

Electronic Supporting Information

A Delayed Curing ROMP Based Thermosetting Resin

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1. General Considerations

All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise specified. Solvents were purchased from Fisher Scientific and used without any further purification. The chromium(III) salen catalyst was synthesized according to a previous report.¹ Catalyst 4 ($\text{H}_2\text{IMes}\{(\text{H}_3\text{C})_2\text{N}-\text{C}_5\text{H}_4\text{N}\}_2\text{Cl}_2\text{Ru}=\text{CHPh}$) was synthesized according to literature procedures.²

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian U400, VXR500, or U500 spectrometer using residual solvent peaks as reference. For ^{31}P NMR, 85 % H_3PO_4 in a glass capillary was used as an external reference. MestReNova (Version 8.1) software was used to process all NMR spectra.

Gel Permeation Chromatography (GPC) was performed on a system equipped with an isocratic pump (Model 1260, Agilent Technology) at a flow rate of 1 mL min^{-1} and a DAWN HELEOS I MALLS detector (Wyatt Technology) and an Optilab rEX refractive index detector (Wyatt Technology). The lasers for both detectors were set to 658 nm. Separations were performed using serially connected size exclusion columns (10^2 \AA , 10^3 \AA , 10^4 \AA , 10^5 \AA , 10^6 \AA Phenogel columns, 5 \mu m , $300 \times 7.8 \text{ mm}$, Phenomenex). The mobile phase consisted DMF + 0.1M LiBr. Samples were filtered through a 0.45 \mu m PTFE filter before analysis. The absolute molecular weights and polydispersity of polymers were determined by using the dn/dc values calculated in the Astra software (Wyatt Technology, Version 6.1.1).

Differential scanning calorimetry (DSC) was conducted on a TA Instruments Q20 with a Liquid Nitrogen Cooling System. Tzero aluminum pans and lids were used to hold samples. Scans were conducted under nitrogen at a flow rate of 50 mL/min. Samples were run under a Heat/Cool/Heat program with heating and cooling rates set to $10 \text{ }^\circ\text{C min}^{-1}$ for T_g determination. The second heating curve was used to calculate T_g using TA Universal Analysis software. For cure exotherm, samples were quickly mixed, weighed, and placed into DSC pre-equilibrated at -20°C . Samples were then heated at a rate of $10 \text{ }^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was conducted on a TA Instruments Q50 under nitrogen using alumina sample pans at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. Dynamic mechanical analysis (DMA) was conducted on a TA Instruments Q800. Samples ($l = 38 \text{ mm}$, $w = 3 \text{ mm}$, $t = 1 \text{ mm}$) were clamped into the instrument and analyzed in tension mode. Samples were subject to an oscillatory strain of 1 Hz with an amplitude of 15 \mu m . Heating was performed at a rate of $3 \text{ }^\circ\text{C min}^{-1}$ until a temperature of $175 \text{ }^\circ\text{C}$ was achieved. All thermal data was processed using TA Universal Analysis (Version 4.5A). Viscosities were measured on a DHR-3 combined motor/transducer rheometer from TA Instruments with a 40 mm diameter and a 1.011 degree cone geometry. The temperature was held at $25 \text{ }^\circ\text{C}$ using a Peltier plate system. The materials were loaded and trimmed and the geometry was brought to the final gap of 30 \mu m . Controlled-velocity tests ramping up and down the shear rate from 1 to 10 s^{-1} revealed no thixotropic or shear-thinning behavior. Final measurements were performed at 3 s^{-1} for a duration of 60 seconds. The average viscosity values were reported.

2. Procedures

A. General Procedures

Polymerization Kinetics of NBMe

In a glass vial was placed 200 mg of NBMe. For polymerizations containing DMAP, 23 μL of a 10 mg mL^{-1} solution in CDCl_3 was added. Then, CDCl_3 was added, followed by 64 μL of a 25 mg mL^{-1} solution of catalyst 1a to bring the total concentration of NBMe to 1.0 M. Samples which required heating (55 $^\circ\text{C}$) were placed in an aluminum heating block. At various times during the reaction, 50 μL of solution was removed and placed into 650 μL of a 0.75 % (v/v) solution of ethyl vinyl ether in CDCl_3 . Conversion was determined by comparing integrations of the olefin protons appearing near δ 6.3 (monomer) and δ 5.5 (polymer).

Rate constants were determined by plotting $\ln([\text{NBMe}])$ vs. time and dividing the resulting slope by [1a] to yield second order rate constants. Due to the difficulty in determining the initiation efficiency of 1a during the course of the reaction, rate constants assume the initiation to be 100 % complete and thus underestimate the value of the true rate constants.

Gel Time and Conversion of NBMe in Bulk

Polymerizations were conducted by adding desired amount of DMAP in DCM (50 mg mL^{-1}) into a vial and allowing to evaporate. NBMe (250 mg) was then added and stirred in the vial to dissolve DMAP. Catalyst 1a was then added in xylenes (50 mg mL^{-1}) and reaction allowed to stand, inverting vials periodically to assess gelation (when inverted samples support their own weight). Conversion of a separate batch of samples was assessed after heating samples to 100 $^\circ\text{C}$ for 1h, and allowing samples to sit overnight. Small samples were then cut from the polymers and dissolved in CDCl_3 for ^1H NMR analysis.

Swelling of Polymers

Polymer samples with mass of \sim 250 mg were placed into 20 mL toluene and allowed to sit at room temperature for 48 h. Samples were removed, gently dabbed with a Kimwipe to remove excess solvent, and weighed. Swelling is defined as:

$$\text{Swelling (\%)} = \frac{M_f - M_0}{M_0} \times 100$$

where M_f is the final mass of the swollen sample and M_0 is the initial mass of the sample.

Gel Fraction

Polymer samples were placed in 20 mL chloroform and heated at 55 $^\circ\text{C}$ for 72 h, replacing the solution with fresh chloroform every 24 h. Samples were then dried in a vacuum oven for 72 h at 110 $^\circ\text{C}$ until constant mass. Gel fraction is defined as:

$$\text{Gel Fraction} = \frac{M_f}{M_0}$$

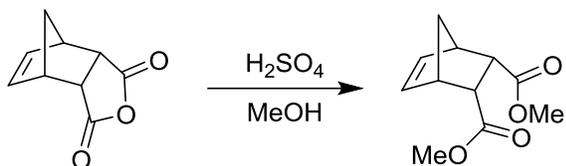
where M_f is the final mass of the dried sample and M_0 is the initial mass.

ROMP Thermosetting Polymerization

Polyester crosslinker (NB-CL) and NBMe were mixed and heated with a heat gun to completely dissolve polyester (once dissolved this formulation remains stable). After cooling to ambient temperature, catalyst 1a (50 mg mL^{-1} in xylenes) was prepared by briefly sonicating and then mixed with the resin for several minutes to ensure a homogenous solution. The resin was poured into molds and cured by heating at $100 \text{ }^\circ\text{C}$ for 1 h.

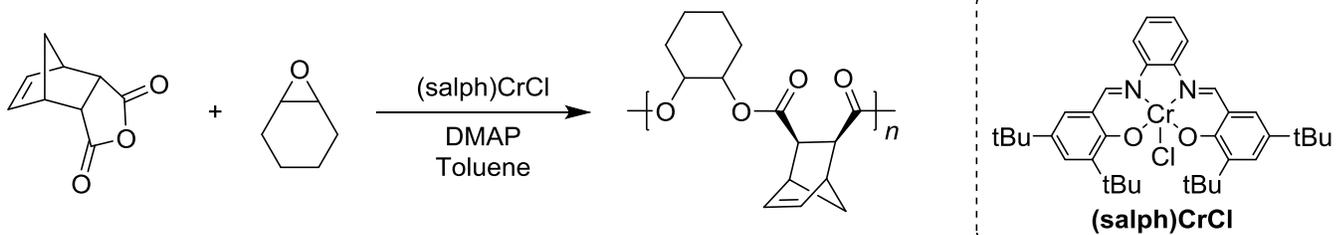
B. Synthetic Procedures

5-Norbornene-2,3-dicarboxylic acid dimethyl ester



The procedure was modified slightly from a previous report.³ In a 1L round bottom flask was mixed *endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (120 g, 731 mmol), methanol (600 mL), and conc. sulfuric acid (1 mL). The reagents were refluxed for 24 h. After cooling to room temperature, 100 mL sat. NaHCO₃ was added to quench the reaction, and the solvent removed *in vacuo* to yield a cloudy paste. Water (200 mL) and sat. NaHCO₃ (100 mL) was added to the residue, which was extracted with 3 x 200 mL diethyl ether. The organic layers were combined, washed with brine, dried over Na₂SO₄, and evaporated to yield a clear colorless oil (131 g, 623 mmol, 85 % yield). **¹H NMR** (500 MHz, CDCl₃): δ 6.26 (t, *J* = 1.2 Hz, 2H), 3.61 (s, 6H), 3.29 (m, 2H), 3.16 (s, 2H), 1.47 (dt, *J* = 8.7, 2.2 Hz, 1H), 1.32 (d, *J* = 9.0 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃): δ 173.01, 134.96, 51.60, 48.75, 48.11, 46.32. **HRMS** (ESI) *m/z* calculated for C₁₁H₁₅O₄ [M+H]⁺: 211.0970, found 211.0980.

poly(*endo*-norbornene anhydride-*alt*-cyclohexene oxide)



The procedure was modified slightly from a previous report.⁴ In a 100 mL round bottom flask was placed *endo* bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (23.9 g, 146 mmol), cyclohexene oxide (14.8 mL, 146 mmol), 4-dimethylaminopyridine (70 mg, 0.573 mmol), *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene chromium chloride (salph)CrCl¹ (160 mg, 0.256 mmol), and toluene (38 mL). Reaction was purged with N₂ for 15 min, then refluxed under N₂ overnight. Solution was diluted in an equal volume dichloromethane, and precipitated into ~700 mL hexanes. Polymer was dried in a vacuum over at 100 °C for 48 h yielding 37.8 g light orange powder (99 % yield). *M_n* = 8.0 kDa; PDI = 1.62. **¹H NMR** (500 MHz, CDCl₃): δ 6.16 (m, 2H), 4.77 (m, 2H), 3.23 (m, 4H), 1.98 (s, 2H), 1.66 (s, 2H), 1.43 (s, 2H), 1.30 (s, 4H).

3. Supplementary Figures

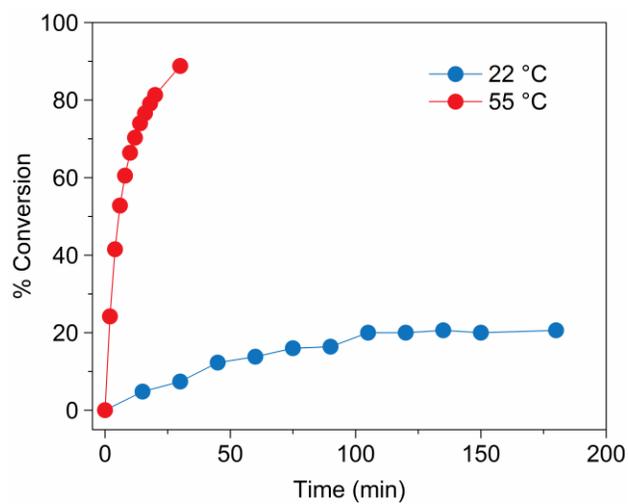


Fig. S1. Conversion of NBMe in CDCl_3 initiated with 4 at various temperatures. $[\text{NBMe}] = 1.0\text{M}$, $[4] = 2.0\text{ mM}$.

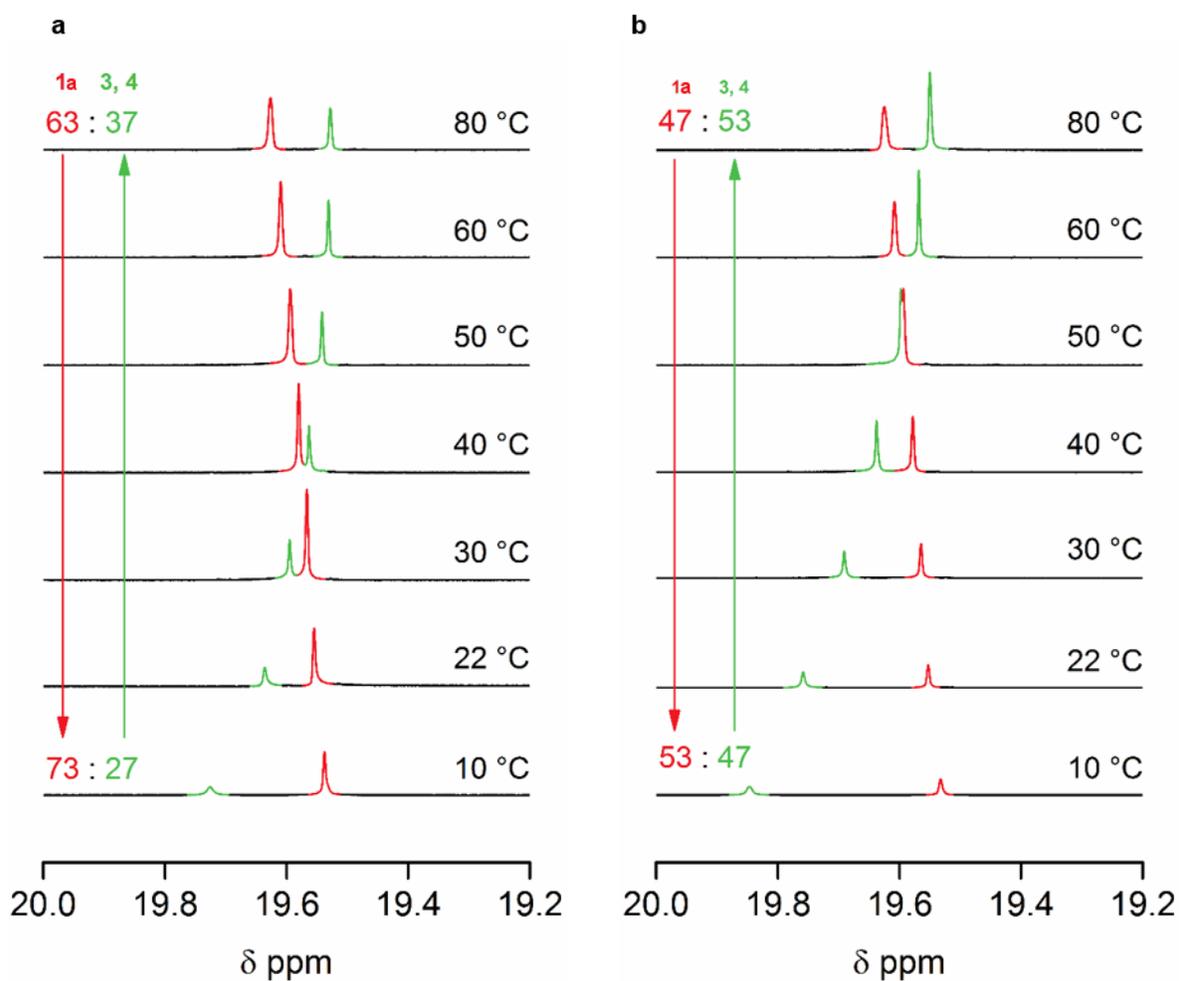
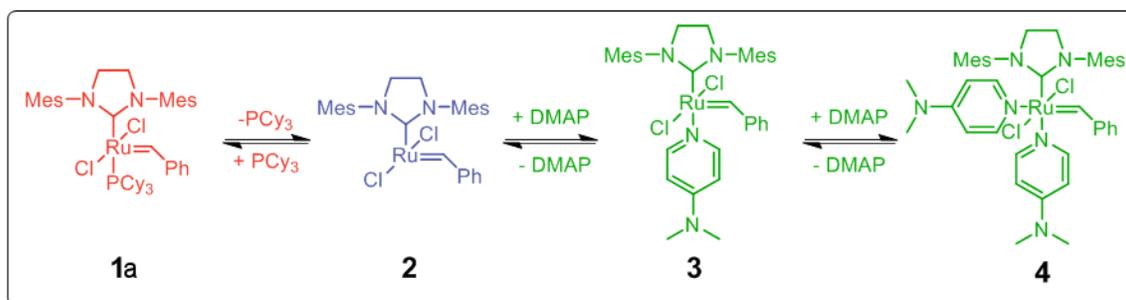


Fig. S2. ¹H NMR of catalyst 1a with (a) 1 equiv DMAP or (b) 2 equiv DMAP in toluene-d₈ at various temperatures. [1a] = 0.025 M. Molar ratios of catalyst species are given at 10 °C and 80 °C. The upfield shift of the green resonance with increasing temperature suggests dissociation of one DMAP ligand, shifting the equilibrium between 3 and 4 towards the pentacoordinate ruthenium complex, 3.

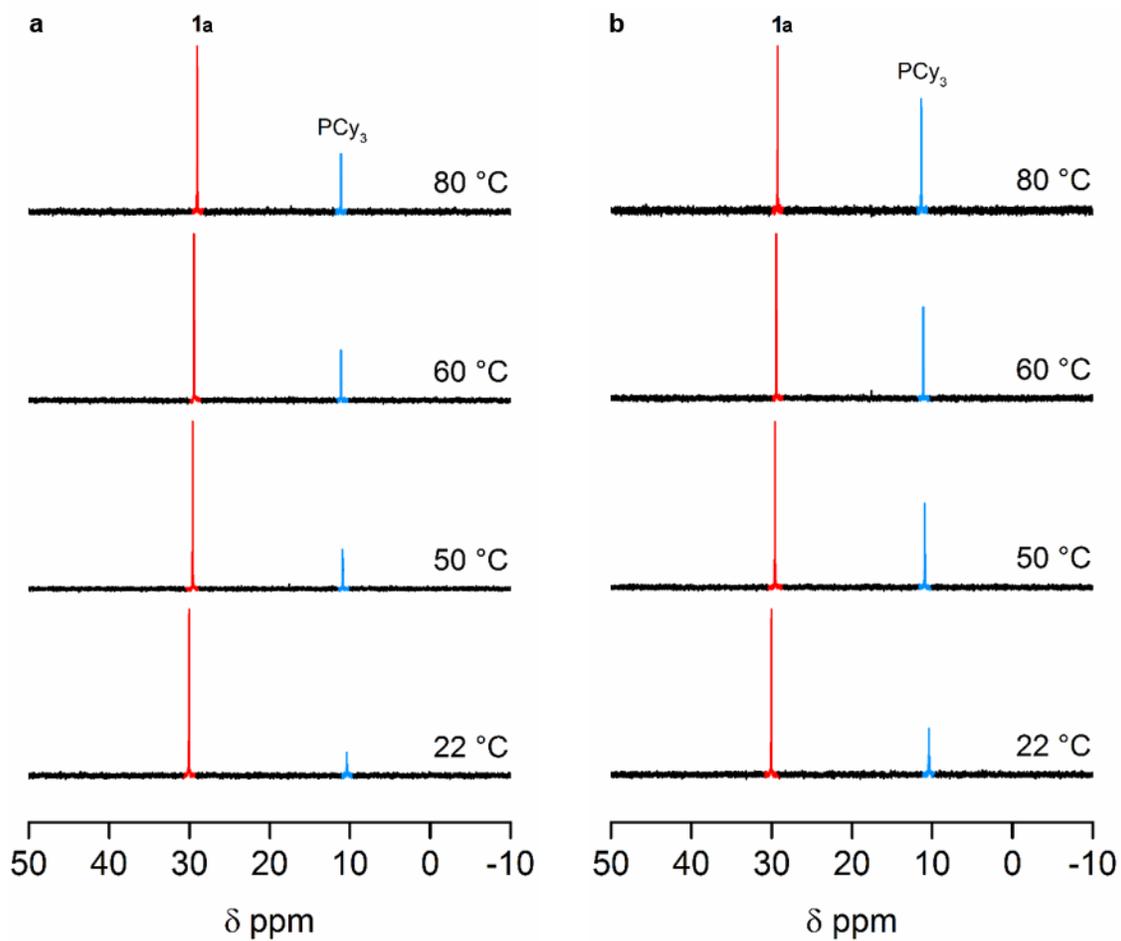
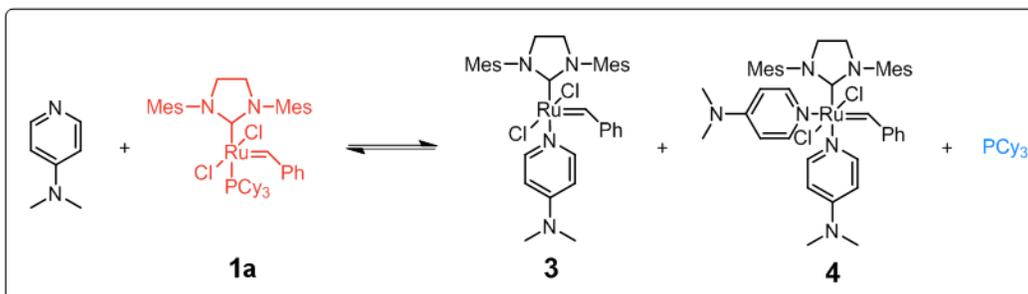


Fig. S3. ^{31}P NMR of catalyst 1a with (a) 1 eq. and (b) 2 eq. DMAP in toluene- d_8 at various temperatures. $[1a] = 0.025$ M.

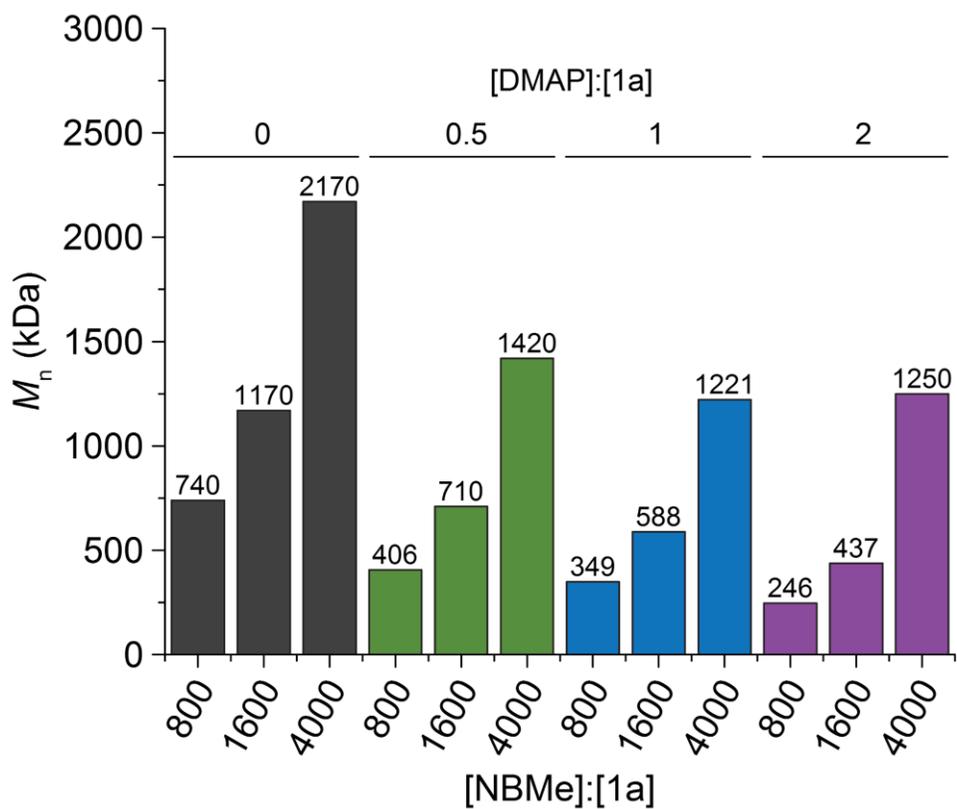


Fig. S4. Molecular weight dependence of PNBMe when polymerized in bulk at 100 °C for 1h at varying [NBMe]:[1a]:[DMAP] ratios. PDI values are typically < 1.1.

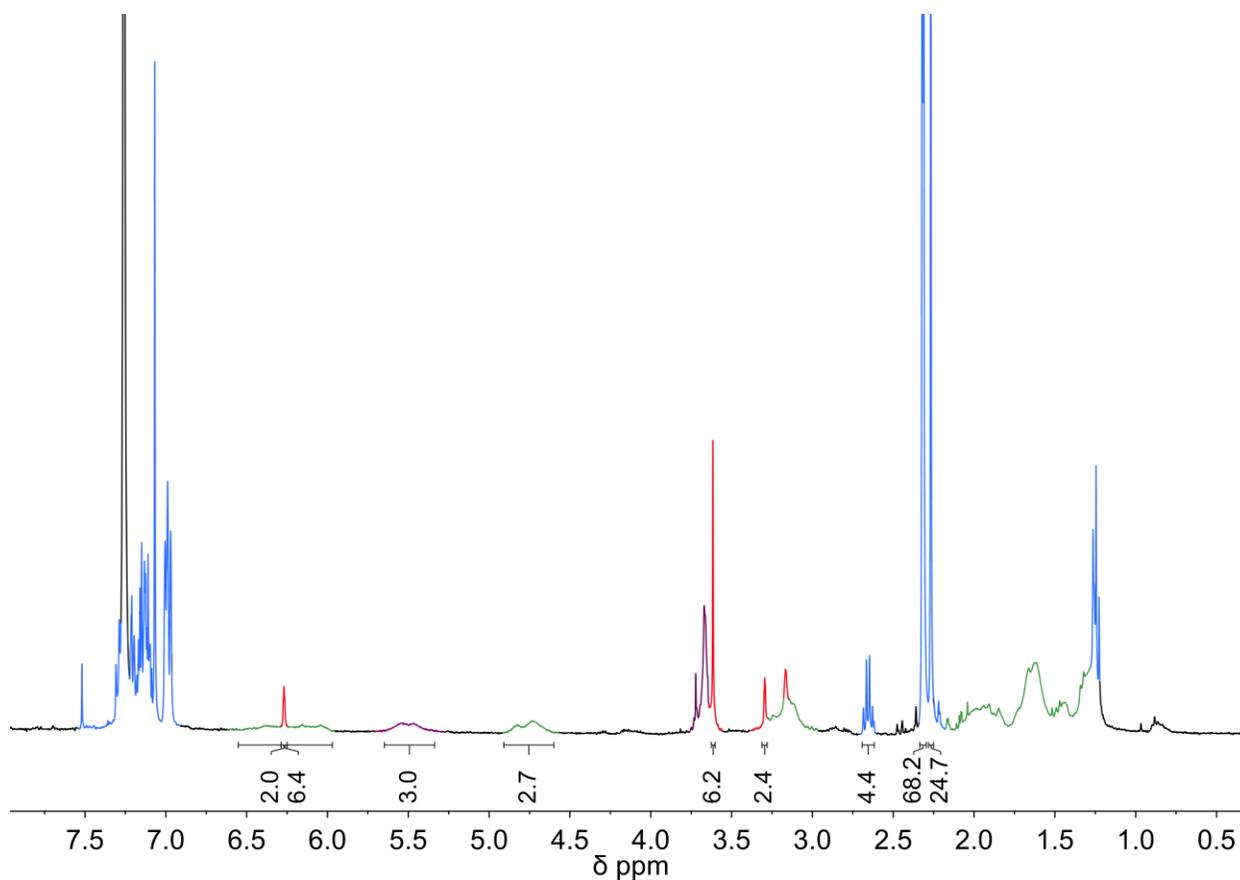
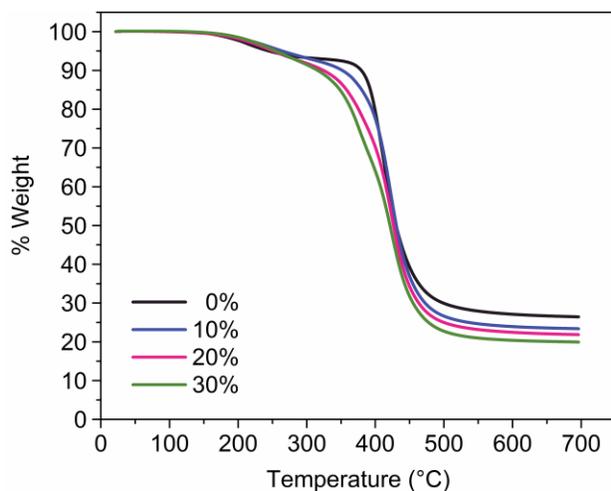


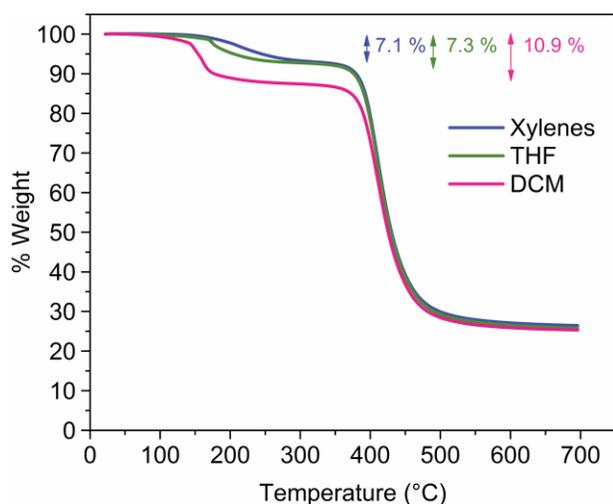
Fig. S5. ^1H NMR in CDCl_3 of chloroform soluble fraction of 20 wt% NB-CL thermoset. Blue indicates xylenes (83%) or ethylbenzene (6%), red indicates unreacted NBMe (3%), green indicates NB-CL (4%), and purple refers to PNBMe (4%). Percentages refer to mol%.



NB-CL wt%	T_d ($^{\circ}\text{C}$) ^a
0%	389
10%	389
20%	369
30%	355

^a Onset point of degradation

Fig. S6. Thermal gravimetric analysis (TGA) of thermosets composed of NBMe containing varying wt% of NB-CL.



Sample	T_d (°C) ^a	Mass Solvent (wt%) ^b
Xylenes	389	8.0
THF	387	8.2
DCM	386	11.8

^a Onset point of degradation ^b Determined from ¹H NMR

Fig. S7. TGA of PNBMe synthesized via bulk polymerization using a solution of 1a (50 mg mL⁻¹) in a variety of solvents to demonstrate 1st stage of weight loss is due to solvent loss. [NBMe]:[1a] = 800:1.

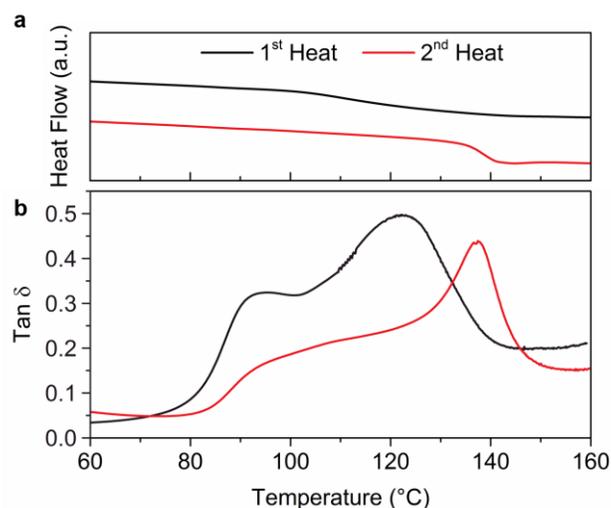


Fig. S8. (a) Second heating DSC traces of PNBMe with a maximum temperature of 175 °C (black) and 300 °C (red). $T_g = 111$ °C (black); $T_g = 138$ °C (red). (b) DMA of PNBMe on 1st heating to 175 °C (black) then slowly cooling to 30 °C, and reheating sample to 175 °C again (red).

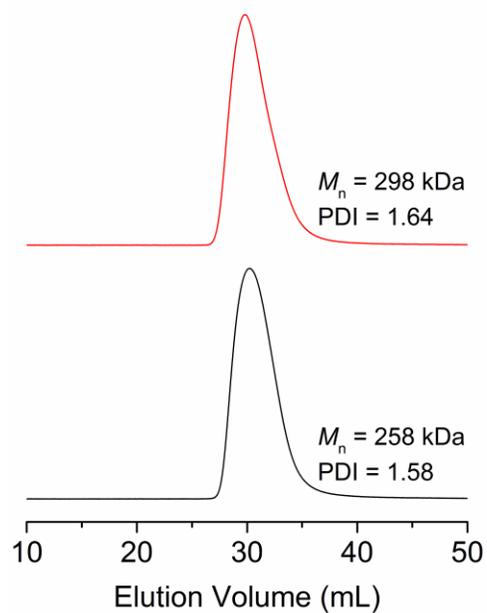


Fig. S9. Normalized light scattering GPC traces from PNBMe samples before (black) and after (red) DMA analysis.

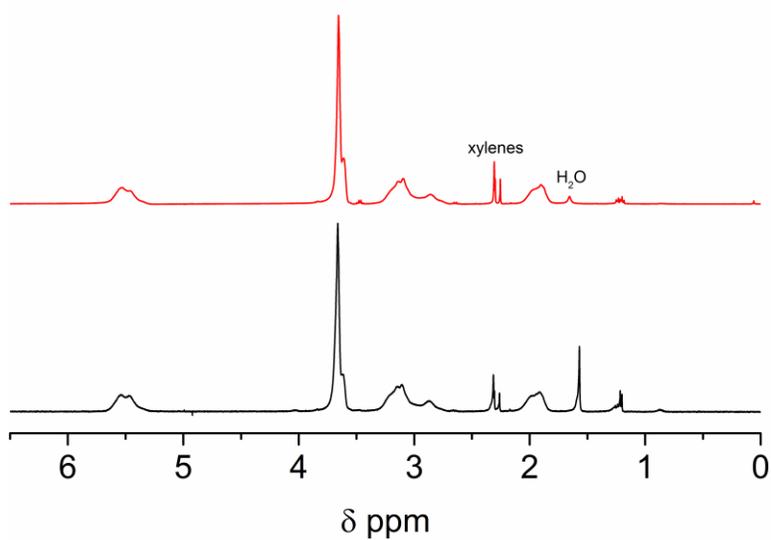
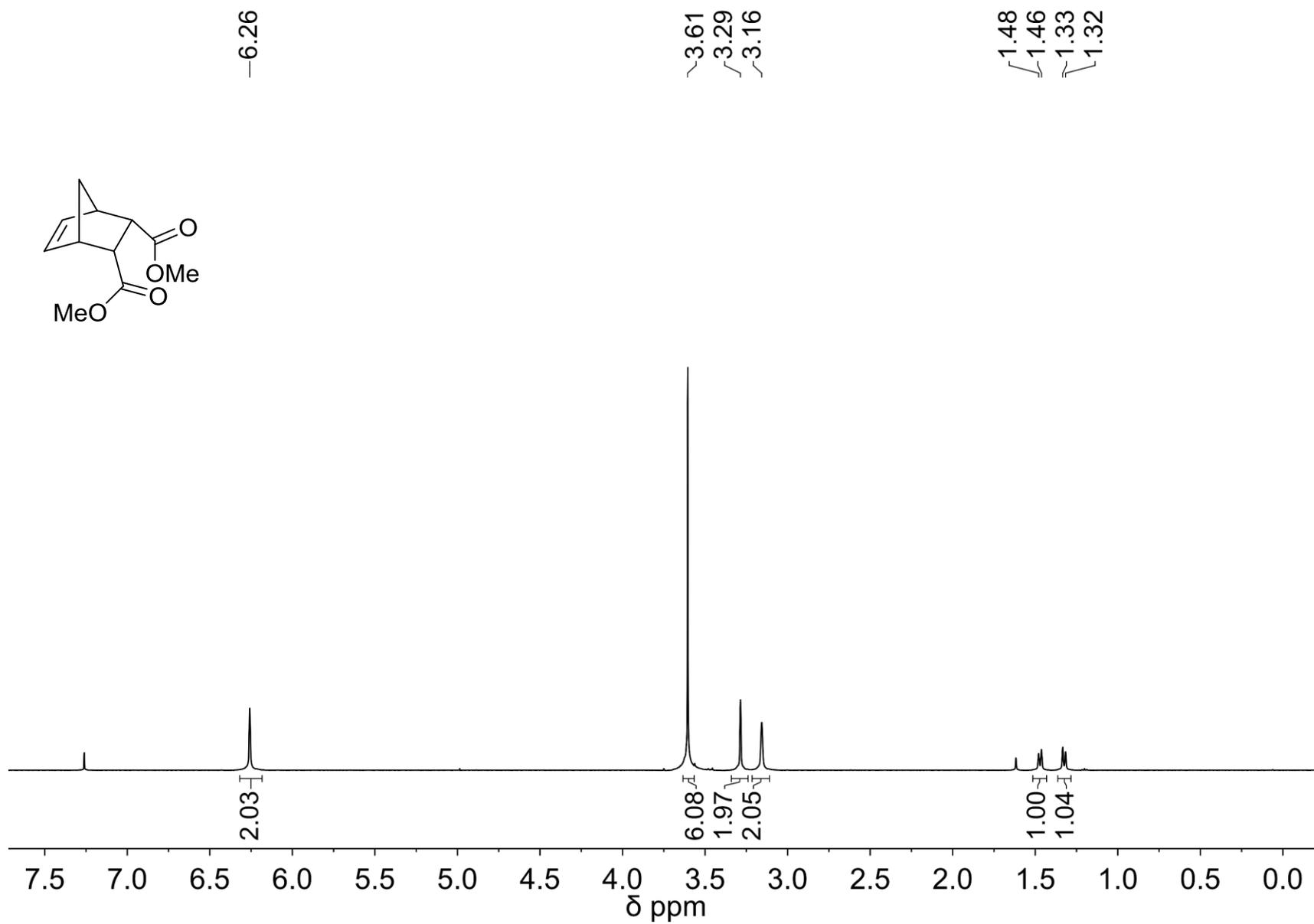
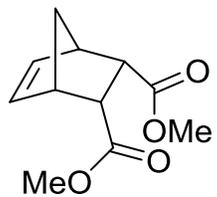
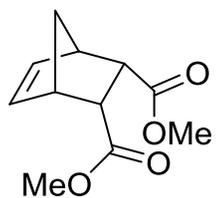


Fig. S10. ^1H NMR analysis of PNBMe samples before (black) and after (red) DMA analysis.

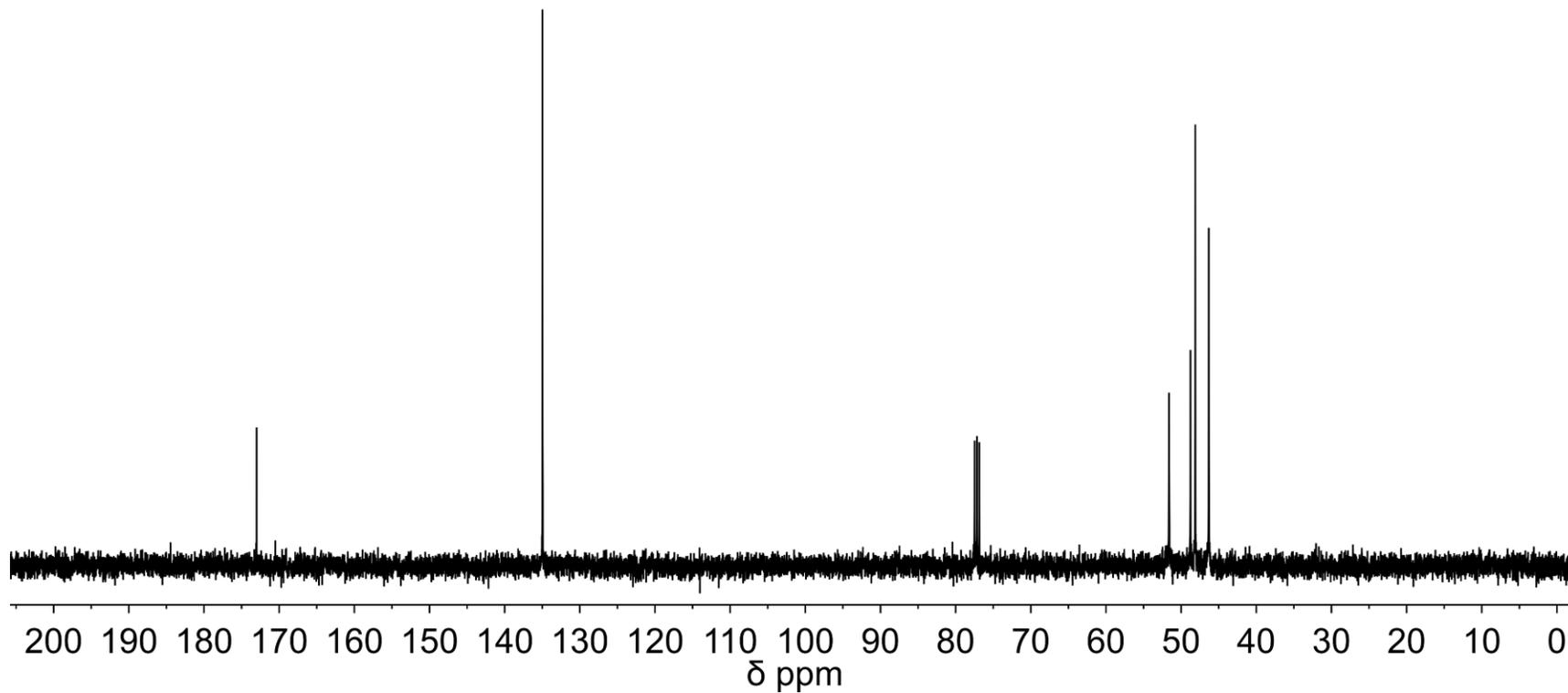


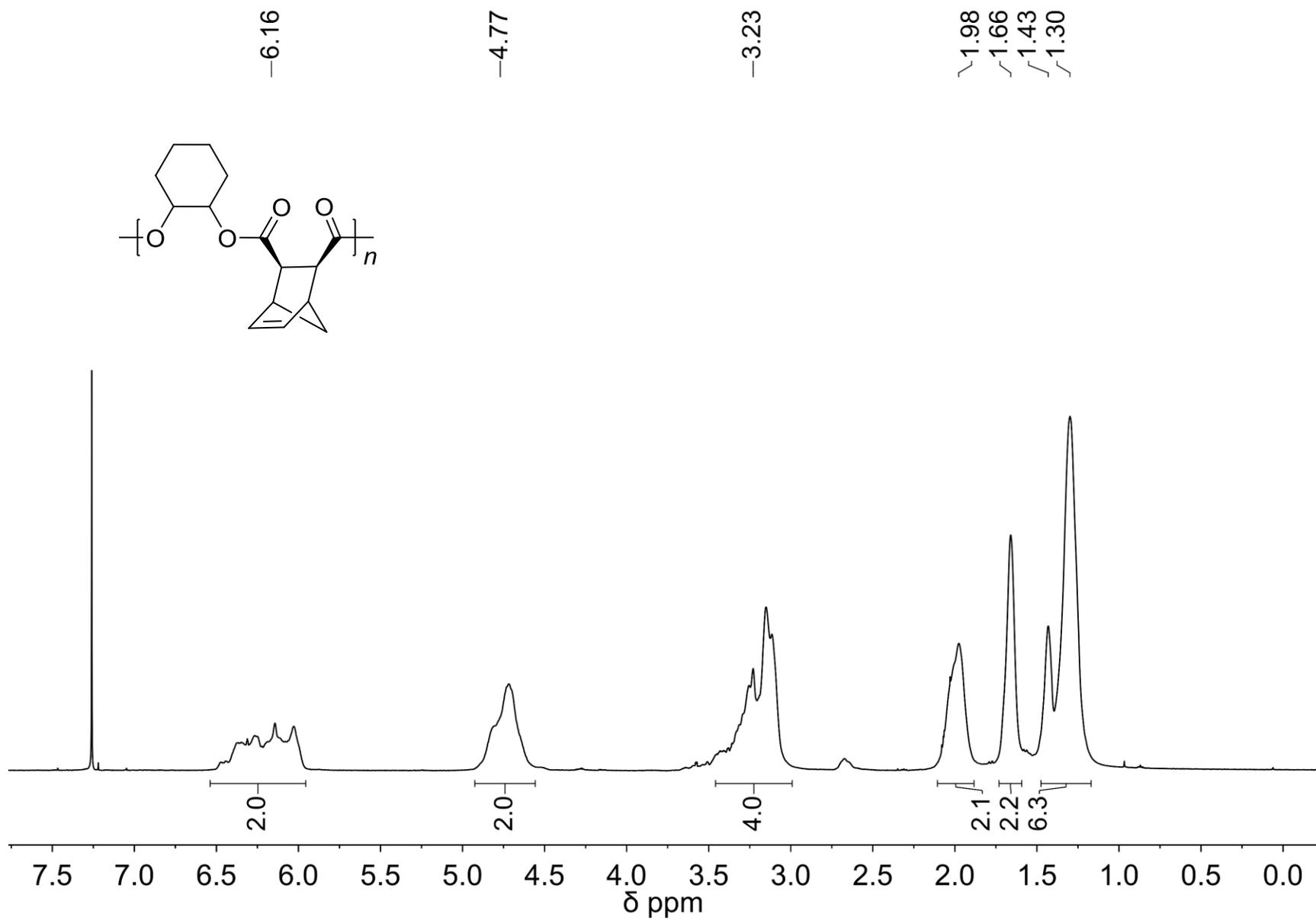


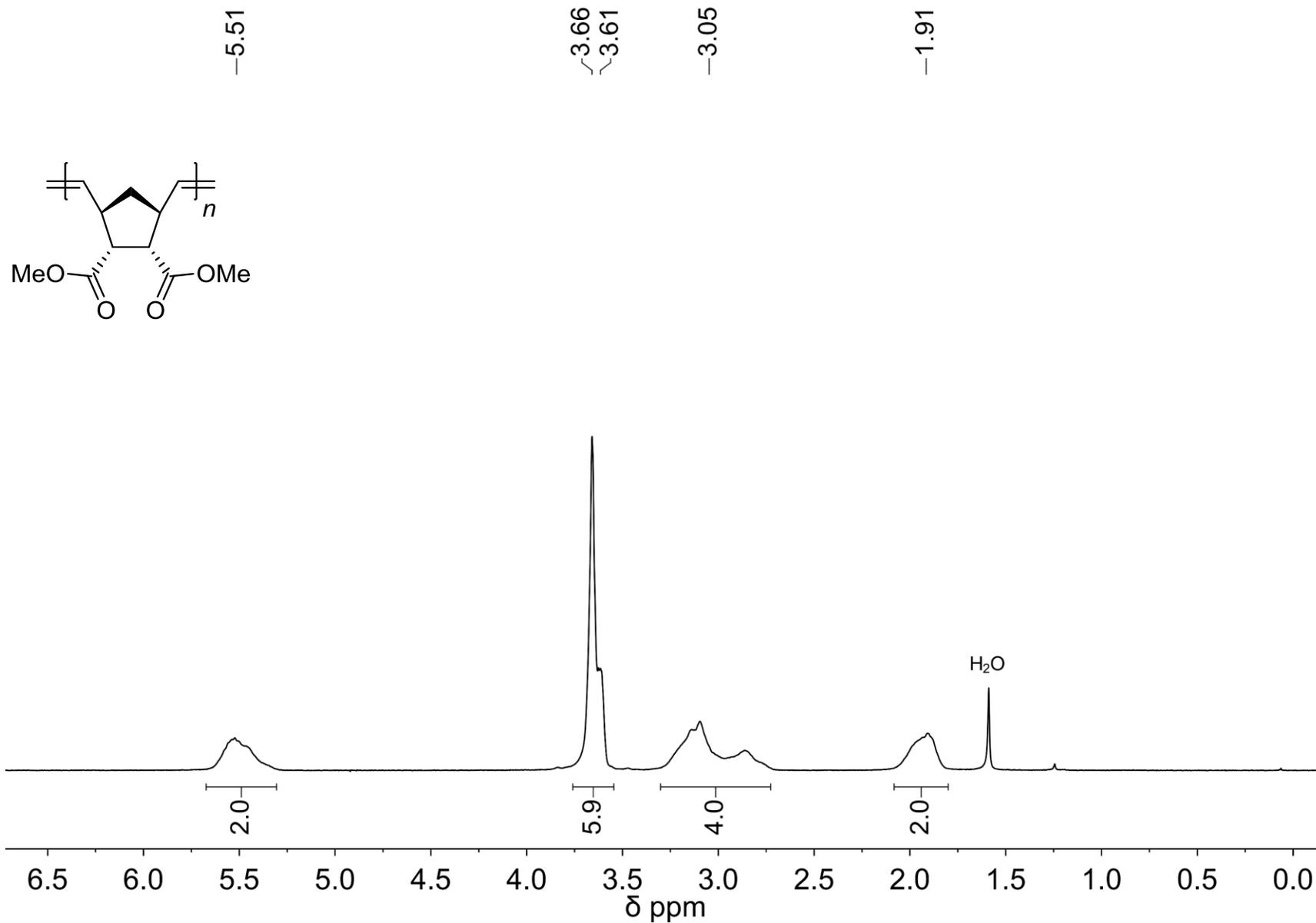
-173.01

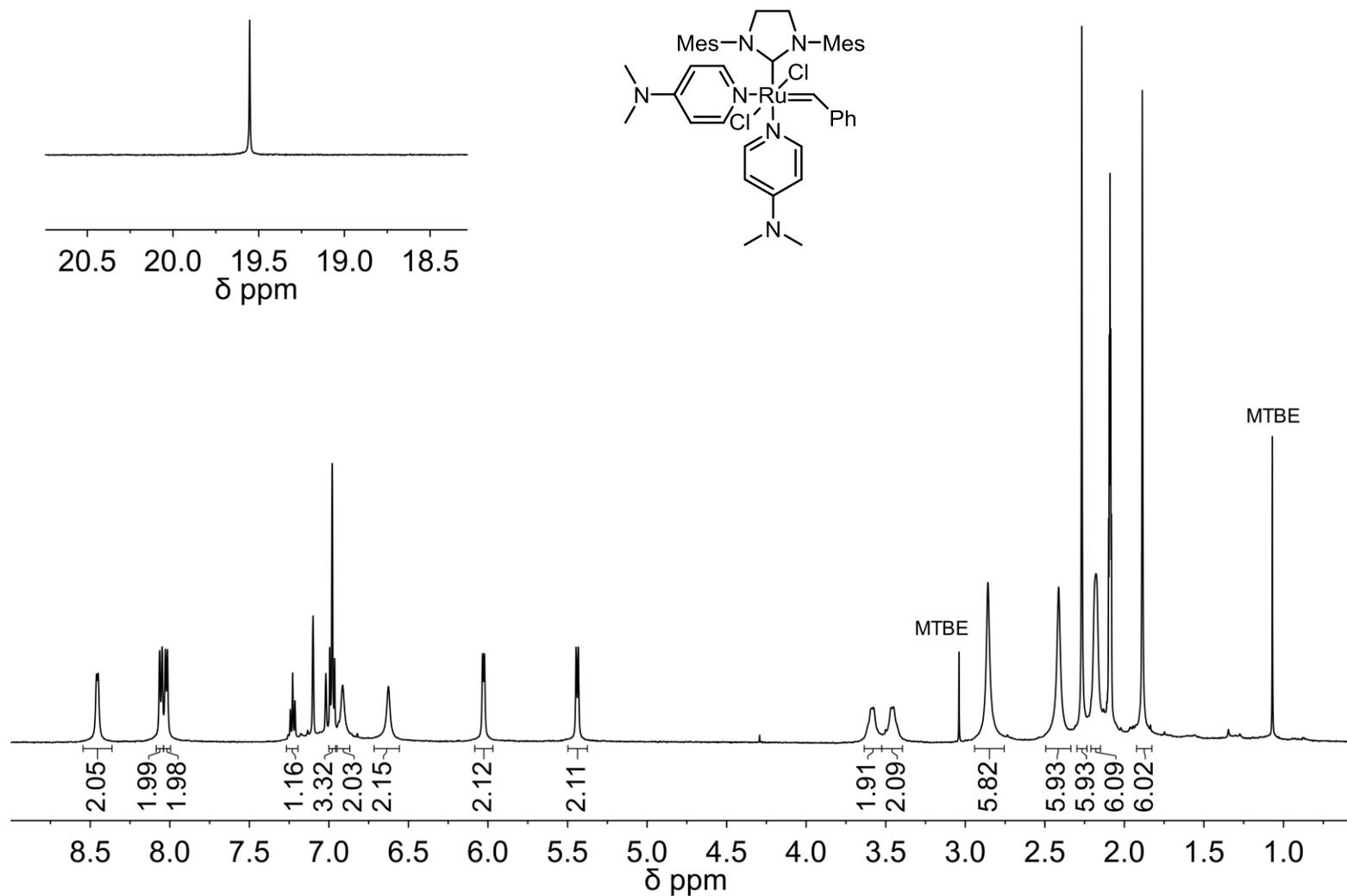
-134.96

51.60
48.75
48.11
46.32









^1H NMR (500 MHz, d_8 -toluene, saturated solution): δ 19.55 (s, 1H), 8.46 (d, J = 4.9 Hz, 2H), 8.06 (d, J = 7.6 Hz, 2H), 8.02 (d, J = 6.7 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 6.99 (t, J = 7.8 Hz, 2H), 6.91 (br s, 2H), 6.63 (br s, 2H), 6.03 (d, J = 5.8 Hz, 2H), 5.44 (d, J = 6.9 Hz, 2H), 3.58 (d, J = 6.4 Hz, 2H), 3.46 (d, J = 7.4 Hz, 2H), 2.86 (br s, 6H), 2.41 (br s, 6H), 2.27 (s, 6H), 2.18 (br s, 6H), 1.89 (s, 6H).

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