# Supplementary Information

for

# Organic nanocage: A promising testbed for catalytic CO<sub>2</sub> conversion

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Nuclear magnetic resonance (NMR) spectroscopy: The solution state <sup>1</sup>H spectra were recorded on Bruker Avance III 500 MHz NMR spectrometers. The residual solvent signals were used as internal standard, and chemical shifts ( $\delta$ ) are reported in parts per million (ppm). The yields of the cyclic carbonates during catalysis were calculated using 1,1,2,2-tetrachloroethane as an external NMR standard.

**Fourier-transform infrared spectroscopy (FTIR):** FTIR measurements were done on Perkin-Elmer Model 2000 FTIR using KBr pellet. Thirty scans were signal-averaged, with a resolution of 8 cm<sup>-1</sup> at ambient temperature.

**Electron spray ionization-gas chromatography mass spectrometry (ESI-GCMS):** ESI-GCMS was carried on Agilent 7890A GC with 5975C MS system spectrometer using 1,1,2,2-tetrachloroethane as an external standard to calculate the yields of the cyclic carbonates.

**Thermogravimetric analysis (TGA):** TGA was carried out using Perkin Elmer TGA-6000 instrument. The sample was heated from 30 °C to 600 °C under nitrogen atmosphere at a rate of 10 °C min<sup>-1</sup>.

**Single-crystal X-ray diffraction (SCXRD):** The crystals of Cg-Im were obtained directly during the course of the reaction in EtOAc and the data was collected using a Bruker APEX II diffractometer employing Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) in phi ( $\phi$ ) and omega ( $\omega$ ) scan. The data collection, integration, scaling unit, cell measurements and absorption corrections were carried using a Bruker Smart Apex II software.

**Powder X-ray diffraction (PXRD):** PXRD experiment was done on PANalytical Empyrean XRD instrument. Data was collected for  $2\theta$  values ranging from 5° to  $60^{\circ}$ .

**Field emission scanning electron microscopy (FESEM):** The surface morphology of all the cages was examined using a Carl Zeiss (Ultraplus) field emission scanning electron microscope. Samples for microscopy were prepared by drop casting a homogeneous dilute CHCl<sub>3</sub> solution (1 mM) of the organic cages over silicon wafer over an adhesive carbon tape. All samples were coated with a thin layer of sputtered gold prior to imaging. FESEM was carried out using an accelerating voltage of 5 kV and 10 kV.

**Transmission electron microscopy (TEM):** The morphology of the cages was examined using FEI TALOS 200S instrument at a working voltage of 200 kV. The samples for TEM analysis were prepared

by drop casting a homogeneous dilute CHCl<sub>3</sub> solution (1 mM) of the organic cages over a carbon coated 400 mesh Cu grid. Energy dispersive X-ray spectroscopy (EDS) was examined at a working voltage of 200 kV using Cu as a reference.

**Gas adsorption studies:** All the gas adsorption measurements were performed on Quantachrome Autosorb QUA211011 equipment. The temperature was maintained using liq.  $N_2$  for the measurements at 77 K and chiller bath for measurements at 273 K and 298 K. Isotherms were analyzed using ASIQwin software. All the samples were treated at room temperature for 24 h under high vacuum before the analysis.

## **II.** Fabrication of organic cages

### (a) Chemicals

All the chemicals were used as received unless stated otherwise. 1,3,5-benzenetricarboxaldehyde (97%), tetrabutylammonium bromide ( $\geq$ 99%), ( $\pm$ )-propylene oxide ( $\geq$ 99.5%), propylene carbonate (99.7%), ethylenediamine ( $\geq$ 98%) were received from Sigma-Aldrich. 1,1,2,2-Tetrachloroethane ( $\geq$ 98%) was received from Sigma-Aldrich and used as an external standard for the % yield calculations.

#### (b) Synthesis of Cg-Im

In a 50 mL beaker, 1 mmol of 1,3,5-benzenetricarboxaldehyde was suspended in 30 mL EtOAc. To the dispersed solution, ethylenediamine (1.5 mmol) in 10 mL of EtOAc was added slowly and the reaction was allowed to continue for 72 h at room temperature. A white colored crystals were isolated (yield: 72%).



Scheme S1 Schematic illustration of the fabrication of Cg-Im through Schiff base condensation reaction.

<sup>1</sup>**H-NMR:** (500 MHz, CDCl<sub>3</sub>) 8.19 (12 H, s), 7.93 (12 H, s), 4.02 (24 H, s). Diffusion coefficient: 4.988 x  $10^{-10}$  m<sup>2</sup> s<sup>-1</sup>.

**MALDI-TOF**: Calculated m/z for  $C_{48}H_{48}N_{12}$  [M<sup>+</sup>] 793.00, found [M<sup>+</sup>] 793.41.

## **Crystallographic details of Cg-Im**

We checked the crystal structure of Cg-Im to confirm the formation of cage structure. The molecular structure obtained from the crystal structure analysis was found to be identical as that of the reported one with CCDC No. 707056.<sup>1</sup>



Figure S1 The molecular structure of Cg-Im obtained from the single crystal analysis.

| Table S1. Crystal data and structure refinement for Cg-Im |  |  |  |  |  |
|---|--|--|--|--|--|
| Temperature   | 100(2) K   |  |  |  |  |
| Wavelength  | 0.71073 Å  |  |  |  |  |
| Crystal system  | Monoclinic   |  |  |  |  |
| Space group   | C2/c   |  |  |  |  |
| Unit cell dimensions                                      | a = 31.92(3) Å, $b = 18.35(3)$ Å, $c = 22.07(2)$ Å                               |  |  |  |  |
|   | $\alpha = 90^{\circ}, \beta = 98.85(4)^{\circ} \text{ and } \gamma = 90^{\circ}$ |  |  |  |  |
| Volume  | .2771(27) Å <sup>3</sup>   |  |  |  |  |
| Z   | 24   |  |  |  |  |
| Density (calculated)                                      | 1.187 mg/m <sup>3</sup>  |  |  |  |  |
| Absorption coefficient                                    | 0.076 mm <sup>-1</sup>   |  |  |  |  |
| F(000)  | 4800   |  |  |  |  |
| Theta range for data collection                           | 2.183 to 25.136°.  |  |  |  |  |
| Reflections collected                                     | 104499   |  |  |  |  |
| Independent reflections                                   | 22320 [R(int) = 0.3873]  |  |  |  |  |
| Completeness to theta =                                   | 98.9 %   |  |  |  |  |
| 25.136°   |  |  |  |  |  |
| Refinement method   | Full-matrix least-squares on   |  |  |  |  |
|   | F <sup>2</sup>   |  |  |  |  |
| Data / restraints / parameters                            | 22320 / 2 / 625  |  |  |  |  |
| Goodness-of-fit on F <sup>2</sup>                         | 1.702  |  |  |  |  |
| Final R indices [I>2sigma(I)]                             | R1 = 0.2086, wR2 = 0.4021  |  |  |  |  |
| R indices (all data)                                      | R1 = 0.4440, wR2 = 0.4633  |  |  |  |  |
| Largest diff. peak and hole                               | 1.471 and -0.565 e.Å <sup>-3</sup>   |  |  |  |  |

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#### (c) Synthesis of Cg-Am

The imine cage (55 mg) was dissolved in a  $CH_2Cl_2/CH_3OH$  mixture (v/v, 1/1, 20 mL) with stirring. To the clear solution, NaBH<sub>4</sub> (55 mg) was added and the reaction was stirred for 15 h at room temperature. Water (1 mL) was then added, and the solution was continuously stirred for 9 h. The solvent was then removed under vacuum. The resulted solid was washed with water and collected by centrifugation, dried at 70 °C under vacuum overnight.



Scheme S2 NaBH<sub>4</sub> reduction of Cg-Im for the synthesis of Cg-Am.

<sup>1</sup>H-NMR: (500 MHz, CDCl<sub>3</sub>) 7.09 (12 H, s), 3.69 (24 H, s), 2.69 (24 H, s).
<sup>13</sup>C-NMR: (126 MHz, CDCl<sub>3</sub>) 140.51, 126.65, 53.77, 48.68.
MALDI-TOF: Calculated m/z for C<sub>48</sub>H<sub>72</sub>N<sub>12</sub> [M<sup>+</sup>] 817.19, found [M<sup>+</sup>] 817.6.

# III. Characterizations of Cg-Im and Cg-Am

#### (a) Fourier-transform infrared spectroscopy (FTIR):

The FTIR spectra of 1,3,5-benzenetricarboxaldehyde (brown), ethylenediamine (blue) and Cg-Im (green) are shown in the Fig. S2. It is noticeable that the peak at 1700 cm<sup>-1</sup> corresponding to the aldehydic carbonyl (C=O) stretching disappears and a new peak emerges at 1650 cm<sup>-1</sup> due to the formation of the imine (C=N) suggesting the Schiff base condensation. Whereas, the peaks at 2830 and 2920 cm<sup>-1</sup> appear due to the sp<sup>3</sup> symmetric as well as asymmetric stretching of the methylene group (-CH<sub>2</sub>-), respectively, which further confirm the formation of imine cage (Cg-Im). The reduction of Cg-Im with NaBH<sub>4</sub> to Cg-Am was confirmed by the disappearance of the peak at 1650 cm<sup>-1</sup>. The FTIR spectrum of Cg-Am after treatment at 120 °C for 12 h suggests no structural change when compared to that obtained at ambient room temperature (Fig. S2b).



**Figure S2** The comparative analysis of FTIR spectra of (a) benzenetricarboxaldehyde (blue), ethylenediamine (orange), Cg-Im (brown), Cg-Am (green) and (b) Cg-Am at ambient room temperature (blue) and after treatment at 120 °C for 12 h (green).

#### (b) Powder X-ray diffraction analysis (PXRD):

The PXRD data of the organic nanocages was measured at a  $2\theta$  range of 5° to 60° as shown in Fig. S3. The analysis revealed a highly crystalline nanocage Cg-Im transforms to nearly an amorphous cage (Cg-Am) after the reduction with NaBH<sub>4</sub>. The cage Cg-Im was found to be highly crystalline as reflected from the PXRD pattern (Figure S3), due to the rigid imine functionality. Whereas, Cg-Am due to the presence of amine functionality, possesses a high degree of flexibility that led to inefficient packing of Cg-Am resulting in amorphous nature.



Figure S3 The PXRD analysis of Cg-Im (green) and Cg-Am (blue).

#### (c) Thermogravimetric analysis (TGA):

The thermogravimetric analysis (TGA) of the organic nanocages showed a high thermal stability up to 320 °C (Fig. 2b). The weight loss (~ 16%) at around 100 °C is due to the presence of the moisture in Cg-Am.

#### (d) Microscopic characterizations

The samples were air dried for 12 h before the microscopic analysis. The Field emission scanning electron microscopy (FESEM) images of Cg-Im revealed a needle like morphology ~1 µm size whereas agglomerates of granular morphology was observed in the case of Cg-Am (Fig. S4). The HR-TEM images of Cg-Im confirm the needle like morphology with the presence of the porous texture. Whereas, a homogeneous distribution of granular morphology with a particle size of 100-150 nm was observed for Cg-Am. The selected area electron diffraction (SAED) pattern also corroborates with the PXRD results showing the crystalline and amorphous nature of Cg-Im and Cg-Am, respectively (Fig. S5).



Figure S4 FESEM images of (a) Cg-Im and (b) Cg-Am taken at a magnification of 30 kX.



**Figure S5** High resolution transmission electron microscopy images of (a) Cg-Im and (b) Cg-Am taken at a magnification of 58 kX. The selected area electron diffraction pattern revealed the crystalline nature of Cg-Im (c) and amorphous nature of Cg-Am (d).

#### (e) Gas adsorption studies of Cg-Im and Cg-Am

#### (i) Nitrogen gas sorption and porosity

The porosity and the surface area of the nanocages were estimated using the  $N_2$  sorption profile obtained at 77 K. The Brunauer–Emmett–Teller (BET) specific surface areas of the nanocages were found to be 104 (Cg-Im) and 5 (Cg-Am) m<sup>2</sup> g<sup>-1</sup> respectively, with a type III sorption profile in each case (Fig. S6, S7).

The nonlocal density functional theory (NLDFT) method was employed to estimate the pore size distribution of the nanocages. It revealed a mesoporous nature with the peak centred at 3.1 (Cg-Im) and 2.8 (Cg-Am) nm of pore width (Fig. S6b, S7b, respectively). The uptake due to the unrestricted monolayermultilayer adsorption was observed at a relative pressure of  $0.15 < P/P_0 < 0.9$ . The high abundance of the interparticular voids<sup>2</sup> is reflected by the sharp adsorption at  $P/P_0 > 0.95$  (Fig.S6a, S7a). The specific surface area plots for Cg-Im and Cg-Am are shown in Fig. S8a, S8b, respectively. The plot was obtained by fitting the BET equation as given below.

$$\frac{P/P_0}{n\left(1-\frac{P}{P_0}\right)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} (P/P_0)$$

Where,  $P/P_0$  refers to the relative pressure,  $n_m$  refers to the specific monolayer capacity, n is the specific amount adsorbed at  $P/P_0$  and C is the BET constant. The low value of S<sub>BET</sub> of Cg-Am refers to the increase in the flexibility as compared to Cg-Im with a surface area of 104 m<sup>2</sup> g<sup>-1</sup>.



**Figure S6** (a) Nitrogen sorption profile of Cg-Im and (b) the pore size distribution profile estimated by the NLDFT method.



**Figure S7** (a) Nitrogen sorption profile of Cg-Am and (b) the pore size distribution profile estimated by the NLDFT method.



Figure S8 The specific BET surface area plot of (a) Cg-Im and (b) Cg-Am.

#### (ii) Carbon dioxide gas sorption

The CO<sub>2</sub> sorption measurements (Fig. S9) showed an uptake of 2.3 and 3.9 wt% at 273 K and 1 bar for Cg-Im and Cg-Am, respectively. (Fig. S9a, S9b, respectively). A large hysteresis (H4) was observed in the case of Cg-Am (Fig. S8b) due to the stronger electrostatic interaction compared to that of the imine cage (Cg-Im) providing more stabilization for CO<sub>2</sub> in the adsorption sites. <sup>3</sup>



Figure S9 The CO<sub>2</sub> sorption isotherm of (a) Cg-Im and (b) Cg-Am measured at 273 K, 1 bar pressure.

#### IV. Catalytic conversion of CO<sub>2</sub> and epoxide into cyclic carbonates by Cg-Am

All the CO<sub>2</sub> conversion experiments were performed with 8.6 mmol of the epoxide and a CO<sub>2</sub> pressure of 2.5 bar. Briefly, TBAB (2.5 mol%) and catalyst (0.025 mmol) were taken in Schlenk-sealed tube and deaerated and filled with CO<sub>2</sub>. Under ice-cold conditions, epoxide of particular interest was added and the CO<sub>2</sub> pressure was set at 2.5 bar and further, allowed to stir at 90 °C. Later, the reaction mixture was cooled and 1,1,2,2-tetrachloroethane was added as an external NMR standard for the calculation of yields. The product formed was isolated by column chromatography using 20% EtOAc/Hexane as eluent. The Cg-Im formed heterogeneous dispersion in the reaction medium, we could easily recover it, and the catalytic conversion was found to be similar in the subsequent cycle (Figure S24). Whereas Cg-Am formed a homogeneous medium with reactants and products, and it was challenging to recover.



**Figure S10** The energy minimized structures of Cg-Am along with various substrates highlighting the possible interactions with oxoanion intermediates of (a) propylene oxide, (b) styrene oxide, (c) cyclohexene oxide, and (d) hexene oxide using molecular mechanics (MM2) calculations.

| S. No. | Epoxide              | Cyclic carbonate                         | Conversion | TON |
|--------|----------------------|--|------------|-----|
| 1.     | گ                    |  | 52         | 169 |
| 2.     | осі                  | o<br>o<br>c                              | 92         | 316 |
| 3.     | ٩                    | °, °, °, °, °, °, °, °, °, °, °, °, °, ° | 34         | 116 |
| 4.     | O<br>Ph              | O<br>O<br>O<br>Ph                        | 53         | 169 |
| 5.     | O<br>O <sub>Ph</sub> | o<br>o<br>o<br>o<br>O<br>Ph              | 59         | 202 |
| 6.     | Ŏ                    |  | 28         | 100 |

**Table S2** The catalytic performance of organic amine cage (Cg-Am, 0.025 mmol) for the cycloaddition of  $CO_2$  and epoxides at 90 °C for 12 h in the presence of 2.5 mol% of TBAB. The substrate scope is indicated along with the turn over number (TON).

# V. A comparative account of catalytic CO<sub>2</sub> conversion by Cg-Am

| S. No. | Catalyst<br>(mmol)                                    | Substrate<br>(mmol) <sup>#</sup> | Pressure<br>(bar) | Temp and<br>reaction<br>time | TBAB<br>(mol%)            | Solvent          | Conv.<br>(%) | Reference  |
|--------|---|----------------------------------|-------------------|------------------------------|---------------------------|------------------|--------------|--|
| 1.     | Cg-Am<br>(0.075)                                      | PO<br>(8.6)                      | 2.5               | 90 °C (9 h)                  | 2.5                       | ×                | 95           | Present study  |
| 2.     | Squaramide- <b>5</b><br>(0.1)                         | HO<br>(2)                        | 10                | 45 °C (18 h)                 | 5<br>(TBAI)               | MEK              | 74           | ACS Catal.<br>2017, <b>7</b> , 3532. <sup>4</sup>                              |
| 3.     | V (V) complex-3                                       | HO<br>(2)                        | 10                | 85<br>(18 h)                 | 0.25<br>(TBAI)            | ×                | 74           | ACS Catal.<br>2017, <b>7</b> , 2367. <sup>5</sup>                              |
| 4.     | Cr(salophen)<br>Complex<br>(2.5%)                     | РО                               | 1 atm             | 0 °C                         | 2.5                       | ×                | 71           | ACS Catal.,<br>2016, <b>6</b> , 5012. <sup>6</sup>                             |
| 5.     | Cavitand 2b<br>(1%)                                   | SO<br>(5)                        | 1                 | 100 °C                       | 1                         | ×                | 85           | ACS Catal.,<br>2015, <b>5</b> , 6748. <sup>7</sup>                             |
| 6.     | Squaramide- <b>15</b><br>(4%)                         | CO<br>(8)                        | 10                | 80 °C<br>(18 h)              | 5                         | MEK              | 36           | ACS Catal.,<br>2017, <b>7</b> ,3532. <sup>4</sup>                              |
| 7.     | Complex <b>2a</b><br>(0.035)                          | PO<br>(70)                       | 20                | 100 °C<br>(2 h)              | -                         | х                | 55           | ACS Catal.,<br>2012, <b>2</b> , 2029. <sup>8</sup>                             |
| 8.     | <b>1a</b><br>(15%)                                    | SO<br>(0.2)                      | 1 atm             | 120 °C<br>(12 h)             | -                         | PhCl             | 41           | ACS Catal.,<br>2016, <b>6</b> , 6906. <sup>9</sup>                             |
| 9.     | B20<br>(10%)  | EPP<br>(2)                       | 10                | 50 °C<br>(4 h)               | 5<br>(TBAI)               | H <sub>2</sub> O | 90           | <i>ACS Catal.,</i> 2016, <b>6</b> , 4871. <sup>10</sup>                        |
| 10.    | <b>1e</b><br>(0.5%)                                   | PO<br>(10)                       | 20                | 100 °C<br>(4 h)              | -                         | ×                | 78           | ACS Catal.,<br>2015, <b>5</b> , 6773. <sup>11</sup>                            |
| 11.    | [Bu4P]Br<br>(2%)                                      | cis-1a<br>(5)                    | 50                | 100 °C                       | 2<br>(FeBr <sub>3</sub> ) | ×                | 81           | ACS Sustainable<br>Chem. Eng.,<br>2016, <b>4</b> , 4805. <sup>12</sup>         |
| 12.    | 3a/KI/18C6<br>(2%)                                    | BO<br>(25)                       | 10                | 100 °C<br>(3 h)              | -                         | ×                | 92           | <i>Adv. Synth.</i><br><i>Catal.</i> , 2016,<br><b>358</b> , 622. <sup>13</sup> |
| 13.    | MoCl <sub>5</sub> /PPh <sub>3</sub> (1:5)<br>(7.3/42) | PO<br>(1430)                     | 1 atm             | 20 °C<br>(7 d)               | -                         | ×                | 78           | Angew. Chem.<br>In. Ed., 1980, <b>19</b> ,<br>317. <sup>14</sup>               |
| 14.    | З <sub>Мд</sub><br>(0.003%)                           | HO<br>(10)                       | 17                | 120 °C<br>(3 h)              | -                         | ×                | 99           | Angew. Chem.<br>Int. Ed., 2015,<br><b>54</b> , 134. <sup>15</sup>              |
| 15.    | Al-catalyst C<br>(1%)                                 | Epoxide (1)                      | 10                | 25 °C<br>(14 h)              | 5                         | MEK              | 99           | Angew. Chem.<br>Int. Ed., 2016,<br><b>55</b> , 3972. <sup>16</sup>             |
| 16.    | Mn- <b>1a</b><br>(0.05%)                              | PO<br>(4)                        | 1 atm             | 25 °C<br>(8 h)               | 2.0                       | ×                | 88           | <i>Chem. Asian J.</i> , 2017, <b>12</b> , 1048. <sup>17</sup>                  |
| 17.    | Catalyst <b>4</b> (0.5%)                              | РО                               | 50                | 50 °C<br>(24 h)              | -                         | ×                | 50           | <i>Chem. Eur. J.</i> , 2014, <b>20</b> , 15005. <sup>18</sup>                  |
| 18.    | IL-ZnTPP<br>(0.1%)                                    | PO<br>(1)                        | 20                | 60 °C<br>(8 h)               | -                         | ×                | 80           | Sustainable<br>Energy Fuels,<br>2018, <b>2</b> , 125. <sup>19</sup>            |

**Table S3.** Catalytic conversion of  $CO_2$  and epoxide into cyclic carbonate by the amine cage, Cg-Am in comparison with other reported small molecular catalysts based on organic and organic-inorganic scaffolds.

| 19. | Complex <b>6</b> (1.5%)                     | РО           | 1  | 25 °C<br>(24 h) | 1.5            | ×    | 59 | <i>Chem. Eur. J.</i> , 2016, <b>22</b> , 2100. <sup>20</sup>         |
|-----|---|--------------|----|-----------------|----------------|------|----|--|
| 20. | Catalyst <b>2</b><br>(2.5%)                 | ECH          | 10 | 85 °C (18 h)    | -              | х    | 80 | <i>Chem. Eur. J.</i> , 2013, <b>19</b> , 2641. <sup>21</sup>         |
| 21. | Catalyst <b>6a</b><br>(2%)                  | BO<br>(13.9) | 10 | 90 °C<br>(2 h)  | -              | ×    | 56 | <i>Green Chem.</i> , 2017, <b>19</b> , 4435. <sup>22</sup>           |
| 22. | Catalyst <b>3g</b><br>(2.5%)                | SO<br>(2.0)  | 1  | 25 °C (24 h)    | 1%<br>(Ylide)  | х    | 96 | <i>Green Chem.</i> , 2017, <b>19</b> , 3908. <sup>23</sup>           |
| 23. | L <sub>2a</sub> BPh <sub>2</sub><br>(0.045) | ECH<br>(45)  | 16 | 100 °C<br>(2 h) | -              | DMAP | 96 | Sustainable<br>Energy Fuels,<br>2019, <b>3</b> , 1066. <sup>24</sup> |
| 24. | Cr<br>(2.5%)                                | SO           | 1  | 25 °C<br>(24 h) | 2.5%<br>(TBAB) | х    | 92 | <i>Organometallics</i> 2019, <b>38</b> , 469. <sup>25</sup>          |

<sup>#</sup>PO: propylene oxide, HO: hexene oxide, SO: styrene oxide, CO: cyclohexene oxide, BO: butene oxide, ECH: epichlorohydrin, EPP: 1,2-epoxy-3-phenoxypropane.

# VI. NMR spectra



Figure S11 <sup>1</sup>H NMR spectrum of Cg-Im after isolation from the reaction mixture in CDCl<sub>3</sub>.



Figure S12 <sup>1</sup>H NMR spectrum of Cg-Am after isolation from the reaction mixture in CDCl<sub>3</sub>.



Figure S13 The <sup>13</sup>C NMR spectrum of Cg-Am obtained in CDCl<sub>3</sub>.



Figure S14 <sup>1</sup>H NMR spectrum of propylene carbonate after isolation from the reaction mixture.



Figure S15 <sup>1</sup>H NMR spectrum of hexene carbonate after isolation from the reaction mixture.



Figure S16<sup>1</sup>H NMR spectrum of 1,2-epoxy-3-phenoxypropane carbonate after isolation from the reaction mixture.



Figure S17 <sup>1</sup>H NMR spectrum of carbonate of epichlorohydrin after isolation from the reaction mixture.



**Figure S18** <sup>1</sup>H NMR spectrum of the reaction mixture of  $CO_2$  and styrene oxide to styrene carbonate with *1,1,2,2*-tetrachloroethane as external standard.



**Figure S19** <sup>1</sup>H NMR spectrum of the reaction mixture of the cycloaddition reaction of  $CO_2$  with cyclohexene oxide to cyclohexene carbonate with *1*,*1*,*2*,*2*-tetrachloroethane as external NMR standard.



**Figure S20** <sup>1</sup>H NMR spectrum of the reaction mixture of the cycloaddition reaction of propylene oxide to propylene carbonate using Cg-Am (0.025 mmol) with 1, 1, 2, 2-tetrachloroethane as external NMR standard (Table 1, entry 3).



**Figure S21** <sup>1</sup>H NMR spectrum of the reaction mixture of  $CO_2$  and propylene oxide to propylene carbonate using Cg-Am (0.075 mmol) with *1,1,2,2*-tetrachloroethane as external NMR standard (Table 1, entry 4).



**Figure S22** <sup>1</sup>H NMR spectrum of the reaction mixture of cycloaddition reaction of  $CO_2$  with hexene oxide to hexene carbonate using Cg-Am with *1,1,2,2*-tetrachloroethane as external NMR standard.



**Figure S23** <sup>1</sup>H NMR spectrum of the reaction mixture of CO<sub>2</sub> and 1,2-epoxy-3-phenoxypropane to the respective carbonate using Cg-Am.



**Figure S24** <sup>1</sup>H NMR spectrum of Cg-Im after the catalytic cycle and recovering the same from the reaction mixture through filtration and washing with EtOAc.

## **VII. References**

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