Supporting Information

Selective Monofluorination of Active Methylene Compounds: the Important Role of ZnCl\textsubscript{2} in Inhibiting Overfluorination

Fanzhou Jiang, Yanchuan Zhao, and Jinbo Hu\textsuperscript{*}

Key Laboratory of Organofluorine Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
345 Ling-Ling Road, Shanghai, 200032 (China)
Fax: (+86) 21-64166128
E-mail: jinbohu@sioc.ac.cn
General Methods:

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used without further purification. The solvent THF was refluxed with sodium and distilled. CH₃CN was distilled from CaH₂. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a 300MHz (Bruker AV300) or 400MHz (Agilent MR400) NMR spectrometer. ¹H NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) at δ 0.0 or to the signal of a residual protonated solvent: CDCl₃ δ 7.26 or (CD₃)₂SO δ 2.50. ¹³C NMR chemical shifts were determined relative to internal TMS at δ 0.0. ¹⁹F NMR chemical shifts were determined relative to CFCl₃ at δ 0.0. Data for ¹H, ¹³C and ¹⁹F NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode.

Preparation of various methylene compounds:

Unless otherwise mentioned, starting materials were purchased from commercial sources and used as received (1a-1i, 4e, 4g). 1j, 4c, 4f, 4h, 4k were prepared in Procedure A. ¹ 4a, 4b, 4d, 4i, 4j were prepared in Procedure B.

Procedure A

Preparation of 1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone (1j):

\[
\begin{array}{c}
\text{H}_3\text{C}-\text{O} & \\
\text{O} & \\
\text{CH}_2\text{Br} & \\
\text{PhSO}_2\text{Na} & \\
\text{DMF, 75 °C} & \\
\end{array}
\]

7j → 1j

Sodium benzenesulfinate (98%, wt%, 1.1 equiv, 3.6850 g, 22 mmol) and 2-bromo-1-(4-methoxyphenyl)ethanone (7j) (98%, wt%, 1.0 equiv, 4.6751 g, 20 mmol) were dissolved in 34 mL DMF. The reaction mixture was stirred at 75 °C for 6 h under N₂ atmosphere until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (4.9196 g) in 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 7.5 Hz, 2H), 7.65 (t, J = 7.1 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 4.66 (s, 2H), 3.87 (s, 3H). MS (ESI, m/z): 291.1 (M + H⁺), 313.1 (M + Na⁺).
Preparation of (benzylsulfonyl)benzene (4c)

\[
\text{CH}_2\text{Br} + \text{PhSO}_2\text{Na} \rightarrow \text{PhSO}_2\text{C}_6\text{H}_4
\]

Sodium benzenesulfinate (98%, wt%, 1.05 equiv, 5.039 g, 30.7 mmol) and (bromomethyl)benzene (8c) (98%, wt%, 1.0 equiv, 5.0 g, 29.2 mmol) were dissolved in 50 mL DMF. The reaction mixture was stirred at 85 °C for 5 h under N\_2 atmosphere until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na\_2SO\_4, filtered and removed under vacuum. The crude product was recrystallization with EtOAc/hexane to provide white solid (5.89 g) in 87% yield. \(^1\)H NMR (300 MHz, CDCl\_3) \(\delta\) 7.67 – 7.56 (m, 3H), 7.50 – 7.41 (m, 2H), 7.36 – 7.22 (m, 3H), 7.08 (d, \(J\) = 6.7 Hz, 2H), 4.31 (s, 2H). MS (ESI, m/z): 233.1 (M + H\(^+\)), 250.1 (M + NH\(_4^+\)), 255.1 (M + Na\(^+\)).

Preparation of 1-methoxy-3-((phenylsulfonyl)methyl)benzene (4f)

\[
\text{CH}_2\text{Br} + \text{PhSO}_2\text{Na} \rightarrow \text{PhSO}_2\text{C}_6\text{H}_4\text{OCH}_3
\]

Sodium benzenesulfinate (98%, wt%, 1.1 equiv, 4.4957 g, 26.8 mmol) and 1-(bromomethyl)-3-methoxybenzene (8f) (98%, wt%, 1.0 equiv, 5.0 g, 24.4 mmol) were dissolved in 42 mL DMF. The reaction mixture was stirred at 80 °C for 6 h under N\_2 atmosphere until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na\_2SO\_4, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (5.5714 g) in 95% yield. \(^1\)H NMR (400 MHz, CDCl\_3) \(\delta\) 7.67 – 7.56 (m, 3H), 7.44 (t, \(J\) = 7.9 Hz, 2H), 7.14 (t, \(J\) = 7.9 Hz, 1H), 6.83 (dd, \(J\) = 8.2, 2.1 Hz, 1H), 6.68 – 6.54 (m, 2H), 4.26 (s, 2H), 3.69 (s, 3H). MS (ESI, m/z): 263.1 (M + H\(^+\)), 280.0 (M + NH\(_4^+\)), 285.1 (M + Na\(^+\)).

Preparation of 1-nitro-3-((phenylsulfonyl)methyl)benzene (4h)

\[
\text{CH}_2\text{Br} + \text{PhSO}_2\text{Na} \rightarrow \text{PhSO}_2\text{C}_6\text{H}_4\text{NO}_2
\]
Sodium benzenesulfinate (98%, wt%, 1.05 equiv, 1.7588 g, 10.5 mmol) and 1-(bromomethyl)-3-nitrobenzene (8h) (97%, wt%, 1.0 equiv, 2.2271 g, 10 mmol) were dissolved in 17 mL DMF. The reaction mixture was stirred at 80 °C for 10 h under N₂ atmosphere until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (1.6502 g) in 60% yield.¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 8.1 Hz, 1H), 7.86 (s, 1H), 7.72 – 7.58 (m, 3H), 7.57 – 7.45 (m, 4H), 4.38 (s, 2H). MS (ESI, m/z): 278.1 (M + H⁺), 295.1 (M + NH₄⁺), 300.1 (M + Na⁺).

Preparation of 1-((methylsulfonyl)methyl)-2-nitrobenzene (4k)

Sodium methanesulfinate (85%, wt%, 1.0 equiv, 2.4021 g, 20 mmol) and 1-(bromomethyl)-2-nitrobenzene (8k) (97%, wt%, 1.0 equiv, 4.4542 g, 20 mmol) were dissolved in 34 mL DMF. The reaction mixture was stirred at 75 °C for 6 h under N₂ atmosphere until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide light green solid (4.1871 g) in 97% yield.¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 8.2 Hz, 1H), 7.76 – 7.62 (m, 2H), 7.62 – 7.53 (m, 1H), 4.78 (s, 2H), 2.89 (s, 3H). MS (ESI, m/z): 216.0 (M + H⁺), 233.1 (M + NH₄⁺), 238.0 (M + Na⁺).

Procedure B

Preparation of 2-(benzylsulfonyl)benzothiazole (4a)

To a mixture of NaH (60%, wt%, 1.3 equiv, 1.0396 g, 26 mmol) and DMF (34 mL), benzothiazole-2-thiol (95%, 1.0 equiv, 3.5208 g, 20 mmol) was dissolved in under N₂ atmosphere. 10 minutes later, (bromomethyl)benzene (98%, wt%, 1.1 equiv, 3.8397 g, 22mmol) was added dropwise. The reaction was stirred at room temperature for 10 h until the almost completion of reaction monitored by TLC. The reaction was
quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was then dissolved in the mixture of CCl$_4$ (30 mL), CH$_3$CN (30 mL) and H$_2$O (75 mL) without purification. NaIO$_4$ (8.5556 g, 40 mmol) and ruthenium trichloride hydrate (ca. 15 mg) was added and the mixture was stirred at room temperature for 5 h until the almost completion of reaction monitored by TLC. The reaction was filtered on diatomite and washed with CH$_2$Cl$_2$. The filtrate was evaporated under vacuum to remove CCl$_4$ and CH$_3$CN, then extraction with CH$_2$Cl$_2$. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (3.4798g) in 60% yield. $^1$H NMR (400 MHz, CDC$_3$) $\delta$ 8.25 (d, $J = 8.3$ Hz, 1H), 7.93 (d, $J = 8.1$ Hz, 1H), 7.68 – 7.61 (m, 1H), 7.61 – 7.54 (m, 1H), 7.34 – 7.21 (m, 5H), 4.74 (s, 2H). MS (ESI, m/z): 290.0 (M + H$^+$), 312.0 (M + Na$^+$).

**Preparation of 2-(benzylsulfonyl)pyridine (4b)**

\[
\begin{align*}
& \text{8b} \quad \text{1) NaH, DMF} \\
& \quad \text{2) PhCH$_2$Br} \\
& \quad \text{9b} \\
& \quad \text{NaIO$_4$, RuCl$_3$·xH$_2$O} \\
& \quad \text{CCl$_4$/ CH$_3$CN/ H$_2$O} \\
& \quad \text{4b}
\end{align*}
\]

To a mixture of NaH (60%, wt%, 1.3 equiv, 1.0396 g, 26 mmol) and DMF (34 mL), pyridine-2-thiol (98%, wt%, 1.0 equiv, 2.2687 g, 20 mmol) was dissolved in under N$_2$ atmosphere. 10 minutes later, (bromomethyl)benzene (98%, wt%, 1.1 equiv, 3.8397 g, 22mmol) was added dropwise. The reaction was stirred at room temperature for 10 h until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was then dissolved in the mixture of CCl$_4$ (30 mL), CH$_3$CN (30 mL) and H$_2$O (75 mL) without purification. NaIO$_4$ (8.5556 g, 40 mmol) and ruthenium trichloride hydrate (ca. 15 mg) was added and the mixture was stirred at room temperature for 5 h until the almost completion of reaction monitored by TLC. The reaction was filtered on diatomite and washed with CH$_2$Cl$_2$. The filtrate was evaporated under vacuum to remove CCl$_4$ and CH$_3$CN, then extraction with CH$_2$Cl$_2$. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (4.1111 g) in 88% yield. $^1$H NMR (400 MHz, CDC$_3$) $\delta$ 8.80 (d, $J = 4.6$ Hz, 1H), 8.07 – 7.72 (m, 2H), 7.64 – 7.43 (m, 1H), 7.30 – 7.20 (m, 3H), 7.20 – 7.14 (m, 2H), 4.64 (s, 2H). MS (ESI, m/z): 234.1 (M + H$^+$), 256.1 (M + Na$^+$).

**Preparation of 2-((2-methylbenzyl)sulfonyl)benzothiazole (4c)**
To a mixture of NaH (60%, wt%, 1.3 equiv, 1.0396 g, 26 mmol) and DMF (34 mL), benzothiazole-2-thiol (95%, wt%, 1.0 equiv, 3.5208 g, 20 mmol) was dissolved in under N\textsubscript{2} atmosphere. 10 minutes later, 1-(bromomethyl)-2-methylbenzene (98%, wt%, 1.1 equiv, 4.1544 g, 22 mmol) was added dropwise. The reaction was stirred at room temperature for 10 h until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and removed under vacuum. The crude product was then dissolved in the mixture of CCl\textsubscript{4} (30 mL), CH\textsubscript{3}CN (30 mL) and H\textsubscript{2}O (75 mL) without purification. NaIO\textsubscript{4} (8.5556 g, 40 mmol) and ruthenium trichloride hydrate (ca. 15 mg) was added and the mixture was stirred at room temperature for 5 h until the almost completion of reaction monitored by TLC. The reaction was filtered on diatomite and washed with CH\textsubscript{2}Cl\textsubscript{2}. The filtrate was evaporated under vacuum to remove CCl\textsubscript{4} and CH\textsubscript{3}CN, then extraction with CH\textsubscript{2}Cl\textsubscript{2}. The organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid (5.3698 g) in 89% yield. m.p.: 125-126\degree C. IR (KBr): 3093, 3063, 3025, 2997, 2943, 2262, 2153, 1932, 1815, 1722, 1552, 1492, 1469, 1455, 1410, 1328, 1316, 1302, 1256, 1237, 1182, 1152, 1138, 1127, 1079, 1047, 1023, 854, 781, 767, 754, 735, 729, 711, 704, 691, 642, 586, 562, 534, 515, 491, 480, 433. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 8.27 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.63 – 7.56 (m, 1H), 7.26 – 7.13 (m, 3H), 7.08 (t, J = 7.0 Hz, 1H), 4.83 (s, 2H), 2.41 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 165.60, 152.59, 138.88, 137.10, 132.04, 131.03, 129.48, 128.06, 127.70, 126.31, 125.46, 124.70, 122.34, 58.39, 19.80. MS (ESI, m/z): 304.0 (M + H\textsuperscript{+}), 326.0 (M + Na\textsuperscript{+}). HRMS (ESI): calcd. For C\textsubscript{15}H\textsubscript{13}N\textsubscript{1}Na\textsubscript{1}O\textsubscript{2}S\textsubscript{2} (M + H\textsuperscript{+}) 326.02799, found 326.02821.

Preparation of 2-((4-methylbenzyl)sulfonyl)pyridine (4i)

To a mixture of NaH (60%, wt%, 1.3 equiv, 1.0396 g, 26 mmol) and DMF (34 mL), pyridine-2-thiol (98%, wt%, 1.0 equiv, 2.2687 g, 20 mmol) was dissolved in under N\textsubscript{2} atmosphere. 10 minutes later, 1-(bromomethyl)-4-methylbenzene (98%, wt%, 1.1 equiv, 4.1544 g, 22 mmol) was added. The reaction was stirred at room temperature for 10 h until the almost completion of reaction monitored by TLC. The reaction was
quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was then dissolved in the mixture of CCl₄ (30 mL), CH₃CN (30 mL) and H₂O (75 mL) without purification. NaIO₄ (8.5556 g, 40 mmol) and ruthenium trichloride hydrate (ca. 15 mg) was added and the mixture was stirred at room temperature for 5 h until the almost completion of reaction monitored by TLC. The reaction was filtered on diatomite and washed with CH₂Cl₂. The filtrate was evaporated under vacuum to remove CCl₄ and CH₃CN, then extraction with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH₂Cl₂/hexane to provide white solid (4.4664 g) in 90% yield. m.p.: 98-99 °C. IR (KBr): 3060, 2999, 2928, 2260, 2188, 1611, 1575, 1561, 1513, 1456, 1425, 1386, 1300, 1289, 1161, 1149, 1125, 1113, 1104, 1082, 1046, 1025, 990, 977, 818, 782, 766, 741, 728, 698, 622, 603, 526, 505, 483. ¹H NMR (400 MHz, CDCl₃) δ 8.81 (d, J = 4.6 Hz, 1H), 7.94 – 7.70 (m, 2H), 7.59 – 7.46 (m, 1H), 7.05 (s, 4H), 4.60 (s, 2H), 2.29 (s, 3H).

Preparation of 1-(benzylsulfonyl)-4-nitrobenzene (4j)

![Diagram](image-url)

To a mixture of NaH (60%, wt%, 1.3 equiv, 1.0396 g, 26 mmol) and DMF (34 mL), 4-nitrobenzenethiol (98%, wt%, 1.0 equiv, 3.1668 g, 20 mmol) was dissolved in under N₂ atmosphere. 10 minutes later, (bromomethyl)benzene (98%, wt%, 1.1 equiv, 3.8397 g, 22mmol) was added dropwise. The reaction was stirred at room temperature for 10 h until the almost completion of reaction monitored by TLC. The reaction was quenched by water. After extraction with EtOAc, the organic layer was washed with brine, and then dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was then dissolved in the mixture of CCl₄ (30 mL), CH₃CN (30 mL) and H₂O (75 mL) without purification. NaIO₄ (8.5556 g, 40 mmol) and ruthenium trichloride hydrate (ca. 15 mg) was added and the mixture was stirred at room temperature for 5 h until the almost completion of reaction monitored by TLC. The reaction was filtered on diatomite and washed with CH₂Cl₂. The filtrate was evaporated under vacuum to remove CCl₄ and CH₃CN, then extraction with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH₂Cl₂/hexane to provide gray solid (3.2333 g) in 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.35 (t, J = 7.4 Hz,
1H), 7.28 (t, J = 7.7 Hz, 2H), 7.08 (d, J = 7.2 Hz, 2H), 4.37 (s, 2H). MS (ESI, m/z): 300.0 (M + Na⁺).

**Monofluorination of various methylene compounds:**

1a-1j were monofluorinated in Condition A, and 4a-4k were monofluorinated in Condition B. The equivalents of base (NaO'Bu or LiHMDS) and ZnCl₂ were based on those of the starting methylene compounds.

**Condition A**

**Monofluorination of bis(phenylsulfonyl)methane (1a)**

\[
\begin{align*}
1a &\xrightarrow{1)} \text{'BuONa, ZnCl₂} \xrightarrow{2)} \text{SelectFluor} \\
&\text{THF, rt} \\
&\text{2a}
\end{align*}
\]

\[\text{'BuONa (2.5 equiv, 360.4 mg, 3.75 mmol) and anhydrous ZnCl₂ (2.5 equiv, 511.1 mg, 3.75 mmol) were dissolved in 12 mL THF. 5 minutes later, bis(phenylsulfonyl)methane (1a) (1.0 equiv, 444.0 mg, 1.5 mmol) was added into the mixture under N₂ atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628 g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid 2a (377.0 mg) in 80% yield.} \]

\[\text{¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 7.7 Hz, 4H), 7.77 (t, J = 7.1 Hz, 2H), 7.61 (t, J = 7.6 Hz, 4H), 5.73 (d, J = 45.8 Hz, 1H).} \]

\[\text{¹⁹F NMR (282 MHz, CDCl₃) δ -168.19 (d, J = 45.9 Hz).} \]

\[\text{¹³C NMR (100 MHz, CDCl₃) δ 135.70, 135.25, 130.14, 129.47, 105.65 (d, J = 266.1 Hz). MS (ESI, m/z): 314.9 (M + H⁺), 332.0 (M + NH₄⁺), 337.0 (M + Na⁺).} \]

**Monofluorination of 1-phenyl-2-(phenylsulfonyl)ethanone (1b)**

\[
\begin{align*}
1b &\xrightarrow{1)} \text{'BuONa, ZnCl₂} \xrightarrow{2)} \text{SelectFluor} \\
&\text{THF, rt} \\
&\text{2b}
\end{align*}
\]

\[\text{'BuONa (2.2 equiv, 317.1 mg, 3.3 mmol) and anhydrous ZnCl₂ (2.5 equiv, 511.1 mg, 3.75 mmol) were dissolved in 12 mL THF. 5 minutes later,} \]
1-phenyl-2-(phenylsulfonyl)ethanone (1b) (1.0 equiv, 394.4 mg, 1.5 mmol) was added into the mixture under N₂ atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid 2b (381.3 mg) in 91% yield.

**1H NMR (400 MHz, CDCl₃)** δ 8.02 (d, J = 7.7 Hz, 2H), 7.88 (d, J = 7.8 Hz, 2H), 7.74 (t, J = 7.1 Hz, 1H), 7.68 (t, J = 7.0 Hz, 1H), 7.58 (t, J = 7.7 Hz, 2H), 7.52 (t, J = 7.7 Hz, 2H), 6.35 (d, J = 48.0 Hz, 1H).

**19F NMR (282 MHz, CDCl₃)** δ -179.60 (d, J = 48.0 Hz).

**13C NMR (100 MHz, CDCl₃)** δ 186.43 (d, J = 17.6 Hz), 135.29, 135.03, 134.52, 133.88, 129.86, 129.76 (d, J = 23.2 Hz), 129.35, 128.84, 100.19 (d, J = 23.2 Hz). MS (EI, m/z): 278 (M⁺, 1.36), 105 (100.00), 77 (65.92), 51 (18.08), 109 (14.77), 141 (8.50), 106 (7.91), 78 (5.67), 50 (5.64).

Monofluorination of 2-(methylsulfonyl)-1-phenylethanone (1c)

1-BuONa (1.8 equiv, 259.5 mg, 2.7 mmol) and anhydrous ZnCl₂ (2.5 equiv, 511.1 mg, 3.75 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-(methylsulfonyl)-1-phenylethanone (1c) (1.0 equiv, 304.4 mg, 1.5 mmol) was added to the mixture under N₂ atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid 2c (282.7 mg) in 87% yield. m.p.: 86-87 °C. IR (KBr): 3356, 3032, 3007, 2976, 2926, 1694, 1596, 1581, 1449, 1417, 1358, 1317, 1257, 1174, 1144, 1096, 1075, 1001, 983, 953, 847, 811, 768, 737, 684, 671, 631, 523, 487, 465, 420. **1H NMR (400 MHz, CDCl₃)** δ 8.05 (d, J = 7.8 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 6.34 (d, J = 47.3 Hz, 1H), 3.05 (s, 3H). **19F NMR (282 MHz, CDCl₃)** δ -182.53 (d, J = 47.4 Hz). MS (EI, m/z): 216 (M⁺, 1.42), 105 (100.00), 77 (43.99), 109 (17.93), 51 (11.56), 106 (8.03), 50 (4.77), 78 (4.36), 83 (3.94). HRMS (EI): calcd. For C₉H₉O₃FS (M⁺) 216.0256, found 216.0257.

Monofluorination of diethyl malonate (1d)
1\textsuperscript{t}BuONa (1.5 equiv, 216.2 mg, 2.25 mmol) and anhydrous ZnCl\textsubscript{2} (2.5 equiv, 511.1 mg, 3.75 mmol) were dissolved in 12 mL THF. 5 minutes later, diethyl malonate (1d) (1.0 equiv, 240.3 mg, 1.5 mmol) was added into the mixture under N\textsubscript{2} atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid 2d (186.7 mg) in 70% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 5.26 (d, \(J = 48.2\) Hz, 1H), 4.32 (qd, \(J = 7.1, 2.6\) Hz, 4H), 1.32 (t, \(J = 7.1\) Hz, 6H). \textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}) \(\delta\) -195.08 (d, \(J = 48.3\) Hz). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 163.94 (d, \(J = 24.0\) Hz), 85.27 (d, \(J = 196.4\) Hz), 62.72, 13.96. MS (EI, m/z): 178 (M\textsuperscript{+}, 0.52), 78 (100.00), 105 (27.99), 106 (24.38), 60 (23.97), 133 (22.25), 77 (10.70), 45 (7.12), 49 (5.84).

Monofluorination of ethyl 3-oxo-3-phenylpropanoate (1e)

\textsuperscript{t}BuONa (1.5 equiv, 216.2 mg, 2.25 mmol) and anhydrous ZnCl\textsubscript{2} (3.0 equiv, 613.4 mg, 4.5 mmol) were dissolved in 12 mL THF. 5 minutes later, ethyl 3-oxo-3-phenylpropanoate (1e) (1.0 equiv, 303.5 mg, 1.5 mmol) was added into the mixture under N\textsubscript{2} atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid 2e (213.6 mg) in 68% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.04 (d, \(J = 8.1\) Hz, 2H), 7.64 (t, \(J = 7.4\) Hz, 1H), 7.50 (t, \(J = 7.8\) Hz, 2H), 5.87 (d, \(J = 48.8\) Hz, 1H), 4.30 (qd, \(J = 7.1, 1.4\) Hz, 2H), 1.26 (t, \(J = 7.1\) Hz, 3H). \textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}) \(\delta\) -190.34 (d, \(J = 48.8\) Hz). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 189.51 (d, \(J = 20.3\) Hz), 164.89 (d, \(J = 24.2\) Hz), 134.52 (s), 133.33 (s), 129.51 (d, \(J = 3.4\) Hz), 128.81 (s), 90.05 (d, \(J = 197.6\) Hz), 62.70 (s), 13.94 (s). MS (EI, m/z): 210 (M\textsuperscript{+}, 0.63), 105 (100.00), 77 (38.81), 51 (9.81), 106 (7.44), 109 (4.80), 78 (4.24), 50 (3.35), 118 (3.13).
Supporting Information

### Monofluorination of 2-(phenylsulfonyl)acetonitrile (1f)

![Chemical Structure of 1f](image)

1. BuONa (2.2 equiv, 317.1 mg, 3.3 mmol) and anhydrous ZnCl$_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-(phenylsulfonyl)acetonitrile (1f) (1.0 equiv, 277.4 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid 2f (275.5 mg) in 92% yield.

1H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, $J = 7.7$ Hz, 2H), 7.85 (t, $J = 7.3$ Hz, 1H), 7.69 (t, $J = 7.6$ Hz, 2H), 5.75 (d, $J = 46.7$ Hz, 1H).

19F NMR (282 MHz, CDCl$_3$) δ -178.95 (d, $J = 46.6$ Hz).

13C NMR (100 MHz, CDCl$_3$) δ 136.50, 132.16, 130.51, 129.90, 129.40, 109.81 (d, $J = 28.9$ Hz), 88.03 (d, $J = 230.9$ Hz). MS (EI, m/z): 199 (M$^+$, 0.80), 77 (100.00), 141 (34.26), 51 (25.39), 50 (8.91), 78 (7.16), 74 (3.82), 58 (3.21), 142 (2.53).

### Monofluorination of ethyl 2-(phenylsulfonyl)acetate (1g)

![Chemical Structure of 1g](image)

1. BuONa (2.5 equiv, 360.4 mg, 3.75 mmol) and anhydrous ZnCl$_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, ethyl 2-(phenylsulfonyl)acetate (1g) (1.0 equiv, 349.4 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid 2g (320.0 mg) in 87% yield. IR (film): 3069, 2984, 1760, 1584, 1476, 1449, 1396, 1372, 1343, 1313, 1275, 1244, 1201, 1159, 1111, 1081, 1022, 954, 856, 838, 763, 713, 687, 631, 597, 567, 543, 524. 1H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, $J = 7.7$ Hz, 2H), 7.75 (t, $J = 7.5$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 2H), 5.57 (d, $J = 48.0$ Hz,
1H), 4.29 (q, \(J = 7.1\) Hz, 2H), 1.28 (t, \(J = 7.1\) Hz, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -180.39 (d, \(J = 48.1\) Hz). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.98 (d, \(J = 23.4\) Hz), 135.32, 134.52, 129.79, 129.40, 97.26 (d, \(J = 232.4\) Hz), 63.51, 13.89. MS (EI, m/z): 246 (M\(^+\), 1.37), 77 (100.00), 141 (62.49), 51 (21.81), 109 (13.71), 78 (13.56), 125 (6.75), 50 (5.98), 182 (5.62). HRMS (EI): m/z calcd. For C\(_{10}\)H\(_{11}\)O\(_4\)F\(_2\)S (M\(^+\)) 246.036, found 246.0365.

### Monofluorination of ethyl 2-cyanoacetate (1h)

\[\text{NC-COOEt} \xrightarrow{1) \text{^tBuONa, ZnCl}_2} \text{THF, r.t.} \xrightarrow{2) \text{SelectFluor}} \text{NC-COOEt-F} \]

\(^{1}\)BuONa (2.2 equiv, 317.1 mg, 3.3 mmol) and anhydrous ZnCl\(_2\) (3.5 equiv, 715.6 mg, 5.25 mmol) were dissolved in 12 mL THF. 5 minutes later, ethyl 2-cyanoacetate (1h) (1.0 equiv, 178.6 mg, 1.5 mmol) was added into the mixture under N\(_2\) atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na\(_2\)SO\(_4\), filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid 2h (118.2 mg) in 60% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.51 (d, \(J = 46.1\) Hz, 1H), 4.40 (q, \(J = 7.1\) Hz, 2H), 1.37 (t, \(J = 7.2\) Hz, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -194.17 (d, \(J = 46.3\) Hz). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.68 (d, \(J = 24.8\) Hz), 111.69 (d, \(J = 29.7\) Hz), 74.33 (d, \(J = 196.5\) Hz), 64.31, 13.86. MS (ESI, m/z): 131.9 (M + H\(^+\)).

### Monofluorination of 3-oxo-3-(pyrrolidin-1-yl)propanenitrile (1i)

\[\text{NC-O} \xrightarrow{1) \text{^tBuONa, ZnCl}_2} \text{THF, r.t.} \xrightarrow{2) \text{SelectFluor}} \text{NC-O-F} \]

\(^{1}\)BuONa (2.2 equiv, 317.1 mg, 3.3 mmol) and anhydrous ZnCl\(_2\) (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, 3-oxo-3-(pyrrolidin-1-yl)propanenitrile (1i) (1.0 equiv, 211.5 mg, 1.5 mmol) was added into the mixture under N\(_2\) atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na\(_2\)SO\(_4\), filtered and removed under vacuum. The crude product was
purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid $2i$ (221.2 mg) in 94% yield. IR (film): 3508, 2979, 2886, 1682, 1444, 1342, 1259, 1231, 1191, 1163, 1098, 1041, 1021, 995, 972, 932, 906, 827, 729, 518. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.62 (d, $J = 46.8$ Hz, 1H), 3.62 – 3.51 (m, 4H), 2.08 – 1.97 (m, 2H), 1.97 – 1.85 (m, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -190.86 (d, $J = 46.8$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.97 (d, $J = 21.4$ Hz), 112.33 (d, $J = 30.3$ Hz), 76.93 (d, $J = 196.0$ Hz), 47.36, 46.15 (d, $J = 4.9$ Hz), 26.18 (d, $J = 1.3$ Hz), 23.49. MS (EI, m/z): 156 (M$^+$, 43.27), 55 (100.00), 98 (91.95), 56 (39.57), 70 (28.57), 41 (26.73), 42 (23.53), 58 (18.95). HRMS (EI): m/z calcd. For C$_7$H$_9$N$_2$OF (M$^+$) 156.0699, found 156.0700.

**Monofluorination of 1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone (1j)**

![Reaction Scheme](image)

$^1$BuONa (2.2 equiv, 317.1 mg, 3.3 mmol) and anhydrous ZnCl$_2$ (3.0 equiv, 613.4 mg, 4.5 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone (1j) (1.0 equiv, 435.5 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then SelectFluor (2.0 equiv, 1.0628g, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 2 h and quenched by 2M HCl until it became clear. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid $2j$ (414.9 mg) in 90% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J = 8.6$ Hz, 2H), 7.87 (d, $J = 7.9$ Hz, 2H), 7.73 (t, $J = 7.5$ Hz, 1H), 7.58 (t, $J = 7.5$ Hz, 2H), 6.98 (d, $J = 8.9$ Hz, 2H), 6.30 (d, $J = 48.0$ Hz, 1H), 3.91 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -179.34 (d, $J = 48.1$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 184.28 (d, $J = 17.3$ Hz), 165.07, 135.19, 134.62, 132.39 (d, $J = 2.8$ Hz), 129.82, 129.30, 126.92, 114.14, 100.20 (d, $J = 231.6$ Hz), 55.67. MS (EI, m/z): 308 (M$^+$, 5.84), 135 (100.00), 77 (22.91), 139 (15.48), 136 (9.43), 92 (6.84), 107 (6.36), 51 (6.33).

**Condition B**

**Monofluorination of 2-(benzylsulfonyl)benzothiazole (4a)**
LiHMDS (2.2 equiv, 552.2 mg, 3.3 mmol) and anhydrous ZnCl$_2$ (3.5 equiv, 715.6 mg, 5.25 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-(benzylsulfonyl)benzothiazole (4a) (1.0 equiv, 434.1 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH$_2$Cl$_2$/hexane to provide white solid 5a (305.4 mg) in 66% yield.  

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.37 – 8.24 (m, 1H), 8.12 – 7.90 (m, 1H), 7.76 – 7.59 (m, 4H), 7.59 – 7.45 (m, 3H), 6.63 (d, $J$ = 45.9 Hz, 1H).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -172.48 (d, $J$ = 45.9 Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.72, 152.80, 137.53, 131.60 (d, $J$ = 1.4 Hz), 128.87, 128.41 (d, $J$ = 0.8 Hz), 128.34, 127.88, 126.23 (d, $J$ = 19.4 Hz), 125.74, 122.34, 101.94 (d, $J$ = 223.1 Hz). MS (ESI, m/z): 308.0 (M + H$^+$), 329.9 (M + Na$^+$).

HRMS (ESI): m/z calcd. For C$_{14}$H$_{10}$F$_1$N$_1$Na$_1$O$_2$S$_2$ (M + Na$^+$) 330.00205, found 330.00308.

**Monofluorination of 2-(benzylsulfonyl)pyridine (4b)**

LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous ZnCl$_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-(benzylsulfonyl)pyridine (4d) (1.0 equiv, 349.6 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH$_2$Cl$_2$/hexane to provide white solid 5d (298.8 mg) in 79% yield. m.p.: 146-147 °C. IR (KBr): 3448, 3068, 2969, 1578, 1492, 1456, 1430, 1410, 1332, 1291, 1257, 1239, 1197, 1170, 1156, 1113, 1083, 1038, 1026, 990, 929, 850, 798, 777, 749, 733, 722, 695, 646, 616, 580, 557, 503, 444, 416, 403. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.84 (d, $J$ = 3.8 Hz, 1H), 8.16 (d, $J$ = 7.8 Hz, 1H), 8.00 (t, $J$ = 7.8 Hz, 1H), 7.62 (d, $J$ = 7.4 Hz, 3H), 7.56 – 7.40 (m, 3H), 6.70 (d, $J$ = 46.0 Hz, 2H).


1H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -175.32 (d, $J = 46.1$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.87, 150.60, 138.23, 131.13 (d, $J = 1.4$ Hz), 128.66, 128.30 (d, $J = 6.3$ Hz), 127.98, 99.49 (d, $J = 219.3$ Hz). MS (ESI, m/z): 251.9 (M + H$^+$), 274.0 (M + Na$^+$). HRMS (ESI): calcd. For C$_{12}$H$_{11}$F$_1$N$_1$O$_2$S (M + H$^+$) 252.04890, found 252.04934.

**Monofluorination of 2-((2-methylbenzyl)sulfonyl)benzothiazole (4c)**

LiHMDS (3.0 equiv, 753.0 mg, 4.5 mmol) and anhydrous ZnCl$_2$ (3.5 equiv, 715.6 mg, 5.25 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-((2-methylbenzyl)sulfonyl)benzothiazole (4c) (1.0 equiv, 455.1 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH$_2$Cl$_2$/hexane to provide white solid 5c (370.8 mg) in 77% yield. m.p.: 148–150 $^\circ$C. IR (KBr): 3029, 2987, 1464, 1348, 1317, 1154, 1125, 1113, 1045, 1022, 761, 737, 716, 697, 652, 612, 594, 562, 544, 513, 485, 464. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.43 – 8.17 (m, 1H), 8.16 – 7.95 (m, 1H), 7.73 – 7.58 (m, 3H), 7.43 (t, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.6$ Hz, 2H), 6.92 (d, $J = 45.7$ Hz, 1H), 2.60 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -170.51 (d, $J = 45.6$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.16, 152.84, 138.36 (d, $J = 4.7$ Hz), 137.53, 131.45 (d, $J = 1.7$ Hz), 131.08, 128.57 (d, $J = 7.8$ Hz), 128.36, 127.84, 126.39, 125.74, 124.86 (d, $J = 18.5$ Hz), 122.35, 99.10 (d, $J = 220.8$ Hz), 19.64. MS (EI, m/z): 321 (M$^+$, 0.97), 123 (100.00), 103 (12.96), 77 (12.29), 256 (12.10), 124 (9.32), 236 (9.14), 242 (8.18), 257 (7.41). HRMS (EI): m/z calcd. For C$_{15}$H$_{12}$NO$_2$FS$_2$ (M$^+$) 321.0294, found 321.0290.

**Monofluorination of (benzylsulfonyl)benzene (4d)**

LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous ZnCl$_2$ (1.0 equiv, 204.5 mg, 1.5 mmol) were dissolved in 12 mL THF. 5 minutes later, (benzylsulfonyl)benzene (4d) (1.0 equiv, 348.5 mg, 1.5 mmol) was added into the
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mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid 5c (282.2 mg) in 75% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J$ = 7.7 Hz, 2H), 7.69 (t, $J$ = 7.4 Hz, 1H), 7.53 (t, $J$ = 7.7 Hz, 2H), 7.49 – 7.42 (m, 1H), 7.42 – 7.33 (m, 4H), 6.07 (d, $J$ = 45.8 Hz, 1H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -175.77 (d, $J$ = 45.7 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.59, 134.53, 130.73, 129.92, 129.01, 128.40, 127.53 (d, $J$ = 6.7 Hz), 102.87 (d, $J$ = 220.8 Hz). MS (ESI, m/z): 268.0 (M + NH$_4^+$), 273.0 (M + Na$^+$), 288.9 (M + K$^+$).

Monofluorination of 1,2-diphenylethanone (4e)

LiHMDS (2.2 equiv, 552.2 mg, 3.3 mmol) and anhydrous ZnCl$_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, 1,2-diphenylethanone (4e) (1.0 equiv, 303.5 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid 5e (265.4 mg) in 83% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J$ = 7.8 Hz, 2H), 7.65 – 7.45 (m, 3H), 7.45 – 7.34 (m, 4H), 6.52 (d, $J$ = 48.6 Hz, 1H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -175.78 (d, $J$ = 48.7 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 194.24 (d, $J$ = 21.3 Hz), 134.20 (d, $J$ = 19.9 Hz), 133.97, 133.75, 129.61 (d, $J$ = 2.6 Hz), 129.07, 129.04, 128.66, 127.36 (d, $J$ = 5.5 Hz), 93.92 (d, $J$ = 185.7 Hz). MS (EI, m/z): 214 (M$^+$, 0.75), 105 (100.00), 77 (39.18), 109 (10.70), 51 (10.46), 106 (7.94), 83 (5.48), 50 (3.27), 78 (2.74).

Monofluorination of 1-methoxy-3-((phenylsulfonyl)methyl)benzene (4f)
LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous ZnCl$_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-methoxy-3-((phenylsulfonyl)methyl)benzene (4f) (1.0 equiv, 393.5 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide white solid 5f (281.5 mg) in 67% yield. m.p.: 122–123 °C. IR (KBr): 3064, 3017, 2962, 2933, 2833, 1610, 1588, 1488, 1458, 1448, 1435, 1323, 1291, 1272, 1234, 1151, 1085, 1071, 1060, 1036, 998, 905, 883, 768, 781, 719, 690, 650, 617, 572, 555, 543. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, 2H), 7.69 (t, $J = 7.3$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 2H), 7.28 (t, 1H), 7.04–6.90 (m, 2H), 6.83 (s, 1H), 6.04 (d, $J = 45.8$ Hz, 1H), 3.74 (s, 3H).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -175.17 (d, $J = 45.8$ Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.44, 134.57, 129.96, 129.68 (d, $J = 19.6$ Hz), 129.49, 129.00, 119.97 (d, $J = 6.8$ Hz), 116.96, 116.95, 112.31 (d, $J = 7.2$ Hz), 102.81 (d, $J = 221.3$ Hz), 55.31. MS (EI, m/z): 280 (M$^+$, 3.64), 139 (100.00), 96 (13.41), 109 (12.94), 77 (10.54), 140 (9.23), 154 (6.67), 51 (6.43), 107 (4.68). HRMS (EI): calcd. For C$_{14}$H$_{13}$O$_3$F$S$ (M$^+$) 280.0569, found 280.0572.

**Monofluorination of (allylsulfonyl)benzene (4g)**

LiHMDS (3.0 equiv, 753.0 mg, 4.5 mmol) and anhydrous ZnCl$_2$ (2.2 equiv, 449.8 mg, 3.3 mmol) were dissolved in 12 mL THF. 5 minutes later, (allylsulfonyl)benzene (4g) (1.0 equiv, 278.9 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide colourless liquid 4g (198.9 mg) in 66% yield. m.p.: 122–123 °C. IR (film): 3648, 3069, 1585, 1479, 1449, 1425, 1329, 1312, 1294, 1232, 1156, 1123, 1085, 1046, 1001, 984, 948, 823, 796, 756, 723, 701, 688, 651, 597, 548, 528, 509. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 7.9$ Hz, 2H), 7.69 (t, $J = 7.3$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 2H), 7.28 (t, 1H), 7.04–6.90 (m, 2H), 6.83 (s, 1H), 6.04 (d, $J = 45.8$ Hz, 1H), 5.68–5.46 (m, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -178.13 (dd, $J = 47.2$, 17.3 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.68, 129.89, 129.13, 125.09 (d, $J = 18.8$ Hz), 124.87, 124.76, 101.82 (d, $J = 219.7$ Hz). MS (ESI, m/z): 218.0 (M + NH$_4^+$), 222.9 (M + Na$^+$). HRMS (ESI): calcd. For C$_9$H$_9$F$_1$Na$_1$O$_2$S$_1$
Supporting Information

(M + Na<sup>+</sup>) 223.01995, found 223.02029.

**Monofluorination of 1-nitro-3-((phenylsulfonyl)methyl)benzene (4h)**

LiHMDS (2.2 equiv, 552.2 mg, 3.3 mmol) and anhydrous ZnCl<sub>2</sub> (1.8 equiv, 368.0 mg, 2.7 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-nitro-3-((phenylsulfonyl)methyl)benzene (4h) (1.0 equiv, 416.0 mg, 1.5 mmol) was added into the mixture under N<sub>2</sub> atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/hexane to provide 5h white solid (417.4 mg) in 94% yield. m.p.: 155 °C. IR(KBr): 3451, 3095, 2957, 1584, 1532, 1449, 1356, 1328, 1311, 1233, 1085, 1046, 903, 830, 781, 756, 738, 717, 688, 641, 580, 559, 510. <sup>1</sup>H NMR (400 MHz, DMSO-D<sub>6</sub>) δ 8.40 (d, J = 8.1 Hz, 1H), 8.23 (s, 1H), 7.95–7.84 (m, 4H), 7.81 (t, J = 7.9 Hz, 1H), 7.72 (t, J = 7.8 Hz, 2H), 7.21 (d, J = 44.6 Hz, 1H). <sup>19</sup>F NMR (282 MHz, DMSO-D<sub>6</sub>) δ -177.23 (d, J = 44.6 Hz). <sup>13</sup>C NMR (100 MHz, DMSO-D<sub>6</sub>) δ 147.90, 135.85, 134.68, 134.51 (d, J = 6.2 Hz), 130.83, 130.67 (d, J = 20.1 Hz), 130.17, 129.87, 126.09, 123.04 (d, J = 7.2 Hz), 100.62 (d, J = 216.0 Hz). MS (EI, m/z): 295 (M<sup>+</sup>, 3.12), 154 (100.00), 108 (37.07), 107 (19.31), 77 (16.23), 51 (9.66), 155 (8.35), 109 (3.83), 50 (3.18). HRMS (EI): calcd. For C<sub>13</sub>H<sub>10</sub>NO<sub>4</sub>F (M<sup>+</sup>) 295.0315, found 295.0318.

**Monofluorination of 2-((4-methylbenzyl)sulfonyl)pyridine (4i)**

LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous ZnCl<sub>2</sub> (1.5 equiv, 306.7 mg, 2.25 mmol) were dissolved in 12 mL THF. 5 minutes later, 2-((4-methylbenzyl)sulfonyl)pyridine (4i) (1.0 equiv, 371.0 mg, 1.5 mmol) was added into the mixture under N<sub>2</sub> atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>,
filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH$_2$Cl$_2$/hexane to provide white solid 5i (310.8 mg) in 78% yield. m.p.: 139-140 °C. IR (KBr): 3822, 3651, 3057, 2962, 1613, 1577, 1560, 1513, 1449, 1427, 1327, 1238, 1184, 1164, 1152, 1110, 1081, 1040, 1021, 990, 831, 787, 777, 752, 735, 619, 637, 606, 562, 549, 503. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.83 (d, $J = 3.9$ Hz, 1H), 8.16 (d, $J = 7.8$ Hz, 1H), 7.69 – 7.57 (m, 1H), 7.51 (d, $J = 7.9$ Hz, 2H), 7.35 – 7.22 (m, 2H), 6.67 (d, $J = 45.9$ Hz, 1H), 2.40 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) δ -174.23 (d, $J = 46.0$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.03, 150.59, 141.56, 138.19, 129.44, 128.31 (d, $J = 6.1$ Hz), 127.91, 124.63, 123.77 (d, $J = 19.5$ Hz), 99.53 (d, $J = 218.8$ Hz), 21.50. MS (ESI, m/z): 287.9 (M + Na$^+$), 552.9 (2M + Na$^+$). HRMS (ESI): calcd. For C$_{13}$H$_{12}$F$_1$N$_1$Na$_1$O$_2$S$_1$ (M + H$^+$) 288.04650, found 288.04662.

Monofluorination of 1-(benzylsulfonyl)-4-nitrobenzene (4j)

![Chemical Structure]

LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous ZnCl$_2$ (3.0 equiv, 613.4 mg, 4.5 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-(benzylsulfonyl)-4-nitrobenzene (4j) (1.0 equiv, 416.0 mg, 1.5 mmol) was added into the mixture under N$_2$ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with CH$_2$Cl$_2$/hexane to provide light green solid 5h (393.2 mg) in 89% yield. m.p.: 167-168 °C. IR (KBr): 3103, 3067, 3038, 2957, 2875, 1963, 1901, 1812, 1608, 1537, 1491, 1480, 1457, 1402, 1346, 1314, 1223, 1234, 1197, 1154, 1112, 1082, 1046, 1030, 1014, 861, 844, 790, 754, 739, 719, 696, 678, 649, 585, 555, 504, 467, 442, 422. $^1$H NMR (400 MHz, DMSO-D$_6$) δ 8.51 (d, $J = 8.7$ Hz, 2H), 8.16 (d, $J = 8.6$ Hz, 2H), 7.66 – 7.42 (m, 5H), 7.12 (d, $J = 44.5$ Hz, 1H). $^{19}$F NMR (282 MHz, DMSO-D$_6$) δ -175.41 (d, $J = 44.5$ Hz). $^{13}$C NMR (100 MHz, DMSO-D$_6$) δ 151.69, 140.88, 131.62, 131.56, 129.06, 128.54 (d, $J = 6.4$ Hz), 127.83 (d, $J = 19.3$ Hz), 125.15, 101.90 (d, $J = 215.1$ Hz). MS (ESI, m/z):312.9 (M + NH$_4^+$), 318.0 (M + Na$^+$). HRMS (ESI): calcd. For C$_{13}$H$_{10}$F$_1$N$_1$Na$_1$O$_2$S$_1$ (M + Na$^+$) 318.02068, found 318.02017.

Monofluorination of 1-((methylsulfonyl)methyl)-2-nitrobenzene (4k)
LiHMDS (2.5 equiv, 627.5 mg, 3.75 mmol) and anhydrous ZnCl₂ (3.5 equiv, 715.6 mg, 5.25 mmol) were dissolved in 12 mL THF. 5 minutes later, 1-((methylsulfonyl)methyl)-2-nitrobenzene (4k) (1.0 equiv, 322.8 mg, 1.5 mmol) was added into the mixture under N₂ atmosphere. The reaction was stirred for half an hour. Then NFSI (2.0 equiv, 947.5 mg, 3.0 mmol) was added into the mixture in a flash. The reaction was allowed at room temperature for 0.5 h and quenched by 20 mL 2M HCl. After extraction with EtOAc, the organic layer was dried over anhydrous Na₂SO₄, filtered and removed under vacuum. The crude product was purified by flash column chromatography on silica gel with EtOAc/hexane to provide light green solid 5k (329.7 mg) in 94% yield. m.p.: 151-152 °C. IR (KBr): 3114, 3032, 3017, 2937, 2870, 1611, 1580, 1527, 1482, 1443, 1410, 1350, 1330, 1315, 1300, 1237, 1188, 1143, 1091, 1057, 1040, 962, 887, 863, 838, 789, 760, 715, 684, 625, 534, 512, 467, 422, 409. ¹H NMR (400 MHz, DMSO-D₆) δ 8.21 (d, J = 8.3 Hz, 1H), 7.94 (t, J = 7.5 Hz, 1H), 7.83 (t, J = 7.0 Hz, 2H), 7.60 (d, J = 5.9 Hz, 1H), 3.28 (s, 3H). ¹⁹F NMR (282 MHz, DMSO-D₆) δ -178.60 (d, J = 45.9 Hz). ¹³C NMR (100 MHz, DMSO-D₆) δ 148.19 (d, J = 3.6 Hz), 134.55 (d, J = 1.0 Hz), 132.41, 129.13 (d, J = 12.3 Hz), 125.90, 122.68 (d, J = 20.8 Hz), 96.92 (d, J = 215.4 Hz), 38.50. MS (ESI, m/z): 250.9 (M + NH₄⁺), 255.9 (M + Na⁺). HRMS (ESI): calcd. For C₈H₆F₁N₁Na₁O₁S₁ (M + Na⁺) 256.00503, found 252.00490.

NMR experiments to gain insight into this ZnCl₂-mediated selective monofluorination
**Experiment A** Comparison of the tendency of deprotonation between (PhSO₂)₂CH₂ and (PhSO₂)₂CHF

(PhSO₂)₂CH₂ (29.6 mg, 0.1 mmol) and (PhSO₂)₂CHF (31.4 mg, 0.1 mmol) were dissolved in 2 mL THF-D₈ in the glove box. 19.5 mg mesitylene was added to the mixture as the internal standard. After 5 minutes, 0.5 mL of the solvent was taken out and indicated by ¹H NMR as a control experiment (entry 1A). Then LiHMDS (12.5 mg, 0.075 mmol) was added with extra 0.3 mL THF-D₈ to guarantee no remaining LiHMDS attached on the schlenk tube. 20 minutes later, 0.5 mL of the solvent was taken out indicated by ¹H NMR (entry 1B). The comparison of ¹H NMR peak integral between entry A and B showed that (PhSO₂)₂CH₂ was almost deprotonated, while (PhSO₂)₂CHF was barely deprotonated. We made the conclusion that (PhSO₂)₂CH₂ has a stronger tendency of deprotonation than (PhSO₂)₂CHF.
**Experiment B** Comparison of the tendency of deprotonation between (PhSO$_2$)$_2$CH$_2$ and (PhSO$_2$)$_2$CHF
(PhSO\(_2\))\(_2\)CH\(_2\) (29.6 mg, 0.1 mmol) and (PhSO\(_2\))\(_2\)CHF (31.4 mg, 0.1 mmol) were dissolved in 2 mL THF-D\(_8\) in the glove box. 16.4 mg mesitylene was added to the mixture as the internal standard. After 5 minutes, 0.5 mL of the solvent was taken out and indicated by \(^1\)H NMR and \(^{19}\)F NMR as a control experiment (entry 2A and 2D). Then NaH (5.7 mg, 0.225 mmol) was added. 20 minutes later, 0.5 mL of the solvent was taken out and indicated by \(^1\)H NMR and \(^{19}\)F NMR (entry 2B and 2E). NFSI (15.8 mg, 0.05 mmol) was added and the mixture was stirred for 30 minutes. The reaction was quenched by 36.0 μL CF\(_3\)COOH and added in 14.2 mg CF\(_3\)Ph as the internal standard. 0.5 mL of the solvent was taken out and indicated by \(^1\)H NMR and \(^{19}\)F NMR (entry 2C and 2F). The crude calculation of fluorinated capability between (PhSO\(_2\))\(_2\)CH\(_2\) and (PhSO\(_2\))\(_2\)CHF were as follows:

1. The comparison of \(^1\)H NMR peak integral between entry 2A and 2B, \(^{19}\)F NMR peak integral between entry 2D and 2E showed that (PhSO\(_2\))\(_2\)CH\(_2\) and (PhSO\(_2\))\(_2\)CHF were almost deprotonated.

2. The comparison of \(^1\)H NMR peak integral between entry 2A and 2C showed that after the reaction was quenched, the concentration of (PhSO\(_2\))\(_2\)CH\(_2\) was reduced by 15.7%, which meant 15.7% was converted into (PhSO\(_2\))\(_2\)CHF. The amount was 15.7%*(1.0 ml/2.0 ml)*0.1 mmol = 0.0079 mmol.

3. According to entry 2F of \(^{19}\)F NMR peak integral, the amount of generation of (PhSO\(_2\))\(_2\)CF\(_2\) was 14.2 mg/(146.11 g/mol)*0.86/2 = 0.0418 mmol

The reaction process was shown as above. We might as well compare the tendency for fluorination between (PhSO\(_2\))\(_2\)CH\(_2\) and (PhSO\(_2\))\(_2\)CHF through the average rate constants \(k_1\) and \(k_2\). The scope of \(k_2/k_1\) could be estimated as follows:
(1) If there were no further transformation of (PhSO₂)₂CHF into (PhSO₂)₂CF until the original (PhSO₂)₂CF had been fluorinated. We would get the maximum ratio of k₂/k₁, which was (0.0418 mmol/ 0.0079 mmol) = 5.3

(2) If further transformation of (PhSO₂)₂CHF into (PhSO₂)₂CF finished before (PhSO₂)₂CF had been fluorinated. We would get the minimum ratio of k₂/k₁. Since the amount of further transformation of (PhSO₂)₂CHF into (PhSO₂)₂CF could not pass 0.0079 mmol, the minimum ratio of k₂/k₁ was (0.05 mmol)/(0.05 mmol + 0.0079 mmol)* (0.0418 mmol/ 0.0079 mmol) = 4.6

The result demonstrated that (PhSO₂)₂CHF showed higher tendency for fluorination.

**Experiment C** Adding (PhSO₂)₂CH₂ into THF-D₈ under the optimized conditions (2.5 equiv of 'BuONa and 2.5 equiv of ZnCl₂)

(PhSO₂)₂CH₂ (59.2 mg, 0.2 mmol) and anhydrous ZnCl₂ (68.2 mg, 0.5 mmol) were dissolved in 2 mL THF-D₈ in the glove box. 17.8 mg mesitylene was added to the mixture as the internal standard. After 5 minutes, 0.5 mL of the solvent was taken out and indicated by ¹H NMR as a control experiment (entry 3A). Then 'BuONa (36.0 mg, 0.375 mmol) was added with extra 0.4 mL THF-D₈ to guarantee no remaining NaOtBu attached on the schlenk tube. 30 minutes later, 0.5 mL of the solvent was taken out indicated by ¹H NMR (entry 3B). The comparison of ¹H NMR peak integral between entry A and B showed that (PhSO₂)₂CH₂ was barely deprotonated.
Table A. Optimized Conditions for Monofluorination of 4a
(R¹ =EWG, R² =Phenyl, Alkenyl)

<table>
<thead>
<tr>
<th>entry</th>
<th>base (equiv)a</th>
<th>ZnCl₂ (equiv)a</th>
<th>time (h)</th>
<th>5a (%)b</th>
<th>6a (%)b</th>
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<tbody>
<tr>
<td>1</td>
<td>2.5 (tBuONa)</td>
<td>2.5</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>2.5 (tBuONa)</td>
<td>2.2</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2.5 (tBuONa)</td>
<td>1.8</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>2.5 (tBuONa)</td>
<td>3.0</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>2.5 (LiHMDS)c</td>
<td>2.5</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>2.5 (LiHMDS)c</td>
<td>2.5</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>2.5 (LiHMDS)</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>2.5 (LiHMDS)</td>
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<td>56</td>
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<tr>
<td>9</td>
<td>3.0 (LiHMDS)</td>
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<td>27</td>
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<tr>
<td>10</td>
<td>2.2 (LiHMDS)</td>
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<tr>
<td>11</td>
<td>1.8 (LiHMDS)</td>
<td>3.5</td>
<td>0.5</td>
<td>53</td>
<td>-</td>
</tr>
</tbody>
</table>

aThe equivalent is relative to that of 1a. bDetermined by ¹⁹F NMR analysis of the crude reaction mixture using PhCF₃ as an internal standard. cEntry 5 used SelectFluor as fluorination reagent, while entry 6 NFSI.

Table B. Screening of different bases.

<table>
<thead>
<tr>
<th>entry</th>
<th>basea</th>
<th>2a (%)b</th>
<th>3a (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₅ONa</td>
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<td>13</td>
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<tr>
<td>2</td>
<td>CH₃ONa</td>
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<tr>
<td>3</td>
<td>C₂H₅ONa</td>
<td>64</td>
<td>10</td>
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<tr>
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<td>tBuONa</td>
<td>73</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>NaHMDS</td>
<td>57</td>
<td>12</td>
</tr>
</tbody>
</table>
"The equivalent of base is 1 equiv relative to that of 1a. \(^b\) Determined by \(^{19}\)F NMR analysis of the crude reaction mixture using PhCF\(_3\) as an internal standard.

Table C. Screening of different bases in the presence of ZnCl\(_2\).

<table>
<thead>
<tr>
<th>entry</th>
<th>base (equiv)(^a)</th>
<th>ZnCl(_2) (equiv)(^a)</th>
<th>2a (%)(^b)</th>
<th>3a (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(^t)BuONa (2.5 equiv)</td>
<td>2.5</td>
<td>91</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>C(_6)H(_5)ONa (2.5 equiv)</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>CH(_3)ONa (2.5 equiv)</td>
<td>2.5</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>C(_2)H(_5)ONa (2.5 equiv)</td>
<td>2.5</td>
<td>39</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>C(_6)H(_5)ONa (2.5 equiv)</td>
<td>2.2</td>
<td>53</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>C(_2)H(_5)ONa (2.5 equiv)</td>
<td>1.8</td>
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<td>19</td>
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<td>7</td>
<td>NaHMDS (2.5 equiv)</td>
<td>2.5</td>
<td>15</td>
<td>39</td>
</tr>
</tbody>
</table>

\(^a\) The equivalent is relative to that of 1a. \(^b\) Determined by \(^{19}\)F NMR analysis of the crude reaction mixture using PhCF\(_3\) as an internal standard.

References

$^{13}$C NMR (100 MHz, CDCl$_3$)
Supporting Information

[Chemical structure image]

[1H NMR spectrum]

1H NMR (500 MHz, CDCl₃)
**Supporting Information**

![Chemical Structure](image)

**$^{19}$F NMR (300 MHz, CDCl$_3$)**

![NMR Spectrum](image)
Supporting Information

$^{19}F$ NMR (202 MHz, CDCl$_3$)
$^{19}F$ NMR (242 MHz, CDCl$_3$)
Supporting Information
Supporting Information