Supporting Information

Unsymmetrical Diaryl Sulfones through Palladium-Catalyzed Coupling of Aryl Iodides and Arenesulfinates

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Melting points were determined with a Büchi apparatus and are uncorrected. Reaction products were purified on axially compressed columns, packed with SiO₂ 25-40 µm (Macherey Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluting with *n*-hexane/ethyl acetate mixtures. ¹H NMR (200 MHz) and ¹³C NMR (50.3 MHz) spectra were recorded with a Bruker Avance 200 spectrometer. IR spectra were recorded with a Jasco FT/IR-430 spectrometer.

Table. Ligands and Solvents in the Reaction of *p*-Iodoanisole with Sodium *p*-Toluenesulfinate **1** in the presence of Pd₂(dba)₃ to give *p*-Methoxyphenyl Toly Sulfone.^a

entry	ligand	solvent	base/salt	reaction time (h)	yield % of <i>p</i> -methoxyphenyl tolyl sulfone
1	Xantphos	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	1	90 ^b
2	-	toluene	Cs ₂ CO ₃ /-	36	-
3	Xantphos	toluene	-/ ⁿ Bu ₄ NCl	24	49
4	Xantphos	toluene	Cs ₂ CO ₃ /-	8	70
5	-	toluene	-	48	-
6	Xantphos	DMSO	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	24	9 ^c
7	Xantphos	DMF	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	24	22 ^d
8	Xantphos	DME	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	36	-
9	PPh ₃	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-
10	(<i>o</i> -tol) ₃ P	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-
11	(<i>o</i> -furyl) ₃ P	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-
12	(<i>p</i> -MeO-C ₆ H ₄) ₃ P	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-
13	(2,4,6-Me ₃ -C ₆ H ₂) ₃ P	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-
14	(<i>p</i> -Cl-C ₆ H ₄) ₃ P	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-
15	Binap	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-
16	MOP	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-
17	dppp	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-
18	dppb	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-
19	1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride ^e	toluene	Cs ₂ CO ₃ / ⁿ Bu ₄ NCl	6	-

^aReactions were conducted on a 0.350 mmol scale in starting aryl iodides in 2 mL of solvent under argon at 80 °C using the following molar ratios: **1**:*p*-iodoanisole: Pd₂(dba)₃:ligand:base:ⁿBu₄NCl (when added) = 1.2:1:0.025:0.05 (bidentate ligands) or 0.1 (monodentate ligands):1.5:1.2. ^b81% in 6 h with toluene sulfinic acid lithium salt. ^c*p*-Iodoanisole was recovered in 70% yield. ^d*p*-Iodoanisole was recovered in 45%. Toluenesulfinic acid 4-methoxyphenyl ester (derived from the competing *O*-arylation process) was isolated in 9% yield. ^e1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride has been shown to generate in situ, in the presence of Cs₂CO₃ as the base, the corresponding carbene ligand: Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804.

Typical procedure for the preparation of unsymmetrical diaryl sulfones: in a Carousel Tube Reaction (Radley Discovery), to a solution of sodium *p*-toluenesulfinate (0.075 g, 0.420 mmol) and *p*-iodoanisole (0.082 g, 0.350 mmol) in 2.0 mL of toluene under argon, Pd₂(dba)₃ (0.008 g, 0.009 mmol) Xantphos (0.010 g, 0.018 mmol), Cs₂CO₃ (0.171 g, 0.525 mmol) and ⁿBu₄NCl (0.117 g, 0.420 mmol) were added. The mixture was warmed at 80 °C and stirred for 1 h. After cooling, the reaction mixture was diluted with ethyl acetate, washed with water, dried over Na₂SO₄ and concentrated under reduced pressure. The reaction mixture was purified by chromatography (silica gel, 35 g; *n*-hexane/ethylacetate 80/20 v/v) to give 0.0825 g of *p*-methoxyphenyl *p*-tolyl sulfone (90 % yield): mp 100-1 °C; lit. mp 90-91 °C;¹ IR (KBr) 2925, 1320, 1152; ¹H NMR (CDCl₃) δ 7.57-7.44 (m, 4H), 7.25 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H); 3.86 (s, 3H); 2.40 (s, 3H); ¹³C NMR (CDCl₃) δ 159.0, 138.1, 136.4, 133.8, 129.5, 128.0, 126.7, 114.2, 55.4, 21.1. Anal calcd for C₁₄H₁₄O₃S C, C, 64.10; H, 5.38. Found C, 64.01; H, 5.36.

Phenyl *p*-tolyl sulfone: mp: 120-1 °C; lit. mp: 119-122 °C;² IR (KBr): 2925, 1593, 1447 cm⁻¹; ¹H NMR (CDCl₃) δ 7.88 (dd, *J*₁ = 7.7 Hz, *J*₂ = 1.5 Hz, 2H), 7.83 (d, *J* = 8.3 Hz), 7.54-7.47 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H); ¹³C NMR (CDCl₃) δ 144.2, 142.0, 138.7, 133.0, 129.9, 129.3, 127.7, 127.5, 21.6; Anal calcd for C₁₃H₁₂O₂S, C, 67.21; H, 5.21. Found C, 67.15; H, 5.19.

Di-*p*-tolyl sulfone: mp: 148-9 °C; lit mp: 158-160 °C;³ IR (KBr): 2924, 1318, 1154 cm⁻¹; ¹H NMR (CDCl₃) δ 7.80 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.9 Hz, 4H), 7.27 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.7 Hz, 4H), 2.38 (s, 6H); ¹³C NMR (CDCl₃) δ 143.9, 139.1, 129.9, 127.6, 21.6. Anal calcd for C₁₄H₁₄O₂S, C, 68.26; H, 5.73. Found C, 68.18; H, 5.71.

***m*-Methylphenyl *p*-tolyl sulfone:** mp 102-3 °C; lit. mp: 115-116 °C;⁴ IR (KBr) 2923, 1320, 1151 cm⁻¹; ¹H NMR (CDCl₃) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.73-7.68 (m, 2H), 7.38-7.24 (m, 4H), 2.38 (s, 3H), 3.36 (s, 3H); ¹³C NMR (CDCl₃) δ 144.1, 141.9, 139.6, 138.9, 133.9, 130.0, 129.2, 127.9, 127.7, 124.7, 21.6, 21.4; Anal calcd for C₁₄H₁₄O₂S, C, 68.26; H, 5.73. Found C, 68.20; H, 5.71.

3,5-Dimethylphenyl *p*-tolyl sulfone: mp 119-120 °C; lit. mp: 113-115 °C;⁵ IR (KBr): 2924, 1299, 1152 cm⁻¹; ¹H NMR (CDCl₃) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.53 (s, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.15 (s, 1H), 2.38 (s, 3H), 2.34 (s, 6H); ¹³C NMR (CDCl₃) δ 144.0, 141.7, 139.4, 139.0, 134.8, 129.9, 127.7, 125.1, 21.6, 21.3; Anal calcd for C₁₅H₁₆O₂S, C, 69.20; H, 6.19. Found C, 69.12; H, 6.17.

***m*-Methoxyphenyl *p*-tolyl sulfone:** mp 75-76 °C; lit. mp: 73 °C;⁶ IR (KBr) 2940, 1314, 1151 cm⁻¹; ¹H NMR (CDCl₃) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.52-7.25 (m, 5H), 7.04 (ddd, *J*₁ = 7.0 Hz, *J*₂ = 2.6 Hz, *J*₃ = 1.1 Hz, 1H), 3.81 (s, 3H), 2.37 (s, 3H); ¹³C NMR (CDCl₃) δ 160.1, 144.3, 143.2, 138.7, 130.4, 130.0, 127.8, 119.8, 119.4, 112.2, 55.7, 21.6. Anal calcd for C₁₄H₁₄O₃S C, C, 64.10; H, 5.38. Found C, 64.01; H, 5.36.

***p*-Fluorophenyl *p*-tolyl sulfone:** mp 85-6 °C; IR (KBr) 2923, 1323, 1152 cm⁻¹; ¹H NMR (CDCl₃) δ 8.02-7.87 (m, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.20-7.07 (m, 2H), 2.38 (s, 3H); ¹³C NMR (CDCl₃) δ 165.4 (d, *J* = 255.5 Hz), 144.5, 138.7, 130.4 (d, *J* = 9.5 Hz), 130.1, 129.6 (d, *J* = 35.2 Hz), 127.7, 116.6 (d, *J* = 22.7 Hz), 21.6; ¹⁹F NMR {H} (CDCl₃) δ -109.40. Anal calcd for C₁₃H₁₁FO₂S C, 62.38; H, 4.43. Found C, 62.30; H, 4.42.

***m*-Fluorophenyl *p*-tolyl sulfone:** wax; IR (neat) 2922, 1320, 1154 cm⁻¹; ¹H NMR (CDCl₃) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.74-7.40 (m, 3H), 7.33-7.21 (m, 3H), 2.39 (s, 3H); ¹³C NMR (CDCl₃) δ 162.5 (d, *J* = 250.5 Hz), 144.8, 138.0, 131.2 (d, *J* = 7.7 Hz), 130.2, 127.9, 127.7 (d, *J* = 11.3 Hz), 123.4 (d, *J* = 3.3 Hz), 120.5 (d, *J* = 21.3 Hz), 114.9 (d, *J* = 24.3 Hz), 21.7; ¹⁹F NMR {H} (CDCl₃) δ -109.72. Anal calcd for C₁₃H₁₁FO₂S C, 62.38; H, 4.43. Found C, 62.31; H, 4.41.

***p*-Chlorophenyl *p*-tolyl sulfone:** mp 119-120 °C; lit. mp 115-117 °C;⁵ IR (KBr) 3091, 1321, 1155 cm⁻¹; ¹H NMR (CDCl₃) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H); ¹³C NMR (CDCl₃) δ 144.6, 140.6, 139.7, 138.3, 130.1, 129.6, 129.0, 127.8, 21.7. Anal calcd for C₁₃H₁₁ClO₂S C, 58.54; H, 4.16. Found C, 58.47; H, 4.18.

***p*-Bromophenyl *p*-tolyl sulfone:** mp 132-3°C; lit. mp 132-134;⁵ IR (KBr) 2923, 1319, 1155 cm⁻¹; ¹H NMR (CDCl₃) δ 7.83-7.73 (m, 4H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H); ¹³C NMR (CDCl₃) δ 144.6, 141.1, 138.2, 132.6, 130.1, 129.1, 128.3, 127.8, 21.7. Anal calcd for C₁₃H₁₁BrO₂S C, 50.17; H, 3.56. Found C, 50.08; H, 3.55.

***p*-Nitrophenyl *p*-tolyl sulfone:** mp 164-5 °C; IR (KBr) 2926, 1351, 1157 cm⁻¹; ¹H NMR (CDCl₃) δ 8.31 (d, *J* = 8.9 Hz, 2H), 8.10 (d, *J* = 8.9 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (CDCl₃) δ 150.3, 147.9, 145.5, 137.1, 130.4, 128.9, 128.2, 124.5, 21.7. Anal calcd for C₁₃H₁₁NO₄S C, 56.31; H, 4.00; N, 5.05. Found C, 56.23; H, 3.99; N, 4.98.

***p*-Carbethoxyphenyl *p*-tolyl sulfone:** mp 87-8 °C; IR (KBr) 2983, 1725, 1324, 1155 cm⁻¹; ¹H NMR (CDCl₃) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (CDCl₃) δ 165.1, 145.8, 144.8, 138.0, 134.5, 130.4, 130.2, 128.0, 127.7, 61.8, 21.7, 14.3. Anal calcd for C₁₆H₁₆O₄S C, 63.14; H, 5.30. Found C, 63.09; H, 5.31.

***m*-Trifluoromethylphenyl *p*-tolyl sulfone:** mp 98-9 °C; lit. mp: 101-2 °C;⁴ IR (KBr) 2923, 1595, 1325 cm⁻¹; ¹H NMR (CDCl₃) δ 8.20 (s, 1H), 8.11(d, *J* = 8.3 Hz, 1H), 7.88-7.76 (m, 3H), 7.70-7.60 (m, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (CDCl₃) δ 144.4, 143.4, 137.7, 131.9 (q, *J* = 33.5 Hz), 130.2, 130.1, 129.7 (q, *J* = 3.4 Hz), 127.9, 124.5 (q, *J* = 3.8 Hz), 123.1 (q, *J* = 273.0 Hz), 21.6; ¹⁹F NMR {H} (CDCl₃) δ -63.26. Anal calcd for C₁₄H₁₁F₃O₂S C, 55.99; H, 3.69. Found C, 55.91; H, 3.67.

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