

Supporting Information

for

BH₃•SMe₂ Addition Enables Molar Mass Control *via* Chain Stabilization in Phosphine-Borane Dehydropolymerization

*Matthew A. Wiebe,^a Jade E. T. Watson,^a Charles Killeen,^a J. Scott McIndoe,^a Anne Staubitz,^{*b} and Ian Manners^a*

^a *Department of Chemistry, University of Victoria, 3800 Finnerty Rd, Victoria, British Columbia, V8P 5C2, Canada*

^b *University of Kiel, Otto-Diels-Institute of Organic Chemistry, Otto-Hahn-Platz 4, 24118 Kiel, Germany*

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General Considerations

Unless otherwise noted, storage and manipulation of chemicals were performed under an inert atmosphere of either N₂ or Ar gas using standard Schlenk techniques, or, carried out in an MBraun 200B glovebox. Further, any glassware used was dried overnight in a 200 °C oven. Toluene was dried using an MBraun Grubbs/Dow solvent purification system¹ and stored over activated 4 Å molecular sieves. 2-Methyl tetrahydrofuran was purchased from Sigma Aldrich and was dried *via* distillation off sodium metal and degassed *via* freeze-pump-thaw cycles. The phosphine-borane adduct, PhPH₂•BH₃ (**1**), was prepared using standard literature procedures.² LiOTf, Mg(OTf)₂, Sc(OTf)₃, LiNTf₂, [Bu₄N][OTf], [Li][B(C₆F₅)₄]•Et₂O, BH₃•SMe₂, and CDCl₃ were all purchased from Sigma Aldrich and used as received. Solvents used in the isolation of polymeric material were purchased from Sigma Aldrich and used as received. **Note: reactions performed in sealed J-Young's NMR tubes are under pressure, care should be taken when handling reaction vessels under pressure.**

Nuclear Magnetic Resonance (NMR) spectroscopy was performed on a Bruker Avance NEO 500 MHz spectrometer. ¹H NMR spectra were referenced to protons in the solvents and heteronuclear spectra were referenced using the recommended IUPAC reference compounds.

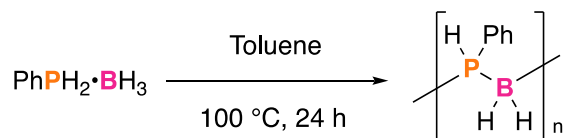
Mass spectrometry experiments were performed with a Waters Synapt G2-Si in positive and negative modes with a capillary voltage of 3.00 kV, a cone voltage of 60 V, and a source offset voltage of 80 V. All samples were prepared in HPLC grade dichloromethane (Supelco, EMD Millipore). An optimal response was obtained using a desolvation gas flow of 100 L h⁻¹, cone gas flow of 100 L h⁻¹, source temperature of 50 °C, and desolvation gas temperature of 150 °C. The scan time was set to 2 s with an inter-scan time of 0.1 s, over a mass range of *m/z* 50-3 000 Da.

Gel-permeation chromatography (GPC) was performed on a Malvern RI max Gel Permeation Chromatograph, equipped with an automatic sampler, a pump, an injector,

and inline degasser. The columns (styrene/divinyl benzene gel, 1xT5000 and 1xT3000) were maintained at 35 °C. Sample elution was detected by means of a differential refractometer. THF (VWR), containing 0.1 wt% [*n*-Bu₄N]Br to prevent column adsorption,³ was used as the eluent at a flow rate of 1 mL min⁻¹. Samples were dissolved in THF (1 mg/mL) and filtered through a 0.2 μm PTFE syringe filter before analysis. Calibration was conducted using commercially available monodisperse polystyrene standards (Aldrich, 1 200 – 4 200 000 Da).

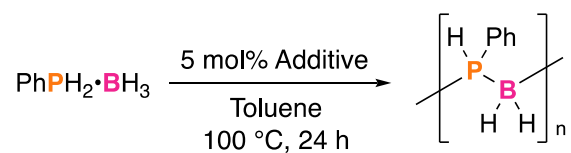
Synthetic Procedures

Thermal Dehydrogenation of **1** in Toluene



To a dram vial the phosphine-borane adduct, **1**, (0.5 mmol, 62 mg) and toluene (250 μL) were added. Then, this solution was transferred to a J-Young's NMR tube. The J-Young's NMR tube was then sealed and removed from the glovebox and placed in a heating block set to 100 $^\circ\text{C}$. The reaction was heated at this temperature over the course of 24 h, after which the heating plate was turned off, and the reaction was left to cool. Once the temperature gauge gave a value below 30 $^\circ\text{C}$, the tubes were removed from the heating block and carefully unsealed to allow the built-up pressure to release. Afterwards, CDCl_3 was added to the tube in open air, and the reactions were assessed by ^{31}P NMR to confirm the reaction was complete and that polyphosphinoborane, **2**, was accessed. In order to isolate the polymeric material (**2**), the resulting solution of **2** was added dropwise to a rapidly stirring solution of $i\text{PrOH}$ at -20 $^\circ\text{C}$, resulting in the precipitation of colourless polymeric material. The vial containing the precipitate and supernatant was then centrifugated at 4 000 revolutions per minute (RPM) for 1 h, before decanting the supernatant and collecting the white precipitate. The precipitate was briefly dried in air and redissolved in THF before the precipitation was repeated in rapidly stirring hexanes that was cooled to -20 $^\circ\text{C}$. Subsequently the precipitation was centrifugated at 4 000 RPM for 5 min, then the precipitate was collected by removal of the supernatant. This precipitate was then dried *in vacuo* overnight, resulting in a white powder in 35% yield (22 mg). Analysis by ^1H , ^{11}B , and ^{31}P NMR spectra that match what was previously reported.⁴ GPC analysis was performed to confirm polymeric material was accessed (**Figure S1** and **Table S1**).

Polymerizations Performed in Toluene with Additives



To a dram vial phosphine-borane adduct (**1**) (0.5 mmol, 62 mg) and toluene (250 μL) were added. Then, in a J-Young's NMR tube 5 mol% (0.025 mmol) of the additive was weighed out and the solution of **1** in toluene was transferred to the tube. The J-Young's NMR tube containing **1** and the additive was then sealed and removed from the glovebox and placed in a heating block set to 100 $^\circ\text{C}$. The reaction was heated at this temperature over the course of 24 h, after which the heating plate was turned off, and the reaction was left to cool to room temperature. Once the temperature gauge gave a value below 30 $^\circ\text{C}$, the tubes were removed from the heating block and carefully unsealed to allow the built-up pressure to release. Afterwards, CDCl_3 was added to the tube in open air, and the reactions were assessed by ^{31}P NMR spectroscopy to confirm the reaction was complete and polyphosphinoborane (**2**) was accessed. Polymer samples were isolated as described above in 30–64% yield. Gel permeation chromatography was used to determine the molar mass of materials accessed (**Figure S1** and **Table S1**).

^1H NMR (500 MHz, 298 K, CDCl_3): δ = 6.85 – 7.52 ppm (5 H, br m, Ar-H), 4.29 ppm (1 H, br d, $^1J_{\text{HP}}$ = 349 Hz, PH), 1.53 ppm (2 H, br, BH_2). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 298 K, CDCl_3): δ = -34.7 ppm (br); ^{31}P NMR (200 MHz, 298 K, CDCl_3): δ = -48.9 ppm (d, $^1J_{\text{PH}}$ = 349 Hz).

**GPC traces of material obtained
from polymerizations performed in toluene**

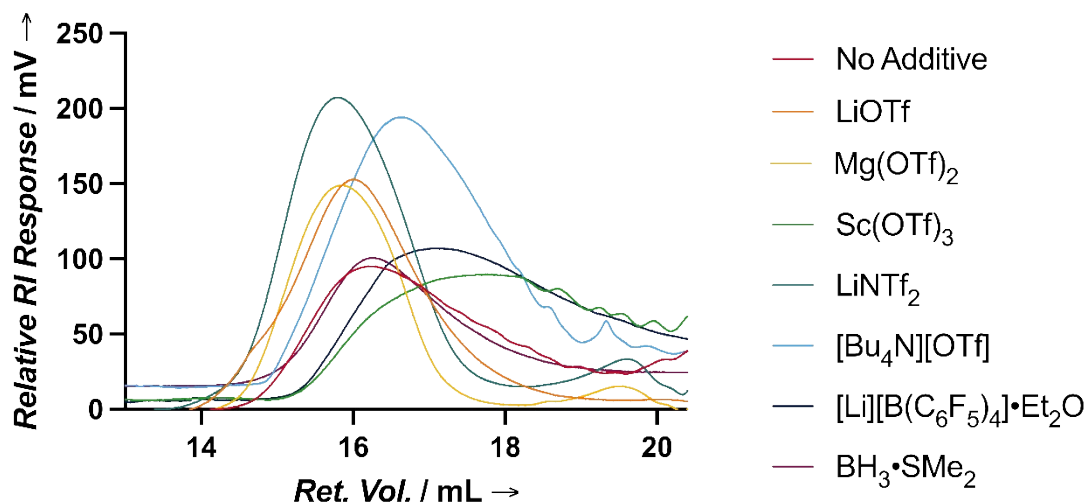
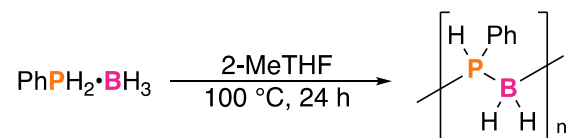
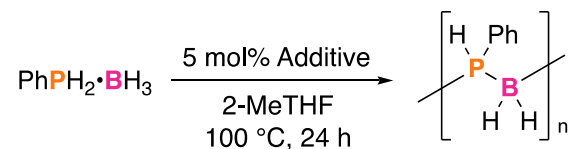


Figure S1: GPC traces of materials obtained from dehydropolymerizations performed in toluene. Samples were prepared as 1 mg•mL solutions in THF and ran with an eluent of THF containing 0.1 wt% of [Bu₄N][Br] with a flow rate of 1 mL•min.



Thermal Dehydropolymerization in 2-MeTHF

To a dram vial phosphine-borane adduct, (**1**) (0.50 mmol, 62 mg) and 2-methyl tetrahydrofuran (250 μL) were added. Then, this solution was transferred to a J-Young's NMR tube. The J-Young's NMR tube was then sealed and removed from the glovebox and placed in a heating block set to 100 $^\circ\text{C}$. The reaction was heated at this temperature over the course of 24 h, after which the heating plate was turned off, and the reaction was left to cool to room temperature. Once the temperature gauge gave a value below 30 $^\circ\text{C}$, the tubes were removed from the heating block and carefully unsealed to allow the built-up pressure to release. Afterwards, CDCl_3 was added to the tube in open air, and the reactions were assessed by ^{31}P NMR spectroscopy to determine the reaction was complete and to confirm that polyphosphinoborane (**2**) was accessed. Afterwards, the polymer was isolated as described above in 70% yield (43 mg). GPC was used to determine the molar mass of materials accessed (**Figure S2** and **Table S1**).



Polymerizations Performed in 2-MeTHF with Additives

To a dram vial, **1** (0.50 mmol, 62 mg) was added. Then, 5 mol% of the additive and 2-MeTHF was added to this vial. Subsequently, the reaction mixtures were transferred to J-Young's NMR tubes. The J-Young's NMR tubes were then sealed, removed from the glovebox, and placed in a heating block set to 100 $^\circ\text{C}$. The reaction was then heated at this temperature for 24 h, after which it was allowed to cool and carefully depressurized. Subsequently, polymer samples were isolated as described for reactions performed in

toluene in 24 – 71% yield. Similarly, GPC was used to assess the materials produced (Figure S2 and Table S1).

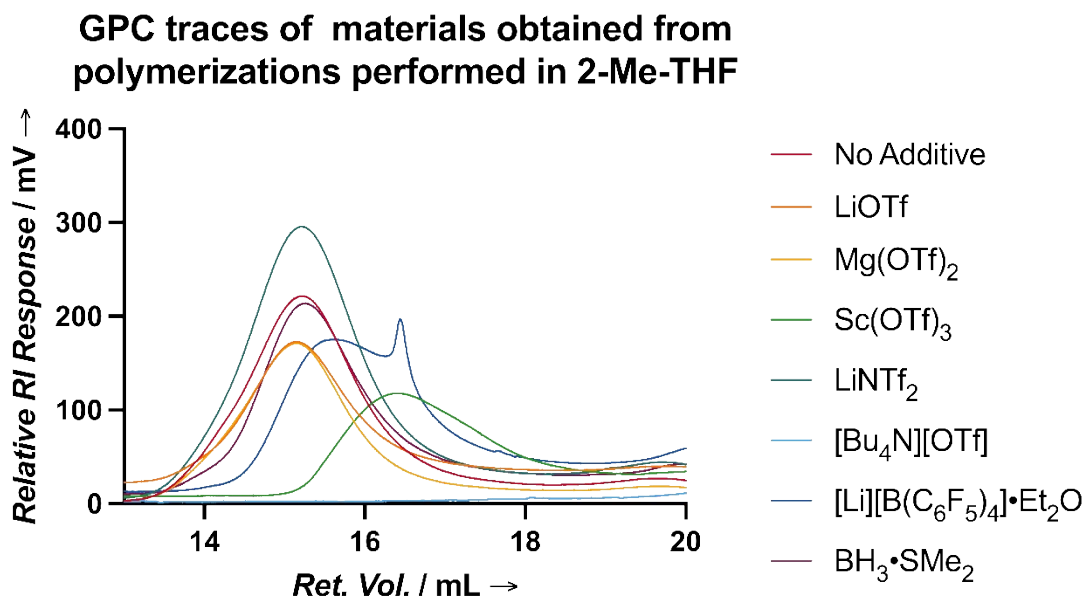
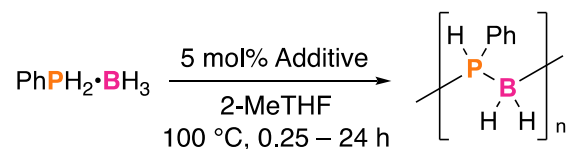


Figure S2: GPC traces of materials obtained from dehydropolymerizations of **1** performed in 2-MeTHF. Samples were prepared as 1 mg•mL solutions in THF and ran with an eluent of THF containing 0.1 wt% of [Bu₄N][Br] with a flow rate of 1 mL•min.

Determination of Conversion and Molar Mass of **2** at 0.25 to 24 h



To determine the approximate rate of dehydropolymerization of **1** to **2** in 2-MeTHF solutions with LiOTf or $\text{BH}_3\cdot\text{SMe}_2$ as additives, reactions were set up in J-Young's NMR tubes with of **1** (0.25 mmol) either of LiOTf or $\text{BH}_3\cdot\text{SMe}_2$ (5 mol%) and total reaction volumes of 125 μL of 2-MeTHF. The J-Young's NMR tubes were sealed, removed from the glove box, and heated for either 6, 16, or 24 h. Afterwards, the tubes were removed from heating and cooled to 20 $^\circ\text{C}$, diluted with of CDCl_3 (750 μL), and monitored by $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy yielding the spectra in **Figures S19 – S22** and represented graphically in **Figure S5** below. Afterwards, the polymers were isolated as described above as white powders in 49–72% yields and analyzed by GPC to determine the molar mass of isolated materials (**Figures S3** and **S4**).

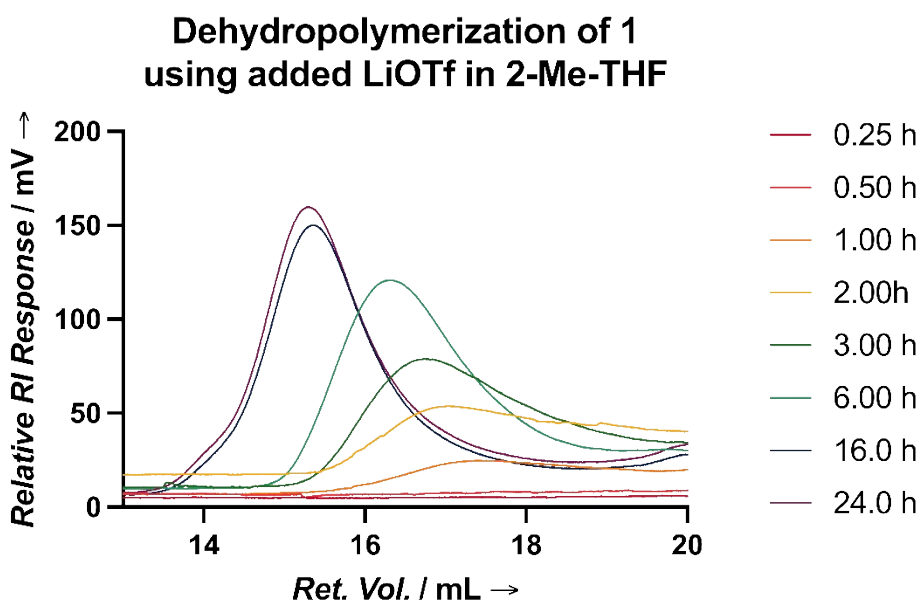


Figure S3: GPC traces of materials obtained from the dehydropolymerization of **1** over 24 h using LiOTf as the catalyst. Samples were prepared as 1 mg•mL solutions in THF and ran with an eluent of THF containing 0.1 wt% of $[\text{Bu}_4\text{N}][\text{Br}]$ with a flow rate of 1 mL•min.

Dehydropolymerization of **1
using added $\text{BH}_3\cdot\text{SMe}_2$ in 2-Me-THF**

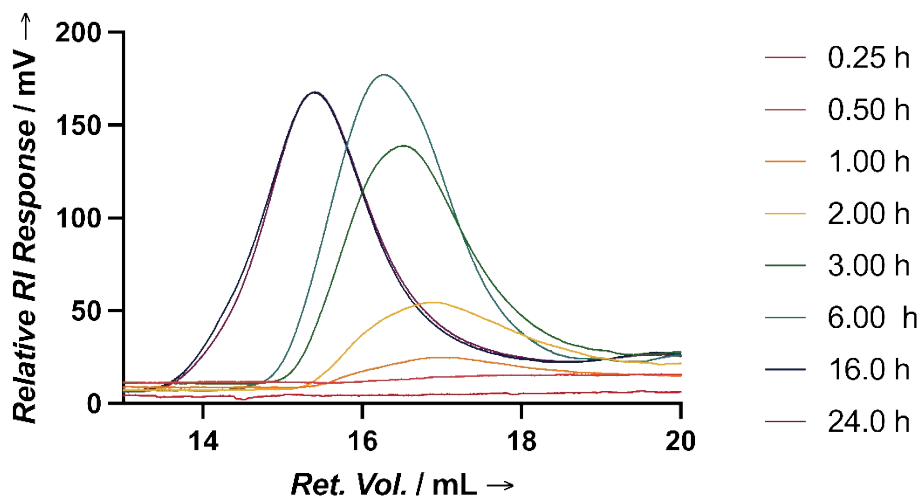


Figure S4: GPC traces of materials obtained from the dehydropolymerization of **1** over 24 h using $\text{BH}_3\cdot\text{SMe}_2$ as the catalyst. Samples were prepared as 1 mg·mL solutions in THF and ran with an eluent of THF containing 0.1 wt% of $[\text{Bu}_4\text{N}][\text{Br}]$ with a flow rate of 1 mL·min.

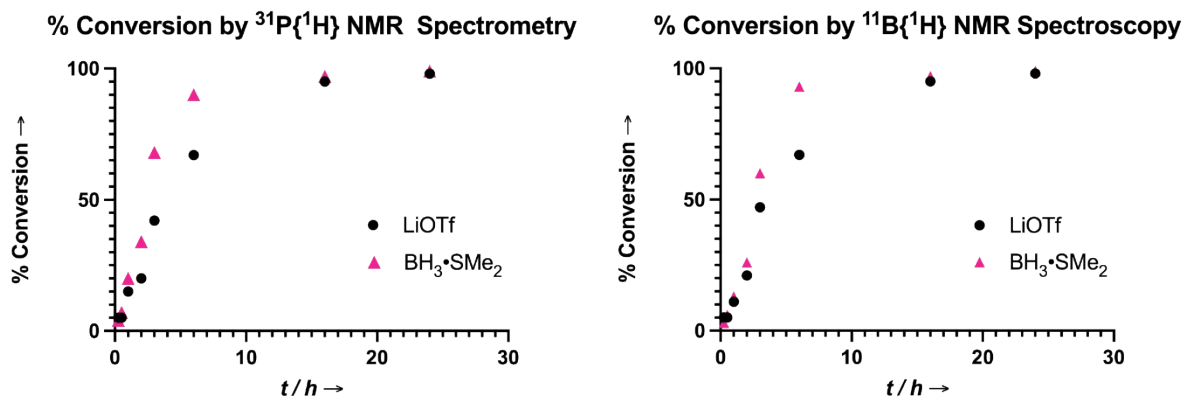
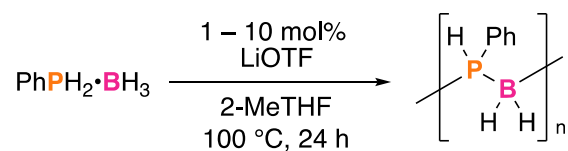


Figure S5: Relative conversion of **1** to dehydrogenated products over 24 h using either $\text{BH}_3\cdot\text{SMe}_2$ or LiOTf as the catalyst. Values were obtained by the relative integrations of products and reactants in their respective NMR spectra.

Polymerizations Performed in 2-MeTHF using LiOTf (1–10 mol%)



First, a solution of LiOTf (1 M) in 2-MeTHF was prepared. Afterwards, in a dram vial, phosphine-borane adduct (**1**) (0.50 mmol, 62 mg) was added. Then, the required amount of the 1 M solution of LiOTf was added to the vial (5 – 50 μL), and solvent was added to the reaction to contain a total volume of 250 μL (i.e., 2 M of **1** in 2-MeTHF). The reaction mixture was transferred to a J-Young's NMR tube and placed in a heating block set to 100 $^\circ\text{C}$. The reaction was then heated for 20 h, after which it was allowed to cool and carefully depressurized. Then, CDCl_3 was added and the reactions were analyzed by ^{31}P NMR spectroscopy to ensure that the reaction had reached completion and that **2** was produced. Polymer samples were isolated as described for reactions performed in toluene in 50 – 74% yield. Similarly, GPC was used to assess the materials produced as presented in **Figure 1** in the main text and the GPC traces obtained are available in **Figure S6** below.

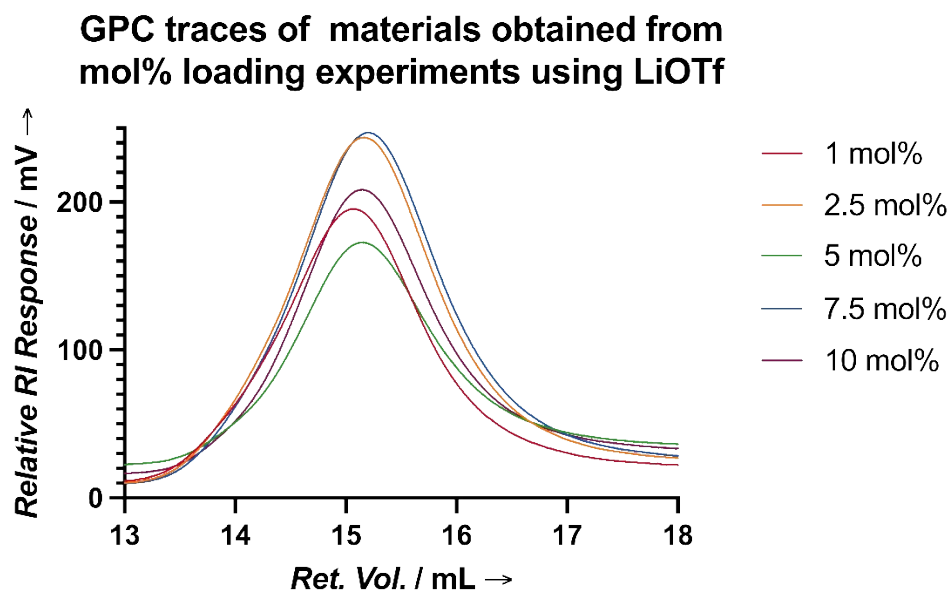
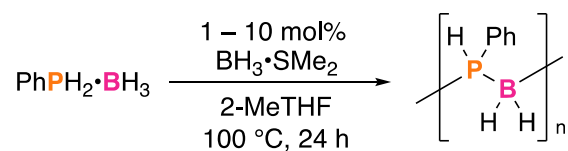


Figure S6: GPC traces of materials obtained from the dehydropolymerization of **1** in 2-MeTHF with 1 – 10 mol% of LiOTf added. Samples were prepared as 1 mg•mL solutions in THF and ran with an eluent of THF containing 0.1 wt% of $[\text{Bu}_4\text{N}][\text{Br}]$ with a flow rate of 1 mL•min.

Polymerizations Performed in 2-MeTHF using $\text{BH}_3\cdot\text{SMe}_2$ (1–10 mol%)



To a dram vial, phosphine-borane adduct was added (**1**) (0.5 mmol, 62 mg). Then, the required amount of 2 M $\text{BH}_3\cdot\text{SMe}_2$ in THF (2.5 – 25 μL) was added to this vial. Afterwards 2-MeTHF (250 μL) was added resulting in an approximately 2 M solution of **1**, with $\text{BH}_3\cdot\text{SMe}_2$. The reaction mixture was transferred to a J-Young NMR tube, sealed, removed from the glovebox and placed in a heating block set to 100 $^\circ\text{C}$. The reaction was then heated at this temperature for 24 h, after which it was allowed to cool and carefully depressurized. Then, CDCl_3 was added and the reactions were monitored by ^{31}P NMR spectroscopy to ensure that the reaction had reached completion and that **2** was produced. Polymer samples were isolated as described for reactions performed in toluene in 63 – 79% yield. Similarly, GPC was used to assess the materials produced (data is presented in figure 1 in the main text, and the GPC traces are presented in **Figure S7** below).

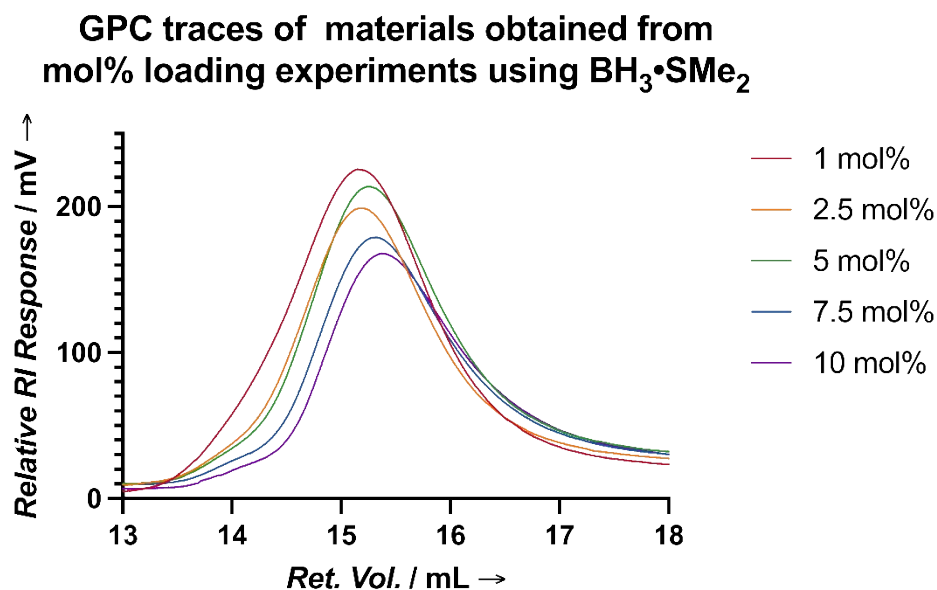


Figure S7: GPC traces of materials obtained from the dehydropolymerization of **1** in 2-MeTHF with 1 – 10 mol% of $\text{BH}_3\cdot\text{SMe}_2$ added. Samples were prepared as 1 mg $\cdot\text{mL}$ solutions in THF and ran with an eluent of THF containing 0.1 wt% of $[\text{Bu}_4\text{N}][\text{Br}]$ with a flow rate of 1 mL $\cdot\text{min}$.

Continued Growth of Polymeric Material 2

To a dram vial, polyphosphinoborane, **2**, was added (**1**) (0.25 mmol, 30 mg) and 250 μL of 2-MeTHF. Afterwards, the solution was transferred to a J-Young NMR tube, sealed, removed from the glovebox and placed in a heating block set to 100 $^{\circ}\text{C}$. The reaction was then heated at this temperature for 24 h, after which it was allowed to cool and carefully depressurized. Then, CDCl_3 was added and the reactions were analysed by ^{31}P NMR spectroscopy, revealing polymeric material was still present (**Figure S8**, ^{31}P $\delta = -48.9$ ppm (d, $^1J_{\text{PH}} = 349$ Hz)). Subsequently, **2** was isolated in 70% yield (21 mg) as described above. Then, GPC was used to assess the material produced (**Figure S9**).

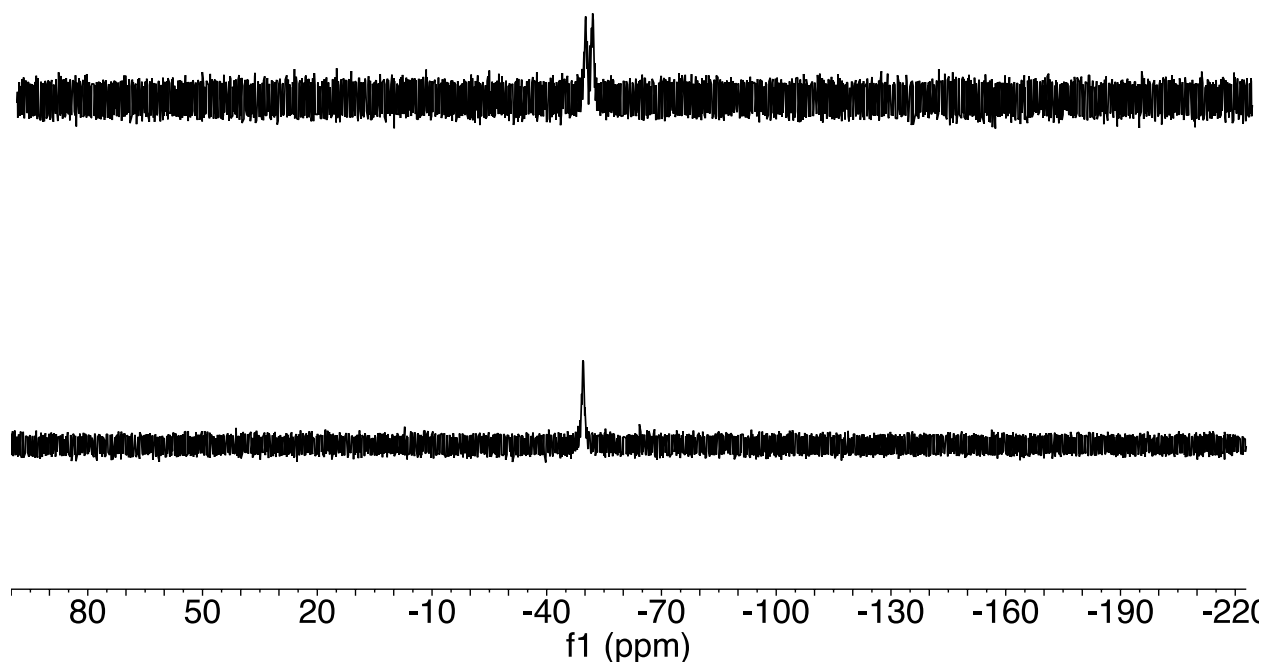


Figure S8: ^{31}P (top) and $^{31}\text{P}\{^1\text{H}\}$ (bottom) NMR spectra (200 MHz, 298 K, CDCl_3) of the reaction product from continued step-growth polymerization of **2**.

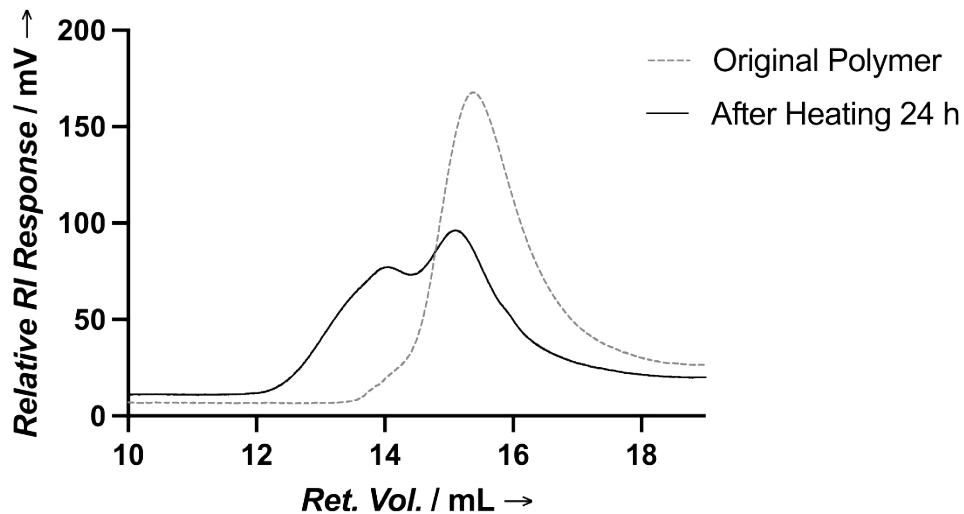


Figure S9: GPC trace of materials obtained from the dehydropolymerization of **1** in 2-MeTHF with 10 mol% of $\text{BH}_3 \cdot \text{SMe}_2$ added (dotted line) overlaid with the GPC trace for the continued step growth polymerization (solid line), revealing material that elutes at a lower retention volume. Samples were prepared as 1 mg•mL solutions in THF and ran with an eluent of THF containing 0.1 wt% of $[\text{Bu}_4\text{N}][\text{Br}]$ with a flow rate of 1 mL•min.

Mass Spectra Obtained for End Group Analysis

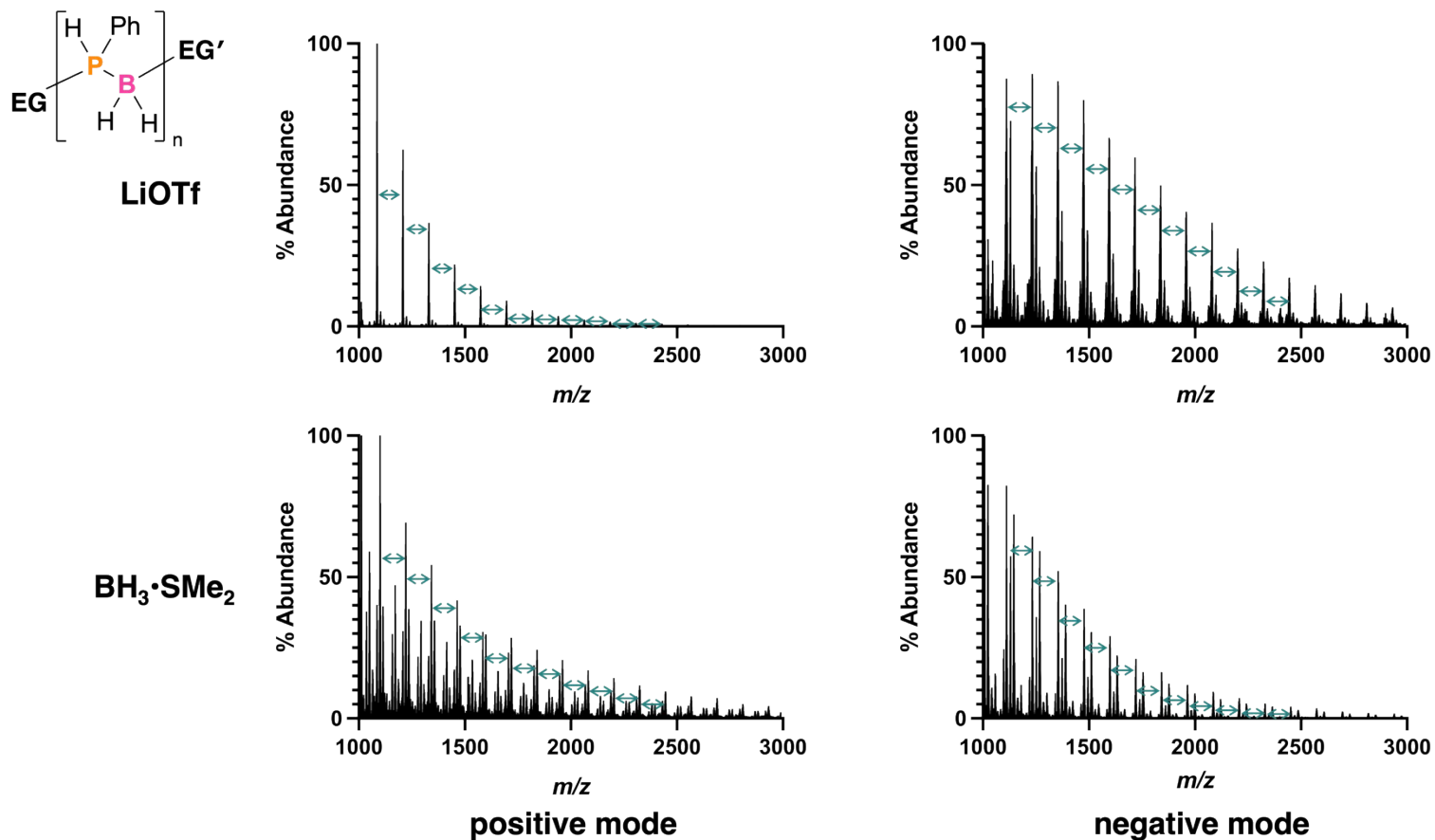
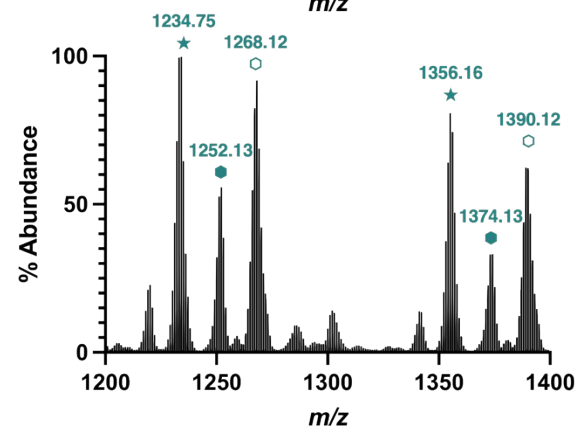
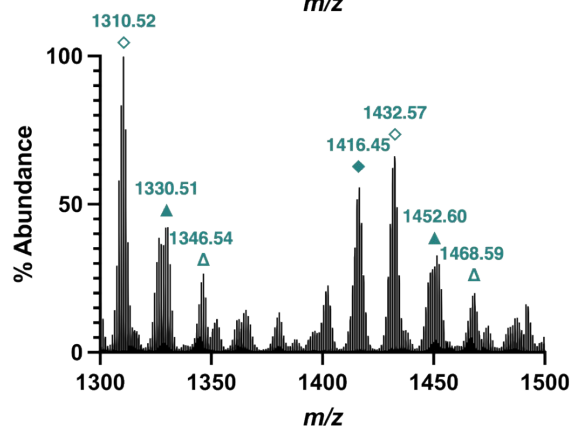
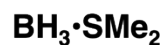
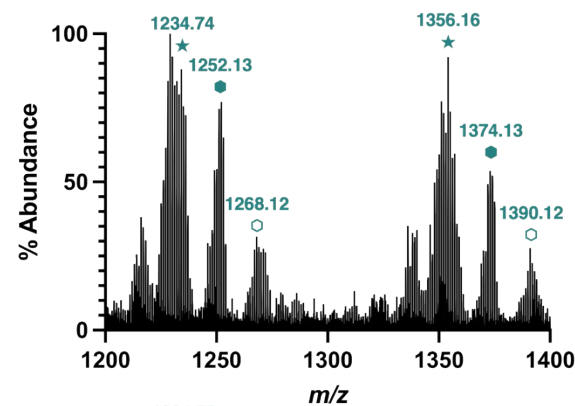
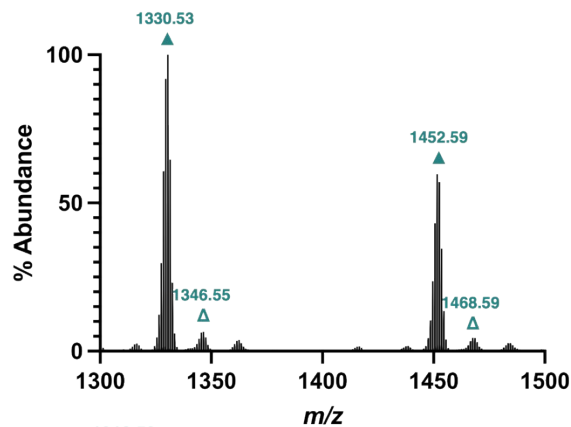
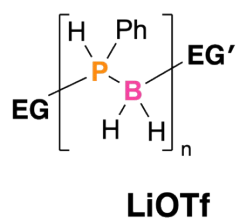


Figure S10: ESI-MS spectra (1 000 – 3 000 m/z) of residual oligomers present in the materials obtained from the dehydropolymerization of **1** in the presence of added LiOTf or $BH_3 \cdot SMe_2$. The turquoise double-headed arrows indicate a spacing of 122 m/z , which is the mass of a monomer un



positive mode

negative mode

Figure S11: ESI-MS spectra of residual oligomers present in materials obtained from the dehydropolymerization of **1** in the presence of either LiOTf or BH₃·SMe₂. Selected peaks are labelled with their found mass and corresponding symbol for the type of oligomer (▲, EG = H, EG' = PhPH₂; Δ, ▲-oxide; ◆, EG = BH₂(SMe₂), EG' = H; ◇, ◆-oxide; ★, EG = BH₃; EG' = H; ●, EG, EG' = unknown end groups with m/z corresponding to either 32 or 154; ○, tentatively assigned as ●-oxide). Calculated masses for each oligomer with 10 and 11 repeat [PhPH–BH₂] units, respectively, are ▲: 1330.50 m/z, 1452.54 m/z, Δ = 1346.49 m/z, 1468.54, ◆ = 1295.51 m/z, 1416.56 m/z, ◇ = 1310.51 m/z, 1432.56 m/z, ★ = 1234.50 m/z.

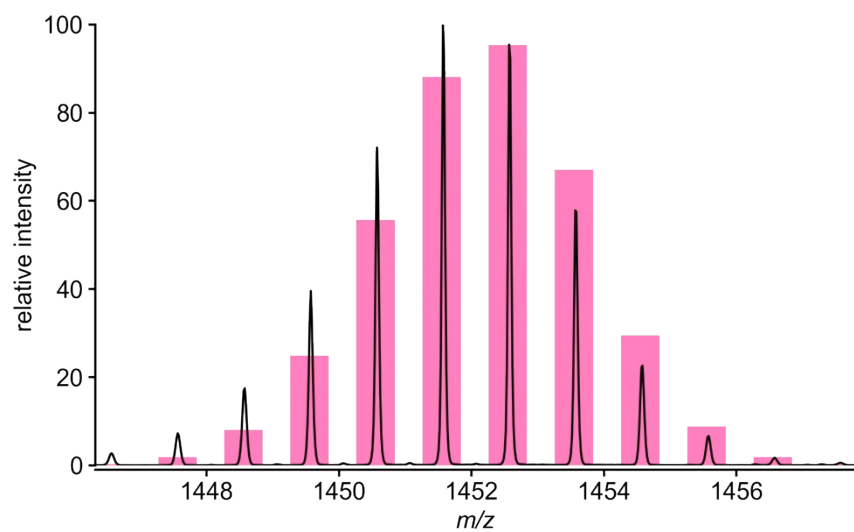


Figure S12: Isotope pattern overlay with signal assigned to H[PhPH-BH₂]₁₁•PhPH₂⁺.

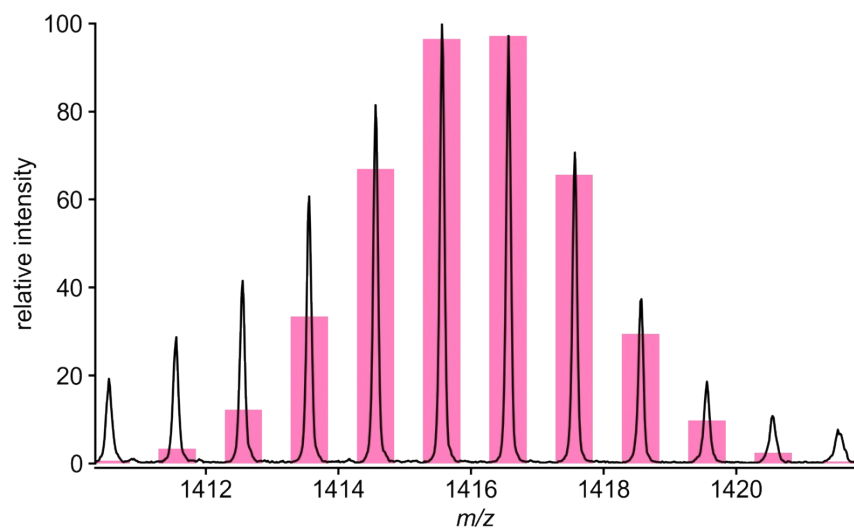


Figure S13: Isotope pattern overlay with signal assigned to [(BH₂(SMe₂)•[PhPH-BH₂]_n•PhPH-BH₂)⁺.

GPC Data

Table S1: Data obtained from the dehydropolymerizations performed within this study as described in the synthetic procedures. (n/a = not applicable). Samples were prepared as 1 mg•mL solutions in THF and ran with an eluent of THF containing 0.1 wt% of [Bu₄N][Br] with a flow rate of 1 mL•min.

Entry	Solvent	1 / mmol	Additive	mol%	Time / h	M_n / g•mol ⁻¹	\bar{D}
1	toluene	0.5	none	n/a	24	12 680	2.00
2	toluene	0.5	LiOTf	5	24	42 200	1.69
3	toluene	0.5	Mg(OTf) ₂	5	24	32 020	1.36
4	toluene	0.5	Sc(OTf) ₃	5	24	12 370	2.26
5	toluene	0.5	LiNTf ₂	5	24	29 260	1.73
6	toluene	0.5	[<i>n</i> Bu ₄ N][OTf]	5	24	13 110	1.68
7	toluene	0.5	[Li][B(C ₆ F ₅) ₄]•Et ₂ O	5	24	10 980	2.29
8	toluene	0.5	BH ₃ •SMe ₂ ^[a]	5	24	27 990	1.70
9	2-MeTHF	0.5	none	n/a	24	80 680	1.66
10	2-MeTHF	0.5	LiOTf	5	24	80 403	1.64
11	2-MeTHF	0.5	Mg(OTf) ₂	5	24	87 570	1.66
12	2-MeTHF	0.5	Sc(OTf) ₃	5	24	24 260	1.64
13	2-MeTHF	0.5	LiNTf ₂	5	24	79 690	1.66
14	2-MeTHF	0.5	[<i>n</i> Bu ₄ N][OTf]	5	24	1 320	1.62
15	2-MeTHF	0.5	[Li][B(C ₆ F ₅) ₄]•Et ₂ O	5	24	45 900	2.29
16	2-MeTHF	0.5	BH ₃ •SMe ₂ ^[a]	5	24	68 930	1.65
17	2-MeTHF	0.5	LiOTf	1	24	92 240	1.64

18	2-MeTHF	0.5	LiOTf	2.5	24	85 120	1.64
19	2-MeTHF	0.5	LiOTf	7.5	24	81 170	1.62
20	2-MeTHF	0.5	LiOTf	10	24	79 330	1.67
21	2-MeTHF	0.5	BH ₃ •SMe ₂ ^[a]	1	24	83 120	1.65
22	2-MeTHF	0.5	BH ₃ •SMe ₂ ^[a]	2.5	24	75 000	1.66
23	2-MeTHF	0.5	BH ₃ •SMe ₂ ^[a]	7.5	24	62 820	1.66
24	2-MeTHF	0.5	BH ₃ •SMe ₂ ^[a]	10	24	57 740	1.66
25^c	2-MeTHF	n/a	n/a	n/a	24	149 420	2.40

[a] Used as a 2 M solution in THF. [b] Approximate mass of the higher molar mass fraction of material. [c] **2** obtained from the continued step-growth polymerization of isolated **2** from entry 24.

NMR Spectra

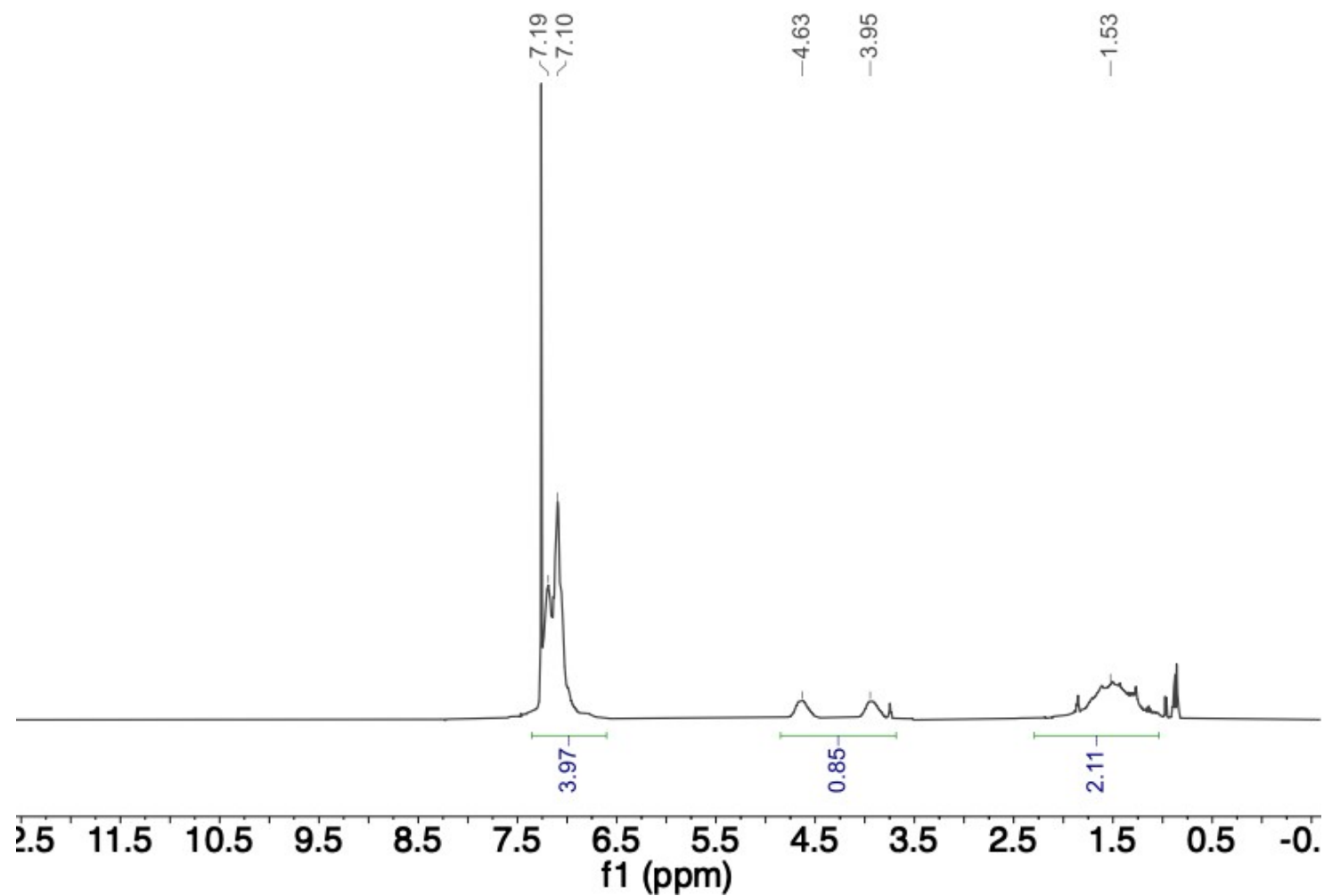


Figure S14: ¹H NMR (500 MHz, CDCl₃, 298 K) of **2** from dehydropolymerization of **1** in 2-MeTHF with added LiOTf.

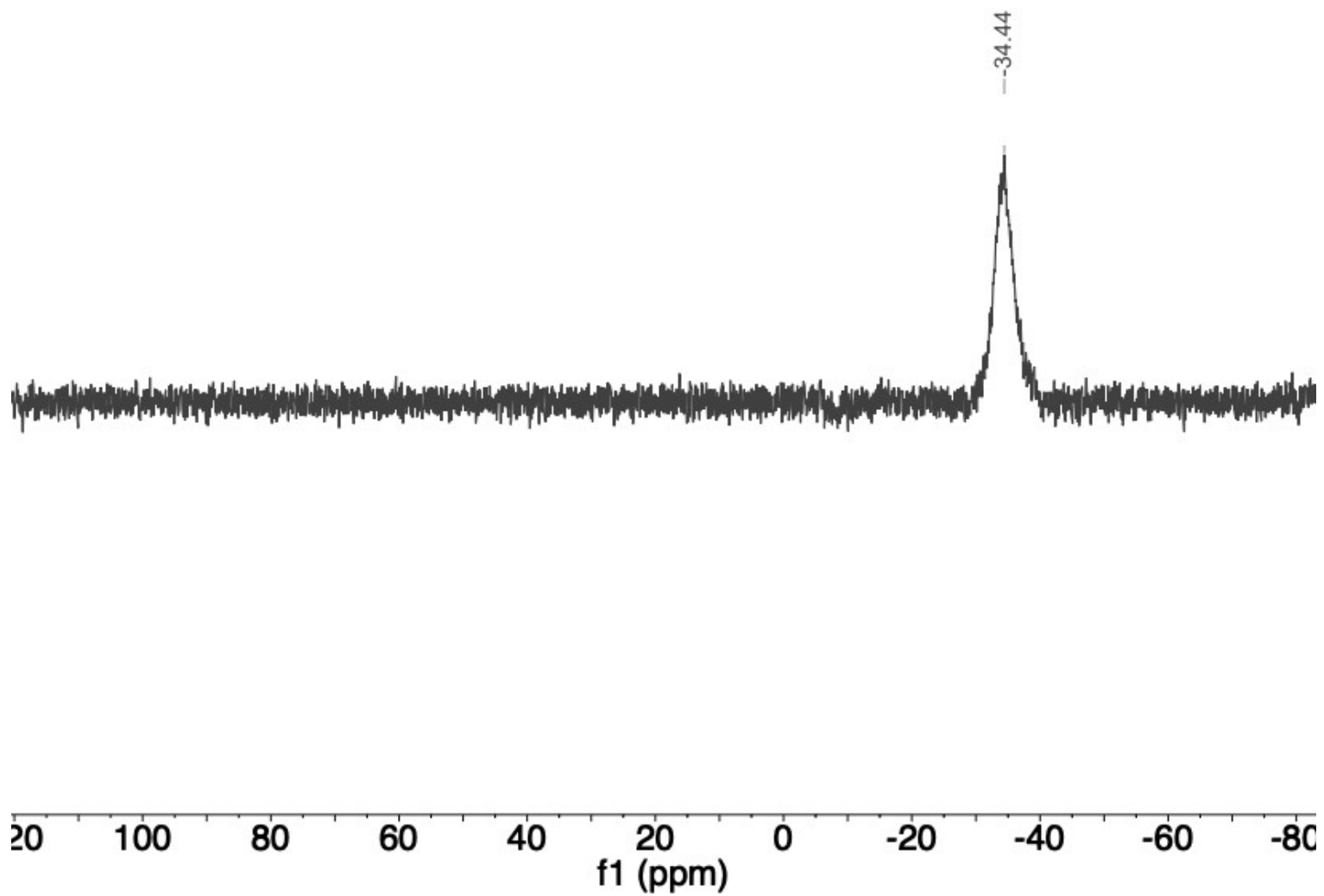


Figure S15: ^{11}B NMR spectrum (161 MHz, CDCl_3 , 298 K) of **2** obtained from the dehydropolymerization of **1** in 2-MeTHF with 5 mol% of LiOTf added.

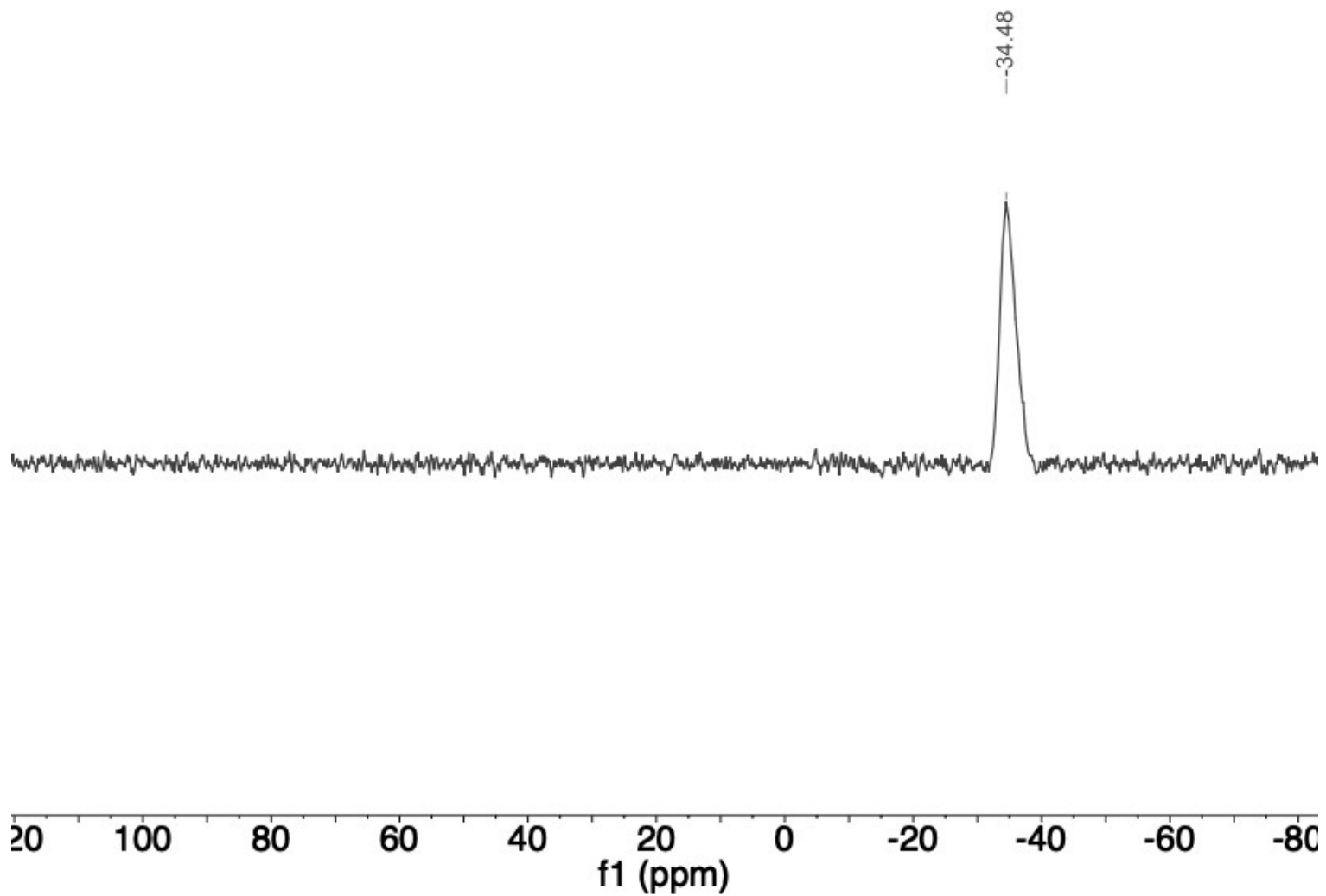


Figure S16: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (161 MHz, CDCl_3 , 298 K) of **2** obtained from the dehydropolymerization of **1** in 2-MeTHF with 5 mol% of LiOTf added.

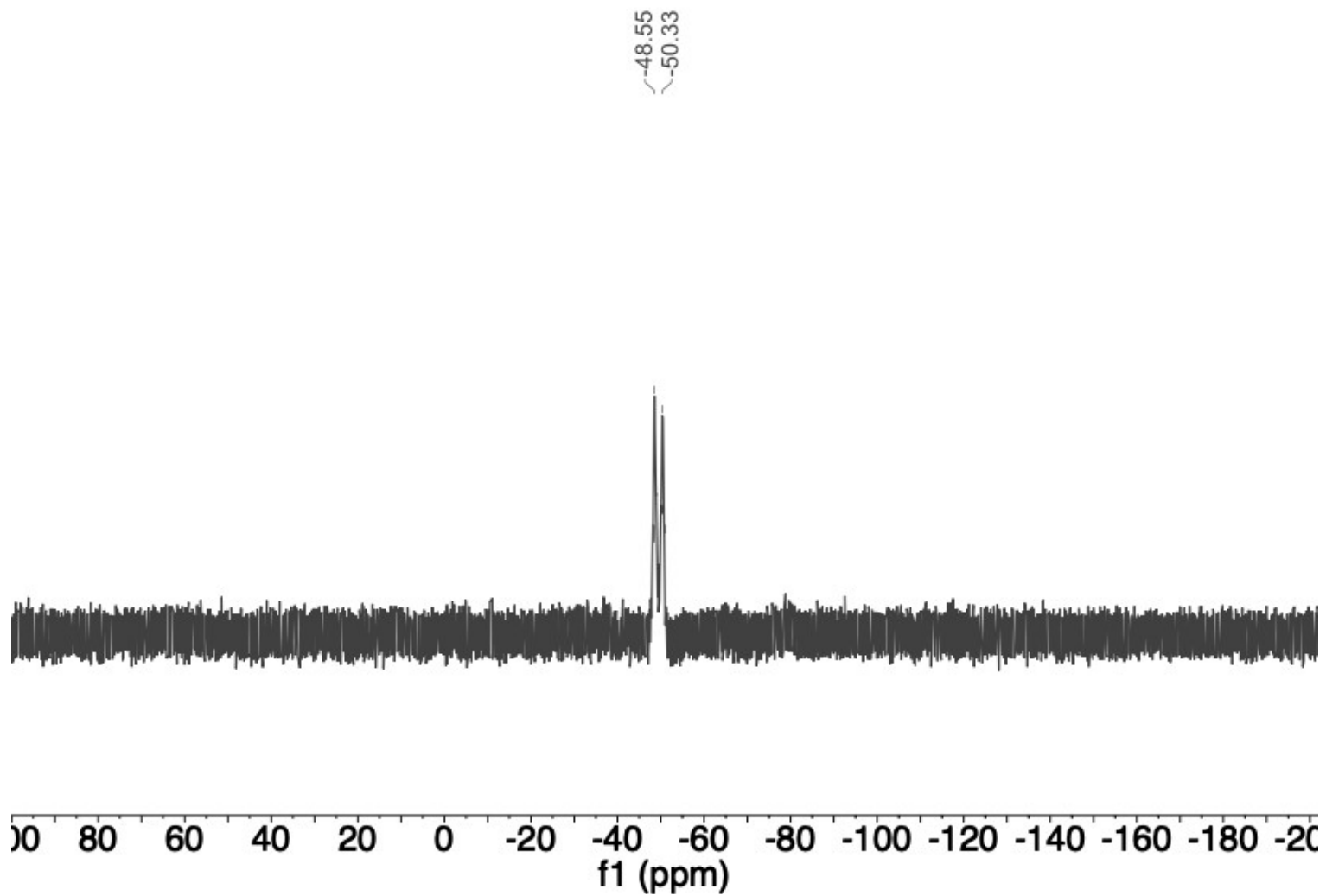


Figure S17: ^{31}P NMR spectrum (201 MHz, CDCl_3 , 298 K) of **2** obtained from the dehydropolymerization of **1** in 2-MeTHF with 5 mol% of LiOTf added.

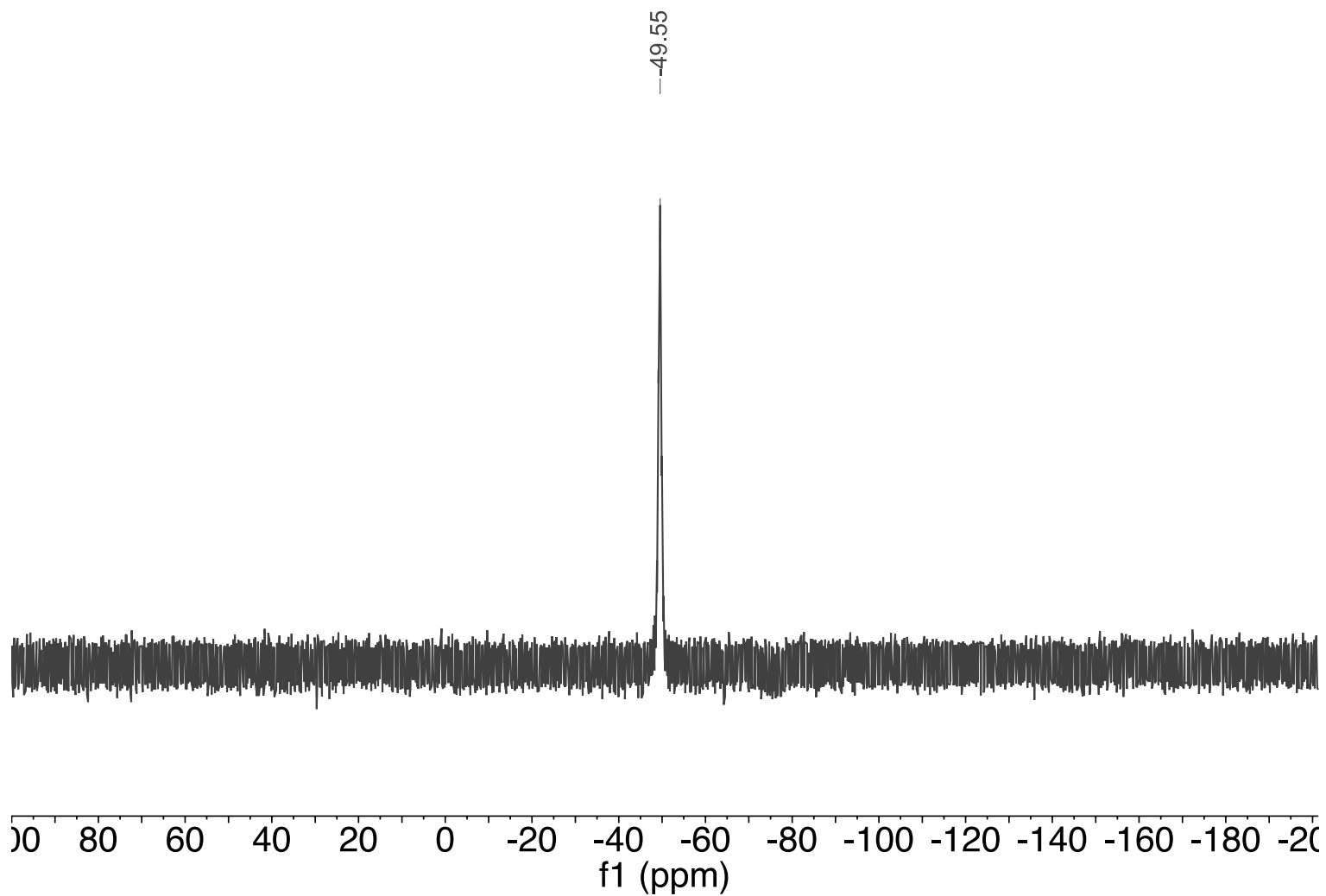


Figure S18: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (201 MHz, CDCl_3 , 298 K) of **2** obtained from the dehydropolymerization of **1** in 2-MeTHF with 5 mol% of LiOTf added.

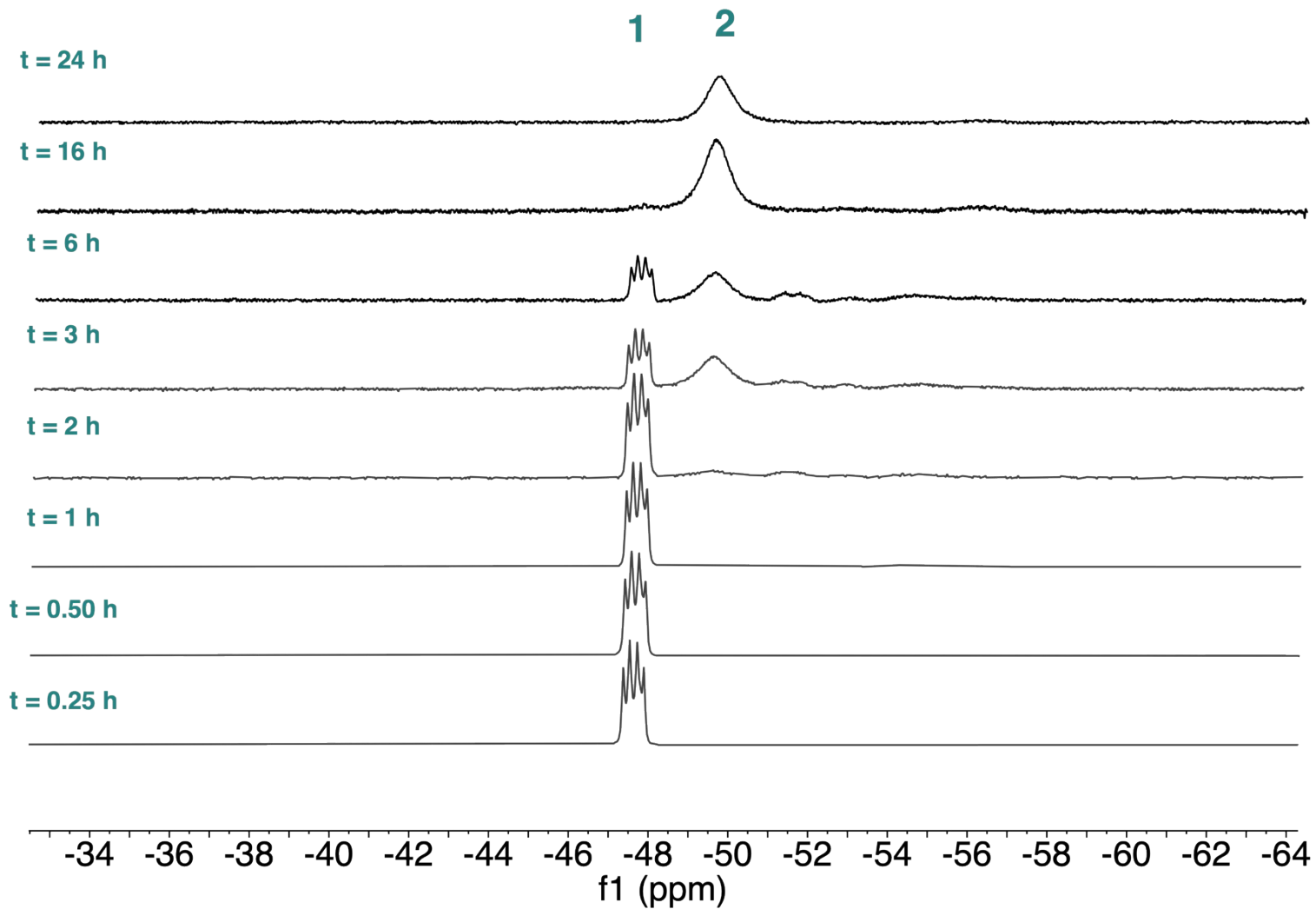


Figure S19: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (201 MHz, 2-MeTHF and CDCl_3 (1:6 ratio), 298 K) of **2** obtained from the dehydropolymerization of **1** in 2-MeTHF with 5 mol% of LiOTf over 24 h.

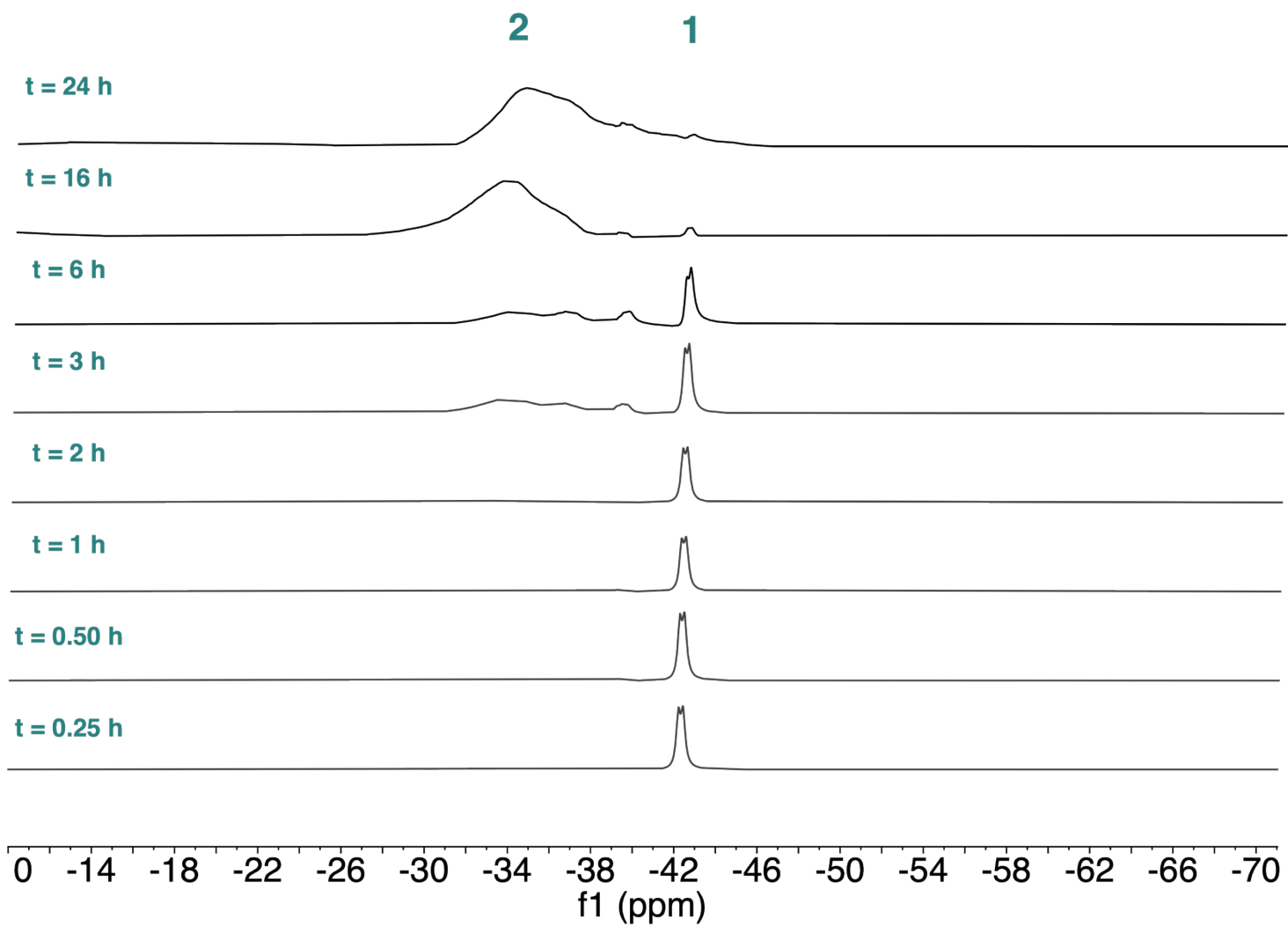


Figure S20: $^{11}\text{B}\{^1\text{H}\}$ NMR spectra (201 MHz, 2-MeTHF and CDCl_3 (1:6 ratio), 298 K) of **2** obtained from the dehydropolymerization of **1** in 2-MeTHF with 5 mol% of LiOTf added over 6 (bottom), 16 (middle), and 24 (top) h.

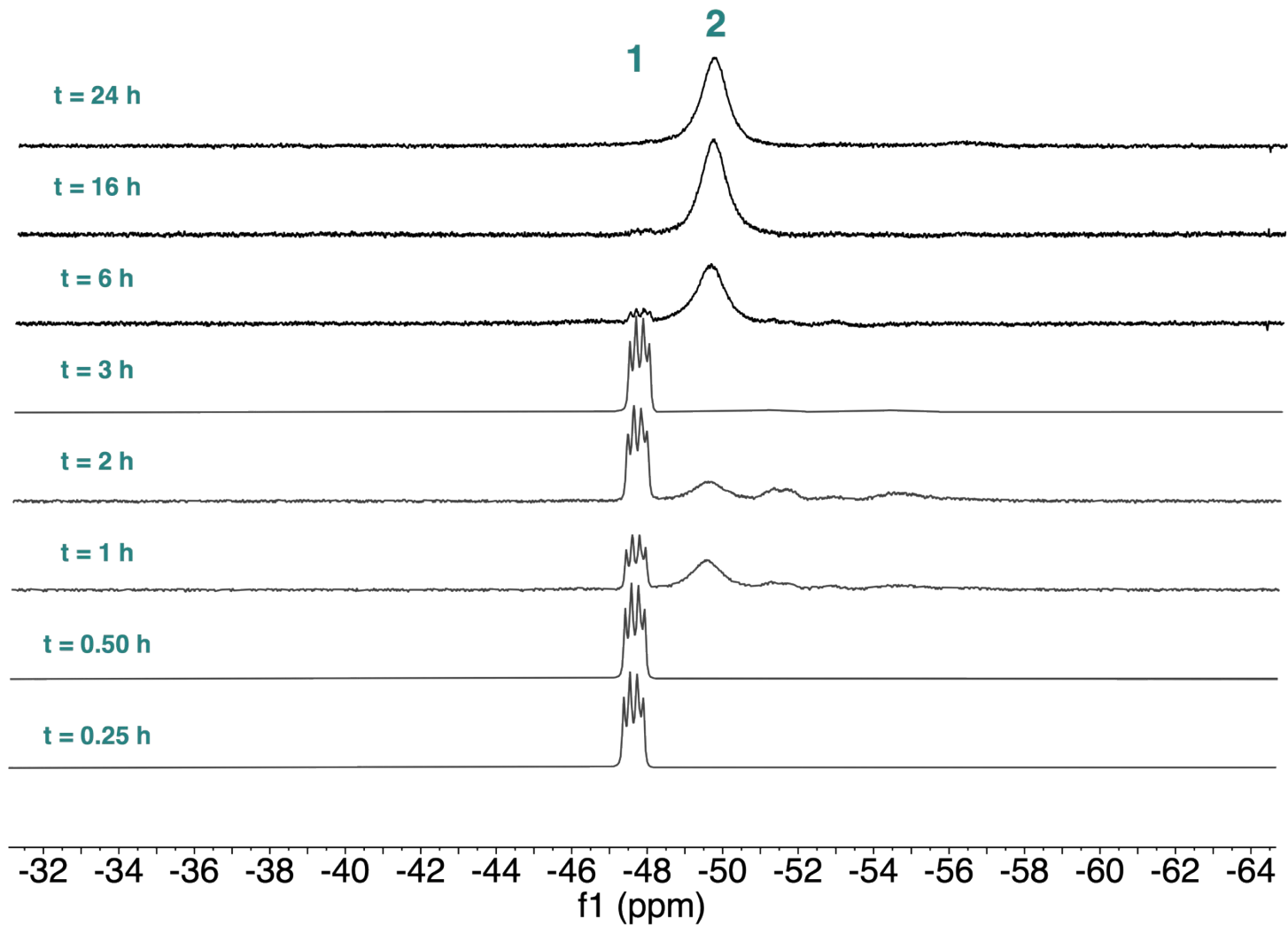


Figure S21: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (201 MHz, 2-MeTHF and CDCl_3 (1:6 ratio), 298 K) of **2** obtained from the dehydropolymerization of **1** in 2-MeTHF with 5 mol% of $\text{BH}_3\cdot\text{SMe}_2$ over 24 h.

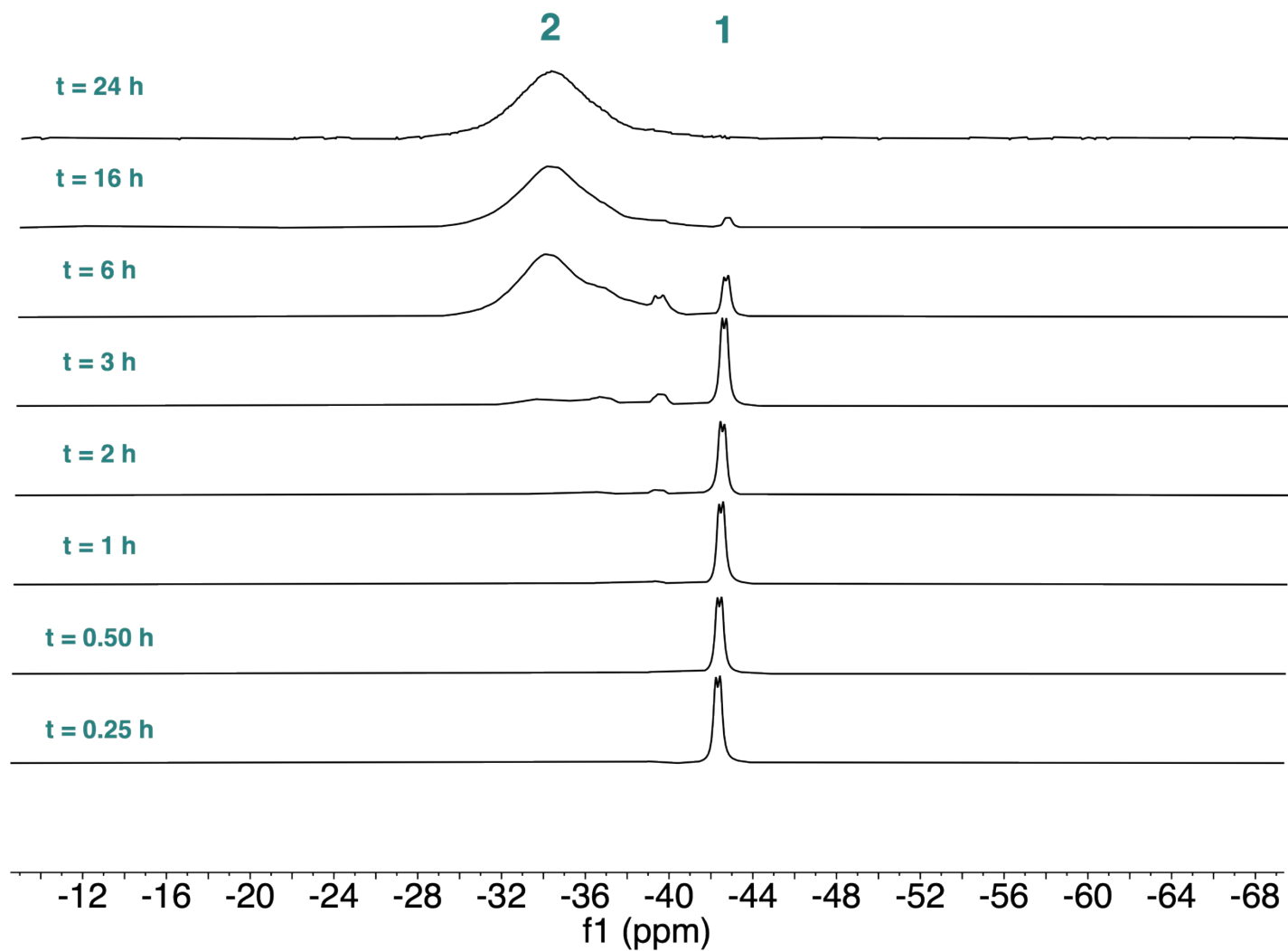


Figure S22: $^{11}\text{B}\{^1\text{H}\}$ NMR spectra (161 MHz, 2-MeTHF and CDCl_3 (1:6 ratio), 298 K) of **2** obtained from the dehydropolymerization of **1** in 2-MeTHF with 5 mol% of LiOTf over 24 h.

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