

Supporting Information

Influence of Solvent on Cyclic Polynorbornene Tacticity

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Syntheses, NMR and Spectra

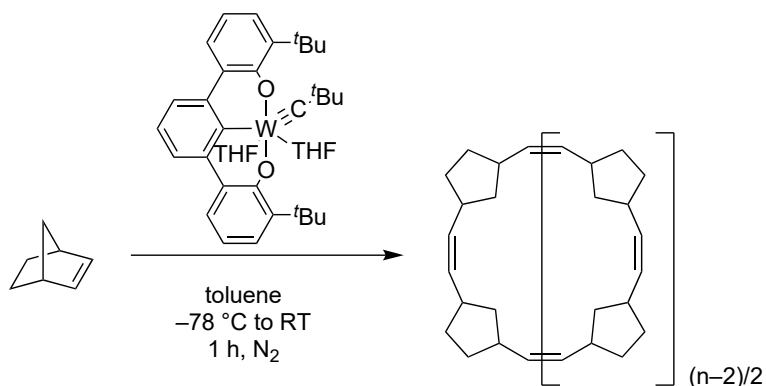
General Considerations

All manipulations were performed under an inert atmosphere using standard Schlenk or glovebox techniques unless otherwise specified. Glassware was oven-dried before use. Pentane, methylene chloride (CH_2Cl_2), toluene, diethyl ether (Et_2O), tetrahydrofuran (THF), and benzene were dried using a GlassContour drying column and stored over 3 Å molecular sieves. Benzene- d_6 (Cambridge Isotopes) was dried over calcium hydride (CaH_2), distilled, and stored over 3 Å molecular sieves. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and 2D NMR spectra were obtained on Varian INOVA (500 MHz) and Bruker (400 MHz and 600 MHz) spectrometers. 2-Bromo-6-*tert*-butylanisole,¹ $[\text{t}^{\text{Bu}}\text{OCO}]\text{H}_2$,² and $[\text{t}^{\text{Bu}}\text{OCO}]\text{W}\equiv\text{C}(\text{t}^{\text{Bu}})(\text{THF})_2$ ³ were prepared according to published methods. MeOTf was purchased from Millipore Sigma and used as received. Norbornene (NB) was purchased from Sigma-Aldrich, dried over Na, distilled under argon, and stored under argon at $-35\text{ }^\circ\text{C}$. Linear polynorbornene (l-PNB) was synthesized following a literature procedure, using the commercially available catalysts, Hoveyda-Grubbs catalyst M2001 for *cis,syndiotactic* l-PNB⁴ and 2,6-diisopropylphenylimidoneophylidene[*racemic*-BIPHEN]molybdenum(VI) for *cis,isotactic* l-PNB.⁵ Complex Hoveyda-Grubbs catalyst M2001 and 2,6-Diisopropylphenylimidoneophylidene[*racemic*-BIPHEN]molybdenum(VI) were purchased from Sigma-Aldrich (CAS 1352916-84-7) and Strem (CAS 300344-02-9) respectively, and used without further purification. Methylene chloride (CH_2Cl_2) was purchased from Fisher Scientific and used as received. *n*-Butyllithium solution (2.5 M in hexanes) was purchased from Acros Organics and Millipore Sigma. 2-Methyltetrahydrofuran (2-MeTHF), anhydrous, >99%, inhibitor-free was purchased from Sigma-Aldrich, and dried

over 3 Å molecular sieves under argon overnight prior to use. 1,3-dichlorobenzene (Alfa Aesar) was dried over CaH₂, distilled under vacuum, and stored over 3 Å molecular sieves. The chemical shifts are reported in δ (ppm), referenced to the solvents for ¹H and ¹³C{¹H} spectra.⁶ Size-exclusion chromatography was performed on an Agilent Infinity II high-temperature GPC system equipped with a refractive index and VS detectors at the Department of Chemistry, University of Warwick. The instrument was run at 140 °C in dichlorobenzene at 1 mL/min. Samples were dissolved as prepared in 5 mL of dichlorobenzene at 135 °C while gently agitating on an Agilent SP260VS high-temperature dissolution unit. Samples were then filtered through 10 µm stainless steel frits before injection and then analyzed by 3rd order conventional calibration prepared from narrow polystyrene in the range of 6,570,000 – 580 g/mol.

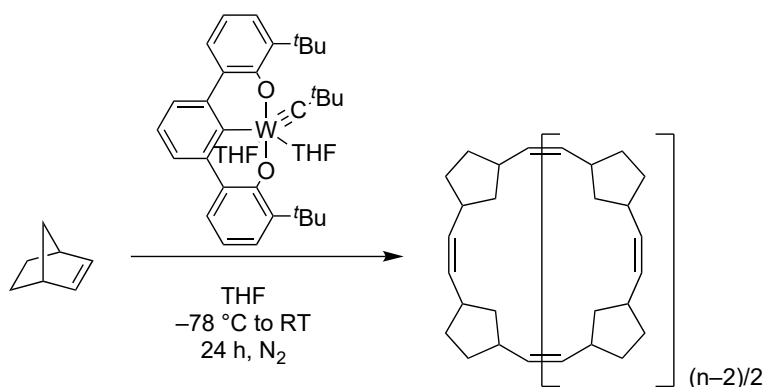
General Polymerization Procedure

Polymerization of norbornene by initiator **1** in toluene



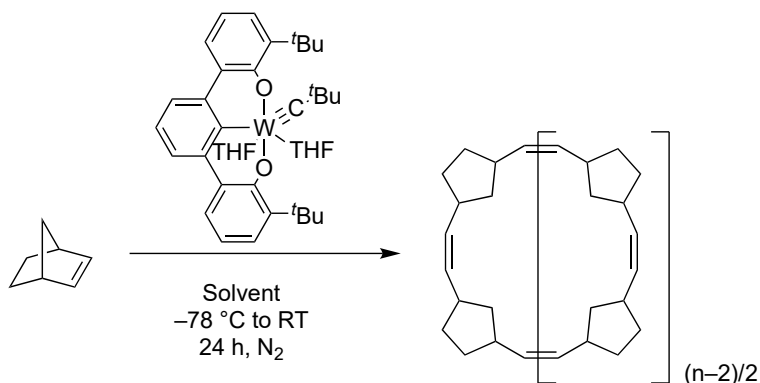
A 20 mL glass vial was charged with norbornene (94.0 mg, 1.00 mmol, 500 equiv), toluene (9.85 mL), and a magnetic stir bar. The norbornene solution was cooled to $-78\text{ }^{\circ}\text{C}$. At ambient temperature, 0.153 mL of a stock solution of **1** (10 mg in 1.0 mL of toluene; 1.53 mg, 0.200×10^{-2} mmol, 1.00 equiv) was added to the norbornene solution with stirring. The reaction was allowed to stir for 1 h at ambient temperature. Then, the reaction mixture was brought outside the glovebox, and added to stirring methanol dropwise to precipitate. Precipitated polynorbornene was isolated by decanting, and dried under vacuum. The obtained polymer was purified again by dissolving in a minimal amount of THF, precipitating in stirring methanol, decanting the supernatant, and then all volatiles were removed under vacuum overnight to yield 92.4 mg of *cis,syndiotactic* cyclic polynorbornene (0.981 mmol, 98% yield, 92 *cis*%, *syndio*>99%). ¹H NMR and ¹³C NMR spectra were consistent with previously reported values.^{7,8}

Polymerization of norbornene by catalyst 1 in THF



A 20 mL glass vial was charged with norbornene (94 mg, 1.00 mmol, 500 equiv), THF (3.85 mL), and a magnetic stir bar. The norbornene solution was cooled to $-78\text{ }^{\circ}\text{C}$. At ambient temperature, 0.153 mL of a stock solution of **1** (10 mg in 1 mL of THF; 1.53 mg, 0.200×10^{-2} mmol, 1.00 equiv) was added to the norbornene solution with stirring. The reaction was allowed to stir for 24 h at room temperature. Then, the reaction mixture was brought outside the glovebox, and added to stirring methanol dropwise to precipitate. Precipitated polynorbornene was isolated by decanting, and dried under vacuum. The obtained polymer was purified again by dissolving in a minimal amount of THF, precipitating in stirring methanol, decanting supernatant, and then all volatiles were removed under vacuum overnight to yield 92.6 mg cyclic polynorbornene (0.983 mmol, 98 % yield, *cis*>99%, *m/r*=1.0:1.0 with the precision of *m* dyad ratio of $\pm 10\%$). ¹H NMR and ¹³C NMR spectra were consistent with previously reported values.^{7,8}

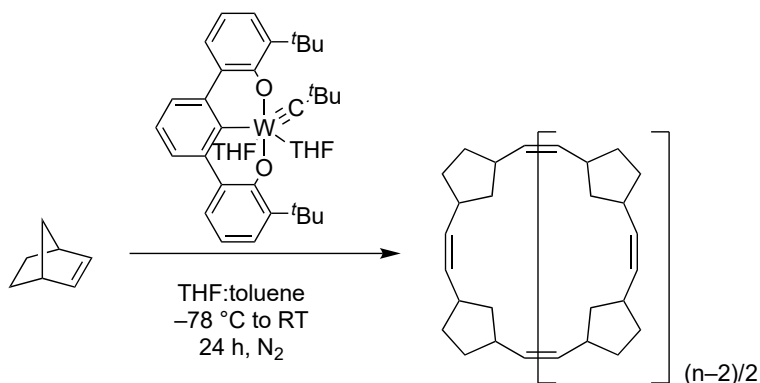
Polymerization of norbornene by catalyst **1** in Et₂O, pyridine, and 2-MeTHF



A 20 mL glass vial was charged with norbornene (94 mg, 1.00 mmol, 500 equiv), solvent (3.85 mL), and a magnetic stir bar. The norbornene solution was cooled to $-78\text{ }^{\circ}\text{C}$. At the ambient temperature, 0.153 mL of a stock solution of **1** (10 mg in 1 mL of solvent; 1.53 mg, 0.200×10^{-2} mmol, 1.00 equiv) was added to the norbornene solution with stirring. The reaction was allowed to stir for 24 h at ambient temperature. Then, the reaction mixture was brought outside the glovebox, and added to stirring methanol dropwise to precipitate. Precipitated polynorbornene was isolated by decanting, and all volatiles were removed under vacuum. The obtained polymer was purified again by dissolving in a minimal amount of THF, precipitating in stirring methanol, decanting the supernatant, and then all volatiles were removed under vacuum overnight.

solvent	Yield (%)	% <i>cis</i>	<i>M_n</i> (g/mol)	<i>M_w</i> (g/mol)	Dispersity
Et ₂ O	87	>99	325,000	1,000,000	3.59
Pyridine	-	-	-	-	-
2-MeTHF	32	97	6760	26,100	3.86

Polymerization of norbornene by catalyst **1** in THF:toluene mixture solutions

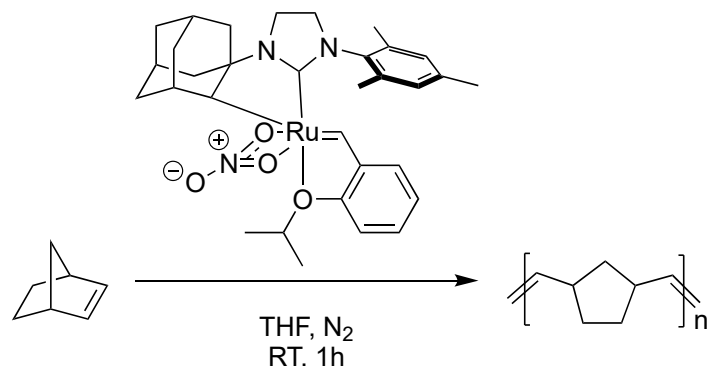


A 20 mL glass vial was charged with norbornene (94 mg, 1.00 mmol, 200 equiv), toluene and THF (total volume 3.62 mL), and a magnetic stir bar. The norbornene solution was cooled to $-78\text{ }^{\circ}\text{C}$. At the ambient temperature, 0.382 mL of a stock solution of **1** (10 mg in 1 mL of THF; 3.82 mg, 0.500×10^{-2} mmol, 1.00 equiv) was added to the norbornene solution with stirring. The reaction was allowed to stir for 24 h at ambient temperature. Then, the reaction mixture was brought outside the glovebox, and added to stirring methanol dropwise to precipitate. Precipitated polynorbornene was isolated by decanting, and dried under vacuum. The obtained polymer was purified again by dissolving in a minimal amount of THF, precipitating in stirring methanol, decanting the supernatant, and dried under vacuum overnight.

*The precision of *m* dyad ratio is $\pm 10\%$.

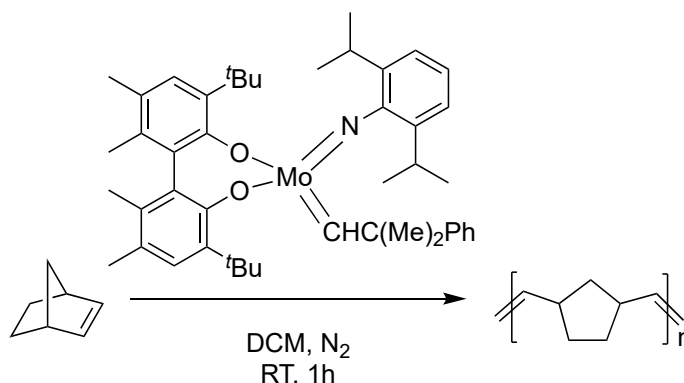
THF:toluene ratio	NB solution THF:toluene volume (mL)	Yield (%)	<i>m</i> : <i>r</i> dyads ratio
1:0	3.62 : 0	93	1.0 : 1.0
1:1	1.62 : 2	86	0.9 : 1.0
1:3	0.62 : 3	>99	0.4 : 1.0
1:9	0.018 : 3.6	96	0.1 : 1.0
0:1	0 : 3.62	99	0 : 1

cis,syndiotactic I-PNB synthesis



To a 20 mL glass vial charged with norbornene (94.0 mg, 1.00 mmol, 500 equiv), THF (3.87 mL), and a magnetic stir bar. The norbornene solution was cooled to -78 °C. At ambient temperature, 0.126 mL of a stock solution of Hoveyda-Grubbs catalyst M2001 (10 mg in 1.0 mL of toluene; 1.26 mg, 0.200×10^{-2} mmol, 1.00 equiv) was added to the norbornene solution with stirring. The reaction was allowed to stir for 1 h at ambient temperature. Then, the reaction mixture was brought outside the glovebox, and added to stirring methanol dropwise to precipitate. Precipitated polynorbornene was isolated by decanting, and all volatiles were under vacuum. The obtained polymer was purified again by dissolving in a minimal amount of THF, precipitating in stirring methanol, decanting the supernatant, and then all volatiles were removed under vacuum overnight to yield 93.3 mg of *cis,syndiotactic* cyclic polynorbornene (0.990 mmol, 99% yield, 94 *cis*%, *syndio*>99%). ¹H NMR and ¹³C NMR spectra were consistent with previously reported values.⁴

cis, isotactic I-PNB synthesis



A 20 mL glass vial was charged with norbornene (94.0 mg, 1.00 mmol, 500 equiv), DCM (3.38 mL), and a magnetic stir bar. The norbornene solution was cooled to -78 °C. At ambient temperature, 0.150 mL of a stock solution of 2,6-diisopropylphenylimidoneophylidene[*racemic*-BIPHEN]molybdenum(VI) (10 mg in 1.0 mL of DCM; 1.26 mg, 0.200×10^{-2} mmol, 1.00 equiv) was added to the norbornene solution with stirring. The reaction was allowed to stir for 1 h at ambient temperature, and quenched with benzaldehyde. Then, the reaction mixture was brought outside the glovebox, and added to stirring methanol dropwise to precipitate. Precipitated polynorbornene was isolated by decanting, and all volatiles were removed under vacuum. The obtained polymer was purified again by dissolving in minimum amount of THF, precipitating in stirring methanol, decanting the supernatant, and then then all volatiles were removed under vacuum overnight to yield 90.0 mg of *cis, syndiotactic* cyclic polynorbornene (0.956 mmol, 96% yield, >99 *cis*%, *iso*>99%). ¹H NMR and ¹³C NMR spectra were consistent with previously reported values.⁵

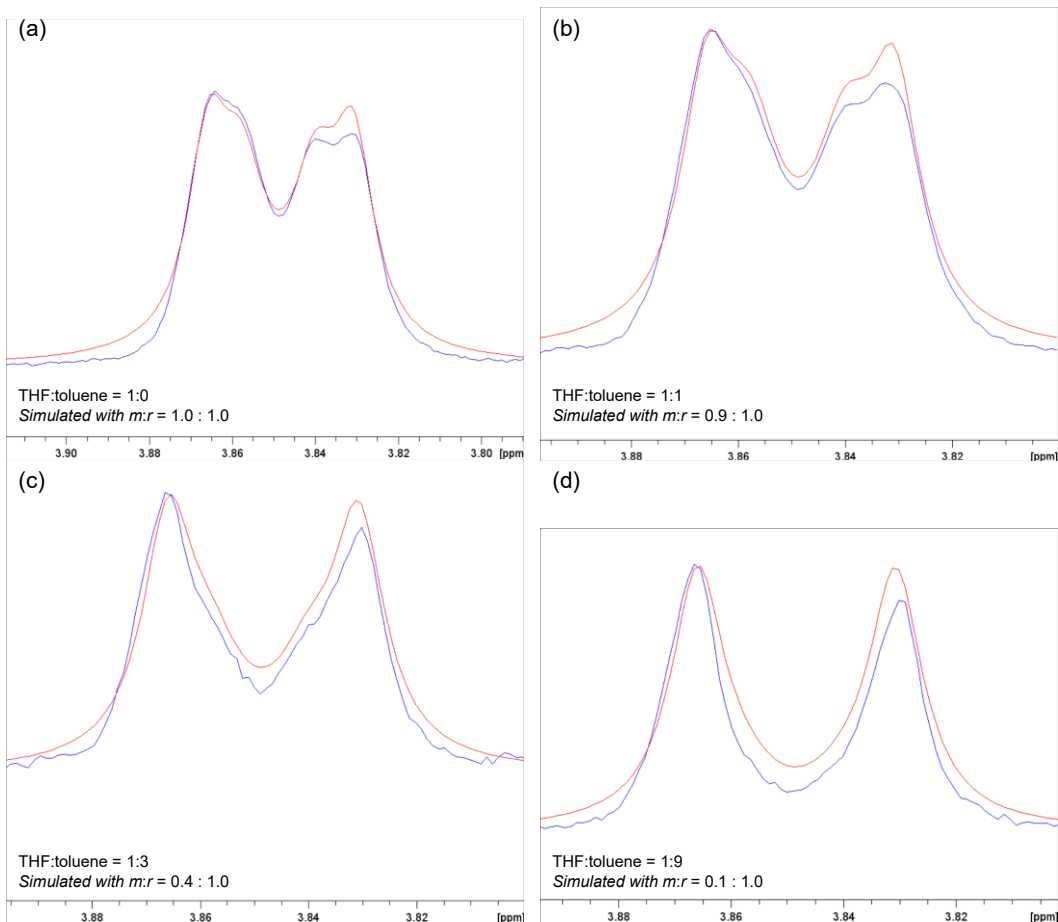


Figure S1. Simulated (red, —) and measured (blue, —) H(1',6') signals of partially brominated c-PNBs synthesized in THF:toluene mixture solution with homonuclear decoupling at 2.61 ppm. THF:toluene ratio is (a) 1:0, (b) 1:1, (c) 1:3, and (d) 1:9. Spectra were simulated for a system of two fragments, syndiotactic (*r* dyad) and isotactic (*m* dyad) H(1',6')s, each consisting of two lines of equal intensity using measured H(1',6') spectra of partially brominated isotactic (>99%) and syndiotactic (>99%) I-PNBs as references. The possible coupling in isotactic H(1',6') was ignored since it is not observed. The coupling effect on the spectra was accounted as a wider line; the linewidths for syndiotactic H(1',6') and isotactic H(1',6') were 7 Hz and 8.5 Hz, correspondingly. The simulated line is more intense on the outside regions due to ignoring the difference in the linewidth for each four peaks considering the relaxation parameters and the dispersion of the chemical shifts in the polymer. The precision of concentration of *m* dyad is $\pm 10\%$.

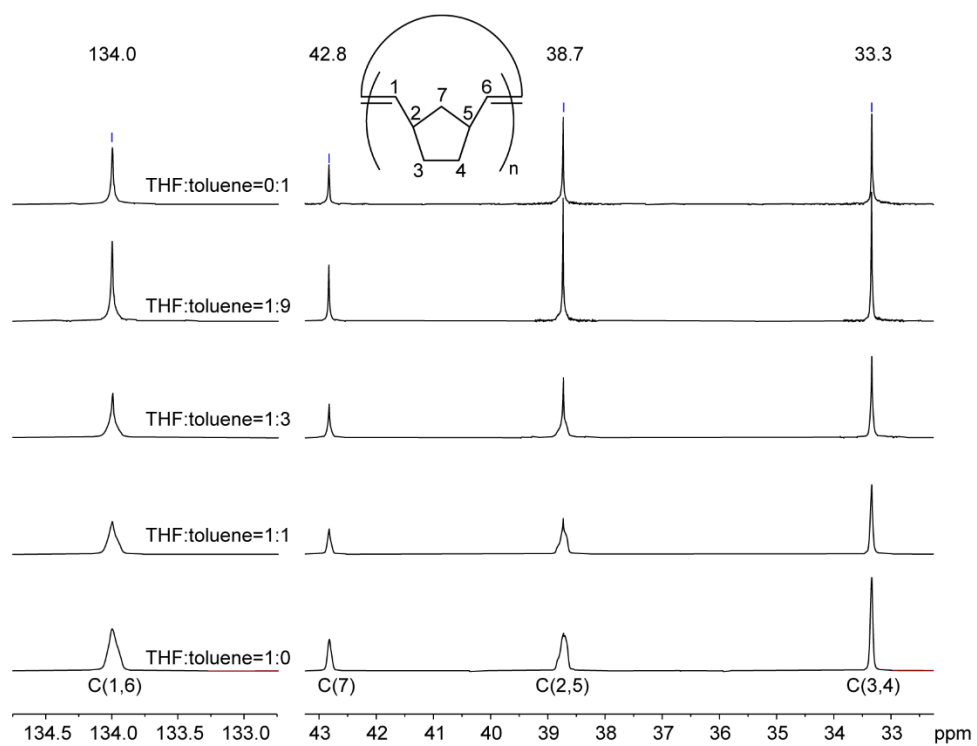


Figure S2. ^{13}C NMR spectra of c-PNBs synthesized by **1** in varying ratio of THF:toluene. The broadening of signals is evidence of r dyad incorporation.

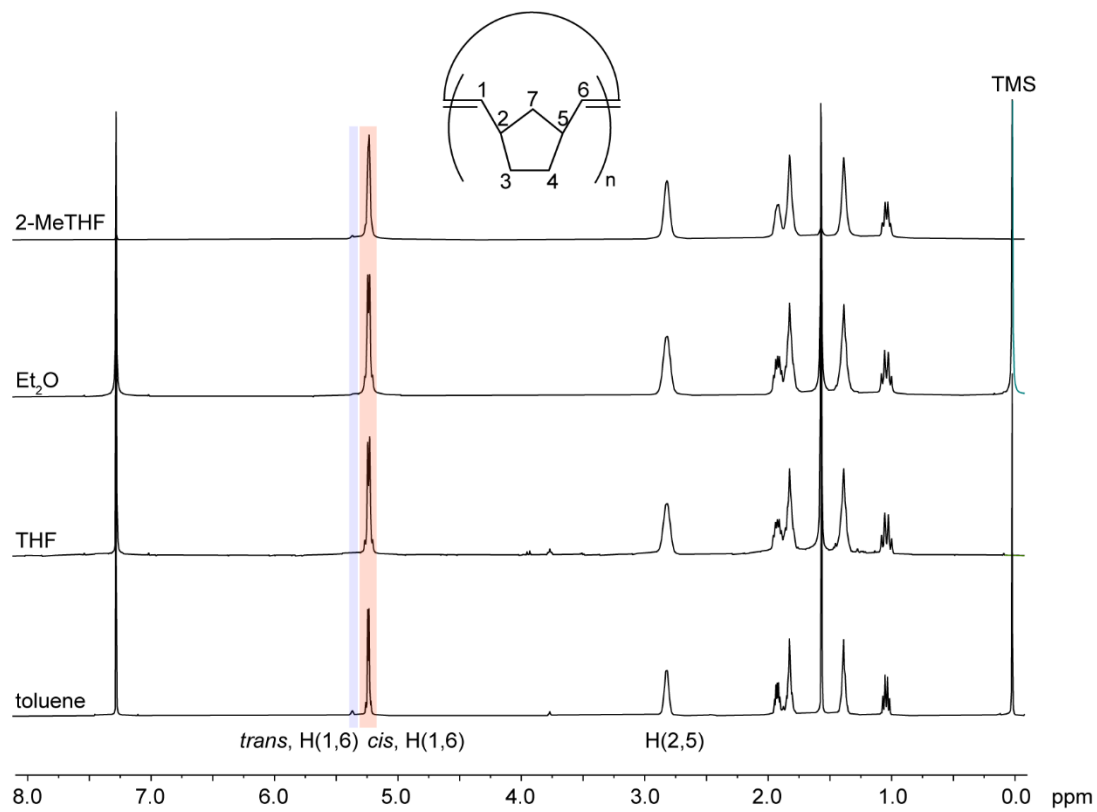


Figure S3. ¹H NMR spectra of c-PNBs synthesized in various solvents demonstrating high *cis* content (CDCl₃, 400.2 MHz, 25 °C).

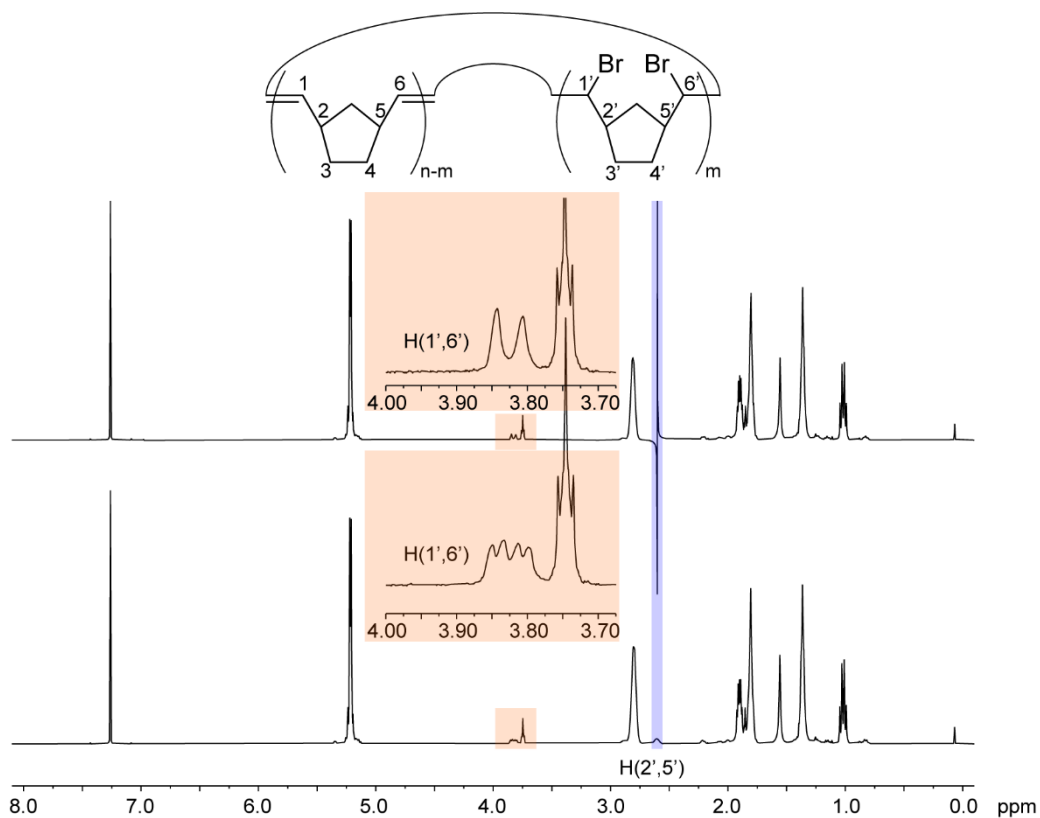


Figure S4. ^1H NMR spectra of c-PNB (partially brominated) synthesized by **1** in 2-MeTHF with (top) and without (bottom) homonuclear decoupling at 2.61 ppm (CDCl_3 , 600.2 MHz, 25 $^\circ\text{C}$).

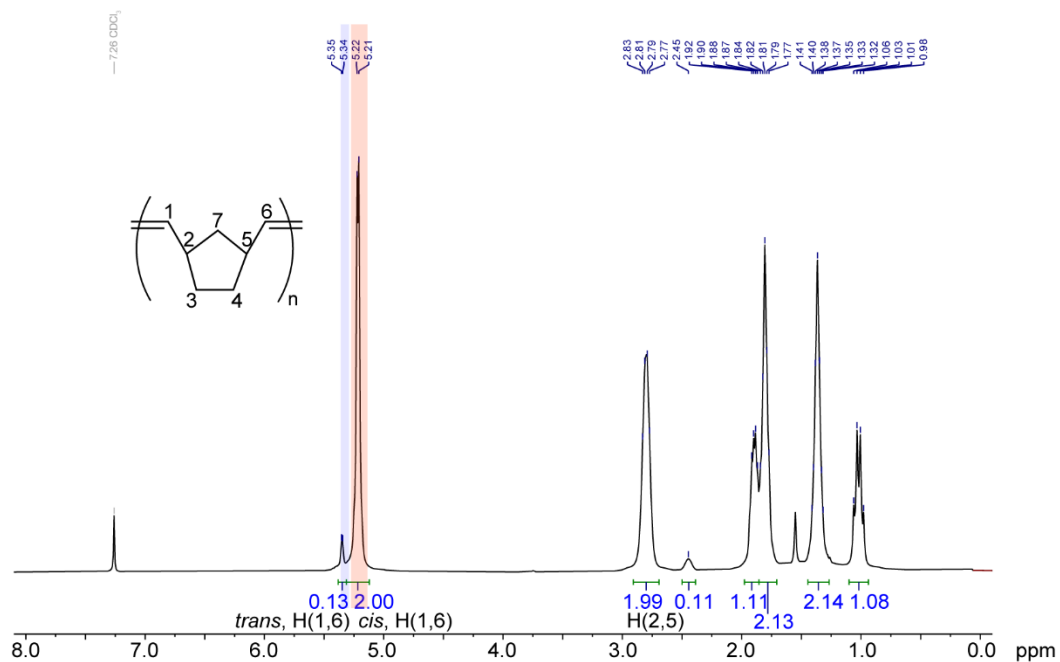


Figure S5. ^1H NMR spectrum of I-PNB *syndiotactic* (CDCl_3 , 400.2 MHz, 25 $^\circ\text{C}$).

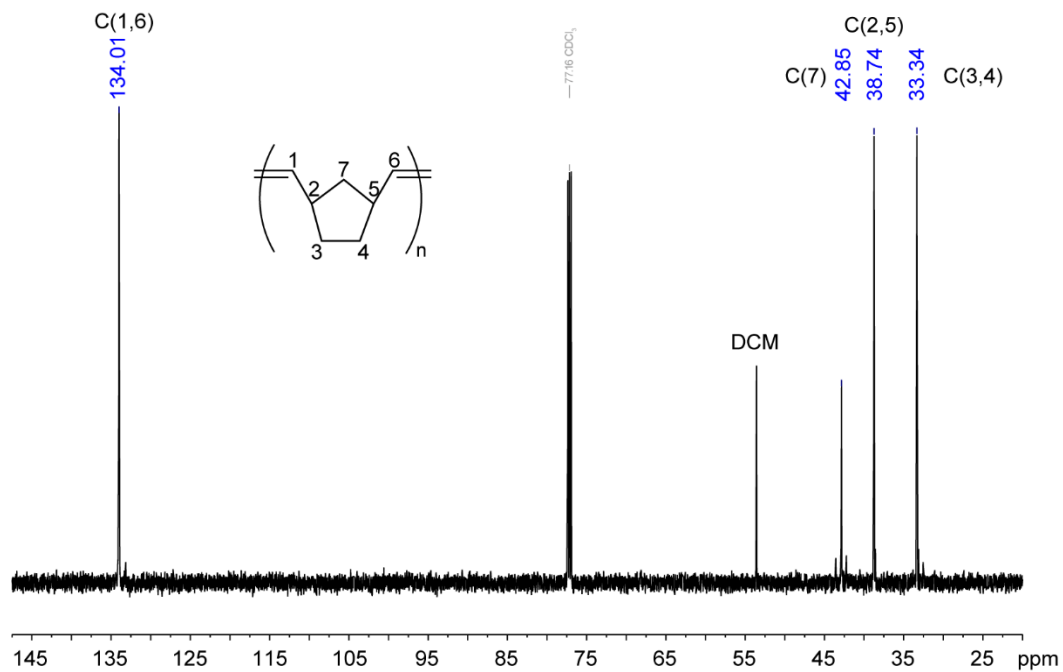


Figure S6. ¹³C NMR spectrum of I-PNB *syndiotactic* (CDCl₃, 100.2 MHz, 25 °C).

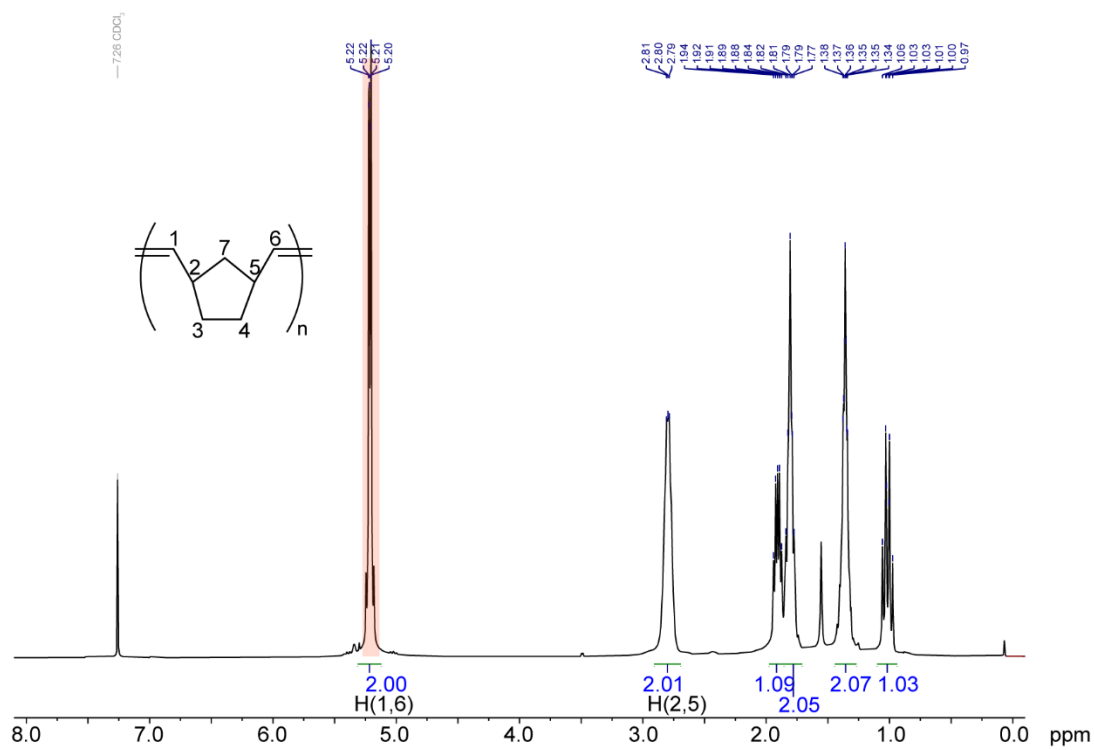


Figure S7. ¹H NMR spectrum of I-PNB *isotactic* (CDCl₃, 400.2 MHz, 25 °C).

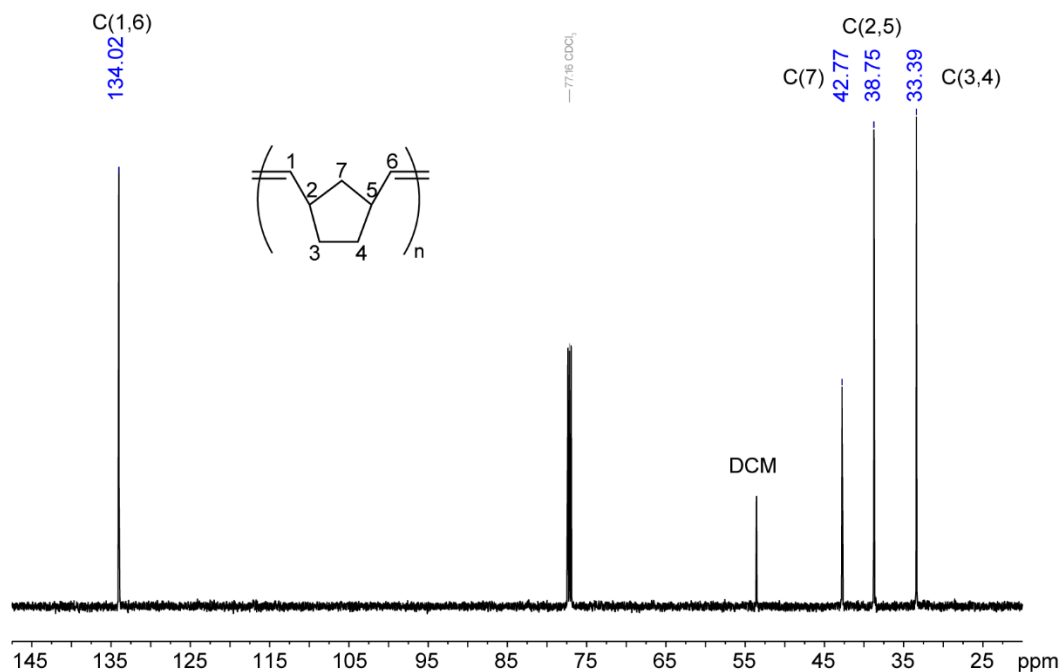


Figure S8. ^{13}C NMR spectrum of I-PNB *isotactic* (CDCl₃, 100.2 MHz, 25 °C).

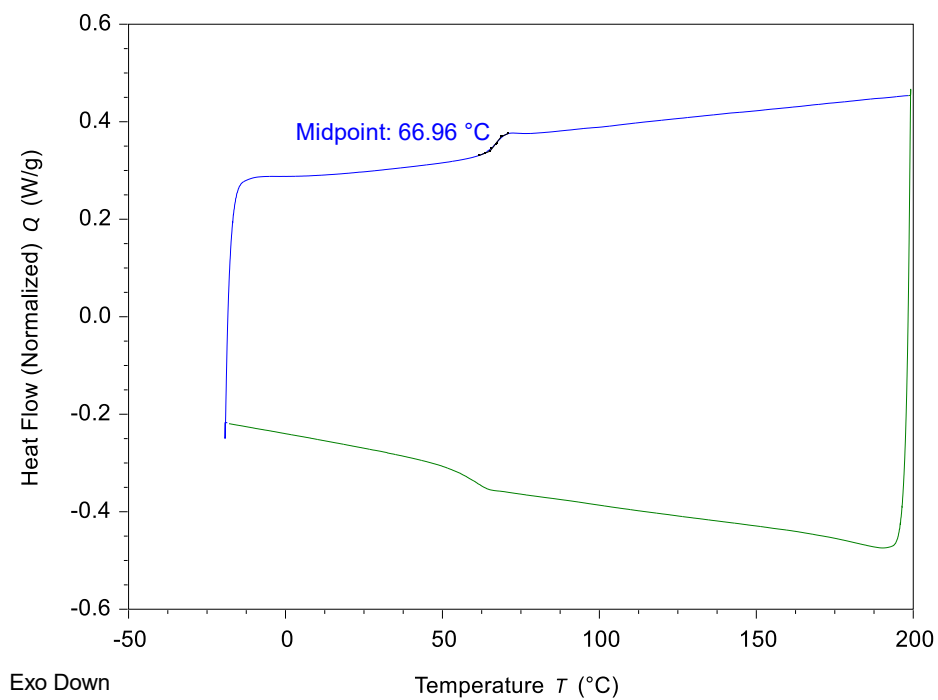


Figure S9. Differential scanning calorimetry (DSC) analysis of c-PNB_{tol}; $T_g = 67.0$ °C

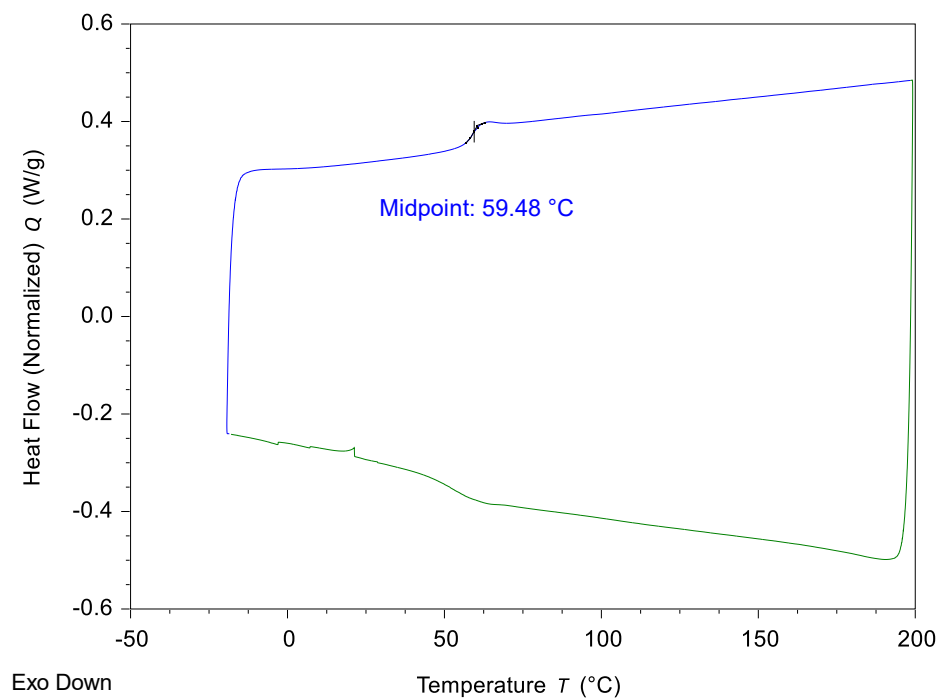


Figure S 10. DSC analysis of c-PNB_{THF}; $T_g = 59.5$ °C.

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