Supporting Information

An Ultrastable Zirconium-phosphonate Framework as Bifunctional Catalyst for Highly Active CO_2 Chemical Transformation

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Supplementary Index

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S1. Materials and Methods

1.1 General information

Materials and Instrument All commercial chemicals were used without further purification except for organo-phosphonate ligand H_8L, which was synthesized by a modified procedure documented previously.[1]

Powder X-ray diffraction (PXRD) was carried out with a MiniFlex 600 X-ray powder diffractometer equipped with a Cu sealed tube (λ = 1.541 78 Å) at 40 kV and 40 mA. Elemental analyses for C, H, and N were performed by a VarioEL analyzer. Thermal gravimetric analysis (TGA) was conducted under an air atmosphere with a heating rate of 10 ^{o}C/min on a SDT 2960 Simultaneous DSC-TGA of TA instruments up to 800 ^{o}C. The infrared (IR) spectra (diamond) were recorded on a Nicolet 7600 FT-IR spectrometer within the 4000-500 cm^{-1} region. ^{1}H 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 ^{1}H spectroscopy.

1.2 Synthesis of compound Zr(H_4L)

$ZrOCl_2 \cdot 8H_2O$ (0.2 mmol, 64 mg) and H_8L (0.2 mmol, 131 mg) were dissolved in a mixed distilled water (3 ml)-methanol (1 ml) in the presence of HF (200 μL) as a mineralizer. The mixture was heated at 180 ^{o}C oven for 3 days. After the autoclave was cooled to room temperature, light-yellow block-shaped single crystals suitable for single-crystal X-ray crystallographic analysis were obtained. Then, the mother liquor was decanted, and the resulting crystals were dried at room temperature overnight. Yield: 96 mg (65 % based on Zr^{IV}). Phase purity was confirmed by PXRD analysis (Figure S2). FTIR (cm^{-1}): 1611 (w), 1582 (w), 1514 (vs), 1419 (s), 1364 (s), 1257 (m), 1172 (m), 1102(w), 1061 (vs), 872 (w), 855 (m), 764 (w), 717 (w), 639 (w). Elemental analysis calca (%) for $ZrSiC_{24}P_4O_{12}H_{20}$ (Mr = 743.6): C, 38.76; H, 2.71. Found: C, 38.88; H, 2.62.

1.3 Single-Crystal X-ray Crystallography

Single-crystal X-ray diffraction (SXRD) data of compound Zr(H_4L) were collected on a Bruker diffractometer using Cu K*α* radiation (λ = 1.54178 Å) at 293 K. Data processing was accomplished with the SAINT processing program.[2] 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.[3] 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 Zr(H_4L) was determined by single-crystal X-ray diffraction.

Crystallographic data for Zr(H_4L) (1502488) 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.

1.4 Stability Test

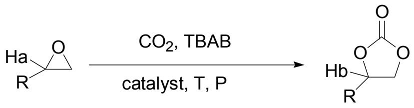
Several batches of about 10 mg of freshly synthesized samples were added into vials containing 4 mL of HCl solutions (2 M, 4 M, 6 M, 8 M, 10 M and concentrated HCl), aqueous solutions (pH = 1-12), pure water, aqua regia and various organic solvents (propanol, isopropanol, ethanol, methanol, acetone, tetrachloromethane, trichloromethane, dichloromethane, n-hexane, acetonitrile, DMF and DMA), respectively. After immersion in those solutions for given times (1, 3, 5 and 7 days) at room temperature or at 100 °C, $Zr(H_4L)$ samples were centrifuged and then dried naturally.

1.5 Catalysis

Typically, $Zr(H_4L)$ (0.01 mmol, 7.4 mg), tetrabutylammonium bromide (TBAB) (0.3 mmol, 90 mg), and epoxides (30 mmol, 2775 mg for epichlorohydrin, 4100 mg for epibromohydrin, 3600 mg for styrene oxide, 4500 mg for 1,2-epoxy-3-phenoxypropane) were added to a 10 mL autoclave reactor. The loading of the catalyst is a 0.33 ‰ ratio based on the epoxide. The reactor was pressurized to 1 MPa with CO_2 under a constant pressure for 10 min to equilibrate the system. When the pressure of CO_2 decreased to 0.5 MPa, the reactor was pressurized to 1 MPa again. After given reaction time, the reactor was put into ice bath for 30 min and depressurized. A small aliquot of the supernatant reaction mixtures was dissolved in 0.8 mL of $CDCl_3$. 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 the next cycle, and the supernatant was collected.

1.6 Cycloaddition of CO_2 to epoxides

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



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

S2 Supplementary tables and figures

Table S1 Crystallographic data for compound Zr(H_4L).

compound	**1**
Formula	$ZrSiC_{24}P_4O_{12}H_{20}$
F_w	743.61
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	9.9688(2)
b, Å	19.2157(4)
c, Å	14.5392(3)
β, °	99.702(2)
V, $Å^3$	2745.26(11)
Z	4
D_c, mg/mm^3	1.799
μ, mm^{-1}	6.500
reflection collected	5132
GOF on F^2	1.054
R_1/wR_2 ($I > 2\sigma(I)$)	0.0489/ 0.1369
R_1/wR_2 (all data)	0.0612/ 0.1514

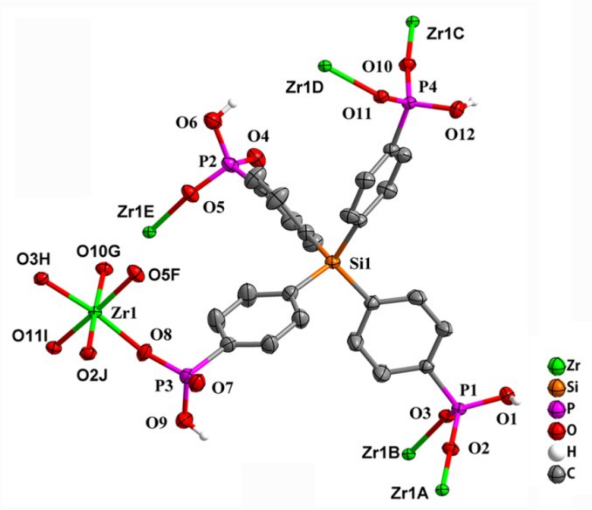


Figure S1 ORTEP representation of the coordination environment in Zr(H_4L) with thermal ellipsoids set at 50% probability. The asymmetric codes: A, -x, 0.5+y, 0.5-z; B, -1+x, 1.5-y,-0.5+z; C, 1-x, 0.5+y, 1.5-z; D, x, 1.5-y, 0.5+z; E, -1+x, y, z; F, 1+x, y, z; G, 1-x, -0.5+y, 1.5-z; H, 1+x, 1.5-y, 0.5+z; I, x, 1.5-y,0.5+z; J, 1-x, -0.5+y, 0.5-z. Hydrogen atoms bonded to carbon atoms are omitted for clarity.

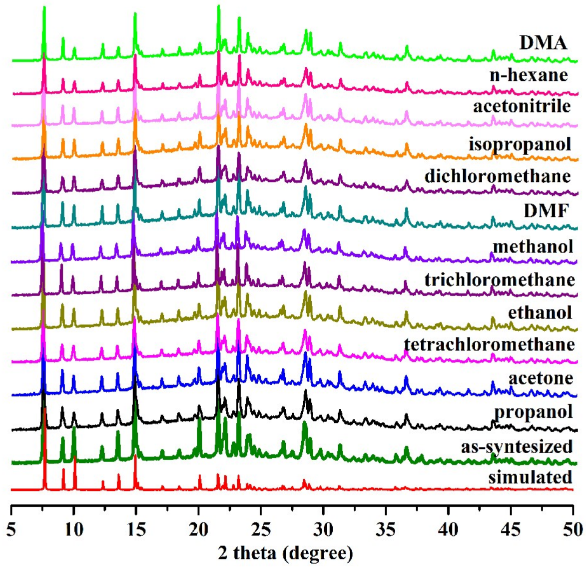


Figure S2 PXRD patterns of Zr(H_4L) upon the treatment with various organic solvents.

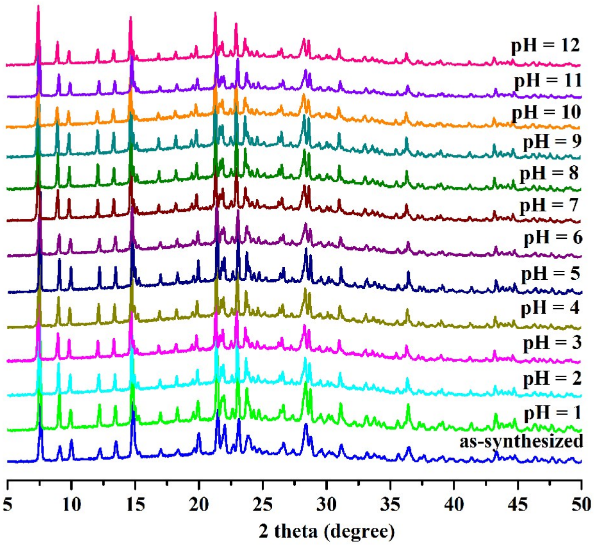


Figure S3 PXRD patterns of Zr(H_4L) upon the treatment using aqueous solution with a wide range of pH values (1 - 12).

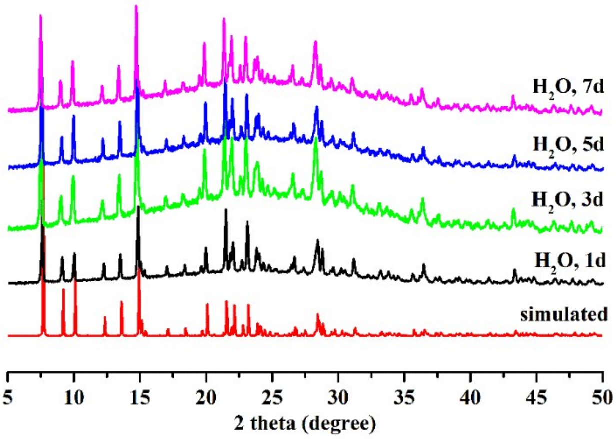


Figure S4 PXRD patterns of Zr(H_4L) upon the treatment with water.

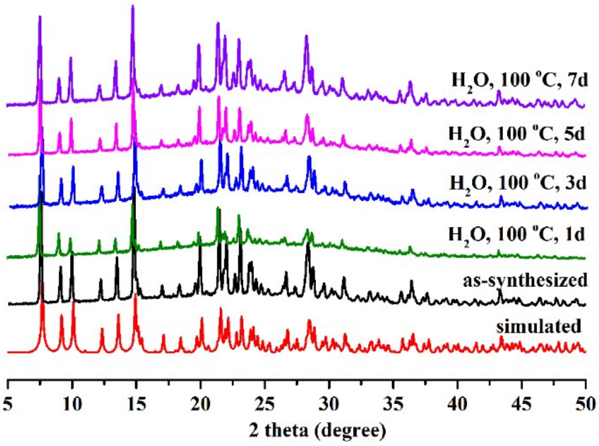


Figure S5 PXRD patterns of Zr(H_4L) upon the treatment with boiling water.

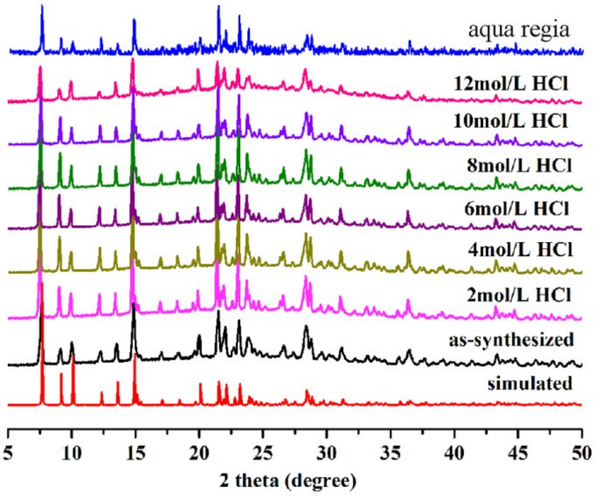


Figure S6 PXRD patterns of Zr(H_4L) after the treatment of HCl solution with different concentrations as well as aqua regia.

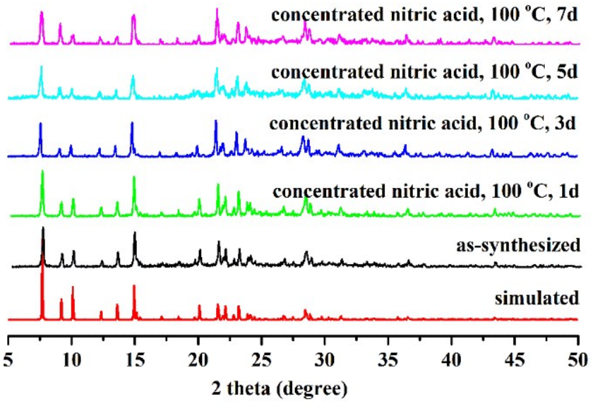


Figure S7 PXRD patterns of Zr(H_4L) upon the treatment with concentrated HNO_3 solution at 100 °C.

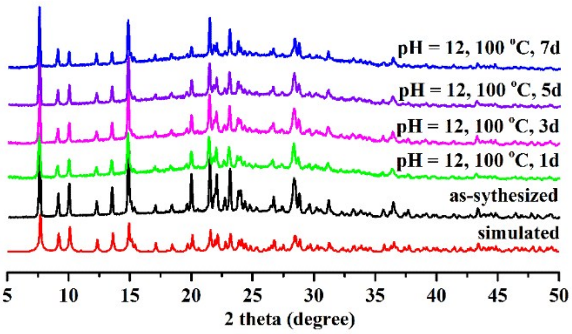


Figure S8 PXRD patterns of Zr(H_4L) upon the treatment with NaOH solution (pH = 12) at 100 °C.

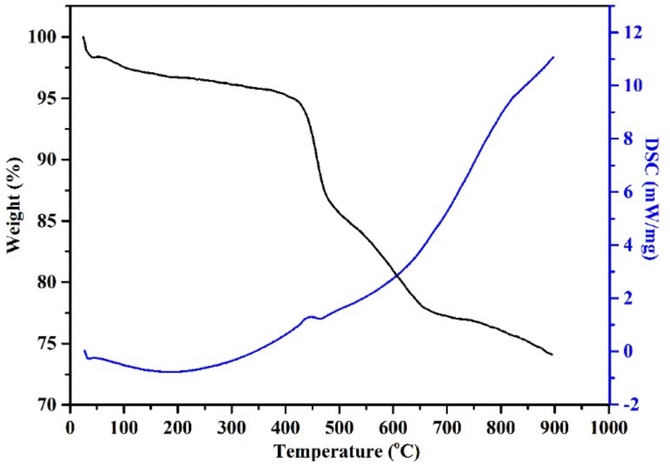
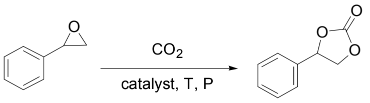


Figure S9 Thermogravimetric analysis data for Zr(H_4L).

Table S2 Comparison of chemical stability conditions of selected stable MOFs.

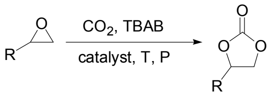
MOFs	Metals	Ligands	Stable conditions	Ref.
PCN-57	Zr	2',3',5',6'-tetramethylterphenyl-4,4''-dicarboxylic acid	pH = 2-11 solutions for 2 days	4
PCN-222	Zr	tetrakis (4-carboxyphenyl) porphyrin	Concentrate HCl or boiling H_2O for 24h	5
PCN-223	Zr	tetrakis (4-carboxyphenyl) porphyrin	pH = 0-10 solutions for 24h	6
PCN-224	Zr	tetrakis (4-carboxyphenyl) porphyrin	pH = 0-11 solutions for 24h	7
PCN-225	Zr	tetrakis (4-carboxyphenyl) porphyrin	Boiling water or pH = 1-11 solutions for 12h	8
PCN-777	Zr	4,4',4''-s-triazine-2,4,6- triyl-tribenzoic acid	pH = 3-11 solutions for 12h	9
UiO-66-$(CH_3)_2$	Zr	2,5-dimethylterephthalic acid	pH = 1-14 solutions for 2h	10
Zr-DTDC	Zr	3,4-Dimethylthieno[2,3-b] thiophene-2,5-dicarboxylicacid	Boiling water or aqueous solutions over a wide pH range (from 8 M HCl to pH of 12) for 1 day; pH = 0-11 solutions or boiling water for 7 days	11
BUT-12	Zr	5'-(4-carboxyphenyl)-2',4',6'-trimethyl-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid	Boling water for 7 days; concentrated HCl for 24 h; NaOH solution for 24 h	12
BUT-13	Zr	6,6',6''- (2,4,6-trimethylbenzene-1,3,5-triyl)tris(2-naphthoic acid)	The same to BUT-12	12
DUT-67	Zr	2,5-Thiophenedicarboxylic	Concentrated HCl for 3 days.	13
DUT-68	Zr	2,5-Thiophenedicarboxylic	Concentrated HCl for 3 days.	13
Zr(H_4L)	Zr	tetraphenylsilane tetrakis-4-phosphonic acid	**Concentrated HNO_3 at 100 ^{o}C for 7 d; pH = 12 aqueous solution at 100 ^{o}C for 7 d; aqua regia for 24h**	**This work**
$Ni_3(BTP)_2$	Ni	1,3,5-tris(1H-pyrazol-4-yl)benzene	Boiling aqueous solutions of pH = 2-14 for 2 weeks.	14
PCN-601	Ni	5,10,15,20-tetra(1H-pyrazol-4-yl)-porphyrin	saturated NaOH at 100 °C for 24 h	15
PCN-250(Fe_2Co)	Fe; Co	3,3',5,5'-Azobenzenetetracarboxylic	pH = 1-11 solutions for 24h.	16
ZIF-8	Zn	2-methylimidazole	8 M NaOH at 100 ^{o}C for	17
PCN-600	Fe	tetrakis (4-carboxyphenyl) porphyrin	pH = 2-11 solutions for 24h.	18
LaBTB	La	1,3,5-tris (4-carboxyphenyl) benzene	pH = 2 solution (60 ^{o}C) or pH = 14 solution (60 ^{o}C or 100 ^{o}C) for 3 days.	19
Eu_2(D-cam)($Himdc$)$_2$	Eu	D-camphoric acid; 4,5-imidazole dicarboxylic	pH = 2-13 solutions for 2 weeks.	20
Cd_3(L)(bipy)$_2$	Cd	hexa[4-(carboxyphenyl) oxamethyl]-3-oxapentane	pH = 2-13 solutions for 24h; water for 7 days.	21

Table S3 Control experiments of cycloaddition of CO_2 and styrene oxide as the model reaction. Reaction conditions: styrene oxide (30 mmol), catalyst (0.01 mmol), and TBAB (0.3 mmol). The yields were determined by ^1H NMR analysis. The optimal reaction was determined to be at 373 K and 1 MPa.



Entry	Catalyst	Co-catalyst	T (K)	P (MPa)	Time (h)	Yield (%)
1	$Zr(H_4L)$	TBAB	298	0.1	12	4
2	$Zr(H_4L)$	TBAB	298	0.1	24	7
3	$Zr(H_4L)$	TBAB	298	0.1	48	8.7
4	$Zr(H_4L)$	TBAB	323	1	12	7
5	$Zr(H_4L)$	TBAB	373	1	6	51
6	$Zr(H_4L)$	TBAB	373	1	12	95
7	$Zr(H_4L)$		373	1	12	0

Table S4 $Zr(H_4L)$-catalyzed coupling of epoxides with CO_2. Reaction conditions: epoxide (30 mmol), catalyst (0.01 mmol, 0.33‰ 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.



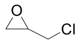
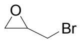
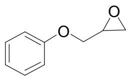
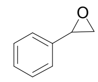
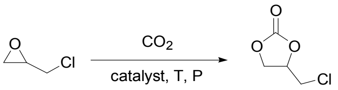
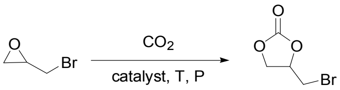
Entry	Substrates	Time (h)	Conversion (%)	TON	TOF (h^{-1})
1		2	91	2730	1365
2		2	97	2910	1455
3		2	64	1830	915
		4	86	2580	645
		6	>99	3000	500
4		6	51.2	1536	256
		12	95.2	2856	238

Table S5 Comparison with different MOF catalysts in the cycloaddition reaction of CO_2 and epichlorohydrin.



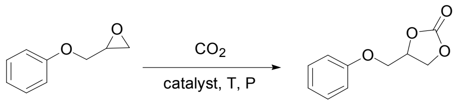
Catalyst	Loading of catalyst (‰)	T (K)	P (MPa)	T (h)	TON	TOF (h^{-1})	Ref.
Gea-MOF-1	1.5	393	2.0	6	593	99	22
CHB (M)	16.1	393	1.2	6	44.6	7	23
Ni(salphen)-MOF	2.8	353	2.0	4	300	75	24
MOF-5	6.5	323	0.1	12	22.3	2	25
$[Cu_4(L_1)]_n$	20	298	0.1	48	425	9	26
$Zr(H_4L)$	0.33	373	1.0	2	2730	1365	**This work**

Table S6 Comparison with the only MOF catalyst reported in the cycloaddition reaction of CO_2 and epibromohydrin. *: the values were obtained through recalculation on the basis of the corresponding calculation formulas.



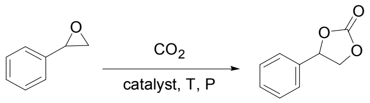
Catalyst	Loading of catalyst (‰)	T (K)	P (MPa)	T (h)	TON	TOF (h^{-1})	Ref.
$[Cu_4(L_1)]_n$	20	298	0.1	48	440*	9*	26
HKUST-1	20	298	0.1	48	285*	6*	26
$Zr(H_4L)$	0.33	373	1.0	2	2910	1455	**This work**

Table S7 Comparison with different MOF catalysts reported in the cycloaddition reaction of CO_2 and 1,2-epoxy-3-phenoxypropane.



Catalyst	Loading of catalyst (‰)	T (K)	P (MPa)	T (h)	TON	TOF (h^{-1})	Ref.
Ni-TCPE-1	0.5	373	1.0	12	2000	167	27
Ni(salphen)-MOF	2.8	353	2.0	4	196.4	49	24
CHB(M)	16.1	393	1.2	6	44	7	23
MOF-5	6.5	323	0.1	3	13.4	5	25
Zr(H_4L)	0.33	373	1.0	6	3000	500	**This work**

Table S8 Comparison with the different MOF catalysts reported in the cycloaddition reaction of CO_2 and styrene oxide. N.A.: Not Available. The article does not list the data.



Catalyst	Loading of catalyst (‰)	T (K)	P (MPa)	T (h)	TON	TOF (h^{-1})	Ref.
Ni-TCPE-1	0.5	373	1.0	12	2000	167	27
Ni-TCPE-2	0.5	373	1.0	12	1720	143	27
Gea-MOF-1	1.5	393	2.0	6	567	95	22
Ni(salphen)-MOF	2.8	353	2.0	4	289	72	24
$L_{Cu'}$	N.A.	393	2.0	6	286	48	28
Co-MOF-74	33.3	373	2.0	4	29	7	29
CHB(M)	16.1	393	1.2	6	35	6	23
Mg-MOF-74	33.3	373	2.0	4	29	7	30
Cr-MIL-101	12.5	298	0.8	48	178	4	31
MOF-5	6.5	323	0.1	15	22	2	25
Hf-NU-1000	40	298	0.1	56	25	0.4	32
Zr(H_4L)	0.33	373	1.0	12	2850	238	**This work**

Table S9 Comparison analysis on catalytic activity of different catalysts. Reaction condition in this work: epoxide (30 mmol), catalyst (0.01 mmol, 0.33‰ based on the catalyst) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K. The conversion was determined by ^{1}H NMR analysis. a, after 20 times of repeating catalytic reaction for 70 h; b, after 5 runs of repeated catalytic reaction for 50 h.

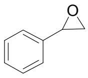
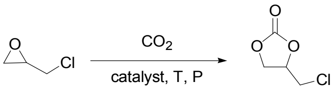
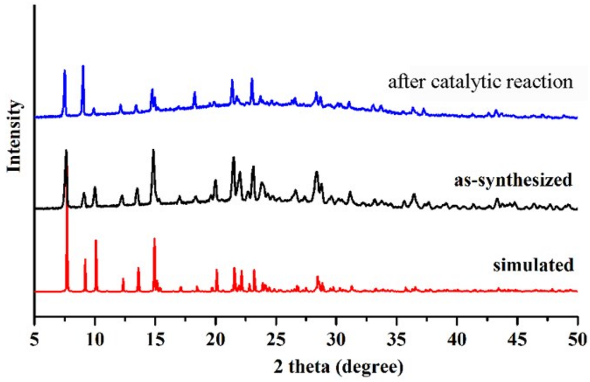
Entry	Substrates	Catalyst (mmol)	P (MPa)	T (K)	t (h)	Conversion (%)
1		TBAB (0.3)	1	373	6	50
2		H_8L/TABA (0.01/0.3)	1	373	6	63
3		Zr(H_4L)/TBAB (0.01/0.3)	1	373	6	95

Table S10 The time-control experiments conducted in coupling of CO_2 with a large excess of epichlorohydrin. Reaction condition: epichlorohydrin (120 mmol), catalyst (0.01 mmol, 0.0083‰ based on the catalyst) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K. The conversion was determined by ^{1}H NMR analysis.



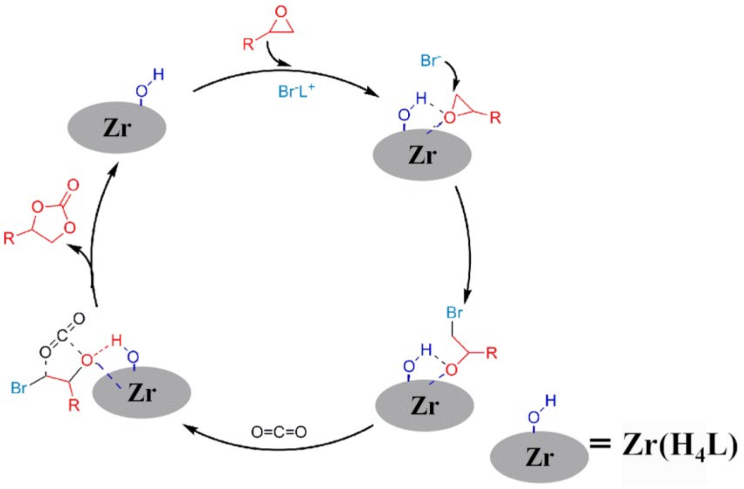
Entry	Catalyst	Co-catalyst	T (K)	P (MPa)	Time (h)	Yield (%)
1	Zr(H_4L)	TBAB	373	1	4	70
2	Zr(H_4L)	TBAB	373	1	6	82
3	Zr(H_4L)	TBAB	373	1	8	93
4	Zr(H_4L)	TBAB	373	1	10	>99



Figurre S10 The powder X-ray diffraction of simulated, experimental and recovered catalyst Zr(H_4L). Results clearly indicate that the crystal structure of the material remains unaltered through the performed catalytic tests.

Table S11 Recyclability test performed by catalytic CO_2 cycloaddition with excess epichlorohydrin under the optimal conditions. The catalyst $Zr(H_4L)$ was collected by centrifugation after each cycle, and then reused by mixing with fresh epoxide and TBAB. It is worth noting that an unavoidable loss of catalyst would bring an inaccurate decrease of conversion as after several runs, as for as the small quantity of catalyst in the recyclable reactions. Reaction conditions: epichlorohydrin (120 mmol), catalyst (0.01 mmol, 0.0083‰ based on the catalyst) and TBAB (0.3 mmol) under a constant CO_2 pressure of 1 MPa. The conversion was determined by ^1H NMR analysis.

Run	Catalyst	Co-catalyst	T (K)	P (MPa)	Time (h)	Yield (%)
1st	$Zr(H_4L)$	TBAB	373	1	10	>99
2ed	$Zr(H_4L)$	TBAB	373	1	10	>99
3rd	$Zr(H_4L)$	TBAB	373	1	10	>99
4th	$Zr(H_4L)$	TBAB	373	1	10	>99
5th	$Zr(H_4L)$	TBAB	373	1	10	98
6th	$Zr(H_4L)$	TBAB	373	1	10	93



Scheme S1 The proposed mechanism for the cycloaddition of CO_2 and epoxide at the solid/liquid interface assisted by bifunctional catalysis from Lewis acid and Brønsted acid (L^+ = tetra-n-butylammonium).

S3 The NMR spectrums

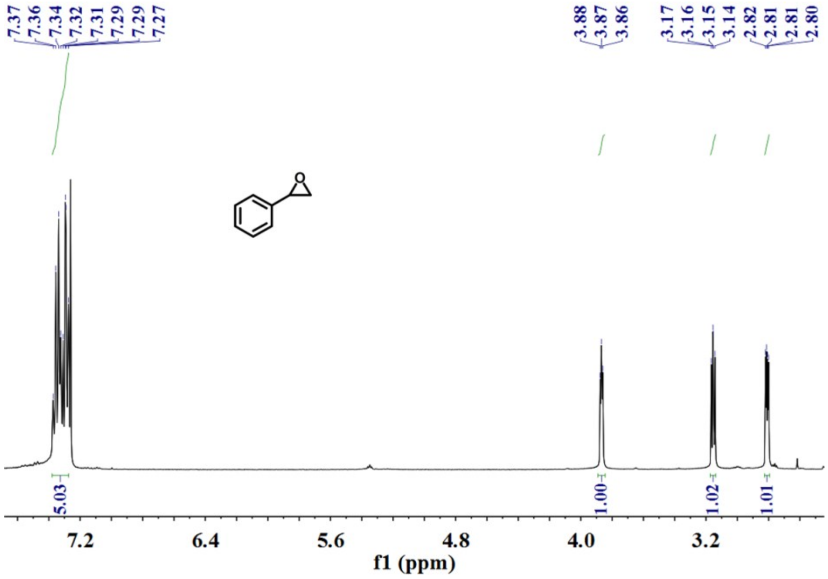


Figure S11 ^{1}H NMR spectra of styrene oxide (400 MHz, $CDCl_3$): δ = 7.27 – 7.37 (m, 5H, Ar-H), 3.87 (t, J=4.0 Hz, 1H, O-CH), 3.16 (q, J=4.0 Hz, 1H, O-CH_2), 2.81 (q, J = 4.0 Hz, 1H, O-CH_2).

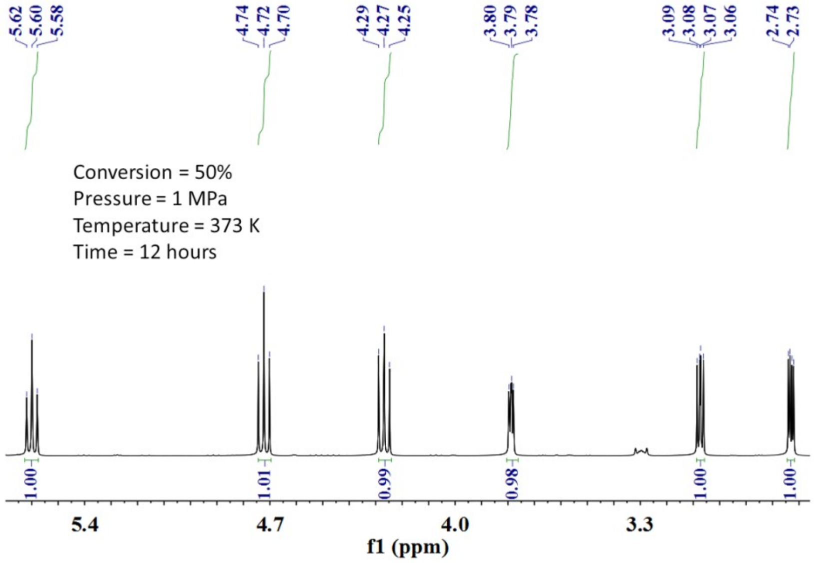


Figure S12 ^{1}H NMR spectra of the cycloaddition product of styrene oxide and CO_2 catalyzed by TBAB ((400 MHz, $CDCl_3$) : δ =7.28 – 7.39 (m, 8H, Ar-H), 7.18 – 7.25 (m, 8H, Ar-H), 5.60 (t, J = 8.0 Hz, 1H, COO-CH), 4.72 (t, J = 8.0 Hz, 1H, COO-CH_2), 4.27 (t, J = 8.0 Hz, 1H, COO-CH_2), 3.79 (t, J = 8.0 Hz, 2.20H, O-CH), 3.07 (q, J = 4.0 Hz, 2.20H, O-CH_2), 2.73 (q, J = 4.0 Hz, 2.20H, O-CH_2). Dosages: epoxide (30 mmol); TBAB (0.3 mmol).

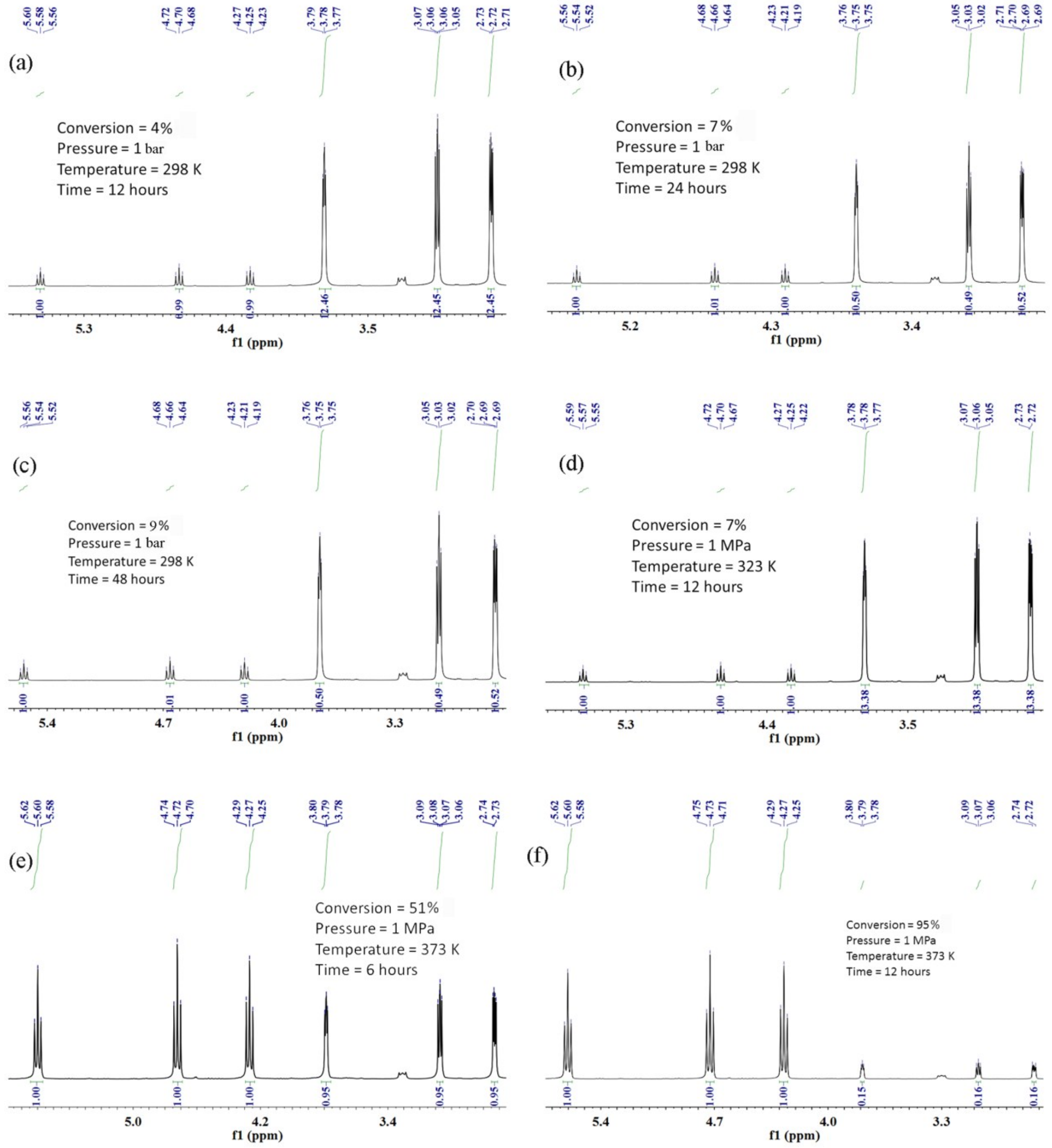


Figure S13 ^{1}H NMR spectra of the cycloaddition product of styrene oxide and CO_2 under different conditions. (400 MHz, $CDCl_3$) : δ =7.28 – 7.39 (m, 8H, Ar-H), 7.18 – 7.25 (m, 8H, Ar-H), 5.60 (t, J = 8.0 Hz, 1H, COO-CH), 4.72 (t, J = 8.0 Hz, 1H,COO-CH_2), 4.27 (t, J = 8.0 Hz, 1H,COO-CH_2), 3.79 (t, J = 8.0 Hz, 2.20H, O-CH), 3.07 (q, J = 4.0 Hz, 2.20H, O-CH_2), 2.73 (q, J = 4.0 Hz, 2.20H, O-CH_2). Dosages: epoxide (30 mmol); catalyst (0.01 mmol, 0.33‰ based on the catalyst); TBAB (0.3 mmol).

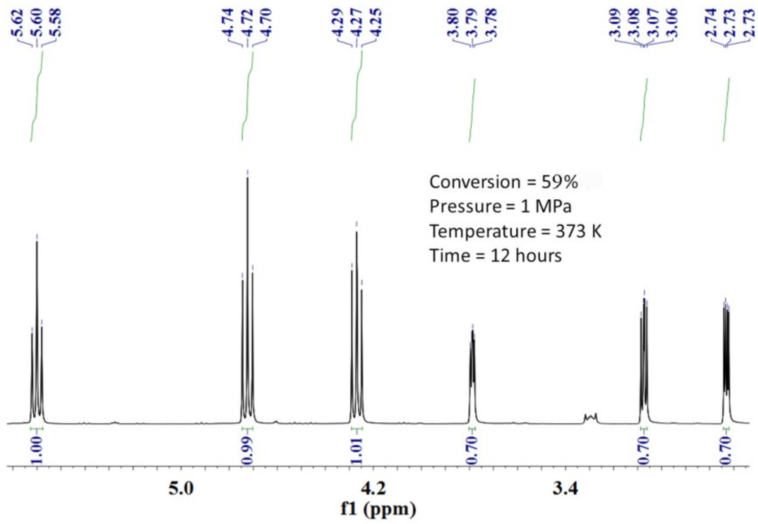


Figure S14 ^{1}H NMR spectra of the cycloaddition product of styrene oxide and CO_2 for filtration test (400 MHz, $CDCl_3$) : δ =7.28 – 7.39 (m, 8H, Ar-H), 7.18 – 7.25 (m, 8H, Ar-H), 5.60 (t, J = 8.0 Hz, 1H, COO-CH), 4.72 (t, J = 8.0 Hz, 1H,COO-CH_2), 4.27 (t, J = 8.0 Hz, 1H,COO-CH_2), 3.79 (t, J = 8.0 Hz, 2.20H, O-CH), 3.07 (q, J = 4.0 Hz, 2.20H, O-CH_2), 2.73 (q, J = 4.0 Hz, 2.20H, O-CH_2). The filtration test was performed from the mixture after 2 hours. After removal of the catalyst, the reaction continued. Reaction conditions: epoxide (30 mmol), catalyst (0.01 mmol, 0.33‰ based on the catalyst) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K. The total reaction time is 12 hours.

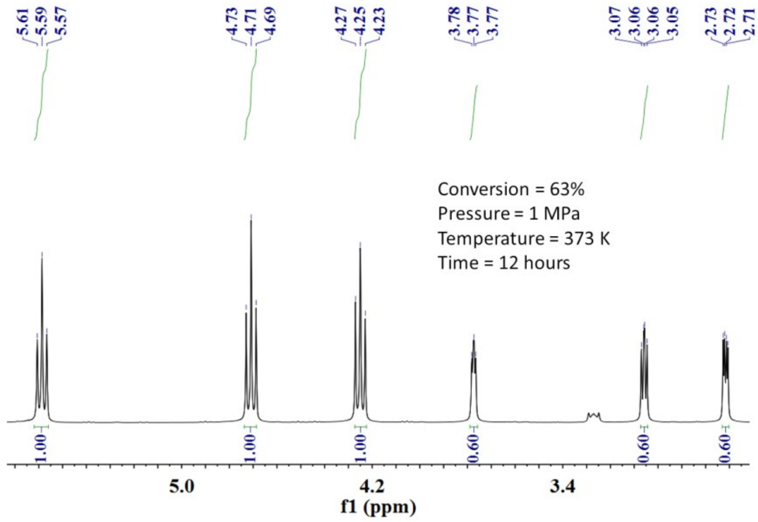


Figure S15 ^{1}H NMR spectra of the cycloaddition product of styrene oxide and CO_2 catalyzed by H_8L (400 MHz, $CDCl_3$) : δ =7.28 – 7.39 (m, 8H, Ar-H), 7.18 – 7.25 (m, 8H, Ar-H), 5.60 (t, J = 8.0 Hz, 1H, COO-CH), 4.72 (t, J = 8.0 Hz, 1H,COO-CH_2), 4.27 (t, J = 8.0 Hz, 1H,COO-CH_2), 3.79 (t, J = 8.0 Hz, 2.20H, O-CH), 3.07 (q, J = 4.0 Hz, 2.20H, O-CH_2), 2.73 (q, J = 4.0 Hz, 2.20H, O-CH_2). Reaction conditions: epoxide (30 mmol), catalyst (0.01 mmol) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K.

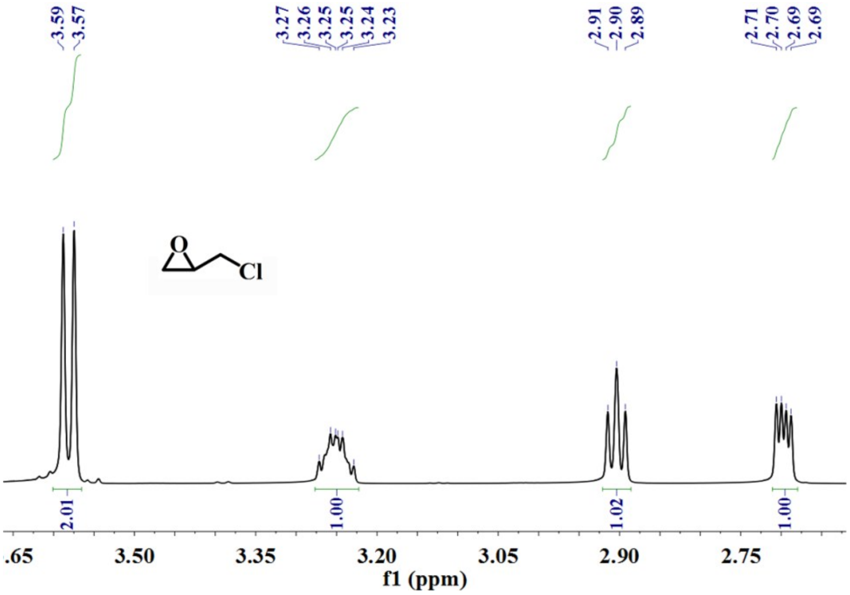


Figure S16 ^{1}H NMR spectra of epichlorohydrin (400 MHz, $CDCl_3$): δ = 3.58 (d, J = 8.0 Hz, 2H, Cl-CH_2), 3.23 – 3.27 (m, 1H, O-CH), 2.90 (t, J = 4.0 Hz, 1H, O-CH_2), 2.70 (q, J = 4.0 Hz, 1H, O-CH_2).

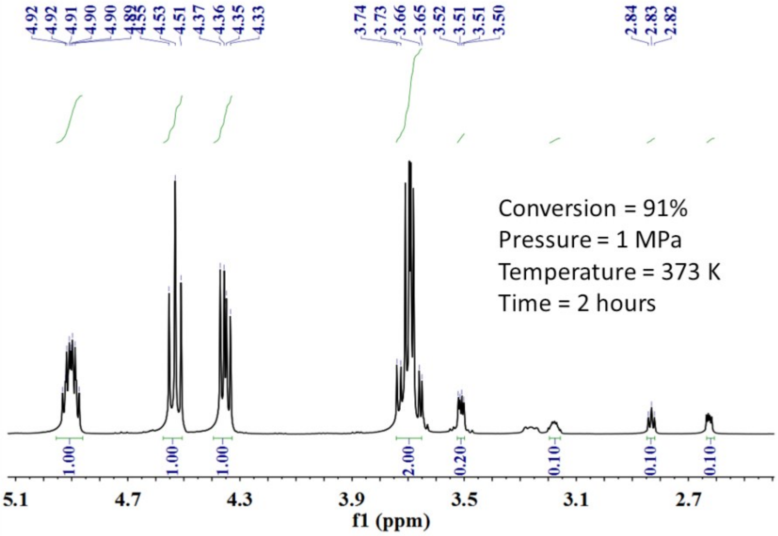


Figure S17 ^{1}H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 catalyzed by Zr(H_4L) for 2h (400 MHz, $CDCl_3$) : δ = 4.88 – 4.93 (m, 1H, COO-CH), 4.53 (t, J = 8.0 Hz, 1H, COO-CH_2), 4.35 (q, J = 8.0 Hz, 1H, COO-CH_2), 3.65 – 3.74 (m, 1H, Cl-CH_2 of product), 3.50–3.52 (m, 0.10H, Cl-CH_2 of epichlorohydrin), 3.16 – 3.20 (m, 1H, O-CH), 2.83 (d, J = 4.0 Hz, 1H, O-CH_2), 2.63 (q, J = 4.0 Hz, 1H, O-CH_2). Reaction conditions: epoxide (30 mmol), catalyst (0.01 mmol) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K.

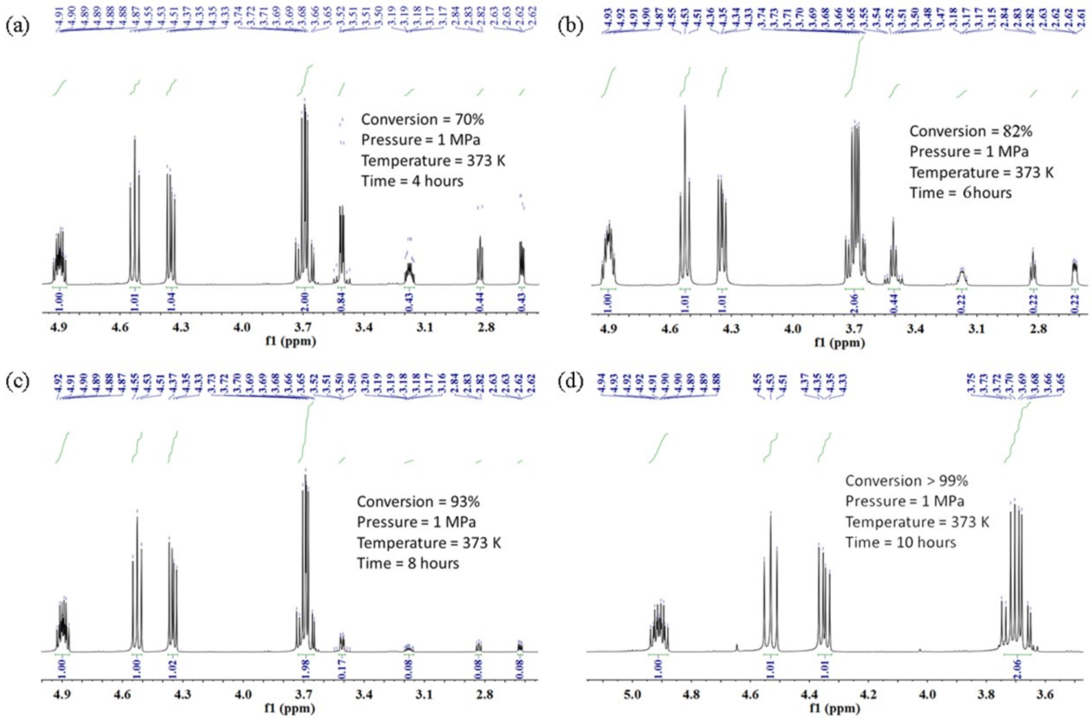


Figure S18 ^{1}H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 catalyzed by $Zr(H_4L)$ for 4h (a), 6h (b), 8h (c) and 10h (d). (400 MHz, $CDCl_3$) : δ = 4.88 – 4.93 (m, 1H, COO-CH), 4.53 (t, J = 8.0 Hz, 1H, COO-CH_2), 4.35 (q, J = 8.0 Hz, 1H, COO-CH_2), 3.65 – 3.74 (m, 1H, Cl-CH_2 of product), 3.50–3.52 (m, 0.10H, Cl-CH_2 of epichlorohydrin), 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). Reaction conditions: epoxide (120 mmol), catalyst (0.01 mmol, 0.33‰ based on the catalyst) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K.

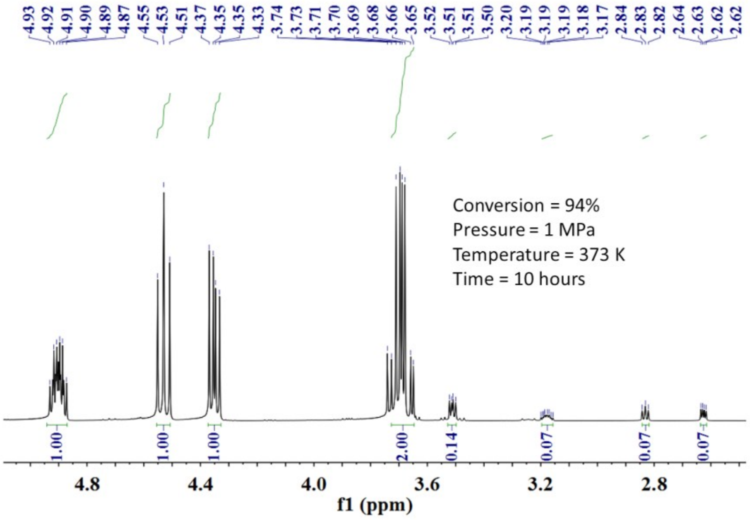


Figure S19 ^{1}H NMR spectra of the cycloaddition product of epichlorohydrin and CO_2 catalyzed by $Zr(H_4L)$ for the 6th recyclability test (400 MHz, $CDCl_3$) : δ = 4.88 – 4.93 (m, 1H, COO-CH), 4.53 (t, J = 8.0 Hz, 1H, COO-CH_2), 4.35 (q, J = 8.0 Hz, 1H, COO-CH_2), 3.65 – 3.74 (m, 1H, Cl-CH_2 of product), 3.50–3.52 (m, 0.10H, Cl-CH_2 of epichlorohydrin), 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). Dosages: epichlorohydrin (120 mmol), catalyst (0.01 mmol, 0.0083‰ based on the catalyst) and TBAB (0.3 mmol).

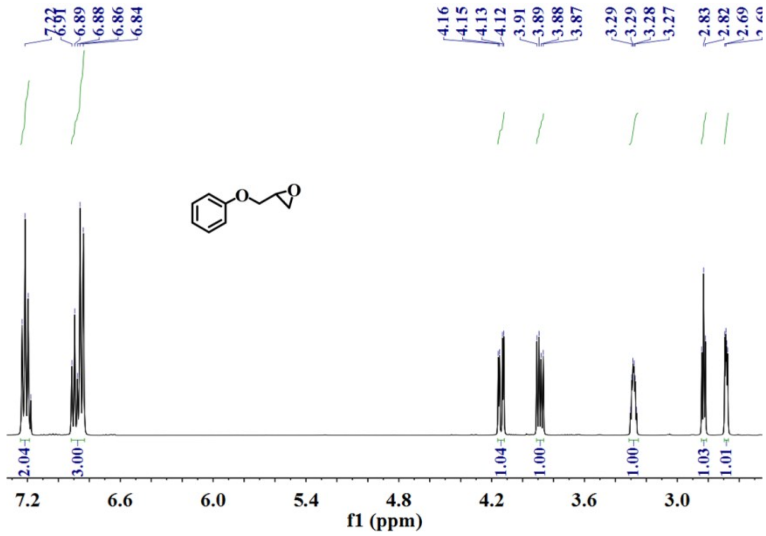
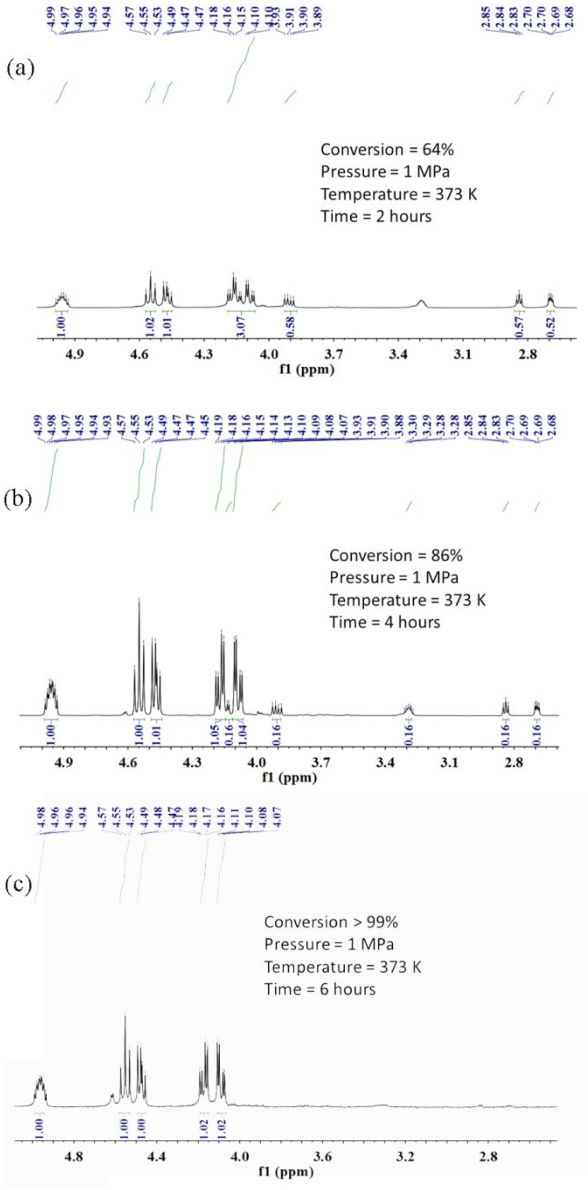


Figure S20 ^{1}H NMR spectra of 1,2-epoxy-3-phenoxypropane (400 MHz, $CDCl_3$) : δ = 7.18 – 7.23 (m, 2H, Ar-H), 6.84 – 6.91 (m, 3H, Ar-H), 4.14 (q, J = 4.0 Hz, 1H, ArO-CH_2), 3.88 (q, J = 4.0 Hz, 1H, ArO-CH_2), 3.26 – 3.30 (m, 1H,O-CH), 2.83 (t, J = 4.0 Hz, 1H,O-CH_2), 2.68 (q, J = 4.00 Hz, 1H,O-CH_2).



Conversion = 64%
Pressure = 1 MPa
Temperature = 373 K
Time = 2 hours

Conversion = 86%
Pressure = 1 MPa
Temperature = 373 K
Time = 4 hours

Conversion > 99%
Pressure = 1 MPa
Temperature = 373 K
Time = 6 hours

Figure S21 ^{1}H NMR of the cycloaddition product of 1,2-epoxy-3-phenoxypropane and CO_2 for 2h (a), 4h (b) and 6h (c) (400 MHz, $CDCl_3$): δ = 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). Reaction conditions: epoxide (30 mmol), catalyst (0.01 mmol, 0.33‰ based on the catalyst) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K.

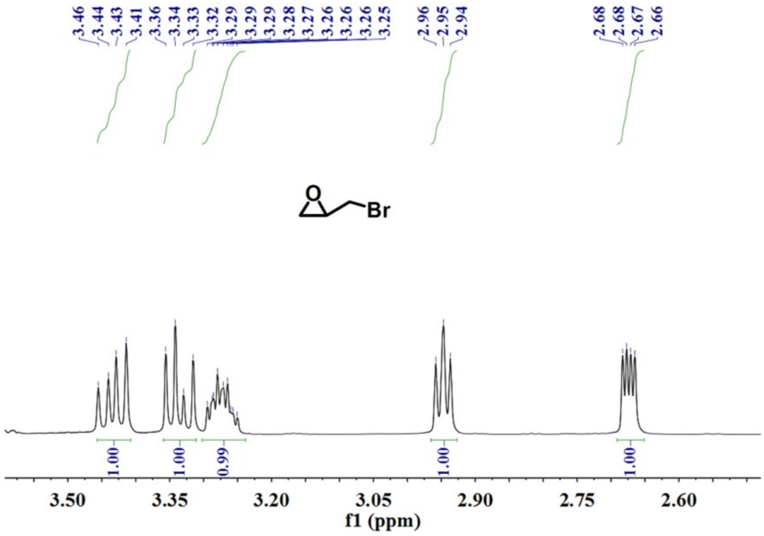
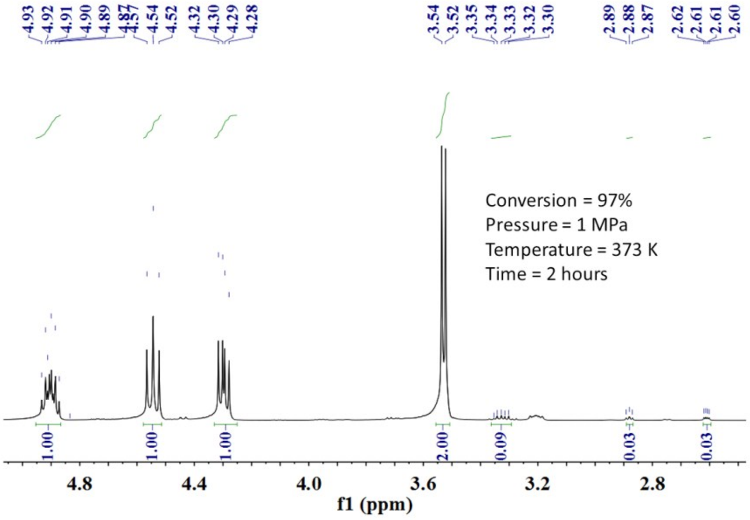


Figure S22 ^{1}H NMR spectra of epibromohydrin (400 MHz, $CDCl_3$): δ = 3.42 (q, J = 8.0 Hz, 1H, Br-CH_2), 3.33 (q, J = 8.0 Hz, 1H, Br-CH_2), 3.25 – 3.29(m, 1H, O-CH), 2.95 (t, J = 4.0 Hz, 1H, O-CH_2), 2.67 (q, J = 4.0 Hz, 1H, O-CH_2).



Conversion = 97%
Pressure = 1 MPa
Temperature = 373 K
Time = 2 hours

Figure S23 ^{1}H NMR spectra of the cycloaddition product of epibromohydrin and CO_2 catalyzed by Zr(H_4L) for 2h (400 MHz, $CDCl_3$) : δ = 4.83 – 4.93 (m, 1H, COO-CH), 4.54 (t, J = 8.0 Hz, 1H, COO-CH_2), 4.29 (q, J = 8.0 Hz, 1H, COO-CH_2), 3.53(d, J=8.0Hz, 2H, Br-CH_2 of product), 3.30–3.35 (m, 0.09H, Br-CH_2 of epibromohydrin and O-CH), 2.88 (t, J = 4.0 Hz, 1H, O-CH_2), 2.61 (q, J = 4.0 Hz, 1H, O-CH_2). Reaction conditions: epoxide (30 mmol), catalyst (0.01 mmol, 0.33‰ based on the catalyst) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K.

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