Electronic Supporting Information

Robust acid-base Ln-MOFs: searching for efficient catalysts in cycloaddition of CO_2 with epoxides and cascade deacetalization-Knoevenagel reactions†

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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) was performed under nitrogen atmosphere on a TG/DSC-QMS analyzer with a heating rate of 20 °C/min. Argon and CO_2 adsorption isotherms were measured on a Micromeritics ASAP 2460 system. The samples were degassed at 200 °C for 12 h prior to the measurements. ^1H NMR spectra were measured on Bruker 500 MHz spectrometer by using tetramethylsilane (TMS) as the internal standard.

S2- Single-crystal X-ray diffraction analysis of MOF 1-Yb

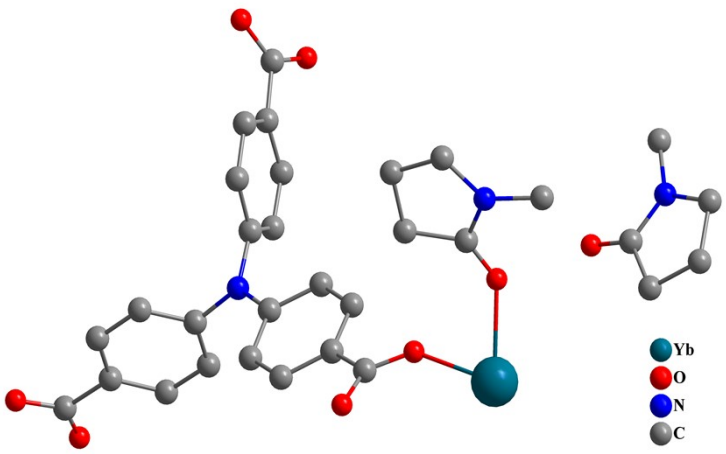


Fig. S1 The asymmetric units in the 1-Yb

Table S1 Crystal data and structure refinements for MOFs 1-Tb and 1-Yb

	1-Tb	1-Yb
Empirical formula	$C_{31}H_{30}N_3O_8Tb$	$C_{31}H_{30}N_3O_8Yb$
Formula weight	731.50	745.62
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	8.8772(3)	8.8416(3)
b/Å	12.9580(3)	12.9176(5)
c/Å	14.1742(3)	14.0990(6)
α/°	113.037(2)	112.907(4)
β/°	93.343(2)	93.312(3)
γ/°	106.968(2)	107.248(3)
Volume/Å^3	1407.29(7)	1388.86(10)
Z	2	2
ρ_{calc}g/cm^3	1.726	1. 7883
μ/mm^{-1}	2.571	3.426
F(000)	732.0	742.0
2θ range for data collection/°	4.892 to 61.284	4.92 to 61.508
Index ranges	-12≤ h ≤ 11 -16 ≤ k ≤ 17 -20 ≤ l ≤ 19	-12 ≤ h ≤ 12 -18 ≤ k ≤ 18 -19 ≤ l ≤ 20
GoF on F^2	1.040	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0294 wR_2 = 0.0605	R1 = 0.0400 wR2 = 0.0974
Final R indexes [all data]	R_1 = 0.0332 wR_2 = 0.0629	R1 = 0.0442 wR2 = 0.1006

S3- The powder X-ray diffraction data analysis

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. The PXRD patterns of as-synthesized 1-Ln solids are in well agreement with their simulated ones, confirming the phase purity of the as-synthesized bulk samples.

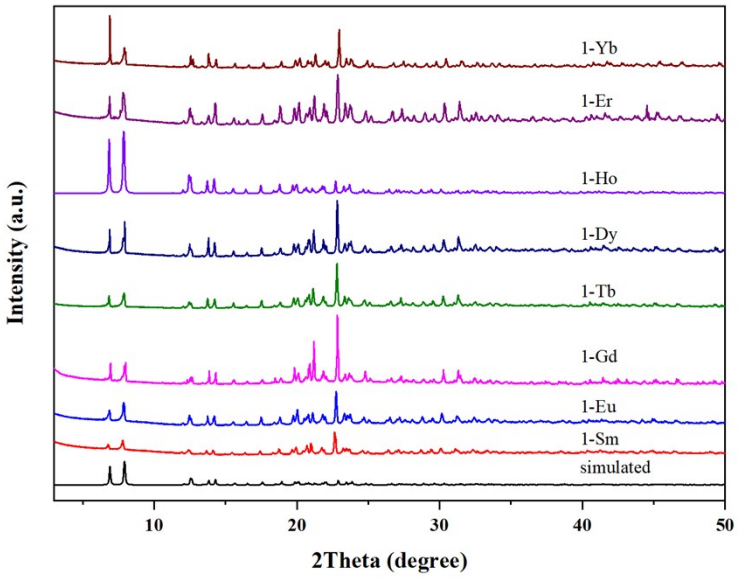


Fig. S2 The PXRD patterns of simulated, as-synthesized, and activated samples after adsorption experiments for 1-Ln.

S4-Fourier-Transform infrared spectrum

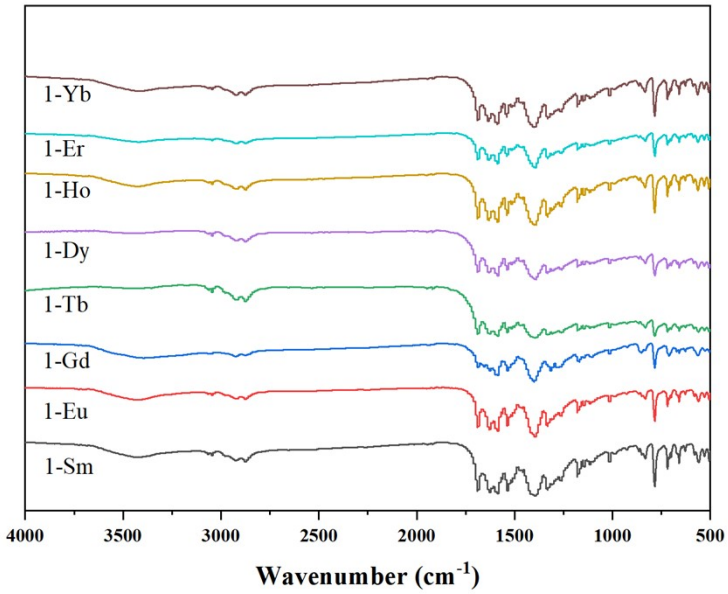


Fig. S3 The FT-IR spectrum of 1-Ln indicating almost identical structures.

S5 - Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere on a Netzsch STA 449F5-QMS403C. TGA plot (black line) shows the sample loses all solvents (water, NMP) with a weight loss of 23.95%(1-Sm), 22.66%(1-Eu), 21.02%(1-Gd), 26.43%(1-Tb), 21.49%(1-Dy), 22.06% (1-Ho), 21.10%(1-Er), 21.63%(1-Yb) before 260 °C. Then, without clear plateau, it started to decompose.

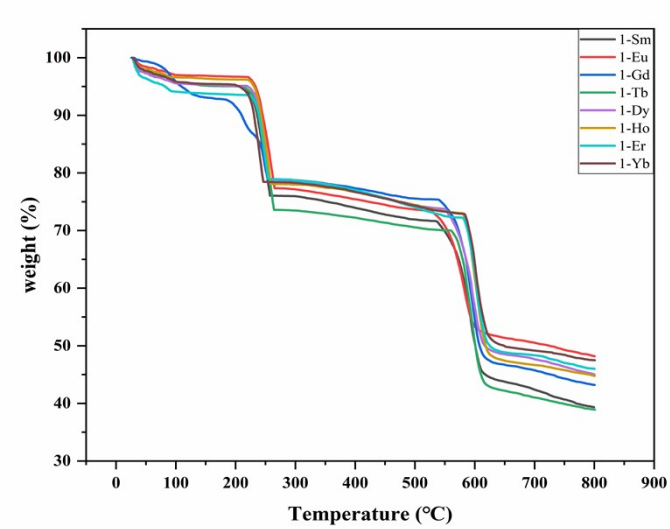


Fig. S4 TGA plot of as-synthsized MOF 1-Ln.

S6 - The adsorption isotherms

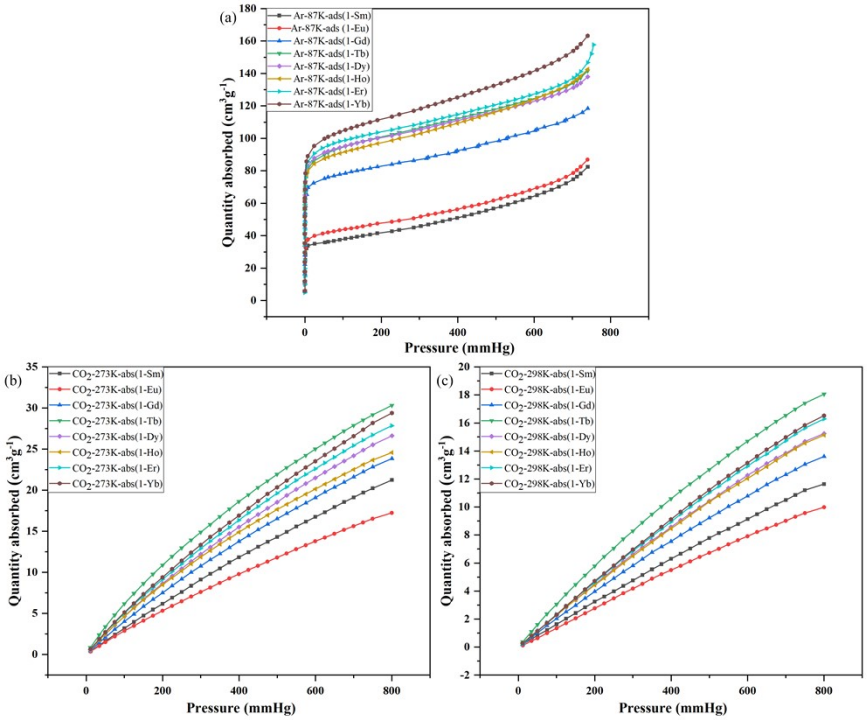


Fig. S5 (a) the Ar adsorption isotherms of 1-Ln at 87 K. (b) the CO_2 adsorption isotherms at 273 K. (c) the CO_2 adsorption isotherms at 298 K.

S7 - Isosteric heat of CO_2 adsorption (Q_{st})

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.

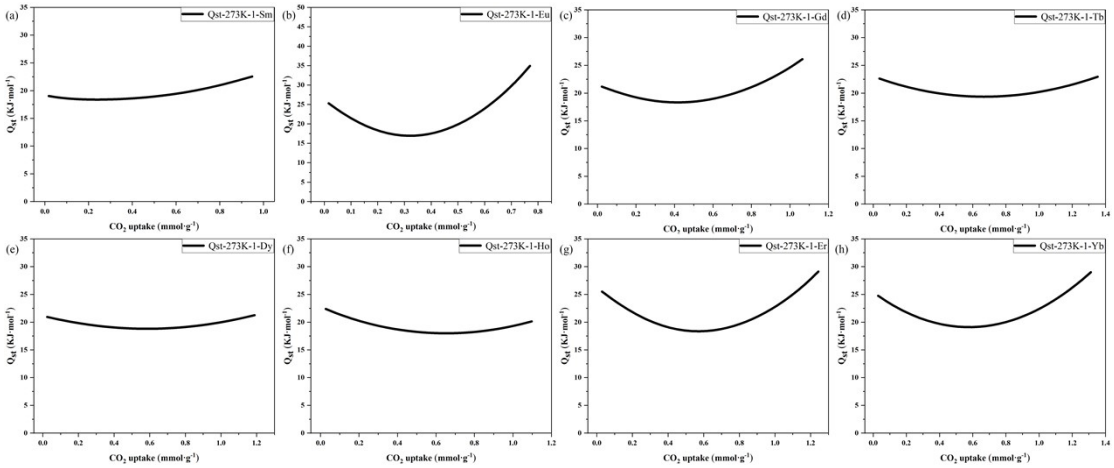
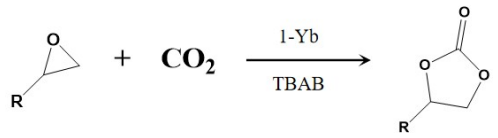
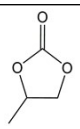
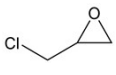
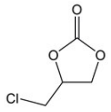
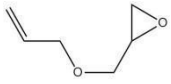
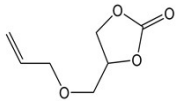
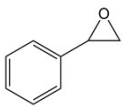
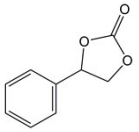


Fig. S6 Isosteric heat of adsorption (Q_{st}) calculated by the viral method, (a) 1-Sm, (b) 1-Eu, (c) 1-Gd, (d)1-Tb, (e) 1-Dy, (f) 1-Ho, (g) 1-Er, (h) 1-Yb.

S8-Catalytic cycloaddition of CO_2 and epoxides

Table S2 Cycloaddition of various epoxides with CO_2 catalyzed by 1-Yb under ambient conditions.



Entry	Epoxides	Product	Yield (%)
1			99.0
2			97.0
3			37.0
4			10.0

The stability of the catalyst is proved by the cycle experiment of the catalyst, 1-Yb was simply filtrated after the reaction was completed and then washed with Purified water and methanol. The recovered 1-Yb could be used for successive five recycling runs. Importantly, the catalytic performance of 1-Yb remained high even after the five recycle runs, [yields of products: 98% (first run), 99%(second run), 97%(third run), 99%(fourth run), 98%(fifth run).

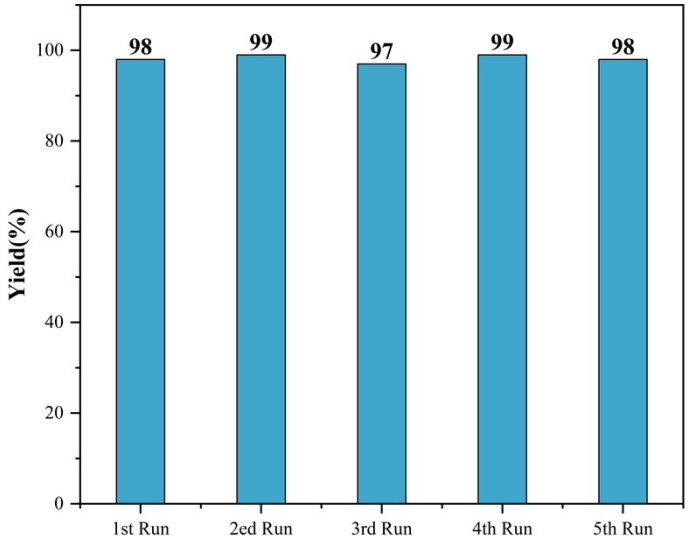


Fig. S7 The reaction results of CO_2-epoxide cycloaddition reaction catalyzed by 1-Yb in recycle experiments. Reaction conditions: 4 mmol of epichlorohydrin, solvent free, CO_2 (1 atm).

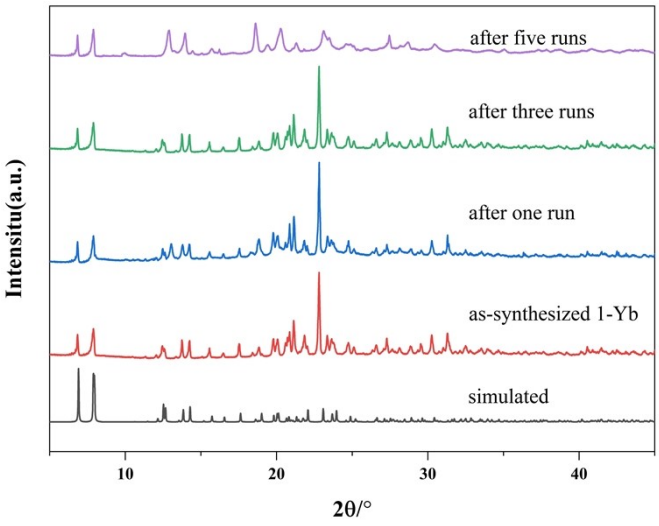


Fig. S8 The PXRD patterns of 1-**Yb** (from bottom to up): the simulated, the as-synthesized, after one recycle run, the one after three recycle runs, the one after five recycle runs.

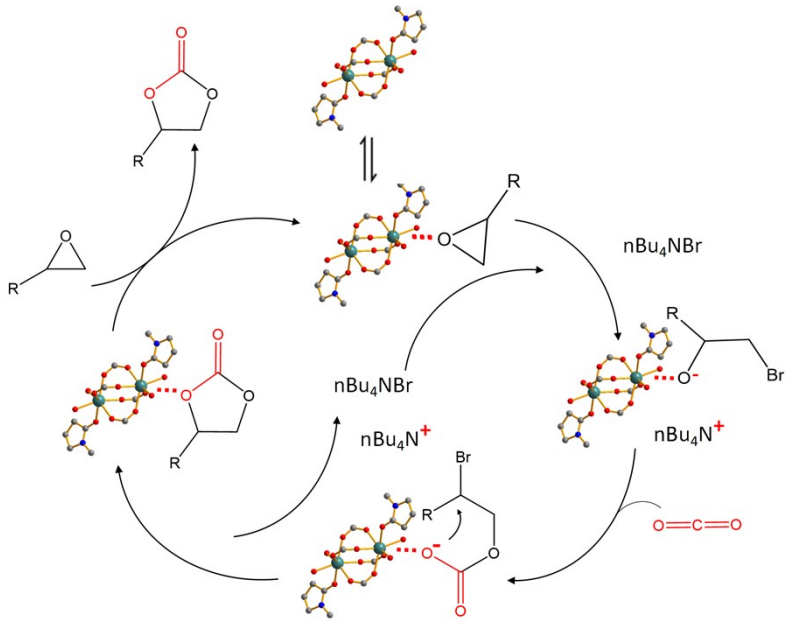


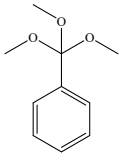
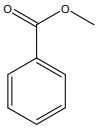
Fig. S9 A plausible mechanism for the CO_2-epoxide cycloaddition reaction over 1-Yb catalyst.

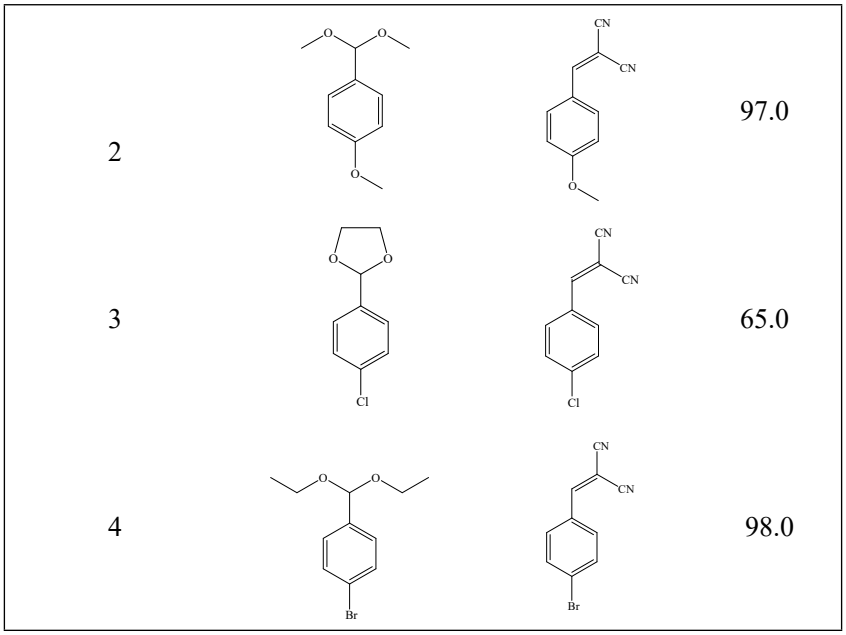
Table S3 Catalytic cycloaddition of CO_2 and epoxides

Entry	Materials	Tem.(℃)	Time(h)	Yield(%)	Ref.
1	NUC-38Yb	60	6	98.0	[1]
2	Compound **1**	80	4	>99.0	[2]
3	NUC-51a	55	6	99.0	[3]
4	NUC-29	65	12	98.3	[5]
5	NUC-54	60	8	99.0	[6]
6	NUC-53	80	4	99.0	[8]
7	MOF **1**	room temperature	48	85.0	[11]
8	JLU-Liu21	80	48	93.0	[12]
9	compound 1	room temperature	48	95.1	[13]
10	1-Yb	room temperature	36	97.0	This work

S9-Catalytic deacetalization-Knoevenagel reactions

Table S4: The deacetalization-Knoevenagel condensation reaction of aldehyde derivatives containing diffffferent groups

Entry	Subtrate	Product	Yield (%)
1			100.0



The stability of the catalyst is proved by the cycle experiment of the catalyst. 1-Yb was simply filtrated after the reaction was completed and then washed with purified water and methanol. The recovered 1-Yb could be used for successive five recycling runs. Notably, the catalytic performance of 1-Yb remained high even after the five recycle runs, [0.5 mol% catalyst: yields of 98% (first run), 97% (second run), 95% (third run), 93% (fourth run), 92% (fifth run); 0.3 mol% catalyst: yields of 86% (first run), 85% (second run), 85% (third run), 83% (fourth run), 82% (fifth run)].

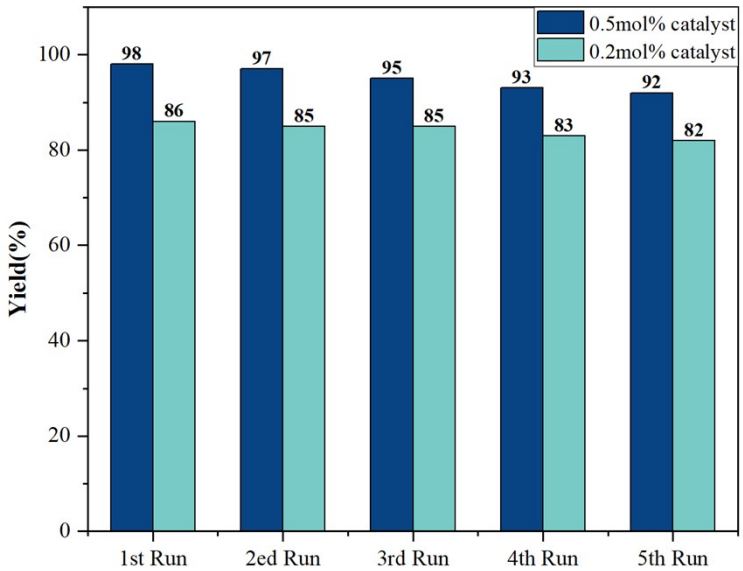


Fig. S10 The reaction results of deacetalization-Knoevenagel condensation catalyzed by 1-Yb in recycle experiments. Reaction conditions: BD (1 mmol), MA (2 mmol), H_2O (3 mmol), catalysts (0.5 mol% and 0.2 mol% respectively), 60 °C, 6 h, N_2 atmosphere.

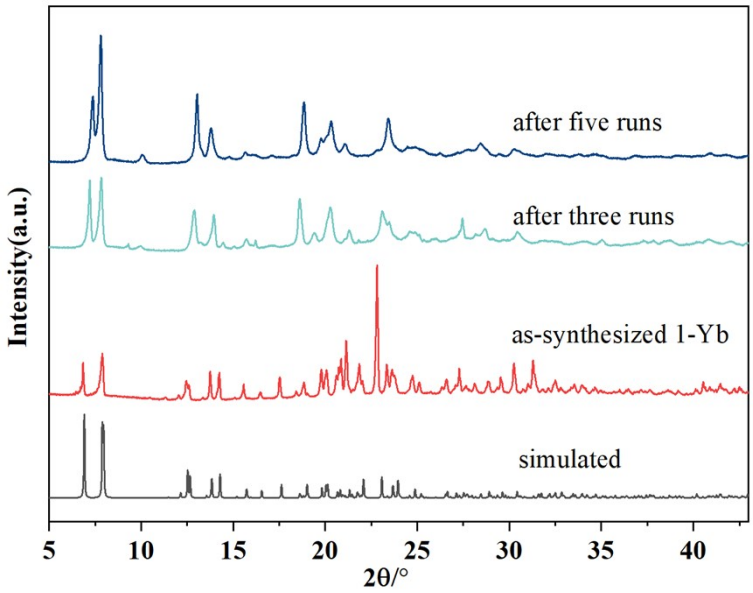


Fig. S11 The PXRD patterns of **1-Yb** (from bottom to up): the simulated, the as-synthesized, the one after three recycle runs, the one after five recycle runs.

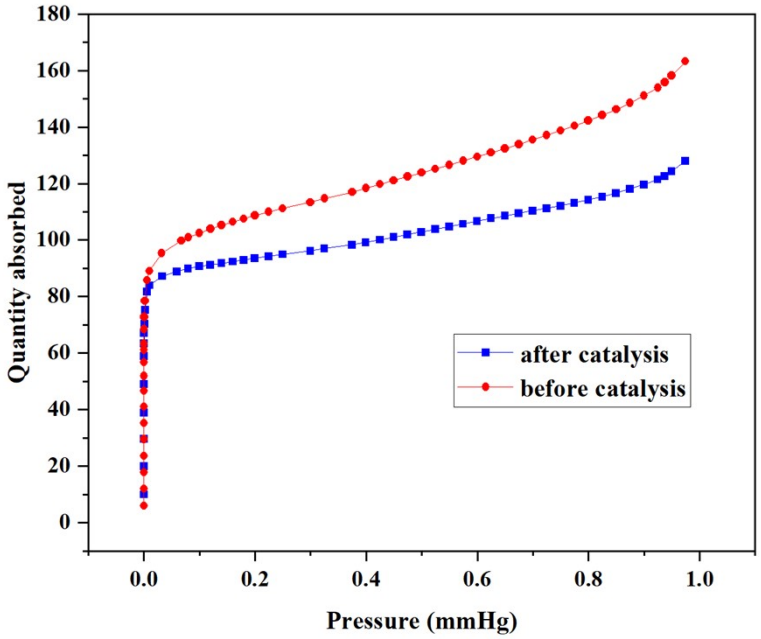


Fig. S12 Ar adsorption of the recovered **1-Yb**, showing the microporosity of the framework.

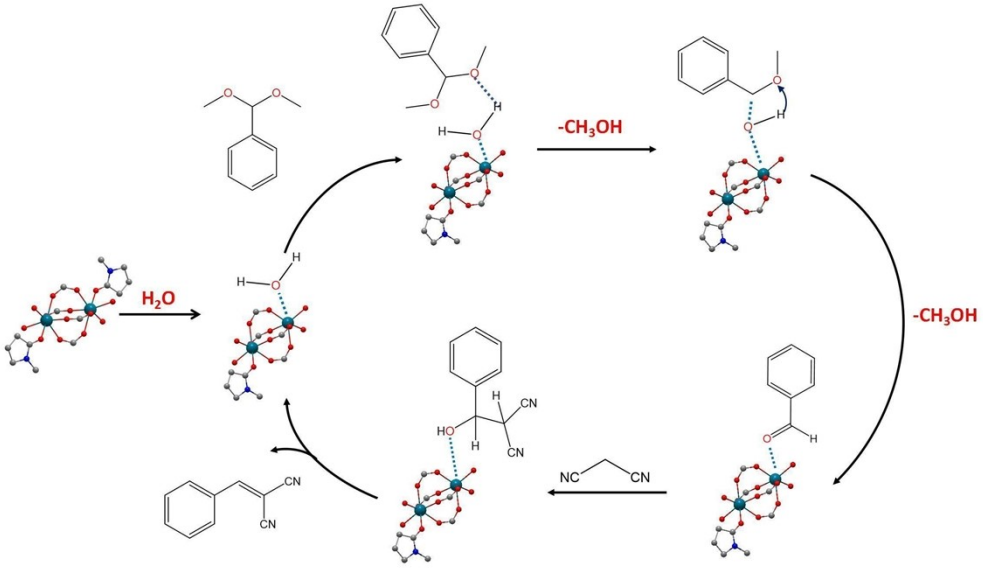


Fig. S13 Plausible reaction mechanism of deacetalization-Knoevenagel condensation reaction catalyzed by 1-Yb.

Table S5 deacetalization-Knoevenagel condensation reaction

Entry	Catalyst	Solvent	Temperature(℃)	Reaction time(h)	Yield(%)	Ref.
1	NUC-51a (1 mol%)	DMSO	70	4	99.3	[3]
2	PCN-222-Co@TpPa-1	DMSO-d_6	50	10	99.3	[4]
3	NUC-29 (1 mol%)	DMSO	70	5	99.2	[5]
4	NUC-54	DMSO	60	5	99.0	[6]
5	Yb-BDC-NH_2	DMSO-d_6	50	24	97.0	[7]
6	Dy-BDC-NH_2	DMSO-d_6	50	24	82.0	[7]
7	Sm-BDC-NH_2	DMSO-d_6	50	24	76.0	[7]
8	NUC-53	DMSO	70	6	99.0	[8]
9	MIL-101(Al)-NH_2	1,4-dioxane	90	3	96.0	[9]
10	Compound **1**	DMF	80	3	93.5	[10]
11	1-Yb	No solvent	60	6	97.0	This work

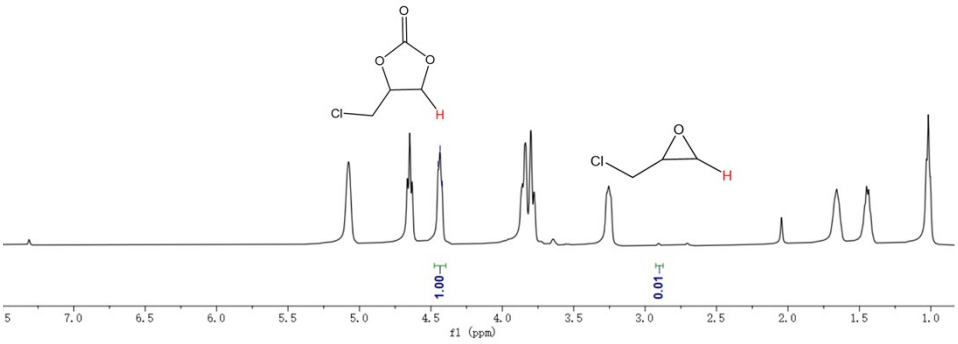


Fig. S14 ^{1}H NMR spectrum of the mixture products under CO_2 atmosphere catalyzed by 1-**Yb** in $CDCl_3$.

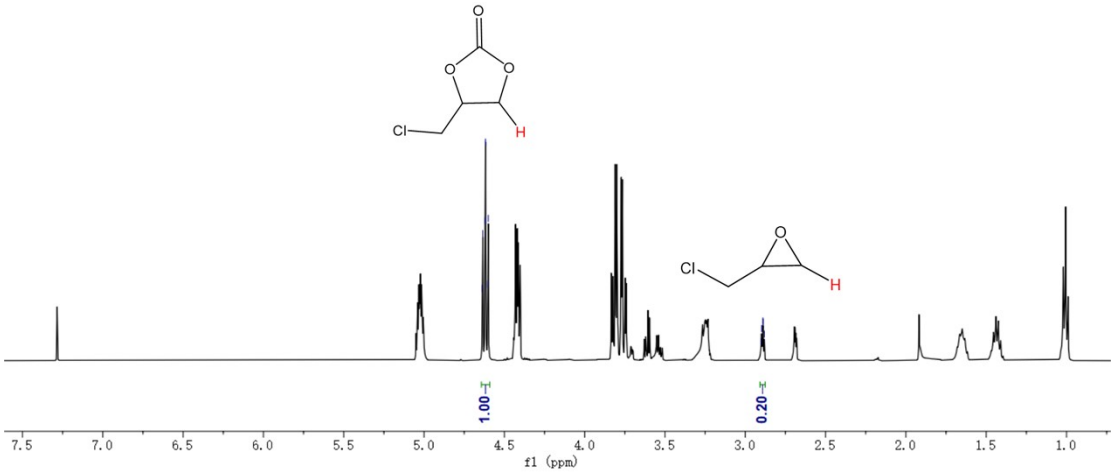


Fig. S15 ^{1}H NMR spectrum of the mixture products under CO_2 atmosphere catalyzed by 1-**Eu** in $CDCl_3$.

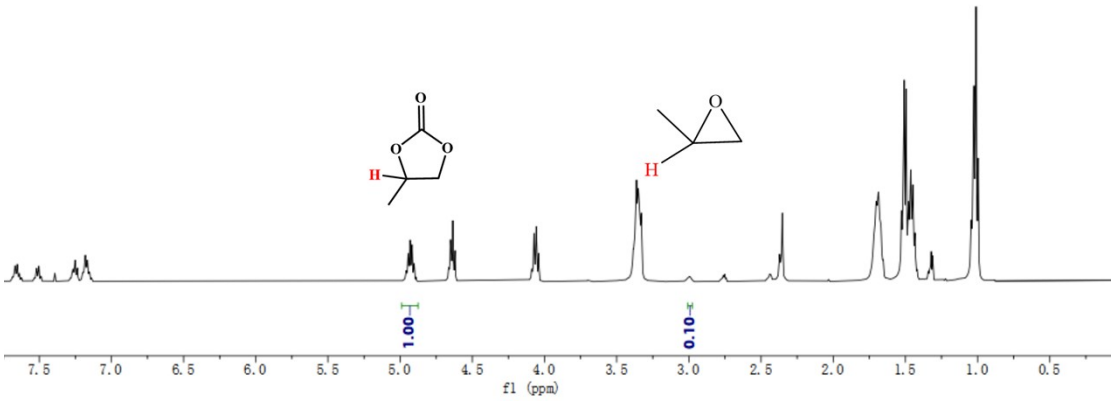


Fig. S16 ^{1}H NMR spectrum of the mixture products under CO_2 atmosphere catalyzed by 1-**Yb** in $CDCl_3$.

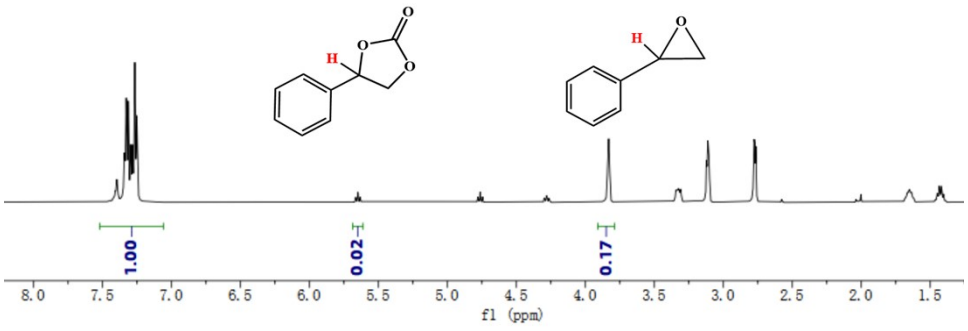


Fig. S17 ^{1}H NMR spectrum of the mixture products under CO_2 atmosphere catalyzed by 1-**Yb** in $CDCl_3$.

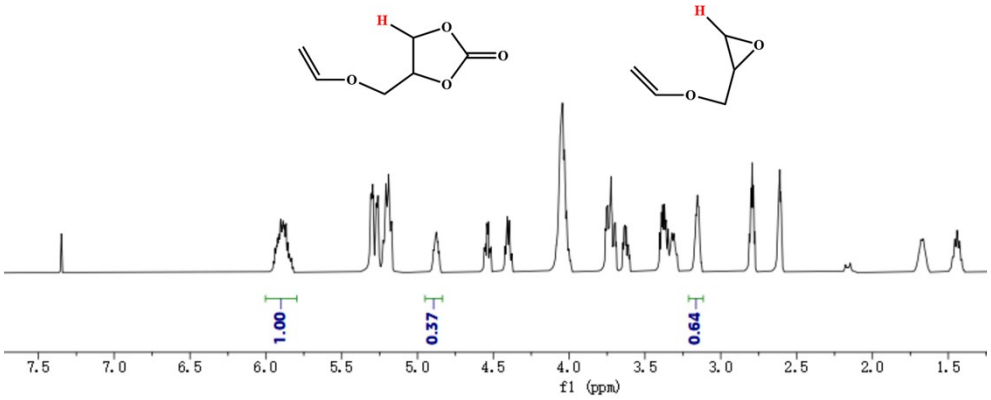


Fig. S18 ^{1}H NMR spectrum of the mixture products under CO_2 atmosphere catalyzed by 1-**Yb** in $CDCl_3$.

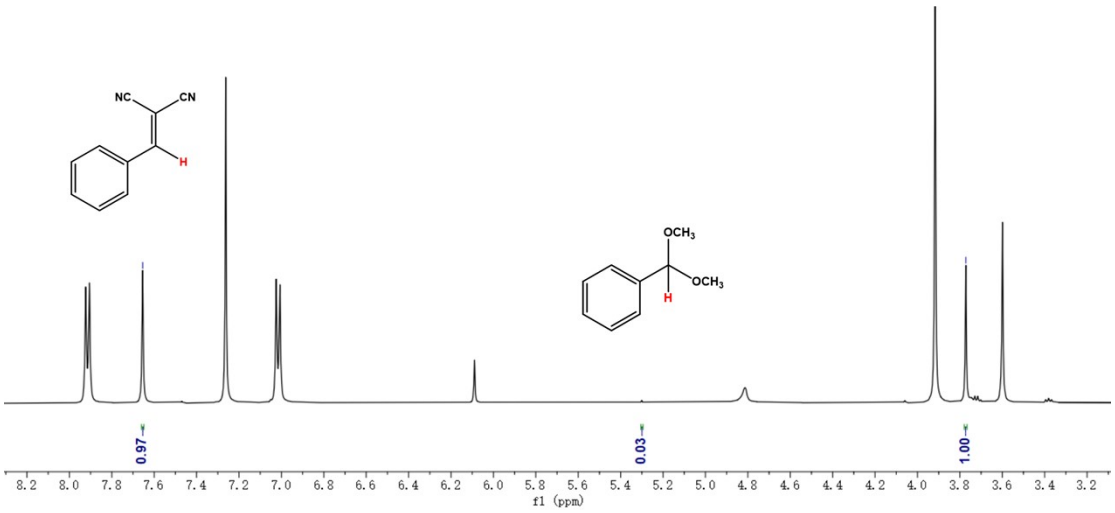


Fig. S19 ^{1}H NMR spectrum of the mixture products under N_2 atmosphere catalyzed by 1-**Yb** in $CDCl_3$.

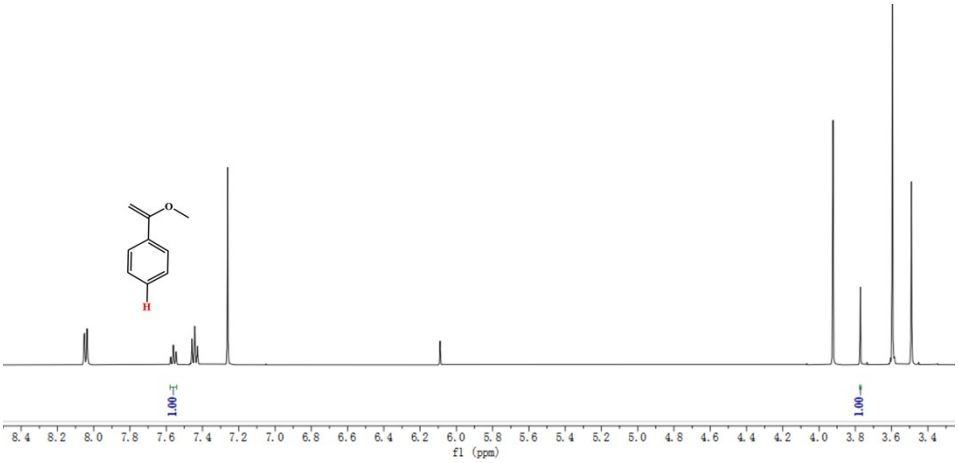


Fig. S20 ^{1}H NMR spectrum of the mixture products under N_2 atmosphere catalyzed by 1-**Yb** in $CDCl_3$.

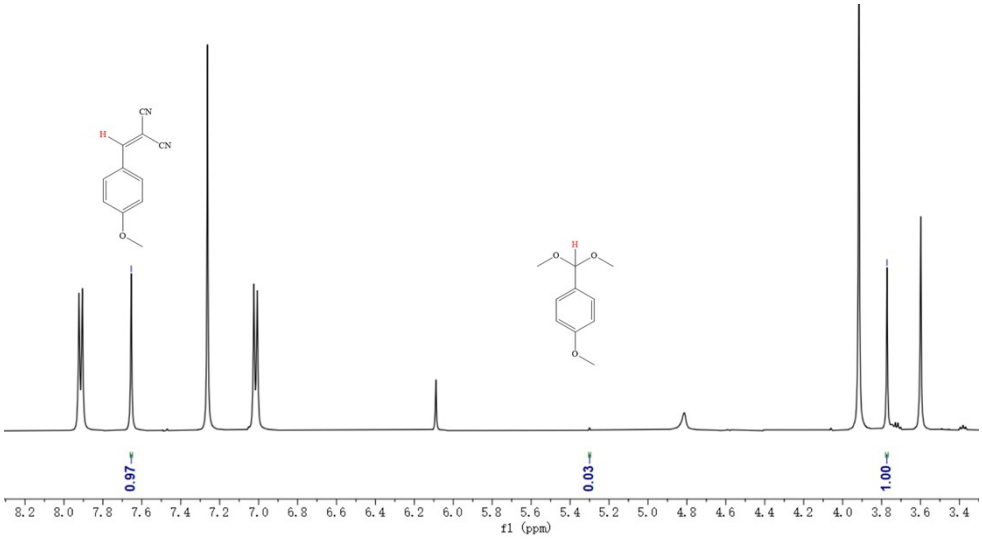


Fig. S21 ^{1}H NMR spectrum of the mixture products under N_2 atmosphere catalyzed by 1-**Yb** in $CDCl_3$.

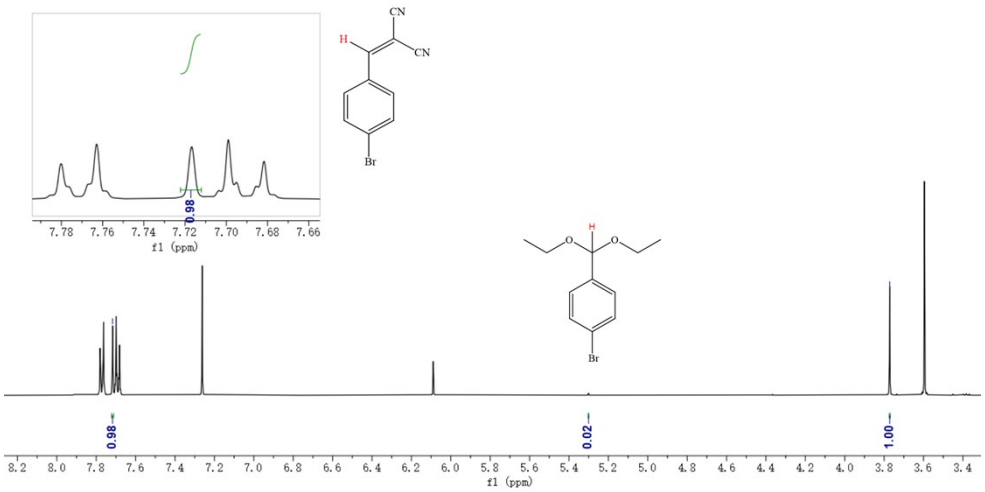


Fig. S22 ^{1}H NMR spectrum of the mixture products under N_2 atmosphere catalyzed by 1-**Yb** in $CDCl_3$.

[1] T. Zhang, H. Chen, S. Liu, H. Lv, X. Zhang, Q. Li, Highly Robust {Ln_4}-organic grameworks (Ln=Ho, Yb) for excellent catalytic performance on cycloaddition reaction of epoxides with CO_2 and Knoevenagel condensation. *ACS Catal.,* **2021**, 11, 14916-14925.
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