Visible Light-promoted Difluoromethylthiolation of Aryldiazonium Salts
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General information
All solvents were purified by standard method. $^1$H NMR spectra were recorded on a 600 MHz or 400 MHz spectrometer. $^{19}$F NMR were recorded on a 376 MHz or 282 MHz spectrometer. $^{13}$C NMR spectra were recorded on a Agilent 151 MHz spectrometer. $^1$H NMR and $^{13}$C NMR chemical shifts were determined relative to internal standard TMS at $\delta$ 0.0 and $^{19}$F NMR chemical shifts were determined relative to CFCl$_3$ as inter standard. Chemical shifts ($\delta$) are reported in ppm, and coupling constants ($J$) are in Hertz (Hz).
All reagents were received from commercial sources. Solvents were purified according to the purification handbook Purification of Laboratory Chemicals.
Details of the fluorescence quenching experiments

A 0.0001 M solution Ru(bpy)$_3$(PF$_6$)$_2$ in CH$_3$CN was prepared. Solution of aryldiazonium salt (1a) in CH$_3$CN was prepared at a concentration of 0.003 M. Similarly, a solution of sodium ascorbate in water was prepared at a concentration of 0.003 M. 3 mL solution of Ru(bpy)$_3$(PF$_6$)$_2$ was added into a quartz cell. The solution was excited at 452 nm. The emission was detected and recorded. Then 25 μL, 50μL, 75μL, and 100μL solutions of quencher were added, respectively. Detection was carried out every time the quencher solution was added.
The spectral data of products

(difluoromethyl)(4-methoxyphenyl)sulfane (3a)

![Chemical Structure]

Colorless oil (79 mg, 83%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.75 (t, $J = 57.2$ Hz, 1H), 3.83 (s, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 161.2, 137.6, 120.9 (t, $J = 275.1$ Hz), 116.1 (t, $J = 3.2$ Hz), 114.9, 55.3; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -92.3 (d, $J = 57.3$ Hz).

(difluoromethyl)(4-ethoxyphenyl)sulfane (3b)

![Chemical Structure]

Colorless oil (84 mg, 82%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 8.3$ Hz, 2H), 6.90 (d, $J = 8.3$ Hz, 2H), 6.74 (t, $J = 57.2$ Hz, 1H), 4.04 (q, $J = 6.9$ Hz, 2H), 1.43 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 160.6, 137.6, 130.0 (t, $J = 275.1$ Hz), 115.9 (t, $J = 3.0$ Hz), 115.4, 63.6, 14.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -92.3 (d, $J = 57.3$ Hz).

(difluoromethyl)(4-phenoxyphenyl)sulfane (3c)

![Chemical Structure]

Pale yellow oil (107 mg, 82%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.56-7.51 (m, 2H), 7.41-7.36 (m, 2H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.05-7.01 (dd, $J = 8.6$, 0.9 Hz, 2H), 7.04-6.96 (m, 2H), 6.79 (t, $J = 57.0$ Hz, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 159.5, 155.9, 137.6, 130.0, 124.3, 120.8 (t, $J = 275.2$ Hz), 119.8 (t, $J = 3.0$ Hz), 118.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -92.0 (d, $J = 57.2$ Hz).

(difluoromethyl)(4-isopropylphenyl)sulfane (3d)

![Chemical Structure]

Colorless oil (73 mg, 72%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 6.78 (t, $J = 57.2$ Hz, 1H), 2.96-2.87 (m, 1H), 1.25 (d, $J = 7.0$ Hz, 6H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 151.0, 135.6, 127.5, 122.7 (t, $J = 3.0$ Hz), 121.2 (t, $J = 274.9$ Hz), 33.9, 23.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -91.6 (d, $J = 57.2$ Hz).

(4-(tert-butyl)phenyl)(difluoromethyl)sulfane (3e)

![Chemical Structure]

Colorless oil (72 mg, 67%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J = 8.3$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 2H), 6.81 (t, $J = 57.2$ Hz, 1H), 1.33 (s, 9H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 153.2, 135.2, 126.5, 122.5 (t, $J = 3.0$ Hz), 121.2 (t, $J = 274.9$ Hz), 34.8, 31.2; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -91.5 (d, $J = 57.1$ Hz).
(4-benzylphenyl)(difluoromethyl)sulfane (3f)

\[
\text{Ph} \quad \text{SCF}_2 \text{H}
\]

Pale yellow oil (66 mg, 53%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.51 (d, \(J = 7.8\) Hz, 2H), 7.31 (d, \(J = 8.3\) Hz, 2H), 7.25-7.18 (m, 5H), 6.80 (t, \(J = 57.1\) Hz, 1H), 4.01 (s, 2H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 143.3, 140.1, 135.6, 129.9, 128.9, 128.6, 126.4, 123.3 (t, \(J = 2.9\) Hz, 121.0 (t, \(J = 275.0\) Hz), 41.6; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -91.5 (d, \(J = 56.9\) Hz). IR (KBr): \(\nu\) = 3093, 3063, 3028, 2973, 2920, 2850, 1593, 1494, 1454, 1434, 1405, 1320, 1180, 1069, 1035, 1018, 850, 801, 758, 720, 698, 657, 587, 502 cm\(^{-1}\). MS (EI): m/z (%) 167 (100). HRMS (EI) for C\(_{14}\)H\(_{12}\)F\(_2\)S: Calcd: 250.0628; Found: 250.0626.

[1,1'-biphenyl]-4-yl(difluoromethyl)sulfane (3g)

\[
\text{Ph} \quad \text{SCF}_2 \text{H}
\]

White solid (73 mg, 62%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.67 (d, \(J = 8.2\) Hz, 2H), 7.64-7.59 (m, 4H), 7.48 (t, \(J = 7.6\) Hz, 2H), 7.40 (t, \(J = 7.3\) Hz, 1H), 6.87 (t, \(J = 56.9\) Hz, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 142.8, 139.8, 135.7, 128.9, 128.0, 127.9, 127.1, 124.8 (t, \(J = 2.9\) Hz), 120.9 (t, \(J = 275.3\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -91.4 (d, \(J = 57.1\) Hz).

(4-chlorophenyl)(difluoromethyl)sulfane (3h)

\[
\text{Cl} \quad \text{SCF}_2 \text{H}
\]

Colorless oil (62 mg, 62%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.52 (d, \(J = 8.5\) Hz, 2H), 7.37 (d, \(J = 8.5\) Hz, 2H), 6.81 (t, \(J = 56.6\) Hz, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 136.7, 136.5, 129.6, 124.2 (t, \(J = 2.9\) Hz), 120.3 (t, \(J = 275.5\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -91.7 (d, \(J = 56.5\) Hz).

(difluoromethyl)(4-iodophenyl)sulfane (3i)

\[
\text{I} \quad \text{SCF}_2 \text{H}
\]

Colorless oil (74 mg, 52%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.2\) Hz, 2H), 7.30 (d, \(J = 8.1\) Hz, 2H), 6.81 (t, \(J = 56.6\) Hz, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 138.5, 136.9, 125.7 (t, \(J = 2.9\) Hz), 120.2 (t, \(J = 275.9\) Hz), 96.4; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -91.8 (d, \(J = 56.4\) Hz).

4-((difluoromethyl)thio)benzonitrile (3j)

\[
\text{NC} \quad \text{SCF}_2 \text{H}
\]

Colorless oil (17 mg, 19%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.67 (s, 4 H), 6.91 (t, \(J = 56.0\) Hz, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 134.5, 132.8 (t, \(J = 2.8\) Hz), 132.7, 119.7 (t, \(J = 277.0\) Hz), 117.9, 113.3; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -91.2 (d, \(J = 56.3\) Hz).
1-(4-((difluoromethyl)thio)phenyl)ethanone (3k)

Colorless oil (17 mg, 17%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 8.3$ Hz, 2 H), 7.64 (d, $J = 8.2$ Hz, 2H), 6.90 (t, $J = 56.4$ Hz, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 197.1, 137.5, 134.1, 132.3 (t, $J = 2.8$ Hz), 129.0, 120.2 (t, $J = 275.8$ Hz), 26.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -91.2 (d, $J = 56.1$ Hz).

ethyl 2-(4-((difluoromethyl)thio)phenyl)acetate (3l)

Colorless oil (64 mg, 52%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 8.2$ Hz, 2 H), 7.32 (d, $J = 8.2$ Hz, 2H), 6.81 (t, $J = 56.9$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.63 (s, 2H), 1.26 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 170.9, 136.1, 135.5, 130.3, 124.7 (t, $J = 3.0$ Hz), 120.9 (t, $J = 275.2$ Hz), 61.1, 39.5, 14.1; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -91.4 (d, $J = 57.1$ Hz). MS (EI): m/z (%) 173 (100). HRMS (EI) for C$_{11}$H$_{12}$O$_2$F$_2$S: Calcd: 246.0526; Found: 246.0530.

2-(4-((difluoromethyl)thio)phenyl)pyridine (3m)

Colorless oil (25 mg, 21%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.71 (d, $J = 4.8$ Hz, 1H), 8.02 (d, $J = 4.8$ Hz, 2H), 7.80 -7.73 (m, 2H), 7.68 (t, $J = 56.9$ Hz, 1H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.24 (d, $J = 7.6$ Hz, 1H), 6.83 (t, $J = 7.7$ Hz, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 156.0, 149.7, 140.6, 137.0, 135.4, 127.8, 126.9 (t, $J = 2.9$ Hz), 122.7, 120.9 (t, $J = 275.6$ Hz), 120.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -91.3 (d, $J = 57.0$ Hz).

(difluoromethyl)(m-tolyl)sulfane (3n)

Colorless oil (45 mg, 52%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.41 (s, 1H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.24 (d, $J = 7.6$ Hz, 1H), 6.83 (t, $J = 7.7$ Hz, 1H), 6.74 (t, $J = 57.0$ Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 139.3, 135.8, 132.2, 130.6, 129.1, 125.8 (t, $J = 2.8$ Hz), 121.2 (t, $J = 275.2$ Hz), 21.2; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -91.7 (d, $J = 56.9$ Hz).

(3-chlorophenyl)(difluoromethyl)sulfane (3o)

Colorless oil (50 mg, 52%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.59 (t, $J = 1.9$ Hz, 1H), 7.47 (d, $J = 7.7$ Hz, 1H), 7.41 (d, $J = 7.8$ Hz, 1H), 7.33 (t, $J = 7.9$ Hz, 1H), 6.74 (t, $J = 56.6$ Hz, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 134.9, 134.8, 133.3, 130.3, 130.2, 127.7 (t, $J = 3.0$ Hz), 120.4 (t, $J = 275.9$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -91.4 (d, $J = 56.5$ Hz).
(difluoromethyl)(o-tolyl)sulfane (3p)

Colorless oil (45 mg, 52%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ = 7.5 Hz, 1H), 7.36-7.30 (m, 2H), 7.22 (td, $J$ = 7.4, 1.9 Hz, 1H), 6.79 (t, $J$ = 56.9 Hz, 1H), 2.51 (s, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 143.0, 136.8, 130.9, 130.2, 126.8, 125.5 (t, $J$ = 2.8 Hz), 121.2 (t, $J$ = 275.0 Hz), 21.3; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -91.5 (d, $J$ = 57.2 Hz).

[1,1'-biphenyl]-2-yl(difluoromethyl)sulfane (3q)

Colorless oil (67 mg, 57%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J$ = 7.7 Hz, 1H), 7.48-7.38 (m, 6H), 7.37-7.35 (m, 2H), 6.66 (t, $J$ = 57.0 Hz, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 146.4, 140.3 135.4, 131.0, 129.6, 129.5, 128.2, 128.0, 127.6, 125.4 (t, $J$ = 2.7 Hz), 120.9 (t, $J$ = 275.1 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -91.5 (d, $J$ = 57.0 Hz).

(2-chlorophenyl)(difluoromethyl)sulfane (3r)

Colorless oil (37 mg, 38%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.66 (dd, $J$ = 7.8, 1.7 Hz, 1H), 7.51(dd, $J$ = 8.0, 1.3 Hz, 1H), 7.36 (td, $J$ = 7.7, 1.6 Hz, 1H), 7.29 (td, $J$ = 7.6, 1.3 Hz, 1H), 6.90 (t, $J$ = 56.9 Hz, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 138.5, 136.7, 131.0, 130.4, 127.6, 126.0 (t, $J$ = 3.2 Hz), 120.3 (t, $J$ = 276.1 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -92.1 (d, $J$ = 56.9 Hz).

(2-bromophenyl)(difluoromethyl)sulfane (3s)

Colorless oil (49 mg, 41%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.68 (td, $J$ = 8.2, 1.5 Hz, 2H), 7.35 (td, $J$ = 7.6, 1.4 Hz, 1H), 7.29-7.25 (m, 1H), 6.91 (t, $J$ = 56.9 Hz, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 136.4, 133.8, 131.0, 128.3 (t, $J$ = 3.3 Hz), 128.2, 120.5 (t, $J$ = 276.1 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -92.2 (d, $J$ = 56.8 Hz).

5-((difluoromethyl)thio)benzo[d][1,3]dioxole (3t)

Colorless oil (63 mg, 62%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.10 (dd, $J$ = 8.0, 1.7 Hz, 1H), 7.04 (d, $J$ = 1.6 Hz, 1H), 6.82 (d, $J$ = 8.0 Hz, 1H), 6.75 (t, $J$ = 57.0 Hz, 1H), 6.02 (s, 2H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 149.5, 148.2, 130.6, 120.8 (t, $J$ = 275.3 Hz), 117.3 (t, $J$ = 3.2 Hz), 115.8, 109.0, 101.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -92.4 (d, $J$ = 56.5 Hz). IR (KBr): $\nu$ = 3077, 3014, 2978.
(difluoromethyl)(2,3-dihydro-1H-inden-5-yl)sulfane (3u)

Colorless oil (62 mg, 62%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.44 (s, 1H), 7.35 (d, \(J = 7.7\) Hz, 1H), 7.25 (d, \(J = 8.4\) Hz, 1H), 6.80 (t, \(J = 57.2\) Hz, 1H), 2.93 (td, \(J = 7.5, 4.6\) Hz, 4H), 2.11 (p, \(J = 7.5\) Hz, 2H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 146.6, 145.8, 133.5, 131.6, 125.2, 122.8 (t, \(J = 2.9\) Hz), 121.3 (t, \(J = 274.7\) Hz), 32.68, 32.66, 25.4; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -91.6 (d, \(J = 57.2\) Hz).

IR (KBr): \(\nu\) = 3068, 3021, 2956, 2869, 2846, 1598, 1569, 1474, 1459, 1437, 1405, 1320, 1296, 1257, 1066, 1035, 884, 864, 821, 792, 757, 704, 541 cm\(^{-1}\). MS (EI): m/z (%) 152 (100). HRMS (EI) for C\(_{10}\)H\(_{10}\)F\(_2\)S: Calcd: 204.0057; Found: 200.0064.

(2-bromo-4-methylphenyl)(difluoromethyl)sulfane (3v)

Colorless oil (58 mg, 46%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.55 (d, \(J = 7.9\) Hz, 1H), 7.53 (d, \(J = 1.2\) Hz, 1H), 7.14 (dd, \(J = 7.9, 1.2\) Hz, 1H), 6.85 (t, \(J = 57.1\) Hz, 1H), 2.35 (s, 3H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 142.1, 136.9, 134.3, 129.5, 129.1, 124.4 (t, \(J = 3.3\) Hz), 120.6 (t, \(J = 276.2\) Hz), 20.9; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -92.4 (d, \(J = 57.2\) Hz). IR (KBr): \(\nu\) = 3054, 2972, 2924, 1590, 1551, 1464, 1381, 1319, 1259, 1210, 1120, 1073, 875, 849, 820, 790, 755, 699, 671, 544 cm\(^{-1}\). MS (EI): m/z (%) 254 (100), 252 (100). HRMS (EI) for C\(_{8}\)H\(_{7}\)F\(_2\)SBr: Calcd: 251.9420; Found: 251.9428.

(2-bromo-4-chlorophenyl)(difluoromethyl)sulfane (3w)

Yellow oil (48 mg, 35%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.71 (d, \(J = 2.2\) Hz, 1H), 7.61 (d, \(J = 8.4\) Hz, 1H), 7.33 (dd, \(J = 8.4, 2.3\) Hz, 1H), 6.87 (t, \(J = 56.7\) Hz, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 137.3, 136.7, 133.4, 129.9, 128.5, 126.0 (t, \(J = 3.2\) Hz), 119.9 (t, \(J = 276.8\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -92.4 (d, \(J = 57.2\) Hz). IR (KBr): \(\nu\) = 3087, 2972, 2928, 1568, 1545, 1418, 1365, 1317, 1297, 1247, 1104, 1077, 1024, 954, 871, 822, 793, 752, 696, 661, 585, 548 cm\(^{-1}\). MS (EI): m/z (%) 274 (100). HRMS (EI) for C\(_{8}\)H\(_{7}\)F\(_2\)SClBr: Calcd: 271.8874; Found: 271.8883.

(5-chloro-2,4-dimethoxyphenyl)(difluoromethyl)sulfane (3x)

White solid (28 mg, 22%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.54 (s, 1H), 6.80 (t, \(J = 57.8\) Hz, 1H),
6.70 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 160.1, 157.8, 138.1, 120.2 (t, \(J = 275.6\) Hz), 114.2, 105.4 (t, \(J = 3.5\) Hz), 96.7, 56.4, 56.3; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) - 93.0 (d, \(J = 57.8\) Hz). IR (KBr): \(\nu\) = 3015, 2970, 2945, 2882, 2851, 1589, 1568, 1500, 1482, 1470, 1462, 1436, 1375, 1296, 1210, 1180, 1094, 1070, 1017, 883, 819, 799, 745, 700, 519 cm\(^{-1}\).

MS (EI): m/z (%) 254 (100). HRMS (EI) for C\(_9\)H\(_9\)O\(_2\)F\(_2\)SCl: Calcd: 253.9980; Found: 253.9986.

(difluoromethyl)(naphthalen-1-yl)sulfane (3y)

Colorless oil (63 mg, 60%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.54 (d, \(J = 8.5\) Hz, 1H), 7.97 (d, \(J = 8.3\) Hz, 1H), 7.92-7.89 (m, 2H), 7.65 (ddd, \(J = 8.4, 6.8, 1.3\) Hz, 1H), 7.58 (ddd, \(J = 8.0, 6.9, 1.1\) Hz, 1H), 7.49 (dd, \(J = 8.2, 7.2\) Hz, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 136.3, 135.2, 134.2, 131.3, 128.6, 127.4, 126.6, 125.8, 125.6, 123.4 (t, \(J = 2.8\) Hz), 121.3 (t, \(J = 275.9\) Hz); \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -91.2 (d, \(J = 57.4\) Hz).

5-((difluoromethyl)thio)benzo[d]thiazole (3z)

Colorless oil (49 mg, 45%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 9.07 (s, 1H), 8.40 (d, \(J = 1.7\) Hz, 1H), 7.99 (d, \(J = 8.3\) Hz, 1H), 7.65 (dd, \(J = 8.3, 1.7\) Hz, 1H), 6.89 (t, \(J = 56.7\) Hz, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 155.4, 153.7, 135.6, 132.1, 130.8, 123.8 (t, \(J = 3.0\) Hz), 122.5, 120.6 (t, \(J = 275.8\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -91.6 (d, \(J = 56.5\) Hz).

5-((difluoromethyl)thio)-2-methoxypyridine (3aa)

Colorless oil (33 mg, 35%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.33 (d, \(J = 2.5\) Hz, 1H), 7.74 (dd, \(J = 8.6, 2.4\) Hz, 1H), 6.76 (d, \(J = 8.6\) Hz, 1H), 6.73 (t, \(J = 56.7\) Hz, 1H), 3.95 (s, 3H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 165.2, 153.9, 145.8, 119.8 (t, \(J = 276.1\) Hz), 113.7 (t, \(J = 3.0\) Hz), 111.8, 53.8; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -92.5 (d, \(J = 56.6\) Hz). MS (EI): m/z (%) 191 (100). HRMS (EI) for C\(_7\)H\(_7\)NOF\(_2\)S: Calcd: 191.0216; Found: 191.0219.

5-((difluoromethyl)thio)-2-methoxy-4-methylpyridine (3ab)

Yellow oil (58 mg, 57%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.29 (s, 1H), 6.68 (t, \(J = 56.6\) Hz, 1H), 6.67 (s, 1H), 3.93 (s, 3H), 2.43 (s, 3H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 165.7, 155.2, 154.9, 120.2 (t, \(J = 276.3\) Hz), 114.2 (t, \(J = 2.7\) Hz), 112.2, 53.7, 20.8; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -92.1 (d, \(J = 56.5\) Hz). MS (EI): m/z (%) 205 (100). HRMS (EI) for C\(_8\)H\(_9\)NOF\(_2\)S: Calcd: 205.0373; Found: 205.0378.
$^1$H, $^{19}$F, $^{13}$C NMR Spectra of Corresponding Compounds

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-methoxyphenyl)sulfane (3a)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-methoxyphenyl)sulfane (3a)
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-methoxyphenyl)sulfane (3a)

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-ethoxyphenyl)sulfane (3b)
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-ethoxyphenyl)sulfane (3b)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-ethoxyphenyl)sulfane (3b)
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-phenoxyphenyl)sulfane (3c)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-phenoxyphenyl)sulfane (3c)
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-phenoxyphenyl)sulfane (3c)

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-isopropylphenyl)sulfane (3d)
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-isopropylphenyl)sulfane (3d)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (difluoromethyl)(4-isopropylphenyl)sulfane (3d)
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (4-([\text{tert}-\text{butyl}])phenyl)(difluoromethyl)sulfane (3e)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (4-([\text{tert}-\text{butyl}])phenyl)(difluoromethyl)sulfane (3e)
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (4-(tert-butyl)phenyl)(difluoromethyl)sulfane (3e)

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (4-benzylphenyl)(difluoromethyl)sulfane (3f)
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (4-benzylphenyl)(difluoromethyl)sulfane (3f)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (4-benzylphenyl)(difluoromethyl)sulfane (3f)
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of [1,1'-biphenyl]-4-yl(difluoromethyl)sulfane (3g)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of [1,1'-biphenyl]-4-yl(difluoromethyl)sulfane (3g)
$\text{^19F NMR (376 MHz, CDCl}_3\text{)}$ spectrum of [1,1'-biphenyl]-4-yl(difluoromethyl)sulfane (3g)

$\text{^1H NMR (600 MHz, CDCl}_3\text{)}$ spectrum of (4-chlorophenyl)(difluoromethyl)sulfane (3h)
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (4-chlorophenyl)(difluoromethyl)sulfane (3h)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (4-chlorophenyl)(difluoromethyl)sulfane (3h)
\[ f_1 \] (ppm)

**1H NMR (600 MHz, CDCl\textsubscript{3}) spectrum of (difluoromethyl)(4-iodophenyl)sulfane (3i)**

**13C NMR (151 MHz, CDCl\textsubscript{3}) spectrum of (difluoromethyl)(4-iodophenyl)sulfane (3i)**
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ spectrum of (difluoromethyl)(4-iodophenyl)sulfane (3i)

$^1\text{H NMR (600 MHz, CDCl}_3\text{)}$ spectrum of 4-((difluoromethyl)thio)benzonitrile (3j)
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of 4-((difluoromethyl)thio)benzonitrile (3j)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 4-((difluoromethyl)thio)benzonitrile (3j)
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 1-(4-((difluoromethyl)thio)phenyl)ethanone (3k)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of 1-(4-((difluoromethyl)thio)phenyl)ethanone (3k)
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 1-(4-((difluoromethyl)thio)phenyl)ethanone (3k)

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of ethyl 2-(4-((difluoromethyl)thio)phenyl)acetate (3l)
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of ethyl 2-(4-((difluoromethyl)thio)phenyl)acetate (3l)
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of ethyl 2-(4-((difluoromethyl)thio)phenyl)acetate (3l)

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 2-(4-((difluoromethyl)thio)phenyl)pyridine (3m)
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of 2-(4-((difluoromethyl)thio)phenyl)pyridine (3m)

![13C NMR spectrum](image)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 2-(4-((difluoromethyl)thio)phenyl)pyridine (3m)

![19F NMR spectrum](image)
$^{1}$H NMR (600 MHz, CDCl$_3$) spectrum of (difluoromethyl)(m-tolyl)sulfane (3n)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (difluoromethyl)(m-tolyl)sulfane (3n)
$^{19}$F NMR (282MHz, CDCl$_3$) spectrum of (difluoromethyl)(m-toly)sulfane (3n)

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (3-chlorophenyl)(difluoromethyl)sulfane (3o)
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (3-chlorophenyl)(difluoromethyl)sulfane (3o)

\[ \text{Cl} \quad \text{SCF}_2\text{H} \]

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (3-chlorophenyl)(difluoromethyl)sulfane (3o)

\[ \text{Cl} \quad \text{SCF}_2\text{H} \]
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (difluoromethyl)(o-tolyl)sulfane (3p)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (difluoromethyl)(o-tolyl)sulfane (3p)
$^{19}$F NMR (282 MHz, CDCl$_3$) spectrum of (difluoromethyl)(o-tolyl)sulfane (3p)

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of [1,1'-biphenyl]-2-yl(difluoromethyl)sulfane (3q)
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of [1,1'-biphenyl]-2-yl(difluoromethyl)sulfane (3q)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of [1,1'-biphenyl]-2-yl(difluoromethyl)sulfane (3q)
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (2-chlorophenyl)(difluoromethyl)sulfane (3r)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (2-chlorophenyl)(difluoromethyl)sulfane (3r)
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (2-chlorophenyl)(difluoromethyl)sulfane (3r)

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (2-bromophenyl)(difluoromethyl)sulfane (3s)
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (2-bromophenyl)(difluoromethyl)sulfane (3s)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (2-bromophenyl)(difluoromethyl)sulfane (3s)
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5-((difluoromethyl)thio)benzo[d][1,3]dioxole (3t)

\[
\begin{align*}
&\text{f$_1$ (ppm)} \\
&2.21 \\
&2.28 \\
&0.97 \\
&1.00 \\
&6.02 \\
&6.66 \\
&6.75 \\
&6.81 \\
&6.82 \\
&6.85 \\
&7.04 \\
&7.04 \\
&7.09 \\
&7.09 \\
&7.11 \\
&7.11 \\
&7.26
\end{align*}
\]

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of 5-((difluoromethyl)thio)benzo[d][1,3]dioxole (3t)

\[
\begin{align*}
&\text{f$_1$ (ppm)} \\
&76.79 \\
&77.00 \\
&77.21 \\
&101.74 \\
&108.95 \\
&115.82 \\
&117.30 \\
&117.32 \\
&117.35 \\
&119.03 \\
&120.85 \\
&122.67 \\
&130.55 \\
&148.17 \\
&149.54
\end{align*}
\]
\textsuperscript{19}F NMR (600 MHz, CDCl\textsubscript{3}) spectrum of 5-((difluoromethyl)thio)benzo[d][1,3]dioxole (3t)

\[ \text{SCF}_2H \]

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) spectrum of (difluoromethyl)(2,3-dihydro-1H-inden-5-yl)sulfane (3u)

\[ \text{SCF}_2H \]
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (difluoromethyl)(2,3-dihydro-1H-inden-5-yl)sulfane (3u)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (difluoromethyl)(2,3-dihydro-1H-inden-5-yl)sulfane (3u)
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (2-bromo-4-methylphenyl)(difluoromethyl)sulfane (3v)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (2-bromo-4-methylphenyl)(difluoromethyl)sulfane (3v)
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (2-bromo-4-methylphenyl)(difluoromethyl)sulfane $(3v)$

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (2-bromo-4-chlorophenyl)(difluoromethyl)sulfane $(3w)$
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (2-bromo-4-chlorophenyl)(difluoromethyl)sulfane (3w)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of (2-bromo-4-chlorophenyl)(difluoromethyl)sulfane (3w)
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (5-chloro-2,4-dimethoxyphenyl)(difluoromethyl)sulfane (3x)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (5-chloro-2,4-dimethoxyphenyl)(difluoromethyl)sulfane (3x)
\[ ^{19}F \text{NMR (376 MHz, CDCl}_3) \text{ spectrum of (5-chloro-2,4-dimethoxyphenyl)(difluoromethyl)sulfane (3x)} \]

\[ ^{1}H \text{NMR (600 MHz, CDCl}_3) \text{ spectrum of (difluoromethyl)(naphthalen-1-yl)sulfane (3y)} \]
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of (difluoromethyl)(naphthalen-1-yl)sulfane (3y)

$^{19}$F NMR (282 MHz, CDCl$_3$) spectrum of (difluoromethyl)(naphthalen-1-yl)sulfane (3y)
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5-((difluoromethyl)thio)benzo[d]thiazole (3z)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of 5-((difluoromethyl)thio)benzo[d]thiazole (3z)
$^{19}\text{F NMR} \ (376 \text{ MHz, CDCl}_3) \ spectrum \ of \ 5-((\text{difluoromethyl})\text{thio})\text{benzo}[d]\text{thiazole} \ (3z)$

$^{1}\text{H NMR} \ (600 \text{ MHz, CDCl}_3) \ spectrum \ of \ 5-((\text{difluoromethyl})\text{thio})-2\text{-methoxypyridine} \ (3aa)$
$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of 5-((difluoromethyl)thio)-2-methoxypyridine (3aa)

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5-((difluoromethyl)thio)-2-methoxypyridine (3aa)
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5-((difluoromethyl)thio)-2-methoxy-4-methylpyridine (3ab)

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of 5-((difluoromethyl)thio)-2-methoxy-4-methylpyridine (3ab)
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 5-((difluoromethyl)thio)-2-methoxy-4-methylpyridine (3ab)

References: