Supporting Information

Introducing the reversible chemistry of CO_2 with diols mediated by organic superbases into polycarbonate synthesis

Yang Chai,[a] Qin Chen,[a] Caijuan Huang,*[a] Qiang Zheng,[b] Michael North[c] and Haibo Xie*[a]

*E-mail: cjhuang98@163.com and hbxie@gzu.edu.cn

[a]Department of Polymeric Materials & Engineering, College of Materials & Metallurgy, Guizhou University, West Campus, Huaxi District, Guiyang 550025, P. R. China.

[b]Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

[c]Green Chemistry Centre of Excellence, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.

S1.0 Experimental section

S1.1 Chemicals and Instruments

Materials. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flask or Schlenk-type bottles in a high-vacuum environment or under dry nitrogen gas. 1,4-di(hydroxymethyl)benzene (DHB), 3-bromopropene, 1,3-dimercaptopropane, benzoin dimethyl ether (DMPA), 2,2'-azobisisobutyronitrile (AIBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), caesium carbonate (Cs_2CO_3), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,1,3,3-tetramethylguanidine (TMG), tetrabutylammonium iodide, 3-chloroperbenzoic acid, p-benzoquinone, Hoveyda-Grubbs catalyst 2nd generation, 1,4-butanediol (BDO), triethylene glycol (TEG) and 1,4-cyclohexanedimethanol (CHDM) were purchased from Aladdin and used as received. Isosorbide (IS) and 6-bromo-1-hexene were purchased from Energy Chemical and used as received. 10-bromo-1-decene was purchased from Accela ChemBio Co. Ltd. Other Reagents were available commercially and used as received.

Instruments

^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. Chemical shifts were referenced to the solvent resonance signals. The data obtained were processed and analyzed by MestReNova software.

Fourier transform infrared (FT-IR) spectra were obtained on a 460 plus spectrometer from JASCO. The measurement resolution was set at 4 cm^{-1}, and the spectra were collected in the range 4000−500 cm^{-1}.

The thermal stability of the polymers was determined by thermogravimetric analysis (TGA) with a SDT Q6000 apparatus from TA Instruments. The samples were heated from 40 to 800 °C at a heating rate of 10 °C/min under a nitrogen flow of 100 mL/min. Glass transition temperatures (T_g) and melting points (T_m) were measured by differential scanning calorimetry (DSC) using a DSC Q2000 from TA Instruments. Measurements of T_g and T_m were recorded with a heating and cooling

rate of 10 °C/min from -70 to 250 °C. Thermal data acquisition was carried out using Thermal Analysis software from TA Instruments.

Gel permeation chromatography (GPC) in tetrahydrofuran (THF) was performed on a system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a Waters 1717 plus autosampler. THF was used as eluent at a flow rate of 1.0 mL/min. The molecular weights were calculated against polystyrene standards.

1.2 Typical Procedure for the synthesis of polymeric monomers

1,4-di(hydroxymethyl)benzene (2.791 g, 20 mmol), DMF (50 ml), and TMG (5.069 g, 40 mmol) were added to a stainless autoclave vessel and then pressurized with CO_2 to 1 MPa. The autoclave was put into an oil bath at 30 °C and 1 MPa for 1 h. Then allyl bromide (10.581 ml, 120 mmol) was added into the autoclave in situ and the reaction was further carried out under 1 MPa of CO_2 at 30 °C for 48 h. The rection mixture was filtered, and the filtrate was then poured into water (60 ml) and extracted with ethyl acetate (60 ml×3). The organic layer was washed with water (60 ml×2) and saturated brine and dried over anhydrous anhydrous Na_2SO_4. Evaporation of solvent follwowed by column chromatography with petroleum ether/ethyl acetate (10: 1- 3: 1) afforded the monomer as a transparent pale yellow liquid. Product **2a-1**. Yield: 44.6%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.87-5.97 (m, 2H), 5.24-5.37 (m, 4H), 5.16 (s, 4H), 4.63 (dt, ^1J = 1.6 Hz, ^2J = 8 Hz, 4H). ^{13}C NMR (100 MHz, CDCl3, ppm): δ 155.0, 135.7, 131.6, 128.6, 119.1, 69.2, 68.7. IR: υ_{max} 3090-2892, 1747, 1649, 1577, 1517, 1449, 1385, 1253, 1077, 953, 789 cm^{-1}.

1.3 Typical Procedure for the synthesis of polymers via thiol-ene click reaction

To a vial, 1,3-propanedithiol (0.566 g, 5 mmol), **2a-1** (1.525 g, 5 mmol), benzoin dimethyl ether (DMPA, 65 mg, 5 mol%) and THF (5 ml) were added. The vial was placed in a previously set UV cross-linker and irradiated at 365 nm for 2 h. The polymers were dissolved in THF, and precipitated in cold methanol, washed three times, and dried under vacuum at 35 °C for 24 h. Product **P3a-1** was a white solid (yield: 98.2%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.14 (s, 4H), 4.24 (t, J = 6.6 Hz, 4H), 2.76-2.44 (m, 8H), 2.17-1.60 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.0, 135.6, 128.6, 77.5, 77.2, 76.8, 69.2, 66.7, 30.8, 29.0, 28.6, 28.2. IR: υ_{max} 2957-2849, 1745, 1517, 1453, 1393, 1253, 1085-849, 789 cm^{-1}.

1.4 Typical Procedure for the synthesis of polymers via ADMET

Monomer **2a-1** (1.257 g, 2.5 mmol) was added to a 50 ml Schlenk tube equipped with a stopcock at 80 °C and exposed to high-vacuum for 1 h. Then Hoveyda-Grubbs catalyst (16 mg, 1 mol%) and p-benzoquinone (5 mg, 2 mol%) were added to Schlenk tube, and heated at 80 °C under high-vacuum for 24 h. Subsequently, THF (10 ml) and ethyl vinyl ether (5 ml) were added to quench the reaction. The obtained product **P4a-1** was precipitated by slow addition into cold methanol. The product was dried in vacuum under 35 °C for 24 h. Product **P4a-1** was a dark green solid (yield: 60.2%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.89 (s, 2H), 5.15 (s, 4H), 4.63 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.8, 135.6, 131.5, 128.6, 77.5, 77.2, 76.8, 69.4, 67.2. IR: υ_{max} 2960, 1740, 1450, 1391, 1235, 1081, 931, 891, 837, 790, 757 cm^{-1}.

1.5 Typical Procedure for the oxidation postmodification of PO3a-1

P3a-1 (0.307 g, 0.741 mmol) and m-chloroperbenzoic acid (m-CPBA, 0.609 g, 3 mmol) were weighed into THF (5 ml) and added to a vial. Then the mixture was stirred at room temperature for 10 h. At the end of the reaction, the product was dropped into cold methanol to precipitate the oxidized polymer. The oxidized polymer was dried in a vacuum oven at 35 °C for 24 h. Product **PO3a-1** was white powder (yield: 96.2%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.40 (s, 4H), 5.14

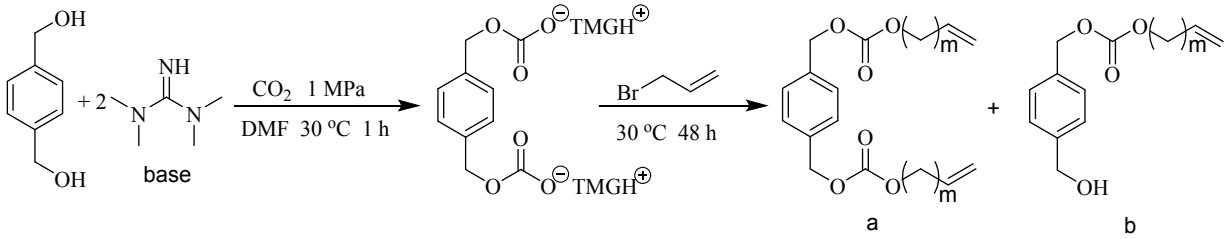
(s, 4H), 4.20 (t, J = 6.3 Hz, 4H), 3.34-3.09 (m, 2H), 2.59-2.39 (m, 5H), 2.24-1.85 (m, 6H). IR: υ_{max} 2965, 1746, 1466, 1401, 1374, 1262, 1129, 1020, 952, 789 cm^{-1}.

1.6 Typical Procedure for the hydrogenation

P4a-3 (200 mg, 0.41 mmol) and pyridine (10 ml) were placed in a 100 ml two-necked flask, and nitrogen was introduced for half an hour. p-Toluenesulfonylhydrazide (0.780 g, 4.1 mmol) and triethylamine (0.576 ml, 4.1 mmol) were added to the flask and reacted at 100 °C for 5 h. After the reaction was completed, it was cooled to room temperature, and then precipitated in 50 ml of methanol and washed three times with methanol. The product was dried under vacuum at 35 °C for 24 h. Product **PH4a-3** was a dark green solid (yield: 98.0%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.14 (d, J = 3.2 Hz, 4H), 4.13 (dd, J = 8.3, 5.1 Hz, 4H), 1.73-1.56 (m, 5H), 1.24 (s, 28H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.3, 135.8, 128.6, 77.5, 77.2, 76.8, 69.1, 68.5, 29.8, 29.7, 29.6, 29.3, 28.7, 25.8. IR: υ_{max} 2921, 2851, 1745, 1456, 1397, 1375, 1257, 1082, 953, 792 cm^{-1}.

2.0 STables

Table S1. Optimization of reaction conditions for the synthesis of diene carbonate monomers[a]



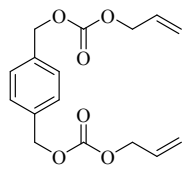
Entry	m	CO_2 (MPa)	T (°C)	t (h)	Base	-Br/-OH	Yield	
							a (%)	b (%)
1	1	1	30	48	TMG	3 equiv.	44.6	37.5
2	1	1	30	48	DBU	3 equiv.	41.5	38.4
3	1	1	30	48	DBN	3 equiv.	13.7	52.7
4	1	1	30	48	TMG	1.5 equiv.	14.8	30.0
5	1	1	50	48	TMG	3 equiv.	28.7	35.6
6	1	1	60	48	TMG	3 equiv.	7.8	41.8
7	1	1	30	12	TMG	3 equiv.	28.0	42.2
8	1	1	30	24	TMG	3 equiv.	35.5	44.9
9	1	2	30	48	TMG	3 equiv.	45.8	33.0
10	1	3	30	48	TMG	3 equiv.	58.8	25.4
11	4	1	30	48	TMG	3 equiv.	40.2	31.2
12	8	1	30	48	TMG	3 equiv.	22.8	35.1
13[b]	4	0.1	60	48	Cs_2CO_3	3 equiv.	70.4	9.8
14[b]	8	0.1	60	48	Cs_2CO_3	3 equiv.	68.6	21.7

[a]The standard conditions involved the use of 1,4-di(hydroxymethyl)benzene (4 mmol), 3-bromopropene (24 mmol) and DMF (10 ml). [b]TBAI was used in the reation. For specific experimental

protocols refer to relevant literature.[1, 2]

3.0 SFigures

3.1 NMR spectra of monomers and polycarbonates



1,4-phenylenebis(methylene) diallyl bis(carbonate)

Product **2a-1**. Transparent pale yellow liquid (yield: 44.6%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.87-5.97 (m, 2H), 5.24-5.37 (m, 4H), 5.16 (s, 4H), 4.63 (dt, ^{1}J = 1.6 Hz, ^{2}J = 8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.0, 135.7, 131.6, 128.6, 119.1, 69.2, 68.7. IR: υ_{max} 3090-2892, 1747, 1649, 1577, 1517, 1449, 1385, 1253, 1077, 953, 789 cm^{-1}.

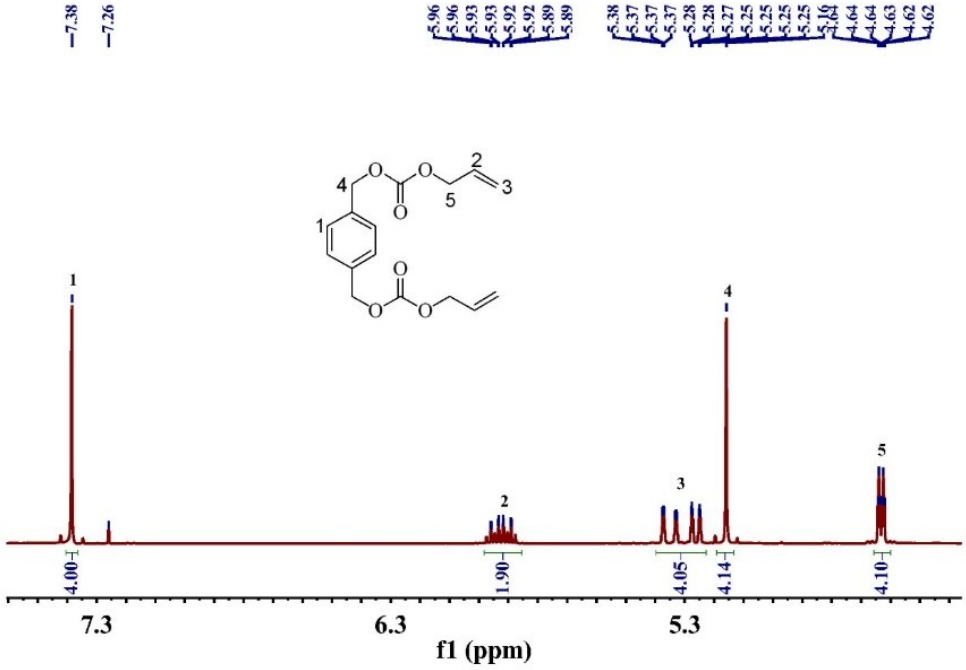


Figure S1. ^{1}H NMR spectrum of **2a-1**

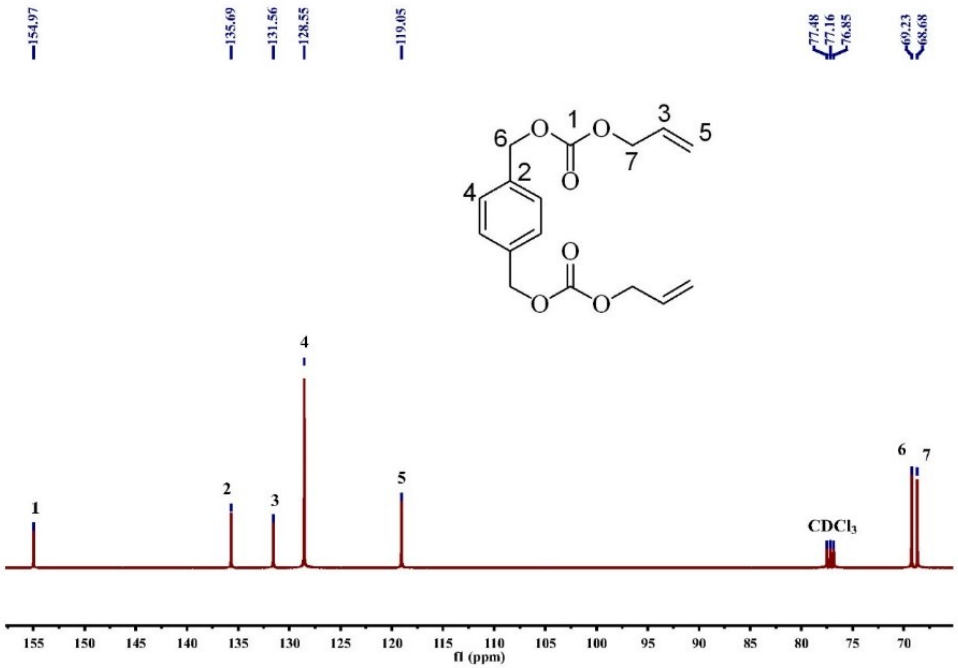
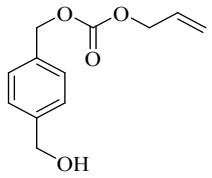


Figure S2. ^{13}C NMR spectrum of **2a-1**



allyl (4-(hydroxymethyl)benzyl) carbonate

Product **2a-1'**. Transparent pale yellow liquid (yield: 37.5%).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 (s, 4H), 5.99-5.85 (m, 1H), 5.31 (ddd, J = 13.8, 11.7, 1.3 Hz, 2H), 5.16 (s, 2H), 4.69 (s, 2H), 4.63 (dt, J = 5.8, 1.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.0, 135.7, 135.6, 131.5, 128.6, 128.6, 128.0, 128.0, 119.1, 77.4, 77.1, 76.8, 69.4, 69.2, 68.7. IR: υ_{max} 3404, 3089-2877, 1745, 1649, 1577, 1513, 1453-1253, 953, 789 cm^{-1}.

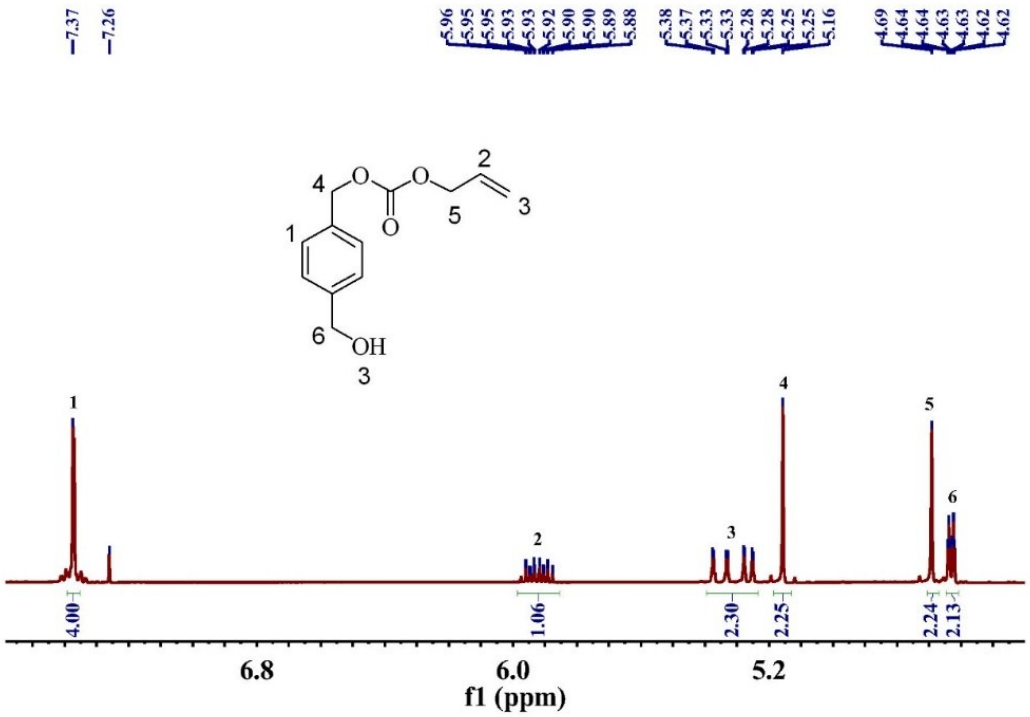


Figure S3. ^{1}H NMR spectrum of **2a-1'**

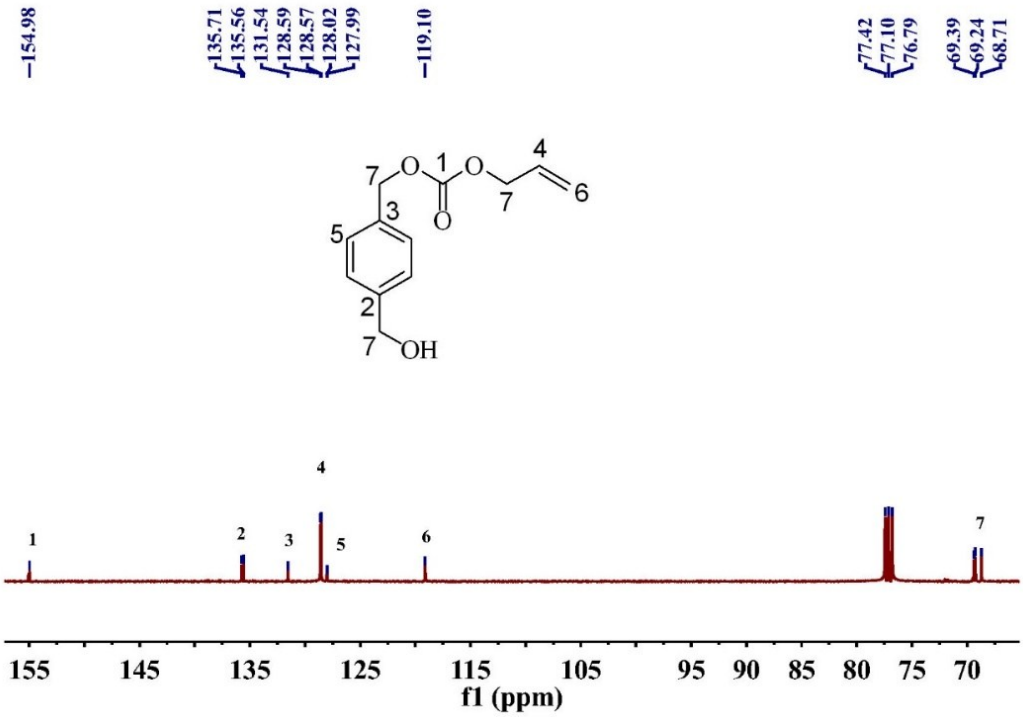
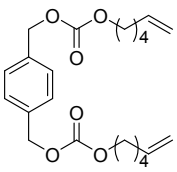


Figure S4. ^{13}C NMR spectrum of **2a-1'**



1,4-phenylenebis(methylene) di(hex-5-en-1-yl) bis(carbonate)

Product **2a-2**. Pale yellow liquid (yield: 40.2%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.77 (dd, J = 17.0, 10.3 Hz, 2H), 5.14 (s, 4H), 5.06-4.89 (m, 4H), 4.15 (t, J = 6.6 Hz, 4H), 2.07 (d, J = 6.9 Hz, 4H), 1.68 (dd, J = 8.4, 6.9 Hz, 4H), 1.56-1.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.3, 138.3, 135.7, 128.6, 115.0, 77.4, 77.1, 76.8, 69.1, 68.2, 33.3, 28.1, 25.0. IR: υ_{max} 3077-2857, 1749, 1637, 1577, 1517, 1453, 1393, 1253, 992, 913, 789 cm^{-1}.

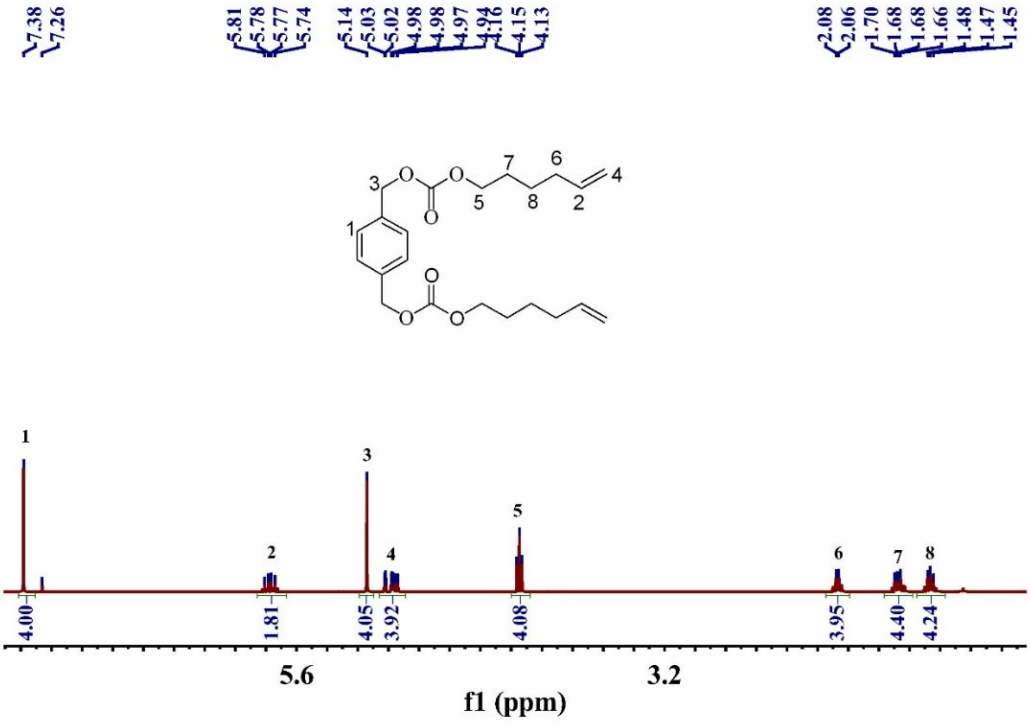


Figure S5. ^{1}H NMR spectrum of **2a-2**

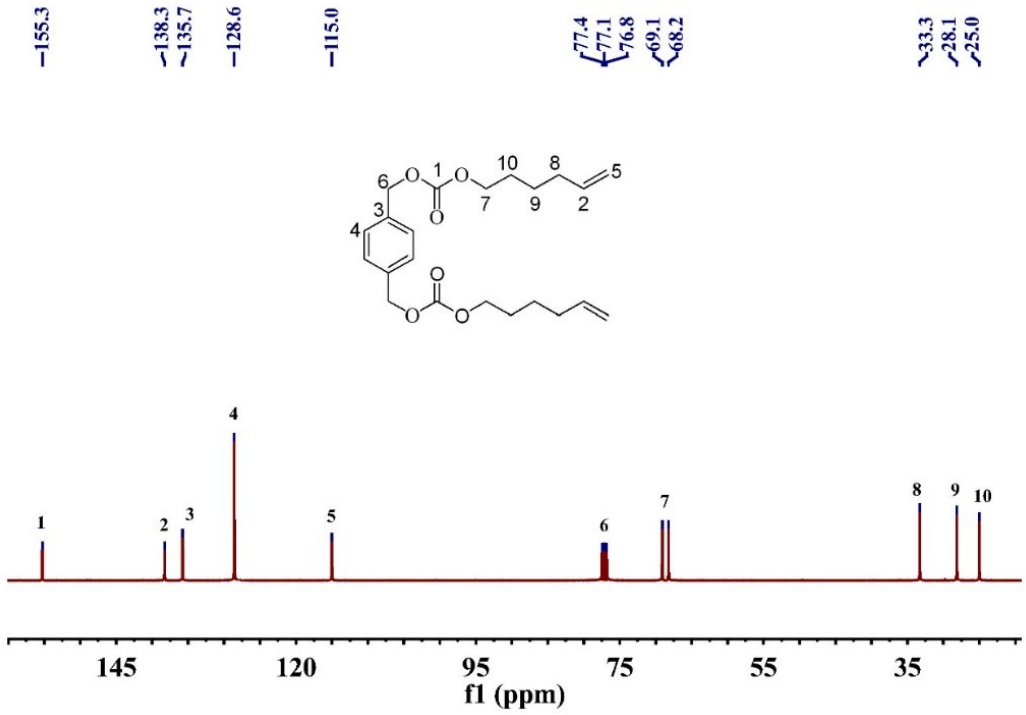
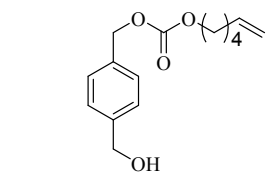


Figure S6. ^{13}C NMR spectrum of **2a-2**



hex-5-en-1-yl (4-(hydroxymethyl)benzyl) carbonate

Product **2a-2'**. Pale yellow liquid (yield: 31.2%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.35 (s, 4H), 5.77 (dd, J = 17.2, 10.4 Hz, 1H), 5.12 (s, 3H), 5.06-4.75 (m, 2H), 4.65 (s, 2H), 4.13 (t, J = 6.8 Hz, 2H), 2.24-1.92 (m, 2H), 1.88-1.58 (m, 2H), 1.58-1.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.3, 141.4, 138.3, 134.7, 128.6, 127.2, 115.0, 77.5, 77.2, 76.9, 69.3, 68.2, 64.9, 33.3, 28.1, 25.0. IR: υ_{max} 3418, 3073-2857, 1737, 1633, 1577, 1513, 1457-1369, 1257, 913, 789 cm^{-1}.

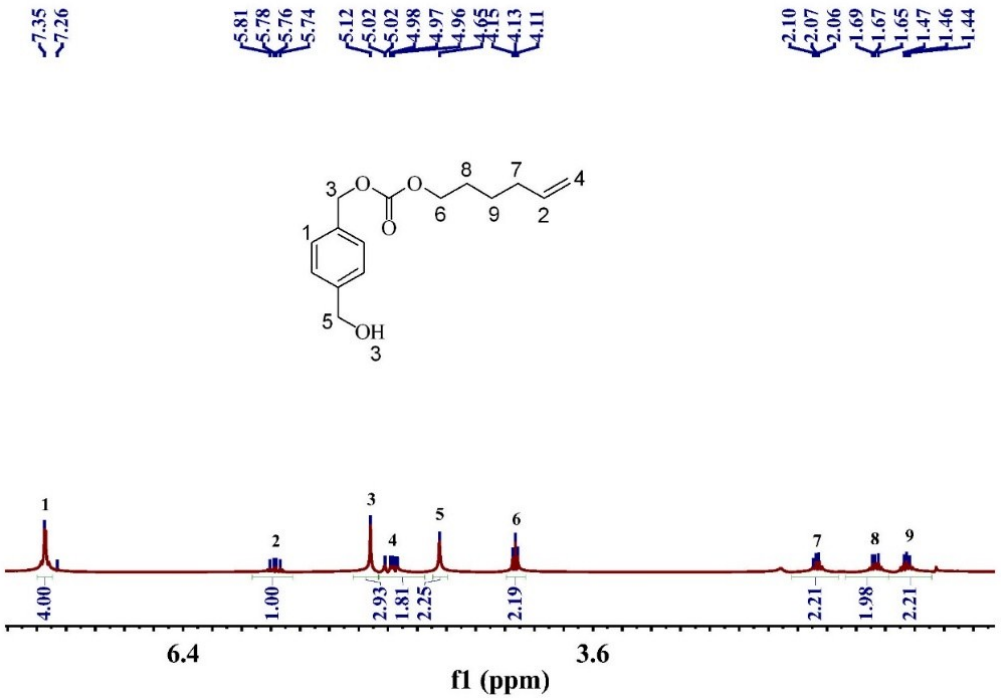


Figure S7. ^{1}H NMR spectrum of **2a-2'**

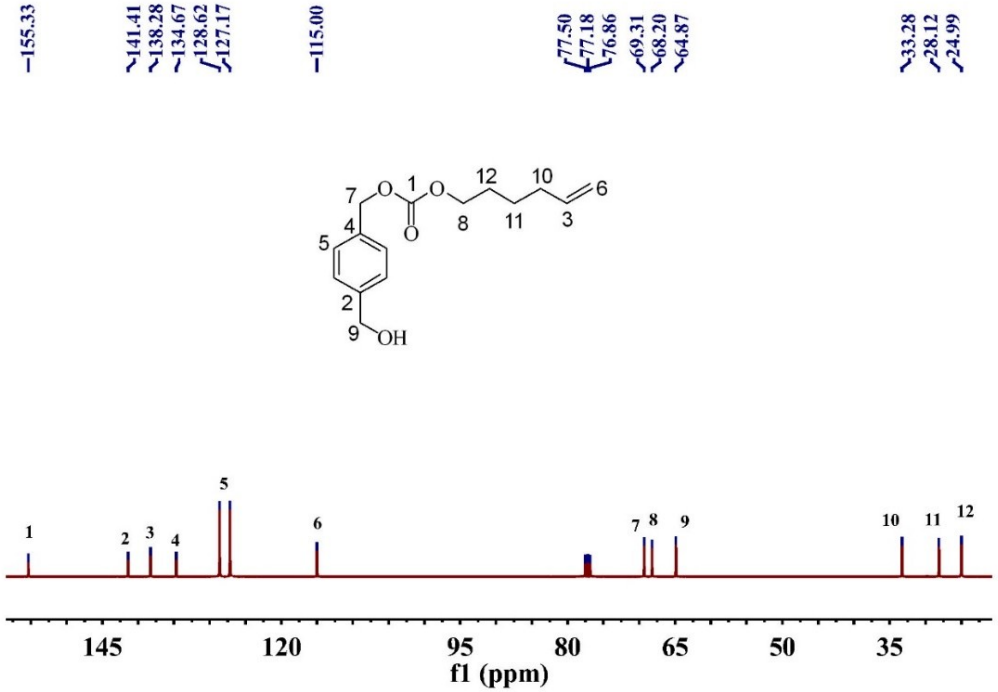
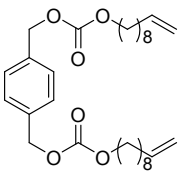


Figure S8. ^{13}C NMR spectrum of **2a-2'**



1,4-phenylenebis(methylene) di(dec-9-en-1-yl) bis(carbonate)

Product **2a-3**. White solid (yield: 22.8%); m.p. 53.3 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.80 (dd, J = 17.0, 10.3 Hz, 2H), 5.14 (s, 4H), 5.05-4.84 (m, 4H), 4.13 (t, J = 6.7 Hz, 4H), 2.03 (dd, J = 6.7, 1.0 Hz, 4H), 1.64 (dd, J = 18.5, 10.6 Hz, 4H), 1.46-1.20 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.3, 141.4, 138.3, 134.7, 128.6, 127.2, 115.0, 77.5, 77.2, 76.9, 69.3, 68.2, 64.9, 33.3, 28.1, 25.0. IR: υ_{max} 3077-2853, 1733, 1637, 1577, 1513, 1477-1373, 1265, 989, 945, 853, 789, 752, 713 cm^{-1}.

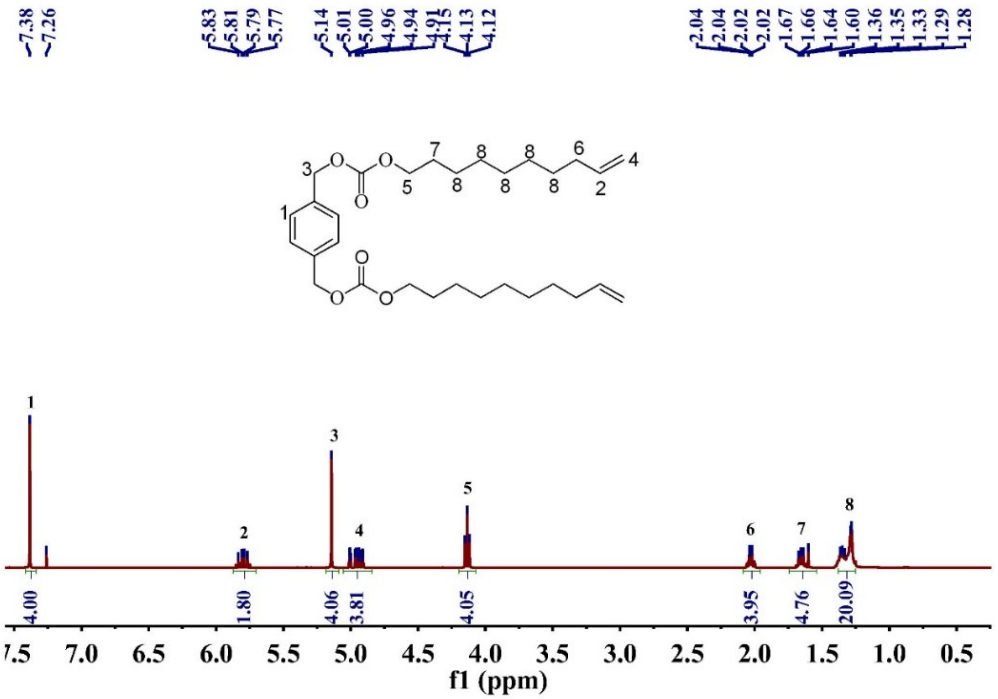


Figure S9. ^{1}H NMR spectrum of **2a-3**

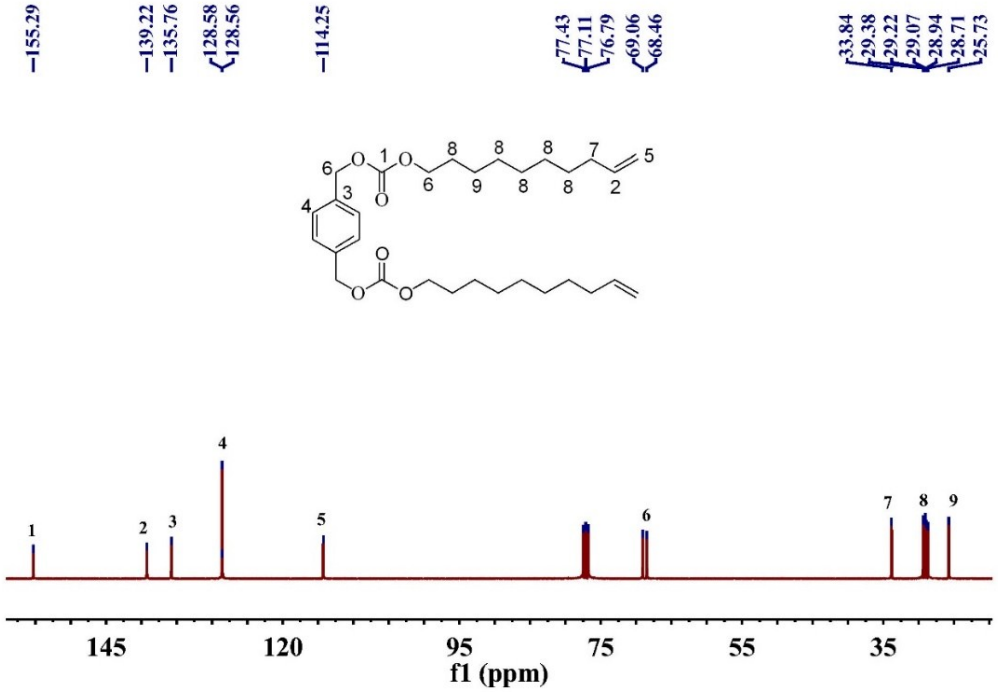
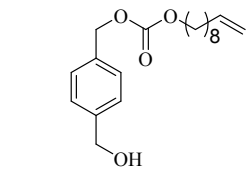


Figure S10. ^{13}C NMR spectrum of **2a-3**



dec-9-en-1-yl (4-(hydroxymethyl)benzyl) carbonate

Product **2a-3'**. Colorless liquid (yield: 35.1%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36 (s, 4H), 5.80 (ddt, J = 17.0, 10.3, 6.8 Hz, 1H), 5.13 (s, 3H), 4.95 (ddd, J = 13.7, 12.5, 2.3 Hz, 2H), 4.68 (s, 2H), 4.13 (t, J = 6.8 Hz, 2H), 2.26-1.86 (m, 2H), 1.81-1.54 (m, 2H), 1.30 (dd, J = 27.8, 17.9 Hz, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.3, 141.3, 139.2, 134.8, 128.6, 127.2, 114.3, 77.4, 77.1, 76.8, 69.3, 68.4, 65.0, 33.8, 29.4, 29.2, 29.1, 28.9, 28.7, 25.7. IR: υ_{max} 3469, 3077-2849, 1749, 1637, 1465, 1405, 1257, 992, 909, 793, 724, 633 cm^{-1}.

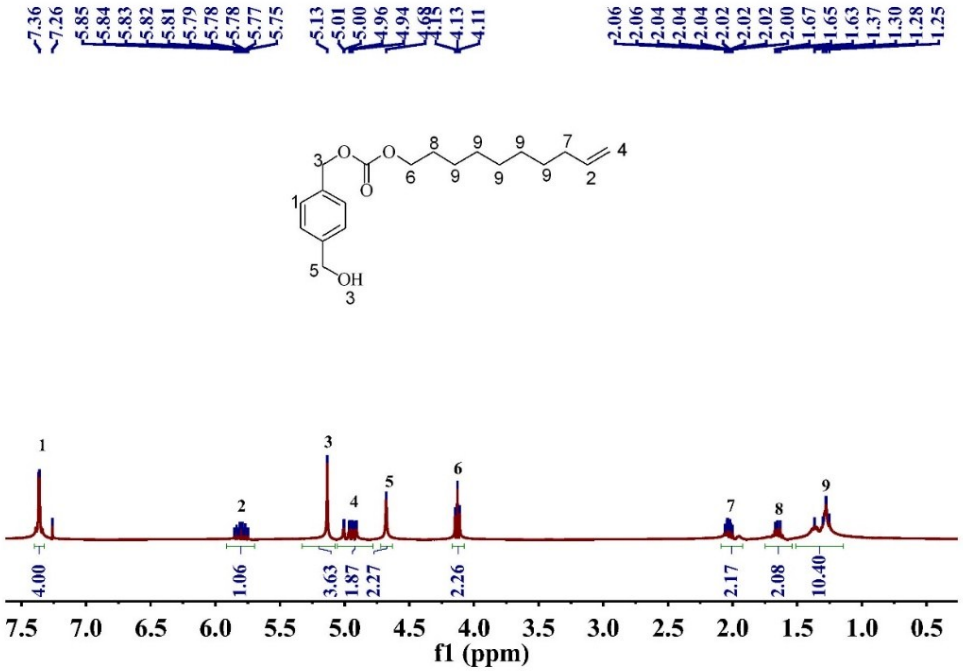


Figure S11. ^{1}H NMR spectrum of **2a-3'**

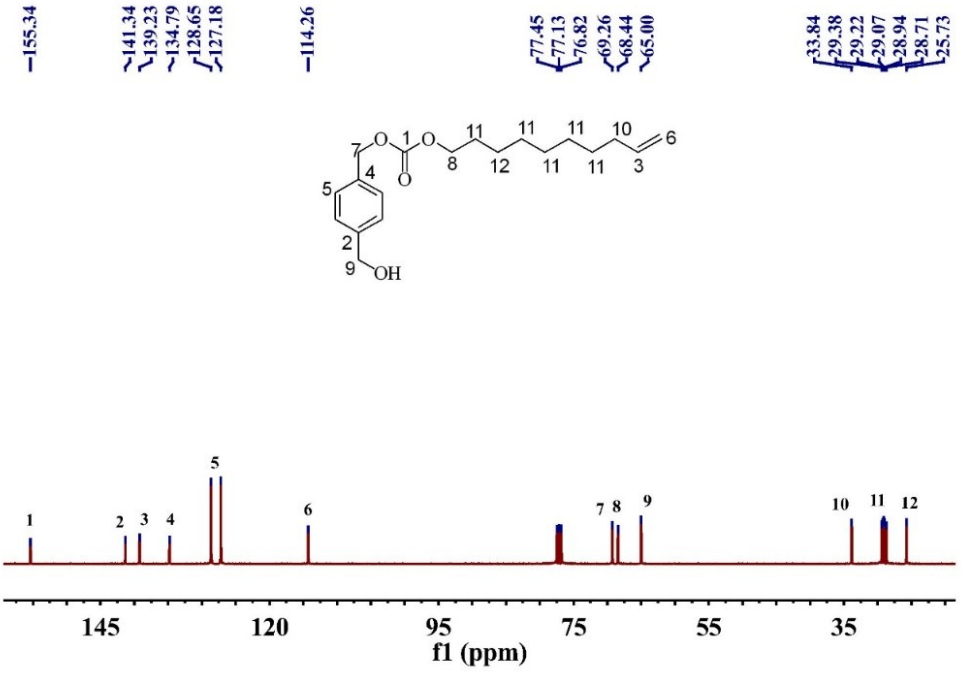
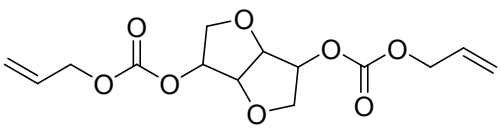


Figure S12. ^{13}C NMR spectrum of **2a-3'**



diallyl (hexahydrofuro[3,2-*b*]furan-3,6-diyl) bis(carbonate)

Product **2b**. Thick pale yellow liquid (yield: 45.8%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.92 (ddd, J = 17.1, 10.4, 3.9 Hz, 2H), 5.42-5.22 (m, 4H), 5.08 (dd, J = 9.9, 4.4 Hz, 2H), 4.89 (t, J = 5.2 Hz, 1H), 4.64 (ddt, J = 7.2, 5.9, 1.2 Hz, 4H), 4.54 (d, J = 4.8 Hz, 1H), 4.12-3.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.4, 131.4, 119.5, 85.9, 81.3, 77.2, 73.3, 70.6, 68.9. IR: υ_{max} 3082-2882, 1748, 1647, 1452, 1364, 1246, 1098-863, 788 cm^{-1}.

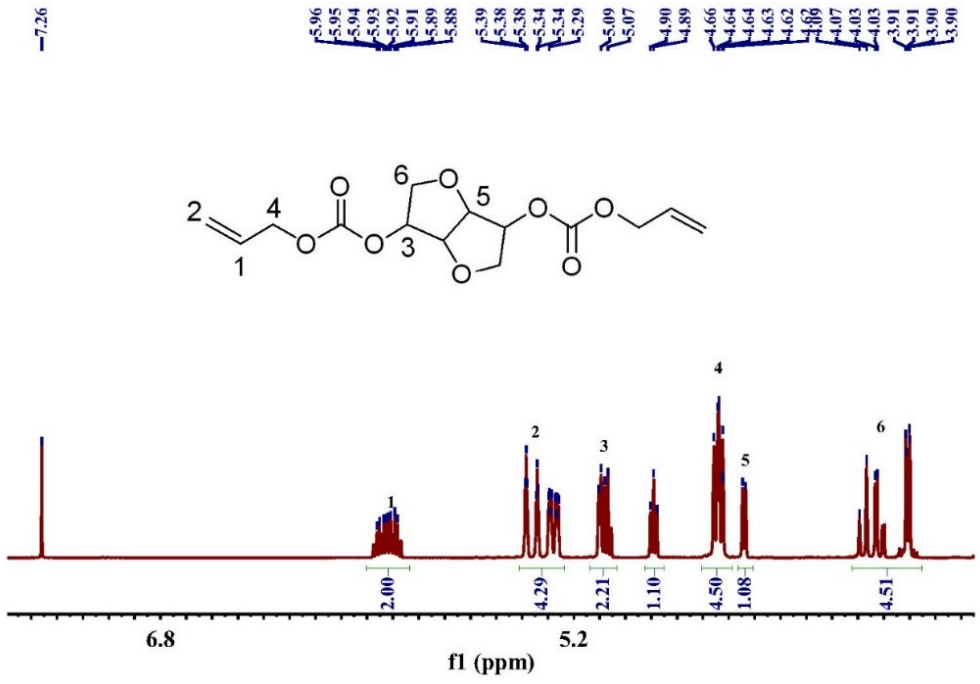


Figure S13. ^{1}H NMR spectrum of **2b**

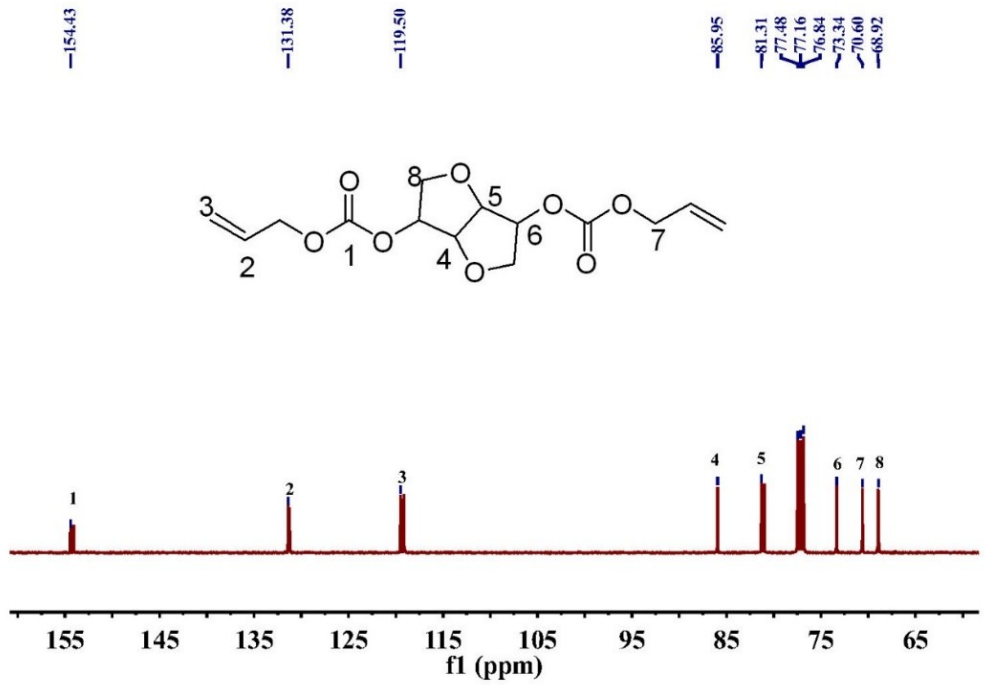
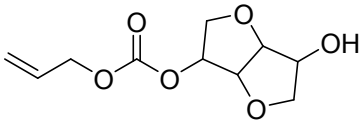


Figure S14. ^{13}C NMR spectrum of **2b**



allyl (6-hydroxyhexahydrofuro[3,2-*b*]furan-3-yl) carbonate

Product **2b'**. Thick pale yellow liquid (yield: 22.5%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.99-5.86 (m, 1H), 5.41-5.23 (m, 3H), 5.06 (d, J = 5.2 Hz, 1H), 4.89 (t, J = 5.1 Hz, 1H), 4.65 (dt, J = 5.8, 1.3 Hz, 2H), 4.36 (dd, J = 25.9, 3.1 Hz, 2H), 3.97-3.83 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.6, 131.3, 119.1, 88.4, 80.6, 77.5, 77.2, 77.1, 76. 9, 75.9, 75.7, 70.4, 68.9. IR: υ_{max} 3465, 3087-2878, 1747, 1649, 1452, 1373, 1255, 1089-832, 788 cm^{-1}.

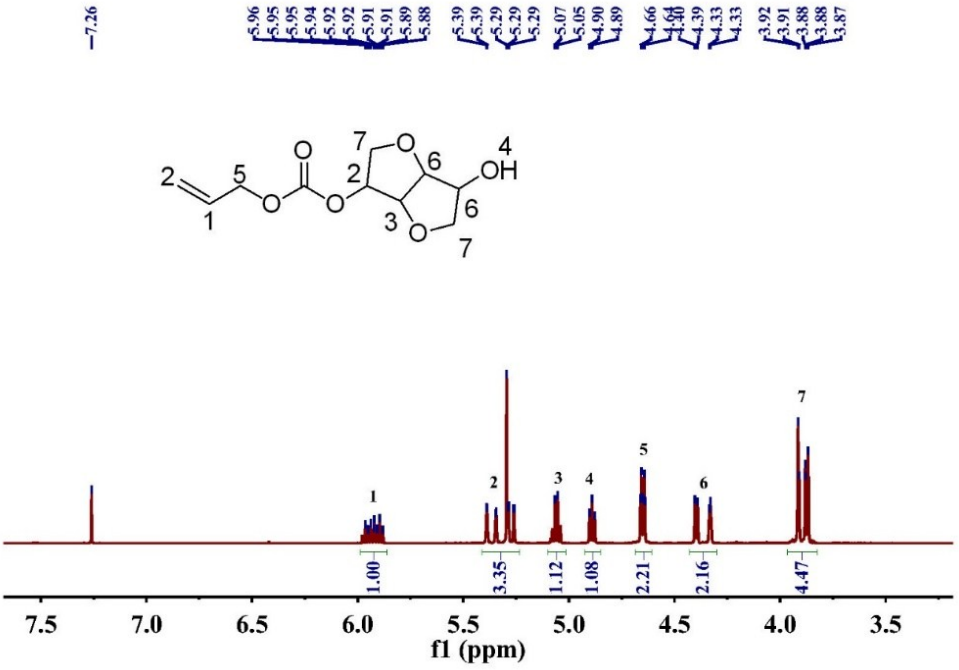


Figure S15. ^{1}H NMR spectrum of **2b'**

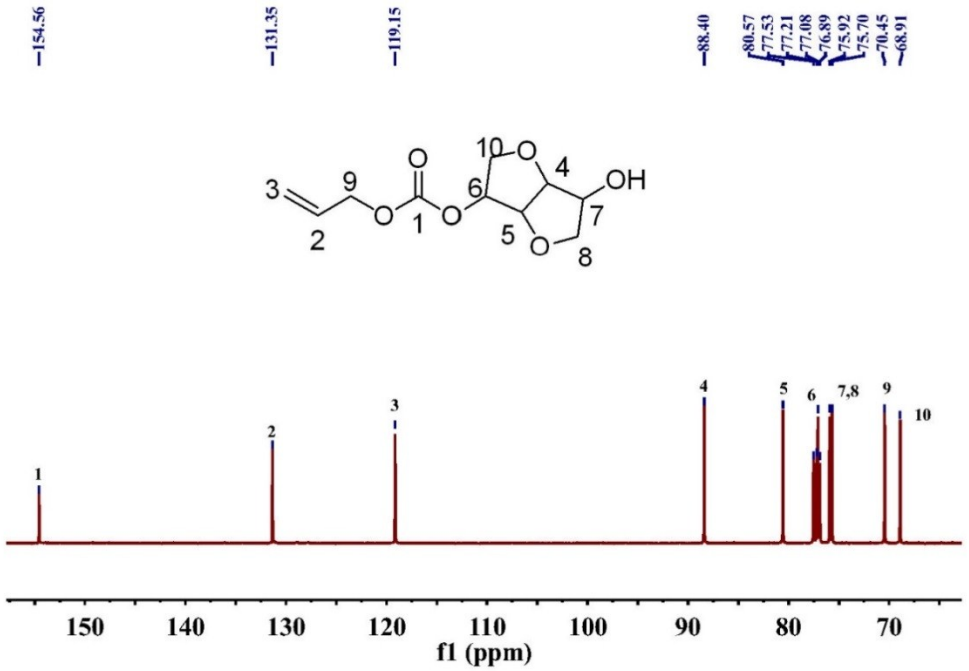
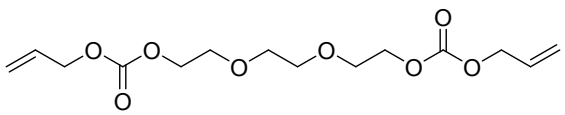


Figure S16. ^{13}C NMR spectrum of **2b'**



diallyl ((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl)) bis(carbonate)

Product **2c**. Transparent pale yellow liquid (yield: 51.7%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.99-5.84 (m, 2H), 5.28 (ddd, J = 13.9, 11.6, 1.3 Hz, 4H), 4.60 (dt, J = 5.7, 1.3 Hz, 4H), 4.26 (dd, J = 5.5, 4.0 Hz, 4H), 3.74-3.66 (m, 4H), 3.63 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.0, 131.6, 119.0, 77.5, 77.2, 76.8, 70.7, 69.0, 68.5, 67.1. IR: υ_{max} 3089-2885, 1749, 1649, 1585, 1453, 1389, 1257, 1133, 1029-873, 789 cm^{-1}.

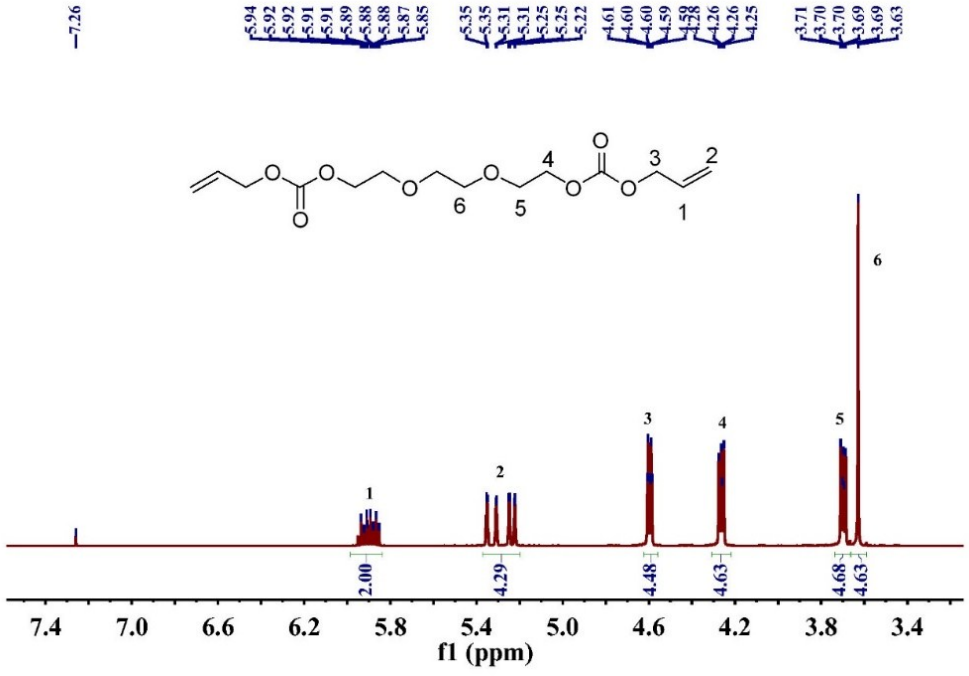


Figure S17. ^{1}H NMR spectrum of **2c**

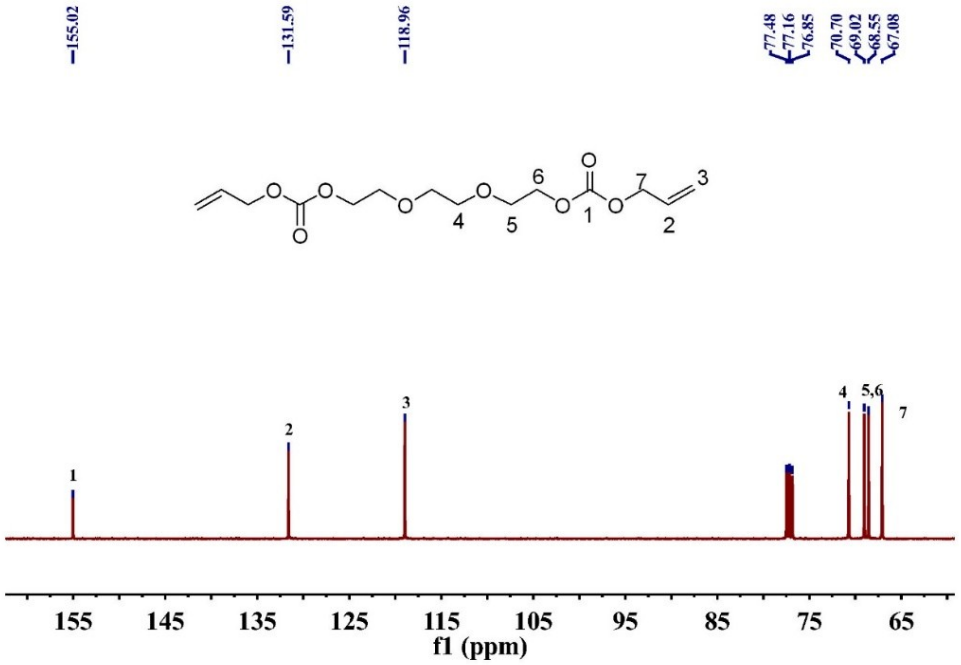
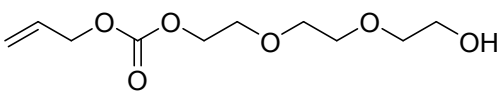


Figure S18. ^{13}C NMR spectrum of **2c**



allyl (2-(2-(2-hydroxyethoxy)ethoxy)ethyl) carbonate

Product **2c'**. Transparent pale yellow liquid (yield: 21.0%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.92 (dd, J = 17.1, 10.6 Hz, 1H), 5.39 -5.23 (m, 2H), 4.62 (d, J = 5.8 Hz, 2H), 4.30 (dd, J = 5.5, 4.0 Hz, 2H), 3.77-3.57 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.0, 131.5, 119.1, 77.5, 77.2, 76.8, 72.7, 70.7, 70.3, 69.0, 68.7, 67.0, 61.8. IR: υ_{max} 3457, 2878, 1748, 1646, 1452, 1382, 1119-871, 785 cm^{-1}.

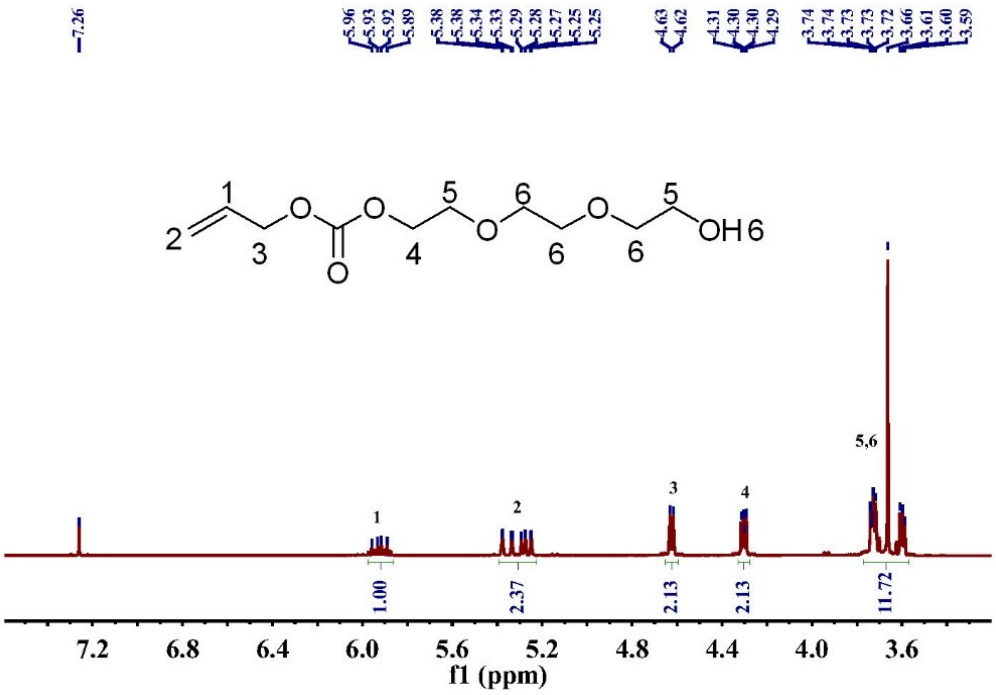


Figure S19. ^{1}H NMR spectrum of **2c'**

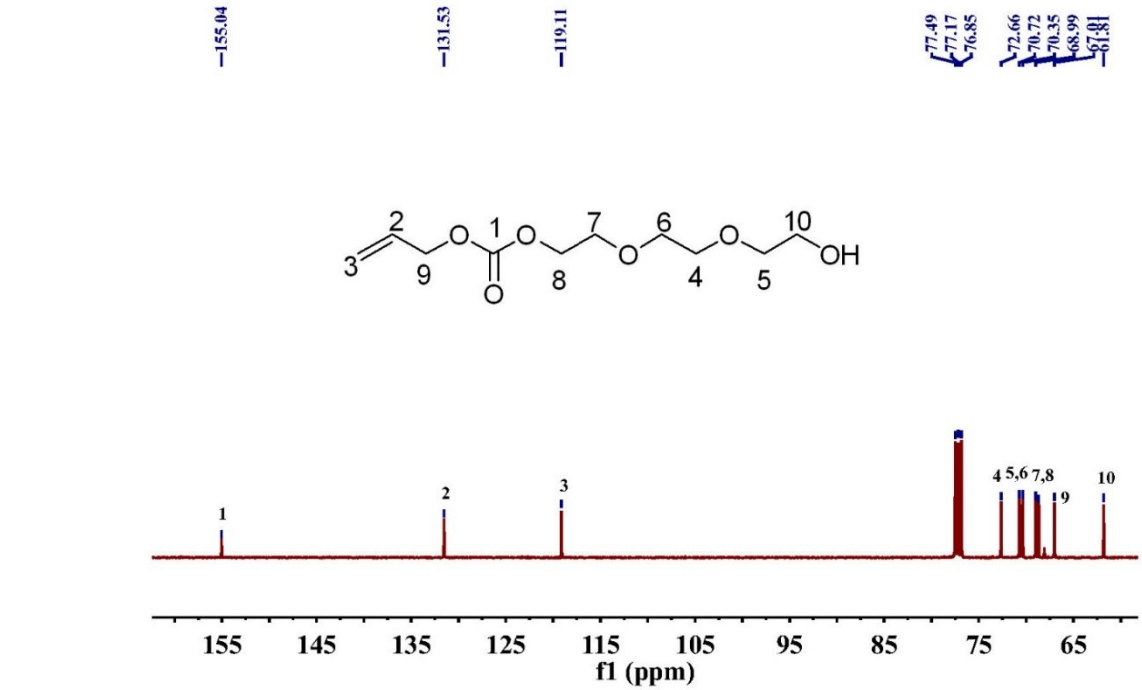
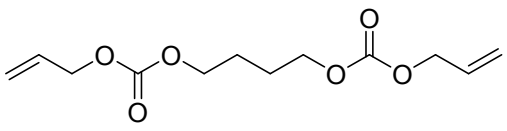


Figure S20. ^{13}C NMR spectrum of **2c'**



diallyl butane-1,4-diyl bis(carbonate)

Product **2d**. Transparent pale yellow liquid (yield: 58.0%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.99-5.85 (m, 2H), 5.30 (ddd, J = 13.8, 11.6, 1.3 Hz, 4H), 4.61 (dt, J = 5.6, 1.2 Hz, 4H), 4.21-4.12 (m, 4H), 1.77 (t, J = 3.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.1, 131.6, 119.1, 77.5, 77.2, 76.8, 68.5, 67.4, 25.2. IR: υ_{max} 3089-2853, 1749, 1649, 1585, 1453-1365, 1253, 949, 789 cm^{-1}.

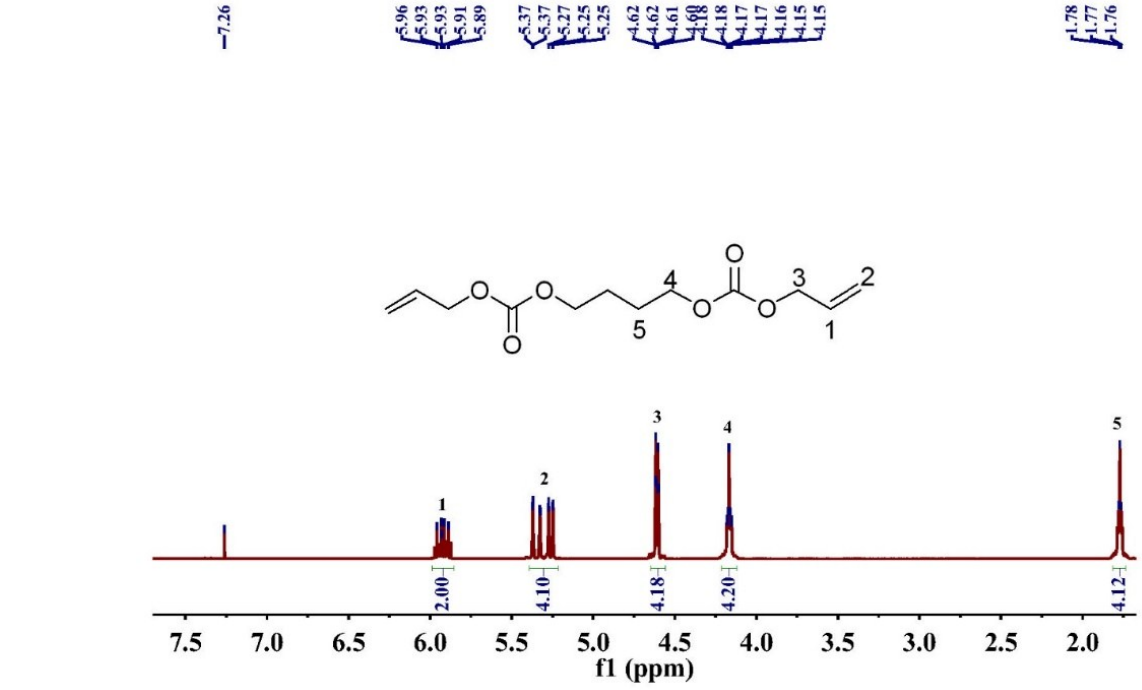


Figure S21. ^{1}H NMR spectrum of **2d**

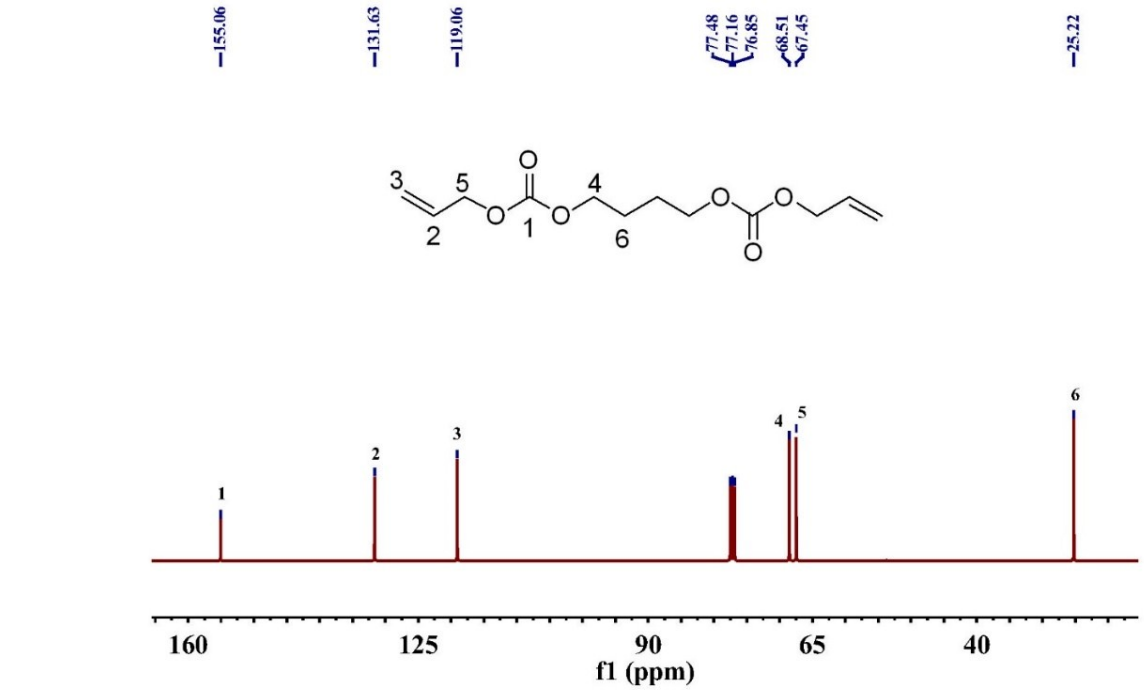
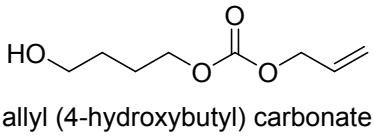


Figure S22. ^{13}C NMR spectrum of **2d**



allyl (4-hydroxybutyl) carbonate

Product **2d'**. Transparent pale yellow liquid (yield: 17.0%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.96-5.88 (m, 1H), 5.41-5.22 (m, 2H), 4.61 (dd, J = 6.8, 1.0 Hz, 2H), 4.18 (t, J = 6.5 Hz, 2H), 3.68 (t, J = 6.3 Hz, 2H), 1.77 (dd, J = 8.8, 6.3 Hz, 2H), 1.70-1.62 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.3, 131.8, 119.2, 77.6, 77.3, 77.0, 68.7, 68.2, 62.5, 29.1, 25.4. IR: υ_{max} 3436, 3089-2873, 1754, 1647, 1585, 1509, 1453-1365, 1257, 1065-945, 789 cm^{-1}.

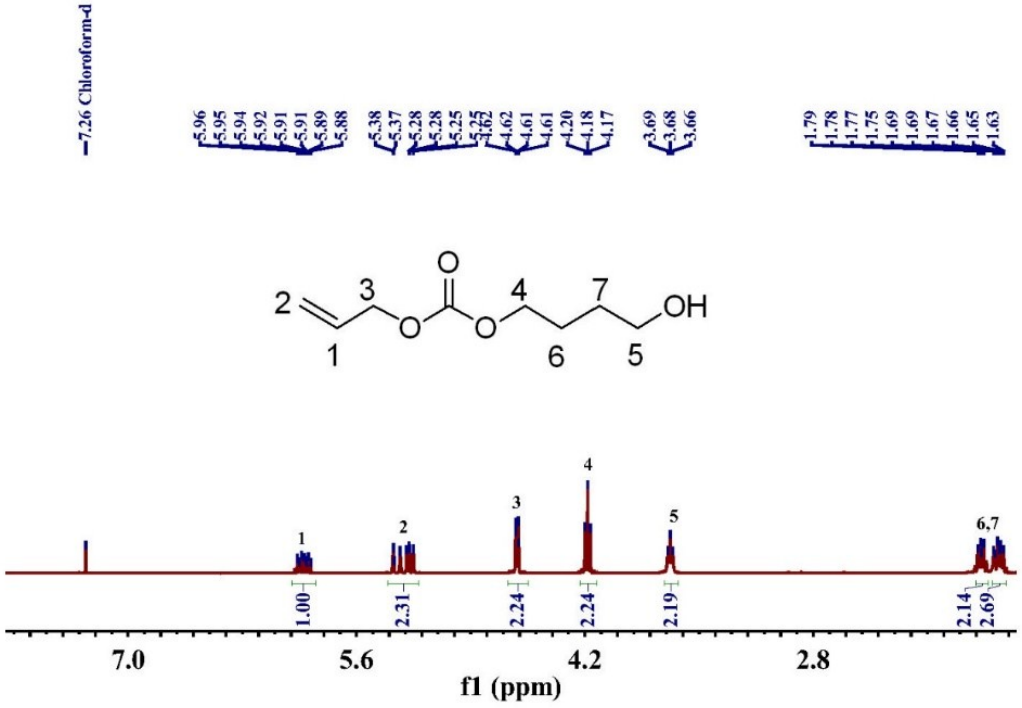


Figure S23. ^{1}H NMR spectrum of **2d'**

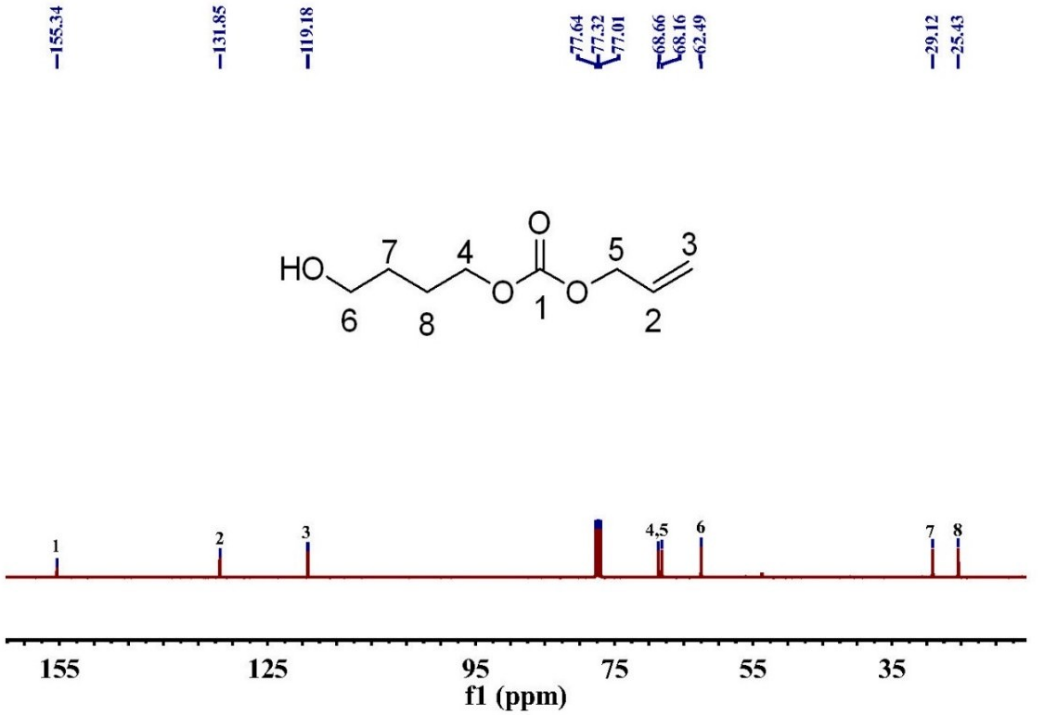
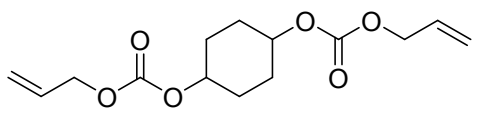


Figure S24. ^{13}C NMR spectrum of **2d'**



diallyl cyclohexane-1,4-diyl bis(carbonate)

Product **2e**. Transparent pale yellow liquid (yield: 41.1%).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.93 (dd, J = 17.2, 10.5 Hz, 2H), 5.42-5.20 (m, 4H), 4.71 (s, 2H), 4.61 (dt, J = 5.9, 1.3 Hz, 4H), 2.02-1.68 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.5, 131.7, 119.0, 77.5, 77.2, 76.8, 73.9, 68.4, 27.2. IR: υ_{max} 3082-2878, 1744, 1643, 1447, 1373, 1250, 1120-840, 788 cm^{-1}.

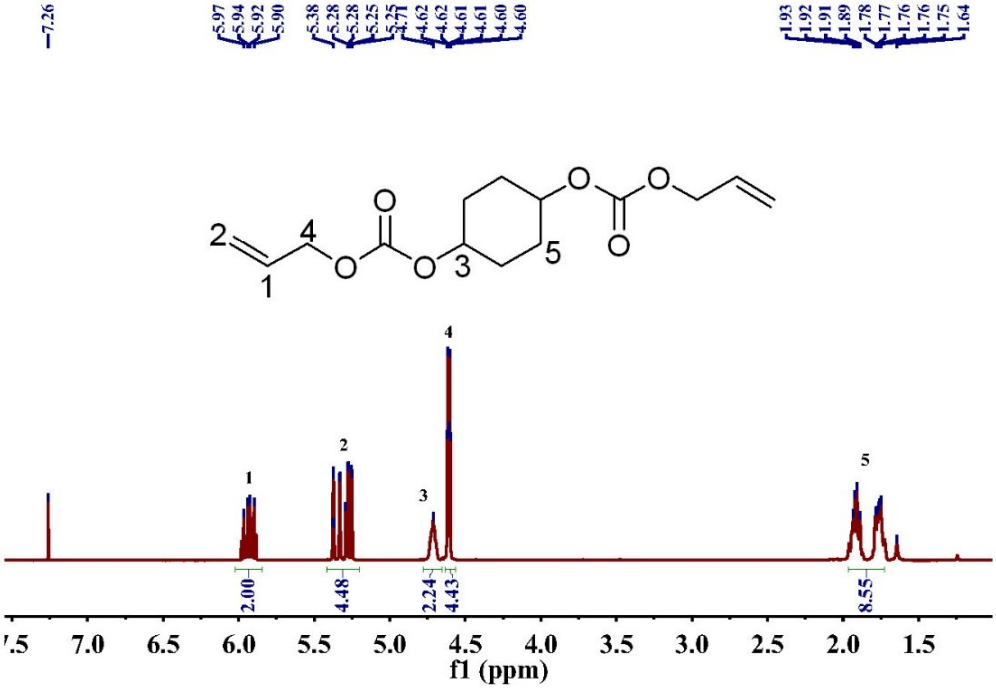


Figure S25. ^{1}H NMR spectrum of **2e**

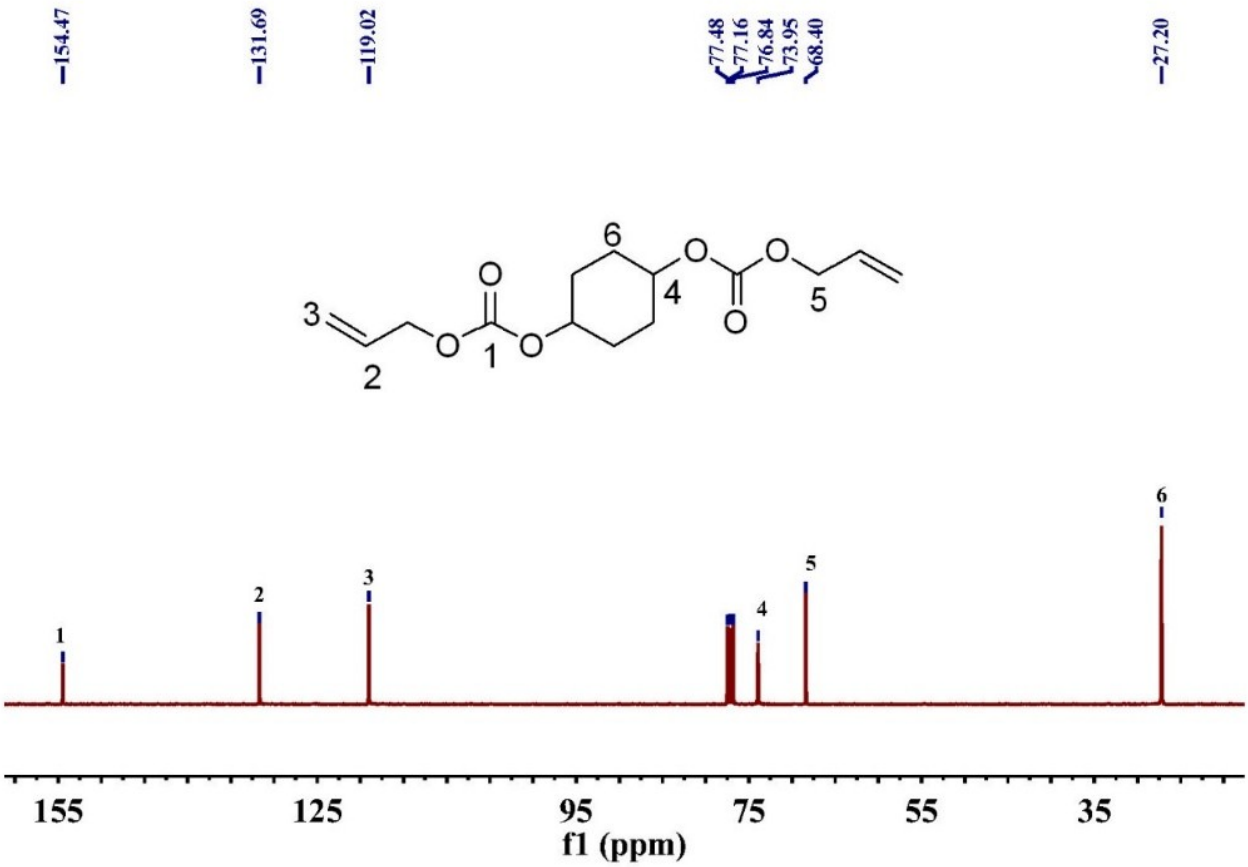
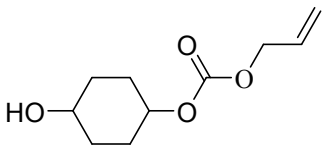


Figure S26. ^{13}C NMR spectrum of **2e**



allyl (4-hydroxycyclohexyl) carbonate

Product **2e'**. Transparent pale yellow liquid (yield: 23.2%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.98-5.84 (m, 1H), 5.41-5.19 (m, 2H), 4.78-4.52 (m, 3H), 3.74 (ddd, J = 13.1, 9.7, 5.2 Hz, 1H), 2.13-1.57 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.5, 131.7, 119.0, 77.5, 77.2, 76.9, 75.9, 68.6, 68.4, 30.4, 27.4. IR: υ_{max} 3412, 3087-2864, 1744, 1647, 1447, 1373, 1255, 1068-928, 788 cm^{-1}.

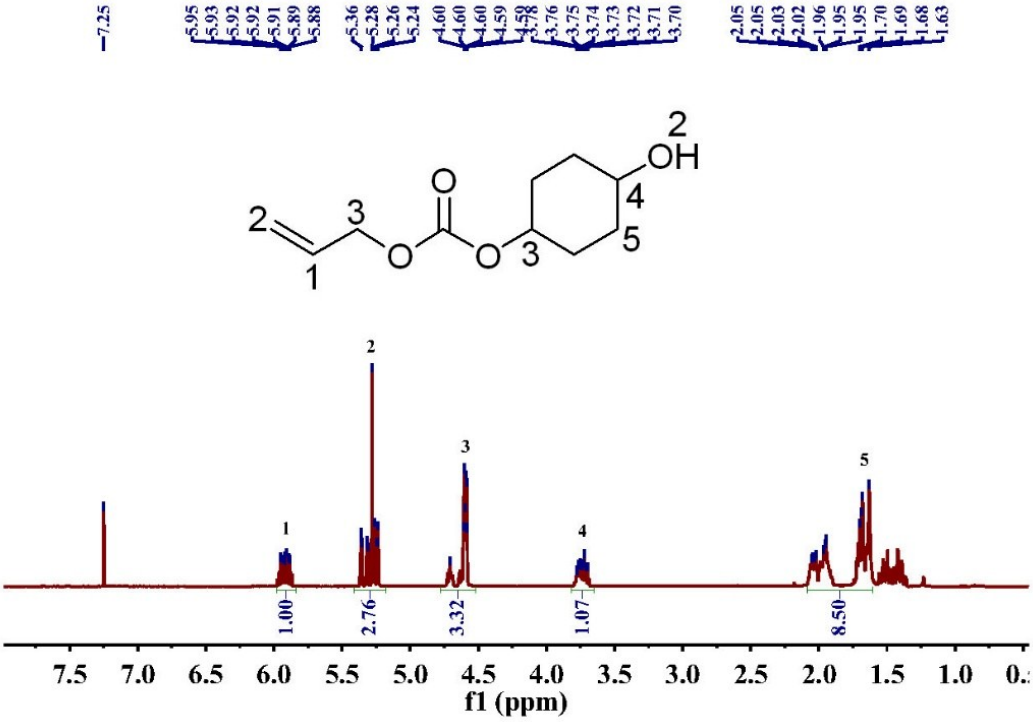


Figure S27**.** ^{1}H NMR spectrum of **2e'**

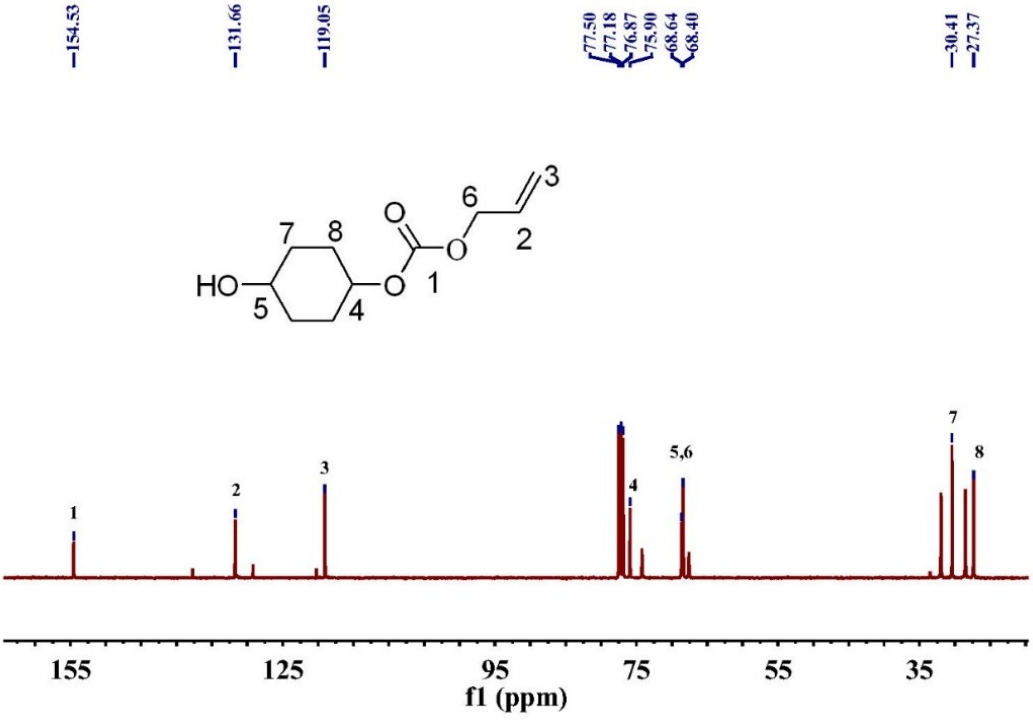
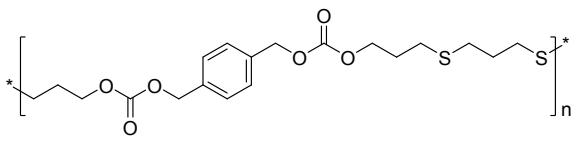


Figure S28**.** ^{13}C NMR spectrum of **2e'**



poly-butyl (4-(3-oxo-2,4-dioxa-8,12-dithiatridecyl)benzyl) carbonate

Product **P3a-1**. White solid (yield: 98.2%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.14 (s, 4H), 4.24 (t, J = 6.6 Hz, 4H), 2.76-2.44 (m, 8H), 2.17-1.60 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.0, 135.6, 128.6, 77.5, 77.2, 76.8, 69.2, 66.7, 30.8, 29.0, 28.6, 28.2. IR: υ_{max} 2957-2849, 1745, 1517, 1453, 1393, 1253, 1085-849, 789 cm^{-1}.

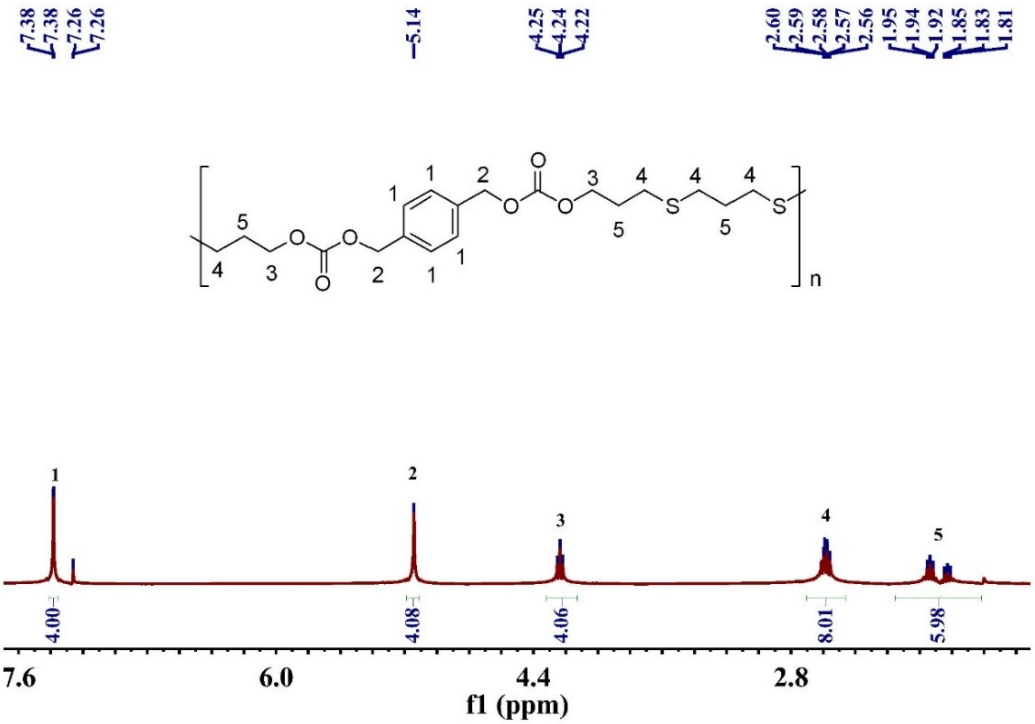


Figure S29. ^{1}H NMR spectrum of **P3a-1**

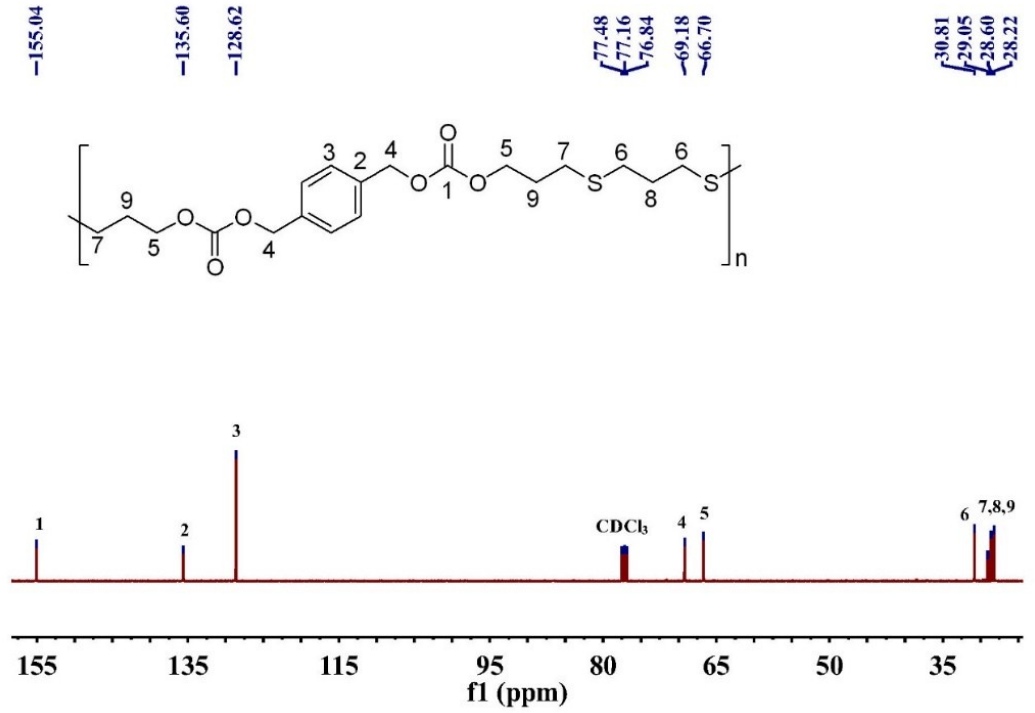
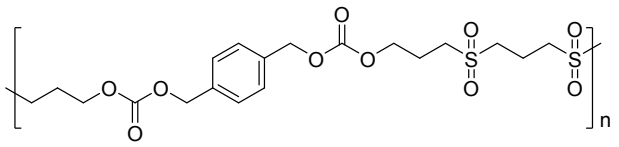


Figure S30. ^{13}C NMR spectrum of **P3a-1**



Product **PO3a-1**. White powder (yield: 96.2%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.40 (s, 4H), 5.14 (s, 4H), 4.19 (t, J = 6.3 Hz, 4H), 3.33 – 3.15 (m, 2H), 2.95–2.66 (m, 1H), 2.12–1.94 (m, 6H). IR: υ_{max} 2965, 1746, 1466, 1401, 1374, 1262, 1129, 1019, 952, 789 cm^{-1}.

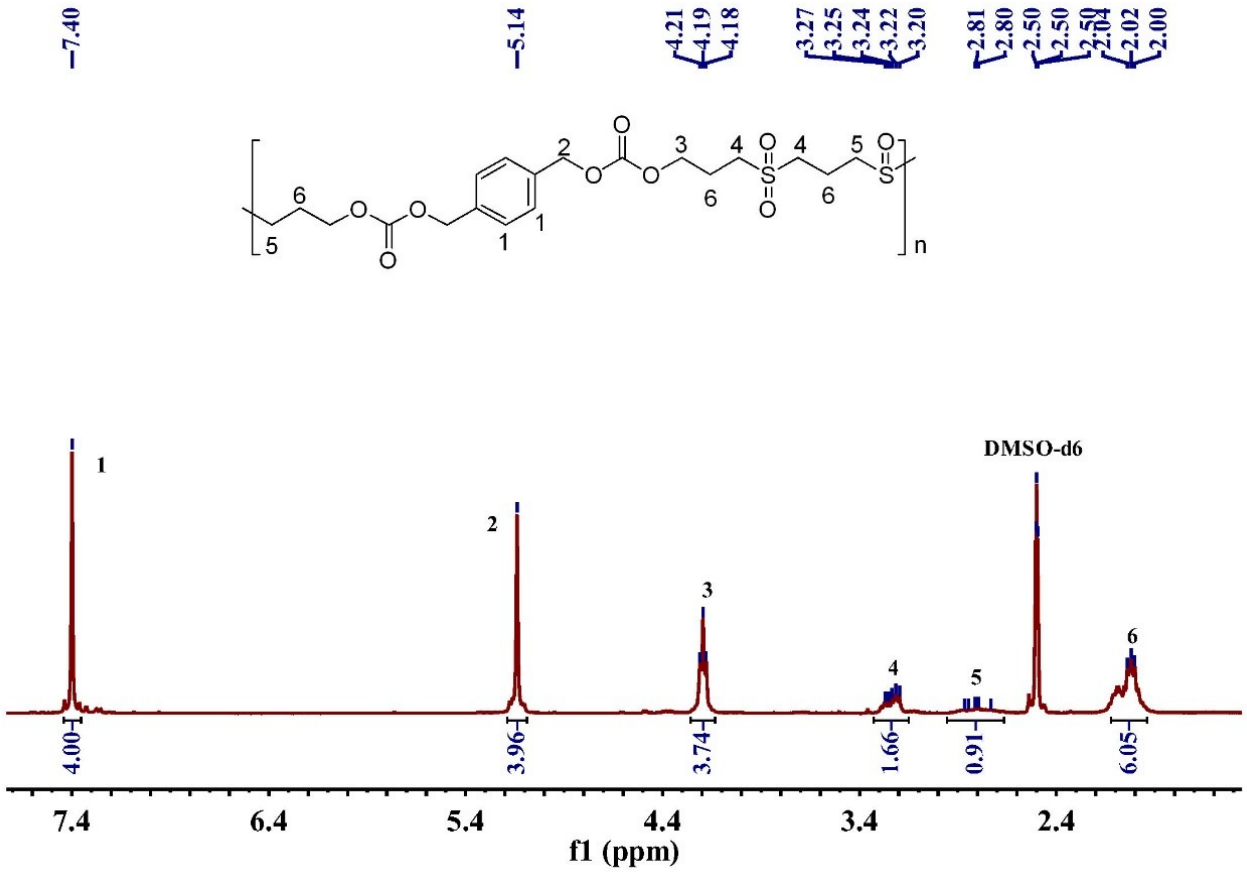
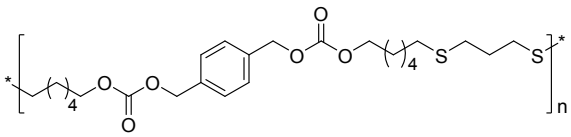


Figure S31. ^{1}H NMR spectrum of **PO3a-1**



poly-hexyl (4-((((((6-((3-mercaptopropyl)thio)hexyl)oxy)carbonyl)oxy)methyl)benzyl) carbonate

Product **P3a-2**. White solid (yield: 94.5%).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.14 (s, 4H), 4.13 (t, J = 6.7 Hz, 4H), 2.54 (dt, J = 39.5, 7.3 Hz, 8H), 1.83 (m, 2H), 1.61 (m, 8H), 1.38 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.2, 135.7, 128.6, 77.5, 77.2, 76.8, 69.1, 68.2, 32.1, 31.0, 29.5, 28.6, 28.5, 25.4. IR: υ_{max} 2929, 2853, 1745, 1453, 1393, 1257, 949, 789 cm^{-1}.

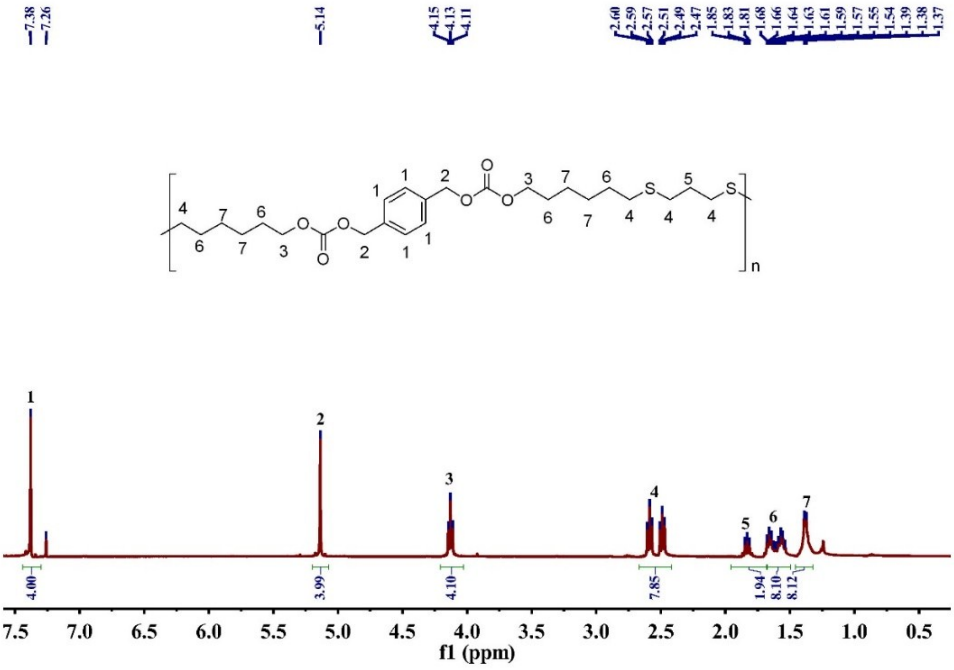


Figure S32. ^{1}H NMR spectrum of **P3a-2**

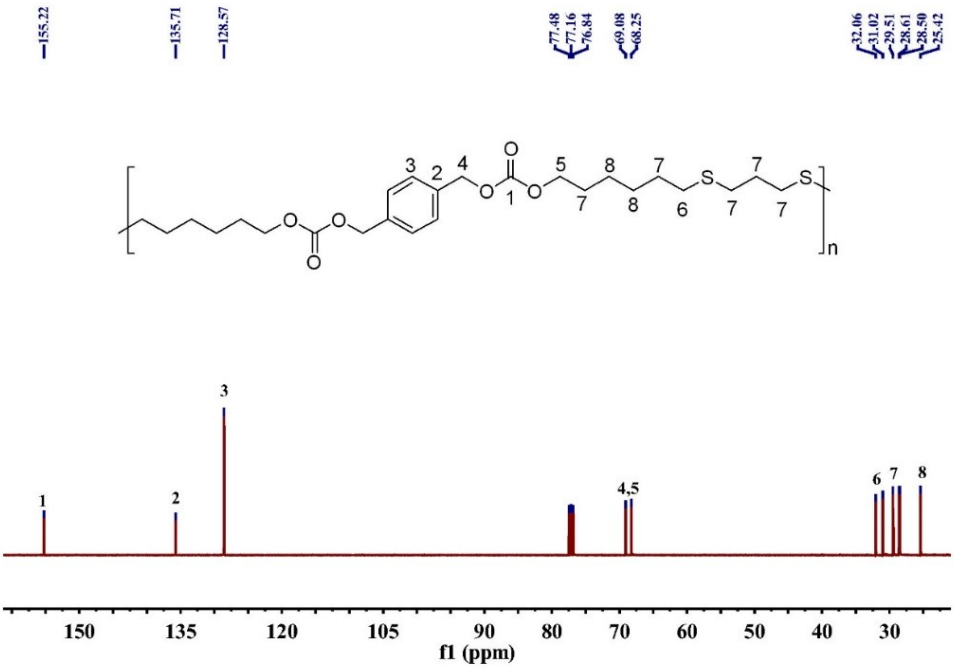
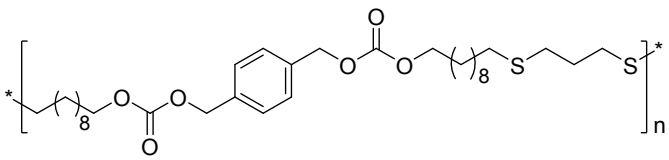


Figure S33. ^{13}C NMR spectrum of **P3a-2**



poly-decyl (4-(((((12-((3-mercaptopropyl)thio)dodecyl)oxy) carbonyl)oxy)methyl)benzyl) carbonate

Product **P3a-3**: White solid (yield: 84.7%).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.14 (d, J = 2.5 Hz, 4H), 4.12 (dd, J = 8.8, 4.6 Hz, 4H), 2.67-2.40 (m, 8H), 1.89-1.77 (m, 2H), 1.75-1.45 (m, 8H), 1.30 (d, J = 31.7 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.2, 135.7, 128.6, 77.5, 77.2, 76.8, 69.0, 68.4, 32.2, 31.0, 29.7, 29.5, 29.3, 29.2, 29.0, 28.7, 25.7. IR: υ_{max} 2920, 2849, 1747, 1469-1369, 1257, 936-717, 605 cm^{-1}.

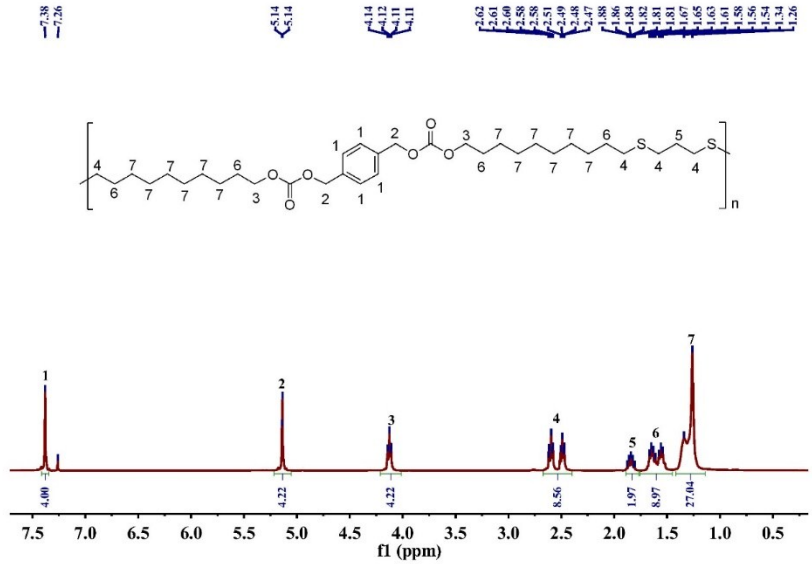


Figure S34. ^{1}H NMR spectrum of **P3a-3**

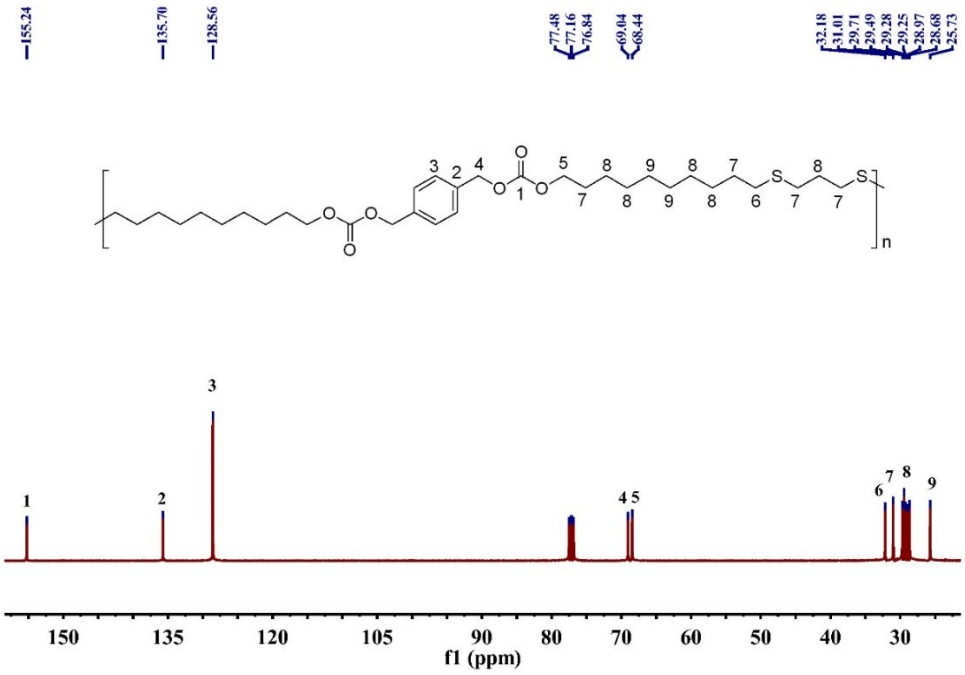
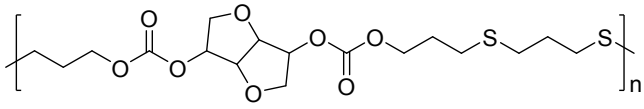


Figure S35. ^{13}C NMR spectrum of **P3a-3**



poly-hexahydrofuro[3,2-*b*]furan-3,6-diyl (3-((3-mercaptopropyl)thio)propyl) propyl bis(carbonate)

Product **P3b**. White solid (yield: 92.7%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.07 (dd, J = 8.9, 4.0 Hz, 2H), 4.87 (t, J = 5.0 Hz, 1H), 4.53 (d, J = 4.7 Hz, 1H), 4.25 (q, J = 6.3 Hz, 4H), 4.12-3.80 (m, 4H), 2.60 (t, J = 7.2 Hz, 8H), 1.90 (ddd, J = 41.1, 10.4, 5.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.3, 85.9, 81.0, 77.5, 77.2, 76.8, 73.3, 70.5, 67.0, 30.9, 29.1, 28.6, 28.5, 28.2. IR: υ_{max} 2956-2878, 1750, 1459-1342, 1254, 1098-863, 788 cm^{-1}.

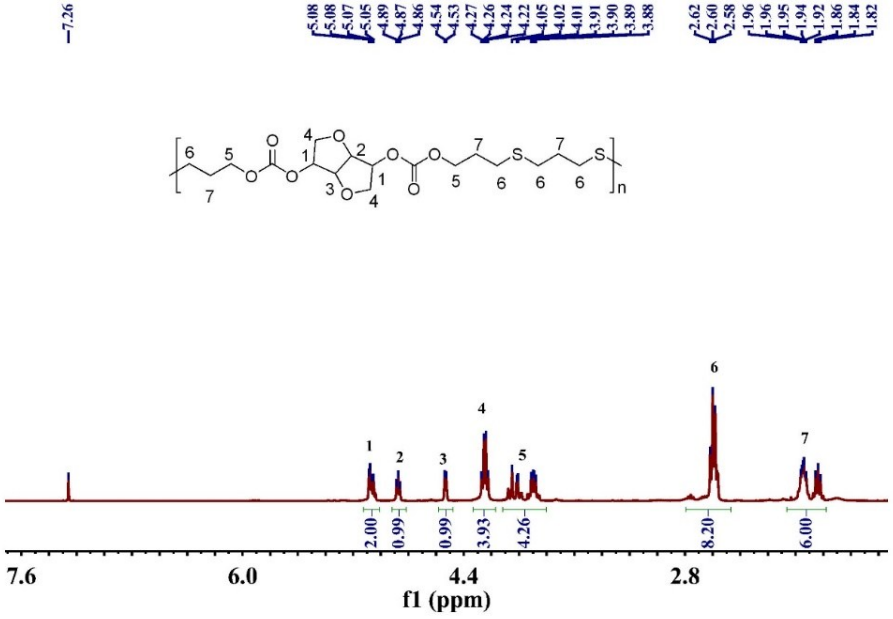


Figure S36**.** ^{1}H NMR spectrum of **P3b**

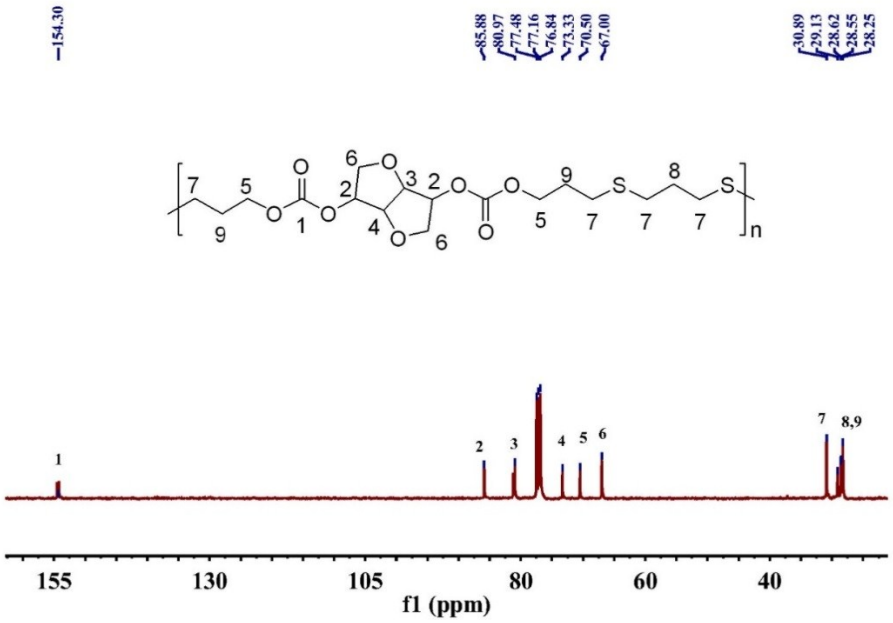
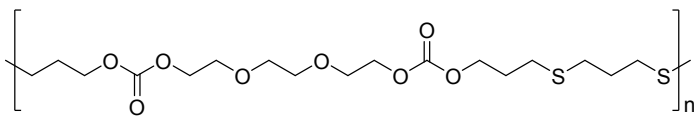


Figure S37**.** ^{13}C NMR spectrum of **P3b**



poly-18-mercapto-10-oxo-3,6,9,11-tetraoxa-15-thiaoctadecyl propyl carbonate

Product **P3c**. White solid (yield: 87.9%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.34-4.16 (m, 8H), 3.76-3.58 (m, 8H), 2.69-2.46 (m, 8H), 2.00-1.76 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.1, 77.5, 77.2, 76.8, 70.6, 69.0, 67.0, 66.6, 30.8, 29.1, 28.6, 28.2. IR: υ_{max} 2951-2855, 1748, 1459, 1399, 1259, 1124-740, 666 cm^{-1}.

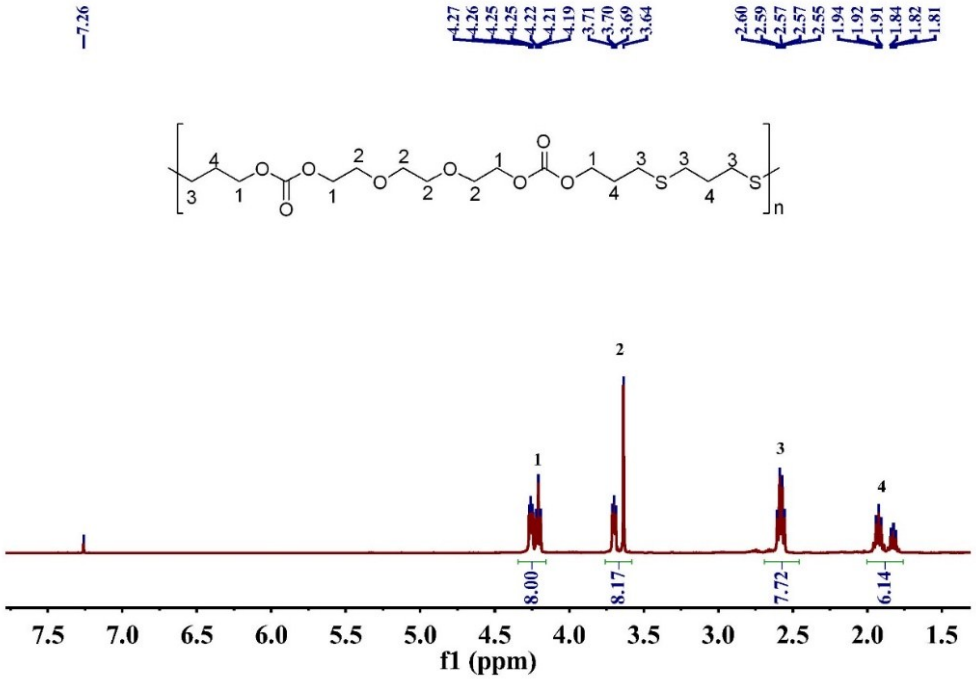


Figure S38. ^{1}H NMR spectrum of **P3c**

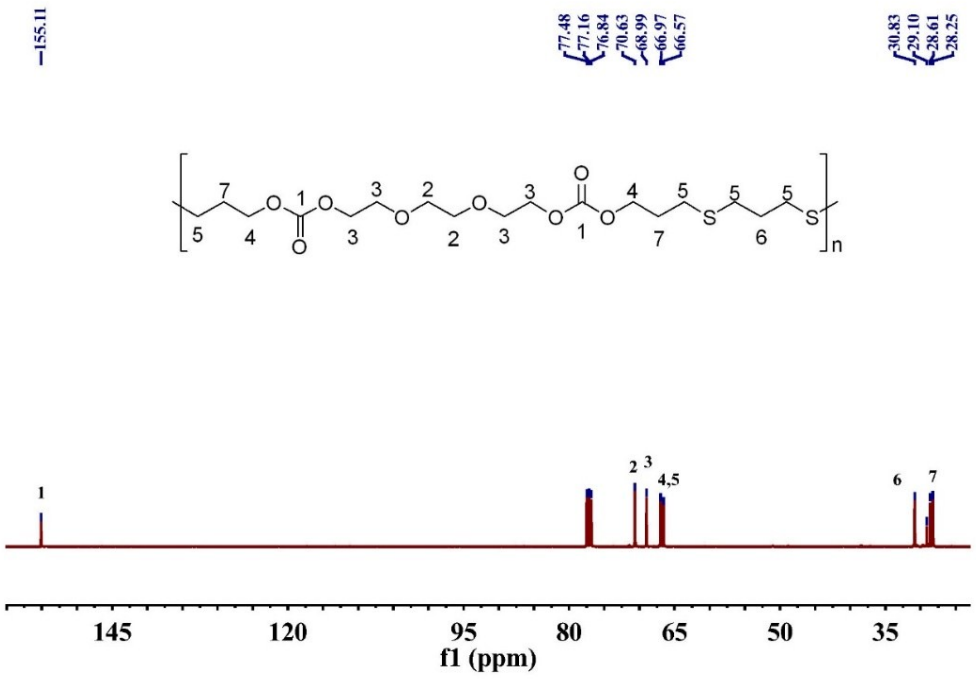
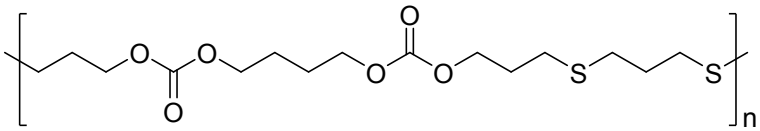


Figure S39. ^{13}C NMR spectrum of **P3c**



poly-butane-1,4-diyl (3-((3-mercaptopropyl)thio)propyl) propyl bis(carbonate)

Product **P3d**. White solid (yield: 89.3%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.20 (dd, J = 18.6, 12.4 Hz, 8H), 2.60 (dd, J = 14.7, 7.4 Hz, 8H), 2.03-1.69 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.2, 77.5, 77.2, 76.8, 67.4, 66.5, 30.9, 29.1, 28.7, 28.3, 25.2. IR: υ_{max} 2965-2855, 1748, 1578, 1459, 1403, 1255, 1054-893, 788 cm^{-1}.

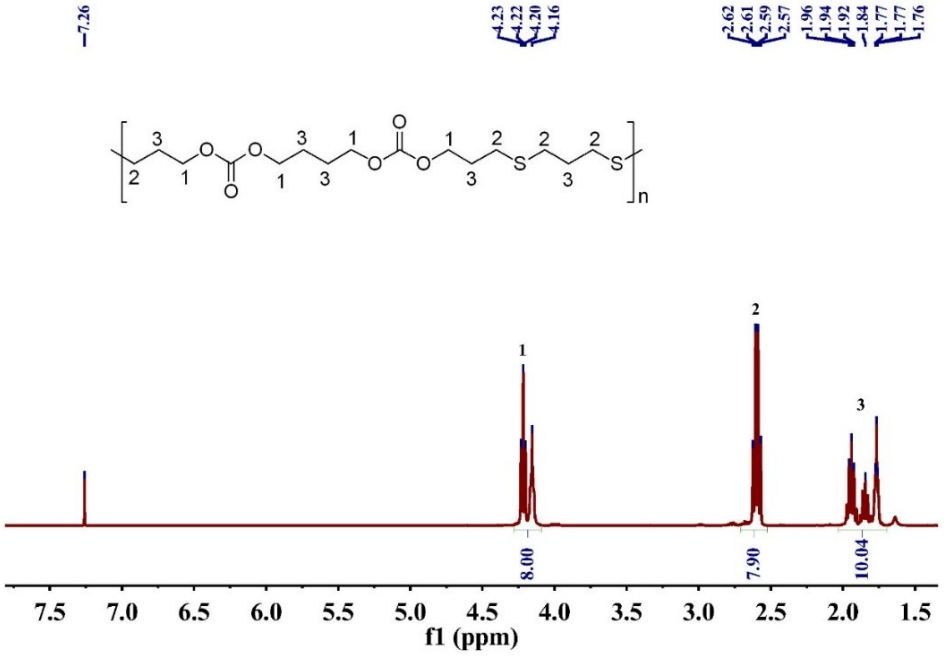


Figure S40. ^{1}H NMR spectrum of **P3d**

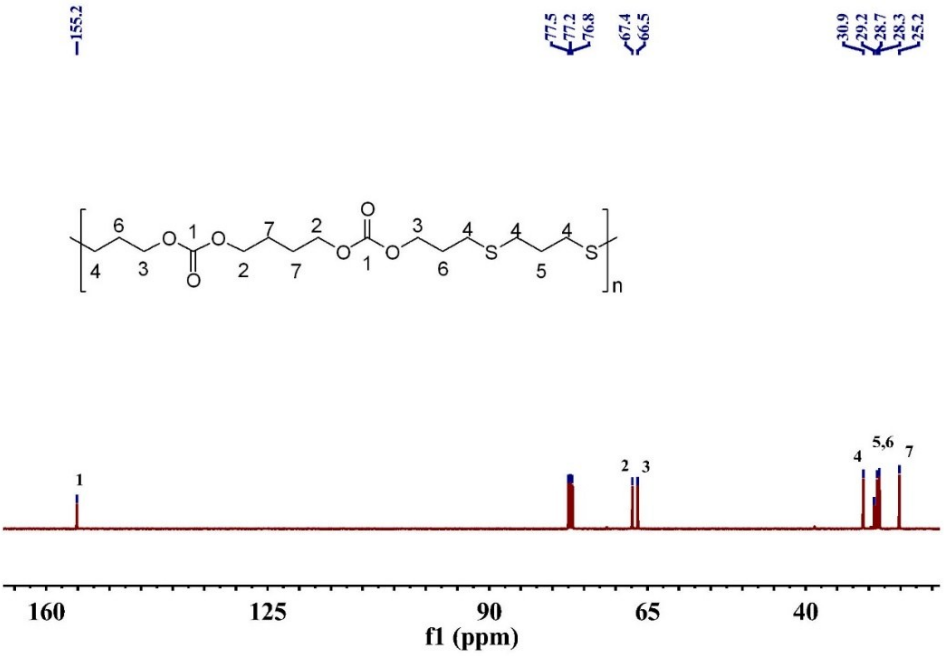
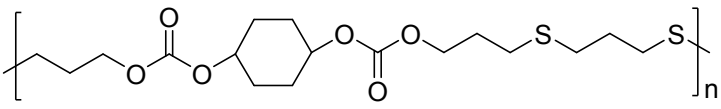


Figure S41. ^{13}C NMR spectrum of **P3d**



poly-cyclohexane-1,4-diyl (3-((3-mercaptopropyl)thio)propyl) propyl bis(carbonate)

Product **P3e**. White solid (yield: 91.5%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.69 (d, J = 4.3 Hz, 2H), 4.21 (t, J = 6.3 Hz, 4H), 2.60 (q, J = 7.3 Hz, 8H), 2.05-1.61 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.4, 77.3, 77.0, 76.6, 74.5, 73.6, 66.2, 30.7, 28.9, 28.5, 28.2 27.4, 27.0. IR: υ_{max} 2956-2846, 1741, 1459-1321, 1259, 1015, 937, 749 cm^{-1}.

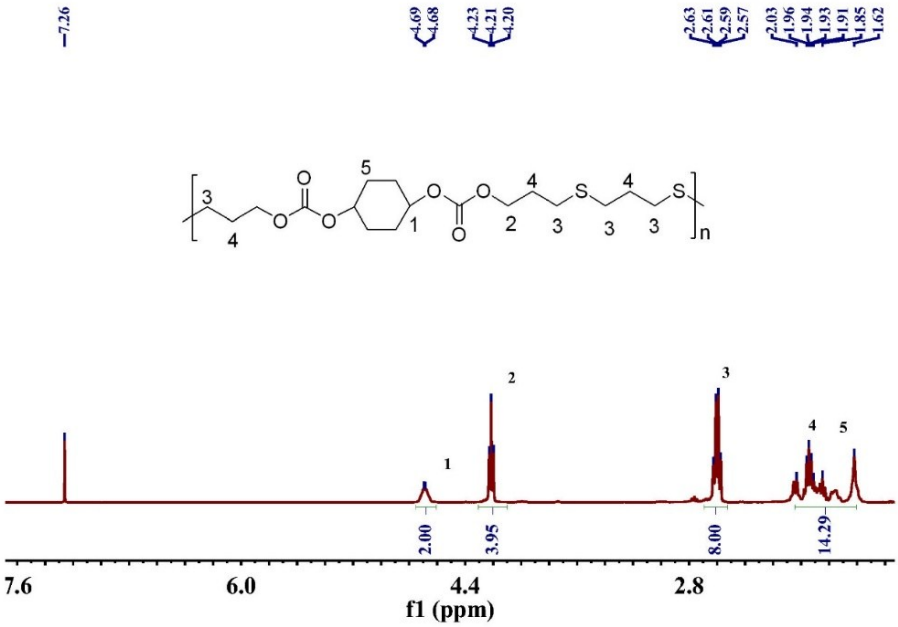


Figure S42. ^{1}H NMR spectrum of **P3e**

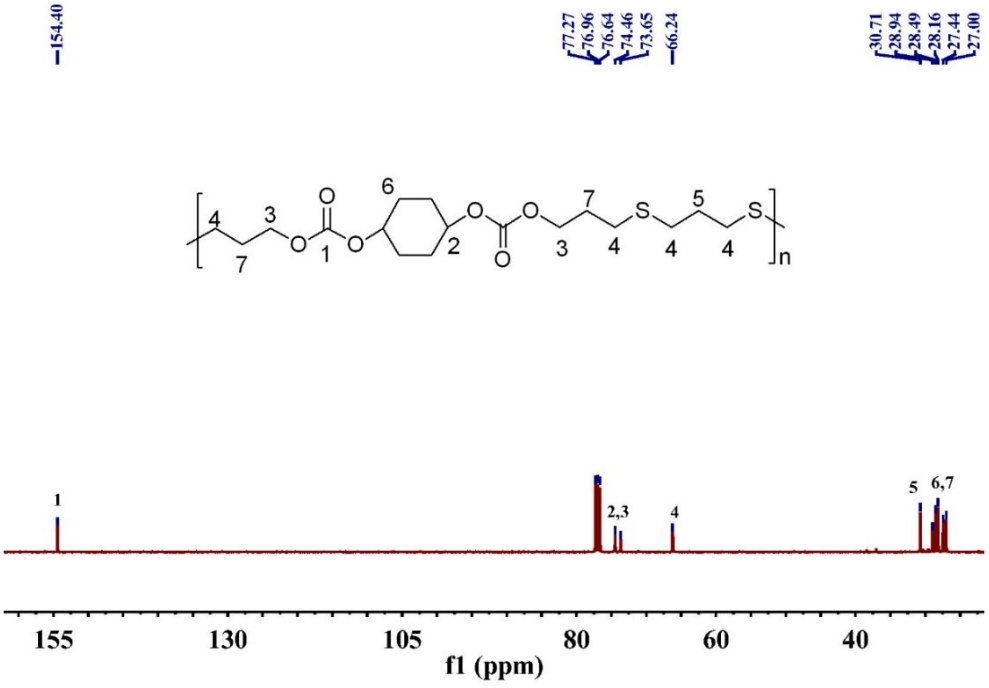
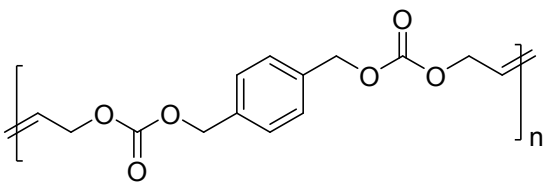


Figure S43. ^{13}C NMR spectrum of **P3e**



Product **P4a-1**. Dark green solid (yield: 60.2%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.89 (s, 2H), 5.15 (s, 4H), 4.63 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.8, 135.6, 131.5, 128.6, 77.5, 77.2, 76.8, 69.4, 67.2. IR: υ_{max} 2960, 1740, 1450, 1391, 1235, 1081, 931, 891, 837, 790, 757 cm^{-1}.

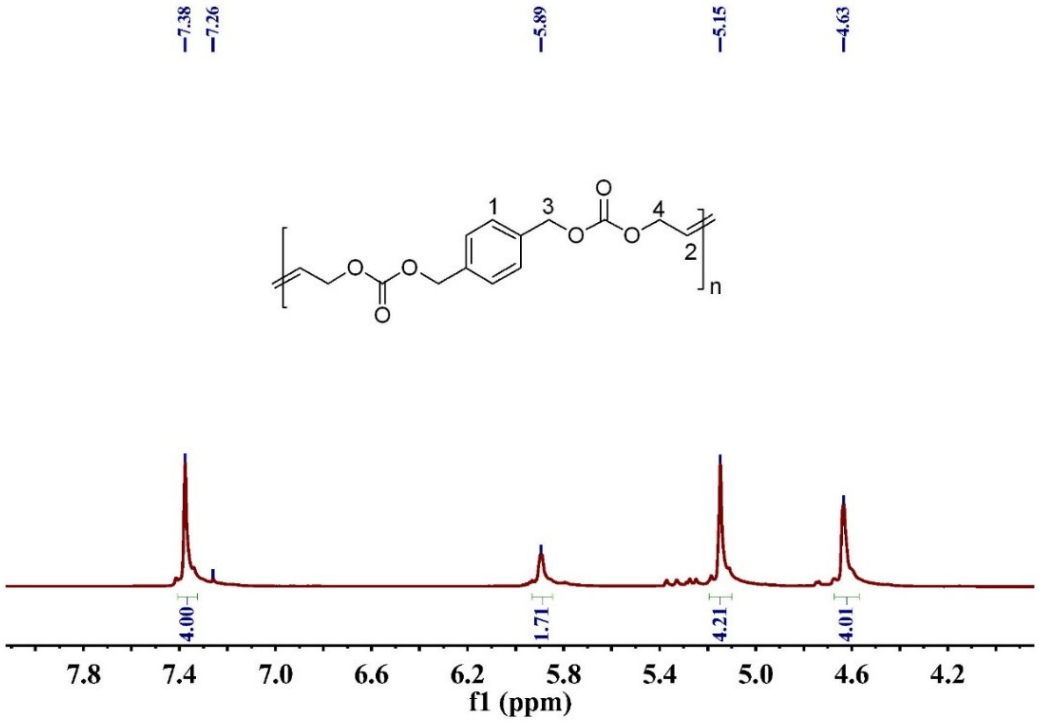


Figure S44**.** ^{1}H NMR spectrum of **P4a-1**

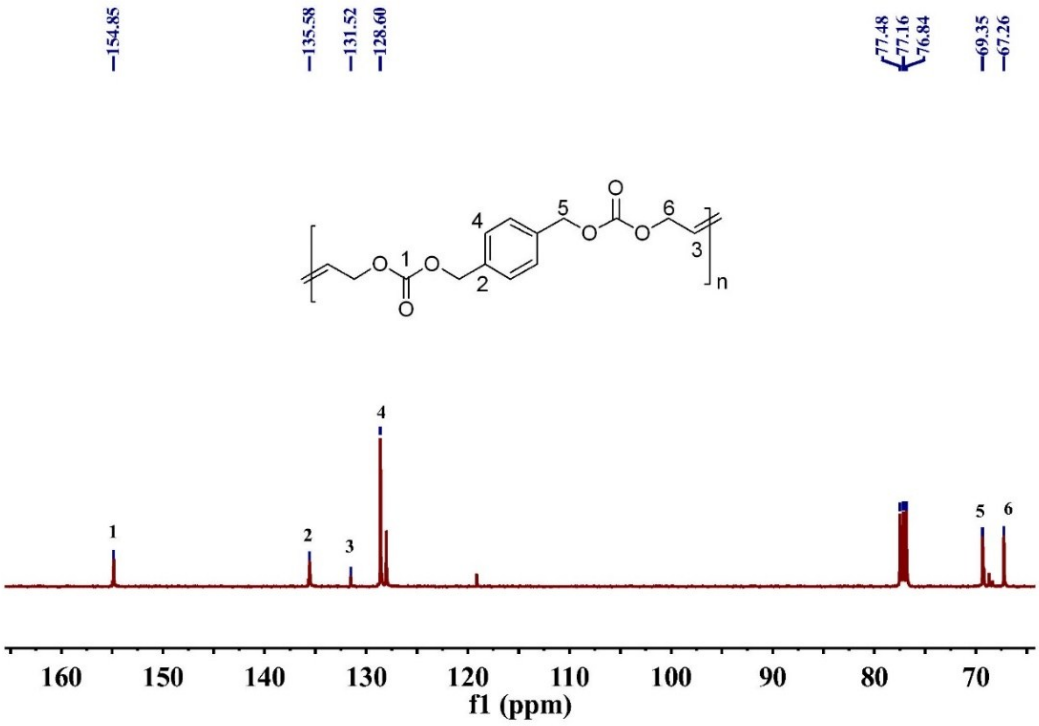
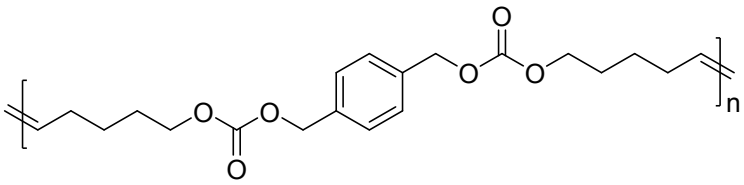


Figure S45**.** ^{13}C NMR spectrum of **P4a-1**



Product **P4a-2**. Dark green solid (yield: 71.6%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 (s, 4H), 5.44-5.29 (m, 2H), 5.13 (s, 4H), 4.12 (t, J = 6.6 Hz, 4H), 2.21-1.89 (m, 4H), 1.83-1.19 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.4, 135.8, 130.4, 128.7, 77.6, 77.3, 77.0, 69.2, 68.4, 32.2, 28.3, 25.8. IR: υ_{max} 2934, 2856, 1743, 1518, 1455, 1396, 1373, 1259, 1087-968, 792 cm^{-1}.

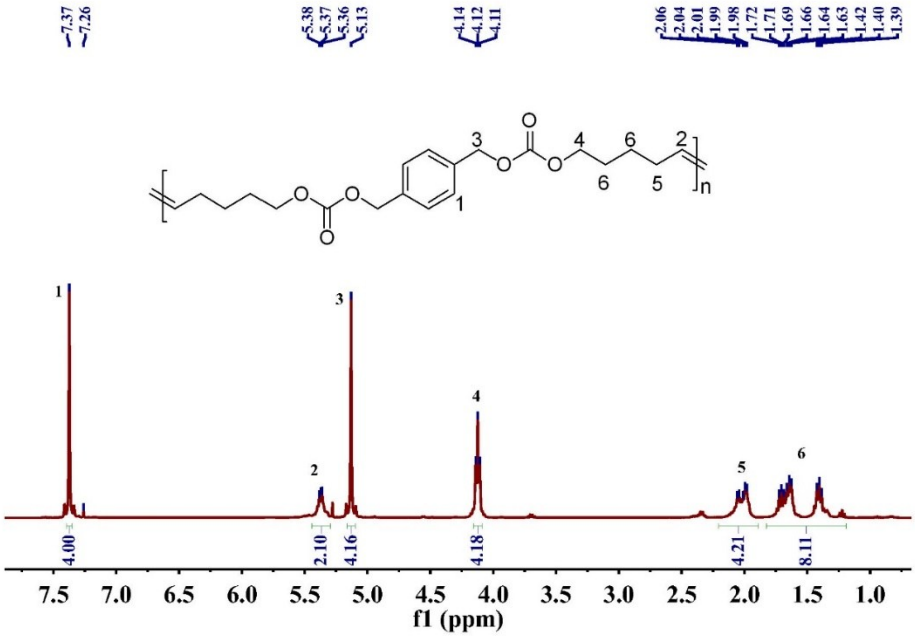


Figure S46. ^{1}H NMR spectrum of **P4a-2**

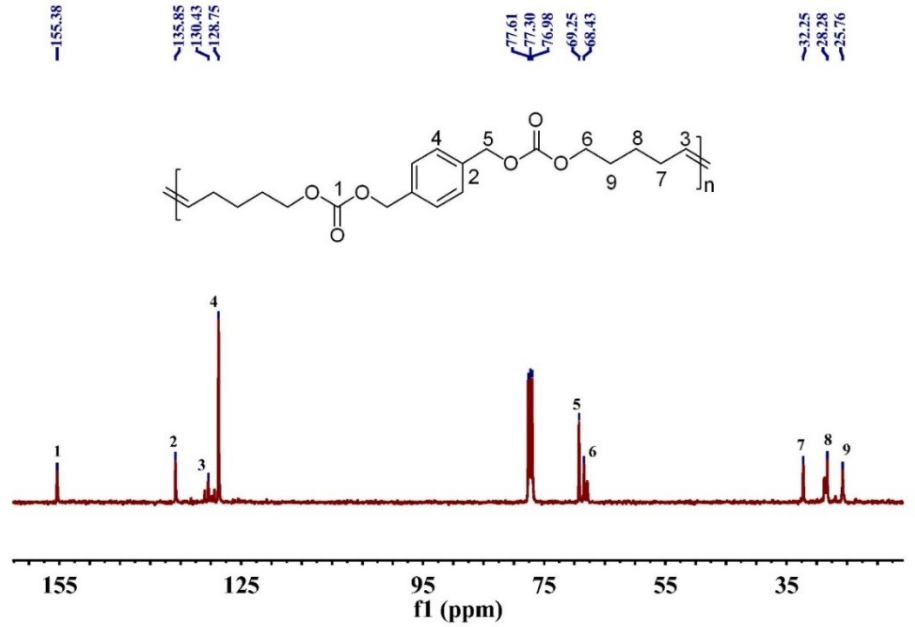
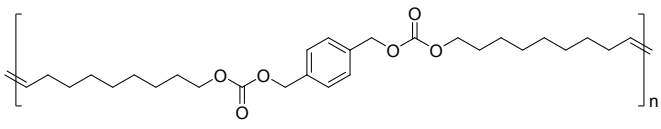


Figure S47. ^{13}C NMR spectrum of **P4a-2**



poly-1,4-phenylenebis(methylene) di(dec-9-en-1-yl) bis(carbonate)

Product **P4a-3**. Dark green solid (yield: 87.4%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (s, 4H), 5.37 (s, 2H), 5.14 (t, J = 16 Hz, 4H), 4.13 (t, J = 8 Hz, 4H), 1.95 (s, 4H), 1.60-1.69 (m, 4H), 1.25 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm)：δ 155.3, 135.7, 130.4, 128.6, 77.5, 77.2, 76.8, 69.1, 68.5, 32.7, 29.6, 29.4, 29.3, 29.2, 28.7, 25.8. IR: υ_{max} 2931, 2853, 1745, 1517, 1457, 1393, 1265, 964, 789 cm^{-1}.

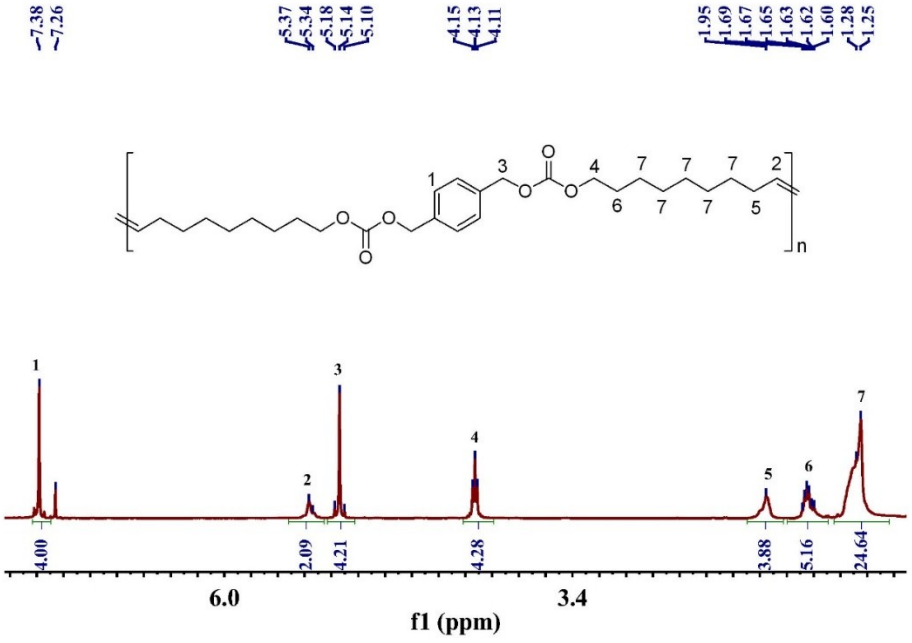


Figure S48. ^{1}H NMR spectrum of **P4a-3**

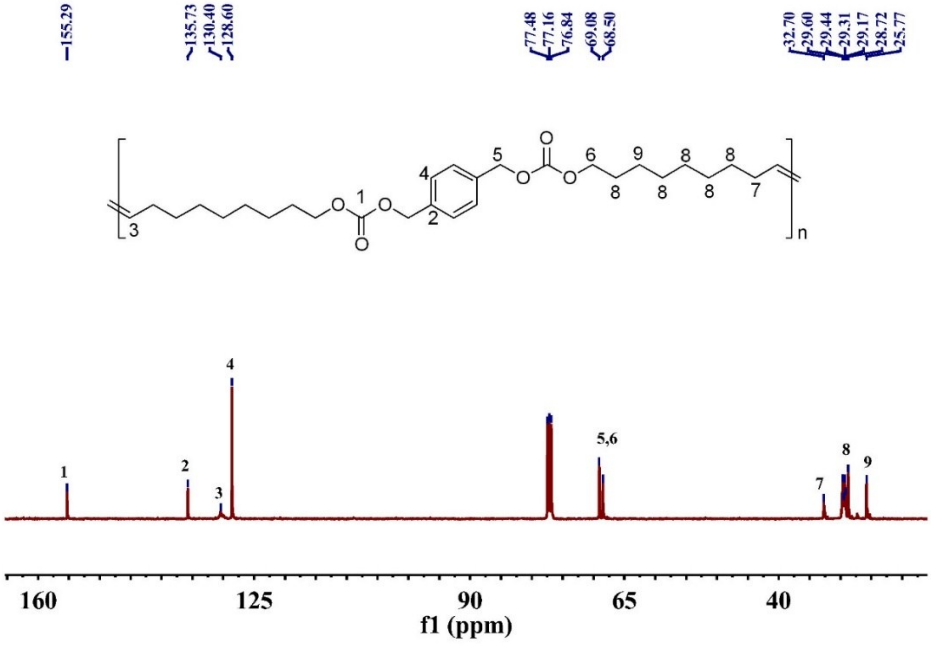
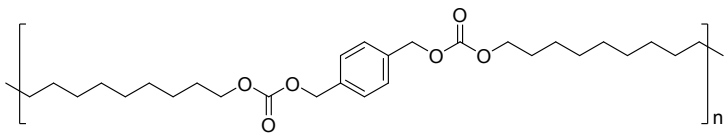


Figure S49. ^{13}C NMR spectra of **P4a-3**



Product **PH4a-3**. Dark green solid (yield: 98%). ^{1}H NMR (400 MHz, CDCl3, ppm): δ 7.38 (s, 4H), 5.14 (d, J = 3.2 Hz, 4H), 4.13 (dd, J = 8.3, 5.1 Hz, 4H), 1.73-1.56 (m, 5H), 1.24 (s, 28H). ^{13}C NMR (100 MHz, CDCl3, ppm): δ 155.3, 135.8, 128.6, 77.5, 77.2, 76.8, 69.1, 68.5, 29.8, 29.7, 29.6, 29.3, 28.7, 25.8. IR: υ_{max} 2921, 2851, 1745, 1456, 1397, 1375, 1257, 1082, 953, 792 cm^{-1}.

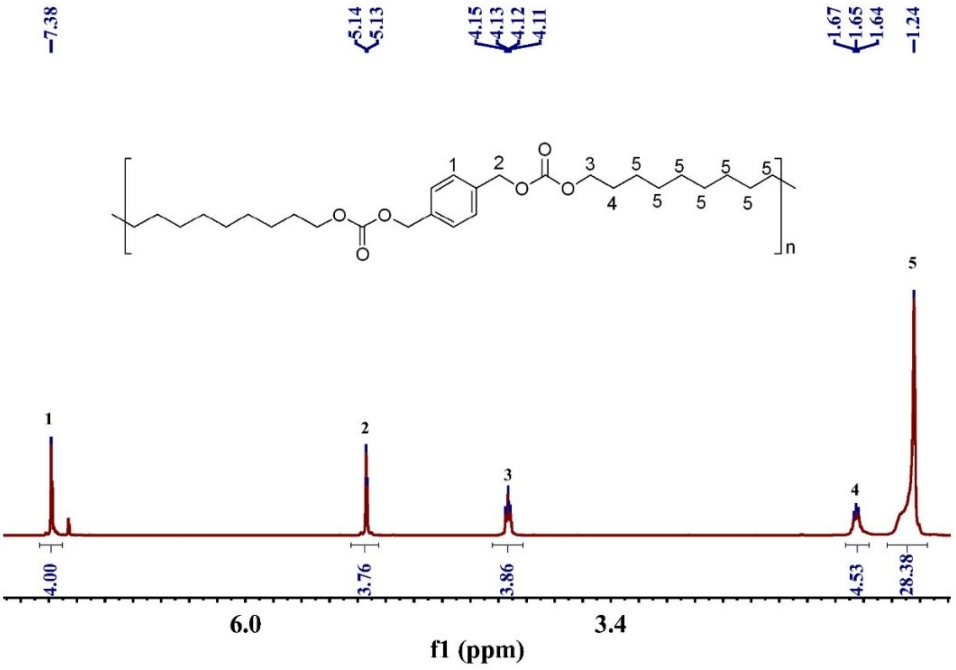


Figure S50. ^{1}H NMR spectrum of **PH4a-3**

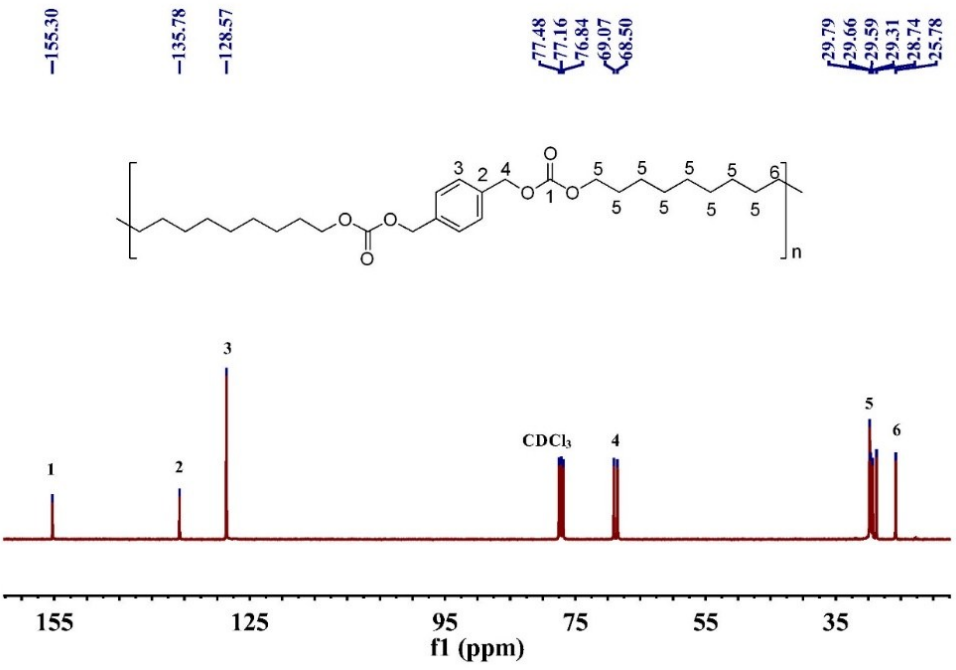


Figure S51. ^{13}C NMR spectrum of **PH4a-3**

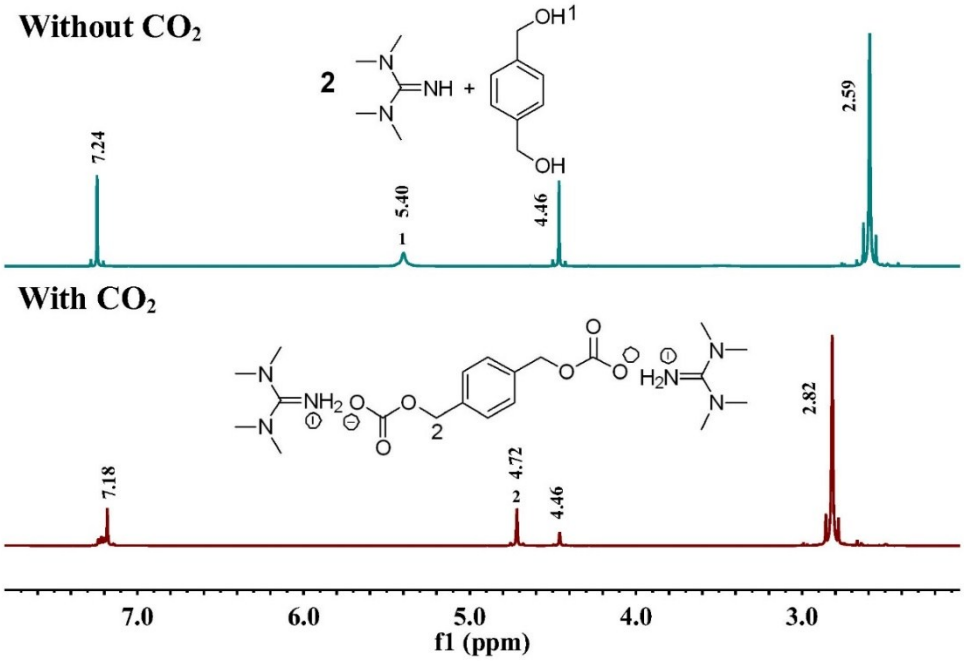


Figure S52. Comparative ^{1}H NMR spectra of TMG–BDM (2:1, molar ratio) in d_6-DMSO without and with CO_2 addition. A new signal assigned to the carbonate carbon appeared at δ = 156.2 ppm after CO_2 addition, which indicated the formation of $2[TMGH]^{+}[O_2COCH_2C_6H_4CH_2OCO_2]^{2-}$.

3.2 FTIR spectra of monomers and polymers

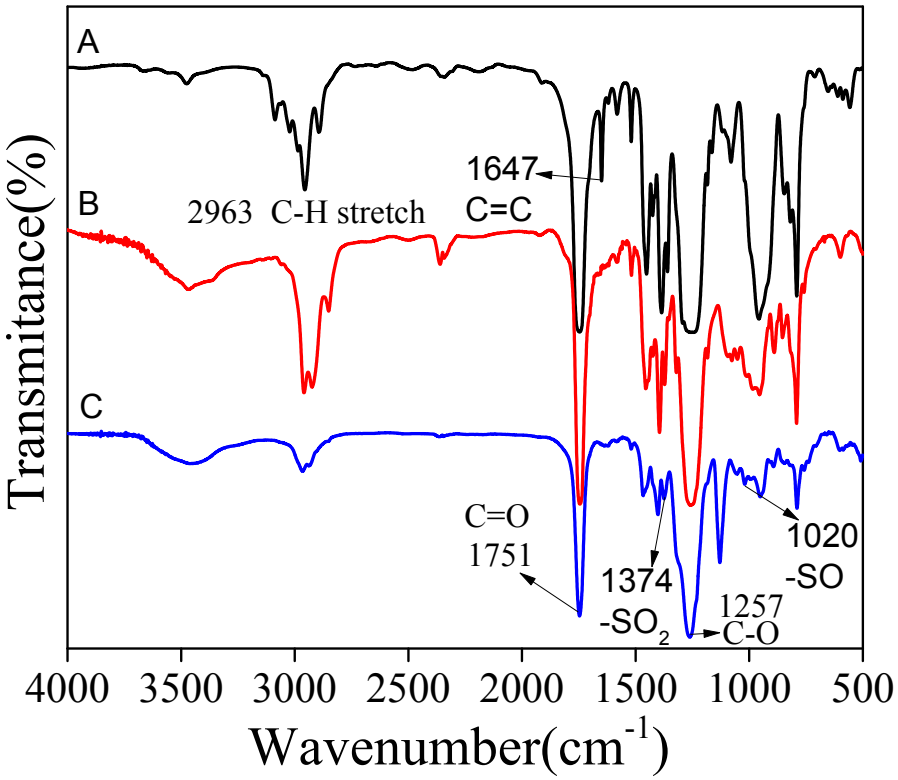


Figure S53. FT-IR spectra of **2a-1**(A), **P3a-1** (B) and **PO3a-1**(C).

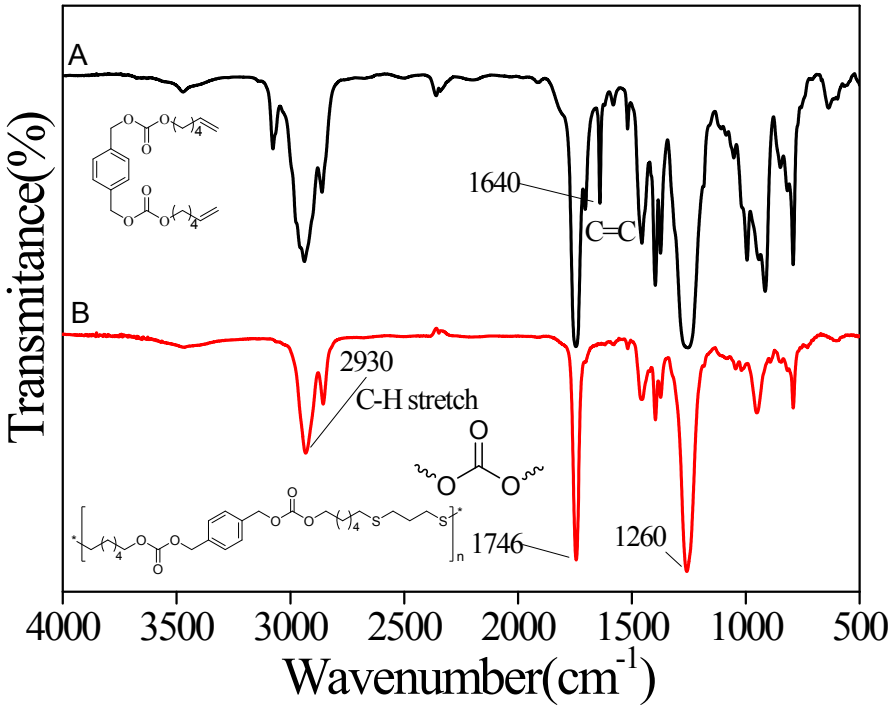


Figure S54. FT-IR spectra of **2a-2** (A) and **P3a-2** (B)

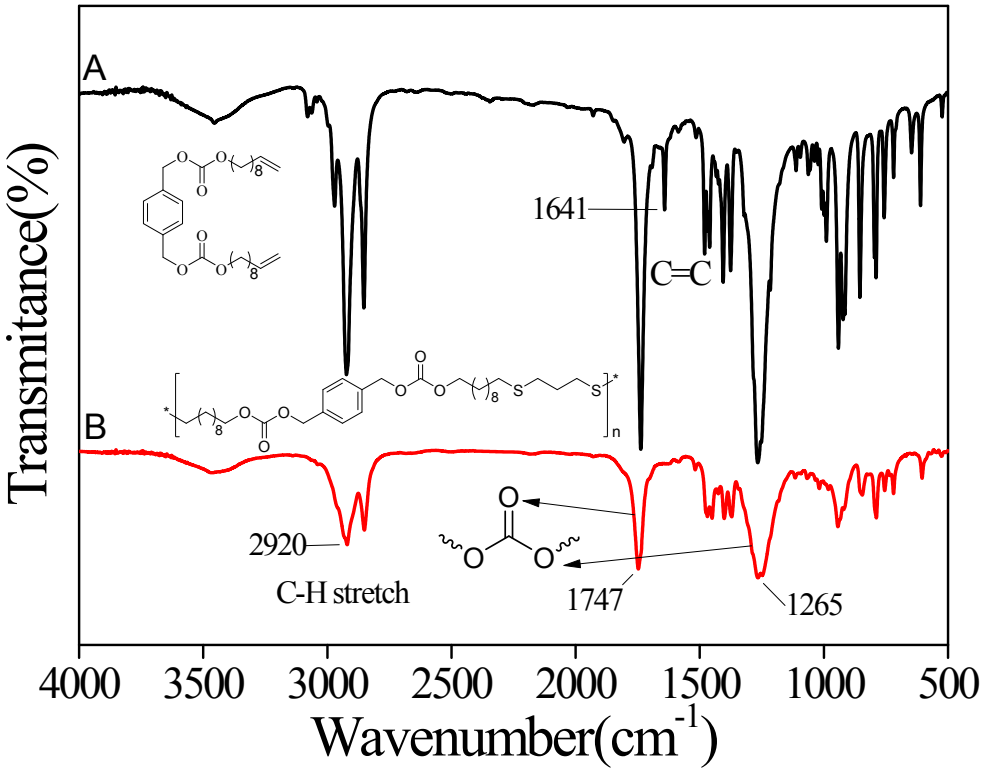


Figure S55. FT-IR spectra of **2a-3** (A) and **P3a-3** (B)

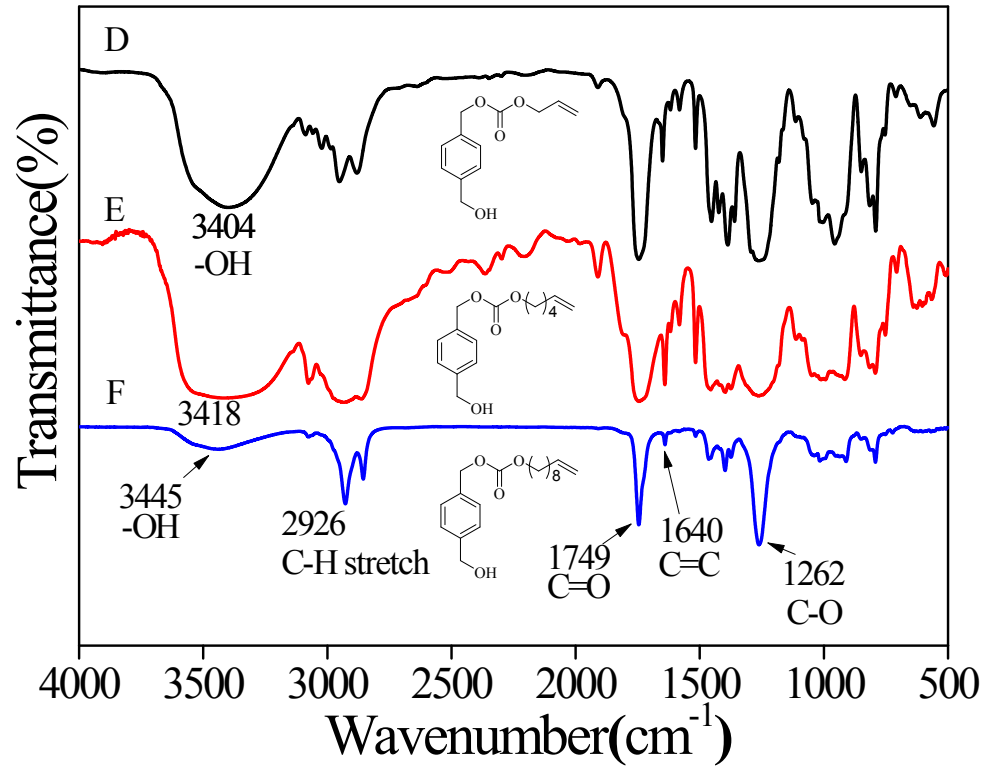


Figure S56. FT-IR spectra of **2a-1'** (D), **2a-2'** (E) and **2a-3'** (F)

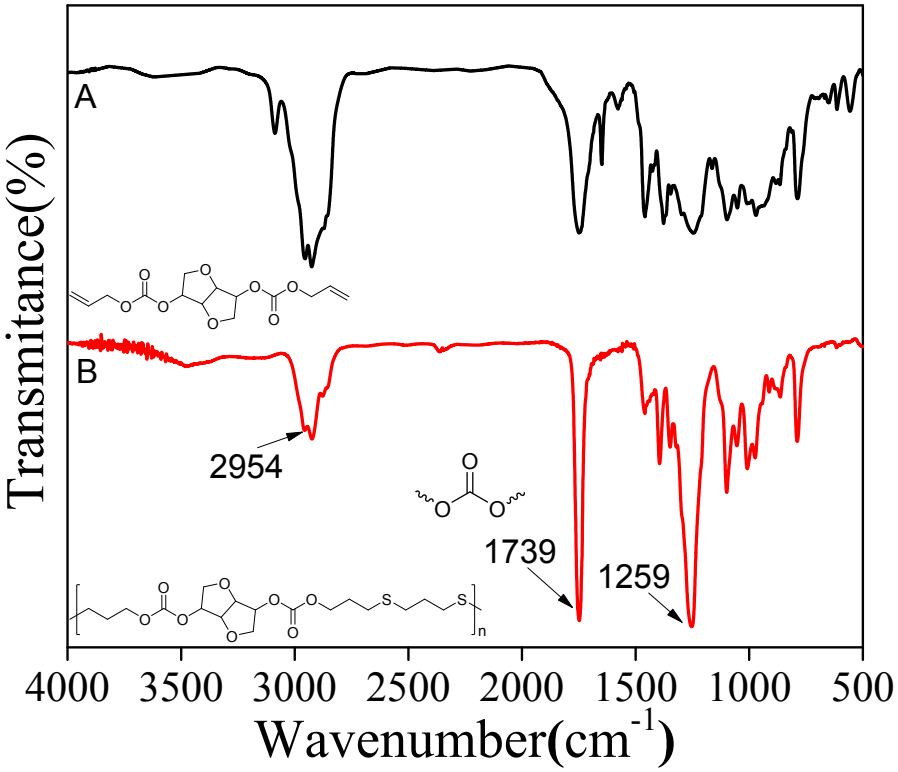


Figure S57. FT-IR spectra of **2b** (A) and **P3b** (B)

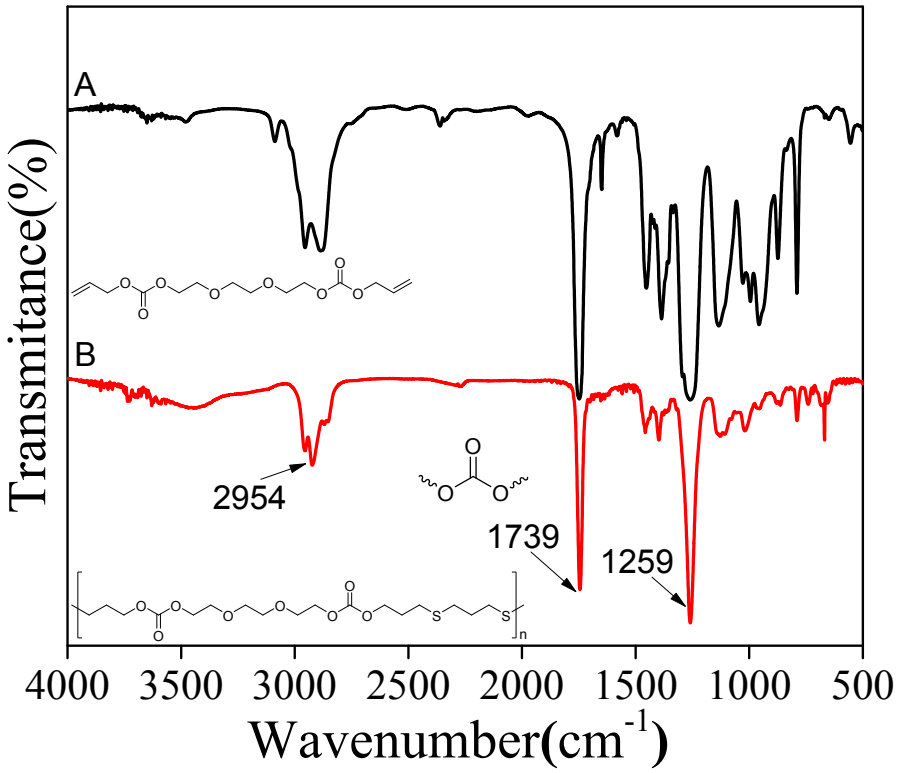


Figure S58. FT-IR spectra of **2c** (A) and **P3c** (B)

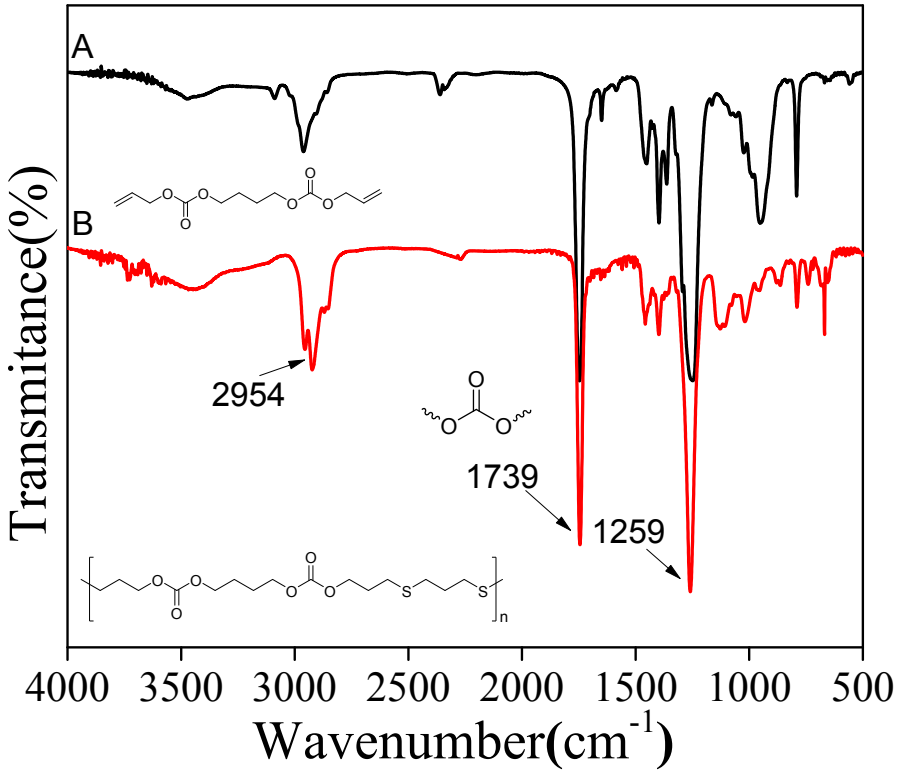


Figure S59. FT-IR spectra of **2d** (A) and **P3d** (B)

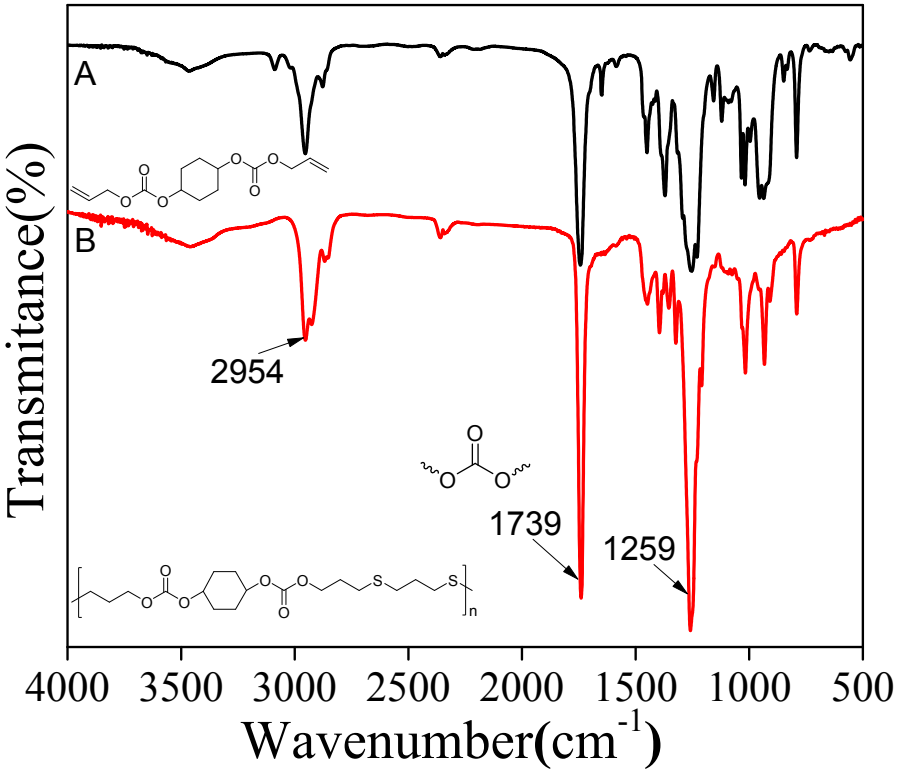


Figure S60. FT-IR spectra of **2e** (A) and **P3e** (B)

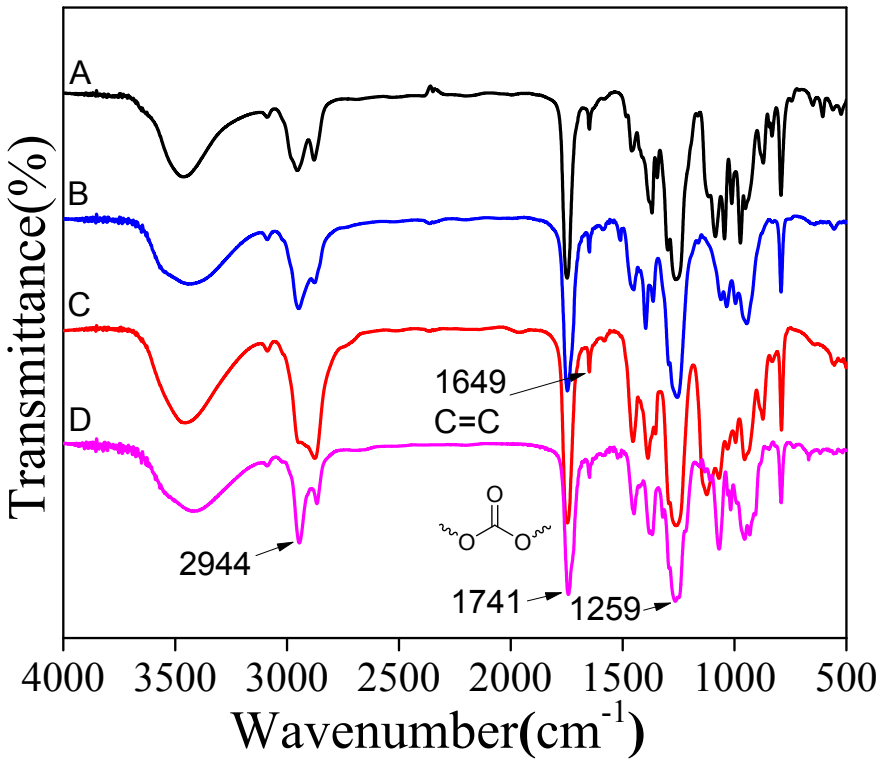


Figure S61. FT-IR spectra of **2b'** (A), **2c'** (B), **2d'** (C) and **2e'** (D)

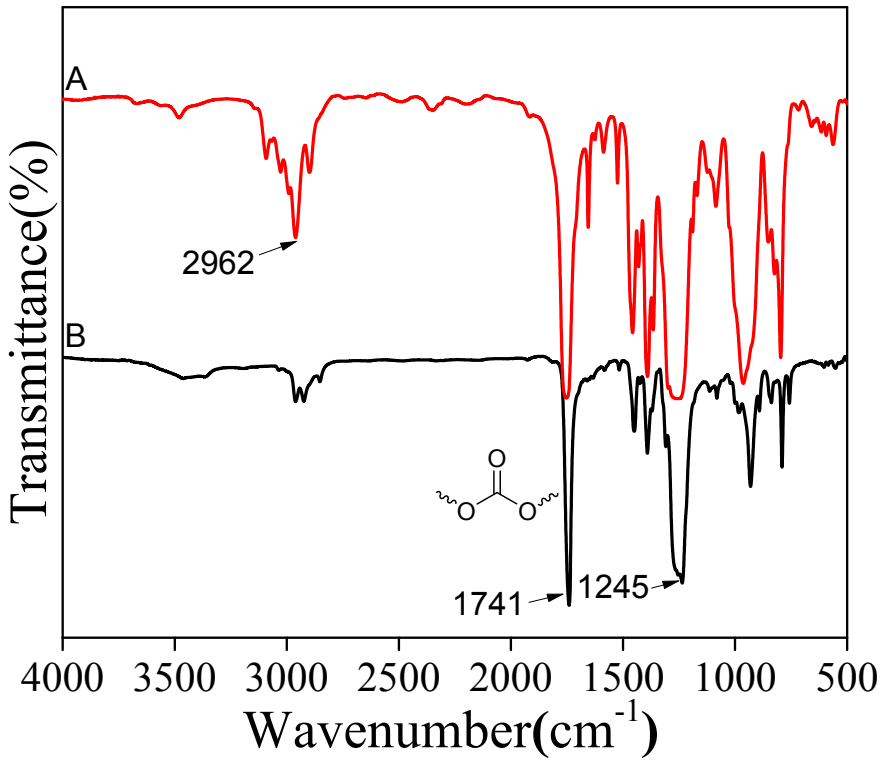


Figure S62. FT-IR spectra of **2a-1** (A) and **P4a-1** (B)

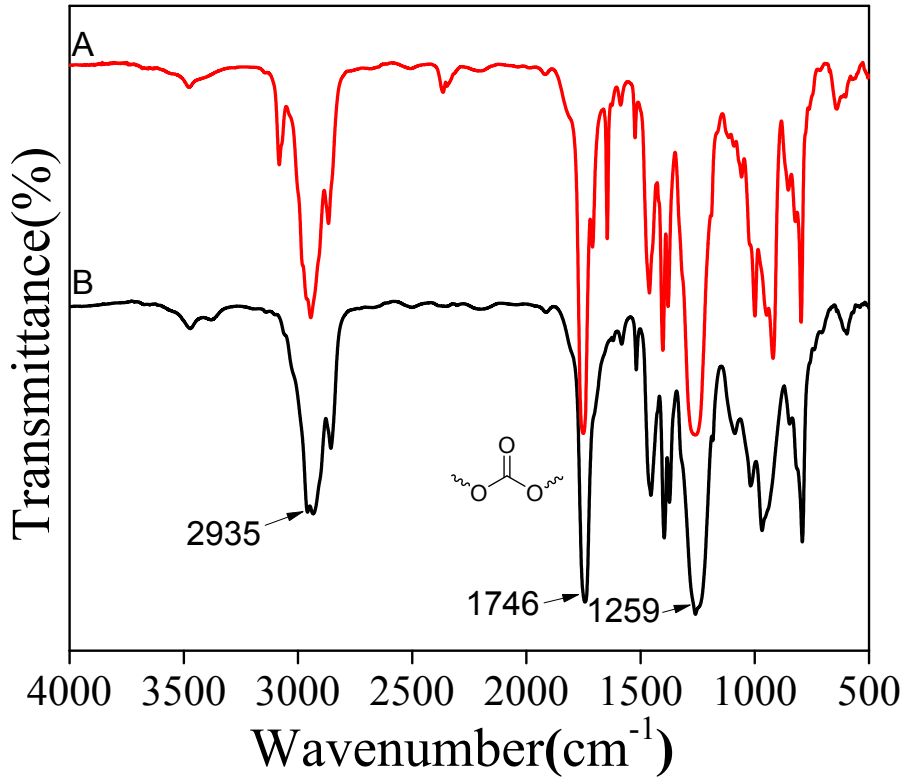


Figure S63**.** FT-IR spectra of **2a-2** (A) and **P4a-2** (B)

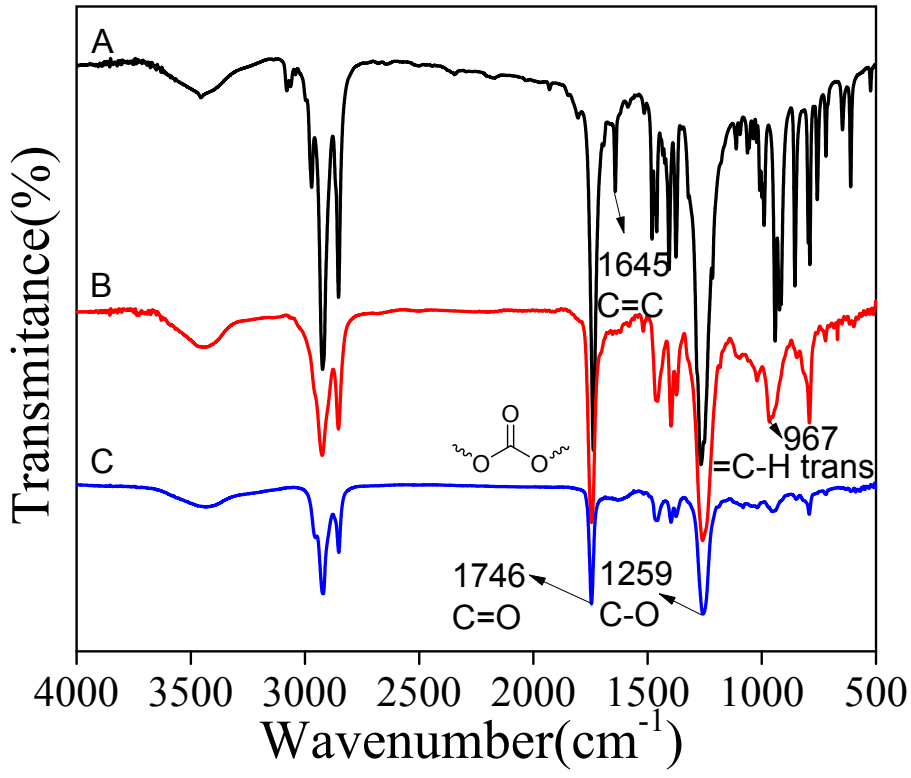


Figure S64. FT-IR spectra of **2a-3** (A), **P4a-3** (B) and **PH4a-3** (C).

3.3. TGA and DSC curves of polymers

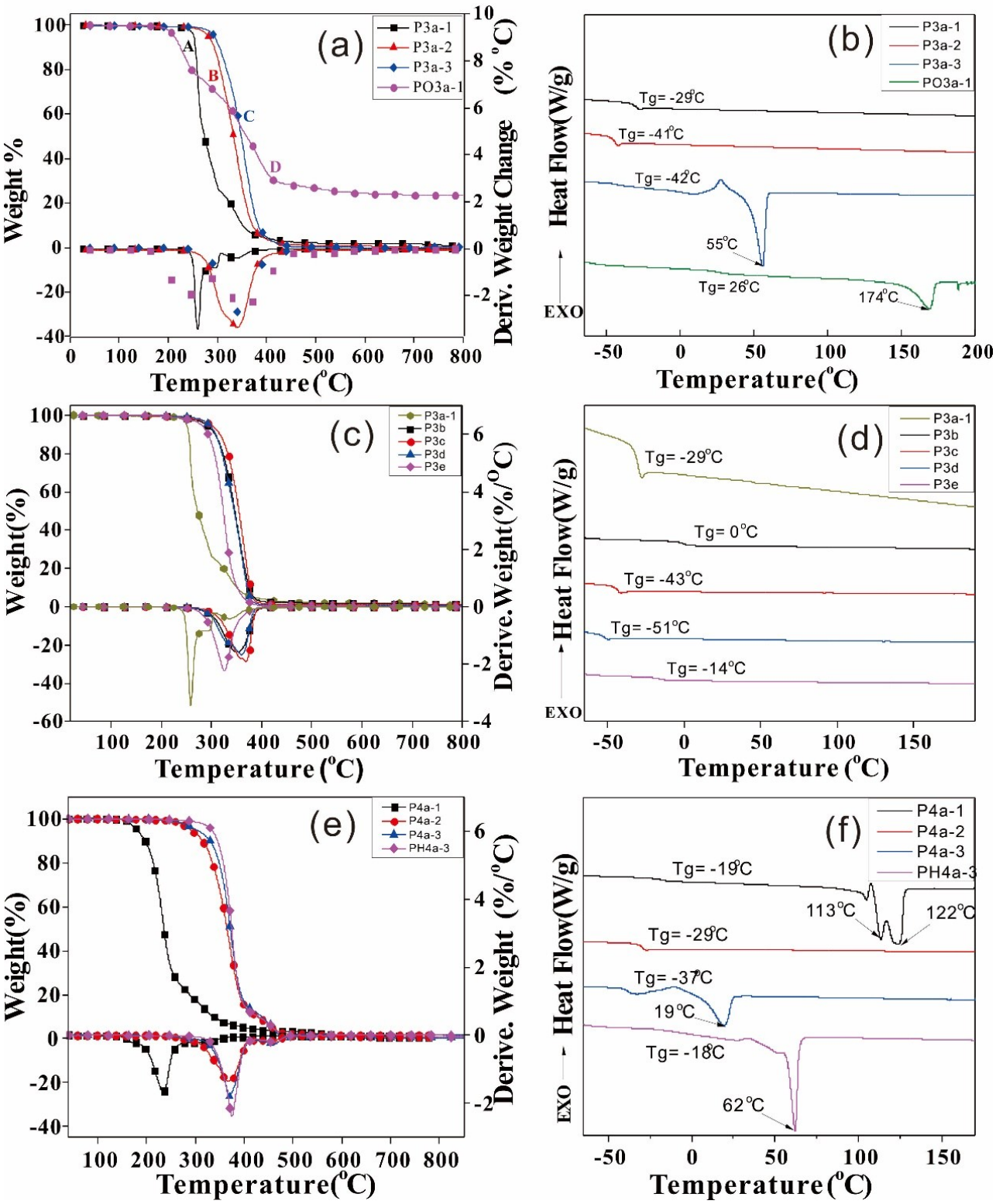


Figure S65. DSC and TGA traces of the polymers.

3.4. XRD plots of the polymers

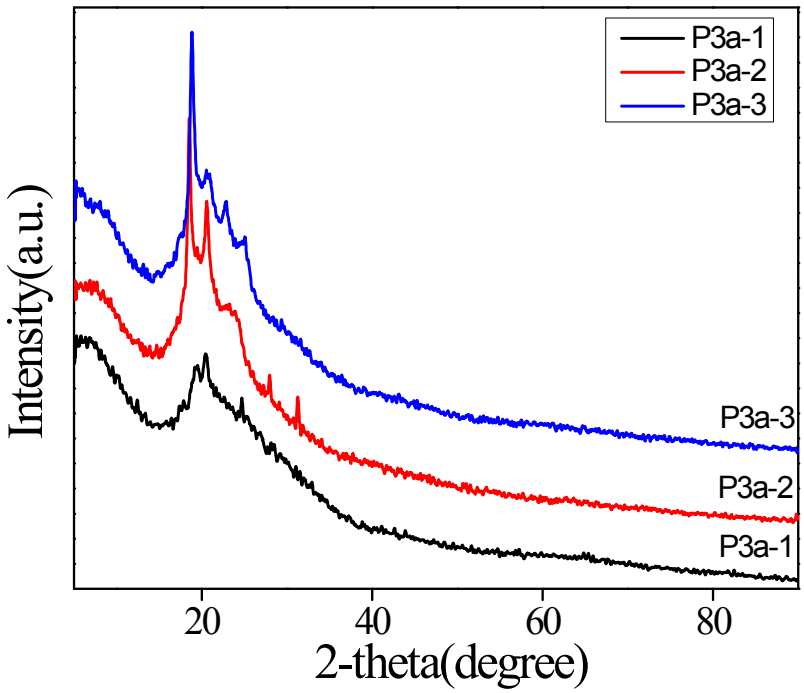


Figure S66. Comparative XRD patterns of polycarbonate with different chain lengths from click chemistry

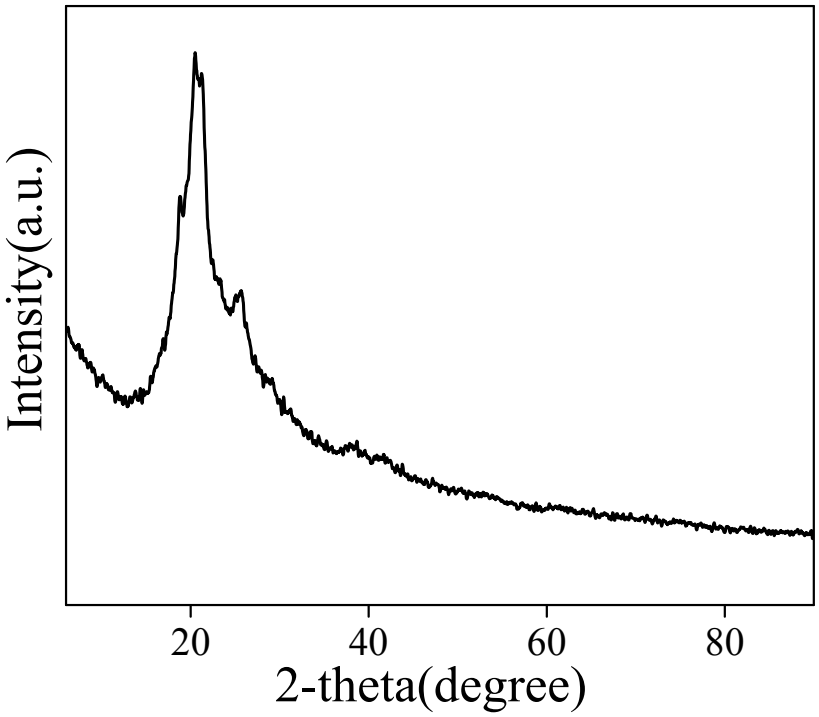


Figure S67. The XRD curve of **PO3a-1**

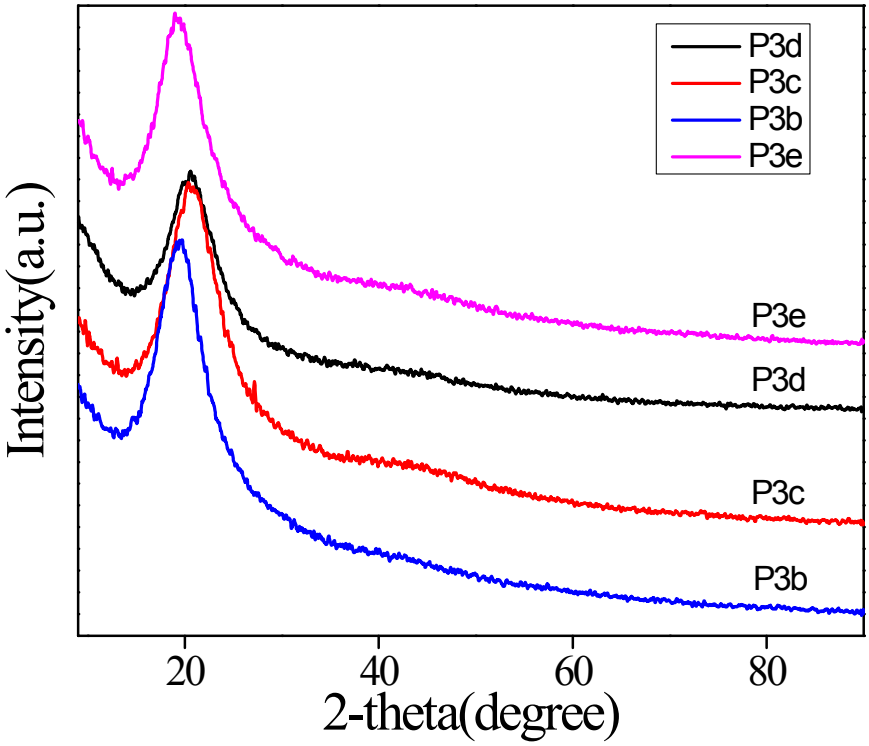


Figure S68. Comparative XRD patterns of polycarbonate from different diols from click chemistry

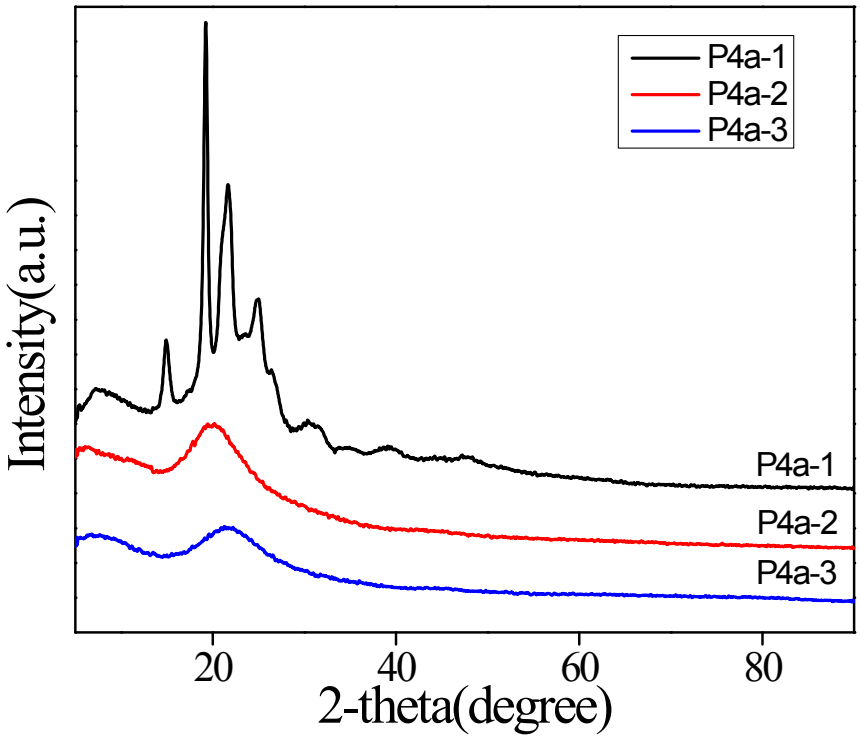


Figure S69. Comparative XRD patterns of polycarbonate with different chain lengths from ADMET polymerization

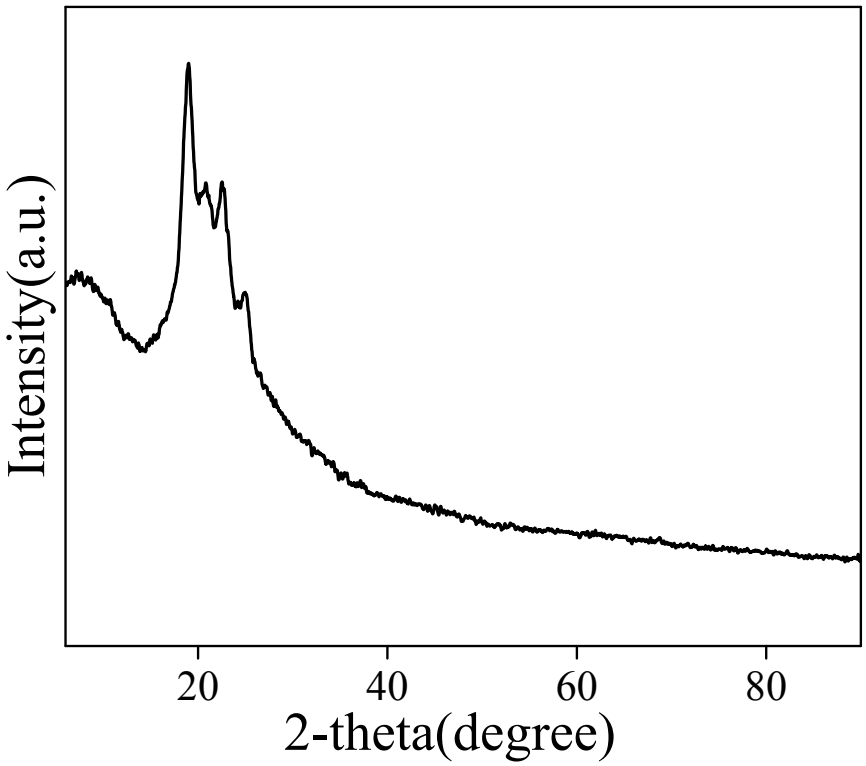


Figure S70. The XRD curve of **PH4a-3**

3.5 GPC curves of polycarbonates

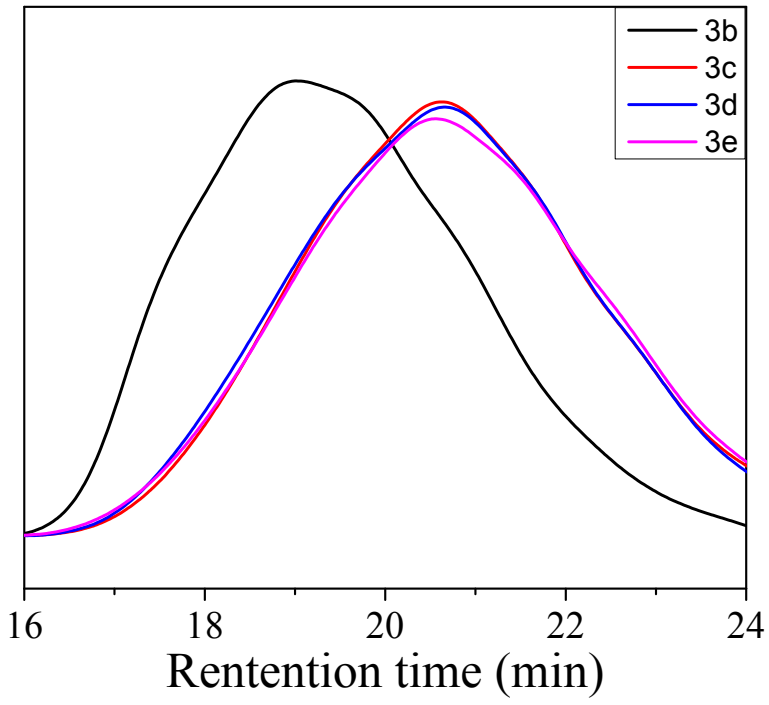


Figure S71. GPC analysis of **P3b**, **P3c**, **P3d** and **P3e**

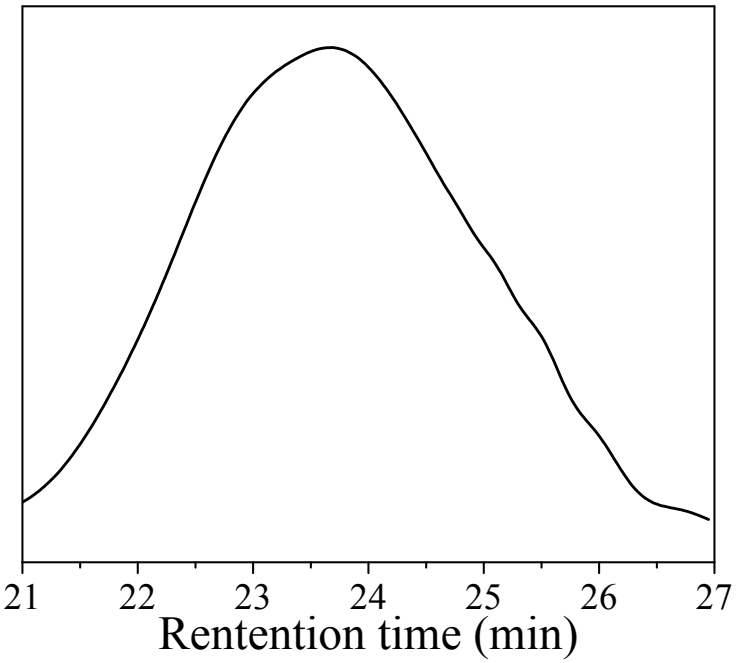


Figure S72. GPC analysis of **P4a-2**

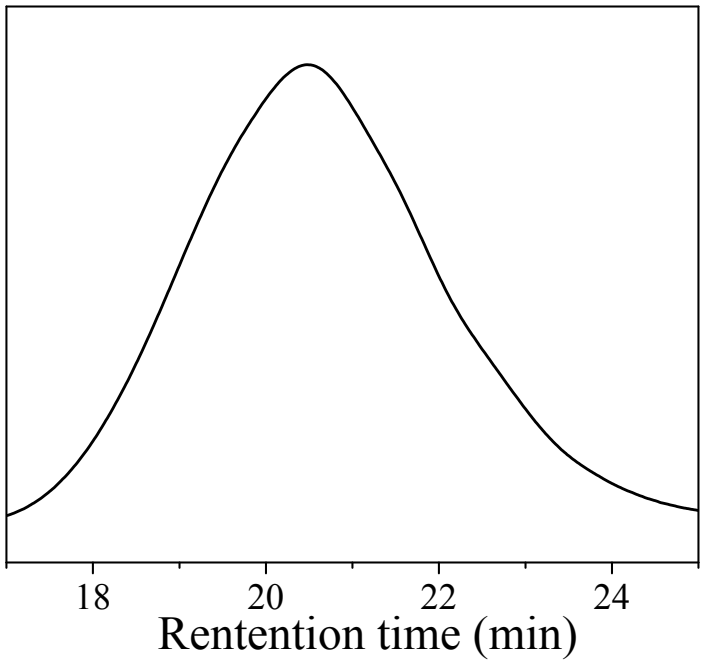


Figure S73. GPC analysis of **P4a-3**

4.0 References

1. V. L. F. Ralph, N. Salvatore, D. Ha and K. W. Jung, *Org. Lett.*, 2000, **2**, 2797–2800.
2. C. F. Salvatore and R. N. Nagle, *Cheminform*, 2002, **33**, 3329–3347.