

Supporting Information

**Gram-Scale Free Radical Polymerization of an Azaborine Vinyl Monomer**

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## 1. General Information

**General Experimental Procedures:** All reactions were conducted under a positive pressure of inert atmosphere (nitrogen or argon), unless stated otherwise. Standard Schlenk techniques were used in all syntheses conducted under inert atmosphere and all glassware was oven-dried overnight in a 175 °C oven and cooled to room temperature under vacuum.

**Instrumentation:**  $^1\text{H}$  NMR,  $^{11}\text{B}$  NMR, and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance III 400 MHz Spectrometer and chemical shifts are reported in parts per million (ppm). Spectra were recorded in chloroform-*d* or dichloromethane-*d*<sub>2</sub> with the residual solvent peak as the internal standard ( $^1\text{H}$  NMR:  $\text{CHCl}_3$ ,  $\delta = 7.26$  ppm;  $\text{CH}_2\text{Cl}_2$ ,  $\delta = 5.32$  ppm.  $^{13}\text{C}$  NMR:  $\text{CHCl}_3$ ,  $\delta = 77.16$  ppm;  $\text{CH}_2\text{Cl}_2$ ,  $\delta = 53.84$  ppm).  $^{11}\text{B}$  NMR spectra are externally referenced to boron trifluoride diethyl etherate ( $\text{BF}_3 \bullet \text{Et}_2\text{O}$ ,  $\delta = 0$  ppm). Carbons bound to boron are not observed due to the quadrupolar relaxation of boron. Broad signals at  $\sim \delta = 2.7$  ppm in the  $^{11}\text{B}$  NMR spectrum are due to boron contained in probe components; all polymer spectra were acquired using quartz NMR tubes from Norell. Multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), 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. Polymer molecular weights were measured by gel permeation chromatography (GPC) on a Tosoh Bioscience EcoSEC GPC workstation using butylated hydroxytoluene stabilized tetrahydrofuran (THF) as the eluent ( $0.35 \text{ mL min}^{-1}$ , 40 °C) through TSKgel SuperMultipore HZ-M guard column (4.6 mm ID x 2.0 cm, 4  $\mu\text{m}$ , Tosoh Bioscience) and a TSKgel SuperMultipore HZ-M column (4.6 mm ID x 15 cm, 4  $\mu\text{m}$ , Tosoh Bioscience). Polystyrene standards (EasiVial PS-M, Agilent) were used to build a calibration curve. Processing was performed using EcoSEC Data Analysis software (Version 1.14, Tosoh Bioscience). Polymers were dissolved in THF ( $1 \text{ mg mL}^{-1}$ ), filtered (Millex-FG Syringe Filter Unit, 0.20  $\mu\text{m}$ , PTFE, EMD Millipore), and injected using an auto-sampler (5  $\mu\text{L}$ ). UV-Vis spectroscopy was performed on a Shimadzu UV-1800 UV-Vis spectrophotometer. The spectra were measured at room temperature in non-stabilized THF in a quartz cuvette (10 mm). Fluorescence spectroscopy was performed on a Photon Technology International, Inc. QuantaMaster 40 spectrofluorometer equipped with an Ushio short-arc xenon gas discharge lamp. The spectra were measured at room temperature in non-stabilized THF in a quartz cuvette (10 mm) and all solutions were dilute ( $\lambda_{\text{max}} < 0.1$  abu) to minimize re-absorption effects. Processing was done using FeliX32 Analysis (Version 1.2, Build 56, Photon Technology International, Inc.). Elemental analysis was performed by Robertson Microlit Laboratories.

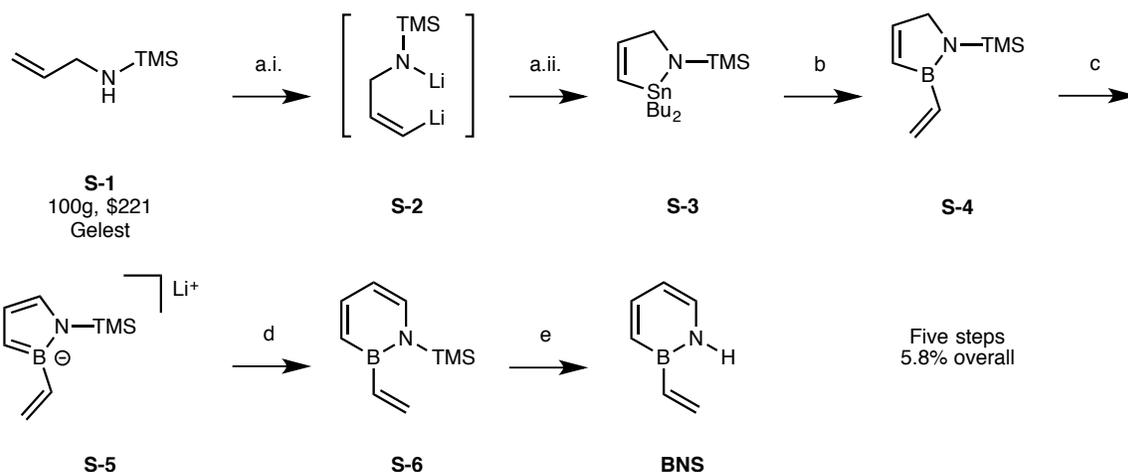
**Materials:** Unless otherwise specified, all chemicals were used as purchased without further purification. Solvents used for column chromatography and polymer workup were reagent grade and used as received. Reaction solvent toluene (Fisher, certified ACS) was dried on a J. C. Meyer Solvent Dispensing 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. 2-Vinylnaphthalene (**2VN**) (Sigma Aldrich, 95%) was sublimed at room temperature and 1.3 Torr, then stored in a glove box freezer (-20 °C) until future use. Triethylamine (Sigma Aldrich, >99%) was dried over potassium hydroxide overnight and distilled under argon just prior to use. UV-Vis and fluorescence studies

were performed in non-stabilized THF from EMD Millipore. GPC studies were performed in butylated hydroxytoluene stabilized THF from EMD Millipore.

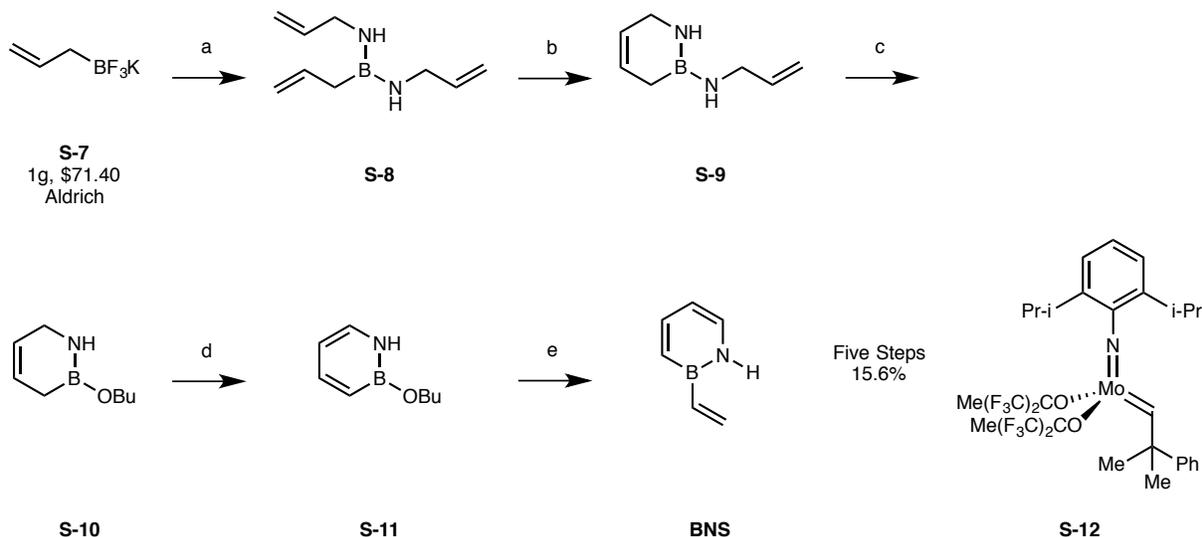
2,2'-Azobis(2-methylpropionitrile) (AIBN) (recrystallized, 99%), AIBN solution (0.2 M, toluene), celite, cyclopentyl methyl ether (CPME) (anhydrous, 99.9%), dichloromethane, hexanes, methanol, potassium hydroxide, potassium vinyltrifluoroborate (95%), and silicon tetrachloride (SureSeal, 99%) were purchased from Sigma Aldrich.

Chloroform-*d* (D, 99.8%) and dichloromethane-*d*<sub>2</sub> (D, 99.8%) were purchased from Cambridge Isotope Laboratories, Inc. Toluene (for polymer elution) was purchased from EMD Milipore. Quinine hemisulfate monohydrate (purum for fluorescence, ≥98%) was purchased from Fluka. 2-Aminophenethyl alcohol (**1**, 97% or 95%) was purchased from Sigma Aldrich (or TCI America).

## 2. Azaborine Vinyl Monomer Syntheses



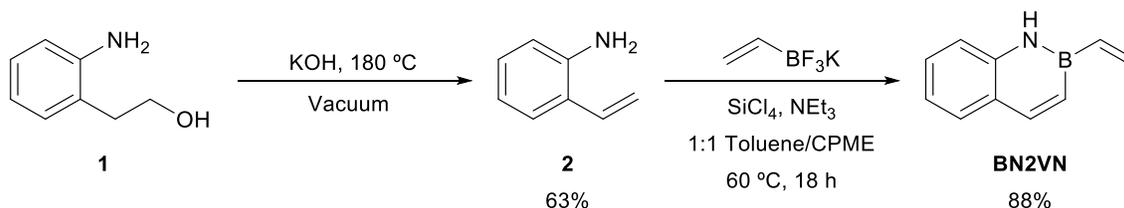
**Figure S1.** Ashe Synthesis of BN Styrene (BNS).<sup>1</sup> a) i. n-BuLi, Et<sub>2</sub>O, 0 → 23 °C, 24 h; ii. Cl<sub>2</sub>Sn(n-Bu)<sub>2</sub>, Et<sub>2</sub>O, -50 °C, 44%; b) BCl<sub>3</sub>, Bu<sub>3</sub>SnCHCH<sub>2</sub>; then S-3, pentane, -78 → 23 °C, 77% c) LDA, Et<sub>2</sub>O, -78 → 23 °C, 72%; d) LDA, Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>, -78 → 23 °C, 34%; e) TBAF, THF, 0 → 23 °C, 70%. TMS = trimethylsilyl, Bu = butyl, LDA = lithium diisopropylamide, TBAF = tetrabutylammonium fluoride.



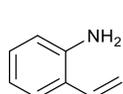
**Figure S2.** Liu Synthesis of BNS.<sup>2</sup> a) allylamine, TMSCl, MeCN, reflux, 57%; b) 3 mol% **S-12**, CH<sub>2</sub>Cl<sub>2</sub>, 94%; c) n-BuOH, CH<sub>2</sub>Cl<sub>2</sub>; d) Pd/C, cyclohexene, 60 °C, 47% (two steps); e) CH<sub>2</sub>CHMgBr, Et<sub>2</sub>O, -30 °C; HCl, 62%. TMS = trimethylsilyl, Bu = butyl.

### 3. Experimental Procedures

#### 3.1 Monomer Synthesis



#### 2-Aminostyrene (2)



This reaction is adapted from Hoveyda *et al.*<sup>3</sup>

An oven-dried 100 mL Schlenk flask equipped with a rare-earth<sup>i</sup> stir bar, short path distillation head, and tared receiving flask was cooled under vacuum and backfilled with argon. To the Schlenk flask was added 2-aminophenethyl alcohol (1) (1 equiv., 15.0 g, 109 mmol) and potassium hydroxide pellets (1 equiv., 6.1 g, 109 mmol). The entire distillation apparatus was purged and backfilled three times with argon, then returned to vacuum and heated to 180 °C. As the potassium hydroxide begins to melt the reaction mixture changes color from brown/purple to green. With continued heating and applied vacuum (1.3 Torr) the clear product distills over (83-90 °C) to the tared receiving flask which was ultimately sealed under argon with a septum and stored in the glove box for future use (yield 6.2 g, 63%).

Note: Depending on the source of 2-aminophenethyl alcohol, there may be contamination with dimethyl sulfoxide (DMSO) which co-distills with 2. DMSO may be removed with successive liquid-liquid extractions with deionized water, however DMSO contamination showed no noticeable effect on subsequent reactions.

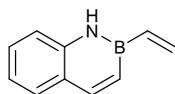
$\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.29 (1 H, ddt, *J* 7.7, 1.6, 0.5), 7.14 – 7.04 (1 H, m), 6.84 – 6.72 (2 H, m), 6.69 (1 H, ddd, *J* 8.0, 1.2, 0.4), 5.64 (1 H, dd, *J* 17.4, 1.5), 5.33 (1 H, dd, *J* 11.0, 1.5), 3.75 (2 H, s).  $\delta_{\text{C}}$  (101 MHz, CDCl<sub>3</sub>) 143.77, 132.87, 128.85, 127.46, 124.22, 119.05, 116.20, 115.82.

$\delta_{\text{C}}$  (101 MHz, CDCl<sub>3</sub>) 143.77, 132.87, 128.85, 127.46, 124.22, 119.05, 116.20, 115.82.

HRMS (EI)  $m/z$  [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>9</sub>N 119.0735; Found 119.07365.

Data collected match published material on this compound,<sup>3,4</sup> therefore no further spectra were obtained.

#### 2-Vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (BN2VN)



This procedure was adapted from Molander *et al.*<sup>4</sup>

An oven-dried 500 mL Schlenk flask equipped with a stir bar and septum sealed reflux condenser was charged with potassium vinyltrifluoroborate (1.1 equiv., 18.6 mmol, 2.49 g) and purged and backfilled three times with argon. 2 (1 equiv., 16.9 mmol, 2.01 g), toluene (75 mL), cyclopentyl methyl ether (CPME) (75 mL), triethylamine (1.5 equiv., 25.3 mmol, 3.5 mL), then silicon tetrachloride (1.1 equiv., 18.6 mmol, 2.1 mL) were added and the reaction mixture was heated to 60 °C for 18 hours with stirring. The reaction mixture was cooled to room temperature, diluted with hexanes (100 mL), and passed through a plug of celite

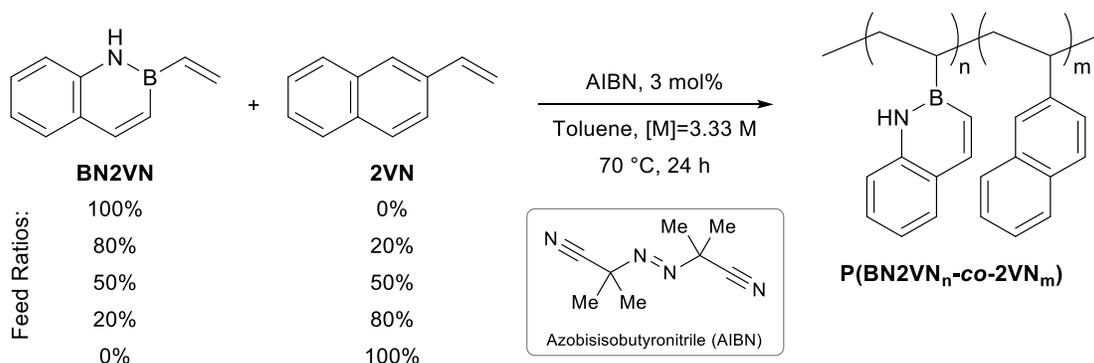
<sup>i</sup> A stronger magnet provided better stirring (Fischer Scientific Catalog No. 14-513-511).

to remove solids, washing with hexanes (100 mL). The eluent was collected and concentrated by rotary evaporation. The product was purified by silica gel chromatography, eluting with hexanes, then ramping to 10% dichloromethane in hexanes. Fractions were concentrated by rotary evaporation and dried on vacuum (for a limited time due to sublimation, usually ~ 5 hours) to yield a white solid which was stored in a glove box freezer (-20 °C) for future use (yield 2.3 g, 88%).

Note: A 40% reduction in amount of toluene and CPME used led to only minor decreases in yield. This is advantageous for large scale reactions (**2**, >2 g), however vigorous stirring is needed to allow the reaction to become homogeneous after addition of silicon tetrachloride. Pure **2** can also be isolated by sublimation at room temperature and 1.3 Torr, following celite filtration.

$\delta_{\text{H}}$ (400 MHz, CD <sub>2</sub> Cl <sub>2</sub> )	8.09 (1 H, d, <i>J</i> 11.5), 7.92 (1 H, s), 7.66 (1 H, ddt, <i>J</i> 7.8, 1.3, 0.6), 7.45 (1 H, ddd, <i>J</i> 8.4, 7.1, 1.5), 7.29 (1 H, ddt, <i>J</i> 8.1, 1.3, 0.6), 7.22 (1 H, ddd, <i>J</i> 7.9, 7.1, 1.2), 7.12 (1 H, dd, <i>J</i> 11.5, 2.0), 6.56 (1 H, dd, <i>J</i> 19.6, 13.3), 6.31 (1 H, dd, <i>J</i> 19.7, 3.7), 6.11 (1 H, dd, <i>J</i> 13.6, 3.5).
$\delta_{\text{C}}$ (101 MHz, CD <sub>2</sub> Cl <sub>2</sub> )	145.46, 140.61, 132.63, 129.86, 128.82, 126.33, 121.52, 118.66.
$\delta_{\text{B}}$ (128 MHz, CD <sub>2</sub> Cl <sub>2</sub> )	32.45.
HRMS (EI)	<i>m/z</i> [M] <sup>+</sup> Calcd for C <sub>10</sub> H <sub>10</sub> BN 155.0906; Found 155.09057.
Anal.	Found: C, 77.4; H, 6.4; N, 9.1. Calc. for C <sub>10</sub> H <sub>10</sub> BN: C, 77.5; H, 6.5; N, 9.0.
Melting point:	66 °C.

## 3.2 Polymerization



### 3.2.1 General Procedure A

An oven-dried 15 mL heavy walled cylindrical pressure vessel equipped with a small stir bar was brought into the glove box and charged with the appropriate monomer(s) (2 mmol total), toluene (0.3 mL), and AIBN (0.2 M in toluene, 3 mol%, 0.06 mmol, 0.3 mL). The pressure vessel was tightly sealed with a Teflon cap, brought out of the glove box, wrapped in aluminum foil, and heated (in a pre-heated pie plate) to 70 °C for 24 hours with vigorous stirring. Polymerization was quenched by opening the reaction flask in air and immediately pipetting the solution into a beaker of methanol (30 mL). Over the course of 30 minutes the polymer precipitated from solution and was isolated by filtering off the methanol solution through a plug of celite. Collected polymer was washed with additional methanol (20 mL), then eluted with toluene (20 mL) into an empty round bottom flask. The toluene polymer solution was concentrated by rotary evaporation, re-dissolved in toluene (5 mL), and once again precipitated into methanol (30 mL). The second precipitation yielded a more powdery precipitate, which was filtered over a plug of celite, washed with methanol (20 mL), and then eluted with dichloromethane (20 mL) into an empty round bottom flask. The polymer solution was concentrated by rotary evaporation, transferred to a tared scintillation vial for storage, dried on the Schenk line for about 30 min, and then finally dried in a vacuum oven for about 36 hours at 85 °C.

#### PBN2VN

Synthesized according to General Procedure A using **BN2VN** (2 mmol, 309.9 mg) (yield 178.1 mg, 58%).

$\delta_{\text{H}}$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 8.17 – 5.43 (5 H, m), 2.26 – 0.46 (3 H, m).

$\delta_{\text{C}}$  (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 144.26, 140.44, 129.67, 128.40, 125.73, 120.92, 118.21.

$\delta_{\text{B}}$  (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 31.2 (br).

Anal. Found: C, 77.1; H, 6.2; N, 9.1. Calc. for C<sub>10</sub>H<sub>10</sub>BN: C, 77.5; H, 6.5; N, 9.0.

#### P(BN2VN<sub>74</sub>-co-2VN<sub>26</sub>)

Synthesized according to General Procedure A using **BN2VN** (1.6 mmol, 248.7 mg) and **2VN** (0.4 mmol, 61.6 mg) (yield 167.6 mg, 54%).

$\delta_{\text{H}}$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 8.32 – 6.04 (6 H, m), 3.13 – 0.21 (3 H, m).

$\delta_{\text{C}}$  (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 144.38, 140.41, 133.91, 132.64, 129.62, 127.97, 125.72, 120.93, 118.18.

$\delta_B$  (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 33.1 (br).

Anal. Found: C, 81.0; H, 6.7; N, 6.8. Calc. for [C<sub>10</sub>H<sub>10</sub>BN]<sub>0.74</sub>[C<sub>12</sub>H<sub>10</sub>]<sub>0.26</sub>: C, 81.6; H, 6.5; N, 6.7.

#### **P(BN2VN<sub>49</sub>-co-2VN<sub>51</sub>)**

Synthesized according to General Procedure A using **BN2VN** (1 mmol, 156.1 mg) and **2VN** (1 mmol, 154.2 mg) (yield 190.5 mg, 61%).

$\delta_H$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 8.07 – 6.37 (6 H, m), 2.38 – 0.39 (3 H, m).

$\delta_C$  (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 144.20, 139.81, 133.39, 132.14, 129.13, 127.52, 127.37, 126.60, 125.67, 125.29, 125.00, 120.50, 117.72, 40.90.

$\delta_B$  (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 33.2 (br).

Anal. Found: C, 85.6; H, 6.2; N, 3.6. Calc. for [C<sub>10</sub>H<sub>10</sub>BN]<sub>0.49</sub>[C<sub>12</sub>H<sub>10</sub>]<sub>0.51</sub>: C, 85.6; H, 6.5; N, 4.4.

#### **P(BN2VN<sub>9</sub>-co-2VN<sub>91</sub>)**

Synthesized according to General Procedure A using **BN2VN** (0.4 mmol, 61.9 mg) and **2VN** (1.6 mmol, 245.6 mg) (yield 171.1 mg, 56%).

$\delta_H$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.95 – 6.12 (7 H, m), 2.26 – 1.22 (3 H, m).

$\delta_C$  (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 142.88, 133.85, 132.59, 127.99, 127.79, 127.23, 126.14, 125.78, 125.44, 41.16.

$\delta_B$  (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 34.5 (br).

Anal. Found: C, 91.0; H, 6.0; N, 0.71. Calc. for [C<sub>10</sub>H<sub>10</sub>BN]<sub>0.09</sub>[C<sub>12</sub>H<sub>10</sub>]<sub>0.91</sub>: C, 92.0; H, 6.5; N, 0.81.

#### **P2VN**

Synthesized according to General Procedure A using **2VN** (2 mmol, 308.4 mg) (yield 271.0 mg, 88%).

$\delta_H$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 8.07 – 6.18 (7 H, m), 2.54 – 1.38 (3 H, m).

$\delta_C$  (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 143.49, 142.98, 133.90, 132.63, 128.03, 127.85, 127.20, 126.14, 125.48, 41.19.

Anal. Found: C, 92.3; H, 6.2; N, 0.12. Calc. for C<sub>12</sub>H<sub>10</sub>: C, 93.5; H, 6.5. Found nitrogen incorporation likely reflects AIBN end groups.

### 3.2.2 Large Scale Polymerization of BN2VN

An oven-dried 15 mL heavy walled cylindrical pressure vessel equipped with a rare-earth<sup>ii</sup> stir bar was brought into the glove box and charged with **BN2VN** (17.9 mmol, 2.77 g), toluene (2.7 mL), and AIBN (0.2 M in toluene, 3 mol%, 0.54 mmol, 2.7 mL). The pressure vessel was tightly sealed with a Teflon cap, brought out of the glove box, wrapped in aluminum foil, and heated (in a pre-heated pie plate) to 70 °C for 24 hours with vigorous stirring. Polymerization was quenched by opening the reaction flask in air and immediately pipetting the solution into a beaker of methanol (200 mL). Over the course of 30 minutes the polymer precipitated from solution and was isolated by filtering off the methanol solution through a plug of celite. Collected polymer was washed with additional methanol (150 mL), then eluted with toluene (250 mL) into an empty round bottom flask. The toluene polymer solution was concentrated by rotary evaporation (to ~ 6 mL) and once again precipitated into methanol (200 mL). The second precipitation yielded a more powdery precipitate, which was filtered over a plug of celite, washed with methanol (150 mL), and then eluted with dichloromethane (200 mL) into an empty round bottom flask. The polymer solution was concentrated by rotary evaporation, divided among tared scintillation vials (3) for storage, concentrated by rotary evaporation, and then finally dried in a vacuum oven for about 36 hours at 85 °C (yield 2.04 g, 74%).

$\delta_{\text{H}}$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 8.30 – 5.46(7 H, m), 2.39 – 0.43 (3 H, m).

$\delta_{\text{C}}$  (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 143.82, 140.13, 129.16, 127.89, 125.23, 120.42, 117.73.

$\delta_{\text{B}}$  (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 32.8 (br).

Anal. Found: C, 77.1; H, 6.2; N, 9.1. Calc. for C<sub>10</sub>H<sub>10</sub>BN: C, 77.5; H, 6.5; N, 9.0.

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<sup>ii</sup> A stronger magnet provided better stirring (Fischer Scientific Catalog No. 14-513-511).

### 3.2.3 Tabulated Details of Reaction Variables

**Table S1.** Influence of initiator concentration, temperature, and solvent on **PBN2VN** molecular weight characteristics.

Entry	AIBN (mol%)	Time (h)	Temperature (°C)	Monomer Concentration (M)	M <sub>n</sub> (Da) <sup>a</sup>	M <sub>w</sub> (Da) <sup>a</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>a</sup>
1	3	24	70	3.33	6040	8660	1.43
2	3	48	70	3.33	4610	5790	1.26
3	1	24	70	3.33	5630	7030	1.25
4	1	48	70	3.33	5460	6770	1.24
5	1	72	85	n/a	8900	13700	1.54

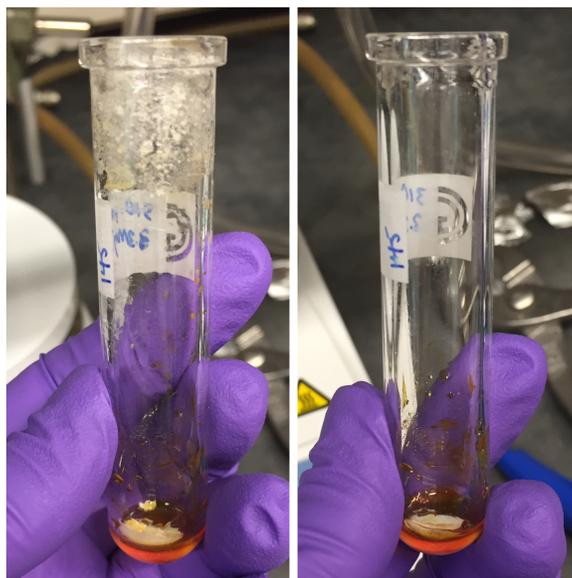
<sup>a</sup> Measured by gel permeation chromatography (GPC) at 254 nm relative to polystyrene standard (THF, 0.35 mL min<sup>-1</sup>, 40 °C).

### 3.2.4 Solvent-Free Polymerization

An oven-dried 2-5 mL microwave vial equipped with a small stir bar was brought into the glove box and charged with **BN2VN** (2 mmol, 310.1 mg) and AIBN (1 mol%, 3.3 mg). The microwave vial was crimped with an aluminum/PTFE/silicone septum seal, brought out of the glove box, wrapped in aluminum foil, and heated (in a pre-heated pie plate) to 85 °C for 72 hours with vigorous stirring. Polymerization was quenched by opening the microwave vial in air, dissolving the solid polymer in dichloromethane (10 mL), and immediately pipetting the solution into a beaker of methanol (30 mL). Over the course of 30 minutes the polymer precipitated from solution and was isolated by filtering off the methanol solution through a plug of celite. Collected polymer was washed with additional methanol (20 mL) then eluted with dichloromethane (20 mL) into an empty round bottom flask. The dichloromethane polymer solution was concentrated by rotary evaporation, re-dissolved in dichloromethane (5 mL), and once again precipitated into methanol (30 mL). The second precipitation yielded a more powdery precipitate, which was filtered over a plug of celite, washed with methanol (20 mL), and then eluted with dichloromethane (20 mL) into an empty round bottom flask. The polymer solution was concentrated by rotary evaporation, transferred to a tared scintillation vial for storage, dried on the Schenk line for about 30 min, and then finally dried in a vacuum oven for about 36 hours at 85 °C (yield 119.5 mg, 39%).

Note: Due to the readiness of **BN2VN** to evaporate and condense at elevated temperatures in the absence of solvent, some monomer amassed at the top of the microwave vial (below, left). In order to limit characterization to the bulk polymer, the microwave vial was inverted and the top two thirds of the microwave vial was rinsed with dichloromethane (below, right). Potential for non-representative polymerization above the bulk is possible due to splashing of the less viscous reaction mixture during early stages of polymerization.

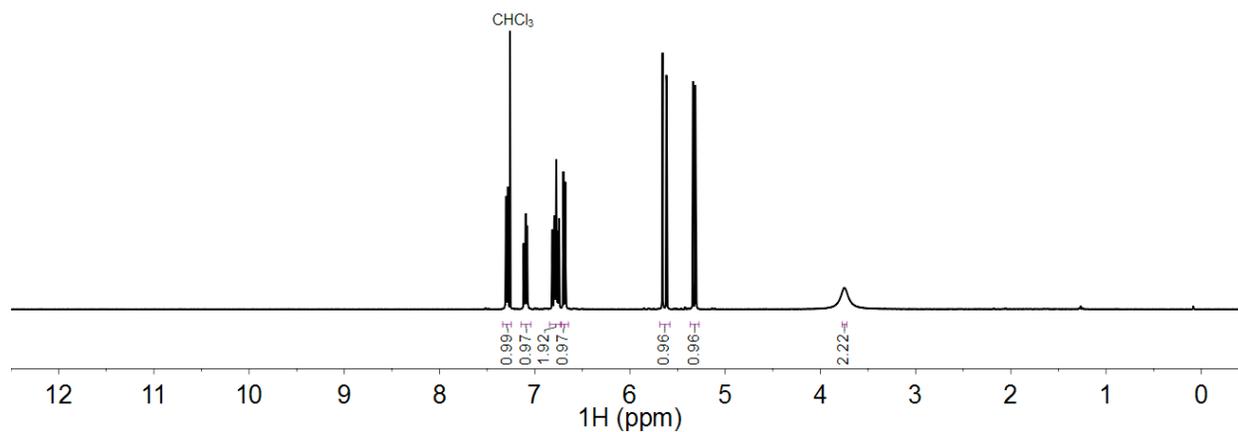
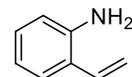
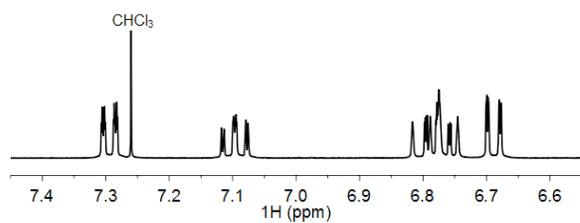
$\delta_{\text{H}}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) 8.19 – 5.43 (6 H, m), 2.56 – 0.32 (3 H, m).



**Figure S3.** Image of bulk polymerization reaction vessel. Left: condensed monomer appears at top of vial and bulk material at bottom. Right: Bulk reaction after removing condensed monomer.

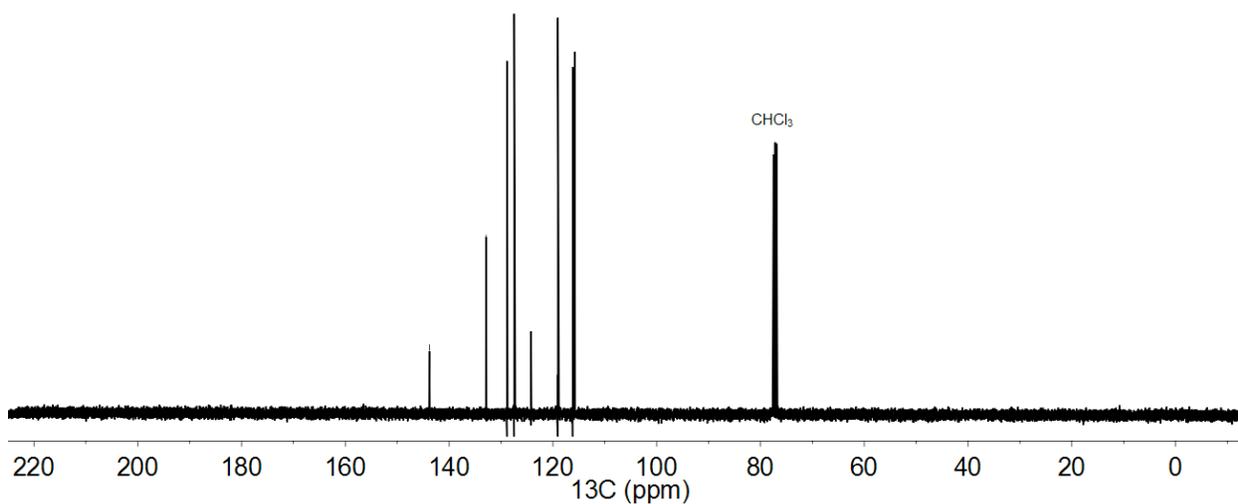
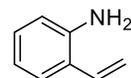
## 4. NMR Spectra

### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz) 2-Aminostyrene (2)

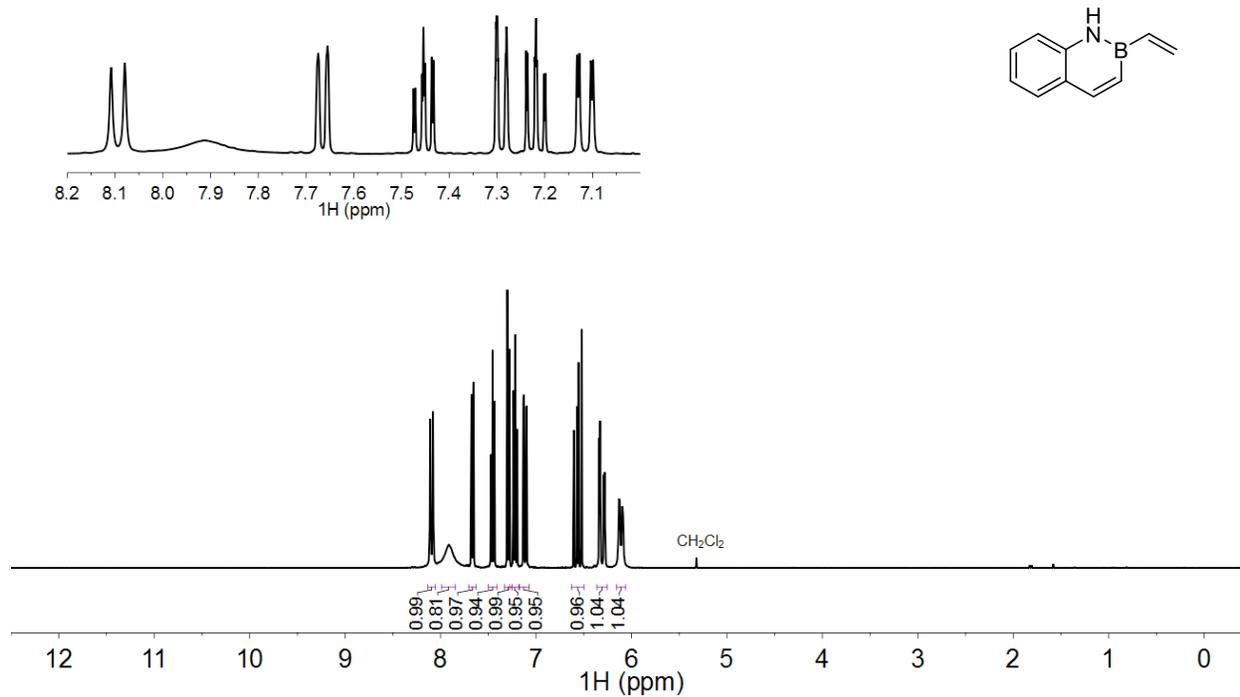


### $^{13}\text{C}$ $\{^1\text{H}\}$ NMR ( $\text{CDCl}_3$ , 101 MHz) 2-Aminostyrene (2)

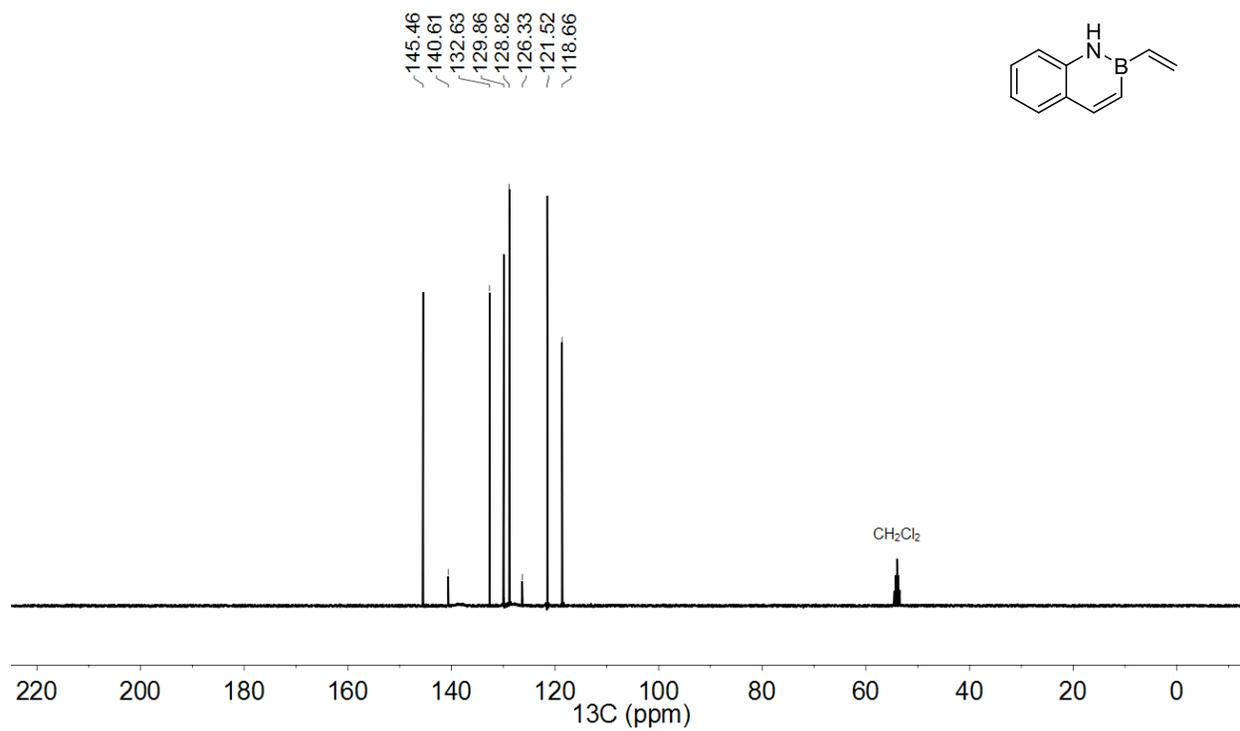
143.77  
132.87  
128.85  
127.46  
124.22  
119.05  
116.20  
115.82



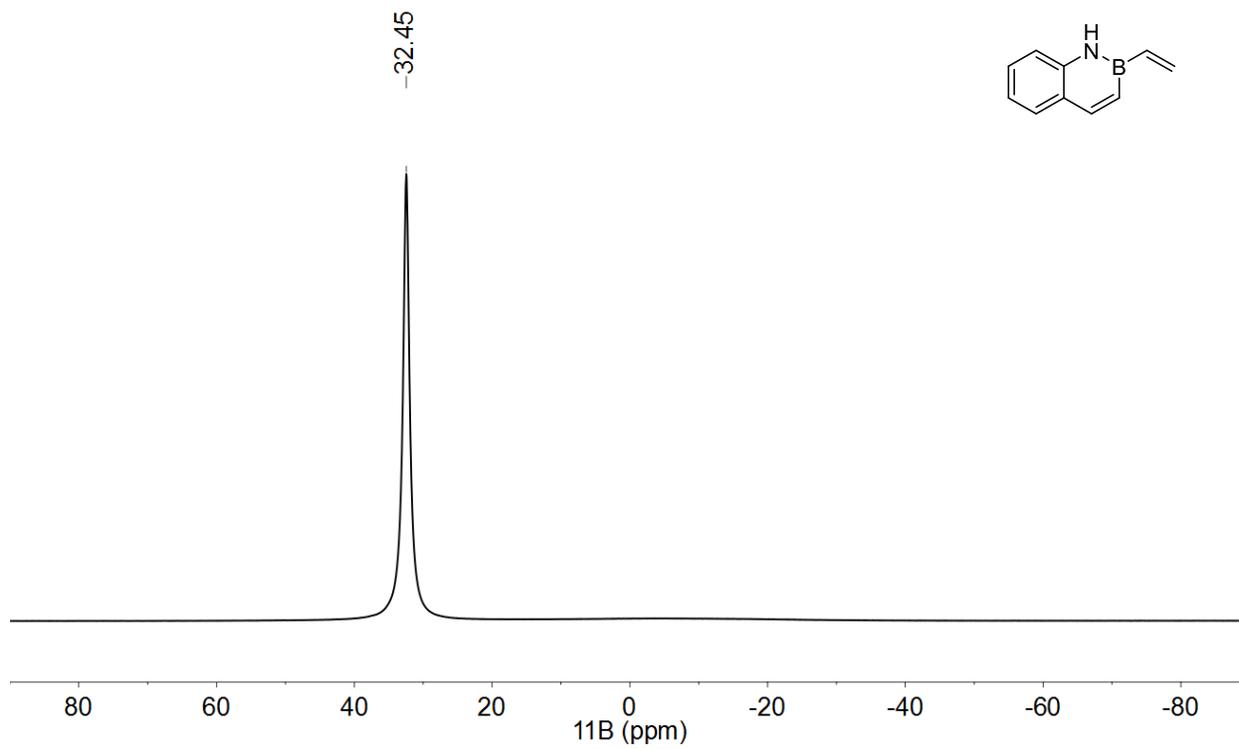
**$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz) 2-Vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (BN2VN)**



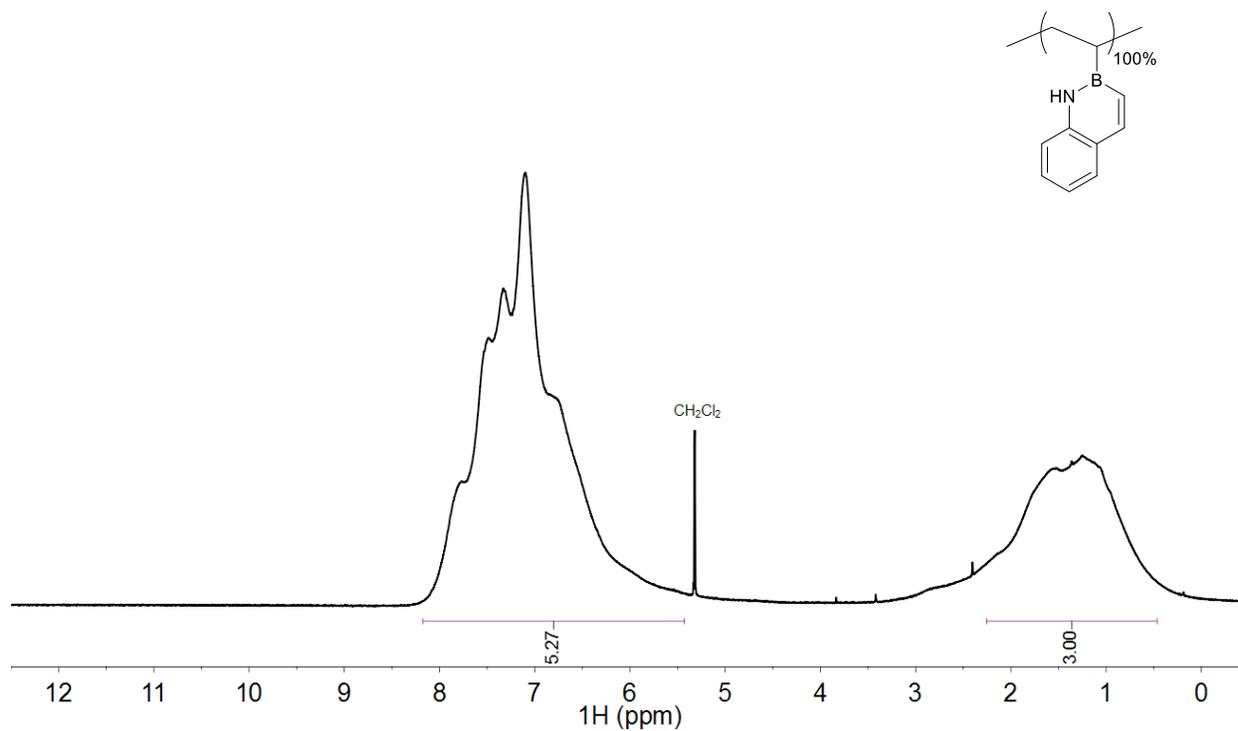
**$^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 101 MHz) 2-Vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (BN2VN)**



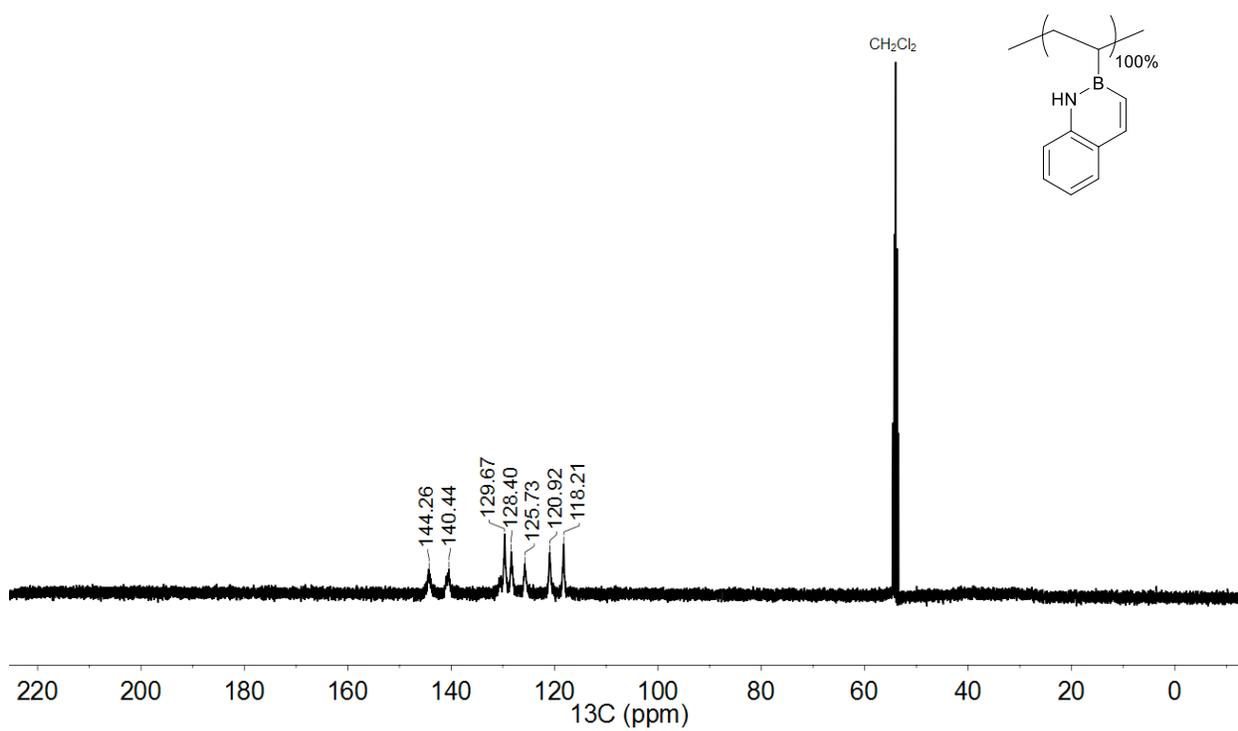
**$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) 2-Vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (BN2VN)**



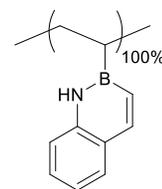
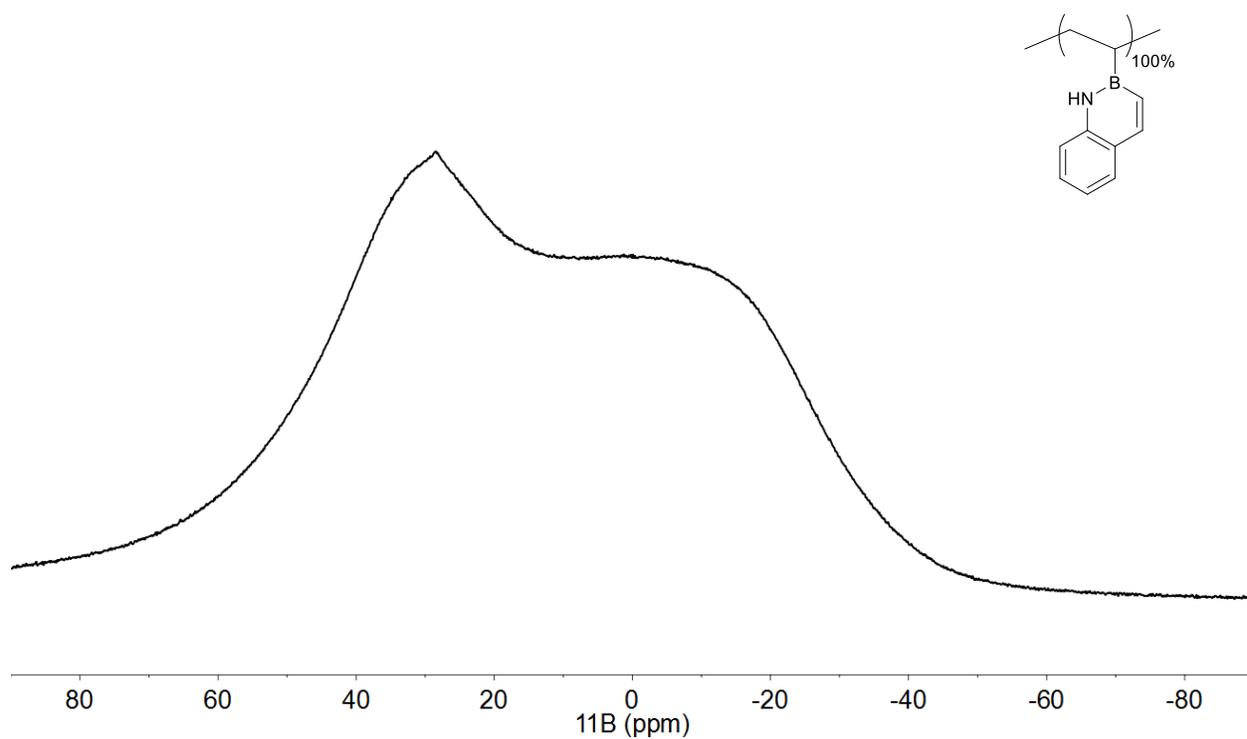
**$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz) PBN2VN**



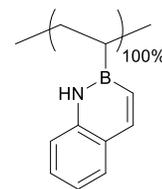
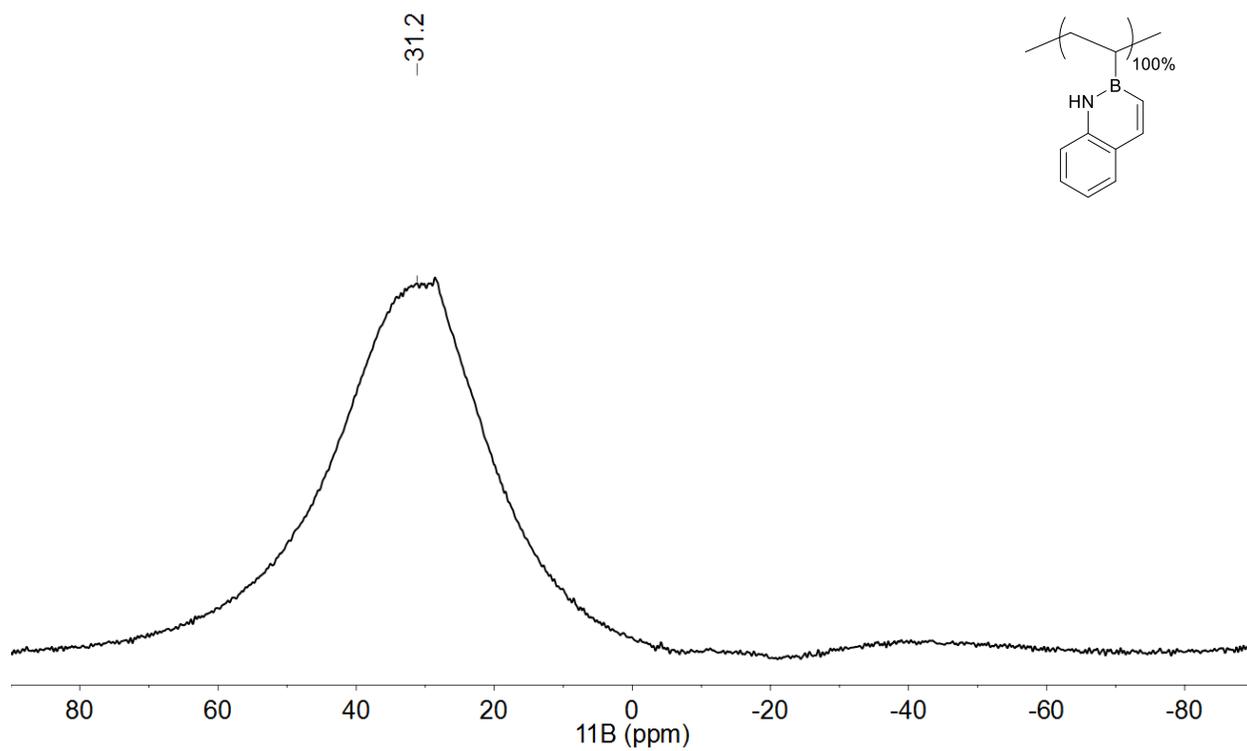
**$^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 101 MHz) PBN2VN**



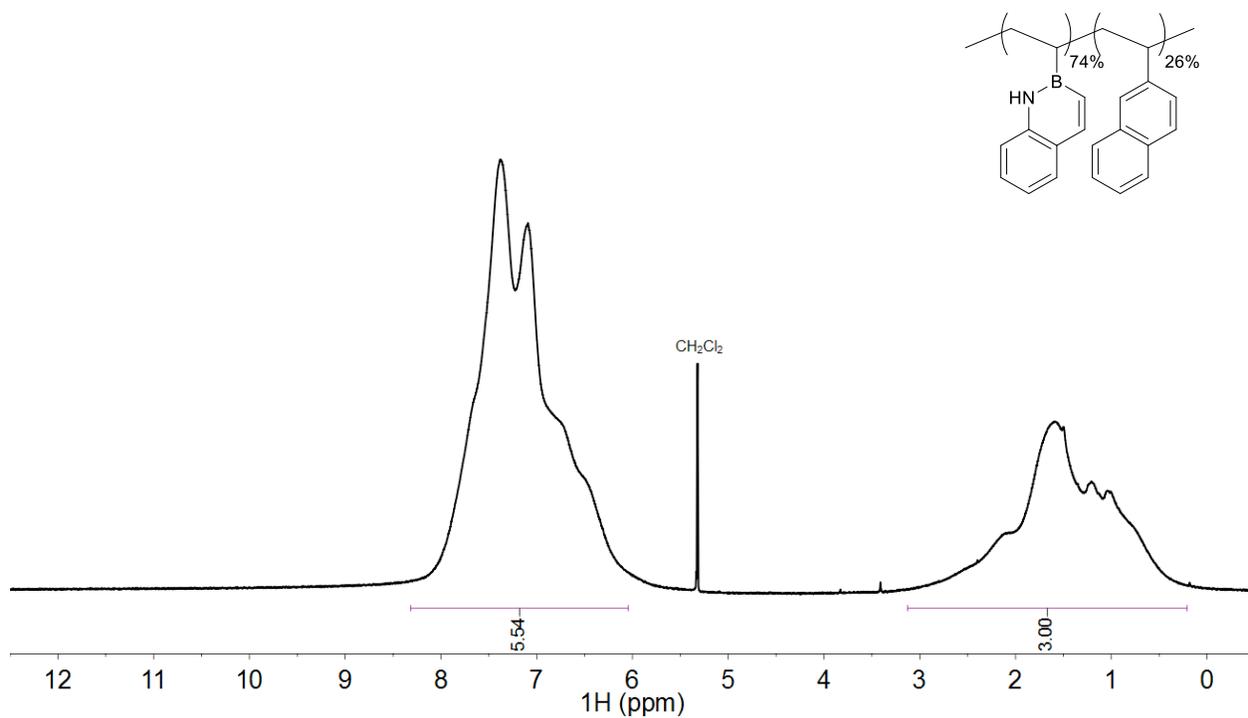
**$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) PBN2VN**



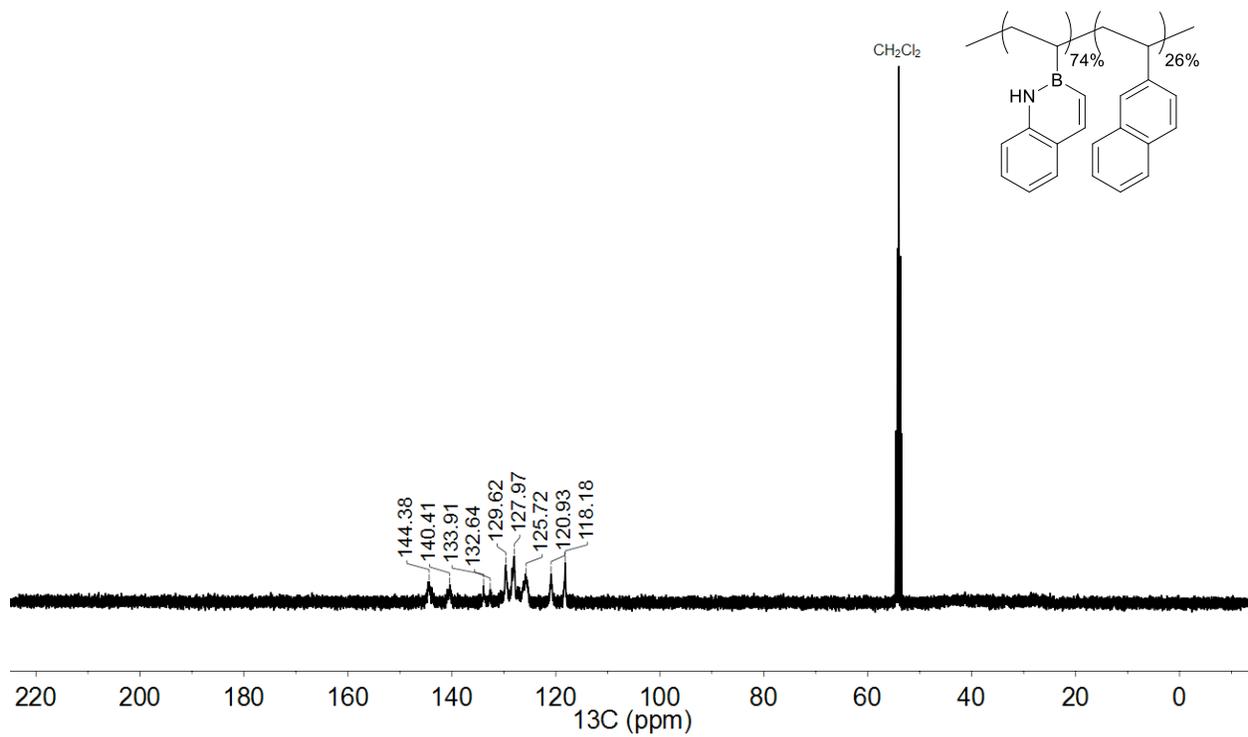
**$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) PBN2VN, Background Subtracted**



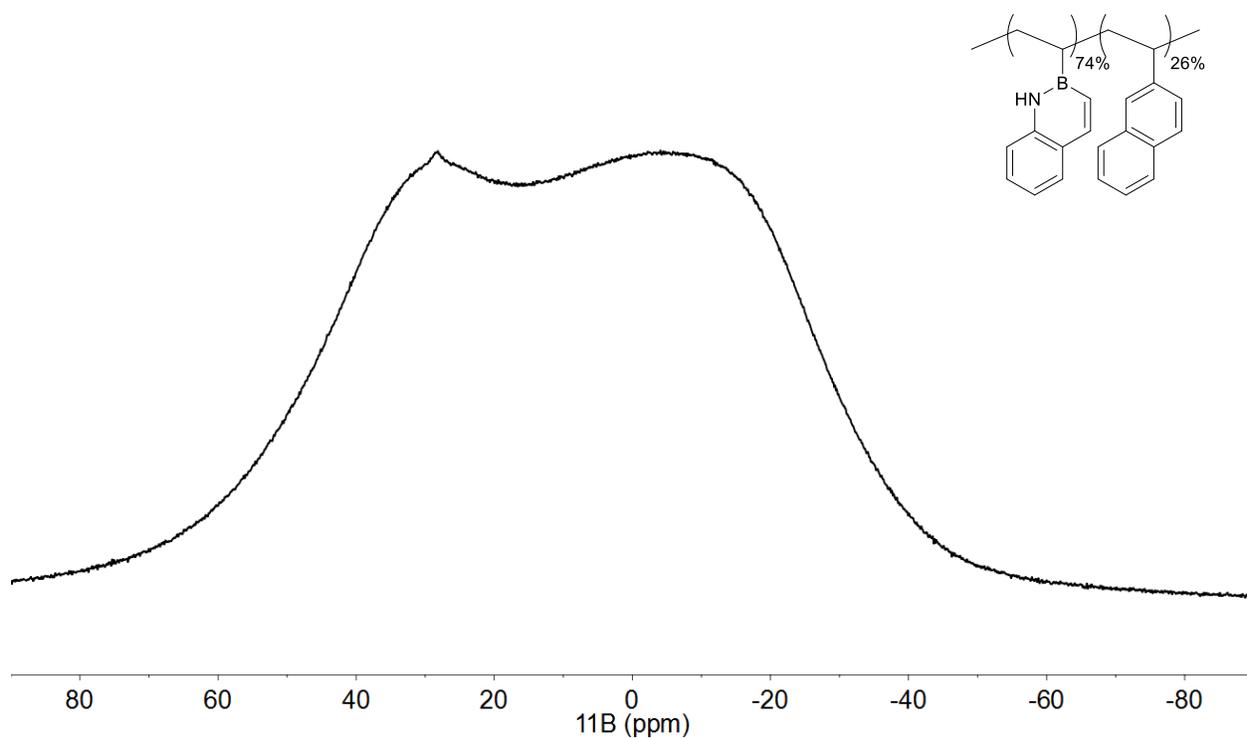
$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz) P(BN2VN<sub>74</sub>-co-2VN<sub>26</sub>)



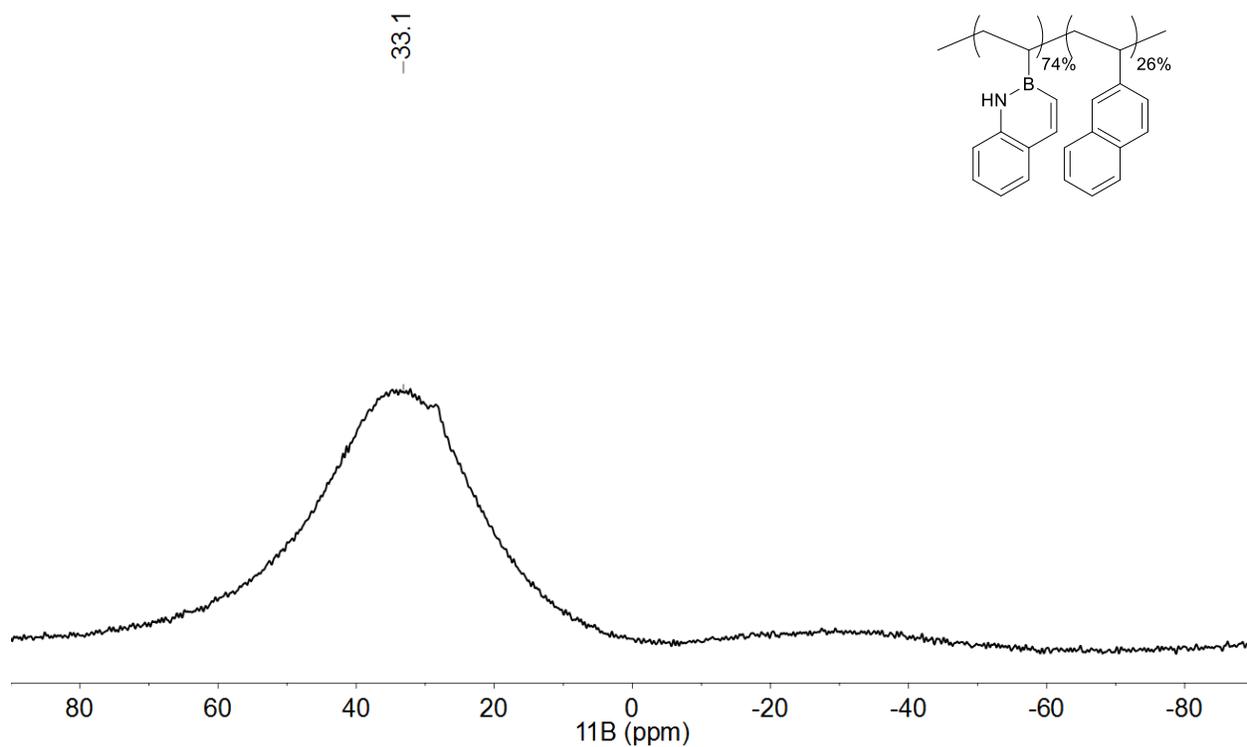
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 101 MHz) P(BN2VN<sub>74</sub>-co-2VN<sub>26</sub>)



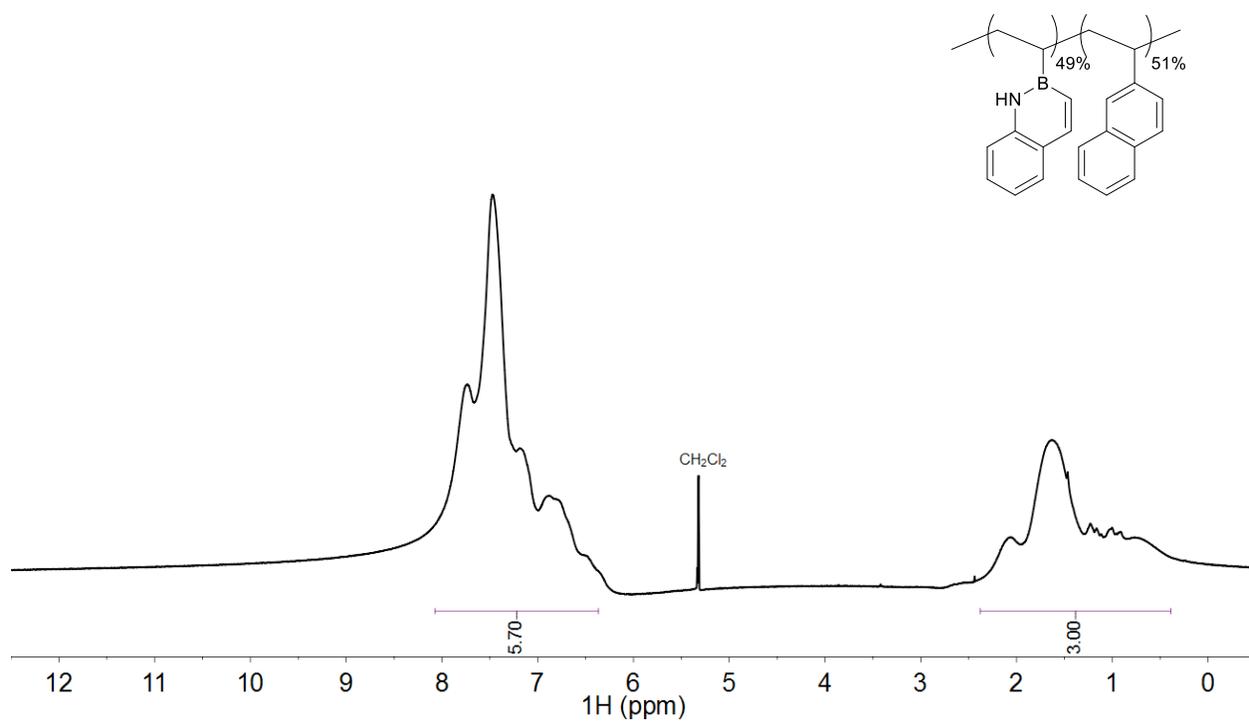
$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) P(BN $_{2}\text{VN}_{74}$ -*co*-2VN $_{26}$ )



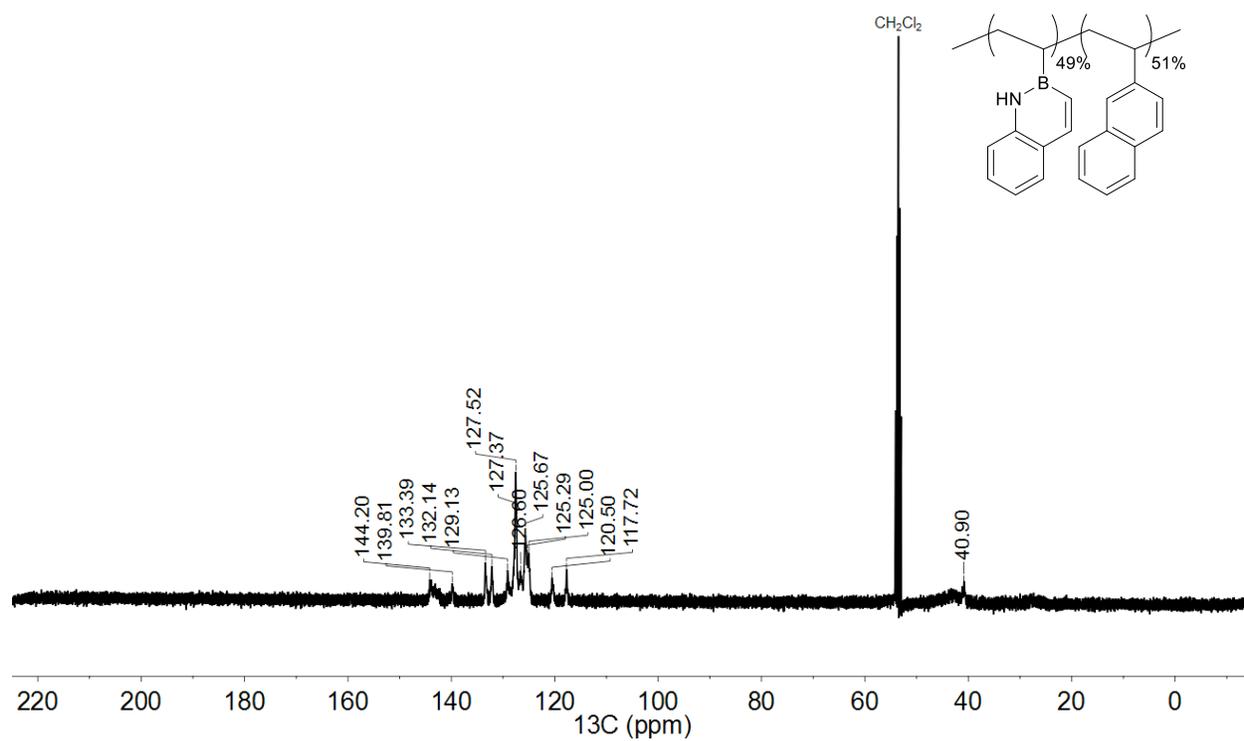
$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) P(BN $_{2}\text{VN}_{74}$ -*co*-2VN $_{26}$ ), Background Subtracted



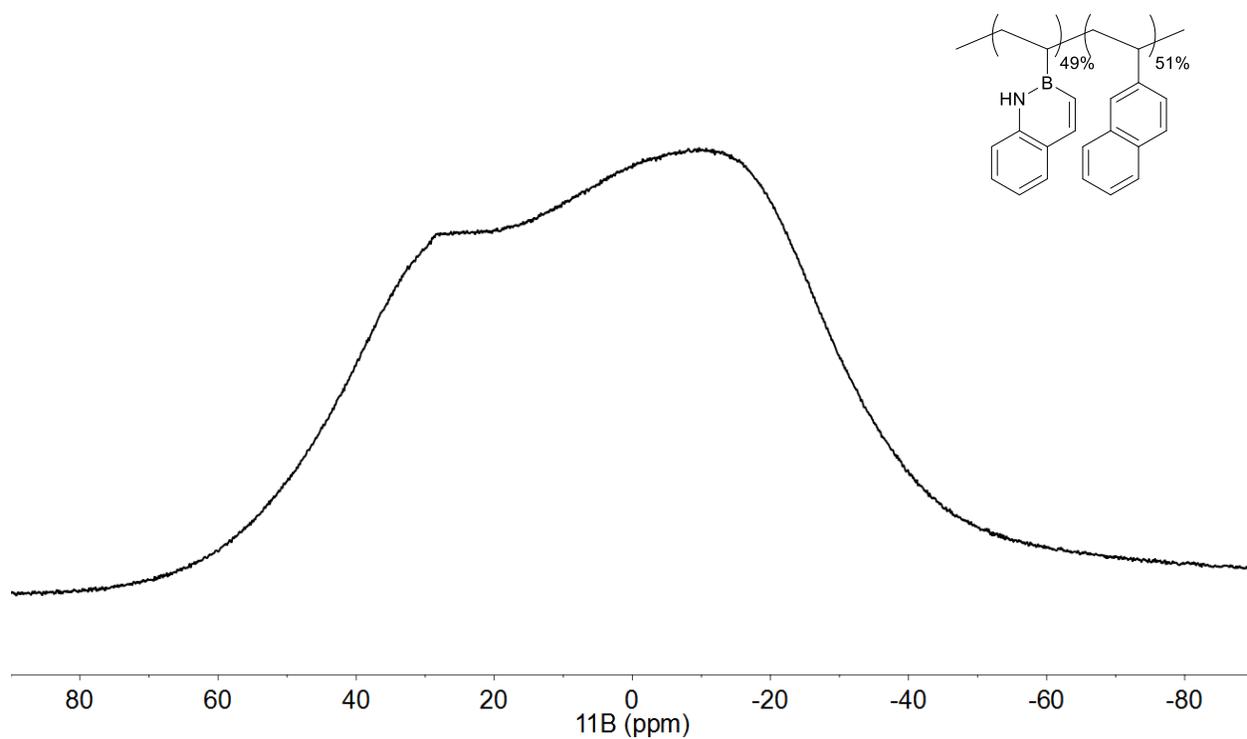
$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz) P(BN2VN<sub>49</sub>-co-2VN<sub>51</sub>)



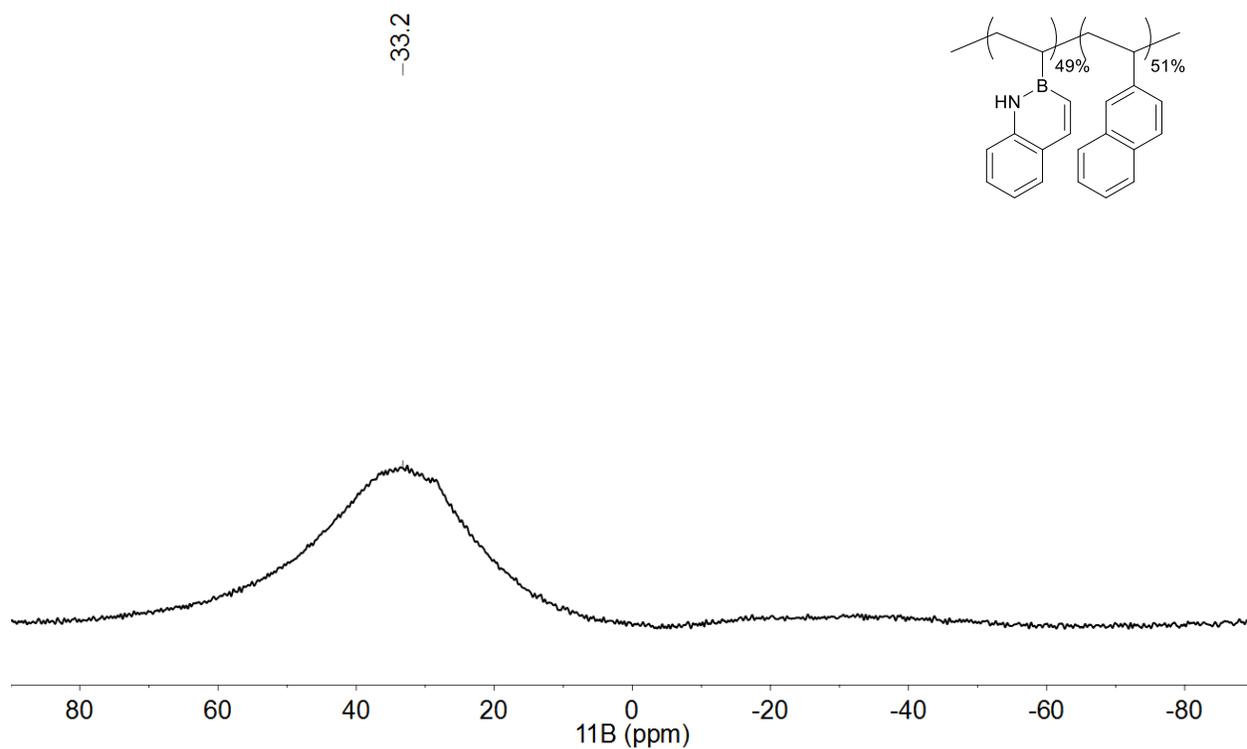
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 101 MHz) P(BN2VN<sub>49</sub>-co-2VN<sub>51</sub>)



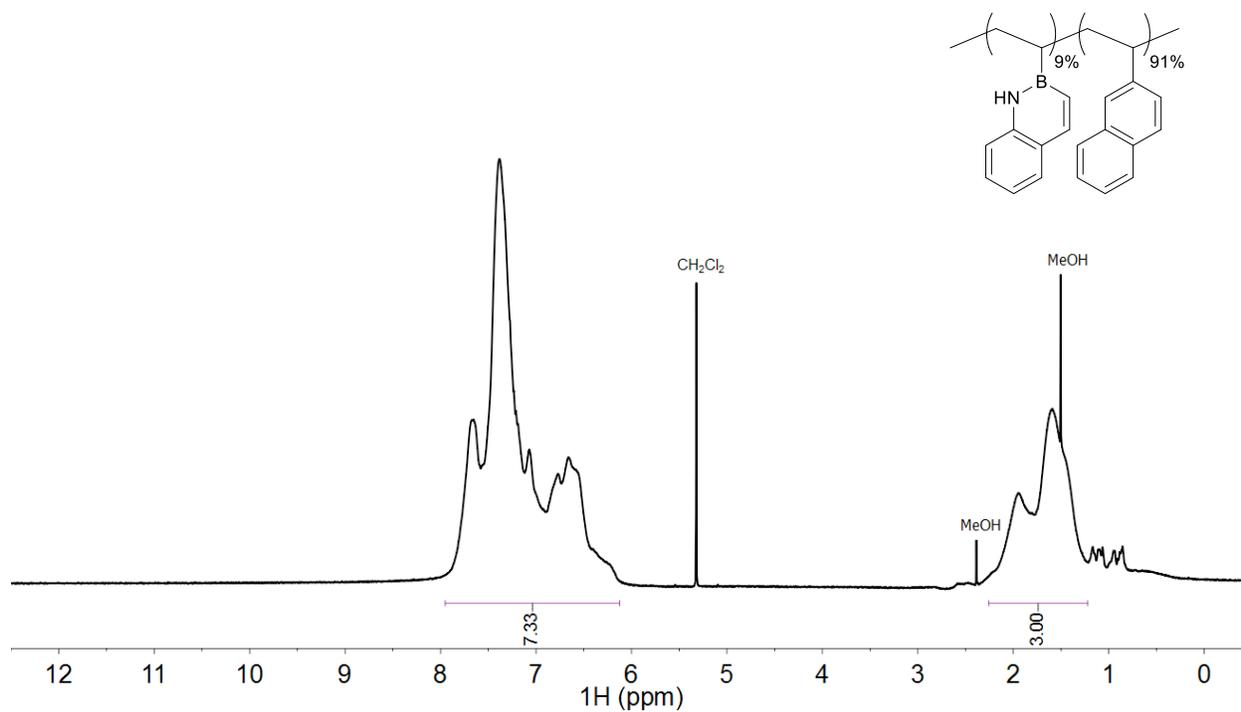
$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) P(BN2VN<sub>49</sub>-co-2VN<sub>51</sub>)



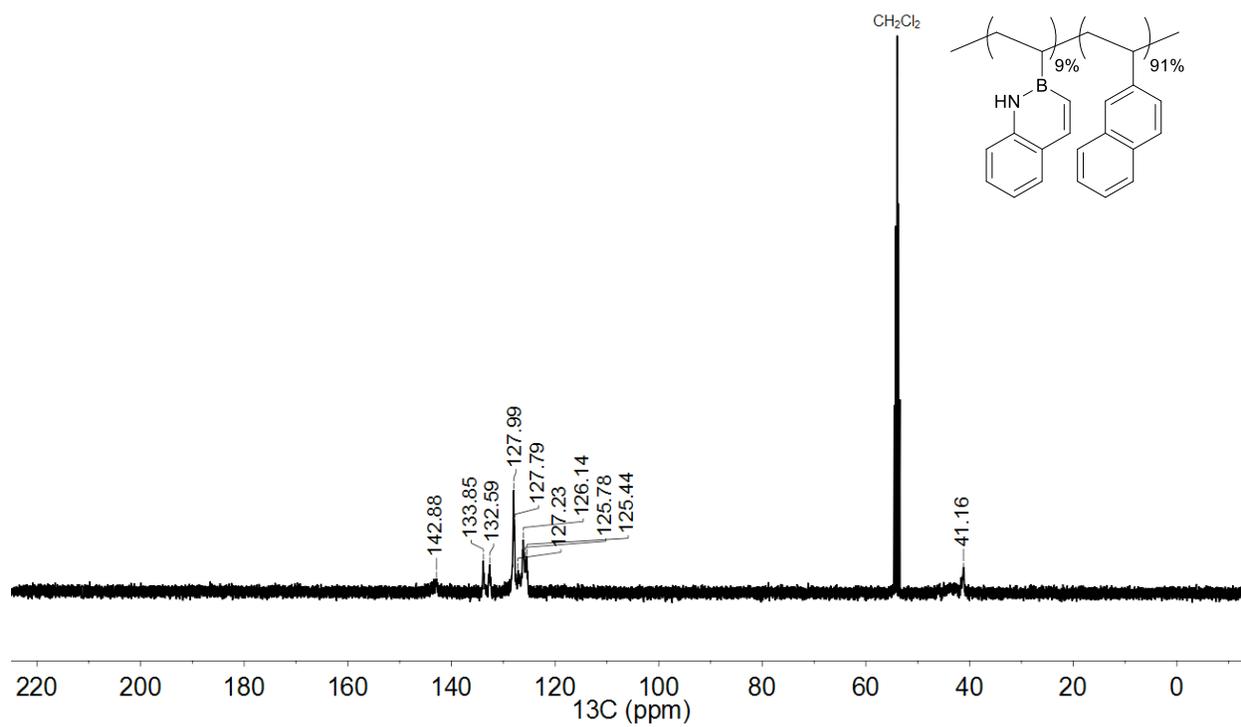
$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) P(BN2VN<sub>49</sub>-co-2VN<sub>51</sub>), Background Subtracted



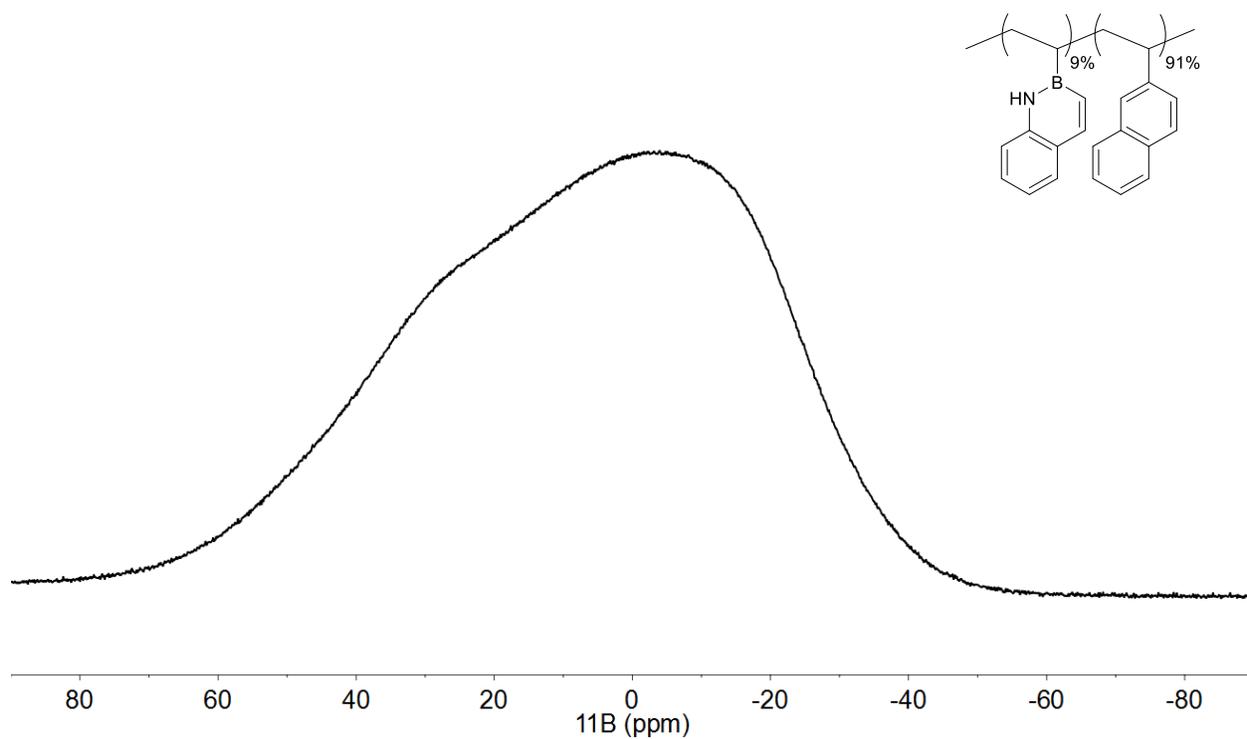
**$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz) P(BN2VN<sub>9</sub>-co-P2VN<sub>91</sub>)**



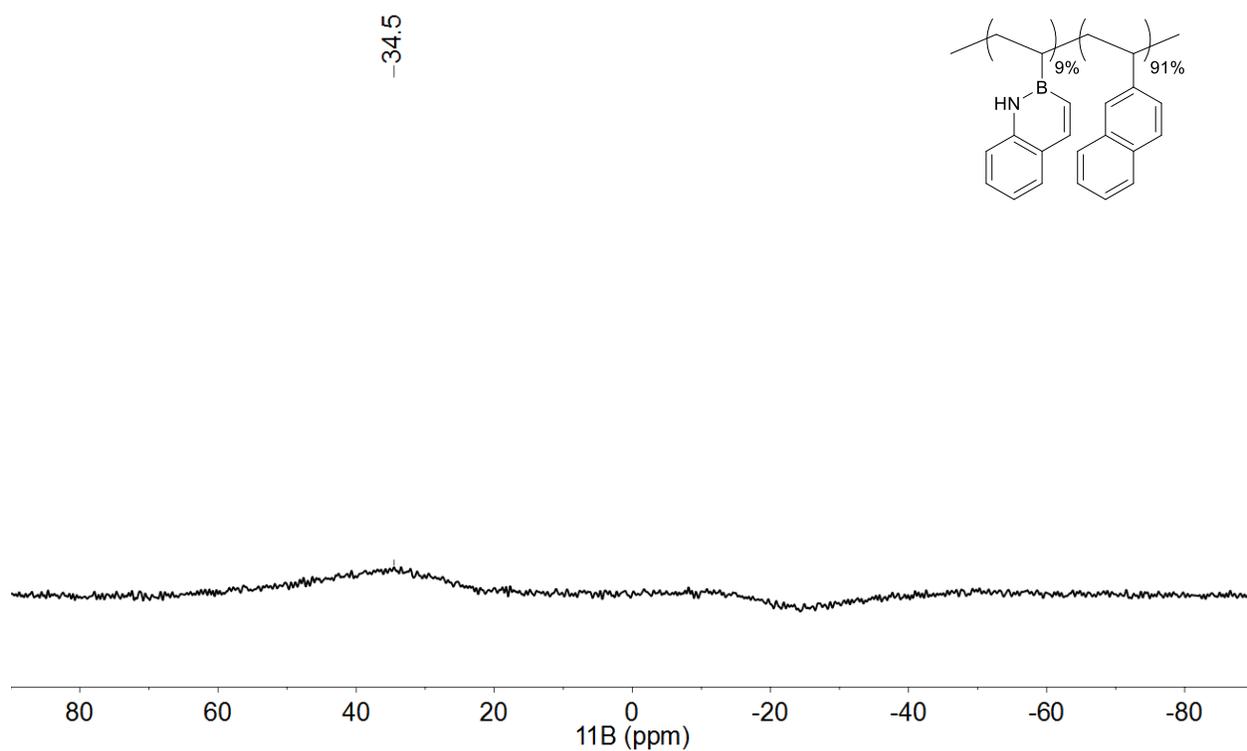
**$^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 101 MHz) P(BN2VN<sub>9</sub>-co-P2VN<sub>91</sub>)**



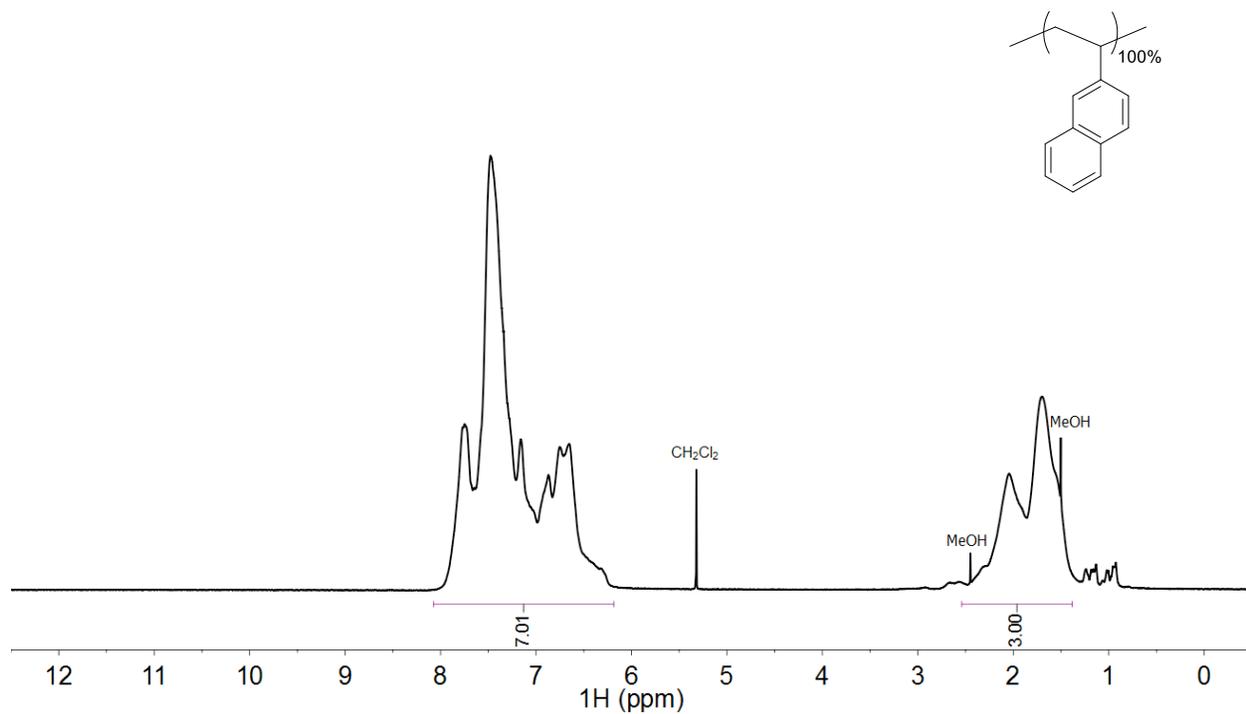
$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) P(BN2VN<sub>9</sub>-*co*-P2VN<sub>91</sub>)



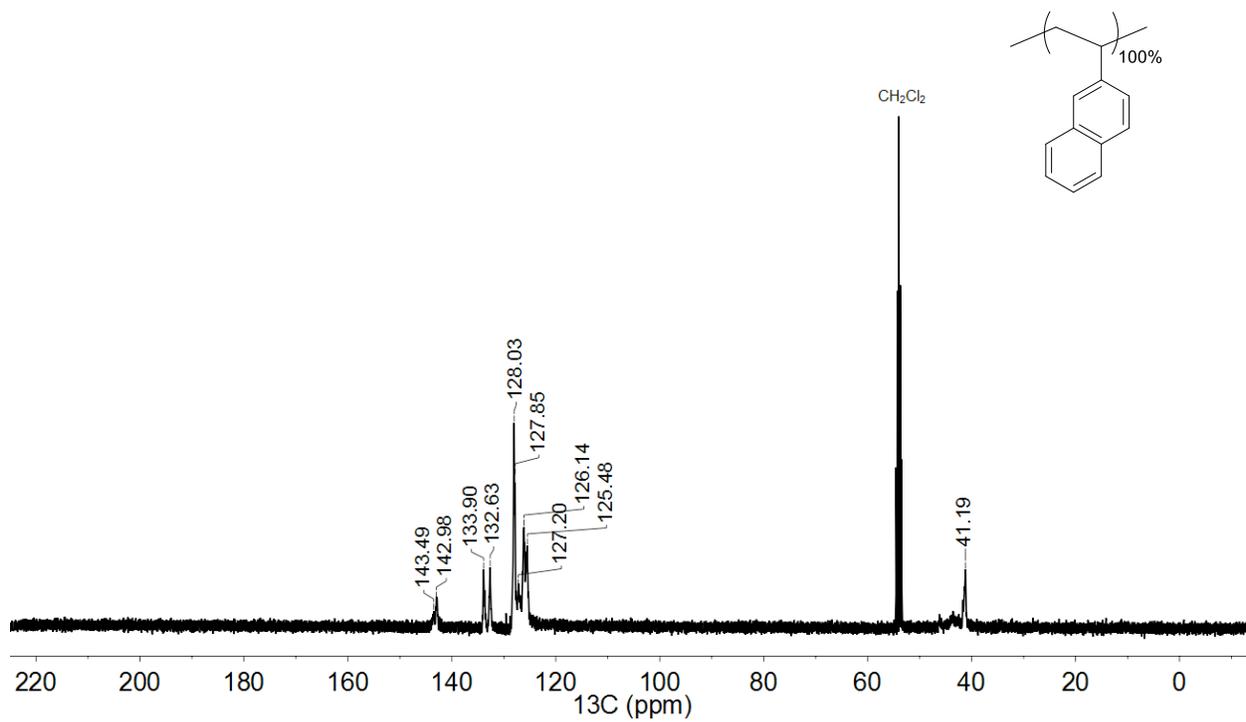
$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) P(BN2VN<sub>9</sub>-*co*-P2VN<sub>91</sub>), Background Subtracted



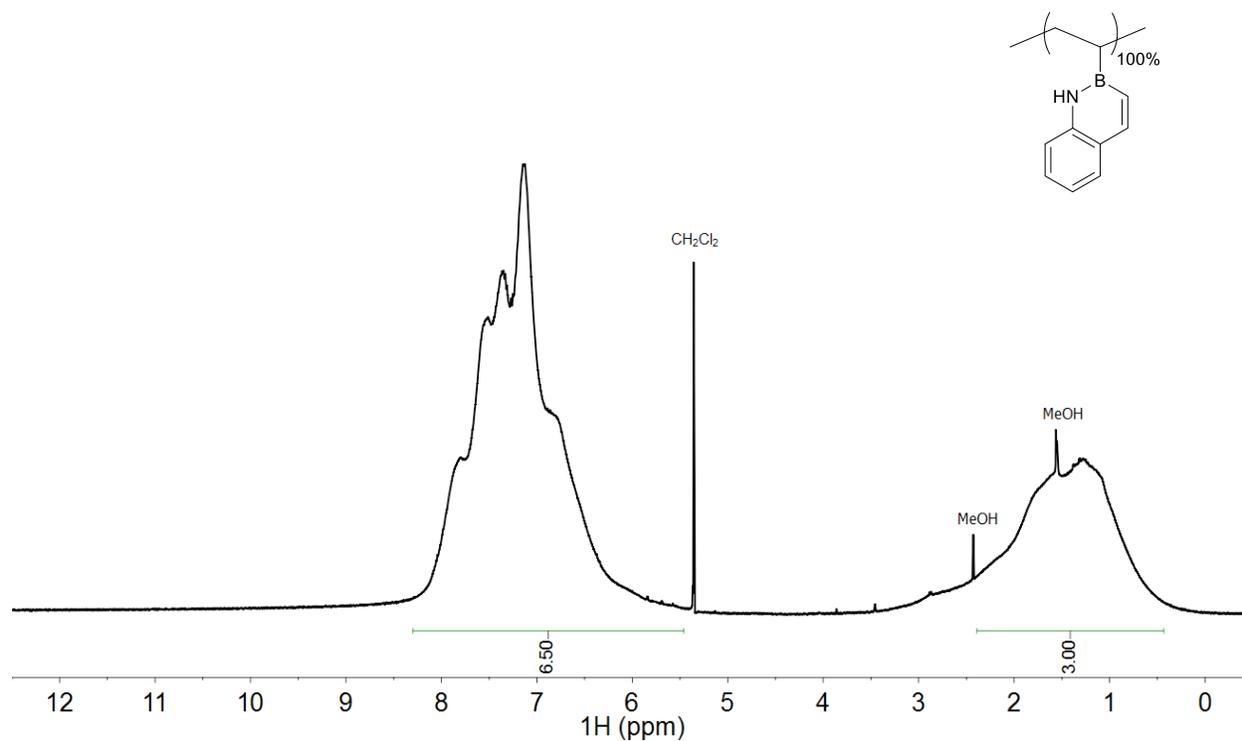
**$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz) P2VN**



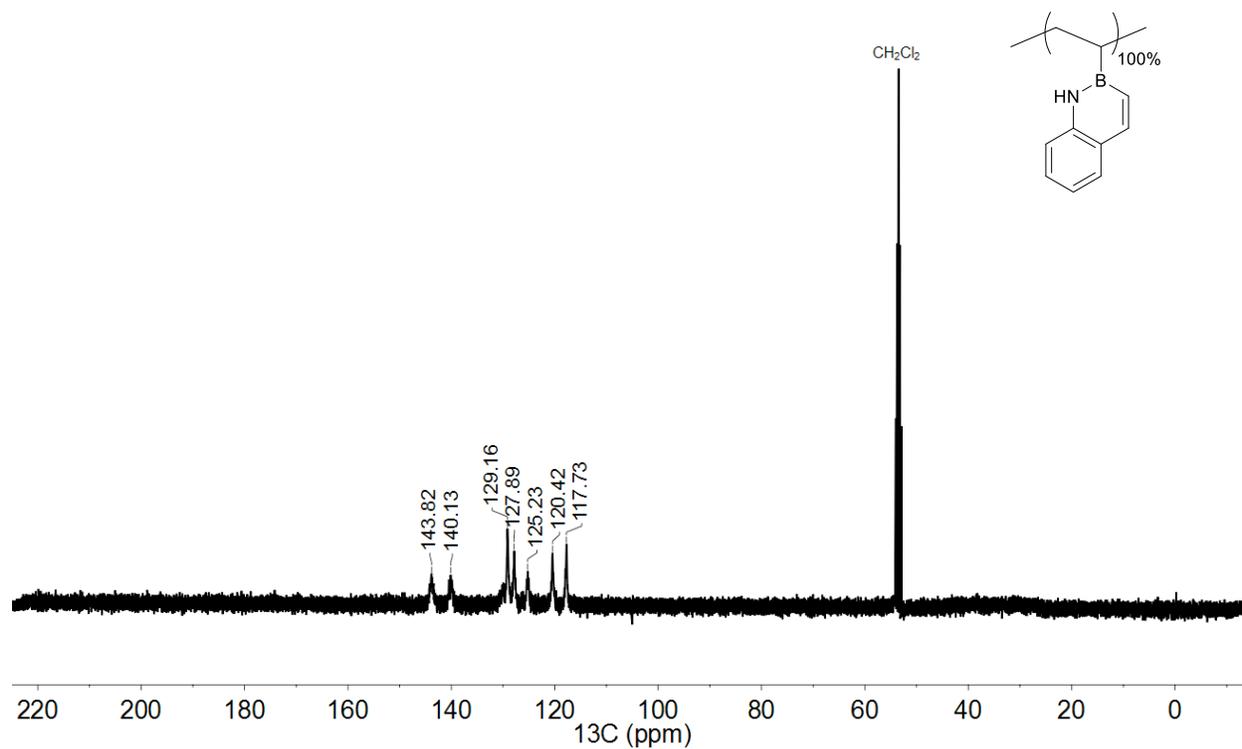
**$^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 101 MHz) P2VN**



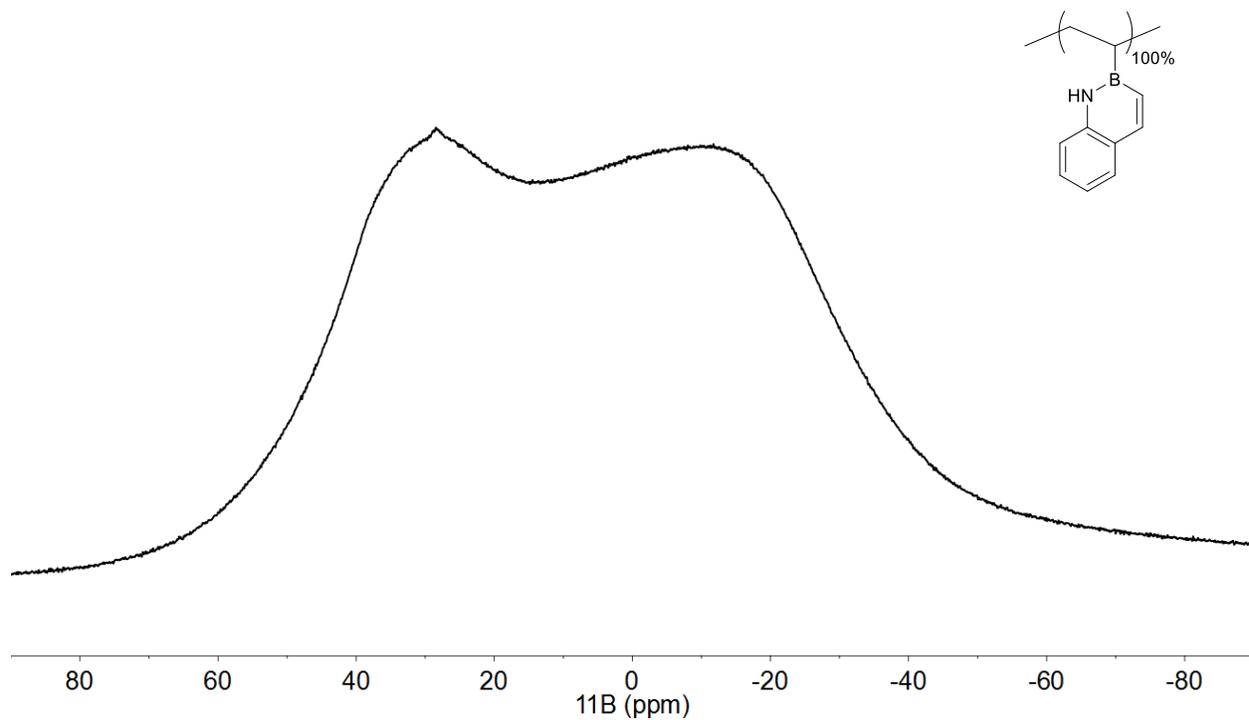
**<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz) PBN2VN- Large Scale**



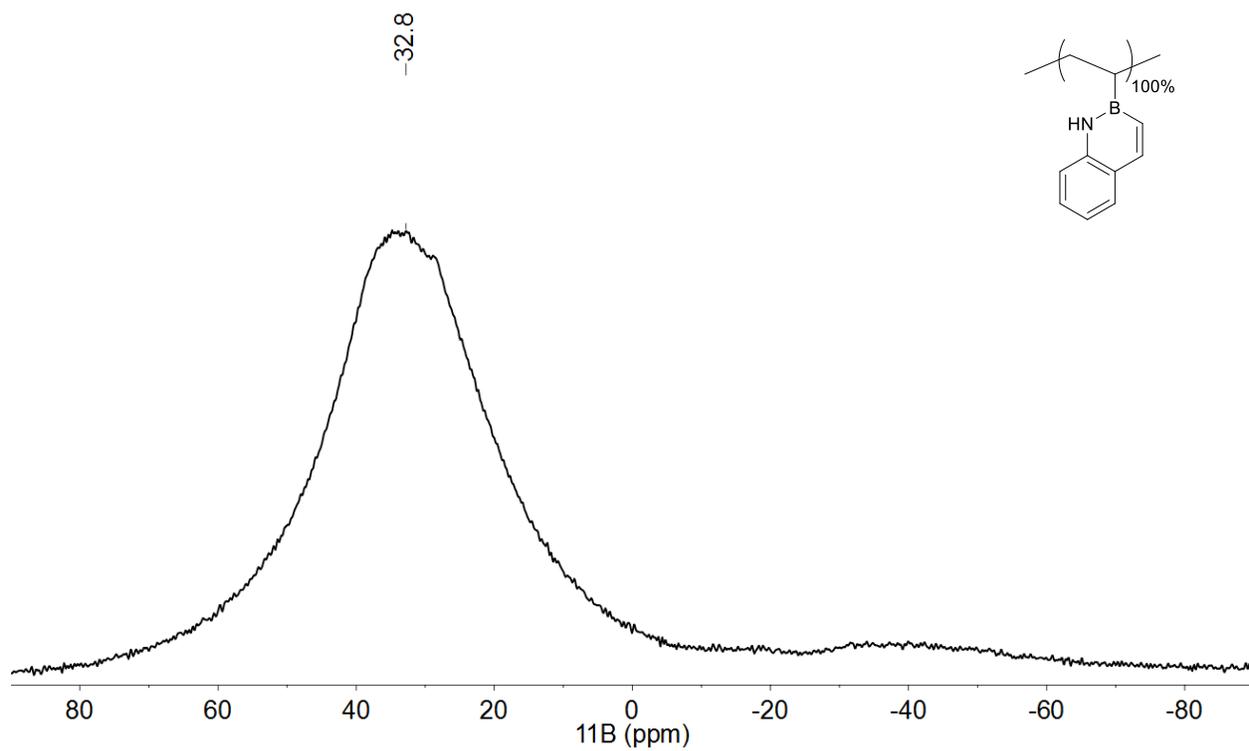
**<sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 101 MHz) PBN2VN- Large Scale**



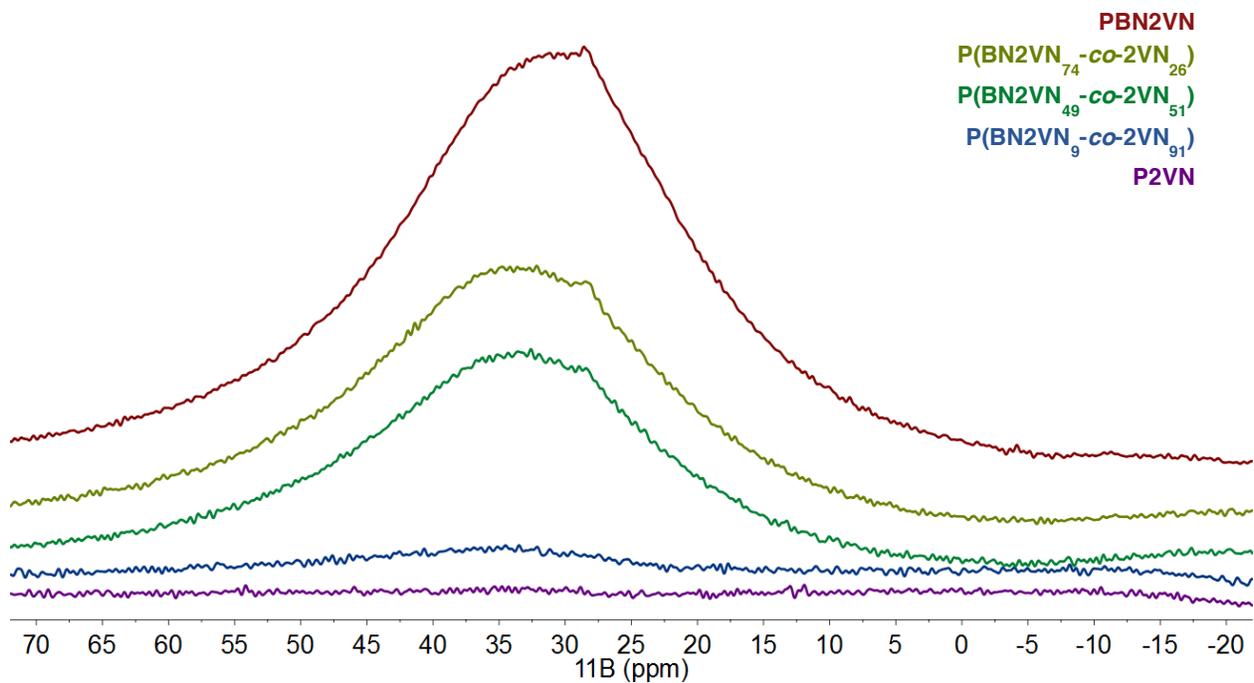
**$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) PBN2VN- Large Scale**



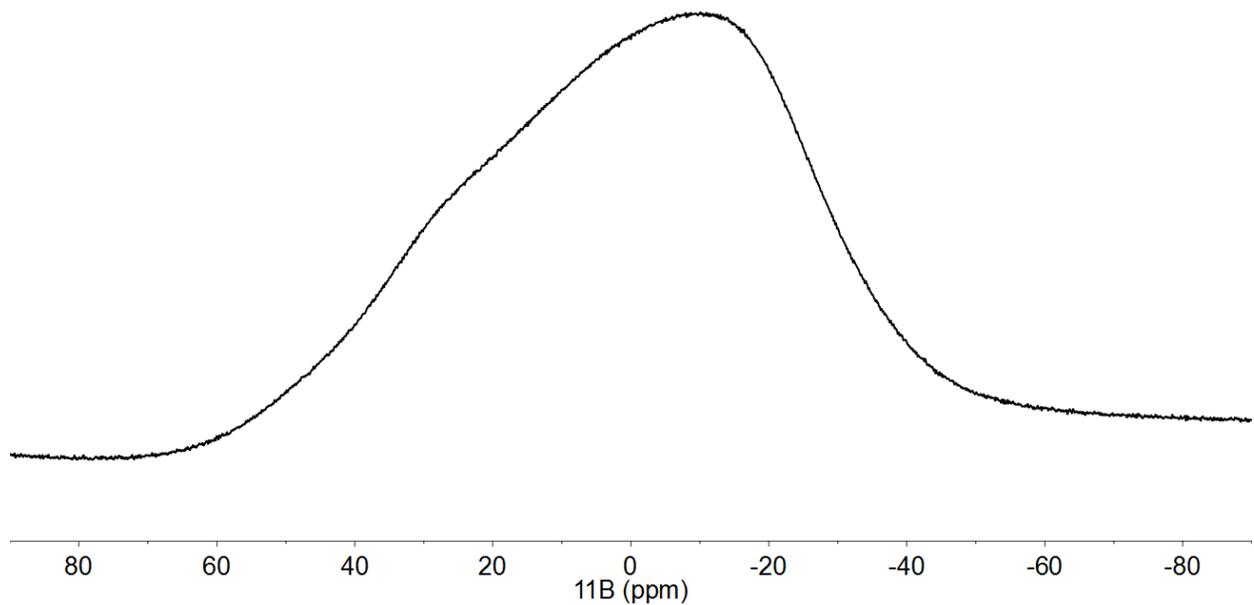
**$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) PBN2VN- Large Scale, Background Subtracted**



**$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) Stacked Background Subtracted Spectra of PBN2VN, P(BN2VN<sub>74</sub>-co-2VN<sub>26</sub>), P(BN2VN<sub>49</sub>-co-2VN<sub>51</sub>), P(BN2VN<sub>9</sub>-co-P2VN<sub>91</sub>), and P2VN**



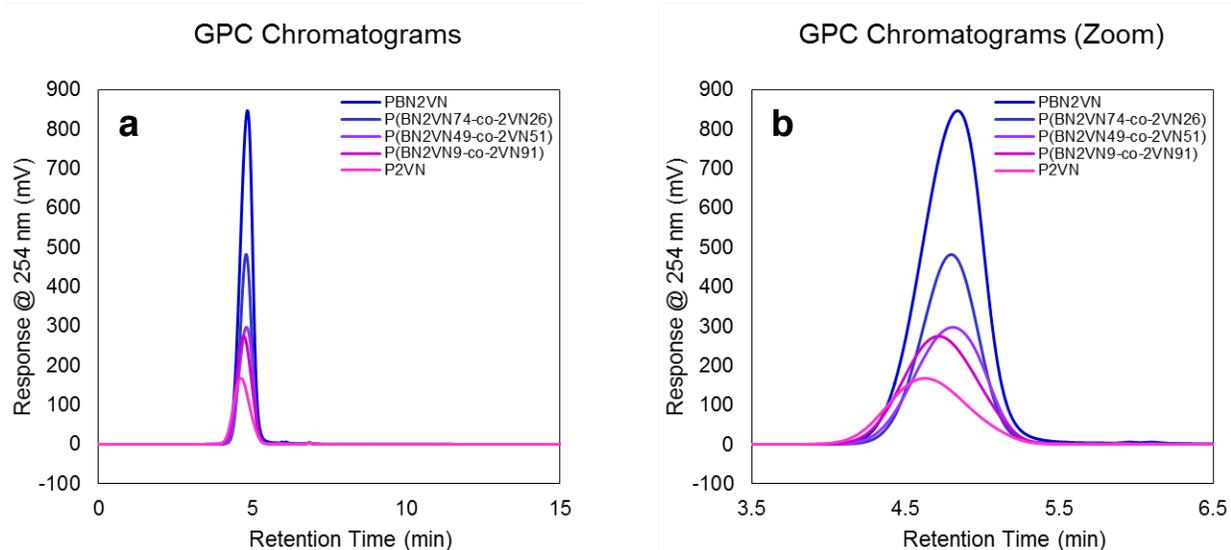
**$^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz) No Analyte: Probe Background**



## 5. Gel Permeation Chromatography

Polymer molecular weights were measured by gel permeation chromatography (GPC) on a Tosoh Bioscience EcoSEC GPC workstation using butylated hydroxytoluene stabilized tetrahydrofuran (THF) as the eluent ( $0.35 \text{ mL min}^{-1}$ ,  $40 \text{ }^\circ\text{C}$ ) through TSKgel SuperMultipore HZ-M guard column (4.6 mm ID x 2.0 cm,  $4 \mu\text{m}$ , Tosoh Bioscience) and a TSKgel SuperMultipore HZ-M column (4.6 mm ID x 15 cm,  $4 \mu\text{m}$ , Tosoh Bioscience). Polystyrene standards (EasiVial PS-M, Agilent) were used to build a calibration curve. Processing was done using EcoSEC Data Analysis software (Version 1.14, Tosoh Bioscience).

Polymers were dissolved in THF ( $1 \text{ mg mL}^{-1}$ ), filtered through a syringe filter (Millex-FG Syringe Filter Unit,  $0.20 \mu\text{m}$ , PTFE, EMD Millipore), and injected using an auto-sampler ( $5 \mu\text{L}$ ).

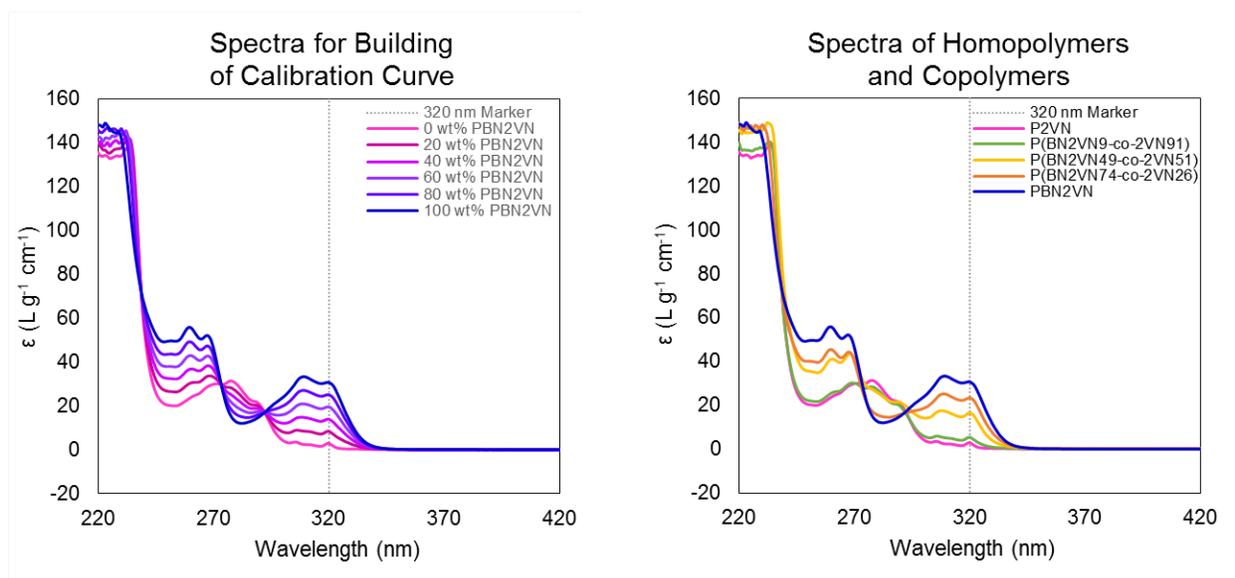


**Figure S4.** GPC chromatograms of homo- and copolymers. Data have not been normalized and correspond to the data in Figure 2d. a) Full window b) zoom.

## 6. Absorbance Spectroscopy

UV-vis spectroscopy was performed on a Shimadzu UV-1800 UV-vis spectrophotometer. The spectra were measured at room temperature in non-stabilized THF in a quartz cuvette (10 mm). All polymer solutions were made to the same concentration (0.021 g/L), with acute attention paid to accuracy of mass measurements and dilution of polymers. A calibration curve was built by taking spectra of the **PBN2VN** solution, **P2VN** solution, and various mixtures of the two (20 w/w, 40 w/w, 60 w/w, and 80 w/w). From the calibration curve the following equation was calculated to determine the incorporation of **BN2VN** within the various random co-polymers:

$$\epsilon_{\text{copolymer}} = (27.8)X + 2.81$$



**Figure S5.** a) UV-vis spectra of **PBN2VN**:**P2VN** blends in THF. b) UV-vis spectra of homo- and copolymers in THF. See Figure 2c for additional data.

## 7. Fluorescence Spectroscopy

Fluorescence spectroscopy was performed on a Photon Technology International, Inc. QuantaMaster 40 spectrofluorometer equipped with an Ushio short-arc xenon gas discharge lamp. The spectra were measured at room temperature in non-stabilized THF in a quartz cuvette (10 mm) and all solutions were dilute ( $\lambda_{\text{max}} < 0.1$  abu) to minimize re-absorption effects. Processing was done using FeliX32 Analysis (Version 1.2, Build 56, Photon Technology International, Inc.).

Relative quantum yields were determined vs. a quinine sulfate standard ( $\Phi_F = 54.6\%$ ) as per the following equation:<sup>5</sup>

$$\Phi_F^a = \frac{F^a f_a n_a^2}{F^s f_s n_s^2} \Phi_F^s$$

$\Phi_F^a$  and  $\Phi_F^s$  : Quantum yield of the analyte (a) and the standard (s), respectively

$F^x$  : Integrated intensity, in photons

$f_x$  : Absorption factor ( $f_x = 1 - 10^{-Abs_x}$ , where Abs = Absorbance at  $\lambda_{\text{ex}}$ )

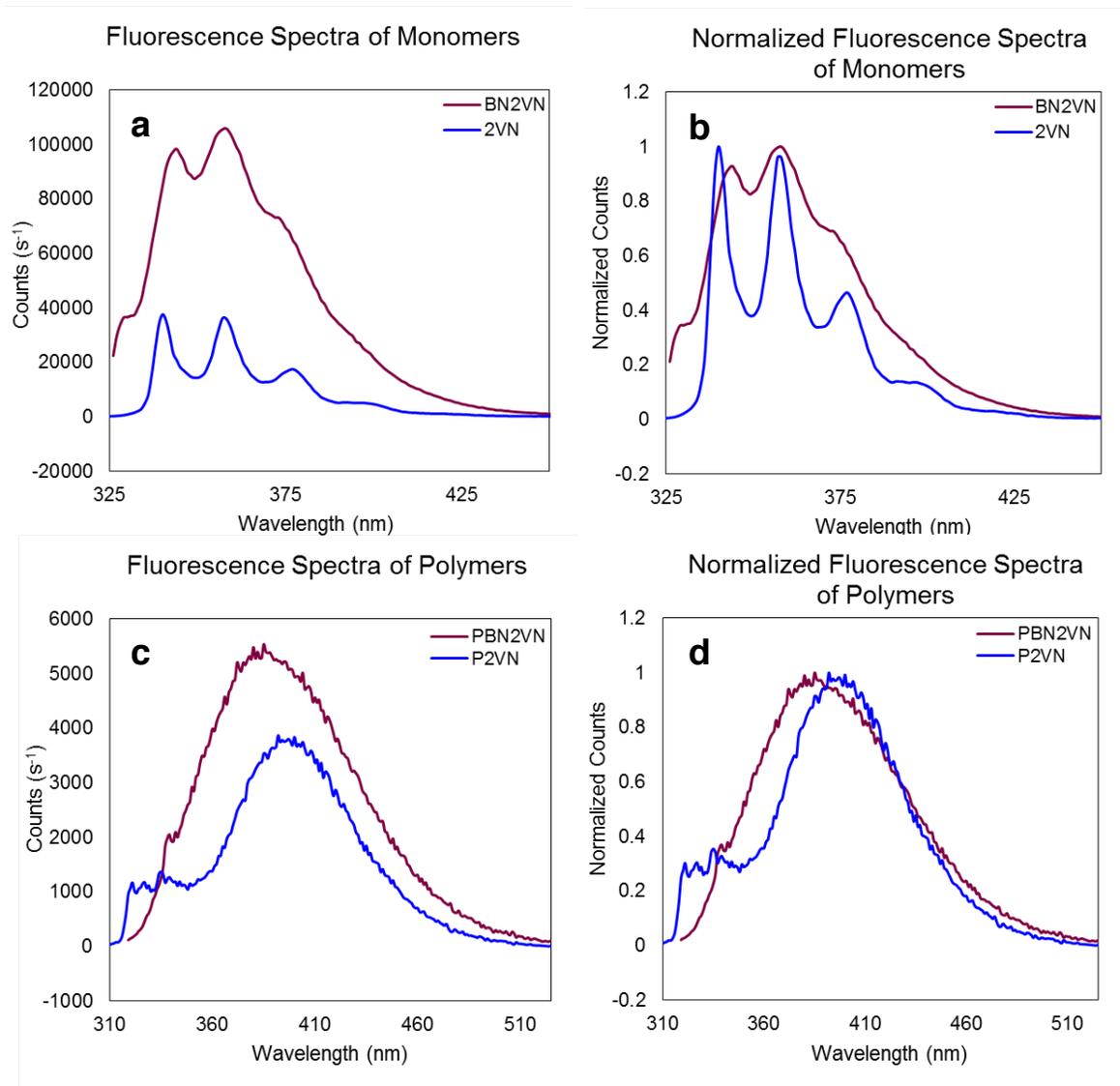
$n_x$  : Refractive index of the solvent used

**Table S2.** Quantum yield determination of monomers and homopolymers.

Compound	Solvent	Solvent Refractive Index	$\lambda_{\text{ex}}^a$ (nm)	Absorbance (abu)	Absorption Factor	Integration (photons)	Quantum Yield
BN2VN	THF	1.407	313	0.0834	0.175	2.97E+06	66%
2VN	THF	1.407	285	0.0810	0.170	1.15E+06	25%
PBN2VN	THF	1.407	309	0.0661	0.141	4.72E+05	8%
P2VN	THF	1.407	277	0.0838	0.176	3.09E+05	7%
Quinine Sulfate	0.5 M H <sub>2</sub> SO <sub>4</sub>	1.346	366	0.0452	0.0989	4.74E+06	54.6% <sup>b</sup>

<sup>a</sup>  $\lambda_{\text{ex}}$  = excitation wavelength

<sup>b</sup> See reference 5



**Figure S6.** a) Raw and b) normalized fluorescence spectra of monomers **BN2VN** and **2VN**. c) Raw and d) normalized fluorescence spectra of homopolymers **PBN2VN** and **P2VN**.

## 8. References

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- 2 E. R. Abbey, A. N. Lamm, A. W. Baggett, L. N. Zakharov and S.-Y. Liu, *J. Am. Chem. Soc.*, 2013, **135**, 12908–12913.
- 3 S. J. Dolman, R. R. Schrock and A. H. Hoveyda, *Org. Lett.*, 2003, **5**, 4899–4902.
- 4 S. R. Wisniewski, C. L. Guenther, O. A. Argintaru and G. A. Molander, *J. Org. Chem.*, 2014, **79**, 365–378.
- 5 A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213–2228.