

*Supporting Information*

**Enhancement of the Catalytic Performance of  
UIO-66 for CO<sub>2</sub> Synthesis of Cyclic Carbonate  
by Natural Nanomaterials as a Carrier**

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# 1、 Experimental section

## 1.1 General information

All chemicals were commercially available and used without further purification. Fourier transform infrared (FT-IR, Burker VERTEX 70) spectroscopic analysis was carried out using pressed KBr disks in the region of 4000–500  $\text{cm}^{-1}$ . The powder X-ray diffraction recorded crystal structures (XRD, Rigaku MiniFlex600 X-ray diffractometer using CuK $\alpha$  radiation). The Brunauer-Emmett-Teller (BET) specific surface area of samples was determined using N<sub>2</sub> adsorption-desorption on an ASAP2020M. Thermal Gravimetric Analyzer (TGA) was performed on a NETZSCH STA449C under a nitrogen atmosphere at a heating rate of 10 °C/min. Scanning electronic microscopy (SEM) images were obtained using an Apreo S electron microscope operating at 30 kV. The surface images were recorded on transmission electron microscopy (TEM, Tecnai G2Tf20) at 200 kV, and 100 K. X-ray photoelectron spectroscopy (XPS) was carried out on XPS spectrometers (PHI-5702). The <sup>1</sup>H NMR data were collected using a JNM-ECS 400 M NMR spectrometer. The Zr<sup>4+</sup> contents in UIO-66-3/ATP samples were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, PQ9000).

## 1.2 Preparation of UIO-66 catalyst

UIO-66 was prepared by mixing terephthalic acid(0.05 mmol), zirconium tetrachloride, and hydrochloric acid in a molar ratio (1:1:1) in 16 mL DMF; the mixture was transferred into a 25 mL PTFE-lined stainless steel reactor, maintained at 393 K for 24 h, the hydrothermal kettle was cooled naturally to room temperature. The white product was separated by centrifugation, washed with DMF to remove excess unreacted terephthalic acid, washed three times with methanol and dried.

## 1.3 Catalytic cycloaddition of CO<sub>2</sub> with epoxides

The following steps are common to the cycloaddition reaction of CO<sub>2</sub> and epoxy compounds. Fill a 30 mL reactor with the catalyst, co-catalyst, and epoxide mixture. The reactor was subjected to three pressurization cycles (with CO<sub>2</sub> at 1.5 MPa) and depressurization, and the final pressure was stabilized at 1 MPa. When the reactor's temperature is raised to the set temperature, place the reactor in a thermostatically heated jacket and mechanically stir the solution at 400 rpm/min. After the defined reaction time, the reaction vessel was cooled to room temperature in cold water, and a

small amount of residue was removed for  $^1\text{H}$  NMR analysis to calculate the reaction yield.

## 2、Catalyst details

**Table S1** Catalytic effect of the amount of catalyst on the synthesis of cyclic carbonate from Styrene oxide

Entry	cat	cat(mg)	Co-cat	Co-cat(mmol)	yield (%) <sup>b</sup>
1	UIO-66-3/ATP	2	TBAB	0.08	78
2	UIO-66-3/ATP	4	TBAB	0.08	88
3	UIO-66-3/ATP	6	TBAB	0.08	76
4	UIO-66-3/ATP	8	TBAB	0.08	82
5	UIO-66-3/ATP	10	TBAB	0.08	93
6	UIO-66-3/ATP	12	TBAB	0.08	92

a. Reaction conditions: Styrene oxide (1.202 g, 10 mmol), TBAB as Co-Cat, 2 h,  $\text{CO}_2$  1 MPa, solvent-free.

b. Yields were determined by  $^1\text{H}$  NMR.

**Table S2** Catalytic effect of the amount of catalyst on the synthesis of cyclic carbonate from oxidized styrene

Entry	Cat	cat(mg)	Co-cat	Co-cat(mmol)	yield (%)
1	UIO-66-3/ATP	10	TBAB	0.08	93
2	UIO-66-3/ATP	10	TBAI	0.08	92
3	UIO-66-3/ATP	10	TBAC	0.08	85
4	UIO-66-3/ATP	10	—	—	1
5	UIO-66	10	—	—	0
6	ATP	10	—	—	1
7	UIO-66-3/ATP	10	TBAB	0.04	75
8	UIO-66-3/ATP	10	TBAB	0.06	80
9	UIO-66-3/ATP	10	TBAB	0.08	93
10	UIO-66-3/ATP	10	TBAB	0.1	94
11	UIO-66-3/ATP	10	TBAB	0.12	89
12	—	—	TBAB	0.08	55
11	UIO-66	10	TBAB	0.08	73

a. Reaction conditions: Styrene oxide (1.202 g, 10 mmol), TBAB as Co-Cat, 2 h,  $\text{CO}_2$  1 MPa, solvent-free.

b. Yields were determined by  $^1\text{H}$  NMR.

**Table S3** Catalytic effect of the amount of catalyst on the synthesis of cyclic carbonate from Styrene oxide

Entry	cat	cat(mg)	Co-cat	Co-cat (mmol)	T (°C)	Time (h)	yield (%)
1	UIO-66-3/ATP	10	TBAB	0.08	60	2	4
2	UIO-66-3/ATP	10	TBAB	0.08	80	2	15
3	UIO-66-3/ATP	10	TBAB	0.08	100	2	44
4	UIO-66-3/ATP	10	TBAB	0.08	120	2	93
5	UIO-66-3/ATP	10	TBAB	0.08	140	2	96
6	UIO-66-3/ATP	10	TBAB	0.08	120	0.5	31
7	UIO-66-3/ATP	10	TBAB	0.08	120	1	59
8	UIO-66-3/ATP	10	TBAB	0.08	120	1.5	75
9	UIO-66-3/ATP	10	TBAB	0.08	120	2	93
10	UIO-66-3/ATP	10	TBAB	0.08	120	2.5	92

a. Reaction conditions: Styrene oxide (1.202 g,10 mmol), TBAB as Co-Cat, 2 h, CO<sub>2</sub> 1 MPa, solvent-free.

b. Yields were determined by <sup>1</sup>H NMR.

**Table S4** Catalytic effect of solvent type on the synthesis of cyclic carbonate from Styrene oxide

Entry	cat	cat(mg)	Co-cat	Co-cat (mmol)	solvent	yield (%)
1	UIO-66-3/ATP	10	TBAB	0.08	pure water	78
2	UIO-66-3/ATP	10	TBAB	0.08	ethyl alcohol	25
3	UIO-66-3/ATP	10	TBAB	0.08	dimethyl sulfoxide	72

a. Reaction conditions: Styrene oxide (1.202 g,10 mmol), TBAB as Co-Cat, 2 h, 120°C, CO<sub>2</sub> 1 MPa, solvent (1 mL) .

b. Yields were determined by <sup>1</sup>H NMR.

**Table S5** Catalytic effect of physical mixture catalysts on the synthesis of cyclic carbonates from styrene oxide

Entry	cat	cat(mg)	Co-cat	Co-cat (mmol)	Time (h)	yield (%)
1	UIO-66•ATP	10	TBAB	0.08	2	74
2	UIO-66•ATP	10	TBAB	—	2	1

a. Reaction conditions: Styrene oxide (1.202 g, 10 mmol), TBAB as Co-Cat, 120°C, CO<sub>2</sub> 1 MPa, solvent-free.

b. Based on the ICP detection of 4% Zr<sup>4+</sup> in UIO-66-3/ATP, it was calculated that 10 mg of the mixture catalyst ( $M_{\text{UIO-66}} = 1.17 \text{ mg}$ ,  $M_{\text{ATP}} = 8.83 \text{ mg}$ ), and the physical mixture was noted as UIO-66•ATP.

b. Yields were determined by <sup>1</sup>H NMR.

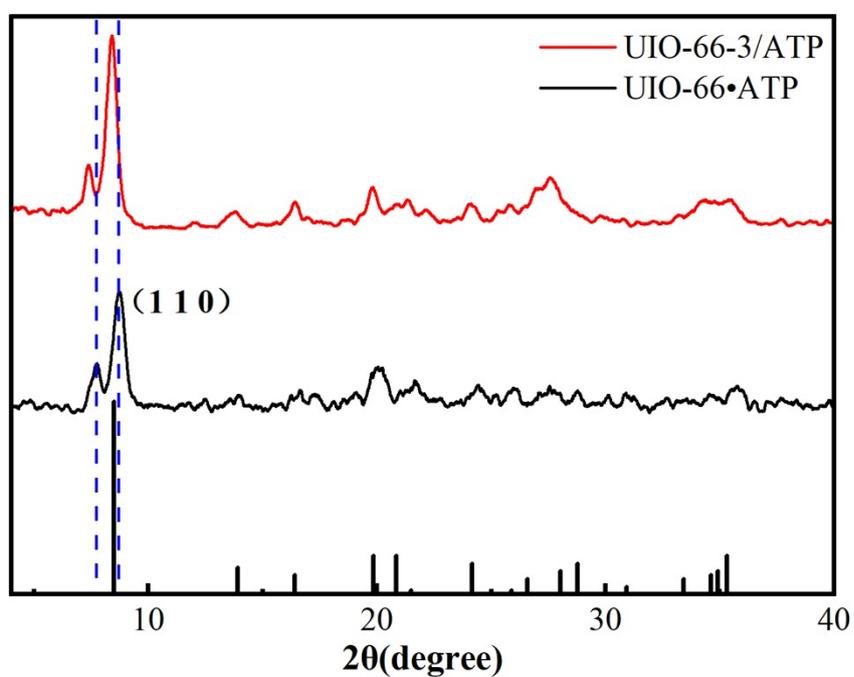


Figure. S1 PXRD spectra of two different catalysts .

### 3、Catalyst characterization

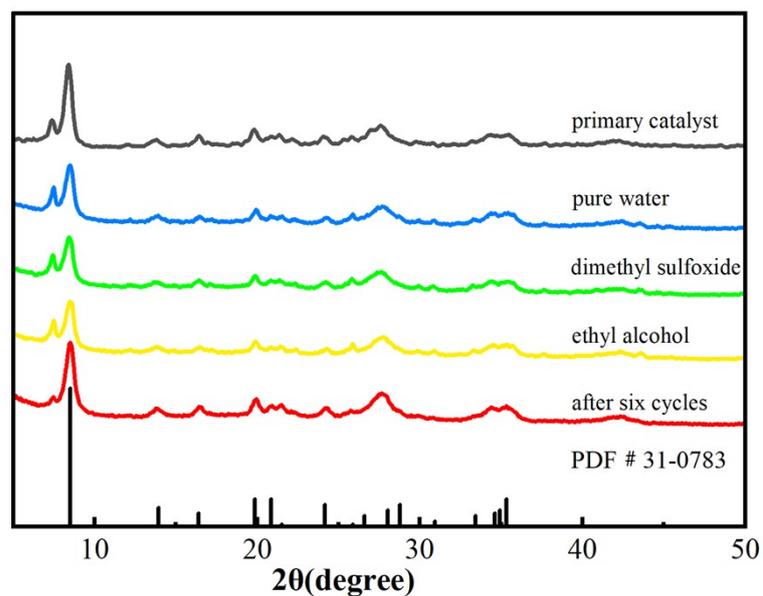


Fig. S2 PXRD spectra of catalysts after reaction with different solvents.

#### 4、<sup>1</sup>H NMR Spectra

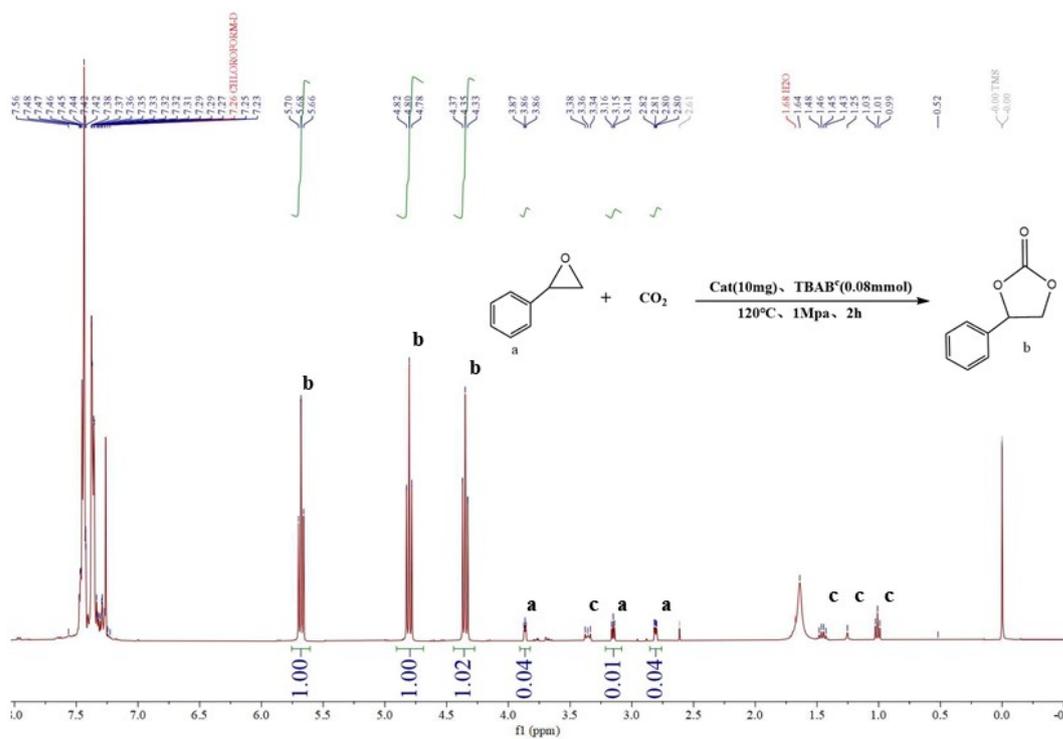
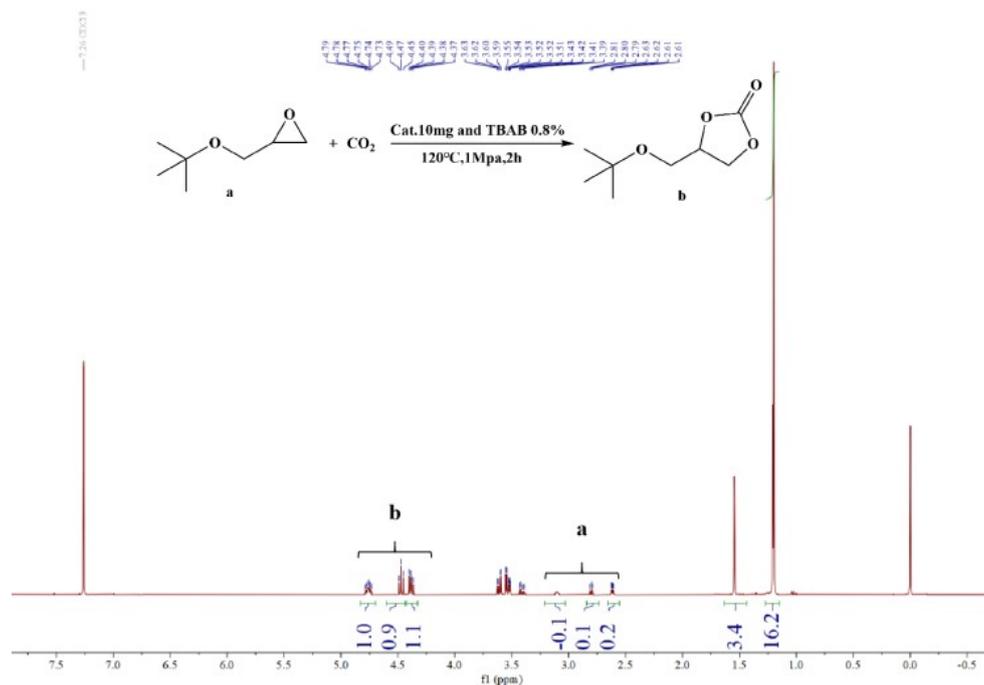


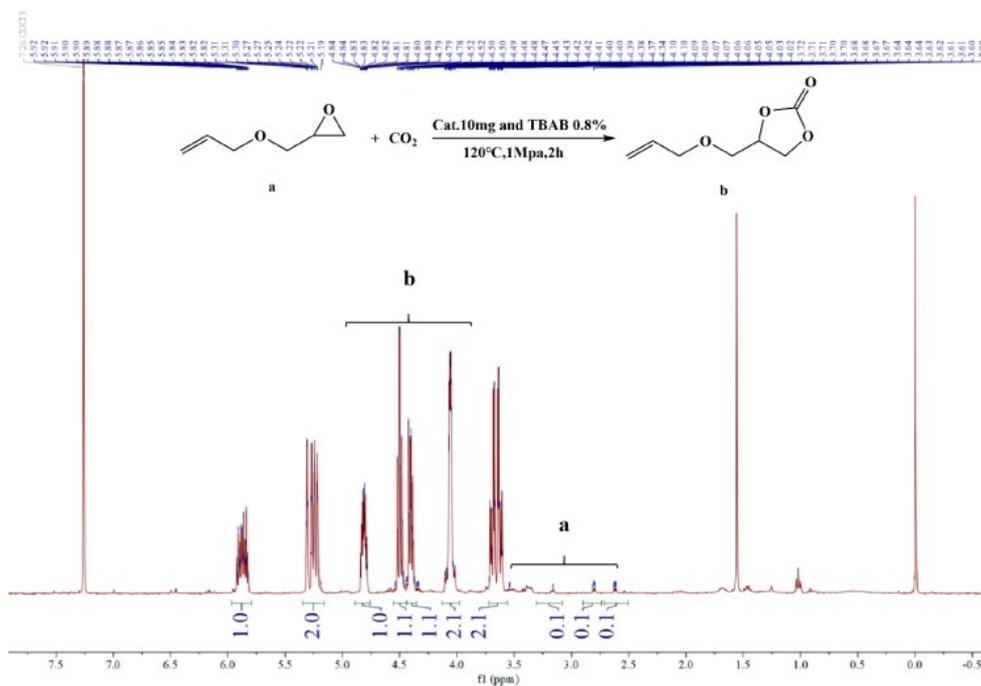
Fig. S3 <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum of the reaction substrate of cycloaddition of CO<sub>2</sub> with styrene oxide catalyzed by UIO-66-3/ATP at 120 °C for 2 h.



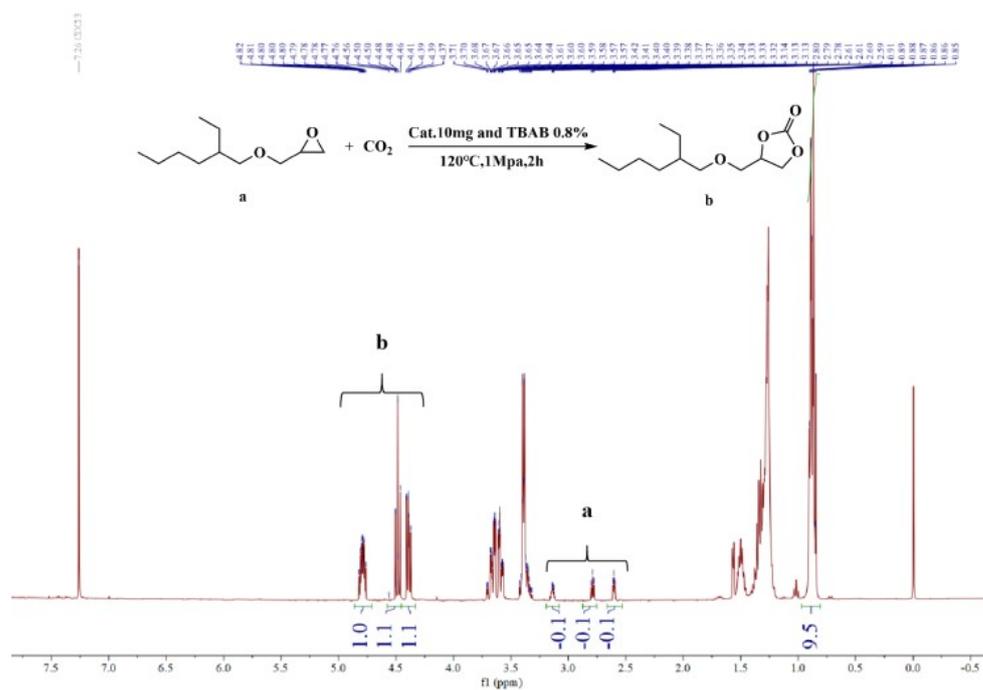




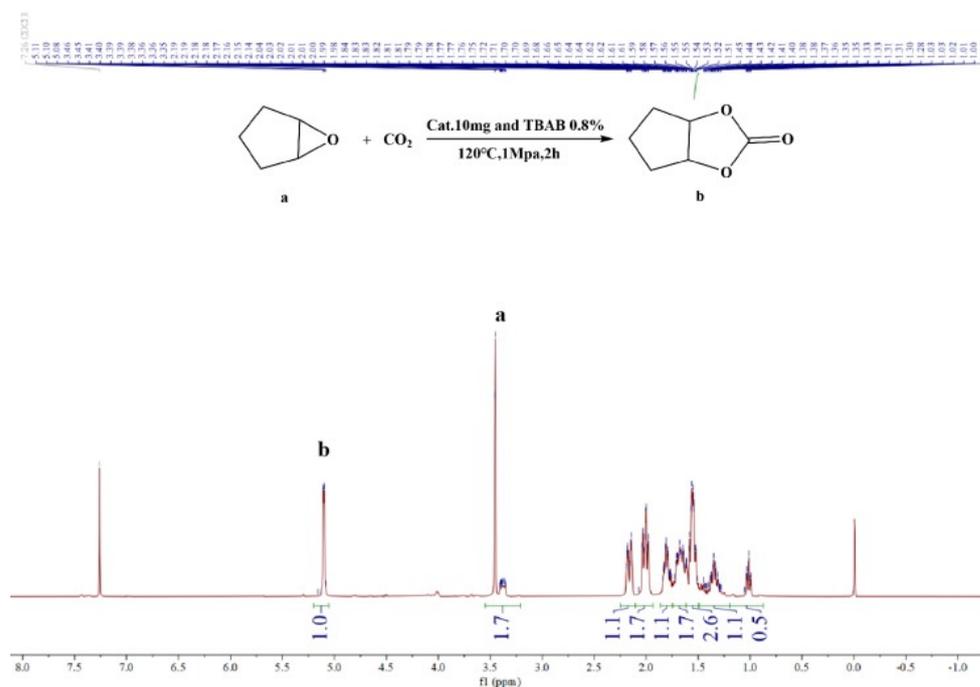
**Fig. S8** <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum of the reaction substrate of cycloaddition of CO<sub>2</sub> with tert-butyl glycidyl ether catalysed by UIO-66-3/ATP at 120 °C for 2 h.



**Fig. S9** <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum of the reaction substrate of cycloaddition of CO<sub>2</sub> with Allyl glycidyl ether catalyzed by UIO-66-3/ATP at 120 °C for 2h.



**Fig. S10** <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum of the reaction substrate of cycloaddition of CO<sub>2</sub> with octyl glycidyl ether catalysed by UIO-66-3/ATP at 120 °C for 2 h.



**Fig. S11** <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum of the reaction substrate of cycloaddition of CO<sub>2</sub> with cyclohexene oxide catalysed by ATP at 120 °C for 2 h.

