Supplemental Materials

Organolanthanide Catalyzed Cyclization/Boration Reaction

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Experimental

General Considerations. All reactions involving the lanthanide metallocenes were performed in a nitrogen filled glove box or in Schlenk-type glassware interfaced to a vacuum-nitrogen double manifold. Toluene, benzene-d_6, and substrates **1**-**5** were distilled from sodium and stored in the glove box. Substrates **1**, **3**, catecholborane, pinacolborane, BH_3•NMe_3, *N,N'*-dimethylethylenediamine, *N,N'*-diethylethylenediamine, and *N,N'*-diisopropylethylenediamine were purchased from Aldrich. Catecholborane and pinacolborane were distilled under an atmosphere of nitrogen prior to use. Substrates **2**, **4**, and **5** were synthesized according to published procedures.[1] The lanthanide metallocenes were prepared according to literature procedures.[2] All 1,3-diaza-2-boracycloalkanes were prepared by the reaction of BH_3•NMe_3 with the corresponding amines.[3]

Cyclopentylmethanol (6). Representative Procedure for Lanthanide Catalyzed Cyclization/Boration. In a nitrogen filled glovebox, the precatalyst (0.010 g, 1.6 mol%) was dissolved in 3 mL of toluene. After the addition of 1,5-hexadiene (**1**) (0.10 g, 1.22 mmol), the resultant reaction mixture was stirred for 10 min at ambient temperature, during which time the color of the solution changed from brown/purple to red. Next, freshly distilled 1,3-dimethyl-1,3-diaza-2-boracyclopentane (0.164 g, 1.30 mmol) was added dropwise over a period of 10 min. After stirring for 18 h the reaction was found to be complete as evidenced by ^{11}B-NMR spectroscopy. The solvent was removed in vacuum. Next, 3 mL of 3M NaOH, 3 mL of THF, and 3 mL of 30% H_2O_2 were added, and the mixture was stirred for 18 h. The resulting suspension was saturated with K_2CO_3, followed by extraction with 4 x 20 mL of ether. The organic layers were combined, washed with 15 mL of saturated NH_4OH, and dried over Na_2SO_4. After removal of the solvent in vacuum, purification of the crude product by flash chromatography followed by Kugelrohr distillation afforded **6** in 86% yield (0.104 g, 1.04 mmol). The identity of **6** was established by comparison of the spectral and analytical data with a commercial sample: (R_f=0.16 in hexane/EtOAc 10:1); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 32.32; ^1H-NMR (500 MHz, $CDCl_3$) δ 3.45 (d, *J*=7.0, 2H), 2.06 (p, *J*=3.6, 1H), 1.71-1.73 (m, 2H), 1.53-1.59 (m, 5H), 1.19-1.23 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 67.44, 42.14, 29.05, 25.43; IR (neat) 3384 (broad, OH), 2951, 1638, 1451, 1032, 932 cm^{-1}; LRMS (CI^+) *m/z* MH^+ 101(5.0), 83 (100.0).

***trans*-2-Phenylcyclopentylmethanol (7).** 3-Phenyl-1,5-hexadiene (**2**) (0.200 g, 1.27 mmol) and 1,3-dimethyl-1,3-diaza-2-boracyclopentane (0.132 g, 1.35 mmol) were reacted according to the general cyclization/boration procedure. The reaction mixture was transferred into a Teflon-valved reaction tube and heated at 80 °C for 18 h to afford **7** in 64% yield (0.152 g, 0.864 mmol). The identity of **7** was established by comparison of spectral data with the literature data;[4a] (R_f=0.18 in hexane/EtOAc 10:1); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 32.89; ^1H-NMR (500 MHz, $CDCl_3$) δ 7.17-7.30 (m, 5H), 3.58-3.61 (m, 1H), 3.45-3.47 (m, 1H), 2.66 (q, *J*=8.0, 1H), 2.09-2.16 (m, 2H), 1.97-2.00 (m, 1H), 1.81-1.84 (m, 1H), 1.70-1.75 (m, 2H), 1.51-1.56 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.38, 128.50, 127.45, 126.11, 65.92, 50.28, 49.14, 35.84, 29.50, 24.58; IR (neat) 3355 (broad, OH), 3025, 2946, 1492, 1451, 1054, 1020, 755, 699 cm^{-1}; HRMS Calcd for

$C_{12}H_{16}O(M+Na)^+$ 199.1201, found 199.1099; LRMS (CI^+) *m/z* $(MH-H_2O)^+$ 159(100.0), 81 (10.0).

Cyclohexylmethanol (8). 1,6-Heptadiene (**3**) (0.100 g, 1.04 mmol) and 1,3-dimethyl-1,3-diaza-2-boracyclopentane (0.108 g, 1.10 mmol) were reacted according to the general cyclization/boration procedure. The reaction mixture was transferred into a Teflon-valved reaction tube and heated at 80 °C for 18 h to afford **8** in 55% yield (0.089 g, 0.605 mmol). The identity of **7** was established by comparison of spectral data with a commercial sample: (R_f=0.19 in hexane/EtOAc 10:1); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 33.33; ^1H-NMR (500 MHz, $CDCl_3$) δ 3.40 (d, *J*=6.4, 2H), 1.63-1.73 (m, 6H), 1.31-1.54 (m, 4H), 0.88-0.91 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 68.72, 40.44, 29.52, 26.55, 25.79; IR (neat) 3384 (broad, OH), 2992, 2852, 1083, 1022, 755, 700 cm^{-1}; LRMS (CI^+) *m/z* MH^+ 97(100.0).

***trans*-2-Phenylcyclohexylmethanol (9).** 3-Phenyl-1,6-heptadiene (**4**) (0.200 g, 1.16 mmol) and 1,3-dimethyl-1,3-diaza-2-boracyclopentane (0.122 g, 1.25 mmol) were reacted according to the general cyclization/boration procedure. The reaction mixture was transferred into a Teflon-valved reaction tube and heated at 80 °C for 18 h to afford **9** in 52% yield (0.114 g, 0.603 mmol). The identity of **9** was established by comparison of spectral data with the literature data:[4b] (R_f=0.17 in hexane/EtOAc 10:1); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 33.18; ^1H-NMR (500 MHz, $CDCl_3$) δ 7.17-7.28 (m, 5H), 3.33-3.37 (m, 1H), 3.18-3.22 (m, 1H), 2.28-2.33 (m, 1H), 1.93-1.96 (m, 1H), 1.80-1.85 (m, 3H), 1.69-1.72 (m, 1H), 1.45-1.54 (m, 1H), 1.32-1.39 (m, 2H), 1.20-1.25 (m, 1H), 0.94-0.98 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.80, 128.57, 127.37, 126.22, 66.55, 47.33, 45.25, 35.45, 29.87, 26.70, 26.08; IR (neat) 3330 (broad, OH), 2923, 1448, 1090, 1034, 891 cm^-

^{1}; HRMS Calcd for $C_{13}H_{18}O(M+Na)^+$ 213.1357, found 213.1255; LRMS (CI^+) *m/z* MH^+ 191 (10.0), 173 (100.0).

Table 1, entry a. Compound **1** and catecholborane (0.155 g, 1.30 mmol) were reacted according to the general cyclization/boration procedure: $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 28.28 (d, $^1J_{B\text{-}H}$=191.6), 12.12.

Table 1, entry b. Compound **1** and pinacolborane (0.171 g, 1.30 mmol) were reacted according to the general cyclization/boration procedure to afford **6** in 50% yield (0.61 g, 0.61 mmol); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 33.87 for precatalyst Cp^*_2Sm•THF; 42% yield (0.51 g, 0.51 mmol); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 33.65 for precatalyst Cp^*_2YMe•THF; and 45% yield (0.55 g, 0.55 mmol); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 33.81 for precatalyst $[Cp^{TMS}{}_2YMe]_2$, respectively.

Table 1, entry c. Compound **1** and 1,3-diethyl-1,3-diaza-2-boracyclopentane (0.163 g, 1.30 mmol) were reacted according to the general cyclization/boration procedure to afford **6** in 45% yield (0.55 g, 0.55 mmol); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 31.85, 27.63 (d, $^1J_{B\text{-}H}$=139.0); Compound **1** and 1,3-diisopropyl-1,3-diaza-2-boracyclopentane (0.163 g, 1.30 mmol) were reacted according to the general cyclization/boration procedure; $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 26.19 (d, $^1J_{B\text{-}H}$=137.2).

Table 1, entry d. The general cyclization/boration procedure afforded **6**, after the reaction mixture was transferred into a Teflon-valved reaction tube and heated at 80 °C for 18 h, in 74% yield (0.90 g, 0.90 mmol); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 32.91 for precatalyst $[Cp^{TMS}{}_2SmMe]_2$; 62% yield (0.75 g, 0.75 mmol); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 33.21, 29.94 (d, $^1J_{B\text{-}H}$=142.6) for precatalyst $[Cp^{TMS}{}_2YMe]_2$; and 40% yield (0.48 g, 0.48 mmol); $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 32.86, 29.60 (d, $^1J_{B\text{-}H}$=140.9) for precatalyst

$[Cp^{TMS}{}_2LuMe]_2$, respectively. The precatalyst $Cp^*{}_2YMe$•THF showed no reactivity: $^{11}B\{^1H\}$-NMR (64.2 MHz) δ 28.95 (d, $^1J_{B\text{-}H}$=140.5).

References

(1) Molander, G.A.; Dowdy, E.D.; Schumann, H. *J. Org. Chem.* **1998**, *63*, 3386.

(2) Precatalyst preparation: (a) Evans, W.J.; Grate, J.W.; Choi, H.W.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 941 for $Cp^*{}_2Sm$•THF. (b) Schumann, H.; Keitsch, M.R.; Demtschuk, J.; Molander, G.A. *J. Organomet. Chem.* **1999**, *582*, 70 for $[Cp^{TMS}{}_2LnMe]_2$. (c) den Haan, K.H.; deBoer, J.L.; Teuben, J.H.; Smeets, W.J.J.; Spek, A.L. *J. Organomet. Chem.* **1987**, *327*, 70 for $Cp^*{}_2YMe$•THF.

(3) Merriam, J.S.; Niedenzu, K. *Inorganic Syntheses* **1972**, *44*, 162.

(4) (a) Fang, C.; Suemune, H.; Sakai, K. *J. Org. Chem.* **1992**, *57*, 4300. (b) Rieke, R.D.; Xiong, H. *J. Org. Chem.* **1991**, *56*, 3109.