

Supporting Information

Amine decorated MOF for Direct Capture of CO₂ from Ambient Air

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Experimental Section

Materials and Measurements

All chemicals were of reagent grade quality and used directly from the commercial vendors (Sigma-Aldrich, Alfa Aesar, and TCI). S. D. Fine Chemicals (India) was the source for all solvents. Prior to their use, these solvents were purified using industry standards. The details of spectroscopic techniques and X-ray structural studies are provided in the Supporting Information.

Physical measurements

The subsequent Data from spectroscopy were gathered. Infrared spectra were obtained using a Perkin-Elmer model 1320 spectrometer (KBr disc, 400–4000 cm^{-1}). Using a "XPERT-3 Panalytical Diffractometer system" with nickel-filtered Cu K ($\lambda = 1.5418$ Å) radiation at 298 K, powder X-ray diffraction (PXRD) patterns were recorded. 45 kV and 40 mA, respectively, were the tube voltage and current, respectively. A Perkin-Elmer Series II, elemental analyzer model 2400 was used to perform microanalyses of all the compounds. Thermogravimetric analysis (TGA) was carried out using "SDT Q 600 TA Instruments" at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in a nitrogen environment. Using Me₄Si as the internal standard, ¹H NMR measurements were taken in CDCl₃ on a JEOL ECX 500 FT (500, 125 MHz) or a JEOL ECS 400 FT (400, 100 MHz) instrument.

X-Ray Structural Studies

Crystal data was acquired using a Bruker SMART CCD diffractometer (Mo K radiation, $\lambda = 0.71073$ Å). SMART¹ was used to collect data frames, index reflections, and calculate lattice parameters; SAINT² was used to integrate the intensity of reflections and scale them; SADABS² was used to correct for absorption; and SHELXTL³ was used to determine the space group and structure as well as perform least-squares refinements on F₂. The SHELXL-2014⁴ programme in Olex-2 software⁵ was used to solve and refine the crystal structure using full-matrix least-squares methods versus F₂. Anisotropic displacement parameters were used for a final refinement of all atoms outside of hydrogen. Calculated positions were locked in for the hydrogen and refined isotropically. Due to the presence of disorder, a satisfactory model of the solvent molecule was not possible. So, the "Solvent mask" instruction of Olex2 has been executed to get rid of the solvent molecules that are in disarray. The following crystallographic data has been submitted to the

Cambridge Crystallographic Data Center (CCDC): 2260842. Tabulated in Table S1 and S2 are selected bond distances and bond angles, as well as a summary of the lattice characteristics of the compound, data collecting settings, and refinement parameters.

Table S1. Crystal and Structure Refinement Data for 1.

| Parameters | 1 |
|--|--|
| Empirical formula | C ₂₄ H ₂₅ N ₅ O ₄ Zn |
| Formula wt | 512.86 |
| Crystal system | Orthorhombic |
| Space group | <i>P6₃/mmc</i> |
| <i>a</i> , Å | 34.992(5) |
| <i>b</i> , Å | 17.836(5) |
| <i>c</i> , Å | 21.716(5) |
| α (deg) | 90 |
| β (deg) | 90 |
| γ (deg) | 90 |
| <i>V</i> , Å ³ | 13553(5) |
| <i>Z</i> | 16 |
| ρ_{calc} g/cm ³ | 1.005 |
| μ , mm ⁻¹ | 0.753 |
| F(000) | 4256 |
| reflns collected | 82395 |
| Independent reflns. | 6425 |
| GOOF | 1.033 |
| Final R indices [<i>I</i> > 2 σ (<i>I</i>)] | R1 = 0.0948 wR2 = 0.2696 |
| R indices (all data) | R1 = 0.1525 wR2 = 0.3174 |

Table S2. Selected bond distances (Å) and bond angles (°) in 1.

| | | | | | | | |
|--------|----------|--------|----------|---------|----------|---------|----------|
| Zn1 N4 | 2.039(6) | Zn1 N5 | 2.034(6) | Zn1 O1A | 1.957(5) | Zn1 O1B | 1.950(5) |
|--------|----------|--------|----------|---------|----------|---------|----------|

| | | | | | |
|------------|----------|------------|----------|-------------|----------|
| N4 Zn1 N5 | 103.4(2) | O1A Zn1 N4 | 105.0(2) | O1A Zn1 N5 | 97.4(2) |
| O1B Zn1 N4 | 124.5(2) | O1B Zn1 N5 | 113.3(2) | O1B Zn1 O1A | 109.7(3) |

Synthesis of 1,4-bis(4-pyridinylmethyl)piperazine(bpmp)

The ligand 1,4-bis(4-pyridinylmethyl)piperazine (bpmp) was synthesized using earlier reported⁶.

Synthesis of $\{[\text{Zn}(\text{TPA})_{0.5}(\text{NH}_2\text{TPA})_{0.5}]\cdot\text{DMF}\cdot 7\text{H}_2\text{O}\}_n$

A mixture of TPA (20 mg, 0.12 mmol), NH₂-TPA (20 mg, 0.11 mmol), bpmp (20 mg, 0.15 mmol), and Zn(NO₃)₂·6H₂O (44.6 mg, 0.15 mmol) was prepared in a 10 mL glass vial containing 4 mL of DMF and 2ml of water . The vial was then heated at 90 °C for 72 hours. The resulting product was a colorless block-shaped crystals. These crystals were harvested, washed repeatedly with DMF, rinsed with acetone, and air-dried, resulting in a high yield of 80% (based on the ligand). Anal. Calcd for C₂₇ H₄₆ N₆ O₁₂ Zn: C, 45.54; H, 6.51; N, 11.8%. Found: C, 44.94; H, 6.21; N, 11.69%. IR (cm⁻¹): 3349 (broad), 3130 (s), 1675 (s), 1613 (s), 1493 (s), 1363(s), 1238 (m), 1085 (s), 955 (s), 829 (s), 758 (s), 672 (s) (Figure S1).

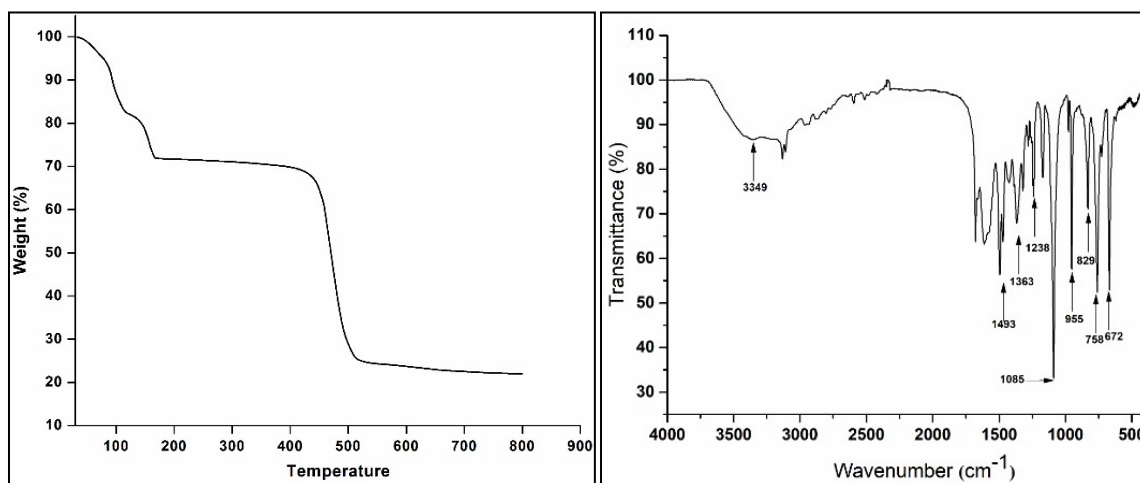


Fig. S1. TGA curve and IR spectrum of 1.

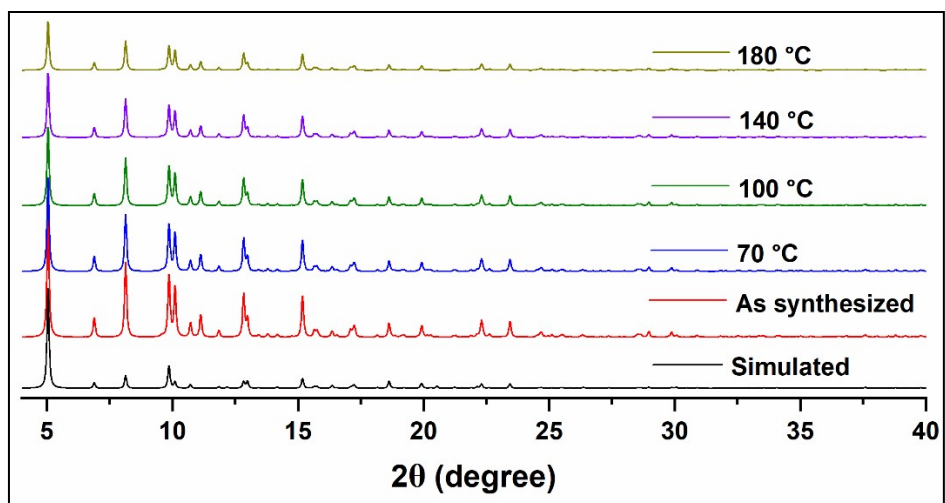


Fig. S2. VTPXRD patterns of **1**.

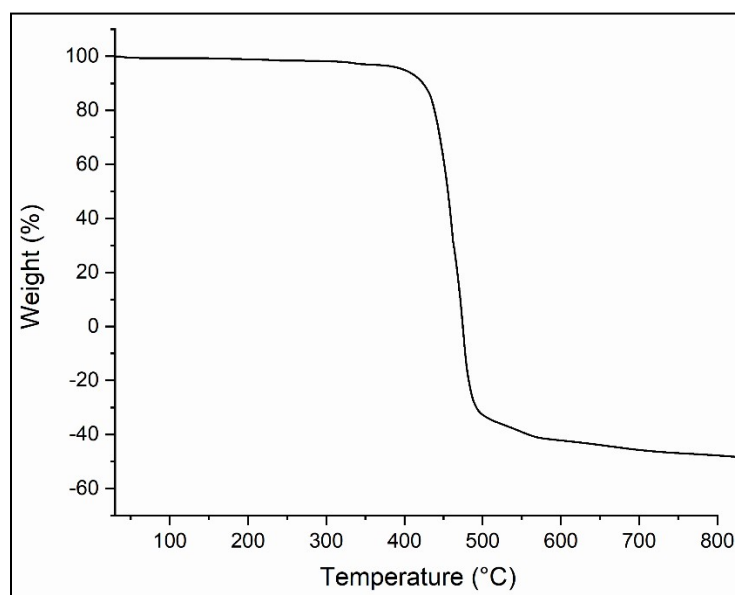


Fig. S3. TGA curve activated **1 (1')**.

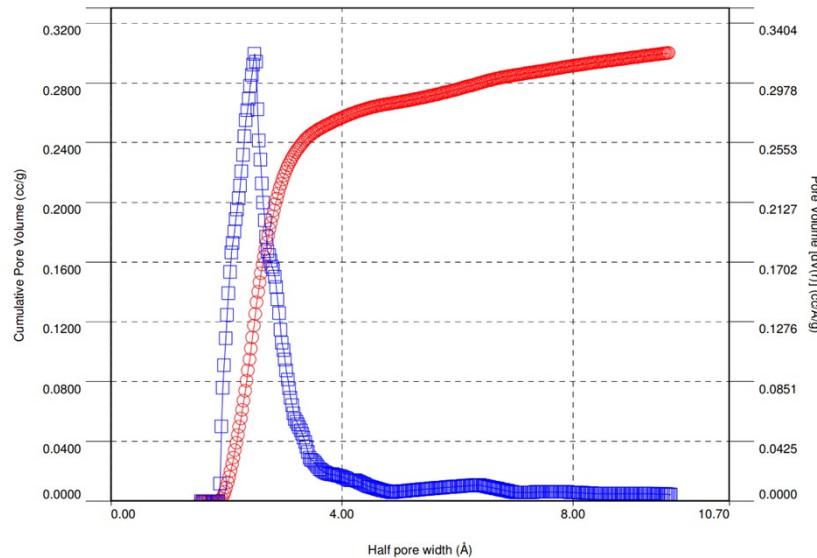


Fig. S4. Pore size distribution in **1'**.

Calculations for Determining Solvents Squeezed Out.

Number of electrons Squeezed out = 1689, therefore, no. of electrons in the formula unit = $1689/z = 1689/16/6 = 105.56$.

The number of electrons in (1 DMF) + (7 H₂O) = (1 × 40) + (7 × 10) = 110 which is in good agreement with the electrons counts calculated (105.56).

TGA analysis:

1DMF (lattice) + 7H₂O (lattice) = (73.09 + 126.07) = 199.16

% weight loss = $(199.16/712.04) \times 100 = 27.97\%$, which is in good agreement with the experimental (27%).

Calculation of Isothermic Heat of CO₂ Adsorption (q_{st})

The process to calculate heat of CO₂ adsorption from Clausius-Clapeyron equation is as follows. Two different adsorption isotherms that were measured at different temperatures T_1 (283K) and T_2 (303K) are needed for the analysis. q_{st} at an adsorption amount can be calculated from the equation below with the difference between the two different pressures (p_1 and p_2) at the same adsorption amount.

Where R is the universal gas constant.

$$q_{st} = \frac{RT_1T_2}{T_2 - T_1} (\ln p_2 - \ln p_1)$$

Ideal Adsorption Solution Theory (IAST):

IAST calculations were employed as described by Prausnitz et al.⁶ The equation that is involved in selectivity calculations has been given below.

$$S_{1,2} = \frac{q_1/q_2}{p_1/p_2}$$

IAST fitting parameters:

Table S3: Parameters for the IAST fitting for CO₂/N₂ at 303 K.

| Constants | Gas A | Gas B |
|-----------|-------------|-------------|
| qA1 | 4.838152821 | 3.901716611 |
| qA2 | 0 | 0 |
| kA1 | 0.000510641 | 3.33582E-06 |
| kA2 | 0 | 0 |
| nA1 | 1.003276328 | 1.221863808 |
| nA2 | 0 | 0 |
| HA1 | 0.002470561 | 1.30154E-05 |
| HA3 | 0 | 0 |

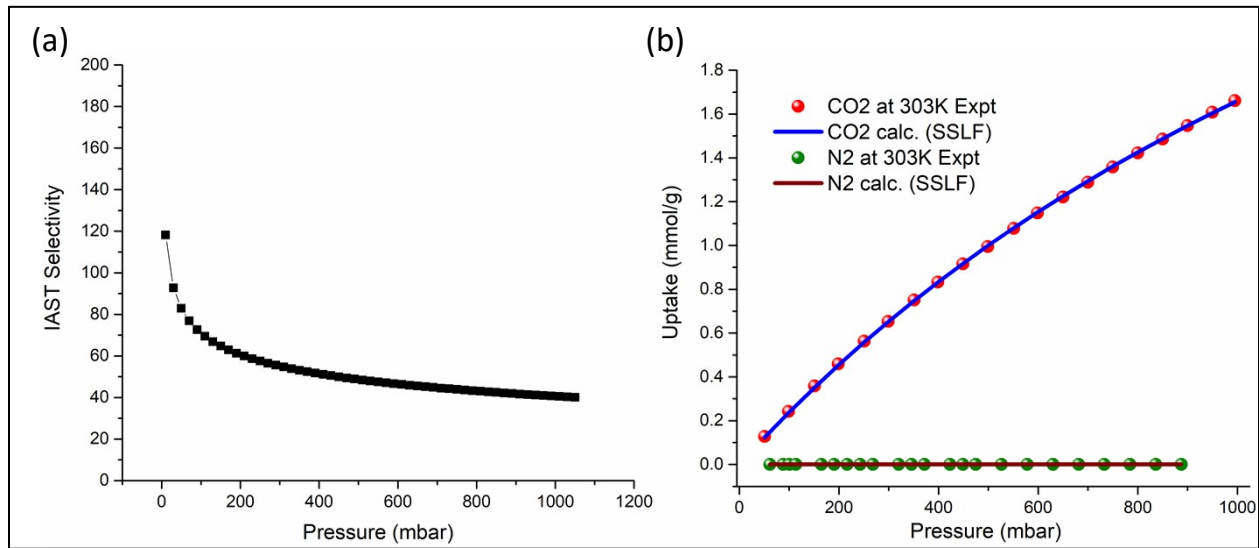


Fig. S5. IAST selectivity for CO₂/N₂ (a) analyses and (b) fitting curves at 303 K.

$$V(r)_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \dots\dots\dots(S1)$$

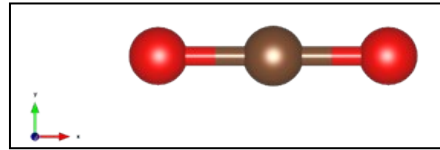


Fig. S6. CO₂ molecule modelled by TraPPE forcefield. Red Oxygen and Brown Carbon.

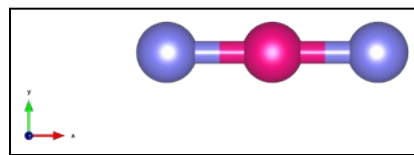


Fig. S7. N₂ molecule modelled by TraPPE forcefield. Purple Nitrogen and pink pseudo atom.

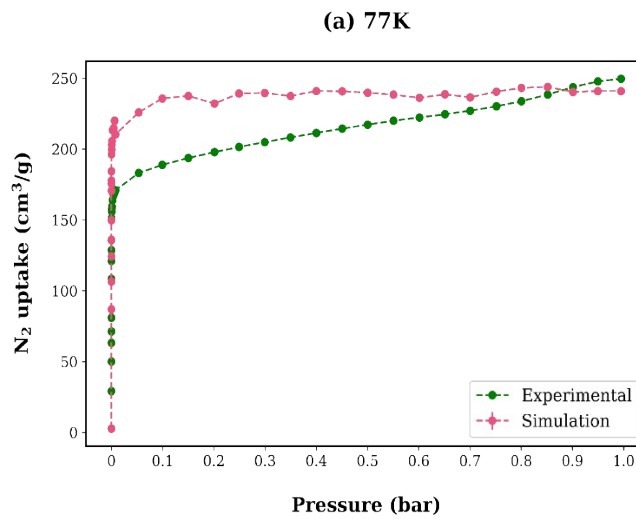


Fig. S8. Experimental and Simulation Isotherm for N₂ at 77 K.

Table S4. The Lennard Jones parameters of the framework atoms, as extracted from the UFF⁷ forcefield.

| Atom | ϵ (K) | σ (Å) |
|------|----------------|--------------|
| C | 52.8384 | 3.431 |
| H | 22.1418 | 2.5711 |
| N | 34.7224 | 3.2607 |

| | | |
|----|---------|--------|
| O | 30.1934 | 3.1182 |
| Zn | 62.3996 | 2.4616 |

Table S5. The Lennard Jones parameters of Nitrogen molecule, as extracted from the TraPPE⁸ forcefield.

| Atom | ϵ (K) | σ (Å) | q (e) |
|------------|----------------|--------------|--------|
| N | 36.0 | 3.310 | -0.482 |
| M (pseudo) | 0.00 | 0.000 | 0.964 |
| N | 36.0 | 3.310 | -0.482 |

Table S6. The Lennard Jones parameters of Carbon dioxide molecule, as extracted from the TraPPE⁹ forcefield.

| Atom | ϵ (K) | σ (Å) | q (e) |
|------|----------------|--------------|--------|
| C | 27.0 | 2.800 | 0.700 |
| O | 79.0 | 3.050 | -0.350 |

Table S7. Void fraction calculation via experiments and various simulation methodologies.

| Void fraction calculation methodology | Void fraction |
|---------------------------------------|---------------|
| Experimental | 0.384 |
| Zeo++ | 0.555 |
| Helium Void fraction | 0.444 |

General Procedure for the Cycloaddition of CO₂ to Epoxides

Epoxide (20 mmol), catalyst **1'** (0.005 mmol as per molecular weight of MOF **1**) and co-catalyst TBAB (1 mmol) were added to an RB that had a septum on top of it. Using an air pump, laboratory air was purge by syringe. After that, the reaction mixture was stirred for 24 hours at room temperature. 5 mL of CH₂Cl₂ was added once the reaction was finished, and the mixture was filtered to remove the catalyst. By using silica gel column chromatography, all cyclic carbonates were purified, and ¹H NMR spectroscopy was used to identify them.

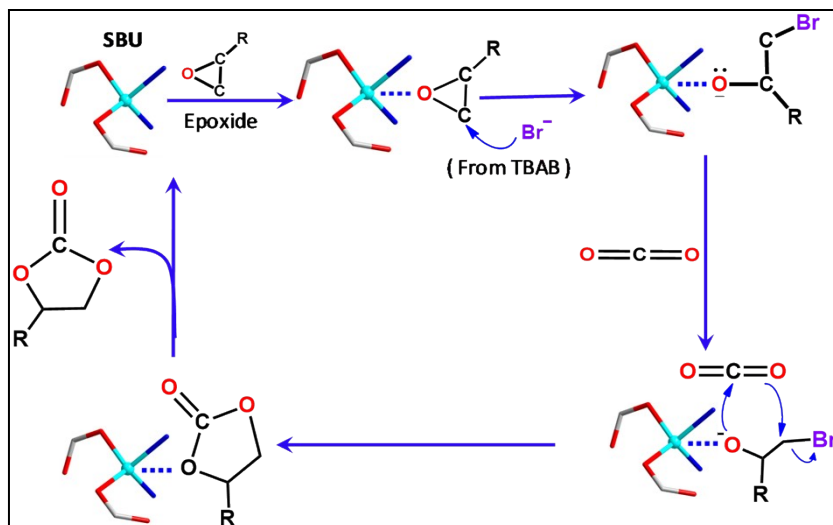


Fig. S9. Proposed mechanism for **1** catalyzed cycloaddition of CO₂ to epoxide in presence of TBAB.

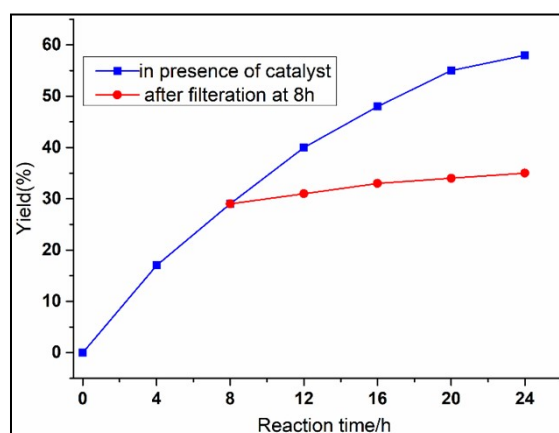


Fig. S10. Evidence of heterogeneous nature of catalysis in the coupling of epoxycyclohydrin with CO₂.

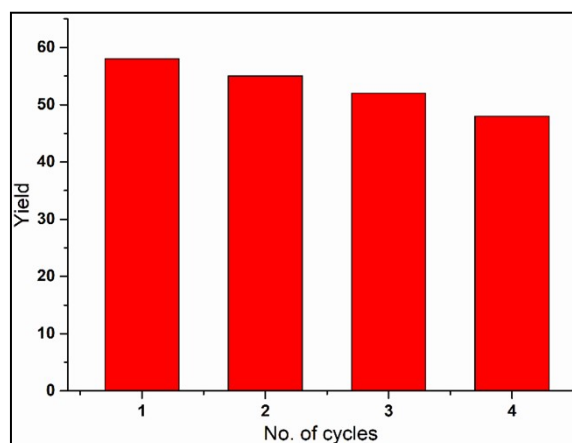


Fig. S11. Recyclability study (four cycles) for catalytic activity of **1** in Coupling of epoxycyclohydrin with CO₂.

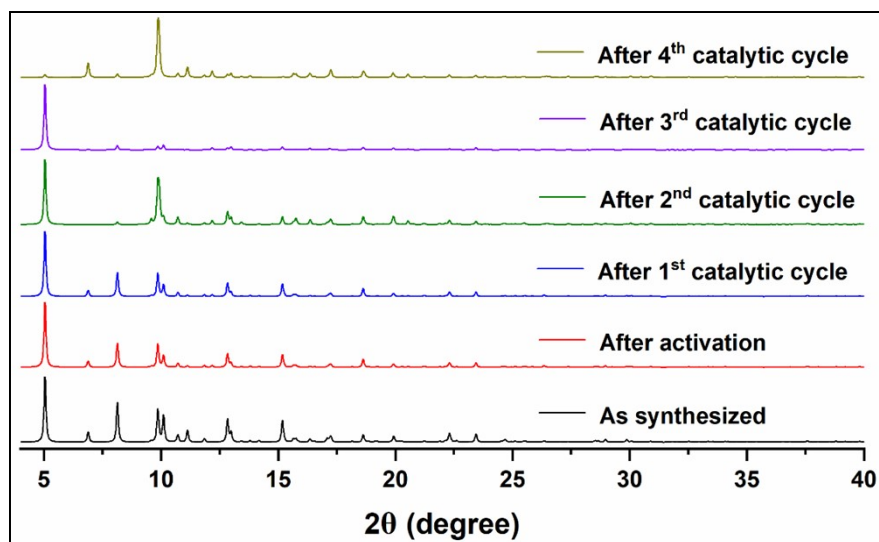


Fig. S12. PXRD patterns of As-synthesized, after activation and after 1st to 4th catalytic cycle of **1'** the Coupling of Epoxides with CO₂.

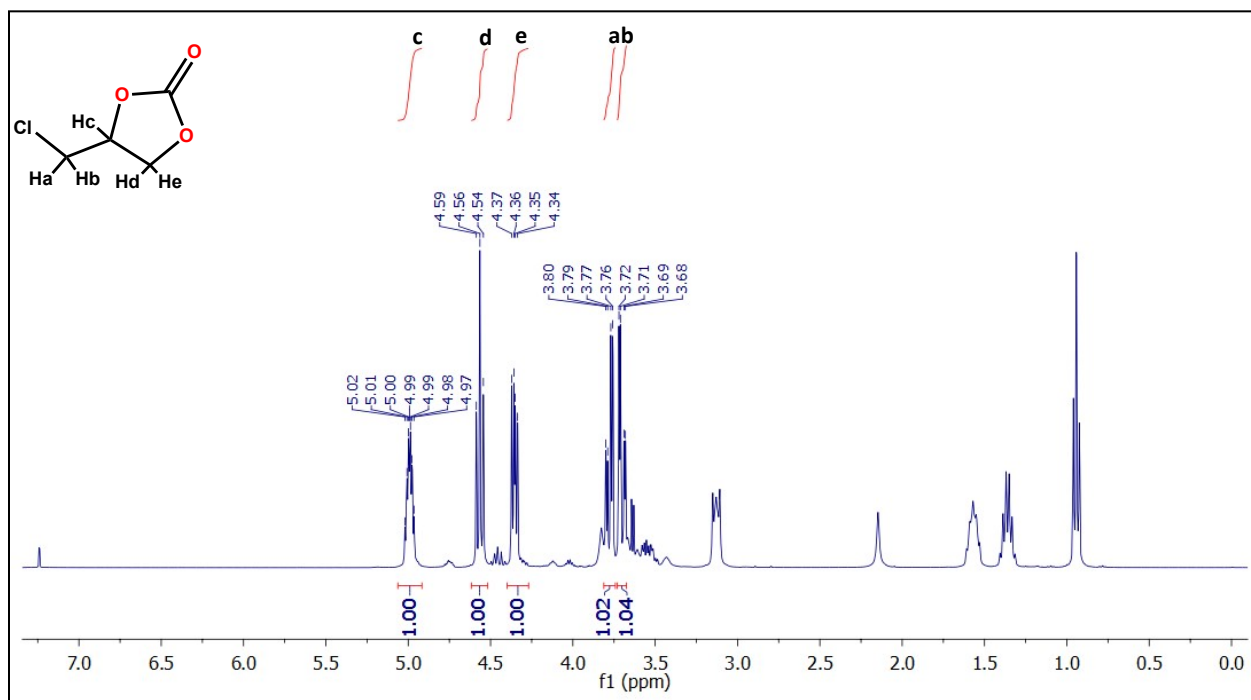


Fig. S13. ¹H NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one in CDCl₃ (Table 1, entry 1). ¹H NMR (500 MHz, CDCl₃): δ 5.02–4.97 (m, 1Hc), 4.56 (t, 1Hd), 4.35 (q, 1He), 3.89 (dd, 1Ha), 3.77 (m, 1Hb).

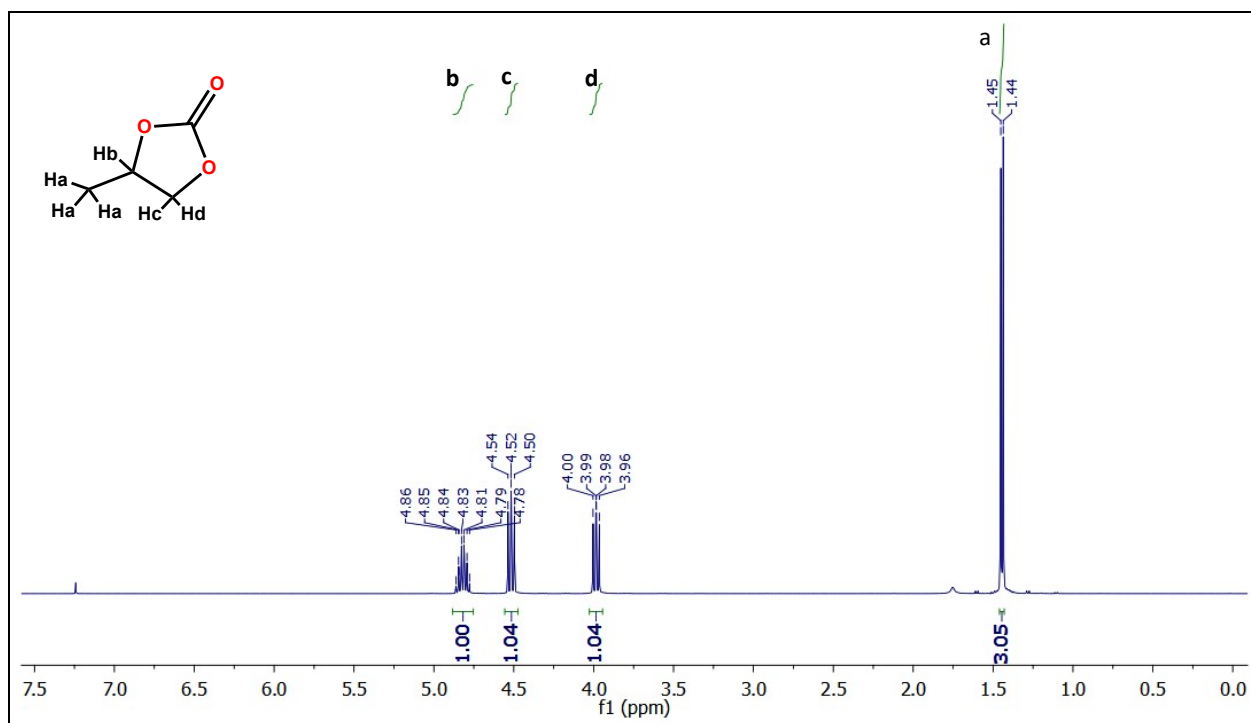


Fig. S14. ^1H NMR spectrum of 4-ethyl-1,3-dioxolan-2-one in CDCl_3 (Table 1, entry 2). ^1H NMR (500 MHz, CDCl_3): δ 4.86–4.78 (m, 1Hb), 4.54–4.50 (m, 1Hc), 4.00–3.96 (m, 1Hd), 1.44 (d, 3a).

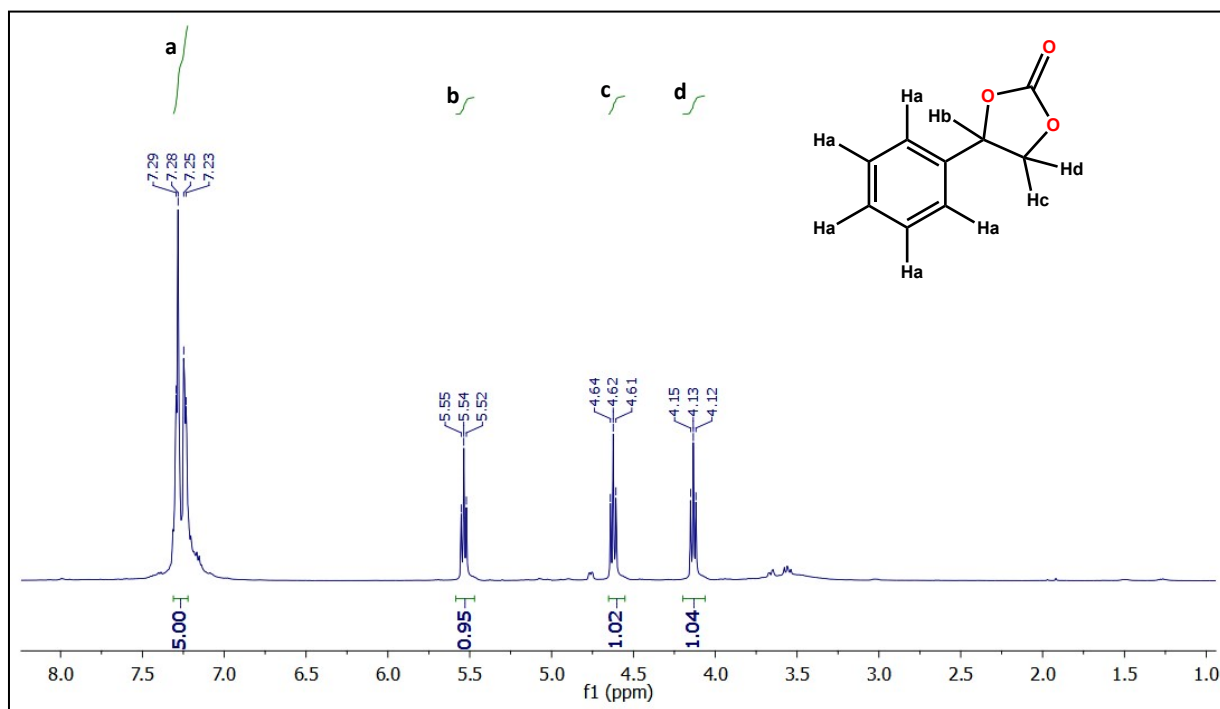


Fig. S15. ^1H NMR spectrum 4-phenyl-1,3-dioxolan-2-one in CDCl_3 (Table 1, entry 3). ^1H NMR (500 MHz, CDCl_3): δ 7.23–7.29 (m, 5Ha), 5.54 (t, 1Hb), 4.62 (t, 1Hc), 4.13 (t, 1Hd).

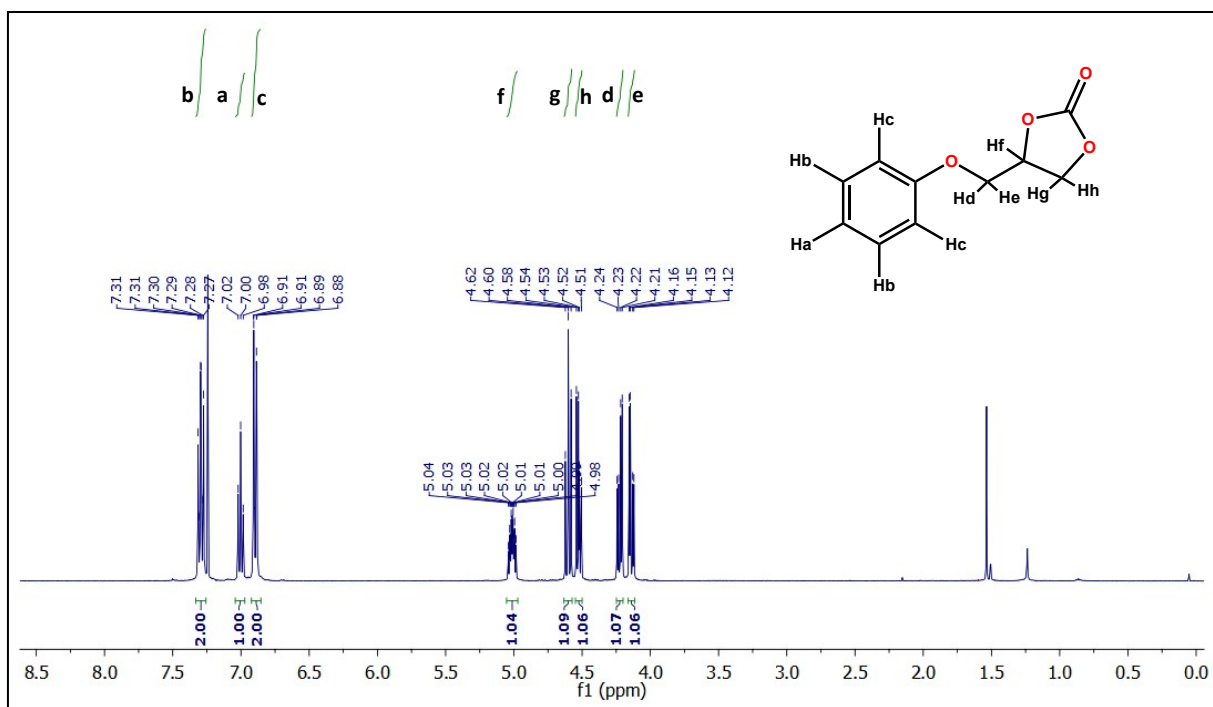


Fig. S16. ^1H NMR spectrum of 4-(phoxymethyl)-1,3-dioxolan-2-one in CDCl_3 (Table 1, entry 4). ^1H NMR (500 MHz, CDCl_3): δ 7.31- 7.27(m, 2Hb), 7.00 (t, 1Ha), 6.91-6.91 (m, 2Hc), 5.04-4.98 (m, 1Hf), 4.60 (t, 1Hg), 4.52 (q, 1Hh, OCH₂), 4.22 (q, 1Hd), 4.13 (q, 1He).

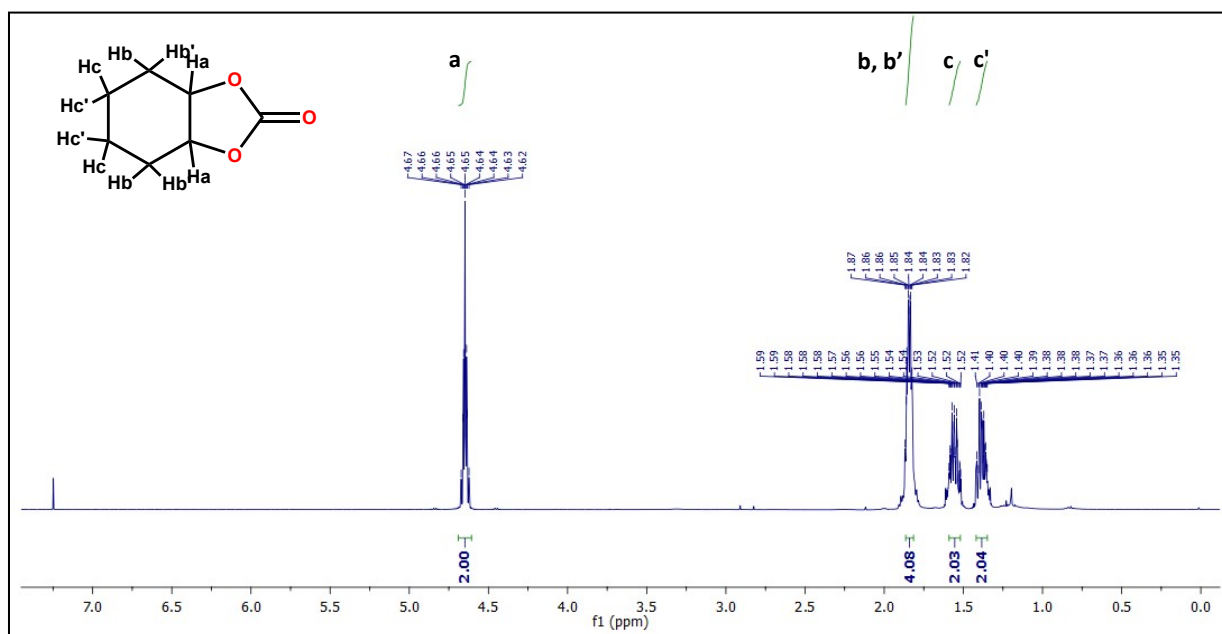


Fig. S17. ^1H NMR spectrum of hexahydrobenzo[d][1,3]dioxol-2-one in CDCl_3 (Table 1, entry 5). ^1H NMR (500 MHz, CDCl_3): δ 4.67-4.62 (m, 2H, Ha), 1.87-1.82 (m, 4Hb\&b'), 1.59-1.52 (m, 2Hc), 1.41-1.35 (m, 2Hc').

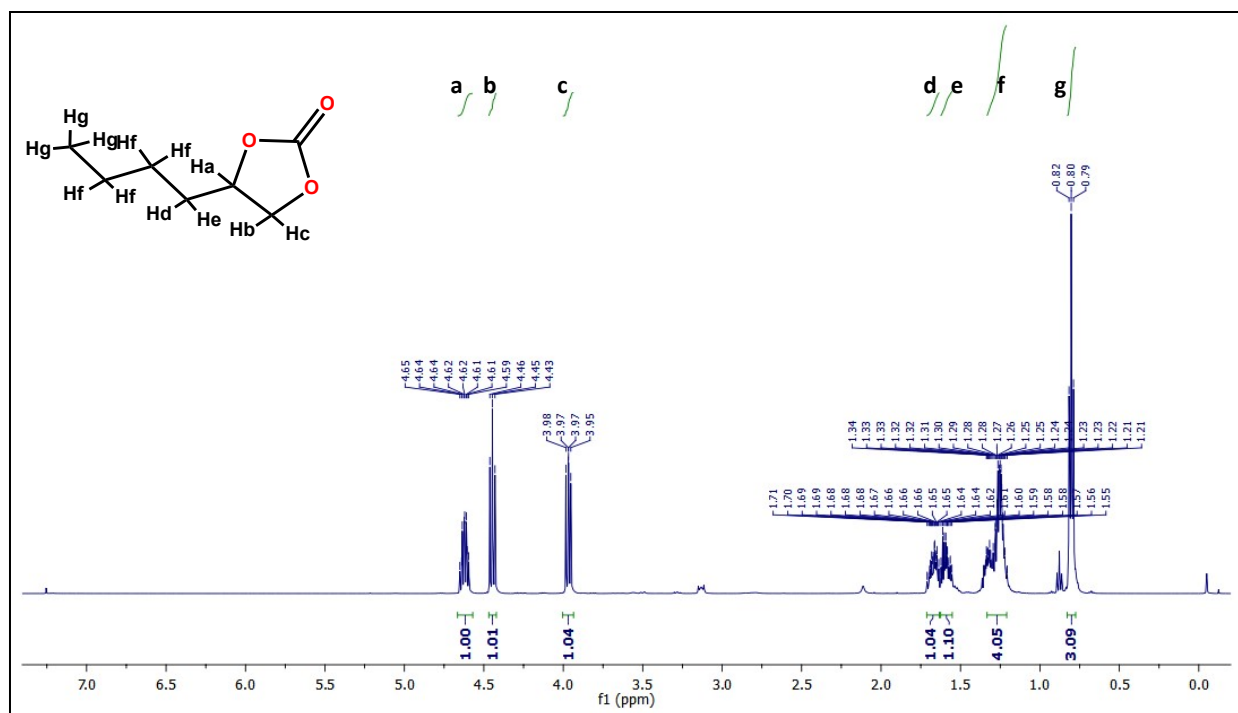


Fig. S18. ¹H NMR spectrum of 4-butyl-1,3-dioxolan-2-one in CDCl₃ (Table 1, entry 5). ¹H NMR (500 MHz, CDCl₃): δ 4.65–4.59 (m, 1Ha), 4.46–4.43 (m, 1Hb), 3.98–3.95 (m, 1Hc), 1.70–1.64 (m, 1Hd), 1.62–1.55 (m, 1He), 1.34–1.21 (m, 4Hf), 0.80 (t, 3Hg).

Calculation of TON and TOF:

Amount of catalyst **1** as per molecular weight (512.86) of activated MOF **1**: 2.56 mg, 0.005 mmol

Amount of epoxide : 20 mmol

Reaction time: 24 hours

| Entry | Epoxide | Product | Conversion % | TON mmol of cyclic carbonate mmol of catalyst used. | TOF ^h TOF 24 |
|-------|---------|---------|--------------|---|-------------------------------|
| 1 | | | 51 | 10.2/0.005 = 2040 | 2040/24 = 85 |
| 2 | | | 43 | 8.6/0.005 = 1720 | 1720/24 = 71.66 |
| 3 | | | 35 | 7/0.005 = 1400 | 1400/24 = 58.33 |
| 4 | | | 20 | 4/0.005 = 800 | 800/24 = 33.33 |
| 5 | | | 38 | 7.6/0.005 = 1520 | 1520/24 = 63.33 |
| 6 | | | 25 | 5/0.005 = 1000 | 1000/24 = 41.66 |

References

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