Supporting Information

Rhodium-Catalyzed Dehydrogenative Borylation of Cyclic Alkenes
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General Information

All manipulations were carried out in an inert atmosphere using standard Schlenk line or glovebox techniques. Tetrahydrofuran and toluene were purified via an SG Water USA solvent column system before they were used. Materials obtained from commercial supplier were used without further purification. Analytical thin-layer chromatography was performed using EM Science silica gel 60 F254 plates. The developed chromatogram was visualized by UV lamp or stained using aqueous potassium permanganate (KMnO4). Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on Silicycle silica gel (230-400 mesh).

$^1$H and $^{13}$C NMR spectra were recorded on Varian Inova 500 MHz spectrometers in CDCl$_3$. Chemical shifts in $^1$H NMR spectra are reported in parts per million (ppm) on the $\delta$ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad), coupling constant in hertz (Hz), and integration. Chemical shifts of $^{13}$C NMR spectra are reported in ppm from the central peak of CDCl$_3$ (77.23 ppm) on the $\delta$ scale. Infrared (IR) spectra were recorded on a Perkin-Elmer 2000 FT-IR. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXII 3 Fourier Transform Mass Spectrometer by Li Li of the Massachusetts Institute of Technology, Department of Chemistry Instrumentation Facility.
Experimental Procedure

Representative Procedure for the Rhodium-Catalyzed Dehydrogenative Borylation of Cyclic Alkenes.

[RhCl(cod)]_2 (6.4 mg, 0.013 mmol), Xantphos (0.014 g, 0.025 mmol) and bis(pinacolato)diboron (0.13 g, 0.50 mmol) were placed in a 10-mL Schlenk tube in a glovebox filled with nitrogen. On the Schlenk line, THF (2.0 mL) was added, and the mixture was stirred for 5 min. Cyclohexene (1a) (0.10 g, 1.2 mmol) was added, and the resulting solution was heated in an oil bath (115 °C) for 24 h. After the mixture was cooled to room temperature, H₂O (10 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure to afford the crude reaction mixture. Chromatographic purification on silica (hexane/ethyl acetate = 30 : 1) yielded mixture of 3a, 3a' and 4a (0.15 g, 3a : 3a' : 4a = 87 : 3 : 10, 3a = 64%, 3a' = 2%, 4a = 7%) as a colorless oil. Yields of 3 and 4 are determined by the weight with the ratio of 3 and 4 (and 3') based on ¹H NMR after column purification.

Representative Procedure for the Rhodium-Catalyzed Dehydrogenative Borylation followed by Suzuki-Miyaura Cross-Coupling Reaction.

[RhCl(cod)]_2 (6.4 mg, 0.013 mmol), Xantphos (0.014 g, 0.025 mmol) and bis(pinacolato)diboron (0.13 g, 0.50 mmol) were placed in a 10-mL Schlenk tube in a glovebox filled with nitrogen. On the Schlenk line, THF (2.0 mL) was added, and the mixture was stirred for 5 min. Cyclohexene (1a) (0.10 g, 1.2 mmol) was added, and the resulting solution was heated in an oil bath (115 °C) for 24 h. After the mixture was cooled to room temperature, the resulting mixture was filtrated on silica and concentrated under reduced pressure. PdCl₂(dppe) (0.022 g, 0.030 mmol) and K₃PO₄ (0.64 g, 3.0 mmol) were placed in a 25-mL round bottom flask in a glovebox. DMF (2.0 mL) was added and the mixture was stirred for 10 min. 4-Bromotoluene (0.17 g, 1.0 mmol) and the solution of the crude reaction mixture in DMF (2.0 mL) were sequentially added. The resulting mixture was then heated in an oil bath (80 °C) for 17 h. After the mixture was cooled to room temperature, saturated aq. NH₄Cl (10 mL) was added and the product was extracted with hexane/ethyl acetate (10 : 1, 10 mL × 3). Combined organic layer was dried over sodium sulfate. Concentration under reduced pressure followed by silica gel column purification (hexane) afforded 5a (0.11 g, 0.64 mmol) in 64% yield as a colorless oil.
Characterization Data

1-Alkenylboronate esters 3a, 3b, 3c and 3d and cross-coupling products 5a and 5c showed the same spectroscopic data in the literature.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-bicyclo[2.2.1]hept-2-ene (3e): IR (neat) 3047, 2976, 2869, 1589, 1469, 1447, 1368, 1310, 1267, 1213, 1146, 1046, 963, 864, 697 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.86–1.00 (m, 2H), 1.10–1.14 (m, 1H), 1.27 (s, 6H), 1.28 (s, 6H), 1.30–1.35 (m, 1H), 1.60–1.68 (m, 2H), 2.89–2.93 (m, 1H), 3.05–3.08 (m, 1H), 6.81 (d, J = 3.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 24.2, 24.7, 24.8, 25.1, 43.5, 43.6, 48.6, 83.1, 151.8; HRMS-ESI (m/z): [M + Na]⁺ Observed: 220.1745. Calculated for C₁₃H₂₁BO₂: 220.1744.

1-(2-Methylphenyl)cycloheptene (5d): IR (neat) 3016, 2921, 2849, 1484, 1447, 1378, 964, 854, 753, 726 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.58–1.67 (m, 4H), 1.80–1.87 (m, 2H), 2.25–2.30 (m, 2H), 2.29 (s, 3H), 2.40–2.45 (m, 2H), 5.75 (t, J = 6.5 Hz, 1H), 7.05–7.10 (m, 1H), 7.10–7.17 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 20.50, 27.21, 27.39, 29.15, 32.90, 34.99, 125.65, 126.46, 128.51, 130.10, 131.24, 134.78, 146.07, 146.77; HRMS-ESI (m/z): Calculated for
Figure S1. $^1$H NMR spectrum of 3e
Figure S2. $^{13}$C NMR spectrum of 3e
Figure S3. $^1$H NMR spectrum of 5d
Figure S4. $^{13}$C NMR spectrum of 5d
Spectra of Previously Reported Compounds

Compound 3a was isolated as an inseparable mixture with hydroboration product 4a (indicated with an asterisk (*) in the following spectra) and allylboronate ester 3a' (indicated with a double asterisk (**) in the following spectra). Compounds 3b, 3c and 3d were isolated as inseparable mixtures with hydroboration products 4b, 4c and 4d (indicated with an asterisk (*) in the following spectra), respectively.
Figure S5. $^1$H NMR spectrum of 3a
Figure S6. $^1$H NMR spectrum of 3b
Figure S7. $^1$H NMR spectrum of 3c
Figure S8. $^1$H NMR spectrum of 3d
Figure S9. $^1$H NMR spectrum of 5a
Figure S10. $^1$H NMR spectrum of 5c
References

