Supporting Information for

Room temperature activation of aryl chlorides in Suzuki-Miyaura coupling using a $[PdCl_2(NHC)]_2$ complex (NHC = *N*-heterocyclic carbene).

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Suzuki-Miyaura Cross-Coupling Reactions: General Procedure.

In a glovebox, a 5 mL screwcap-vial fitted with a septum equipped with a magnetic stirring bar was charged with sodium methoxide (40.5 mg, 0.75 mmol), and the boronic acid (0.525 mmol). Outside the glovebox, the required amount of catalyst solution (catalyst loading 0.1 mol %) was injected through the septum, followed by addition of technical grade degassed ethanol (1 mL). The mixture was then stirred at room temperature unless otherwise indicated. After 15 min, the aryl halide (0.5 mmol) was injected, and the reaction was monitored by gas chromatography. When the reaction reached completion, or no further conversion was observed by gas chromatography, the solvent was removed under vacuum and the resulting solid was filtered on a pad of silica (using a hexanes/ethyl acetate mixture, depending on the polarity of the product). When necessary the product was purified by flash chromatography on silica gel. For reactions carried out under aerobic conditions, all solids were weighted in air. The solvents were dried over molecular sieves and all liquids were injected in vials opened to air.

4-methylbiphenyl[4] (Table 1): The procedure afforded, after flash chromatography on silica gel (hexanes), 78.2 mg (93%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, $J_{H\text{-}H}$=7.8 Hz, 2H), 7.58 (d, $J_{H\text{-}H}$=7.8 Hz, 2H), 7.50 (t, $J_{H\text{-}H}$=7.5 Hz, 2H), 7.40 (t, $J_{H\text{-}H}$=7.8 Hz, 1H), 7.33 (d, $J_{H\text{-}H}$=7.8 Hz), 2.47 (s, CH_3, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 141.23, 138.43, 137.06, 129.54, 128.77, 127.05, 127.03, 21.16.

3-phenylanisole[1] (Table 2, Entry 1): The procedure afforded, after flash chromatography on silica gel (hexanes/ AcOEt, 95/5), 80.1 mg (87%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, J_{H-H}=7.5 Hz, Ph-*H*, 2H), 7.50 (t, J_{H-H}=7.5 Hz, Ph-*H*, 2H), 7.44-7.39 (m, Ph-*H*, 2H), 7.25 (d, J_{H-H}=7.7 Hz, Ph-*H*, 1H), 7.21-7.19 (m, Ph-*H*, 1H), 6.96 (dd, J_{H-H}=8.2 Hz, J_{H-H}=2.6 Hz, Ph-*H*, 1H), 3.92 (s, O-CH_3, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 160.01, 142.83, 141.17, 129.80, 128.79, 127.46, 127.25, 119.74, 112.97, 112.73, 55.33.

2-phenylanisole[4] (Table 2, Entry 2): The procedure afforded, after flash chromatography on silica gel (hexanes/AcOEt, 95/5), 88.4 mg (96%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, J_{H-H}=8.0 Hz, Ph-*H*, 2H), 7.60 (t, J_{H-H}=7.6 Hz, Ph-*H*, 2H), 7.54-7.47 (m, Ph-*H*, 3H), 7.22 (td, J_{H-H}=7.4 Hz, J_{H-H}=1.1 Hz, Ph-*H*, 1H), 7.15 (dd, J_{H-H}=8.2 Hz, J_{H-H}=0.8 Hz, Ph-*H*, 1H), 3.95 (s, O-CH_3, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 156.67, 138.77, 131.08, 130.92, 129.75, 128.81, 128.17, 127.10, 121.03, 111.44, 55.67.

2-methylbiphenyl[1] (Table 2, Entry 3): The procedure afforded, after flash chromatography on silica gel (hexanes), 72.3 mg (86%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54-7.49 (m, 2H, Ph-*H*), 7.46-7.42 (m, 3H, Ph-*H*), 7.39-7.34 (m, 4H, Ph-*H*), 2.39 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 142.07, 135.42, 130.39, 129.89, 129.29, 128.15, 127.34, 126.85, 125.85, 20.56.

2,6-dimethylbiphenyl[4] (Table 2, Entry 4): The procedure afforded, after flash chromatography on silica gel (hexanes), 65.6 mg (72%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (m, Ph-*H*, 2H), 7.37 (m, Ph-*H*, 1H), 7.24-7.12 (m, Ph-*H*, 5H), 2.07 (s, CH_3, 6H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 136.07, 129.03, 128.42, 127.27, 126.61, 20.86.

2,4,4',6-tetramethylbiphenyl[2] (Table 2, Entry 5): The procedure afforded, after flash chromatography on silica gel (hexanes), 86.2mg (82%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 (d, J_{H-H}=7.8 Hz, 2H), 7.08 (d, J_{H-H}=7.6 Hz, 2H), 6.99 (s, 2H), 2.46 (s, C*H*$_3$, 3H), 2.39 (s, C*H*$_3$, 3H), 2.07 (s, C*H*$_3$, 6H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 139.05, 138.04, 136.42, 136.17, 135.98, 21.27, 21.05, 20.81.

2,6-dimethoxy-4'-methylbiphenyl[3] (Table 2, Entry 6): The procedure afforded, after flash chromatography on silica gel (hexanes/AcOEt, 95/5), 89.0 mg (78%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (m, Ph-*H*, 5H), 6.78 (d, J_{H-H}=8.3 Hz, Ph-*H*, 2H), 3.85 (s, O-C*H*$_3$, 6H), 2.53 (s, C*H*$_3$, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 157.88, 136.38, 131.17, 130.86, 128.64, 128.57, 119.62, 101.31, 56.00, 21.50.

2,2',6-trimethylbiphenyl[4] (Table 2, Entry 7) (2-methylphenyl boronic acid + 2-chloro-*m*-xylene)**:** The procedure afforded, after flash chromatography on silica gel (hexanes), 78.5 mg (80%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.29 (m, 3H, Ph-*H*), 7.26-7.22 (m, 1H, Ph-*H*), 7.19-7.16 (m, 2H, Ph-*H*), 7.10-7.08 (m, 1H, Ph-*H*), 2.04 (s, 3H, C*H*$_3$), 2.02 (s, 6H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 141.14, 140.60, 135.91, 135.66, 130.02, 128.90, 127.27, 127.05, 126.97, 126.10, 20.38, 19.44.

2,2',6-trimethylbiphenyl[4] (Table 2, Entry 8) (2,6-dimethylphenyl boronic acid + 2-chlorotoluene)**:** The procedure afforded, after flash chromatography on silica gel (hexanes), 35.3 mg (36%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.29 (m, 3H, Ph-*H*), 7.26-7.22 (m, 1H, Ph-*H*), 7.19-7.16 (m, 2H, Ph-*H*), 7.10-7.08 (m, 1H, Ph-*H*), 2.04 (s, 3H, C*H*$_3$), 2.02 (s, 6H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 141.14, 140.60, 135.91, 135.66, 130.02, 128.90, 127.27, 127.05, 126.97, 126.10, 20.38, 19.44.

2,6-dimethoxy-2'-methylbiphenyl[5] (Table 2, Entry 9): The procedure afforded, after flash chromatography on silica gel (hexanes/AcOEt, 95/5), 95.9 mg (84%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.21 (m, Ph-*H*, 5H), 6.73 (d, J_{H-H}=8.4 Hz, Ph-*H*, 2H), 3.78 (s, O-C*H*$_3$, 6H), 2.16 (s, C*H*$_3$, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 157.78, 137.40, 134.28, 130.81, 129.58, 128.71, 127.26, 125.27, 119.02, 101.05, 55.89, 19.79.

2,2',6-trimethoxybiphenyl[3] (Table 2, Entry 10): The procedure afforded, after flash chromatography on silica gel (hexanes/AcOEt, 95/5), 35.4 mg (29%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.34 (m, Ph-*H*, 2H), 7.26 (dd, J_{H-H}=7.4 Hz, J_{H-H}=1.7 Hz, Ph-*H*, 1H), 7.08 (qd, J_{H-H}=7.4 Hz, J_{H-H}=1.1 Hz, Ph-*H*, 2H), 3.82 (s, O-C*H*$_3$, 3H), 3.79 (s, O-C*H*$_3$, 6H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 128.17, 157.56, 132.22, 128.78, 128.57, 123.69, 120.33, 116.40, 111.33, 104.33, 56.07, 55.88.

2-phenylpyridine[6] (Table 3, Entry 1): The procedure afforded, after flash chromatography on silica gel (hexanes/AcOEt, 85/15), 53.5 mg (69%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.73 (m, Ph-*H*, 1H), 8.04-8.01 (m, Ph-*H*, 2H), 7.77-7.75 (m, Ph-*H*, 2H), 7.51 (t, J_{H-H} = 7.1Hz, 2H), 7.47-7.42 (m, Ph-*H*, 1H), 7.27-7.23 (m, Ph-*H*, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 149.70, 139.44, 136.75, 128.97, 128.76, 126.94, 122.11, 120.57.

2-(*o*-tolyl)-pyridine[6] (Table 3, Entry 2): The procedure afforded, after flash chromatography on silica gel (hexanes/AcOEt, 85/15), 83.8 mg (99%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.73 (d, J_{H-H}=5.0 Hz, Ph-*H*, 1H), 7.75 (td, J_{H-H}=7.7 Hz, J_{H-H}=1.8 Hz, Ph-*H*, 2H), 7.45-7.41 (m, PH-*H*, 2H), 7.34-7.28 (m, Ph-*H*, 3H), 7.25 (m, Ph-*H*, 1H), 2.41 (s, C*H*$_3$, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 160.08, 149.24, 140.49, 136.11, 135.76, 130.76, 129.65, 128.28, 125.90, 124.10, 121.63, 20.31.

3-phenylpyridine[6] (Table 3, Entry 3): The procedure afforded, after flash chromatography on silica gel (hexanes/AcOEt, 85/15), 70.6 mg (91%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.72 (d, J_{H-H}=4.9 Hz, Ph-*H*, 1H), 8.04-8.02 (m, Ph-*H*, 2H), 7.74 (m, Ph-*H*, 1H), 7.74 (d, J_{H-H}=1.4 Hz, Ph-*H*, 1H), 7.51 (t, J_{H-H}=7.0 Hz, Ph-*H*, 2H), 7.25-7.21 (m, Ph-*H*, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 149.67, 139.40, 136.78, 128.99, 128.78, 126.95, 122.12, 120.58.

3-(*o*-tolyl)-pyridine[6] (Table 3, entry 4): The procedure afforded, after flash chromatography on silica gel (hexanes/AcOEt, 85/15), 59.2 mg (70%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (m, Ph-*H*, 2H), 7.67 (dt, J_{H-H}=7.8 Hz, J_{H-H}=1.9 Hz, Ph-*H*, 1H), 7.37 (m, Ph-*H*, 1H), 7.34-7.27 (m, Ph-*H*, 3H), 7.25-7.22 (m, Ph-*H*, 1H), 2.30 (s, C*H*$_3$, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 149.87, 128.03, 138.07, 137.51, 136.56, 135.59, 130.59, 129.88, 128.14, 126.11, 123.05, 20.36.

2-phenylthiophene[4] (Table 3, Entry 5): The procedure afforded, after flash chromatography on silica gel (hexanes/AcOEt, 95/5), 69.7 mg (87%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (m, Ph-*H*, 2H), 7.45 (t, J_{H-H}=7.7 Hz, Ph-*H*, 2H), 7.40-7.33 (m, Ph-*H*, 3H), 7.15 (dd, J_{H-H}=5.1 Hz, J_{H-H}=3.6 Hz, Ph-*H*, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 144.52, 134.50, 128.97, 128.08, 127.54, 126.04, 124.88, 123.17.

2-(*o*-tolyl)thiophene[7] (Table 3, Entry 6): The procedure afforded, after flash chromatography on silica gel (hexanes/AcOEt, 95/5), 68.8 mg (79%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49-7.46 (m, Ph-*H*, 1H), 7.39 (dd, J_{H-H}=5.0 Hz, J_{H-H}=1.2 Hz, Ph-*H*, 1H), 7.35-7.25 (m, Ph-*H*, 3H), 7.16-7.12 (m, Ph-*H*, 2H), 2.49 (s, C*H*$_3$, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 143.19, 135.16, 134.24, 130.77, 130.54, 127.85, 127.11, 126.42, 125.94, 125.14, 21.18.

References and Notes

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