Supporting Information for

Mechanochemically accessing a challenging-to-synthesize depolymerizable polymer

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I. General Procedures

Materials

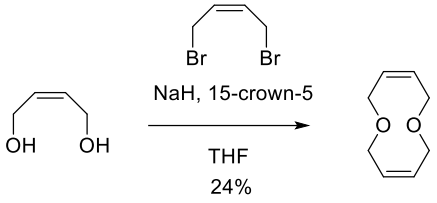
Tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF) were obtained from Sigma-Aldrich and dried by immersing in 4 Å molecular sieves desiccant (beads, 4-8 mesh, Sigma-Aldrich) overnight before use. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. Other solvents were purchased from Fisher Chemical and used without further purification. All other chemicals were purchased from Sigma-Aldrich or Fisher Chemical without further purification before use unless specified.

Instruments

All GPC experiments were carried out using Tosoh EcoSEC HLC-8320 GPC with two 17393 TSKgel columns (7.8 mm ID x 30 cm, 13 μm) and one 17367-TSKgel Guard Column (7.5 mm ID x 7.5 cm, 13 μm) using preservative-free HPLC grade THF (obtained from Fisher Chemical) at a flow rate of 1 mL min^{-1} at 40°C. Purification by preparative GPC were done by LaboACE LC-5060 which was connected to two JAIGEL-2HR columns using HPLC grade chloroform with 0.75% ethanol as preservative (obtained from Fisher Chemical) at a flow rate of 10 mL min^{-1}. ^{1}H and ^{13}C NMR spectra were collected on a Varian 500 MHz spectrometer using $CDCl_3$ as the solvent and referenced to residual solvent peak (δ = 7.26 in ^{1}H, 77.16 in ^{13}C). X-ray crystallographic study was carried out using Bruker ApexII Duo with comounted Mo and Cu microfocus radiation sources and Quazar optics for increased source brightness. ESI-MS spectra were recorded on a Waters Synapt HDMS quadrupole/time-of-flight (Q-ToF) mass spectrometer (Waters, Beverly, MA) in positive ion mode. Samples were prepared to a final concentration of 1 μg mL^{-1} in methanol. Each sample was introduced to the electrospray source via direct infusion at a flow rate of 5 μL/min, with source parameters as follows: capillary voltage: 3.15 kV; cone voltage: 35 V; sampling cone voltage: 3.2 V; source temperature: 90 °C; desolvation temperature: 150 °C. High resolution-atmospheric pressure chemical ionization mass spectra (HR-APCI-MS) were acquired using a Waters Synapt HDMS Quadrupole/Time-of-Flight (Q-ToF) Mass Spectrometer (Waters, Beverly, MA) equipped with an atmospheric solids analyses probe (ASAP) in positive ion mode.

II. Synthesis

Synthesis of DHF dimer



DHF dimer

To a suspension of sodium hydride (powder, 90%, 1.2 g, 50 mmol, 5 equiv.) in dry THF (400 mL) was added *cis*-2-butene-1,4-diol (881 mg, 10 mmol,1 equiv.) and 15-crown-5 (4.4 g, 20 mmol, 2 equiv.), and the mixture was stirred for 1 h under N_2. *Cis*-1,4-dibromo-2-butene (2.13 g, 10 mmol, 1 equiv.) in THF (10 mL) and additional 490 mL THF were added to the reaction mixture. The reaction was allowed to stir for 1 day before it was quenched by adding several drops of water. After removal of THF on a rotavapor, the residue was purified by column chromatography (ethyl acetate/hexane = 1:2) to obtain **DHF dimer** as a white solid (340 mg; yield: 24%).

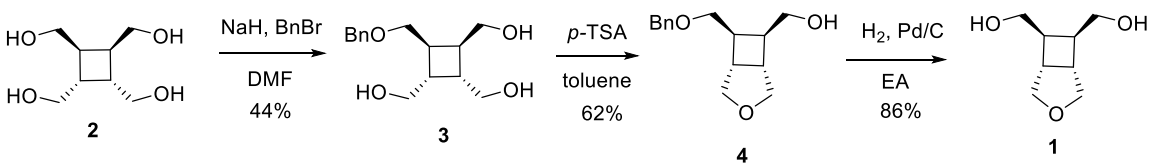
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.87 – 5.71 (m, 4H), 4.26 – 4.08 (m, 8H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 132.02, 59.98.

MS (ASAP) m/z: calcd for $C_8H_{13}O_2$ $[M+H]^+$, 141.0916; found 141.0938.

Alternative Synthesis of 1

In addition to previously reported route,[1] a more efficient synthetic route was developed for the synthesis of **1.**



Cyclobutane tetraol **2** was prepared according to a reported procedure.[2]

((1S,2S,3S,4S)-4-((benzyloxy)methyl)cyclobutane-1,2,3-triyl)trimethanol (3)

To a vigorously stirred, 15 mL DMF solution of **2** (1 g, 5.67 mmol,1.0 equiv.) was added NaH (60% in oil, 150 mg, 6.24 mmol, 1.1 equiv.) in dry DMF (15 mL) under N_2 at 0 °C. After 40 min of stirring at room temperature, benzyl bromide (970 mg, 5.67 mmol,1.0 equiv.) was added quickly to the reaction mixture using a syringe, and the reaction was allowed to stir overnight. Vacuum distillation was applied to remove DMF, and the residue was purified by column chromatography (MeOH/DCM = 1/12) to obtain **3** as colorless oil (664 mg, yield: 44%).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.42 – 7.27 (m, 5H), 4.54 (s, 2H), 3.90 – 3.77 (m, 2H), 3.77 – 3.68 (m, 2H), 3.68 – 3.61 (m, 2H), 3.58 – 3.46 (m, 2H), 2.88 (s, 3H), 2.47 – 2.21 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 137.38, 128.73, 128.20, 128.10, 73.74, 70.07, 62.43, 62.39, 62.35, 38.46, 38.21, 38.05, 35.47.

MS (ESI) m/z: calcd for $C_{15}H_{22}O_4Na$ $[M+Na]^+$, 289.141; found 289.1400.

((1S,5S,6S,7S)-7-((benzyloxy)methyl)-3-oxabicyclo[3.2.0]heptan-6-yl)methanol (4)

To **3** (400 mg, 1.5 mmol,1.0 equiv.) in toluene (30 mL) was added *p*-toluenesulfonic acid monohydrate (14 mg, 0.075 mmol, 0.05 equiv.), and the reaction was heated to reflux using Dean-Stark apparatus for 16 hours. After removal of toluene on a rotavapor, the residue was purified by column chromatography (ethyl acetate/hexane = 3/1) to obtain **4** as colorless oil (231 mg, yield: 62%).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.39 – 7.24 (m, 5H), 4.53 (s, 2H), 3.86 (d, J = 9.0 Hz, 2H), 3.77 (dd, J = 11.6, 10.0 Hz, 1H), 3.73 (t, J = 10.0 Hz, 1H), 3.54 – 3.39 (m, 4H), 3.29 (s, 1H), 2.52 – 2.28 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 137.27, 128.55, 128.53, 127.99, 127.94, 73.44, 73.43, 73.36, 70.00, 62.19, 41.16, 38.53, 38.45, 38.22.

MS (ESI) m/z: calcd for $C_{15}H_{20}O_3Na$ $[M+Na]^+$, 271.1300; found 271.1310.

((1R,5S,6R,7S)-3-oxabicyclo[3.2.0]heptane-6,7-diyl)dimethanol (1)

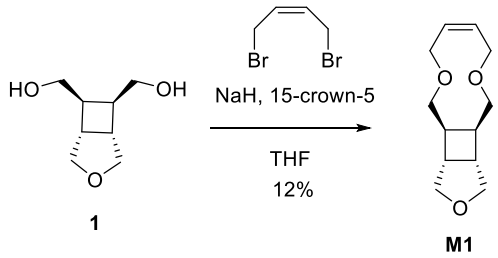
A mixture of 5 wt% Pd/C (10 mg), **4** (200 mg, 0.8 mmol) and ethyl acetate (8 mL) was charged into a pressure bottle settled on a hydrogenation apparatus (3920 Shaker Hydrogenation Apparatus, Parr Instrument Company). The reaction mixture was shaken at room temperature under 35 psi hydrogen pressure for 20 h. Pd/C was filtered over celite. After removal of the solvent on a rotavapor, the residue was purified by flash column chromatography (ethyl acetate) to obtain **1** as colorless oil (109 mg, yield: 86%).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 4.29 (s, 2H), 3.81 (d, *J* = 9.4 Hz, 2H), 3.79 – 3.71 (m, 2H), 3.57 – 3.47 (m, 2H), 3.44 – 3.34 (m, 2H), 2.45 – 2.34 (m, 2H), 2.33 – 2.18 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 73.43, 61.94, 40.70, 38.15.

MS (ESI) m/z: calcd for $C_8H_{14}O_3Na$ $[M+Na]^+$, 181.0840; found 181.0856.

Synthesis of M1



(3aR,3bS,11aR,11bS,*Z*)-1,3,3a,3b,4,6,9,11,11a,11b-decahydrofuro[3',4':3,4] cyclobuta[1,2-c][1,6]dioxecine (M1)

To a suspension of sodium hydride (powder, 90%, 228 mg, 9.48 mmol, 5 equiv.) in dry THF (100 mL) was added **1** (300 mg, 1.9 mmol,1 equiv.) and 15-crown-5 (837 mg, 3.8 mmol, 2 equiv.), and the mixture was stirred for 1 h under N_2. *Cis*-1,4-dibromo-2-butene (406 mg, 1.9 mmol, 1 equiv.) in THF (10 mL) and additional 80 mL THF were then added to the reaction mixture. The reaction was allowed to stir for 1 day before it was quenched by adding several drops of water. After removal of THF on a rotavapor, the residue was purified by column chromatography (ethyl acetate/hexane = 1:1) to obtain **M1** as white solid (48 mg, yield: 12%).

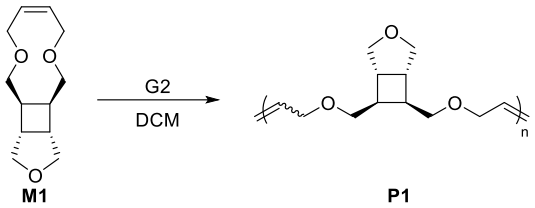
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.70 (t, *J* = 3.3 Hz, 2H), 4.47 – 4.30 (m, 2H), 4.11 – 3.96 (m, 2H), 3.95 – 3.77 (m, 4H), 3.59 – 3.50 (m, 2H), 3.49 – 3.40 (m, 2H), 2.44 – 2.34 (m, 2H), 2.35 – 2.23 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 130.57, 73.49, 69.70, 67.01, 40.11, 39.15.

MS (ESI) m/z: calcd for $C_{12}H_{18}O_3Na$ $[M+Na]^+$, 233.1148; found 233.1074.

III. Polymer Synthesis

Synthesis of P1



P1 of different molecular weights were made by ROMP of **M1**. The following is an example of the procedure.

To a vial was added **M1** (100 mg, 0.48 mmol, 1 equiv.) and **G2** (0.4 mg, 0.000476 mmol, 0.001 equiv., in 480 μL of DCM stock solution). The reaction was gently stirred for 3 hours, and excess amount of ethyl vinyl ether (150 μL) was added and stirred for 30 minutes to terminate the polymerization. The solvent was then removed on a rotavaper and subjected to prepGPC for further purification to yield transparent viscous oil, which was dried under vacuum overnight to afford 75 mg of polymer **P1**. (75 mg, yield: 75%, M_n = 154 kDa, $Đ$ = 1.97)

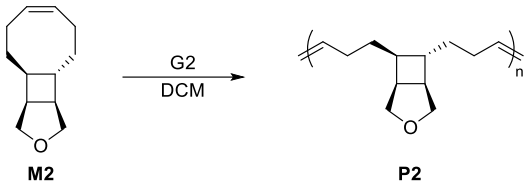
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.8-5.65 (m, 2H), 4.05-3.89 (m, 4H), 3.86 (d, *J* = 9.4 Hz, 2H), 3.65 – 3.54 (m, 2H), 3.54 – 3.41 (m, 4H), 2.64 (m, 2H), 2.35 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 129.43, 129.38, 73.77, 71.00, 70.73, 66.81, 40.50, 38.56.

Supplementary Table 1. M_n and $Đ$ of **P1** synthesized.

[M1]/[G2]	[M1]	M_n (kDa)	$Đ$	Use
25	0.5 M	5	1.96	Sonication Control Study
400	1 M	35	1.88	Initial Sonication Study
400	1 M	58	1.65	Sonication Kinetic Study
500	1 M	68	2.12	Thermal Analysis
1000	1 M	89	1.83	Sonication Kinetic Study
1000	1 M	154	1.97	Sonication for Depolymerization Study

Synthesis of P2

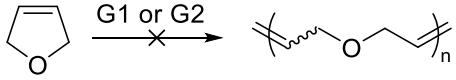


M2 P2

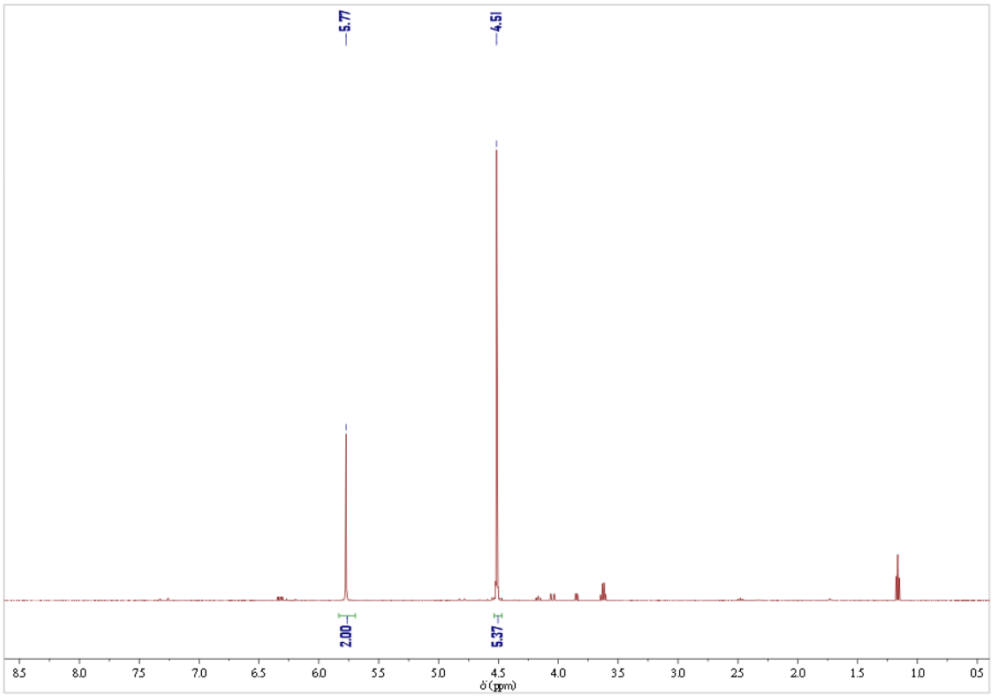
M2 was prepared according to previously described procedure.[1] To a vial was added **M2** (325 mg, 1.82 mmol, 1.000 equiv.) and **G2** (1.55 mg, 1.82 μmol, 0.001 equiv., in 910 μL of DCM solution). The reaction was gently stirred overnight, and 100 μL ethyl vinyl ether was added and stirred for 30 minutes to quench the polymerization. The concentrated mixture was precipitated three times in cold MeOH. The collected polymer was dried under vacuum overnight to afford polymer **P2** as white fibers. (205 mg, yield: 63%, M_n = 87.5 kDa, $Đ$ = 1.83)

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.43 – 5.26 (m, 2H), 4.01 (d, *J* = 9.8 Hz, 1H), 3.68 (d, *J* = 8.9 Hz, 1H), 3.42 – 3.32 (m, 2H), 2.83 – 2.73 (m, 1H), 2.48 – 2.37 (m, 1H), 2.04 – 1.75 (m, 5H), 1.53 – 1.48 (m, 2H), 1.48 – 1.29 (m, 3H).

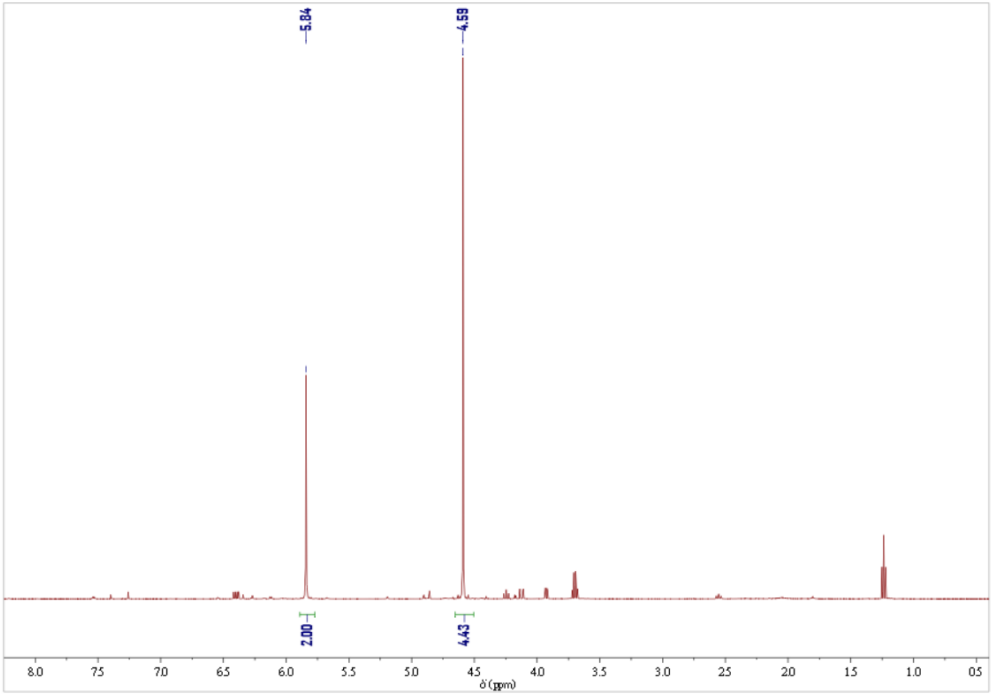
Synthesis of PDHF (from DHF)



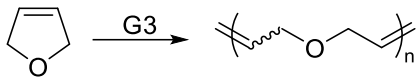
To a vial was added freshly distilled DHF (1 equiv.) and Grubbs catalyst (0.001 equiv.), and the reaction was allowed to proceed for 24 h. Excess amount of ethyl vinyl ether was added, and the mixture was stirred for 30 min before aliquots were taken for ^{1}H NMR characterization.



Supplementary Fig. 1: ^{1}HNMR of DHF reacting with **G1**.



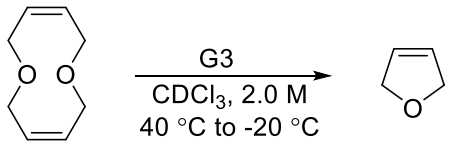
Supplementary Fig. 2: ^{1}HNMR of DHF reacting with **G2**.



To a vial was added freshly distilled DHF (200 mg, 2.85 mmol, 1 equiv.) and G3 (3.1 mg, 0.0035 mmol, 0.00123 equiv.), and the reaction was allowed to proceed for 24 h. Excess amount of ethyl vinyl ether (200 μL) was added, and the mixture was stirred for 30 min. The reaction mixture was precipitated in cold methanol to obtain **PDHF** as a brown oil (17 mg, yield: 9%, M_n = 14 kDa, $Đ$ = 2.12).

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.87 – 5.67 (m, 2H), 4.10 – 3.84 (m, 4H).

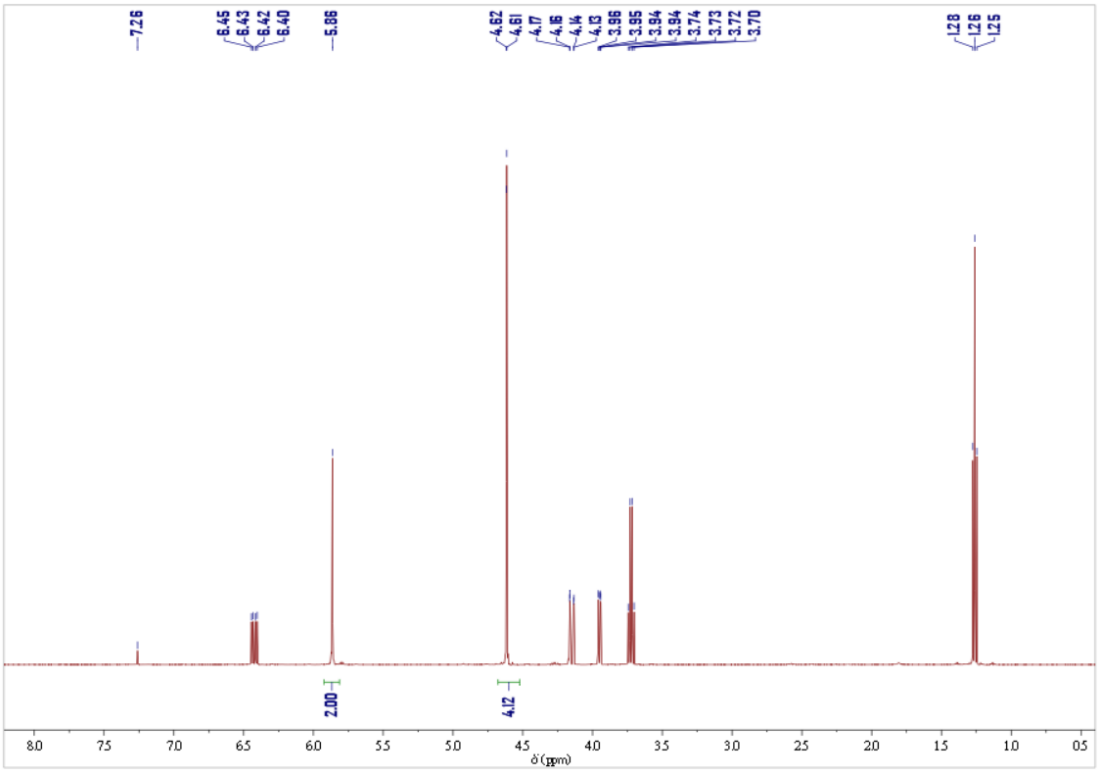
Synthesis of PDHF (from DHF dimer)



DHF dimer

DHF dimer (60 mg, 0.43 mmol, 1 equiv.) and a stir bar was charged in a small vial. **G3** (0.38 mg, 0.00043 mmol, 0.001 equiv., in 143 μL of $CDCl_3$ stock solution) was added. The vial was sealed and heated to 40 °C, and the reaction was stirred at this temperature for 5 min. The vial was then put in a freezer (-20 °C) and left there for 16 h. The reaction was taken out from the freezer, and excess amount of cold ethyl vinyl ether (100 μL) was added to quench the reaction. The vial was put back to freezer left there for 30 min before ^{1}H NMR characterization.

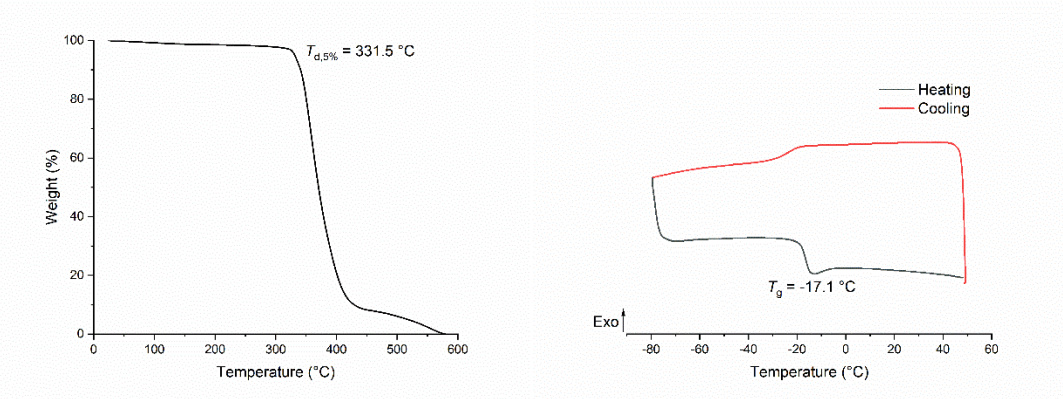
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.90 – 5.87 (m, 2H), 4.68 – 4.52 (m, 4H).



Supplementary Fig. 3: ^{1}HNMR of **DHF dimer** reacting with **G3**.

IV. Thermal Properties of Polymers

Thermogravimetric analysis (TGA) was performed using a TA Discovery TGA 550 at a ramp rate of 10 °C/min under nitrogen flow. Thermal decomposition onset temperature T_d was reported at the temperature at which 5% mass loss. Differential scanning calorimetry (DSC) was determined with a TA Instrument of Discovery DSC 250 using hermetic aluminum pans under nitrogen atmosphere using a heat-cool-heat cycle at a heating ramp rate of 10 °C/min and a cooling ramp rate of 5 °C/min. Results were processed with TA TRIOS software and shown from the cooling and the second heating curve.



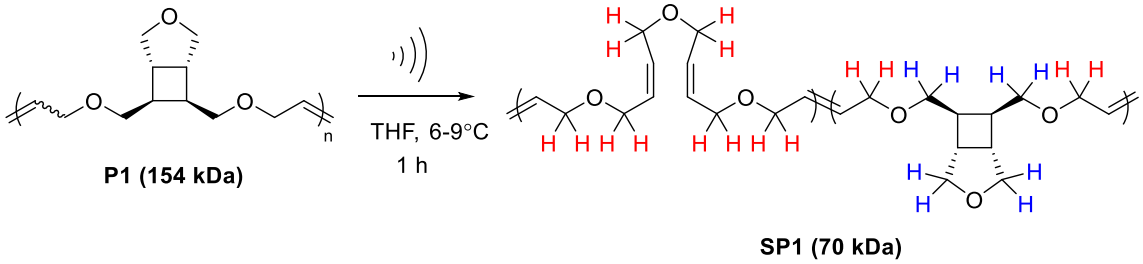
Supplementary Fig. 4: Thermal characterizations: TGA curves (left) and DSC curves (right) of **P1 (**68 kDa, *Đ* = 2.12).

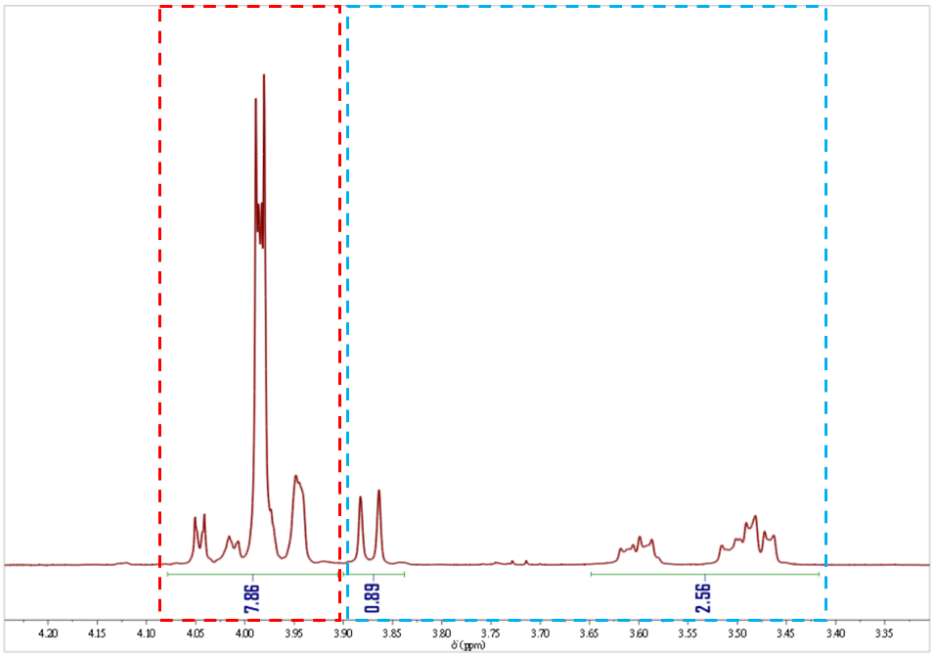
V. Sonication Experiments

General

Sonication experiments were conducted using a Vibracell model VCX500 (Sonics & Materials) with a standard solid probe (tip diameter = 13 mm, titanium alloy Ti-6Al-4V) operated at 20 kHz. 1 mg/1 mL THF solution of **P1** was made and transferred to a reaction vessel (made by U Akron Glassblowing Shop) and was then deoxygenated by bubbling through N_2 for 30 minutes. The solution was sonicated under N_2 using a pulse sequence 1 s on / 1 s off at an energy density of 9.3 W/cm^2 (AMPL = 25%). The energy density was calibrated according to the previous literature.[3] The temperature of the solution was maintained by placing the vessel in an ice/water bath. Ring opening percentage and molecular weight changes were tracked by ^{1}H NMR and GPC, respectively.

Calculation of % Ring Opening of P1 from ^{1}H NMR





Supplementary Fig. 5: ^{1}H NMR for 1 h of sonication of 154 kDa **P1**.

$$8 \text{ methylene H (blue) in nonactivated region} = 2.56 + 0.89 = 3.45$$

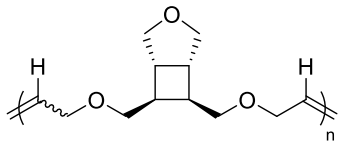
$$\text{nonactivated region allylic H (red)} = \frac{3.45}{8} \times 4 = 1.725$$

$$\text{activated region allylic H (red)} = 7.86 - 1.725 = 6.135$$

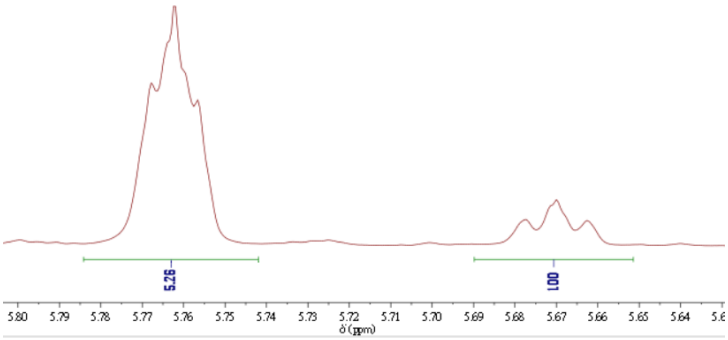
$$\text{activated: nonactivated} = \frac{6.135}{12} : \frac{1.725}{4} = 0.511 : 0.431$$

$$\%\text{RO} = \frac{0.511}{0.511 + 0.431} = 54\%$$

Calculation of *Z*/*E* Ratio for Mechanochemically Generated Olefins from P1 to SP2

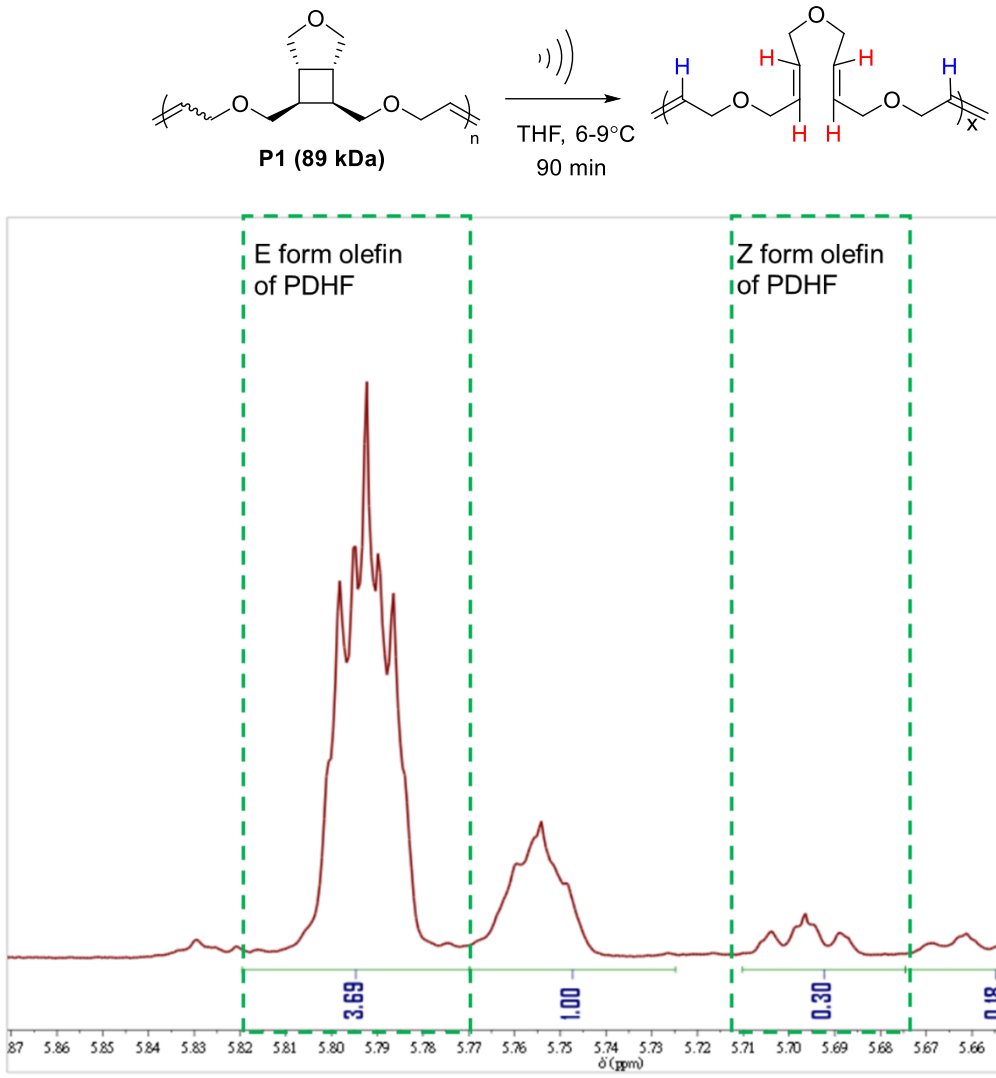


P1 (89 kDa)



Supplementary Fig. 6: ^{1}HNMR for **P1** (olefin region).

$$\text{original olefin: E form : Z form} = \frac{5.26}{1}$$



Supplementary Fig. 7: ^{1}HNMR for **SP1** (olefin region).

$$\text{PDHF olefinic H} = 3.69 + 0.3 = 3.99$$

$$\text{blue H (original olefin)} = \frac{3.99}{6} \times 2 = 1.33$$

$$\text{E form of original olefin} = \frac{5.26}{1 + 5.26} \times 1.33 = 1.12$$

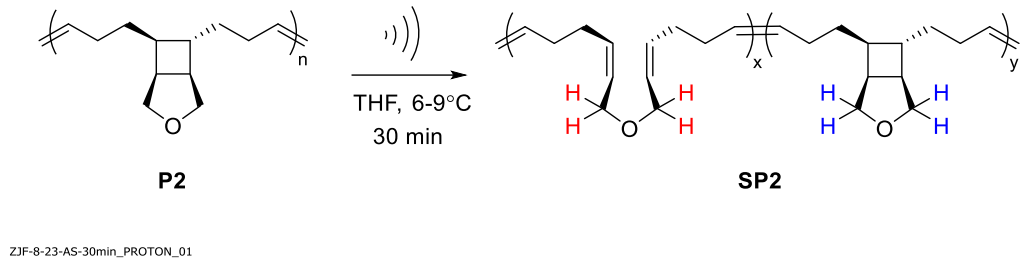
$$\text{Z form of original olefin} = \frac{1}{1 + 5.26} \times 1.33 = 0.21$$

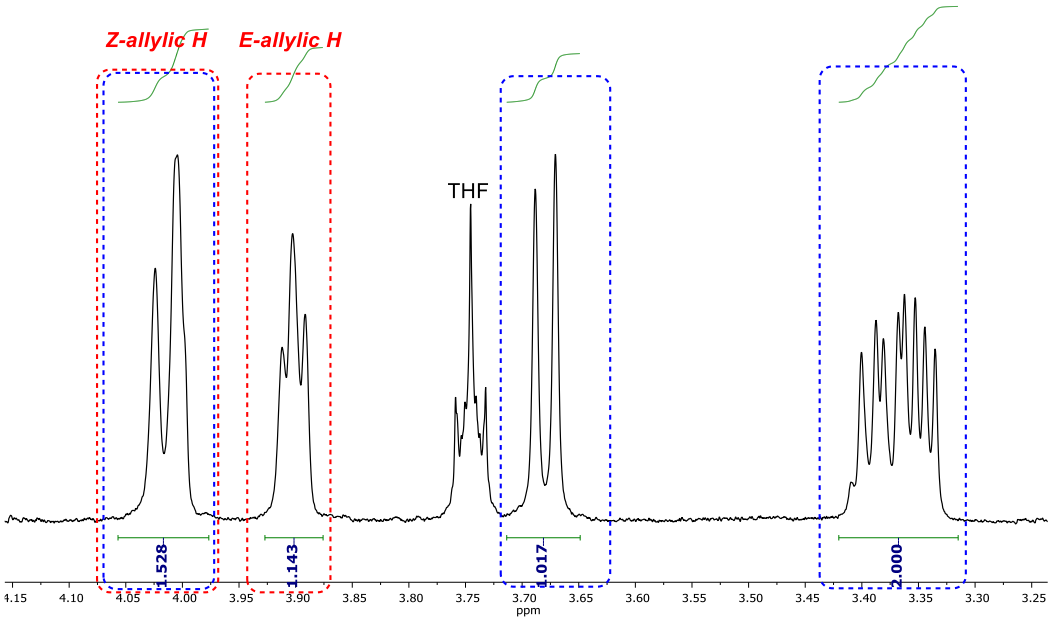
$$\text{E form of new olefin} = 3.69 - 1.12 = 2.57$$

$$\text{Z form of new olefin} = 0.3 - 0.21 = 0.09$$

$$\frac{\text{Z}}{\text{E}} \text{ ratio of new olefins} = \frac{0.09}{2.57} = 0.035$$

Calculation of % Ring Opening of P2 from ^{1}H NMR





Supplementary Fig. 8: Partial ^{1}HNMR for 88 kDa **SP2** after 30 minutes of sonication.

(**Note**: two peaks overlapped in the region from 4.05 ppm to 3.98 ppm)

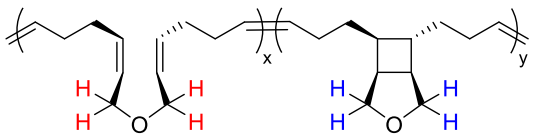
$$\text{THF H (blue)} = 1.017 \times 2 + 2.000 = 4.034$$

$$\text{allylic H (red)} = 1.528 - 1.017 + 1.143 = 1.654$$

$$\frac{x}{y} = \frac{1.654}{4.034}$$

$$\%\mathrm{RO} = \frac{\mathrm{x}}{\mathrm{x}+\mathrm{y}} = \frac{1.654}{1.654+4.034} = 29.1\%$$

Calculation of Z/E Ratio for Mechanochemically Generated Olefins from P2 to SP2



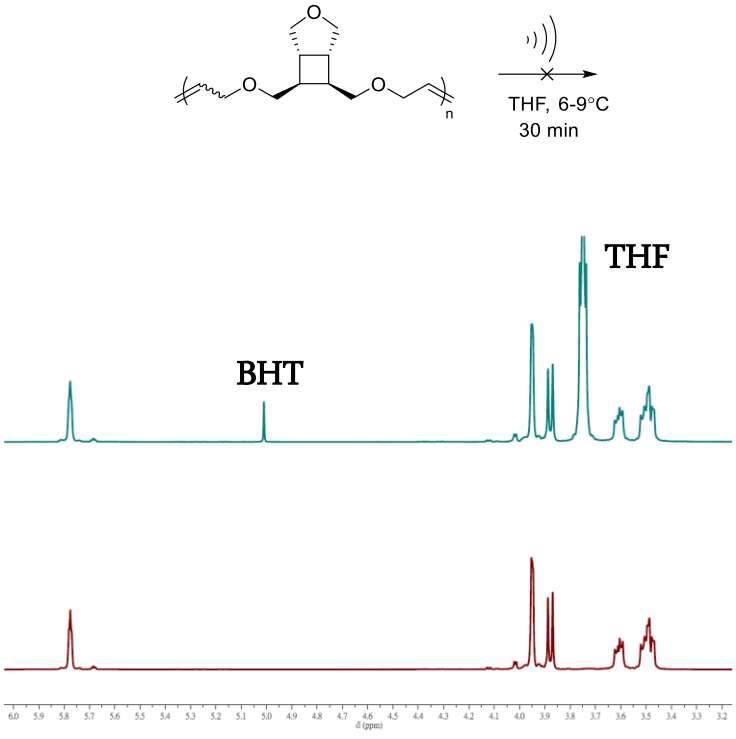
SP2

$$\frac{\mathrm{Z}}{\mathrm{E}} = \frac{1.528-1.017}{1.143} = 0.447$$

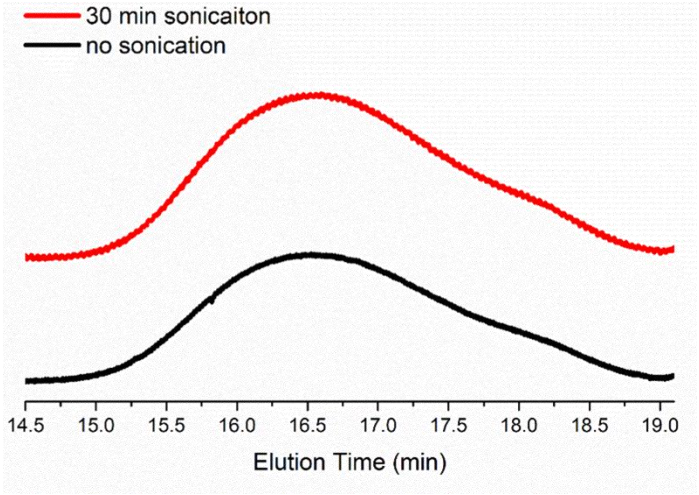
Supplementary Table 2. Summary of %RO and Z/E ratio after sonication for 89 kDa **P1** and 88 kDa **P2.**

SP1			SP2			
Time	%RO	Z/E	Time	%RO	Z/E	%EZ
2 min	6.5%	0.0755	2 min	4.3%	0.1030	18.7%
4 min	12.1%	0.0628	4 min	8.0%	0.3170	48.1%
8 min	20.0%	0.0329	8 min	13.4%	0.3995	57.1%
15 min	28.2%	0.0352	15 min	19.8%	0.3657	53.6%
30 min	37.6%	0.0374	30 min	29.1%	0.4470	61.8%
60 min	47.5%	0.0369				
90 min	52.7%	0.0341				

Sonication Control Study for 5 kDa P1



Supplementary Fig. 9: ^{1}HNMR for 5 kDa **P1** before sonication (bottom, red) and after sonication (top, blue).



Supplementary Fig. 10: GPC for 5 kDa **P1** before sonication (bottom, black) and after sonication (top, red).

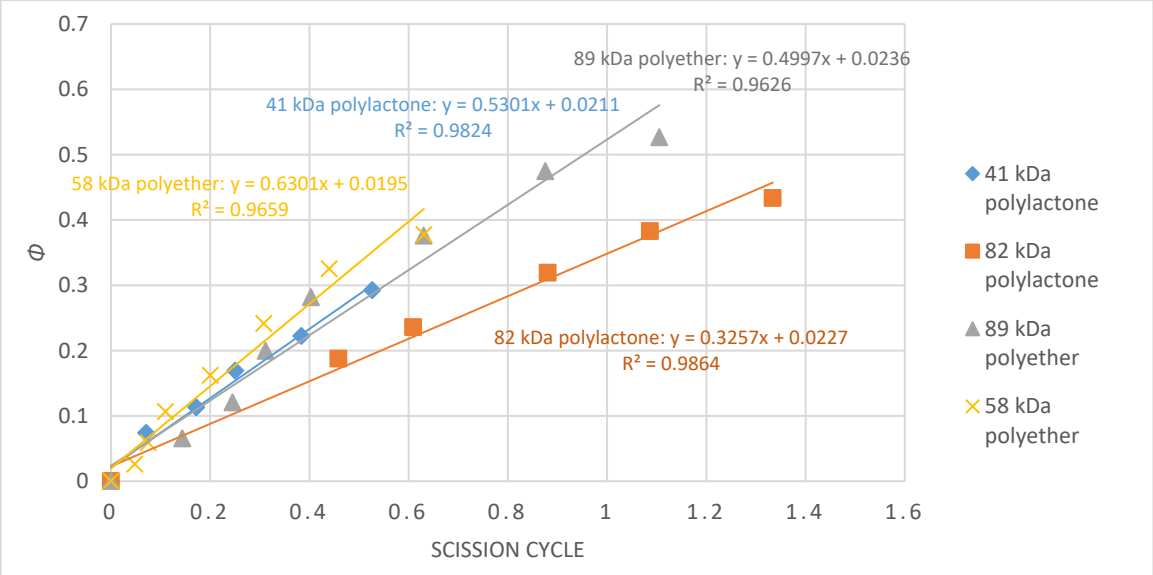
Calculation of Scission Cycle from M_n Changes [4]

$$SC = [\ln(M_{n(0)}) - \ln(M_{n(t)})]/\ln(2)$$

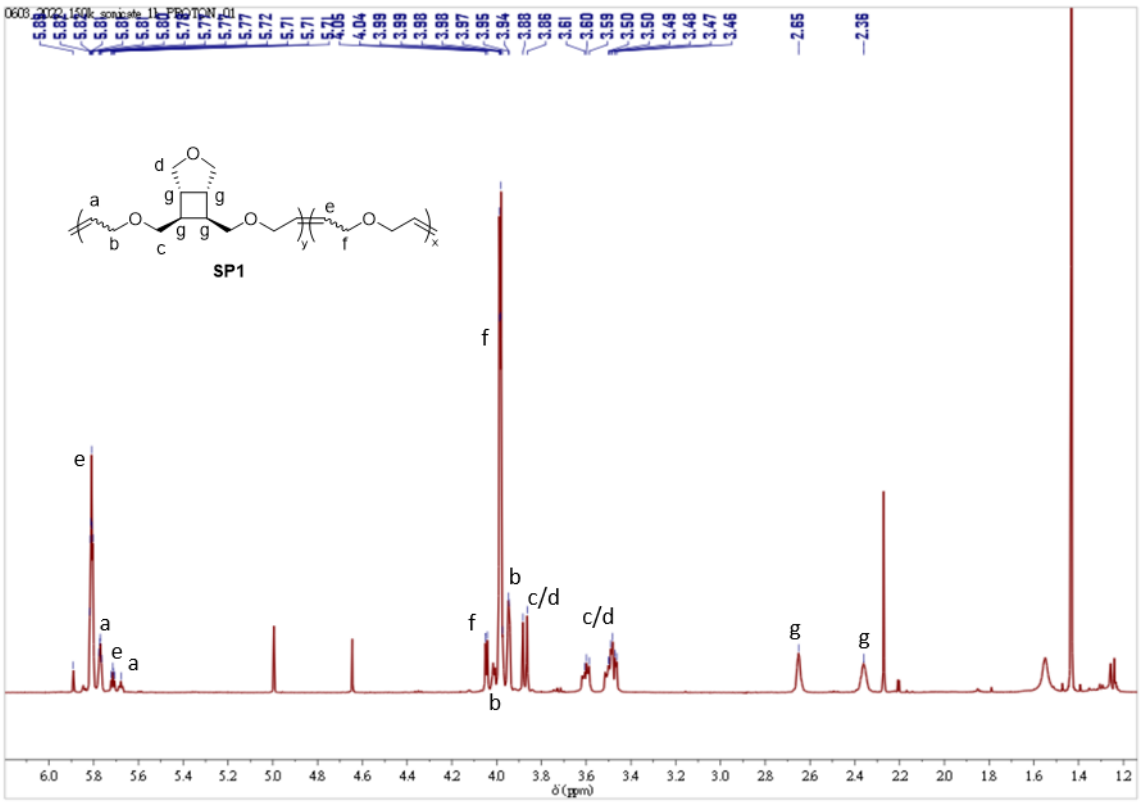
For 89 kDa **P1** sonicated 90 minutes:

$$SC = [\ln(89375) - \ln(41546)]/\ln(2) = 1.11$$

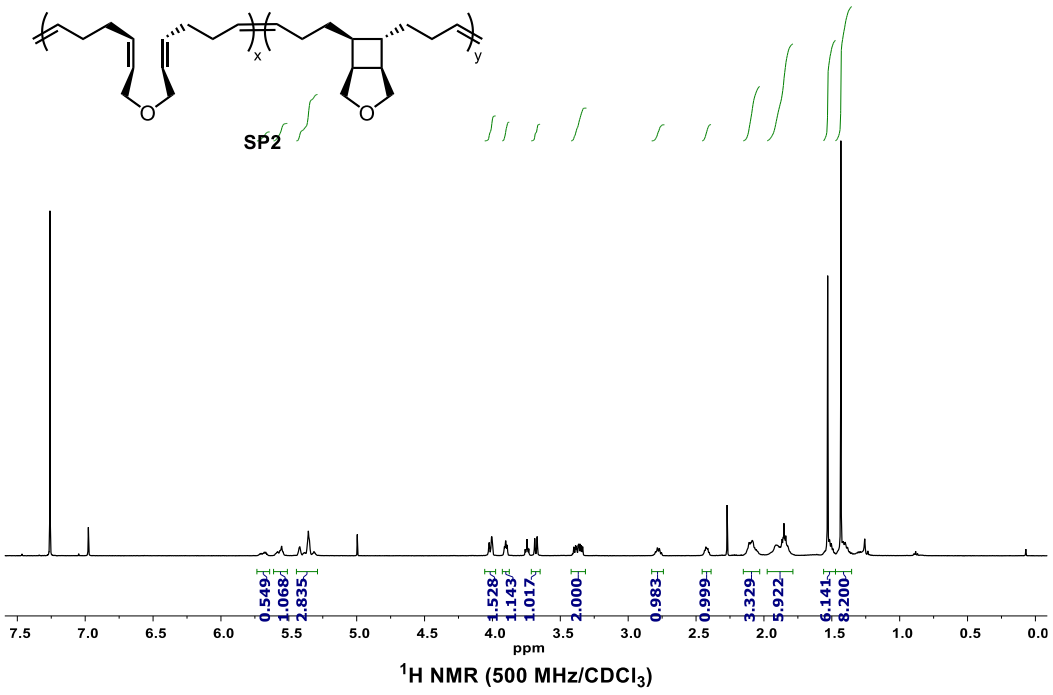
Extent of Ring Opening (ϕ) vs Scission Cycle



Supplementary Fig. 11: Extent of ring opening (ϕ) vs scission cycle for **P1** (this work) and a poly(*trans*-cyclobutane-fused lactone) (previous work) of different initial molecular weights.[5] The extent of ring opening per chain scission ϕ = 0.63 and 0.50 for 58 kDa and 89 kDa **P1**, respectively; ϕ = 0.53 and 0.33 for 41 kDa and 82 kDa poly(*trans*-cyclobutane-fused lactone), respectively.



Supplementary Fig. 12: ^{1}H NMR for **SP1**.



Supplementary Fig. 13: ^{1}H NMR for **SP2**.

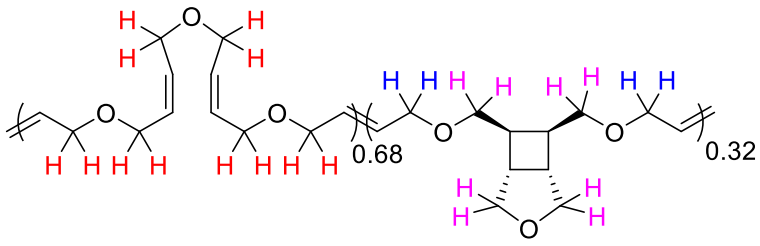
VI. Depolymerization Experiments

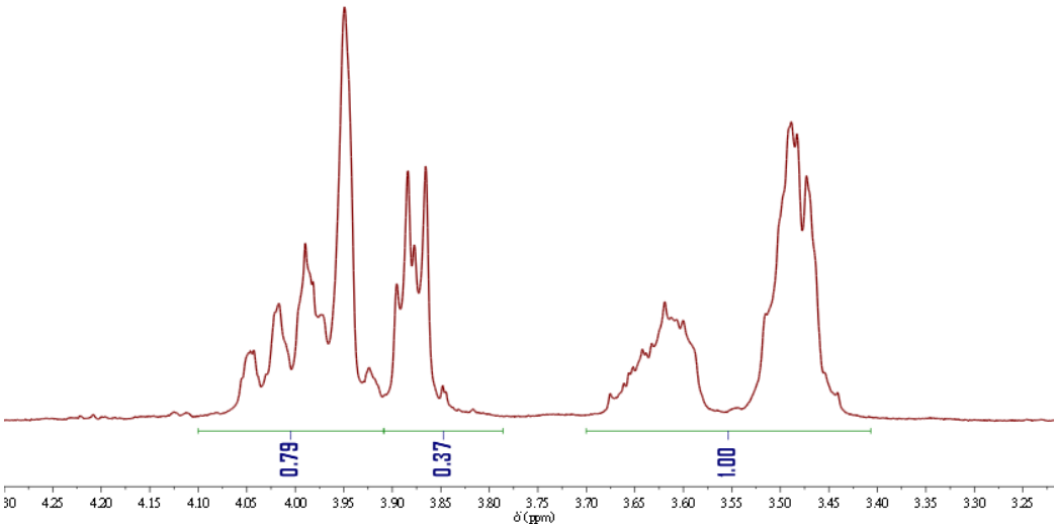
General

The sonicated sample **SP1** (33 mg, %RO = 68%) was dried and reacted with 0.8 mol% of **G2** (2.7 mg, 0.0031 mmol, 0.008 equiv., in 6.3 mL of degassed $CDCl_3$ stock solution) to olefin (0.06 M, 1.0 equiv) under the protection of N_2 for 6 hours at 30 °C. Aliquots were taken out at different reaction periods, and excess amount of ethyl vinyl ether (100 μL) was added and left standing for 30 minutes before ^{1}HNMR and GPC analysis.

Calculation of Depolymerization Percentage

6 hours of depolymerization of 44 kDa **SP1** with 68% ring opening is used as an example for the calculation:





Supplementary Fig. 14: ^{1}HNMR of **SP1** reacting with **G2** for 6h.

$$\text{aliphatic H (pink H)} = 1 + 0.37 = 1.37$$

$$\text{inactivated } \mathbf{P1} \text{ H (blue H)} = \frac{1.37}{8}(4) = 0.685$$

$$\frac{0.685}{4} = 0.32\text{n} \Rightarrow \text{n} = 0.535$$

$$\text{activated allylic H (red H)} = 0.79 - 0.685 = 0.105$$

$$\text{activated allylic H (red H)} = \frac{0.105}{12} = 0.00875 = 0.01635\ \text{n}$$

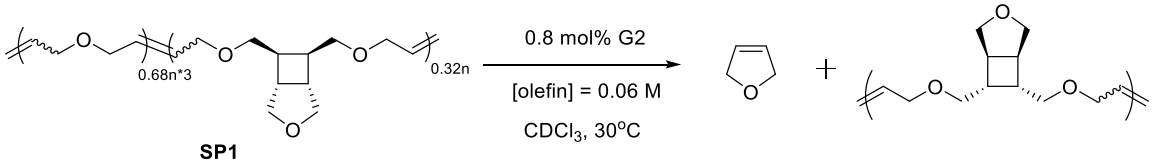
$$= \text{nondepolymerized activated region}$$

$$\text{depolymerization fraction} = \frac{0.68\text{n} - 0.01635\text{n}}{0.68\ \text{n}}$$

$$= \frac{(\text{activated region}) - (\text{nondepolymerized activated region})}{\text{activated region}}$$

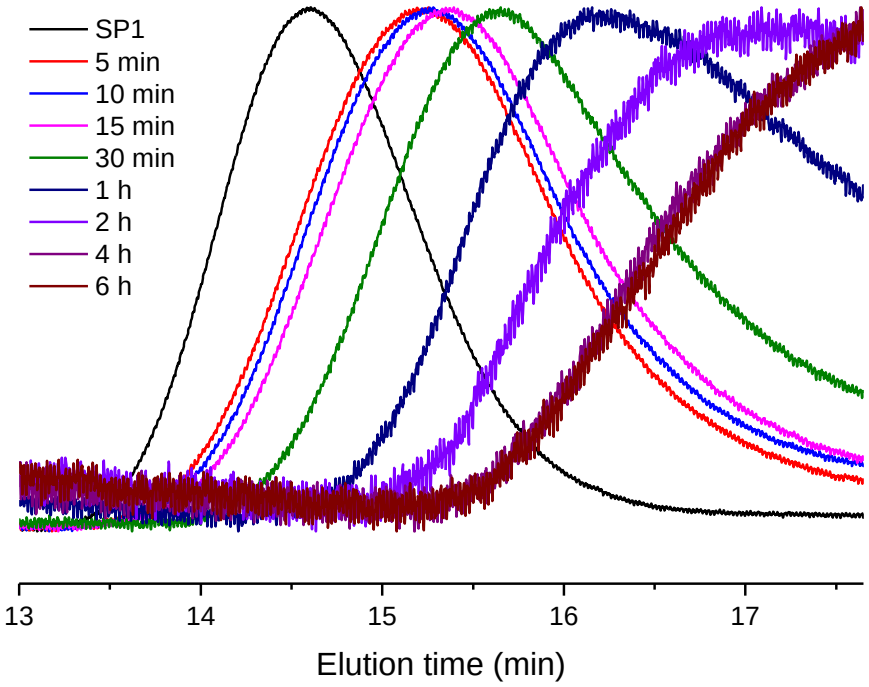
$$= 0.975 \sim 0.98$$

Depolymerization Results for 44 kDa SP1

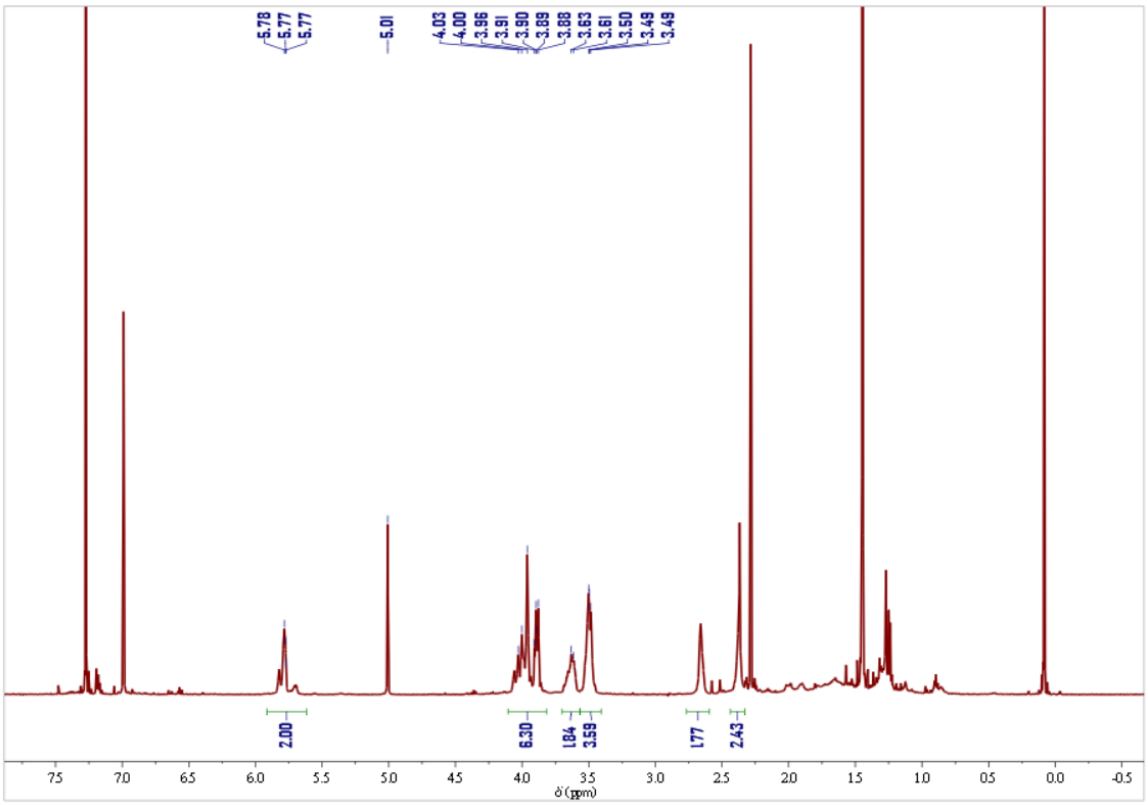


Supplementary Table 3. Summary of depolymerization kinetic study for 44kDa **SP1.**

Reaction Time (min)	Depolymerization (%)	M_n (Da)
360	97.6	4889
240	97.4	5159
120	95.6	6344
60	88.4	8376
30	69.6	13389
15	46.0	18436
10	42.3	20527
5	36.3	21170
0	0	44238

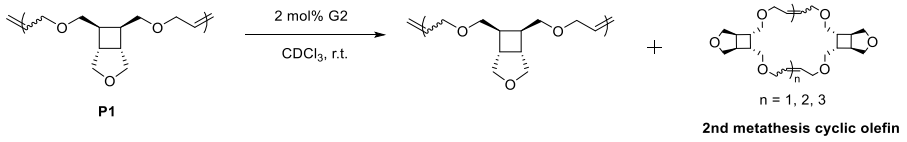


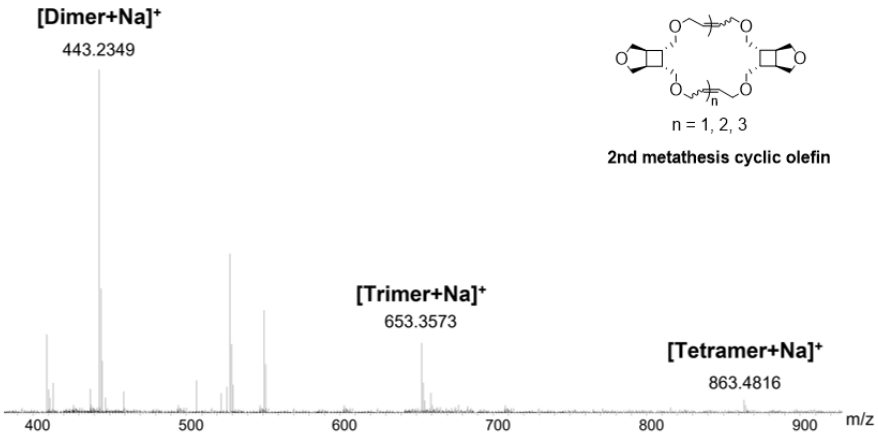
Supplementary Fig. 15: GPC traces of depolymerized **SP1** with different reaction time.



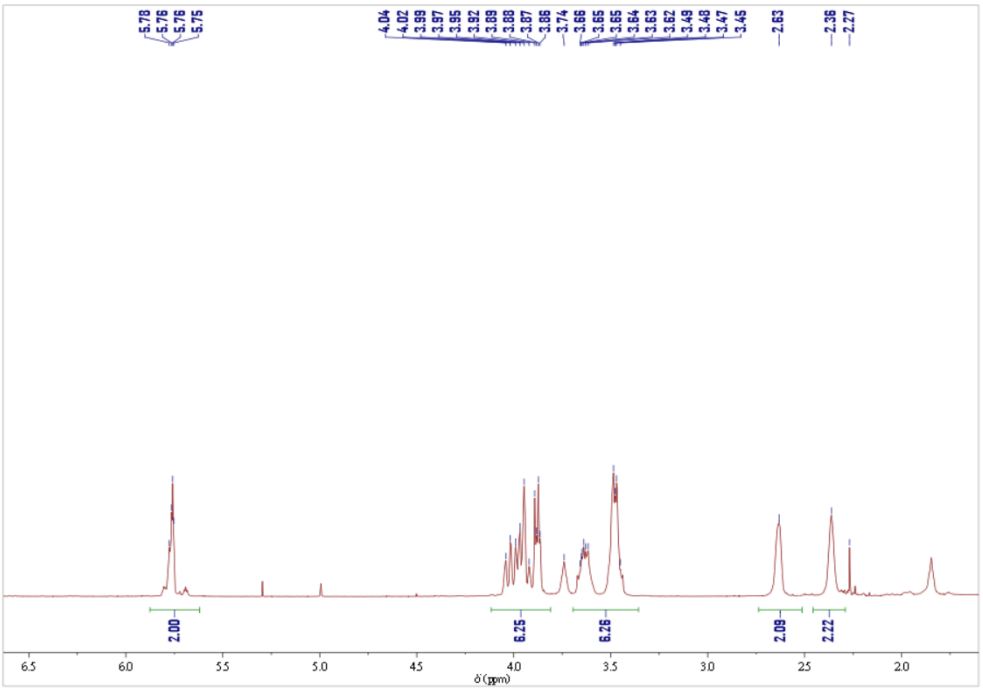
Supplementary Fig. 16: ^{1}HNMR of **SP1** reacting with **G2**.

Mass Spectrometry and ^{1}HNMR Results for P1 Reacting with G2

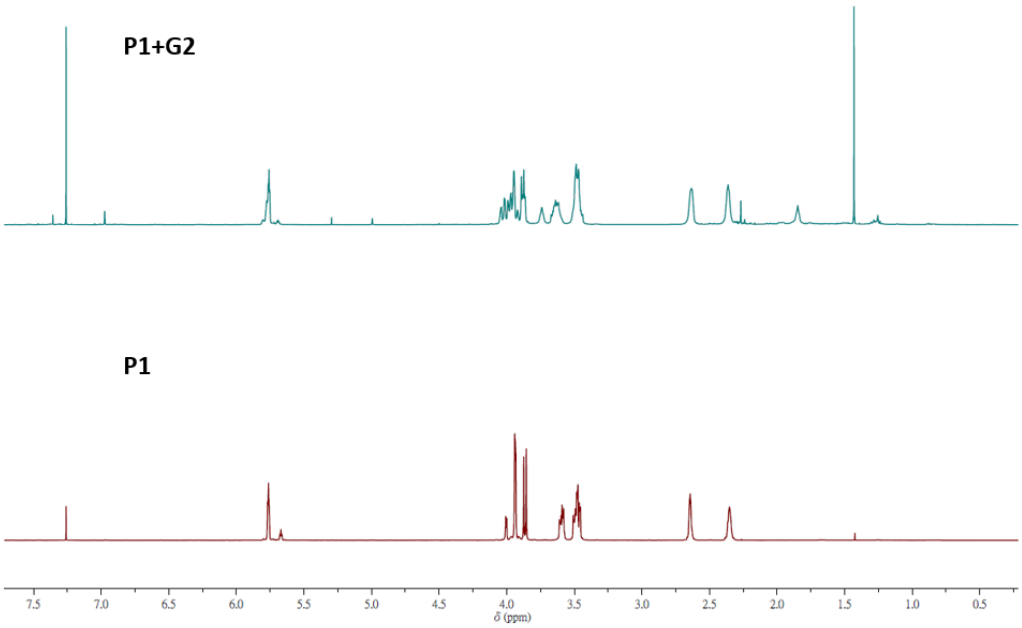




Supplementary Fig. 17: Mass spectrometry of **P1** reacting with **G2** for 1 day.

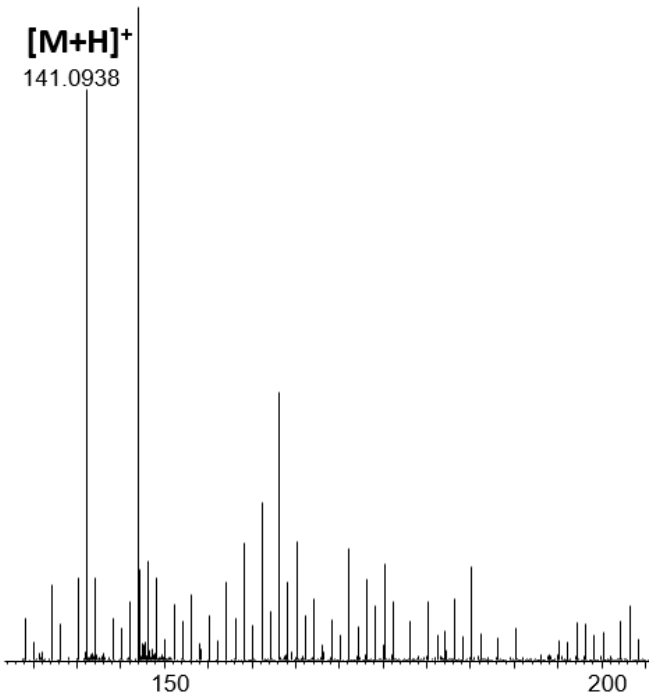


Supplementary Fig. 18: ^{1}HNMR of **P1** reacting with **G2** for 1 day.

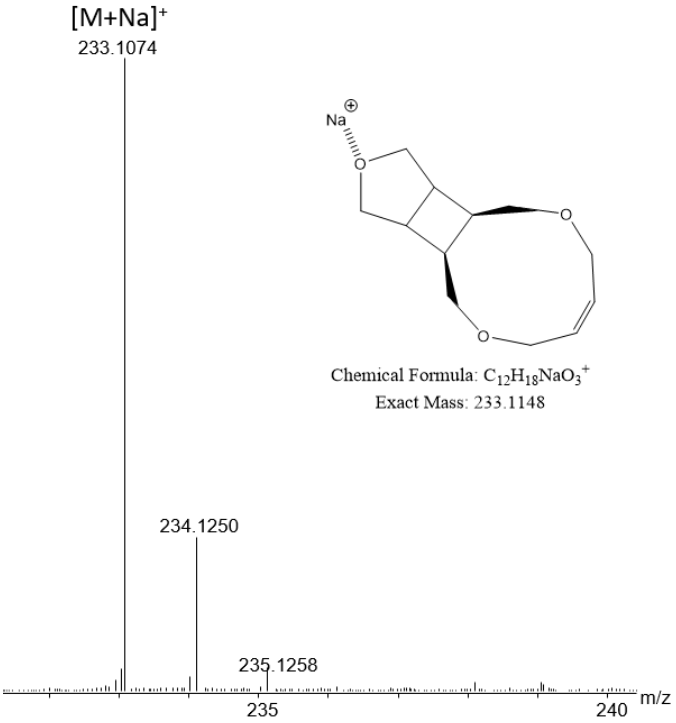


Supplementary Fig. 19: Comparison of ^{1}HNMR of **P1** and **P1** reacting with **G2** for 1 day.

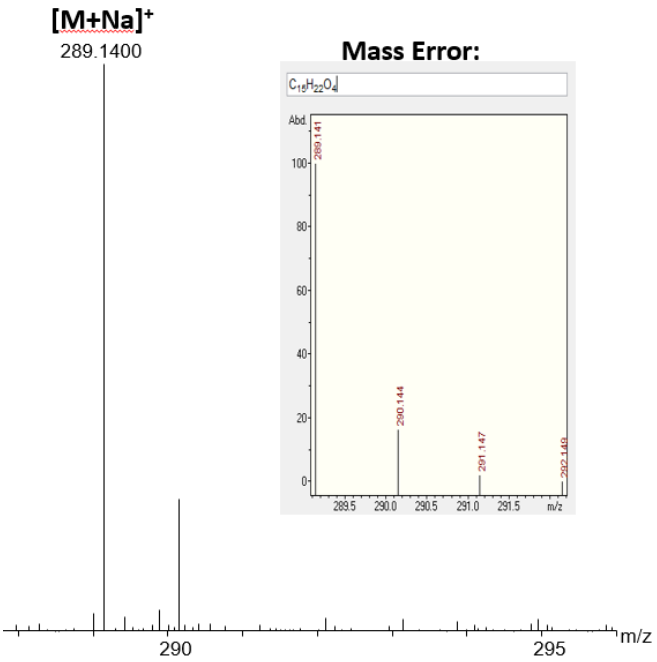
VII. Mass Spectrometry



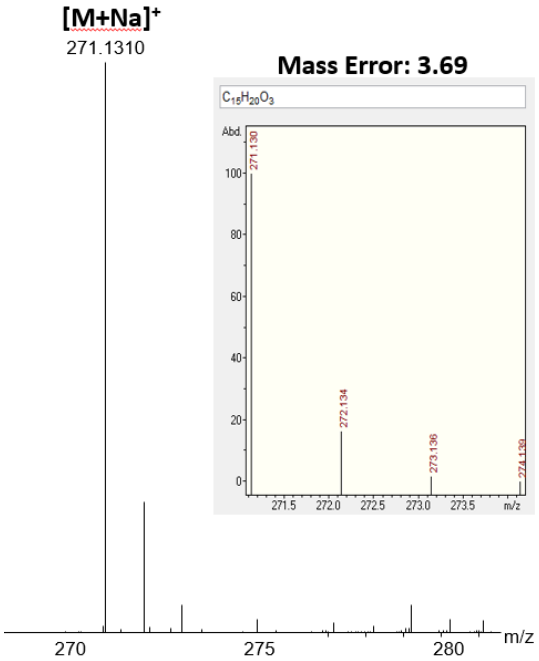
Supplementary Fig. 20: ASAP-MS spectrum for compound **DHF dimer**.



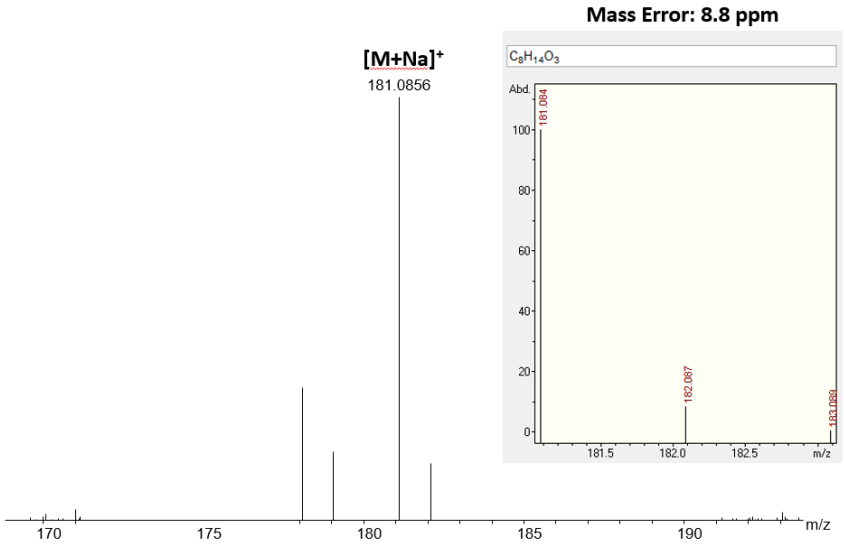
Supplementary Fig. 21: ESI-MS spectrum for compound **M1**.



Supplementary Fig. 22: ESI-MS spectrum for compound **3**.



Supplementary Fig. 23: ESI-MS spectrum for compound **4**.



Supplementary Fig. 24: ESI-MS spectrum for compound **1**.

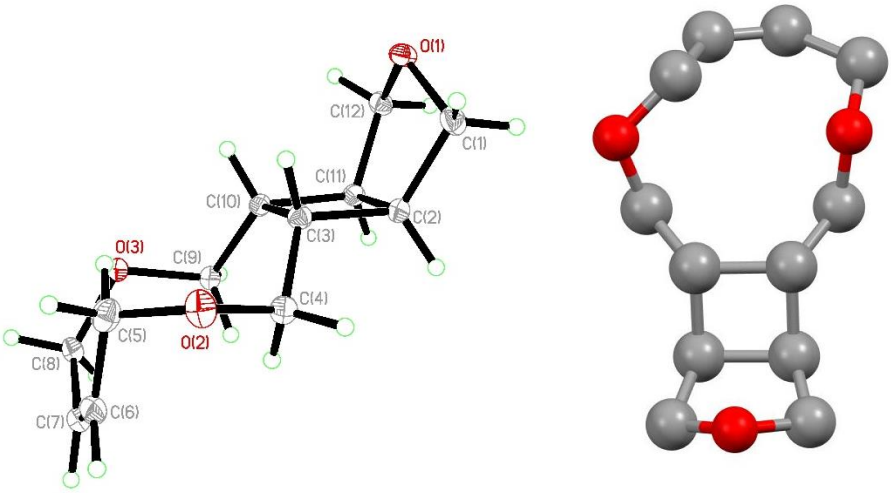
VIII. X-Ray Crystallographic Study

X-Ray Crystallographic Study of M1

Single crystal of **M1** was obtained by making a saturated solution of **M1** with EA/Hexane (1:5) at r.t. The solution was left for 1 day to afford transparent needle-like single crystals. X-ray intensity data were measured on a Bruker CCD-based and PHOTON II CPAD-based diffractometer with dual Cu/Mo ImuS microfocus optics (Mo Kα radiation, λ =0.71073 Å). Crystals were mounted on a cryoloop using Paratone oil and placed under a steam of nitrogen at 100 K (Oxford Cryosystems). The detector was placed at a distance of 5.00 cm from the crystal. The data were corrected for absorption and the structures were refined using the Bruker SHELXTL Software Package (Version 6.1),[2] and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of F^2 converged. CCDC 2179611 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

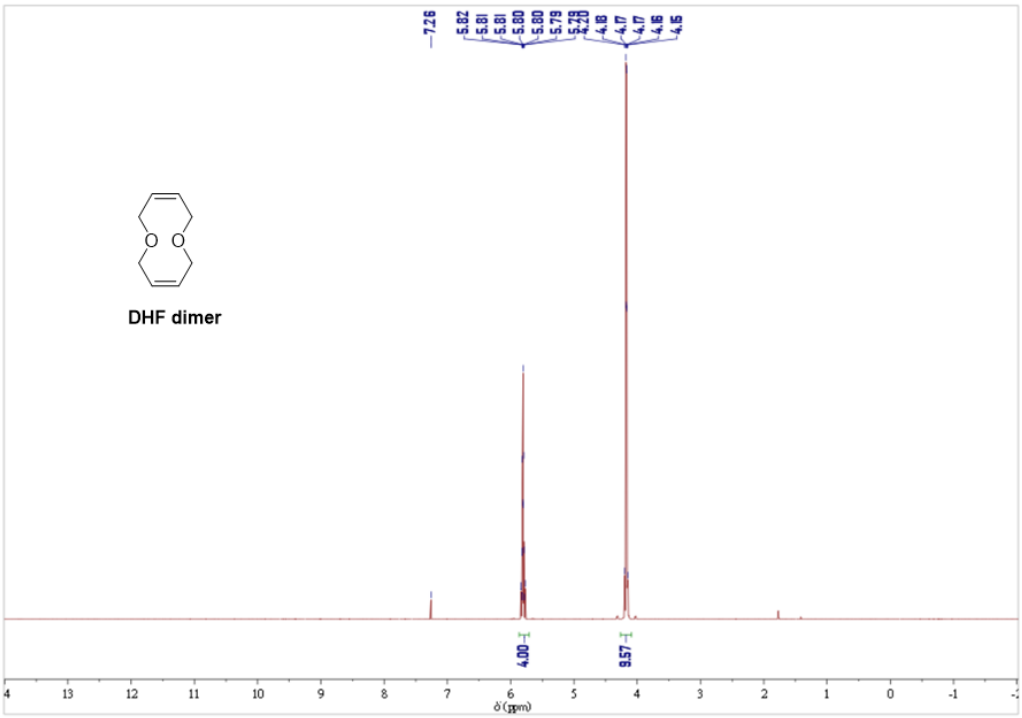
Supplementary Table 4. Crystal data and structure refinement parameters.

Compound	**M1**
CCDC	2179611
Empirical formula	$C_{12}H_{18}O_3$
Formula weight	210.26
Crystal system	monoclinic
Space group	P2(1)/n
a/ Å	5.5345(4)
b/ Å	15.2895(11)
c/ Å	12.7056(10)
α(°)	90
β(°)	98.571(3)
γ(°)	90
Volume ($Å^3$)	1063.14(14)
Z	4
Dc (Mg/m^3)	1.314
μ (mm^{-1})	0.093
F(000)	456
reflns collected	2639
indep. reflns	2178
GOF on F^2	0.939
R1 (on F_o^2, $I > 2\sigma(I)$)	0.0437
wR2 (on F_o^2, $I > 2\sigma(I)$)	0.1361
R1 (all data)	0.0532
wR2 (all data)	0.1439

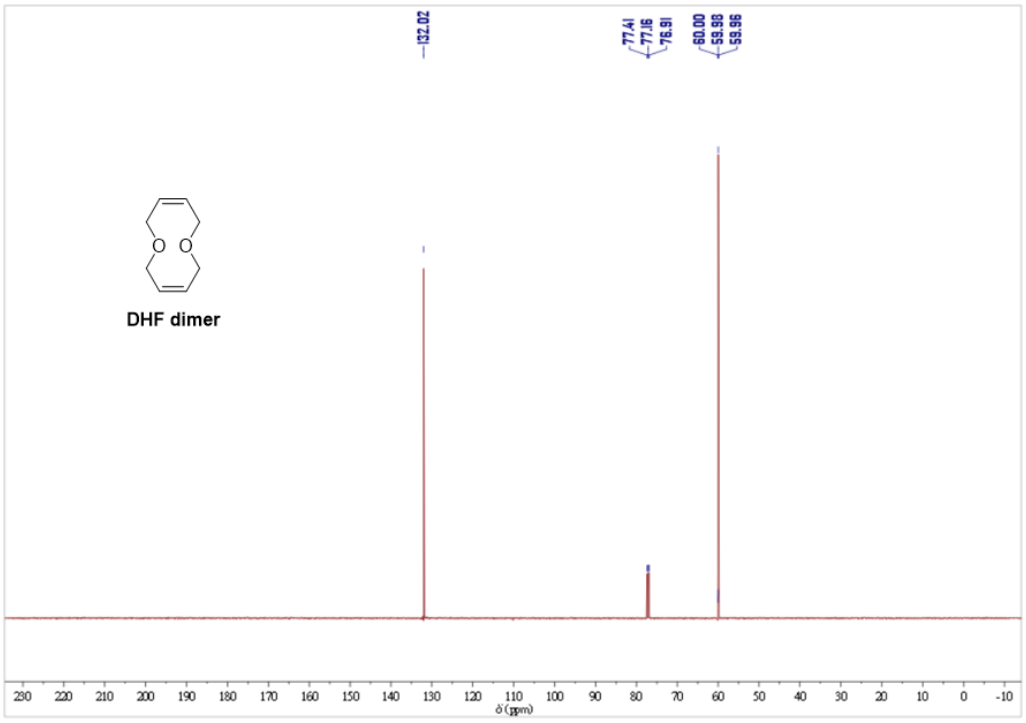


Supplementary Fig. 25: Left: Molecular structure of **M1** with 35% thermal ellipsoids. Right: Ball and stick diagram of **M1** orthogonal to the rings with hydrogen atom positions omitted for clarity.

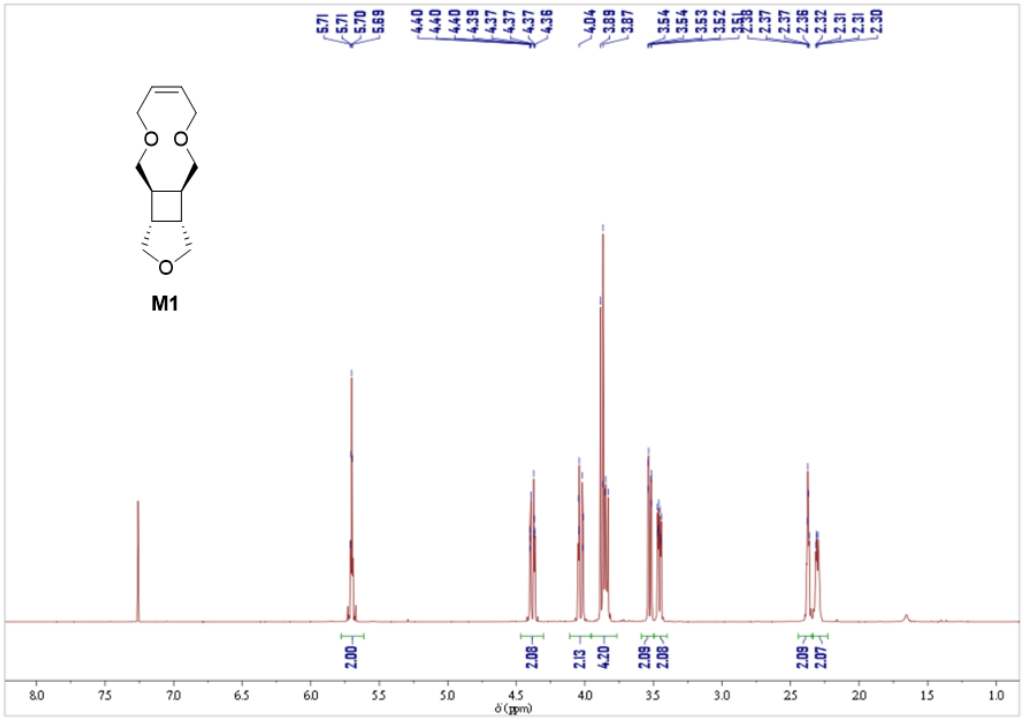
IX. ^{1}H and ^{13}C NMR Spectra



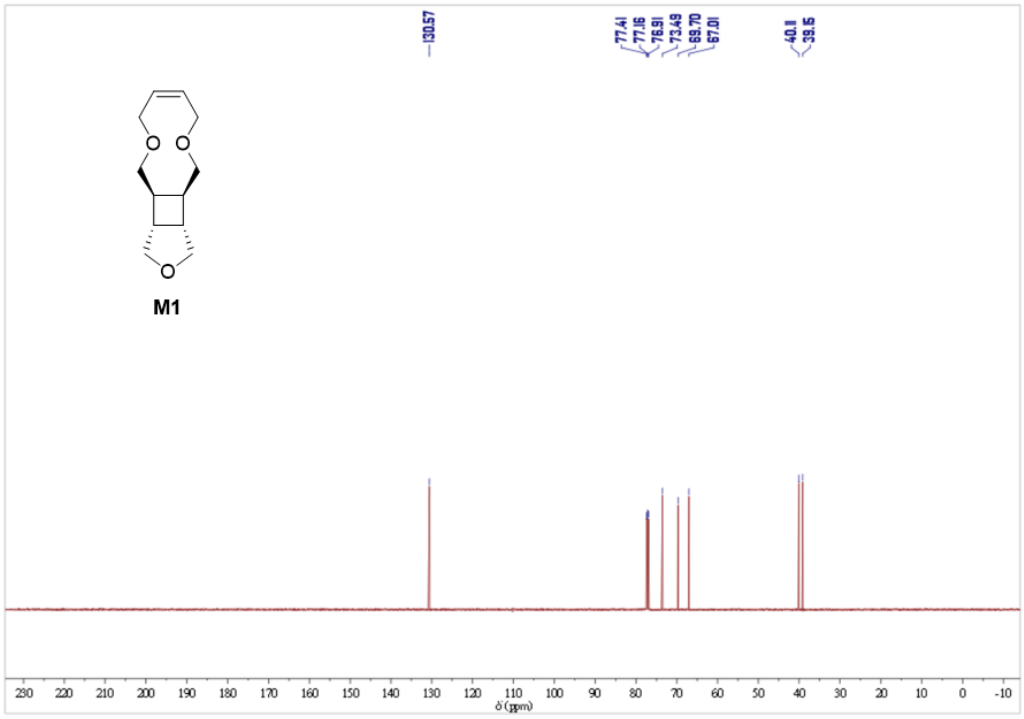
Supplementary Fig. 26: ^{1}H NMR spectrum for **DHF dimer**.



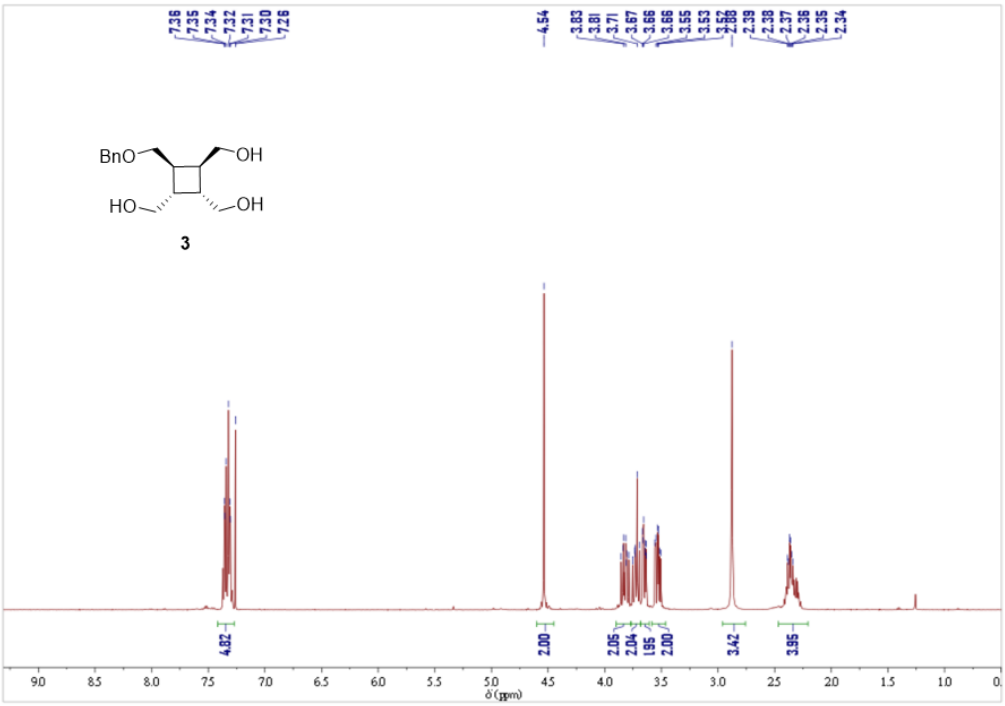
Supplementary Fig. 27: ^{13}C NMR spectrum for **DHF dimer**.



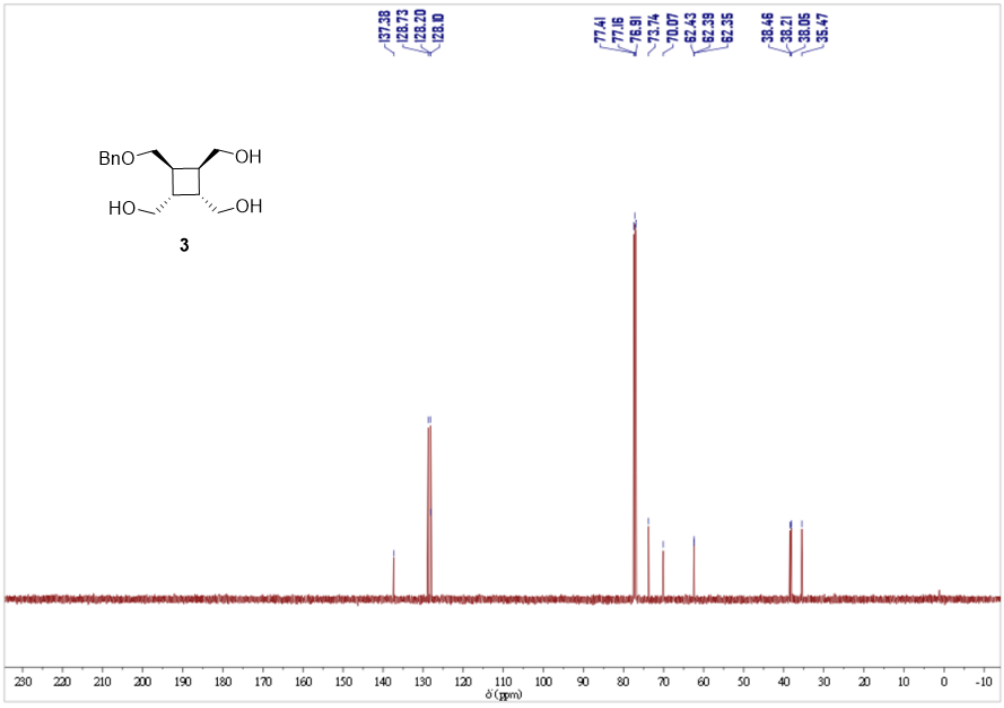
Supplementary Fig. 28: ^{1}H NMR spectrum for **M1**.



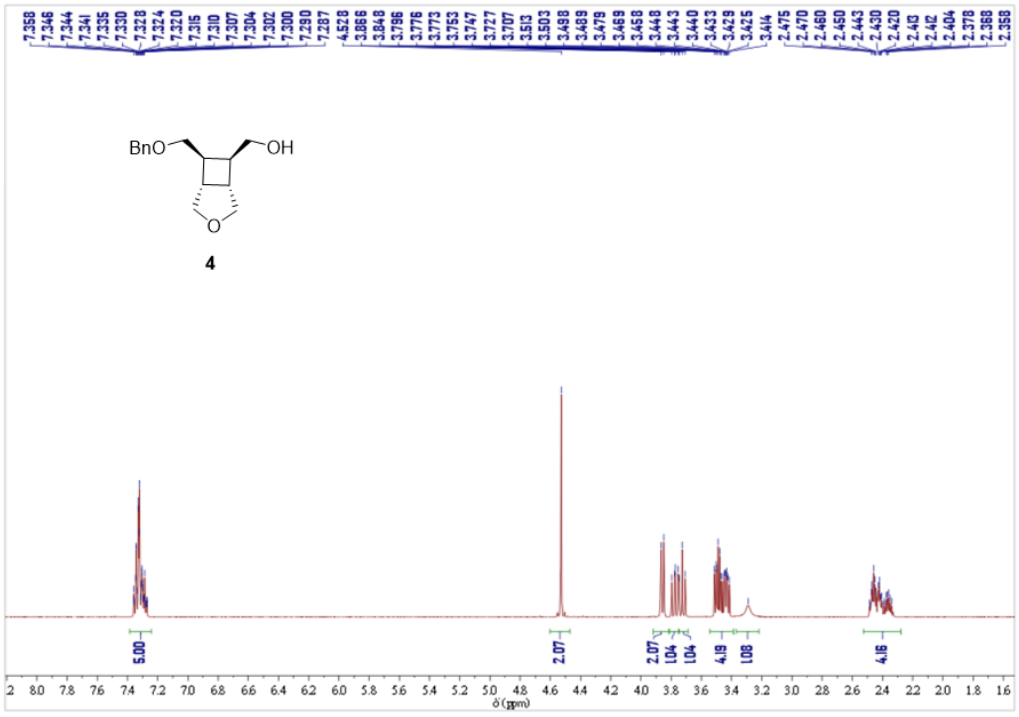
Supplementary Fig. 29: ^{13}C NMR spectrum for **M1**.



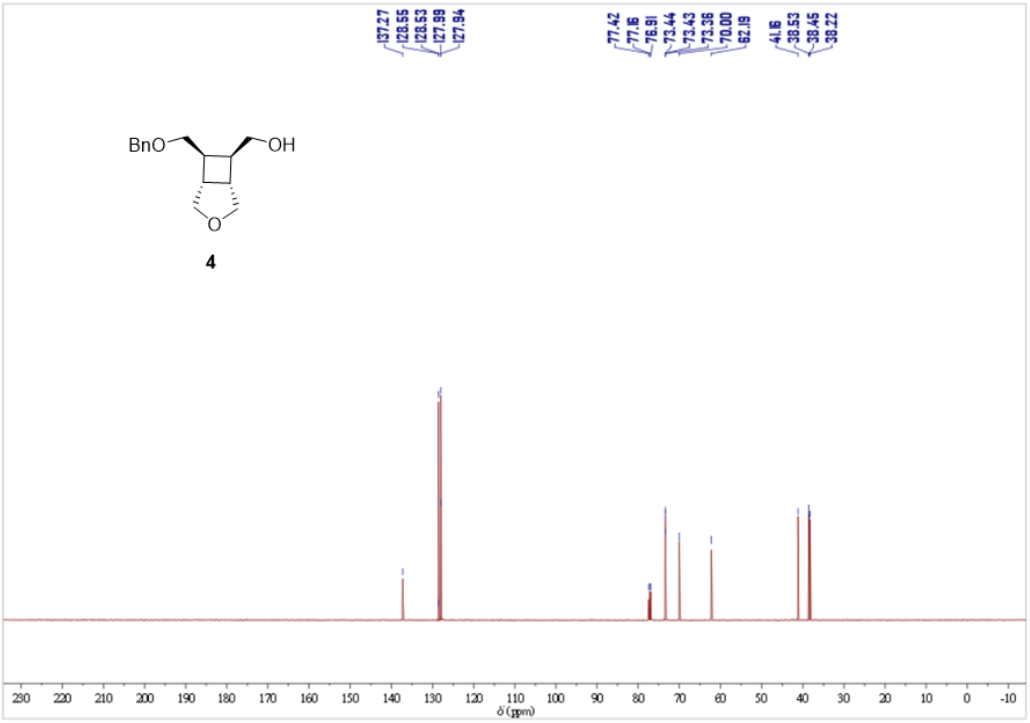
Supplementary Fig. 30: ^{1}H NMR spectrum for **3**.



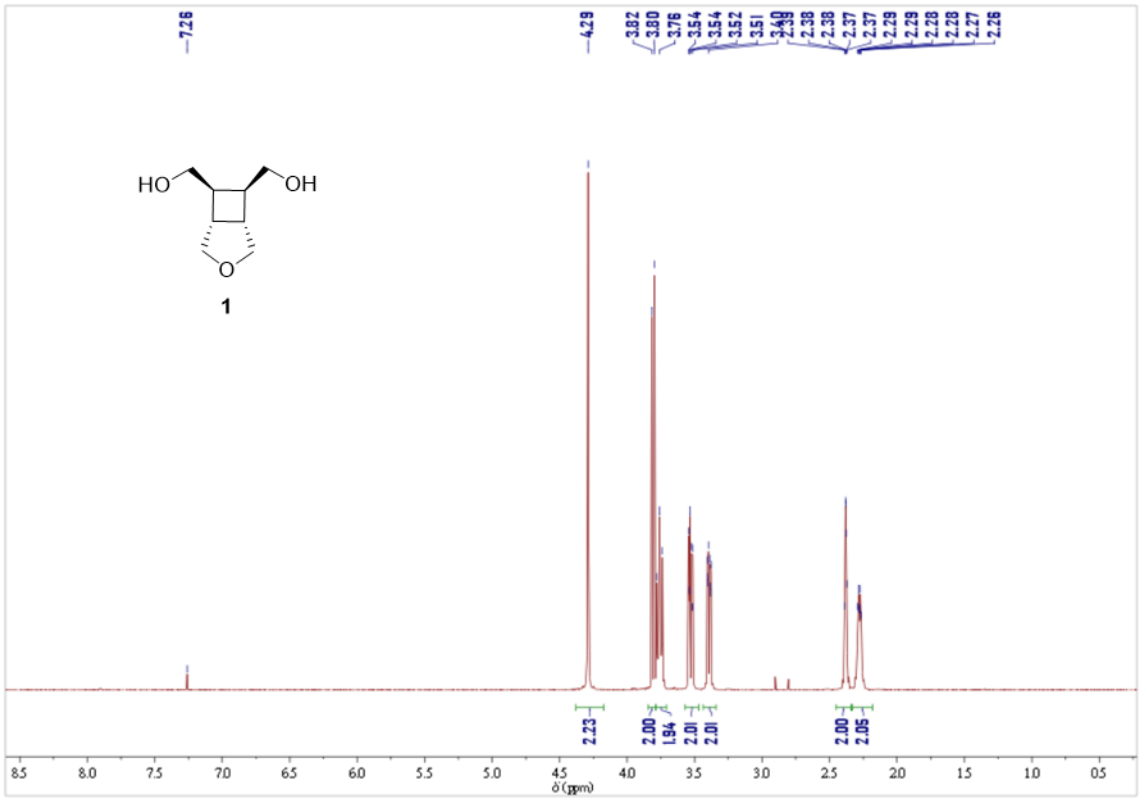
Supplementary Fig. 31: ^{13}C NMR spectrum for **3**.



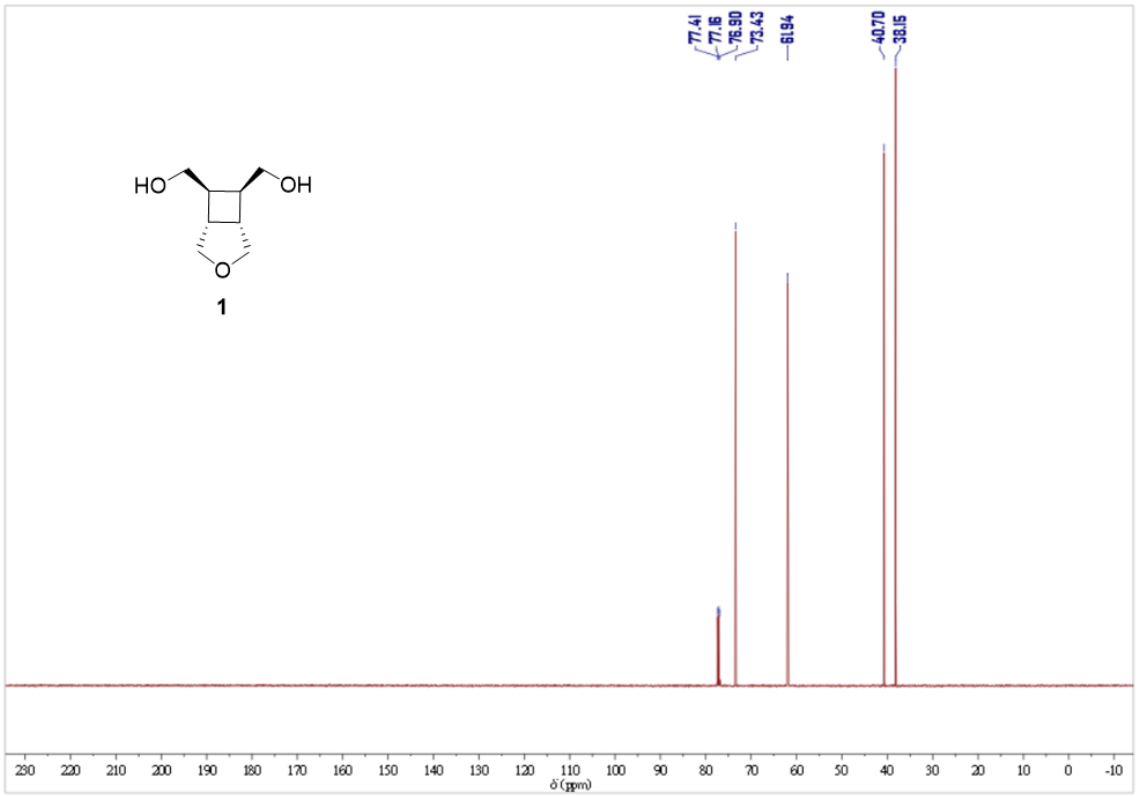
Supplementary Fig. 32: ^{1}H NMR spectrum for **4**.



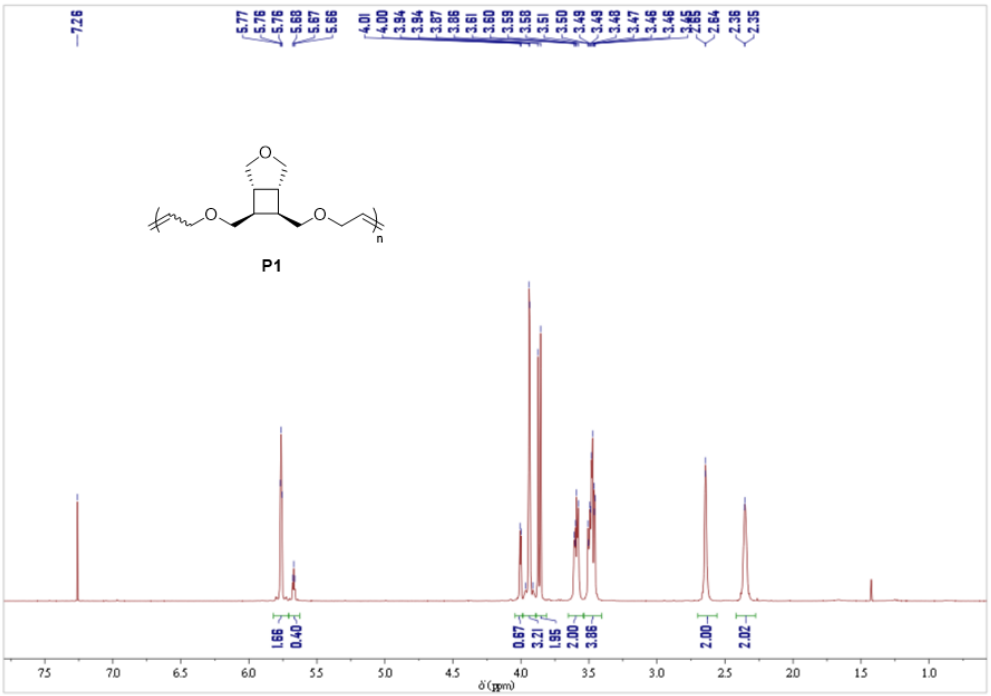
Supplementary Fig. 33: ^{13}C NMR spectrum for **4**.



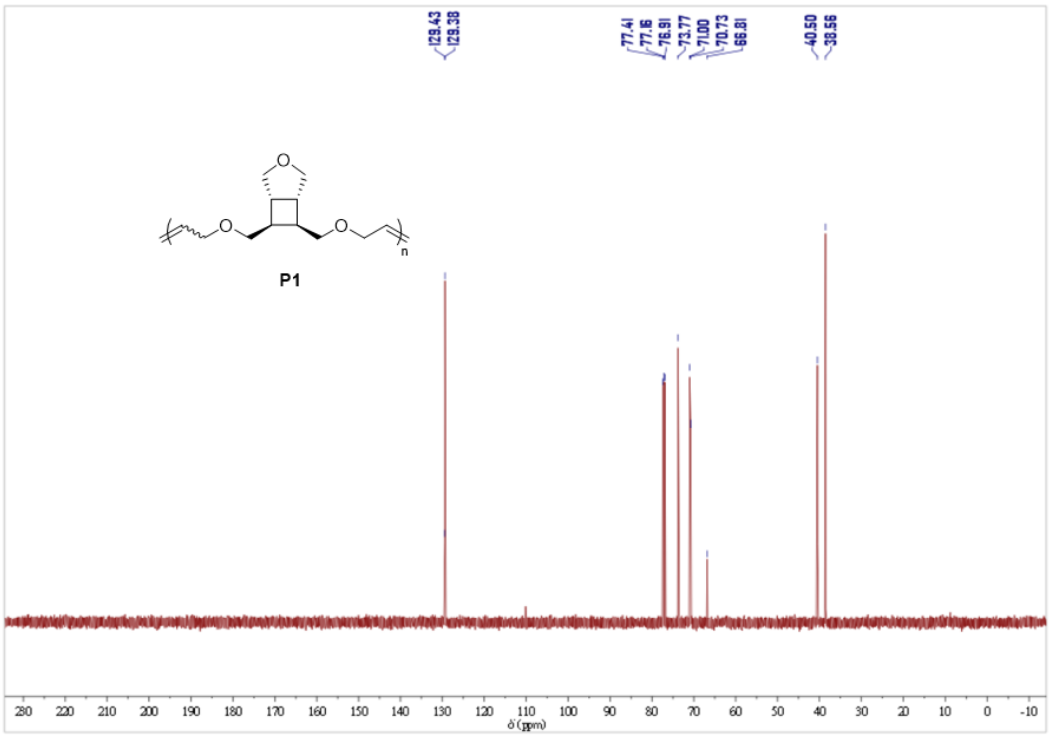
Supplementary Fig. 34: ^{1}H NMR spectrum for **1**.



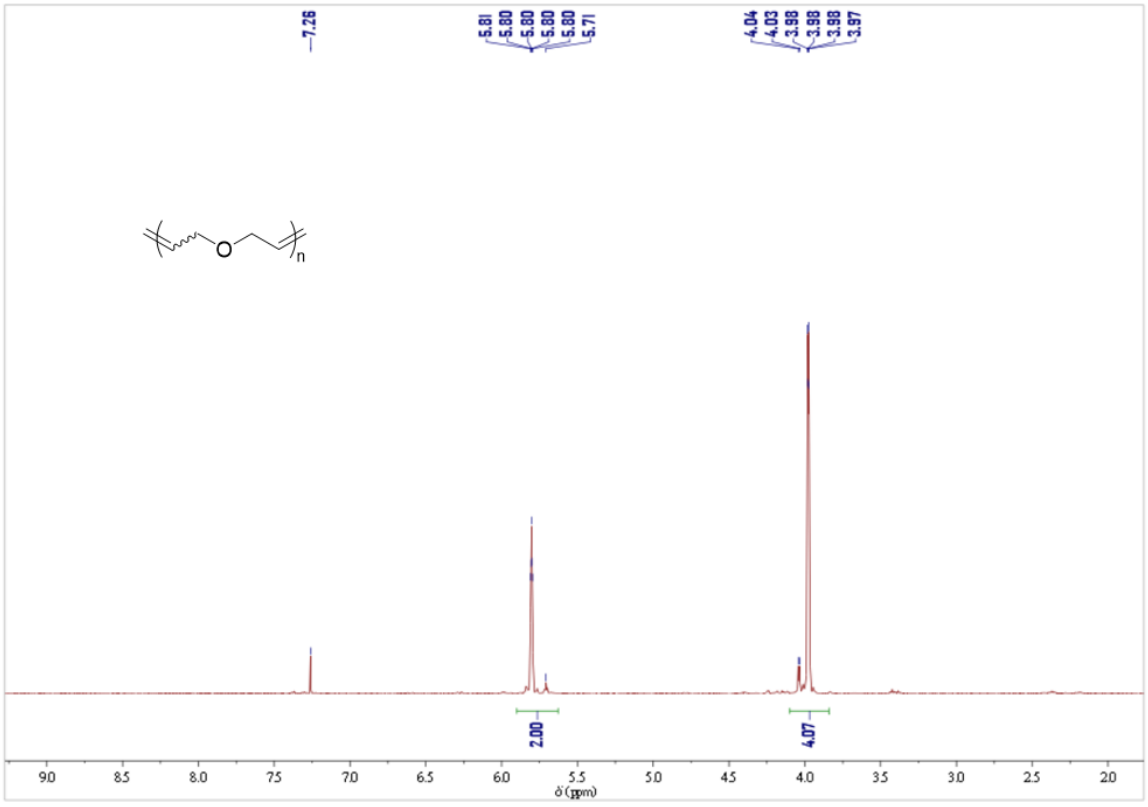
Supplementary Fig. 35: ^{13}C NMR spectrum for **1**.



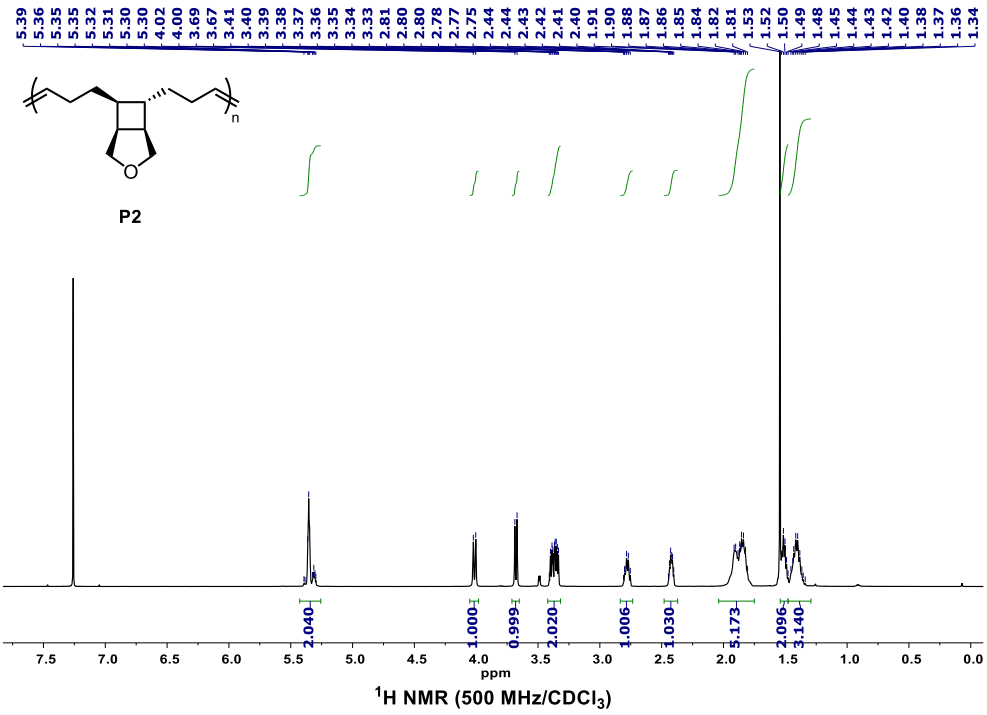
Supplementary Fig. 36: ^{1}H NMR spectrum for **P1**.



Supplementary Fig. 37: ^{13}C NMR spectrum for **P1**.



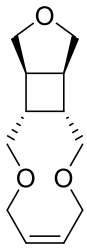
Supplementary Fig. 38: ^{1}H NMR spectrum for PDHF**.**



Supplementary Fig. 39: ^{1}HNMR of **P2**

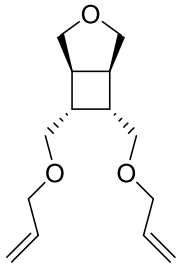
X. Optimized Geometries

Optimized geometries from DFT calculations at B3LYP/6-31g(d,p) level.



C 1.82361 -0.88345 0.64603
C 1.81376 0.68218 0.61001
C 3.27873 1.05566 0.40650
O 3.83313 -0.04102 -0.32341
C 3.26841 -1.22626 0.24418
O -1.64044 -1.16030 -0.85465
C -0.60278 -1.36564 0.10010
C -2.92441 -1.50701 -0.36033

C -3.48978 -0.59463 0.71258
C -3.30664 0.72493 0.83333
C -2.48702 1.57673 -0.10682
O -1.10310 1.49375 0.22909
C -0.20747 1.57144 -0.87244
C 0.96114 0.61852 -0.69039
C 0.73502 -0.91445 -0.46844
H 1.53925 -1.37304 1.58282
H 1.32669 1.18476 1.44787
H 3.43423 1.96052 -0.18945
H 3.79251 1.18010 1.37496
H 3.34856 -2.02138 -0.50335
H 3.84138 -1.52926 1.13586
H -0.53841 -2.44058 0.34756
H -0.82610 -0.81918 1.02307
H -3.58711 -1.50757 -1.23608
H -2.91463 -2.53966 0.02682
H -4.11755 -1.09461 1.45009
H -3.77210 1.23238 1.67602
H -2.63707 1.23123 -1.13704
H -2.82573 2.62291 -0.05365
H -0.72946 1.31893 -1.80525
H 0.17210 2.60243 -0.97625
H 1.62233 0.75366 -1.55513
H 0.97892 -1.52919 -1.34310



C 2.38906 0.68181 0.23723
C 2.20818 -0.28707 -0.98123
C 3.55778 -1.00226 -1.07522
O 4.11553 -0.93143 0.23823

C 3.81119 0.38020 0.71888
O -0.32383 1.67065 0.32574
C 0.04922 0.80606 1.39474
C -1.42247 2.50896 0.65203
C -1.68785 3.43084 -0.50028
C -3.34130 -2.68538 0.31443
C -2.45118 -1.96437 -0.65328
O -1.17383 -1.79093 -0.05930
C -0.23993 -1.16169 -0.93019
C 1.09163 -1.04974 -0.21089
C 1.23758 -0.05117 0.98686
C -2.88393 3.61620 -1.05573
C -4.57044 -2.29303 0.64423
H 2.20708 1.74219 0.05456
H 1.89187 0.16433 -1.92598
H 3.48737 -2.05930 -1.34948
H 4.21476 -0.49359 -1.80112
H 3.92381 0.36840 1.80746
H 4.52086 1.11482 0.30213
H -0.79680 0.16060 1.67285
H 0.31950 1.41211 2.27763
H -2.31882 1.91201 0.88590
H -1.18052 3.09661 1.55688
H -0.82071 3.97967 -0.86481
H -2.92156 -3.59629 0.73866
H -2.34929 -2.55613 -1.58211
H -2.89206 -0.99465 -0.93743
H -0.11086 -1.76563 -1.84669
H -0.60549 -0.16939 -1.22819
H 1.40989 -2.05746 0.07886
H 1.58570 -0.56446 1.89116
H -3.76213 3.07388 -0.71337
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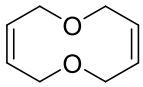
H -5.00679 -1.38287 0.23936



C 0.50826 0.21790 2.30930
C 1.53866 0.05505 1.47163
C -0.95249 -0.13526 2.14375
O -1.36389 -0.55086 0.85705
C -1.49258 0.53021 -0.08445
C -1.53866 -0.05505 -1.47163
C -0.50826 -0.21790 -2.30930
C 0.95249 0.13526 -2.14375
O 1.36389 0.55086 -0.85705
C 1.49258 -0.53021 0.08445
H 0.71799 0.67302 3.27876
H 2.51229 0.41511 1.79917
H -1.19602 -0.96558 2.82129
H -1.55495 0.72445 2.48841
H -2.42549 1.07673 0.12583
H -0.65448 1.22284 0.01361
H -2.51229 -0.41511 -1.79917
H -0.71799 -0.67302 -3.27876
H 1.55495 -0.72445 -2.48841
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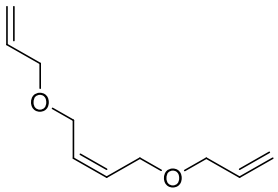

C 0.60753 -2.00316 -0.35206
C 1.90549 -1.68201 -0.31961
C 2.59647 -0.71044 0.60159
O 3.25762 0.3228 -0.13153
O -1.47361 -0.87682 -0.2435
C -0.47641 -1.50521 0.55807
C 2.36485 1.2446 -0.76641

C 1.66551 2.14878 0.21327
C -3.64747 0.05664 -0.43842
C -2.64405 -0.5491 0.49573
C -4.28538 1.20414 -0.21492
C 0.34023 2.22233 0.34691
H 0.26063 -2.70013 -1.11366
H 2.56478 -2.13102 -1.06184
H 1.9061 -0.28326 1.33895
H 3.3968 -1.21883 1.15142
H -0.0967 -0.80338 1.31333
H -0.92275 -2.35745 1.10145
H 3.00609 1.83211 -1.43342
H 1.6264 0.71558 -1.3841
H 2.31504 2.76481 0.83496
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H -2.4108 0.14731 1.31751
H -3.05728 -1.46633 0.95437
H -5.02849 1.58838 -0.90684
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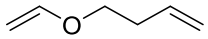
H -0.32707 1.60021 -0.24588

C -1.20139 -0.06956 0.00737
C -0.57230 1.10565 0.03694
C 0.91858 0.85610 -0.05116
C 0.97279 -0.68948 0.05916
O -0.39324 -1.17171 -0.05730
H -2.26097 -0.29389 0.01649
H -1.04378 2.07771 0.06947
H 1.33864 1.21905 -0.99915
H 1.48702 1.33723 0.75307
H 1.56223 -1.16661 -0.72768
H 1.35672 -1.01611 1.03234



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C -2.00354 -0.44075 -0.07942
C -1.19023 0.74127 -0.53351
C 0.24114 0.73332 0.00145
O 0.90675 -0.40853 -0.53853
C 2.95552 0.13674 0.64125
C -3.15820 -0.36080 0.58109
H 2.58103 -1.50611 -0.64706
H -1.58677 -1.41745 -0.31939
H -1.13597 0.75945 -1.63060
H -1.67112 1.67483 -0.21847
H 0.77399 1.64588 -0.30067
H 0.24875 0.68054 1.09877
H 2.60623 1.03669 1.13148
H 3.97781 -0.16807 0.82791
H -3.70494 -1.24847 0.88496
H -3.60439 0.59700 0.83994

C 0.00000 1.17241 0.37105
C 0.00000 0.66529 -1.04492
C 0.00000 -0.66529 -1.04492
C 0.00000 -1.17241 0.37105
O 0.00000 0.00000 1.18998
H -0.88592 1.78774 0.59766
H 0.88592 1.78774 0.59766
H 0.00000 1.31618 -1.91197
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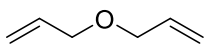

C 1.17134 -0.58121 0.15862

C 2.33689 0.32987 0.40191
C -2.33689 0.32987 -0.40191
C -1.17134 -0.58121 -0.15862
O 0.00000 0.20591 0.00000
C 3.49027 0.26926 -0.26078
C -3.49027 0.26926 0.26078
H 1.04502 -1.26584 1.01789
H 1.34851 -1.20969 -0.73036
H 2.19410 1.06231 1.19484
H -2.19410 1.06231 -1.19484
H -1.34851 -1.20969 0.73036
H -1.04502 -1.26584 -1.01789
H 3.65106 -0.44737 -1.06273
H 4.31935 0.92947 -0.02528
H -4.31935 0.92947 0.02528
H -3.65106 -0.44737 1.06273

XI. Reference

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