Supporting Information

A Study on the Selectivity of Arylzinc Reagents in Cross-coupling Reactions with Chemically Equivalent and Pseudo-equivalent Dibromopyridines

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Experimental

Typical procedures: (a) Preparation of 5-bromo-2-(2'-ethoxycarbonyl)phenyl pyridine (1a): Into a 25 mL round-bottomed flask were added $Pd(PPh_3)_2Cl_2$ (0.12 g, 2.0 mol %), 2,5-dibromopyridine (1.18 g, 5.0 mmol) and 10.0 mL of 2-(ethoxycarbonyl)phenylzinc bromide (0.5 M in THF, 5.0 mmol) under an argon atmosphere at room temperature. The resulting mixture was stirred at room temperature for 0.5 h. Quenched with saturated NH_4Cl solution, then extracted with ethyl ether (10 mL × 3). Washed with saturated $NaHCO_3$, $Na_2S_2O_3$ solution and brine, then dried over anhydrous $MgSO_4$. Purification by column chromatography on silica gel (10% ethyl acetate/90% heptane) afforded 1.02 g of **1a** in 67% isolated yield as a colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.69 (s, 1H), 7.85 (dt, *J* = 8.0 Hz, 2H), 7.56-7.45 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.3, 157.3, 149.9, 139.8, 138.8, 131.5, 131.2, 130.0, 129.7, 128.6, 124.1, 119.4, 61.1, 13.9; GC-MS (EI, 70 eV): *m/z* (%) 307 (M+2, 19), 305 (18), 262 (100), 235 (23), 153 (35).

(b) Preparation of 2-bromo-6-(4'-ethoxycarbonyl)phenyl pyridine (3a): Into a 25 mL round-bottomed flask were added $Pd(PPh_3)_2Cl_2$ (0.06 g, 2.0 mol %), 2,6-dibromopyridine (0.60 g, 2.5 mmol) and 5.0 mL of 4-(ethoxycarbonyl)-phenylzinc bromide (0.5 M in THF, 2.5 mmol) under an argon atmosphere at room temperature. The resulting mixture was stirred at room temperature for 0.5 h. Quenched with saturated NH_4Cl solution, then extracted with ethyl ether (10 mL × 3). Washed with saturated $NaHCO_3$, $Na_2S_2O_3$ solution and brine, then dried over anhydrous $MgSO_4$. Purification by column chromatography on silica gel (10% ethyl acetate/90% heptane) afforded 0.31 g of **3a** in 50% isolated yield as a white solid; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.15 (d, *J* = 7.8 Hz, 2H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 166.5, 157.6, 142.6, 141.8, 139.3, 131.6, 130.2, 127.4, 127.1, 119.7, 61.4, 14.6; GC-MS (EI, 70 eV): *m/z* (%) 307 (M+2, 56), 305 (M^+, 55), 277 (38), 262 (100), 232 (24), 153 (41).