Supporting Information

Pyridine-catalyzed Desulfonative Borylation of Benzyl Sulfones

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1. General:

Unless otherwise noted, all manipulations were performed under an atmosphere of dry argon or nitrogen. Reactions were performed in oven-dried vials with Teflon-lined caps or flame-dried flasks. All solvents were distilled from either calcium hydride or sodium metal prior to use. C₆H₅CF₃ was stored over molecular sieves (4Å) in a nitrogen-atmosphere glove box. Work-up purifications were performed using commercial reagent-grade solvents. Commercial reagents were purchased from Sigma-Aldrich, Alfa Aesar, Oakwood Chemical, Frontier Scientific, or Cambridge Isotopes Laboratories and used as received with the following exceptions: sodium methoxide was prepared from dry methanol and sodium metal. Thin layer chromatography was performed on aluminum-backed silica plates and visualized by UV (254, 365 nm). All GC-MS analyses were performed using an Agilent Technologies 5975CVL-MSD (triple axis detector) with a capillary measuring 30 m by 250 µm by 0.25 µm nominal, 250 inlet, splitless detector. High-resolution mass spectra (HRMS) were obtained from a Thermo Fisher Scientific Exactive (ESI) or an Applied Biosystems/MDS Sciex QSTar XL QqTOF instrument (EI). NMR spectra were recorded on a Bruker Avance 400 (¹H: 400.13, ¹³C: 100.62) instrument operating at the denoted spectrometer frequency given in mega Hertz (MHz) for the specified nucleus. All NMR samples were prepared using CDCl₃. To specify the signal multiplicity, the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, and m = multiplet; br indicates a broad resonance. Shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an external standard for ¹H- and ¹³C NMR spectra and calibrated against the solvent residual peak.
2: Preparation of Diarylmethyl Sulfones

General Procedure 1:

To a flame-dried flask containing a magnetic stir bar under an atmosphere of dry argon was added the diaryl methyl alcohol (1.0 equiv), TsOH-5H2O (1.5 equiv), NaSO2Ph (1.5 equiv), and dry DCM (0.5 M). The reaction mixture was stirred at room temperature for 16 h. Upon reaction completion, the reaction mixture was diluted DCM and water was added. The organic phase was extracted with DCM, washed with 1 M NaOH, brine, dried over sodium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography or recrystallization.

Sulfone 1a

The following compound was synthesized with alcohol (1.0 g, 5.4 mmol), TsOH-5H2O (1.5 g, 1.5 equiv), NaSO2Ph (1.1 mg, 1.2 equiv) and DCM (27 mL, 0.2 M). Purification by recrystallization from DCM/hexane gave 1a (1.2 g, 71%) as a colorless solid.

\[ ^1H\text{ NMR (400 MHz, CDCl}_3): \delta 5.31 (s, 1H), 7.30-7.38 (m, 8H), 7.49-7.56 (m, 5H), 7.62-7.64 (m, 2H). \]

\[ ^13C\text{ NMR (101 MHz, CDCl}_3): \delta 76.4, 128.56, 128.59, 128.6, 128.9, 129.9, 132.9, 133.4, 138.2. \]

HRMS (ESI): m/z calcd for \([C_{19}H_{16}O_2S+Na]: 331.0763, \text{ found } 331.0760.\]

Sulfone 1b

The following compound was synthesized with alcohol (1.6 g, 2 mmol), TsOH-5H2O (12.8 g, 1.75 equiv), NaSO2Ph (1.3 g, 1.15 equiv) and DCM (50 mL, 0.15 M). Purification by recrystallization from CHCl3/MeOH gave 1b (2.0 g, 80%) as a colorless solid.

\[ ^1H\text{ NMR (400 MHz, CDCl}_3): \delta 3.78 (s, 3H), 5.26 (s, 1H), 6.84 (dt, J = 2.2, 8.8 Hz, 2H), 7.29-7.33 (m, 3H), 7.36 (tt, J = 1.8, 7.8 Hz, 2H), 7.45 (dt, J = 2.2, 8.8 Hz, 2H), 7.49-7.55 (m, 3H), 7.62-7.63 (m, 2H). \]

\[ ^13C\text{ NMR (101 MHz, CDCl}_3): \delta 55.2, 75.8, 114.1, 124.7, 128.4, 128.5, 128.6, 128.9, 129.8, 131.2, 133.2, 133.3, 138.3, 159.8. \]
**HRMS (ESI):** \( m/z \) calcd for \([C_{20}H_{18}O_3S+Na]\): 361.0869, found 361.0869.

**Sulfone 1d**

The following compound was synthesized with alcohol (456 mg, 2 mmol), TsOH-5H.O (570 mg, 1.5 equiv), NaSO\(_2\)Ph (492 mg, 1.5 equiv) and DCM (10 mL, 0.5 M).

Purification by recrystallization from CHCl\(_3\)/hexane gave **1d** (434 mg, 62%) as a colorless solid.

**\(^{1}H\) NMR (400 MHz, CDCl\(_3\)):** \( \delta \) 5.22, 5.93 (d, \( J = 1.2 \) Hz, 1H), 5.95 (d, \( J = 1.2 \) Hz, 1H), 6.71 (d, \( J = 8.8 \) Hz, 1H), 6.89 (dd, \( J = 1.8, 4.1 \) Hz, 1H), 7.15 (d, \( J = 1.7 \) Hz, 1H), 7.29-7.32 (m, 3H), 7.39 (t, \( J = 8.2 \) Hz, 2H), 7.49-7.54 (m, 3H), 7.65 (m, 2H).

**\(^{13}C\) NMR (101 MHz, CDCl\(_3\)):** \( \delta \) 76.0, 101.3, 108.3, 110.0, 124.1, 126.2, 128.5, 128.6, 128.7, 128.9, 129.7, 133.1, 133.4, 138.2, 147.8, 147.9.

**HRMS (ESI):** \( m/z \) calcd for \([C_{20}H_{16}O_4S+Na]\): 375.0662, found 375.0677.

**Sulfone 1e**

The following compound was synthesized with alcohol (1.1 g, 4.7 mmol), TsOH-5H.O (1.2 g, 1.5 equiv), NaSO\(_2\)Ph (919 mg, 1.2 equiv) and DCM (0.2 M). Purification by recrystallization from AcOEt/hexane gave **1e** (933 mg, 55%) as a colorless solid.

**\(^{1}H\) NMR (400 MHz, CDCl\(_3\)):** \( \delta \) 5.50, 7.32-7.36 (m, 5H), 7.47-7.51 (m, 3H), 7.60-7.70 (m, 5H), 7.79-7.82 (m, 3H), 8.01 (s, 1H).

**\(^{13}C\) NMR (101 MHz, CDCl\(_3\)):** \( \delta \) 76.5, 126.3, 126.6, 127.0, 127.5, 128.2, 128.4, 128.60, 128.64, 128.7, 129.0, 129.6, 130.0, 130.4, 132.9, 133.0, 133.5, 138.2.

**HRMS (ESI):** \( m/z \) calcd for \([C_{23}H_{18}O_3S+Na]\): 381.0920, found 381.0932.

**Sulfone 1f**

The following compound was synthesized with alcohol (395 mg, 2.0 mmol), TsOH-5H.O (570 mg, 1.5 equiv), NaSO\(_2\)Ph (492 mg, 1.5 equiv) and DCM (10 mL, 0.2 M). Purification by recrystallization from AcOEt/hexane gave **1f** (228 mg, 35%) as a colorless solid.

**\(^{1}H\) NMR (400 MHz, CDCl\(_3\)):** \( \delta \) 2.31 (s, 3H), 5.26 (s, 1H), 7.13 (d, \( J = 7.6 \) Hz, 1H), 7.21 (t, \( J = 7.6 \) Hz, 1H), 7.26-7.39 (m, 7H), 7.50-7.54 (m, 3H), 7.61-7.64 (m, 2H).

**\(^{13}C\) NMR (101 MHz, CDCl\(_3\)):** \( \delta \) 21.4, 76.5, 126.9, 128.52, 128.54, 128.55, 128.6, 129.0, 129.4, 129.9,
HRMS (ESI): \textit{m/z} calcd for [C_{20}H_{18}O_S+Na]: 345.0931, found 345.0929.

**Sulfone 1g**

The following compound was synthesized with alcohol (484 mg, 2.4 mmol), Sulfone (492 mg, 1.25 equiv), TsOH·5H_2O (570 mg, 1.25 equiv), and DCM (10 mL, 0.24 M). Purification by recrystallization from CH_2Cl_2/hexane gave 1g (349 mg, 44\%) as a pale yellow solid.

\textbf{1H NMR (400 MHz, CDCl_3):} δ 2.11 (s, 3H), 5.60 (s, 1H), 7.06 (d, \textit{J} = 7.5 Hz, 1H), 7.20 (dt, \textit{J} = 3.1, 7.4 Hz, 1H), 7.28-7.33 (m, 4H), 7.38 (t, \textit{J} = 8.4 Hz, 2H), 7.47-7.56 (m, 3H), 7.62-7.65 (m, 2H).

\textbf{13C NMR (101 MHz, CDCl_3):} δ 19.7, 71.3, 126.5, 128.5, 128.5, 128.6, 128.9, 130.3, 130.7, 131.8, 132.7, 133.5, 136.8, 138.7.

**HRMS (ESI):** \textit{m/z} calcd for [C_{20}H_{18}O_S+Na]: 345.0920, found 345.0925.

**Sulfone 1h**

The following compound was synthesized with alcohol (428 mg, 2 mmol), TsOH·5H_2O (570 mg, 1.5 equiv), NaSO_2Ph (492 mg, 1.5 equiv), and DCM (10 mL, 0.5 M). Purification by recrystallization from CH_2Cl_2/hexane gave 1h (382 mg, 56\%) as a colorless solid.

\textbf{1H NMR (400 MHz, CDCl_3):} δ 3.51 (s, 3H), 6.10 (s, 1H), 6.68 (d, \textit{J} = 8.3 Hz, 1H), 7.03 (dt, \textit{J} = 1.0, 7.6 Hz, 1H), 7.25 (dd, \textit{J} = 1.7, 8.6 Hz, 1H), 7.30-7.37 (m, 5H), 7.35 (tt, 1.3, 7.5 Hz, 1H), 7.58-7.64 (m, 4H);

\textbf{13C NMR (101 MHz, CDCl_3):} δ 55.4, 66.5, 110.5, 120.7, 121.8, 128.2, 128.3, 128.5, 128.9, 129.7, 130.0, 130.2, 133.1, 133.2, 138.8, 156.7.

**HRMS (ESI):** \textit{m/z} calcd for [C_{20}H_{18}O_S+Na]: 361.0869, found 361.0873.

**Sulfone 1i**

The following compound was synthesized with alcohol (468 mg, 2 mmol), NaSO_2Ph (570 mg, 1.5 equiv), TsOH·5H_2O (492 mg, 1.5 equiv), and DCM (0.5 M). Purification by recrystallization from AcOEt/hexane gave 1i (220 mg, 30\%) as a colorless solid.

\textbf{1H NMR (400 MHz, CDCl_3):} δ 6.25 (s, 1H), 7.27-7.34 (m, 5H), 7.39-7.42 (m, 2H), 7.46 (tt, \textit{J} = 1.2, 7.5 Hz, 1H), 7.51-7.54 (m, 2H), 7.59 (t, \textit{J} = 8.0 Hz, 1H), 7.65-7.68 (m, 2H), 7.80-7.85 (m, 3H), 8.50 (dd, \textit{J} = 0.8, 7.4 Hz, 1H).
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 70.7, 121.9, 125.2, 125.6, 126.7, 127.3, 128.5, 128.60, 128.62, 128.9, 129.0, 129.1, 129.2, 130.3, 131.4, 133.0, 133.5, 133.9, 138.4.

HRMS (ESI): $m/z$ calcd for [$C_{23}$H$_{18}$O$_2$S$+$Na]: 381.0920, found 381.0920.

**Sulfone 1j**

The following compound was synthesized with alcohol (950 mg, 5 mmol), NaSO$_2$Ph (984 mg, 1.2 equiv), TsOH-5H$_2$O (1.3 g, 1.5 equiv), and DCM (0.2 M). Purification by recrystallization from MeOH gave 1j (809 mg, 52%) as a colorless solid.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.56, 6.98 (dd, $J$ = 3.6, 7.4 Hz, 1H), 7.24 (m, 1H), 7.31-7.39 (m, 6H), 7.50-7.55 (m, 3H), 7.61-7.64 (m, 2H)

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 72.2, 126.9, 127.1, 128.5, 128.6, 129.0, 129.1, 129.6, 130.0, 132.4, 133.6, 133.8, 137.4.

HRMS (ESI): $m/z$ calcd for [$C_{17}$H$_{14}$O$_2$S$_2$$+$Na]: 337.0327, found 337.0332.

**Sulfone 1k**

To a flame-dried flask containing a magnetic stir bar under an atmosphere of dry argon was added the 4,4’-dimethoxybenzophenon (1.0 g, 4.1 mmol), NaBH$_4$ (188 mg, 1.2 equiv) and methanol (21 mL). Upon reaction completion, the reaction mixture was quenched with sat. NaHCO$_3$aq and extracted with AcOEt. The organic phase was dried over sodium sulfate and concentrated in vacuo. The obtained alcohol was used without further purification, and reacted with NaSO$_2$Ph (773 mg, 1.15 equiv), TsOH-5H$_2$O (1.4 g, 1.75 equiv) in DCM (0.15 M). Purification by recrystallization from MeOH gave 1k (880 mg, 58%) as a colorless solid.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.77 (s, 6H), 5.22 (s, 1H), 6.82-6.85 (m, 4H), 7.36 (t, $J$ = 7.8 Hz, 2H), 7.41-7.45 (m, 4H), 7.50 (dt, $J$ = 0.9, 7.5 Hz, 1H), 7.61-7.64 (m, 2H)

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 55.2, 75.1, 114.0, 125.0, 128.5, 128.9, 131.1, 132.3, 138.3, 159.7.

HRMS (ESI): $m/z$ calcd for [$C_{21}$H$_{20}$O$_4$S$_2$+Na]: 391.0975, found 391.0982.

**Sulfone 1n**

The following compound was synthesized with alcohol (910 mg, 5 mmol), TsOH-5H$_2$O (1.4 g, 1.5 equiv), NaSO$_2$Ph (984 mg, 1.2 equiv), and DCM (25 mL, 0.2 M).
Purification by column chromatography on silica gel (EtOAc:hexane = 1:1) gave 1m (607 mg, 40%) as a colorless solid.

**1H NMR (400 MHz, CDCl3):** δ 0.04-0.10 (m, 1H), 0.32-0.39 (m, 1H), 0.57-0.64 (m, 1H), 0.72-0.79 (m, 1H), 1.48-1.56 (m, 1H), 3.27 (d, J = 10.6 Hz, 1H), 7.20 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.47 (t, J = 7.7 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H) 7.70-7.73 (m, 2H)

**13C NMR (101 MHz, CDCl3):** δ 3.6, 7.5, 10.5, 75.3, 128.6, 128.8, 129.1, 131.1, 131.8, 133.6, 134.8, 138.0.

**HRMS (ESI):** m/z calcd for [C16H15O2SCl+Na]: 329.0374, found 329.0375.

**Synthesis of 1c**

The following compound was synthesized with alcohol (456 mg, 2 mmol), 2-(phenylsulfonyl)acetonitrile (506 mg, 1.2 equiv), BF3·Et2O (0.12 mL, 0.3 equiv), and CH3CN (3 mL, 0.3 M). Purification by recrystallization from EtOAc/hexane gave 1c (260 mg, 51%) as a colorless solid.

**1H NMR (400 MHz, CDCl3):** δ 5.28 (s, 1H), 7.28-7.33 (m, 5H), 7.38 (t, J = 7.8 Hz, 2H), 7.47-7.55 (m, 5H), 7.62-7.63 (m, 2H)

**13C NMR (101 MHz, CDCl3):** δ 75.6, 128.70, 128.75, 128.79, 128.8, 128.9, 129.8, 131.2, 131.4, 132.5, 133.6, 134.8, 137.9.

**HRMS (ESI):** m/z calcd for [C19H15ClO2+Na]: 365.0374, found 365.0365.

**Sulfone 1l**

A flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added benzyl sulfone (696 mg, 3 mmol) and dry THF (10 mL). A solution of NaHMDS (605 mg, 1.05 equiv) in dry THF (3 mL) was added drop wise to the reaction mixture, at -78 °C under argon. After 15 min, a solution of methyl iodide (0.21 mL, 1.05 equiv) in dry THF (2 mL) was added, the mixture was stirred at room temperature for 1 h. Sat. NH4Claq was added to the reaction mixture, and the layers were separated. The organic phase was extracted with EtOAc three
times, dried over Na₂SO₄ and concentrated under reduced pressure. The crude reaction mixture was purified by recrystallization from Hexane/CH₂Cl₂ to afford sulfone 1l (537 mg, 73%)

**¹H NMR (400 MHz, CDCl₃):** δ 1.75 (d, J = 7.2 Hz, 3H), 4.23 (q, J = 7.2 Hz, 1H), 7.11-7.14 (m, 2H), 7.21-7.28 (m, 3H), 7.36-7.40 (m, 2H), 7.52-7.57 (m, 2H).

**¹³C NMR (101 MHz, CDCl₃):** δ 13.9, 66.0, 128.3, 128.6, 128.7, 129.1, 129.3, 133.4, 133.7, 136.8.

**HRMS (ESI):** m/z calcd for [C₁₄H₁₄O₂S+Na]: 269.0607, found 269.0610.

**Sulfone 1o**

A flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added benzyl sulfone (464 mg, 2 mmol), 5-bromo-1-pentene (0.28 mL, 1.2 equiv) and dry THF (15 mL). A solution of NaHMDS (605 mg, 1.05 equiv) in dry THF (5 mL) was added drop wise to the reaction mixture at 0 ºC under argon. The mixture was stirred at room temperature for 16 h. Sat. NH₄Claq was added to the reaction mixture, and the layers were separated. The organic phase was extracted with EtOAc three times, dried over Na₂SO₄ and concentrated under reduced pressure. The crude reaction mixture was purified by column chromatography (Hexane/AcOEt = 1:15) to afford sulfone 1o (428 mg, 71%).

**¹H NMR (400 MHz, CDCl₃):** δ 1.12-1.32 (m, 2H), 1.88-2.03 (m, 2H), 2.03-2.20 (m, 1H), 2.36 (ddt, J = 3.7, 7.9, 9.2 Hz, 1H), 3.96 (dd, J = 3.7, 11.6 Hz, 1H), 4.66-5.09 (m, 2H), 5.61 (m, 1H), 7.01 (m, 2H), 7.09 – 7.23 (m, 3H), 7.29 (m, 2H), 7.38-7.62 (m, 3H).

**¹³C NMR (101 MHz, CDCl₃):** δ 26.0, 26.7, 33.2, 71.5, 115.2, 128.4, 128.5, 128.7, 129.0, 129.8, 132.3, 133.3, 137.4, 137.6.

**HRMS (ESI):** m/z calcd for [C₁₈H₂₁O₂S+H]: 301.1268, found 301.1257.
3. Optimization of reaction conditions

3.1. Effect of substituents on the sulfonyl group

Yield was determined by crude $^1$H NMR (1,3,5-trimethoxy benzene was used as internal standard).

3.2. Screening of pyridine catalysts

Yield was determined by crude $^1$H NMR (1,3,5-trimethoxy benzene was used as internal standard).
3.3. Screening of solvents

Yields were determined by GC.

3.4. Effect of the equivalent of reagents and catalyst

Yields were determined by GC. \(^b\)Reaction temperature: 90 °C. Yield was determined by crude \(^1\)H NMR (1,3,5-trimethoxy benzene was used as internal standard).
3.5. Optimization of reaction conditions

![Chemical Reaction Diagram]

<table>
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<th>Entry</th>
<th>Base</th>
<th>cat. (mol%)</th>
<th>temp. (°C)</th>
<th>conc. (M)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>NaOMe</td>
<td>4-PhPy (15)</td>
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<td>2.0</td>
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<td>62</td>
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<tr>
<td>2</td>
<td>NaOMe</td>
<td>4-PhPy (5)</td>
<td>90</td>
<td>2.0</td>
<td>94</td>
<td>67</td>
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<tr>
<td>3</td>
<td>NaOMe</td>
<td>4-PhPy (5)</td>
<td>120</td>
<td>2.0</td>
<td>98</td>
<td>51</td>
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<tr>
<td>4</td>
<td>NaOMe</td>
<td>4-AnthPy (5)</td>
<td>90</td>
<td>2.0</td>
<td>93</td>
<td>71</td>
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<tr>
<td>5</td>
<td>NaOMe</td>
<td>4-AnthPy (5)</td>
<td>90</td>
<td>1.0</td>
<td>90</td>
<td>69 (66)b</td>
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<tr>
<td>6</td>
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<td>50</td>
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<td>7</td>
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<td>4-AnthPy (5)</td>
<td>90</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
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</table>

*aYield was determined by crude 1H NMR (1,3,5-trimethoxy benzene was used as internal standard).*

*bIsolated yield*

3.5. Optimization of reaction conditions for an electron rich substrate

![Chemical Reaction Diagram]

<table>
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<th>Entry</th>
<th>B.pin. (equiv)</th>
<th>Cat. (mol%)</th>
<th>Base</th>
<th>Conc. (M)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
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<td>1.3</td>
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<td>NaOEt</td>
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<tr>
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<td>75</td>
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<tr>
<td>4</td>
<td>3.0</td>
<td>4-PhPy (10)</td>
<td>NaOEt</td>
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<td>75</td>
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<tr>
<td>5</td>
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<tr>
<td>6</td>
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<td>47</td>
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<tr>
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<td>4-AnthPy (10)</td>
<td>NaOEt</td>
<td>0.50</td>
<td>16</td>
<td>(62)</td>
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</table>

*aYield was determined by crude 1H NMR (1,3,5-trimethoxy benzene was used as internal standard).*

*cIsolated yield ‘Reaction was conducted under Air.*
4: Borylation of Sulfones

In a nitrogen-atmosphere glove box, 4-anthracenyl pyridine (5-10 mol%), NaOMe or EtOMe (1.3 equiv), Bpin (1.3-2.0 equiv), and sulfone (1.0 equiv) were weighed followed by C\textsubscript{6}H\textsubscript{5}CF\textsubscript{3} (0.5-1 M) into an 1-dram oven dried vial containing a magnetic stir bar. The vial was capped with a Teflon-lined cap and sealed with electrical tape before removing from the glove box. The mixture was stirred at 90 ºC for 24-48 h. The reaction mixture was cooled down to room temperature. The reaction was quenched with sat. NH\textsubscript{4}Cl\textsubscript{aq} and extracted with EtOAc three times. The collected organic phase was dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography to afford the desired product.

Boronic ester 2a

The following compound was synthesized with sulfone 1a (62 mg, 0.2 mmol), 4-anthracenyl pyridine (2.5 mg, 5 mol%), NaOMe (14 mg, 1.3 equiv), Bpin (66 mg, 1.3 equiv) in C\textsubscript{6}H\textsubscript{5}CF\textsubscript{3} (0.2 mL, 1 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:50) gave 2a (39 mg, 66%) as a colorless solid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 1.15 (s, 12H), 3.79 (s, 1H), 7.07-7.10 (m, 2H), 7.15-7.20 (m, 8H).

Data were consistent with those reported in the literature\textsuperscript{1}

Boronic ester 2b

The following compound was synthesized with sulfone 1b (34 mg, 0.1 mmol), 4-anthracenyl pyridine (2.5 mg, 10 mol%), NaOEt (9 mg, 1.3 equiv), Bpin (52 mg, 2 equiv) in C\textsubscript{6}H\textsubscript{5}CF\textsubscript{3} (0.2 mL, 0.5 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:50) gave 2b (20 mg, 61%) as a colorless solid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 1.14 (s, 12H), 3.68 (s, 1H), 3.72 (s, 1H), 6.73 (d, \textit{J} = 8.8 Hz, 2H), 7.03-7.07 (m, 1H), 7.11 (d, \textit{J} = 8.7 Hz, 2H), 7.16 (d, \textit{J} = 5.8 Hz, 4H).

Data were consistent with those reported in the literature\textsuperscript{2}
Boronic ester 2c

The following compound was synthesized with sulfone 1c (69 mg, 0.2 mmol), 4-anthracenyl pyridine (5 mg, 5 mol%), NaOMe (14 mg, 1.3 equiv), Bpin. (66 mg, 1.3 equiv) in C6H5CF3 (0.2 mL, 1 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:75) gave 2c (34 mg, 52%) as a colorless solid.

\textbf{1H NMR (400 MHz, CDCl3):}\ δ 1.15 (s, 6H), 1.15 (s, 6H), 3.74 (s, 1H), 7.09-7.21 (m, 9H)

\textbf{13C NMR (101 MHz, CDCl3):}\ δ 24.5, 24.6, 83.9, 125.8, 128.5, 128.5, 129.0, 130.4, 131.4, 140.7, 141.6.

\textbf{HRMS (TOF-EI):}\ m/z calcd for [C19H22O2BCl]: 328.1401, found 328.1412.

Boronic ester 2d

The following compound was synthesized with sulfone 1d (35 mg, 0.1 mmol), 4-anthracenyl pyridine (2.5 mg, 10 mol%), NaOEt (9 mg, 1.3 equiv), Bpin. (52 mg, 2 equiv) in C6H5CF3 (0.2 mL, 0.5 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:30) gave 2d (19 mg, 54%) as a colorless solid.

\textbf{1H NMR (400 MHz, CDCl3):}\ δ 1.26 (s, 12H), 3.79 (s, 1H), 5.92 (s, 2H), 6.74 (s, 2H), 6.81 (s, 1H), 7.17-7.20 (m, 1H), 7.25-7.31 (m, 4H).

\textbf{13C NMR (101 MHz, CDCl3):}\ δ 24.6, 83.7, 100.7, 108.1, 109.8, 122.0, 125.6, 128.4, 128.9, 135.9, 142.3, 145.5, 147.6.

\textbf{HRMS (EI):}\ m/z calcd for [C20H23O4B]: 338.1693, found 338.1699.

Boronic ester 2e

The following compound was synthesized with sulfone 1e (72 mg, 0.2 mmol), 4-anthracenyl pyridine (5 mg, 5 mol%), NaOMe (14 mg, 1.3 equiv), Bpin. (66 mg, 1.3 equiv) in C6H5CF3 (0.2 mL, 1 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:30) gave 2e (24 mg, 54%) as a colorless solid.

\textbf{1H NMR (400 MHz, CDCl3):}\ δ 1.16 (s, 12H), 3.95 (s, 1H), 7.09 (dt, J = 1.5, 7.0 Hz, 1H), 7.16-7.24 (m, 4H), 7.29-7.36 (m, 3H), 7.61 (s, 1H), 7.67-7.71 (m, 3H).

\textbf{13C NMR (101 MHz, CDCl3):}\ 24.60, 24.63, 83.8, 125.9, 125.6, 125.7, 127.1, 127.5, 127.7, 127.8, 128.2, 128.4, 129.2, 131.9, 133.7, 139.7, 141.9.
HRMS (TOF-EI): m/z calcd for [C\textsubscript{23}H\textsubscript{25}O\textsubscript{2}B]: 344.1948, found 344.1950.

**Boronic ester 2f**

The following compound was synthesized with sulfone \textbf{1f} (322 mg, 1 mmol), 4-anthracenyl pyridine (13 mg, 5 mol%), NaOMe (240 mg, 1.3 equiv), Bpin. (330 mg, 1.3 equiv) in C,H,CF\textsubscript{3} (1 mL, 1 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:50) gave \textbf{2f} (177 mg, 57\%) as a colorless solid:

\textbf{1H NMR (400 MHz, CDCl}\textsubscript{3}): \textit{\delta} 1.25 (s, 12H), 2.32 (s, 3H), 3.84 (s, 1H), 7.00 (d, \textit{J} = 7.5 Hz, 1H), 7.08-7.11 (m, 2H), 7.16-7.20 (m, 2H), 7.26-7.28 (m, 4H).

Data were consistent with those reported in the literature.

\textbf{Boronic ester 2g}

The following compound was synthesized with sulfone \textbf{1g} (65 mg, 0.2 mmol), 4-anthracenyl pyridine (5 mg, 5 mol%), NaOMe (14 mg, 1.3 equiv), Bpin. (66 mg, 1.3 equiv) in C,H,CF\textsubscript{3} (0.2 mL, 1 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:30) gave \textbf{2g} (20 mg, 32\%) as a colorless solid.

\textbf{1H NMR (400 MHz, CDCl}\textsubscript{3}): \textit{\delta} 1.15 (s, 6H), 1.16 (s, 6H), 2.19 (s, 3H), 3.93 (s, 1H), 6.57-7.80 (m, 9H);

\textbf{13C NMR (101 MHz, CDCl}\textsubscript{3}): \textit{\delta} 20.1, 24.6, 24.7, 83.7, 125.4, 125.8, 125.9, 128.3, 129.1, 129.3, 130.4, 136.7, 140.1, 141.7.

HRMS (ESI): m/z calcd for [C\textsubscript{20}H\textsubscript{25}O\textsubscript{2}B+Na]: 331.1856, found 331.1840.

\textbf{Boronic ester 2h}

The following compound was synthesized with sulfone \textbf{1h} (34 mg, 0.1 mmol), 4-anthracenyl pyridine (2.5 mg, 10 mol%), NaOEt (9 mg, 1.3 equiv), Bpin. (52 mg, 2 equiv) in C,H,CF\textsubscript{3} (0.2 mL, 0.5 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:30) gave \textbf{2h} (12 mg, 37\%) as a colorless solid.

\textbf{1H NMR (400 MHz, CDCl}\textsubscript{3}): \textit{\delta} 1.12 (s, 6H), 1.16 (s, 6H), 3.76 (s, 3H), 3.81 (s, 1H), 6.73-6.78 (m, 3H), 7.05-7.09 (m, 1H), 7.10-7.14 (m, 1H), 7.18-7.24 (m, 4H).

\textbf{13C NMR (101 MHz, CDCl}\textsubscript{3}): 24.5, 24.7, 55.1, 83.3, 109.5, 120.5, 125.6, 126.5, 128.4, 128.8, 130.1, 131.8, 140.5, 156.6.
HRMS (ESI): $m/z$ calcd for $[C_{20}H_{25}O_3B+Na]$: 347.1802, found 347.1794.

Boronic ester 2i

The following compound was synthesized with sulfone 1i (36 mg, 0.1 mmol), 4-anthracenyl pyridine (2.5 mg, 10 mol%), NaOEt (9 mg, 1.3 equiv), B.pin (52 mg, 2 equiv) in C.H.CF (0.2 mL, 0.5 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:50) gave 2i (16 mg, 47%) as a colorless solid.

$^1$H NMR (400 MHz, CDCl3): $\delta$ 1.23 (s, 6H), 1.25 (s, 6H), 4.58 (s, 1H), 7.18-7.24 (m, 1H), 7.28-7.32 (m, 4H), 7.37-7.42 (m, 2H), 7.44-7.49 (m, 2H), 7.73 (d, $J = 7.7$ Hz, 1H), 7.86 (dd, $J = 3.4$, 6.2 Hz, 1H), 8.11 (dd, $J = 3.4$, 6.2 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl3): $\delta$ 24.5, 24.7, 83.8, 124.2, 125.3, 125.6, 125.7, 126.4, 126.5, 128.4, 128.7, 129.4, 132.3, 134.0, 138.2, 141.4.

HRMS (ESI): $m/z$ calcd for $[C_{23}H_{25}O_2B+Na]$ 367.1840, found 367.1822.

Boronic ester 2j

The following compound was synthesized with sulfone 1j (63 mg, 0.2 mmol), 4-anthracenyl pyridine (5 mg, 5 mol%), NaOMe (14 mg, 1.3 equiv), B.pin (66 mg, 1.3 equiv) in C.H.CF (0.2 mL, 1 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:75) gave 2j (20 mg, 33%) as a yellow solid.

$^1$H NMR (400 MHz, CDCl3): $\delta$ 1.24 (s, 12H), 4.03 (s, 1H), 6.91-6.96 (m, 2H), 7.11 (dd, $J = 1.3$, 5.1 Hz, 1H), 7.16-7.19 (m, 1H), 7.25-7.26 (m, 4H).

$^{13}$C NMR (101 MHz, CDCl3): $\delta$ 24.5, 24.6, 84.0, 123.7, 125.4, 125.9, 126.7, 128.4, 128.5, 128.7, 141.9, 145.1.

HRMS (ESI): $m/z$ calcd for $[C_{17}H_{21}O_2BS+H]$ 301.1428, found 301.1442.

Boronic ester 2k

The following compound was synthesized with sulfone 1k (37 mg, 0.1 mmol), 4-anthracenyl pyridine (2.5 mg, 10 mol%), NaOEt (9 mg, 1.3 equiv), B.pin (52 mg, 2 equiv) in C.H.CF (0.2 mL, 0.5 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:30) gave 2k (34 mg, 96%) as a colorless solid.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.15 (s, 12H), 3.66 (s, 1H), 3.69 (s, 6H), 6.73 (d, $J = 8.6$ Hz, 4H), 7.08 (d, $J = 8.6$ Hz, 4H).

Data were consistent with those reported in the literature.

Boronic ester 2l

The following compound was synthesized with sulfone 1l (49 mg, 0.2 mmol), 4-anthracenyl pyridine (5 mg, 10 mol%), NaOEt (18 mg, 1.3 equiv), B.pin. (104 mg, 2 equiv) in C.H.CF. (0.4 mL, 0.5 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:50) gave 2l (35 mg, 72%) as a colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.16 (s, 6H), 1.17 (s, 6H), 1.29 (d, $J = 7.5$ Hz, 3H), 2.40 (q, $J = 7.5$ Hz, 1H), 6.98-7.13 (m, 1H), 7.12-7.23 (m, 4H).

Data were consistent with those reported in the literature.

Boronic ester 2m

The following compound was synthesized with sulfone 1m (70 mg, 0.3 mmol), 4-anthracenyl pyridine (8 mg, 10 mol%), NaOEt (25 mg, 1.3 equiv), B.pin. (152 mg, 2 equiv) in C.H.CF. (0.5 mL, 0.5 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:50) gave 2m (33 mg, 50%) as a colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.25 (s, 12H), 2.31 (s, 2H), 7.12-7.28 (m, 5H).

Data were consistent with those reported in the literature.

Boroninc ester 2n

The following compound was synthesized with sulfone 1n (153 mg, 0.5 mmol), 4-anthracenyl pyridine (13 mg, 10 mol%), NaOEt (44 mg, 1.3 equiv), B.pin. (260 mg, 2 equiv) in C.H.CF. (1 mL, 0.5 M). Purification by column chromatography on silica gel (EtOAc:hexane = 1:50) gave 2n (109 mg, 75%) as a colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.04 (ddd, $J = 5.1, 5.1, 14.6$ Hz, 1H), 0.25 (ddd, $J = 5.1, 5.1, 14.6$ Hz, 1H), 0.44-0.50 (m, 1H), 0.54-0.60 (m, 1H), 1.06-1.13 (m, 1H), 1.22 (s, 12H), 1.69 (d, $J = 9.6$ Hz), 7.19-7.24 (m, 4H).
$^{13}$C NMR (101 MHz, CDCl$_3$): 4.8, 4.9, 13.0, 24.6, 83.5, 128.3, 129.5, 130.9, 141.7.

HRMS (EI): $m/z$ calcd for [C$_{16}$H$_{22}$O$_2$BCl]: 292.1404, found 292.1411.
5: Preparation of Diarylmethyl Sulfones

Preparation of cyclic sulfones 4a, 4c

Cyclic sulfone 4a  

Sulfone (1.5 g, 6 mmol) was dissolved in MeOH (0.1 M) and Pd/C (600 mg, 10 wt%) was added to the solution. The mixture was stirred at 50 ºC for 24 h under hydrogen (1 atm). The reaction mixture was filtered through Celite and washed with MeOH three times. The filtrate was concentrated under reduced pressure, and the crude product was purified by recrystallization from MeOH to give cyclic sulfone 4a (880 mg, 57%) as a colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.38 (s, 3H), 3.61 (d, $J$ = 8.4 Hz, 2H), 4.65 (t, $J$ = 8.4 Hz, 1H), 7.24 (d, $J$ = 7.8 Hz, 2H), 7.35 (d, $J$ = 8.1 Hz, 2H), 7.44 (dt, $J$ = 1.0, 7.5 Hz, 1H), 7.50 (dt, $J$ = 1.0, 7.5 Hz, 1H), 7.60 (dt, $J$ = 1.3, 7.6 Hz, 1H), 7.78 (dd, $J$ = 1.3, 7.5 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$): 21.2, 32.7, 67.1, 122.2, 126.9, 127.0, 128.9, 129.1, 129.6, 133.3, 136.4, 138.4, 139.3.

HRMS (ESI): m/z calcd for [C$_{15}$H$_{14}$O$_2$S+H]: 259.0787, found 275.0787.

Cyclic sulfone 4c  

Sulfone (408 mg, 1.5 mmol) was dissolved in MeOH (0.1 M) and Pd/C (150 mg, 10 wt%) was added to the solution. The mixture was stirred at 50 ºC for 7 days under hydrogen (1 atm). The reaction mixture was filtered through Celite and washed with MeOH three times. The filtrate was concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (CHCl$_3$:hexane = 4:1) to give cyclic sulfone 4c (71 mg, 7%) as a colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.61 (dd, $J$ = 8.0, 9.0 Hz, 2H), 4.63 (dd, $J$ = 8.0, 9.0 Hz, 1H), 6.94-6.98 (m, 2H), 7.38-7.45 (m, 3H), 7.50 (dt, $J$ = 1.0, 7.6 Hz, 1H), 7.60 (dt, $J$ = 1.3, 7.6 Hz, 1H), 7.79 (d, $J$ = 7.7 Hz, 1H).
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 32.9, 55.3, 66.9, 114.5, 121.7, 122.4, 127.0, 129.0, 130.5, 133.3, 136.4, 138.4, 160.5.

HRMS (ESI): $m/z$ calcd for [C$_{15}$H$_{14}$O$_3$S]+H: 275.0736, found 275.0726.

**Cyclic sulfone 4b**

To a flame-dried flask containing a magnetic stir bar under an atmosphere of dry argon was added 2-(4-chlorophenyl)-1-benzothiophene (488 mg, 2 mmol), mCPBA (988 mg, 2.2 equiv) and dry DCM (0.1 M). The reaction mixture was stirred at room temperature for 16 h. Upon reaction completion, the reaction mixture was diluted DCM and water was added. The organic phase was extracted with DCM, washed with 1 M NaOH, brine, dried over sodium sulfate, and concentrated in vacuo. The crude product was dissolved in MeOH (0.1 M) and Pd/C (160 mg, 10 wt%) was added to the solution. The mixture was stirred at 50 ºC for 24 h under hydrogen (1 atm). The reaction mixture was filtered through Celite and washed with MeOH three times. The filtrate was concentrated under reduced pressure, and the crude product was recrystallized from MeOH to give 4b (256 mg, 66%) as a colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.55-3.69 (m, 2H), 4.64 (dd, $J$ = 7.8, 9.0 Hz, 1H), 7.39-7.46 (m, 5H), 7.52 (t, $J$ = 7.5 Hz, 1H), 7.62 (dt, $J$ = 1.2, 7.6 Hz, 1H), 7.79 (d, $J$ = 7.6 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$): 32.9, 66.6, 122.4, 127.0, 128.6, 129.0, 129.20, 129.24, 130.6, 133.6, 135.6, 136.0, 138.2.

HRMS (ESI): $m/z$ calcd for [C$_{14}$H$_{11}$O$_2$SCl]+H: 279.0237, found 279.0241.
6. Borylation and functionalization of benzo thiophene derivatives

Boronic ester 5a

In a nitrogen-atmosphere glove box, Aryl Pyridine (7.8 mg, 30 mol%), NaOEt (7.0 mg, 1.3 equiv), Bpin (33 mg, 1.3 equiv), Sulfones 4a (26 mg, 0.1 mmol) were weighed followed by C6H5CF3 (0.5 M) into a 1-dram oven dried vial containing a magnetic stir bar. The vial was capped with a Teflon-lined cap and sealed with electrical tape before removing from the glove box. The mixture was stirred at 100 ºC for 17 h. After cooling to room temperature, solvent was removed under reduced pressure. To this vial were added methyl iodide (31 µL, 5 equiv) and DMSO (0.5 mL) under argon. The mixture was stirred at 80 ºC for 2 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc, and 10% brine was added to the solution. The mixture was extracted with EtOAc three times. The collected organic phase was dried over Na2SO4, filtered and concentrated under reduced pressure. The crude was purified by column chromatography (EtOAc/Hex = 1:7.5) to afford 5a (31 mg, 78%) as a colorless solid.

1H NMR (400 MHz, CDCl3): δ 1.11 (s, 6H), 1.14 (s, 6H), 2.29 (s, 3H), 2.85 (dd, J = 9.0, 7.1 Hz, 1H), 3.03 (s, 3H), 3.31 (dd, J = 14.4, 7.2 Hz, 1H), 3.57 (dd, J = 14.4, 9.0 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.31-7.40 (m, 2H), 7.46 (td, J = 7.4, 1.5 Hz, 1H), 8.02 (dd, J = 7.8, 1.5 Hz, 1H).

13C NMR (101 MHz, CDCl3): δ 21.0, 24.5, 24.6, 35.9, 44.7, 83.5, 126.6, 128.6, 129.2, 129.6, 131.4, 133.1, 135.2, 138.7, 138.8, 142.0.

HRMS (ESI): m/z calcd for [C22H29O4BS+H]: 401.1950, found 401.1952.

Gram scale synthesis of 5a

In a nitrogen-atmosphere glove box, Aryl Pyridine (200 mg, 20 mol%), NaOMe (274 mg, 1.3 equiv), Bpin (1.29 g, 1.3 equiv), Sulfones 4a (1.0 g, 1.0 equiv) were weighed followed by C6H5CF3 (0.5 M) into a 50 mL Schlenk flask containing a magnetic stir bar. The mixture was stirred at 100 ºC for 10 h. After cooling to room temperature, solvent was removed under reduced pressure. To this flask were added methyl iodide (1.2 mL, 5 equiv) and DMSO (0.2 M) under argon. The mixture was stirred at 80 ºC for 16
h. After cooling to room temperature, the reaction mixture was diluted with EtOAc, and 10% brine was added to the solution. The mixture was extracted with EtOAc three times. The collected organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude was purified by column chromatography (EtOAc/Hex = 1:7.5) to afford 5a (0.92 g, 60%) as a colorless solid.

Boronic ester 5b

In a nitrogen-atmosphere glove box, Aryl Pyridine (6.8 mg, 10 mol%), NaOEt (23.8 mg, 1.3 equiv), B.pin.(140 mg, 2 equiv), Sulfones 4b (76 mg, 0.27 mmol) were weighed followed by C.HCF, (0.5 M) into a 1-dram oven dried vial containing a magnetic stir bar. The vial was capped with a Teflon-lined cap and sealed with electrical tape before removing from the glove box. The mixture was stirred at 100 ºC for 17 h. After cooling to room temperature, solvent was removed under reduced pressure. To this vial were added methyl iodide (84 µL, 5 equiv) and DMSO (0.2 M) under argon. The mixture was stirred at 80 ºC for 3 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc, and 10% brine was added to the solution. The mixture was extracted with EtOAc three times. The collected organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude was purified by column chromatography (EtOAc/Hex = 1:7.5) to afford 5b (34.9 mg, 31%) as a colorless solid.

1H NMR (300 MHz, CDCl₃): δ 1.14 (s, 6H), 1.16 (s, 6H), 2.89 (dd, J = 7.1, 8.7 Hz, 1H), 3.28 (s, 3H), 3.30 (dd, J = 7.1, 14.1 Hz, 1H), 3.57 (dd, J = 8.7, 14.1 Hz, 1H), 7.13-7.27 (m, 4H), 7.41-7.31 (m, 2H), 7.47 (dt, J = 1.5, 7.5 Hz, 1H), 8.04 (dd, J = 1.5, 7.9 Hz, 1H).

13C NMR (101 MHz, CDCl₃): δ 24.5, 24.6, 37.3, 44.1, 44.8, 124.7, 126.9, 128.0, 128.3, 129.1, 129.2, 129.8, 130.1, 131.6, 133.2, 133.9.

HRMS (ES): m/z calcd for [C₂₁H₂₆O₄BSCl]: 420.1337, found 420.1339.

Boronic ester 5c

In a nitrogen-atmosphere glove box, Aryl Pyridine (2.5 mg, 10 mol%), NaOEt (8.8 mg, 1.3 equiv), B.pin.(52 mg, 2 equiv), Sulfones 4c (27 mg, 0.1 mmol) were weighed followed by C.HCF, (0.5 M) into a 1-dram oven dried vial containing a magnetic stir bar. The vial was capped with a Teflon-lined cap and sealed with electrical tape before removing from the glove box. The mixture was stirred at 100 ºC for 17 h. After
cooling to room temperature, solvent was removed under reduced pressure. To this vial were added methyl iodide (31 µL, 5 equiv) and DMSO (0.5 mL) under argon. The mixture was stirred at 80 °C for 2 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc, and 10% brine was added to the solution. The mixture was extracted with EtOAc three times. The collected organic phase was dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude was purified by column chromatography (EtOAc/Hex = 1:7.5) to afford 5c (15 mg, 36%) as a colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.11 (s, 6H), 1.14 (s, 6H), 2.83 (dd, $J = 8.8, 7.2$ Hz, 1H), 3.04 (s, 3H), 3.29 (dd, $J = 14.3, 7.3$ Hz, 1H), 3.55 (dd, $J = 14.4, 8.8$ Hz, 1H), 3.77 (s, 3H), 6.75-6.85 (m, 2H), 7.11-7.16 (m, 2H), 7.34 (dd, $J = 7.9, 6.6$ Hz, 2H), 7.42-7.48 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$): 24.8, 24.9, 25.3, 36.4, 45.0, 55.5, 83.9, 114.3, 127.0, 129.9, 130.0, 131.8, 133.4, 134.2, 139.1, 142.2, 158.1.

HRMS (ESI): $m/z$ calcd for [C$_{22}$H$_{29}$O$_5$BS+H]: 401.1909, found 401.1902.

**Boronic ester 6a**

In a nitrogen-atmosphere glove box, Aryl Pyridine (23 mg, 30 mol%), NaOEt (27 mg, 1.3 equiv), B.pin (99 mg, 1.3 equiv), Sulfones 4a (78 mg, 1.0 equiv) were weighed followed by C$_6$H$_5$CF$_3$ (0.5 M) into a 1 dram oven dried vial containing a magnetic stir bar. The vial was capped with a Teflon-lined cap and sealed with electrical tape before removing from the glove box. The mixture was stirred at 100 °C for 17 h. After cooling to room temperature, solvent was removed under reduced pressure. To this vial were added benzyl bromide (71 µL, 2 equiv), potassium iodide (50 mg, 1 equiv) and DMF (1.2 mL) under argon. The mixture was stirred at r.t. °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc, and 10% brine was added to the solution. The mixture was extracted with EtOAc three times. The collected organic phase was dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude was purified by column chromatography (EtOAc/Hex = 1:10) to afford 6a (62 mg, 44%) as a colorless solid.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.15 (s, 6H), 1.17 (s, 6H), 2.28 (s, 3H), 2.84 (t, $J = 7.9$ Hz, 1H), 3.26 (dd, $J = 7.5, 14.3$ Hz, 1H), 3.48 (dd, $J = 8.2, 14.3$ Hz, 1H), 4.28 (d, $J = 3.3$ Hz, 2H), 7.01-7.07 (m, 4H), 7.09-7.16 (m, 3H), 7.18-7.25 (m, 2H), 7.28-7.32 (m, 1H), 7.33-7.39 (m, 2H), 7.60 (dd, $J = 1.4, 7.9$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$): 21.0, 24.5, 24.6, 36.2, 62.7, 65.4, 83.5, 126.2, 127.0, 127.6, 128.1, 128.4,
128.6, 128.7, 129.2, 130.9, 131.2, 131.3, 133.1, 135.1, 136.2, 138.9, 142.6.

**HRMS (ESI):** m/z calc for [C\(_{28}\)H\(_{33}\)O\(_4\)BS+H]: 477.2265, found 477.2265.

Boronic ester 7a

In a nitrogen-atmosphere glove box, Aryl Pyridine (5.9 mg, 15 mol%), NaOMe (11 mg, 1.3 equiv), B.pin (50 mg, 1.3 equiv), Sulfones 4a (39 mg, 1.0 equiv) were weighed followed by C.H.CF, (0.5 M) into a 1-dram oven dried vial containing a magnetic stir bar. The vial was capped with a Teflon-lined cap and sealed with electrical tape before removing from the glove box. The mixture was stirred at 100 ºC for 17 h. After cooling to room temperature, solvent was removed under reduced pressure. To this vial were added allyl bromide (65 µL, 5 equiv) and DMSO (1.5 mL) under argon. The mixture was stirred at 50 ºC for 12 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc, and 10% brine was added to the solution. The mixture was extracted with EtOAc three times. The collected organic phase was dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The crude was purified by column chromatography (EtOAc/Hex = 1:12) to afford 7a (21 mg, 33%) as a colorless solid.

**\(^1\)H NMR (400 MHz, CDCl\(_3\)):** δ 1.13 (s, 6H), 1.16 (s, 6H), 2.29 (s, 3H), 2.83 (t, \(J = 7.9\) Hz, 1H), 3.33 (dd, \(J = 7.4, 14.4\) Hz, 1H), 3.54 (dd, \(J = 8.4, 14.4\) Hz, 1H), 3.76 (d, \(J = 7.4\) Hz, 3H), 5.1 (dd, \(J = 1.2, 17.0\) Hz, 1H), 5.27 (ffzd, \(J = 10.1\) Hz, 1H), 5.56-5.76 (m, 1H), 7.04 (d, \(J = 8.0\) Hz, 2H), 7.11 (d, \(J = 8.0\) Hz, 2H), 7.31-7.35 (m, 2H), 7.44 (dt, \(J = 1.4, 7.6\) Hz, 1H), 7.91 (dd, \(J = 1.3, 8.0\) Hz, 1H).

**\(^{13}\)C NMR (101 MHz, CDCl\(_3\)):** 21.0, 24.5, 24.6, 36.2, 60.8, 83.5, 124.4, 124.7, 128.7, 129.2, 131.1, 131.4, 133.1, 135.1, 136.6, 138.9, 142.4.

**HRMS (ESI):** m/z calc for [C\(_{28}\)H\(_{33}\)O\(_4\)BS+H]: 427.2129, found 427.2109.

Boronic ester 8a

In a nitrogen-atmosphere glove box, Aryl Pyridine (5.9 mg, 15 mol%), NaOMe (11 mg, 1.3 equiv), B.pin (50 mg, 1.3 equiv), Sulfones 4a (39 mg, 1.0 equiv) were weighed followed by C.H.CF, (0.5 M) into a 1-dram oven dried vial containing a magnetic stir bar. The vial was capped with a Teflon-lined cap and sealed with electrical tape before removing from the glove box. The mixture was stirred at 100 ºC for 17 h. After cooling to room temperature, solvent was removed under reduced pressure. To this vial were added
diphenyl iodonium iodide (189 mg, 3 equiv) and DMF (1.5 mL) under argon. The mixture was stirred at 90 °C for 16 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc, and 10% brine was added to the solution. The mixture was extracted with EtOAc three times. The collected organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude was purified by column chromatography (EtOAc/Hex = 1:10) to afford 8a (31 mg, 45%) as a colorless solid.

H NMR (300 MHz, CDCl₃): δ 1.13 (s, 6H), 1.15 (s, 6H), 2.28 (s, 3H), 2.56 (t, J = 7.8 Hz, 1H), 3.07 (dd, J = 14.5, 8.0 Hz, 1H), 3.38 (dd, J = 14.5, 7.5 Hz, 1H), 6.92 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 7.05-7.12 (m, 1H), 7.30-7.38 (m, 2H), 7.33-7.38 (m, 2H), 7.51-7.59 (m, 1H), 7.82-7.89 (m, 2H), 8.17-8.26 (m, 1H).

C NMR (101 MHz, CDCl₃): δ 21.0, 24.6, 35.3, 83.4, 126.3, 127.6, 128.5, 129.0, 129.8, 131.6, 132.9, 134.7, 138.7, 138.8, 141.9, 142.1.

HRMS (ESI): m/z calcd for [C₂₇H₃₁O₄BS+H]: 463.2114, found 463.2109.

Boronic ester 9a

In a nitrogen-atmosphere glove box, Aryl Pyridine (15 mg, 30 mol%), NaOMe (14 mg, 1.3 equiv), Bpin₂ (66 mg, 1.3 equiv), Sulfones 4a (52 mg, 1.0 equiv) were weighed followed by C₆H₅CF₃ (0.5 M) into a 1-dram oven dried vial containing a magnetic stir bar. The vial was capped with a Teflon-lined cap and sealed with electrical tape before removing from the glove box. The mixture was stirred at 100 °C for 17 h. After cooling to room temperature, solvent was removed under reduced pressure. To this mixture in THF (0.2 M) was added sulfuryl chloride (20 µL, 1 equiv) dropwise at –40 °C under argon. The orange suspension was warmed to room temperature, and diethyl amine (0.1 mL, 0.5 equiv) was added to the reaction. After stirring for 2 h the reaction mixture was quenched with sat. NH₄Cl and diluted with EtOAc. The mixture was extracted with EtOAc three times. The collected organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude was purified by column chromatography (EtOAc/Hex = 1:5) to afford 9a (45 mg, 49%) as a colorless solid.

H NMR (400 MHz, CDCl₃): δ 1.11 (t, J = 7.1 Hz, 6H), 1.14 (s, 6H), 1.17 (s, 6H), 2.29 (s, 3H), 2.82 (t, J = 7.7 Hz, 1H), 3.22 (dd, J = 7.7, 14.6 Hz, 1H), 3.29 (q, J = 7.1 Hz, 4H), 3.54 (dd, J = 7.8, 14.6 Hz, 1H), 3.76 (d, J = 7.4 Hz, 3H), 7.03 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 7.16 (dd, J = 1.5, 7.7 Hz, 1H), 7.23 (dt, J = 1.5, 7.5 Hz, 1H), 7.30 (dt, J = 1.6, 7.5 Hz, 1H), 7.90 (dd, J = 1.5, 7.8 Hz, 1H).
$^{13}$C NMR (101 MHz, CDCl$_3$): 13.7, 21.0, 24.5, 24.6, 35.4, 40.8, 83.4, 125.8, 128.6, 129.0, 129.8, 131.4, 131.8, 134.7, 138.3, 139.2, 141.5.

HRMS (ESI): $m/z$ calcd for [C$_{25}$H$_{36}$O$_4$BS+H]: 458.2536, found 458.2557.
7: Reference

