Supporting Information

A General Copper Catalyzed Sulfonylation of Arylboronic acids

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General: NMR spectra were recorded on a Bruker ARX 300 spectrometer, operating at 300 MHz for ¹H NMR, 75 MHz for ¹³C NMR were reported downfield from CDCl₃ (δ: 7.27 ppm) for ¹H NMR. For ¹³C NMR, chemical shifts were reported in the scale relative to the solvent of CDCl₃ (δ: 77.0 ppm) used as an internal reference. Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector. Column chromatographies were performed with silica gel Merck 60 (70-230 mesh ASTM).

General Procedure for Cu(OAc)₂ Catalyzed Sulfonylation of Aryl Boronic Acid: To a round bottom flask equipped with an air drying tube was added aryl boronic acid (0.5 mmol) to DMSO (2 mL). To the mixture was added Cu(OAc)₂ (20 mol%), 1-benzylimidazole (40 mol%), sodium sulfinate (0.75 mmol), K₂CO₃ (1 mmol) and 4 Å MS (1.25 g). The mixture was stirred for 22 h at 60 °C and then filtered on a Celite pad aluted with EtOAc. The filtrate was diluted with EtOAc and aqueous ammonium chloride and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography to afford the desired product.

Methylsulfonylbenzene **5a**¹

¹H NMR (CDCl₃, 300 MHz) δ: 3.04 (s, 3H), 7.52-7.68 (m, 3H), 7.90-7.96 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ: 44.35, 127.19, 129.26, 133.61, 140.42; MS (EI): *m/z* 156 (M⁺).

2-(Methylsulfonyl)naphthalene **5b**²

¹H NMR (CDCl₃, 300 MHz) δ : 3.13 (s, 3H), 7.61-7.73 (m, 2H), 7.88-8.06 (m, 4H), 8.54 (br s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ : 44.5, 122.08, 127.74, 127.95, 129.00, 129.24, 129.36, 129.69, 132.11, 135.23, 137.35; MS (EI): m/z 206 (M⁺).

1-(Methylsulfonyl)naphthalene **5c**³

¹H NMR (CDCl₃, 300 MHz) δ : 3.22 (s, 3H), 7.57-7.76 (m, 3H), 7.96-8.01 (m, 1H), 8.11-8.17 (m, 1H), 8.32-8.37 (m, 1H), 8.71-8.76 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ : 44.21, 123.84, 124.43, 126.99, 128.59, 128.73, 129.28, 129.60, 134.14, 135.13, 135.51; MS (EI): m/z 206 (M⁺).

4-(Methylsulfonyl)biphenyl **5d**^{3,4}

¹H NMR (CDCl₃, 300 MHz) δ : 3.11 (s, 3H), 7.41-7.55 (m, 3H), 7.59-7.66 (m, 2H), 7.79 (d, J = 8.7 Hz, 2H), 8.02 (d, J = 8.7 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ : 44.61, 127.38, 127.91, 127.98, 128.67, 129.09, 139.05, 139.11, 146.71; MS (EI): m/z 232 (M⁺).

Ethyl(4-(methylsulfonyl)phenyl)sulfane **5e**

Mp: 87-88 °C (hexane+ethyl acetate); IR (KBr): ν (cm⁻¹) = 1585, 1559, 1475, 1456, 1446, 1410, 1396, 1384, 1323, 1304, 1255, 1154, 1100, 1083, 962, 948, 819, 775, 735, 571, 531, 488, 460; ¹H NMR (CDCl₃, 300 MHz) δ : 1.39 (t, J = 7.4 Hz, 3H), 3.04 (q, J = 7.4 Hz, 2H), 3.05 (s, 3H), 7.38 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ : 13.71, 25.96, 44.62, 126.61, 127.65, 136.42, 146.02; MS (EI): m/z 216 (M⁺); HRMS Calcd for C₉H₁₂O₂S₂ 216.0273, Found 216.0270.

1-Methoxy-4-(methylsulfonyl)benzene **5f**^{3,5}

¹H NMR (CDCl₃, 300 MHz) δ : 3.03 (s, 3H), 3.88 (s, 3H), 7.02 (d, J = 9 Hz, 2H), 7.86 (d, J = 9 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ : 44.77, 55.64, 114.42, 129.46, 132.18, 163.61; MS (EI): m/z 186 (M^+).

1-Bromo-3-(methylsulfonyl)benzene **5g**⁶

¹H NMR (CDCl₃, 300 MHz) δ : 3.07 (s, 3H), 7.43-7.50 (s, 1H), 7.75-7.81 (m, 1H), 7.85-7.91 (m, 1H), 8.07-8.10 (m, 1); ¹³C NMR (CDCl₃, 75 MHz) δ : 44.40, 123.27, 125.90, 130.33, 130.90, 136.76, 142.25; MS (m/z): 236 (M^+).

1-(Methylsulfonyl)-2-(trifluoromethyl)benzene **5h**⁷

¹H NMR (CDCl₃, 300 MHz) δ : 3.19 (s, 3H), 7.75-7.84 (m, 2H), 7.89-7.96 (m, 1H), 8.28-8.37 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ : 44.98 (q, ⁴ J_{C-F} = 3.3 Hz), 122.64 (q, ¹ J_{C-F} = 273.6 Hz), 128.33 (q, ³ J_{C-F} = 6.4 Hz), 128.78 (q, ² J_{C-F} = 33.5 Hz), 132.03, 132.82, 133.86, 139.22-139.22 (bm); MS (EI): m/z 224 (M^+).

4-(Methylsulfonyl)phenol **5i**^{5a}

¹H NMR (CDCl₃, 300 MHz) δ : 3.07 (s, 3H), 6.98 (d, J = 8.9 Hz, 2H), 7.79 (d, J = 8.8 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ : 44.89, 116.20, 129.69, 131.38, 160.99; MS (EI): m/z 172 (M^+).

1-(Methylsulfonyl)-4-vinylbenzene **5j**⁸

¹H NMR (CDCl₃, 300 MHz) δ : 3.05 (s, 3H), 5.46 (d, J = 11 Hz, 1H), 5.91 (d, J = 17.5 Hz, 1H), 5.46 (dd, J = 11, 17.7 Hz, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ : 44.49, 117.96, 126.88, 127.66, 135.13, 139.24, 142.80; MS (EI): m/z 182 (M^+).

1-Chloro-3-(methylsulfonyl)benzene **5k**⁹

¹H NMR (CDCl₃, 300 MHz) δ : 3.07 (s, 3H), 7.49-7.56 (m, 1H), 7.60-7.65 (m, 1H), 7.80-7.86 (m, 1H), 7.92-7.95 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ : 44.37, 125.45, 127.50, 130.70, 133.84, 135.52, 142.12; MS (EI): m/z 190 (M⁺).

4-Tosylbiphenyl **5l**

Mp: 206-207 °C (hexane); IR (KBr): ν (cm⁻¹) = 1594, 1480, 1399, 1386, 1320, 1307, 1292, 1155, 1111, 1076, 1005, 840, 819, 764, 718, 708, 692, 678, 647, 584, 559, 529, 488; ¹H NMR (CDCl₃, 300 MHz) δ : 2.18 (s, 3H), 7.29-7.36 (m, 2H), 7.37-7.51 (m, 3H), 7.53-7.60 (m, 2H), 7.66-7.73 (m, 2H), 7.84-7.91 (m, 2H), 7.96-8.03 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ : 21.56, 127.31, 127.68, 127.86, 128.01, 128.51, 129.01, 129.93, 138.75, 139.21, 140.49, 144.15, 145.96; MS (EI): m/z 308 (M⁺); HRMS Calcd for C₁₉H₁₆O₂S 308.0866, Found 308.0860.

Ethyl(4-(phenylsulfonyl)phenyl)sulfane **5m**

Mp: 91 °C (hexane+ethyl acetate); IR (KBr): ν (cm⁻¹) = 1583, 1478, 1446, 1393, 1381, 1317, 1299, 1283, 1177, 1156, 1113, 1087, 1071, 1009, 999, 826, 818, 793, 769, 749, 721, 703, 683, 619, 570, 564, 505; ¹H NMR (CDCl₃, 300 MHz) δ : 1.27 (t, J = 7.34 Hz, 3H), 2.91 (d, J = 7.38 Hz, 2H), 7.20-7.27 (m, 2H), 7.38-7.52 (m, 3H), 7.70-7.77 (m, 2H), 7.82-7.89 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ : 13.73, 25.93, 126.56, 127.42, 127.95, 129.23, 133.04, 137.38, 141.79, 145.46; MS (EI): m/z 278 (M⁺); HRMS Calcd for C₁₄H₁₄O₂S₂ 278.0430, Found 278.0432.

4-(Methylsulfonyl)pyridine **5n**¹⁰

¹H NMR (CDCl₃, 300 MHz) δ : 3.10 (s, 3H), 7.79-7.83 (m, 2H), 8.91-8.95 (s, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ : 43.80, 120.42, 148.27, 151.40; MS (EI): m/z 157 (M⁺).

3-(Methylsulfonyl)thiophene **5o**¹¹

¹H NMR (CDCl₃, 300 MHz) δ : 3.10 (s, 3H), 7.40-7.43 (m, 1H), 7.45-7.50 (m, 1H), 8.08-8.11 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ : 44.74, 125.43, 128.51, 131.85, 141.07; MS (EI): m/z 162 (M⁺).

(*E*)-(2-(Methylsulfonyl)vinyl)benzene **5p**¹²

¹H NMR (CDCl₃, 300 MHz) δ : 3.04 (s, 3H), 6.93 (d, J = 15.5 Hz, 1H), 7.39-7.56 (m, 5H), 7.64 (d, J = 15.5 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ : 43.25, 126.10, 128.54, 129.13, 131.37, 132.01, 143.99; MS (EI): m/z 182 (M⁺).

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