1,2-Fluorosulfenylation of unactivated alkenes with thiols and fluoride source promoted by bromodimethylsulfonium bromide

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1 General Information

All reactions involving air or moisture sensitive reagents were carried out in flame dried glass ware under argon atmosphere using standard Schlenk techniques. Solvents were either freshly distilled or obtained in extra–dry grade from commercial sources, and store over molecular sieves (3 Å). Diethyl ether (Et₂O) was distilled over sodium/benzophenone and stored over activated molecular sieves (3 Å). Dichloromethane (CH₂Cl₂) was refluxed over CaH₂ and used as freshly distilled. Otherwise noted, commercially available chemicals were purchased from Energy Chemical. Column chromatography was performed with silica gel (300–400 mesh). Merck silica gel 60 F254 plates were used for thin layer chromatography (TLC) with UV light (254/366 nm) or KMnO₄ (1.5 g in 200 mL H₂O, 5 g NaHCO₃) as the staining. The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz (¹H), 101 MHz (¹³C) and 376 MHz (¹⁹F) in CDCl₃ with tetramethylsilane as the internal standard. Chemical shifts (δ) were reported in parts per million (ppm). Splitting patterns were designated as s, singlet; d, doublet; t; dd, doublet of doublets; m, multiplet. High–resolution mass spectra were obtained with an AB Triple 5600 mass spectrometer by ESI on a TOF mass analyzer.
2 General Procedures

2.1 Preparation of (bromodimethyl)sulfonyl bromide (BDMS)

\[ \text{S} + \text{Br}_2 \xrightarrow{\text{MeCN}} \text{Br}_2 \text{S} \text{Br} \]

Dimethyl sulfide (12.4 g, 200 mmol, 1 equiv) were diluted in 40 mL dry acetonitrile (MeCN) in a
dry 250 mL flask. A solution of bromine (10.3 mL, 200 mmol, 1 equiv) in 40 mL MeCN was added
dropwise over 15 minutes at room temperature. The resulting orange powder was washed with
hexane (10 mL X 3) and dried under vacuo (40.3 g, 180 mmol, 92%).

2.2 Alkenes synthesized according to the published procedures

Compounds 1g, 1h, 1k, 1l, 1m, 1n, 1o, 1p, 1q, 1r, 1s, 1t, 1w, 1x, 1y, and 1z were prepared
according to the literature procedure.

2.3 General procedure for preparation of \( \beta \)-fluoro thioethers (vicinal
fluorosulfonylation of alkenes)

A dry Schlenk flask, charged with BDMS (99.9 mg, 0.45 mmol, 1.5 equiv) and RSH (0.45 mmol,
1.5 equiv), was vacuumed and refilled with nitrogen (3 cycles). Dry THF (3 mL) were injected to the flask at 0 °C with an ice bath. Corresponding alkene (0.30 mmol, 1.0 equiv) and AgF (114.2 mg, 0.90 mmol, 3.0 equiv) were then added to the flask while stirring. When the addition was completed, the mixture was allowed to stir for a further 10 h at room temperature. The reaction mixture was filtered by celite, and the filtrate was concentrated in vacuo. The crude product was then purified by column chromatography.

2.4 Procedure for gram scale synthesis of 3ka

A dry Schlenk flask, charged with BDMS (2.5 g, 11.36 mmol, 1.5 equiv) and 4-chlorothiophenol (1.6 g, 11.36 mmol, 1.5 equiv), was vacuumed and refilled with nitrogen (3 cycles). Dry THF (20 mL) were injected to the flask at 0 °C with an ice bath. Corresponding (2-methylallyl)benzene (1.0 g, 7.57 mmol, 1.0 equiv) and AgF (2.9 g, 22.71 mmol, 3.0 equiv) were then added to the flask while stirring. When the addition was completed, the mixture was allowed to stir for a further 10 h at room temperature. The reaction mixture was filtered by celite, and the filtrate was concentrated in vacuo. The crude product was then purified by column chromatography to give 3ka as a yellow oil (1.85 g, 83% yield).

2.5 General procedure for fluorosulfenylation of ethylene

A dry Schlenk flask, charged with BDMS (99.9 mg, 0.45 mmol, 1.0 equiv) and RSH (0.45 mmol, 1.0 equiv), was vacuumed and refilled with nitrogen (3 cycles). Dry THF (3 mL) were injected to the flask at 0 °C with an ice bath. The solution was bubbled with a needle-tipped ethylene cylinder for 2–3 minutes. AgF (114.2 mg, 0.90 mmol, 3.0 equiv) were added to the flask. When the addition was completed, the mixture was allowed to stir for a further 10 h at room temperature. The reaction mixture was filtered by celite, and the filtrate was concentrated in vacuo. The crude product was then purified by column chromatography.

3 Characterization data

Trans-(4-chlorophenyl)(2-fluorocyclohexyl)sulfane (3aa)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 54.9 mg (75% yield) of 3aa as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, $J = 8.4$ Hz, 2H), 7.28 – 7.26 (m, 2H), 4.45 – 4.26 (m, 1H), 3.15 – 3.07 (m, 1H), 2.20 – 2.05 (m, 2H), 1.77 – 1.53 (m, 3H), 1.45 – 1.25 (m, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ −170.1. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 134.2, 133.5, 132.4, 129.0, 93.3 (d, $J = 178.6$ Hz), 51.1 (d, $J = 18.4$ Hz), 31.3 (d, $J = 18.9$ Hz), 30.9, 24.4, 22.8 (d, $J = 9.0$ Hz). HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{12}$H$_{15}$ClFS 245.0562; Found 245.0564.

Trans-(4-chlorophenyl)(2-fluorocyclopentyl)sulfane (3ba)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 53.8 mg (78% yield) of 3ba as a yellow oil. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 – 7.27 (m, 4H), 4.99 – 4.84 (m, 1H), 3.73 – 3.65 (m, 1H), 2.36 – 2.27 (m, 1H), 2.12 – 1.81 (m, 4H), 1.64 – 1.55 (m, 1H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 165.3 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 134.0, 132.6, 131.1, 129.2, 99.8 (d, $J$ = 180.8 Hz), 50.9 (d, $J$ = 24.1), 31.6 (d, $J$ = 21.5), 30.4, 22.7 ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{11}$H$_{13}$ClF$_2$S 231.0405; Found 231.0406.

**Trans–(4–chlorophenyl)(2–fluorocyclooctyl)sulfane (3ca)**

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 67.7 mg (83% yield) of 3ca as a yellow oil. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 – 7.25 (m, 4H), 4.73 – 4.57 (m, 1H), 3.47 – 3.89 (m, 1H), 2.06 – 1.95 (m, 3H), 1.80 – 1.57 (m, 5H), 1.56 – 1.26 (m, 4H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 158.1 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 133.7, 133.5, 133.2, 129.0, 96.9 (d, $J$ = 172.0 Hz), 53.2 (d, $J$ = 21.2 Hz), 31.9 (d, $J$ = 22.5 Hz), 28.5 (d, $J$ = 6.2 Hz), 26.0, 25.3, 25.2, 24.2 (d, $J$ = 6.8 Hz) ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{14}$H$_{19}$ClF$_2$S 273.0875; Found 273.0883.

**(4–Chlorophenyl)(5–fluorooctan–4–yl)sulfane (3da)**

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 68.2 mg (83% yield) of 3da as a colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.26 (m, 4H), 4.60 – 4.44 (m, 1H), 3.17 – 3.08 (m, 1H), 1.83 – 1.60 (m, 4H), 1.56 – 1.33 (m, 4H), 0.96 – 0.92 (m, 6H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 181.7 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 133.9, 133.5, 133.2, 129.0, 95.1 (d, $J$ = 176.4 Hz), 53.7 (d, $J$ = 20.6 Hz), 34.2 (d, $J$ = 21.3 Hz), 32.3 (d, $J$ = 5.1 Hz) 20.2, 18.6 (d, $J$ = 3.6 Hz), 13.8, 13.8 ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{14}$H$_{21}$ClF$_2$S 275.1031; Found 275.1038.

**(4–Chlorophenyl)(2–fluorohexyl)sulfane (3ea)**

According to the general procedure for preparation of β-fluoro thioethers, the crude product was
purified using silica gel chromatography (PE) to give 64.2 mg (87% yield) of 3ea as a yellow oil. 
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.25 (m, 4H), 4.67 – 4.49 (m, 1H), 3.20 – 2.99 (m, 2H), 1.76 – 1.64 (m, 2H), 1.49 – 1.30 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ –177.1 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 134.3, 132.5, 131.2, 129.1, 92.4 (d, J = 173.6 Hz), 38.8 (d, J = 23.8 Hz), 33.9 (d, J = 20.7 Hz), 26.9 (d, J = 3.8 Hz), 22.4, 13.9 ppm. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for C$_{12}$H$_{16}$ClFSNa 269.0537; Found 269.0542.

(4-Chlorophenyl)(2-fluoro-4-phenylbutyl)sulfane (3fa)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.25 (m, 4H), 4.67 – 4.49 (m, 1H), 3.20 – 2.99 (m, 2H), 1.76 – 1.64 (m, 2H), 1.49 – 1.30 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ –177.1 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 134.3, 132.5, 131.2, 129.1, 92.4 (d, J = 173.6 Hz), 38.8 (d, J = 23.8 Hz), 33.9 (d, J = 20.7 Hz), 26.9 (d, J = 3.8 Hz), 22.4, 13.9 ppm. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for C$_{16}$H$_{19}$ClFSNa 309.0875; Found 309.0880.

(4-Chlorophenyl)(2-fluoro-4-(p-toly)butyl)sulfane (3ga)

According to the general procedure for preparation of $\beta$-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 86.0 mg (93% yield) of 3ga as a yellow oil. 
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.18 (m, 9H), 7.12 – 7.06 (m, 4H), 4.69 – 4.51 (m, 1H), 3.24 – 2.99 (m, 2H), 2.89 – 2.68 (m, 2H), 2.11 – 1.95 (m, 2H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ –178.6 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.8, 134.0, 132.8, 131.5, 129.1, 128.5, 126.1, 126.1, 128.4, 91.4 (d, J = 174.4 Hz), 38.9 (d, J = 23.5 Hz), 35.8 (d, J = 20.8 Hz), 31.0 (d, J = 3.9 Hz) ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{16}$H$_{19}$ClFS 309.0875; Found 309.0880.

(4-(4-Bromophenyl)-2-fluorobutyl)(4-chlorophenyl)sulfane (3ha)

According to the general procedure for preparation of $\beta$-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 100.4 mg (90% yield) of 3ha as a yellow oil. 
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.24 (m, 4H), 7.12 – 7.06 (m, 4H), 4.68 – 4.50 (m, 1H), 3.22 – 2.99 (m, 2H), 2.83 – 2.63 (m, 2H), 2.34 – 1.93 (m, 2H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ –176.6 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.8, 134.0, 132.8, 132.7, 131.5, 129.2, 129.1, 128.3, 91.5 (d, J = 174.2 Hz), 38.8 (d, J = 23.6 Hz), 35.9 (d, J = 20.9 Hz), 30.6 (d, J = 3.9 Hz), 21.0 ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{17}$H$_{19}$ClFS 309.0875; Found 309.0880.
According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 71.4 mg (85% yield) of 3ia as a yellow oil. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.21 (m, 9H), 4.90 – 4.72 (m, 1H), 3.19 – 3.02 (m, 4H) ppm. 

\(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –175.2 ppm. 

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 136.0 (d, \(J = 4.4\) Hz), 133.9, 132.6, 131.2, 129.4, 129.1, 128.6, 126.9, 92.5 (d, \(J = 177.6\) Hz), 40.2 (d, \(J = 21.2\) Hz), 37.8 (d, \(J = 23.5\) Hz) ppm. 

HRMS (ESI) m/z: [M + H]\(^+\) Calcd for C\(_{16}\)H\(_{16}\)BrClFS 372.9823; Found 372.9826.

(4-Chlorophenyl)(2-fluoro-3-phenylpropyl)sulfane (3ia)

\[
\text{\begin{tikzpicture}
\node at (-1.5,0) {\includegraphics[width=0.3\textwidth]{3ia.png}};
\end{tikzpicture}}
\]

4-((4-Chlorophenyl)thio)-3-fluorobutan-1-ol (3ja)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 5:1) to give 53.4 mg (76% yield) of 3ja as a yellow oil. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 – 7.25 (m, 4H), 4.91 – 4.73 (m, 1H), 3.81 (t, \(J = 6.0\) Hz, 2H), 3.26 – 3.06 (m, 2H), 2.03 – 1.91 (m, 2H) 1.55 (br, 1H) ppm. 

\(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –179.2 ppm. 

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 134.0, 132.8, 131.4, 129.2, 90.4 (d, \(J = 172.9\) Hz), 58.8 (d, \(J = 4.4\) Hz), 39.0 (d, \(J = 23.2\) Hz), 36.8 (d, \(J = 20.3\) Hz) ppm. 

HRMS (ESI) m/z: [M + Na]\(^+\) Calcd for C\(_{10}\)H\(_{12}\)ClFOSNa 257.0174; Found 257.0177.

(4-Chlorophenyl)(2-fluoro-2-methyl-3-phenylpropyl)sulfane (3ka)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 75.9 mg (86% yield) of 3ka as a yellow oil. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 – 7.24 (m, 9H), 3.19 – 3.00 (m, 4H), 1.41 (d, \(J = 21.6\) Hz, 3H) ppm. 

\(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –141.2 ppm. 

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 135.8 (d, \(J = 3.6\) Hz), 135.1, 132.3, 130.9, 130.4, 129.0, 128.3, 126.8, 96.5 (d, \(J = 176.1\) Hz), 44.9 (d, \(J = 22.3\) Hz), 43.2 (d, \(J = 25.6\) Hz), 24.2 (d, \(J = 24.0\) Hz) ppm. 

HRMS (ESI) m/z: [M + Na]\(^+\) Calcd for C\(_{16}\)H\(_{16}\)ClFNSNa 317.0537; Found 317.0530.

(4-Chlorophenyl)(2-fluoro-2-methyl-3-(p-tolyl)propyl)sulfane (3la)

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According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 73.9 mg (80% yield) of 3la as a yellow oil. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.23 (m, 4H), 7.11 (s, 4H), 3.17 – 2.95 (m, 4H), 2.33 (s, 3H), 1.39 (d, $J = 21.6$ Hz, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ −141.2 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 136.4, 135.2, 132.7 (d, $J = 4.0$ Hz), 132.3, 130.9, 130.3, 129.0, 128.9, 96.5 (d, $J = 175.9$ Hz), 44.5 (d, $J = 22.4$ Hz), 43.2 (d, $J = 25.5$ Hz), 24.2 (d, $J = 24.2$ Hz), 21.0 ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{17}$H$_{19}$ClFS 309.0875; Found 309.0884.

(4–Chlorophenyl)(2–fluoro–3–(4–methoxyphenyl)–2–methylpropyl)sulfane (3ma)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 10:1) to give 86.5 mg (89% yield) of 3ma as a yellow oil. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.23 (m, 4H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 3.80 (s, 3H), 3.17 – 2.93 (m, 4H), 1.39 (d, $J = 21.6$ Hz, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ −141.4 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.5, 135.2, 131.4, 130.9, 129.0, 127.8 (d, $J = 3.7$ Hz), 113.6, 96.6 (d, $J = 175.7$ Hz), 55.2, 44.0 (d, $J = 22.4$ Hz), 43.1 (d, $J = 25.7$ Hz), 24.1 (d, $J = 24.0$ Hz) ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{17}$H$_{19}$ClFOS 325.0824; Found 325.0816.

(4–Chlorophenyl)(2–fluoro–3–(4–fluorophenyl)–2–methylpropyl)sulfane (3na)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 68.3 mg (73% yield) of 3na as a yellow oil. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.24 (m, 4H), 7.21 – 7.18 (m, 2H), 7.01 – 6.97 (m, 2H), 3.16 – 2.93 (m, 4H), 1.38 (d, $J = 21.6$ Hz, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ −116.0, −141.7 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.9 (d, $J = 246.0$ Hz), 135.0, 132.4, 131.8 (dd, $J = 7.8$, 1.4 Hz), 131.5 (t, $J = 3.0$ Hz), 131.0 (d, $J = 1.2$ Hz), 129.1, 115.1 (d, $J = 21.4$ Hz), 96.4 (d, $J = 177.0$ Hz), 43.9 (d, $J = 22.2$ Hz), 43.2 (d, $J = 25.8$ Hz), 24.1 (d, $J = 24.0$ Hz) ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{16}$H$_{16}$ClF$_2$S 313.0624; Found 313.0616.

(4–Chlorophenyl)(3–(4–chlorophenyl)–2–fluoro–2–methylpropyl)sulfane (3oa)
According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 74.8 mg (76% yield) of 3oa as a yellow oil. 

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.29 – 7.22 (m, 6H), 7.14 (d, \( J = 8.0 \text{ Hz}, 2H \)), 3.14 – 2.91 (m, 4H), 1.36 (d, \( J = 21.6 \text{ Hz}, 3H \)) ppm. 

\[ ^19F \text{ NMR (376 MHz, CDCl}_3 \] \( \delta \) –141.5 ppm. 

\[ ^13C \text{ NMR (101 MHz, CDCl}_3 \] \( \delta \) 134.9, 134.2 (d, \( J = 2.8 \text{ Hz} \)), 132.8, 132.5, 131.8, 131.0, 129.1, 128.4, 96.3 (d, \( J = 176.5 \text{ Hz} \)), 44.0 (d, \( J = 22.3 \text{ Hz} \)), 43.2 (d, \( J = 25.9 \text{ Hz} \)), 24.1 (d, \( J = 23.9 \text{ Hz} \)) ppm. 

HRMS (ESI) m/z: [M + H]^+ Calcd for C\text{16}H\text{16}ClFS 329.0328; Found 329.0334.

(3–(4-Bromophenyl)–2–fluoro–2–methylpropyl)(4–chlorophenyl)sulfane (3pa)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 50:1) to give 80.3 mg (72% yield) of 3pa as a yellow oil. 

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.42 (d, \( J = 8.4 \text{ Hz}, 2H \)), 7.31 – 7.24 (m, 4H), 7.15 – 7.10 (m, 2H), 3.16 – 2.91 (m, 4H), 1.38 (d, \( J = 21.2 \text{ Hz}, 3H \)) ppm. 

\[ ^19F \text{ NMR (376 MHz, CDCl}_3 \] \( \delta \) –141.4 ppm. 

\[ ^13C \text{ NMR (101 MHz, CDCl}_3 \] \( \delta \) 134.9, 134.7 (d, \( J = 2.5 \text{ Hz} \)), 134.8, 132.5, 132.1, 131.3, 131.0, 129.1, 120.9, 96.2 (d, \( J = 176.5 \text{ Hz} \)), 44.1 (d, \( J = 22.3 \text{ Hz} \)), 43.2 (d, \( J = 25.9 \text{ Hz} \)), 24.1 (d, \( J = 23.9 \text{ Hz} \)) ppm. 

HRMS (ESI) m/z: [M + H]^+ Calcd for C\text{16}H\text{16}BrClFS 372.9823; Found 372.9814.

Methyl 4–(3–((4–chlorophenyl)thio)–2–fluoro–2–methylpropyl)benzoate (3qa)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 50:1) to give 66.5 mg (63% yield) of 3qa as a yellow oil. 

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 8.00 (d, \( J = 8.0 \text{ Hz}, 2H \)), 7.35 – 7.26 (m, 6H), 3.94 (s, 3H), 3.22 – 3.03 (m, 4H), 1.41 (d, \( J = 21.2 \text{ Hz}, 3H \)) ppm. 

\[ ^19F \text{ NMR (376 MHz, CDCl}_3 \] \( \delta \) –141.2 ppm. 

\[ ^13C \text{ NMR (101 MHz, CDCl}_3 \] \( \delta \) 166.9, 141.1 (d, \( J = 2.5 \text{ Hz} \)), 134.8, 132.5, 131.0, 130.4, 129.5, 129.1, 128.8, 96.2 (d, \( J = 177.2 \text{ Hz} \)), 52.0, 44.7 (d, \( J = 22.1 \text{ Hz} \)), 43.4 (d, \( J = 25.8 \text{ Hz} \)), 24.2 (d, \( J = 24.0 \text{ Hz} \)) ppm. 

HRMS (ESI) m/z: [M + H]^+ Calcd for C\text{18}H\text{19}ClFO\text{2}S 353.0773; Found 353.0774.

(2–Fluoro–2–methyl–4–phenylbutyl)(phenyl)sulfane (3ra)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was
purified using silica gel chromatography (PE) to give 70.2 mg (76% yield) of 3ra as a yellow oil.  
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.36 – 7.26 (m, 6H), 7.23 – 7.16 (m, 3H), 3.21 (d, \(J = 17.2\) Hz, 2H), 2.75 – 2.67 (m, 2H), 2.16 – 1.96 (m, 2H), 1.50 (d, \(J = 21.6\) Hz, 3H) ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta \) -142.2 ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta \) 141.3, 135.1, 132.5, 131.2, 129.1, 128.5, 128.2, 126.0, 96.5 (d, \(J = 173.8\) Hz), 43.8 (d, \(J = 26.1\) Hz), 40.7 (d, \(J = 22.5\) Hz), 29.8 (d, \(J = 5.4\) Hz), 24.1 (d, \(J = 24.3\) Hz) ppm. HRMS (ESI) m/z: [M + H]\(^+\) Calcd for C\(_{17}\)H\(_{19}\)ClF\(_3\)S 309.0875; Found 309.0878.

(4-Chlorophenyl)(2-fluoro-2-phenylethyl)sulfane (3sa)[6]

According to the general procedure for preparation of \(\beta\)-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 69.4 mg (87% yield) of 3sa as a yellow oil.  
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.38 – 7.24 (m, 9H), 5.59 – 5.44 (m, 1H), 3.48 – 3.22 (m, 2H) ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta \) -171.7 ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta \) 138.3 (d, \(J = 20.1\) Hz), 133.9, 132.8, 131.6, 129.2, 128.9 (d, \(J = 1.9\) Hz), 128.6, 125.7 (d, \(J = 6.5\) Hz), 92.6 (d, \(J = 176.8\) Hz), 41.0 (d, \(J = 27.1\) Hz) ppm.

Methyl 4-(2-((4-chlorophenyl)thio)-1-fluoroethyl)benzoate (3ta)[6]

According to the general procedure for preparation of \(\beta\)-fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 50:1) to give 80.7 mg (83% yield) of 3ta as a yellow oil.  
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 8.03 (d, \(J = 8.0\) Hz, 2H), 7.38 (d, \(J = 8.0\) Hz, 2H), 7.31 – 7.24 (m, 4H), 5.64 – 5.49 (m, 1H), 3.91 (s, 3H), 3.45 – 3.22 (m, 2H) ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta \) -174.8 ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta \) 166.5, 143.0 (d, \(J = 20.2\) Hz), 133.5, 133.0, 131.8, 130.5 (d, \(J = 1.5\) Hz), 129.8, 129.2, 125.6 (d, \(J = 7.0\) Hz), 91.9 (d, \(J = 178.5\) Hz), 52.2, 40.9 (d, \(J = 26.4\) Hz) ppm.

(4-Chlorophenyl)(2-fluoro-2-(4-nitrophenyl)ethyl)sulfane (3ua)

According to the general procedure for preparation of \(\beta\)-fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 50:1) to give 60.6 mg (65% yield) of 3ua as a yellow oil.  
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 8.23 (d, \(J = 8.8\) Hz, 2H), 7.50 (d, \(J = 8.4\) Hz, 2H), 7.33 – 7.26 (m, 4H), 5.70 – 5.55 (m, 1H), 3.47 – 3.23 (m, 2H) ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta \) -175.6 ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta \) 148.1, 145.1 (d, \(J = 20.6\) Hz), 133.4, 133.1, 132.0, 129.3, 126.5 (d, \(J = 7.3\) Hz), 123.8, 91.3 (d, \(J = 180.1\) Hz), 40.9 (d, \(J = 26.0\) Hz) ppm. HRMS (ESI) m/z: [M +
H]^+ Calcd for C\textsubscript{14}H\textsubscript{12}ClFNO\textsubscript{2}S 312.0256; Found 312.0245.

\((4\text{–Chlorophenyl})(2\text{–}(4\text{–chlorophenyl})\text{–}2\text{–fluoroethyl})\text{sulfane (3va)}\)\(^{[6]}\)

According to the general procedure for preparation of \(\beta\)–fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 70.2 mg (78\% yield) of 3va as a yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 (d, \(J = 8.4\) Hz, 2H), 7.31 – 7.24 (m, 6H), 5.56 – 5.41 (m, 1H), 3.45 – 3.18 (m, 2H) ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –171.5 ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 136.7 (d, \(J = 20.7\) Hz), 134.8 (d, \(J = 2.2\) Hz), 133.5, 133.0, 131.8, 129.2, 128.8, 127.2 (d, \(J = 6.6\) Hz), 91.9 (d, \(J = 177.6\) Hz), 40.9 (d, \(J = 27.1\) Hz) ppm.

\((R)\text{–}2,5,7,8\text{–Tetramethyl}\text{–}2\text{–}((4S,8R)\text{–}4,8,12\text{–trimethyltridecylic)chroman\text{–}6\text{–yl}}\text{4\text{–}}((4\text{–chlorobenzyl})\text{thio})\text{fluoromethyl}\text{benzoate (3wa)}\)

According to the general procedure for preparation of \(\beta\)–fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 50:1) to give 138.7 mg (64\% yield) of 3wa as a yellow oil. The diastereoselectivity for this compound is not determined (one signal observed in \(^{19}\)F NMR). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.30 (d, \(J = 8.0\) Hz, 2H), 7.51 (d, \(J = 8.0\) Hz, 2H), 7.33 (dd, \(J = 23.6, 8.8\) Hz, 4H), 5.73 – 5.58 (m 1H), 3.54 – 3.30 (m, 2H), 2.67 (t, \(J = 6.6\) Hz, 2H), 2.18 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 1.93 – 1.79 (m, 2H), 1.66 – 1.55 (m, 4H), 1.49 – 1.42 (m, 4H), 1.37 – 1.27 (m, 10H), 1.22 – 1.09 (m, 6H), 0.93 – 0.90 (m, 12H) ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –174.5 ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 164.5, 149.5, 143.5 (d, \(J = 20.2\) Hz), 140.5, 133.5, 133.0, 131.8, 130.4, 130.0 (d, \(J = 1.4\) Hz), 129.2, 126.8, 125.8 (d, \(J = 7.0\) Hz), 125.0, 123.1, 117.5, 91.9 (d, \(J = 178.9\) Hz), 75.0, 40.9 (d, \(J = 26.4\) Hz), 40.4, 39.6, 39.3, 37.4, 37.2, 32.7, 31.2, 31.0, 27.9, 24.8, 24.4, 24.1 23.6, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 13.0, 12.2, 11.8 ppm. HRMS (ESI) \(m/z\): [M + H]^+ Caled for C\textsubscript{44}H\textsubscript{61}ClFOS 723.4008; Found 723.4009.

\((3S,8S,9S,10R,13R,14S,17R)\text{–}10,13\text{–Dimethyl}\text{–}17\text{–}((R)\text{–}6\text{–methylheptan}–2\text{–yl})\text{–}2,3,4,7,8,9,10,11,12,13,14,15,16,17\text{–tetracadehydroy–}1\text{H–cyclopenta[a]phenanthren–}3\text{–yl}4\text{–}((4\text{–chlorophenyl})\text{thio})\text{–}1\text{–fluoroethyl}\text{benzoate (3xa)}\)
According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 50:1) to give 107.9 mg (53% yield) of 3xa as a yellow oil. The diastereoselectivity for this compound is not determined (one signal observed in $^{19}$F NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.31 – 7.24 (m, 4H), 5.64 – 5.49 (m, 1H), 5.42 (d, $J = 4.8$ Hz, 1H), 4.90 – 4.82 (m, 1H), 3.45 – 3.21 (m, 2H), 2.46 (d, $J = 8.4$ Hz, 2H), 2.04 – 1.89 (m, 1H), 1.86 – 1.79 (m, 1H), 1.76 – 1.68 (m, 1H), 1.60 – 1.45 (m, 6H), 1.39 – 1.25 (m, 6H), 1.22 – 1.12 (m, 5H), 1.07 (s, 3H), 1.04 – 0.97 (m, 3H), 0.92 (d, $J = 6.4$ Hz, 3H), 0.88 – 0.85 (m, 6H), 0.69 (s, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ –174.5 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.4, 142.8 (d, $J = 20.2$ Hz), 139.5, 133.5, 133.1, 131.8, 131.3, 129.8, 129.2, 125.5 (d, $J = 6.9$ Hz), 122.9, 92.0 (d, $J = 178.6$ Hz), 74.8, 56.7, 56.1, 50.0, 42.3, 41.0 (d, $J = 26.4$ Hz), 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.9, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 11.8 ppm. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for C$_{42}$H$_{56}$ClFO$_2$SNa 701.3566; Found 701.3553.

(1R,2S,5R)—2—Isopropyl—5—methylcyclohexyl 4—(2—[(4—chlorophenyl)thio]—1—fluoroethyl)benzoate (3ya)

According to the general procedure for preparation of β—fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 50:1) to give 90.1 mg (67% yield) of 3ya as a yellow oil. The diastereoselectivity for this compound is not determined (one signal observed in $^{19}$F NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.32 – 7.24 (m, 4H), 5.64 – 5.49 (m, 1H), 4.97 – 4.91 (m, 1H), 3.46 – 3.22 (m, 2H), 2.15 – 2.10 (m, 1H), 1.98 – 1.91 (m, 1H), 1.77 – 1.71 (m, 2H), 1.59 – 1.53 (m, 2H), 1.16 – 1.06 (m, 2H), 0.94 – 0.91 (m, 7H), 0.80 (d, $J = 6.8$ Hz, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ –174.4 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.4, 142.8 (d, $J = 20.2$ Hz), 139.5, 133.5, 133.1, 131.8, 131.3, 129.8, 129.2, 125.6 (d, $J = 6.8$ Hz), 92.0 (d, $J = 178.8$ Hz), 75.1, 47.2, 41.0 (d, $J = 26.6$ Hz), 40.9, 34.3, 31.4, 26.5, 23.6, 22.0, 20.7, 16.5 ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{25}$H$_{31}$ClFO$_2$S 449.1712; Found 449.1712.
According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 50:1) to give 99.2 mg (57% yield) of 3za as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.35 – 7.31 (m, 4H), 7.27 – 7.21 (m, 3H), 7.17 – 7.14 (m, 1H), 6.92 (t, $J = 8.2$ Hz, 2H), 5.67 – 5.52 (m, 1H), 3.47 – 3.23 (m, 2H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ –175.4 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.4, 151.0, 146.8, 144.1 (d, $J = 20.2$ Hz), 141.6, 133.4, 133.1, 131.8, 130.5, 130.3, 129.5, 129.2, 128.8 (d, $J = 1.4$ Hz), 128.1, 127.1, 125.9, 125.7 (d, $J = 7.0$ Hz), 124.5, 120.5, 120.2, 91.8 (d, $J = 179.0$ Hz), 40.9 (d, $J = 26.2$ Hz) ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{27}$H$_{18}$Cl$_4$FO$_3$S 580.9709; Found 580.9717.

Trans–(4-bromophenyl)(2–fluorocyclohexyl)sulfane (3ab)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 57.9 mg (67% yield) of 3ab as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.42 (m, 4H), 4.45 – 4.27 (m, 1H), 3.16 – 3.09 (m, 1H), 2.20 – 2.05 (m, 2H), 1.77 – 1.55 (m, 3H), 1.46 – 1.25 (m, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ –170.1 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 134.3, 133.1, 131.9, 121.5, 93.3 (d, $J = 178.6$ Hz), 50.9 (d, $J = 18.4$ Hz), 31.3 (d, $J = 19.3$ Hz), 30.9 (d, $J = 4.0$ Hz), 24.4, 22.8 (d, $J = 9.0$ Hz) ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{12}$H$_{15}$BrFS 289.0056; Found 289.0069.

Trans–(2–fluorocyclohexyl)(4–fluorophenyl)sulfane (3ac)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 40.4 mg (59% yield) of 3ac as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.46 (m, 2H), 7.00 (t, $J = 8.8$ Hz, 2H), 4.42 – 4.25 (m, 1H), 3.07 – 3.00 (m, 1H), 2.19 – 2.03 (m, 2H), 1.77 – 1.51 (m, 3H), 1.44 – 1.27 (m, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ –113.8, –170.2 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.6 (d, $J = 248.9$ Hz), 136.0 (d, $J = 8.2$ Hz), 128.5 (d, $J = 3.3$ Hz), 115.9 (d, $J = 21.9$ Hz), 93.2 (d, $J = 178.3$ Hz), 51.6 (d, $J = 18.2$ Hz), 31.4 (d, $J = 19.0$ Hz), 30.9 (d, $J = 4.0$ Hz), 24.4, 22.9 (d, $J = 9.1$ Hz) ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{12}$H$_{15}$F$_2$S 229.0857; Found 229.0856.

Trans–(2–fluorocyclohexyl)(p–tolyl)sulfane (3ad)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 51.1 mg (76% yield) of 3ad as a yellow oil. 

1H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 4.46 – 4.29 (m, 1H), 3.13 – 3.05 (m, 1H), 2.34 (s, 3H), 1.62 – 1.39 (m, 3H), 1.47 – 1.39 (m, 1H), 1.35 – 1.25 (m, 2H) ppm. 

19F NMR (376 MHz, CDCl₃) δ −170.5 ppm. 

13C NMR (101 MHz, CDCl₃) δ 137.6, 133.7, 129.8, 129.6, 93.0 ppm. 

The anti-stereochemistry of product 3ad was consistent with the literature.

**Trans-(4-(tert-butyl)phenyl)(2-fluorocyclohexyl)sulfane (3ae)**

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 52.7 mg (66% yield) of 3ae as a yellow oil. 

1H NMR (400 MHz, CDCl₃) δ 7.41 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.49 – 4.32 (m, 1H), 3.17 – 3.10 (m, 1H), 2.20 – 2.07 (m, 2H), 1.76 – 1.57 (m, 4H), 1.50 – 1.42 (m, 2H), 1.31 (s, 9H) ppm. 

19F NMR (376 MHz, CDCl₃) δ −170.6 ppm. 

13C NMR (101 MHz, CDCl₃) δ 150.7, 133.1, 130.1, 125.9, 93.0 (d, J = 177.9 Hz), 50.7 (d, J = 18.6 Hz), 34.5, 31.2, 30.9 (d, J = 19.5 Hz), 30.7, 24.1, 22.7 (d, J = 8.4 Hz) ppm. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₆H₂₄FS 267.1577; Found 267.1572.

**Trans-(2-fluorocyclohexyl)(naphthalen-2-yl)sulfane (3af)**

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 52.3 mg (67% yield) of 3af as a yellow oil. 

1H NMR (400 MHz, CDCl₃) δ 7.97 (s, 1H), 7.83 – 7.77 (m, 3H), 7.56 – 7.45 (m, 3H), 4.55 – 4.38 (m, 1H), 3.34 – 3.27 (m, 1H), 3.23 – 2.12 (m, 2H), 1.77 – 1.59 (m, 3H), 1.55 – 1.46 (m, 1H), 1.38 – 1.27 (m, 2H) ppm. 

19F NMR (376 MHz, CDCl₃) δ −170.3 ppm. 

13C NMR (101 MHz, CDCl₃) δ 133.5, 132.3, 131.6, 131.2, 130.2, 128.3, 127.6, 127.4, 126.5, 126.2, 93.1 (d, J = 178.3 Hz), 50.6 (d, J = 18.7 Hz), 31.1 (d, J = 19.4 Hz), 30.8, 24.2, 22.7 (d, J = 8.5 Hz) ppm. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₆H₁₈FS 261.1108; Found 261.1111.

**Trans-(2-fluorocyclohexyl)(m-tolyl)sulfane (3ag)**

According to the general procedure for preparation of β-fluoro thioethers, the crude product was
purified using silica gel chromatography (PE) to give 41.7 mg (62% yield) of 3ag as a yellow oil.  
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.26 (m, 2H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 4.50 – 4.33 (m, 1H), 3.22 – 3.14 (m, 1H), 2.34 (s, 3H), 2.20 – 2.06 (m, 2H), 1.77 – 1.58 (m, 3H), 1.51 – 1.42 (m, 1H), 1.38 – 1.27 (m, 2H) ppm.  
$^{19}$F NMR (376 MHz, CDCl$_3$) δ –170.5 ppm.  
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 138.6, 133.5, 133.4, 129.8, 128.6, 128.2, 93.0 (d, $J = 177.9$ Hz), 50.4 (d, $J = 18.8$ Hz), 30.9 (d, $J = 19.4$ Hz), 30.7, 24.1, 22.6 (d, $J = 8.4$ Hz), 21.3 ppm.  
HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{18}$FS 225.1108; Found 225.1115.

Trans–(2–fluorocyclohexyl)(o–tolyl)sulfane (3ah)

According to the general procedure for preparation of β–fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 49.1 mg (73% yield) of 3ah as a yellow oil.  
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.45 (m, 1H), 7.23 – 7.14 (m, 3H), 4.56 – 4.38 (m, 1H), 3.24 – 3.17 (m, 1H), 2.21 – 2.06 (m, 2H), 1.77 – 1.59 (m, 3H), 1.55 – 1.47 (m, 1H), 1.42 – 1.27 (m, 2H) ppm.  
$^{19}$F NMR (376 MHz, CDCl$_3$) δ –170.6 ppm.  
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.1, 133.5, 132.7, 130.3, 127.2, 126.3, 93.3 (d, $J = 177.9$ Hz), 49.9 (d, $J = 18.8$ Hz), 30.8 (d, $J = 19.4$ Hz), 30.4, 24.0, 22.5 (d, $J = 8.1$ Hz), 20.9 ppm.  
HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{18}$FS 225.1108; Found 225.1117.

Trans–(2,6–dimethylphenyl)(2–fluorocyclohexyl)sulfane (3ai)

According to the general procedure for preparation of β–fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 41.4 mg (58% yield) of 3ai as a yellow oil.  
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.12 (s, 3H), 4.58 – 4.40 (m, 1H), 3.01 – 2.93 (m, 1H), 2.56 (s, 6H), 2.21 – 2.10 (m, 1H), 1.98 – 1.91 (m, 1H), 1.75 – 1.56 (m, 3H), 1.53 – 1.45 (m, 1H), 1.42 – 1.26 (m, 2H) ppm.  
$^{19}$F NMR (376 MHz, CDCl$_3$) δ –170.6 ppm.  
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.4, 132.5, 128.2, 128.1, 94.2 (d, $J = 177.6$ Hz), 50.8 (d, $J = 18.6$ Hz), 30.9 (d, $J = 19.3$ Hz), 30.3 (d, $J = 3.9$ Hz), 24.0, 22.6 (d, $J = 8.1$ Hz), 22.3 ppm.  
HRMS (ESI) m/z: [M + Na]$^+$ Calcd for C$_{14}$H$_{19}$FSNa 261.1084; Found 261.1075

Trans–(2–fluorocyclohexyl)thio)phenol (3aj)

According to the general procedure for preparation of β–fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 10:1) to give 44.1 mg (65% yield) of 3aj as a yellow oil.  
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.38 (m, 2H), 6.80 – 6.77 (m, 2H), 5.30 (br, 1H), 4.41 – 4.23 (m, 1H), 3.00 – 2.92 (m, 1H), 2.19 – 1.99 (m, 2H), 1.73 – 1.51 (m, 3H), 1.42 – 1.27 (m,
Trans–butyl(2–fluorocyclohexyl)sulfane (3ak)

According to the general procedure for preparation of β–fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 45.6 mg (80% yield) of 3ak as a yellow oil. 1H NMR (400 MHz, CDCl3) δ 4.48–4.30 (m, 1H), 2.77–2.69 (m, 1H), 2.64 (t, J = 7.6 Hz, 2H), 2.15–2.04 (m, 2H), 1.78–1.63 (m, 2H), 1.59–1.54 (m, 3H), 1.43–1.30 (m, 7H), 1.25 (s, 14H), 0.90 (t, J = 6.6 Hz, 3H) ppm. 19F NMR (376 MHz, CDCl3) δ −170.0 ppm. 13C NMR (101 MHz, CDCl3) δ 95.8 (d, J = 177.1 Hz), 47.6 (d, J = 18.3 Hz), 32.1, 31.8 (d, J = 2.6 Hz), 31.4 (d, J = 19.3 Hz), 30.8 (d, J = 5.2 Hz), 24.5, 22.9 (d, J = 9.1 Hz), 22.0, 13.7 ppm. HRMS (ESI) m/z: [M + H]+ Calcd for C12H16FOS 227.0900; Found 227.0895.

Trans–dodecyl(2–fluorocyclohexyl)sulfane (3al)

According to the general procedure for preparation of β–fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 49.0 mg (54% yield) of 3al as a yellow oil. 1H NMR (400 MHz, CDCl3) δ 8.41–8.39 (m, 1H), 7.50–7.46 (m, 1H), 7.32–7.22 (m, 6H), 7.00–6.97 (m, 1H), 3.61–3.56 (m, 2H), 3.18–2.95 (m, 2H), 1.37 (d, J = 21.2 Hz, 3H) ppm. 19F NMR (376 MHz, CDCl3) δ −142.0 ppm. 13C NMR (101 MHz, CDCl3) δ 157.9, 149.2, 136.2 (d, J = 2.6 Hz), 136.0, 130.5 (d, J = 1.3 Hz), 128.2, 126.7, 122.4, 119.6, 96.6 (d, J = 175.1 Hz), 44.9 (d, J = 22.1 Hz), 37.7 (d, J = 25.3 Hz), 23.6 (d, J = 23.9 Hz) ppm. HRMS (ESI) m/z: [M + H]+ Calcd for C18H36FS 303.2512; Found 303.2512.

2–((2–Fluoro–2–methyl–3–phenylpropyl)thio)pyridine (3am)

According to the general procedure for preparation of β–fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 44.6 mg (57% yield) of 3am as a yellow oil. 1H NMR (400 MHz, CDCl3) δ 8.41–8.39 (m, 1H), 7.50–7.46 (m, 1H), 7.32–7.22 (m, 6H), 7.00–6.97 (m, 1H), 3.61–3.56 (m, 2H), 3.18–2.95 (m, 2H), 1.37 (d, J = 21.2 Hz, 3H) ppm. 19F NMR (376 MHz, CDCl3) δ −142.0 ppm. 13C NMR (101 MHz, CDCl3) δ 157.9, 149.2, 136.2 (d, J = 2.6 Hz), 136.0, 130.5 (d, J = 1.3 Hz), 128.2, 126.7, 122.4, 119.6, 96.6 (d, J = 175.1 Hz), 44.9 (d, J = 22.1 Hz), 37.7 (d, J = 25.3 Hz), 23.6 (d, J = 23.9 Hz) ppm. HRMS (ESI) m/z: [M + H]+ Calcd for C15H17FNS 262.1060; Found 262.1068.
2-((2-Fluoro-2-methyl-3-phenylpropyl)thio)thiophene (3an)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE) to give 40.7 mg (51% yield) of 3an as a yellow oil. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 – 7.33 (m, 1H), 7.32 – 7.27 (m, 3H), 7.26 – 7.23 (m, 2H), 7.19 – 7.17 (m, 1H), 7.01 – 6.96 (m, 1H), 3.16 – 2.98 (m, 4H), 1.42 (d, $J$ = 21.6 Hz, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –141.1 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 135.9 (d, $J$ = 3.4 Hz), 135.0, 133.6, 130.4, 129.2, 128.2, 127.5, 126.8, 96.4 (d, $J$ = 175.8 Hz), 48.1 (d, $J$ = 25.1 Hz), 44.7 (d, $J$ = 22.2 Hz), 23.9 (d, $J$ = 24.0 Hz) ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{14}$H$_{16}$FS$_2$ 267.0672; Found 267.0680.

Methyl N-((tert-butoxycarbonyl)-S-(2-fluoro-2-methyl-3-phenylpropyl)-D-cysteinate (3ao)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 5:1) to give 61.2 mg (53% yield) of 3ao as a yellow oil. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 – 7.21 (m, 5H), 5.35 (br, 1H), 4.52 (br, 1H), 3.76 – 3.72 (m, 3H), 3.09 – 2.94 (m, 4H), 2.78 – 2.64 (m, 2H), 1.44 (s, 9H), 1.36 (d, $J$ = 21.6 Hz, 3H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –142.5 ppm (major). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.4, 155.1, 138.5 (d, $J$ = 20.0 Hz), 128.8, 128.5, 125.6 (d, $J$ = 6.6 Hz), 94.1 (d, $J$ = 176.0 Hz), 80.1, 53.3, 52.5, 44.7 (d, $J$ = 22.6 Hz), 41.4 (d, $J$ = 24.8 Hz), 35.9, 28.2, 23.9 (d, $J$ = 24.1 Hz) ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{29}$FNO$_4$S 386.1796; Found 386.1791.

Methyl N-((tert-butoxycarbonyl)-S-(2-fluoro-2-phenylethyl)-D-cysteinate (3ap)

According to the general procedure for preparation of β-fluoro thioethers, the crude product was purified using silica gel chromatography (PE:EA = 5:1) to give 50.4 mg (47% yield) of 3ap as a yellow oil. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.33 (m, 5H), 5.61 – 5.46 (m, 1H), 5.35 (br, 1H), 4.55 – 4.51 (m, 1H), 3.75 (s, 3H), 3.12 – 2.84 (m, 4H), 1.44 (s, 9H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –172.6 ppm (major). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.4, 155.1, 138.5 (d, $J$ = 20.0 Hz), 128.8, 128.5, 125.6 (d, $J$ = 6.6 Hz), 94.1 (d, $J$ = 176.0 Hz), 80.2, 53.3, 52.6, 38.8 (d, $J$ = 26.6 Hz), 35.2, 28.2 ppm. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{17}$H$_{25}$FNO$_4$S 358.1483; Found 358.1483.

(4-Chlorophenyl)(2-fluoroethyl)sulfane (5)
According to the general procedure for fluorosulfenylation of ethylene, the crude product was purified using silica gel chromatography (PE) to give 46.2 mg (54% yield) of 5 as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.26 (m, 4H), 4.53 (dt, $J_1$ = 47.2 Hz, $J_2$ = 6.4 Hz, 2H), 3.18 (dt, $J_1$ = 18.0 Hz, $J_2$ = 6.8 Hz, 2H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ −212.9 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 133.3, 133.0, 131.6, 129.2, 81.5 (d, $J = 173.4$ Hz), 34.0 (d, $J = 21.7$ Hz) ppm.

(2-Fluoroethyl)(4-fluorophenyl)sulfane (6)[8]

According to the general procedure for fluorosulfenylation of ethylene, the crude product was purified using silica gel chromatography (PE) to give 33.7 mg (43% yield) of 6 as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.39 (m, 2H), 7.04 – 6.98 (m, 2H), 4.51 (dt, $J_1$ = 47.2 Hz, $J_2$ = 6.4 Hz, 2H), 3.13 (dt, $J_1$ = 18.0 Hz, $J_2$ = 6.8 Hz, 2H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ −114.3, −213.2 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.2 (d, $J = 248.5$ Hz), 133.4 (d, $J = 8.1$ Hz), 129.6 (d, $J = 3.5$ Hz), 116.2 (d, $J = 22.1$ Hz), 81.5 (d, $J = 173.1$ Hz), 34.9 (d, $J = 21.4$ Hz) ppm.

(2-Fluoroethyl)(4-methoxyphenyl)sulfane (7)[8]

According to the general procedure for fluorosulfenylation of ethylene, the crude product was purified using silica gel chromatography (PE:EA = 50:1) to give 34.3 mg (41% yield) of 7 as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.38 (m, 2H), 6.87 – 6.83 (m, 2H), 4.49 (dt, $J_1$ = 46.8 Hz, $J_2$ = 6.8 Hz, 2H), 3.80 (s, 3H), 3.07 (dt, $J_1$ = 17.6 Hz, $J_2$ = 6.8 Hz, 2H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ −213.0 ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.4, 134.2, 124.7, 114.7, 81.6 (d, $J = 172.7$ Hz), 55.3, 35.5 (d, $J = 21.0$ Hz) ppm.

4 Reference

5  NMR Spectra

$^1$H NMR of 3aa (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3aa (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3aa (101 MHz, CDCl$_3$)

$^1$H NMR of 3ba (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3ba (376 MHz, CDCl$_3$)

\[ \text{F} - \text{S} - \text{Cl} \]

$^{13}$C NMR of 3ba (101 MHz, CDCl$_3$)

\[ \text{F} - \text{S} - \text{Cl} \]
$^1$H NMR of 3ca (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3ca (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3ca (101 MHz, CDCl$_3$)

$^1$H NMR of 3da (400 MHz, CDCl$_3$)
\(^{19}\text{F NMR of 3da} \ (376 \text{ MHz, CDCl}_3)\)

\begin{center}
\includegraphics[width=\textwidth]{f_nmr.png}
\end{center}

\(^{13}\text{C NMR of 3da} \ (101 \text{ MHz, CDCl}_3)\)

\begin{center}
\includegraphics[width=\textwidth]{c_nmr.png}
\end{center}
$^1$H NMR of 3ea (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3ea (376 MHz, CDCl$_3$)
$^{13}$C NMR of $3\text{ea}$ (101 MHz, CDCl$_3$)

$^1$H NMR of $3\text{fa}$ (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3fa (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3fa (101 MHz, CDCl$_3$)
$^1$H NMR of 3ga (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3ga (376 MHz, CDCl$_3$)
\( ^{13} \text{C} \) NMR of 3\( \text{ga} \) (101 MHz, CDCl\(_3\))

\( ^{1} \text{H} \) NMR of 3\( \text{ha} \) (400 MHz, CDCl\(_3\))
$^{19}$F NMR of 3ha (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3ha (101 MHz, CDCl$_3$)
$^1$H NMR of 3ia (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3ia (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3ia (101 MHz, CDCl$_3$)

$^1$H NMR of 3ja (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3ja (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3ja (101 MHz, CDCl$_3$)
**1H NMR of 3ka (400 MHz, CDCl₃)**

![1H NMR spectrum of 3ka](image)

**19F NMR of 3ka (376 MHz, CDCl₃)**

![19F NMR spectrum of 3ka](image)
$^{13}$C NMR of 3ka (101 MHz, CDCl$_3$)

$^1$H NMR of 3la (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3la (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3la (101 MHz, CDCl$_3$)
$^1$H NMR of 3\text{ma} (400 MHz, CDCl$_3$)

\[ \text{MeO} - \text{F} - \text{S} - \text{Cl} \]

$^{19}$F NMR of 3\text{ma} (376 MHz, CDCl$_3$)

\[ \text{MeO} - \text{F} - \text{S} - \text{Cl} \]
$^{13}$C NMR of 3na (101 MHz, CDCl$_3$)

1H NMR of 3na (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3na (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3na (101 MHz, CDCl$_3$)
$^1$H NMR of 3oa (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3oa (376 MHz, CDCl$_3$)
\( ^{13}\text{C} \) NMR of 3oa (101 MHz, CDCl\(_3\))

\( ^{1}\text{H} \) NMR of 3pa (400 MHz, CDCl\(_3\))
$^{19}$F NMR of $3\text{pa}$ (376 MHz, CDCl$_3$)

\[
\begin{align*}
\text{Br} & \quad \text{S} & \quad \text{F} & \quad \text{Cl} \\
\end{align*}
\]

$^{13}$C NMR of $3\text{pa}$ (101 MHz, CDCl$_3$)

\[
\begin{align*}
\text{Br} & \quad \text{S} & \quad \text{F} & \quad \text{Cl} \\
\end{align*}
\]
$^1$H NMR of 3qa (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3qa (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3qa (101 MHz, CDCl$_3$)

$^1$H NMR of 3ra (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3ra (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3ra (101 MHz, CDCl$_3$)
$^{1}H$ NMR of 3sa (400 MHz, CDCl$_3$)

$^{19}F$ NMR of 3sa (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3sa (101 MHz, CDCl$_3$)

$^1$H NMR of 3ta (400 MHz, CDCl$_3$)
$^{19}$F NMR of $3\text{ta}$ (376 MHz, CDCl$_3$)

$^{13}$C NMR of $3\text{ta}$ (101 MHz, CDCl$_3$)
$^1$H NMR of 3ua (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3ua (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3ua (101 MHz, CDCl$_3$)

$^1$H NMR of 3va (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3va (376 MHz, CDCl$_3$)

\[
\begin{align*}
\text{Cl} & \quad \text{F} \\
\text{F} & \quad \text{S} \\
\text{S} & \quad \text{Cl}
\end{align*}
\]

$^{13}$C NMR of 3va (101 MHz, CDCl$_3$)

\[
\begin{align*}
\text{Cl} & \quad \text{F} \\
\text{F} & \quad \text{S} \\
\text{S} & \quad \text{Cl}
\end{align*}
\]
$^1$H NMR of 3wa (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3wa (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3wa (101 MHz, CDCl$_3$)

$^1$H NMR of 3xa (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3xa (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3xa (101 MHz, CDCl$_3$)
$^{1}$H NMR of 3ya (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3ya (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3ya (101 MHz, CDCl$_3$)

$^1$H NMR of 3za (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3za (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3za (101 MHz, CDCl$_3$)
$^{1}\text{H NMR of 3ab (400 MHz, CDCl}_3)$

$^{19}\text{F NMR of 3ab (376 MHz, CDCl}_3)$
$^{13}$C NMR of 3ab (101 MHz, CDCl$_3$)

$^1$H NMR of 3ac (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3ac (376 MHz, CDCl₃)

$^{13}$C NMR of 3ac (101 MHz, CDCl₃)
$^1$H NMR of 3ad (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3ad (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3ad (101 MHz, CDCl$_3$)

$^1$H NMR of 3ae (400 MHz, CDCl$_3$)
$^{19}$F NMR of $3ae$ (376 MHz, CDCl$_3$)

$^{13}$C NMR of $3ae$ (101 MHz, CDCl$_3$)
$^1$H NMR of 3a$\text{f}$ (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3a$\text{f}$ (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3af (101 MHz, CDCl$_3$)

$^{1}$H NMR of 3ag (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3ag (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3ag (101 MHz, CDCl$_3$)
$^1$H NMR of 3ah (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3ah (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3ah (101 MHz, CDCl$_3$)

$^1$H NMR of 3ai (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3ai (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3ai (101 MHz, CDCl$_3$)
$^1$H NMR of 3aj (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3aj (376 MHz, CDCl$_3$)
$^{13}$C NMR of 3aj (101 MHz, CDCl$_3$)

$^1$H NMR of 3ak (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3ak (376 MHz, CDCl$_3$)

C NMR of 3ak (101 MHz, CDCl$_3$)
\(^1\)H NMR of 3al (400 MHz, CDCl\(_3\))

\(^{19}\)F NMR of 3al (376 MHz, CDCl\(_3\))
$^{13}$C NMR of 3al (101 MHz, CDCl$_3$)

$^1$H NMR of 3am (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3am (376 MHz, CDCl$_3$)

$^{13}$C NMR of 3am (101 MHz, CDCl$_3$)
$^1$H NMR of 3an (400 MHz, CDCl₃)

$^{19}$F NMR of 3an (376 MHz, CDCl₃)
$^{13}$C NMR of 3an (101 MHz, CDCl$_3$)

$^1$H NMR of 3ao (400 MHz, CDCl$_3$)
$^{19}$F NMR of 3ao (376 MHz, CDCl$_3$)

![F NMR spectrum of 3ao](image)

$^{13}$C NMR of 3ao (101 MHz, CDCl$_3$)

![C NMR spectrum of 3ao](image)
$^1$H NMR of 3ap (400 MHz, CDCl$_3$)

$^{19}$F NMR of 3ap (376 MHz, CDCl$_3$)
$^{13}$C NMR of $3a_p$ (101 MHz, CDCl$_3$)

![13C NMR spectrum of 3a_p](image)

$^1$H NMR of 5 (400 MHz, CDCl$_3$)

![1H NMR spectrum of 5](image)
$^{19}$F NMR of 5 (376 MHz, CDCl$_3$)

$^{13}$C NMR of 5 (101 MHz, CDCl$_3$)
**$^1$H NMR of 6 (400 MHz, CDCl$_3$)**

![H NMR spectrum of 6](image1)

**$^{19}$F NMR of 6 (376 MHz, CDCl$_3$)**

![F NMR spectrum of 6](image2)
$^{13}$C NMR of 6 (101 MHz, CDCl$_3$)

$^1$H NMR of 7 (400 MHz, CDCl$_3$)
$^{19}$F NMR of 7 (376 MHz, CDCl$_3$)

$^{13}$C NMR of 7 (101 MHz, CDCl$_3$)