Sequential Chelation-Assisted Aromatic C-H Functionalisation via Catalytic meta-Sulfonation

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Electronic Supplementary Information

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Considerations</td>
<td>2</td>
</tr>
<tr>
<td>Experimental Procedures</td>
<td>2</td>
</tr>
<tr>
<td>NMR Spectra</td>
<td>18</td>
</tr>
<tr>
<td>X-ray Crystallographic Data</td>
<td>61</td>
</tr>
<tr>
<td>References</td>
<td>67</td>
</tr>
</tbody>
</table>
General considerations

Unless otherwise noted, all reagents and catalysts were commercially available and purchased from Sigma-Aldrich Company Ltd and were used without further purification. Silica gel plates (GF<sub>254</sub>) were used for TLC monitoring and silica gel (230-400 mesh) was used for flash column chromatography. Dried solvents were obtained by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. The <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded on Bruker Avance 250, 300 and 500 instruments with TMS as the internal standard. The mass spectra were run on a microTOF electrospray time of flight (ESI-TOF) coupled to an Agilent 1200 LC system (University of Bath). IR spectra were recorded on Perkin-Elmer 1600 FT IR spectrometer with only selected absorbance quoted as ν in cm<sup>-1</sup>. All capillary melting points were recorded using a Bibby Scientific melting point apparatus Stuart SMP10 digital.

CCDC 944822 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General sulfonation procedure<sup>1</sup>

![Chemical reaction diagram]

To a nitrogen-purged carousel tube was added [Ru(ρ-cymene)Cl<sub>2</sub>]<sub>2</sub> (0.1 mmol, 0.060 g), phenylpyridine derivative (2 mmol), sulfonylchloride (6 mmol), potassium carbonate (4 mmol, 0.552 g), and acetonitrile (5 mL). The reaction was heated to 120 °C with stirring for 15 h before being cooled to rt. The reaction mixture was washed with brine, extracted with dichloromethane, dried over MgSO<sub>4</sub> and the solvent removed. The crude mixture was then purified by flash column chromatography.
2-(3-((4-bromophenyl)sulfonyl)-4-methylphenyl)pyridine (18a)

According to the general procedure, from 2-(p-tolyl)pyridine (2 mmol, 0.341 ml) and 4-bromophenylsulfonyl chloride (6 mmol, 1.533 g), the title compound was obtained by flash column chromatography eluting with hexane/EtOAc (4:1), followed by recrystallisation from ethanol to give a white solid (46 % yield). m.p. 196-198 °C. IR (neat, cm⁻¹) ν 2974.01, 1570.40, 1431.29, 1308.22, 1105.96, 1067.43, 1006.20, 808.79, 771.38, 742.25, 614.92. ¹H NMR (250 MHz, CDCl₃) δ 8.80 (d, J = 1.9 Hz, 1H), 8.70 (d, J = 4.7 Hz, 1H), 8.18 (dd, J = 7.9, 1.9 Hz, 1H), 7.84 – 7.73 (m, 2H), 7.74 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 7.34 (d, J = 8.0 Hz, 1H), 7.31 – 7.25 (m, 1H), 2.45 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 155.3, 149.8, 140.3, 138.8, 138.5, 138.1, 137.2, 133.5, 132.4, 132.1, 129.3, 128.4, 127.8, 122.9, 120.6, 20.2. HRMS calcd [M+H]⁺: 389.9941; Found: 389.9960.

2-(3-((4-nitrophenyl)sulfonyl)phenyl)pyridine (16a)

According to the general procedure, from 2-phenylpyridine (2 mmol, 0.286 ml) and 4-nitrophenylsulfonyl chloride (6 mmol, 1.330 g), the title compound was obtained by flash column chromatography eluting with hexane/EtOAc (4:1), followed by recrystallisation from ethanol to give a yellow solid (28 % yield). m.p. 158-161 °C. IR (neat, cm⁻¹) ν 3647.47, 2980.90, 1605.98, 1586.68, 1531.19, 1460.08, 1350.13, 1301.12, 1150.01, 1102.82, 735.54, 679.08. ¹H NMR (300 MHz, CDCl₃) δ 8.71 (dt, J = 4.8, 1.4 Hz, 1H), 8.61 (t, J = 1.7 Hz, 1H), 8.34 (d, J = 9.0 Hz, 2H), 8.27 (ddd, J = 7.8, 1.7, 1.1 Hz, 1H), 8.17 (d, J = 9.0 Hz, 2H), 8.00 (ddd, J = 7.8, 1.9, 1.1 Hz, 1H), 7.86 – 7.74 (m, 2H), 7.66 (t, J = 7.8 Hz, 1H), 7.31 (ddd, J = 6.6, 4.8, 1.7 Hz, OCH₃).
According to the general procedure, from 2-(2-methoxy)phenylpyridine (2 mmol, 0.372 g) and p-toluenesulfonyl chloride (6 mmol, 1.144 g) in MeCN (5 ml), the title compound was obtained by flash column chromatography eluting with CH₂Cl₂/2-propanol (1:0.01) to give a white solid (12 % yield). m.p. 160-163 °C. IR (neat, cm⁻¹) ν 2924.21, 1590.54, 1464.65, 1140.51, 1088.93, 989.91, 776.29, 685.44, 654.76. ¹H NMR (500 MHz, CDCl₃) δ 8.68 (d, J = 4.7 Hz, 1H), 8.17 (dd, J = 7.9, 1.8 Hz, 1H), 7.93 (dd, J = 7.7, 1.7 Hz, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 3.6 Hz, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.24 (q, J = 4.7 Hz, 1H), 3.35 (s, 3H), 2.39 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 156.3, 154.5, 150.0, 144.0, 138.9, 137.5, 136.5, 135.6, 135.0, 130.0, 129.4, 128.2, 124.4, 124.2, 122.7, 62.2, 21.7. HRMS calcd [M+Na]⁺: 340.1008; Found: 340.1090.

White solid (37 % yield). m.p. 118-120 °C. IR (neat, cm⁻¹) ν 2923.63, 1734.13, 1594.80, 1376.42, 1255.79, 1141.35, 1088.46, 870.59, 782.12, 662.51, 681.39. ¹H NMR (500 MHz, CDCl₃) 8.54 (d, J = 4.5 Hz, 1H), 7.62 – 7.36 (m, 1H), 7.26 (s, 1H), 7.12 – 7.07 (m, 1H), 7.04 (t, J
= 8.0 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 6.57 (dd, J = 7.7, 0.8 Hz, 1H), 3.72 (s, 2H).

\[ ^{13}C\text{ NMR (75 MHz, CDCl}_3\] \( \delta \) 156.8, 156.2, 148.2, 141.6, 135.7, 128.9, 128.1, 123.6, 121.4, 109.4, 55.8. \HRMS\ calcd [M+H]: 369.1603; Found: 369.1744.

\[ HNMR (300 MHz, CDCl}_3\] \( \delta \) 8.68 – 8.50 (m, 1H), 8.24 (d, J = 2.2 Hz, 1H), 7.89 (dd, J = 8.5, 2.1 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.7 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.23 – 7.08 (m, 4H), 2.26 (s, 3H), 2.08 (s, 3H). \[ ^{13}C\text{ NMR (75 MHz, CDCl}_3\] \( \delta \) 168.7, 153.9, 151.6, 149.5, 144.5, 139.9, 138.2, 136.7, 134.2, 130.5, 130.1, 128.9, 127.8, 124.7, 123.7, 123.1, 21.6, 21.0. \HRMS\ calcd [M+H]: 368.0879; Found: 368.1026.
**General bromination procedure**

To a clean, dry carousel tube, Cu(OAc)$_2$ (1 mmol, 0.182 g) the required substrate (1 mmol), C$_2$Cl$_4$Br$_2$ (2 mmol, 0.651 g) and acetonitrile (5 mL) were added. The reaction was heated to 130 °C with stirring for 24 h before being cooled to rt. The reaction mixture was washed with sat. aq. NaHSO$_3$, extracted with dichloromethane, filtered through celite, dried over MgSO$_4$ and the solvent removed. The crude mixture was then purified by column chromatography. Adapted from ref. 2

**2-(2-bromophenyl)pyridine (5a)**

According to the general procedure, from 2-phenylpyridine (1 mmol, 0.143 ml), the title compound was obtained after purification by flash column chromatography eluting with hexane/EtOAc/NEt$_3$ (4:1:0.01) to give a colourless oil (61 % yield). $^1$H NMR (250 MHz, CDCl$_3$) 8.73 (ddd, $J =$ 4.9, 1.7, 0.9 Hz, 1H), 7.76 (td, $J =$ 7.7, 1.8 Hz, 1H), 7.69 (dd, $J =$ 8.0, 1.0 Hz, 1H), 7.61 (d, $J =$ 7.9 Hz, 1H), 7.55 (dd, $J =$ 7.6, 1.8 Hz, 1H), 7.41 (td, $J =$ 7.5, 1.2 Hz, 1H), 7.35 – 7.20 (m, 2H). In accordance with the literature.[^2]
2-(2-bromo-5-tosylphenyl)pyridine (6)

According to the general procedure, from 2-(3-tosylphenyl)pyridine (1 mmol, 0.309 g), the title compound was obtained after purification by flash column chromatography eluting with hexane/EtOAc/NEt₃ (4:1:0.01) to give a white solid (87% yield). **m.p.** 198-200 °C. **IR** (neat, cm⁻¹) v 2925.64, 1592.48, 1478.05, 1402.41, 1311.17, 1296.68, 1151.63, 1107.45, 814.28, 692.52, 646.22. **¹H NMR** (300 MHz, CDCl₃) δ 8.61 (d, J = 4.7 Hz, 1H), 8.50 (d, J = 2.3 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.02 (t, J = 8.5 Hz, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.84 (dd, J = 8.7, 2.1 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.40 – 7.31 (m, 2H), 7.15 (d, J = 8.7 Hz, 1H), 2.46 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 164.2, 155.9, 145.6, 143.8, 139.4, 138.7, 131.4, 130.8, 130.0, 127.4, 126.5, 122.7, 119.7, 118.6, 21.6. **HRMS** calcd [M+H]⁺: 389.9986; Found: 390.0062.

2-(2-bromo-5-(phenylsulfonfyl)phenyl)pyridine (12)

According to the general procedure, from 2-(3-(phenylsulfonfyl)phenyl)pyridine (1 mmol, 0.295 g), the title compound was obtained after purification by flash column chromatography eluting with hexane/EtOAc/NEt₃ (4:1:0.01) to give a white solid (83% yield). **m.p.** 169-172 °C. **IR** (neat, cm⁻¹) v 2922.43, 1586.95, 1450.07, 1301.29, 1146.74, 1097.84, 770.57, 710.85, 681.18, 610.70. **¹H NMR** (300 MHz, CDCl₃) δ 8.66 (d, J = 4.3 Hz, 1H), 8.08 (s, 1H), 7.9 (d, J = 6.9 Hz, 2H), 7.77 (d, J = 1.2 Hz, 2H), 7.73 (dd, J = 7.7, 1.7 Hz, 1H), 7.56 – 7.38 (m, 4H), 7.29 (ddd, J = 7.7, 5.0, 1.0 Hz, 1H). **¹³C NMR** (75 MHz, CDCl₃) δ 156.7, 149.8, 142.6, 141.2, 141.1, 136.3, 134.5, 133.6, 130.4, 129.5, 128.4, 127.8, 124.6, 123.2. **HRMS** calcd [M+Na]⁺: 395.9669; Found: 395.9677.
2-(2-bromo-5-((4-(tert-butyl)phenyl)sulfonyl)phenyl)pyridine (13)

According to the general procedure from 2-(3-((4-(tert-butyl)phenyl)sulfonyl)phenyl)pyridine (1 mmol, 0.351 g), the title compound was obtained after purification by flash column chromatography eluting with hexane/EtOAc/NEt₃ (4:1:0.01) to give a yellow solid (75 % yield). m.p. 125-128 °C. IR (neat, cm⁻¹) ν 3087.76, 2964.17, 1587.64, 1449.26, 1303.98, 1150.38, 1096.65, 1084.27, 825.14, 752.36, 703.10. ¹H NMR (300 MHz, CDCl₃) δ δ 8.70 (dd, J = 4.9, 1.7, 1.0 Hz, 1H), 8.08 (t, J = 1.3 Hz, 1H), 7.85 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 1.3 Hz, 2H), 7.77 (dd, J = 7.7, 1.8 Hz, 1H), 7.54 (dt, J = 7.9, 1.0 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.32 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H), 1.29 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 157.5, 156.7, 149.6, 142.4, 141.5, 138.0, 136.3, 134.4, 130.3, 128.4, 127.7, 127.6, 126.5, 124.6, 123.2, 36.2, 31.0. HRMS calcd [M+Na]+: 452.0295; Found: 452.0303.

2-(2-bromo-5-((4-fluorophenyl)sulfonyl)phenyl)pyridine (14)

According to the general procedure, from 2-(3-((4-fluorophenyl)sulfonyl)phenyl)pyridine (1 mmol, 0.312 g), the title compound was obtained after purification by flash column chromatography eluting with hexane/EtOAc/NEt₃ (4:1:0.01) to give a white solid (72 % yield). m.p. 152-156 °C. IR (neat, cm⁻¹) ν 3072.24, 2924.20, 1585.21, 1431.07, 1107.95, 844.09, 770.87, 660.61. ¹H NMR (300 MHz, CDCl₃) δ 8.62 (d, J = 4.4 Hz, 1H), 8.06 (s, 1H), 7.92 (dd, J = 8.7, 5.0 Hz, 2H), 7.72 (m, 3H), 7.50 (d, J = 7.8 Hz, 1H), 7.24 (ddd, J = 7.2, 4.7, 1.5, 1H), 7.09 (t, J = 8.5 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 165.6 (d, J = 256.6 Hz), 156.5, 149.7,
142.6, 141.0, 137.07 (d, J = 3.2 Hz), 136.4, 134.6, 130.66 (d, J = 9.7 Hz), 130.4, 128.3, 128.0, 124.6, 123.3, 116.8 (d, J = 22.7 Hz). HRMS calcd [M+H]+: 391.9756; Found: 391.9783.

2-(2-bromo-5-((4-bromophenyl)sulfonyl)phenyl)pyridine (15)

According to the general procedure, from 2-(3-((4-bromophenyl)sulfonyl)phenyl)pyridine (1 mmol, 0.373 g), the title compound was obtained after purification by flash column chromatography eluting with hexane/EtOAc/NEt₃ (4:1:0.01) to give a white solid (71% yield). m.p. 126-130 °C. IR (neat, cm⁻¹) ν 2923.07, 2853.05, 1734.97, 1592.02, 1577.81, 1388.60, 1325.98, 1151.23, 1102.27, 1007.87, 816.21, 748.19, 707.40. ¹H NMR (250 MHz, CDCl₃) 8.68 (d, J = 4.2 Hz, 1H), 8.06 (d, J = 1.8 Hz, 1H), 7.77 (td, J = 9.3, 8.4, 3.0 Hz, 5H), 7.60 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 7.9 Hz, 1H), 7.31 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 156.4, 149.8, 142.6, 140.6, 140.0, 136.4, 134.7, 132.8, 130.4, 129.3, 128.9, 128.4, 128.1, 124.6, 123.3. HRMS calcd [M+H]+: 451.8955; Found: 451.8961.

2-(2-bromo-5-((4-nitrophenyl)sulfonyl)phenyl)pyridine (16)

According to the general procedure, from 2-(3-((4-nitrophenyl)sulfonyl)phenyl)pyridine (1 mmol, 0.339 g), the title compound was obtained after purification by flash column chromatography eluting with hexane/EtOAc/NEt₃ (4:1:0.01) to give a white solid (68% yield). m.p. 143-146 °C. IR (neat, cm⁻¹) ν 1587.41, 1448.43, 1334.44, 1345.95, 1102.50, 1014.51, 854.16, 827.64, 737.62, 630.44. ¹H NMR (300 MHz, CDCl₃) δ 8.68 (d, J = 4.8 Hz, 1H), 8.30 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 9.0 Hz, 2H), 8.08 (d, J = 2.2 Hz, 1H), 7.84 (d, J = 8.4 Hz,
According to the general procedure, from 2-(3-((4-bromophenyl)sulfonyl)-4-methylphenyl)pyridine (1 mmol, 0.387 g), the title compound was obtained after purification by flash column chromatography eluting with hexane/EtOAc/NEt$_3$ (4:1:0.01) to give a white solid (72 % yield). m.p. 94-98 °C. IR (neat, cm$^{-1}$) ν 1591.70, 1403.26, 1322.65, 1156.75, 1133.94, 1105.20, 1060.85, 1014.39, 826.42, 717.312. $^1$H NMR (250 MHz, CDCl$_3$) δ 8.72 (ddd, $J = 4.8, 1.7, 0.9$ Hz, 1H), 8.14 – 8.04 (m, 3H), 7.90 – 7.71 (m, 5H), 7.58 (dt, $J = 7.9, 0.9$ Hz, 1H), 7.35 (ddd, $J = 7.6, 4.9, 1.1$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 156.3, 149.7, 144.6, 142.8, 140.1, 136.3, 135.1 (q, $J = 33.1$ Hz), 134.7, 131.9, 130.6, 129.3, 128.5, 128.4 (d, $J = 10.8$ Hz), 126.6 (q, $J = 3.7$ Hz), 124.9, 124.6, 123.3, 121.2. HRMS calcd [M+H]$^+$: 441.9724; Found: 441.9737.

According to the general procedure, from 2-(3-((4-bromophenyl)sulfonyl)-4-methylphenyl)pyridine (1 mmol, 0.387 g), the title compound was obtained after purification by flash column chromatography eluting with hexane/EtOAc/NEt$_3$ (4:1:0.01) to
give a white solid (76 % yield). **m.p.** 162-166 °C. **IR** (neat, cm⁻¹) ν 3088.98, 2927.31, 1712.99, 1571.77, 1456.70, 1304.32, 1148.64, 1058.78, 1007.94, 892.75, 825.23, 751.21, 733.05. **¹H NMR** (250 MHz, CDCl₃) δ 7.74 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 8.36 (s, 1H), 7.87 – 7.71 (m, 3H), 7.69 – 7.54 (m, 4H), 7.35 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 2.43 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 156.5, 149.6, 139.6, 139.8, 139.1, 138.0, 137.4, 136.3, 132.5, 132.3, 129.3, 128.7, 128.0, 124.8, 123.1, 19.8. **HRMS** calcd [M+H]⁺: 467.9013; Found: 467.9096.

2-(2-bromo-5-(naphthalen-2-ylsulfonyl)phenyl)pyridine (19)

![Chemical structure](Image)

According to the general procedure, from 2-(3-(naphthalen-2-ylsulfonyl)phenyl)pyridine (1 mmol, 0.343 g), the title compound was obtained after purification by flash column chromatography eluting with hexane/EtOAc/NET₃ (2:1:0.01) to give a white solid (79 % yield). **m.p.** 185-188 °C. **IR** (neat, cm⁻¹) ν 2983.19, 1587.56, 1462.81, 1432.10, 1303.05, 1152.97, 1102.41, 992.06, 801.02, 773.41, 655.85. **¹H NMR** (300 MHz, CDCl₃) δ 8.69 (d, J = 4.3 Hz, 1H), 8.57 (s, 1H), 8.14 (d, J = 2.0 Hz, 1H), 7.97 – 7.75 (m, 7H), 7.64 – 7.53 (m, 3H), 7.33 (dd, J = 7.5, 0.8, 1H). **¹³C NMR** (75 MHz, CDCl₃) δ 156.4, 149.4, 142.1, 141.3, 137.8, 136.7, 135.2, 134.6, 132.3, 130.5, 129.9, 129.5, 129.4, 129.3, 128.7, 128.0, 127.8, 127.7, 124.8, 123.3, 122.6. **HRMS** calcd [M+H]⁺: 424.0007; Found: 424.0029.

Other transformations

2-(2-methoxyphenyl)pyridine (3a)

![Chemical structure](Image)
To a clean, dry carousel tube, PdCl₂ (0.05 mmol, 8.87 mg), 2-phenylpyridine (2 mmol, 0.286 ml), t-butylhydroperoxide (70 % solution in water, 6 mmol, 1.04 ml) and chlorobenzene (5 ml) were added. The reaction was heated to 140 °C with stirring for 24 h before being cooled to rt. The reaction mixture was filtered through celite and the solvent removed. The crude mixture was then purified by flash column chromatography eluting with dichloromethane to give the phenolic intermediate.

The intermediate (1 mmol, 0.172 g) was added to a slurry of K₂CO₃ (4 mmol, 0.552 g) in DMF and stirred for 1 h at rt before Mel (1.2 mmol, 0.118 g) was added and stirred for 1 h at rt. The reaction mixture was quenched with water, extracted with ethyl acetate, dried over MgSO₄ and the solvent removed to give the title compound as a white solid (52 % yield over two steps). ¹H NMR (300 MHz, CDCl₃) 8.70 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.87 – 7.74 (m, 2H), 7.68 (td, J = 7.7, 1.9 Hz, 1H), 7.37 (ddd, J = 8.3, 7.4, 1.8 Hz, 1H), 7.19 (ddd, J = 7.4, 4.9, 1.2 Hz, 1H), 7.08 (td, J = 7.5, 1.1 Hz, 1H), 6.99 (d, J = 9.0 Hz, 1H), 3.84 (s, 3H). In accordance with the literature.³

2-(2-acetoxyphenyl)pyridine (4a)

To a clean, dry carousel tube, Pd(OAc)₂ (0.05 mmol, 11.2 mg), 2-phenylpyridine (1 mmol, 0.143 ml), Phil(OAc)₂ (1.5 mmol, 0.483 g), Ac₂O (1 ml) and toluene (5 ml) were added. The reaction was heated to 100 °C with stirring for 3 h before being cooled to rt. The reaction mixture was filtered through celite and the solvent removed. The crude mixture was then purified by flash column chromatography eluting with hexane/EtOAc/NEt₃ (4:1:0.01) to give the title compound as a yellow oil (39 % yield). ¹H NMR (300 MHz, CDCl₃) δ 8.69 (d, J = 4.8 Hz, 1H), 7.79 – 7.64 (m, 2H), 7.54 (d, J = 7.9 Hz, 1H), 7.50 – 7.27 (m, 2H), 7.27 – 7.11 (m, 2H), 2.17 (s, 3H). In accordance with the literature.⁴
2-(2-acetoxy-5-tosylphenyl)pyridine (4c)

To a clean, dry carousel tube, Pd(OAc)$_2$ (0.05 mmol, 11.2 mg), 2-(3-tosylphenyl)pyridine (1 mmol, 0.309 g), Phl(OAc)$_2$ (3 mmol, 0.966 g), Ac$_2$O (3 mL) and toluene (3 mL) were added. The reaction was heated to 100 °C with stirring for 3 h before being cooled to rt. The reaction mixture was filtered through celite and the solvent removed. The crude mixture was then purified by flash column chromatography eluting with hexane/EtOAc/NEt$_3$ (4:1:0.01) to give the title compound as a white solid (82 % yield). For full compound data see page 5.

2-(2-chloro-5-tosylphenyl)pyridine (7)

To a clean, dry carousel tube, Cu(OAc)$_2$ (1 mmol, 0.182 g), 2-(3-tosylphenyl)pyridine (1 mmol, 0.309 g), C$_2$Cl$_6$ (2 mmol, 0.473 g) and acetonitrile (5 mL) were added. The reaction was heated to 130 °C with stirring for 24 h before being cooled to rt. The crude mixture was washed with sat. aq. NaHSO$_3$, extracted with dichloromethane, filtered through celite, dried over MgSO$_4$ and the solvent removed. The crude mixture was then purified by flash column chromatography eluting with hexane/EtOAc/NEt$_3$ (1:1:0.01) to give the title compound as a white solid (67 % yield). m.p. 97-101 °C. IR (neat, cm$^{-1}$) ν 2152.91, 1590.52, 1287.65, 1148.57, 1085.32, 1030.71, 825.16, 791.91, 752.62, 713.33, 674.09. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.64 (d, J = 4.3 Hz, 1H), 8.08 (d, J = 2.3 Hz, 1H), 7.85 – 7.63 (m, 4H), 7.51 (dd, J = 8.1, 2.8 Hz, 2H), 7.30 – 7.13 (m, 3H), 2.30 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 155.1, 149.8, 144.6, 141.0, 140.3, 138.1, 137.6, 136.3, 131.2, 130.7, 130.1, 128.4, 127.8, 124.8, 123.2, 21.7. HRMS calcd [M+H$^+$]: 344.0512; Found: 344.0493.
2-(2-hydroxy-5-tosylphenyl)pyridine (8)

To a clean, dry carousel tube, PdCl₂ (0.05 mmol, 8.87 mg), 2-(3-tosylphenyl)pyridine (1 mmol, 0.309 g), t-butylhydroperoxide (70 % solution in water, 3 mmol, 0.52 ml) and chlorobenzene (5 ml) were added. The reaction was heated to 140 °C with stirring for 24 h before being cooled to rt. The reaction mixture was filtered through celite and the solvent removed. The crude mixture was then purified by flash column chromatography eluting with dichloromethane to give the title compound as an amorphous white solid (43 % yield). IR (neat, cm⁻¹) ν 3323.50, 1640.05, 1570.75, 1466.92, 1431.36, 1323.30, 1308.41, 1177.80, 1148.60, 1106.44, 1006.46, 839.95, 770.88, 678.37. ¹H NMR (300 MHz, CDCl₃) δ 15.26 (bs, 1H), 8.42 (d, J = 4.3 Hz, 1H), 8.36 (d, J = 2.2 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.83 (td, J = 8.0, 1.7 Hz, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.71 (dd, J = 8.8, 2.2 Hz, 1H), 7.27 (td, J = 9.0, 1.5 Hz, 1H), 7.20 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.7 Hz, 1H), 2.30 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 164.4, 156.1, 145.7, 143.8, 139.4, 138.4, 131.4, 130.6, 129.9, 127.3, 126.4, 122.7, 119.8, 119.5, 118.7, 21.6. HRMS calcd [M+H]⁺: 326.0850; Found: 326.0865.

4-methyl-N-(2-(pyridine-2-yl)-4-tosylphenyl)benzenesulfonamide (9)

To a clean, dry carousel tube, Cu(OAc)₂ (1 mmol, 0.182 g), 2-(3-tosylphenyl)pyridine (1 mmol, 0.309 g), toluene-4-sulfonamide (2 mmol, 0.342 g) and PrCN (5 mL) were added. The reaction was heated to 130 °C with stirring for 24 h before being cooled to rt. The reaction mixture was washed with sat. aq. NaHSO₃, extracted with dichloromethane, filtered through celite, dried over MgSO₄ and the solvent removed. The crude mixture was then purified by
flash column chromatography eluting with hexane/EtOAc/NET₃ (1:1:0.01) to give the title compound as a white solid (10 % yield). m.p. 205-206 °C. IR (neat, cm⁻¹) ν 2924.44, 1593.54, 1495.49, 1394.67, 1314.40, 1152.79, 1114.37, 1090.45, 932.08, 811.93, 690.87, 657.57. ¹H NMR (300 MHz, CDCl₃) δ 13.19 (s, 1H), 8.66 (d, J = 3.6 Hz, 1H), 8.24 (s, 1H), 7.86 (t, J = 7.8 Hz, 1H), 7.74 (dt, J = 17.0, 8.5 Hz, 4H), 7.59 (d, J = 8.1 Hz, 2H), 7.41 – 7.32 (m, 1H), 7.31 – 7.23 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H), 2.33 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 155.6, 147.3, 144.3, 143.9, 141.8, 138.6, 138.2, 136.5, 136.3, 130.0, 129.7, 129.3, 127.9, 127.6, 127.0, 124.9, 123.1, 122.4, 120.7, 21.6, 21.5. HRMS calcd [M+H⁺]: 479.1099; Found: 479.1086.

2,2'-(4,4'-ditosyl-[1,1'-biphenyl]-2,2'-diyl)dipyridine (10)

To a clean, dry carousel tube, [RuCl₂(p-cymene)]₂ (0.025 mmol, 0.030 g), 2-(3-tosylphenyl)pyridine (1 mmol, 0.309 g), FeCl₃ (0.8 mmol, 0.129 g) and chlorobenzene (5 ml) were added. The reaction was heated to 110 °C with stirring for 16 h before being cooled to rt. The reaction mixture was then diluted with dichloromethane, filtered through celite and the solvent removed. The crude mixture was then purified by flash column chromatography eluting with hexane/EtOAc/NET₃ (1:1:0.01) to give the title compound as a white solid (81 % yield). m.p. 107-110 °C. IR (neat, cm⁻¹) ν 2919.63, 1589.75, 1317.58, 1151.31, 1105.79, 809.11, 749.59, 708.67, 672.43, 660.01. ¹H NMR (300 MHz, CDCl₃) δ 8.25 (d, J = 4.1 Hz, 2H), 8.00 (d, J = 1.6 Hz, 2H), 7.81 – 7.72 (m, 6H), 7.35 (td, J = 7.5, 1.8, 2H), 7.22 (dd, J = 8.4, 3.7 Hz, 6H), 7.03 (dd, J = 7.2, 2.1, 2H), 6.84 (d, J = 7.8 Hz, 2H), 2.33 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 156.2, 149.6, 144.4, 143.8, 141.6, 140.9, 138.4, 136.1, 132.1, 130.0, 129.2, 127.1, 127.8, 124.1, 122.3, 21.6. HRMS calcd [M+H⁺]: 617.1569; Found: 617.1603.
2,2'-(4,4'-di-(4-bromophenyl)sulfonyl-[1,1'-biphenyl]-2,2'-diyl)dipyridine (11)

To a clean, dry carousel tube, [RuCl₂(p-cymene)]₂ (0.025 mmol, 0.030 g), 2-(3-(4-bromophenyl)sulfonyl)pyridine (1 mmol, 0.309 g), FeCl₃ (0.8 mmol, 0.129 g) and chlorobenzene (5 ml) were added. The reaction was heated to 110 °C with stirring for 16 h before being cooled to rt. The reaction mixture was then diluted with dichloromethane, filtered through celite and the solvent removed. The crude mixture was then purified by flash column chromatography eluting with hexane/EtOAc/NEt₃ (1:1:0.01) to give the title compound as a white solid (63 % yield). m.p. 126-130 °C. IR (neat, cm⁻¹) ν 1571.65, 1469.64, 1389.10, 1321.65, 1153.12, 1106.40, 1066.69, 1008.78, 813.03, 740.14, 629.35. ¹H NMR (300 MHz, CDCl₃) δ 8.27 (d, J = 3.7 Hz, 1H), 8.01 (s, 1H), 7.78 – 7.73 (m, 3H), 7.58 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.28 – 7.17 (m, 1H), 7.10 – 6.99 (m, 1H), 6.88 (d, J = 7.8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 155.9, 149.4, 144.1, 141.0, 140.8, 140.4, 136.3, 132.7, 132.2, 129.3, 128.7, 127.2, 124.2, 122.5. HRMS calcd [M+H]⁺: 746.9471; Found: 746.9445.

Suzuki coupling

2-(2-(4-methylthio)phenyl)-5-tosylphenyl)pyridine

To a nitrogen-purged carousel tube, Pd(PPh₃)₄ (0.01 mmol, 0.012 g), 2-(2-bromo-5-tosylphenyl)pyridine (0.5 mmol, 0.195 g), trimethyl((5-methyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane⁵ (0.75 mmol, 243 g) K₂CO₃ (1 mmol, 0.138 g) and
EtOH (6 ml) were added. The reaction was heated to 100 °C with stirring for 12 h before being cooled to rt. The reaction mixture was then washed with sat. aq. NaHCO₃, extracted with dichloromethane, dried over MgSO₄ and the solvent removed. The crude mixture was then purified by flash column chromatography eluting with hexane/EtOAc/NEt₃ (2:1:0.01) to give the title compound as a white solid (84% yield). **m.p.** 175-178 °C. **IR** (neat, cm⁻¹) ν 1592.92, 1458.79, 1315.74, 1280.01, 1153.96, 1094.88, 838.12, 816.69, 709.05, 662.40. **¹H NMR** (300 MHz, CDCl₃) δ 8.59 (d, J = 5.5 Hz, 1H), 8.21 (d, J = 1.9 Hz, 1H), 7.96 (dd, J = 8.1, 2.0 Hz, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.1 Hz, 1H), 7.44 (dd, J = 7.7, 1.7 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.14 (ddd, J = 7.5, 4.9, 1.0 Hz, 1H), 7.07 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 7.9 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 157.4, 149.6, 144.7, 144.3, 141.0, 140.4, 138.6, 138.5, 136.0, 135.9, 131.4, 130.0, 129.9, 129.8, 127.9, 127.4, 125.9, 125.3, 122.2, 21.7, 15.5. **HRMS** calcd [M+H]⁺: 432.1092; Found: 432.1090.
X-ray crystallographic data for

2-(2-bromo-5-((4-bromophenyl)sulfonyl)-4-methylphenyl)pyridine (19)
Table 1. Crystal data and structure refinement for k12cgf3.

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Table 2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for k12cgf3. 
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Table 3. Bond lengths [Å] for k12cge3.

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Table 4. Bond lengths [Å] and angles [deg] for k12cgf3.

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### Table 5. Anisotropic displacement parameters \((\text{A}^2 \times 10^3)\) for k12cgf3.
The anisotropic displacement factor exponent takes the form:
\[-2 \pi^2 \left[ h^2 a^* a^{**} U_{11} + \ldots + 2hka^{*}b^{**} U_{12} \right]\]

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### Table 6. Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($A^2 \times 10^3$) for k12cgf3.

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### References