Supporting Information

Catalyst-Free gem-Chlorosulfurization of Difluoromethyl-Substituted Diazo Compound with Disulfide and PhICl₂

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1. General information

Nuclear magnetic resonance spectra (\( ^1\)H NMR, \( ^{13}\)C NMR and \( ^{19}\)F NMR) were recorded with Bruker Avance III 400 (400 MHz, \( ^1\)H NMR at 400 MHz, \( ^{13}\)C NMR at 100 MHz, \( ^{19}\)F NMR at 376MHz) or Bruker Ascend TM 500 (500 MHz, \( ^1\) H NMR at 500 MHz, \( ^{13}\)C NMR at 125 MHz, \( ^{19}\)F NMR at 470MHz) respectively, using CDCl\(_3\) as reference standard (δ 7.26 ppm) for \( ^1\)H NMR and (δ 77.0 ppm) for \( ^{13}\)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 (diazo compounds 1, disulfides 2) were prepared according to literature procedures \(^1\)-\(^3\).

2. General experimental procedure

Procedure for the synthesis of \( p\)-toluenesulfonyl difluorodiazoethane 1a:

\[
\begin{align*}
\text{p-Methylthiophenol (1.24 g, 10 mmol, 1.0 equiv.)} & \xrightarrow{\text{NaH, BrCF}_2\text{COOEt}} \xrightarrow{\text{DMSO, 40 ℃, 15h}} \text{I} \\
\text{Ts-\( \text{CF}_2\text{CH}_2\text{OH} \)} & \xrightarrow{\text{NaBH}_4, \text{EtOH, 0 ℃}} \xrightarrow{\text{EtOH/HOAc, 120 ℃}} \text{III} \\
\text{H}_2\text{O}_2 & \xrightarrow{\text{Ts-\( \text{CF}_2\text{CH}_2\text{OTf} \)}Py, \text{CH}_3\text{CN}} \xrightarrow{\text{NH}_3\text{H}_2\text{O}, \text{CH}_3\text{CN, 40 ℃, 24h}} \text{IV} \\
1) \text{HCl (2N), DCM} & \xrightarrow{\text{yellow solid}} \xrightarrow{\text{55% yield for 6 steps}} 1a \\
2) \text{NaNO}_2, 0 ℃, 10min & \xrightarrow{\text{N}_2} \text{TsF}_2\text{C}_\equiv\text{N}_2 \\
\end{align*}
\]

\( p\)-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 ℃. 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 ℃. 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\(_4\) (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 × 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 difluorodiazoethane (TsCF₂CHN₂) is easier to obtain than that of phenylsulfone difluorodiazoethane (PhSO₂CF₂CHN₂)⁴, whose total reaction is yield of about 55%.

General procedure for the gem-chlorosulfurization of diazo compound with disulfide and PhICl₂.

A mixture of disulfide 2 (0.1 mmol, 0.5 equiv.), PhICl₂ 3a (0.14 mmol, 0.7 equiv.) was stirred in CH₂Cl₂ (2 mL) at room temperature, then a solution of diazo compound 1 (0.2 mmol, 1.0 equiv.) in CH₂Cl₂ (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 disulfide 2a (0.55 g, 2.5 mmol, 0.5 equiv.), PhICl 3a (0.96 g, 3.5 mmol, 0.7 equiv.) was stirred in CH$_2$Cl$_2$ (20 mL) at room temperature, then a solution of TsCF$_2$CHN$_2$ 1a (1.23 g, 5 mmol, 1.0 equiv.) in CH$_2$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 1.54 g 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.), ZnCl$_2$ (41 mg, 0.3 mmol, 1.5 equiv.) was stirred in CICH$_2$CH$_2$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:

\[
\text{Ts-}N_2 + \text{PhS-SPh} + \text{PhICl}_2 \rightarrow \text{MeO-}O\text{Me} + \text{MeO-}O\text{Me} \rightarrow \text{SPh-}O\text{Me-}O\text{Me} \quad 8a, 80\%
\]

A mixture of diphenyl disulfide 2a (22 mg, 0.1 mmol, 0.5 equiv.), PhICl 3a (39 mg, 0.14 mmol, 0.7 equiv.), 1,3,5-trimethoxybenzene (50 mg, 0.3 mmol, 1.5 equiv.), TsCF\textsubscript{2}CHN\textsubscript{2} 1a (50 mg, 0.2 mmol, 1.0 equiv.) and ZnCl\textsubscript{2} (41 mg, 0.3 mmol, 1.5 equiv.) was stirred in ClCH\textsubscript{2}CH\textsubscript{2}Cl (3 mL) at 60 °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 of the product 8a in 80% yield.
3. X-Ray structure of product 4c (CCDC 1996733):

![Chemical structure diagram]

**Bond precision:** C-C ~ 0.0057 Å  
**Wavelength:** 1.54184 Å

**Cell:**
- a = 8.7553(2) Å  
- b = 6.4721(3) Å  
- c = 28.2921(10) Å  
- alpha = 90°  
- beta = 97.357(3)°  
- gamma = 90°

**Temperature:** 100 K

**Calculated**  
**Reported**
- Volume: 1589.98(10) Å³  
- Space group: P 21/c  
- Hall group: -P 2ybc  
- Molecular formula: C15 H12 Cl F3 O2 S2  
- Sum formula: C15 H12 Cl F3 O2 S2  
- Mr: 380.82  
- Z: 4  
- Dx, g cm⁻³: 1.591  
- μ (mm⁻¹): 4.941  
- F000: 776.0  
- F000': 782.46  
- h,k,l max: 11,8,35  
- Nref: 3314  
- Tmin, Tmax: 0.580, 0.781  
- Tmin’: 0.355

**Correction method:** # Reported T Limits: Tmin-0.409 Tmax-1.000  
**AbsCorr = MULTI-SCAN**

**Data completeness:** 0.942  
**θ(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, 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, CDCl\(_3\)): \(\delta\) 147.31, 134.93, 130.79, 130.22, 130.13, 130.05, 129.66, 129.48, 119.47 (dd, \(J_{CF} = 296.1, 293.8\) Hz), 64.90 (dd, \(J_{CF} = 25.3, 22.9\) Hz), 21.92 ppm; \(^{19}\text{F NMR}\) (376 MHz, 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 C\(_{15}\)H\(_{13}\)O\(_2\)F\(_2\)S\(_2\)ClNa 384.9906 [M+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, 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, CDCl\(_3\)): \(\delta\) 159.38, 147.19, 135.85, 131.71, 130.87, 130.29, 130.06, 121.18, 119.55 (dd, \(J_{CF} = 292.5, 290.0\) Hz), 117.63, 111.38, 62.12 (dd, \(J_{CF} = 25.0, 22.5\) Hz), 55.98, 21.91 ppm; \(^{19}\text{F NMR}\) (470 MHz, CDCl\(_3\)): \(\delta\) -101.33 (dd, \(J = 231.7\) Hz), -102.39 (dd, \(J = 231.6\) Hz) ppm; \(^{HRMS}\) (m/z) (ESI): calc. for C\(_{16}\)H\(_{15}\)O\(_3\)F\(_2\)S\(_2\)ClNa 415.0011 [M+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, 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; $^{13}$C NMR (125 MHz, CDCl$_3$): δ 162.90 (d, J$_{CF}$ = 248.8 Hz), 147.40, 137.21, 132.66 (d, J$_{CF}$ = 8.8 Hz), 130.82, 130.10 (d, J$_{CF}$ = 12.5 Hz), 124.98 (d, J$_{CF}$ = 3.8 Hz), 119.41 (dd, J$_{CF}$ = 296.2, 292.8 Hz), 116.56 (d, J$_{CF}$ = 17.5 Hz), 116.47 (d, J$_{CF}$ = 22.5 Hz), 62.70 (dd, J$_{CF}$ = 27.4, 22.3 Hz), 21.90 ppm; $^{19}$F NMR (470 MHz, CDCl$_3$): δ -101.26 (d, J = 231.3 Hz), -102.26 (d, J = 231.6 Hz), -105.46 (s) ppm; HRMS (m/z) (ESI): calc. for C$_{15}$H$_{12}$O$_2$F$_2$S$_2$ClNa 402.9812 [M+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). $^1$H NMR (500 MHz, CDCl$_3$): δ 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; $^{13}$C NMR (125 MHz, CDCl$_3$): δ 159.98, 147.30, 130.83, 130.79, 130.25, 130.12, 126.68, 119.53, 119.44 (dd, J$_{CF}$ = 295.0, 292.5 Hz), 116.07, 65.07 (dd, J$_{CF}$ = 25.2, 23.0 Hz), 55.47, 21.91 ppm; $^{19}$F NMR (470 MHz, CDCl$_3$): δ -97.79 (d, J = 230.0 Hz), -102.98 (d, J = 229.9 Hz) ppm; HRMS (m/z) (ESI): calc. for C$_{16}$H$_{15}$O$_3$F$_2$S$_2$ClNa 415.0011 [M+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). $^1$H NMR (500 MHz, CDCl$_3$): δ 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; $^{13}$C NMR (125 MHz, CDCl$_3$): δ 147.44, 137.30, 133.47, 133.21, 131.42, 130.81, 130.73, 130.18, 130.03, 122.87, 119.32 (dd, J$_{CF}$ = 296.4, 294.1 Hz), 64.18 (dd, J$_{CF}$ = 25.4, 23.2 Hz), 21.94 ppm; $^{19}$F NMR (470 MHz, CDCl$_3$): δ -97.73 (d, J = 230.0 Hz), -103.02 (d, J = 230.2 Hz) ppm; HRMS (m/z) (ESI): calc. for C$_{16}$H$_{12}$O$_2$F$_2$S$_2$ClBrNa 462.9011, 464.8988 [M+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). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{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; \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \delta 147.25, 140.56, 135.24, 130.78, 130.10, 129.98, 119.52 (dd, J\textsubscript{CF} = 296.2, 293.6 Hz), 65.06 (dd, J\textsubscript{CF} = 25.4, 22.6 Hz), 21.90, 21.34 ppm; \textsuperscript{19}F NMR (470 MHz, CDCl\textsubscript{3}): \delta -97.94 (d, J = 229.8 Hz), -102.72 (d, J = 229.8 Hz) ppm; HRMS (m/z) (ESI): calc. for C\textsubscript{16}H\textsubscript{15}O\textsubscript{2}F\textsubscript{2}S\textsubscript{2}ClNa 399.0062 [M+Na]\textsuperscript{+}; found 399.0064.

(1-Chloro-2,2-difluoro-2-tosylethyl)(4-methoxyphenyl)sulfane 4g:
Yield: 89%, 70 mg. Colorless solid, m.p. = 105-107 \degree C. R_{f} = 0.2 (PE:EtOAc = 5:1). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{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; \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \delta 161.43, 147.24, 137.56, 130.78, 130.10, 119.63, 119.56 (dd, J\textsubscript{CF} = 295.0, 292.5 Hz), 114.92, 64.97 (dd, J\textsubscript{CF} = 25.4, 22.3 Hz), 55.42, 21.90 ppm; \textsuperscript{19}F NMR (470 MHz, CDCl\textsubscript{3}): \delta -97.81 (d, J = 229.7 Hz), -102.67 (d, J = 229.6 Hz); HRMS (m/z) (ESI): calc. for C\textsubscript{16}H\textsubscript{15}O\textsubscript{2}F\textsubscript{2}S\textsubscript{2}ClNa 415.0009 [M+Na]\textsuperscript{+}; 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). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{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
(1-Chloro-2,2-difluoro-2-tosylethyl)(4-chlorophenyl)sulfane 4i:

Yield: 80%, 63 mg. Colorless solid, m.p. = 106-108 °C. R<sub>f</sub> = 0.2 (PE:EtOAc = 10:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.87 (d, J = 7.9 Hz, 2H), 7.62 (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; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 147.40, 136.79, 136.62, 130.77, 130.16, 130.08, 129.66, 127.63, 119.38 (dd, J<sub>CF</sub> = 296.3, 294.3 Hz), 64.16 (dd, J<sub>CF</sub> = 25.3, 22.9 Hz), 21.91 ppm; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ -97.13 (d, J = 229.7 Hz), -103.22 (d, J = 229.7 Hz) ppm; HRMS (m/z) (ESI): calc. for C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>F<sub>2</sub>S<sub>2</sub>ClNa 400.9855 [M+Na]<sup>+</sup>; found 400.9853.

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

Yield: 88%, 68 mg. Colorless oil. R<sub>f</sub> = 0.3 (PE:EtOAc = 10:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 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; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 147.24, 139.24, 132.01, 131.73, 130.81, 130.33, 130.10, 129.37, 119.51 (dd, J<sub>CF</sub> = 295.9, 293.5 Hz), 65.41 (dd, J<sub>CF</sub> = 25.4, 22.9 Hz), 21.91, 21.18 ppm; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ -98.48 (d, J = 230.3 Hz), -102.57 (d, J = 230.1 Hz) ppm; HRMS (m/z) (ESI): calc. for C<sub>17</sub>H<sub>17</sub>O<sub>2</sub>F<sub>2</sub>S<sub>2</sub>ClNa 413.0219 [M+Na]<sup>+</sup>; 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. Rf = 0.3 (PE:EtOAc = 10:1). $^1$H NMR (500 MHz, CDCl$_3$): δ 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; $^{13}$C NMR (125 MHz, CDCl$_3$): δ 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; $^{19}$F NMR (470 MHz, CDCl$_3$): δ -97.48 (d, $J = 230.4$ Hz), -103.22 (d, $J = 230.3$ Hz) ppm; HRMS (m/z) (ESI): calc. for C$_{15}$H$_{11}$O$_2$F$_2$S$_2$Cl$_3$Na 452.9126 [M+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. Rf = 0.4 (PE:EtOAc = 10:1). $^1$H NMR (500 MHz, CDCl$_3$): δ 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; $^{13}$C NMR (125 MHz, CDCl$_3$): δ 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; $^{19}$F NMR (470 MHz, CDCl$_3$): δ -97.91 (d, $J = 229.9$ Hz), -102.76 (d, $J = 229.9$ Hz) ppm; HRMS (m/z) (ESI): calc. for C$_{19}$H$_{15}$O$_2$F$_2$S$_2$Cl$_3$Na 435.0062 [M+Na]$^+$; found 435.0065.

3-((1-chloro-2,2-difluoro-2-tosylethyl)(thio)-2-methylfuran 4m:
Yield: 82%, 60 mg. Colorless oil. Rf = 0.3 (PE:EtOAc = 5:1). $^1$H NMR (500 MHz, CDCl$_3$): δ 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; $^{13}$C NMR (125 MHz, CDCl$_3$): δ 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; \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) -100.00 (d, \(J = 229.8\) Hz), -102.16 (d, \(J = 229.9\) Hz) ppm; HRMS (m/z) (ESI): calc. for C\(_{14}\)H\(_{13}\)O\(_3\)F\(_2\)S\(_2\)ClNa 388.9855 [M+Na]\(^+\); found 388.9857.

2-((1-Chloro-2,2-difluoro-2-tosylethyl)thio)thiophene 4n:
Yield: 81%, 59 mg. Light yellow oil. \(R_f = 0.2\) (PE:EtOAc = 10:1). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 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; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 147.37, 138.55, 133.29, 130.83, 130.15, 130.06, 127.98, 125.87, 119.35 (dd, \(J_{CF} = 297.0, 293.3\) Hz), 64.31 (dd, \(J_{CF} = 26.0, 22.3\) Hz), 21.93 ppm; \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) -99.81 (d, \(J = 230.7\) Hz), -101.60 (d, \(J = 230.7\) Hz) ppm; HRMS (m/z) (ESI): calc. for C\(_{13}\)H\(_{11}\)O\(_2\)F\(_2\)S\(_2\)ClNa 390.9470 [M+Na]\(^+\); found 390.9462.

(1-Chloro-2,2-difluoro-2-tosylethyl)(cyclohexyl)sulfane 4o:
Yield: 78%, 57 mg. Colorless oil. \(R_f = 0.4\) (PE:EtOAc = 10:1). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 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; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 147.15, 130.74, 130.38, 130.04, 119.62 (dd, \(J_{CF} = 294.4, 293.8\) Hz), 61.42 (dd, \(J_{CF} = 24.8, 23.7\) Hz), 45.53, 33.14, 32.98, 25.47, 21.88 ppm; \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) -96.35 (d, \(J = 228.7\) Hz), -104.42 (d, \(J = 228.7\) Hz) ppm; HRMS (m/z) (ESI): calc. for C\(_{15}\)H\(_{19}\)O\(_2\)F\(_2\)S\(_2\)ClNa 391.0375 [M+Na]\(^+\); 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). \(^1\)H NMR (500 MHz, 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; \(^1\)C NMR (125 MHz, 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; \(^1\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) -95.94 (d, \(J = 230.4\) Hz), -103.88 ppm; HRMS (m/z) (ESI): calc. for C\(_{16}\)H\(_{15}\)O\(_2\)F\(_2\)S\(_2\)ClNa 399.0062 [M+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). \(^1\)H NMR (500 MHz, 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; \(^1\)C NMR (125 MHz, 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; \(^1\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) -96.54 (d, \(J = 229.8\) Hz), -103.81 ppm; HRMS (m/z) (ESI): calc. for C\(_{13}\)H\(_{15}\)O\(_4\)F\(_2\)S\(_2\)ClNa 394.9961 [M+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). \(^1\)H NMR (500 MHz, 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; \(^1\)C NMR (125 MHz, 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; \(^1\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) -96.05 (d, \(J = 229.8\) Hz), -101.45 (d, \(J = 229.2\) Hz) ppm; HRMS (m/z) (ESI): calc. for C\(_{13}\)H\(_{13}\)O\(_2\)F\(_2\)S\(_2\)ClSeNa 432.9348 [M+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 ºC. Rf = 0.3 (PE:EtOAc = 10:1). ¹H NMR (500 MHz, CDCl₃): δ 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; ¹³C NMR (125 MHz, CDCl₃): δ 147.16, 140.33, 136.78, 130.75, 130.38, 130.28, 130.07, 122.52, 120.09 (dd, JCF = 295.7, 289.0 Hz), 52.55 (dd, JCF = 30.0, 23.0 Hz), 21.90, 21.36 ppm; ¹⁹F NMR (470 MHz, CDCl₃): δ -96.00 (d, J = 229.0 Hz), -101.54 (d, J = 229.0 Hz) ppm; HRMS (m/z) (ESI): calc. for C₁₆H₁₅O₂F₂SClSeNa 446.9504 [M+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 ºC. Rf = 0.2 (PE:EtOAc = 10:1). ¹H NMR (500 MHz, CDCl₃): δ 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; ¹³C NMR (125 MHz, CDCl₃): δ 147.31, 138.37, 132.66, 130.74, 130.16, 130.13, 125.04, 124.51, 119.91 (dd, JCF = 295.9, 289.5 Hz), 52.01 (dd, JCF = 30.0, 23.0 Hz), 21.92 ppm; ¹⁹F NMR (470 MHz, CDCl₃): δ -96.61 (d, J = 229.0 Hz), -100.82 (d, J = 229.0 Hz) ppm; HRMS (m/z) (ESI): calc. for C₁₅H₁₂O₂F₂SClSeBrNa 510.8450, 512.8434 [M+Na]⁺; found 510.8457, 512.8409.

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

Yield: 84%, 77 mg. Yellow solid, m.p.= 88-90 ºC. Rf = 0.4 (PE:EtOAc = 10:1). ¹H NMR (500 MHz, CDCl₃) δ 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; ¹³C NMR (125 MHz,
CDCl$_3$): δ 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; $^{19}$F NMR (470 MHz, CDCl$_3$) δ -95.99 (d, $J = 229.1$ Hz), -101.46 (d, $J = 229.0$ Hz) ppm.

HRMS (m/z) (ESI): calc. for C$_{19}$H$_{15}$O$_2$F$_2$SClSeNa 482.9504 [M+Na]$^+$; found 482.9495.

2-((1-Chloro-2,2-difluoro-tosylethyl)selanyl)thiophene 4v:
Yield: 82%, 68 mg. Light yellow oil. R$_f$ = 0.2 (PE:EtOAc = 10:1). $^1$H NMR (500 MHz, CDCl$_3$): δ 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, $J_{CF} = 15.9, 10.1$ Hz, 1H), 2.48 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): δ 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; $^{19}$F NMR (470 MHz, CDCl$_3$): δ -96.26 (d, $J = 229.3$ Hz), -101.81 (d, $J = 229.2$ Hz) ppm; HRMS (m/z) (ESI): calc. for C$_{13}$H$_{11}$O$_2$F$_2$SClSeNa 438.8911 [M+Na]$^+$; 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). $^1$H NMR (500 MHz, CDCl$_3$): δ 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; $^{13}$C NMR (125 MHz, CDCl$_3$): δ 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; $^{19}$F NMR (470 MHz, CDCl$_3$): δ -71.89 (s) ppm; HRMS (m/z) (ESI): calc. for C$_9$H$_8$O$_3$SClNa 278.9829 [M+Na]$^+$; found 278.9836.

(1-Chloro-2,2,3,3,3-pentafluoropropyl)(4-methoxyphenyl)sulfane 4x:
Yield: 75%, 46 mg. Colorless oil. Rf= 0.4 (PE:EtOAc = 10:1). \(^1\)H NMR (500 MHz, 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; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta \) 161.49, 137.45, 119.66, 115.03, 65.28 (dd, \(J_{CF} = 27.4, 25.5 \) Hz), 55.43 ppm (Carbon with directly attached fluorine appear as broad multiplets and are not reported); \(^{19}\)F NMR (470 MHz, 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 C\(_{10}\)H\(_8\)O\(_5\)SClNa \(328.9797 \) [M+Na]\(^+\); found 328.9790.

(1-Chloro-2,2,3,3,4,4,4-heptafluorobutyl)(4-methoxyphenyl)sulfane 4y:
Yield: 71%, 50 mg. Colorless oil. Rf= 0.4 (PE:EtOAc = 10:1). \(^1\)H NMR (500 MHz, 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; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta \) 160.50, 136.48, 118.62, 114.01, 64.47 (t, \(J_{CF} = 26.6 \) Hz), 54.37 ppm (Carbon with directly attached fluorine appear as broad multiplets and are not reported); \(^{19}\)F NMR (470 MHz, 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 C\(_{11}\)H\(_8\)O\(_5\)SClNa \(378.9765 \) [M+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. Rf= 0.2 (PE:EtOAc = 10:1). \(^1\)H NMR (500 MHz, 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; \(^{13}\)C NMR (125 MHz, 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 C\(_{15}\)H\(_{13}\)O\(_2\)SCl \(291.0252 \) [M-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). \(^1\)H NMR (500 MHz, 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; \(^1\)C NMR (125 MHz, 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 C\(_{11}\)H\(_{13}\)O\(_3\)SClNa 283.0166 [M+Na]\(^+\); found 283.0164.

Diethyl (chloro(phenylthio)methyl)phosphonate 4B:
Yield: 85%, 50 mg. Yellow oil. R_f = 0.2 (PE:EtOAc = 2:1). \(^1\)H NMR (500 MHz, 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; \(^1\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 132.75, 132.27\) (d, \(J_{CP} = 9.7\) Hz), 129.38, 129.05, 64.71, 64.66, 61.06 (d, \(J_{CP} = 162.6\) Hz), 16.46, 16.41 ppm; \(^{31}\)P NMR (202 MHz, CDCl\(_3\)): \(\delta 13.98 – 13.62\) (m, 1P) ppm; HRMS (m/z) (ESI): calc. for C\(_{11}\)H\(_{15}\)O\(_3\)PSClNa 317.0139 [M+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). \(^1\)H NMR (500 MHz, 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; \(^1\)C NMR (125 MHz, 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 C\(_{15}\)H\(_{17}\)O\(_2\)SCl 291.0252 [M-H]\(^-\); found 291.0256.
(2,2-Difluoro-2-tosyl-1-(2,4,6-trimethoxyphenyl)ethyl)(phenyl)sulfane 8a:
Quantitative yield, 98 mg. Colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 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; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 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, \(J_{CF} = 295.0, 287.0\) Hz), 104.55, 91.43, 90.80, 56.28, 55.83, 55.30, 45.09 ppm; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -92.85 (d, \(J = 226.2\) Hz), -100.16 (d, \(J = 226.2\) Hz) ppm; HRMS (m/z) (ESI): calc. for C\(_{24}\)H\(_{24}\)O\(_5\)F\(_2\)S\(_2\)Na 517.0931 [M+Na]\(^+\); found 517.0928.

(1-(2,5-Dimethoxyphenyl)-2,2-difluoro-2-tosylethyl)(phenyl)sulfane 8b:
Quantitative yield, 93 mg. Colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 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; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 153.34, 150.87, 146.38, 133.61, 130.76, 130.56, 129.72, 128.88, 128.29, 123.02 (dd, \(J_{CF} = 293.0, 287.0\) Hz), 122.91, 122.88, 115.39, 115.12, 112.33, 56.70, 55.54, 45.32 (dd, \(J_{CF} = 25, 21\) Hz), 21.76 ppm; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -92.85 (d, \(J = 226.2\) Hz), -102.76 (d, \(J = 233.0\) Hz) ppm; HRMS (m/z) (ESI): calc. for C\(_{23}\)H\(_{22}\)O\(_4\)F\(_2\)S\(_2\)Na 487.0825 [M+Na]\(^+\); found 487.0832.

5. References:
6. NMR spectra