

Supporting Information

Rhodium-catalysed addition reaction of aryl- and alkenylboronic acids to isocyanates

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General. All reactions were carried out with standard Schlenk techniques under an argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300.07 MHz and ^{13}C at 75.46 MHz) spectrometer or a JEOL ECA-600P (^{13}C at 150.92 MHz) spectrometer. All NMR data were obtained in CDCl_3 . Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm. Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.0 ppm. High resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica 60 PF₂₅₄ (Merck).

Materials. Anhydrous THF was purchased from Kanto Chemical Co., Inc. 1,4-Dioxane was freshly distilled from sodium benzophenone ketyl. Phenyl isocyanate (**1a**), *m*-tolyl isocyanate (**1c**), 4-chlorophenyl isocyanate (**1f**) and cyclohexyl isocyanate (**1k**) were purchased from Tokyo Kasei Kogyo Co., Ltd. *p*-Tolyl isocyanate (**1b**), *o*-tolyl isocyanate (**1d**), 4-methoxyphenyl isocyanate (**1e**) and ethyl 4-isocyanatobenzoate (**1g**) were purchased from Aldrich Chemical Co. *m*-Nitrophenyl isocyanate (**1h**) and *n*-hexyl isocyanate (**1j**) were purchased from Wako Pure Chemical Industries, Ltd. All isocyanates, except for **1h**, were used after bulb-to-bulb distillation. **1h** was used without further purification. All other commercially available resources were used without further purification. $[\text{Rh}(\text{OH})(\text{cod})]_2$ was prepared according to the reported procedure.¹ 2-(1-Pentenyl)phenyl isocyanate (**1i**) was prepared by Suzuki-Miyaura coupling of 2-iodoaniline and (*E*)-1-pentenylboronic acid ($\text{Pd}(\text{PPh}_3)_4$ and KOH in THF/ H_2O , reflux), followed by isocyanation.² Phenylboroxine was prepared from the phenylboronic acid by azeotropic removal of water from its toluene solution and purified by washing the crude boroxine repeatedly with hexane.³

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³ F.-X. Chen, A. Kina and T. Hayashi, *Org. Lett.*, **2006**, 8, 341.

General procedure. To an oven-dried flask was added [Rh(OH)(cod)]₂ (2.3 mg, 5.0 μmol, 5 mol% Rh), organoboronic acid **2** (0.60 mmol, 3.0 equiv.) and a solution of isocyanate **1** (0.20 mmol, 1.0 equiv.) in dry THF (2.0 mL). The reaction mixture was stirred at room temperature for 12 h under an argon atmosphere, and then quenched with addition of water (2.0 mL). The resulting aqueous solution was extracted with ethyl acetate (4 x 10 mL). The combined extracts were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (chloroform/ethyl acetate 20:1 or 10:1) to give the corresponding amide **3**.

Compounds **3aa**,⁴ **3ab**,⁴ **3af**,⁵ **3ah**,⁶ **3ba**,⁷ **3ca**,⁷ **3ea**,⁷ **3fa**,⁷ **3ha**,⁸ **3ja**⁹ and **3ka**¹⁰ are known and their spectral data were compared with those of authentic specimens. The analytical data of other products **3ac**, **3ad**, **3ae**, **3ag**, **3ai**, **3da**, **3ga** and **3ia** are as follows.

3ac: IR (KBr): 3233, 1651, 1539, 1441, 1325 cm⁻¹; ¹H NMR (300 MHz): δ = 2.47 (s, 3H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.16–7.27 (m, 2H), 7.29–7.40 (m, 3H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.72 (br s, 1H); ¹³C NMR (75 MHz): δ = 19.8, 119.8, 124.4, 125.7, 126.5, 128.9, 130.1, 131.1, 136.2, 137.9, 168.0 (one carbon missing); HRMS (EI⁺): Calcd for C₁₄H₁₃NO, M⁺ 211.0997. Found m/z 211.0997.

3ad: IR (KBr): 3243, 1651, 1595, 1541, 1441, 1329 cm⁻¹; ¹H NMR (300 MHz): δ = 3.83 (s, 3H), 7.06 (ddd, *J* = 7.7, 2.7, 1.7 Hz, 1H), 7.14 (tt, *J* = 7.2, 1.5 Hz, 1H), 7.30–7.44 (m, 5H), 7.60–7.68 (m, 2H), 8.01 (br s, 1H); ¹³C NMR (75 MHz): δ = 55.4, 112.3, 117.9, 118.6, 120.1, 124.5, 128.9, 129.6, 136.3, 137.8, 159.8, 165.5; HRMS (EI⁺): Calcd for C₁₄H₁₃NO₂, M⁺ 227.0946. Found m/z 227.0947.

3ae: IR (KBr): 3345, 1655, 1534, 1441, 1320 cm⁻¹; ¹H NMR (300 MHz): δ = 7.15 (t, *J* = 7.5 Hz, 1H), 7.23–7.41 (m, 3H), 7.53–7.68 (m, 3H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.93–8.00 (m, 1H), 8.07 (br s, 1H); ¹³C NMR (75 MHz): δ = 120.3, 122.8, 124.8, 125.5, 129.0, 130.1, 134.6, 136.8, 137.4, 164.3 (one carbon missing); HRMS (EI⁺): Calcd for C₁₃H₁₀BrNO, M⁺ 274.9946. Found m/z 274.9946.

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3ag: IR (KBr): 3332, 1651, 1538, 1441, 1320, 1258 cm^{-1} ; ^1H NMR (300 MHz): δ = 7.10–7.18 (m, 1H), 7.30–7.40 (m, 3H), 7.49 (dd, J = 5.0, 1.4 Hz, 1H), 7.57–7.65 (m, 2H), 7.83 (br s, 1H), 7.98 (dd, J = 3.0, 1.2 Hz, 1H); ^{13}C NMR (150 MHz): δ = 120.2, 124.5, 126.1, 126.9, 128.7, 129.1, 137.7, 137.8, 161.1; HRMS (Cl^+): Calcd for $\text{C}_{11}\text{H}_9\text{NOS}$, M^+ 203.0405. Found m/z 203.0403.

3ai: IR (KBr): 3266, 1667, 1603, 1541, 1441, 1345 cm^{-1} ; ^1H NMR (300 MHz): δ = 0.95 (t, J = 7.2 Hz, 3H), 1.51 (sextet, J = 7.3 Hz, 2H), 2.21 (qd, J = 7.4, 1.4 Hz, 2H), 5.92 (dt, J = 15.3, 1.5 Hz, 1H), 6.99 (dt, J = 15.2, 7.1 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 7.23 (br s, 1H), 7.28–7.37 (m, 2H), 7.56 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz): δ = 13.7, 21.5, 34.1, 120.0, 124.1, 128.8, 138.0, 146.1, 164.3 (one carbon missing); HRMS (EI^+): Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}$, M^+ 189.1154. Found m/z 189.1152.

3da: IR (KBr): 3245, 1649, 1522, 1489, 1309 cm^{-1} ; ^1H NMR (300 MHz): δ = 2.32 (s, 3H), 7.12 (t, J = 7.8 Hz, 1H), 7.18–7.30 (m, 2H), 7.43–7.60 (m, 3H), 7.79 (br s, 1H) 7.84–7.96 (m, 3H); ^{13}C NMR (75 MHz): δ = 17.9, 123.2, 125.3, 126.7, 126.9, 128.7, 129.4, 130.4, 131.7, 134.8, 135.6, 165.5 (one carbon missing); HRMS (EI^+): Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}$, M^+ 211.0997. Found m/z 211.0997.

3ga: IR (KBr): 3332, 1705, 1657, 1530, 1410, 1281 cm^{-1} ; ^1H NMR (300 MHz): δ = 1.40 (t, J = 7.1 Hz, 3H), 4.37 (q, J = 7.1 Hz, 2H), 7.46–7.63 (m, 3H), 7.71–7.78 (m, 2H), 7.85–7.91 (m, 2H), 7.97 (br s, 1H), 8.07 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz): δ = 14.4, 60.9, 119.2, 126.0, 127.0, 128.7, 130.7, 132.0, 134.4, 142.0, 165.9, 166.0; HRMS (EI^+): Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3$, M^+ 269.1052. Found m/z 269.1051.

3ia: IR (KBr): 3245, 1651, 1522, 1482, 1308 cm^{-1} ; ^1H NMR (300 MHz): δ = 0.96 (t, J = 7.4 Hz, 3H), 1.51 (sextet, J = 7.3 Hz, 2H), 2.23 (qd, J = 7.1, 1.4 Hz, 2H), 6.15 (dt, J = 15.6, 6.9 Hz, 1H), 6.49 (d, J = 15.3 Hz, 1H), 7.15 (td, J = 7.5, 0.9 Hz, 1H), 7.30 (td, J = 7.8, 1.8 Hz, 1H), 7.38 (dd, J = 7.8, 1.5 Hz, 1H), 7.46–7.61 (m, 3H), 7.80–7.97 (m, 3H), 8.08 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz): δ = 13.7, 22.5, 35.4, 122.9, 124.8, 125.0, 126.9, 127.2, 127.6, 128.7, 130.4, 131.7, 134.1, 134.8, 135.9, 165.3; HRMS (EI^+): Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}$, M^+ 265.1467. Found m/z 265.1467.