

**Metal-assisted synthesis of salen-based porous organic polymer for high efficient
fixation of CO₂ into cyclic carbonates**

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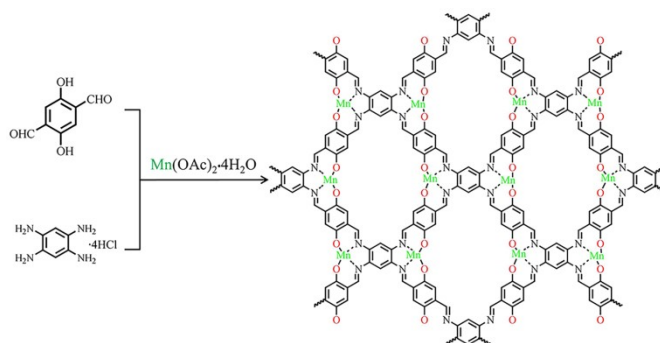
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Materials and characterizations

All chemicals were obtained from commercial suppliers and used without further purification. Fourier transform infrared (FTIR) spectra were recorded in the range of 400–4000 cm^{-1} on a Nicolet 6700 FT-IR spectrometer with KBr pellets. X-ray photoelectron spectroscopy (XPS) were performed using an ESCALAB 250 spectrometer with a monochromatic X-ray source (Al $K\alpha$ $h\nu=1486.6$ eV). The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max 2550 X-ray diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5406$ Å). The content of metal in products were determined with inductively coupled plasma (ICP) analyses carried out on a Perkin-Elmer Optima 3300 DV ICP instrument. Elemental analyses (C, H, and N) were performed with a Vario MICRO (Elementar, Germany). Surface morphologies were characterized using a JSM-7800 F field emission scanning electron microscope (SEM) at an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) were conducted on a FEI Tecnai G2S-Twin with a field emission gun operating at 200 kV. Thermal gravimetric analyses (TGA) were carried out on a TGA Q500 thermogravimetric analyzer in air atmosphere at a heating rate of 10 $^{\circ}\text{C min}^{-1}$. The Micromeritics ASAP 2020 instrument was used to evaluate the adsorption properties of N_2 , CO_2 with the samples degassed at 120 $^{\circ}\text{C}$ for 10 h before testing under high vacuum. Solution-state ^1H spectra were recorded on a Varian Mercury spectrometer operating at frequency of 300 MHz.

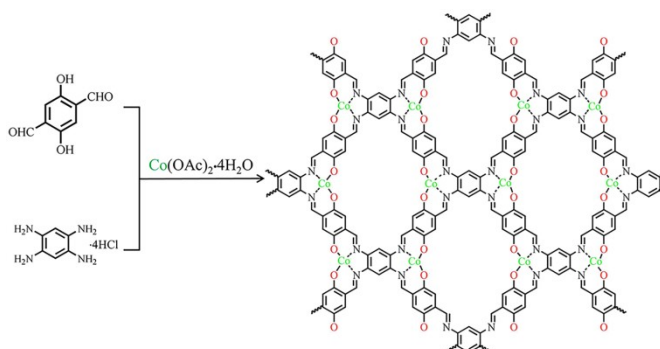
Experimental section

Synthesis of Mn-salen-POP



A mixture of mesitylene/1,4-dioxane (0.5 mL/1.5 mL), 1,2,4,5-benzenetetramine tetrahydrochloride (BTA) (20 mg, 0.07 mmol), 2,5-dihydroxy-1,4-benzenedicarboxaldehyde (HBC) (27 mg, 0.14 mmol) and 0.28 mmol $\text{Mn(OAc)}_2 \cdot 4\text{H}_2\text{O}$ was degassed in a pyrex tube (5 mL) by three freeze-pump-thaw cycles. The tubes were sealed off and heated at 150 °C for 3 days. The resulting products were collected by filtration and washed with H_2O (3×20 mL), DMF (3×20 mL) and MeOH (3×20 mL), respectively. The sample was transferred to a Soxhlet extractor and washed with tetrahydrofuran (THF) (24 h) then dried at 80 °C under vacuum for 24 h to give black powders with 81% yields.

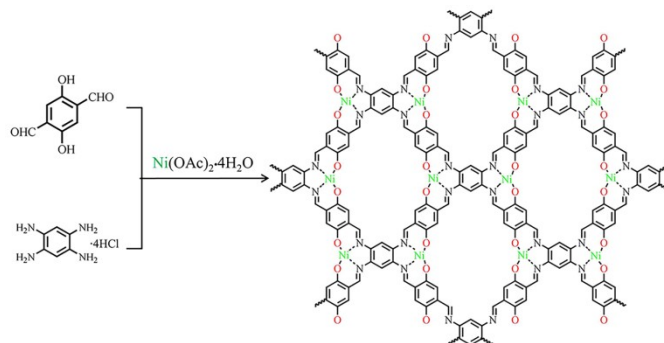
Synthesis of Co-salen-POP



A mixture of mesitylene/1,4-dioxane (0.5 mL/1.5 mL), BTA (20 mg, 0.07 mmol), HBC (27 mg, 0.14 mmol) and 0.28 mmol $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$ was degassed in a pyrex tube (5 mL) by three freeze-pump-thaw cycles. The tubes were sealed off and heated at 150 °C for 3 days. The resulting products were collected by filtration and washed with H_2O (3×20 mL), DMF (3×20 mL) and MeOH (3×20 mL), respectively. The

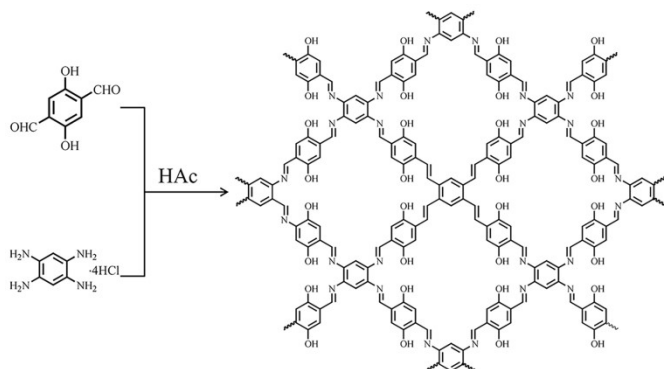
sample was transferred to a Soxhlet extractor and washed with THF (24 h) then dried at 80 °C under vacuum for 24 h to give black powders with 84% yields.

Synthesis of Ni-salen-POP



A mixture of mesitylene/1,4-dioxane (0.5 mL/1.5 mL), BTA (20 mg, 0.07 mmol), HBC (27 mg, 0.14 mmol) and 0.28 mmol $\text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O}$ was degassed in a pyrex tube (5 mL) by three freeze-pump-thaw cycles. The tubes were sealed off and heated at 150 °C for 3 days. The resulting products were collected by filtration and washed with H_2O (3×20 mL), DMF (3×20 mL) and MeOH (3×20 mL), respectively. The sample was transferred to a Soxhlet extractor and washed with THF (24 h) then dried at 80 °C under vacuum for 24 h to give black powders with 87% yields.

Synthesis of salen-POP



A mesitylene/1,4-dioxane/6M HAc (0.5 mL/1.5 mL/0.2 mL) mixture of BTA (20 mg, 0.07 mmol), HBC (27 mg, 0.14 mmol) in a Pyrex tube (5 mL) was degassed by three freeze-pump-thaw cycles. The tube was sealed off and heated at 150 °C for 3 days. The formed black precipitate was collected by filtration and washed with H_2O

(3 × 20 mL), DMF (3 × 20 mL) and MeOH (3 × 20 mL). **salen-POP** was further purified by soxhlet extraction with THF (24 h), then dried at 80 °C under vacuum for 24 h to give black powders.

Synthesis of salen-POP/Co

Salen-POP (100 mg) was dispersed in 6 mL ethanol and the mixture was added into the solution of Co(OAc)₂·4H₂O (100 mg, 0.4 mmol). The mixture was refluxed at 80 °C for 12 h. After filtration, the obtained material was fully washed with ethanol and then dried under vacuum at 60 °C for 12 h.

Experiment of CO₂ fixation under 0.1 MPa

For this reaction, styrene oxide (10 mmol), **Co-salen-POP** (30 mg, 0.82 mol%), TBAB (0.1 mmol, 1 mol%) were added into a 10 mL reaction tube. The reaction was carried out at 100 °C in the presence of carbon dioxide provided by the carbon dioxide cylinder. After a certain amount of time, the reaction was stopped. After dissolving a small portion of the product in DMSO-*d*₆ reagent and separating the catalyst through a Nylon filter membrane, the resulting clear solution was characterized by ¹H NMR. The yields were calculated according to the ¹H NMR spectra.

The detailed process of isolated yield calculation

Co-salen-POP (30 mg), phenyl glycidyl (10 mmol) and TBAB (0.1 mmol) were added into the reactor. After purging the reactor with CO₂ to remove air three times, the autoclave was pressurized to 1.0 MPa with CO₂. The temperature was raised to 100 °C in 30 minutes and the reaction proceeded for 5 minutes with stirring at 300 rpm. In the end of reaction, the reactor was quickly cooled to room temperature in an ice water bath and the CO₂ pressure was released from the autoclave. After dissolving

the mixture in ethyl acetate and filtering out the catalyst, the resulting solution was removed under reduced pressure to obtain the product. The isolated yield of corresponding cyclic carbonate of phenyl glycidyl ether was calculated by the formula: $\text{isolated yield} = \text{experimental yield (1.918 g)} / \text{theoretical yield (1.948 g)}$.

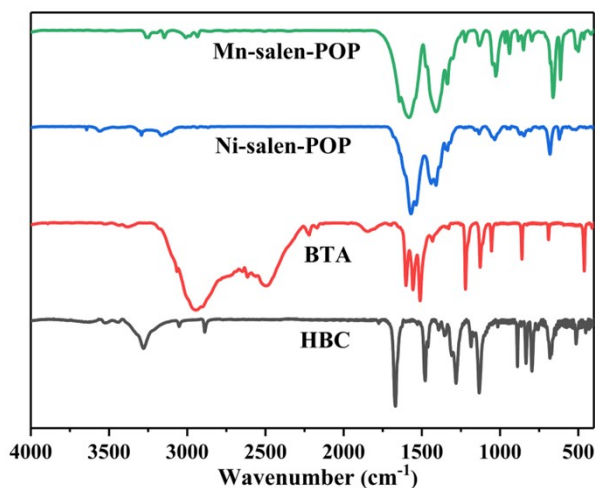


Fig. S1 FTIR spectra of **Mn-salen-POP** and **Ni-salen-POP**.

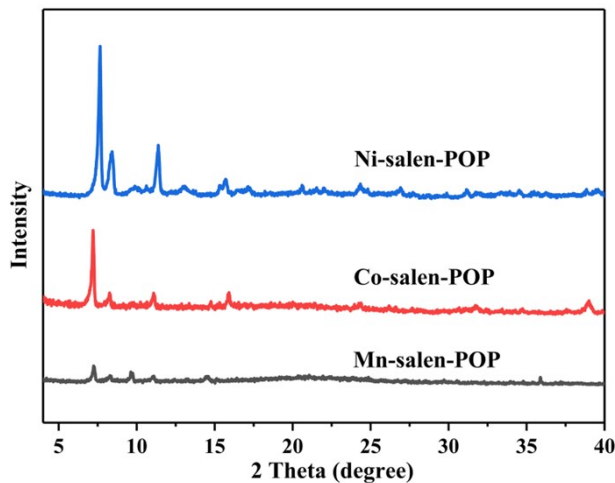


Fig. S2 Powder XRD patterns of **Mn-salen-POP**, **Co-salen-POP** and **Ni-salen-POP**.

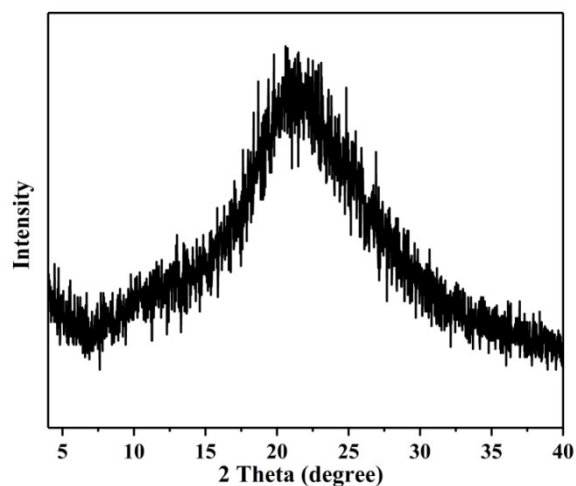


Fig. S3 Powder XRD pattern of salen-POP.

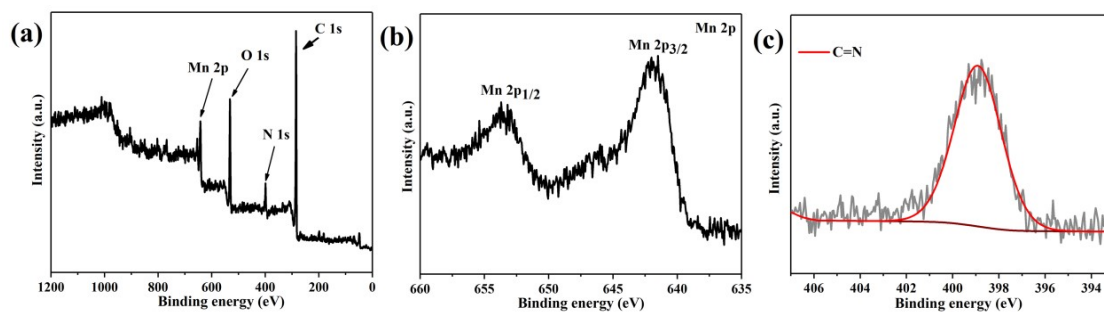


Fig. S4 (a) XPS survey spectra of Mn-salen-POP. (b) Mn 2p spectra of Mn-salen-POP. (c) N 1s spectra of Mn-salen-POP.

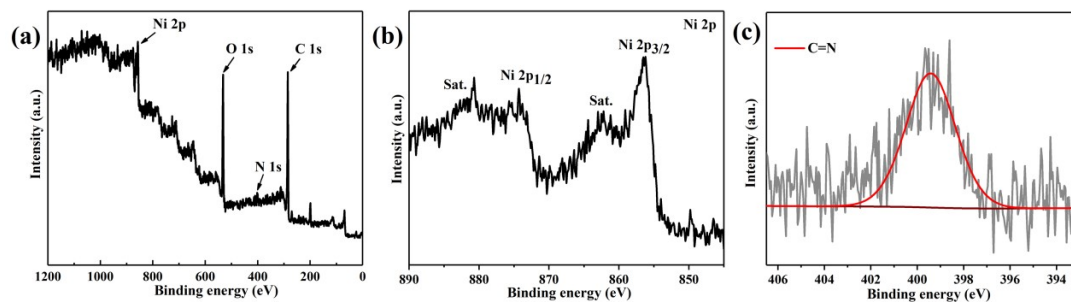


Fig. S5 (a) XPS survey spectra of Ni-salen-POP. (b) Ni 2p spectra of Ni-salen-POP. (c) N1s spectra of Ni-salen-POP.

Table S1 CHN elemental analysis and ICP results of metal for catalysts.

| M-Salen-POP | CHN Elemental Analysis (wt%) | | | Metal content (wt%) |
|---|------------------------------|------|------|---------------------|
| | C | H | N | |
| Mn-salen-POP | 19.48 | 3.38 | 2.58 | 15.39 |
| Ni-salen-POP | 23.24 | 3.43 | 2.77 | 17.29 |
| Co-salen-POP | 17.73 | 3.10 | 3.53 | 16.13 |
| Co-salen-POP (after 5 cycles) | 17.63 | 3.12 | 3.51 | 16.06 |

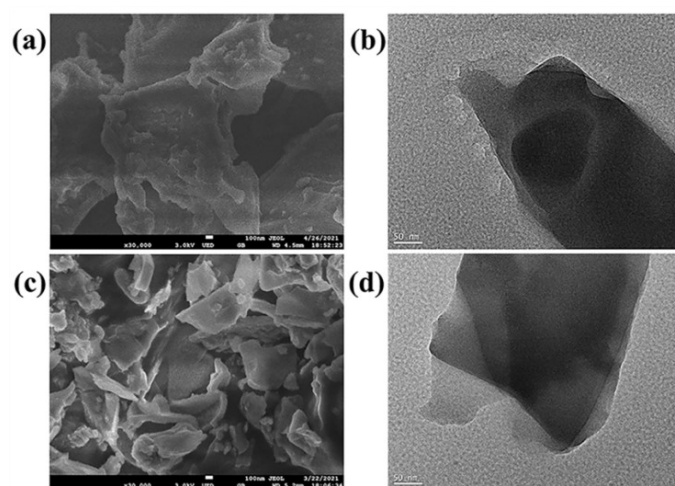


Fig. S6 (a, b) SEM and TEM images of **Mn-salen-POP**. (c, d) SEM and TEM images of **Ni-salen-POP**.

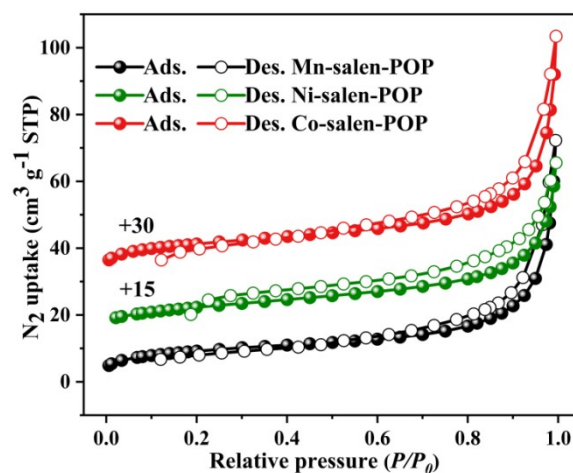


Fig. S7 N₂ adsorption–desorption isotherms of **Mn-salen-POP**, **Ni-salen-POP** and **Co-salen-POP**.

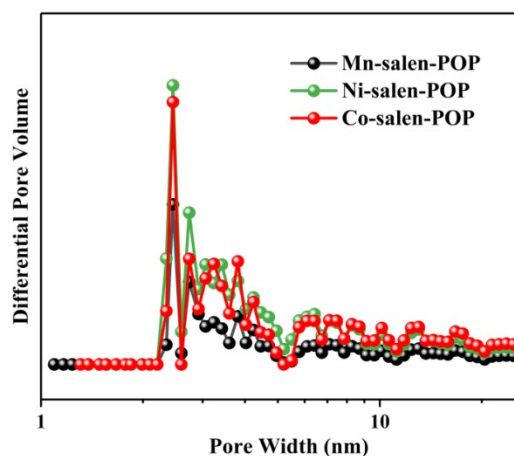


Fig. S8 Pore size distributions of **Mn-salen-POP**, **Ni-salen-POP** and **Co-salen-POP**.

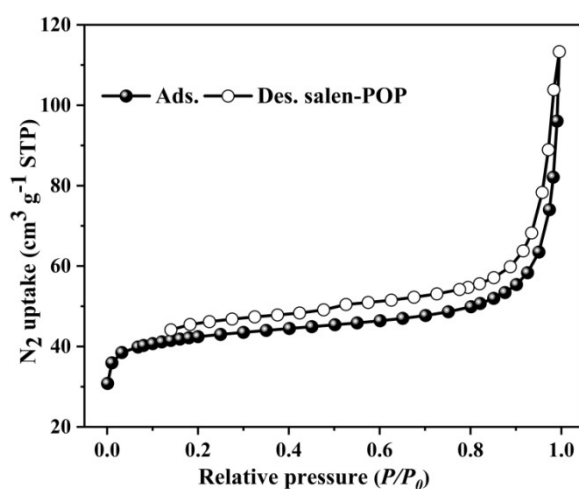


Fig. S9 N_2 adsorption-desorption isotherms of salen-POP.

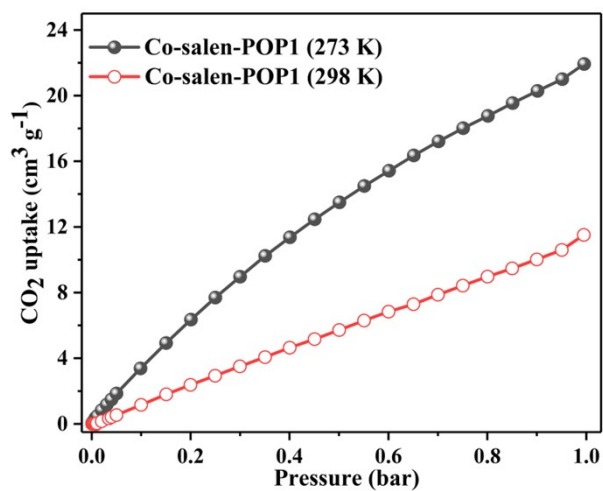


Fig. S10 Adsorption isotherms of CO_2 of **Co-salen-POP** at 273 and 298 K.

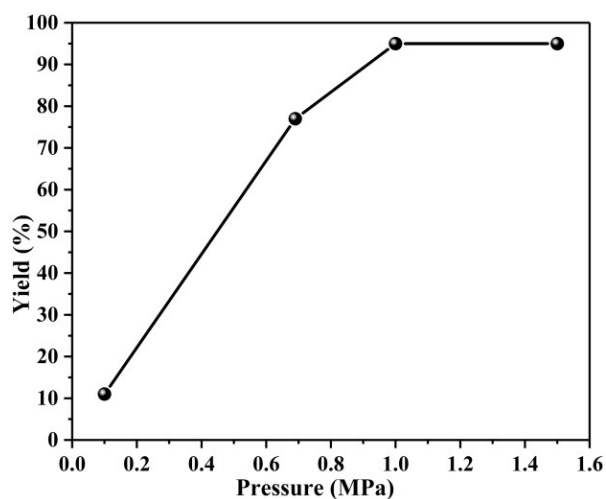


Fig. S11 Yields of styrene carbonate depending on reaction pressure under 100 °C for 30 min using **Co-salen-POP** (30 mg) as catalyst and TBAB (0.1mmol) as co-catalyst.

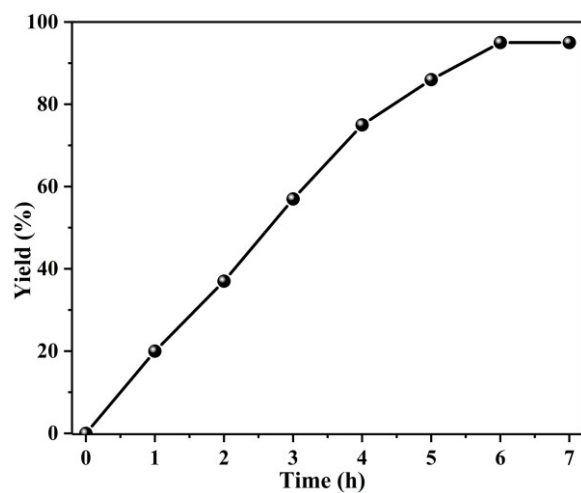


Fig. S12 Kinetic curve for the cycloaddition reactions of styrene epoxide and CO₂ catalyzed by **Co-salen-POP** (30 mg, 0.82 mol%) with the aid of TBAB (0.1 mmol, 1mol%) at 100 °C and 0.1 MPa CO₂.

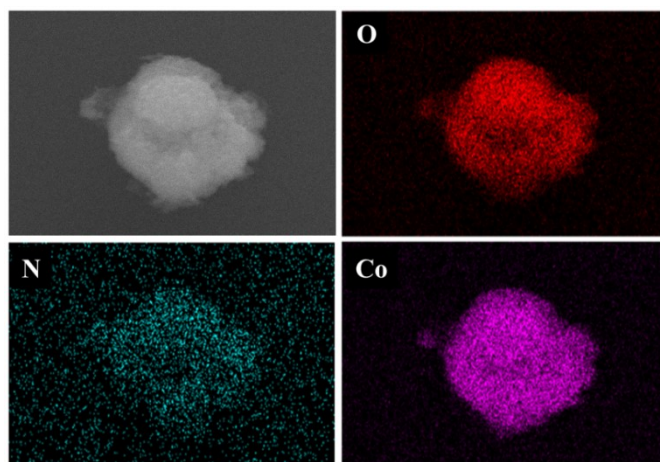


Fig. S13 SEM & EDS Mapping of **Co-salen-POP** after five catalysis.

Table S2 Comparison of the activity of **Co-salen-POP** in the PO cycloaddition reaction with the other salen-based POP catalysts.

| Catalyst | Catalyst (mol%) | T (°C) | Pressure (MPa) | TBAB (mol%) | Time (h) | Yield (%) | Ref. |
|---------------------|--------------------|-----------|-------------------|----------------|-------------|--------------|------------------|
| Co-salen-POP | 0.54 | 100 | 1 | 1 | 1/12 | 97 | This work |
| COF-salen-Co | 0.1 | 100 | 2 | 1 | 3 | 91 | S1 |
| Co-CMP-2 | 0.41 | 100 | 3 | 7.2 | 1 | 98.7 | S2 |
| Co-CMP | 0.488 | 100 | 3 | 7.2 | 1 | 98.1 | S3 |
| Zn-CMP | 0.1 | 120 | 3 | 1.8 | 1 | 74.8 | S4 |
| Zn@SBMMP | 0.48 | 80 | 2 | 1.8 | 4 | 95 | S5 |
| Co-salen-TBB-Py | 0.19 | 80 | 0.5 | none | 8 | 97.8 | S6 |
| BSPOP-Co | 0.2 | 25 | 0.1 | 4 | 18 | 92 | S7 |

Table S3 Comparison of the activity of **Co-salen-POP** in the PO cycloaddition reaction with the reported metalated porous organic polymers and MOFs.

| Catalyst | Catalyst (mol%) | T (°C) | Pressure (MPa) | TBAB (mol%) | Time (h) | Yield (%) | Ref. |
|----------------------------|--------------------|-----------|-------------------|----------------|-------------|--------------|------|
| PAF-ZnBr ₂ | 1.7 | 90 | 1 | 2 | 1 | 71 | S8 |
| Zn-TPAMP | 0.011 | 100 | 2 | 6.5 | 1 | 99 | S9 |
| Al-HCP | 0.25 | 40 | 1 | 2 | 1 | 99 | S10 |
| P-POF-Zn | 0.1 | 120 | 3 | 0.5 | 2.5 | 95 | S11 |
| Al-iPOP-2 | 0.1 | 40 | 1 | 0.2 | 3 | 99 | S12 |
| Bp-POF-Cu | 0.1 | 100 | 1 | 0.5 | 6 | 99 | S13 |
| Co-Phen-POP | 0.025 | 25 | 1 | 7.2 | 48 | 83.6 | S14 |
| Zn/HAzo-POP1 | 0.062 | 100 | 3 | 7.2 | 0.5 | 90 | S15 |
| Zn@ah-PMF | 0.0085 | 100 | 2 | 0.6 | 0.5 | 79 | S16 |
| IL-MIL-101-NH ₂ | 0.88 | 120 | 1.3 | none | 1 | 91 | S17 |
| CPP-IL _{0.05} | 1.0 | 100 | 0.1 | none | 24 | 96 | S18 |

The detailed process of yield calculation by solution-state ¹H NMR.

The yields of propylene oxide, epichlorohydrin, styrene oxide, allyl glycidyl ether, phenyl glycidyl ether, *o*-tolyl glycidyl ether and cyclohexene oxide to corresponding cyclic carbonates catalyzing by **Co-salen-POP** were calculated according to the following equation. As all of the epoxides and cyclic carbonates are known compounds, the characteristic peaks were pointed out according to reference.

$$\text{Yield}(\%) = \frac{I_{H_{a'}}}{I_{H_a} + I_{H_{a'}}} \times 100\%$$

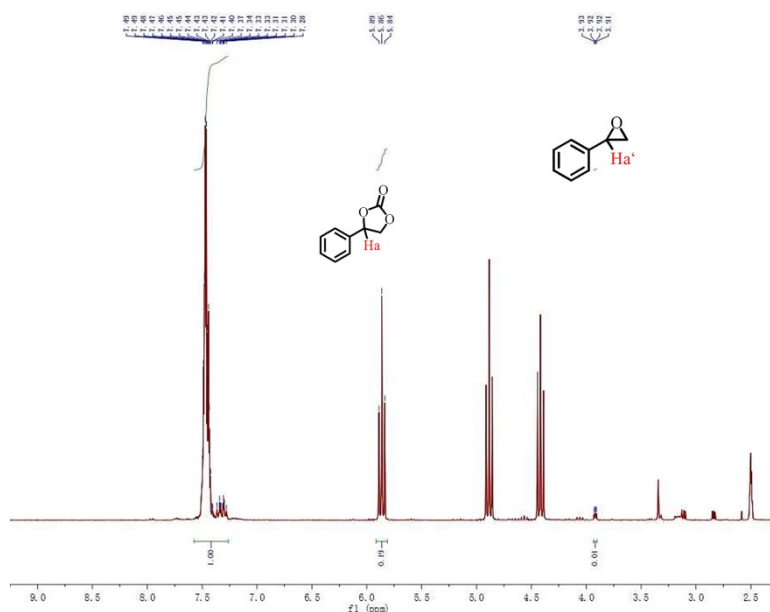


Fig. S14 Solution-state ¹H NMR of the crude products in the cycloaddition reaction catalyzed by the **Co-salen-POP** catalyst with styrene epoxide as substrate (DMSO-*d*₆ as solvent).

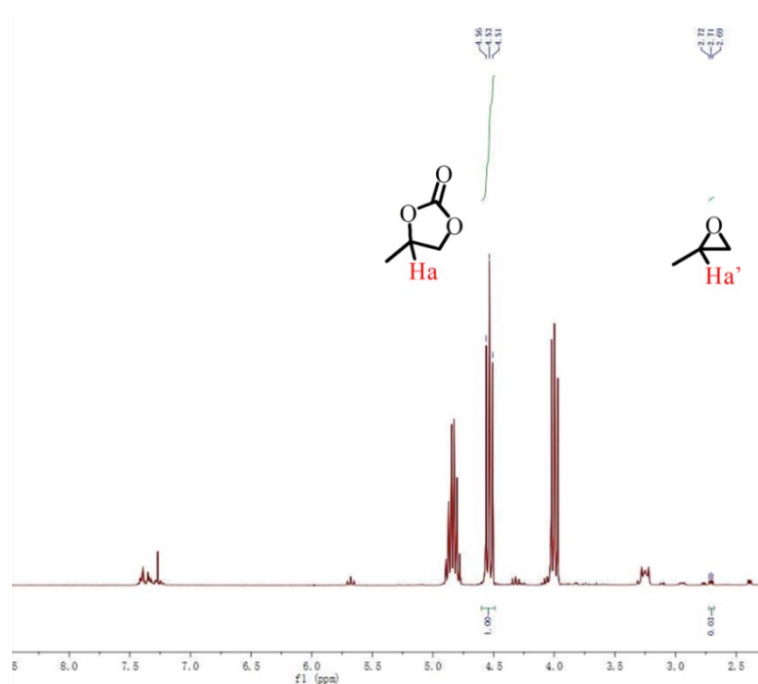


Fig. S15 Solution-state ¹H NMR of the crude products in the cycloaddition reaction catalyzed by the **Co-salen-POP** catalyst with propylene oxide as substrate (CDCl₃ as solvent).

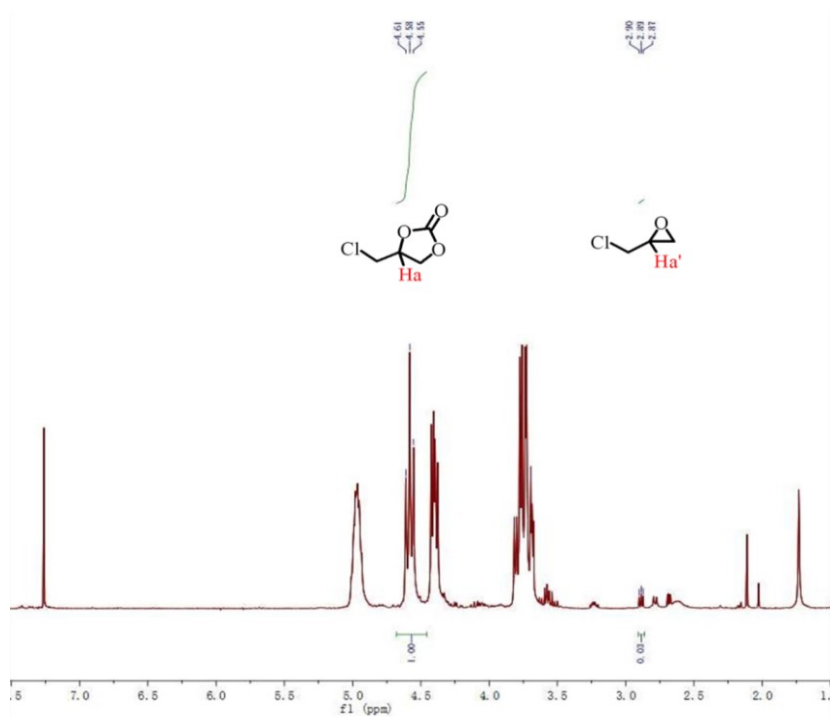


Fig. S16 Solution-state ¹H NMR of the crude products in the cycloaddition reaction catalyzed by the **Co-salen-POP** catalyst with epichlorohydrin as substrate (CDCl₃ as solvent).

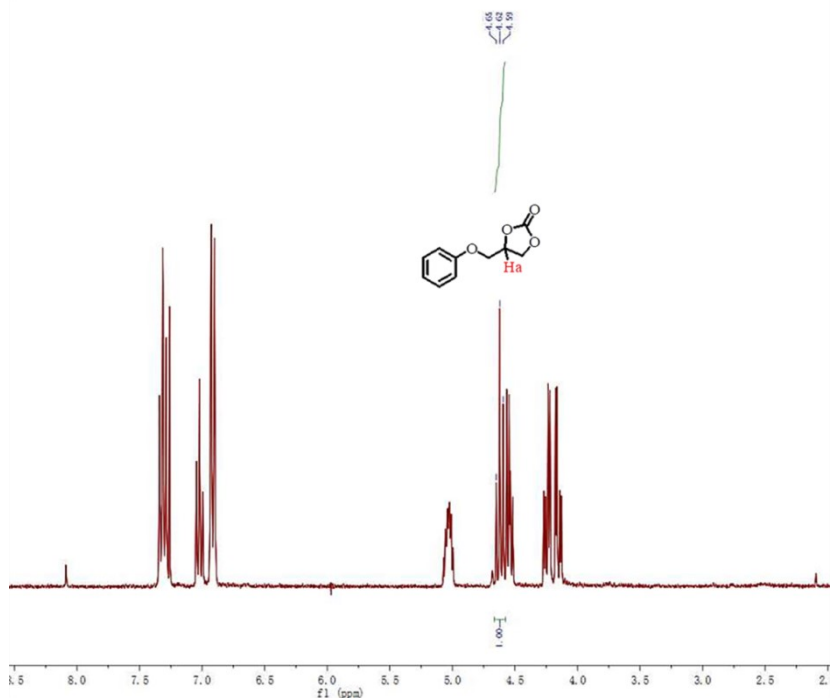


Fig. S17 Solution-state ¹H NMR of the crude products in the cycloaddition reaction catalyzed by the **Co-salen-POP** catalyst with phenyl glycidyl ether as substrate (CDCl₃ as solvent).

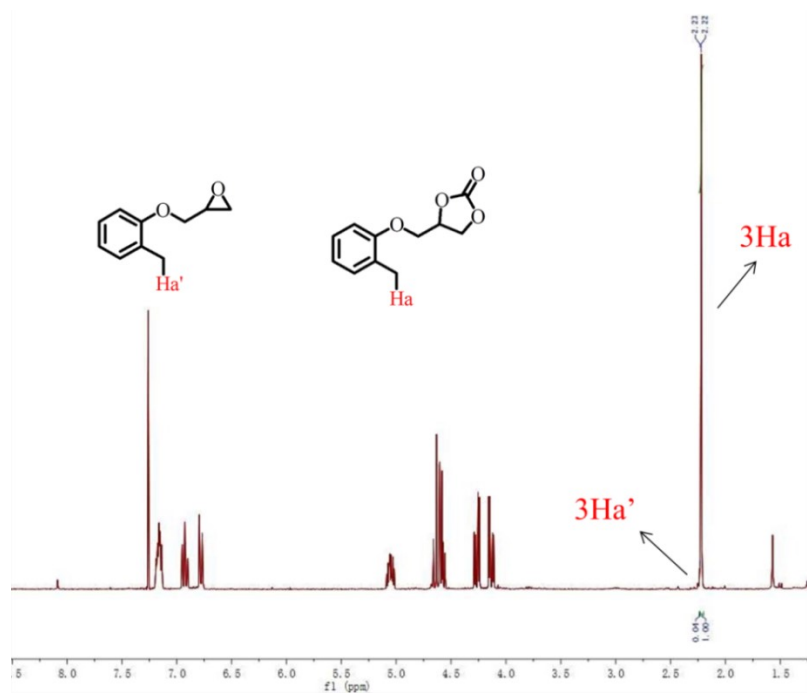


Fig. S18 Solution-state ¹H NMR of the crude products in the cycloaddition reaction catalyzed by the **Co-salen-POP** catalyst with *o*-tolyl glycidyl ether as substrate (CDCl₃ as solvent).

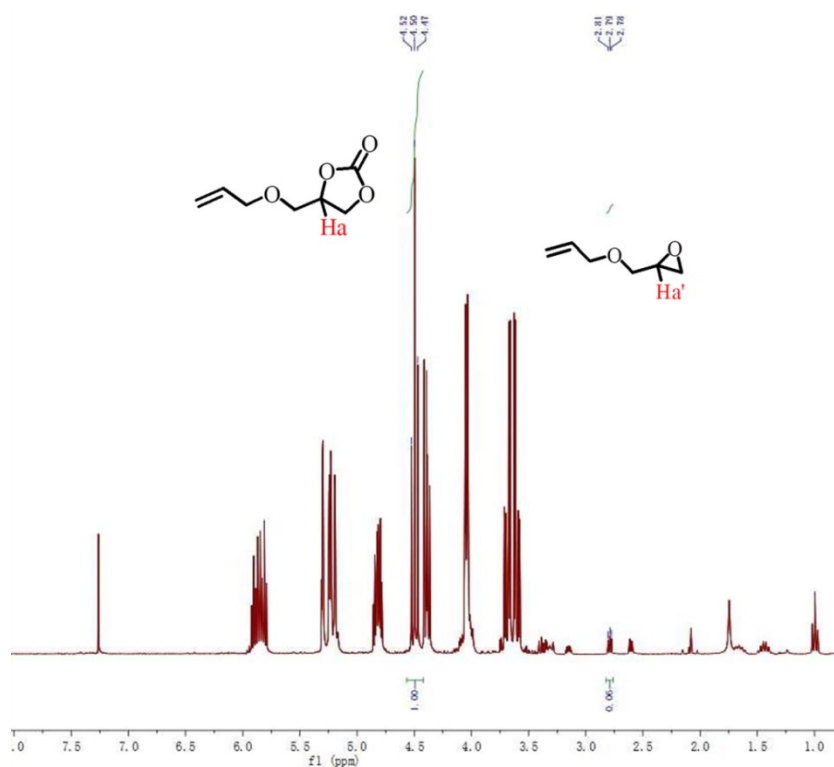


Fig. S19 Solution-state ¹H NMR of the crude products in the cycloaddition reaction catalyzed by the **Co-salen-POP** catalyst with allyl glycidyl ether as substrate (CDCl₃ as solvent).

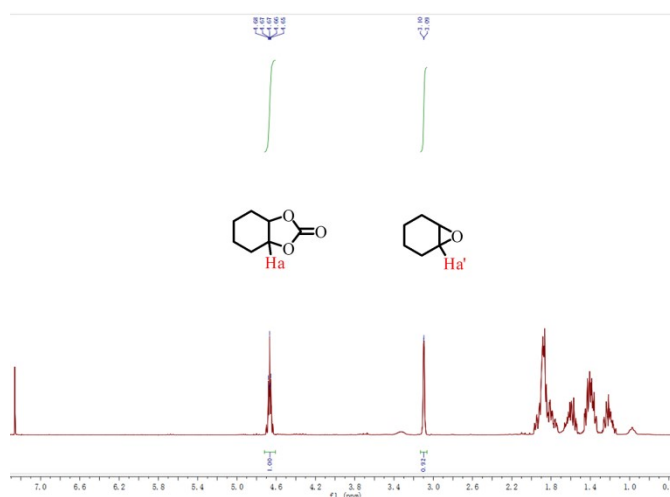


Fig. S20 Solution-state ^1H NMR of the crude products in the cycloaddition reaction catalyzed by the **Co-salen-POP** catalyst with cyclohexene oxide as substrate (CDCl_3 as solvent).

Table S3 Details of reagents used in this work.

| Reagent | Manufacturer | Purity (%) |
|----------------------------------|---|-------------|
| TBAB | Tianjin guangfu fine chemical research institute | 99 |
| Styrene epoxide | Aladdin | ≥ 95 |
| Propylene oxide | Aladdin | ≥ 99.5 |
| Epichlorohydrin | Tianjin fuchen chemical reagent factory | 98 |
| Allyl glycidyl ether | Aladdin | 99 |
| Phenyl glycidyl ether | Macklin | > 98 |
| 2-methylphenyl glycidyl ether | Aladdin | 95 |
| Ethyl acetate | Tianjin fuyu fine chemical company limited | 99 |
| DMSO- d_6 | Aldrich | 99.9 |
| CDCl_3 | Aladdin | 99 |
| 1,4-dioxane | Tianjin fuyu fine chemical company limited | 99.5 |

| | | |
|--|--|------|
| mesitylene | Macklin | 97 |
| 1,2,4,5-benzenetetramine tetrahydrochloride | Zhenzhou Alfa chemical company | 95 |
| 2,5-dihydroxy-1,4- benzenedicarboxaldehyde | Zhenzhou Alfa chemical company | 96 |
| Co(OAc) ₂ ·4H ₂ O | China National Pharmaceutical Group Corporation | 99.5 |
| Mn(OAc) ₂ ·4H ₂ O | China National Pharmaceutical Group Corporation | 99.5 |
| Ni(OAc) ₂ ·4H ₂ O | China National Pharmaceutical Group Corporation | 99.5 |

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