Supporting Information

A Zeolitic Metal Cluster Carboxylic Framework for Selective Carbon Dioxide Chemical Fixation Through the Super-large Cage

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Table of Contents

Section S1. Crystallographic data of ZCF-1

Table S1. Selected bond lengths (Å) and bond angles (º) for **ZCF-1**.

ZCF-1			
Zn(1)-O(11)	1.9253(6)	O(9)-Zn(1)#6	2.291(19)
Zn(1)-O(3)	1.96(3)	O(10)-Zn(1)#7	1.96(3)
O(11)-Zn(1)#2	1.9253(6)	O(11)-Zn(1)-O(3)	116.0(7)
O(11)-Zn(1)#1	1.9253(6)	Zn(1)#2-O(11)-Zn(1)#3	104.59(3)
O(11)-Zn(1)#3	1.9253(6)	Zn(1)#1-O(11)-Zn(1)	104.59(3)
O(4)-Zn(1)#3	2.06(2)	Zn(1)-O(11)-Zn(1)#3	111.967(17)
O(7)-Zn(1)#3	2.06(4)	Zn(1)#1-O(11)-Zn(1)#2	111.969(17)
O(8)-Zn(1)#2	2.61(2)	Zn(1)#1-O(11)-Zn(1)#3	111.965(17)
O(2)-Zn(1)#4	2.13(3)	Zn(1)#2-O(11)-Zn(1)	111.967(17)
O(1)-Zn(1)#5	2.00(3)		

Symmetry codes: #1: x, -y+1, -z+2; #2: -x+1/2, y+1/2, -z+3/2; #3: -x+1/2, -y+3/2, z-1/2; #4 x+1/2, y-1/2, z-1/2; #5: -x+1, y, -z+1; #6: x+1/2, y+1/2, z-1/2; #7: x+1/2, -y+3/2, -z+3/2.

Section S2. Structural Figures

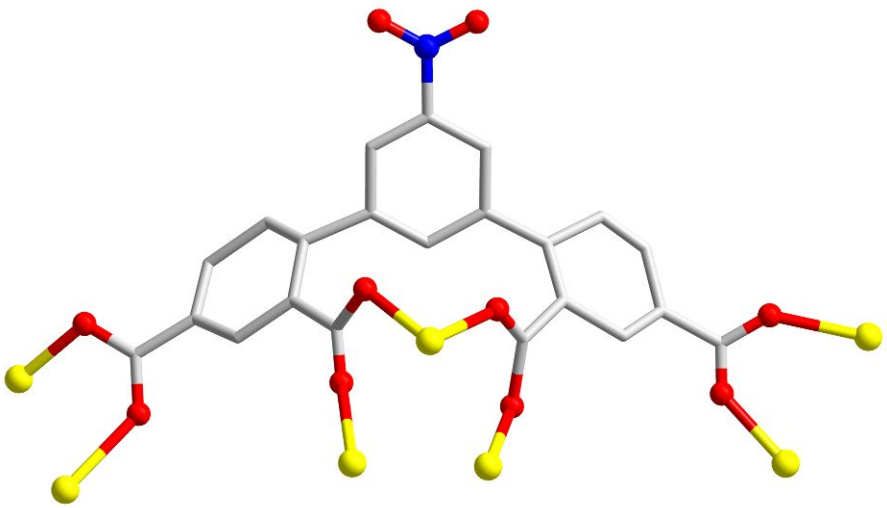


Figure S1. The coordination modes of L^{4-} in **ZCF-1**.

Section S3. Characterization of ZCF-1

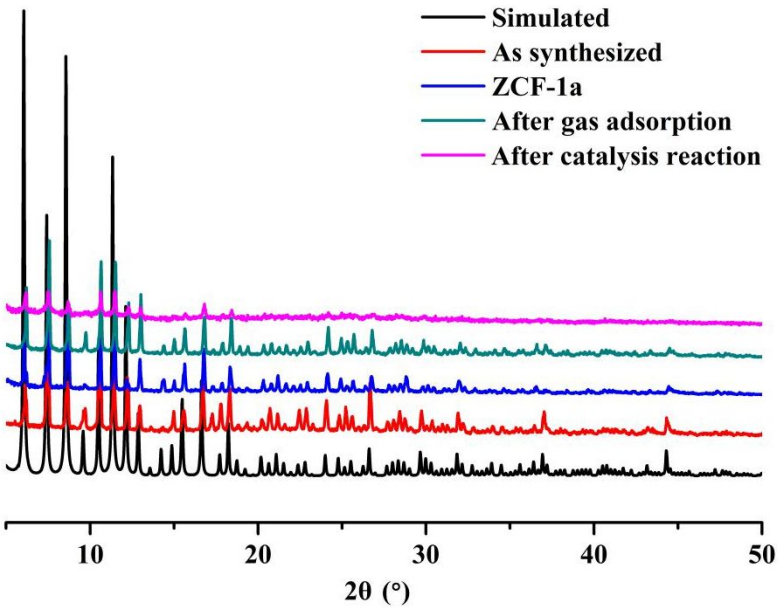


Figure S2. PXRD patterns of **ZCF-1** (simulated from the crystallographic information; as synthesized; desolvated-**1a**; after gas adsorption and after 5th time recycling and reusing of **ZCF-1a** under the same reaction conditions).

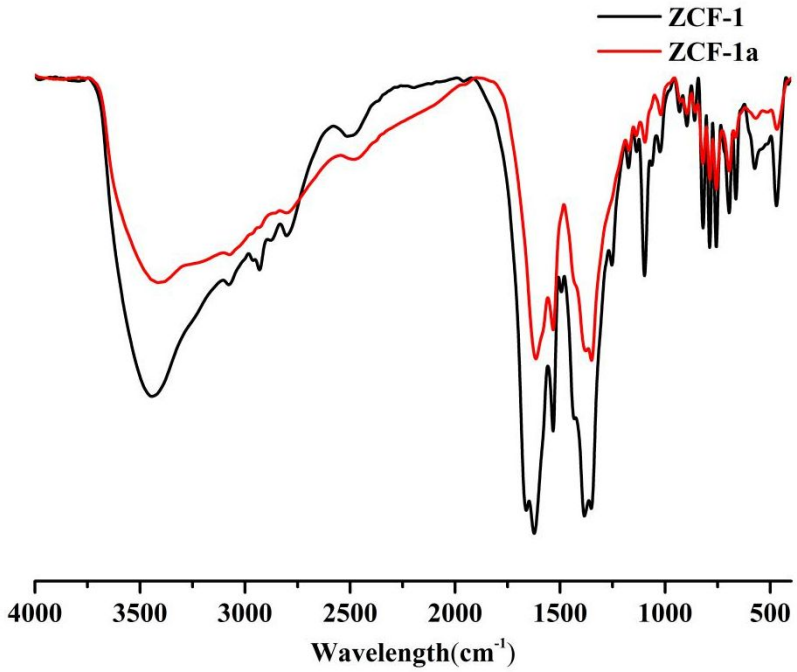


Figure S3. The FT-IR spectra of complexes **ZCF-1** and **ZCF-1a**.

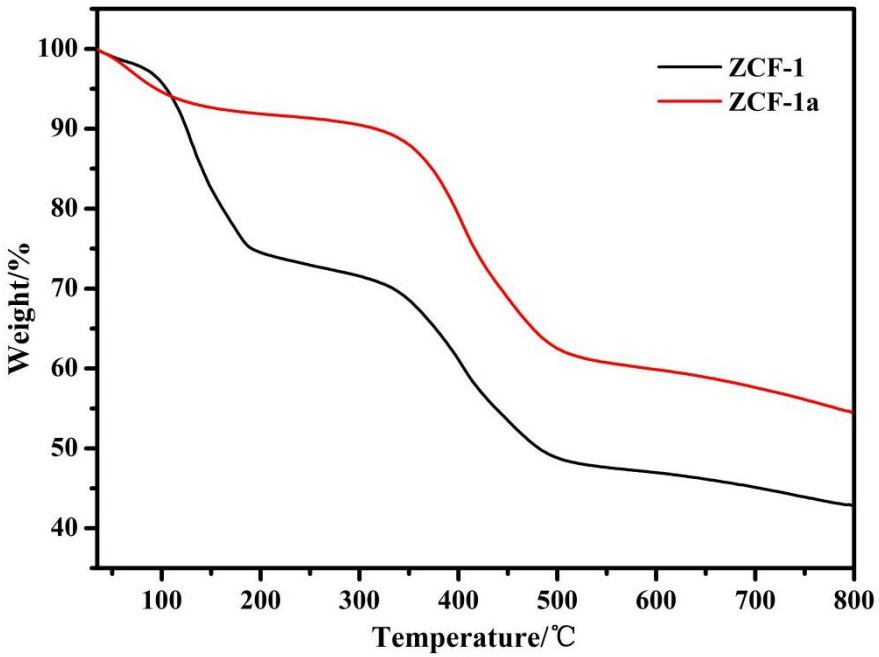


Figure S4. TGA curves of the as-synthesized **ZCF-1** and desolvated sample **ZCF-1a**.

Section S4. Gas sorption studies

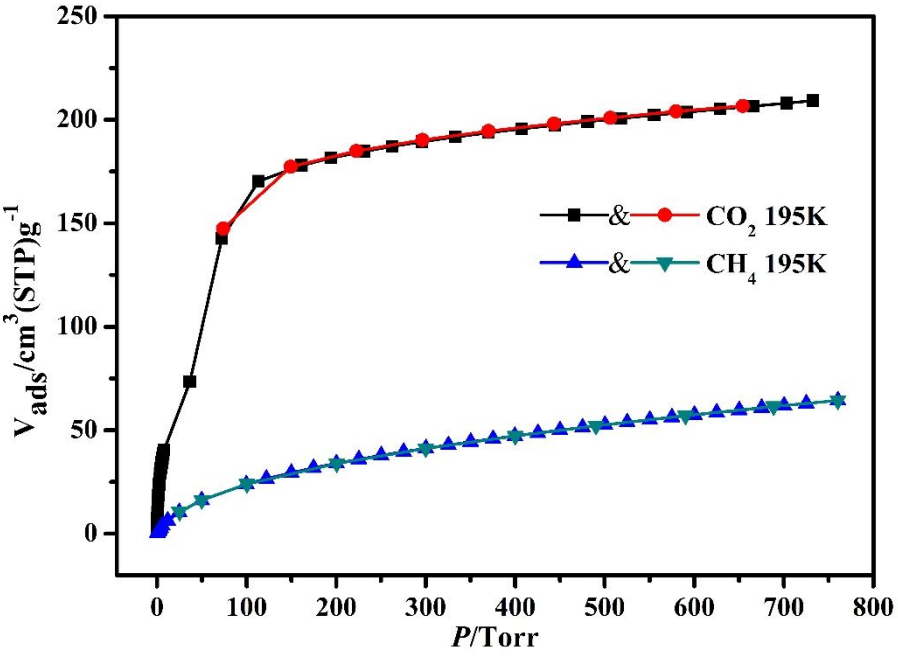


Figure S5. Sorption isotherms of **ZCF-1a**: CO_2 and CH_4 at 195 K.

IAST adsorption selectivity calculation

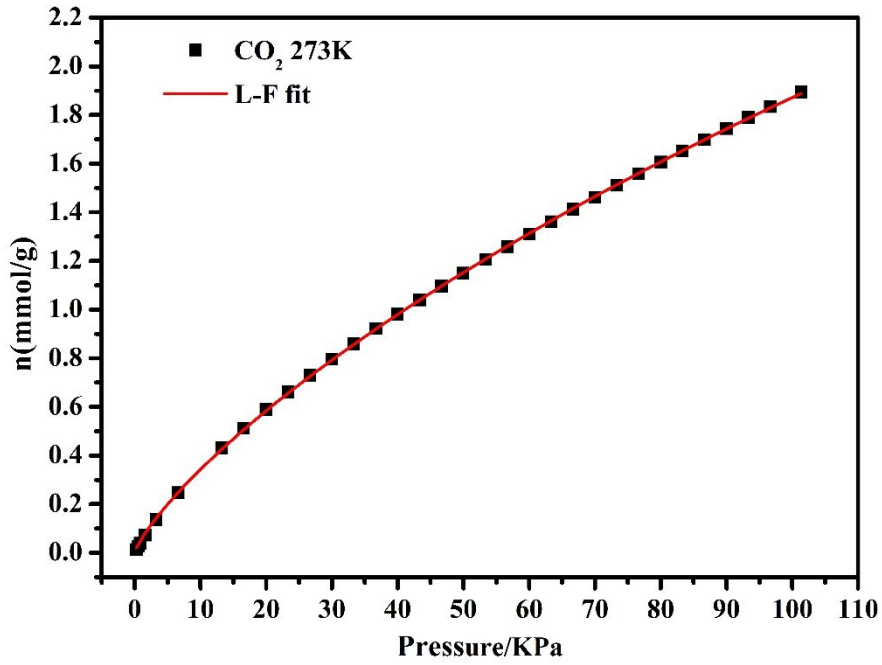
The experimental isotherm data for pure CO_2 and CH_4 (measured at 273 and 298 K) were fitted using a Langmuir-Freundlich (L-F) model

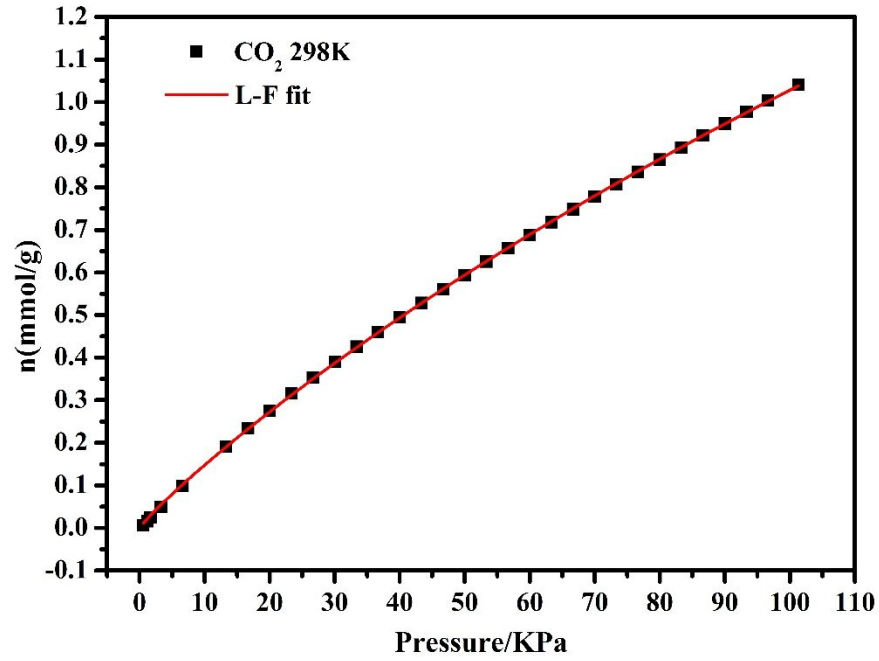
$$q = \frac{a * b * p^c}{1 + b * p^c}$$

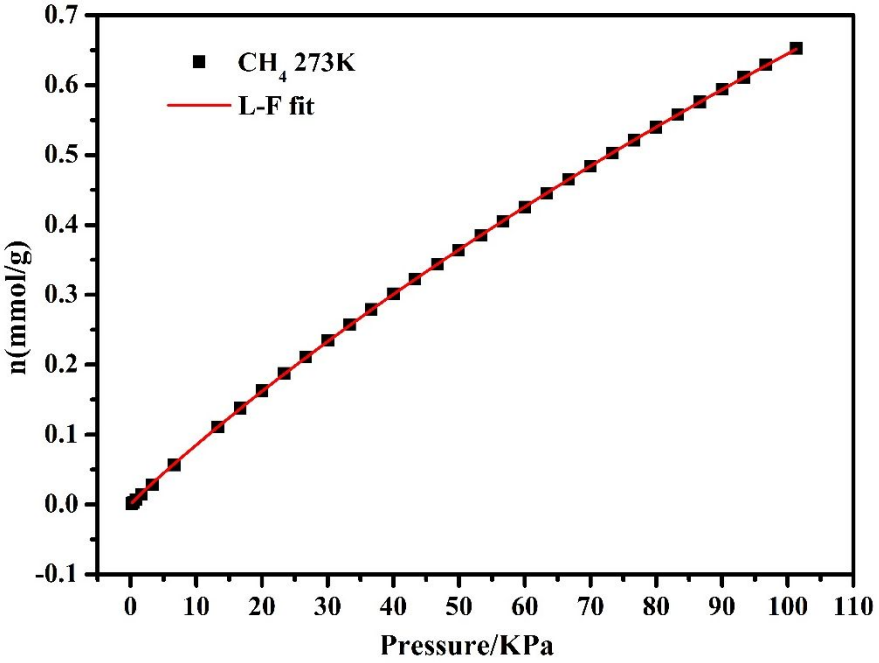
Where q and p are adsorbed amounts and pressures of component i, respectively. The adsorption selectivities for binary mixtures of CO_2/CH_4 at 273 and 298 K, defined by

$$S_{ads} = (q_1/q_2)/(p_1/p_2)$$

Where qi is the amount of i adsorbed and pi is the partial pressure of i in the mixture.




CO2 298K
L-F fit
n(mmol/g)
Pressure/KPa
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0
10
20
30
40
50
60
70
80
90
100
110


CH4 273K
L-F fit
n(mmol/g)
Pressure/KPa
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0
10
20
30
40
50
60
70
80
90
100
110

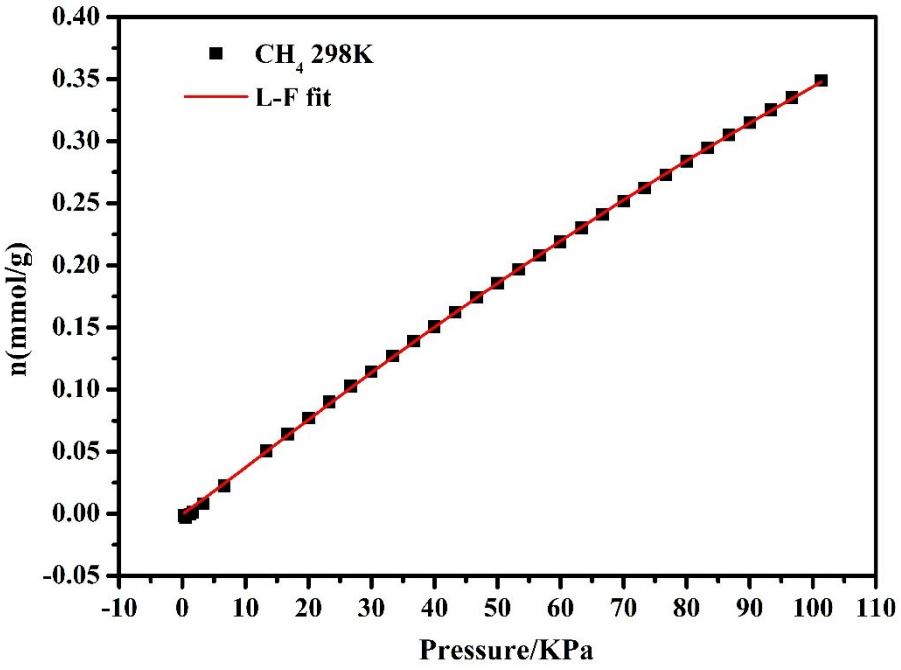


Figure S6. CO_2 adsorption isotherms of **ZCF-1a** at 273K with fitting by L-F model: a = 12.08917, b = 0.00466, c = 0.79744, Chi^2 = 2.45703E-5, R^2 = 0.99993; CO_2 adsorption isotherms of **ZCF-1a** at 298K with fitting by L-F model: a = 5.97343, b = 0.00311, c = 0.91279, Chi^2 = 7.75954E-6, R^2 = 0.99993; CH_4 adsorption isotherms of 1a at 273K with fitting by L-F model: a = 3.60092, b = 0.00271, c = 0.95283, Chi^2 = 9.1752E-7, R^2 = 0.99998; CH_4 adsorption isotherms of **ZCF-1a** at 298K with fitting by L-F model: a = 1.62025, b = 0.00206, c = 1.05793, Chi^2 = 3.79877E-6, R^2 = 0.9997.

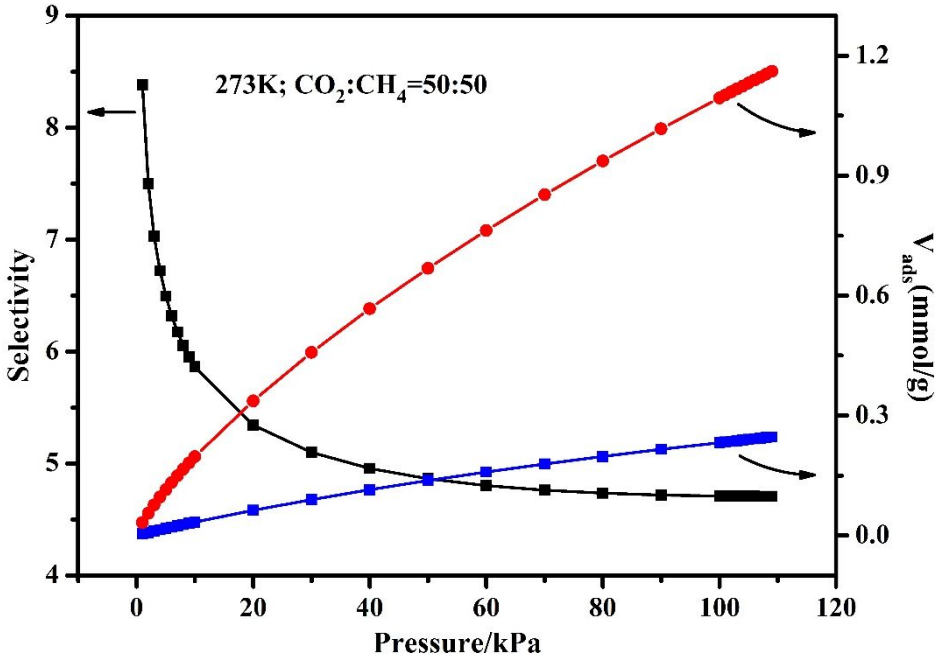


Figure S7. IAST adsorption selectivities of **ZCF-1a** for equimolar mixture of CO_2 and CH_4 (50:50) at 273 K.

Calculation of sorption heat for CO_2 uptake using Virial 2 model

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} aiN^i + \sum_{i=0}^{n} biN^i \qquad Q_{st} = -R \sum_{i=0}^{m} aiN^i$$

The above equation was applied to fit the combined CO_2 isotherm data for desolvated **ZCF-1**at 273 and 298 K, where *P* is the pressure, *N* is the adsorbed amount, *T* is the temperature, ai and bi are virial coefficients, and m and n are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and *R* is the universal gas constant.

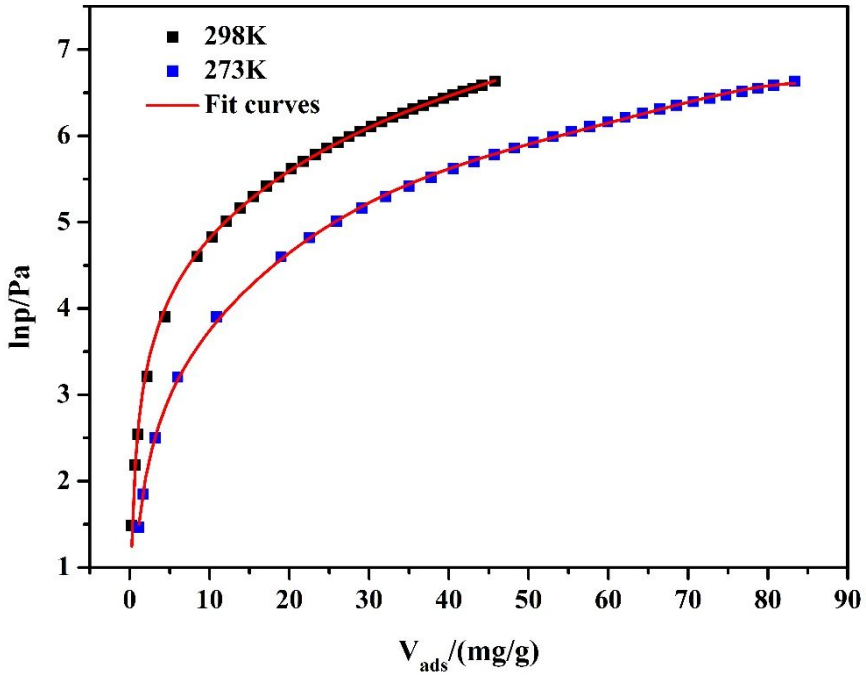


Figure S8. Virial analysis of the CO_2 adsorption data at 273 and 298 K for **ZCF-1**. Fitting results: a0= -3980.13187, a1 = 52.23, a2 = -0.13927, a3 = -0.01806, a4 =2.30859E-4, a5 = -1.04375E-6; b0 = 15.93357, b1 = -0.20084, b2 = 0.00255; Chi^2 = 0.00173, R^2 = 0.99906.

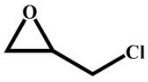
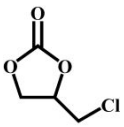
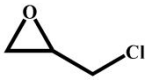
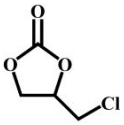
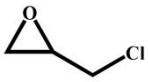
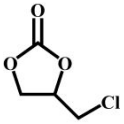
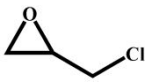
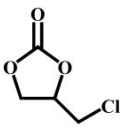
Table S2. Comparison of CO_2/CH_4 selectivity calculated by the IAST method for the equimolar mixture at 1 atm and 298 K of **ZCF-1a** with the selected MOFs.

MOFs	Selectivity	References

BUT-11	9.0	1
UiO-66	6.87	2
ZCF-1a	4.1	**This work**
JLU-Liu37	3.8	3
DMOF	3.2	4
ZIF-25	2.53	5
MIL-53(Al)	2.3	6
$Cu_3(BTC)_2$	2.28	6
MOF-205	2.2	7
UMCM-1	1.82	6

Section S5. Catalyst studies of cycloaddition of CO_2 to epoxides

Table S3. Exploration of Optimal Reaction Conditions for the cycloaddition reaction of CO_2

Entry	Catalyst	Epoxides	Products	Yield [%]
1	**ZCF-1a**			6.2
2[a]	**ZCF-1a**/TBAB			91.3
3[b]	**ZCF-1a**/TBAB			95.3
4[c]	**ZCF-1a**/TBAB			98.6

Reaction condition: Epichlorohydrin (20 mmol); **ZCF-1a** (0.2 mmol); TBAB (2 mmol); dioxygen gas: CO_2 containing balloon; reaction 6 h; [a] 40°C. [b] 55 °C. [c] 70 °C.

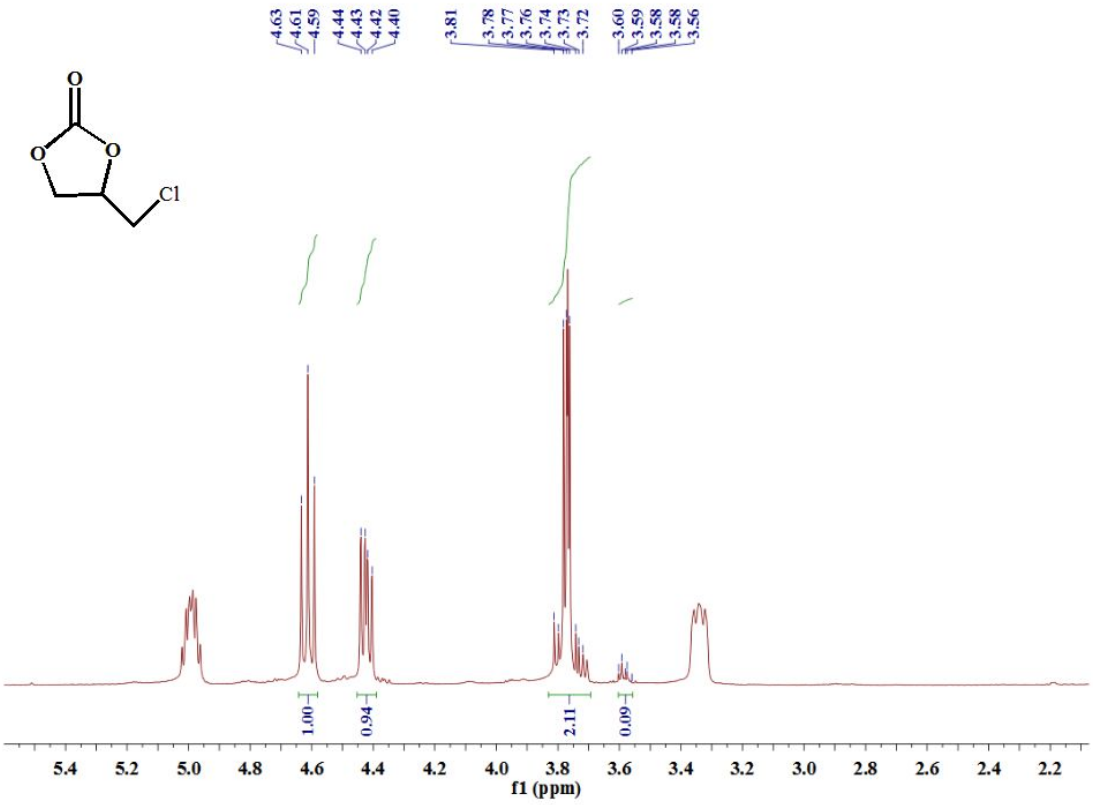


Figure S9. [1]H NMR spectra of 4-cloromethyl-1,3-dioxolan-2-one (Table 1, entry 1).

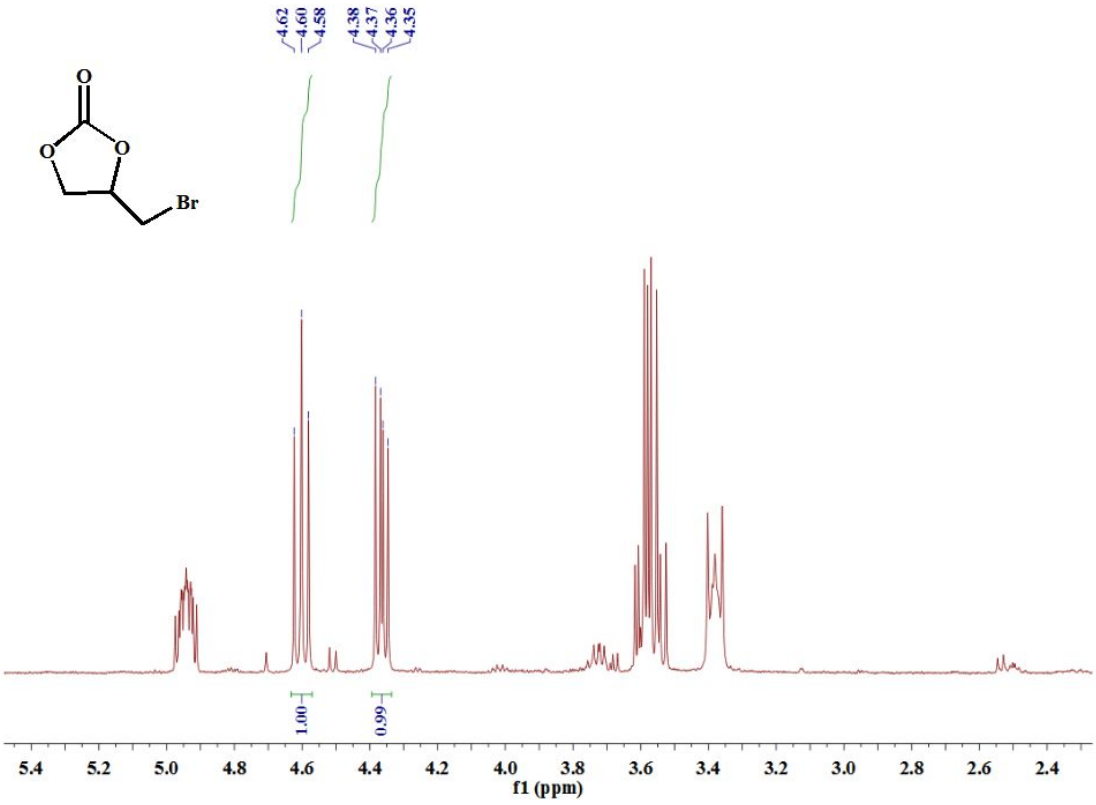


Figure S10. [1]H NMR spectra of 4-bromomethyl-1,3-dioxolan-2-one (Table 1, entry 2).

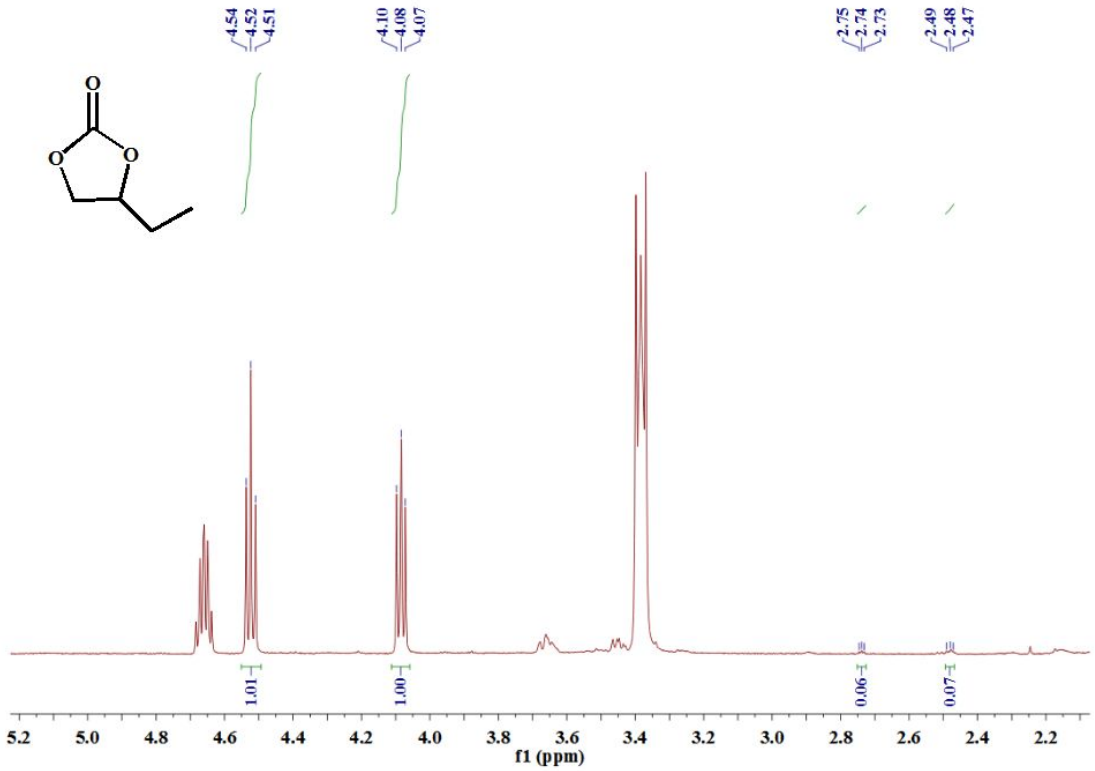


Figure S11. ^{1}H NMR spectra of 4-ethyl-1,3-dioxolan-2-one (Table 1, entry 3).

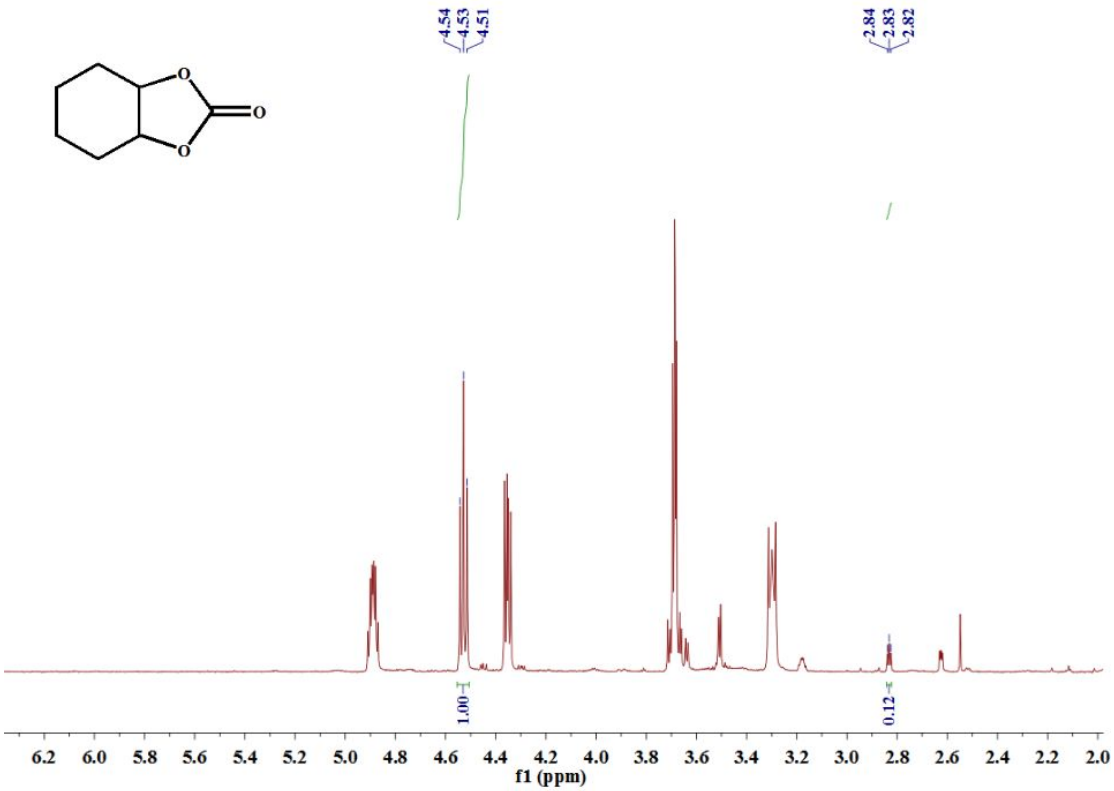


Figure S12. [1]H NMR spectra of hexahydro-benzo[1,3]dioxol-2-one (Table 1, entry 4).

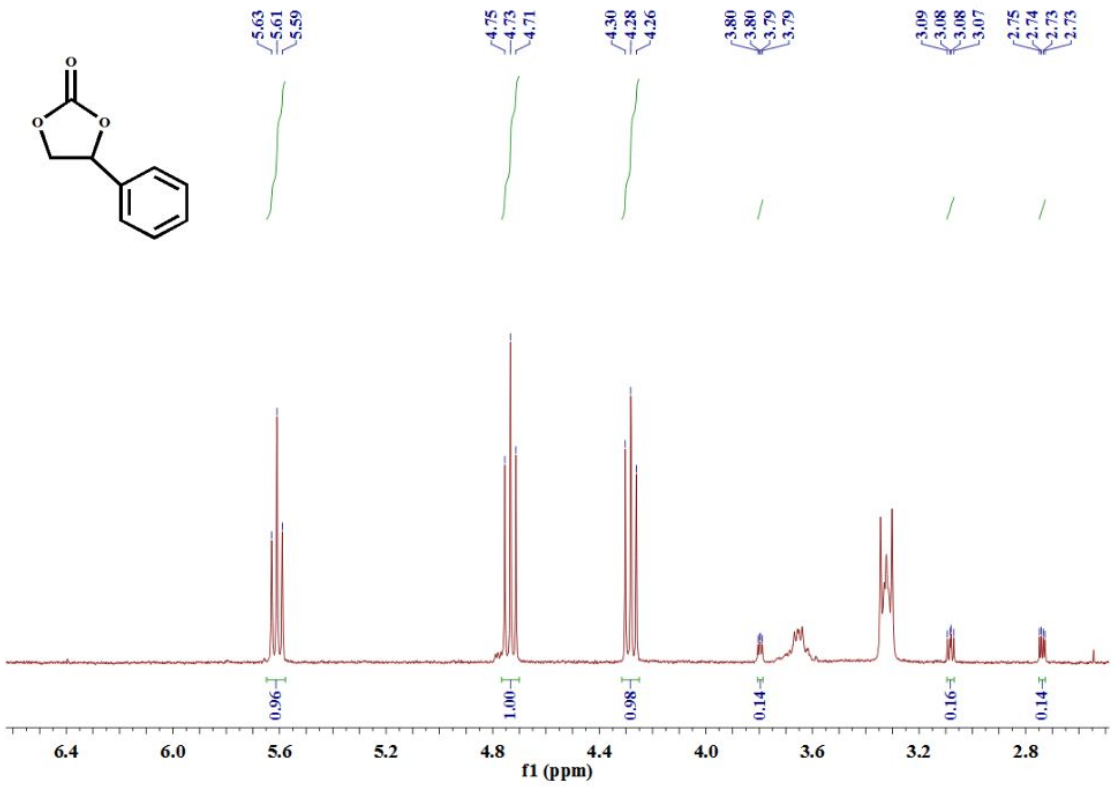


Figure S13. [1]H NMR spectra of styrene carbonate (Table 1, entry 5).

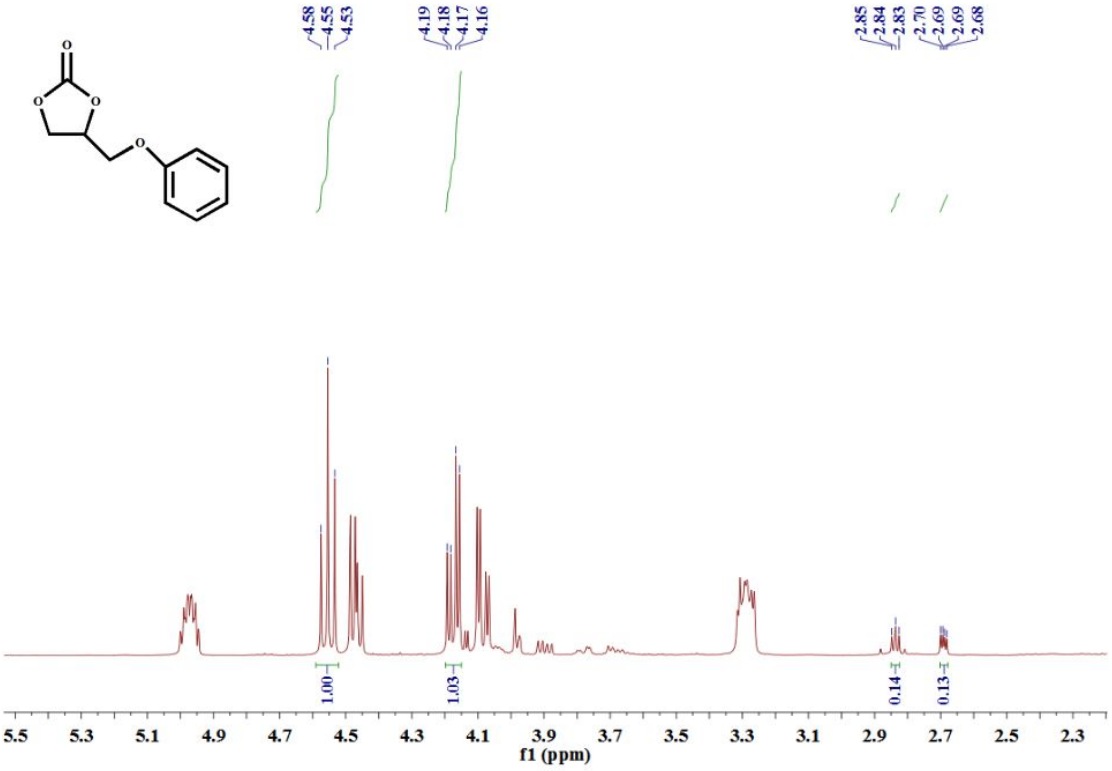


Figure S14. [1]H NMR spectra of 4-(phenoxymethyl)-1,3-dioxolan-2-one (Table 1, entry 6).

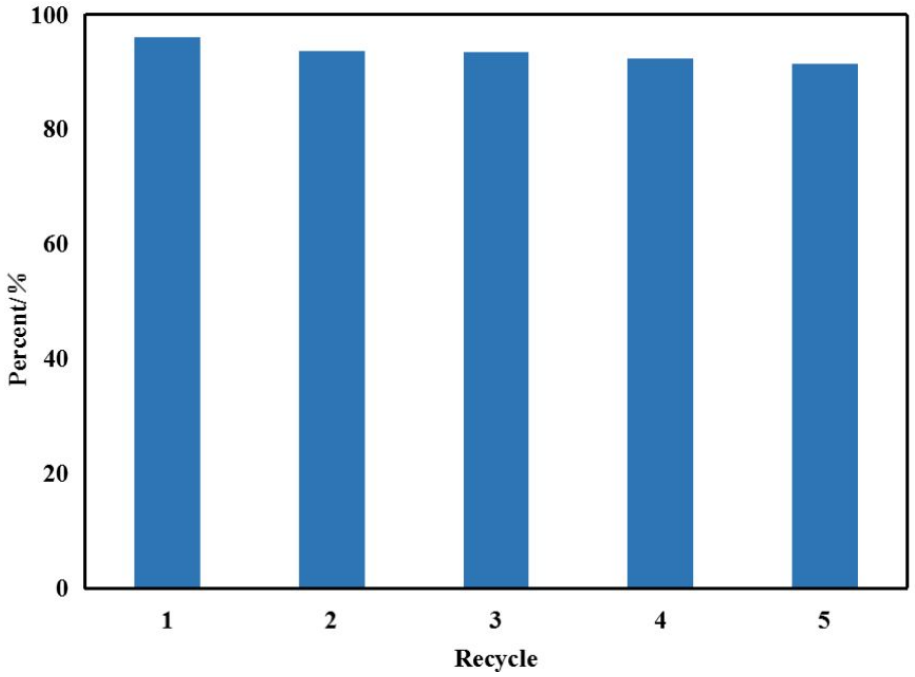


Figure S15. Recyclability of **ZCF-1a** for the coupling reaction of CO_2 with epichlorohydrin under optimal reaction conditions.

Table S4. Comparison of the catalytic activity of **ZCF-1a** with the reported MOFs.

Entry	Catalyst	Reaction conditions	Yield(%)	Reference
1	Salen-Co(23%)⊂(Br^-)Etim-UiO-66	120 °C, 0.1MPa, 12 h	86	8
2	{[Co_6(TATAB)$_4$(DABCO)$_3$(H_2O)$_3$]·12DMF·9H_2O}$_n$	80 °C, 0.1MPa, 15 h	55	9
3	InDCPN-Cl	80 °C, 0.1MPa, 24 h	88	10
4	[Zn_2(TCA)(BIB)$_{2.5}$]·(NO_3)	80 °C, 0.1MPa, 4 h	59.5	11
5	Cu/NC-0.5	40 °C, 0.1MPa, 48 h	70	12
6	{[Zn(CHDC)(L)]·H_2O}$_n$	80 °C, 1.0MPa, 18 h	87	13
	{[Cd(CHDC)(L)]·H_2O}$_n$	80 °C, 1.0MPa, 18 h	85	13
7	CoMOF-1′	60 °C, 0.1MPa, 12 h	84	14
8	[Zn_6(TATAB)$_4$(DABCO)$_3$(H_2O)$_3$]·12DMF·9H_2O	100 °C, 0.1MPa, 16 h	50	15
9	MIL-101-N(*n*-Bu)$_3$Br	80 °C, 2.0MPa, 8 h	40.1	16
	MIL-101-P(*n*-Bu)$_3$Br	80 °C, 2.0MPa, 8 h	36.9	16
10	(I^-)Meim-UiO-66	120 °C, 0.1MPa, 24 h	76	17

11	**ZCF-1a**	70 °C, 0.1Mpa, 6 h	88.3	**This work**

Substrate : Epoxide = Glycidyl phenyl ether

Entry	**Catalyst**	**Reaction conditions**	**Yield(%)**	**Reference**
1	Salen-Co(23%)⊂(Br^-)Etim-UiO-66	120 °C, 0.1MPa, 12 h	84	8
2	[Ni(btzip)(H_2btzip)]·2 DMF·2H_2O	80 °C, 2.0 MPa, 4 h	40	18
3	MOF-892	80 °C, 0.1 MPa, 16 h	82	19
	MOF-893	80 °C, 0.1 MPa, 16 h	63	19
	MOF-894	80 °C, 0.1 MPa, 16 h	66	19
4	Cu-MOPF	100 °C, 0.1MPa, 4 h	69	20
5	[Zn_2(TCA)$(BIB)_{2.5}$]·(NO_3)	80 °C, 0.1MPa, 4 h	51.3	11
6	Cu/NC-0.5	80 °C, 0.1MPa, 4 h	52	12
7	{[Zn(CHDC)(L)]·H_2O}$_n$	80 °C, 1.0MPa, 18 h	72	13
	{[Cd(CHDC)(L)]·H_2O}$_n$	80 °C, 1.0MPa, 18 h	70	13
8	@MIL-101	70 °C, 0.1MPa, 48 h	81	21
9	MIL-101	100 °C, 0.2MPa, 4 h	63	22
	CuBTC	100 °C,0.2MPa, 4 h	48	22
	IRMOF-3	100 °C, 0.2MPa, 4 h	33	22
	ZIF-8	100 °C,0.2MPa, 4 h	11	22

10	{[Co_6(TATAB)$_4$(DABCO)$_3$(H_2O)$_3$]·12DMF·9H_2O}n	80 °C, 0.1MPa 15 h	82	9
11	In_2(OH)(btc)(Hbtc)$_{0.4}$(L)$_{0.6}$	80℃, 2 MPa, 4 h	73.2	23
12	[Mn_5L(H_2O)$_6$·(DMA)$_2$]·5DMA·4C_2H_5OH	80℃, 2 MPa, 4 h	44	24
13	IL-ZIF-90	120℃, 1 MPa, 3 h	81	25
14	Ni-TCPE2	100℃, 1 MPa, 12 h	86.2	26
15	(I^-)Meim-UiO-66	120 °C, 0.1MPa, 24 h	46	17
16	**ZCF-1a**	70 °C, 0.1Mpa, 6 h	87	**This work**

Substrate : Epoxide = Styrene oxide

Section S6. References

1. Yu, J. M.; Xie, L. H.; Li, J. R.; Ma, Y. G.; Seminario, J. M.; Balbuena, P. B. CO_2 Capture and Separations Using MOFs: Computational and Experimental Studies. *Chem. Rev.* **2017**, 117, 9674-9754.

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computational investigation of methane adsorption and selectivity in a series of isoreticular zeolitic imidazolate frameworks. *J. Phys. Chem. C* **2013**, 117, 10326-10335.

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