

Organocatalytic Ring-opening Polymerization of Thionolactones: Anything O Can Do, S Can Do Better

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Supporting Information

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General Considerations: All chemicals were used as received unless stated otherwise. Hexamethyldisiloxane (HMDO), P₄S₁₀, cycloheptanone, cyclooctanone, 3-chloroperbenzoic acid (*m*-CPBA) and 2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) were supplied by Acros Organics. Sodium thiosulfate (Na₂S₂O₃•5H₂O) was purchased from Allied Chemical. Sigma-Aldrich provided ω-pentadecalactone (PDL). Acetonitrile, potassium carbonate, sodium carbonate, sodium bicarbonate, sodium sulfate, magnesium sulfate, benzyl alcohol, benzoic acid, ethyl acetate, dichloromethane, toluene and hexane were purchased from Fisher Scientific. Acetone-*d*₆, chloroform-*d* and benzene-*d*₆ were supplied by Cambridge Isotope Laboratories and distilled from CaH₂ under a nitrogen atmosphere. Benzyl alcohol was distilled from CaH₂ under high vacuum. Toluene was dried on an Innovated Technologies solvent purification system with alumina columns and nitrogen working gas. **1** [3,5-bis(trifluoromethyl)phenyl]-3-cyclohexyl-thiourea (CyTU), and **2** 1,1',1''-(nitrioltris(ethane-2,1-diy))tris(3-(3,5-bis(trifluoromethyl)phenyl)urea (Tris-U2C) were synthesized and purified according to literature procedures.^{1,2} Triclocarban (TCC), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were purchased from Tokyo Chemical Industry (TCI). The syntheses of ζ-heptalactone (HL)³ and η-nonalactone (NL)⁴ were performed according to literature procedures.

All polymerization reactions were performed in an MBRAUN or INERT stainless-steel glovebox equipped with a gas purification system under a nitrogen atmosphere using glass vials and magnetic stir bars which were baked overnight at 140 °C. NMR experiments were performed on a Bruker Avance III 300 MHz or 400 MHz spectrometer. The chemical shifts for proton (¹H) and carbon (¹³C) NMR were recorded in parts per million (ppm) relative to a residual solvent. Size exclusion chromatography (SEC) was performed at 30 °C in dichloromethane (DCM) using an Agilent Infinity GPC system equipped with three Agilent PLGel columns 7.5 mm × 300 mm (pore sizes: 10³, 10⁴, and 10⁵ Å). *M_n* and *M_w/M_n* were determined versus polystyrene standards (500 g/mol – 3,150 kg/mol; Polymer Laboratories). UV-vis were acquired on a Perkin-Elmer Lambda 1050 single beam spectrometer.

Mass spectrometry experiments were performed using a Thermo Electron (San Jose, CA, USA) LTQ Orbitrap XL mass spectrometer affixed with electrospray ionization (ESI) interface in positive ion mode. Collected mass spectra were averaged for at least 50 scans. Tune conditions for

infusion experiments (10 $\mu\text{L}/\text{min}$ flow, sample concentration 2 $\mu\text{g}/\text{mL}$ in 50/50 v/v water/methanol) were as follows: ion spray voltage, 4000 V; capillary temperature, 275 $^{\circ}\text{C}$; sheath gas (N_2 , arbitrary units), 15; auxiliary gas (N_2 , arbitrary units), 2; capillary voltage, 21 V; and tube lens, 90 V; multipole 00 offset, -4.25 V; lens 0 voltage, - 5.00; multipole 1 offset, - 8.50 V; Multipole RF Amplitude, 400 V; Ion trap's AGC target settings for Full MS was 3.0×10^4 and FT's 2.0×10^5 (with 3 and 2 averaged microscans, respectively). Prior to analysis, the instrument was calibrated for positive ions using Pierce LTQ ESI positive ion calibration solution (lot #PC197784). Thermogravimetric analysis (TGA) was performed using a TGA Q500 from TA Instruments under a N_2 atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 25 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$.

The surface analysis of the crosslinked polymer was carried out using a Thermo Scientific Photoelectron Spectrometer (XPS) equipped with a 180° double-focusing hemispherical analyzer and a monochromatized Al K_{α} radiation source. The surface was bombarded with electrons using a flood gun. Binding energy (BE) corrections were done using the position of C-H/C-C at 284.7 eV as a reference. The sample was dried under reduced pressure ($10^{-9} - 10^{-10}$ mbar) overnight before analysis. The sampling spot size was 200 μm .

Synthesis of ζ -thionoheptalactone (tnHL)

This synthesis of ζ -thionoheptalactone (tnHL) was performed according to literature procedure.⁵ The crude product mixture was purified by silica-gel column chromatography (3:7 ethyl acetate:hexanes). Characterization matched the literature.⁵

Synthesis of η -thionononalactone (tnNL)

The synthesis of η -thionononalactone (tnNL) was adapted from a literature procedure.⁵ NL (3.00 g, 21.11 mmol), HMDO (8.20 mL, 35.25 mmol) and P₄S₁₀ (2.51 g, 5.27 mmol) were dissolved in acetonitrile (23 mL) and stirred at 80 °C for 4 hours. The reaction mixture was cooled in an ice-water bath and quenched with distilled water (2 mL/mmol of P₄S₁₀) and sodium carbonate (8 mmol/mmol of P₄S₁₀) over a period of 30 minutes. The reaction mixture was then vigorously stirred at 0 °C for an additional 30 mins. The reaction mixture was extracted with ethyl acetate (3 x 50 mL) and concentrated in vacuo to yield a yellow-orange oil. Following silica gel column chromatography (1:10 ethyl acetate:hexanes) and Kugelrohr distillation (60 °C, 200 mTorr), a pale yellow oil was obtained (0.67 g, 4.64 mmol, 22 % yield).

Synthesis of ω -thionopentadecalactone (tnPDL)

This synthesis of ω -thionopentadecalactone (tnPDL) was performed according to a literature procedure.⁵ Following silica-gel column chromatography (1:99 ethyl acetate:hexanes) and Kugelrohr distillation (120 °C, 100 mTorr), the characterization matched the literature.⁵

Synthesis of thiono-ethylene brassylate (tnEB)

The synthesis of tnEB was adapted from a literature procedure.^{6,7} Ethylene brassylate (13 mL, 50 mmol), HMDO (17 mL, 80 mmol) and P₄S₁₀ (11.11 g, 25 mmol) were dissolved in *o*-xylene (50 mL) and refluxed for 9 hours. The reaction mixture was cooled in an ice-water bath and quenched with distilled water (2 mL/mmol of P₄S₁₀) and sodium carbonate (8 mmol/mmol of P₄S₁₀) over a period of 30 minutes. The reaction mixture was then vigorously stirred at 0 °C for an additional 30 mins. The reaction mixture was extracted with dichloromethane (3 x 100 mL) and concentrated in vacuo to yield a yellow oil. Following silica gel chromatography (ethyl acetate:hexanes 5:95), a

yellow oil was obtained (7.54 g, mmol, 25 mmol, 50% yield). HRMS m/z calcd ($C_{15}H_{27}O_2S_2^+$) 303.1447, found 303.1436. 1H NMR (400 MHz, $CDCl_3$) δ 4.72 (s, 4H), 2.75 (t, $J=7.2$, 4H), 1.70 (p, $J=7.1$, 4H), 1.37 – 1.11 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 25.9, 26.0, 26.2, 26.9, 45.9, 68.3, 223.4.

Ring-Opening Polymerization of tnNL

In an N_2 -filled glovebox, tnNL (0.100 g, 0.6318 mmol) was added to a 20 mL scintillation vial equipped with a stir bar. TCC (0.0100 g, 0.031 mmol), BEMP (0.008 g, 0.031 mmol) and benzyl alcohol (0.0007 g, 0.006 mmol) were added to another 20 mL scintillation vial in the glovebox. Benzene (0.315 mL, 2 M in tnNL) was divided equally between the two vials. The contents of the vials were stirred for about 2 mins at moderate speed after which the mixture of tnNL in benzene was transferred to the other vial and stirred for 4 hours. The polymer was then precipitated with hexanes. The supernatant was decanted and remaining volatiles were removed under reduced pressure to yield the polymer (60.8% yield; $M_w/M_n = 1.7$; M_n (GPC) = 24,200; M_n (NMR) = 19,100). ^{13}C NMR spectra display characteristic resonances of a polymer with a thionoester repeat at 224 ppm.

Ring-Opening Polymerization of tnPDL

In an N_2 -filled glovebox, tnPDL (0.250 g, 0.975 mmol) was added to a 20 mL scintillation vial equipped with a stir bar. TCC (0.015 g, 0.048 mmol), MTBD (0.007 g, 0.048 mmol) and benzyl alcohol (0.001 g, 0.0097 mmol) were added to another 20 mL scintillation vial. Toluene (0.195 mL, 5M in tnPDL) was divided equally between the two vials and stirred to dissolve. The solution of tnPDL was transferred to the other vial via Pasteur pipette and then heated to 100 °C and stirred for 4.5 hours in the glovebox. The polymer was then precipitated with hexanes. The supernatant was decanted and remaining volatiles were removed under reduced pressure to yield the polymer (62% yield; $M_w/M_n = 1.8$; M_n (GPC) = 34,400; M_n (NMR) = 21,000). ^{13}C NMR spectra display characteristic resonances of a polymer with a thionoester repeat unit at 224 ppm.

Co-polymerization of tnPDL and PDL

In an N₂-filled glovebox, PDL (120 mg, 0.50mmol), tnPDL (128 mg, 0.50 mmol), TCC (0.015 g, 0.050 mmol), BEMP (0.013 g, 0.050 mmol) and benzyl alcohol (0.001 g, 0.01 mmol) were added to a 20 mL scintillation vial with a stir bar. The vial was then heated to 100 °C and stirred for 5 hours in the glovebox. The polymer was then precipitated with hexanes. The supernatant was decanted and remaining volatiles were removed under reduced pressure to yield the polymer (80% yield; $M_w/M_n = 1.6$; M_n (GPC) = 33,800).

Synthesis of P(tnPDL-*b*-CL) polymer

The ROP of tnPDL was carried out as above. After completion, the homopolymer was washed with methanol and volatiles were removed under reduced pressure. The chain extension of PtnPDL was conducted. In one 20 mL vial, PtnPDL (250 mg, 0.975 mmol), TCC (0.015 g, 0.048 mmol), BEMP (0.013 g, 0.048 mmol) were dissolved in CH₂Cl₂. In a second vial, CL (0.111 g, 0.976 mmol) was dissolved in CH₂Cl₂ (total CH₂Cl₂ volume 1.95 mL), and the contents of the CL vial transferred to the other via Pasteur pipette. The reaction solution as stirred for 9 hours. The polymer was precipitated from hexanes, the supernatant decanted and the product placed under high vacuum (75 % yield; $M_w/M_n = 2.8$; M_n (GPC) = 37,600).

Determination of Thermodynamics of ROP

For HL, tnHL, NL and tnNL:

An NMR tube was loaded with tnHL (e.g., 0.100 g, 0.693 mmol), TBD (0.0048 g, 0.035 mmol), benzyl alcohol (0.0008 g, 0.0069 mmol) in C₆D₆ (1 M in monomer). The [M]_{eq} was measured versus temperature via ¹H NMR from 298 K to 333 K by heating the sample in a variable temperature NMR probe. Data points were taken in duplicate, once while heating and once while cooling, and the [M]_{eq} values are within error of each other. The ΔH° , ΔS° and T_{ceiling} for the ROP of tnHL were determined from a van't Hoff plot where the error was calculated from linear regression at 95% confidence interval.

For PDL, tnPDL, EB and tnEB:

In an N₂-filled glovebox, a 20 mL scintillation vial equipped with a stir bar was loaded with tnPDL (e.g., 0.100 g, 0.390 mmol), TCC/BEMP (5 mol% each, 0.0195 mmol), benzyl alcohol (0.0004 g, 0.0039 mmol) in toluene (0.5 M in monomer). The vial was heated to perform the polymerization, and reaction progress was monitored via ¹H NMR by withdrawing aliquots. When the reaction had reached equilibrium, the temperature was increased and aliquots were withdrawn after the reaction reached equilibrium at different temperatures (from 90 °C to 150 °C) and the [M]_{eq} was analyzed via ¹H NMR. The ΔH°, ΔS° and T_{ceiling} for the ROP of tnPDL were determined from a van't Hoff plot of the data where the error was propagated from ¹H NMR integrations (±5%).

Example Synthesis of Cross-Linked Polymers

The polyhomo(thionolactone) or co-polymer was dissolved in CH₂Cl₂, transferred to a 6-8 kDa dialysis bag and stirred in methanol overnight. The purified homopolymer was then dried under reduced pressure. The homopolymer was then weighed (200 mg), transferred to a 100 mL beaker and dissolved in 4 mL of CH₂Cl₂. To the beaker with the dissolved polymer, 20 mL aqueous NaOCl was added (household bleach, 5.25 %). The reaction mixture was then vigorously stirred for 18 hours. A solid white polymer precipitated. The polymer was then filtered and blotted on paper towels to remove excess solvent. The polymer was then washed with water to remove excess NaOCl. The polymer was then dried under reduced pressure. The product recovery was > 99.99 % (200 mg).

Hydrolytic Degradation Studies of PtnPDL-CLP

Polymer samples (approximately 25 mg of the cross-linked polymer) were transferred to empty 20 mL scintillation vials. Each vial was charged with 10 mL of aqueous 0.25 M HCl, aqueous 0.25 M NaOH solution, or distilled water. All vials were vigorously stirred for the duration of the study. Samples were acquired by removing polymer pieces from the solution and blotting to remove the aqueous solution from the surface. Polymer samples were then dried under high vacuum overnight and weighed. The percent mass loss is given by $[\text{mass}]_o - [\text{mass}]_i / [\text{mass}]_o$.⁶ The same steps were repeated over a ten days period daily.

Determination of Crosslink Density

The crosslink density was determined at room temperature from literature methods.⁸ The swelling ratio was calculated using equation 1 where W_d is the pre-immersion weight of the crosslinked polymer, and W_s is the weight after immersion in THF⁹

$$\text{Swelling ratio} = \frac{(W_s - W_d)}{(W_d)} \quad (1)$$

The porosity of the polymer was calculated from equation 2, where V is the volume of the crosslinked polymer disk ($\rho_{THF} = 0.8892 \text{ g/mL}$).⁹ Results were averaged of three measurements.

$$\text{Porosity \%} = \frac{(W_s - W_d)}{V\rho} \times 100 \quad (2)$$

For crosslinked densities, the Flory-Huggins polymer-solvent interaction parameter (χ) was calculated using equation 3. δ_1 and δ_2 are the solubility parameters of the solvent (δ_1 (THF) = 18.30 $\text{J}^{1/2} \text{ cm}^{-3/2}$) and the polymer respectively, V_s is the molar volume of the solvent.¹⁰ The δ_2 value is estimated from the Hansen solubility parameters of PPDL (17.5 $\text{J}^{1/2} \text{ cm}^{-3/2}$) and PCL (19.5 $\text{J}^{1/2} \text{ cm}^{-3/2}$).^{11,12,13} The solubility parameter of PCL was used for PtnCL-CLP and PtnHL-CLP, and that of PPDL for PtnPDL-CLP and P(tnPDL-*b*-CL)-CLP.

$$\chi = \frac{(\delta_1 - \delta_2)^2 V_s}{RT} \quad (3)$$

The crosslinked densities were calculated based on Flory-Rehner equation 4.¹⁰

$$-\ln(1 - V_p) + V_p + \chi V_p^2 = V_s n \left[V_p^{\frac{1}{3}} + \frac{V_p}{2} \right] \quad (4)$$

V_p is the volume fraction of polymer in the swollen weight, and n is the crosslinked density of the polymer. Errors are taken from the standard deviation of three measurements.

Procedure for Gold Extraction with Varying Amounts of PtnPDL-CLP

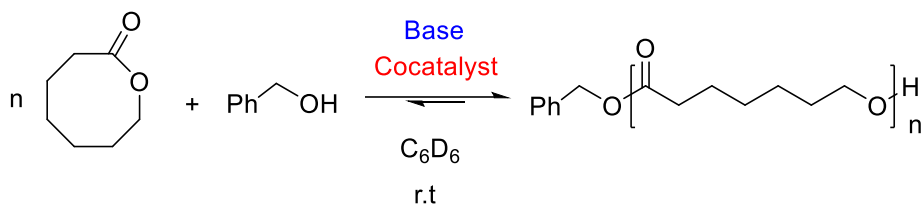
A 100 ppm Au³⁺ solution was prepared by dissolving 10 mg of NaAuCl₄•2H₂O salt in 50 mL of deionized water. The absorbance was measured for a diluted series of the Au³⁺ solution with different concentrations (5 ppm, 25 ppm, 50 ppm and 75 ppm) using a UV-Vis spectrophotometer to construct a calibration curve. To 10 mL samples of 100 ppm Au³⁺ solution, 25 mg, 50 mg and 100 mg of small PtnPDL-CLP pieces were added. The solutions were stirred for three days and the remaining concentrations of Au³⁺ were measured at different time periods using UV-Vis to calculate the extraction efficiency.

Procedure for Gold Recovery After Heating to 1000 °C

To a 10 mL solution of 100 ppm Au³⁺ solution in deionized water, 50 mg of small PtnPDL-CLP pieces were added and stirred for 3 days. The supernatant was removed, and the polymer was dried under high vacuum at room temperature to afford 53.20 mg solid grey polymer. The polymer was heated in air to 1000 °C and held for 30 minutes to afford 0.45 mg of gold metal. The recovery of extracted gold metal was 99%.

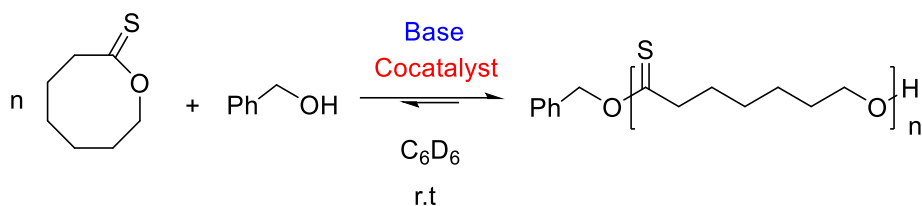
Tables

Table S1. ROP of HL with urea/base cocatalyst system.^a



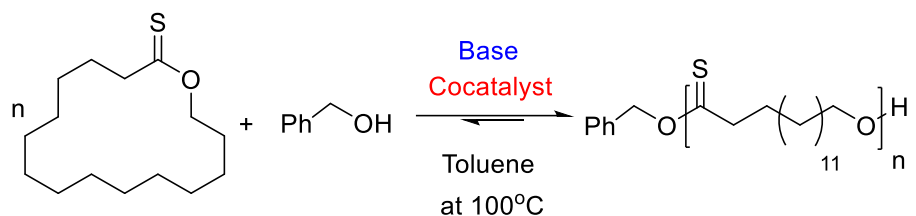
Entry	base	cocatalyst	[M] ₀ /[I] ₀	conv. ^b (%)	time (h)	M_n^c (g/mol)	M_w/M_n^c
1 ^d	TBD	-	100	93	2	24,600	1.59
2	BEMP	TCC	100	88	0.06	12,600	1.04
3	MTBD	TCC	200	90	8.5	32,100	1.02
4	MTBD	TCC	100	90	5	19,200	1.02
5	MTBD	TCC	50	91	2	11,500	1.03
6	MTBD	TCC	25	90	1	6,100	1.04
7	DBU	TCC	100	89	21	18,200	1.03
8 ^e	BEMP	2	100	98	0.83	23,800	1.13
9 ^e	MTBD	2	100	89	2	24,300	1.13
10 ^e	DBU	2	100	89	18	17,800	1.03

a. Reaction conditions: HL (2 M, 0.78 mmol, 1 equiv), benzyl alcohol initiator (I), TCC/base (5 mol %, 0.039 mmol each) in C₆D₆. b. Monomer conversion was monitored via ¹H NMR. c. M_n and M_w/M_n were determined by GPC (CH₂Cl₂) versus polystyrene standards. d. TBD (1 mol %, 0.0078 mmol). e. **2**/base (1.67 mol %, 0.013 mmol each).

Table S2. ROP of tnHL with urea/base cocatalyst system ^a

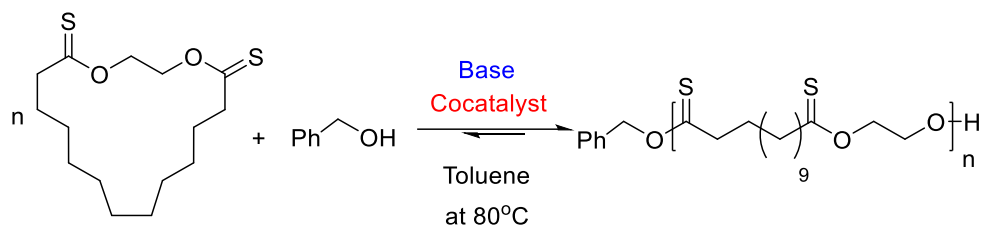
Entry	Base	Cocatalyst	[M] ₀ /[I] ₀	Conv. ^b (%)	Time (h)	<i>M_n</i> ^c (g/mol)	<i>M_w</i> / <i>M_n</i> ^c
1	BEMP	TCC	100	92	0.63	14,700	1.19
2	MTBD	TCC	200	89	6.75	28,700	1.14
3	MTBD	TCC	100	90	4	16,200	1.03
4	MTBD	TCC	50	88	2.25	8,700	1.03
5	MTBD	TCC	25	90	1	4,900	1.02
6 ^d	MTBD	2	100	85	12	11,700	1.19
7 ^e	TBD	-	100	89	0.35	19,400	1.13

a. Reaction conditions: tnHL (2 M, 1.04 mmol, 1 eq), benzyl alcohol as initiator, TCC/base (5 mol %, 0.052 mmol each) in C₆D₆. b. Monomer conversion was monitored via ¹H NMR. c. *M_n* and *M_w*/*M_n* were determined by GPC (CH₂Cl₂) versus polystyrene standards. d. **2**/base (1.67 mol %, 0.017 mmol each). e. TBD (1 mol %, 0.010 mmol).

Table S3. ROP of tnPDL with urea/base cocatalyst system ^a

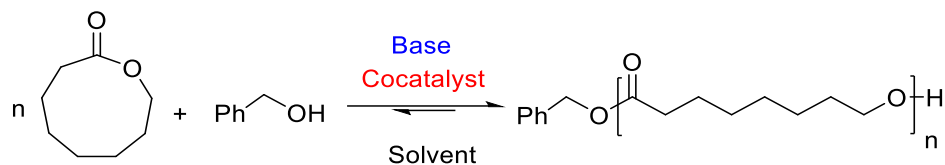
Entry	Base	Cocatalyst	conv. ^b (%)	time (h)	M_n^c (g/mol)	M_w/M_n^c
1 ^d	TBD	-	85	6	35,000	1.93
2	BEMP	TCC	90	5	35,800	1.80
3	MTBD	TCC	93	4.5	34,400	1.80

a. Reaction conditions: tnPDL (5 M, 0.974 mmol, 1 eq), benzyl alcohol (1 mol %, 0.0097 mmol) TCC/base (5 mol %, 0.0478 mmol each) in toluene at 100 °C. b. Monomer conversions were monitored via ¹H NMR. c. M_n and M_w/M_n were determined by GPC (CH₂Cl₂) versus polystyrene standards. d. TBD (2 mol%, 0.0194 mmol).

Table S4. ROP of tnEB with urea/base cocatalyst system^a

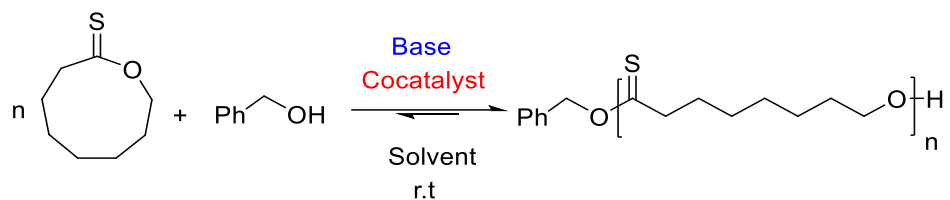
Entry	Base	Cocatalyst	Conv. ^b (%)	Time(h)	M_n^c (g/mol)	M_w/M_n^c
1	BEMP	TCC	64	4.5	10,600	1.90
2	MTBD	TCC	67	8	8,900	1.80
3 ^d	BEMP	2	6	77	-	-
4 ^d	MTBD	2	29	77	-	-

a. Reaction conditions: tnEB (2 M, 1.32 mmol, 1 eq), benzyl alcohol (1 mol %, 0.0132 mmol), TCC/base (5 mol%, 0.0661 mmol each) in toluene at 80 °C. b. Monomer conversion were monitored via ¹H NMR. c. M_n and M_w/M_n were determined by GPC (CH₂Cl₂) versus polystyrene standards. d. **2**/base (1.67 mol%, 0.022 mmol each).

Table S5. ROP of NL with urea base cocatalyst system^a

Entry	Base	Cocatalyst	Solvent	[M] ₀ /[I] ₀	Conv. ^b (%)	Time (h)	<i>M_n</i> ^c (g/mol)	<i>M_w</i> / <i>M_n</i> ^c
1 ^d	TBD	-	toluene	100	85	76	12,100	1.68
2	BEMP	TCC	acetone- <i>d</i> ₆	100	96	25	18,000	1.80
3	MTBD	TCC	acetone- <i>d</i> ₆	100	27	24	9,200	1.31
5	BEMP	TCC	benzene- <i>d</i> ₆	100	80	48	22,000	1.57
6 ^e	BEMP	2	benzene- <i>d</i> ₆	200	84	22	27,600	1.50
7 ^e	BEMP	2	benzene- <i>d</i> ₆	100	90	10	23,200	1.30
8 ^e	BEMP	2	benzene- <i>d</i> ₆	50	87	5.5	11,300	1.50
9 ^f	BEMP	2	toluene	100	97	3	29,000	1.55

a. Reaction conditions: NL (2 M, 0.703 mmol, 1 eq), benzyl alcohol as initiator TCC/base (5 mol %, 0.0351 mmol each), b. Monomer conversions were monitored via ¹H NMR. c. *M_n* and *M_w*/*M_n* were determined by GPC (CH₂Cl₂) versus polystyrene standards d. TBD (5 mol %, 0.0351 mmol) e. **2**/base (1.67 mol %, 0.0117 mmol each) f. **2**/base (1.67 mol%, 0.0117 mmol each) in toluene at 80°C.

Table S6. ROP of tnNL with urea/base cocatalyst system^a

Entry	Base	Cocatalyst	Solvent	[M] ₀ /[I] ₀	Conv. ^b (%)	Time (h)	M _n ^c (g/mol)	M _w /M _n ^c
1	BEMP	TCC	acetone- <i>d</i> ₆	100	95	4	23,500	1.81
2	MTBD	TCC	acetone- <i>d</i> ₆	100	75	48	14,800	1.73
3	BEMP	TCC	benzene- <i>d</i> ₆	200	94	7.75	26,400	1.50
4	BEMP	TCC	benzene- <i>d</i> ₆	100	99	4	24,200	1.70
5	BEMP	TCC	benzene- <i>d</i> ₆	50	93	2.5	12,500	1.50

a. Reaction conditions: tnNL (2 M, 0.632 mmol, 1 eq), benzyl alcohol as initiator, TCC/base (5 mol %, 0.0315 mmol each), b. Monomer conversion were monitored via ¹H NMR. c. M_n and M_w/M_n were determined by GPC (CH₂Cl₂) versus polystyrene standards.

Figures

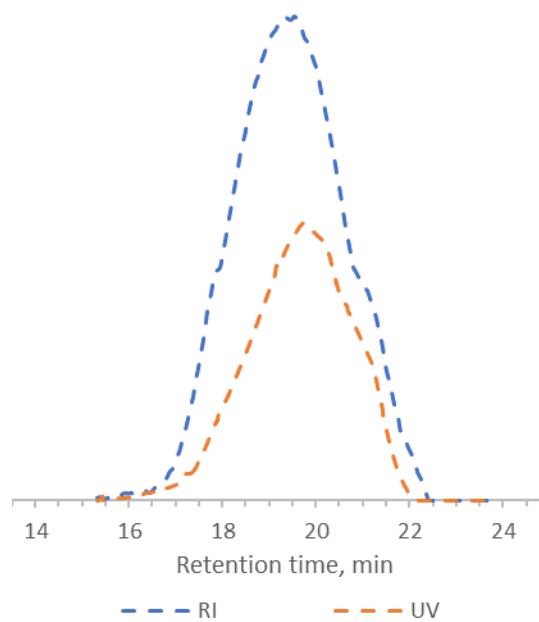


Figure S1. RI and UV GPC traces of the ROP initiated from pyrenebutanol for tnNL. Conditions: tnNL (0.631 mmol, 2 M in acetone- d_6), 1-pyrenebutanol (2 mol %, 0.012 mmol), TCC/BEMP (5 mol %, 0.0315 mmol each) in acetone- d_6 .

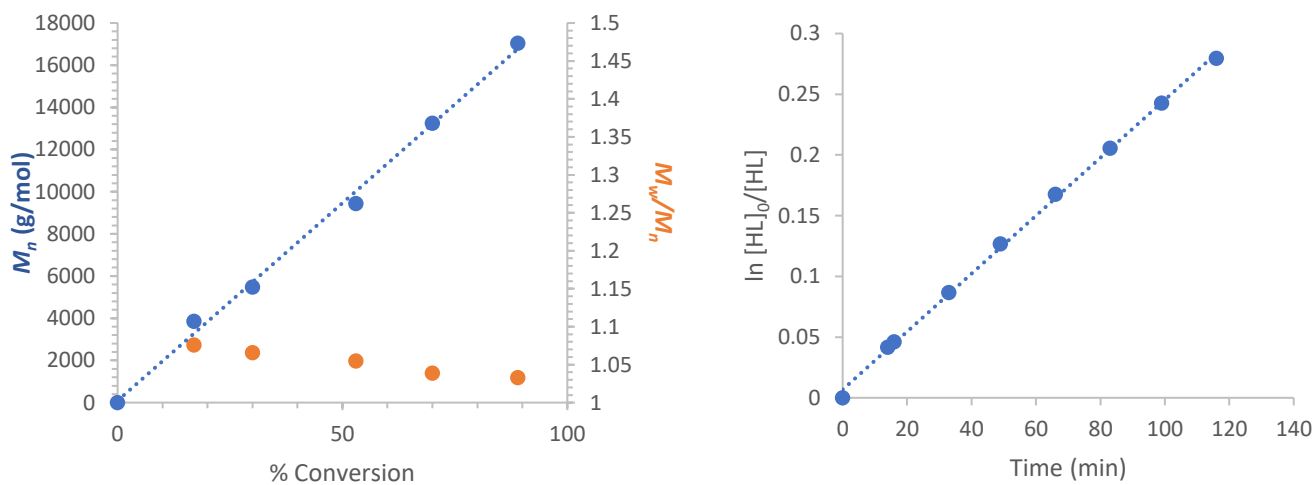


Figure S2. (Left) M_n versus conversion. (Right) First order evolution of $[HL]$ versus time; Reaction conditions: HL (0.78 mmol, 2M in C_6D_6), benzyl alcohol (1 mol %, 0.0078 mmol) catalyzed by TCC/MTBD (5 mol %, 0.039 mmol each) in C_6D_6 .

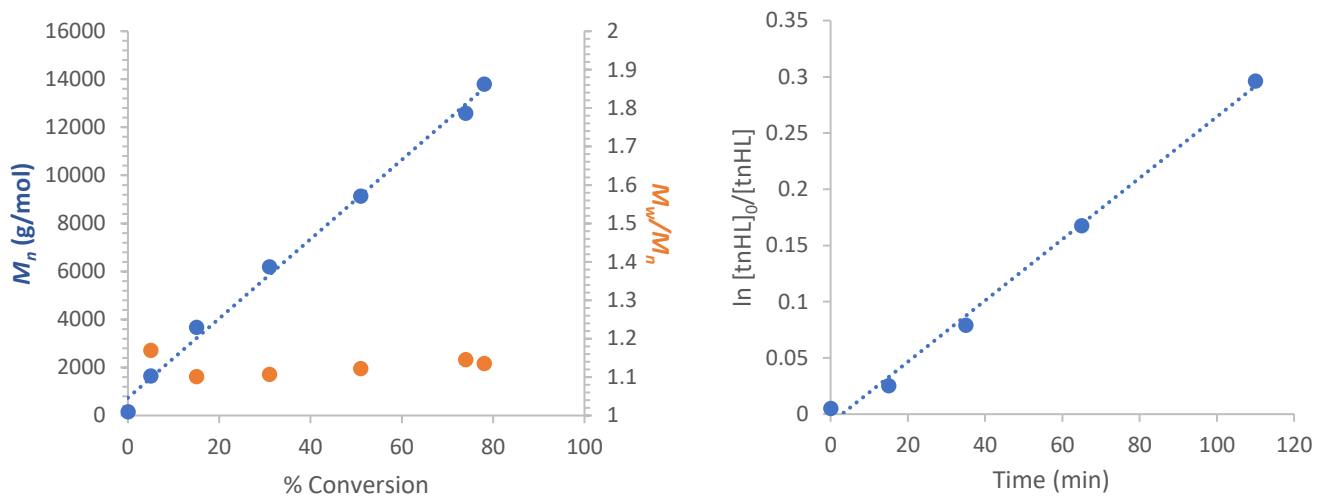


Figure S3. (Left) M_n versus conversion. (Right) First order evolution of $[tnHL]$ versus time. Reaction conditions: tnHL (1.04 mmol, 2M in C_6D_6), benzyl alcohol (1 mol %, 0.010 mmol), TCC/MTBD (5 mol %, 0.034 mmol each) in C_6D_6

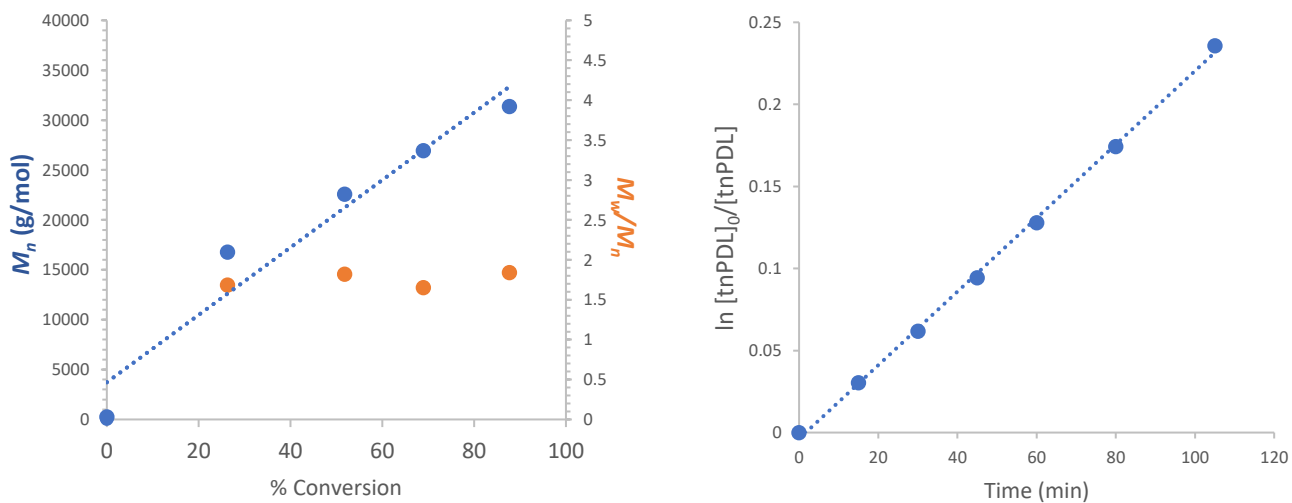


Figure S4. (Left) M_n versus conversion. (Right) First order evolution of $[tnPDL]$ versus time. Reaction conditions: tnPDL (0.974 mmol, 5M in toluene), benzyl alcohol (1 mol %, 0.0097 mmol) catalyzed by TCC/MTBD (5 mol %, 0.0478 mmol each) in toluene at 100 °C.

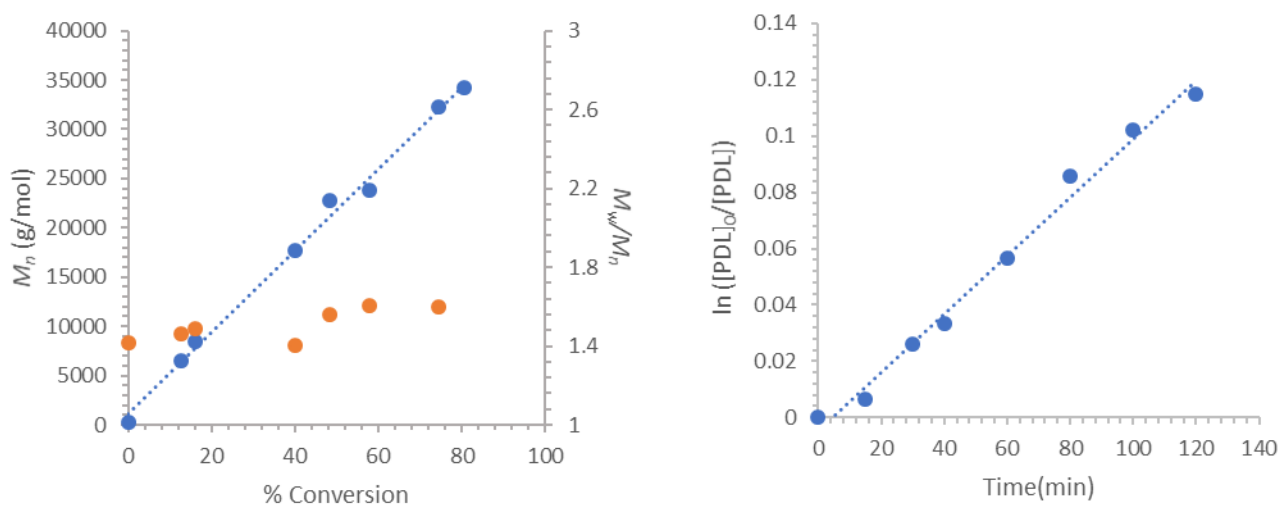


Figure S5. (Left) M_n versus conversion. (Right) First order evolution of [PDL] versus time. Reaction conditions: PDL (1.05 mmol, 5M in toluene), benzyl alcohol (1 mol%, 0.0105 mmol) catalyzed by TCC/MTBD (5 mol %, 0.0525 mmol each) in toluene at 100 °C.

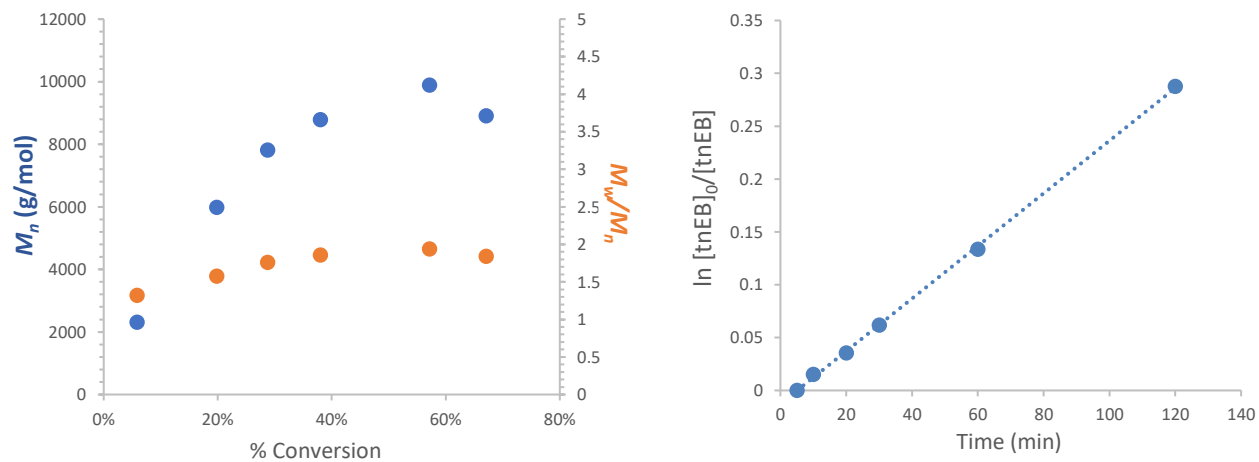


Figure S6. (Left) M_n versus conversion. (Right) First order evolution of [tnEB] versus time. Reaction conditions: tnEB (1.32 mmol, 2M in toluene), benzyl alcohol (1 mol %, 0.0132 mmol) catalyzed by TCC/BEMP (5 mol %, 0.0661 mmol each) in toluene at 80 °C.

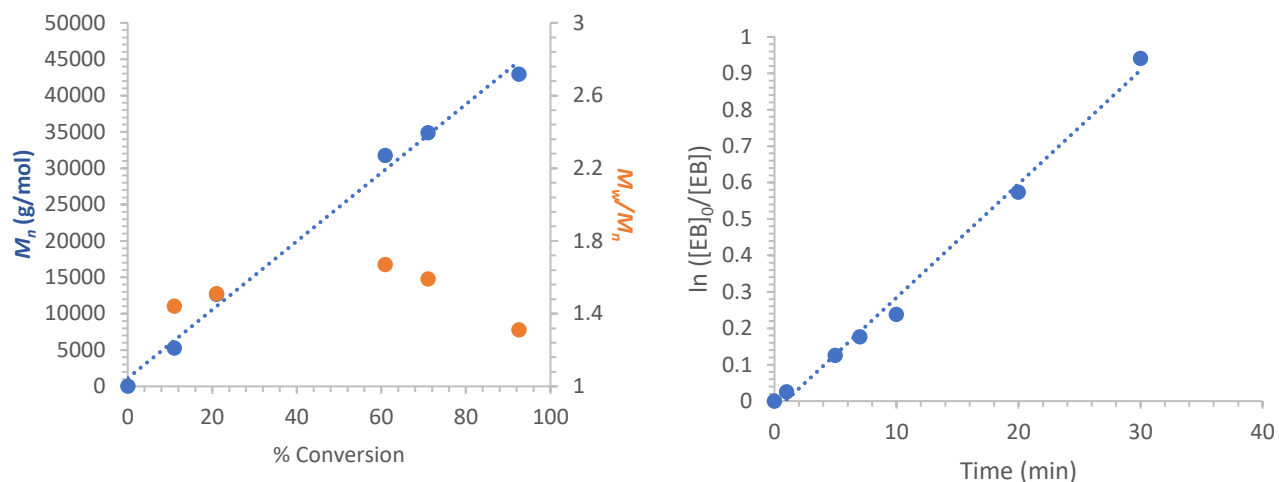


Figure S7. (Left) M_n versus conversion. (Right) First order evolution of [EB] versus time. Reaction conditions: EB (2.95 mmol), benzyl alcohol (1 mol %, 0.0295 mmol) catalyzed by TCC/BEMP (2 mol %, 0.0590 mmol each) at 80 °C under solvent-free conditions.

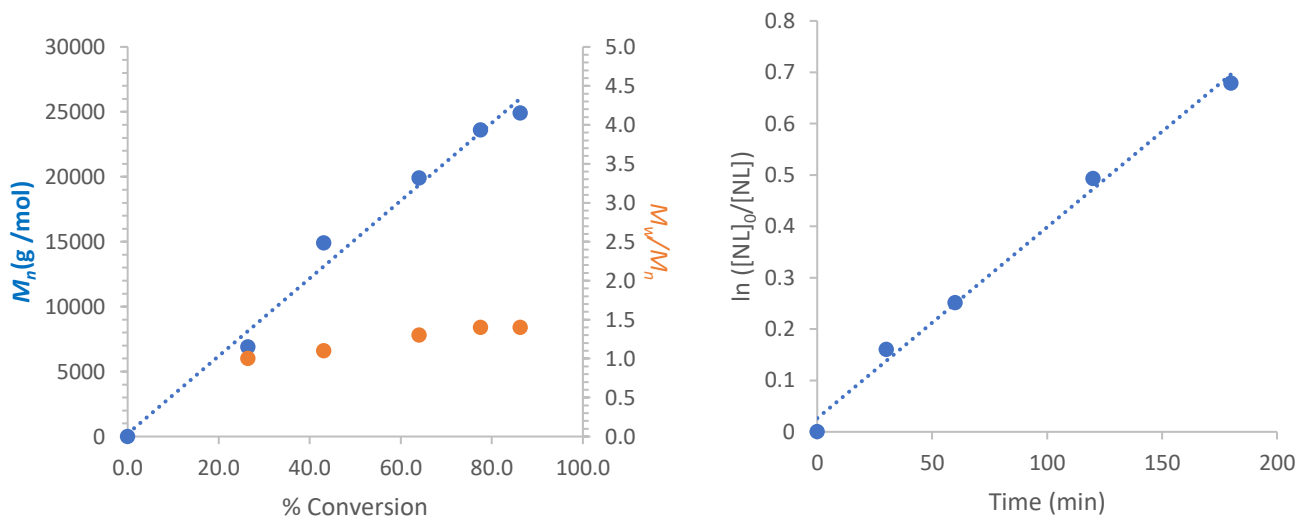


Figure S8. (Left) M_n versus conversion. (Right) First order evolution of [NL] versus time. Reaction conditions: NL (0.703 mmol, 2M in C_6D_6), benzyl alcohol (1 mol %, 0.00703 mmol) catalyzed by **2**/BEMP (1.67 mol %, 0.0117 mmol each) in C_6D_6 .

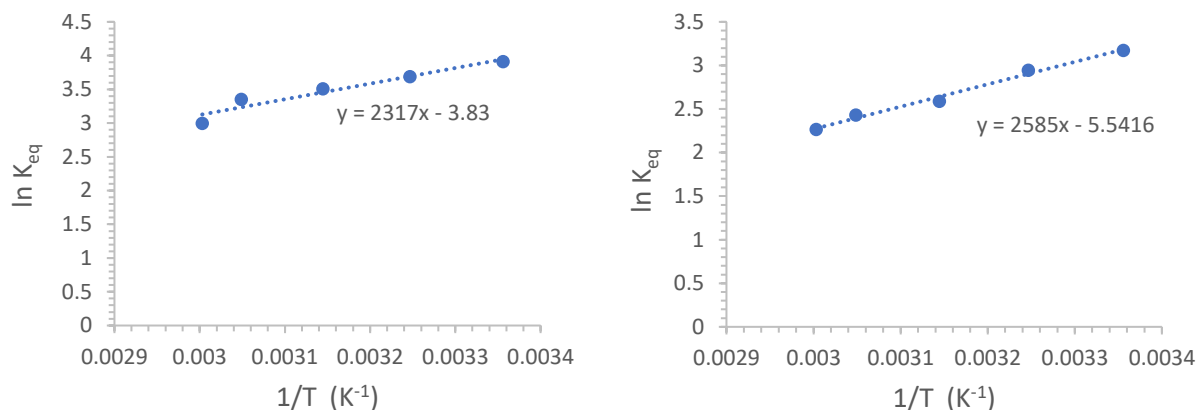


Figure S9. (Left) Van't Hoff plot for the ROP of HL (0.780 mmol, 0.5M in C_6D_6) from benzyl alcohol (1 mol %, 0.0078 mmol) catalyzed by TBD (5 mol %, 0.039 mmol). (Right) Van't Hoff plot for the ROP of tnHL (0.694 mmol, 1M in C_6D_6) from benzyl alcohol (1 mol %, 0.0069 mmol) catalyzed by TBD (5 mol %, 0.039 mmol).

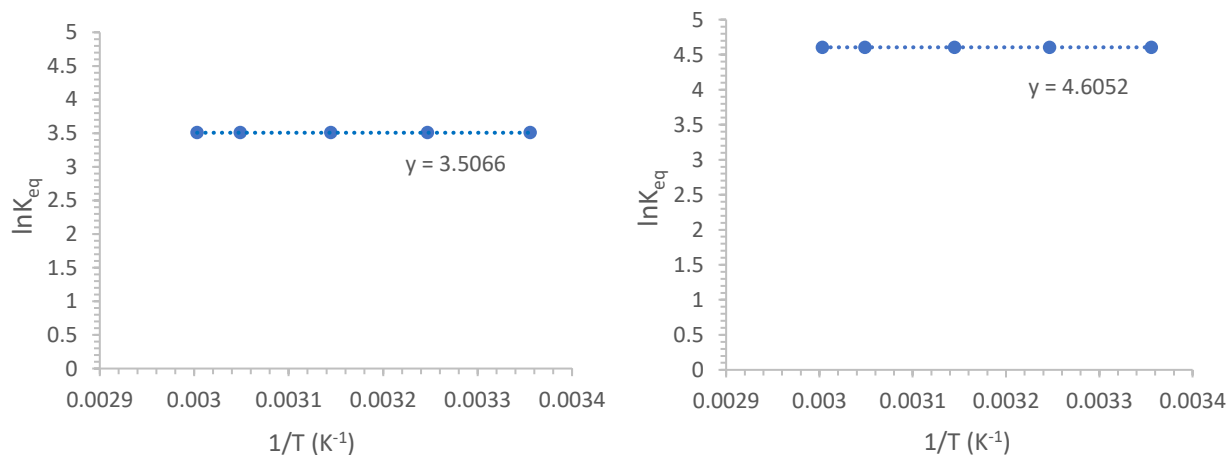


Figure S10. (Left) Van't Hoff plot for the ROP of NL (0.703 mmol, 0.5M in C_6D_6) from benzyl alcohol (1 mol %, 0.0070 mmol) catalyzed by TCC/BEMP (5 mol %, 0.0352 mmol each). (Right) Van't Hoff plot for the ROP of tnNL (0.632 mmol, 0.5M in C_6D_6) from benzyl alcohol (1 mol %, 0.0063 mmol) catalyzed by TCC/BEMP (5 mol %, 0.0315 mmol each).

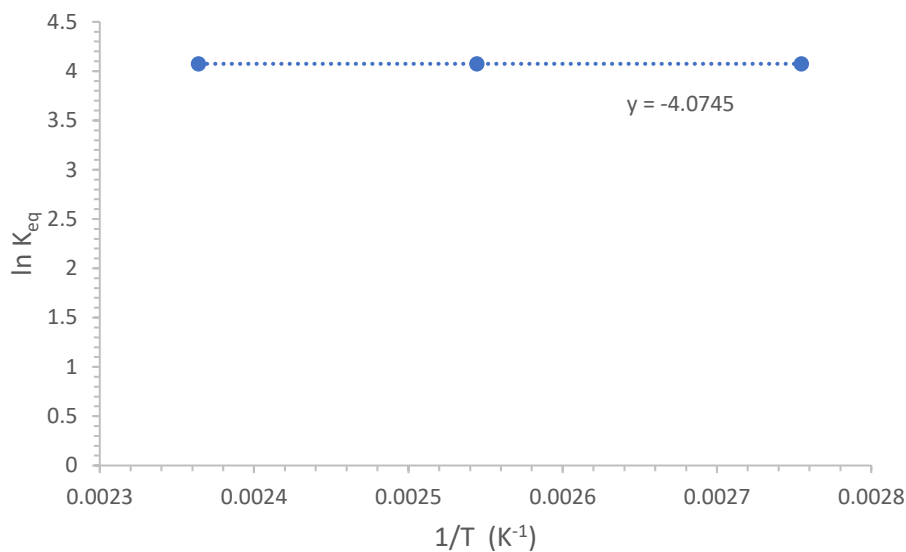


Figure S11. Van't Hoff plot for the ROP of tnPDL(0.390 mmol, 0.5 M in toluene) from benzyl alcohol (1 mol %, 0.0039 mmol) catalyzed by TCC/BEMP (5 mol% each, 0.0195 mmol each).

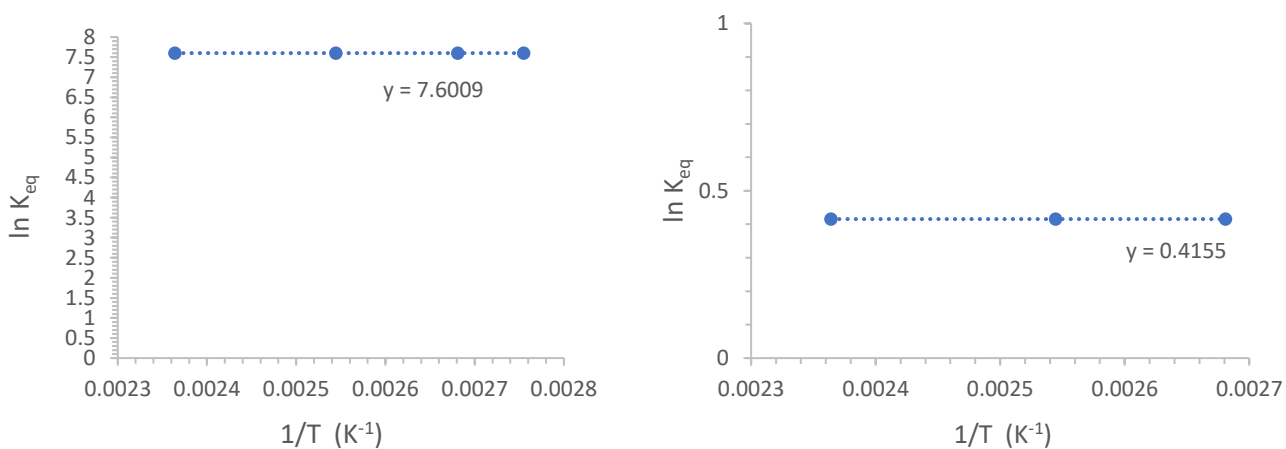


Figure S12. (Left) Van't Hoff plot for the ROP of EB (0.370 mmol, 0.5 M in toluene) from benzyl alcohol (1 mol %, 0.0037 mmol) catalyzed by TCC/BEMP (5 mol %, 0.0185 mmol each). (Right) Van't Hoff plot for the ROP of tnEB (1.32 mmol, 2 M in toluene) from benzyl alcohol (1 mol% 0.013 mmol) catalyzed by TCC/BEMP (5 mol%, 0.066 mmol each)

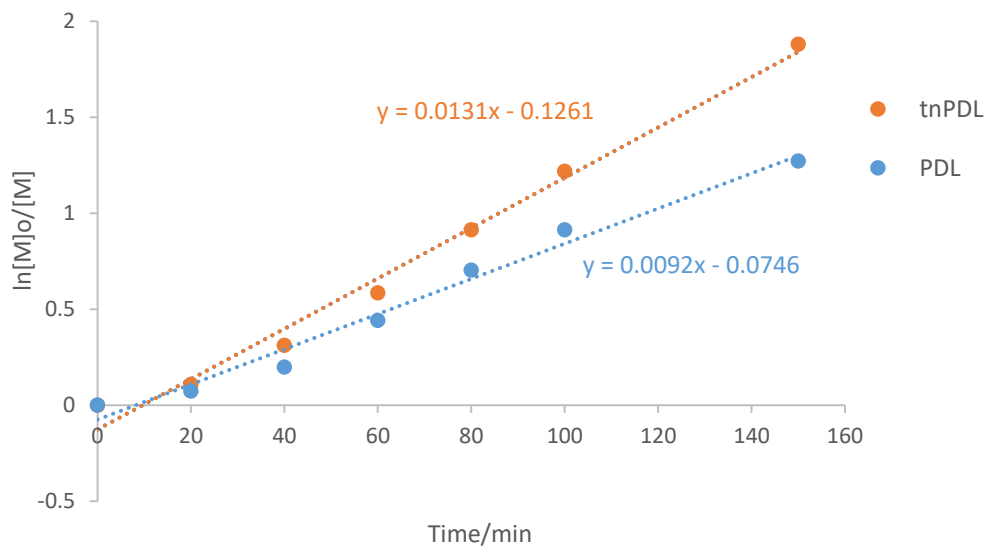


Figure S13. First order evolution of monomer concentrations versus time for the one-pot copolymerization of tnPDL and PDL. Reaction conditions: tnPDL and PDL (0.50 mmol each), benzyl alcohol (0.010 mmol) catalyzed by TCC/BEMP (0.0504 mmol each) in toluene (0.200 mL) at 100 °C.

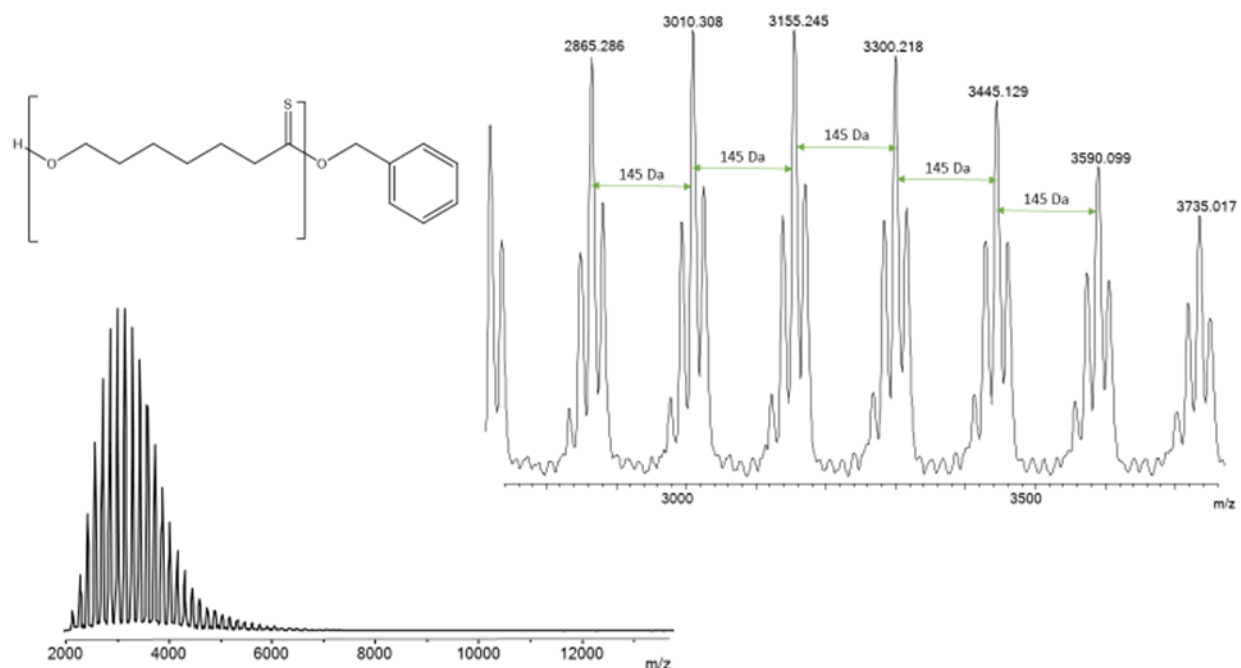


Figure S14. MALDI-ToF mass spectrum of PtnHL homopolymer ($[M]_o/[I]_o=25$)

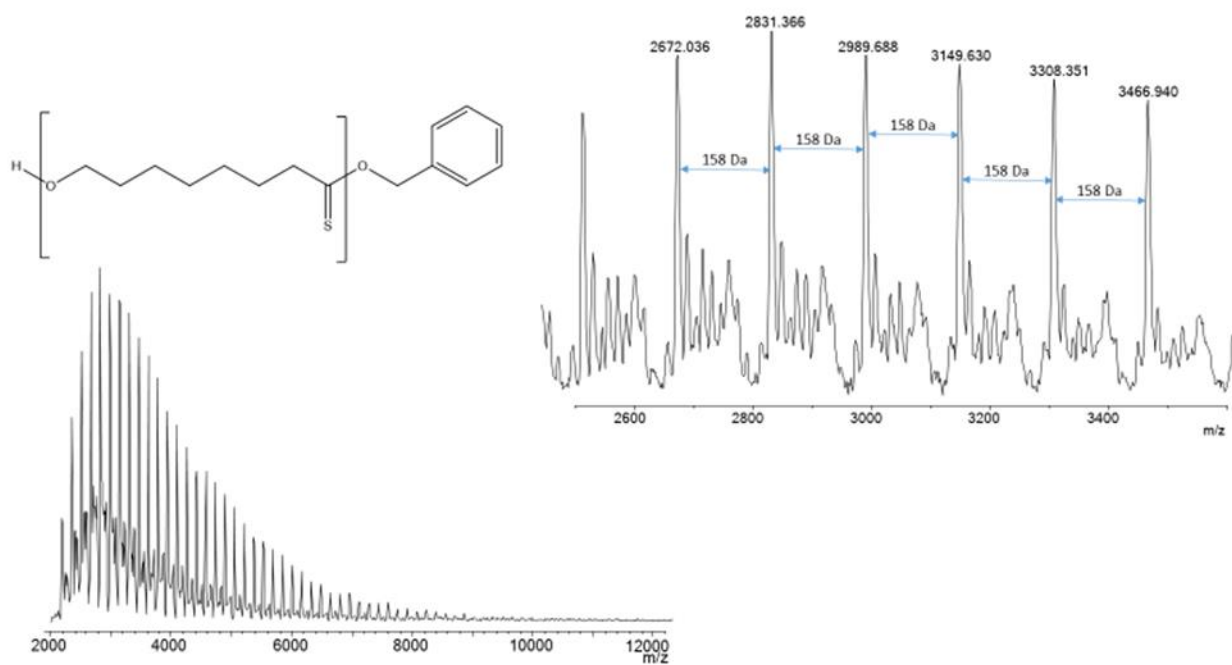


Figure S15. MALDI-ToF mass spectrum of PtnNL homopolymer ($[M]_o/[I]_o=25$)

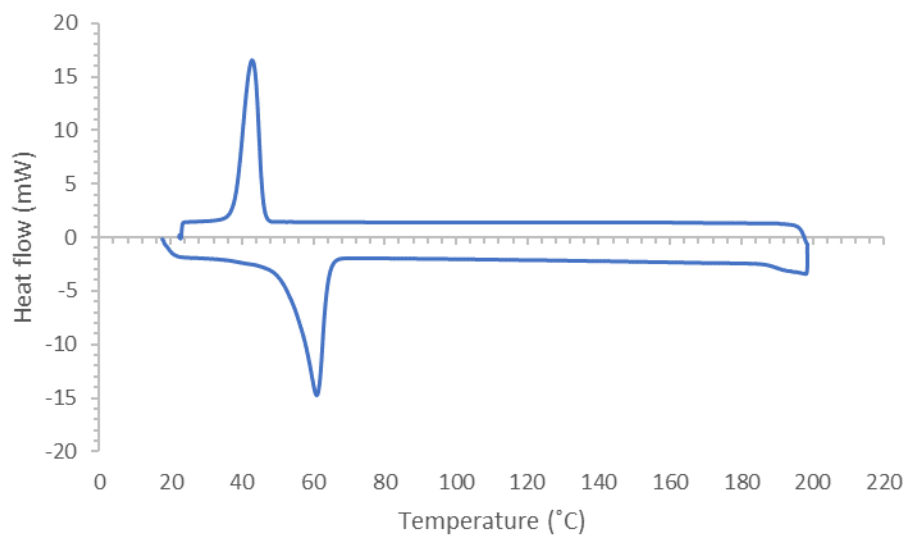


Figure S16. Differential scanning calorimetry spectrum of PHL homopolymer

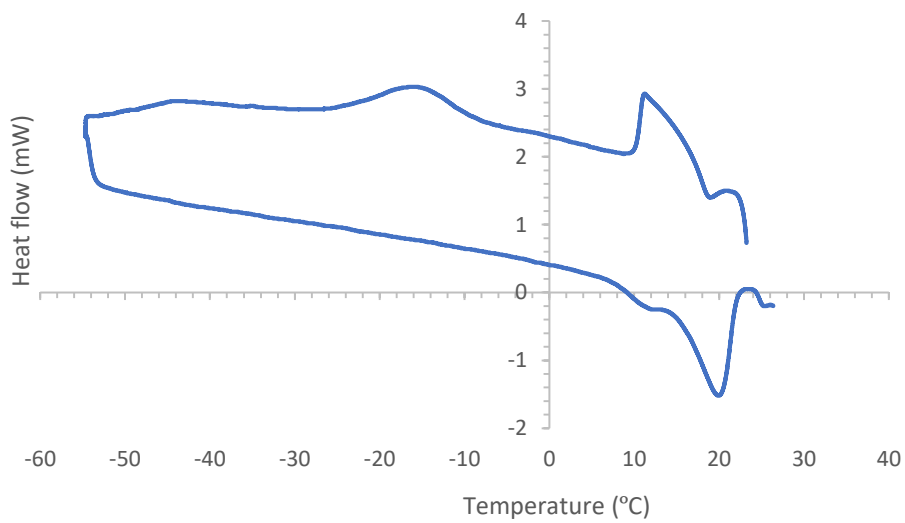


Figure S17. Differential scanning calorimetry spectrum of PtnHL homopolymer

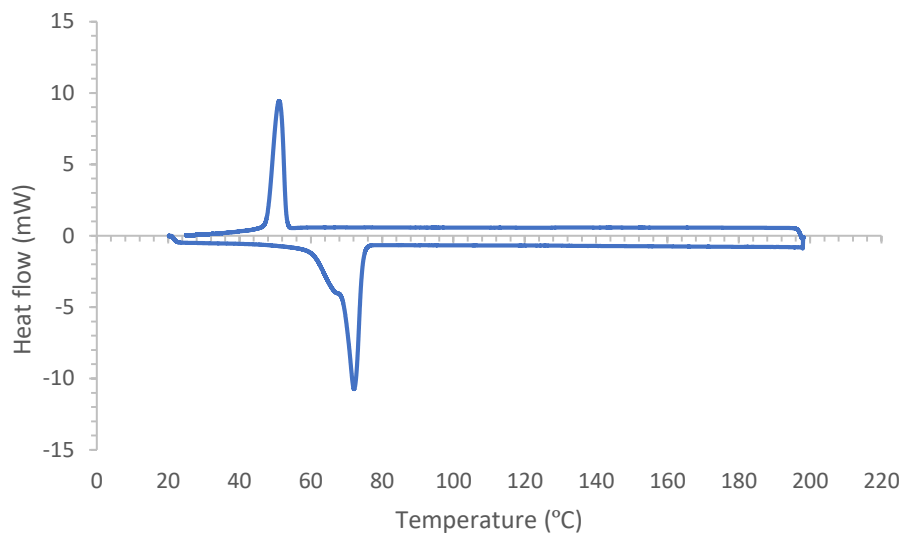


Figure S18. Differential scanning calorimetry spectrum of PNL homopolymer

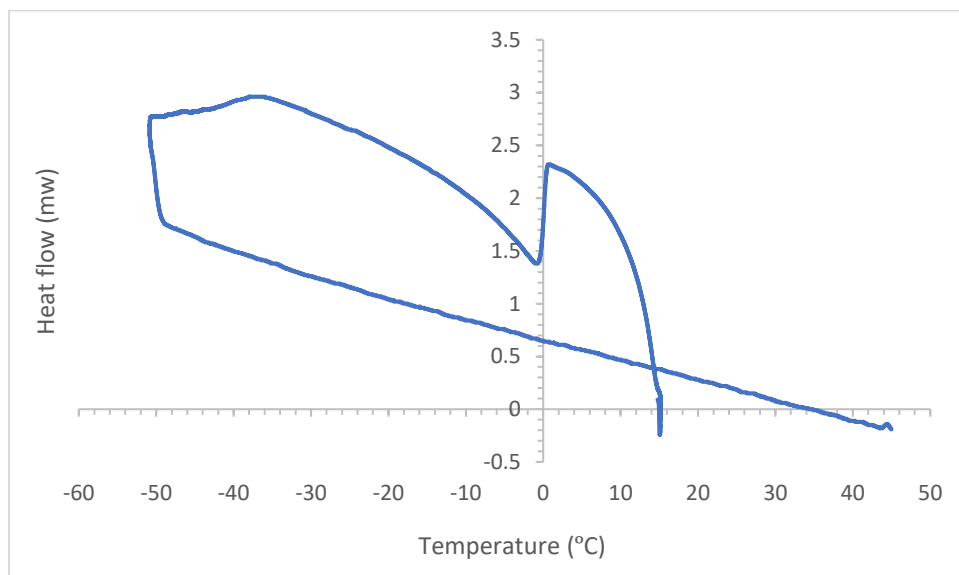


Figure S19. Differential scanning calorimetry spectrum of PtnNL homopolymer

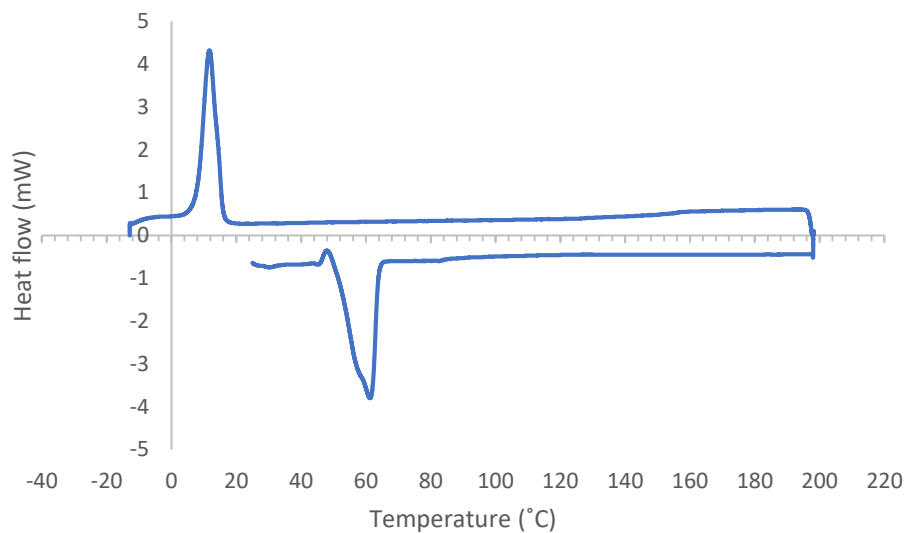


Figure S20. Differential scanning calorimetry spectrum of PtnPDL homopolymer

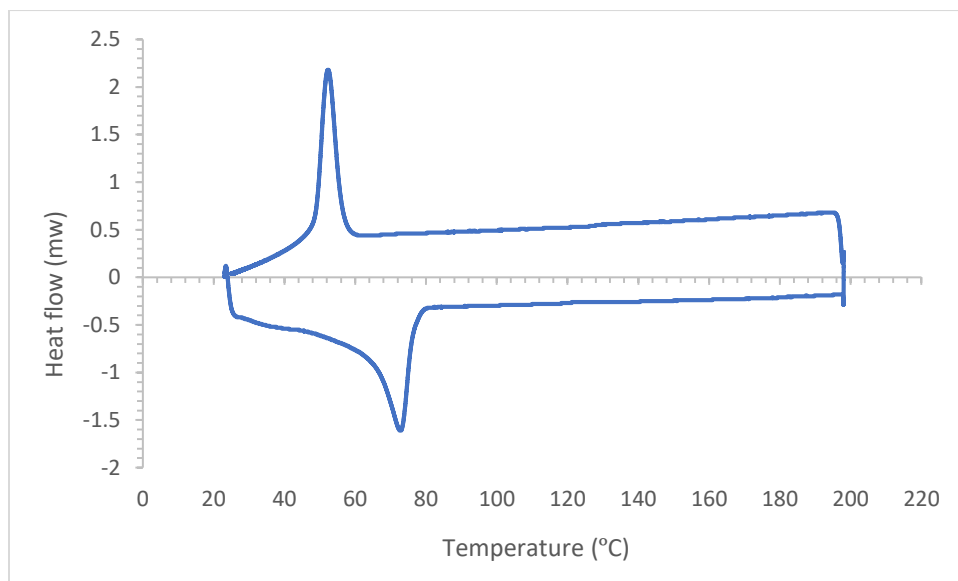


Figure S21. Differential scanning calorimetry spectrum of PtnEB homopolymer

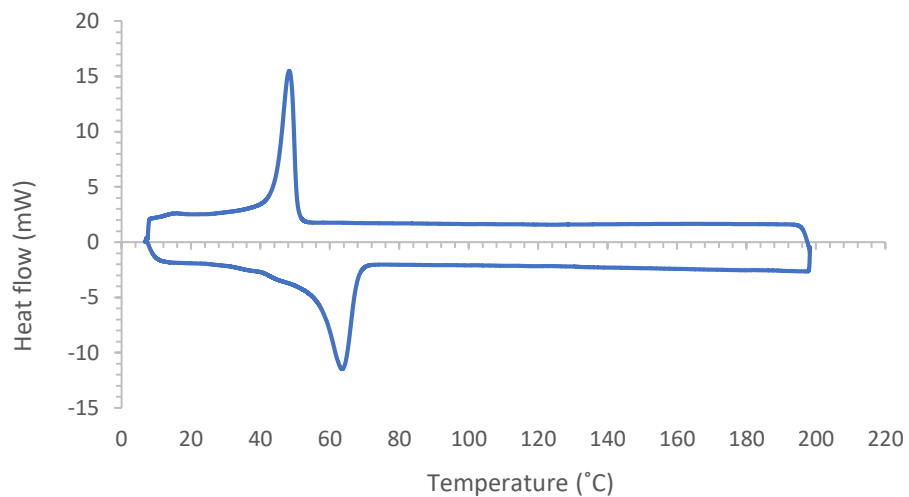


Figure S22. Differential scanning calorimetry spectrum of P(tnPDL-co-PDL) copolymer

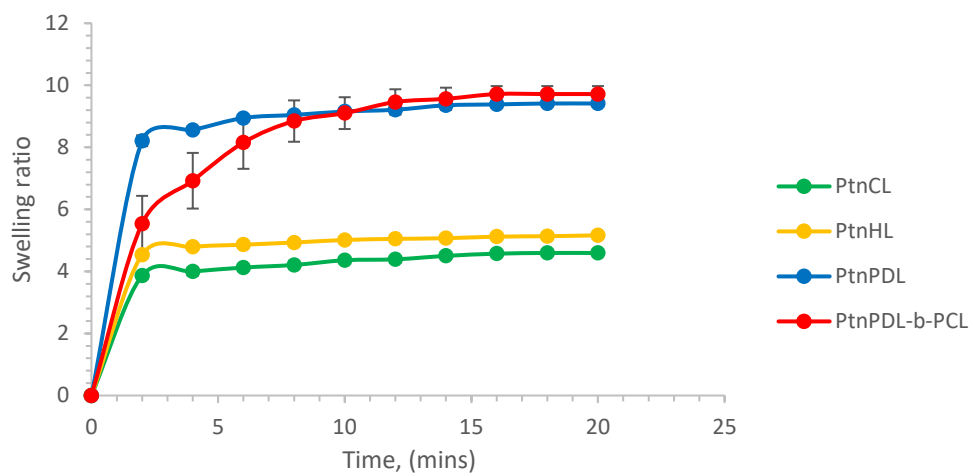


Figure S23. Swelling ratios of crosslinked polymers in THF

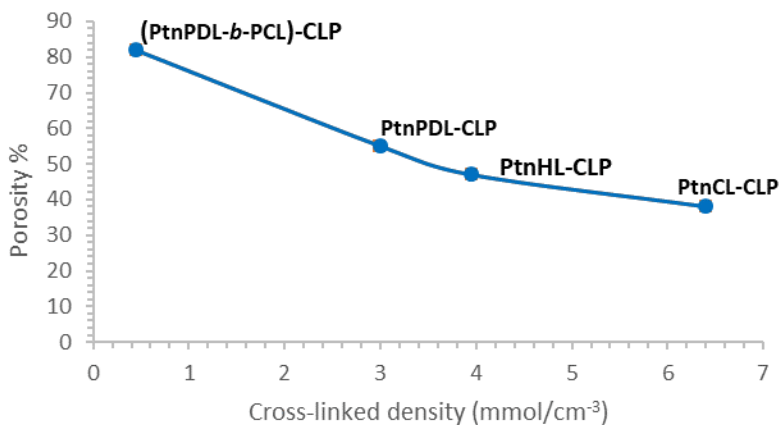


Figure S24. Dependence of porosity on cross-linked density of CLPs

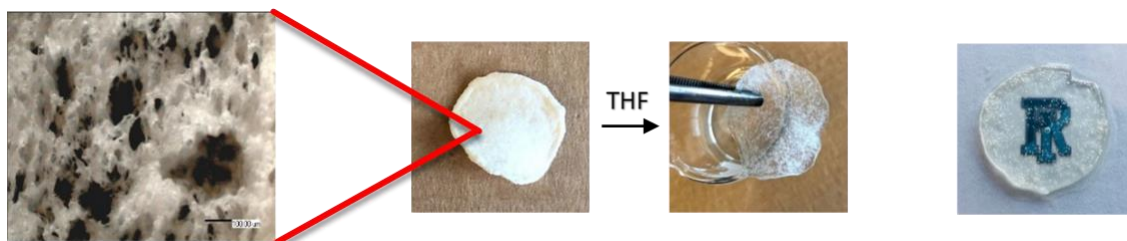


Figure S25. Images of the transparent P(tnPDL-*b*-CL)-CLP after immersed in THF

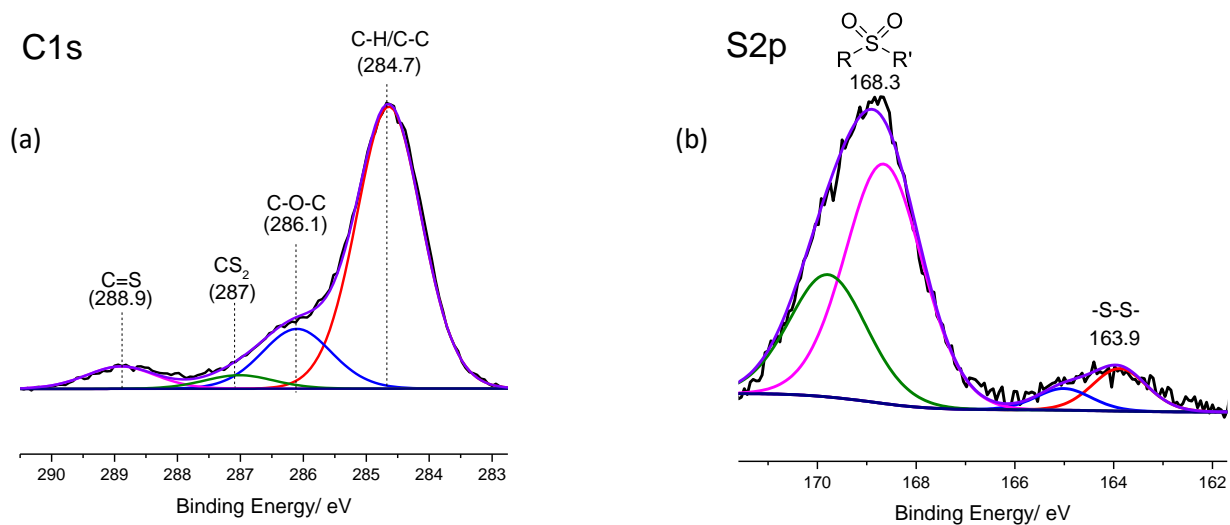


Figure S26. (a) XPS spectrum for the C 1s (b) XPS spectrum for the S 2p

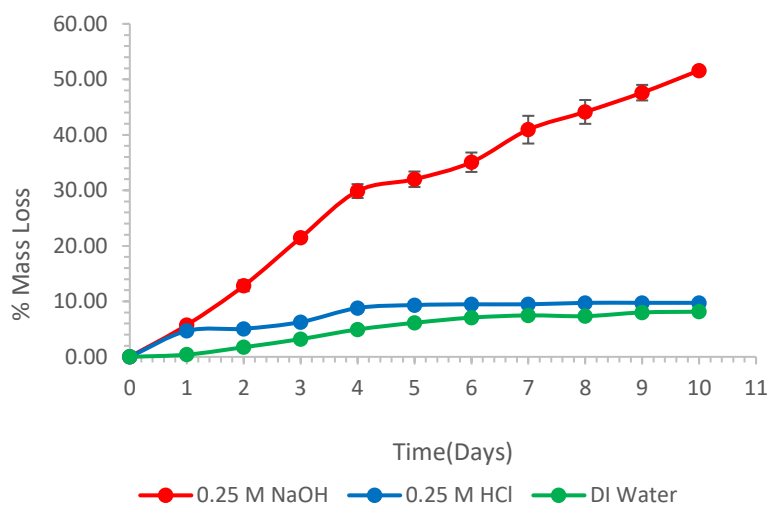


Figure S27. Percent mass loss for PtnPDL-CLP in acidic (0.25 M HCl), basic (0.25 M NaOH), and neutral (distilled water) conditions versus time. The results shown are an average of three replicates.

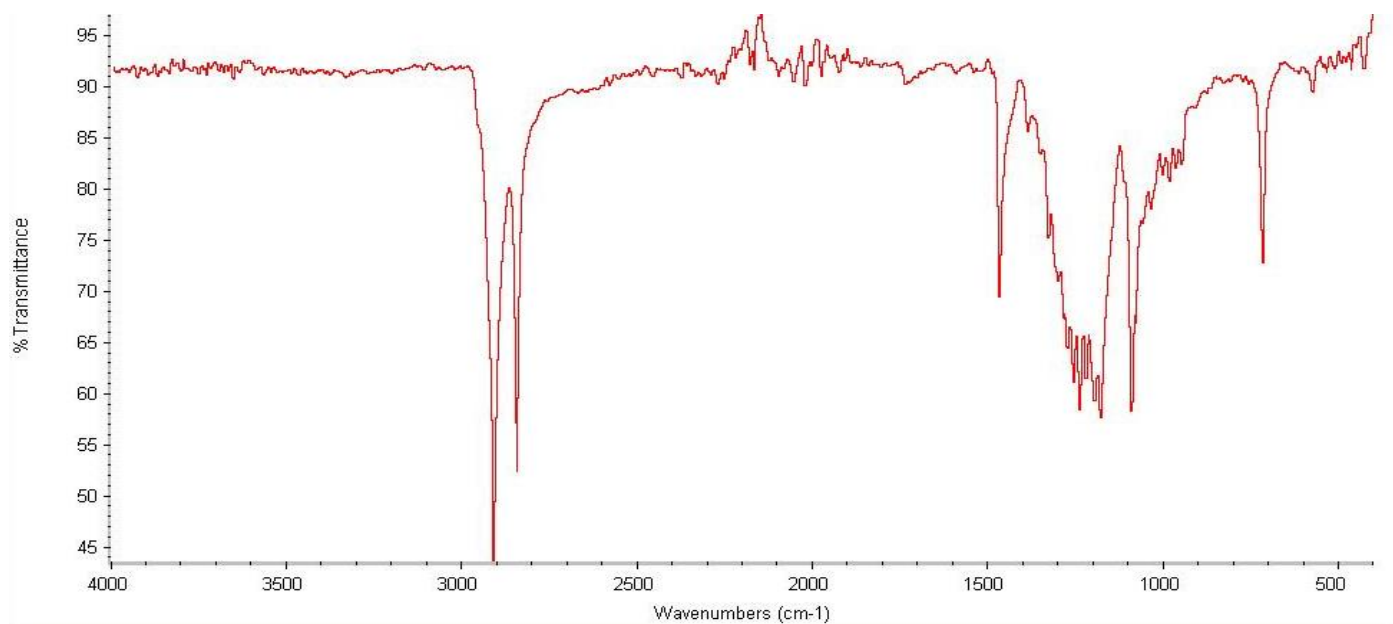


Figure S28. Solid-state IR spectrum of PtnPDL.

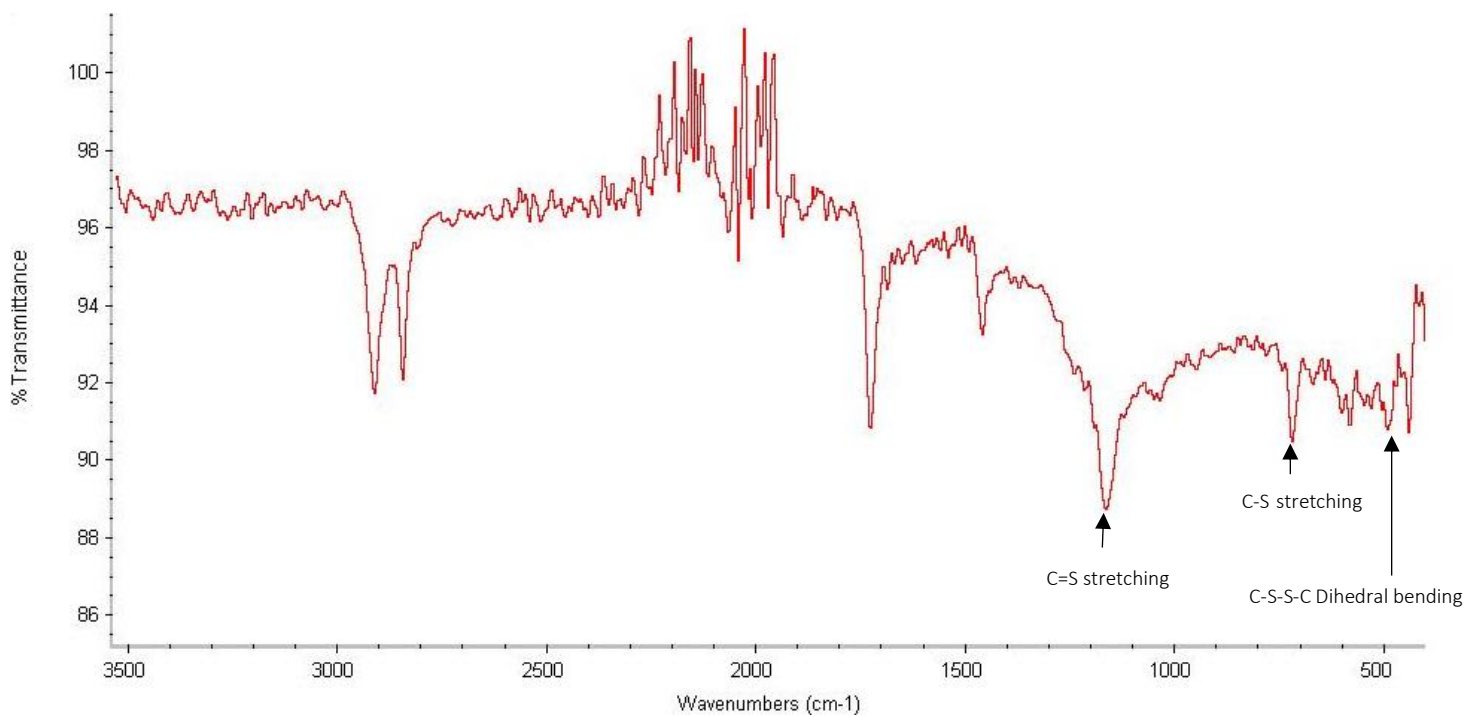


Figure S29. Solid-state IR spectrum of the crosslinked polymer (PtnPDL-CPL).

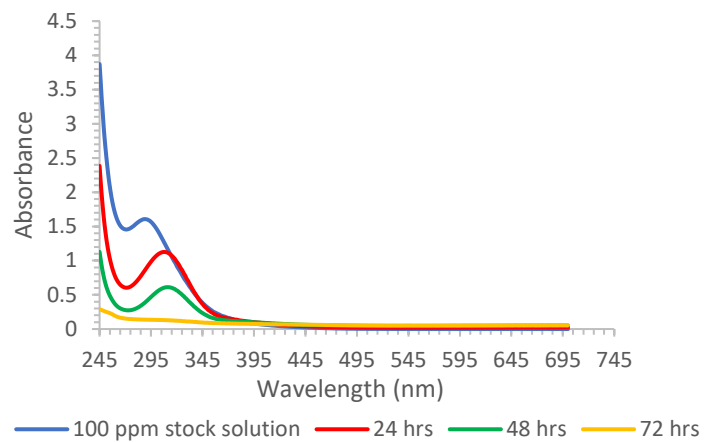


Figure S30. UV-vis spectrum for the Au³⁺ (100 ppm aqueous solution) extraction with PtnPDL-CLP (100 mg).

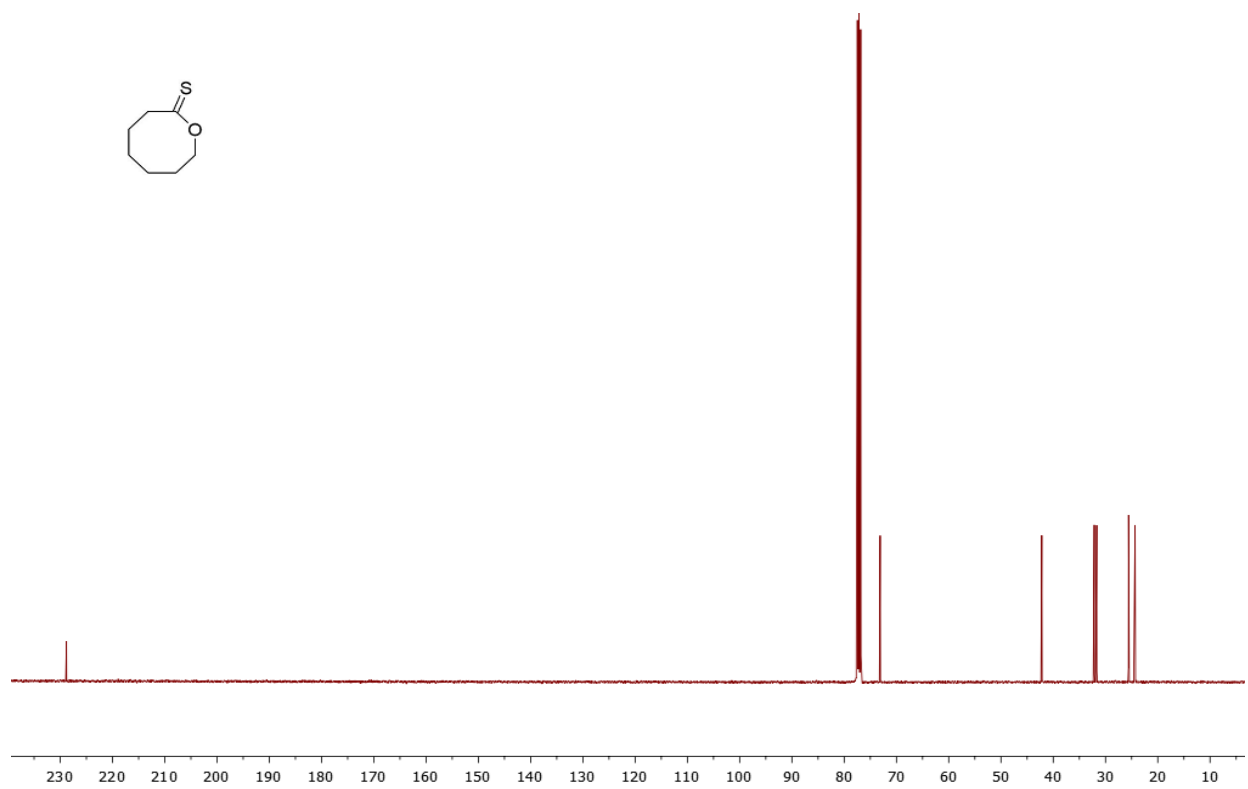
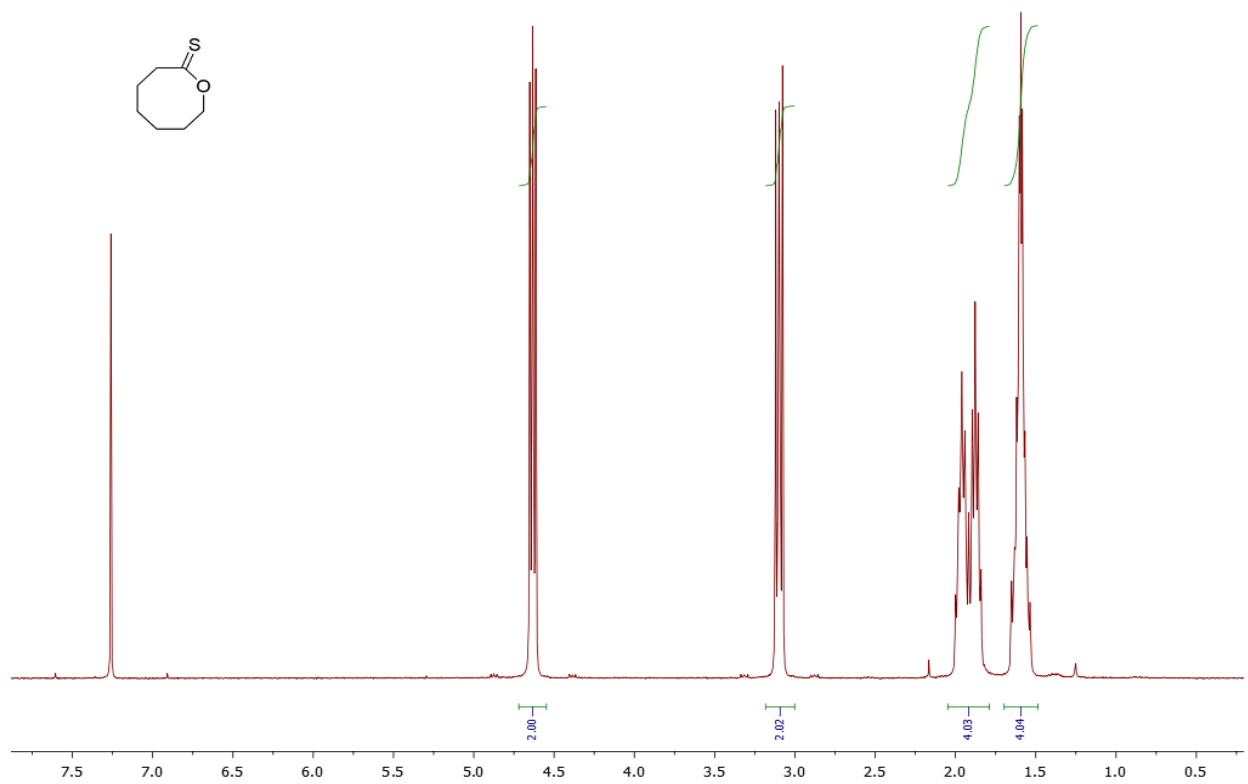


Figure S31. (Upper) ¹H NMR (CDCl₃, 300 MHz, ppm) spectrum of tnHL. (Lower) ¹³C NMR (CDCl₃, 100 MHz, ppm) spectrum of tnHL.

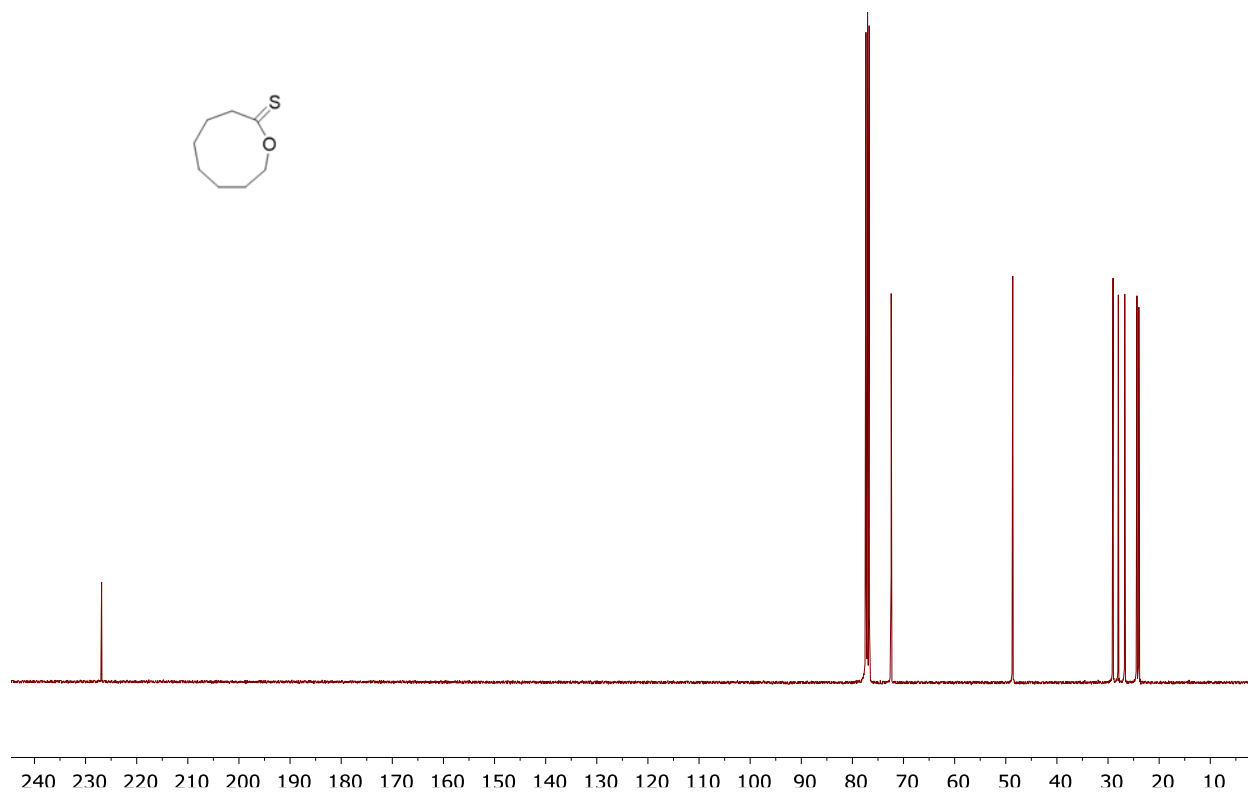
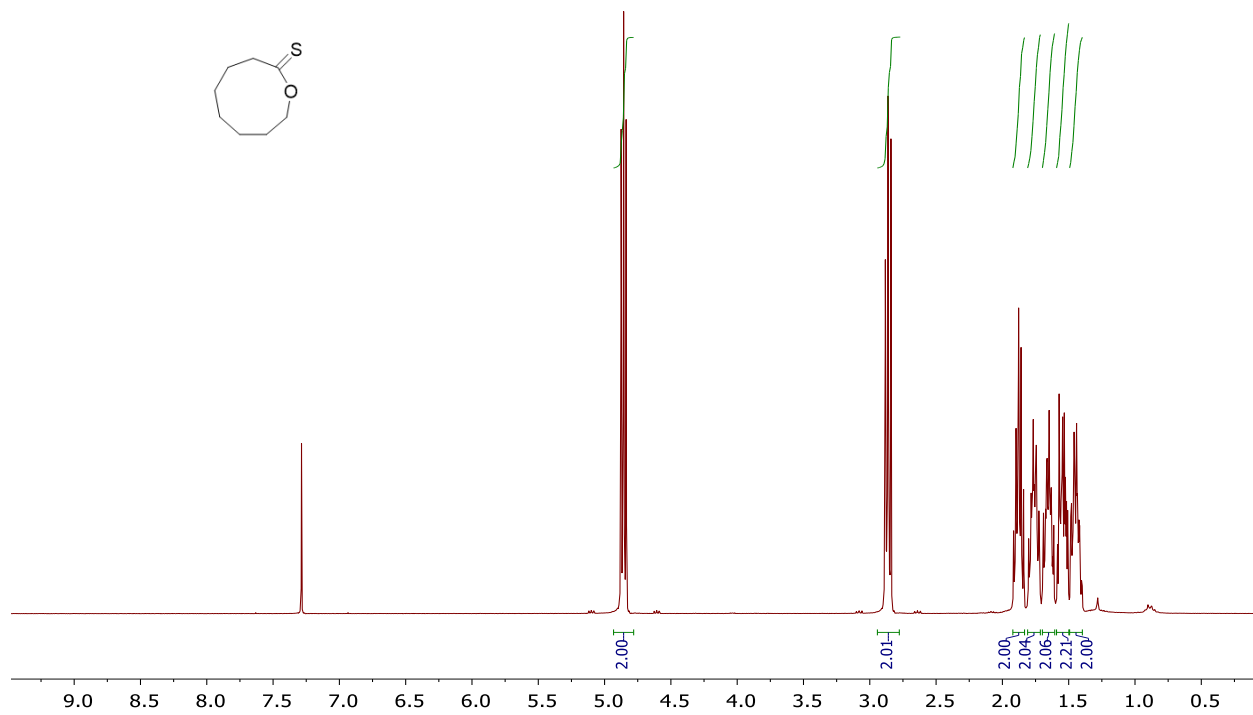


Figure S32. (Upper) ¹H NMR (CDCl₃, 300 MHz, ppm) spectrum of tnNL. (Lower) ¹³C NMR (CDCl₃, 100 MHz, ppm) spectrum of tnNL.

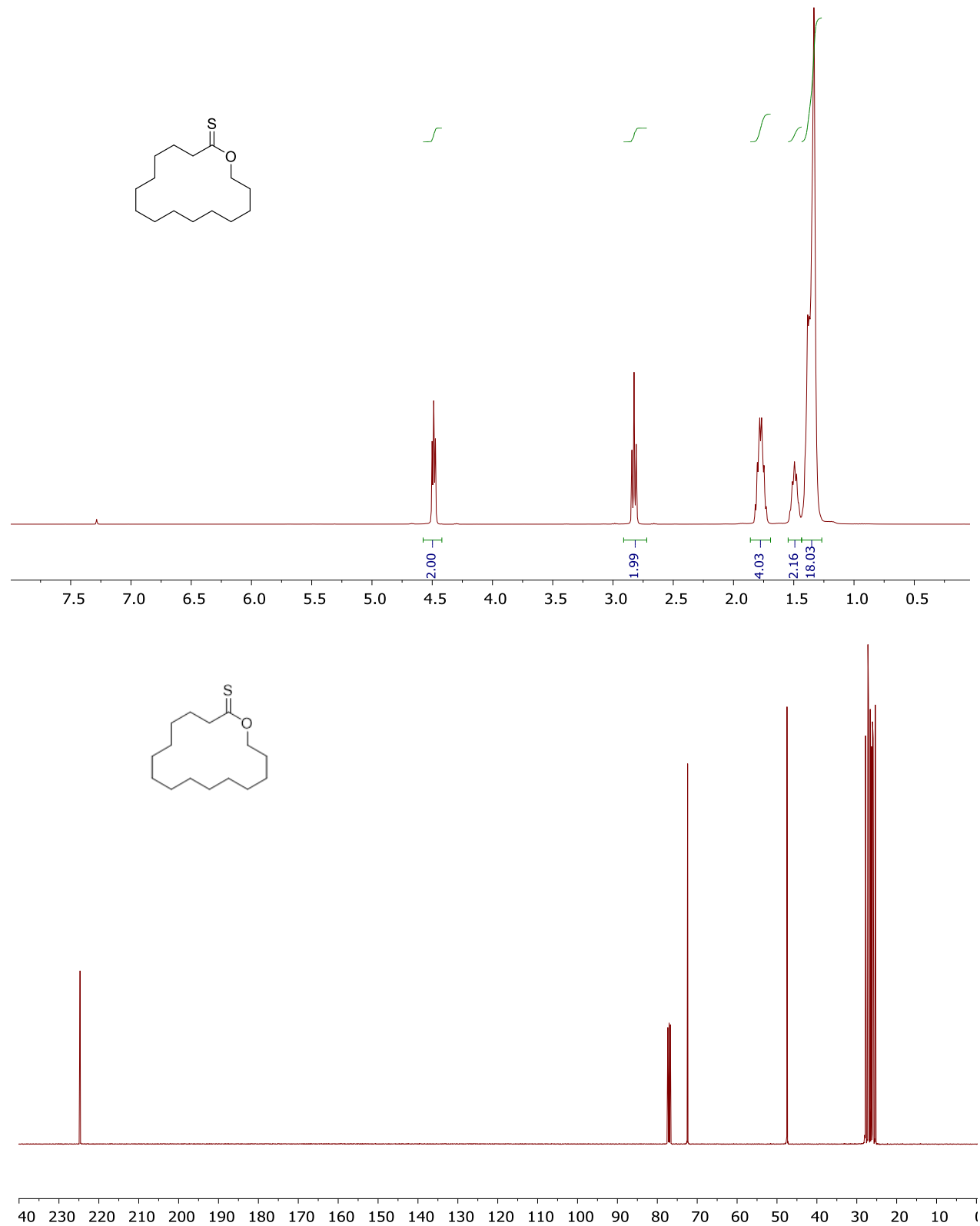


Figure S33. (Upper) ^1H NMR (CDCl_3 , 300 MHz, ppm) spectrum of tnPDL. (Lower) ^{13}C NMR (CDCl_3 , 100 MHz, ppm) spectrum of tnPDL.

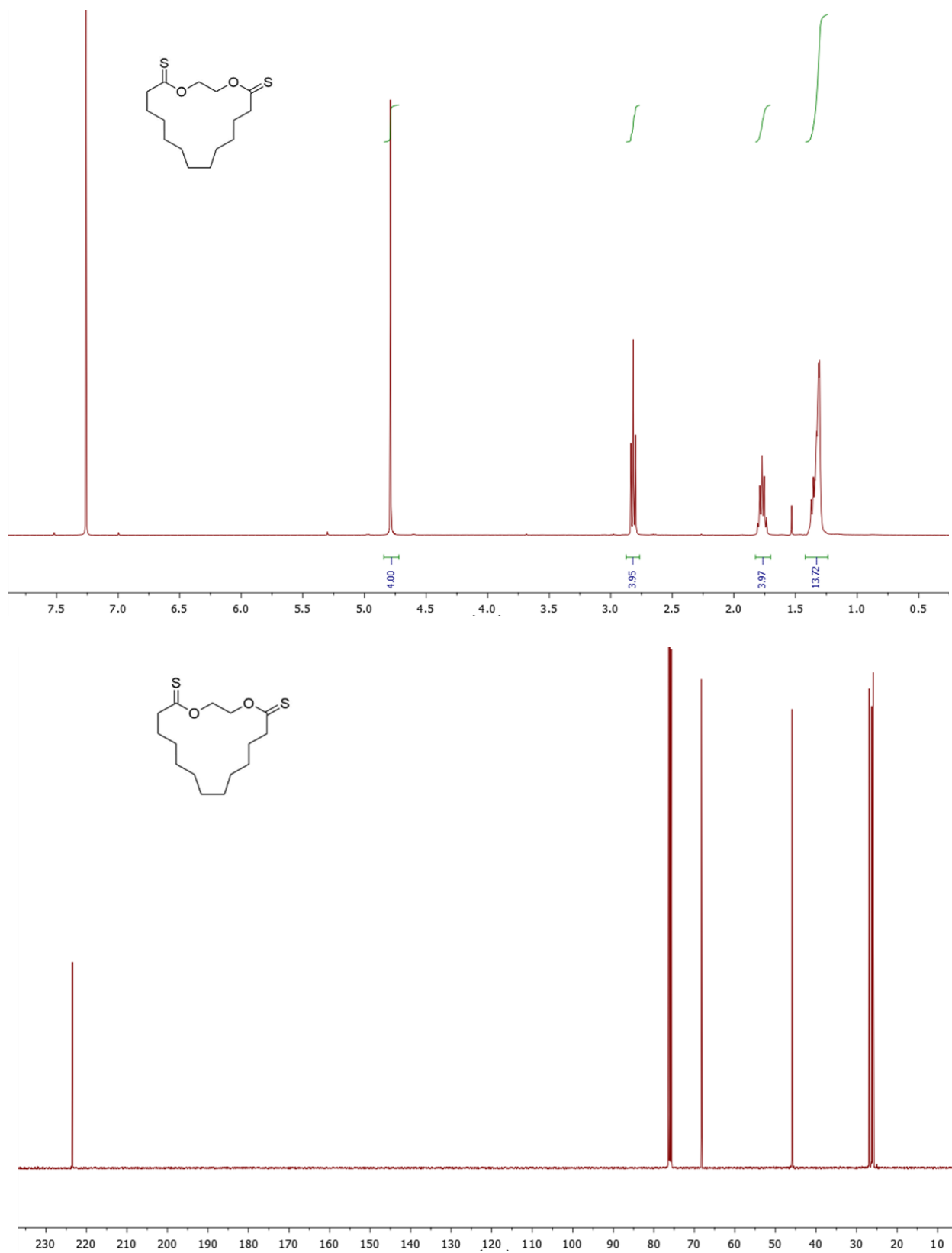


Figure S34. (Upper) ^1H NMR (CDCl_3 , 300 MHz, ppm) spectrum of tnEB. (Lower) ^{13}C NMR (CDCl_3 , 100 MHz, ppm) spectrum of tnEB.

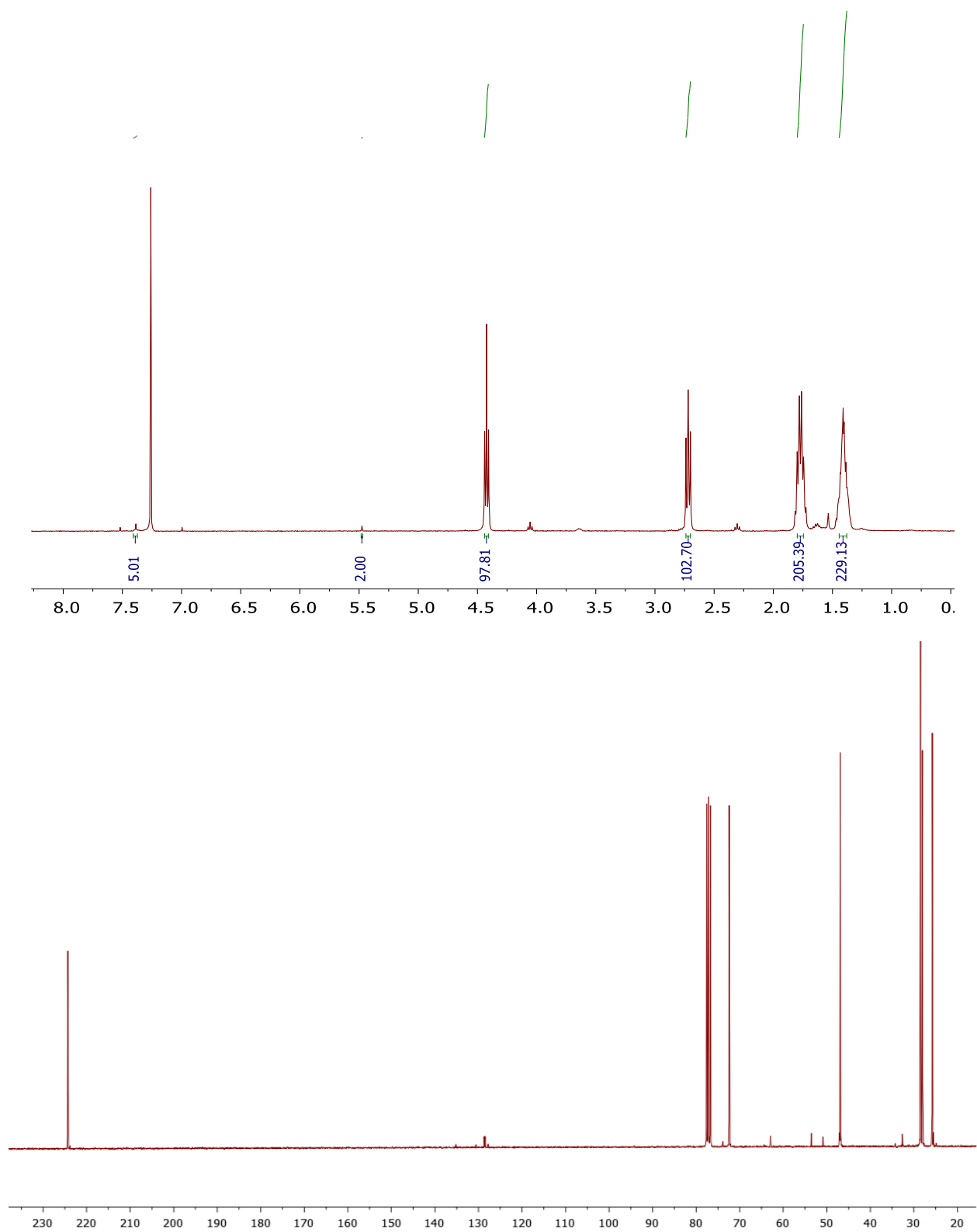


Figure S35. (Upper) ^1H NMR (CDCl_3 , 400 MHz, ppm) spectrum of PtnHL. (Lower) ^{13}C (75 MHz, CDCl_3) spectrum of PtnHL

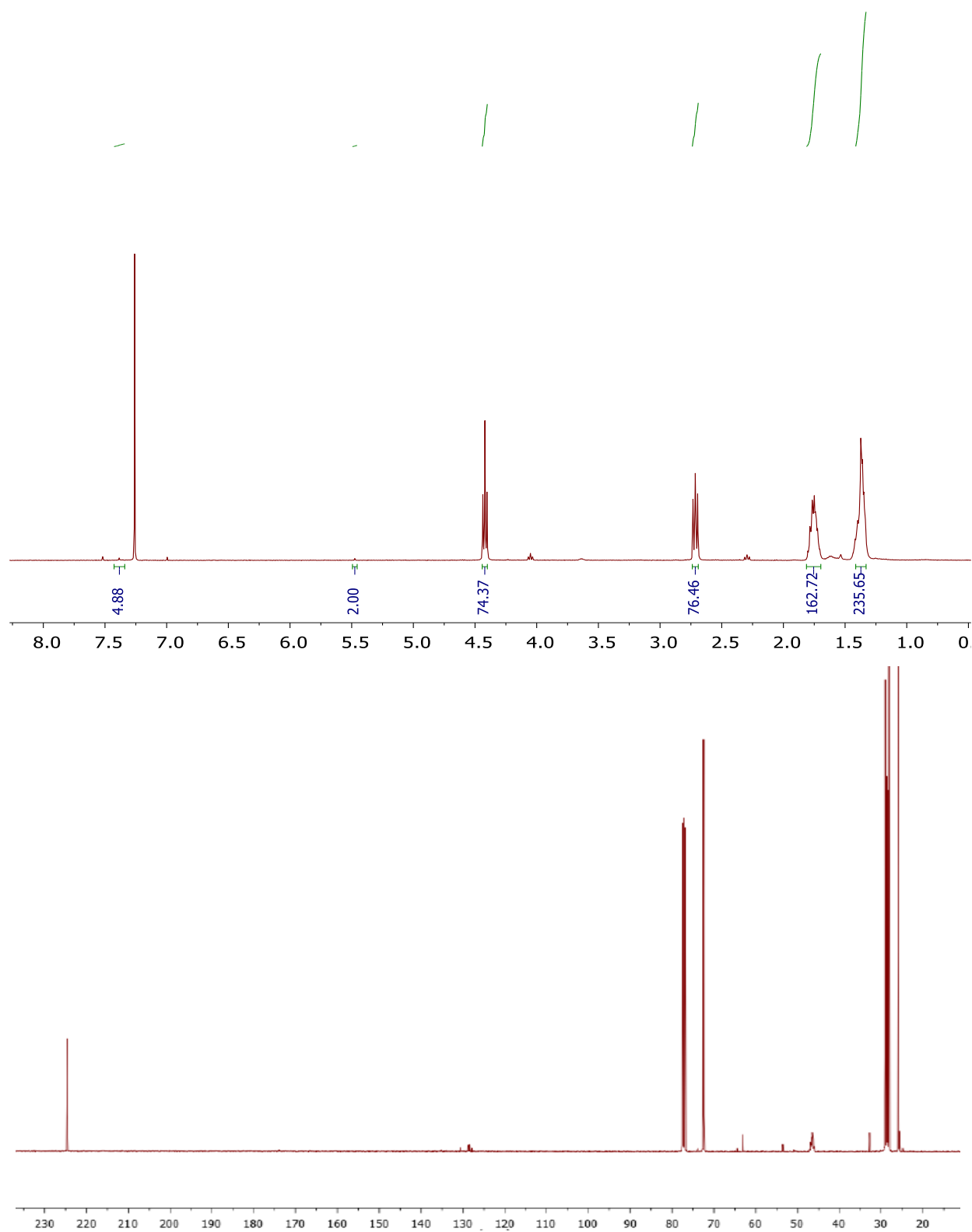


Figure S36. (Upper) ^1H NMR (CDCl_3 , 400 MHz, ppm) spectrum of PtnNL. (Lower) ^{13}C NMR (100 MHz, CDCl_3) spectrum of PtnNL.

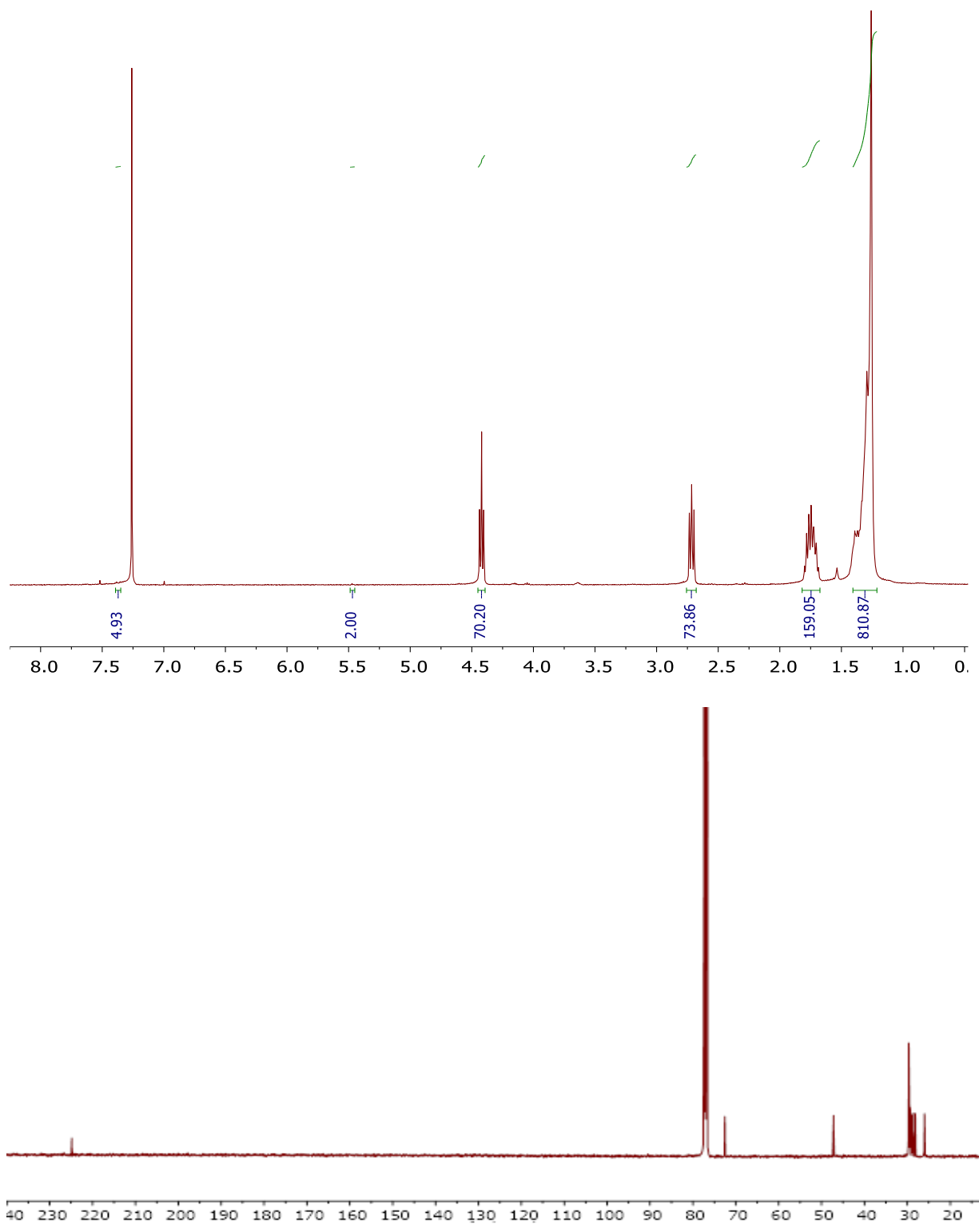


Figure S37. (Upper) ¹H NMR (CDCl₃, 400 MHz, ppm) spectrum of PtnPDL. (Lower) ¹³C NMR (100 MHz, CDCl₃) spectrum of PtnPDL.

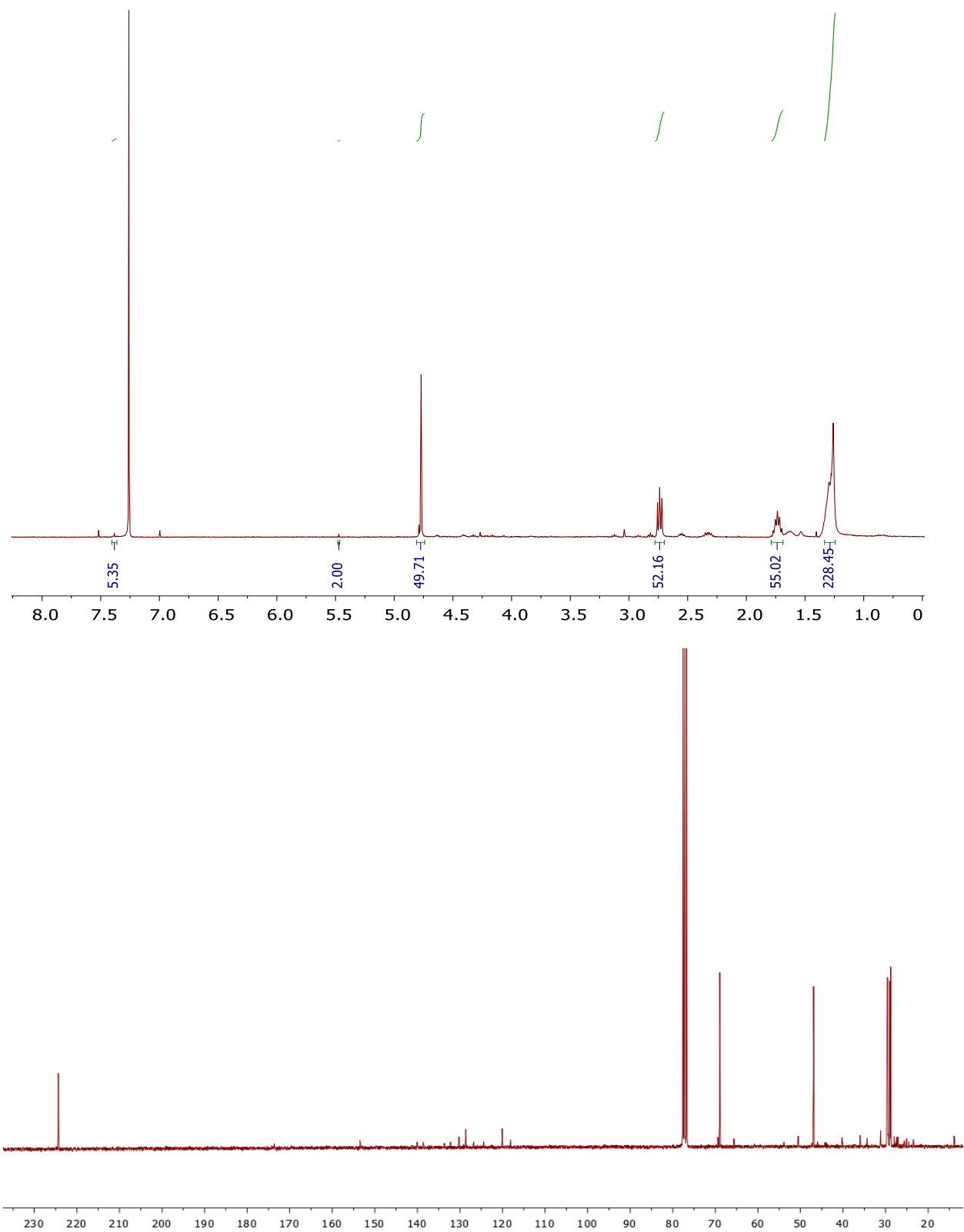


Figure S38. (Upper) ^1H NMR (CDCl_3 , 400 MHz, ppm) spectrum of PtnEB. (Lower) ^{13}C NMR (75 MHz, CDCl_3) spectrum of PtnEB.

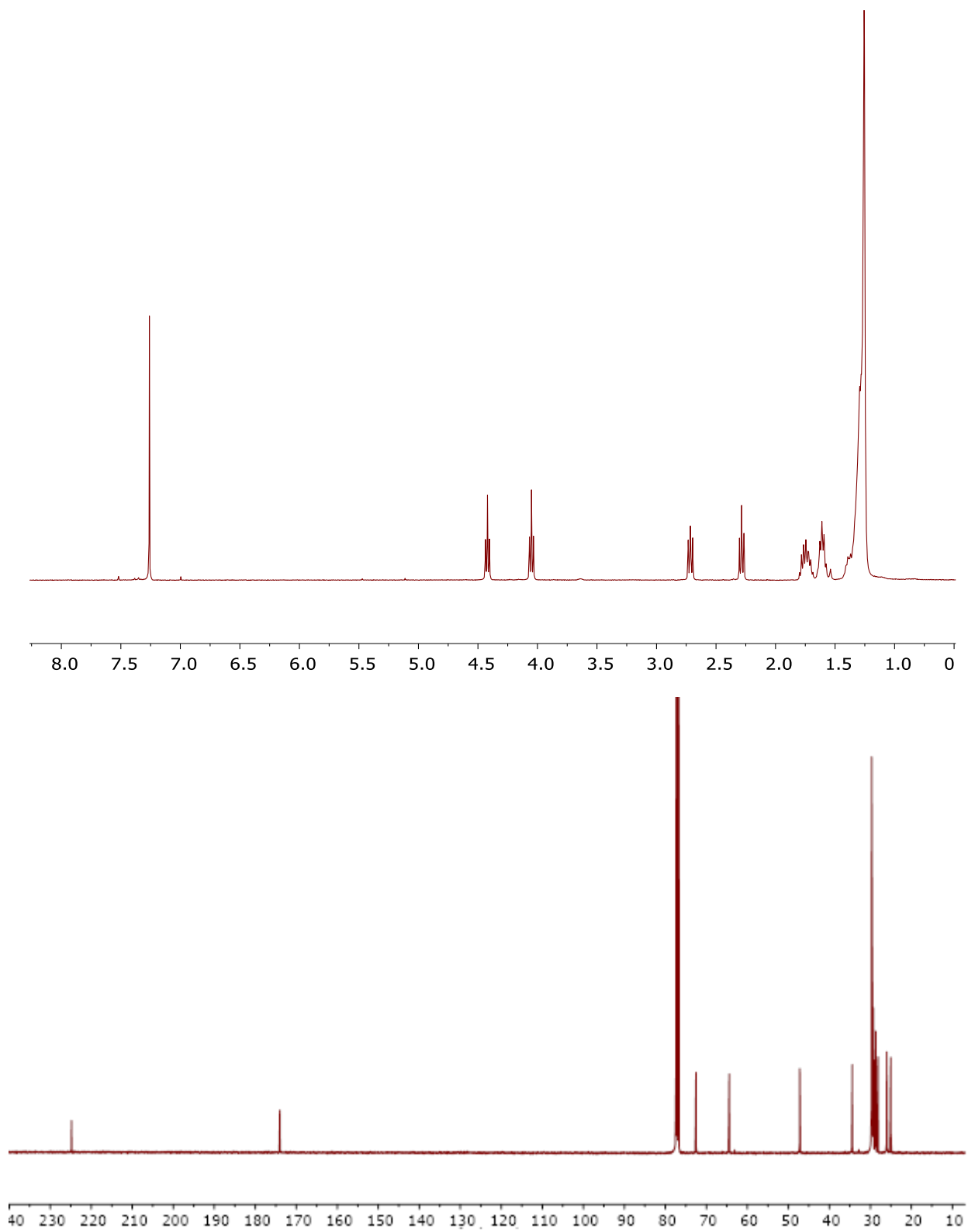


Figure S39. (Upper) ^1H NMR (CDCl_3 , 400 MHz, ppm) spectrum of P(tnPDL-co-PDL) (1:1). (Lower) ^{13}C NMR (100 MHz, CDCl_3) spectrum of P(tnPDL-co-PDL) (1:1)

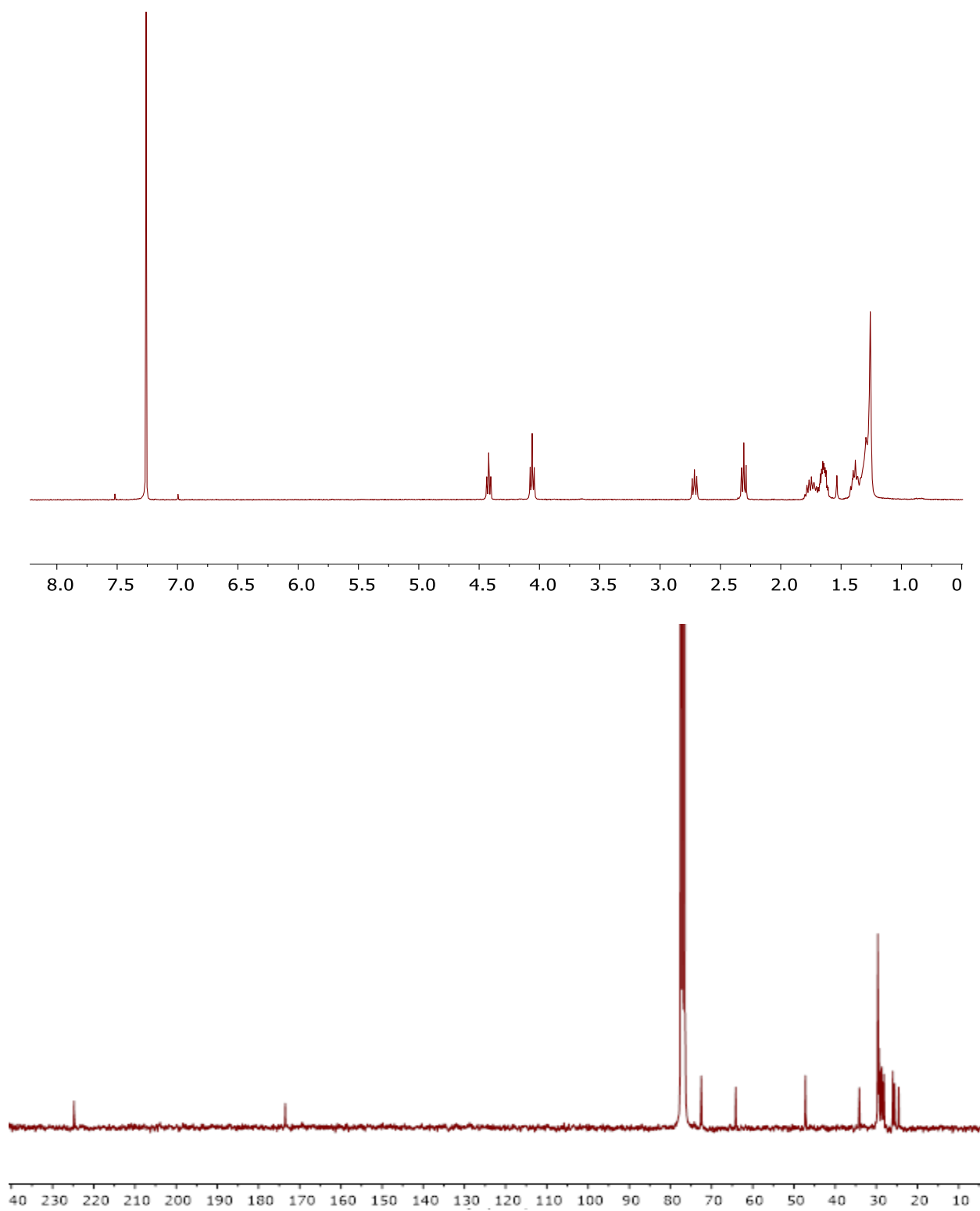


Figure S40. (Upper) ¹H NMR (CDCl₃, 400 MHz, ppm) spectrum of P(tnPDL-*b*-CL) (1:1). (Lower) ¹³C NMR (100 MHz, CDCl₃) spectrum of P(tnPDL-*b*-CL) (1:1).

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