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Generation of aminoborane monomers RR'NH=BH_2 from amine-boronium cations [RR'NH-BH_2L]$^+$: metal catalyst-free formation of polyaminoboranes at ambient temperature

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Supplementary Information

Experimental Notes:

Unless otherwise stated, all manipulations were undertaken under an atmosphere of argon or nitrogen using standard glovebox (M-Braun O_2 < 0.1 ppm, H_2O < 0.1 ppm) and Schlenk line techniques and all glassware was oven and vacuum dried prior to use. $Me_2NH{\cdot}BH_3$ was purchased from Sigma-Aldrich and purified by sublimation prior to use, $MeNH_2{\cdot}BH_3$ and $[H(OEt_2)_2][B(C_6F_5)_4]$ were synthesized according to literature protocols,[1] HOTf, HCl (2M in Et_2O) and $AlCl_3$ were purchased from Acros Organics and Sigma Aldrich respectively and used as received, ^{i}Pr$_2$EtN was purchased from Sigma Aldrich and distilled from CaH_2 prior to use, 2,6-di-*tert*butylpyridine (DTBP) was purchased from Sigma Aldrich and stirred over 3 Å molecular sieves prior to use. Common laboratory solvents (Et_2O, DCM, Hexane, THF) were purified using a Grubbs type purification system.[2]

NMR spectra were recorded using a JEOL ECP-300 (300 MHz) spectrometer and a Varian-400 (400 MHz) spectrometer. Deuterated solvents were obtained from Sigma Aldrich and distilled from CaH_2 prior to use. Spectra of air sensitive compounds were recorded using NMR tubes fitted with J-Young valves and spectra of boron-containing compounds were recorded in quartz NMR tubes. ESI-MS of **8** was carried out on a Brüker Daltonics Apex IV (FT-ICR) in a 1 mgmL^{-1} DCM/MeCN solution. CI-MS of **3** and **4** was carried out on a VG Analytical Autospec in a 1 mgmL^{-1} solution in MeCN. Gel Permeation Chromatography (GPC) was carried out using a Viscotek VE2001 instrument (VE3580 refractometer detector), using a flow rate of 1 mLmin^{-1} of THF containing 0.1 w/w % nBu$_4$NBr, calibrated using polystyrene standards. The columns used were of grade GP5000HHR followed by GP2500HHR. All samples were dissolved in the eluent (0.5 mgmL^{-1}) and filtered using 0.45 mm

PTFE membranes prior to analysis. Dynamic Light Scattering measurements were made using a Malvern Zetasizer Nanoseries with data analysis carried out in DTS Nano. Samples were prepared by dissolving in THF (0.5-1 mgmL^{-1}) and filtered using 0.45 mm PTFE membranes prior to analysis.

Amine-Boronium Cation Synthesis

Synthesis of $[Me_2NH{\cdot}BH_2(OEt_2)][B(C_6F_5)_4]$ (1)

In a glovebox, $Me_2NH{\cdot}BH_3$ (7 mg, 0.12 mmol) was weighed into a vial, dissolved in Et_2O (0.5 mL) and added to a solution of $[H(OEt_2)_2][B(C_6F_5)_4]$ (100 mg, 0.12 mmol). After the effervescence had ceased (ca. 1 min), the solvent was removed *in vacuo* to yield **1** as a white solid. Further purification can be achieved by recrystallization from DCM/hexane. Yield = 60 mg, 62%

$[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$ **(2)** was synthesized using an analogous method, using $MeNH_2{\bullet}BH_3$ (5 mg, 0.12 mmol) and $[H(OEt_2)_2][B(C_6F_5)_4]$ (100 mg, 0.12 mmol). Yield = 61 mg, 64%

Crystals of **1** suitable for analysis by X-ray diffraction were obtained from layering a DCM solution with hexane.

For 1:

^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.49 (6H, t, $^3J_{HH}$ = 7 Hz, (C$\underline{H_3}$CH$_2$)$_2$O), 1.47 (6H, d, $^3J_{HH}$ = 7 Hz, (C$\underline{H_3}$)$_2$NH), 4.30 (4H, q, $^3J_{HH}$ = 7 Hz, (CH$_3$C$\underline{H_2}$)$_2$O), 6.83 (1H, br, (CH$_3$)$_2$N$\underline{H}$)

^{13}C{^{1}H} NMR (76 MHz, CD_2Cl_2): δ 12.9 (s, ($\underline{C}$H$_3$CH$_2$)$_2$O), 30.4 (s, ($\underline{C}$H$_3$)NH$_2$), 79.2 (s, (CH$_3\underline{C}$H$_2$)$_2$O), 124.6 (br, C_6F_5), 136.7 (d, $^1J_{CF}$ = 242 Hz, C_6F_5), 138.7 (d, $^1J_{CF}$ = 244 Hz, C_6F_5), 148.5 (d, $^1J_{CF}$ = 241 Hz, C_6F_5)

^{11}B NMR (96 MHz, CD_2Cl_2): δ 3.7 (br, t, J_{BH} = 121 Hz, $[Me_2NH{\cdot}\underline{B}H_2(OEt_2)]^+$), -17.6 (s, $[B(C_6F_5)_4]^-$)

^{19}F NMR (283 MHz, CD_2Cl_2): δ -133.2 (br, s, *ortho*), -162.7 (t, *meta*), -167.4 (br, t, *para*)

For 2:

^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.47 (6H, t, $^{3}J_{HH}$ = 7 Hz, (C$\underline{H_3}$CH$_2$)$_2$O), 2.60 (3H, t, $^{3}J_{HH}$ = 7 Hz, (C$\underline{H_3}$)NH$_2$), 4.31 (4H, q, $^{3}J_{HH}$ = 7 Hz, (CH$_3$C$\underline{H_2}$)$_2$O), 6.69 (2H, br, (CH$_3$)N$\underline{H_2}$)

^{13}C{^{1}H} NMR (76 MHz, CD_2Cl_2): δ 12.8 (s, ($\underline{C}$H$_3$CH$_2$)$_2$O), 40.3 (s, ($\underline{C}$H$_3$)NH$_2$), 79.3 (s, (CH$_3$$\underline{C}H_2$)$_2$O), 124.6 (br, C_6F_5), 136.7 (d, $^{1}J_{CF}$ = 242 Hz, C_6F_5), 138.7 (d, $^{1}J_{CF}$ = 244 Hz, C_6F_5), 148.5 (d, $^{1}J_{CF}$ = 241 Hz, C_6F_5)

^{11}B NMR (96 MHz, CD_2Cl_2): δ 1.7 (br, t, $^{1}J_{BH}$ = 121 Hz, [MeNH$_2$•$\underline{B}$H$_2$(OEt$_2$)]$^{+}$), -17.6 (s, [B(C$_6$F$_5$)$_4$]$^{-}$)

^{19}F NMR (283 MHz, CD_2Cl_2): δ -133.2 (br, s, *ortho*), -162.7 (t, *meta*), -167.4 (br, t, *para*)

Synthesis of Me_2NH•BH_2OTf (3)

In a glovebox, Me_2NH•BH_3 (1.00 g, 16.9 mmol) was weighed into a Schlenk flask. The reaction flask was removed from the glovebox and the solid dissolved in DCM (40 mL). The solution was cooled to -78 °C, and trifluoromethanesulfonic acid (1.50 mL, 2.53 g, 16.9 mmol), suspended in DCM (20 mL) in a dropping funnel and added dropwise. Once the addition was complete, the solution was allowed to warm to room temperature and the solvent removed *in vacuo* to yield **3** as a spectroscopically pure, colourless oil. Further purification of this oil by distillation is precluded by its decomposition at high temperature. However, the product may be cooled to -78 °C, at which temperature it is solid, and washed with cold hexanes (-78 °C) to remove any minor impurities. Yield = 3.23 g, 92%

$MeNH_2$•BH_2OTf (**4**) was synthesized using an analogous method using $MeNH_2$•BH_3 (1.00 g, 22.3 mmol) and HOTf (1.97 mL, 3.35 g, 22.3 mmol). Yield = 2.84 g, 66%

Compounds **3** and **4** were found to be temperature sensitive, therefore both **3** and **4** were stored at -40 °C.

For 3:

^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.55 (6H, d, $^{3}J_{HH}$ = 6 Hz, (C$\underline{H_3}$)$_2$NH), 2.58 (2H, br, B$\underline{H_2}$OTf), 4.61 (1H, bs, Me$_2$N$\underline{H}$)

$^{13}C\{^1H\}$ NMR (76 MHz, CD_2Cl_2): δ 39.5 (s, ($\underline{C}H_3)_2NH$), 118.9 (q, $^1J_{CF}$ = 318 Hz, $\underline{C}F_3$)

^{11}B NMR (96 MHz, CD_2Cl_2): δ -0.4 (bt, $^1J_{BH}$ = 121 Hz)

^{19}F NMR (283 MHz, CD_2Cl_2): δ - 76.3 (s, C$\underline{F_3}$)

CI-MS – [MH^+-H_2]: Calculated = 206.0270 m/z, Observed = 206.0270 m/z

For 4:

^1H NMR (300 MHz, CD_2Cl_2): δ 2.59 (3H, t, $^3J_{HH}$ = 6 Hz, (C$\underline{H_3}$)NH_2), 2.68 (2H, br, B$\underline{H_2}$OTf), 4.29 (2H, bs, MeN$\underline{H_2}$)

$^{13}C\{^1H\}$ NMR (76 MHz, CD_2Cl_2): δ 30.0 (s, ($\underline{C}H_3)NH_2$), 119.4 (q, $^1J_{CF}$ = 318 Hz, $\underline{C}F_3$)

^{11}B NMR (96 MHz, CD_2Cl_2): δ -2.2 (t, $^1J_{BH}$ = 121 Hz)

^{19}F NMR (283 MHz, CD_2Cl_2): δ -76.4 (s, C$\underline{F_3}$)

CI-MS – [MH^+-H_2]: Calculated = 192.0113 m/z, Observed = 192.0144 m/z

Synthesis of $Me_2NH{\bullet}BH_2Cl$ (5)

$Me_2NH{\bullet}BH_3$ (500 mg, 8.49 mmol) was weighed into a Schlenk flask and dissolved in Et_2O (20 mL). A 2M solution of HCl in Et_2O (4.67 mL, 9.34 mmol, 1.1 equiv.) was added dropwise and effervescence observed. After addition was complete, the reaction was stirred for 1 h, filtered *via* cannula and the solvent removed *in vacuo* to yield **5** as a white solid. This material was deemed pure by NMR spectroscopy, and as such purification of the crude material was not required. Further purification can be achieved by sublimation (25 °C , 3 x 10^{-2} Torr) Yield = 549 mg, 69%.

$MeNH_2{\bullet}BH_2Cl$ (**6**) was synthesized using an analogous method, using $MeNH_2{\bullet}BH_3$ (500 mg, 11.1 mmol) and HCl (2M in Et_2O) (6.12 mL, 12.2 mmol) and purified by recrystallization from Et_2O**.** Yield = 644 mg, 73%

Crystals of **6** suitable for analysis by X-ray diffraction were obtained from layering a DCM solution with hexane at -40 °C .

It should also be noted that **5** and **6** should be stored at -40 °C as they are found to slowly decompose at room temperature to yield unidentified decomposition products.

For 5:

^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.51 (2H, bq, $^{1}J_{BH}$ = 121 Hz, B$\underline{H_2}$Cl), 2.68 (6H, d, $^{3}J_{HH}$ = 6 Hz, (C$\underline{H_3}$)$_2$NH), 4.05 (1H, bt, $^{3}J_{HH}$ = 43 Hz, Me$_2$N$\underline{H}$)

^{13}C{^{1}H} NMR (76 MHz, CD_2Cl_2): δ 41.0 (s, ($\underline{C}$H$_3$)$_2$NH)

^{11}B NMR (96 MHz, CD_2Cl_2): δ -4.2 (t, $^{1}J_{BH}$ = 121 Hz)

For 6:

^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.62 (3H, t, $^{3}J_{HH}$ = 6 Hz, C$\underline{H_3}$), 2.68 (2H, bq, $^{1}J_{BH}$ = 120 Hz, B$\underline{H_2}$Cl), 4.05 (2H, bt, $^{3}J_{HH}$ = 43 Hz, MeN$\underline{H_2}$)

^{13}C NMR (76 MHz, CD_2Cl_2): δ 31.2 (s, $\underline{C}$H$_3$)

^{11}B NMR (96 MHz, CD_2Cl_2): δ -6.8 (t, $^{1}J_{BH}$ = 121 Hz)

Details of X-Ray Diffraction Studies of 2 and 6

X-ray diffraction experiments were carried out at 100 K on a Bruker APEX II diffractometer using Mo-Ka radiation (λ = 0.71073 Å). The data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated[3] from several series of exposures measuring 0.5° in ω or φ. Absorption corrections were based on equivalent reflections using SADABS.[4] The structures were solved using direct methods or Patterson methods in XS and structures were refined against all Fo^2 data with hydrogen atoms on carbon atoms riding in calculated positions using SHELXL-97. [5] All images were generated using OLEX2.[6]

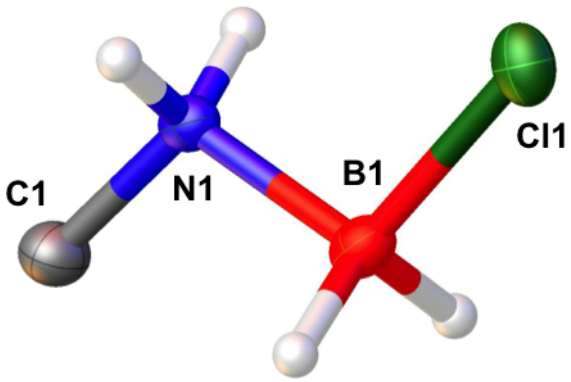

Figure S1 – Representation of the molecular structure of **6**. The hydrogen atoms of the methyl group are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) C1-N1 1.4853(10), B1-N1 1.5810(11), B1-Cl1 1.8984(9), N1 B1 Cl1 107.55(5), C1 N1 B1 111.56(6).

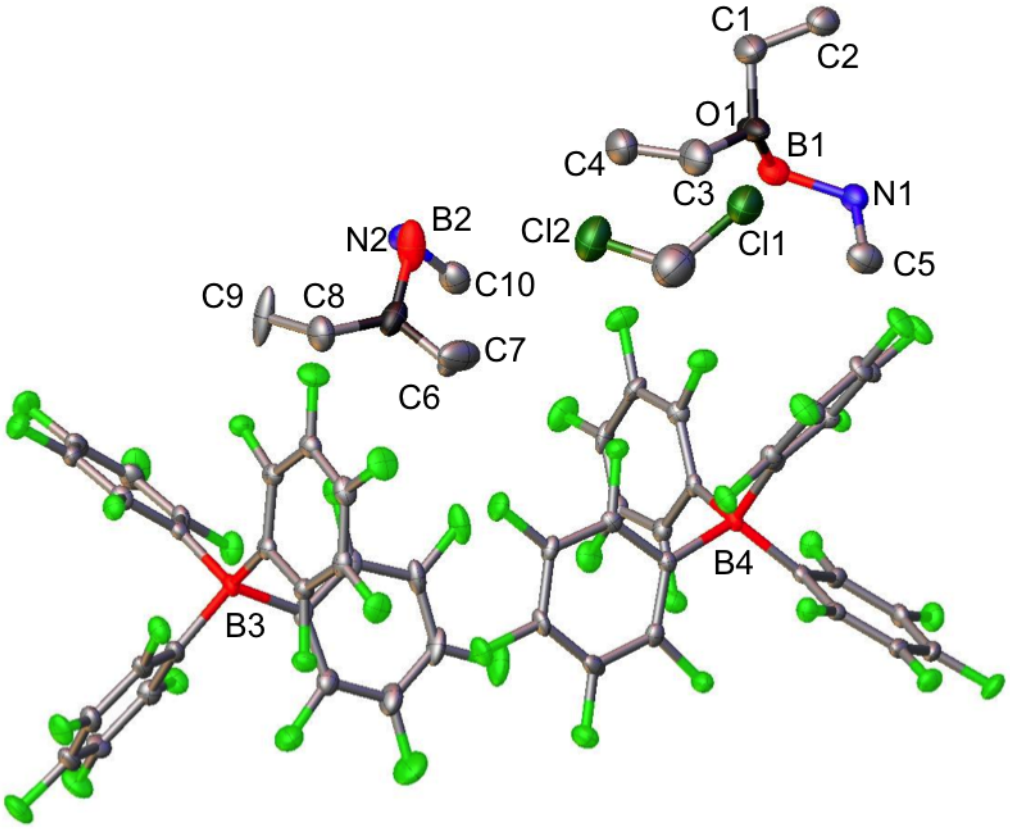

Figure S2 – Unit cell view of $[MeNH_2 \bullet BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**), showing two inequivalent boronium cations and associated $[B(C_6F_5)_4]^-$ counterions.

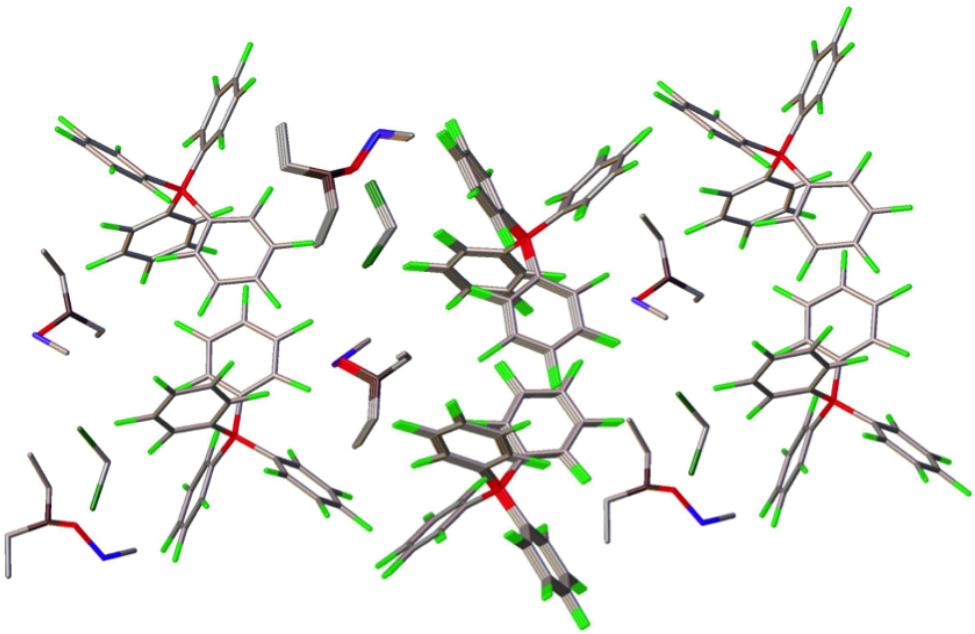

Figure S3 – Expanded solid state structure of $[MeNH_2 \bullet BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**)

It should be noted that each unit cell contained two inequivalent $[MeNH_2 \bullet BH_2(OEt_2)]^+$ moieties (Figure S2). One $[MeNH_2 \bullet BH_2(OEt_2)]^+$ moiety shows appreciable disorder and as such has been disregarded when comparing bond lengths and angles. Figure S3 illustrates the extended solid state structure of $[MeNH_2 \bullet BH_2(OEt_2)][B(C_6F_5)_4]$.

^{11}B NMR Spectra of 2, 4 and 6

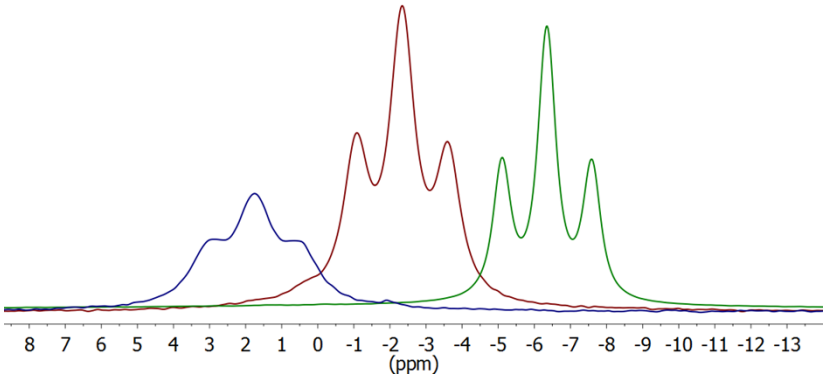

Figure S4 - ^{11}B NMR spectra (96 MHz, d_2-DCM, 25°C) of **2**, **4**, and **6**

Identification	$[MeNH_2•BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**)	$MeNH_2•BH_2Cl$ (**6**)
Empirical formula	$C_{59}H_{36}B_4Cl_2F_{40}N_2O_2$	CH_7BClN
Formula weight	1679.04	79.34
Temperature/K	100(2)	100(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	*Pnma*
a/Å	8.8098(2)	12.7715(12)
b/Å	21.0038(6)	6.5471(6)
c/Å	17.4138(5)	5.2055(5)
α/°	90.00	90.00
β/°	98.837(2)	90.00
γ/°	90.00	90.00
Volume/Å^3	3183.99(15)	435.26(7)
Z	2	4
ρ_{calc}mg/mm^3	1.751	1.211
μ/mm^{-1}	0.267	0.662
F(000)	1668.0	168.0
Crystal size/mm^3	0.26 × 0.16 × 0.12	0.35 × 0.1 × 0.04
2Θ range for data collection	3.88 to 54.96°	6.38 to 71.38°
Index ranges	$-11 \le h \le 7$, $-27 \le k \le 27$, $-22 \le l \le 22$	$-20 \le h \le 20$, $-10 \le k \le 10$, $-8 \le l \le 8$
Reflections collected	30403	10841
Independent reflections	14515[R(int) = 0.0383]	1044[R(int) = 0.0206]
Data/restraints/parameters	14515/1/989	1044/0/34
Goodness-of-fit on F^2	1.036	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0615, wR_2 = 0.1609	R_1 = 0.0199, wR_2 = 0.0518
Final R indexes [all data]	R_1 = 0.0870, wR_2 = 0.1798	R_1 = 0.0237, wR_2 = 0.0540
Largest diff. peak/hole / e Å^{-3}	0.82/-1.23	0.57/-0.22

Table S1 - Crystal data and structure refinement for $[MeNH_2•BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**) and $MeNH_2•BH_2Cl$ (**6**)

Atom	Atom	Length/ Å	Atom	Atom	Length/ Å
B1	N1	1.602(8)	B1	O1	1.514(8)
N1	C5	1.496(7)	O1	C1	1.500(7)
O1	C3	1.467(7)	C1	C2	1.461(9)
C3	C4	1.500(10)	B2	N2	1.627(9)
B2	O2	1.438(10)	N2	C10	1.442(8)
O2	C6	1.452(6)	O2	C8	1.517(7)
C6	C7	1.535(10)	C8	C9	1.472(8)

Table S2 – Selected bond lengths for $[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**)

Reaction of $[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$ (2) with $[^nBu_4N]Cl$

$[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**) was synthesized *in situ* by slow addition of a solution of $MeNH_2{\bullet}BH_3$ (2.7 mg, 0.06 mmol) in Et_2O (0.25 mL) to a solution of $[H(OEt_2)_2][B(C_6F_5)_4]$ (50 mg, 0.06 mmol) in Et_2O (0.25 mL) at room temperature in a glove-box. A solution of $[^nBu_4N]Cl$ (16.7 mg, 0.06 mmol) in Et_2O (0.25 mL) was then added dropwise and the resulting solution transferred to a quartz NMR tube. The ^{11}B NMR spectrum in Figure S5 was then obtained.

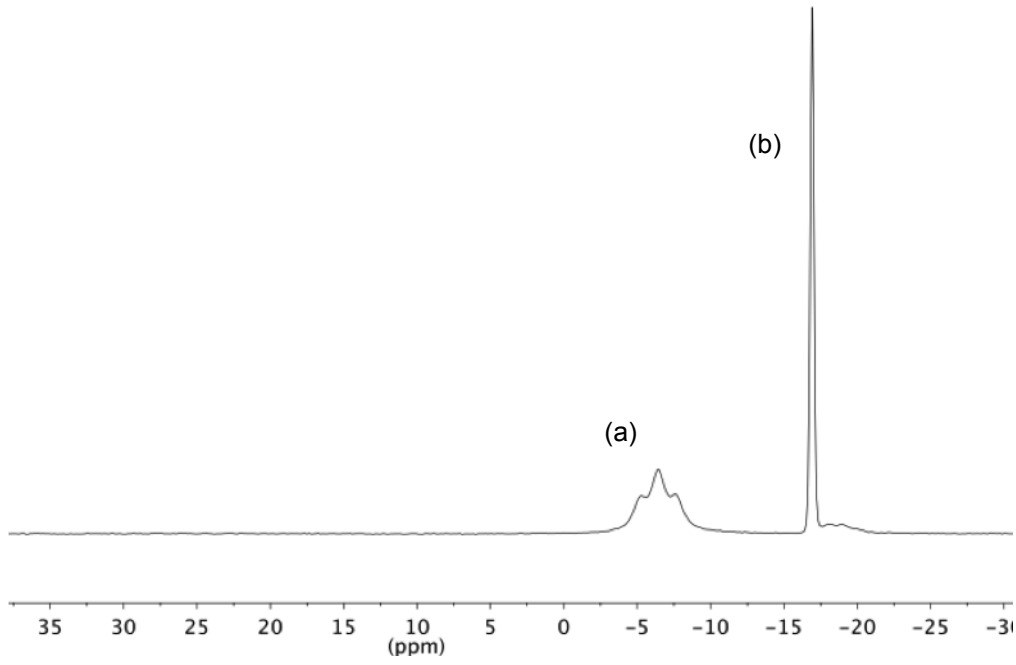

Figure S5 – ^{11}B NMR spectrum of $[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**) + $[^nBu_4N]Cl$ (5 mins, 25°C, Et_2O). (a) δ = -6.8 ppm (t, $^1J_{BH}$ = 121 Hz, $MeNH_2{\bullet}BH_2Cl$ (**6**)), (b) δ = -17.0 ppm (s, $[B(C_6F_5)_4]^-$

Reaction of $[MeNH_2•BH_2(OEt_2)][B(C_6F_5)_4]$ (2) with $[^nBu_4N][OTf]$

$[MeNH_2•BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**) was synthesized *in situ* by slow addition of a solution of $MeNH_2•BH_3$ (2.7 mg, 0.06 mmol) in Et_2O (0.25 mL) to a solution of $[H(OEt_2)_2][B(C_6F_5)_4]$ (50 mg, 0.06 mmol) in Et_2O (0.25 mL) at room temperature in a glove-box. The solution was removed from the glovebox, and added dropwise to a stirred solution of $[^nBu_4N][OTf]$ (23.5 mg, 0.06 mmol) in Et_2O (0.25 mL) at 0 °C the resulting solution transferred to a quartz NMR tube. The $^{11}B\{^1H\}$ NMR spectrum in Figure S6 was then obtained.

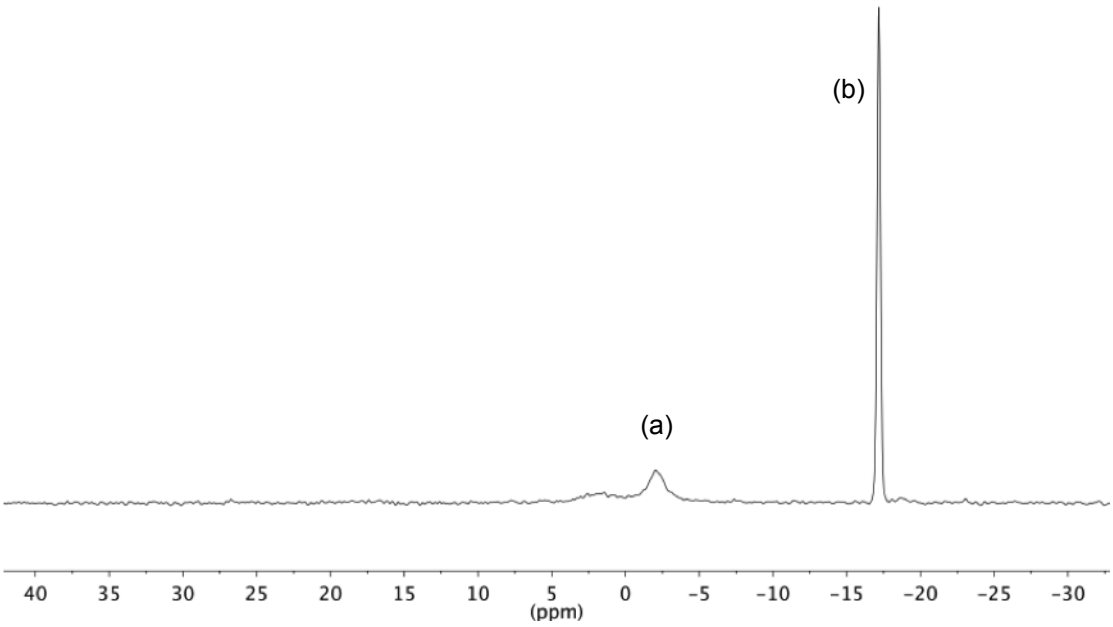

Figure S6 - $^{11}B\{^1H\}$ NMR spectrum of $[MeNH_2•BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**) + $[^nBu_4N][OTf]$ (5 mins, 25°C, Et_2O). (a) δ = -2.2 ppm (s, $MeNH_2•BH_2OTf$ (**4**)), (b) δ = -17.0 ppm (s, $[B(C_6F_5)_4]^-$

Reaction of $Me_2NH•BH_2OTf$ (3) with $^iPr_2EtN$

In a glovebox, $Me_2NH•BH_2OTf$ (**3**) (20 mg, 0.097 mmol) was dissolved in DCM (0.7 mL) and transferred to a quartz NMR tube. $^iPr_2EtN$ (0.17 mL, 0.97 mmol) was added *via* syringe, and ^{11}B and $^{11}B\{^1H\}$ NMR spectra obtained immediately. Figure S7 shows the ^{11}B NMR spectrum of the reaction after ~1 min.

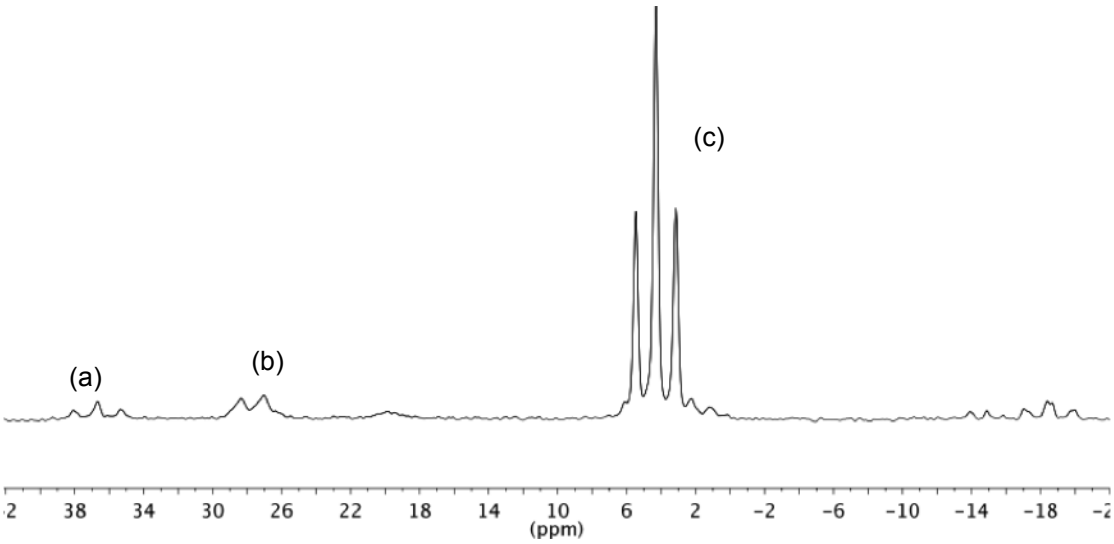

Figure S7 - ^{11}B NMR spectrum of $Me_2NH{\bullet}BH_2OTf$ (**3**)+ $^{i}Pr_2EtN$ (~1 min, 25°C, DCM). (a) δ = 36.6 ppm (t, $^{1}J_{BH}$ = 130 Hz, $Me_2N{=}BH_2$), (b) δ = 28.0 ppm (d, $^{1}J_{BH}$ = 126 Hz, $HB(NMe_2)_2$), (c) δ = 4.3 ppm (t, $^{1}J_{BH}$ = 110 Hz, $(Me_2N\text{-}BH_2)_2$)

Reaction of $Me_2NH{\bullet}BH_2Cl$ (5) with $^{i}Pr_2EtN$

In a glovebox, $Me_2NH{\bullet}BH_2Cl$ (**5**) (20 mg, 0.21 mmol) was dissolved in DCM (0.7 mL) and transferred to a quartz NMR tube. $^{i}Pr_2EtN$ (0.37 mL, 2.1 mmol) was added *via* syringe, and ^{11}B and $^{11}B\{^{1}H\}$ NMR spectra obtained immediately. Figure S8 shows the ^{11}B NMR spectrum of the reaction after ~1 min.

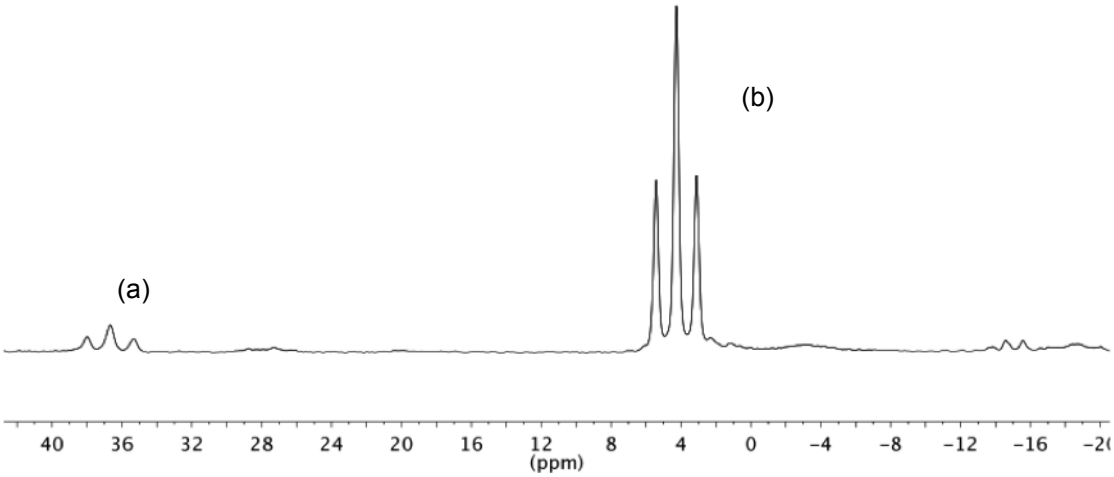

Figure S8 - ^{11}B NMR spectrum of $Me_2NH{\bullet}BH_2Cl$ (**5**) + $^{i}Pr_2EtN$ (~1 min, 25°C, DCM). (a) δ = 36.6 ppm (t, $^{1}J_{BH}$ = 130 Hz, $Me_2N{=}BH_2$), (b) δ = 4.3 ppm (t, $^{1}J_{BH}$ = 110 Hz, $(Me_2N\text{-}BH_2)_2$)

Reaction of $[Me_2NH•BH_2(OEt_2)][B(C_6F_5)_4]$ (1) with DTBP (2,6-di-*tert*-butylpyridine)

$[Me_2NH•BH_2(OEt_2)][B(C_6F_5)_4]$ (**1**) was synthesized *in situ* by slow addition of a solution of $Me_2NH•BH_3$ (14 mg, 0.24 mmol) in Et_2O (0.25 mL) to a solution of $[H(OEt_2)_2][B(C_6F_5)_4]$ (100 mg, 0.12 mmol) in Et_2O (0.25 mL) at room temperature in a glove-box. An excess of $Me_2NH•BH_3$ was used to ensure full conversion of $[H(OEt_2)_2][B(C_6F_5)_4]$. DTBP (0.26 mL, 1.2 mmol) was added *via* syringe and the $^{11}B\{^1H\}$ NMR spectrum shown in Figure S9 was obtained after ~1 min.

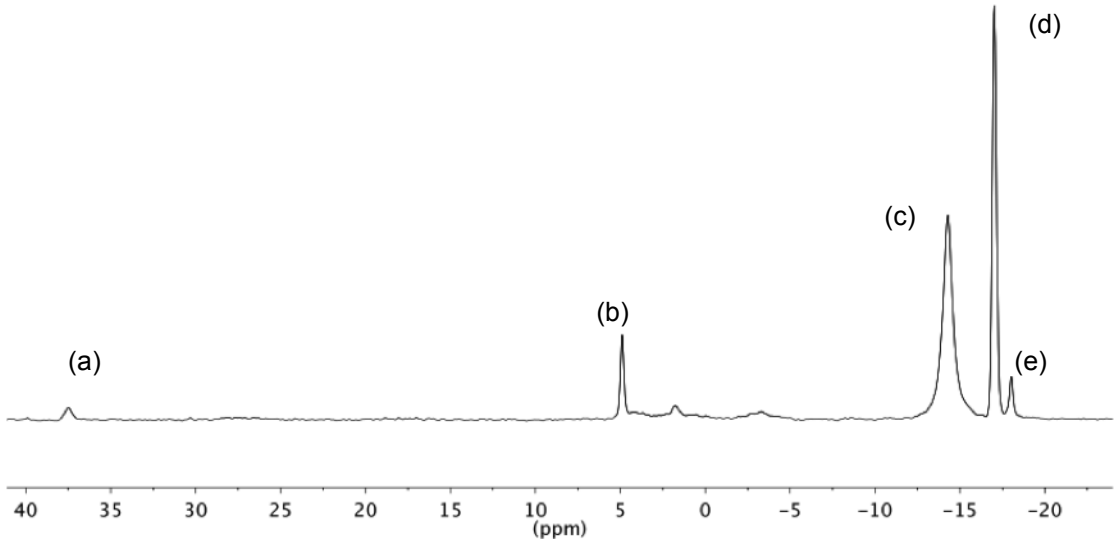

Figure S9 - $^{11}B\{^1H\}$ NMR spectrum of $[Me_2NH•BH_2(OEt_2)][B(C_6F_5)_4]$ (**1**)+ DTBP (~1 min, 25°C, Et_2O). (a) δ = 36.6 ppm (s, $Me_2N=BH_2$), (b) δ = 4.9 ppm (s, $(Me_2N\text{-}BH_2)_2$), (c) δ = -14.3 ppm (s, Excess $Me_2NH•BH_3$), (d) δ = -17.0 ppm (s, $[B(C_6F_5)_4]^-$). (e) δ = -18.0 ppm (s, $Me_2N(B_2H_5)$)

Reaction of $[MeNH_2•BH_2(OEt_2)][B(C_6F_5)_4]$ (2) with DTBP

$[MeNH_2•BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**) was synthesized *in situ* by slow addition of a solution of $Me_2NH•BH_3$ (10 mg, 0.2 mmol) in Et_2O (0.25 mL) to a solution of $[H(OEt_2)_2][B(C_6F_5)_4]$ (184.5 mg, 0.2 mmol) in Et_2O (0.25 mL) at room temperature in a glove-box. DTBP (0.4 mL, 2.0 mmol) was added *via* syringe and the ^{11}B NMR spectrum shown in Figure S10 was obtained after ~1 min. Analysis of the resultant product by ESI-MS showed no polymeric species and GPC showed no peaks associated with a material of molecular weight > 5,000 $gmol.^{-1}$

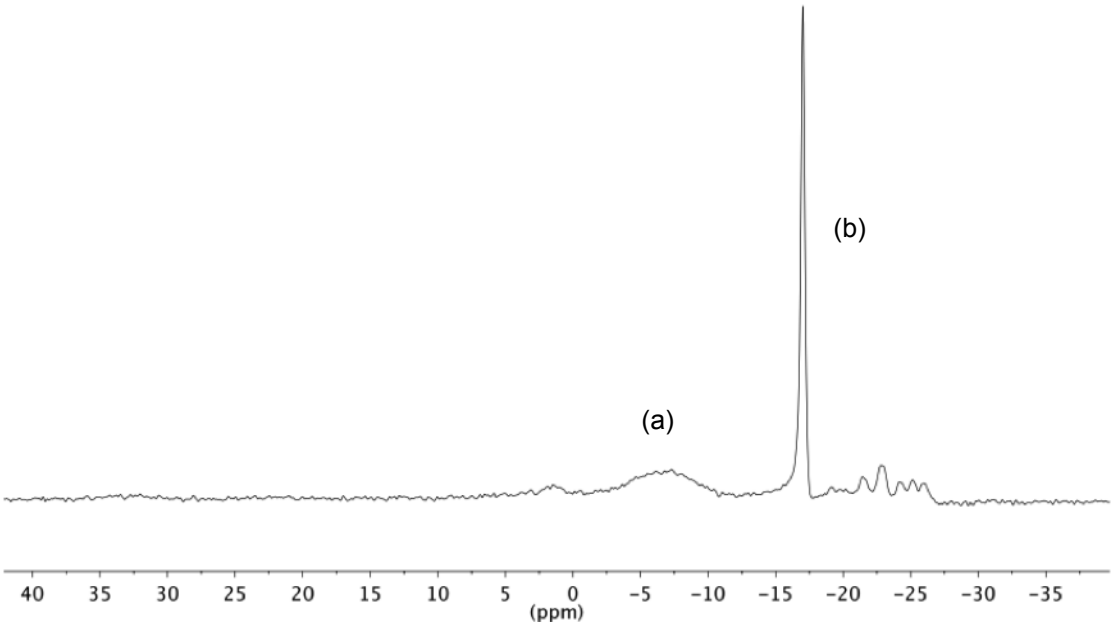

Figure S10 - $^{11}B\{^1H\}$ NMR spectrum of $[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**)+ DTBP (~1 min, 25 °C, Et_2O). (a) δ = -7.0 ppm (s, $[MeNH_2\text{-}BH_2]_n$), (b) δ = -17.0 ppm (s, $[B(C_6F_5)_4]^-$)

Procedure for Cyclohexene Trapping Reaction

Prior to the addition of DTBP, 2.5 eq. of cyclohexene was added to the reaction mixture *via* syringe. The base was then added and the ^{11}B NMR spectra obtained. An ^{11}B NMR spectrum, indicating the peak for $MeNH{=}BCy_2$ is indicated below (Figure S11). It shows the less clean nature of the reaction in the presence of cyclohexene, and the relative reduction in the yield of polyaminoborane (**8**). The broader peaks between 0 ppm to -5 ppm in Figure S11 are attributed to branchpoints in the resulting polyaminoborane.[7]

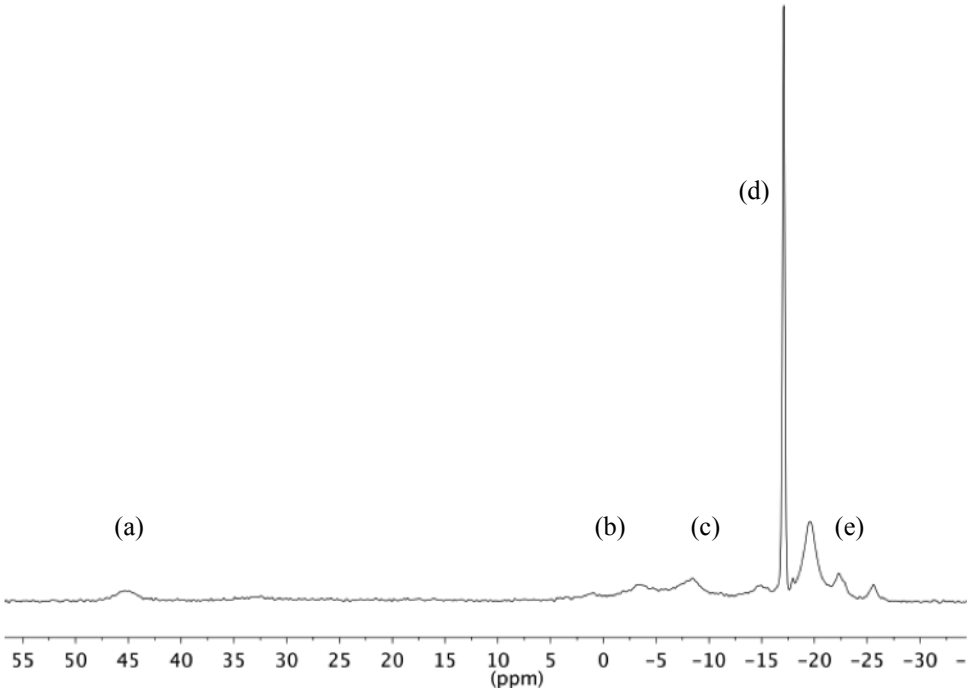

Figure S11 - $^{11}B\{^{1}H\}$ NMR spectrum of $[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**)+ DTBP + Cyclohexene (~1 min, 25 °C, DCM). (a) δ = 45.4 ppm (s, $MeNH{=}BCy_2$), (b) δ = 1.7 ppm (s, unreacted $[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$), (c) δ = -6.9 ppm (s, $[MeNH_2\text{-}BH_2]_n$), (d) δ = -17.6 ppm (s, $[B(C_6F_5)_4]^-$), (e) δ = -18.6 ppm (s, $MeNH_2{\bullet}BH_3$)

Direct Observation of $MeNH{=}BH_2$ (9) by Low Temperature NMR Spectroscopy

$[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**) was synthesized *in situ* by slow addition of a solution of $Me_2NH{\bullet}BH_3$ (5 mg, 0.12 mmol) in Et_2O (0.25 mL) to a solution of $[H(OEt_2)_2][B(C_6F_5)_4]$ (100 mg, 0.12 mmol) in Et_2O (0.25 mL) at room temperature in a glove-box. The solution was transferred to a quartz NMR tube and cooled to -78 °C. DTBP (0.1 mL, 1.2 mmol) was added *via* syringe and the tube inserted into a pre-cooled NMR probe (-60 °C). The sample was allowed to warm to -10 °C and the following spectrum was obtained.

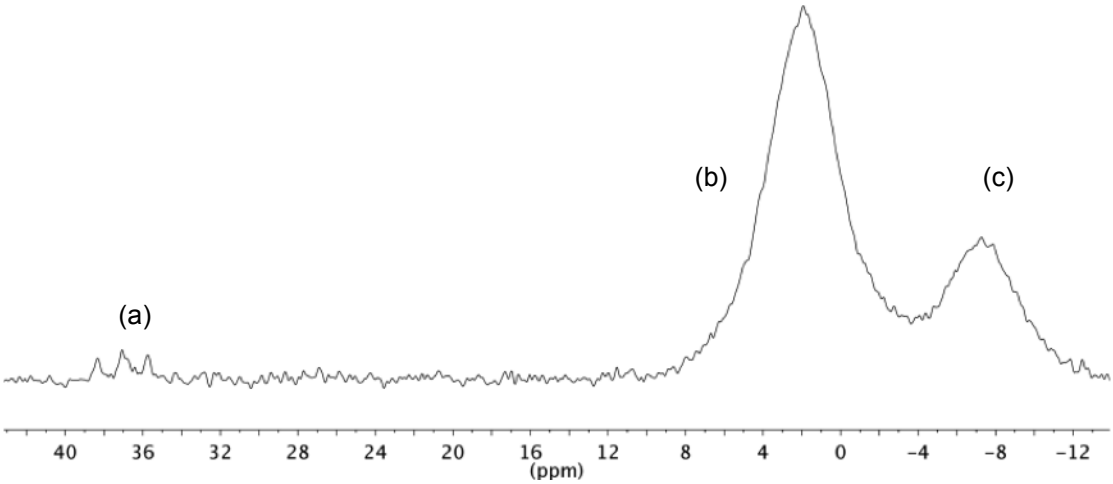

Figure S12 – Low temperature ^{11}B NMR (-10 °C) of $[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$ (**2**) + DTBP in Et_2O. $[B(C_6F_5)_4]$ peak excluded for clarity. (a) δ = 37.1 ppm (t, J_{BH} = 130 Hz, $MeNH{=}BH_2$), (b) δ = 1.9 ppm (bs, $[MeNH_2{\bullet}BH_2(OEt_2)][B(C_6F_5)_4]$, (c) δ = -7.2 ppm (bs, $[MeNH\text{-}BH_2]_n$)

Reaction of $MeNH_2{\bullet}BH_2Cl$ (6) with $^{i}Pr_2EtN$

In a glovebox, $MeNH_2{\bullet}BH_2Cl$ (**6**) (20 mg, 0.25 mmol) was dissolved in DCM (0.7 mL) and transferred to a quartz NMR tube. The NMR tube was removed from the glovebox, and using a Schlenk line, $^{i}Pr_2EtN$ (0.4 mL, 2.5 mmol) was added rapidly *via* syringe. An ^{11}B NMR spectrum of the reaction mixture was obtained after ~ 1 min (Figure S13). Analysis of this polymer by ESI-MS showed no polymeric species and GPC showed no peaks associated with a material of molecular weight > 5,000 gmol.$^{-1}$.

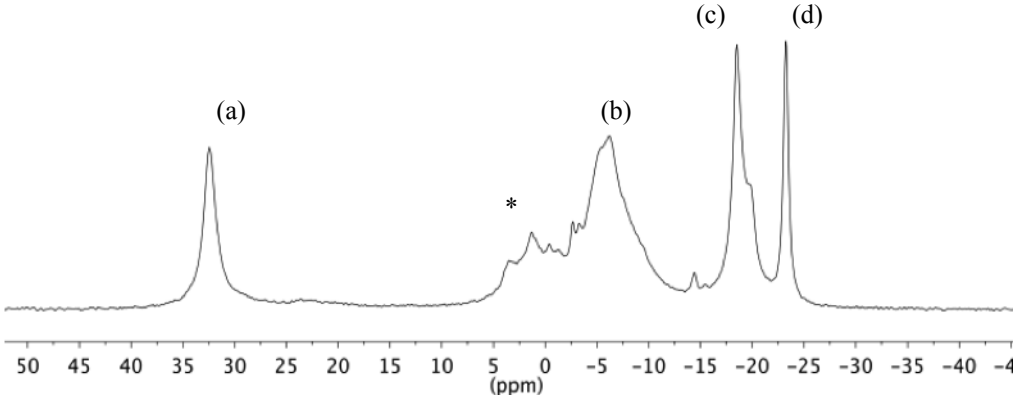

Figure S13 - $^{11}B\{^{1}H\}$ NMR spectrum of $MeNH_2{\bullet}BH_2Cl$ (**6**) + $^{i}Pr_2EtN$ (~1 min, 25 °C, DCM). (a) δ = 32.2 ppm (s, $(MeN\text{-}BH)_3$), (b) δ = -6.9 ppm (s, $[MeNH_2\text{-}BH_2]_n$), (c) δ = -18.6 ppm (s, $MeNH_2{\bullet}BH_3$), (d) δ = -23.4 ppm (s, $MeNH(B_2H_5)$),

* These peaks are tentatively attributed to the presence of chain branching[7] or byproducts from hydrogen transfer reactions.

Reaction of $MeNH_2 \bullet BH_2OTf$ (4) with $^iPr_2EtN$

In a glovebox, $MeNH_2 \bullet BH_2OTf$ (**4**) (500 mg, 2.59 mmol) was weighed into a Schlenk flask and dissolved in DCM (1 mL). On a Schlenk line, $^iPr_2EtN$ (0.45 mL, 2.59 mmol) was added rapidly *via* syringe and an ^{11}B NMR spectrum of the crude reaction mixture obtained (Figure S14). Isolation of the polymer was subsequently attempted through repeated precipitations (x3) of a DCM solution into a large volume of rapidly stirred hexanes to yield a white solid. The solid was still found to contain [$^iPr_2EtN$-H][OTf], which precluded calculation of an isolated yield. ESI-MS of the polymer was obtained from a 1 $mgmL^{-1}$ solution in MeCN/DCM and is shown in Figure S16. Analysis of this polymer by GPC showed no peaks associated with a material of molecular weight > 5,000 $gmol.^{-1}$

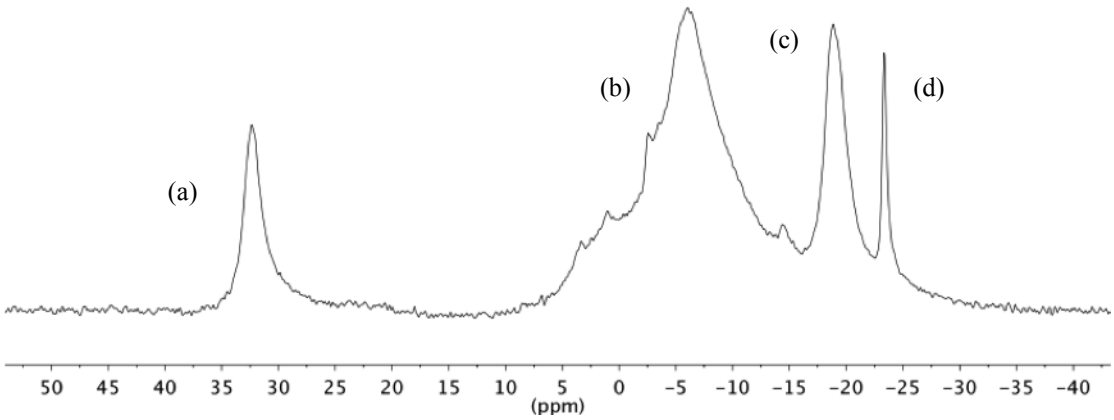

Figure S14 - $^{11}B\{^1H\}$ NMR spectrum of $MeNH_2 \bullet BH_2OTf$ (**4**)+ $^iPr_2EtN$ (~1 min, 25°C, DCM). (a) δ = 32.2 ppm (s, $(MeN\text{-}BH)_3$), (b) δ = -6.9 ppm (s, $[MeNH_2\text{-}BH_2]_n$), (c) δ = -18.6 ppm (s, $MeNH_2 \bullet BH_3$), (d) δ = -23.4 ppm (s, $MeNH(B_2H_5)$)

In addition, this reaction was carried out at low temperature (0 °C) in an attempt to give a cleaner reaction, however the product distribution remained the same. (Figure S15)

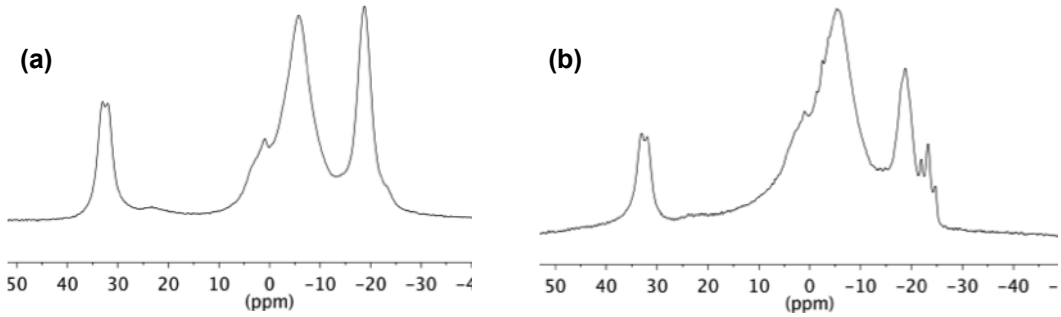

Figure S15 - $^{11}B\{^{1}H\}$ NMR spectrum of $MeNH_2 \bullet BH_2OTf$ (**4**) + $^{i}Pr_2EtN$ (~1 min, DCM). (**a**) is carried out at 0 °C and (**b**) at 25 °C. See Figure S14 for peak assignments.

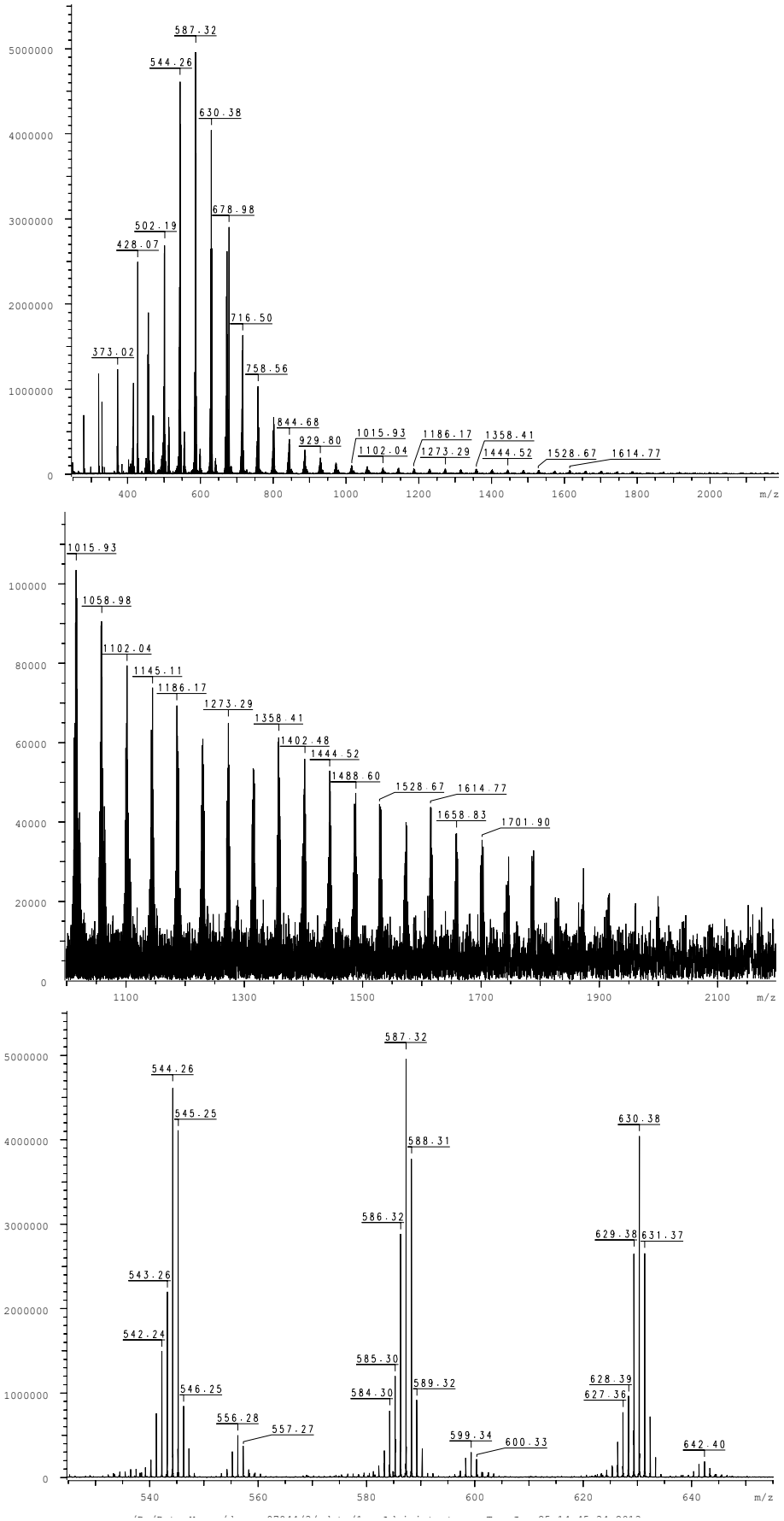

Figure S16 – Poly (*N*-methylyaminoborane) **8** derived from $MeNH_2$•BH_2OTf (**4**) in negative ion ESI-MS (-110V capillary voltage)

From Figure S16 it is clear that there are two product distributions present in the sample, the lower intensity distribution can be assigned to cyclic species. For example the peak at 556.28 m/z can be attributed to a polymer of the form $[MeNH\text{-}BH_2]_{13}$ losing H^+ upon ionization. (observed 556.28 m/z, calculated 556.78 m/z). The more intense distribution however appears to correspond to a linear species. For example, the peak at 544.26 m/z can be tentatively assigned as $MeNH_2\text{-}[BH_2\text{-}MeNH]_{12}\text{-}H$. Taking into account the isotopic distributions present in these materials, the most intense peak corresponds to $MeNH_2\text{-}[BH_2\text{-}MeNH]_{12}\text{-}H$ assuming loss of H^+ to generate a negative ion would be 545.76 m/z. We therefore propose a loss of H_2 upon ionization to give the observed distribution - this is also observed in the CI-MS of species **3** and **4**.

Peaks Assigned to Cyclic Product (8_C) $[MeNH\text{-}BH_2]_x$

428 (x = 10), 470 (x = 11), 513 (x = 12), 556 (x = 13), 599 (x = 14), 642 (x = 15)

Peaks Assigned to Linear Product (8_L) $MeNH_2\text{-}[BH_2\text{-}MeNH]_x\text{-}H$

458 (x = 10), 502 (x = 11), 544 (x = 12), 587 (x = 13), 630 (x = 14), 674 (x = 15), 717 (x = 16), 759 (x = 17), 802 (x = 18), 845 (x = 19), 888 (x = 20), 930 (x = 21), 973 (x = 22), 1016 (x = 23), 1059 (x = 24), 1102 (x = 25), 1145 (x = 26), 1186 (x = 27), 1229 (x = 28), 1273 (x = 29), 1315 (x = 30), 1358 (x = 31), 1402 (x = 32), 1445 (x = 33), 1489 (x = 31), 1529 (x = 32), 1573 (x = 33), 1614 (x = 34), 1659 (x = 35), 1702 (x = 36), 1746 (x = 37), 1788 (x = 38). Peaks can be observed further up to x ~44, but cannot be accurately assigned.

NB: As noted in the manuscript, both 10 equiv. and 1 equiv. of base were used in reactions with **2**, **4** and **6**. 10 equiv. of base was used to ensure a high rate of deprotonation, in order to generate the highest possible concentration of the reactive monomer $MeNH{=}BH_2$ in solution, thus promoting the formation of higher molecular weight polymers. The use of 1 equiv. of base was explored to ascertain whether the reaction was cleaner with a lower concentration of base. The effect of the concentration of base on the product distribution as monitored by ^{11}B NMR spectroscopy in all cases was found to be negligible.

Procedure for Cyclohexene Trapping Reaction

An identical procedure was employed as for the previous trapping reaction. The ^{11}B NMR spectrum, indicating the peak for $MeNH{=}BCy_2$ is indicated below (Figure S17). Again it shows the less clean nature of the reactions in the presence of cyclohexene, and the relative reduction in the yield of polyaminoborane (**8**). There are again unidentified products, which are not labeled, e.g. the peak at -11 ppm. The broader peaks between 0 ppm to -5 ppm in Figure S17 are again attributed to branchpoints in the resulting polyaminoborane and side products from hydrogen transfer reactions.[7]

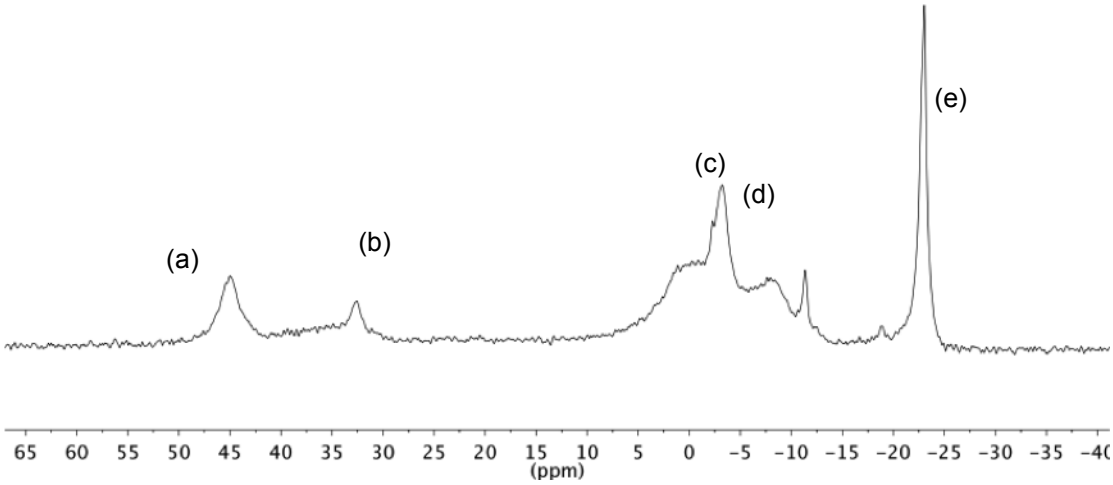

Figure S17 - $^{11}B\{^1H\}$ NMR spectrum of $MeNH_2{\bullet}BH_2OTf$ (**4**) + $^{i}Pr_2EtN$ + Cyclohexene (~1 min, 25 °C, DCM). (a) δ = 45.4 ppm (s, $MeNH{=}BCy_2$), (b) δ = 32.7 ppm (s, $(MeN\text{-}BH)_3$), (c) δ = -2.2 ppm (s, unreacted $MeNH_2{\bullet}BH_2OTf$), (d) δ = -6.6 ppm (s, $[MeNH_2\text{-}BH_2]_n$), (e) δ = -22.0 ppm (s, $MeNH(B_2H_5)$)

Isolation of poly(*N*-methylaminoborane) (8)

Isolation of **8** generated from **4** was precluded by the similar solubility of $[^{i}Pr_2EtN\text{-}H][OTf]$ and **8** in common organic solvents. In addition, column chromatography did not result in good product separation. To combat this the new species $[MeNH_2{\bullet}BH_2(OEt_2)][AlCl_4]$ was synthesized by reaction of **6** with $AlCl_3$ in Et_2O.

Synthesis of $[MeNH_2{\bullet}BH_2(OEt_2)][AlCl_4]$

A solution of $AlCl_3$ (840 mg, 6.30 mmol) in Et_2O (20 mL) was added dropwise to a stirred solution of $MeNH_2{\bullet}BH_2Cl$ (500 mg, 6.30 mmol) in Et_2O (20 mL) *via* syringe,

resulting in a cloudy solution. Upon standing, the reaction mixture phase separated (Et_2O/[$MeNH_2$•$BH_2(OEt_2)$][$AlCl_4$]) and in order to obtain a crude ^{11}B NMR, a small amount of DCM (< 5 mL) was added to dissolve the product. The solvent was subsequently removed *in vacuo* to yield spectroscopically pure [$MeNH_2$•$BH_2(OEt_2)$][$AlCl_4$] as a colourless oil (1.32 g, 73%).

For [$MeNH_2$•$BH_2(OEt_2)$][$AlCl_4$]

^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.51 (6H, t, $^3J_{HH}$ = 7 Hz, ($C\underline{H_3}CH_2)_2O$), 2.62 (3H, d, $^3J_{HH}$ = 6 Hz, ($C\underline{H_3}$)NH_2), 4.37 (4H, q, $^3J_{HH}$ = 7 Hz, ($CH_3C\underline{H_2}$)$_2O$), 4.61 (2H, br, (CH_3)$N\underline{H_2}$)

$^{13}C\{^1H\}$ NMR (76 MHz, CD_2Cl_2): δ 13.2 (s, ($\underline{C}H_3CH_2)_2O$), 30.1 (s, ($\underline{C}H_3$)NH_2), 79.0 (s, ($CH_3\underline{C}H_2)_2O$)

^{11}B NMR (96 MHz, CD_2Cl_2): δ 1.4 (t, $^1J_{BH}$ = 121 Hz)

Reaction of [$MeNH_2$•$BH_2(OEt_2)$][$AlCl_4$] with DTBP

[$MeNH_2$•$BH_2(OEt_2)$][$AlCl_4$] (746 mg, 2.6 mmol) was then dissolved in DCM (1 mL) and DTBP (0.58 mL, 2.6 mmol) was added rapidly *via* syringe. Precipitation of [DTBP-H][$AlCl_4$] was immediately observed. The product was extracted using cold (-78^{o}C) DCM and the solvent removed *in vacuo* to yield a white solid. This polymer was purified by repeated precipitation from THF into a solution of rapidly stirred hexanes and dried overnight *in vacuo*. Yield (104 mg, 93%).

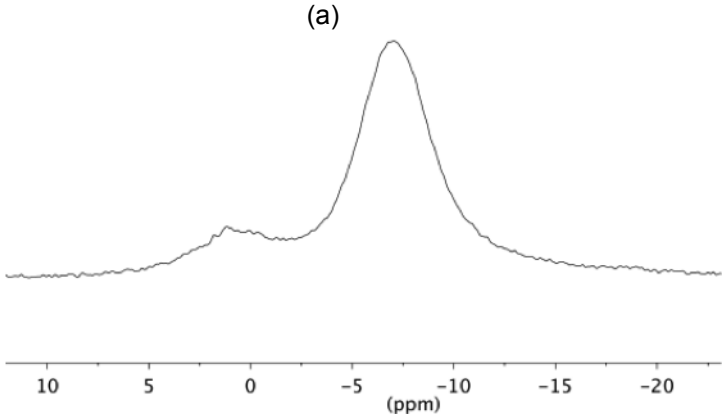

Figure S18 - $^{11}B\{^1H\}$ NMR spectrum of **8** produced from [$MeNH_2$•$BH_2(OEt_2)$][$AlCl_4$]. (a) δ = -7.05 (bs, [$MeNH\text{-}BH_2]_n$),

Figure S18 shows a peak at ~ 0 ppm, which was initially thought to be an impurity in the sample. However, despite further precipitation of the product using the same

methodology, the peak was found to persist (Figure S19). This peak is associated with the polymer and probably arises from branch points.[7] ESI-MS of this species indicated a DP_n of up to 20.

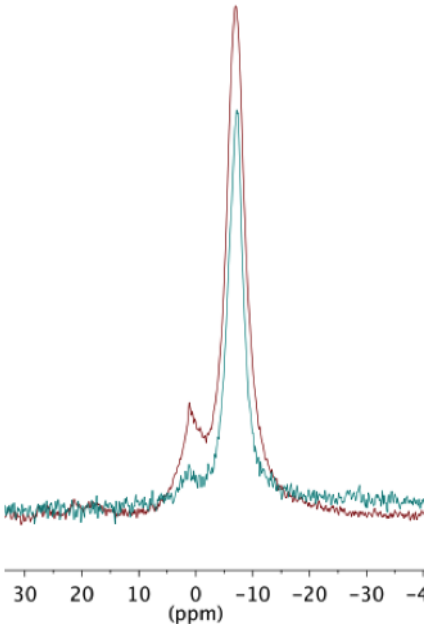

Figure S19 – ^{11}B NMR spectrum of the polymer shown in Figure S18 (red) and after further reprecipitation (blue).

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