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Construction of a bifunctional Zn(II)-organic framework containing basic amine functionality for selective capture and room temperature fixation of CO_2

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Contents:

Materials and Methods

Gas adsorption measurements

Catalytic cycloaddition reactions of CO_2 with epoxides

Theoretical calculations

X-ray crystallography

Fig. S1 PXRD patterns of **Zn-DAT** MOF (a) simulated pattern from single-crystal X-ray diffraction, (b) as-synthesized sample (c) activated and (d) recycled sample after five catalytic cycles.

Fig. S2 FT-IR spectrum of **Zn-DAT** MOF.

Fig. S3 PXRD patterns for **Zn-TAZ** MOF (a') simulated pattern from single-crystal X-ray diffraction, (b') as-synthesized sample (c') activated and (d') after the catalytic reaction.

Table S1 Crystal data and structure refinement parameters for **Zn-DAT** MOF.

Table S2 Selected bond length (Å) and angles (°) for **Zn-DAT** MOF.

Table S3 Selected hydrogen bonding geometry (Å, °) for **Zn-DAT** MOF.

Fig. S4 3D view of **Zn-DAT** MOF showing the pore size along the crystallographic *c*- and *b*-axis.

Fig. S5 (a) 5-connected Zn(II) node and (b) 8-connected Zn(II) node OF **Zn-DAT** MOF.

Analysis of gas adsorption isotherms

Fig. S6 N_2 adsorption-desorption isotherm of (a) **Zn-DAT** (b) **Zn-TAZ** MOFs carried out at 77 K.

Fig. S7 Carbon dioxide adsorption isotherm for (a) **Zn-DAT** and (b) **Zn-TAZ** MOFs carried out at 273 K.

Fig. S8 Carbon dioxide adsorption isotherm for (a) **Zn-DAT** and (b) **Zn-TAZ** MOFs carried out at 298 K.

Fig. S9 Enthalpy of carbon dioxide for (a) **Zn-DAT** and (b) **Zn-TAZ** MOFs calculated using Clausius-Clapeyron equation calculations.

Fig. S10 Gas selectivity for **Zn-DAT** MOF calculated following the Henrys law from the CO_2, N_2, Ar and H_2 isotherms carried out at 273 K.

Fig. S11 Linear fitting of CO_2, Ar, H_2 and N_2 isotherms used for calculation of Henry's selectivity constants for **Zn-DAT** MOF.

Table S4 Optimization table for catalytic cycloaddition reaction of CO_2 with epichlorohydrin (ECH).

Fig. S12-S24 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of CO_2 with various epoxides.

Table S5 Optimized geometries of epoxides using Gaussian09[1] at B3LYP/6-311g (d,p) level.

Table S6 Cartesian coordinates for optimized geometries of **Zn-DAT** MOF with CO_2 molecules.

Materials and methods

All reagents used in this study were commercially available and used as received without further purification. 2, 5-thiophene dicarboxylic acid was purchased from Alfa Aesar, Chemical Co. 3,5-diamino-1,2,4-triazole and $Zn(NO)_3.6H_2O$ were purchased from Sigma Aldrich Chemical Co. N, N' dimethylformamide (DMF) was obtained from S. D. Fine Chem. Limited. Thermogravimetric analysis (TGA) of **Zn-DAT** MOF was carried out using Mettler Toledo Thermogravimetric analyzer in the N_2 atmosphere. The phase-purity of the MOF samples was confirmed by powder XRD recorded on a PANalytical's X'PERT PRO diffractometer using CuK_α radiation (k = 1.542 Å; 40 kV, 20 MA). Fourier transform infrared (FT-IR) spectra of **Zn-DAT** MOF was recorded on a Perkin Elmer FTIR spectrometer.

Gas adsorption measurements

Gas adsorption measurements were performed on a Quantachrome's QUADRASORB SI automatic volumetric instrument using ultrapure (99.995%) H_2, Ar, N_2 and CO_2 gases. The **Zn-DAT** MOF sample (~ 0.10 g) was activated by heating at 393 K under vacuum (18 mTorr) for 15 hours. The temperatures, 273 and 298 K were achieved by using water chiller with appropriate coolants. Whereas, 77 K and 195 K temperatures were achieved by using liquid nitrogen and dry ice-acetone mixture as coolants, respectively. The dead volume of the sample cell was determined using He gas (99.995%).

Catalytic cycloaddition reactions of CO_2 with epoxides

The cycloaddition reaction of CO_2 with various epoxides was carried out in a glass reactor (50 mL) under RT and 0.1/0.8 MPa pressure of CO_2. Before starting catalytic reactions, the **Zn-DAT**/**Zn-TAZ** MOF was activated at 373 K for 12 h under vacuum to remove guest solvent molecules. The reactants were taken in the reactor at room temperature and it was flushed with CO_2 twice and the required pressure (0.1/0.8 MPa) of CO_2 was introduced and the contents

were allowed to stir at RT. After 24 h, the excess CO_2 was released slowly and the **Zn-DAT** MOF catalyst was separated from the reaction mixture by filtration and centrifugation. The catalytic conversions were determined by ^{1}H NMR spectra of the filtrate. The recovered catalyst was washed with methanol three times and activated at 373 K under vacuum for 12 h and reused for the subsequent catalytic cycles.

Theoretical calculations

To understand the interaction of CO_2 with **Zn-DAT** MOF was studied by density functional theory (DFT) calculations. All the calculations were performed with DMOL^3 package.[2] Generalized gradient approximations (GGA) along with Perdew, Bruke, and Ernzerhof (PBE) exchange-correlation functional was used. Double numeric polarization (DNP) basis set with DFT-D Grimme function has been used to accurately demonstrate the weak van der Waal's interactions.

The average CO_2 interaction energy (E_{Int}) with **Zn-DAT** MOF was determined using the following relation,

$$E_{Int} = \frac{1}{2}[E(MOF + 2CO_2) - E(MOF) - 2E(CO_2)]$$

Here, $E(MOF + 2CO_2)$ is the total energy of two molecules of CO_2 interacting with **Zn-DAT** MOF, $E(MOF)$ and $2E(CO_2)$ are the energy of **Zn-DAT** MOF and the energy of CO_2 molecules, respectively.

X-ray crystallography

Single crystal X-ray structural data of **Zn-DAT** MOF was collected on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. The SAINT^3 program was used for integration of diffraction profiles and absorption correction was made with SADABS program.[4] The structures were solved by SIR 92[5] and refined by full-

matrix least square method using SHELXL-2013[6] and WinGX system, Ver 2013.3.[7] The non-hydrogen atoms in all the structures were located from the difference Fourier map and refined anisotropically. All the hydrogen atoms were fixed by HFIX and placed in ideal positions and included in the refinement process using riding model with isotropic thermal parameters. The disordered guest solvent molecules were treated with SQUEEZE option of PLATON[8] multipurpose software. Therefore, the formula of **Zn-DAT** MOF was confirmed based on the elemental analyses and TGA. The potential solvent accessible area or void space was calculated using the PLATON software. All the crystallographic and structure refinement data of the **Zn-DAT** MOF are summarized in Table S1. Selected bond lengths and angles are given in Table S2 and selected hydrogen bond details of the **Zn-DAT** MOF are summarized in Table S3. The crystallographic information file is deposited with the CCDC number 1918936.

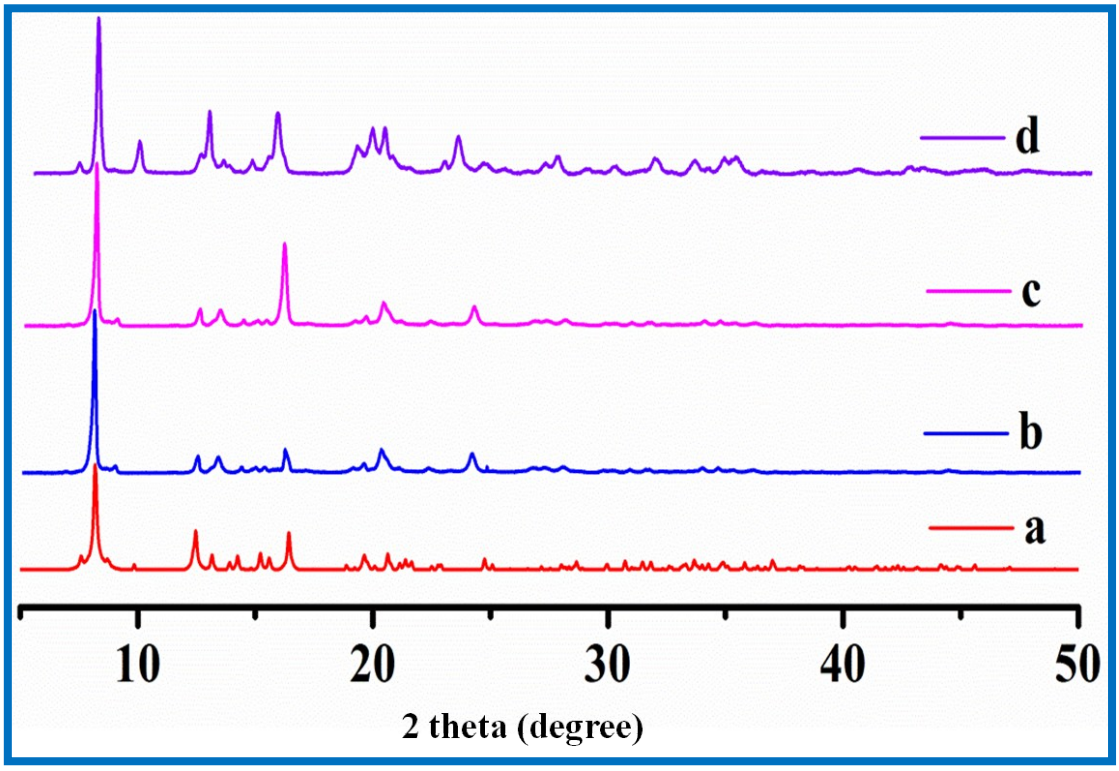


Fig. S1 PXRD patterns of **Zn-DAT** MOF (a) simulated pattern from single crystal X-ray diffraction, (b) as-synthesized sample (c) activated and (d) recycled sample after five catalytic cycles.

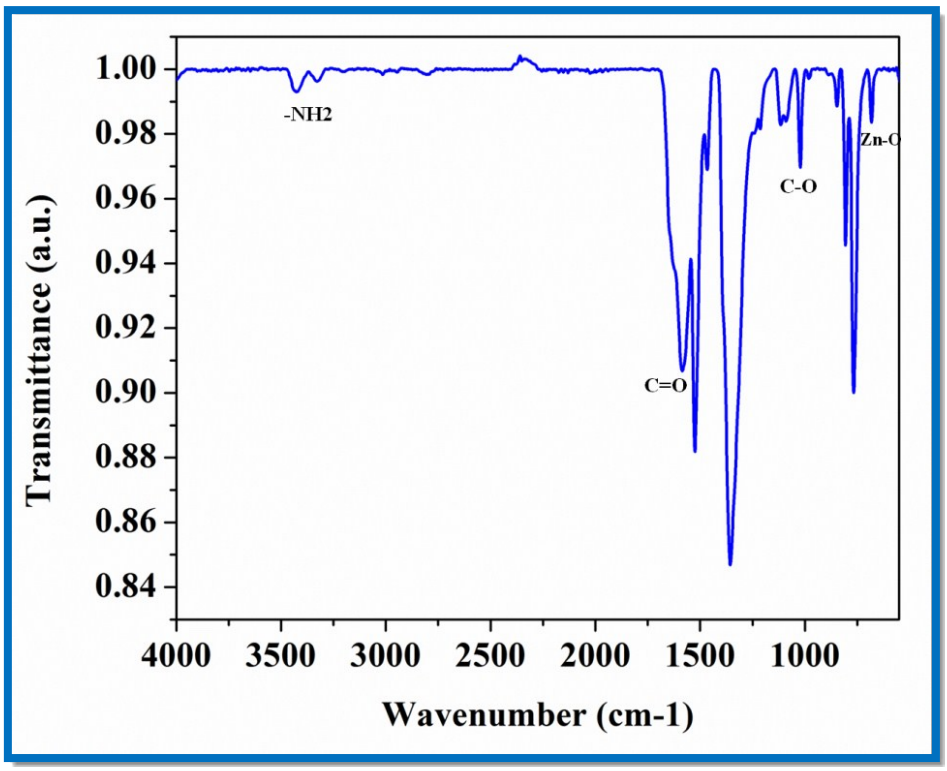


Fig. S2 FT-IR spectrum of **Zn-DAT** MOF.

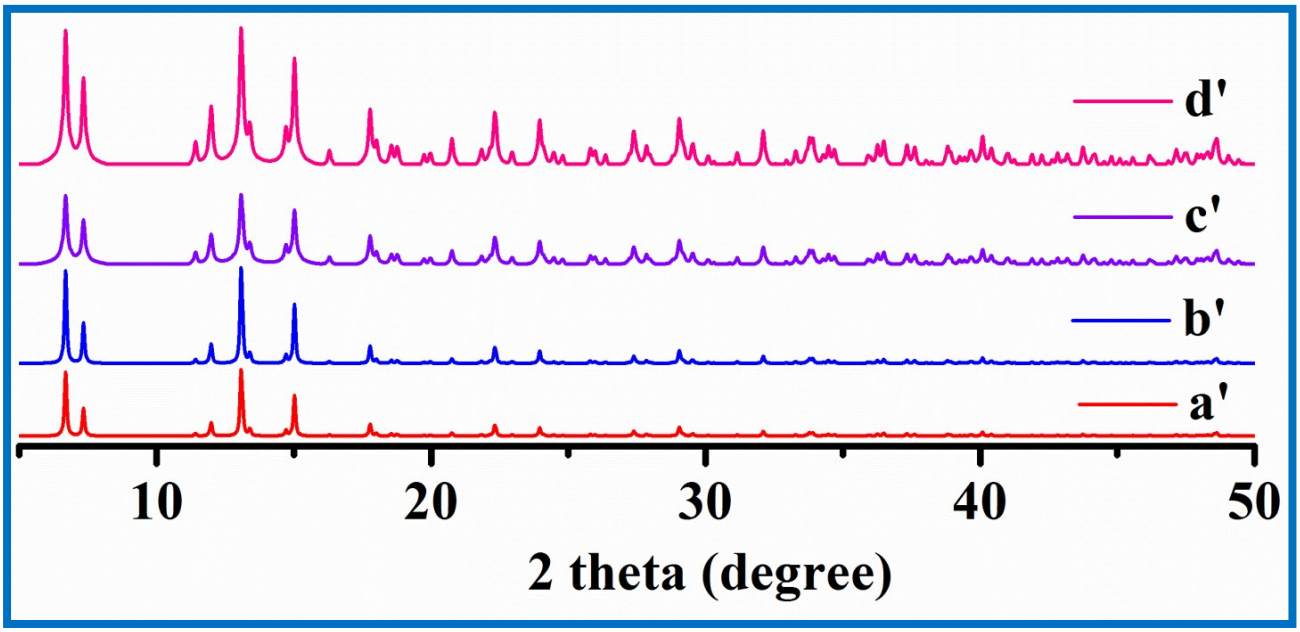


Fig. S3 PXRD patterns for **Zn-TAZ** MOF (a') simulated pattern from single crystal X-ray diffraction, (b') as-synthesized sample (c') activated and (d') after reaction.

Table S1. Crystal data and structure refinement parameters for **Zn-DAT** MOF.

Parameters	**Zn-DAT** MOF
Empirical formula	$C_{14}H_8N_5O_8S_2Zn_2$
Formula mass	569.17
Crystal system	Monoclinic
Space group	C2/m
a/ Å	18.054(4)
b/ Å	20.290(4)
c/Å	12.812(3)
α (degree)	90
β (degree)	128.191(5)
γ (degree)	90
V ($Å^3$)	3688.7(14)
Z	4
M (mm^{-1})	1.443
F (000)	1132
T (K)	298
λ (Mo Kα) (Å)	0.71073
$\theta_{min\ (deg)}$	2.3
$\theta_{max\ (deg)}$	26.8
total data	18973
unique data	3940
R_{int}	0.042
Data [1 > 2σ(I)]	2817
$^aR_1$	0.0787
wR_2	0.2664
S	1.23
CCDC	1918936

$^aR_1 = \sum \| F_0 | - | F_c \| / \sum | F_o |$, $wR_2 = [\ \sum w(F_o^2-F_c^2)^2/\sum w(Fo^2)^2]^{1/2}$

Table S2. Selected bond length (Å) and angles (°) for **Zn-DAT** MOF.

Zn1-O1	1.955(4)	$O3^{vi}$-Zn2-N2	102.29(18)
Zn1-N1	1.972(4)	$O4^{viii}$-Zn2-N2	101.1(2)
Zn1-$O1^{i}$	1.955(4)	$O3^{vi}$-Zn2-$O4^{iv}$	84.4(2)
Zn1-$N1^{i}$	1.972(4)	$O3^{vi}$-Zn2-$O4^{iv}$	156.6(2)
Zn2-N2	1.993(6)	$O4^{iv}$-Zn2-$O4^{viii}$	90.01(18)
Zn2-$O4^{iv}$	2.031(5)	$O3^{vi}$-Zn2-$O3^{vi}$	91.7(2)
Zn2-$O3^{vi}$	2.020(5)	$O3^{vi}$-Zn2-$O4^{viii}$	156.6(2)
Zn2-$O3^{vi}$	2.020(5)	$O3^{vii}$-Zn2-$O4^{viii}$	84.4(2)
Zn2-$O4^{viii}$	2.031(5)	Zn1-O1-C1	117.4(4)
O1-Zn1-N1	116.8(2)	$Zn2^{v}$-O3-C6	127.3(4)
O1 -Zn1-$O1^{i}$	108.21(18)	$Zn2^{iii}$-O4-C6	129.9(5)
O1-Zn1-N^{i}	102.92(19)	Zn1-N1-C7	128.2(3)
$O1^{i}$-Zn1-N1	102.92(19)	Zn1-N1-$N1^{ii}$	125.1(3)
N1-Zn1-N^{i}	109.83(16)	$N1^{ii}$-N1-C7	105.7(4)
$O1^{i}$-Zn1-N^{i}	116.8(2)	Zn2-N2-C7	127.5(3)
$O4^{iv}$ -Zn2-N2	101.1(2)	Zn2-N2-$C7^{ii}$	127.5(3)
$O3^{vi}$-Zn2-N2	102.29(18)		

i = 1-x,y,-z, ii = x,2-y,z, iii = -1/2+x,-1/2+y,-1+z, iv = 1/2+x,1/2+y,1+z, *v* = 3/2-x,-1/2+y,z, vi = 3/2-x,1/2+y,-z, vii = 3/2-x,3/2-y,-z, viii = 1/2+x,3/2-y,1+z.

Table S3. Selected hydrogen bonding interactions (Å) and angles (°) for **Zn-DAT** MOF.

D–H···A	H···A	D···A	D–H···A
N3-H3A…O2	2.1000	2.874(7)	149.00
N3-H3B…O3	2.5700	3.252(8)	137.00

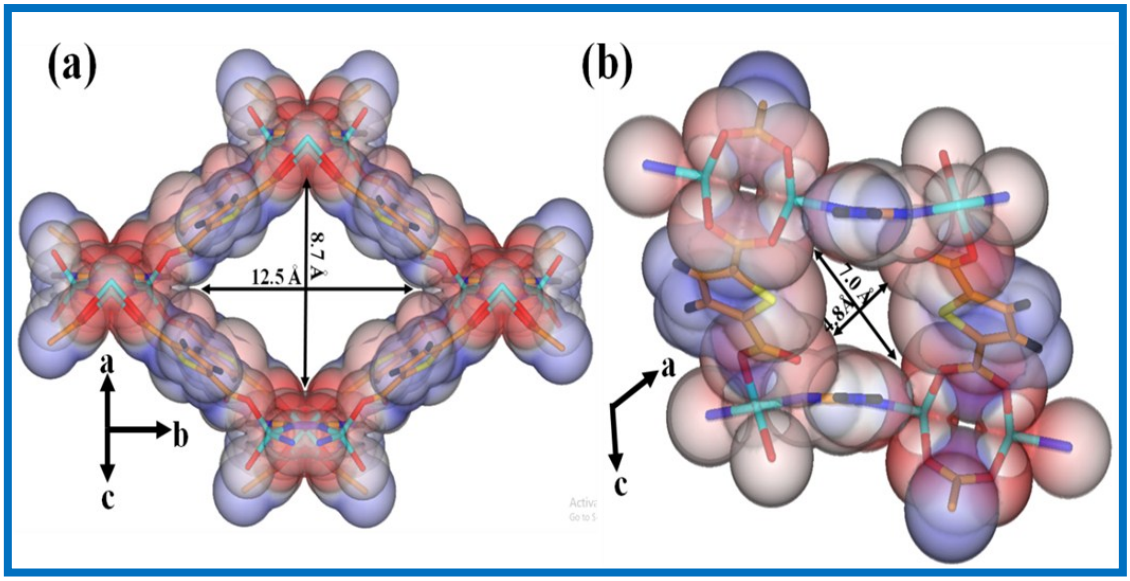


Fig. S4 3D view of **Zn-DAT** MOF showing the pore size along the crystallographic *c*- and *b*-axis.

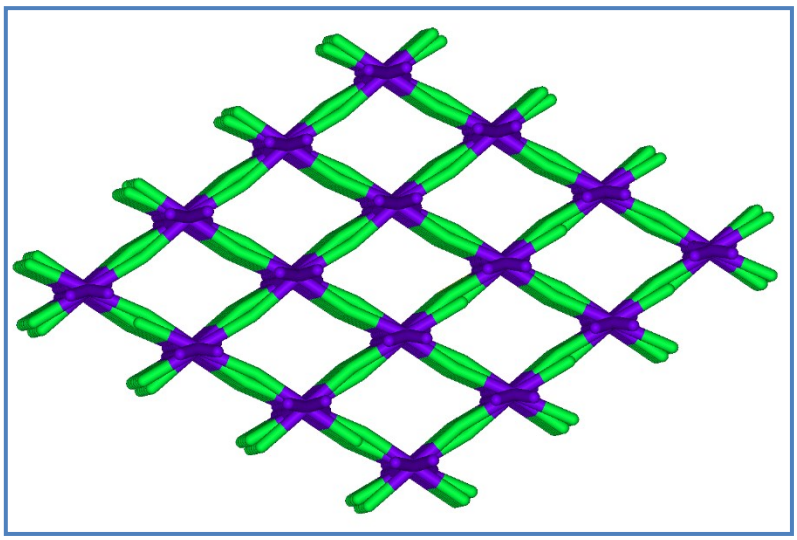


Fig. S5 TOPOS view of the 6-connected uni-nodal net of **Zn-DAT** MOF.

Analysis of gas adsorption isotherms

Clausius-Clapeyron Equation[9] was used to calculate the enthalpies of carbon dioxide adsorption. By using Langmuir Freundlich equation[10] an accurate fit was retrieved which gives a precise prediction of carbon dioxide adsorbed at saturation. A modification of Clausius-Clapeyron equation is used for calculations.

$$\ln\left[\frac{P_1}{P_2}\right] = \Delta H_{ads} \; X \left[\frac{T_2 - T_1}{R \; X \; T_2 T_1}\right] \text{------(i)}$$

where, P_1 and P_2 = pressures for isotherm at 273K and 298K respectively.

T_1 and T_2 = temperatures for isotherm at 273K and 298K respectively.

ΔH_{ads} = Enthalpy of adsorption.

R = Universal gas constant = 8.314 J/K/mol.

Pressure is a function of amount of gas adsorbed which was determined by using the Langmuir-Freundlich fit.

$$\frac{Q}{Q_m} = \frac{B \; X \; P^{(1/t)}}{1 + (B \; X \; P^{(1/t)})} \text{ ------(ii)}$$

where, Q = moles of gas adsorbed.

Q_m = moles of gas adsorbed at saturation.

B and t = constants.

P = Pressure.

By rearranging equation (ii) we get equation (iii)

$$P = \left[\frac{Q/Q_m}{B - (B \; X \; Q/Q_m)} \right]^t \quad \text{------(iii)}$$

Substituting equation (iii) into equation (i) we get

$$\Delta H_{ads} = \frac{R \; X \; T_1 \; X \; T_2}{T_2 - T_1} \; \ln \frac{\left[\frac{Q/Q_{m1}}{B - (B \; X \; Q/Q_{m1})} \right]^{t1}}{\left[\frac{Q/Q_{m2}}{B - (B \; X \; Q/Q_{m2})} \right]^{t2}} \quad \text{------(iv)}$$

In equation (iv), subscript 1 and 2 are representing data corresponding to 273K and 298K in case of carbon dioxide gas.

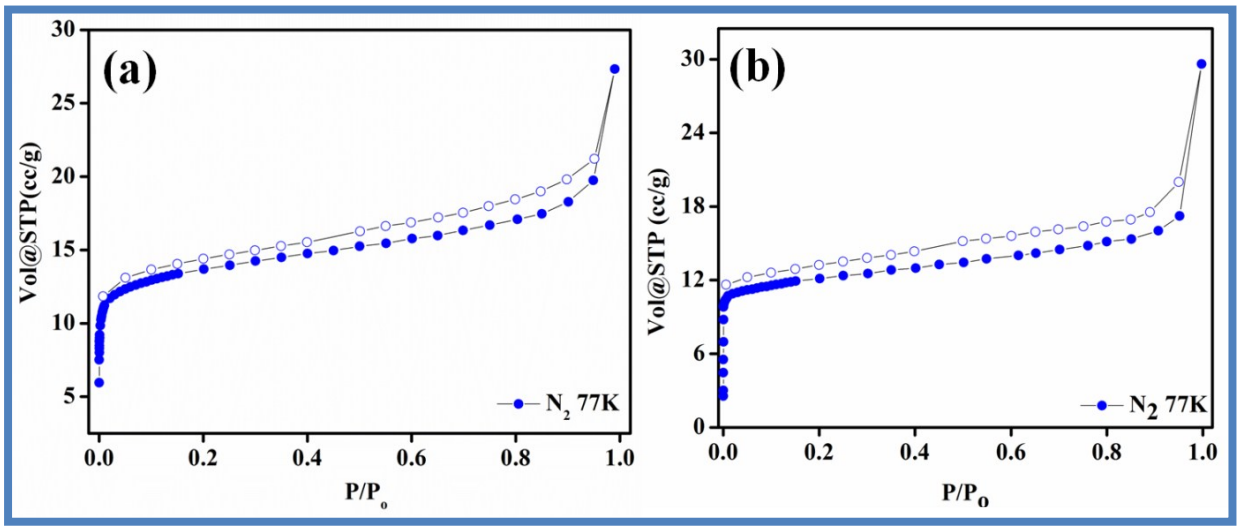


Fig. S6 N_2 adsorption-desorption isotherms of (a) **Zn-DAT** (b) **Zn-TAZ** MOF carried out at 77 K.

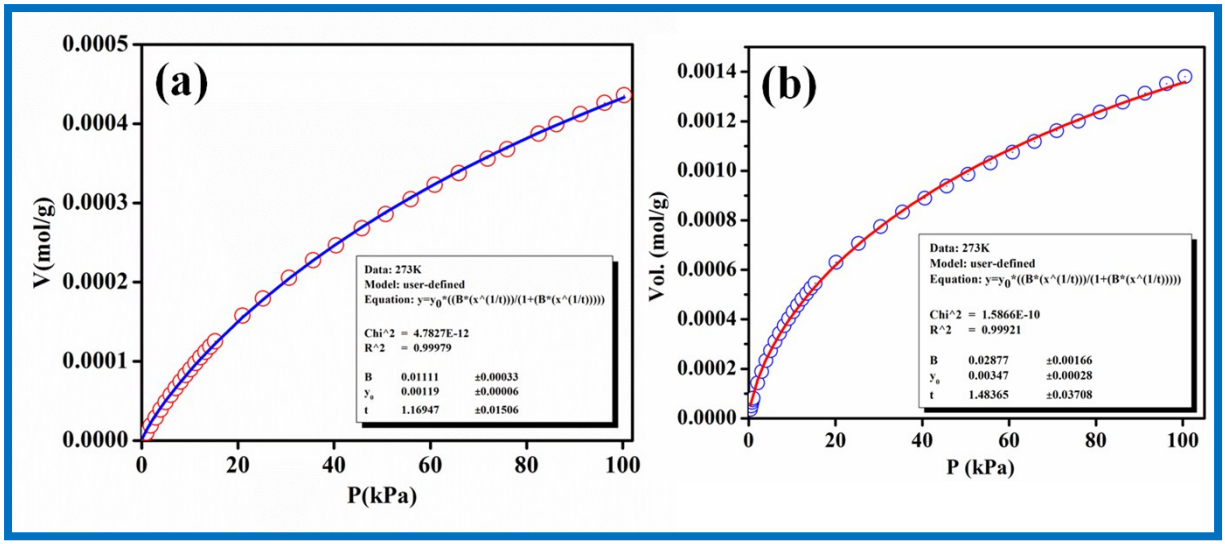


Fig. S7 Carbon dioxide adsorption isotherms of **Zn-DAT** (a) and **Zn-TAZ** (b) MOFs carried out at 273 K. The solid line shows the best fit to the data using the Langmuir-Freundlich Equation.

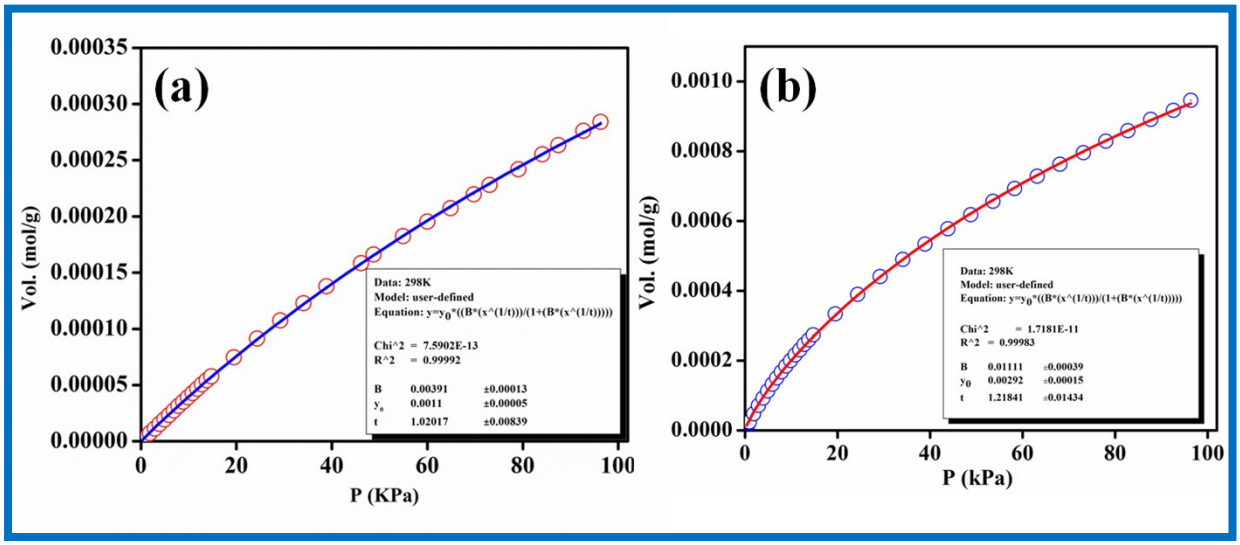


Fig. S8 Carbon dioxide adsorption isotherm for **Zn-DAT** (a) and **Zn-TAZ** (b) MOFs carried out at 298 K. The solid line shows the best fit to the data using the Langmuir-Freundlich Equation.

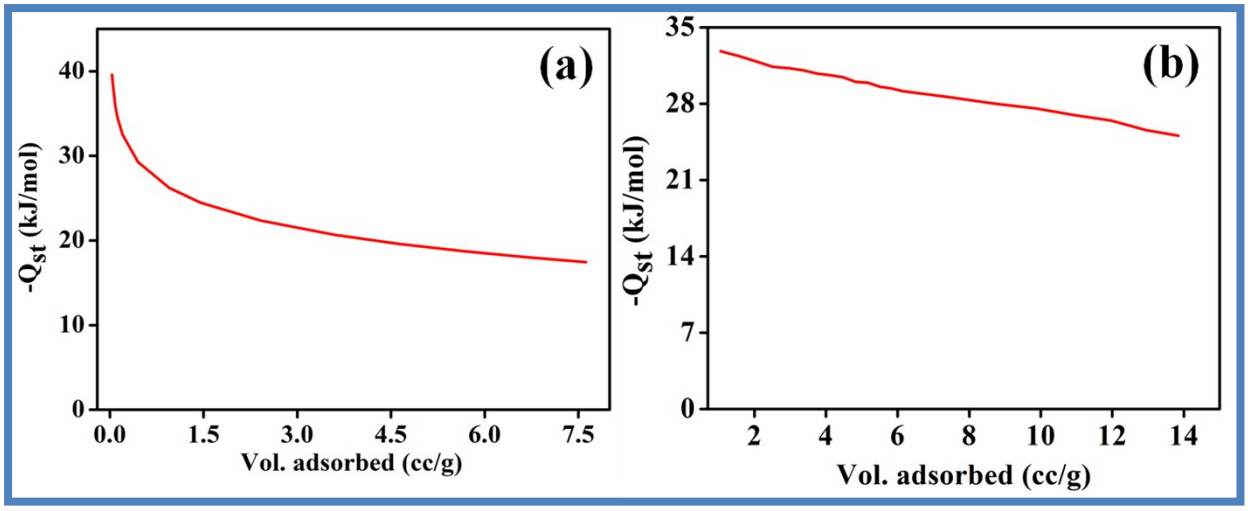


Fig. S9 Enthalpy of carbon dioxide for **Zn-DAT** (a) and for **Zn-TAZ** (b) MOFs calculated using the Clausius-Clapeyron equation.

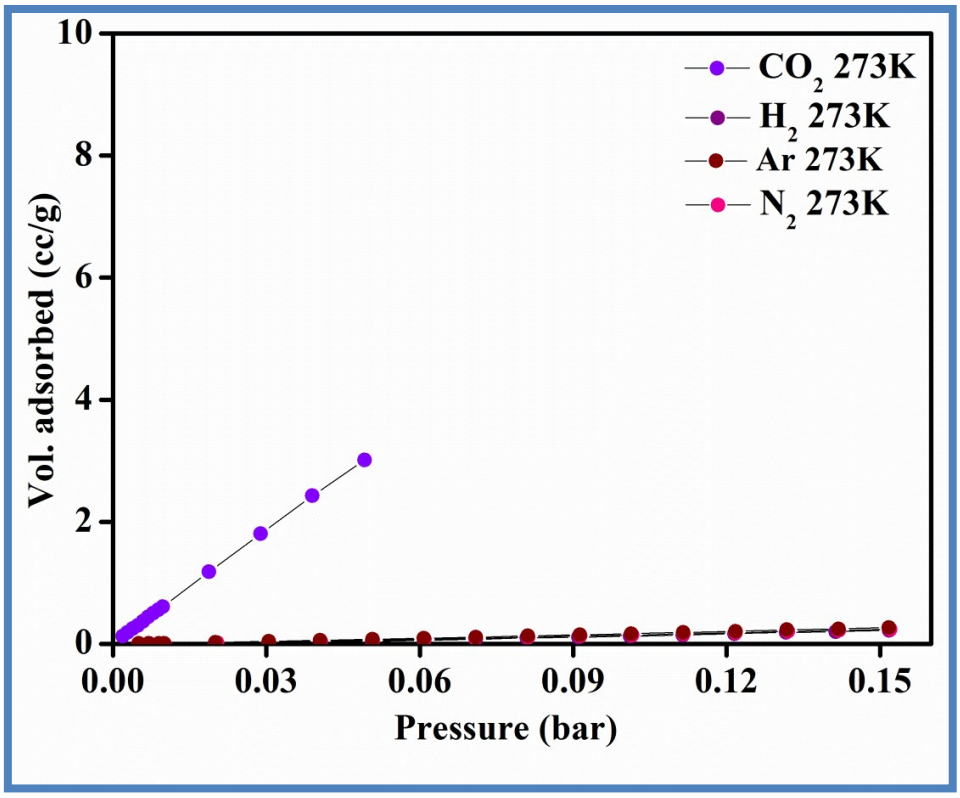


Fig. S10 Gas selectivity for **Zn-DAT** MOF calculated following the Henry's law from the CO_2, N_2, Ar and H_2 isotherms carried out at 273 K.

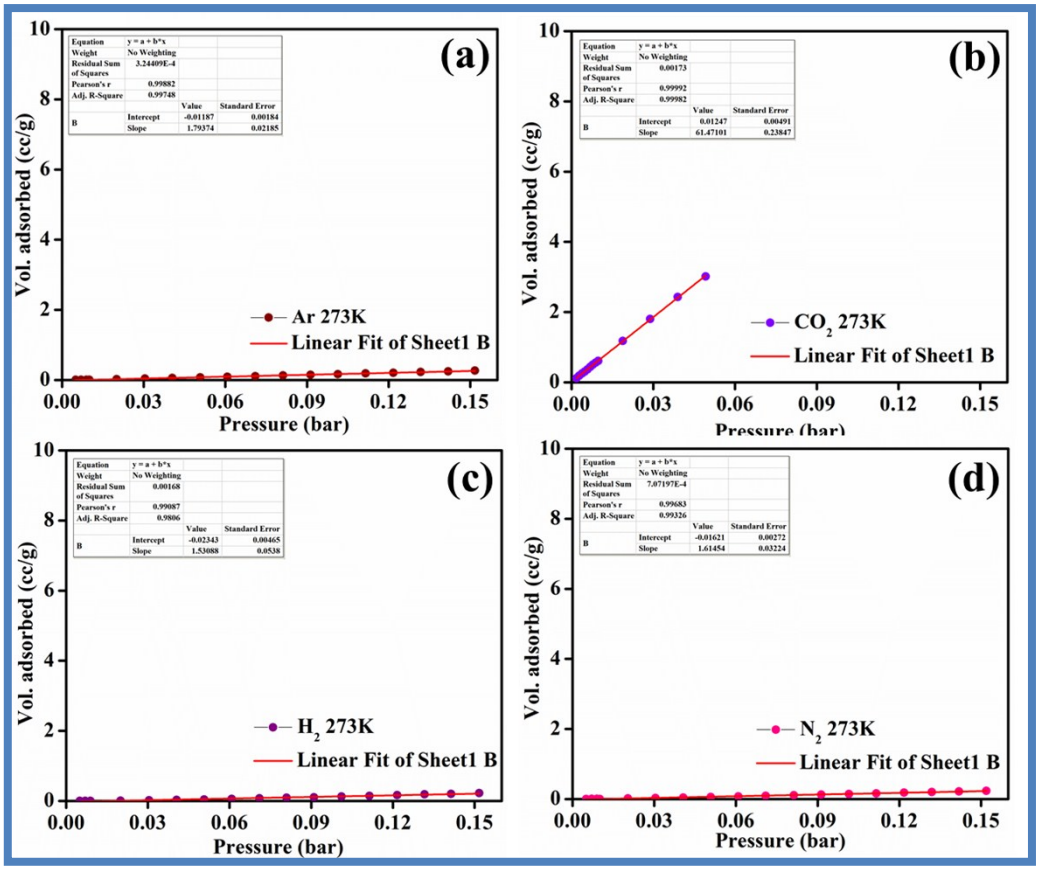


Fig. S11 Linear fitting of CO_2, Ar, H_2 and N_2 isotherms used for calculation of Henry's selectivity constants for **Zn-DAT** MOF.

Table S4. Optimization of catalytic cycloaddition reaction of CO_2 with epichlorohydrin (ECH) catalysed by **Zn-DAT** MOF.

Entry number	Catalyst (mol %)	Cocatalyst (mol %)	Temperature (°C)	Pressure (MPa)	Time (h)	Yield (%)
1	0.0	0.0	RT	0.8	24	00.0
2	0.4	0.0	RT	0.8	24	00.0
3	0.0	4.0	RT	0.8	24	44.5
4	0.4	4.0	RT	0.8	24	>99

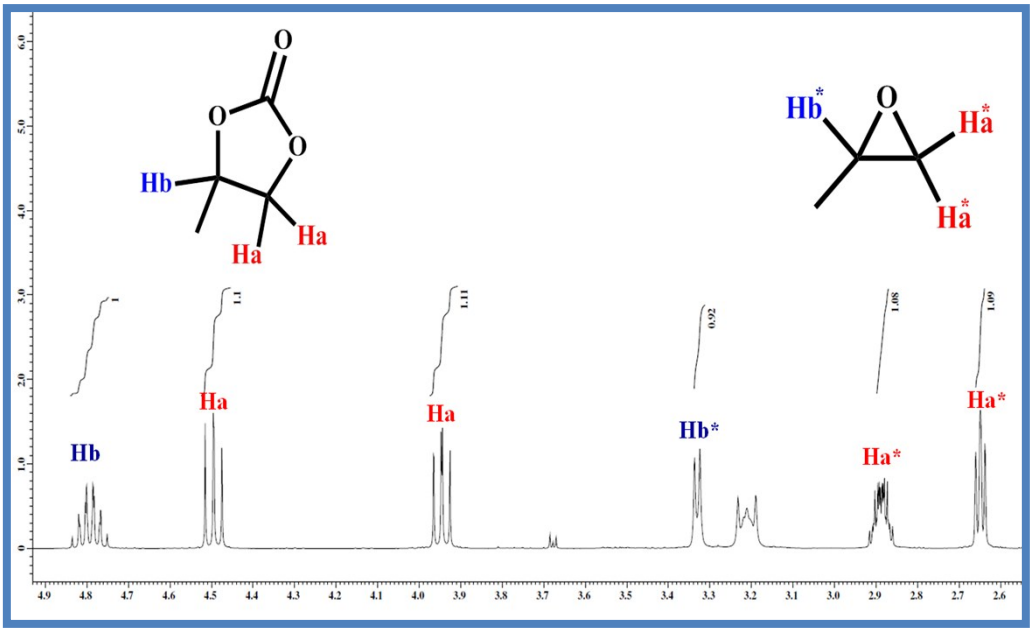


Fig. S12 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of propylene oxide (PO) using **Zn-DAT** MOF as catalyst (Table 1, entry no. 1).

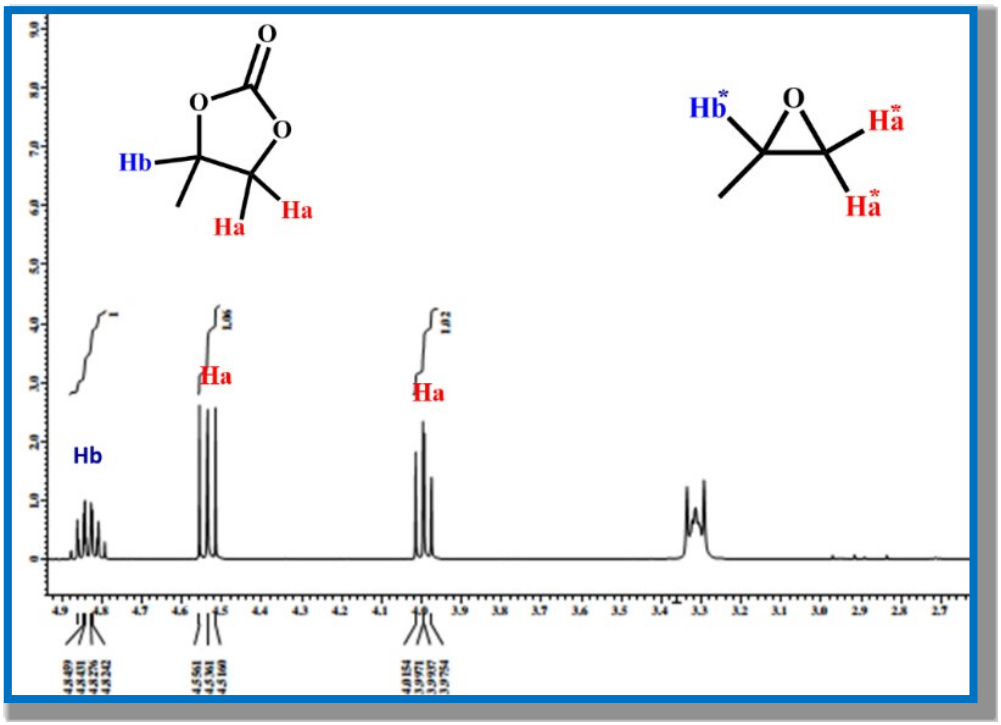


Fig. S13 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of PO with CO_2 using **Zn-DAT** MOF as catalyst (Table 1, entry no. 2).

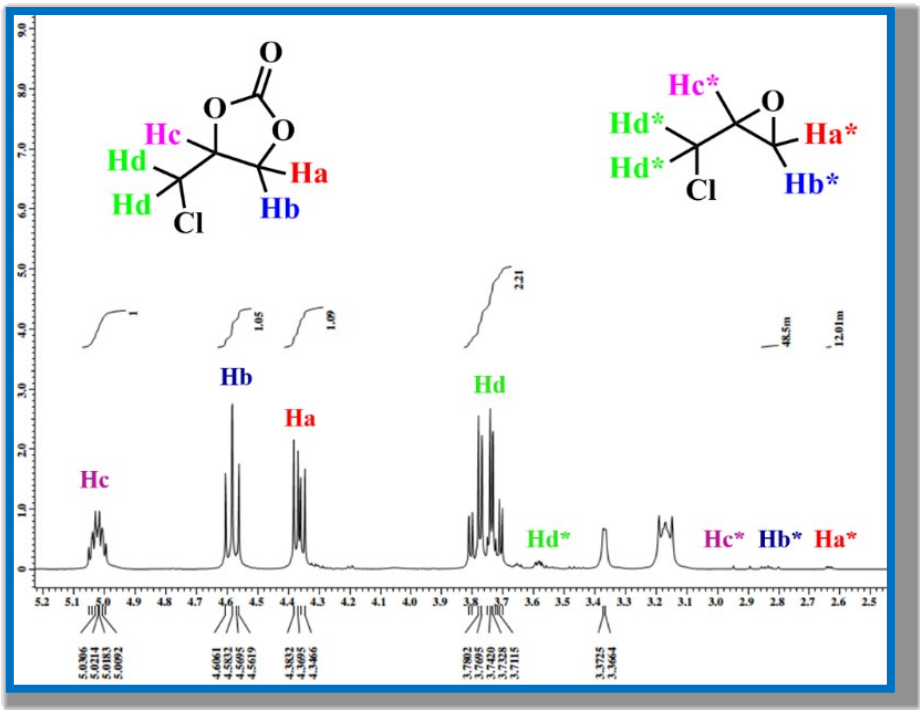


Fig. S14 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of epichlorohydrin (ECH) with CO_2 using **Zn-DAT** MOF as catalyst (Table 1, entry no. 3 and Table S5, entry no. 4).

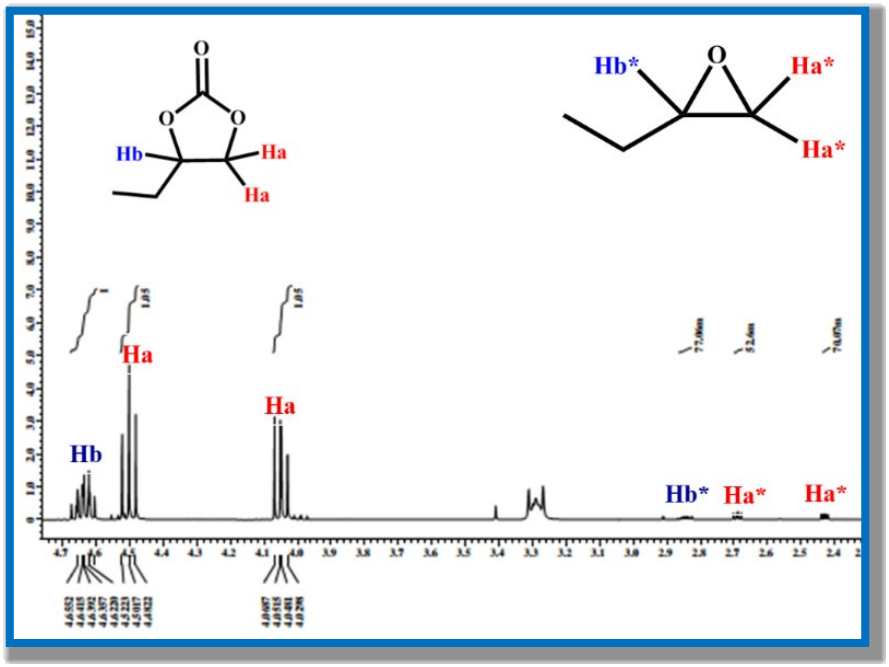


Fig. S15 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of 1, 2-epoxybutane using **Zn-DAT** MOF as catalyst (Table 1, entry no. 5).

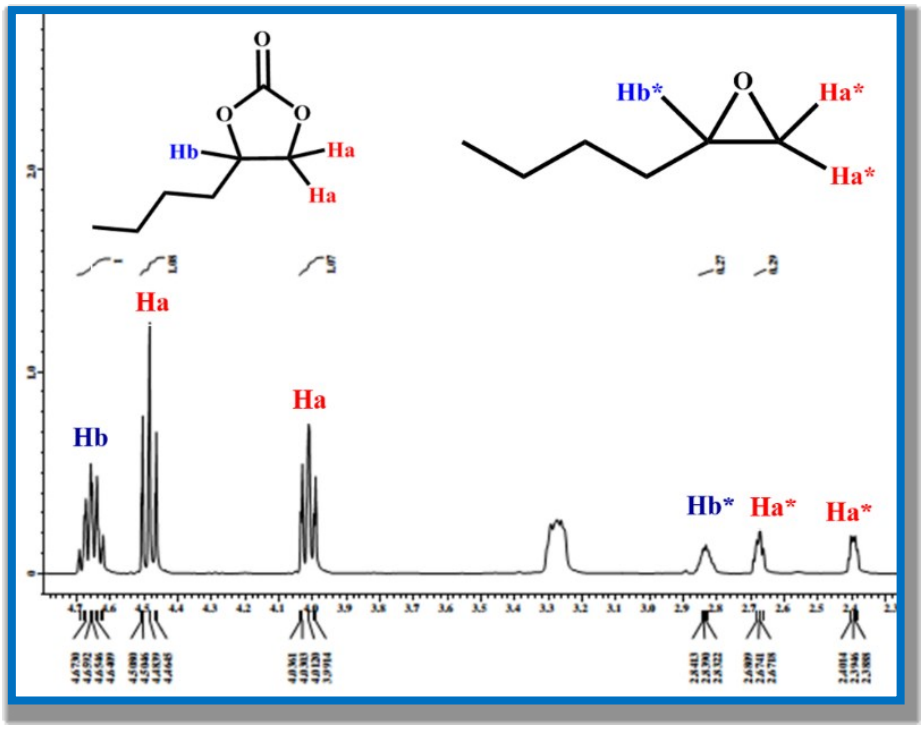


Fig. S16 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of 1, 2-epoxyhexane with CO_2 using **Zn-DAT** MOF as catalyst (Table 1, entry no. 7).

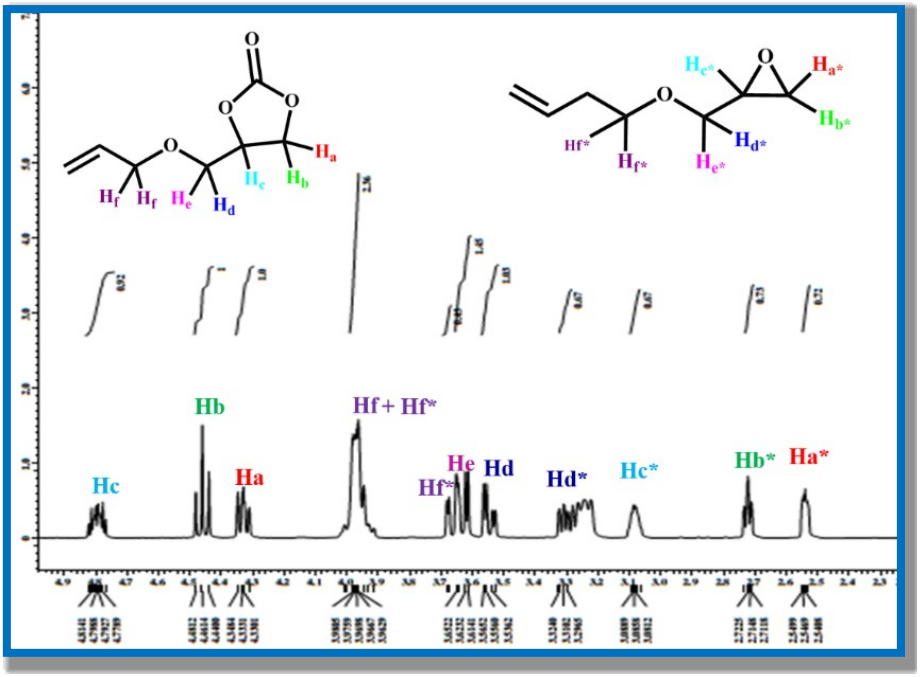


Fig. S17 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of allyl glycidyl ether with CO_2 using **Zn-DAT** MOF as catalyst (Table 1, entry no. 8).

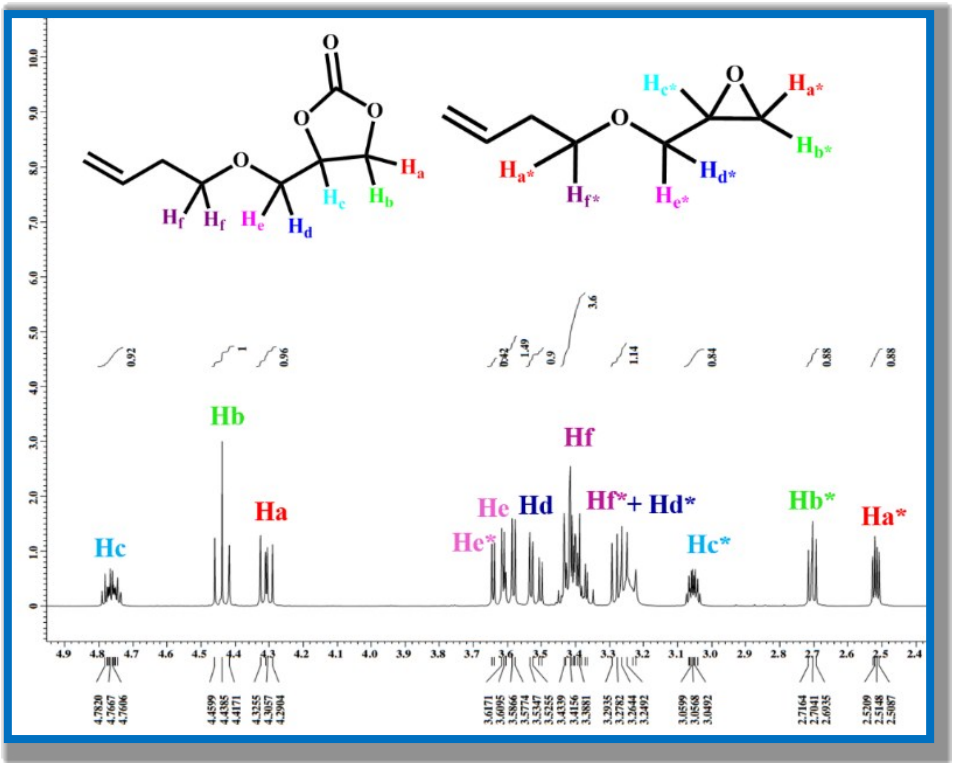


Fig. S18 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of butyl glycidyl ether with CO_2 using **Zn-DAT** MOF as catalyst (Table 1, entry no. 9).

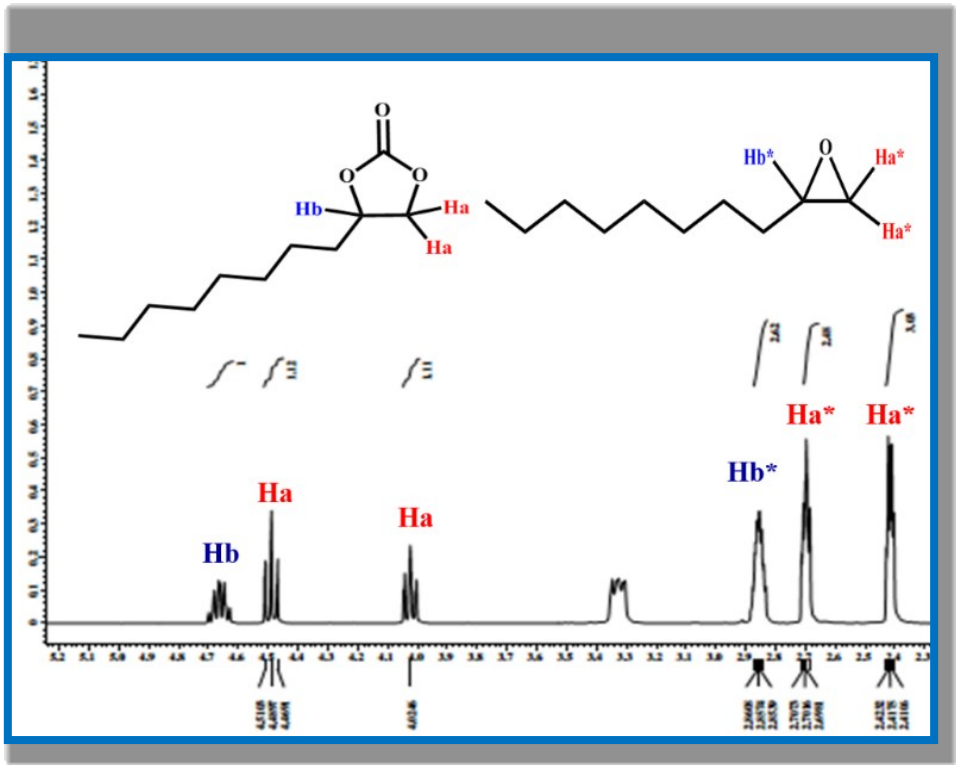


Fig. S19 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of 1, 2-epoxydecane with CO_2 using **Zn-DAT** MOF as catalyst (Table 1, entry no. 10).

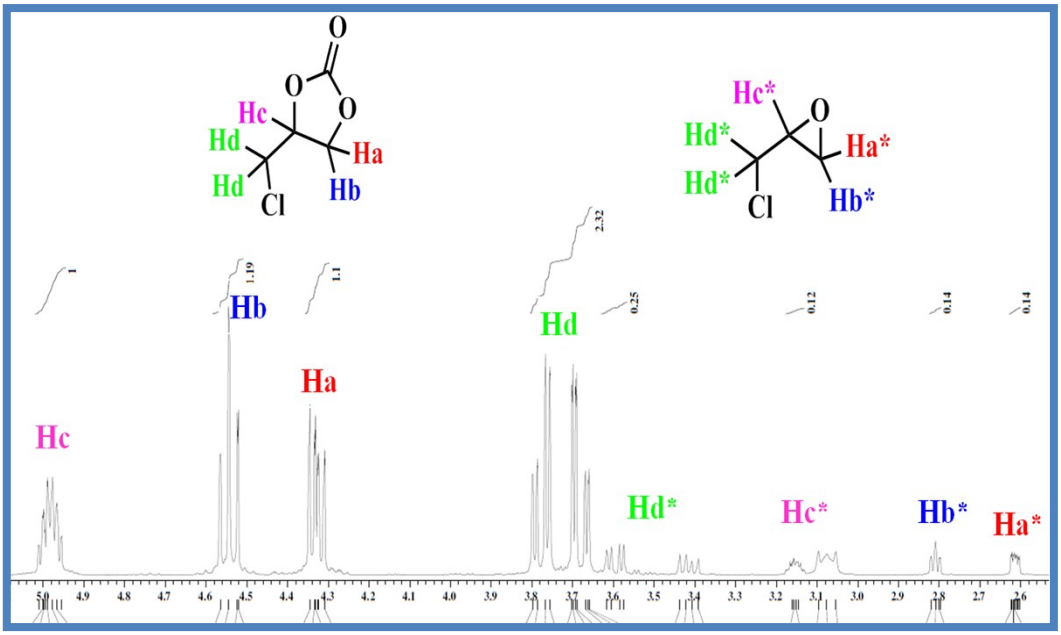


Fig. S20 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of epichlorohydrin (ECH) with CO_2 using **Zn-TAZ** MOF as catalyst (Table 1, entry no. 4).

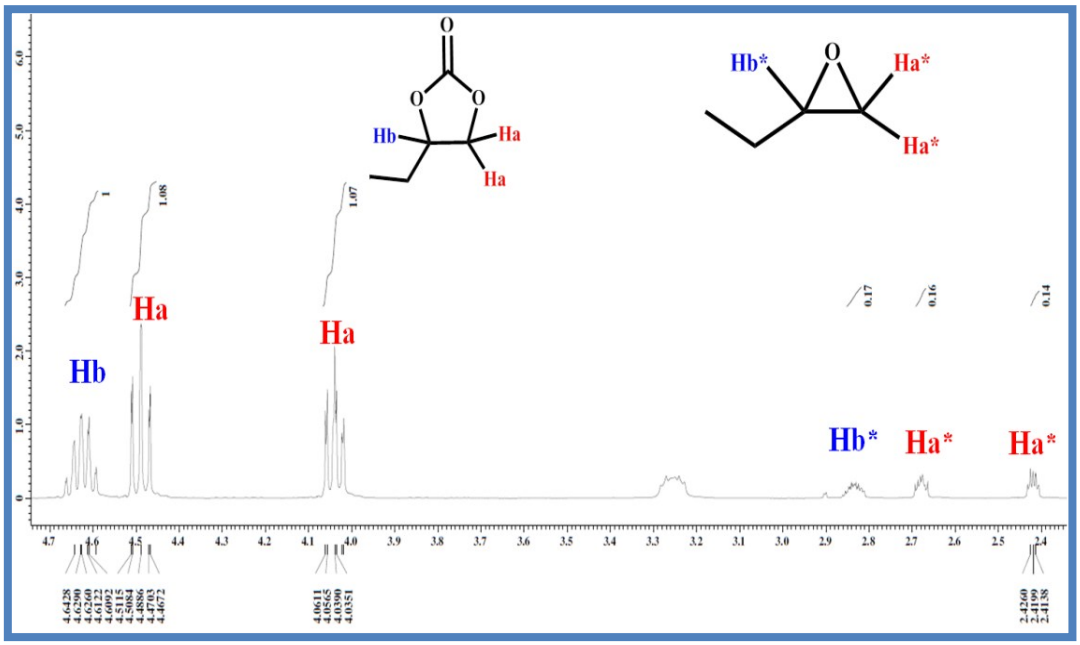


Fig. S21 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of 1, 2-epoxybutane using **Zn-TAZ** MOF as catalyst (Table 1, entry no. 6).

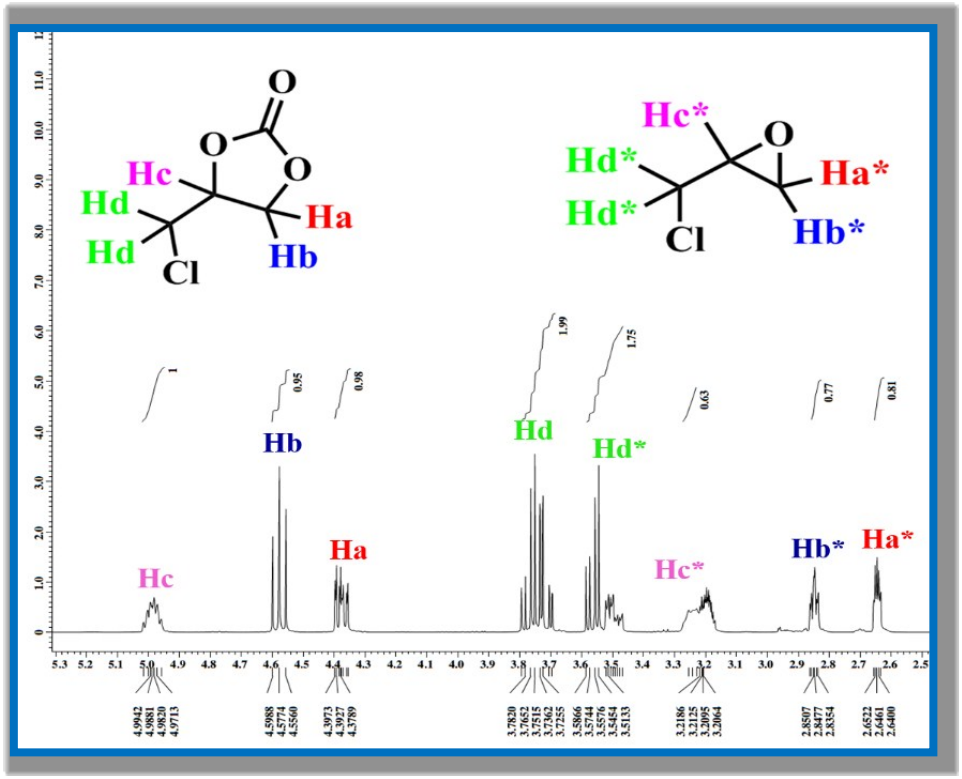


Fig. S22 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of epichlorohydrin (ECH) with CO_2 using TATAB as catalyst. (Table S5, entry no. 3).

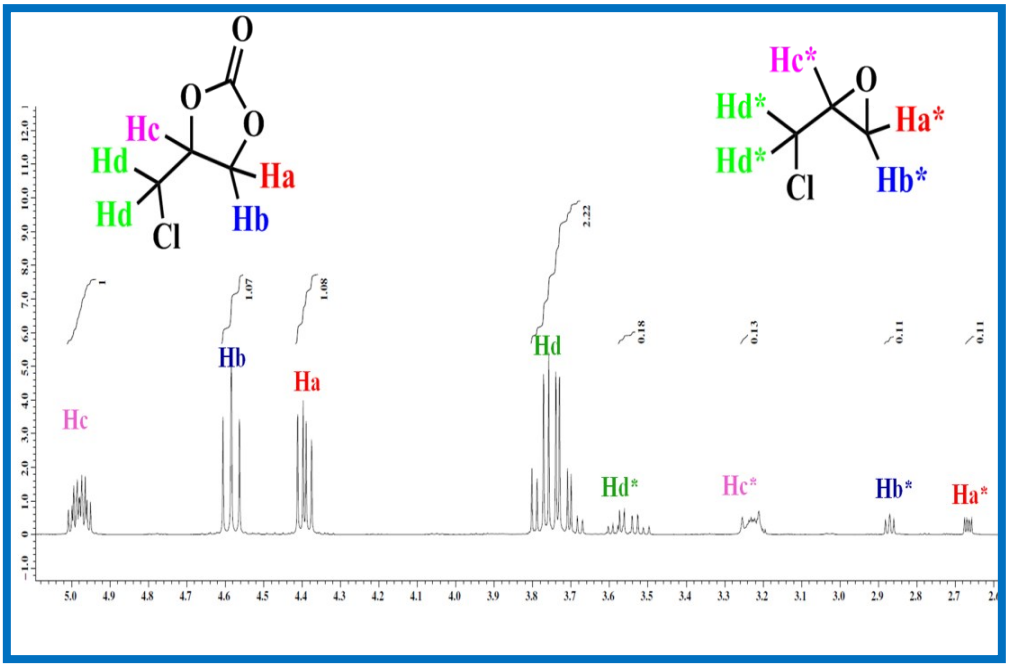


Fig. S23 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of epichlorohydrin with CO_2 using **Zn-DAT** MOF recycled after five cycles.

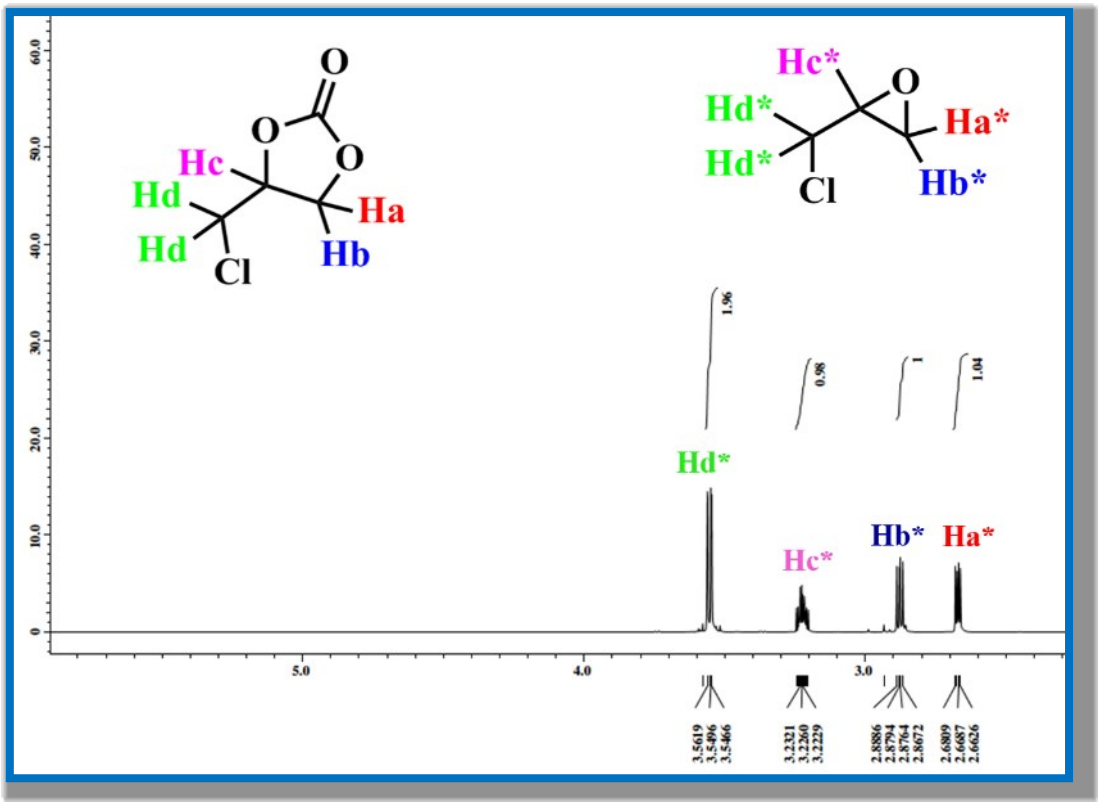


Fig. S24 ^{1}HNMR ($CDCl_3$, 400 MHz) spectra for the cycloaddition reaction of epichlohydrin using **Zn-DAT** MOF as catalyst without TBAB as co-catalyst (Table S4, entry no. 2).

Table S5. Optimized geometries of epoxides using Gaussian09[11] at B3lYP/6-311g (d,p) level.

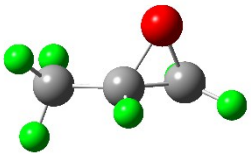
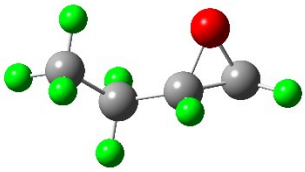
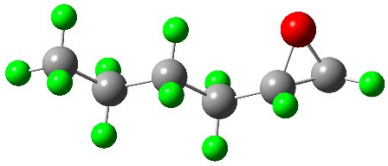
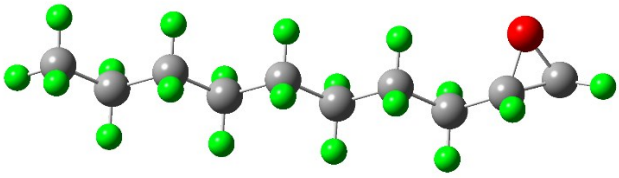
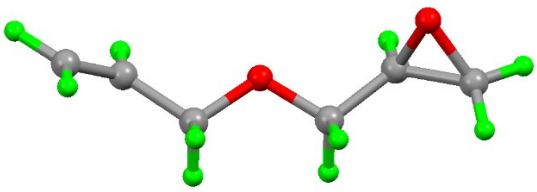
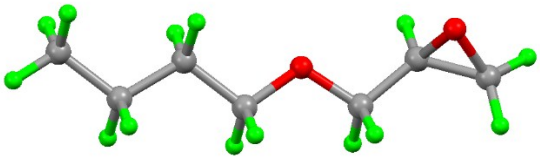
Substrates	Optimized structure	Dimensions
1,2-epoxy propane		4.35 X 3.41 Å^2
1,2-epoxy butane		5.648 X 3.39 Å^2
1,2-epoxy hexane		8.198 X 3.39 Å^2
1,2-epoxy decane		13.321 X 3.39 Å^2
allyl glycidyl ether		~8.901 X 3.140 Å^2
butyl glycidyl ether		~ 10.462 X 3.140 Å^2

Table S6. Cartesian coordinates of optimized geometries for

1. Zn-DAT MOF

Zn	10.48800000	39.33600000	20.62400000
Zn	11.20100000	58.26200000	20.50300000
Zn	20.80000000	48.94500000	19.77100000
Zn	12.09100000	48.92800000	29.98100000
Zn	11.20000000	43.17400000	20.37700000
Zn	10.47600000	62.21700000	20.65800000
Zn	20.80000000	52.54900000	19.78900000
Zn	12.03000000	52.56800000	30.04100000
Zn	15.51300000	40.65600000	23.72300000
Zn	15.49300000	60.82000000	23.76500000
Zn	15.04800000	50.86100000	13.55400000
Zn	5.64900000	50.84500000	24.61000000
Zn	17.14900000	40.61500000	26.07200000
Zn	17.13000000	60.85700000	26.11400000
Zn	16.79100000	50.75900000	15.77400000
Zn	7.18500000	50.73500000	27.01400000
S	14.20500000	54.49500000	17.82900000
S	14.29500000	44.07200000	28.36300000
S	8.34900000	54.70700000	22.76600000
S	18.23600000	44.39000000	21.67400000
S	8.29700000	46.92500000	22.70600000
S	18.20400000	57.07300000	21.71600000
S	14.19200000	47.03000000	17.84100000
S	14.28900000	57.39700000	28.40600000
N	14.07900000	40.74900000	22.28900000
N	14.05400000	60.73700000	22.33900000
N	17.83500000	50.75700000	17.51900000
N	8.70600000	50.71800000	28.40200000
O	15.50300000	52.32200000	16.29300000
O	6.06900000	52.37200000	27.65900000
O	15.81500000	41.91400000	26.97000000
O	15.95800000	62.46600000	26.68700000
O	16.34000000	52.29800000	12.86800000
O	6.82600000	52.33600000	23.87800000
O	16.80400000	42.15300000	23.03400000
O	16.87200000	62.28000000	23.28000000
O	16.28900000	49.37000000	12.74400000
O	7.00300000	49.35100000	23.97700000
O	16.88200000	39.18900000	23.23200000
O	16.77900000	59.31600000	23.07000000
O	15.47200000	49.26400000	16.40400000
O	5.62500000	49.46700000	27.53000000
O	15.96600000	39.00900000	26.63800000
O	15.79900000	59.55600000	27.01200000
O	11.80300000	38.19100000	19.18100000
O	11.74300000	57.41200000	18.81200000
O	21.26400000	47.51300000	18.27200000

O	12.07700000	47.31300000	28.83800000
O	10.60600000	37.76600000	22.02500000
O	11.24700000	57.40300000	22.44800000
O	20.44300000	47.63400000	21.20600000
O	12.42800000	47.98500000	31.78300000
O	10.90000000	43.98000000	22.17600000
O	10.67600000	63.85700000	22.00100000
O	20.43100000	53.84300000	21.24000000
O	12.37300000	53.51100000	31.83400000
O	11.74900000	44.06200000	18.71700000
O	11.86200000	63.22900000	19.15600000
O	21.25900000	54.00200000	18.31400000
O	12.04200000	54.17200000	28.88500000
N	12.14700000	40.34000000	21.26700000
N	12.44800000	59.83800000	21.04800000
N	22.43600000	50.15500000	20.15100000
N	13.76800000	50.18800000	29.87500000
N	9.25800000	40.79000000	19.50600000
N	9.65700000	59.62000000	19.49300000
N	19.34800000	50.04200000	19.00100000
N	10.50500000	50.03000000	29.54300000
N	9.65000000	41.87400000	19.53000000
N	9.25400000	60.68800000	19.44900000
N	19.34900000	51.45700000	19.00800000
N	10.47000000	51.44000000	29.57700000
N	12.51100000	41.64500000	20.94800000
N	12.10600000	61.15400000	21.34700000
N	22.43600000	51.33200000	20.15300000
N	13.74000000	51.35300000	29.91000000
O	13.97500000	52.24100000	14.60400000
O	4.68200000	52.20900000	25.85300000
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O	14.49200000	62.33400000	24.95200000
O	17.80900000	52.16800000	14.61300000
O	8.12900000	52.09900000	25.73200000
O	17.91000000	42.30800000	25.01300000
O	18.34900000	62.05300000	25.00600000
O	17.65800000	49.27400000	14.56500000
O	8.02200000	49.10500000	25.99000000
O	18.35900000	39.41200000	24.95800000
O	17.88300000	59.15900000	25.05000000
O	14.06100000	49.31200000	14.62300000
O	4.53700000	49.32500000	25.53100000
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N	14.29300000	58.45400000	21.66900000
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N	18.06900000	53.10700000	17.83500000

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H	13.69100000	37.92700000	22.02300000
H	13.96400000	57.67300000	21.06400000
H	18.33100000	47.67100000	18.47000000
H	9.88600000	47.70000000	28.61900000
H	18.33000000	53.83600000	18.50100000
H	9.77200000	53.77000000	28.59500000
H	14.02000000	43.80100000	20.98600000
H	13.75600000	63.53900000	22.06000000
H	13.45800000	38.55300000	23.53700000
H	15.22400000	58.44000000	22.08700000
H	17.17100000	48.29600000	17.32900000
H	8.58900000	48.26800000	27.65500000
H	17.19400000	53.22900000	17.32100000
H	8.28700000	53.20300000	27.92800000
H	15.27600000	43.03800000	22.02500000
H	13.45500000	62.95100000	23.57200000
C	13.70700000	53.83900000	16.30000000
C	14.14200000	43.56200000	26.71200000
C	8.60800000	53.84500000	24.25300000
C	18.39800000	43.86900000	23.32300000
C	8.59700000	47.62500000	24.27000000
C	18.36300000	57.59100000	23.36600000
C	13.71800000	47.70600000	16.31300000
C	14.13900000	57.89700000	26.75100000
O	13.48700000	56.47100000	19.92800000
O	13.31500000	46.11800000	30.33400000
O	9.49900000	57.06600000	21.10600000
O	19.34100000	46.37100000	19.66800000
O	9.28700000	44.73900000	20.80400000
O	19.32400000	55.10800000	19.70800000
O	13.45500000	45.00100000	19.89200000
O	13.28700000	55.35500000	30.38400000
C	12.90700000	55.64600000	17.79300000
C	13.17700000	45.37600000	28.09200000
C	9.65900000	55.78900000	23.12800000
C	19.33300000	45.70900000	21.95100000
C	9.56200000	45.76100000	22.94300000
C	19.30100000	55.75500000	21.99300000
C	12.90700000	45.86800000	17.76400000
C	13.17800000	56.08700000	28.13700000
C	14.44700000	52.72100000	15.68700000
C	14.94100000	42.43300000	26.18900000
C	7.79300000	52.67600000	24.64200000
C	17.65200000	42.69300000	23.82700000
C	7.81500000	48.77400000	24.77000000
C	17.62200000	58.77300000	23.86600000
C	14.46600000	48.84100000	15.73500000

C	14.92900000	59.03300000	26.22900000
C	12.72400000	56.56800000	18.93500000
C	12.84600000	46.31000000	29.17400000
C	10.14100000	56.80900000	22.18000000
C	19.71200000	46.62100000	20.85700000
C	9.90500000	44.77600000	21.89400000
C	19.69100000	54.85200000	20.89700000
C	12.71400000	44.91600000	18.88000000
C	12.82500000	55.16400000	29.22000000
C	13.10200000	39.85100000	22.05000000
C	13.62900000	59.60900000	21.67600000
C	18.40900000	49.67500000	18.10900000
C	9.44100000	49.65000000	28.81300000
C	18.41000000	51.83300000	18.11900000
C	9.39500000	51.80000000	28.85200000
C	13.68000000	41.87100000	21.59800000
C	13.08400000	61.64400000	22.10100000
C	12.12900000	55.51200000	16.65200000
C	12.72000000	45.39900000	26.78000000
C	10.24900000	55.49100000	24.34700000
C	19.79700000	45.72800000	23.26000000
C	10.18800000	45.92600000	24.16800000
C	19.76300000	55.73300000	23.30300000
C	12.14500000	46.01500000	16.61300000
C	12.72800000	56.05500000	26.82300000
H	11.01700000	45.28800000	24.46900000
C	12.58400000	54.48400000	15.80100000
C	13.25900000	44.36200000	25.99700000
C	9.65200000	54.39000000	24.98900000
C	19.27200000	44.67800000	24.03600000
C	9.64100000	46.98000000	24.92400000
C	19.23600000	56.78100000	24.08000000
C	12.60700000	47.06100000	15.78800000
C	13.26200000	57.09100000	26.03500000
H	12.77900000	54.37000000	31.37000000
H	11.58200000	53.79700000	32.32200000
H	12.82300000	47.12100000	31.32400000
H	11.63400000	47.71100000	32.27300000
C	14.93200000	62.82100000	26.04300000
C	17.95200000	62.52600000	23.89800000
H	18.63600000	63.24900000	23.40700000
H	14.34200000	63.65500000	26.48100000
H	12.33400000	62.52700000	18.67000000
H	11.40800000	63.76000000	18.47800000
H	11.61800000	63.61400000	22.37600000
H	10.05200000	63.80900000	22.74700000
C	17.39100000	52.61900000	13.50800000
H	18.02200000	53.39600000	13.02600000
C	17.27900000	48.92900000	13.41100000
H	17.88400000	48.14100000	12.91300000

O	13.68700000	50.25600000	11.97900000
H	14.28700000	49.64200000	11.51100000
H	13.12400000	49.66900000	12.52100000
H	12.32900000	38.84600000	18.68500000
H	11.35400000	37.64800000	18.50900000
H	11.56300000	37.96700000	22.39200000
H	9.98300000	37.86400000	22.76700000
C	5.05600000	52.69200000	26.96200000
C	4.73500000	49.02200000	26.74900000
H	4.41200000	53.49600000	27.37900000
H	4.04000000	48.27200000	27.18300000
O	4.50700000	50.29100000	22.86200000
H	5.17900000	49.77700000	22.37300000
H	3.92500000	49.61300000	23.25800000
O	18.50700000	60.17500000	27.63700000
H	19.04600000	59.57400000	27.08600000
H	17.90800000	59.57600000	28.12500000
C	14.94100000	38.65500000	25.99400000
C	17.96100000	38.94000000	23.85100000
H	14.34900000	37.82100000	26.42900000
H	18.64500000	38.21700000	23.36000000
O	18.52600000	41.27700000	27.60100000
H	19.07200000	41.88200000	27.06200000
H	17.93300000	41.87300000	28.10100000
H	22.10600000	54.46100000	18.45000000
H	20.54100000	54.62700000	18.65900000
H	22.11400000	47.06000000	18.40500000
H	20.55100000	46.87800000	18.60900000
H	19.46200000	56.95700000	25.13100000
H	20.46100000	54.97300000	23.64800000
H	11.25800000	56.14200000	16.47700000
H	12.13100000	54.18900000	14.85400000
H	12.16000000	47.36600000	14.84200000
H	11.28200000	45.38000000	16.41900000
H	19.49800000	44.49900000	25.08700000
H	20.49400000	46.48800000	23.60700000
H	9.99300000	47.29900000	25.90400000
H	12.03300000	46.16500000	26.42600000
H	13.05000000	44.18800000	24.94200000
H	13.05100000	57.26200000	24.97900000
H	12.04800000	55.28000000	26.47600000
H	11.08900000	56.07600000	24.71300000
H	9.96600000	53.96000000	25.94000000

2. Zn-DAT MOF with two CO_2 molecules

Zn	10.22400000	39.53100000	20.84100000
Zn	11.67700000	58.15400000	20.88200000
Zn	20.74000000	49.06400000	20.01400000
Zn	12.47200000	49.22600000	29.67400000
Zn	11.27700000	43.23400000	20.46000000

Zn	10.02700000	61.85900000	21.24100000
Zn	20.75000000	52.67200000	19.92800000
Zn	12.10200000	52.85500000	29.88800000
Zn	15.47900000	40.56800000	23.62900000
Zn	15.54600000	61.16000000	23.77700000
Zn	15.01500000	50.84000000	13.59600000
Zn	5.98900000	50.87300000	24.53300000
Zn	17.05800000	40.57100000	26.00600000
Zn	17.09800000	61.02500000	26.14100000
Zn	16.89900000	50.77300000	15.71100000
Zn	7.42400000	50.74200000	26.98200000
S	14.50500000	54.59600000	17.84500000
S	14.36200000	44.19500000	28.09400000
S	9.00700000	54.59500000	23.11700000
S	18.23600000	44.34400000	21.65600000
S	8.76400000	46.93700000	22.86200000
S	18.32300000	57.42400000	21.69700000
S	14.28400000	47.08300000	17.91100000
S	14.02900000	57.75900000	28.25800000
N	14.08500000	40.62100000	22.14800000
N	14.14300000	61.08800000	22.30700000
N	18.00900000	50.81300000	17.41200000
N	8.83100000	50.77200000	28.46900000
O	15.64300000	52.33700000	16.32600000
O	6.63300000	52.68800000	27.14300000
O	15.64700000	41.84800000	26.82900000
O	16.03900000	62.69100000	26.76900000
O	16.23500000	52.22100000	12.71700000
O	7.36900000	52.23700000	23.93700000
O	16.82400000	42.01800000	22.94700000
O	16.89400000	62.65800000	23.39800000
O	16.27100000	49.30000000	12.86900000
O	7.25800000	49.24000000	24.05300000
O	16.81600000	39.05400000	23.23100000
O	16.91500000	59.71300000	23.08600000
O	15.55700000	49.28900000	16.36500000
O	5.60500000	49.97900000	27.59400000
O	15.93600000	38.92700000	26.56300000
O	15.57900000	59.83400000	26.89600000
O	11.04400000	38.85100000	18.84400000
O	11.96600000	57.33000000	19.12100000
O	21.44600000	47.58700000	18.67400000
O	12.43500000	47.62100000	28.51100000
O	10.46500000	37.81800000	22.01800000
O	12.19200000	56.88800000	22.52100000
O	20.11600000	47.81700000	21.40900000
O	12.95200000	48.29900000	31.44600000
O	11.15800000	43.80100000	22.49900000
O	10.28800000	63.69600000	22.38800000
O	20.13700000	53.92300000	21.32500000

O	12.57200000	53.74900000	31.67000000
O	11.89900000	44.05900000	18.77700000
O	11.17100000	62.76100000	19.38500000
O	21.38400000	54.12000000	18.54700000
O	11.86700000	54.50100000	28.81100000
N	12.06500000	40.31700000	21.26400000
N	12.53500000	59.94100000	21.23900000
N	22.32200000	50.28800000	20.58800000
N	14.00100000	50.63400000	29.42300000
N	9.02000000	41.05400000	19.85100000
N	9.28700000	58.96500000	19.10000000
N	19.43700000	50.14300000	18.99300000
N	10.76500000	50.20800000	29.44700000
N	9.52900000	42.08600000	19.72900000
N	8.76100000	59.94500000	19.08600000
N	19.42600000	51.55400000	18.97200000
N	10.60800000	51.60500000	29.54900000
N	12.51300000	41.56900000	20.84400000
N	11.99200000	61.14200000	21.70100000
N	22.33000000	51.46100000	20.54600000
N	13.87800000	51.79300000	29.49500000
O	14.05400000	52.27100000	14.69600000
O	5.02700000	52.43700000	25.55100000
O	14.64400000	42.07100000	24.79800000
O	14.50800000	62.53700000	25.09400000
O	17.76200000	52.17700000	14.41700000
O	8.78000000	51.53200000	25.57600000
O	17.77700000	42.30100000	24.99300000
O	18.38100000	62.18100000	25.06100000
O	17.78500000	49.26700000	14.57100000
O	7.84000000	48.83000000	26.20600000
O	18.32400000	39.40700000	24.90900000
O	17.78300000	59.27100000	25.13700000
O	14.01900000	49.35700000	14.69200000
O	4.72900000	49.55800000	25.53300000
O	14.42200000	39.12900000	24.87800000
O	14.61800000	59.62100000	24.84800000
N	12.92500000	38.50600000	22.60500000
N	14.72800000	58.98900000	21.33600000
N	18.25900000	48.46400000	17.75700000
N	9.45600000	48.45600000	28.47800000
N	18.21700000	53.17400000	17.68100000
N	8.95000000	53.14800000	28.79900000
N	14.52600000	42.78900000	21.24500000
N	12.82700000	63.07400000	22.88000000
H	13.55800000	37.86200000	22.11600000
H	14.43400000	58.12000000	20.85000000
H	18.49800000	47.74300000	18.44100000
H	10.30000000	47.88100000	28.44300000
H	18.43900000	53.91800000	18.34200000

H	9.63600000	53.89900000	28.73300000
H	14.15100000	43.65200000	20.80200000
H	13.39900000	63.73600000	22.34400000
H	13.29600000	38.56700000	23.58000000
H	15.61400000	59.00300000	21.84900000
H	17.39600000	48.32600000	17.23000000
H	8.83500000	48.33900000	27.66000000
H	17.33300000	53.26600000	17.17600000
H	8.12000000	53.23800000	28.19900000
H	15.39100000	42.82900000	21.78600000
H	13.24200000	63.06000000	23.83400000
C	13.85600000	53.86000000	16.41200000
C	14.14200000	43.63200000	26.46800000
C	9.45700000	53.29800000	24.18100000
C	18.17900000	43.91300000	23.33700000
C	8.61300000	47.36400000	24.53800000
C	18.19800000	57.75100000	23.39800000
C	13.76700000	47.75800000	16.39500000
C	13.88700000	58.22600000	26.59200000
O	14.03900000	56.75200000	19.85300000
O	13.66000000	46.37700000	29.97900000
O	10.11100000	57.10700000	21.75500000
O	19.36700000	46.43700000	19.76000000
O	9.85500000	44.82700000	21.00700000
O	19.44900000	55.38400000	19.71900000
O	13.52900000	45.05500000	20.00600000
O	13.09600000	55.75800000	30.26300000
C	13.15900000	55.68600000	17.93500000
C	13.37400000	45.59000000	27.77300000
C	10.59600000	55.28600000	23.23500000
C	19.05100000	45.83100000	22.03800000
C	9.75300000	45.56700000	23.26000000
C	19.08600000	55.89400000	22.01700000
C	12.99800000	45.91800000	17.86400000
C	12.88200000	56.47400000	28.02300000
C	14.56700000	52.74300000	15.76200000
C	14.85600000	42.42400000	25.99900000
C	8.46900000	52.27500000	24.59100000
C	17.55100000	42.65300000	23.79100000
C	7.85000000	48.55900000	24.95100000
C	17.59000000	58.99900000	23.90900000
C	14.50000000	48.88000000	15.77300000
C	14.75200000	59.30800000	26.07000000
C	13.07700000	56.65200000	19.05100000
C	13.15300000	46.57800000	28.83500000
C	10.97700000	56.48600000	22.48200000
C	19.52300000	46.74300000	20.98600000
C	10.27800000	44.69200000	22.19800000
C	19.57300000	55.02500000	20.93200000
C	12.81800000	44.95300000	18.96900000

C	12.60000000	55.53800000	29.11600000
C	13.02600000	39.79600000	22.01700000
C	13.84200000	59.94100000	21.61900000
C	18.56100000	49.74800000	18.05300000
C	9.68700000	49.75900000	28.78200000
C	18.54400000	51.90500000	18.02000000
C	9.45300000	51.89600000	28.92300000
C	13.73900000	41.72700000	21.40700000
C	12.97900000	61.78100000	22.31400000
C	12.25200000	55.47100000	16.90700000
C	12.90400000	45.60300000	26.46400000
C	11.43200000	54.51700000	24.03700000
C	19.25300000	45.97600000	23.40600000
C	9.94800000	45.44900000	24.62600000
C	19.21400000	55.65800000	23.38100000
C	12.20900000	46.06100000	16.73200000
C	12.41300000	56.43500000	26.71500000
H	10.53700000	44.64100000	25.05800000
C	12.65400000	54.44100000	16.03300000
C	13.33400000	44.48200000	25.72200000
C	10.78000000	53.40000000	24.59000000
C	18.76300000	44.88200000	24.14200000
C	9.29600000	46.46800000	25.35300000
C	18.71800000	56.71600000	24.16400000
C	12.64500000	47.10900000	15.89800000
C	12.98100000	57.43400000	25.89800000
H	12.81500000	54.67700000	31.21700000
H	11.82000000	53.90900000	32.26400000
H	13.27800000	47.41400000	30.97800000
H	12.19200000	48.06900000	32.00700000
C	14.97600000	63.02200000	26.17500000
C	17.99600000	62.78300000	24.01200000
H	18.71500000	63.51100000	23.58300000
H	14.37500000	63.82200000	26.65600000
H	11.81100000	62.04500000	19.21700000
H	10.61600000	62.80300000	18.58600000
H	11.25600000	63.55600000	22.71200000
H	9.72400000	63.70000000	23.18100000
C	17.30500000	52.57300000	13.30600000
H	17.91900000	53.32800000	12.77000000
C	17.31700000	48.88700000	13.46000000
H	17.89400000	48.09400000	12.93600000
O	13.70900000	50.17900000	11.99100000
H	14.34700000	49.59000000	11.54300000
H	13.15400000	49.57200000	12.52000000
H	11.79300000	39.46600000	18.72500000
H	10.43100000	39.05300000	18.11400000
H	11.43200000	37.99400000	22.39300000
H	9.86000000	37.77800000	22.77900000
C	5.58300000	53.04200000	26.50700000

C	4.75000000	49.48500000	26.80200000
H	5.11000000	53.99100000	26.83800000
H	3.92000000	48.91800000	27.27200000
O	4.90200000	50.29600000	22.76500000
H	5.53600000	49.67500000	22.35500000
H	4.21800000	49.72000000	23.15900000
O	18.27000000	60.25100000	27.77400000
H	18.78100000	59.57000000	27.29400000
H	17.57600000	59.74800000	28.24300000
C	14.88800000	38.60200000	25.94100000
C	17.91900000	38.87300000	23.83200000
H	14.30300000	37.75900000	26.36800000
H	18.61700000	38.15200000	23.35700000
O	18.33500000	41.22600000	27.60900000
H	18.92900000	41.83000000	27.12300000
H	17.70900000	41.82200000	28.06800000
H	22.24600000	54.52700000	18.73700000
H	20.67000000	54.78800000	18.85200000
H	22.27400000	47.15400000	18.94200000
H	20.69600000	46.94900000	18.92300000
H	18.71400000	56.74700000	25.25300000
H	19.66400000	54.74100000	23.75900000
H	11.33300000	56.05000000	16.82500000
H	12.10300000	54.09400000	15.15900000
H	12.17800000	47.41000000	14.96100000
H	11.34800000	45.41800000	16.55500000
H	18.81000000	44.77800000	25.22500000
H	19.74600000	46.85400000	23.82000000
H	9.30500000	46.55100000	26.43900000
H	12.28300000	46.40800000	26.07200000
H	13.07500000	44.28000000	24.68200000
H	12.78300000	57.55600000	24.83200000
H	11.69800000	55.68600000	26.37900000
H	12.47600000	54.77900000	24.19800000
H	11.23000000	52.66500000	25.25600000
C	14.00300000	46.14500000	22.63200000
O	15.01800000	45.55100000	22.66100000
O	12.99500000	46.74800000	22.63800000
C	14.61200000	55.25900000	22.21000000
O	15.22000000	56.15800000	22.66400000
O	14.03100000	54.33000000	21.78700000

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