Supplementary Information

Efficient Catalytic Conversion of Terminal/ Internal Epoxides to Cyclic Carbonates by Porous Co(II) MOF at Ambient Conditions:

Structure Property Correlation and Computational Studies

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S1. EXPERIMENTAL AND CHARACTERIZATION SECTION

Materials and General Methods

All reagents and solvents were purchased from commercial sources and were used without further purification. N-donor, (*E*)-N'-(pyridin-4-ylmethylene) isonicotinohydrazide (**L**) was synthesized according to our previous report.^{S1} Distilled water was used for synthetic manipulations. CHNS analyses were done using elementar vario MICRO CUBE analyzer. IR spectra were recorded using KBr pellet method on a Perkin–Elmer GX FTIR spectrometer. For each IR spectra 10 scans were recorded at 4 cm⁻¹ resolution. ¹H & ¹³C NMR spectra for the ligand and cyclic bicarbonate derivatives were recorded on JEOL, JNM-ECZ 600R (600 MHz) spectrometer at

temperature 25 °C and was calibrated with respect to internal reference TMS. TGA analysis was carried out using Mettler Toledo Star SW 8.10. TG analysis was performed in nitrogen environment while the heating rate was ramped from room temperature to 600 °C at 10°C/min. Powder X-ray diffraction (PXRD) and variable temperature XRD (VT-XRD) data were collected using a PANalytical Empyrean (PIXcel 3D detector) system with CuK_α radiation. Single crystal structures were determined using BRUKER SMART APEX (CCD) diffractometer. N₂ and CO₂ adsorption-desorption isotherm and BET surface area was measured on a Micromeritics, 3 Flex instrument. Solid state UV–Vis spectra were recorded using Shimadzu UV-3101PC spectrometer and BaSO₄ as a reference. Field Emission-Scanning Electron Microscopy (FE-SEM) micrographs were recorded using a JEOL JSM-7100F instrument employing an 15-kV accelerating voltage.

Hydrothermal Synthesis of {[Co(OBA)(L)].xG}_n (CoMOF-1): H₂OBA (26 mg, 0.1 mmol), L (23 mg, 0.1 mmol) and Co(NO₃)₂.6H₂O (30 mg, 0.1 mmol) were dispersed in 6 mL H₂O:MeOH:EtOH:DMF (2:2:1:1) and then sealed in 14 mL Teflon-lined autoclave, which was heated at 90 °C for 72 h. After slow cooling to room temperature for 5 °C / 2 h, red plates shaped crystals were obtained. Yield *ca*. 68%. Elemental analysis (%) C₃₅H₄₈N₆O₁₃Co, calc.: C, 51.28; H, 5.90; N, 10.25; found: C, 52.56; H, 6.12; N, 9.56. FTIR cm⁻¹ (KBr): 3432 (br), 1684 (w), 1596 (s), 1560 (s), 1535 (w), 1496 (w), 1418 (s), 1281 (w), 1252 (s), 1163 (m), 1142 (w), 1100 (w), 1067 (w), 1016 (w), 940 (w), 924 (w), 882 (w), 783 (m), 696 (w), 659 (w), 539 (w).

Conventional (reflux) synthesis of CoMOF-1: Bulk materials of **CoMOF-1** was synthesized *via* conventional reflux method. 10 mmol of $Co(NO_3)_2.6H_2O$, 10 mmol H_2OBA , 20 mmol NaOH and 10 mmol **L** in 100 mL $H_2O:MeOH:EtOH:DMF$ (5:4:0.5:0.5/v:v) solvent were refluxed in a 200 mL round bottom flask at *ca* 100 °C for 8 h. The resulting baby pink colour precipitates were filtered

and washed with H₂O:MeOH (1:1/v:v) followed by acetone then dried at 100 °C in oven. Yield *ca.* 89%. For **CoMOF-1**: Elemental analysis (%) calc.: C, 51.28; H, 5.90; N, 10.25; found: C, 51.57; H, 5.83; N, 10.50. FTIR cm⁻¹ (KBr): 3437 (br), 1686 (w), 1598 (s), 1562 (s), 1533 (w), 1502 (w), 1413 (s), 1284 (w), 1252 (s), 1162 (m), 1144 (w), 1102 (w), 1069 (w), 1016 (w), 942 (w), 924 (w), 883 (w), 784 (m), 696 (w), 660 (w), 539 (w).

Activation of CoMOF-1: The activated CoMOF-1 (CoMOF-1') was prepared via solvent exchange of reaction solvent with DCM for 48 h, followed by heating at 150 °C for 24 h in oven. The PXRD data of the activated material well matched with the simulated generated from the SCXRD data and confirmed phase purity as well as crystallinity of CoMOF-1 after activation. For CoMOF-1': Elemental analysis (%) calc.: C, 57.68; H, 3.35; N, 10.35; found: C, 55.93; H, 3.43; N, 10.03. FTIR cm⁻¹ (KBr): 3438 (br), 1697 (w), 1597 (s), 1561 (m), 1534 (w), 1500 (w), 1411 (s), 1282 (m), 1248 (s), 1162 (m), 1143 (w), 1101 (w), 1069 (w), 1015 (w), 940 (w), 924 (w), 881 (w), 784 (m), 696 (m), 659 (w), 538 (w).

General Procedure for the Cycloaddition of CO₂ and Epoxide

Terminal Epoxide: Cycloaddition of terminal epoxide subtracts and CO₂ was performed in a 5-mL Glass tube equipped with a magnetic stirrer. For each reaction, terminal epoxide (8.7 mmol) and the **CoMOF-1'** (1.8 mol%) and co-catalyst TBAB (or TBAI, KI; 2.5 mol%), wherever applicable were introduced into the Glass tube without solvent. The Glass tube was then pressurized with CO₂ 1 atm at room temperature. The reaction mixture was then heated to the desired temperature (RT/ 40/ 60 $^{\circ}$ C), and stirring was set at 600 rpm. When the reaction time was elapsed, cycloaddition was stopped and cooled to RT. The reaction mixture was centrifuged to separate the catalyst, 2 times washing with ethyl acetate and the products were isolated (in ethyl acetate)

and identified with a gas chromatograph using dodecane as an internal standard (Bruker 450-GC; equipped with a capillary column HP-5, 30m × 0.25 mm; using a flame ionization detector).

Internal Epoxide: Synthesis of cyclic carbonate from internal epoxide and CO₂ was performed in 25-mL stainless-steel autoclave reactor with a magnetic stirrer. For each reaction batch, internal epoxide (20 mmol) and **CoMOF-1'** (2.8 mol%) and co-catalyst TBAB (or TBAI, KI; 5 mol%), wherever applicable were introduced the reactor without solvent. The autoclave reactor was then pressurized with CO₂ to pre-set pressure at room temperature. The reaction mixture was then heated to the desired temperature, and stirring was set at 600 rpm. When the reaction time was elapsed, cycloaddition was stopped and cooled to RT. The reaction mixture was centrifuged to separate the catalyst, 2 times washing with ethyl acetate and the products were isolated (in ethyl acetate) and identified with a gas chromatograph using dodecane as an internal standard (Bruker 450-GC; equipped with a capillary column HP-5, 30m × 0.25 mm; using a flame ionization detector).

Catalyst Recyclability

After each catalytic reaction, **CoMOF-1'** catalyst were recovered by centrifugation, then washed with water, acetone and dried in vacuum at 150 °C for the next catalytic reaction under the same reaction conditions up to 6 recycle. Chemical stability of recovered catalyst analysed by PXRD, FTIR and FE-SEM analysis technique. For **CoMOF-1'** (Terminal epoxide): FTIR cm⁻¹ (KBr): 3443 (br), 1686 (w), 1598 (s), 1561 (m), 1531 (w), 1501 (w), 1420 (s), 1286 (m), 1252 (s), 1164 (m), 1145 (w), 1102 (w), 1071 (w), 1015 (w), 942 (w), 925 (w), 883 (w), 783 (w), 696 (w), 659 (w), 539 (w). For **CoMOF-1'** (Internal epoxide): FTIR cm⁻¹ (KBr): 3445 (br), 1686 (w), 1597 (s), 1563 (m), 1531 (w),

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1502 (w), 1420 (s), 1286 (m), 1252 (s), 1163 (m), 1145 (w), 1102 (w), 1071 (w), 1016 (w), 942 (w), 924 (w), 883 (w), 783 (w), 696 (w), 659 (w), 539 (w).

X-ray Crystallography

The crystallographic data and refinement for **CoMOF-1** is provided in **Table S1**. Crystal of suitable size was selected from the mother liquor and immersed in paratone oil and then mounted for data collection. Single crystal X-ray data was collected at 150 K using a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo-K α radiation (λ = 0.71069 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were obtained from International Tables for X-ray Crystallography. The data integration and reduction were processed using SAINTPLUS software.⁵² An empirical absorption correction was applied to the collected reflections with SADABS using XPREP.^{S3} The structure was solved by the direct method using SHELXTL^{S4} and was refined on F² by a full-matrix least-squares technique using the SHELXL-2014^{S5} program package. Non-hydrogen atoms were refined anisotropically and the hydrogen atoms attached to the organic moiety were stereochemically fixed. The void volumes of the framework was estimated by the *PLATON* program.^{S6} The solvent molecules present in **CoMOF-1** could not be refined because of their highly disordered nature. Hence, SQUEEZE function of the PLATON program was used to eliminate the contribution of the electron density in the solvent region from the intensity data.⁵⁷ The solvent accessible void volume and the corresponding electron counts/unit cell estimated was 942 Å³/193 eÅ⁻³ for **CoMOF-1**. Furthermore, the accessible solvent volume is 31% of unit cell volume as calculated by PLATON.

Identification code	CoMOF-1		
Chemical formula	CoC ₂₆ H ₁₈ N ₄ O ₆		
Formula weight (g/mol)	541.37		
Crystal Color	Red		
Crystal Size (mm)	0.20 x 0.13 x 0.06		
Temperature (K)	150 (2)		
Crystal System	Monoclinic		
Space Group	P2/c		
a(Å)	12.625(4)		
b(Å)	9.350(3)		
c(Å)	26.835(7)		
α(°)	90		
β(°)	107.011(12)		
γ(°)	90		
Z	4		
V(Å ³)	3029.1(16)		
Density (Mg/m ³)	1.187		
μ(mm⁻¹)	0.607		
F(000)	1108		
Reflections Collected	11097		
Independent Reflections	5260		
R _{int}	0.0456		
Number of parameters	334		
GOF on F ²	1.096		
Final R₁/wR₂ (I ≥2σ(I)	0.0716/0.1630		
Weighted R ₁ /wR ₂ (all data)	0.0903/0.1699		
CCDC number	1864042		

Table S1. Crystal Data and Refinement Parameters for CoMOF-1.

This electron count corresponds to disordered methanol, water and DMF molecules (tentatively 3 methanol, 2 water and 2 DMF molecules) present in the unit cell as solvent of crystallization. The contribution of the guest solvent molecules were removed, and final refinement was performed. The disordered solvent molecules are not included in the molecular formula of **CoMOF-1** in the structure refinement, CIF file and crystallographic Table. CCDC reference number for **CoMOF-1** is 1864042 and this data can be obtained free of charge from The Cambridge Crystallographic Data Center via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

Characterization and Chemical Stability of CoMOF-1

CoMOF-1 synthesised by different approaches, hydrothermal synthesis for harvesting crystals and conventional reflux method for synthesis of the bulk material, was characterised by various analytical techniques, such as FTIR, PXRD, TGA and FE-SEM for the assessment of thermal/chemical stability and phase purity. Guest free CoMOF-1 obtained by solvent exchanged with DCM for 48 h followed by heating at 150 °C in oven for 24 h and designated as CoMOF-1'. Interestingly, MOFs synthesised by both routes showed phase pure material with different degree of solvent encapsulation exposed by the physico-chemical analysis. PXRD data of the compounds synthesized by reflux method as well as activated material is in good agreement with the simulated single crystal X-ray (SXRD) data suggesting the bulk phase purity of the compound (Figure S1). CHN analysis of MOFs synthesized via different routes advocate the elemental composition of MOF with following empirical formula, $\{[Co(OBA)(L)] \cdot xG\}_n$ where G = methanol, water or DMF as mentioned in crystallographic section. The infrared spectra of MOF in the range 400-4000 cm⁻¹ was dominated by the vibrational modes of the ligands and lattice solvent molecules. The symmetric and antisymmetric stretching modes of the lattice water molecules as well as $\mu(N-H)$ of vibrations of L was very broad and lie in the range 3100-3400 cm⁻¹. The characteristic carboxylate peaks with symmetric and antisymmetric $v_{C=0}$ bands was observed at ca., 1420 and 1598 (s) cm⁻¹ respectively (Figure S2). Bands in the range of 1600 cm⁻¹ to 1300 cm⁻¹ ¹ with medium intensity were credited to stretching modes of the pyridyl rings of L ligands and

the aromatic rings of the OBA ligands. Thermal stability of the MOF was established by TGA data measured up to 600 °C and variable temperature powder XRD (VT-PXRD) analysis. The TGA plot of **CoMOF-1** synthesized by both methods disclosed two step weight loss in which the first step involving observed weight loss of 13-15% around 120 °C corresponding to escape of lattice methanol and water molecules. Further 10-12% weight loss in the temperature range 120-280 corresponds to loss of lattice DMF molecules. Degradation of the MOF structural framework commences at around ~300°C by loss of organic ligand moiety. TGA data of CoMOF-1' (activated MOF) showed negligible weight loss compared to as synthesized materials suggesting removal of guest solvent molecules (Figure S3). VT-PXRD data revealed major peaks of the pristine compound is retained by the CoMOF-1 up to 300 °C, displaying the crystalline nature and thermal stability of the compound (Figure S4). For catalysis, gas adsorption, and chemical stability experiments bulk material of CoMOF-1 synthesised by reflux method has been used after activation and designated as CoMOF-1'. Thus, chemical stability using CoMOF-1' in a variety of organic solvents was investigated by soaking the material in respective medium for one-week as well as in acidic and basic media by soaking in 0.1 M and 0.01 M aqueous acidic (HCl, HNO₃, H₂SO₄) and basic (NaOH, KOH) solution for 6 and 12 h respectively. Approximately 50 mg of the sample was dispersed uniformly in a 25-mL vial containing the respective media to make uniform suspension. The solid material was recovered by filtration, washed thoroughly with water/methanol and acetone followed by drying at ambient temperatures. PXRD data of the recovered solid samples showed good agreement with the simulated single crystal data suggesting the chemical stability of the material in different solvents and acidic/ basic medium (Figure S5&6). FE-SEM analysis of MOF synthesized via conventional reflux method showed plate

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shaped morphology (**Figure S7**). The robustness and chemical stability of the MOF can be attributed to the structural features such as coordinatively saturated metal site in which carboxylate group involve in versatile coordination in the formation of extended dimeric metal clustres and axially pillared by the Schiff base ligands in the formation of the 3D framework.



Figure S1. Comparison of PXRD data of **CoMOF-1** synthesized by hydrothermal/conventional reflux, and activated framework with simulated SXRD.



Figure S2. FTIR recorded for **CoMOF-1** (synthesized by different routes, activated framework and recovered after 6th catalytic recycle) dispersed in KBr pellets.



Figure S3. TGA plot for the **CoMOF-1** (synthesized by hydrothermal/reflux method and activated MOF).



Figure S4. VT-PXRD data for CoMOF-1 from room temperature to 350 °C.



Figure S5. PXRD data of CoMOF-1' dispersed for a 1 week in various organic solvents.



Figure S6. PXRD data of **CoMOF-1'** dispersed in aqueous acid (HCl, HNO₃, H₂SO₄) and base (NaOH, KOH) solutions of 0.1 M for 6 h and 0.01M for 12 h.



Figure S7. FE-SEM Images of **CoMOF-1** as synthesized (reflux) (a) and recovered after 6th catalytic recycle for terminal and internal epoxide conversion (b,c).



Figure S8. (a) Horvath-Kawazoe Differential Pore Volume Plot for the micropore size determination in **CoMOF-1**; (b) BJH Desorption dV/dD Pore Volume plot for the mesopore determination in **CoMOF-1**.

S2. COMPUTATIONAL METHODS

Microscopic models for the host framework

The experimentally elucidated structure of **CoMOF-1'** was initially geometry optimized at the Density Functional Theory (DFT) level using the CP2K package.⁵⁸⁻⁵¹¹ In these simulations, the positions of atoms of the framework were relaxed while the unit cell parameters were kept fixed at the values determined experimentally. All the structural optimizations were done using Perdew-Burke-Ernzerhof (PBE)⁵¹² functional along with a combined Gaussian basis set and pseudopotential. For Carbon, Nitrogen, Oxygen, and Hydrogen, a triple zeta (TZVP-MOLOPT) basis set was considered, while a double zeta (DZVP-MOLOPT) was applied for Cobalt.⁵¹³ The pseudopotentials used for all of the atoms were those derived by Goedecker, Teter and Hutter.⁵¹⁴ The van der Waals effects interactions were taken into account via the use of semi-empirical dispersion corrections as implemented in the DFT-D3 method.⁵¹⁵ The atomic point charges for all framework atoms of the **CoMOF-1'** (**Figure S9**) were obtained using the REPEAT method proposed by Campana et al.,⁵¹⁶ which was recently implemented into the CP2K code based on a restrained electrostatic potential framework.⁵¹⁷



Figure S9. The single unit cell (1×1×1 simulation box) considered for the DFT calculations viewed along *c* for **CoMOF-1**′. (Gray, carbon; blue, nitrogen; white, hydrogen; red, oxygen; violet, green).

Force fields

The interaction between the **CoMOF-1'** framework and the CO₂ molecules was modelled using the sum of a 12-6 Lennard-Jones (LJ) contribution and a coulombic term. The Universal force field (UFF) was adopted to describe the LJ parameters for the atoms of the **CoMOF-1'** framework (**Figure S9 and Table S2**).^{S18} In this work, CO₂ has been modeled as a rigid molecule through the EPM2 intermolecular potential (**Table S3**).^{S19}

Atomic		UFF		
type	σ (Å)	<i>ℰ /</i> k _B (K)		
С	3.431	52.841		
н	2.571	22.143		
Ν	3.261	34.724		
0	3.118	30.195		
Со	2.562	7.045		

Table S2. LJ potential parameters for the atoms of the CoMOF-1'.

Table S3. Potential parameters and partial charges for the adsorbates.

Atomic type	σ (Å)	<i>ℰ</i> /k _B (K)	q (e)
CO ₂ _C	2.757	28.129	0.6512
CO2_O	3.033	80.507	-0.3256

GCMC Simulations

Grand Canonical Monte Carlo (GCMC) simulations were carried out at two different temperatures, 273 K and 298 K, for **CoMOF-1'** in order to predict the single component adsorption of CO₂. These calculations were performed using the RASPA simulation code.⁵²⁰ The simulation box was made of 6 (2×3×1) unit cells of **CoMOF-1'**. Short-range dispersion forces were

truncated at a cutoff radius of 12 Å while the interactions between unlike force field centers a and b were treated by means of the Lorentz-Berthelot combination rules; $\varepsilon_{ab} = \sqrt{\varepsilon_a \varepsilon_b}$, $\sigma_{ab} =$ $(\sigma_a + \sigma_b)/2$, where ε_a and σ_a are the LJ parameters for the species a. The long-range electrostatic interactions were handled using the Ewald summation technique. The fugacities for each adsorbed species at a given thermodynamic condition were computed with the Peng-Robinson equation of state (EoS).^{S21} For each state point, 5×10^7 Monte Carlo steps have been used for both equilibration and production runs. Three types of trials were considered for the molecules: (i) translation or rotation, (ii) creation/deletion and (iii) exchange of molecular identity. The adsorption enthalpy at low coverage (Δh) for each gas was calculated through configurational-bias Monte Carlo simulations performed in the NVT ensemble using the revised Widom's test particle insertion method.⁵²² Additionally, in order to gain insight into the configurational distribution of the adsorbed species in CoMOF-1', some additional data were calculated at different pressure including the radial distribution functions (RDF) between the guests and the host.



Computational predictions

Figure S10. Comparison of the single component simulated isotherms for CO₂ (red) with the experimental data (blue) in **CoMOF-1'** at 273 K (a) and 298 K (b).



Figure S11. Comparison of the simulated adsorption enthalpy (red) for CO₂ with the experimental data (blue) in **CoMOF-1'**.



Figure S12. Radial distribution functions (RDF) between CO_2 and the atoms of the MOF framework (Carbonyl group of amide functions, $O_{carbonyl}$: red, and Organic Oxygen, $O_{organic}$: blue, Organic carbon, $C_{organic}$: black, Organic hydrogen, $H_{organic}$: green,) extracted from the single component adsorption in **CoMOF-1'** at 1 bar and 298 K: Carbon of CO_2 : C_{CO2} (a) and Oxygen of CO_2 : C_{CO2} (b).



Figure S13. Maps of the occupied positions of CO₂ (green) in 500 equilibrated frames for a given pressure of 1 bar and at 298 K for **CoMOF-1'**, color code for the atoms: C (dark grey), N (blue), O (red), Co (violet), H (light grey).



Figure S14. Effect of temperature (°C)(a), reaction time (b), and catalyst loading (c) on styrene carbonate formation. (Reaction conditions: SO = 8.7 mmol (1.0 mL at 25 °C), Catalyst mol%: **CoMOF-1'** = 1.8 mol% (except c); tetrabutyl ammonium bromide (TBAB) = 2.5 mol%, P_{CO2} = 1.0 bar, 60 °C (except a), 12 h except (b), 600 rpm)



Figure S15. Effect of pressure (a), temperature (b), reaction time (c), and catalyst loading (d) on cyclohexene carbonate formation. (Reaction conditions: CHO = 20 mmol (3.0 mL at 25 °C), Catalyst mol%: **CoMOF-1'** = 2.8 mol% (except d); tetrabutyl ammonium bromide (TBAB) = 5 mol%, P_{CO2} = 30 bar (except a), 8 h (except c), 100 °C (except d), 600 rpm)

Computational Methods for catalytic mechanism

Periodic DFT calculations were carried out in the mixed Gaussian plane wave scheme as implemented in the CP2K code package^{S8-S11} with Grimme's D3 dispersion corrections by keeping the same functional and basis set used as for the geometry optimization of **CoMOF-1'**. This basis set and energy cutoff parameters have been considered based on the previous calculation by Ye *et al.*,^{S23} where they validated that PBE functional with a plane wave cutoff energy of 500 Ry and suggested as the best option for exploring the catalytic mechanism involves MOF. The Br-nucleophile incorporated **CoMOF-1'** (**Figure S16**) was considered was considered as the model catalyst for exploring the reaction mechanism. The lattice constants of the optimized unit cell are a = 12.715, b = 9.399, c = 27.119 Å and $\alpha = 90.0^{\circ}$, $\beta = 107.011^{\circ}$, $\gamma = 90.0^{\circ}$. The TBAB provides the

halide ion (bromide) nucleophile for the epoxide ring opening, this simplified Br- nucleophile incorporated **CoMOF-1'** catalyst model helps to avoid any complication as blocking TBAB cocatalyst to the pore aperture of **CoMOF-1'** for the substrate and CO₂. In this work, we examined the case of one Br- per **CoMOF-1'** unit cell. We found that fully relaxing the geometry and cell parameters of **CoMOF-1'** gave lattice constants that were almost identical to the relaxed **CoMOF-1'** values.



Figure S16. Mechanistic pathways of the intermediates and transitions states in the cycloaddition of cyclohexane epoxide and CO₂ using **CoMOF-1'** catalyst with Br- ion.

Furthermore, optimizing the structure with chemisorbed cyclohexane epoxide or CO_2 in **CoMOF-1'** also perturbed the lattice constants and energies by a very minor amount. Therefore, we held the lattice constants fixed at the ground state **CoMOF-1'** values for most calculations to save computational time. For the calculation, the total relative energy of the Br- nucleophile incorporated **CoMOF-1'** (catalyst + nucleophile), CO_2 , and cyclohexane epoxide (isolated reactants) was consider to zero energy and the optimized structures of reactant complexes are depicted in **scheme 1**. In the case of each stages of catalytic reaction (e.g. IC, Int, TS, FC etc.), the relative energies were computed with respect to the sum of the total energies of the corresponding gas phase molecules as represented in Equation 1.

$$E_{relative} = E_{stage} - \left(E_{Co-MOF-1+Br} - E_{CO_2} - E_{Cyclohexane\ epoxide}\right) \tag{1}$$

Where E_{stage} , $E_{Co-MOF-1+Br}$, E_{CO_2} and $E_{Cyclhexane\ epoxide}$ represents the total energies of the **CoMOF-1'** + Br⁻ with adsorbates at each reaction stage, the empty **CoMOF-1'** + Br⁻ catalyst, gas phase CO₂ and gas phase Cyclohexane epoxide, respectively. Equation 1 defines negative values as exothermic and positive values as endothermic processes. Transition states along the reaction pathway were determined by using the climbing image nudged elastic band (CI-NEB) method. Transition states were confirmed through frequency analysis, verifying that the transition complex had only one imaginary frequency vibrational mode.



Scheme 1. Energy profile diagram of the intermediates and transitions states calculated using Periodic DFT calculation in the cycloaddition of cyclohexene oxide and CO₂ to form cyclohexene carbonate, using the **CoMOF-1'** catalyst.

¹H & ¹³C NMR analysis of cyclic carbonate products

The cyclic carbonate products involve in this study are all well-known compounds. ¹H and ¹³C NMR spectra of products matched well with reported in the literature.^{524-529,35} ¹H and ¹³C NMR data of the cyclic carbonate products are as follows.



Styrene carbonate: ¹H NMR (600 MHz, CDCl₃) δ 7.47 – 7.34 (m, 5H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.1 Hz, 1H), 4.35 (t, *J* = 8.5 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 154.87, 135.86, 129.84, 129.34, 125.94, 71.24.



4-(chloromethyl)-1,3-dioxolan-2-one: ¹H NMR (600 MHz, CDCl₃) δ 5.04 – 4.91 (m, 1H), 4.60 (t, J = 8.6 Hz, 1H), 4.42 (dd, J = 9.0, 5.7 Hz, 1H), 3.80 (dd, J = 12.6, 5.7 Hz, 1H), 3.74 (dd, J = 12.5, 3.5 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 154.27, 74.35, 67.06, 43.73.



4-(phenoxymethyl)-1,3-dioxolan-2-one: ¹H NMR (600 MHz, CDCl₃) δ 7.44 – 7.17 (m, 2H), 7.09 – 6.82 (m, 3H), 5.15 – 4.93 (m, 1H), 4.69 – 4.46 (m, 2H), 4.20 (ddd, *J* = 53.0, 10.7, 3.9 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 157.82, 154.72, 129.78, 122.09, 114.68, 74.15, 66.94, 66.33.



4-hexyl-1,3-dioxolan-2-one: ¹H NMR (600 MHz, CDCl₃) δ 4.81 – 4.01 (m, 3H), 1.74 (d, J = 69.9 Hz, 2H), 1.38 (d, J = 97.1 Hz, 8H), 0.89 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 155.26, 69.51, 33.88, 31.55, 28.83, 24.36, 22.49, 14.02.



2-((2,4-dibromophenoxy)methyl)oxirane: ¹H NMR (600 MHz, CDCl₃) δ 7.70 – 7.63 (m, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 5.05 (dq, *J* = 6.9, 3.5 Hz, 1H), 4.64 (d, *J* = 6.9 Hz, 2H), 4.32 – 4.11 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 154.56, 153.59, 135.93, 131.51, 115.09, 114.84, 113.67, 73.86, 68.40, 66.14.



Hexahydrobenzo[d][1,3]dioxol-2-one: ¹H NMR (600 MHz, CDCl₃) δ 4.71 (s, 2H), 1.90 (s, 4H), 1.62 (s, 2H), 1.44 (s, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 155.43, 75.81, 26.74, 19.13.



4,4-dimethyl-1,3-dioxolan-2-one: ¹H NMR (600 MHz, CDCl₃) δ 4.18 (s, 2H), 1.54 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 154.60, 81.81, 75.29, 25.83.



4,5-dimethyl-1,3-dioxolan-2-one: ¹H NMR (600 MHz, CDCl₃) δ 4.34 (s, 2H), 1.46 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 154.64, 80.01, 18.38.



Tetrahydro-4H-cyclopenta[d][1,3]dioxol-2-one: ¹H NMR (600 MHz, CDCl₃) δ 5.14 (s, 2H), 2.12 (s, 2H), 1.73 (s, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 155.61, 82.04, 33.10, 21.59.



4,5-diphenyl-1,3-dioxolan-2-one: ¹H NMR (600 MHz, CDCl₃) δ 7.41 (s, 6H), 7.31 (d, J = 24.9 Hz,

4H), 5.42 (s, 2H). 13 C NMR (151 MHz, CDCl₃) δ 154.15, 134.81, 129.86, 129.28, 126.17, 85.39.



Figure S17. ¹H-NMR of the isolated styrene carbonate.



Figure S18. ¹³C-NMR of the isolated styrene carbonate.



Figure S19. ¹H-NMR of the isolated 4-(chloromethyl)-1,3-dioxolan-2-one.



Figure S20. ¹³C-NMR of the isolated 4-(chloromethyl)-1,3-dioxolan-2-one.



Figure S21. ¹H-NMR of the isolated 4-(phenoxymethyl)-1,3-dioxolan-2-one.



Figure S22. ¹³C-NMR of the isolated 4-(phenoxymethyl)-1,3-dioxolan-2-one.



Figure S23. ¹H-NMR of the isolated 4-hexyl-1,3-dioxolan-2-one.



Figure S24. ¹³C-NMR of the isolated 4-hexyl-1,3-dioxolan-2-one.



Figure S25. ¹H-NMR of the isolated 2-((2,4-dibromophenoxy)methyl)oxirane.



Figure S26. ¹³C-NMR of the isolated 2-((2,4-dibromophenoxy)methyl)oxirane.



Figure S27. ¹H-NMR of the isolated hexahydrobenzo[d][1,3]dioxol-2-one.



Figure S28. ¹³C-NMR of the isolated hexahydrobenzo[d][1,3]dioxol-2-one.



Figure S29. ¹H-NMR of the isolated 4,4-dimethyl-1,3-dioxolan-2-one.



Figure S30. ¹³C-NMR of the isolated 4,4-dimethyl-1,3-dioxolan-2-one.



Figure S31. ¹H-NMR of the isolated 4,5-dimethyl-1,3-dioxolan-2-one.



Figure S32. ¹³C-NMR of the isolated 4,5-dimethyl-1,3-dioxolan-2-one.



Figure S33. ¹H-NMR of the isolated tetrahydro-4H-cyclopenta[d][1,3]dioxol-2-one.



Figure S34. ¹³C-NMR of the isolated tetrahydro-4H-cyclopenta[d][1,3]dioxol-2-one.



Figure S35. ¹H-NMR of the isolated 4,5-diphenyl-1,3-dioxolan-2-one.



Figure S36. ¹³C-NMR of the isolated 4,5-diphenyl-1,3-dioxolan-2-one.

No	Catalyst	Temp.	Pressure	Time	Viold	Homogeneous/	Pof
NO.	Catalyst	(°C)	(MPa)	(h)	Tield	Heterogeneous	Rel.
1	PAD-3	120	1	15	94	hetero	30
	V(V)						
2	aminotriphenolate	85	1	18	71	homo	31
	complexes						
3	SQA-15	80	3	18	88	homo	32
4	[Fe(CNN)2]I2	80	1	24	94	homo	33
5	Fe(III) complexes (1d)	100	1	12	91		34
	4(5)-						
6	(Hydroxymethyl)imidaz	120	5	6	78	homo	35
	ole and						
7	Amidinate Aluminium	50	1	24	83		36
	Complexes						
-	Bimetallic	-0	4	24	47		07
8	Aluminium(Salphen)	50	1	24	17		37
0		70	2	24	00	hama	20
9	Co2L crown other	70	Z	24	90	потто	38
10	Cd2+-Crown etner	45	1	48	98		39
11	Resorcinarenes	100	0.5	64	/1	homo	40
	Ionic Bare Farth Metal	100	0.5	04	71	nomo	40
12	Complexes	90	1	48	40		41
	pyridine-bridged						
13	pincer-type	90	1	5	81	homo	42
	imidazolium salts						
	[AlMe2{κ2-		_				
14	mbpzbdeape}]l2 (70	1	18	54	homo	43
	Robust						
15	Metalloporphyrin	120	1.7	32	90	homo	44
	Catalysts						
16	(salalen)Ti(IV)Cl.	120	4	8	99	homo	45
17	Ti-ZIF	100	2.5	8	95	Hetero/MOF	46
18		100	3	8	99	Hetero/MOF	This
10		100	5	5	55		work

Table S4. Catalyst for internal epoxide conversion (compared substrate = cyclohexane oxide).



Figure S37. Recyclability of **CoMOF-1'** up to 6 catalytic cycles for styrene oxide and cyclohexene oxide conversion (up); PXRD data of **CoMOF-1'** recovered after 6 catalytic recycle for cycloaddition reaction of internal/terminal epoxide compared with PXRD data of as synthesized.



Figure S38. (a) XPS survey spectrum of **CoMOF-1** (as synthesized and catalytic recycled) shows the peaks of C, N, O, and Co elements; (b) High resolution XPS spectrum of Co 2p showed two peaks at ~781 (Co $2p_{3/2}$) and ~796 eV and (Co $2p_{1/2}$) for both materials, indicating that the Co(II) state is predominant in **CoMOF-1**.^{S47-48}



Figure S39. Hot filtration test for cycloaddition reactions catalysed by **CoMOF-1'** for metal leaching. [Hot filtration was done at half reaction time].

|--|

CoMOF-1					
Co(1)-O(1)	1.996(3)	Co(1)-N(1)	2.149(3)		
Co(1)-O(2)#1	2.024(3)	Co(1)-N(4)#3	2.155(3)		
Co(1)-O(5)#2	2.126(3)	Co(1)-O(4)#2	2.303(4)		
O(1)-Co(1)-O(2)#1	119.56(13)	N(1)-Co(1)-O(4)#2	88.16(12)		
O(1)-Co(1)-O(5)#2	151.98(12)	N(4)#3-Co(1)-O(4)#2	91.72(12)		
O(2)#1-Co(1)-O(5)#2	88.45(12)	C(1)-O(1)-Co(1)	138.4(3)		
O(1)-Co(1)-N(1)	86.54(13)	C(1)-O(2)-Co(1)#1	141.3(3)		
O(2)#1-Co(1)-N(1)	88.58(12)	C(14)-O(4)-Co(1)#4	86.8(2)		
O(5)#2-Co(1)-N(4)#3	93.90(13)	C(14)-O(5)-Co(1)#4	95.4(3)		
O(1)-Co(1)-N(4)#3	90.49(13)	C(15)-N(1)-Co(1)	120.7(3)		
O(2)#1-Co(1)-N(4)#3	93.15(12)	C(19)-N(1)-Co(1)	122.7(3)		
O(5)#2-Co(1)-N(4)#3	88.59(13)	C(25)-N(4)-Co(1)#5	123.8(3)		
N(1)-Co(1)-N(4)#3	177.02(14)	C(24)-N(4)-Co(1)#5	119.7(3)		
O(1)-Co(1)-O(4)#2	93.41(12)	O(2)-C(1)-O(1)	124.8(4)		
O(2)#1-Co(1)-O(4)#2	146.58(12)	O(5)-C(14)-O(4)	119.2(4)		
O(5)#2-Co(1)-O(4)#2	58.64(11)				
Symmetry transformation: #1 -x,1-y,-z #2 +x,-y,-1/2+z #3 1+x,-1+y,+z					
#4 +x,-y,1/2+z #5 1+x,1+y,+z					

Table S6. Details of hydrogen bonding interactions observed in the structure of CoMOF-1:

D-H···A	d(H…A) (Å)	d(D…A) (Å)	∠D-H…A (°)	
CoMOF-1				
N(3)-H(3C)…O(4) ¹	2.06	2.893(5)	162	
C(26)-H(26)…O(4) ¹	2.46	3.328(6)	156	
Symmetry code: 1. 1-x,1+y,1/2-z				

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