

## Supporting Information

### Synthesis and Controlled Organobase-Catalyzed Ring-Opening

### Polymerization of Morpholine-2, 5-Dione Derivatives and Monomer

### Recovery by Acid-Catalyzed Degradation of the Polymers

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## 1. Materials and methods

### *Materials*

All reagents were purchased from commercial suppliers and used directly unless otherwise specified. Ethyl isocyanoacetate (98%, Heowns); 4-methylbenzenesulfonic acid (99%, Xiya Reagent); boric acid (99.5%, Xilong); molecular sieves 4Å ; Amberlyst (R) 15 ion-exchange resin (Acros); acetaldehyde, 40% solution in H<sub>2</sub>O; propionaldehyde (98%, Energy Chemical); butyraldehyde (98%, Energy Chemical); isobutyraldehyde (98%, Ourchem); 10-undecenal (94%, TCI); undecanal (98%, Adamas); phenylpropylaldehyde (95%, Energy Chemical); benzyl alcohol (Superdry, 99%, J&K); triazabicyclo[4.4.0]dec-5-ene (TBD, 98%, J&K); diazabicyclo[5.4.0]undec-7-ene (DBU, 98%, J&K); cyclohexylamine (99%, Sinopharm); 3,5-bis(trifluoromethyl)-2-chlorophenylisothiocyanate (99%, J&K); *rac*-Lactide (99%, J&K; recrystallized from dry toluene prior to use); caprolactam (CP; Sinopharm; recrystallized from dry toluene prior to use); trimethoxymethane (99%, J&K); *L*-Leucine ethyl ester hydrochloride(98%; J&K); *L*-Phenylalanine (99%; J&K); *rac*-Phenylalanine (99%, J&K); phosphorus oxychloride (99.5%, Energy Chemical); *N*-methyl morpholine (NMM, 99%, Macklin); thionyl chloride (99%, Macklin); trifluoromethanesulfonic acid (TfOH, 99%, J&K), trifluoromethanesulfonimide (HNTf<sub>2</sub>, 99%, J&K), diphenyl phosphate (DPP, 99%, TCI). 1-(3,5-Bis (trifluoromethyl)-phenyl-3-cyclohexyl-2-thiourea) (TU) was synthesized according to previously reported procedure.<sup>1</sup>

### *General characterization and instrumentation*

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 MHz or 500 MHz spectrometers and are reported as δ values in ppm relative to the reported solvent (CDCl<sub>3</sub> referenced to 7.26). Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), and combinations thereof.

Electrospray ionization (ESI) mass spectrum were recorded on a Bruker Apex IV or Bruker Solarix XR Fourier transform mass spectrometer in the positive ion mode with high resolution.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum were recorded on a Bruker Autoflex III mass spectrometer equipped with a 355 nm laser. α-Cyano-4-hydroxycinnamic acid was used as the matrix and the spectrum were acquired in linear mode.

Elemental analysis was performed on ElementarVario MICRO CUBE (Germany) with twice parallel test.

Size exclusion chromatography (SEC) was performed on a Waters system equipped with a Waters 1525 binary HPLC pump, a Waters 2414 refractive index detector, and three Waters Styragel HT columns (HT2, HT3, HT4) thermostated at 35 °C. THF was used as eluent at a flow rate of 1.0 mL/min. The calibration was made against linear polystyrene standards, and the data was collected and processed with Breeze software.

Recycling preparative HPLC was performed on a JAI LaboACE LC-5060 series equipped with two JAIGEL HR columns (2HR, 2.5 HR), a UV detector, and a RI detector. Chloroform (added 0.05% ethanol) was used as eluent at a flow rate of 8.0 mL/min. The data was collected and processed with the JAI Scan software.

Differential scanning calorimetry (DSC) was performed on a TA Q100 differential scanning calorimeter under a nitrogen atmosphere of 50 mL/min. The heating rate was set to 10 °C/min.

Thermal gravimetric analysis (TGA) was performed on a Q600-SDT thermogravimetric analyzer (TA Co. Ltd.) at a heating rate of 10 °C/min under a nitrogen flow of 100 mL/min.

Thermal gravimetric-infrared-gas chromatography/mass spectrometry (TG-IR-GC MS) was performed on a Perkin Elmer analysis system equipped with a Perkin Elmer Clarus 6000 GC/MS, a Perkin Elmer Frontier FT-IR, Pyris 1 TGA and TL9000 temperature control module. The heating rate was 20 °C/min.

Single crystal X-ray diffraction data was collected at room temperature (150K) using graphite-monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) on a SuperNova X-ray Diffraction System from Agilent Technologies. Data reduction and empirical absorption correction were performed using the CrysAlisPro program. The structure was solved by using SHELXT program. All non-hydrogen atoms could be located directly from the difference Fourier maps. Framework hydrogen atoms were placed geometrically and constrained using the riding model to the parent atoms. Final structure refinement was done using the SHELXL program by minimizing the sum of squared deviations of  $F^2$  using a full-matrix technique.

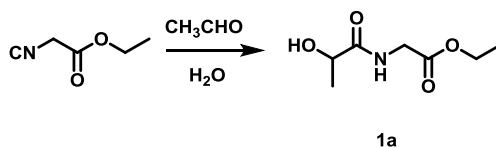
The enantiomeric excess (ee%) was also acquired on high performance liquid chromatography (HPLC) equipped with a JASCO PU-2089 pump, a AS-2055 automatic sampler, a UV-2070 UV-Vis spectrometer, a CD-2095 circular dichroism spectrometer and a Daicel Chiralpak IC column at a flow rate of 1.0 mL/min with isopropanol/hexane = 20/80 as the eluent.

The specific optical rotation was acquired on a JASCO Model P-1030 digital polarimeter in a 50 mm cell at 25 °C.

## 2. Preparation and characterization of monomers 2a-2i

### 2.1 Synthesis of monomer 2a

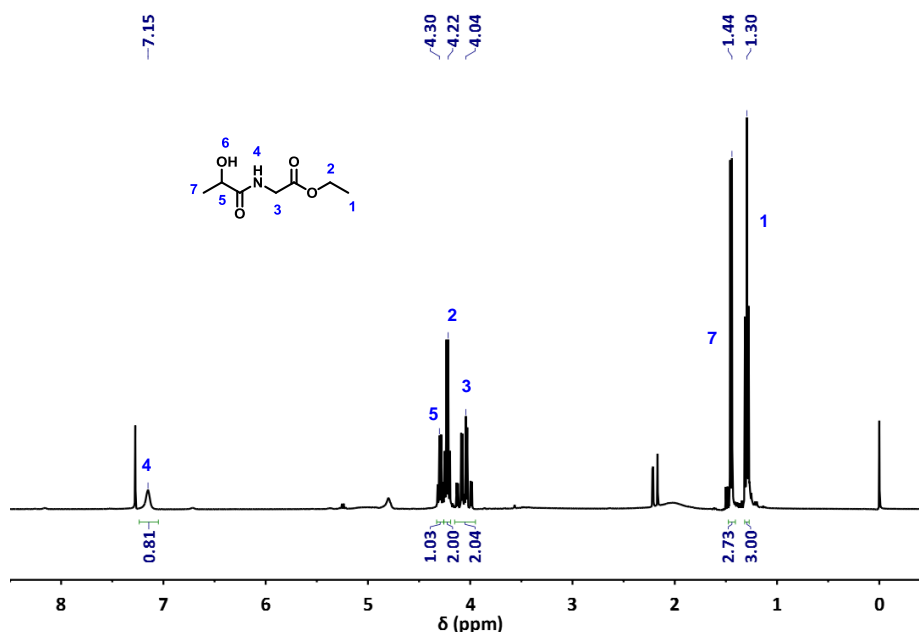
Ethyl 2-(2-hydroxy propanamido) acetate (**1a**)<sup>2</sup>



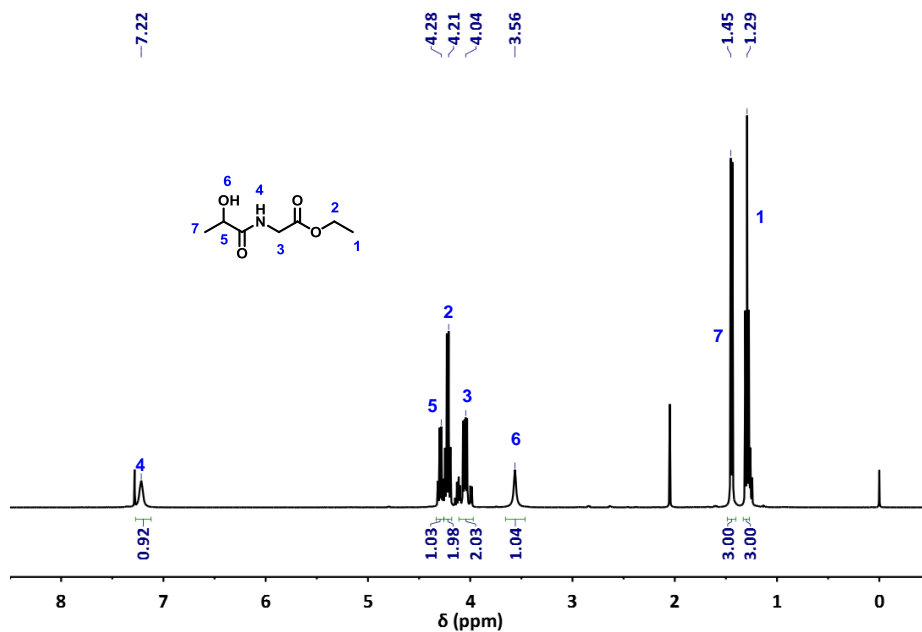
In a 250 mL round bottom flask, ethyl isocyanoacetate (5 g, 0.044 mol) was dissolved in 40% acetaldehyde solution (125 mL), and the reaction mixture was vigorously stirred at room temperature for 12 h. The reaction mixture was concentrated *in vacuo* to provide the crude product which was used directly in the next step without further purification. Optionally, the crude product can be further purified by flash column chromatography (EtOAc/PE=1/1), affording a colorless oil (6.77 g, 88%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.22 (s, 1H), 4.28 (q, 1H), 4.21 (q, 2H), 4.04 (m, 2H), 3.56 (s, 1H), 1.45 (d, 3H), 1.29 (t, 3H).

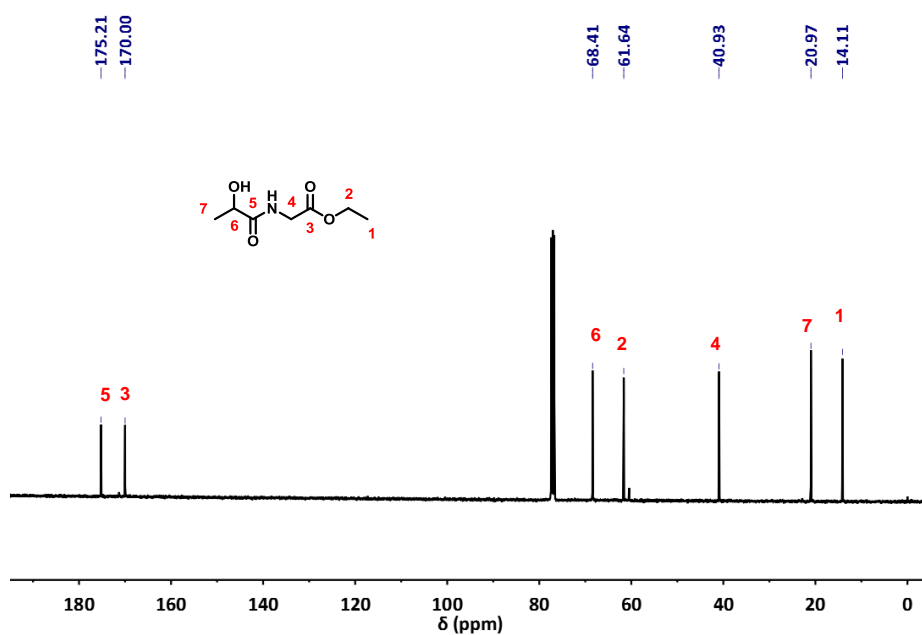
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 175.21, 170.00, 68.41, 61.64, 40.93, 20.97, 14.11.



**Figure S1.** <sup>1</sup>H NMR spectrum of crude compound **1a** in CDCl<sub>3</sub>.

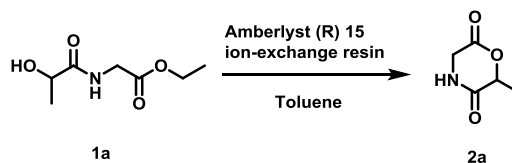


**Figure S2.** <sup>1</sup>H NMR spectrum of purified compound **1a** in CDCl<sub>3</sub>.



**Figure S3.** <sup>13</sup>C NMR spectrum of purified compound **1a** in CDCl<sub>3</sub>.

6-Methyl-morpholine-2, 5-dione (**2a**)<sup>3</sup>



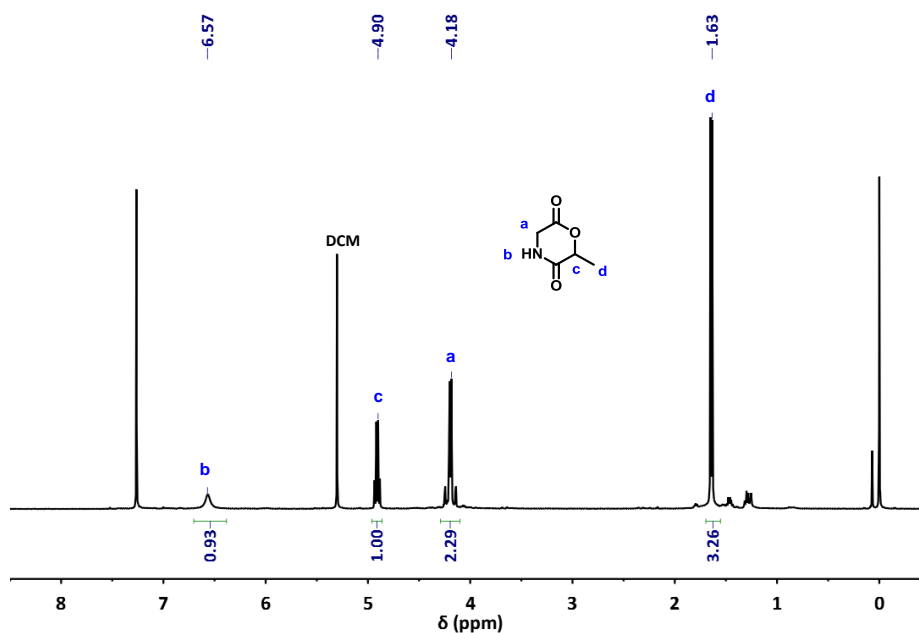
In a 1000 mL round bottom flask equipped with a Soxhlet extractor (filled with 4Å molecular sieve) and a reflux condenser, compound **1a** (3.5 g, 0.02 mol) and a catalytic amount of Amberlyst (R) 15 ion-exchange resin were added into 500 mL of toluene. The reaction mixture was allowed to reflux for 48 h. and then cooled to room temperature, filtered to remove the ion exchange resin, and finally concentrated to remove the solvent under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/PE = 1/1) to provide the desired product (**2a**) as a white solid (2.37 g, 87%).  $T_m = 99.3$  °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.07 (s, 1H), 4.90 (q,  $J = 7.0$  Hz, 1H), 4.18 (m, 2H), 1.63 (d,  $J = 7.0$  Hz, 3H).

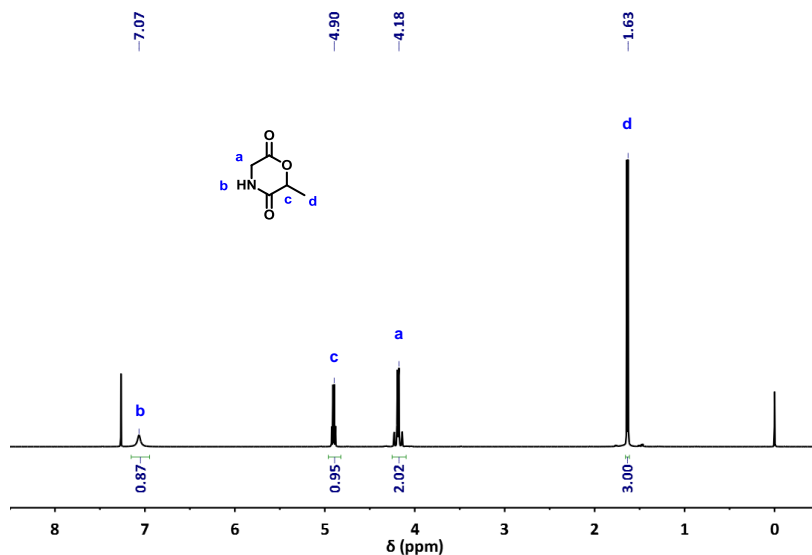
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 168.72, 165.15, 74.74, 43.73, 16.88.

HRMS (FAB+):  $m/z$  [M+H]<sup>+</sup> calcd. for C<sub>5</sub>H<sub>8</sub>NO<sub>3</sub>: 130.0425; found: 130.0498.

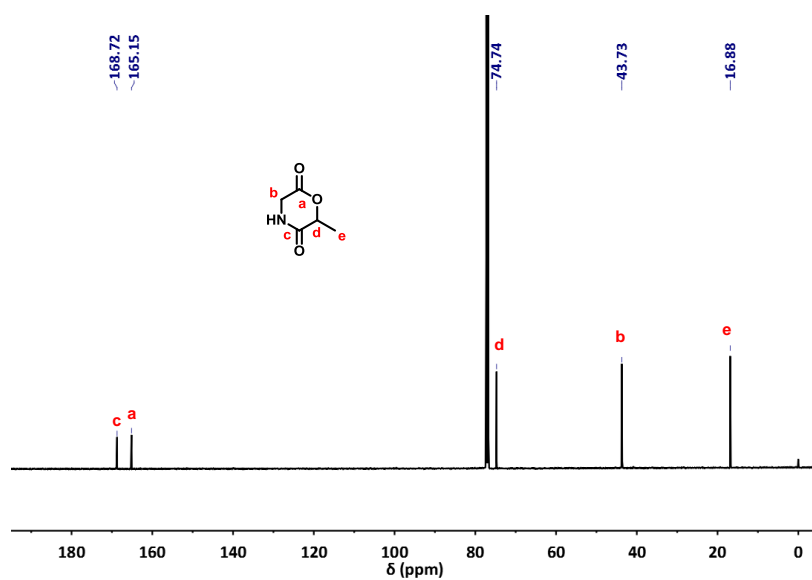
Elemental analysis: calcd. for C<sub>5</sub>H<sub>7</sub>NO<sub>3</sub>: C, 46.51; H, 5.46; N, 10.85. Found: C, 46.55; H, 5.38; N, 10.86.



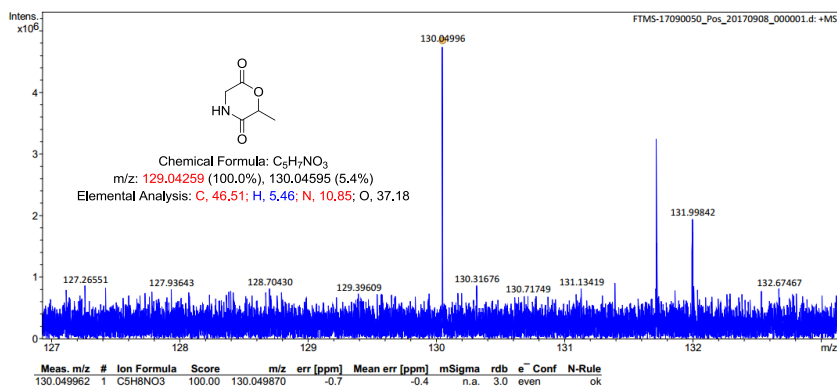
**Figure S4.** <sup>1</sup>H NMR spectrum of crude monomer **2a** in CDCl<sub>3</sub>.



**Figure S5.**  $^1\text{H}$  NMR spectrum of purified monomer **2a** in  $\text{CDCl}_3$ .



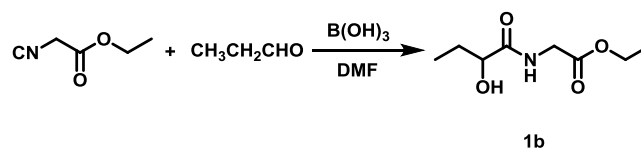
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of purified monomer **2a** in  $\text{CDCl}_3$ .



**Figure S7.** ESI-MS spectrum of monomer **2a**.

## 2.2 Synthesis of monomer 2b

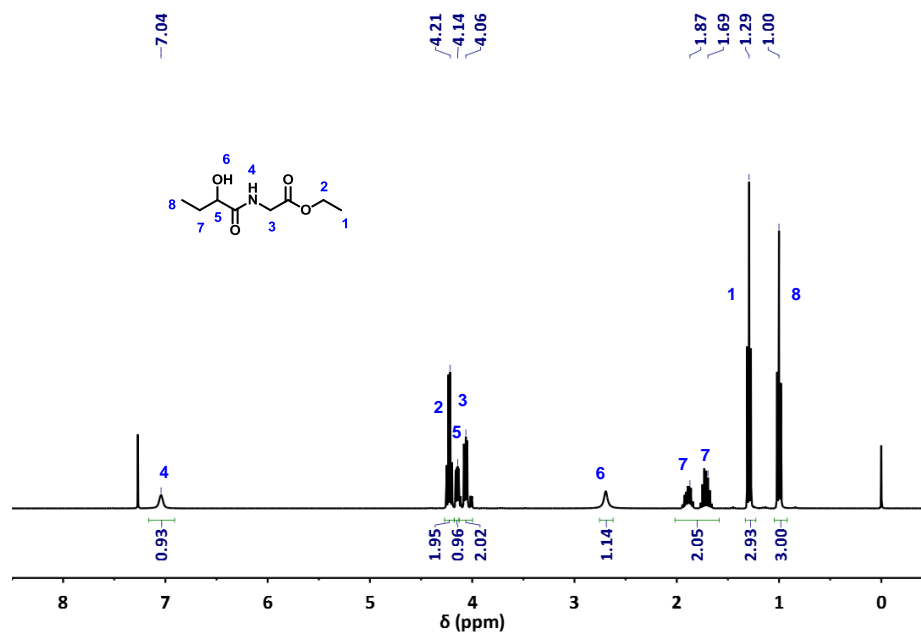
Ethyl 2-(2-hydroxy butanamido) acetate (**1b**)<sup>4</sup>



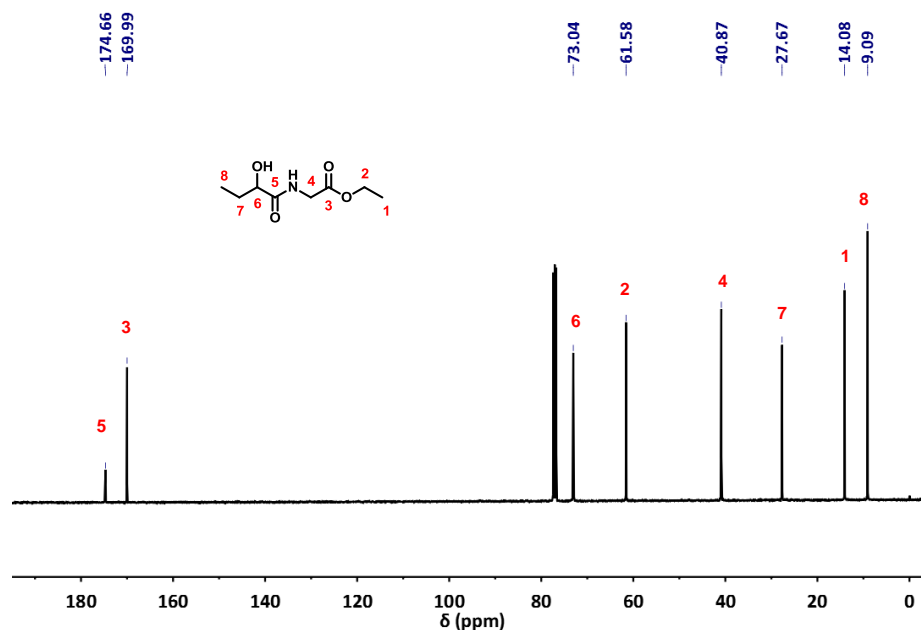
In a 500 mL round bottom flask, propionaldehyde (5.8 g, 0.1 mol), ethyl isocyanoacetate (11.3 g, 0.1 mol) and boric acid (7.2 g, 0.12 mol) were dissolved in DMF (200 mL). The reaction mixture was stirred for 48 h at room temperature and quenched with H<sub>2</sub>O (100 mL). Then the reaction mixture was concentrated in *vacuo*. The crude product was further purified by flash column chromatography (EtOAc/PE=1/1), affording a white solid (16.1 g, 85%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.04 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.14 (dd, *J* = 7.3, 4.1 Hz, 1H), 4.06 (m, 2H), 2.69 (s, 1H), 1.87 (m, *J* = 15.0, 7.5, 4.1 Hz, 1H), 1.69 (m, *J* = 14.6, 7.3 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 174.66, 169.99, 73.04, 61.58, 40.87, 27.67, 14.08, 9.09.

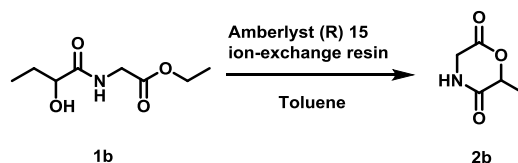


**Figure S8.** <sup>1</sup>H NMR spectrum of compound **1b** in CDCl<sub>3</sub>.



**Figure S9.**  $^{13}\text{C}$  NMR spectrum of compound **1b** in  $\text{CDCl}_3$ .

#### 6-Ethyl-morpholine-2, 5-dione (**2b**)



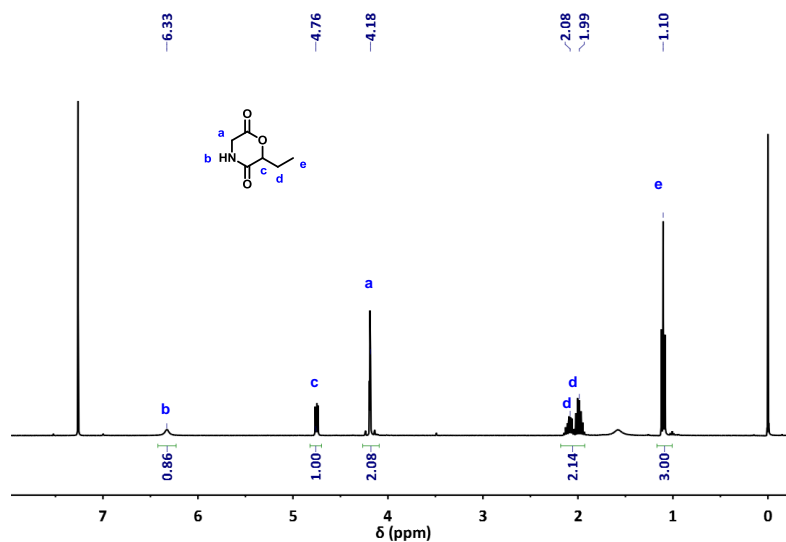
In a 1000 mL round bottom flask equipped with a Soxhlet extractor (filled with 4Å molecular sieve) and a reflux condenser, compound **1b** (3.8 g, 0.02 mol) and a catalytic amount of Amberlyst (R) 15 ion-exchange resin were added in 500 mL of toluene. The reaction mixture was allowed to reflux for 48 h., and then cooled to room temperature, filtered to remove the ion exchange resin, and concentrated to remove the solvent under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/PE = 1/1) to provide the desired product (**2b**) as a white solid (2.03 g, 71%).  $T_m = 95.0\text{ }^\circ\text{C}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.33 (s, 1H), 4.76 (dd,  $J = 7.3, 4.7$  Hz, 1H), 4.18 (m, 2H), 2.08 (m, 1H), 1.99 (m, 1H), 1.10 (t,  $J = 7.4$  Hz, 3H).

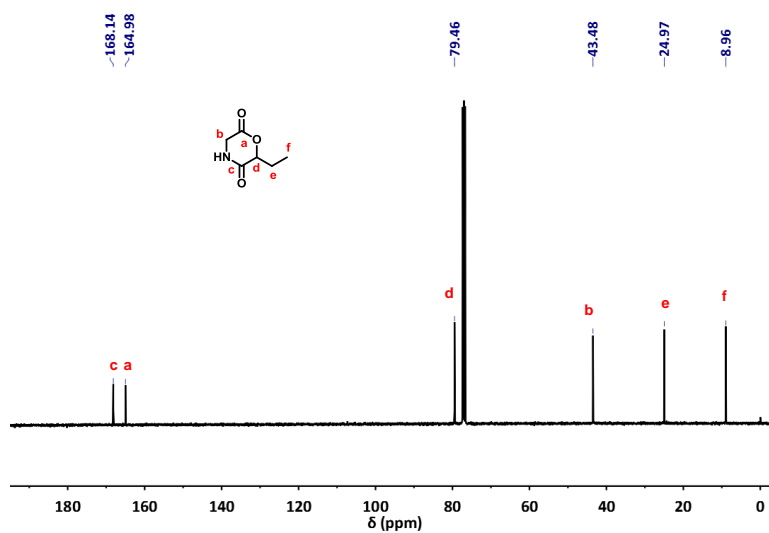
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 168.14, 164.98, 79.46, 43.48, 24.97, 8.96;

HRMS (FAB+):  $m/z$   $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_6\text{H}_{10}\text{NO}_3$ : 144.0582; found: 144.0655;

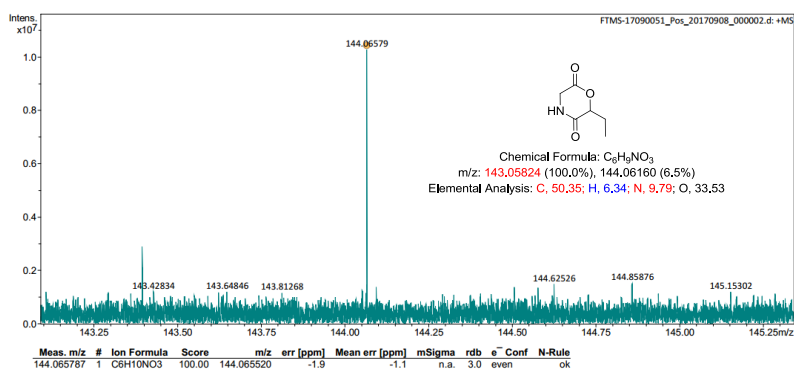
Elemental Analysis: calcd. for  $\text{C}_6\text{H}_9\text{NO}_3$ , C, 50.35; H, 6.34; N, 9.79. Found: C, 48.17; H, 6.61; N, 9.36.



**Figure S10.** <sup>1</sup>H NMR spectrum of monomer **2b** in CDCl<sub>3</sub>.



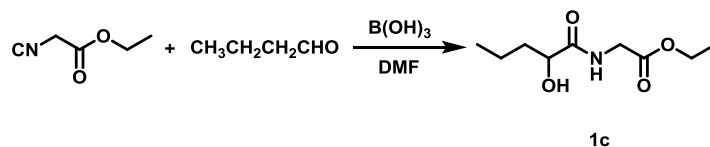
**Figure S11.** <sup>13</sup>C NMR spectrum of monomer **2b** in CDCl<sub>3</sub>.



**Figure S12.** ESI-MS spectrum of monomer **2b**.

### 2.3 Synthesis of monomer 2c

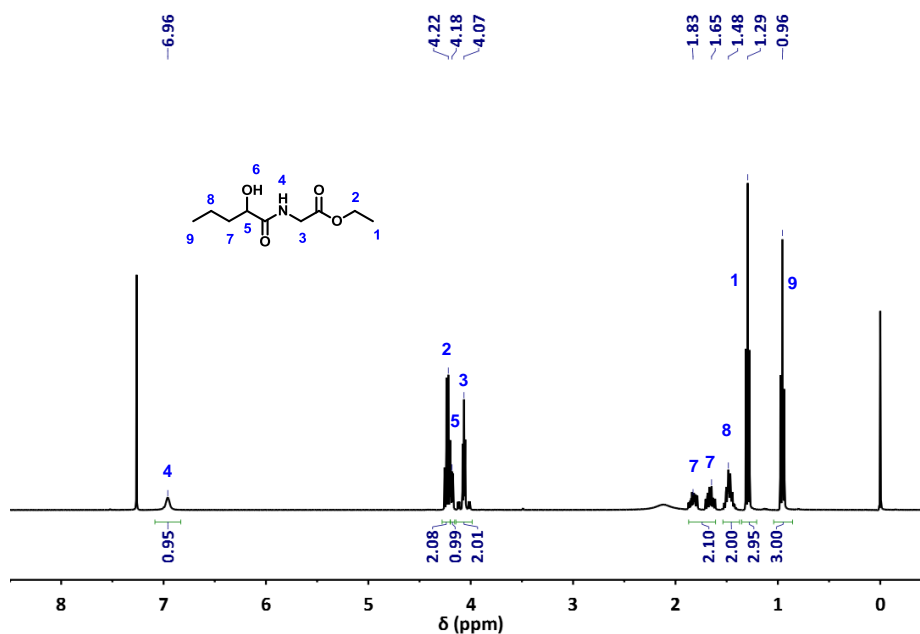
Ethyl 2-(2-hydroxy penanamido) acetate (**1c**)



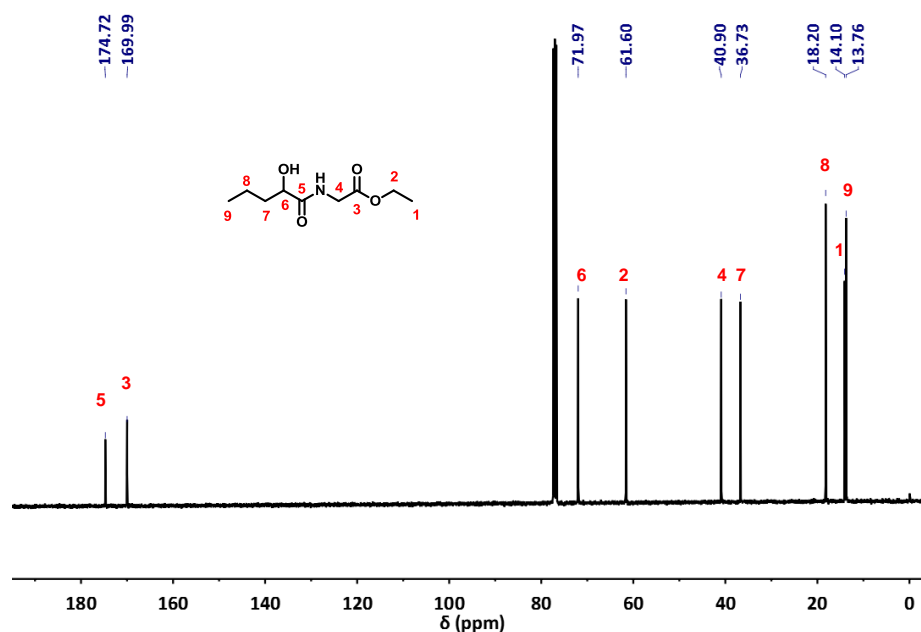
In a 500 mL round bottom flask, butyraldehyde (7.2 g, 0.1 mol), ethyl isocyanacetate (11.3 g, 0.1 mol) and boric acid (7.2 g, 0.12 mol) were dissolved in DMF (200 mL). The reaction mixture was stirred for 48 h at room temperature and quenched with H<sub>2</sub>O (100 mL). Then the reaction mixture was concentrated in *vacuo*. The crude product was purified by flash column chromatography (EtOAc/PE=1/1), affording a white solid (16.6 g, 82%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.96 (s, 1H), 4.22 (q, *J* = 14.2, 7.1 Hz, 2H), 4.18 (dd, *J* = 7.8, 3.6 Hz, 1H), 4.07 (m, 2H), 2.12 (s, 1H), 1.83 (m, 1H), 1.65 (m, 1H), 1.48 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 174.72, 169.99, 71.97, 61.60, 40.90, 36.73, 18.20, 14.10, 13.76.

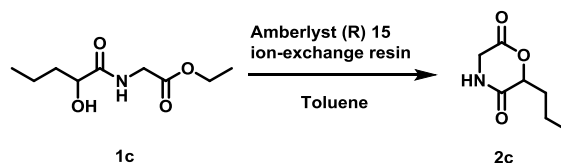


**Figure S13.** <sup>1</sup>H NMR spectrum of compound **1c** in CDCl<sub>3</sub>.



**Figure S14.**  $^{13}\text{C}$  NMR spectrum of compound **1c** in  $\text{CDCl}_3$ .

#### 6-Propyl-morpholine-2, 5-dione (**2c**)



In a 1000 mL round bottom flask equipped with a Soxhlet extractor (filled with 4Å molecular sieve) and a reflux condenser, compound **1c** (4.0 g, 0.02 mol) and a catalytic amount of Amberlyst (R) 15 ion-exchange resin were added into 500 mL of toluene. The reaction mixture was allowed to reflux for 48 h., and then cooled to room temperature, filtered to remove the ion exchange resin, and concentrated to remove the solvent under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/PE = 1/1) to provide the desired product (**2c**) as a white solid (2.45 g, 78%).  $T_m = 115.0$  °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.55 (s, 1H), 4.78 (dd,  $J = 8.1, 4.5$  Hz, 1H), 4.18 (m, 2H), 2.02 (m, 1H), 1.90 (m, 1H), 1.60 (m, 2H), 0.99 (t, 3H)

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 168.48, 165.00, 78.29, 43.44, 33.56, 17.88, 13.51;

HRMS (FAB+):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_7\text{H}_{11}\text{NNaO}_3$ : 180.0739; found: 180.0631;

Elemental analysis: calcd. for  $\text{C}_7\text{H}_{11}\text{NO}_3$ , C, 53.49; H, 7.05; N, 8.91. Found: C, 53.57; H, 7.12; N, 8.92.

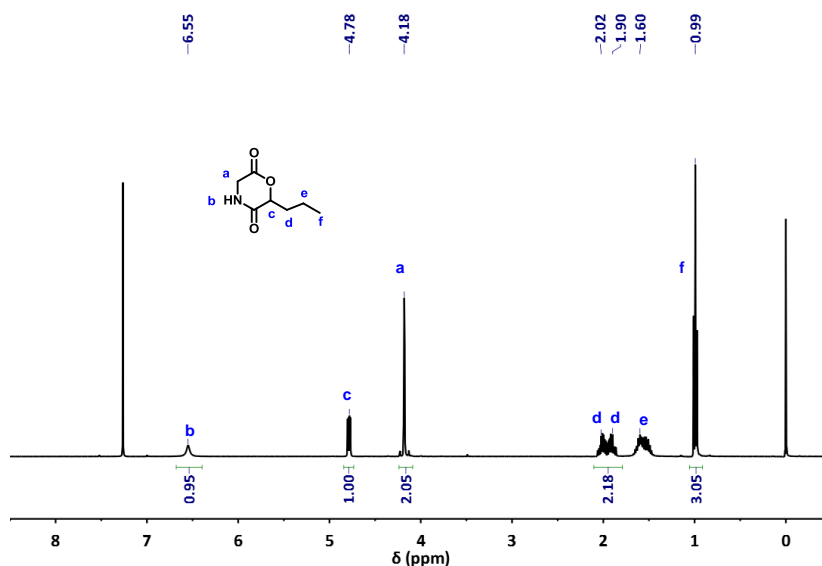


Figure S15.  $^1\text{H}$  NMR spectrum of monomer **2c** in  $\text{CDCl}_3$ .

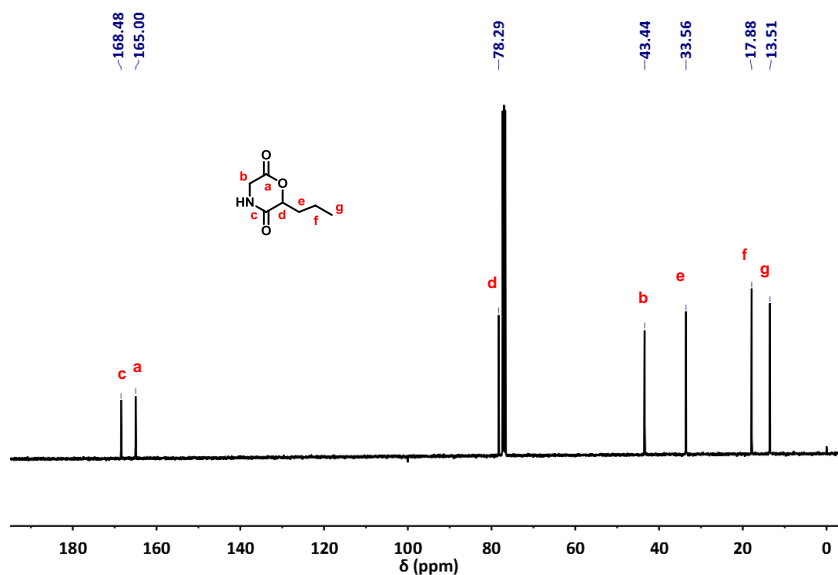


Figure S16.  $^{13}\text{C}$  NMR spectrum of monomer **2c** in  $\text{CDCl}_3$ .

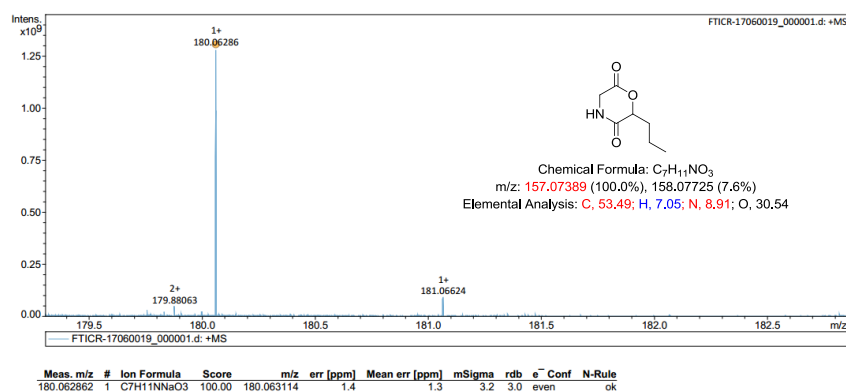
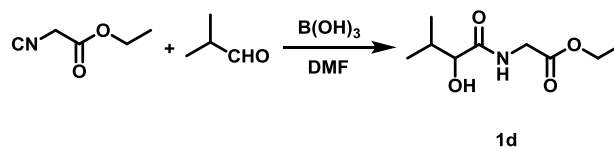


Figure S17. ESI-MS spectrum of monomer **2c**.

## 2.4 Synthesis monomer 2d

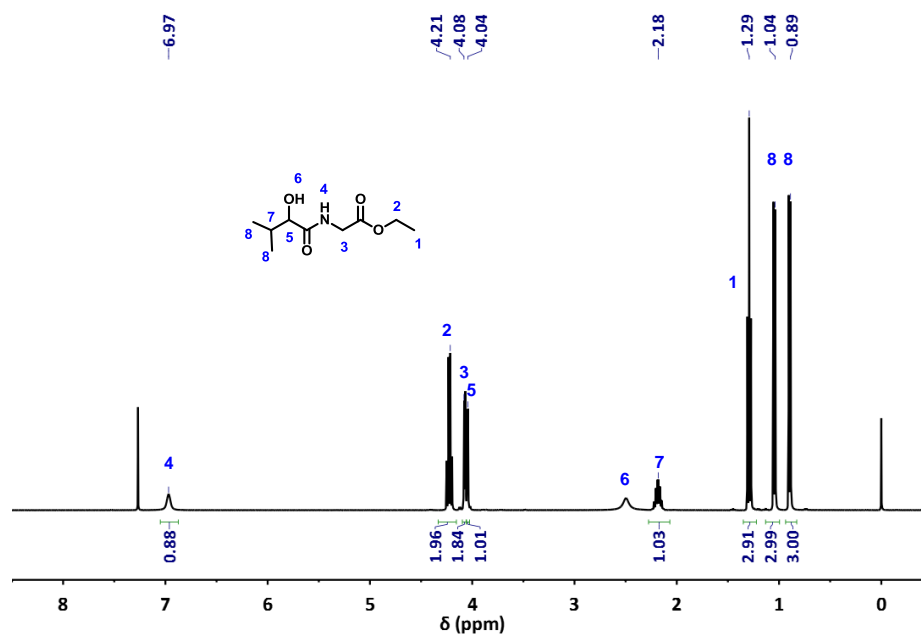
Ethyl 2-(2-hydroxy-3-methyl-butanamido) acetate (**1d**)



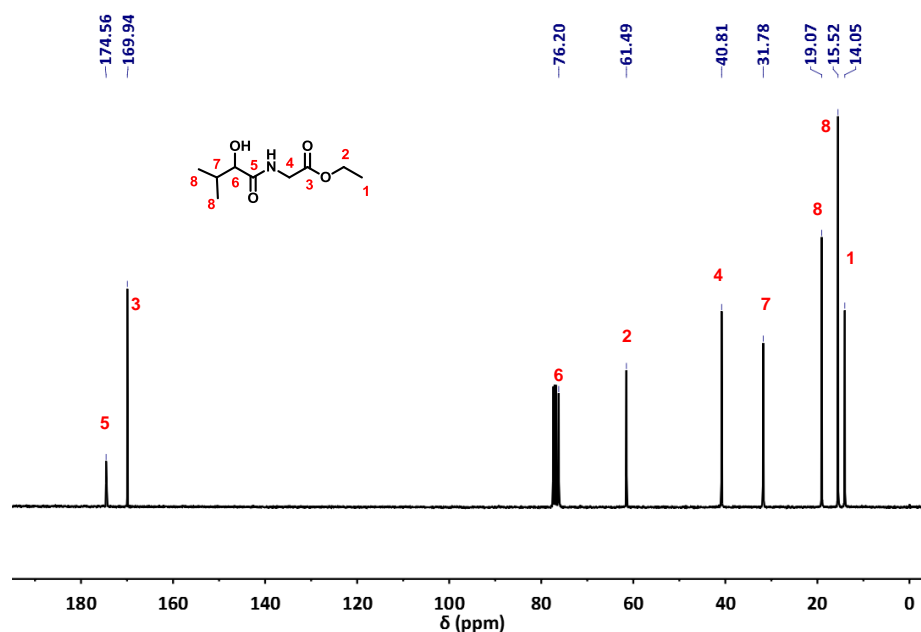
In a 500 mL round bottom flask, isobutyraldehyde (7.2 g, 0.1 mol), ethyl isocyanacetate (11.3 g, 0.1 mol) and boric acid (7.2 g, 0.12 mol) were dissolved in DMF (200 mL). The reaction mixture was stirred for 48 h at room temperature and quenched with H<sub>2</sub>O (100 mL). Then the reaction mixture was concentrated in *vacuo*. The crude product was purified by flash column chromatography (EtOAc/PE=1/1), affording a white solid (17.4 g, 86%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.97 (s, *J* = 13.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.08 (m, 2H), 4.04 (d, *J* = 3.2 Hz, 1H), 2.49 (s, 1H), 2.18 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 174.56, 169.94, 76.20, 61.49, 40.81, 31.78, 19.07, 15.52, 14.05.

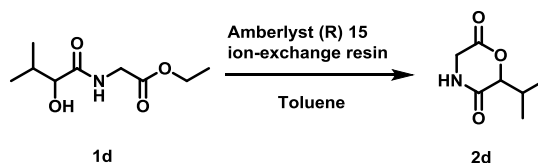


**Figure S18.** <sup>1</sup>H NMR spectrum of compound **1d** in CDCl<sub>3</sub>.



**Figure S19.** <sup>13</sup>C NMR spectrum of compound **1d** in CDCl<sub>3</sub>.

#### 6-Isopropyl-morpholine-2, 5-dione (**2d**)



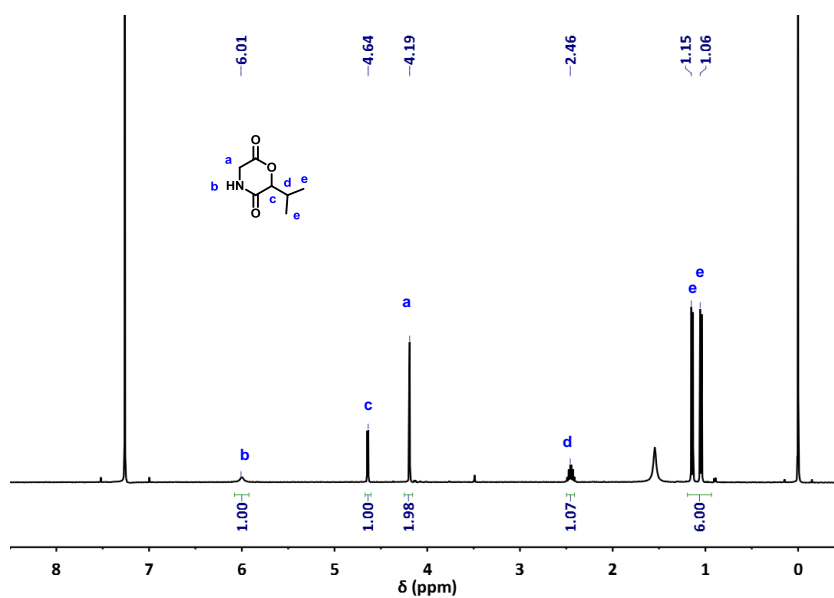
In a 500 mL round bottom flask equipped with a Soxhlet extractor (filled with 4Å molecular sieve) and a reflux condenser, compound **1d** (2.5 g, 0.012 mol) and a catalytic amount of Amberlyst (R) 15 ion-exchange resin were added into 300 mL of toluene. The reaction mixture was allowed to reflux for 48 h., and then cooled to room temperature, filtered to remove the ion exchange resin, and concentrated to remove the solvent under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/PE = 1/1) to provide the desired product (**2d**) as a white solid (1.45 g, 75%).  $T_m = 153.1$  °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.01(s, 1H), 4.64 (d,  $J = 4.1$  Hz, 1H), 4.19 (d,  $J = 2.4$  Hz, 2H), 2.46 (m, 1H), 1.15 (d,  $J = 7.0$  Hz, 3H), 1.06 (d,  $J = 6.8$  Hz, 3H).

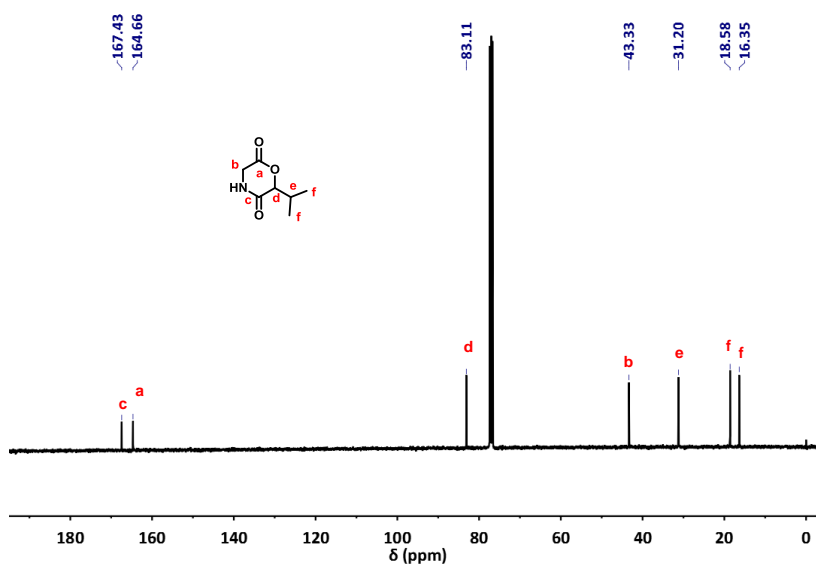
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 167.43, 164.66, 83.11, 43.33, 31.20, 18.58, 16.35.

HRMS (FAB<sup>+</sup>):  $m/z$  [M+H]<sup>+</sup> calcd. for C<sub>7</sub>H<sub>12</sub>NO<sub>3</sub>: 158.0739; found:158.0812.

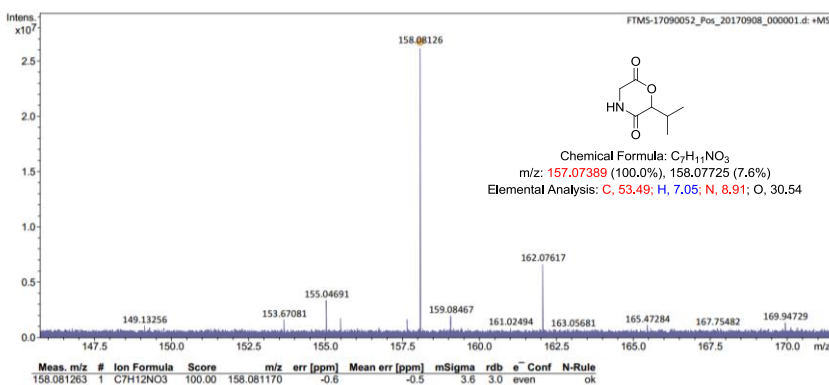
Elemental Analysis: calcd. for C<sub>7</sub>H<sub>11</sub>NO<sub>3</sub>, C, 53.49; H, 7.05; N, 8.91. Found: C, 53.49; H, 7.12; N, 8.91.



**Figure S20.** <sup>1</sup>H NMR spectrum of compound **2d** in CDCl<sub>3</sub>.



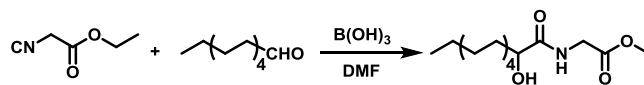
**Figure S21.** <sup>13</sup>C NMR spectrum of compound **2d** in CDCl<sub>3</sub>.



**Figure S22.** ESI-MS spectrum of monomer **2d**.

## 2.5 Synthesis of monomer 2e

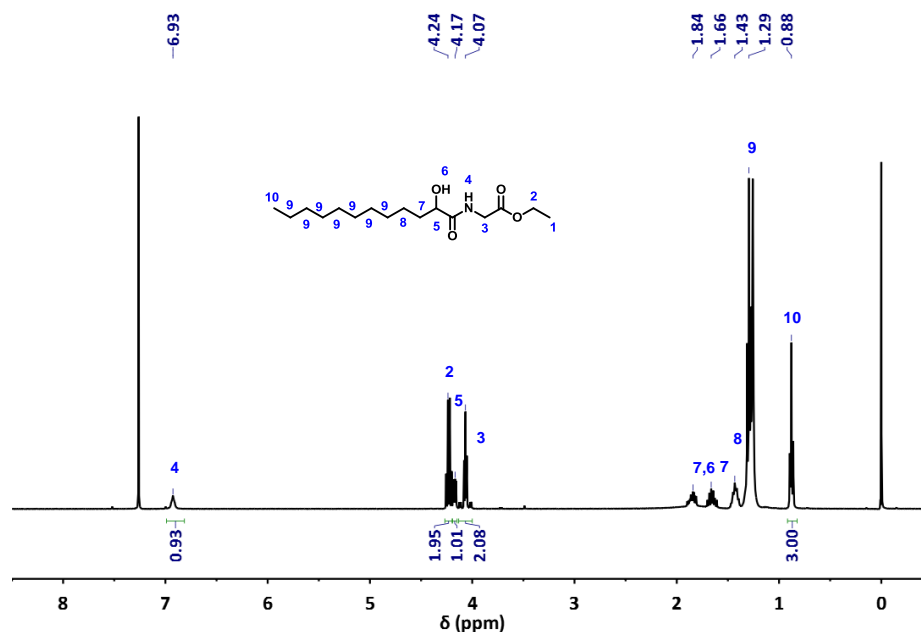
Ethyl 2-(2-hydroxy dodecanamido) acetate (**1e**)

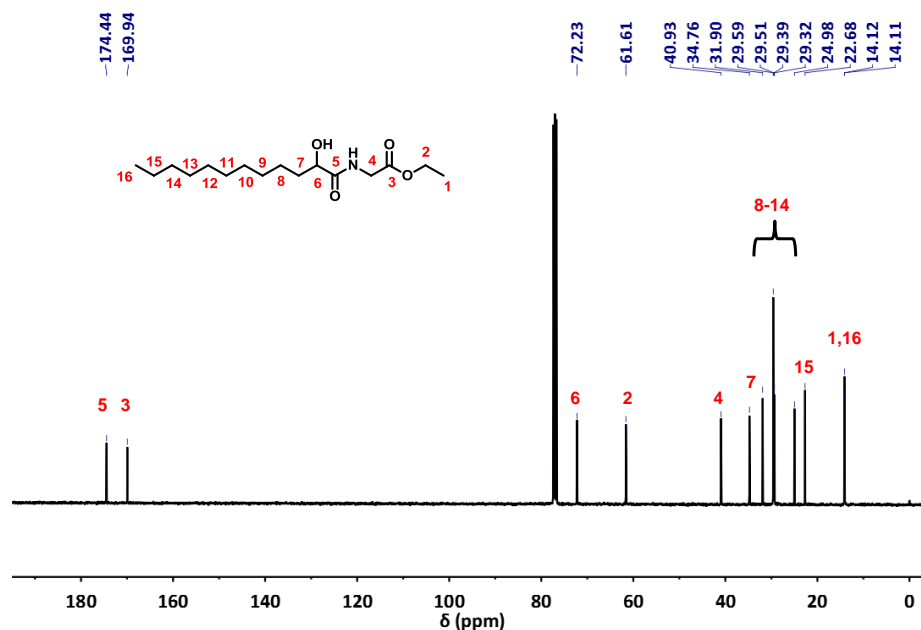


In a 500 mL round bottom flask, undecanal (18.4 g, 0.1 mol), ethyl isocyanooacetate (11.3 g, 0.1 mol) and boric acid (7.2 g, 0.12 mol) were dissolved in DMF (200 mL). The reaction mixture was stirred for 48 h at room temperature and quenched with H<sub>2</sub>O (100 mL). Then the reaction mixture was concentrated in *vacuo*. The crude product was purified by flash column chromatography (EtOAc/PE=1/1), affording a white solid (27.4 g, 91%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.93 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.17 (dd, *J* = 8.0, 3.8 Hz, 1H), 4.07 (m, 2H), 1.84 (m, 1H), 1.66 (m, 1H), 1.43 (m, 2H), 1.29 (m, 17H), 0.88 (t, *J* = 6.9 Hz, 3H).

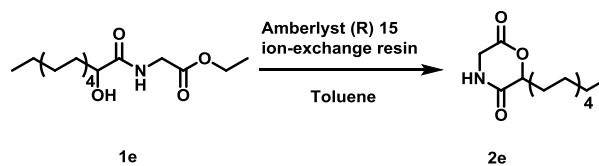
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 174.44, 169.94, 72.23, 61.61, 40.93, 34.76, 31.90, 29.59, 29.51, 29.39, 29.32, 24.98, 22.68, 14.12, 14.11.





**Figure S24.**  $^{13}\text{C}$  NMR spectrum of compound **1e** in  $\text{CDCl}_3$ .

#### 6-Decyl-morpholine-2, 5-dione (**2e**)



In a 500 mL round bottom flask equipped with a Soxhlet extractor (filled with  $4\text{\AA}$  molecular sieve) and a reflux condenser, compound **1e** (3.5 g, 0.012 mol) and a catalytic amount of Amberlyst (R) 15 ion-exchange resin were added into 300 mL of toluene. The reaction mixture was allowed to reflux for 48 h., and then cooled to room temperature, filtered to remove the ion exchange resin, and concentrated to remove the solvent under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/PE = 1/1) to provide the desired product (**2e**) as a white solid (2.40 g, 81%).  $T_m = 114.7\text{ }^\circ\text{C}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.38 (s, 1H), 4.77 (dd,  $J = 8.0, 4.5$  Hz, 1H), 4.18 (m, 2H), 2.03 (m, 1H), 1.91 (m, 1H), 1.57 (m, 16H), 0.88 (t,  $J = 6.9$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 164.94, 78.62, 43.50, 31.89, 31.64, 29.55, 29.51, 29.34, 29.30, 29.08, 24.52, 22.68, 14.12.

HRMS (FAB $^+$ ):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{14}\text{H}_{25}\text{NNaO}_3$ : 278.1834; found: 278.1726.

Elemental Analysis: calcd. for  $\text{C}_{14}\text{H}_{25}\text{NO}_3$ , C, 65.85; H, 9.87; N, 5.49. Found: C, 65.50; H, 10.02; N, 5.43.

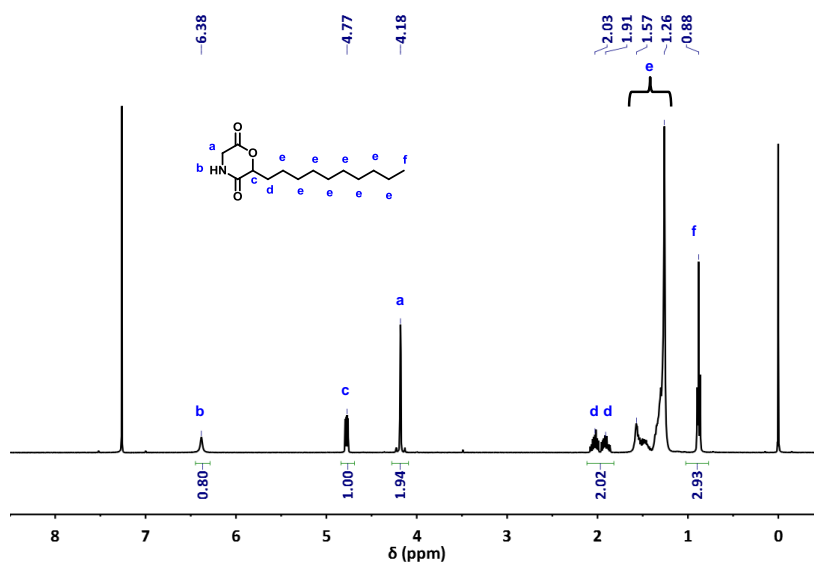


Figure S25.  $^1\text{H}$  NMR spectrum of monomer **2e** in  $\text{CDCl}_3$ .

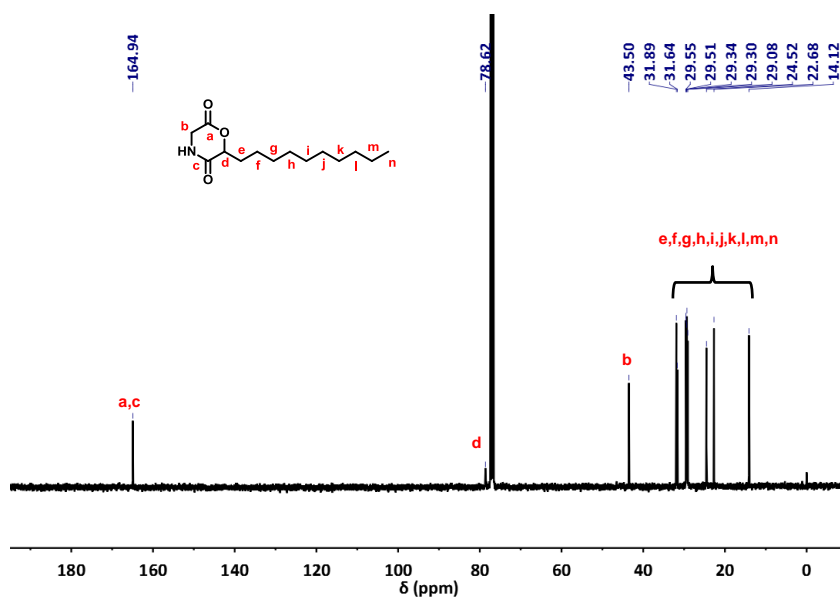


Figure S26.  $^{13}\text{C}$  NMR spectrum of monomer **2e** in  $\text{CDCl}_3$ .

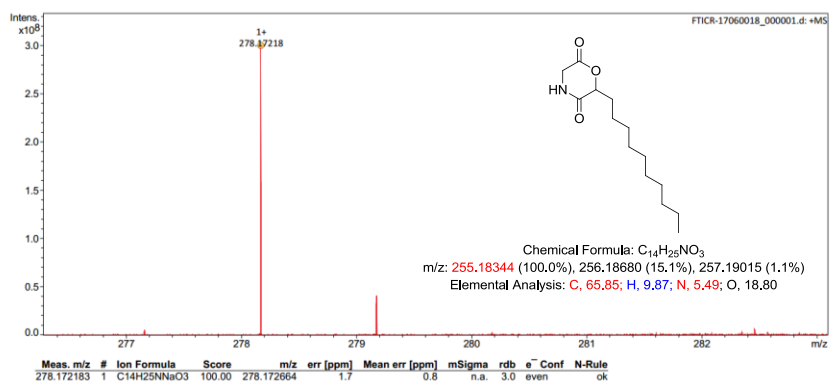
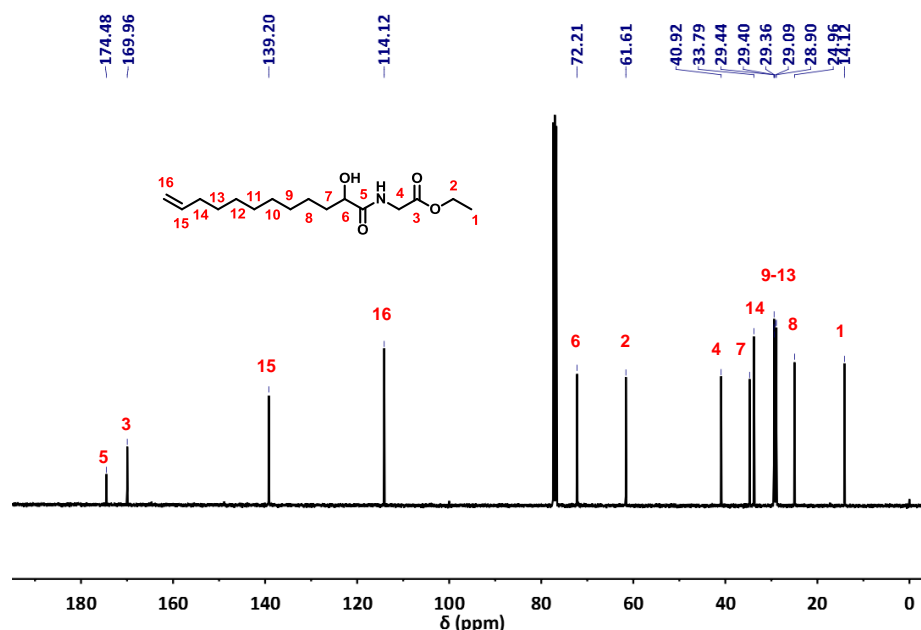


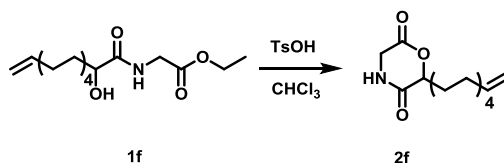
Figure S27. ESI-MS spectrum of monomer **2e**.





**Figure S29.**  $^{13}\text{C}$  NMR spectrum of compound **1f** in  $\text{CDCl}_3$ .

6-(Dec-9-en-1-yl)-morpholine-2,5-dione (**2f**)



In a 1000 mL round bottom flask equipped with a Soxhlet extractor (filled with 4Å molecular sieve) and a reflux condenser, compound **1f** (6.0 g, 0.02 mol) and TsOH (1.0 g, 0.006 mol) were added in 500 mL of  $\text{CHCl}_3$ . The reaction mixture was allowed to reflux for 48 h., and then cooled to room temperature, and washed successively with 300 mL sat.  $\text{NaHCO}_3$  and 300 mL  $\text{H}_2\text{O}$ . The organic layer was dried with anhydrous  $\text{MgSO}_4$ , and concentrated to remove the solvent under reduced pressure. The crude product was purified by silica gel chromatography ( $\text{EtOAc/PE} = 1/1$ ) to provide the desired product (**2f**) as a white solid (4.25 g, 84%).  $T_m = 102.8\text{ }^\circ\text{C}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.13 (s, 1H), 5.82 (m, 1H), 4.95 (m, 2H), 4.77 (dd,  $J = 8.0, 4.5$  Hz, 1H), 4.18 (t,  $J = 2.2$  Hz, 2H), 2.03 (m, 3H), 1.56 (m, 1H), 1.29 (m, 12H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 168.35, 164.96, 139.16, 114.18, 78.52, 43.48, 33.77, 31.61, 29.32, 29.27, 29.04, 28.87, 24.51.

HRMS (FAB<sup>+</sup>):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{14}\text{H}_{25}\text{NNaO}_3$ : 276.1678; found: 276.1570;

Elemental Analysis: calcd. for  $\text{C}_{14}\text{H}_{25}\text{NO}_3$ , C, 66.37; H, 9.15; N, 5.53. Found: C, 66.29; H, 9.31; N, 5.48.

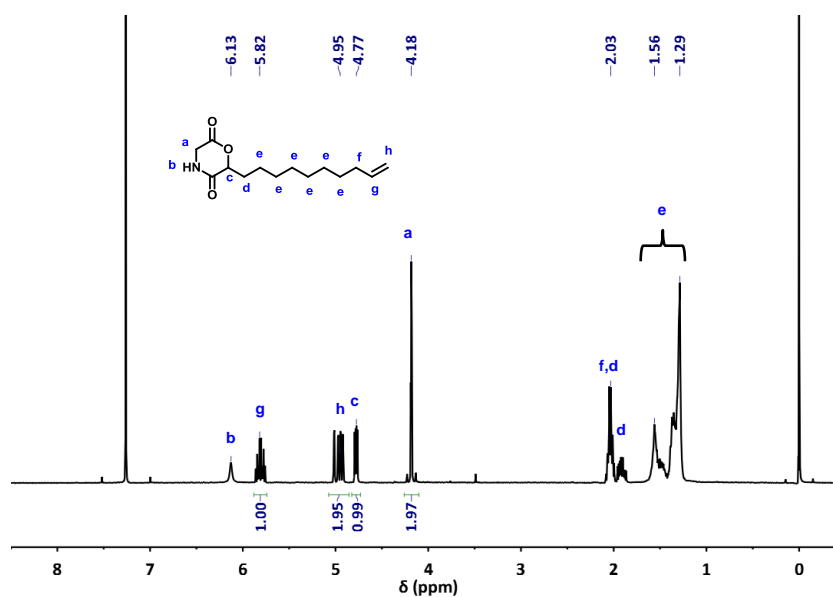


Figure S30. <sup>1</sup>H NMR spectrum of monomer **2f** in CDCl<sub>3</sub>.

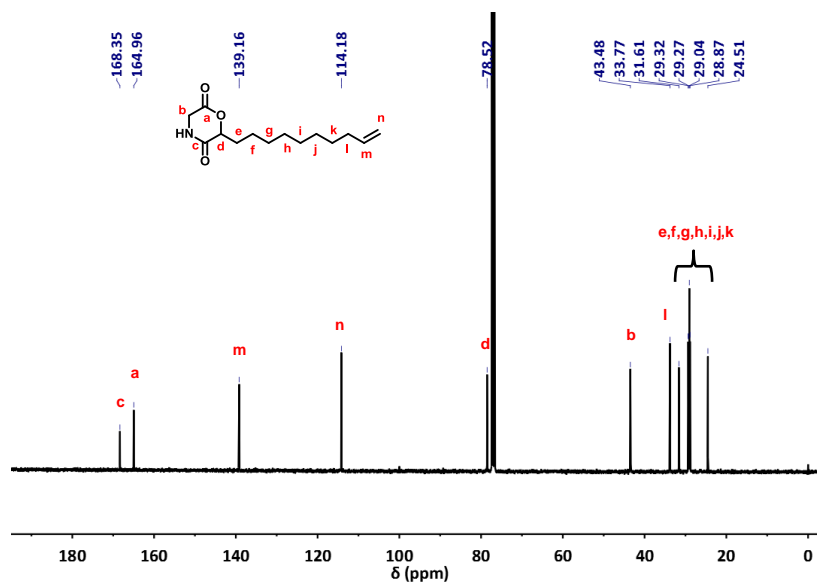


Figure S31. <sup>13</sup>C NMR spectrum of monomer **2f** in CDCl<sub>3</sub>.

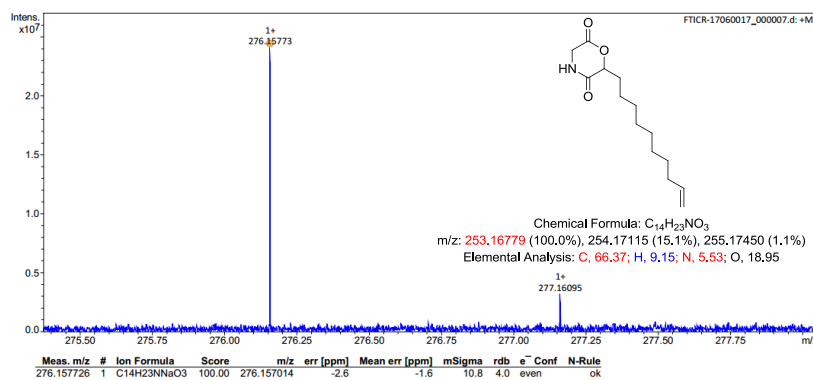
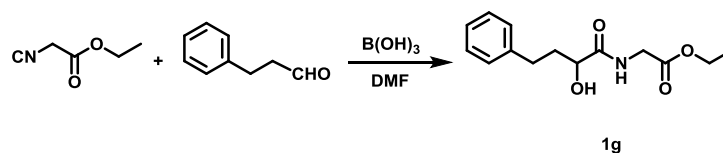


Figure S32. ESI-MS spectrum of monomer **2f**.

## 2.7 Synthesis of monomer **2g**

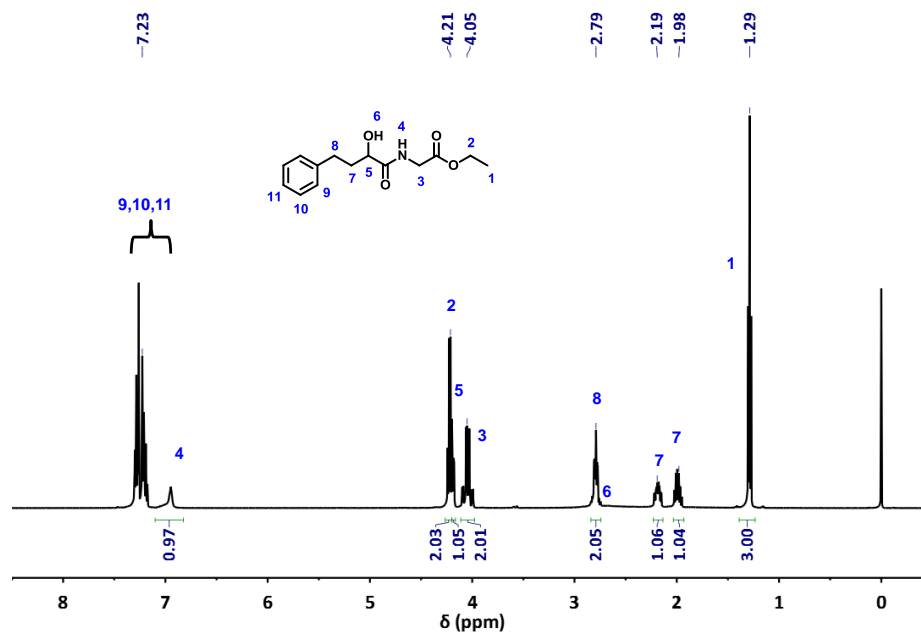
Ethyl-2-(2-hydroxy-4-phenylbutanamido) acetate (**1g**)



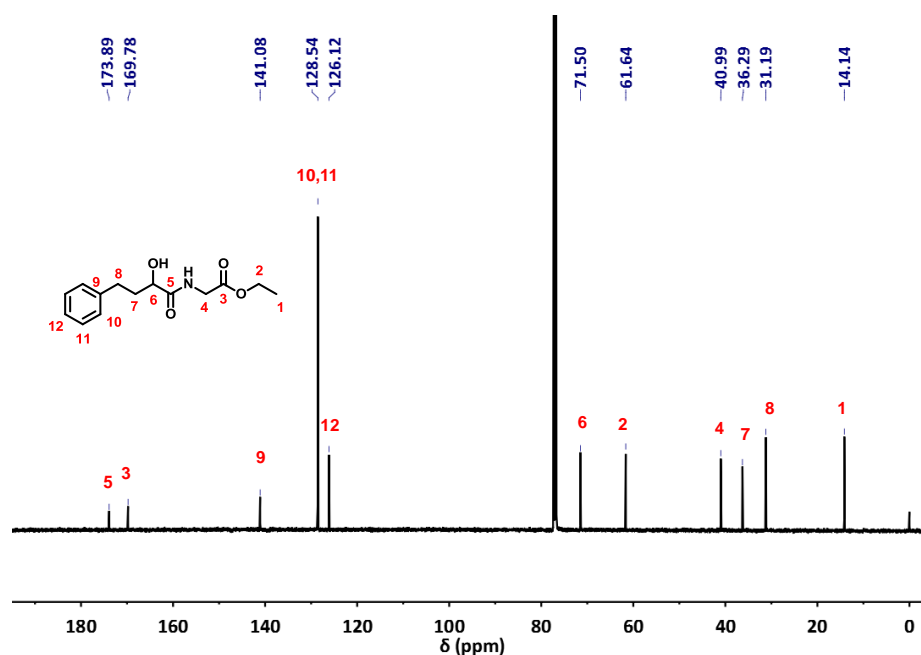
In a 100 mL round bottom flask, phenylpropylaldehyde (1.8 g, 0.013 mol), ethyl isocyanoacetate (1.5 g, 0.013 mol) and boric acid (1.0 g, 0.015 mol) were dissolved in DMF (50 mL). And the reaction mixture was stirred for 48 h at room temperature and quenched with H<sub>2</sub>O (20 mL). Then the reaction mixture was concentrated in *vacuo*. The crude product was purified by flash column chromatography (EtOAc/PE = 1/1), affording a white solid (3.0 g, 87%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.23 (m, 5H), 6.95 (s, 1H), 4.21 (q, *J* = 14.2, 7.1 Hz, 2H), 4.18 (dd, *J* = 8.0, 3.8 Hz, 1H), 4.05 (m, 5.4 Hz, 2H), 2.79 (m, 2H), 2.19 (m, 1H), 1.98 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 173.89, 169.78, 141.08, 128.54, 126.12, 71.50, 61.64, 40.99, 36.29, 31.19, 14.14.

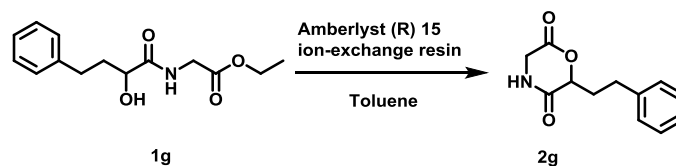


**Figure S33.** <sup>1</sup>H NMR spectrum of compound **1g** in CDCl<sub>3</sub>.



**Figure S34.**  $^{13}\text{C}$  NMR spectrum of compound **1g** in  $\text{CDCl}_3$ .

6-(3-Phenyl)-propyl-morpholine-2, 5-dione (**2g**)



In a 500 mL round bottom flask equipped with a Soxhlet extractor (filled with 4Å molecular sieve) and a reflux condenser, compound **1g** (2.5 g, 0.0094 mol) and a catalytic amount of Amberlyst (R) 15 ion-exchange resin were added in 240 mL of toluene. The reaction mixture was allowed to reflux for 48 h., and then cooled to room temperature, filtered to remove the ion exchange resin, and concentrated to remove the solvent under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/PE = 1/1) to provide the desired product (**2g**) as a white solid (1.53 g, 74%).  $T_m = 130.0\text{ }^\circ\text{C}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.29 (m, 5H), 6.96 (s, 1H), 4.72 (ddd,  $J = 8.6, 4.1, 2.3$  Hz, 1H), 4.16 (m, 2H), 2.91 (m, 1H), 2.82 (m, 1H), 2.36 (m, 1H), 2.23 (m, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.98, 164.89, 139.82, 128.65, 128.61, 126.46, 77.08, 43.58, 43.55, 32.77, 30.45.

HRMS (FAB $^+$ ):  $m/z$   $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{12}\text{H}_{13}\text{NNaO}_3$ :242.0895; found:242.0788.

Elemental Analysis: calcd. for  $\text{C}_{12}\text{H}_{13}\text{NO}_3$ , C, 65.74; H,5.98; N, 6.39. Found: C, 64.82; H, 6.18; N, 6.18.

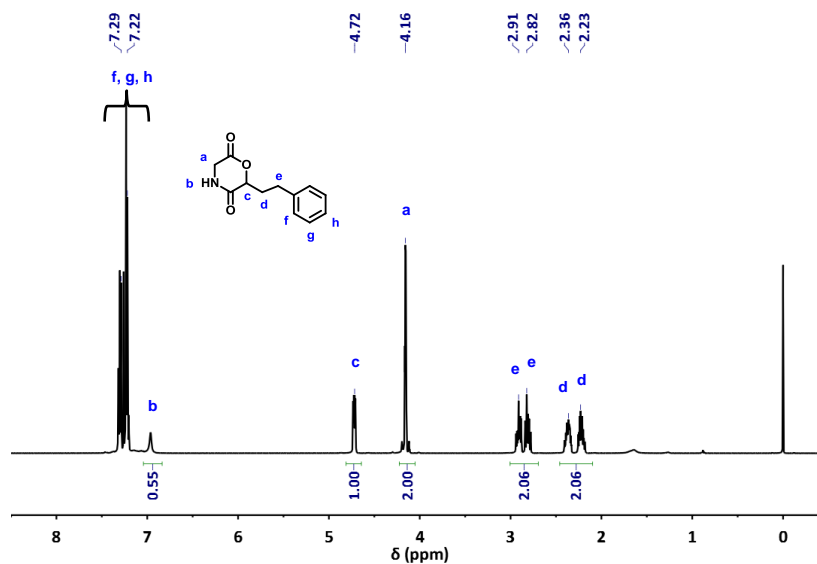


Figure S35. <sup>1</sup>H NMR spectrum of monomer **2g** in CDCl<sub>3</sub>.

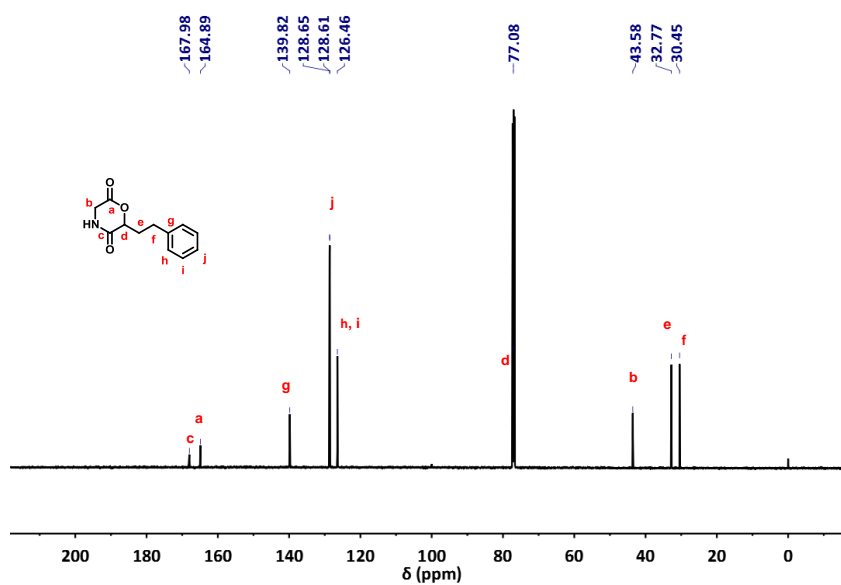


Figure S36. <sup>13</sup>C NMR spectrum of monomer **2g** in CDCl<sub>3</sub>.

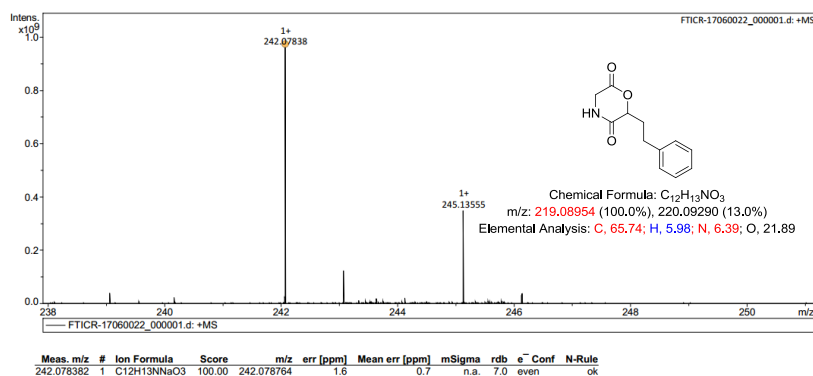
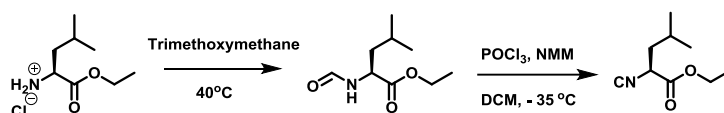


Figure S37. ESI-MS spectrum of monomer **2g**.

## 2.8 Synthesis of isocyanides from amino acids <sup>5</sup>

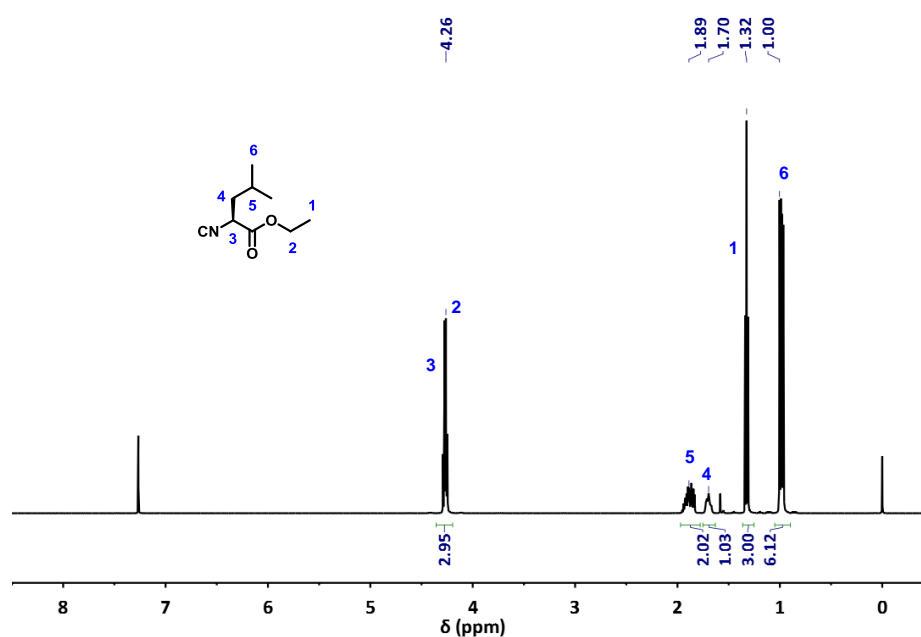


### Ethyl 2-isocyano-4-methylpentanoate

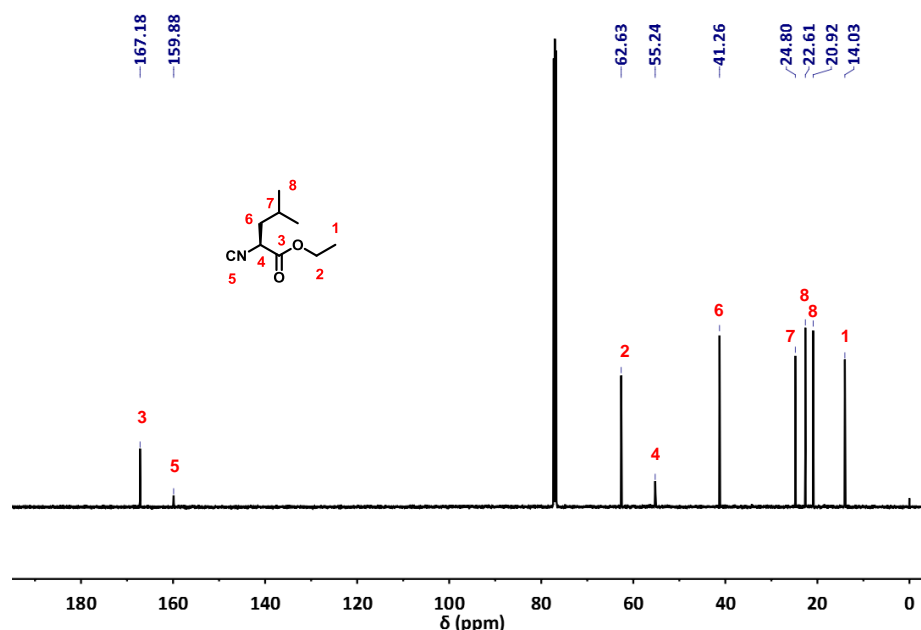
In a 500 mL round bottom flask, *L*-leucine ethyl ester hydrochloride (15 g, 0.076 mol) was suspended in trimethoxymethane (100 mL), and the reaction mixture was vigorously stirred at 45°C for 48 h. Then the reaction mixture was concentrated in *vacuo*. The crude product and NMM (19.5 g, 0.38 mol) were dissolved in DCM (150 mL) and chilled to -35 °C. Subsequently, a solution of POCl<sub>3</sub> (8.6 g, 0.11 mol) in DCM (25 mL) was added dropwise over 1 h and stirred for another 2 h at this temperature. The reaction was quenched with saturated NaHCO<sub>3</sub> solution (50 mL). The organic layer was separated and concentrated in *vacuo*. The crude product was purified by flash column chromatography (EtOAc/PE=1/15), affording a colorless oil (10.5 g, 81% yield for two steps).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 4.27 (dd, 1H), 4.26 (q, 2H), 1.89 (m, 2H), 1.70 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.00 (dd, *J* = 12.1, 6.6 Hz, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 167.18, 159.88, 62.63, 55.24, 41.26, 24.80, 22.61, 20.92, 14.0.

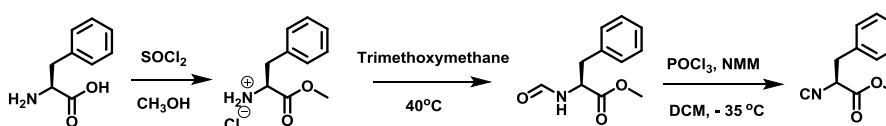


**Figure S38.** <sup>1</sup>H NMR spectrum of ethyl 2-isocyano-4-methylpentanoate in CDCl<sub>3</sub>.



**Figure S39.**  $^{13}\text{C}$  NMR spectrum of ethyl 2-isocyano-4-methylpentanoate in  $\text{CDCl}_3$ .

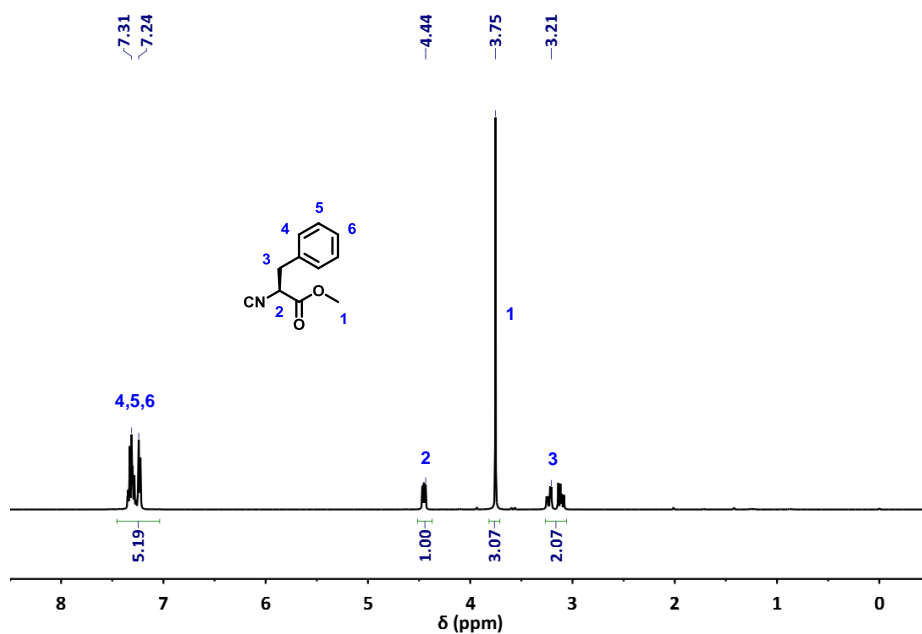
#### Methyl 2-isocyano-3-phenylpropanoate



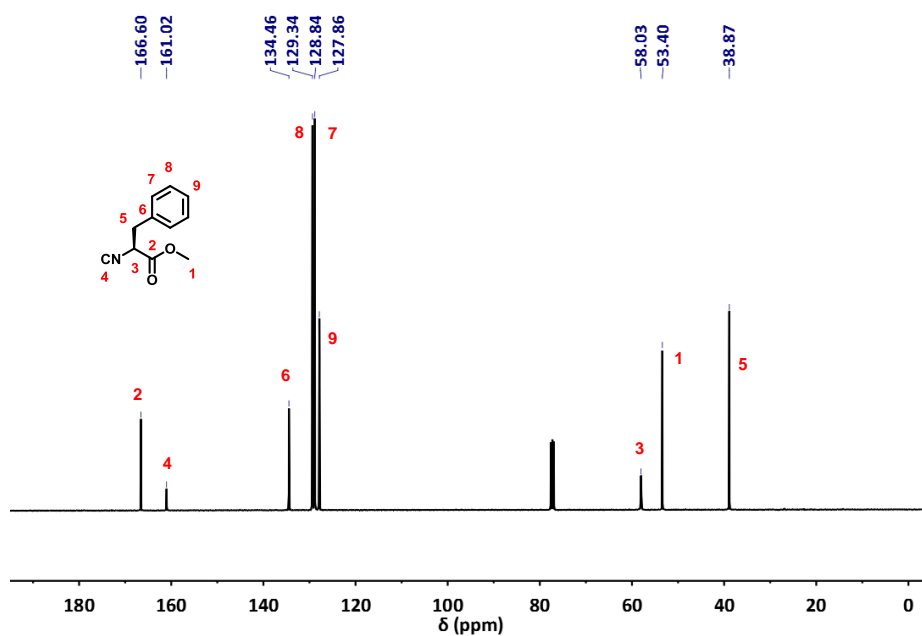
In a 1000 mL round bottom flask, *L*-phenylalanine (50 g, 0.3 mol) was suspended in methanol (500 mL), and  $\text{SOCl}_2$  was dropwise added under vigorous stirring at  $0^\circ\text{C}$ . The reaction mixture was vigorously stirred at room temperature for 12 h., and then concentrated under vacuum. Without any purification, the crude product was suspended in trimethoxymethane (300 mL), and the reaction mixture was vigorously stirred at  $45^\circ\text{C}$  for 48 h. The reaction mixture was concentrated in *vacuo*. The crude product and NMM (77 g, 1.5 mol) were dissolved in DCM (400 mL) and chilled to  $-35^\circ\text{C}$ . Subsequently, a solution of  $\text{POCl}_3$  (34 g, 0.45 mol) in DCM (100 mL) was added dropwise over 1 h. and stirred for another 2 h. at this temperature. The reaction was quenched with saturated  $\text{NaHCO}_3$  solution (50 mL). The organic layer was separated and concentrated in *vacuo*. The crude product was purified by flash column chromatography (EtOAc/PE=1/10), affording a colorless oil (43 g, 76% yield for three steps).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.27 (m, 5H), 4.44 (dd,  $J = 8.3, 4.9$  Hz, 1H), 3.75 (s, 3H), 3.21 (m, 2H)

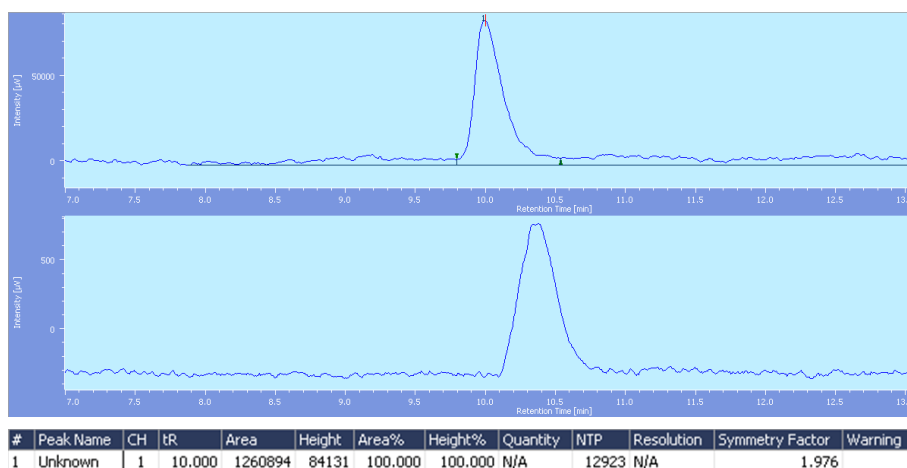
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.60, 161.02, 134.46, 129.34, 128.84, 127.86, 58.03, 53.40, 38.87.



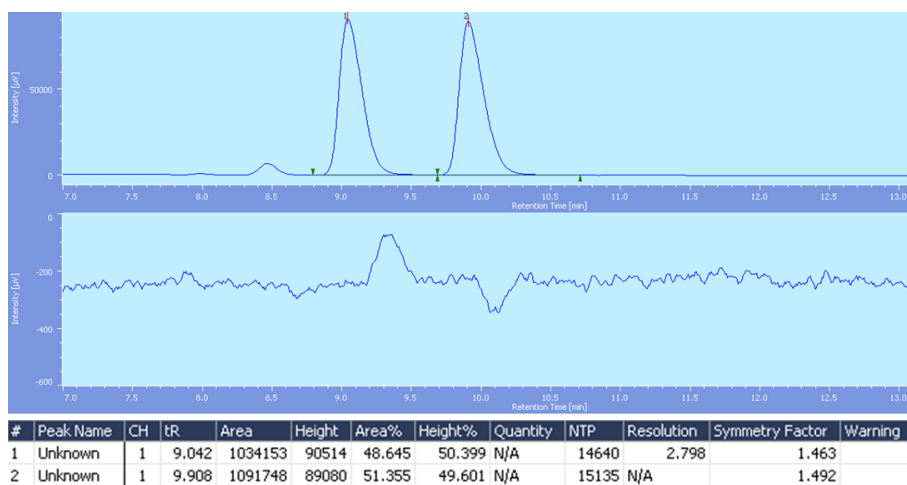
**Figure S40.** <sup>1</sup>H NMR spectrum of methyl 2-isocyano-3-phenylpropanoate in CDCl<sub>3</sub>.



**Figure S41.** <sup>13</sup>C NMR spectrum of methyl 2-isocyano-3-phenylpropanoate in CDCl<sub>3</sub>.



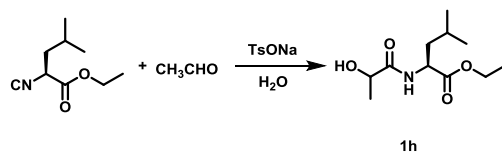
**Figure S42.** Chiral HPLC chromatogram of methyl 2-isocyano-3-phenylpropanoate derived from *L*-phenylalanine, (Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min,  $\lambda = 254$  nm).



**Figure S43.** Chiral HPLC chromatogram of *rac*-ethyl 2-isocyano-3-phenylpropanoate derived from *rac*-phenylalanine, (Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min,  $\lambda = 254$  nm).

## 2.9 Synthesis of monomer 2h

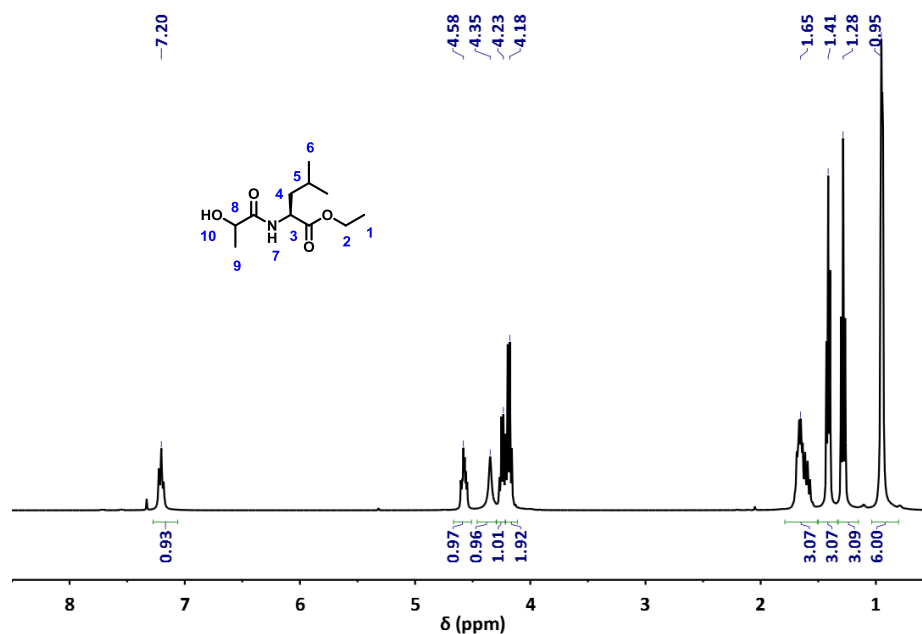
Ethyl 2-(2-hydroxy propanamido)-3-(3-methyl butanyl) propanoate (**1h**)

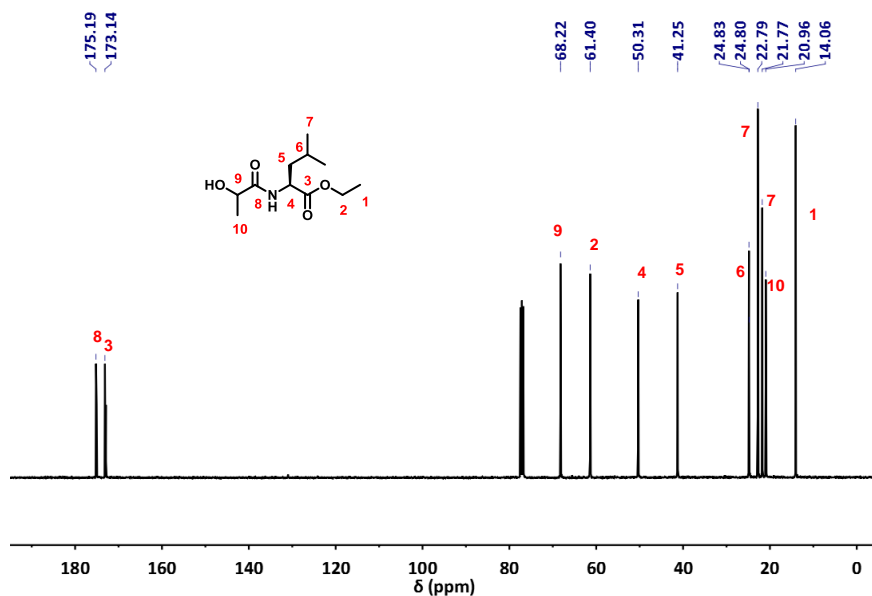


In a 250 mL round bottom flask, ethyl 2-isocyano-4-methylpentanoate (5 g, 0.03 mol) and sodium *p*-toluenesulfonate (TsONa, 1.8 g, 0.009 mol) were dissolved in 40% acetaldehyde solution (100 mL), and the reaction mixture was vigorously stirred at room temperature for 12 h. The reaction mixture was concentrated *in vacuo* to provide the crude product which was used directly in the next step. Optionally, the crude product can be further purified by flash column chromatography (EtOAc/PE=1/1), affording a colorless oil (5.81 g, 85%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.20 (t,  $J = 8.0$  Hz, 1H), 4.58 (m, 1H), 4.35 (s, 1H), 4.23 (m, 3H), 1.65 (m, 3H), 1.41 (m, 3H), 1.28 (t,  $J = 7.1$  Hz, 3H), 0.95 (m, 6H).

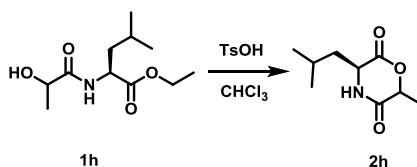
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 175.19, 175.04, 173.14, 172.90, 68.22, 61.40, 61.34, 50.38, 50.31, 41.29, 41.25, 24.83, 24.80, 22.79, 21.77, 20.96, 20.87, 14.06.





**Figure S45.** <sup>13</sup>C NMR spectrum of compound **1h** in CDCl<sub>3</sub>.

(3S)-3-Isobutyl-6-methyl-morpholine-2, 5-dione (**2h**)



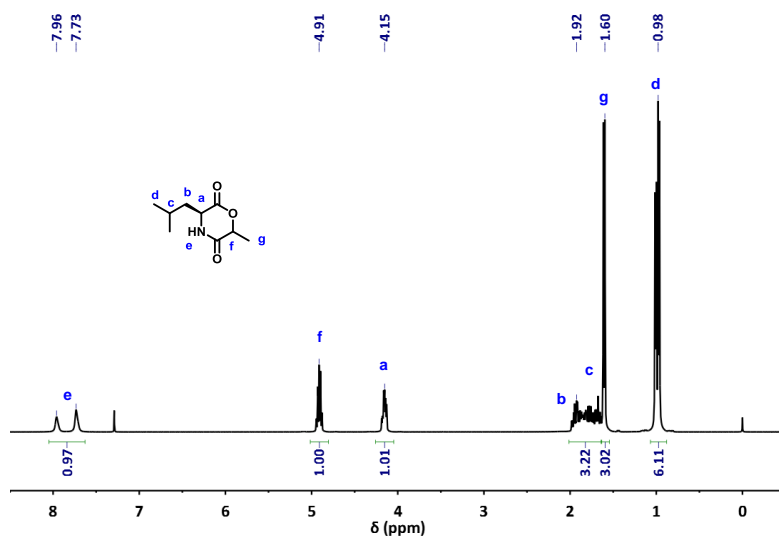
In a 1000 mL round bottom flask equipped with a Soxhlet extractor (filled with 4Å molecular sieve) and a reflux condenser, compound **1h** (5.8 g, 0.025 mol) and TsOH (1.25 g, 0.0075 mol) were added into 600 mL of CHCl<sub>3</sub>. The reaction mixture was allowed to reflux for 48 h., and then was cooled to room temperature, and washed successively with 375 mL of saturated NaHCO<sub>3</sub> solution and 375 mL of H<sub>2</sub>O. The organic layer was collected and dried with anhydrous MgSO<sub>4</sub>, and concentrated to remove the solvent under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/PE = 3/7) to provide the desired product (**2h**) as a white solid (3.80 g, 82%). *T<sub>m</sub>* = 166.3 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.84 (d, *J* = 91.1 Hz, 1H), 4.91 (m, 1H), 4.15 (m, 1H), 1.92 (m, 3H), 1.60 (d, *J* = 6.9 Hz, 3H), 0.98 (dd, *J* = 14.6, 6.3 Hz, 6H).

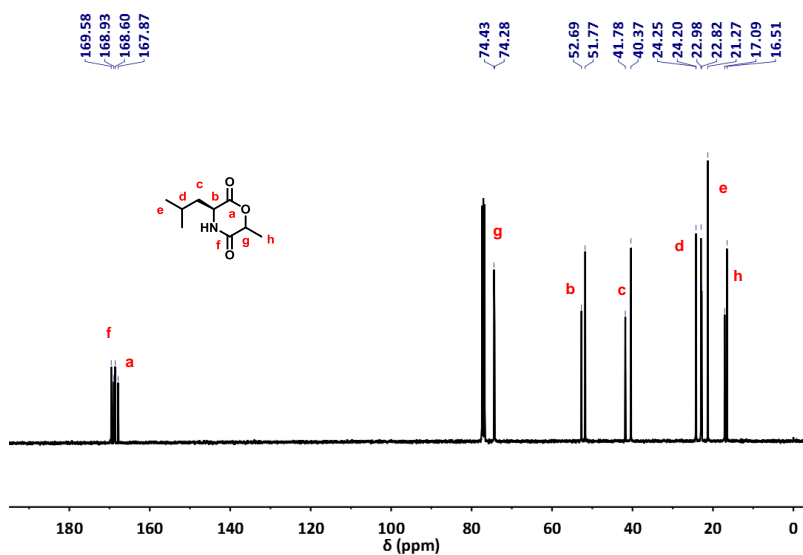
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 169.58, 168.93, 168.60, 167.87, 74.43, 74.28, 52.69, 51.77, 41.78, 40.37, 24.25, 24.20, 22.98, 22.82, 21.27, 17.09, 16.51.

HRMS (FAB<sup>+</sup>): *m/z* [M+H]<sup>+</sup> calcd. for C<sub>9</sub>H<sub>16</sub>NO<sub>3</sub>:186.1052; found:186.1124.

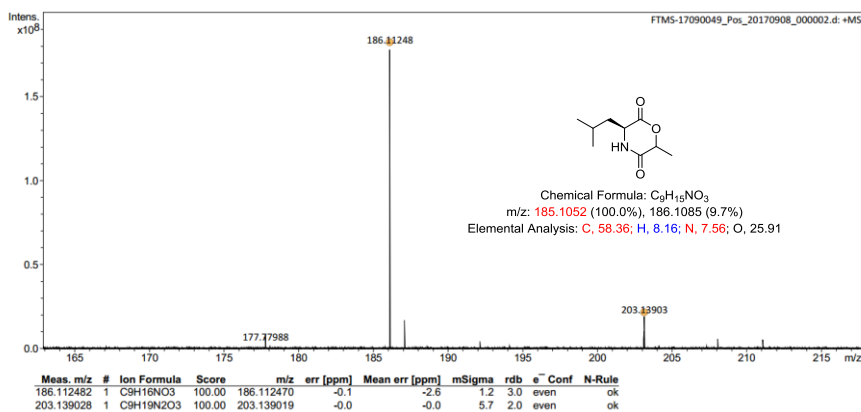
Elemental Analysis: calcd. for C<sub>9</sub>H<sub>15</sub>NO<sub>3</sub>, C, 58.36; H,8.16; N, 7.56. Found: C, 58.38; H, 8.30; N, 7.56.



**Figure S46.**  $^1\text{H}$  NMR spectrum of monomer **2h** in  $\text{CDCl}_3$ .



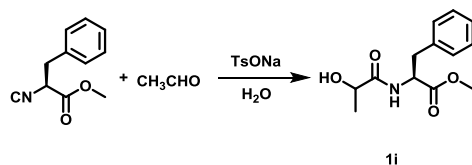
**Figure S47.**  $^{13}\text{C}$  NMR spectrum of monomer **2h** in  $\text{CDCl}_3$ .



**Figure S48.** ESI-MS spectrum of monomer **2h**.

## 2.10 Synthesis of monomer 2i

Methyl 2-(2-hydroxy propanamido)-3-phenyl propanoate (**1i**)



In a 1000 mL round bottom flask, methyl 2-isocyano-3-phenylpropanoate (30 g, 0.16 mol) and sodium *p*-toluenesulfonate (TsONa, 6 g, 0.03 mol) were dissolved in 40% acetaldehyde solution (500 mL), and the reaction mixture was vigorously stirred at room temperature for 12 h. The reaction mixture was concentrated *in vacuo* to provide the crude product which was used directly in the next step. Optionally, the crude product can be further purified by flash column chromatography (EtOAc/PE = 1/1), affording a colorless oil (35.8 g, 90%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (m, 5H), 4.83 (m, 1H), 4.13 (m, 1H), 3.88 (m, 1H), 3.69 (s, 3H), 3.08 (m, 2H), 1.32 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.84, 174.75, 172.10, 171.93, 135.82, 135.73, 129.24, 129.20, 128.61, 128.58, 127.17, 68.25, 68.15, 52.90, 52.65, 52.42, 52.39, 37.94, 37.93, 20.91, 20.89.

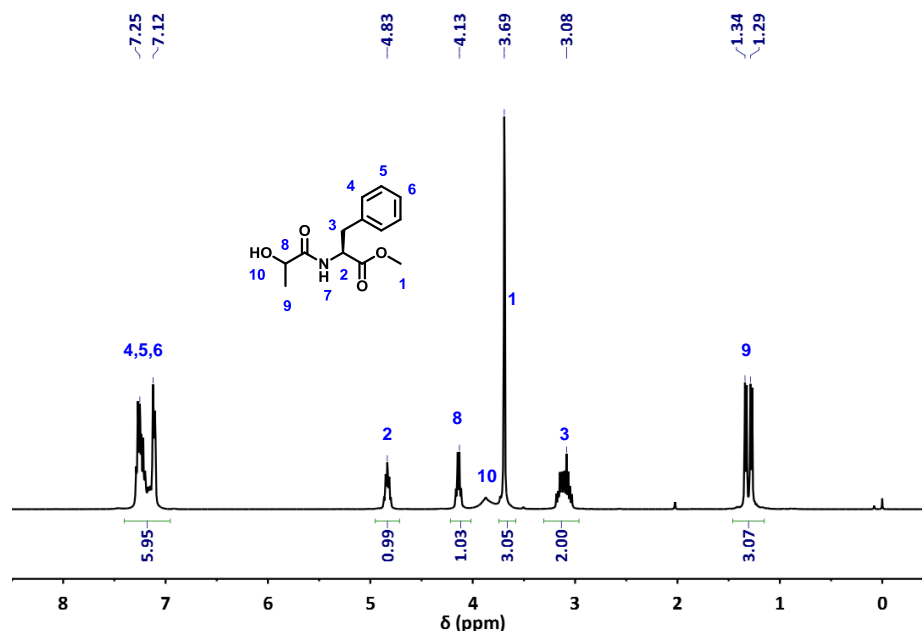
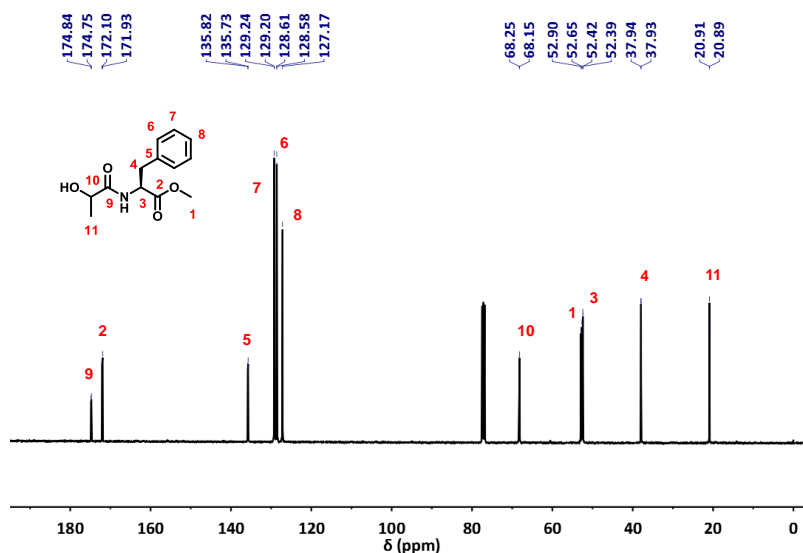
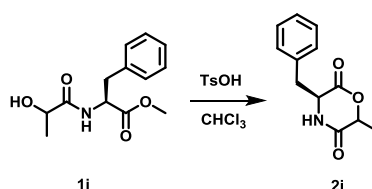


Figure S49.  $^1\text{H}$  NMR spectrum of compound **1i** in  $\text{CDCl}_3$ .



**Figure S50.** <sup>13</sup>C NMR spectrum of compound **1i** in CDCl<sub>3</sub>.

(3*S*)-3-Benzyl 6-methyl-morpholine-2, 5-dione (**2i**)



In a 1000 mL round bottom flask equipped with a Soxhlet extractor (filled with 4Å molecular sieve) and a reflux condenser, compound **1i** (5.0 g, 0.02 mol) and TsOH (1.0 g, 0.006 mol) were added into 500 mL of CHCl<sub>3</sub>. The reaction mixture was allowed to reflux for 12 h., cooled to room temperature, and washed successively with 300 mL of saturated NaHCO<sub>3</sub> solution and 300 mL of H<sub>2</sub>O. The organic layer was collected, dried with anhydrous MgSO<sub>4</sub>, and concentrated to remove the solvent under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/PE = 3/7) to provide the desired product (**2i**) as a white solid (3.50 g, 80%). *T<sub>m</sub>* = 99.6 °C.  $[\alpha]_{365}^{25} = +51.4 \text{ deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$  (*c* = 2.0\*10<sup>-3</sup> g/mL in THF).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.30 (m, 5H), 6.15 (d, 1H), 4.84 (m, 0.5H), 4.44 (m, 1H), 4.11 (m, 0.5H), 3.22 (m, 2H), 1.45 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 168.54, 168.43, 167.09, 166.93, 134.53, 134.41, 129.78, 129.57, 129.25, 128.04, 127.93, 74.86, 74.32, 55.78, 54.68, 39.98, 38.17, 17.57, 16.97.

HRMS (FAB<sup>+</sup>): *m/z* [M+H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>14</sub>NO<sub>3</sub>: 220.0895; found: 220.0968.

Elemental Analysis: calcd. for C<sub>12</sub>H<sub>14</sub>NO<sub>3</sub>, C, 65.74; H, 5.98; N, 6.39. Found: C, 65.65; H, 5.91; N, 6.39.

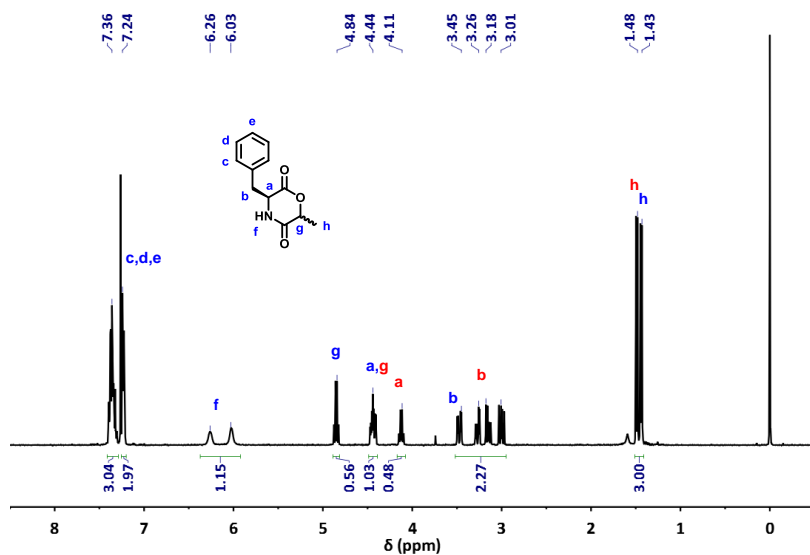


Figure S51. <sup>1</sup>H NMR spectrum of monomer **2i** in CDCl<sub>3</sub>.

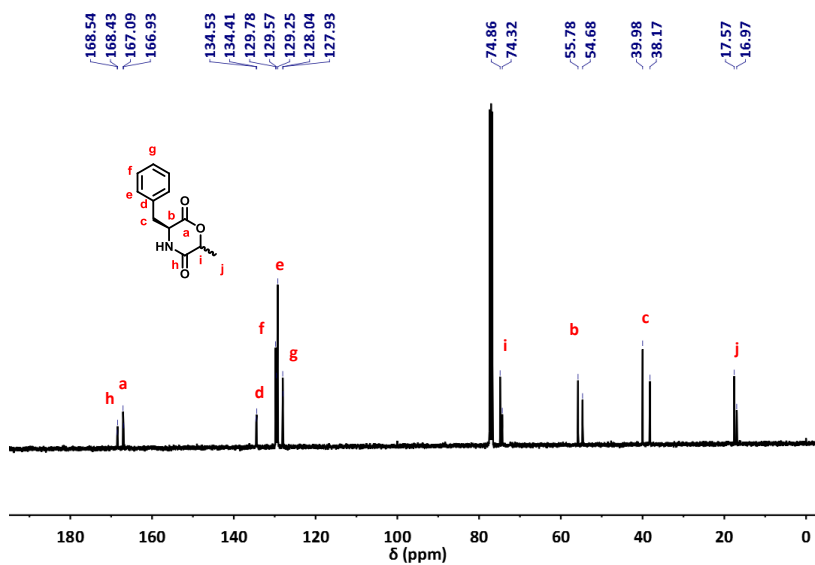


Figure S52. <sup>13</sup>C NMR spectrum of monomer **2i** in CDCl<sub>3</sub>.

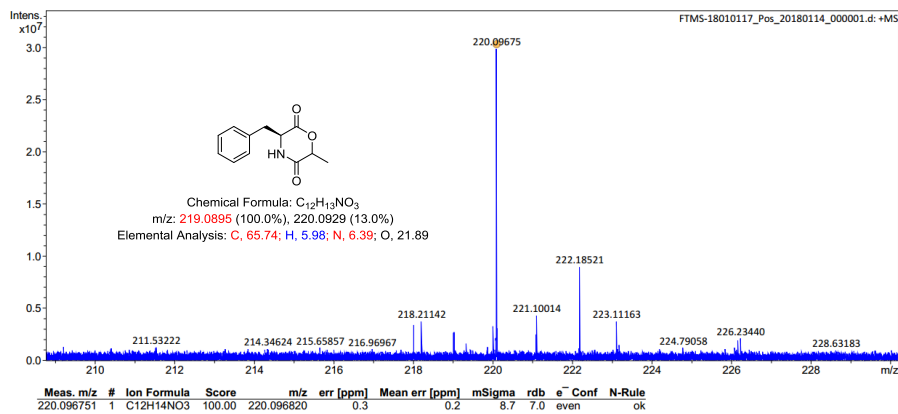


Figure S53. ESI-MS spectrum of monomer **2i**.

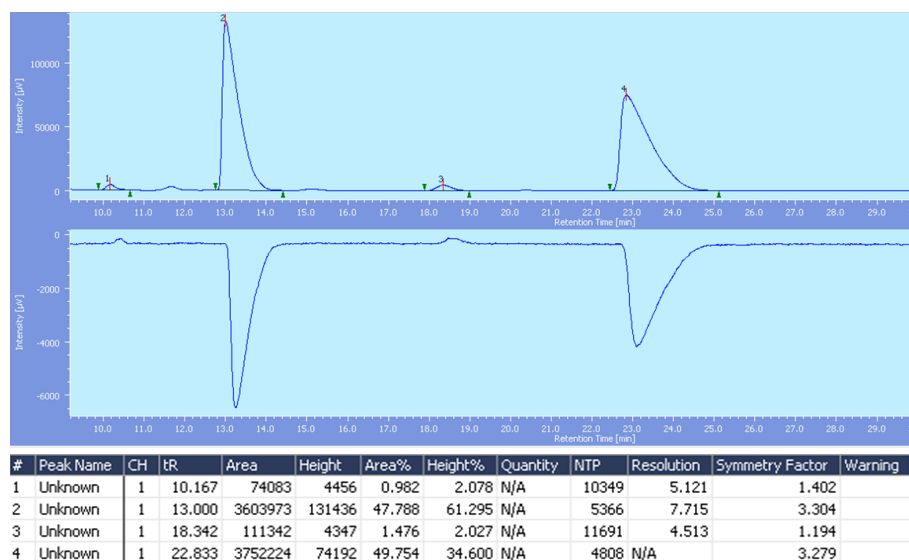
## 2.11. Separation and characterization of 3-benzyl-6-methyl-morpholine-2, 5-dione (**2i**) diastereoisomers

(3*S*, 6*R*)-3-benzyl-6-methyl -morpholine-2, 5-dione ((3*S*,6*R*)-**2i**)

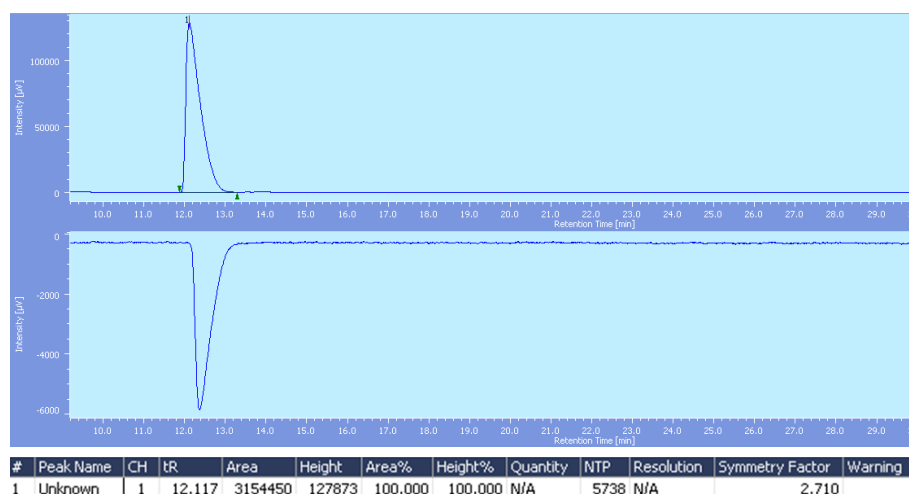
$[\alpha]_{365}^{25} = +244.9 \text{ deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$  ( $c = 2.0 \cdot 10^{-3} \text{ g/mL}$  in THF).

(3*S*, 6*S*)-3-benzyl-6-methyl -morpholine-2, 5-dione ((3*S*,6*S*)-**2i**)

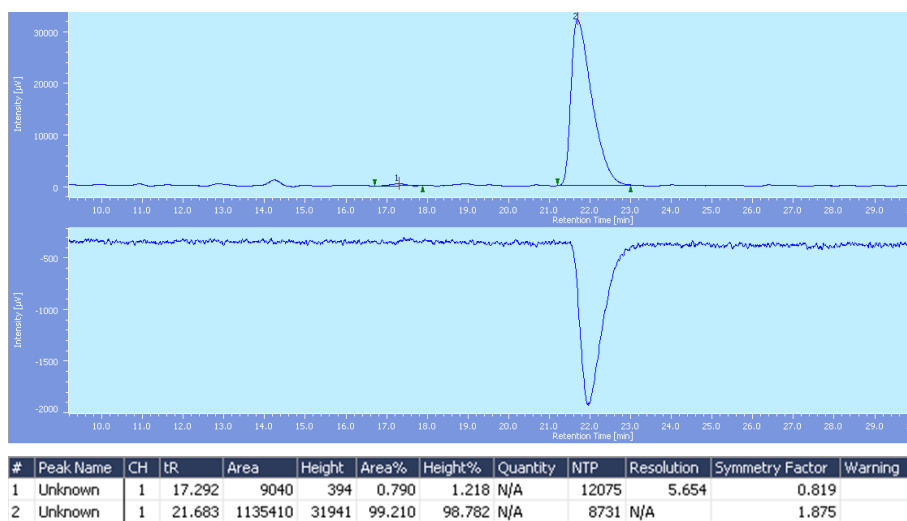
$[\alpha]_{365}^{25} = -338.3 \text{ deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$  ( $c = 2.0 \cdot 10^{-3} \text{ g/mL}$  in THF).



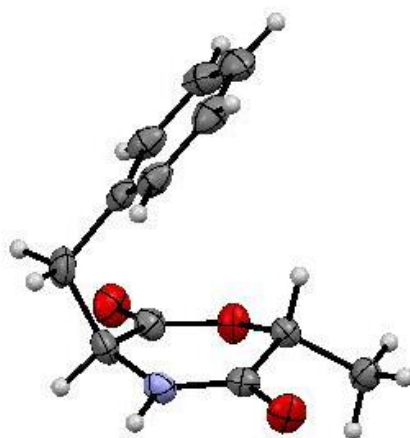
**Figure S54.** HPLC chromatogram of (3*S*,6*S*/*R*)-**2i** separated by chiral column into diastereoisomers with minor racemization (Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min,  $\lambda = 254 \text{ nm}$ ,  $t_1 = 10.1 \text{ min}$ ;  $t_2 = 13.0 \text{ min}$ ;  $t_3 = 18.3 \text{ min}$ ;  $t_4 = 22.8 \text{ min}$ ).



**Figure S55.** HPLC chromatogram of (3*S*,6*R*)-**2i**, (Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min,  $\lambda = 254 \text{ nm}$ ).



**Figure S56.** HPLC chromatogram of (3*S*,6*S*)-**2i**, (Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min,  $\lambda$ = 254 nm).

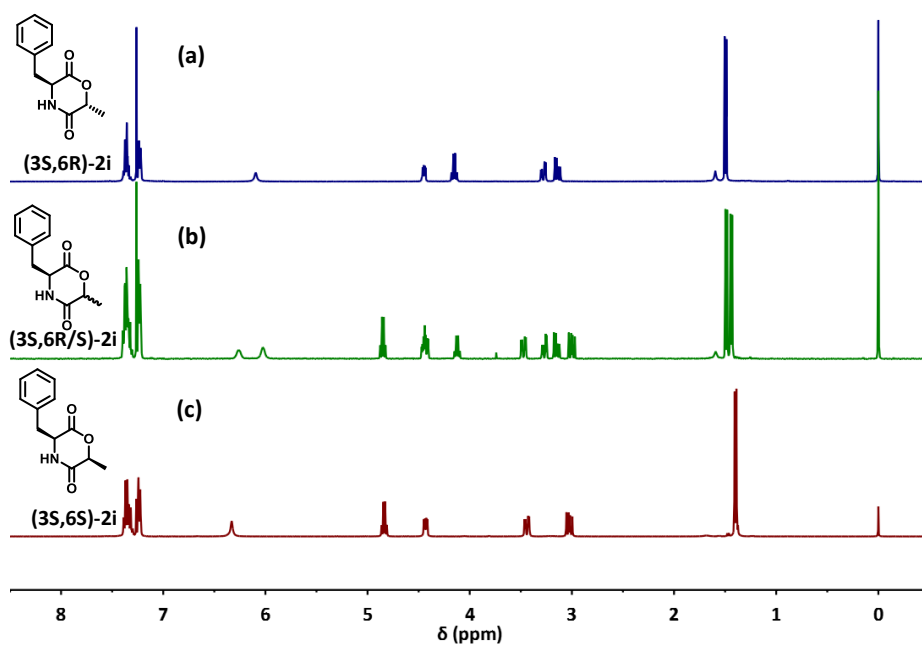


**Figure S57.** The molecular structure of monomer (3*S*, 6*R*)-**2i**, and the hydrogen atoms are omitted for clarity.

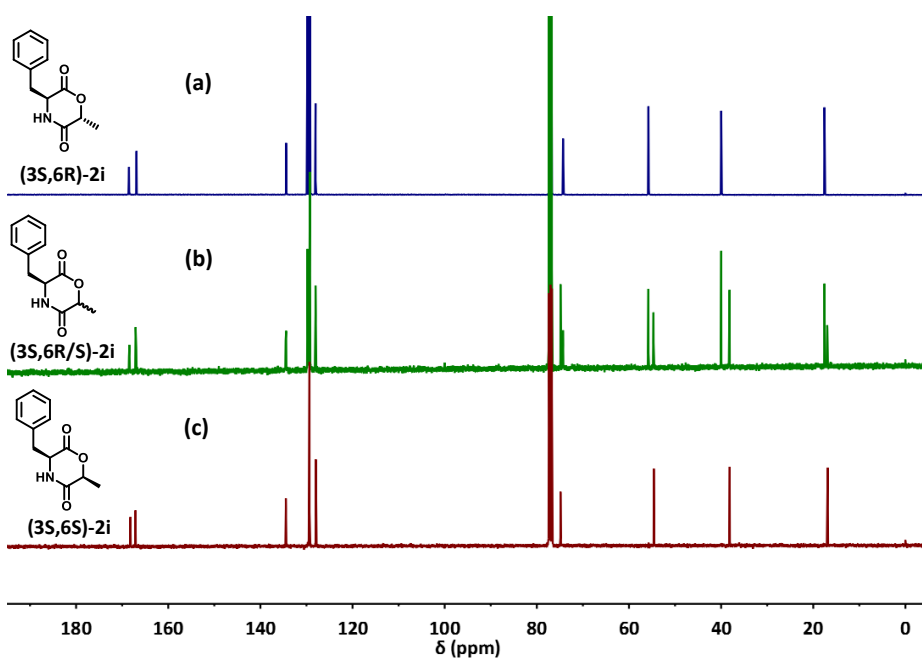
Crystallographic data of (3S, 6R)-**2i** has been deposited with the Cambridge Crystallographic Data Centre as supplementary information (nos. CCDC 1862221), Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Crystal data, data collection and processing parameters for (3S, 6R)-**2i** are summarized in Table S1.

**Table S1. Crystal data and structure refinement for (3S, 6R)-**2i**.**

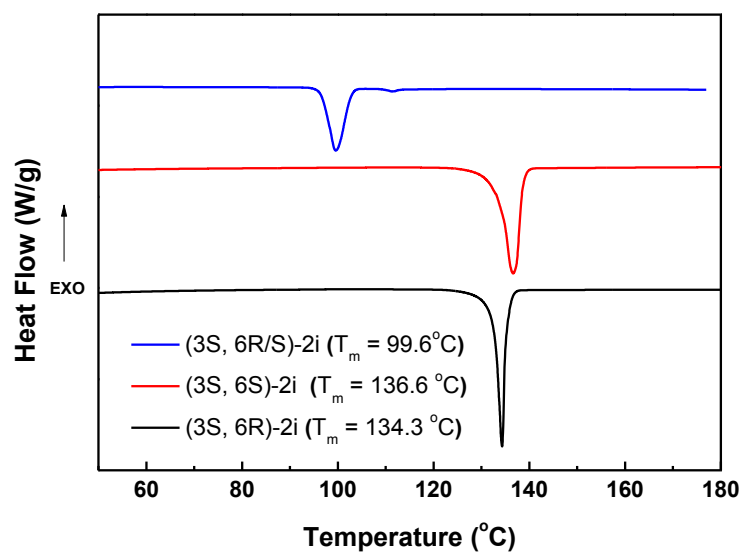
Identification code	(3S, 6R)- <b>2i</b>
Empirical formula	C <sub>12</sub> H <sub>13</sub> NO <sub>3</sub>
Formula weight	219.23
Temperature/K	149.7(4)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	6.5387(2)
b/Å	10.7125(3)
c/Å	15.1777(5)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1063.13(6)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.370
μ/mm <sup>-1</sup>	0.817
F(000)	464.0
Crystal size/mm <sup>3</sup>	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	10.106 to 148.148
Index ranges	-8 ≤ h ≤ 7, -11 ≤ k ≤ 13, -18 ≤ l ≤ 16
Reflections collected	2670
Independent reflections	1834 [R <sub>int</sub> = 0.0242, R <sub>sigma</sub> = 0.0320]
Data/restraints/parameters	1834/1/149
Goodness-of-fit on F <sup>2</sup>	1.025
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0381, wR <sub>2</sub> = 0.1005
Final R indexes [all data]	R <sub>1</sub> = 0.0389, wR <sub>2</sub> = 0.1024
Largest diff. peak/hole / e Å <sup>-3</sup>	0.15/-0.25
Flack parameter	-0.13(17)



**Figure S58.**  $^1\text{H}$  NMR spectra of (a) monomer (3S, 6R)-**2i**; (b) monomer (3S, 6R/S)-**2i** (diastereoisomer) and (c) monomer (3S, 6S)-**2i** in  $\text{CDCl}_3$ .



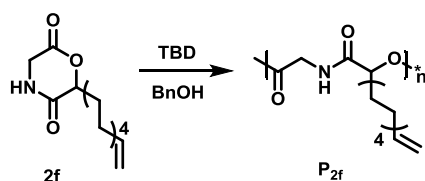
**Figure S59.**  $^{13}\text{C}$  NMR spectra of (a) monomer (3S, 6R)-**2i**; (b) monomer (3S, 6R/S)-**2i** (diastereoisomer) and (c) monomer (3S, 6S)-**2i** in  $\text{CDCl}_3$ .



**Figure S60.** DSC thermograms of monomer (3S, 6R/S)-2i (blue line), (3S, 6S)-2i (red line) and (3S, 6R)-2i (black line) (first-heating-scan curves (10 °C/min)).

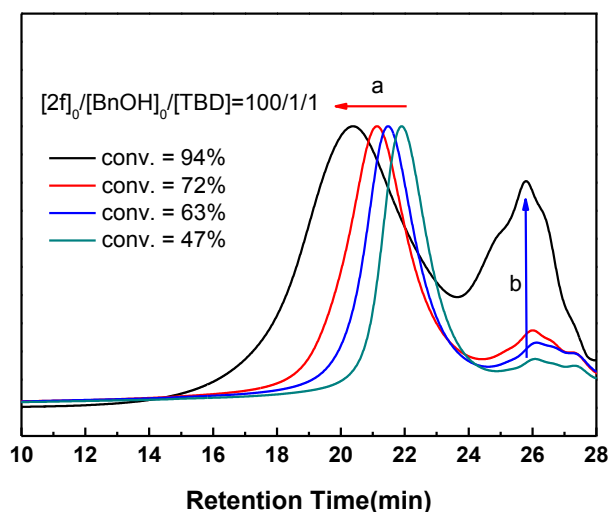
### 3. General procedure for the ROP of MDs

*ROP of 2f catalyzed by TBD: Representative example (entry 1, table 1).*



In a N<sub>2</sub>-filled glovebox, monomer **2f** (160 mg, 0.64 mmol) and BnOH (0.7 mg, 0.0064 mmol) were dissolved in DCM (0.9 mL) in a 4 mL vial containing a micro stir bar. After the monomer was dissolved completely, 0.1 mL of TBD solution (0.064 mol/L in DCM) was added to the vial. After 2 h., 0.5 mL of benzoic acid solution (0.064 mol/L in DCM) was added to quench the reaction. The polymer was purified by three successive precipitations from diethyl ether and dried in *vacuo*.

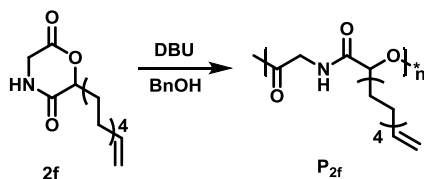
In another experiment, the kinetics of the polymerization was followed. Samples (0.1 mL) were taken out periodically and transferred into NMR tubes, and quickly quenched by adding 0.05 mL of benzoic acid solution (0.064 mol/L in DCM). Solvents were removed in *vacuo* and then each sample was characterized by <sup>1</sup>H NMR to obtain the monomer conversions and SEC to obtain the molecular weight and dispersity. The time-dependent SEC traces of the polymerization were shown below.



**Figure S61.** SEC traces of polymer **P<sub>2f</sub>** at different conversions.

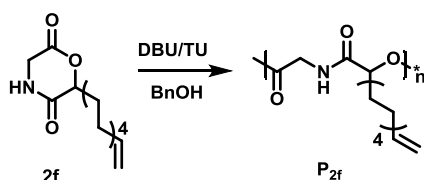
( $[2f]_0/[BnOH]_0/[TBD] = 100/1/1$ ,  $[2f]_0 = 0.64$  mol/L, T: 25 °C, solvent: DCM)

**ROP of 2f catalyzed by DBU: Representative example (entry 2, table 1).**



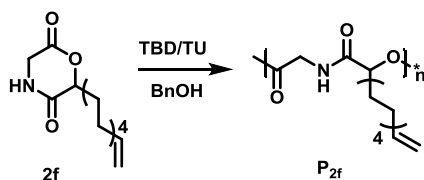
In a N<sub>2</sub>-filled glovebox, monomer **2f** (160 mg, 0.64 mmol) and BnOH (0.7 mg, 0.0064 mmol) were dissolved in DCM (0.9 mL) in a 4 mL vial containing a micro stir bar. After the monomer was dissolved completely, 0.1 mL of DBU solution (0.064 mol/L in DCM) was added to the vial. After 230 min., 0.5 mL of benzoic acid solution (0.064 mol/L in DCM) was added to quench the reaction. The polymer was purified by three successive precipitations from diethyl ether and dried in *vacuo*.

**ROP of 2f catalyzed by DBU/TU: Representative example (entry 3, table 1)**



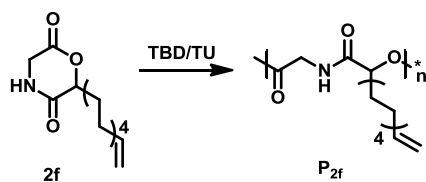
In a N<sub>2</sub>-filled glovebox, monomer **2f** (160 mg, 0.64 mmol), TU (11.8 mg, 0.032 mmol) and BnOH (0.7 mg, 0.0064 mmol) were dissolved in DCM (0.9 mL) in a 4 mL vial containing a micro stir bar. After the monomer was dissolved completely, 0.1 mL of DBU solution (0.064 mol/L in DCM) was added to the vial. After 300 min., 0.5 mL of benzoic acid solution (0.064 mol/L in DCM) was added to quench the reaction. The polymer was purified by three successive precipitations from diethyl ether and dried in *vacuo*.

**ROP of 2f catalyzed by TBD/TU: Representative example (entry 6, table 1)**



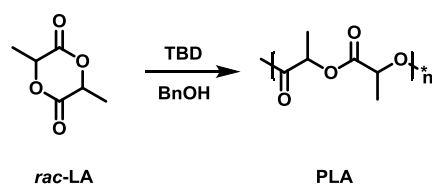
In a N<sub>2</sub>-filled glovebox, monomer **2f** (160 mg, 0.64 mmol), TU (11.8 mg, 0.032 mmol) and BnOH (0.7 mg, 0.0064 mmol) were dissolved in DCM (0.9 mL) in a 4 mL vial containing a micro stir bar. After the monomer was dissolved completely, 0.1 mL of TBD solution (0.064 mol/L in DCM) was added to the vial. After 120 min., 0.5 mL of benzoic acid solution (0.064 mol/L in DCM) was added to quench the reaction. The polymer was purified by three times precipitation from diethyl ether and dried in *vacuo*.

**ROP of 2f catalyzed by TBD (no BnOH)**

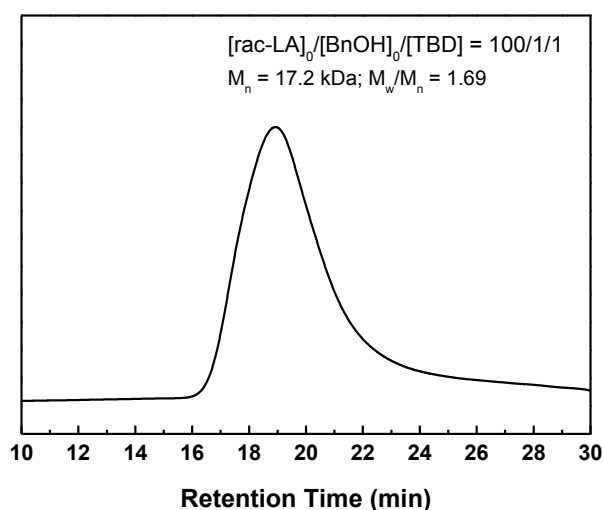


In a N<sub>2</sub>-filled glovebox, monomer **2f** (160 mg, 0.64 mmol) was dissolved in DCM (0.9 mL) in a 4 mL vial containing a micro stir bar. After the monomer was dissolved completely, 0.1 mL of TBD containing the (0.064 mol/L in DCM) was added to the vial. The reaction was stirred at room temperature. When the reaction finished, 0.5 mL of benzoic acid solution (0.064 mol/L in DCM) was added to quench the reaction. The polymer was purified by three successive precipitations from diethyl ether and dried in *vacuo*.

### ROP of *rac*-LA catalyzed by TBD



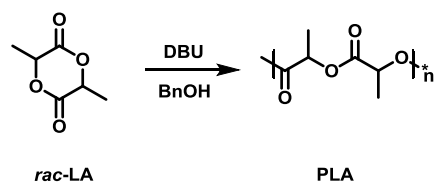
In a N<sub>2</sub>-filled glovebox, *rac*-LA (92 mg, 0.64 mmol) and BnOH (0.7 mg, 0.0064 mmol) were dissolved in DCM (0.9 mL) in a 4 mL vial containing a micro stir bar. After the monomer was dissolved completely, 0.1 mL of TBD solution (0.064 mol/L in DCM) was added to the vial. The reaction was stirred at room temperature. When the reaction finished, 0.5 mL of benzoic acid solution (0.064 mol/L in DCM) was added to quench the reaction. The polymer was purified by three successive precipitations from diethyl ether and dried in *vacuo*.



**Figure S62.** SEC trace of PLA catalyzed by TBD in the presence of BnOH.

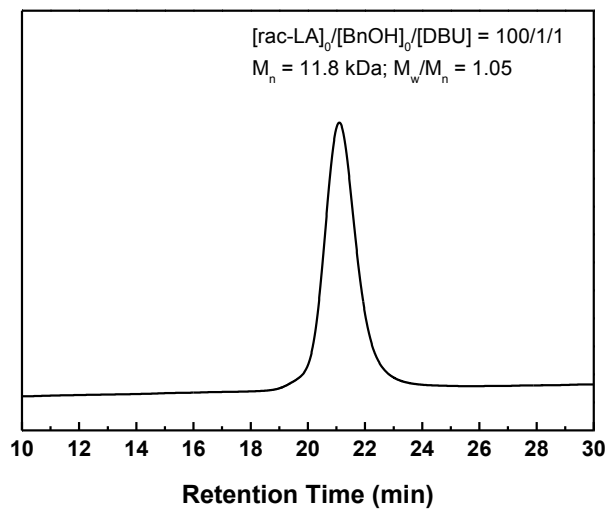
( $[rac\text{-LA}]_0/[BnOH]_0/[TBD] = 100/1/1$ ,  $[rac\text{-LA}]_0 = 0.64$  mol/L, T: 25 °C, solvent: DCM)

### ROP of *rac*-LA catalyzed by DBU



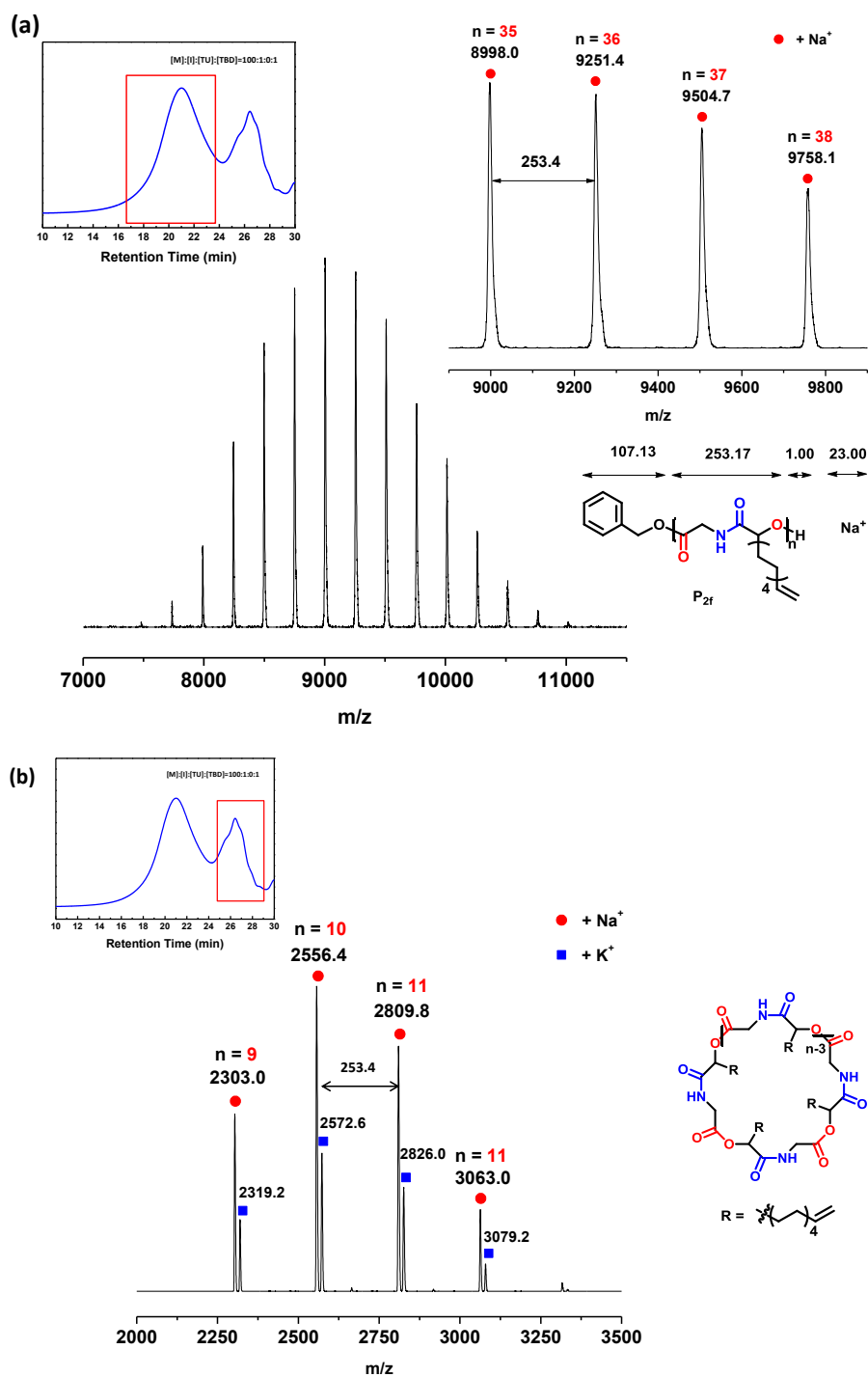
In a N<sub>2</sub>-filled glovebox, *rac*-LA (92 mg, 0.64 mmol) and BnOH (0.7 mg, 0.0064 mmol) were dissolved in DCM (0.9 mL) in a 4 mL vial containing a micro stir bar. After the monomer was dissolved completely, 0.1 mL of DBU solution (0.064 mol/L in DCM) was added to the vial. The reaction was stirred at room temperature. When the reaction

finished, 0.5 mL of benzoic acid solution (0.064 mol/L in DCM) was added to quench the reaction. The polymer was purified by three successive precipitations from diethyl ether and dried in *vacuo*.



**Figure S63.** SEC trace of PLA catalyzed by DBU in the presence of BnOH.

( [rac-LA]<sub>0</sub>/[BnOH]<sub>0</sub>/[DBU]= 100/1/1, [rac-LA]<sub>0</sub>=0.64 mol/L,T: 25 °C, solvent: DCM)



**Figure S64.** MALDI-TOF mass spectra of linear  $\text{P}_{2f}$  and cyclic  $\text{P}_{2f}$  separated by recycling preparative HPLC (a) BnOH-initiated linear  $\text{P}_{2f}$  (b) cyclic  $\text{P}_{2f}$ .

#### 4. ROP kinetic studies and characterization of polymers

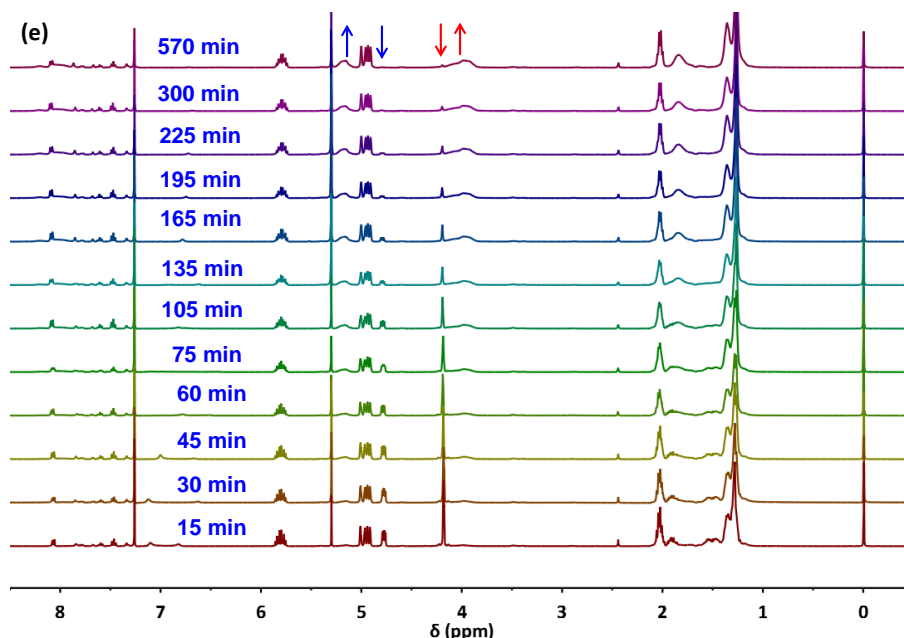
##### *Kinetic studies of the ROP of 2f catalyzed by DBU/TU*

In a N<sub>2</sub>-filled glovebox, monomer **2f** (320 mg, 1.28 mmol), TU (23.6 mg, 0.064 mmol) and BnOH (1.4 mg, 0.0128 mmol) were dissolved in DCM (1.8 mL) in a 4 mL vial containing a micro stir bar. After the monomer was dissolved completely, the polymerization was started by rapid addition of 0.2 mL of DBU solution (0.064 mol/L in DCM) to the vial under vigorous stirring. After the prescribed time, samples (0.1 mL) were taken out and transferred into NMR tubes, and quickly quenched by adding 0.05 mL of benzoic acid solution (0.064 mol/L in DCM). Solvents were removed in *vacuo* and then each sample was characterized by <sup>1</sup>H NMR to obtain the monomer conversions and SEC to obtain the molecular weight and dispersity.

The polymerization kinetic of monomer **2c** and **2g** was followed in the same way.

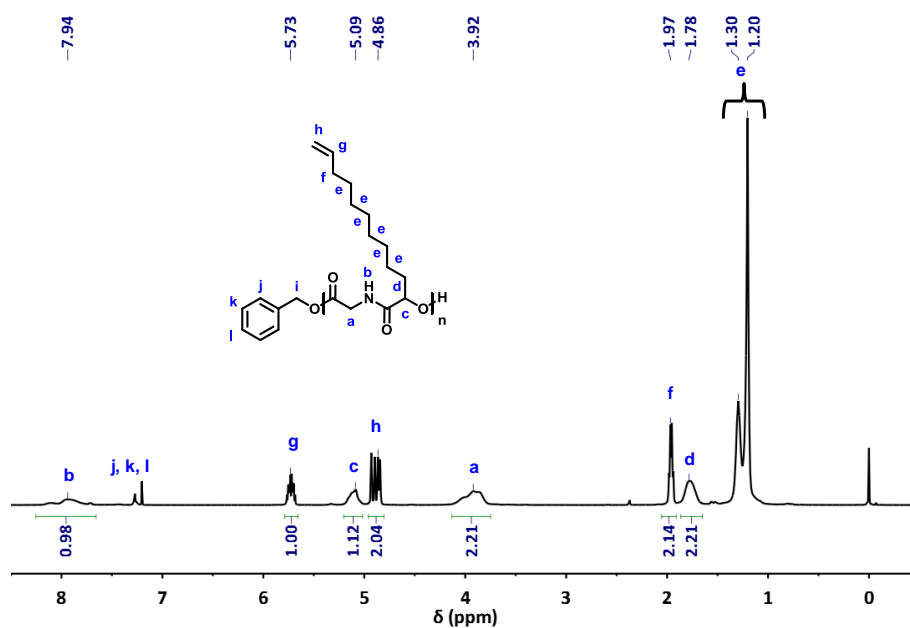
##### *Kinetic studies of the ROP of 2f catalyzed by TBD/TU*

The experimental procedure was the same as for the ROP of **2f** catalyzed by DBU/TU, with TBD replacing DBU.

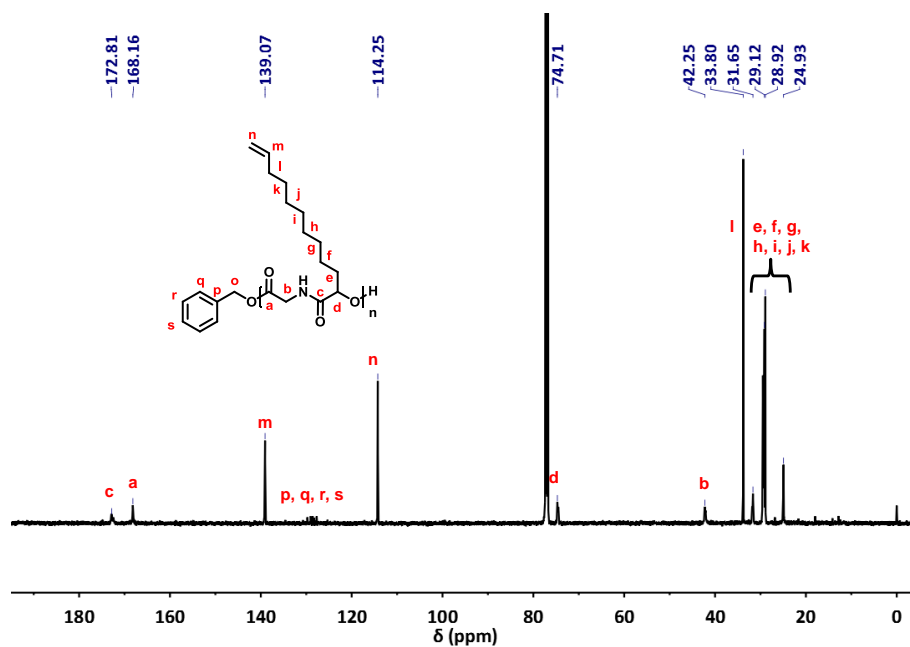


**Figure S65.** Time-dependent *in-situ* <sup>1</sup>H NMR spectra of ROP of **2f** catalyzed by DBU/TU.

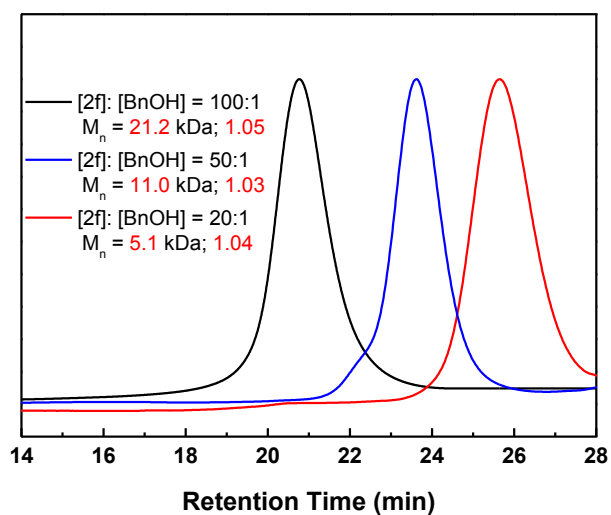
([**2f**]<sub>0</sub>/[BnOH]<sub>0</sub>/[DBU]/[TU] = 100/1/1/5, [**2f**]<sub>0</sub> = 0.64 mol/L, T: 25 °C, solvent: DCM).



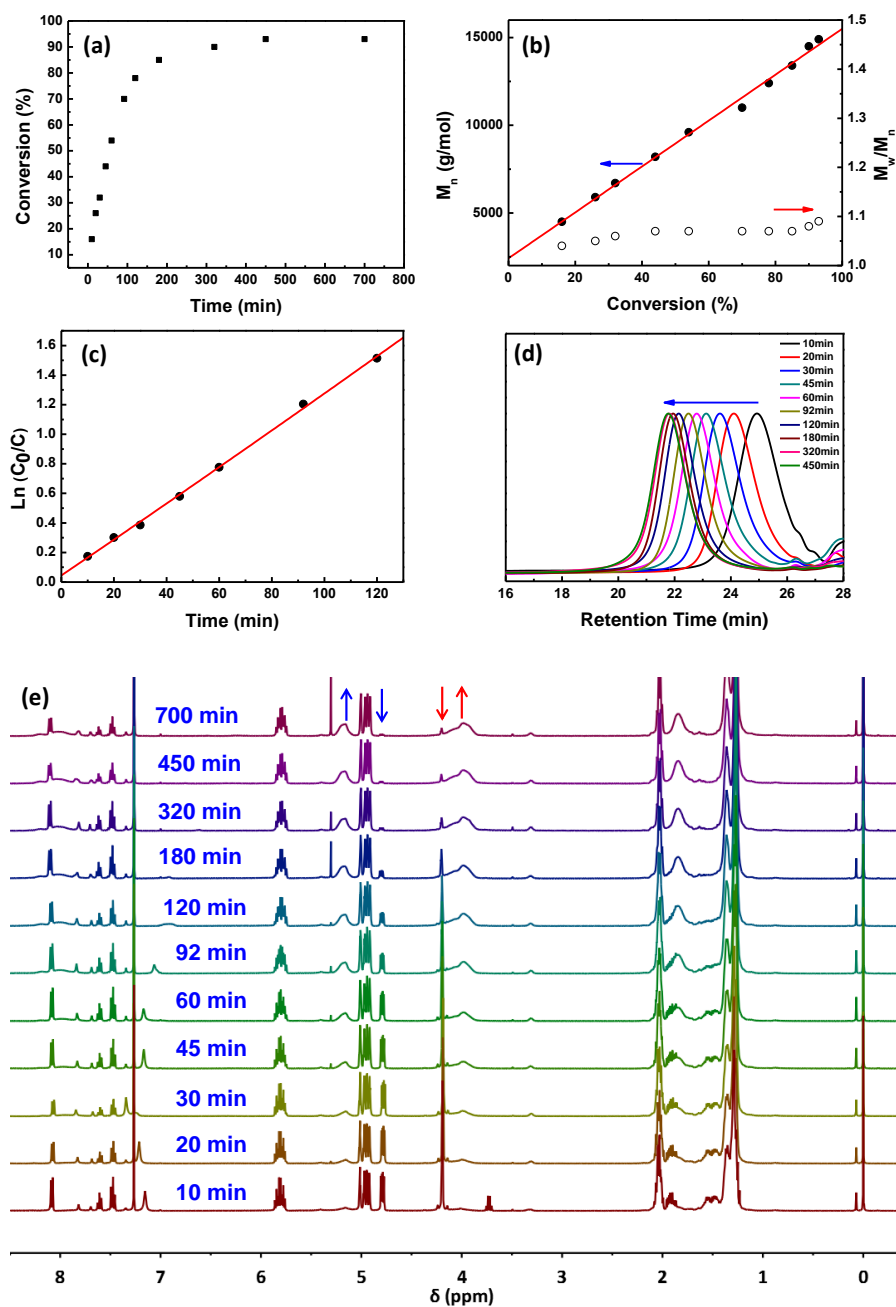
**Figure S66.**  $^1\text{H}$  NMR spectrum of **P<sub>2f</sub>** in  $\text{CDCl}_3$ .  
 ( $[\mathbf{2f}]_0/[\text{BnOH}]_0/[\text{DBU}]_0/[\text{TU}]_0 = 100/1/1/5$ , quenched at 44% conversion)



**Figure S67.**  $^{13}\text{C}$  NMR spectrum of **P<sub>2f</sub>** in  $\text{CDCl}_3$ .  
 ( $[\mathbf{2f}]_0/[\text{BnOH}]_0/[\text{DBU}]_0/[\text{TU}]_0 = 100/1/1/5$ , quenched at 44% conversion)



**Figure S68.** SEC traces of  $P_{2f}$  obtained at different  $[2f]_0/[BnOH]_0$  ratios. ( $[2f]_0/[BnOH]_0/[DBU]/[TU] = 100/x/1/5$ ,  $[2f]_0 = 0.64$  mol/L, T: 25 °C, solvent: DCM).



**Figure S69.** ROP kinetics of **2f** catalyzed by TBD/TU

( $[\mathbf{2f}]_0/[\text{BnOH}]_0/[\text{TBD}]/[\text{TU}] = 100/1/1/5$ ,  $[\mathbf{2f}]_0 = 0.64 \text{ mol/L}$ , T: 25 °C, solvent: DCM).

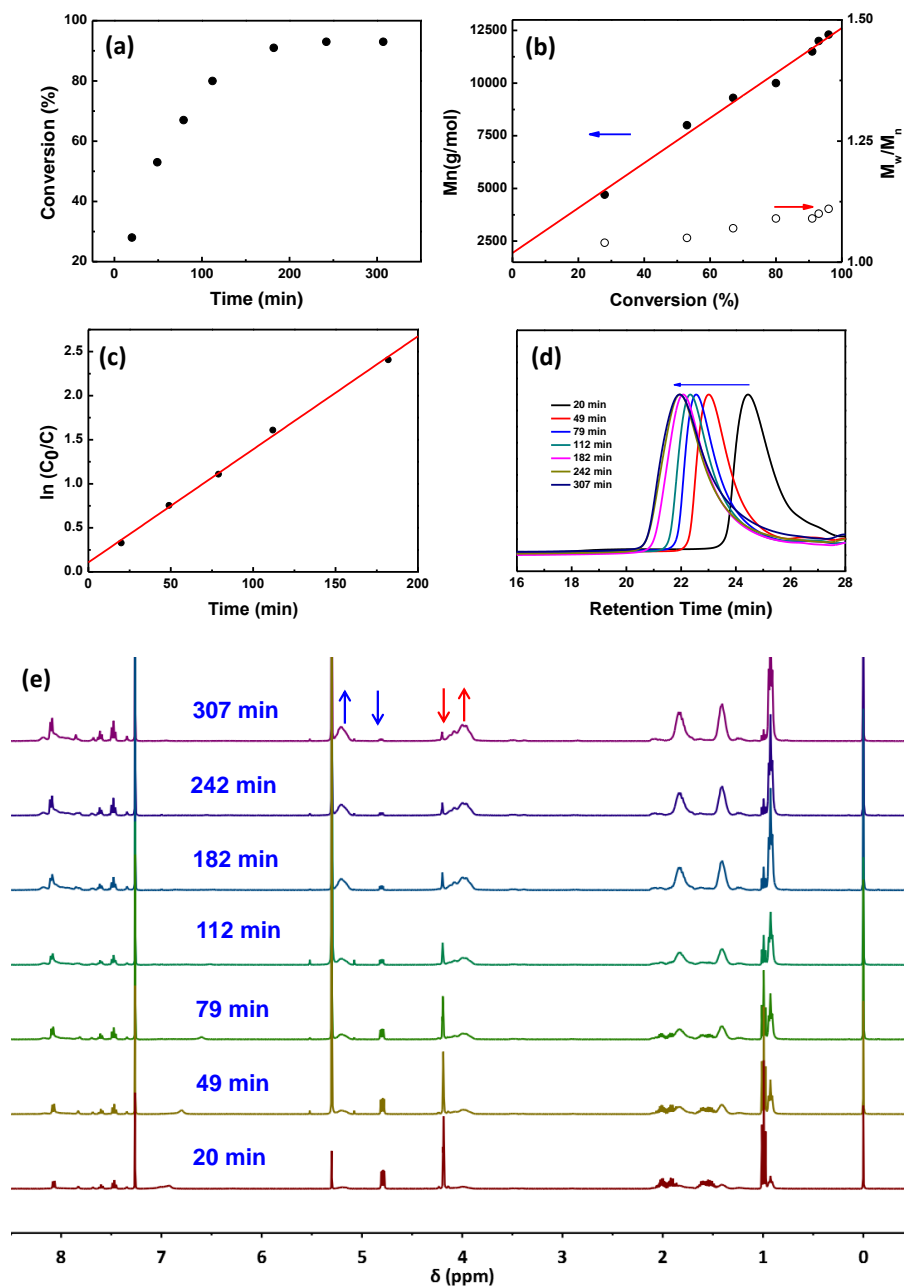
(a) Conversion versus time plot of **2f**.

(b) Plots of  $M_n$  and  $\bar{D}$  versus **2f** conversions.

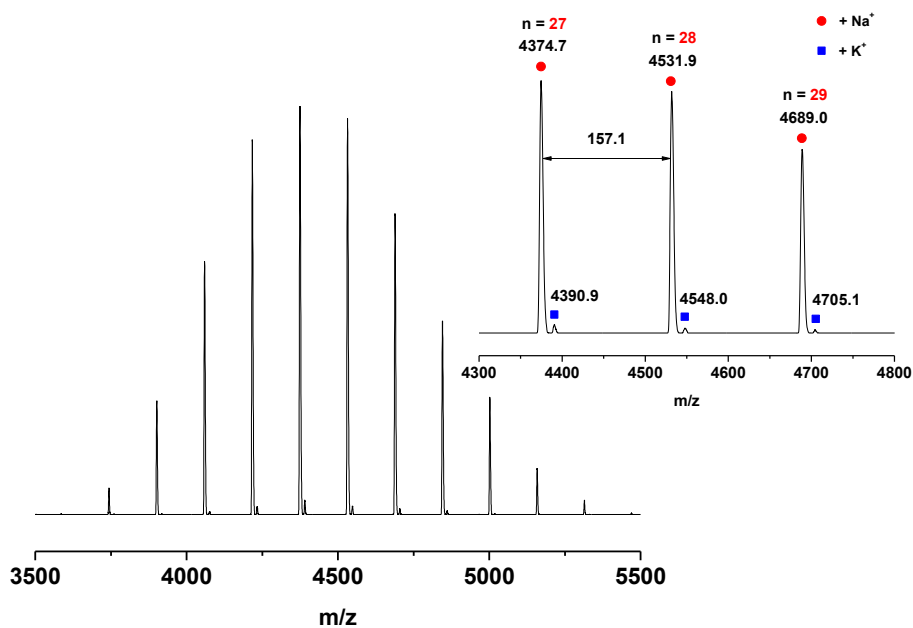
(c) Semilogarithmic kinetic plot of **2f** versus time.

(d) SEC traces of  $\mathbf{P}_{2f}$  obtained at different polymerization time.

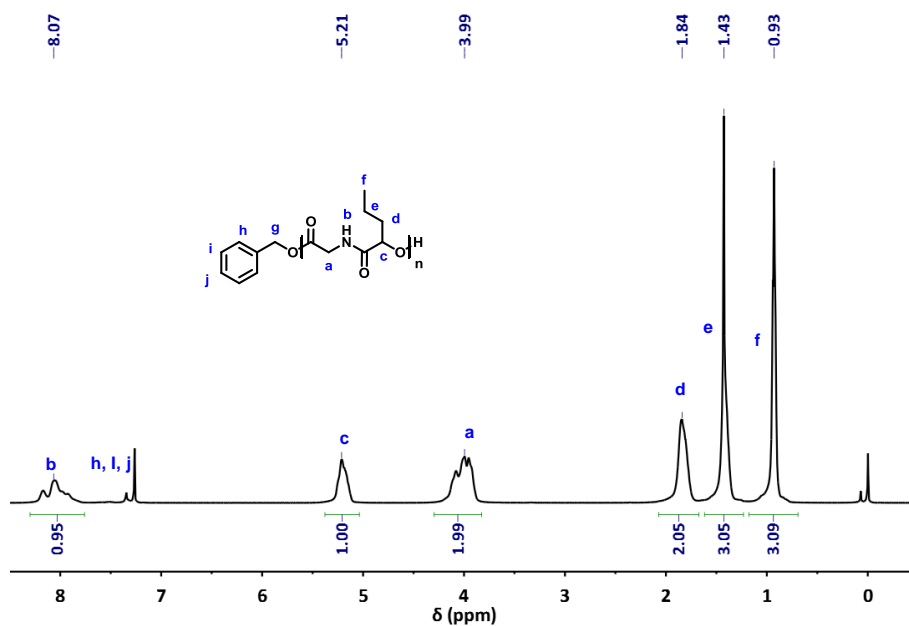
(e) Time-dependent *in-situ*  $^1\text{H}$  NMR spectra of the polymerization mixture.



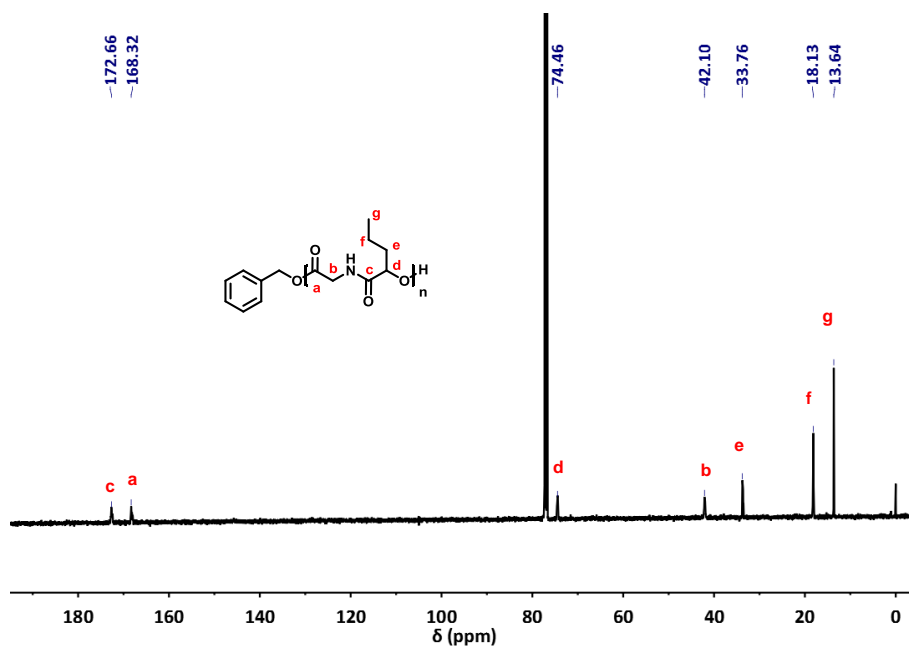
**Figure S70.** ROP kinetics of **2c** catalyzed by DBU/TU  
 ( $[2\mathbf{f}]_0/[BnOH]_0/[DBU]/[TU] = 100/1/1/5$ ,  $[2\mathbf{c}]_0 = 0.64$  mol/L, T: 25 °C, solvent: DCM).  
 (a) Conversion versus time plot of **2c**.  
 (b) Plots of  $M_n$  and  $\bar{D}$  versus **2c** conversions.  
 (c) Semilogarithmic kinetic plot of **2c** versus time.  
 (d) SEC traces of  $\mathbf{P}_{2c}$  obtained at different polymerization time.  
 (e) Time-dependent *in-situ*  $^1\text{H}$  NMR spectra of the polymerization mixture.



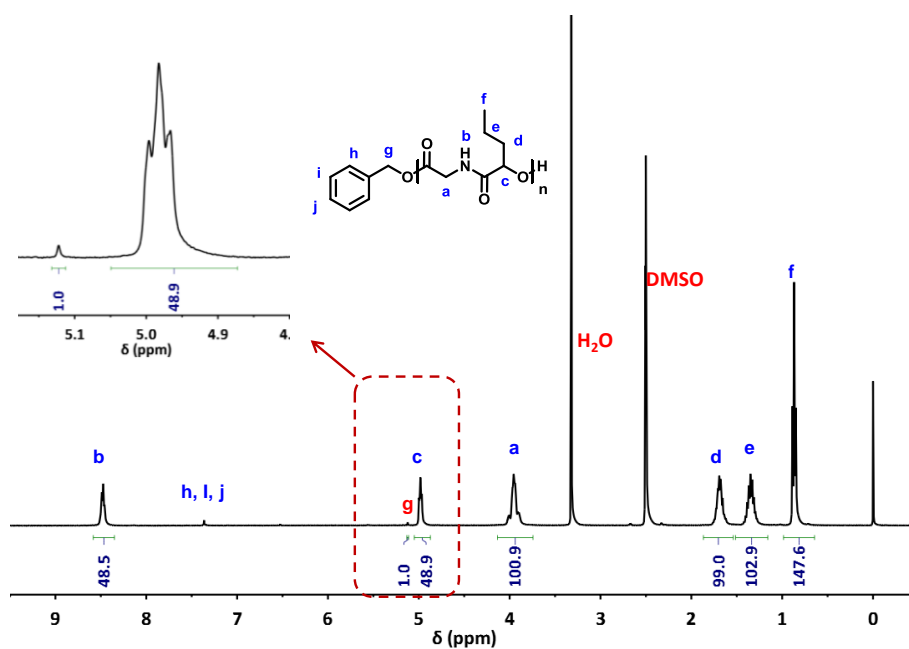
**Figure S71.** MALDI-TOF mass spectrum of linear  $P_{2c}$ .  
 ( $[2c]_0/[BnOH]_0/[TBD]/[TU] = 100/1/1/5$ , quenched at 38% conversion)



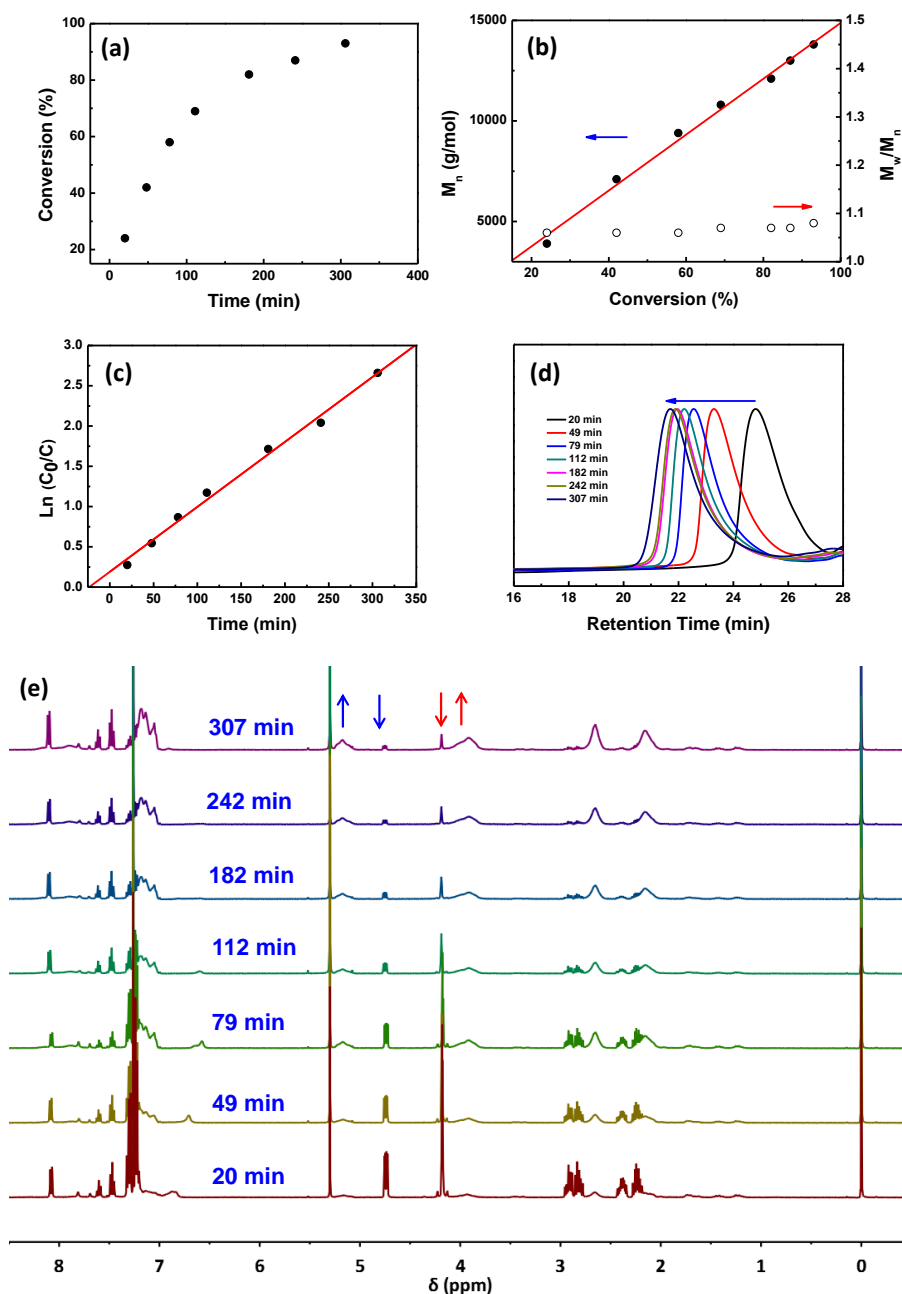
**Figure S72.**  $^1H$  NMR spectrum of  $P_{2c}$  in  $CDCl_3$ .  
 ( $[2c]_0/[BnOH]_0/[TBD]/[TU] = 100/1/1/5$ , quenched at 91% conversion)



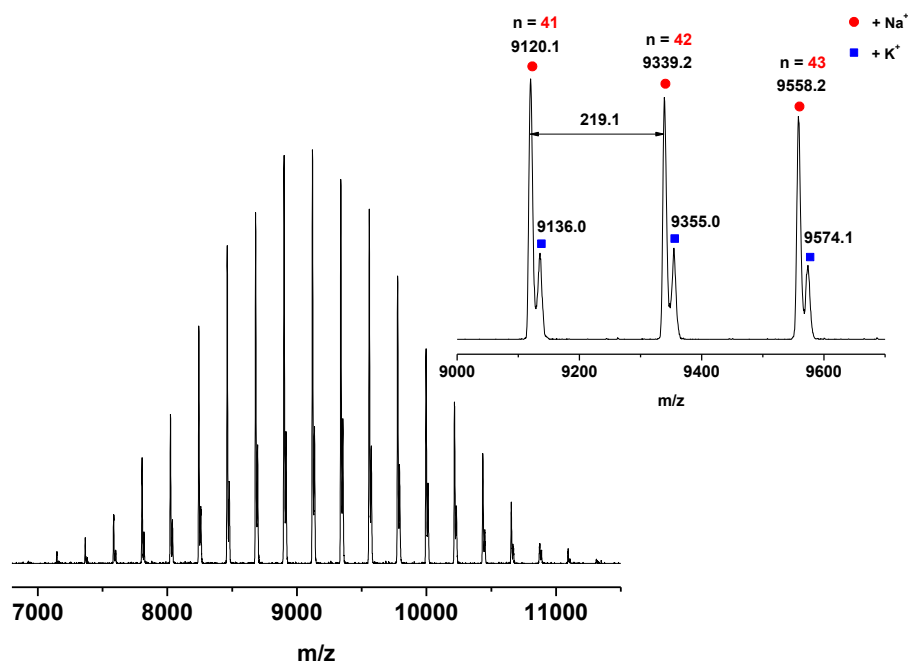
**Figure S73.**  $^{13}\text{C}$  NMR spectrum of polymer  $P_{2c}$  in  $\text{CDCl}_3$ .  
 ( $[\text{2c}]_0/[\text{BnOH}]_0/[\text{TBD}]/[\text{TU}] = 100/1/1/5$ , quenched at 91% conversion)



**Figure S74.**  $^1\text{H}$  NMR spectrum of  $P_{2c}$  in  $\text{DMSO-}d_6$ .  
 ( $[\text{2c}]_0/[\text{BnOH}]_0/[\text{TBD}]/[\text{TU}] = 100/1/1/5$ , quenched at 91% conversion)

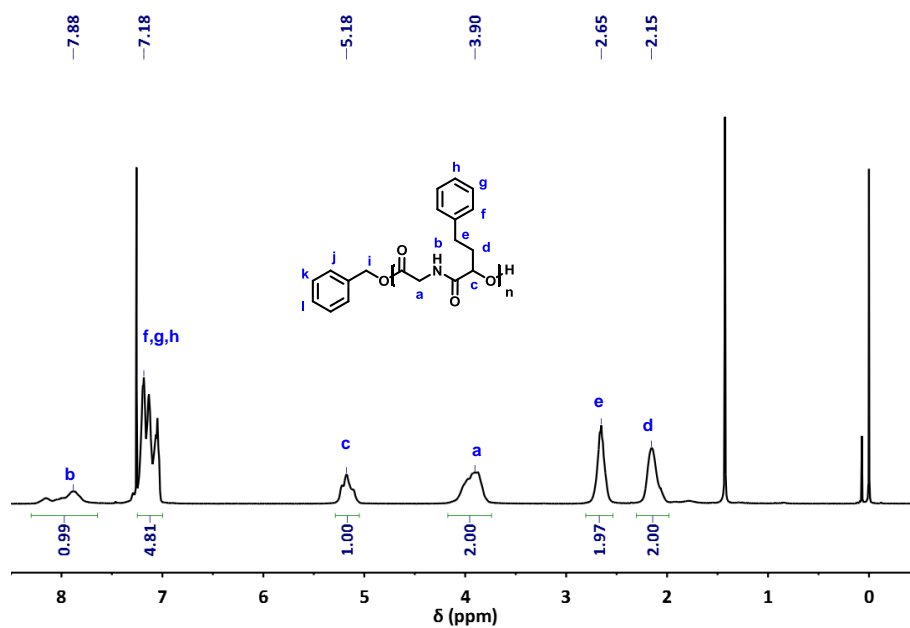


**Figure S75.** ROP kinetics of **2g** catalyzed by DBU/TU  
 ( $[\mathbf{2g}]_0/[\text{BnOH}]_0/[\text{DBU}]/[\text{TU}] = 100/1/1/5$ ,  $[\mathbf{2g}]_0 = 0.64 \text{ mol/L}$ ,  $T: 25 \text{ }^\circ\text{C}$ , solvent: DCM).  
 (a) Conversion versus time plot of **2g**.  
 (b) Plots of  $M_n$  and  $\bar{D}$  versus **2g** conversions.  
 (c) Semilogarithmic kinetic plot of **2g** versus time.  
 (d) SEC traces of  $\mathbf{P}_{2g}$  obtained at different polymerization time.  
 (e) Time-dependent *in-situ*  $^1\text{H}$  NMR spectra of the polymerization mixture.



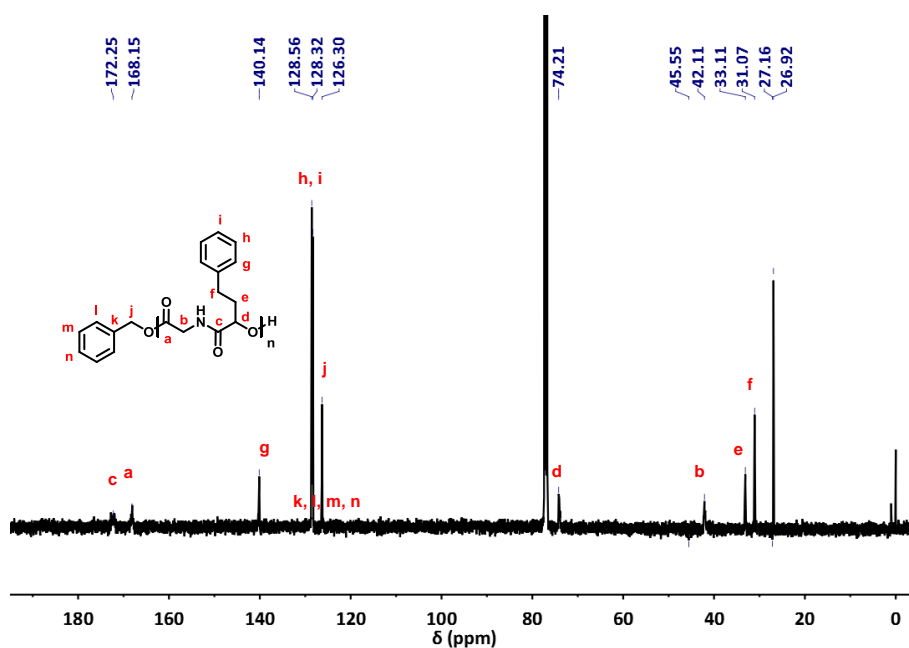
**Figure S76.** MALDI-TOF mass spectrum of linear  $P_{2g}$ .

( $[2g]_0/[BnOH]_0/[DBU]/[TU] = 100/2/1/5$ , quenched at 89% conversion)

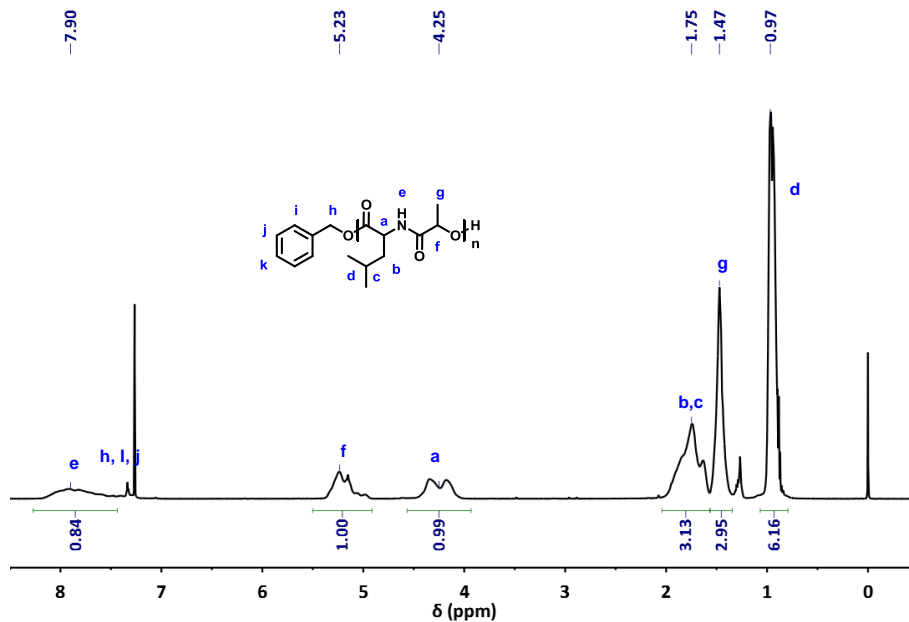


**Figure S77.**  $^1H$  NMR spectrum of  $P_{2g}$  in  $CDCl_3$ .

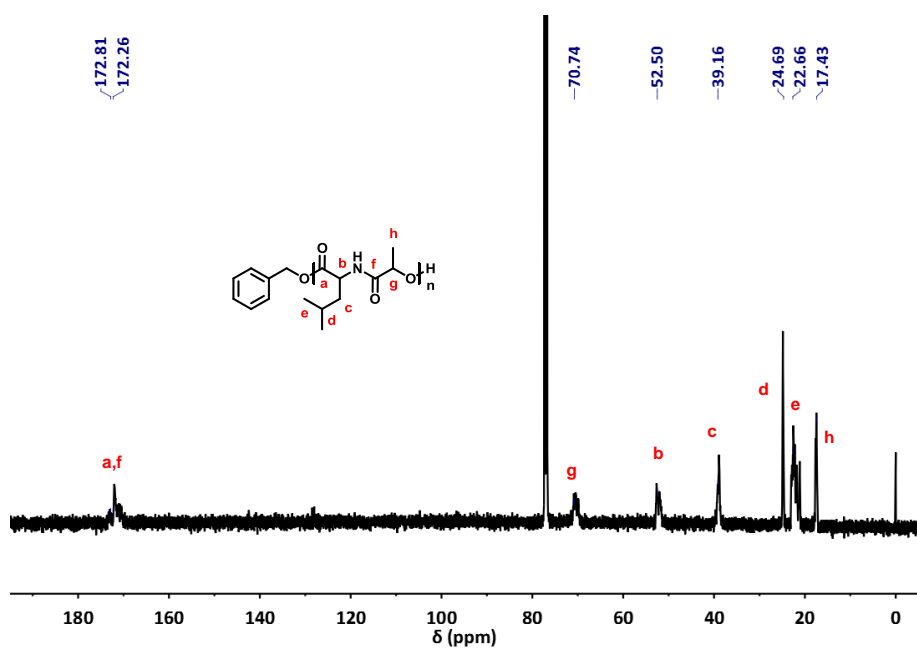
( $[2g]_0/[BnOH]_0/[DBU]/[TU] = 100/2/1/5$ , quenched at 89% conversion)



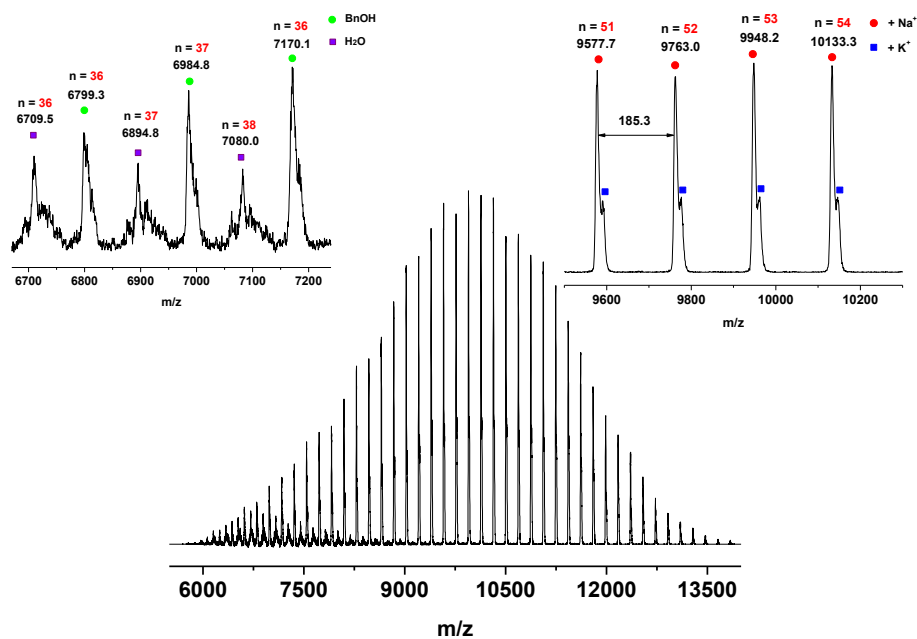
**Figure S78.** <sup>13</sup>C NMR spectrum of **P<sub>2g</sub>** in CDCl<sub>3</sub>.  
 ([**2g**]<sub>0</sub>/[BnOH]<sub>0</sub>/[DBU]/[TU] = 100/2/1/5, quenched at 89% conversion)



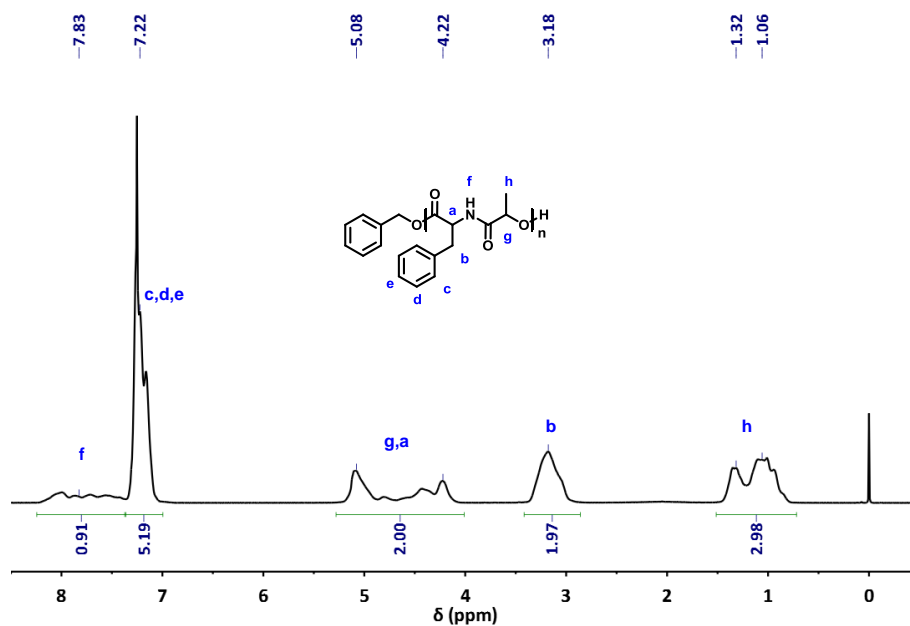
**Figure S79.** <sup>1</sup>H NMR spectrum of **P<sub>2h</sub>** in CDCl<sub>3</sub>.  
 ([**2h**]<sub>0</sub>/[BnOH]<sub>0</sub>/[TBD]/[TU] = 100/1/1/5, quenched at 88% conversion)



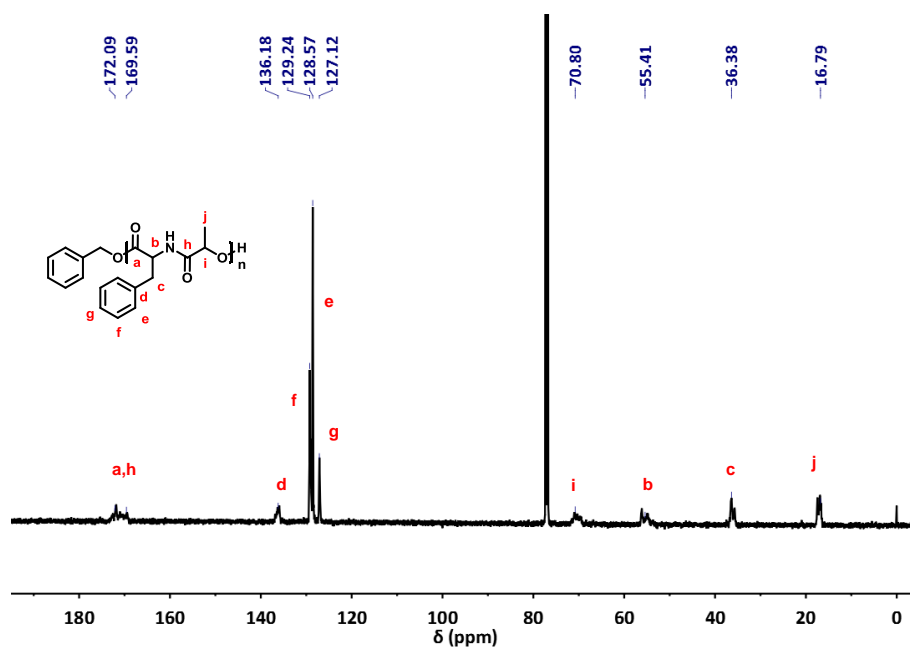
**Figure S80.**  $^{13}\text{C}$  NMR spectrum of  $\text{P}_{2\text{h}}$  in  $\text{CDCl}_3$ .  
 ( $[\mathbf{2h}]_0/[\text{BnOH}]_0/[\text{TBD}]/[\text{TU}] = 100/1/1/5$ , quenched at 88% conversion)



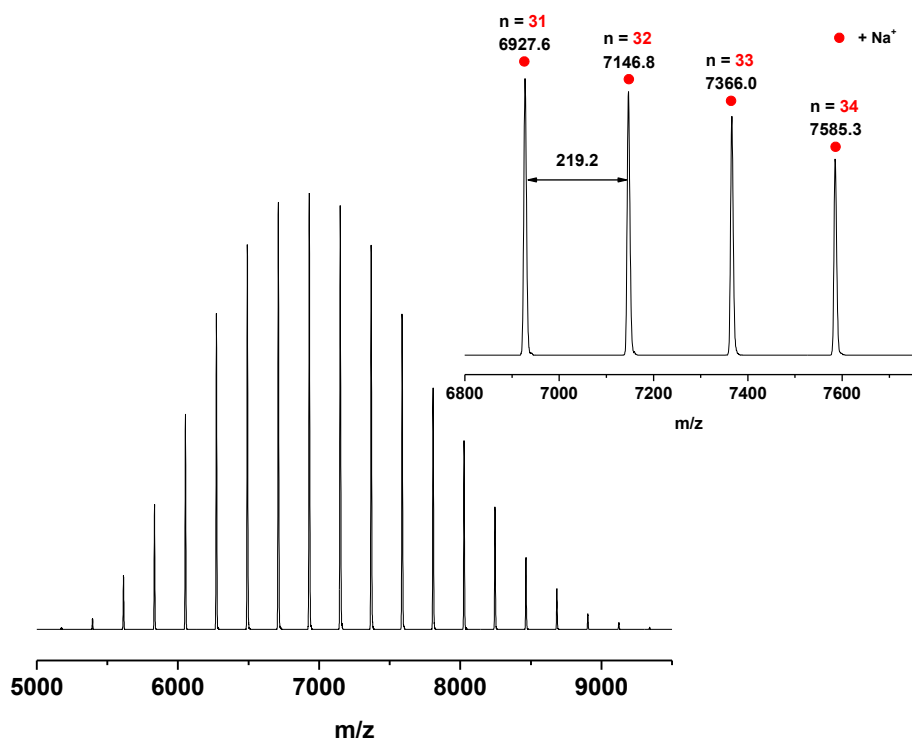
**Figure S81.** MALDI-TOF mass spectrum of linear  $\text{P}_{2\text{h}}$ .  
 ( $[\mathbf{2h}]_0/[\text{BnOH}]_0/[\text{TBD}]/[\text{TU}] = 100/1/1/5$ , quenched at 88% conversion)



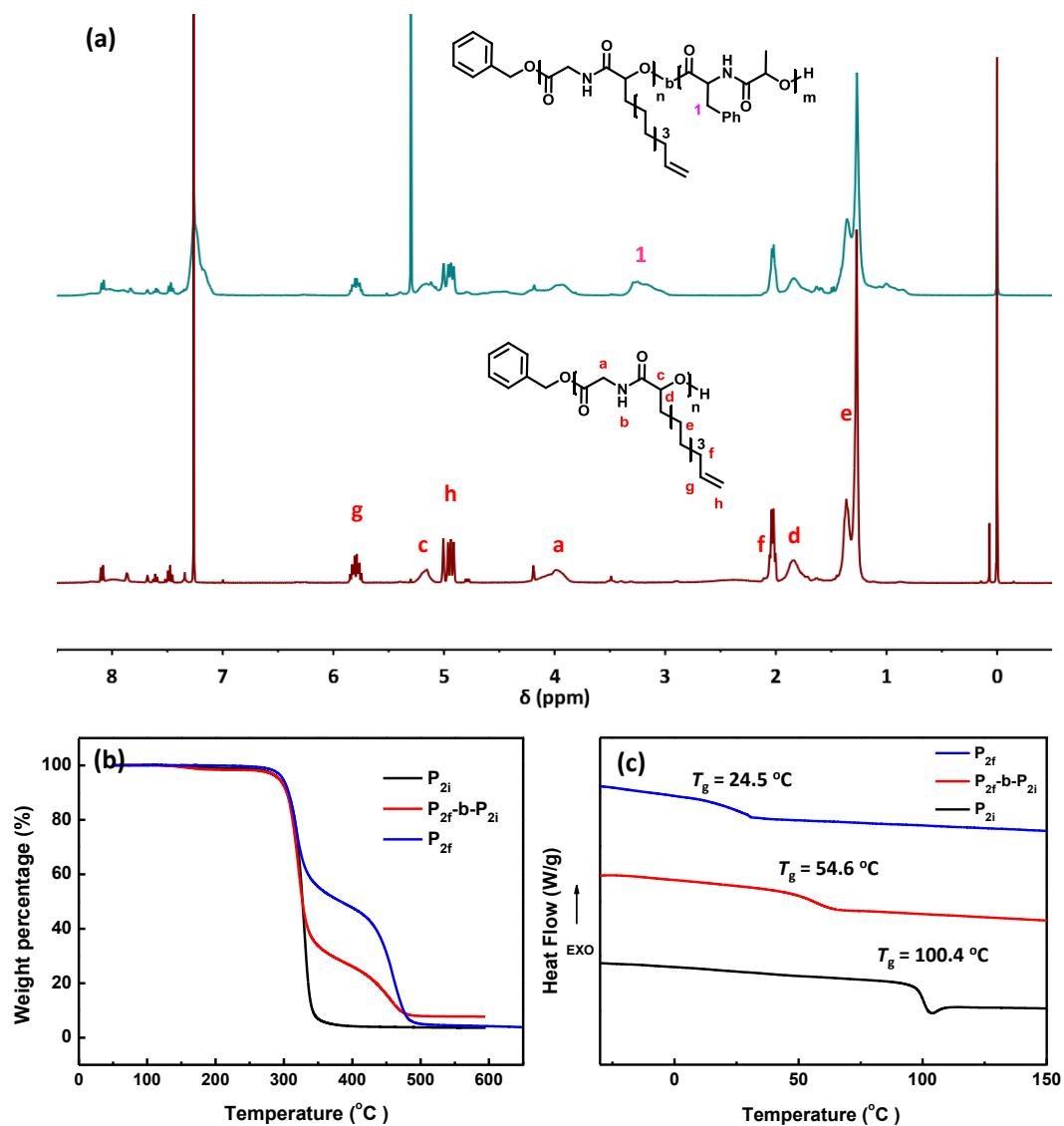
**Figure S82.**  $^1\text{H}$  NMR spectrum of  $\text{P}_{2i}$  in  $\text{CDCl}_3$ .  
 ( $[\text{2i}]_0/[\text{BnOH}]_0/[\text{TBD}]/[\text{TU}] = 100/2/1/5$ , quenched at 82% conversion)



**Figure S83.**  $^{13}\text{C}$  NMR spectrum of  $\text{P}_{2i}$  in  $\text{CDCl}_3$ .  
 ( $[\text{2i}]_0/[\text{BnOH}]_0/[\text{TBD}]/[\text{TU}] = 100/2/1/5$ , quenched at 82% conversion)

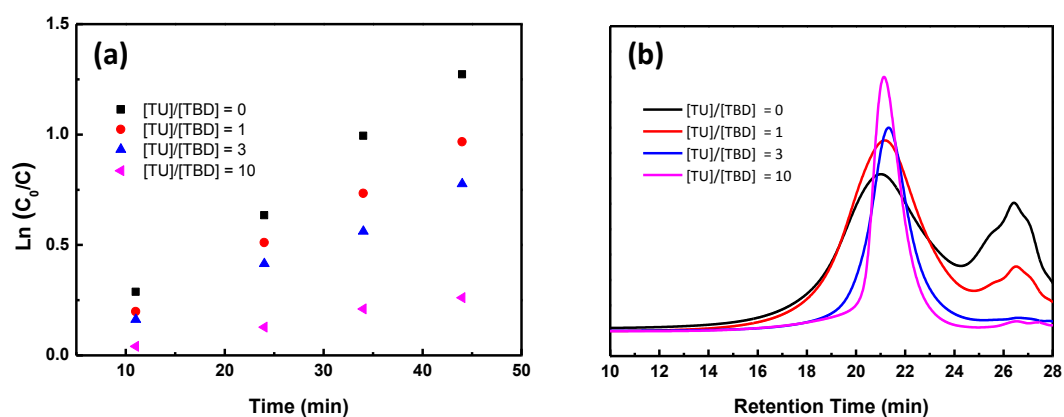


**Figure S84.** MALDI-TOF mass spectrum of linear  $P_{2i}$ .  
( $[2i]_0/[BnOH]_0/[TBD]/[TU] = 100/2/1/5$ , quenched at 82% conversion)



**Figure S85.** (a) <sup>1</sup>H NMR spectra of **P**<sub>2f</sub> and **P**<sub>2f</sub>-*b*-**P**<sub>2i</sub>. (b) TGA curves of **P**<sub>2f</sub>, **P**<sub>2f</sub>-*b*-**P**<sub>2i</sub> and **P**<sub>2i</sub>. (c) DSC second –heating –scan curves of **P**<sub>2f</sub>, **P**<sub>2f</sub>-*b*-**P**<sub>2i</sub> and **P**<sub>2i</sub>.

### ROP of **2f** at varied ratios of [TU]/[TBD]

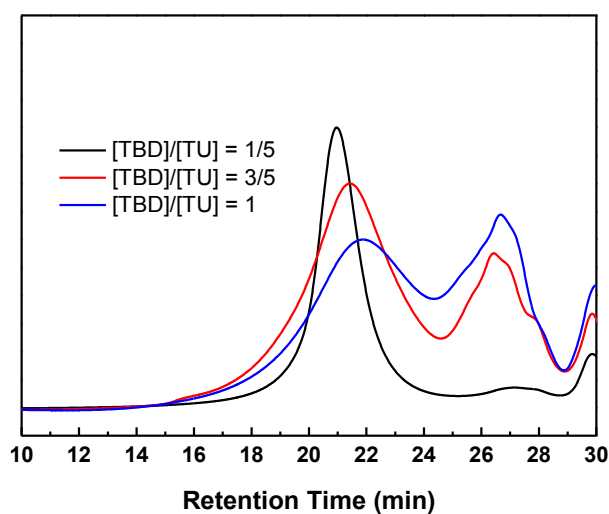


**Figure S86.** ROP of **2f** at different [TU]/[TBD] ratios.

( $[2f]_0/[TBD] = 100/1$ ,  $[2f]_0 = 0.64$  mol/L, T: 25 °C, solvent: DCM)

(a) The polymerization rates decreased as the amount of TU increased.

(b) The controllability of polymerization increased as the amount of TU increased.



**Figure S87.** SEC traces of  $P_{2f}$  obtained at different [TBD]/[TU] ratios.

( $[2f]_0/[TU] = 100/5$ ,  $[2f]_0 = 0.64$  mol/L, T: 25 °C, solvent: DCM).

The controllability of the polymerization decreased as the ratio of [TBD]/[TU] increased.

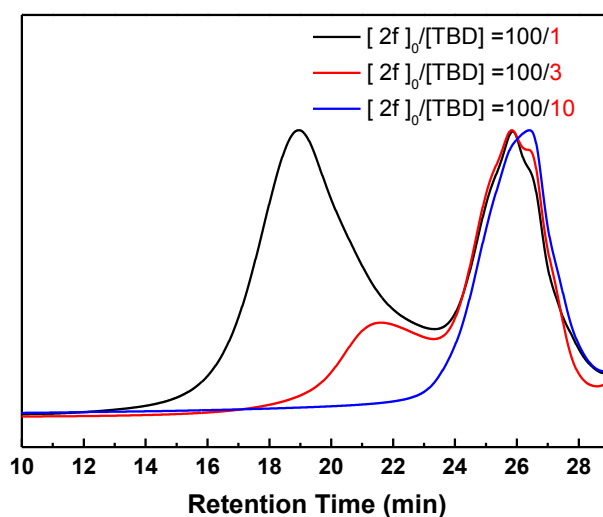
**Table S2| TBD-catalyzed ROP of MDs in the absence of BnOH**

Entry	Monomer (M)	Conc. (mol/L)	Ratio (M:C:I:TU)	Time (min)	Conv. (%) <sup>a</sup>	M <sub>n</sub> <sup>SEC</sup> (kDa) <sup>b</sup>	Đ <sup>b</sup>
1	2f	0.64	100:1:0:0	300	89	-	-
2	2f	0.64	100:3:0:0	150	87	-	-
3	2f	0.64	100:10:0:0	65	72	-	-
4	2c	0.64	100:1:0:0	76	77	-	-
5	2g	0.32	100:1:0:0	242	88	-	-

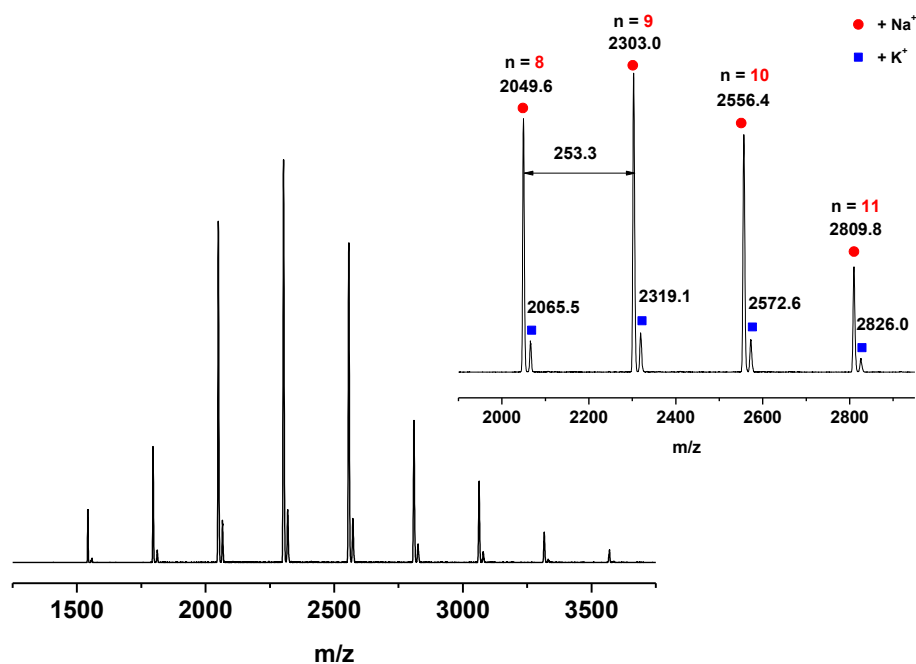
All polymerizations were conducted in DCM (1 mL) in the absence of initiator BnOH at 25 °C, the polymers were not purified for <sup>1</sup>H NMR and SEC characterizations.

<sup>a</sup>The monomer conversion was determined by <sup>1</sup>H NMR spectroscopy.

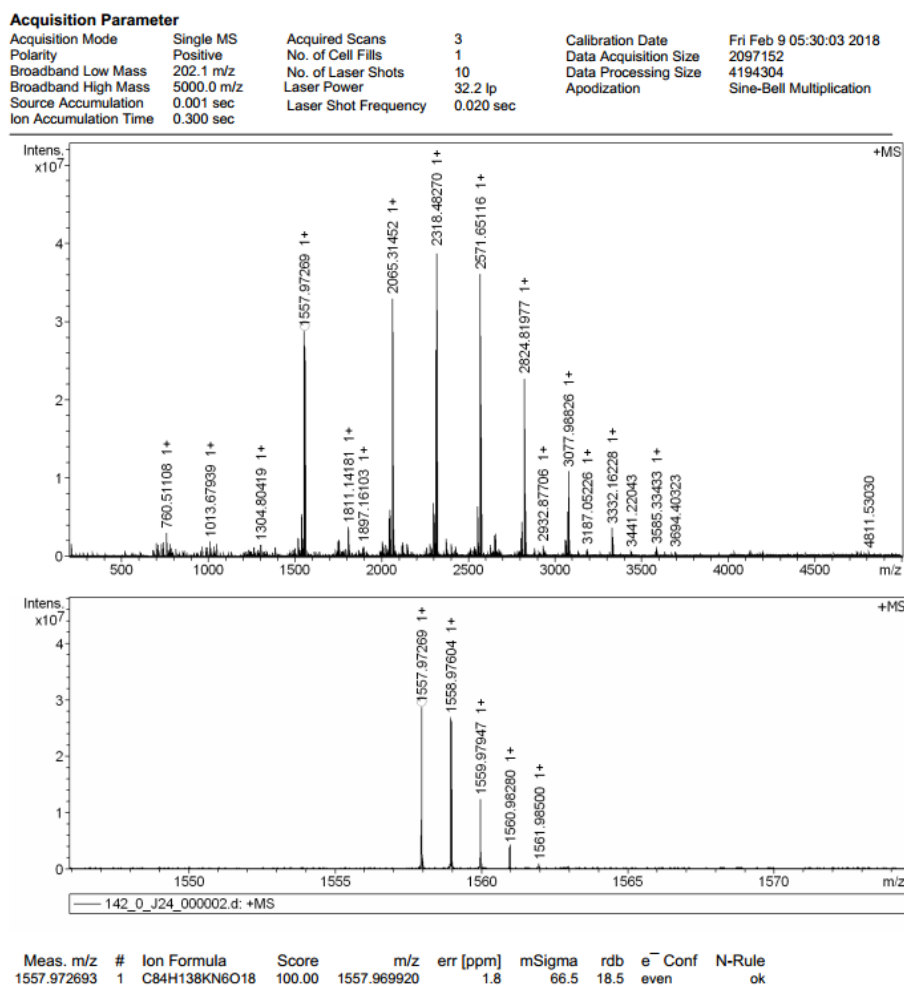
<sup>b</sup>Molar mass and dispersity were measured with SEC and calibrated with polystyrene standard. - the SEC trace was bimodal distribution, data could not to be determined.



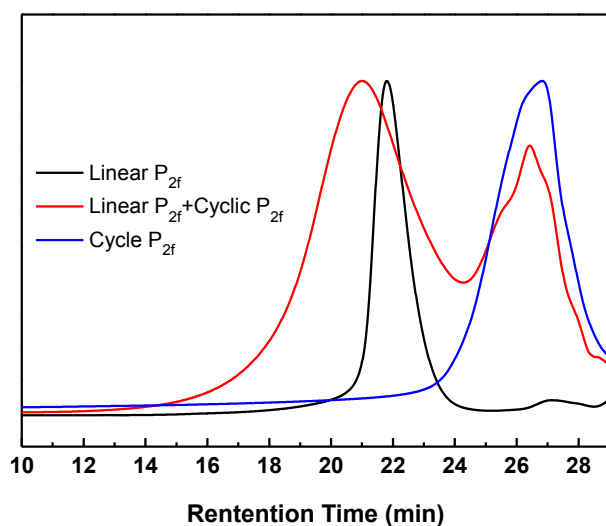
**Figure S88.** SEC traces of **P**<sub>2f</sub> obtained by the TBD-catalyzed ROP of **2f** in the absence of BnOH.



**Figure S89.** MALDI-TOF mass spectrum of cyclic  $P_{2f}$  ( $[2f]_0/[TBD] = 100/1$ )



**Figure S90.** High resolution MALDI-TOF mass spectrum of cyclic  $P_{2f}$  ( $[2f]_0/[TBD] = 100/1$ )

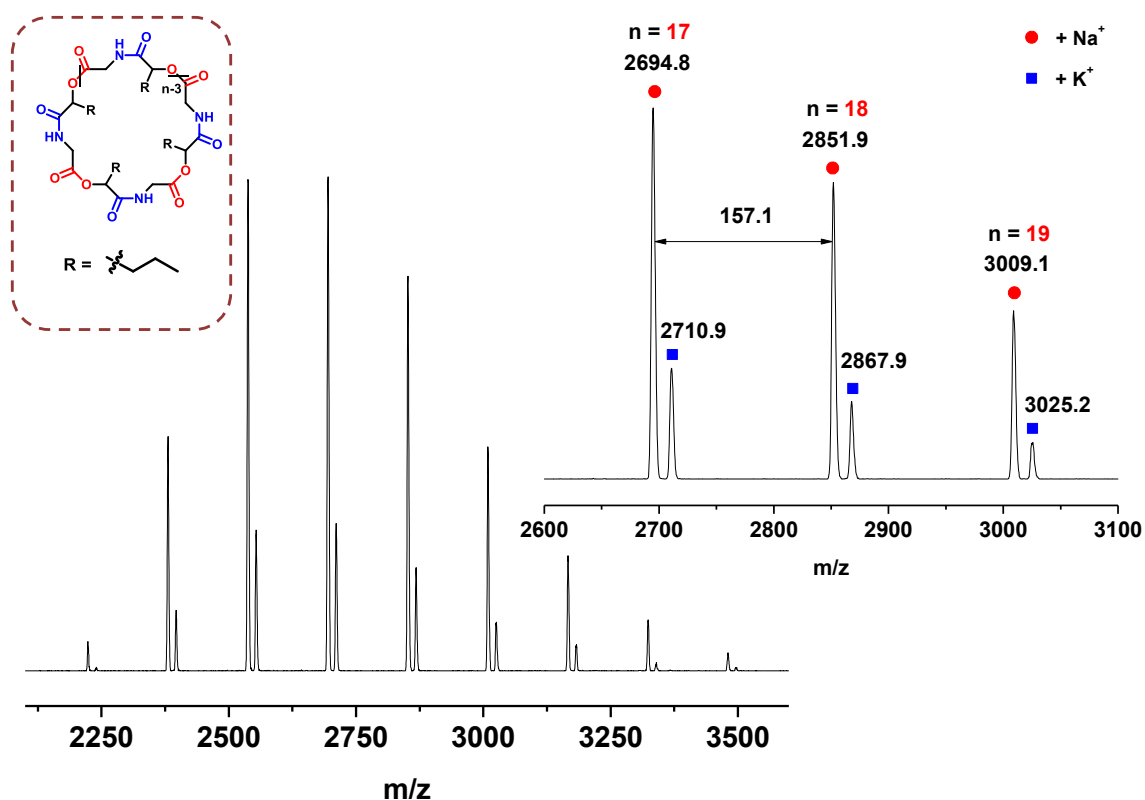


**Figure S91.** Topology control of  $P_{2f}$  under different polymerization conditions.

Linear  $P_{2f}$ ,  $[2f]_0/[TBD]/[BnOH]_0/[TU] = 100/1/1/5$

Linear  $P_{2f}$  + Cyclic  $P_{2f}$ ,  $[2f]_0/[TBD]/[BnOH]_0 = 100/1/1$

Cyclic  $P_{2f}$ ,  $[2f]_0/[TBD] = 100/10$



**Figure S92.** MALDI-TOF mass spectrum of cyclic  $P_{2c}$  ( $[2c]_0/[TBD] = 100/1$ ).

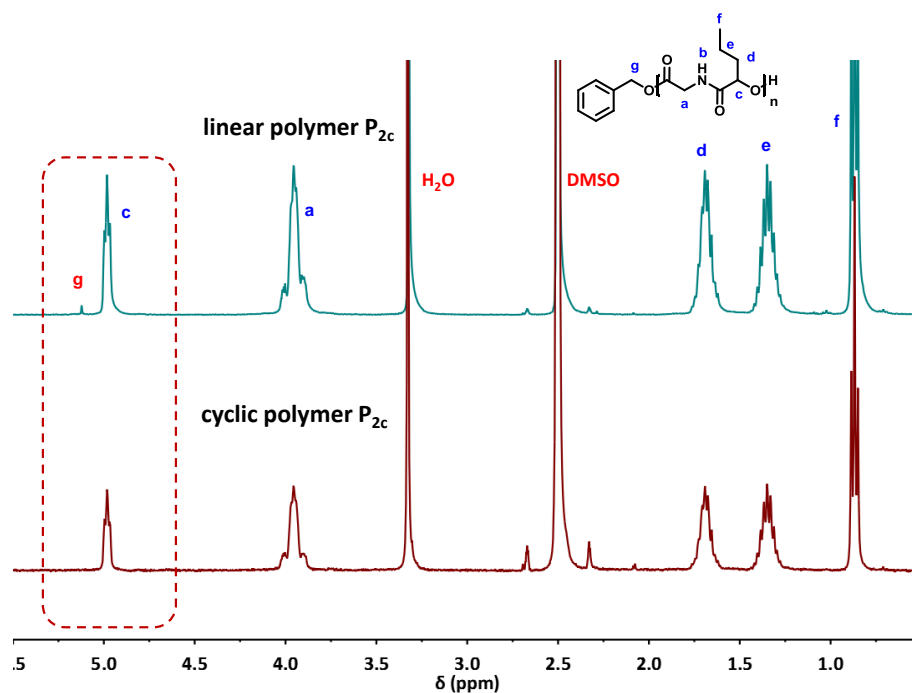


Figure S93. Overlay of the  $^1\text{H}$  NMR spectra of linear  $\text{P}_{2c}$  and cyclic  $\text{P}_{2c}$  in  $\text{DMSO-}d_6$ .

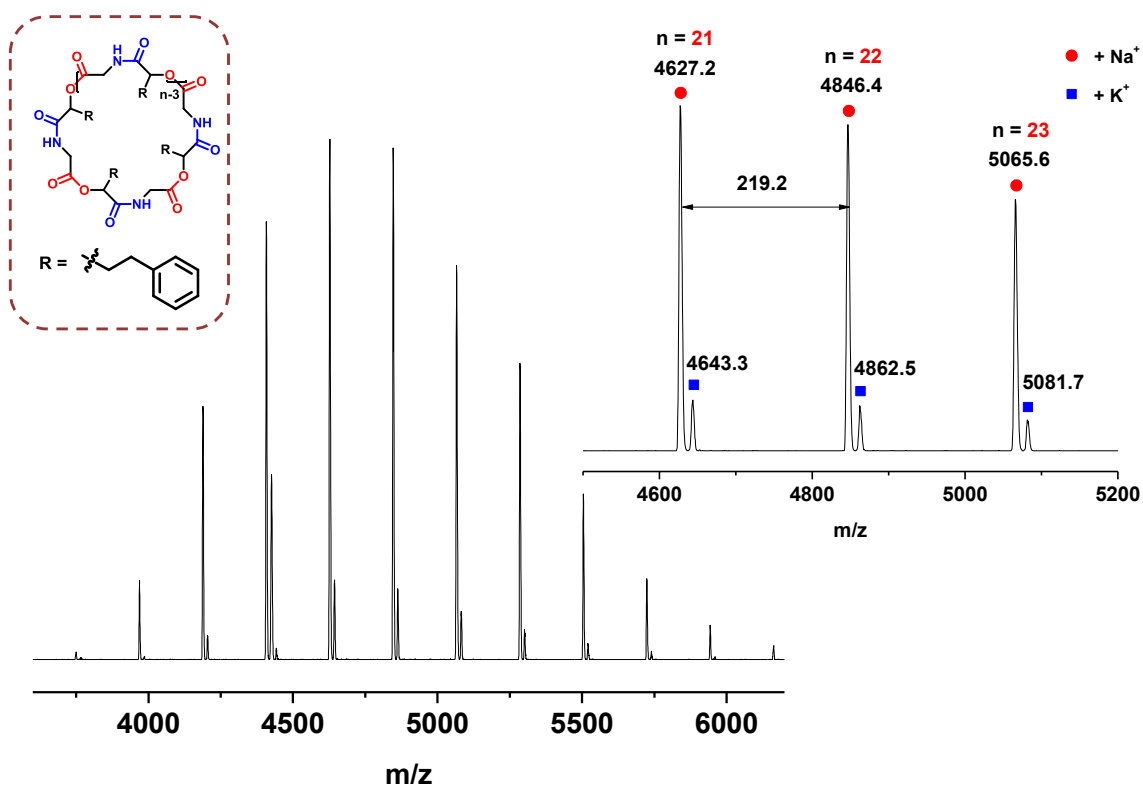
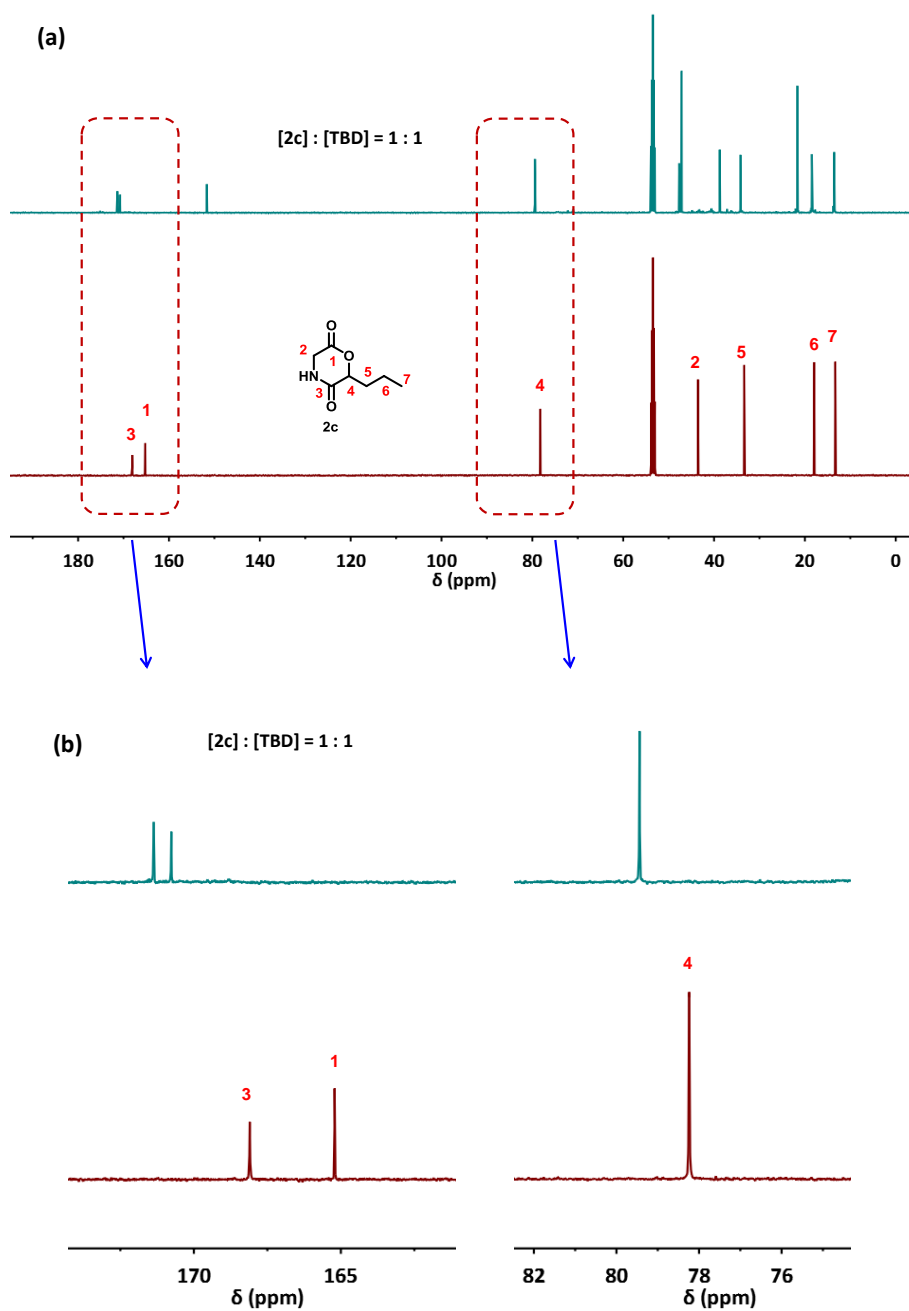


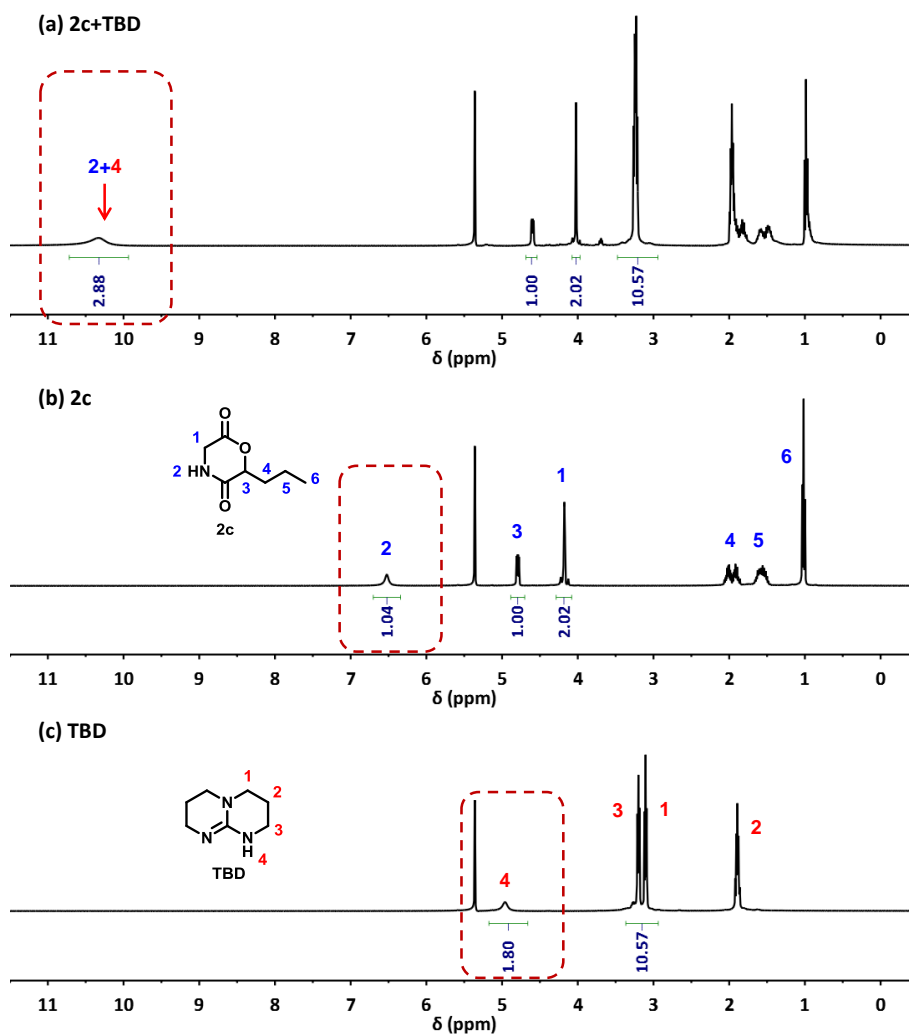
Figure S94. MALDI-TOF mass spectrum of cyclic  $\text{P}_{2g}$  ( $[\text{2g}]_0/[\text{TBD}] = 100/1$ ).

## 5. Mechanism of the TBD-catalyzed ROP of MDs

### Interactions between monomer **2c**, TBD, and TU

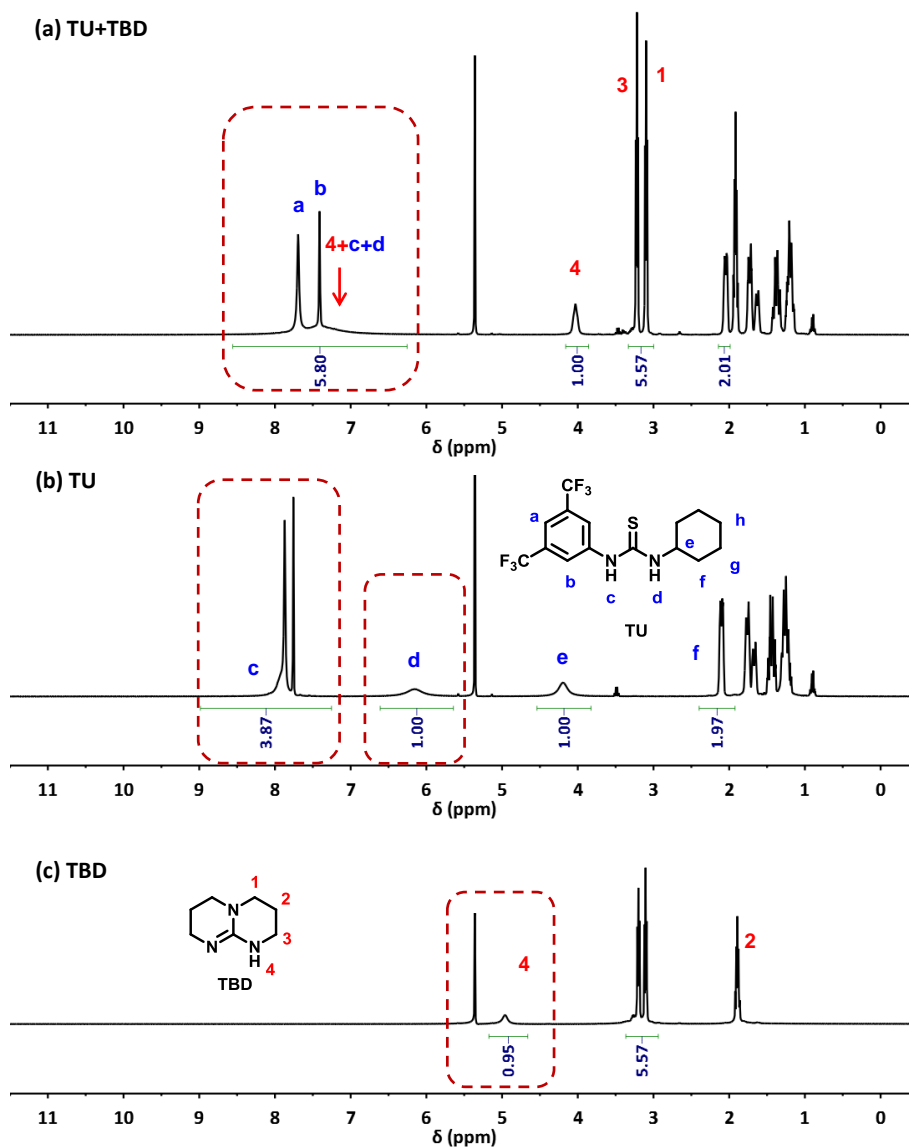


**Figure S95.**  $^{13}\text{C}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$ . (a) **2c**/TBD ( $\approx 1/1$ ); **2c**, ( $[2c] = 0.17 \text{ mol/L}$ ). (b) Enlarged spectrum.



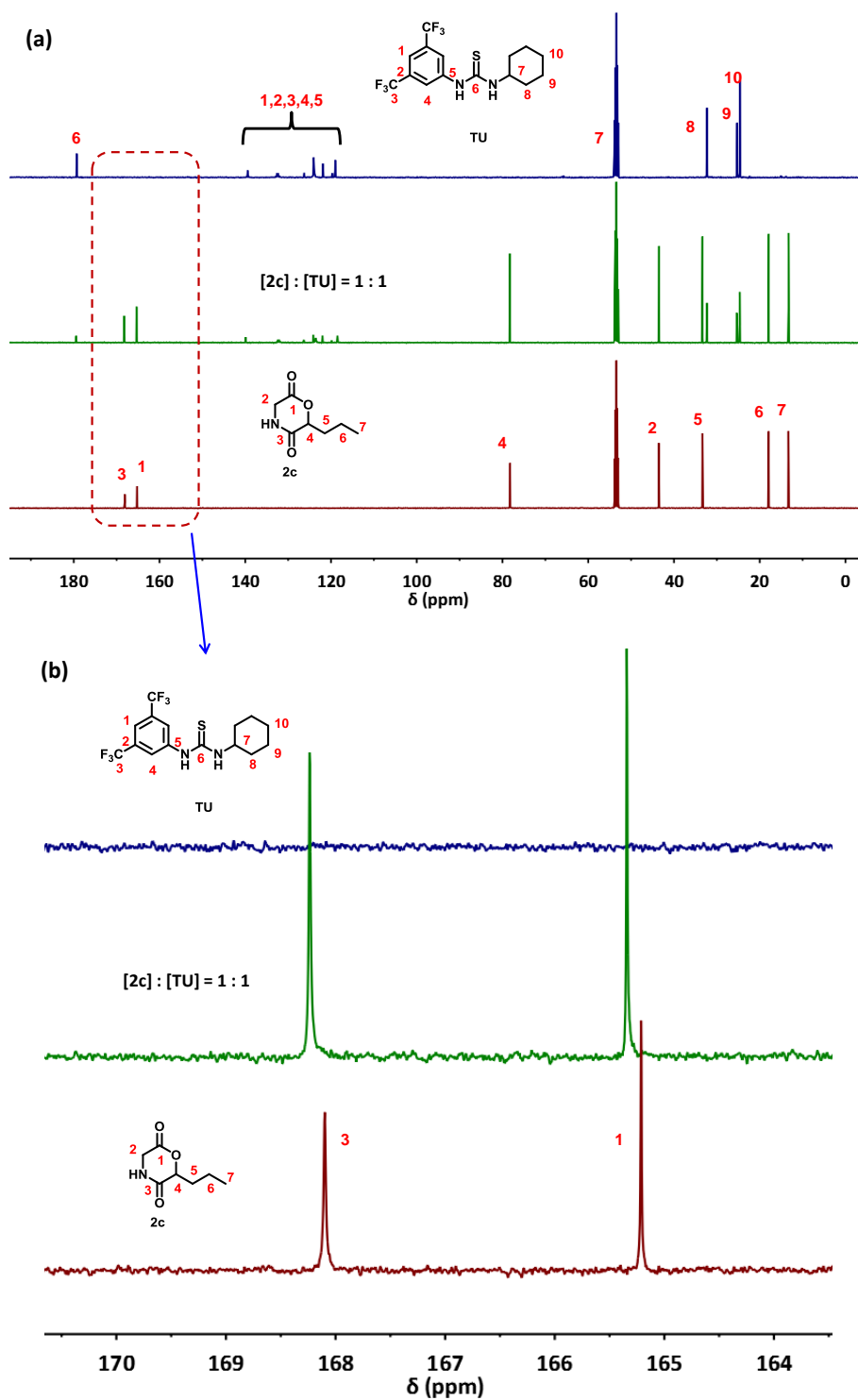
**Figure S96.**  $^1\text{H}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$ . (a) **2c**/TBD ( $\approx 1/1$ ); (b) **2c**; (c) TBD ( $[\mathbf{2c}] = [\text{TBD}] = 0.05 \text{ mol/L}$ ).

According to the integration of the  $^1\text{H}$  NMR, the active hydrogen of **2c** and TBD shifted to 10.4 ppm when they were mixed, which indicated that the active hydrogen of **2c** and TBD were in fast exchange equilibrium.



**Figure S97.**  $^1\text{H}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$ . (a) TU/TBD ( $\approx 1/1$ ); (b) TU; (c) TBD ( $[\mathbf{2c}] = [\text{TBD}] = 0.05 \text{ mol/L}$ ).

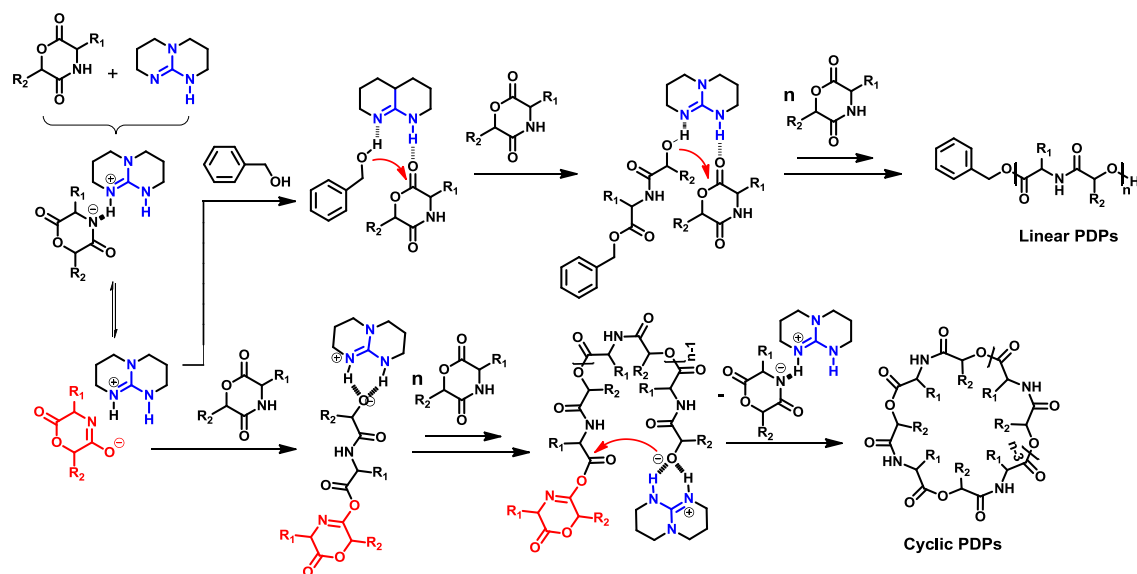
According to the integration of the  $^1\text{H}$  NMR, the active hydrogen of TU and TBD shifted to 7.4 ppm when they were mixed, which indicated that the active hydrogen of TU and TBD were also in fast exchange equilibrium like  $\mathbf{2c}$  and TBD.



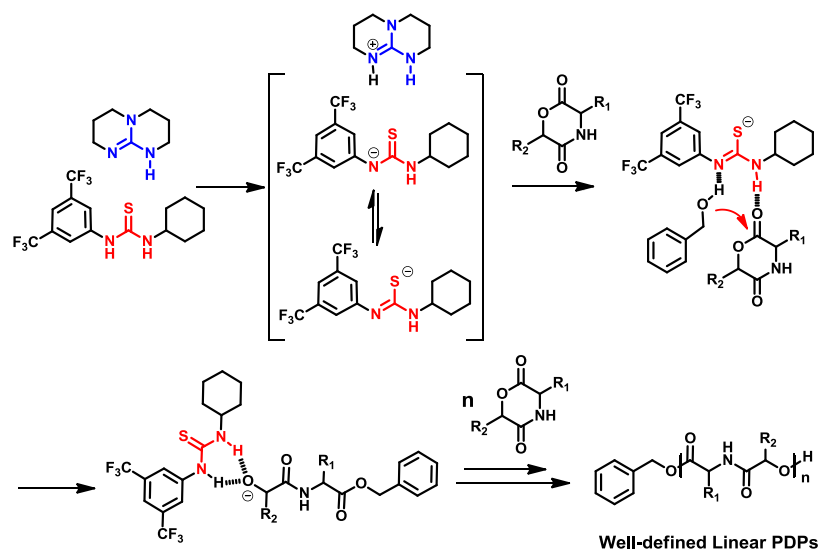
**Figure S98.**  $^{13}\text{C}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$ . (a) TU;  $\mathbf{2c}/\text{TU}$  ( $\approx 1/1$ );  $\mathbf{2c}$ , ( $[\mathbf{2c}] = 0.17 \text{ mol/L}$ ) (b) enlarged spectrum.

The  $^{13}\text{C}$  NMR spectrum suggested there are interactions between TU and  $\mathbf{2c}$ , but the interaction is less than TBD and  $\mathbf{2c}$ .

(a) Linear and cyclic PDPs formation catalyzed by TBD

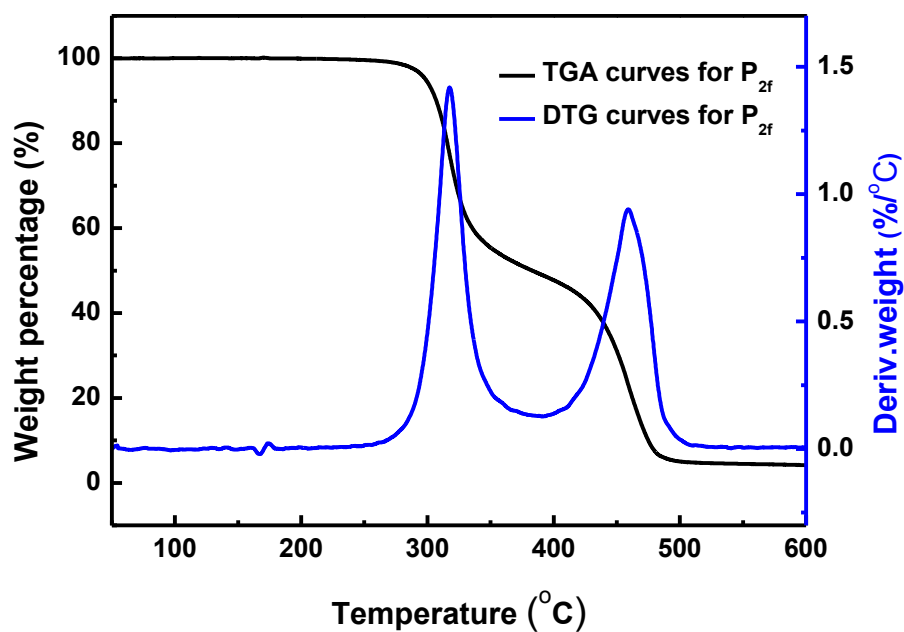


(b) Living ROP of MDs catalyzed by TBD/TU



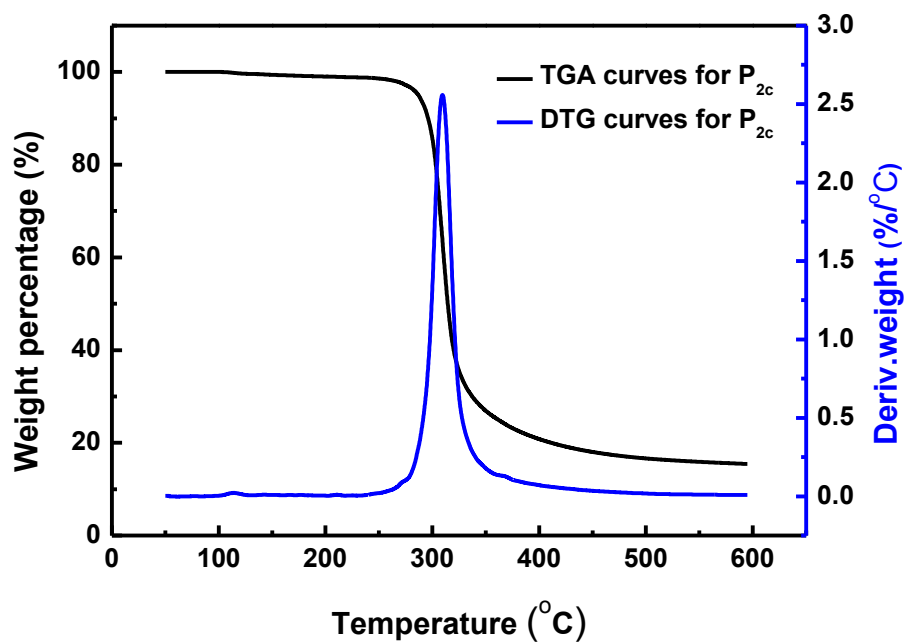
**Figure S99.** Proposed mechanism of ROP of MDs catalyzed by TBD and TBD/TU.

## 6. Thermal properties of polymers P<sub>2f</sub>, P<sub>2c</sub>, P<sub>2g</sub>, P<sub>2h</sub>, and P<sub>2i</sub>



**Figure S100.** TGA and DTG curves of P<sub>2f</sub>.

$T_{\max 1} = 318\text{ }^{\circ}\text{C}$ ,  $T_{\max 2} = 459\text{ }^{\circ}\text{C}$ ,  $T_{d, 5\%} = 295\text{ }^{\circ}\text{C}$ .



**Figure S101.** TGA and DTG curves of P<sub>2c</sub>.  $T_{\max} = 309\text{ }^{\circ}\text{C}$ ,  $T_{d, 5\%} = 293\text{ }^{\circ}\text{C}$ .

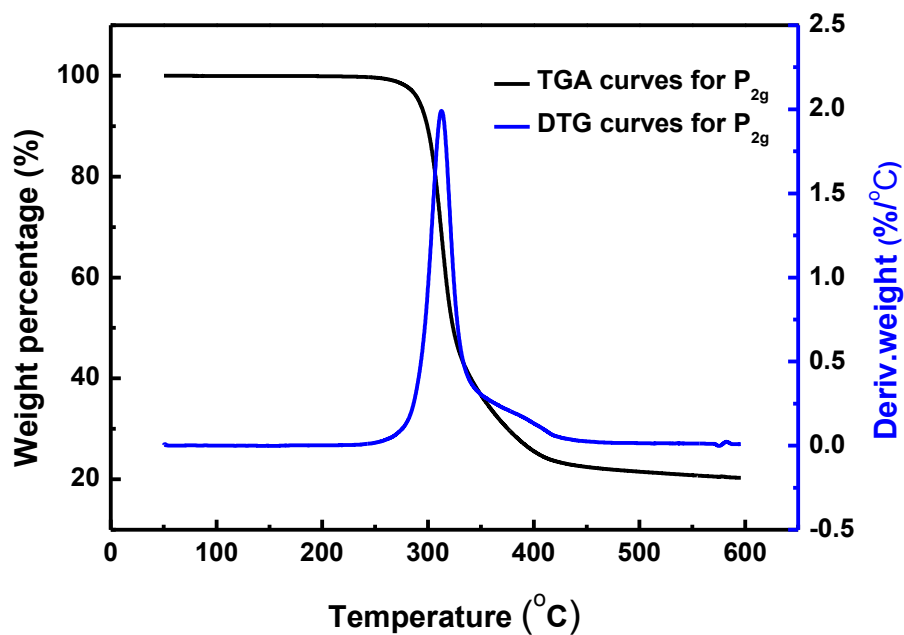


Figure S102. TGA and DTG curves of  $P_{2g}$ .  $T_{\max} = 313^{\circ}\text{C}$ ,  $T_{d, 5\%} = 294^{\circ}\text{C}$ .

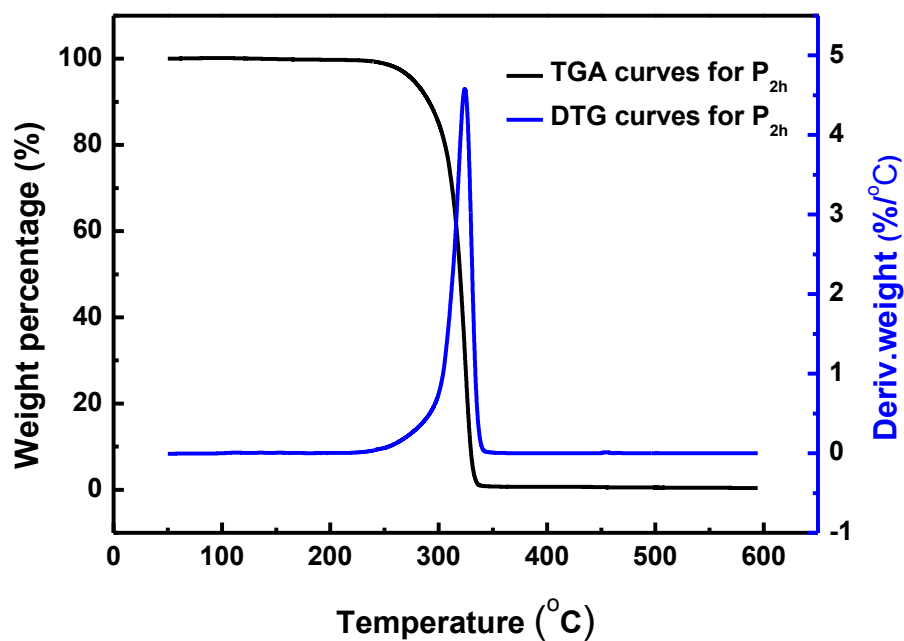
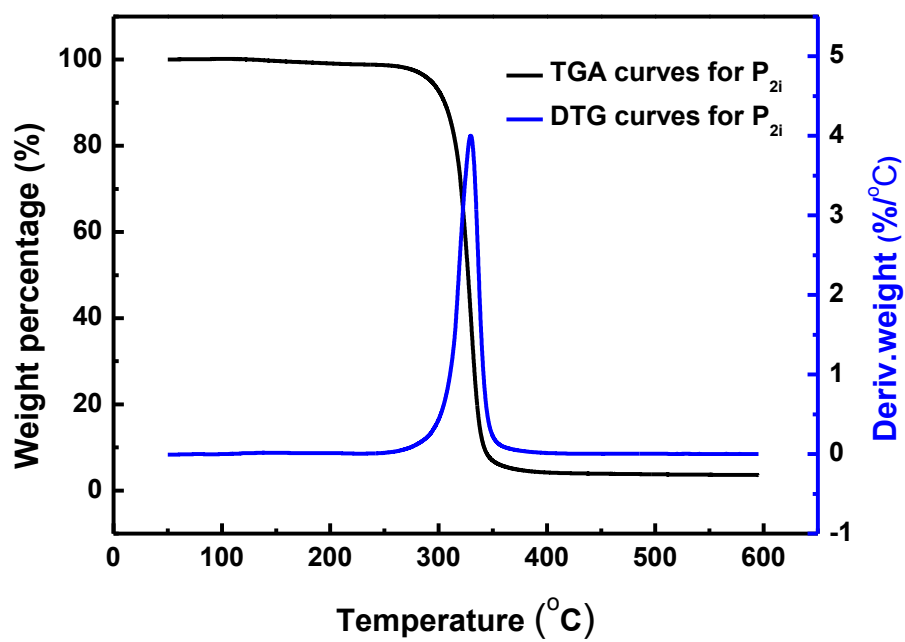
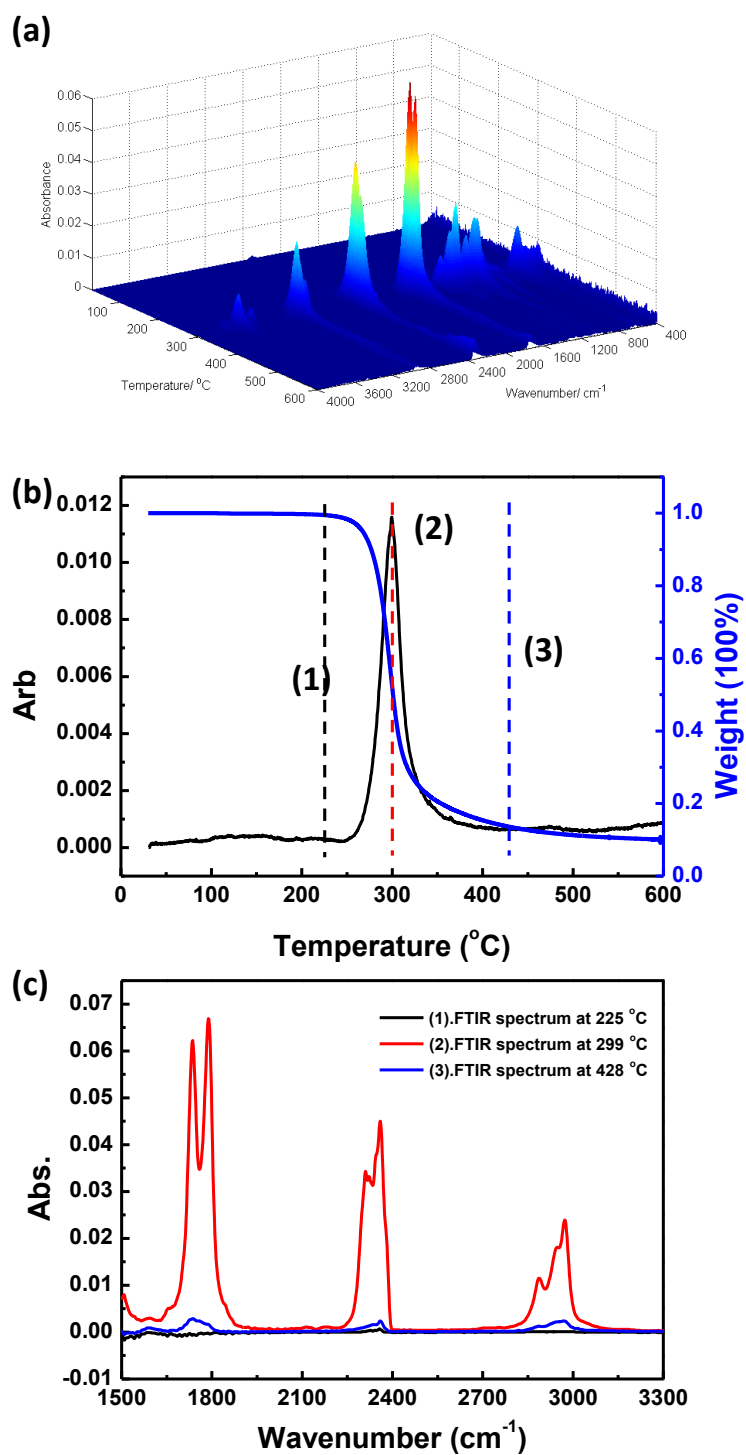


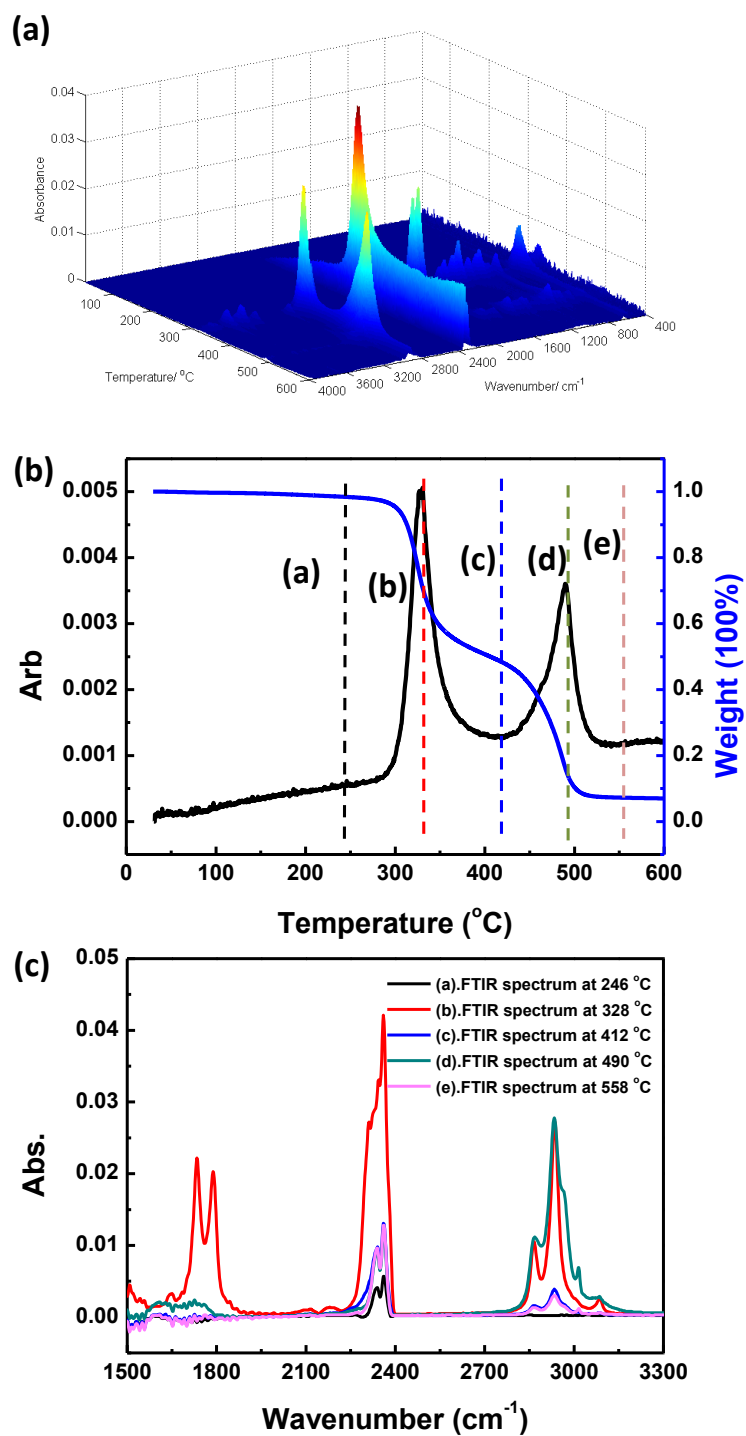
Figure S103. TGA and DTG curves for  $P_{2h}$ .  $T_{\max} = 324^{\circ}\text{C}$ ,  $T_{d, 5\%} = 293^{\circ}\text{C}$ .



**Figure S104.** TGA and DTG curves for P<sub>2i</sub>. T<sub>max</sub> = 330 °C, T<sub>d,5%</sub> = 294 °C.



**Figure S105.** (a) TGA-FTIR 3D spectrum of polymer  $\mathbf{P}_{2c}$ , (b) Gram-Schmidt curve and TGA curve of polymer  $\mathbf{P}_{2c}$ , (c) FTIR spectrum of polymer  $\mathbf{P}_{2c}$  at different decomposition temperatures.

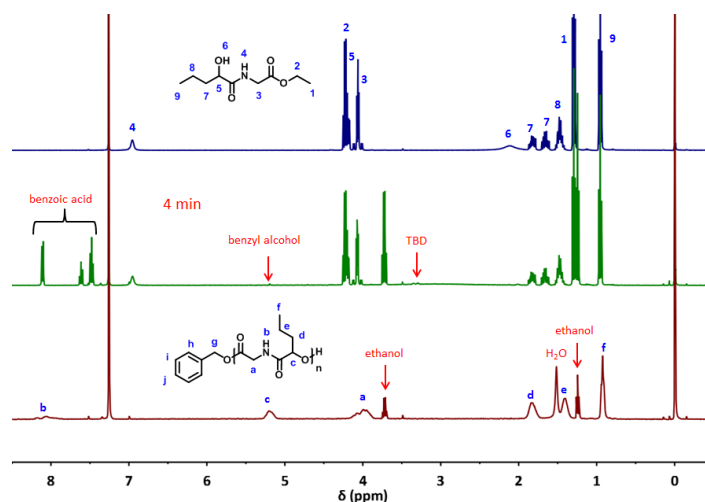


**Figure S106.** (a) TGA-FTIR 3D spectrum of polymer  $P_{2f}$ , (b) Gram-Schmidt curve and TGA curve of polymer  $P_{2f}$ , (c) FTIR spectrum of polymer  $P_{2f}$  at different decomposition temperatures.

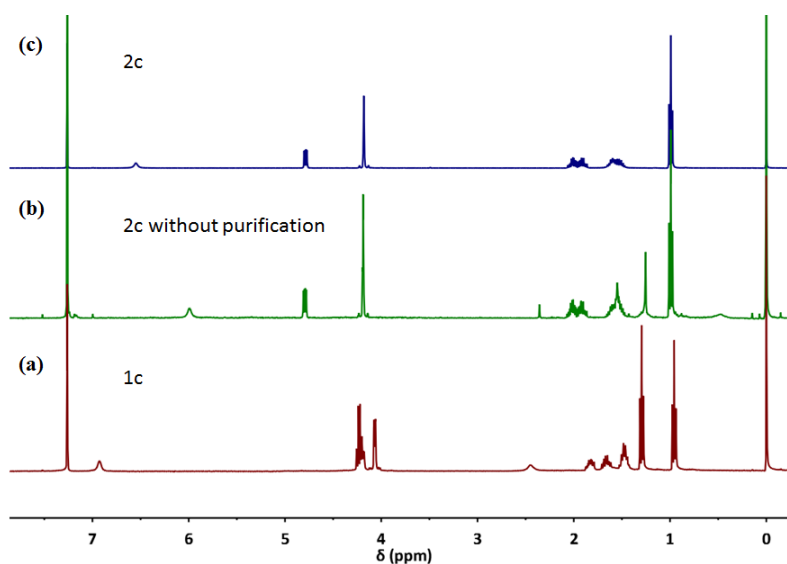
## 7. Chemical recyclability of polymer

### *TBD-catalyzed alcoholysis of PMD using P<sub>2c</sub> as an example.*

In a N<sub>2</sub>-filled glovebox, P<sub>2c</sub> (15.7 mg) was dissolved with mixed solvent (EtOH/ DCM = 2/1, 0.9 mL) in a 2 mL vial containing a micro stir bar. After P<sub>2c</sub> was dissolved completely, the degradation was triggered by rapid adding 0.1 mL of TBD solution (0.005 mol/L in DCM) to the vial under vigorous stirring. Samples (0.1 mL solution) were taken out periodically and quickly quenched by benzoic acid. The quenched reaction solution was analyzed by <sup>1</sup>H NMR to follow the degradation process.



**Figure S107.** <sup>1</sup>H NMR spectra for the TBD-catalyzed fast and quantitative alcoholysis of P<sub>2c</sub>. (0.5% TBD, solvent: EtOH/ DCM = 2/1, T: 25 °C, [P<sub>2c</sub>] = 0.1 mol/L).



**Figure S108.** <sup>1</sup>H NMR spectrum of (a) compound 1c obtained by TBD-catalyzed degradation of P<sub>2c</sub>; (b) crude monomer 2c product after cyclization of 1c in toluene catalyzed by Amberlyst (R) 15 ion-exchange resin. (c) monomer 2c.

### *Acid-catalyzed depolymerization of PMDs using $P_{2i}$ as an example.*

$P_{2i}$  (44 mg, produced by  $[2i]_0/[BnOH]_0/[TBD]/[TU]=100/1/1/5$ ) was dissolved in 2 mL of toluene in a Schlenk tube containing a micro stir bar. Then a catalytic amount of Amberlyst (R) 15 ion-exchange resin was added to the Schlenk tube. The degradation was triggered by putting the Schlenk tube in the 120°C oil bath. Samples (0.2 mL solution) were taken out periodically, and analyzed by  $^1H$  NMR and SEC to follow the degradation process.

### 8. References

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