

Supporting Information for

Processable Epoxy-Telechelic Polyalkenamers and Polyolefins for Photocurable Elastomers

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Table of Contents

Materials	3
Characterization	3-6
Representative Synthetic Methods	
Diepoxy-telechelic polyalkenamer (P-5)	6-7
(<i>Z</i>)-dibenzyl oct-4-ene-1,8-diyl bis(carbonate) (CTA 2)	7-8
Dicarboxybenzyl-telechelic polyalkenamer (P-5-Cbz)	8-9
Dihydroxy-telechelic polyolefin (PH-5-OH)	9
Diepoxy-telechelic polyolefin (PH-5)	10-11
Supplementary Figures and Tables	11-29
NMR and FTIR Spectra	30-41
References	42

Materials

All chemicals and reagents were purchased from commercial suppliers and used without further purification. 3-Ethyl-*cis*-cyclooctene,¹ (*Z*)-1,4,-bis(oxiran-2-ylmethoxy)but-2-ene,² and (*Z*)-Oct-4-ene-1,8-diol³ were prepared using methods previously reported. Sylanto-7MS was generously donated by Synthos S.A. Anhydrous THF and DCM were obtained from a solvent purification system (Pure Process Technology). Anhydrous chloroform used for ROMP was washed with deionized water (to remove ethanol inhibitor), distilled over calcium hydride, and stored over 4 Å molecular sieves. TLC analysis was conducted using glass-backed thin-layer silica gel chromatography plates (60 Å, 250 µm thickness, F-254 indicator). Column chromatography was performed using Sigma-Aldrich 70-230 mesh, 60 Å pore diameter silica gel.

Characterization

Nuclear magnetic resonance (NMR): Number-average molecular weight (M_n) was determined by ¹H-NMR end group analysis assuming $F = 2$. Regioregularity, or head-to-tail content, was determined by integration of head-to-tail, head-to-head, and tail-to-tail olefinic proton peaks according to the assignments made by Kobayashi et al.¹ 1D- (¹H, ¹³C) and 2D- (COSY, HSQC, HMBC) spectra were recorded on either an AM-400, AV-500, or HD-500 Bruker Avance III spectrometer. Chemical shifts (δ values) are reported in parts per million and referenced to the residual solvent signal (CDCl₃ ¹H singlet = 7.26, ¹³C triplet = 77.16). Characteristic splitting patterns due to spin-spin coupling are identified as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sep = septet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, dq = doublet of quartets, brs = broad singlet, app = apparent. All coupling constants are measured in hertz (Hz).

Size exclusion chromatography (SEC): THF-SEC was performed using an Agilent 1260 series instrument (1.0 mL/min, 25 °C). Separation was achieved using a single Waters Styragel guard column and three successive Waters Styragel columns (HR6, HR4, and HR1) packed with rigid 5 μm styrene-divinylbenzene particles. Number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity (\mathcal{D}) were determined using a Wyatt Technology DAWN Heleos II multiangle laser light scattering (MALS) detector and a Wyatt OPTILAB T-rEX refractive index detector (based on a 10-point calibration curve with polystyrene standards). CHCl_3 -SEC was performed using an HP/Agilent 1100/1200 series instrument (1.0 mL/min, 35 °C). Separation was achieved using a single Waters Styragel guard column and two successive Malvern VISCOTEK columns (I-MBMMW-3078) packed with rigid 10 μm styrene-divinylbenzene particles (mixed bed). Number-average molecular weight (M_n) and dispersity (\mathcal{D}) were determined using an HP 1047A refractive index detector (based on a 10-point calibration curve with polystyrene standards).

Thermal analyses: Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 under nitrogen atmosphere at a heating rate of 10 °C/min. Differential Scanning Calorimetry (DSC) was performed on a TA Instruments Discovery DSC calibrated with an indium standard using hermetically-sealed, aluminum T-zero pans. Scans were conducted under nitrogen atmosphere at a heating rate of 10 °C/min.

Photorheology: Photorheology was conducted on a TA Instruments DHR-3 rheometer equipped with a UV-curing accessory, 20 mm quartz lower parallel plate, 20 mm aluminum upper parallel

plate, and unfiltered Excelitas Omnicure S2000 high-pressure mercury vapor lamp (320-500 nm, 0.7 W/cm²). Data was collected during a steady state period (60 s) with 0.1% strain and 1.0 Hz in the “Fast Sampling” mode, after which point the lamp shutter was opened and samples exposed for the remainder of the experiment. Axial force was minimized by making slight adjustments in gap distance. Strain sweeps (0.1 to 100%) were conducted before and after curing to ensure a linear response prior to frequency sweeps (0.1 to 100 rad/s). Gel points were analyzed using the Modulus Crossover function within the TRIOS software and plateau moduli are reported as an average of the final 30 s during curing.

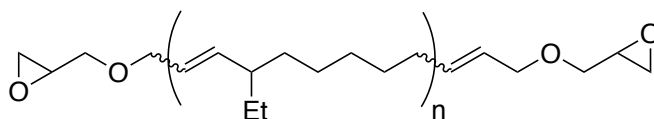
Gel fraction: Approximately 80–100 mg of each cross-linked sample was immersed in DCM (20 mL) and left stirring 48 h. The solvent was decanted and swollen samples dried in a vacuum oven at 60 °C for 24 h. The dried gel mass was measured and gel fraction calculated by taking the ratio of final mass to initial mass.

Oscillatory shear rheology: Measurements were performed on a TA Instruments Rheometric Series ARES Classic using 25 mm diameter parallel plates under a nitrogen atmosphere. Prior to performing frequency sweeps, a strain sweep was performed from 0.1 to 10% and a linear response in the signal was observed. The P-25 sample was then equilibrated at the desired temperature for 10 min before performing a frequency sweep from 0.01 to 100 rad/s at an oscillating strain of 1.0% for the polyalkenamer and 0.1% for the polyolefin. Each sweep was performed at: 23, 0, –15, –25, –35, –45 °C for polyalkenamer and 25, 0, –15, –30, –40, –50 °C for polyolefin. Time–temperature superposition was then used to generate a master curve (reference temperature of 273 K). The plateau modulus (G_N) was defined as the shear storage modulus (G') at $\tan \delta_{\min}$. Entanglement

molar mass (M_e) was calculated from the G_N using the following relationship: $M_e = \rho RT \cdot (G_N)^{-1}$, where ρ is the sample density (0.862 ± 0.007 g/cm³ for polyalkenamer and 0.869 ± 0.004 g/cm³ for polyolefin at 295 K, measured using Archimedes' principle with a density determination kit for Excellence XP/XS analytical balances, Mettler Toledo), T is the absolute temperature, and R is the universal gas constant.

Tensile testing: Measurements performed using a Shimadzu Autograph AGS-X series instrument to conduct uniaxial extension measurements at room temperature with rectangular-shaped specimens [ca. 1 mm (T) x 2 mm (W) with a gauge length of ca. 20 mm]. Rubber grips were used and the test speed was set to a ramp rate of 5 mm·min⁻¹. The data obtained were analyzed using the *Trapezium* software. The extension to break tests were performed with 3 replicates per crosslinked elastomer sample, and the values are reported as a range of data for each specimen.

Representative procedure for synthesis of diepoxy-telechelic polyalkenamer (P-5)

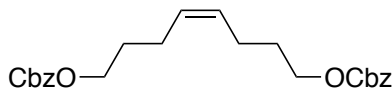


3-EtCOE (20.8 g, 150 mmol), (*Z*)-1,4,-bis(oxiran-2-ylmethoxy)but-2-ene (820 mg, 4.1 mmol), and *p*-BQ (544 mg, 5.0 mmol) were placed into a two-neck, 250 mL round bottom flask containing a Teflon-coated magnetic stir bar and then dissolved in anhydrous chloroform (80 mL, 1.8 M). Several quick vacuum-argon cycles were performed so as to prevent loss of volatile reagents. The system was further sparged with argon for 30 minutes under vigorous stirring and then the flask was immersed in an oil bath preset to 40 °C. A ruby solution of G2 catalyst (42.3 mg, 0.05 mmol) in chloroform (2 mL) was then injected into the reaction. Following 2 h, the reaction was quenched

with ethyl vinyl ether (2.9 mL, 30 mmol) and left stirring an additional 20 min. The crude polyalkenamer was isolated by precipitation into methanol at $-78\text{ }^{\circ}\text{C}$ and left stirring 1 h, after which methanol was decanted. The resulting deep-green, viscous polymer was dissolved in hexane and left stirring with 20 wt. % activated charcoal. The charcoal was removed via filtration and process repeated 1-2 more times until a colorless solution resulted. Butylated hydroxytoluene (BHT, 10 mg) was added and the solvent removed via rotary evaporation. Further drying in a vacuum oven at $60\text{ }^{\circ}\text{C}$ overnight afforded 17.0 g of a colorless, transparent, slightly viscous prepolymer (79% yield).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) = 5.31 (dt, $J = 15.2, 6.7$ Hz, H5), 5.07 (dd, $J = 15.2, 8.8$ Hz, H6), 3.96 4.07 (m, H4), 3.68 (ddd, $J = 11.4, 3.2, 1.8$ Hz, H3), 3.40 (ddd, $J = 11.4, 5.8, 2.1$ Hz, H3'), 3.13-3.18 (m, H2), 2.80 (dd, $J = 4.2, 4.9$ Hz, H1), 2.61 (dd, $J = 5.0, 2.7$ Hz, H1'), 1.92-2.04 (m, H12), 1.70-1.82 (m, H7), 1.08-1.46 (m, H8-11,13), 0.82 (t, $J = 7.5$ Hz, H14); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ (ppm) = 139.6, 134.8, 130.4, 126.0, 72.3, 70.4, 51.0, 44.7, 44.6, 44.4, 35.4, 32.8, 30.0, 29.4, 28.4, 27.3, 11.9. FTIR (neat, cm^{-1}): 2958, 2922, 2852, 1741, 1460, 1377, 1303, 1096, 967, 847, 776, 724.

Representative procedure for synthesis of (*Z*)-dibenzyl oct-4-ene-1,8-diyl bis(carbonate)

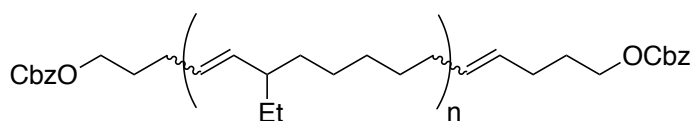


(*Z*)-oct-4-ene-1,8-diol (6.3 g, 44 mmol), 4-dimethylaminopyridine (1.07 g, 8.74 mmol), pyridine (21.0 mL, 261 mmol), and 180 mL dichloromethane (0.2 M) were added to a 1 L round bottom flask containing a Teflon-coated magnetic stir bar. The reaction mixture was cooled to $0\text{ }^{\circ}\text{C}$, and benzyl chloroformate (25.0 mL, 175 mmol) was added to the flask slowly by syringe over 20 minutes. After 18 hours, the reaction mixture was quenched with hydrochloric acid (300 mL, 4

M). The aqueous layer was extracted with diethyl ether (3 x 100 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated by rotary evaporation. The product was purified by silica gel column chromatography (5% to 10% ethyl acetate/hexane) to give 11.4 g of a yellow oil (63% yield).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) = 7.29-7.41 (m, 10H), 5.35-5.41 (m, 2H), 5.15 (s, 4H), 4.13 (t, J = 6.6 Hz, 4H), 2.07-2.14 (m, 4H), 1.71 (tt, J = 7.6, 6.7 Hz, 4H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ (ppm) = 155.3, 135.4, 129.5, 128.7, 128.6, 128.5, 69.6, 67.7, 28.6, 23.4.

Representative procedure for synthesis of dicarboxybenzyl-telechelic polyalkenamer (P-5-Cbz)

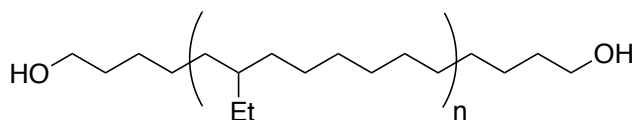


3-EtCOE (15.08 g, 109 mmol) and (*Z*)-dibenzyl oct-4-ene-1,8-diyl bis(carbonate) (1.29 g, 3.1 mmol) were filtered through basic alumina and placed into a two-neck, 250 mL round bottom flask containing a Teflon-coated magnetic stir bar and then dissolved in anhydrous chloroform (58 mL, 1.9 M). Several quick vacuum-argon cycles were performed so as to prevent loss of volatile reagents. The system was further sparged with argon for 20 minutes under vigorous stirring and then the flask was immersed in an oil bath preset to 40 °C. A ruby solution of G2 catalyst (22.9 mg, 0.027 mmol) in chloroform (2 mL) was then injected directly into the reaction. Following 2.5 h, the reaction was quenched with ethyl vinyl ether (2 mL, 21 mmol) and left stirring an additional 30 min. The crude polyalkenamer was isolated by precipitation into methanol and left stirring 1 h, after which methanol was decanted. This was repeated twice more to remove residual ruthenium.

BHT (10 mg) was added and the solvent was removed in a vacuum oven at 65 °C overnight, affording 11.5 g of an orange, transparent, slightly viscous prepolymer (70% yield).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) = 7.30-7.41 (m, 10H), 5.27-5.39 (m, 37H), 5.16 (s, 4H), 4.97-5.12 (m, 32H), 4.16 (t, $J = 6.5$ Hz, 4H), 1.92-2.03 (m, 69H), 1.70-1.80 (m, 36H), 1.09-1.43 (m, 347H), 0.82 (t, $J = 7.3$ Hz, 103H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ (ppm) = 155.4, 136.3, 135.5, 134.8, 130.4, 130.0, 128.7, 128.6, 128.5, 69.6, 67.8, 44.7, 39.1, 35.4, 32.8, 30.0, 29.4, 28.4, 27.3, 11.9.

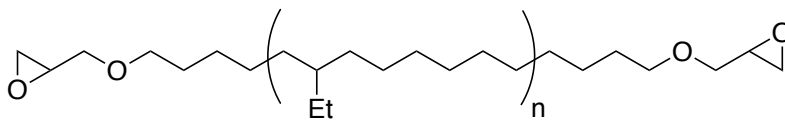
Representative procedure for synthesis of dihydroxy-telechelic polyolefin (PH-5-OH)



P-5-Cbz (11.5 g, 2.21 mmol) was dissolved in a minimum amount of toluene and added to a high-pressure reactor (Parr Series 4520 Bench Top Reactor, 1L). 10 wt. % Pd/C (1.55 g, 13 wt. % to polymer) was added to the reactor. The reaction mixture was purged 4 times with argon (60 psig). The reaction mixture was heated to 45 °C, and hydrogen (480 psig) was introduced. After 72 hours, the reaction mixture was filtered through Celite® with THF. The filtrate was concentrated by rotary evaporation and dried in a vacuum oven at 70 °C overnight to afford 10.3 g of a yellow, transparent, slightly viscous prepolymer (90 % yield).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) = 3.61-3.68 (m, 4H), 1.54-1.61 (m, 5H), 1.03-1.47 (m, 630H), 0.83 (t, $J = 7.4$ Hz, 109H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ (ppm) = 63.3, 39.0, 33.4, 30.4, 30.0, 26.9, 26.0, 11.0.

Representative procedure for synthesis of diepoxy-telechelic polyolefin (PH-5)



PH-5-OH (5.6 g, 1.08 mmol) was dissolved in allyl bromide (23 mL, 266 mmol) and added to a 120 mL pressure vessel containing a Teflon-coated magnetic stir bar. Sodium hydroxide (11 g, 275 mmol) was dissolved in 15 mL water and added to the pressure vessel with tetrabutylammonium bromide (177 mg, 0.55 mmol). The reaction was heated to 60 °C and stirred vigorously for 72 hours. The organic layer was precipitated into methanol, after which methanol was decanted. The polymer was dissolved in minimal dichloromethane, and precipitation was repeated once more. The isolated polymer was dissolved in minimal dichloromethane, and BHT (10 mg) was added. Additional allyl bromide and dichloromethane were removed by drying in a vacuum oven at 65 °C overnight to afford 4.89 g of a colorless, transparent, slightly viscous polymer (87% yield).

The resulting polymer was dissolved in 35 mL dichloromethane and added to a 100 mL round-bottom flask containing a Teflon-coated magnetic stir bar. 3-chloroperoxybenzoic acid (2.33 g, \leq 77%, 10.4 mmol) was added to the flask, and the reaction was left at room temperature overnight. The reaction mixture was precipitated into methanol, after which methanol was decanted. This was repeated three more times after dissolving the polymer in a minimal amount of dichloromethane. The isolated polymer was dried in a vacuum oven at 70 °C overnight to afford 2.79 g of a colorless, transparent, slightly viscous prepolymer (57 % yield).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 3.69 (dd, $J = 11.6, 3.0$ Hz, 2H), 3.43-3.55 (m, 4H), 3.39 (dd, $J = 11.5, 5.8$ Hz, 2H) 3.12-3.17 (m, 2H), 2.77-2.82 (m, 2H), 2.59-2.63 (m, 2H), 1.53-1.63 (m, 9H), 1.16-1.35 (m, 814H), 0.83 (t, $J = 7.2$ Hz, 138H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ (ppm) = 71.9,

71.6, 51.1, 44.5, 39.0, 33.4, 30.4, 30.0, 26.9, 26.0, 11.0. FTIR (neat, cm^{-1}): 2959, 2921, 2852, 1756, 1460, 1378, 1362, 1174, 1110, 943, 908, 829, 771, 721, 650, 576, 423.

Supplementary Figures and Tables

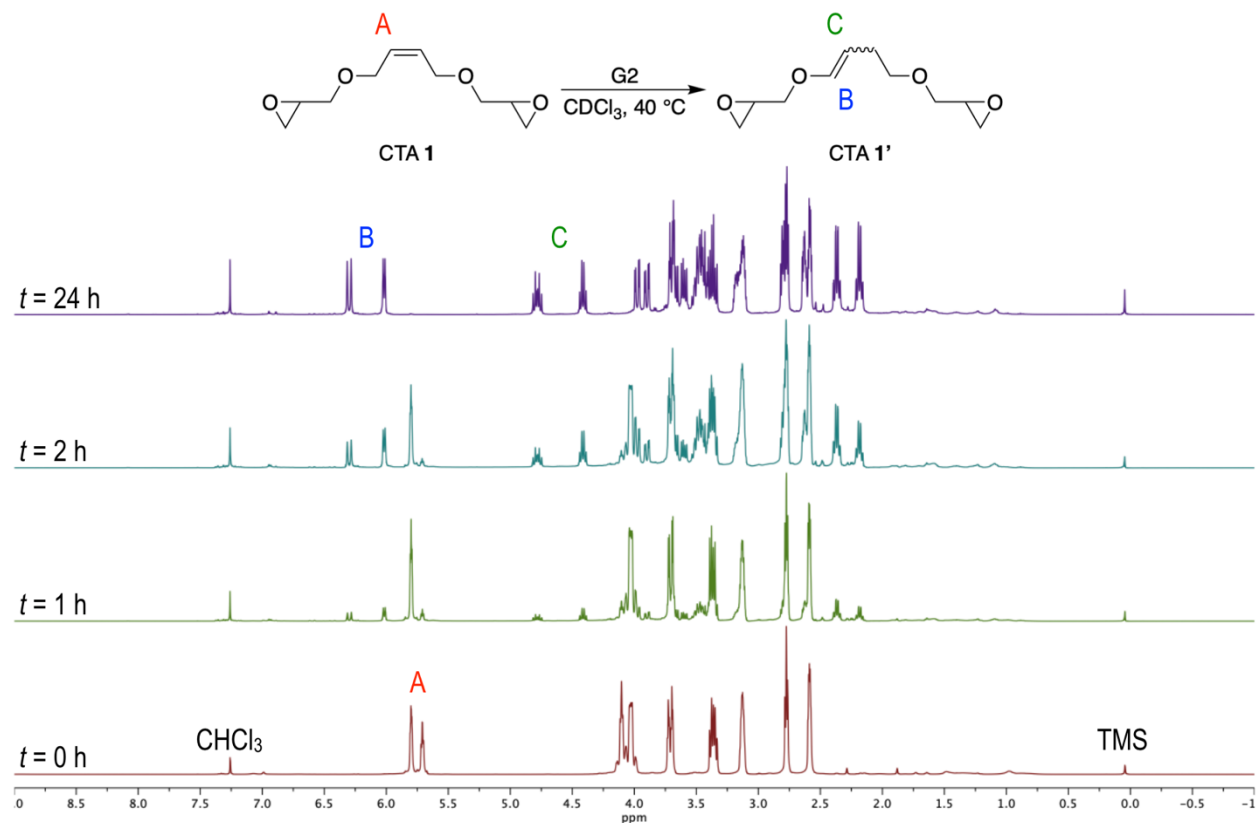


Figure S1. $^1\text{H-NMR}$ overlay of CTA **1** monitoring olefin isomerization.

Table S1. Additive (*p*-BQ) optimization during ROMP between 3-EtCOE and CTA **1**.

Entry	Monomer:CTA: <i>p</i> -BQ:G2	Conversion (%) ^a			Yield (%)	$M_{n,\text{theo}}$ (kg/mol) ^b	$M_{n,\text{NMR}}$ (kg/mol) ^c	HT (%) ^d	$M_{n,\text{SEC}}$ (kg/mol) ^e	\bar{D} ^e
		1 h	2 h	22 h						
1	3100:90:0:1	7	7	7	0.1	5.1	3.7	93	10	2.8
2	3100:90:20:1	16	17	17	0.7	5.1	2.6	95	4.5	1.3
3	3100:90:40:1	39	40	42	29	5.1	4.1	96	5.3	1.3
4	3100:90:60:1	69	72	72	66	5.1	4.8	97	5.1	1.4
5	3100:90:80:1	89	91	92	83	5.1	5.2	96	6.4	1.4
6	3100:90:100:1	97	97	98	87	5.1	5.3	95	8.1	1.2

^aDetermined by $^1\text{H-NMR}$ using integral ratio of polyalkenamer/monomer (dd, 5.07 ppm/m, 5.64 ppm). ^b $M_{n,\text{theo}} = \text{MW}_{3\text{EtCOE}} \cdot [r_{3\text{EtCOE}} / (r_{\text{CTA}} + r_{\text{G2}})] + \text{MW}_{\text{CTA}}$. ^cDetermined by $^1\text{H-NMR}$ end group analysis assuming $F = 2$. ^d*trans*-head-to-tail content. ^eDetermined by SEC in THF (1.0 mL/min, 25 °C) using a MALS detector.

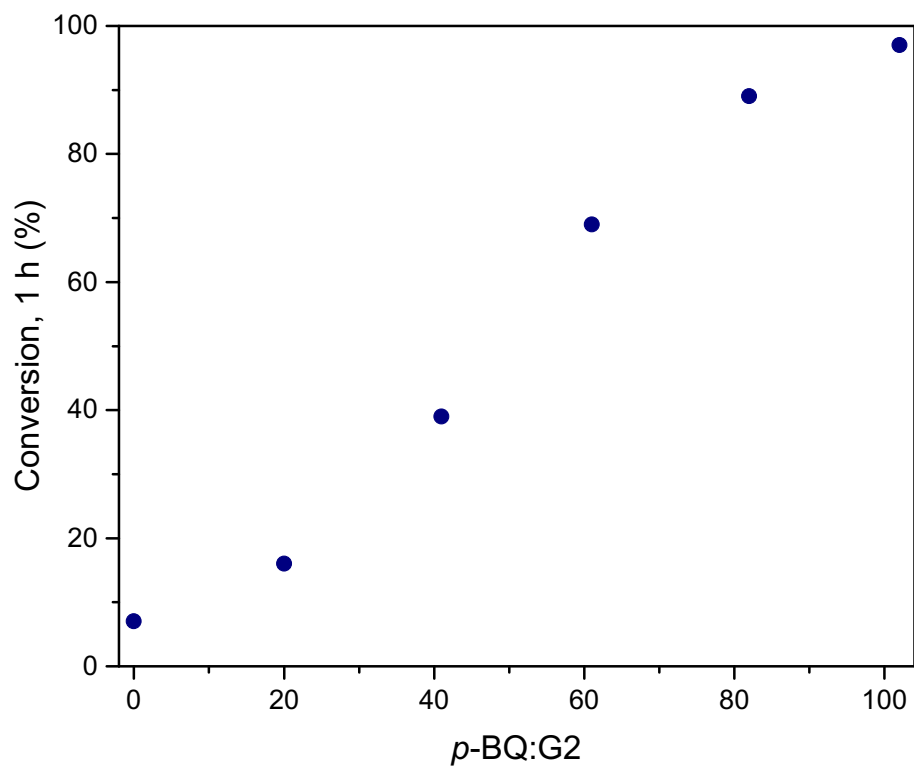


Figure S2. Romp conversion-molar equivalents p -BQ:G2 during additive optimization.

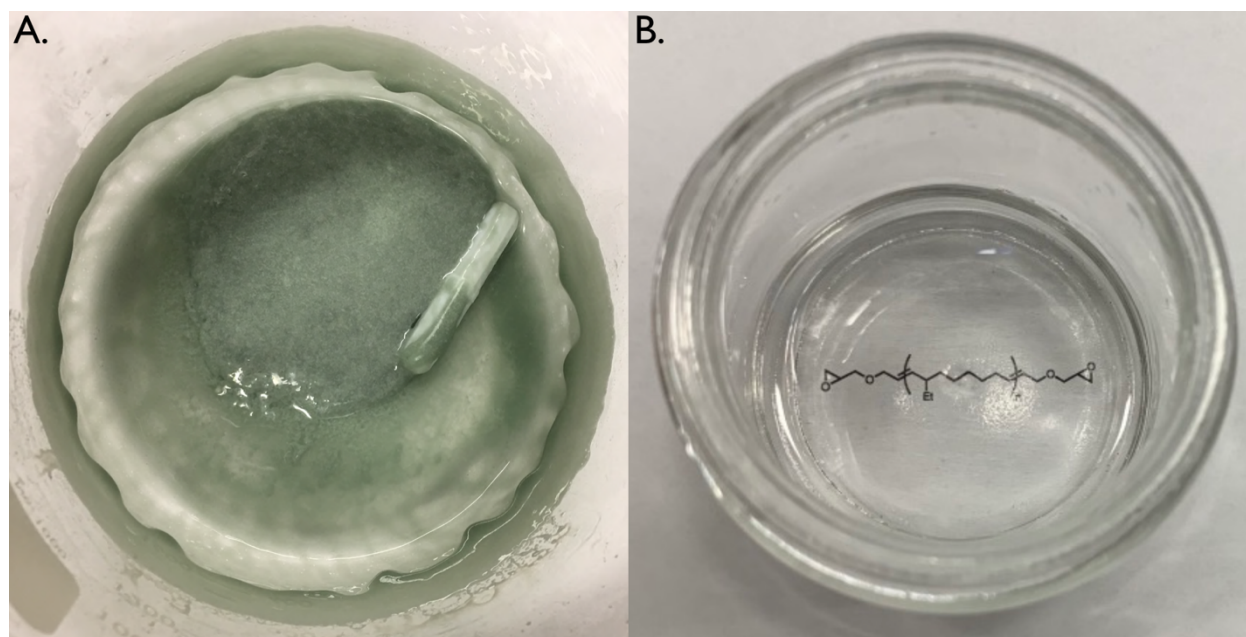


Figure S3. (A) Crude prepolymer. (B) Colorless, transparent prepolymer obtained following purification.

Table S2. Characterization of diepoxy-telechelic polyalkenamer prepolymers.

Prepolymer	Monomer:CTA:p-BQ:G2	Conversion (%) ^a	$M_{n,theo}$ (kg/mol) ^b	$M_{n,NMR}$ (kg/mol) ^c	$M_{n,SEC}$ (kg/mol) ^d	$M_{w,SEC}$ (kg/mol) ^d	P_{SEC} ^d	T_d (°C) ^e	T_g (°C) ^f
P-5	3000:80:100:1	99	5.0	5.3	6.0	9.1	1.5	372	-61
P-11	3000:40:100:1	99	10	11	11	14	1.3	393	-59
P-19	3000:30:100:1	99	15	19	20	27	1.4	383	-58
P-25	3000:20:100:1	>99	20	25	19	26	1.3	351	-58

^aDetermined by ¹H-NMR using integral ratio of polyalkenamer/monomer (dd, 5.07 ppm/m, 5.64 ppm). ^b $M_{n,theo} = MW_{SEC} [P_{SEC} / (r_{CTA} + r_{G2})] + MW_{CTA}$. ^cDetermined by ¹H-NMR end group analysis assuming F = 2. ^dDetermined by SEC in THF (1.0 mL/min, 25 °C) with a MALS detector. ^e5% weight loss determined by TGA at 10 °C/min in N₂. ^fDetermined by DSC (2nd heating cycle) at 10 °C/min.

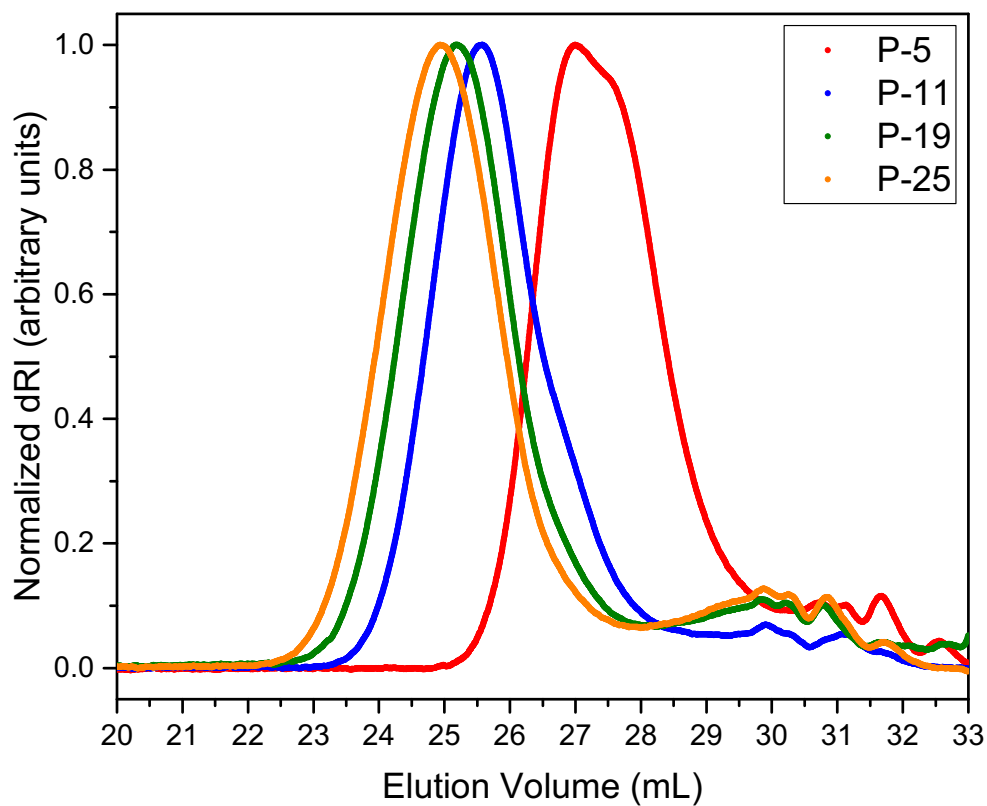


Figure S4. SEC traces (THF, 1.0 mL/min, 25 °C, RI) of epoxy-telechelic polyalkenamers with varying molar masses.

Table S3. Summary of photorheology using P-5 and iodonium PAGs.

Entry	PAG	[PAG] (wt. %)	t_{gel} (s) ^a	G_N (MPa) ^b	Gel Fraction ^c
1	1	0.1	291	0.04	0.62
2	1	0.5	75	0.71	0.90
3	1	1.0	68	0.70	0.89
4	1	2.0	166	0.64	0.88
5	2	0.1	192	0.79	0.91
6	2	0.5	243	0.80	0.90
7	2	1.0	276	0.73	0.89
8	2	2.0	305	0.73	0.89

^aDetermined using the “Modulus Crossover” function within the TA Instruments TRIOS software. ^bAverage value for final 30 s of photocuring. ^cApproximately 100 mg of polymer was dissolved in 20 mL DCM and left stirring 48 h. Sol removed and gel dried at 60 °C for 24 h.

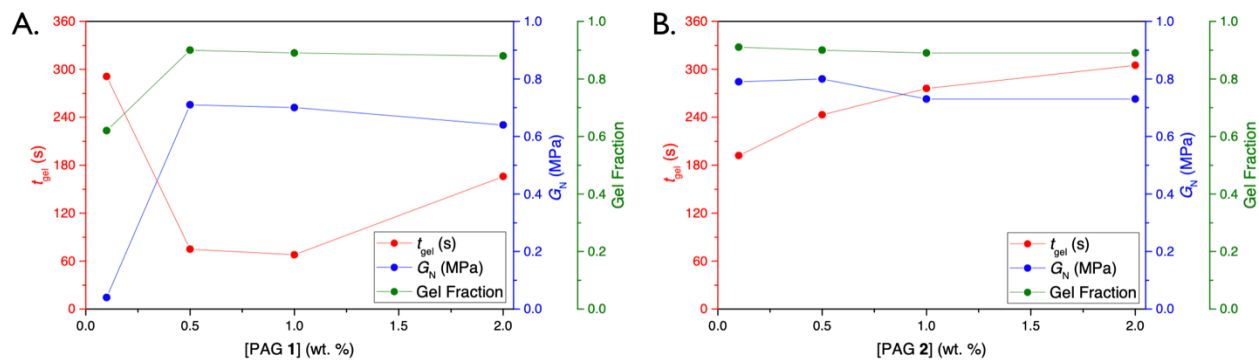


Figure S5. Photoreology of P-5 using various concentration of PAG 1 (A) and PAG 2 (B).

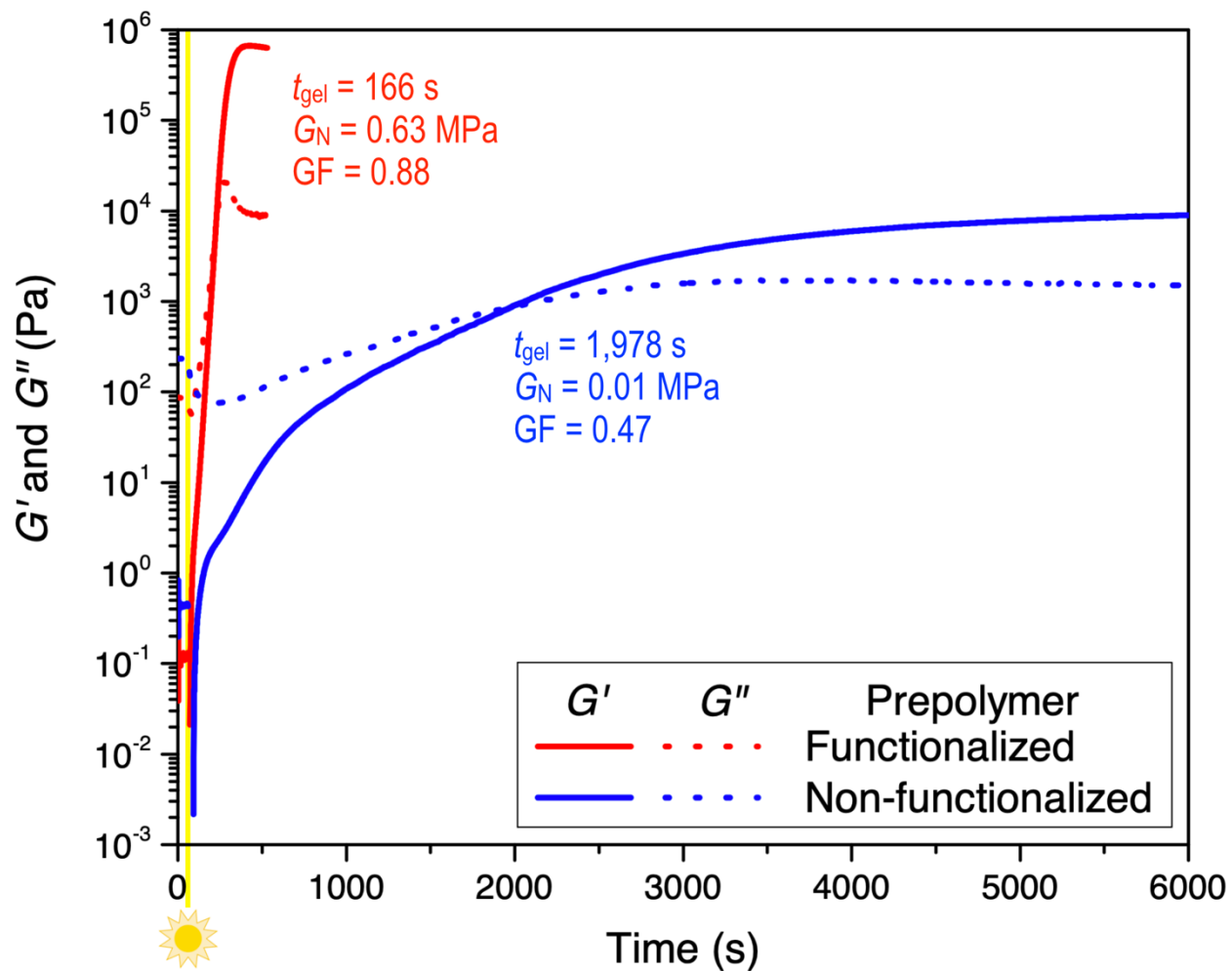


Figure S6. Photorheology (20 mm parallel plates, 0.1 % strain, 1.0 Hz, gap = 1.1 mm) of functionalized vs. non-functionalized polyalkenamer using PAG 1 (2.0 wt. %). Samples were exposed to unfiltered UV light (320-500 nm, 0.7 W/cm²) after a 60 s steady state period.

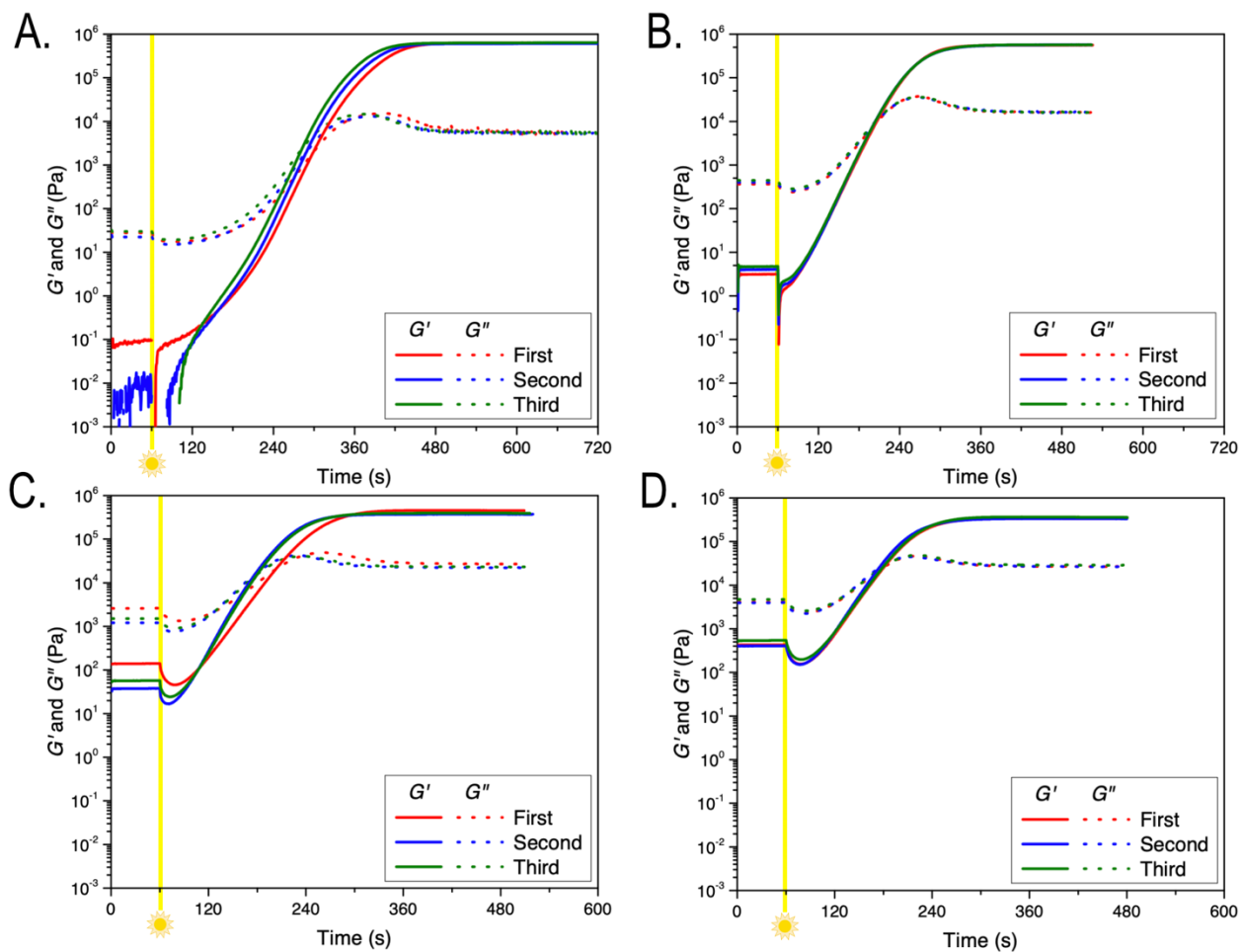


Figure S7. Photorheology of epoxy-telechelic polyalkenamer prepolymers using PAG 2 (0.5 wt. %). Unfiltered UV light (0.7 W/cm^2) turned on after 60 s steady state. (A) 5.3 kg/mol; (B) 11 kg/mol; (C) 19 kg/mol; (D) 25 kg/mol.

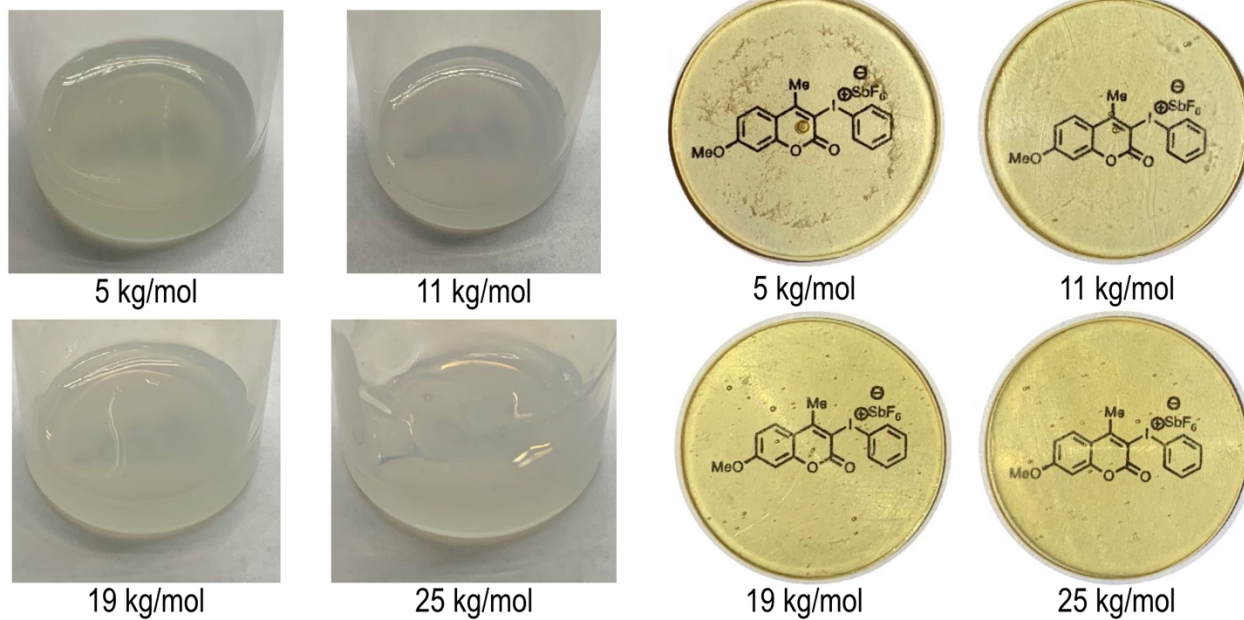


Figure S8. Prepolymer containing 0.5 wt. % PAG 2 (left) and corresponding elastomer following UV-irradiation (right).

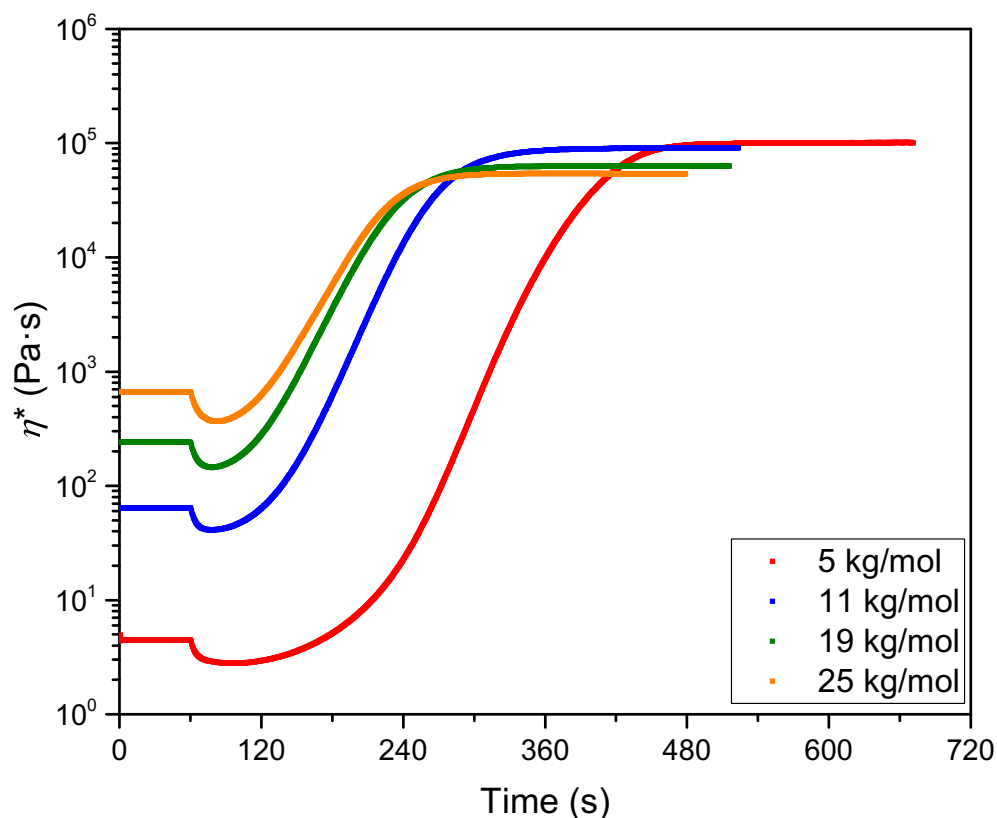


Figure S9. Complex viscosity observed during photorheology (20 mm parallel plates, 0.1% strain, 1.0 Hz, 1.0 mm gap) of epoxy-telechelic polyalkenamers with PAG 2 (0.5 wt. %); samples were exposed to UV light after a 60 s steady state period.

Table S4. Prepolymer curing characteristics and elastomer thermal properties.

Prepolymer ^a	Precure η^* (kPa·s) ^b	Postcure η^* (kPa·s) ^c	T_d (°C) ^d	T_g (°C) ^e
P-5	0.004-0.005	97-102	338-348	-57 to -58
P-11	0.06-0.07	89-91	377-379	-56 to -57
P-19	0.2-0.4	59-72	357-364	-56
P-25	0.6-0.8	53-57	345-351	-56

^aAll measurements performed in triplicate and range of data reported. ^bAverage of initial 60 s prior to UV exposure. ^cAverage of final 30 s following UV exposure. ^d5% mass loss determined by TGA at 10 °C/min in N₂. ^eDetermined by DSC (2nd heating cycle) at 10 °C/min.

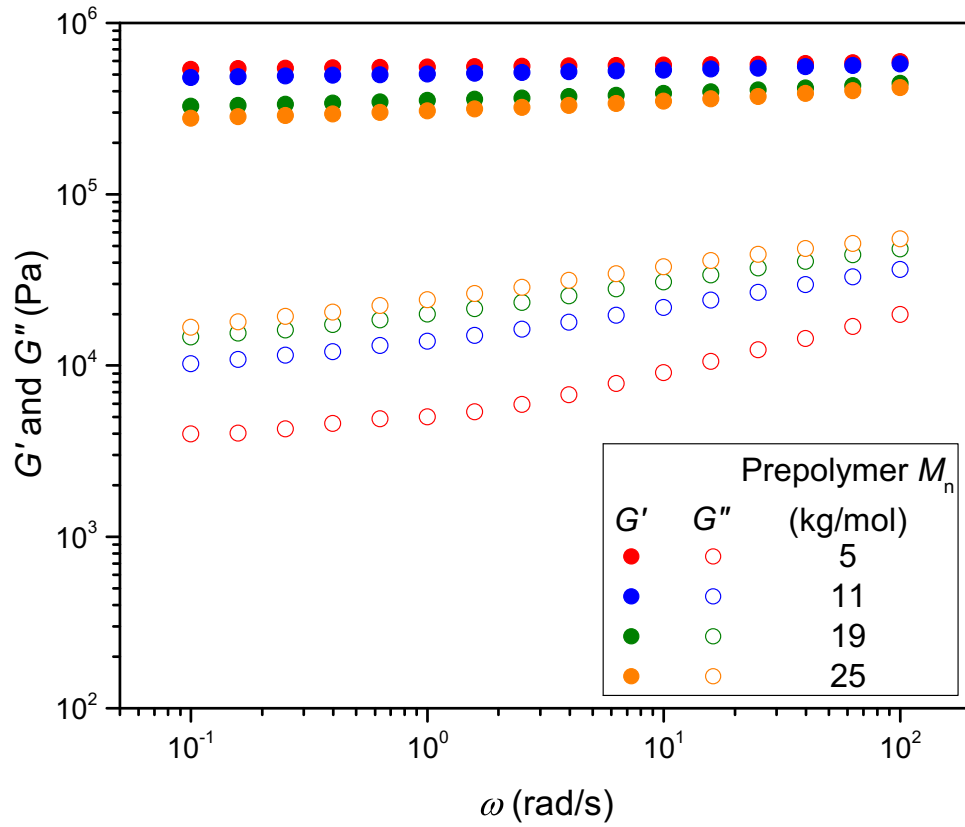


Figure S10. Elastomer frequency sweep (10 % strain, 0.1 to 100 rad/s), conducted post-cure with UV light off. $m_{G'} = 0.01-0.06$ Pa/rad \cdot sec $^{-1}$; $m_{G''} = 0.2$ Pa/rad \cdot sec $^{-1}$.

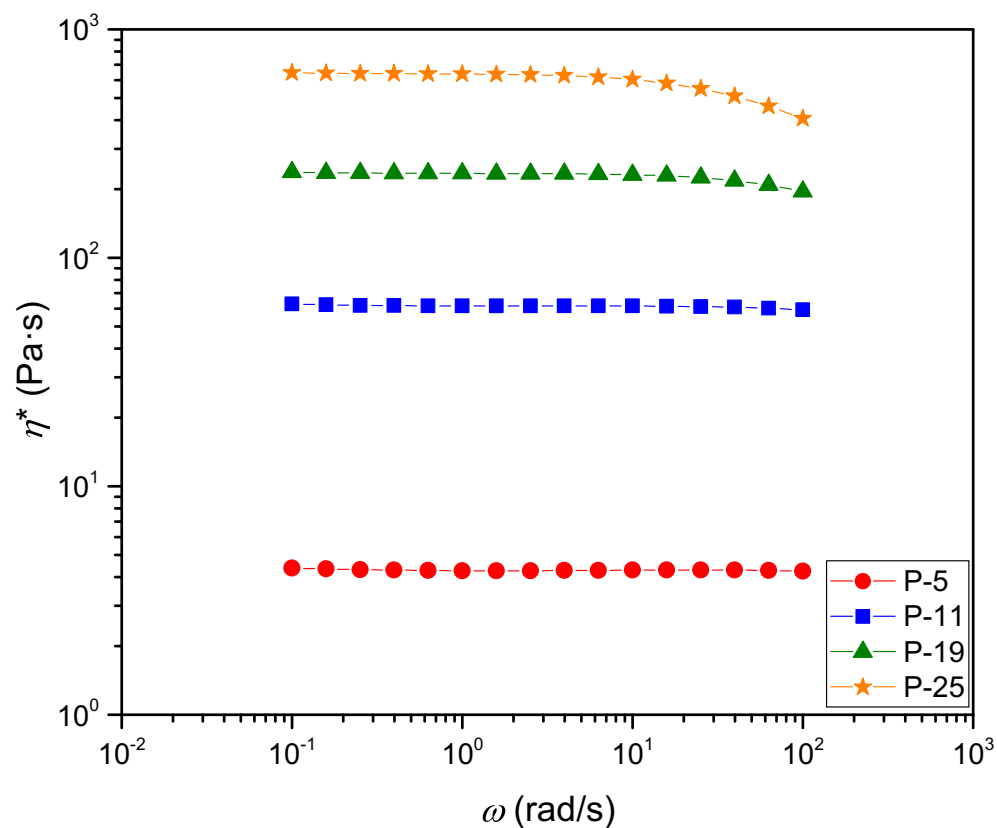


Figure S11. Pre-cure complex viscosity-frequency relationship showing that the prepolymers behave as a Newtonian liquid (10 % strain). Therefore, complex viscosity may be used as a proxy for shear viscosity.⁴

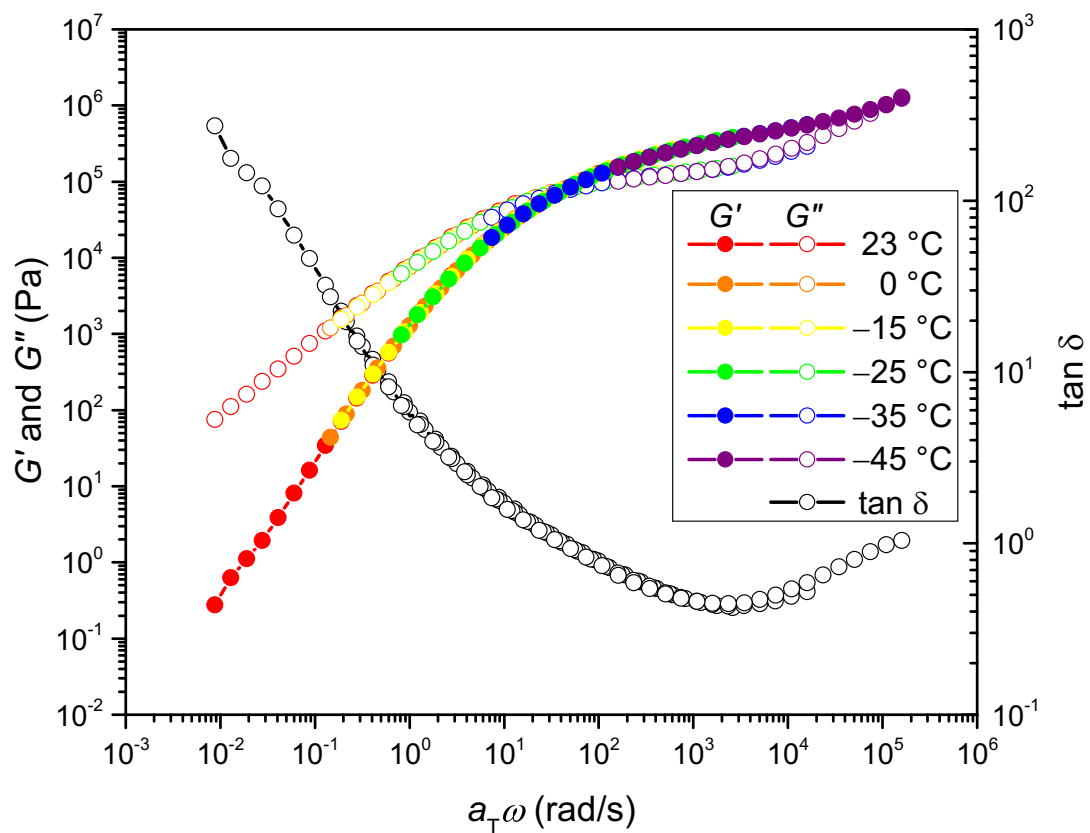


Figure S12. Master curve for P-25 obtained through time-temperature superposition; shift factors obtained by shifting $\tan \delta$.

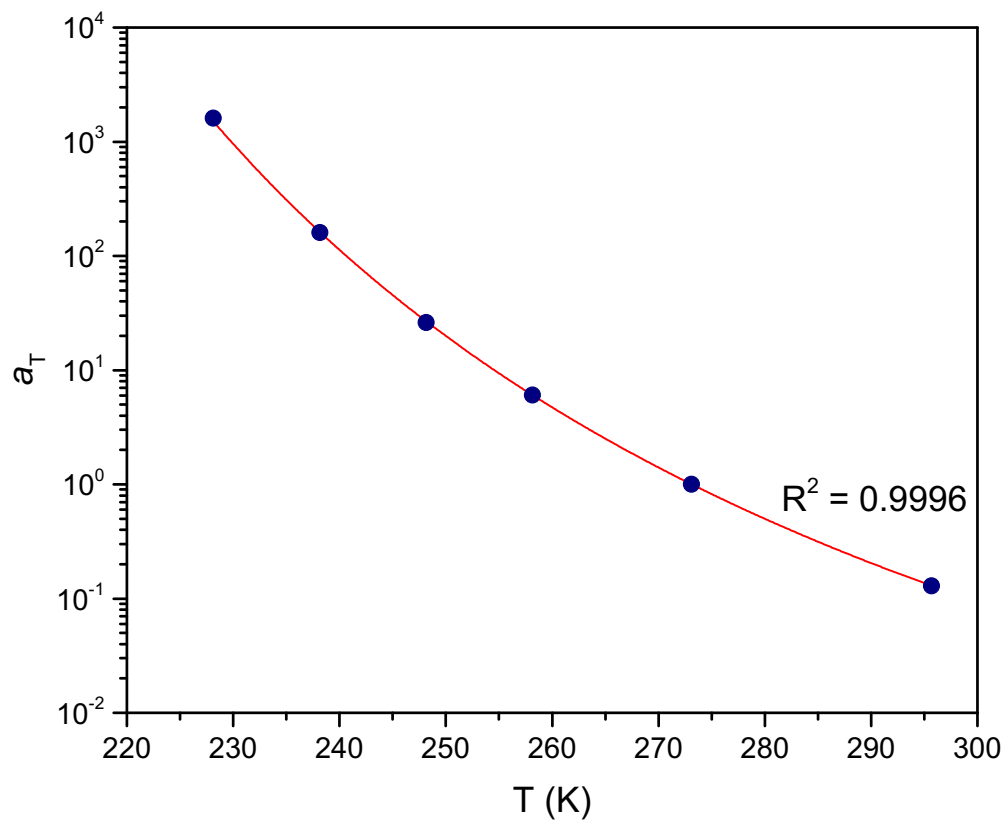


Figure S13. Master curve shift factors for P-25 obtained via time-temperature superposition of $\tan \delta$. Data fit to Williams-Landel-Ferry model, $\log(a_T) = -C_1(T - T_r)/(C_2 + (T - T_r))$; $T_r = 273$ K, $C_1 = 5.99$, $C_2 = 129.8$ K.

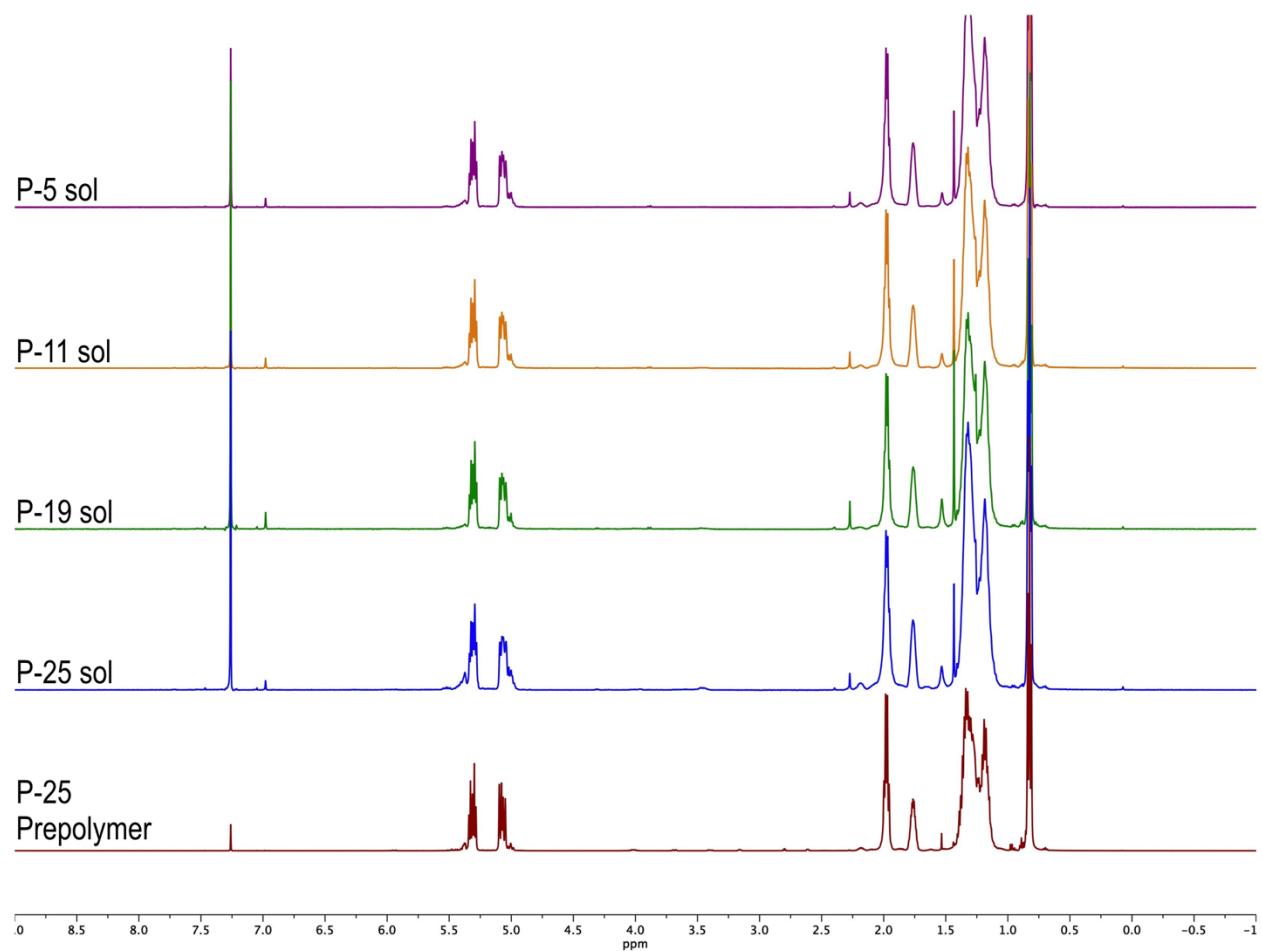


Figure S14. ¹H-NMR (500 MHz, CDCl₃) overlay of P-25 prepolymer and concentrated elastomer sol fractions.

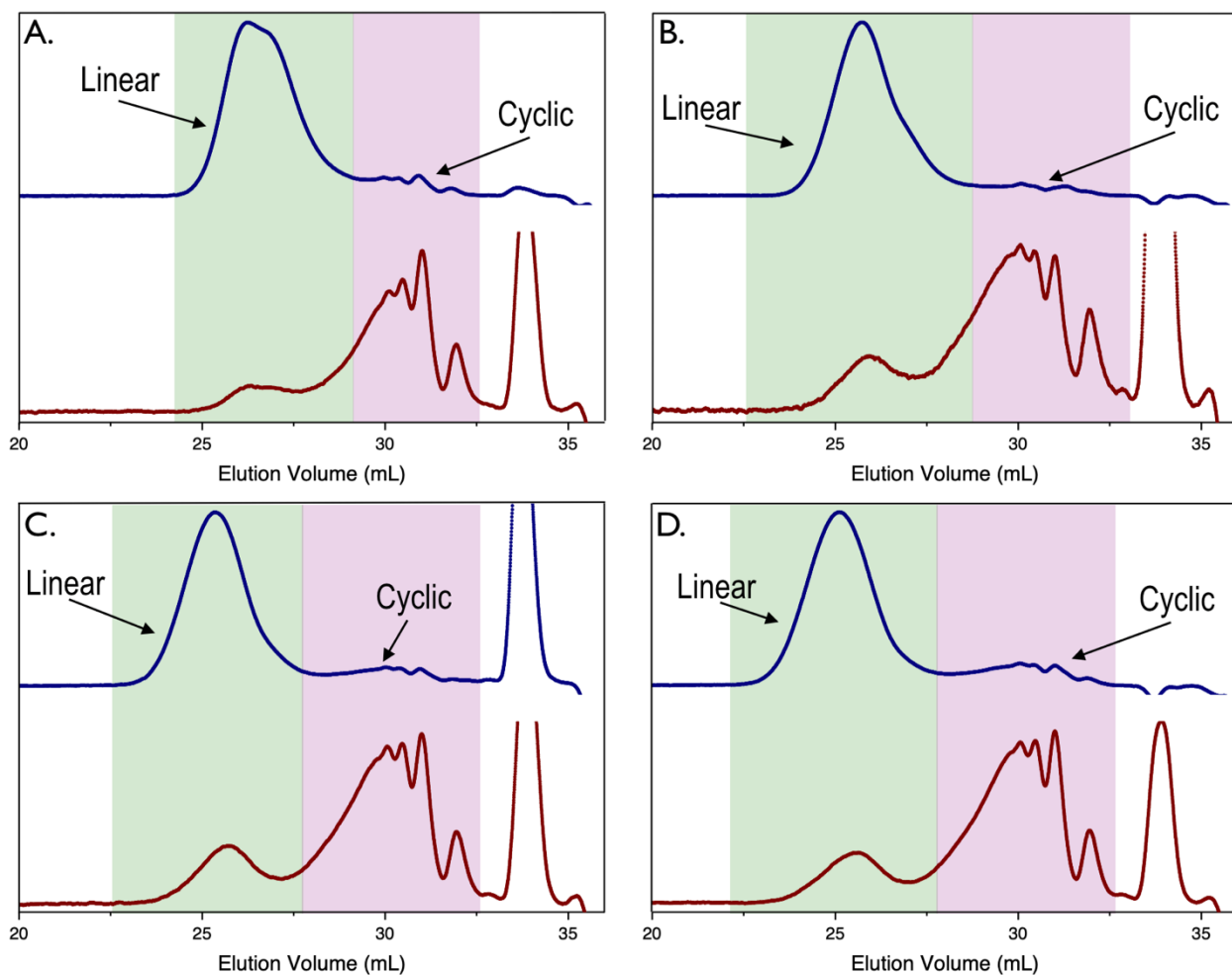


Figure S15. SEC traces (THF, 1.0 mL/min, 25 °C, RI) for prepolymer (blue) and elastomer sol fraction (red). Green (linear) and magenta (cyclic) regions indicate area used for integration.

(A) 5.3 kg/mol; (B) 11 kg/mol; (C) 19 kg/mol; (D) 25 kg/mol.

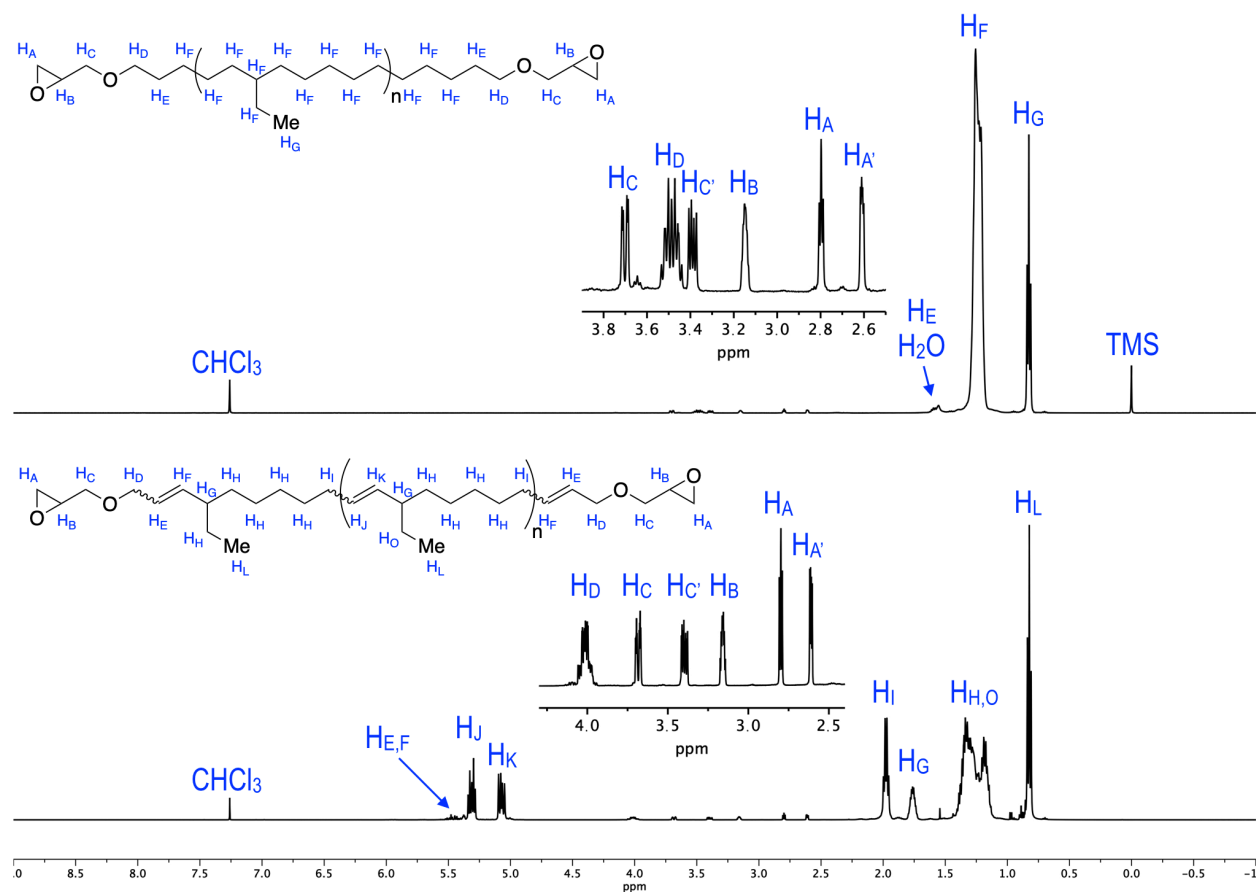


Figure S16. A comparison of the ¹H-NMR spectra (500 MHz, CDCl₃) for both prepolymers: polyolefin PH-5 (top) and polyalkenamer P-5 (bottom); the enhanced regions display their respective end group signals.

Table S5. Characterization of polyolefin prepolymers.

Prepolymer ^a	M_n (kg/mol)			$M_{w,SEC}$ (kg/mol) ^c	D_{SEC} ^c
	Theoretical ^a	NMR ^b	SEC ^c		
P-5-Cbz	5.0	5.2	8.8	12	1.3
PH-5-OH	-	5.2	9.0	11	1.3
PH-5	-	6.7	9.2	13	1.4

^a $M_{n,theo} = MW_{3EICOE} * [n_{3EICOE} / (n_{CTA} + n_{G2})] + MW_{CTA}$. ^bDetermined by ¹H-NMR end group analysis assuming F = 2. ^cDetermined by SEC in THF (1.0 mL/min, 25 °C) using a MALS detector.

Table S6. Summary of P-5 vs. PH-5 photorheology using PAG 2 (0.5 wt. %).

Prepolymer ^a	t_{gel} (s) ^b	G_N (MPa) ^c	Precure η^* (kPa·s) ^d	Gel Fraction ^e
P-5	222-239	0.61-0.64	0.004-0.005	0.87-0.88
PH-5	113-122	0.86-0.89	0.022-0.024	0.86-0.89

^aAll measurements performed in triplicate and range of data reported. ^bDetermined using the "Modulus Crossover" function within the TA Instruments TRIOS software. ^cAverage value for final 30 s of photocuring. ^dAverage of initial 60 s prior to UV exposure. ^eApproximately 100 mg of polymer was dissolved in 20 mL DCM and left stirring 48 h. Sol removed and gel dried at 60 °C for 24 h.

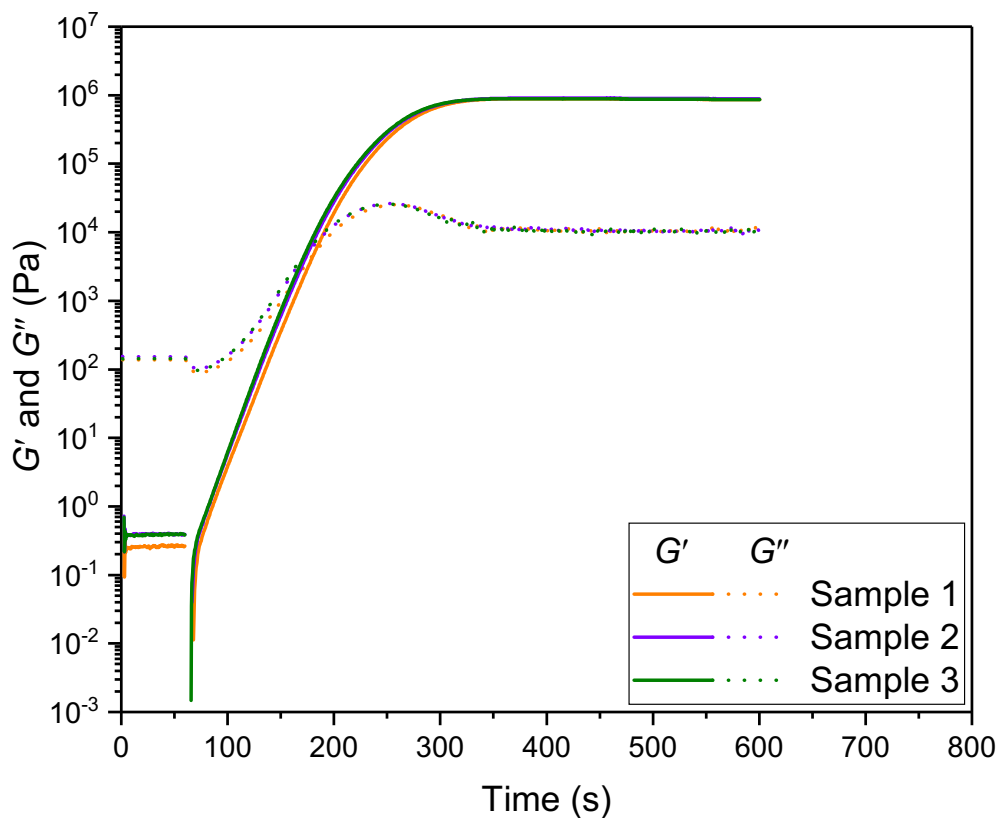


Figure S17: Photocuring (20 mm parallel plates, 0.1 % strain, 1.0 Hz, gap = 1.1 mm) of **PH-5** using PAG 2 (0.5 wt. %), in triplicate. Samples exposed to unfiltered UV light (320-500 nm, 0.7 W/cm²) after a 60 s steady state period.

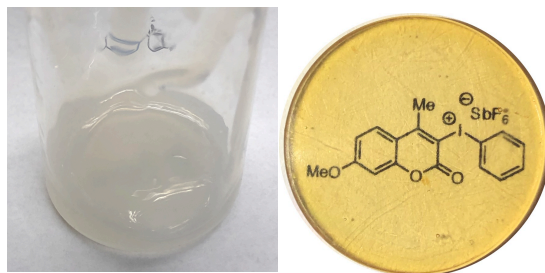


Figure S18. PH-5 prepolymer containing 0.5 wt. % PAG 2 (left) and corresponding elastomer following UV-irradiation (right).

Table S7. Thermal characterization of polyolefin prepolymer and elastomer.

Sample	T_d (°C) ^a	T_g (°C) ^b
PH-5 Prepolymer	378	-73
PH-5 Elastomer	361	-71

^a5% mass loss determined by TGA at 10 °C/min in N₂. ^bDetermined by DSC (2nd heating cycle) at 10 °C/min.

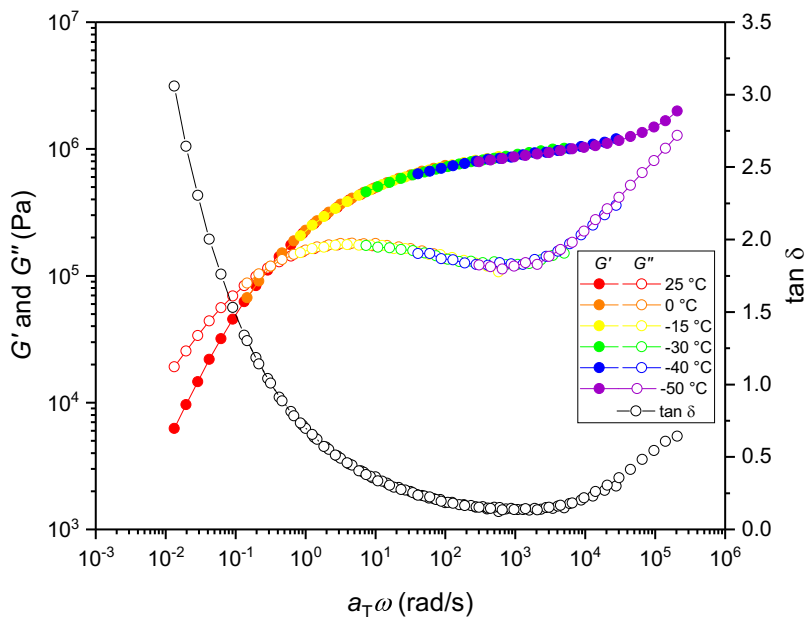


Figure S19. Master curve for non-functionalized polyolefin with $M_n = 55$ kg/mol obtained through time-temperature superposition; shift factors obtained by shifting $\tan \delta$.

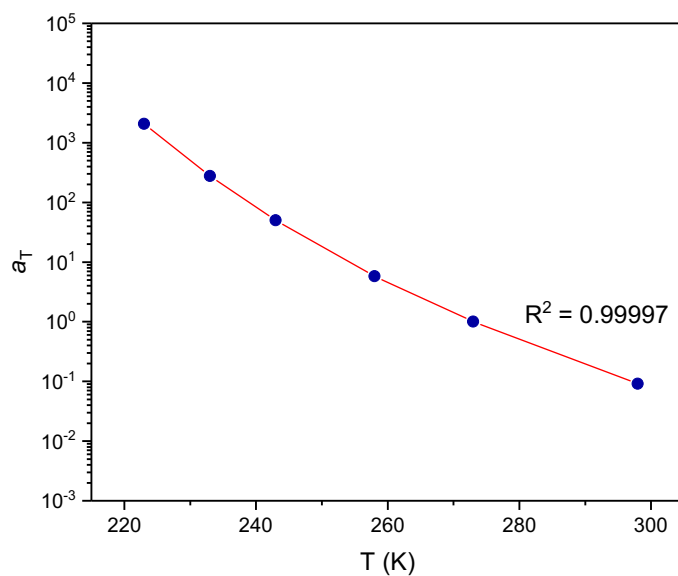


Figure S20. Master curve shift factors for non-functionalized polyolefin with $M_n = 55$ kg/mol obtained via time-temperature superposition of $\tan \delta$. Data fit to Williams-Landel-Ferry model, $\log(a_T) = -C_1(T - T_r)/(C_2 + (T - T_r))$; $T_r = 273$ K, $C_1 = 8.17$, $C_2 = 173.5$ K.

Table S8. Summary of tensile properties for polyalkenamer elastomers.

Sample	ϵ_b (%)	σ_b (MPa)	E (MPa)
P-5	29-47	0.2-0.4	1.39-1.43
P-11	202-320	1.1-1.5	1.4-1.5
P-19	367-491	0.8-1.0	1.0-1.1
P-25	632-739	0.8-1.0	0.8-1.0

Determined at 5 mm·min⁻¹ using at least 3 rectangular tensile bars per sample. Values reported as range of data.

Table S9. Summary of tensile properties for P-5 and PH-5 elastomers.

Sample	ϵ_b (%)	σ_b (MPa)	E (MPa)
P-5	29-47	0.2-0.4	1.39-1.43
PH-5	22-46	0.4-0.6	2.0-2.2

Determined at 5 mm·min⁻¹ using at least 3 rectangular tensile bars per sample. Values reported as range of data.

Table S10. Summary of mass-based equilibrium swelling ratios for photo-cured elastomers.

Sample	Q_m
P-5	2.1-2.2
P-11	2.0-2.4
P-19	2.6-2.9
P-25	2.6-3.0
PH-5	1.0-1.3

10-48 mg of gel was swollen in 20 mL DCM for 48 h, removed from solvent, quickly patted dry with Kimwipe, and then weighed. $Q_m = (M_{wet} - M_{dry})/M_{dry}$.

Table S11. Prepolymer D variation by SEC.

Prepolymer	THF-SEC w/ MALS ^a	THF-SEC w/o Cyclics ^b		THF-SEC w/ Cyclics ^b		CHCl ₃ -SEC w/o Cyclics ^c		CHCl ₃ -SEC w/ Cyclics ^c	
	D	Peak Region (min)	D	Peak Region (min)	D	Peak Region (min)	D	Peak Region (min)	D
P-5	1.5	24.0-29.3	1.7	24.0-32.2	3.3	13.5-18.4	1.5	13.5-20.4	8.3
P-11	1.3	23.3-28.8	1.8	23.3-32.3	4.5	12.6-18.3	1.6	12.6-20.6	13
P-19	1.4	22.5-28.1	1.8	22.5-31.4	6.0	12.1-17.6	1.5	12.1-20.6	16
P-25	1.3	22.3-28.0	1.8	22.3-32.3	9.8	12.0-17.4	1.6	12.0-20.5	23

^aDetermined by SEC in THF (1.0 mL/min, 25 °C) using a MALS detector. M_n and D were found to be unaffected by inclusion/omission of cyclic oligomers. ^bDetermined by SEC in THF (1.0 mL/min, 25 °C) using an RI detector against PS standards. ^cDetermined by SEC in CHCl₃ (1.0 mL/min, 35 °C) using an RI detector against PS standards.

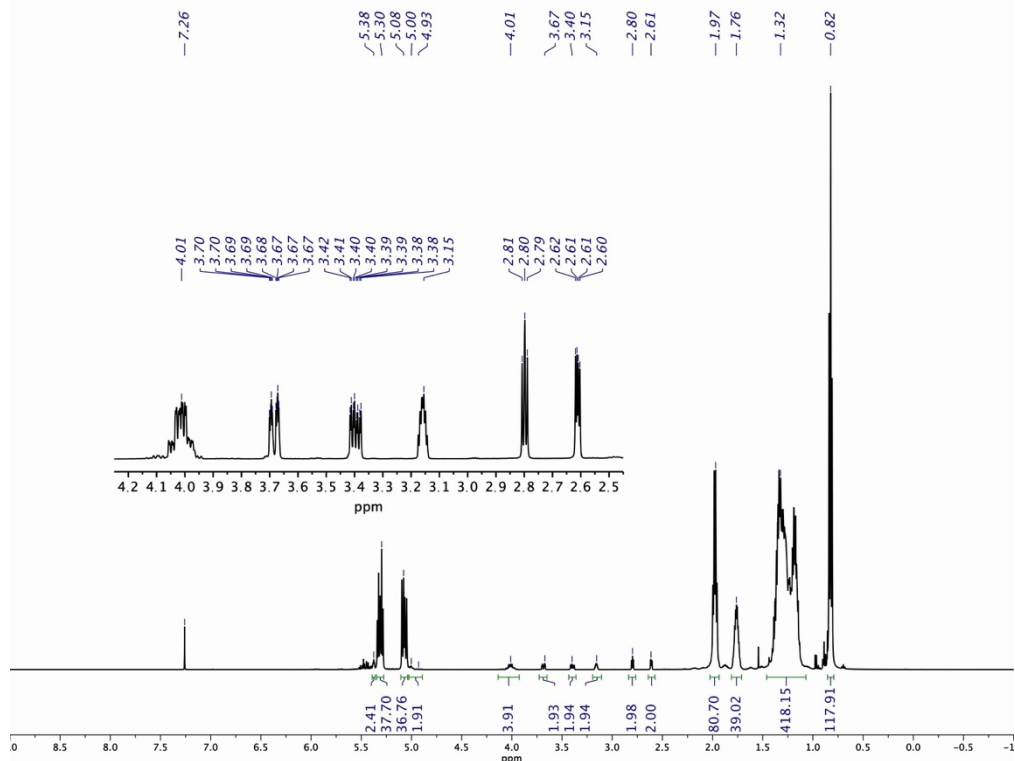


Figure S21. ¹H-NMR spectrum (500 MHz, CDCl₃) of P-5.

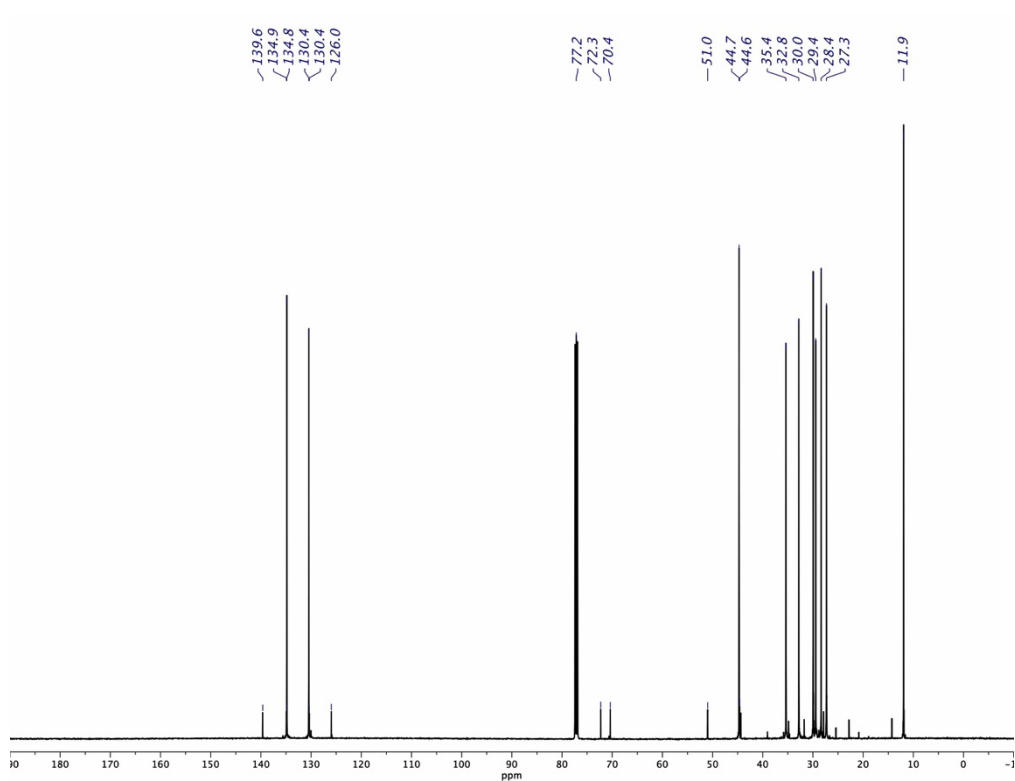


Figure S22. ¹³C-NMR spectrum (125 MHz, CDCl₃) of P-5.

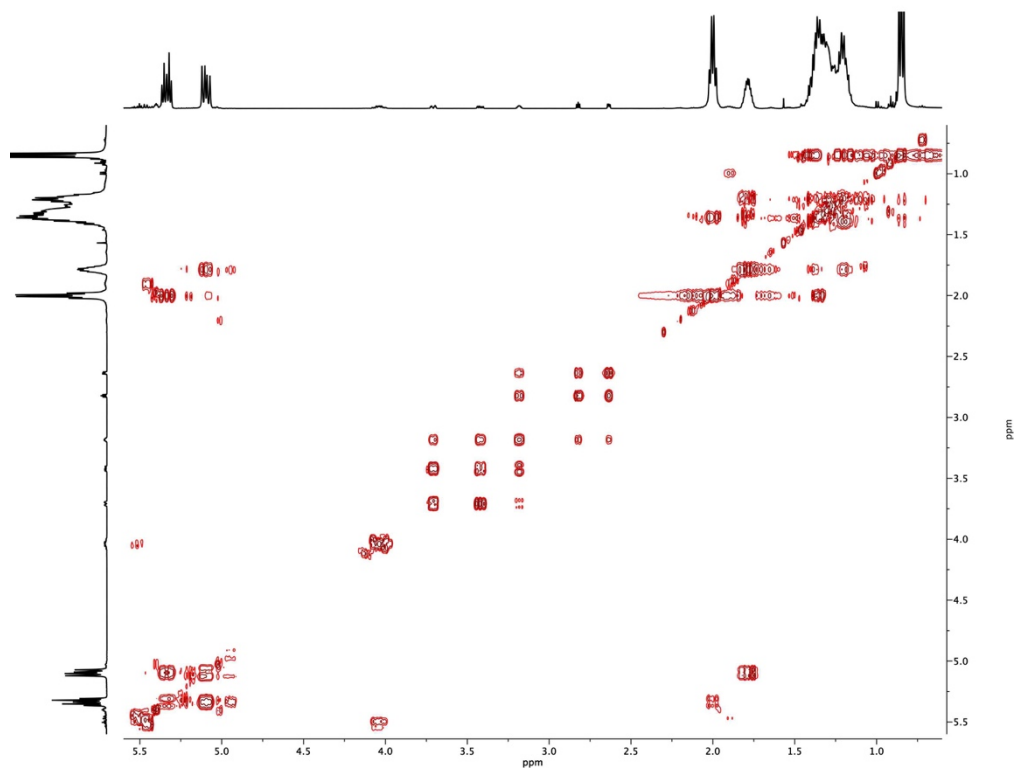


Figure S23. 2D-COSY spectrum of P-5.

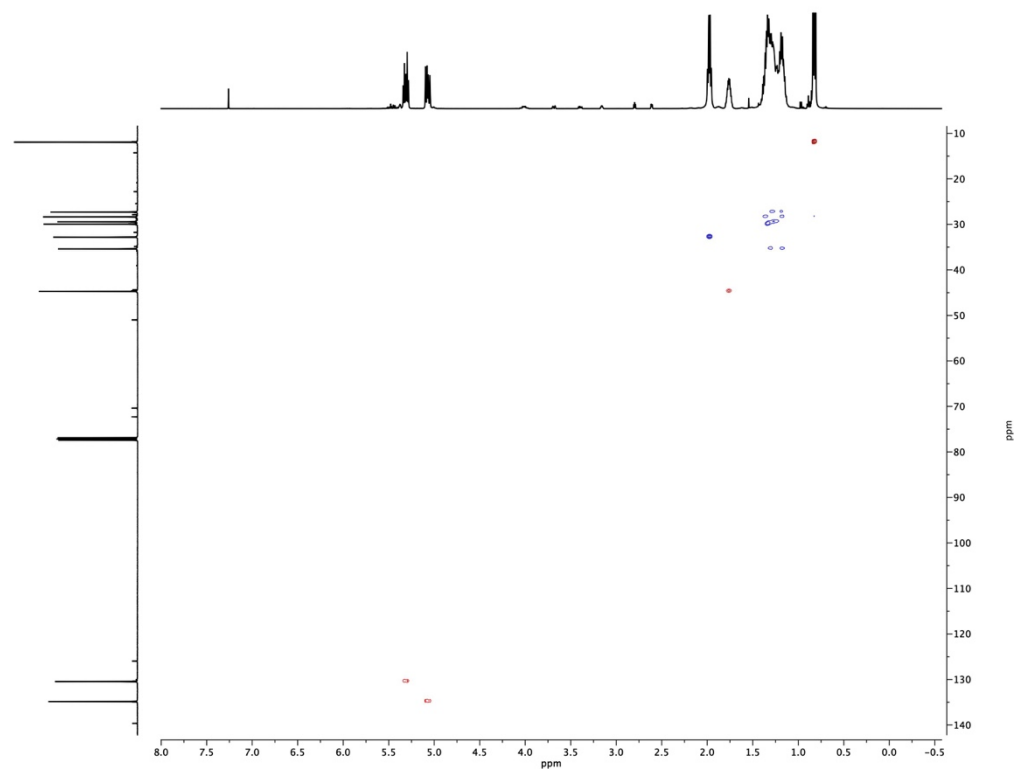


Figure S24. 2D-HSQC spectrum of P-5.

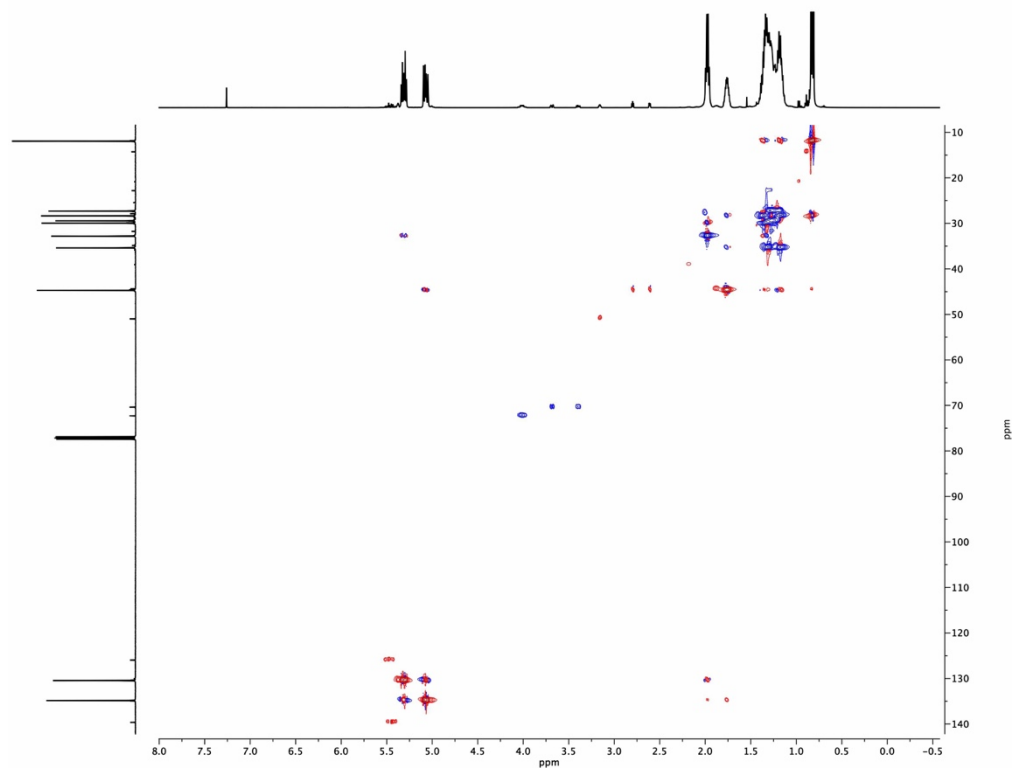


Figure S25. 2D-HSQC spectrum of P-5 (increased intensity).

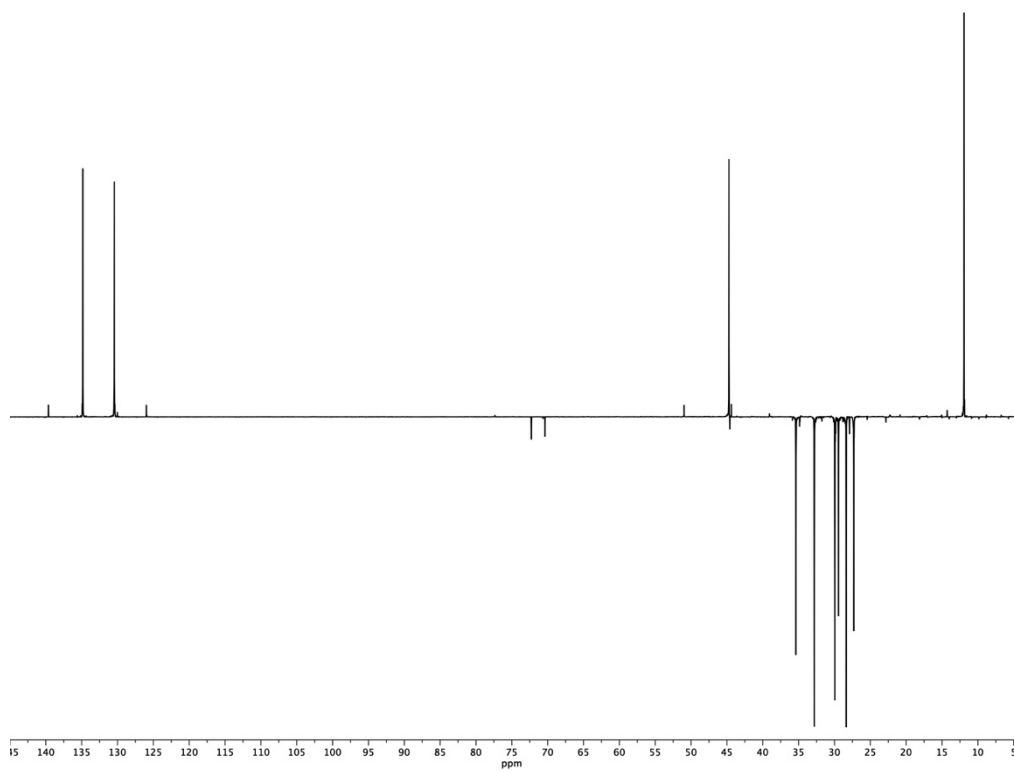


Figure S26. DEPT-135 spectrum of P-5.

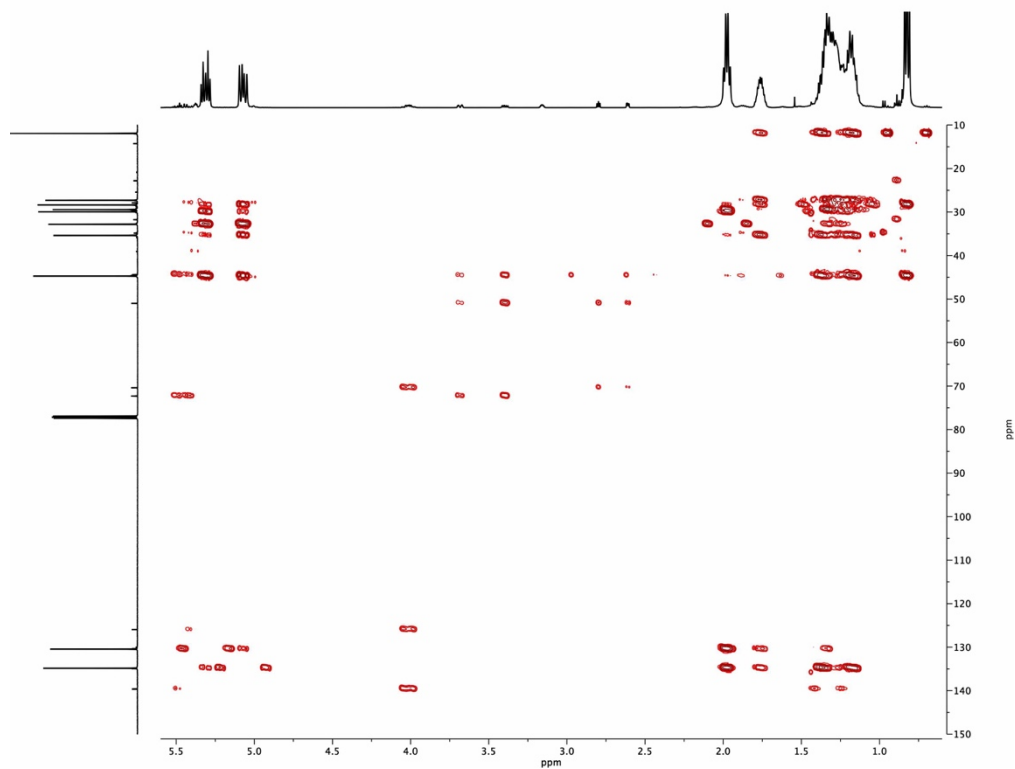


Figure S27. 2D-HMBC spectrum of P-5.

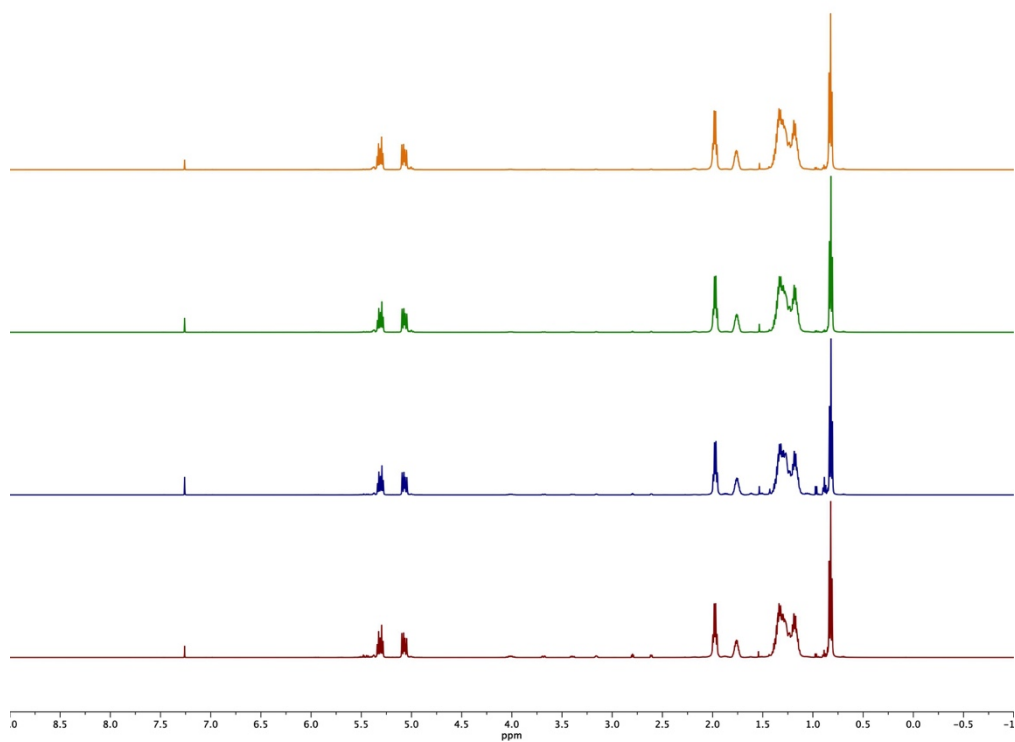


Figure S28. ^1H -NMR overlay of P-5 (maroon), P-11 (navy blue), P-19 (green), P-25 (orange).

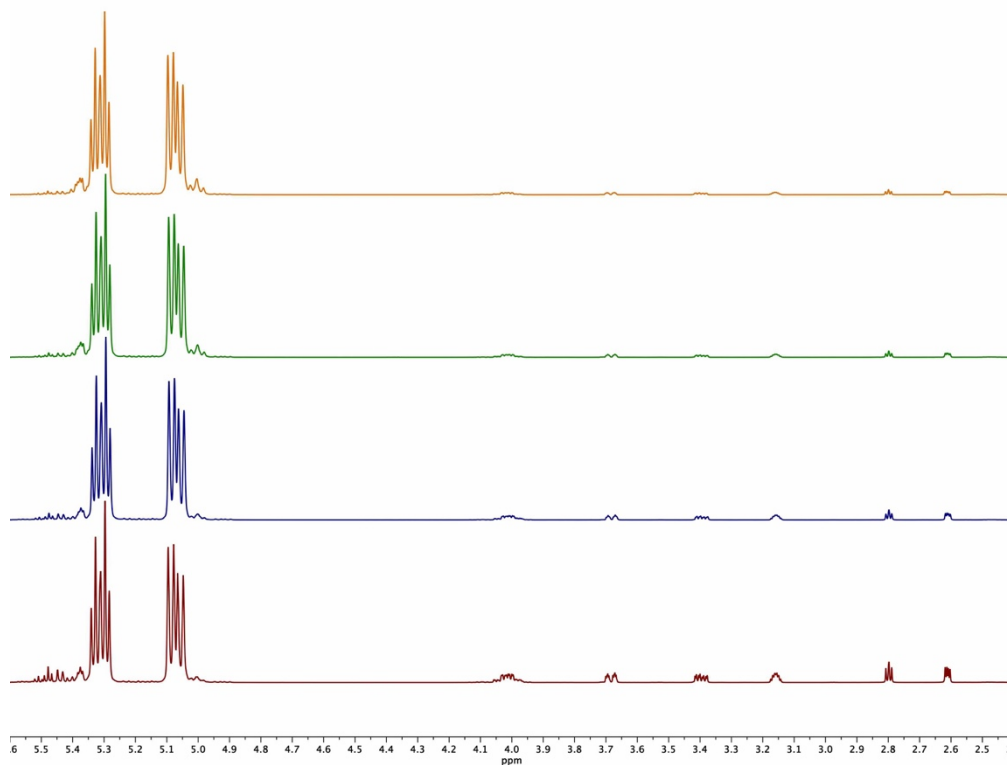


Figure S29. Expanded ^1H -NMR overlay of P-5 (maroon), P-11 (navy blue), P-19 (green), P-25 (orange).

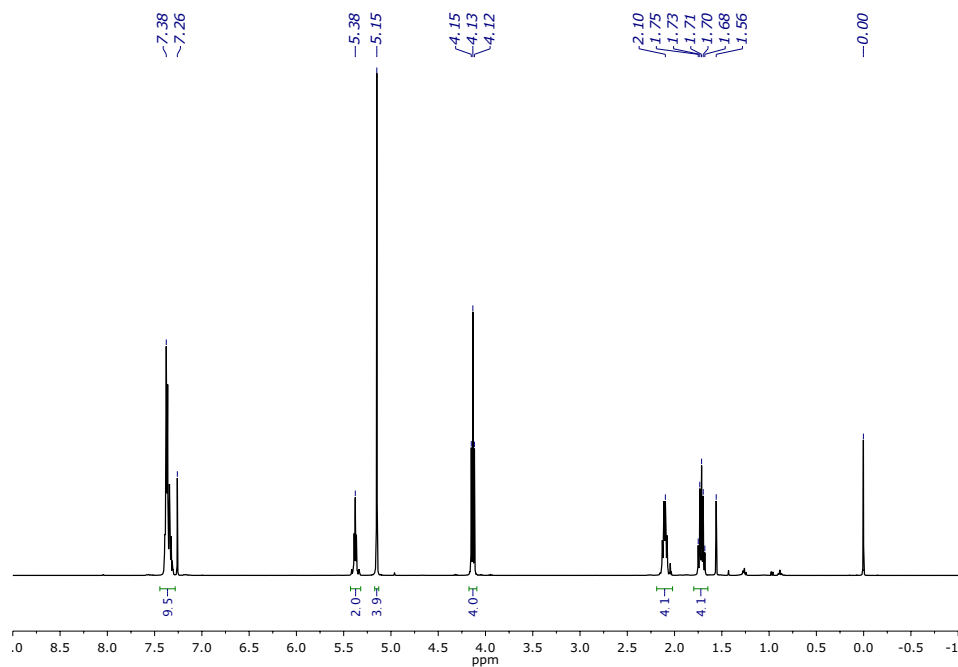


Figure S30. ^1H -NMR spectrum (400 MHz, CDCl_3) of CTA **2**.

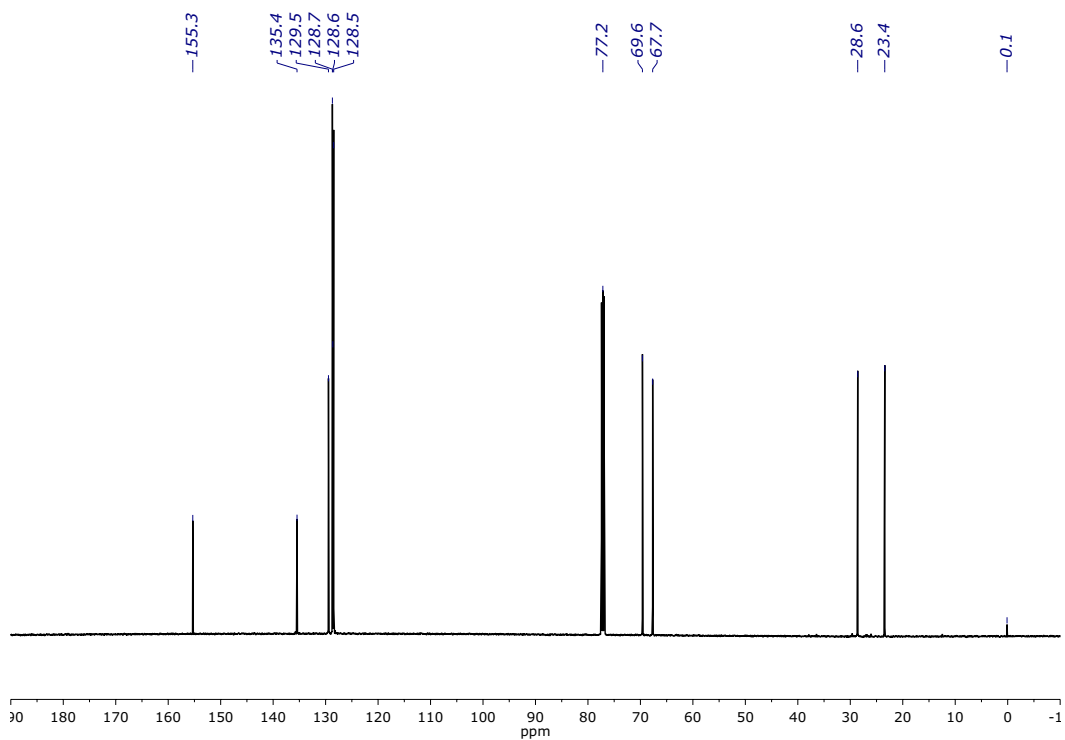


Figure S31. ^{13}C -NMR spectrum (125 MHz, CDCl_3) of CTA **2**.

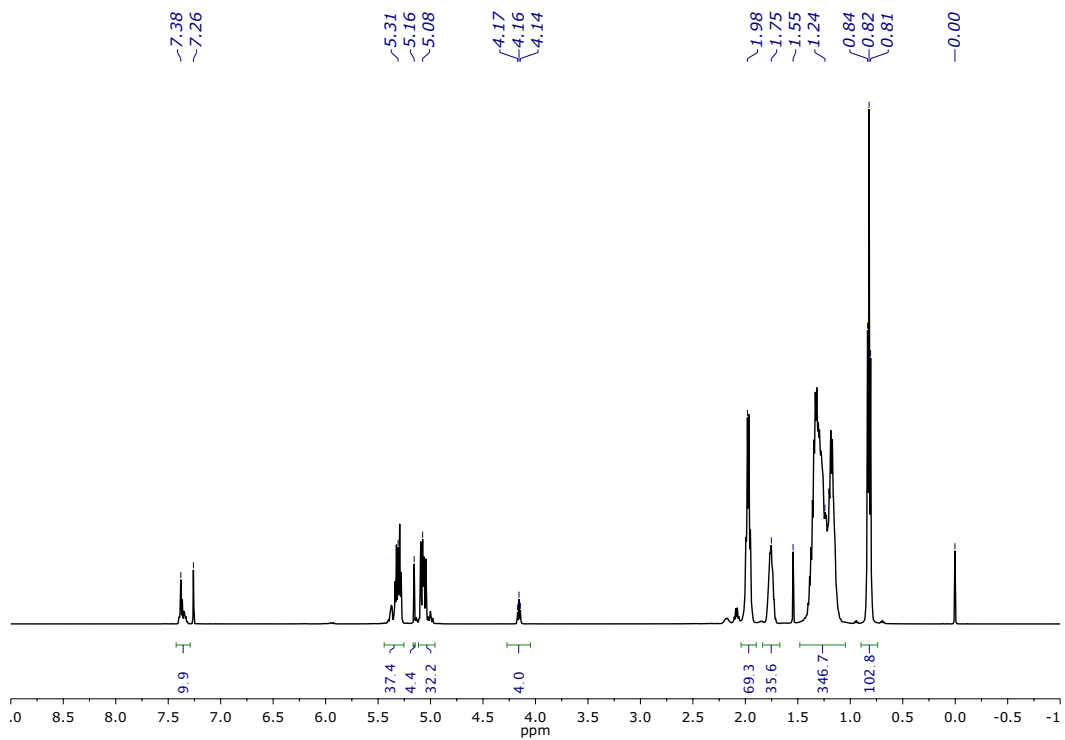


Figure S32. ^1H -NMR spectrum (500 MHz, CDCl_3) of P-5-Cbz.

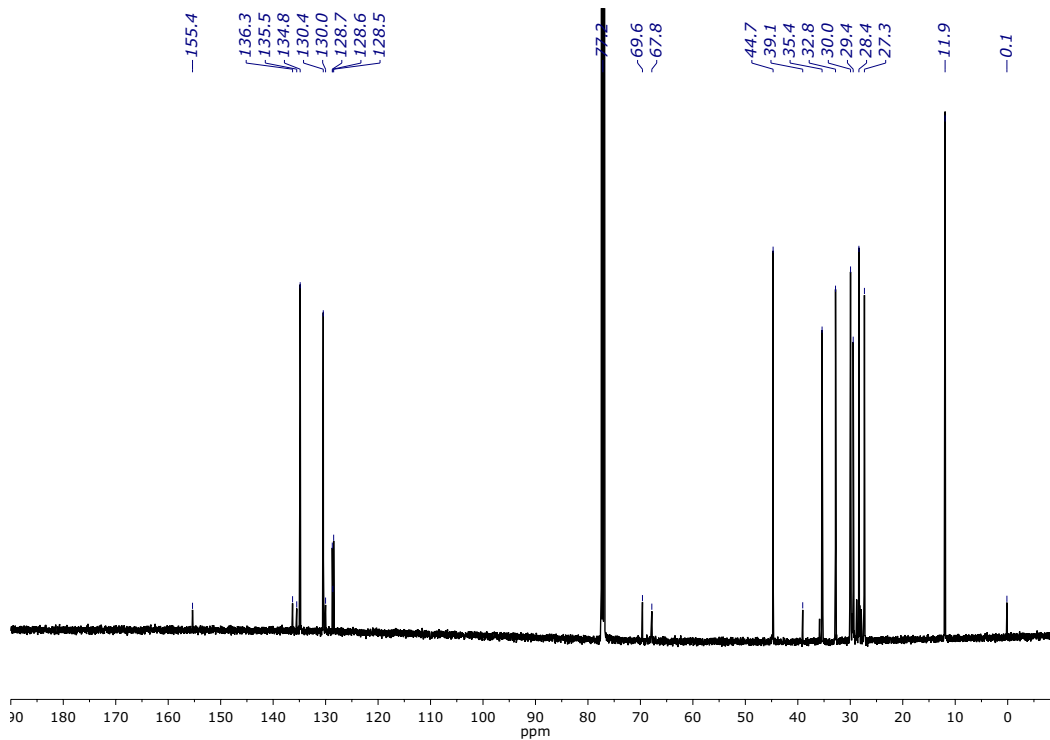


Figure S33. ^{13}C -NMR spectrum (125 MHz, CDCl_3) of P-5-Cbz.

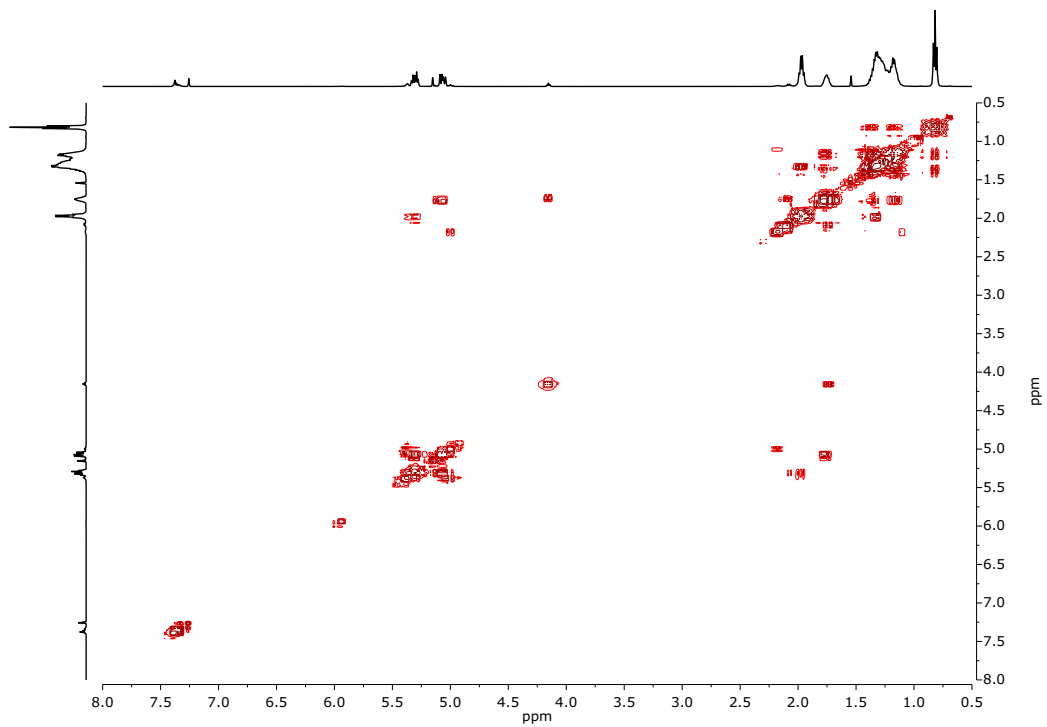


Figure S34. 2D-COSY spectrum of P-5-Cbz.

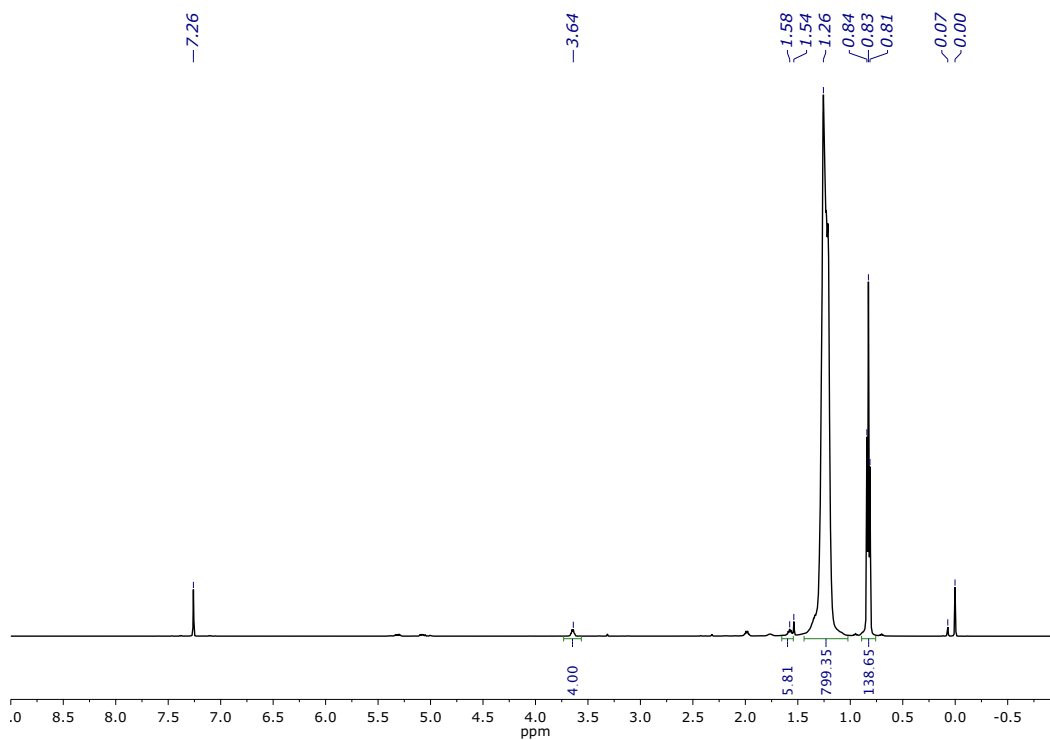


Figure S35. ^1H -NMR spectrum (500 MHz, CDCl_3) of PH-5-OH.

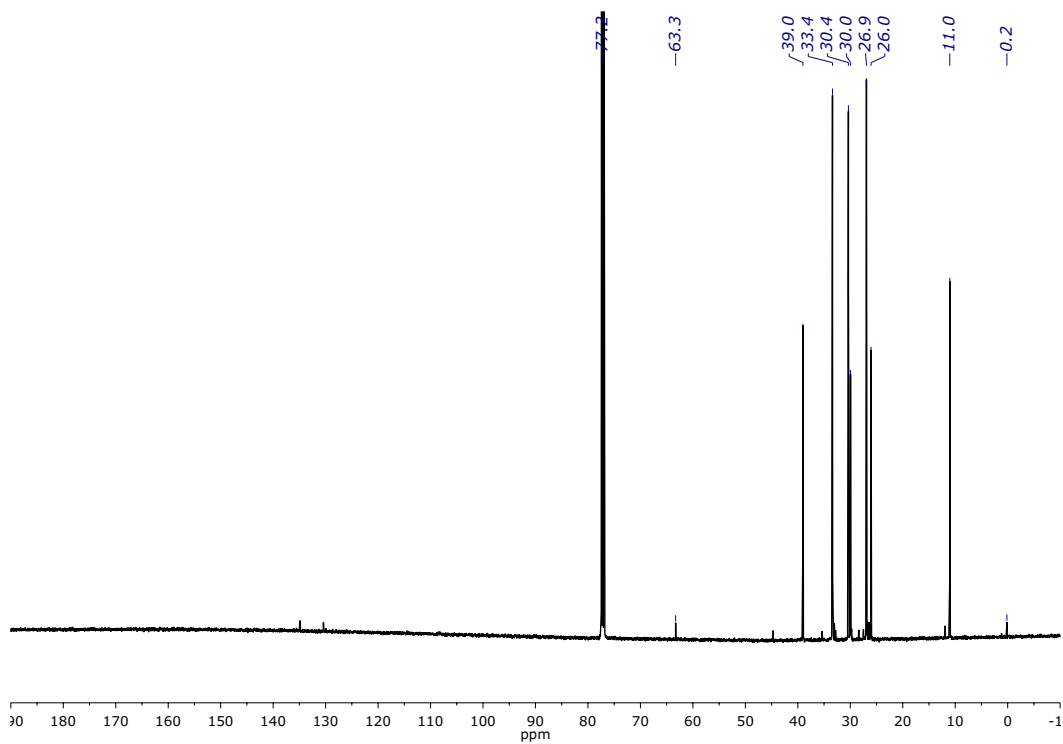


Figure S36. ^{13}C -NMR spectrum (125 MHz, CDCl_3) of PH-5-OH.

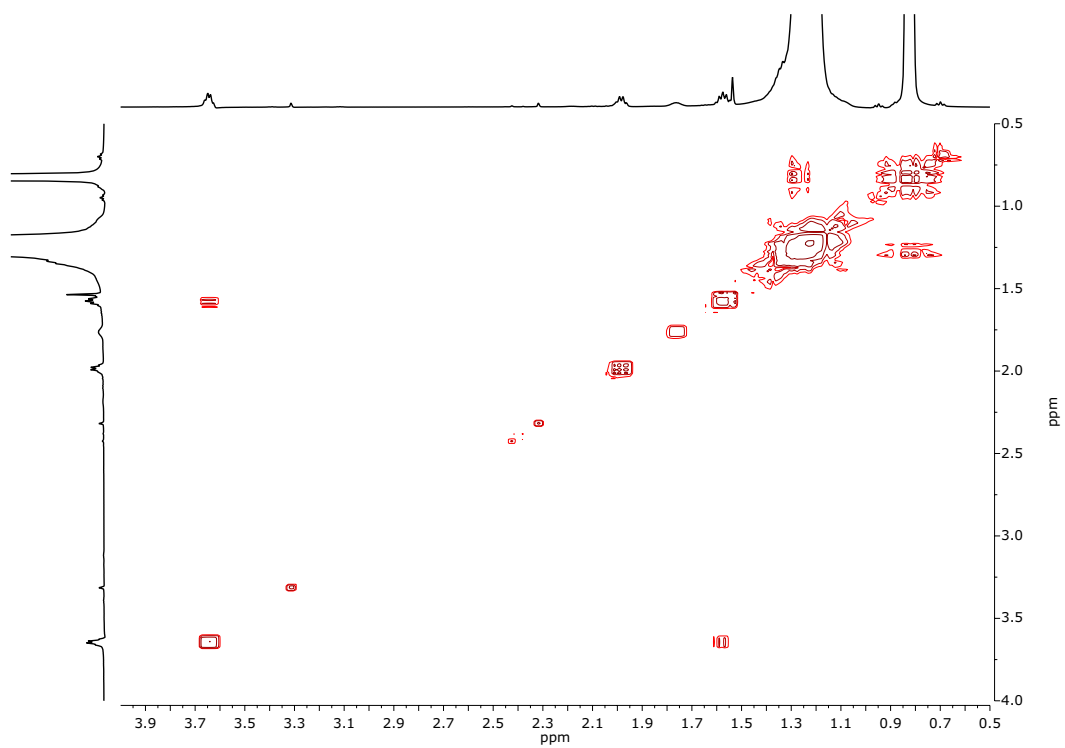


Figure S37. 2D-COSY spectrum of PH-5-OH.

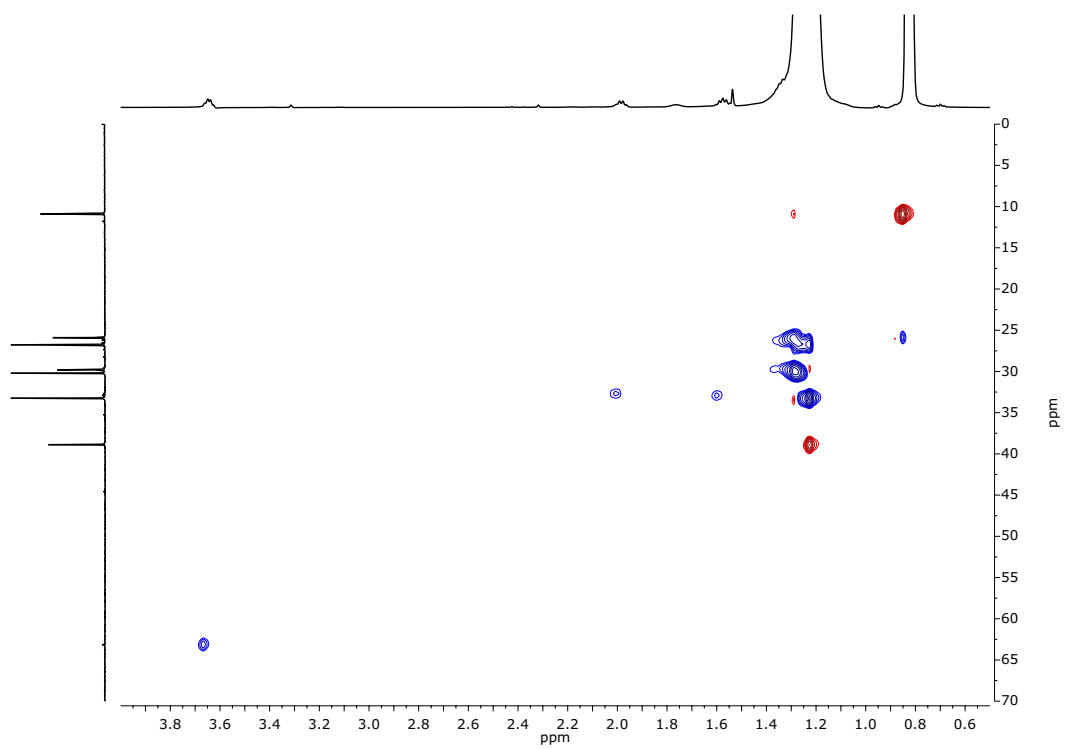


Figure S38. 2D-HSQC spectrum of PH-5-OH.

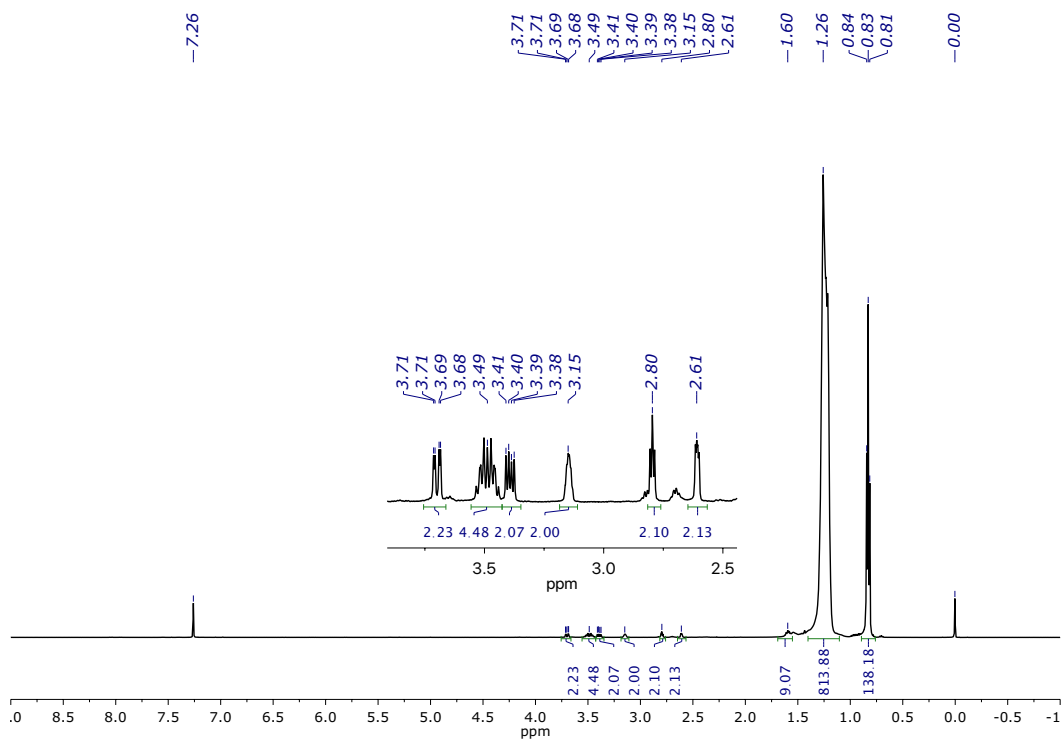


Figure S39. ^1H -NMR spectrum (500 MHz, CDCl_3) of PH-5.

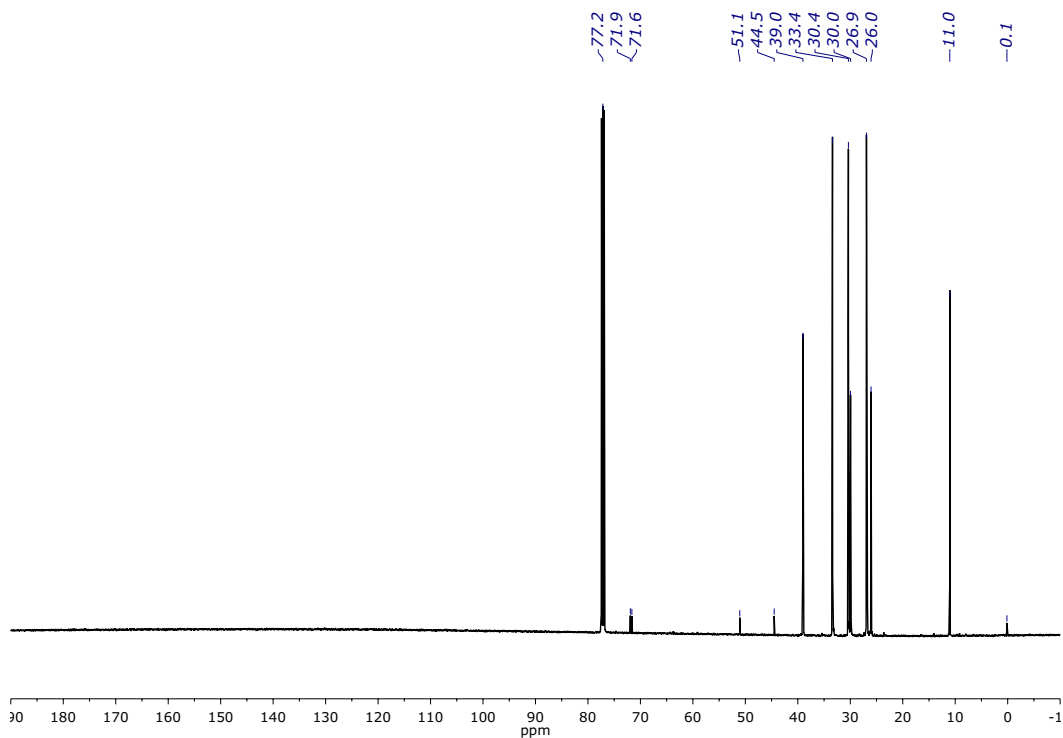


Figure S40. ^{13}C -NMR spectrum (125 MHz, CDCl_3) of PH-5.

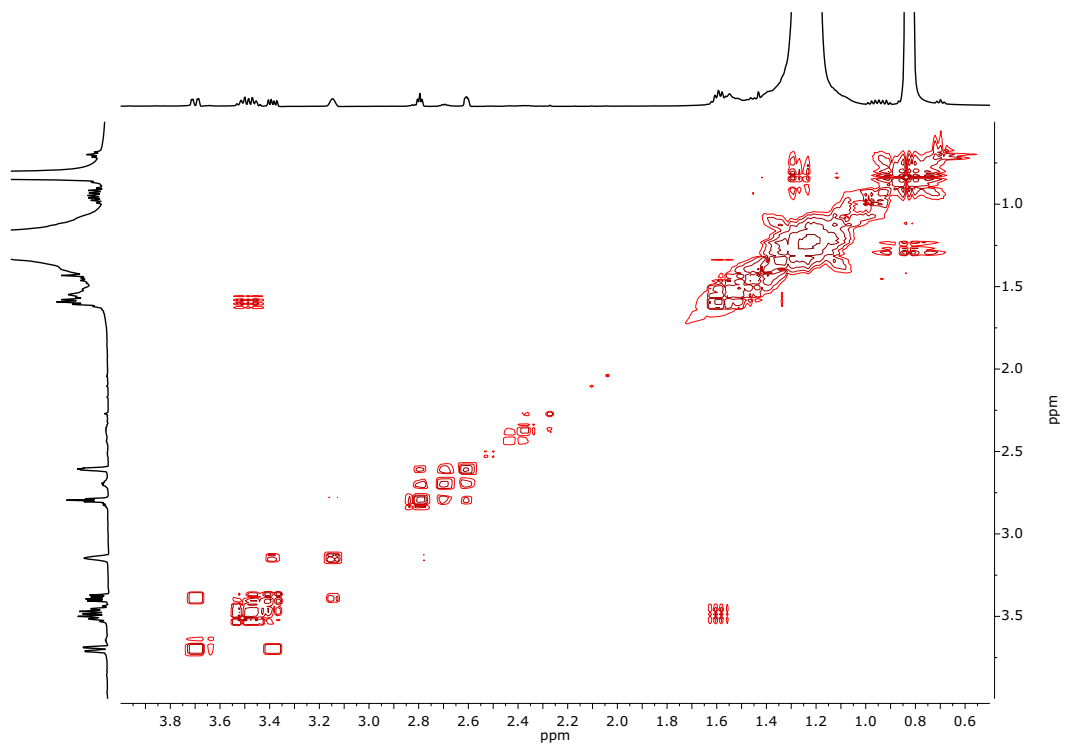


Figure S41. 2D-COSY spectrum of PH-5.

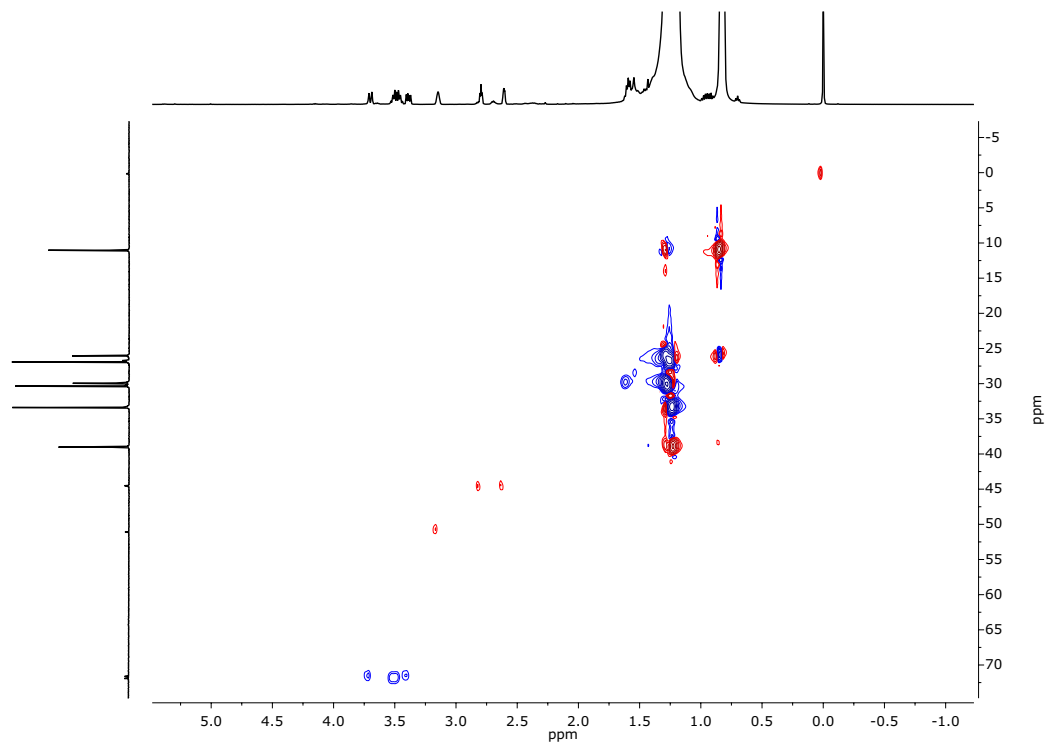


Figure S42. 2D-HSQC spectrum of PH-5.

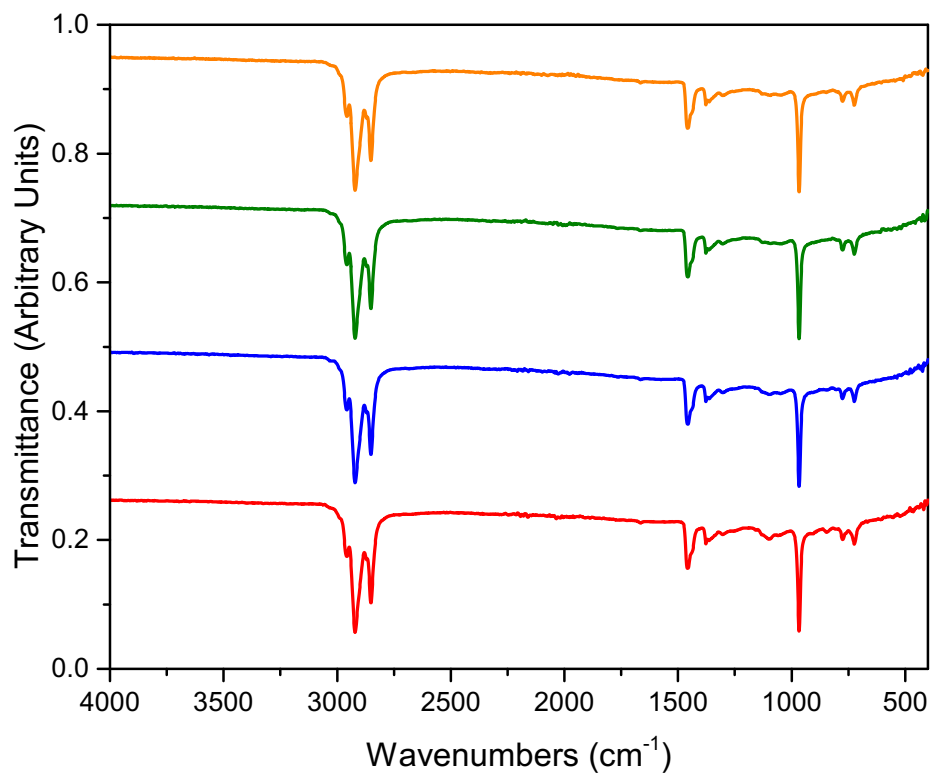


Figure S43. FTIR spectrum overlay of P-5 (red), P-11 (blue), P-19 (green), and P-25 (orange).

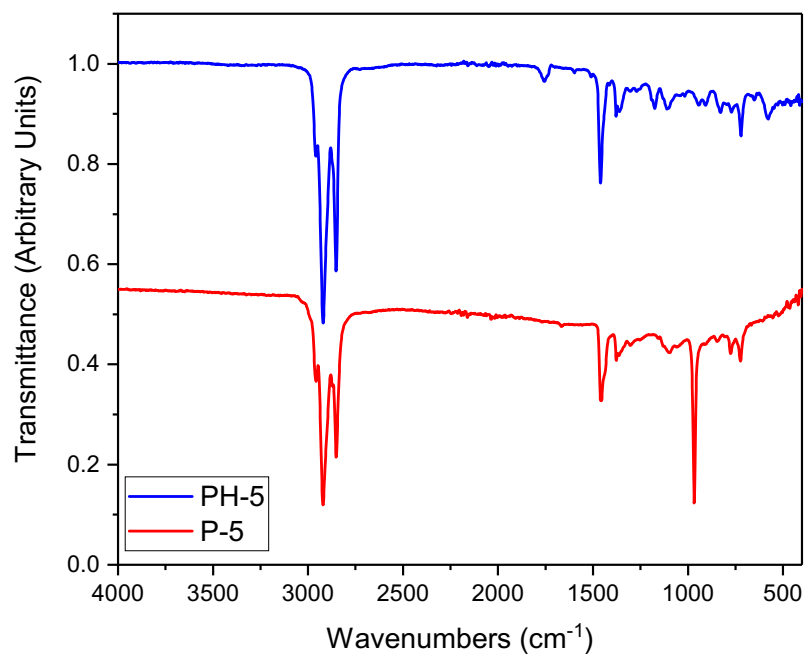


Figure S44. FTIR spectrum overlay of P-5 and PH-5.

References

1. Kobayashi, S.; Pitet, L. M.; Hillmyer, M. A. Regio- and Stereoselective Ring-Opening Metathesis Polymerization of 3-Substituted Cyclooctenes. *J. Am. Chem. Soc.* **2011**, *133*, 5794–5797.
2. Maughon, B. R.; Morita, T.; Bielawski, C. W.; Grubbs, R. H. Synthesis of Cross-Linkable Telechelic Poly(Butenylene)s Derived from Ring-Opening Metathesis Polymerization. *Macromolecules* **2000**, *33*, 1929–1935.
3. Matson, J. B.; Grubbs, R. H. Monotelechelic Poly(Oxa)Norbornenes by Ring-Opening Metathesis Polymerization Using Direct End-Capping and Cross-Metathesis. *Macromolecules* **2010**, *43*, 213–221.
4. Cox, W. P.; Merz, E. H. Correlation of Dynamic and Steady Flow Viscosities. *Journal of Polymer Science* **1958**, *28*, 619–622.