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Supporting Information

A Mild and Base-free Synthesis of Unsymmetrical Diaryl Sulfones from Aryl Boronic Acids and Aryl Sulfonyl Hydrazides

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Table of Contents

Materials and methods S2

Analytical data S3

References S6
Materials and Methods

Hydrogen nuclear magnetic resonance spectra ($^1$H NMR) were obtained at 300 MHz. Spectra were recorded in CDCl$_3$ solutions. Carbon-13 nuclear magnetic resonance spectra ($^{13}$C NMR) were obtained at 75 MHz. Spectra were recorded in CDCl$_3$ solutions. Chemical shifts are reported in ppm relative to the TMS ($^1$H NMR) and to the solvent ($^{13}$C NMR). Melting points were obtained of a XT4A melting point apparatus and were uncorrected. Gas chromatography mass spectra (GC/MS) were recorded on a Saturn 2000GC/MS instrument. Thin layer chromatography (TLC) was performed using Merck Silica Gel GF254, 0.25 mm thickness.

General procedure for the coupling of aryl boronic acids and aryl sulfonyl hydrazides

Aryl boronic acids (1.2 mmol), aryl sulfonyl hydrazides (1.0 mmol), cupric acetate (1.5 mmol), and EtOH (2.0 mL) were taken in a 25 mL two-neck flask. The reaction mixture was stirred at room temperature for 6 hours in air. The solution was evaporated under reduced pressure and water (20 mL) was added and then the mixture was extracted with EtOAc (4×10 mL). The extracts were combined and washed by brine (3×10 mL), dried over MgSO$_4$, filtered, and evaporated, and purified by chromatography on silica gel to obtain the desired products with ethyl acetate/hexane (v/v=1:5 ~ 1:10). The products were characterized by their spectral and analytical data and compared with those of the known compounds.
Characterization data

**phenyl p-tolyl sulfone (Table 2, entry 1)** [1]

$^1\text{H}$ NMR (300 MHz, CDCl$_3$): $\delta$ 7.94-7.92 (m, 2H), 7.84-7.82 (m, 2H), 7.55-7.48 (m, 3H), 7.31-7.27 (m, 2H), 2.39 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 144.2, 141.9, 138.6, 133.0, 129.9, 129.2, 127.7, 127.5, 21.6. GC-MS (EI, m/z): 232 [M+].

**Di-p-tolyl sulfone (Table 2, entry 2)** [1]

$^1\text{H}$ NMR (300 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 8.2$ Hz, 4H), 7.26 (d, $J = 8.0$ Hz, 4H), 2.36 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 143.9, 139.0, 129.9, 127.5, 21.5. GC-MS (EI, m/z): 246[M+].

**m-Methylphenyl p-tolyl sulfone (Table 2, entry 3)** [1]

$^1\text{H}$ NMR (300 MHz, CDCl$_3$): $\delta$ 7.84-7.72 (m, 4H), 7.36-7.26 (m, 4H), 2.37 (s, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 144.1, 141.8, 139.5, 138.8, 133.8, 129.9, 129.1, 127.7, 127.6, 21.5, 21.3. GC-MS (EI, m/z): 246[M+].

**p-Ethylphenyl p-tolyl sulfone (Table 2, entry 4)**

$^1\text{H}$ NMR (300 MHz, CDCl$_3$): $\delta$ 7.85-7.81 (m, 4H), 7.31-7.27 (m, 4H), 2.68-2.66 (m, 2H), 2.38 (s, 6H), 1.22 (m, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 144.0, 139.1, 139.0, 129.9, 128.7, 127.6, 28.8, 21.6, 15.1. GC-MS (EI, m/z): 260[M+]. Anal calcd for C$_{15}$H$_{16}$O$_2$S C, 69.20; H, 6.19. Found C, 69.12; H, 6.15.

**p-Methoxyphenyl p-tolyl sulfone (Table 2, entry 5)** [2]

$^1\text{H}$ NMR (300 MHz, CDCl$_3$): $\delta$ 7.87-7.78 (m, 4H), 7.25 (d, $J = 8.1$ Hz, 2H), 6.93 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H), 2.36 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 163.2, 143.8, 139.3, 133.4, 129.9, 129.6, 127.3, 114.5, 55.7, 21.5. GC-MS (EI, m/z): 262[M+].

**p-Chlorophenyl p-tolyl sulfone (Table 2, entry 6)** [1]

$^1\text{H}$ NMR (300 MHz, CDCl$_3$): $\delta$ 7.88-7.80 (m, 4H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 2.39 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 144.6, 140.5, 139.6, 138.2, 130.1, 129.6, 129.0,
127.7, 21.6. GC-MS (EI, m/z): 267[M+].

**m-Chlorophenyl p-tolyl sulfone (Table 2, entry 7)** [3]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.91-7.80 (m, 4H), 7.51-7.40 (m, 2H), 7.33-7.28 (m, 2H), 2.39 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 144.8, 143.7, 137.8, 135.4, 133.2, 130.6, 130.1, 129.9, 127.8, 127.5, 125.6, 21.6. GC-MS (EI, m/z): 267 [M+].

**p-Fluorophenyl p-tolyl sulfone (Table 2, entry 8)** [1]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.97-7.92 (m, 2H), 7.81 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.3$ Hz, 2H), 7.19-7.13 (m, 2H), 2.39 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 167.0, 163.6, 144.4, 138.5, 138.1, 130.4, 130.2, 130.0, 127.6, 116.7, 116.4, 21.5. GC-MS (EI, m/z): 250[M+].

**m-Fluorophenyl p-tolyl sulfone (Table 2, entry 9)** [1]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J = 8.2$ Hz, 2H), 7.72 (d, $J = 7.8$ Hz, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.49-7.47 (m, 1H), 7.33-7.24 (m, 3H), 2.41 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 164.1, 160.8, 144.6, 138.0, 131.1, 130.0, 129.8, 127.8, 123.3, 120.3, 120.1, 115.0, 114.6, 21.6. GC-MS (EI, m/z): 250[M+].

**p-Bromophenyl p-tolyl sulfone (Table 2, entry 10)** [1]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J = 8.2$ Hz, 2H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.49-7.47 (m, 1H), 7.33-7.24 (m, 3H), 2.41 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 164.5, 141.1, 138.5, 138.2, 132.5, 130.0, 129.0, 128.9, 128.2, 127.7, 21.5. GC-MS (EI, m/z): 311[M+].

**naphthyl p-tolyl sulfone (Table 2, entry 11)** [4]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.56 (s, 1H), 7.94-7.82 (m, 6H), 7.60-7.57 (m, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 2.36 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 144.2, 138.8, 138.7, 134.9, 132.2, 129.9, 129.6, 129.4, 129.1, 128.8, 127.9, 127.8, 127.6, 127.5, 122.6, 21.6. GC-MS (EI, m/z): 282[M+].

**m-Nitrophenyl p-tolyl sulfone (Table 2, entry 12)** [5]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.74 (s, 1H), 8.39 (d, $J = 8.3$ Hz, 1H), 8.27 (d, $J = 7.7$ Hz, 1H), 7.87 (d, $J = 8.2$ Hz, 2H), 7.77-7.72 (m, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 2.42 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 148.4, 145.4, 144.2, 137.0, 133.0, 130.8, 130.4, 128.0, 127.5, 122.7, 21.6. GC-MS (EI, m/z): 277[M+].
**m-Trifluoromethylphenyl p-tolyl sulfone (Table 2, entry 13)**

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.20 (s, 1H), 8.12 (d, $J$=7.8Hz, 1 H), 7.86-7.79 (m, 3 H), 7.67-7.65 (m, 1H), 7.33 (m, 2H), 2.40 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 144.9, 143.3, 137.6, 130.8, 130.2, 129.8, 129.6, 127.9, 127.5, 124.4, 122.7, 21.6. GC-MS (EI, m/z): 300[M+].

![m-Trifluoromethylphenyl p-tolyl sulfone](image)

**3,5-Ditrifluoromethylphenyl p-tolyl sulfone (Table 2, entry 14)**

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.37 (s, 2H), 8.04 (s, 1H), 7.86 (d, $J$=8.3Hz, 2H), 7.37 (d, $J$=8.1Hz, 2H), 2.44 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 145.6, 145.1, 136.7, 133.8, 133.4, 132.9, 132.4, 130.5, 128.1, 127.7, 126.6, 124.2, 120.5, 21.6. GC-MS (EI, m/z): 368[M+]. Anal calcd for C$_{15}$H$_{10}$F$_6$O$_2$S C, 48.92; H, 2.74. Found C, 48.87; H, 2.70.

![3,5-Ditrifluoromethylphenyl p-tolyl sulfone](image)

**p-acetylyphenyl p-tolyl sulfone (Table 2, entry 15)**

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.03 (m, 4H), 7.83 (d, $J$=8.2Hz, 2H), 7.32 (d, $J$=8.1Hz, 2 H), 2.62 (s, 3H), 2.41 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 196.9, 161.0, 145.8, 144.9, 140.1, 137.6, 130.9, 130.2, 129.1, 127.9, 127.8, 115.4, 26.9, 21.6. GC-MS (EI, m/z): 274[M+].

![p-acetylyphenyl p-tolyl sulfone](image)

**Diphenyl Sulfone (Table 2, entry 16)**

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.96-7.93 (m, 4H), 7.58-7.47 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 141.5, 133.3, 129.3, 127.6. GC-MS (EI, m/z): 218 [M+].

![Diphenyl Sulfone](image)

**p-Ethylphenyl phenyl sulfone (Table 2, entry 17)**

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.94 (d, $J$=7.5Hz, 2H), 7.85 (d, $J$=9.1Hz, 2H), 7.54-7.36 (m, 3 H), 7.32 (d, $J$=9.1Hz, 2H), 2.72-2.64 (m, 2H), 1.25-1.19 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 150.3, 141.9, 138.7, 133.0, 129.2, 128.8, 127.8, 127.5, 28.8, 15.1. GC-MS (EI, m/z): 246 [M+].

![p-Ethylphenyl phenyl sulfone](image)

**m-Fluorophenyl phenyl sulfone (Table 2, entry 18)**

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.95 (d, $J$=8.5Hz, 2H), 7.75 (d, $J$=8.5Hz, 1H), 7.66-7.49 (m, 5 H), 7.27-7.26 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 164.1, 160.8, 143.6, 140.9, 133.6, 131.2, 131.1, 129.5, 127.8, 123.4, 120.6, 120.4, 115.1, 114.8. GC-MS (EI, m/z): 236 [M+]. Anal calcd for C$_{12}$H$_{9}$FO$_2$S C, 61.00; H, 3.84. Found C, 60.57; H, 3.83.
**p-Methoxyphenyl phenyl sulfone (Table 2, entry 19)** [6]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.93-7.86 (m, 4H), 7.53-7.46 (m, 3H), 6.98-6.95 (m, 2 H), 3.83 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 163.4, 142.3, 133.0, 132.9, 129.8, 129.2, 127.3, 114.5, 55.7. GC-MS (EI, m/z): 248 [M+].

**p-Fluorophenyl phenyl sulfone (Table 2, entry 20)** [6]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.99-7.92 (m, 4H), 7.58-7.49 (m, 3H), 7.18-7.15 (m, 2 H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 167.1, 163.7, 141.4, 137.6, 133.4, 130.5, 130.4, 129.4, 127.6, 116.8, 116.5. GC-MS (EI, m/z): 236 [M+].

**p-Chlorophenyl phenyl sulfone (Table 2, entry 21)** [6]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.95-7.87 (m, 4H), 7.58-7.45 (m, 5H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 141.1, 140.1, 139.9, 133.5, 129.6, 129.4, 129.3, 129.1, 127.6. GC-MS (EI, m/z): 252 [M+].

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