

## Supporting Information

### Controlled Ring-Opening Polymerization of Xylose-derived Lactones towards Sustainable Polyesters

Xiao-Yue Wang, Wei Wang, Wang-Long Wei, Wei-Min Ren and Xiao-Bing Lu and Hui Zhou\*

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## 1. Materials and instrumentation

All manipulations involving air and moisture sensitive compounds were carried out in a glove box or using standard Schlenk techniques under dry nitrogen atmosphere. Chemicals, solvents and catalysts, unless otherwise stated, were purchased from Energy Chemical, TCI and Adamas, and used as received without purification. Toluene, tetrahydrofuran (THF) and 1, 4-dioxane were distilled from sodium/benzophenone under nitrogen atmosphere. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) was dried by  $\text{CaH}_2$  before use.

**Nuclear magnetic resonance (NMR).** All the NMR spectra were recorded on a Bruker 400 or 600 MHz type spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for  $^1\text{H}$  NMR and against the solvent  $\text{CDCl}_3$  at 77.0 ppm for  $^{13}\text{C}$  NMR, respectively.

**Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS).** MALDI-TOF mass spectrometric measurements were performed on a Shimadzu Axima CFR MALDI-TOF MS mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) (J&K, 97%), was used as a matrix.  $\text{CF}_3\text{COONa}$  (J&K, 98%) was added for ion formation.

**Gel permeation chromatography (GPC).** Molecular weights and molecular weight distributions of the resultant polymers were measured by GPC analysis at 35 °C and a flow rate of 1.0 mL/min, with as the eluent and polystyrene as the standards, on an Agilent 1260 instrument coupled with an Agilent RI detector and equipped with two PL gel columns.

**Thermo-gravimetric analysis (TGA).** The Mettler-Toledo TGA /SDTA851e and NETZSCH DSC 206 thermal analyzer were used for thermogravimetric and differential thermal analysis to examine the thermal stability. The decomposition behavior of polyesters was studied from 25 °C to 500 °C with a heating rate of 10 °C/min under the nitrogen flow.

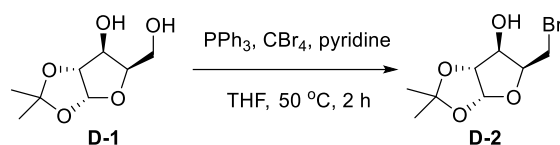
**Differential scanning calorimetry (DSC).** DSC analysis of the samples were performed on a NETZSCH DSC 206 equipment and heated from -30 °C to 100 °C at a

heating rate of 10 °C/min under a constant nitrogen flow.

**Dynamic light scattering (DLS).** DLS was used to determine the hydrodynamic diameter ( $D_h$ ) and polydispersity of the vesicle structure formed by the linear poly(**DM-1**)-*b*-polyether-*b*-poly(**DM-1**) triblock and star-shaped copolymers in aqueous solution, and measurements were performed using a nanoparticle size and Zeta potential analyzer (Nanozs 90).

**Scan electron microscopy.** The surface morphologies of were characterized by field emission scanning electron microscopy (Nova NanoSEM 450) with a voltage of 3.0 kV.

## 2. Synthesis of xylose-derived seven-membered monomers.



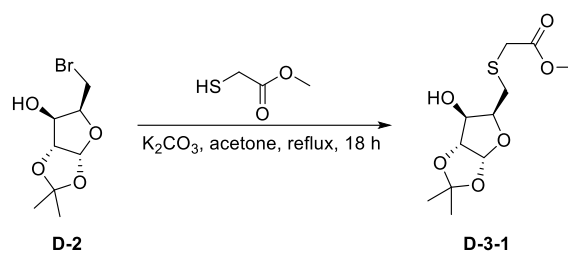
**Scheme S1.** Synthesis of **D-2** via Appel reaction

1,2-*O*-isopropylidene-*D*-xylofuranose (**D-1**) (7.6 g, 40 mmol), triphenylphosphine (13.6 g, 1.3 equiv.) and carbon tetrabromide (14.6 g, 1.1 equiv.) were placed in a round bottom flask at room temperature and THF (100 mL) was added to dissolve them completely. After the reaction solution was stirred well, pyridine (9.9 mL, 3.2 equiv.) was added. The reaction mixture was stirred at 50 °C for 2 h. After the reaction, the reaction liquid was filtered, and the filtrate was concentrated under vacuum to obtain the crude liquid mixture, which was further purified by column chromatography (PE: EA= 4:1) to obtain the desired product as white solid **D-2**. (7.96 g, yield 79%).

**D-2:** <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 5.9 (d,  $J = 3.6$  Hz, 1H), 4.5 (d,  $J = 3.6$  Hz, 1H), 4.4 (m, 1H), 4.3 (m, 1H), 3.6 – 3.5 (m, 2H), 2.0 (d,  $J = 5.4$  Hz, 1H), 1.5 (s, 3H), 1.3 (s, 3H). **HRMS** (ESI,  $m/z$ ): calcd for C<sub>8</sub>H<sub>13</sub>BrO<sub>4</sub>: [M+Cl]<sup>-</sup> 288.9664, found: 288.9669. All the results were in good agreement with literature values. [S1]

**L-2:** **L-2** was synthesized according to the same procedure as that described for **D2**, using 1,2-*O*-isopropylidene-*L*-xylofuranose (**L-1**) as the starting material. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.9 (d,  $J = 3.6$  Hz, 1H), 4.6 (d,  $J = 3.6$  Hz, 1H), 4.4 (m, 1H), 4.3 (m, 1H), 3.5 – 3.4 (m, 2H), 2.0 (d,  $J = 5.4$  Hz, 1H), 1.5 (s, 3H), 1.3 (s, 3H). **HRMS** (ESI,  $m/z$ ): calcd for C<sub>8</sub>H<sub>13</sub>BrO<sub>4</sub>: [M+Cl]<sup>-</sup> 288.9664, found: 288.9661. All the results

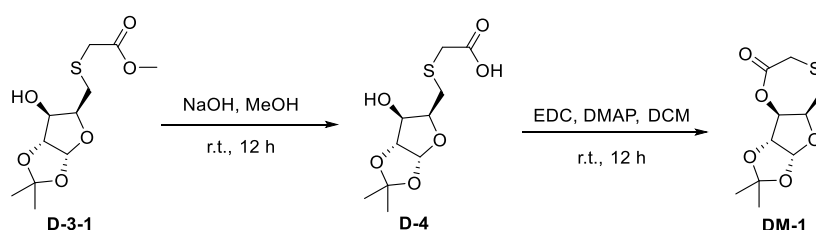
were in good agreement with literature values.<sup>[S1]</sup>



**Scheme S2.** Synthesis of **D-3-1**

**D**-bromoxyfuran (**D-2**) (1.27 g, 5 mmol) and anhydrous potassium carbonate (1.04 g, 1.5 equiv.) were added to a round-bottomed flask at room temperature and dissolved in acetone (20 mL). Methyl thioglycolate (0.54 mL, 1.2 equiv.) was added and the reaction mixture was refluxed at 75 °C for 18 h. After cooling, the reaction mixture was filtered, and the filtrate was concentrated in vacuum to afford colorless, viscous **D-3-1** in quantitative yield. The crude product was used directly in the next reaction without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.8 (d, *J* = 3.7 Hz, 1H), 4.4 (d, *J* = 3.7 Hz, 1H), 4.2 (m, 2H), 3.6 (s, 3H), 3.4 (d, *J* = 5.3 Hz, 1H), 3.3 (m, 2H), 2.8 (m, 2H), 1.4 (s, 3H), 1.2 (s, 3H).

**L-3**: **L-3** was synthesized according to the same procedure as that described for **D-3-1**, using **L-2** as the starting material. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.8 (d, *J* = 3.7 Hz, 1H), 4.4 (d, *J* = 3.7 Hz, 1H), 4.2 – 4.1 (m, 2H), 3.7 (s, 3H), 3.3 – 3.2 (m, 2H), 2.9 (m, 5.9 Hz, 1H), 2.8 (m, 1H), 1.4 (s, 3H), 1.2 (s, 3H).



**Scheme S3.** Synthesis of cyclic lactone **DM-1**

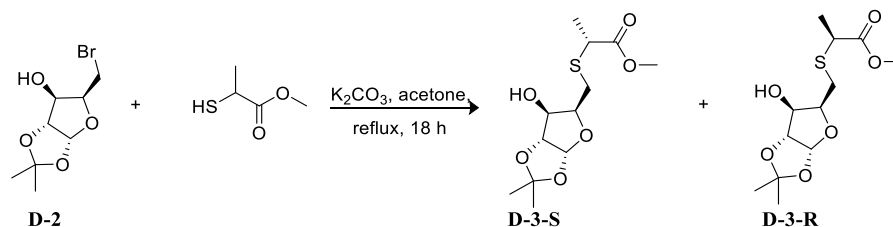
**D-3-1** (2.0 g, 7.2 mmol) and sodium hydroxide (2.9 g, 10 equiv.) were added into a round-bottom flask at 0 °C. The reactants were dissolved in methanol (100 mL) and the reaction mixture was stirred overnight at room temperature. After the reaction was completed, glacial acetic acid was added dropwise to adjust the pH of the solution to 6. Subsequently, after the solvent was removed, the mixture was diluted with H<sub>2</sub>O (50 mL)

and extracted with DCM (3×100 mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to obtain crude **D-4**, which was used directly in the subsequent reaction without further purification.

In a 100 mL Schlenk flask, to a solution of **D-4** (2.0 g, 7.6 mmol) in 50 mL DCM, 4-dimethylaminopyridine (DMAP) (11.4 mmol, 1.5 equiv.) and EDC (8.4 mmol, 1.1 equiv.) were added sequentially at 0 °C. Then, the mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction solution was filtered, and the filtrate was concentrated under vacuum to obtain the crude mixture. Then, the resultant mixture was further purified by column chromatography (PE: EA= 3:1) to afford the desired product **DM-1** as a white solid (66% yield).

**DM-1:** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.0 (d, *J* = 3.7 Hz, 1H), 4.7 (m, 2H), 4.60 (s, 1H), 3.7-3.4 (m, 2H), 3.0 – 2.7 (m, 2H), 1.5 (s, 3H), 1.3 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.3, 112.6, 105.4, 83.5, 82.6, 79.8, 29.7, 28.6, 27.0, 26.5. **FT-IR** (neat) 2989, 1751, 1376, 1247, 1218, 1077, 1021 cm<sup>-1</sup>. **HRMS** (ESI, *m/z*): calcd for C<sub>10</sub>H<sub>14</sub>NaO<sub>5</sub>S<sup>+</sup> 269.0454, found: 269.0455.

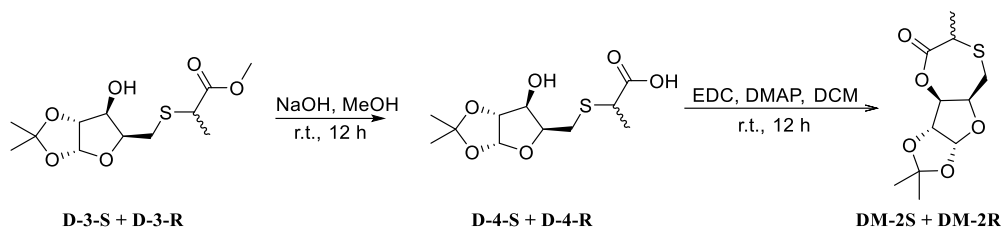
**LM:** **LM** was synthesized according to the same procedure as that described for **DM**. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.0 (d, *J* = 3.7 Hz, 1H), 4.8 (m, 2H), 4.6 (m, 3.0 Hz, 1H), 3.6 (m, 2H), 3.0 – 2.7 (m, 2H), 1.5 (s, 3H), 1.3 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.3, 112.6, 105.4, 83.5, 82.6, 79.8, 29.7, 28.5, 27.0, 26.5. **FTIR** (neat) 2991, 1751, 1450, 1375, 1258, 1163, 1076, 1024 cm<sup>-1</sup>. **HRMS** (ESI, *m/z*): calcd for C<sub>10</sub>H<sub>14</sub>NaO<sub>5</sub>S<sup>+</sup> 269.0454, found: 269.0435.



**Scheme S4.** Synthesis of **D-3-S** and **D-3-R**

*D*-bromoxyfuran (**D-2**) (1.27 g, 5.0 mmol) and anhydrous potassium carbonate (1.04 g, 1.5 equiv.) were added to a round-bottomed flask at room temperature and dissolved in acetone (20 mL). Methyl 2-mercaptoacetate (1.18 g, 1.5 equiv.) was added and

the reaction mixture was refluxed at 75 °C for 18 h. After cooling, the reaction mixture was filtered, and the filtrate was concentrated in vacuum to obtain colorless viscous the mixture of **D-3-S** and **D-3-R** in quantitative yield. The crude product was used directly in the next reaction without further purification.



### Scheme S5. Synthesis of cyclic lactone **DM-2S** and **DM-2R**

The mixture of **D-3-S/D-3-R** (1.5 g, 5.0 mmol) and sodium hydroxide (2.0 g, 10.0 equiv.) were added to a round-bottom flask at 0 °C. The reactants were dissolved in methanol (50 mL) and the reaction mixture was stirred overnight at room temperature. After the reaction was completed, glacial acetic acid was added dropwise to adjust the pH of the solution to 6. Subsequently, after the solvent was removed, the mixture was diluted with H<sub>2</sub>O (50 mL) and extracted with DCM (3×100 mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to obtain the mixture of **D-4-S/D-4-R**, which was used directly in the subsequent reaction without further purification.

In a 100 mL Schlenk flask, to a solution of **D-4-S/D-4-R** (1.4 g, 5.0 mmol) in 50 mL DCM, 4-dimethylaminopyridine (DMAP) (7.5 mmol, 1.5 equiv.) and EDC (5.5 mmol, 1.1 equiv.) were added sequentially at 0 °C. Then, the mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction solution was filtered, and the filtrate was concentrated under vacuum to obtain the crude mixture. Then, the resultant mixture was further purified by column chromatography (PE: EA= 3:1) to afford the desired product **DM-2S** (30% yield) and **DM-2R** (32% yield), respectively.

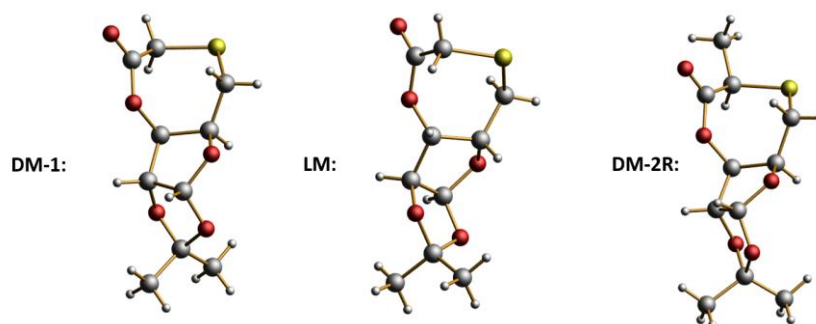
**DM-2R**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.9 (d, *J* = 3.7 Hz, 1H), 4.8(m, 1H), 4.7 (d, *J* = 3.8 Hz, 1H), 4.6 (m, 1H), 3.9 (d, *J* = 6.6 Hz, 1H), 2.8 (m, 2H), 1.5 (s, 3H), 1.4 (m,

3H), 1.3 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  169.2, 112.4, 105.4, 83.7, 81.8, 79.7, 36.2, 29.4, 27.0, 26.4, 17.7. **FTIR** (neat) 2987, 2934, 1750, 1376, 1214, 1153, 1088, 1020  $\text{cm}^{-1}$ . **HRMS** (ESI,  $m/z$ ): calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_5\text{S}$ :  $[\text{M}+\text{Na}]^+$  283.0610, found: 283.0613.

**DM-2S**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.0 (d,  $J = 3.7$  Hz, 1H), 5.1 (d,  $J = 2.9$  Hz, 1H), 4.7 (d,  $J = 3.7$  Hz, 1H), 4.5 (m, 1H), 4.1 (m,  $J = 7.3$  Hz, 1H), 3.1 – 2.8 (m, 2H), 1.6 (d,  $J = 7.2$  Hz, 3H), 1.5 (s, 3H), 1.3 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 112.5, 106.1, 83.2, 82.2, 79.5, 43.5, 30.6, 27.0, 26.4, 18.2. **FTIR** (neat) 2986, 2935, 1735, 1376, 1216, 1084, 1020  $\text{cm}^{-1}$ . **HRMS** (ESI,  $m/z$ ): calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_5\text{S}$ :  $[\text{M}+\text{Na}]^+$  283.0610, found: 283.0615.

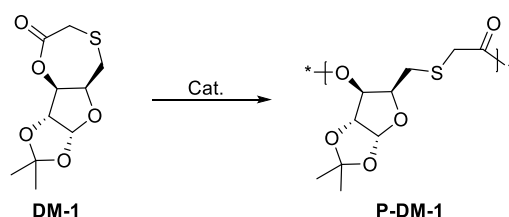
### 3. Crystal data and structure refinement for monomer **DM-1**, **LM** and **DM-2R**

Single crystals of lactones **DM-1**, **LM** and **DM-2R** suitable for X-ray structural analysis were obtained from chloroform or dichloromethane solution at room temperature. Diffraction data were collected at 273 K on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  [S2]. All nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL crystallographic software packages [3]. **CCDC**: 2407919 (**DM-1**), **CCDC**: 2407920 (**LM**), **CCDC**: 2407921 (**DM-2R**), contain 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/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure S1.** X-ray crystallographic structure of **DM-1**, **LM** and **DM-2R**. **C**: black, **O**: red, **S**: yellow, **H**: white.

#### 4. General procedure for the ring-opening polymerization of xylose-derived seven-membered monomers



**Scheme S6.** Ring opening polymerization of **DM-1** to **P-DM-1**

Polymerizations were performed in 3 mL glass reactor inside the glovebox. In a typical polymerization reaction, **DM-1** (0.5 mmol), BDI-Zn (0.005 mmol, 1.0 mol%), 4-methylbenzyl alcohol (0.005 mmol, 1.0 mol%) and THF (0.5 mL) was added into a 3 mL vial under argon atmosphere. The vial was sealed, and then the mixture was stirred at room temperature. After 12 hours the vial was removed out of the glovebox and the polymerization was quenched with a THF solution of benzoic acid (0.1 mL, 10 mg/mL), and a 20  $\mu$ L of aliquot was taken from the reaction mixture and prepared for  $^1\text{H}$  NMR analysis to obtain the percent monomer conversion. The quenched mixture was precipitated from cold methanol, centrifuged (4000 rpm, 3 minutes, 3 times) to remove any unreacted monomer, and dried in a vacuum oven to a constant weight to afford the desired polyester **P-DM-1**.

**P-DM-1:**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  5.9 (d,  $J = 3.8$  Hz, 1H), 5.2 (d,  $J = 2.9$  Hz, 1H), 4.6 (d,  $J = 3.8$  Hz, 1H), 4.5 – 4.4 (m, 1H), 3.4 (d,  $J = 15.2$  Hz, 1H), 3.3 (d,  $J = 15.0$  Hz, 1H), 2.9 (m, 1H), 2.8 (m, 1H), 1.5 (s, 3H), 1.3 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 112.4, 104.8, 83.2, 79.4, 34.1, 30.6, 26.8, 26.4.

**P-LM:**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  5.9 (d,  $J = 3.8$  Hz, 1H), 5.2 (d,  $J = 2.9$  Hz, 1H), 4.6 (d,  $J = 3.8$  Hz, 1H), 4.5 (m, 1H), 3.4 (d,  $J = 15.1$  Hz, 1H), 3.3 (d,  $J = 15.2$  Hz, 1H), 2.9 (m, 1H), 2.8 (m, 1H), 1.5 (s, 3H), 1.3 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 112.4, 104.9, 83.2, 79.4, 53.5, 34.2, 30.6, 26.8, 26.4.

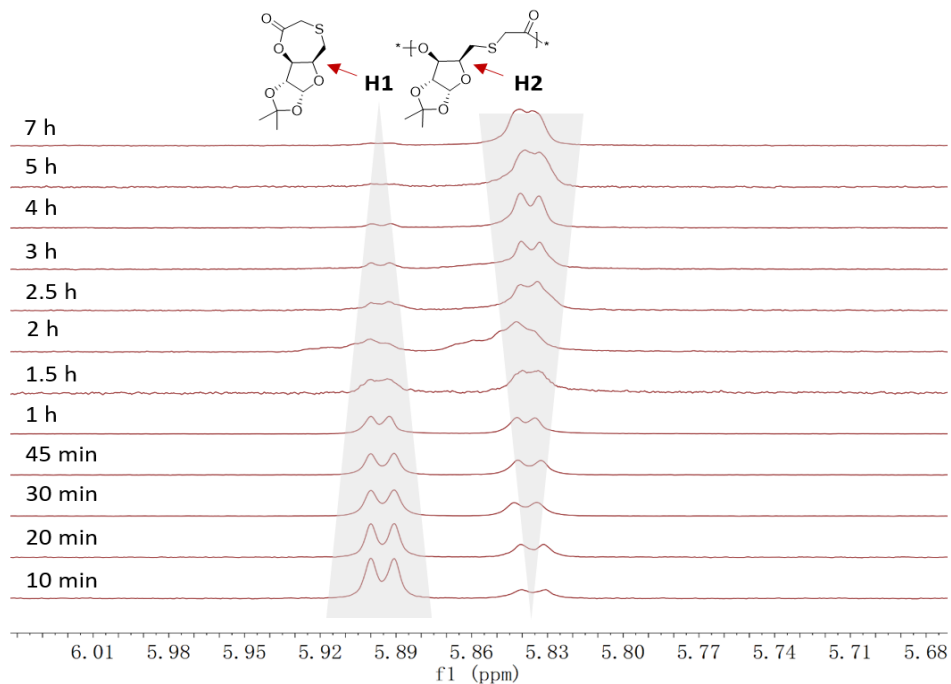
**P-DM-2S:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.9 (m,  $J = 4.2$  Hz, 1H), 5.2 (d,  $J = 3.3$  Hz, 1H), 4.6 – 4.5 (m, 1H), 4.46 – 4.40 (m, 1H), 3.6 – 3.4 (m, 1H), 3.0 (m, 1H), 2.9 (m, 1H), 2.8 (m, 1H), 1.5 (s, 3H), 1.4 (m, 3H), 1.3 (d,  $J = 2.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,

DMSO-*d*<sub>6</sub>)  $\delta$  171.5, 111.3, 104.3, 82.5, 78.2, 76.5, 40.6, 28.3, 26.3, 26.0, 17.

**Table S1.** Kinetic experiments of ring opening polymerization of **DM-1**.<sup>[a]</sup>

Entry	t [min]	Conv. <sup>[b]</sup> (%)	$M_{n,calcd}$ <sup>[c]</sup> (kg/mol)	$M_{n,SEC}$ <sup>[d]</sup> (kg/mol)	$\mathcal{D}$ <sup>[e]</sup>
1	10	22	5.4	6.8	1.09
2	20	36	8.9	9.4	1.07
3	30	44	10.8	10.9	1.07
4	45	46	11.3	12.9	1.08
5	60	59	14.5	13.3	1.07
6	90	66	16.2	15.0	1.13
7	120	73	18.0	16.6	1.13
8	150	79	19.4	16.9	1.13
9	180	85	20.9	17.2	1.16
10	240	88	21.3	18.3	1.16
11	300	91	22.4	19.0	1.12
12	360	92	22.6	19.6	1.13

<sup>[a]</sup> Polymerization conditions:  $[\mathbf{DM-1}]_0/[\mathbf{BDI-Zn}]_0/[\mathbf{I}]_0 = 100:1:1$ ,  $\mathbf{I} = p$ -methylbenzyl alcohol, 1.0 M in  $\text{CH}_2\text{Cl}_2$  at room temperature; <sup>[b]</sup> Monomer conversions were measured by  $^1\text{H}$  NMR of the quenched solution; <sup>[c]</sup> Theoretical molar weight ( $M_{n, calcd}$ ) was calculated from  $M_w[\mathbf{M}] \times ([\mathbf{M}]/[\mathbf{I}]) \times \text{Conv.} + M_w[\mathbf{I}]$ ; <sup>[d]</sup> Number-average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) was determined by GPC (THF eluent) using polystyrene standards; <sup>[e]</sup> Polydispersity index ( $\mathcal{D}$ ) =  $M_w/M_n$ .



**Figure S2.** Zoomed-in region of stacked  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) of the crude reaction mixtures from **BDI-Zn**-catalyzed ROP of **DM-1** at different reaction times.

## 5. GPC traces of polyesters

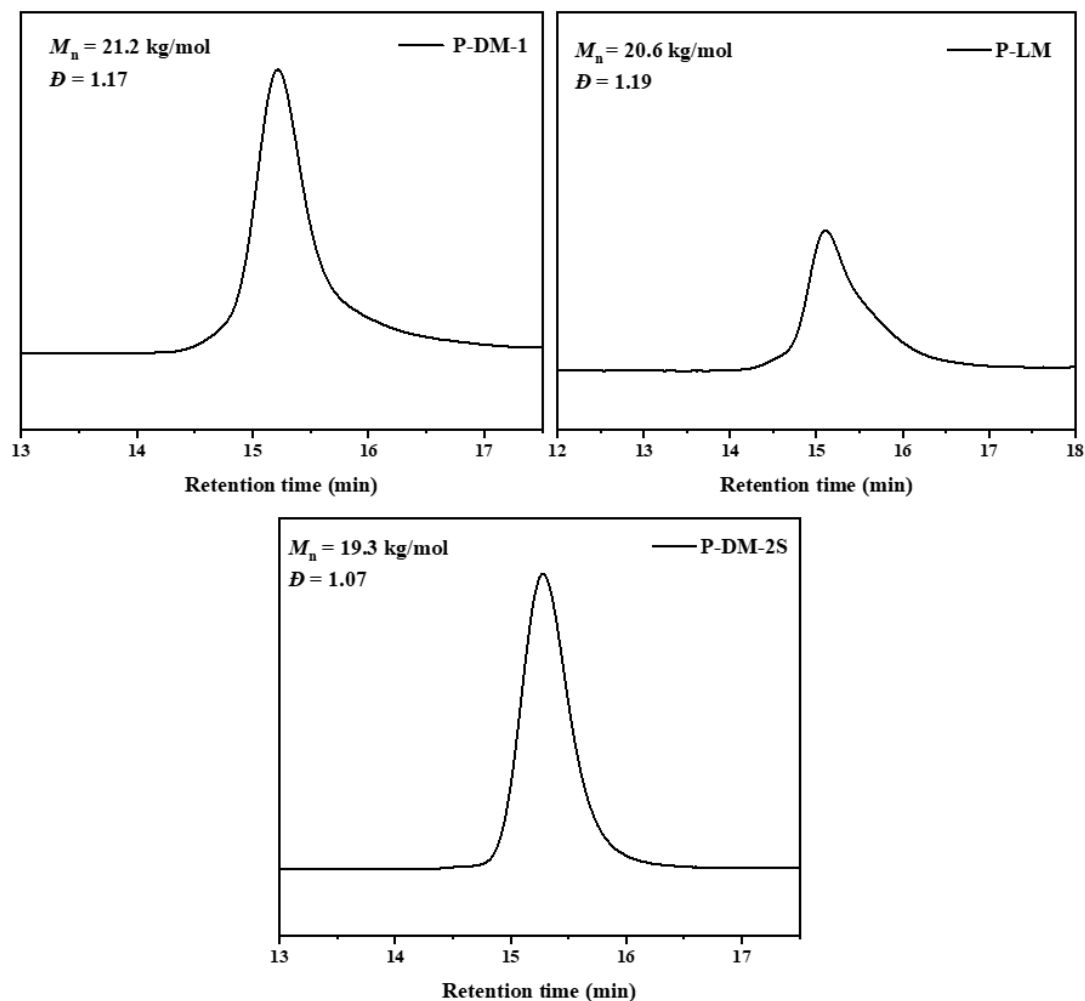
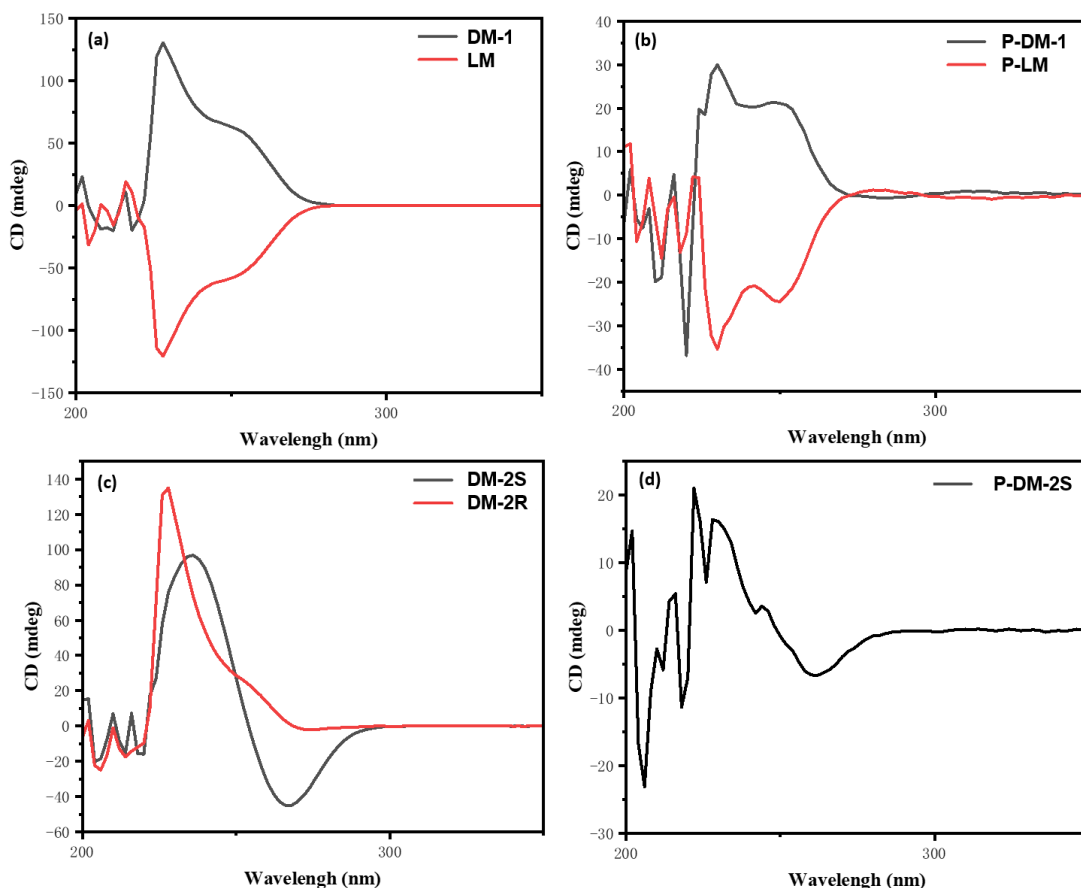


Figure S3. GPC curves of P-DM-1, P-LM and P-DM-2S

## 6. Circular dichroism (CD) spectroscopy

In order to explore the chirality of the obtained monomers **DM** and **LM**, as well as the resultant polyesters, we also conducted the optical activity tests by circular dichroism (CD) spectroscopy in a  $\text{CH}_2\text{Cl}_2$  solution at room temperature. As shown in Figure S4, the CD analysis revealed that **DM-1** and **LM** showed positively signed and negatively signed Cotton effects at 228 nm, respectively. Similar to the results of the monomers, **P-DM-1** showed a strong positive band at 230 nm, and **P-LM** showed a strong negative band at the same wavelength, indicating the inversed configuration based on the ring-opening polymerization.

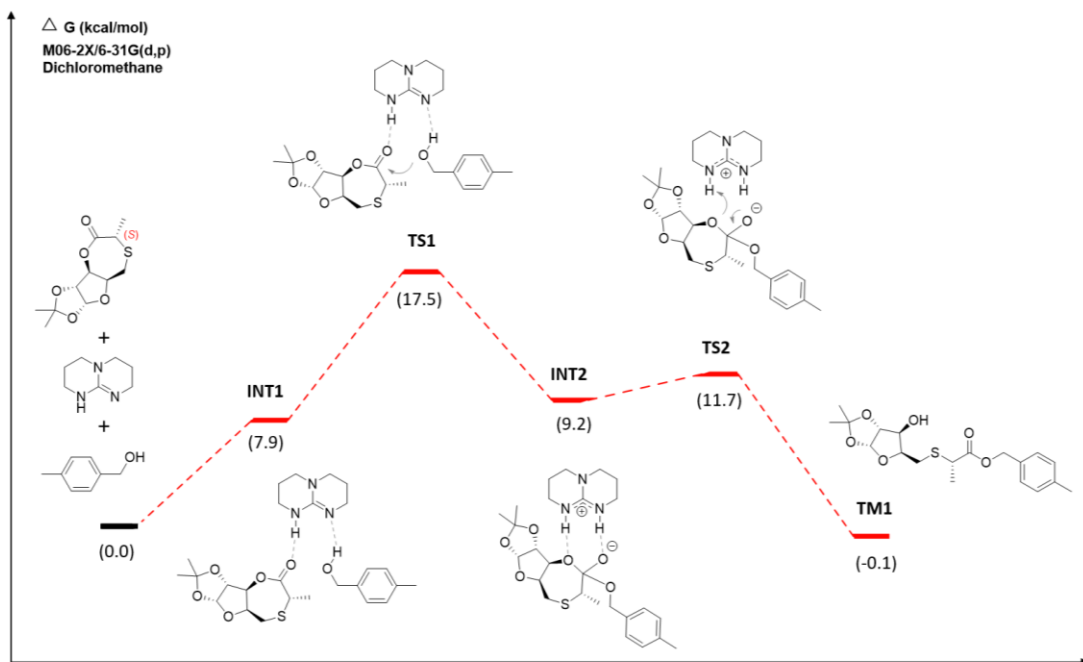


**Figure S4.** CD spectra of xylosed-derived **DM**, **LM** monomers and the resultant polyesters recorded in  $\text{CH}_2\text{Cl}_2$ .

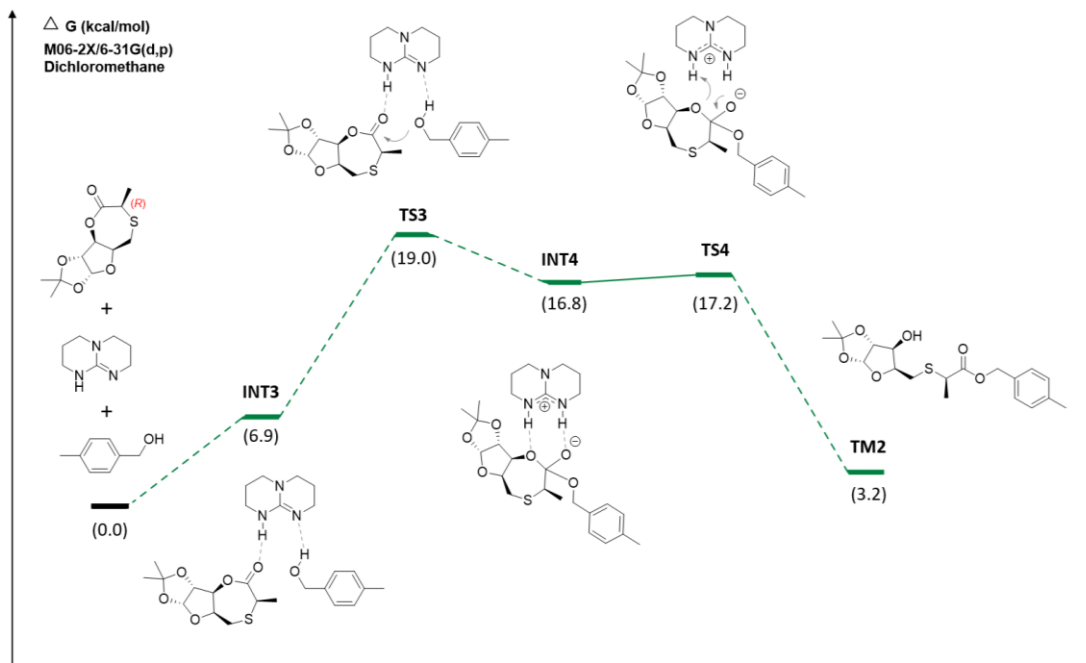
### 7. Density functional theory (DFT) calculations for TBD-catalyzed ROP of **DM-2R** and **DM-2S**.

In order to clearly investigate the reactivity of ring-opening polymerization of **DM-2R** and **DM-2S**, density functional theory (DFT) calculation was performed with Gaussian 16.<sup>[S4]</sup> All geometries of the reactants, products, intermediates (**INT**), and transition states (**TS**) involved in this mechanistic study were fully optimized in  $\text{CH}_2\text{Cl}_2$  solvent using SMD solvent model at the M06-2X/6-31G (d, p) level of theory. Intrinsic reaction coordinate (**IRC**) scans were conducted when necessary to check that the transition state correctly connects the two relevant minima. To improve the accuracy of the energy, the single point energy of each optimized structure was calculated at the M06-2X (SMD,  $\text{CH}_2\text{Cl}_2$ )/6-311++G (d, p) level. The relative free energy ( $\Delta G_{\text{sol}}$ ) was obtained by combining the single-point energy with Gibbs free energy correction at the

M06-2X/6-31G (d, p) level.

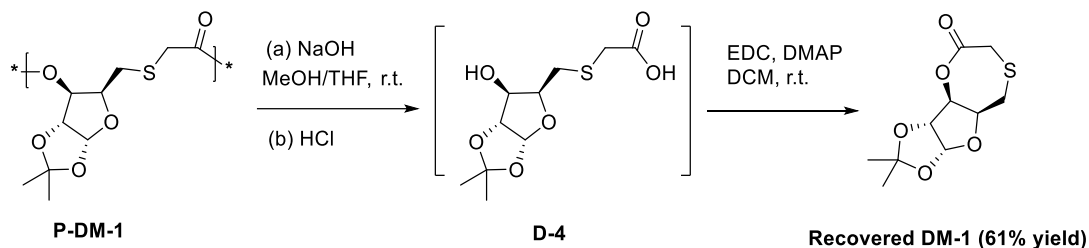


**Figure S5.** The possible mechanism of TBD-catalyzed ROP of **DM-2S**.



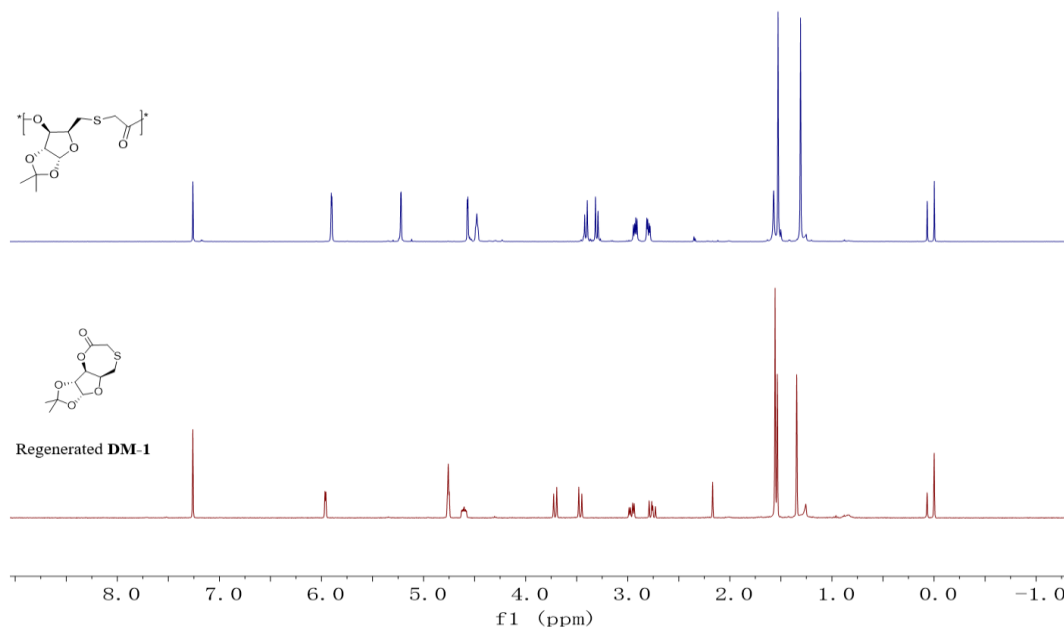
**Figure S6.** The possible mechanism of TBD-catalyzed ROP of **DM-2R**.

## 8. Chemical recycling of P-DM-1

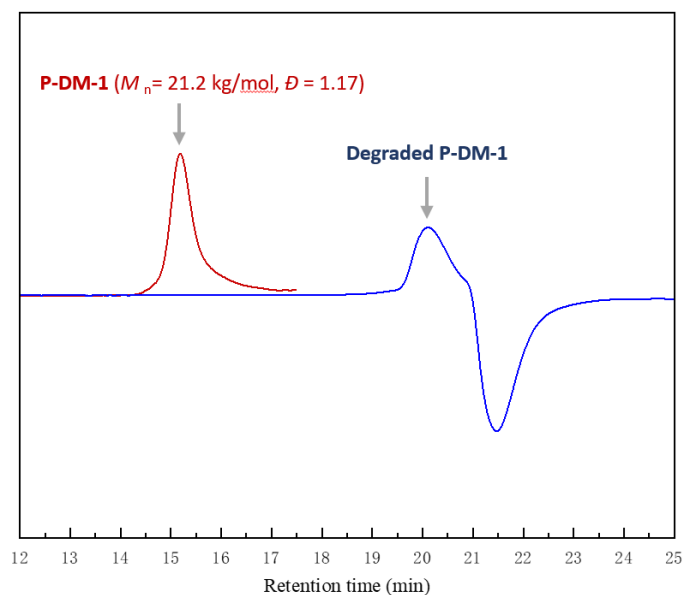


**Scheme S7.** Chemical recycling of **P-DM-1**.

To a solution of **P-DM-1** (0.12 g, 0.5 mmol relative to the repeating units) in THF (1.0 mL) and H<sub>2</sub>O (0.5 mL) was added NaOH (0.04 g, 1.0 mmol). The reaction was allowed to stir at room temperature. After completion of the reaction monitored by TLC, EtOAc (15 mL) and H<sub>2</sub>O (15 mL) were added. The phases were separated and the aqueous phase was washed with EtOAc (3 × 15 mL). The water fraction was acidified with 1.0 M hydrochloric acid to pH 2-3, and then extracted with EtOAc. The organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo to obtain the crude **D-4**, which was used directly in the next reaction without further purification.



**Figure S7.** Stacked <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of **P-DM-1** and regenerated **DM-1**.

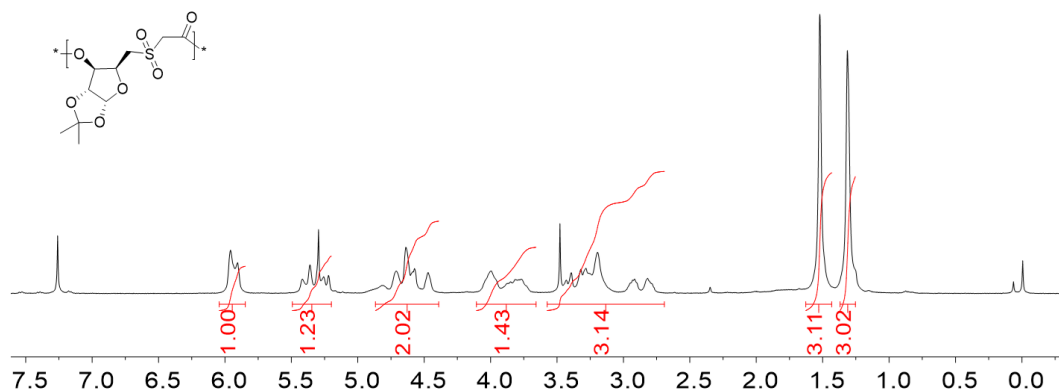


**Figure S8.** GPC traces of **P-DM-1** before and after degradation.

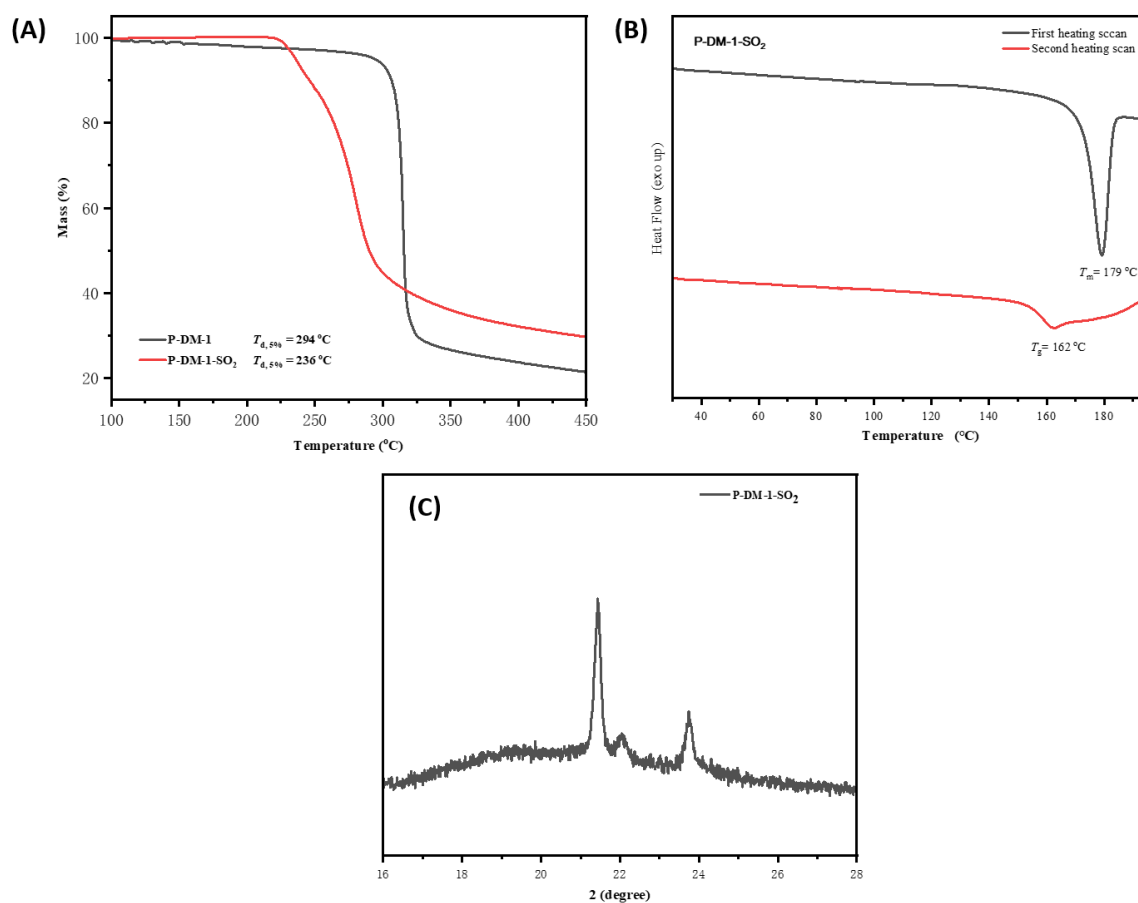
In a 100 mL Schlenk flask, to a solution of crude **D-4** in 30 mL DCM, 4-dimethylaminopyridine (DMAP) (7.5 mmol) and EDC (5.5 mmol) were added sequentially at 0 °C. Then, the mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction solution was filtered, and the filtrate was concentrated under vacuum to obtain the crude mixture. Then, the resultant mixture was further purified by column chromatography (PE: EA= 3:1) to afford the regenerated **DM-1** as a white solid (75 mg, 61% yield).

## 9. Oxidation Procedure

Oxidation procedure of **P-DM-1** was according to the reported literature. In a 100 mL Schlenk flask, **P-DM-1** ((0.24 g, 1.0 mmol relative to the repeating units) was dissolved in dichloromethane (5.0 mL) and stirred at 0°C, 5 mL diethyl ether solution of 3-chloroperbenzoic acid (0.2 g, 85 wt.%, 2.0 equiv.) was added dropwise into the above solution. The mixture was stirred at room temperature for 24 h, then the solvent was removed under reduced pressure. The quenched mixture was precipitated from cold methanol, centrifuged (4000 rpm, 3 minutes, 3 times) to remove any unreacted monomer, and dried in a vacuum oven to a constant weight to afford the desired polymers **P-DM-1-SO<sub>2</sub>**.

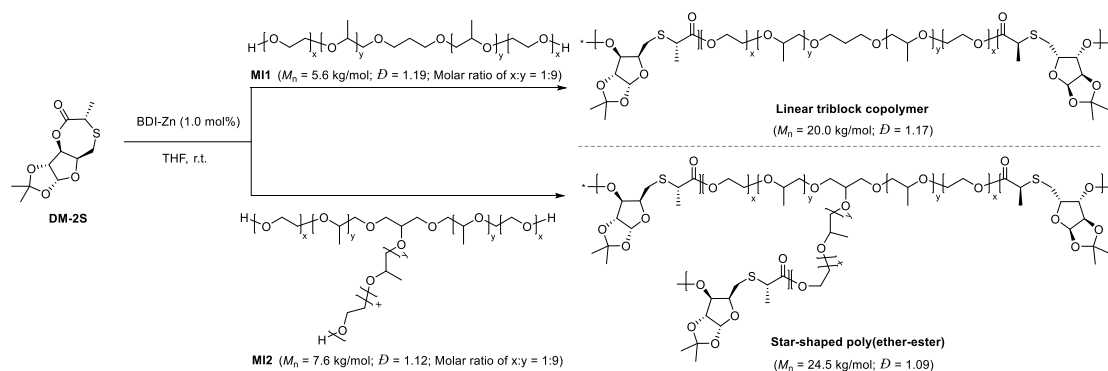


**Figure S9.** <sup>1</sup>H-NMR spectrum of **P-DM-1-SO<sub>2</sub>**.



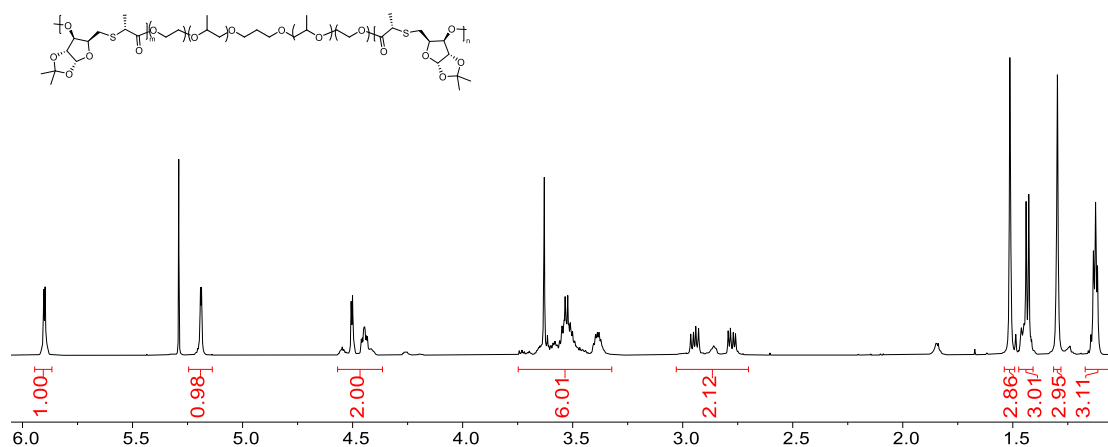
**Figure S10.** (A) TGA curves of **P-DM-1** and **P-DM-1-SO<sub>2</sub>**; (B) DSC curves of **P-DM-1-SO<sub>2</sub>**; (C) XRD pattern of **P-DM-1-SO<sub>2</sub>**.

## 10. Procedure for polyether polyols-initiated ROP

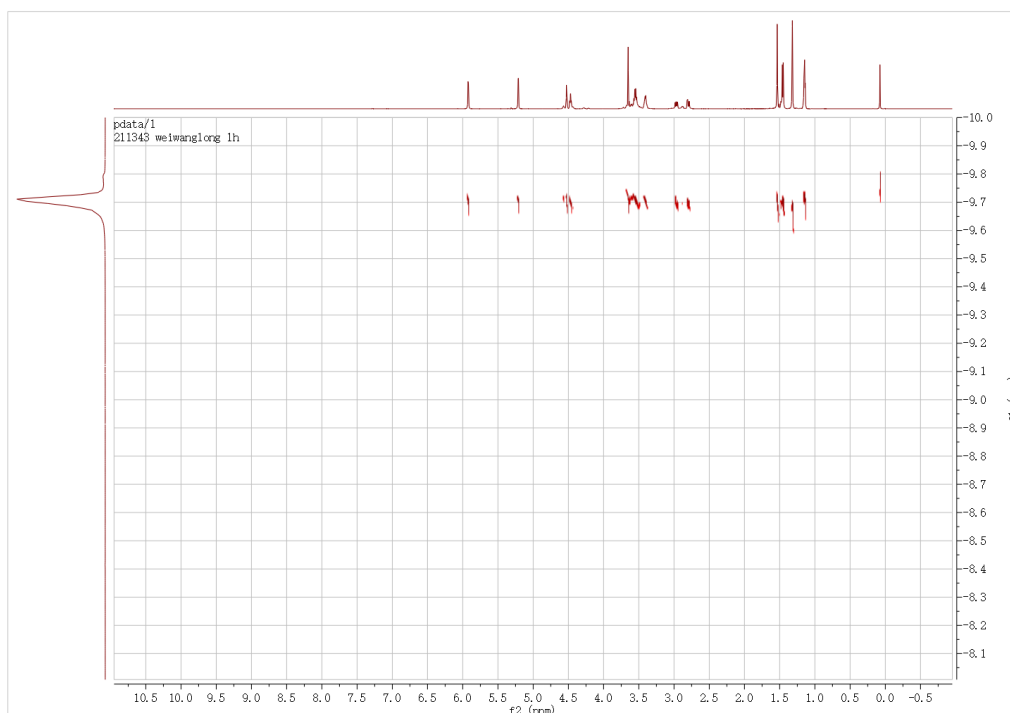


**Scheme S8.** Polyether polyols-initiated ROP of **DM-2S** in the presence of BDI-Zn.

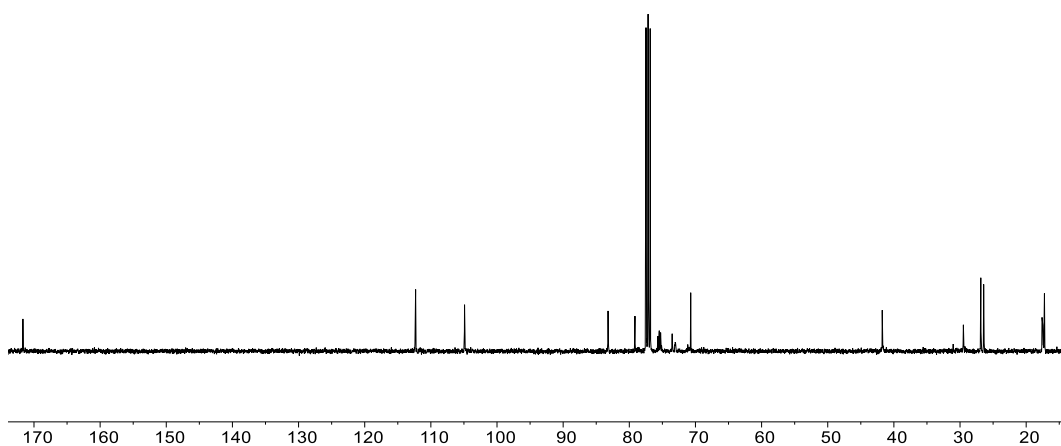
The block copolymerization is carried out at ambient temperature in a 4 mL glass reactor in the glove box. Polyether polyols (**EO**) with a molecular weight of 5000 was added to the catalyst solution of THF, and after 10 minutes monomer (**DM**) was added to the reaction mixture. After a period of time, 500  $\mu\text{L}$  benzoic acid/wet chloroform (10 mg  $\text{mL}^{-1}$ ) was added to the quenching polymerization reaction, and 20  $\mu\text{L}$  of the reaction mixture was obtained by  $^1\text{H}$  NMR analysis. The quenched mixture is precipitated into 10 mL cold methanol, centrifugated (4500 RPM, 10 min, 3 times), washed with cold methanol to remove any unreacted monomers, and dried to a fixed weight in a vacuum oven.



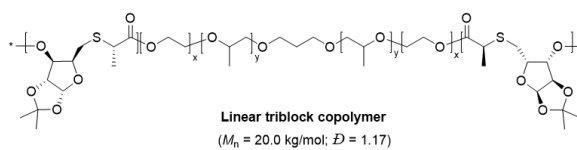
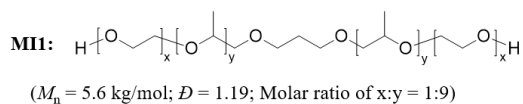
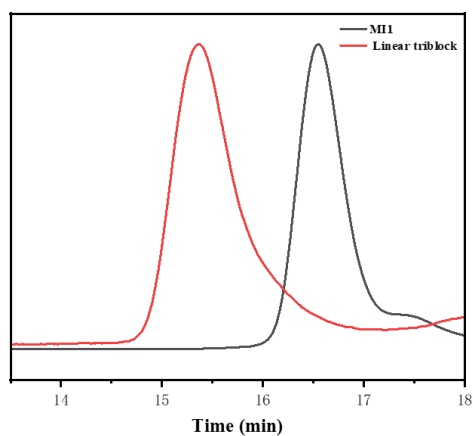
**Figure S11.**  $^1\text{H}$ -NMR spectrum of linear triblock copolymer.



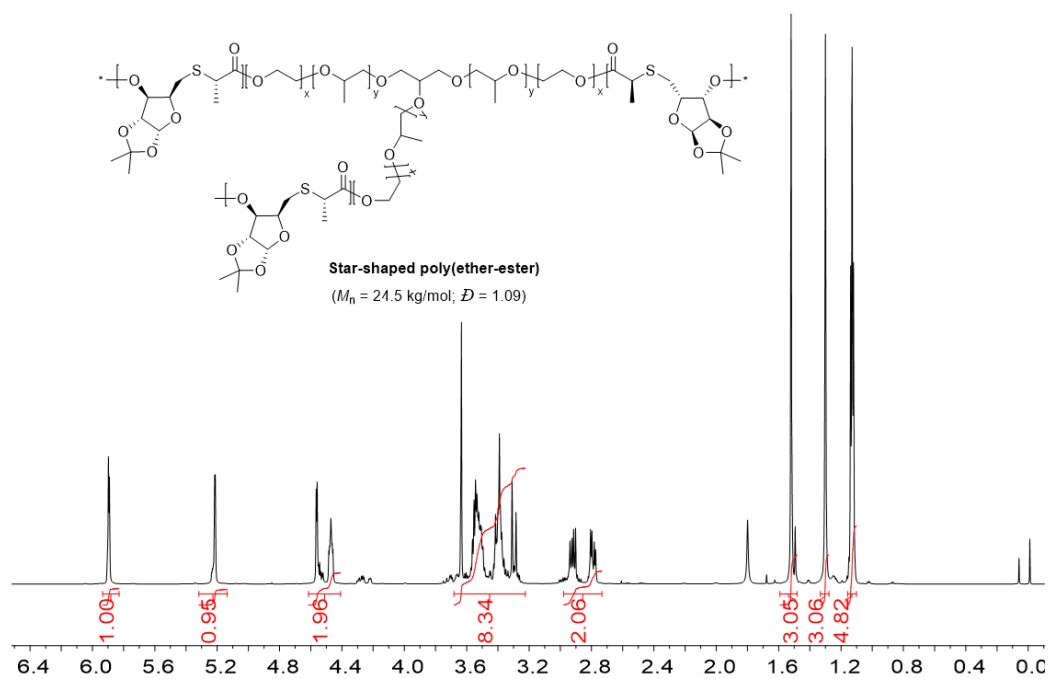
**Figure S12.** DOSY NMR spectrum of linear triblock copolymer.



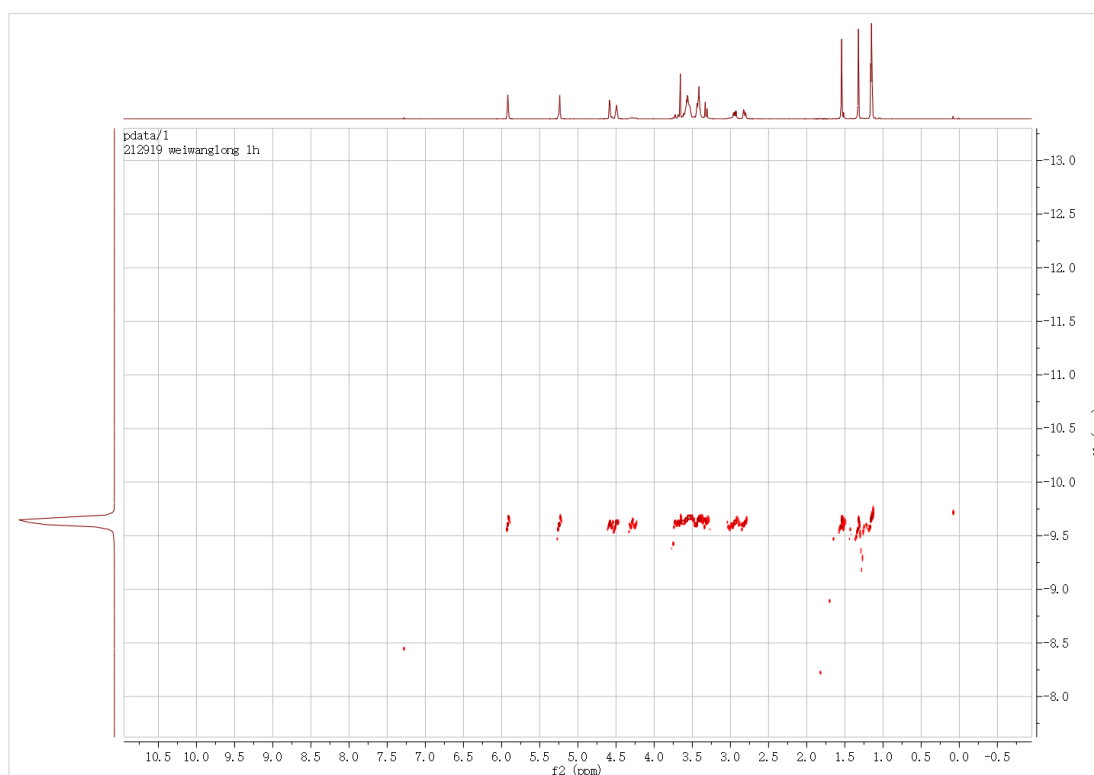
**Figure S13.**  $^{13}\text{C}$ -NMR spectrum of linear triblock copolymer.



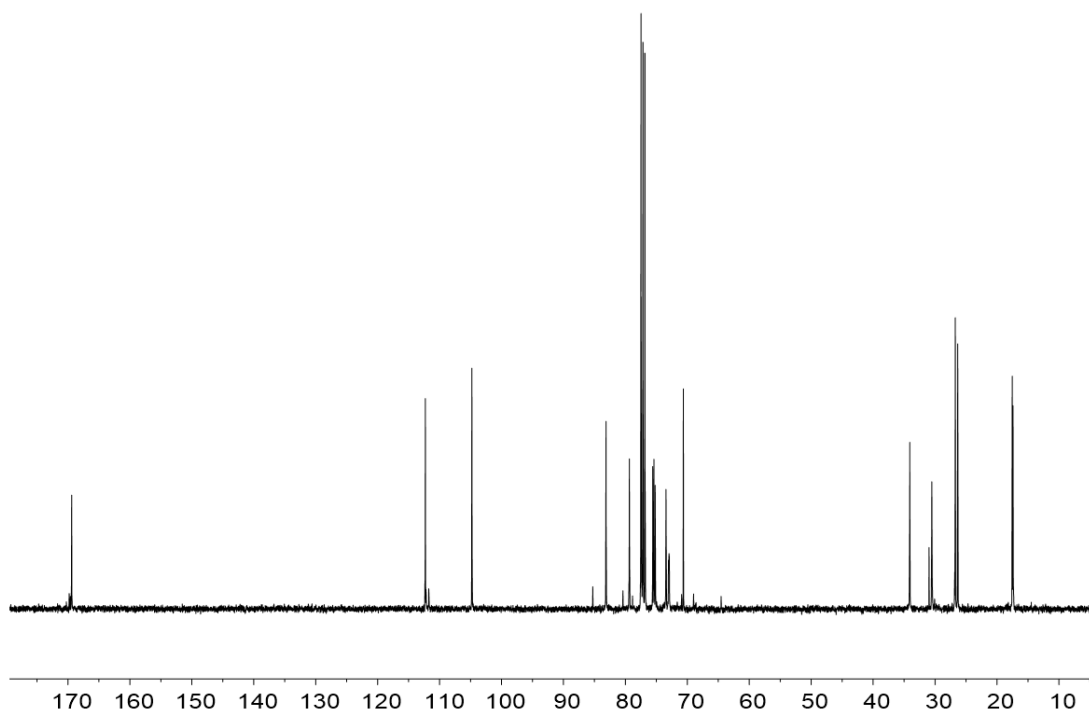
**Figure S14.** DSC curves of linear triblock copolymer and M11



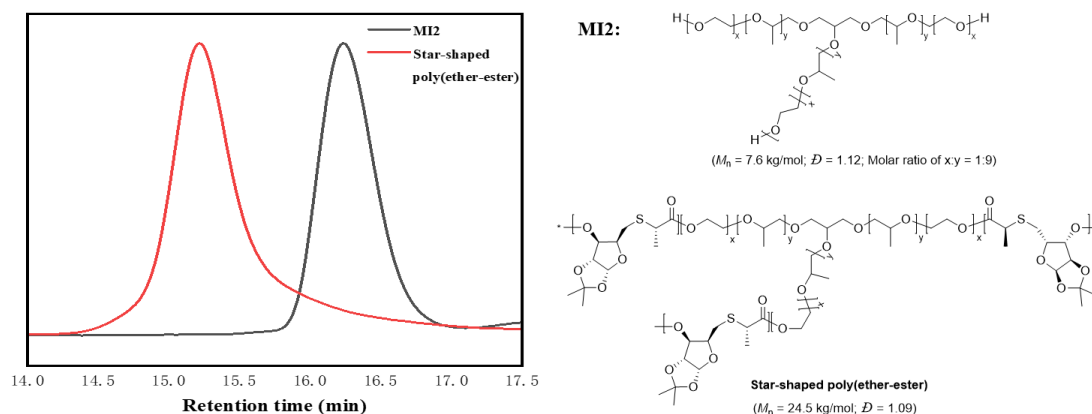
**Figure S15.** <sup>1</sup>H-NMR spectrum of star-shaped poly(ether-ester).



**Figure S16.** DOSY NMR spectrum of star-shaped poly(ether-ester).



**Figure S17.**  $^{13}\text{C}$  -NMR spectrum of star-shaped poly(ether-ester).



**Figure S18.** DSC curves of star-shaped poly(ether-ester) and MI2.

### 11. Self-assembly of the resultant amphiphilic block polymers

Firstly, 20 mg of the resultant amphiphilic block polymers was dissolved in 2 mL of THF. Then, the solution was slowly added dropwise to 100 mL of distilled water under intensely stirring. After sonicating for 5 minutes, the solution was let stand for 24 hours before SEM characterization.

## 12. NMR spectra

Mar19-2024.1270.1.1r

1

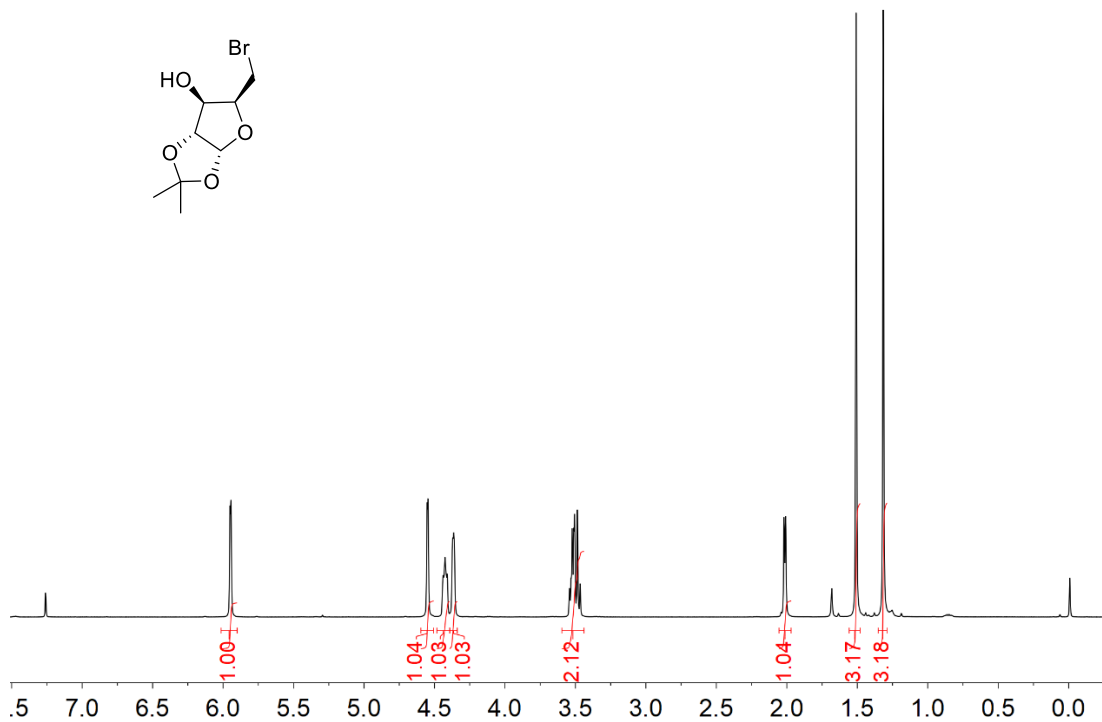


Figure S19. <sup>1</sup>H-NMR spectrum of D-2.

20230523-58.1.1.1r

1-20-TM

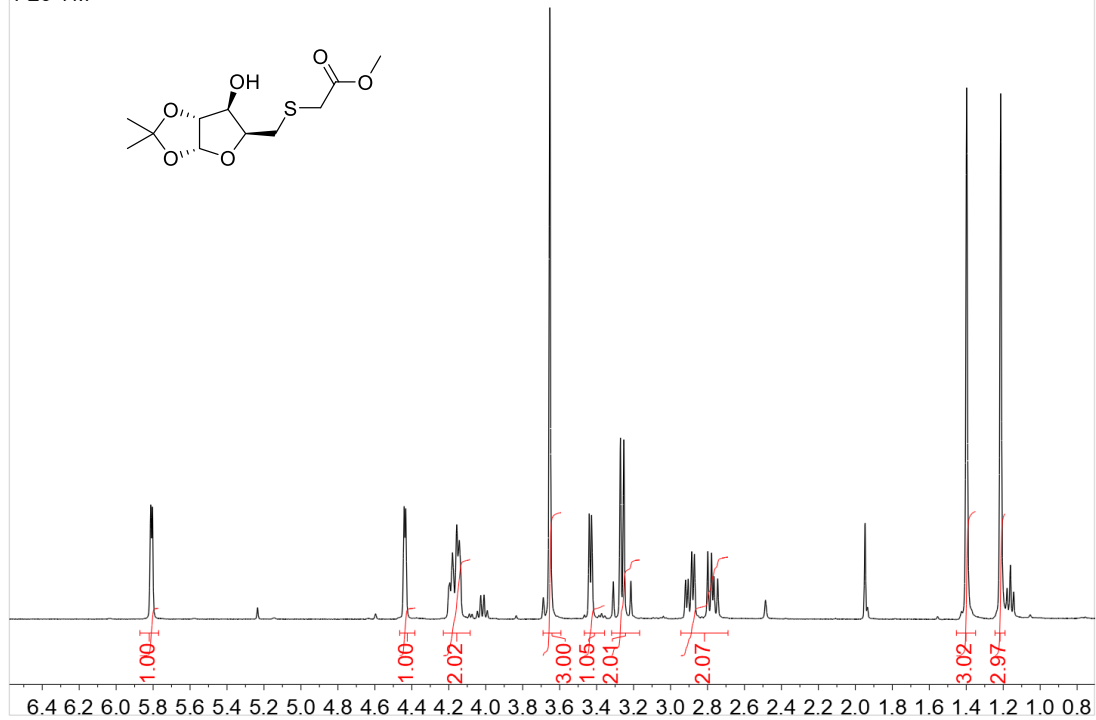


Figure S20. <sup>1</sup>H-NMR spectrum of D-3-1.

ch. 23110702, 1, 1r  
d

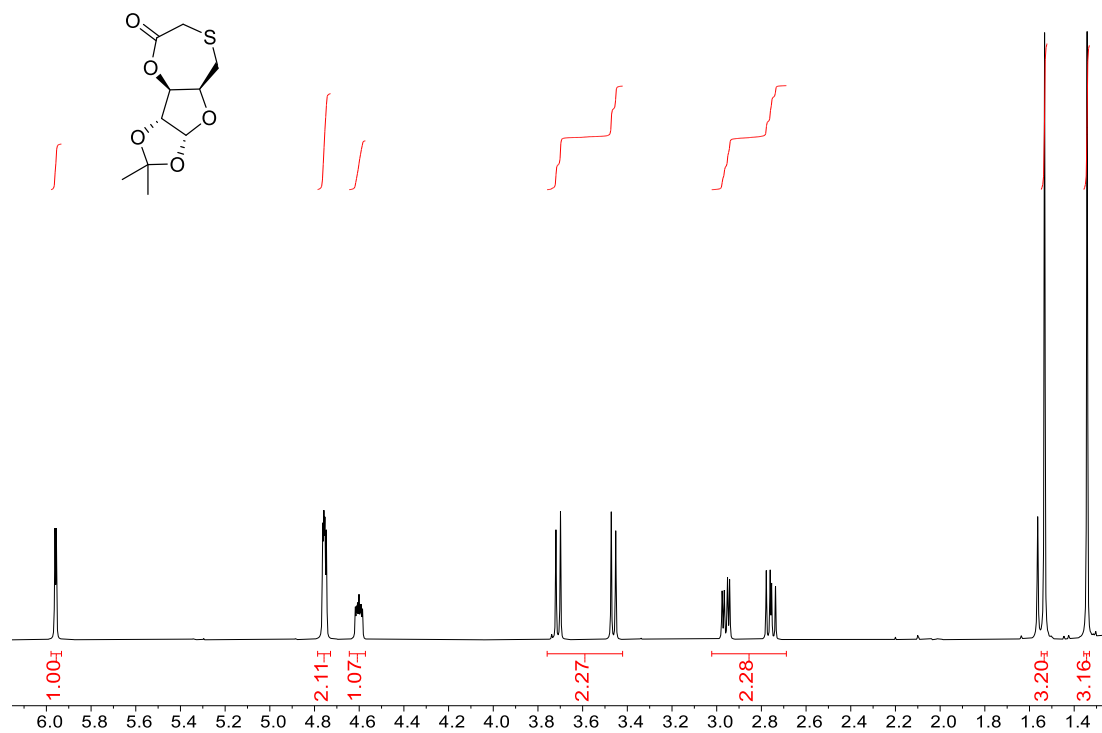


Figure S21. <sup>1</sup>H-NMR spectrum of DM-1.

Jun19-2023, 770, 1, 1r  
1-22-1m

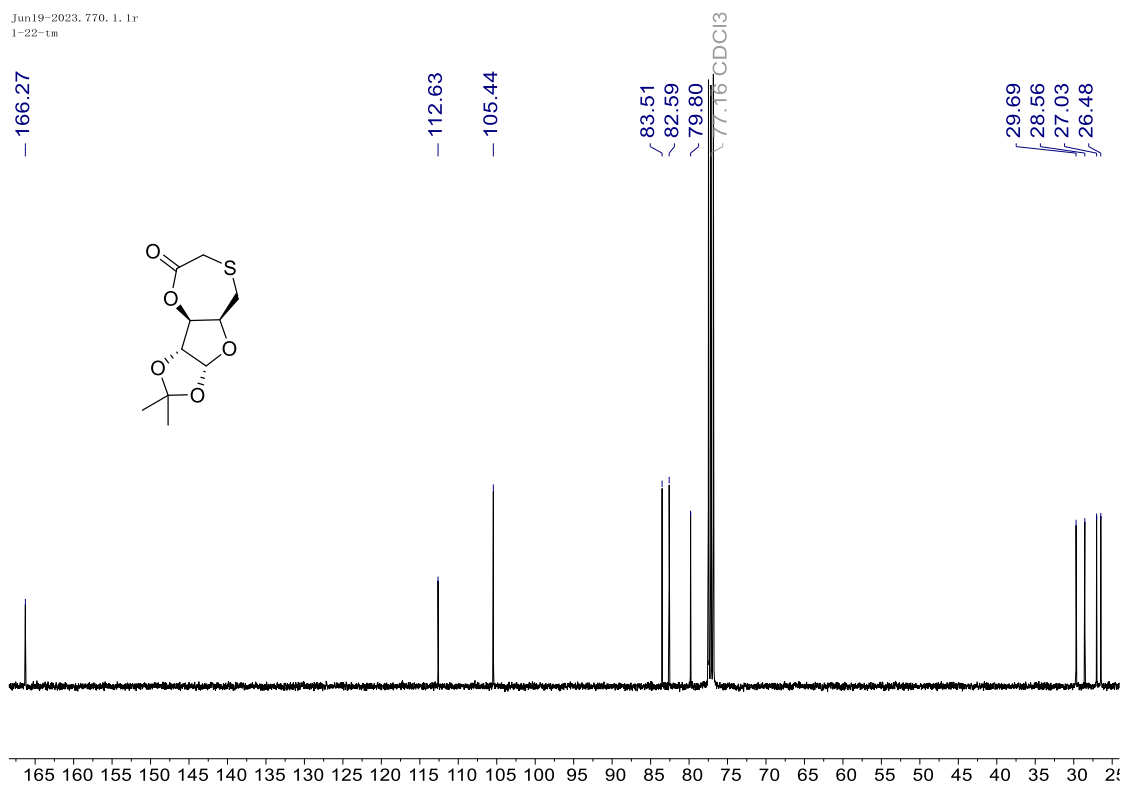


Figure S22. <sup>13</sup>C-NMR spectrum of DM-1.

ch. 23072103. 1. 1r  
4H-H

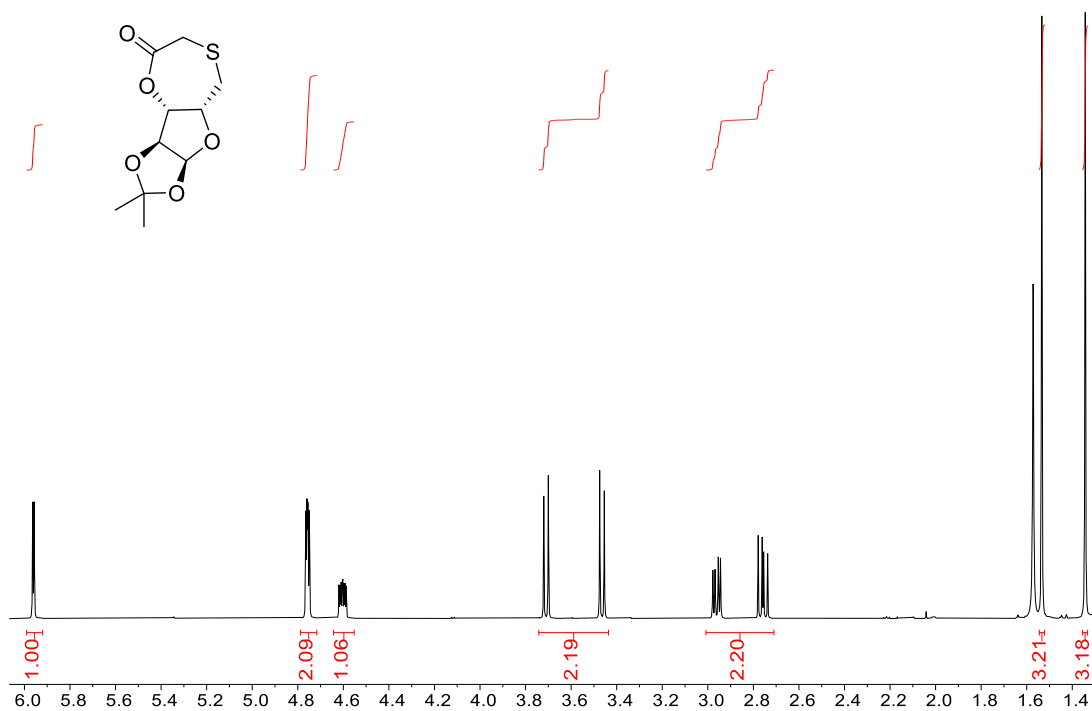


Figure S23. <sup>1</sup>H-NMR spectrum of LM

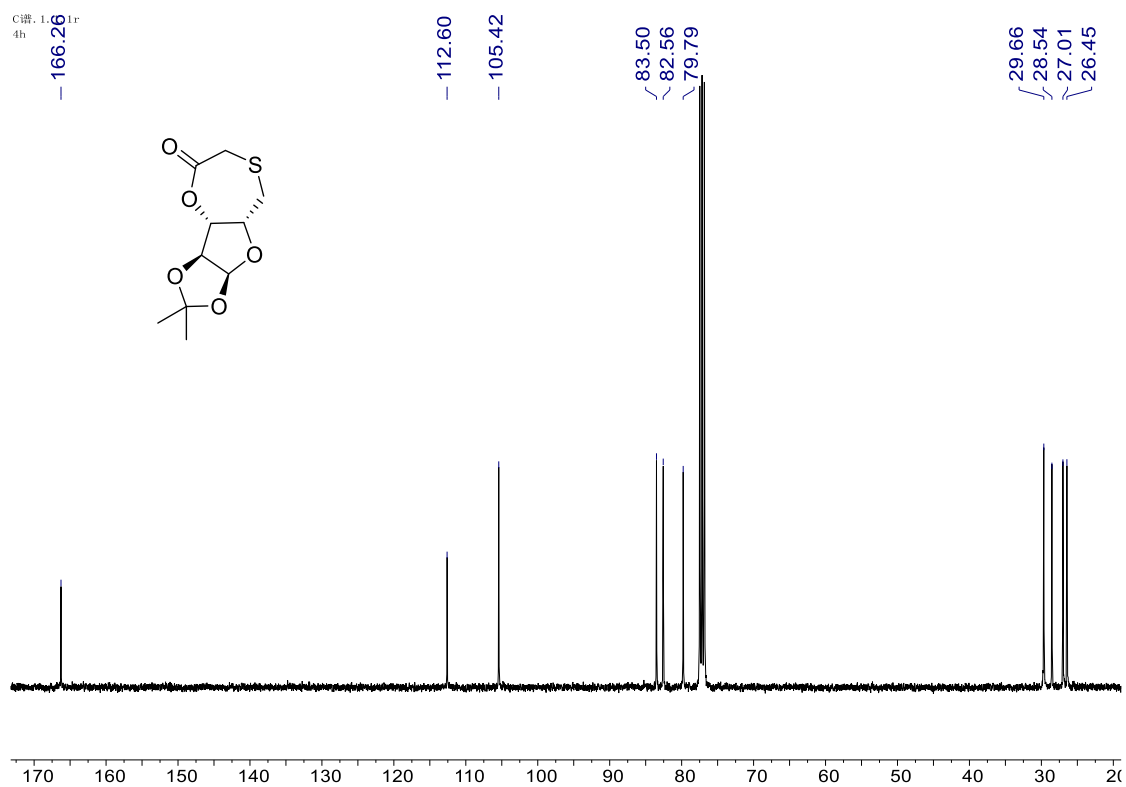


Figure S24. <sup>13</sup>C-NMR spectrum of LM.

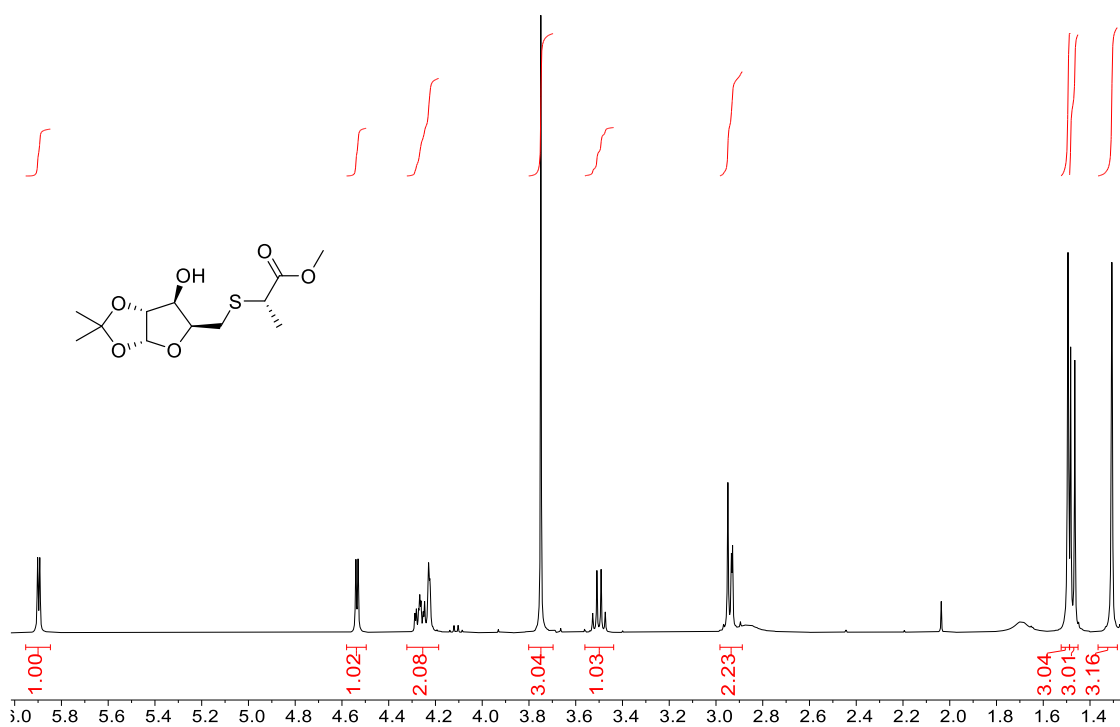


Figure S25. <sup>1</sup>H-NMR spectrum of D-3-S.

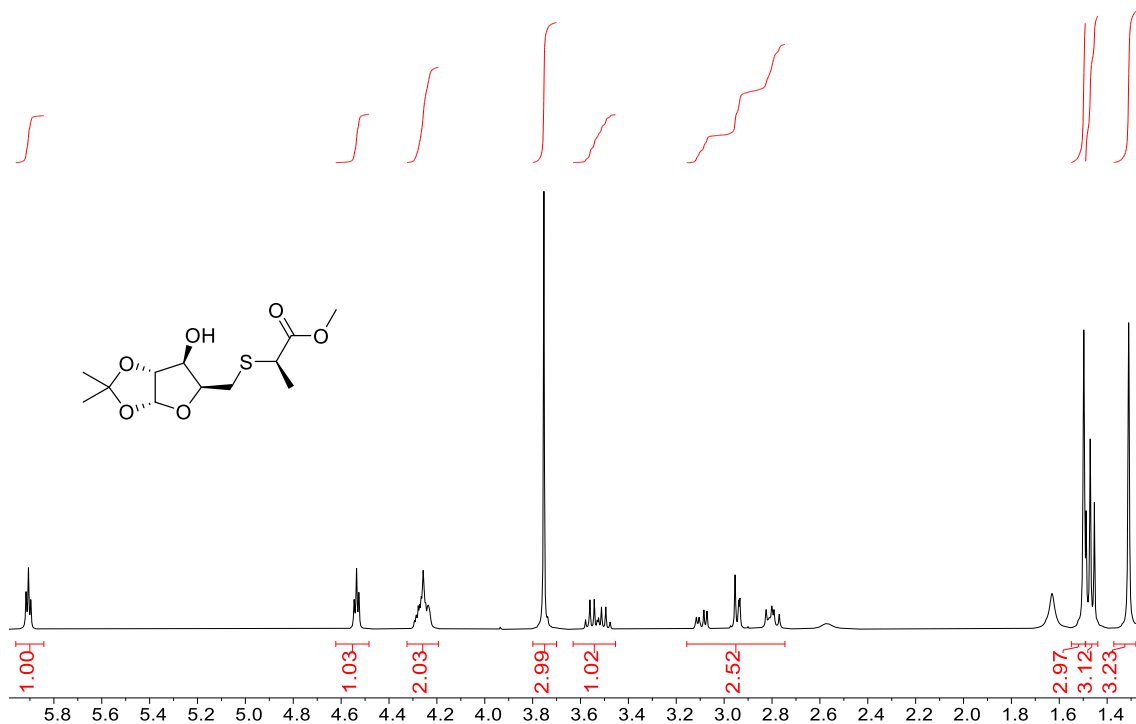


Figure S26. <sup>1</sup>H-NMR spectrum of D-3-R.



pdata/1  
s

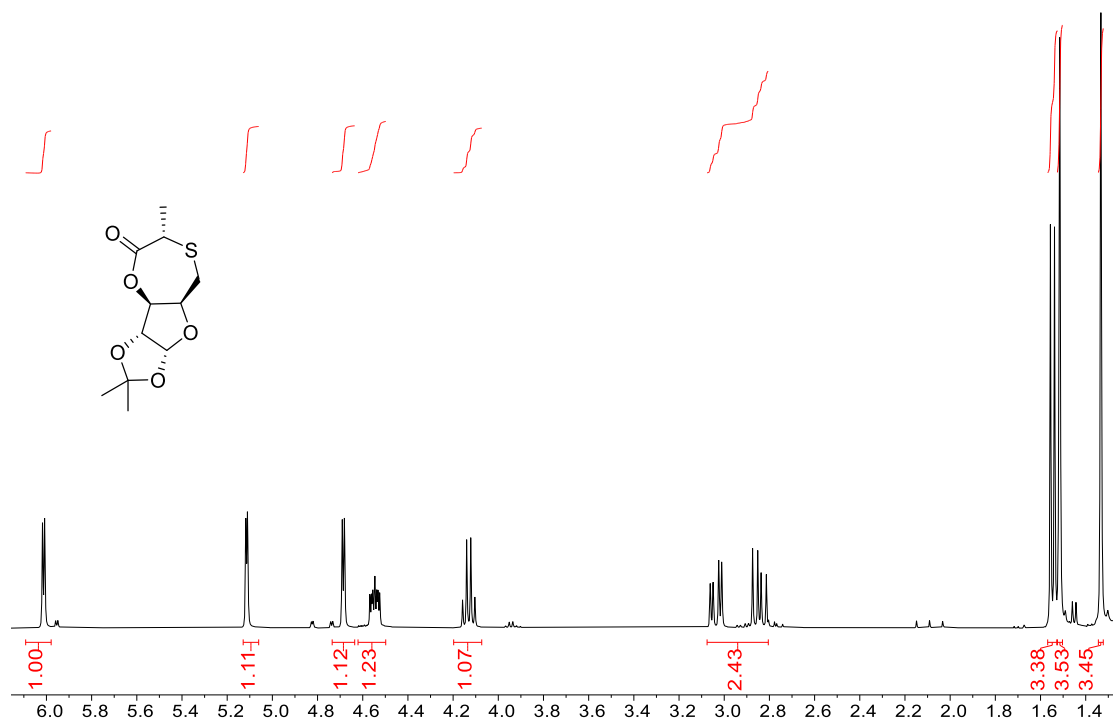


Figure S29. <sup>1</sup>H-NMR spectrum of DM-2S.

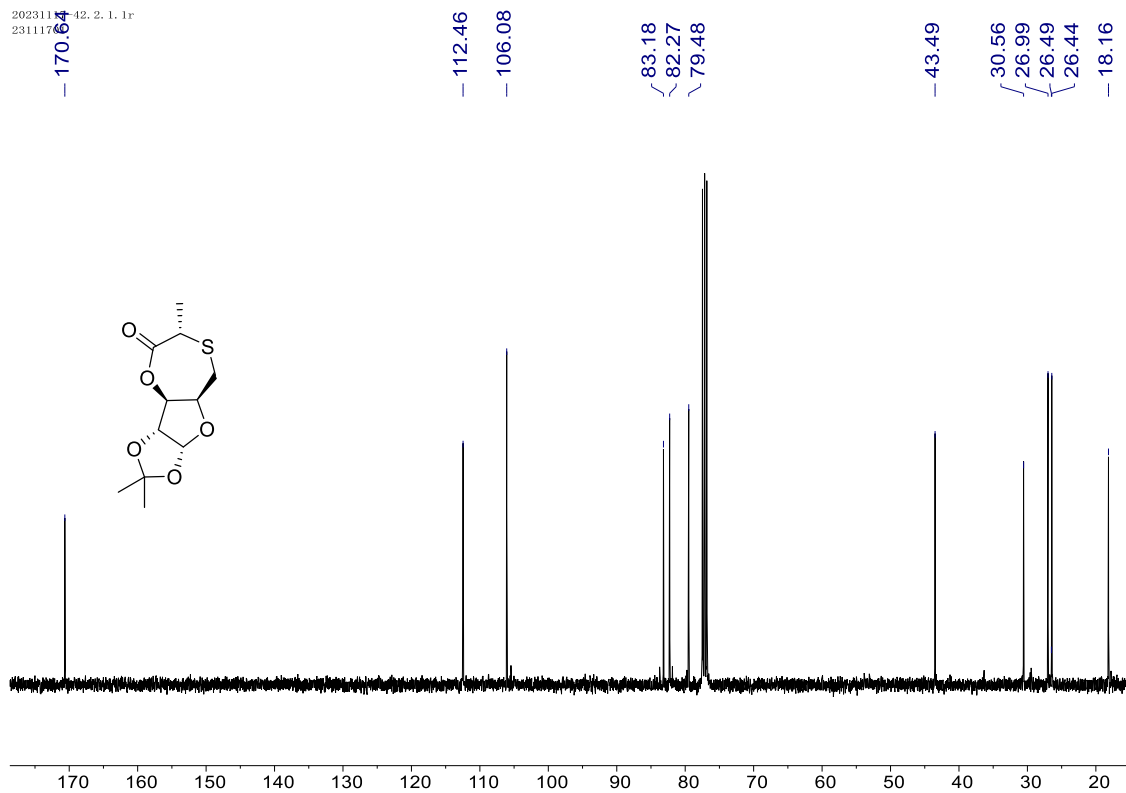


Figure S30. <sup>13</sup>C-NMR spectrum of DM-2S.

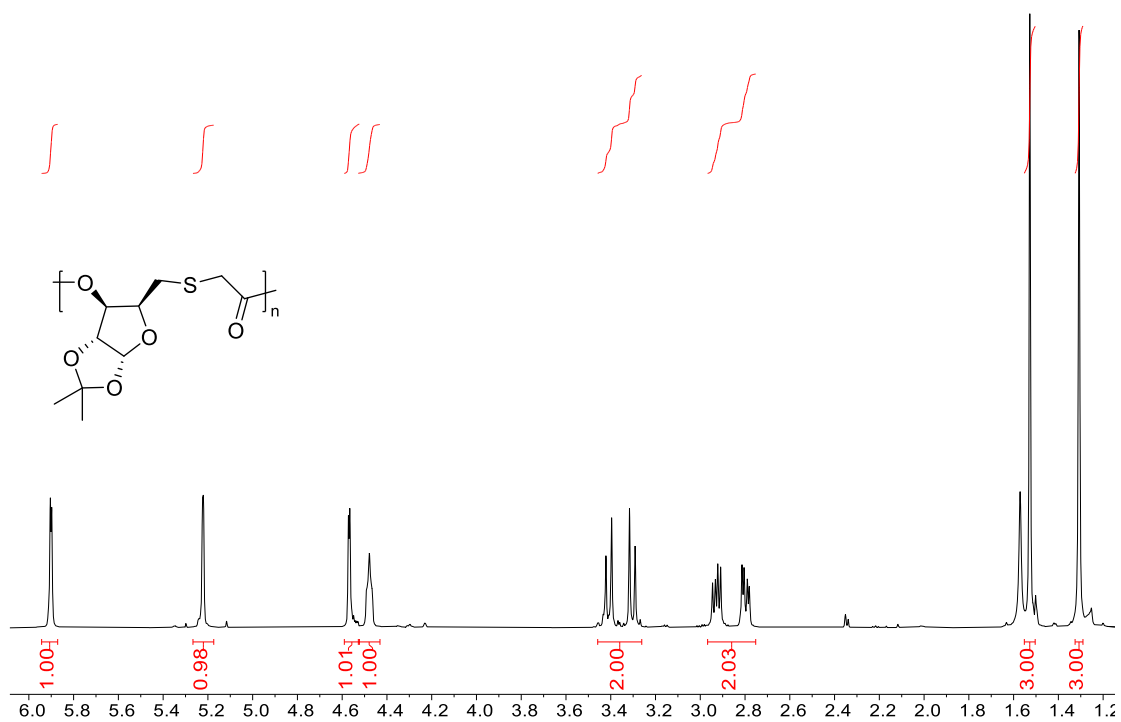


Figure S31. <sup>1</sup>H-NMR spectrum of P(DM-1).

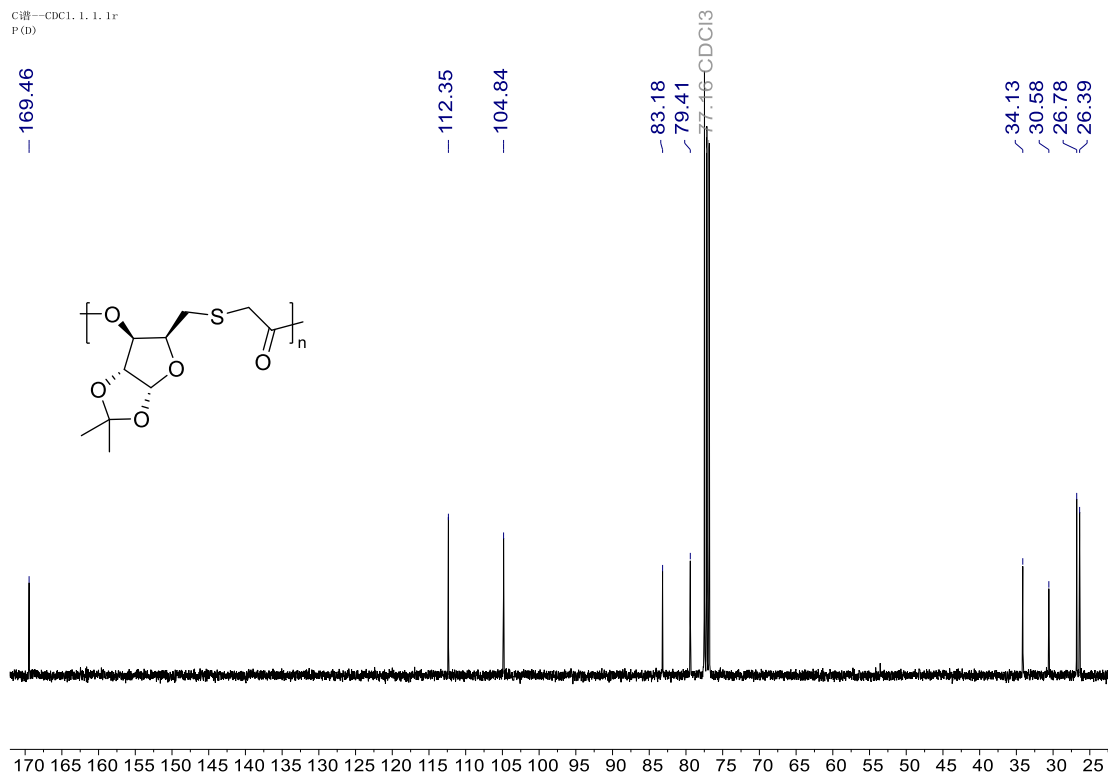


Figure S32. <sup>13</sup>C-NMR spectrum of P(DM-1).

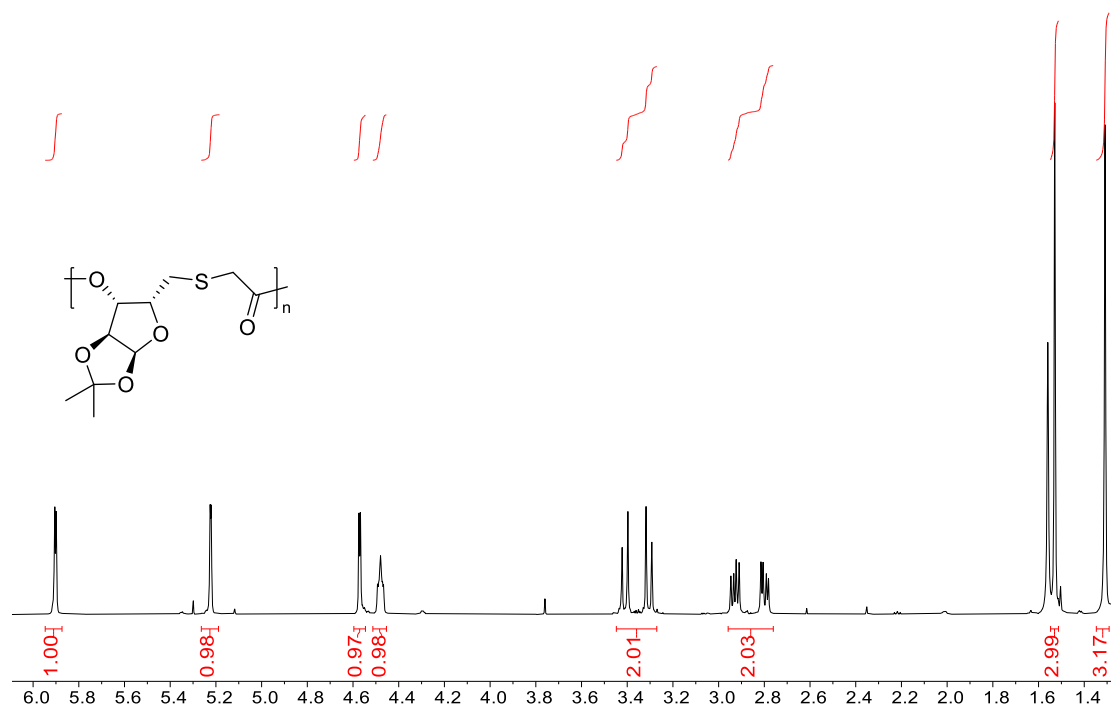


Figure S33. <sup>1</sup>H-NMR spectrum of P(LM).

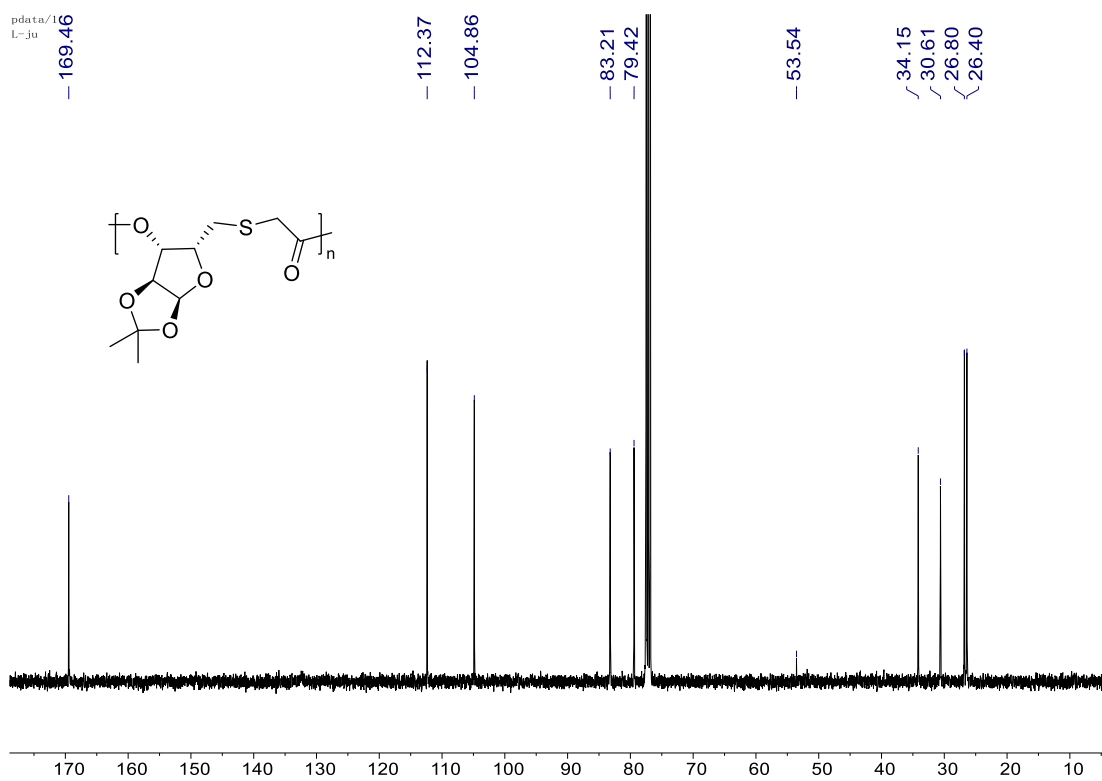


Figure S34. <sup>13</sup>C-NMR spectrum of P(LM).

D-S-H. 540. 1. 1r  
S-JU

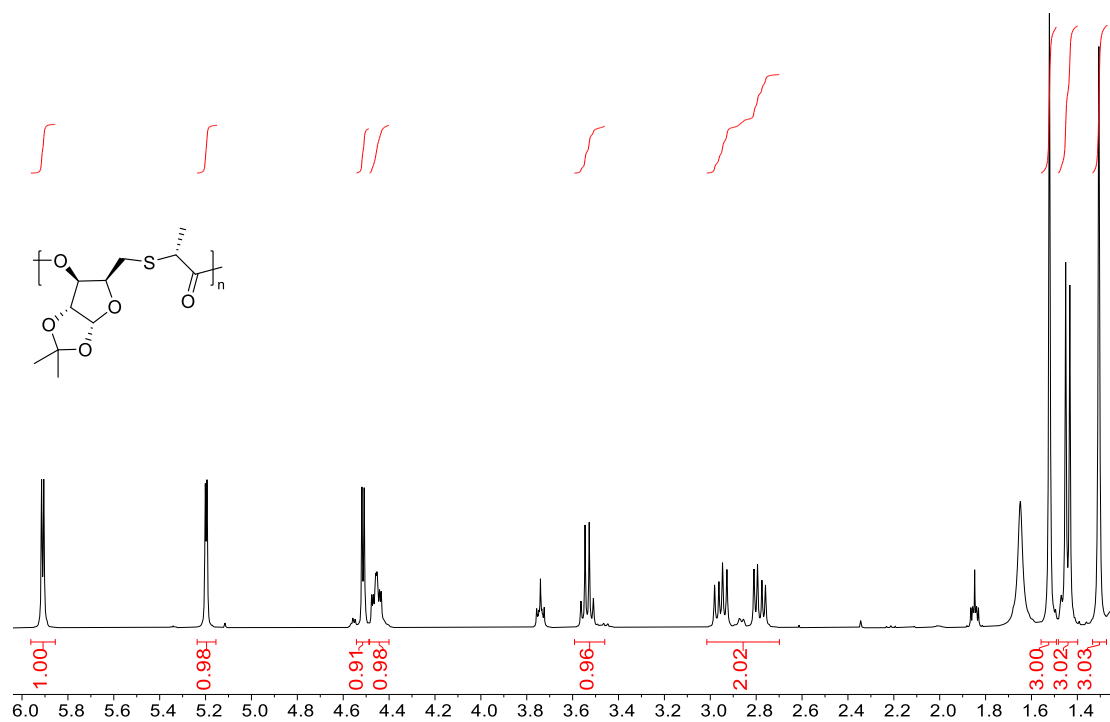


Figure S35. <sup>1</sup>H-NMR spectrum of P(DM-2S).

ww1. 120602. 1. 1r  
D-S-ju

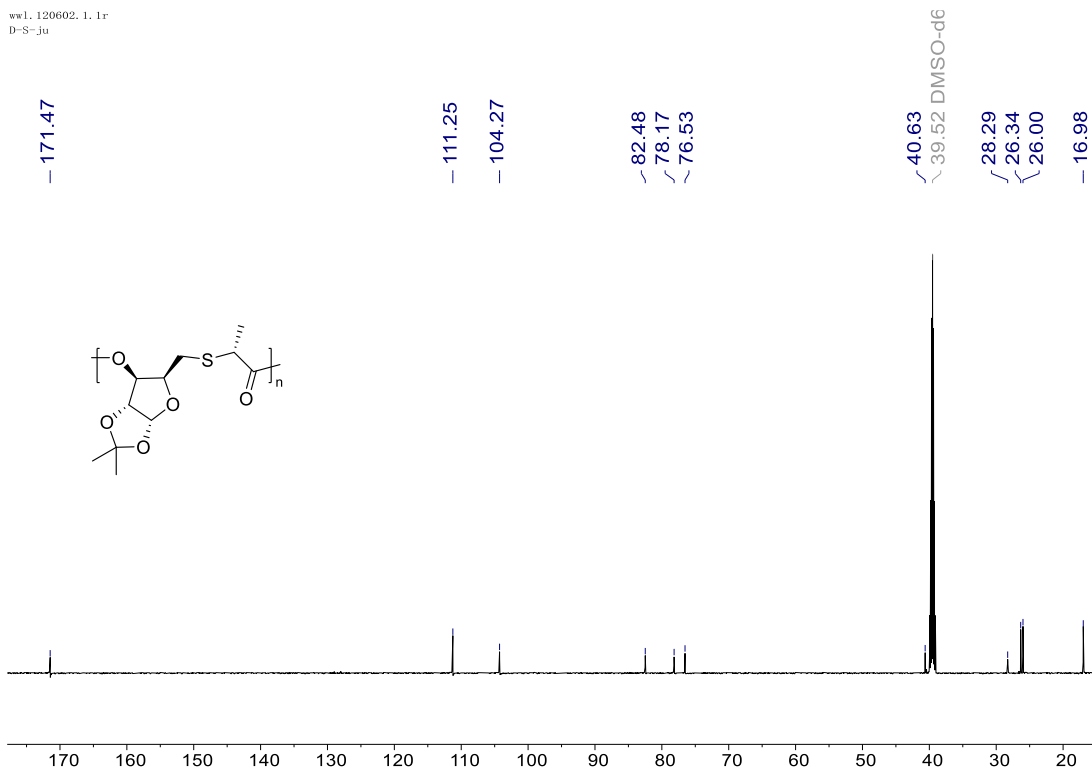
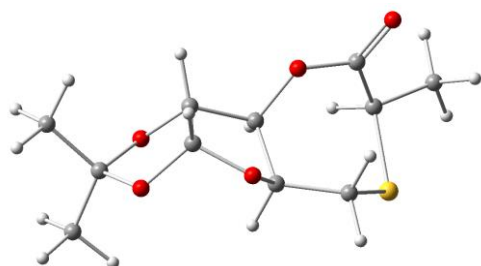


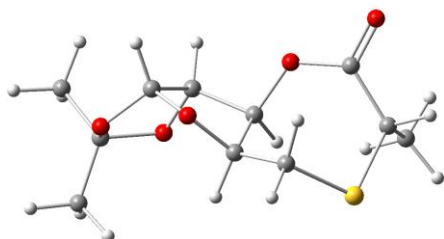
Figure S36. <sup>13</sup>C-NMR spectrum of P(DM-2S).

### 13. Geometries for all the optimized compounds and transition state



	DM-2R		
C	2.17531	0.35122	0.92040
O	1.09004	-0.21736	0.21077
C	1.35693	-1.58255	-0.13200
C	2.46143	-2.02581	0.83132
C	3.2523	-0.73268	0.97786
O	1.86535	-2.36545	2.06485
O	3.99919	-0.483	-0.19858
C	3.78879	0.86324	-0.63500
O	2.78517	1.39865	0.22925
C	0.08174	-2.39216	0.00048
C	5.0561	1.6731	-0.44525
C	3.2947	0.84341	-2.06945
S	-1.08159	-1.98885	-1.35042
C	-2.95397	-1.30717	0.46677
O	-2.5656	-1.33296	1.61418
C	-2.67591	-2.40645	-0.53665
C	-3.7533	-2.57383	-1.59928
O	-3.63006	-0.28895	-0.07719
C	-3.84565	0.87898	0.73547
C	-2.82946	1.94698	0.41726
C	-3.23568	3.27317	0.2664
C	-2.30098	4.27033	-0.00812
C	-0.95464	3.94323	-0.15169
C	-0.54441	2.61729	-0.01087
C	-1.47611	1.62504	0.28160
H	1.81406	0.74048	1.87394
H	1.75215	-1.63497	-1.15572
H	3.05916	-2.84392	0.41405
H	3.87513	-0.69721	1.87905
H	2.56254	-2.66219	2.66599
H	0.31546	-3.46003	-0.03013
H	-0.3881	-2.15504	0.95726
H	5.37344	1.61894	0.5992
H	5.85032	1.27799	-1.08333
H	4.87753	2.71812	-0.71029
H	3.16267	1.86638	-2.43088

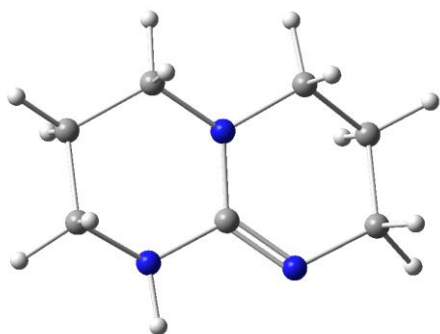
H	4.01981	0.33408	-2.70918
H	2.33408	0.32547	-2.12167
H	-2.53116	-3.32991	0.02883
H	-3.51719	-3.42868	-2.23619
H	-4.72237	-2.74806	-1.12406
H	-3.83437	-1.68012	-2.22185
H	-4.85421	1.2223	0.49812
H	-3.80414	0.58783	1.78779
H	-4.28911	3.52531	0.35936
H	-2.62803	5.29928	-0.12285
H	-0.22805	4.71769	-0.37779
H	0.50128	2.34687	-0.13241
H	-1.13146	0.60141	0.3976



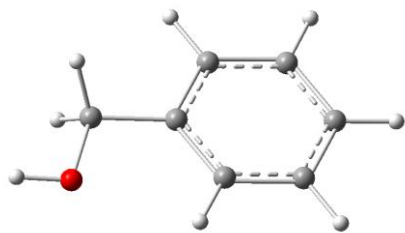
**DM-2S**

C	-1.67377	-0.28642	-1.25133
O	-0.6799	0.60138	-1.68226
C	0.12085	0.9586	-0.55931
C	0.23245	-0.34165	0.23802
C	-1.16548	-0.92715	0.0697
O	1.12191	-1.25891	-0.40214
O	-2.00224	-0.37807	1.06424
C	-3.21978	0.00816	0.43723
O	-2.84193	0.40345	-0.87628
C	1.44623	1.50534	-1.04995
C	-3.78327	1.2023	1.17188
C	-4.18084	-1.1698	0.37184
S	2.62915	1.63137	0.32549
C	2.46472	-1.15665	-0.35849
O	3.10887	-1.95556	-0.99054
C	3.16802	-0.12338	0.51884
C	3.1541	-0.5479	1.99088
H	-1.87832	-0.97889	-2.07077
H	-0.39255	1.70014	0.06835
H	0.48448	-0.19285	1.28805
H	-1.16787	-2.02115	0.0689
H	1.3257	2.51343	-1.45163
H	1.8511	0.87692	-1.84857
H	-4.69354	1.54727	0.67643

H	-4.02529	0.92624	2.20077
H	-3.04687	2.00883	1.17703
H	-4.44739	-1.49392	1.38078
H	-5.08961	-0.87991	-0.16101
H	-3.72	-2.00909	-0.15806
H	4.1983	-0.16328	0.16435
H	3.77878	0.13407	2.57298
H	3.57232	-1.55433	2.08302
H	2.15124	-0.54239	2.42159

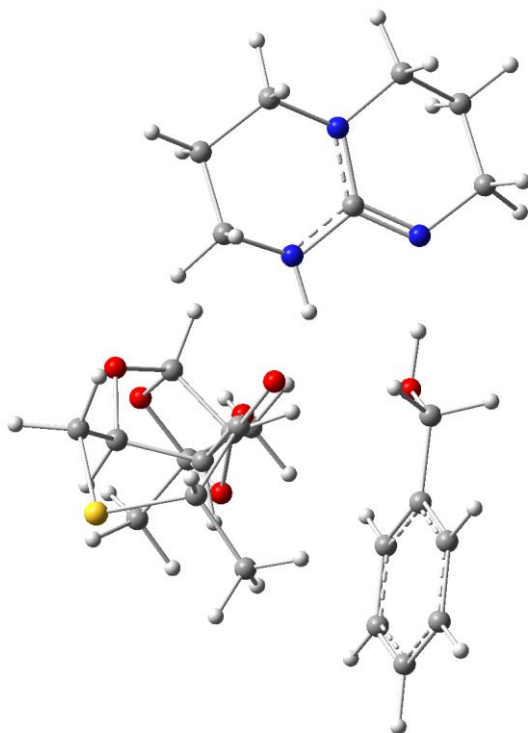


<b>TBD</b>			
C	-2.42439	0.6736	-0.31056
C	-2.40839	-0.75596	0.20117
N	-1.15445	-1.37224	-0.20876
C	0.06225	-0.72646	-0.03258
N	0.02379	0.65769	-0.09042
C	-1.19764	1.3944	0.22204
N	1.1175	-1.45961	0.07042
C	2.41733	-0.81231	0.17111
C	2.43792	0.61121	-0.37503
C	1.25868	1.37151	0.20744
H	-1.06196	-2.35867	-0.00197
H	-3.32873	1.19061	0.02003
H	-2.40591	0.66963	-1.40509
H	-3.22859	-1.33647	-0.22821
H	-2.53325	-0.75768	1.29501
H	-1.10675	2.38771	-0.22928
H	-1.29185	1.53787	1.31086
H	2.73821	-0.79998	1.22355
H	3.15262	-1.42715	-0.36101
H	2.3467	0.59389	-1.46664
H	3.37507	1.11517	-0.12217
H	1.17793	2.3718	-0.23034
H	1.38408	1.49655	1.29506



**BnOH**

C	1.35631	-1.35086	-0.00007
C	-0.00697	-1.05261	-0.00021
C	-0.43583	0.27358	-0.00025
C	0.51627	1.29786	0.00002
C	1.87491	1.00103	0.00019
C	2.30014	-0.32817	0.00009
H	1.67912	-2.38774	-0.0001
H	-0.74505	-1.84693	-0.00037
H	0.18645	2.33449	0.0001
H	2.60358	1.80608	0.0004
H	3.36028	-0.56179	0.0002
C	-1.90289	0.63047	-0.00032
H	-2.11882	1.2498	0.88295
H	-2.11899	1.24866	-0.88437
O	-2.68096	-0.54784	0.00054
H	-3.61055	-0.2875	0.00016

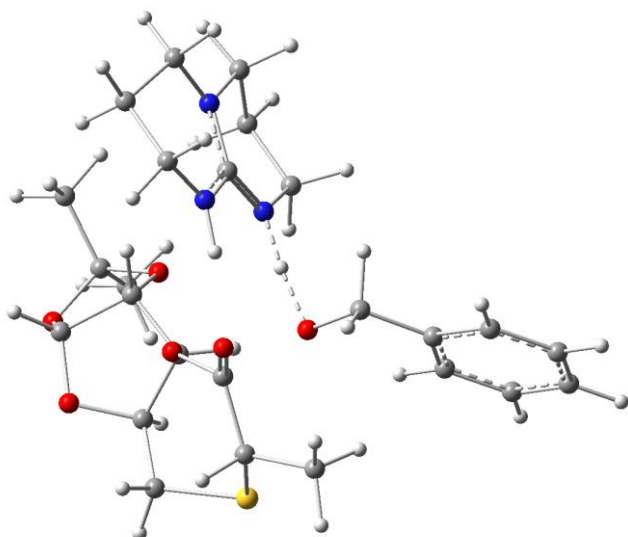


**INT1**

C	0.01185	2.55868	-0.40716
O	-0.33873	2.73634	0.94045

C	-1.59402	2.10038	1.1667
C	-1.53099	0.83454	0.31005
C	-0.77298	1.32285	-0.92027
O	-0.69007	-0.15529	0.91169
O	-1.70979	1.86061	-1.83407
C	-1.18423	3.09624	-2.30209
O	-0.46076	3.62473	-1.19539
C	-1.75804	1.85078	2.65221
C	-2.33489	4.0206	-2.62614
C	-0.24597	2.86359	-3.47753
S	-3.1705	0.74817	2.95044
C	-1.04249	-0.92576	1.95868
O	-0.21565	-1.69563	2.38411
H	1.10118	2.48334	-0.45679
H	-2.41831	2.72169	0.78999
H	-2.50752	0.4231	0.05076
H	-0.14866	0.53737	-1.35715
H	-1.96629	2.7829	3.18148
H	-0.845	1.42488	3.08012
H	-1.95272	4.99507	-2.93836
H	-2.93232	3.60017	-3.43838
H	-2.96341	4.1452	-1.74168
H	-0.79573	2.42771	-4.31529
H	0.19629	3.8108	-3.79563
H	0.56042	2.18043	-3.19343
C	3.46359	1.37006	2.18288
C	2.19166	0.58571	1.91515
N	2.24784	0.0616	0.55713
C	3.3901	-0.49919	0.03031
N	4.58607	-0.12553	0.59162
C	4.65997	0.47077	1.92296
N	3.25844	-1.27247	-1.00759
C	4.43905	-1.85076	-1.63246
C	5.70114	-1.03827	-1.37316
C	5.80717	-0.76689	0.11815
H	1.39801	-0.3793	0.22142
H	3.4854	1.72235	3.21701
H	3.50454	2.24087	1.52001
H	1.31153	1.23021	1.98174
H	2.08099	-0.22161	2.65293
H	5.59199	1.04219	1.97312
H	4.71454	-0.31683	2.69009
H	4.58624	-2.87722	-1.26595
H	4.25371	-1.93073	-2.70888

H	5.64746	-0.08473	-1.9094
H	6.58849	-1.57404	-1.72076
H	6.63993	-0.09112	0.33603
H	5.9881	-1.70362	0.66682
C	-3.38615	-1.97519	-2.09868
C	-2.01446	-1.78923	-1.916
C	-1.25429	-2.74394	-1.23795
C	-1.89093	-3.89115	-0.75172
C	-3.25693	-4.08142	-0.93832
C	-4.01211	-3.12017	-1.61186
H	-3.96275	-1.22305	-2.62973
H	-1.5238	-0.90905	-2.31801
H	-1.3049	-4.6439	-0.22824
H	-3.73373	-4.98054	-0.55907
H	-5.07756	-3.26738	-1.75978
C	0.2338	-2.57363	-1.03455
H	0.42824	-2.47458	0.04748
H	0.73542	-3.50076	-1.35685
O	0.71201	-1.46336	-1.74685
H	1.70437	-1.41087	-1.57322
C	-3.4077	-1.72225	1.6884
H	-3.51577	-1.31485	0.68015
H	-3.036	-2.74685	1.61064
H	-4.39414	-1.74949	2.15861
C	-2.44768	-0.90108	2.55347
H	-2.31955	-1.4146	3.5069

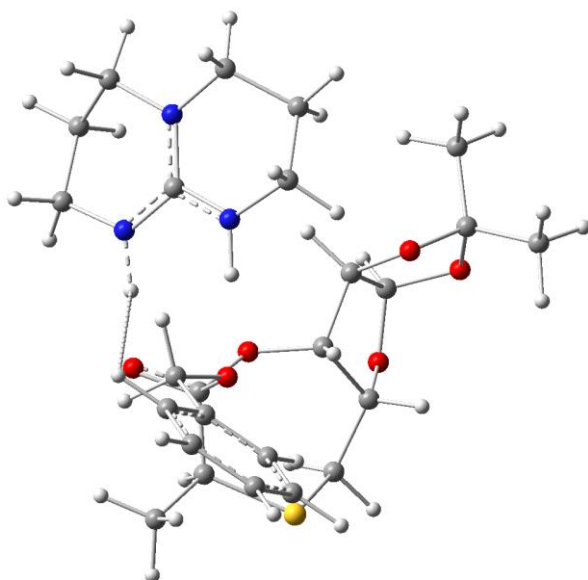


**TS1**

C	3.08584	-2.02516	-0.51653
O	2.27773	-3.08043	-0.93888
C	1.01935	-2.96711	-0.26994

C	0.73639	-1.46364	-0.23884
C	2.14178	-0.90016	-0.01341
O	0.29564	-0.95762	-1.49532
O	2.39969	-0.8231	1.37549
C	3.68781	-1.38022	1.61205
O	3.8358	-2.38833	0.62334
C	0.0013	-3.80301	-1.01614
C	3.69007	-2.02239	2.98029
C	4.77187	-0.32335	1.44399
S	-1.69368	-3.31865	-0.57594
C	-1.02947	-0.79274	-1.84139
O	-1.2455	0.07498	-2.68071
H	3.748	-1.75777	-1.34421
H	1.11349	-3.31013	0.77069
H	0.04808	-1.17899	0.55544
H	2.28424	0.05837	-0.51991
H	0.12578	-4.86368	-0.78902
H	0.1363	-3.66406	-2.09289
H	4.65808	-2.49126	3.17145
H	3.50829	-1.26463	3.74623
H	2.90523	-2.78031	3.02831
H	4.68671	0.43803	2.22356
H	5.75713	-0.79087	1.51494
H	4.68589	0.16124	0.46582
C	2.36328	3.57405	-2.44659
C	0.99394	3.01095	-2.78515
N	0.52126	2.19145	-1.67991
C	0.85564	2.38994	-0.38997
N	1.78341	3.32929	-0.07941
C	2.29412	4.25476	-1.08918
N	0.30102	1.61183	0.52414
C	0.5823	1.74856	1.9461
C	1.94442	2.38369	2.1644
C	2.04853	3.64537	1.32292
H	-0.11284	1.42162	-1.90249
H	2.67609	4.2946	-3.20537
H	3.09945	2.7643	-2.41287
H	1.03312	2.37704	-3.67358
H	0.29076	3.8293	-2.98644
H	3.28898	4.57101	-0.76463
H	1.65791	5.14906	-1.1397
H	-0.20088	2.35146	2.42548
H	0.55262	0.7485	2.38775
H	2.71915	1.67388	1.85751

H	2.09106	2.6253	3.21997
H	3.056	4.06612	1.37467
H	1.34586	4.41079	1.67983
C	-4.81877	-0.22394	2.56967
C	-3.73373	-0.06392	1.70735
C	-3.79549	0.84442	0.65046
C	-4.96579	1.58807	0.4668
C	-6.04921	1.43265	1.3266
C	-5.97884	0.52407	2.38375
H	-4.7581	-0.93639	3.38757
H	-2.824	-0.64317	1.83126
H	-5.02501	2.29429	-0.35921
H	-6.95211	2.01606	1.17083
H	-6.82422	0.39948	3.05358
C	-2.60673	1.04048	-0.27483
H	-2.95656	1.03985	-1.3216
H	-2.22797	2.06815	-0.1008
O	-1.59713	0.10856	-0.08132
H	-0.53916	0.87272	0.21915
C	-3.42556	-1.63913	-1.82259
H	-3.72808	-1.28452	-0.8347
H	-3.6005	-0.84644	-2.55274
H	-4.03721	-2.50456	-2.08871
C	-1.95191	-2.01941	-1.83006
H	-1.7191	-2.49339	-2.79328

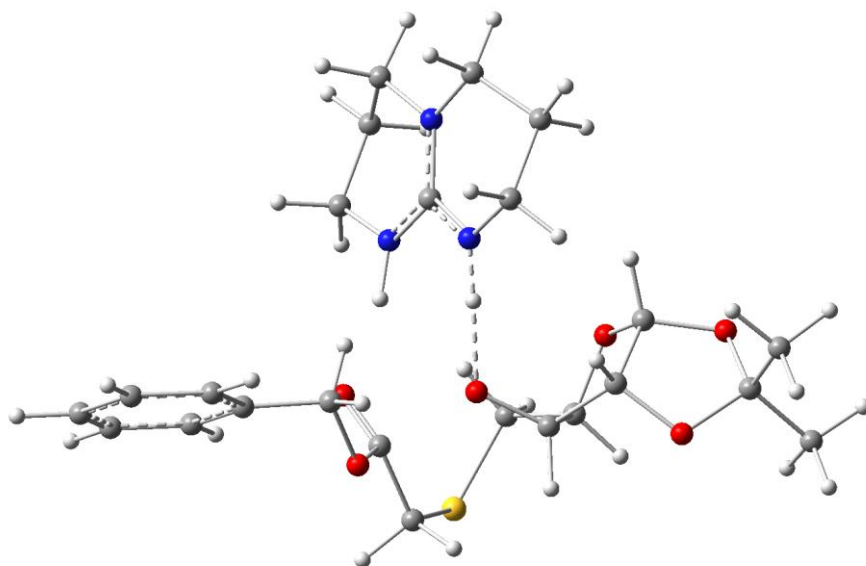


### INT2

C	2.64855	-2.43524	-0.70068
O	1.71645	-3.13779	-1.45717
C	0.41988	-2.94568	-0.87762

C	0.42098	-1.49007	-0.38608
C	1.88207	-1.31787	0.05085
O	0.14587	-0.56476	-1.41745
O	2.01414	-1.66239	1.41995
C	3.13906	-2.52325	1.54732
O	3.18456	-3.24581	0.32748
C	-0.6036	-3.2621	-1.94945
C	2.88383	-3.48614	2.68447
C	4.41456	-1.7098	1.72463
S	-2.26045	-2.63073	-1.55272
C	-1.17341	0.03298	-1.55788
O	-1.0664	1.14615	-2.2261
H	3.4418	-2.09783	-1.37353
H	0.2981	-3.61043	-0.01033
H	-0.24587	-1.35218	0.46702
H	2.2544	-0.31071	-0.15615
H	-0.68104	-4.34131	-2.09931
H	-0.28092	-2.80549	-2.88907
H	3.71505	-4.18951	2.77217
H	2.78694	-2.93663	3.6238
H	1.96153	-4.03855	2.49243
H	4.37198	-1.13828	2.65556
H	5.2808	-2.37545	1.75647
H	4.54177	-1.01468	0.88828
C	2.77302	3.89072	-2.10356
C	1.30808	3.57722	-2.36026
N	0.79347	2.65251	-1.35974
C	1.32301	2.54488	-0.15102
N	2.40781	3.25876	0.22899
C	2.94216	4.29933	-0.64863
N	0.77512	1.66502	0.70879
C	1.22846	1.44712	2.07576
C	2.70273	1.79376	2.17048
C	2.92343	3.18399	1.59589
H	-0.03053	1.96171	-1.68748
H	3.10977	4.69883	-2.75683
H	3.38555	3.00638	-2.30586
H	1.17046	3.11143	-3.33955
H	0.72098	4.5046	-2.35096
H	3.99917	4.42237	-0.40025
H	2.43699	5.25473	-0.45383
H	0.64694	2.06304	2.77317
H	1.06154	0.39555	2.31838
H	3.28689	1.0608	1.60264

H	3.0336	1.76639	3.21112
H	3.98987	3.41884	1.5522
H	2.43816	3.94138	2.22606
C	-4.87686	-0.70526	2.22849
C	-3.83113	-0.38497	1.36185
C	-3.58216	0.94447	1.01976
C	-4.39188	1.94855	1.56053
C	-5.43581	1.62953	2.42289
C	-5.68182	0.29806	2.76077
H	-5.06065	-1.74386	2.48743
H	-3.19794	-1.16077	0.94168
H	-4.19923	2.98762	1.30212
H	-6.05702	2.41937	2.83461
H	-6.49461	0.0477	3.4355
C	-2.47333	1.32695	0.06595
H	-2.88448	1.69816	-0.87722
H	-1.90254	2.16202	0.50128
O	-1.61189	0.23029	-0.17016
H	0.0081	1.09137	0.35863
C	-3.54068	-0.39255	-2.40845
H	-4.04349	-0.34173	-1.43697
H	-3.48574	0.61346	-2.83067
H	-4.1441	-1.01977	-3.06956
C	-2.12949	-0.95342	-2.2765
H	-1.69925	-1.08356	-3.27519

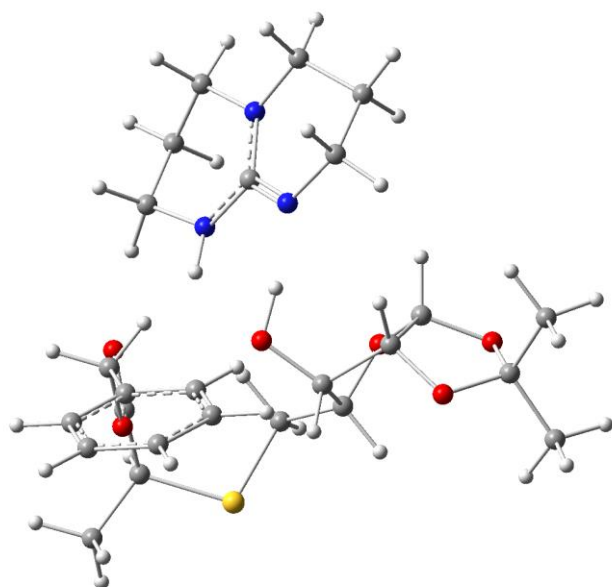


**TS2**

C	-3.19875	0.19189	-0.1989
O	-2.75833	0.07947	1.12319
C	-2.18479	-1.22257	1.32368
C	-1.50459	-1.53826	-0.02422

C	-2.5291	-0.94875	-0.9986
O	-0.27668	-0.92129	-0.14448
O	-3.58741	-1.8702	-1.20394
C	-4.80114	-1.14068	-1.20336
O	-4.58455	-0.05701	-0.30509
C	-1.20951	-1.09755	2.47525
C	-5.89934	-2.02708	-0.65892
C	-5.10424	-0.599	-2.59456
S	-0.28953	-2.61811	2.8569
C	1.2988	-1.69841	0.69259
O	1.76598	-0.75142	1.33973
H	-2.98291	1.21018	-0.53775
H	-2.9759	-1.95299	1.54567
H	-1.46114	-2.62646	-0.19205
H	-2.06673	-0.63799	-1.94222
H	-1.73829	-0.85239	3.40084
H	-0.49904	-0.30159	2.2502
H	-6.83604	-1.46791	-0.59928
H	-6.04487	-2.88862	-1.31502
H	-5.62315	-2.37547	0.3387
H	-5.24523	-1.42285	-3.2988
H	-6.01247	0.00835	-2.57115
H	-4.27752	0.02691	-2.9451
C	0.68861	-2.92331	1.35407
H	1.53073	-3.53941	1.6874
H	0.13058	-3.50572	0.62203
C	0.86463	3.96779	2.49892
C	1.47827	2.58311	2.38888
N	0.8447	1.85557	1.29722
C	0.28782	2.44053	0.22798
N	0.19704	3.78251	0.15057
C	0.87994	4.62974	1.13028
N	-0.19333	1.64705	-0.72917
C	-0.72296	2.17489	-1.97835
C	-1.35401	3.53651	-1.73594
C	-0.34615	4.43677	-1.04059
H	1.06515	0.85345	1.21814
H	1.43098	4.57337	3.20949
H	-0.1673	3.89226	2.85519
H	1.32821	2.00963	3.30656
H	2.55805	2.66	2.21132
H	0.3477	5.58337	1.15639
H	1.90966	4.82536	0.80368
H	0.07544	2.25556	-2.72684

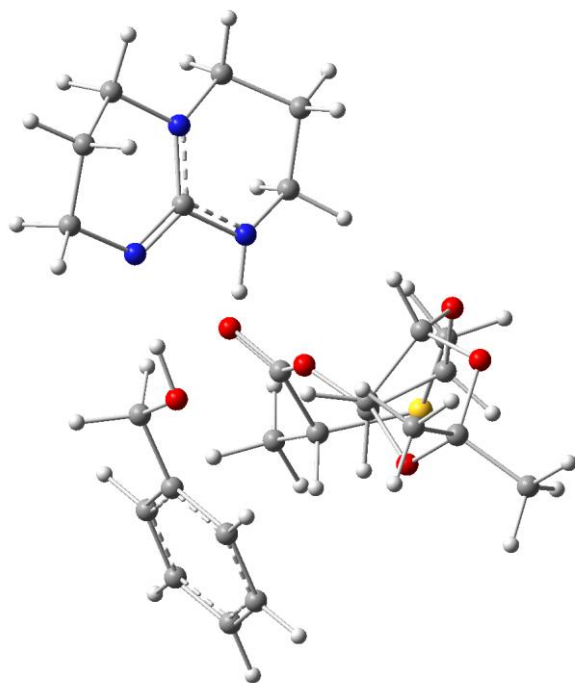
H	-1.46149	1.46466	-2.35738
H	-2.24215	3.42477	-1.10518
H	-1.65795	3.99165	-2.68108
H	-0.81932	5.3666	-0.71451
H	0.47389	4.69715	-1.72253
C	6.03884	-1.28232	-0.06295
C	4.6471	-1.27773	-0.0734
C	3.95099	-1.13015	-1.27698
C	4.66902	-0.9893	-2.46492
C	6.06333	-0.9867	-2.45504
C	6.75141	-1.13514	-1.25351
H	6.57096	-1.40006	0.87641
H	4.08247	-1.38108	0.84888
H	4.13274	-0.88632	-3.40517
H	6.61021	-0.87887	-3.38691
H	7.83707	-1.14037	-1.24365
C	2.44196	-1.09511	-1.28683
H	2.08219	-0.12185	-0.93774
H	2.0664	-1.25383	-2.30239
O	1.88825	-2.12056	-0.46993
H	-0.24231	0.59743	-0.51037



			<b>TM1</b>
C	2.196	1.93607	0.54254
O	1.80822	1.16839	1.64651
C	0.40191	1.34213	1.84668
C	-0.16589	1.39637	0.41884
C	0.91254	2.2317	-0.27604
O	-0.29857	0.12796	-0.15856
O	0.67256	3.60655	-0.04161

C	1.91773	4.21329	0.26597
O	2.66055	3.20706	0.94405
C	-0.08714	0.1865	2.6948
C	1.67247	5.37039	1.20788
C	2.64414	4.62149	-1.00886
S	-1.86925	0.38841	3.04945
C	-2.21703	-1.75253	1.33512
O	-1.38897	-2.59447	1.04846
H	2.98545	1.38961	0.01971
H	0.21341	2.30459	2.34688
H	-1.13208	1.90995	0.38723
H	0.99708	2.00363	-1.34497
H	0.47407	0.14054	3.63047
H	0.06493	-0.74423	2.14247
H	2.62352	5.82099	1.50093
H	1.06005	6.12953	0.71559
H	1.15403	5.0104	2.09925
H	2.06348	5.37237	-1.55057
H	3.62433	5.03801	-0.76411
H	2.78932	3.75233	-1.65812
C	2.87391	-4.32396	0.76217
C	1.42907	-3.86694	0.67736
N	1.40403	-2.47493	0.25668
C	2.23534	-1.97128	-0.71204
N	3.3773	-2.67714	-0.98824
C	3.5459	-4.06846	-0.57649
N	1.91642	-0.82293	-1.24449
C	2.76862	-0.25784	-2.27961
C	4.21825	-0.70567	-2.15144
C	4.25164	-2.22184	-2.0628
H	0.49439	-2.0275	0.29111
H	2.92531	-5.38844	1.00326
H	3.39192	-3.76439	1.54753
H	0.93008	-3.93105	1.64638
H	0.8755	-4.50848	-0.02393
H	4.62112	-4.26083	-0.51136
H	3.13585	-4.7446	-1.34191
H	2.38802	-0.53674	-3.2733
H	2.70746	0.83544	-2.22227
H	4.66006	-0.28057	-1.24318
H	4.80914	-0.36853	-3.00723
H	5.26178	-2.57931	-1.84019
H	3.94614	-2.66852	-3.02083
C	-3.61039	1.62894	-2.88658

C	-2.9212	0.68602	-2.1288
C	-3.53507	-0.51917	-1.77715
C	-4.84397	-0.7701	-2.19088
C	-5.53454	0.17235	-2.95032
C	-4.91822	1.37304	-3.2977
H	-3.12784	2.56266	-3.159
H	-1.89956	0.8628	-1.80082
H	-5.32131	-1.70806	-1.91848
H	-6.55154	-0.03044	-3.27154
H	-5.45527	2.10744	-3.89021
C	-2.78778	-1.51172	-0.93304
H	-3.15687	-2.53106	-1.08149
H	-1.71602	-1.47567	-1.13346
O	-3.00027	-1.14946	0.44971
H	0.57555	-0.1595	-0.59456
C	-3.97252	-1.34245	3.10106
H	-4.52661	-0.63042	2.48544
H	-4.37408	-2.34325	2.91998
H	-4.12359	-1.09526	4.15422
C	-2.48473	-1.3107	2.76113
H	-1.92575	-1.99507	3.40284

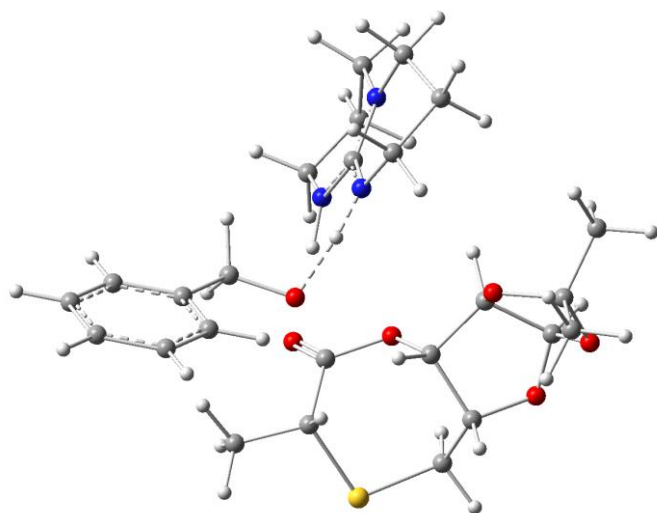


### INT3

C	-0.01954	2.5989	0.48112
O	-0.52449	2.26953	1.7502
C	-1.74676	1.54945	1.59318
C	-1.52214	0.70925	0.33461

C	-0.68286	1.63465	-0.53521
O	-0.70223	-0.42355	0.63691
O	-1.56639	2.46284	-1.26736
C	-1.05965	3.7889	-1.19962
O	-0.44574	3.87873	0.08288
C	-1.97223	0.72514	2.84597
C	-2.22052	4.75462	-1.2608
C	-0.0234	4.01949	-2.28994
S	-3.33848	-0.4612	2.66683
C	-1.20972	-1.54329	1.19649
O	-0.44365	-2.42092	1.50671
H	1.07117	2.54979	0.53874
H	-2.58546	2.23543	1.41613
H	-2.44044	0.41476	-0.17475
H	0.01369	1.08227	-1.17364
H	-2.25189	1.3661	3.68534
H	-1.05064	0.20291	3.12042
H	-1.85734	5.77961	-1.15777
H	-2.73495	4.65813	-2.21967
H	-2.92019	4.53612	-0.45116
H	-0.48683	3.92038	-3.27459
H	0.40156	5.02167	-2.19516
H	0.78642	3.28816	-2.2072
C	-2.71567	-1.64115	1.38099
H	-3.18804	-1.38326	0.42658
C	3.32465	0.49519	2.63038
C	2.06567	-0.07687	2.00376
N	2.23357	-0.09266	0.55623
C	3.40842	-0.4819	-0.04824
N	4.55796	-0.37789	0.69538
C	4.52294	-0.30773	2.15401
N	3.35275	-0.83936	-1.29807
C	4.5742	-1.21253	-1.99671
C	5.82019	-0.59272	-1.3774
C	5.80625	-0.86245	0.11779
H	1.41167	-0.35715	0.02359
H	3.26196	0.45281	3.72047
H	3.44043	1.54235	2.33127
H	1.19687	0.54718	2.22918
H	1.86798	-1.08525	2.39484
H	5.45683	0.15996	2.48039
H	4.49434	-1.32107	2.58314
H	4.67771	-2.30747	-2.00204
H	4.47862	-0.90611	-3.0438

H	5.82254	0.48923	-1.54797
H	6.72657	-1.00905	-1.82506
H	6.62615	-0.33895	0.61933
H	5.92987	-1.93819	0.31495
C	-3.26741	-0.98869	-2.60592
C	-1.87643	-0.94636	-2.493
C	-1.17255	-2.04662	-2.00176
C	-1.88364	-3.19404	-1.63261
C	-3.26965	-3.24287	-1.75644
C	-3.96881	-2.13573	-2.24024
H	-3.80122	-0.12122	-2.98357
H	-1.32756	-0.05523	-2.78047
H	-1.34178	-4.05468	-1.24503
H	-3.80629	-4.14247	-1.46884
H	-5.04991	-2.16987	-2.33287
C	0.3322	-2.02641	-1.86709
H	0.58823	-2.32082	-0.83492
H	0.75029	-2.80624	-2.52532
O	0.8472	-0.76146	-2.1871
H	1.83238	-0.78092	-1.97058
C	-3.11795	-3.05009	1.7908
H	-4.2029	-3.10957	1.90975
H	-2.81433	-3.76236	1.02063
H	-2.64127	-3.32668	2.73295

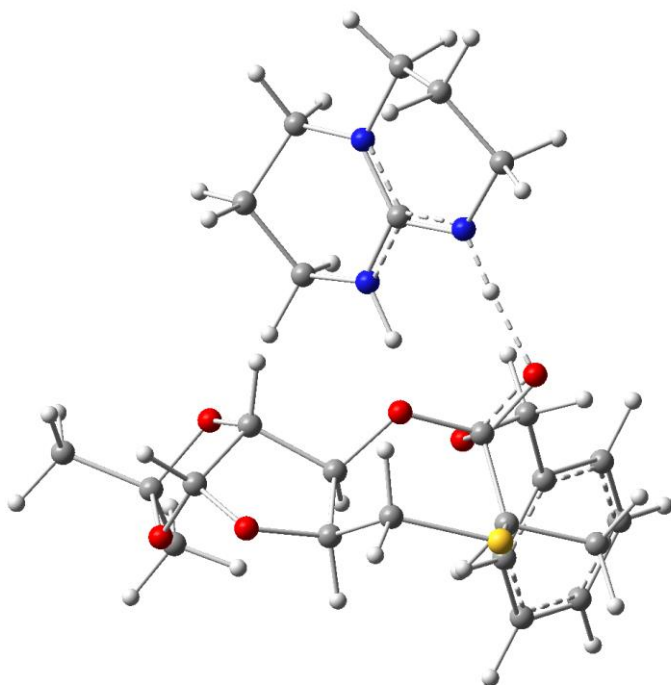


**TS3**

C	3.47689	-1.42585	-0.35496
O	3.02385	-2.27418	-1.35703
C	1.6633	-2.65047	-1.10523
C	1.03934	-1.43439	-0.38694
C	2.23642	-0.76089	0.28618
O	0.45176	-0.54827	-1.3258
O	2.28066	-1.15345	1.6464

C	3.60137	-1.60583	1.9295
O	4.06442	-2.15301	0.7059
C	1.0587	-2.92379	-2.47188
C	3.5233	-2.70565	2.96278
C	4.47564	-0.43501	2.35833
S	-0.70577	-3.36035	-2.47332
C	-0.89662	-0.69585	-1.59179
O	-1.37057	0.092	-2.40691
H	4.20278	-0.74088	-0.80208
H	1.62749	-3.53582	-0.458
H	0.31911	-1.70711	0.38478
H	2.20533	0.32635	0.17204
H	1.56471	-3.77648	-2.93184
H	1.22451	-2.04585	-3.09864
H	4.52113	-3.10404	3.15986
H	3.10994	-2.31282	3.89457
H	2.88047	-3.50629	2.5906
H	4.08393	0.00828	3.27765
H	5.49917	-0.7747	2.53509
H	4.4948	0.33323	1.57888
C	-1.49406	-2.09405	-1.38458
H	-1.3519	-2.40791	-0.35277
C	0.78823	4.52495	-2.44118
C	-0.41811	3.60428	-2.51055
N	-0.35026	2.62353	-1.4358
C	0.27955	2.82983	-0.2669
N	0.95479	3.98216	-0.05718
C	0.91099	5.07435	-1.02913
N	0.23713	1.86513	0.64417
C	0.85272	1.98697	1.95883
C	1.99857	2.98401	1.91461
C	1.51253	4.26996	1.26398
H	-0.70558	1.68475	-1.63704
H	0.6759	5.34982	-3.14807
H	1.69542	3.96972	-2.69892
H	-0.44626	3.05607	-3.45441
H	-1.34319	4.18865	-2.43245
H	1.83571	5.64576	-0.91583
H	0.07128	5.74492	-0.80244
H	0.10422	2.30887	2.69439
H	1.2075	0.99524	2.25626
H	2.82969	2.57522	1.3291
H	2.36121	3.19098	2.92403
H	2.33916	4.96986	1.1199

H	0.75971	4.76157	1.89443
C	-4.40125	-1.60637	2.68729
C	-3.41384	-1.03847	1.88169
C	-3.70509	0.05356	1.06477
C	-5.00606	0.56775	1.06419
C	-5.99341	0.00523	1.86772
C	-5.69335	-1.08649	2.68414
H	-4.16075	-2.45736	3.31833
H	-2.40097	-1.42914	1.87052
H	-5.24389	1.41625	0.42535
H	-6.99957	0.4143	1.85591
H	-6.46307	-1.528	3.3098
C	-2.62775	0.68031	0.19386
H	-3.018	0.78411	-0.83743
H	-2.48409	1.72077	0.55132
O	-1.43203	-0.01411	0.2019
H	-0.42745	1.0015	0.44841
C	-2.97887	-2.10484	-1.71611
H	-3.37797	-3.12123	-1.65268
H	-3.52241	-1.48557	-0.99971
H	-3.1469	-1.71437	-2.72148

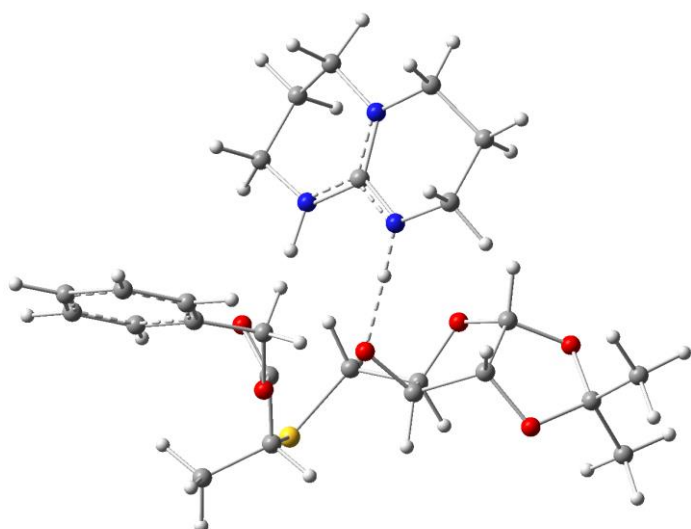


**INT4**

C	1.71004	-3.51427	-0.12594
O	1.03156	-3.82336	-1.28876
C	-0.05253	-2.89765	-1.49519
C	0.20362	-1.69753	-0.5399

C	1.54661	-2.02201	0.13672
O	0.31429	-0.47046	-1.22159
O	1.52644	-1.89895	1.54109
C	1.26726	-3.19646	2.1096
O	1.06729	-4.07283	1.01292
C	-0.01149	-2.49263	-2.9592
C	-0.00497	-3.15118	2.93068
C	2.48579	-3.60957	2.9187
S	-1.48049	-1.56104	-3.51114
C	-0.8991	0.28201	-1.4412
O	-0.63789	1.34801	-2.1167
H	2.73598	-3.88419	-0.21965
H	-0.99464	-3.40474	-1.25693
H	-0.56751	-1.63987	0.23481
H	2.3449	-1.40394	-0.28142
H	0.0204	-3.39454	-3.57579
H	0.89103	-1.90607	-3.1399
H	-0.21824	-4.13906	3.34672
H	0.10732	-2.43994	3.75279
H	-0.84101	-2.84106	2.29903
H	2.66108	-2.89035	3.72306
H	2.33039	-4.59911	3.35576
H	3.36971	-3.63817	2.27563
C	-2.0045	-0.64477	-2.01162
H	-2.27916	-1.38209	-1.25043
C	3.71556	3.33941	-1.87736
C	2.23263	3.23932	-2.19106
N	1.55308	2.41827	-1.19803
C	2.01806	2.2288	0.03047
N	3.18198	2.78128	0.44166
C	3.88407	3.73318	-0.41869
N	1.3243	1.44048	0.86845
C	1.64573	1.27021	2.27813
C	3.15025	1.36874	2.45499
C	3.63981	2.66415	1.82736
H	0.62836	1.94346	-1.52196
H	4.18933	4.08425	-2.52054
H	4.20211	2.37453	-2.05121
H	2.06478	2.78046	-3.16867
H	1.78658	4.24167	-2.21431
H	4.93781	3.71308	-0.13045
H	3.50659	4.74983	-0.24541
H	1.14093	2.0355	2.88188
H	1.27775	0.28804	2.57732

H	3.63071	0.51301	1.96951
H	3.41227	1.35617	3.51525
H	4.73237	2.69513	1.81009
H	3.2892	3.5276	2.4085
C	-4.96146	0.22238	1.98553
C	-3.76109	0.3523	1.28583
C	-3.25934	1.61491	0.97092
C	-3.9772	2.74746	1.37002
C	-5.17413	2.61999	2.06716
C	-5.67149	1.35352	2.37796
H	-5.3408	-0.76692	2.22413
H	-3.20002	-0.52507	0.97937
H	-3.59131	3.73588	1.12946
H	-5.72112	3.50839	2.36861
H	-6.60527	1.25228	2.92232
C	-1.96532	1.79197	0.20552
H	-2.14558	2.30391	-0.74668
H	-1.30165	2.45028	0.78962
O	-1.32048	0.56225	-0.02629
H	0.49206	0.97905	0.49852
C	-3.23791	0.15953	-2.40174
H	-4.00258	-0.48112	-2.84955
H	-3.67403	0.63002	-1.516
H	-2.95947	0.94195	-3.11161

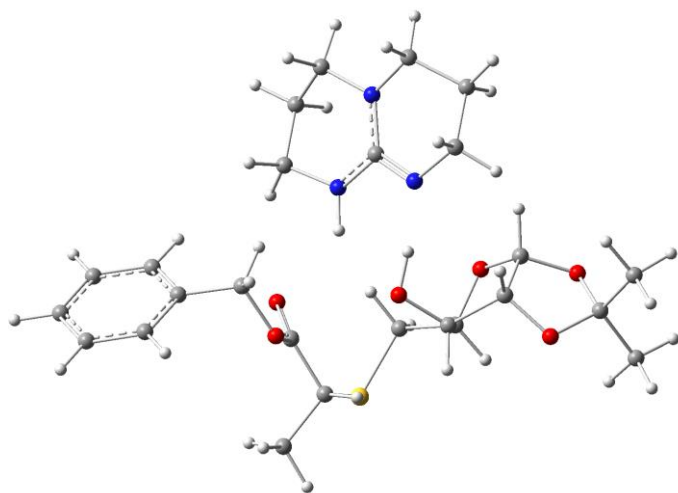


**TS4**

C	-3.27367	0.20812	-0.13724
O	-2.79115	-0.04127	1.15059
C	-2.1799	-1.34106	1.18239
C	-1.52687	-1.47704	-0.20707
C	-2.59086	-0.80755	-1.08282
O	-0.3203	-0.81246	-0.27911

O	-3.62687	-1.72938	-1.37914
C	-4.86028	-1.04325	-1.26203
O	-4.6534	-0.07814	-0.23602
C	-1.17342	-1.33074	2.31257
C	-5.92092	-2.02501	-0.81587
C	-5.20899	-0.33768	-2.56653
S	-0.20707	-2.86137	2.46631
C	1.31074	-1.61628	0.43186
O	1.74564	-0.74387	1.19587
H	-3.10186	1.2663	-0.35906
H	-2.94639	-2.11437	1.33492
H	-1.45664	-2.53685	-0.5015
H	-2.15978	-0.37012	-1.99021
H	-1.67807	-1.22283	3.27711
H	-0.49067	-0.49225	2.17225
H	-6.87136	-1.5071	-0.66737
H	-6.05686	-2.79939	-1.57466
H	-5.61282	-2.4899	0.12319
H	-5.34181	-1.06856	-3.36824
H	-6.13341	0.2333	-2.44923
H	-4.40809	0.35307	-2.84835
C	0.79339	-2.95976	0.93578
H	0.20872	-3.42874	0.14357
C	0.735	3.80166	2.82158
C	1.38542	2.45659	2.54975
N	0.74208	1.82833	1.40366
C	0.13685	2.5035	0.41721
N	0.00466	3.84274	0.48473
C	0.69069	4.60378	1.53061
N	-0.34777	1.79959	-0.60581
C	-0.92118	2.43805	-1.78188
C	-1.58242	3.74839	-1.38603
C	-0.5843	4.60088	-0.61988
H	0.98192	0.8452	1.21983
H	1.30395	4.34745	3.57712
H	-0.28334	3.65603	3.19483
H	1.27872	1.78499	3.4048
H	2.45698	2.58607	2.35386
H	0.13227	5.53214	1.6712
H	1.70441	4.8656	1.20007
H	-0.14317	2.6185	-2.53445
H	-1.6496	1.75014	-2.21766
H	-2.45363	3.54627	-0.75419
H	-1.91905	4.2902	-2.27258

H	-1.07566	5.47647	-0.18775
H	0.21196	4.95645	-1.28692
C	6.00587	-0.91536	-0.28974
C	4.61518	-0.97616	-0.29639
C	3.90037	-0.6503	-1.45284
C	4.59861	-0.26599	-2.59823
C	5.99112	-0.19782	-2.5907
C	6.69816	-0.52449	-1.43614
H	6.55263	-1.17259	0.61264
H	4.06673	-1.26696	0.59506
H	4.04791	-0.02298	-3.50379
H	6.52264	0.10033	-3.48942
H	7.78287	-0.47906	-1.42944
C	2.39108	-0.68282	-1.45492
H	1.99215	0.21498	-0.97177
H	2.01485	-0.71291	-2.4821
O	1.88917	-1.83608	-0.79144
H	-0.35308	0.73054	-0.49759
C	1.99782	-3.85004	1.2588
H	1.67076	-4.81719	1.65096
H	2.5807	-4.02407	0.35128
H	2.63594	-3.36883	2.00511



**TM2**

C	-3.53902	-0.05982	0.32762
O	-2.66799	-0.36468	1.37683
C	-1.96788	-1.57396	1.05593
C	-1.71464	-1.45505	-0.45516
C	-3.03627	-0.83511	-0.91703
O	-0.61264	-0.64828	-0.76635
O	-4.00051	-1.85627	-1.09157
C	-5.21853	-1.39772	-0.52609
O	-4.83067	-0.57805	0.56939

C	-0.73695	-1.61337	1.93841
C	-5.98961	-2.59036	-0.00707
C	-6.00099	-0.57238	-1.53918
S	0.30326	-3.09202	1.75264
C	1.88714	-1.506	0.06757
O	2.08712	-0.71464	0.9631
H	-3.57835	1.02846	0.23323
H	-2.61186	-2.44417	1.24911
H	-1.58702	-2.44187	-0.91456
H	-2.91836	-0.22016	-1.81663
H	-1.0497	-1.63253	2.98648
H	-0.13287	-0.71894	1.78572
H	-6.90897	-2.25719	0.47995
H	-6.25033	-3.25526	-0.83391
H	-5.37582	-3.13429	0.71425
H	-6.275	-1.18969	-2.39843
H	-6.91062	-0.17874	-1.079
H	-5.39707	0.27067	-1.88965
C	1.19699	-2.85188	0.18264
H	0.51062	-2.92541	-0.66322
C	1.23912	3.69913	2.10165
C	1.64665	2.37823	1.47356
N	0.49442	1.8161	0.7894
C	-0.38556	2.56633	0.05113
N	-0.41551	3.91431	0.29796
C	0.65622	4.59432	1.02096
N	-1.17364	1.93643	-0.77605
C	-2.11869	2.69823	-1.5785
C	-2.52755	4.00668	-0.91558
C	-1.27145	4.76487	-0.52079
H	0.56755	0.84922	0.49544
H	2.10235	4.18839	2.55911
H	0.48865	3.52031	2.87808
H	1.97303	1.65804	2.22666
H	2.48683	2.54172	0.78075
H	0.22812	5.50033	1.4604
H	1.44652	4.90868	0.32247
H	-1.68466	2.91076	-2.56669
H	-3.00374	2.07638	-1.75853
H	-3.12095	3.79929	-0.01811
H	-3.1345	4.6145	-1.59181
H	-1.51901	5.65099	0.07164
H	-0.73104	5.10536	-1.41673
C	6.28495	0.26167	0.45273

C	4.94216	0.38355	0.10104
C	4.46319	-0.20747	-1.06915
C	5.34179	-0.9329	-1.87862
C	6.68205	-1.06205	-1.52572
C	7.15565	-0.46187	-0.3594
H	6.65024	0.72779	1.36258
H	4.25323	0.931	0.73786
H	4.97021	-1.394	-2.79048
H	7.35805	-1.62548	-2.16139
H	8.20171	-0.55795	-0.0852
C	3.01102	-0.09636	-1.45562
H	2.51848	0.72314	-0.92588
H	2.90116	0.04874	-2.53151
O	2.30651	-1.32477	-1.18826
H	-0.89788	0.3264	-0.82224
C	2.24608	-3.9669	0.08109
H	1.76548	-4.9461	0.1438
H	2.76685	-3.896	-0.87635
H	2.97963	-3.88331	0.88773

## 14. References

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- [S3] G. M. Sheldrick, SHELXTL Structure Determination Programs, version 5.0, PC; Siemens Analytical Systems, Madison, WI, 1994.
- [S4] G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16, Program for Quantum Chemical Calculations*, Gaussian, Inc., Wallingford CT (USA), **2016**.