Supporting Information for

A Synthesis of Aromatic Five- and Six-membered B-N Heterocycles via Ring Closing Metathesis

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Experimental Section

General Remarks: All reactions were carried out under an atmosphere of argon or nitrogen. Solvents were dried using standard procedures. The mass spectra were determined using a VG-70-S spectrometer and the NMR spectra were obtained using either a Varian INOVA 400, Bruker WH 300 or AM 300 spectrometer. The ^{1}H NMR spectra and ^{13}C NMR spectra were calibrated by using signals from solvents referenced to Me_4Si. The ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. The combustion analyses were determined by the analytical service department of the Department of Chemistry, The University of Michigan.

Tributylvinyltin[18] and allyltributyltin[20a] were prepared by literature procedures. All other compounds are commercially available.

Phenyl vinyl boron chloride (**11**). A solution of tributylvinyltin (16.8 g, 53 mmol) in 20 mL of pentane was added dropwise with stirring to a solution of phenylboron dichloride (7.0 g, 44 mmol) in 20 mL of pentane at -78 °C. After addition the reaction mixture was allowed to warm to 25 °C and stirred for 6 h. The solvent was removed in vacuo and the product (5.15 g, 78% yield) was obtained by vacuum distillation as a clear liquid (bp, 31-34 °C at 0.05 torr). *^{1}H NMR* (C_6D_6, 400 MHz): δ 8.02(d, J=8.0 Hz, 2H, ortho-ArH), 7.22(t, J=8.0Hz, 1H, para-ArH), 7.13(t, J=8.0Hz, 2H, meta-ArH), 6.83(dd, J=18.6, 13.7Hz, 1H, H_α), 6.60(dd, J=18.6, 4.0Hz, 1H, cis-Hβ), 6.06(bd, J=13.7Hz, 1H, trans-Hβ). *^{11}B NMR* (C_6D_6, 115.5 MHz): δ 58.5. *^{13}C NMR* (C_6D_6, 100.6MHz): δ 142.9, 139.7(br), 137.1, 136.9(br), 134.5, 128.6; *HRMS* (EI, m/z) calcd

for $C_8H_8{}^{11}B^{35}Cl$ (M^+), 150.0408; found, 150.0409. Anal. Calcd. for C_8H_8BCl: C, 63.88; H, 5.36. Found: C, 63.61; H, 5.27.

N-methylallylaminophenylvinylborane (**1c**). A solution of N-methylallylamine (3.02 g, 42.5 mmol) in 10 mL of CH_2Cl_2 was added to a solution of **11** (6.4 g, 42.7 mmol) in 20 mL of CH_2Cl_2 at -78 °C with stirring. The mixture was stirred for 1 h. Triethylamine (4.3 g, 42.6 mmol) was then added and a white precipitate formed immediately. The reaction mixture was allowed to warm to 25 °C with stirring for 3 h. The solid was removed by filtration and the solvent was removed in vacuo. Vacuum distillation of the residue gave **1c** (6.13 g, 78% yield) as a clear liquid (bp, 70-74 °C at 0.05 torr). The ^1H NMR and ^{13}C NMR spectra were consistent with **1c** existing as two B-N rotomers in the ratio of 1:1. *^1H NMR* (C_6D_6, 400 MHz): δ 7.43 (d, J=8 Hz, 4H, ArH); 7.30 (m, 6H, ArH); 6.66 (dd, J=18, 14 Hz, 1H, BCH), 6.57 (dd, J=18, 14 Hz, 1H, BCH'); 6.01 (m, 2H, B-vinyl), 5.70 (dd, J=18, 4Hz, 2H, B-vinyl), 5.62 (m, 1H, N-allyl (CH)), 5.52 (m, 1H, N-allyl-(CH')), 5.00 (m, 4H, N-allyl (CH)), 3.64 (dt, J=5.1, 1.5 Hz, 2H, NCH_2), 3.44 (dt, J=5.5, 1.5 Hz, 2H, N CH_2'); 2.70 (s, 3H, NCH_3); 2.57 (s, 3H, N CH_3'). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 39.2. ^{13}C NMR (C_6D_6, 100.6 MHz): shows two sets of signals. HRMS (EI, m/z) for $C_{12}H_{16}{}^{11}BN$ (M^+) calcd, 185.1376; found, 185.1376. Anal. Calcd. for $C_{12}H_{16}BN$: C, 77.88; H, 8.71; N, 7.57. Found: C, 77.66; H, 8.71; N, 7.50.

1,5-Dihydro-1-methyl-2-phenyl-1,2-azaborole (**3c**). A solution of **1c** (6.0 g, 32.4 mmol) in 320 mL of CH_2Cl_2 was added to a solution of bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (Grubbs' catalyst) (1.33 g, 1.62 mmol) in 20 mL of CH_2Cl_2 at 25 °C. The mixture was stirred at 25 °C for 10 h after which the color had changed from purple-red to dark brown. The solvent was removed in vacuo and the product (4.37 g, 86%) was distilled (bp=60-65 °C at 0.05 torr). *^1H NMR* (C_6D_6, 400 Hz): δ 7.75 (d, J=7.0 Hz, 2H, ArH), 7.30 (m, 3H, ArH); 6.88 (d, J=8.6 Hz, 1H, alkene), 6.60 (d, J=8.6 Hz, 1H, alkene), 3.42 (brs, 2H, N CH_2), 2.82 (s, 3H, N CH_3). *^{11}B NMR* (C_6D_6, 115.5 MHz): δ 39.0. *^{13}C NMR* (C_6D_6, 100.6 MHz): δ 148.3 (C(4)); 134.3 (Ph); 128.7 (Ph), 128.1 (Ph); 63.9 (C(5)), 34.3 (CH_3). C(3), Ph(i)

not observed. HRMS (EI, m/z calcd for $C_{10}H_{12}{}^{11}BN$ (M^+), 157.1063; found, 157.1068. Anal. calcd for $C_{10}H_{12}BN$: C, 76.49; H, 7.70; N, 8.92. Found: C, 76.47; H, 7.49, N, 8.52.

Lithium 1-methyl-2-phenyl-1,2-azaborolide (**5c**). A solution of **3c** (2.30 g, 14.6 mmol) in 14 mL of ether was added to a solution of LDA (1.57 g, 14.6 mmol) in 10 mL of ether at -78 °C. The reaction mixture was stirred at -78 °C for 2 h and allowed to warm to 25 °C for 3 h. A white solid formed and the color of the solution became slightly yellow. The solvent was removed under vacuum and the residue was washed with pentane (3x30 mL). The residue was dried under vacuum to give the product a white solid (1.93 g, 81%). *^1H NMR* (THF-d_8, 400 MHz): δ 7.56 (d, J=8.0 Hz, 2H, ArH), 7.05 (t, J=8.0 Hz, 2H, ArH), 6.87 (t, J=8.0 Hz, 1H, ArH), 5.87 (d, J=3.7 Hz, 2H, H_3 & H_4), 4.47 (t, J=3.7 Hz, 1H, H_5), 3.51 (s, 3H, Me). *^{11}B NMR* (THF-d_8, 115.5 MHz): δ 29.9. *^{13}C NMR* (THF-d_8, 100.6 MHz): δ 133.9 (Ar), 127.2 (Ar), 123.8 (Ar), 115.2 (C_4); 111.8 (C_5), 36.2 (Me). C(3) not observed.

[1-Methyl-2-phenyl-1,2-azaborolyl][pentamethyl-cyclopentadienyl]ruthenium(II) (**12c**). A solution of **5c** (0.30 g, 1.8 mmol) in 4 mL of THF was added dropwise to a suspension of $[Cp^*RuCl]_4$ (1.25 g, 1.8 mmol) in 10 mL of THF at -78 °C. The mixture was stirred at -78 °C for 1 h and allowed to warm with stirring to 25 °C for 4 h. The solvent was removed in vacuo leaving a solid residue which was extracted with pentane (3x20 mL). The product was obtained by recrystallization from pentane as colorless crystals, (0.34 g, 47%), mp, 49 °C. *^1H NMR* (C_6D_6, 360 MHz): δ 7.76 (d, J=8.0 Hz, 2H, ArH), 7.39 (t, J=8.0 Hz, 2H, ArH), 7.26 (t, J=8.0 Hz, 1H, ArH), 4.72 (s, 1H, H_3), 4.34 (d, J=4.5 Hz, 1H, H_4), 3.82 (d, J=4.5 Hz, 1H, H_5), 2.49 (s, 3H, NCH_3), 1.75 (s, 15H, CpMe). *^{13}C NMR* (C_6D_6, 100.6 MHz): δ 134.3 (Ar); 127.6(Ar); 126.8 (Ar); 84.2 (C(4)); 82.9 (Cp*(c)); 78.0 (C(3)); 38.2 (NMe); 11.6 (CpMe). C(5) not observed. *^{11}B NMR* (C_6D_6, 115.5 MHz): δ 11.4. HRMS (EI, m/z): calcd for $C_{20}H_{26}{}^{11}BNRu$: 393.1202; found, 393.1189. Anal. Calcd for $C_{20}H_{26}BNRu$: C, 61.23; H, 6.68; N, 3.57; Found: C, 60.97; H, 6.70; N, 3.51.

N-Allyl-N-ethylamino allylboron chloride (**14**). Ethylallylamine (12.8 g, 0.15 mol) was added dropwise with stirring at -78 °C to a solution of allylboron dichloride (0.15 mol) which had

been prepared from allyltributyltin (59.8 g, 0.18 mol) and BCl_3 (17.6 g, 0.15 mol) by literature methods.[20] The mixture was stirred at -78 °C for 20 min and then allowed to warm to 0 °C for 30 min. After recooling to -78 °C triethylamine (16.7 g, 0.165 mol) was added via a syringe. White solid formed on addition. The reaction mixture was stirred at 30 °C for 4 h. The solid was removed by filtration and the volatiles were removed under vacuum. The product (17.5 g, 68%) was obtained by distillation (bp, 36 °C at 0.05 torr). The H NMR spectrum of **14** was consistent with it being in the form of two BN rotomers in the ratio of 1:1. *^1H NMR* ($CDCl_3$, 300 MHz): δ 5.9 (m, 2CH, 2H); 5.75 (m, 2 CH, 2H), 5.15 (m, 2 vinyl CH_2, 4H); 4.98 (m, 2 vinyl CH_2, 4H), 3.85 (d, J=5.1 Hz, CH_2N, 2H), 3.62 (d, J=5.5 Hz, CH_2N', 2H), 3.21 (q, J=7 Hz, CH_2N, 2H); 3.16 (q, J=7 Hz, CH_2N', 2H), 2.03 (d, J=7.7 Hz, CH_2B, 2H); 1.96 (d, J=7.7 Hz, CH_2B', 2H), 1.07 (t, J=7 Hz, CH_3, 3H), 1.02 (t, J=7 Hz, CH_3', 3H). *^{11}B NMR* (115.5 MHz, C_6D_6): δ 37.4. HRMS (EI, m/z): calcd for $C_9H_{14}{}^{11}BN^{35}Cl$, 182.0908; found 182.0914.

N-allyl-N-ethylamino allylphenylborane (**2e**). A solution of phenyllithium (96 mmol) in ether cyclohexane was added to a solution of **14** (17.5 g, 96 mmol) in 35 mL of ether at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and allowed to warm to 25 °C for 4 h. The solvent was removed in vacuo and the residue was extracted with pentane. After filtration the solvent was removed and the product (16.5 g, 81%) was obtained by distillation, bp 74-77 °C at 0.05 torr. The ^1H NMR spectrum was consistent with **2e** in the form of two B-N rotomers in the ratio of 1:1. *^1H NMR* (C_6D_6, 400 MHz): δ 7.30-7.05 (m, 10H, 2Ph); 5.8 (m, 2H, 2CH vinyl) 5.58 (m, 1H, CH vinyl), 5.48 (m, 1H, CH vinyl), 4.83-5.0 (m, 8H, $4CH_2$ vinyl), 3.54 (dt, J=5.1 Hz, 2H, NCH_2), 3.40 (dt, J=5.5 Hz, 2H, NCH_2'); 3.02 (q, J=7.0 Hz, 2H, Et), 2.83 (q, J=7.0 Hz, 2H, Et'), 2.08 (d, J=7.7 Hz, 2H, BCH_2); 2.00 (d, J=7.7 Hz, 2H, BCH_2'); 0.88 (t, J=7.0 Hz, 3H, Et); 0.72 (q, J=7.0 Hz, 3H, Et'). *^{11}B NMR* (115.5 MHz, C_6D_6): δ 42.5. *HRMS* (EI, m/z): calcd for $C_{14}H_{20}{}^{11}BN$, 213.1689; found 213.1683.

1-Ethyl-3,6-dihydro-2-phenyl-1,2-azaborine (**4e**). A solution of **2e** (4.0 g, 21.6 mmol) in 180 mL of CH_2Cl_2 was added to a solution of bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (0.89 g, 1.08 mmol) in 30 mL of CH_2Cl_2. The mixture was stirred at 25

°C for 10 h during which the color changed from purple-red to dark brown. The solvent was removed in vacuo and the product (3.0 g, 86%) was obtained as colorless liquid (bp, 52-54 °C at 0.05 torr). *^{1}H NMR* (300 MHz, C_6D_6): δ 7.36 (d, J=8.0 Hz, 2H, ArH), 7.24 (t, J=8.0 Hz, 2H, ArH), 6.70 (t, J=8.0 Hz, 1H, ArH), 5.90 (dm, J=10.2 Hz, 1H, alkene), 5.46 (dm, J=10.2 Hz, alkene), 3.40 (m, 2H, CH_2N), 2.95 (q, J=7.1 Hz, 2H, CH_2(Et), 1.79 (m, 2H, CH_2B), 0.84 (t, J=7.1 Hz, 3H, CH_3). *^{13}C NMR* (75.5 MHz, C_6D_6): δ 131.2, 129.0, 127.9, 127.6 (ArC), 126.0, 124.7 (C=C), 48.1, 46.4, 19.8 (b), 15.1. *^{11}B NMR* (115.5 MHz, C_6D_6): δ 41.2. HRMS (EI, m/z): calcd for $C_{12}H_{16}{}^{11}BN$, 185.1376; found, 185.1384. Anal. calcd for $C_{12}H_{16}BN$: C, 77.88; H, 8.71; N, 7.57. Found: C, 78.42; H, 8.80; N, 7.67.

1-Ethyl-2-phenyl-1,2-azaborine (**6e**). A solution of **4e** (3.0 g, 16.2 mmol) in 15 mL of pentane was added dropwise to a solution of DDQ (4.04 g, 17.8 mmol) in 30 mL of pentane at 25 °C. The color changed quickly from bright yellow to brown. The reaction mixture was stirred at 35 °C for 24 h. After filtration the solvent was removed which gave the product as a yellow oil. A pure sample of **6e** (1.79 g, 58%) was obtained by column chromotography (silica gel, hexane). ^{1}H NMR (360 MHz, C_6D_6): δ 7.54 (d, J=8.0 Hz, 2H, ArH), 7.32~7.00 (m, 5H, ArH and CH=), 6.72 (d, J=7.0 Hz, 1H, CH=), 6.20 (t, J=7.0 Hz, 1H, CH=), 3.40 (q, J=7.2 Hz, 2H, NCH_2), 0.84 (t, J=7.2 Hz, 3H, CH_3). *^{13}C NMR* (100.6 MHz, C_6D_6): δ 142.9 137.9, 133.9(b), 133.0, 131.1, 127.6, 111.8, 48.1 (NCH_2), 18.2 (CH_3). *^{11}B NMR* (115.5 MHz, C_6D_6): δ 35.4. *HRMS* (EI, m/z): clacd for $C_{12}H_{14}{}^{11}BN$, 183.1219; found, 183.1226. Anal. calcd for $C_{12}H_{14}BN$: C, 78.73; H, 7.71; N, 7.65; Found: C, 78.59; H, 7.65; N, 7.48. UV (hexane): max 236, 286 nm.