

Supporting Information

Synthesis of isocyanate-free polyurethane concocting multiple cyclic carbonates catalysed by a new microporous zinc phosphonate via CO₂ fixation

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Experimental

Material characterizations

The Powder X-ray diffraction analysis of ZnGLy was performed in Bruker AXS D-8 Advanced SWAX diffractometer using Cu-K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The model structure and the extended framework were carried out using the EXPO2014 and VESTA crystallography softwares. For microscopic study high resolution transmission electron microscopic (TEM) images of ZnGLy was studied using JEOL JEM 2010 transmission electron microscope. The self-assembled morphology as well as the particle size of the material was analyzed by a JEOL JSM-7500F field emission scanning electron microscope. N₂ adsorption/desorption isotherm of ZnGLy was measured at 77 K from the Autosorb-iQ surface area analyzer of Quantachrome Instruments, USA. Utilizing non-local density functional theory (NLDFT), a pore size distribution plot was created using N₂ sorption at 77 K on carbon as a benchmark. The product was analysed by ^1H NMR spectroscopy using Bruker ADVANCED III-400 and 600 MHz instrument. The HSQC NMR also performed with ADVANCED III-400. The pressure reactions of few substrates were performed by using high pressure reactor provided by Amar Equipment Pvt. Ltd. The ^{31}P CP MAS NMR of ZnGLy characterized through ECX400-Jeol 400 MHz high resolution multinuclear FT-NMR spectrometer for solids. The CO₂ DRIFT study was performed under 25 °C. Initially ultrapure argon (Ar) was purged at a flow rate of 15 ml/min. Both the KBr and the ZnGLy samples were kept in a vacuum oven for 48 h prior measurement.

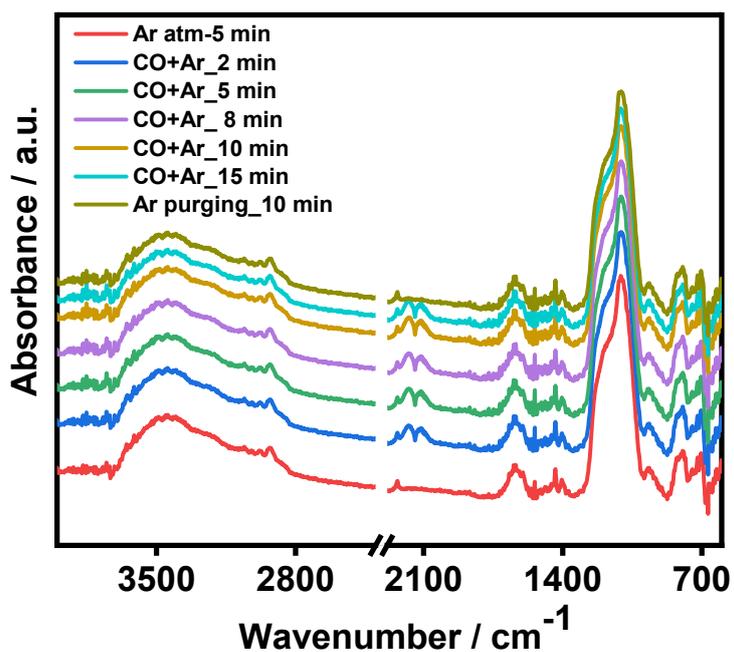


Figure S1a. In-situ DRIFT IF after CO adsorption at different time interval.

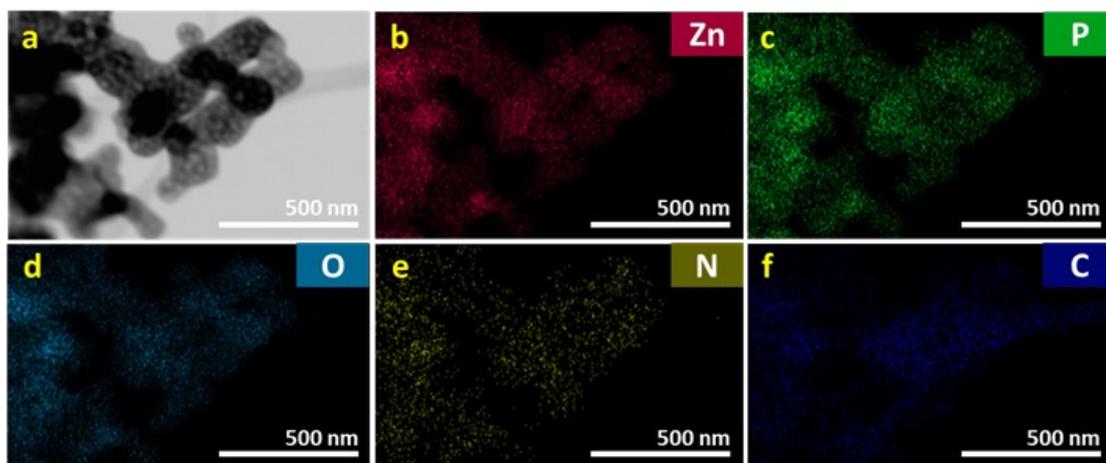
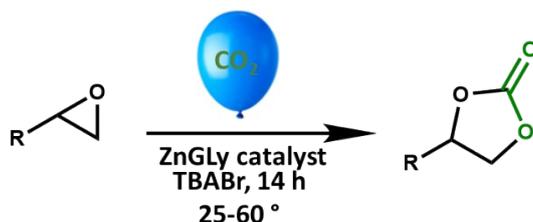


Figure S2. (a) HR-TEM image of ZnGLy material and the corresponding elemental map of (b) Zn, (c) P, (d) O, (e) N, and (f) C.

Synthesis of Cyclic carbonate

In this typical reaction, a pre-dried round bottle flask (RB) filled with epichlorohydrin (5 mmol), TBABr (0.8 mmol) as co-catalyst and ZnGLy catalyst (20 mg). Then the RB was sealed by a stop cork and CO₂ was purged into the system three times to evacuated the air through

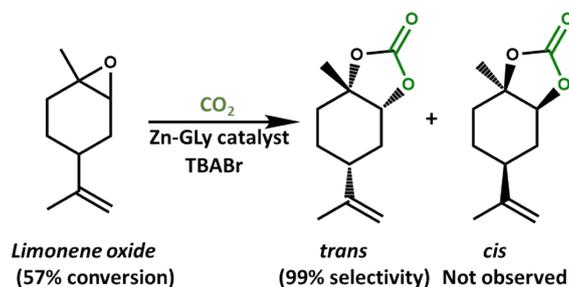
a balloon source and finally fitted with a balloon. After that, the reaction mixture was stirred for 14-24 h at 60 °C to completion the reaction. Then the product was washed with a 50:50 mixture of EtOAc:H₂O. Then the mixture was dried over Na₂SO₄. The final product was further purified by column chromatography. The final product was analyzed through ¹H NMR spectroscopy.



Scheme S1. General scheme for cyclic carbonate synthesis.

Synthesis of limonene carbonate

limonene carbonate was synthesized in a pre-dried stainless-steel autoclave which was charged with limonene oxide (5 mmol), TBABr (0.8 mmol) and Zn-Gly (20 mg). Then CO₂ was purged up to 30 bar pressure. After completion of reaction the mixture was poured into water (10 ml) and washed with EtOAc (10 ml) three times and dried over Na₂SO₄ collected under reduced pressure. The final product was characterized through ¹H NMR in CDCl₃ in 400 MHz NMR and FT-IR spectroscopy.



Scheme S2. General scheme for limonene carbonate synthesis.

Table S1. Optimization of cyclic carbonate synthesis from bio-derived epoxide limonene oxide.

Entry	CO ₂ pressure (Mpa)	Catalyst (mg)	Time (h)	Yield (%)
1	0.1	10	14	-
2	0.5	10	14	8
3	0.5	10	24	17
4	1	10	24	31
5	1	10	24	39
6	2	10	24	54
7	3	10	24	57

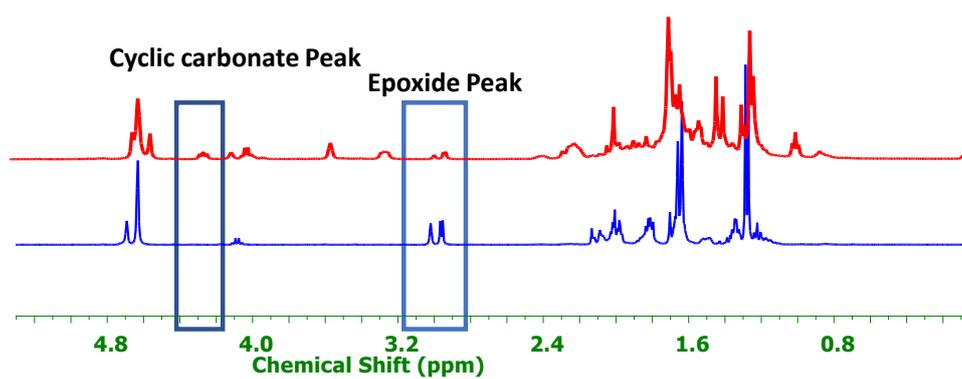


Figure S3a. ¹H NMR of after and before reaction of limonene oxide with CO₂.

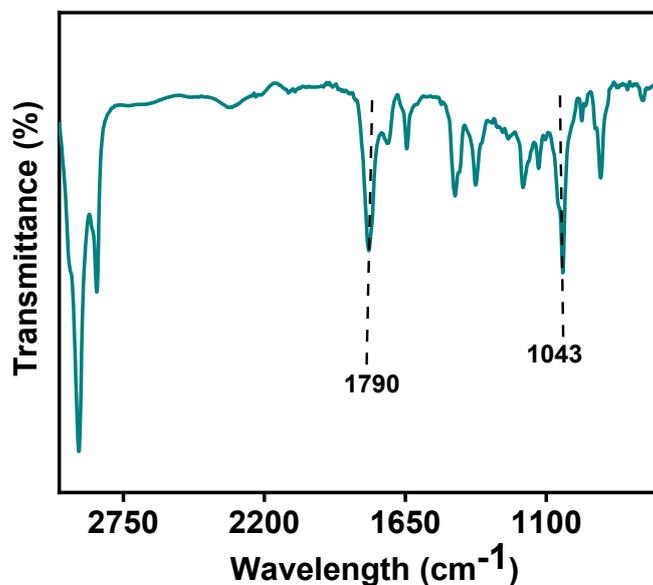
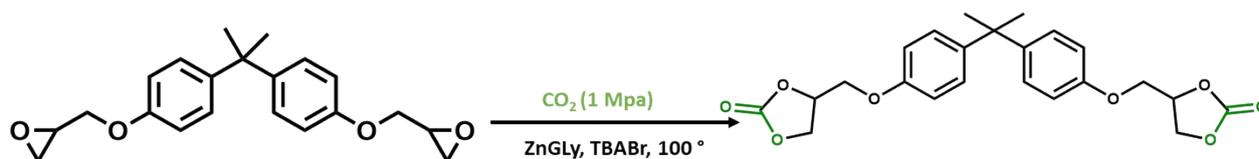


Figure S3b. FT-IR spectra of limonene oxide.

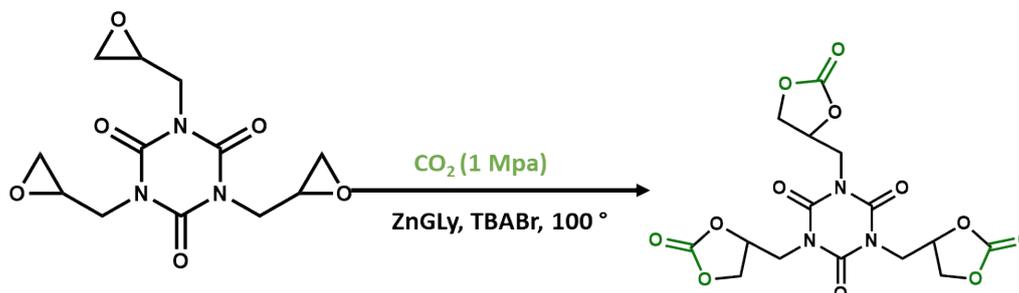
Synthesis of 4,4'-(((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one)

This reaction was conducted in a pre-dried high pressure autoclave. In this typical reaction, the pre-dried autoclave was charged with 2,2-bis(4-glycidyloxyphenyl)propane (2 mmol), TBABr (0.8 mmol) as co-catalyst and ZnGLy catalyst (20 mg). Then the autoclave was sealed CO₂ was purged into the system and pressurised at 1 Mpa pressure. After that, the reaction mixture was stirred for 24 h at required temperature for completion of reaction. Then the product was washed with a 50:50 mixture of EtOAc:H₂O. Then the mixture was dried over Na₂SO₄. Then the product was purified by column chromatography. The final product was formed as a white solid analyzed through ¹H NMR spectroscopy.



Scheme S3. General scheme for of 4,4'-(((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) synthesis.

Synthesis of 1,3,5-tris((2-oxo-1,3-dioxolan-4-yl)methyl)-1,3,5-triazinane-2,4,6-trione



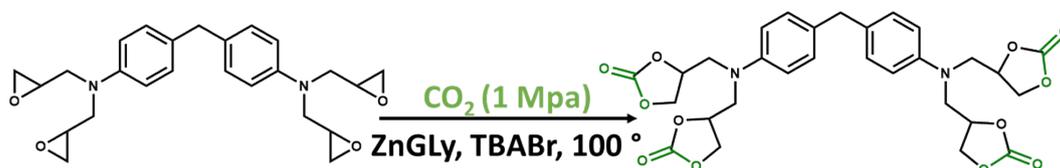
Scheme S4. General scheme for 1,3,5-tris((2-oxo-1,3-dioxolan-4-yl)methyl)-1,3,5-triazinane-2,4,6-trione synthesis.

A high pressure autoclave that had been pre-dried was used for this reaction. In this typical process, epoxide (2 mmol), TBABr (0.8 mmol) as co-catalyst, and ZnGly catalyst were charged into the pre-dried autoclave (20 mg) in DMC as a green solvent. The autoclave was then sealed. The system was pressurised with CO₂ to a pressure of 1 MPa. To finish the reaction, the reaction mixture was then agitated for 24 hours at 100 °C. The product was then rinsed with a 50:50 solution of EtOAc and water. The mixture was then dried using Na₂SO₄. The end result was a white substance that underwent ¹H NMR spectroscopic analysis.

Synthesis of 4,4',4'',4'''-(((methylenebis(4,1-phenylene))bis(azanetriyl)))tetrakis(methylene)tetrakis(1,3-dioxolan-2-one)

This reaction was conducted in a pre-dried high pressure autoclave. In this typical reaction, the pre-dried autoclave was charged with 2,2-bis(4-glycidyoxyphenyl)propane (2 mmol), TBABr (0.8 mmol) as co-catalyst and ZnGly catalyst (20 mg). Then the autoclave was sealed CO₂ was purged into the system and pressurised at 1 Mpa pressure. After that, the reaction

mixture was stirred for 24 h at 100 °C to completion the reaction. Then the product was washed with a 50:50 mixture of EtOAc:H₂O. Then the mixture was dried over Na₂SO₄. The final product was formed as a white solid analyzed through ¹H NMR spectroscopy.



Scheme S5. General scheme for Synthesis of 4,4',4'',4'''-(((methylenebis(4,1-phenylene))bis(azanetriyl))tetrakis(methylene))tetrakis(1,3-dioxolan-2-one) synthesis.

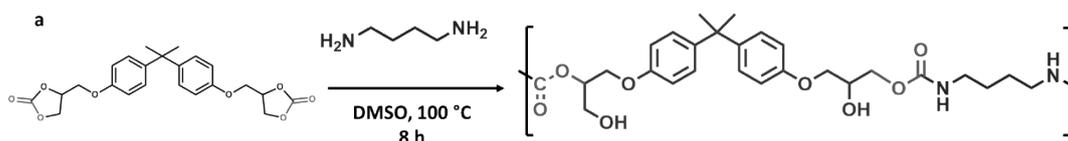
Table S2. Comparison table of cyclic carbonate synthesis.

Entry	Catalyst	Type	Pressure	Time (h)	Yield (%)	Ref.
1	NHC-CAP-1 (Zn ²⁺)	Heterogeneous	2 MPa	3	95	1
2	ImBr-MOF-545(Mn)	Heterogeneous	0.5 MPa	1.5	98.4	2
3	MOF-5	Heterogeneous	6 MPa	4	97.6	3
4	Iron (II) Bis-CNN	Homogeneous	1 MPa	24	99	4
5	IL-ZNTPP	Heterogeneous	2 MPa	30	97	5
6	Pd@Eu-MOF	Heterogeneous	2 MPa	24	98	6
7	Cu ₇ (H ₁ L) ₂ (TPT) ₃ (H ₂ O) ₆	Heterogeneous	1 MPa	12	99	7
8	66Pym-RXs and 67BPym-Mel	Heterogeneous	0.5 MPa	24 h	99	8
9	ZnGly	Heterogeneous	balloon	14	99	This work

Synthesis of Non-isocyanate poly(hydroxy)urethane NIPU

In a 50 ml round bottom-flask charged with 4,4'-(((propane-2,2-diylbis(4,1-phenylene))bis(oxy)) bis(methylene))bis(1,3- dioxolan-2-one) (600 mg, 1.76 mmol) , 1,4-diaminobutane (157 mg, 1.77 mmol) and DMSO. Then, the mixture was heated at 100 °C for 8 h under N₂ atmosphere. After completion of reaction, the mixture poured into water and white precipitate was formed. The precipitate was filtered of and few amounts of precipitate dissolved in DMSO-d₆ for ¹H NMR study.

^1H NMR (400 MHz, DMSO-d_6): δ = 1.335 (m, NHCH_2CH_2), 1.560 (s, CCH_3), 2.929 (m, CONHCH_2), 3.565 (m, CH_2OH), 3.879–3.996 (m, OCHCH_2O , $\text{OCH}_2\text{CHCH}_2\text{O}$), 4.843 (m, CHCH_2OH). 4.967 (s, CH_2OH), 5.252 (s, CHOH), 6.802–6.821 (d, OCCHCHC), 7.075–7.094 (d, OCCHCHC), 7.20 (m, OCONHCH_2) ppm.



Scheme S6. General scheme for NIPU synthesis.

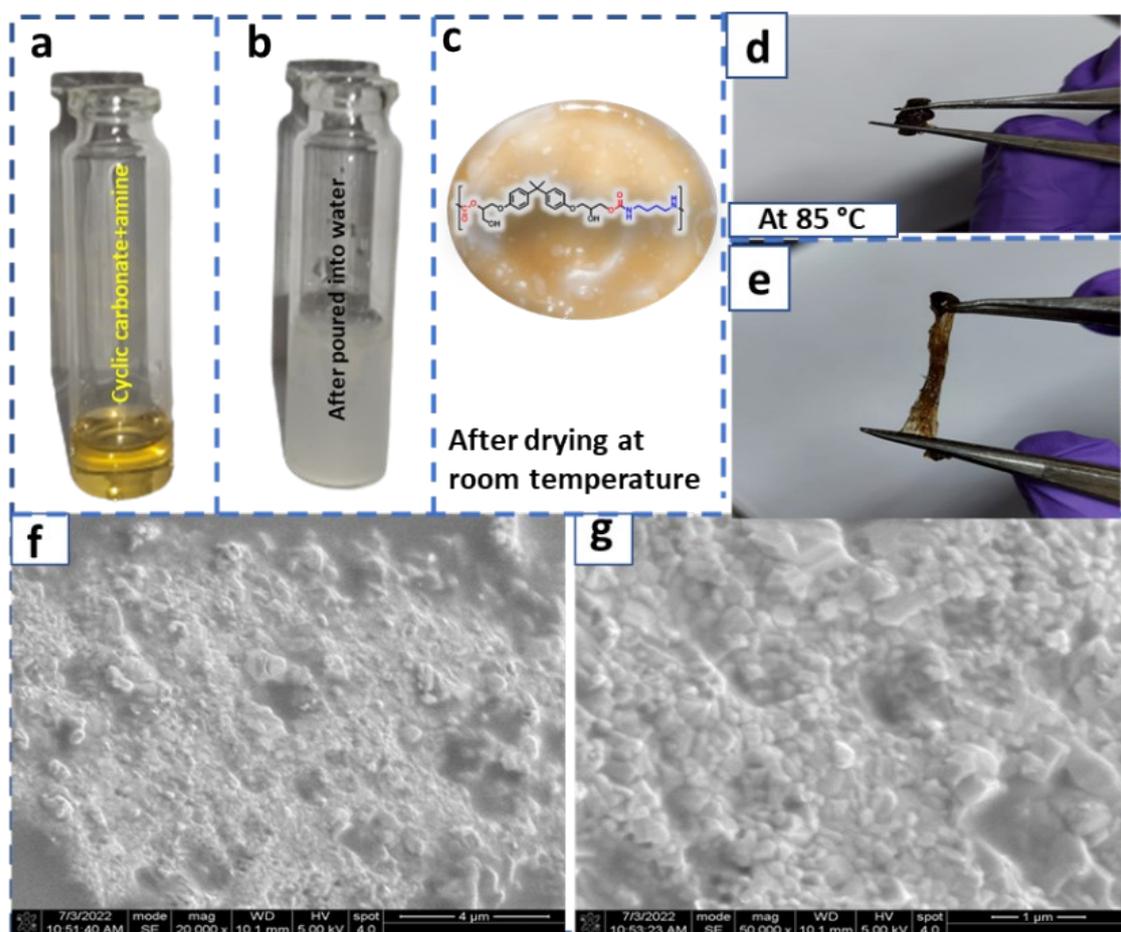


Figure S4. Cyclic carbonate and amine mixture before (a) and after (b) poured into water, drying at room temperature (c), after formation of adhesive (d,e), SEM images of PHU (f,g).

Table S3. Calculated Mn, Mw, and Đ (Mw/Mn) values for PHU.

Entry	Temperature (°C)	M _n /10 ⁴	M _w /10 ⁴	M _z /10 ⁴	Đ (M _w /M _n) PDI
1.	80	0.9341	0.9179	0.9501	1.017
2.	100	1.0414	1.0135	1.0674	1.027

Propylene carbonate

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 4.90-4.81 (m, 1H), 4.53-4.57 (q, 8.4 Hz, 1H), 4.01-4.04 (q, 8.4 Hz, 1H), 1.49-1.51 (d, 3H).

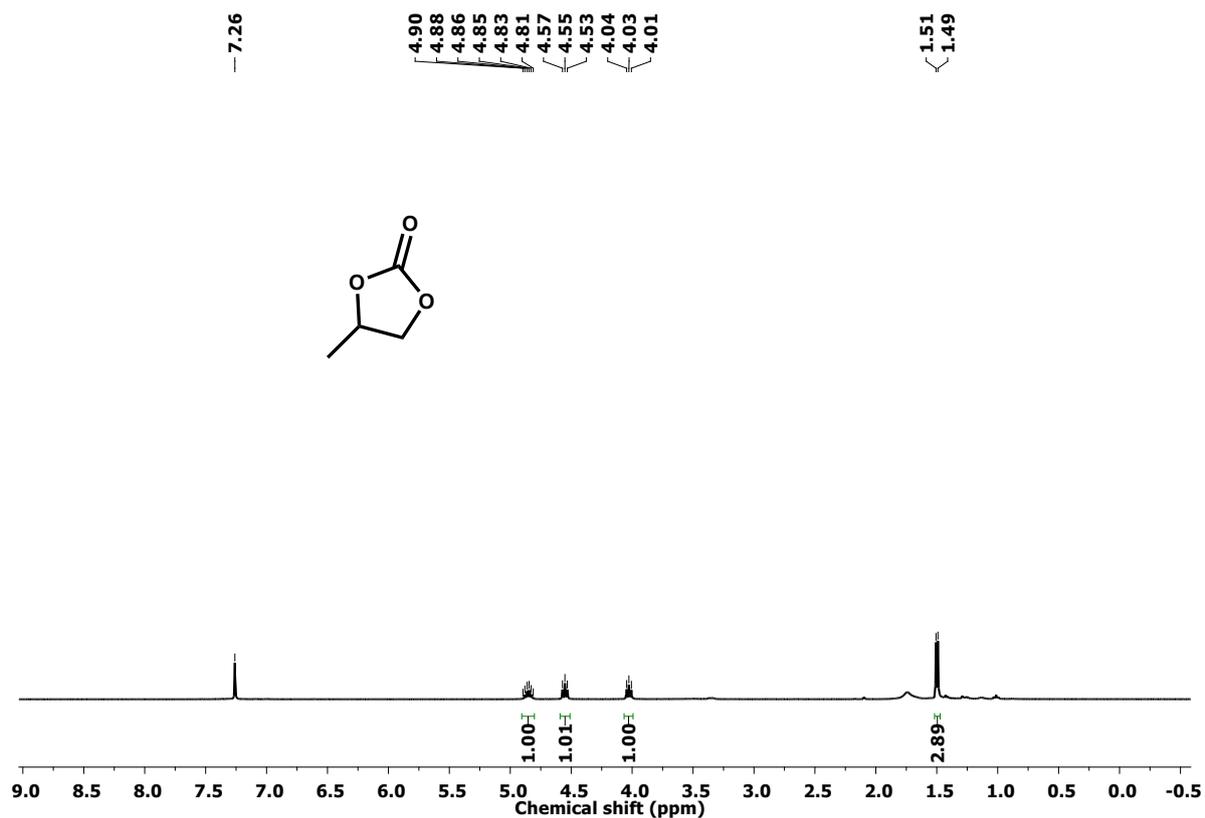


Figure S 5a. ¹H NMR of propylene carbonate.

4-chloromethyl-1,3-dioxolan-2-one

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 5.01-4.95 (m, 1H), 4.57 (t, Hz, 1H), 4.39 (q, $J=5.7, 8.8$ Hz, 1H), 3.81(dd, 1H), 3.68- 3.77 (dd, 1H).

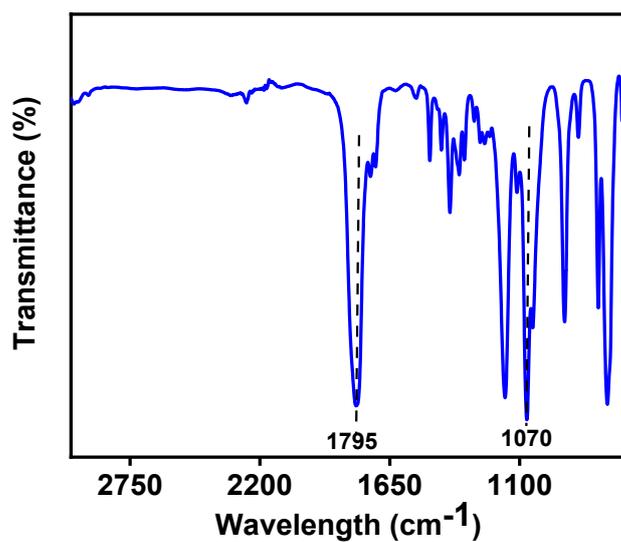
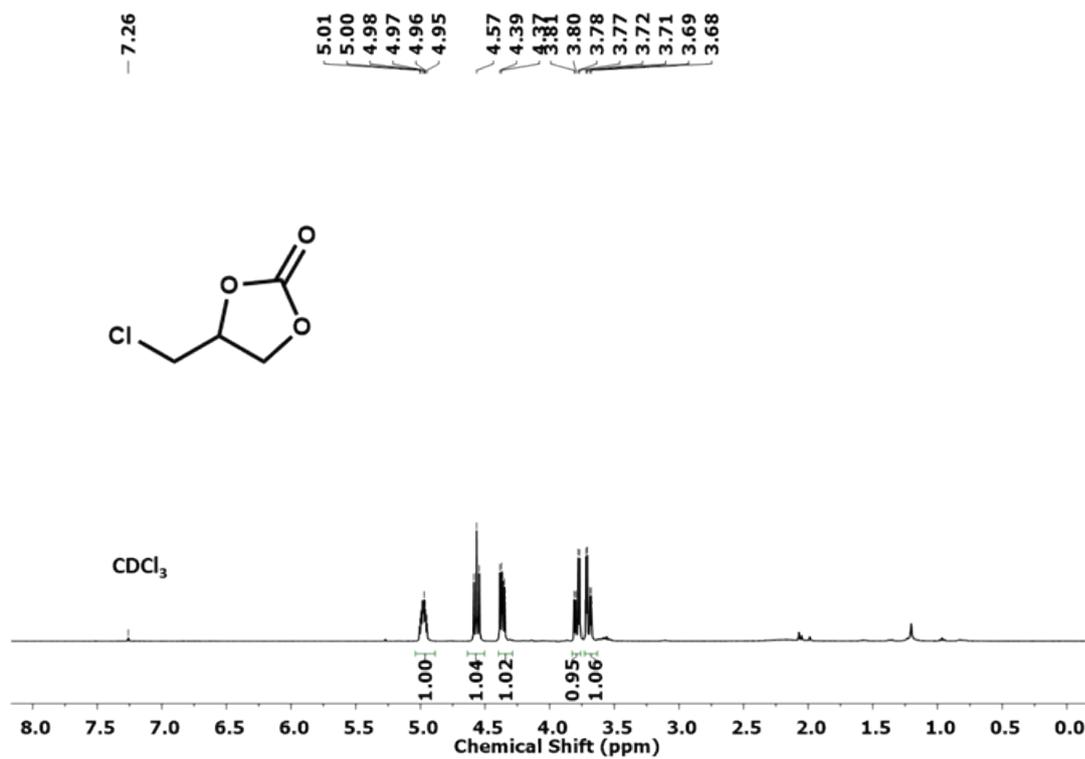


Figure S 5b. $^1\text{H NMR}$ and FT-IR of 4-chloromethyl-1,3-dioxolan-2-one.

4-((allyloxy)methyl)-1,3-dioxolan-2-one

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 5.88-5.78 (m, 1H), 5.26-5.16 (m, 2H), 4.77-4.81 (m, 1H), 4.49 (m, 1H), 4.49 (m, 1H), 4.02 (m, 2H), 3.68 (m, 1H), 3.55 (m, 1H).

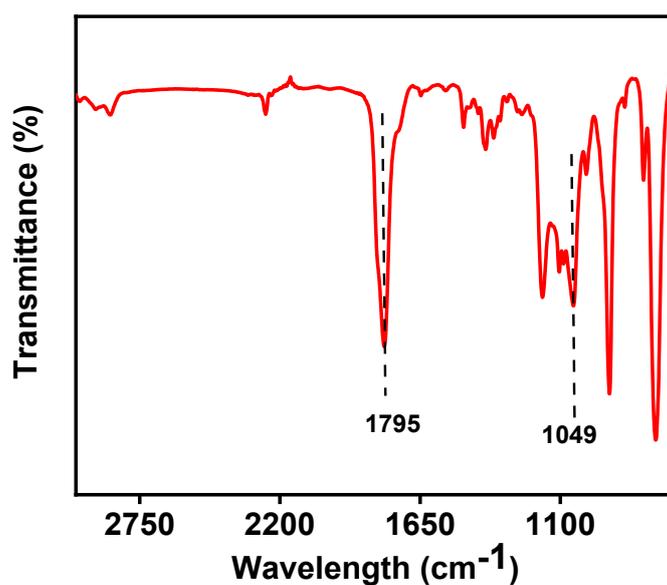
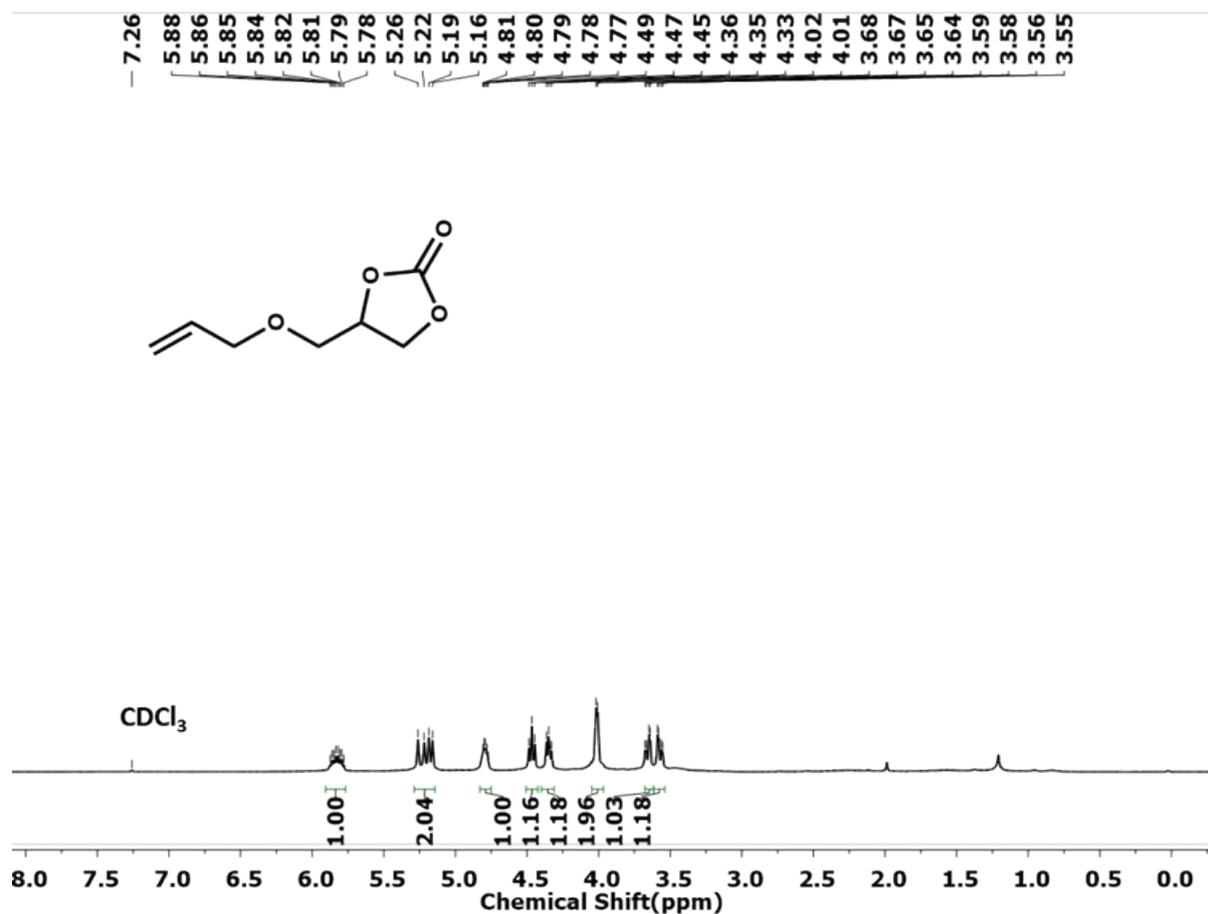


Figure S 5c. $^1\text{H NMR}$ and FT-IR of 4-((allyloxy)methyl)-1,3-dioxolan-2-one.

4-(butoxymethyl)-1,3-dioxolan-2-one

^1H NMR (CDCl_3 , 600 MHz) δ (ppm): 4.78-4.77 (m, 1H), 4.43-4.45 (t, 1H), 4.30-4.32 (t, 1H), 3.62 (m, 1H), 3.53 (m, 1H), 3.43 (t, 2H), 1.48 (m, 2H), 1.28-1.30 (m, 2H), 0.82-0.85 (t, 3H).

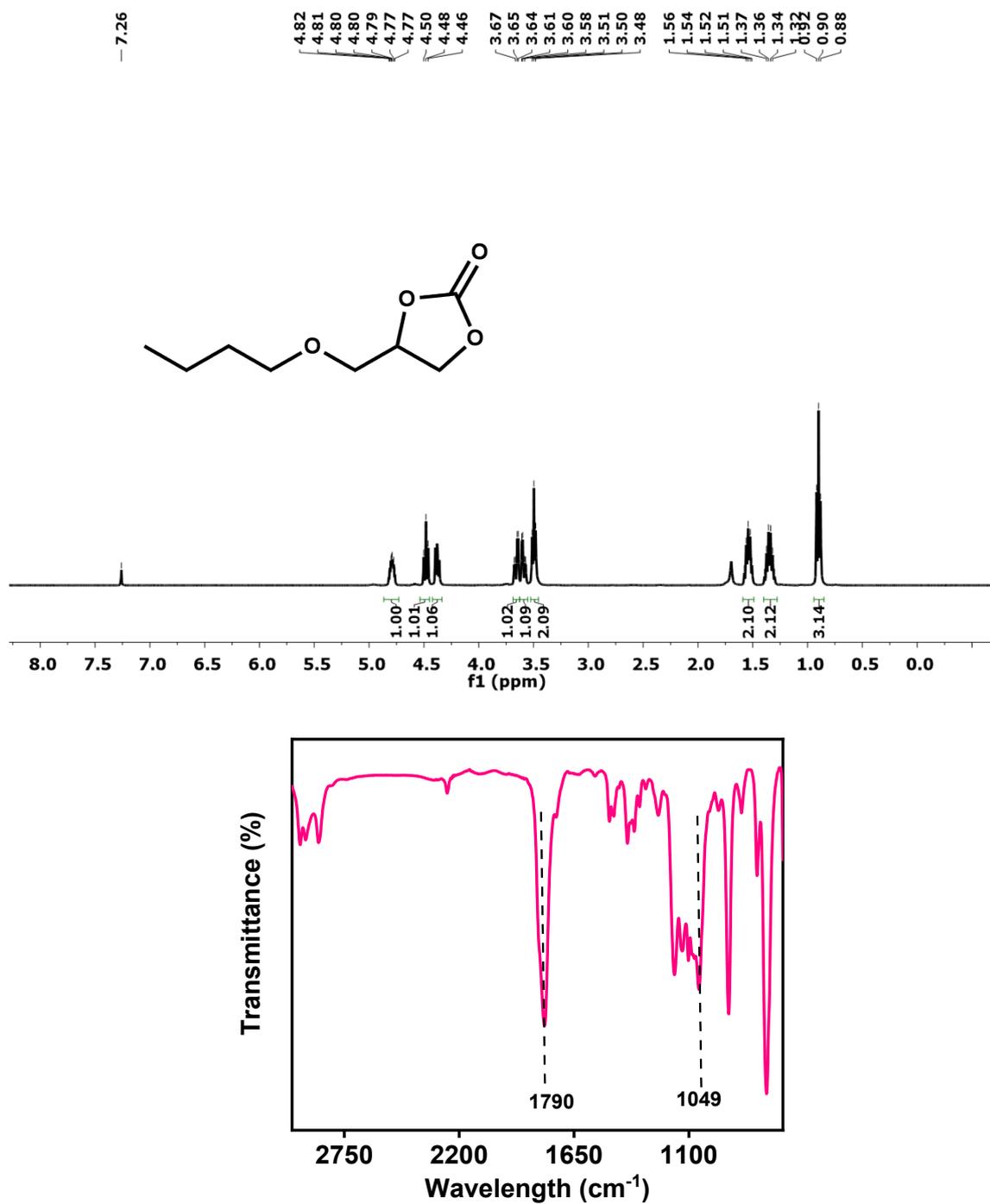


Figure S 5d. ^1H NMR and FT-IR of 4-(butoxymethyl)-1,3-dioxolan-2-one.

Styrene carbonate

^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.40-7.34 (m, 5H), 5.63-5.67 (t, $J=8$ Hz, 1H), 4.75-4.79 (t, $J=8$ Hz, 1H), 4.27-4.32 (t, $J=8$ Hz, 1H).

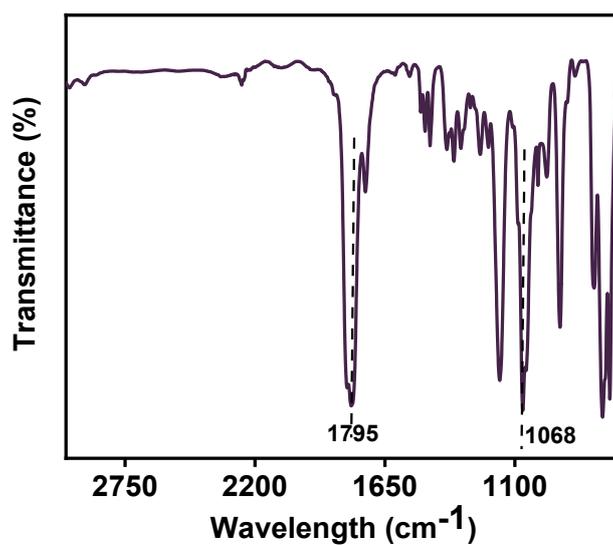
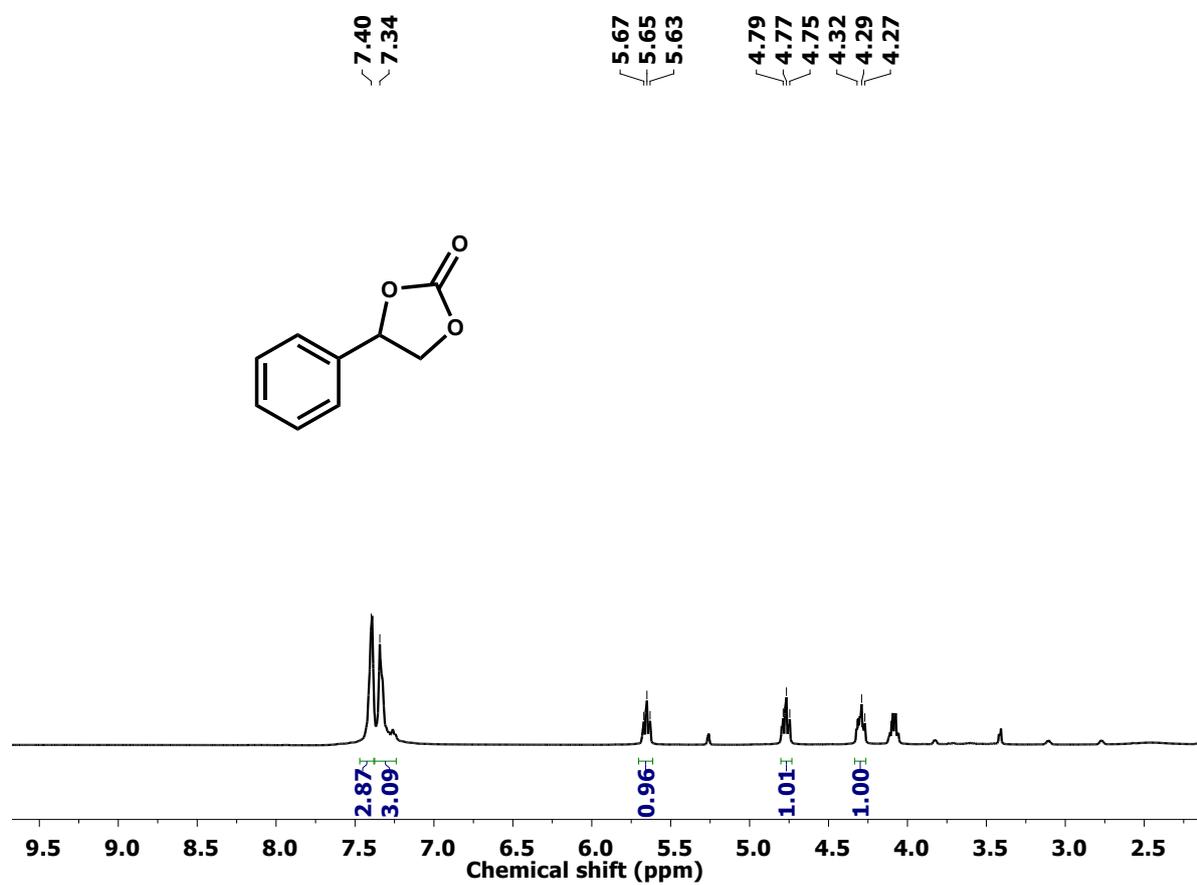


Figure S 5e. ^1H NMR and FT-IR of Styrene carbonate.

Hexahydro-benzo [1,3] dioxol-2-one

^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 4.68 (m, 2H), 1.86-1.85 (m, 4H), 1.68 (m, 2H), 1.41 (m, 2H).

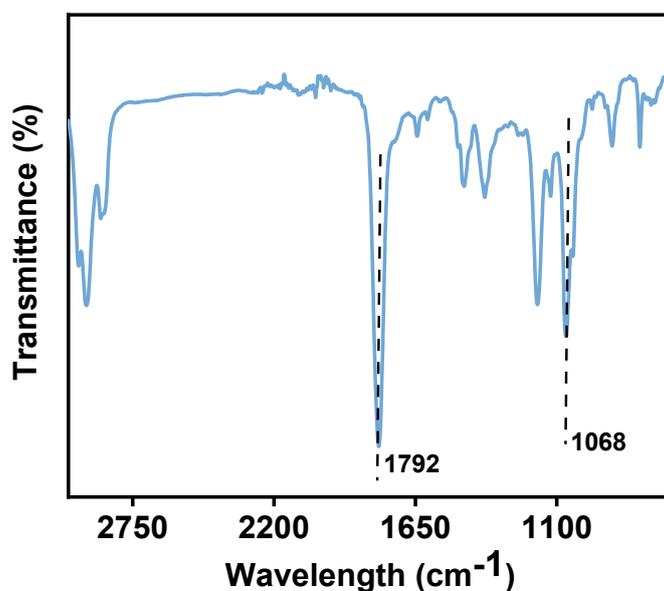
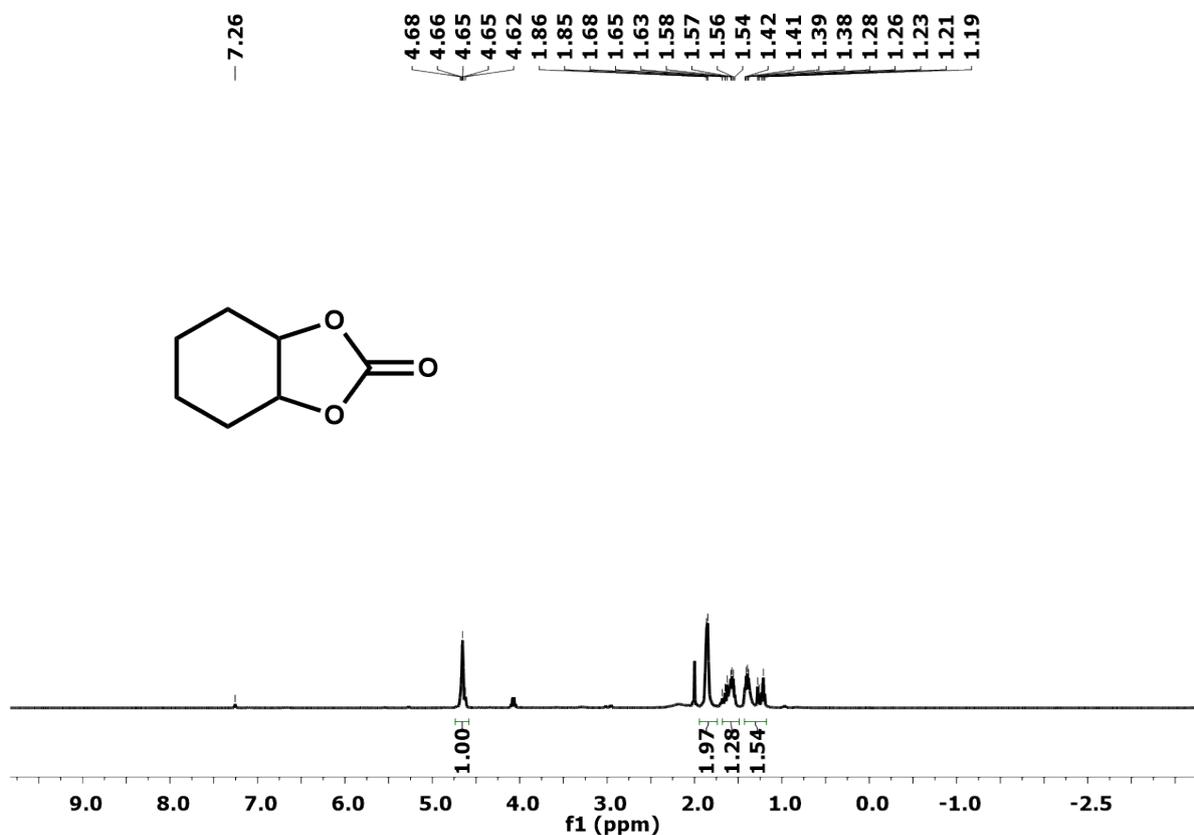


Figure S 5f. ^1H NMR and FT-IR of Hexahydro-benzo [1,3] dioxol-2-one.

4-(tert-butoxymethyl)-1,3-dioxolan-2-one

^1H NMR (CDCl_3 , 600 MHz) δ (ppm): 4.78-4.73 (m, 1H), 4.444-4.48 (t, 1H), 4.34-4.38 (m, 1H), 3.8-3.62 (dd, 10.3 Hz, 1H), 3.49-3.52 (dd, 1H), 1.18 (s, 9H).

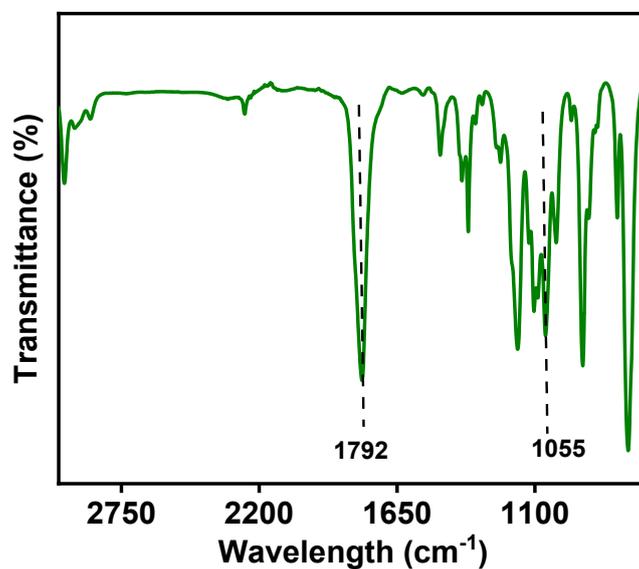
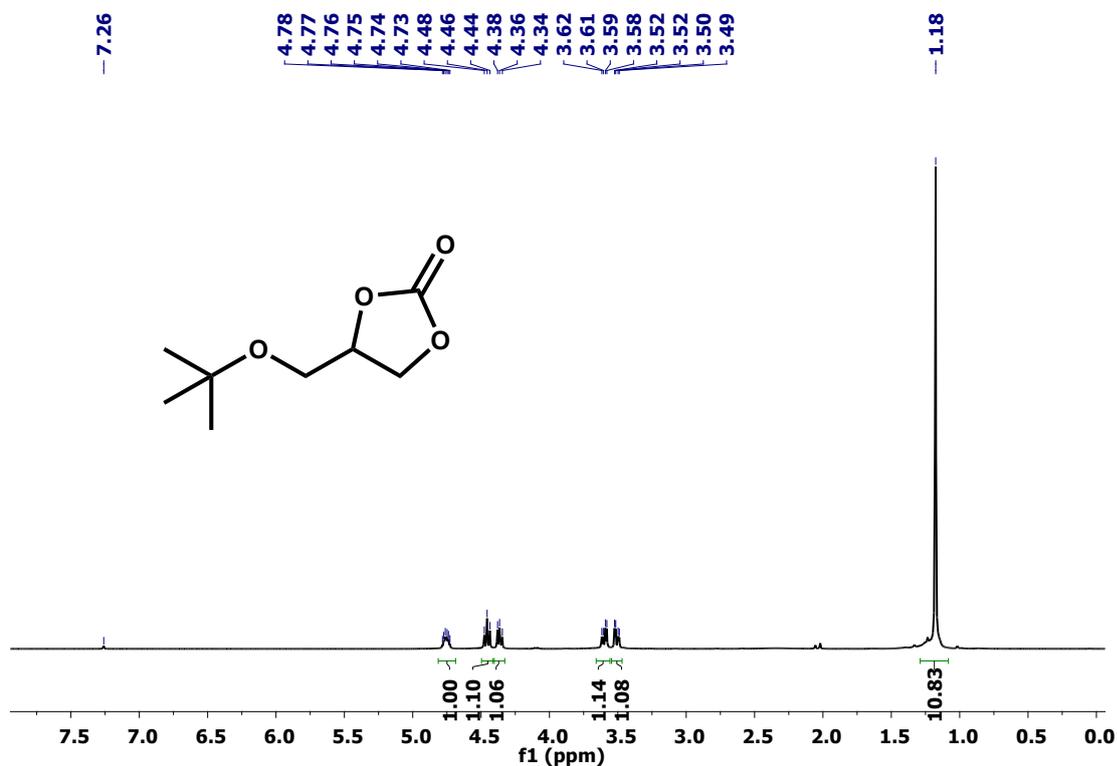


Figure S 5g. ^1H NMR and FT-IR of 4-(tert-butoxymethyl)-1,3-dioxolan-2-one.

4,4'-(((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one)

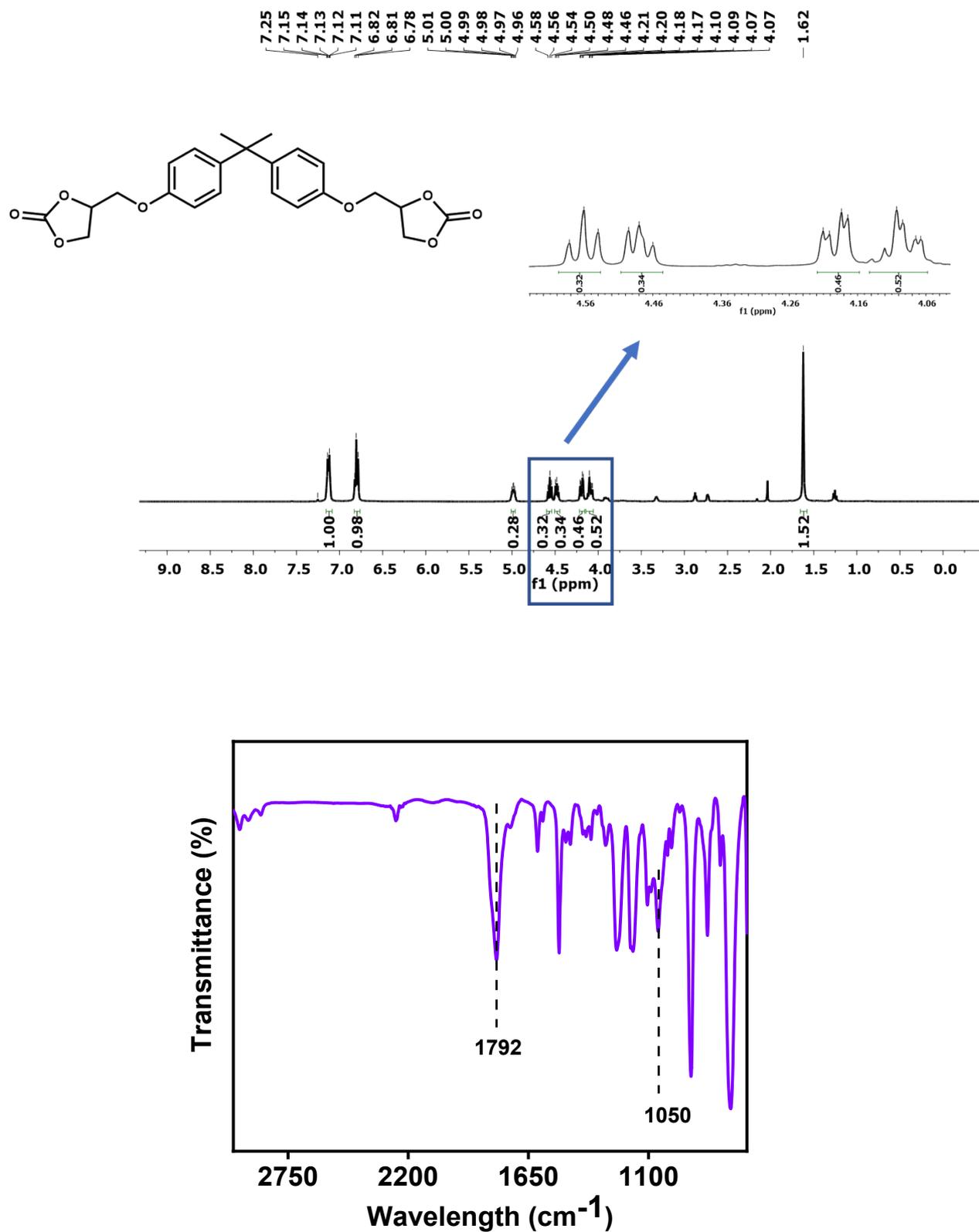


Figure S5h. ¹H NMR and FT-IR of 4,4'-(((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one).

1,3,5-tris((2-oxo-1,3-dioxolan-4-yl)methyl)-1,3,5-triazinane-2,4,6-trione

^1H NMR (400 MHz, DMSO- d_6 , mixture of stereoisomers): δ = 3.97 (m, 3H), 4.05 (m, 3H), 4.34 (m, 3H), 4.56-4.60 (t, J = 8.3 Hz, 3H), 4.98-4.95 (m, 3H) ppm.

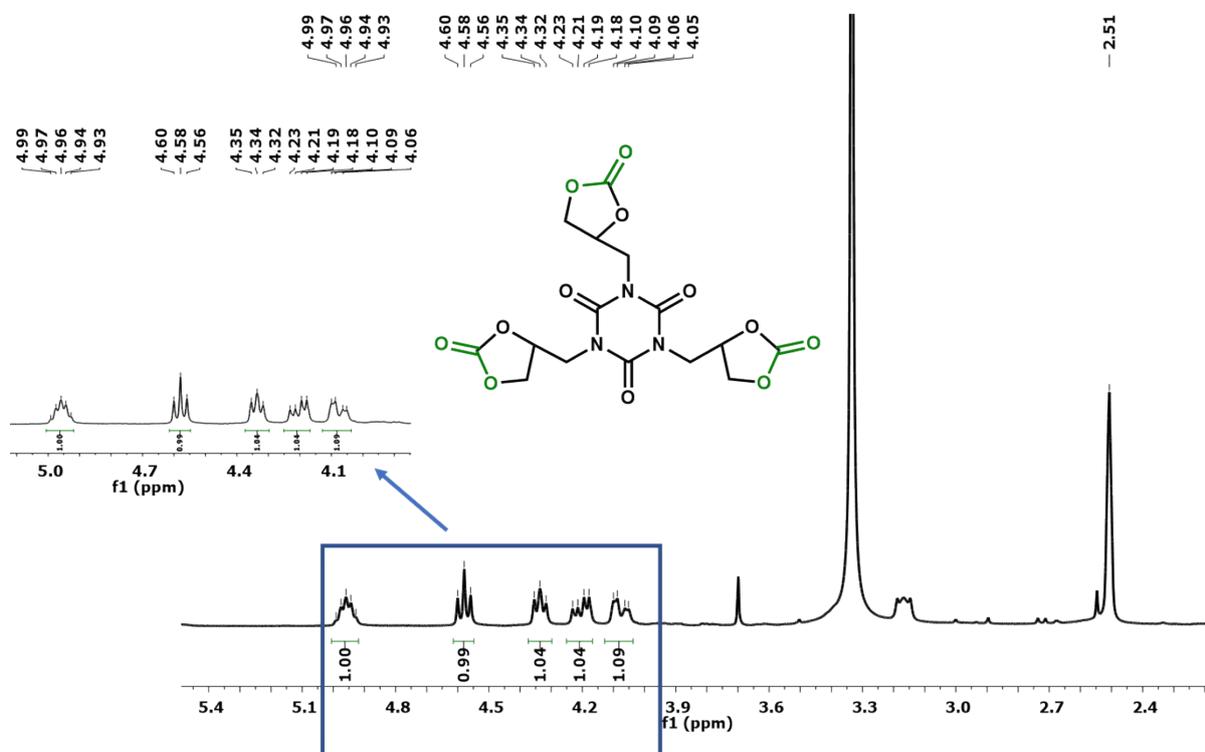


Figure S5i. ^1H NMR of 1,3,5-tris((2-oxo-1,3-dioxolan-4-yl)methyl)-1,3,5-triazinane-2,4,6-trione in DMSO- d_6 (400 MHz) .

4,4',4'',4'''-(((methylenebis(4,1-phenylene))bis(azanetriyl))tetrakis(methylene))tetrakis(1,3-dioxolan-2-one)

^1H NMR (400 MHz, DMSO-d_6): δ = 3.59-3.83 (m, 10H), 4.14-4.17 (ddd, 7.2 Hz, 1.9 Hz, 4H), 4.53-4.59 (td, 4H), 4.94-4.97 (m, 4H), 6.74- 6.81 (m, 4H), 6.99-7.04 (d, 4H) ppm.

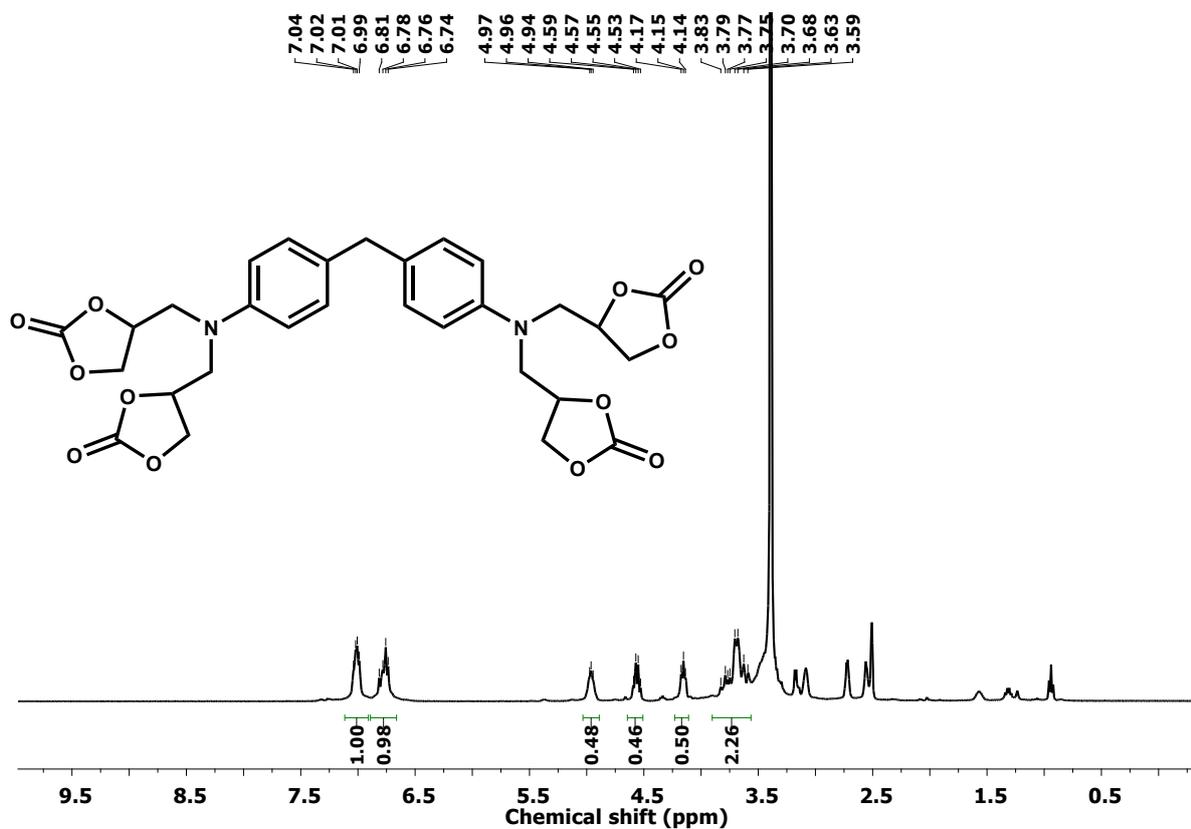


Figure S5j. ^1H NMR of 4,4',4'',4'''-(((methylenebis(4,1-phenylene))bis(azanetriyl))tetrakis(methylene))tetrakis(1,3-dioxolan-2-one) in DMSO-d_6 (400 MHz).

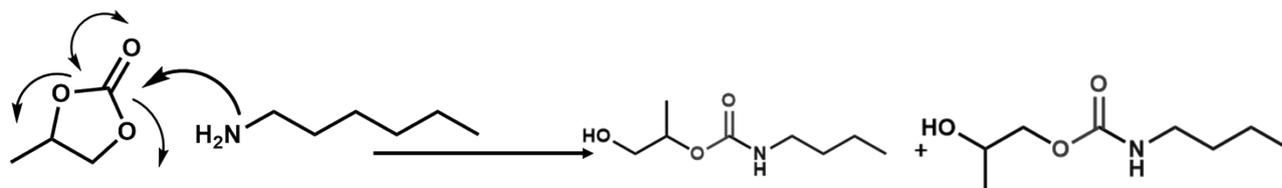


Figure S5. Mechanistic ring opening of five membered cyclic carbonate with amine.

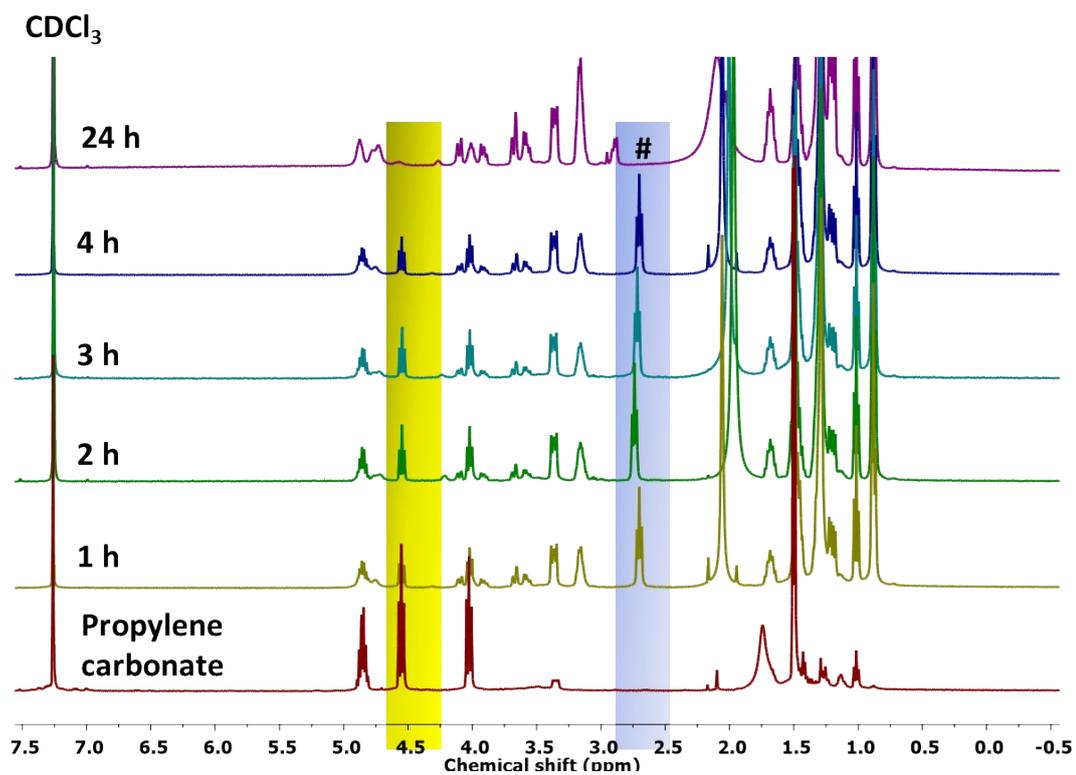
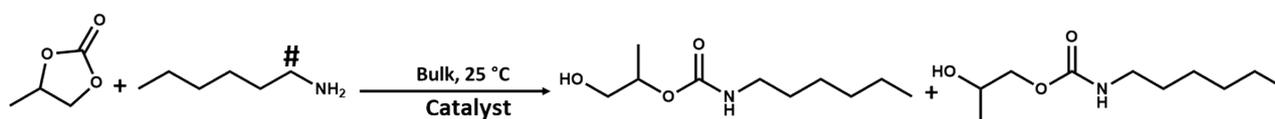


Figure S6a. Stacked ^1H NMR plot of aminolysis reaction between cyclic carbonate with amine in CDCl_3 (400 MHz).

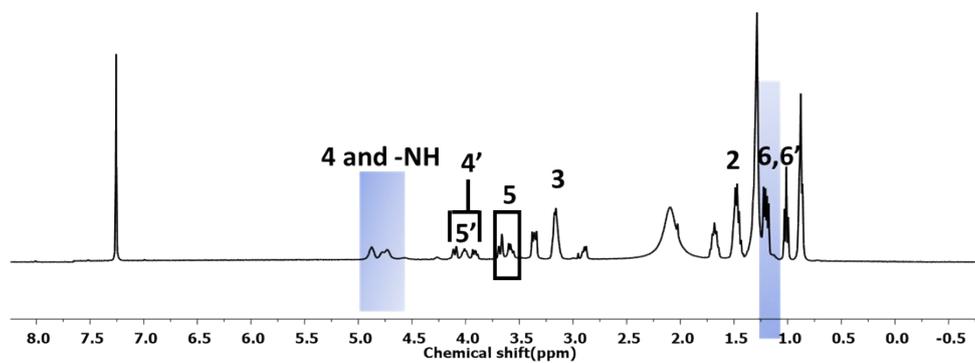
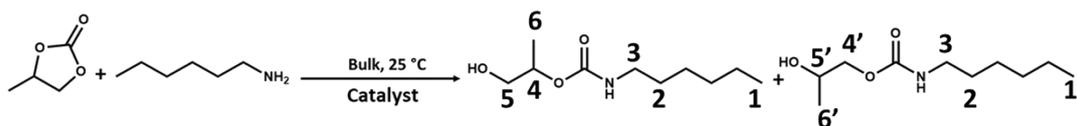


Figure S6b. ^1H NMR of two isomer formed during aminolysis reaction in CDCl_3 (400 MHz).⁷

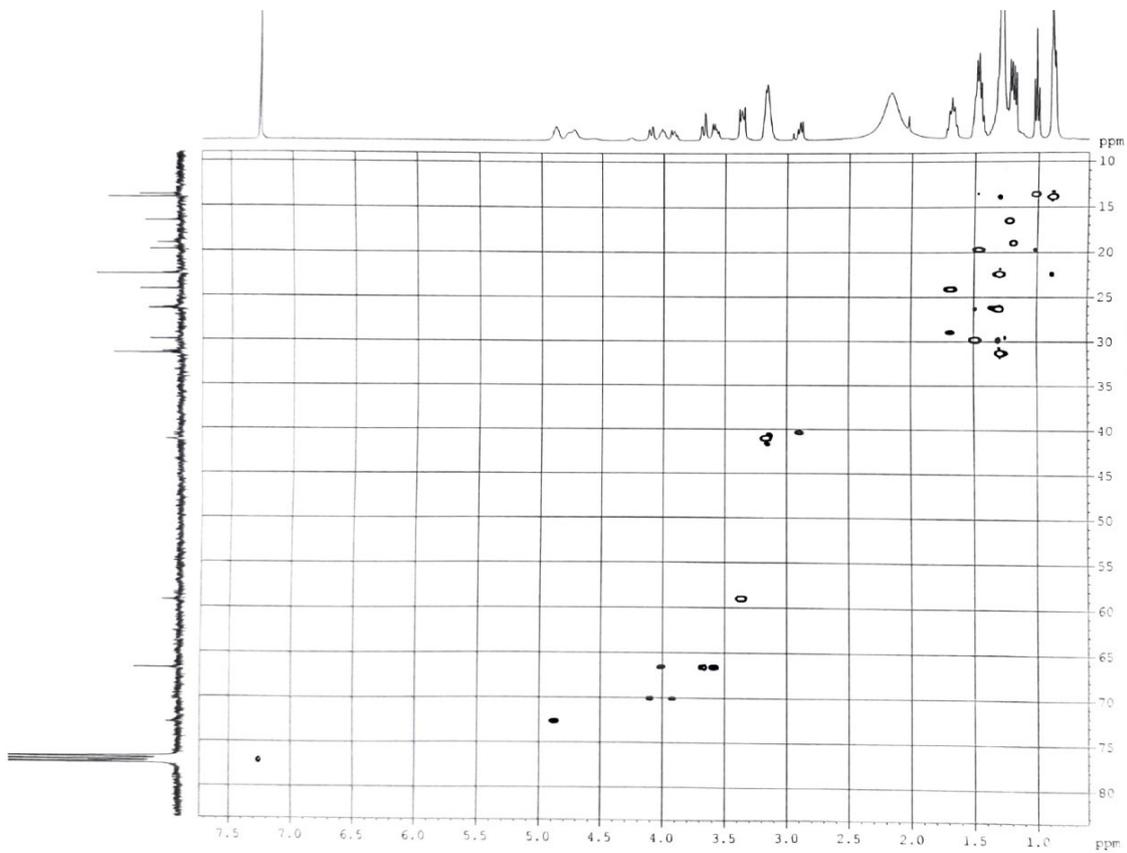


Figure S6c. HSQC plot of ^1H - ^{13}C NMR of two isomers formed during aminolysis reaction in CDCl_3 (400 MHz).⁷

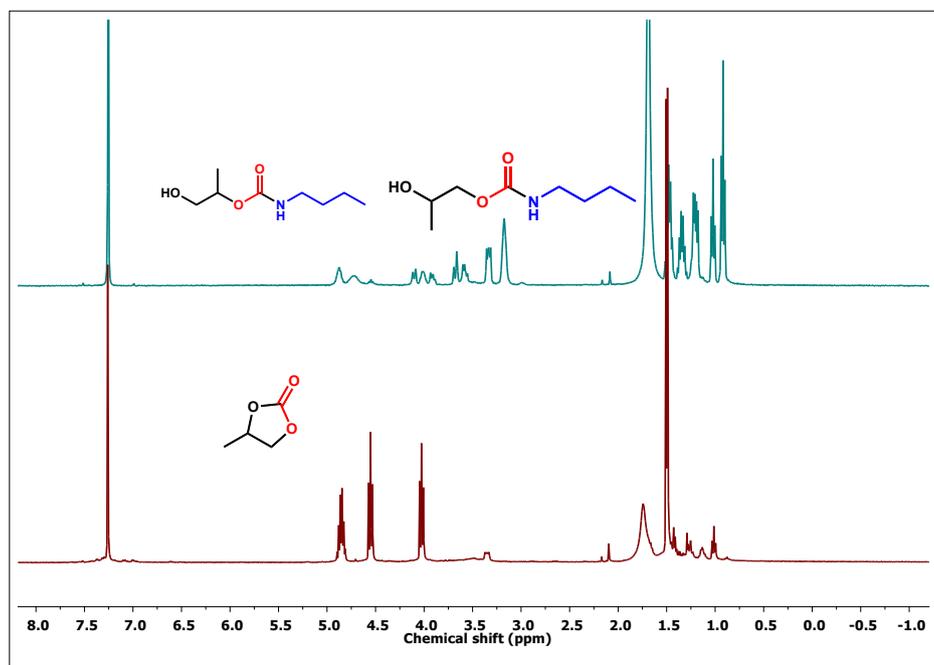
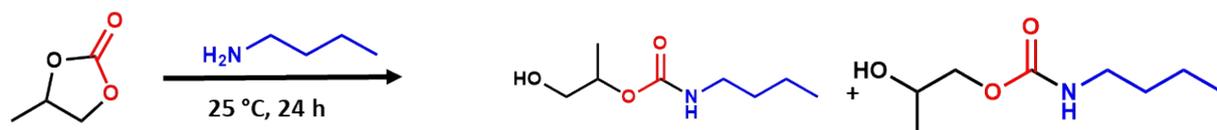


Figure S6d. ^1H NMR after and before aminolysis reaction between propylene oxide and butylamine in CDCl_3 (400 MHz).

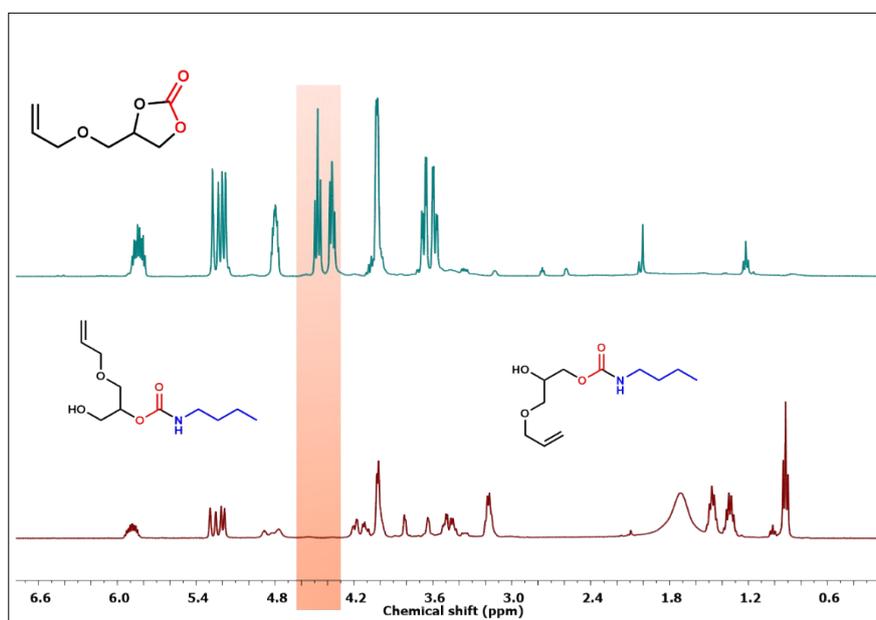
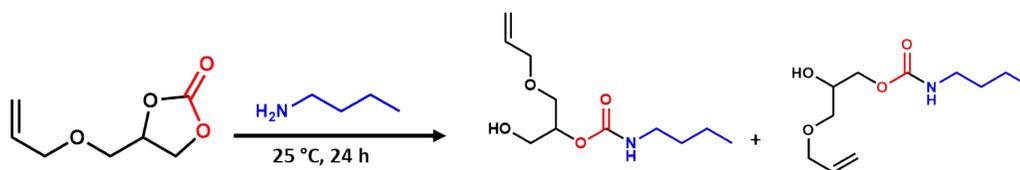


Figure S6e. ^1H NMR after and before aminolysis reaction between allylglycidyl ether and butylamine in CDCl_3 (400 MHz).

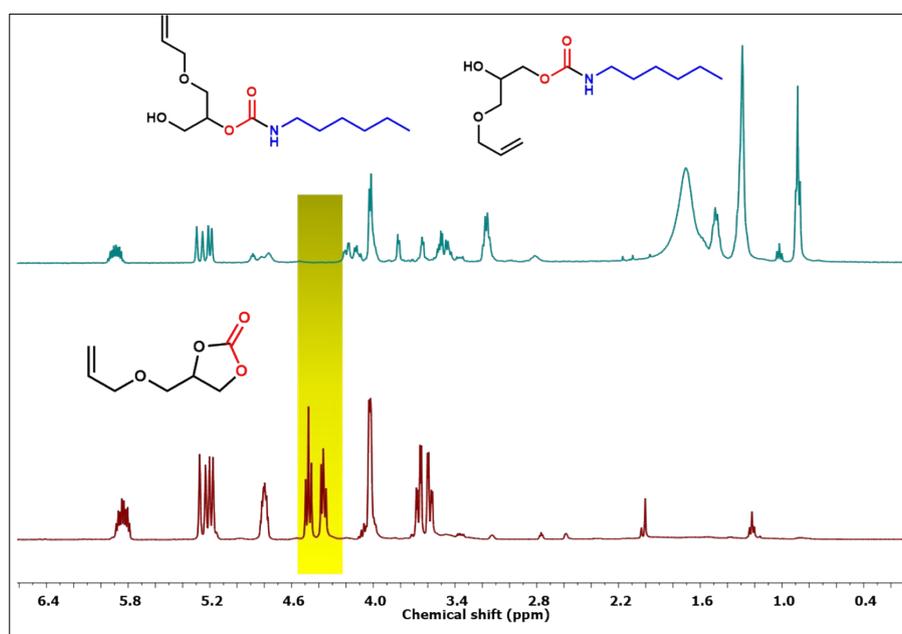
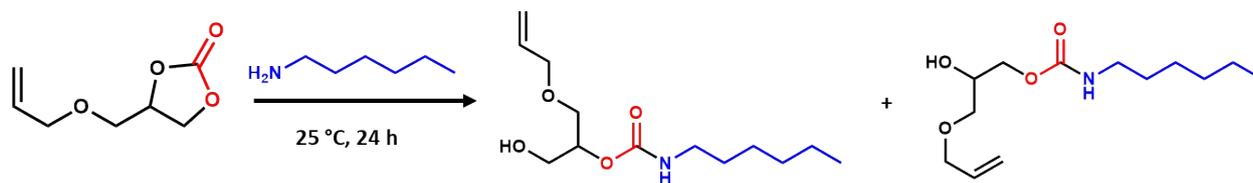


Figure S6f. ^1H NMR after and before aminolysis reaction between allylglycidyl ether and hexylamine in CDCl_3 (400 MHz).

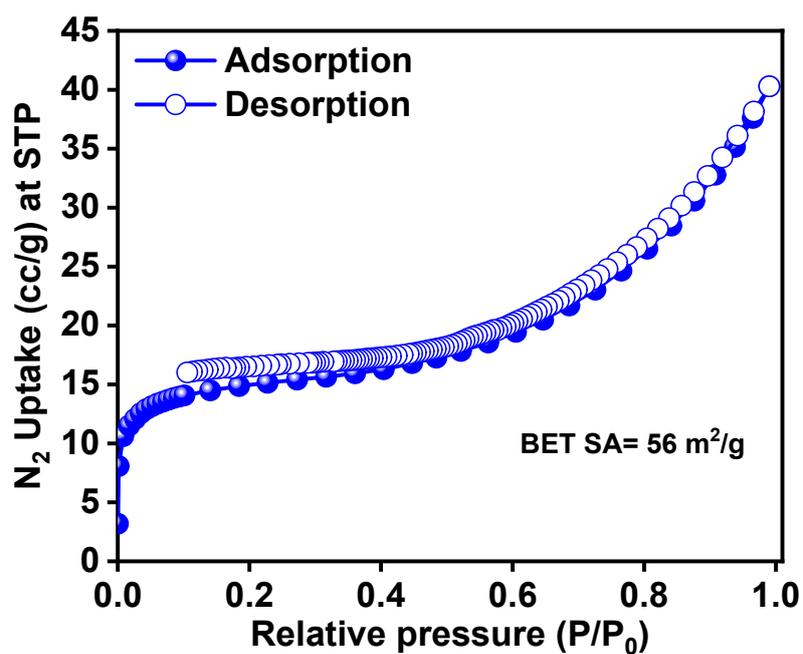


Figure S7. BET isotherm of ZnGLy after 5th cycle.

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