

Supporting Information

**Integrating Metal Complex Units into Knitted
Hyperscrosslinked Polymers for Enhanced Efficiency of
Cyclization Reactions with CO₂**

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1. Methods

Fourier transform infrared spectroscopy (FT-IR) was carried out by a Nicolet 6700 research infrared spectrometer. The chemical structure of the catalyst was tested by ^{13}C NMR (Solid State Nuclear Magnetic Resonance) using an all-digital superconducting nuclear magnetic resonance spectrometer (NMR) 600 MHz. X-ray photoelectron spectroscopy (XPS) was obtained by ESCALAB 250Xi (Thermo Fisher). X-ray diffraction (XRD) was obtained by Bruker D8 ADVANCE. Field emission transmission electron microscopy (TEM) and element distribution energy spectrum (EDS-mapping) of the obtained materials were tested by Talos F200S. The scanning electron microscope (SEM) of the obtained materials were tested by Hitachi SU8220. The samples were tested by the ASAP2020 surface area meter and the microporous physical adsorption meter, and then analyzed by the Brunauer-Emmett-Teller (BET) method and the non-local density functional theory (NLDFT) method to obtain the results of specific surface area and pore size analysis. The CO_2 adsorption experiment was also carried out on the ASAP2020 automatic physical adsorption instrument. The pore size distribution of the sample was calculated by the nonlocal density functional theory (NLDFT) method. (TGA) was detected with a STA449F5 thermogravimetric analyzer. Gas chromatographic (GC) analyses were performed on an Agilent 7820A gas chromatograph equipped with a flame ionization detection detector.

2. Materials

Benzaldehyde, pyrrole and o-toluidine were purchased from Macklin. Imidazole, *N*-methylimidazole, anhydrous iron (III) chloride, triphenylchloromethane, *N*-chlorosuccinimide Cobalt acetate tetrahydrate, aluminium phthalocyanine and *N,N'*-bis(salicylidene) ethylenediamine were obtained from Energy Chemical. Dimethoxymethane, propylene oxide, epichlorohydrin, epibromohydrin, allyl glycidyl ether, styrene oxide, 2-methyl-3-butyn-2-ol, 3-methyl-1-pentyne-3-ol, 3,5-dimethyl-1-hexyn-3-ol, 2-phenyl-3-butyn-2-ol and 1-ethynyl-1-cyclohexanol were purchased from J&K Scientific Ltd. 1,2-Epoxyhexane, phenyl glycidyl ether and benzyl chloride were used as received from TCI Shanghai Ltd. Other commercially available chemicals were provided from the local suppliers without further purification.

3. Experimental Section

3.1 Synthesis of 5,10,15,20-tetraphenylporphyrin (TPP).

A mixture of benzaldehyde (1.06 g, 10 mmol) was added to 200 mL of propionic acid in a 500 mL double-necked round-bottomed flask under a nitrogen atmosphere. When the reaction solution is stirred at 100°C for 1 h, the equivalent amount of pyrrole (0.67 g, 10 mmol) was injected via a syringe and then kept the reaction mixture refluxing at 140°C for 4 h. The resulting suspension was cooled to room temperature, filtered under reduced pressure, and then washed with methanol, finally dried to obtain 0.5 g of 5,10,15,20-tetraphenylporphyrin (TPP) as a bright-purple powder. ¹H NMR (400 MHz, CDCl₃) δ -2.77 (s, 1H), 8.84 (s, 4H), 8.23 (d, 4H), 7.76- 7.74 (m, 6H).

3.2 Synthesis of aluminium 5,10,15,20-tetraphenylporphyrin chloride (Al-TPP).

Under a nitrogen atmosphere, 1.6 mmol of TPP was dissolved in 30 mL of anhydrous dichloromethane. After continuous and vigorous stirring, 1.8 mmol of diethyl aluminium chloride in 1.0 M *n*-hexane was slowly dripped into the ice water bath with a syringe for 1 h, and then the reactor was transferred to the oil bath and kept at room temperature for additional 6 h. After the reaction, the excess solvent was removed by rotary evaporation and washed with methanol to obtain **Al-TPP** as a dark purple solid. ¹H NMR (400 MHz, CDCl₃) δ 9.00 (s, 2H), 8.20 (d, 2H), 7.87 (m, 3H).

3.3 Synthesis of cobalt 5,10,15,20-tetraphenylporphyrin (Co-TPP)

Under a nitrogen atmosphere, 0.5 mmol of TPP and 3 mmol of Co(OAc)₂·4H₂O were mixed in 30 mL of chloroform-acetic acid solution (v/v=1/1). The reaction solution was stirred at 120°C for 4 h. After the reaction, the mixture was filtered and washed with methanol to obtain **Co-TPP** as a bright purple solid.

3.4 Synthesis of (3-(1,3-bis(imidazolomethyl)phenyl) triphenylmethane bromide (IL).

(3-Methylphenyl)triphenylmethane (1.53 mmol, 0.512 g), NCS (1.99 mmol, 0.266 mg), benzoyl peroxide (0.01 g) and 20 mL of anhydrous carbon tetrachloride were added to a 100 mL round-bottom flask under a nitrogen atmosphere. The reaction was heated to 80°C

and stirred for 16 h. After the reaction, it was cooled to room temperature, the yellow filtrate was concentrated and 50 mL of ethanol was added to remove the impurities. Finally, (3-chloromethylphenyl) triphenylmethane as a yellow solid was obtained. Then, imidazole (6 mmol, 0.4 g), (3-chloromethylphenyl) triphenylmethane (11.9 mmol, 4.4 g), K_2CO_3 (18 mmol, 2.5 g) was added in 100 mL of anhydrous acetonitrile. The reactor was stirred under reflux for 48 h under a nitrogen atmosphere. After the reaction, the solvent was removed by vacuum distillation and 140 mL of deionized water was added. The mixture was extracted with CH_2Cl_2 (5×30 mL), the organic phase was dried overnight with anhydrous magnesium sulfate. After the solvent was removed by vacuum distillation, the targeted product was obtained as a yellow powder. 1H NMR (400 MHz, $DMSO-d_6$) δ 9.26 (s, 1H), 7.66-7.64 (d, 2H), 7.34-7.12 (m, 39H), 5.37(s, 4H).

3.5 Synthesis of 1,3-dibenzyl-imidazolium chloride.

Imidazole (6 mmol, 0.4 g), K_2CO_3 (18 mmol, 2.5 g) and benzyl chloride (11.9 mmol, 2.3 g) were added to a 100 mL round-bottom flask including 60 mL of anhydrous acetonitrile under a nitrogen atmosphere. The mixture was stirred at room temperature for 48 h. After the reaction, the solvent was removed by vacuum distillation and 140 mL of deionized water was added. The aqueous phase was extracted with CH_2Cl_2 (5×30 mL), and the organic phase was dried overnight with anhydrous magnesium sulfate. After the solvent was removed by vacuum distillation, the targeted product was obtained as a yellow oil. 1H NMR (400 MHz, $DMSO-d_6$) 7.90 (d, 2H), 7.44 (m, 10H), 5.50(s, 1H), 5.55(s, 4H).

3.6 Synthesis of Ag-NHC

IL (100 mg) and Ag_2O (100 mg) were added to a 25 mL round-bottomed flask containing 10 mL of anhydrous dichloromethane under a nitrogen atmosphere. Then, the mixture was stirred at room temperature for 48 h under darkness. After the reaction, the resulting black powder was filtered and washed with methylene chloride.

3.7 Synthesis of Al-HCP

Al-TPP (1 mmol), IL (1 mmol) and FDA (8 mmol) were added into a 15-mL Schleck tube equipped with 10 mL of anhydrous 1,2-dichloroethane under a nitrogen atmosphere. After stirring for 1 h, anhydrous $FeCl_3$ (8 mmol) was added into the reaction mixture and stirred at 80°C for 24 h. The resulting suspension was cooled to room temperature and washed

with methylene chloride, methanol and DMF, respectively. The obtained solid powder was further purified in a mixture of methanol/dichloromethane (v/v=1:1) with a Soxhlet extractor for 24 h and dried under vacuum at 70°C.

3.8 Synthesis of Co-HCP

Under a nitrogen atmosphere, **Co-TPP** (1 mmol), IL (1 mmol) and FDA (8 mmol) were added into a 15-mL Schleck tube equipped with 10 mL of anhydrous 1,2-dichloroethane. After stirring for 1 h, anhydrous FeCl₃ (8 mmol) was added into the reaction mixture and stirred at 80°C for 24 h. The resulting suspension was cooled to room temperature and washed with methylene chloride, methanol and DMF, respectively. The solid powder was further purified in a methanol/dichloromethane (v/v=1:1) mixture with a Soxhlet extractor for 24 h and dried under vacuum at 70°C.

3.9 Synthesis of Al-HCP-o

Al-TPP (1 mmol), 1,3-dibenzylimidazolium chloride (1 mmol); FDA (8 mmol) and 10 mL of anhydrous 1,2-dichloroethane was added into a 15-mL Schleck tube under a nitrogen atmosphere. After stirring for 1 h, anhydrous FeCl₃ (8 mmol) was added into the reaction mixture and stirred at 80°C for 24 h. The reaction suspension was cooled to room temperature and washed separately with DMF, methylene chloride and methanol. The obtained solid powder underwent further purification in a 1:1(v/v) mixture of methanol and dichloromethane with a Soxhlet extractor for 24 h and dried under vacuum at 70°C.

3.10 Synthesis of Al-HCP-p

Under a nitrogen atmosphere, aluminium phthalocyanine (**Al-Pc**, 1 mmol), IL (1 mmol) and FDA (8 mmol) were added into a 15-mL Schleck tube equipped with 10 mL of anhydrous 1,2-dichloroethane. After stirring for 1 h, anhydrous FeCl₃ (8 mmol) was added into the reaction mixture and stirred at 80°C for 24 h. The resulting suspension was cooled to room temperature and washed successively with methylene chloride, DMF and methanol. The obtained solid powder was further purified in a 1:1(v/v) mixture of dichloromethane and methanol by means of a Soxhlet extractor for 24 h. and dried under vacuum at 70°C.

3.11 Synthesis of Al-HCP-s

A 15-mL Schleck tube was pre-equipped with 10 mL of anhydrous 1,2-dichloroethane, received the addition of **Al(Salen)** (1 mmol), IL (1 mmol) and FDA (8 mmol) under a nitrogen

atmosphere. After a period of 1 hour of continuous stirring, anhydrous FeCl_3 (8 mmol) was added into the reaction mixture and stirred continuously at 80°C for 24 h. The resulting suspension was cooled to the ambient temperature and washed with methylene chloride, methanol and DMF, respectively. The obtained solid powder was further purified in a mixture of methanol/dichloromethane (with a volume ratio of 1:1) using a Soxhlet extractor over a duration of 24 h and dried under vacuum conditions at 70°C .

3.12 Synthesis of Ag-HCP

Ag-NHC (1 mmol) and FDA (8 mmol) were added into a 15-mL Schleck tube equipped with 10 mL of anhydrous 1,2-dichloroethane under a nitrogen atmosphere. After stirring for 1 h, anhydrous FeCl_3 (8 mmol) was added into the reaction mixture and stirred at 80°C for 24 h. The resulting suspension was cooled to room temperature and washed with methylene chloride, methanol and DMF, respectively.

3.13 Typical process of CO_2 cycloaddition with epoxides

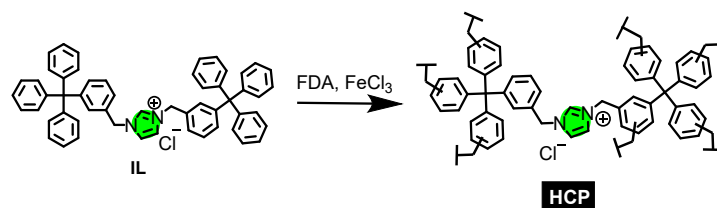
Epichlorohydrin (3 mmol) and catalyst (10 mg) were added to a 10 mL stainless steel reactor. The reactor was purged/evacuated with CO_2 for three times to remove any residual air and moisture. Then, CO_2 was flushed to 10 bar at room temperature. After keeping the reactor at the required temperature in an oil bath for the desired reaction times, the reactor was cooled to room temperature, and the remaining CO_2 was slowly drained from the reactor. The yields and selectivities of the products were determined by GC.

3.14 Typical procedure of CO_2 carboxylative cyclization with propargylic alcohols

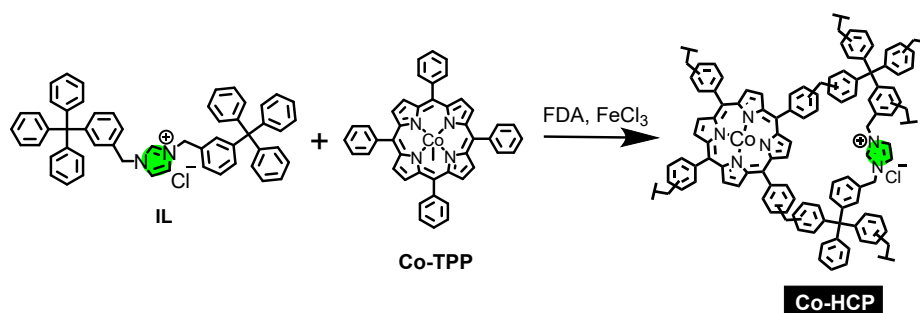
2-Methyl-3-butyn-2-ol (1.0 mmol), DBU (1.0 mmol), catalyst (10 mg) and CH_3CN (5 mL) were loaded into a 10 mL Schleck glass tube. The remaining moisture and air were removed by blowing nitrogen gas and the reactor was connected to a CO_2 balloon. After the reaction mixture is stirred at room temperature for the required time, the CO_2 was slowly expelled.

The yields and selectivities of the products were determined by GC. The catalyst was collected by simple centrifugation or filtration, washed with methanol and methylene chloride and then can be used for the next round of production without further purification.

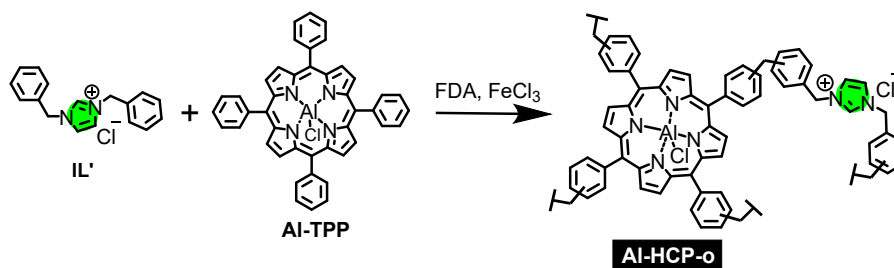
4. Figures



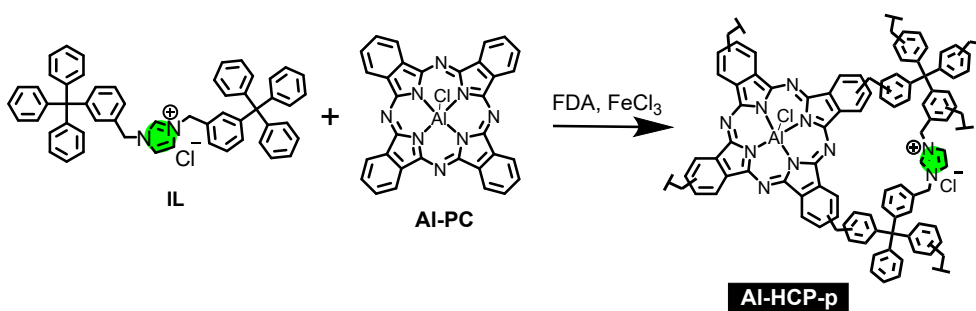
Scheme S1. Synthesis of HCP



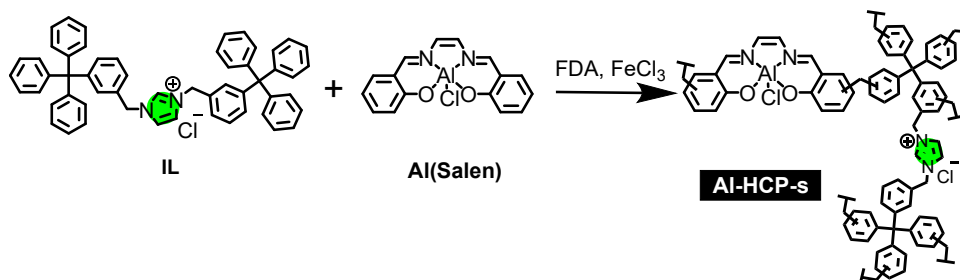
Scheme S2. Synthesis of Co-HCP



Scheme S3. Synthesis of Al-HCP-o



Scheme S4. Synthesis of Al-HCP-p



Scheme S5. Synthesis of Al-HCP-s

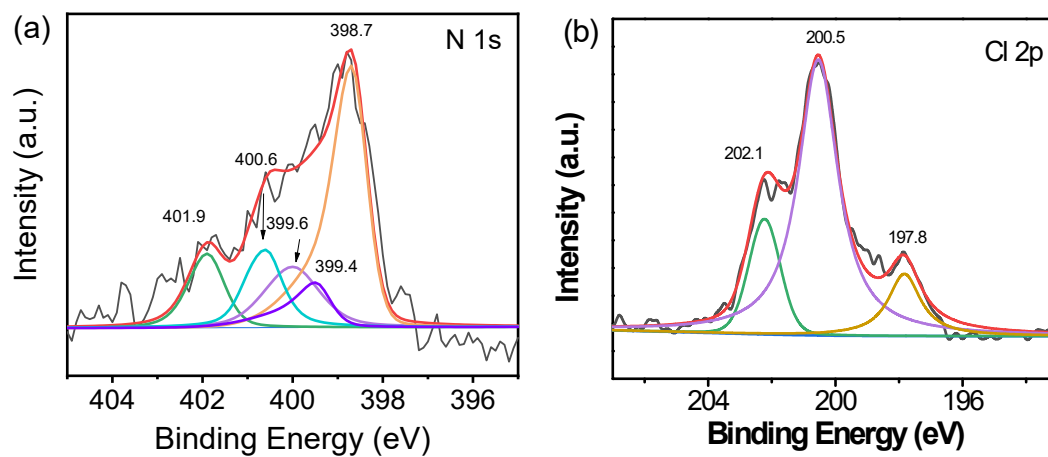


Fig. S1 (a) N 1s and (b) Cl 2p XPS spectra of Al-HCP

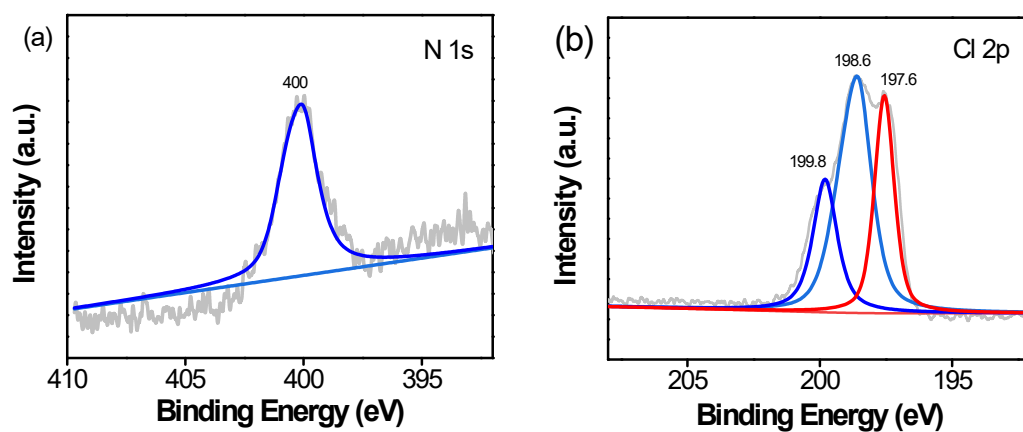


Fig. S2 (a) N 1s and (b) Cl 2p XPS spectra of Ag-HCP

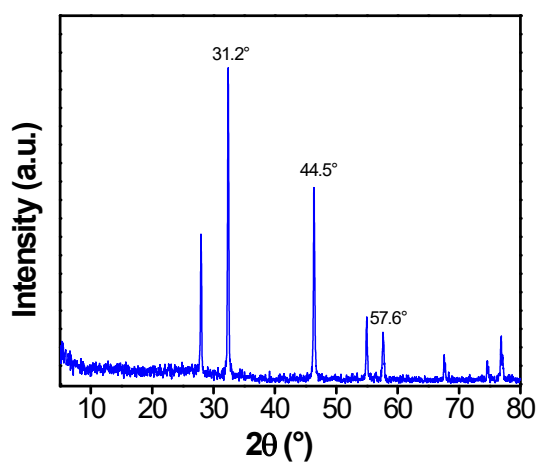


Fig. S3 Powder XRD curve of Ag-HCP

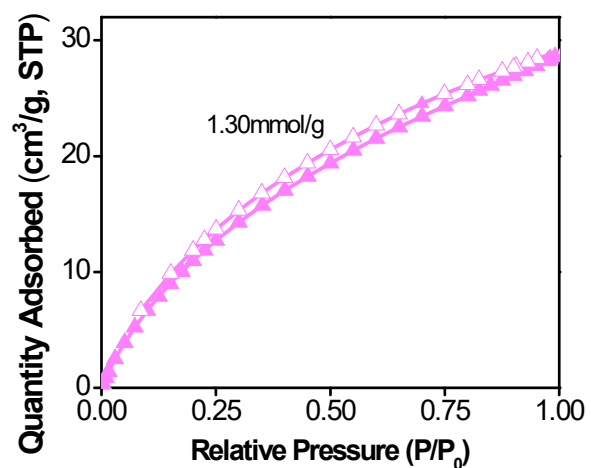


Fig. S4 CO₂ adsorption isotherm of Al-HCP

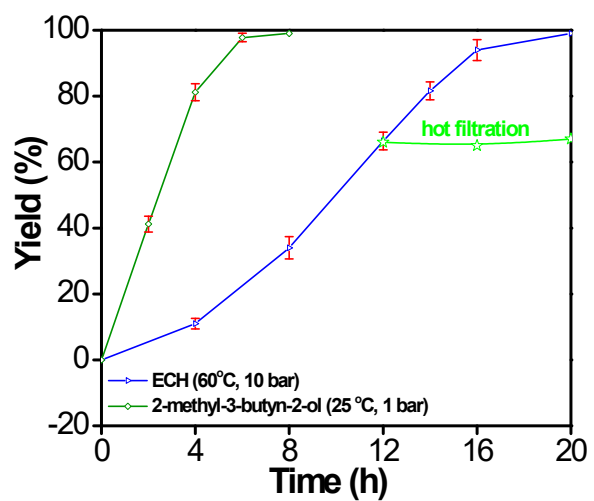


Fig. S5 Kinetic curves of CO₂ cycloaddition with ECH (blue) and carboxylative cyclization of CO₂ with 2-methyl-3-butyn-2-ol (green)

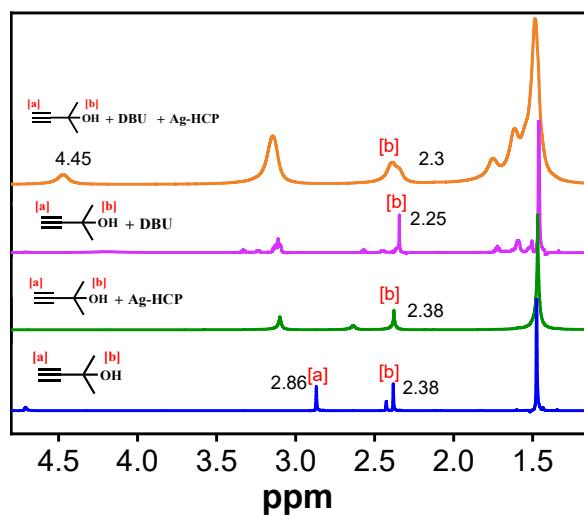


Fig. S6 ¹H NMR spectra of 2-methyl-3-butyn-2-ol (blue), the mixture of 2-methyl-3-butyn-2-ol and **Ag-HCP** (green), the mixture of 2-methyl-3-butyn-2-ol and DBU (purple) and the mixture of 2-methyl-3-butyn-2-ol, DBU and **Ag-HCP** (orange)

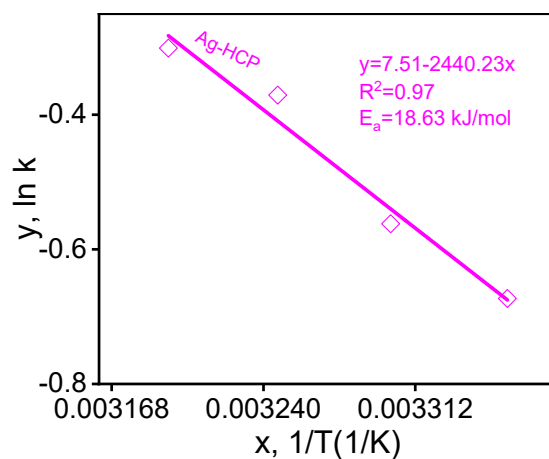


Fig. S7 The fitting curve of the natural logarithm of the observed pseudo-first-order rate constant ($\ln k$) against the reciprocal absolute temperature ($1/T$).

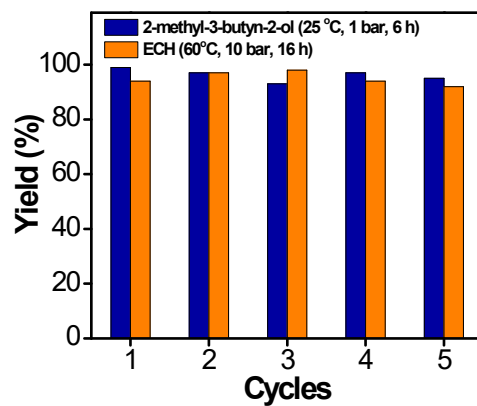


Fig. S8 Recyclability of Al-HCP and Ag-HCP

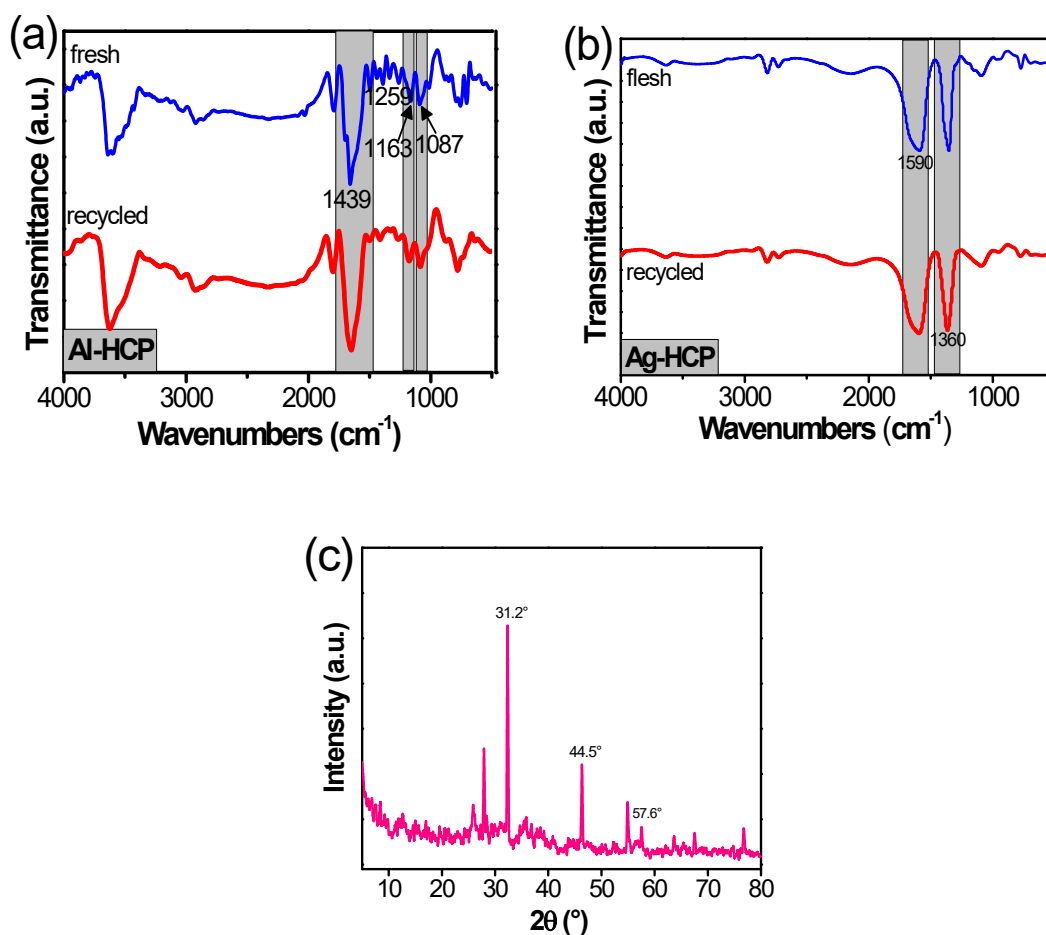


Fig. S9 (a, b) FT-IR spectra of fresh and recycled Al-HCP and Ag-HCP; (c) Powder XRD curve of or Ag-HCP after being reused five times

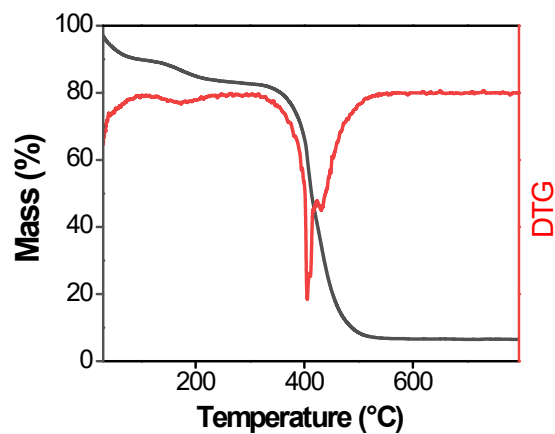


Fig. S10 TGA curves of Al-HCP

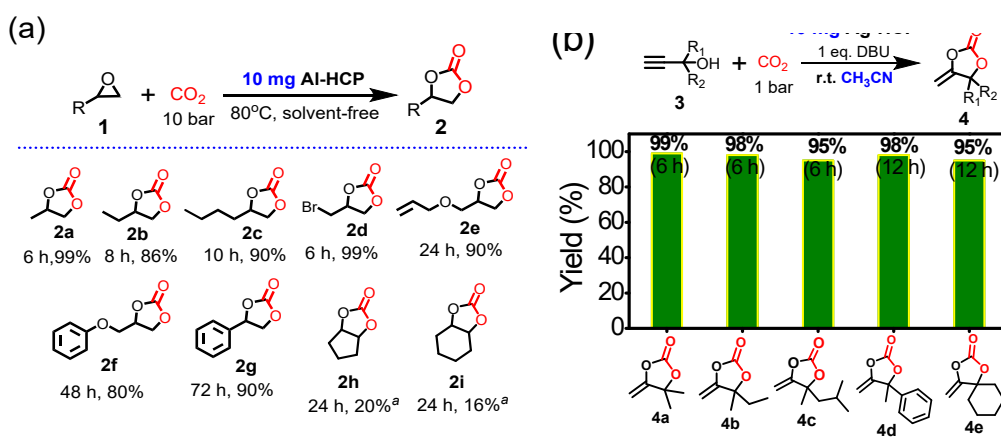


Fig. S11 Substrate generality of (a) Al-HCP and (b) Ag-HCP. ^a reaction condition: reaction temperature 140 °C.

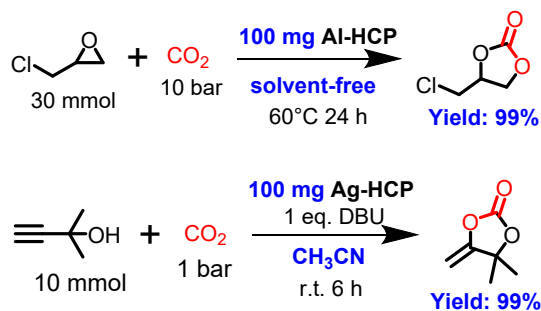


Fig. S12 Large-scale experiments of CO_2 cycloaddition with ECH and carboxylative cyclization of CO_2 with 2-methyl-3-butyn-2-ol

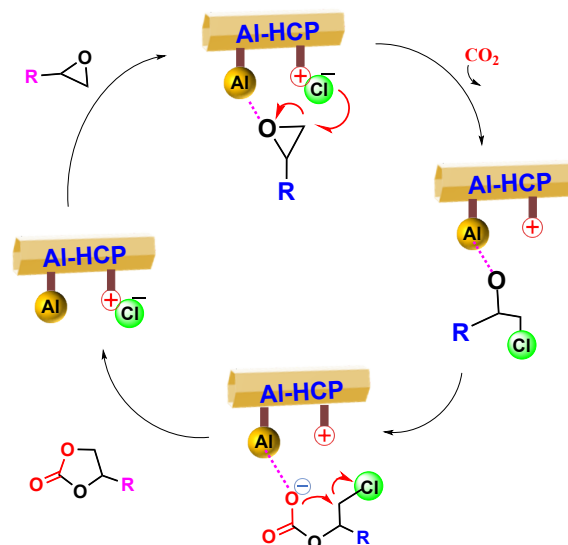


Fig. S13 Possible reaction mechanism for the cycloaddition of CO_2 with epoxides over AI-HCP

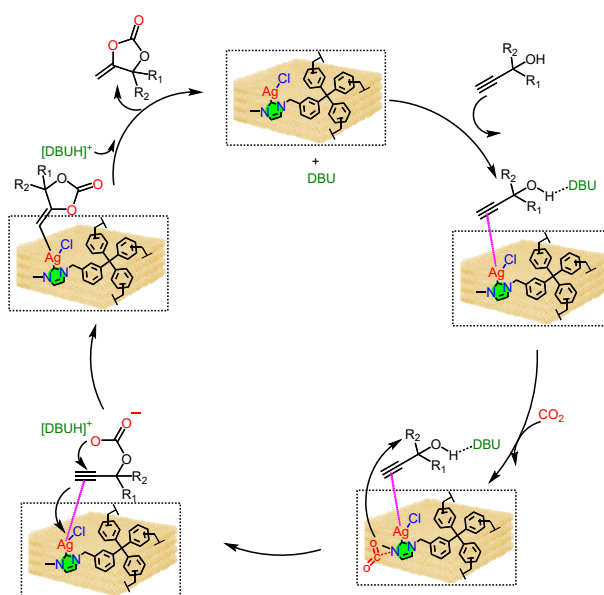


Fig. S14 Possible reaction mechanism for the carboxylative cyclization of propargyl alcohols with CO_2

5. NMR spectra

