Supplementary Information

Closed-Loop Recycling of Lignin-Based Sustainable Polymers with an All-Hydrocarbon Backbone

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1. General Information....2
1.1 Materials....2
1.2 Characterizations....2
2. Synthesis....3
2.1 Monomer synthesis....3
2.1.1 Synthesis of 9-oxabicyclo[6.1.0]non-4-ene....3
2.1.2 Synthesis of *cis*-cyclooctene-*trans*-5,6-doil....3
2.1.3 Synthesis of 1....4
2.1.4 Synthesis of M1....4
2.1.5 Synthesis of 2....5
2.1.6 Synthesis of 3....5
2.1.7 Synthesis of 4....5
2.1.8 Synthesis of C2....6
2.1.9 Synthesis of C3....6
2.1.10 Synthesis of C4....7
2.1.11 Synthesis of M2....7
2.1.12 Synthesis of M3....8
2.1.13 Synthesis of M4....8
2.2 Polymerization procedure....9
2.2.1 Synthesis of P1....9
2.2.2 Synthesis of P1'....10
2.2.3 Synthesis of P2....10
2.2.4 Synthesis of P3....11
2.2.5 Synthesis of P4....11
3. DFT calculation of the ring strain energy....12
4. Depolymerization studies....12
4.1 Depolymerization procedure for P1-P4....12
4.2 Depolymerization results....12

4.3 Depolymerization kinetic study 14
4.4 Recovered monomer for repolymerization towards multiple recycling 14
5. NMR spectra 15
Reference 27

1. General Information

1.1 Materials

All reagents were purchased from the *Sigma-Aldrich*, *Alfa Aesar*, J*&K Chemicals*, *Energy Chemicals*, *Aladdin Reagents, Meryer Chemicals* or *Leyan Chemicals* and used without further purification unless otherwise stated. All the synthetic steps were carried out under an inert argon atmosphere using standard Schlenk technique unless otherwise stated. All solvents were extra dry for reactions unless otherwise stated.

1.2 Characterizations

Nuclear magnetic resonance (NMR) experiments (^{1}H and ^{13}C) were recorded on a Bruker Avance NEO 400 instrument by using deuterated chloroform as a solvent. Chemical shifts were calibrated to the proton resonance of solvent (7.26 and 77.0 ppm for ^{1}H NMR and ^{13}C NMR spectroscopies, respectively).

High-resolution mass spectra (HRMS) were recorded by a Waters Xevo G2-XS QTof mass spectrometer which utilized an ESI ionization source.

Gel permeation chromatography (GPC) curves were measured with Malvern Viscotek 270 by using THF as the mobile phase at 40 °C. The flow rate was 1 mL/min, and the injection volume was 100 μL. A refractive index detector was employed to characterize the number average molecular weight (M_n) and molecular weight distribution ($Đ$) through conventional calibration by using narrow-distributed polystyrene as an internal standard.

Glass transition temperature (T_g) was characterized with a Netzsch differential scanning calorimeter (DSC) calibrated with an indium standard. The heating and cooling rates were fixed at 10 °C/min from -30 °C to 150 °C. T_g was determined from the second heating ramp.

The thermal degradation properties of the samples were probed through thermogravimetry by using a Netzsch TG 209 F1 system (Netzsch Instruments). The samples were heated from 30 °C to 800 °C at a rate of 20 °C/min under nitrogen protection.

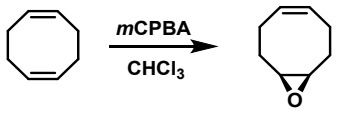
Rectangular polymer specimens were prepared with solution-casting polymer solutions (in toluene) onto mica substrates. After the specimens were vacuum dried at

110 °C overnight, the film could be easily peeled off from substrates and cut into several rectangular specimens (length = 50 mm, thickness = 0.2 μm, and width = 10 mm). Tensile tests were performed on MTS CMT8502 at a strain speed of 15 mm/min at ambient temperature (~15 °C).

2. Synthesis

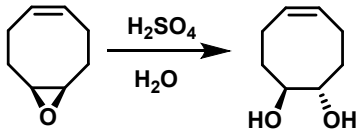
2.1 Monomer synthesis

2.1.1 Synthesis of 9-oxabicyclo[6.1.0]non-4-ene



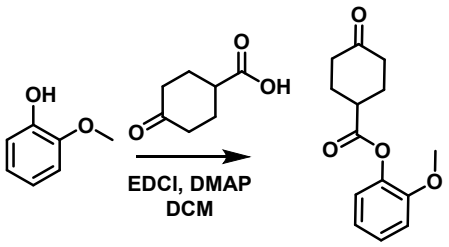
1,5-cyclooctadiene (15.67 g, 144.85 mmol) dissolved in 20 mL THF, *m*CPBA (20 g, 115.9 mmol) dissolved in 224 mL $CHCl_3$ was added into the solution dropwise at 0 °C within 2 h. The mixture was kept at 0 °C and stirred for another hour until the reaction was completed. 100 mL saturated $NaHSO_3$ solution was added into the reaction mixture to quench unreacted *m*CPBA. The organic phase was washed with $NaHCO_3$ and saturated brine in sequence. The organic phase was further dried with $MgSO_4$. After solvent evaporation, the crude product was purified via silica gel column chromatography using EA: hexane=1:2 to EA: hexane=1:1 as eluent. The product was obtained as a colorless liquid (16.05 g, 89.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.65 – 5.47 (m, 2H), 3.03 (s, 2H), 2.44 (m, 2H), 2.21 – 1.92 (m, 6H).

2.1.2 Synthesis of *cis*-cyclooctene-*trans*-5,6-doil



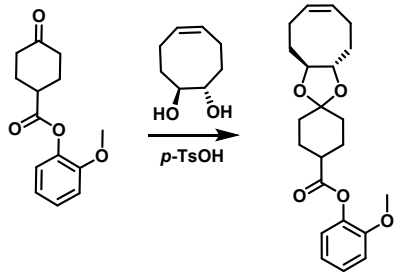
9-Oxabicyclo[6.1.0]non-4-ene (2.13 g, 17.2 mmol) was dispersed in H_2O (31.4 mL, 1.744 mol) using ultrasonication, and then concentrated H_2SO_4 (53.25 μL) was added into the solution. The reaction was stirred at room temperature overnight. The resultant mixture was extracted using EA. The organic phase was washed with saturated $NaHCO_3$ solution, deionized water, saturated brine and dried over $MgSO_4$. After solvent evaporation, the crude product was purified via silica gel column chromatography using EA: PE=1.8:1 as eluent. The product was obtained as a colorless liquid (1.45 g, 59.5% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.72 – 5.49 (m, 2H), 3.80 – 3.51 (m, 2H), 2.87 (s, 2H), 2.48 – 2.27 (m, 2H), 2.24 – 1.99 (m, 4H), 1.67 – 1.42 (m, 2H).[1]

2.1.3 Synthesis of 1



Guaiacol (0.719 g, 5.79 mmol), DMAP (0.068 g, 0.579 mmol), and 4-oxocyclohexane-1-carboxylic acid (0.823 g, 5.79 mmol) were dissolved in 60 mL DCM. Then EDCl (1.11 g, 5.79 mmol) was added into the system in one batch. The reaction was stirred at room temperature overnight. The resultant mixture was washed with deionized water, saturated brine and dried over Na_2SO_4. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=4:1 as eluent). The product was obtained as a white solid (1.09 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (m, 1H), 7.03 (dd, *J*=7.8, 1.5, 1H), 6.98 (m, 2H), 3.81 (s, 3H), 3.06 (m, 1H), 2.60 (m, 2H), 2.42 (m, 2H), 2.30 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 210.15, 172.26, 150.88, 139.57, 126.98, 122.57, 120.78, 112.33, 55.74, 40.11, 39.43, 28.40. HRMS m/z (ESI) calcd for $C_{14}O_4H_{16}Na$ $(M + Na)^+$ 271.0941, found 271.0943.

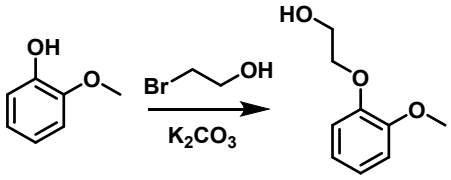
2.1.4 Synthesis of M1



1 (1.00 g, 4.02 mmol), *p*-TsOH (0.138 g, 0.805 mmol), and *cis*-cyclooctene-*trans*-5,6-doil (0.572 g, 4.02 mmol) were dissolved in 55 mL toluene. The reaction mixture was refluxed overnight. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=6:1 as eluent). The product was obtained as a white solid (1.11 g, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (m, 1H), 6.99 (dd, *J*=7.8, 1H), 6.97 – 6.90 (m, 2H), 5.65 (m, 2H), 3.93 (m, 2H), 3.80 (s, 3H), 2.62 (m, 1H), 2.33 – 1.80 (m, 12H), 1.7-1.4 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.34, 151.11, 139.90, 129.59, 129.49, 126.69, 122.75, 120.72, 112.37, 106.96, 80.74, 80.66, 55.82, 41.41, 35.10, 34.64, 31.82, 31.68, 26.29, 26.13,

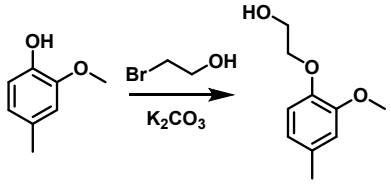
21.92, 21.90. HRMS m/z (ESI) calcd for $C_{22}O_5H_{28}Na$ $(M + Na)^+$ 395.1829, found 395.1832.

2.1.5 Synthesis of 2



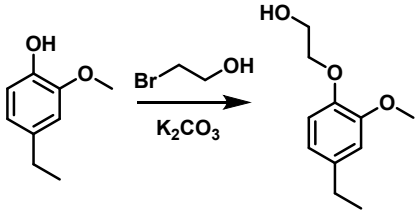
Guaiacol (9.78 g, 78.8 mmol), K_2CO_3 (12.0 g, 86.7 mmol), and 2-bromoethanol (8.87 g, 70.9 mmol) were dissolved in 95 mL acetone. The reaction mixture was refluxed overnight. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=1:3 as eluent). The product was obtained as a light yellow liquid (2.07 g, 15.6% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01 – 6.87 (m, 4H), 4.12 (m, 2H), 3.92 (m, 2H), 3.86 (s, 3H), 2.63 (br, 1H).

2.1.6 Synthesis of 3



2-Methoxy-4-methylphenol (10.9 g, 78.8 mmol), K_2CO_3 (12.0 g, 86.7 mmol), and 2-bromoethanol (8.87 g, 70.9 mmol) were dissolved in 95 mL acetone. The reaction mixture was refluxed overnight. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=1:3 as eluent). The product was obtained as a light yellow liquid (1.45 g, 10.1% yield). ^{1}H NMR (400 MHz, CDCl3) δ = 6.84 (d, *J*=7.9, 1H), 6.70 (d, *J*=10.8, 2H), 4.10 (m, 2H), 3.89 (d, *J*=3.8, 2H), 3.85 (s, 3H), 2.52 (br, 1H), 2.31 (s, 3H).

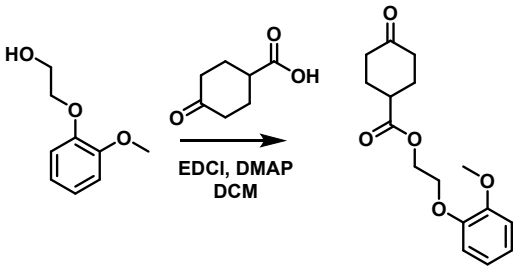
2.1.7 Synthesis of 4



4-Ethyl-2-methoxyphenol (12.0 g, 78.8 mmol), K_2CO_3 (12.0 g, 86.7 mmol), and 2-bromoethanol (8.87 g, 70.9 mmol) were dissolved in 95 mL acetone. The reaction mixture was refluxed overnight. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=1:3 as

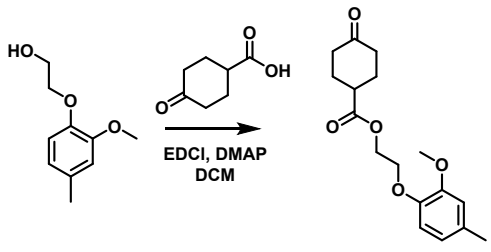
eluent). The product was obtained as a light yellow liquid (1.41 g, 10% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.87 (d, *J*=7.9, 1H), 6.73 (d, *J*=9.3, 2H), 4.51 (s, 3H), 3.89 (s, 2H), 3.86 (s, 3H), 2.60 (dd, *J*=15.1, 7.5, 2H), 2.41 (br, 1H), 1.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.63, 145.76, 138.35, 119.74, 115.23, 111.58, 71.69, 61.16, 55.68, 28.44, 15.71. HRMS m/z (ESI) calcd for $C_{11}O_3H_{16}Na$ $(M + Na)^+$ 219.0991, found 219.0998.

2.1.8 Synthesis of C2



2 (1.03 g, 6.12 mmol), DMAP (0.074 g, 0.612 mmol), and 4-oxocyclohexane-1-carboxylic acid (0.871 g, 6.12 mmol) were dissolved in 60 mL DCM. Then EDCl (1.17 g, 6.12 mmol) was added into the system in one batch. The reaction was stirred at room temperature overnight. The resultant mixture was washed with deionized water, saturated brine and dried over Na_2SO_4. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=2:1 as eluent). The product was obtained as a white solid (1.40 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.99 – 6.94 (m, 1H), 6.93 – 6.88 (m, 3H), 4.50 (m, 2H), 4.25 (m, 2H), 3.85 (s, 3H), 2.80 (m, 1H), 2.49 (m, 2H), 2.32 (m, 2H), 2.19 (m, 2H), 2.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 210.12, 174.03, 149.73, 147.71, 122.06, 120.74, 114.41, 111.98, 67.10, 63.07, 55.74, 40.37, 39.56, 28.35. HRMS m/z (ESI) calcd for $C_{16}O_5H_{20}Na$ $(M + Na)^+$ 315.1203, found 315.1210.

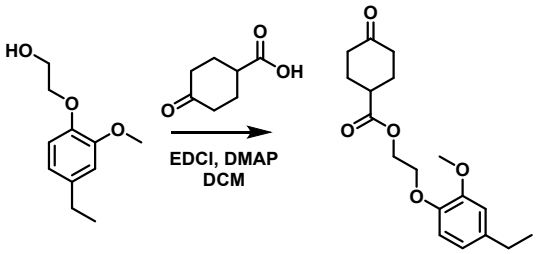
2.1.9 Synthesis of C3



3 (0.985 g, 5.40 mmol), DMAP (0.066 g, 0.540 mmol), and 4-oxocyclohexane-1-carboxylic acid (0.768 g, 5.40 mmol) were dissolved in 50 mL DCM. Then EDCl (1.03 g, 5.40 mmol) was added into the system in one batch. The reaction was stirred at room temperature overnight. The resultant mixture was washed with deionized water,

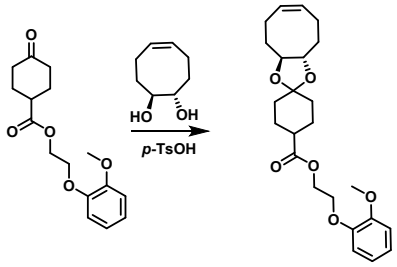
saturated brine and dried over Na_2SO_4. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=2:1 as eluent). The product was obtained as a colorless solid (0.869 g, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.79 (d, *J*=7.6, 1H), 6.70 (m, 2H), 4.47 (s, 2H), 4.22 (s, 2H), 3.82 (s, 3H), 2.80 (m, 1H), 2.45 (m, 2H), 2.33 (m, 2H), 2.29 (s, 3H), 2.18 (m, 2H), 2.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 210.02, 173.99, 149.60, 145.51, 131.90, 120.81, 114.91, 113.09, 67.52, 63.16, 55.69, 40.36, 39.52, 28.33, 20.95. HRMS m/z (ESI) calcd for $C_{17}O_5H_{22}Na$ $(M + Na)^+$ 329.1368, found 329.1369.

2.1.10 Synthesis of C4



4 (1.12 g, 5.71 mmol), DMAP (0.070 g, 0.571 mmol), and 4-oxocyclohexane-1-carboxylic acid (0.813 g, 5.71 mmol) were dissolved in 55 mL DCM. Then EDCl (1.10 g, 5.71 mmol) was added into the system in one batch. The reaction was stirred at room temperature overnight. The resultant mixture was washed with deionized water, saturated brine and dried over Na_2SO_4. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=2:1 as eluent). The product was obtained as light yellow solid (0.915 g, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.82 (d, *J*=8.0, 1H), 6.72 (m, 2H), 4.47 (m, 2H), 4.21 (m, 2H), 3.83 (s, 3H), 2.80 (m, 1H), 2.59 (m, 2H), 2.45 (m, 2H), 2.31 (m, 2H), 2.15 (m, 2H), 2.03 (m, 2H), 1.23 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 209.89, 173.75, 149.28, 145.32, 138.09, 119.19, 114.36, 111.56, 67.09, 62.88, 55.41, 40.08, 39.28, 28.13, 28.05, 15.43. HRMS m/z (ESI) calcd for $C_{18}O_5H_{24}Na$ $(M + Na)^+$ 343.1516, found 343.1522.

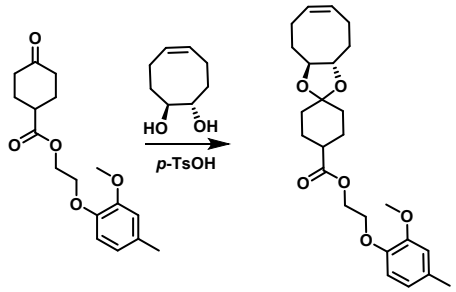
2.1.11 Synthesis of M2



C2 (0.411 g, 1.41 mmol), *p*-TsOH (0.048 g, 0.280 mmol), and *cis*-cyclooctene-

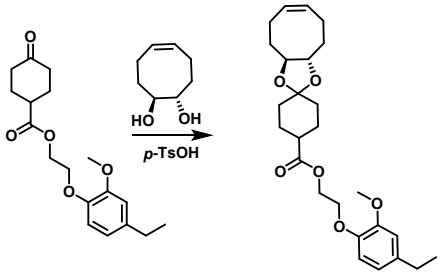
trans-5,6-doil (0.200 g, 1.41 mmol) were dissolved in 19 mL toluene. The reaction mixture was refluxed overnight. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=5:1 as eluent). The product was obtained as a white solid (0.532 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 – 6.84 (m, 4H), 5.63 (m, 2H), 4.42 (m, 2H), 4.22 (m, 2H), 3.91 (s, 2H), 3.86 (s, 3H), 2.35 (m, 1H), 2.22 (m, 2H), 2.19 – 2.07 (m, 4H), 1.91 (m, 2H), 1.86 – 1.71 (m, 4H), 1.65 – 1.40 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.86, 149.57, 147.63, 129.21, 129.11, 121.67, 120.51, 114.44, 111.88, 106.51, 80.32, 80.25, 67.04, 62.35, 60.00, 55.55, 41.17, 34.85, 34.34, 31.43, 31.29, 25.85, 25.68, 21.55, 21.51, 20.67, 13.83. HRMS m/z (ESI) calcd for $C_{24}O_6H_{32}Na$ $(M + Na)^+$ 439.2091, found 439.2093.

2.1.12 Synthesis of M3



C3 (0.829 g, 2.71 mmol), *p*-TsOH (0.096 g, 0.541 mmol), and *cis*-cyclooctene-*trans*-5,6-doil (0.401 g, 2.71 mmol) were dissolved in 37 mL toluene. The reaction mixture was refluxed overnight. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=5:1 as eluent). The product was obtained as a light yellow solid (1.097 g, 94% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.80 (d, *J*=8.0, 1H), 6.70 (m, 2H), 5.63 (m, 2H), 4.39 (s, 2H), 4.18 (s, 2H), 3.90 (m, 2H), 3.83 (s, 3H), 2.40 – 2.02 (m, 10 H), 1.89 (m, 2H), 1.85 – 1.71 (m, 4H), 1.58 – 1.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.22, 149.72, 145.71, 131.84, 129.56, 129.45, 120.91, 115.16, 113.24, 106.87, 80.67, 80.59, 67.76, 62.78, 55.85, 41.52, 35.20, 34.68, 31.77, 31.63, 26.19, 26.03, 21.89, 21.85, 21.02. HRMS m/z (ESI) calcd for $C_{25}O_6H_{34}Na$ $(M + Na)^+$ 453.2247, found 453.2254.

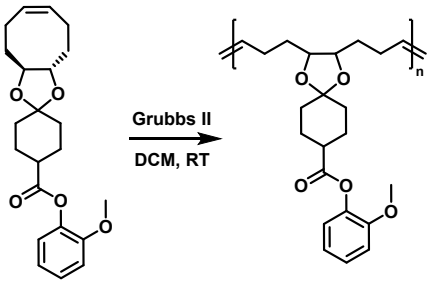
2.1.13 Synthesis of M4



C4 (0.911 g, 2.84 mmol), *p*-TsOH (0.098 g, 0.541 mmol), and *cis*-cyclooctene-*trans*-5,6-doil (0.489 g, 2.84 mmol) were dissolved in 37 mL toluene. The reaction mixture was refluxed overnight. The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (PE: EA=5:1 as eluent). The product was obtained as a light yellow liquid (1.23 g, 97% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.82 (d, *J*=8.0, 1H), 6.72 (m, 2H), 5.63 (m, 2H), 4.40 (s, 2H), 4.18 (s, 2H), 3.90 (s, 2H), 3.84 (s, 3H), 2.58 (m, 2H), 2.34 (m, 1H), 2.30 – 2.05 (m, 6H), 1.95 – 1.70 (m, 6H), 1.57 – 1.38 (m, 4H), 1.28 – 1.17 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.15, 149.63, 145.75, 138.20, 129.47, 129.36, 119.52, 114.85, 111.94, 106.77, 80.57, 80.50, 67.54, 62.70, 55.77, 41.42, 35.10, 34.58, 31.69, 31.55, 28.39, 26.11, 25.94, 21.80, 21.77, 15.70. HRMS m/z (ESI) calcd for $C_{26}O_6H_{36}Na(M + Na)^+$ 467.2404, found 467.2408.

2.2 Polymerization procedure

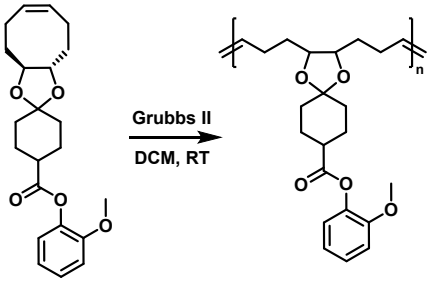
2.2.1 Synthesis of P1



M1 (494 mg, 1.32 mmol) was dissolved in anhydrous DCM (0.663 mL). The solution was purged with nitrogen for 10 min. Grubbs II (2.25 mg, 2.64 μmol) was added to initiate the polymerization. After the reaction mixture was stirred at room temperature for 45 min, several drops of EVE were added to stop polymerization. The polymer solution was precipitated into methanol three times. The polymer products were dried under high vacuum overnight. **P1** was obtained as white solid (352 mg, 71.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (m, 1H), 7.00 (d, *J*=6.8, 1H), 6.93 (br,

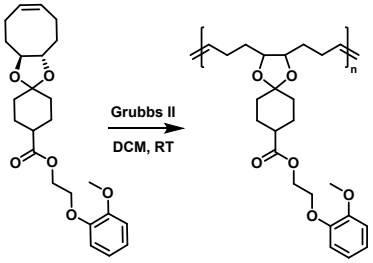
2H), 5.52 – 5.30 (m, 2H), 3.79 (s, 3H), 3.63 (s, 2H), 2.62 (br, 1H), 2.30 – 1.75 (m, 10H), 1.70 – 1.48 (m, 6H).

2.2.2 Synthesis of P1'



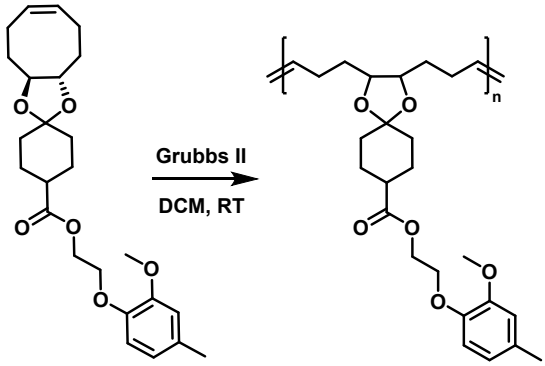
M1 (494 mg, 1.32 mmol) was dissolved in anhydrous THF (0.663 mL). The solution was purged with nitrogen for 10 min. Grubbs III (0.777 mg, 0.880 μmol) was added to initiate the polymerization. After the reaction mixture was stirred at room temperature for 60 min, several drops of EVE were added to stop polymerization. The polymer solution was precipitated into methanol three times. The polymer products were dried under high vacuum overnight. **P1'** was obtained as white solid (383 mg, 77.5%). ^{1}H NMR of **P1'** is the same as **P1**.

2.2.3 Synthesis of P2



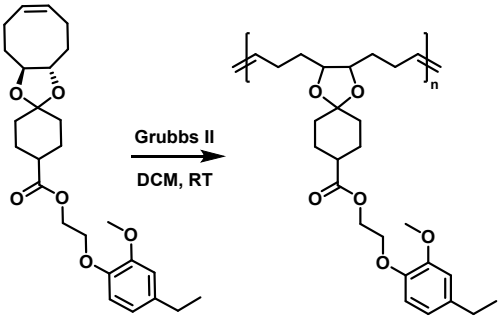
M2 (412 mg, 0.99 mmol) was dissolved in anhydrous DCM (0.5 mL). The solution was purged with nitrogen for 10 min. Grubbs II (1.68 mg, 1.98 μmol) was added to initiate the polymerization. After the reaction mixture was stirred at room temperature for 120 min, several drops of EVE were added to stop polymerization. The polymer solution was precipitated into methanol three times. The polymer products were dried under high vacuum overnight. **P2** was obtained as a white solid (291 mg, 70.6%). 1H NMR (400 MHz, $CDCl_3$) δ = 6.98 – 6.84 (m, 4H), 5.50 – 5.40 (s, 2H), 4.42 (m, 2H), 4.22 (m, 2H), 3.85 (s, 3H), 3.59 (s, 2H), 2.35 (m, 1H), 2.30 – 2.13 (m, 2H), 2.12 – 1.98 (m, 2H), 1.98 – 1.87 (m, 2H), 1.86 – 1.67 (m, 4H), 1.58 – 1.46 (m, 6H).

2.2.4 Synthesis of P3



M3 (490 mg, 1.13 mmol) was dissolved in anhydrous DCM (0.569 mL). The solution was purged with nitrogen for 10 min. Grubbs II (1.93 mg, 2.27 μmol) was added to initiate the polymerization. After the reaction mixture was stirred at room temperature for 15 min, several drops of EVE were added to stop polymerization. The polymer solution was precipitated into methanol three times. The polymer products were dried under high vacuum overnight. **P3** was obtained as a white solid (353 mg, 72.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.80 (d, *J*=8.0, 1H), 6.70 (m, 2H), 5.50 – 5.33 (m, 2H), 4.40 (s, 2H), 4.18 (s, 2H), 3.83 (s, 3H), 3.59 (s, 2H), 2.35 (m, 1H), 2.29 (s, 3H), 2.25 –1.98 (m, 4H), 1.97 –1.67 (m, 6H), 1.60 – 1.45 (m, 6H).

2.2.5 Synthesis of P4

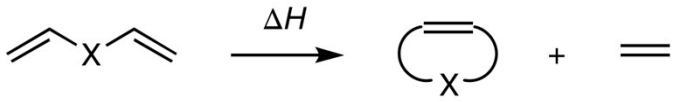


M4 (499 mg, 1.12 mmol) was dissolved in anhydrous DCM (0.561 mL). The solution was purged with nitrogen for 10 min. Grubbs II (1.90 mg, 2.24 μmol) was added to initiate the polymerization. After the reaction mixture was stirred at room temperature for 80 min, several drops of EVE were added to stop polymerization. The polymer solution was precipitated into methanol three times. The polymer products were dried under high vacuum overnight. **P4** was obtained as a colorless solid (365 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.83 (d, *J*=7.9, 1H), 6.72 (m, 2H), 5.50 – 5.32 (m, 2H), 4.41 (s, 2H), 4.19 (s, 2H), 3.84 (s, 3H), 3.59 (s, 2H), 2.58 (q, 2H), 2.35 (m, 1H), 2.30 – 1.98 (m, 4H), 1.98 – 1.66 (m, 6H), 1.53 (br, 6H), 1.21 (t, *J*=7.4, 3H).

3. DFT calculation of the ring strain energy

The computation of ring strain energy of different monomers was conducted by calculating the enthalpy change of the ring-closing metathesis reaction shown below using density functional theory (DFT) at the B3LYP/6-31G(d,p) with G09 software.[2] After geometry optimization and frequency calculation, this equation was used directly to calculate the ΔH for the ring strain using the equation below:

$$\text{Ring strain energy} = \Delta H = (H_{\text{ring}} + H_{\text{ethylene}}) - H_{\text{diene}}$$



in which the H_{diene} represents the enthalpy for the ring-opened alkenes; H_{ring} represents the enthalpy for the cyclic monomer; and H_{ethylene} represents the enthalpy for ethylene.

4. Depolymerization studies

4.1 Depolymerization procedure for P1-P4

General procedure: the polymers were dissolved in deuterated chloroform ($CDCl_3$) at a concentration of 20 mM ([olefin]=20 mM) and heated at 50 °C in the presence of 1 mol% Grubbs II catalyst for 2 h.

4.2 Depolymerization results

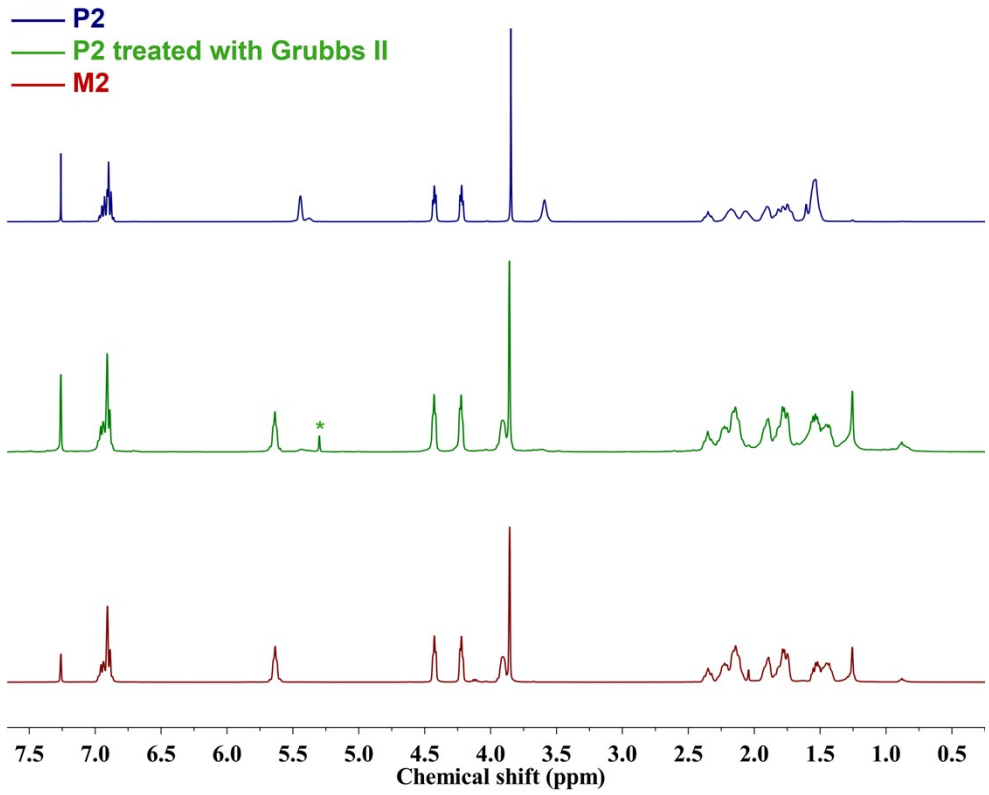


Figure S1. Depolymerization studies of **P2** using ^{1}H NMR spectroscopy.

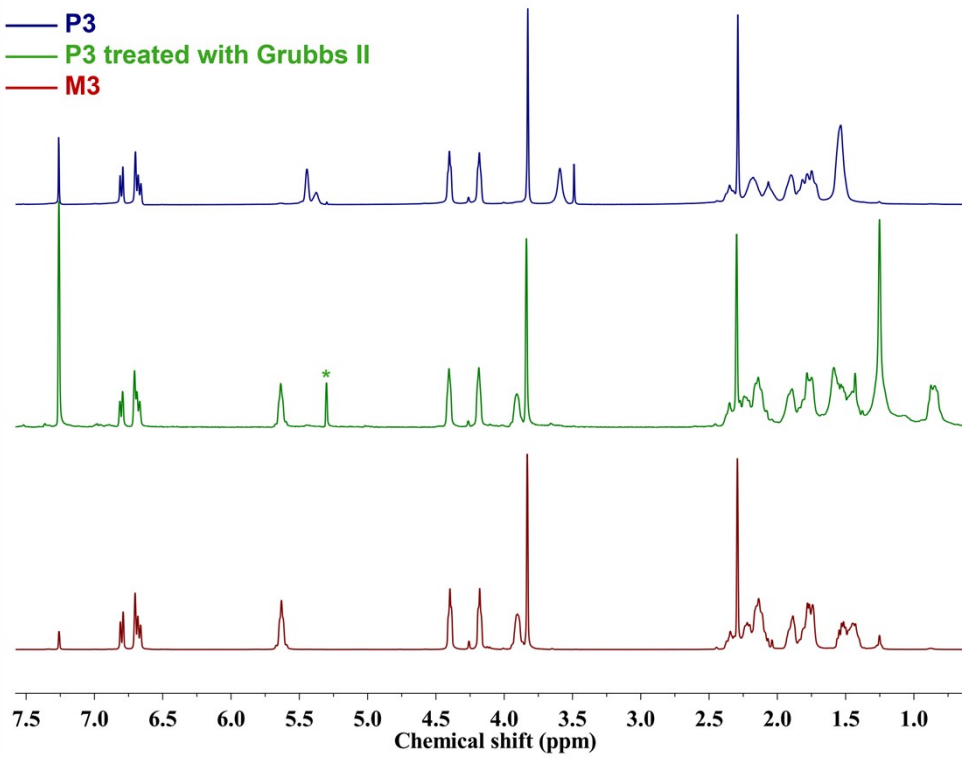


Figure S2. Depolymerization studies of **P3** using ^{1}H NMR spectroscopy.

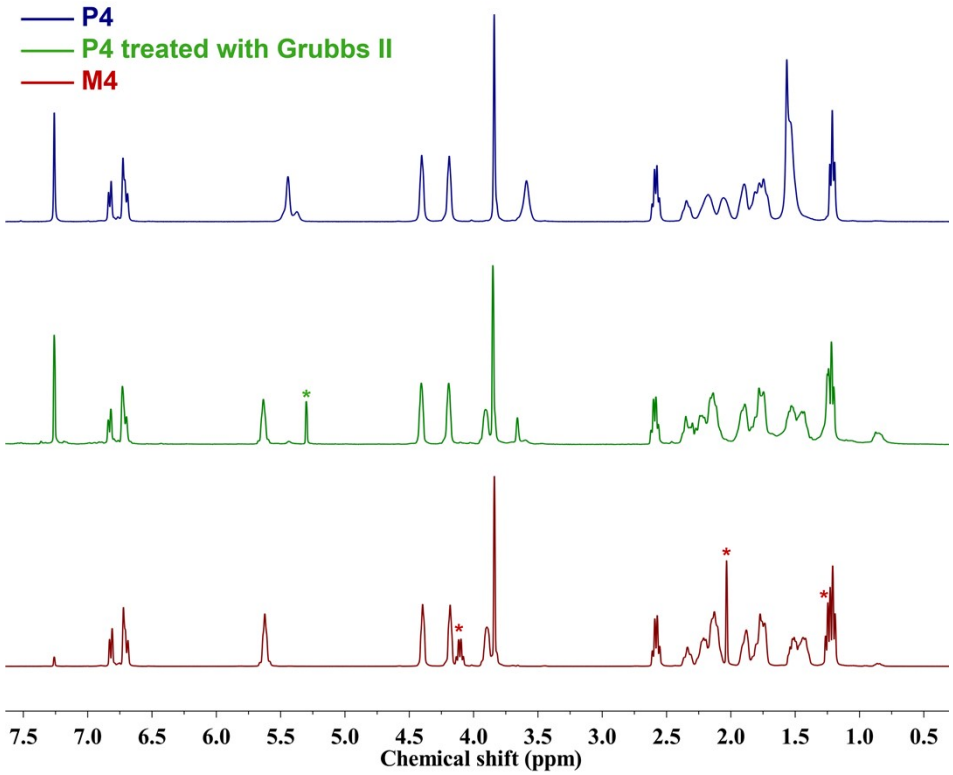


Figure S3. Depolymerization studies of **P4** using ^{1}H NMR spectroscopy.

4.3 Depolymerization kinetic study

P1 was dissolved in deuterated chloroform ($CDCl_3$) at a concentration of 20 mM ([olefin]=20 mM) and heated at 50 °C in the presence of 1 mol% Grubbs II catalyst. Aliquot was taken out at a few time intervals and quenced by EVE. These samples were directly used for HNMR test to determine the depolymerization conversion. Then the solvent was removed for GPC measurement.

4.4 Recovered monomer for repolymerization towards multiple recycling

After the depolymerization process finished, EVE was added into the reaction mixture to quench the catalyst. The mixture was stirred with Quadrapure TU overnight, filtered through a silica plug and concentrated on a rotavap, which was collected with the identical purity as the pristine monomer, and can be used for repolymerization. The polymerization process is the same as illustrated in Part 2.2.

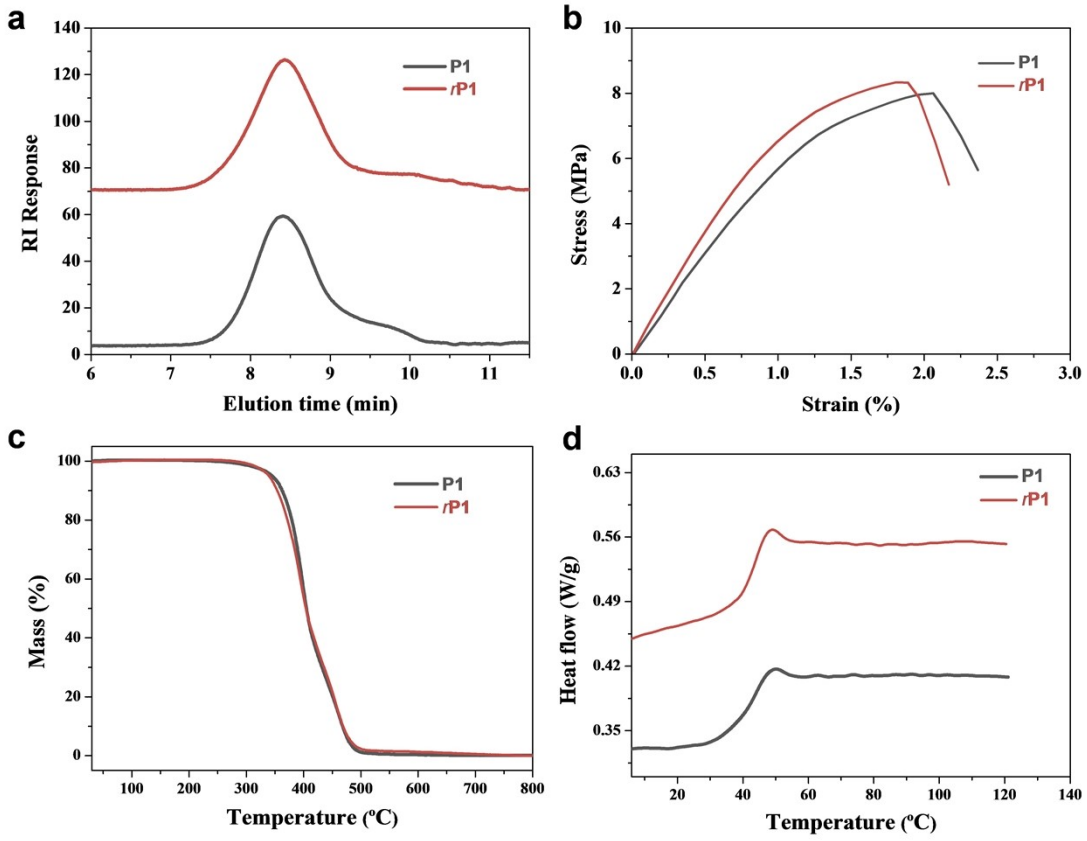


Figure S4. (a) GPC results of *r***P1** prepared from the recovered **M1**; (b) tensile testing results of *r***P1** prepared from the recovered **M1**; (c) TGA results of *r*P1 prepared from the recovered **M1**; (d) DSC results of *r***P1** prepared from the recovered **M1**.

5. NMR spectra

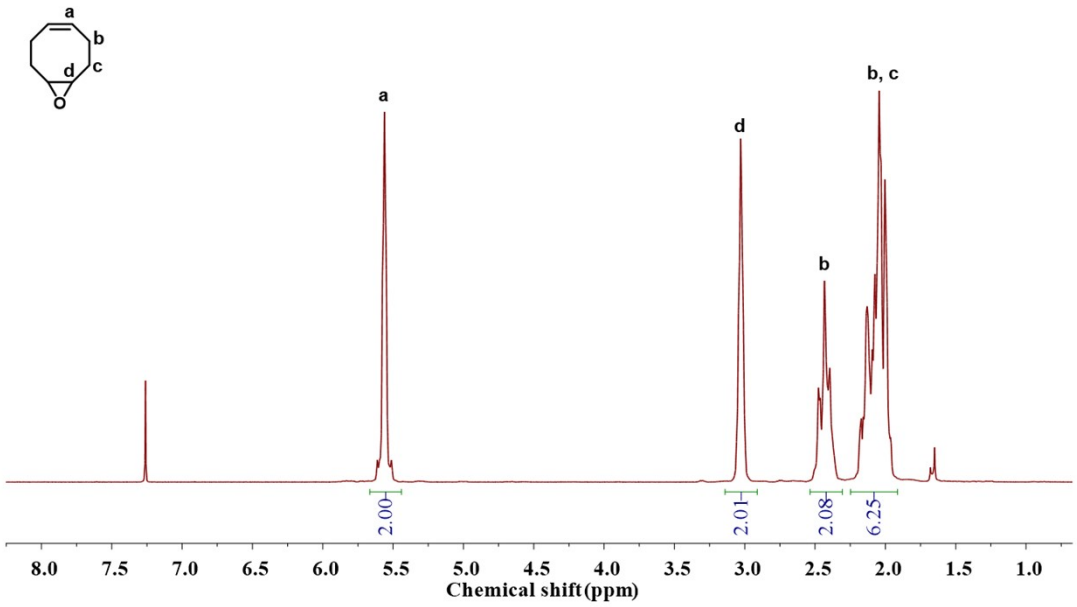


Figure S5. ^{1}H NMR spectrum of 9-oxabicyclo[6.1.0]non-4-ene in $CDCl_3$.

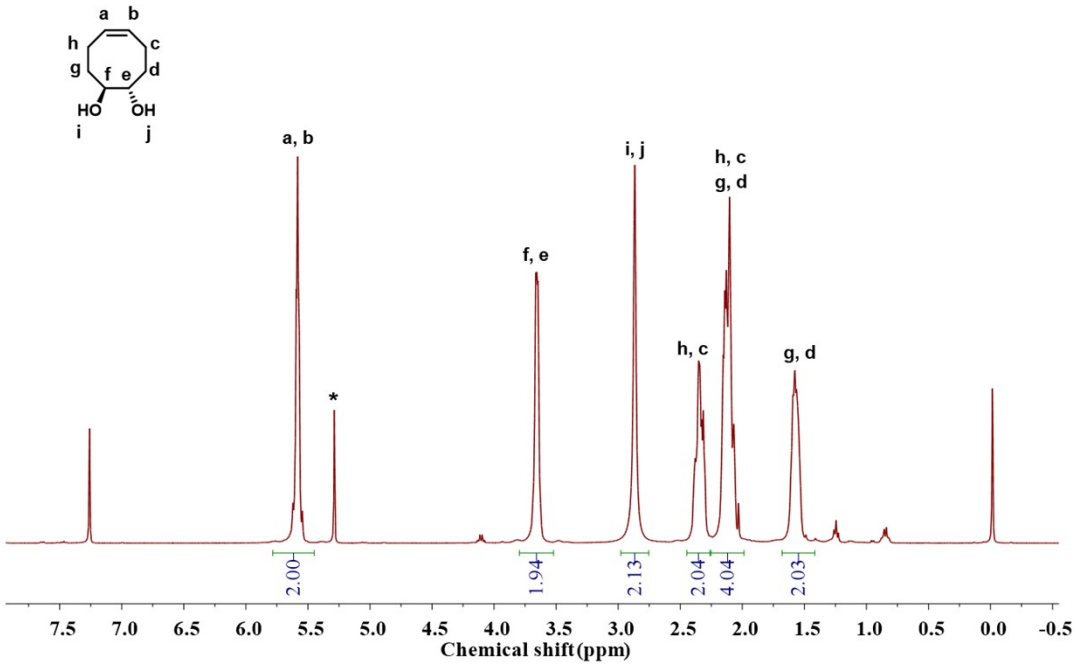


Figure S6. ^{1}H NMR spectrum of *cis*-cyclooctene-*trans*-5,6-doil in $CDCl_3$.

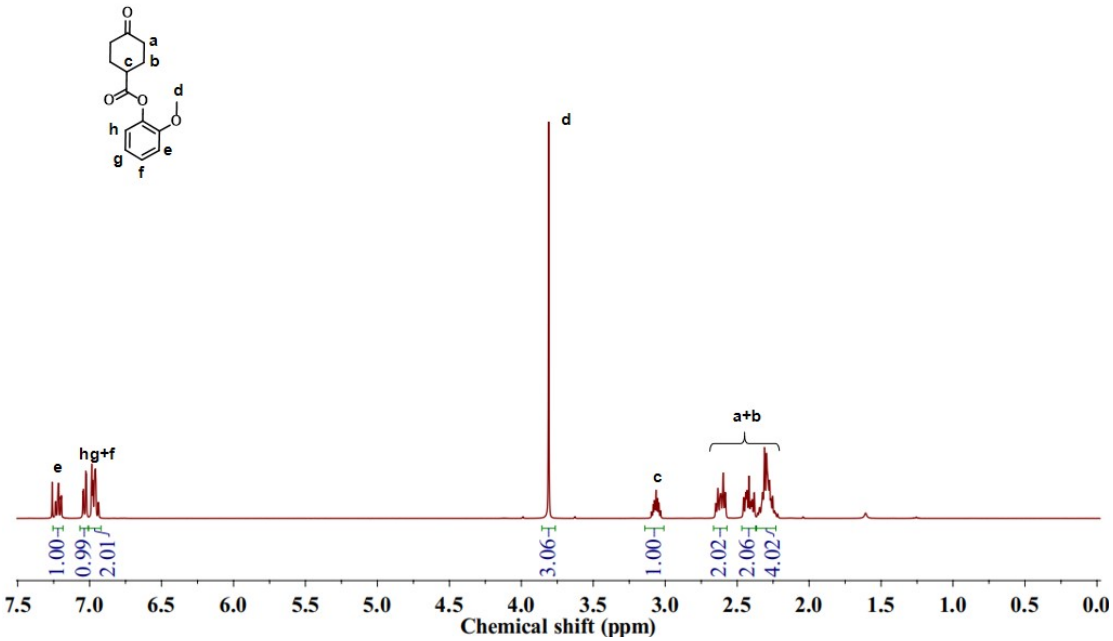


Figure S7. ^{1}H NMR spectrum of **1** in $CDCl_3$.

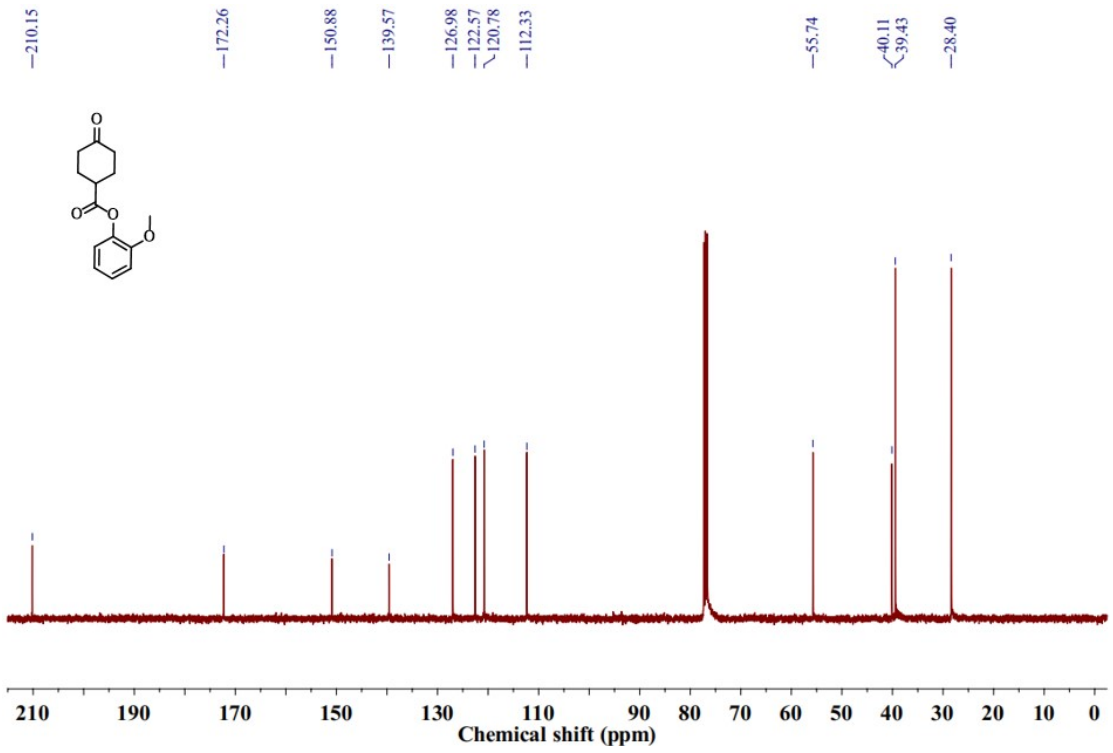


Figure S8. ^{13}C NMR spectrum of **1** in $CDCl_3$.

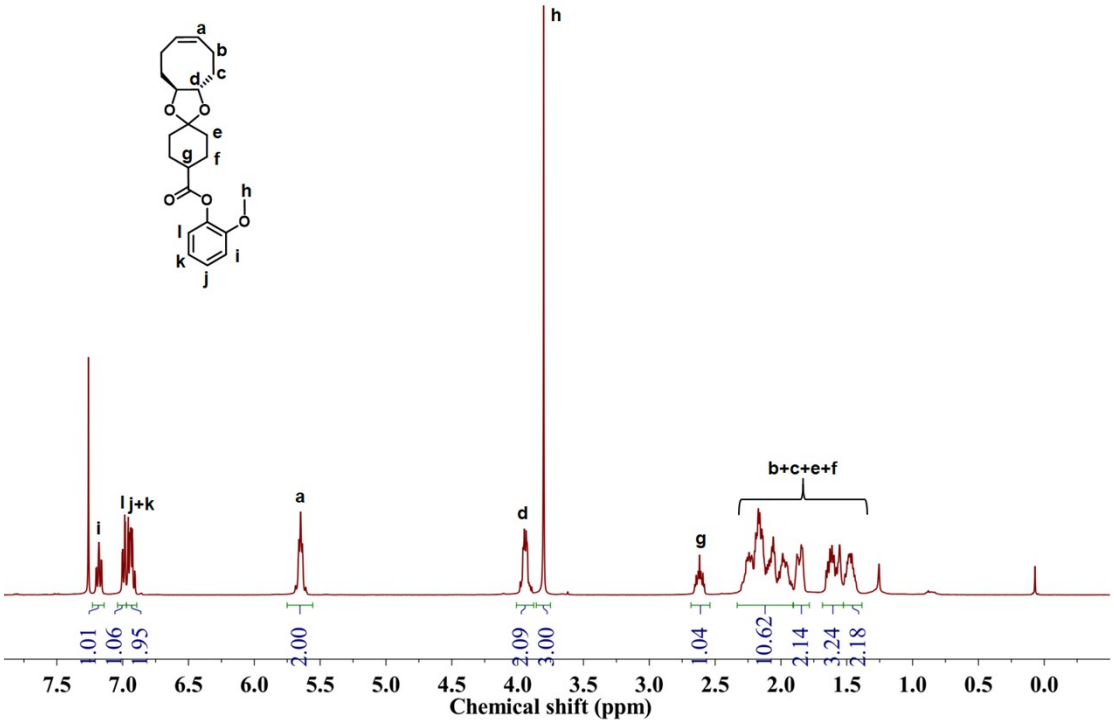


Figure S9. ^{1}H NMR spectrum of **M1** in $CDCl_3$.

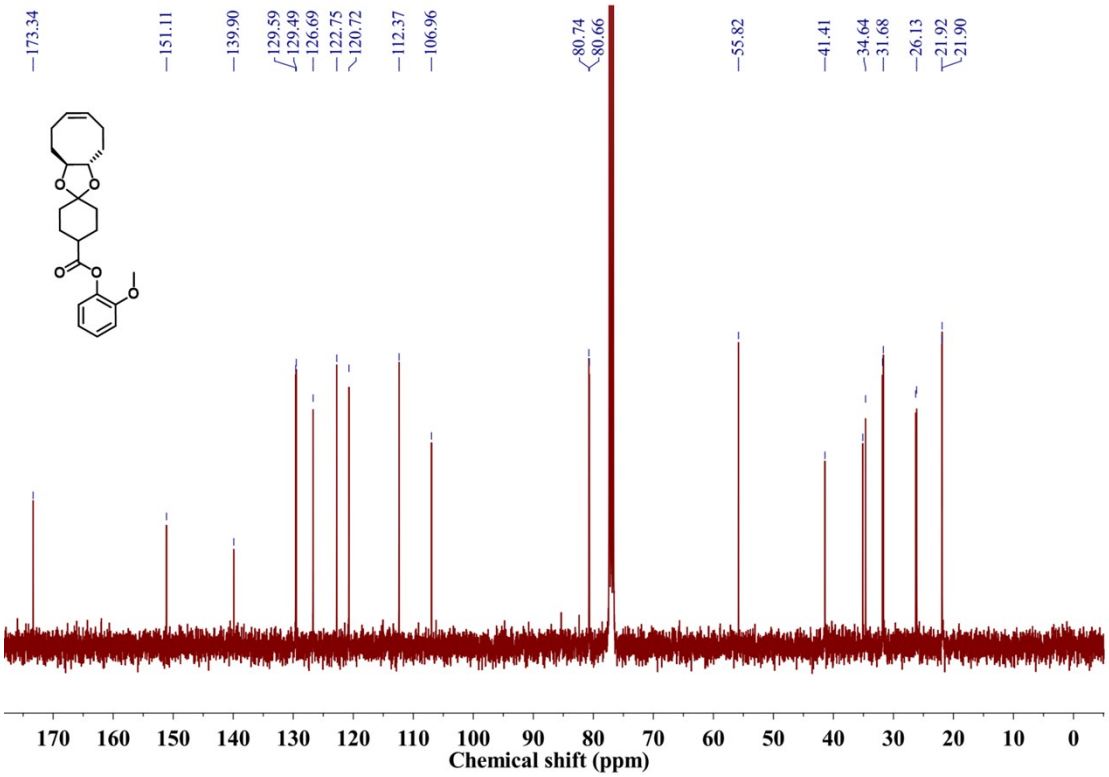


Figure S10. ^{13}C NMR spectrum of **M1** in $CDCl_3$.

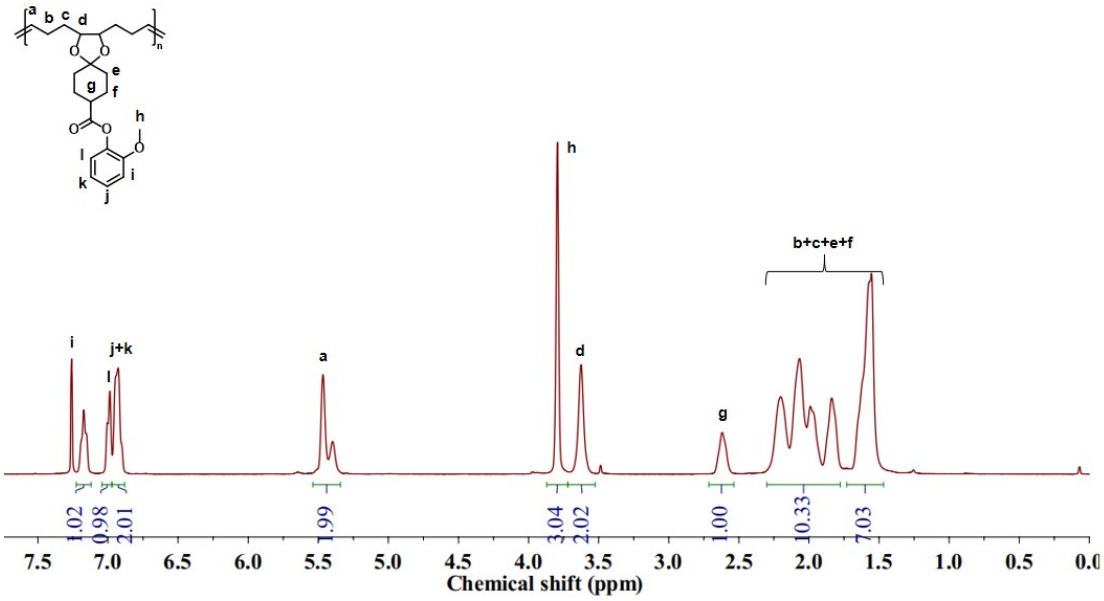


Figure S11. ^{1}H NMR spectrum of **P1** in $CDCl_3$.

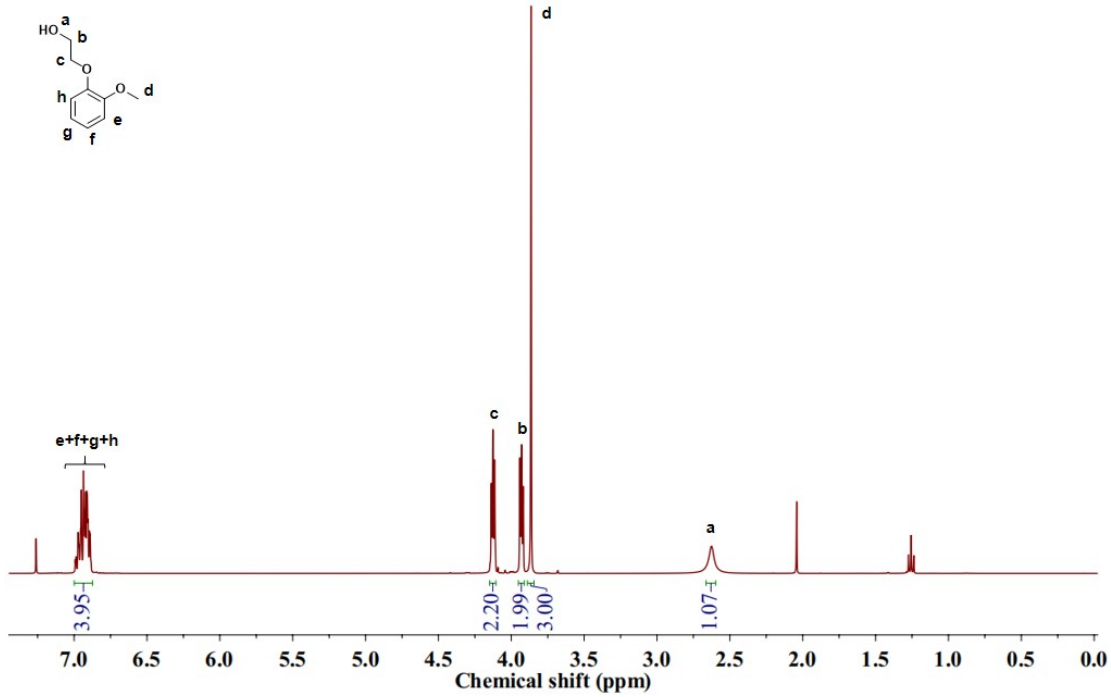


Figure S12. ^{1}H NMR spectrum of **2** in $CDCl_3$.

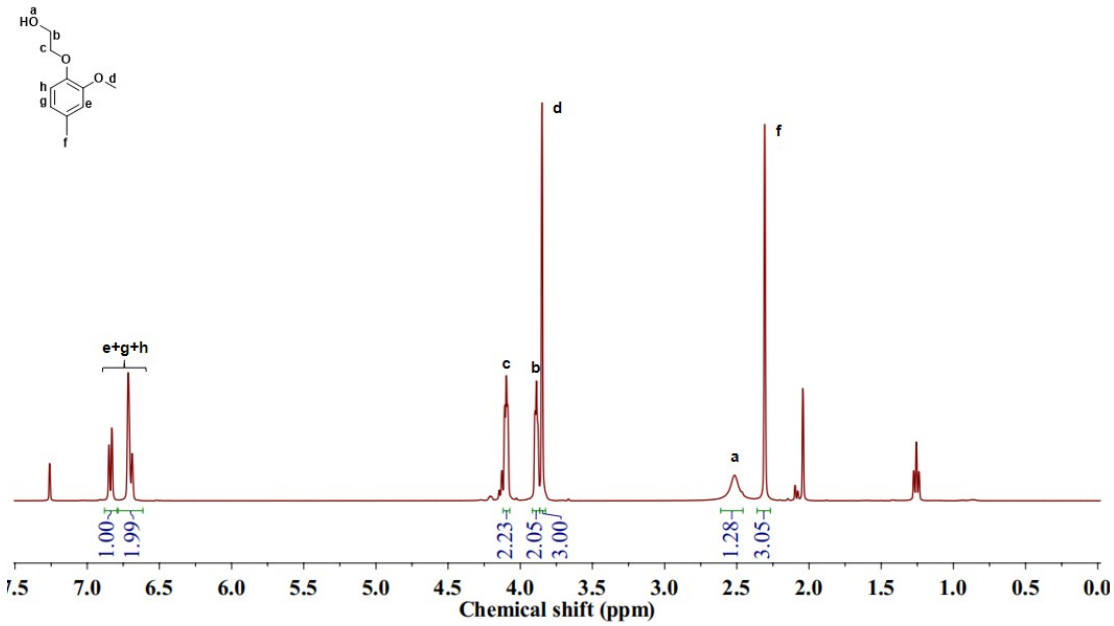


Figure S13. ^{1}H NMR spectrum of **3** in $CDCl_3$.

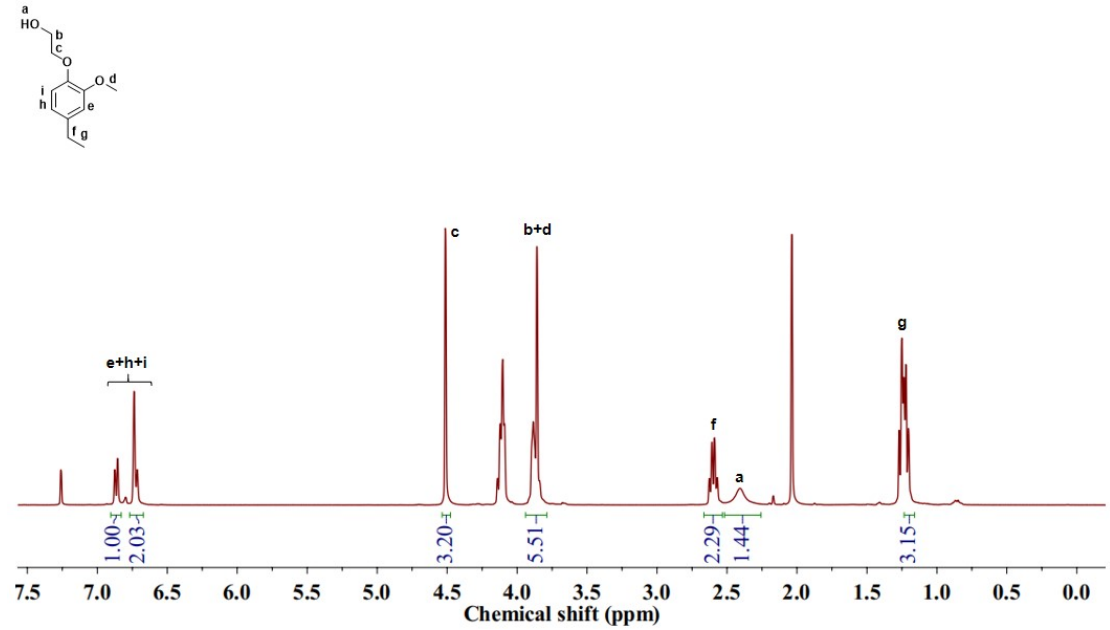


Figure S14. ^{1}H NMR spectrum of **4** in $CDCl_3$.

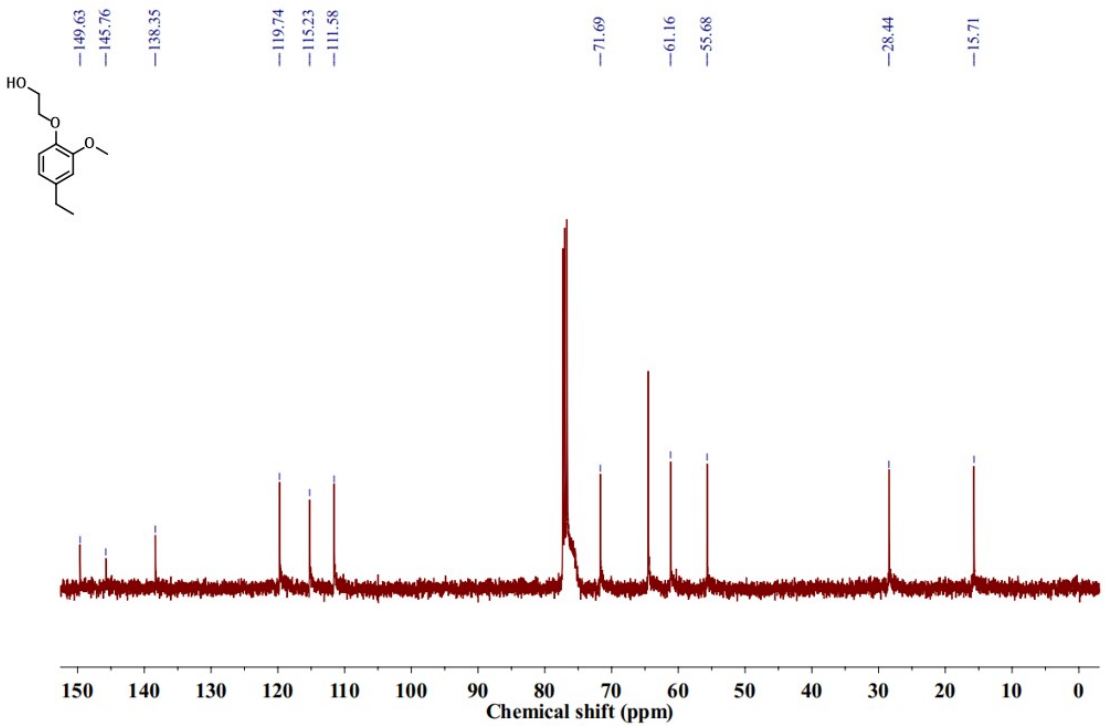


Figure S15. ^{13}C NMR spectrum of **4** in $CDCl_3$.

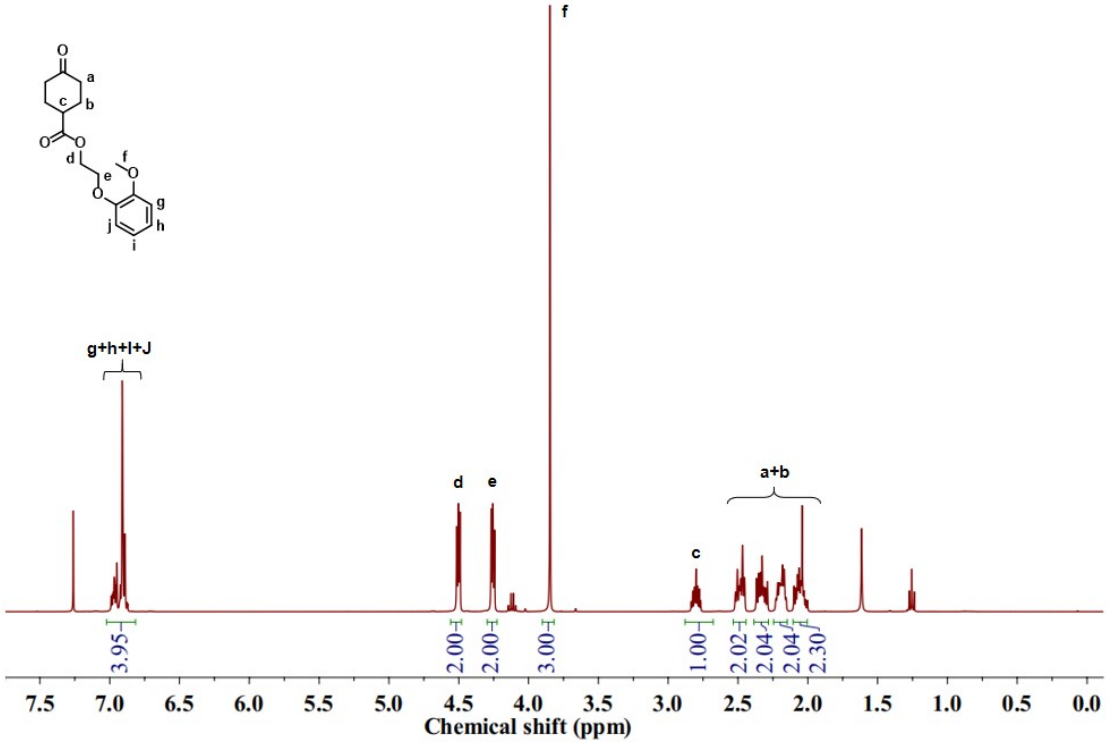


Figure S16. ^{1}H NMR spectrum of **C2** in $CDCl_3$.

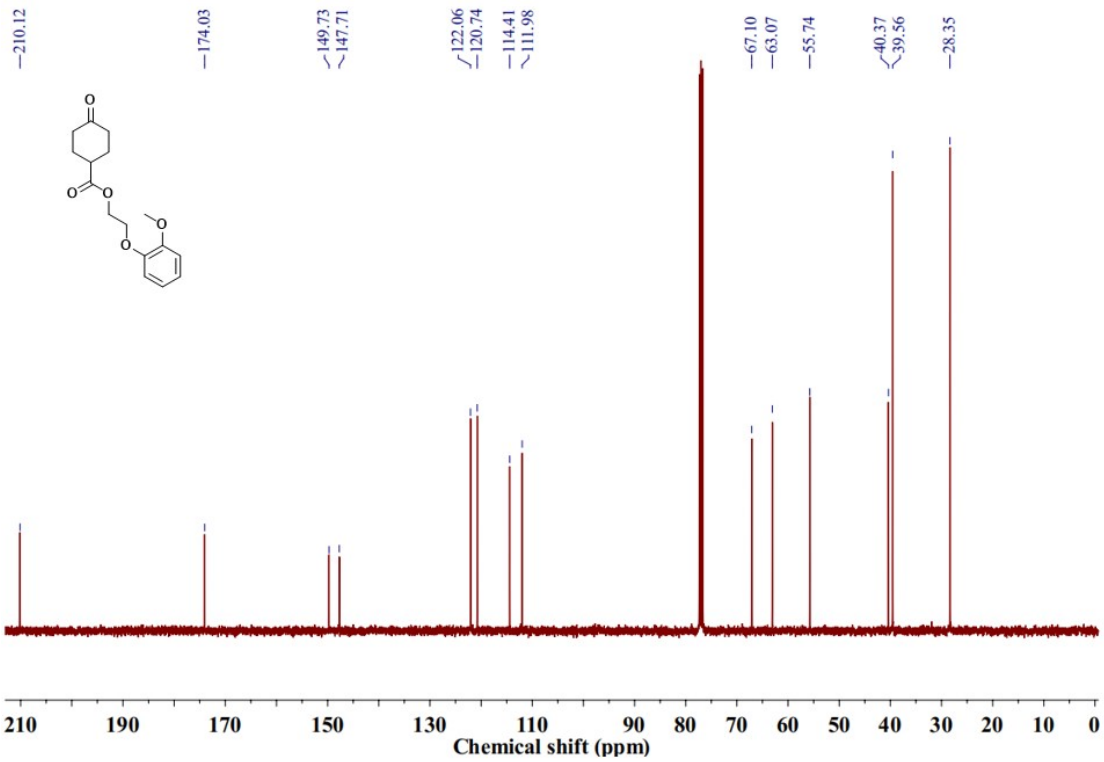


Figure S17. ^{13}C NMR spectrum of **C2** in $CDCl_3$.

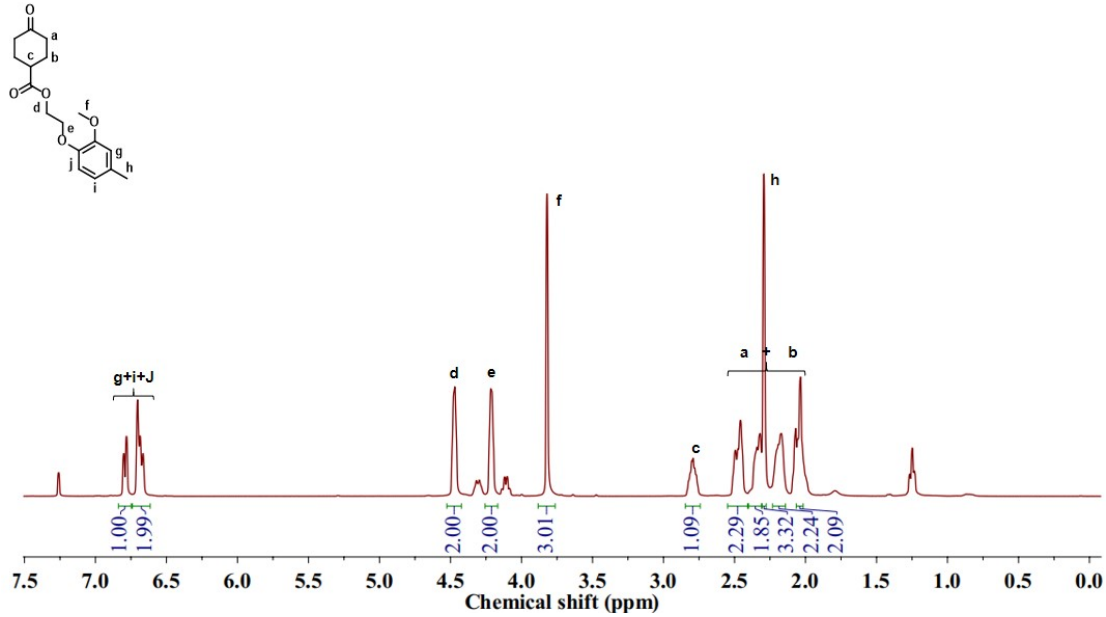


Figure S18. ^{1}H NMR spectrum of **C3** in $CDCl_3$.

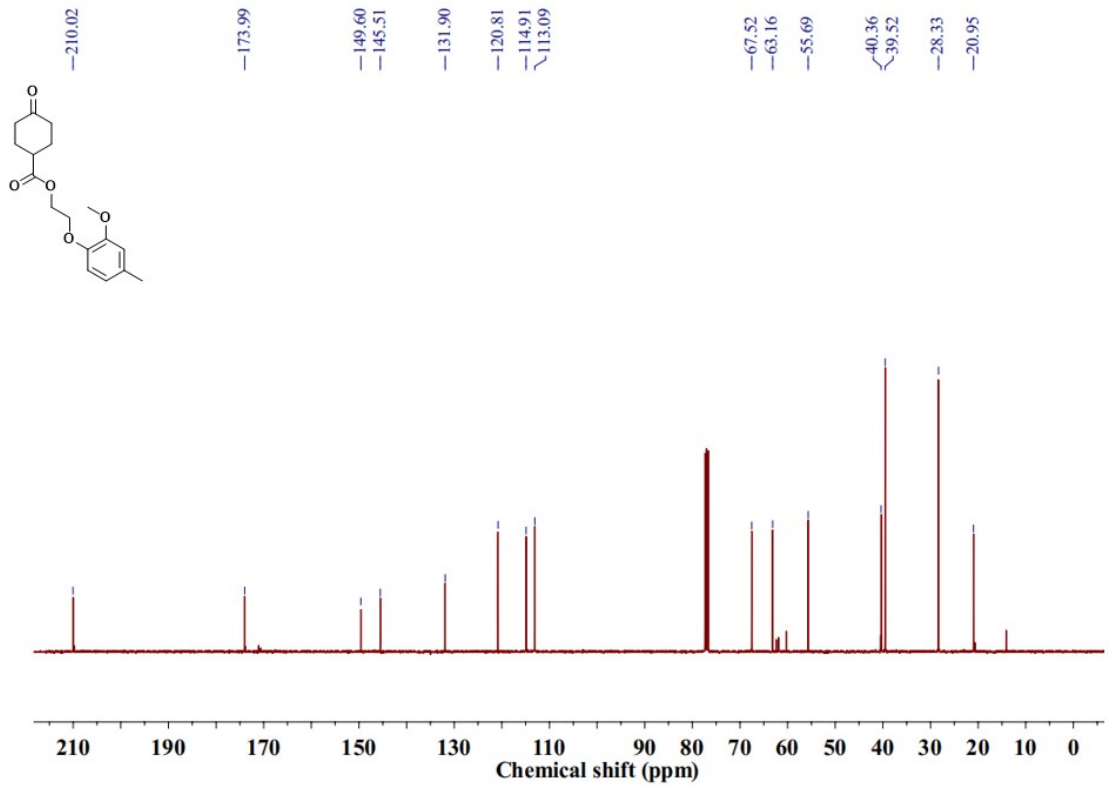


Figure S19. ^{13}C NMR spectrum of **C3** in $CDCl_3$.

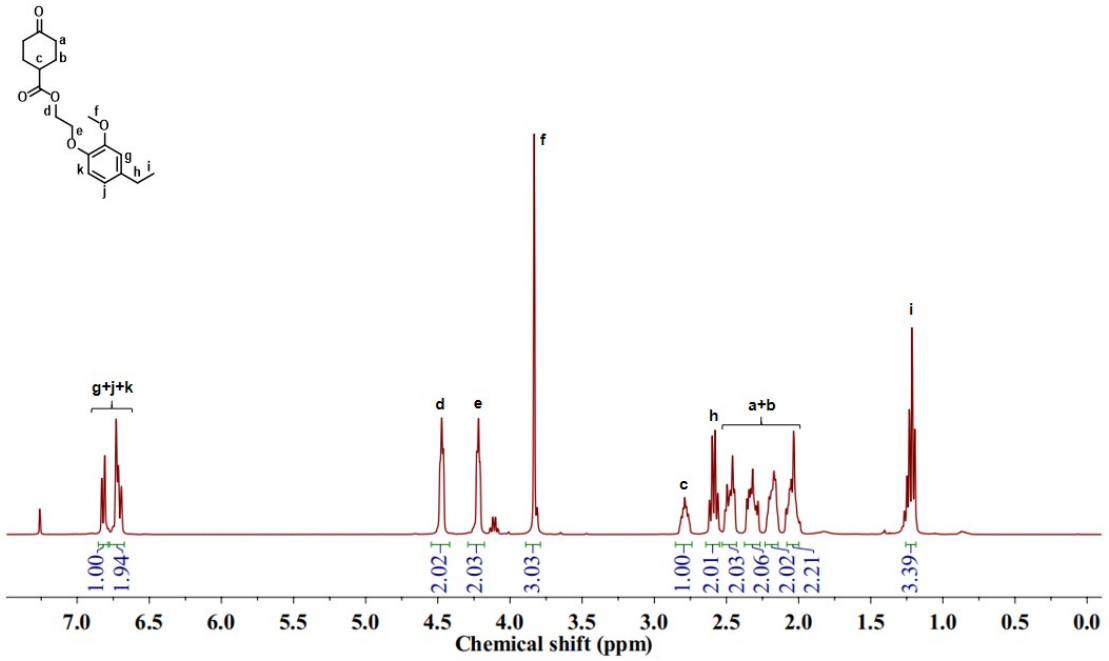


Figure S20. ^{1}H NMR spectrum of **C4** in $CDCl_3$.

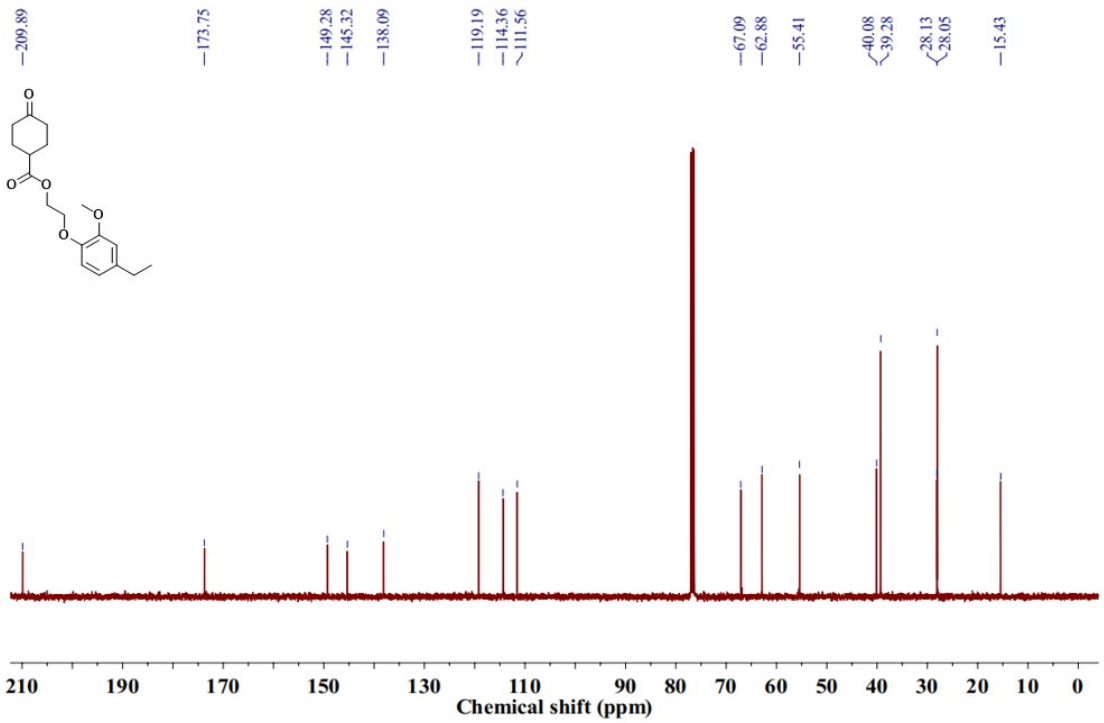


Figure S21. ^{13}C NMR spectrum of **C4** in $CDCl_3$.

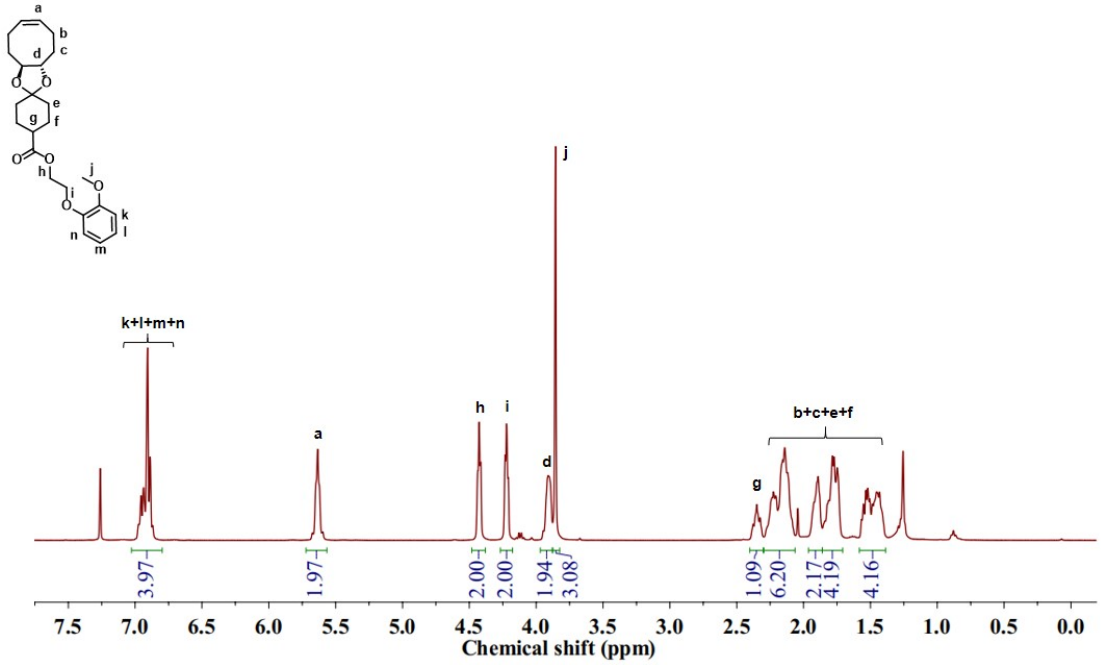


Figure S22. ^{1}H NMR spectrum of **M2** in $CDCl_3$.

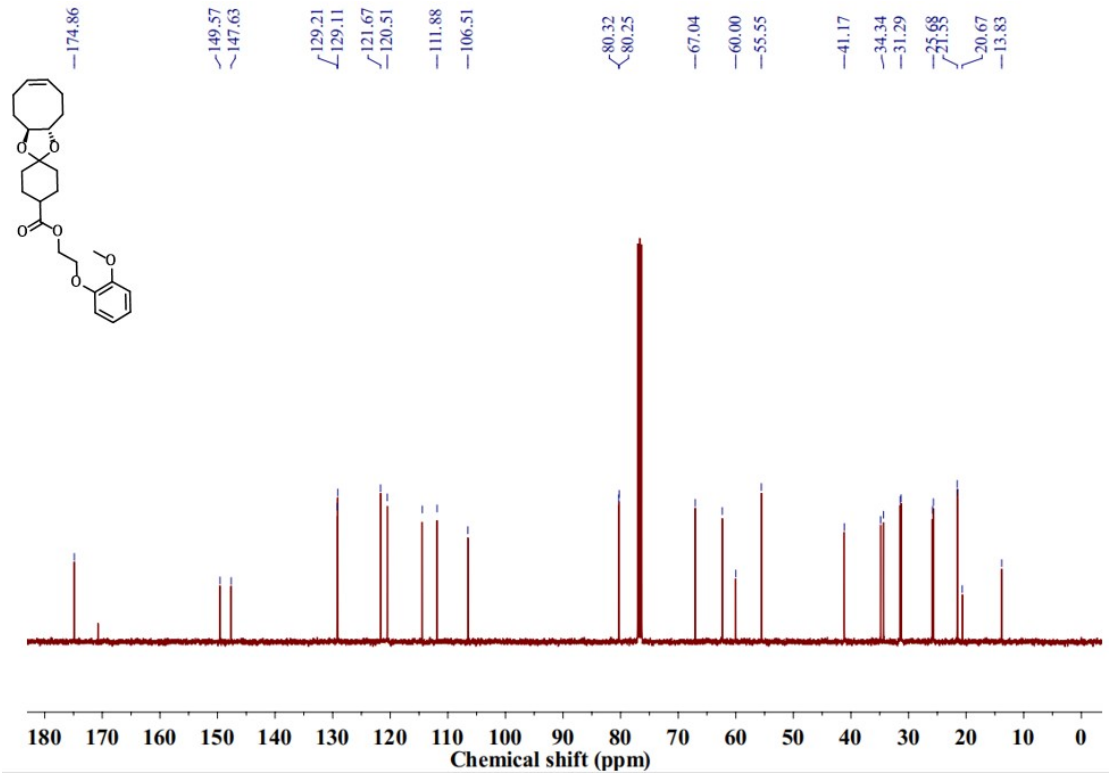


Figure S23. ^{13}C NMR spectrum of **M2** in $CDCl_3$.

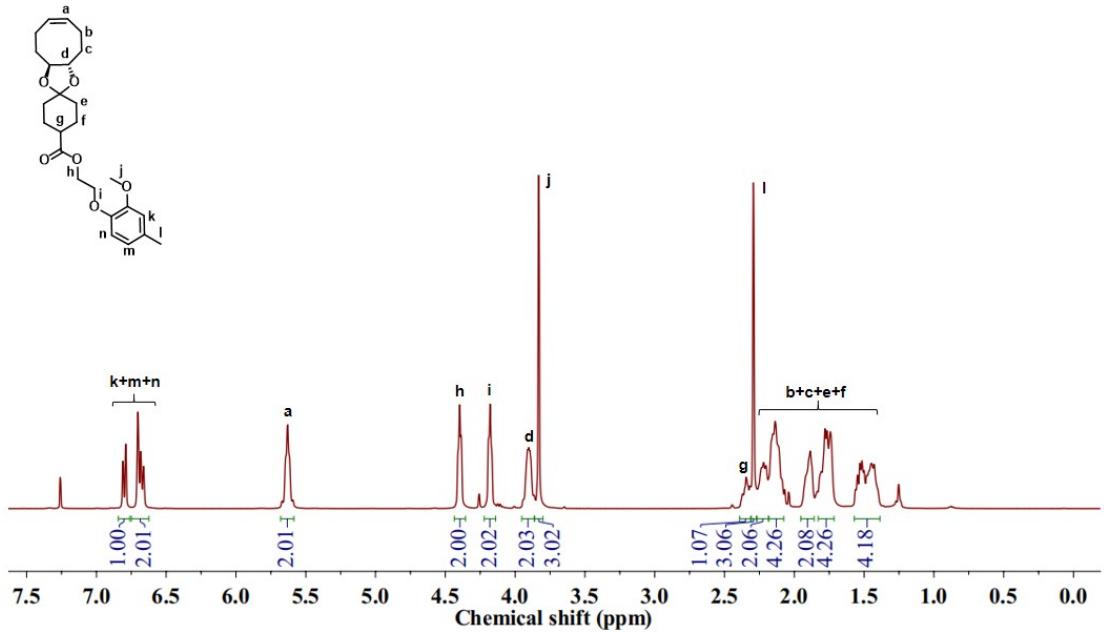


Figure S24. ^{1}H NMR spectrum of **M3** in $CDCl_3$.

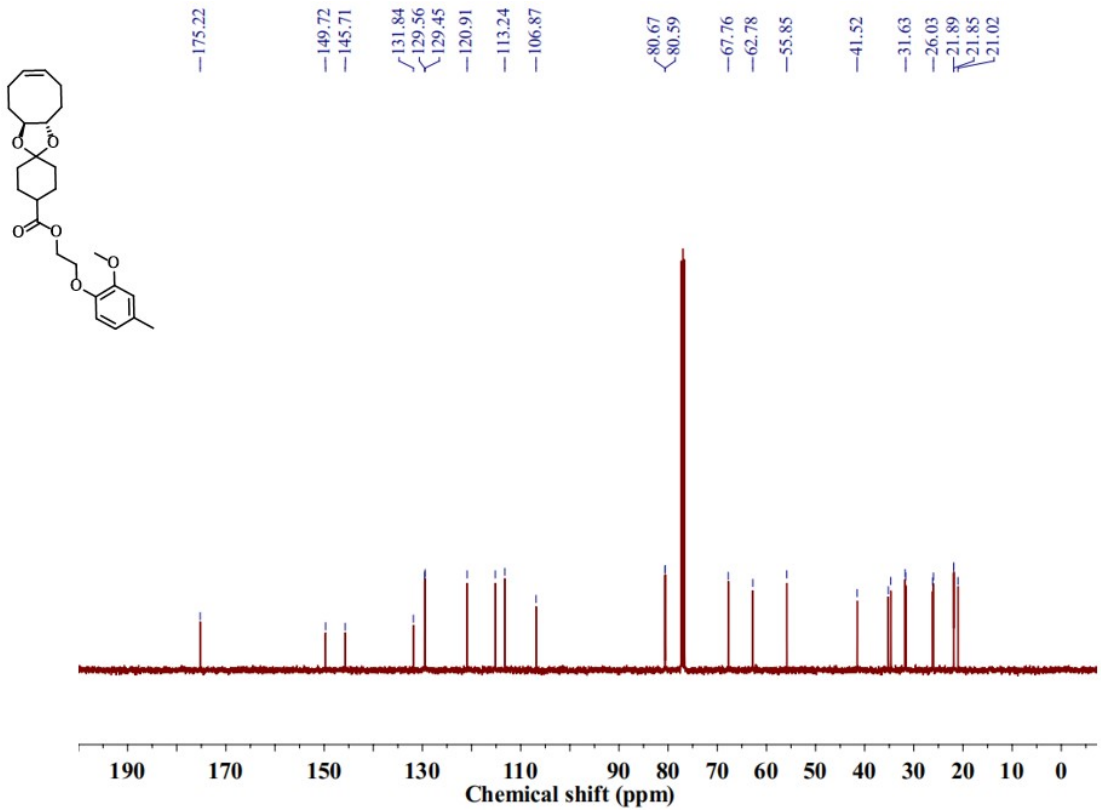


Figure S25. ^{13}C NMR spectrum of **M3** in $CDCl_3$.

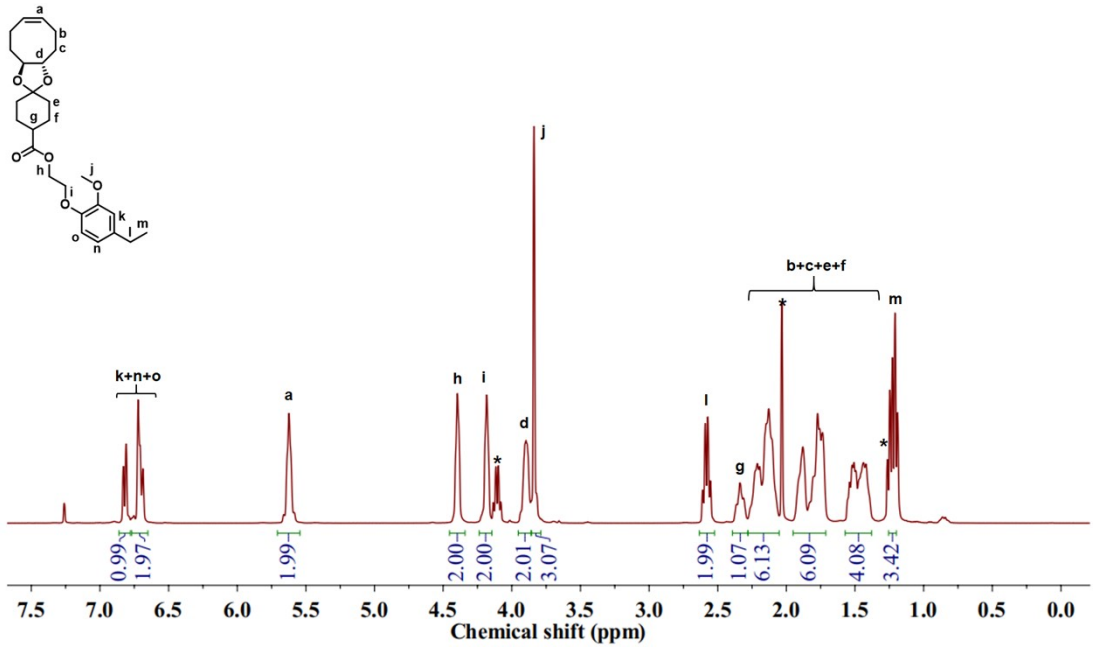


Figure S26. ^{1}H NMR spectrum of **M4** in $CDCl_3$.

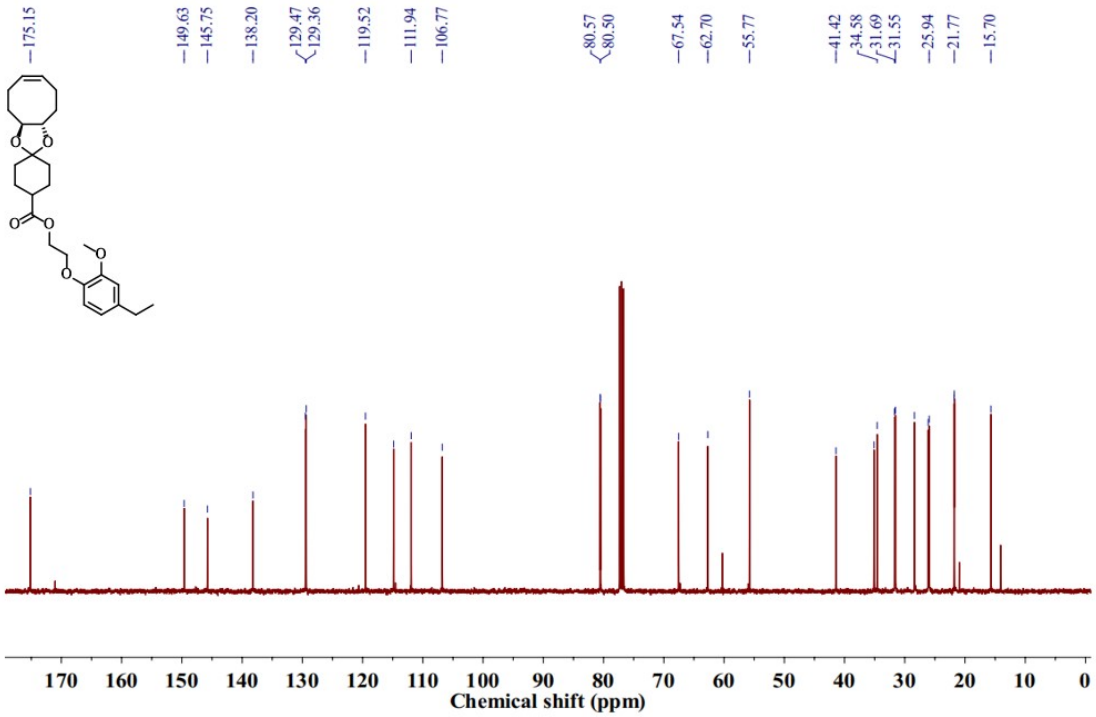


Figure S27. ^{13}C NMR spectrum of **M4** in $CDCl_3$.

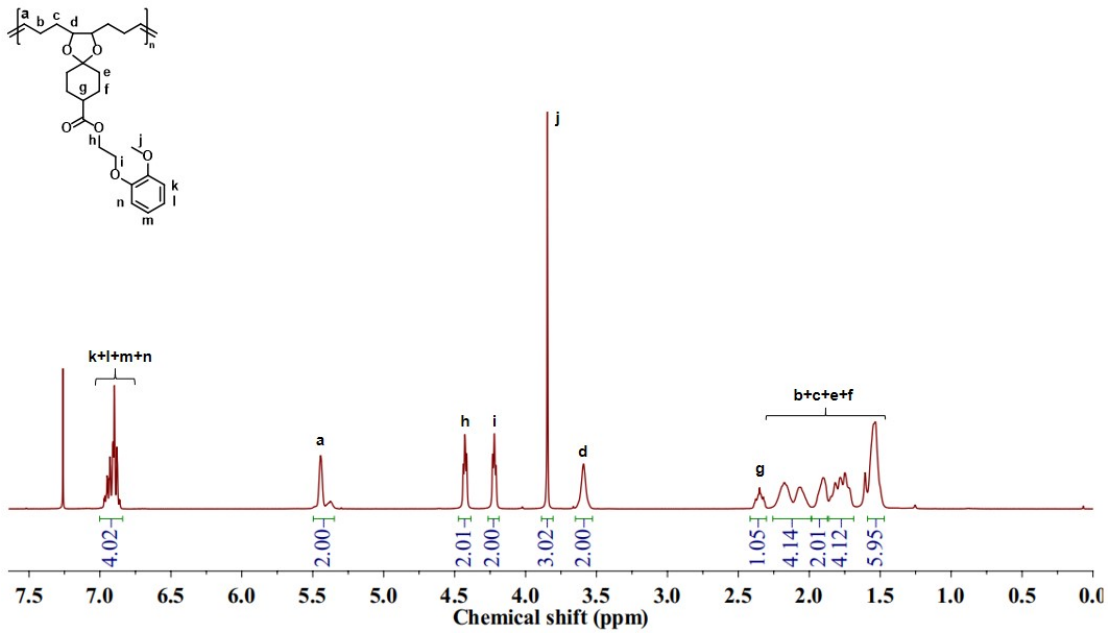


Figure S28. ^{1}H NMR spectrum of **P2** in $CDCl_3$.

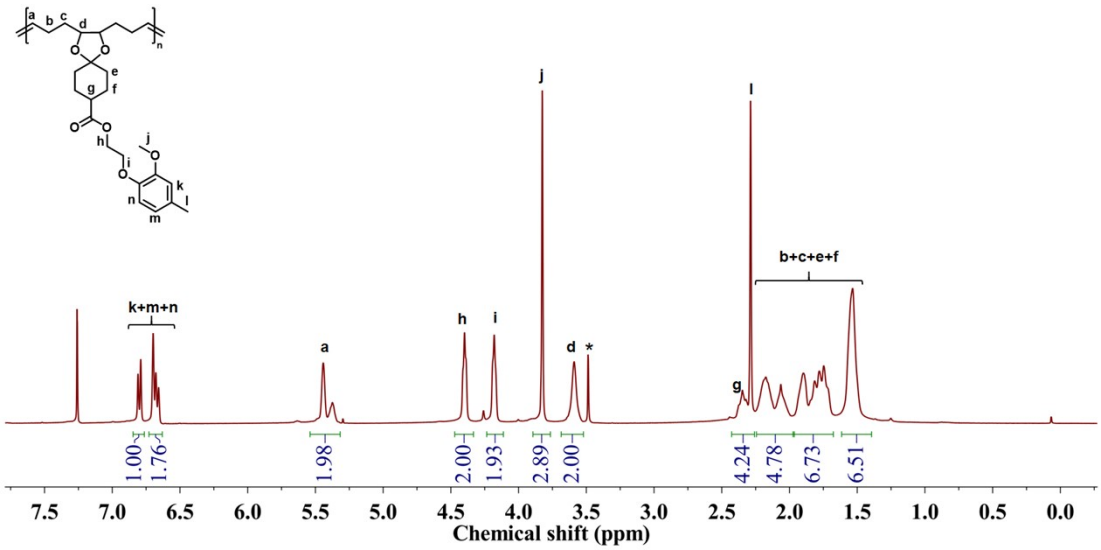


Figure S29. ^{1}H NMR spectrum of **P3** in $CDCl_3$.

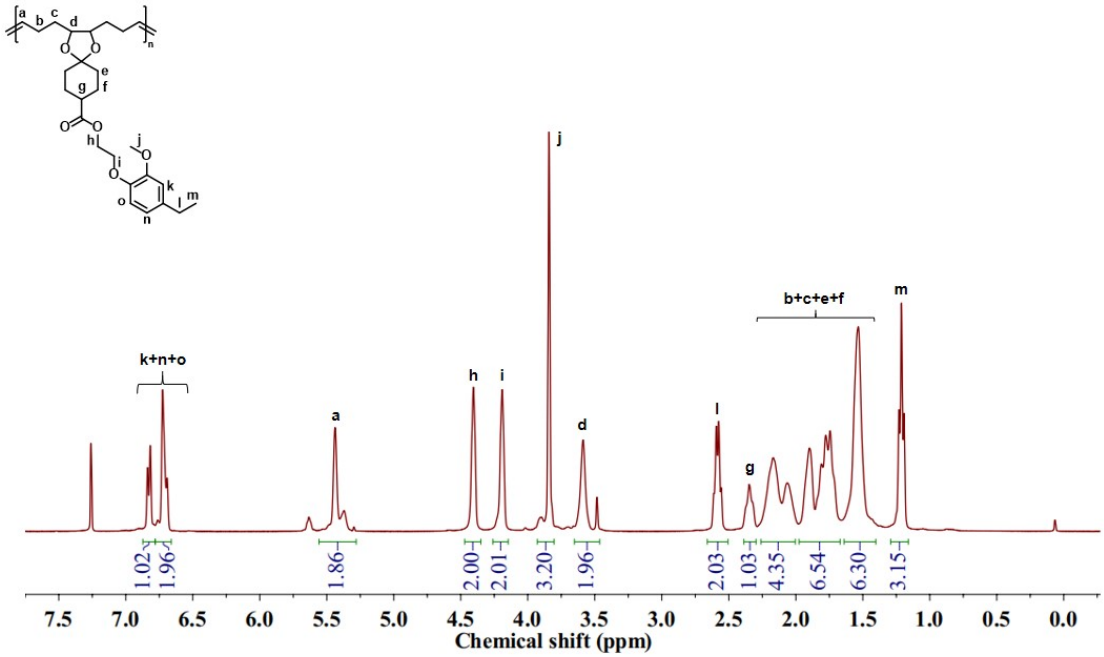


Figure S30. ^{1}H NMR spectrum of **P4** in $CDCl_3$.

Reference

(1) Zhang, H.; Zhou, Z.; Chen, X.; Yu, B.; Luo, Z.; Li, X.; Rahman, M. A.; Sha, Y. Sequence-Controlled Metallopolymers: Synthesis and Properties. *Macromolecules* **2021,** *54* (19), 9174-9184.

(2) M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi,

N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.