Supporting Information

Palladium Phosphinous Acid-Catalyzed NaOH-promoted Cross-Coupling Reactions of Arylsiloxanes with Aryl Chlorides and Bromides in Water

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Experimental Procedures

General Procedures. All chemicals were of reagent grade. Reactions were carried out using a high pressure vessel (i.d. 31.7cm) made of 4.0mm Pyrex 7740 heavy wall glass and equipped with a 4mm bore valve and Aegis backing o-ring. Flash chromatography was carried out on Kieselgel 60, particle size 0.032-0.063 mm. NMR spectra were obtained at 300 MHz (^1H NMR) and 75 MHz (^{13}C NMR) using CDCl_3 as the solvent. Chemical shifts are reported in ppm relative to TMS. 4-Methylbiphenyl, **26**, and 2-phenylthiophene, **28**, are commercially available.

Cross-coupling procedure.

A mixture of 100 mg aryl halide and 7 mol% of POPd1, and 2 equivalents of aryltrimethoxysilane, was stirred in 5 mL 0.5 M NaOH at 135°C for 24h using a closed vessel. The reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with Et_2O . The combined organic layers were washed with brine, dried over MgSO_4 , and the solvents were removed under vacuum. The residue was purified by flash chromatography on silica gel, vide infra.

3-Phenylpyridine, 5.^[1] Purification by chromatography on silica gel using hexanes:ethyl acetate 5:1. ^1H NMR (300 MHz, CDCl_3) δ 7.33-7.51 (m, 4H), 7.56-7.61 (m, 2H), 7.88 (ddd, $J=0.6\text{Hz}$, $J=1.7\text{Hz}$, $J=7.8\text{Hz}$, 1H), 8.59 (dd, $J=1.7\text{Hz}$, $J=4.7\text{Hz}$, 1H), 8.85 (dd,

$J=0.9\text{Hz}$, $J=2.5\text{Hz}$, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 123.7, 127.3, 128.3, 129.3, 134.5, 136.8, 138.1, 148.5, 148.6. EI-MS (70eV): m/z (%) = 155 (100, M^+), 78 (5, M^+-Ph), 77 (10, M^+-py).

2-(3-Pyridyl)furan, 10.^[2] Purification by chromatography on silica gel using hexanes:ethyl acetate:triethylamine 100:10:1. ^1H NMR (300 MHz, CDCl_3) δ 6.70 (d, $J=2.8$ Hz, 1H), 7.29 (dd, $J=4.9\text{Hz}$, $J=7.9\text{Hz}$, 1H), 7.51 (d, $J=2.8$ Hz, 1H), 7.73-7.77 (m, 2H), 8.50 (dd, $J=1.6\text{Hz}$, $J=4.9\text{Hz}$, 1H), 8.75 (d, $J=1.4\text{Hz}$, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 108.8, 123.8, 128.6, 133.2, 139.1, 144.4, 147.3, 148.3. EI-MS (70eV): m/z (%) = 145 (68, M^+), 117 (33, M^+-CO), 116 (54, M^+-CO , -H), 89 (100, M^+-CO , -H, -HCN).

2-(3-Pyridyl)thiophen, 11.^[3] Purification by chromatography on silica gel using hexanes:ethyl acetate:triethylamine 100:10:1. ^1H NMR (300 MHz, CDCl_3) δ 7.12 (dd, $J=4.2\text{Hz}$, $J=8.3\text{Hz}$, 1H), 7.30 (dd, $J=4.9\text{Hz}$, $J=7.9\text{Hz}$, 1H), 7.35 (d, $J=4.2\text{Hz}$, 2H), 7.85 (ddd, $J=1.4\text{Hz}$, $J=2.2\text{Hz}$, $J=7.9\text{Hz}$, 1H), 8.51 (dd, $J=1.4\text{Hz}$, $J=4.9\text{Hz}$, 1H), 8.88 (d, $J=2.2\text{Hz}$, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 123.8, 124.4, 126.2, 128.5, 130.6, 133.2, 140.6, 147.2, 148.6. EI-MS (70eV): m/z (%) = 161 (100, M^+), 134 (28, M^+-HCN), 108 (M^+-HCN , $-\text{C}_2\text{H}_2$).

4-(3-pyridyl)toluene, 12.^[4] Purification by chromatography on silica gel using hexanes:ethyl acetate:triethylamine 100:10:1. ^1H NMR (300 MHz, CDCl_3) δ 2.41 (s, 3H), 7.27 (d, $J=8.2\text{Hz}$, 2H), 7.32 (dd, $J=4.9\text{Hz}$, $J=7.9\text{Hz}$, 1H), 7.47 (d, $J=8.2\text{Hz}$, 2H), 7.93 (ddd, $J=2.0\text{Hz}$, $J=2.0\text{Hz}$, $J=7.9\text{Hz}$, 1H), 8.58 (bs, 1H), 8.89 (bs, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.5, 123.7, 127.2, 130.0, 134.3, 135.1, 138.2, 148.3. EI-MS (70eV): m/z (%) = 169 (100, M^+), 141 (12, $\text{M}^+-\text{C}_2\text{H}_2$), 91 (10, C_7H_7^+).

4-(3-pyridyl)aniline, 13.^[5] Purification by chromatography on silica gel using hexanes:ethyl acetate:triethylamine 100:10:1. ¹H NMR (300 MHz, CDCl₃) δ 3.75 (bs, 2H), 6.76 (d, *J*=8.5Hz, 2H), 7.30 (dd, *J*=5.0Hz, *J*=8.0Hz, 1H), 7.37 (d, *J*=8.5Hz, 2H), 7.79 (ddd, *J*=2.2Hz, *J*= 2.2Hz, *J*=8.0Hz, 1H), 8.47 (d, *J*=5.0Hz, 1H), 8.77 (bs, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 115.7, 123.7, 127.8, 128.2, 133.8, 136.9, 146.9, 147.1, 147.5. EI-MS (70eV):*m/z* (%) = 169 (100, M⁺-H), 142 (14, M⁺-H, -HCN), 117 (9, M⁺-HCN, -C₂H₂).

2-Methyl-4-phenylquinoline, 14. Purification by chromatography on silica gel using hexanes:diethylether:triethylamine 50:50:1. ¹H NMR (300 MHz, CDCl₃) δ 2.78 (s, 3H), 7.23 (s, 1H), 7.43 (ddd, *J*= 1.4, *J*= 7.6, *J*= 8.5, 1H), 7.47-7.51 (m, 5H), 7.69 (ddd, *J*=1.4Hz, *J*=7.6Hz, *J*=8.4Hz, 1H), 7.86 (dd, *J*=1.4Hz, *J*=8.4Hz, 1H), 8.08 (dd, *J*=1.4Hz, *J*=8.5Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 25.4, 122.1, 125.0, 125.5, 125.6, 128.2, 128.5, 128.9, 129.2, 129.5, 138.0, 148.2, 148.3, 158.3. EI-MS (70eV):*m/z* (%) = 219 (100, M⁺), 204 (50, M⁺-Me), 142 (2, M⁺-Ph), 127 (10, M⁺-Me, -Ph). Anal. Calcd. For C₁₆H₁₃N: C, 87.64; H, 5.98; N, 6.39. Found: C: 87.52; H, 5.82; N, 6.35.

2-Cyanobiphenyl, 23.^[6] Purification by chromatography on silica gel using hexanes:diethylether 5:1. ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.59 (m, 7H), 7.65 (ddd, *J*=1.4Hz, *J*=7.7 Hz, *J*=7.7Hz, 1H), 7.77 (dd, *J*=0.8Hz, *J*=7.7Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 111.5, 118.9, 127.7, 128.9, 130.3, 133.0, 133.9, 138.3, 145.7. EI-MS (70eV):*m/z* (%) = 179 (100, M⁺), 153 (25, M⁺-CN), 76 (37, M⁺-CN, -Ph).

3-Acetylbiphenyl, 24.^[7] Purification by chromatography on silica gel using hexanes:dichloromethane 1:1. ¹H NMR, CDCl₃ : 2.99, (s, 1H); 7.38-7.63, (m, 6H); 7.80 (ddd, *J*=0.8Hz, *J*=3.0Hz, *J*=7.7Hz, 1H), 7.93 (ddd, *J*=0.6Hz, *J*=2.8 Hz, *J*=7.7Hz, 1H),

8.18 (dd, $J=0.6\text{Hz}$, $J=3.3\text{Hz}$, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 27.1, 127.2, 127.4, 128.0, 129.1, 129.2, 131.9, 137.9, 140.0, 142.0, 194.0. EI-MS (70eV): m/z (%) = 196 (90, M^+), 181 (100, M^+-Me), 77 (20, Ph).

2-Phenylnaphthalene, 25.^[8] Purification by chromatography on silica gel using hexanes:dichloromethane 10:1. ^1H NMR CDCl_3 : 7.37 (m, 1H), 7.45-7.50 (m, 4H), 7.71-7.76 (m, 3H), 7.81-7.91 (m, 3H), 8.03 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 126.0, 126.2, 126.4, 126.7, 127.8, 127.9, 128.1, 128.7, 128.9, 129.3, 133.1, 134.1, 138.9, 141.5. EI-MS (70eV): m/z (%) = 204 (100, M^+), 127 (5, M^+-Ph), 77 (3, Ph).

4-Phenylquinoline, 27.^[9] Purification by chromatography on silica gel using hexanes:ethyl acetate:triethylamine 100:10:1. ^1H NMR (75 MHz, CDCl_3) δ 7.34 (d, $J=4.4\text{Hz}$, 1H), 7.50-7.52 (m, 6H), 7.73 (dd, $J=7.0\text{Hz}$, $J=8.2\text{Hz}$, 1H), 7.92 (d, $J=7.0\text{Hz}$, 1H), 8.18 (d, $J=8.2\text{Hz}$, 1H), 8.95 (d, $J=4.4\text{Hz}$, 1H). ^{13}C NMR (300 MHz, CDCl_3) δ 121.5, 126.1, 126.8, 128.6, 128.8, 129.5, 129.7, 130.0, 138.2, 148.7, 148.8, 150.0. EI-MS (70eV): m/z (%) = 205 (85, M^+), 204 (100, M^+-H), 77 (10, Ph).

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