

Supporting Information

A Ni^{II}-cluster based MOF as an efficient heterogeneous catalyst for chemical transformation of CO₂

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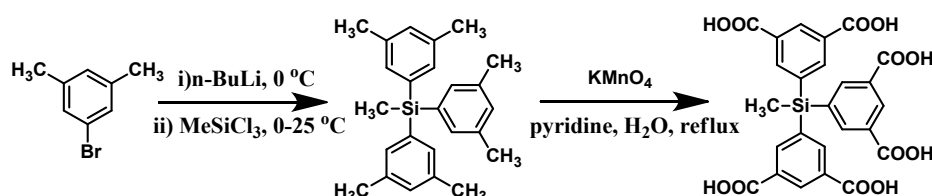
S1. Materials and Methods

1.1 General information

Materials and Instrument

All materials are commercially available and were used without further purification except for 5,5',5''-(methylsilanetriyl)trisophthalic acid (H_6L), which was synthesized in our laboratory.

Powder X-ray diffraction (PXRD) was carried out at 40 kV and 40 mA on a MiniFlex 600 X-ray powder diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$) over 2θ range of 5-50° at room temperature. The infrared (IR) spectra (diamond) were recorded on a Nicolet 7600 FT-IR spectrometer within the 4000-500 cm^{-1} region. Thermal gravimetric analysis (TGA) was conducted on a SDT 2960 Simultaneous DSC-TGA of TA instruments with a heating rate of 10 °C/min up to 900 °C under an air atmosphere. Elemental analyses for C, H, and N were performed by a VarioEL analyzer. ^1H NMR spectra were carried out in CDCl_3 solvent on a Bruker 400 MHz spectrometer. The chemical shift is given in dimensionless δ values and is referenced relative to TMS in ^1H spectroscopy. Inductively coupled plasma (ICP) analyses were conducted on a Perkin-Elmer Optima 3300DV spectrometer.



Scheme 1 The synthesis of 5,5',5''-(methylsilanetriyl)trisophthalic acid.

1.2 Single-Crystal X-ray Crystallography

Single-crystal X-ray diffraction (SXRD) data of compound $\{[\text{Ni}_4\text{L}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_6]\cdot 2(\text{H}_2\text{O})\cdot \text{DMA}\}_n$ were collected on a Bruker diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 293 K. Data processing was accomplished with the SAINT processing program.¹ The structure was solved by the direct methods and refined by full-matrix least-squares fitting on F^2 using the SHELXTL crystallographic software package.² Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. The final formula of $\{[\text{Ni}_4\text{L}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_6]\cdot 2(\text{H}_2\text{O})\cdot \text{DMA}\}_n$ was determined by single-crystal X-ray diffraction, TGA and elemental analysis.

Crystallographic data for $\{[\text{Ni}_4\text{L}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_6]\cdot 2(\text{H}_2\text{O})\cdot \text{DMA}\}_n$ (1872271) has been deposited with Cambridge Crystallographic Data Centre. Data can be obtained free of charge upon request at www.ccdc.cam.ac.uk/data_request/cif. Crystal data and structure refinement is summarized in Table S1.

1.3 Catalysis

In a typical reaction, the catalytic reaction was conducted in a 20 mL autoclave reactor using the epoxides (20 mmol, 1850 mg for epichlorohydrin, 2733 mg for epibromohydrin, 2400 mg for styrene oxide, 3000 mg for 1,2-epoxy-3-phenoxypropane, 1420 mg for glycidol) with CO_2 purged at 1 MPa under solvent free environment catalyzed by the activated sample (0.005mmol, 4 mg)

and co-catalyst of tetrabutylammonium bromide (TBAB, 0.3 mmol) for different intervals. The loading of the catalyst is a 0.025% ratio based on the epoxide. After given reaction time, a small aliquot of the supernatant reaction mixtures was dissolved in 0.6 mL of CDCl₃. The obtained solution was filtered through a syringe filter (PTFE) to be analyzed by ¹H NMR for calculating the conversion of the epoxide. For the recycle experiment, the catalyst was separated by centrifugation for 5 min after the reaction, and the supernatant was collected. The residual solid was washed with dichloromethane and centrifuged three times before being applied the next catalytic conditions.

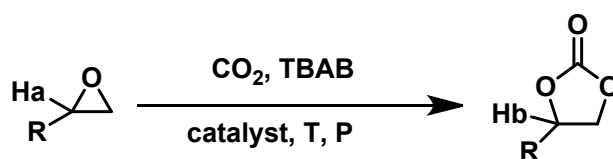
For the recyclable experiment, the catalyst was isolated by centrifugation after the reaction, washed with dichloromethane for three times and dried in air. The recovered catalyst was reused in the following reactions under the same conditions as the first run.

1.4 ICP procedure

Firstly, the filter liquor after catalytic reaction is incinerated at about 500 degrees in the ceramic crucible; secondly, the alkali is dissolved; thirdly, the acid is neutralized; finally, the solution is added to the instrument for analysis.

1.5 Cycloaddition of CO₂ to epoxides

The conversion was calculated from ¹H NMR according to the following equation.



$$\text{conversion} = \frac{{}^1\text{Hb}}{({}^1\text{Ha} + {}^1\text{Hb})}$$

The TON (turnover number) and TOF (turnover frequency) were calculated according to the following equations.

$$\text{TON} = \frac{n(\text{epoxide})}{n(\text{catalyst})}$$

$$\text{TOF} = \frac{n(\text{epoxide})}{n(\text{catalyst}) \times h}$$

S2 Supplementary tables and figures

Table S1 Crystallographic data

Formula	Ni ₄ SiC ₂₉ O ₂₃ H ₃₉ N
F_w	1032.47
Crystal system	orthorhombic
Space group	<i>P n m a</i>
<i>a</i> , Å	12.260(3)
<i>b</i> , Å	18.225(5)
<i>c</i> , Å	19.795(5)
<i>V</i> , Å ³	4423(2)
<i>Z</i>	4
D_c , mg/mm ³	1.340
μ , mm ⁻¹	1.767
reflection collected	26769
GOF on F^2	1.048
R_1/wR_2 ($I > 2\sigma(I)$)	0.0588 / 0.1692
R_1/wR_2 (all data)	0.0765 / 0.1786

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right]^{1/2}$$

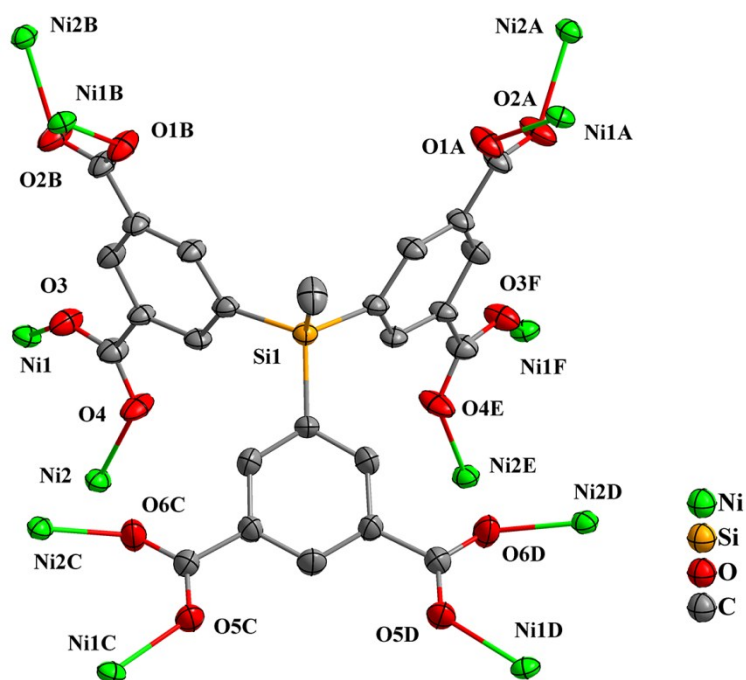


Figure S1. ORTEP representation of the asymmetric unit in **1** with thermal ellipsoids set at 50% probability. The asymmetric codes for the coordinated atoms: A, $-0.5+x, 1.5-y, 1.5-z$; B, $-0.5+x, y, 1.5-z$; C, $-1+x, y, z$; D, $-x, -0.5+y, 1-z$; E, $1-x, -0.5+y, 1-z$; F, $x, 1.5-y, z$.

Hydrogen atoms bonded to carbon atoms are omitted for clarity.

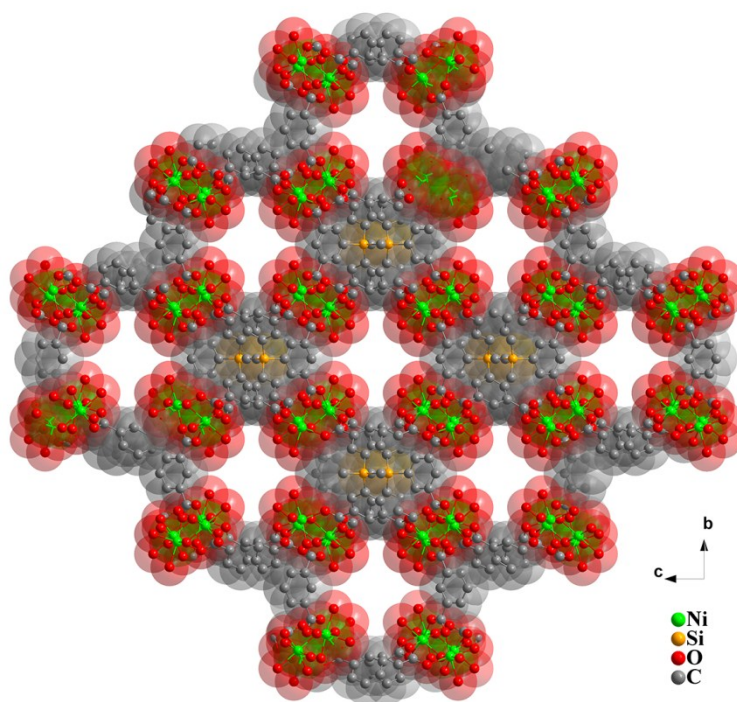


Figure S2. Space-filling view of the structure of **1** showing pores along the a -axis. For clarity the hydrogen atoms have been omitted.

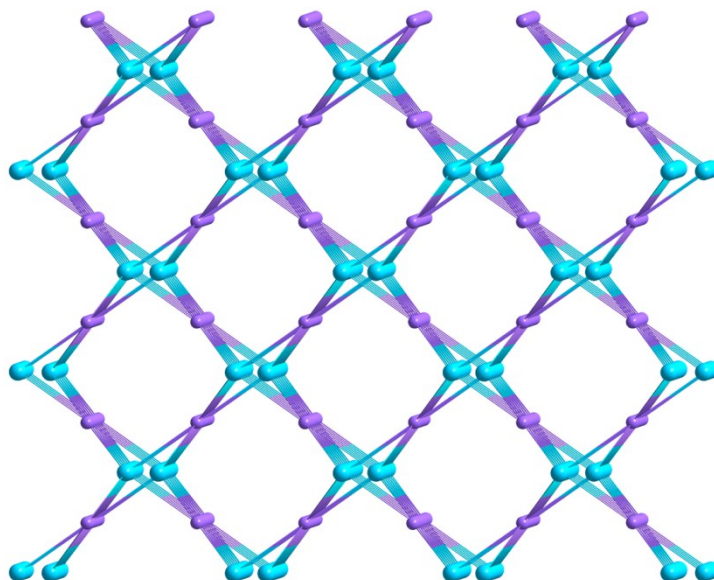


Figure S3. Simplified 6,6-connected net of the compound **1**.

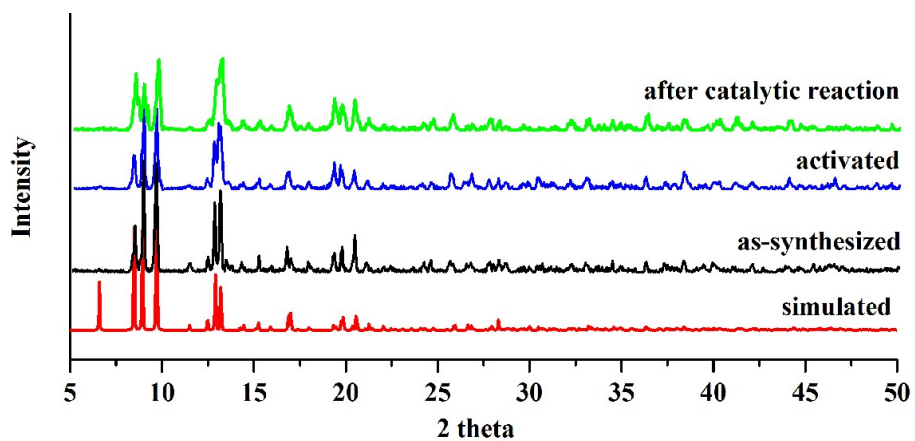


Figure S4. Powder X-ray (PXRD) patterns for the simulated, as-synthesized and activated samples of compound 1, as well as that after the catalytic reaction.

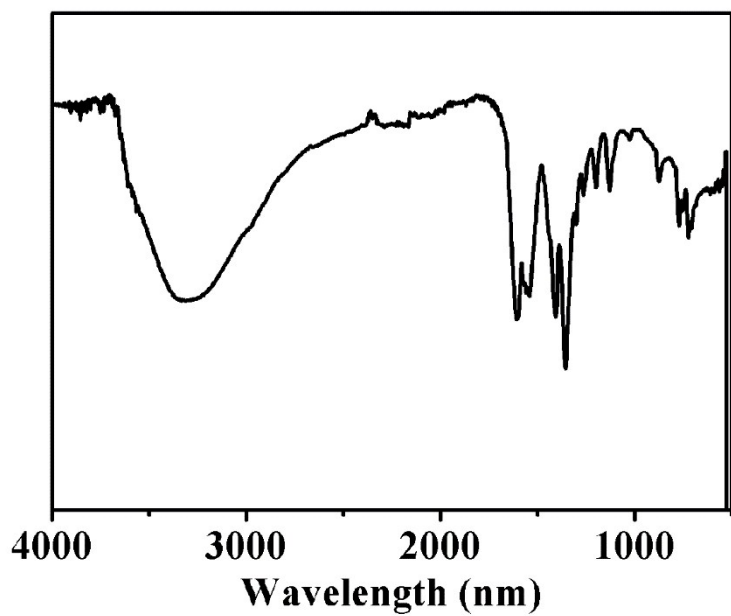


Figure S5. Infrared spectra of the compound 1.

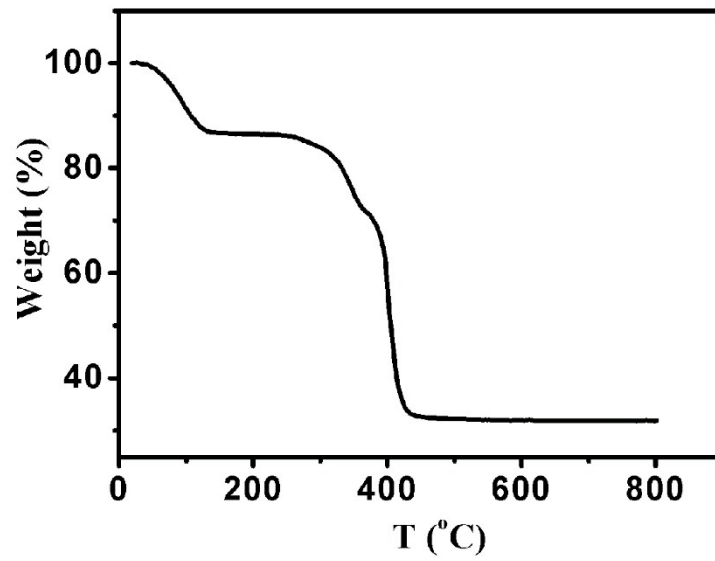


Figure S6 TG curve of compound 1.

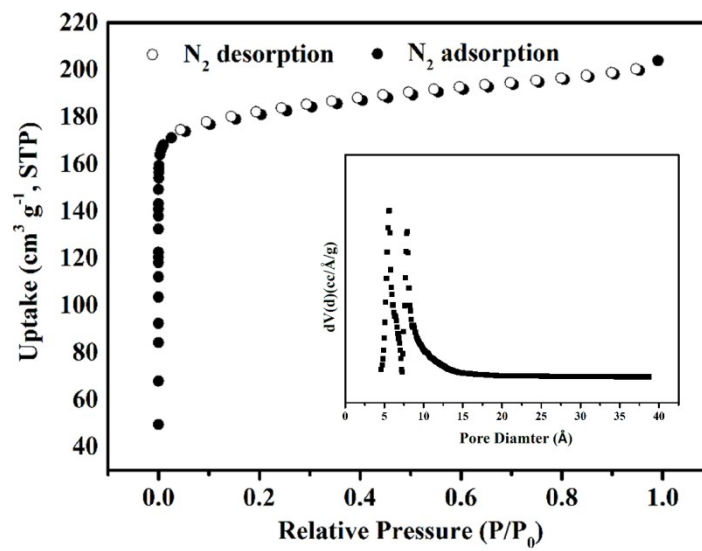


Figure S7. The N₂ sorption isotherm at 77K (P₀ = 101 KPa). Inset: the pore size distribution base on N₂ adsorption analysis.

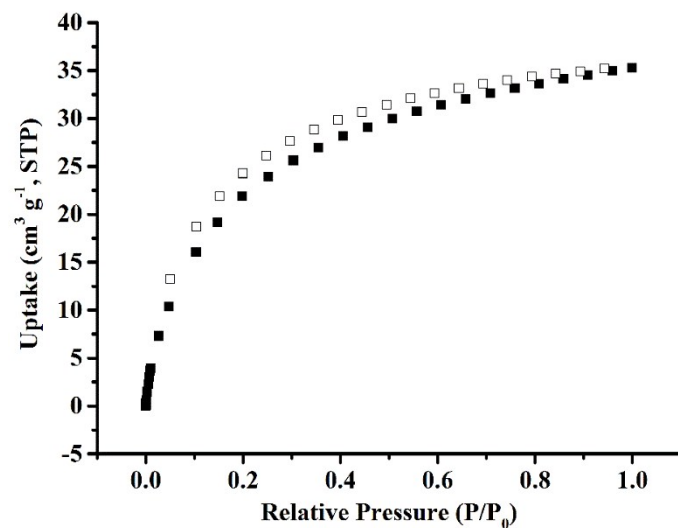


Figure S8. The CO₂ sorption isotherm at 273 K ($P_0 = 101$ KPa).

The sorption behaviour of compound **1** toward CO₂ was studied at 273 K and under 1bar, which is reversible and do not reach the saturated adsorption. It shows a maximum CO₂ uptake of 35 cm³ g⁻¹ at 273K.

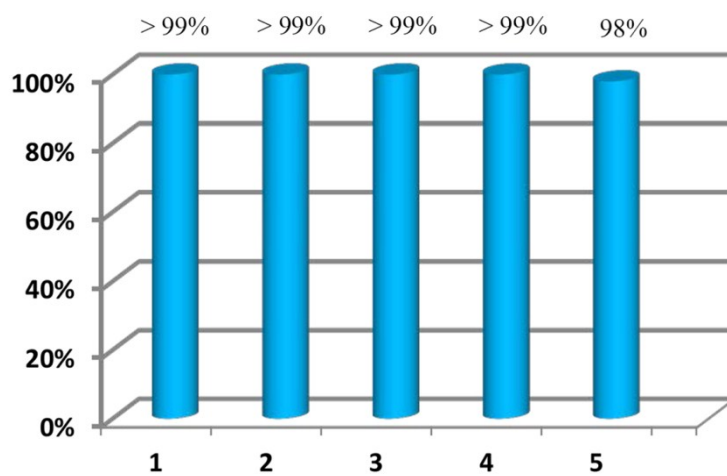
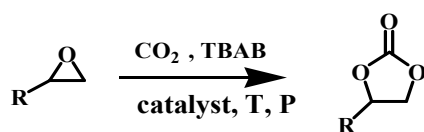
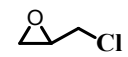
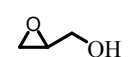
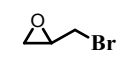
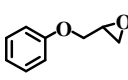
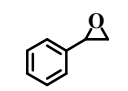


Figure S9. Histogram of recyclability study (five cycles) for catalytic activities of catalyst **1** in coupling of epichlorohydrin with CO₂.

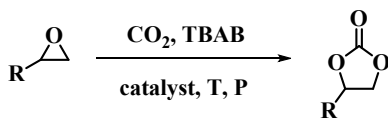
Table S2 Compound 1 catalyzed coupling of epoxides with CO₂.



Entry	Substrate	Time(h)	conversion(%)	TON	TOF
1		3	>99	4000	1333
2		3	>99	4000	1333
3		3	>99	4000	1333
3		3	64	2560	853
		6	85	3400	567
		9	>99	4000	444
4		3	28	1120	373
		6	50	2000	333
		9	59	2360	262
		12	68	2720	227

Reaction conditions: epoxide (20 mmol), catalyst (0.005 mmol, based on [Ni₄] cluster), and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K. The yields were determined by ¹H NMR analysis.

Table S3 Comparison with different MOF catalysts in the cycloaddition reaction of CO₂ and the same epoxies under similar conditions.



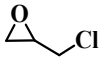
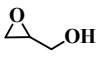
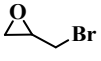
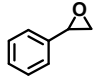
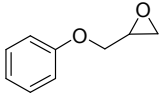
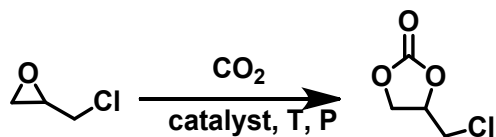
Substrate	Catalyst	T (°C)	P (MPa)	T (h)	TON	TOF (h ⁻¹)	Ref.
	Gea-MOF-1	120	2.0	6	593	99	3
	CHB(M)	120	1.2	6	44.6	7	4
	Ni(salphen)-MOF	80	2.0	4	300	75	5
	[Cu ₂ L]	100	1.0	2	1904	952	6
	{Ni ₄ L(OH) ₂ }	100	1.0	3	4000	1333	This work
	{[Eu(BTB)(phen)]}	70	0.1	12	19.6	1.6	7
	[Cu ₂ L]	100	1.0	2	2000	1000	6
	{Ni ₄ L(OH) ₂ }	100	1.0	3	4000	1333	This work
	[Cu ₄ (L ₁) _n]	25	0.1	48	440.0	9.2	8
	{Ni ₄ L(OH) ₂ }	100	1.0	3	4000	1333	This work
	Ni-TCPE-1	100	1.0	12	2000	167	9
	Ni-TCPE-2	100	1.0	12	1720	143	9
	Gea-MOF-1	120	2.0	6	567	95	3
	L _{cu'}	120	2.0	4	289	72	10
	{Ni ₄ L(OH) ₂ }	100	1.0	12	2680	223	This work
	Ni-TCPE-1	100	1.0	12	2000	167	9
	Ni(salphen)-MOF	80	2.0	4	196	49	5
	CHB(M)	120	1.2	6	44	7	4
	{Ni ₄ L(OH) ₂ }	100	1.0	9	4000	444	This work

Table S4 The time-control experiments conducted in coupling of CO₂ with a large excess of epichlorohydrin. Reaction condition: epichlorohydrin (120 mmol), catalyst (0.005 mmol, 0.0042 % based on the catalyst) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K. The conversion was determined by ¹H NMR analysis.



Entry	Catalyst	Co-catalyst	T (K)	P (MPa)	Time (h)	Yield (%)
1	{Ni ₄ L(OH) ₂ }	TBAB	373	1	6	84
2	{Ni ₄ L(OH) ₂ }	TBAB	373	1	10	91
3	{Ni ₄ L(OH) ₂ }	TBAB	373	1	14	>99

S3 The NMR spectrums

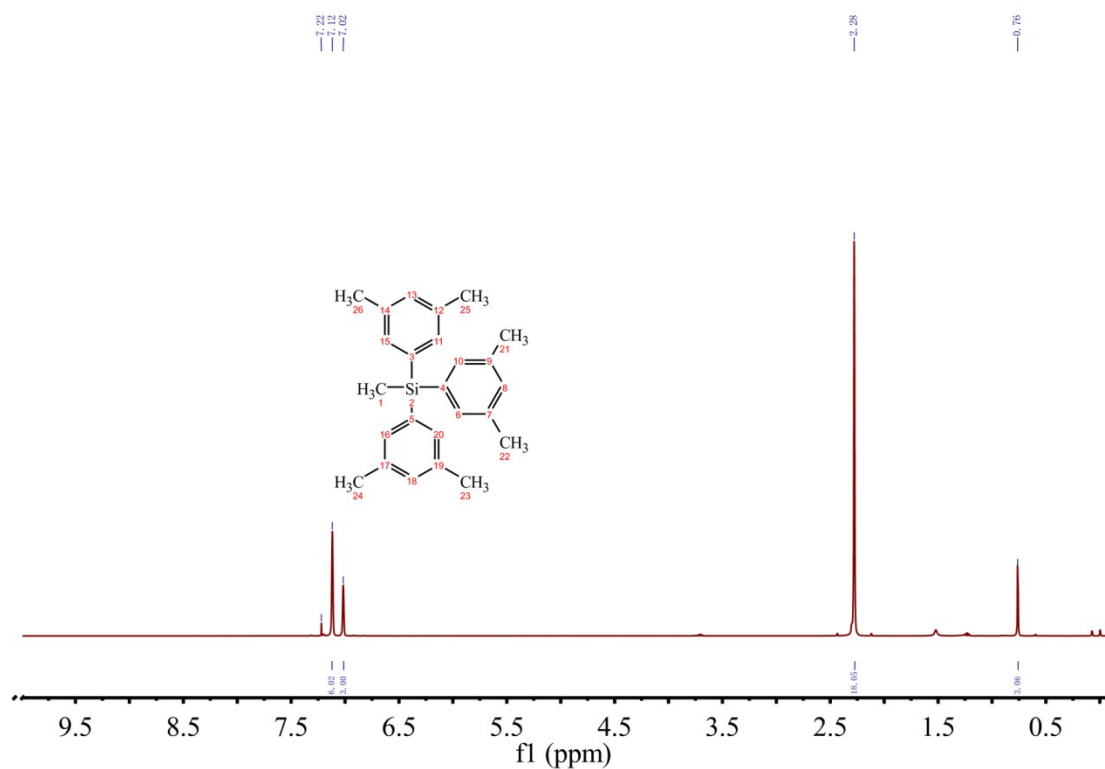


Figure S10. The ¹H-NMR spectrum of tris(3,5-dimethylphenyl)(methyl)silane

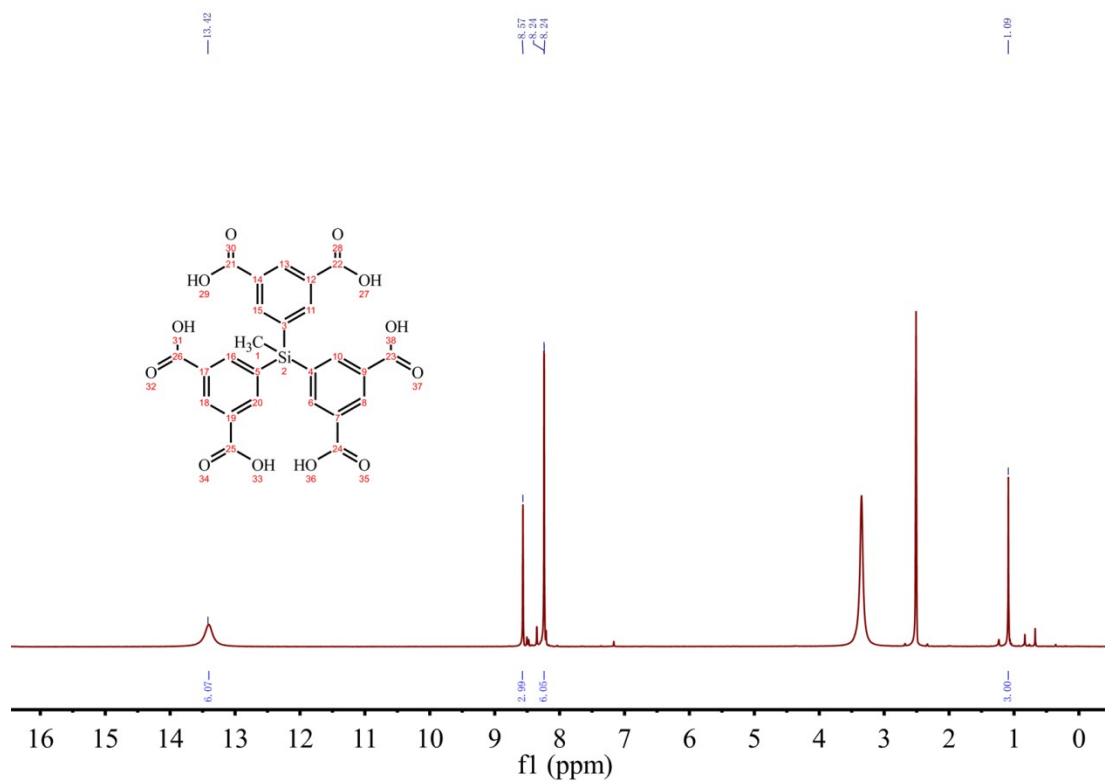


Figure S11. The ¹H-NMR spectrum of 5,5',5''-(methylsilanetriyl)trisophthalic acid.

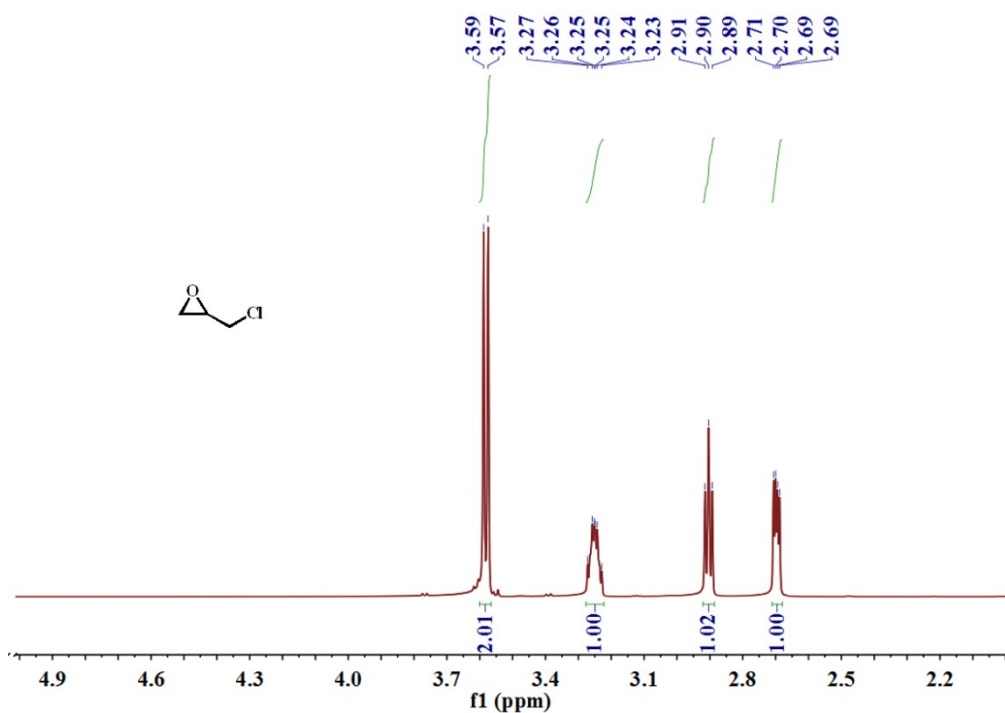


Figure S12 ^1H NMR spectra of epichlorohydrin (400 MHz, CDCl_3): $\delta = 3.58$ (d, $J = 8.0$ Hz, 2H, Cl- CH_2), 3.23 – 3.27 (m, 1H, O-CH), 2.90 (t, $J = 4.0$ Hz, 1H, O- CH_2), 2.70 (q, $J = 4.0$ Hz, 1H, O- CH_2).

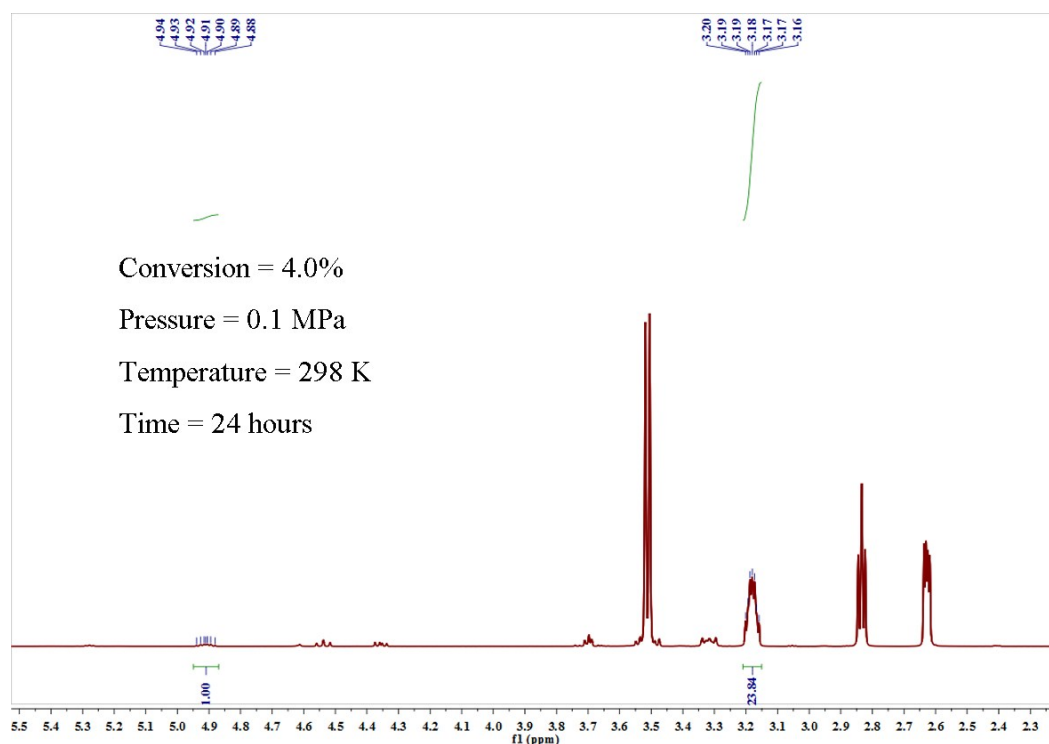


Figure S13. ^1H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 (400 MHz, CDCl_3): $\delta = 4.88 - 4.93$ (m, 1H, COO-CH), 4.53 (t, $J = 8.0$ Hz, 1H, COO- CH_2), 4.35 (q, $J = 8.0$ Hz, 1H, COO- CH_2), 3.65 – 3.74 (m, 1H, Cl- CH_2 of product), 3.50–3.52 (m, 0.10 H, Cl- CH_2 of chloromethyl-cyclopropane), 3.16 – 3.20 (m, 1H, O- CH_2), 2.83 (d, $J = 4.0$ Hz, 1H, O- CH_2), 2.63 (q, $J = 4.0$ Hz, 1H, O- CH_2).

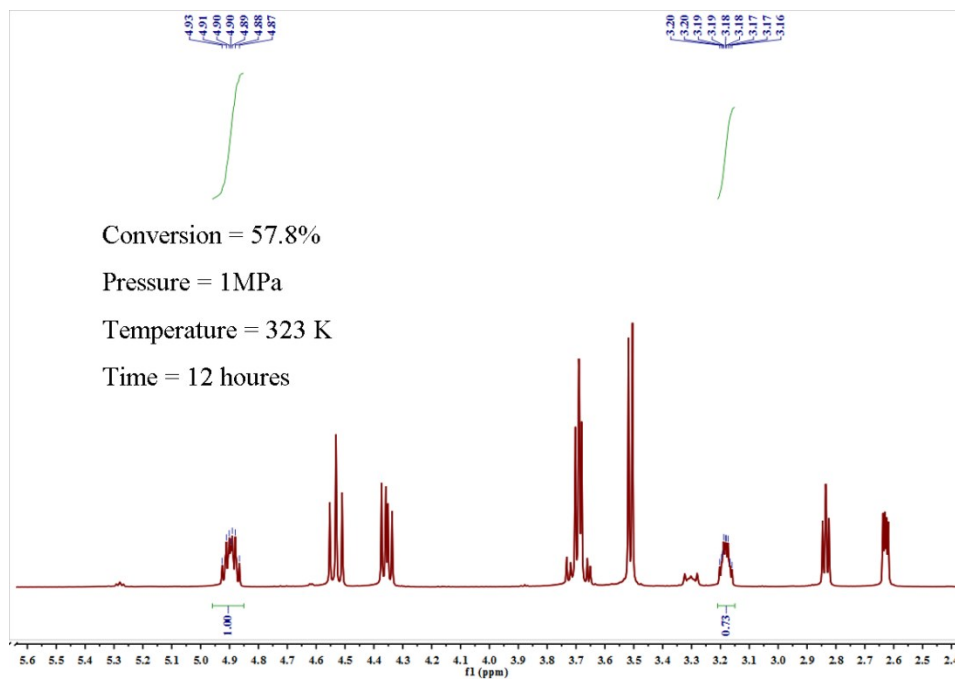


Figure S14 ^1H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 (400 MHz, CDCl_3)

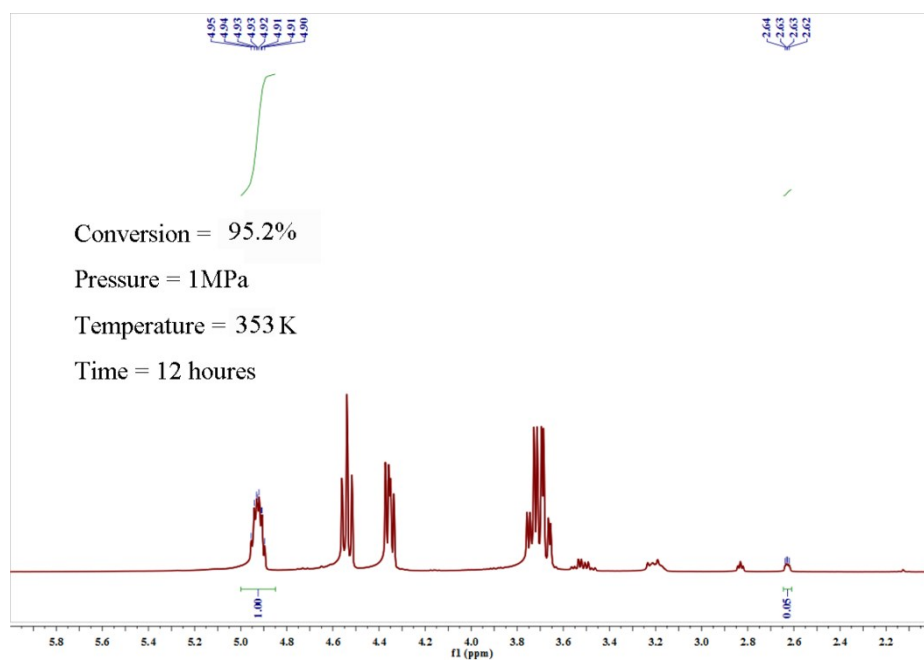


Figure S15 ^1H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 (400 MHz, CDCl_3)

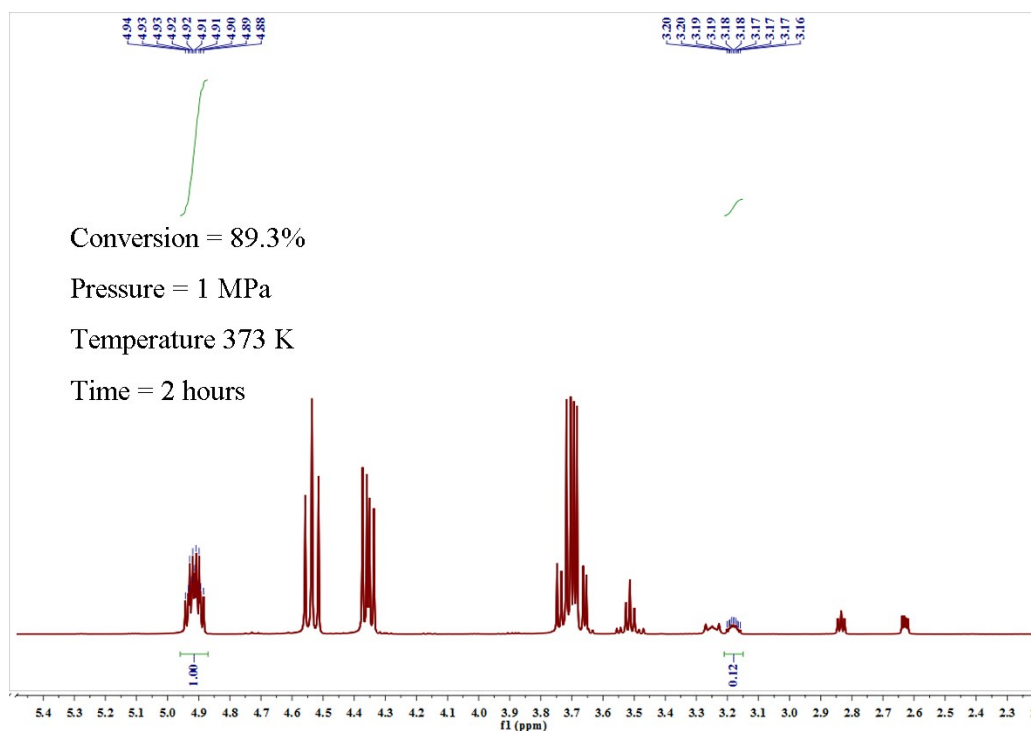


Figure S16 ^1H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 (400 MHz, CDCl_3)

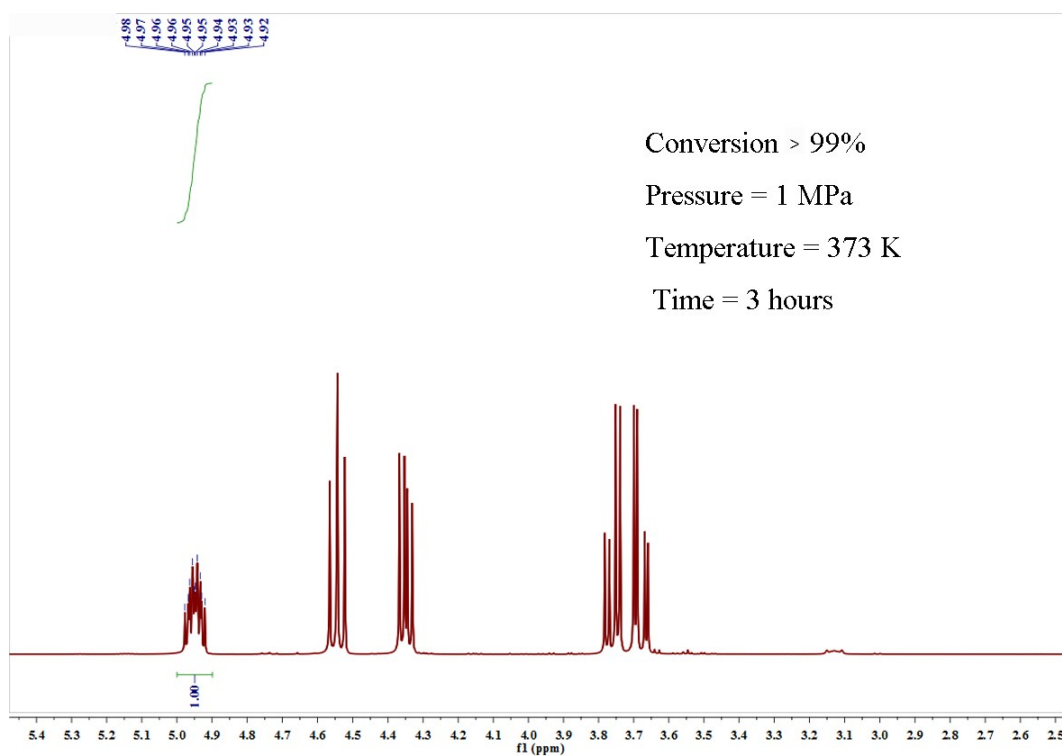


Figure S17 ^1H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 (400 MHz, CDCl_3)

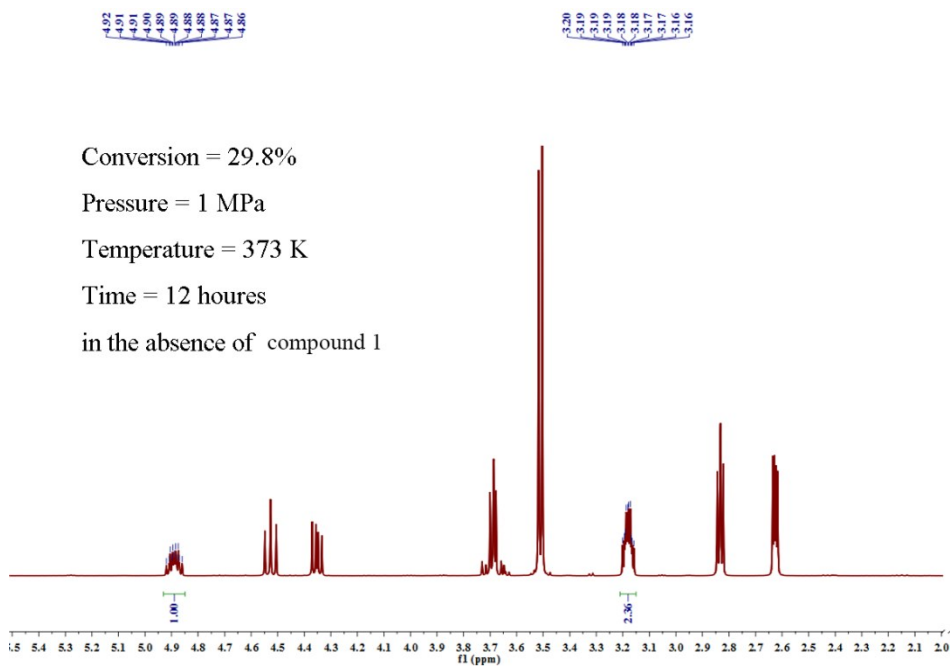


Figure S18 ^1H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 (400 MHz, CDCl_3)

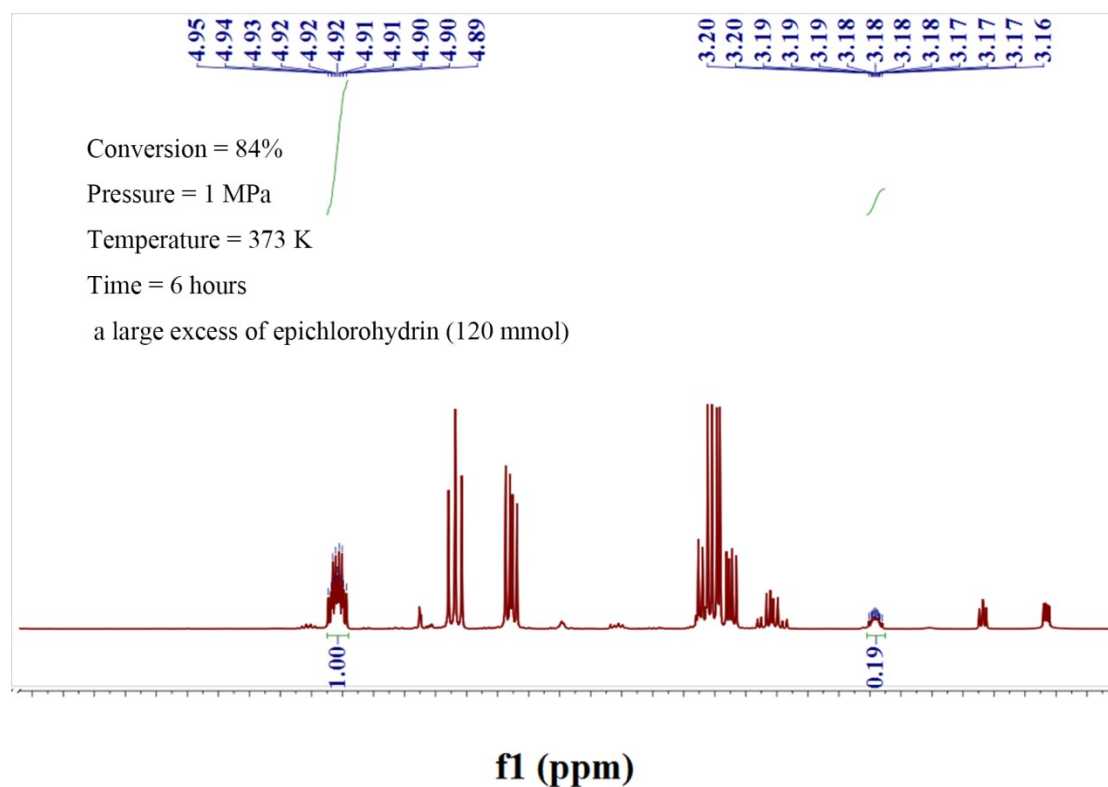


Figure S19. ^1H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 (400 MHz, CDCl_3)

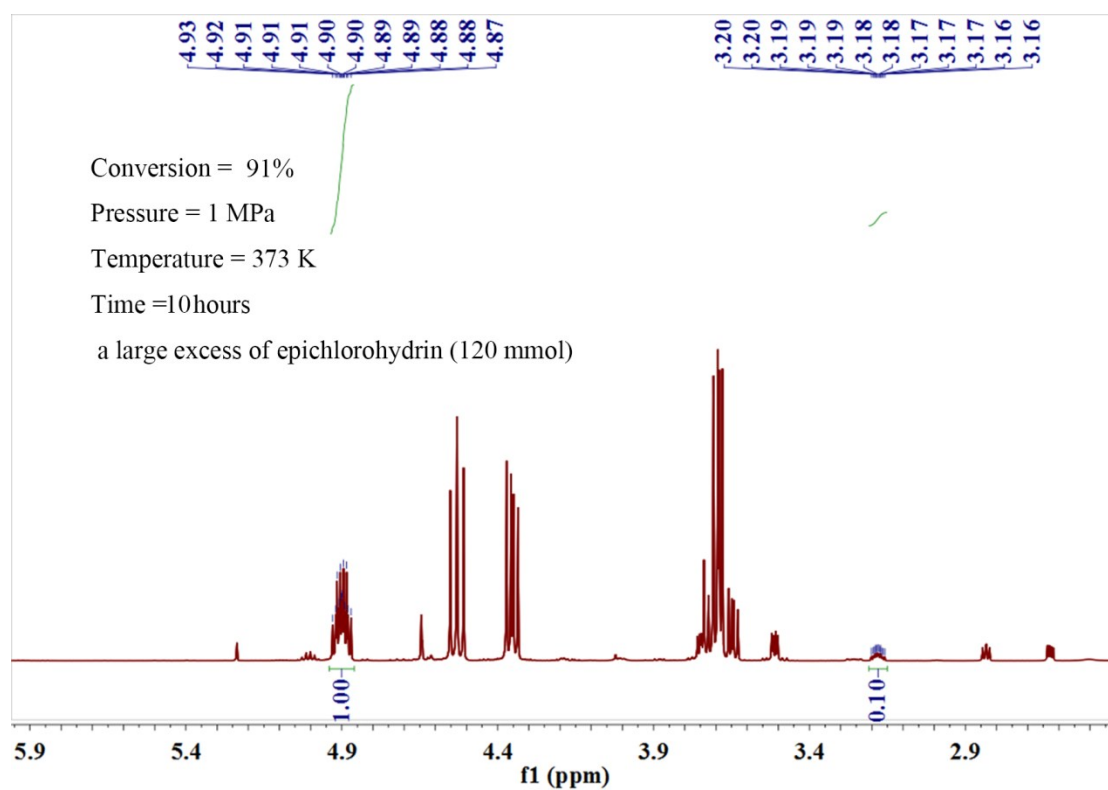


Figure S20. ^1H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 (400 MHz, CDCl_3)

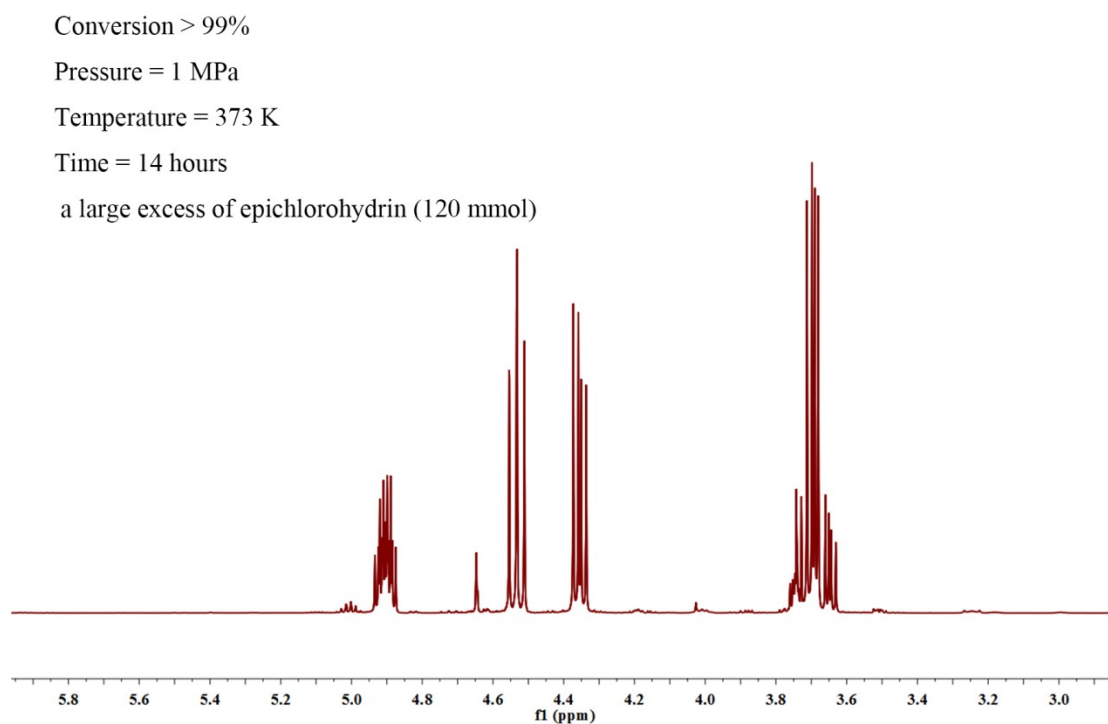


Figure S21. ^1H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 (400 MHz, CDCl_3).

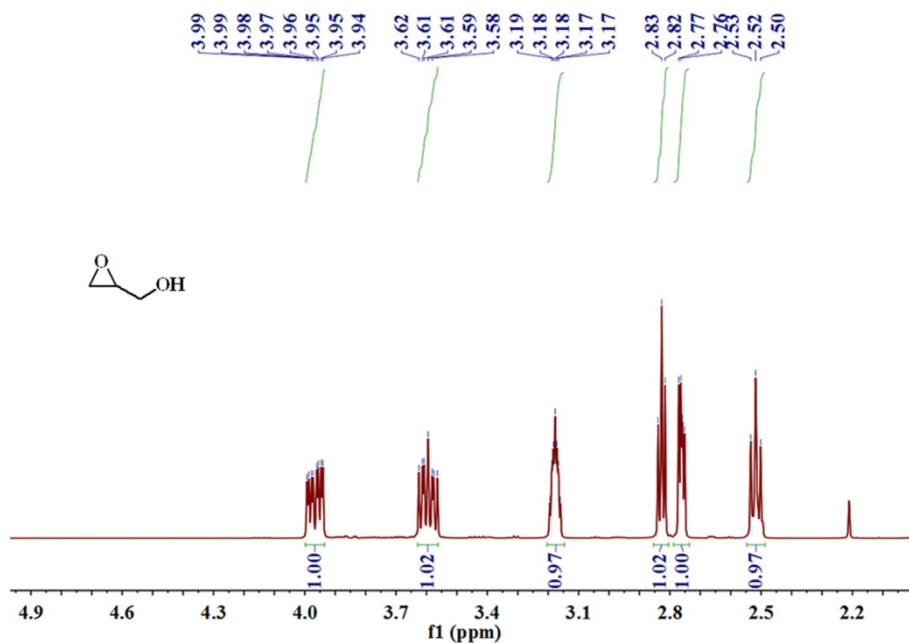


Figure S22. ^1H NMR spectra of glycidol (400 MHz, CDCl_3): $\delta = 3.94 - 3.99$ (m, 1H, HO- CH_2), 3.56 - 3.62 (m, 1H, HO- CH_2), 3.16 - 3.19 (m, 1H, O-CH), 2.83 (t, $J = 4.0$ Hz, 1H, O- CH_2), 2.76 (q, $J = 4.0$ Hz, 1H, O- CH_2), 2.52 (t, $J = 4.0$ Hz, 1H, -OH).

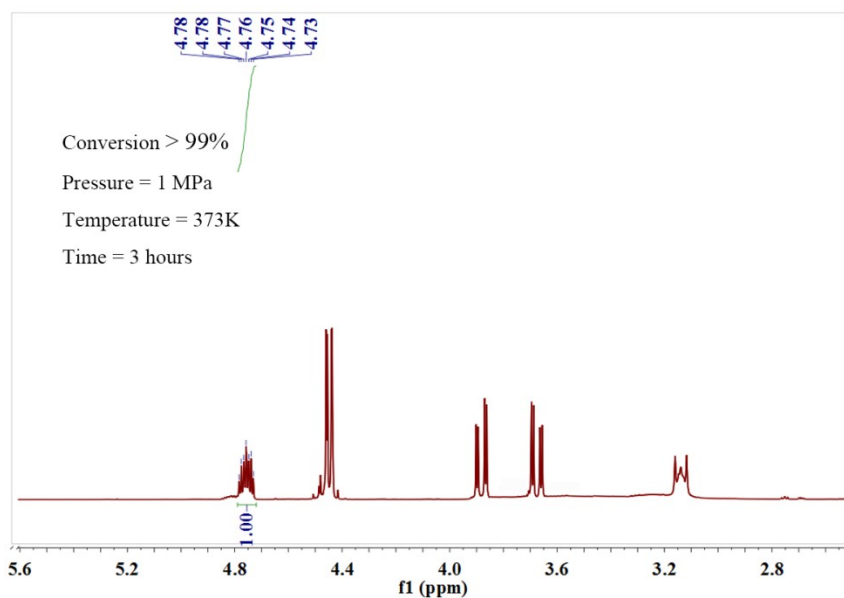


Figure S23. ^1H NMR spectra of the cycloaddition product of cyclopropyl-methanol with CO_2 (400 MHz, CDCl_3): $\delta = 4.73 - 4.78$ (m, 1H, COO-CH), 4.39 - 4.48 (m, 2H, HO- CH_2), 3.91 (dd, $J = 12.0$ Hz, 4.0 Hz, 1H, COO- CH_2), 3.65 (dd, $J = 12.0, 4.0$ Hz, 1H, COO- CH_2), 2.73 (br, 1H, -OH).

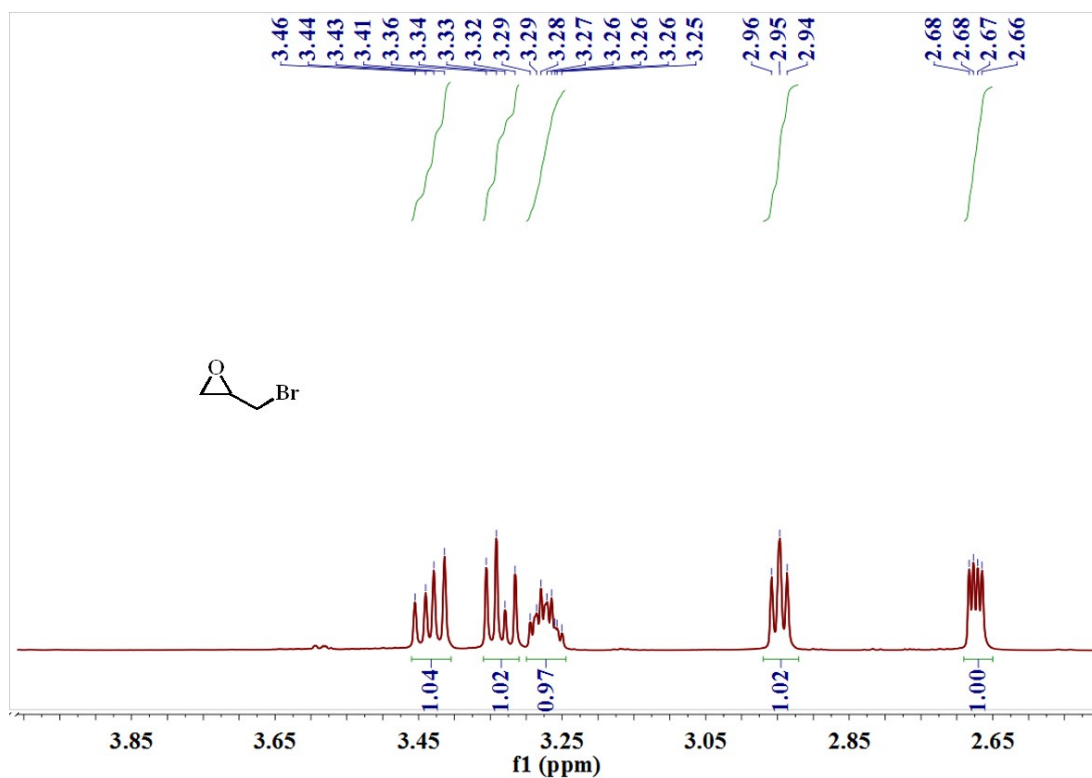


Figure S24. ^1H NMR spectra of epibromohydrin (400 MHz, CDCl_3): $\delta = 3.42$ (q, $J = 8.0$ Hz, 1H, Br- CH_2), 3.33 (q, $J = 8.0$ Hz, 1H, Br- CH_2), 3.25 – 3.29 (m, 1H, O- CH^*), 2.95 (t, $J = 4.0$ Hz, 1H, O- CH_2), 2.67 (q, $J = 4.0$ Hz, 1H, O- CH_2).

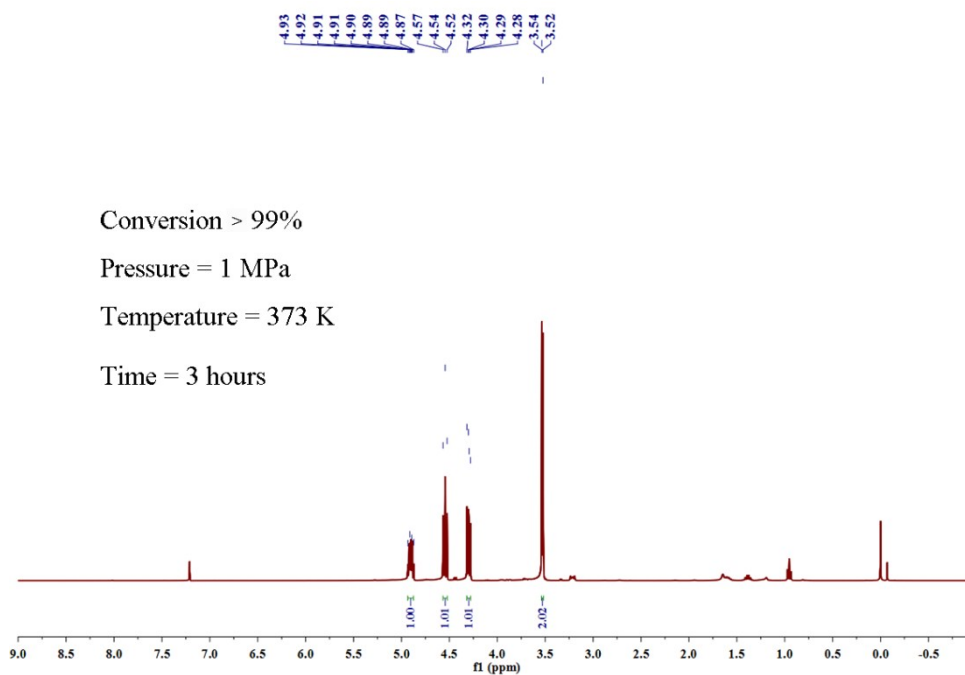


Figure S25. ^1H NMR spectra of the cycloaddition product of epibromohydrin and CO_2 for 3h (400 MHz, CDCl_3): $\delta = 4.88 - 4.95$ (m, 1H, COO- CH^* of product).

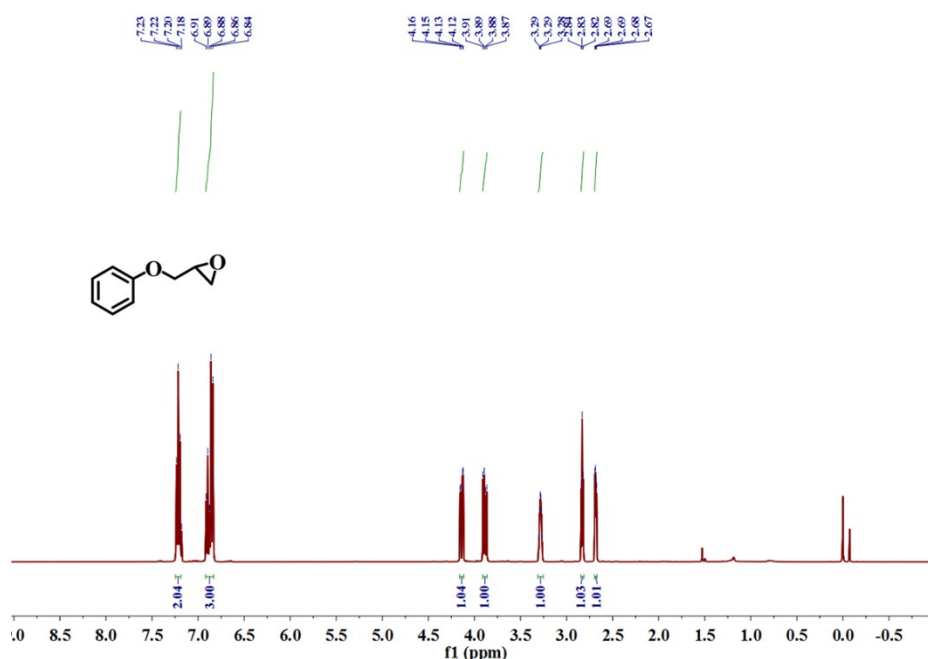


Figure S26. ^1H NMR spectra of 1,2-epoxy-3-phenoxypropane (400 MHz, CDCl_3) : $\delta = 7.18 - 7.23$ (m, 2H, Ar-H), 6.84 – 6.91 (m, 3H, Ar-H), 4.14 (q, $J = 4.0$ Hz, 1H, ArO-CH₂), 3.88 (q, $J = 4.0$ Hz, 1H, ArO-CH₂), 3.26 – 3.30 (m, 1H, O-CH), 2.83 (t, $J = 4.0$ Hz, 1H, O-CH₂), 2.68 (q, $J = 4.00$ Hz, 1H, O-CH₂).

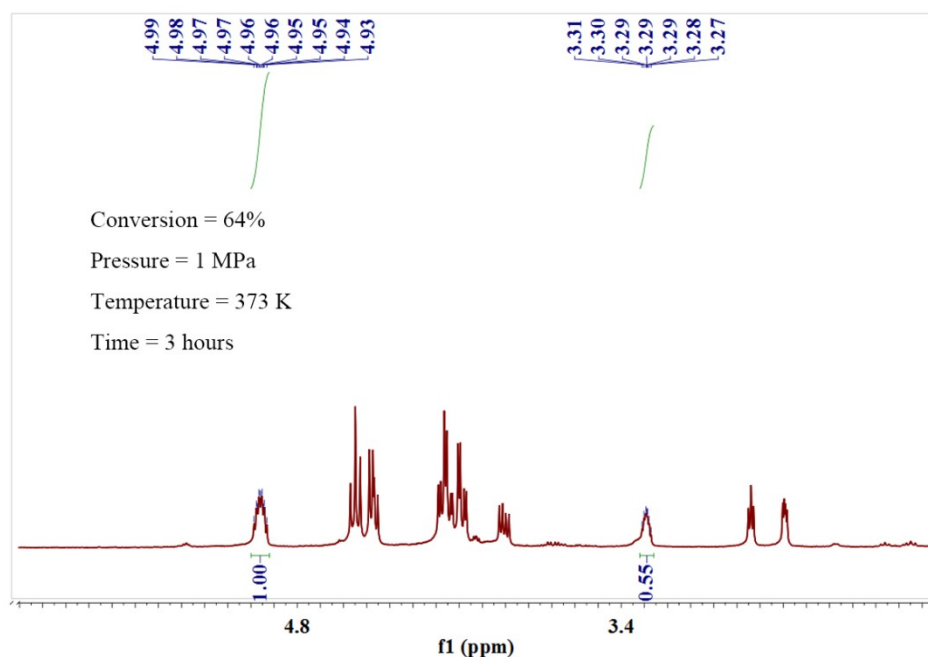


Figure S27. ^1H NMR of the cycloaddition product of 1,2-epoxy-3-phenoxypropane and CO_2 for 2h (400 MHz, CDCl_3): $\delta = 7.20 - 7.27$ (m, 3.12H, Ar-H), 6.88 – 6.97 (m, 1.47H, Ar-H), 6.83 – 6.87 (m, 2.79H, Ar-H), 4.93 – 4.99 (m, 1H, COO-CH), 4.55 (t, $J = 8.0$ Hz, 1H, COO-CH₂), 4.47 (t, $J = 8.0$ Hz, 1H, COO-CH₂), 4.19 – 4.13 (m, 1.46H, 1H - ArO-CH₂ of product and 0.46H - ArO-CH₂ of 1,2-epoxy-3-phenoxypropane), 4.07 (dd, $J = 8.0$ Hz, 4.0 Hz, 1H, ArO-CH₂ of product), 3.90 (q, $J = 8.0$ Hz, 0.46H, ArO-CH₂ of 1,2-epoxy-3-phenoxypropane), 3.28 – 3.31 (m, 0.46H, O-CH), 2.84 (t, $J = 4.0$ Hz, 0.46H, O-CH₂), 2.70 (q, $J = 4.0$ Hz, 0.46H, O-CH₂).

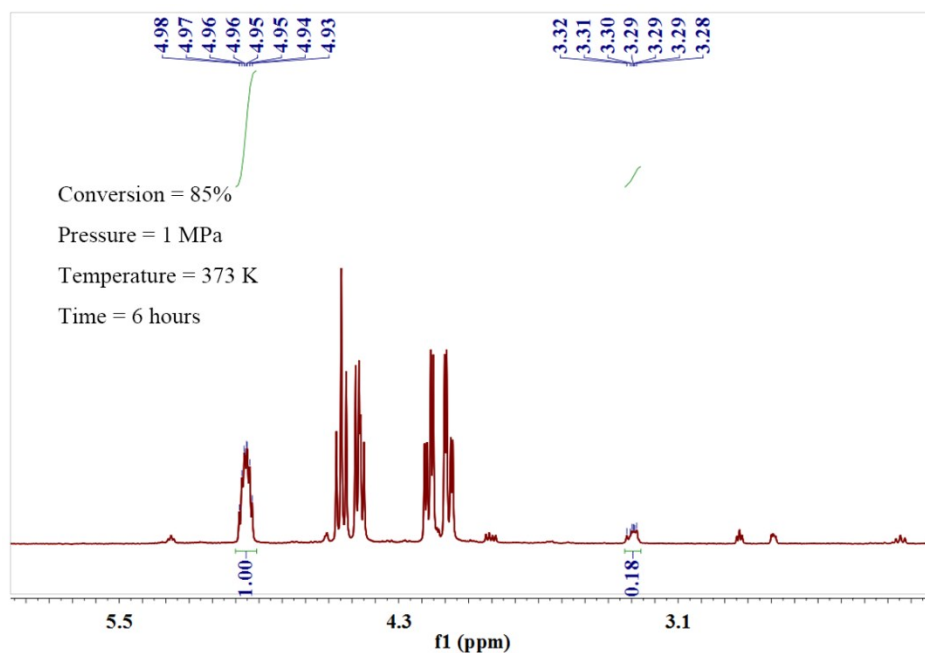


Figure S28. ^1H NMR of the cycloaddition product of 1,2-epoxy-3-phenoxypropane and CO_2 for 2h (400 MHz, CDCl_3): $\delta = 7.20 - 7.27$ (m, 3.12H, Ar-H), 6.88 – 6.97 (m, 1.47H, Ar-H), 6.83 – 6.87 (m, 2.79H, Ar-H), 4.93 – 4.99 (m, 1H, COO-CH), 4.55 (t, $J = 8.0$ Hz, 1H, COO- CH_2), 4.47 (t, $J = 8.0$ Hz, 1H, COO- CH_2), 4.19 – 4.13 (m, 1.46H, 1H - ArO- CH_2 of product and 0.46H - ArO- CH_2 of 1,2-epoxy-3-phenoxypropane), 4.07 (dd, $J = 8.0$ Hz, 4.0 Hz, 1H, ArO- CH_2 of product), 3.90 (q, $J = 8.0$ Hz, 0.46H, ArO- CH_2 of 1,2-epoxy-3-phenoxypropane), 3.28 – 3.31 (m, 0.46H, O-CH), 2.84 (t, $J = 4.0$ Hz, 0.46H, O- CH_2), 2.70 (q, $J = 4.0$ Hz, 0.46H, O- CH_2).

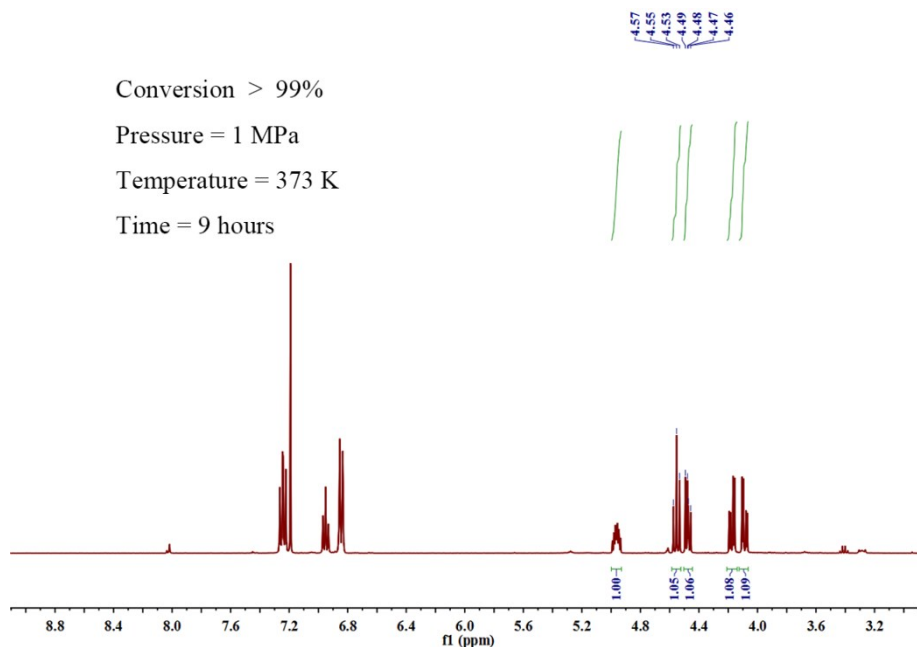


Figure S29 ^1H NMR spectra of the cycloaddition product of 1,2-epoxy-3-phenoxypropane and CO_2 for 6h (400 MHz, CDCl_3): $\delta = 7.24$ (t, $J = 8.0$ Hz, 2H, Ar-H), 6.95 (t, $J = 8.0$ Hz, 1H, Ar-H), 6.84 (d, $J = 8.0$ Hz, 2H, Ar-H), 4.94 – 4.99 (m, 1H, COO-CH), 4.55 (t, $J = 8.0$ Hz, 1H, COO- CH_2), 4.48 (t, $J = 8.0$ Hz, 1H, COO- CH_2), 4.18 (dd, $J = 8.0$ Hz, 4.0 Hz, 1H, ArO- CH_2 of product), 4.08 (dd, $J = 8.0$ Hz, 4.0 Hz, 1H, ArO- CH_2 of product).

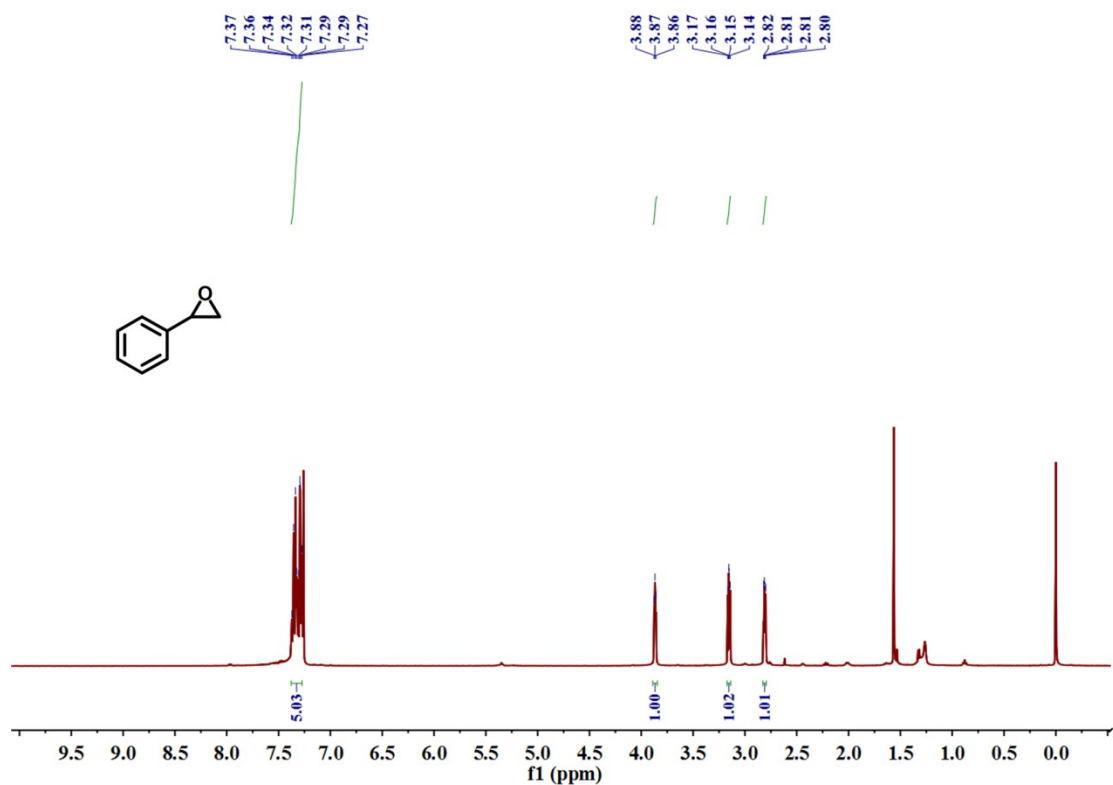


Figure S30. ^1H NMR spectra of styrene oxide (400 MHz, CDCl_3): $\delta = 7.27 - 7.37$ (m, 5H, Ar-H), 3.87 (t, $J=4.0$ Hz, 1H, O-CH), 3.16 (q, $J=4.0$ Hz, 1H, O- CH_2), 2.81 (q, $J = 4.0$ Hz, 1H, O- CH_2).

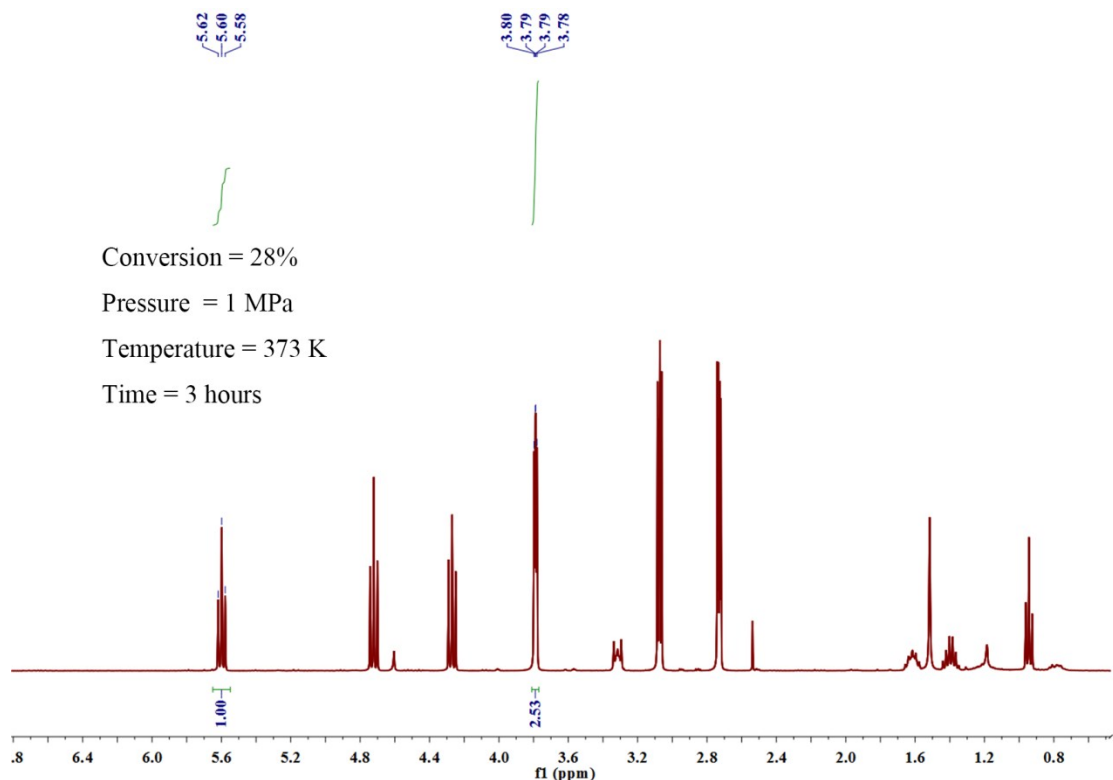


Figure S31. ^1H NMR spectra of the cycloaddition product of styrene oxide and CO_2 for 4h (400 MHz, CDCl_3): $\delta = 7.29 - 7.38$ (m, 5H, Ar-H), 7.19 - 7.26 (m, 2.58H, Ar-H), 5.60 (t, $J = 8.0$ Hz, 1H, COO-CH), 4.73 (t, $J = 8.0$ Hz, 1H, COO- CH_2), 4.27 (t, $J = 8.0$ Hz, 1H, COO- CH_2), 3.79 (q, $J = 4.0$ Hz, 0.70H, O-CH), 3.08 (q, $J = 4.0$ Hz, 0.70H, O- CH_2), 2.73 (q, $J = 4.0$ Hz, 0.70H, O- CH_2).

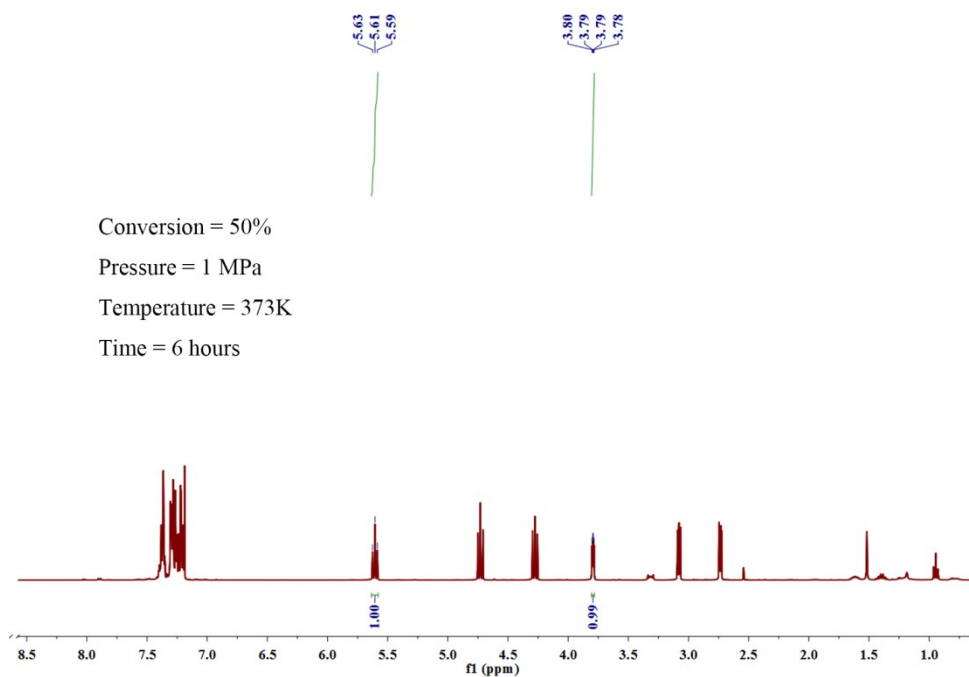


Figure S32. ^1H NMR spectra of the cycloaddition product of styrene oxide and CO_2 for 4h (400 MHz, CDCl_3): δ = 7.29 – 7.38 (m, 5H, Ar-H), 7.19 – 7.26 (m, 2.58H, Ar-H), 5.60 (t, J = 8.0 Hz, 1H, COO-CH), 4.73 (t, J = 8.0 Hz, 1H, COO- CH_2), 4.27 (t, J = 8.0 Hz, 1H, COO- CH_2), 3.79 (q, J = 4.0 Hz, 0.70H, O-CH), 3.08 (q, J = 4.0 Hz, 0.70H, O- CH_2), 2.73 (q, J = 4.0 Hz, 0.70H, O- CH_2).

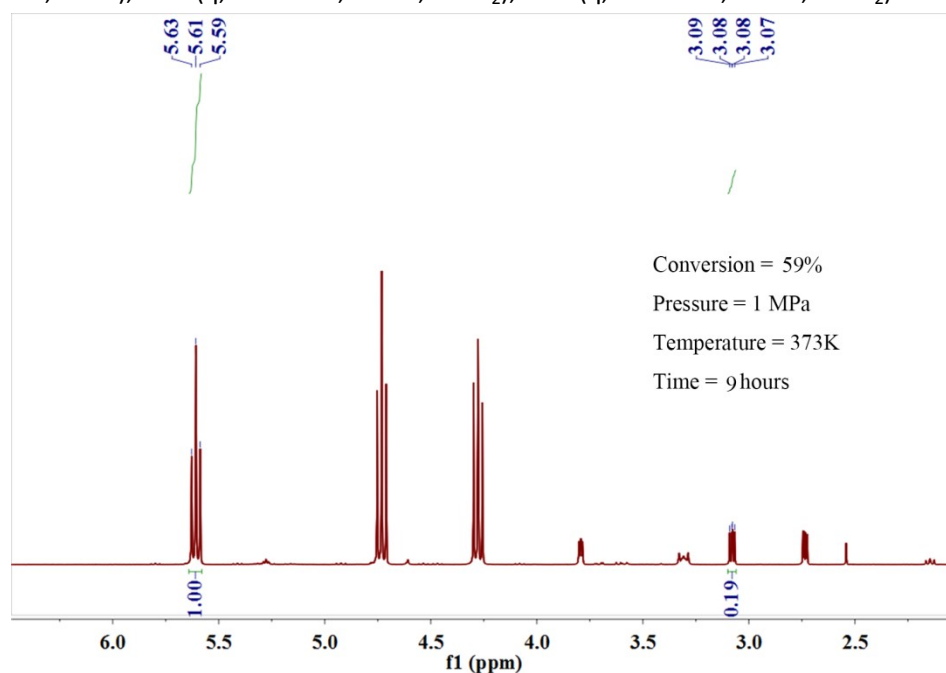


Figure S33. ^1H NMR spectra of the cycloaddition product of styrene oxide and CO_2 for 4h (400 MHz, CDCl_3): δ = 7.29 – 7.38 (m, 5H, Ar-H), 7.19 – 7.26 (m, 2.58H, Ar-H), 5.60 (t, J = 8.0 Hz, 1H, COO-CH), 4.73 (t, J = 8.0 Hz, 1H, COO- CH_2), 4.27 (t, J = 8.0 Hz, 1H, COO- CH_2), 3.79 (q, J = 4.0 Hz, 0.70H, O-CH), 3.08 (q, J = 4.0 Hz, 0.70H, O- CH_2), 2.73 (q, J = 4.0 Hz, 0.70H, O- CH_2).

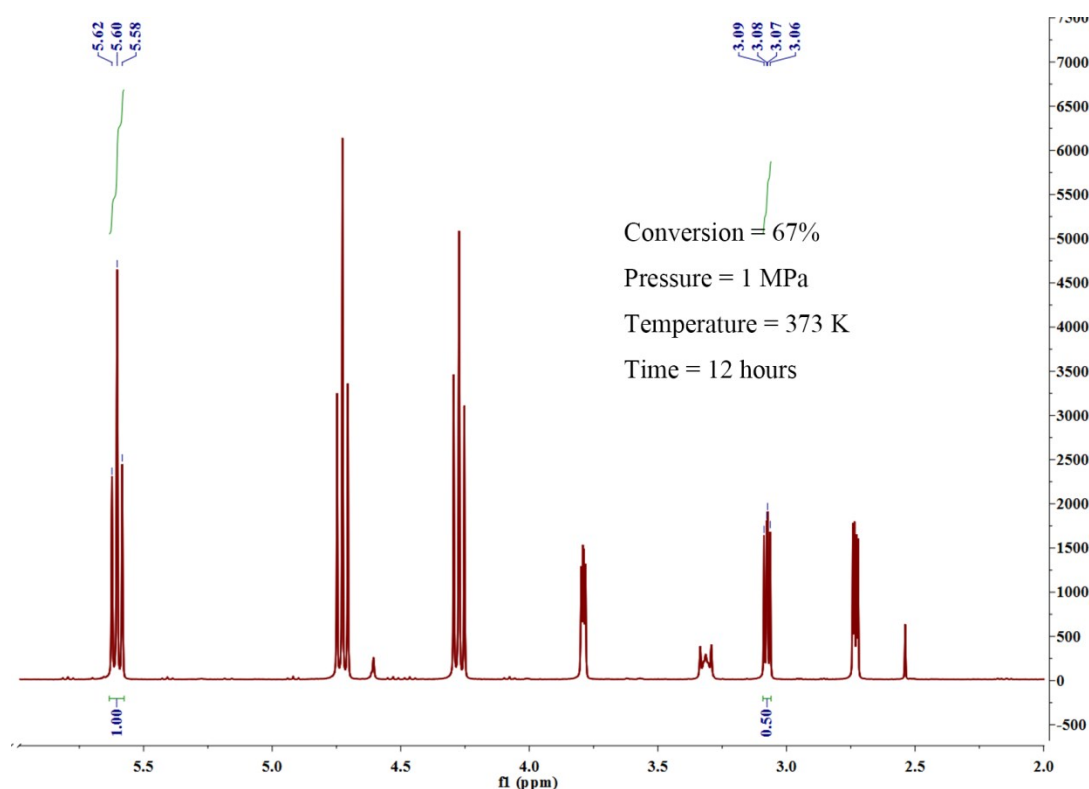


Figure S34. ^1H NMR spectra of the cycloaddition product of styrene oxide and CO_2 for 4h (400 MHz, CDCl_3): $\delta = 7.29 - 7.38$ (m, 5H, Ar-H), $7.19 - 7.26$ (m, 2.58H, Ar-H), 5.60 (t, $J = 8.0$ Hz, 1H, COO-CH), 4.73 (t, $J = 8.0$ Hz, 1H, COO- CH_2), 4.27 (t, $J = 8.0$ Hz, 1H, COO- CH_2), 3.79 (q, $J = 4.0$ Hz, 0.70H, O-CH), 3.08 (q, $J = 4.0$ Hz, 0.70H, O- CH_2), 2.73 (q, $J = 4.0$ Hz, 0.70H, O- CH_2).

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