Electronic Supporting Information

Azaborine Benzylic Ion Stability and Reactivity in Ionic Polymerization

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Table of Contents

1. General Information

Instrumentation: ^{1}H NMR, ^{11}B NMR, and ^{13}C {1H} NMR spectra were recorded on a Bruker Avance III 400 MHz Spectrometer or a Bruker Avance 300 MHz Spectrometer and chemical shifts are reported in parts per million (ppm). Spectra were recorded in chloroform-*d*, benzene- d_6, or dimethylsulfuoxide-d_6 with the residual solvent peak as the internal standard (^{1}H NMR: $CHCl_3$, δ = 7.26 ppm; C_6D_6, δ = 7.16 ppm; DMSO, δ = 2.50 ppm. ^{13}C NMR: $CHCl_3$, δ = 77.16 ppm; C_6D_6, δ = 128.06 ppm; DMSO, δ = 39.52 ppm). ^{11}B NMR spectra are externally referenced to boron trifluoride diethyl etherate ($BF_3{\bullet}Et_2O$, δ = 0 ppm). Carbons bound to boron are not observed due to the quadrupolar relaxation of boron. Broad signals at ~ δ = 2.7 ppm in the ^{11}B NMR spectrum are due to boron contained in probe components. Multiplicities are as indicated: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), h (heptet), m (multiplet), and br (broad). Coupling constants, J, are reported in Hertz (Hz) and integration is provided, along with assignments, as indicated. Mass spectrometry and high-resolution mass spectrometry were performed in the Department of Chemistry at Johns Hopkins University using a VG Instruments VG70S/E magnetic sector mass spectrometer with electron ionization (EI) (70 eV). The UNIlab Plus Glove Box by MBRAUN was maintained under nitrogen atmosphere. All column chromatography was performed on a Teledyne ISCO Combiflash Rf+ using Redisep Rf silica columns. Prep TLC was performed with the 20x20 1000-micron silica gel GF plate by Uniplate.

Materials: Unless otherwise specified, all chemicals were used as purchased without further purification. Solvents used for column chromatography and polymer workup were reagent grade and used as received. Reaction solvent THF, toluene, dichloromethane (DCM) (Sigma Aldrich), HPLC grade) was dried on a J. C. Meyer Solvent Dispensing System (SDS) using stainless steel columns packed with neutral alumina and Q5 reactant, a copper (II) oxide oxygen scavenger, following the manufacturer's recommendations for solvent preparation and dispensation. Triethylamine (Sigma Aldrich, >99%) was dried over potassium hydroxide overnight and distilled under argon just prior to use. Styrene was filtered through a column of aluminum oxide to remove inhibitor. 1M NaOH solution was made by dissolving 40 g of NaOH in 1 L of water. Aluminum chloride($AlCl_3$)(99.99%), benzaldehyde (99.5%), benzene (anhydrous) (99.8%), boron trifluoride diethyl etherate ($BF_3{\bullet}OEt_2$), n-butyl lithium solution (n-BuLi)(2.5 M, hexanes), cyclopentyl methyl ether (CPME) (anhydrous, 99.9%), dichloromethane (DCM), hexanes, hydrochloric acid (37%), methanol (MeOH), potassium hydroxide, potassium isopropyl trifluoroborate (97%), potassium vinyltrifluoroborate (95%), silicon tetrachloride ($SiCl_4$) (SureSeal, 99%), $SnCl_4$ solution (1.0 M, methylene chloride), sodium borohydride ($NaBH_4$)(≥98%), sodium hydroxide (NaOH)(97.0%), styrene (99.4%), and sulfuric acid (H_2SO_4) (95-98%) were purchased from Sigma Aldrich. Anhydrous sodium sulfate was purchased from Milipore. Chloroform-*d* ($CDCl_3$)(D, 99.8%), DMSO-d_6 and benzene-d_6 (D, 99.5%) were purchased from Cambridge Isotope Laboratories, Inc. Silica gel (siliaflash P60) was purchased from Silicycle. Ammonia 7N methanol was purchased from Acros. Triethylamine was purchased from Fisher Scientific.

2. Supplemental figures

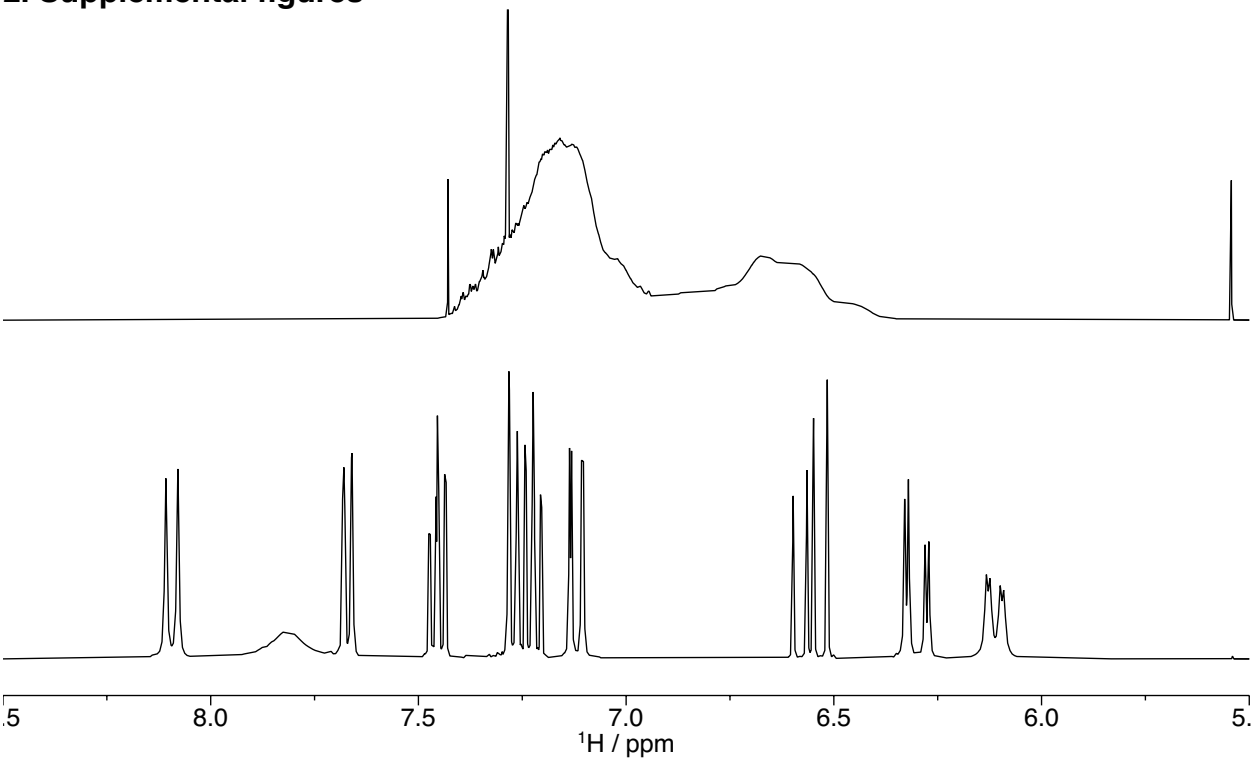


Figure S1. $AlCl_3$ ([monomer]/[$AlCl_3$], 1.00:0.05). Top: styrene after 16 h. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) consistent with PS. Bottom: BN2VN after 16 h. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) consistent with recovered monomer.

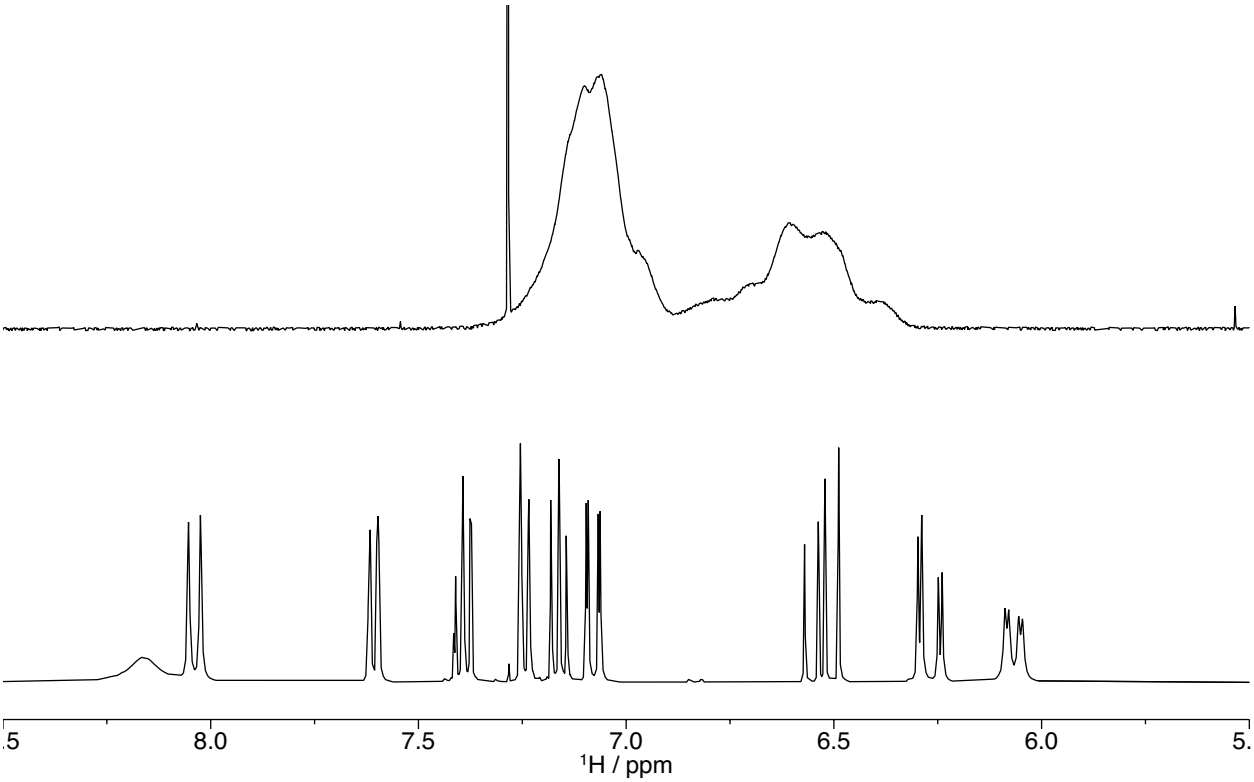


Figure S2. $BF_3 \bullet OEt_2$ ([monomer]/[$BF_3 \bullet Et_2O$], 1.00:0.05). Top: styrene after 1 h. ^1H NMR spectrum (400 MHz, $CDCl_3$) consistent with PS. Bottom: BN2VN after 18 h. ^1H NMR spectrum (400 MHz, $CDCl_3$) consistent with recovered monomer.

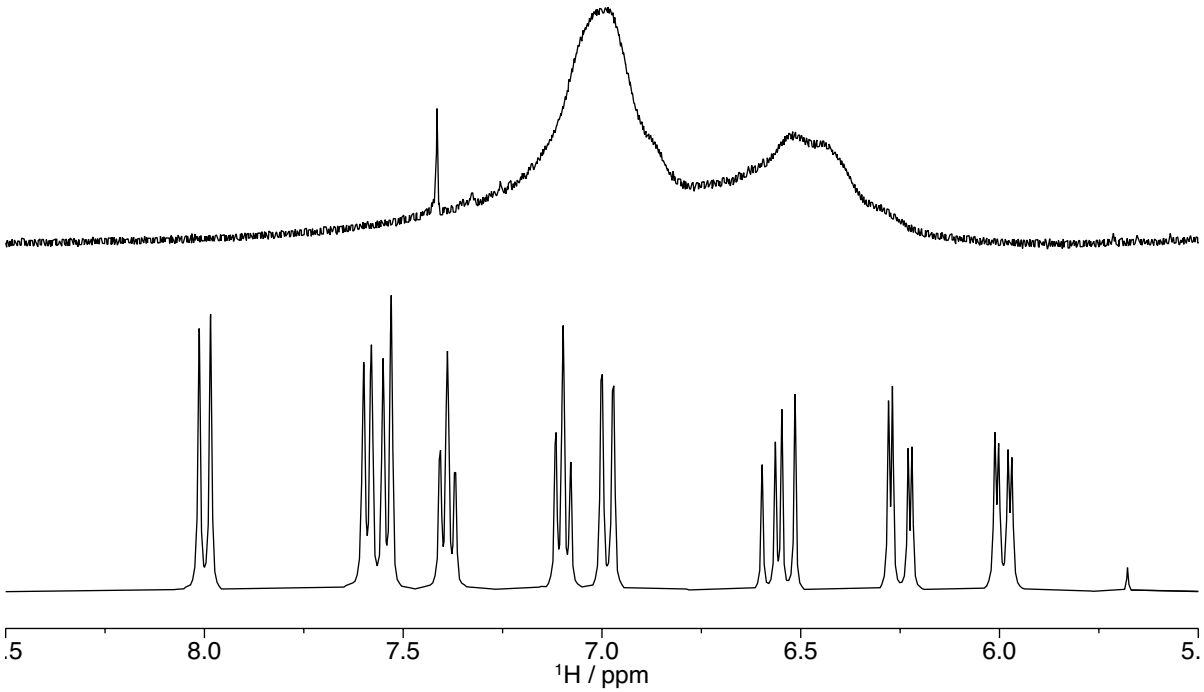


Figure S3. $SnCl_4$ ([monomer]/[$SnCl_4$], 1.00:0.05). Top: styrene after 1 h. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) consistent with PS. Bottom: BN2VN after 18 h. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) consistent with recovered monomer.

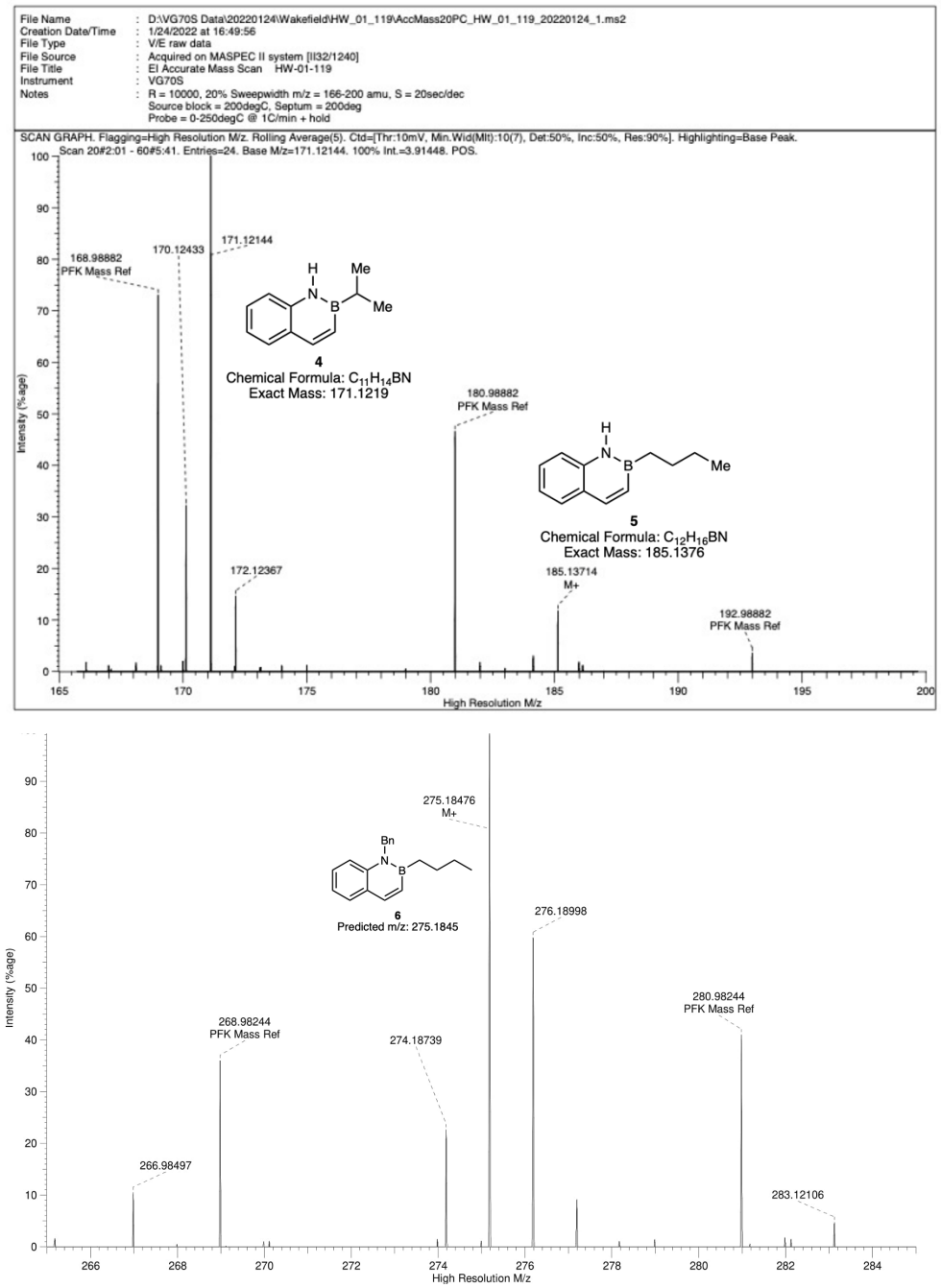


Figure S4. Electron ionization mass spectrometry (EI-MS) of nucleophilic substitution of compound **4** (top) and compound **3** (bottom) with n-BuLi. Both starting material (**3** or **4**) and substitution product (**5** or **6**) can be identified.

3. Experimental Procedures

3.1 Cationic Polymerization

Acid
BF_3OEt_2
$AlCl_3$
$SnCl_4$
$B(C_6F_5)_3$

3.1.1 General procedure for cationic polymerization with $AlCl_3$

An oven dried 15 mL heavy walled cylindrical pressure vessel equipped with a stir bar was charged with monomer (BN2VN or styrene, 5 mmol) and DCM (5 mL). The reaction vessel was then lowered into an ice bath to cool to 0 °C. $AlCl_3$ (33.0 mg, 0.25 mmol) was added to initiate the reaction and the reaction mixture was allowed to stir, while warming to room temperature. The reaction was monitored by taking aliquots for ^1H NMR spectroscopy. After completion (2 h for styrene, 16 h for BN2VN), the reaction was quenched with 2.0 mL of 1% NaOH in ethanol and then precipitated in 150 mL solution of 1:1 hexane/ethanol. In the case of styrene, a white solid was precipitated, isolated by filtration, and dried in vacuo overnight at 70 °C (153. mg, 28.5% yield). No BN2VN polymerization was observed.

3.1.2 General procedure for cationic polymerization with $BF_3{\bullet}OEt_2$

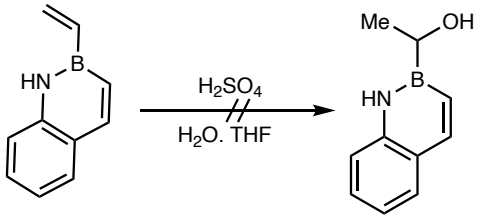
An oven dried 15 mL heavy walled cylindrical pressure vessel equipped with a stir bar was charged with the monomer (BN2VN or styrene, 5 mmol). The monomer was then place in an ice bath to cool to 0 °C. $BF_3{\bullet}OEt_2$ (0.50 mL of a stock solution, 0.617 mL in 10 mL CH_2Cl_2) was added to initiate the reaction and allowed to stir, while warming to room temperature. The reaction was monitored by taking aliquots for ^1H NMR spectroscopy. After completion (1 h for styrene, 18 h for BN2VN), the reaction was quenched by addition of MeOH (2.0 mL) then washed with water (50 mL). In the case of styrene, a white solid was isolated by filtration dried in vacuo overnight at 70 °C (539.0 mg, 98.8% yield). No BN2VN polymerization was observed.

3.1.4 General procedure for cationic polymerization with SnCl4

An oven dried 15 mL heavy walled cylindrical pressure vessel equipped with a stir bar was charged with the monomer (BN2VN or styrene, 5 mmol) and DCM (0.5 mL). The reaction vessel was lowered into a 0 °C ice bath to cool. $SnCl_4$ (0.25 mmol) was added to initiate the reaction and allowed to stir, while warming to room temperature. The

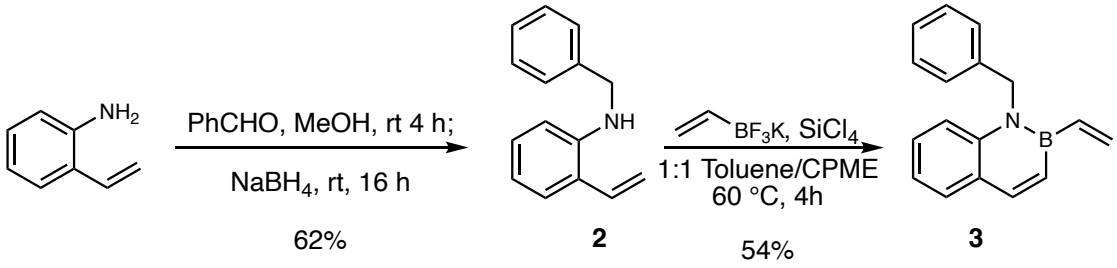
reaction was monitored by taking aliquots for ^{1}H NMR spectroscopy. After completion (2 h for styrene, 18 h for BN2VN), the reactions were quenched with 2 mL of ammonia (7N) in methanol, washed with 15 mL of 0.2 M hydrochloric acid, and dried in vacuo at 70 °C. In the case of styrene, solid polymer was isolated by filtration (435. mg, 83.2% yield). No BN2VN polymerization was observed.

3.2 Attempted Hydration of BN2VN



An oven dried microwave vial was charged with BN2VN (387.5 mg, 2.5 mmol, 1.0 equiv.), water (0.450 mL, 25 mmol, 10 equiv.) and THF (2.0 mL), then lowered into a 0 °C ice bath. Dilute H_2SO_4 (1.34 mL, 25 mmol, 10 equiv.) was added to the cooled flask to initiate the reaction. The reaction was stirred for 3 hours, while warming to room temperature, and monitored by TLC (1:3 DCM/hexane). After 3 hours, the reaction was quenched with the dropwise addition of a saturated aqueous solution of $NaHCO_3$ until a neutral pH was achieved. The aqueous layer was separated from the organic layer and extracted by 10 mL of ethyl acetate by 3 times. The organic layers were combined and concentrated by rotatory evaporation. The crude was purified via preparatory TLC with 25% ethyl acetate and 75% hexane. The product was 2-aminostyrene (62.7 mg, 52.6% yield), instead of the secondary alcohol. The spectra of the 2-aminostyrene product matched spectra previously reported.[1]

3.3 Synthesis of BN Naphthalenes



3.3.1. Synthesis *of N*-benzyl-2-vinylaniline (2)

Procedures are adapted from Marhold et al.[2]

In an oven dried 100 mL Schlenk flask, 2-vinylaninline (1.19 g, 10.0 mmol, 1.00 equiv.) was dissolved by MeOH (40 mL), and then benzaldehyde (1.33 mL, 13.0 mmol, 1.30 equiv.) was added to the reaction mixture. The reaction was stirred at room temperature. After 4 hours, the reaction was cooled in an ice bath to 0 °C. $NaBH_4$ (1.14 g, 30.0 mmol, 3.00 equiv.) was added and the reaction stirred overnight while warming to room temperature. The reaction was quenched with aqueous solution of 1M NaOH (20 mL).

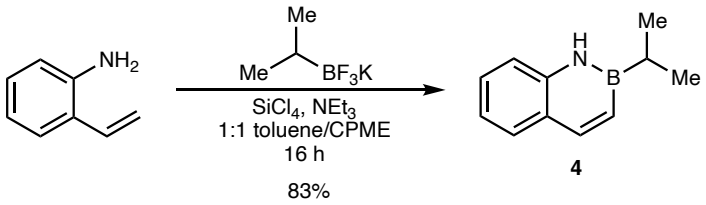
The aqueous layer was separated from the organic layer and extracted by 40 mL of hexanes by 3 times. The organic layer was dried with anhydrous $NaSO_4$ and then concentrated by rotatory evaporation. The crude was purified via automated column chromatography with 100% hexanes then with a gradient to 25% DCM/75% hexanes yielding **2** as a yellow oil (1.30 g, 62%). **2** was stored in a -10 °C freezer, for further uses. The spectra were consistent with data reported for this compound[3]

δ_H (400 MHz, $CDCl_3$)	7.55 – 7.37 (m, 5H), 7.33 – 7.24 (m, 1H), 6.98 – 6.84 (m, 2H), 6.77 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.77 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.44 (dd, *J* = 11.0, 1.6 Hz, 1H), 4.47 (d, *J* = 0.7 Hz, 2H), 4.33 (s, 1H).
δ_C (101 MHz, $CDCl_3$)	145.19, 139.38, 133.05, 129.14, 128.81, 127.65, 127.54, 127.42, 124.43, 117.72, 116.47, 111.15, 77.54, 48.45.

3.3.2. Synthesis of 1-benzyl-2-vinyl-1,2,3,4-tetrahydrobenzo[e][1,2]azaborinine (3). Procedures are adapted from Molander et al.[3]

An oven dried 100 mL 3-neck flask equipped with a stir bar and a reflux condenser was charged with potassium vinyl trifluoroborate (295. mg, 2.20 mmol, 1.00 equiv.) and purged and backfilled with nitrogen. Compound **2** (691 mg, 3.30 mmol, 1.50 equiv.) was added the flask and dissolved by toluene (2.20 mL) and CPME (2.20 mL). Silicon tetrachloride (0.26 mL, 2.20 mmol, 1.00 equiv.) was added dropwise via syringe. The reaction mixture was then heated at 60 °C for 4 hours. The reaction was cooled to room temperature and diluted with hexanes (8.00 mL). The solution was passed through silica plug by washing with 300 mL of 1:3 DCM:hexanes. The filtrate was dried over anhydrous $NaSO_4$ and concentrated by rotatory evaporation. The crude was purified via automated column chromatography with 100% hexanes then with a gradient to 30% DCM/70% hexanes yielding **3** as a brown solid that was then stored in a lab freezer (-10 °C) for further uses (yield 292. mg, 54.1%).

δ_H (400 MHz, $CDCl_3$)	8.07 (d, *J* = 11.5 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.39 – 7.15 (m, 10H), 6.68 (dd, *J* = 19.4, 13.5 Hz, 1H), 6.31 (dd, *J* = 19.4, 3.8 Hz, 1H), 6.10 (dd, *J* = 13.6, 3.8 Hz, 1H), 5.44 (s, 2H).
δ_C (101 MHz, CDCl3)	145.03, 138.66, 133.57, 130.20, 128.75, 128.46, 127.02, 125.94, 120.80, 116.15, 77.36, 77.04, 76.73, 51.16.
δ_B NMR (128 MHz, $CDCl_3$)	34.41.
ATR-IR Spectroscopy	3059, 3028, 2952, 1602, 1551, 1416, 1218, 805, 762, 729, 707, 693, 501, 483, 461
HRMS (EI)	m/z $[M]^+$ Calc 245.1376 for $C_{17}H_{16}BN$; Found 245.1376.



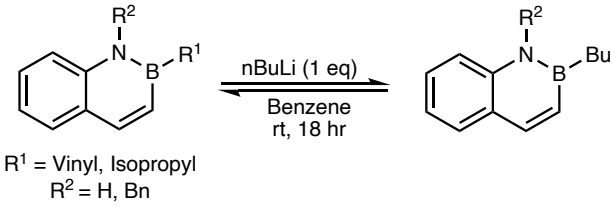
3.3.3. Synthesis of 2-isopropyl-1,2-dihydrobenzo[*e*][1,2]azaborinine (4)

Procedures are adapted from van de Wouw et al.[1]

An oven dried 100 mL 3-neck flask equipped with a stir bar and a reflux condenser was charged with potassium isopropyl trifluoroborate (347. mg, 2.31 mmol, 1.10 equiv.) then purged and backfilled with nitrogen. 2-Vinylaniline (0.25 mL, 2.10 mmol, 1.00 equiv.), CPME (10 mL), toluene (10 mL), triethylamine (0.44 mL, 3.15 mmol, 1.5 eq), and silicon tetrachloride (0.27 mL, 2.31 mmol, 1.1 eq) were added to the reaction vessel. The flask was heated to 60 °C and allowed to stir for 18 hours. The reaction was cooled to room temperature, diluted with hexanes (16.0 mL), eluted through a silica gel plug and washed with 300 mL of 1:3 DCM:hexanes. The eluent was dried with $NaSO_4$ before being concentrated by rotatory evaporation. **4** was purified by silica gel chromatography eluting with hexane, then ramping to 25% DCM in hexanes. Eluted fractions were concentrated by rotatory evaporation and dried on vacuum yielding a white powdery solid before storing in a freezer (-10 °C) (yield 298. mg, 82.9%). The spectra were consistent with data reported for this compound.[4,5]

δ_H (400 MHz, $CDCl_3$)	8.01 (d, J = 11.5 Hz, 1H), 7.64 (t, J = 12.0 Hz, 2H), 7.42 (t, J = 7.7 Hz, 1H), 7.35 – 7.13 (m, 2H), 6.90 (dd, J = 11.6, 2.0 Hz, 1H), 1.55 (h, J = 7.3 Hz, 1H), 1.20 (d, J = 7.3, 6H).
δ_C (101 MHz, $CDCl_3$)	144.52, 139.97, 129.30, 127.96, 125.37, 120.64, 117.91, 19.75.

3.4 Anionic Reactivity of Azaborine

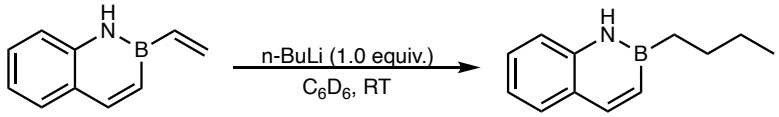


3.4.1 General procedure for n-BuLi substitution

An oven dried 10 mL Schlenk flask under an argon atmosphere was charged with BN naphthalene (1.00 equiv.) and dissolved in C_6D_6 (0.5 mL) at room temperature. A ~0.75M solution of *n*-BuLi in C_6D_6 was made by adding 0.6 mL of a 2.0M n-BuLi solution in hexanes to 1.4 mL of C_6D_6 and titrated by diphenyl acetic acid.[6] *n*-BuLi (1.00 equiv.) was added to initiate the reaction. The reaction vessel was then sealed with copper wire and brought into a nitrogen filled glovebox to stir at room temperature overnight. While in the

glovebox, reaction aliquots were taken and placed into a J. Young tube to preform NMR experiments. The next day, the reaction was brought out of the glovebox and quenched with 2 mL of a solution of 1:1 IPA:hexane and then washed with 2 mL of saturated aqueous NH_4Cl solution. The aqueous layer was separated from the organic layer and extracted by 8 mL of hexanes by 3 times. The organic layer was then concentrated by rotatory evaporation and the crude was analyzed by ^1H NMR spectroscopy.

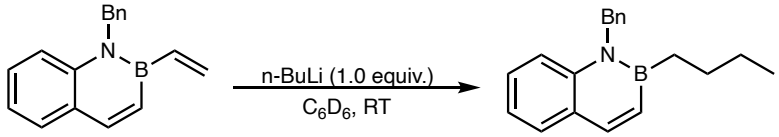
3.4.2 Procedure for *n*-BuLi substitution with BN2VN



BN2VN **5**
68.5% NMR

Synthesized 5 on a 50.0 mg (0.32 mmol, 1.00 equiv.) scale according to the general procedure 3.4.1 (0.32 mmol, 1.00 equiv., 0.5 mL C_6D_6). δ_H (400 MHz, $CDCl_3$) 7.96 (d, J = 11.6 Hz, 1H), 7.67 (s, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.23 (d, J = 8.2 Hz, 1H), 7.18 – 7.12 (m, 1H), 6.85 (d, J = 11.5 Hz, 1H), 1.66 – 1.56 (m, 2H), 1.48 – 1.37 (m, 2H), 1.32 – 1.26 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). δ_C (101 MHz, $CDCl_3$) 144.04, 140.18, 129.30, 127.91, 125.30, 120.52, 117.75, 77.35, 36.83, 28.09, 25.73, 14.14.

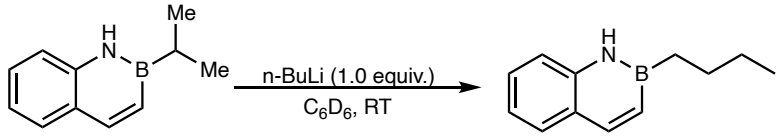
3.4.3 Procedure for *n*-BuLi substitution with 3



3 **6**
85% NMR

Synthesized 5 on a 50.0 mg (0.20 mmol, 1.00 equiv.) scale according to the general procedure 3.4.1 (0.20 mmol, 1.00 equiv., 0.5 mL C_6D_6).

3.4.4 Procedure for *n*-BuLi substitution with 4



4 **7**
90% NMR

Synthesized 5 on a 50.0 mg (0.29 mmol, 1.00 equiv.) scale according to the general procedure 3.4.1 (0.29 mmol, 1.00 equiv., 0.5 mL C_6D_6).

4. Computational Methods

All the DFT calculations are performed with the Gaussian 09 package. Geometries were optimized using the B3LYP functional with the 6-31G(d,p) basis. No symmetry restrictions were applied to geometry optimization. Frequency calculations were done at the same level of theory on optimized geometries, and no imaginary frequencies were shown, confirming optimized geometries as local minima on their potential surfaces. Energies of

ethyl benzene, ethyl 1,2-azaborines and their cations are shown in Table SX. The enthalpy of reaction for hydride transfer between a benzylic cation and ethyl 1,2-azaborines was calculated as following: $\Delta H = (E_{BN\ cation} + E_{ethyl\ benzene}) - (E_{BN} + E_{benzylic\ cation})$ and converted to kcal mol^{-1} (1 E_h = 627.510 kcal mol^{-1}).

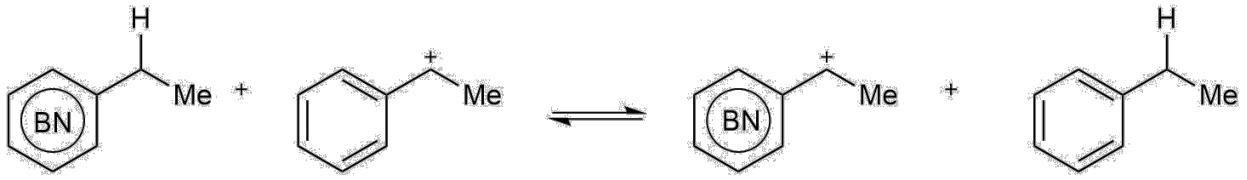
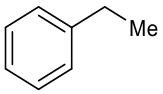
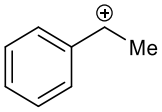
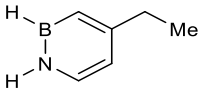
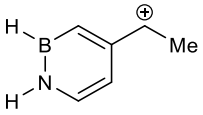
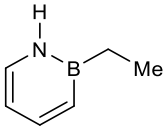
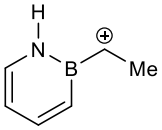
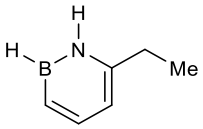
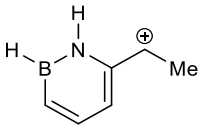
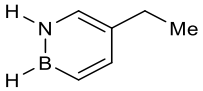
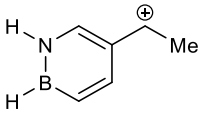
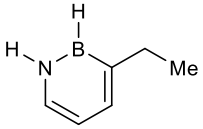
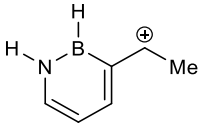
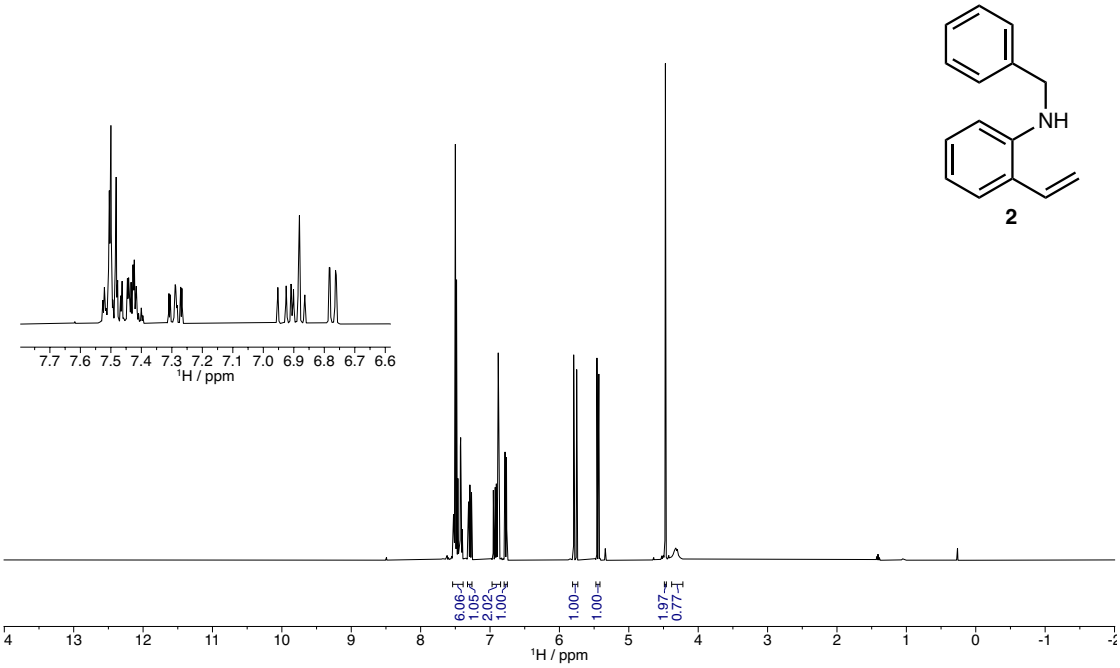


Table SX. Energies of ethyl benzene, ethyl 1,2-azaborines and their cations.

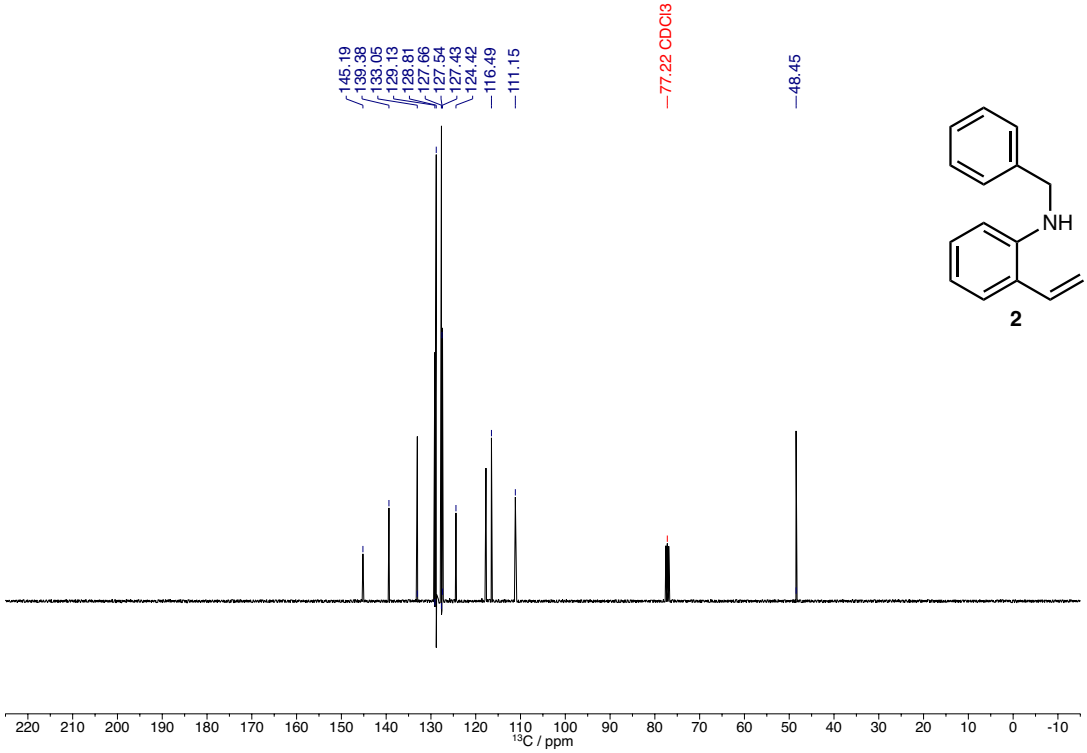
Ethyl benzene or ethyl 1,2-azaborines	Energy / E_h	Cations	Energy / E_h
	-310.8951		-310.0099
	-314.3259		-313.4271
	-314.3323		-313.4382
	-314.3286		-313.4367
	-314.3252		-313.4524
	-314.3250		-313.4634

5. NMR Spectra

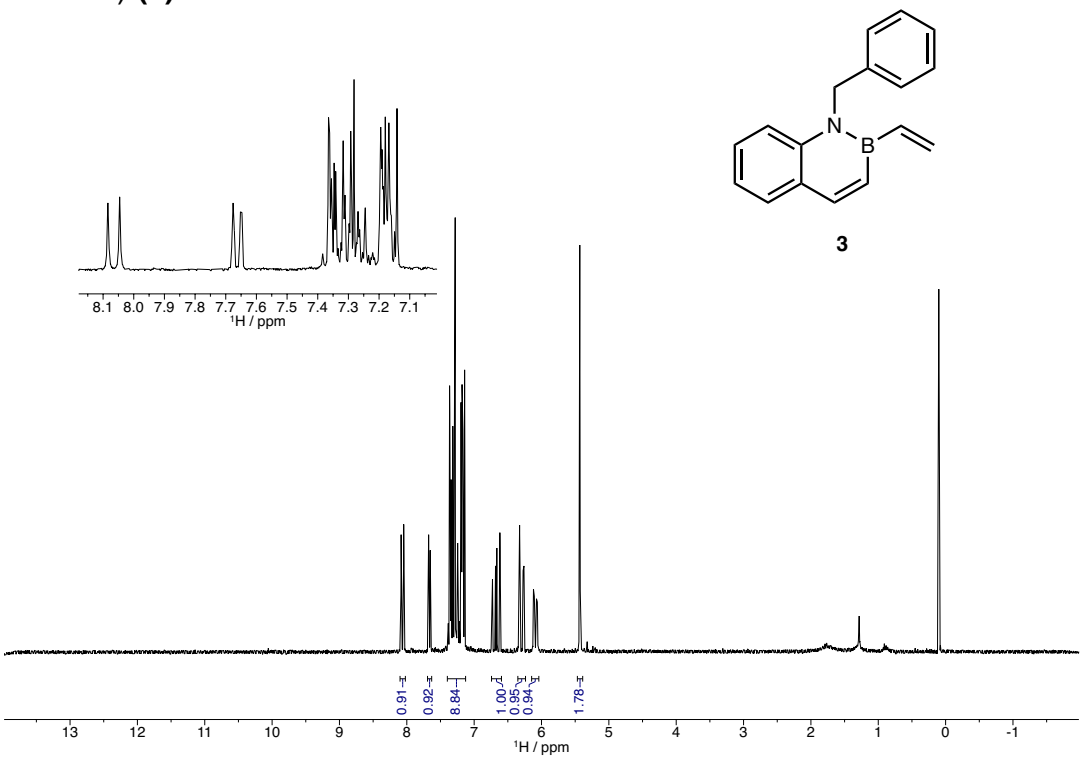
^{1}H NMR (400 MHz, $CDCl_3$) *N*-benzyl-2-vinylaniline (N-Bn 2-VA) **(2)**



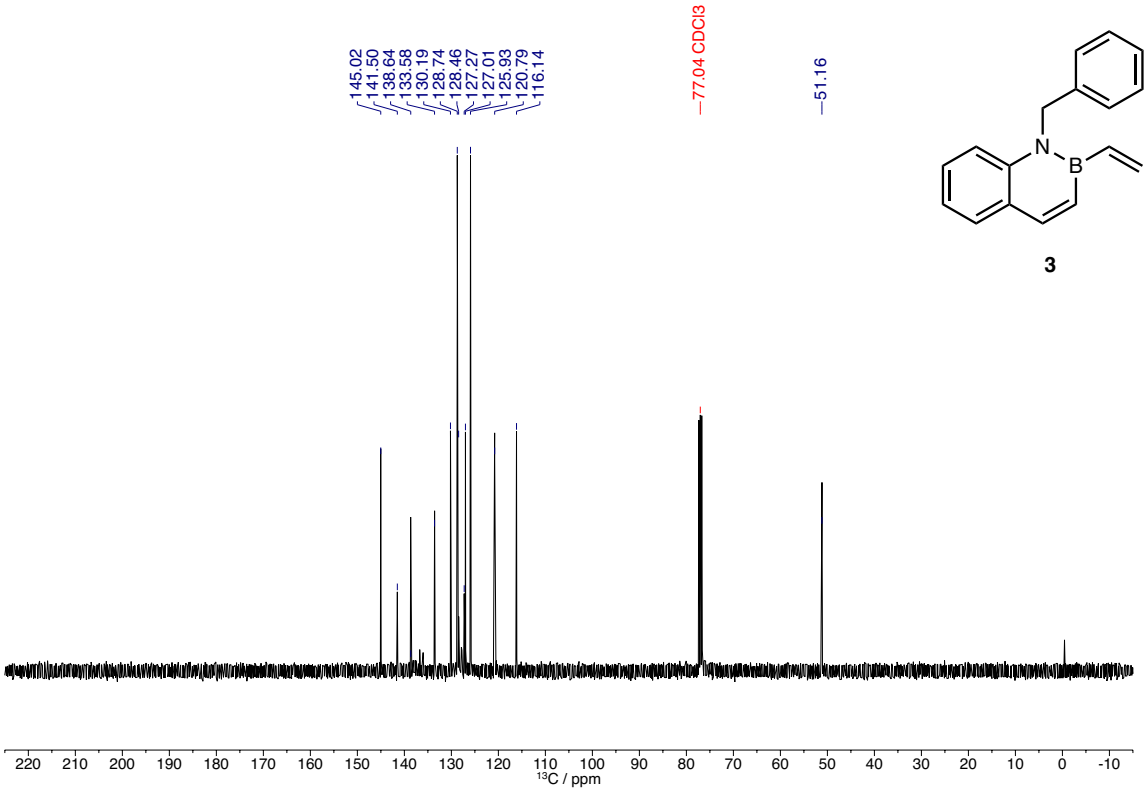
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) *N*-benzyl-2-vinylaniline (N-Bn 2-VA) **(2)**



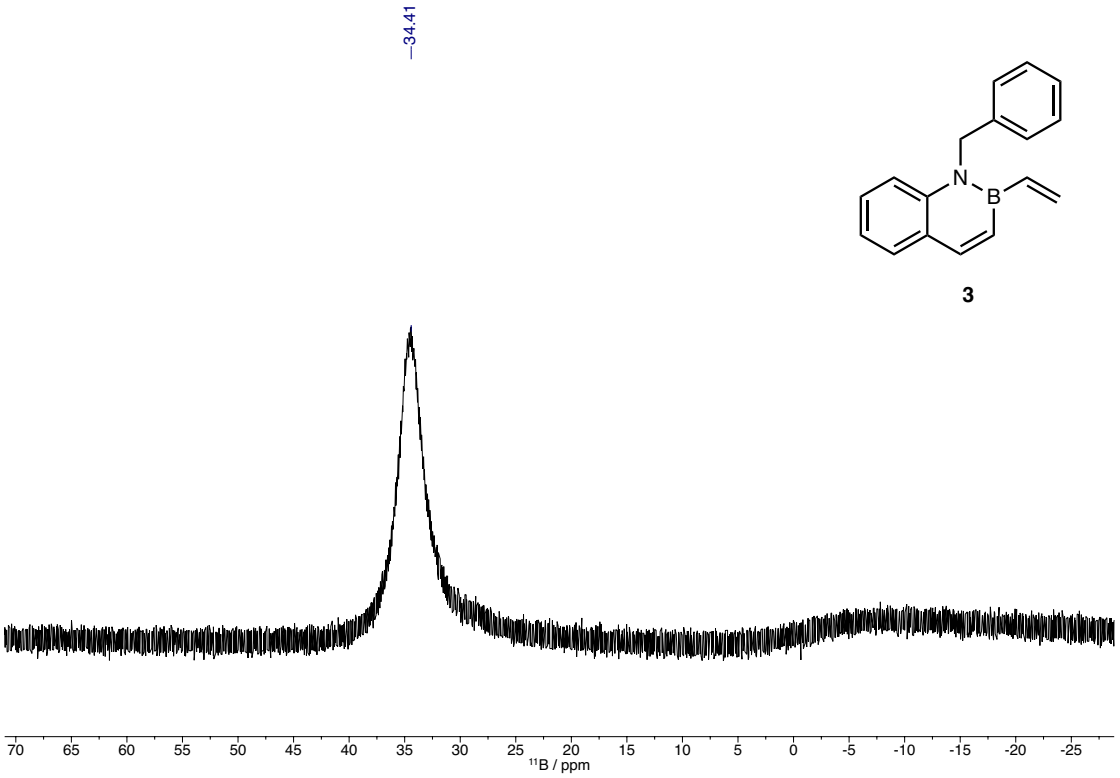
^{1}H NMR (400 MHz, $CDCl_3$) 1-benzyl-2-vinyl-1,2,3,4-tetrahydrobenzo[e][1,2]azaborinine (N-Bn BN2VN) **(3)**



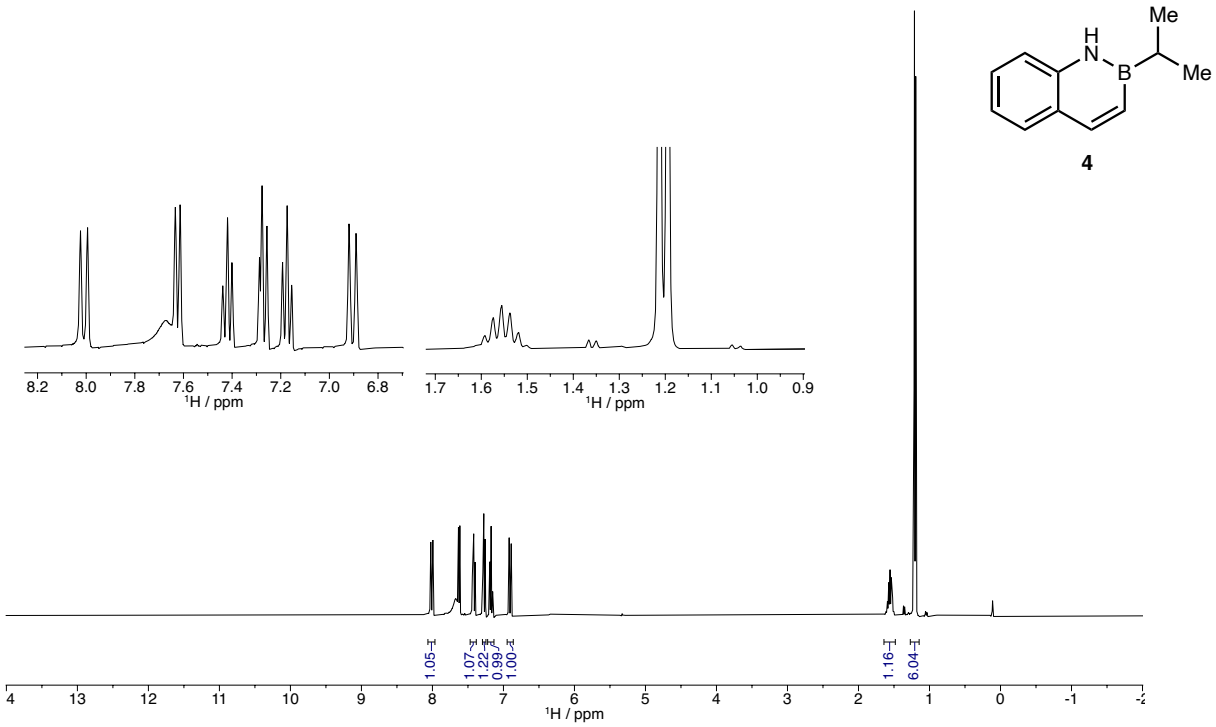
^{13}C {^{1}H} NMR (101 MHz, CDCl3) 1-benzyl-2-vinyl-1,2,3,4 tetrahydrobenzo[e][1,2]azaborinine (N-Bn BN2VN) **(3)**



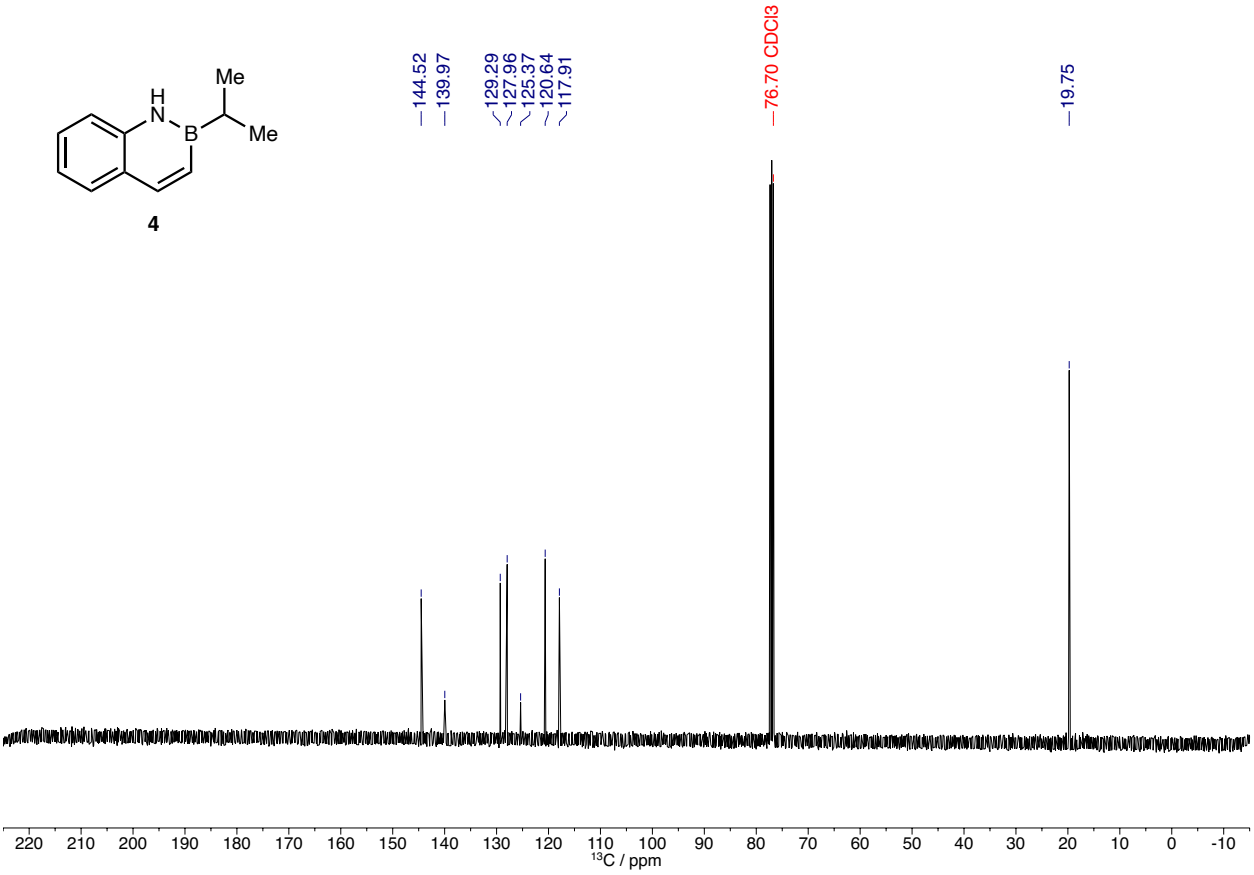
^{11}B NMR (128 MHz, $CDCl_3$) 1-benzyl-2-vinyl-1,2,3,4 tetrahydrobenzo[e][1,2]azaborinine (N-Bn BN2VN) **(3)**



^{1}H NMR (400 MHz, $CDCl_3$) 2-isopropyl-1,2-dihydrobenzo[*e*][1,2]azaborinine (BN2IN) **(4)**



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) 2-isopropyl-1,2-dihydrobenzo[*e*][1,2]azaborinine (BN2IN) **(4)**



5. References

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