Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

A Sustainable Protocol for the Spontaneous Synthesis of Zinc-Glutamate MOF: Efficient Catalyst for Room Temperature CO_2 Fixation Reactions in Wet Conditions

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S1. Experimental

S1.1 Reagents and Methods

L-Glutamic acid (>99 %), $ZnSO_4.7H_2O$ (>99 %), NaOH and (±)-propylene oxide (PO, >99 %) were purchased from Aldrich, Korea and used as received. Doubly distilled water was used for catalyst synthesis. Toluene for GC/internal standard (anhydrous, >99.8%) was purchased from Aldrich. CO_2 of 99.999% purity was used for cycloadditions without further purification.

S1.2 Synthesis of the Catalyst: Instant synthesis of aquazinc(II) glutamate hydrate

Rapid room temperature synthesis of zinc-glutamate-MOF was performed by the direct mixing of L-Glutamic acid (0.294g, 2 mmol), NaOH (0.200g, 5mmol) and $ZnSO_4.7H_2O$ (0.575g, 2 mmol) in aqueous solution. The readily precipitated white material was filtered and dried in air (Fig. S1).

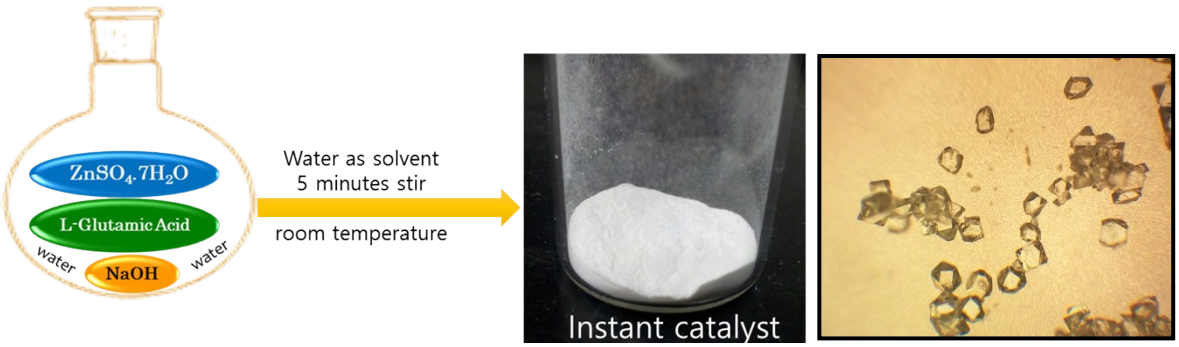

Fig. S1: Scheme for the synthesis of ZnGlu at room temperature, and the images of romm temperature synthesized MOF compared with the single crystals (right).

S1.3 Characterization

Powder X-ray diffraction (XRD) patterns were obtained with a Philips PANalytical X'pert PRO power diffractometer operating at 40 kV and 30 mA by using Ni-filtered CuKa radiation (l=1.5404). The diffractograms were recorded in the 2θ range of 5–50° (Fig. S2). FTIR spectra were obtained with an Avatar 370 Thermo Nicolet spectrophotometer at a resolution of 4 cm^{-1} (Fig. S3). The material surface was observed with an S-4200 field-emission

scanning electron microscope (Hitachi). Thermogravimetric analysis (TGA) was conducted using an AutoTGA 2950 apparatus under a nitrogen flow of 100 mL min^{-1} while heating from room temperature at a rate of 10 °C min^{-1} (Fig. S4). CD spectra was recorded in a JASCO-J715 Spectrophotometer and the solid state spectra was recorded in KBr pellete (Fig. S5). BET measurements (Fig. S7) was recorded in a micromeritics ASAP 2020 instrument after activating the sample at 120 °C for 6 h.

S1.4 Cycloaddition of CO_2 with PO or 2-MeAz

Synthesis of propylene carbonate from PO (or 2-MeAz) and CO_2 (Scheme 1) was performed in a 25 mL stainless-steel autoclave equipped with a magnetic stirrer. For each typical operation, PO (42.9 mmol) or 2-MeAz (28.3 mmol) and zinc-glutamate catalyst (and cocatalyst, wherever applicable) were introduced to the reactor without solvent. The reactor was then pressurized with CO_2 to the preset pressure at room temperature and stirring was set at 600 rpm. When the desired time was elapsed, cycloaddition was stopped and the reaction was cooled externally to 0 °C using ice bath. Toluene was added as internal standard cum solvent for PO, while THF was added as GC solvent (and biphenyl as internal standard) in the case of 2-MeAz. The mixture was centrifuged to separate the catalyst, and the products were identified with a gas chromatograph (GC, Agilent HP 6890 A) equipped with a capillary column (HP-5, 30 m x 0.25 mm) using a flame ionization detector.

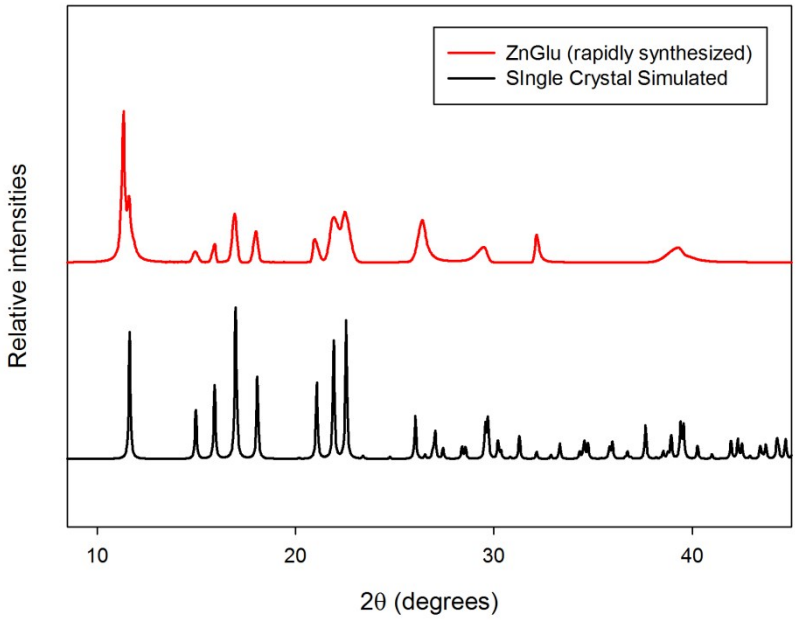

Fig. S2: XRD Spectra of rapidly synthesized ZnGlu in comparison with single crystal simulated pattern.

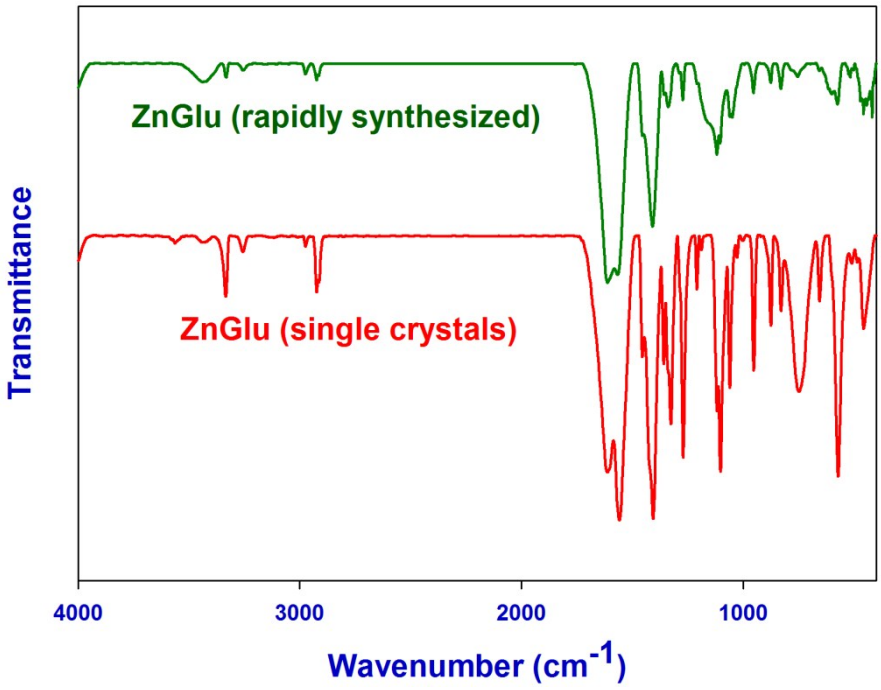

Fig. S3: FTIR Spectra of rapidly synthesized ZnGlu in comparison with single crystal.

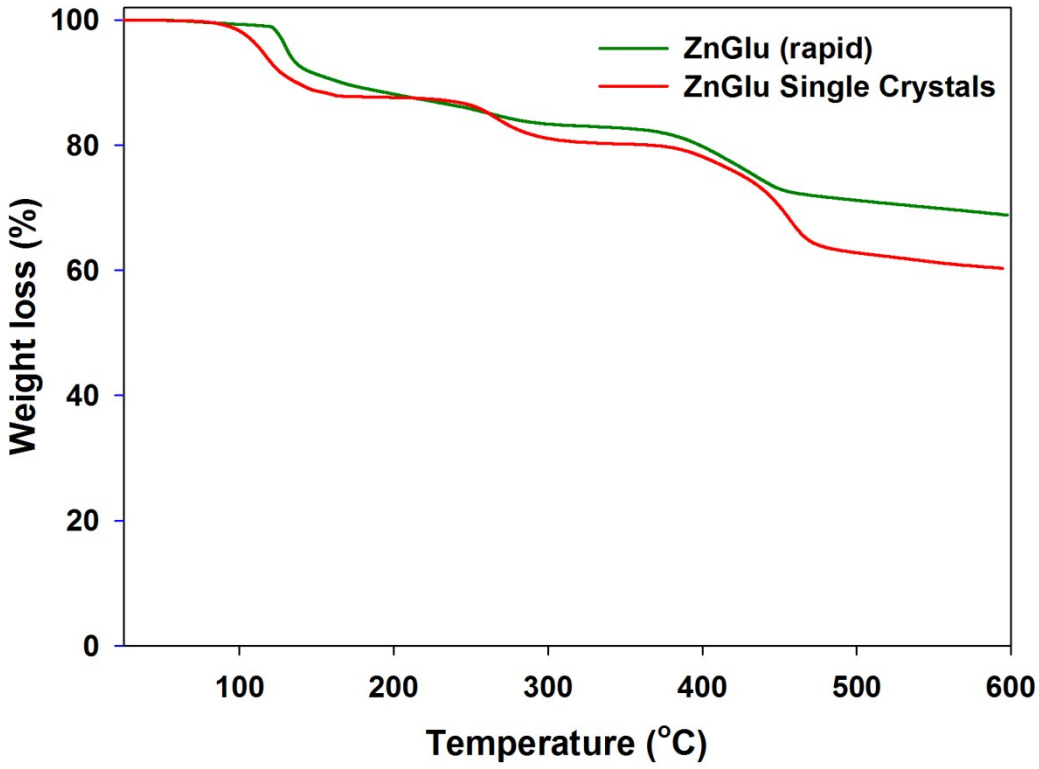

Fig. S4: TGA curves of rapidly synthesized ZnGlu and single crystals of ZnGlu.

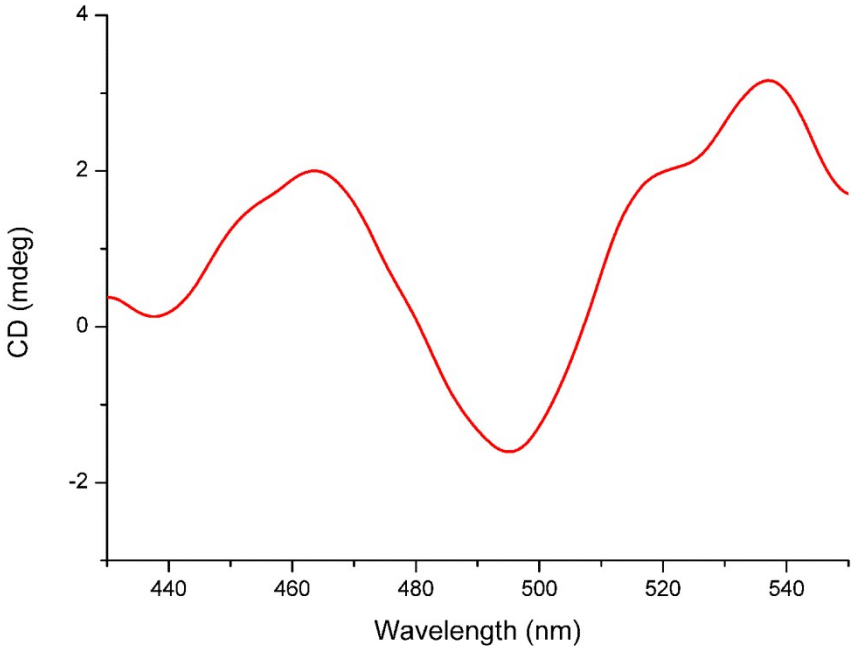

Fig. S5: Solid state CD spectra of ZnGlu

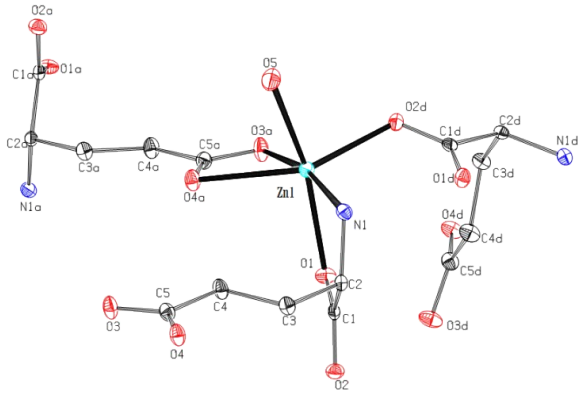

Fig. S6: ORTEP diagram showing the octahedral coordination environment around Zinc.

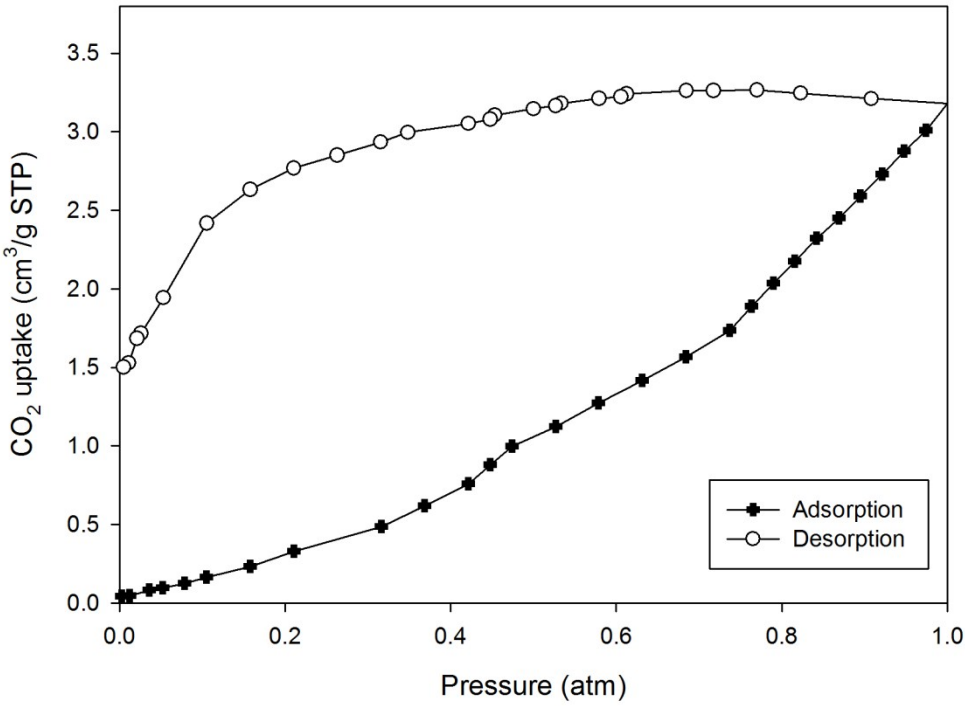

Fig. S7: CO_2 uptake by ZnGlu (a) adsorption curve (b) desorption curve.

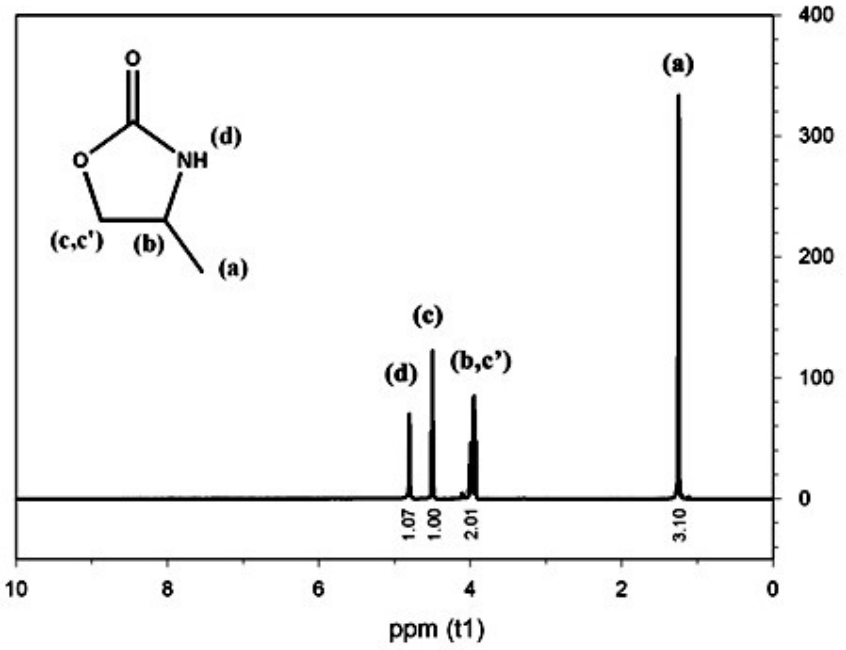

Fig. S8: [1]H-NMR of the isolated 4-methyl-2-oxazolidinone

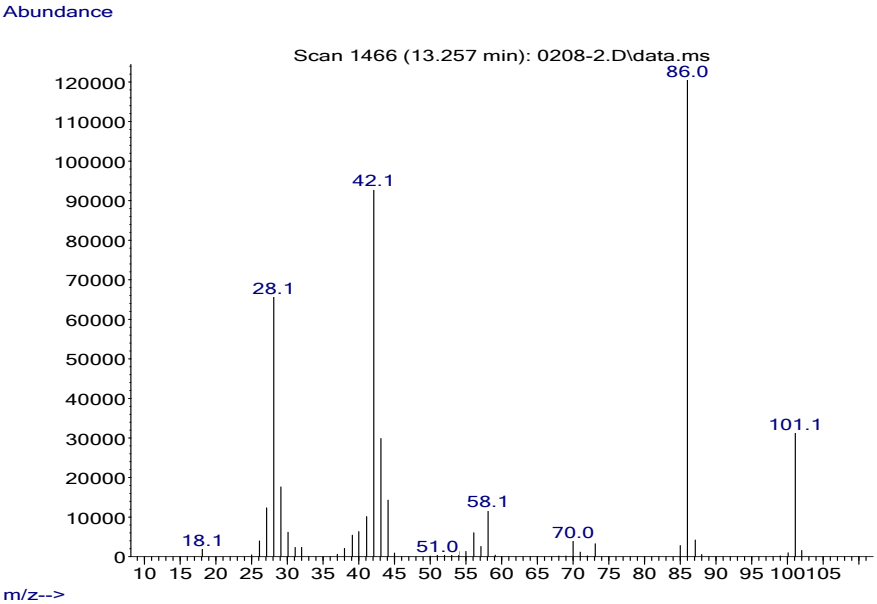

Fig. S9: GC-MS fragmentation pattern of 4-methyl-2-oxazolidinone, RT=13.25 min

S1.5 Catalyst Recycling

After the CO_2 cycloaddition reaction at optimum conditions, it was mixed with (GC/internal standard) and centrifugation was performed to recover the catalyst. The supernatant was taken for further GC analysis and for ICP-OES to verify if any leaching occurred during the reaction. The recovered catalyst was washed several times with water and dried in air for a day, and used for further run.

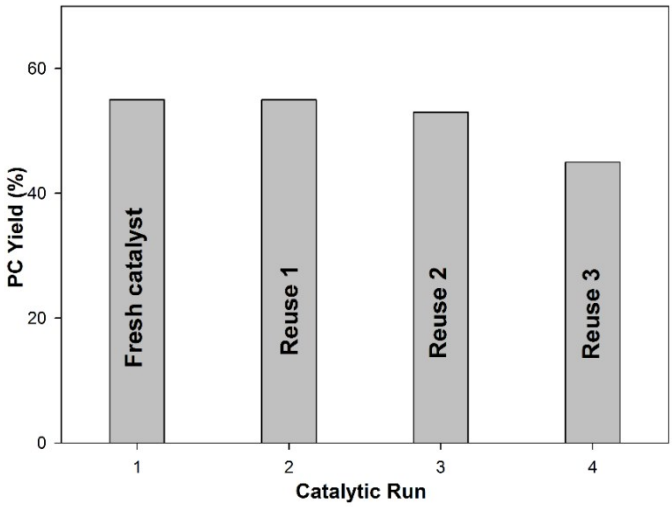

Fig. S10: Recycling test for zinc-glutamate-MOF (conditions same as Table 1, entry 5).

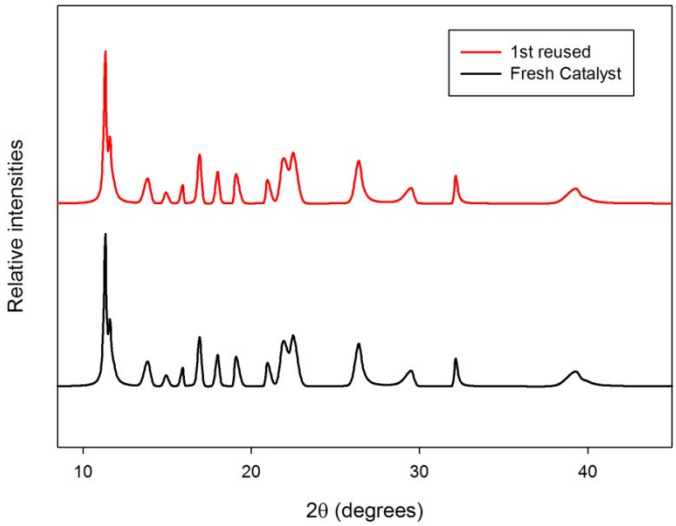

Fig. S11: XRD analysis of the recycled catalyst (first reuse) compared to the fresh one.

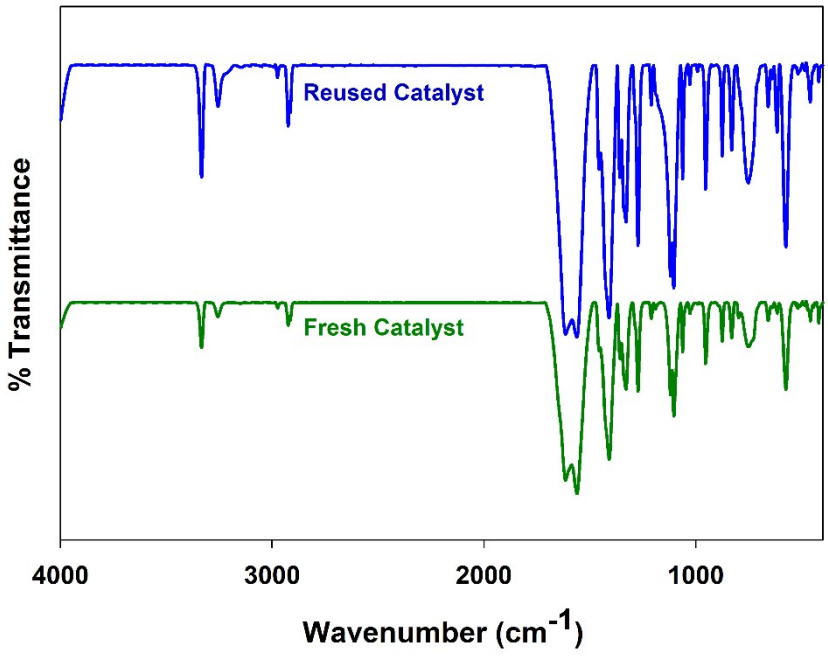

Fig. S12: FT-IR spectrum of the fresh catalyst compared to first reused catalyst.

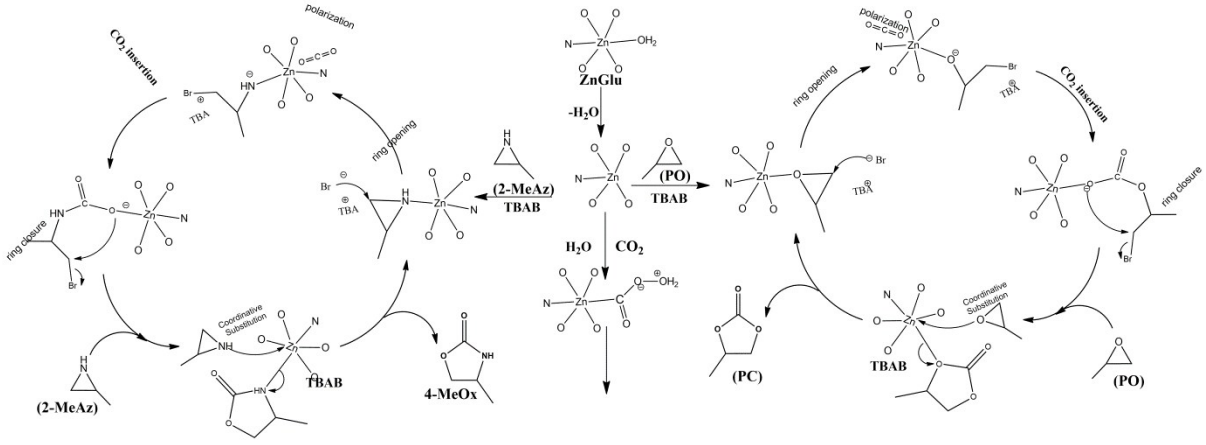

Fig. S13: Mechanism for the cycloaddition of CO_2 with PO and 2-MeAz to form PC and 4-MeOx, using ZnGlu/TBAB.