# A new 2D lanthanum based microporous MOF for efficient synthesis of cyclic carbonates through $CO_2$ fixation

Sabuj Kanti Das,[a] Anirban Ghosh,[a] Sudip Bhattacharjee,[a] Avik Chowdhury,[a] Partha Mitra,[b] Asim Bhaumik*,[a]

[a]School of Materials Sciences, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700 032, India.
Address for correspondence. E-mail: msab@iacs.res.in

[b]School of Chemical Sciences, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700 032, India

| No. | Contents |
|---|---|
| Table S1 | Crystal data and structure refinement for La-5-SIP-MOF. |
| Table S2 | Bond distance and bond angles obtained from CIF of La-5-SIP-MOF. |
| Figure S1 | 2D layered view of La-5-SIP MOF. |
| Figure S2 | FT-IR spectra of 5-NaSIP ligand and La-5-SIP-MOF. |
| Figure S3 | FTIR of reused catalyst. |
| Figure S4 | PXRD of reused catalyst. |
| Figure S5 | TGA profile diagram of La-5-SIP-MOF. |
| Section S1 | Acid Digestion test. |
| Figure S6 | $^1$H NMR of La-5-SIP MOF after acid digestion |
| Figure S7 | UHR-TEM images of La-5-SIP-MOF before and after catalysis. |
| Figure S8 | Optimization of solvent in terms of yield. |
| Figure S9 | Time vs conversion plot after hot filtration test in the cycloadditon of $CO_2$ over epichlorohydrine by La-5-SIP-MOF. |
| Figure S10 | $^1$H NMR of pure epichlorohydrine and after 30 minutes of reaction. |
| Table S3 | $^1$H NMR data of cyclic carbonates. |
| Table S4 | Comparison table of Catalytic activity with previously reported catalyst |
| Figure S11 (a-h) | Proton NMR spectra of the cyclic carbonates |
| Section S2 | Calculation of Turnover Number (TON) and Turnover frequency (TOF) |

**Table S1**. Crystal data and structure refinement for La-5- SIP MOF

| | |
|---|---|
| Empirical formula | $C_8 H_{11} La O_{11} S$ |
| Formula weight | 446.07 |
| Temperature | 293 K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Orthorhombic, Pna2(1) |
| Unit cell dimensions | a= 7.2429(17) Å,<br>b= 16.825(4) Å,<br>c = 10.555(3) Å,<br>α = 90°<br>β= 90°<br>γ = 90° |
| Volume | 1286.3(5) $Å^3$ |
| Z, Calculated density | 4, 2.303 $Mg/m^3$ |
| Absorption coefficient | 3.540 mm-1 |
| F (000) | 848 |
| Theta range for data collection | 2.28 to 26.49° |
| Limiting indices | -7<=h<=9, -21<=k<=21,<br>-12<=l<=13 |
| Absorption correction | Semi-empirical from equivalents |
| Max. And min. Transmission | 0.615 and 0.702 |
| Refinement method | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 2572 / 1 / 190 |
| Goodness-of-fit on F2 | 1.093 |
| R factor (%) | R= 2.17, wR2 = 5.56 |
| Cell formulae units, Z | 4 |

**Table S2.** Bond distance and bond angles obtained from CIF of La-5-SIP-MOF

| | | | |
|---|---|---|---|
| La(1)-O4 | 2.511 | La(1)-O(6) | 2.518 |
| La(1)-O(56) | 2.548 | La(1)-O(52) | 2.574 |
| La(1)-O(1) | 2.573 | La(1)-O(3) | 2.581 |
| La(1)-O(2) | 2.592 | La1 O55 | 2.592 |
| La1 O51 | 2.616 | La1 C100 | 2.949 |
| La1 C4 | 2.960 | O4 S1 | 1.467 |
| C4 O51 | 1.249 | C4 O52 | 1.263 |
| C4 C8 | 1.519 | C100 O2 | 1.261 |
| C100 O1 | 1.258 | C100 C5 | 1.528 |
| O4 La1 O6 | 140.67 | O4 La1 O56 | 71.12 |
| O6 La1 O56 | 71.86 | O4 La1 O52 | 134.20 |
| O6 La1 O52 | 70.96 | O56 La1 O52 | 108.28 |
| O4 La1 O1 | 133.07 | O6 La1 O1 | 78.37 |
| O56 La1 O1 | 148.15 | O52 La1 O1 | 71.24 |
| O4 La1 O3 | 85.73 | O6 La1 O3 | 69.77 |
| O56 La1 O3 | 70.50 | O52 La1 O3 | 138.77 |
| O1 La1 O3 | 88.95 | O4 La1 O2 | 83.67 |
| O6 La1 O2 | 115.80 | O56 La1 O2 | 136.69 |
| O52 La1 O2 | 114.49 | O1 La1 O2 | 50.42 |
| O3 La1 O2 | 73.07 | O52 La1 O55 | 70.75 |
| O1 La1 O55 | 80.51 | O3 La1 O55 | 142.68 |
| O2 La1 O55 | 72.67 | O4 La1 O51 | 91.56 |
| O6 La1 O51 | 87.88 | O56 La1 O51 | 69.83 |

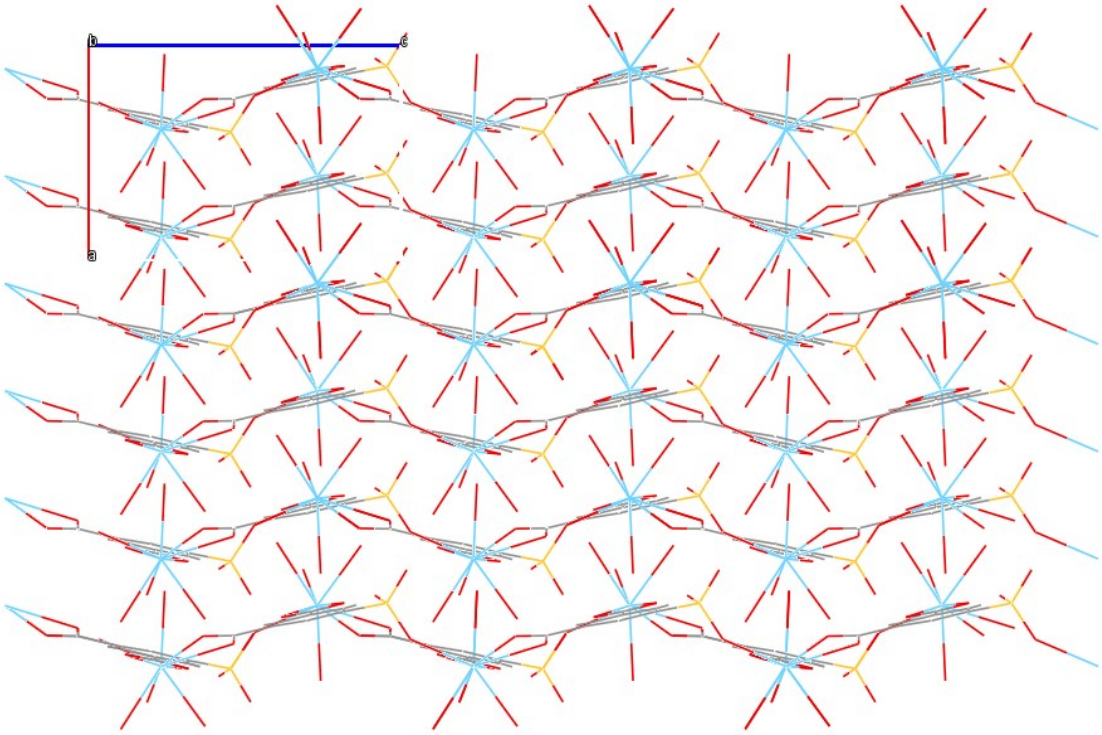


**Figure S1:** 2D layer view of La-5-SIP-MOF.

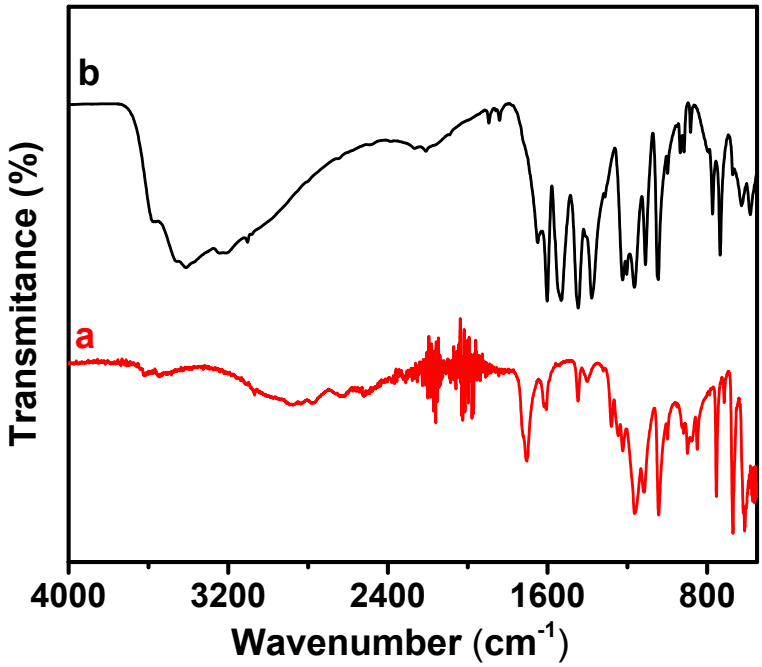



**Figure S2:** FT-IR spectra of 5-NaSIP ligand (a) and La-5-SIP-MOF (b).

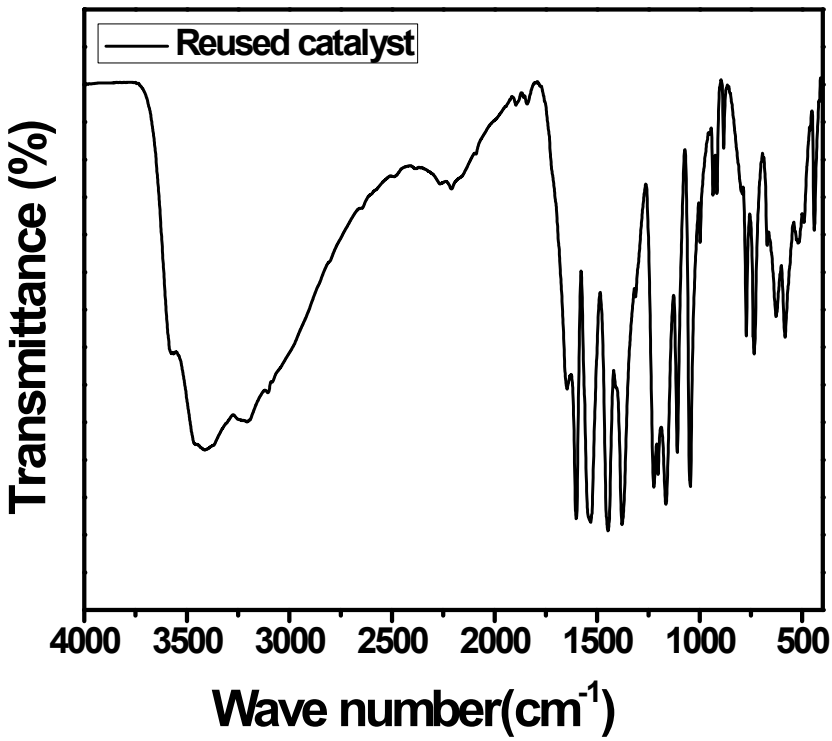



**Figure S3:** FTIR spectrum of reused catalyst.

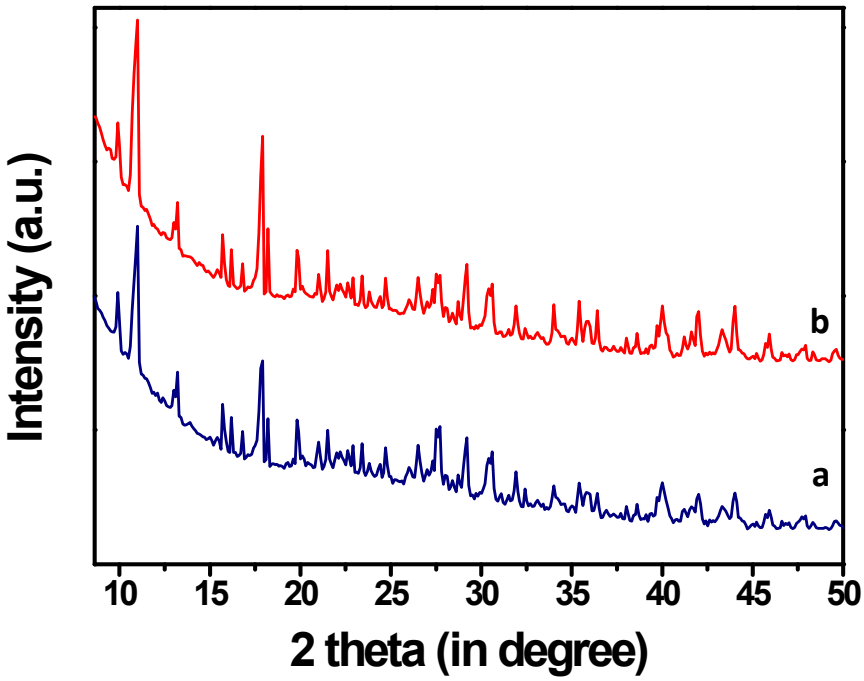



**Figure S4:** PXRD of reused catalyst (a) and activated catalyst (b).

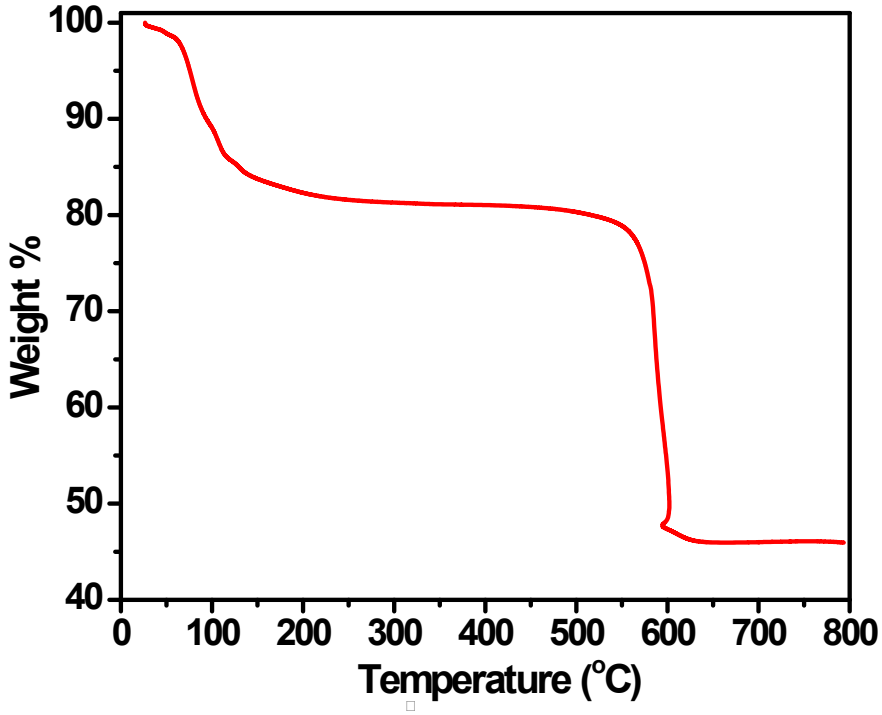



**Figure S5:** TGA profile diagram of La-5-SIP-MOF.

**Section S1:** Acid digestion test

To perform the acid digestion test, 5 mg of the La-5-SIP-MOF material was taken along with 20µl of HF and 0.5ml DMSO-$d^6$ in an eppendorf tube and then the solution was sonicated for 30 min. The portion of the solution was taken in a NMR tube to obtain $^1$HNMR analysis. Two major peaks at 8.42 and 8.36 ppm was appeared with 1:2 ratio for the H(b) and H(a) protons respectively. Which indicates the structural integrity is retained for the ligand in this La-5-SIP-MOF.

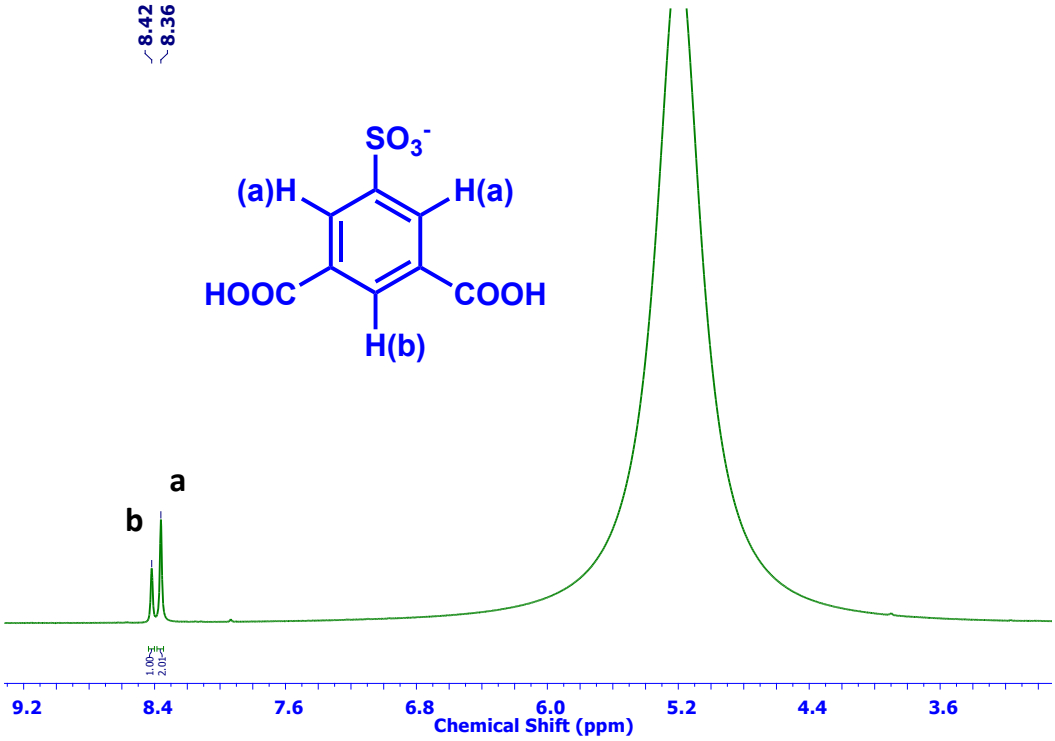



**Figure S6:** $^1$H NMR of La-5-SIP-MOF after acid digestion.

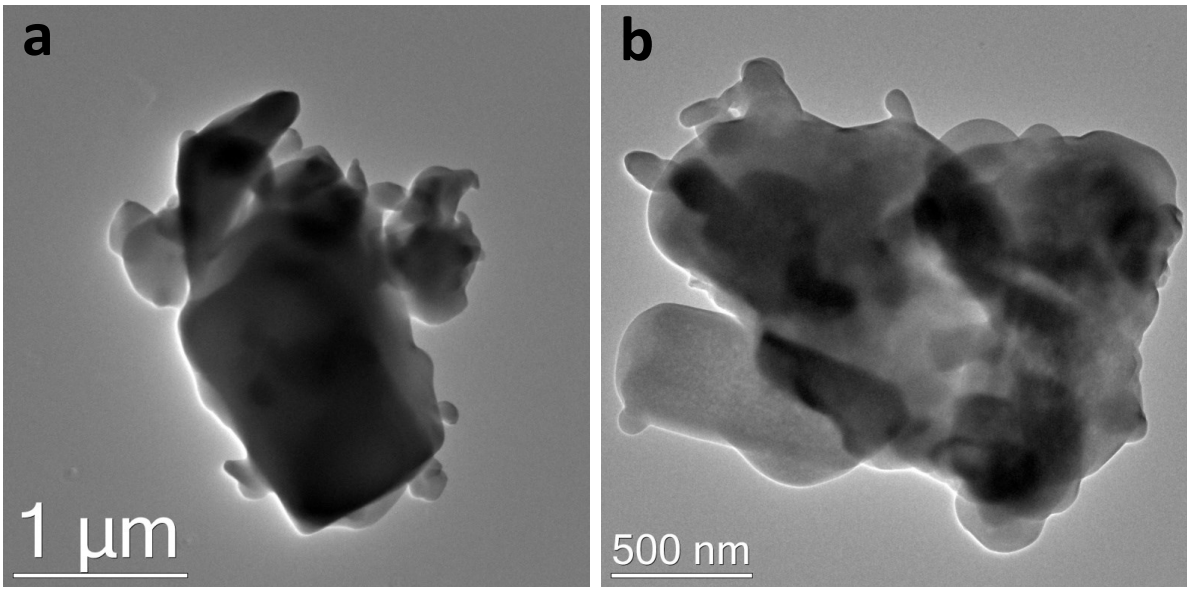



**Figure S7:** UHR-TEM images of La-5-SIP-MOF: a. before catalysis; b. after catalysis.

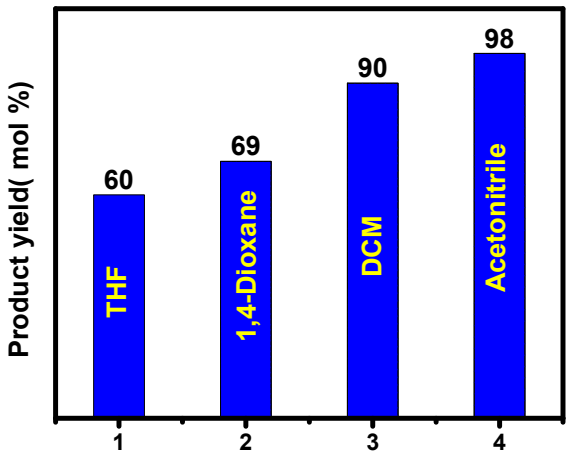



**Figure S8:** Optimization of the product yield over different solvents used in the $CO_2$ fixation over epichlorohydrine.

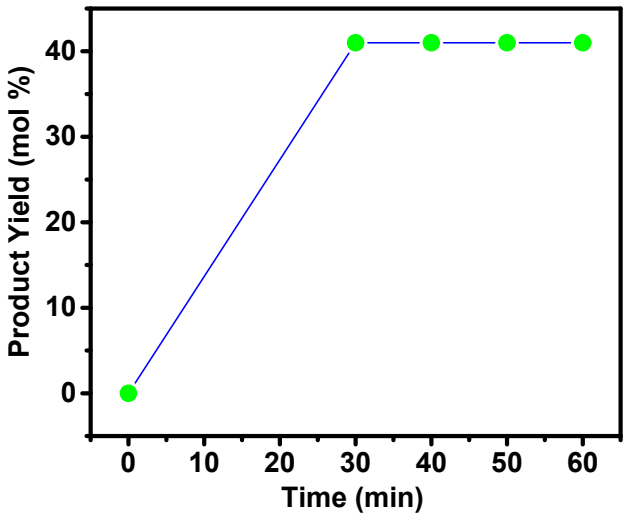



**Figure S9:** Time vs conversion test after hot filtration in the $CO_2$ fixation over epichlorohydrine.

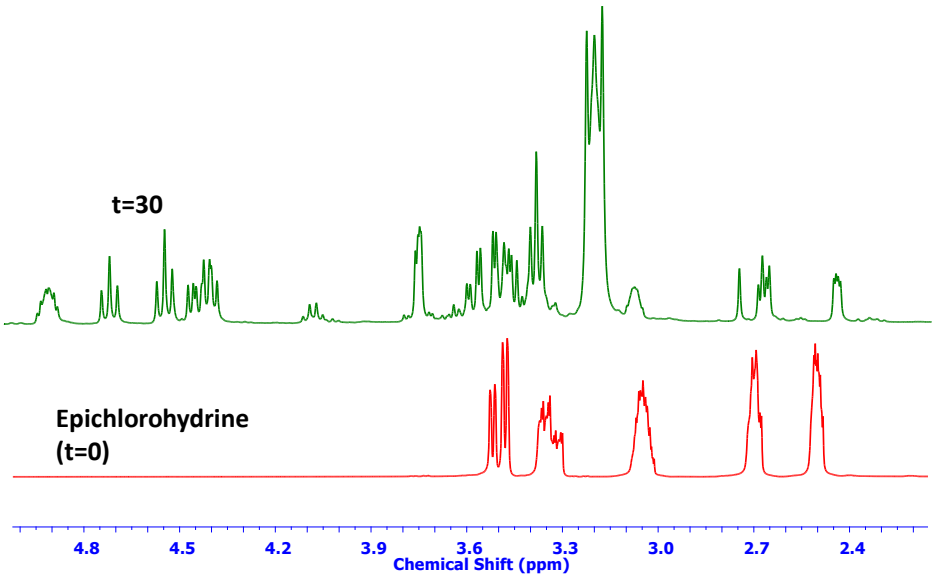
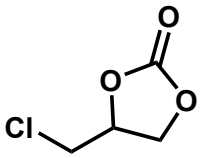
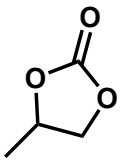
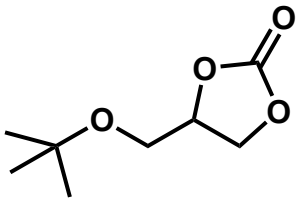
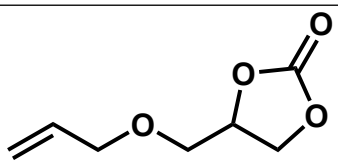
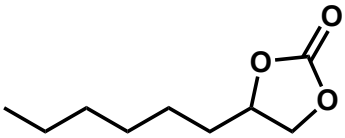
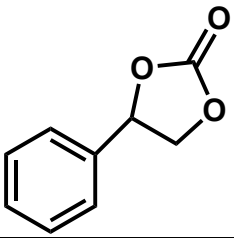
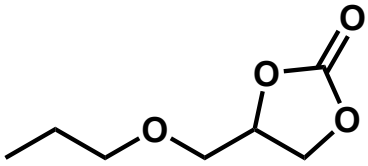



**Figure S10:** $^1H$ NMR of pure epichlorohydrine and after 30 min of $CO_2$ fixation reaction.

**Table S3:** $^{1}$H NMR data of cyclic carbonates**.**

| Entry | Product | $^{1}$H NMR |
|---|---|---|
| **1.** |  | $^{1}$H NMR (400 MHz, TMS, $CDCl_3$): δ (ppm) 4.98-4.92(m,1H), 4.61-4.57(t,H), 4.43-4.40(dd,1H), 3.79-3.71(m, 2H). |
| |  | $^{1}$H NMR (400 MHz, TMS, $CDCl_3$): δ (ppm) 4.87-4.82(m,1H), 4.57-4.53(t,1H), 4.04-4(t,1H), 1.49-1.48(d,3H). |
| **2.** |  | $^{1}$H NMR (400 MHz, TMS, $CDCl_3$): δ (ppm), 4.79-4.73(m,1H), 4.48-4.44(t,1H), 4.38-4.35(dd,1H), 3.62-3.58(), 3.53-3.49(ddd,2H), 1.18(s,9H). |
| **4.** |  | $^{1}$H NMR (400 MHz, TMS, $CDCl_3$): δ (ppm) 5.92-5.81(m,1H), 5.30-5.21(dd,1H), 4.83-4.79(m,1H),4.49-4.39(m,2H), 3.74-3.62(m, 2H). |
| **5.** |  | $^{1}$H NMR (400 MHz, TMS, $CDCl_3$): δ (ppm) 4.84-4.80(m,1H), 4.55(m,1H), 4.05(m,1H), 1.69-1.50(m), 1.69-1.61(m,2H), 1.50-1.22(m,8H), 1-0.83(m,3H). |
| **6.** |  | $^{1}$H NMR (400 MHz, TMS, $CDCl_3$): δ (ppm) 7.434-7.351(m,3H), 7.341-7.259(m,2H), 5.699-5.646(t,1H), 4.820-4.765(t, 1H), 4.359-4.304(t, 1H). |
| **7.** |  | $^{1}$H NMR (400 MHz, TMS, $CDCl_3$): δ (ppm) 4.76(m,1H), 4.45(t,1H),4.34(dd,1H) 3.56(qd,2H),3.46(t,2H) 1.59-1.54-1.30(m,3H), 0.90(t,3H). |

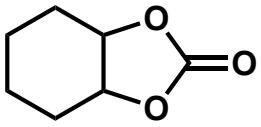
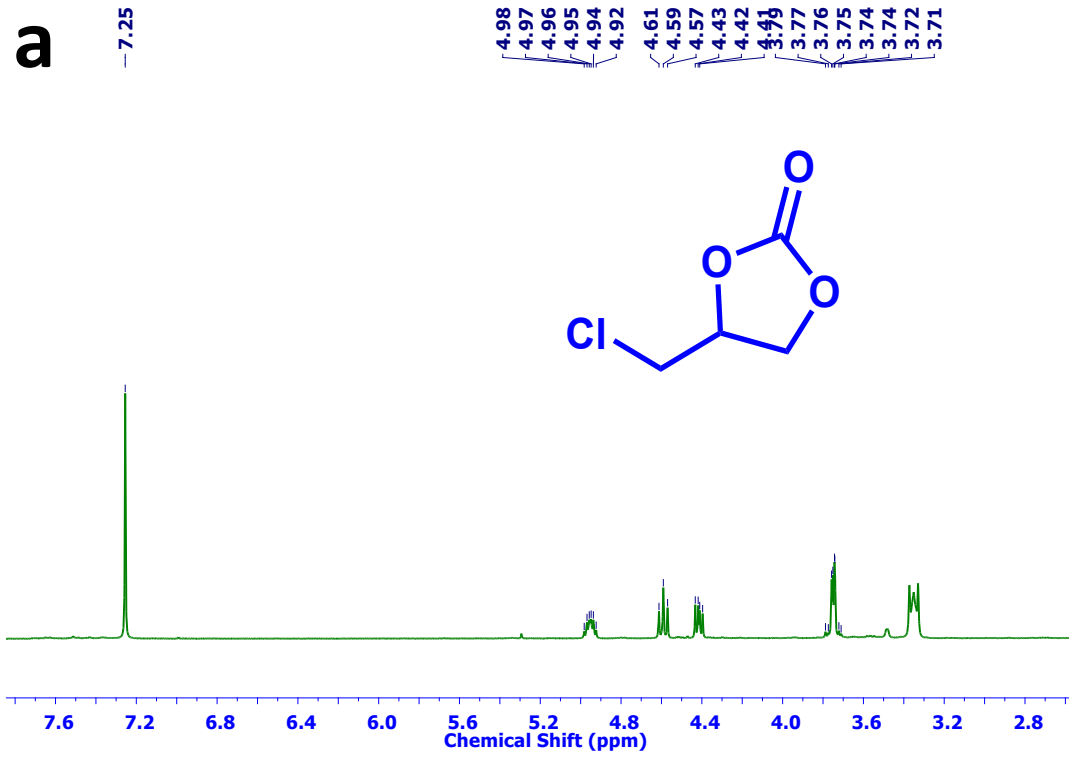
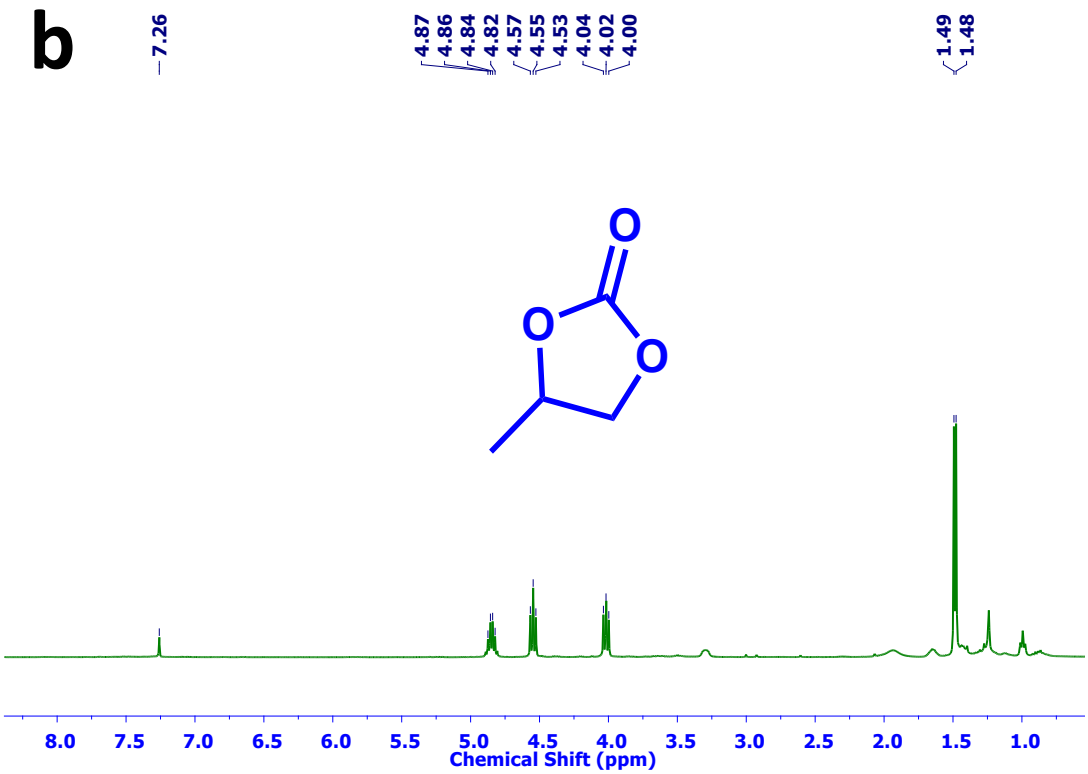
| | | |
|---|---|---|
| **8.** |  | $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.68-4.63(m,2H), 1.90-1.87(m,4H), 1.68-1.62(m,2H),1.47-1.42(m,2H). |

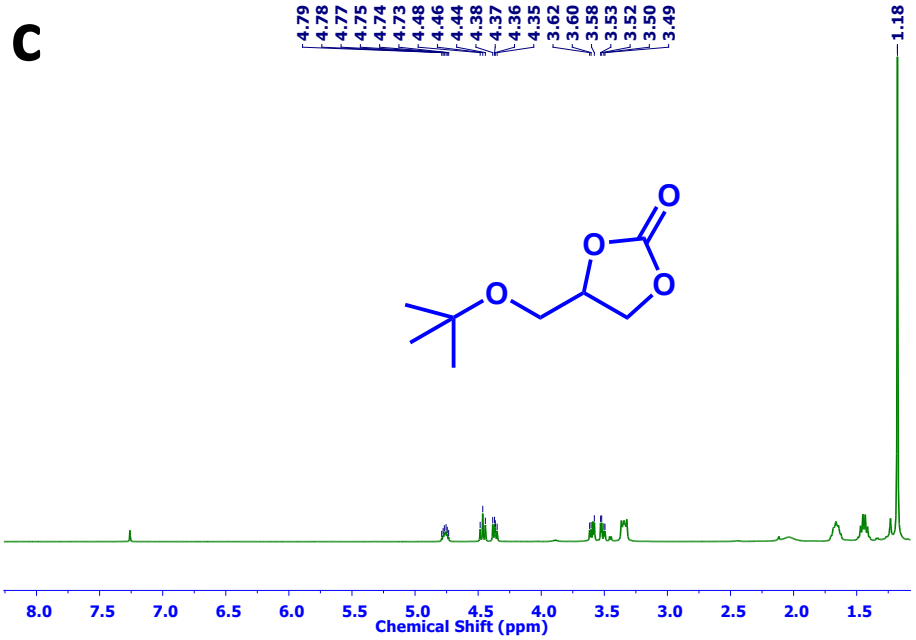
**Table S4.** Comparison table of catalytic activity of La-5-SIP-MOF for $CO_2$ fixation over epichlorohydrine.with previously reported catalyst.

| **Catalyst** | **Pressure (MPa)** | **Temperature (°C)** | **Time (h)** | **TON** | **TOF ($h^{-1}$)** | **Ref.** |
|---|---|---|---|---|---|---|
| Zn@SBMMP | 2 | 80 | 10 | 204 | 20.4 | 1 |
| Al-CMP | 3 | 100 | 1 | 187 | 187 | 2 |
| Co-CMP | 3 | 100 | 1 | 201 | 201 | 2 |
| Al (Salen)/PS | 10 | 80 | 6 | 47 | 7.8 | 3 |
| Al (Salen)/PEA | 10 | 80 | 6 | 7 | 1.16 | 3 |
| Cr-MIL-101 | 0.8 | RT | 24 | 247 | 10.29 | 4 |
| $Ce_2NDC_3$ | 0.1 | RT | 8 | 360 | 45 | 5 |
| Al1cat | 0.1 | 110 | 48 | 41 | 0.85 | 6 |
| La-5-SIP-MOF | 0.5 | RT | 1 | 141.53 | 141.53 | This Work |

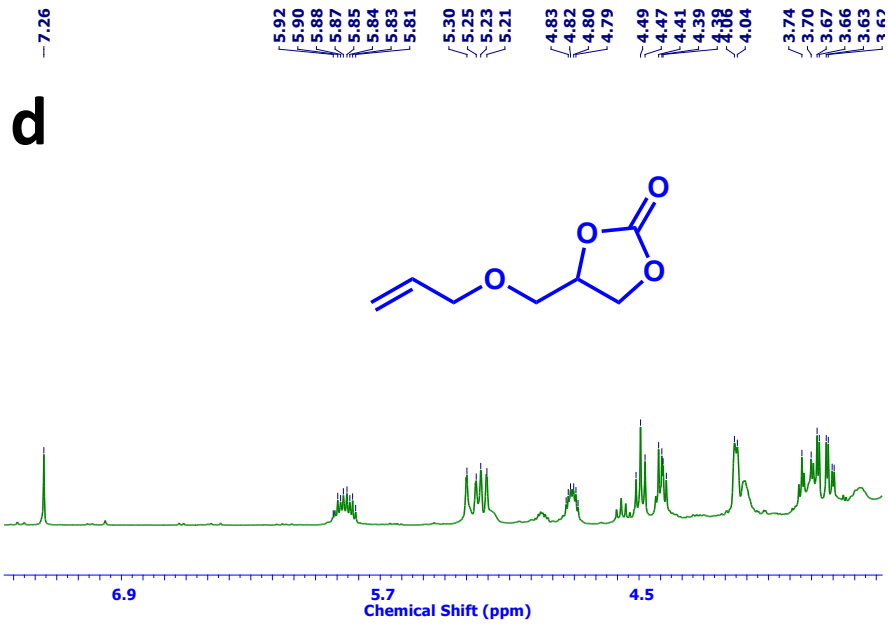

a
7.25
4.98
4.97
4.96
4.95
4.94
4.92
4.61
4.59
4.57
4.43
4.42
3.77
3.76
3.75
3.74
3.74
3.72
3.71
O
O
O
Cl
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
Chemical Shift (ppm)

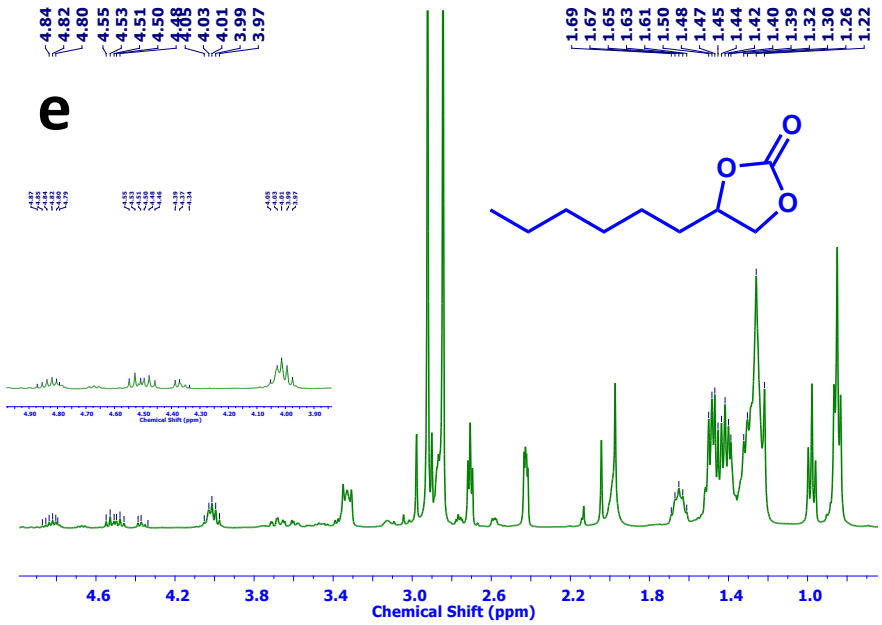

b
7.26
4.87
4.86
4.84
4.82
4.57
4.55
4.53
4.04
4.02
4.00
1.49
1.48
O
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

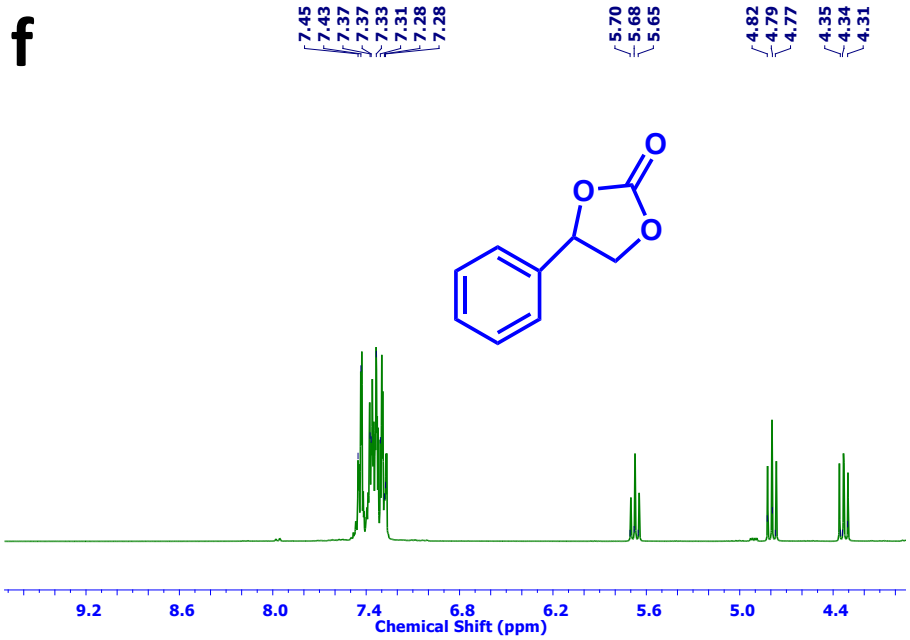
**c**


4.79
4.78
4.77
4.75
4.74
4.73
4.48
4.46
4.44
4.38
4.37
4.36
4.35
3.62
3.60
3.58
3.53
3.52
3.50
3.49
1.18
O
O
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
Chemical Shift (ppm)

**d**


7.26
5.92
5.90
5.88
5.87
5.85
5.84
5.83
5.81
5.30
5.25
5.23
5.21
4.83
4.82
4.80
4.79
4.49
4.47
4.41
4.39
4.04
3.74
3.70
3.67
3.66
3.63
O
O
O
O
6.9
5.7
4.5
Chemical Shift (ppm)


e
4.84
4.82
4.80
4.55
4.53
4.51
4.50
4.03
4.01
3.99
3.97
1.69
1.67
1.65
1.63
1.61
1.50
1.48
1.47
1.45
1.44
1.42
1.40
1.39
1.32
1.30
1.26
1.22
O
O
O
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
Chemical Shift (ppm)


f
7.45
7.43
7.37
7.37
7.33
7.31
7.28
7.28
5.70
5.68
5.65
4.82
4.79
4.77
4.35
4.34
4.31
O
O
O
9.2
8.6
8.0
7.4
6.8
6.2
5.6
5.0
4.4
Chemical Shift (ppm)

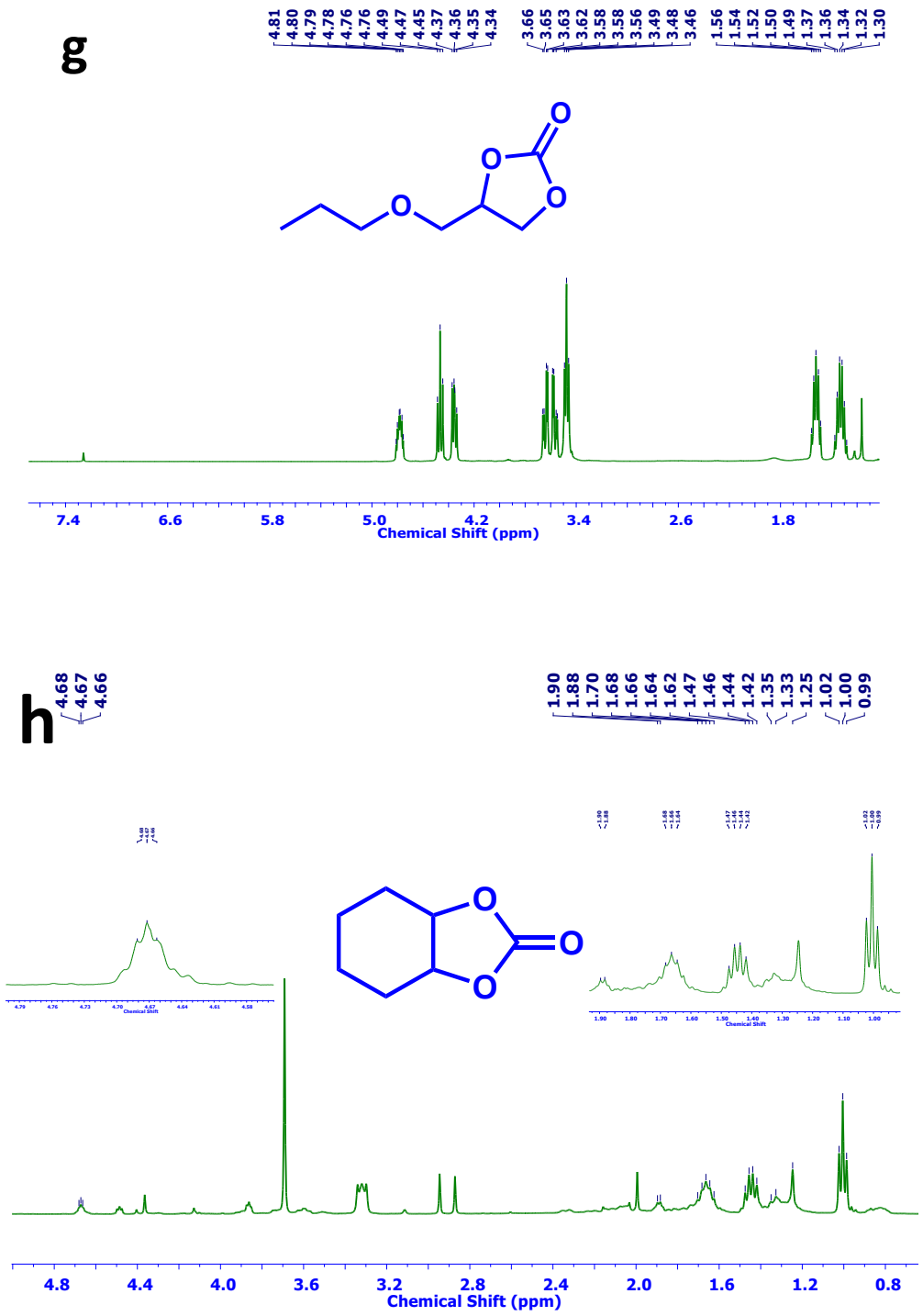



**Figure S11 (a-h):** $^{1}$H NMR spectrum of cyclic carbonates.

**Section S2:** Calculation of Turnover Number (TON) and Turnover frequency (TOF).

$$TON = \frac{No.\,moles\ of\ product\ formed}{No.\ of\ moles\ of\ active\ site\ in\ the\ catalyst}$$

Here we used 6mg of catalyst for cyclic carbonate conversion.

The molecular formulae of La-5-SIP-MOF = C8 H3 La O11 S

The formulae weight of our La-5-SIP-MOF = 446.07

So, from formulae weight we can say that one equivalent of La-5-SIP-MOF contains one equivalent of La atom.

The molecular weight of one La atom is 138.9057.

Thus, the moles of catalyst required = 6 mg.

So, $0.013 \times 10^{-3}$ moles of catalyst required.

We get 98% of products which equivalent to 1.196 × $10^{-3}$ mol.

Thus, $TON = \frac{1.196 \times 10^{-3}}{0.013 \times 10^{-3}}$ = 150.76

Now,

$$TOF = \frac{TON}{Time} h^{-1}$$

As the reaction was conducted for 1 hour, the TOF is equal to TON.

**Section S3:** Synthesis procedure of cyclic carbonate

The reaction was carried out in a high pressure autoclave reactor. Here a dried autoclave of inner volume 100 ml charged with 2-(chloromethyl)oxirane (2 mmol), 6 mg La-5-SIP MOF, along with TBABr (0.062 mmol) as a co-catalyst and acetonitrile (10ml) as solvent. Then the reactor was sealed and purged with $CO_2$ (5 bar) at room temperature. The reaction was carried out under continuous stirring for 1 h. After that, the reaction mixture was filtered to separate the catalyst and extracted with ethyl acetate. Solvents were evaporated under reduced pressure. The colourless liquid formed after evaporation was characterised by $^1$H NMR in $CDCl_3$.

**References:**


1. S. Bhunia, R. A. Molla, V. Kumari, S. M. Islam and A. Bhaumik, *Chem. Commun.,* 2015, **51**, 15732-15735.
2. M. Alvaro, C. Baleizao, E. Carbonell, M. E. Ghoul, H. Garcí and B. Gigante, *Tetrahedron,* 2005, **61**, 12131-12139.
3. Y. M. Shen, W. L. Duan and M. Shi, *J. Org. Chem.,* 2003, **68**, 1559-1156.
4. O. V. Zalomaeva, A. M. Chibiryaev, K. A. Kovalenko, O. A. Kholdeeva, B. S. Balzhinimaev and V. P. Fedin, *J. Catal.,* 2013, **298**, 179-185.
5. S. K. Das, S. Chatterjee, S. Bhunia, A. Mondal, P. Mitra, V. Kumari, A. Pradhan, A. Bhaumik, *Dalton Trans.,* 2017, **46**, 13783-13792.
6. S. Supasitmongkol and P. Styring, *Catal. Sci. Technol.,* 2014, **4**, 1622-1630.