Supporting Information

Mechanochemical Generation of Acid-Degradable Poly(Enol Ether)s

Jinghui Yang, Yan Xia*
Department of Chemistry, Stanford University, Stanford, California 94305, United States.

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1. General Information

Grubbs 3rd generation catalyst was prepared following literature procedure.[1] Other reagents were obtained from commercial vendors and used as received unless otherwise noted. Flash column chromatography was performed using F60 silica gel (40-63 μm, 230-400 mesh, 60Å) purchased from Silicycle. Analytical thin-layer chromatography (TLC) was carried out on 250 μm 60-F254 silica gel plates purchased from EMD Millipore, and visualization was effected by observation of fluorescence-quenching with ultraviolet light and staining with potassium permanganate or cerium ammonium sulfate as developing agents.

^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Inova 600, Varian Inova 500, Varian Mercury 400, or Varian Inova 300 spectrometers operating respectively at 600, 500, 400, and 300 MHz for ^{1}H and at 150, 125, 100, and 75 MHz for ^{13}C. Chemical shifts are reported in parts per million (ppm) relative to residual protonated solvent for ^{1}H ($CHCl_3$ = δ 7.26) and relative to carbon resonances of the solvent for ^{13}C ($CDCl_3$ = δ 77.0). Peak multiplicities are annotated as follows: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet. LC-MS (ESI) data were collected on a Waters Alliance e2695 separations module with an XBridge 3.5 μm 2.1x50 mm C18 column in series with a 2489 UV/visible light detector and an Acquity QDa detector using MeCN/water containing 0.1% formic acid as the eluent.

Gel permeation chromatography (GPC) was carried out in THF on two PolyPore columns (Agilent) connected in series with a DAWN multiangle laser light scattering (MALLS) detector and an Optilab T-rEX differential refractometer (both from Wyatt Technology). MW of polymers were determined by GPC MALLS analysis. dn/dc values were obtained for each injection assuming 100% elution from the columns.

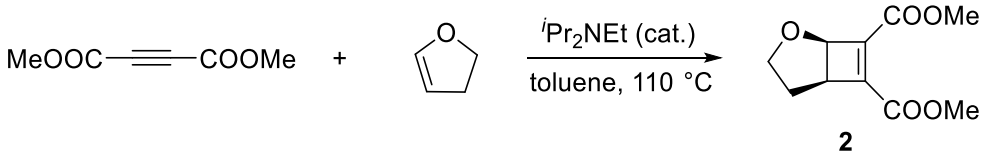
Differential scanning calorimetry (DSC) experiments were performed on a TA Instrument DSC Q2000 using Tzero aluminum pans at a heating or cooling rate of 10 °C min^{-1} under an atmosphere of nitrogen. Thermal gravimetric analysis (TGA) plots were recorded with a Mettler Toledo AG-TGA/SDTA851e at a heating rate of 10 °C min^{-1} under an atmosphere of nitrogen.

Ultrasonication was performed in a 10 mL ultrasonic vessel (Ace Glass 9843-25) with a Branson 450 sonifier equipped with a 1/8'' (3 mm diameter) tapered microtip. The distance between the tip and bottom of the vessel was 1 cm. The vessel was connected to the horn with a bushing and an O-ring to ensure airtightness. The power was calibrated according to reported procedures.[2] Sonication was performed using pulsed ultrasound (1.0 s on, 1.0 s off) at 20 kHz under Ar with an output of 9.2 W/cm^2. The vessel was placed in an ice bath to maintain a temperature inside the vessel of 6–9 °C throughout sonication experiments. All sonication times in this manuscript refer to on-time.

2. Synthetic Procedures

2.1. Synthesis of monomers

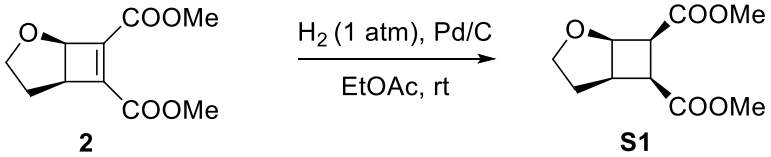
*2.1.1 Synthesis of compound **2***



The thermal cycloaddition reaction was adapted from a literature procedure[3]: dimethyl acetylenedicarboxylate (25.58 g, 22.05 mL, 180 mmol), 2,3-dihydrofuran (37.85 g, 40.84 mL, 540 mmol) and *N,N*-diisopropylethylamine (2.33 g, 3.13 mL, 18 mmol) were dissolved in toluene (45 mL). The solution was transferred into three 120 mL pressure tubes equipped with stir bars (approximately equal volumes). The pressure tubes were heated at 110 °C for one hour behind a blast shield. The reaction mixture was combined and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (33% to 50% EtOAc/hexanes) to afford **2** (6.82 g, 18%) as a yellow oil, which solidified upon cooling in freezer.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.02 (d, *J* = 3.3 Hz, 1 H), 4.14 – 4.07 (m, 1 H), 3.85 – 3.78 (m, 1 H), 3.77 (s, 3 H), 3.75 (s, 3 H). 3.51 (dd, *J* = 8.1 Hz, 3.4 Hz, 1 H), 1.90 (dd, *J* = 13.1 Hz, 5.2 Hz, 1 H), 1.72 – 1.60 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.80, 160.03, 143.59, 139.79, 77.68, 68.48, 52.41, 52.28, 46.63, 25.93. MS (ESI) calcd. for $C_{10}H_{12}O_5$ [M+H$^+$]: 213.08; found: 213.17.

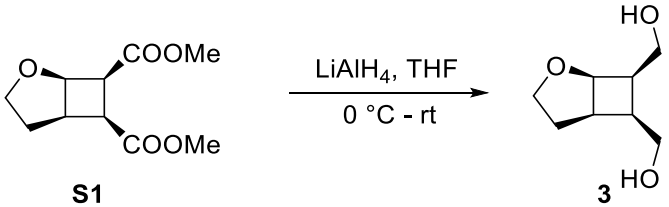
*2.1.2 Synthesis of compound **S1***



To a 250 mL round bottom flask was added **2** (7.10 g, 33.4 mmol) and 10 wt.% Pd/C (120 mg) in EtOAc (70 mL). The solution was sparged with N_2 for 5 min before exchanging for a balloon of H_2. The reaction was then stirred at room temperature under H_2 atmosphere for 19 hours. Once the reaction was complete (monitored by ^{1}H NMR), the reaction mixture was sparged with N_2 and filtered through a short plug of silica gel. The filtrate was concentrated *in vacuo* to yield **S1** (7.14 g, 99%) as a slightly yellow oil.

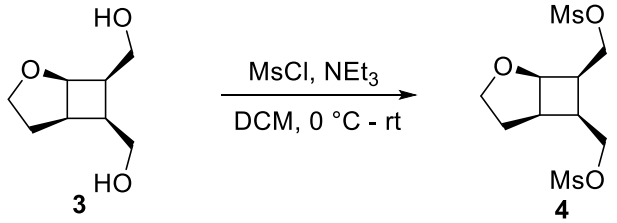
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.58 (t, *J* = 6.7 Hz, 1 H), 4.03 – 3.96 (m, 1 H), 3.78 – 3.72 (m, 1 H), 3.65 – 3.60 (m, 1 H), 3.59 (s, 3 H), 3.56 (s, 3H), 3.24 – 3.18 (m, 1H), 3.16 – 3.08 (m, 1H), 2.70 - 2.60 (m, 1H), 1.95 – 1.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.58, 170.37, 76.11, 71.43, 51.88, 51.44, 47.27, 41.69, 35.17, 27.51. MS (ESI) calcd. For $C_{10}H_{14}O_5$ [M+Na$^+$]: 237.07; found: 237.15.

*2.1.3 Synthesis of compound **2***



To a 500 ml round bottom flask was added $LiAlH_4$ (4.26 g, 112 mmol) and 30 mL THF at 0 °C. Then a solution of **S1** (8.00 g, 37.3 mmol) in 70 mL THF was added over 10 minutes. Once addition was complete, the reaction mixture was allowed to stir vigorously at room temperature for one hour. The reaction was quenched at 0 °C by adding 4.3 mL water, then 4.3 mL 15% aq. NaOH, then 12.8 mL water. The quenched reaction mixture was allowed to stir at room temperature for 15 min. The reaction mixture was then filtered and the solid was washed excessively with EtOAc. The filtrate were combined, concentrated and purified by flash column chromatography on silica gel (0% to 5% MeOH/DCM) to yield diol **3** (5.18 g, 88%) as a slight yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.58 – 4.54 (m, 1 H), 4.00 – 3.93 (m, 1 H), 3.92 – 3.82 (m, 3 H), 3.75 – 3.68 (m, 1 H), 3.66 – 3.56 (m, 2 H), 3.51 (br, 1H), 3.12 – 3.04 (m, 1H), 2.88 – 2.70 (m, 2H), 1.88 – 1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 78.71, 71.46, 59.64, 58.72, 41.71, 38.84, 36.26, 26.80. MS (ESI) calcd. For $C_8H_{14}O_3$ [M+Na^+]: 181.08; found: 181.19.

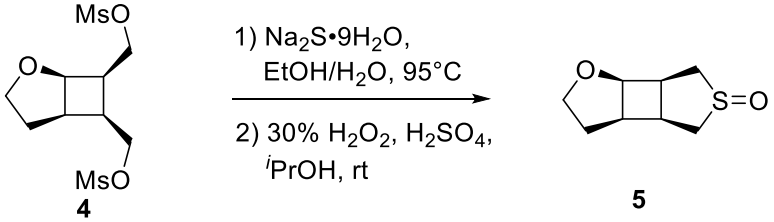
*2.1.4 Synthesis of compound **3***



3 **4**

To a 250 mL round bottom flask was added **3** (5.02 g, 31.7 mmol) and triethylamine (9.63 g, 13.27 mL, 95.2 mmol) in 95 mL dry dichloromethane under an atmosphere of N_2. Methanesulfonyl chloride (9.08 g, 6.14 mL, 79.3 mmol) was added dropwise into the reaction mixture at 0 °C. The reaction mixture was allowed to stir at room temperature for one hour. Then 100 mL water was added and the organic layer was removed. The aqueous layer was extracted twice with dichloromethane. The combined organics were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified through flash column chromatography on silica gel (100% EA) to yield **4** (9.12 g, 91%) as a slightly yellow oil, which solidified slowly.
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.57 – 4.52 (m, 1 H), 4.40 – 4.23 (m, 4 H), 4.02 – 3.91 (m, 2 H), 3.20 – 3.14 (m, 1 H), 3.03 – 2.94 (m, 8 H), 2.03 – 1.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 77.73, 71.08, 66.62, 65.81, 38.99, 37.55, 37.43, 37.27, 33.73, 26.81. MS (ESI) calcd. For $C_{10}H_{18}O_7S_2$ [M+Na^+]: 337.05; found: 337.07.

*2.1.5 Synthesis of compound **5***



4 **5**

To a 250 mL round bottom flask was added dimesylate **4** (8.58 g, 27.3 mmol) and $Na_2S{\cdot}9H_2O$ (7.87 g, 32.8 mmol) in 40 mL EtOH and 16 mL H_2O under an atmosphere of N_2. The reaction mixture was heated at 95 °C for 24 hours then cool down to 0 °C. H_2SO_4 was added as a 0.35 M solution in *i*-PrOH (31.2 mL, 10.9 mmol), followed by the addition of 30% hydrogen peroxide (7.0 mL, 68.3 mmol). The reaction mixture was allowed to warm to room temperature. After 16

hours the reaction mixture was returned to 0 °C followed by slowly addition of saturated NaHCO3 solution (40 mL) and saturated Na_2SO_3 solution (20 mL). Chloroform (100 mL) was added and the layers were separated. The aqueous layer was extracted twice with chloroform. The combined organics were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified through flash column chromatography on silica gel (0 - 20% MeOH/EtOAc) to yield **5** (3.20 g, 68%) as a slightly yellow oil. **5** was isolated as a 5:1 mixture of diastereomers that are separable chromatographically. The mixture is inconsequential: both diastereomers react the same in the following reaction.

Major isomer:

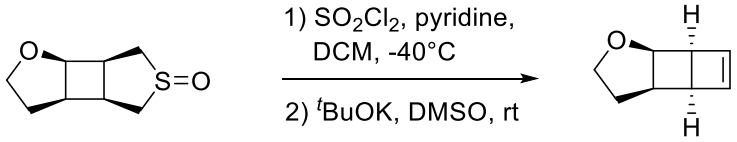
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.49 – 4.45 (m, 1 H), 3.89 – 3.77 (m, 2 H), 3.62 – 3.52 (m, 2 H), 3.22 – 3.14 (m, 1 H), 3.12 – 3.05 (m. 1H) 3.04 – 2.97 (m, 1 H), 2.94 – 2.88 (m, 1H), 2.76 – 2.70 (m, 1H), 2.02 – 1.90 (m, 1H), 1.82 – 1.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 76.61, 70.94, 54.25, 52.50, 41.65, 39.75, 36.84, 27.42.

Minor isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.57 – 4.53 (m, 1 H), 4.30 – 4.24 (m, 1 H), 4.05 -3.99 (m, 1 H), 3.42 – 3.32 (m, 2 H), 3.26 – 3.20 (m. 1H), 3.04 (dd, J = 12.6, 8.1 Hz, 1 H), 2.97 – 2.85 (m, 2 H), 2.77 (dd, J = 12.3, 8.8 Hz, 1 H), 2.03 – 1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 77.40, 71.22, 52.88, 50.30, 39.88, 36.97, 33.18, 27.87.

MS (ESI) calcd. For $C_8H_{12}O_2S$ [M+H$^+$]: 173.07; found: 173.11.

*2.1.6 Synthesis of monomer **1***



5 **1**

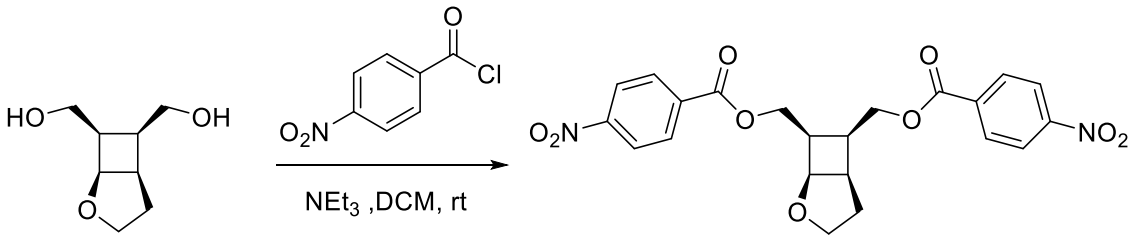
To a 100 mL flame-dried round bottom flask was charged with **5** (2.50 g, 14.5 mmol) and pyridine (2.29 g, 2.34 mL, 29.0 mmol) in 29 mL dry DCM under N_2 atmosphere at -40°C. SO_2Cl_2 (1.96 g, 1.17 mL, 14.5 mmol) was added dropwise by cannula over 5 minutes. The reaction mixture was allowed to stir at -40 °C for 1 hour. After this time, the reaction was quenched by addition of 1M HCl (50 mL). The layers were separated and the aqueous layer was extracted twice with DCM. The combined organics were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude *α*-chlorosulfoxide was directly used in the next step without further purification.

To a 100 mL flame-dried round bottom flask was charged with *tert*-butoxide (4.88 mol, 43.5 mmol) in 20 mL dry DMSO under N_2 atmosphere. A solution of crude *α*-chlorosulfoxide in DMSO (20 mL) was added by cannula over 15 minutes. The reaction mixture was allowed to stir for 12 hours at room temperature. After this time, 50 mL water was added and the reaction mixture was extracted three times with pentane (50 mL×3). The combined organics were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* by rotary evaporation at 0 °C and 200 mbar until a final volume of 20 mL was obtained. The crude mixture was purified by column chromatography (5% Ethyl ether/Pentane) to yield a solution of **1** in ether and pentane. The solvent was carefully removed by rotary evaporation at 0 °C and 200 mbar to a volume of 5 mL. A gentle flow of N_2 was passed to remove the residue solvents and yielded **1** (820 mg, 46%) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 – 6.32 (m, 1 H), 6.29 – 6.27 (m, 1 H), 4.65 (dd, J = 7.8, 5.8 Hz, 1 H), 4.08 (q, J = 7.9 Hz, 1H), 3.91- 3.86 (m, 1H), 3.31 – 3.28 (m, 1H), 3.11 – 3.07 (m, 1H),

3.05 – 2.99 (m, 1H), 1.95 -1.85 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.66, 138.99, 78.57, 74.37, 47.07, 40.35, 40.05, 29.47. MS (ESI) calcd. For $C_8H_{10}O$ [M+H$^+$]: 123.08; found: 122.98.

*2.1.7 Synthesis of compound **S2***



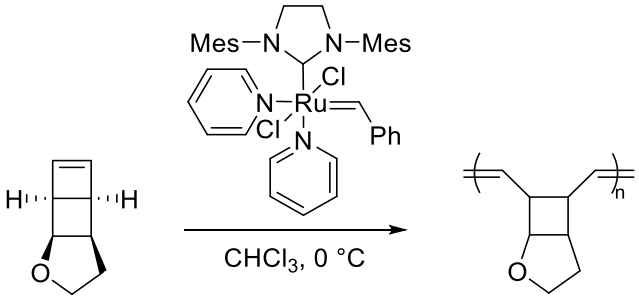
3 **S2**

To a 20 mL vial was charged with diol **3** (25.0 mg, 0.158 mmol) and triethylamine (88 μL, 0.64 mmol) in 2 mL DCM. With stirring, 4-nitrobenzoyl chloride (88.0 mg, 0.474 mmol) was added into the reaction in one portion. The reaction mixture was allowed to stir at room temperature for 1 h. Then 10 mL water was added and the organic layer was removed. The aqueous layer was extracted twice with dichloromethane. The combined organics were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified through flash column chromatography on silica gel (33% EtOAc/Hexanes) to yield **S2** (59.2 mg, 82%) as a white crystalline solid. Single crystals of **S2** were obtained by diffusing hexanes into a DCM solution.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 – 8.20 (m, 4 H), 8.16 – 8.13 (m, 4H), 4.70 – 4.67 (m, 1 H), 4.62 – 4.57 (m, 2 H), 4.55 – 4.50 (m, 2 H), 4.13 – 4.02 (m, 2 H), 3.29 – 3.23 (m, 1 H), 3.17 – 3.10 (m, 2H), 2.11 – 1.97 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.53, 164.42, 150.61, 150.52, 135.47, 135.21, 130.69, 130.66, 123.55, 123.47, 78.13, 71.22, 63.25, 61.69, 39.17, 37.54, 33.30, 27.07. MS (ESI) calcd. For $C_{22}H_{20}N_2O_9$ [M$^+$]: 456.12; found: 456.22.

2.2. Synthesis of polymers

*2.2.1 ROMP of monomer **1***

General procedure of ring-opening metathesis polymerization of **1** and its copolymerization with NBE-EtHex.

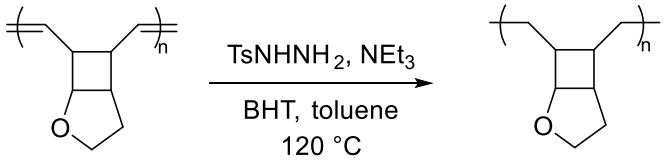


(1 M)

To a 0.5 dram vial with a stir bar was added the desired amount of monomer, then $CHCl_3$ was added to make a 1 M solution. The solution was then cooled to 0 °C. When stirring, the desired amount of **G3** stock solution was quickly injected. After stirring at 0 °C for 15 min, the reaction was quenched by several drops of ethyl vinyl ether. Solvents were evaporated *in vacuo* to a minimal extent, followed by addition of excess methanol. The polymer was collected by

centrifugation (3000 rpm, 10 min) and dried under high vacuum. The polymer was white when freshly prepared and gradually turned slightly yellow in several hours when stored under ambient conditions.

2.2.2 Hydrogenation of ROMP polymer



To a 20 mL vial with a stir bar was added freshly prepared ROMP polymer (61 mg), $TsNHNH_2$ (466 mg, 2.5 mmol, 5 equiv.) and BHT (5mg). Then NEt_3 (253 mg, 348 μL, 2.5 mmol, 5 equiv) and anhydrous toluene (5 mL) were added under nitrogen atmosphere. The vial was connected to a nitrogen balloon before heating at 120 °C for 16 h. The solution was cooled down to room temperature and added into 50 mL methanol. The precipitate was collected through filtration and washed with methanol three times to yield hydrogenated polymer as a white solid (51 mg, 82%).

3. X-Ray Crystallographic Analysis

3.1 General X-ray data collection

Single crystals of **S2** were prepared by diffusing a dichloromethane solution into hexanes. A suitable crystal was selected and measured on a D8 Venture diffractometer. The crystal was kept at 100.0 K during data collection. Using Apex3,[4] the structure was solved with the ShelXT[5] structure solution program using intrinsic phasing. Using Olex2[6] refined with the XL[7] refinement package using least squares minimization. The absolute structure was determined using anomalous dispersion. The direct Flack parameter[8] was determined from 2128 selected quotients during refinement using XL.

The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 2023034 (**S2**). These data can be obtained free of charge from CCDC via http://www.ccdc.cam.ac.uk/data_request/cif.

3.2 Crystallographic data

Table S1. Crystal data and structure refinement for **S2**.

	S2
Empirical formula	$C_{22}H_{20}N_2O_9$
Formula weight	456.40
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.8601(4)
b/Å	20.5081(11)
c/Å	7.3450(4)
α/°	90
β/°	92.7080(10)

γ/°	90
Volume/Å^3	1032.20(10)
Z	2
ρ_{calc}g/cm^3	1.468
μ/mm^{-1}	0.983
F(000)	476.0
Crystal size/mm^3	0.72 × 0.3 × 0.13
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.624 to 160.476
Index ranges	-8 ≤ h ≤ 8, -26 ≤ k ≤ 26, -8 ≤ l ≤ 9
Reflections collected	56702
Independent reflections	4448 [R_{int} = 0.0230, R_{sigma} = 0.0141]
Data/restraints/parameters	4448/1/229
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0281, wR_2 = 0.0775
Final R indexes [all data]	R_1 = 0.0282, wR_2 = 0.0776
Largest diff. peak/hole / e Å^{-3}	0.24/-0.16
Flack parameter	0.002(48)

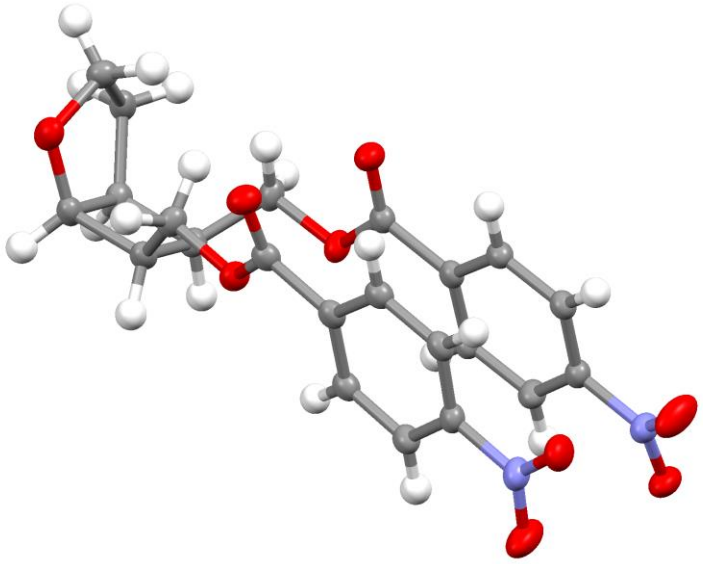
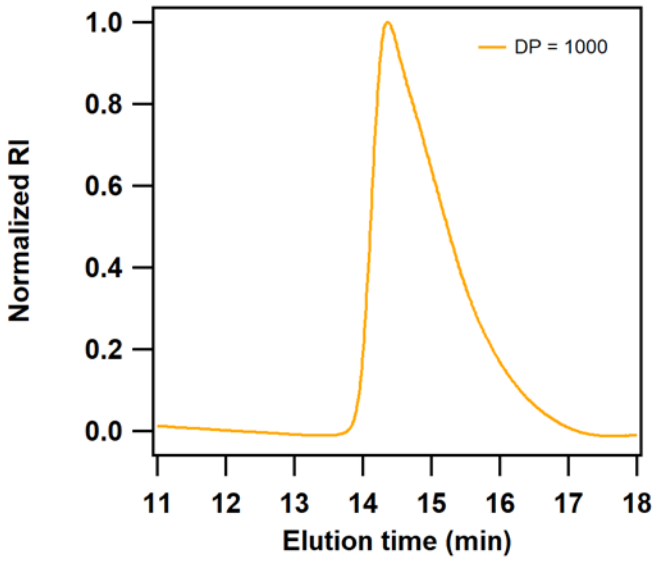


Figure S1. Single crystal structure of **S2** indicates the cyclobutane is in an *endo* configuration.

4. Supporting Figures and Tables



DP_{theory}	$M_{n,\ theory}$	$M_{n,\ MALLS}$	$Đ$
1000	122	78.2	1.32

Figure S2. GPC trace of poly(**1**) obtained from ROMP at room temperature (polymerization conditions: $[M]_0$ = 1 M in $CHCl_3$, reaction time = 15 min).

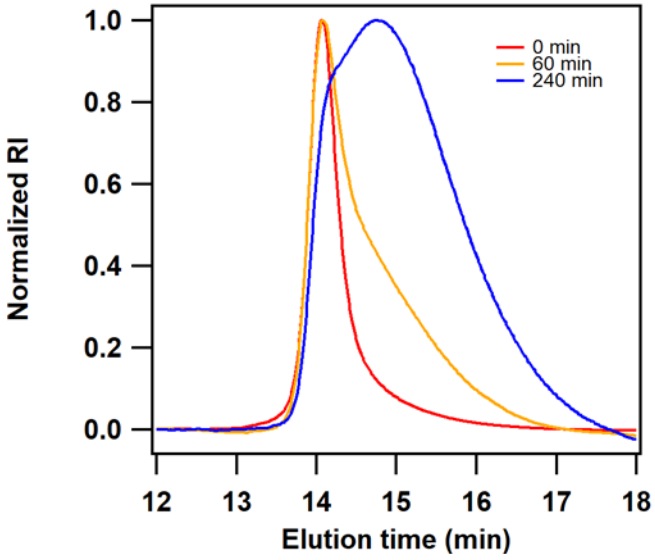


Figure S3. GPC traces of poly(**1**) showing peak broadening upon leaving quenched polymerization solution for the indicated times under ambient condition (polymerization condition: $[M]_0$ = 1 M, $[M]_0$/[**G3**] = 1000, reaction time = 15 min, temperature = 0 °C).

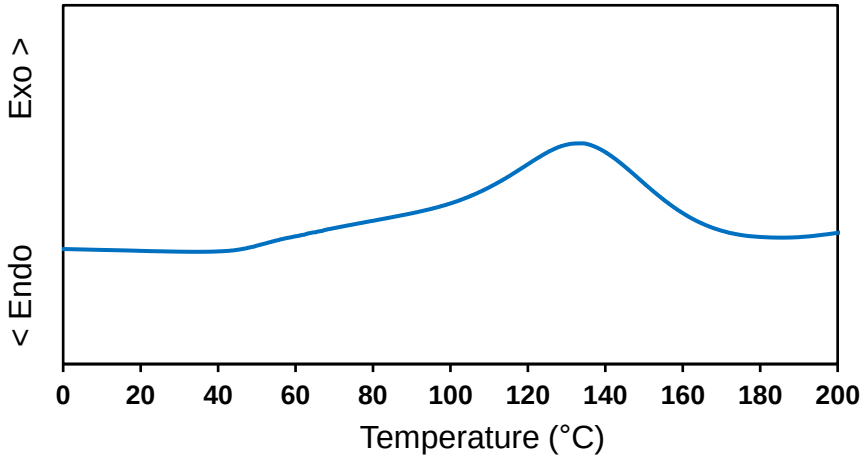


Figure S4. DSC curve of **P1** indicating thermal decomposition beginning at 46 °C.

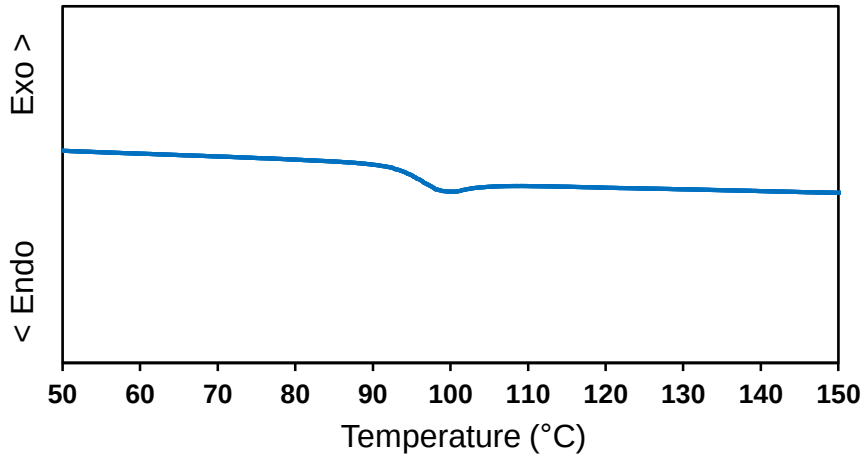


Figure S5. DSC curve of polymer **P1-H** indicating a T_g of 94 °C.

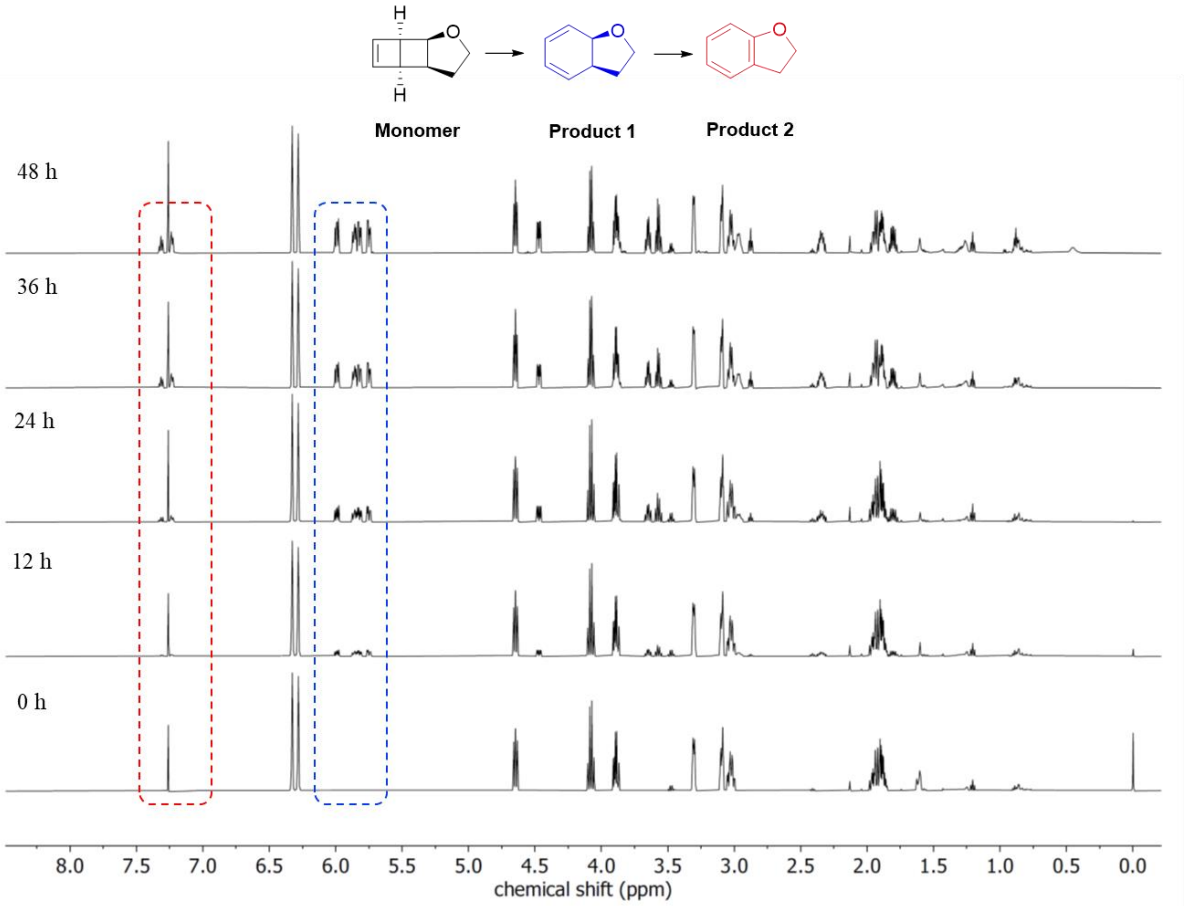


Figure S6. ^{1}H NMR analysis of thermal decomposition products of monomer **1** (heated at 65 °C in $CDCl_3$).

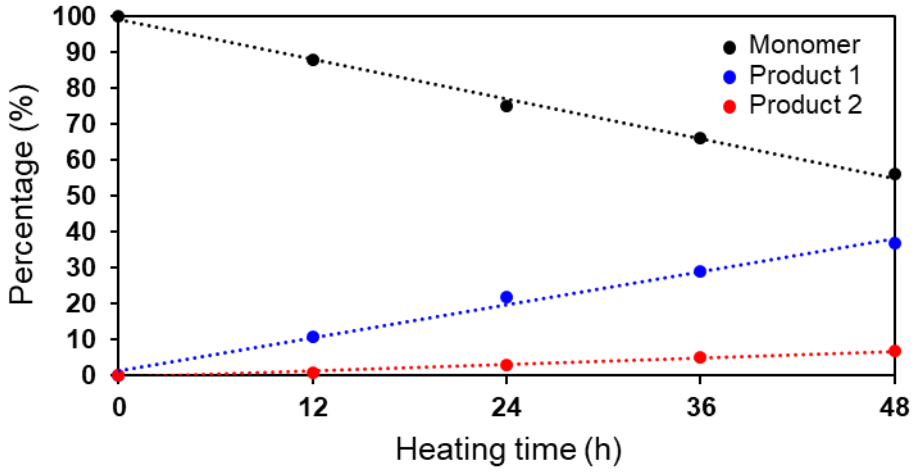


Figure S7. The change of product distribution overtime when monomer **1** was heated at 65 °C in $CDCl_3$.

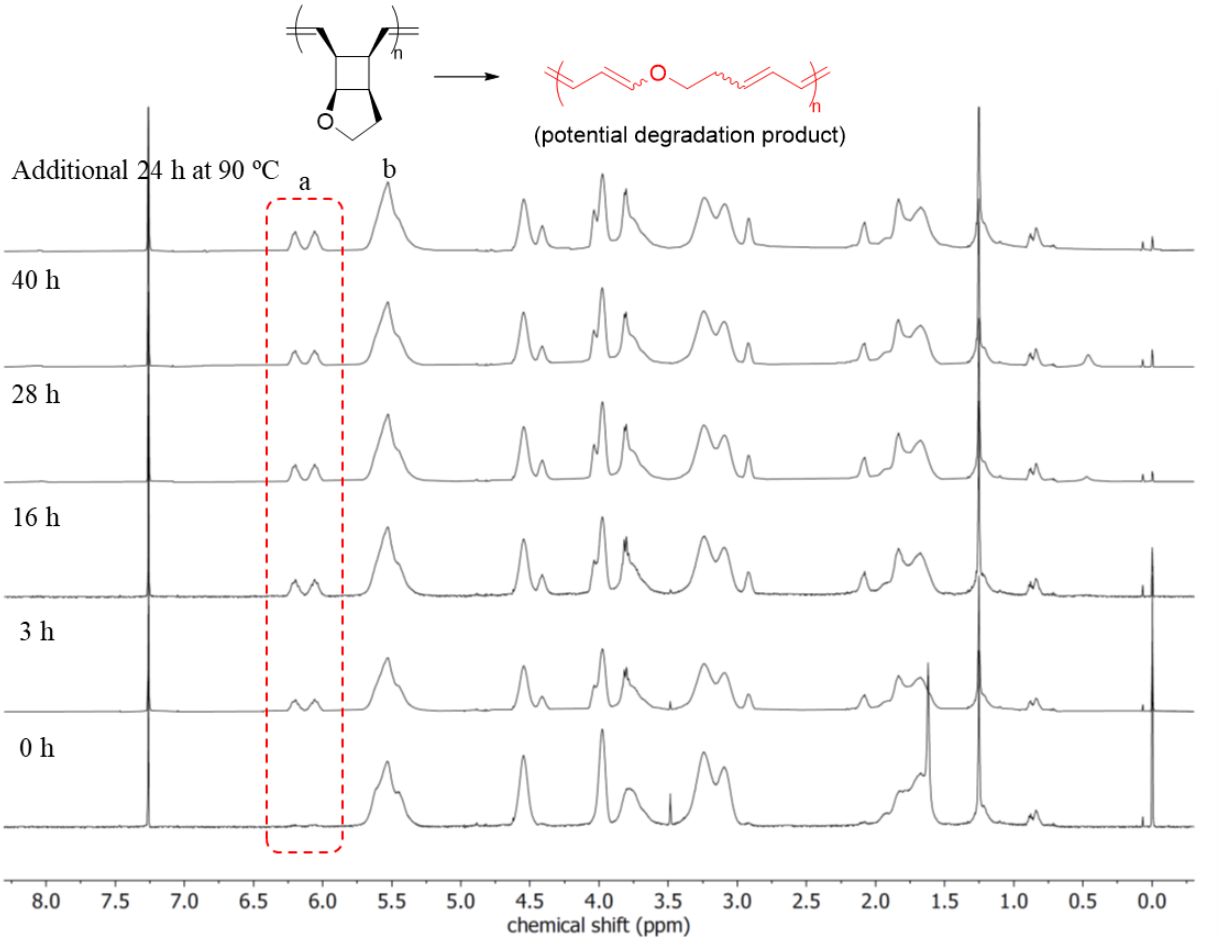


Figure S8. ^{1}H NMR analysis of the thermal decomposition of **P2** (heated at 65 °C in $CDCl_3$), the red box indicated peaks from hypothesized conjugated olefins from thermal ring-opening.

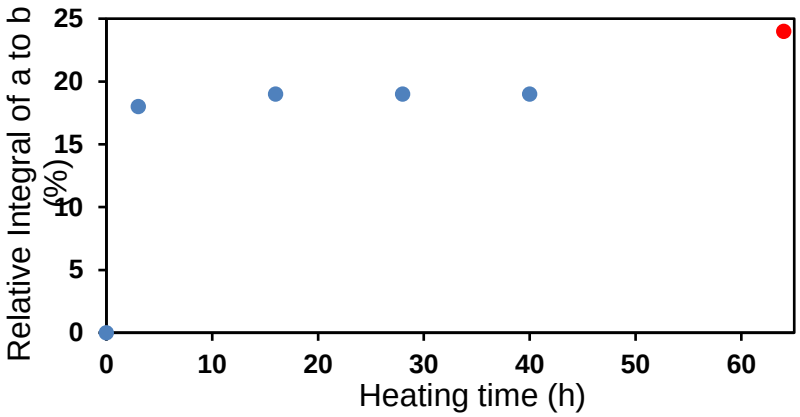


Figure S9. The relative integral of peak a (olefins between 6.0 ppm and 6.3 ppm) to peak b (olefins between 5.3 ppm to 5.7 ppm) at different heating times (**P2** was initially heated at 65 °C in $CDCl_3$ for 40 h, followed by heating at 90 °C for additional 24 h).

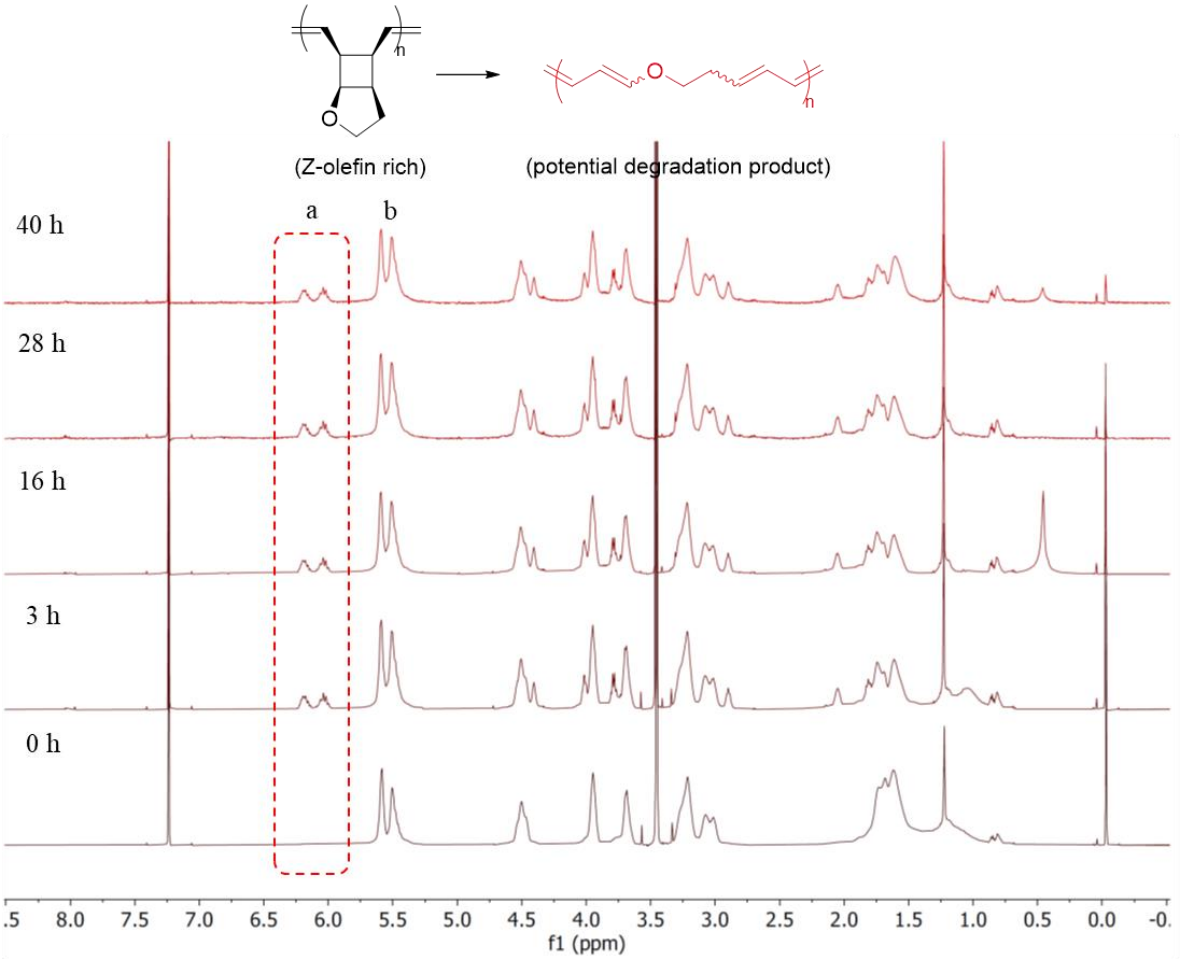


Figure S10. ^{1}H NMR analysis of the thermal decomposition of *Z*-olefin rich poly(**1**) (heated at 65 °C in $CDCl_3$).

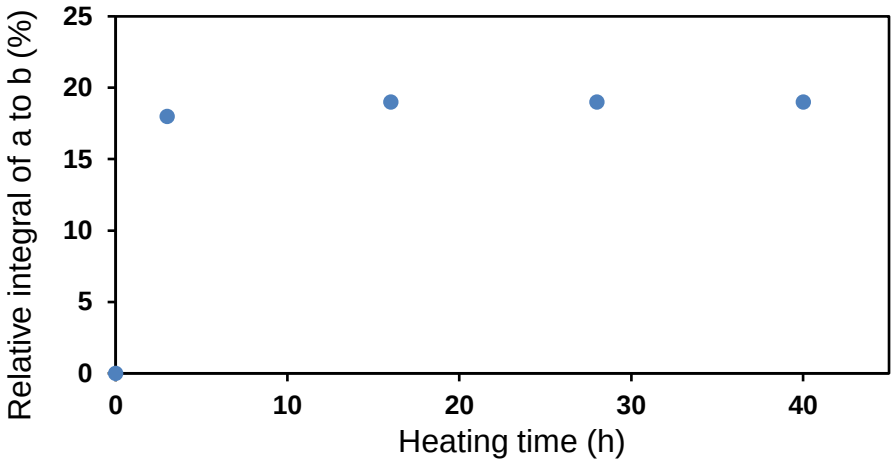


Figure S11. The relative integral of peak a (olefins between 6.0 ppm and 6.3 ppm) to peak b (olefins between 5.3 ppm to 5.7 ppm) at different heating times.

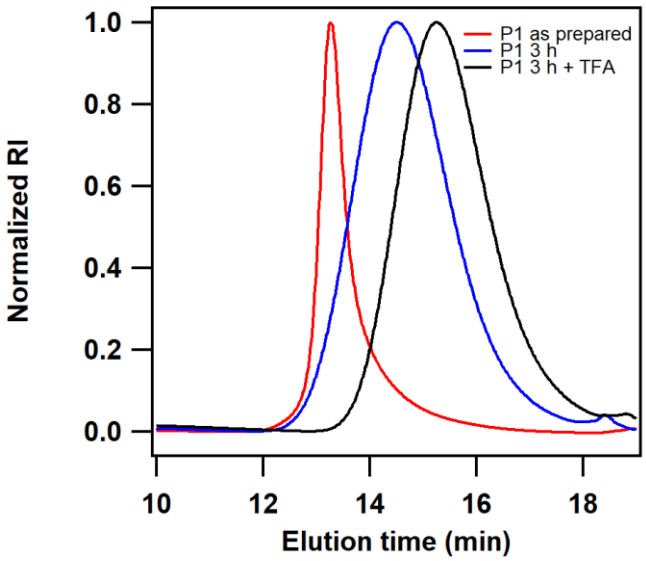


Figure S12. GPC traces of **P1** after heating at 65 °C for 3 h in THF (blue trace) followed by addition of 10 mM TFA (black trace). The decrease of molecular weight after acid treatment indicates enol ether as a plausible decomposition product, and adventitious acid or water may have already caused enol ether hydrolysis and decrease in polymer molecular weight during heating.

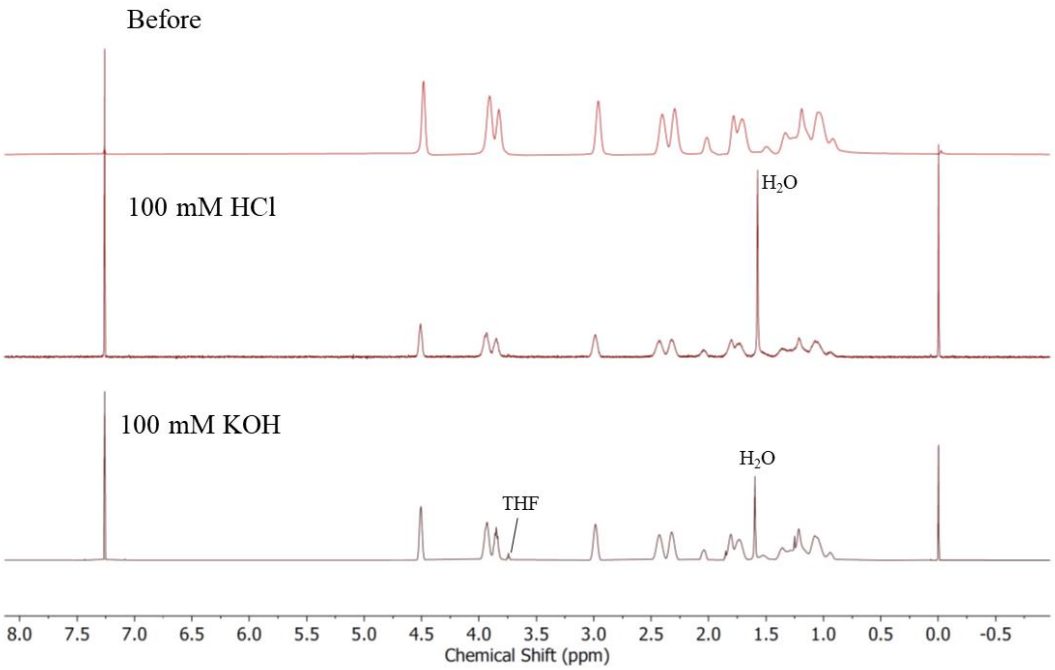


Figure S13. ^{1}H NMR spectra of **P2-H** before and after treated with either 100 mM HCl in THF or 100 mM KOH in 9:1 (v/v) THF/H_2O for 72 h.

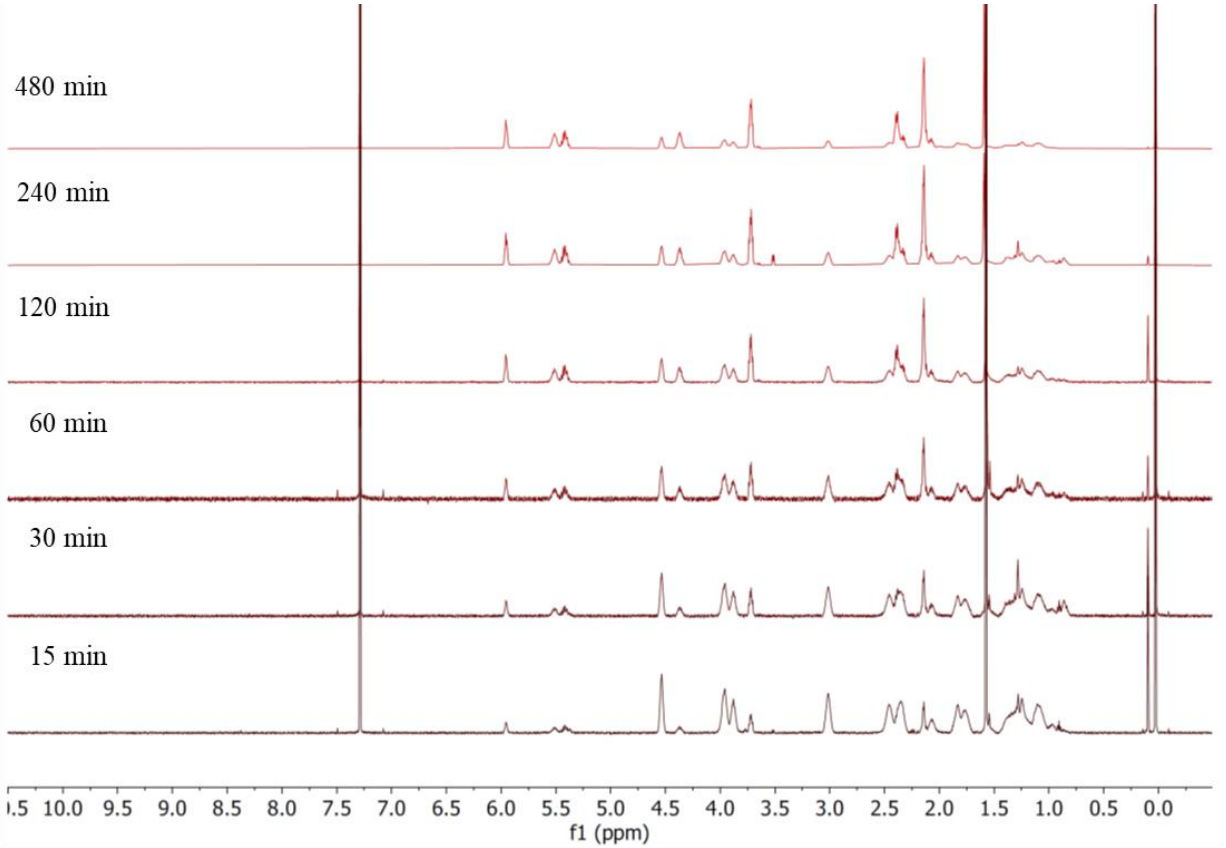


Figure S14. ^{1}H NMR spectra of **P1-H** at different sonication times.

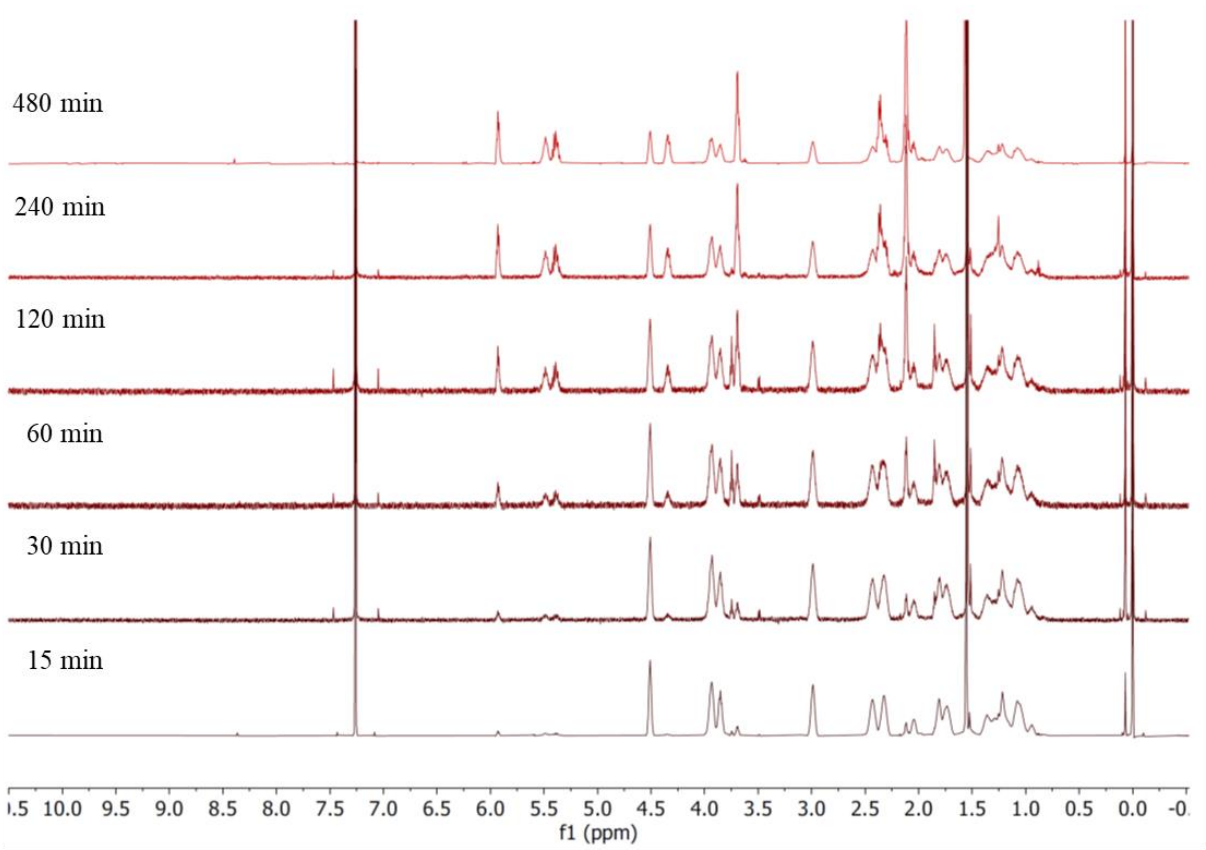


Figure S15. ^{1}H NMR spectra of **P2-H** at different sonication times.

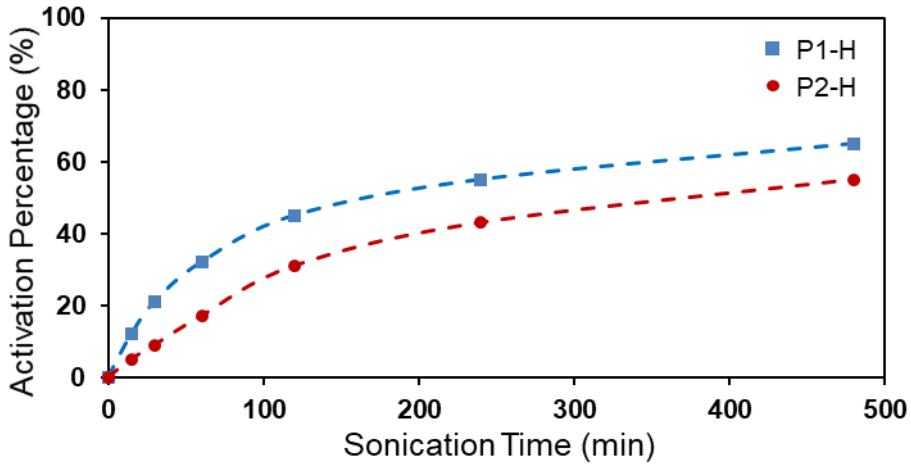


Figure S16. Plot of activation percentage versus time for **P1-H** and **P2-H**.

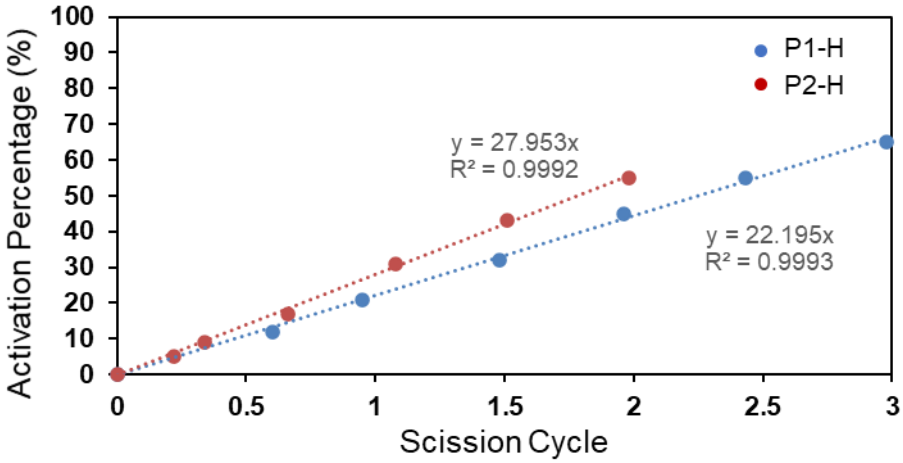


Figure S17. Activation percentage versus scission cycle for **P1-H** and **P2-H**. The activation percentage per scission cycle for **P1-H** and **P2-H** is 22% and 28%, respectively.

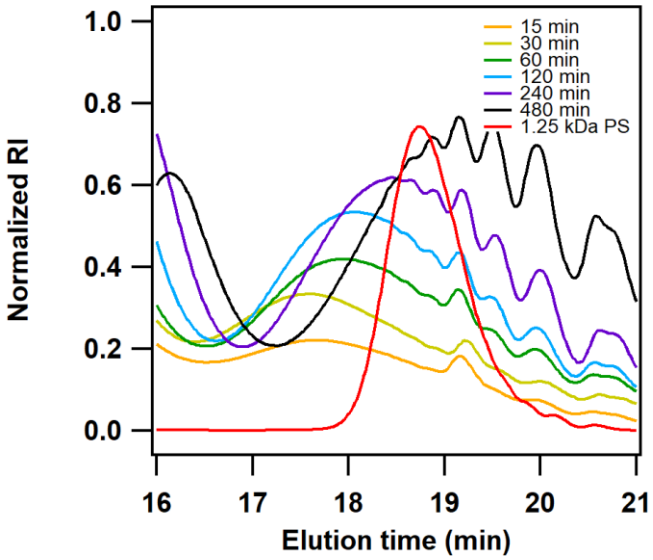


Figure S18. GPC traces of **P1-H** at different sonication times after 10 mM TFA treatment. The red trace is a PS standard (M_n = 1.25 kDa) for comparison of MW.

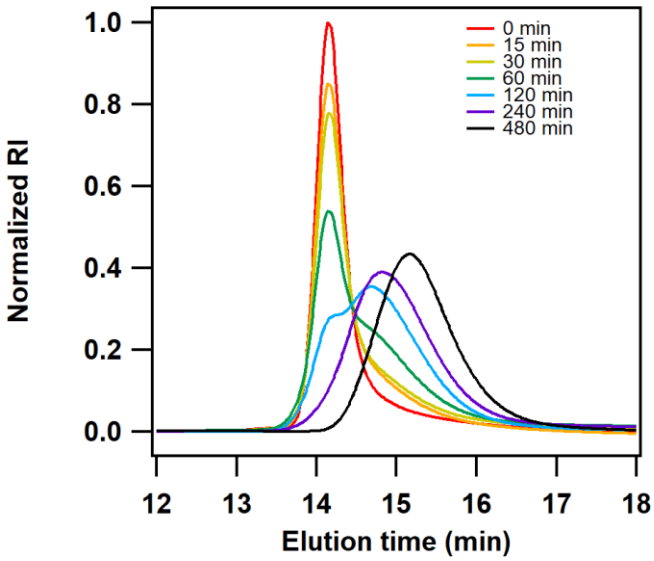


Figure S19. GPC traces of **P2-H** at different sonication times (sonication condition: 1 mg/mL solution in THF).

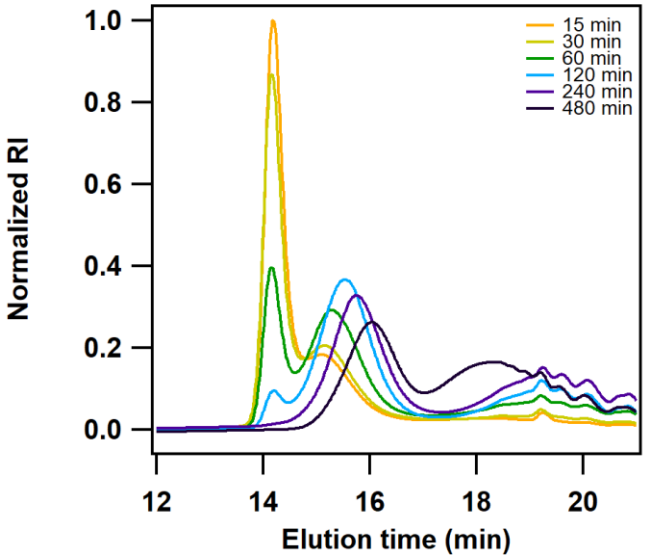


Figure S20. GPC traces of **P2-H** at different sonication times after 10 mM TFA treatment.

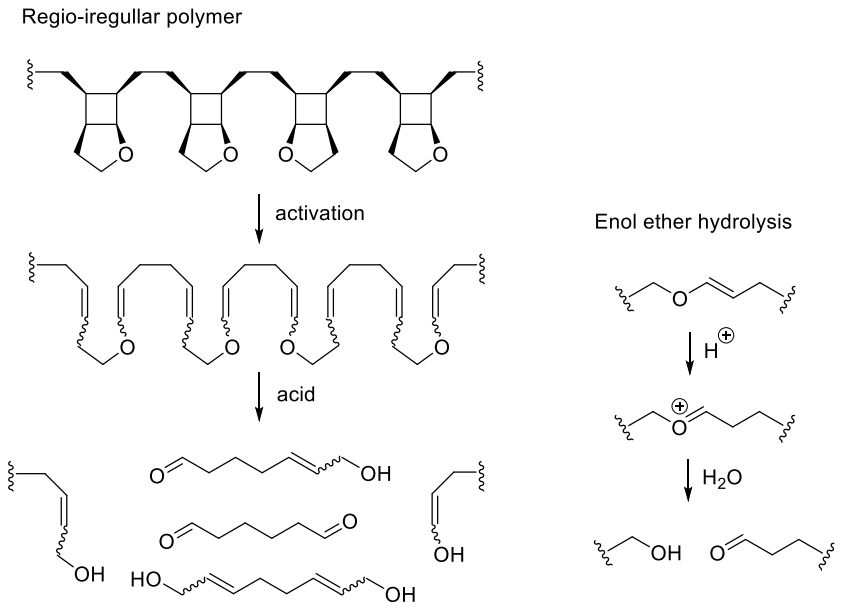


Figure S21. Several possible small molecule hydrolysis products due to the regio-irregular placement of the pendent cyclic ether rings.

Table S2. Summary of sonication experiment of **P1-H**.

Time (min)	M_n (kDa)	Scission Cycle[a]	Activation %
0	141	0	0
15	93.4	0.60	12
30	73.1	0.95	21
60	50.8	1.48	32
120	36.4	1.96	45
240	26.2	2.43	55
480	18.0	2.98	65

[a] Scission cycle was calculated using following equation: Scission Cycle = $[\ln(M_{n,0}/M_{n,t})]/\ln 2$.

Table S3. Summary of sonication experiment of **P2-H**.

Time (min)	M_n (kDa)	Scission Cycle	Activation %
0	74.0	0	0
15	63.4	0.22	5
30	58.3	0.34	9
60	46.9	0.66	17
120	35.0	1.08	31
240	25.9	1.51	43
480	18.7	1.98	55

Table S4. Summary of MW analysis after acidic degradation for sonicated **P1-H**.

Time (min)	M_n after sonication (kDa)	M_n of $\mathbf{P_{unactivated}}$ (kDa)
0	141	141
15	93.4	69.0
30	73.1	45.6
60	50.8	32.1
120	36.4	23.7
240	26.2	15.7
480	18.0	9.6

Table S5. Summary of MW analysis after acidic degradation for sonicated **P2-H**.

Time (min)	M_n after sonication (kDa)	M_n of $\mathbf{P_{unactivated}}$ (kDa)
0	74.0	74.0
15	63.4	55.0
30	58.3	47.4
60	46.9	30.2
120	35.0	20.8
240	25.9	14.1
480	18.7	10.7

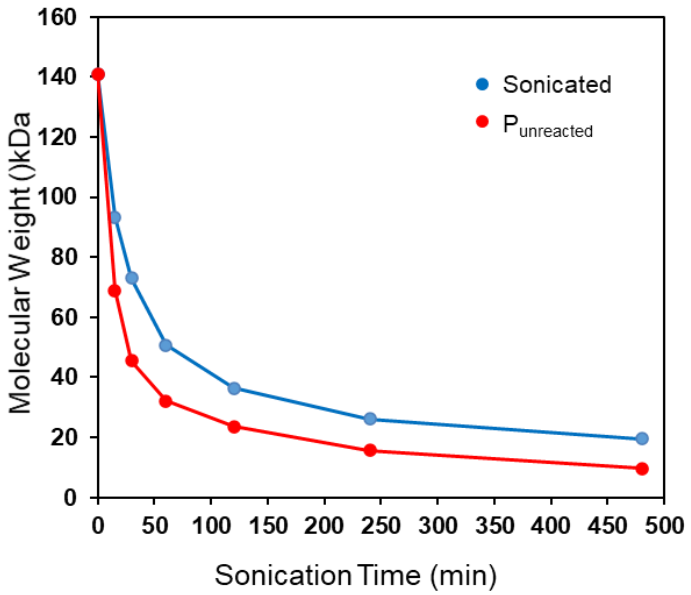


Figure S22. M_n of sonicated **P1-H** before acidic degradation (blue curve) and $\mathbf{P_{unreacted}}$ at different sonication times (red curve). $\mathbf{P_{unreacted}}$ refers to the unactivated polymer segments that are presumably located toward the ends of the polymer chain.

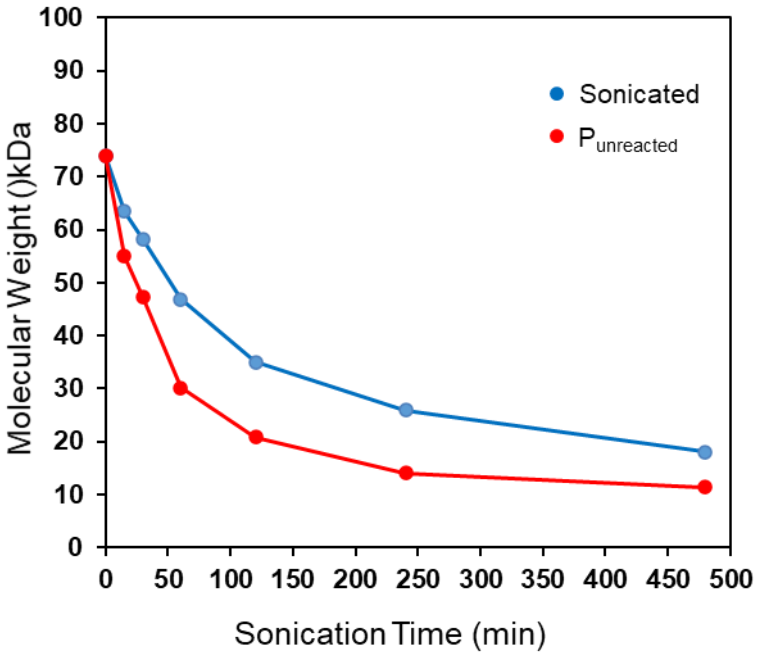


Figure S23. M_n of sonicated **P2-H** before acidic degradation (blue curve) and **P$_{unreacted}$** at different sonication times (red curve). **P$_{unreacted}$** refers to the unactivated polymer segments that are presumably located toward the ends of the polymer chain.

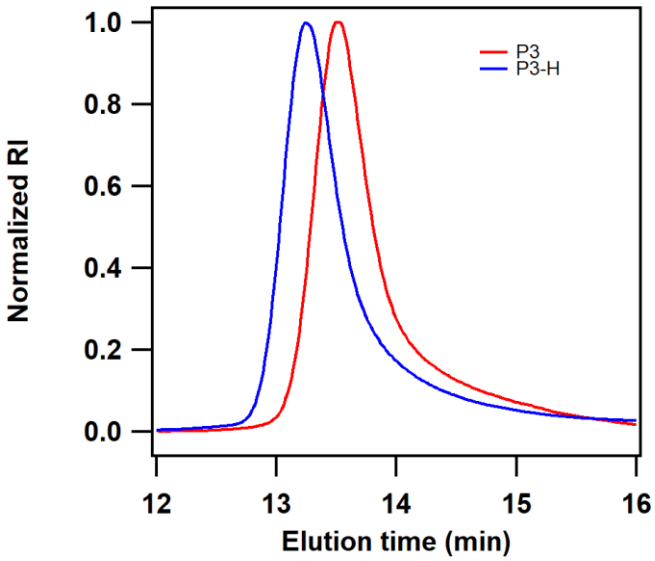


Figure S24. GPC traces of **P3** and **P3-H**.

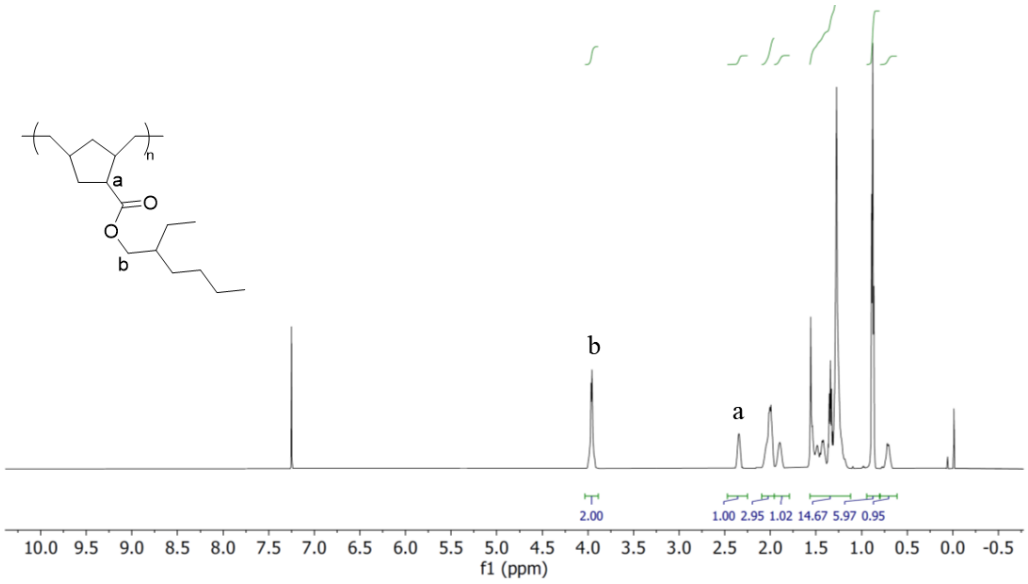


Figure S25. ^{1}H NMR spectrum of hydrogenated poly(NBE-EtHex). The relative integration of proton a and b implies that the side chain ester is preserved under the hydrogenation condition.

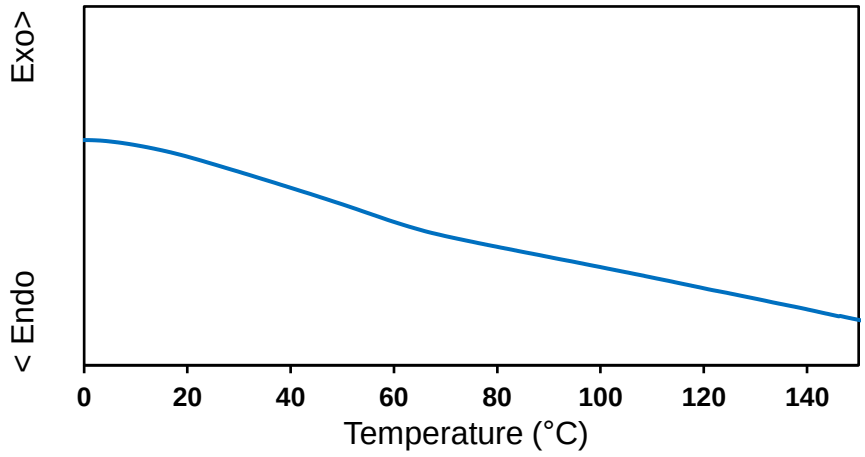


Figure S26. DSC curve of polymer **P3-H** indicating a T_g of 56 °C.

5. Additional NMR Spectra

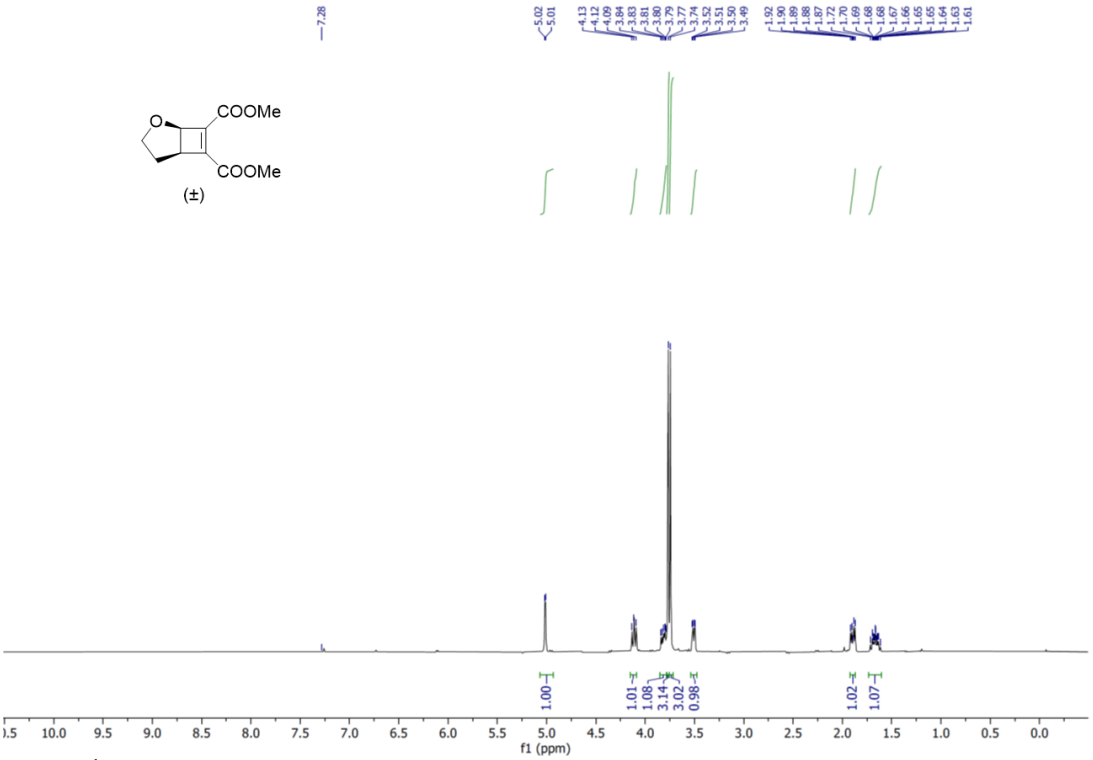


Figure S27. ^{1}H NMR spectrum of **2**.

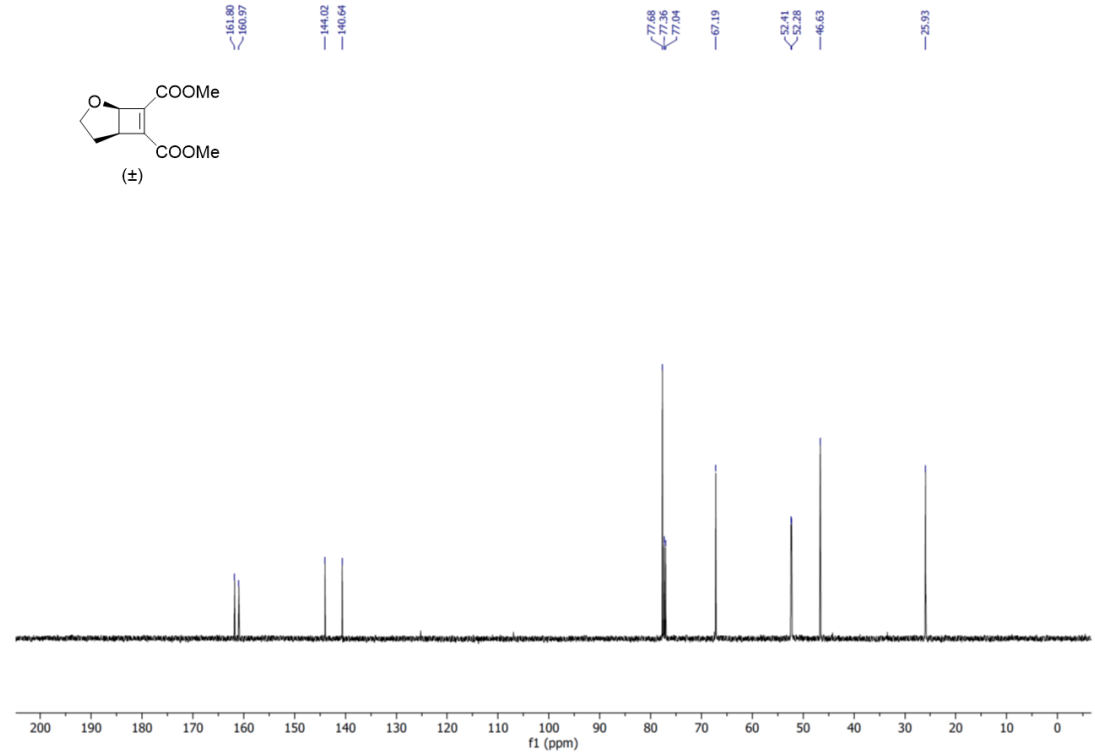


Figure S28. ^{13}C NMR spectrum of **2**.

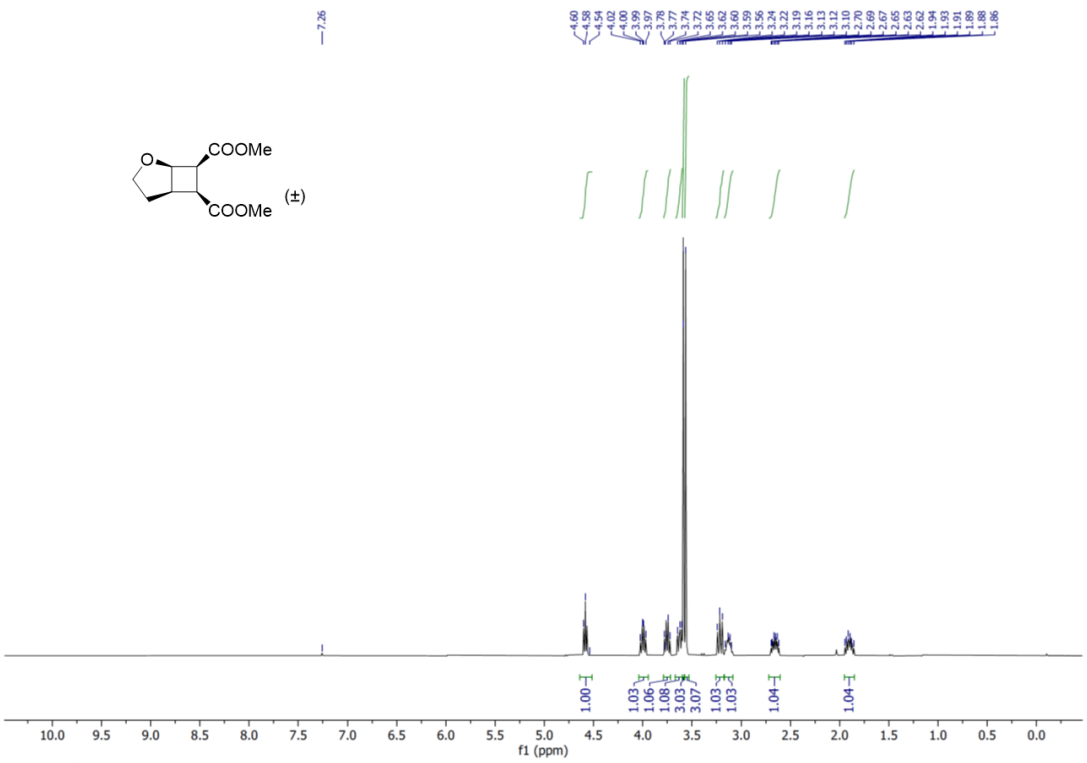


Figure 29. ^{1}H NMR spectrum of **S1**.

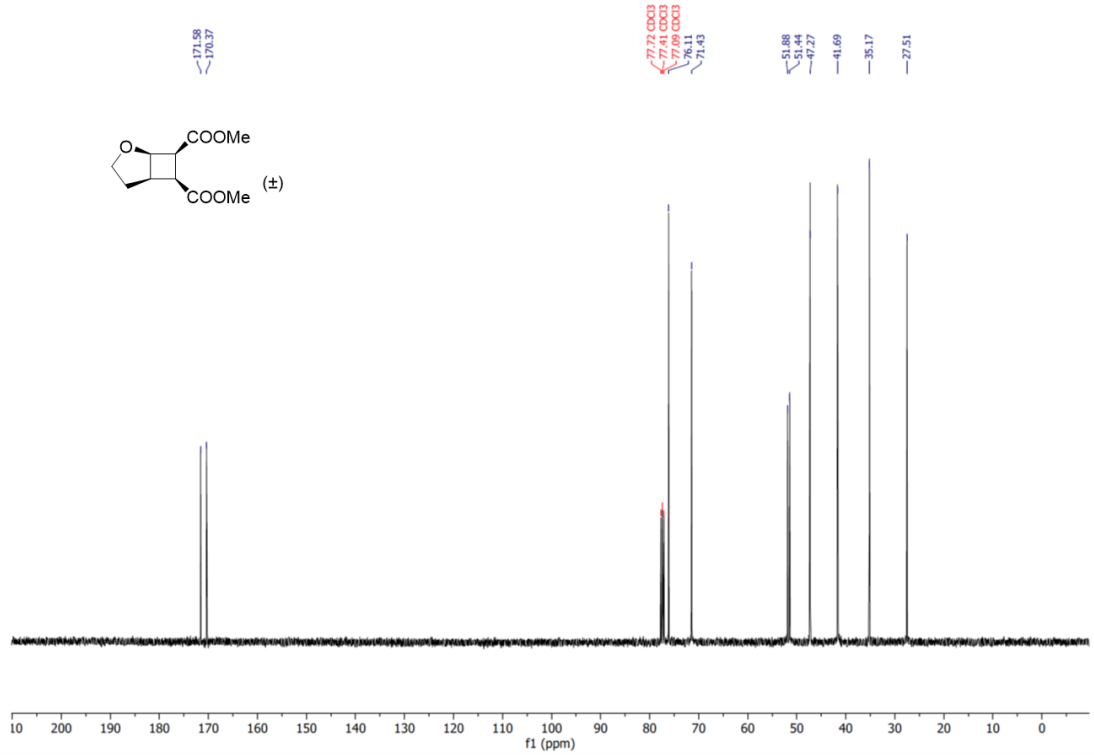


Figure S30. ^{13}C NMR spectrum of **S1**.

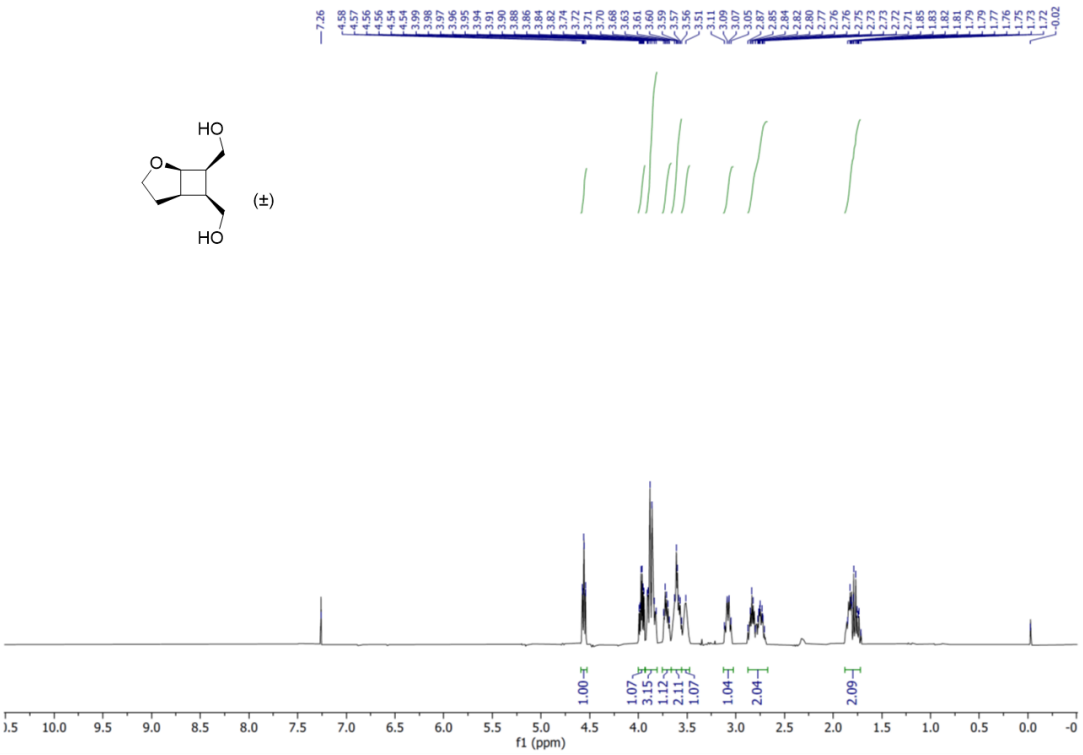


Figure S31. ^{1}H NMR spectrum of **3**.

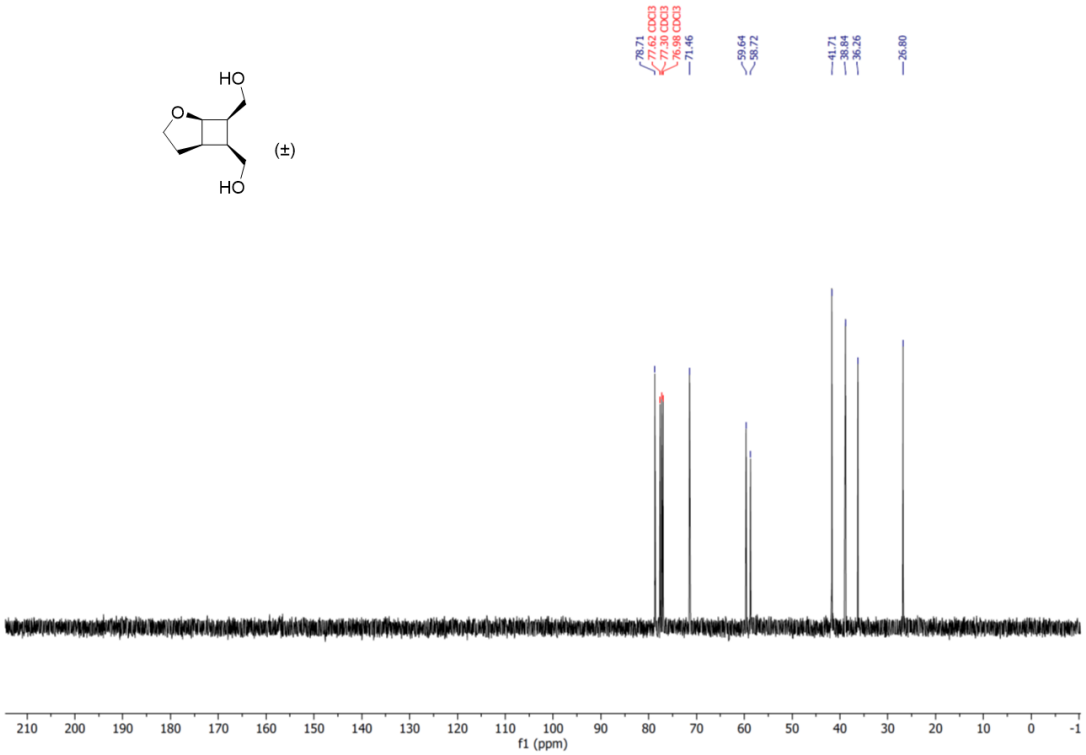


Figure S32. ^{1}H NMR spectrum of **3**.

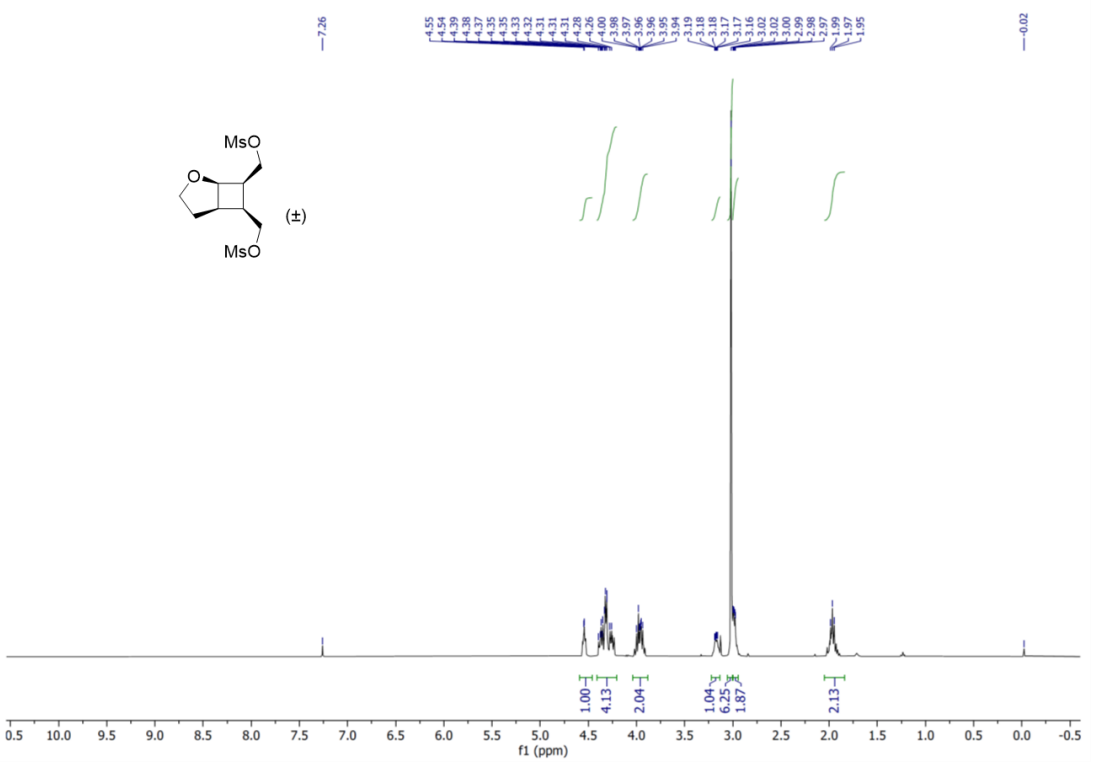


Figure S33. ^{1}H NMR spectrum of **4**.

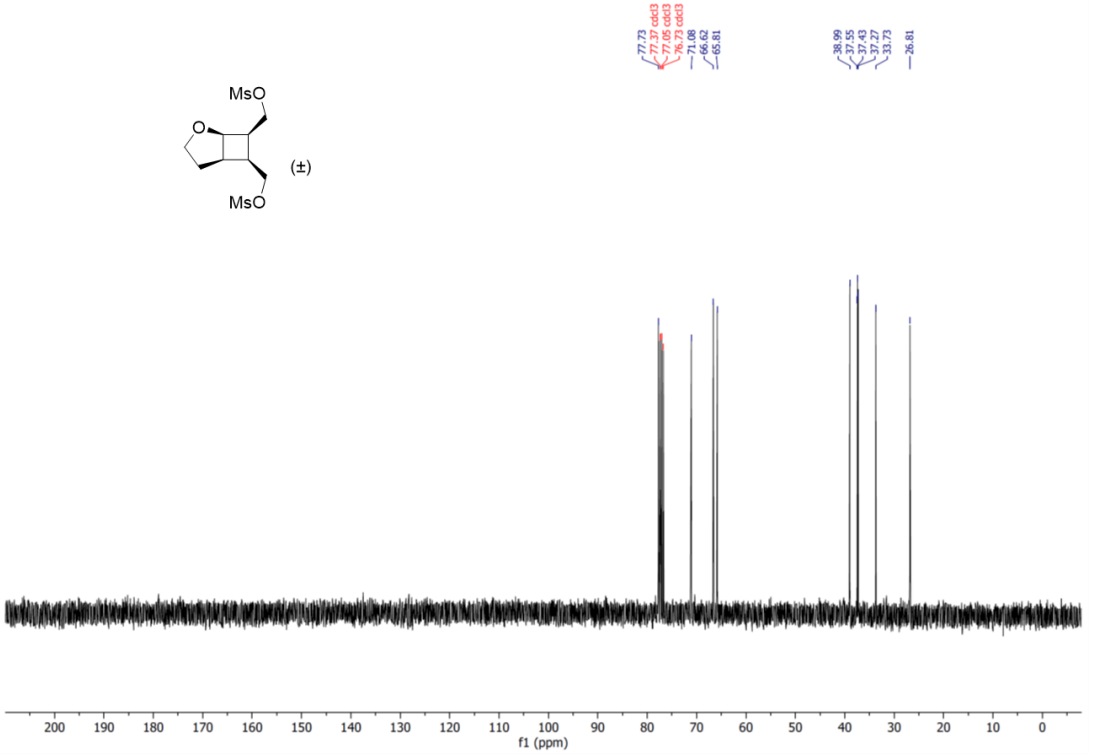


Figure S34. ^{13}C NMR spectrum of **4**.

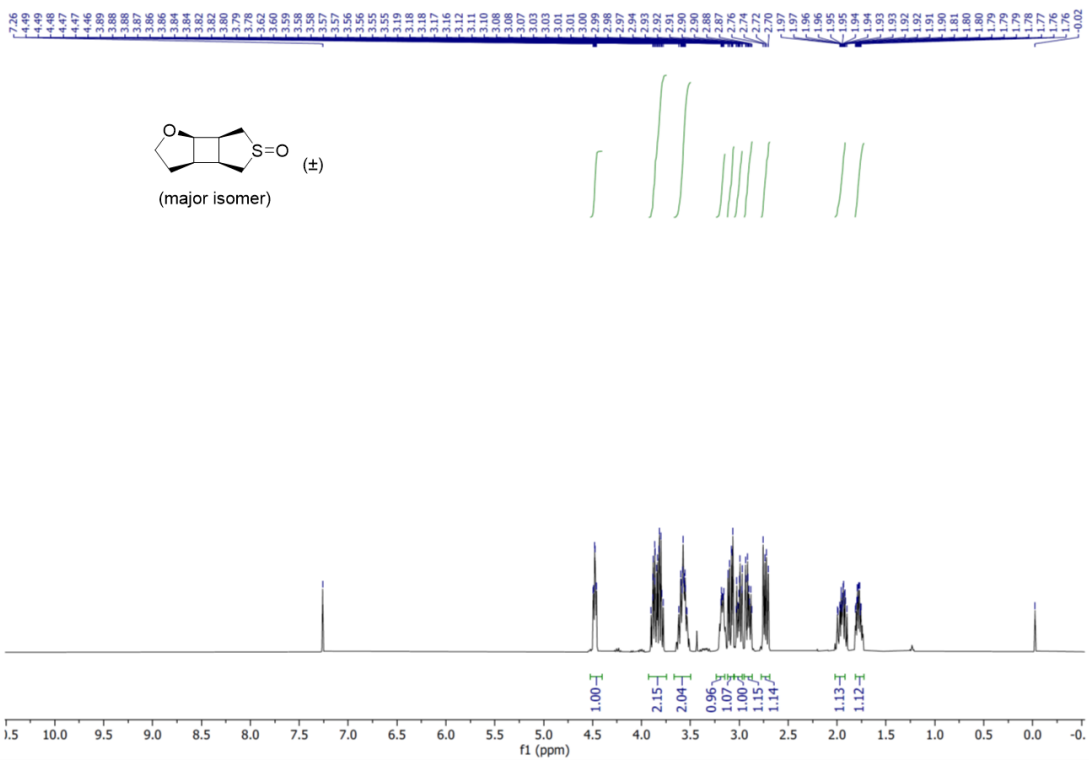


Figure S35. ^{1}H NMR spectrum of **5**.

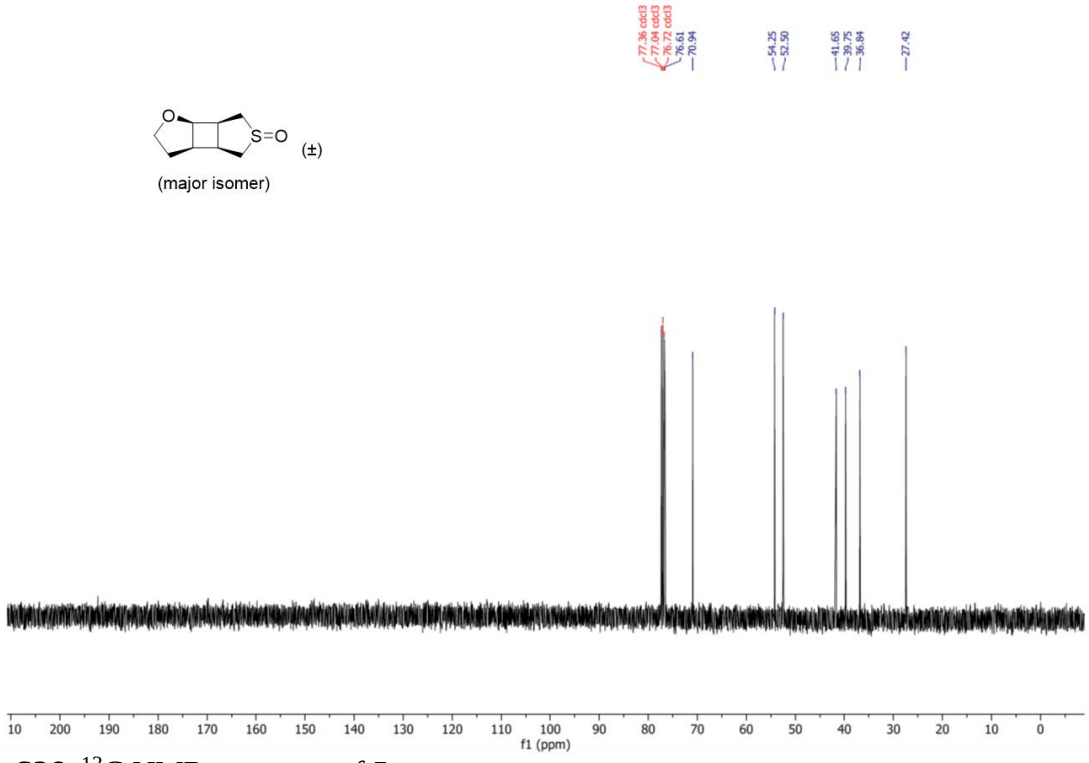


Figure S36. ^{13}C NMR spectrum of **5**.

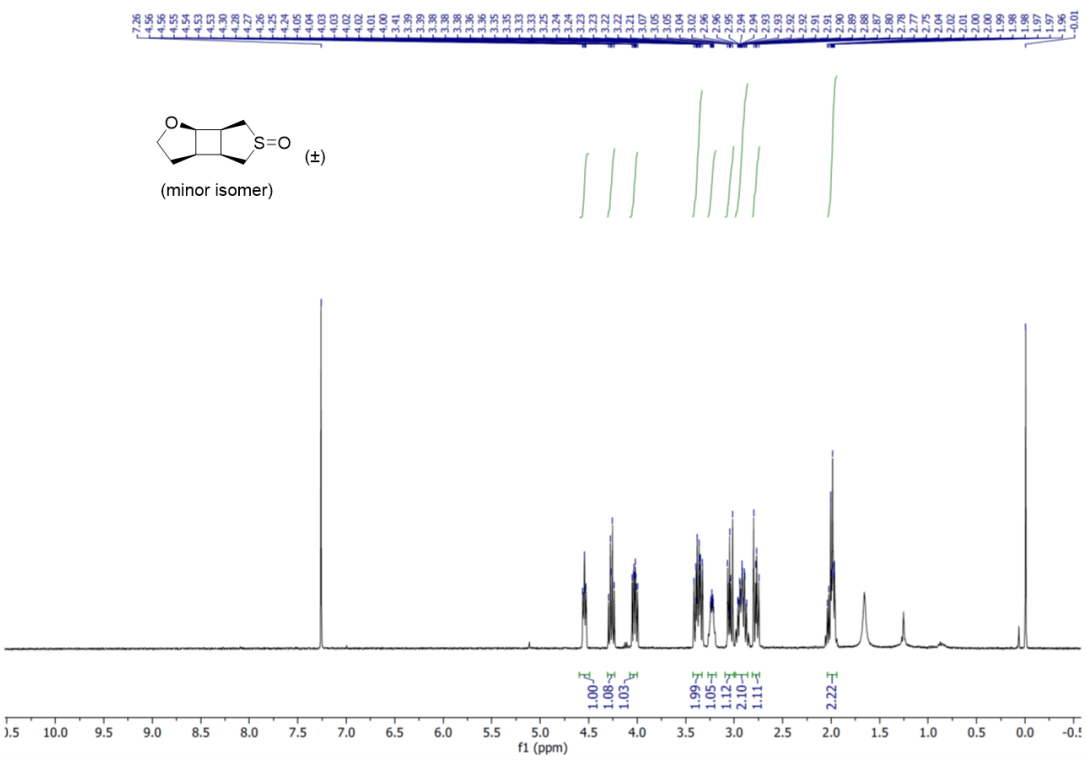


Figure S37. ^{1}H NMR spectrum of **5**.

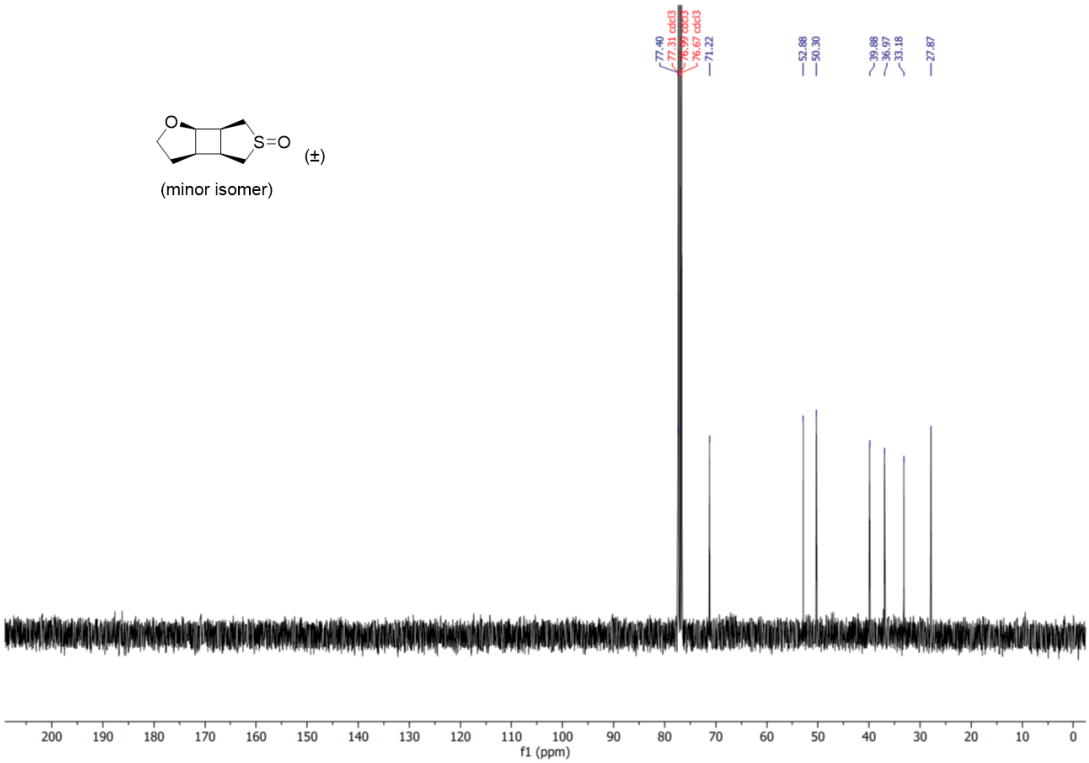


Figure S38. ^{13}C NMR spectrum of **5**.

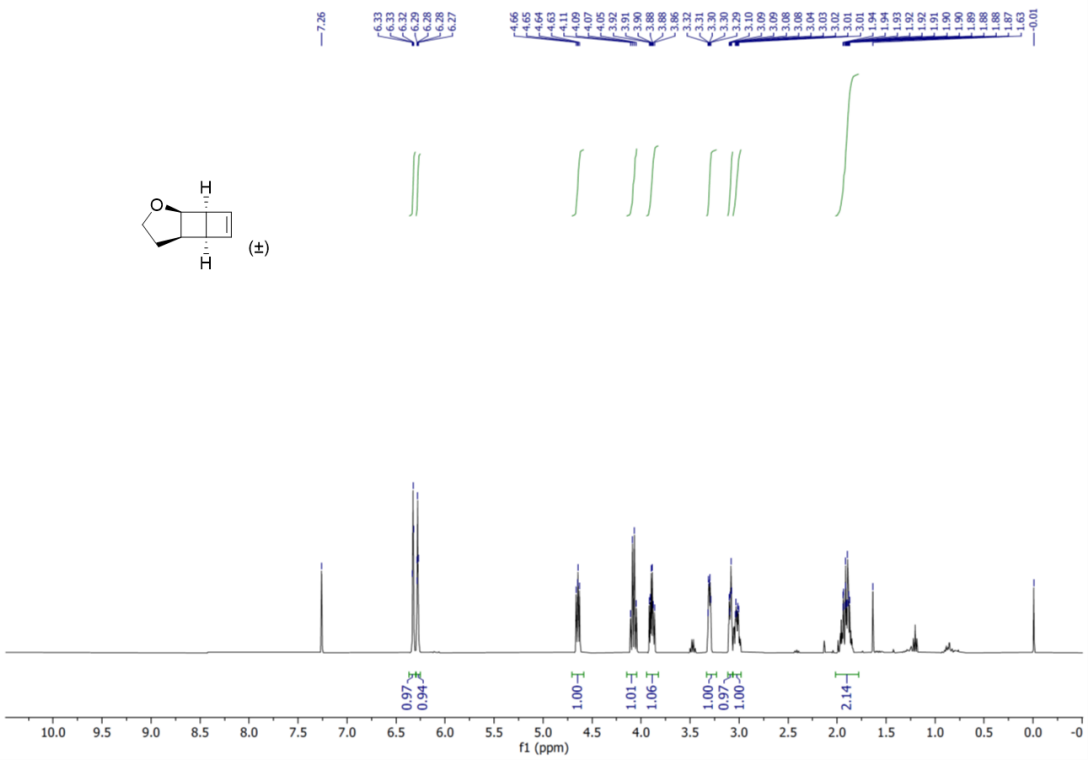


Figure S39. ^{1}H NMR spectrum of **1**.

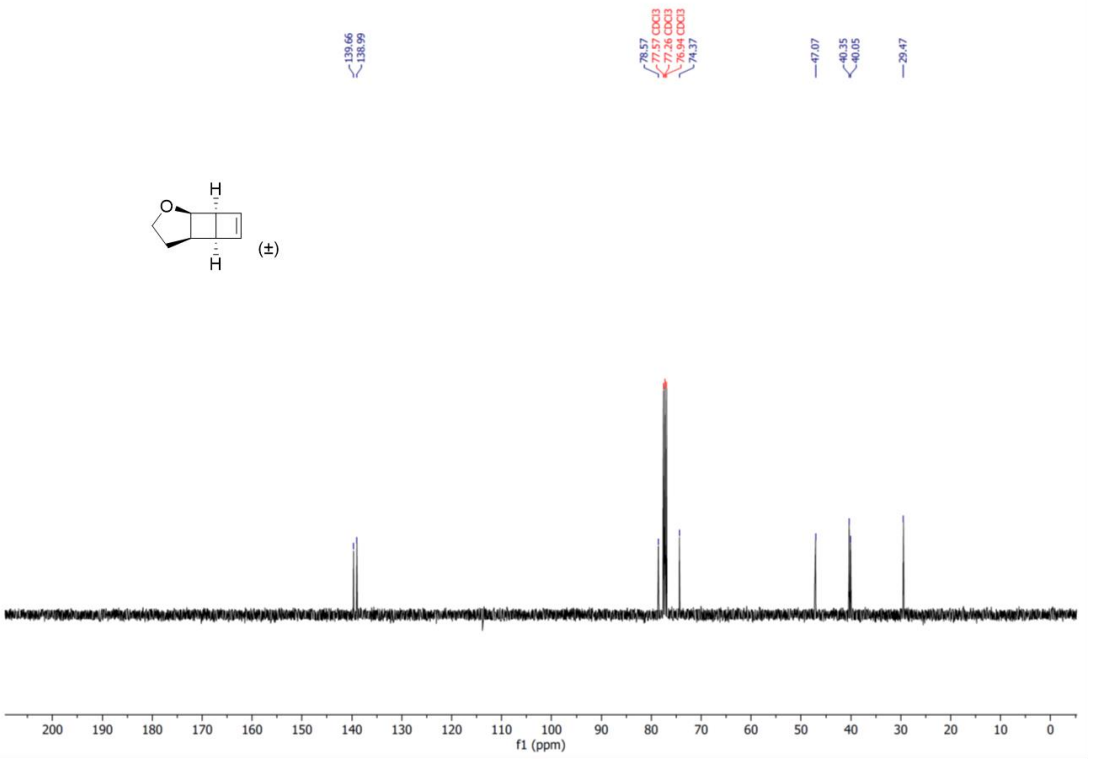


Figure S40. ^{13}C NMR spectrum of **1**.

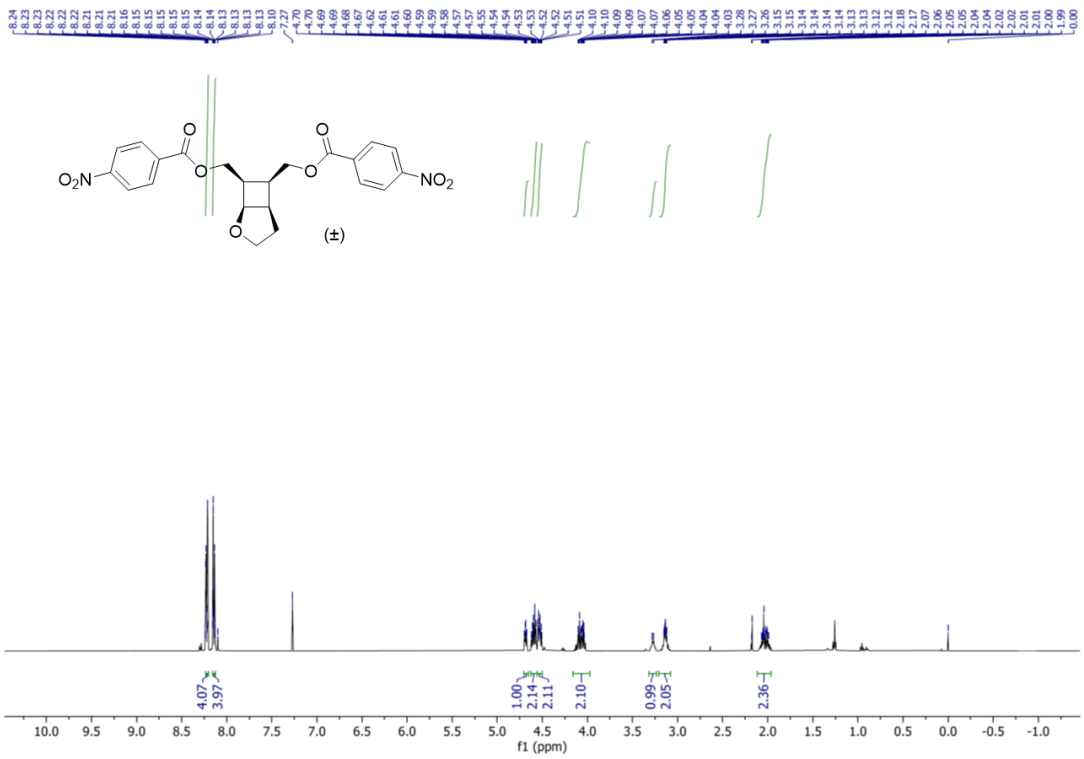


Figure S41. ^{1}H NMR spectrum of **S2**.

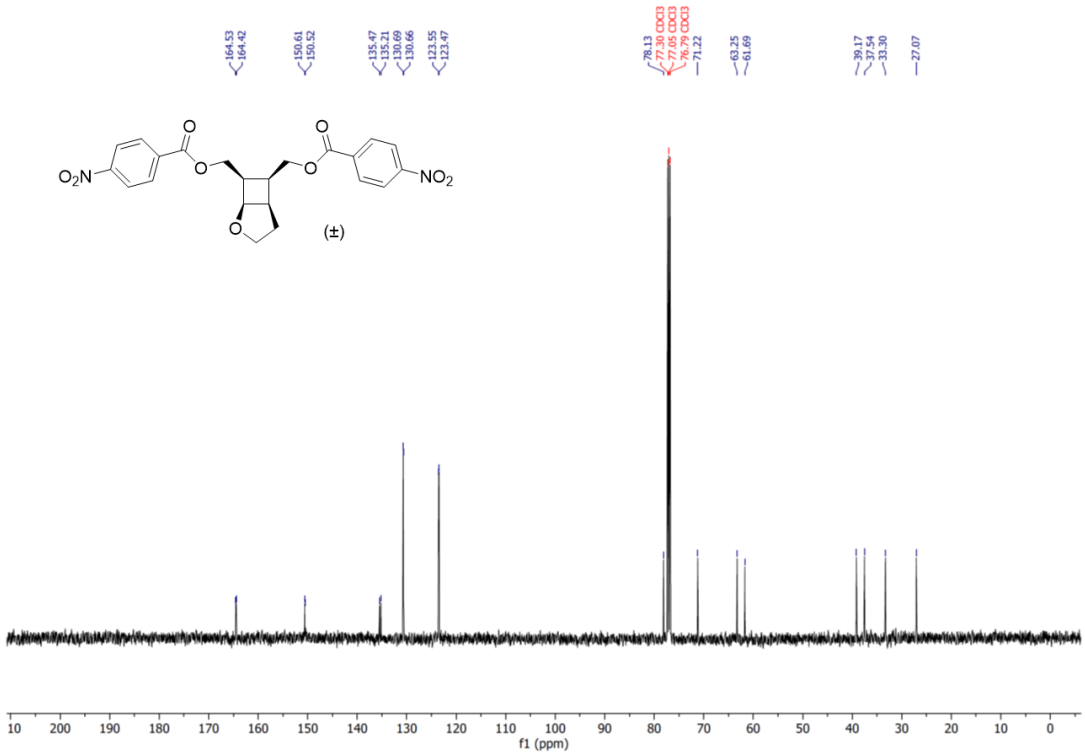


Figure S42. ^{13}C NMR spectrum of **S2**.

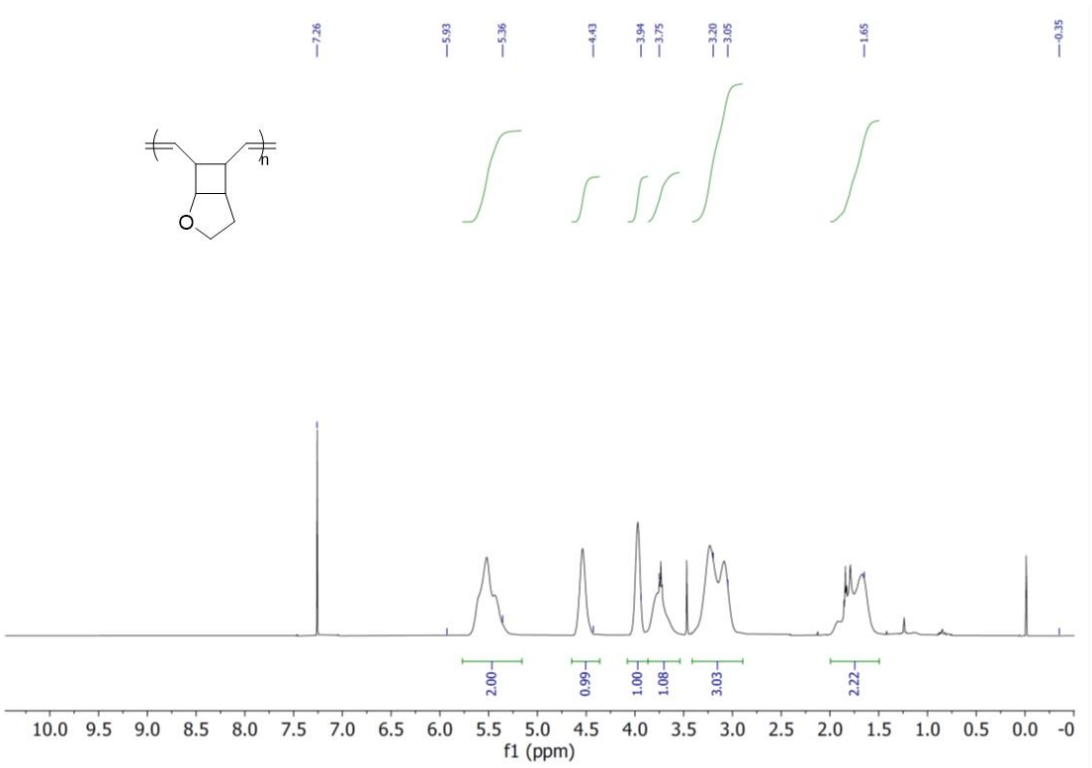


Figure S43. ^{1}H NMR spectrum of **P1**.

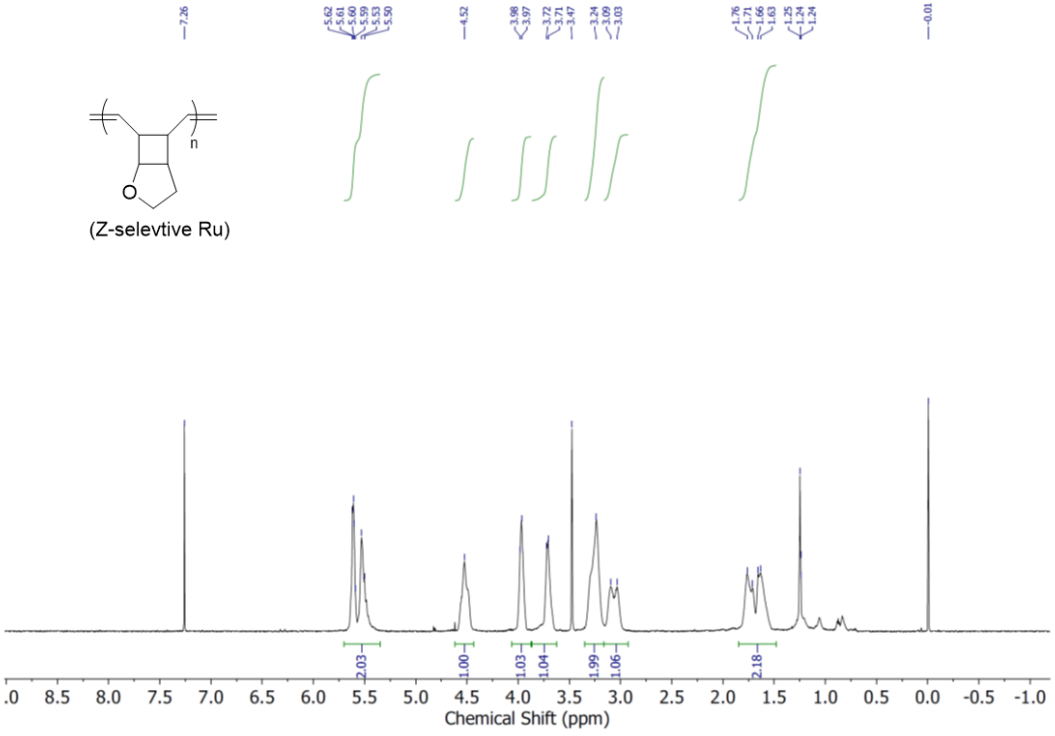


Figure S44. ^{1}H NMR spectrum of **P1** prepared using Z-selective Grubbs catalyst.

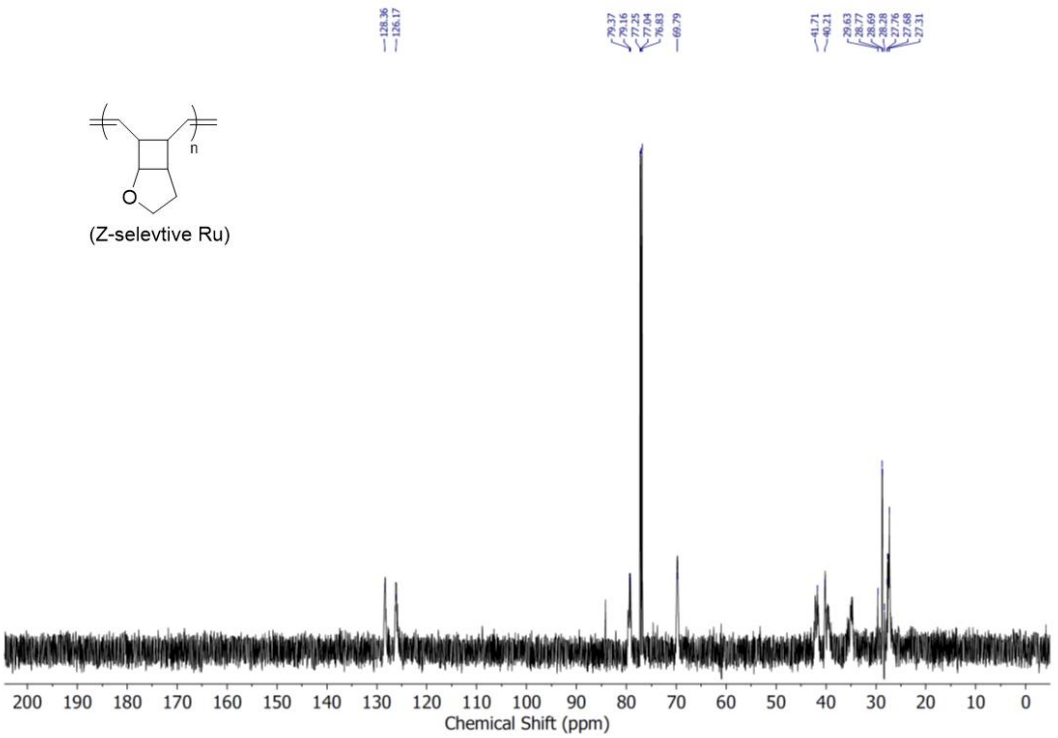


Figure S45. ^{13}C NMR spectrum of **P1** prepared using Z-selective Grubbs catalyst.

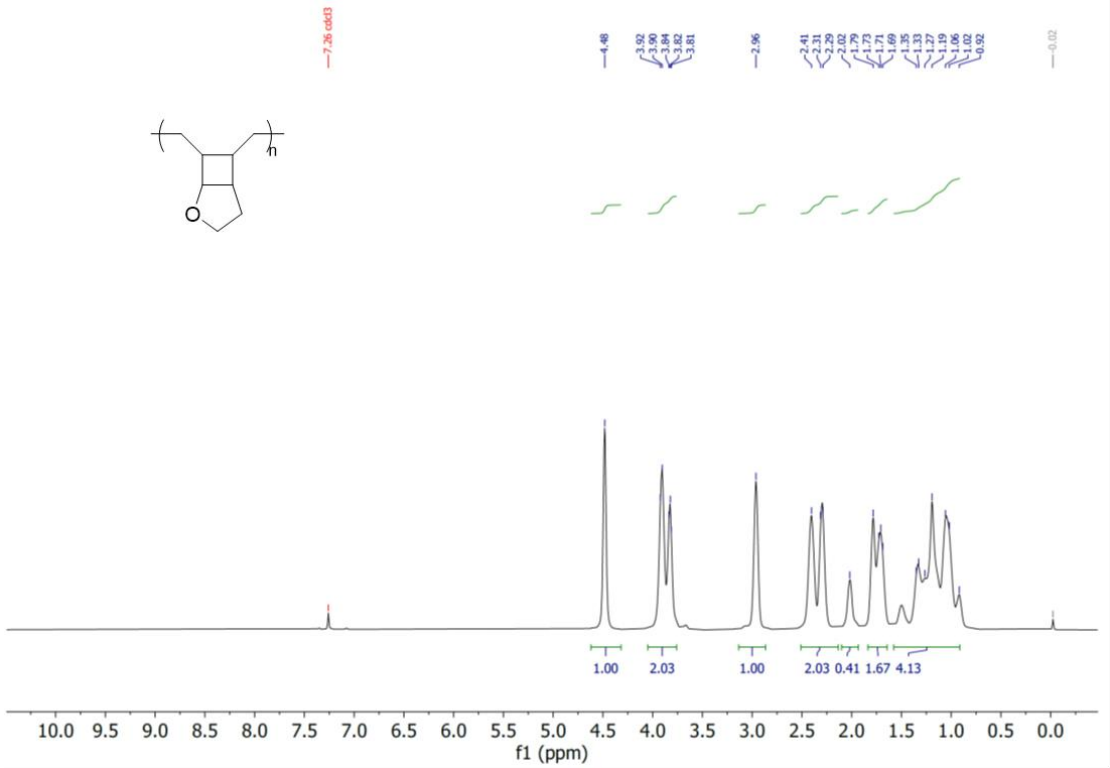


Figure S46. ^{1}H NMR spectrum of **P1-H**.

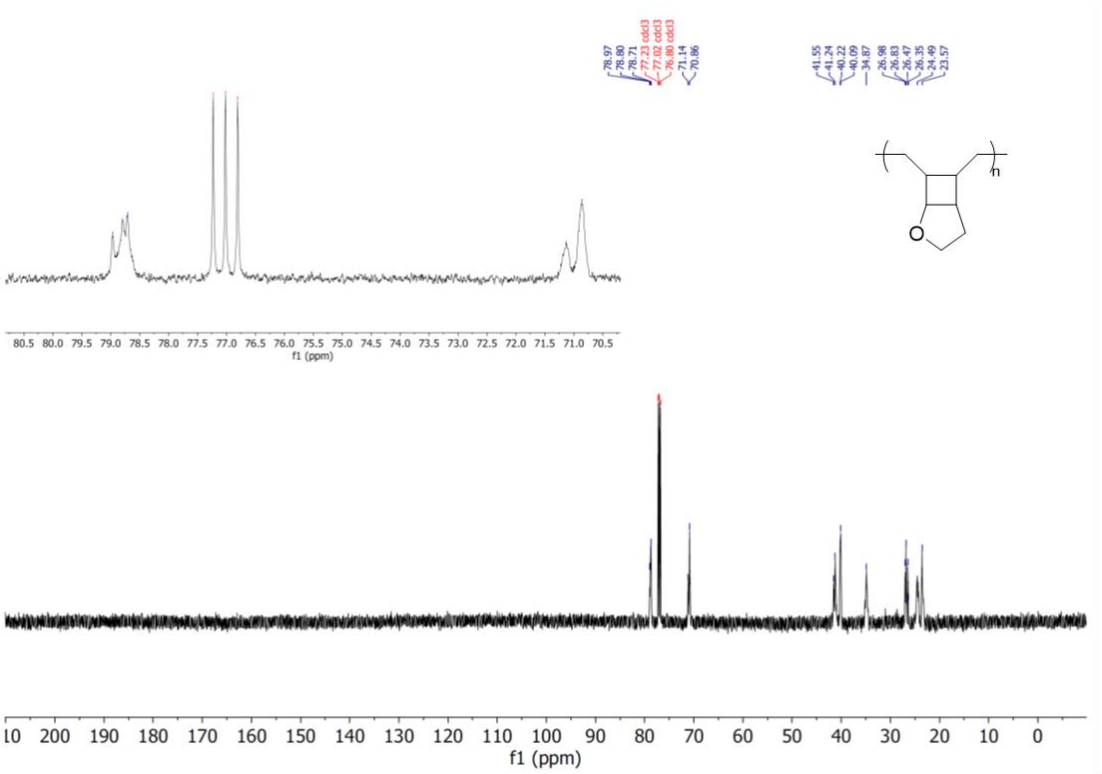


Figure S47. ^{13}C NMR spectrum of **P1-H**.

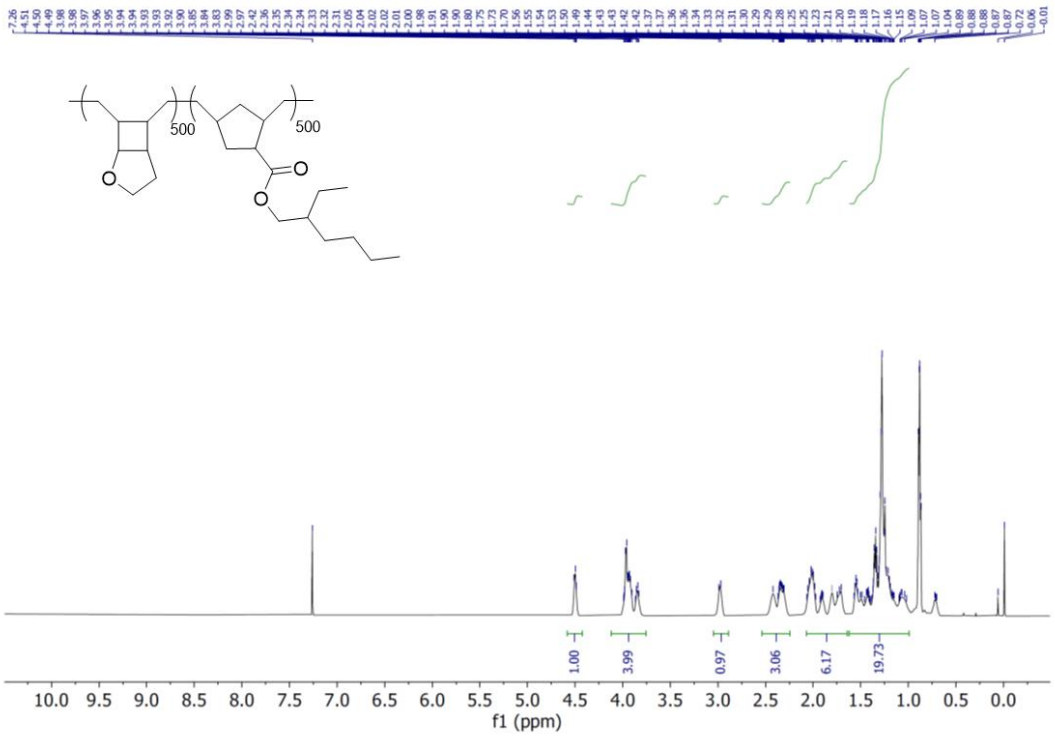


Figure S48. ^{1}H NMR spectrum of **P3-H**.

6. References

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