Supporting Information

Use of Highly Active Palladium-phosphinous Acid Catalysts in Stille, Heck, Amination and Thiation

Reactions of Chloroquinolines

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Procedures for the chromatographic purification of quinolines **3**, **4**, **5**, and **16** and NMR spectroscopy and mass spectrometry data:

2-*n*-Butyl-4-chloroquinoline (3). Flash chromatography (hexane/CH₂Cl₂ 3:1) gave a yellow oil (76 %). ¹H NMR: 0.97 (t, *J* = 7.1Hz, 3H), 1.45 (m, 2H), 1.78 (m, 2H), 2.90 (t, *J* = 7.7Hz, 2H), 7.40 (s, 1H), 7.57 (ddd, *J* = 1.1Hz, 8.2Hz, 8.2Hz, 1H), 7.65 (ddd, *J* = 1.6Hz, 8.2Hz, 8.5Hz, 1H), 8.05 (dd, *J* = 1.1Hz, 8.5Hz, 1H), 8.18 (dd, *J* = 1.6Hz, 8.2Hz, 1H). ¹³C NMR: 13.9, 22.6, 31.8, 38.8, 121.1, 123.6, 124.6, 126.3, 128.9, 130.0, 142.1, 148.4, 162.7. EI-MS (70 eV): *m/z* (%): 219 (30, M⁺), 204 (100, M⁺-Me), 162 (32, M⁺-C₄H₉), 127 (5, M⁺-Cl, -C₄H₉).

2-*tert*-Butyl-4-chloroquinoline (4). Purification by flash chromatography (hexane/CH₂Cl₂ 5:1) gave a yellow oil (68 %). ¹H NMR: 1.50 (s, 9H), 7.57 (ddd, *J* = 1.6Hz, 7.6Hz, 7.7Hz, 1H), 7.64 (s, 1H), 7.75(ddd, *J* = 1.1Hz, 7.6Hz, 7.6Hz, 1H), 8.12 (dd, 1.1Hz, 7.7Hz, 1H), 8.20 (dd, *J* = 1.6Hz, 7.6Hz, 1H). ¹³C NMR: 30.1, 38.1, 118.33 123.6, 124.3, 126.5, 129.6, 129.8, 142.1, 148.2, 169.3. EI-MS (70 eV): *m/z* (%): 219 (42, M⁺), 204 (100, M⁺-Me), 177 (70, M⁺-C₃H₆), 162 (25, M⁺-C₄H₉), 127 (50, M⁺-Cl, -C₄H₉).

4-Chloro-2-phenylquinoline (5). Flash chromatography (hexane/CH₂Cl₂ 50:1) gave yellow crystals (67 %), mp 50-52 °C. ¹H NMR: 7.48-7.56 (m, 3H), 7.62 (ddd, *J* = 1.2Hz, 7.6Hz, 7.6Hz, 1H), 7.78 (ddd, *J* = 1.4Hz, 7.6Hz, 7.6Hz, 1H), 7.98 (s, 1H), 8.12-8.22 (m, 3H), 8.24 (dd, *J* = 1.4Hz, 7.6Hz, 1H). ¹³C NMR: 119.0, 123.8, 125.2, 127.1, 127.4, 128.8, 129.6, 129.9, 130.4, 138.4, 142.9, 148.9, 157.0. EI-MS (70 eV): *m/z* (%): 239 (95, M⁺), 204 (100, M⁺-Cl), 162 (5, M⁺-Ph), 127 (8, M⁺-Cl, -Ph).

***N*-(2-Phenyl-4-quinolyl)aniline (16).** Flash chromatography (hexane/Et₂O 6:1) gave a yellow oil (72 %, using *t*-BuOK). ¹H NMR: 6.64 (s, 1H), 7.20 (dd, *J* = 7.2Hz, 7.2Hz, 1H), 7.33-7.53 (m, 9H), 7.71 (ddd, *J* = 1.4Hz, 7.7Hz, 8.3Hz, 1H), 7.91 (dd, *J* = 1.1Hz, 7.7Hz, 1H), 7.97-8.03 (m, 2H), 8.12 (dd, *J* = 0.8Hz, 8.1Hz, 1H). ¹³C NMR: 100.6, 119.6, 122.6, 124.7, 125.4, 127.7, 128.8, 129.2, 129.8, 130.0, 133.5, 140.0, 141.4, 146.5, 148.0, 153.6. EI-MS (70 eV): *m/z* (%): 296 (100, M⁺), 219 (40, M⁺-Ph), 142 (10, M⁺-2 Ph), 127 (5, M⁺-Ph, -NHPh).