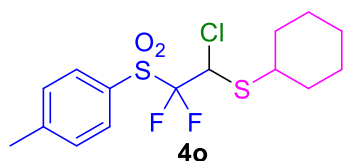
Yield: 82%, 60 mg. Colorless oil.  $R_f$  = 0.3 (PE:EtOAc = 5:1).  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 (d,  $J$  = 7.9 Hz, 2H), 7.42 (d,  $J$  = 8.0 Hz, 2H), 7.32 (s, 1H), 6.49 (s, 1H), 5.53 (t,  $J$  = 12.3 Hz, 1H), 2.49 (s, 3H), 2.41 (s, 3H) ppm;  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.00, 147.27, 141.14, 130.77, 130.30, 130.11, 119.45 (dd,  $J_{CF}$  = 296.7, 292.9 Hz), 115.60, 105.07, 63.42 (dd,  $J_{CF}$  = 26.3, 22.2 Hz),

21.90, 12.12 ppm; **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>): δ -100.00 (d, *J* = 229.8 Hz), -102.16 (d, *J* = 229.9 Hz) ppm; **HRMS** (*m/z*) (ESI): calc. for C<sub>14</sub>H<sub>13</sub>O<sub>3</sub>F<sub>2</sub>S<sub>2</sub>ClNa 388.9855 [M+Na]<sup>+</sup>; found 388.9857.



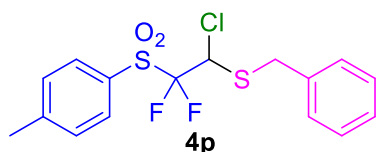
**2-((1-Chloro-2,2-difluoro-2-tosylethyl)thio)thiophene 4n:**

Yield: 81%, 59 mg. Light yellow oil. *R<sub>f</sub>* = 0.2 (PE:EtOAc = 10:1). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 5.3 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 3H), 7.08 (dd, *J* = 6.2, 2.4 Hz, 1H), 5.57 (t, *J* = 12.0 Hz, 1H), 2.49 (s, 3H) ppm; **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>): δ 147.37, 138.55, 133.29, 130.83, 130.15, 130.06, 127.98, 125.87, 119.35 (dd, *J<sub>CF</sub>* = 297.0, 293.3 Hz), 64.31 (dd, *J<sub>CF</sub>* = 26.0, 22.3 Hz), 21.93 ppm; **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>): δ -99.81 (d, *J* = 230.7 Hz), -101.60 (d, *J* = 230.8 Hz) ppm; **HRMS** (*m/z*) (ESI): calc. for C<sub>13</sub>H<sub>11</sub>O<sub>2</sub>F<sub>2</sub>S<sub>3</sub>ClNa 390.9470 [M+Na]<sup>+</sup>; found 390.9462.



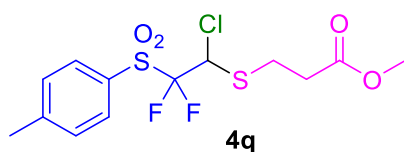
**(1-Chloro-2,2-difluoro-2-tosylethyl)(cyclohexyl)sulfane 4o:**

Yield: 78%, 57 mg. Colorless oil. *R<sub>f</sub>* = 0.4 (PE:EtOAc = 10:1). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.76 (dd, *J* = 15.8, 9.3 Hz, 1H), 3.16-3.12 (m, 1H), 2.49 (s, 3H), 2.09-2.04 (m, 2H), 1.82-1.79 (m, 2H), 1.54-1.44 (m, 2H), 1.42-1.32 (m, 2H), 1.30-1.26 (m, 2H) ppm; **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 147.15, 130.74, 130.38, 130.04, 119.62 (dd, *J<sub>CF</sub>* = 294.4, 293.8 Hz), 61.42 (dd, *J<sub>CF</sub>* = 24.8, 23.7 Hz), 45.53, 33.14, 32.98, 25.47, 21.88 ppm; **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>): δ -96.35 (d, *J* = 228.7 Hz), -104.42 (d, *J* = 228.7 Hz) ppm; **HRMS** (*m/z*) (ESI): calc. for C<sub>15</sub>H<sub>19</sub>O<sub>2</sub>F<sub>2</sub>S<sub>2</sub>ClNa 391.0375 [M+Na]<sup>+</sup>; found 391.0378.



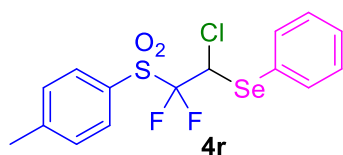
**Benzyl(1-chloro-2,2-difluoro-2-tosylethyl)sulfane 4p:**

Yield: 75%, 57 mg. Colorless oil.  $R_f$  = 0.3 (PE:EtOAc = 10:1).  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.84 (d,  $J$  = 8.0 Hz, 2H), 7.40 (d,  $J$  = 8.1 Hz, 2H), 7.39 – 7.29 (m, 5H), 5.47 (dd,  $J$  = 15.7, 9.3 Hz, 1H), 4.07 (s, 2H), 2.48 (s, 3H) ppm;  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.25, 134.79, 130.79, 130.15, 130.08, 129.43, 128.89, 128.03, 119.70 (dd,  $J_{\text{CF}}$  = 295.0, 293.9 Hz), 61.00 (t,  $J_{\text{CF}}$  = 25.0 Hz), 35.65, 21.90 ppm;  **$^{19}\text{F}$  NMR** (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -95.94 (d,  $J$  = 230.4 Hz), -103.88 (d,  $J$  = 230.4 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{F}_2\text{S}_2\text{ClNa}$  399.0062  $[\text{M}+\text{Na}]^+$ ; found 399.0063.



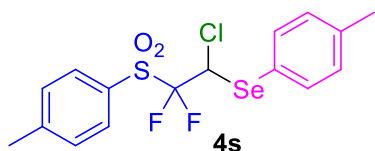
**Methyl 3-((1-chloro-2,2-difluoro-2-tosylethyl)thio)propanoate 4q:**

Yield: 73%, 54 mg. Colorless oil.  $R_f$  = 0.2 (PE:EtOAc = 10:1).  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (d,  $J$  = 8.0 Hz, 2H), 7.41 (d,  $J$  = 8.0 Hz, 2H), 5.70 (dd,  $J$  = 15.1, 9.9 Hz, 1H), 3.72 (s, 3H), 3.20 – 3.06 (m, 2H), 2.74 (t,  $J$  = 7.2 Hz, 2H), 2.48 (s, 3H) ppm;  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.64, 147.32, 130.78, 130.10, 130.10, 119.53 (dd,  $J_{\text{CF}}$  = 295.7, 293.9 Hz), 61.29 (dd,  $J_{\text{CF}}$  = 25.1, 24.0 Hz), 52.07, 33.91, 26.36, 21.90 ppm;  **$^{19}\text{F}$  NMR** (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -96.54 (d,  $J$  = 229.8 Hz), -103.81 (d,  $J$  = 229.8 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{13}\text{H}_{15}\text{O}_4\text{F}_2\text{S}_2\text{ClNa}$  394.9961  $[\text{M}+\text{Na}]^+$ ; found 394.9955.



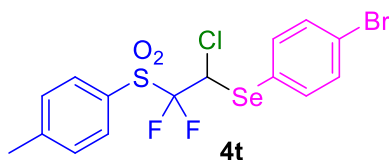
**(1-Chloro-2,2-difluoro-2-tosylethyl)(phenyl)selane 4r:**

Yield: 88%, 72 mg. Light yellow oil.  $R_f$  = 0.4 (PE:EtOAc = 10:1).  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (d,  $J$  = 7.8 Hz, 2H), 7.74 (d,  $J$  = 7.6 Hz, 2H), 7.43 (dd,  $J$  = 16.7, 8.0 Hz, 3H), 7.37 (t,  $J$  = 7.3 Hz, 2H), 5.71 (dd,  $J$  = 15.8, 10.4 Hz, 1H), 2.48 (s, 3H) ppm;  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.21, 136.60, 130.75, 130.32, 130.09, 129.93, 129.49, 126.13, 120.04 (dd,  $J_{\text{CF}}$  = 295.8, 289.1 Hz), 52.59 (dd,  $J_{\text{CF}}$  = 29.9, 23.1 Hz), 21.91 ppm;  **$^{19}\text{F}$  NMR** (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -96.05 (d,  $J$  = 229.1 Hz), -101.45 (d,  $J$  = 229.2 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{F}_2\text{SClSeNa}$  432.9348  $[\text{M}+\text{Na}]^+$ ; found 432.9345.



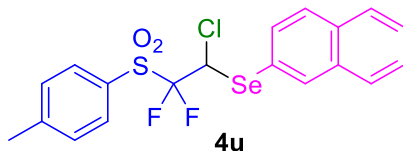
**(1-Chloro-2,2-difluoro-2-tosylethyl)(p-tolyl)selane 4s:**

Yield: 85%, 72 mg. Light yellow solid, m.p.= 71-73 °C.  $R_f$  = 0.3 (PE:EtOAc = 10:1).  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (d,  $J$  = 7.9 Hz, 2H), 7.62 (d,  $J$  = 7.5 Hz, 2H), 7.41 (d,  $J$  = 7.9 Hz, 2H), 7.17 (d,  $J$  = 7.6 Hz, 2H), 5.66 (dd,  $J$  = 16.0, 10.3 Hz, 1H), 2.48 (s, 3H), 2.38 (s, 3H) ppm;  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.16, 140.33, 136.78, 130.75, 130.38, 130.28, 130.07, 122.52, 120.09 (dd,  $J_{\text{CF}}$  = 295.7, 289.0 Hz), 52.55 (dd,  $J_{\text{CF}}$  = 30.0, 23.0 Hz), 21.90, 21.36 ppm;  **$^{19}\text{F}$  NMR** (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -96.00 (d,  $J$  = 229.0 Hz), -101.54 (d,  $J$  = 229.0 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{F}_2\text{SClSeNa}$  446.9504  $[\text{M}+\text{Na}]^+$ ; found 446.9509.



**(4-Bromophenyl)(1-chloro-2,2-difluoro-2-tosylethyl)selane 4t:**

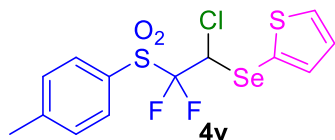
Yield: 81%, 79 mg. Light yellow solid, m.p.= 111-113 °C.  $R_f$  = 0.2 (PE:EtOAc = 10:1).  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 (d,  $J$  = 8.0 Hz, 2H), 7.60 (d,  $J$  = 8.1 Hz, 2H), 7.49 (d,  $J$  = 8.1 Hz, 2H), 7.41 (d,  $J$  = 8.0 Hz, 2H), 5.68 (dd,  $J$  = 15.2, 10.8 Hz, 1H), 2.48 (s, 3H) ppm;  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.31, 138.37, 132.66, 130.74, 130.16, 130.13, 125.04, 124.51, 119.91 (dd,  $J_{\text{CF}}$  = 295.9, 289.5 Hz), 52.01 (dd,  $J_{\text{CF}}$  = 29.8, 23.0 Hz), 21.92 ppm;  **$^{19}\text{F}$  NMR** (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -96.61 (d,  $J$  = 229.0 Hz), -100.82 (d,  $J$  = 229.0 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{F}_2\text{SClSeBrNa}$  510.8450, 512.8434  $[\text{M}+\text{Na}]^+$ ; found 510.8457, 512.8409.



**(1-Chloro-2,2-difluoro-2-tosylethyl)(naphthalen-2-yl)selane 4u:**

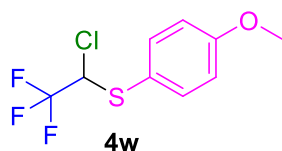
Yield: 84%, 77 mg. Yellow solid, m.p.= 88-90 °C.  $R_f$  = 0.4 (PE:EtOAc = 10:1).  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (s, 1H), 7.85 (dd,  $J$  = 21.9, 8.6 Hz, 5H), 7.78 (d,  $J$  = 8.5 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.40 (d,  $J$  = 8.0 Hz, 2H), 5.80 (dd,  $J$  = 15.8, 10.3 Hz, 1H), 2.48 (s, 3H) ppm;  **$^{13}\text{C}$  NMR** (125 MHz,

CDCl<sub>3</sub>):  $\delta$  147.22, 136.82, 133.64, 133.49, 132.55, 130.77, 130.31, 130.10, 129.08, 128.07, 127.84, 127.46, 126.82, 123.34, 120.10 (dd,  $J_{CF}$  = 295.8, 289.1 Hz), 52.58 (dd,  $J_{CF}$  = 30.0, 23.2 Hz), 21.90 ppm; **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>)  $\delta$  -95.99 (d,  $J$  = 229.1 Hz), -101.46 (d,  $J$  = 229.0 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for C<sub>19</sub>H<sub>15</sub>O<sub>2</sub>F<sub>2</sub>SClSeNa 482.9504 [M+Na]<sup>+</sup>; found 482.9495.



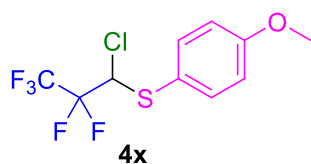
**2-((1-Chloro-2,2-difluoro-2-tosylethyl)selanyl)thiophene 4v:**

Yield: 82%, 68 mg. Light yellow oil.  $R_f$  = 0.2 (PE:EtOAc = 10:1). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.85 (d,  $J$  = 7.9 Hz, 2H), 7.67 (d,  $J$  = 1.3 Hz, 1H), 7.40 (d,  $J$  = 7.9 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.25 (s, 1H), 5.58 (dd,  $J$  = 15.9, 10.1 Hz, 1H), 2.48 (s, 3H) ppm; **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  147.23, 133.94, 133.81, 130.75, 130.27, 130.10, 126.82, 119.92 (dd,  $J_{CF}$  = 295, 287.5 Hz), 118.70, 51.97 (dd,  $J_{CF}$  = 30.1, 23.0 Hz), 21.91 ppm; **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>):  $\delta$  -96.26 (d,  $J$  = 229.3 Hz), -101.81 (d,  $J$  = 229.2 Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for C<sub>13</sub>H<sub>11</sub>O<sub>2</sub>F<sub>2</sub>S<sub>2</sub>ClSeNa 438.8911 [M+Na]<sup>+</sup>; found 438.8920.



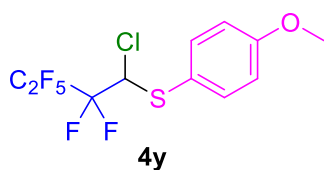
**(1-Chloro-2,2,2-trifluoroethyl)(4-methoxyphenyl)sulfane 4w:**

Yield: 70%, 36 mg. Colorless oil.  $R_f$  = 0.5 (PE:EtOAc = 10:1). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.56 (d,  $J$  = 8.4 Hz, 2H), 6.92 (d,  $J$  = 8.4 Hz, 2H), 5.15 (q,  $J$  = 6.5 Hz, 1H), 3.83 (s, 3H) ppm; **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  160.43, 136.51, 121.83 (q,  $J_{CF}$  = 277.5 Hz), 118.39, 113.93, 64.64 (q,  $J_{CF}$  = 34.8 Hz), 54.39 ppm; **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>):  $\delta$  -71.89 (s) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for C<sub>9</sub>H<sub>8</sub>OF<sub>3</sub>SClNa 278.9829 [M+Na]<sup>+</sup>; found 278.9836.



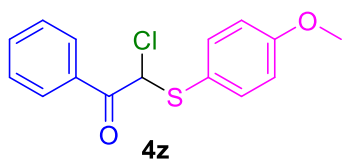
**(1-Chloro-2,2,3,3,3-pentafluoropropyl)(4-methoxyphenyl)sulfane 4x:**

Yield: 75%, 46 mg. Colorless oil.  $R_f$  = 0.4 (PE:EtOAc = 10:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.56 (d,  $J$  = 8.3 Hz, 2H), 6.92 (d,  $J$  = 8.3 Hz, 2H), 5.21 (t,  $J$  = 12.0 Hz, 1H), 3.84 (s, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.49, 137.45, 119.66, 115.03, 65.28 (dd,  $J_{\text{CF}}$  = 27.4, 25.5 Hz), 55.43 ppm (Carbon with directly attached fluorine appear as broad multiplets and are not reported);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.55 (s, 3F), -114.73 (d,  $J$  = 268.6 Hz, 1F), -115.64 (d,  $J$  = 268.6 Hz, 1F) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{10}\text{H}_8\text{OF}_5\text{SClNa}$  328.9797  $[\text{M}+\text{Na}]^+$ ; found 328.9790.



**(1-Chloro-2,2,3,3,4,4,4-heptafluorobutyl)(4-methoxyphenyl)sulfane 4y:**

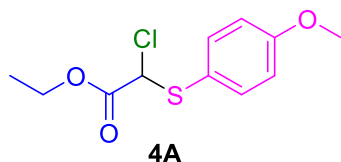
Yield: 71%, 50 mg. Colorless oil.  $R_f$  = 0.4 (PE:EtOAc = 10:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.57 (d,  $J$  = 8.4 Hz, 2H), 6.93 (d,  $J$  = 8.4 Hz, 2H), 5.28 (t,  $J$  = 12.1 Hz, 1H), 3.84 (s, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.50, 136.48, 118.62, 114.01, 64.47 (t,  $J_{\text{CF}}$  = 26.6 Hz), 54.37 ppm (Carbon with directly attached fluorine appear as broad multiplets and are not reported);  $^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -80.77 (t,  $J$  = 10.9 Hz, 3F), -109.59 – -114.34 (m, 2F), -122.39 – -123.55 (m, 2F) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{11}\text{H}_8\text{OF}_7\text{SClNa}$  378.9765  $[\text{M}+\text{Na}]^+$ ; found 378.9771.



**2-Chloro-2-((4-methoxyphenyl)thio)-1-phenylethan-1-one 4z:**

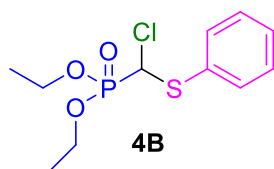
Yield: 86%, 50 mg. Yellow solid, m.p. = 95-97 °C.  $R_f$  = 0.2 (PE:EtOAc = 10:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02 (d,  $J$  = 7.8 Hz, 2H), 7.62 (t,  $J$  = 7.3 Hz, 1H), 7.50 (t,  $J$  = 7.5 Hz, 2H), 7.46 (d,  $J$  = 8.0 Hz, 2H), 6.89 (d,  $J$  = 8.0 Hz, 2H), 6.33 (s, 1H), 3.82 (s, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.05, 161.26, 136.96, 134.04, 133.33, 129.29, 128.86, 120.37, 114.94, 69.33, 55.40 ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{SCl}$  291.0252  $[\text{M}-\text{H}]^-$ ; found 291.0247.





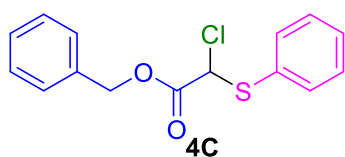
**Ethyl 2-chloro-2-((4-methoxyphenyl)thio)acetate 4A:**

Yield: 82%, 43 mg. Yellow solid, m.p.= 80-82 °C.  $R_f$ = 0.3 (PE:EtOAc = 5:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.52 (d,  $J$  = 7.7 Hz, 2H), 6.90 (d,  $J$  = 7.7 Hz, 2H), 5.41 (s, 1H), 4.22 (q,  $J$  = 7.1 Hz, 2H), 3.81 (s, 3H), 1.28 (t,  $J$  = 7.1 Hz, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.04, 161.25, 137.06, 120.36, 114.81, 65.32, 62.81, 55.40, 13.99 ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{11}\text{H}_{13}\text{O}_3\text{SClNa}$  283.0166  $[\text{M}+\text{Na}]^+$ ; found 283.0164.



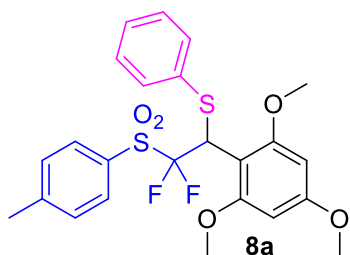
**Diethyl (chloro(phenylthio)methyl)phosphonate 4B:**

Yield: 85%, 50 mg. Yellow oil.  $R_f$ = 0.2 (PE:EtOAc = 2:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 (dd,  $J$  = 6.5, 3.0 Hz, 2H), 7.42 – 7.32 (m, 3H), 5.25 (d,  $J$  = 12.6 Hz, 1H), 4.35 – 4.23 (m, 4H), 1.42 – 1.33 (m, 6H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  132.75, 132.27 (d,  $J_{\text{CP}}$  = 9.7 Hz), 129.38, 129.05, 64.71, 64.66, 61.06 (d,  $J_{\text{CP}}$  = 162.6 Hz), 16.46, 16.41 ppm;  $^{31}\text{P NMR}$  (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.98 – 13.62 (m, 1P) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{11}\text{H}_{16}\text{O}_3\text{PSClNa}$  317.0139  $[\text{M}+\text{Na}]^+$ ; found 317.0147.



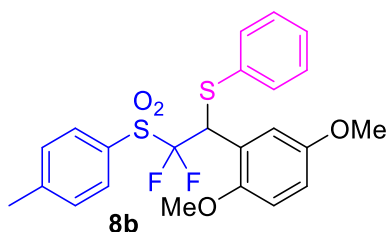
**Benzyl 2-chloro-2-(phenylthio)acetate 4C:**

Yield: 80%, 46 mg. Yellow oil.  $R_f$ = 0.2 (PE:EtOAc = 5:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.56 – 7.50 (m, 2H), 7.42 – 7.36 (m, 6H), 7.36 – 7.33 (m, 2H), 5.58 (s, 1H), 5.21 (d,  $J$  = 8.5 Hz, 2H) ppm;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.77, 134.66, 134.35, 130.11, 129.70, 129.32, 128.71, 128.69, 128.49, 68.38, 64.62 ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{SCl}$  291.0252  $[\text{M}-\text{H}]^-$ ; found 291.0256.



**(2,2-Difluoro-2-tosyl-1-(2,4,6-trimethoxyphenyl)ethyl)(phenyl)sulfane 8a:**

Quantitative yield, 98 mg. Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (d,  $J = 8.2$  Hz, 2H), 7.55 – 7.50 (m, 2H), 7.33 – 7.27 (m, 5H), 6.16 (d,  $J = 2.2$  Hz, 1H), 6.12 (d,  $J = 2.2$  Hz, 1H), 5.81 (dd,  $J = 20.7, 13.0$  Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.82 (s, 3H), 2.45 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.87, 160.47, 158.05, 146.00, 136.52, 132.07, 130.97, 130.61, 129.60, 128.86, 127.41, 122.69 (dd,  $J_{\text{CF}} = 295.0, 287.0$  Hz), 104.55, 91.43, 90.80, 56.28, 55.83, 55.30, 45.09 (dd,  $J_{\text{CF}} = 25.0, 21.0$  Hz), 21.76 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -92.85 (d,  $J = 226.2$  Hz), -100.16 (d,  $J = 226.2$  Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{24}\text{H}_{24}\text{O}_5\text{F}_2\text{S}_2\text{Na}$  517.0931  $[\text{M}+\text{Na}]^+$ ; found 517.0928.



**(1-(2,5-Dimethoxyphenyl)-2,2-difluoro-2-tosylethyl)(phenyl)sulfane 8b:**

Quantitative yield, 93 mg. Colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72 (d,  $J = 8.2$  Hz, 2H), 7.46 (dd,  $J = 6.4, 3.0$  Hz, 2H), 7.31 (s, 1H), 7.30 – 7.26 (m, 4H), 6.87 – 6.79 (m, 3H), 5.82 (s, 1H), 3.83 (s, 3H), 3.67 (s, 3H), 2.45 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.34, 150.87, 146.38, 133.61, 130.76, 130.56, 129.72, 128.88, 128.29, 123.02 (dd,  $J_{\text{CF}} = 293.0, 287.0$  Hz), 122.91, 122.88, 115.39, 115.12, 112.33, 56.70, 55.54, 45.32 (dd,  $J_{\text{CF}} = 25.0, 21.0$  Hz), 21.76 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -95.29 (d,  $J = 233.2$  Hz), -102.76 (d,  $J = 233.0$  Hz) ppm; **HRMS** ( $m/z$ ) (ESI): calc. for  $\text{C}_{23}\text{H}_{22}\text{O}_4\text{F}_2\text{S}_2\text{Na}$  487.0825  $[\text{M}+\text{Na}]^+$ ; found 487.0832.

**5. References:**

1. J. Li, C. Ma, D. Xing, W. Hu, *Org. Lett.* **2019**, *21*, 2101.
2. J. Li, D. Xing, W. Hu, *Mol. Divers.* DOI: 10.1007/s11030-020-10100-7.
3. Q. Chen, Y. Huang, X. Wang, J. Wu, G. Yu, *Org. Biomol. Chem.* **2018**, *16*, 171.
4. J.-L. Zeng, Z. Chen, F.-G. Zhang, J.-A. Ma, *Org. Lett.* **2018**, *20*, 4562.

## 6. NMR spectra

