Electronic Supporting Information

A robust and porous titanium metal-organic framework for gas adsorption, CO2 capture and conversion

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S1 Materials and Instruments

All chemicals were commercially available and used without further purification. IR spectra were recorded on a Nicolet-iS50 FT-IR spectrophotometer with KBr pellets in the region of 4000-400 cm^{-1}. The powder X-ray diffraction (PXRD) data were collected on a Rigaku SmartLab 9 kW Advance diffractionmeter with Cu-Kα radiation (λ=1.5418 Å) at 298 K. Thermogravimetric analysis (TGA) and mass spectrum was performed under nitrogen atmosphere on a Netzsch STA 449F5-QMS403C simultaneous TG/DSC-QMS analyzer with a heating rate of 20 °C/min. N_2 and CO_2 adsorption isotherms were measured on a Micromeritics ASAP 2460 system. The sample were degassed at 150 °C for 12 h prior to the measurements. ^{1}H and ^{13}C NMR spectra were measured on Bruker 500 MHz spectrometer by using tetramethylsilane (TMS) as the internal standard. SEM-Energy-dispersive X-Ray analysis (EDX) Particle morphologies and dimensions were studied with a Thermo Fisher Scientific FIB-SEM GX4 scanning electron microscope at an accelerating voltage of 20 kV.

Table S1 The reported Ti-MOFs with various Ti-O clusters

Entry	Metalcluster/core	Materials	Surface area	Ref
1	TiO_6	ZTOF-2	S_{BET} = 1878 $m^2\ g^{-1}$	[1]
2	TiO_6	NTU-9		[2]
3	TiO_6	MIL-167		[3]
4	TiO_6	MIL-168		[3]
5	TiO_6	1-Ti		[4]
6	TiO_6	MUV-11	S_{BET} = 756 $m^2\ g^{-1}$	[5]
7	$TiO_4(\mu_2\text{-}O)_2$	ACM-1	S_{BET} = 1212 $m^2\ g^{-1}$	[6]
8	$TiO_6(\mu_2\text{-}O)$	COK-47	S_{BET} = 573 $m^2\ g^{-1}$	[7]
9	$TiO_6(\mu_2\text{-}O)$	COK-47-bdc		[7]
10	$TiO_6(\mu_2\text{-}O)$	COK-47-bpyrdc		[7]
11	$Ti(C_2O_2)_3$	Ti-CAT-5	S_{BET} = 450 $m^2\ g^{-1}$	[8]
12	Ti_2O_{11}	MIL-169		[3]
13	Ti_3O	Ti-MIL-101		[9]
14	$Ti_3(OH)_2$	Ti_3-BPDC	S_{BET} = 636 $m^2\ g^{-1}$	[10]

| 15	$Ti_3(\mu_3\text{-}O)$	COK-69	$S_{BET} = 29.13\ m^2\,g^{-1}$	[11]
16	$Ti_3(\mu_3\text{-}O)$	MIL-100(Ti)	$S_{BET} = 1321\ m^2\,g^{-1}$	[12]
17	$Co_2Ti(\mu_3\text{-}O)$	CTOF-1	$S_{BET} = 637\ m^2\,g^{-1}$	[13]
18	$Co_2Ti(\mu_3\text{-}O)$	CTOF-2	$S_{BET} = 618\ m^2\,g^{-1}$	[13]
19	$Co2Ti(\mu3\text{-}O)\ (COO)6$	PFC-20-Co_2Ti		[14]
20	$Ni2Ti(\mu3\text{-}O)\ (COO)6$	PFC-20-Ni_2Ti		[14]
21	$Mn2Ti(\mu3\text{-}O)\ (COO)6$	PFC-20-Mn_2Ti		[14]
22	$Co_2Ti(\mu_3\text{-}O)$	Co_2Ti-bdc-tpt	$S_{BET} = 1369.8\ m^2\,g^{-1}$	[15]
23	$Mg_2Ti(\mu_3\text{-}O)$	Mg_2Ti-bdc-tpt	$S_{BET} = 1460.6\ m^2\,g^{-1}$	[15]
24	$Mg_2Ti(\mu_3\text{-}O)$	Mg_2Ti-bdc-tppy	$S_{BET} = 1599.1\ m^2\,g^{-1}$	[15]
25	$Mg_2Ti(\mu_3\text{-}O)$	Mg_2Ti-bdc-tpbz	$S_{BET} = 1661.7\ m^2\,g^{-1}$	[15]
26	$Zn_3Ti(\mu_3\text{-}OH)$	ZTOF-1	$S_{BET} = 1045\ m^2\,g^{-1}$	[16]
27	$Ti_2Ca_2(\mu_3\text{-}O)_2(H_2O)_4$	MUV-10	$S_{BET} = 1041\ m^2\,g^{-1}$	[17]
28	$Ti_2Ca_2(\mu_3\text{-}O)_2(\mu_2\text{-}H_2O)_2(H_2O)_4$	LCU-402	$S_{BET} = 1460\ m^2\,g^{-1}$	This work
29	$[Ti_5(OAc)_2(OH)_6]_n$	Ti-TBP	$S_{BET} = 527.7\ m^2\,g^{-1}$	[18]
30	$(Ti_6O_9)_n$	MIL-177-HT	$S_{BET} = 690\ m^2\,g^{-1}$	[19]
31	$Ti_6(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6$	ZSTU-1	$S_{BET} = 536\ m^2\,g^{-1}$	[20]
32	$Ti_6(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6$	ZSTU-2	$S_{BET} = 628\ m^2\,g^{-1}$	[20]
33	$Ti_6(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6$	ZSTU-3	$S_{BET} = 861\ m^2\,g^{-1}$	[20]
34	Ti_6O_6	MOF-901	$S_{BET} = 550\ m^2\,g^{-1}$	[21]
35	Ti_6O_6	MOF-902	$S_{BET} = 400\ m^2 g^{-1}$	[22]
36	Ti_7O_6	PCN-22	$S_{BET} = 1284\ m^2\,g^{-1}$	[23]
37	$Ti_8O_8(OH)_4$	MIL-125	$S_{BET} = 1550\ m^2\,g^{-1}$	[24]
38	$Ti_8O_8(OH)_4$	NH_2-MIL-125	$S_{BET} = 1302\ m^2\,g^{-1}$	[25]
39	$Ti_8(\mu_2\text{-}O)_8(OAC)_8$	MIP-207	$S_{BET} = 570\ m^2\,g^{-1}$	[26]
40	$Ti_8Zr_2O_{12}$	PCN-415	$S_{BET} = 1550\ m^2\,g^{-1}$	[27]
41	$Ti_8Zr_2O_{12}$	PCN-416	$S_{BET} = 1337\ m^2\,g^{-1}$	[27]
42	$Ti_{12}O_{15}$	MIL-177-LT	$S_{BET} = 730\ m^2\,g^{-1}$	[19]
43	$Ti_n(\mu_2\text{-}O)_n$	DGIST-1	$S_{BET} = 1957.3\ m^2\,g^{-1}$	[28]
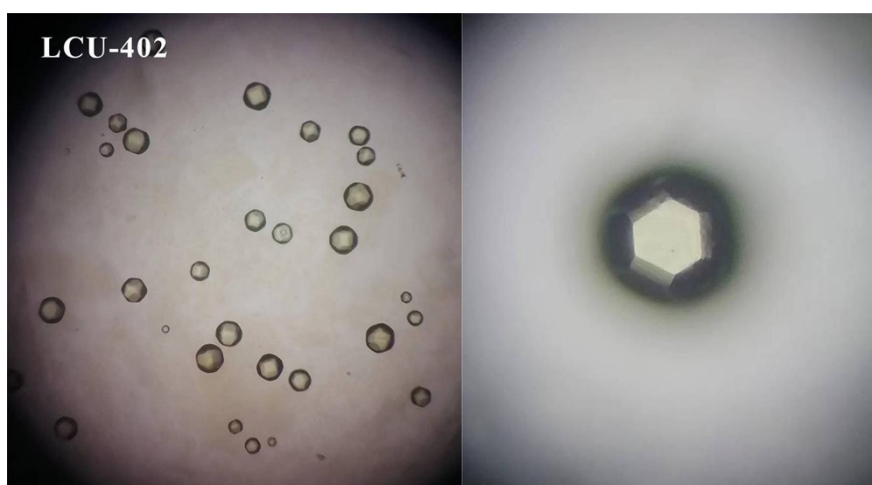
Fig. S1 Photographs of single crystals of LCU-402

S2 Scanning Electron Microscopy (SEM-EDX)

Particle morphologies, dimensions, and SEM-Energy-dispersive X-Ray analysis (EDX) of LCU-402 solids were studied with a Thermo Fisher Scientific FIB-SEM GX4 scanning electron microscope at an accelerating voltage of 20 kV. Mapping of LCU-402 showing Ti (roseo) and Ca (yellow) confirms that element distribution is homogeneous.
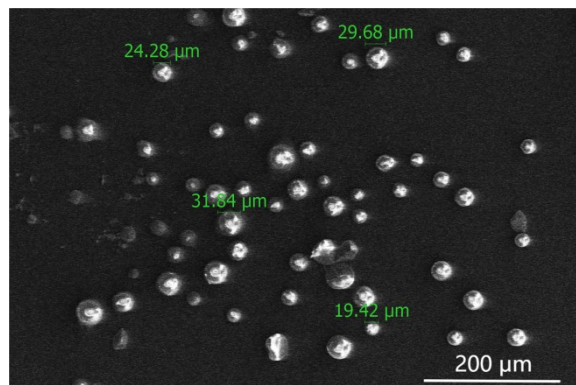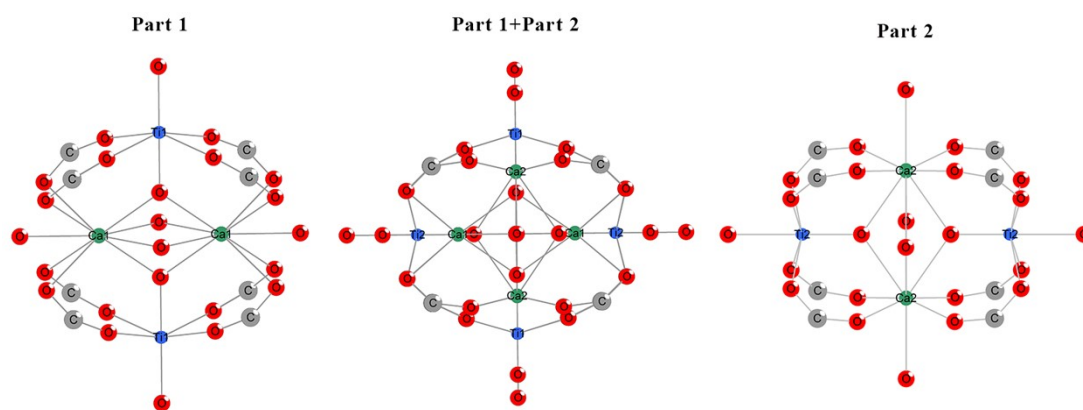

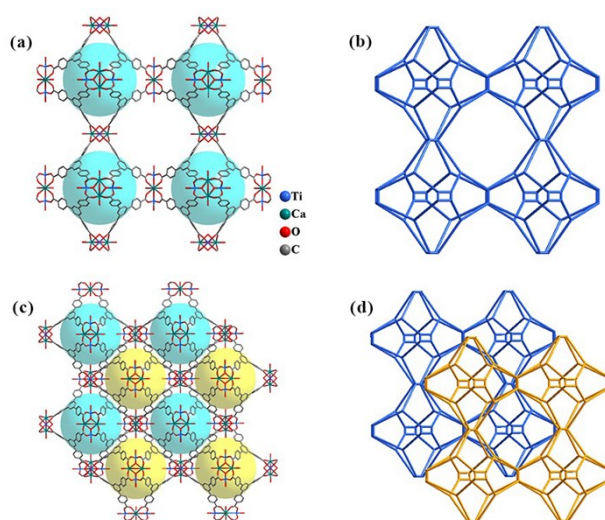**Fig. S2** Scanning Electron Microscopy (SEM) images of LCU-402.
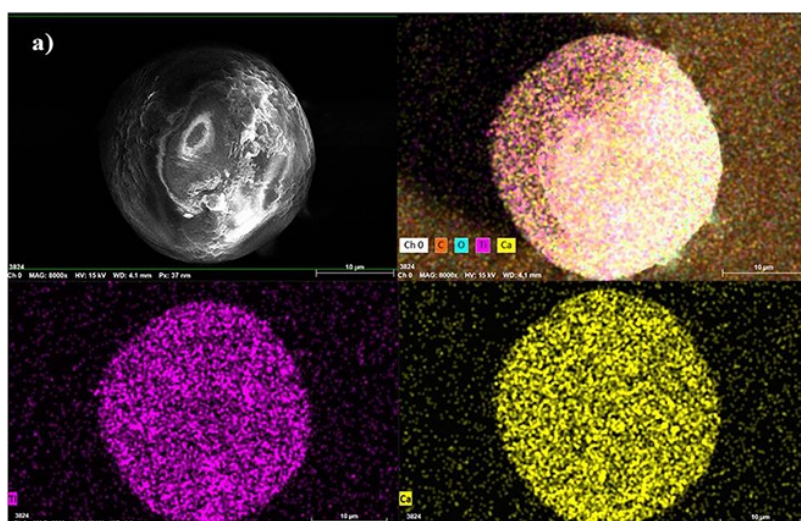
Fig. S3 Mapping of LCU-402 showing Ti (pink) and Ca (yellow)
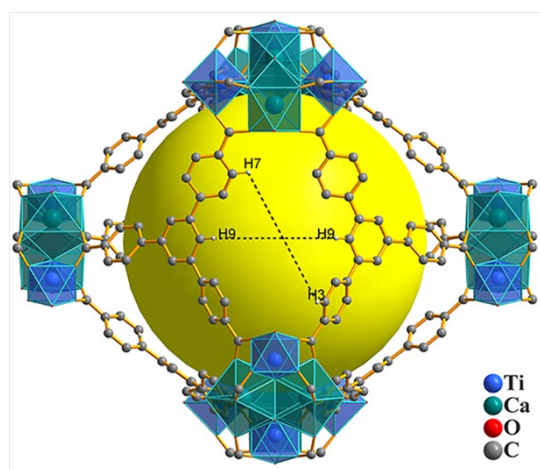
S3 Single-crystal X-ray diffraction analysis of LCU-402

Fig. S4 ORTEP representation (50% probability) of the secondary building unit showing the two fragments PART 1 and PART 2 separately.

Fig. S5 8-c SBU links 3-c BTB and (3,8)-connected augmented the net.

Fig. S6 the distance of H9···H9 and H3···H7

Table S2 Crystal data and structure refinements for LCU-402

	BTB-Ti-Ca
Empirical formula	$C_{36}H_{25.31}CaO_{11.65}Ti$
Formula weight	732.32
Crystal system	cubic
Space group	*Im-3*
a/Å	26.4097(2)
b/Å	26.4097(2)
c/Å	26.4097(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	18420.0(4)
Z	12
ρ_{calc}g/cm^3	0.792
μ/mm^{-1}	2.215
F(000)	4518.0
2θ range for data collection/°	6.694 to 144.74
Index ranges	$-24 \leq h \leq 31$, $-31 \leq k \leq 29$, $-32 \leq l \leq 32$
GoF on F^2	1.045
Final R indexes [I>=2σ (I)]	R1 = 0.0701, wR2 = 0.2013
Final R indexes [all data]	R1 = 0.0909, wR2 = 0.2218

S4 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere on a Netzsch STA 449F5-QMS403C. TGA plot (black line) shows the LCU-402 loses all solvents (water, DMF) with a weight loss of 34.9% before 250 °C. Then, with clear plateau, it started to decompose.
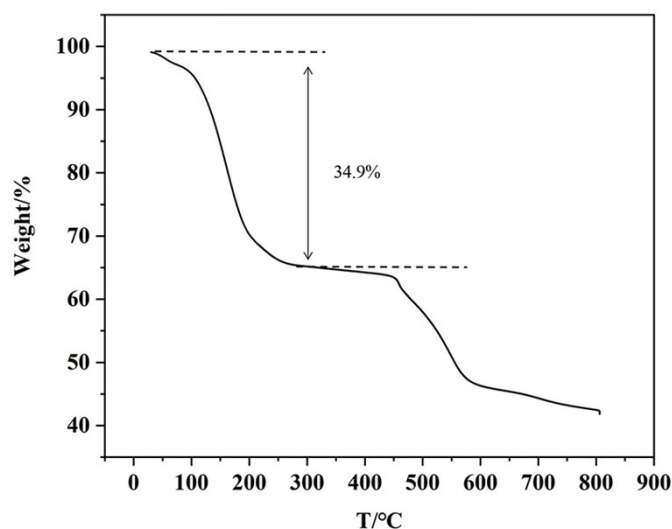

Fig. S7 TGA plot of as-synthsized LCU-402

S5 LCU-402 Pore size distribution

N_2 and CO_2 adsorption isotherms were measured on a Micromeritics ASAP 2460 system. The sample were degassed at 150 °C for 12 h prior to the measurements. Pore size distribution was analysed by using the solid density functional theory (NLDFT) for the adsorption branch assuming a cylindrical pore model.
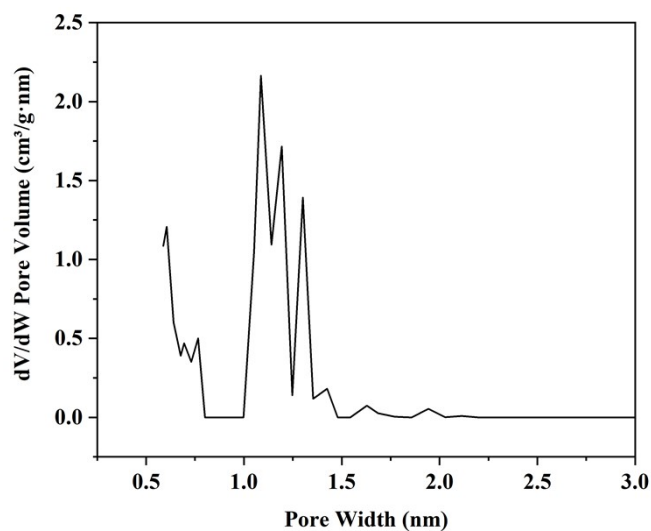

Fig. S8 LCU-402 Pore Size Distribution

S6 Isosteric heat of CO_2 adsorption (Qst)

The adsorption heat (Q_{st}) of hydrogen for the desolvated LCU-402 is fitted by Virial method using the data obtained from 273 K and 298 K with the following Equation:

$$Ln(P) = Ln(N) + \frac{1}{T}\sum_{i=0}^{m} a_i * N_i + \frac{1}{T}\sum_{j=0}^{m} a_j * N_j$$
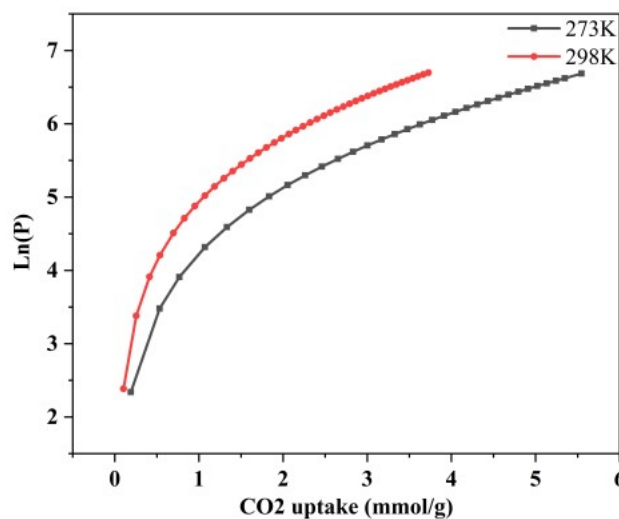
N: adsorbed quantity (mg/g);
P: pressure (mmHg);
T: temperature (K);
a_i, b_j: constant;
R: 8.314 J·mol^{-1}·K^{-1};
The isosteric enthalpy of adsorption (Q_{st}):

$$Q_{st} = Ln(P) = -R * \sum_{i=0}^{m} a_i * N_i$$

Fig. S9 Nonlinear curve fitting of CO_2 sorption isotherms for LCU-402 at 273 K and 298 K.

Table S3 Fit curve equation and factor.

		Value	Standard Error
273K	a0*	-2360.88925	11.35166
	a1*	99.60839	12.11314
	a2*	-44.62595	3.84775
	a3*	16.47407	1.47966
	a4*	-2.68098	0.29351
	a5*	0.16618	0.02099
	b0*	12.56056	0.03924
	b1*	0.08971	0.04187
	b2*	-0.02043	0.00978
	k	273	0
	a0*	-2360.88925	11.35166
	a1*	99.60839	12.11314

	a2*	-44.62595	3.84775
	a3*	16.47407	1.47966
	a4*	-2.68098	0.29351
298K	a5*	0.16618	0.02099
	b0*	12.56056	0.03924
	b1*	0.08971	0.04187
	b2*	-0.02043	0.00978
	k	298	0

$$y = Ln(x) + 1/k*(a0 + a1*x + a2*x^2 + a3*x^3 + a4*x^4 + a5*x^5) + (b0 + b1*x + b2*x^2)$$

Isosteric heat of CO_2 adsorption (Qst) was calculated by using the viral equation based on the isotherms at 273 K and 298 K.

S6 Isosteric heat of CO2 adsorption (Qst)

Isosteric heat of CO_2 adsorption (Q_{st}) was calculated by using the viral equation based on the isotherms at 273 K and 298 K.
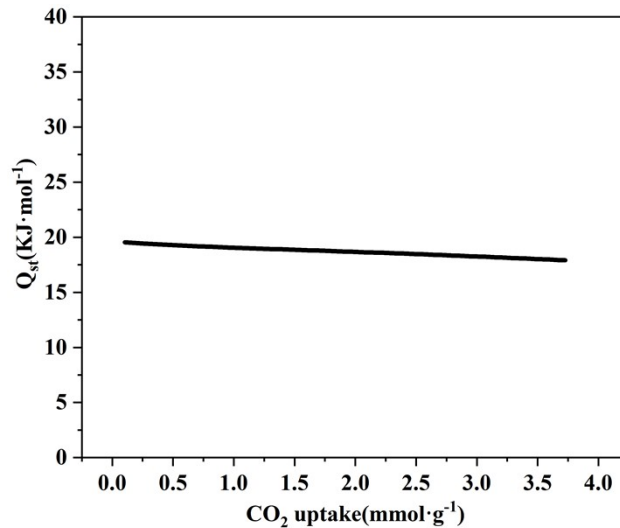
Fig. S10 Isosteric heat of adsorption (Q_{st}) calculated by the viral method

S7 IAST selectivity of LCU-402 for C_2H_6/C_2H_4 mixtures.

For adsorption isotherm data measured at 298 K, it was performed using the single point Langmuir-Freundlich isotherm model shown in Equation

$$q = q_{sat} \frac{bp^v}{1 + bp^v}$$

q: Adsorption quantity mmol/g

q_{sat} :The saturated adsorption amount of the site mmol/g

b: Single-point Langmuir-Freundlich constant of a gas component at the adsorption site kPa

V: Single-point Langmuir-Freundlich isotherm index

P: Separation pressure of the gas components kPa

Table S4 Fit curve equation and factor.

		Value	Standard Error
	A1	8.62414	0.11905
C_2H_4	B1	0.01887	2.65735E-4
	C1	0.94081	0.00909
	A1	10.13142	0.21346
C_2H_6	B1	0.02708	5.10528E-4
	C1	0.86876	0.01333

Based on the fitting parameters of the single-point Langmuir-Freundlich isotherm model at 298 K, the selectivity of LCU-402 to the C_2H_6 and C_2H_4 components was calculated using the ideal solution adsorption theory (IAST).
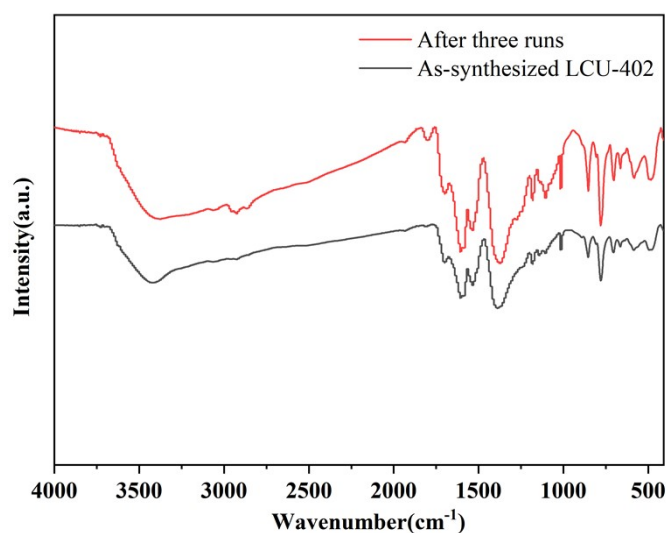
$$S_{ads} = \frac{q_1 / q_2}{y_1 / y_2}$$

S_{ads} : selectivity

q: adsorption quantity

y: molar fraction in the mixture gas

S7 Fourier-Transform infrared spectrum

Fig. S11 The FT-IR spectrum of LCU-402 as-synthesized and after three catalytic runs.

S8 Cycloaddition reaction of CO_2 with epoxides

Details of experiments and calculation procedures of catalytic efficiency:

In a typical catalytic reaction under 1 bar, epoxide (4 mmol), TBAB (1 mmol, 5 mol%), LCU-402 (0.5 mol% for open Ti sites) were put into a 15 mL Schlenk tube with solvent free environment. After centrifuging to recycle the catalyst, a little supernatant reaction mixture was taken to get analyzed by ^{1}H NMR.

The yields of propylene oxide, epichlorohydrin, epibromohydrin, 1,2-epoxyoctane, and allyl glycidyl ether (H_a for epoxides and $H_{a'}$ for carbonates, respectively) catalyzed by the LCU-402 were calculated according to the following equation.

$$Yield(\%) = \frac{I_{H_{a'}}}{I_{H_a} + I_{H_{a'}}} \times 100\%$$

The yield of styrene oxide to styrene carbonate were determined by calculation of the ^{1}H NMR integrals of corresponding highlighted protons in styrene oxide (H_a), styrene carbonate ($H_{a'}$) and phenyl group (H_b-H_f) (from styrene oxide, styrene carbonate and other by-products) according to the following equation.

$$Yield(\%) = \frac{5 \times I_{H_{a'}}}{I_{H_b - H_f}} \times 100\%$$

Figure S12. Image of the region on which EDX analysis was taken;elements ratio % from EDX analysis for organic part is represented in the table below.

Table S5 The element content determined by EDX analysis.

| Element	Atomic number	Normalized mass %	Atom %	Abs.error %
O	8	40.82	52.43	6.06
Si	14	32.96	24.12	1.39
K	19	10.74	5.65	0.48
Al	13	8.47	6.45	0.44
C	6	7.01	11.35	1.85
Ti	22	0.00	0.00	0.02
Ca	20	0.00	0.00	0.00
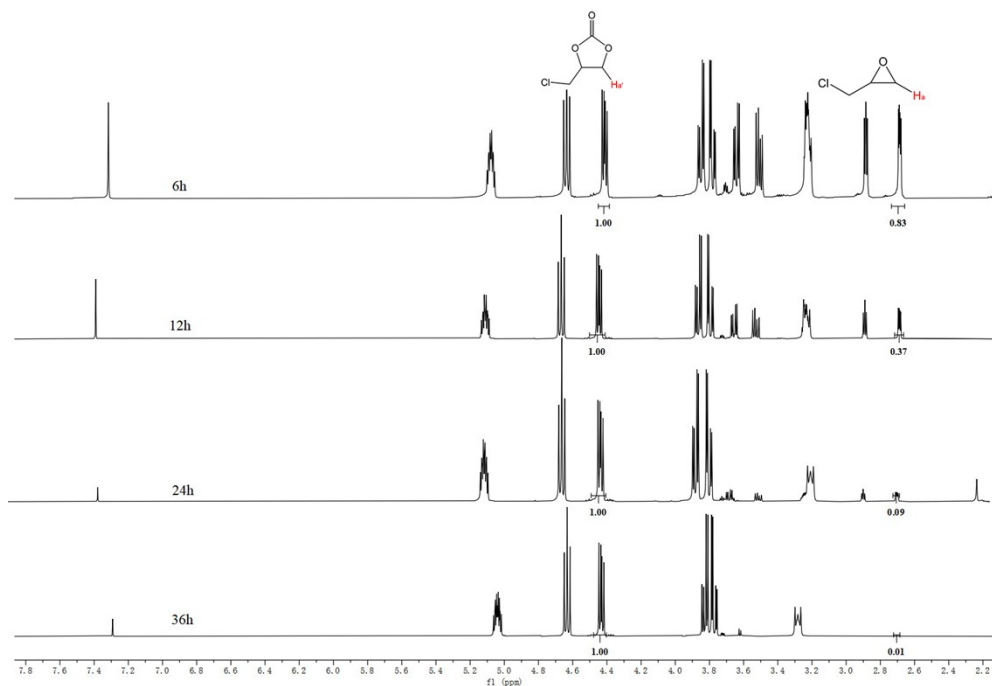
**Fig. S13** ^{1}H NMR spectrum of the mixture products under 0.15atm CO_2 atmosphere catalyzed by LCU-402 in CDCl$_3$.
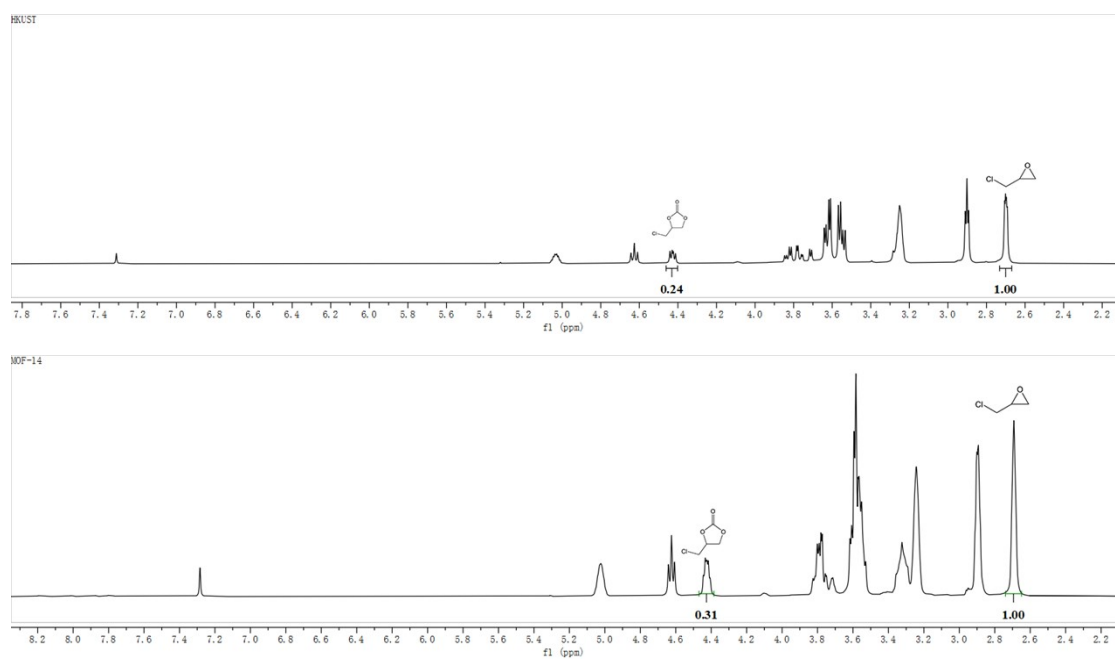
Fig. S14 ^{1}H NMR spectrum of the mixture products under 0.15atm CO_2 atmosphere catalyzed by HKUST-1 and MOF-14 in $CDCl_3$.
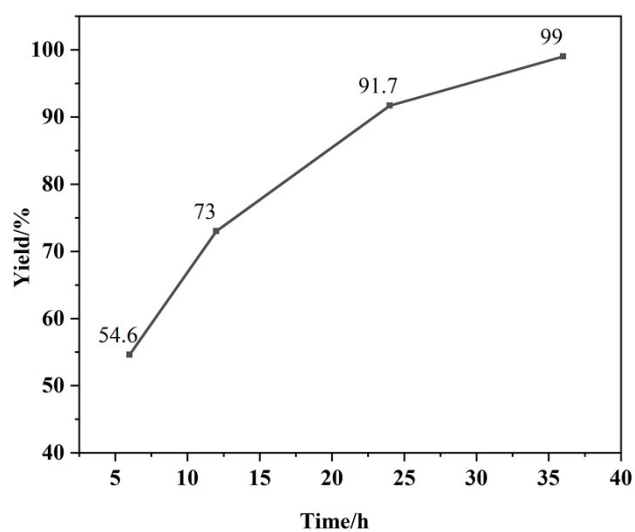
Fig. S15 Continuous sampling experiment of LCU-402 for cycloaddition reaction of epichlorohydrin with 0.15atm CO_2.
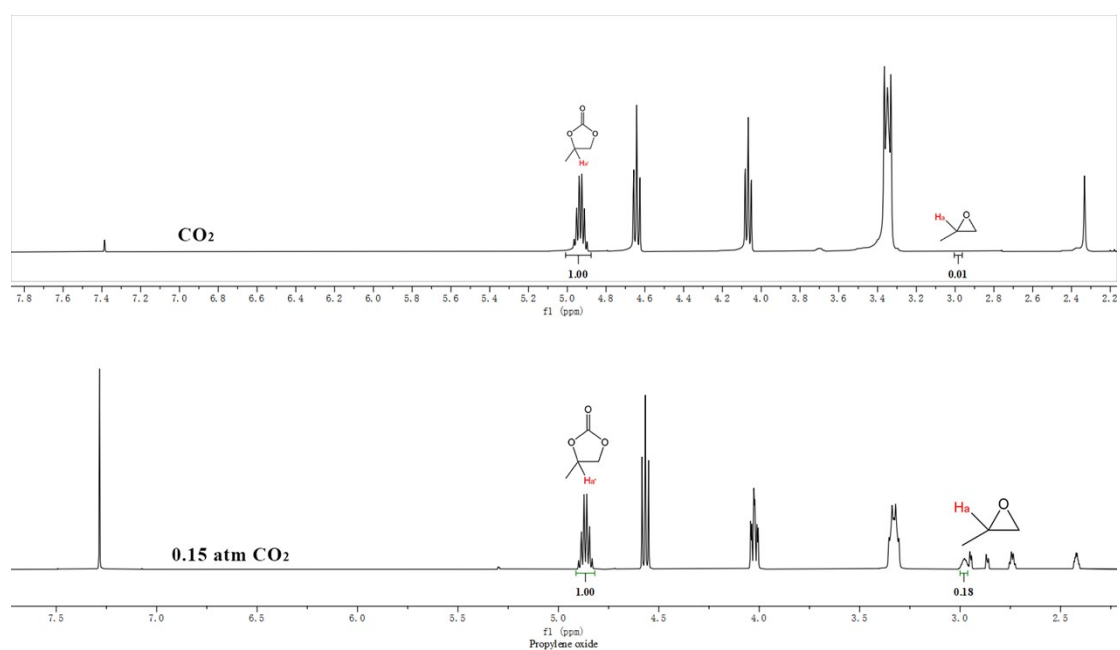
Fig. S16 ^{1}H NMR spectrum for the cycloaddition reaction of propylene epoxide under CO_2 and 0.15atm CO_2 atmosphere catalyzed by LCU-402.
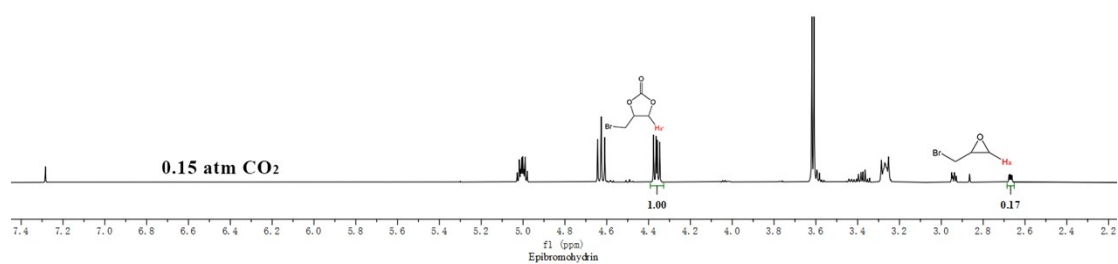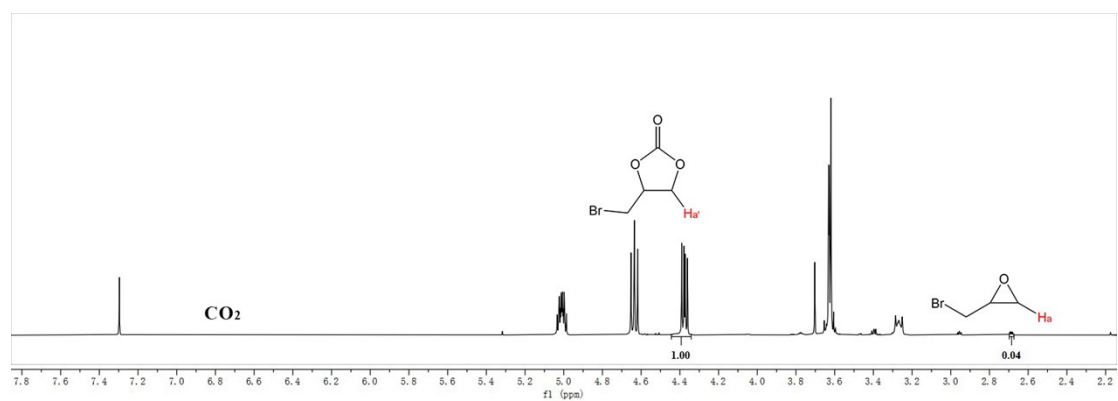
Fig. S17 ^{1}H NMR spectrum for the cycloaddition reaction of epoxy bromine propane under CO_2 and 0.15atm CO_2 atmosphere catalyzed by LCU-402.
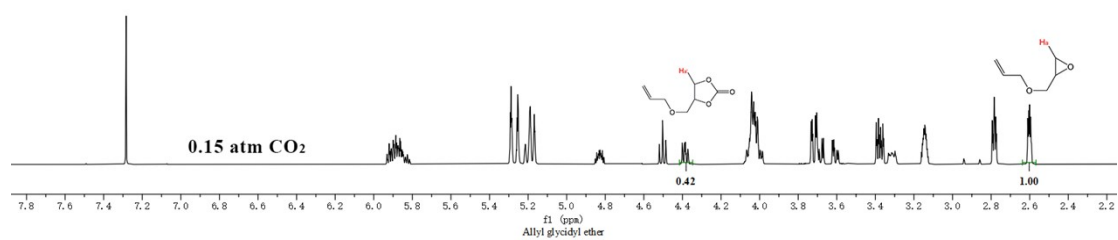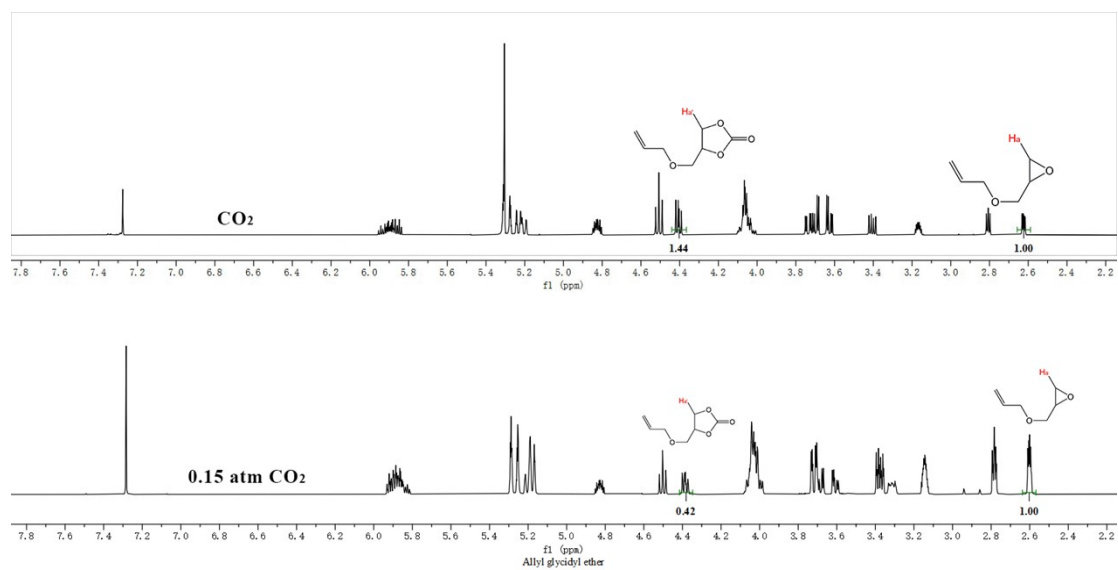
Fig. S18 ^{1}H NMR spectrum for the cycloaddition reaction of allyl glycidyl ether under CO_2 and 0.15 atm CO_2 atmosphere catalyzed by LCU-402.

Fig. S19 ^{1}H NMR spectrum for the cycloaddition reaction of cyclooxygen octane under CO_2 and 0.15 atm CO_2 atmosphere catalyzed by LCU-402.

Fig. S20 ^{1}H NMR spectrum for the cycloaddition reaction of styrene oxide under CO_2 and 0.15atm CO_2 atmosphere catalyzed by LCU-402.

Fig. S21 ^1H NMR spectrum of the mixture products under 0.15atm CO_2 atmosphere catalyzed by LCU-402 in $CDCl_3$.


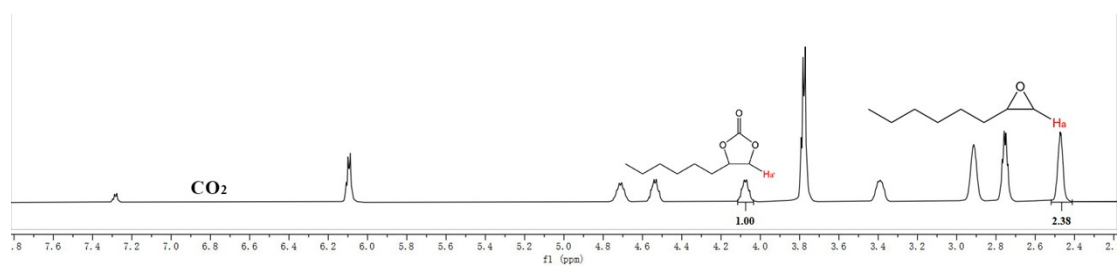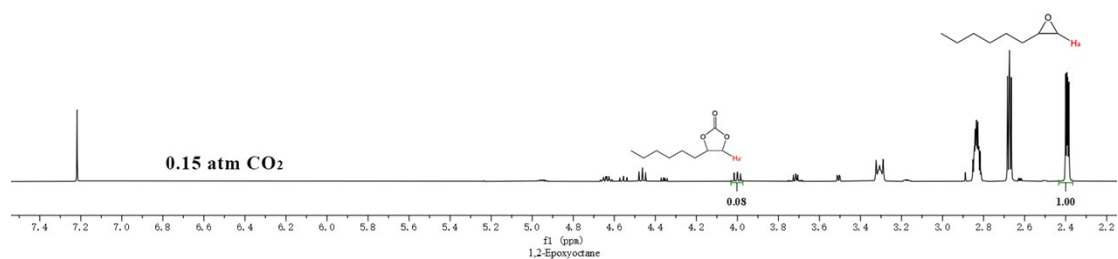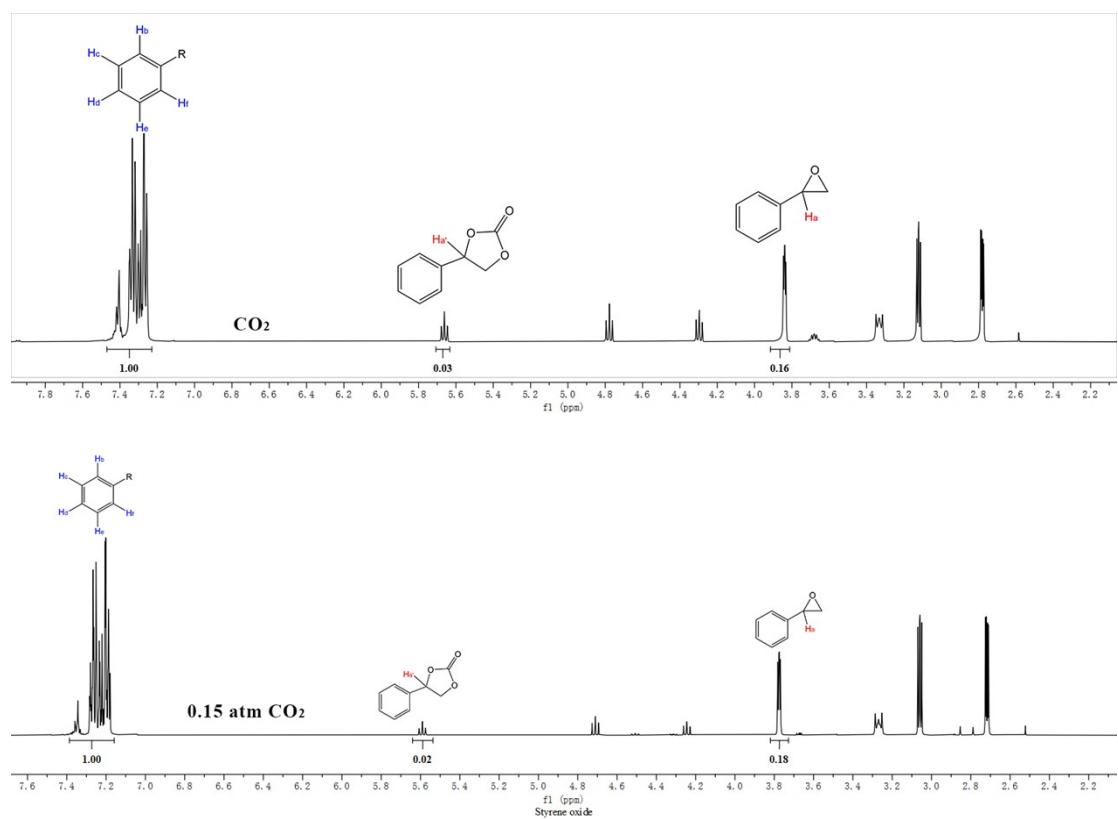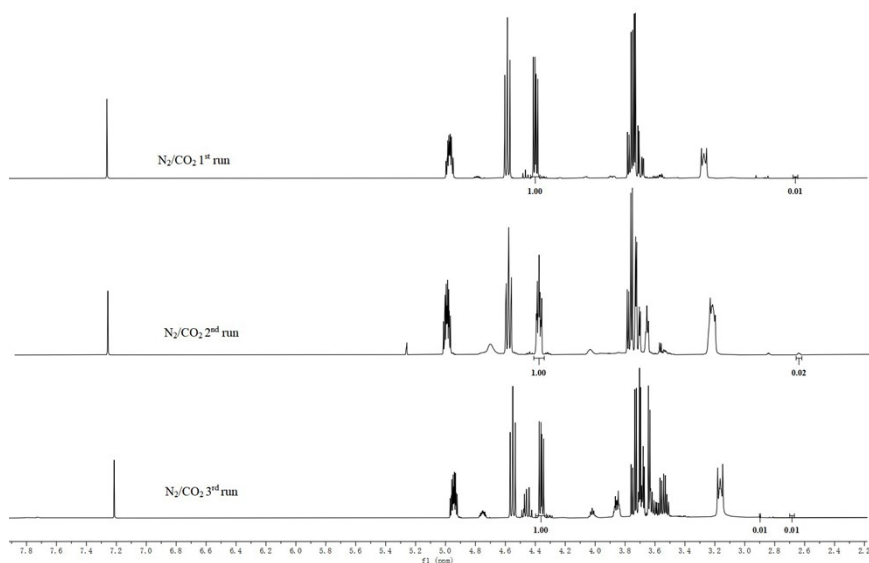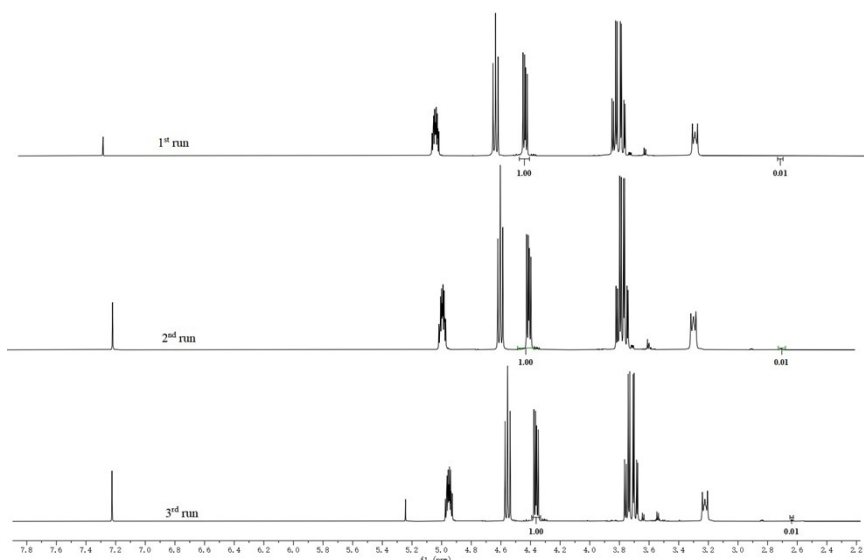**Fig. S22** ^1H NMR spectrum of the mixture products under CO_2 atmosphere catalyzed by LCU-402 in $CDCl_3$.

References

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