Supplemental Information

1,2-Migratory Ring Expansion of a BN-Naphthalene

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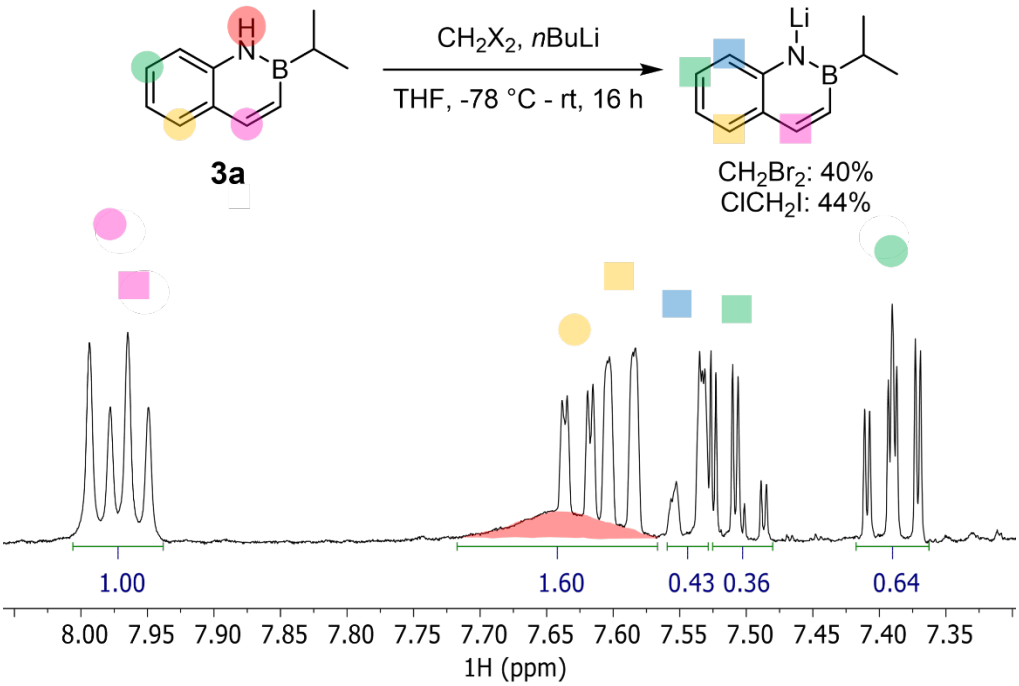


Figure S1. Cropped ^{1}H NMR spectrum of the roughly 60:40 mixture produced by subjecting **3a** to standard Matteson Homologation conditions, emphasizing that the proton on the BN starting material (red highlighted area) is not present in the product.

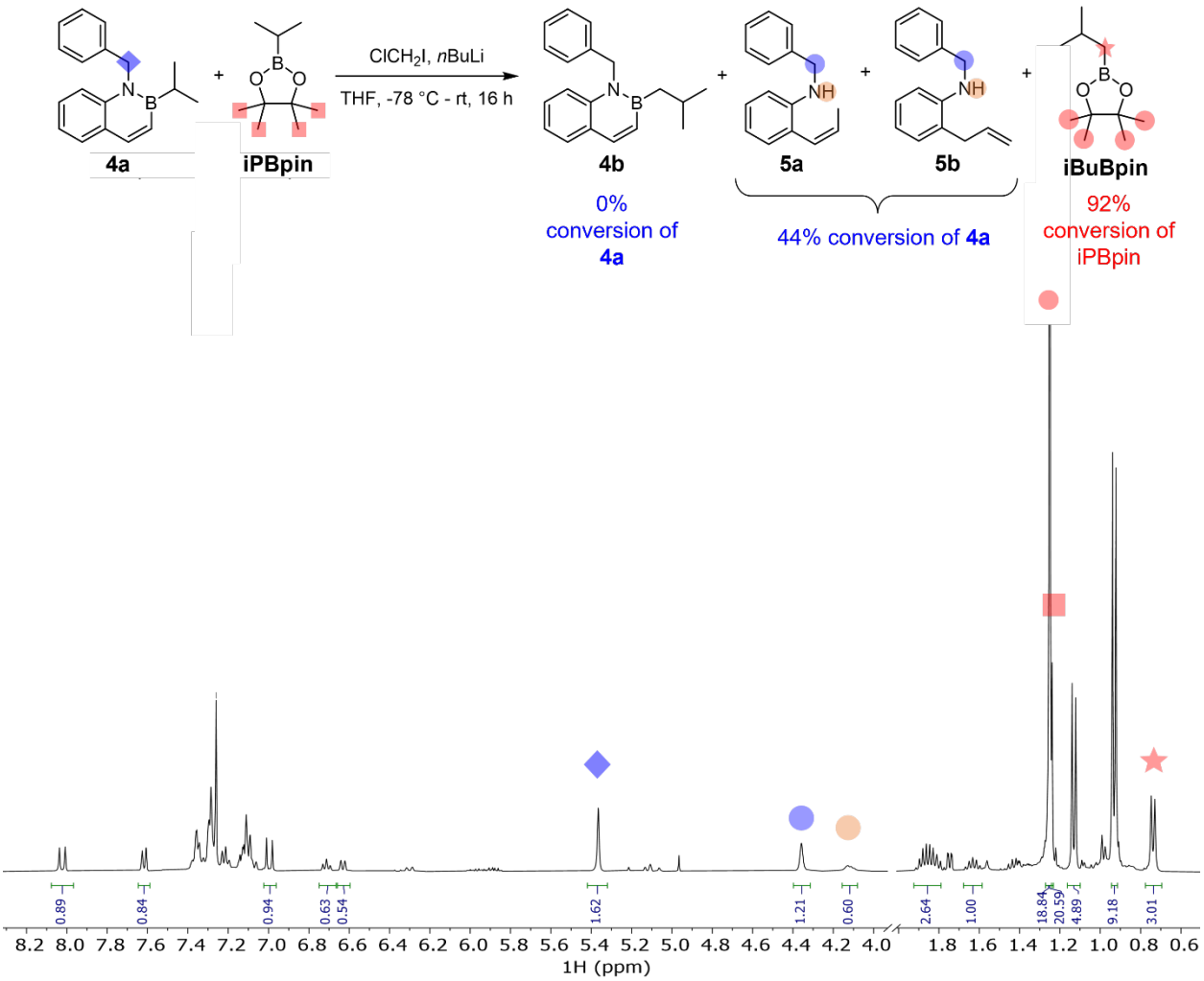


Figure S2. Cropped ^{1}H NMR spectrum of the crude product mixture from the Matteson homologation of iPBpin in the presence of **4a**.

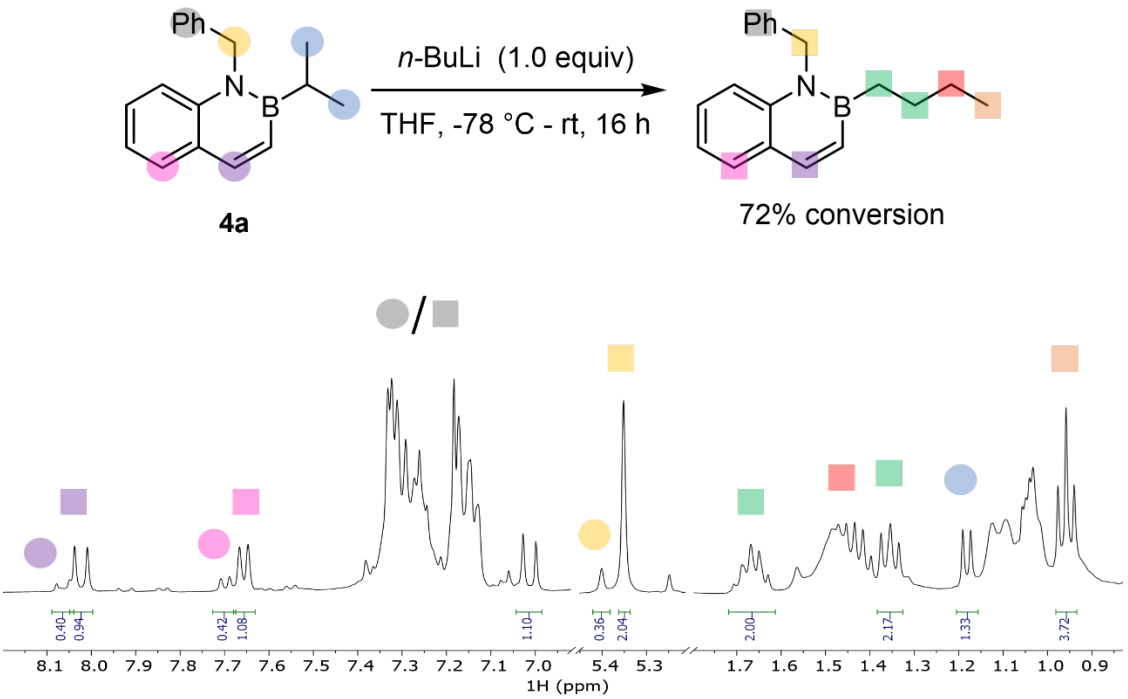


Figure S3. Cropped ^{1}H NMR spectrum of the crude product mixture from substitution of **4a** with 1.0 equivalents of *n*-BuLi to form (N-Bn)-*n*BuBN.

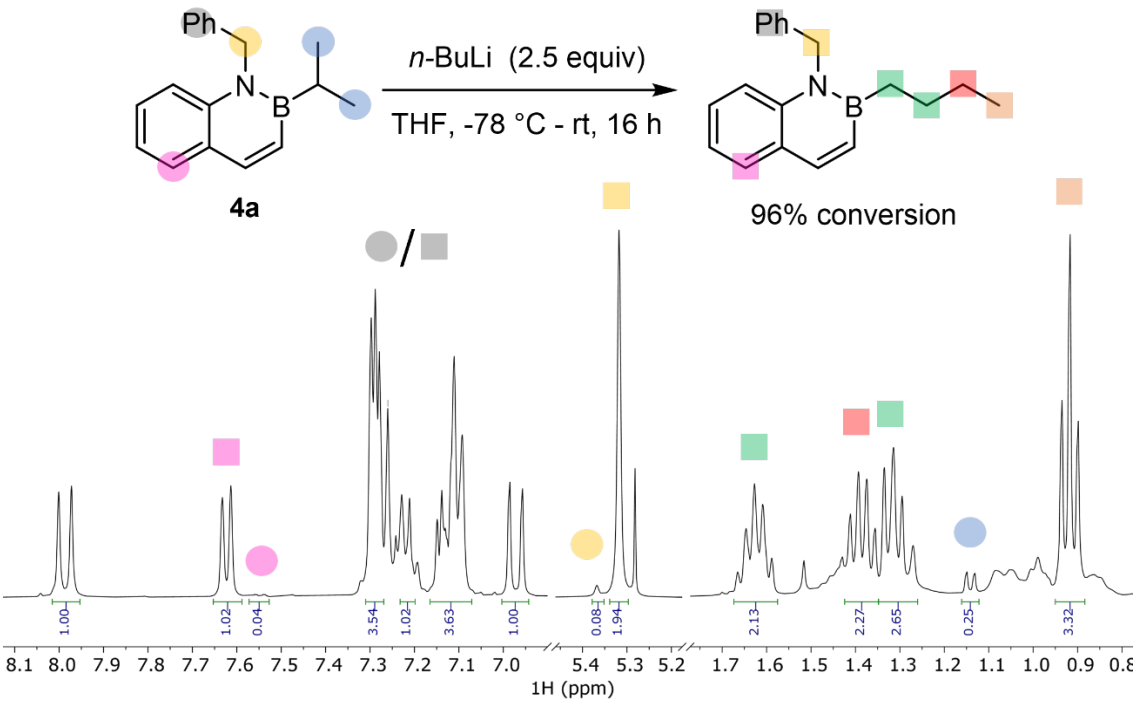


Figure S4. Cropped ^{1}H NMR spectrum of the crude product mixture from substitution of **4a** with 2.5 equivalents of *n*-BuLi to form (N-Bn)-*n*BuBN.

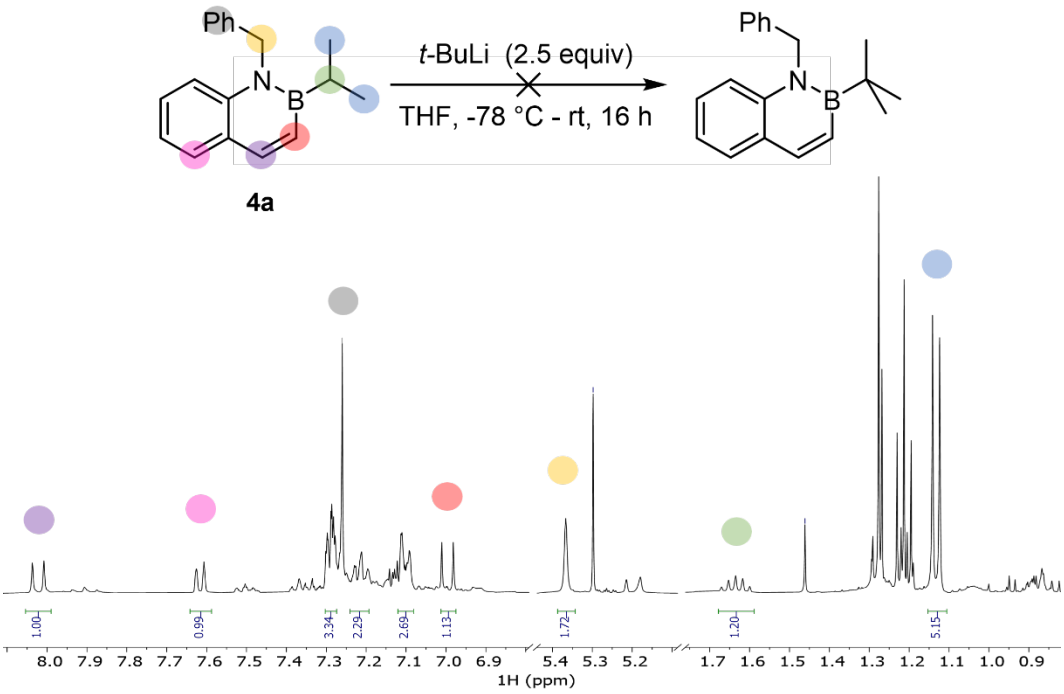


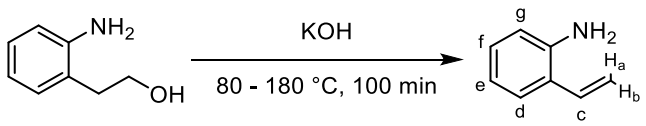
Figure S5. Cropped ^{1}H NMR spectrum of the crude product mixture from reaction of **4a** with 2.5 equivalents of *t*-BuLi, which did not result in substitution to form (N-Bn)-*t*BuBN and instead the starting material was recovered.

2 | General Information

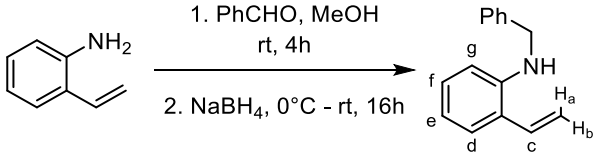
All experiments were performed using standard Schlenk techniques, except the synthesis of **1**, which was carried out under aerobic conditions. Air-sensitive reagents which were not dispensed using standard Schlenk techniques were stored and dispensed under an inert nitrogen atmosphere using an MBraun UNIlab Pro glovebox. Moisture-sensitive potassium trifluoroborate reagents were stored in a desiccator with Drierite™. Glassware for air- and moisture-sensitive experiments were dried overnight in an oven at 175 °C. Reactions maintained at cryogenic temperatures for >8 hr were cooled with a Neslab CryoControl 100 Immersion Cooler. Solvents THF and toluene were dried on a J. C. Meyer Solvent Dispensing System (SDS) with alumina-packed stainless-steel columns. All column chromatography was performed on a Teledyne ISCO Combiflash Rf+ using Redisep Rf silica columns. Prep TLC was performed with 20x20 1000 um silica gel FG plates by Uniplate. Mass spectrometry and high-resolution mass spectrometry were performed in the Johns Hopkins University Department of Chemistry with a VG Instruments VG70S/E magnetic sector mass spectrometer with electric ionization (EI, 70 eV). NMR spectra were recorded at room temperature on a Bruker Avance 400 MHz spectrometer. The proton and carbon chemical shifts are reported here in ppm and referenced using the respective signals of the deuterated solvent (^{1}H: $CDCl_3$ – δ = 7.26; ^{13}C: – δ = 77.2), while boron chemical shifts were referenced to an external standard (^{11}B: BF_3•Et_2O - δ = 0.0).

2-aminophenyl ethanol, potassium hydroxide, benzaldehyde, sodium borohydride, 2-iodopropane, *n*-butyllithium solution 1.6 M in hexanes, *tert*-butyllithium solution 1.7 M in pentane, zinc chloride solution 1.0 M in ether, dibromomethane, silicon tetrachloride, triethylamine, sodium hydroxide, ammonium chloride, methanol, dichloromethane, hexanes (mixture of isomers), and anhydrous cyclopentyl methyl ether were purchased from Sigma Aldrich and used as received. Anhydrous sodium sulfate was purchased from EMD Millipore and used as received. Chloroform-*d* was purchased from Cambridge Isotope Laboratories and dried over 4Å molecular sieves before use. Chloroiodomethane was purchased from Sigma Aldrich and distilled before use. All potassium trifluoroborates were purchased from Ambeed and used as received. Isopropylboronic acid pinacol ester was purchased from Thermo Scientific Chemicals and used as received.

3 | Experimental Procedures

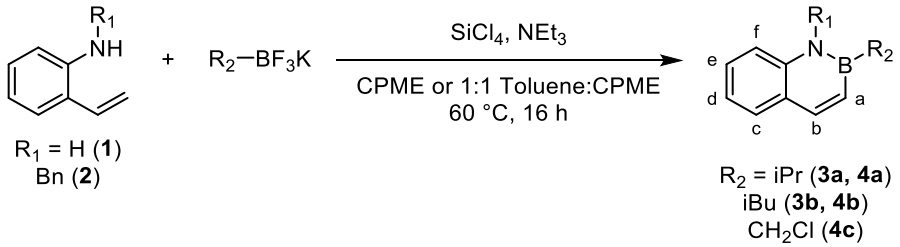


3.1 Synthesis of 2-Vinylaniline (1): To a 50 mL round bottom flask equipped with a stir bar were added 2-aminophenylethanol (23.9 g, 0.139 mol, 1.0 equiv) and potassium hydroxide (9.76 g, 0.139 mol, 1.0 equiv) under atmospheric conditions. The flask was attached to a distillation path and placed under reduced pressure (<1 mtorr) while increasing the temperature from 80 to 180 °C in increments of 10 °C every 10 min. 2-vinylaniline (**1**) was collected as a colorless clear oil between 120 and 140 °C (12.6 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.30 (d, *J* = 7.7 Hz, 1H, H_d), 7.10 (t, *J* = 6.8 Hz, 1H, H_c), 6.78 (td, *J* = 11.6, 7.3 Hz, 2H, $H_{e,f}$), 6.69 (d, *J* = 8.0 Hz, 1H, H_g), 5.64 (d, *J* = 17.4 Hz, 1H_a), 5.33 (d, *J* = 11.1 Hz, 1H, H_b), 3.74 (s, 2H, N*H*$_2$) ppm; ^{13}C NMR (400 MHz, $CDCl_3$, 298K) δ 143.8, 132.8, 128.8, 127.4, 124.1, 119.0, 116.2, 115.7 ppm.

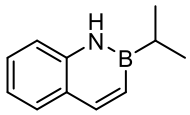


1 **2**

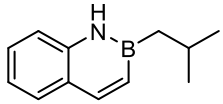
3.2 Synthesis of (N-Benzyl)-2-Vinylaniline (2): To an oven-dried Schlenk flask equipped with a stir bar was added **1** (10.2 g, 0.086 mol, 1.0 equiv). The flask was then placed under vacuum with stirring for 20 minutes to remove dissolved air in **1**. Anhydrous methanol (342 mL, 0.25 M) was then added, though reagent-grade methanol could be used if sparged for 45 min. The flask was then brought into the glovebox, and to it was added benzaldehyde (11.4 mL, 0.112 mol, 1.3 equiv) which had been filtered through an alumina plug. The flask was then brought out of the glovebox, put on the Schlenk line, and stirred at rt for 4 hours. After 4 hours, an aliquot was taken to ensure full conversion to the imine by ^{1}H NMR. The reaction was then cooled to 0 °C and $NaBH_4$ (11.4 g, 0.301 mol, 3.5 equiv) was then added under positive Argon flow, after which the reaction was allowed to warm to rt and stir for 16 hours. The reaction was quenched with 180 mL 1M $NaOH_{(aq)}$, extracted 3 times with hexanes, and concentrated under vacuum to give **2** as a yellow oil (15.8g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.37 (m, 4H, Ar), 7.30 (m, 2H, $H_{e,f}$), 7.16 (td, *J* = 7.72, 1.68 Hz, 1H, H_c), 6.78 (m, 2H, Ar, H_d), 6.65 (d, *J* = 8.2 Hz, 1H, H_g), 5.64 (d, *J* = 17.3 Hz, 1H, H_a), 5.32 (d, *J* = 11.1 Hz, 1H, H_b), 4.37 (s, 2H, NC*H*$_2$Ar), 4.18 (s, 1H, N*H*) ppm; ^{13}C NMR (400 MHz, $CDCl_3$, 298K) δ 145.2, 139.4, 133.0, 129.1, 128.8, 127.6, 127.5, 127.4, 124.4, 117.6, 116.5, 111.1, 48.4 ppm.



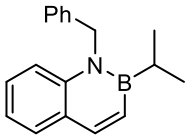
3.3 General Procedure: Synthesis of Borazaronaphthalenes (3a-b, 4a-c): To an oven-dried Schlenk flask equipped with a stir bar was added vinylaniline (1.5 equiv), which was then placed under vacuum to remove dissolved air in **2** until bubbling ceased. The appropriate potassium trifluoroborate (1.0 equiv) was then added under positive Argon flow, and the reaction vessel was then purged and backfilled. To this was added anhydrous cyclopentyl methyl ether (CPME) or 1:1 anhydrous toluene:anhydrous CPME (0.5 M total) to dissolve **2**. To the flask was then added NEt_3 (1.5 equiv), followed by $SiCl_4$ dropwise (1.5 equiv), taking care to avoid vigorous bubbling. The reaction then stirred for 15 min at rt, then for 16 hours at 60 °C. After 16 hours, the CPME was removed under reduced pressure to yield a brownish solid, which was resuspended in 16 mL hexanes and stirred for 2 hr. After this, 16 mL DI H_2O was added and the mixture was stirred for a further 2 hr. The mixture was then filtered to remove all undissolved solids, the layers were separated, and the organic layer was washed 3 times with sat. $NH_4Cl_{(aq)}$. Organic layers were then combined, dried over Na_2SO_4, and concentrated under vacuum to yield the crude material, which was then purified by column chromatography in 100% hexanes.



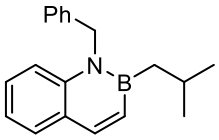
*3.3.1 Synthesis of 2-isopropylborazaronaphthalene (**3a**):* The title compound was synthesized according to General Procedure 3.3 on a 4.2 mmol scale using **1** and potassium trifluoro(isopropyl)borate in 1:1 toluene:CPME, and was obtained as a white crystalline solid (507.7 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.99 (d, *J* = 11.5 Hz, 1H, H_b), 7.66 (s, 1H, N*H*), 7.60 (d, *J* = 7.8 Hz, 1H, H_c), 7.40 (t, *J* = 7.6 Hz, 1H, H_e), 7.24 (d, *J* = 3.8 Hz, 1H, H_f), 7.16 (t, *J* = 7.4 Hz, 1H, H_d), 6.88 (d, *J* = 11.5 Hz, 1H, H_a), 1.54 (hept, *J* = 7.2 Hz, 1H, BC*H*), 1.18 (d, *J* = 7.3 Hz, 6H, 2CH_3) ppm; ^{11}B{^{1}H} (400 MHz, $CDCl_3$, 298 K) δ 13.8 ppm; ^{13}C NMR (400 MHz, $CDCl_3$, 298K) δ 114.7, 140.1, 129.4, 128.1, 125.5, 120.8, 118.0, 119.9 ppm.



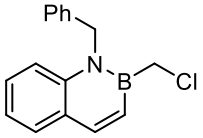
*3.3.2 Synthesis of 2-isobutylborazaronaphthalene (**3b**):* The title compound was synthesized according to General Procedure 3.3 on a 1.4 mmol scale, using **1** and potassium trifluoro(isobutyl)borate in 1:1 toluene:CPME, and was obtained as a white solid (222.0 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.94 (d, *J* = 11.5 Hz, 2H), 7.65 (s, 1H, N*H*), 7.59 (d, *J* = 7.7 Hz, 1H, H_c), 7.38 (td, *J* = 7.1, 1.6 Hz, 1H, H_e), 7.21 (d, *J* = 7.5 Hz, 1H, H_f), 7.14 (td, *J* = 7.0, 1.2 Hz, 1H, H_d), 6.83 (dd, *J* = 11.5, 2.0 Hz, 1H, H_a), 2.17 – 1.96 (m, 1H, BCH_2CH), 1.21 (d, *J* = 7.2 Hz, 2H, BCH_2CH), 0.99 (d, *J* = 6.6 Hz, 6H, 2CH_3) ppm; ^{11}B{^{1}H} (400 MHz, $CDCl_3$, 298 K) δ 38.0 ppm; ^{13}C NMR (400 MHz, $CDCl_3$, 298K) 144.1, 140.3, 129.4, 128.0, 125.4, 120.7, 117.9, 26.4, 25.8 ppm; HRMS (EI) m/z calculated for $C_{12}H_{16}BN$ $[M]^+$ 185.1376, found 185.0380.



*3.3.3 Synthesis of (N-benzyl)-2-isopropylborazaronaphthalene (**4a**):* The title compound was synthesized according to General Procedure 3.3 on a 2.5 mmol scale, using **2** and potassium trifluoro(isopropyl)borate in CPME, and was obtained as a white crystalline solid (228.0 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.02 (d, *J* = 11.5 Hz, 1H, H_b), 7.62 (d, *J* = 8.6 Hz, 1H, H_f), 7.29 (m, 4H, Ar), 7.21 (m, 1H, Ar), 7.12 (m, 3H, $H_{c,d,e}$), 6.99 (d, *J* = 11.5 Hz, 1H, H_a), 5.37 (s, 2H, NCH_2Ar), 1.63 (hept, *J* = 7.1 Hz, 1H, C*H*), 1.13 (d, *J* = 7.1 Hz, 6H, 2CH_3) ppm; ^{11}B{^{1}H} (400 MHz, $CDCl_3$, 298 K) δ 40.4 ppm; ^{13}C NMR (400 MHz, $CDCl_3$, 298K δ 145.3, 141.5, 139.0, 130.2, 128.8, 128.4, 1267.0, 125.9, 120.6, 116.5, 50.4, 20.8 ppm. Anal. calcd for $C_{18}H_{20}BN$: C, 82.78; H, 7.72; N, 5.36%. Found: C, 81.35; H, 7.51; N, 5.38%.



*3.3.4 Synthesis of (N-benzyl)-2-isobutylborazaronaphthalene (**4b**):* The title was synthesized according to General Procedure 3.3 on a 1.67 mmol scale, using **2** and potassium trifluoro(isobutyl)borate in CPME, and was obtained as a white solid (85.0 mg, 19% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.99 (d, *J* = 11.4 Hz, 1H, H_b), 7.63 (d, *J* = 7.7 Hz, 1H, H_f), 7.27 (m, 5H, Ar), 7.13 (m, 3H, $H_{c,d,e}$), 6.98 (d, *J* = 11.5 Hz, 1H, H_a), 5.34 (s, 2H, NCH_2Ar), 2.17 (m, 6.6 Hz, 1H, BCH_2C*H*), 1.29 (d, *J* = 7.2 Hz, 2H, BCH_2CH), 0.99 (d, *J* = 6.5 Hz, 6H, 2CH_3) ppm; ^{11}B{^{1}H} (400 MHz, $CDCl_3$, 298 K) δ 39.8 ppm; ^{13}C NMR (400 MHz, $CDCl_3$, 298K) δ 144.3, 141.8, 138.8, 130.2, 128.8, 128.3, 127.0, 125.9, 116.2, 50.7, 26.5, 25.8 ppm; HRMS (EI) m/z calculated for $C_{19}H_{22}BN$ $[M]^+$ 275.1845, found 275.1845.



*3.3.5 Synthesis of (N-benzyl)-2-(chloromethyl)borazaronaphthalene (**4c**):* The title compound was synthesized according to General Procedure 3.3 on a 7.5 mmol scale, using **2** and potassium trifluoro(chloromethyl)borate in CPME and was obtained as a white crystalline solid (810.9 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.14 (d, *J* = 11.4 Hz, 1H, H_b), 7.70 (d, *J* = 7.0 Hz, 1H, H_f), 7.41 (m, 2H, Ar and H_c), 7.26 (m, 4H, Ar), 7.17 (d, *J* = 11.4 Hz, 2H, $H_{d,e}$), 7.10 (d, *J* = 6.8 Hz, 1H, H_d), 5.33 (s, 2H, NCH_2Ar), 3.57 (s, 2H, BCH_2Br) ppm; ^{11}B{^{1}H} (400 MHz, $CDCl_3$, 298 K) δ 35.8 ppm; ^{13}C NMR (400 MHz, $CDCl_3$, 298K) δ 146.5, 141.1, 137.8, 130.6, 129.0, 127.3, 127.2, 125.8, 121.4, 116.3, 50.8 ppm; HRMS (EI) m/z calculated for $C_{16}H_{15}ClBN$ $[M]^+$ 267.0986 (Cl^{35}), found 267.0981, and 269.0957 (Cl^{37}), found 269.0966.

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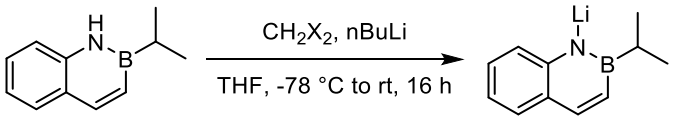


3.4 Deprotonation of Compound 3a Under Matteson Homolgation Conditions: To an oven-dried 10 mL Schlenk flask equipped with a stir bar was added **3a** (80.0 mg, 0.468 mmol, 1.0 equiv), and THF (0.78 mL, 0.6 M) in the glovebox. If using chloroiodomethane as the dihalomethane (47.8 µL, 0.655 mmol, 1.4 equiv), it was also added in the glovebox. The flask was then sealed, brought out of the glovebox, put on the Schlenk line, and cooled to -78 °C using a dry ice/isopropanol bath. If using dibromoomethane as the

dihalomethane, it was then added via syringe (85.0 µL, 1.218 mmol, 2.5 equiv). After 15 minutes of stirring at -78 °C, nBuLi (1.1 equiv for $ClCH_2I$ or 2.0 equiv for CH_2Br_2) was added dropwise over 45 min using a syringe pump, taking care that the solution should cool before reaching the solution by flowing down the inside of the flask, which was held at an angle in the bath (**Figure S10**). Following addition, the reaction was stirred for 16 hours while slowly warming up to rt. The reaction was then quenched with methanol, opened to air, and concentrated under vacuum. The resulting viscous oil was redissolved in minimal DCM, washed 3 times with sat. $NH_4Cl_{(aq)}$, dried over Na_2SO_4, and concentrated under vacuum to yield the crude mixture as an oily yellow solid. Conversion was then estimated by ^1H NMR (**Figure S1**, CH_2Br_2 40%, $ClCH_2I$ 44%).

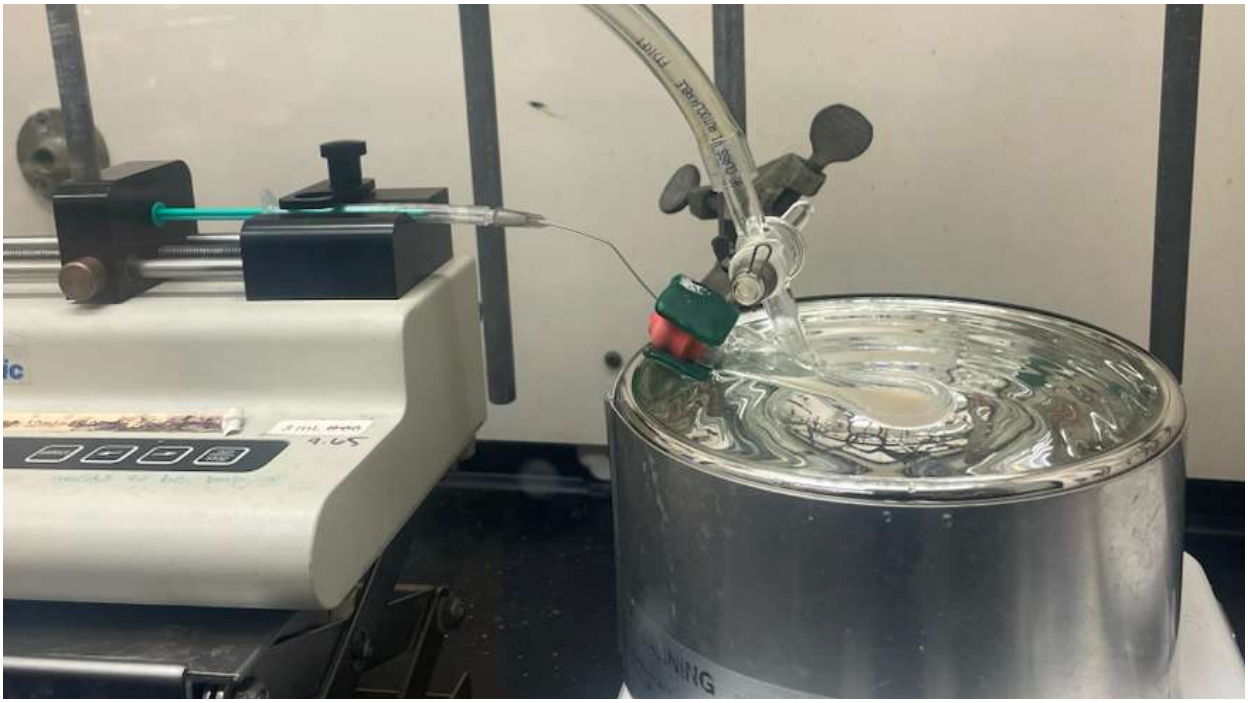
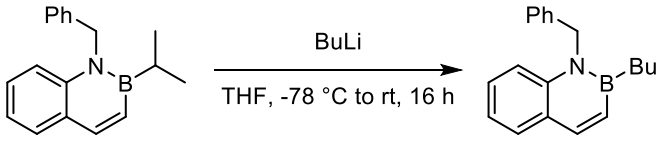
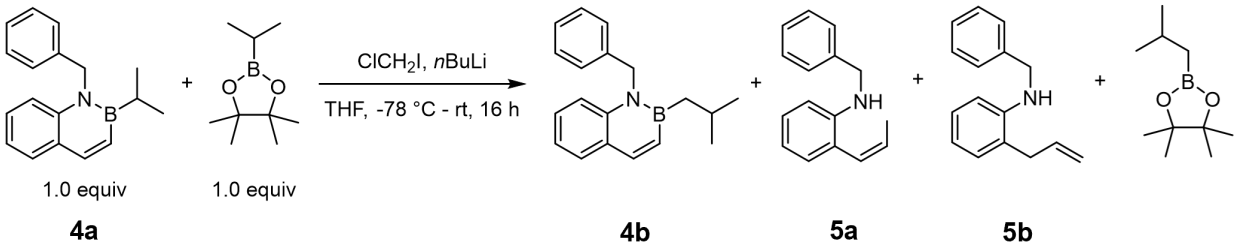


Figure S10. Photograph displaying a mock-up experimental setup for dropwise addition from a syringe pump of a butyllithium reagent down the side of the 10 mL Schlenk flask vessel to pre-cool it, as used in Experimental Procedures 3.4-9.

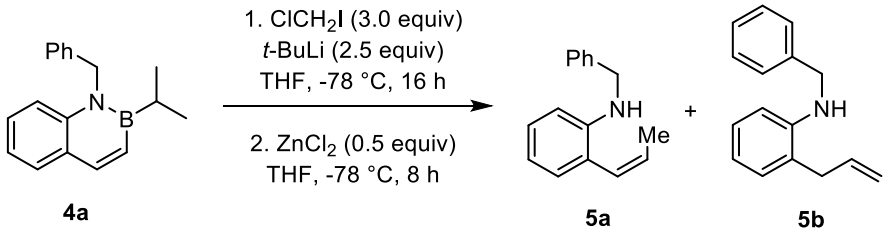


3.5 Substitution of Compound 4a with Butyllithium: To an oven-dried 10 mL Schlenk flask was added **4a** (150 mg, 0.574 mmol, 1.0 equiv) in the glovebox and dissolved in THF (0.975 mL, 0.6 M). The flask was then sealed, brought out of the glovebox, put on the Schlenk line, and cooled to -78 °C using a dry ice/isopropanol bath. After 15 minutes of stirring at -78 °C, BuLi (1.0 or 2.5 equiv) was added dropwise over 45 min using a syringe pump, taking care that the reagent should cool before reaching the solution by flowing down the inside of the flask, which was held at an angle in the bath (**Figure S10**). Following addition, the reaction was stirred for 16 hours while slowly warming up to rt. The reaction was then quenched with methanol, opened to air, and then concentrated under vacuum. The resulting viscous oil was redissolved

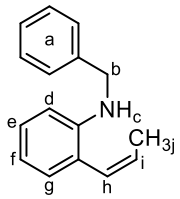
in minimal DCM, washed 3 times with saturated $NH_4Cl_{(aq)}$, dried over Na_2SO_4, and concentrated under vacuum to yield the crude as a brown oil. Conversion was then estimated by ^1H NMR (**Figure S2-4**).



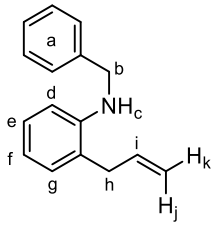
3.6 Matteson Homologation of iPrBpin in the Presence of Compound 4a: To an oven-dried 10 mL Schlenk flask equipped with a stir bar was added **4a** (145 mg, 0.554 mmol, 1.0 equiv), chloroiodomethane (266 µL, 1.66 mmol, 3.0 equiv), and THF (0.780 mL, 0.6 M) in the glovebox. The flask was then sealed, brought out of the glovebox and put on the Schlenk line. To it was added isopropylboronic acid pinacol ester (104 uL, 0.554 mmol, 1.0 equiv). The reaction was then cooled to -78 °C using a dry ice/isopropanol bath. After 15 minutes of stirring at -78 °C, nBuLi (865 µL, 1.384 mmol, 2.5 equiv) was added dropwise over 45 min using a syringe pump, taking care that the reagent should cool before reaching the solution by flowing down the inside of the flask, which was held at an angle in the bath (**Figure S10**). Following addition, the reaction was stirred for 16 hours while slowly warming up to rt. The reaction was then quenched with methanol, opened to air, and then concentrated under vacuum. The resulting viscous oil was redissolved in minimal DCM, washed 3 times with saturated $NH_4Cl_{(aq)}$, dried over Na_2SO_4, and concentrated under vacuum to yield the crude mixture as an oily brown solid. Conversion (iPrBpin to iBuBpin; **4a** to **4b**/**5a**/**5b**) was then estimated by ^1H NMR (**Figure S6**).



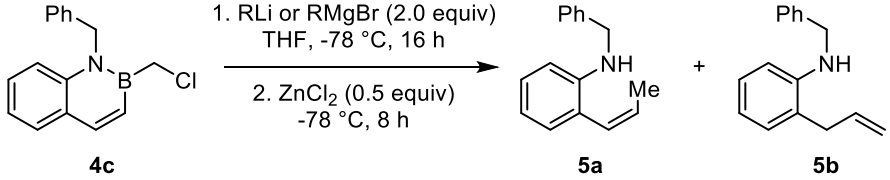
3.7 Ring-Expansion of Compound 4a: To an oven-dried 10 mL Schlenk flask equipped with a stir bar was added **4a** (90.0 mg, 0.345 mmol, 1.0 equiv), and THF (0.780 mL, 0.6 M) in the glovebox. If using chloroiodomethane as the dihalomethane (62.8 µL, 0.861 mmol, 2.5 equiv), it was also added in the glovebox. The flask was then sealed, brought out of the glovebox, put on the Schlenk line, and cooled to -78 °C in a bath of isopropanol maintained by an immersion cooler. If using dibromomethane (60.1 µL, 0.861 mmol, 2.5 equiv), it was then added via syringe. After 15 minutes of stirring at -78 °C, tBuLi (405 µL, 0.689 mmol, 2.0 equiv) was added dropwise over 45 min using a syringe pump, taking care that the reagent should cool before reaching the solution by flowing down the inside of the flask, which was held at an angle in the bath (**Figure S10**). Following addition, the reaction was stirred for 16 hours at -78 °C, after which 1.0 M $ZnCl_2$ in Et_2O (173.0 µL, 0.173 mmol, 0.5 equiv) was added via rapid dropwise addition down the side of the flask, and the reaction was stirred for an additional 8 hours at -78 °C. The reaction was then quenched with dropwise addition of methanol and the immersion cooler was turned off, allowing the reaction to gradually warm up to room temperature overnight. The next day, the reaction was concentrated under vacuum. The resulting viscous oil was redissolved in minimal DCM, washed 3 times with saturated $NH_4Cl_{(aq)}$, dried over Na_2SO_4, and concentrated under vacuum to yield the crude mixture as an oily brown solid. Conversion to **5** was estimated from the crude mixture by ^1H NMR. Pure **5a** and **5b** were isolated for structural validation via preparatory thin layer chromatography in hexanes.



*3.7.1 (Z)-N-benzyl-2-(prop-1-en-1-yl)aniline (**5a**)*: Obtained as a light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.35 (m, 4H$_a$), 7.28 (m, 1H$_a$), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H$_e$), 7.07 (dt, *J* = 7.4, 1.2 Hz, 1H$_g$), 6.71 (td, *J* = 7.4 Hz, 1H$_f$), 6.64 (dt, *J* = 8.1 Hz, 1H$_d$), 6.30 (d, *J* = 11.2 Hz, 1H$_h$), 5.88 (dq, *J* = 11.2, 6.9 Hz, 1H$_i$), 4.36 (s, 2H$_b$), 4.17 (s(broad), 1H$_c$), 1.74 (dd, *J* = 6.9, 1.8 Hz, 3H$_j$); ^{11}B{^{1}H} (400 MHz, $CDCl_3$, 298 K) No peaks observed; ^{13}C NMR (400 MHz, $CDCl_3$, 298K) δ 129.7, 129.5, 128.8, 128.2, 127.5, 127.3, 126.0, 116.8, 110.4, 48.3, 14.7 ppm; HRMS (EI) m/z calculated for $C_{16}H_{17}N$ [M]$^+$ 223.1361, found 223.1365.



*3.7.2 2-allyl-N-benzylaniline (**5b**)*: Obtained as a light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.35 (m, 4H$_a$), 7.28 (m, 1H$_a$), 7.13 (td, *J* = 7.6, 1.7 Hz, 1H$_e$), 7.07 (d, *J* = 7.2 Hz, 1H$_g$), 6.72 (td, *J* = 7.4, 1.3 Hz, 1H$_f$), 6.64 (d, *J* = 8.0 Hz, 1H$_d$), 5.97 (ddt, *J* = 16.4, 10.2, 6.2 Hz, 1H$_i$), 5.12 (dd, *J* = 11.4, 1.7 Hz, 1H$_j$), 5.08 (dd, *J* = 17.0, 1.7 Hz, 1H$_k$), 4.36 (s, 2H$_b$), 4.15 (s(broad), 1H$_c$), 3.33 (d, *J* = 9.8 Hz, 2H$_h$) ppm; ^{11}B{^{1}H} (400 MHz, $CDCl_3$, 298 K) No peaks observed; ^{13}C NMR (400 MHz, $CDCl_3$, 298K) δ 136.1, 130.0, 128.8, 127.9, 127.6, 127.3, 117.6, 116.5, 48.4, 36.7 ppm; HRMS (EI) m/z calculated for $C_{16}H_{17}N$ [M]$^+$ 223.1361, found 223.1367.



3.8 Ring-Expansion of 4c: To an oven-dried 10 mL Schlenk flask was added **4c** (100.0 mg, 0.374 mmol, 1.0 equiv) in the glovebox and dissolved in THF (0.623 mL, 0.6 M). The flask was then sealed, brought out of the glovebox, put on the Schlenk line, and cooled to -78 °C in a bath of isopropanol maintained by an immersion cooler. After 15 minutes of stirring at -78 °C, the alkyl organometallic reagent (2.0 equiv) was added dropwise over 45 min using a syringe pump, taking care that the reagent should cool before reaching the solution by flowing down the inside of the flask, which was held at an angle in the bath (**Figure S10**). Following addition, the reaction was stirred for 16 hours at -78 °C, after which 1.0 M $ZnCl_2$ in Et_2O (187 µL, 0.187 mmol, 0.5 equiv) was added via rapid dropwise addition down the side of the flask, and the reaction was stirred for an additional 8 hours at -78 °C. The reaction was then quenched with dropwise addition of methanol and the immersion cooler was turned off, allowing the reaction to gradually warm up to room temperature overnight. The next day, the reaction was concentrated under vacuum. The resulting viscous oil was redissolved in minimal DCM, washed 3 times with saturated $NH_4Cl_{(aq)}$, dried over Na_2SO_4, and concentrated under vacuum to yield the crude mixture as a brown goo. Conversion to **5a** and **5b** was estimated by ^{1}H NMR.

4 | NMR Spectroscopy (^{1}H, ^{11}B, ^{13}C):

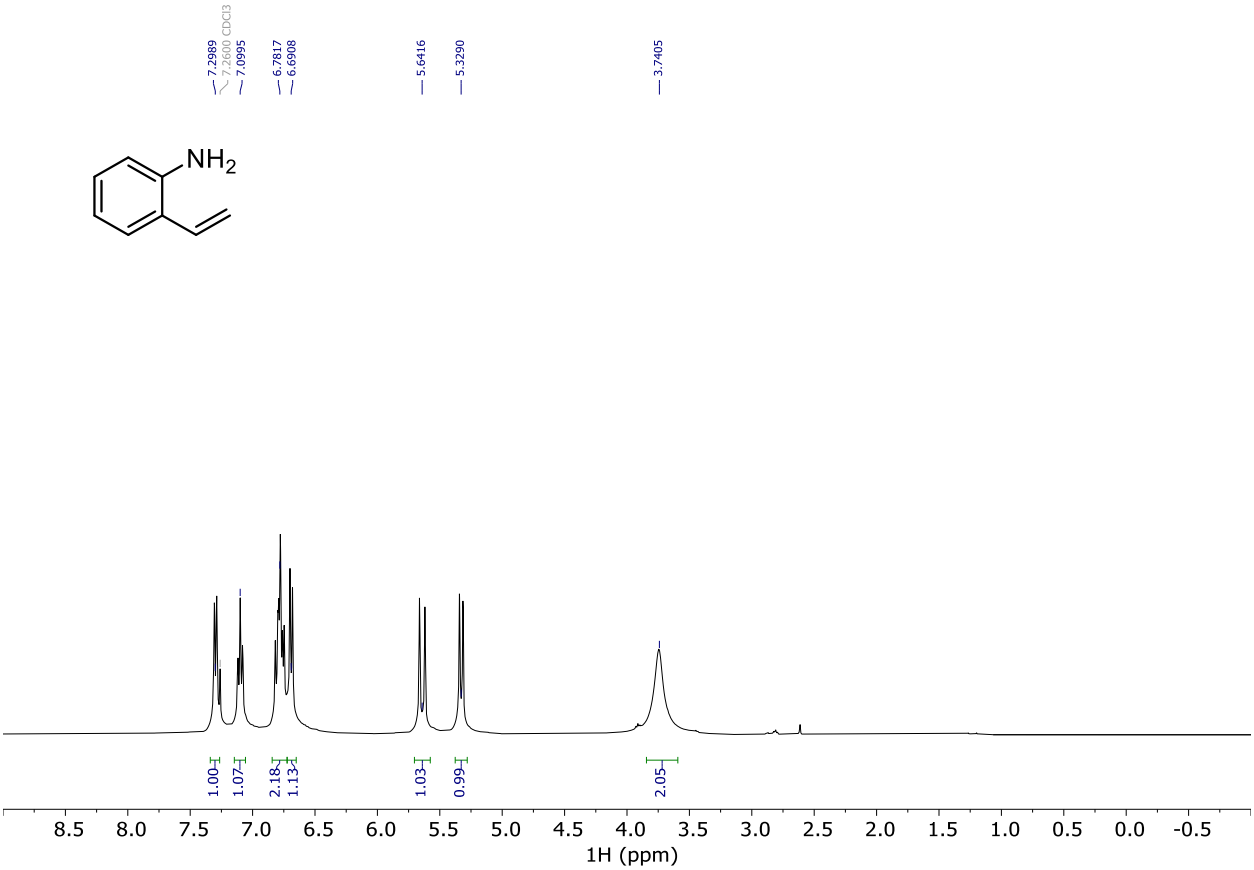


Figure S11. ^{1}H NMR spectrum of 2-Vinylaniline (**1**) in $CDCl_3$.

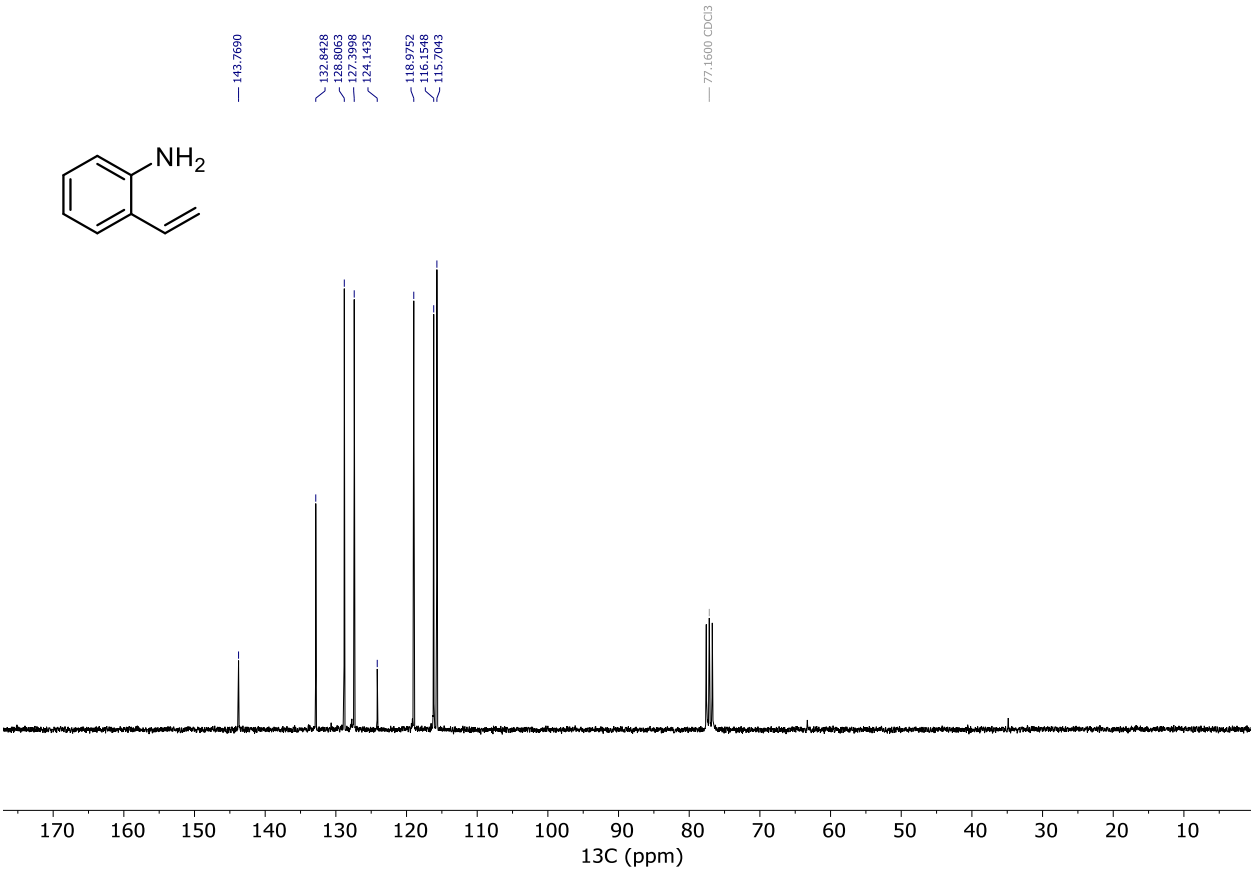


Figure S12. ^{13}C NMR spectrum of 2-Vinylaniline (**1**) in $CDCl_3$.

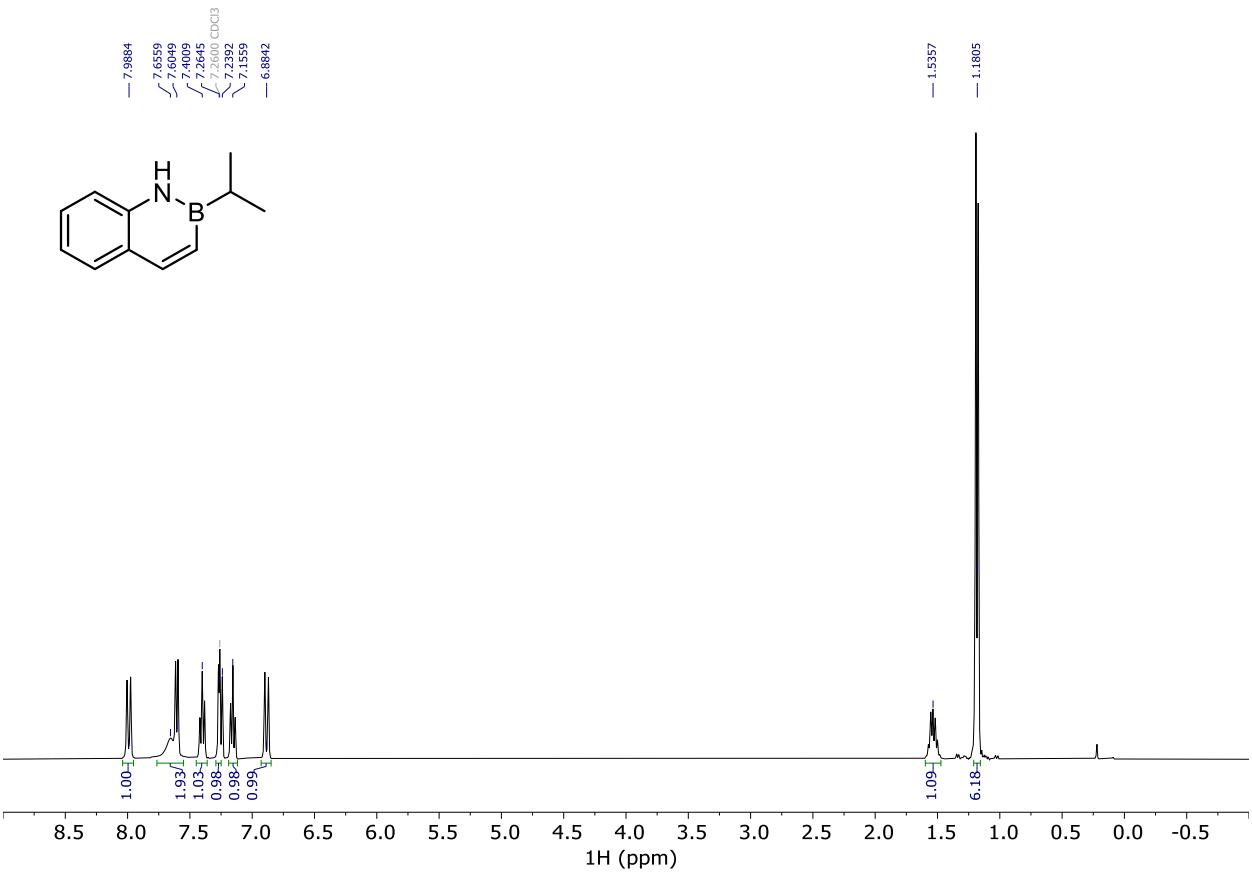


Figure S13. ^{1}H NMR Spectrum of 2-isopropylborazaronaphthalene (**3a**) in $CDCl_3$.

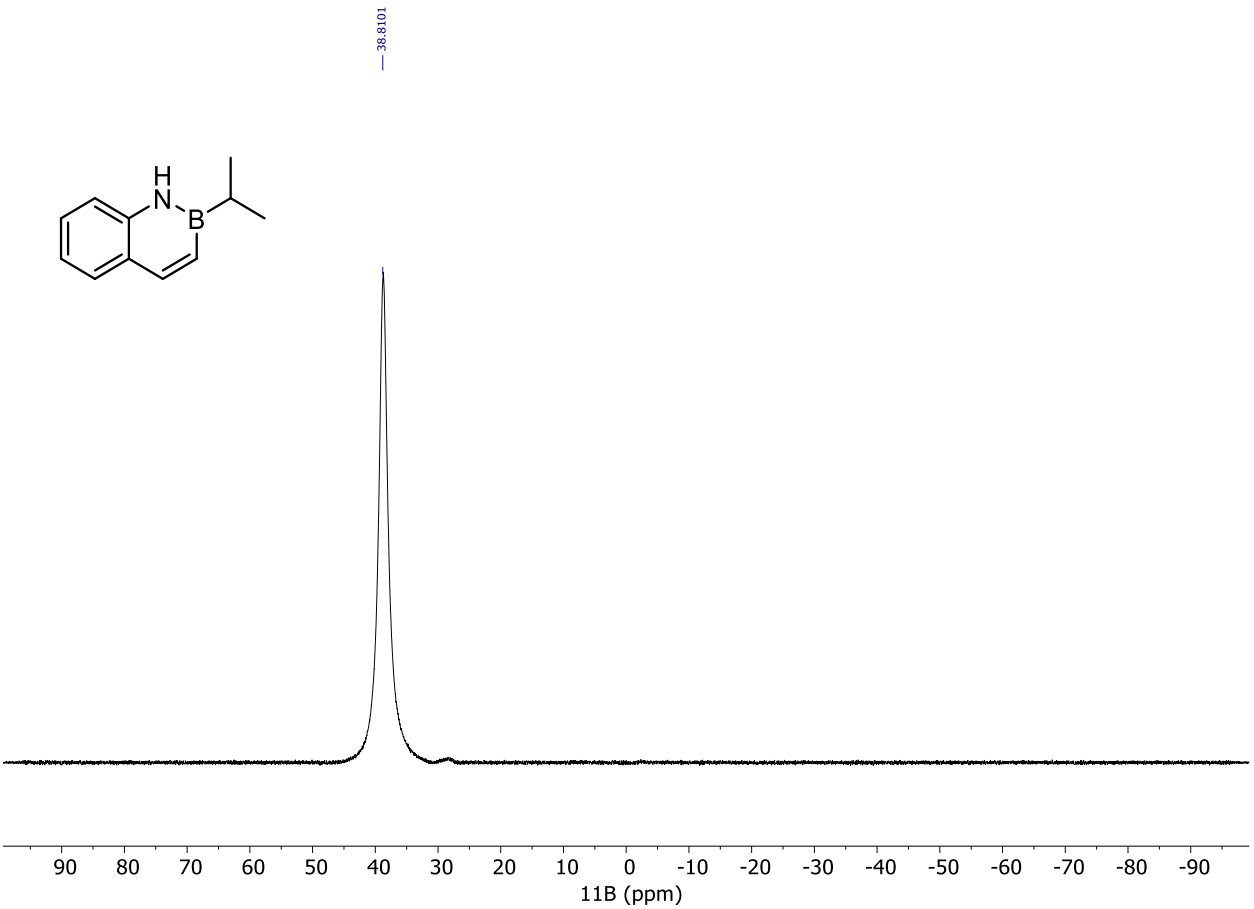


Figure S14. ^{11}B NMR Spectrum of 2-isopropylborazaronaphthalene (**3a**) in $CDCl_3$.

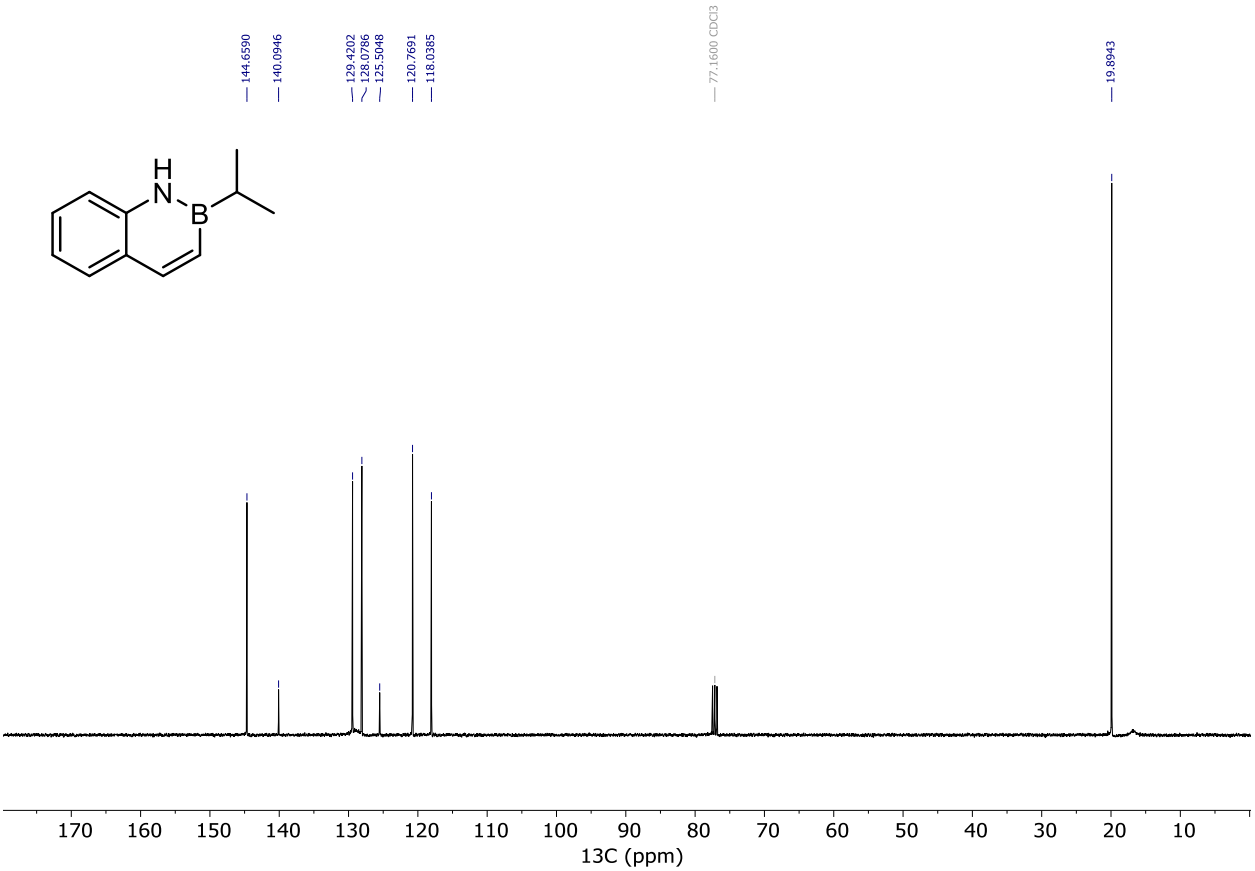


Figure S15. ^{13}C NMR Spectrum of 2-isopropylborazaronaphthalene (**3a**) in $CDCl_3$.

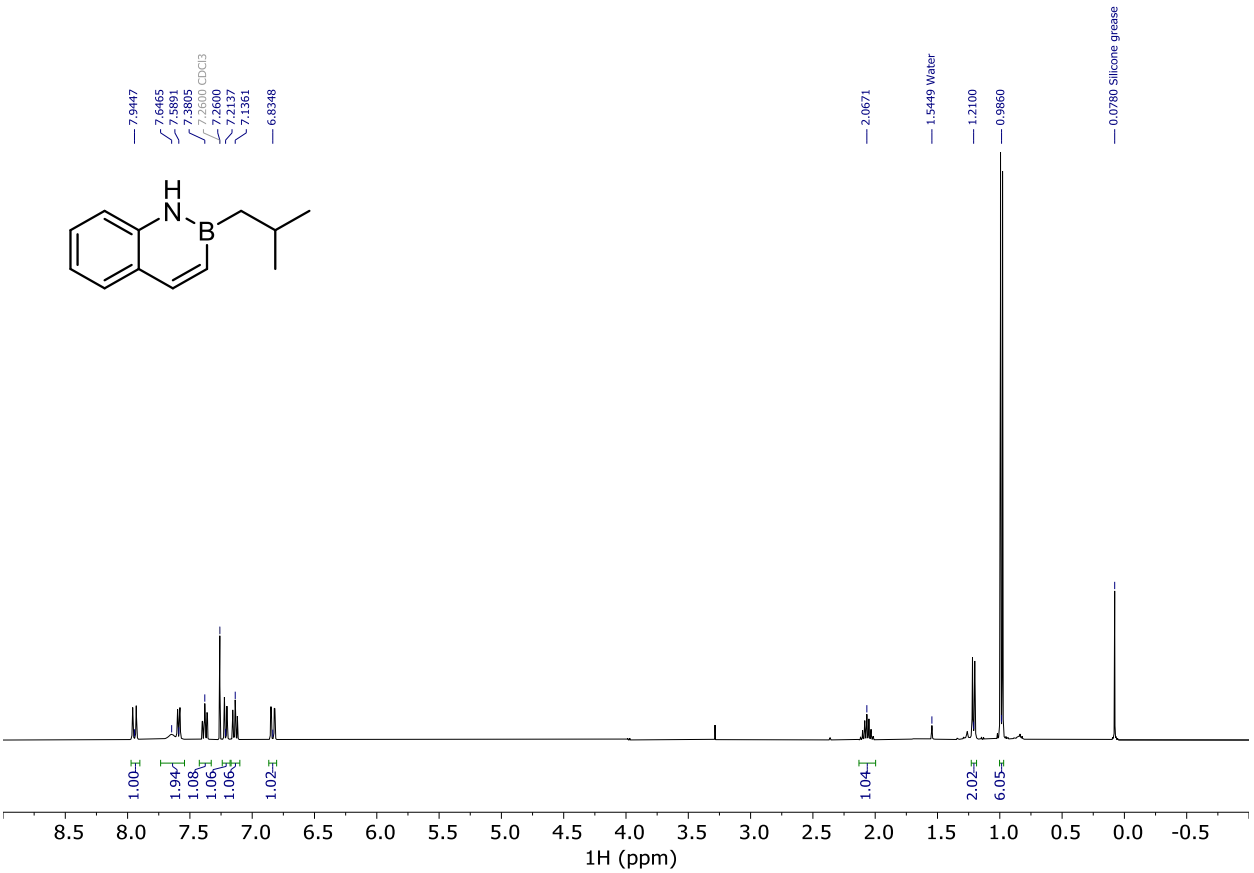


Figure S16. ^{1}H NMR Spectrum of 2-isobutylborazaronaphthalene (**3b**) in $CDCl_3$.

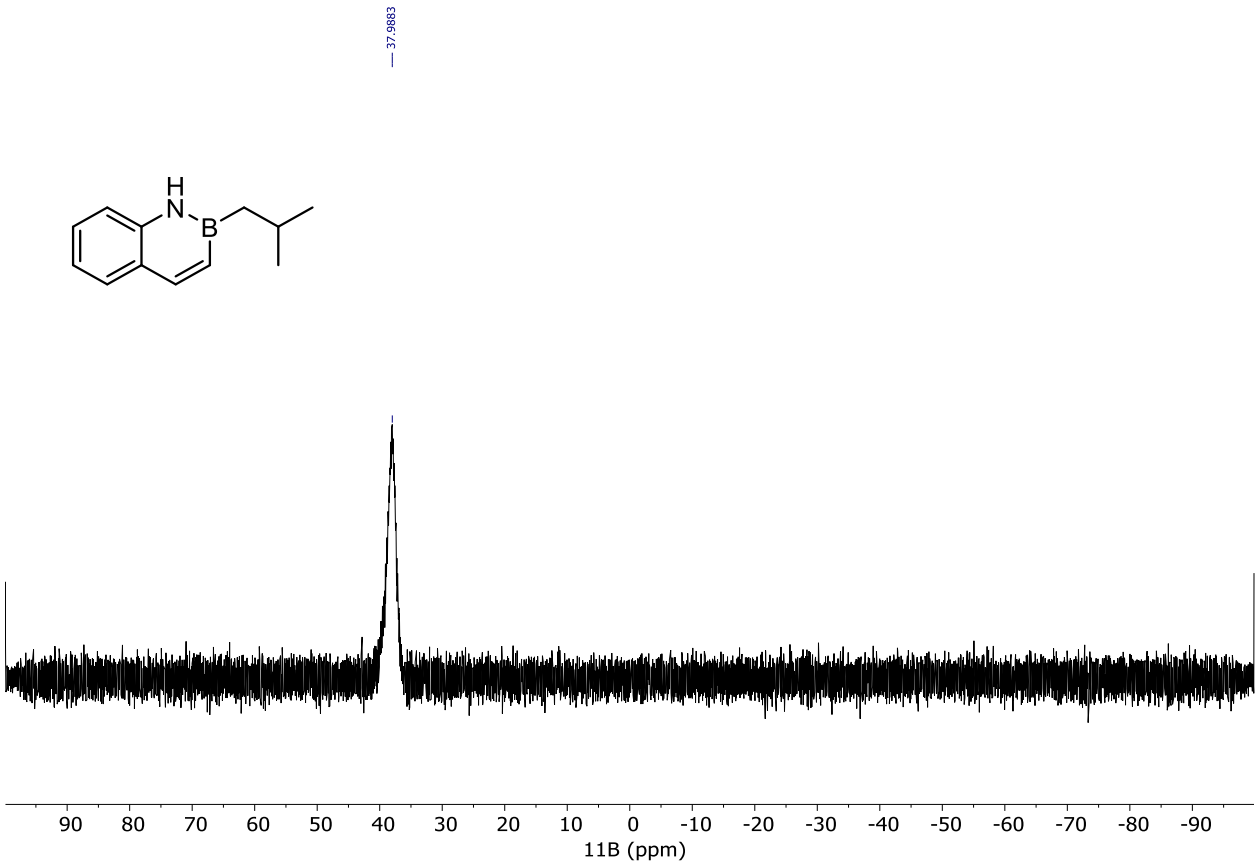


Figure S17. ^{11}B NMR Spectrum of 2-isobutylborazaronaphthalene (**3b**) in $CDCl_3$

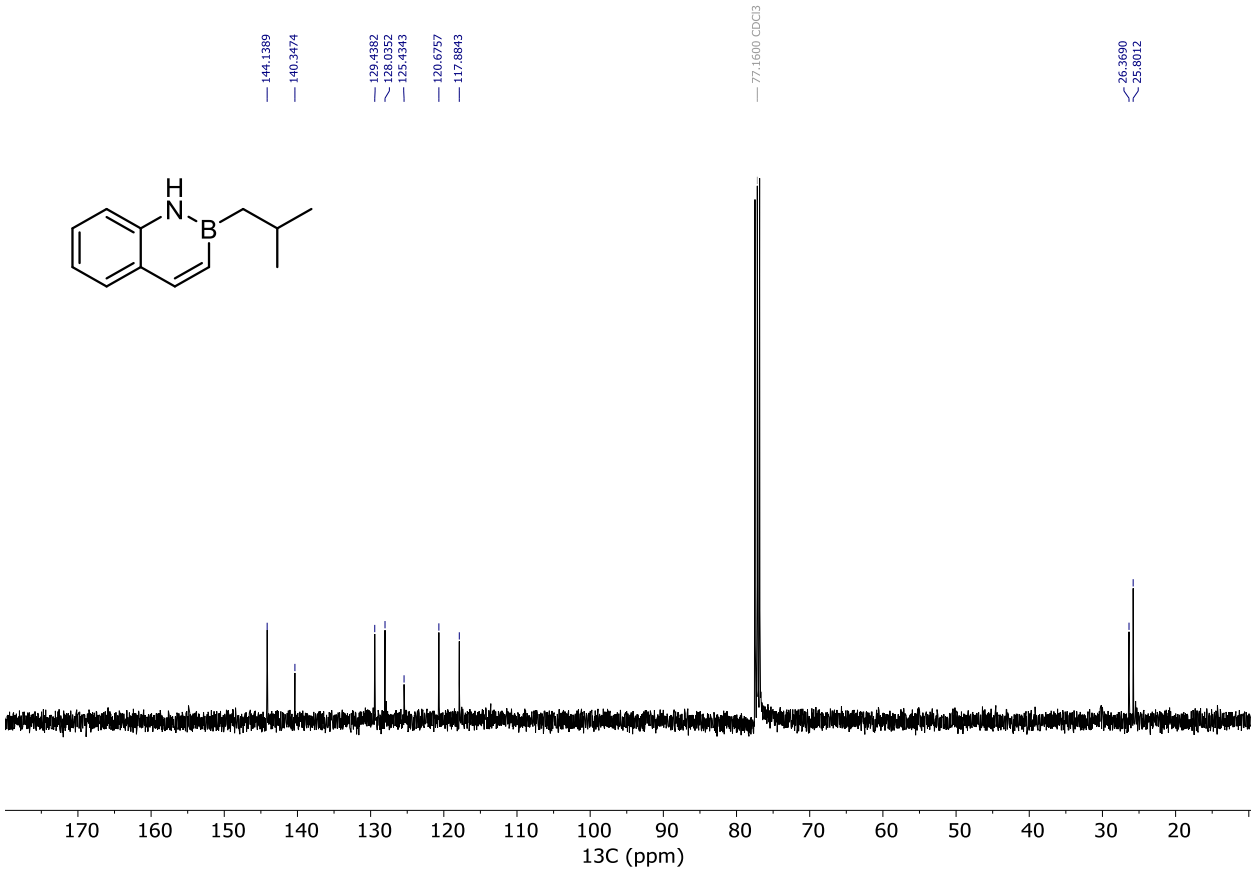


Figure S18. ^{13}C NMR Spectrum of 2-isobutylborazaronaphthalene (**3b**) in $CDCl_3$.

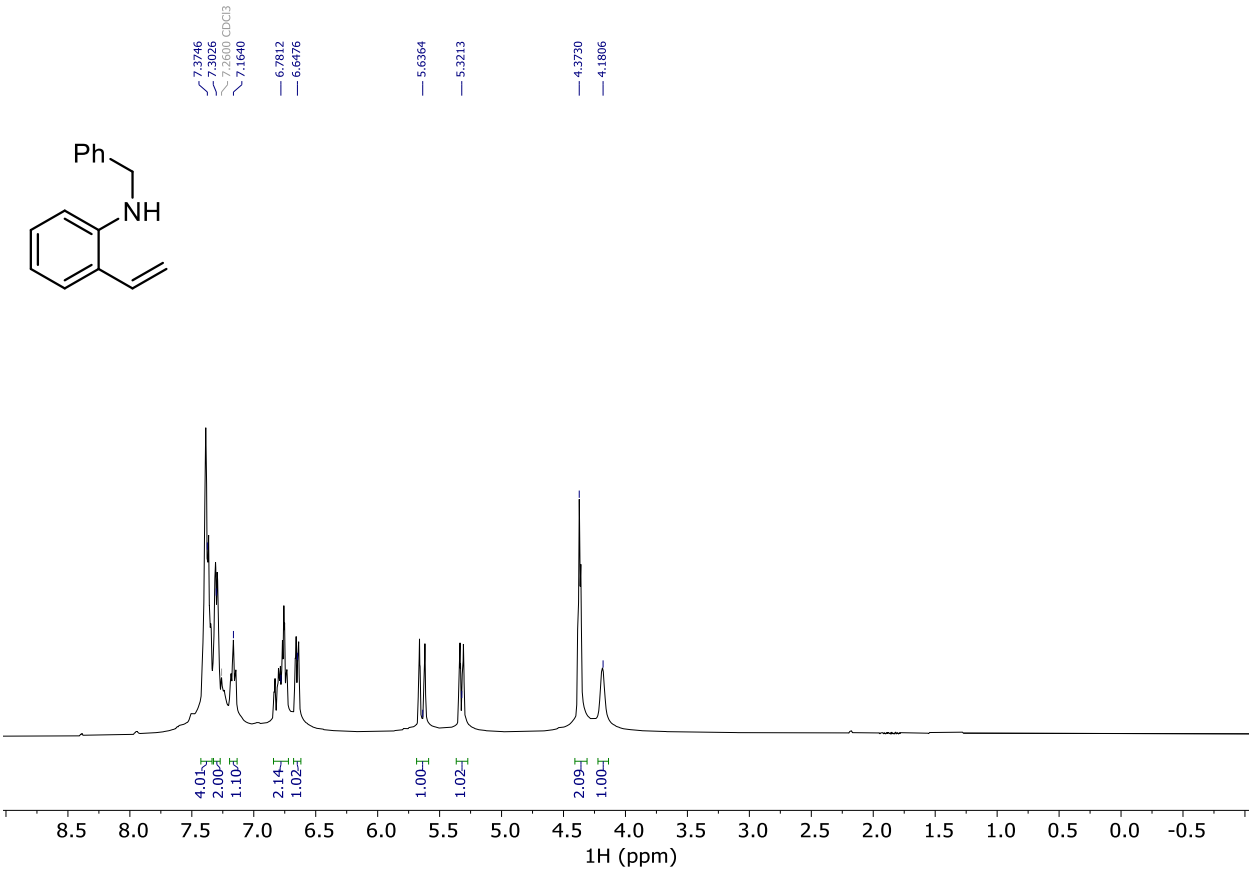


Figure S19. ^{1}H NMR spectrum of (N-Benzyl)-2-Vinylaniline (**2**) in $CDCl_3$.

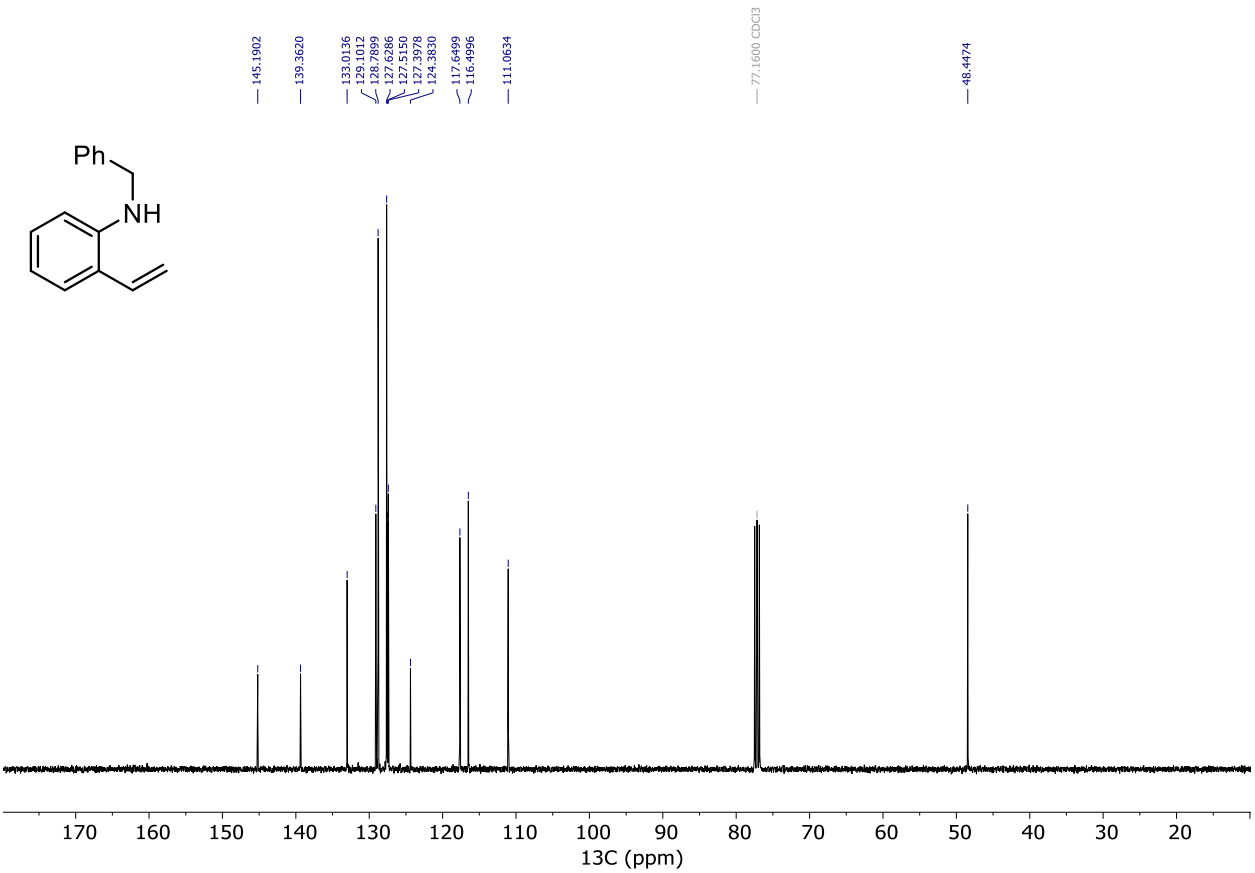


Figure S20. ^{13}C NMR spectrum of (N-Benzyl)-2-Vinylaniline (**2**) in $CDCl_3$.

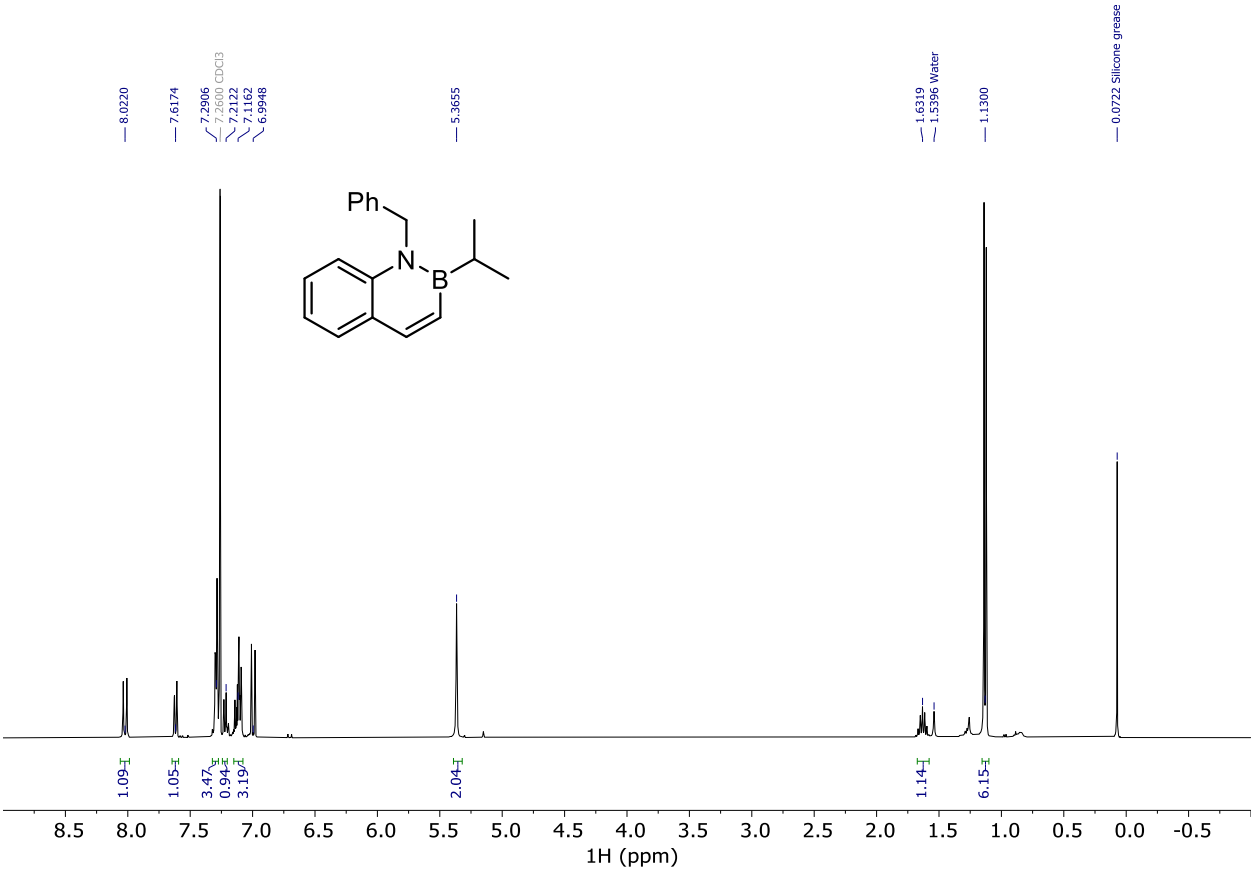


Figure S21. ^{1}H NMR Spectrum of (N-benzyl)-2-isopropylborazaronaphthalene (**4a**) in $CDCl_3$.

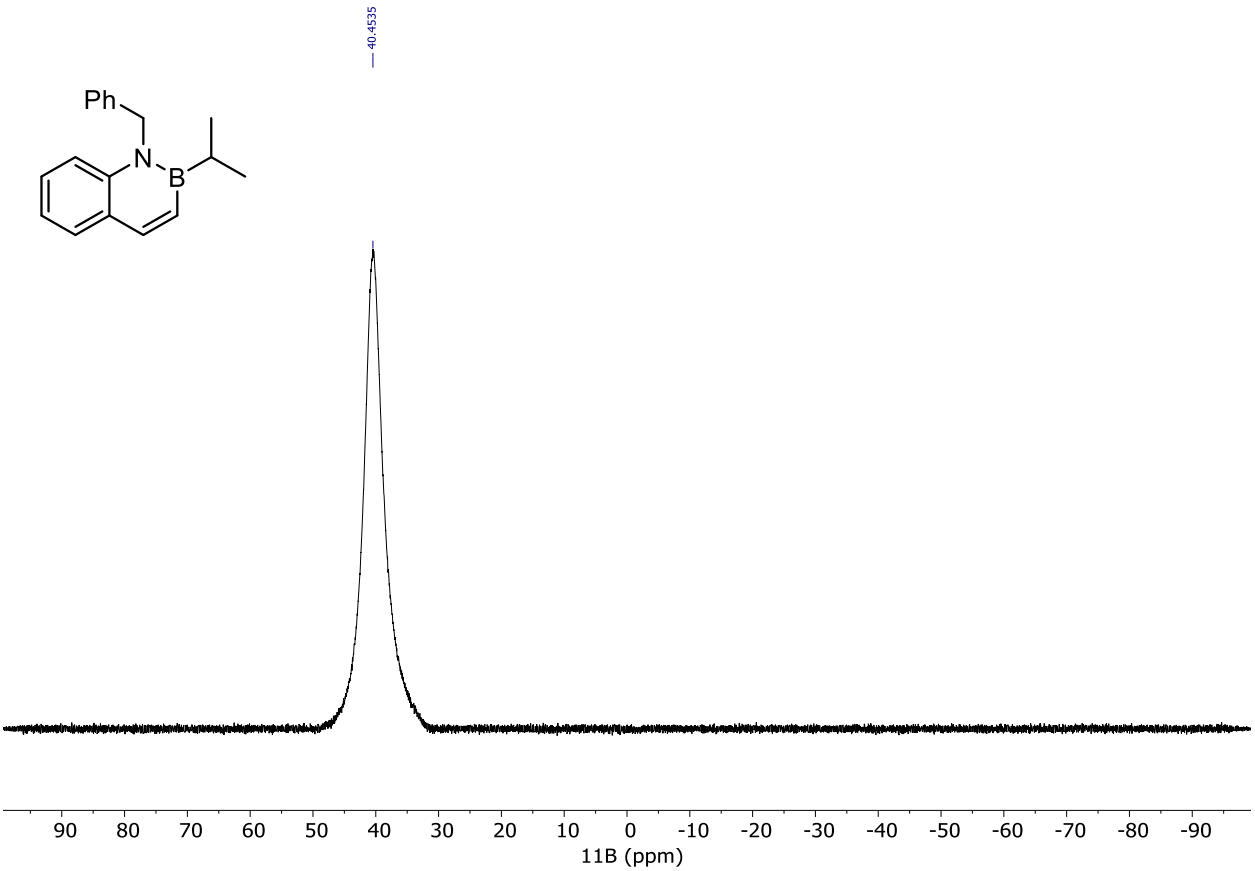


Figure S22. ^{11}B NMR Spectrum of (N-benzyl)-2-isopropylborazaronaphthalene (**4a**) in $CDCl_3$.

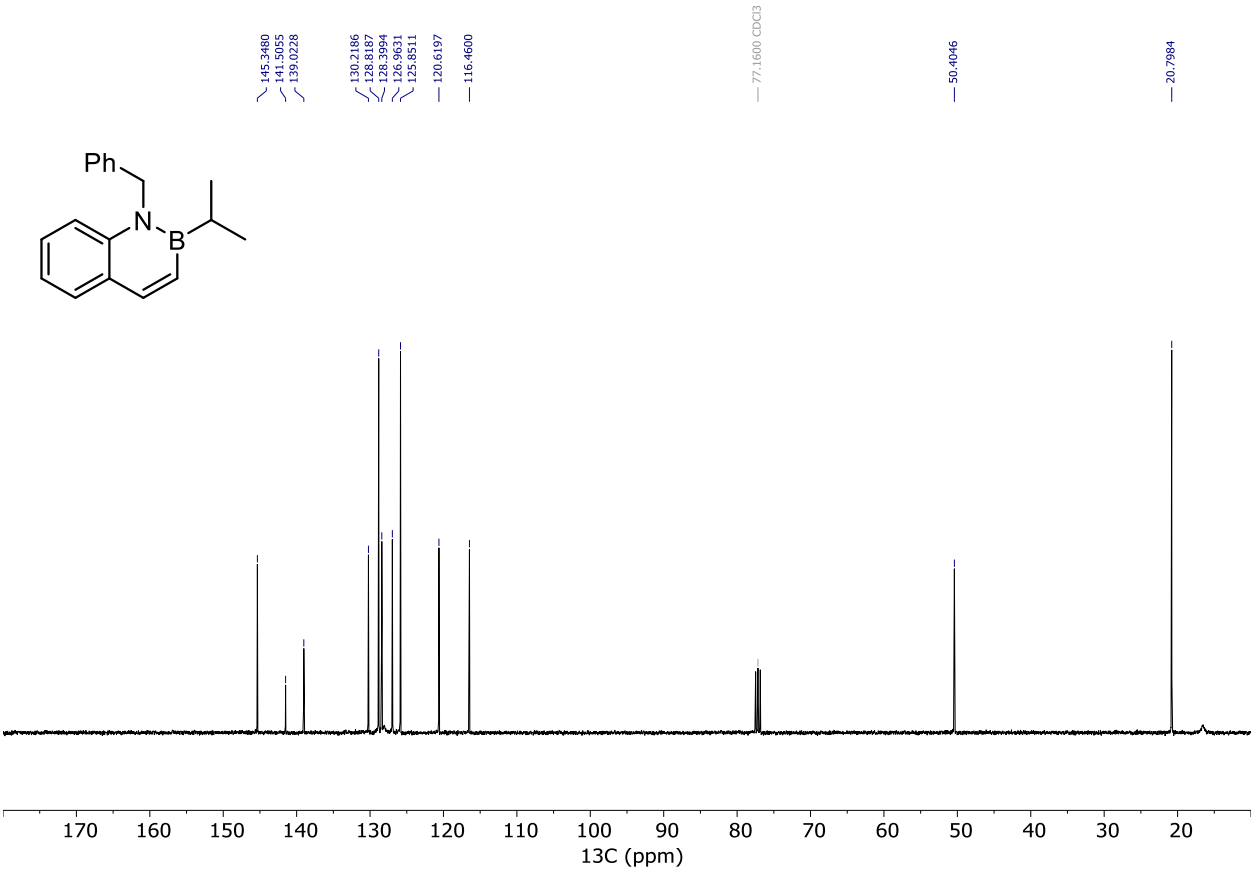


Figure S23. ^{13}C NMR Spectrum of (N-Benzyl)-2-isopropylborazaronaphthalene (**4a**) in $CDCl_3$.

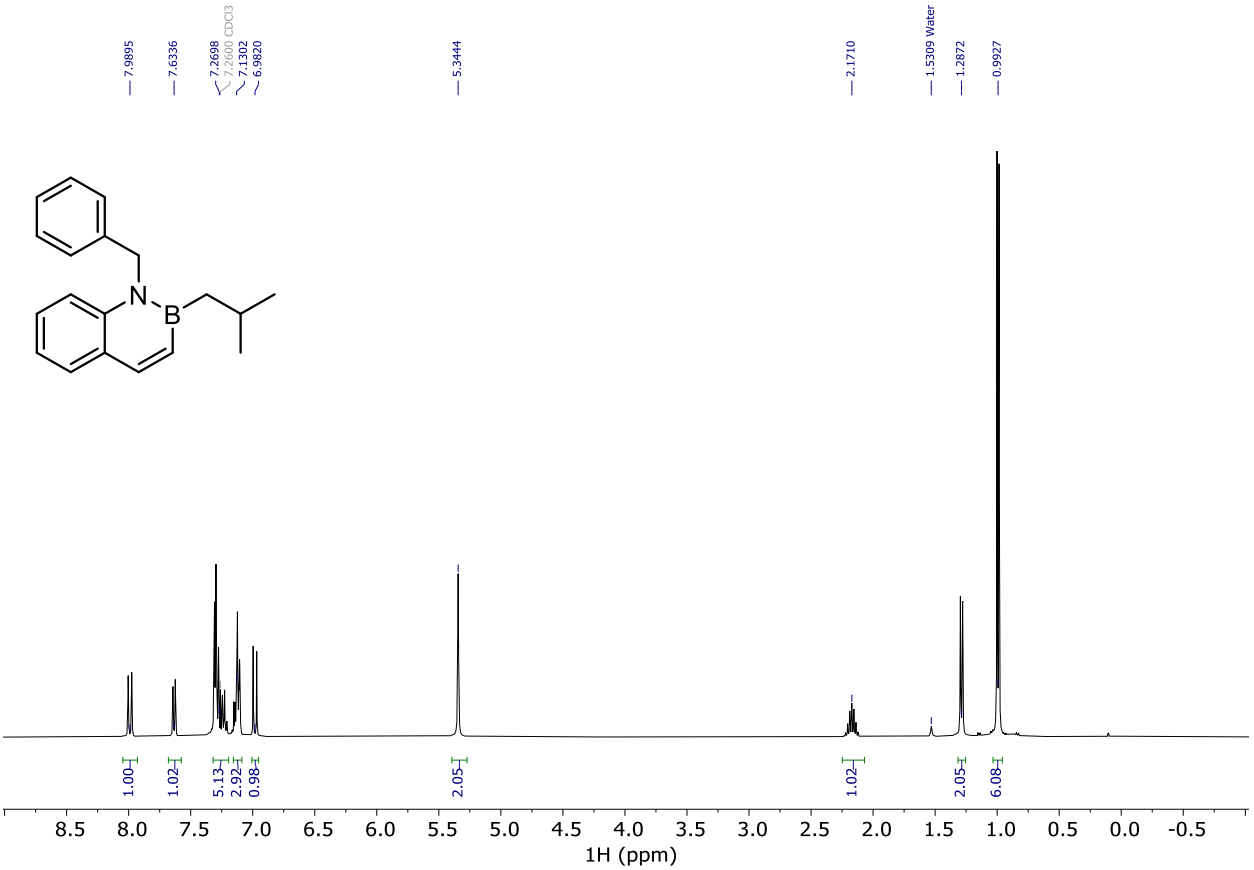


Figure S24. ^{1}H NMR Spectrum of (N-benzyl)-2-isobutylborazaronaphthalene (**4b**) in $CDCl_3$.

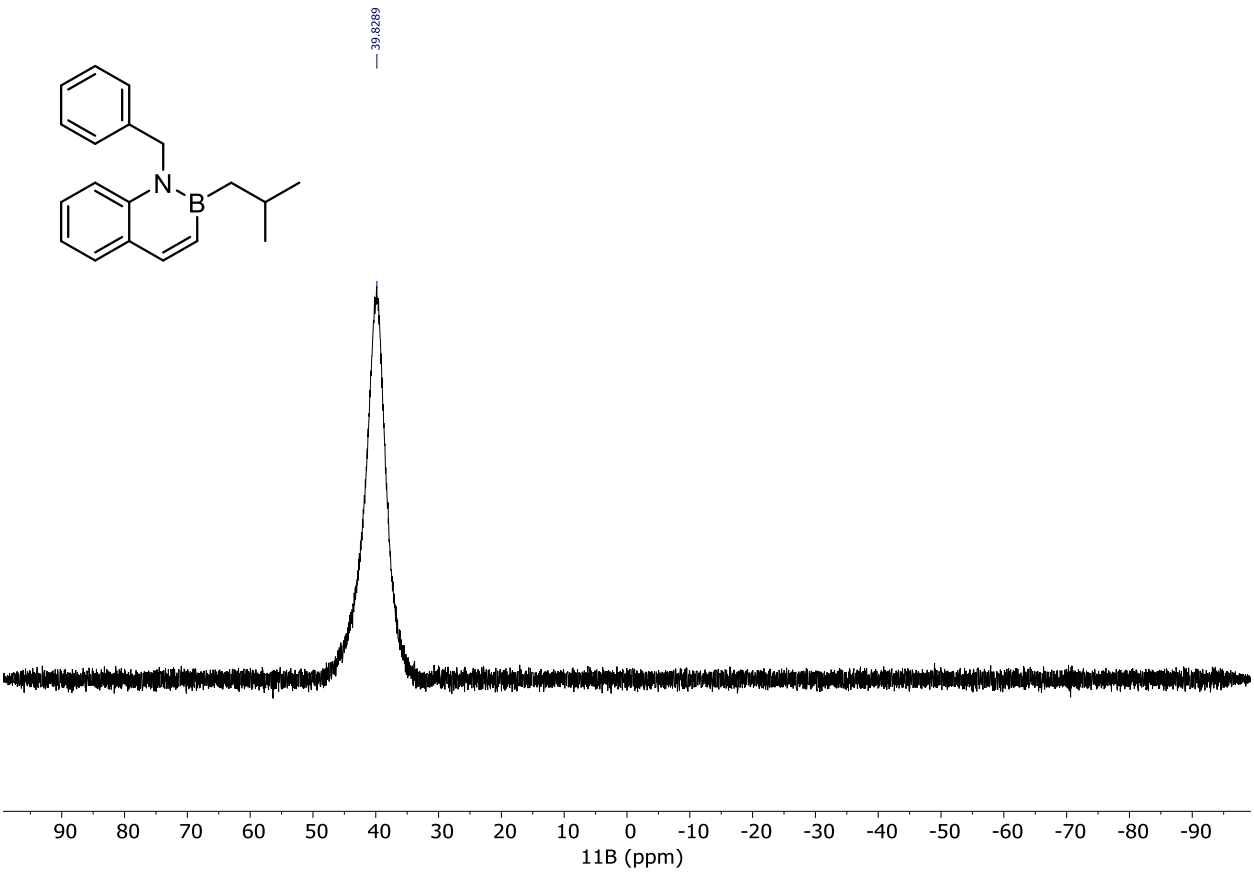


Figure S25. ^{11}B NMR Spectrum of (N-benzyl)-2-isobutylborazaronaphthalene (**4b**) in $CDCl_3$.

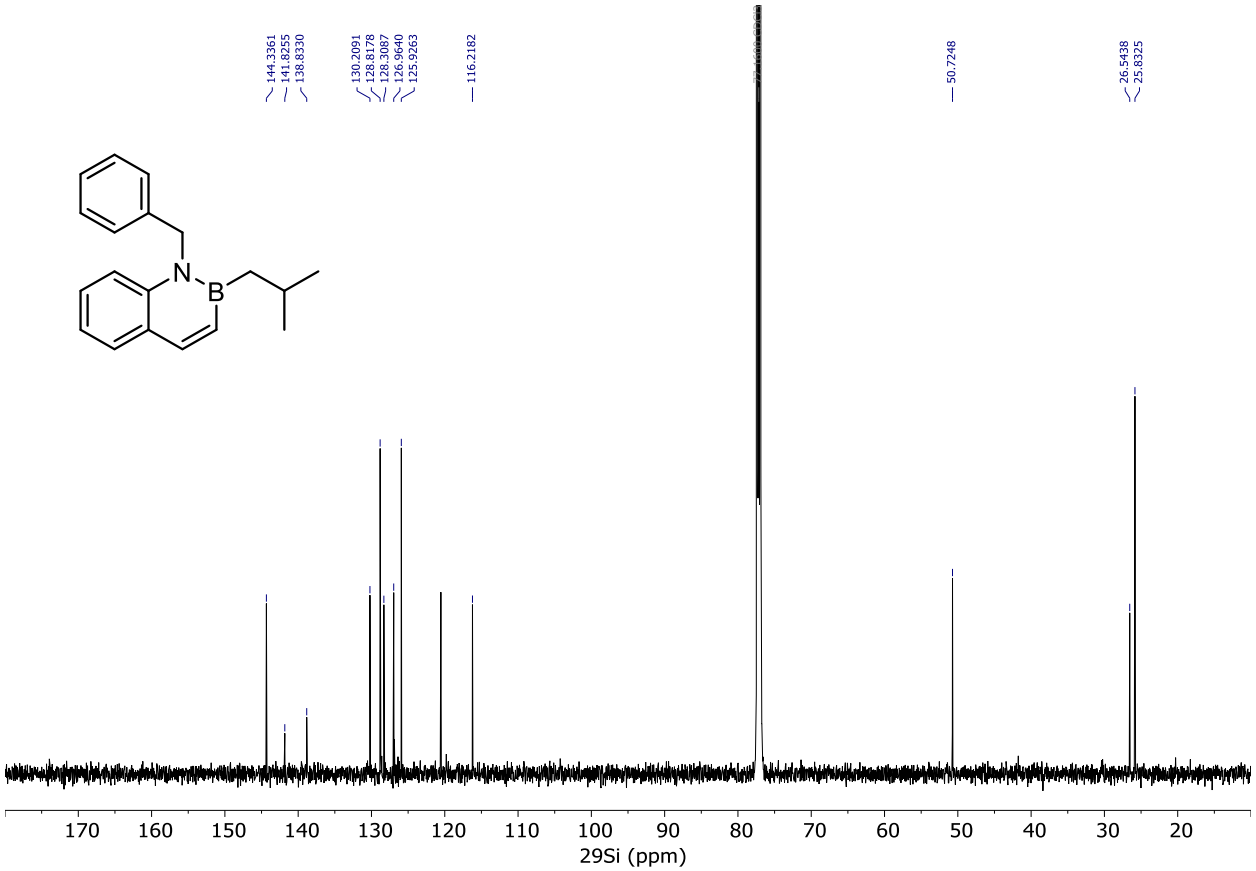


Figure S26. ^{13}C NMR Spectrum of (N-benzyl)-2-isobutylborazaronaphthalene (**4b**) in $CDCl_3$.

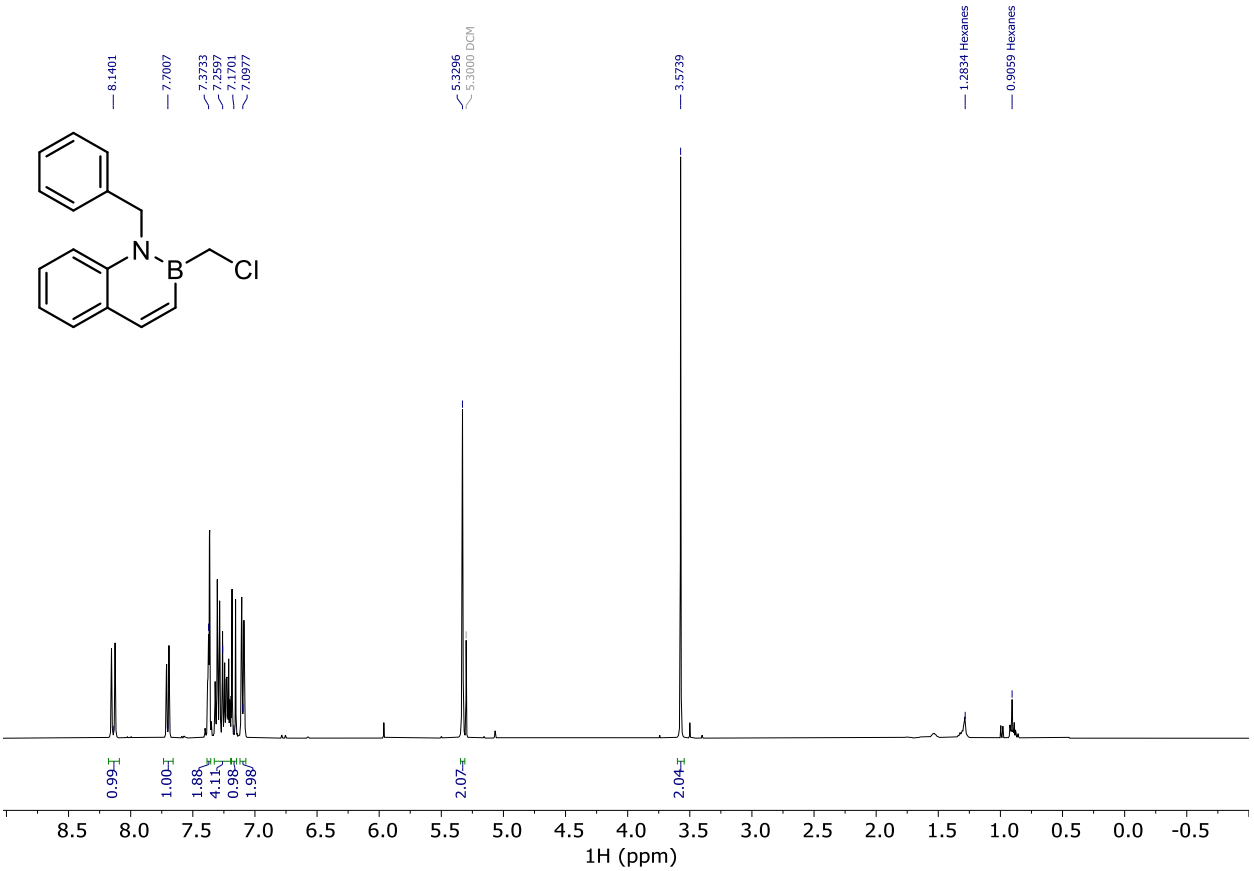


Figure S27. Spectrum of (N-benzyl)-2-(chloromethyl)borazaronaphthalene (**4c**) in $CDCl_3$.

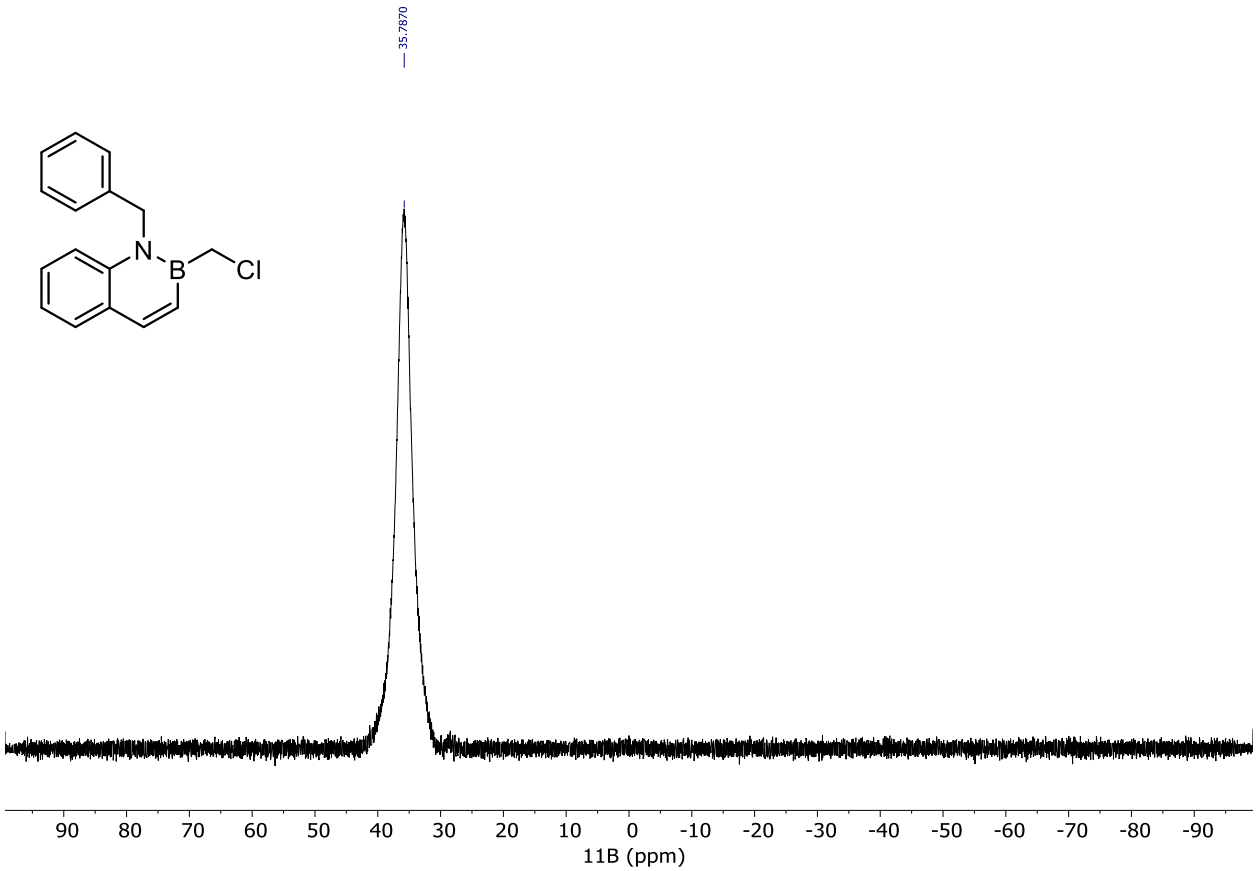


Figure S28. ^{11}B NMR Spectrum of (N-benzyl)-2-(chloromethyl)borazaronaphthalene (**4c**) in $CDCl_3$.

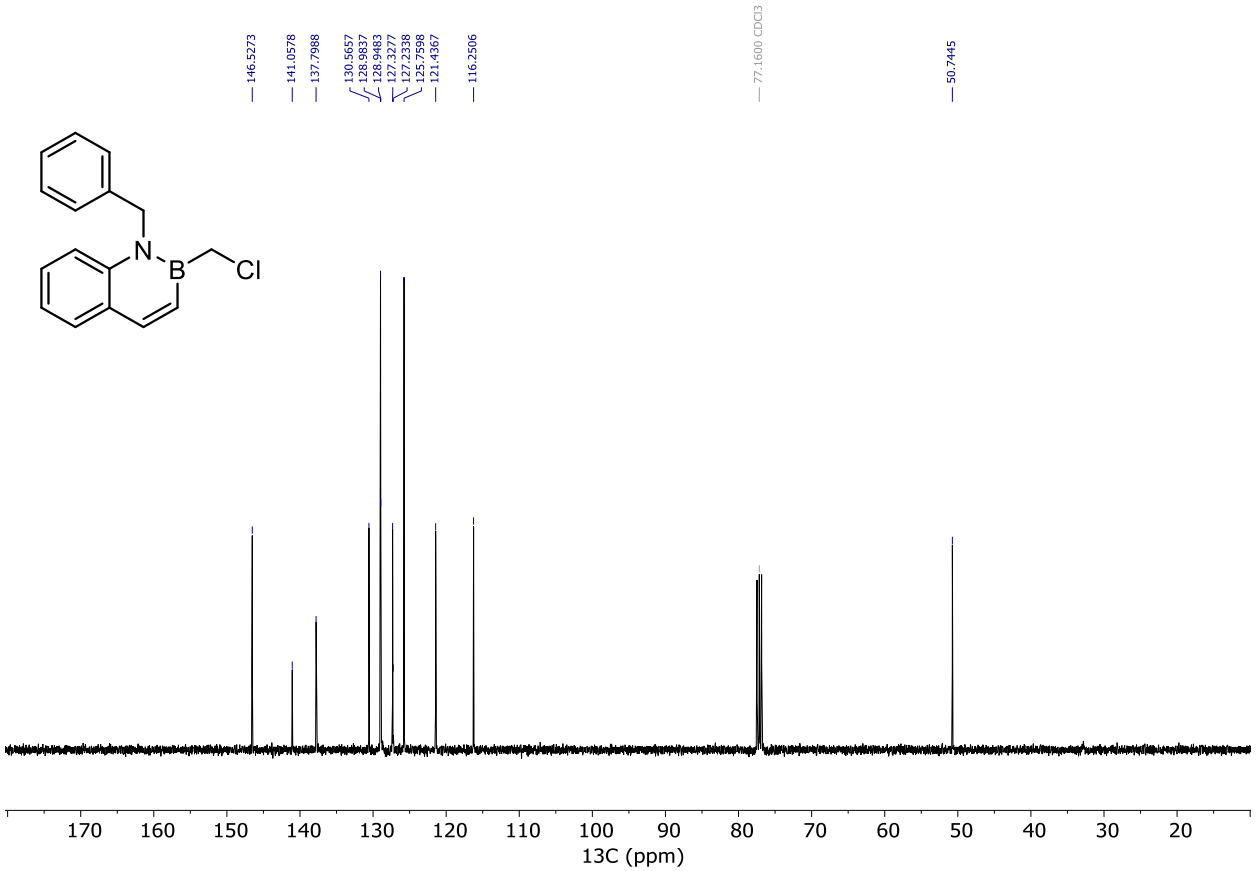


Figure S29. ^{13}C NMR Spectrum of (N-benzyl)-2-(chloromethyl)borazaronaphthalene (**4c**) in $CDCl_3$.

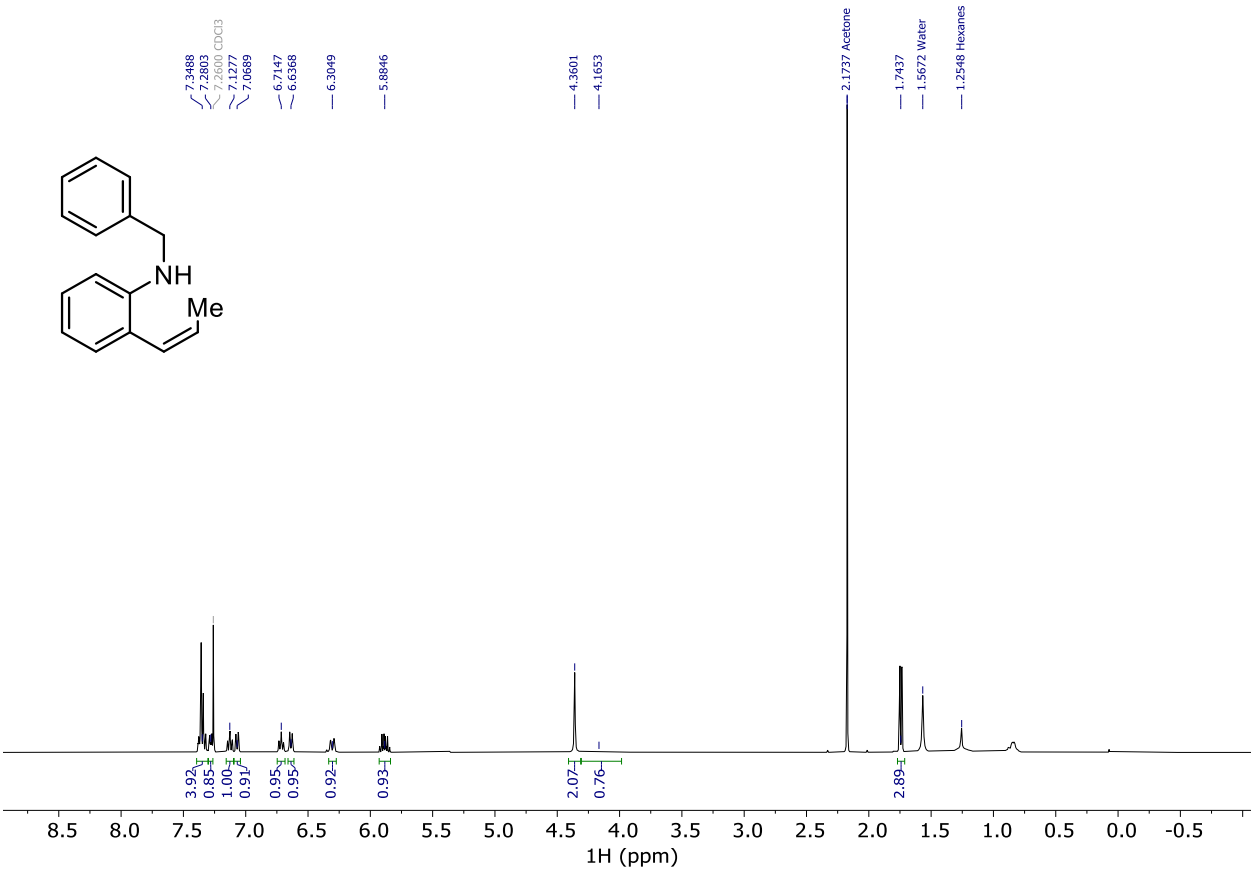
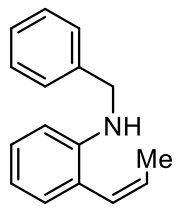


Figure S30. ^{1}H NMR Spectrum of (Z)-N-benzyl-2-(prop-1-en-1-yl)aniline (**5a**) in $CDCl_3$.



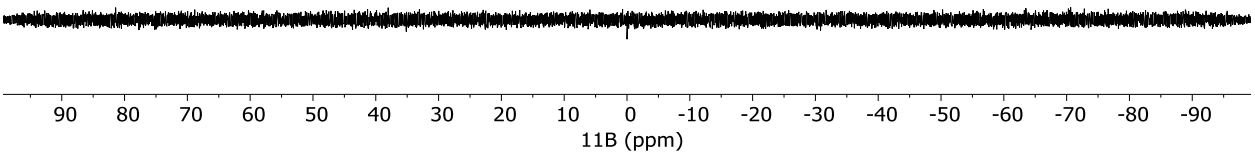


Figure S31. ^{11}B NMR Spectrum of (Z)-N-benzyl-2-(prop-1-en-1-yl)aniline (**5a**) in $CDCl_3$.

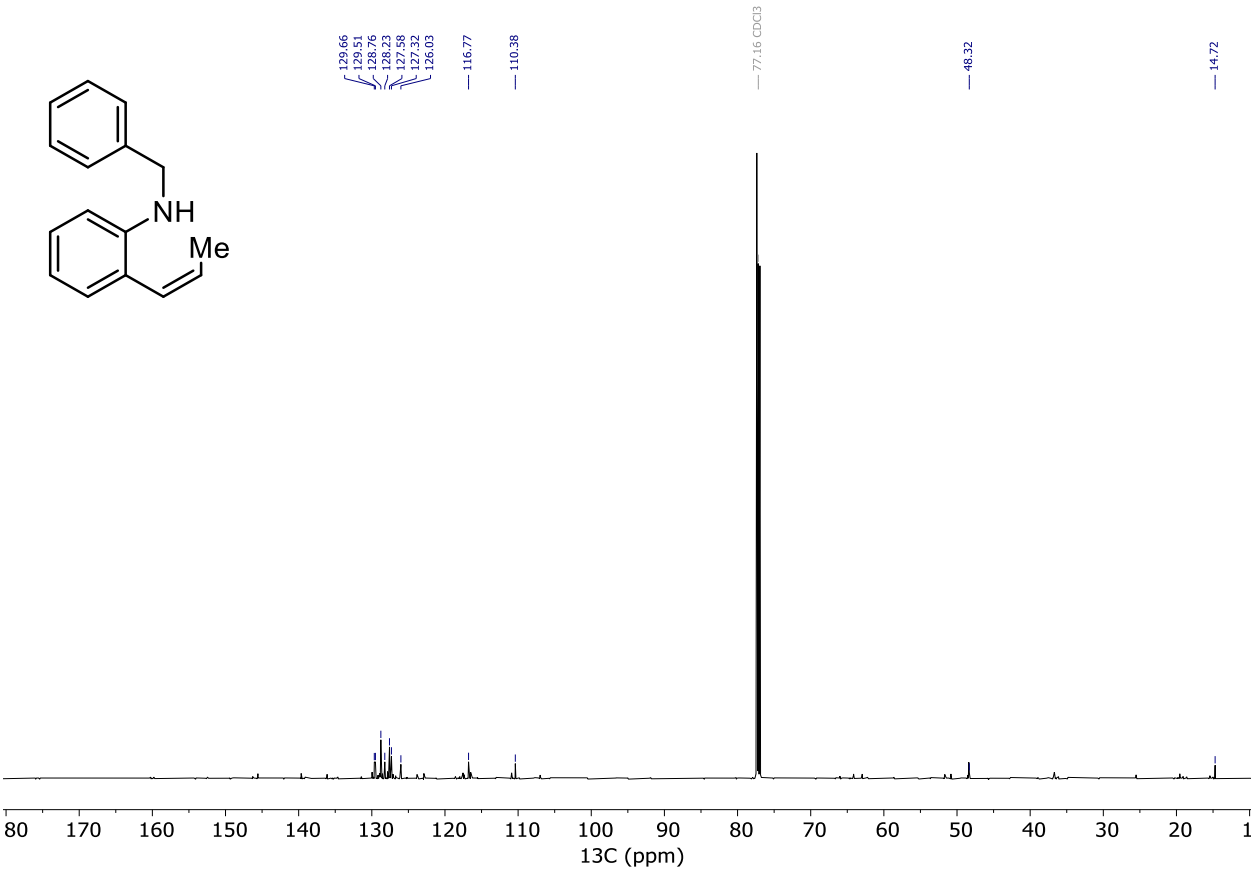


Figure S32. ^{13}C NMR Spectrum of (Z)-N-benzyl-2-(prop-1-en-1-yl)aniline (**5a**) in $CDCl_3$.

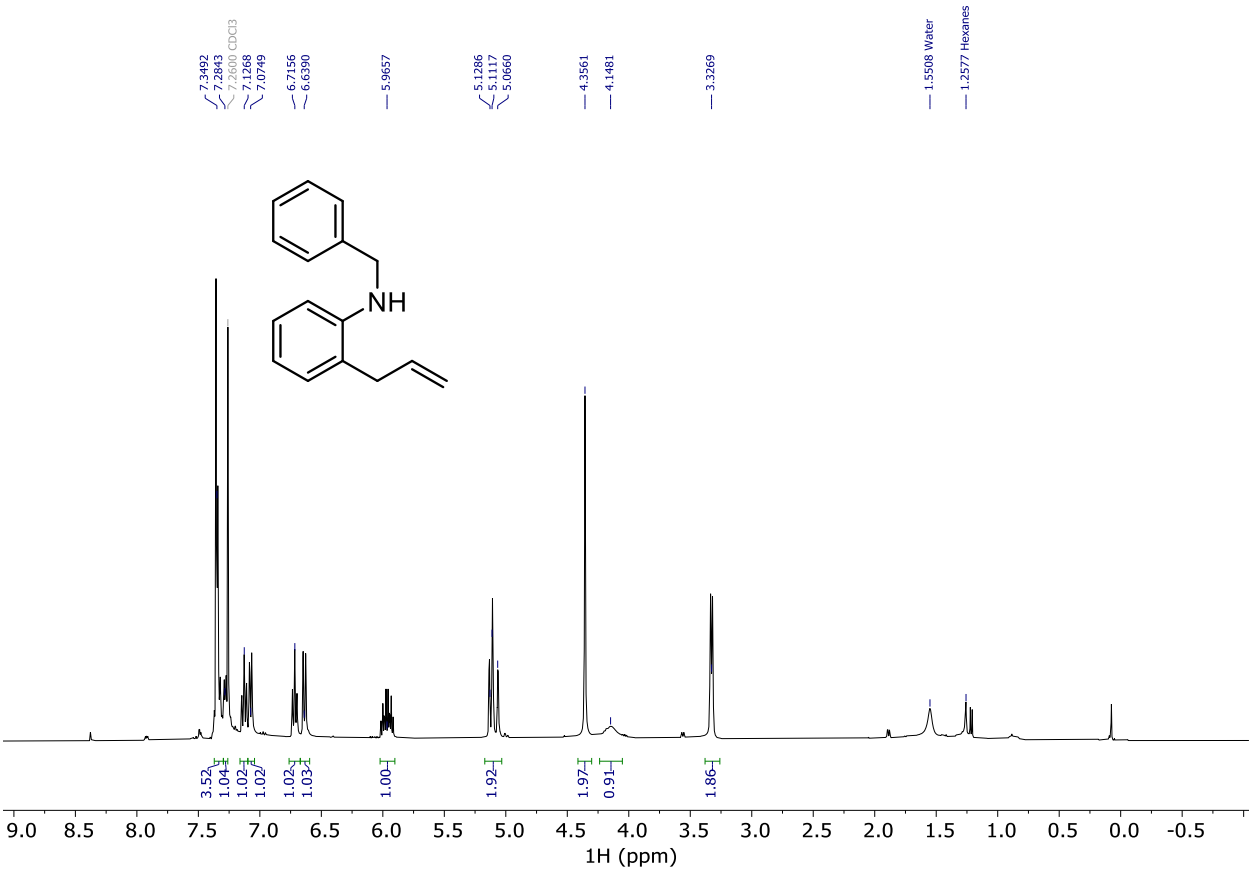
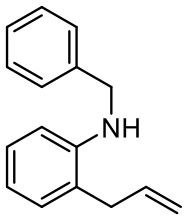


Figure S33. ^{1}H NMR Spectrum of 2-allyl-*N*-benzylaniline (**5b**) in $CDCl_3$.



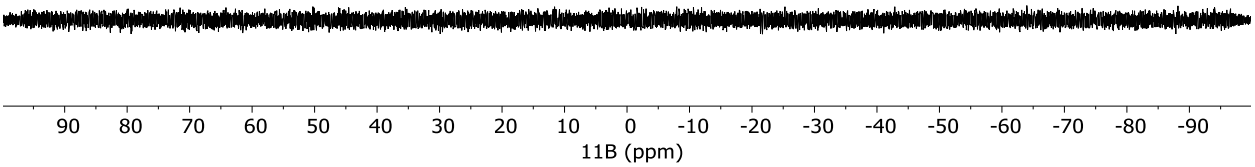


Figure S34. ^{11}B NMR Spectrum of 2-allyl-*N*-benzylaniline (**5b**) in $CDCl_3$.

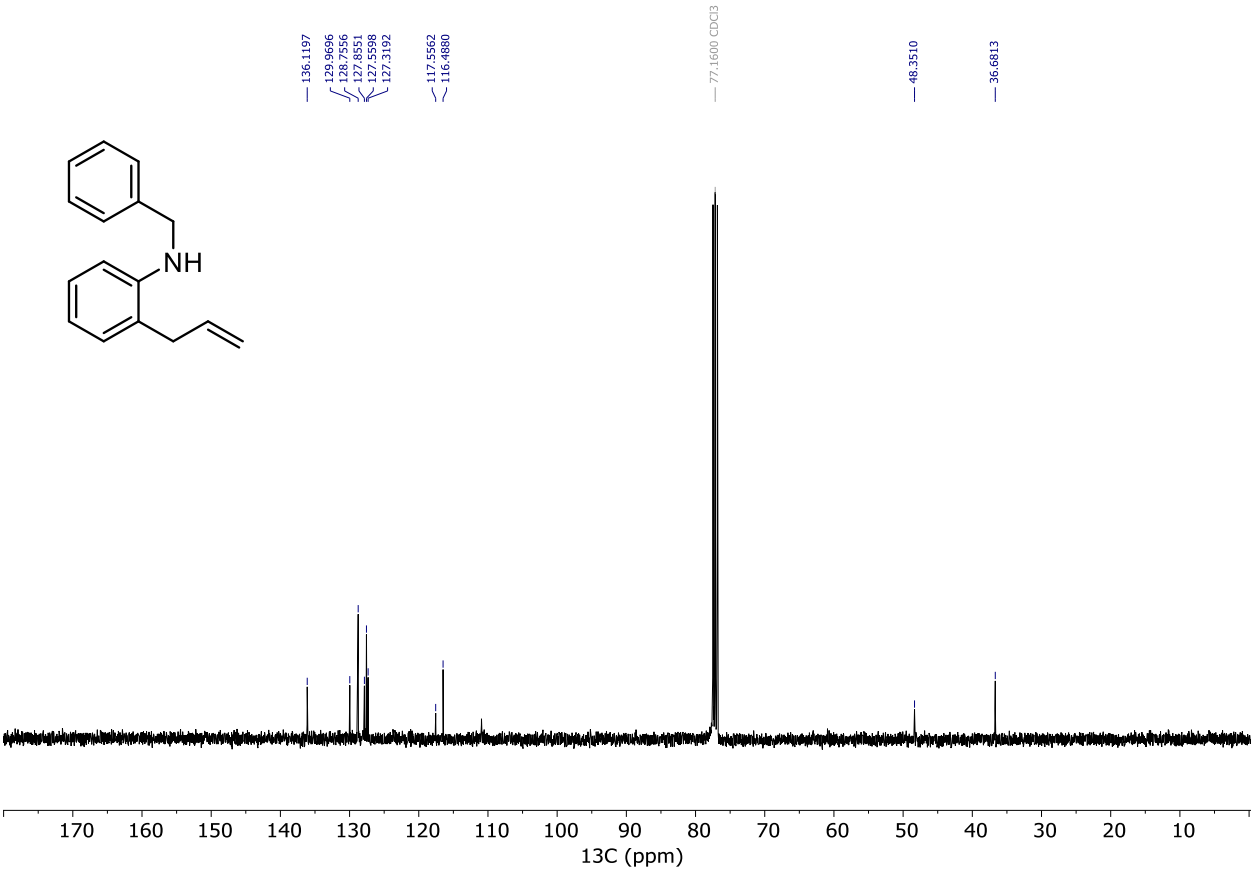


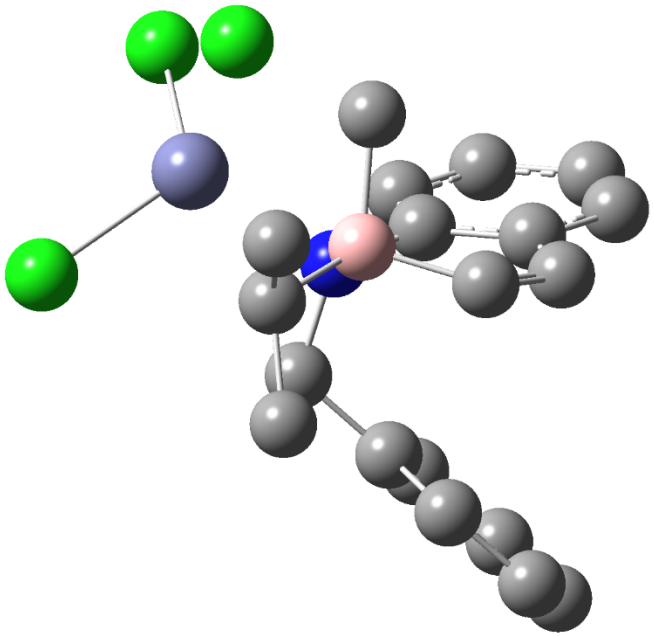
Figure S35. ^{13}C NMR Spectrum of 2-allyl-*N*-benzylaniline (**5b**) in $CDCl_3$.

5 | Computational Methods

All calculations were performed in Gaussian 16. Geometry optimizations were done using the B3LYP density functional, Grimme's D3 dispersion correction with Becke-Johnson damping, and the def2-SVP basis set (B3LYP-D3(BJ)/def2-SVP).[1] Optimizations used the conductor-like polarizable continuum model (CPCM) with parameters for THF.[2] Harmonic frequency calculations were conducted analytically to confirm that optimized geometries had located minima on the potential energy surface and had no imaginary frequencies. Intrinsic reaction coordinate calculations were performed on all transition states confirming saddle points were connected via a minimum energy pathway between the two proposed intermediates, and harmonic frequency calculations were conducted to confirm that transition states had a single, strong imaginary frequency. All transition-state optimizations utilized the transit-guided quasi-Newtonian algorithm implemented in Gaussian 16[3]. Single-point energies were calculated at the B3LYP-D3(BJ)/def2-TZVP (SMD, THF) for all optimized DFT geometries, labelled B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP (SMD, THF). All single-point calculations utilized the CPCM model to calculate the electrostatic solvation energy in addition to Truhlar's SMD solvation model (non-electrostatic component) with parameters for THF.[4]

6 | Computational Data

Figure S36. Optimized structure and atomic coordinates of **I•ZnCl$_2$**



Tag	Symbol	X	Y	Z
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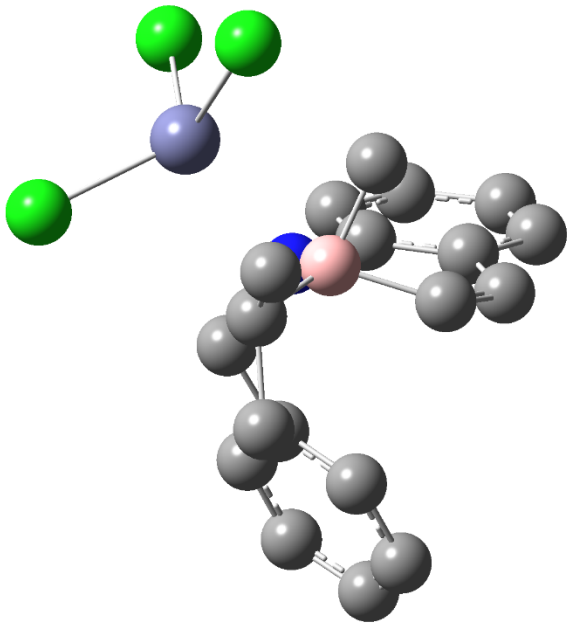
2	H	-1.1481480	1.2955330	0.0842460
3	C	-0.3803810	-0.1292340	-1.2500170
4	H	-0.4369910	0.5203760	-2.1327950
5	C	0.1405830	-1.4773690	-1.4822500
6	C	0.3077320	-1.9478580	-2.7985250
7	H	0.0225050	-1.2889300	-3.6236710
8	C	0.8272760	-3.2129670	-3.0666370
9	H	0.9438190	-3.5527880	-4.0987460
10	C	1.1969060	-4.0381710	-2.0013900
11	H	1.6040880	-5.0352550	-2.1861330
12	C	1.0455250	-3.5876150	-0.6876490
13	H	1.3318570	-4.2460360	0.1319240
14	C	0.5132180	-2.3248990	-0.4050130
15	C	1.8738410	-1.4620740	1.3759320
16	H	2.4410800	-2.3781410	1.5982160
17	H	1.7990830	-0.9235860	2.3238230
18	C	2.6790960	-0.6918240	0.3483020
19	C	2.5189090	0.6837670	0.1268330
20	H	1.7889180	1.2408840	0.7092770
21	C	3.2729690	1.3463000	-0.8451450

22	H	3.1314260	2.4189850	-1.0002790
23	C	4.2000060	0.6434200	-1.6211210
24	H	4.7850930	1.1618720	-2.3849860
25	C	4.3758210	-0.7268540	-1.4076180
26	H	5.0990730	-1.2886970	-2.0040880
27	C	3.6237570	-1.3810760	-0.4286900
28	H	3.7612760	-2.4529560	-0.2684430
29	B	-0.7209320	-0.7542330	1.2139960
30	N	0.4709460	-1.8444490	0.9701750
31	C	-0.6982840	-0.0228920	2.6986450
32	C	-2.1184850	-1.5811780	0.9711640
33	H	-3.0166730	-0.9551960	1.0063600
34	H	-2.1372020	-2.1809330	0.0529170
35	C	-2.0971830	0.5035810	3.0700850
36	H	-2.8326300	-0.3051340	3.1844000
37	H	-2.0763780	1.0613070	4.0237690
38	H	-2.4832750	1.2005290	2.3041560
39	C	0.2820400	1.1518390	2.8626850
40	H	0.0847670	1.9452480	2.1205000
41	H	0.1808810	1.6188470	3.8593250
42	H	1.3370680	0.8664600	2.7571010
43	Cl	-2.4476690	-2.8742940	2.3117300
44	Zn	0.0213420	-3.3863930	2.3481580
45	Cl	0.9802010	-2.9422550	4.3573950
46	Cl	-0.0755690	-5.5979510	1.8600830
47	H	-0.4296460	-0.7767290	3.4587530

Energy: -3977.74736792 hartree

Figure S37. Optimized structure and atomic coordinates of the ring-expansion transition state



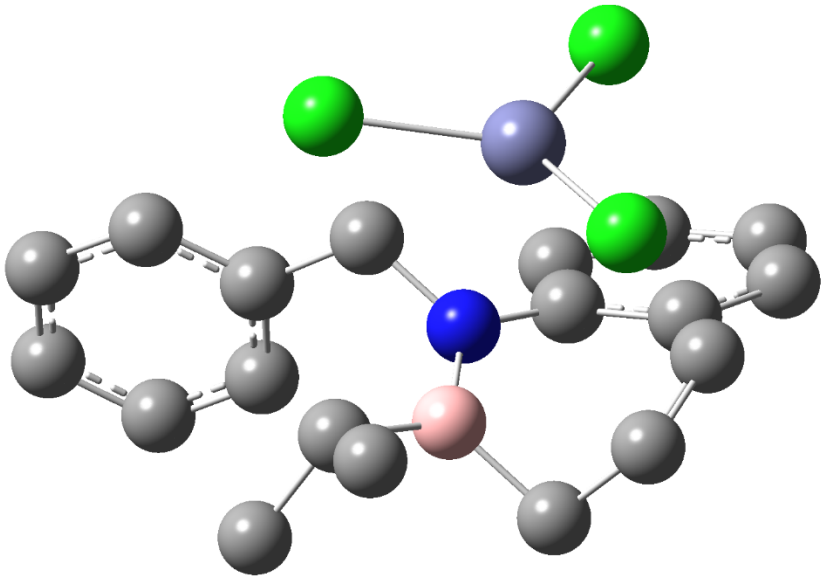
Tag	Symbol	X	Y	Z
1	C	-1.7992170	0.5340540	-0.2941640
2	H	-2.2749050	1.5131090	-0.1813820
3	C	-1.4784780	0.0907460	-1.5328350
4	H	-1.6416060	0.7073120	-2.4252530
5	C	-0.8373970	-1.1985050	-1.7556890
6	C	-0.6978580	-1.6767420	-3.0753980
7	H	-1.1317540	-1.0871280	-3.8875210
8	C	-0.0158040	-2.8549380	-3.3563040
9	H	0.0788270	-3.2073220	-4.3858890
10	C	0.5569360	-3.5747260	-2.3008310
11	H	1.1030580	-4.5006410	-2.4969820
12	C	0.4304090	-3.1207660	-0.9896770
13	H	0.8617390	-3.7053990	-0.1797200
14	C	-0.2816720	-1.9508980	-0.6837990
15	C	1.0513630	-1.2362590	1.1944530
16	H	1.5168090	-2.1907510	1.4773410
17	H	0.9482010	-0.6870910	2.1355950
18	C	2.0004630	-0.5284720	0.2504740
19	C	1.6988990	0.7019440	-0.3537230
20	H	0.7367320	1.1739550	-0.1653380
21	C	2.6114170	1.3196710	-1.2121380
22	H	2.3544100	2.2760020	-1.6748900
23	C	3.8467340	0.7211690	-1.4821710
24	H	4.5591350	1.2058460	-2.1543490
25	C	4.1586670	-0.5050480	-0.8890330
26	H	5.1167690	-0.9883670	-1.0963130
27	C	3.2386620	-1.1222260	-0.0362950

28	H	3.4805140	-2.0891930	0.4130090
29	B	-1.4714090	-0.4207320	1.0017970
30	N	-0.3316480	-1.4823210	0.6768010
31	C	-1.3363700	0.3837390	2.4206850
32	C	-0.4079160	1.6082120	2.3823200
33	H	-0.7692090	2.3609310	1.6600400
34	H	-0.3599360	2.1057220	3.3677120
35	H	0.6244520	1.3615920	2.0969800
36	C	-2.7054110	0.8160870	2.9662530
37	H	-3.2373440	1.4784560	2.2590450
38	H	-3.3504970	-0.0523610	3.1622690
39	H	-2.6013500	1.3801730	3.9099650
40	C	-2.8762420	-1.0152340	0.6511460
41	H	-3.0004800	-1.7169990	-0.1766590
42	H	-3.7883820	-0.4596040	0.8761300
43	Cl	-3.3748670	-2.7513990	2.2045950
44	Zn	-1.0418890	-3.1022630	2.0306660
45	Cl	-0.0000130	-2.7179110	4.0304440
46	Cl	-0.7158110	-5.2352600	1.2983650
47	H	-0.9233900	-0.3292940	3.1547110

Energy: -3977.73881757 hartree

Imaginary frequency: -254.74

Figure S38. Optimized geometry of **6•ZnCl$_3$**



Tag	Symbol	X	Y	Z
1	C	4.5701700	0.5996010	16.7231330
2	H	3.9858200	0.4370000	15.8131510
3	C	4.9824670	-0.4709590	17.4298350
4	H	4.8029120	-1.4769500	17.0410470
5	C	5.6777300	-0.3708640	18.7136690
6	C	6.7240950	-1.2751580	18.9884190
7	H	6.9880590	-2.0018290	18.2152870
8	C	7.4142010	-1.2697920	20.1951660
9	H	8.2261310	-1.9793620	20.3708780
10	C	7.0495230	-0.3449240	21.1811860
11	H	7.5795010	-0.3145080	22.1364090
12	C	5.9999750	0.5387060	20.9496200
13	H	5.7189400	1.2402830	21.7352490
14	C	5.2900650	0.5481590	19.7306610
15	C	3.2844680	1.4692160	20.7853350
16	H	3.5599930	0.6587790	21.4749220
17	H	2.2498130	1.2493640	20.4933300
18	C	3.3155590	2.7974160	21.5079180
19	C	4.4281870	3.6488180	21.4720200
20	H	5.2983760	3.3699050	20.8750800
21	C	4.4232000	4.8625790	22.1666370
22	H	5.2996880	5.5141830	22.1241640
23	C	3.2997430	5.2471350	22.9043530
24	H	3.2926210	6.1981300	23.4424970
25	C	2.1794920	4.4092130	22.9381510
26	H	1.2900840	4.7063580	23.4996910

27	C	2.1892760	3.1973650	22.2436310
28	H	1.3049870	2.5538190	22.2535540
29	B	3.7906030	2.0836790	18.4078960
30	N	4.1502190	1.3811680	19.5990010
31	C	2.4398650	2.9134210	18.2621030
32	C	2.7584130	4.4203550	18.3288700
33	H	3.4573400	4.7168510	17.5275050
34	H	1.8427080	5.0242540	18.2007340
35	H	3.2141100	4.7033350	19.2894120
36	C	1.7031570	2.5895670	16.9506070
37	H	2.3209230	2.8336640	16.0694710
38	H	1.4265780	1.5283550	16.8765960
39	H	0.7759690	3.1834340	16.8681610
40	C	4.8083500	2.0037690	17.1947870
41	H	5.8486540	2.1264340	17.5428590
42	H	4.6061430	2.7403070	16.4064450
43	Cl	0.0331180	0.2900400	19.5937670
44	Zn	1.6298670	-1.0034440	18.6220400
45	Cl	1.4643430	-1.3793040	16.4099050
46	Cl	2.9961620	-2.1427960	19.9829370
47	H	1.7490050	2.6762430	19.0846500

Energy: -3977.81850111 hartree

7 | Single Crystal X-Ray Crystallography Data

2-isopropylborazaronaphthalene (3a)

All reflection intensities were measured at 110.00(10) K using a Rigaku XtaLAB Synergy R (equipped with a rotating-anode X-ray source and HyPix-6000HE detector) with Cu *K*α radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.42.49, Rigaku OD, 2022). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXT-2018/2 (Sheldrick, 2018) and was refined on F^2 with SHELXL-2019/3 (Sheldrick, 2018)[5]. Analytical numeric absorption correction using a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryostream 1000 from Oxford Cryosystems. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 U_{eq} of the attached C atoms. The H atom attached to N1 was found from difference Fourier map, and its coordinates were refined pseudofreely using the DFIX instruction in order to keep the N–H distance to be within an acceptable range.

The structure is ordered. The absolute configuration could not be established by anomalous-dispersion effects in diffraction measurements on the crystal as there are no anomalous scatterers in the crystal.

Table S1. Crystallographic data for 2-isopropylborazaronaphthalene

	2-isopropylborazaronaphthalene
Crystal data	
Chemical formula	$C_{11}H_{14}BN$
M_r	171.04
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	110
a, *b*, *c* (Å)	5.80606 (12), 7.55044 (15), 11.4439 (2)
β (°)	96.1273 (19)
V (Å^3)	498.82 (2)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.49
Crystal size (mm)	0.45 × 0.32 × 0.04
Data collection	
Diffractometer	XtaLAB Synergy R, HyPix
Absorption correction	Analytical *CrysAlis PRO* 1.171.43.90 (Rigaku Oxford Diffraction, 2023) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.864, 0.982
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10074, 1904, 1857
R_{int}	0.025
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.088, 1.09
No. of reflections	1904
No. of parameters	124
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained

	refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, -0.13
Absolute structure	Flack x determined using 823 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.25 (19)

(N-benzyl)-2-isopropylborazaronaphthalene (4a)

All reflection intensities were measured at 243.00(10) K* using a Rigaku XtaLAB Synergy R (equipped with a rotating-anode X-ray source and HyPix-6000HE detector) with Cu *K*α radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.42.49, Rigaku OD, 2022). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXT-2018/2 (Sheldrick, 2018) and was refined on F^2 with SHELXL-2019/3 (Sheldrick, 2018)[5]. Analytical numeric absorption correction using a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryostream 1000 from Oxford Cryosystems. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 23, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 U_{eq} of the attached C atoms.

*The crystal was initially flash-cooled from room temperature to 110 K, but the resulting diffraction pattern indicated non-single crystal behavior. However, when cooled more gradually to 243 K, the crystal behaved as a single crystal, producing a clean diffraction pattern

The structure is ordered.

Table S2. Crystallographic data for (N-benzyl)-2-isopropylborazaronaphthalene

	(N-benzyl)-2-isopropylborazaronaphthalene
Crystal data	
Chemical formula	$C_{18}H_{20}BN$
M_r	261.16
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	243
a, *b*, *c* (Å)	9.63386 (7), 8.72627 (8), 36.3137 (3)
V (Å^3)	3052.81 (4)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.48
Crystal size (mm)	0.54 × 0.31 × 0.28
Data collection	
Diffractometer	XtaLAB Synergy R, HyPix
Absorption correction	Analytical *CrysAlis PRO* 1.171.43.90 (Rigaku Oxford Diffraction, 2023) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.858, 0.910
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32666, 2988, 2794
R_{int}	0.018
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.044, 0.120, 1.06
No. of reflections	2988
No. of parameters	184
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, -0.24

(N-benzyl)-2-(chloromethyl)borazaronaphthalene (4c)

All reflection intensities were measured at 110.00(10) K using a Rigaku XtaLAB Synergy R (equipped with a rotating-anode X-ray source and HyPix-6000HE detector) with Cu *K*α radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.42.49, Rigaku OD, 2022). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXT-2018/2 (Sheldrick, 2018) and was refined on F^2 with SHELXL-2019/3 (Sheldrick, 2018)[5]. Analytical numeric absorption correction using a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryostream 1000 from Oxford Cryosystems. The H atoms were placed at calculated positions using the instructions AFIX 23 or AFIX 43 with isotropic displacement parameters having values 1.2 U_{eq} of the attached C atoms.

The structure is mostly ordered. The asymmetric unit contains one molecule of the target compound and one site that includes some amount of very disordered lattice solvent molecules (possibly dichloromethane), and the latter contribution was removed from the final refinement using the SQUEEZE procedure in Platon (Spek, 2009)[6].

Table S3. Crystallographic data for (N-benzyl)-2-(chloromethyl)borazaronaphthalene

	(N-benzyl)-2-(chloromethyl)borazaronaphthalene
Crystal data	
Chemical formula	$C_{16}H_{15}BClN$
M_r	267.55
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110
a, *b*, *c* (Å)	8.15626 (17), 8.98468 (18), 11.7166 (2)
α, β, γ (°)	100.8560 (17), 93.9083 (17), 108.2052 (19)
V (Å^3)	793.58 (3)
Z	2
Radiation type	Cu *K*α
μ (mm^{-1})	1.99
Crystal size (mm)	0.24 × 0.15 × 0.13
Data collection	
Diffractometer	XtaLAB Synergy R, HyPix
Absorption correction	Analytical *CrysAlis PRO* 1.171.43.90 (Rigaku Oxford Diffraction, 2023) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.737, 0.833
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25296, 3103, 3047
R_{int}	0.022
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.034, 0.089, 1.06
No. of reflections	3103
No. of parameters	173
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, -0.34

Computer programs: *CrysAlis PRO* 1.171.42.49 (Rigaku OD, 2022), *SHELXT2018*/2 (Sheldrick, 2018), *SHELXL2019*/3 (Sheldrick, 2018), *SHELXTL* v6.10 (Sheldrick, 2008).

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[6]Plek, A, L. *Acta Cryst*. **2009**, *D65*, 148-55. https://doi.org/10.1107/S090744490804362X