Supporting Information

Palladium-Catalyzed Borylation of Phenyl Bromides and Application in One-Pot Suzuki-Miyaura Biphenyl Synthesis

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General Procedure for the Synthesis of Phenylboronates 3 (Table 1). To a solution of phenyl halide (1.00 mmol) in dioxane (1.00 mL) were added, under argon, triethylamine (558 μ L, 4.00 mmol), palladium(II) acetate (11.2 mg, 0.05 mmol), DPEphos (53.8 mg, 0.10 mmol), and pinacolborane (3.00 mL, 1.0 M solution in THF, 3.00 mmol). The reaction mixture was heated at 100 °C. The reaction was followed by TLC until disappearance of starting material or maximum 20 h. After cooling to room temperature, the reaction mixture was quenched by adding a sat. solution of NH_4Cl , and the aqueous phase was extracted with diethyl ether. After drying over MgSO_4 , the solution was filtered and evaporated under vacuum. The resulting oil was purified by flash chromatography (SiO_2 deactivated with 5% Et_3N).

Pinacol (2-methoxyphenyl)boronate (Table 1, entry 1): identical spectroscopic data to those previously described.¹

Pinacol (3-methoxyphenyl)boronate (Table 1, entry 2): identical spectroscopic data to those previously described.²

¹Baudoin, O.; Guénard, D.; Guéritte, F. *J. Org. Chem.* **2000**, *65*, 9268.

²Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390.

Pinacol (4-methoxyphenyl)boronate (Table 1, entry 3): identical spectroscopic data to those previously described.³

Pinacol (2-aminophenyl)boronate (Table 1, entry 4): identical spectroscopic data to those previously described.¹

Pinacol (3-aminophenyl)boronate (Table 1, entry 5):⁴ ¹H NMR (300 MHz, CDCl₃): δ = 7.15 (d, J = 8.4 Hz, 1H), 7.16 (s, 1H), 6.77 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 8.3 Hz, 1H), 3.65 (br, s, 2H), 1.25 (s, 12H) ppm; ¹³C NMR (75.5 MHz, CDCl₃): δ = 146.4, 129.3, 125.0, 118.6, 115.1, 83.7, 24.9 ppm.

Pinacol (4-aminophenyl)boronate (Table 1, entry 6): identical spectroscopic data to those previously described.³

Pinacol phenylboronate (Table 1, entry 7): identical spectroscopic data to those previously described.³

Pinacol (2,4,6-trimethylphenyl)boronate (Table 1, entry 8): identical spectroscopic data to those previously described.⁵

Pinacol (2-nitrophenyl)boronate (Table 1, entry 10): identical spectroscopic data to those previously described.^{1,3}

Pinacol (3-*N,N*-dimethylaminophenyl)boronate (Table 1, entry 14): identical spectroscopic data to those previously described.⁶

Pinacol (4-*N,N*-dimethylaminophenyl)boronate (Table 1, entry 15): identical spectroscopic data to those previously described.³

Pinacol (2-methylphenyl)boronate (Table 1, entry 16): identical spectroscopic data to those previously described.³

Pinacol (3-methylphenyl)boronate (Table 1, entry 17): identical spectroscopic data to those previously described.²

Pinacol (4-methylphenyl)boronate (Table 1, entry 18): identical spectroscopic data to those previously described.³

General Procedure for the Synthesis of Biphenyls 5 (Table 2). To a solution of *N,N*-dimethyl-4-bromoaniline (0.212 g, 1.00 mmol), palladium(II) acetate (11.2 mg, 0.05 mmol)

³ Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **2000**, *65*, 164.

⁴ Vogels, C. M.; Wellwood, H. L.; Biradha, K.; Zaworotko, M. J.; Westcott, S. A. *Can. J. Chem.* **1999**, *77*, 1196.

⁵ Wong, K.-T.; Chien, Y.-Y.; Liao, Y.-L.; Lin, C.-C.; Chou, M.-Y.; Leung, M.-k. *J. Org. Chem.* **2002**, *67*, 1041.

⁶ Cho, J.-Y.; Iverson, C. N.; Smith III., M. R. *J. Am. Chem. Soc.* **2000**, *122*, 12868.

and DPEphos (53.8 mg, 0.10 mmol) in dioxane (1.00 mL) was added, under argon, a solution of triethylamine (419 μ L, 3.00 mmol), and pinacolborane (2.00 mL, 1.0 M solution in THF, 2.00 mmol) in dioxane (1.00 mL). The reaction mixture was heated at 100 °C for 3 h and then cooled to room temperature. Flame dried CsF (1.22 g, 8.0 mmol) and more dioxane (5.00 mL) were added. 45 min later 2-bromotoluene (0.120 mL, 0.171 g, 1.00 mmol) and palladium(II) acetate (11.2 mg, 0.05 mmol) in dioxane (4.00 mL) were added. The mixture was heated to 100 °C under stirring for 20 h and then cooled to room temperature and filtered through celite. Brine was added, and the aqueous phase was extracted with CH₂Cl₂. After drying over MgSO₄, the solvents were removed under vacuum, and the residue was purified by flash chromatography (SiO₂).

4-(*N,N*-Dimethylamino)-2'-methyl-1,1'-biphenyl (5a): identical spectroscopic data to those previously described.⁷

4-(*N,N*-Dimethylamino)-4'-methyl-1,1'-biphenyl (5b): identical spectroscopic data to those previously described.⁸

4-(*N,N*-Dimethylamino)-2-carbonitrile-1,1'-biphenyl (5c): identical spectroscopic data to those previously described.⁹

4-(*N,N*-Dimethylamino)-4-carbonitrile-1,1'-biphenyl (5d): identical spectroscopic data to those previously described.¹⁰

4-(*N,N*-Dimethylamino)-2-nitro-1,1'-biphenyl (5e): ¹H NMR (300 MHz, CDCl₃): δ = 7.75 (dd, J = 8.1, 1.2 Hz 1H), 7.55 (td, J = 7.5, 1.2 Hz, 1H), 7.46-7.35 (m, 2H), 7.21 (d, J = 9.0 Hz, 2H), 6.75 (d, J = 8.7 Hz, 2H), 3.00 (s, 6H); ¹³C NMR (75.5 MHz, CDCl₃): δ = 150.3, 149.4, 136.3, 132.0, 131.8, 128.7, 127.0, 124.5, 124.0, 112.3, 40.3 ppm. – C₁₄H₁₄N₂O₂ (242.28) : calcd. C 69.41, H 5.82, N 11.56; found C 68.85, H 6.08, N 11.06.

4-(*N,N*-Dimethylamino)-4-nitro-1,1'-biphenyl (5f): identical spectroscopic data to those previously described.¹⁰

4-Methoxy-1,1'-biphenyl-4-carbonitrile (5g): identical spectroscopic data to those previously described.¹¹

⁷ Littke, A.F.; Dai, C.; Fu, G.C. *J. Amer. Chem. Soc.* **2000**, *122*, 4020.

⁸ Inada, K.; Miyaura, N. *Tetrahedron* **2000**, *56*, 8657.

⁹ Quast, H.; Schmitt, E. *Liebigs Ann. Chem.* **1970**, *732*, 43.

¹⁰ Amatore, C.; Jutand, A.; Negri, S.; Fauvarque, J.-F. *J. Organomet. Chem.* **1990**, *390*, 389.

¹¹ Alam, N.; Amatore, C.; Combella, C.; Pinson, J.; Savéant, J.-M.; Thiébaud, A.; Verpeaux, J.-N. *J. Org. Chem.* **1988**, *53*, 1496.