

## Supporting Information

### **A copper-phosphonate network as High-Performance Heterogeneous Catalyst for CO<sub>2</sub> Cycloaddition Reactions and Alcoholysis of Epoxides**

Jing Ai,<sup>a,b</sup> Xue Min,<sup>a,c</sup> Chao-Ying Gao,<sup>a,c</sup> Hong-Rui Tian,<sup>a</sup> Song Dang<sup>\*a</sup> and Zhong-Ming Sun<sup>\*a</sup>

<sup>a</sup> State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, China

<sup>b</sup> University of Science and Technology of China, Hefei, Anhui 230026, China.

<sup>c</sup> University of Chinese Academy of Sciences, Beijing 100049, P. R. China

\*Corresponding Authors. E-mail: szm@ciac.ac.cn; dangsong@ciac.ac.cn

### Supplementary Index

Contents

S1. Methods

S2. Supplementary tables and figures

S3. The NMR spectrums

S4. References

## S1. Methods

### 1.1 General information

Powder X-ray diffraction (PXRD) was carried out with a MiniFlex 600 X-ray powder diffractometer equipped with a Cu sealed tube ( $\lambda = 1.54178 \text{ \AA}$ ) at 40 kV and 40 mA. Inductively coupled plasma (ICP) analyses of Cu and elemental analyses of C, H, and N were conducted on a Perkin-Elmer Optima 3300DV spectrometer and a Perkin-Elmer 2400 elemental analyzer, respectively. Thermal gravimetric analysis (TGA) was conducted under an air atmosphere with a heating rate of  $10^\circ\text{C}/\text{min}$  on a SDT 2960 Simultaneous DSC-TGA of TA instruments up to  $800^\circ\text{C}$ . The infrared (IR) spectra (diamond) were recorded on a Nicolet 7600 FT-IR spectrometer within the  $4000\text{--}500 \text{ cm}^{-1}$  region.  $^1\text{H}$  NMR spectra were carried out in  $\text{CDCl}_3$  solvent on a Bruker 400 MHz spectrometer. The chemical shift is given in dimensionless  $\delta$  values and is referenced relative to TMS in  $^1\text{H}$  spectroscopy.

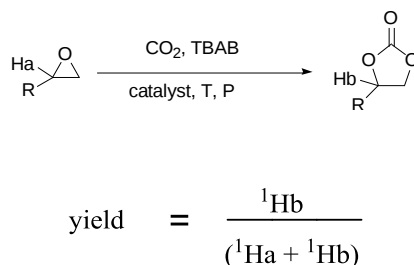
### 1.2 Single-Crystal X-ray Crystallography

Single-crystal X-ray diffraction (SXRD) data of compound **1** were collected on a Bruker diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) at 293 K. Data processing was accomplished with the SAINT processing program.<sup>1</sup> 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.<sup>2</sup> 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. Additionally, in order to avoid symmetrical operation for nitrogen-containing ancillary ligand (TPT: [5-(4-(1H-1,2,4-triazol-1-yl)phenyl)-1H-tetrazole]), N34/C34, N35/C35 and N36/C36 were defined in the same position, respectively. The final formula of compound **1** was determined by single-crystal X-ray diffraction.

Crystallographic data for  $\text{Cu}_7(\text{H}_1\text{L})_2(\text{TPT})_3(\text{H}_2\text{O})_6$  (1524015) 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](http://www.ccdc.cam.ac.uk/data_request/cif). Crystal data and structure refinement is summarized in Table S1.

### 1.3 Cycloaddition of $\text{CO}_2$ to epoxides

The yield was calculated from  $^1\text{H}$  NMR according to the following equation.



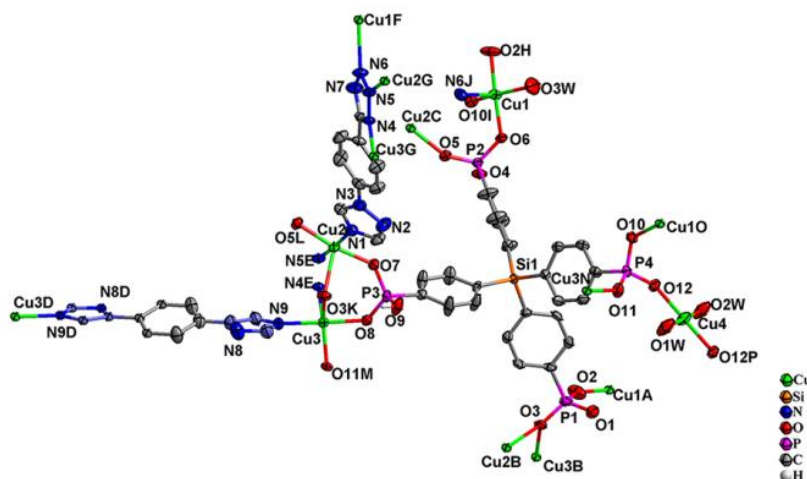
## S2 Supplementary tables and figures



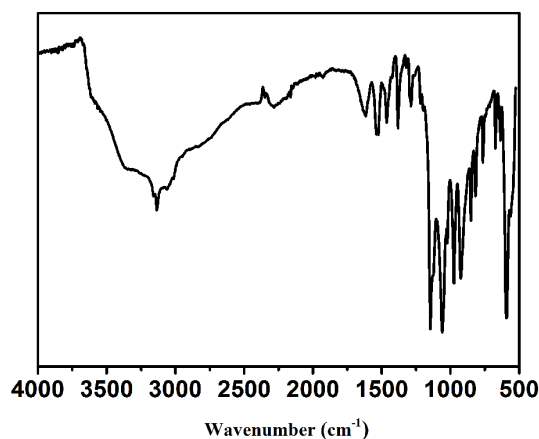
**Scheme S1.** Chemical structure of ligand  $\text{H}_8\text{L}$  and TPT.

**Table S1** Crystallographic data for compound **1**

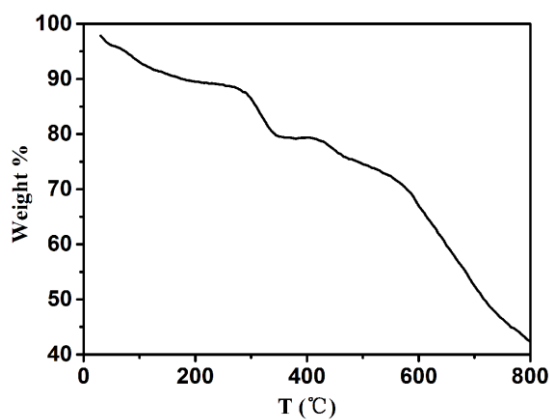
| compound                        | <b>1</b>                                                                               |
|---------------------------------|----------------------------------------------------------------------------------------|
| Formula                         | $\text{Cu}_7\text{Si}_2\text{C}_{75}\text{P}_8\text{O}_{28}\text{N}_{21}\text{H}_{52}$ |
| $F_w$                           | 2444.09                                                                                |
| Crystal system                  | monoclinic                                                                             |
| Space group                     | $P2_1/c$                                                                               |
| a, Å                            | 13.6147(10)                                                                            |
| b, Å                            | 17.8396(13)                                                                            |
| c, Å                            | 20.1820(14)                                                                            |
| $\beta$ , °                     | 94.425(2)                                                                              |
| V, Å <sup>3</sup>               | 4887.2(6)                                                                              |
| Z                               | 2                                                                                      |
| $D_c$ , mg/mm <sup>3</sup>      | 1.661                                                                                  |
| $\mu$ , mm <sup>-1</sup>        | 1.734                                                                                  |
| reflection collected            | 3304                                                                                   |
| GOF on $F^2$                    | 1.027                                                                                  |
| $R_1/wR_2$ ( $I > 2\sigma(I)$ ) | 0.0524/ 0.1231                                                                         |
| $R_1/wR_2$ (all data)           | 0.0792/ 0.1358                                                                         |



**Fig. S1.** ORTEP representation of the coordination environment in compound **1** with thermal ellipsoids set at 50% probability. The asymmetric codes: A,  $-0.5+x, 0.5-y, 0.5+z$ ; B,  $-0.5+x, 1.5-y, -0.5+z$ ; C,  $1.5-x, -0.5+y, 0.5-z$ ; D,  $1-x, 2-y, -z$ ; E,  $-1+x, y, z$ ; F,  $2.5-x, 0.5+y, 0.5-z$ ; G,  $1+x, y, z$ ; H,  $0.5+x, 0.5-y, -0.5+z$ ; I,  $-0.5+x, 0.5-y, -0.5+z$ ; J,  $2.5-x, -0.5+y, 0.5-z$ ; K,  $0.5+x, 1.5-y, -0.5+z$ ; L,  $1.5-x, 0.5+y, 0.5-z$ ; M,  $-0.5+x, 1.5-y, -0.5+z$ ; N,  $0.5+x, 1.5-y, 0.5+z$ ; O,  $0.5+x, 0.5-y, 0.5+z$ ; P,  $2-x, 1-y, 2-z$ . Hydrogen atoms bonded to carbon atoms are omitted for clarity.

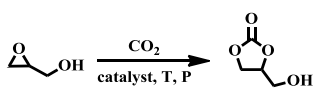


**Fig. S2.** Infrared spectra of compound **1**.



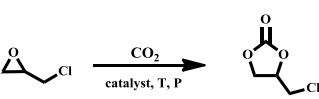
**Fig. S3.** Thermogravimetric analysis data for compound **1**.

**Table S2** Comparison with the only MOF catalyst reported in the cycloaddition reaction of CO<sub>2</sub> and glycidol. \*: the values were obtained through calculation on the basis of the corresponding calculation formulas.



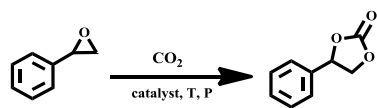
| Entry | Catalyst                       | T (°C) | P (MPa) | T (h) | TON  | TOF  | Ref.             |
|-------|--------------------------------|--------|---------|-------|------|------|------------------|
| 1     | {[Eu(BTB)(phen)]} <sub>n</sub> | 70     | 0.1     | 12    | 20*  | 1.7* | 3                |
| 2     | 1                              | 100    | 1.0     | 3     | 1429 | 476  | <b>This work</b> |

**Table S3** Comparison with different MOF catalysts in the cycloaddition reaction of CO<sub>2</sub> and epichlorohydrin.



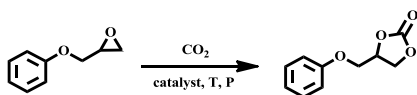
| Entry | Catalyst        | T (°C) | P (MPa) | T (h) | TON  | TOF | Ref.             |
|-------|-----------------|--------|---------|-------|------|-----|------------------|
| 1     | Gea-MOF-1       | 120    | 2.0     | 6     | 593  | 99  | 4                |
| 3     | CHB (M)         | 120    | 1.2     | 6     | 44.6 | 7   | 5                |
| 2     | Ni(salphen)-MOF | 80     | 2.0     | 4     | 300  | 75  | 6                |
| 4     | MOF-5           | 50     | 0.1     | 12    | 22.3 | 2   | 7                |
| 5     | 1               | 100    | 1.0     | 3     | 1429 | 476 | <b>This work</b> |

**Table S4** Comparison with the different MOF catalysts reported in the cycloaddition reaction of CO<sub>2</sub> and styrene oxide.

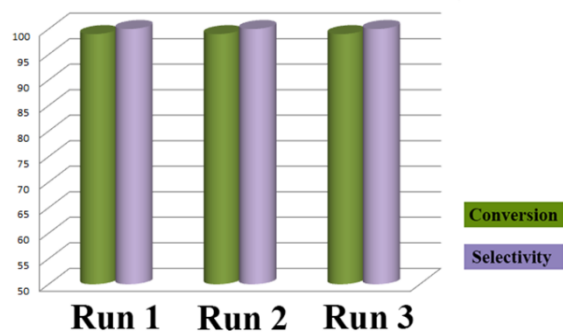


| Entry | Catalyst        | T (°C) | P (MPa) | T (h) | TON  | TOF | Ref.             |
|-------|-----------------|--------|---------|-------|------|-----|------------------|
| 1     | Ni-TCPE1        | 100    | 1.0     | 12    | 2000 | 167 | 8                |
| 2     | Ni-TCPE2        | 100    | 1.0     | 12    | 1720 | 143 | 8                |
| 3     | Gea-MOF-1       | 120    | 2.0     | 6     | 567  | 95  | 4                |
| 4     | 1-Mn            | 80     | 2.0     | 4     | 352  | 88  | 9                |
| 5     | Ni(sal)-MOF     | 80     | 2.0     | 4     | 289  | 72  | 6                |
| 6     | L <sub>Cu</sub> | 120    | 2.0     | 6     | 286  | 48  | 10               |
| 7     | Co-MOF-74       | 100    | 2.0     | 4     | 29   | 7   | 11               |
| 8     | CHB(M)          | 120    | 1.2     | 6     | 35   | 6   | 5                |
| 9     | Mg-MOF-74       | 100    | 2.0     | 4     | 29   | 7   | 12               |
| 10    | 1               | 100    | 1.0     | 12    | 1429 | 119 | <b>This work</b> |

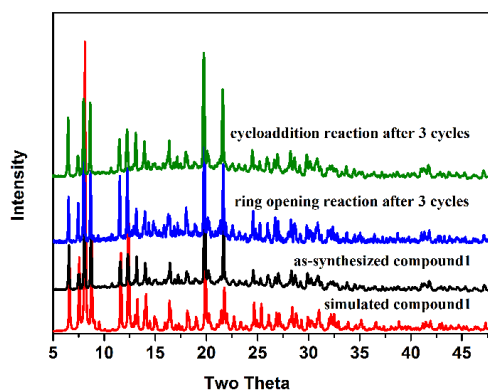
**Table S5** Comparison with different MOF catalysts reported in the cycloaddition reaction of CO<sub>2</sub> and 1,2-epoxy-3-phenoxypropane.



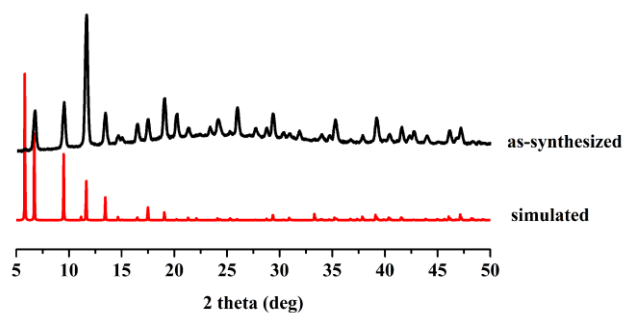
| Entry | Catalyst    | T (°C) | P (MPa) | T (h) | TON   | TOF | Ref.             |
|-------|-------------|--------|---------|-------|-------|-----|------------------|
| 1     | Ni-TCPE1    | 100    | 1.0     | 12    | 2000  | 167 | 8                |
| 2     | Ni(sal)-MOF | 80     | 2.0     | 4     | 196.4 | 49  | 6                |
| 3     | CHB(M)      | 120    | 1.2     | 6     | 44    | 7   | 5                |
| 4     | MOF-5       | 50     | 0.1     | 3     | 13.4  | 5   | 7                |
| 5     | 1           | 100    | 1.0     | 12    | 1429  | 119 | <b>This work</b> |



**Fig. S4.** Recycle and selectivity experiments with styrene oxide for the ring-opening reaction with compound 1.

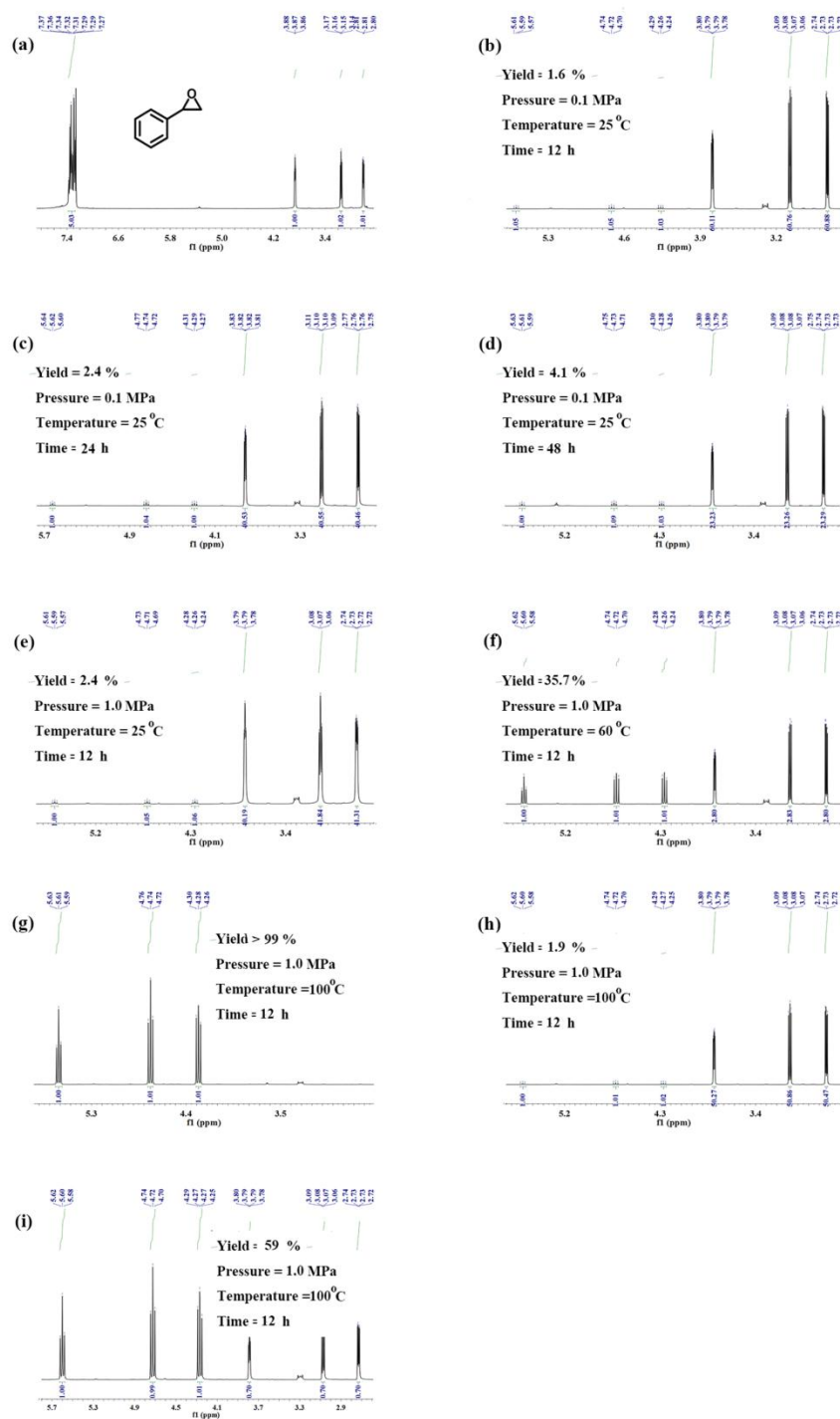


**Fig. S5.** Powder XRD patterns for compound 1 before and after three runs of two catalytic reactions.

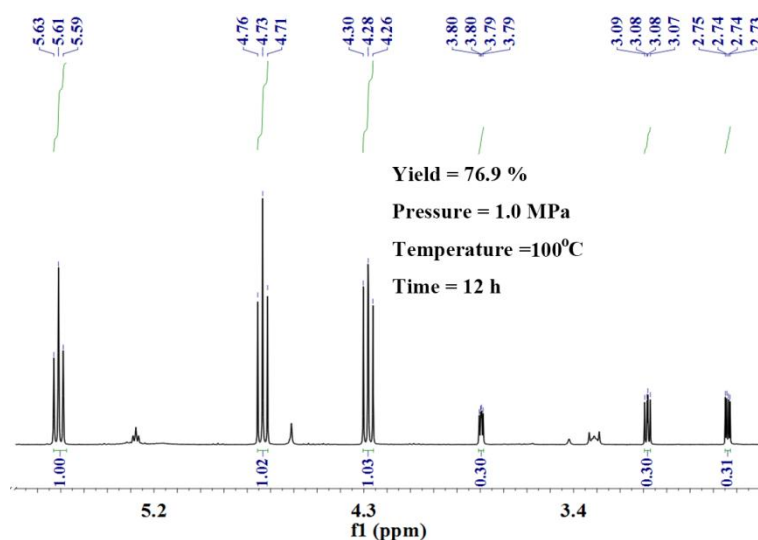


**Fig. S6.** Powder XRD patterns of the simulated and as-synthesized HKUST-1.

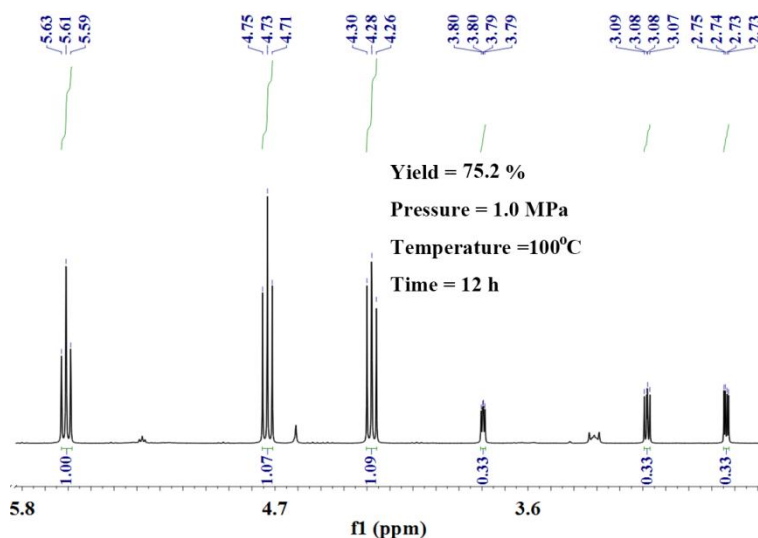
### S3. The NMR spectrums



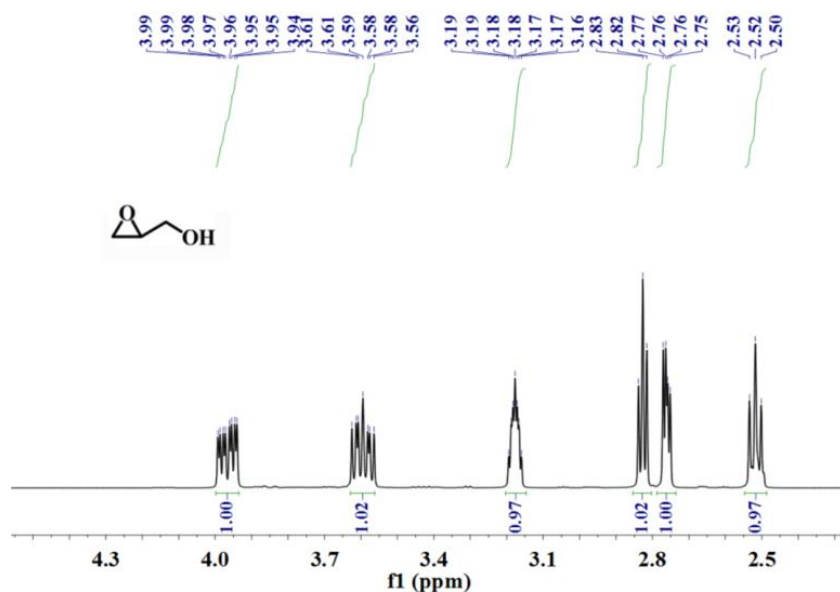
**Fig. S7.** (a)  $^1\text{H}$  NMR spectra of styrene oxide (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.27 – 7.37 (m, 5H, Ar-H), 3.87 (t,  $J$ =4.0 Hz, 1H, O-CH), 3.16 (q,  $J$ =4.0 Hz, 1H, O-CH<sub>2</sub>), 2.81 (q,  $J$  = 4.0 Hz, 1H, O-CH<sub>2</sub>); (b-i)  $^1\text{H}$  NMR spectra of the cycloaddition product of styrene oxide and  $\text{CO}_2$  under different conditions (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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<sub>2</sub>), 4.27 (t,  $J$  = 8.0 Hz, 1H, COO-CH<sub>2</sub>), 3.79 (t,  $J$  = 8.0 Hz, 2.20H, O-CH), 3.07 (q,  $J$  = 4.0 Hz, 2.20H, O-CH<sub>2</sub>), 2.73 (q,  $J$  = 4.0 Hz, 2.20H, O-CH<sub>2</sub>). Dosages in b-i: epoxide (20 mmol); catalyst (2  $\mu\text{mol}$  of compound **1** except for i); TBAB (0.3 mmol except for h).



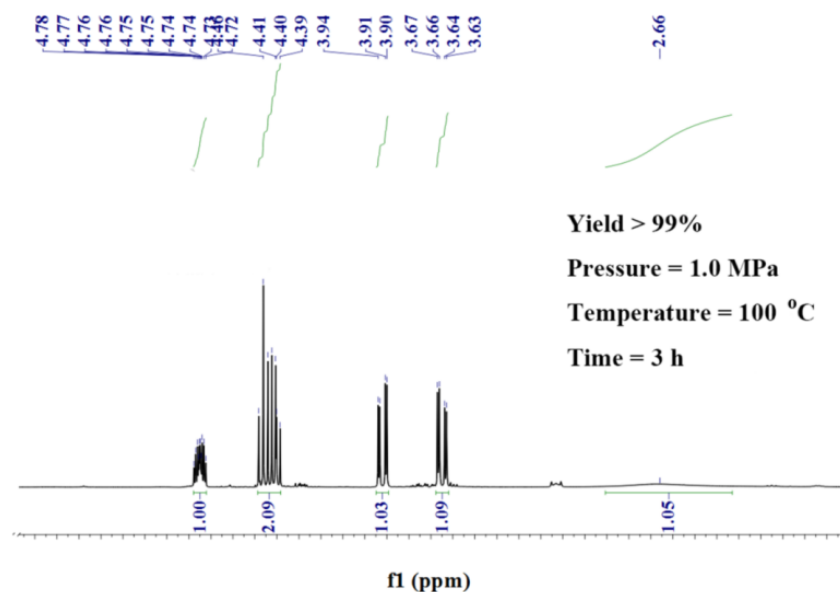
**Fig. S8.**  $^1\text{H}$  NMR spectra of the cycloaddition product of styrene oxide and  $\text{CO}_2$  catalyzed by  $\text{Cu}(\text{OAc})_2$  for 12h (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 7.28 – 7.39 (m, 8H, Ar-H), 7.18 – 7.25 (m, 8H, Ar-H), 5.60 (t,  $J$  = 8.0 Hz, 1H, COO-CH), 4.72 (t,  $J$  = 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 (20 mmol) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100  $^\circ\text{C}$ .



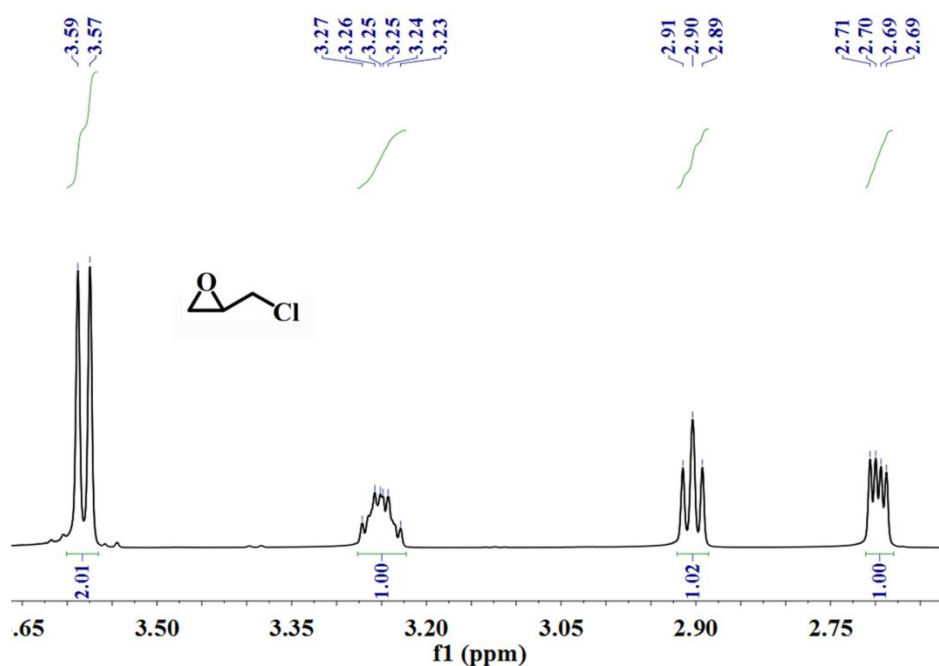
**Fig. S9.**  $^1\text{H}$  NMR spectra of the cycloaddition product of styrene oxide and  $\text{CO}_2$  catalyzed by  $\text{H}_8\text{L}$  for 12h (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 7.28 – 7.39 (m, 8H, Ar-H), 7.18 – 7.25 (m, 8H, Ar-H), 5.60 (t,  $J$  = 8.0 Hz, 1H, COO-CH), 4.72 (t,  $J$  = 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 (20 mmol) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100  $^\circ\text{C}$ .



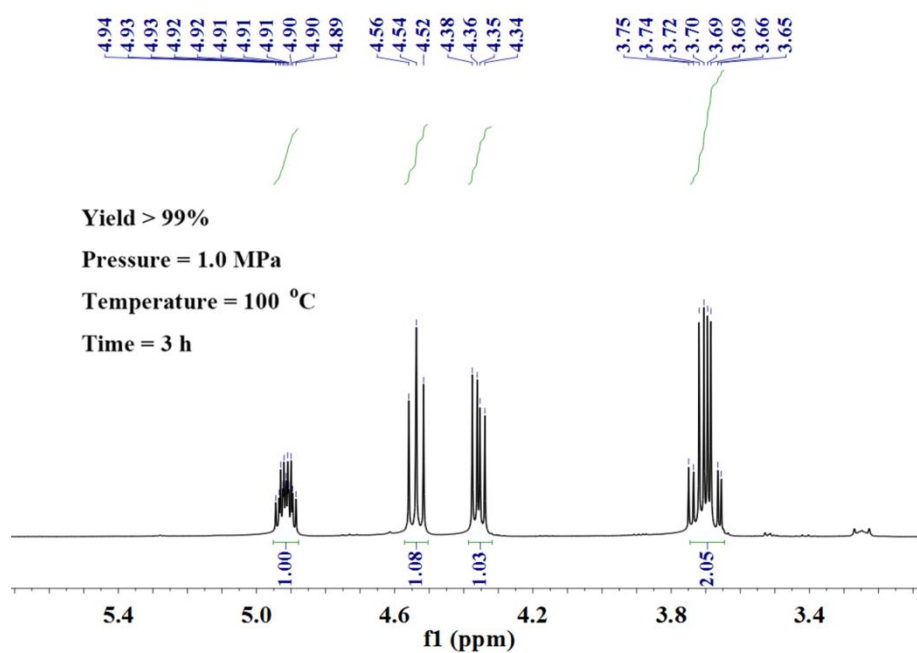
**Fig. S10.**  $^1\text{H}$  NMR spectra of glycidol (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.94 – 3.99 (m, 1H, HO- $\text{CH}_2$ ), 3.56 – 3.62 (m, 1H, HO- $\text{CH}_2$ ), 3.16 – 3.19 (m, 1H, O-CH), 2.83 (t,  $J$  = 4.0 Hz, 1H, O- $\text{CH}_2$ ), 2.76 (q,  $J$  = 4.0 Hz, 1H, O- $\text{CH}_2$ ), 2.52 (t,  $J$  = 4.0 Hz, 1H, -OH).



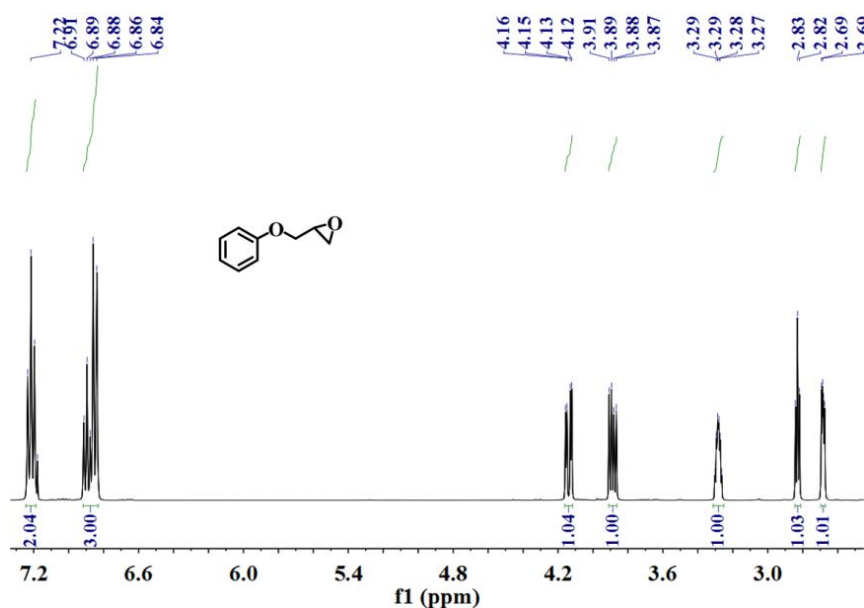
**Fig. S11**  $^1\text{H}$  NMR spectra of the cycloaddition product of glycidol with  $\text{CO}_2$  catalyzed by compound **1** for 3h (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.73 – 4.78 (m, 1H, COO-CH), 4.39 – 4.48 (m, 2H, HO- $\text{CH}_2$ ), 3.91 (dd,  $J$  = 12.0 Hz, 4.0 Hz, 1H, COO- $\text{CH}_2$ ), 3.65 (dd,  $J$  = 12.0, 4.0 Hz, 1H, COO- $\text{CH}_2$ ), 2.73 (br, 1H, -OH). Reaction conditions: epoxide (20 mmol), catalyst (2  $\mu\text{mol}$ ) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100  $^\circ\text{C}$ .



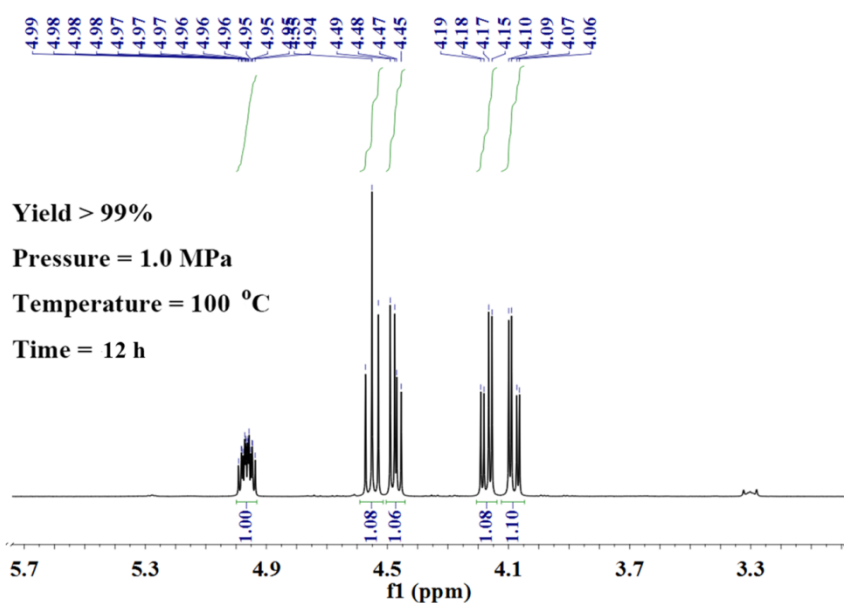
**Fig. S12.** <sup>1</sup>H NMR spectra of epichlorohydrin (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.58 (d,  $J$  = 8.0 Hz, 2H, Cl-CH<sub>2</sub>), 3.23 – 3.27 (m, 1H, O-CH), 2.90 (t,  $J$  = 4.0 Hz, 1H, O-CH<sub>2</sub>), 2.70 (q,  $J$  = 4.0 Hz, 1H, O-CH<sub>2</sub>).



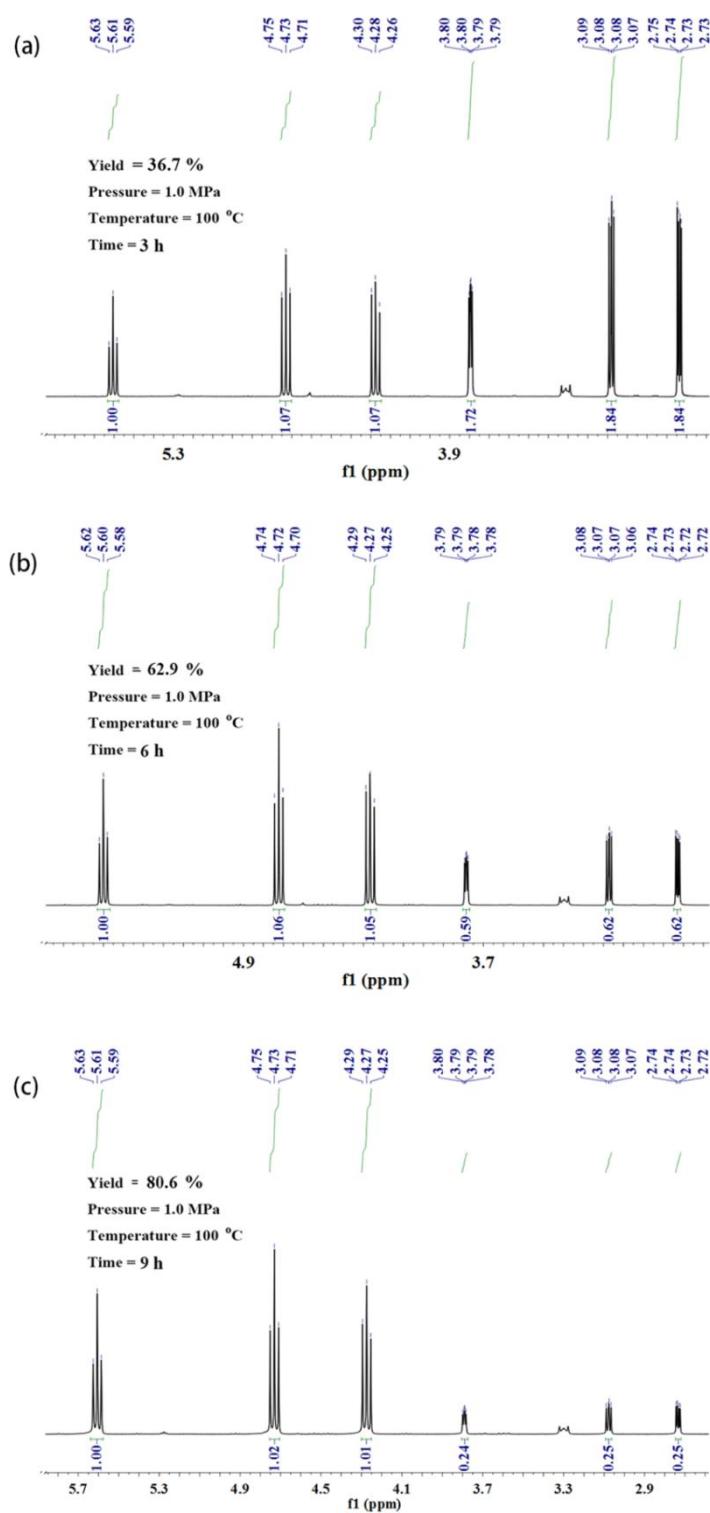
**Fig. S13.** <sup>1</sup>H NMR spectra of the cycloaddition product of epichlorohydrin and CO<sub>2</sub> catalyzed by compound **1** for 3h (400 MHz, CDCl<sub>3</sub>) :  $\delta$  = 4.88 – 4.93 (m, 1H, COO-CH), 4.53 (t,  $J$  = 8.0 Hz, 1H, COO-CH<sub>2</sub>), 4.35 (q,  $J$  = 8.0 Hz, 1H, COO-CH<sub>2</sub>), 3.65 – 3.74 (m, 1H, Cl-CH<sub>2</sub> of product), 3.50–3.52 (m, 0.10H, Cl-CH<sub>2</sub> of epichlorohydrin), 3.16 – 3.20 (m, 1H, O-CH), 2.83 (d,  $J$  = 4.0 Hz, 1H, O-CH<sub>2</sub>), 2.63 (q,  $J$  = 4.0 Hz, 1H, O-CH<sub>2</sub>). Reaction conditions: epoxide (20 mmol), catalyst (2  $\mu$ mol) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100 °C.



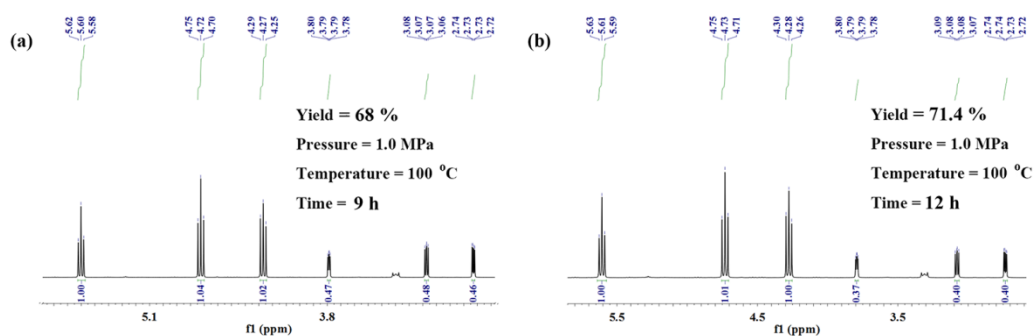
**Fig. S14.**  $^1\text{H}$  NMR spectra of 1,2-epoxy-3-phenoxypropane (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 7.18 – 7.23 (m, 2H, Ar-H), 6.84 – 6.91 (m, 3H, Ar-H), 4.14 (q,  $J$  = 4.0 Hz, 1H, ArO-CH<sub>2</sub>), 3.88 (q,  $J$  = 4.0 Hz, 1H, ArO-CH<sub>2</sub>), 3.26 – 3.30 (m, 1H, O-CH), 2.83 (t,  $J$  = 4.0 Hz, 1H, O-CH<sub>2</sub>), 2.68 (q,  $J$  = 4.00 Hz, 1H, O-CH<sub>2</sub>).



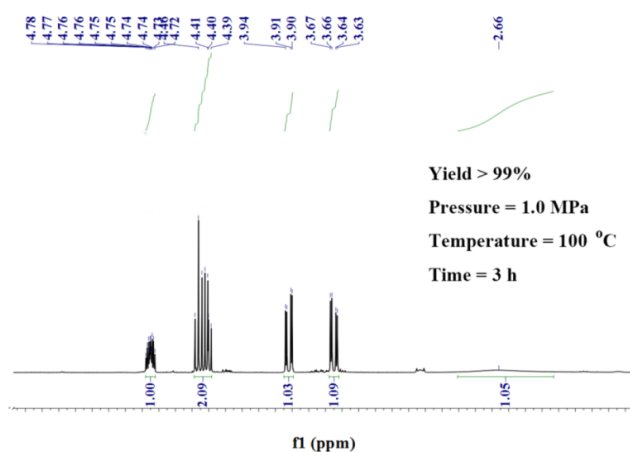
**Fig. S15.**  $^1\text{H}$  NMR of the cycloaddition product of 1,2-epoxy-3-phenoxypropane and  $\text{CO}_2$  catalyzed by compound **1** for 12h (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.20 – 7.27 (m, 3.12H, Ar-H), 6.88 – 6.97 (m, 1.47H, Ar-H), 6.83 – 6.87 (m, 2.79H, Ar-H), 4.93 – 4.99 (m, 1H, COO-CH), 4.55 (t,  $J$  = 8.0 Hz, 1H, COO-CH<sub>2</sub>), 4.47 (t,  $J$  = 8.0 Hz, 1H, COO-CH<sub>2</sub>), 4.19 – 4.13 (m, 1.46H, 1H - ArO-CH<sub>2</sub> of product and 0.46H - ArO-CH<sub>2</sub> of 1,2-epoxy-3-phenoxypropane), 4.07 (dd,  $J$  = 8.0 Hz, 4.0 Hz, 1H, ArO-CH<sub>2</sub> of product), 3.90 (q,  $J$  = 8.0 Hz, 0.46H, ArO-CH<sub>2</sub> 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<sub>2</sub>), 2.70 (q,  $J$  = 4.0 Hz, 0.46H, O-CH<sub>2</sub>). Reaction conditions: epoxide (20 mmol), catalyst (2  $\mu\text{mol}$ ) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100 °C.



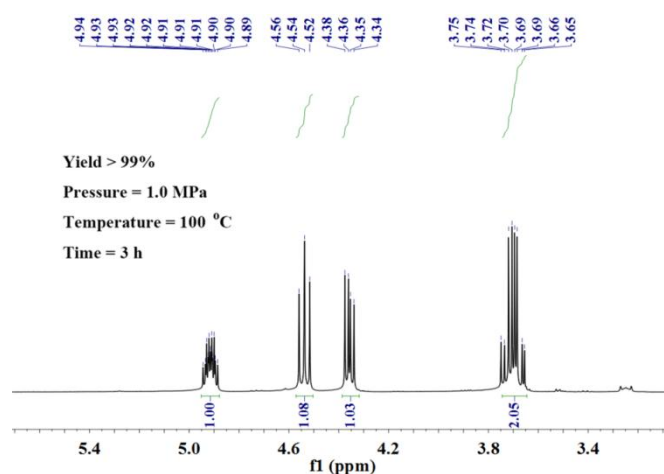
**Fig. S16.**  $^1\text{H}$  NMR spectra of the cycloaddition product of styrene oxide and  $\text{CO}_2$  catalyzed by compound **1** for 3h (a), 6h (b) and 9h (c) (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 7.28 – 7.39 (m, 8H, Ar-H), 7.18 – 7.25 (m, 8H, Ar-H), 5.60 (t,  $J$  = 8.0 Hz, 1H, COO-CH), 4.72 (t,  $J$  = 8.0 Hz, 1H, COO-CH<sub>2</sub>), 4.27 (t,  $J$  = 8.0 Hz, 1H, COO-CH<sub>2</sub>), 3.79 (t,  $J$  = 8.0 Hz, 2.20H, O-CH), 3.07 (q,  $J$  = 4.0 Hz, 2.20H, O-CH<sub>2</sub>), 2.73 (q,  $J$  = 4.0 Hz, 2.20H, O-CH<sub>2</sub>). Reaction conditions: epoxide (20 mmol), catalyst (2  $\mu\text{mol}$ ) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100 °C.



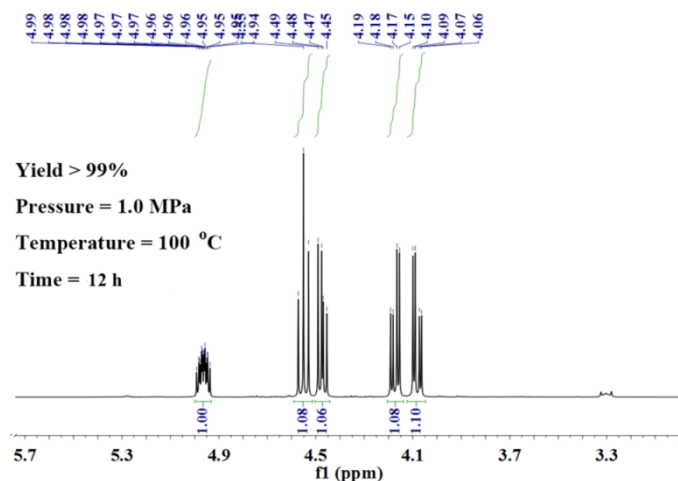
**Fig. S17.**  $^1\text{H}$  NMR spectra of the cycloaddition product of styrene oxide and  $\text{CO}_2$  for filtration test (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.28 – 7.39 (m, 8H, Ar-H), 7.18 – 7.25 (m, 8H, Ar-H), 5.60 (t,  $J$  = 8.0 Hz, 1H, COO-CH), 4.72 (t,  $J$  = 8.0 Hz, 1H, COO-CH<sub>2</sub>), 4.27 (t,  $J$  = 8.0 Hz, 1H, COO-CH<sub>2</sub>), 3.79 (t,  $J$  = 8.0 Hz, 2.20H, O-CH), 3.07 (q,  $J$  = 4.0 Hz, 2.20H, O-CH<sub>2</sub>), 2.73 (q,  $J$  = 4.0 Hz, 2.20H, O-CH<sub>2</sub>). The filtration test was performed from the mixture after 6 hours. After removal of the catalyst, the reaction continued. Reaction conditions: epoxide (20 mmol) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100 °C. The total reaction time is 12 hours.



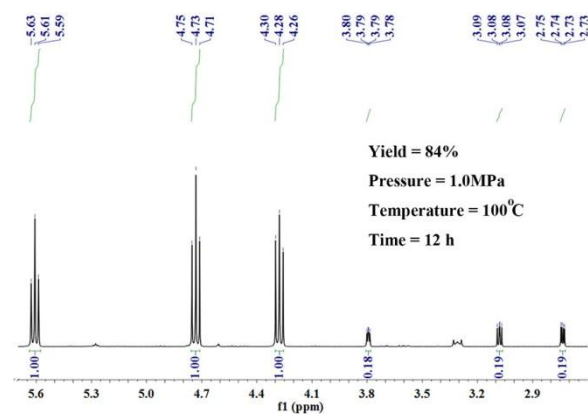
**Fig. S18.**  $^1\text{H}$  NMR spectra of the cycloaddition product of glycidol with  $\text{CO}_2$  catalyzed by HKUST-1 for 3h (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.73 – 4.78 (m, 1H, COO-CH), 4.39 – 4.48 (m, 2H, HO-CH<sub>2</sub>), 3.91 (dd,  $J$  = 12.0 Hz, 4.0 Hz, 1H, COO-CH<sub>2</sub>), 3.65 (dd,  $J$  = 12.0, 4.0 Hz, 1H, COO-CH<sub>2</sub>), 2.73 (br, 1H, -OH). Reaction conditions: epoxide (20 mmol) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100 °C.



**Fig. S19.**  $^1\text{H}$  NMR spectra of the cycloaddition product of epichlorohydrin and  $\text{CO}_2$  catalyzed by HKUST-1 for 3h (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.88 – 4.93 (m, 1H, COO-CH), 4.53 (t,  $J$  = 8.0 Hz, 1H, COO- $\text{CH}_2$ ), 4.35 (q,  $J$  = 8.0 Hz, 1H, COO- $\text{CH}_2$ ), 3.65 – 3.74 (m, 1H, Cl- $\text{CH}_2$  of product), 3.50–3.52 (m, 0.10H, Cl- $\text{CH}_2$  of epichlorohydrin), 3.16 – 3.20 (m, 1H, O-CH), 2.83 (d,  $J$  = 4.0 Hz, 1H, O- $\text{CH}_2$ ), 2.63 (q,  $J$  = 4.0 Hz, 1H, O- $\text{CH}_2$ ). Reaction conditions: epoxide (20 mmol) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100 °C.



**Fig. S20.**  $^1\text{H}$  NMR of the cycloaddition product of 1,2-epoxy-3-phenoxypropane and  $\text{CO}_2$  catalyzed by HKUST-1 for 12h (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 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- $\text{CH}_2$ ), 4.47 (t,  $J$  = 8.0 Hz, 1H, COO- $\text{CH}_2$ ), 4.19 – 4.13 (m, 1.46H, 1H - ArO- $\text{CH}_2$  of product and 0.46H - ArO- $\text{CH}_2$  of 1,2-epoxy-3-phenoxypropane), 4.07 (dd,  $J$  = 8.0 Hz, 4.0 Hz, 1H, ArO- $\text{CH}_2$  of product), 3.90 (q,  $J$  = 8.0 Hz, 0.46H, ArO- $\text{CH}_2$  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- $\text{CH}_2$ ), 2.70 (q,  $J$  = 4.0 Hz, 0.46H, O- $\text{CH}_2$ ). Reaction conditions: epoxide (20 mmol) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100 °C.



**Fig. S21.**  $^1\text{H}$  NMR spectra of the cycloaddition product of styrene oxide and  $\text{CO}_2$  catalyzed by HKUST-1 for 12h (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 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<sub>2</sub>), 4.27 (t,  $J$  = 8.0 Hz, 1H, COO-CH<sub>2</sub>), 3.79 (t,  $J$  = 8.0 Hz, 2.20H, O-CH), 3.07 (q,  $J$  = 4.0 Hz, 2.20H, O-CH<sub>2</sub>), 2.73 (q,  $J$  = 4.0 Hz, 2.20H, O-CH<sub>2</sub>). Reaction conditions: epoxide (20 mmol) and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 100 °C.

#### S4. References

1. SMART and SAINT software package, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
2. (a) O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339; (b) G. M. Sheldrick, *Acta Cryst.*, A, 2008, **64**, 112; (c) G. M. Sheldrick, *Acta Cryst. C.*, 2015, **71**, 3.
3. H. Xu, B. Zhai, C. S. Cao and B. Zhao, *Inorg. Chem.*, 2016, **55**, 9671.
4. V. Guillerme, Ł. J. Weseliński, Y. Belmabkhout, A. J. Cairns, V. D'Elia, Ł. Wojtas, K. Adil and M. Eddaoudi, *Nature Chem.*, 2014, **6**, 673.
5. A. C. Kathalikkattil, D. W. Kim, J. Tharun, H. G. Soek, R. Roshan and D. W. Park, *Green Chem.*, 2014, **16**, 1607.
6. Y. W. Ren, Y. C. Shi, J. X. Chen, S. R. Yang, C. R. Qi and H. F. Jiang, *RSC Adv.*, 2013, **3**, 2167.
7. J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang and B. Han, *Green Chem.*, 2009, **11**, 1031.
8. Z. Zhou, C. He, J. Xiu, L. Yang and C. Duan, *J. Am. Chem. Soc.*, 2015, **137**, 15066.
9. W. Jiang, J. Yang, Y. -Y. Liu, S. -Y. Song and J. -F. Ma, *Chem. Eur. J.*, 2016, **22**, 1.
10. D. De, T. K. Pal, S. Neogi, S. Senthilkumar, D. Das, S. S. Gupta and P. K. Bharadwaj, *Chem. Eur. J.*, 2016, **22**, 3387.
11. H.-Y. Choa, D.-A. Yanga, J. Kima, S.-Y. Jeongb and W.-S. Ahna, *Catalysis Today.*, 2012, **185**, 35.
12. D.-A. Yang, H.-Y. Cho, J. Kim, S.-T. Yang and W.-S. Ahn, *Energy Environ. Sci.*, 2012, **5**, 6465.
13. E. E. Macias, P. Ratnasamy and M. A. Carreon, *Catalysis Today.*, 2012, **198**, 215.