Supporting Information

Copper-Mediated Aerobic (Phenylsulfonyl)difluoromethylation of Arylboronic Acids with Difluoromethy Phenyl Sulfone

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1. General Information

Commercial reagents were used without further purification. DMF and NMP were distilled over CaH₂, and stored over activated molecular sieve. CuCl and CuI were purified according to reported procedures.¹ Difluoromethyl phenyl sulfone (1) was prepared using known procedure.² ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a 400 MHz NMR spectrometer. ¹H NMR spectroscopy chemical shifts were determined relative to internal Me₄Si (TMS) at δ 0.0 or to the signal of the residual protonated solvent CDCl₃ δ 7.26. ¹³C NMR spectroscopy chemical shifts were determined relative to internal TMS at δ 0.0. For the isolated compounds, ¹⁹F NMR spectroscopy chemical shifts were determined relative to CFCl₃ at δ 0.0; for the reaction mixtures, ¹⁹F NMR spectroscopy chemical shifts were determined relative to PhCF₃ at δ –62.0. Data for ¹H, ¹³C and ¹⁹F NMR spectra are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). FT-IR spectra were obtained with a Nicolet 380 spectrophotometer. Mass spectra were obtained on an Agilent LC-MS 1100 instrument. High resolution mass data were recorded on a Thermo Fisher Scientific LTQ FT Ultra instrument. GC–MS data were recorded on a Finnigan 4021 instrument. Elemental analysis was performed with Elementer Vario EL III instrument. Melting points were recorded on a SGW X-4 melting point apparatus and are uncorrected. All reactions were monitored by TLC or ¹⁹F NMR spectroscopy.

2. Preparation of “PhSO₂CF₂Cu” Generated from PhSO₂CF₂H

\[
\text{PhSO}_2\text{CF}_2\text{H} \quad \text{1 (1.6 equiv)} \quad \text{CuCl (0.2 mmol)} \quad \text{¹BuONa (2.0 equiv)} \quad \text{DMF, -20°C, 30 min} \quad \text{“PhSO}_2\text{CF}_2\text{Cu”}
\]

In a glovebox, CuCl (20 mg, 0.2 mmol) and ¹BuONa (38.5 mg, 0.4 mmol) were added to an oven-dried 10-mL Schlenk tube equipped with a stirring bar. The Schlenk tube was sealed with a septum and brought to the bench. DMF (1 mL) was added and
stirred vigorously at room temperature for 10 min, and then difluoromethyl phenyl sulfone (I) (45 μL, 0.32 mmol) was added at −20°C for 30 min under an argon atmosphere. The reaction was monitored by 19F NMR spectroscopy using PhCF3 (25 μL) as an internal standard (Figure S1).

**Figure S1.** Preparation of “PhSO2CF2Cu” generated from PhSO2CF2H

### 3. Transformation of “[PhSO2CF2Cu]−” into [PhSO2CF2Cu]

In a glovebox, CuCl (20 mg, 0.2 mmol) and tBuONa (38.5 mg, 0.4 mmol) were added to an oven-dried 10-mL Schlenk tube equipped with a stirring bar. The Schlenk tube was sealed with a septum and brought to the bench. DMF (1 mL) was added and stirred vigorously at rt for 10 min, and then difluoromethyl phenyl sulfone (I) (45 μL, 0.32 mmol) was added at −20°C for 30 min under an argon atmosphere. The reaction was monitored by 19F NMR spectroscopy using PhCF3 (25 μL) as an internal standard (Figure S2, a). The same sample was monitored again by 19F NMR spectroscopy at rt after 5 min (Figure S2, b).
4. The Stability of “PhSO₂CF₂Cu” under Different Conditions

In a glovebox, CuCl (50 mg, 0.5 mmol, 1.0 equiv) and t-BuONa (96 mg, 1.0 mmol) were added to an oven-dried 10-mL Schlenk tube equipped with a stirring bar. The Schlenk tube was sealed with a septum and brought to the bench. DMF (2 mL) was added and stirred vigorously at rt for 20 min, and then difluoromethyl phenyl sulfone (1) (113 μL, 0.8 mmol) and 18-crown-6 (132 mg, 0.5 mmol) was added at -20℃ for 30
min under an argon atmosphere. The reaction was monitored at rt after 5 min by $^{19}$F NMR spectroscopy using PhCF$_3$ (25.5 μL) as an internal standard (81% yield for “PhSO$_2$CF$_2$Cu”). The same sample was stored in refrigerator (about -12°C) and was monitored again by $^{19}$F NMR spectroscopy after 5 h, 13 h, 24 h, 37 h, 61 h, 109 h (Figure S3).

![Figure S3. The stability of “PhSO$_2$CF$_2$Cu” under different conditions](image)

5. (Phenylsulfonyl)difluoromethylation of Arylboronic Acids with “PhSO$_2$CF$_2$Cu” Generated from PhSO$_2$CF$_2$H

5.1 Screening of Reaction Conditions

In a glovebox, CuCl (50 mg, 0.5 mmol) and tBuONa (96 mg, 1.0 mmol) were added to an oven-dried 10-mL Schlenk tube equipped with a stirring bar. The Schlenk tube was sealed with a septum and brought to the bench. DMF (2 mL) was added and stirred vigorously at rt for 20 min, and then difluoromethyl phenyl sulfone (1) (113 μL, 0.8 mmol) was added at -20°C for 45 min under an argon atmosphere. The pregenerated “PhSO$_2$CF$_2$Cu” and additive were added respectively into
(2-(trifluoromethoxy)phenyl)boronic acid (2a) (purity 98%, 42 mg, 0.2 mmol, 1.0 equiv) in DMF (2 mL) for 4 h under an air atmosphere. The reaction mixture was monitored by $^{19}$F NMR spectroscopy using PhCF$_3$ as an internal standard.

**Table S1.** Screening of Reaction Conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>additive (equiv)</th>
<th>temp.</th>
<th>yield$^a$ of 3a (B) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−</td>
<td>0°C</td>
<td>16 (28)</td>
</tr>
<tr>
<td>2</td>
<td>−</td>
<td>rt</td>
<td>67 (18)</td>
</tr>
<tr>
<td>3</td>
<td>Et$_3$N·3HF (0.8)</td>
<td>rt</td>
<td>0 (0)</td>
</tr>
<tr>
<td>4</td>
<td>H$_2$O (0.5)</td>
<td>rt</td>
<td>68 (19)</td>
</tr>
<tr>
<td>5</td>
<td>H$_2$O (1.0)</td>
<td>rt</td>
<td>60 (21)</td>
</tr>
<tr>
<td>6</td>
<td>1,10-phen (1.0)</td>
<td>rt</td>
<td>0 (0)</td>
</tr>
<tr>
<td>7$^b$</td>
<td>18-crown-6 (2.5)</td>
<td>rt</td>
<td>68 (11)</td>
</tr>
<tr>
<td>8</td>
<td>K$_3$PO$_4$ (1.0)</td>
<td>rt</td>
<td>68 (18)</td>
</tr>
<tr>
<td>9</td>
<td>KOAc (1.0)</td>
<td>rt</td>
<td>60 (27)</td>
</tr>
<tr>
<td>10$^c$</td>
<td>Cu(OAc)$_2$ (5 mol %)</td>
<td>rt</td>
<td>69 (19)</td>
</tr>
<tr>
<td>11</td>
<td>AgNO$_3$ (0.5)</td>
<td>rt</td>
<td>72 (15)</td>
</tr>
<tr>
<td>12</td>
<td>AgNO$_3$ (1.0)</td>
<td>rt</td>
<td>73 (10)</td>
</tr>
<tr>
<td>13</td>
<td>AgNO$_3$ (0.5) + Cu(OAc)$_2$·H$_2$O (0.2)</td>
<td>rt</td>
<td>75 (7)</td>
</tr>
<tr>
<td>14$^d$</td>
<td>AgNO$_3$ (0.5) + Cu(OAc)$_2$·H$_2$O (0.2)</td>
<td>rt</td>
<td>77 (9)</td>
</tr>
<tr>
<td>15$^d$</td>
<td>AgNO$_3$ (0.6) + Cu(OAc)$_2$·H$_2$O (0.3)</td>
<td>rt</td>
<td>80 (7)</td>
</tr>
<tr>
<td>16$^e$</td>
<td>AgNO$_3$ (0.6) + Cu(OAc)$_2$·H$_2$O (0.3)</td>
<td>rt</td>
<td>0 (−)</td>
</tr>
</tbody>
</table>

$^a$Yields were determined by $^{19}$F NMR spectroscopy.

$^b$18-crown-6 was added after the addition of 1 in the generation of “PhSO$_2$CF$_2$Cu”.

$^c$The reaction was conducted for 3 h and 1 (3.2 equiv) was used.

$^d$The reaction was conducted with 0.4 mmol of 2a for 6 h.

$^e$The reaction was conducted under argon atmosphere.
5.2 (Phenylsulfonyl)difluoromethylation of Arylboronic Acids with “PhSO$_2$CF$_2$Cu” Generated from PhSO$_2$CF$_2$H

Method A

![Chemical structure with reagents and reaction conditions]

**Standard procedure for 0.2 mmol scale:**

In a glovebox, CuCl (50 mg, 0.5 mmol) and tBuONa (96 mg, 1.0 mmol) were added to an oven-dried 10-mL Schlenk tube equipped with a stirring bar. The Schlenk tube was sealed with a septum and brought to the bench. DMF (2 mL) was added and stirred vigorously at rt for 20 min, and then difluoromethyl phenyl sulfone (1) (113 μL, 0.8 mmol) was added at −20°C for 45 min under an argon atmosphere. The pregenerated “PhSO$_2$CF$_2$Cu”, AgNO$_3$ (20.5 mg, 0.12 mmol), and Cu(OAc)$_2$·H$_2$O (12 mg, 0.06 mmol) were added respectively into a solution of arylboronic acid (0.2 mmol, 1.0 equiv) in DMF (2 mL) at rt for 4 h under an air atmosphere. After addition of dichloromethane (5 mL), 1N HCl solution (1 mL), and H$_2$O (10 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane (3×5 mL). The combined organic layer was washed with brine (2×10 mL), dried over MgSO$_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel.

**Standard procedure for 0.4 mmol scale:**

In a glovebox, CuCl (100 mg, 1.0 mmol) and tBuONa (192 mg, 2.0 mmol) were added to an oven-dried 10-mL Schlenk tube equipped with a stirring bar. The Schlenk tube was sealed with a septum and brought to the bench. DMF (4 mL) was added and stirred vigorously at rt for 20 min, and then difluoromethyl phenyl sulfone (1) (113 μL, 1.6 mmol) was added at -20°C for 45 min under an argon atmosphere. The
pregenerated “PhSO$_2$CF$_2$Cu”, AgNO$_3$ (41 mg, 0.24 mmol), and Cu(OAc)$_2$·H$_2$O (24 mg, 0.12 mmol) were added respectively into a solution of arylboronic acid (0.4 mmol, 1.0 equiv) in DMF (4 mL) at rt for 6 h under an air atmosphere. After addition of dichloromethane (10 mL), 1N HCl solution (1.5 mL), and H$_2$O (10 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane (3×10 mL). The combined organic layer was washed with brine (2×10 mL), dried over MgSO$_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel.

Method B

\[
\begin{array}{c}
\text{R} - \text{B(OH)$_2$} \\
2e, 2i, 2q-2t \\
\xrightarrow{\text{PhSO$_2$CF$_2$Cu$^*$ (2.0–2.5 equiv)}} \\
\text{DMF, air, rt, 4 h} \\
\text{CF$_2$SO$_2$Ph} \\
3e, 3i, 3q-3t
\end{array}
\]

Standard procedure:

In a glovebox, CuCl (50 mg, 0.5 mmol) and tBuONa (96 mg, 1.0 mmol) were added to an oven-dried 10-mL Schlenk tube equipped with a stirring bar. The Schlenk tube was sealed with a septum and brought to the bench. DMF (2 mL) was added and stirred vigorously at rt for 20 min, and then difluoromethyl phenyl sulfone (1) (113 µL, 0.8 mmol) was added at -20°C for 45 min under an argon atmosphere. The pregenerated “PhSO$_2$CF$_2$Cu$^*$” was added into a solution of arylboronic acid (0.2 mmol, 1.0 equiv) in DMF (2 mL) at rt for 4 h under an air atmosphere. After addition of dichloromethane (5 mL), 1N HCl solution (1 mL), H$_2$O (10 mL) and the organic layer was separated and the aqueous layer was extracted with dichloromethane (3×5 mL). The combined organic layer was washed with brine (2×10 mL), dried over MgSO$_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel.

(Note: The generation of “PhSO$_2$CF$_2$Cu$^*$” is crucial for obtaining all products in good
yields.)

1-(Difluoro(phenylsulfonyl)methyl)-2-(trifluoromethoxy)benzene (3a)

For 0.4 mmol scale, the standard procedure of method A was followed to provide 3a by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (105 mg, 75%). M.p.: 93-95 °C. IR (KBr): 3092, 1609, 1493, 1449, 1341, 1251, 1172, 1061, 945, 773, 763, 598 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.38-7.44 (m, 2H, ArH), 7.60-7.64 (m, 3H, ArH), 7.70 (d, J = 7.6 Hz, 1H, ArH), 7.78 (t, J = 7.4 Hz, 1H), 7.99 (d, J = 8.0 Hz, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 119.2 (t, J = 21.5 Hz), 120.2 (q, J = 257.9 Hz), 120.9 (q, J = 1.5 Hz), 121.2 (t, J = 287.7 Hz), 126.4, 129.3, 130.8 (t, J = 6.9 Hz), 131.0, 132.7, 134.1, 135.5, 147.8 (q, J = 1.4 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ −56.6 (s, 3F), −98.4 (s, 2F). MS (ESI, m/z): 369.9 (M⁺NH₄)+, 374.8 (M⁺Na)+. HRMS (ESI): calcd. For C₁₄H₁₃O₂NF₅S (M⁺NH₄)+: 370.0527, found: 370.0531.

1-(Difluoro(phenylsulfonyl)methyl)-2-(trifluoromethyl)benzene (3b)

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3b by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (44 mg, 65%). M.p.: 117-118 °C. IR (KBr): 3067, 1584, 1448, 1351, 1304, 1284, 1172, 1037, 933, 772, 720, 685, 589, 544 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.64 (t, J = 7.6 Hz, 2H, ArH), 7.72-7.74 (m, 2H, ArH), 7.78 (t, J = 7.6 Hz, 1H, ArH), 7.90-7.98 (m, 2H, ArH), 8.03 (d, J = 7.8 Hz, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 121.5 (t, J = 288.0 Hz), 122.7 (q, J = 272.2 Hz), 125.1 (t, J = 22.6 Hz), 127.9 (q, J = 6.6 Hz), 129.4, 129.5 (q, J = 32.8 Hz), 131.0, 131.7 (t, J = 7.7 Hz), 131.8, 132.5, 132.7, 135.5. ¹⁹F NMR (376 MHz, CDCl₃): δ −58.0 (t, J = 18.8 Hz, 3F), −94.4 (q, J = 19.1 Hz,
2F). MS (ESI, m/z): 353.9 (M+NH₄)⁺, 358.8 (M+Na)⁺. HRMS (ESI): calcd. For C₁₄H₁₀O₂F₅S (M+H)⁺: 337.0311, found: 337.0316.

2-(Difluoro(phenylsulfonyl)methyl)benzaldehyde (3c)

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3c by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (39 mg, 66%). M.p.: 102-103 °C. IR (KBr): 3080, 2929, 1696, 1596, 1457, 1340, 1249, 1170, 1064, 939, 823, 761, 687, 595 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (t, J = 7.8 Hz, 2H, ArH), 7.72-7.74 (m, 3H, ArH), 7.81 (t, J = 7.6 Hz, 1H, ArH), 8.03 (d, J = 7.8 Hz, 2H, ArH), 8.18 (d, J = 6.0 Hz, 1H, ArH), 10.50 (s, 1H, CHO). ¹³C NMR (100 MHz, CDCl₃): δ 122.6 (t, J = 286.6 Hz), 127.1 (t, J = 21.5 Hz), 129.0, 129.5 (t, J = 8.8 Hz), 129.6, 131.0, 132.0, 132.8, 133.1, 135.9, 136.3, 190.4 (t, J = 5.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ −92.8 (s, 2F). MS (ESI, m/z): 296.8 (M+H)⁺, 313.9 (M+NH₄)⁺, 318.9 (M+Na)⁺. HRMS (ESI): calcd. For C₁₄H₁₁O₂F₂S (M+H)⁺: 297.0390, found: 297.0391.

2-(Difluoro(phenylsulfonyl)methyl)benzonitrile (3d)

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3d by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (41 mg, 70%). M.p.: 149-150 °C. IR (KBr): 3075, 2237, 1579, 1446, 1340, 1287, 1170, 1060, 939, 770, 711, 597, 543 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.67 (t, J = 8.0 Hz, 2H, ArH), 7.71-7.84 (m, 5H, ArH), 8.07 (d, J = 8.0 Hz, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 112.3 (t, J = 3.6 Hz), 116.1, 120.8 (t, J = 287.7 Hz), 128.9 (t, J = 21.8 Hz), 129.6, 130.1 (t, J = 6.5 Hz), 131.2, 131.8, 132.6, 132.7, 135.1, 136.0. ¹⁹F
NMR (376 MHz, CDCl₃): δ −99.6 (s, 2F). MS (ESI, m/z): 293.9 (M+H)⁺, 310.9 (M+NH₄)⁺, 315.8 (M+Na)⁺. HRMS (ESI): calcd. For C₁₄H₁₄O₂N₂F₂S (M+NH₄)⁺: 311.0656, found: 311.0660.

![CF₂SO₂Ph](image)

1-(Difluoro(phenylsulfonyl)methyl)-2-(methylsulfonyl)benzene (3e)

For 0.2 mmol scale, the standard procedure of method B was followed to provide 3e by column chromatography on silica gel (petroleum ether/EtOAc, 10:1 to 5:1, v/v) as a white solid (44 mg, 64%). M.p.: 164-165 °C. IR (KBr): 3118, 2937, 1583, 1454, 1353, 1319, 1249, 1169, 1143, 1047, 949, 775, 732, 686, 597 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.29 (s, 3H, CH₃), 7.65 (t, J = 7.6 Hz, 2H, ArH), 7.80-7.83 (m, 3H, ArH), 8.01-8.06 (m, 3H, ArH), 8.42-8.46 (m, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 45.0 (t, J = 4.3 Hz), 121.6 (t, J = 288.6 Hz), 125.3 (t, J = 22.6 Hz), 129.5, 131.1, 131.91 (t, J = 7.6 Hz), 131.92, 132.3, 133.1, 133.3, 135.8, 141.2. ¹⁹F NMR (376 MHz, CDCl₃): δ −90.9 (s, 2F). MS (ESI, m/z): 346.9 (M+H)⁺, 363.9 (M+NH₄)⁺, 368.8 (M+Na)⁺. HRMS (ESI): calcd. For C₁₄H₁₄O₂F₂S₂ (M+H)⁺: 347.0215, found: 347.0218.

![CF₂SO₂Ph](image)

1-(Difluoro(phenylsulfonyl)methyl)-2-fluorobenzene (3f)

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3f by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (43 mg, 75%). M.p.: 105-106 °C. IR (KBr): 3079, 1614, 1493, 1449, 1340, 1261, 1171, 1106, 1062, 939, 764, 687, 597, 545 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.16-7.20 (m, 1H, ArH), 7.26-7.30 (m, 1H, ArH), 7.55-7.64 (m, 4H, ArH), 7.77 (t, J = 7.6 Hz, 1H, ArH), 8.01 (d, J = 7.6 Hz, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 114.5 (td, ²J₉,ₐ = 22.2 Hz, ²J₉,₂ = 10.9 Hz), 117.2 (d, ²J₉,₂ = 21.2 Hz), 121.2 (td, ¹Jₙ,ₐ = 286.6
Hz, $^3J_{F-C} = 3.7$ Hz), 124.2 (d, $^3J_{F-C} = 3.6$ Hz), 129.3, 130.2 (t, $^3J_{F-C} = 6.6$ Hz), 131.0, 132.6, 134.7 (d, $^3J_{F-C} = 8.7$ Hz), 135.5, 160.7 (dt, $^1J_{F-C} = 257.4$ Hz, $^3J_{F-C} = 2.9$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): δ −99.7 (d, $J = 22.9$ Hz 2F), −110.8 (m, 1F). MS (ESI, m/z): 303.9 (M+NH$_4$)$^+$, 308.8 (M+Na)$^+$. HRMS (ESI): calcd. For C$_{13}$H$_{13}$O$_2$NF$_3$S (M+NH$_4$)$^+$: 304.0610, found: 304.0614.

![1-Chloro-2-(difluoro(phenylsulfonyl)methyl)benzene](image)

1-Chloro-2-(difluoro(phenylsulfonyl)methyl)benzene (3g)

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3g by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (42 mg, 70%). M.p.: 101-102 °C. IR (KBr): 3084, 1592, 1473, 1453, 1341, 1245, 1166, 1107, 1042, 938, 759, 728, 687, 596, 541 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.38-7.41 (m, 1H, ArH), 7.48-7.49 (m, 2H, ArH), 7.62 (t, $J = 7.8$ Hz, 2H, ArH), 7.67 (d, $J = 8.0$ Hz, 1H, ArH), 7.77 (t, $J = 7.2$ Hz, 1H, ArH), 8.00 (d, $J = 8.0$ Hz, 2H, ArH). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 121.6 (t, $J = 288.0$ Hz), 124.7 (t, $J = 20.7$ Hz), 126.7, 129.4, 131.0, 131.2 (t, $J = 7.6$ Hz), 132.2, 132.8, 133.4, 134.1 (t, $J = 2.5$ Hz), 135.5. $^{19}$F NMR (376 MHz, CDCl$_3$): δ −97.2 (s, 2F). MS (ESI, m/z): 319.8 (M+NH$_4$)$^+$, 324.7 (M+Na)$^+$. HRMS (ESI): calcd. For C$_{13}$H$_{13}$O$_2$NF$_3$S (M+NH$_4$)$^+$: 320.0315, found: 320.0318.

![1-Bromo-2-(difluoro(phenylsulfonyl)methyl)benzene](image)

1-Bromo-2-(difluoro(phenylsulfonyl)methyl)benzene (3h)

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3h by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (49 mg, 71%). M.p.: 119-121 °C. IR (KBr): 3067, 1590, 1450, 1340, 1245, 1164, 1108, 1029, 933, 755, 723, 686, 592 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): δ
1-(Difluoro(phenylsulfonyl)methyl)-2-nitrobenzene (3i)

For 0.2 mmol scale, the standard procedure of method B was followed to provide 3i by column chromatography on silica gel (petroleum ether/EtOAc, 15:1 to 10:1, v/v) as a white solid (44 mg, 70%). M.p.: 128-129 °C. IR (KBr): 3101, 1543, 1452, 1368, 1253, 1175, 1108, 1058, 939, 853, 765, 686, 599, 540 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.61-7.65 (m, 3H, ArH), 7.70-7.75 (m, 2H, ArH), 7.79 (t, J = 7.6 Hz, 1H, ArH), 7.91 (d, J = 7.2 Hz, 1H, ArH), 8.00 (d, J = 8.0 Hz, 2H, ArH).¹³C NMR (100 MHz, CDCl₃): δ 119.4 (t, J = 22.9 Hz), 120.4 (t, J = 288.0 Hz), 124.3, 129.5, 130.8 (t, J = 6.5 Hz), 131.1, 131.4, 132.2, 133.8, 135.9, 149.7.¹⁹F NMR (376 MHz, CDCl₃): δ −96.0 (s, 2F). MS (ESI, m/z): 363.7 (M+NH₄)⁺, 368.8 (M+Na)⁺. HRMS (ESI): calcd. For C₁₃H₁₃O₂NBrF₂S (M+NH₄)⁺: 363.9809, found: 363.9813.

1-(Difluoro(phenylsulfonyl)methyl)-3-nitrobenzene (3j)

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3j by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (43 mg, 69%). M.p.: 138-140 °C. IR (KBr): 3101, 1628, 1541, 1448, 1358, 1267, 1167, 1066, 978, 712, 595, 544 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (t, J = 7.8 Hz, 2H, ArH), 7.67 (t, J = 7.8 Hz, 2H, ArH), 8.00 (d, J = 8.0 Hz, 2H, ArH).
2H, ArH), 7.74 (t, J = 8.0 Hz, 1H, ArH), 7.81 (t, J = 7.6 Hz, 1H, ArH), 8.02-8.04 (m, 3H, ArH), 8.46 (d, J = 8.4 Hz, 1H, ArH), 8.52 (s, 1H, ArH). $^1$C NMR (100 MHz, CDCl$_3$): δ 120.6 (t, J = 285.8 Hz), 123.2 (t, J = 6.6 Hz), 127.2, 128.8 (t, J = 23.0 Hz), 129.6, 130.1, 131.0, 131.9, 133.7 (t, J = 5.4 Hz), 135.9, 148.2. $^{19}$F NMR (376 MHz, CDCl$_3$): δ −102.4 (s, 2F). MS (ESI, m/z): 335.9 (M+Na$^+$). HRMS (ESI): calcd. For C$_{13}$H$_{13}$O$_4$N$_2$F$_2$S (M+Na$^+$): 331.0554, found: 331.0559.

![1-(Difluoro(phenylsulfonyl)methyl)-4-nitrobenzene (3k)](image)

1-(Difluoro(phenylsulfonyl)methyl)-4-nitrobenzene (3k)

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3k by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (38 mg, 61%). M.p.: 153-155 °C. IR (KBr): 3122, 1613, 1537, 1448, 1344, 1272, 1166, 1094, 1065, 858, 731, 685, 594 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.67 (t, J = 7.6 Hz, 2H, ArH), 7.83 (t, J = 7.4 Hz, 1H, ArH), 7.90 (d, J = 8.8 Hz, 2H, ArH), 8.03 (d, J = 8.0 Hz, 2H, ArH), 8.37 (d, J = 8.8 Hz, 2H, ArH). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 120.8 (t, J = 285.9 Hz), 123.7, 129.4 (t, J = 5.8 Hz), 129.6, 131.0, 132.0, 132.8 (t, J = 22.3 Hz), 135.9, 150.4. $^{19}$F NMR (376 MHz, CDCl$_3$): δ −102.7 (s, 2F). MS (ESI, m/z): 335.8 (M+Na$^+$). HRMS (ESI): calcd. For C$_{13}$H$_{13}$O$_4$N$_2$F$_2$S (M+Na$^+$): 331.0554, found: 331.0559.

![5-(Difluoro(phenylsulfonyl)methyl)-2-fluoropyridine (3l)](image)

5-(Difluoro(phenylsulfonyl)methyl)-2-fluoropyridine (3l)

For 0.4 mmol scale, the standard procedure of method A was followed to provide 3l by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (82 mg, 71%). M.p.: 133-134 °C. IR (KBr): 3062, 1601, 1487, 1447, 1397, 1338, 1264, 1169, 1071, 952, 846, 753, 716, 685, 606 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): δ
7.11 (dd, \( J = 8.6 \) Hz, \( J = 2.6 \) Hz, 1H, ArH), 7.67 (t, \( J = 8.0 \) Hz, 2H, ArH), 7.82 (t, \( J = 7.6 \) Hz, 1H, ArH), 8.03 (d, \( J = 8.0 \) Hz, 2H, ArH), 8.11-8.15 (m, 1H, ArH), 8.53 (s, 1H, ArH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 110.0 (d, \( ^{2}J_{F-C} = 37.2 \) Hz), 120.7 (t, \( ^{1}J_{F-C} = 285.1 \) Hz), 121.2 (td, \( ^{2}J_{F-C} = 23.3 \) Hz, \( ^{4}J_{F-C} = 4.4 \) Hz), 129.6, 131.0, 131.8, 135.9, 141.1 (dt, \( ^{3}J_{F-C} = 9.5 \) Hz, \( ^{3}J_{F-C} = 4.7 \) Hz), 148.1 (dt, \( ^{3}J_{F-C} = 16.8 \) Hz, \( ^{3}J_{F-C} = 6.6 \) Hz), 165.8 (d, \( ^{1}J_{F-C} = 244.3 \) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) –61.5 (d, \( J = 4.1 \) Hz, 1F), –102.5 (s, 2F). MS (ESI, m/z): 287.8 (M+H\(^{+}\)). HRMS (ESI): calcd. For C\(_{12}\)H\(_{9}\)O\(_{2}\)NF\(_{3}\)S (M+H\(^{+}\)): 288.0296, found: 288.0301.

![2-Chloro-5-(difluoro(phenylsulfonyl)methyl)pyridine (3m)](image)

**2-Chloro-5-(difluoro(phenylsulfonyl)methyl)pyridine (3m)**

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3m by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (49 mg, 81%). M.p.: 137-139 \(^{\circ}\)C. IR (KBr): 3049, 1589, 1461, 1339, 1277, 1168, 1116, 1070, 842, 741, 685, 598 cm\(^{-1}\). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.48 (d, \( J = 8.4 \) Hz, 1H, ArH), 7.64 (t, \( J = 7.8 \) Hz, 2H, ArH), 7.79 (t, \( J = 7.4 \) Hz, 1H, ArH), 7.94 (dd, \( J = 8.4 \) Hz, \( J = 2.0 \) Hz, 1H, ArH), 8.00 (d, \( J = 8.0 \) Hz, 2H, ArH), 8.63 (s, 1H, ArH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 120.7 (t, \( J = 285.2 \) Hz), 122.2 (t, \( J = 23.0 \) Hz), 124.4, 129.6, 131.0, 131.7, 135.9, 138.1 (t, \( J = 5.1 \) Hz), 148.9 (t, \( J = 6.5 \) Hz), 155.8. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) –103.1 (s, 2F). MS (ESI, m/z): 303.8 (M+H\(^{+}\)). HRMS (ESI): calcd. For C\(_{12}\)H\(_{9}\)O\(_{2}\)NClF\(_{2}\)S (M+H\(^{+}\)): 304.0002, found: 304.0005.

![2-Bromo-5-(difluoro(phenylsulfonyl)methyl)pyridine (3n)](image)

**2-Bromo-5-(difluoro(phenylsulfonyl)methyl)pyridine (3n)**

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3n by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a
white solid (54 mg, 78%). M.p.: 138-139 °C. IR (KBr): 3045, 1582, 1456, 1339, 1276, 1169, 1097, 1068, 954, 844, 736, 685, 601, 541 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.63-7.67 (m, 3H, ArH), 7.79-7.85 (m, 2H, ArH), 8.01 (d, \(J = 8.0\) Hz, 2H, ArH), 8.61 (s, 1H, ArH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 120.7 (t, \(J = 285.8\) Hz), 122.6 (t, \(J = 22.9\) Hz), 128.2, 129.6, 131.0, 135.9, 137.6 (t, \(J = 5.1\) Hz), 146.8 (t, \(J = 1.8\) Hz), 149.1 (t, \(J = 6.2\) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) −68.3 (s, 3F), −103.4 (s, 2F). MS (ESI, m/z): 347.7 (M+H\(^+\)). HRMS (ESI): calcd. For C\(_{12}\)H\(_9\)O\(_2\)BrF\(_2\)S (M+H\(^+\)): 347.9495, found: 347.9500.

\[
\begin{align*}
\text{CF}_2\text{SO}_2\text{Ph} \\
\text{F}_3\text{C}
\end{align*}
\]

**5-(Difluoro(phenylsulfonyl)methyl)-2-(trifluoromethyl)pyridine (3o)**

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3o by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (55 mg, 82%). M.p.: 112-113 °C. IR (KBr): 3058, 1582, 1448, 1340, 1280, 1171, 1101, 1024, 956, 861, 723, 686, 609, 583, 539 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.67 (t, \(J = 7.8\) Hz, 2H, ArH), 7.81-7.87 (m, 2H, ArH), 8.04 (d, \(J = 8.0\) Hz, 2H, ArH), 8.23 (d, \(J = 8.4\) Hz, 1H, ArH), 8.99 (s, 1H, ArH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 121.0 (q, \(J = 273.2\) Hz), 120.2 (q, \(J = 2.1\) Hz), 120.3 (t, \(J = 285.8\) Hz), 126.2 (t, \(J = 23.2\) Hz), 129.6, 131.1, 131.6, 136.0, 137.5 (t, \(J = 5.5\) Hz), 148.9 (t, \(J = 6.2\) Hz), 151.5 (q, \(J = 35.2\)). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) −68.3 (s, 3F), −103.4 (s, 2F). MS (ESI, m/z): 337.8 (M+H\(^+\)). HRMS (ESI): calcd. For C\(_{13}\)H\(_9\)OF\(_2\)S (M+H\(^+\)): 338.0264, found: 338.0269.

\[
\begin{align*}
\text{CF}_2\text{SO}_2\text{Ph} \\
\text{Cl}
\end{align*}
\]

**2-Chloro-3-(difluoro(phenylsulfonyl)methyl)pyridine (3p)**

For 0.2 mmol scale, the standard procedure of method A was followed to provide
3p by column chromatography on silica gel (petroleum ether/EtOAc, 20:1 to 10:1, v/v) as a white solid (44 mg, 73%). M.p.: 142-143 °C. IR (KBr): 3080, 1582, 1449, 1410, 1341, 1284, 1176, 1116, 1046, 937, 808, 743, 687, 597, 547 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.40 (dd, J = 8.0 Hz, J = 4.8 Hz, 1H, ArH), 7.63 (t, J = 7.8 Hz, 2H, ArH), 7.78 (t, J = 7.4 Hz, 1H, ArH), 7.99 (d, J = 7.6 Hz, 2H, ArH), 8.02 (dd, J = 7.6 Hz, J = 2.0 Hz, 1H, ArH), 8.57 (d, J = 4.8 Hz, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 120.5 (t, J = 287.6 Hz), 122.0, 122.4 (t, J = 22.2 Hz), 129.6, 131.0, 132.2, 135.9, 140.3 (t, J = 7.0 Hz), 150.1, 152.7. ¹⁹F NMR (376 MHz, CDCl₃): δ −98.9 (s, 2F). MS (ESI, m/z): 303.8 (M+H)⁺. HRMS (ESI): calcd. For C₁₂H₉O₂NClF₂S (M+H)⁺: 304.0002, found: 304.0005.

\[
\begin{array}{c}
\text{O} \\
\text{CF₂SO₂Ph}
\end{array}
\]

2-(Difluoro(phenylsulfonyl)methyl)benzofuran (3q)

For 0.2 mmol scale, the standard procedure of method B was followed to provide 3q by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (39 mg, 63%). M.p.: 106-108 °C. IR (KBr): 3075, 1582, 1449, 1351, 1298, 1166, 1064, 979, 881, 753, 682, 626, 575 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.34 (m, 2H, ArH), 7.43 (t, J = 7.8 Hz, 1H, ArH), 7.56 (d, J = 8.0 Hz, 1H, ArH), 7.61 (t, J = 7.8 Hz, 2H, ArH), 7.67 (d, J = 8.0 Hz, 1H, ArH), 7.77 (t, J = 7.4 Hz, 1H, ArH), 8.02 (d, J = 7.2 Hz, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 112.2, 112.5 (t, J = 3.3 Hz), 117.4 (t, J = 283.3 Hz), 122.5, 124.1, 126.5, 127.2, 129.5, 131.0, 132.6, 135.7, 141.6 (t, J = 30.3 Hz), 156.1. ¹⁹F NMR (376 MHz, CDCl₃): δ −102.9 (s, 2F). MS (ESI, m/z): 325.9 (M+NH₄)⁺. HRMS (ESI): calcd. For C₁₅H₁₄O₃NF₂S (M+NH₄)⁺: 326.0655, found: 326.0657.

\[
\begin{array}{c}
\text{O} \\
\text{CF₂SO₂Ph}
\end{array}
\]
4-(Difluoro(phenylsulfonyl)methyl)dibenzo[\(b,d\)]furan (3r)

For 0.2 mmol scale, the standard procedure of method B was followed to provide 3r by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (43 mg, 60%). M.p.: 186-188 °C. IR (KBr): 3071, 1581, 1478, 1423, 1338, 1282, 1193, 1169, 1045, 966, 848, 758, 684, 599, 538 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.37 (t, \(J = 7.4\) Hz, 1H, ArH), 7.44-7.57 (m, 5H, ArH), 7.69 (t, \(J = 7.8\) Hz, 2H, ArH), 7.95 (d, \(J = 7.6\) Hz, 1H, ArH), 8.00 (d, \(J = 8.0\) Hz, 2H, ArH), 8.15 (d, \(J = 7.6\) Hz, 1H, ArH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 111.6 (t, \(J = 23.4\) Hz), 112.1, 120.7, 121.7 (t, \(J = 286.5\) Hz), 122.6, 122.7, 123.3, 125.0, 126.0, 127.0 (t, \(J = 7.4\) Hz), 128.1, 129.1, 131.1, 132.9, 135.3, 135.5 (t, \(J = 2.2\) Hz), 156.4. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -100.0 (s, 2F). MS (ESI, m/z): 375.9 (M\(+\)NH\(_4\))^\(+\), 380.9 (M+Na)^\(+\). HRMS (ESI): calcd. For C\(_{19}\)H\(_{16}\)O\(_3\)NF\(_2\)S (M\(+\)NH\(_4\))^\(+\): 376.0808, found: 376.0813.

![structure of 3r](image)

2-(Difluoro(phenylsulfonyl)methyl)benzo[\(b\)]thiophene (3s)

For 0.2 mmol scale, the standard procedure of method B was followed to provide 3s by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a pink solid (49 mg, 76%). M.p.: 141-143 °C. IR (KBr): 3066, 1581, 1523, 1448, 1346, 1238, 1167, 1036, 830, 751, 682, 600, 531 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.40-7.47 (m, 2H, ArH), 7.61 (t, \(J = 7.8\) Hz, 2H, ArH), 7.76 (t, \(J = 7.6\) Hz, 1H, ArH), 7.80 (s, 1H, ArH), 7.87 (d, \(J = 9.2\) Hz, 2H, ArH), 8.03 (d, \(J = 8.0\) Hz, 2H, ArH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 120.7 (t, \(J = 284.0\) Hz), 122.5, 125.2, 125.3, 126.7, 127.4 (t, \(J = 26.2\) Hz), 129.3 (t, \(J = 5.8\) Hz), 129.4, 131.0, 132.5, 135.5, 138.3, 141.6. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -93.6 (s, 2F). MS (ESI, m/z): 346.7 (M+Na)^\(+\). HRMS (ESI): calcd. For C\(_{13}\)H\(_{14}\)O\(_2\)NF\(_2\)S\(_2\) (M+Na)^\(+\): 342.0425, found: 342.0429.
2-(Difluoro(phenylsulfonyl)methyl)thiophene (3t)

For 0.2 mmol scale, the standard procedure of method B was followed to provide 3t by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (30 mg, 55%). M.p.: 99-100 °C. IR (KBr): 3131, 1525, 1424, 1339, 1259, 1171, 1093, 1033, 863, 719, 686, 602, 539 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.15-7.17 (m, 1H, ArH), 7.54-7.55 (m, 1H, ArH), 7.60-7.64 (m, 3H, ArH), 7.77 (t, J = 7.4 Hz, 1H, ArH), 8.01 (d, J = 7.6 Hz, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 120.8 (t, J = 283.6 Hz), 127.3 (t, J = 27.0 Hz), 127.7, 129.3, 130.9, 131.5, 132.0 (t, J = 5.5 Hz), 132.6, 135.4. ¹⁹F NMR (376 MHz, CDCl₃): δ −92.8 (s, 2F). MS (ESI, m/z): 291.8 (M+NH₄)⁺, 296.7 (M+Na)⁺. HRMS (ESI): calcd. For C₁₁H₁₂O₂NF₂S₂ (M+NH₄)⁺: 292.0269, found: 292.0272.

1-(Difluoro(phenylsulfonyl)methyl)-2-methoxybenzene (3u)

For 0.2 mmol scale, the standard procedure of method A was followed to provide 3u by column chromatography on silica gel (petroleum ether/EtOAc, 20:1, v/v) as a white solid (27 mg, 45%). M.p.: 83-84 °C. IR (KBr): 3045, 2847, 1604, 1585, 1495, 1450, 1333, 1300, 1247, 1162, 1045, 924, 753, 688, 596, 530 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.69 (s, 3H, OCH₃), 6.94 (d, J = 8.4 Hz, 1H, ArH), 7.02 (t, J = 7.4 Hz, 1H, ArH), 7.50 (t, J = 8.2 Hz, 2H, ArH), 7.56 (t, J = 7.4 Hz, 2H, ArH), 7.71 (t, J = 7.6 Hz, 1H, ArH), 7.93 (d, J = 7.6 Hz, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 55.9, 112.4, 115.1 (t, J = 20.8 Hz), 120.3, 122.5 (t, J = 287.3 Hz), 129.0, 130.2 (t, J = 7.6 Hz), 130.8, 133.8, 134.1, 135.0, 158.8 (t, J = 2.1 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ −97.5 (s, 2F). MS (ESI, m/z): 316.0 (M+NH₄)⁺. Anal. calcd. For C₁₄H₁₂F₂O₃S (%): C, 56.37; H, 4.05. Found: C, 56.39; H, 3.95.
6. Synthesis of Difluoromethylated Aromatics by Reductive Desulfonylation

![Chemical structure](image)

**Standard procedure:**

The reductive desulfonylation procedure was according to our previous report.[3] HOAc/NaOAc (1:1) solution (1.5 mL) was added into a suspension of 3 (0.2 mmol, 1.0 equiv), Magnesium turning (72 mg, 3.0 mmol) in DMF (2 mL) at rt under an argon atmosphere. The reaction was monitored by TLC until the starting material 3 was consumed completely.

1-(Difluoromethyl)-2-(trifluoromethoxy)benzene (4a)

According to standard procedure, after stirring at rt for 3 h, PhCF\(_3\) (26.5 \(\mu\)L,) as an internal standard was added into the reaction mixture, and monitored by \(^{19}\)F NMR spectroscopy in 76% yield. Characterization of 4a: \(^{19}\)F NMR (376 MHz, unlocked): \(\delta\) −56.9 (s, 3F), −113.2 (d, \(J = 54.5\) Hz, 2F). GC−MS (EI): \(m/z = 212.2\).

1-(Difluoromethyl)-2-fluorobenzene (4b)[4]

According to standard procedure, after stirring at rt for 3 h, PhCF\(_3\) (26 \(\mu\)L) as an internal standard was added into the reaction mixture, and monitored by \(^{19}\)F NMR spectroscopy in 86% yield. Characterization of 4b: \(^{19}\)F NMR (376 MHz, unlocked): \(\delta\) −113.1 (dd, \(^2J_{H-F} = 54.3\) Hz, \(^4J_{H-F} = 3.9\) Hz, 2F), −119.4 (m, 1F). GC−MS (EI): \(m/z =\)
2-(Difluoromethyl)benzo[b]thiophene (4c)

HOAc/NaOAc (1:1) solution (1.5 mL) was added into a suspension of 3s (0.2 mmol, 1.0 equiv), Magnesium turning (72 mg, 3.0 mmol) in DMF (2 mL) at rt under an argon atmosphere. After stirring at rt for 3 h, dichloromethane (5 mL), and H₂O (10 mL) was added, and then the organic layer was separated and the aqueous layer was extracted with dichloromethane (3×5 mL). The combined organic layer was washed with brine (2×10 mL), dried over MgSO₄, filtered and concentrated in vacuo to obtain the crude product. The crude product was purified by a flash column chromatography on silica gel using pentane as eluent to afford 4c as light yellow oil (25 mg, 68%). IR (KBr): 2924, 2852, 1461, 1369, 1260, 1150, 1061, 1036, 801, 745, 689 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 6.93 (t, J = 55.8 Hz, 1H, CF₂H), 7.41-7.43 (m, 2H, ArH), 7.53 (s, 1H, ArH), 7.82-7.89 (m, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 111.9 (t, J = 236.2 Hz), 122.7, 124.5 (t, J = 7.3 Hz), 124.7, 124.9, 125.9, 136.4 (t, J = 25.5 Hz), 138.3, 140.2. ¹⁹F NMR (376 MHz, CDCl₃): δ −104.0 (dd, 2J_H-F = 52.3 Hz, 4J_H-F = 2.6 Hz, 2F). MS (EI, m/z): 184 (M⁺, 100). HRMS (EI): calcd. For C₉H₆F₂S (M⁺): 184.0158, found: 184.0156.

(Note: The product 4c was isolated in a moderate yield because of its volatility.)

7. References

8. $^{19}$F, $^1$H and $^{13}$C NMR Spectra of isolated Products
\[ \text{CF}_2\text{SO}_2\text{Ph} \]

3a

\[ \text{OCF}_3 \]

\[ {^{13}}\text{C NMR (CDCl}_3, \text{ 100 Mz)} \]

\[ \text{CF}_2\text{SO}_2\text{Ph} \]

3b

\[ \text{CF}_3 \]

\[ {^{19}}\text{F NMR (CDCl}_3, \text{ 376 Mz)} \]
$^{13}$C NMR (CDCl$_3$, 100 MHz)

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

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

$^{13}$C NMR (CDCl$_3$, 100 Mz)
$^{19}$F NMR (CDCl$_3$, 376 MHz)

$^1$H NMR (CDCl$_3$, 400 MHz)
19F NMR (CDCl₃, 376 MHz)

1H NMR (CDCl₃, 400 MHz)
$\text{CF}_2\text{SO}_2\text{Ph}$

3k

$^{19}\text{F NMR (CDCl}_3, 376 \text{ Mz)}$

$\text{O}_2\text{N}$

$\text{CF}_2\text{SO}_2\text{Ph}$

3k

$^1\text{H NMR (CDCl}_3, 400 \text{ Mz)}$
$^{13}$C NMR (CDCl₃, 100 MHz)

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

$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{19}$F NMR (CDCl$_3$, 376 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)

$^{19}$F NMR (CDCl$_3$, 376 MHz)
$\text{CF}_2\text{SO}_2\text{Ph}$

$3q$

$^{13}\text{C NMR (CDCl}_3, 100 \text{ Mz)}$

$\text{CF}_2\text{SO}_2\text{Ph}$

$3r$

$^{19}\text{F NMR (CDCl}_3, 376 \text{ Mz)}$
$^{19}$F NMR (CDCl$_3$, 376 Mz)

$^1$H NMR (CDCl$_3$, 400 Mz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)

$^{19}$FNMR (CDCl$_3$, 376 MHz)
$^{19}$F NMR (CDCl$_3$, 376 MHz)

$^1$H NMR (CDCl$_3$, 400 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)

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

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