

# **An Efficient Copper Catalyst for the Formation of Sulfones from Sulfinic Acid Salts and Aryl Iodides**

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## **Supporting Information**

**General Considerations:** All reactions were carried out in sealed test tubes under a nitrogen atmosphere. *N,N'*-dimethylethylenediamine was purchased from Aldrich and used without further purification. Copper (I) triflate ((CuOTf)<sub>2</sub> PhH) was purchased from Aldrich. All other reagents were commercially available and were used without further purification. All solids were weighed in the air. Flash column chromatography was performed with Silica gel 60 (230-400 mesh). <sup>1</sup>H and <sup>13</sup>C NMR were recorded on a Bruker 500 MHz instrument with chemical shifts reported relative to residual deuterated solvent peaks. All spectra were taken in acetone-d<sub>6</sub> and, in addition to the multiplet at 2.07 ppm due to acetone, exhibit a strong singlet at 2.88 ppm and a weak singlet at 2.84 ppm due to residual water absorbed by acetone-d<sub>6</sub>. HPLC analyses were performed on an Alliance Waters 2690 system with a Waters 990 Photodiode Array Detector. All yields reported in this publication refer to isolated yields of compounds estimated to be >95% pure as determined by <sup>1</sup>H NMR.

## **General Procedure for the Copper-Catalyzed Coupling of Sulfinic Acid Salts with Aryl Halides.**

(a) Used in the case that the aryl iodide is a solid at room temperature

To a sealable tube with an 8 x 1.5 mm stir bar was added 0.05 mmol of (CuOTf)<sub>2</sub> PhH, 1.20 mmol of the sodium sulfinate, and 1.00 mmol of the aryl iodide under an air

atmosphere. The aperture of the tube was then covered with a rubber septum and a nitrogen atmosphere was established. *N,N'*-dimethylethylenediamine (0.10 mmol) and anhydrous DMSO (1 mL) were added via syringe. The septum was replaced by a teflon coated screw cap and the reaction vessel was placed in a 110 °C oil bath. After stirring for approximately 20 h, the reaction mixture was allowed to cool to room temperature, diluted with 10 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was washed with water (2 x 20 mL) and brine (1 x 20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through silica gel, and concentrated. In some cases, further purification by flash column chromatography was required to obtain a pure product. In all cases, the yields reported in the publication represent the isolated yield of products of >95% purity as determined by <sup>1</sup>H NMR.

(b) Used in the case that the aryl iodide is a liquid at room temperature

To a sealable tube with an 8 x 1.5 mm stir bar was added 0.05 mmol of (CuOTf)<sub>2</sub> PhH and 1.20 mmol of the sodium sulfinate under an air atmosphere. The aperture of the tube was then covered with a rubber septum and a nitrogen atmosphere was established. *N,N'*-dimethylethylenediamine (0.10 mmol), the aryl iodide (1.00 mmol), and anhydrous DMSO (1 mL) were added via syringe. The septum was replaced by a teflon coated screw cap and the reaction vessel was placed in a 110 °C oil bath. After stirring for approximately 20 h, the reaction mixture was allowed to cool to room temperature, diluted with 10 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was washed with water (2 x 20 mL) and brine (1 x 20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through silica gel, and concentrated. In some cases, further purification by flash column chromatography was required to obtain a pure product. In all cases, the yields reported in the publication represent the isolated yield of products of >95% purity as determined by <sup>1</sup>H NMR.

**1-methanesulfonyl-naphthalene (Table 1, Entry 1).** General procedure (b) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 mL (0.10 mmol) *N,N'*-dimethylethylenediamine, and 146 mL (1.00

mmol) 1-iodonaphthalene. The title compound (197 mg, 96%) was obtained as a white solid. M.P. 102 °C (lit.<sup>1</sup> 102-103 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 8.78 (d, 1H, J = 8.7 Hz), 8.33 (t, 1H, J = 4.3 Hz), 8.32 (d, 1H, J = 6.3 Hz), 8.16 (d, 1H, J = 8.2), 7.80 (td, 1H, J = 8.5, 1.4 Hz), 7.73-7.77 (m, 2H), 3.30 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 137.18, 135.70, 135.06, 130.07, 130.04, 129.32, 129.26, 127.77, 125.42, 124.91, 44.38. MS (APCI)<sup>+</sup> m/z (rel intens) 207 (M + H, 35), 128 (M – SO<sub>2</sub>Me, 100).

**2-methanesulfonyl-thiophene (Table 1, Entry 2).** General procedure (b) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 110 L (1.00 mmol) 2-iodothiophene. The title compound (102 mg, 63%) was obtained as a beige solid after purification by flash column chromatography eluted with 2:1 hexanes:ethyl acetate. M.P. 47 °C (lit.<sup>2</sup> 47 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 8.02 (dd, 1H, J = 5.0, 1.3 Hz), 7.78 (dd, 1H, J = 3.8, 1.2 Hz), 7.28 (dd, 1H, J = 5.0, 3.8 Hz), 3.26 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 143.26, 134.65, 134.06, 128.85, 45.97. HRMS (FAB)<sup>+</sup> m/z calcd for C<sub>5</sub>H<sub>6</sub>O<sub>2</sub>S<sub>2</sub>K (M + K)<sup>+</sup>, 200.9447; found, 200.9446.

**1-(4-methanesulfonyl-phenyl)-ethanone (Table 1, Entry 3).** General procedure (a) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 246 mg (1.00 mmol) 4-iodoacetophenone. The title compound (144 mg, 73%) was obtained as a light orange solid. M.P. 124 °C (lit.<sup>3</sup> 127 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 8.24 (d, 2H, J = 6.6 Hz), 8.11 (d, 2H, 6.6 Hz), 3.21 (s, 3H), 2.70 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 197.41, 145.66, 141.70, 129.82, 128.46, 43.98, 27.04.

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<sup>1</sup> Otto, R.; Passing, A.; Troeger, J. *J. Prakt. Chem.* **1893**, 47, 102.

<sup>2</sup> Burton, H.; Davy, W. A. *J. Chem. Soc.* **1948**, 525.

<sup>3</sup> Leclerc, G.; Mann, A.; Wermuth, C-G. *J. Med. Chem.* **1977**, 20, 1657.

**1-methanesulfonyl-2-methyl-benzene<sup>4</sup>** (Table 1, Entry 4). General procedure (b) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 127 L (1.00 mmol) 2-iodotoluene. The title compound (129 mg, 76%) was obtained as an oil. <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 7.99 (d, 1H, J = 8.0 Hz), 7.62 (t, 1H, J = 7.5 Hz), 7.48 (t, 1H, J = 6.6 Hz), 7.46 (d, 1H, J = 7.1 Hz), 3.15 (s, 3H), 2.72 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 140.24, 138.36, 134.30, 133.46, 129.59, 127.39, 43.70, 20.13. MS (APCI)<sup>+</sup> m/z (rel intens) 171 (M + H, 100), 91 (M – SO<sub>2</sub>Me, 80).

**2-methanesulfonyl-biphenyl** (Table 1, Entry 5). General procedure (b) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 177 L (1.00 mmol) 2-iodobiphenyl, except the reaction time was 64 h. The title compound (173 mg, 75%) was obtained as a white solid after purification by flash column chromatography eluted with 3:1 hexanes:ethyl acetate. M.P. 101 °C (lit.<sup>5</sup> 100-101 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 8.19 (dd, 1H, J = 8.0, 1.3 Hz), 7.78 (td, 1H, J = 7.5, 1.3 Hz), 7.68 (td, 1H, J = 7.9, 1.4 Hz), 7.47-7.52 (m, 5H), 7.44 (dd, 1H, J = 7.5, 1.2 Hz), 2.70 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 140.24, 138.36, 134.30, 133.46, 129.59, 127.39, 43.70, 20.13. MS (APCI)<sup>+</sup> m/z (rel intens) 233 (M + H, 100), 154 (M – SO<sub>2</sub>Me, 65).

**1-methanesulfonyl-3,5-dimethyl-benzene** (Table 1, Entry 6). General procedure (b) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 144 L (1.00 mmol) 3,5-dimethyliodobenzene. The title compound (167 mg, 91%)

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<sup>4</sup> Hyatt, J. A.; White, A. W. *Synthesis*, **1984**, 214.

<sup>5</sup> Emrick, D. D.; Truce, W. E. *J. Org. Chem.* **1960**, 25, 1103.

was obtained as a white solid. M.P. 83 °C (lit.<sup>6</sup> 81-82.5 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 7.57 (s, 2H), 7.38 (s, 1H), 3.09 (s, 3H), 2.43 (s, 6H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 142.10, 140.08, 135.57, 125.38, 44.25, 21.06. MS (APCI)<sup>+</sup> m/z (rel intens) 185 (M + H, 70), 106 (M – SO<sub>2</sub>Me, 100).

**1-methanesulfonyl-4-nitro-benzene (Table 1, Entry 7).** General procedure (a) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 249 mg (1.00 mmol) 4-nitroiodobenzene. The title compound (171 mg, 85%) was obtained as a yellow solid. M.P. 125 °C. <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 8.52 (d, 2H, J = 8.8 Hz), 8.28 (d, 2H, J = 8.8 Hz), 3.29 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 147.30, 129.87, 129.10, 125.32, 43.87. Note: The product was obtained as a 12:1 mixture of the desired product and 1,4-bis(methanesulfonyl)-benzene, as determined by <sup>1</sup>H NMR: 8.25 (s, 4H), 3.26 (s, 6H). HRMS (FAB)<sup>+</sup> m/z calcd for C<sub>7</sub>H<sub>8</sub>NO<sub>2</sub>S (M + H)<sup>+</sup>, 202.0174; found, 202.0174.

**1-methanesulfonyl-4-methoxy-benzene (Table 1, Entry 8).** General procedure (a) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 234 mg (1.00 mmol) 4-iodoanisole. The title compound (161 mg, 86%) was obtained as a white solid. M.P. 120 °C (lit.<sup>7</sup> 120 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 7.89 (d, 2H, J = 8.9 Hz), 7.16 (d, 2H, J = 8.9 Hz), 3.94 (s, 3H), 3.08 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 164.44, 134.06, 130.27, 115.20, 56.14, 44.63. MS (APCI)<sup>+</sup> m/z (rel intens) 187 (M + H, 30), 108 (M – SO<sub>2</sub>Me, 100), 78 (20).

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<sup>6</sup> Koptiyug, V. A.; Gerasimova, T. N. *J. Gen. Chem. USSR*(Eng. Trans), **1962**, 32, 3718.

<sup>7</sup> Suter, C. M.; Hansen, H. L. *J. Am. Chem. Soc.* **1932**, 54, 4101.

**1-methanesulfonyl-4-trifluoromethyl-benzene (Table 1, Entry 9).** General procedure (b) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 147 L (1.00 mmol) 4-trifluoromethyliodobenzene. The title compound (187 mg, 83%) was obtained as a white solid. M.P. 103-104 °C. <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 8.22 (d, 2H, J = 8.2 Hz), 8.05 (d, 2H, J 8.2 Hz), 3.25 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 145.83, 135.46, 135.20, 134.94, 134.68, 129.14, 127.64, 127.32, 127.29, 127.26, 127.23, 125.48, 123.31, 121.15, 43.95. HRMS (FAB)<sup>+</sup> *m/z* calcd for C<sub>8</sub>H<sub>8</sub>F<sub>3</sub>O<sub>2</sub>S (M + H)<sup>+</sup>, 225.01975; found, 225.01971.

**1-methanesulfonyl-4-methylsulfanyl-benzene (Table 1, Entry 10).** General procedure (a) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 250 mg (1.00 mmol) 4-iodothioanisole. The title compound (181 mg, 90%) was obtained as a white solid. M.P. 98 °C (lit.<sup>8</sup> 98-99 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 7.85 (d, 2H, J = 8.1 Hz), 7.50 (d, 2H, J = 8.1 Hz), 3.11 (s, 3H), 2.61 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 147.51, 137.90, 128.40, 126.10, 44.38, 14.46. MS (APCI)<sup>+</sup> *m/z* (rel intens) 203 (M + H, 40), 124 (M – SO<sub>2</sub>Me, 100).

**1-chloro-4-methanesulfonyl-benzene (Table 1, Entry 11).** General procedure (a) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 238 mg (1.00 mmol) 4-chloriodobenzene. The title compound (148 mg, 78%) was obtained as a white solid. M.P. 96 °C (lit.<sup>9</sup> 98 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 7.99 (d, 2H, J = 8.6 Hz), 7.72 (d, 2H, J = 8.6 Hz), 3.18 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 140.91,

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<sup>8</sup> Burton, H.; Hu, P. F. *J. Chem. Soc.* **1948**, 604.

<sup>9</sup> Gilbert, E. E. *J. Org. Chem.* **1963**, 28, 1945.

140.04, 130.26, 129.95, 44.17. HRMS (FAB)<sup>+</sup> *m/z* calcd for C<sub>7</sub>H<sub>7</sub>O<sub>2</sub>SClK (M + K)<sup>+</sup>, 228.9491; found, 228.9492.

Note: The product was obtained as a 24:1 mixture of the desired product and 1,4-bis(methanesulfonyl)-benzene, as determined by <sup>1</sup>H NMR: 8.25 (s, 4H), 3.26 (s, 6H).

***N*-(4-methanesulfonyl-phenyl)-acetamide (Table 1, Entry 12).** General procedure (a) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 204 mg (2.00 mmol) methanesulfinic acid, sodium salt, 11 mL (0.10 mmol) *N,N'*-dimethylethylenediamine, and 261 mg (1.00 mmol) 4-iodoacetanilide. The crude product was stirred as a suspension in 10 mL of a 1:1 mixture of ethyl acetate and hexanes for approximately 30 min, and the title compound (58 mg, 27%) was obtained by filtration as a white solid. M.P. 184 °C (lit.<sup>10</sup> 183-184 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 9.58 (s, broad, 1H), 7.89 (d, 2H, *J* = 9.1 Hz), 7.87 (d, 1H, *J* = 9.1 Hz), 3.09 (s, 3H), 2.15 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 169.65, 144.88, 136.00, 129.22, 119.55, 44.49, 24.35. MS (APCI)<sup>+</sup> *m/z* (rel intens) 214 (M + H, 35), 93 (100).

**1-methanesulfonyl-naphthalene (Table 1, Entry 13).** General procedure (b) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 123 mg (1.20 mmol) methanesulfinic acid, sodium salt, 11 mL (0.10 mmol) *N,N'*-dimethylethylenediamine, and 146 mL (1.00 mmol) 1-bromonaphthalene. The title compound (50 mg, 24%) was obtained as a white solid after purification by flash column chromatography eluted with a gradient of 3:1 to 2:1 hexanes:ethyl acetate. <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 8.78 (d, 1H, *J* = 8.7 Hz), 8.33 (t, 1H, *J* = 4.3 Hz), 8.32 (d, 1H, *J* = 6.3 Hz), 8.16 (d, 1H, *J* = 8.2), 7.80 (td, 1H, *J* = 8.5, 1.4 Hz), 7.73-7.77 (m, 2H), 3.30 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 137.18, 135.70, 135.06, 130.07, 130.04, 129.32, 129.26, 127.77, 125.42, 124.91, 44.38.

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<sup>10</sup> Gilman, H.; Lindblad, A. E. *J. Am. Chem. Soc.* **1946**, 68, 982.

**1,1'-sulfonylbis-benzene (Table 2, Entry 1).** General procedure (b) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 263 mg (1.60 mmol) benzenesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 112 L (1.00 mmol) iodobenzene. The title compound (153 mg, 70%) was obtained as a white solid. M.P. 125 °C (lit.<sup>11</sup> 128-129 °C). <sup>1</sup>H NMR (500 MHz, acetone-D<sub>6</sub>): 8.01 (m, 4H), 7.68-7.72 (m, 2H), 7.62-7.66 (m, 4H). <sup>13</sup>C NMR (125 MHz, acetone-D<sub>6</sub>): 142.88, 134.17, 130.32, 128.35. MS (APCI)<sup>+</sup> m/z (rel intens) 219 (M + H, 70), 141 (M – Ph, 60), 77 (100).

**1,1'-sulfonylbis(4-methyl-benzene) (Table 2, Entry 2).** General procedure (a) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 257 mg (1.20 mmol) 4-toluenesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 218 mg (1.00 mmol) 4-iodotoluene. The title compound (173 mg, 70%) was obtained as a white solid. M.P. 159 °C (lit.<sup>12</sup> 158 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 7.85 (d, 4H, J = 8.2 Hz), 7.42 (d, 4H, J = 8.2 Hz), 2.41 (s, 6H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 144.93, 140.43, 130.75, 128.29, 21.34. MS (APCI)<sup>+</sup> m/z (rel intens) 247 (M + H, 100), 155 (M – Tol, 100), 91 (60).

**1-methoxy-4-(toluene-4-sulfonyl)-benzene (Table 2, Entry 3).** General procedure (a) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 257 mg (1.20 mmol) 4-toluenesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 234 mg (1.00 mmol) 4-iodoanisole, except the reaction time was 48 h. The title compound (197 mg, 75%) was obtained as a white solid after purification by flash column chromatography eluted with a gradient of 3:1 to 2:1 hexanes:ethyl acetate. M.P.

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<sup>11</sup> Sato, K.; Hyodo, M.; Aoki, M.; Zheng, X-Q.; Noyori, R. *Tetrahedron*, **2001**, 57, 2469.

<sup>12</sup> Meyer, H. *Ann.* **1923**, 433, 336.



105 °C (lit.<sup>13</sup> 103 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 7.91 (d, 2H, J = 8.9 Hz), 7.84 (d, 2H, J = 8.4 Hz), 7.41 (d, 2H, J = 8.4 Hz), 7.12 (d, 2H, J = 8.9 Hz), 3.90 (s, 3H), 2.41 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 164.25, 144.68, 140.88, 134.77, 130.71, 130.48, 128.09, 115.40, 56.11, 21.32. MS (APCI)<sup>+</sup> m/z (rel intens) 263 (M + H, 100), 171 (M – Tol, 55), 155 (M – PhOMe, 30), 91 (PhOMe, 30).

**2-(toluene-4-sulfonyl)-thiophene (Table 2, Entry 4).** General procedure (b) was followed using 25 mg (0.05 mmol) (CuOTf)<sub>2</sub> PhH, 257 mg (1.20 mmol) 4-toluenesulfinic acid, sodium salt, 11 L (0.10 mmol) *N,N'*-dimethylethylenediamine, and 110 L (1.00 mmol) 2-iodothiophene. The title compound (103 mg, 43%) was obtained as a white solid after purification by flash column chromatography eluted with 3:1 hexanes:ethyl acetate. M.P. 120 °C (lit.<sup>14</sup> 113-114 °C). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>): 7.98 (dd, 1H, J = 5.0, 1.3 Hz), 7.91 (d, 2H, J = 8.3 Hz), 7.78 (dd, 1H, J = 3.8, 1.4 Hz), 7.46 (d, 2H, J = 8.3 Hz), 7.22 (dd, 1H, J = 5.0, 3.8 Hz), 2.44 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>): 145.26, 144.46, 140.47, 135.28, 134.23, 130.88, 129.01, 128.00, 21.38. MS (APCI)<sup>+</sup> m/z (rel intens) 238 (M + H, 90), 155 (M – thiophenyl, 25), 147 (M-tol, 100), 99 (tolyl, 95).

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<sup>13</sup> Proctor, T.; *J. Chem. Soc.* **1957**, 2312.

<sup>14</sup> Voronkov et al; CHCCAL; *Chem. Heterocle. Compd*(Eng. Trans.), **1975**, 11, 1131.