Supporting Information

Ambient Conversion of CO_2 and Epoxides to Cyclic Carbonates Using 3D Amide-Functionalized MOFs

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Table S1. SC-XRD Experimental details of ZnMOF.

Crystal data	**ZnMOF**
CCDC	2097251
Chemical formula	$C_{40}H_{46}N_6O_{12}Zn$
M_r	868.20
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	296
a, b, *c* (Å)	13.2667 (11), 13.8534 (12), 22.0429 (19)
α, β, γ (°)	90, 93.349 (2), 90
V (Å^3)	4044.3 (6)
Z	4
Density (calculated)g/cm^{-3}	1.426
F(000)	1816
Radiation type	Mo *K*α
Wavelength (λ)	0.71073
μ (mm^{-1})	0.678
Crystal size (mm)	0.28 × 0.23 × 0.20
Data Collection	
Diffractometer	Bruker APEX-II CCD
Absorption correction	multi-scan
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16769, 4637, 3883
Theta range for data collection (°)	1.851 to 27.528
R_{int}	0.044
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Data Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.038, 0.109, 1.05
No. of reflections	4637
No. of parameters	271
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.25

Table S2. Selected bond lengths (Ǻ) and bond angles (°) in ZnMOF. Symmetry codes are (ii) 1-x, y, 1/2-z; (iv) 1/2+x, -1/2+y, z; (v) 1/2-x, -1/2+y, 1/2-z.

Bond lengths		**Bond angles**	
Zn1—O1	1.9592 (14)	O^{ii}—Zn1—O1	99.37 (9)
Zn1—O1^{ii}	1.9592 (14)	O1^{ii}—Zn1—O4^{iv}	107.61 (6)
Zn1—O4^{iv}	1.9612 (13)	O1—Zn1—O4^{iv}	117.92 (6)
Zn1—O4^{v}	1.9612 (13)	O1^{ii}—Zn1—O4^{v}	117.92 (6)
O1—C1	1.274 (2)	O1—Zn1—O4^{v}	107.61 (6)
O2—C1	1.236 (2)	O4^{iv}—Zn1—O4^{v}	106.88 (9)

Table S3. Hydrogen-bond geometry (Å, º) for ZnMOF.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	<(*D*—H···*A*)º
N1—H1···O6^{vi}	0.86	2.06	2.859 (2)	153
N2—H2*A*···O5^{i}	0.89	2.10	2.851 (3)	142
N2—H2*B*···O2^{vii}	0.89	2.23	2.827 (3)	124
N2—H2*B*···O3	0.89	2.37	2.962 (3)	124
N2—H2*B*···O4^{i}	0.89	2.40	2.989 (2)	124
C16—H16*A*···O3	0.96	2.50	3.062 (4)	117
C17—H17*C*···O2^{vii}	0.96	2.51	3.009 (4)	112

Symmetry codes: (i) −*x*, *y*, −*z*+1/2; (vi) −*x*+1, −*y*, −*z*; (vii) −*x*+1/2, *y*+1/2, −*z*+1/2.

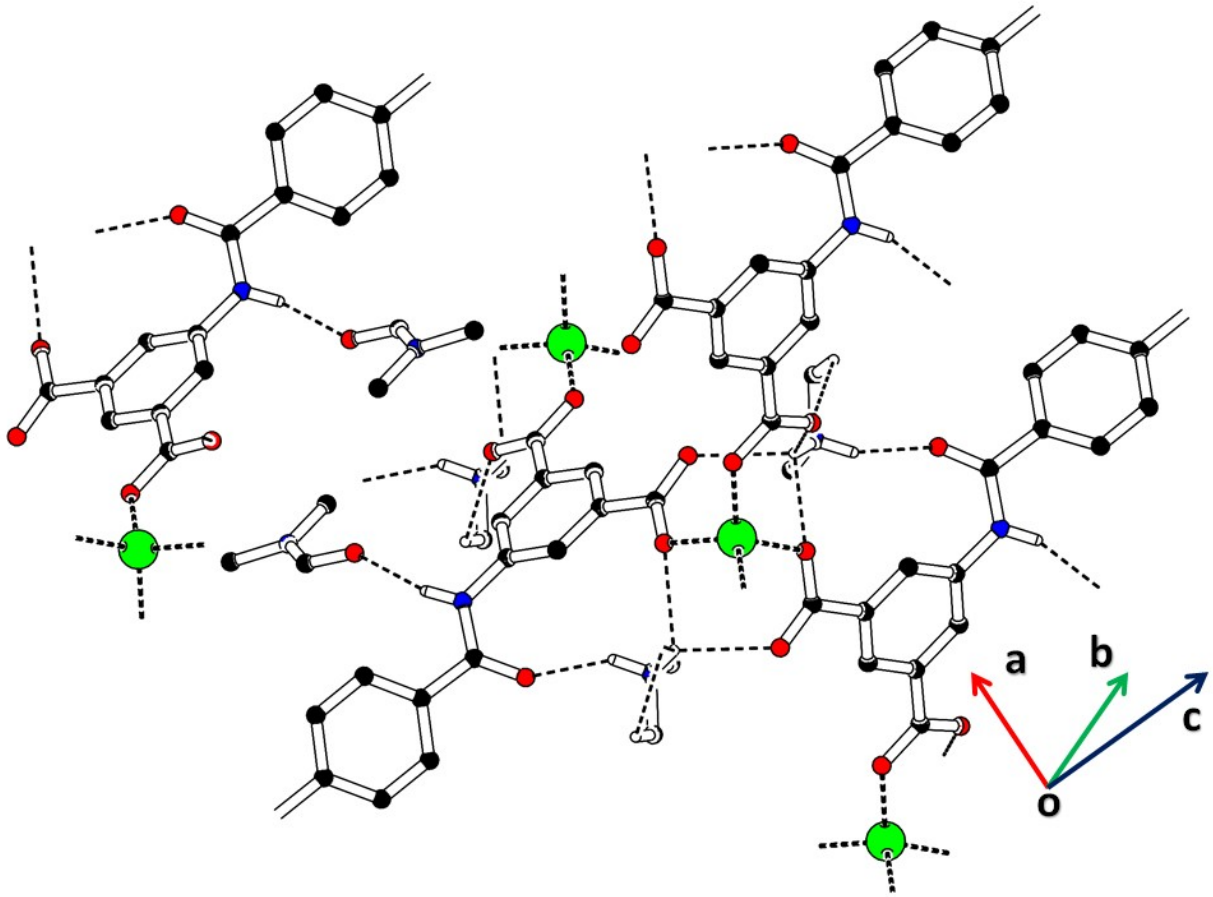


Figure S1. Packing diagram of ZnMOF. Only selected H-atoms are shown for clarity.

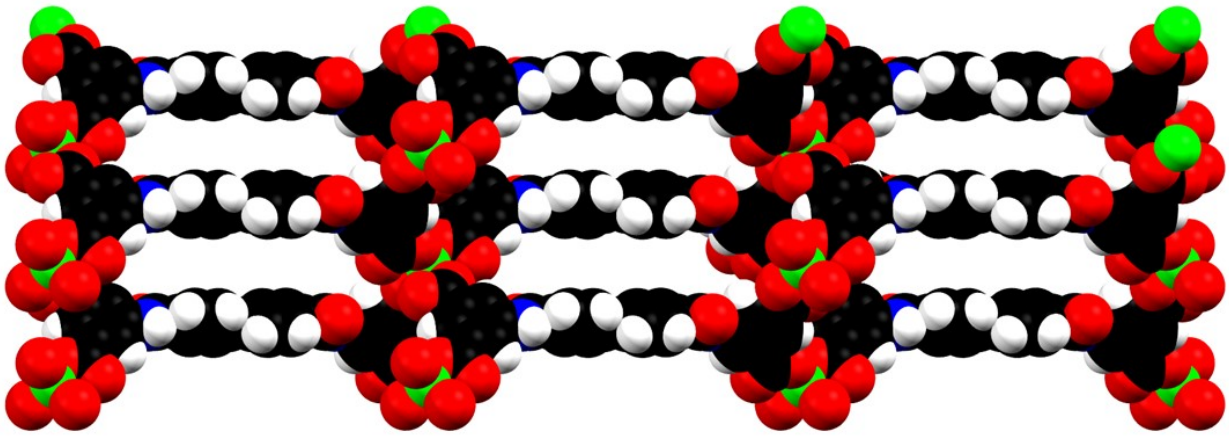


Figure S2. Graphical representation of channels (15 × 7.6) $Å^2$ along *a*-axis.

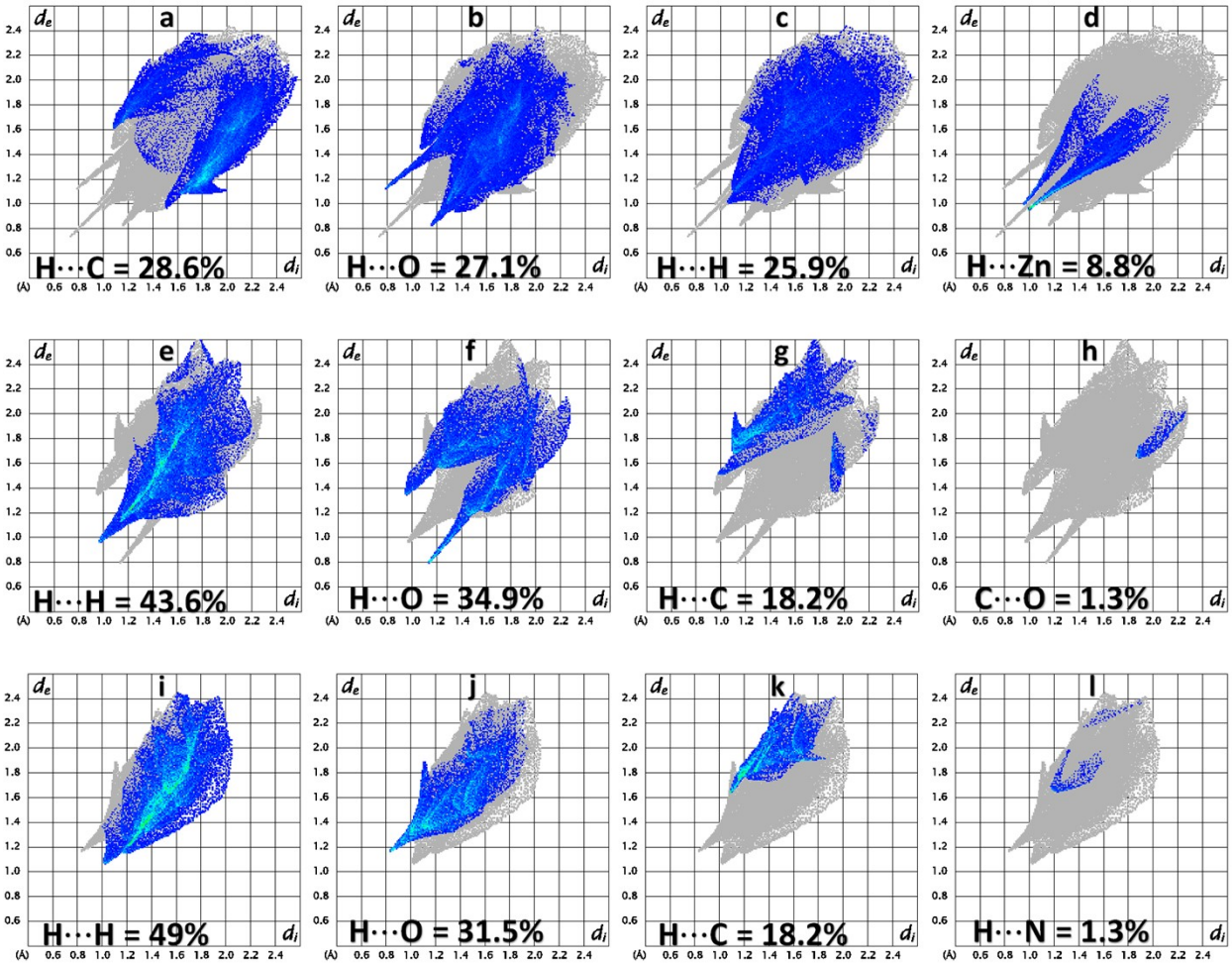


Figure S3. Important 2D fingerprint plots of (a-d) ZnMOF, **(e-h)** DMF, and **(i-l)** DHMA.

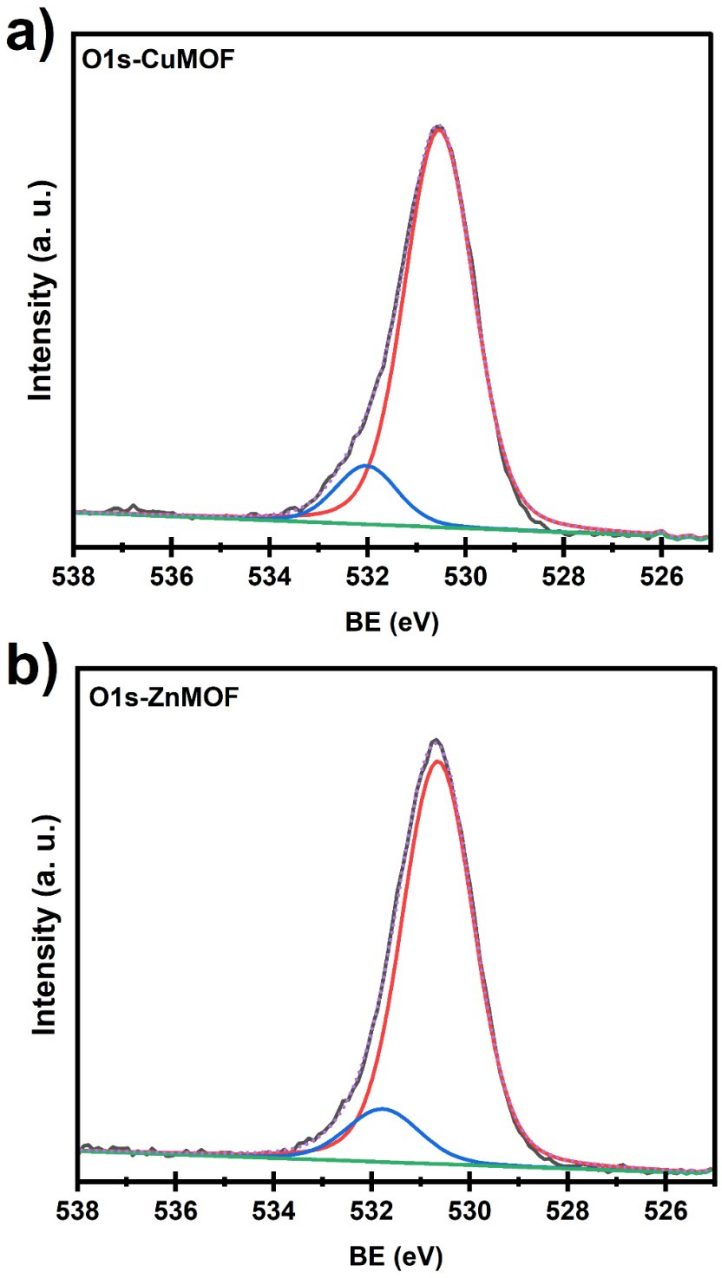


Figure S4. The O 1s XPS spectra of Cu-MOFs (a) and Zn-MOF (b).

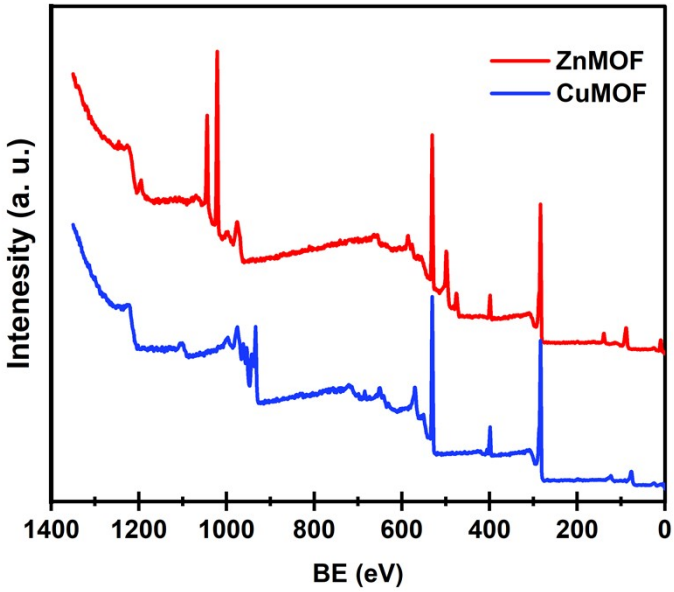


Figure S5. XPS survey of both Cu- and Zn-MOF

Table S4. The cycloaddition of epoxides and CO_2 from the literature catalysed by TBAB.

Catalyst/TBAB (mmol)	**Substrate**	**Substrate Loading** (mmol)	**Reaction Conditions**			**Conversion** (%)	**TON**	**TOF**	**Ref.**
			T (°C)	**P** (bar)	**t** (h)				
0.5	PO	25	40	20	24	13	-	-	[1]
2.5mol%	SO	17.4	80	10	12	02	-	-	[2]
0.01	ECH	10	120	1	3	39	390	130	[3]

SO = Styrene oxide; ECH = Epichlorohydrin, PO = Propylene oxide

NMR Spectra of Carbon Dioxide Fixation Reactions

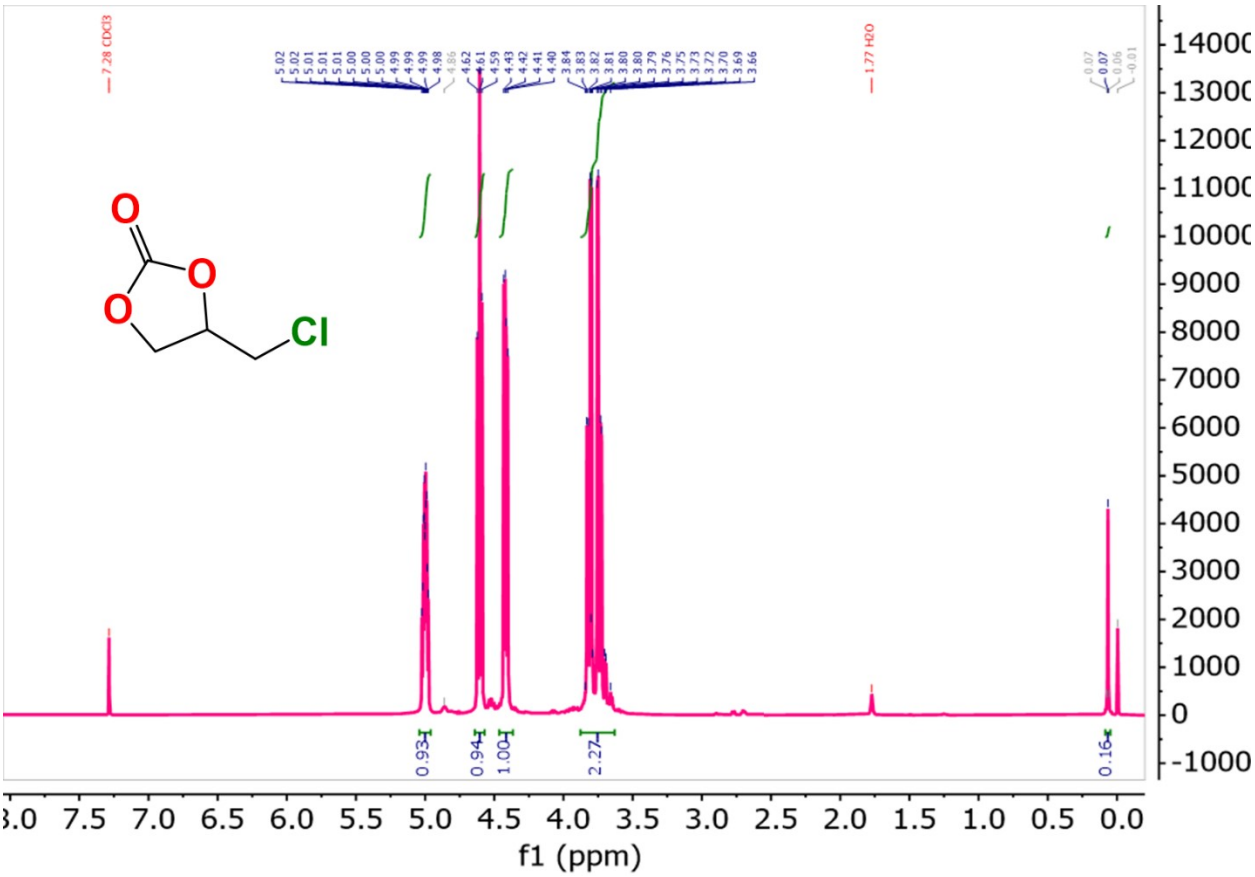


Figure S6: ^{1}H-NMR spectrum in $CDCl_3$ of the reaction mixture obtained from the conversion of epichlorohydrin.

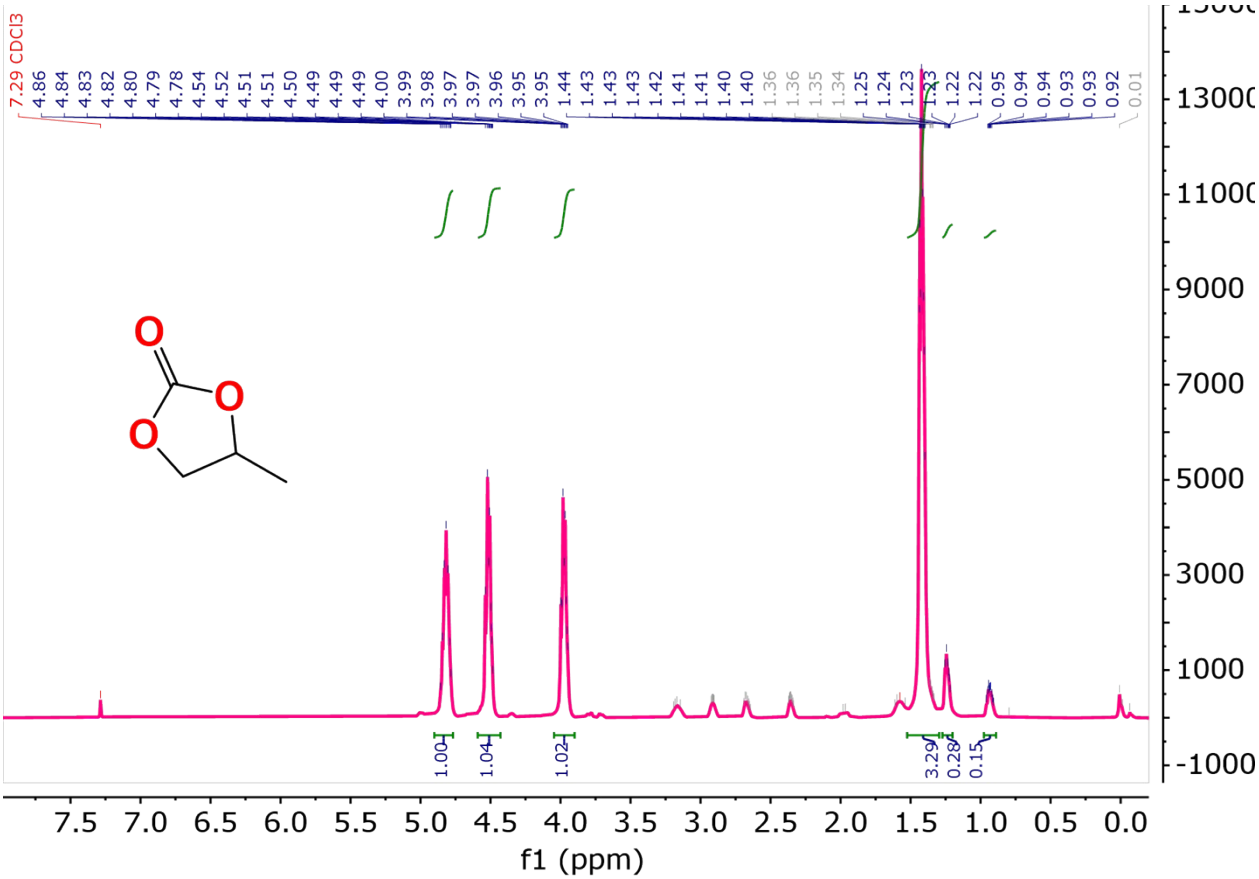


Figure S7: ^{1}H-NMR spectrum in $CDCl_3$ of the reaction mixture obtained from the conversion of propylene oxide.

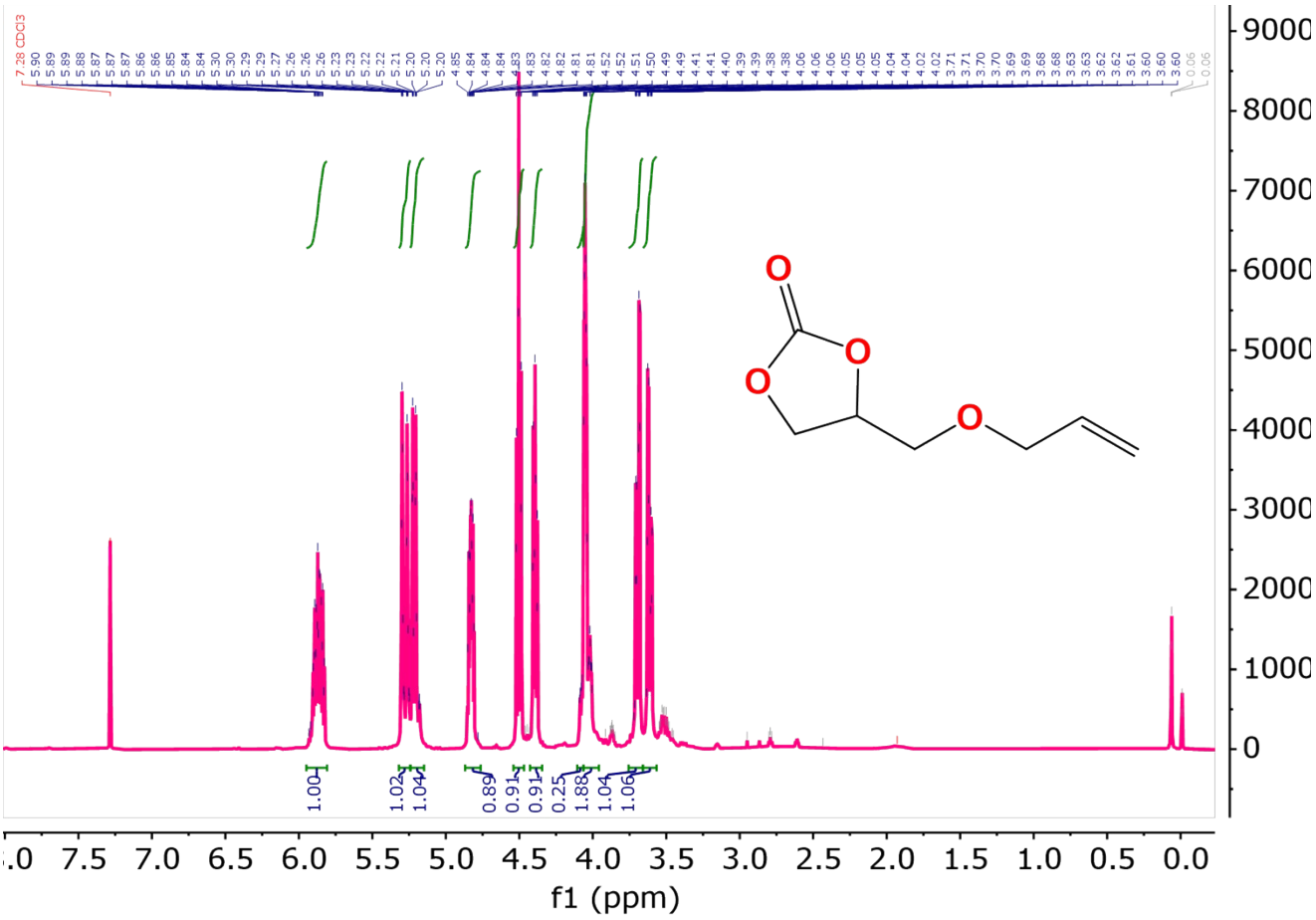


Figure S8: ^{1}H-NMR spectrum in $CDCl_3$ of the reaction mixture obtained from the conversion of allyl glycidyl ether

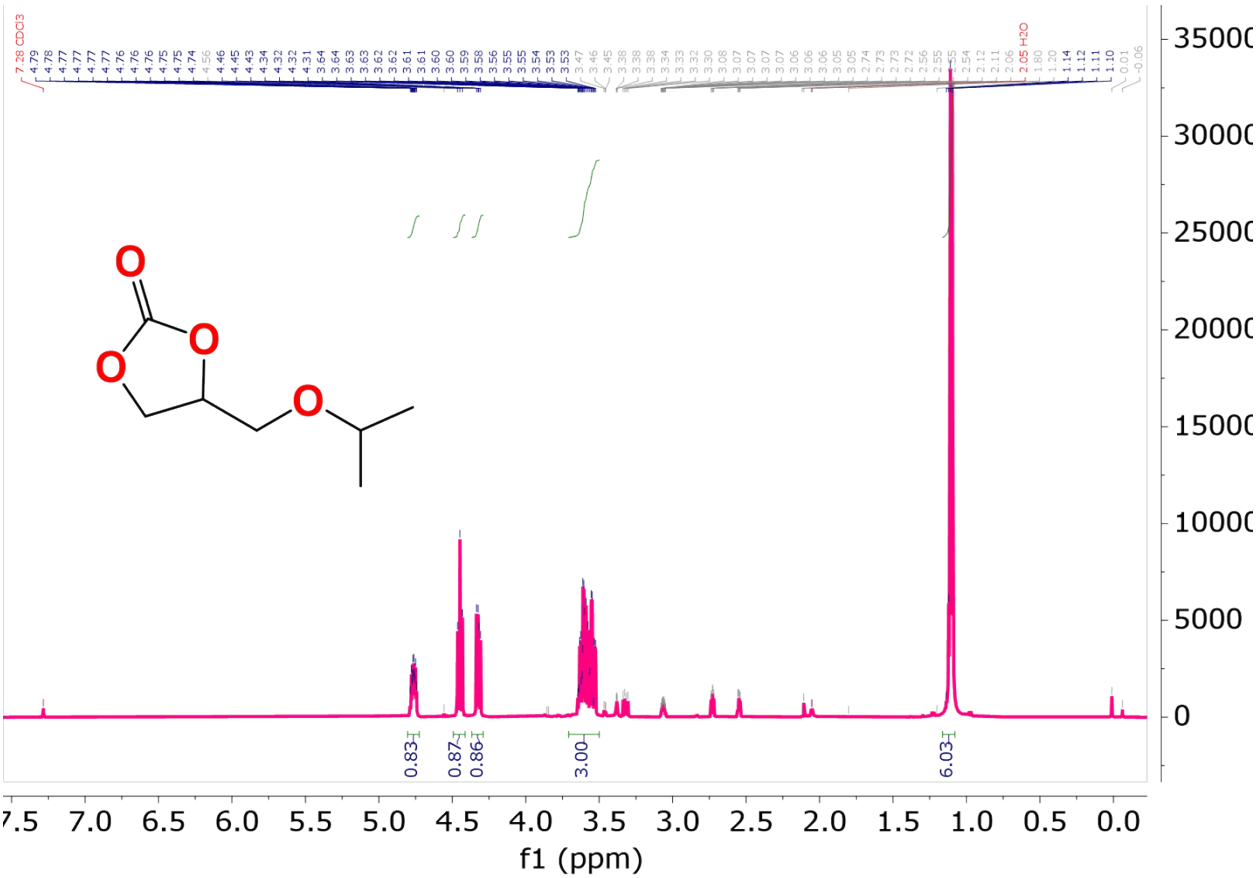
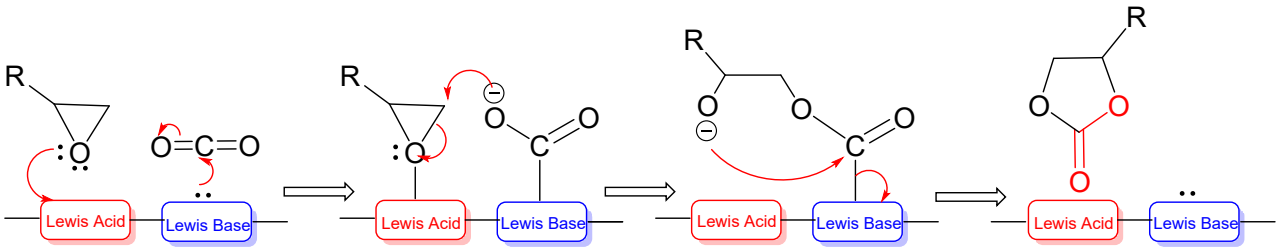


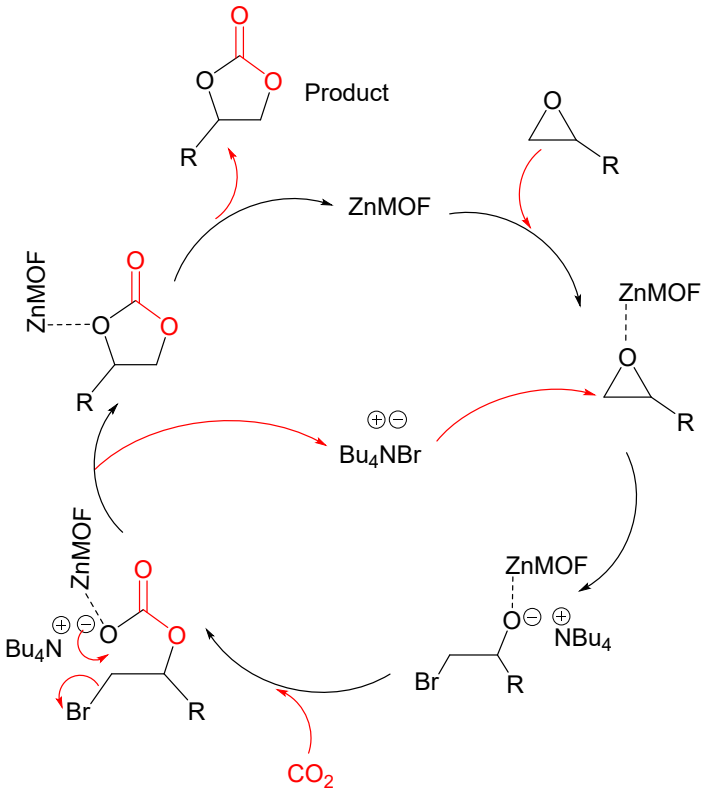
Figure S9: ^{1}H-NMR spectrum in $CDCl_3$ of the reaction mixture obtained from the conversion of glycidyl isopropyl ether.

The proposed mechanism in the absence of TBAB



Scheme S1. Catalytic mechanism involving Lewis Acid and Lewis Base sites of the MOF for the cycloaddition of CO_2 to epoxide.

The proposed mechanism in the presence of TBAB



Scheme S2. Catalytic mechanism involving MOF and cocatalyst TBAB for the cycloaddition of CO_2 to epoxide.

The carbon dioxide sorption-desorption

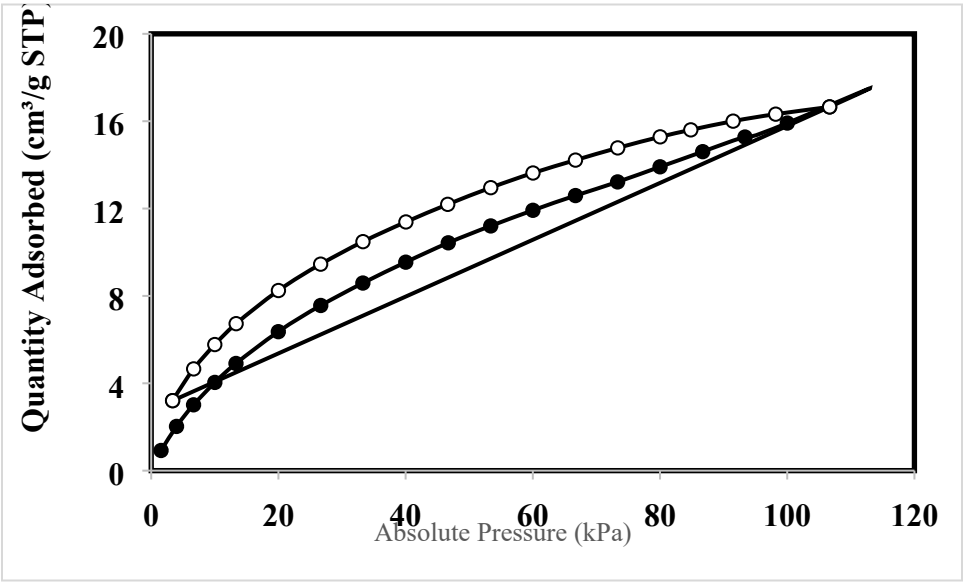


Figure S10: CO_2 sorption (black-colored filled circles)-desorption (empty circles) at 273 K.

The FTIR of the as-synthesized and recovered catalyst

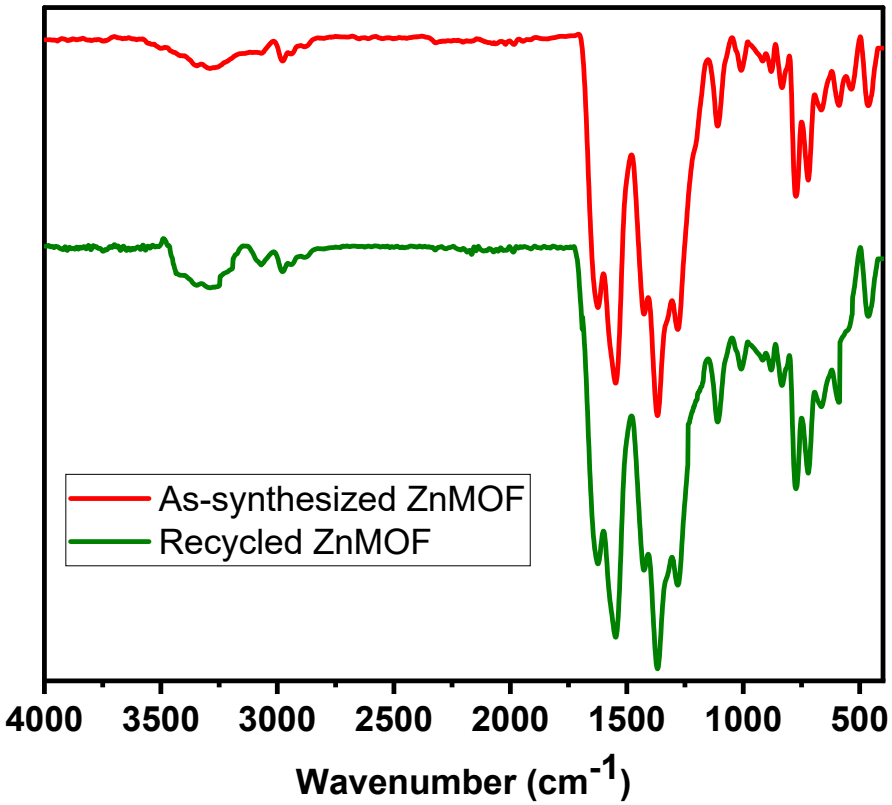


Figure S11: The FTIR of the as-synthesized and recycled (after 5th catalytic run) of ZnMOF

References

1. L. Xu, M.-K. Zhai, X.-C. Lu and H.-B. Du, *Dalton Trans.*, 2016, 45, 18730-18736.
2. U. Patel, P. Patel, B. Parmar, A. Dadhania and E. Suresh, *Crystal Growth & Design*, 2021, 21, 1833-1842.
3. S. Suleman, H. A. Younus, N. Ahmad, Z. A. K. Khattak, H. Ullah, J. Park, T. Han, B. Yu and F. Verpoort, *Appl. Catal. A: Gen.*, 2020, 591, 117384.