

Supplementary Information for
**Vinyl-Addition Polymerizations of Cycloallenes: Synthetic Access to Congeners
of Cyclic-Olefin Polymers**

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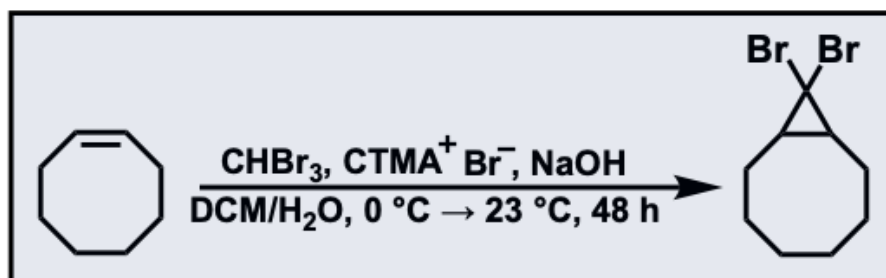
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1. <u>General Considerations</u>	

1.1 Materials and Methods

The following compounds were prepared according to literature procedures: 9,9-dibromobicyclo[6.1.0]nonane,¹ 1,2-cyclononadiene,² 1,1-dibromo-2-hexylcyclopropane,³ 1,2-nonadiene,⁴ $[(\pi\text{-allyl})\text{NiOCOCF}_3]_2$,⁵ and *trans*- $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{SbPh}_3)_2]$.⁶ All other reagents and solvents were obtained from commercial sources and used without further purification. Unless otherwise noted, solvents were dried on an MBraun solvent purification system or Pure Solve solvent purification system with 3Å molecular sieves and degassed with three freeze-pump-thaw cycles. Oxygen and water sensitive manipulations were performed in a N₂-filled MBraun glovebox or using standard Schlenk techniques. All polymerizations were performed in a N₂-filled glovebox. ¹H and ¹³C NMR spectroscopic data were collected on a Bruker 400 MHz NMR, Varian 300 MHz NMR, a Varian 500 MHz NMR, or a Varian 600 MHz spectrometer. Chemical shifts (δ) are reported in ppm using the residual solvent as reference. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q500. Dynamic mechanical analysis (DMA) was performed on a TA Instruments DMA Q800 with a film tension clamp. Gel permeation chromatography (GPC) data, unless otherwise stated, were collected on an Omnisec Resolve and Omnisec Reveal system using triple detection with detectors in series: UV, light scattering, viscometer, and refractive index and three Viscotek styrene divinylbenzene copolymer columns (in series T3000, T4000, and T5000) at a flow rate of 1 mL/min and thermostatted to 30 °C using either tetrahydrofuran (THF) or chloroform (CHCl₃) as the eluent. Molecular weight and dispersity data reported are from triple detection. Poly(1,2-cyclotridecadiene) was analyzed via GPC using 1,2,4-trichlorobenzene (TCB) as the eluent using a Malvern High Temperature OMNISEC system equipped with one TSK gel column thermostatted to 150 °C. Molecular weight and polydispersity data are reported using triple detection: refractive index, viscometer, low angle light scattering and right angle light scattering.

2. Monomer Synthesis

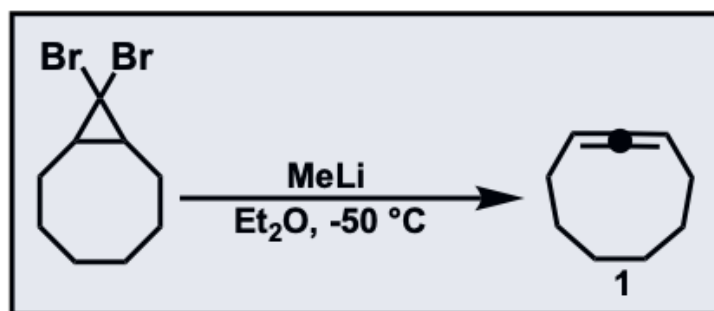
2.1 Synthesis of 9,9-Dibromobicyclo[6.1.0]nonane



Scheme S1: Synthesis of 9,9-Dibromobicyclo[6.1.0]nonane.

9,9-Dibromobicyclo[6.1.0]nonane was synthesized following a modified procedure.¹ A 250 mL 2-neck flask was charged with a Teflon stir bar, cyclooctene (11 g; 99.81 mmol), bromoform (CHBr_3 , 50.4 g; 199.62 mmol), DCM (30 mL), EtOH (2 mL), and cetyltrimethylammonium bromide ($\text{CTMA}^+ \text{Br}^-$, 250 mg; 0.686 mmol). The mixture was cooled to $0\text{ }^\circ\text{C}$ and NaOH (15.96 g; 399 mmol; 50% w/w in water) was added dropwise via cannula over the course of 10 minutes. The resulting mixture was left to stir for 48 hours while warming to room temperature ($23\text{ }^\circ\text{C}$). The reaction mixture was neutralized with 2 M HCl and diluted with water (50 mL). The organic phase was separated, and the aqueous phase was extracted with DCM (2 x 30 mL). The combined organic layers were washed with water (1 x 100 mL), brine (1 x 100 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under vacuum, after which the crude product was dissolved in hexanes and filtered through a plug of silica gel. Residual bromoform and cyclooctene were removed under vacuum (5 torr) with gentle heating ($55\text{ }^\circ\text{C}$) for 16 h to afford 9,9-Dibromobicyclo[6.1.0]nonane (17 g; 60% yield) as a colorless oil. Spectral data are consistent with known reports¹. ^1H NMR (CDCl_3 7.26), $\delta = 1.07 - 1.25$ (m, 2 H), 1.30 - 1.70 (m, 10 H), 2.00 - 2.10 (m, 2 H); ^{13}C (CDCl_3) $\delta = 25.3, 26.3, 27.8, 33.2, 37$. Spectral data are shown in Figures S6 and S7.

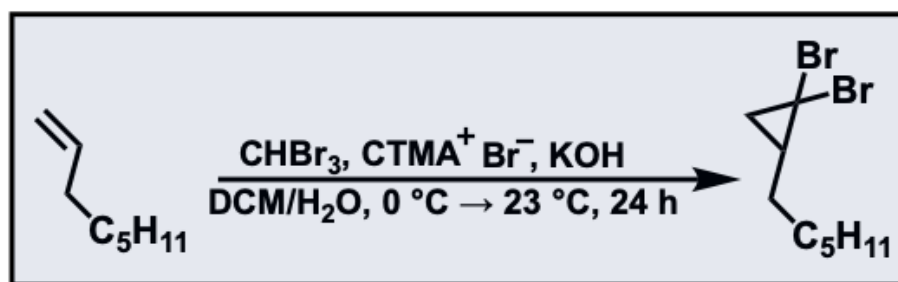
2.2 Synthesis of 1



Scheme S2: Synthesis of 1.

1,2-Cyclononadiene was synthesized following a modified procedure.² A flame dried 250 mL round bottom flask was charged with a Teflon stir bar, 9,9-Dibromobicyclo[6.1.0]nonane (14.3 g; 50.7 mmol), and diethyl ether (Et₂O, 25 mL) before cooling the solution to -50 °C (5 minute isotherm). Methyl lithium (1.6 M in Et₂O; 36 mL; 57.6 mmol) was added slowly and the reaction was stirred at -50 °C for 30 minutes. The reaction mixture was warmed to 0 °C and quenched with water (6 mL). The mixture was then warmed to room temperature (23 °C) and further diluted with water (20 mL). The organic phase was separated, and the aqueous layer was extracted with Et₂O (2 x 20 mL). The combined organic layers were washed with water (1 x 40 mL), brine (1 x 40 mL) dried over anhydrous sodium sulfate and filtered. Solvent was removed under vacuum to yield a pale-yellow oil. Vacuum distillation (2 Torr) at 45 °C afforded **1** as a colorless oil (5.5 g; 89% yield). Spectral data are consistent with literature reports.² ¹H NMR (CDCl₃ 7.26), δ = 1.38-1.40 (m, 2H), 1.54-1.67 (m, 6H), 1.74-1.82 (m, 2H), 2.18-2.27 (m, 2H), 5.26 (m, 2H); ¹³C (CDCl₃) δ = 25.5, 27.5, 28.2, 92.6, 205.8. Spectral data are shown in Figures S8 and S9.

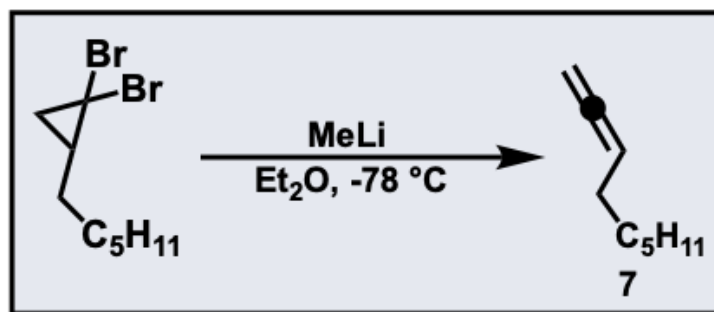
2.3 Synthesis of 1,1-dibromo-2-hexylcyclopropane



Scheme S3: Synthesis of 1,1-dibromo-2-hexylcyclopropane.

1,1-dibromo-2-hexylcyclopropane was synthesized following a modified procedure.³ A 250 mL 2-neck flask was charged with a Teflon stir bar, 1-octene (10 g; 89.1 mmol), bromoform (CHBr₃, 33.6 g; 133 mmol), DCM (100 mL), and cetyltrimethylammonium bromide (CTMA⁺ Br⁻, 3.27 g, 8.91 mmol). The mixture was cooled to 0 °C, and KOH (25.00 g; 445 mmol; 50% w/w in water) was added dropwise via cannula over the course of 30 minutes. The resulting mixture was left to stir for 24 hours while warming to room temperature (23 °C), after which time the reaction mixture was neutralized using 6 M HCl. The organic phase was separated, and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layers were washed with water (2 x 50 mL), brine (1 x 50 mL), dried over anhydrous magnesium sulfate, and filtered. Solvent was removed under vacuum, after which the crude product was dissolved in hexanes and filtered through a plug of silica gel. Vacuum distillation (2 Torr) at 85 °C afforded 1,1-dibromo-2-hexylcyclopropane as a colorless oil (20.0 g, 79% yield). Spectral data are consistent with literature reports.³ ¹H NMR (CDCl₃ 7.26), δ = 0.92 (t, 3H), 1.22 (t, 1H), 1.28–1.42 (m, 6H), 1.43-1.65 (m, 5H), 1.76 (dd, 1H); ¹³C (CDCl₃) δ = 14.1, 22.6, 28.3, 28.6, 29.0, 29.7, 31.5, 31.7, 32.6. Spectral data are shown in Figures S10 and S11.

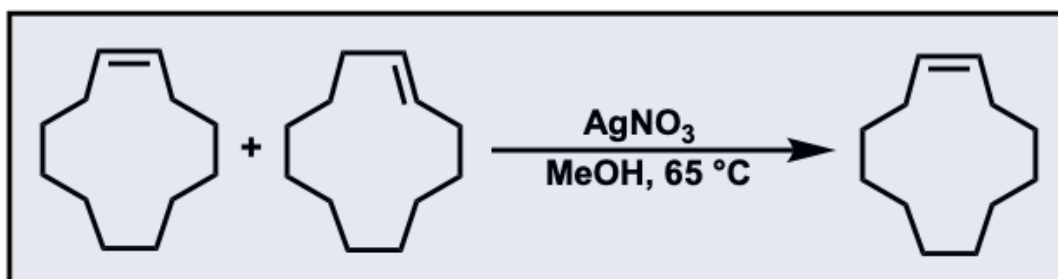
2.4 Synthesis of 7



Scheme S4: Synthesis of 7.

1,2-nonadiene (7) was synthesized following a modified procedure.⁴ A 100 mL Schlenk flask was charged with a Teflon stir bar, 1,1-dibromo-2-hexylcyclopropane (10 g, 35.2 mmol), and diethyl ether (Et₂O, 25 mL) before cooling the solution to -78 °C (x minutes isotherm). Methyl lithium (1.56 M in Et₂O; 27 mL; 42.2 mmol) was added dropwise over the course of 15 minutes and the reaction was stirred at -78 °C for 20 minutes. The reaction mixture was warmed to room temperature (23 °C) and allowed to stir for 1 hour. The mixture was quenched with water (25 mL) the organic phase separated, and the aqueous layer was extracted with Et₂O (2 x 50 mL). The combined organic layers were washed with water (2 x 50 mL), brine (1 x 50 mL), dried over magnesium sulfate, and filtered. Solvent was removed under vacuum, and vacuum distillation (60 torr) at 70 – 80 °C, afforded **7** as a colorless oil (4.0g, 93% yield). Spectral data are consistent with literature reports.⁴ ¹H NMR (CDCl₃ 7.26), δ = 5.10 (quint, 1H), 4.66 (dt, 2H), 2.03-1.98 (m, 2H), 1.43-1.26 (m, 8H), 0.90 (t, 3H); ¹³C NMR (CDCl₃): δ = 208.7, 90.1, 74.5, 31.6, 29.1, 28.7, 28.2, 22.6, 14.0. Spectral data are shown in Figures S12 and S13.

2.5 Separation of *cis*-cyclododecene

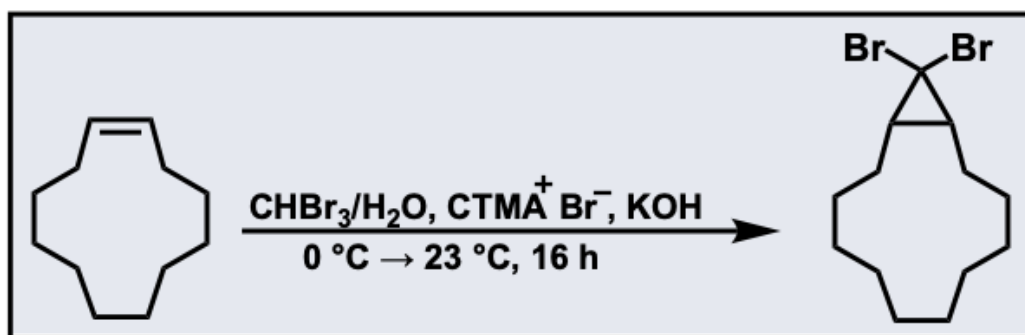


Scheme S5: Separation of *cis*-cyclododecene.

***Cis*-cyclododecene** was isolated following a previously reported procedure.⁷ Commercially available cyclododecene (7 g; 42.09 mmol; 65% *cis* via ¹H NMR spectroscopy) was added to a boiling (65 °C) MeOH solution of silver nitrate (AgNO₃, 4.28 g; 25.18 mmol, 0.92 equivalent relative to *trans* cyclododecene). The boiling solution was stirred for 5 minutes at 65 °C. The solution was cooled to room temperature and subsequently stored at -20 for 16 hours, after which time white needles crystallized within

the flask. The white needles were collected on a medium porosity fritted funnel and transferred to a 150 mL beaker equipped with a stir bar. A mixture of water (30 mL) and Et₂O (30 mL) was added followed by vigorous stirring for 5 minutes at 23 °C. The organic layer was separated, and the aqueous layer was washed with Et₂O (2 x 30 mL). The combined organic layers were washed with water (1 x 100 mL), brine (1 x 100 mL), dried over anhydrous sodium sulfate, and filtered. Solvent was removed under vacuum to afford *cis*-cyclododecene (94% *cis* via ¹H NMR spectroscopy) as a colorless oil (3.16 g; 64% yield). Spectral data are consistent with literature reports.⁸ ¹H NMR (CDCl₃ 7.26), δ = 5.32 (quint, 2H), 2.16-2.07 (m, 4H), 1.48-1.41 (quint, 4H), 1.37-1.31 (s, 10H), 1.30-1.22 (m, 6H); ¹³C NMR (CDCl₃): δ = 130.43, 27.00, 24.68, 24.41, 23.99, 22.11. Spectral data are shown in Figures S14 and S15.

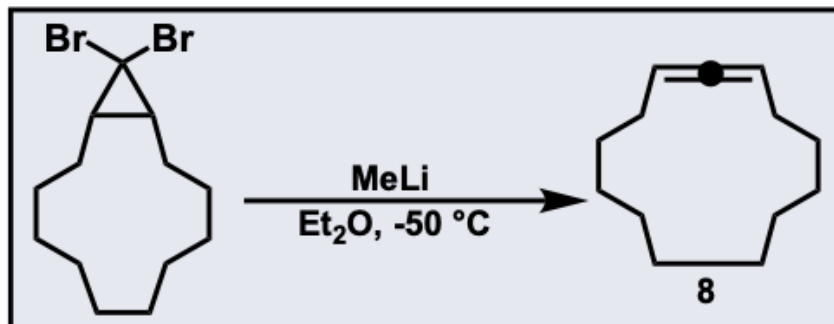
2.6 Synthesis of 13,13-dibromobicyclo[10.1.10]decane



Scheme S6. Synthesis of 13,13-dibromobicyclo[10.1.10]decane.

13,13-dibromobicyclo[10.1.10]decane was synthesized following a modified procedure.⁹ A 250 mL round bottom flask was charged with a Teflon stir bar, *cis*-cyclododecene (3.16 g; 19.06 mmol), bromoform (CHBr₃, 5 mL; 57.18 mmol), cetyltrimethylammonium bromide (CTMA⁺ Br⁻, 228 mg; 0.625 mmol) and EtOH (1 mL). The mixture was cooled to 0 °C and KOH (9.6 g; 171.5 mmol; 50% w/w in water) was added dropwise via syringe over the course of 6 minutes. The resulting mixture was left to stir for 48 hours while warming to room temperature (23 °C). The reaction mixture was diluted with water (50 mL) and hexanes (30 mL). The organic phase was separated, and the aqueous layer was extracted with hexanes (2 x 30 mL). The combined organic layers were washed with water (1 x 60 mL), brine (1 x 90 mL), dried over anhydrous sodium sulfate and filtered. Solvent was removed under vacuum. Unreacted cyclododecene was removed via vacuum distillation (5 torr) at 90 °C. The product was taken up in hexanes, filtered through a plug of silica gel, and removal of solvent under vacuum afforded 13,13-dibromobicyclo[10.1.10]decane as colorless crystals (4.3 g; 67% yield). ¹H NMR (CDCl₃ 7.26), δ = 1.73-1.65 (m, 2H), 1.65-1.49 (m, 4H), 1.49-1.31 (m, 10H), 1.29-1.15 (m, 4H); ¹³C NMR (CDCl₃): δ = 34.29, 26.88, 26.72, 26.06, 24.06, 22.64. Spectral data are shown in Figures S16 and S17.

2.7 Synthesis of 8

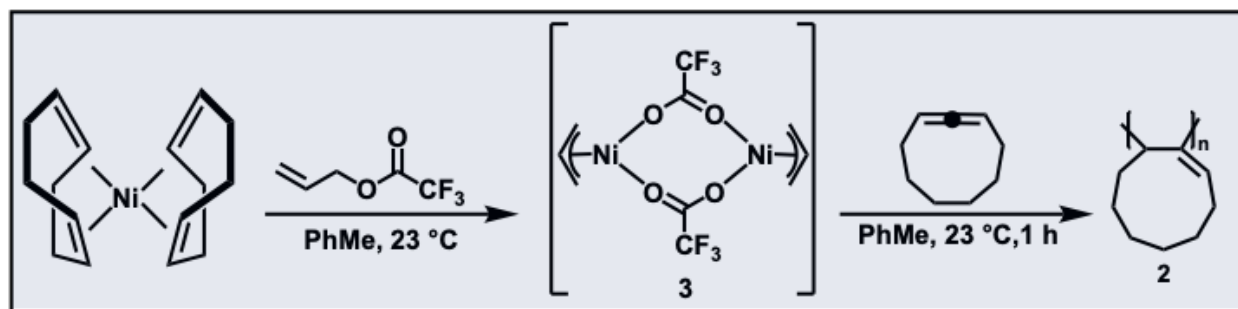


Scheme S7. Synthesis of **8**.

1,2-cyclotridecadiene (8) was synthesized following a modified procedure.⁹ A flame dried 50 mL round bottom flask was charged with a Teflon stir bar, 13,13-dibromobicyclo[10.1.10]decane (4 g; 11.83 mmol), and diethyl ether (Et₂O, 15 mL) before cooling to solution to -40 °C (5 minute isotherm). Methyllithium (1.6 M in Et₂O; 8.13 mL; 13.01 mmol) was slowly added and the reaction was stirred at -40 °C for 1 hour. The reaction mixture was warmed to 0 °C and slowly quenched with water (5 mL). The mixture was then warmed to room temperature (23 °C) and further diluted with water (10 mL). The organic phase was separated, and the aqueous layer was extracted with Et₂O (3 x 15 mL). The combined organic layers were washed with water (1 x 60 mL), brine (1 x 60 mL brine), dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified via vacuum distillation (15 torr) at 95 °C to afford **8** as a colorless oil (1.5 g; 71% yield). Spectral data are consistent with literature reports.⁹ ¹H NMR (CDCl₃ 7.26), δ = 5.08 (quint, 2H), 2.15-1.95 (m, 4H), 1.62-1.50 (m, 4H), 1.50-1.37 (m, 8H), 1.37-1.23 (m, 8H); ¹³C NMR (CDCl₃): δ = 204.31, 91.34, 27.47, 27.19, 27.12, 26.76, 26.52. Spectral data shown in figures S18 and S19.

3. Polymer Synthesis

3.1 General Procedure for Vinyl-Addition Polymerization of **1** with **3**



Scheme S8: Generation of **3** *in situ* and Synthesis of **2**

In an N₂ filled glovebox, bis(1,5-cyclooctadiene)nickel(0) (12.4 mg; 0.045 mmol) was dissolved in toluene (1.75 mL). Allyltrifluoroacetate (5.8 μL, 0.045mmol) was added with stirring at 23 °C for 20 minutes, which generated [$\{(\pi\text{-allyl})\text{NiOCOCF}_3\}_2$] *in-situ* ([Ni] = 0.026 M). An aliquot (0.15 mL, 0.004 mmol Ni) of this freshly prepared catalyst solution was added to a solution of **1** (100 mg; 0.818 mmol) in toluene (8.0 mL) and stirred for 1 hour at 23 °C. The polymerization was quenched via exposure to air and solvent was removed *in vacuo*. Polymeric material was then dissolved in minimal CHCl₃ and precipitated from MeOH. The white powder was collected on a medium porosity fritted funnel and dried for 16 hours *in vacuo*. Representative spectral data are shown in Figures S20 and S21. Representative GPC data shown in Figure S41.

7 was polymerized following the procedure outlined in section 3.1 with the following modifications: **3**, (0.26 mL; 0.0068 mmol Ni), **7** (3.3 mmol), and toluene (20 mL) were used. The polymerization was conducted for 16 hours, quenched via exposure to air, concentrated to a minimal volume, and precipitated from MeOH. Representative spectral data shown in Figures S22 and S23. GPC data shown in Figure S42.

3.2 General Procedure for the Vinyl-Addition Polymerization of **1** with **3** - **6**

In an N₂ filled glovebox, a 7 mL vial was charged with a Teflon stir bar and a solution of catalyst **3**, **5**, or **6** (0.004 mmol Ni/Pd in 0.5 mL toluene) activated with AgSbF₆ (1 equiv. with respect to Ni) or a solution of catalyst **4** (0.004 mmol Ni in 0.5 mL toluene). **1** (100 mg, 0.818 mmol) was added to the catalyst solution and stirred at 23 °C for 1 hour (catalysts **4** and **6**) or 24 hours (catalyst **5** and **3**). The polymerization was sparged with air and solvent was removed *in vacuo*. GPC data are shown in Figures S43 – S46. Results are tabulated in Table 1.

3.3 General Procedure for Quenching the Polymerization of **1** with **3**

In an N₂ filled glovebox, bis(1,5-cyclooctadiene)nickel(0) (12.4 mg; 0.045 mmol) was dissolved in toluene (2.0 mL). Allyltrifluoroacetate (5.8 μL, 0.045mmol) was added with stirring at 23 °C for 20 minutes, which generated [$\{(\pi\text{-allyl})\text{NiOCOCF}_3\}_2$] *in-situ* ([Ni] = 0.023 M). An aliquot (0.11 mL, 0.0025 mmol Ni) of this freshly prepared catalyst solution was added to a solution of **1** (25 mg; 0.205 mmol) in toluene (2.0 mL) and stirred for 1 hour at 23 °C. Excess quenching agent was added (0.10 mL; Table S1), and the mixture was stirred for 30 min. Polymeric material was precipitated upon addition to MeOH and dried *in vacuo* for 16 hours. GPC analyses were conducted to determine if high M_n impurities were present, and the findings from this study are summarized in Table S1.

Table S1: Quenching agent study for polymerization of **1** with **3**

Entry	Quenching Agent	High M_n Shoulder	M_n^{expt} (Da)	\bar{D}	Yield (%)
1	12 M HCl (degassed)	Present	20,600	1.18	90
2	Trifluoroacetic acid (degassed)	Present	21,000	1.23	98
3	MeOH (dry, degassed)	Present	20,700	1.2	78
4	Air Sparge	Present	23,000	1.21	89
5	MeOH (dry, O ₂)	Present	23,400	1.24	98
6	MeCN (dry, degassed)	Present	23,900	1.16	99

All polymerizations conducted for 1 hour using $[1]_0 = 0.1$ M. See section 3.3.

3.4 Additional Catalyst Study to Avoid the High M_n Impurity

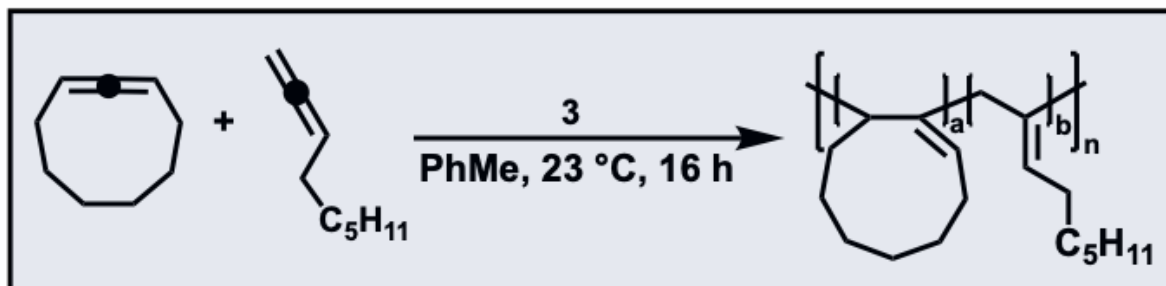
In an N₂ filled glovebox, bis(1,5-cyclooctadiene)nickel(0) (12.4 mg; 0.045 mmol) was dissolved in toluene (1.75 mL). Allyltrifluoroacetate (5.8 μ L, 0.045 mmol) was added with stirring at 23 °C for 10 minutes, which generated $[\{(\pi\text{-allyl})\text{NiOCOCF}_3\}_2]$ *in-situ* ([Ni] = 0.026 M). PPh₃ (11.8 mg; 0.045 mmol) or SbPh₃ (15.0 mg; 0.045 mmol) was added with stirring at 23 °C for 10 minutes. An aliquot (0.38 mL, 0.010 mmol Ni) of this freshly prepared catalyst solution was added to a solution of **1** (100 mg; 0.818 mmol) in toluene (8.0 mL) and stirred for 1 hour at 23 °C. The polymerization was quenched with 0.1 mL of dried and degassed MeOH and stirred for 30 min at 23 °C. The solution was then added to MeOH to precipitate any polymeric material. The white powder was collected on a medium porosity fritted funnel and dried for 16 hours *in vacuo*.

In an N₂ filled glovebox, **6** (3.0 mg; 0.010 mmol) and silver trifluoroacetate (4.4 mg; 0.021 mmol) were dissolved in toluene (1.0 mL) and stirred at 23 °C for 5 minutes. The resulting solution was filtered through a 0.2 μ m syringe filter into a solution of **1** (100 mg; 0.818 mmol) in toluene (8.0 mL) and stirred for 1 hour at 23 °C. The polymerization was quenched with 0.1 mL of dried and degassed MeOH and stirred for 30 min at 23 °C. The solution was then added to excess MeOH to precipitate any polymeric material. The white powder was collected on a medium porosity fritted funnel and dried for 16 hours *in vacuo*.

Table S2: The polymerization of **1** with various catalytic species

Entry	Catalyst	[1] ⁰	Time (h)	Additive	High M_n Shoulder	M_n^{expt} (Da)	\bar{D}	Yield (%)
1	3	0.1	1	PPh ₃	N/A	N/A	N/A	N/A
2	3	0.1	1	SbPh ₃	present	27,400	1.16	96
3	6	0.1	1	AgTFA	present	10,800	1.14	81

3.5 General procedures for Statistical and Block Copolymerizations of **1** and **7**



Scheme S9: Statistical Copolymerization of **1** and **7**

Statistical copolymers were synthesized following the same procedure outlined in section 3.1. Note: both monomers were combined in a single vessel prior to addition of **3**. The solution was then stirred at 23 °C for 16 hours. The polymerization was quenched via exposure to air, concentrated to a minimal volume, precipitated from MeOH, collected on a medium porosity fritted funnel, and dried in a vacuum oven (65 °C) for 16 hours. Representative spectral data shown in Figures S26 – S31. Representative GPC data shown in Figures S47 – S49.

4. Polymerization Kinetics

4.1 General Procedure for the kinetic experiment for **1** and **7**

In an N₂ filled glovebox, a 3 mL vial was charged with **1** or **7** (30 mg; 0.25 mmol), *d*₈-toluene (0.5 mL) and trimethoxybenzene (4.8 mg; 0.026 mmol; used with **7**) or mesitylene (2.5 μL; 0.018 mmol; used with **1**) as an internal standard. The solution was transferred to a septa-capped NMR tube and an initial (T₀) ¹H NMR spectrum was collected. A separate 1 mL vial was charged with bis(1,5-cyclooctadiene)nickel(0) (12 mg; 0.044 mmol), a Teflon stir bar, *d*₈-toluene (1 mL), and allyltrifluoroacetate (5.7 μL; 0.044 mmol).

Stirring at 23 °C for 20 minutes generated **3** *in situ* ([Ni] = 0.044 M). An aliquot (0.14 mL; 0.0062 mmol Ni) was drawn up by an air-tight syringe and the needle tip inserted into a rubber septum. The solution of **3** was quickly injected into the NMR tube (followed by mixing via inversion). ¹H NMR spectra were collected every two minutes over the course of 30 minutes (for **1**) or one hour (for **7**). Monomer consumption was determined via integration of the allene vinyl protons (δ = 5.1 – 5.3 for **1**; δ = 4.5 – 4.8 for **7**) versus the internal standard (δ = 6.1 – 6.3 for trimethoxybenzene; δ = 6.6 – 6.8 for mesitylene). The kinetics experiments were completed in triplicate for **1** and **7**, and error was determined by the standard deviation of the three trials. Kinetics plot comparing the rates of polymerization of **1** and **7** are shown in Figure 1.

5. Determination of Living Character for the Polymerization of 1 and 7 with 3

5.1 Molecular Weight as a Function of Monomer Conversion Procedure

In an N₂ filled glovebox, a 7 mL vial was charged with a Teflon stir bar, **1** (150 mg; 1.23 mmol), mesitylene (170 μ L; 1.23 mmol; used as an internal standard) and an aliquot was removed via capillary action and diluted with CDCl₃ for ¹H NMR spectroscopic analysis (T₀). After which toluene (3 mL) was added. In a separate 7 mL vial, a stock solution of **3** ([Ni] = 0.026 M) was prepared as previously described in section 3.1. An aliquot (0.2 mL; 0.0052 mmol Ni) of this freshly prepared stock solution was added to the vial containing **1** and stirred at 23 °C. Aliquots (0.2 mL) were removed every ~4 minutes, quenched via exposure to air, diluted with CDCl₃ (0.5 mL) and analyzed by ¹H NMR spectroscopy. The NMR samples were transferred to 3 mL vials, concentrated to a residue, and dried *in vacuo* for 16 hours. The aliquots were dissolved in HPLC-THF (2 mL) and analyzed by GPC to determine the number average molecular weight (M_n) of any polymeric species (Table S1). The calculated M_n data were plotted as a function of monomer conversion, which revealed a linear correlation (Figure 2B).

Table S3: Living Plot Molecular Weight and Conversion Data for **1**

Entry	Monomer	Reaction Time (min)	Conversion (%)	M_n (Da)	\bar{D}
0	1	0	0	-	-
1	1	4	40	16000	1.18
2	1	8	65	26000	1.19
3	1	13	87	36000	1.19
4	1	18	94	40470	1.16

This procedure was also conducted for **7** with the following amount/time modifications: **3** (0.13 mL; 0.0034 mmol Ni); aliquots removed every 5 to 10 minutes. The aliquots were

analyzed as previously described in section 5.1 (Table S2). The calculated M_n data were plotted as a function of monomer conversion, which revealed a linear conversion Figure S1.

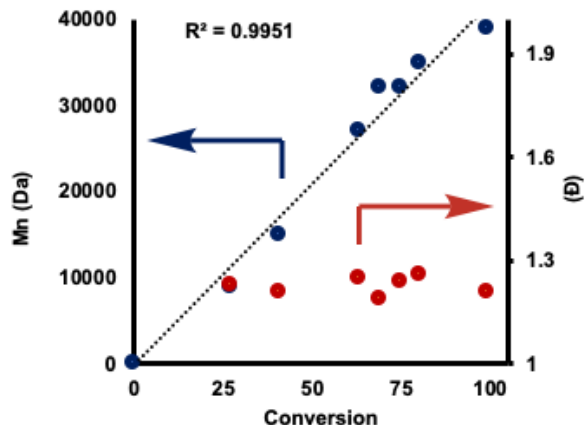


Figure S1: Number average molecular weight (M_n) as a function of monomer conversion (blue) and Dispersity (\bar{D}); red) for polymerization of **7**.

Table S4: Living Plot Molecular Weight and Conversion Data for **7**

Entry	Monomer	Reaction Time (min)	Conversion (%)	M_n (Da)	\bar{D}
0	7	0	0	-	-
1	7	9	27	9000	1.23
2	7	15	41	15000	1.21
3	7	35	63	27000	1.25
4	7	45	69	32000	1.19
5	7	65	75	32000	1.24
6	7	85	80	35000	1.26
7	7	115	99	39000	1.21

5.2 General Procedure for Chain Extension

In an N_2 filled glovebox, a stock solution of **3** ($[Ni] = 0.0133$ M) was prepared as described in section 3.1. A separate 20 mL vial was charged with a Teflon stir bar, **1** (100 mg; 0.8188 mmol), and toluene (1 mL). An aliquot (0.6 mL; 0.00799 mmol Ni) of the stock solution of **3** was added to the solution of **1**, and stirred at 23 °C. After 20 minutes, an aliquot (0.15 mL) was removed, quenched via exposure to air, diluted with $CDCl_3$ (0.55

mL) and analyzed by ^1H NMR spectroscopy (which confirmed full conversion of **1**). At this point, another portion of **1** (100 mg; 0.8188 mmol) in toluene (1.6 mL) was added to the polymerization mixture and allowed to stir. After 20 minutes another aliquot (0.15 mL) was removed from the turbid solution, and ^1H NMR spectroscopic analysis confirmed quantitative conversion of **1**. The NMR aliquots were concentrated to a residue under vacuum and analyzed by GPC to determine the number average molecular weight (M_n) of any polymeric species (Table S2). The observed data were consistent with successful chain extension (Figure 2A).

Table S5: Molecular Weight Data for Chain Extension of **1**

Entry	Extensions	M_n (Da)	Target M_n (Da)	\bar{D}
1	0	18,910	12,000	1.16
2	1	33,800	24,000	1.14

6. Thermomechanical Data

6.1. Representative TGA Thermograms

Representative thermal data for poly(1,2-cyclononadiene) (**2**), poly(1,2-nonadiene), and poly(1,2-cyclotridecadiene) are shown below. The TGA thermograms indicate decomposition onsets near 350 °C.

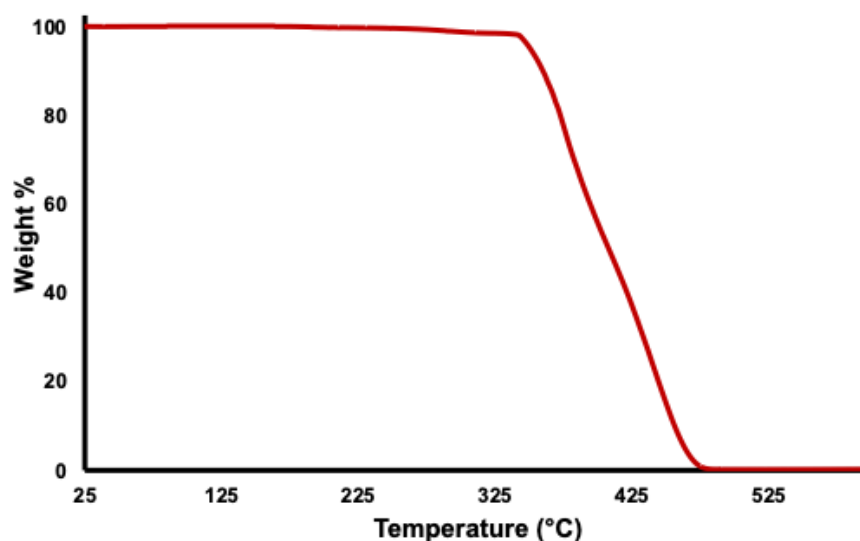


Figure S2: Representative **2** TGA thermogram (Heating Rate: 10 °C/min in N_2)

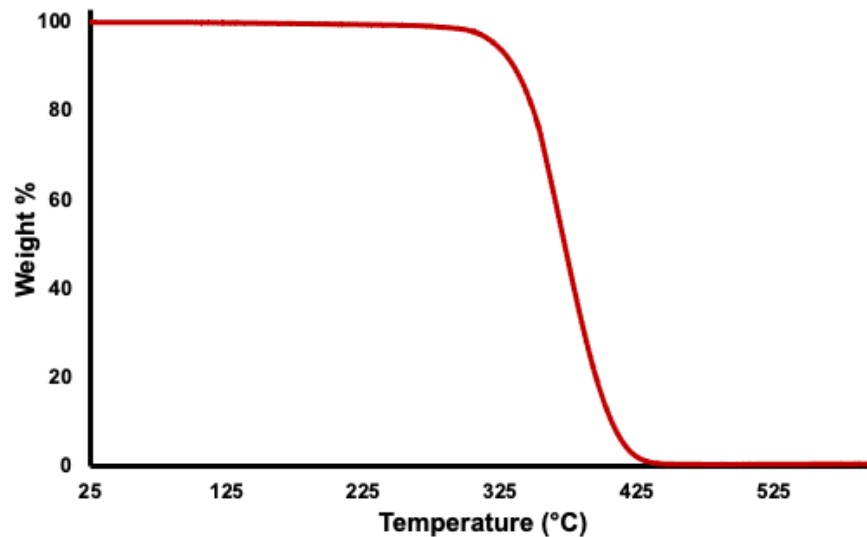


Figure S3: Representative poly(1,2-nonadiene) TGA thermogram (Heating Rate: 10 °C/min in N₂)

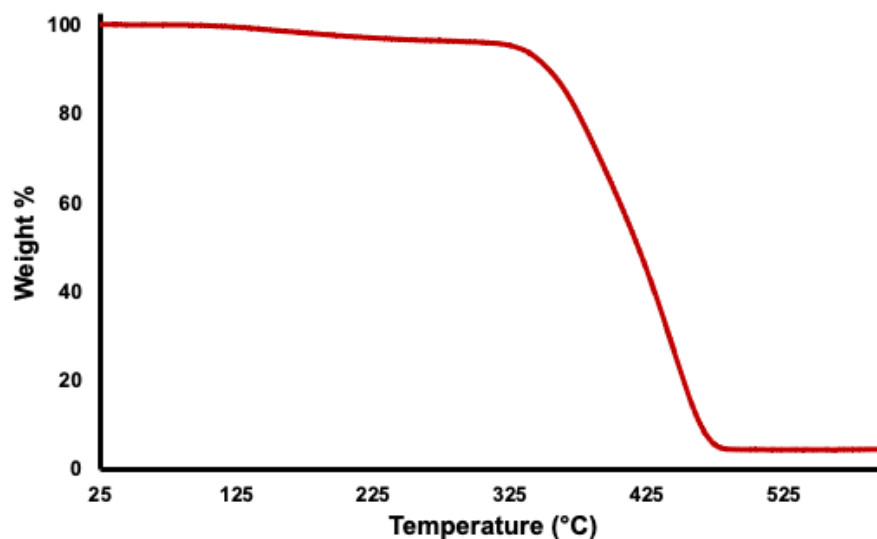


Figure S4: Representative poly(1,2-cyclotridecadiene) TGA thermogram (Heating Rate: 10 °C/min in N₂)

6.2. Differential Scanning Calorimetry (DSC) of poly(1,2-nonadiene)

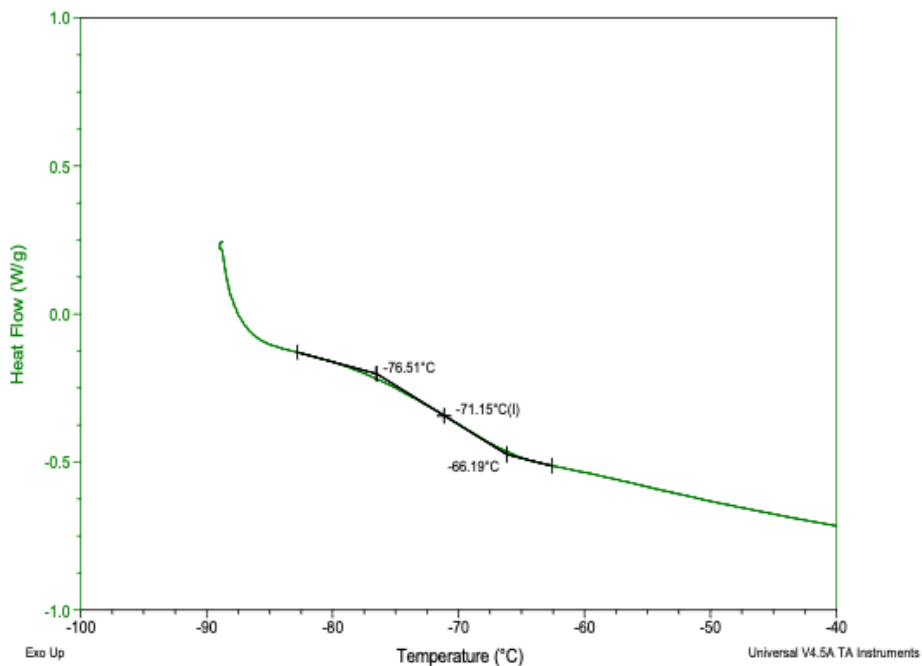


Figure S5: Representative DSC thermogram of poly(1,2-nonadiene). Second heating cycle (Heating Rate: 10 °C/min).

6.3. General Procedure for Stress Strain Experiments

A rectangular film of the respective polymer was cast from CHCl₃ (5 w% polymer) and analyzed using DMA (film tension clamp at 0.1% strain/min). Representative Stress v. Strain plots are shown in Figure 3.

7. NMR Data

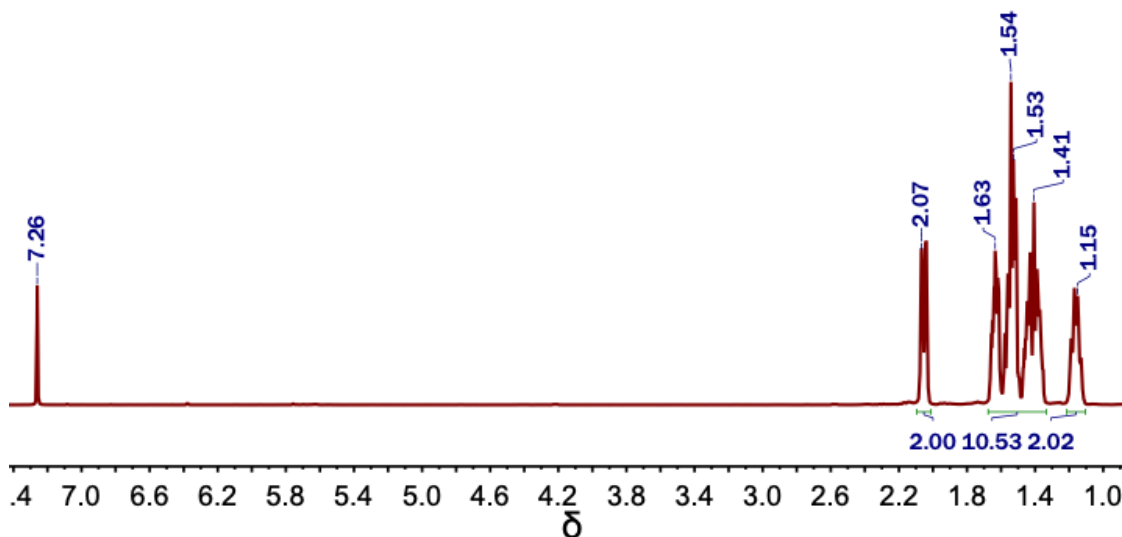


Figure S6: ^1H NMR spectrum of 9,9-Dibromobicyclo[6.1.0]nonane in CDCl_3 .

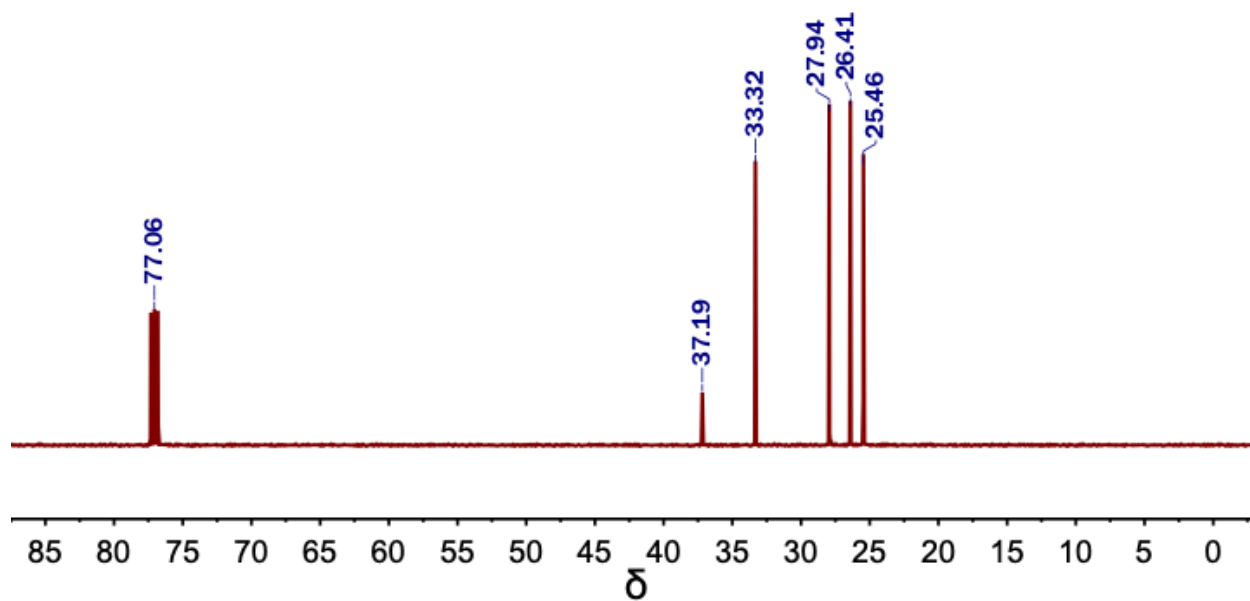


Figure S7: ^{13}C NMR spectrum of 9,9-Dibromobicyclo[6.1.0]nonane in CDCl_3 .

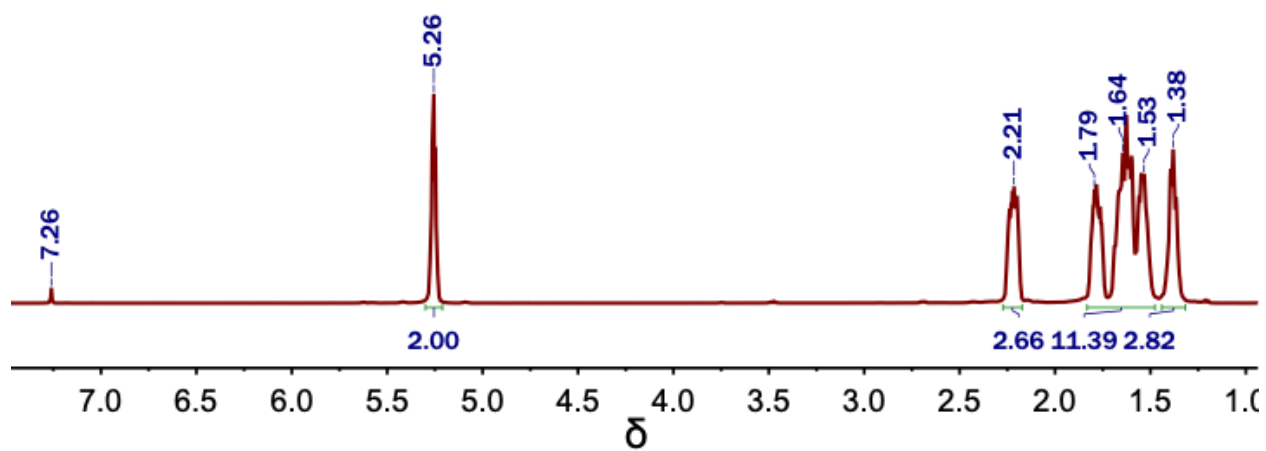


Figure S8: ^1H NMR spectrum of Cyclononadiene (**1**) in CDCl_3 .

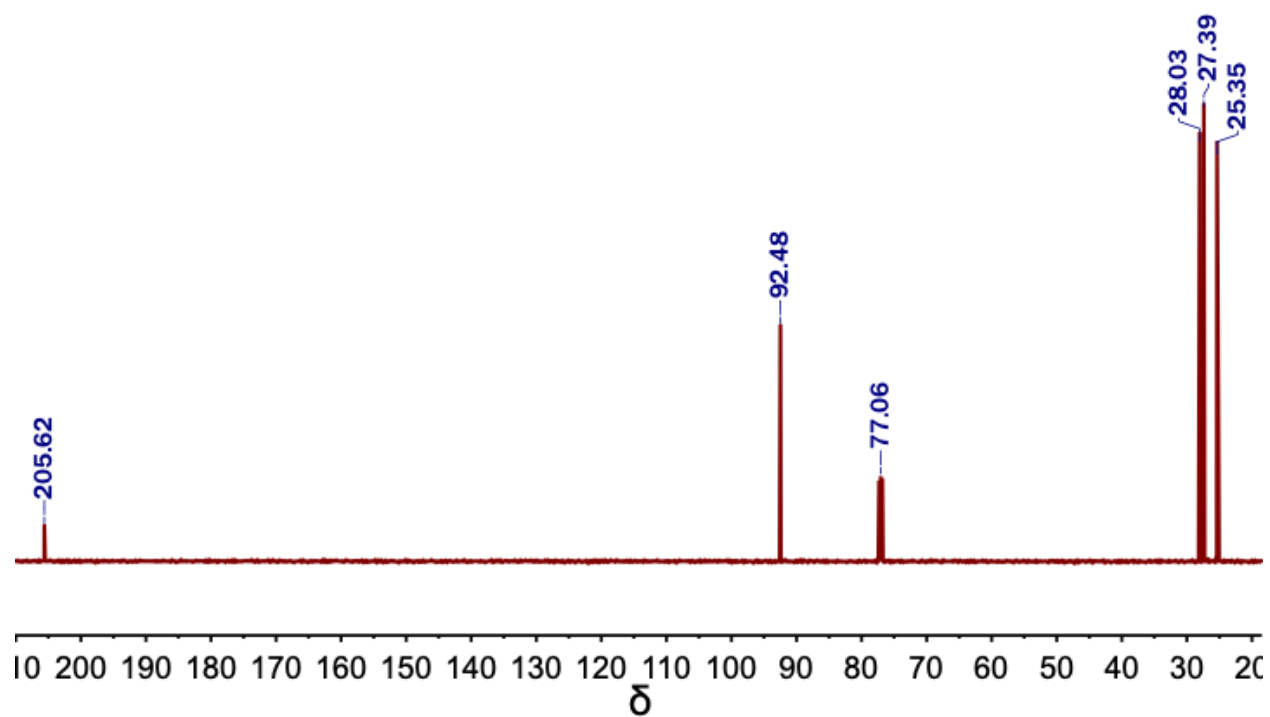


Figure S9: ^{13}C NMR spectrum of Cyclononadiene (**1**) in CDCl_3 .

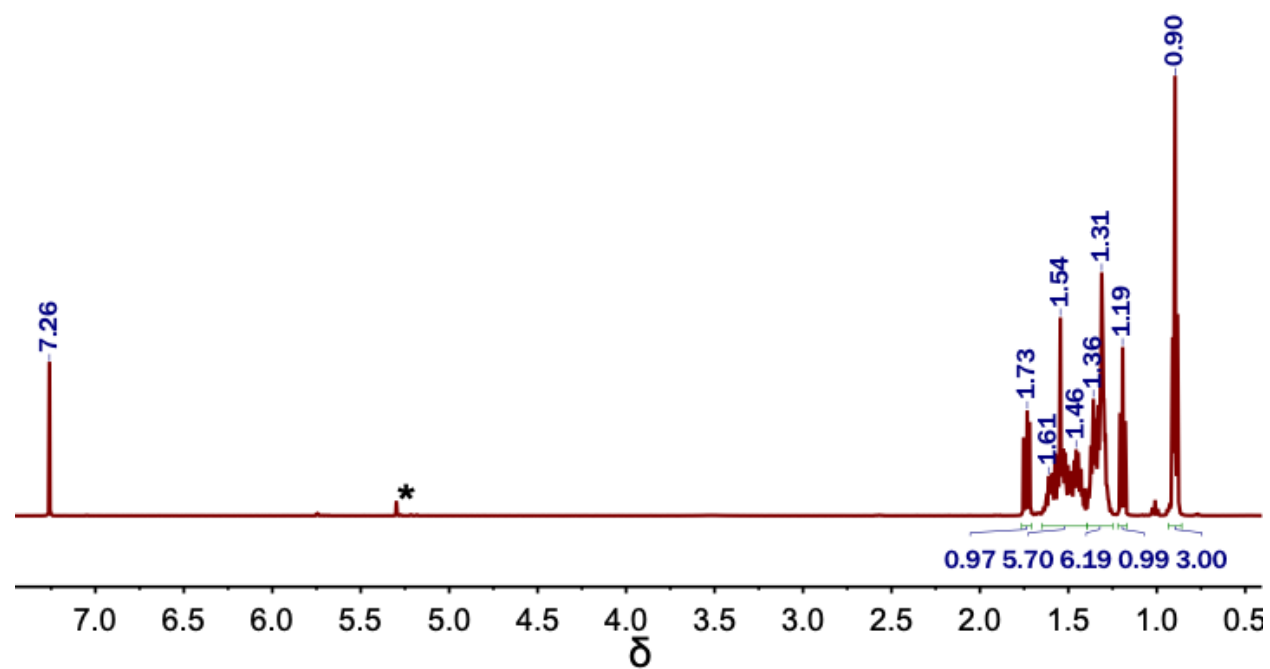


Figure S10: ^1H NMR spectrum of 1,1-dibromo-2-hexylcyclopropane in CDCl_3 . Residual solvent (DCM: $\delta = 5.30$) denoted with *.

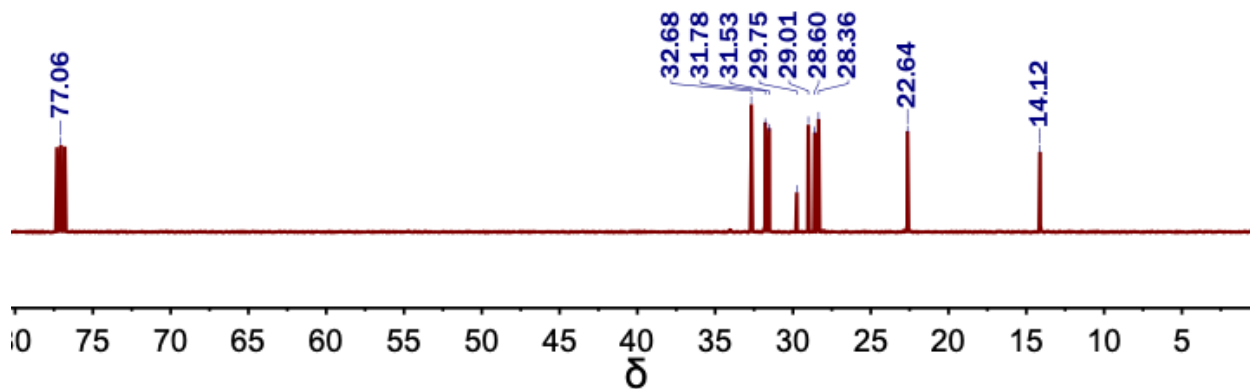


Figure S11: ^{13}C NMR spectrum of 1,1-dibromo-2-hexylcyclopropane in CDCl_3 .

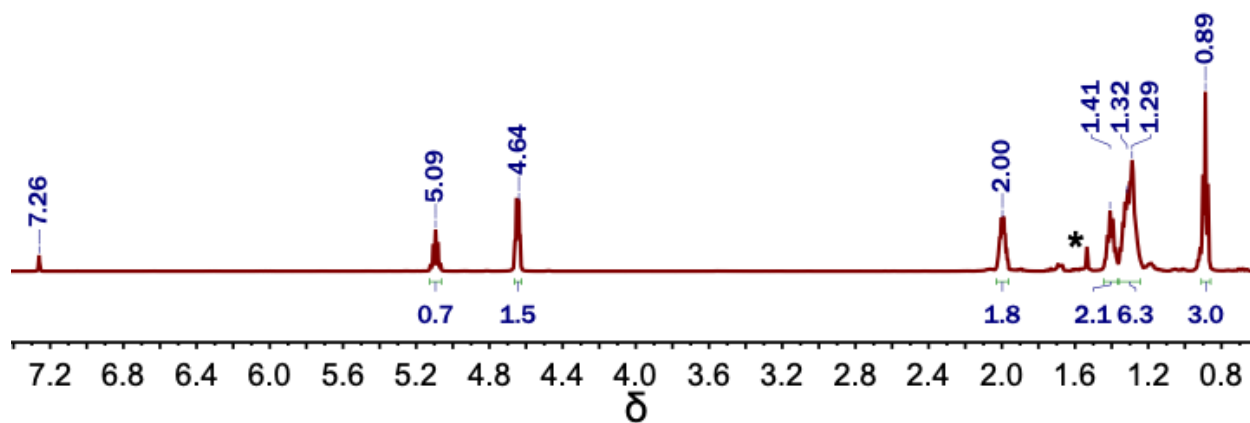


Figure S12: ^1H NMR spectrum of 1,2-nonadiene (**7**) in CDCl_3 . Residual solvent (H_2O : $\delta = 1.56$) denoted by *.

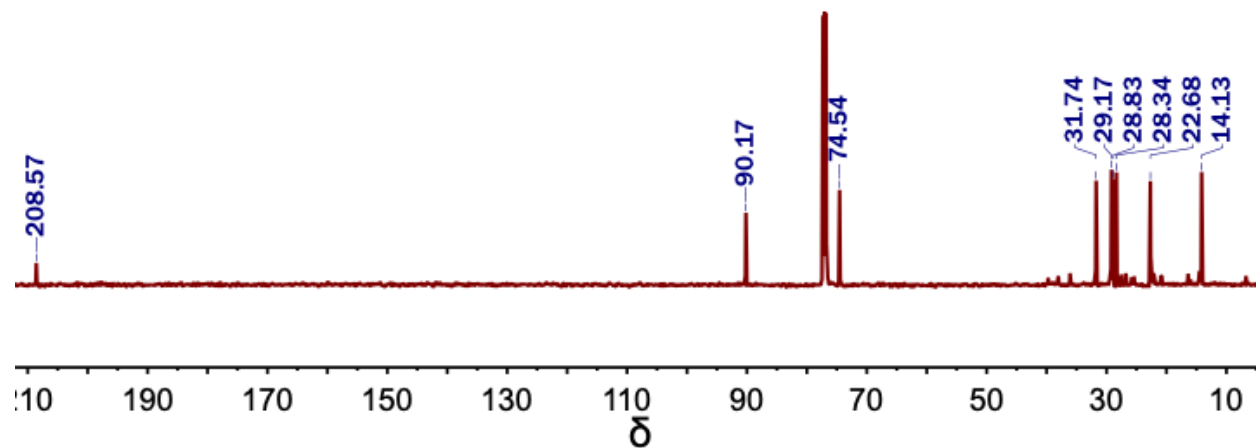


Figure S13: ^{13}C NMR spectrum of 1,2-nonadiene (**7**) in CDCl_3 .

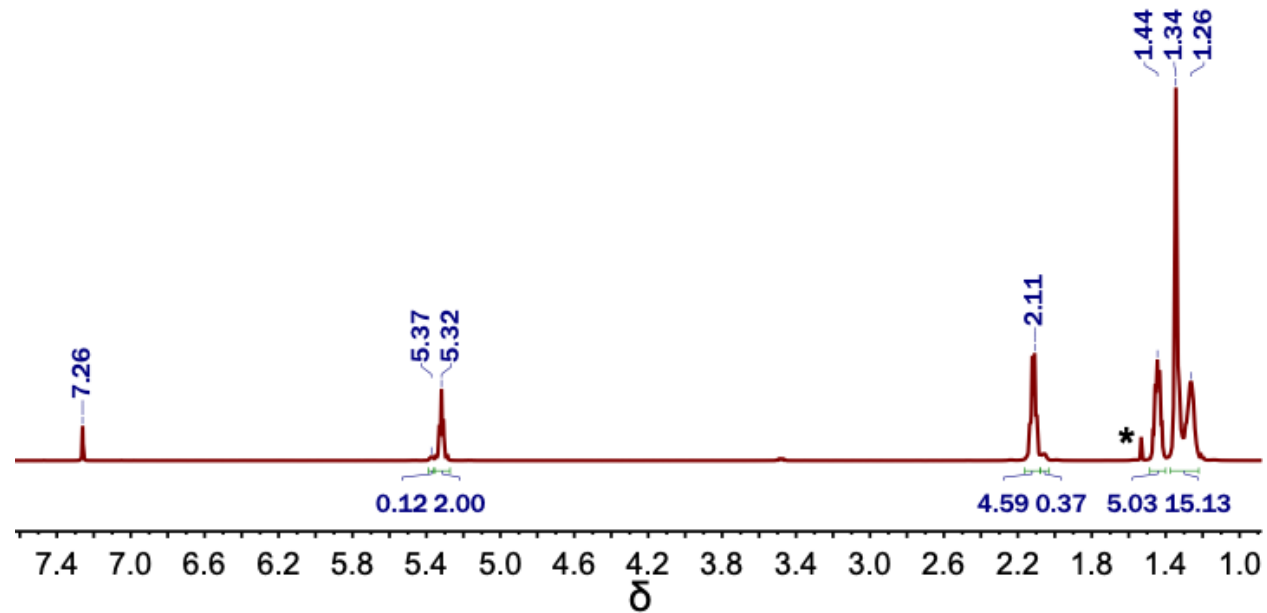


Figure S14: ^1H NMR spectrum of *cis*-cyclododecene in CDCl_3 . Residual solvent (H_2O : $\delta = 1.56$) denoted by *. *Cis:trans* ratio determined by relative integration of *cis* ($\delta = 5.32$) and *trans* ($\delta = 5.37$) resonances.

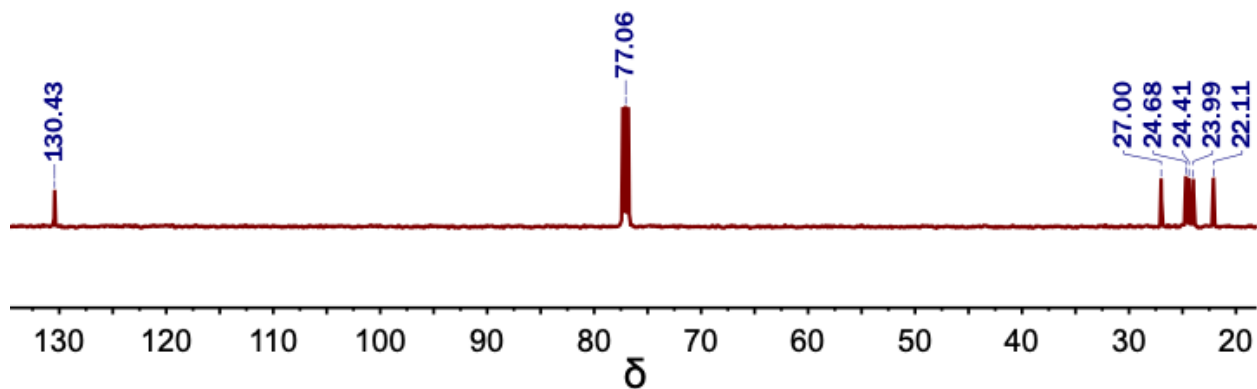


Figure S15: ^{13}C NMR spectrum of *cis*-cyclododecene in CDCl_3 .

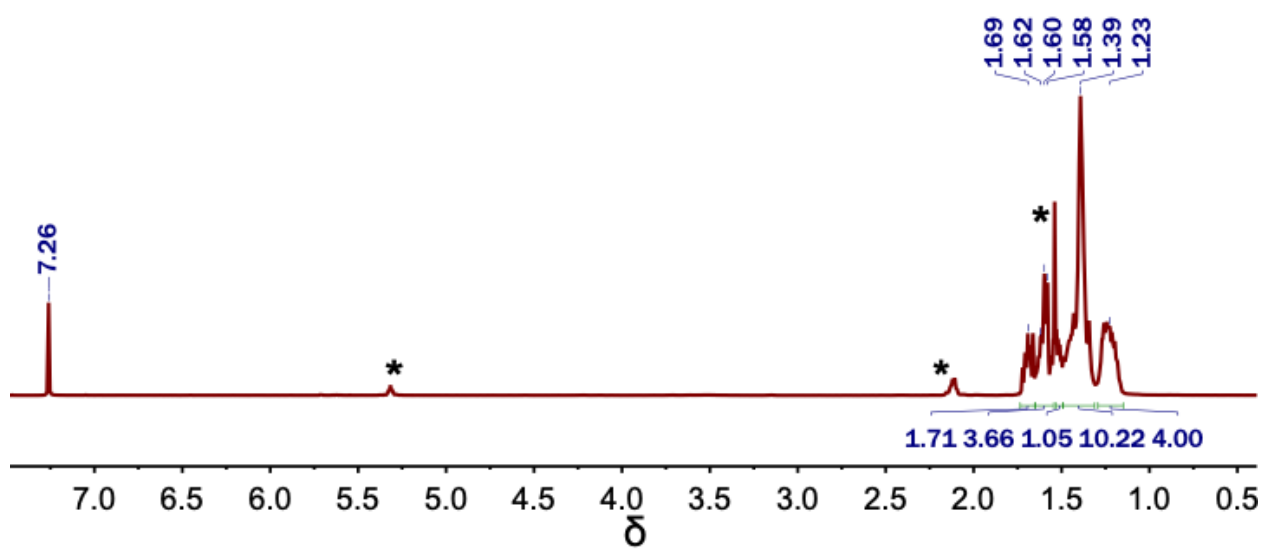


Figure S16: ^1H NMR spectrum of 13,13-dibromobicyclo[10.1.10]decane in CDCl_3 . Residual solvent (H_2O : $\delta = 1.56$) and *cis*-cyclododecene ($\delta = 5.32, 2.10$) denoted by *.

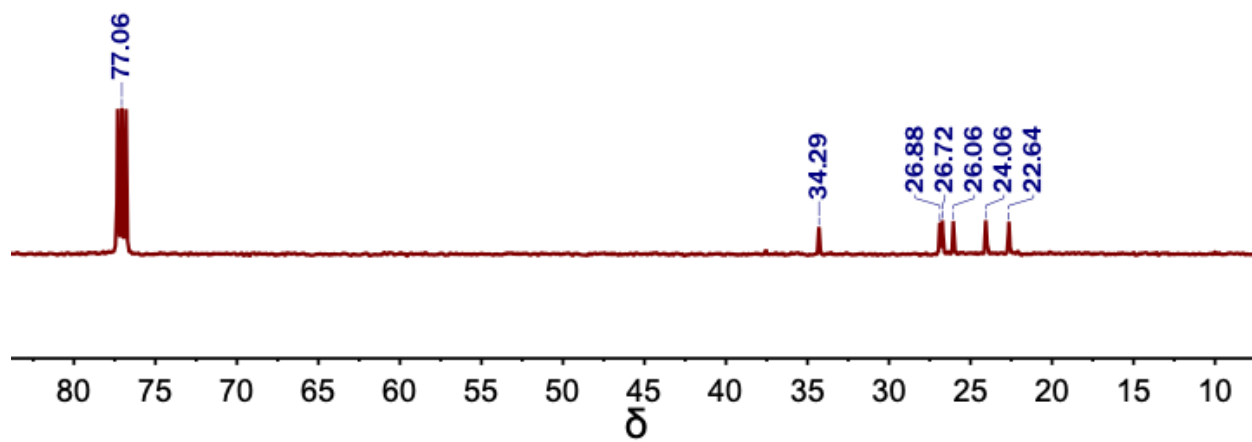


Figure S17: ^1H NMR spectrum of 13,13-dibromobicyclo[10.1.10]decane in CDCl_3 .

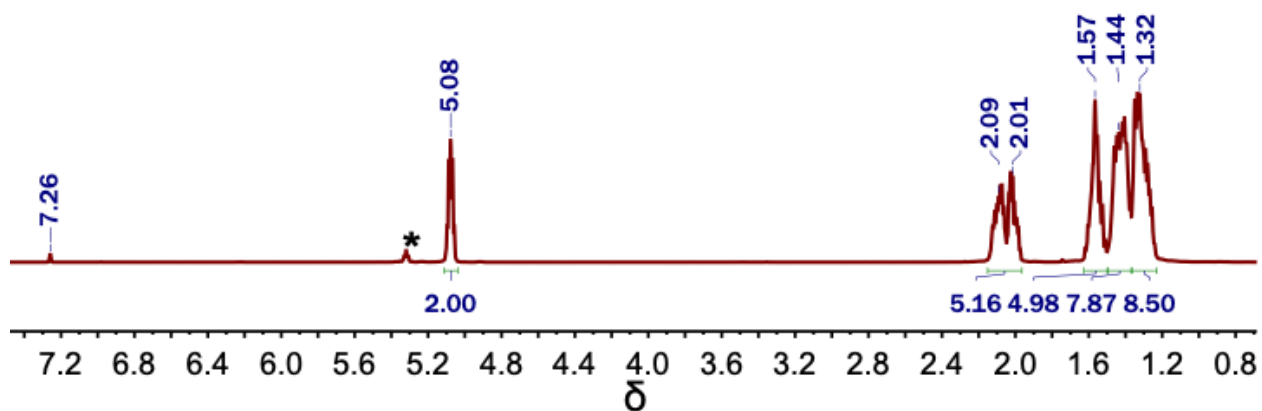


Figure S18: ^1H NMR spectrum of 1,2-cyclotridecadiene (**8**) in CDCl_3 . Residual *cis*-cyclododecene ($\delta = 5.32$) denoted by *.

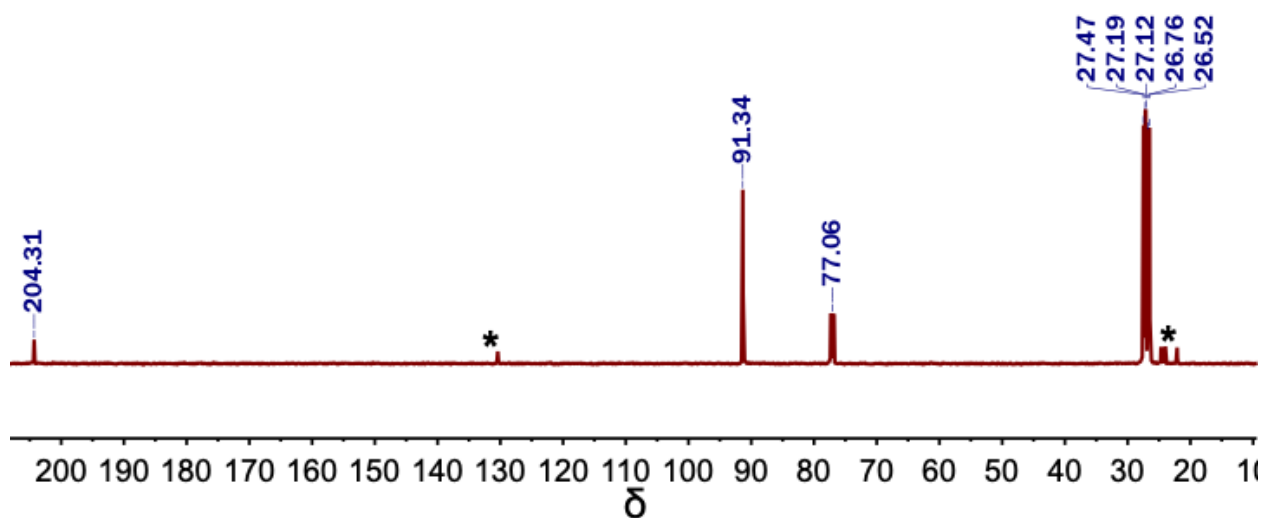


Figure S19: ^{13}C NMR spectrum of 1,2-cyclotridecadiene (**8**) in CDCl_3 . Residual *cis*-cyclododecene ($\delta = 130.43, 24.65, 24.38, 23.95, 22.08$) denoted by *.

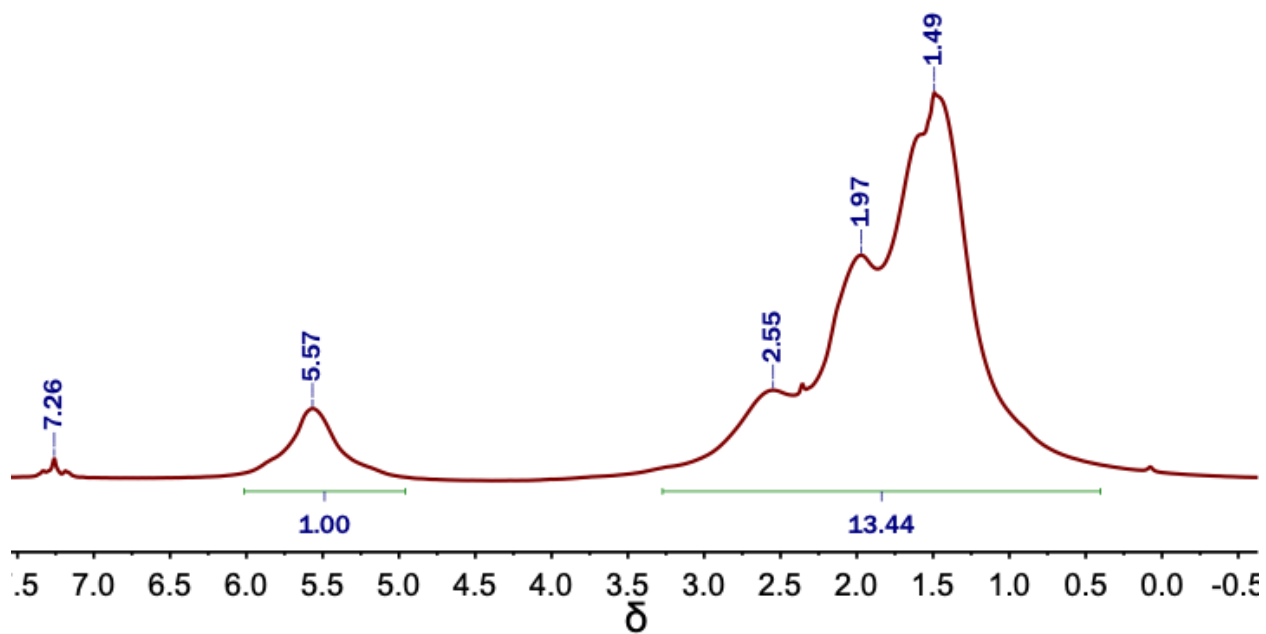


Figure S20. ^1H NMR spectrum of poly(cyclononadiene) (**2**) in CDCl_3 .

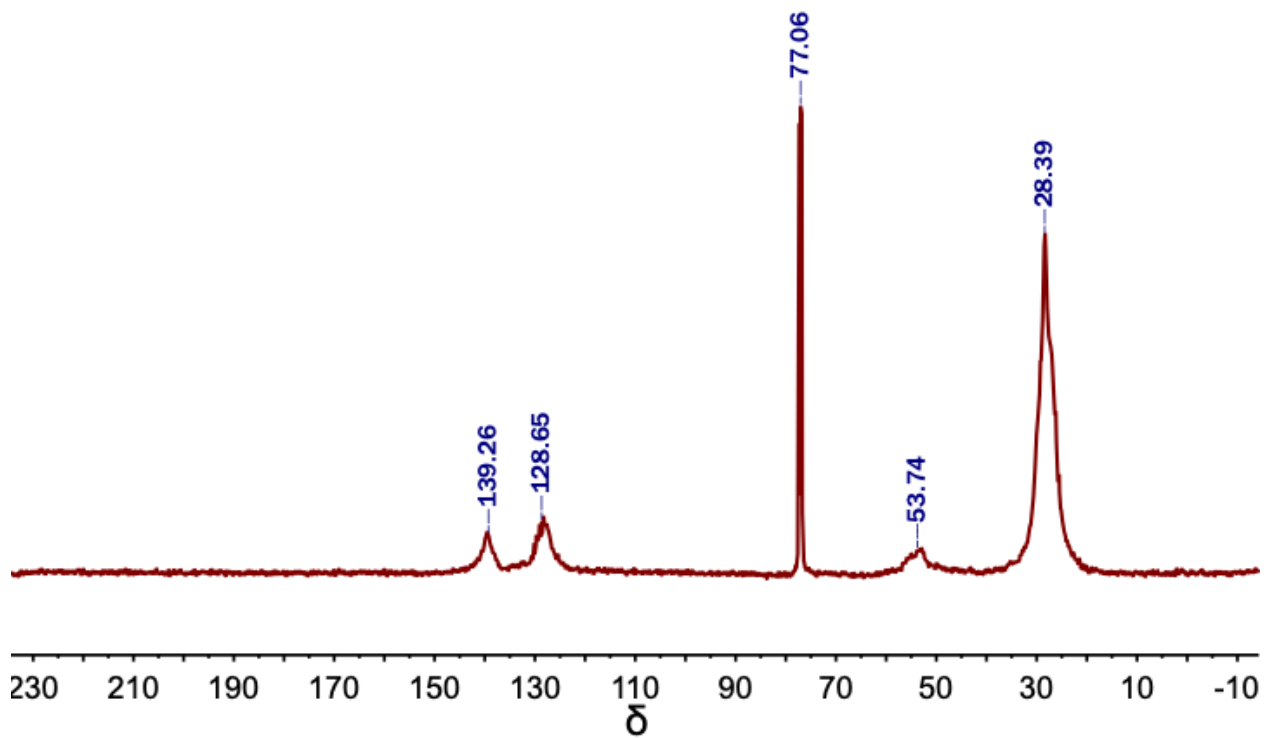


Figure S21: ^{13}C NMR spectrum of poly(cyclononadiene) (**2**) in CDCl_3 .

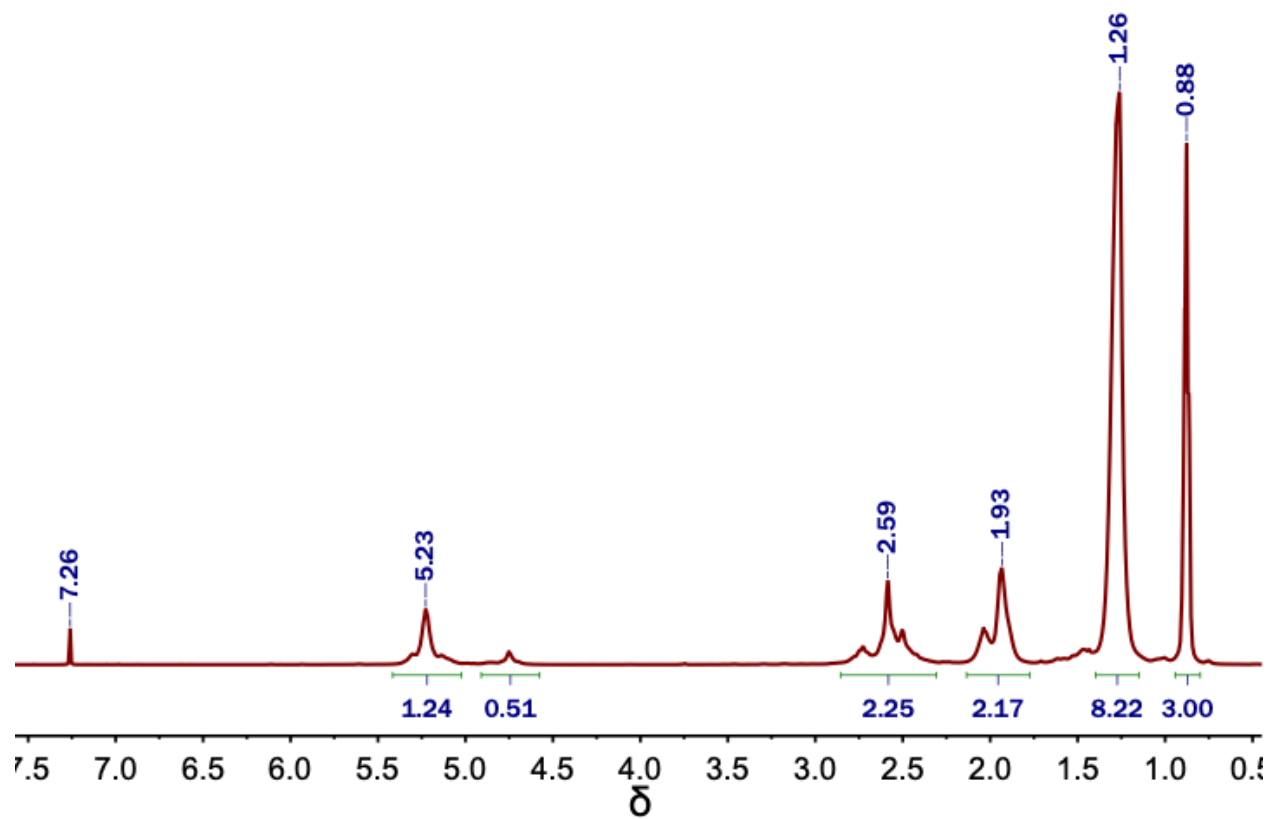


Figure S22: ^1H NMR spectrum of poly(1,2-nonadiene) in CDCl_3 .

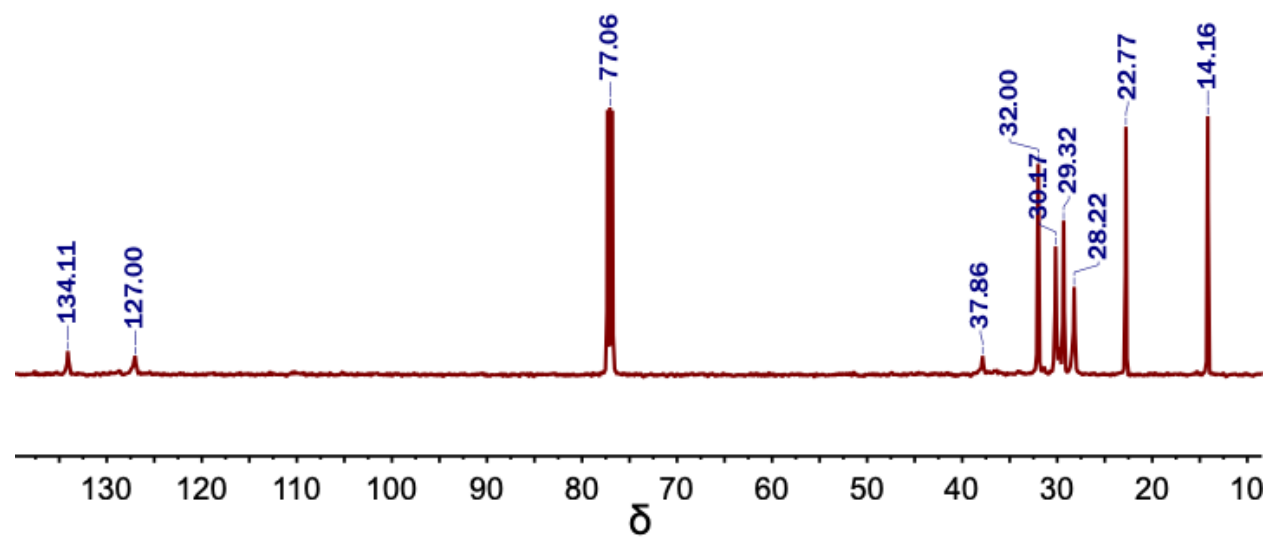


Figure S23: ^{13}C NMR spectrum of poly(1,2-nonadiene) in CDCl_3 .

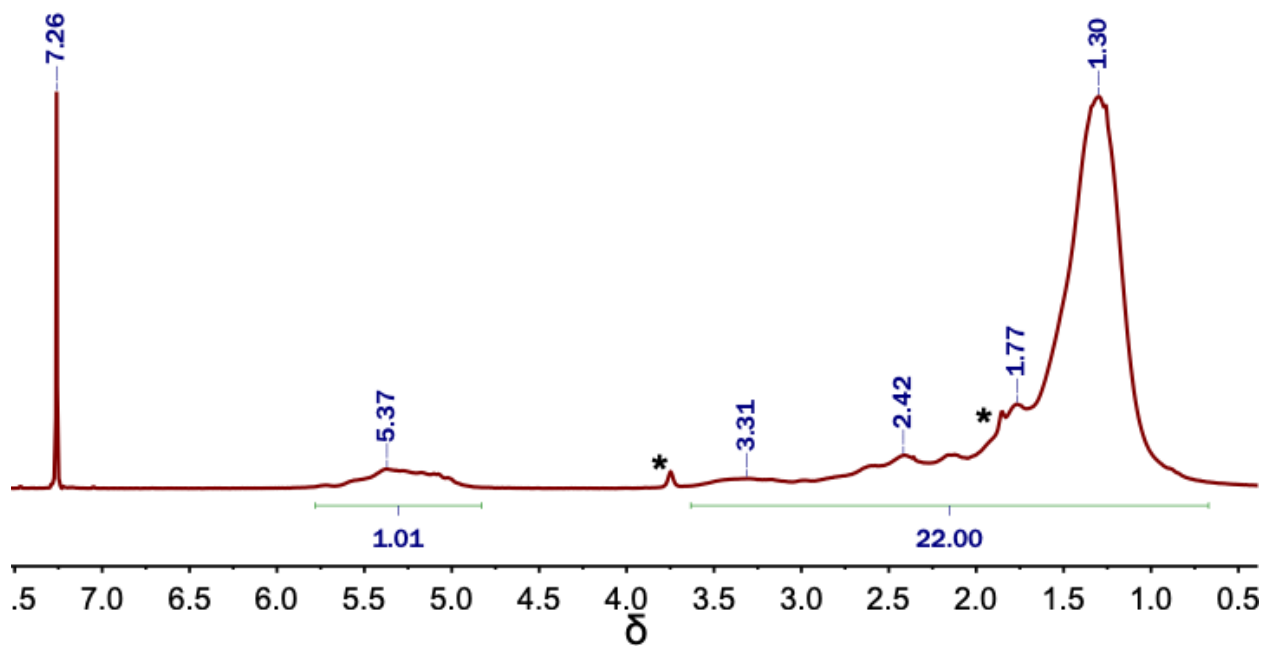


Figure S24: ^1H NMR spectrum of poly(1,2-cyclotridecadiene) in CDCl_3 . Residual Solvent (THF: $\delta = 3.74, 1.85$) denoted by *.

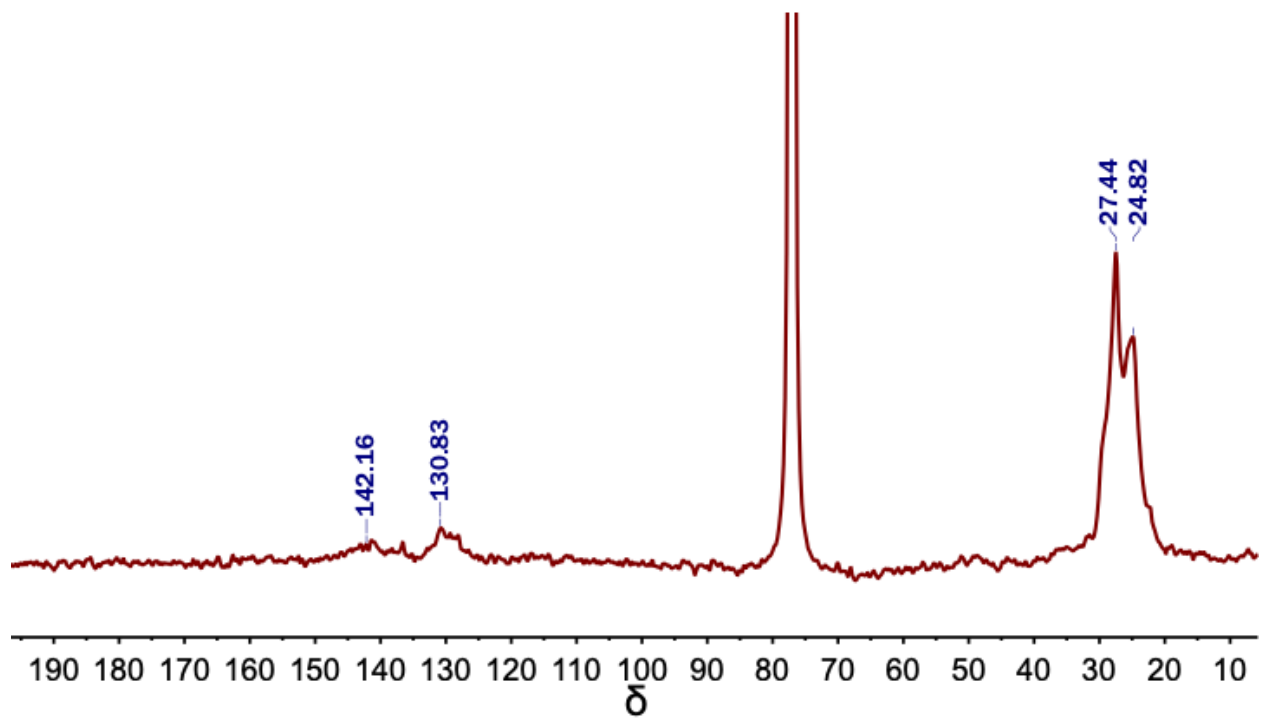


Figure S25: ^{13}C NMR spectrum of poly(1,2-cyclotridecadiene) in CDCl_3 .

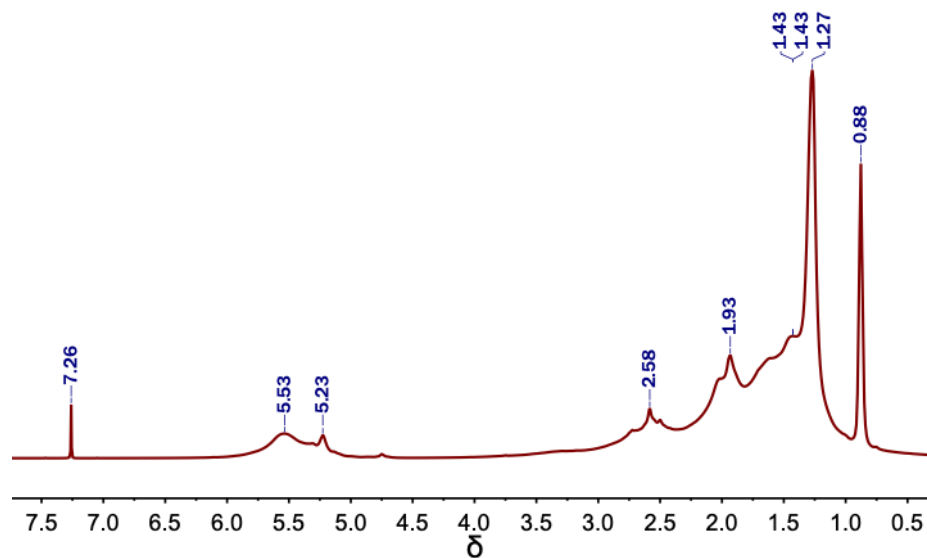


Figure S26: ^1H NMR spectrum of 70:30 (1:7) statistical copolymer in CDCl_3 .

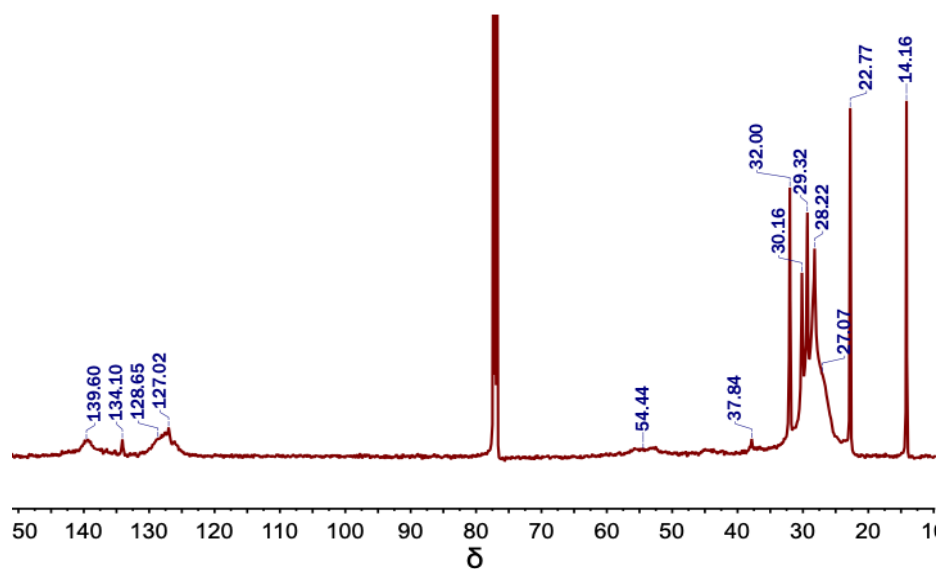


Figure S27: ^{13}C NMR spectrum of 70:30 (1:7) statistical copolymer in CDCl_3 .

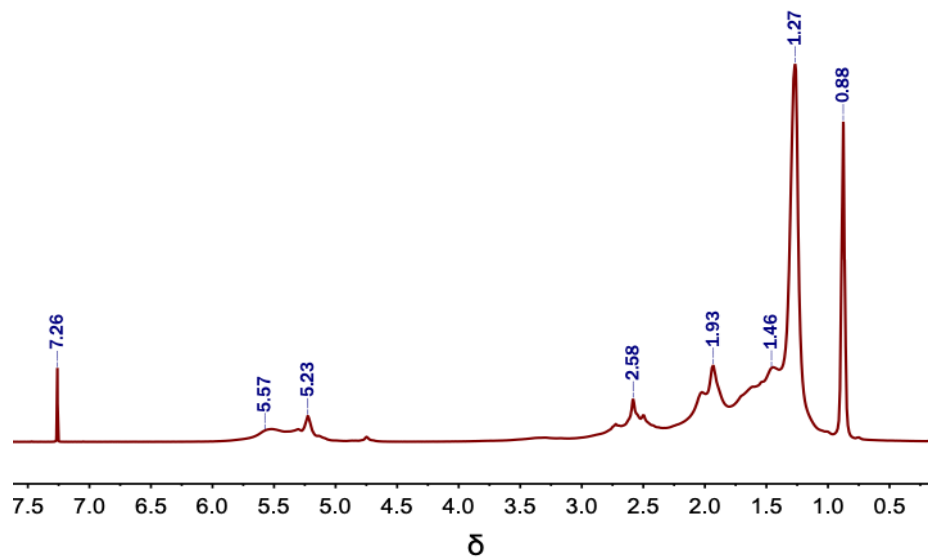


Figure S28: ^1H NMR spectrum of 50:50 (1:7) statistical copolymer in CDCl_3 .

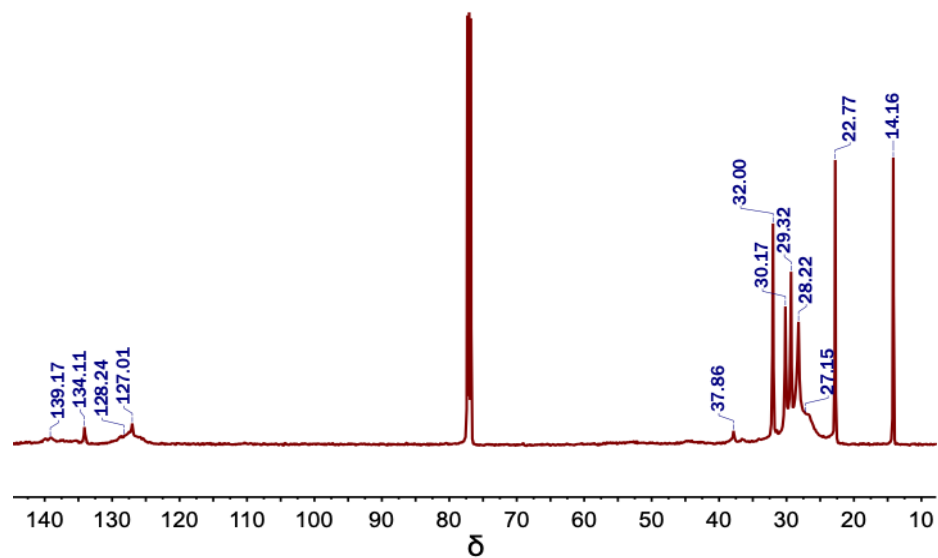


Figure S29: ^{13}C NMR spectrum of 50:50 (1:7) statistical copolymer in CDCl_3 .

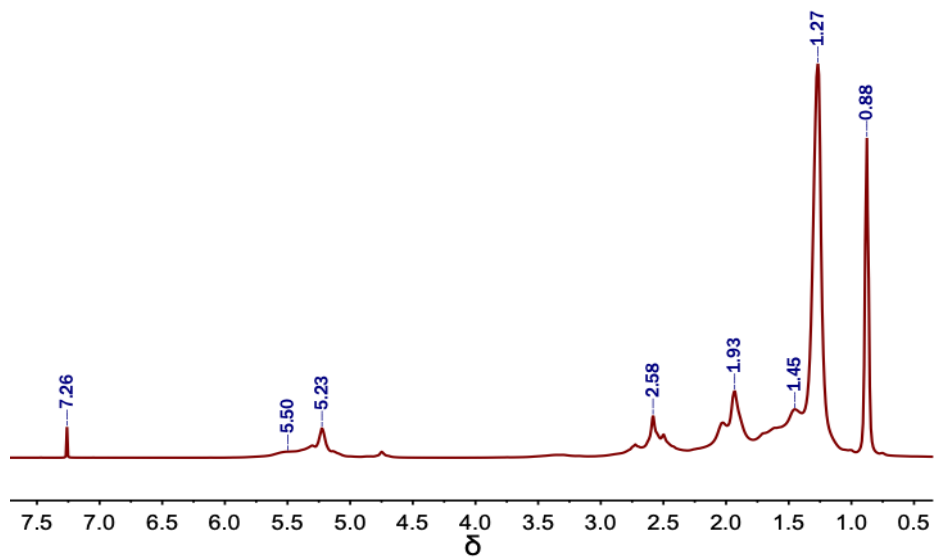


Figure S30: ^1H NMR spectrum of 30:70 (1:7) statistical copolymer in CDCl_3 .

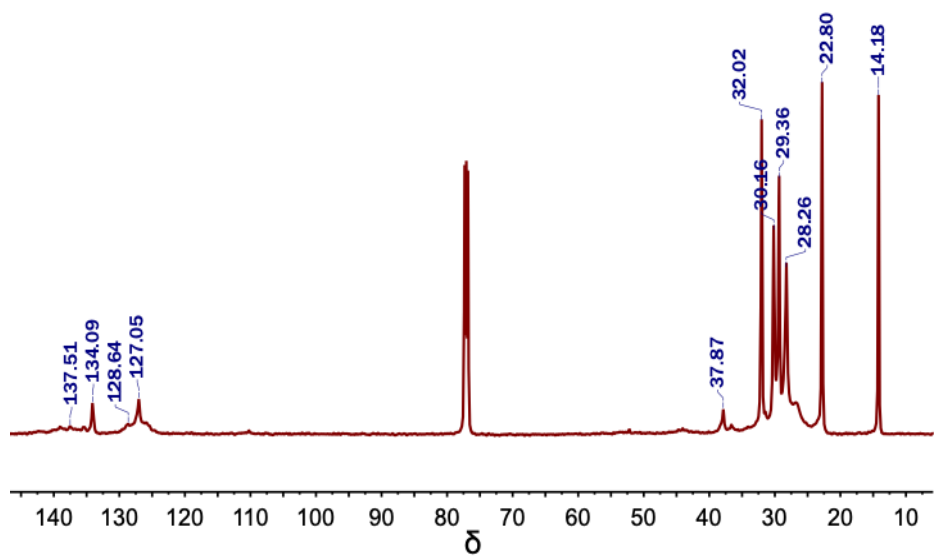


Figure S31: ^{13}C NMR spectrum of 30:70 (1:7) statistical copolymer in CDCl_3 .

9. Raw GPC Data for Polymers

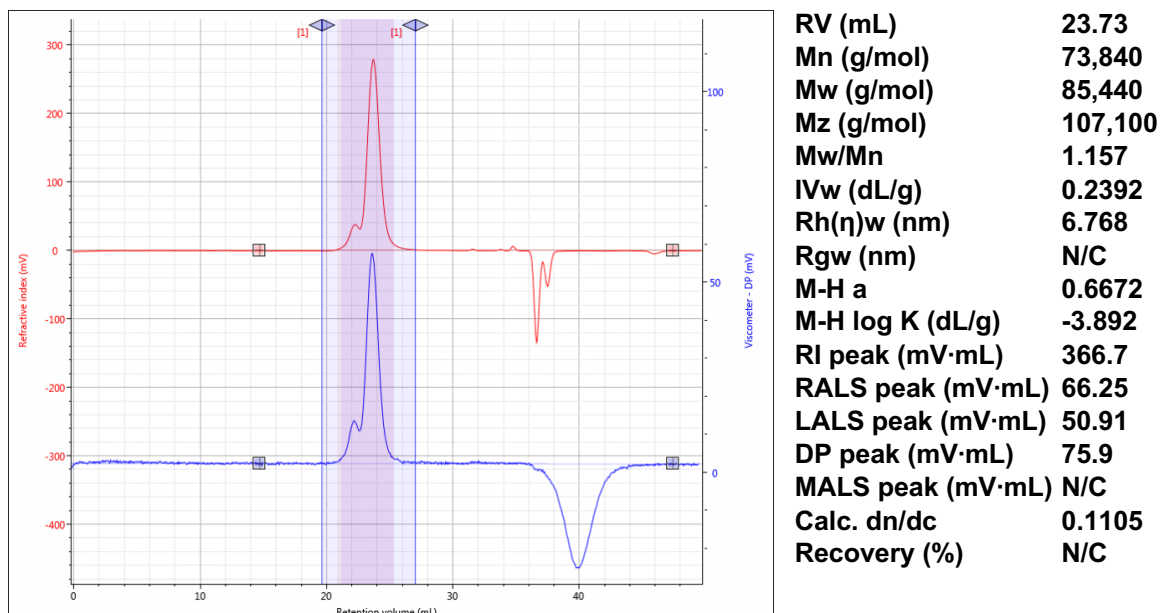


Figure S32: GPC trace of the polymerization of **1** with **3** in CHCl_3 (1 h).

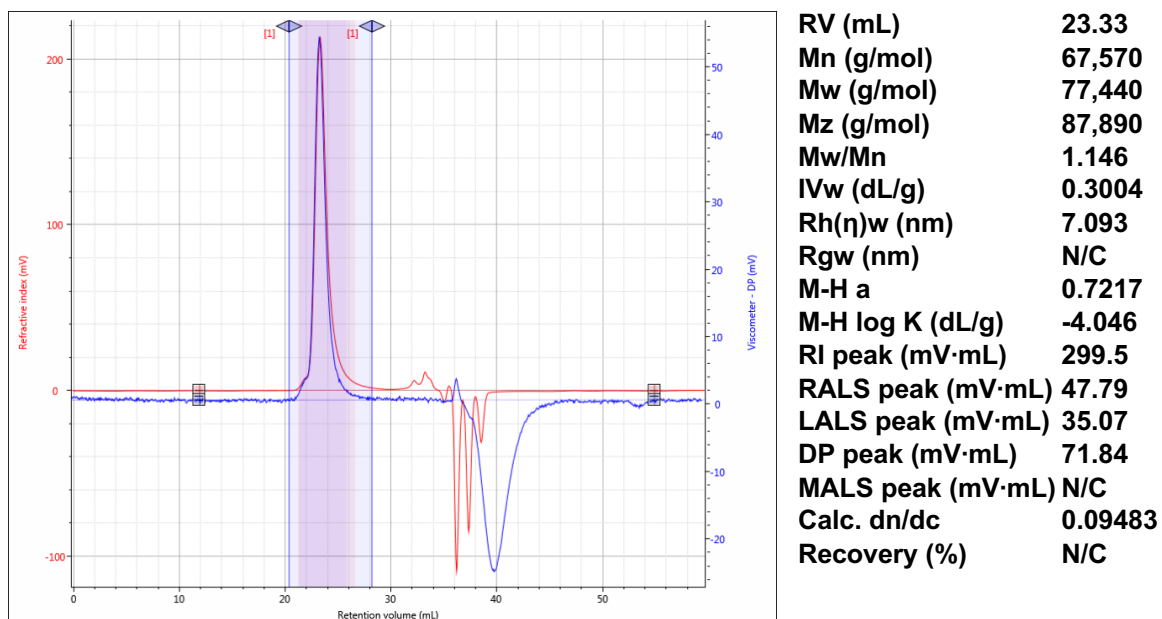
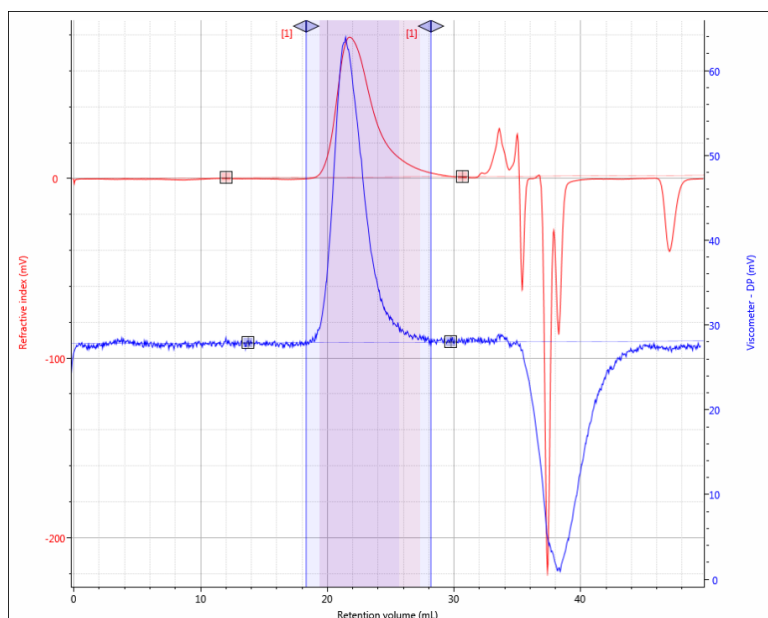
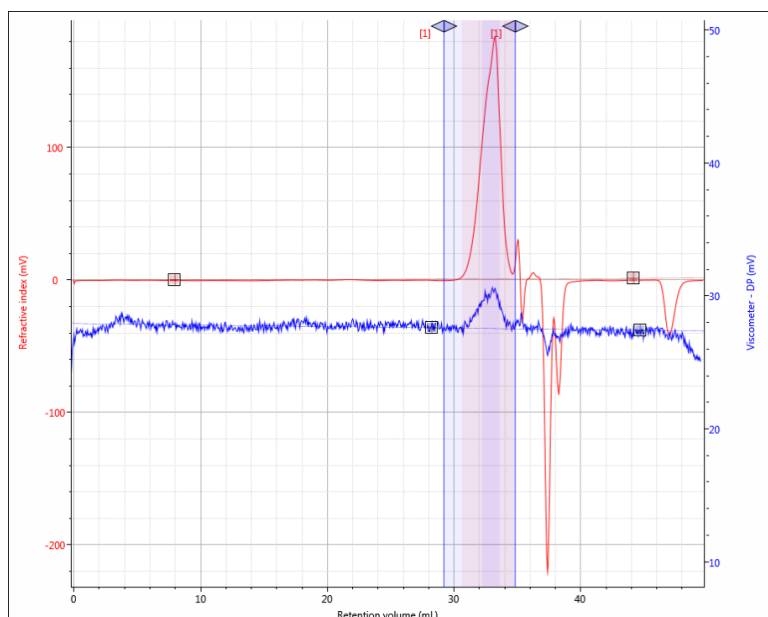


Figure S33: GPC trace of the polymerization of **7** with **3** (2 h).



RV (mL)	21.79
Mn (g/mol)	128,200
Mw (g/mol)	211,000
Mz (g/mol)	369,200
Mw/Mn	1.646
IVw (dL/g)	0.4547
Rh(η)w (nm)	11.01
Rgw (nm)	6.66
M-H a	0.5896
M-H log K (dL/g)	-3.452
RI peak (mV·mL)	263.3
RALS peak (mV·mL)	118.3
LALS peak (mV·mL)	93.04
DP peak (mV·mL)	99.63
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1126
Recovery (%)	N/C

Figure S34: GPC trace of the polymerization of **1** with **4** (1 h).



RV (mL)	33.25
Mn (g/mol)	33,650
Mw (g/mol)	45,040
Mz (g/mol)	187,600
Mw/Mn	1.338
IVw (dL/g)	0.02087
Rh(η)w (nm)	2.189
Rgw (nm)	N/C
M-H a	0.6906
M-H log K (dL/g)	-4.805
RI peak (mV·mL)	305.8
RALS peak (mV·mL)	29.97
LALS peak (mV·mL)	23.29
DP peak (mV·mL)	5.596
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.109
Recovery (%)	N/C

Figure S35: GPC trace of the polymerization of **1** with activated **5** (24 h).

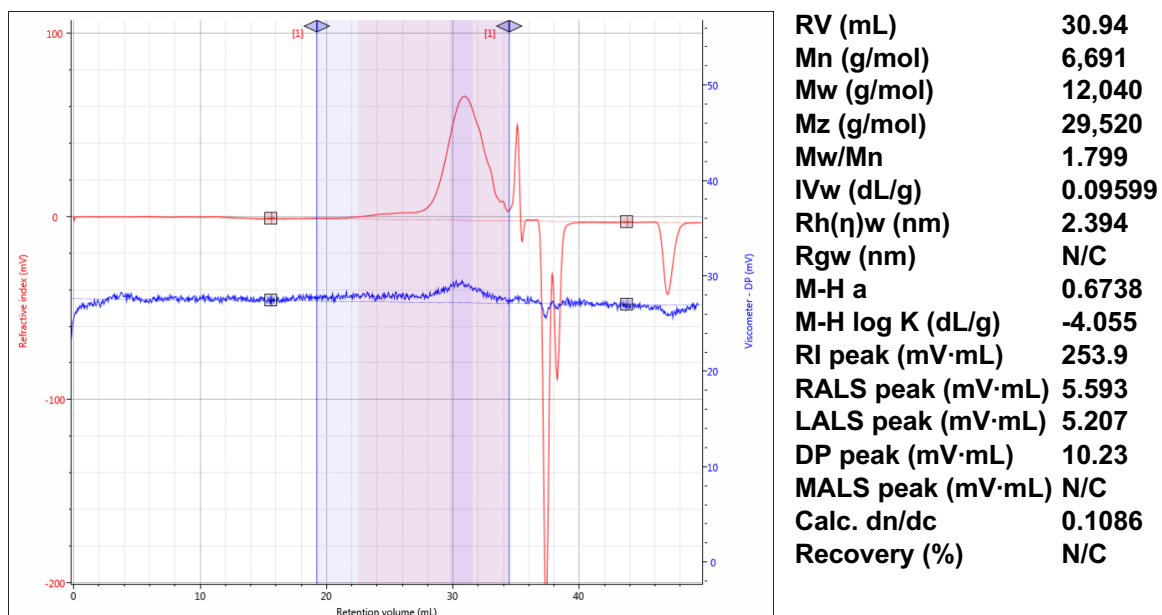


Figure S36: GPC trace of the polymerization of **1** with activated **6** (1 h).

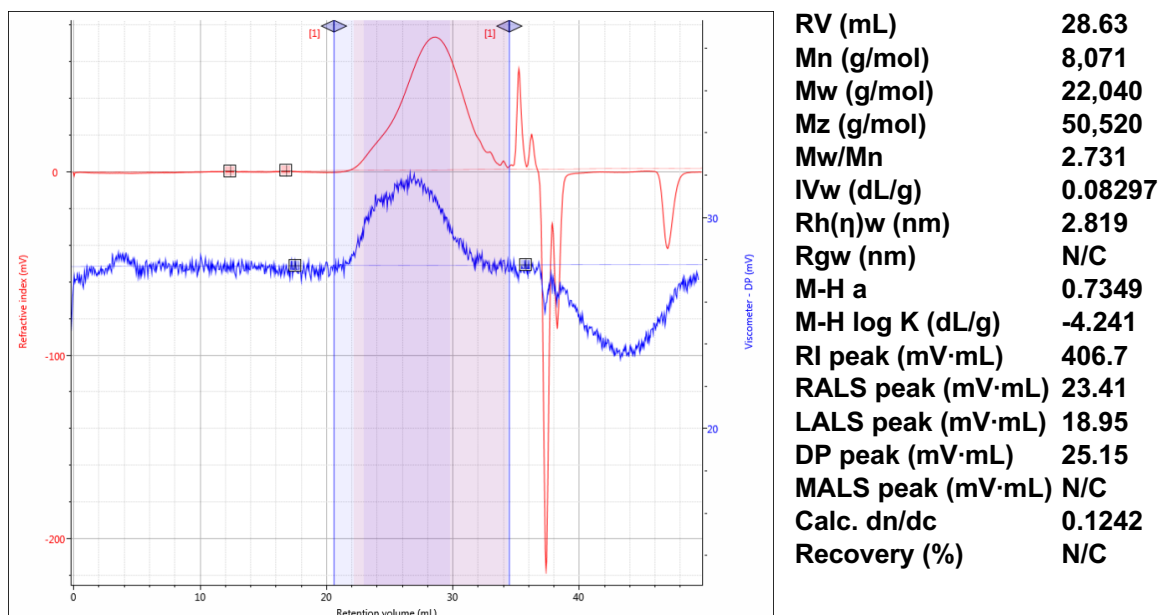
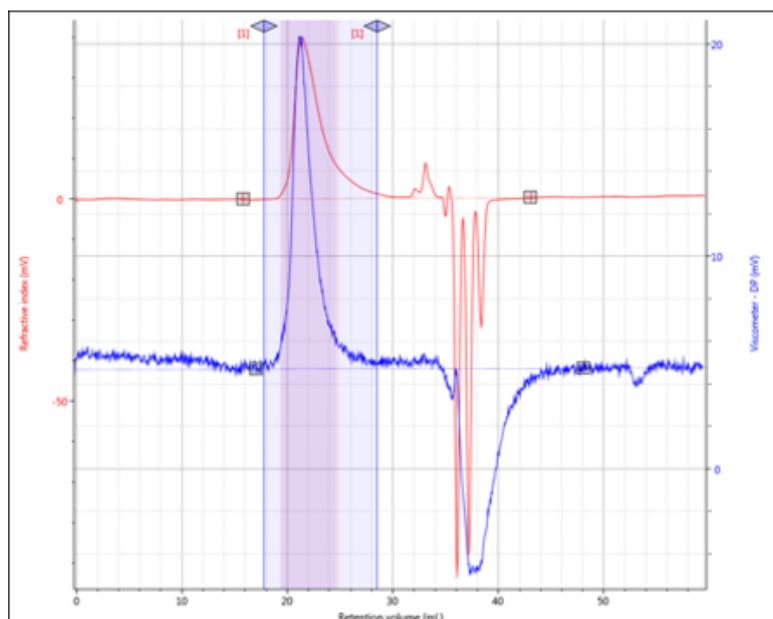
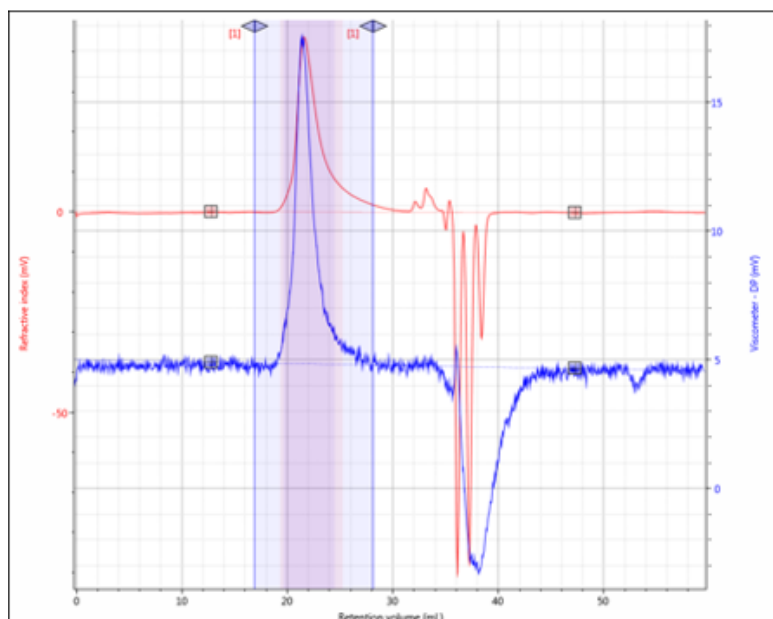


Figure S37: GPC trace of the polymerization of **1** with activated **3** (24 h).



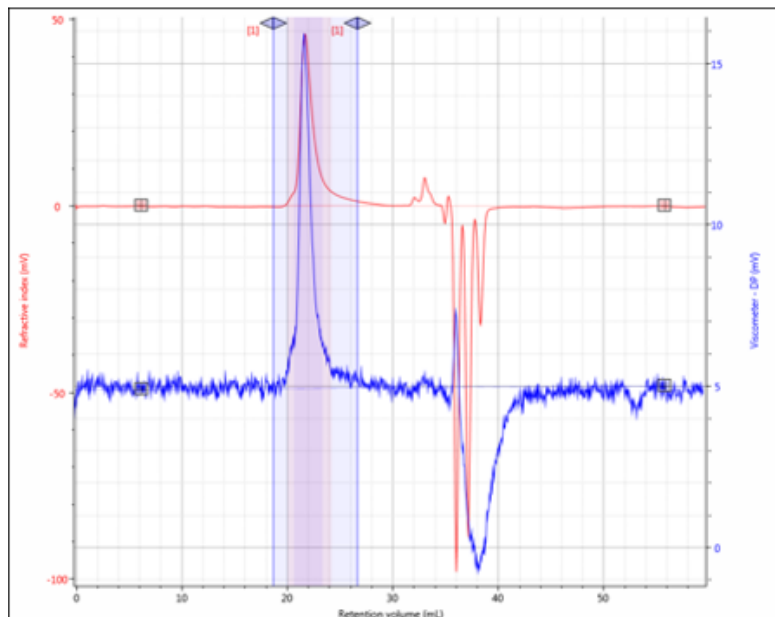
RV (mL) 21.43
Mn (g/mol) 99,270
Mw (g/mol) 174,100
Mz (g/mol) 257,500
Mw/Mn 1.754
IVw (dL/g) 0.4834
Rh(η)w (nm) 10.6
Rgw (nm) 8.074
M-H a 0.4886
M-H log K (dL/g) -2.861
RI peak (mV·mL) 122.1
RALS peak (mV·mL) 52.59
LALS peak (mV·mL) 39.58
DP peak (mV·mL) 38.47
MALS peak (mV·mL) N/C
Calc. dn/dc 0.1163
Recovery (%) N/C

Figure S38: Raw GPC data for 70:30 (1:7) statistical copolymer



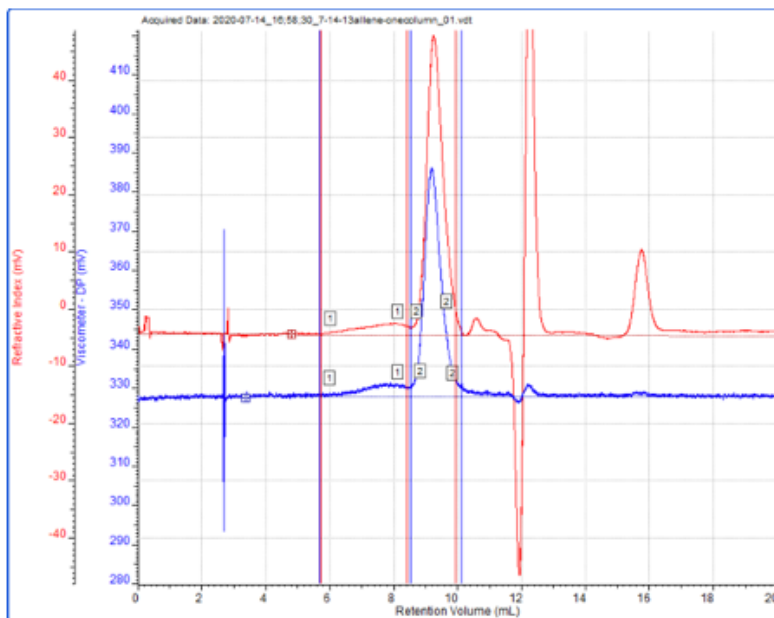
RV (mL) 21.63
Mn (g/mol) 98,360
Mw (g/mol) 181,800
Mz (g/mol) 297,500
Mw/Mn 1.849
IVw (dL/g) 0.4433
Rh(η)w (nm) 10.39
Rgw (nm) 9.095
M-H a 0.4434
M-H log K (dL/g) -2.667
RI peak (mV·mL) 116.9
RALS peak (mV·mL) 62.29
LALS peak (mV·mL) 47.05
DP peak (mV·mL) 27.8
MALS peak (mV·mL) N/C
Calc. dn/dc 0.137
Recovery (%) N/C

Figure S39: Raw GPC data for 50:50 (1:7) statistical copolymer



RV (mL) 21.71
Mn (g/mol) 129,100
Mw (g/mol) 178,400
Mz (g/mol) 237,100
Mw/Mn 1.382
IVw (dL/g) 0.4881
Rh(η)w (nm) 10.84
Rgw (nm) N/C
M-H a 0.9802
M-H log K (dL/g) -5.498
RI peak (mV·mL) 73
RALS peak (mV·mL) 45.56
LALS peak (mV·mL) 33.84
DP peak (mV·mL) 16.76
MALS peak (mV·mL) N/C
Calc. dn/dc 0.1613
Recovery (%) N/C

Figure S40: Raw GPC data for 30:70 (1:7) statistical copolymer



RV (mL) 9.217
Mn (Daltons) 47,289
Mw (Daltons) 94,522
Mz (Daltons) 1.141e6
Mw/Mn 1.999
IVw (dL/g) 0.0510
Rh(η)w (nm) 3.711
Rgw (nm) N/C
M-H a 0.260
M-H log K (dL/g) -2.508
RI peak (mV·mL) 32.12
RALS peak (mV·mL) 4.68
LALS peak (mV·mL) 1.76
DP peak (mV·mL) 36.81
MALS peak (mV·mL) N/C
Calc. dn/dc 0.0194
Recovery (%) N/C

Figure S41: High temperature GPC trace of poly(1,2-cyclotridecadiene).

10. References

- (1) Shea, K. J.; Kim, J. S. Influence of Strain on Chemical Reactivity. Relative Reactivity of Torsionally Distorted Double Bonds in MCPBA Epoxidations. *J. Am. Chem. Soc.* **1992**, *114* (8), 3044–3051.
- (2) Campbell, K. A.; House, H. O.; Surber, B. W.; Trahanovsky, W. S. Enones with Strained Double Bonds. 10. Use of Flash Vacuum Pyrolysis to Obtain Bicyclo[3.3.1]Non-1-En-3-One. *J. Org. Chem.* **1987**, *52* (12), 2474–2481.
- (3) Becker, J. Y.; Zinger, B. Electrochemical Oxidation of Alkyl-Substituted Allenes in Methanol. *Tetrahedron* **1982**, *38* (11), 1677–1682.
- (4) Moore, W. R.; Ward, H. R. The Formation of Allenes from Gem-Dihalocyclopropanes by Reaction with Alkylolithium Reagents^{1,2}. *J. Org. Chem.* **1962**, *27* (12), 4179–4181.
- (5) Zhu, Y.-Y.; Yin, T.-T.; Li, X.-L.; Su, M.; Xue, Y.-X.; Yu, Z.-P.; Liu, N.; Yin, J.; Wu, Z.-Q. Synthesis and Chiroptical Properties of Helical Polyallenes Bearing Chiral Amide Pendants. *Macromolecules* **2014**, *47* (20), 7021–7029.
- (6) Gmernicki, K. R.; Hong, E.; Maroon, C. R.; Mahurin, S. M.; Sokolov, A. P.; Saito, T.; Long, B. K. Accessing Siloxane Functionalized Polynorbornenes via Vinyl-Addition Polymerization for CO₂ Separation Membranes. *ACS Macro Lett.* **2016**, *5* (7), 879–883.
- (7) Ohno, M.; Okamoto, M. Cis-CYCLODODECENE. *Org. Synth.* **1969**, *49* (30).
- (8) Han, X.; Hu, J.; Chen, C.; Yuan, Y.; Shi, Z. Copper-Catalysed, Diboron-Mediated Cis-Dideuterated Semihydrogenation of Alkynes with Heavy Water. *Chem. Commun.* **2019**, *55* (48), 6922–6925.
- (9) Erden, I.; Cao, W.; Price, M.; Colton, M. A Three-Carbon (N+1+2) Ring Expansion Method for the Synthesis of Macrocyclic Enones. Application to Muscone Synthesis. *Tetrahedron* **2008**, *64* (23), 5497–5501.