

# **A Thiol-Containing Zirconium MOF Functionalized with Silver Nanoparticles for Synergistic CO<sub>2</sub> Cycloaddition Reactions**

Rajesh Patra and Debajit Sarma\*

*Department of Chemistry, Indian Institute of Technology Patna*

*Patna, Bihar [debajit@iitp.ac.in](mailto:debajit@iitp.ac.in)*

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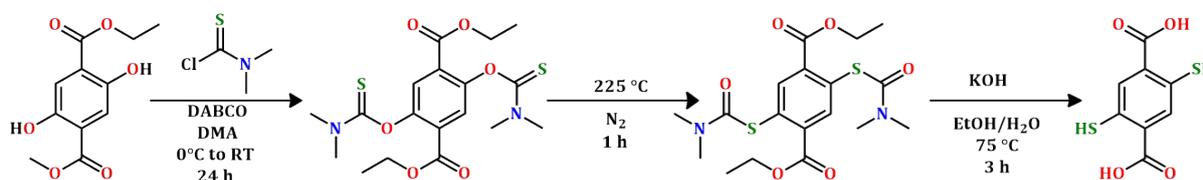
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## Physical Measurements

The powder X-ray diffraction (PXRD) were recorded on a PANalytical's X'PERT PRO diffractometer by using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ; 40 kV, 20 mA). Infra-red (IR) spectra was recorded in Perkin Elmer FTIR instrument.  $^1\text{H}$  was recorded in BRUKER-400 spectrometer at frequency of 400 MHz. TGA( Thermogravimetric analysis) of the samples was performed by using an Q600(TA Instruments) under continuous nitrogen flow (100 mL/min) from room temperature to 800 °C (rate 10 °C min<sup>-1</sup>). A Field Emission Scanning Electron Microscope (FESEM; ZEISS GEMINISEM500 equipped with an energy-dispersive X-ray spectroscopy detector) was used to characterized the surface morphology of the compounds. A transmission electron microscope (JEOL-JEM-F200) operating at 200 kV was used to characterize the synthesized catalyst. The  $\text{N}_2$  and  $\text{CO}_2$  gas adsorption studies were performed by using Quantachrome Autosorb iQ2 analyzer. XPS experiment was done in Omicron Nano tech instrument ( $\text{MgK}\alpha$  radiation at 1253.6 eV). In each elements carbon correction was done with respect to 284.8 eV and for deconvolution of the experimental data Shirley background was used.

## Experimental Section

### Synthesis of thiol ligand 2,5-dimercaptoterephthalic acid ( $H_2DMBD$ )



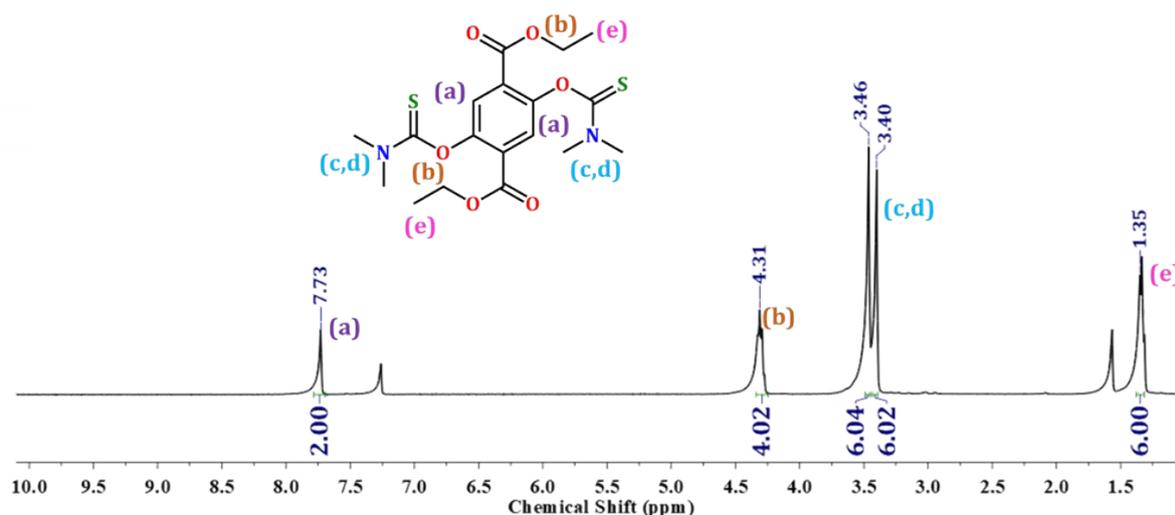
**Reaction scheme 1:** Synthesis of 2,5-dimercaptoterephthalic acid ( $H_2DMBD$ ).

The synthesis of 2,5-dimercaptoterephthalic acid ( $H_2DMBD$ ) was done by the three step organic transformation (**Reaction scheme 1**) by following the previously reported procedure.<sup>1-3</sup> 1 g of 2,5-dihydroxyterephthalic acid diethyl ester and 1.8 g of DABCO was dissolved in dry DMA (10 mL) and then the round bottom flask (RB) was cooled to 0 °C. In another round-bottom flask (RB), 1.9 g of dimethylthiocarbamoyl chloride dissolved in dry DMA (5 mL) and added in other RB under an inert atmosphere and stirred for 18 h. After that, the reaction mixture was filtered, washed with deionized water (60 mL), and dried under vacuum. 1.6 g of 2,5 bis((dimethylcarbamothioyl)oxy)terephthalate was formed as a white compound confirmed by proton NMR (**Figure S1**). ( $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$ 7.73 (s,2H), 4.31 (s,4H), 3.46 (s,6H), 3.40 (s,6H) 1.35 (t,6H).

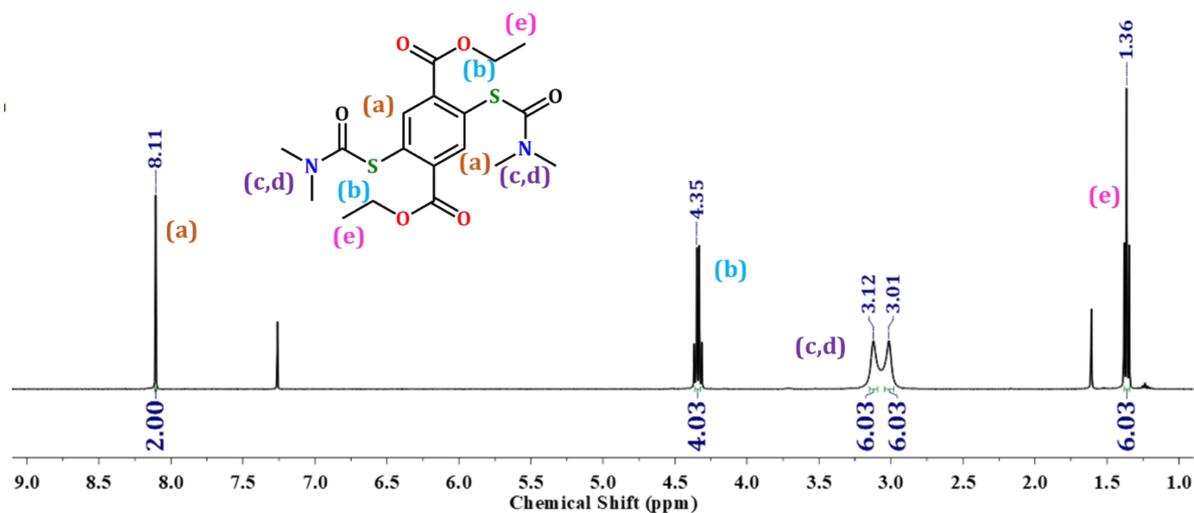
0.8 g of 2,5-bis(dimethylthiocarbamoyloxy)terephthalic acid diethyl ester was taken in a round-bottom flask and heated under an inert atmosphere at 225 °C for 1.5 h. Then the round-bottom flask was cooled to room temperature, and 30 mL of ethanol was added and refluxed for 2 h at 80 °C in an inert atmosphere. After completion of the reaction and slow cooling, pale brown crystals were formed as a compound. Then the compounds were collected by filtration, and 1 g of diethyl 2,5-bis((dimethylcarbamoylthio)oxy)terephthalate was collected as a solid product and confirmed by proton NMR (**Figure S2**). ( $^1H$  NMR (400 MHz,  $\delta CDCl_3$ ): 8.11(s,

2H, CHAr), 4.34 (q, J=7.1 Hz, 4H, CH<sub>2</sub>), 3.12 (s, 6H, CH<sub>3</sub>), 3.02 (s, 6H, CH<sub>3</sub>), 1.37 (t, J=7.1 Hz, 6H, CH<sub>3</sub>)).

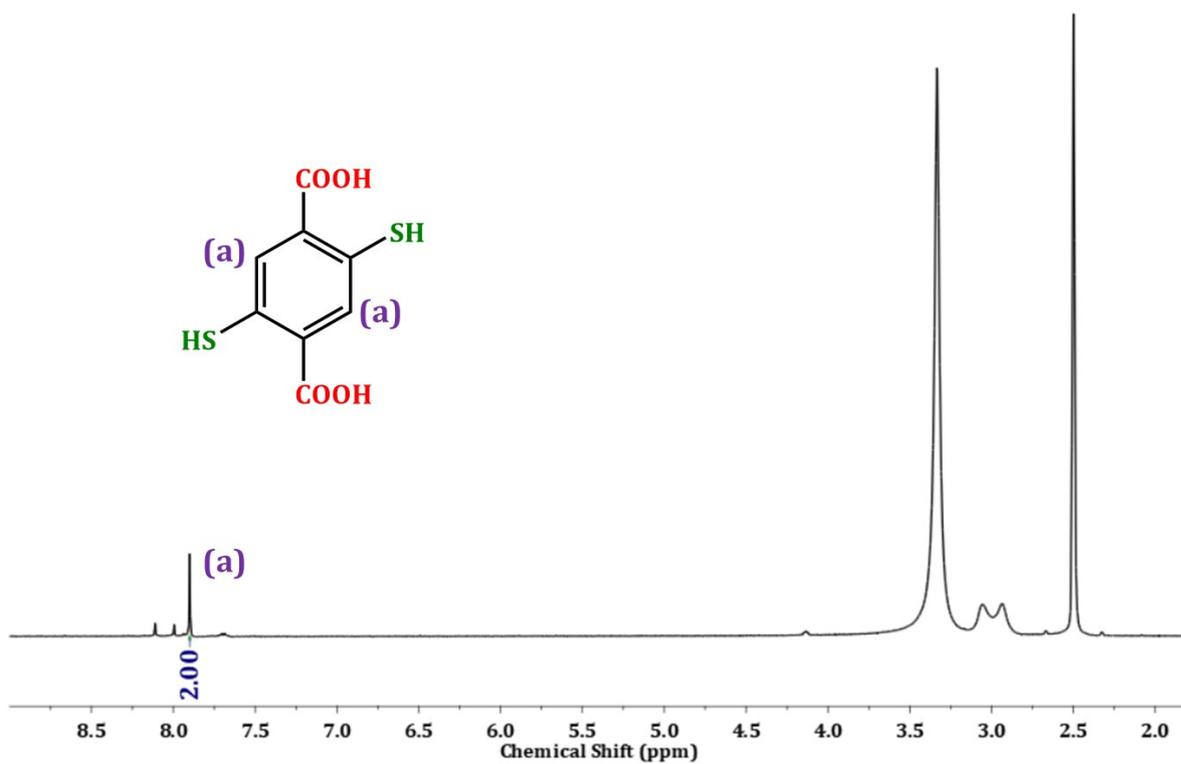
0.5 g of 2,5-bis(dimethylthiocarbamoylsulfanyl)terephthalic acid diethyl ester was dissolved in 40 mL 2 M KOH in EtOH/H<sub>2</sub>O (1:1) and refluxed for 3 h. The reaction mixture was then cooled and concentrated HCl (10 mL) was added. A bright yellow precipitate was formed, filtered, and washed extensively with water, yielding 2,5-dimercapto-1,4-benzenedicarboxylic acid confirmed by proton NMR (**Figure S3**). (<sup>1</sup>H NMR (400 MHz, DMSO): δ7.90 (s, 2H, CHAr).



**Figure S1:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of 2,5- bis((dimethylcarbamothioyl)oxy) terephthalate.

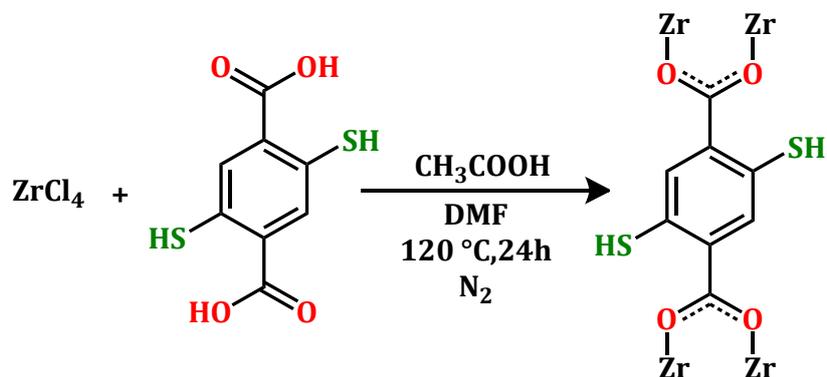


**Figure S2:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of diethyl 2,5-bis ((dimethylcarbamoyl)thio)terephthalate.



**Figure S3:** <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) spectrum of 2,5-dimercaptoterephthalic acid (H<sub>2</sub>DMBD).

## Synthesis of thiol MOF Zr-DMBD



**Reaction scheme 2:** Synthesis of MOF Zr-DMBD.

## Synthesis of thiol MOF Zr-DMBD

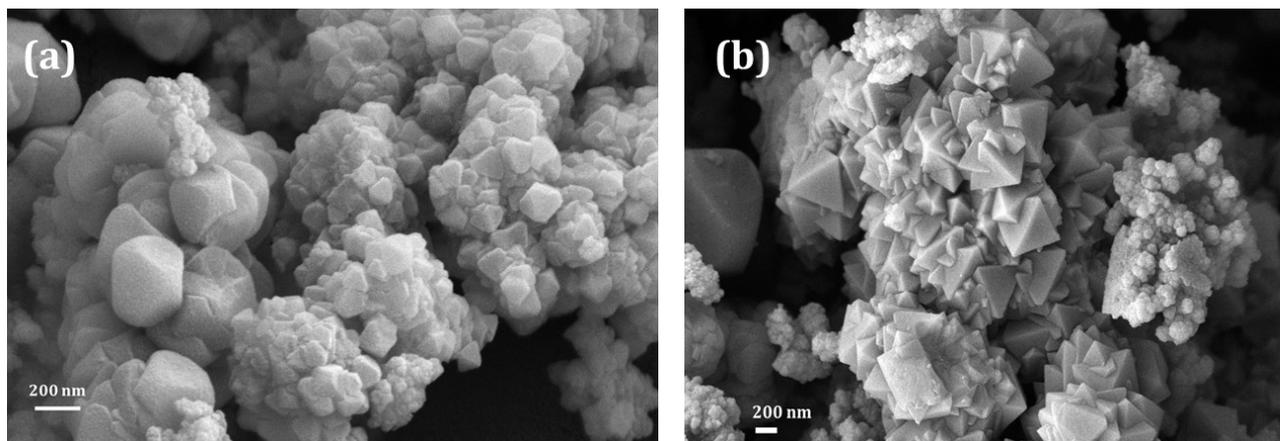
Thiol MOF Zr-DMBD was synthesized by following the reported procedure (**Reaction scheme 2**).<sup>2, 3</sup> In brief, 95 mg (0.41 mmol) of 2,5-dimercaptoterephthalic acid (H<sub>2</sub>DMBD) and 96 mg (0.41 mmol) ZrCl<sub>4</sub> was taken in a Pyrex glass tube inside a glovebox, then 16 ml of anhydrous DMF was added which makes clear yellow solution. After 10 minutes of sonication, 3.9 ml of CH<sub>3</sub>COOH (3.94 g, 65.7 mmol) was added to the glass tube, removed from the glovebox, and kept in a preheated oven for 24 h at 120 °C to get light yellow precipitation. After natural cooling, the light-yellow powder was collected by centrifugation and washing with DMF. Finally, after washing with dichloromethane (DCM), the compound was dried for 12 h at 60 °C in a vacuum oven to get 110 mg compound.

## Synthesis of thiol MOF Ag@Zr-DMBD

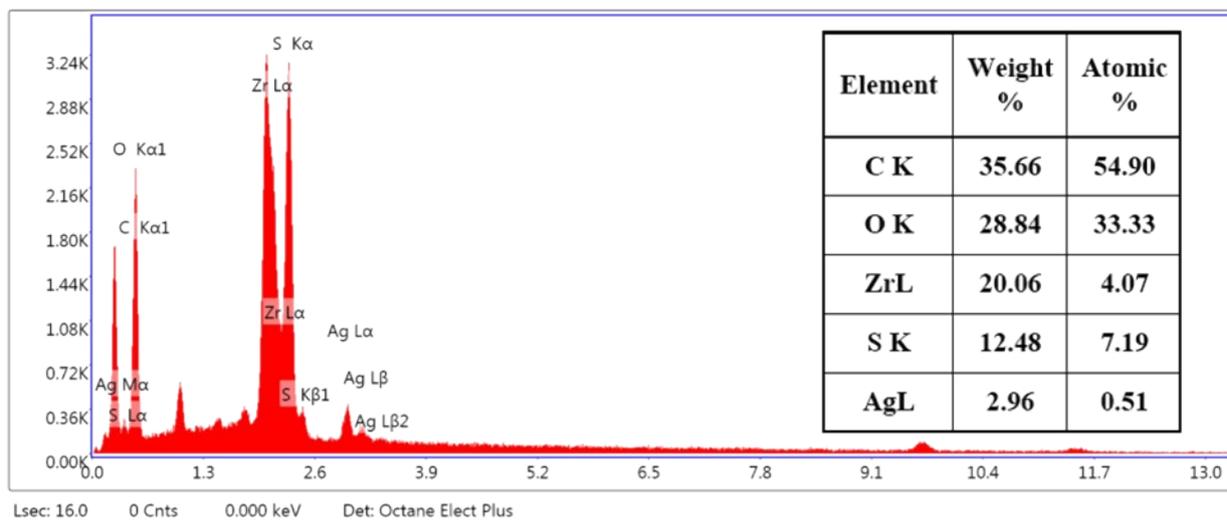
In 10 ml of an acetonitrile solution of 10 mg (0.06 mmol) AgNO<sub>3</sub>, 50 mg of Zr-DMBD was added and stirred for 8 hours at room temperature in nitrogen atmosphere; after that, the compound was collected by filtration using excess acetonitrile to avoid unreacted AgNO<sub>3</sub>. The compound was collected after drying at 40 °C in a vacuum oven for 12 h to get 54 mg Zr-DMBD-Ag(I). Finally, the 10 ml ethanolic solution of 10 mg (0.26 mmol) NaBH<sub>4</sub> was added

to 10 ml ethanolic suspension of Zr-DMBD-Ag(I) and stirred in the dark for 30 min at 0 °C to get 48 mg Ag@Zr-DMBD. The catalyst was collected by centrifugation and then dried in a vacuum oven for 12 h at 60 °C to make an activated catalyst.

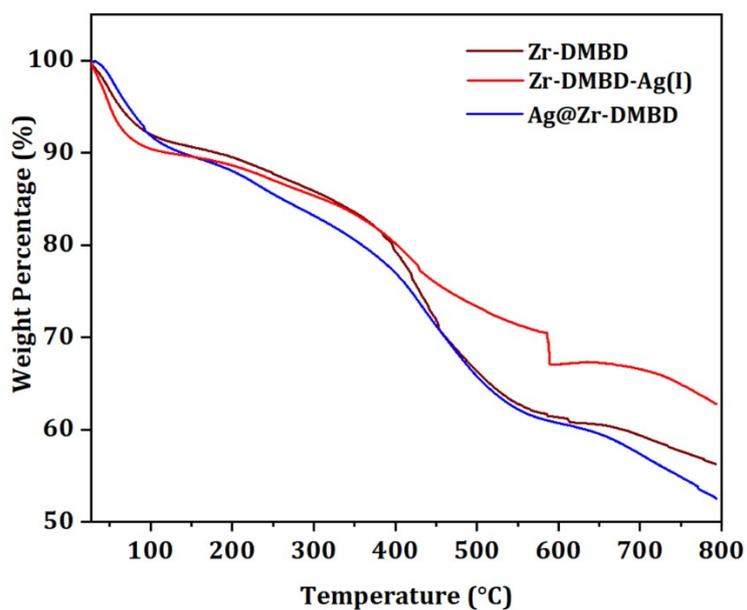
## Characterizations



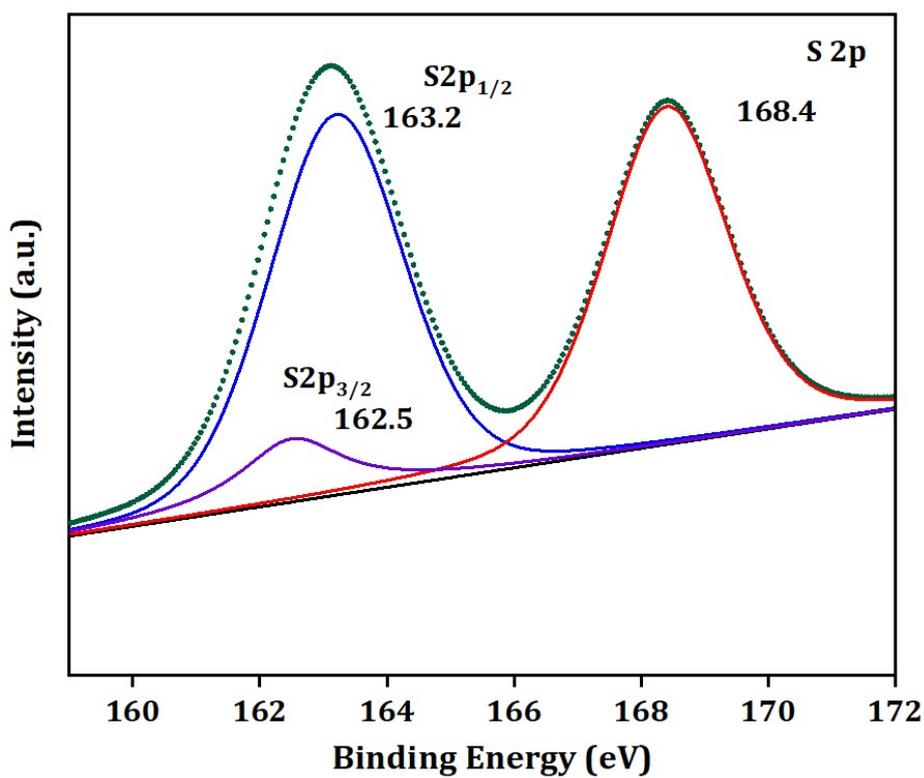
**Figure S4:** SEM images of (a) Zr-DMBD (b) Zr-DMBD-Ag(I).



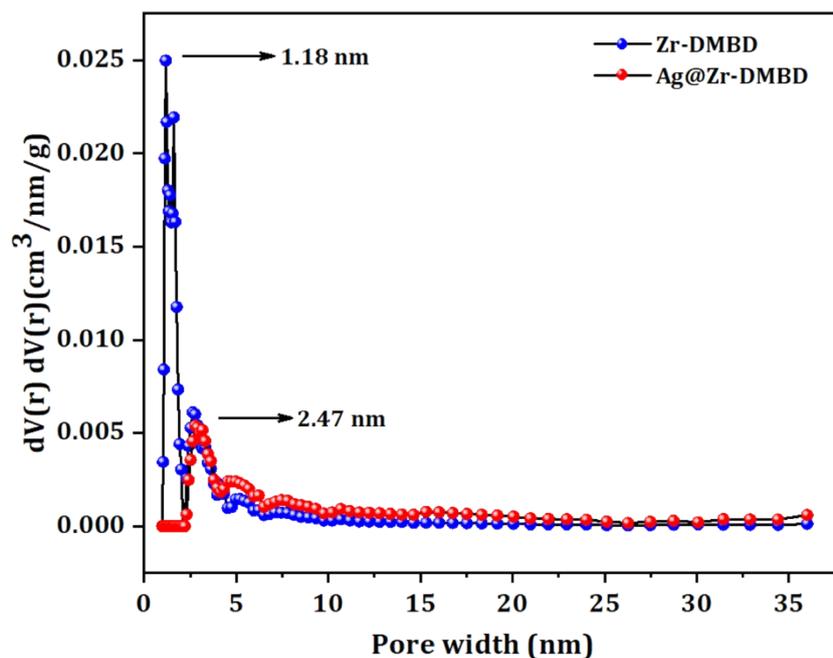
**Figure S5:** SEM-EDX analysis of Ag@Zr-DMBD.



**Figure S6:** Thermogravimetric analysis (TGA) of Zr-DMBD and Zr-DMBD-Ag(I) and Ag@Zr-DMBD.



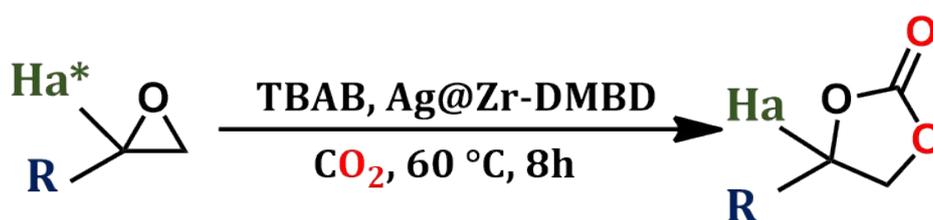
**Figure S7:** XPS spectrum of S 2p for Ag@Zr-DMBD.



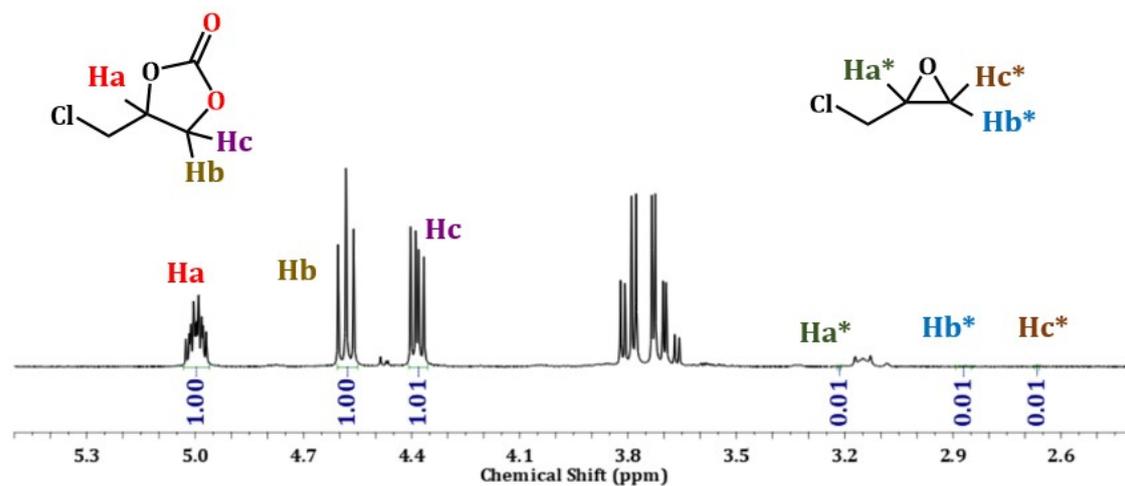
**Figure S8:** Pore size distribution plot of Zr-DMBD and Ag@Zr-DMBD.

### Terminal epoxide CO<sub>2</sub> fixation to cyclic-carbonate: a general protocol

The catalytic conversion of terminal epoxides was performed in a 25 ml round bottom flask (RB) by taking 5 mmol of the substrate, with the contentious flow of CO<sub>2</sub> in presence of TBAB as a co-catalyst without any solvents. After different time interval the aliquot of the reaction is collected and <sup>1</sup>H NMR was checked to measure the conversion of the terminal epoxide to cyclic Carbonate. The conversion of the substrate to the product is calculated by the following formula.

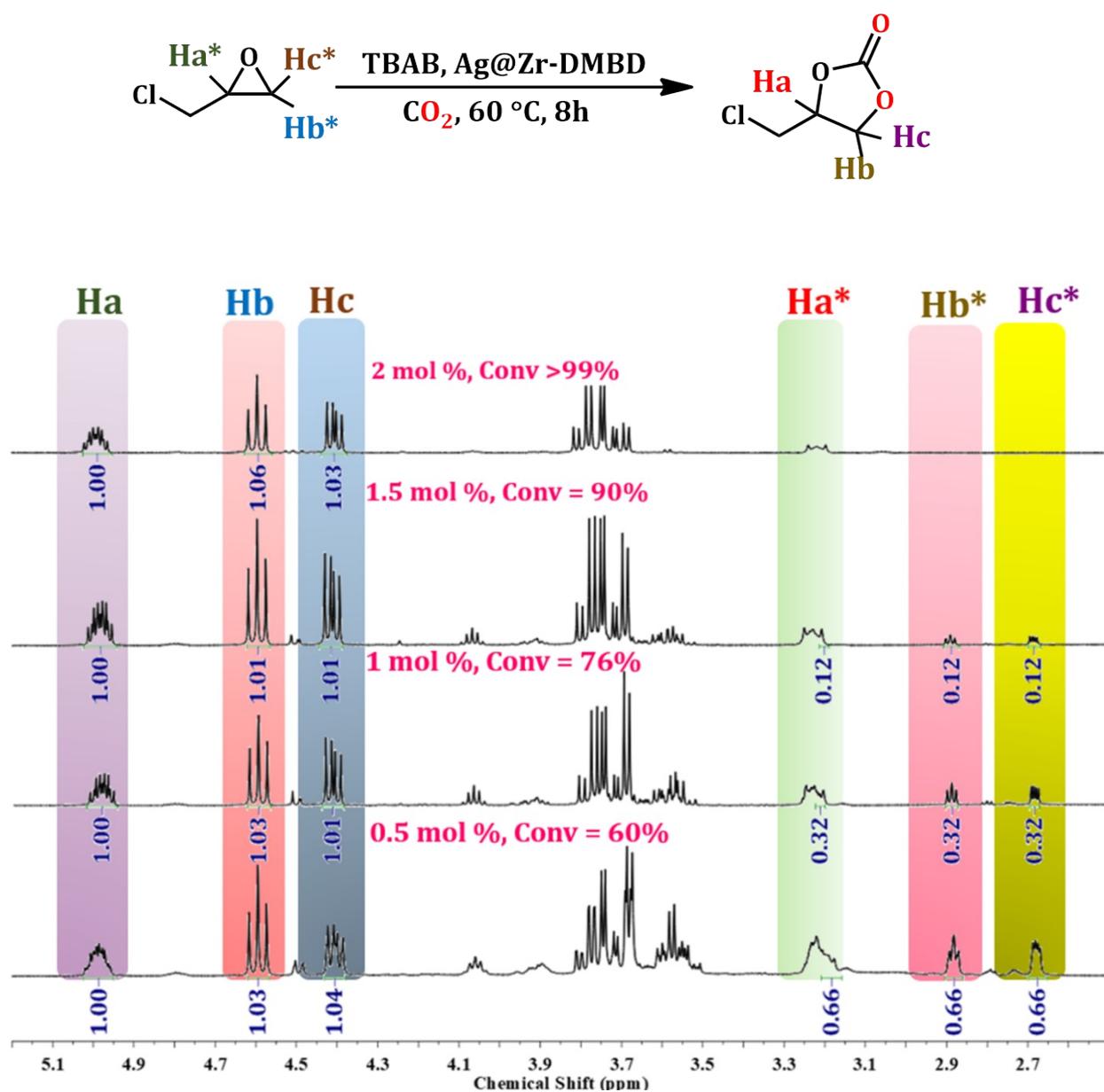


$$\text{Conversion} = \frac{Ha}{Ha + Ha^*} \times 100 \%$$

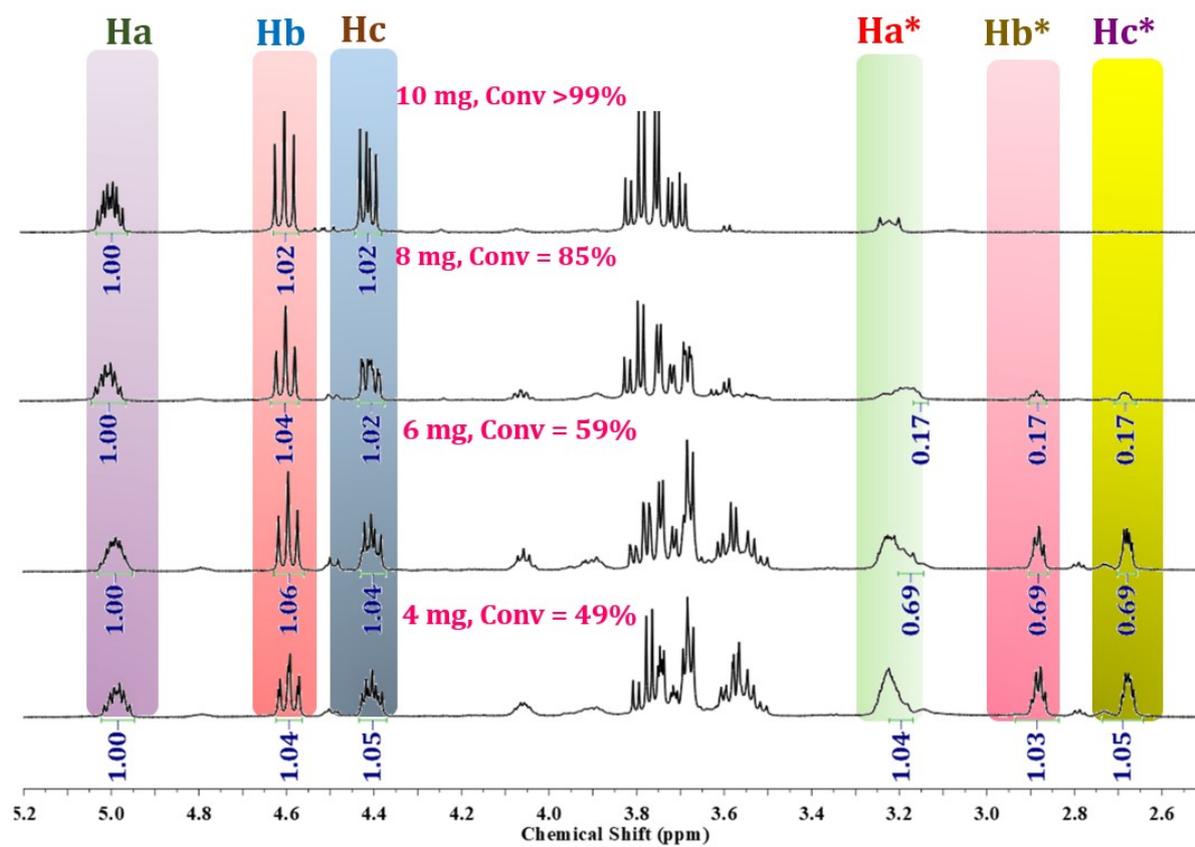


**Figure S9:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra for the cycloaddition of epichlorohydrin by Ag@Zr-DMBD.

## Kinetic study

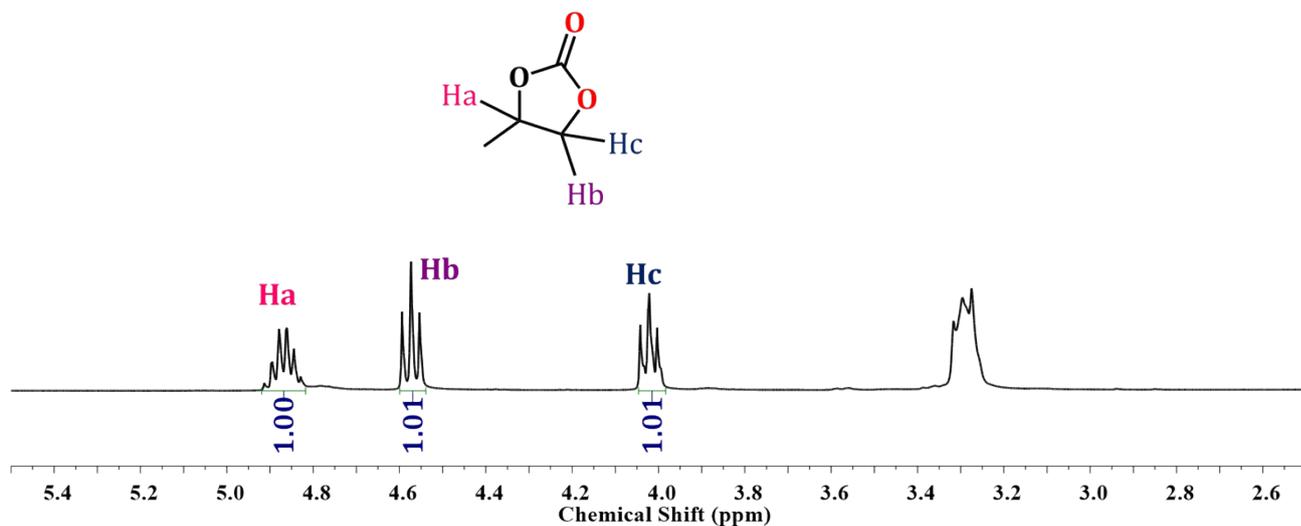


**Figure S10:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra for the cycloaddition of epichlorohydrin by Ag@Zr-DMBD with respect to co-catalyst (TBAB) amount (Kinetic study).

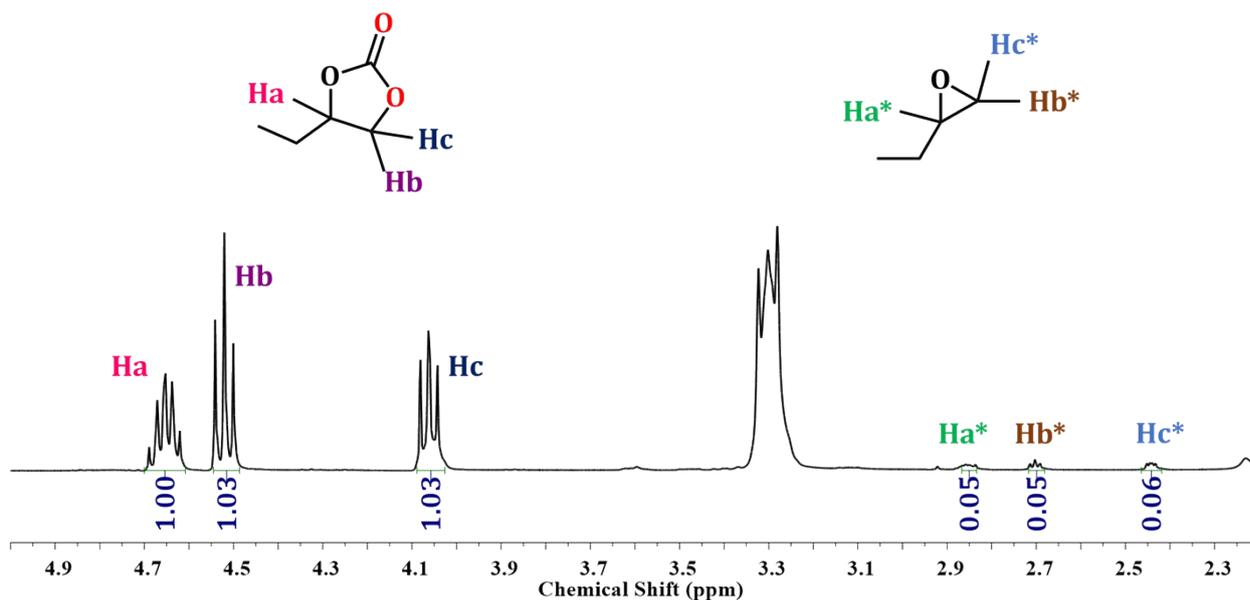


**Figure S11:**  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz) spectra for the cycloaddition of epichlorohydrin by Ag@Zr-DMBD with respect to catalyst amount (Kinetic study).

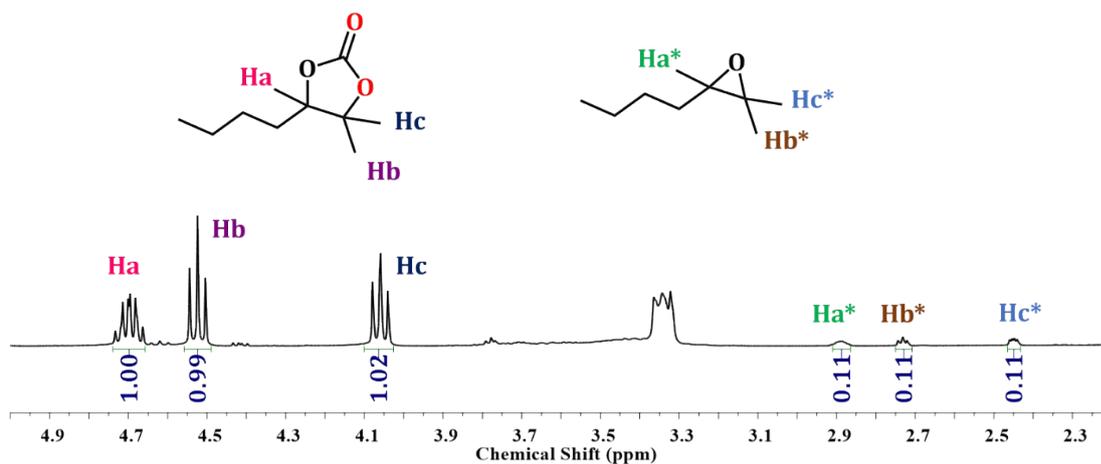
## Substrate Scope



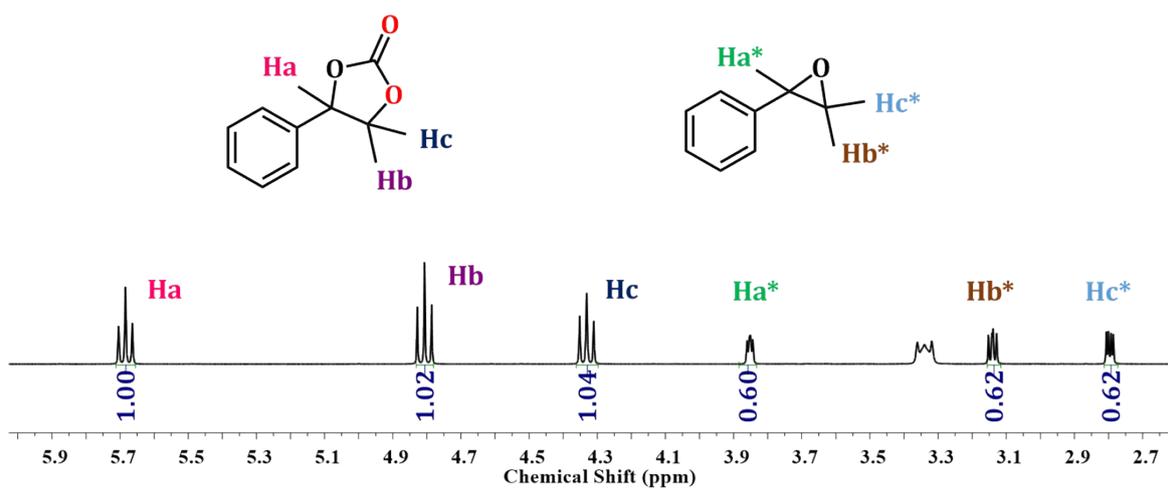
**Figure S12:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra for the Propylene oxide cycloaddition reaction with CO<sub>2</sub> using the catalyst Ag@Zr-DMBD.



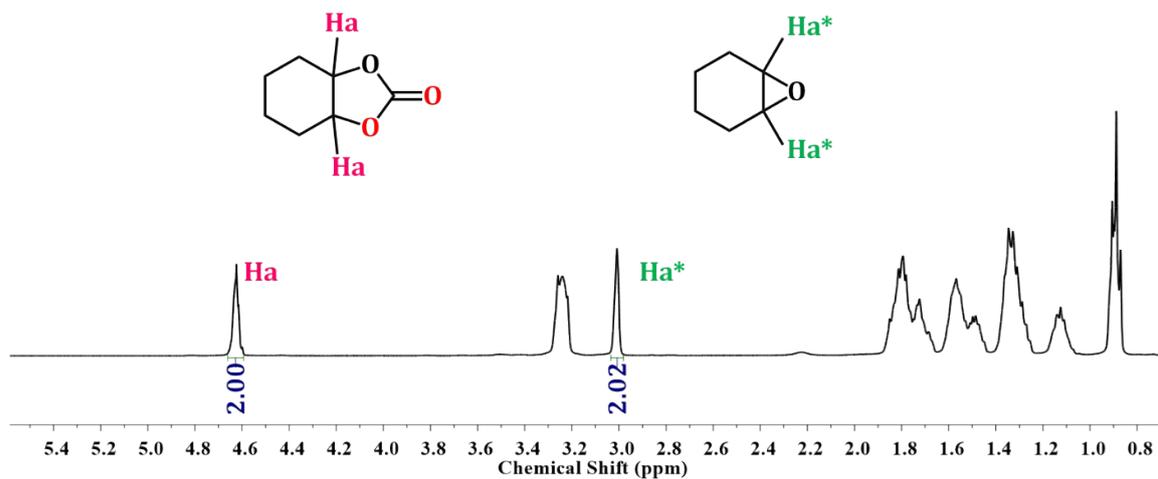
**Figure S13:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra for the 1,2-Epoxybutane cycloaddition reaction with CO<sub>2</sub> using the catalyst Ag@Zr-DMBD.



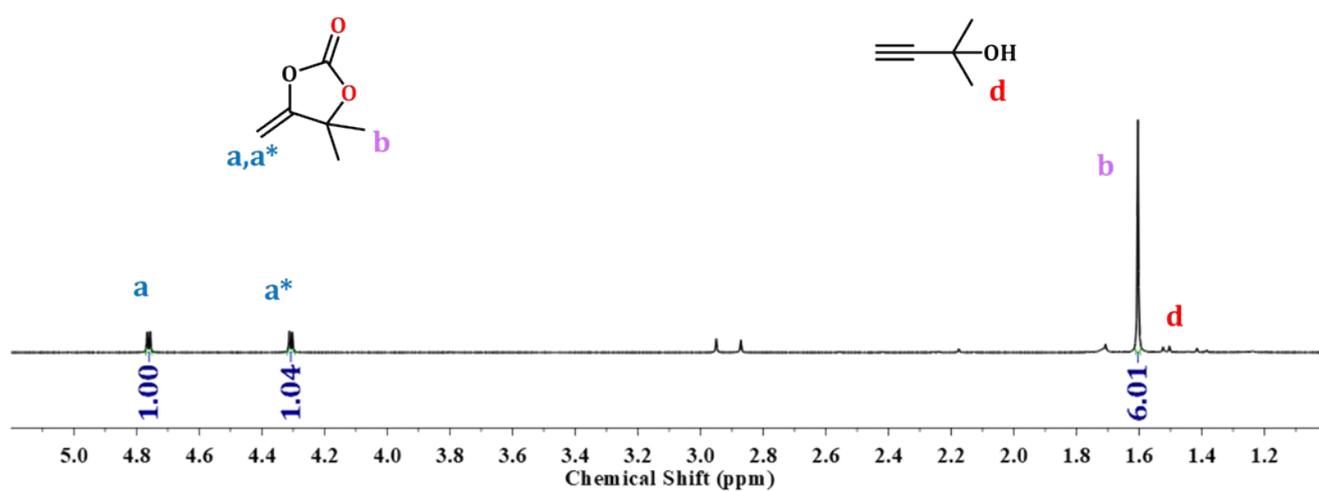
**Figure S14:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectra for the 1,2-Epoxyhexane cycloaddition reaction with  $\text{CO}_2$  using the catalyst  $\text{Ag@Zr-DMBD}$ .



**Figure S15:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectra for the cycloaddition reaction of Styrene oxide cycloaddition reaction with  $\text{CO}_2$  using the catalyst  $\text{Ag@Zr-DMBD}$ .

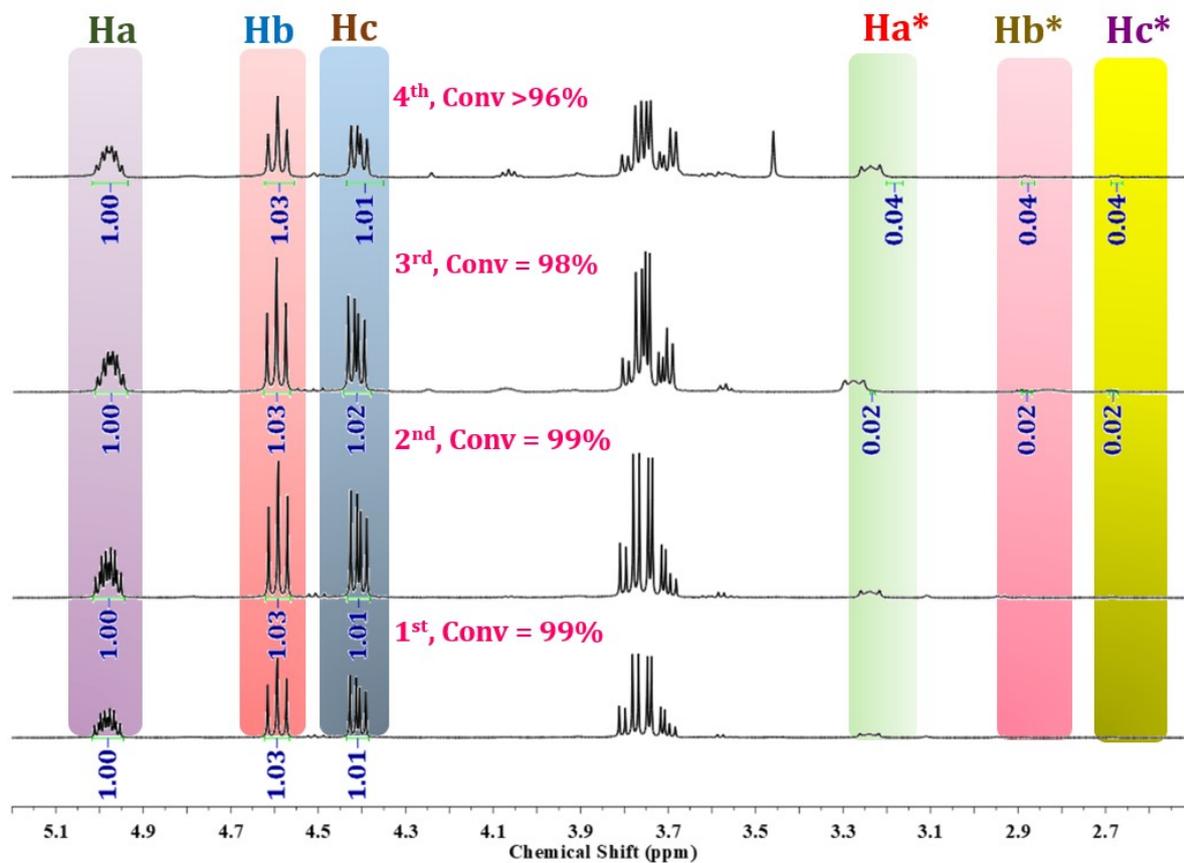


**Figure S16:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectra for the cycloaddition reaction of 1,2-cyclohexane oxide cycloaddition reaction with  $\text{CO}_2$  using the catalyst  $\text{Ag@Zr-DMBD}$ .

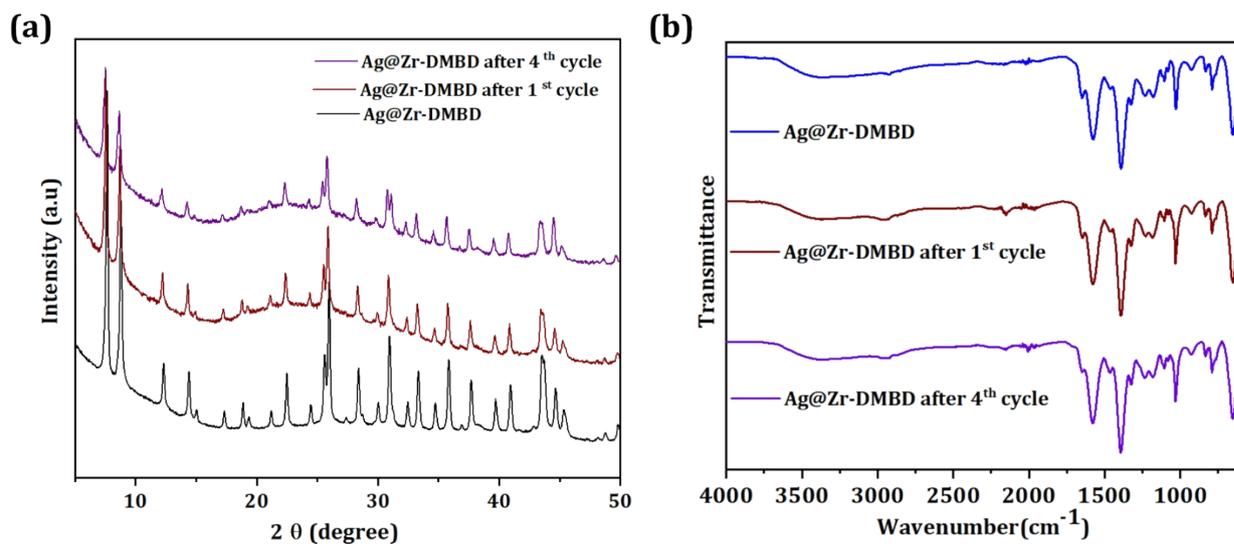


**Figure S17:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectra for the cycloaddition reaction of 2-Methyl-3-butyn-2-ol cycloaddition reaction with  $\text{CO}_2$  using the catalyst  $\text{Ag@Zr-DMBD}$ .

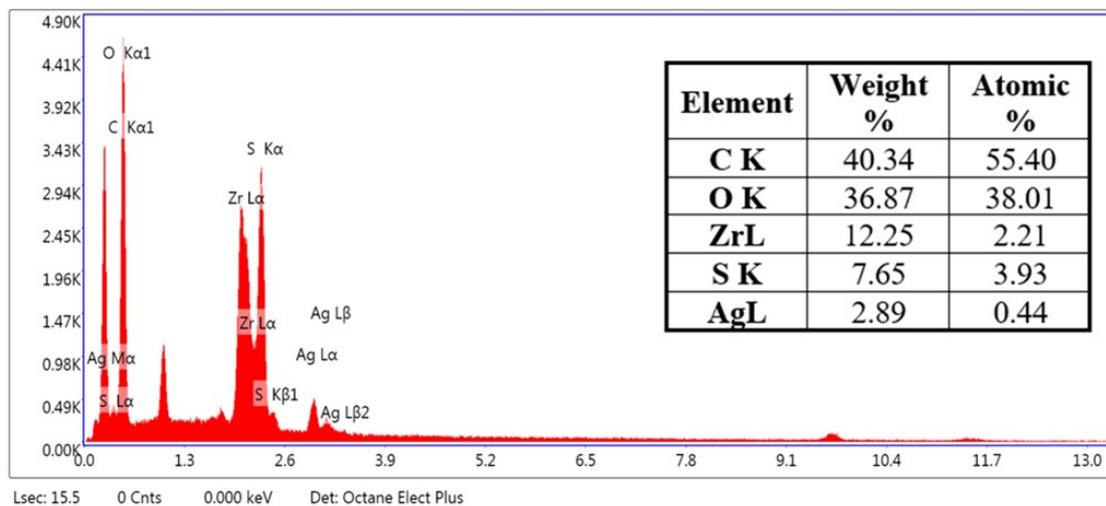
## Recyclability test of the catalyst (Ag@Zr-DMBD)



**Figure S18:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra for the cycloaddition of epichlorohydrin by Ag@Zr-DMBD in different cycle of reactions (recyclability).



**Figure S19** (a) PXRD pattern of synthesised Ag@Zr-DMBD, Ag@Zr-DMBD after 1<sup>st</sup> cycle and after 4<sup>th</sup> cycle. (b) IR spectra of synthesised Ag@Zr-DMBD, Ag@Zr-DMBD after 1<sup>st</sup> cycle and after 4<sup>th</sup> cycle.



**Figure S20: SEM-EDX analysis of Ag@Zr-DMBD after catalysis.**

## Comparison Table

**Table S1:** Analysing the catalytic activity of Ag@Zr-DMBD in comparison to the other reported literature for CO<sub>2</sub> fixation of the epichlorohydrin.

Sl No.	Catalyst	Pressure (bar)	Temperature (°C)	Conversion (%)	Time (h)	Ref.
1	Al fumarate	10	50	95	6	4
2	MIL-101(Cr)	8	RT	82	24	5
3	ZIF-67	8	95	99	8	6
4	ZIF-8	7	80	44	4	7
5	ZIF-8-NH <sub>2</sub>	7	80	73	4	7
6	[Ni(H <sub>2</sub> O) (Hpdcd) (H <sub>2</sub> O) <sub>2</sub> ].DMF	1	100	80	72	8
7	Zn-DABCO	8	100	99	12	9
8	Ni-DABCO (100)	8	100	75	12	9
9	SYSU-Zn@IL2	10	80	99	12	10
10	Pd@MTiO <sub>2</sub>	1	80	98.0	2	11
11	[Ag <sub>10</sub> (H <sub>3</sub> L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (4,4'-bipy)]	10	100	87	6	12
12	Ag (4.8 mol%)/α-Fe <sub>2</sub> O <sub>3</sub>	1	105	86	20	13
13	Au (4.8 mol%)/α-Fe <sub>2</sub> O <sub>3</sub>	1	105	91	20	13
14	Au@Zn MOF	1	80	99	8	14
15	Ag@In MOF	1	80	99	8	15
16	6%-Ag/TUD-1	10	60	98	4	16
17	Ag@MOF-s-SH	1	80	68.4	3	17
18	Ag@Zr-DMBD	1	60	99	8	This Work

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