

Ionic Fe(III)-porphyrin frameworks for one-pot synthesis of cyclic carbonates from olefins and CO₂

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Materials and methods

All reagents used in this study were commercially available and used as received without further purification. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Pyrrole, 4-pyridine carboxaldehyde, 1, 4-bis(bromomethyl) benzene, and ZnCl_2 were purchased from Sigma Aldrich Chemical Co. The powder XRD measurements were recorded on a PANalytical's X'PERT PRO diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$; 40 kV, 20 MA). Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Perkin Elmer FTIR spectrometer. UV-Vis (Diffuse Reflectance) spectra were recorded on a Shimadzu spectrophotometer using BaSO_4 as a reference. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Scientific NEXSA photoemission spectrometer using Al $\text{K}\alpha$ (1486.6 eV) X-ray radiation. The analysis of obtained data was carried out using advantage software. ^1H NMR spectra were recorded in CDCl_3 on a JEOL JNM-ECS400 spectrometer operating at a frequency of 400 MHz.

Experimental Section

Synthesis of 5, 10, 15, 20-tetrakis (4-pyridyl)-porphyrin [H_2TPyP]

In a 250 mL round-bottom flask, 4-pyridine carboxaldehyde (25 mmol, 2.815 g) was dissolved in propionic acid (50 mL) with stirring. Pyrrole (25 mmol, 1.68 g) was then added dropwise. The solution was refluxed at 140 °C for 12 h. Then, the reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. After the removal of the solvent, the precipitation was done in DMF at a low temperature. The precipitate was filtered, washed with diethyl ether, and dried under vacuum to obtain a purple solid of H_2TPyP . ^1H NMR (400 MHz, CDCl_3) δ 8.94 (d, 8H, δ 8.83 (s, 8H, δ 8.07 (d, 8H, δ -2.83 (s, 2H)

Synthesis of 5, 10, 15, 20-tetrakis (4'-pyridyl)Zn(II)porphyrin, [Zn-TPyP]

In a 250 mL round bottom flask, TPyP (0.5 mmol, 0.31 g) and ZnCl₂ (8 mmol, 1.00 mg) were dissolved in methanol (15 mL) and chloroform (60 mL). The resulting mixture was refluxed for 28 h. After cooling to room temperature, the solvent was removed under reduced pressure using a rotary evaporator. The obtained red solid was washed with methanol in sintered glass crucible and dried under vacuum. ¹H NMR (400 MHz, DMSO-d₆) δ 8.96 (d, 8H), δ 8.85 (s, 8H), δ 8.09 (d, 8H).

Synthesis of 5, 10, 15, 20-tetrakis (4'-pyridyl)Fe(III)porphyrin, [Fe-TPyP]

In a 250 mL round bottom flask, TPyP (0.5 mmol, 0.31 g) and FeCl₃.6H₂O (8 mmol, 1.60 g) were dissolved in methanol (15 mL) and chloroform (60 mL). The resulting mixture was refluxed for 28 h. After cooling to room temperature, the solvent was removed under reduced pressure using a rotary evaporator. The obtained red solid was washed with methanol in sintered glass crucible and dried under a vacuum.

Synthesis of metal-porphyrin-based ionic porous polymer (M-IPOP1, M = Zn, Fe)

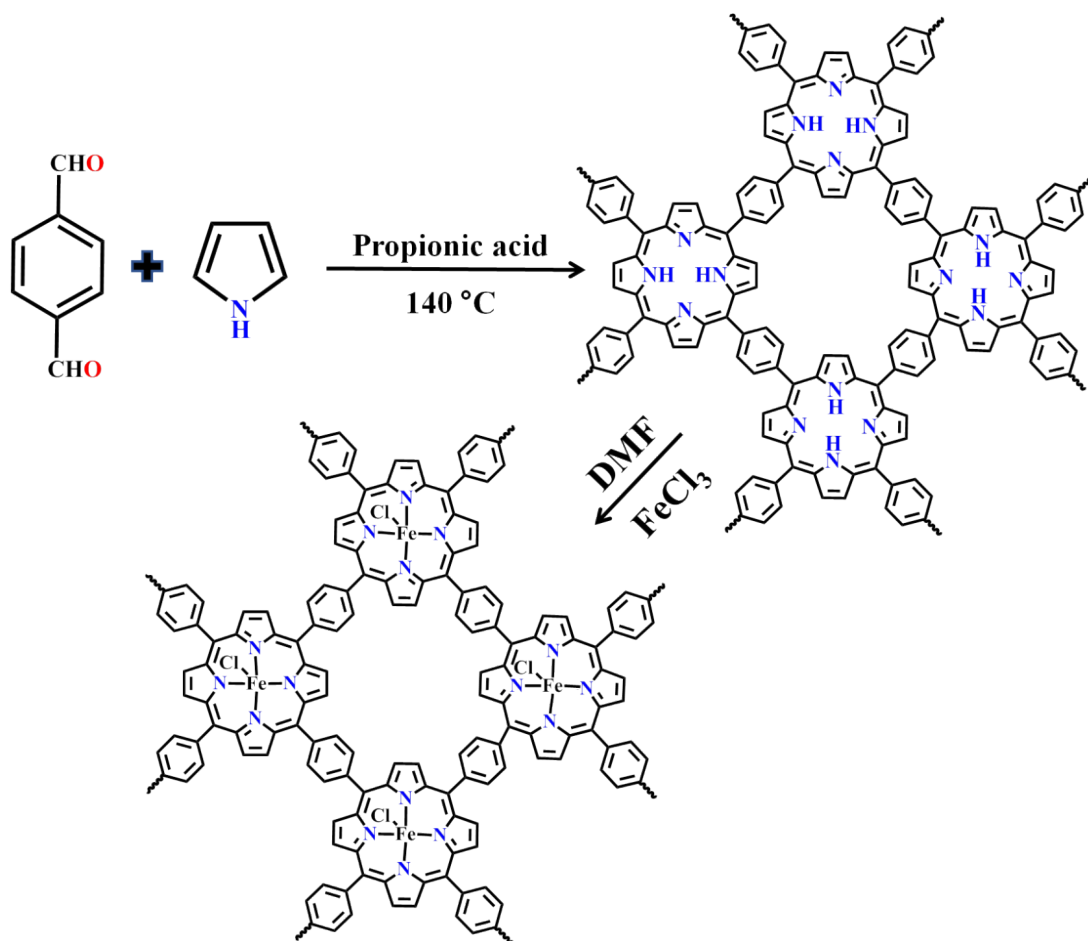
To a suspension of M-TPyP (0.5 mmol) in 25 mL of THF, 1,4-bis(bromomethyl)benzene (BBMBr) (1 mmol, 0.264 g) was added and the resulting mixture was refluxed under N₂ atmosphere. After 90 h, the reaction mixture was cooled down to RT, and the solid of M-IPOP1 formed was washed thoroughly with chloroform. The product was further purified by washing with chloroform in a soxhlet apparatus for 36 h and dried at 80 °C under vacuum for 12 h.

Synthesis of metal-porphyrin-based ionic porous polymer (Fe-IPOP2)

To a suspension of Fe-TPyP (0.5 mmol) in 25 mL of THF, 4, 4'-bis(bromomethyl)biphenyl (1 mmol) was added, and the resulting mixture was refluxed under an N₂ atmosphere for 90 h and then it was cooled down to RT. The solid of Fe-IPOP2 formed was washed thoroughly with chloroform. The product was further purified by washing with chloroform in a soxhlet apparatus for 36 h and dried at 80 °C under vacuum for 12 h.

Synthesis of Fe-POP

The Fe-POP was synthesized by following the previously reported procedure with a slight modification (Scheme S2)¹. Briefly, terephthalaldehyde (10 mmol, 1.3 g) was mixed in 80 mL of propionic acid and separately pyrrole (20 mmol, 1342 mg) was dissolved in 20 mL of propionic acid and this solution was added to terephthalaldehyde solution in a drop-wise manner and the resulting mixture was refluxed for 12 h. After cooling to RT, the black ppt of POP polymer formed was obtained by filtration, washed thoroughly with CH₂Cl₂, CH₃OH, and H₂O, respectively, and dried under vacuum at 100 °C for 12 h. Then 50 mg of POP was dispersed by 15 mL DMF and FeCl₃·6H₂O (2 mmol) was added to this solution, and the resulting mixture was heated to 150 °C with stirring for 6 h. After cooling to RT, the Fe-POP polymer formed was filtered and thoroughly washed with water and CH₃OH to remove unreacted metal salt and then dried at 100 °C under vacuum for 12 h.



Scheme S1. Synthesis scheme of Fe-POP.

Catalytic epoxidation of olefins

A mixture of catalyst (20 mg), olefins (1 mmol), and PhIO (1.5 mmol) was mixed in dichloromethane (2 mL) in a Schlenk tube (90 mL). The resulting mixture was stirred at RT for 18 h. After which time, the mixture was centrifuged to separate the catalyst, the solvent was evaporated, and the conversion was determined by ^1H NMR spectroscopy. The recovered catalyst after was washed with dichloromethane/methanol and dried under vacuum and reused for successive cycles.

The catalytic one-pot cyclic carboxylation of olefins with CO₂

The one-pot cyclic carboxylation of olefins with CO₂ was carried out in a 50 mL glass reactor. Prior to catalytic reactions, the catalyst was activated at 100 °C for 12 h under vacuum to remove guest solvent molecules. In a typical reaction, olefins (1 mmol), and the activated catalyst (20 mg) were taken in the reactor at RT. Then, CO₂ was flushed into the reactor three times to remove air and finally 1 bar was introduced and the reaction mixture was allowed to stir at 80 °C for 24 h. After this time, the mixture was cooled to RT and the catalyst was separated from the reaction mixture by simple centrifugation and the conversion was determined from ¹H NMR analysis of the filtrate. The recovered catalyst was washed with methanol thoroughly and activated at 100 °C under vacuum for 12 h and reused for subsequent catalytic cycles.

Analysis of gas adsorption isotherms

Clausius-Clapeyron equation² was used to calculate the enthalpies of carbon dioxide adsorption and by using Langmuir Freundlich equation³ an accurate fit was retrieved for precise prediction of carbon dioxide adsorbed at saturation. A modified Clausius-Clapeyron equation was used for calculations.

$$\ln(P_1/P_2) = \Delta H_{ads}(T_2 - T_1/R.T_1.T_2) \dots\dots(1)$$

where P₁ and P₂ = Pressures for isotherm at 273K and 298K, respectively.

T₁ and T₂ = Temperatures for isotherm at 273K and 298K, respectively.

ΔH_{ads} = Enthalpy of adsorption.

R = Universal gas constant = 8.314 J/K/mol.

The pressure is a function of the amount of gas adsorbed which was determined by using the Langmuir-Freundlich fit.

$$Q/Q_m = B.P^{(1/t)}/1 + (B.P^{(1/t)}) \dots\dots\dots (2)$$

where Q = moles of gas adsorbed.

Q_m = moles of gas adsorbed at saturation.

B and t = constants.

P = Pressure.

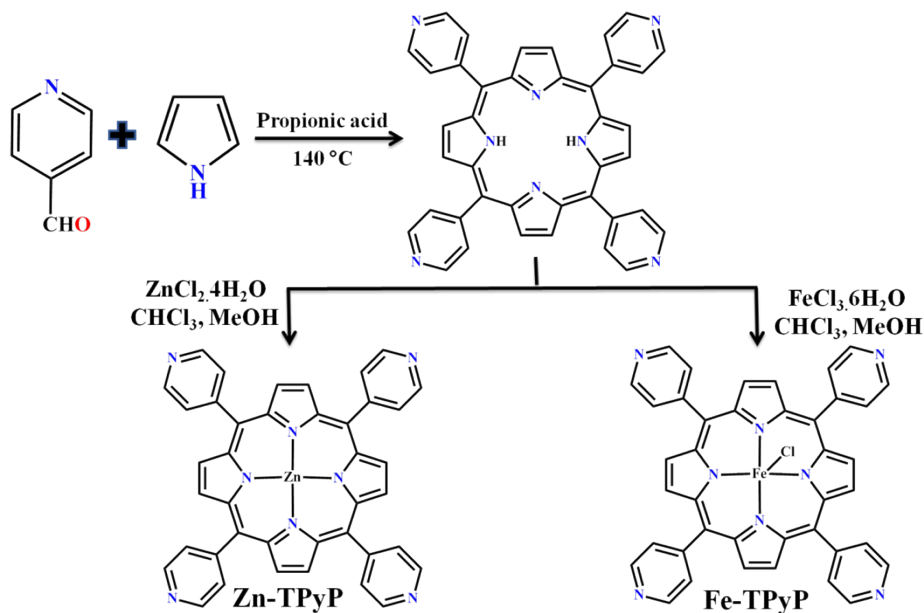
By rearranging equation (2) we get equation (3)

$$P = [(Q/Q_m)/\{B - (B.(Q/Q_m))\}]^t \dots\dots\dots(3)$$

Substituting equation (3) into equation (1) we get

$$\Delta H_{ads} = \{R.T_1.T_2/(T_2 - T_1)\} \cdot \ln \frac{[(Q/Q_{m1})/\{B - (B.Q/Q_{m1})\}]^{t_1}}{[(Q/Q_{m2})/\{B - (B.Q/Q_{m2})\}]^{t_2}} \dots\dots\dots(4)$$

In equation (4), subscripts 1 and 2 represents data corresponding to 273K and 298K in the case of carbon dioxide gas.



Scheme S2. Synthesis scheme of Zn/Fe-TPyP.

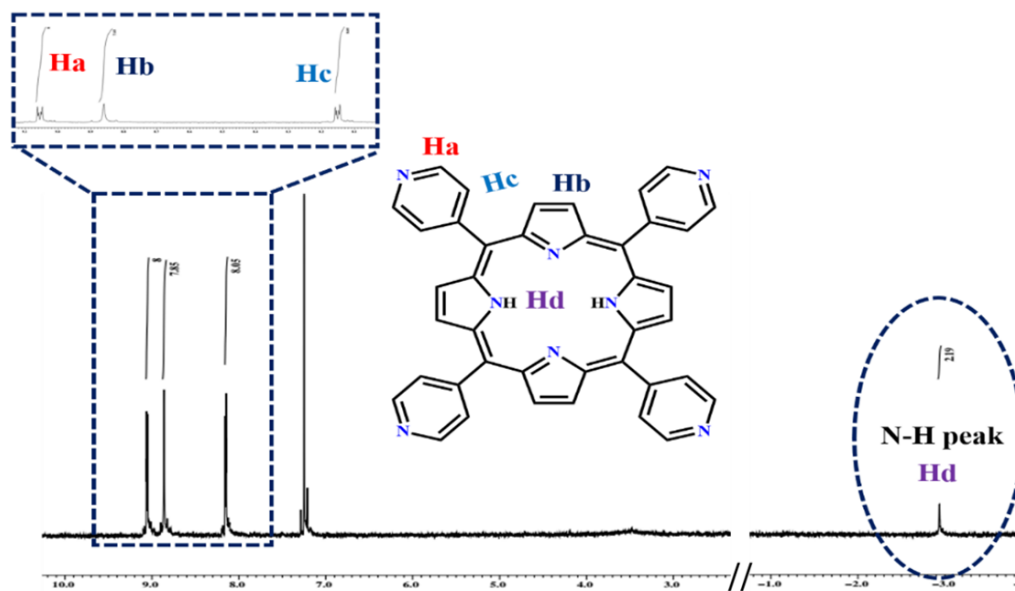


Fig. S1 ¹H NMR (400MHz, CDCl₃, 20 °C) spectrum of H₂TPyP.

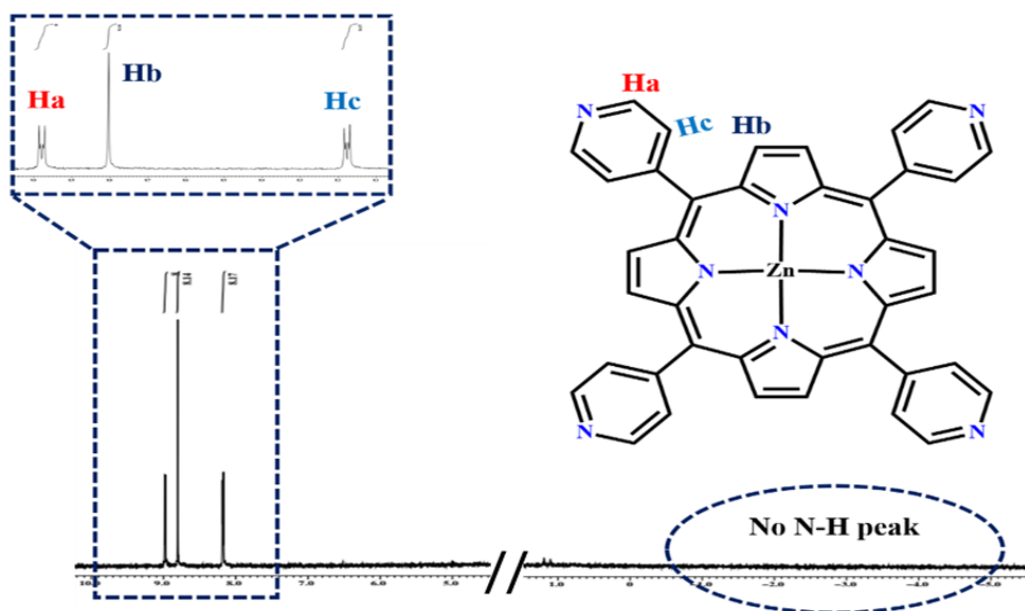


Fig. S2 ¹H NMR (400 MHz, DMSO, 20 °C) spectrum of Zn-TPyP.

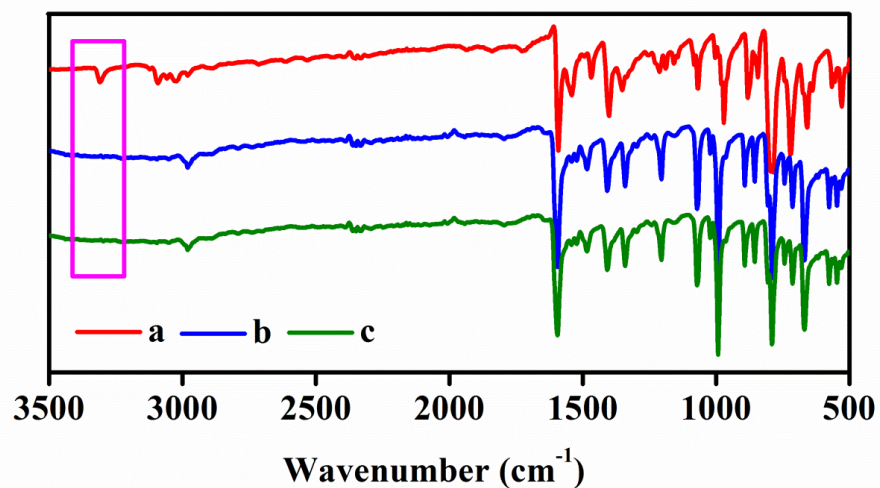


Fig. S3 FT-IR spectra (solid, 1 mg sample, 20 °C) of (a) H₂TPyP, (b) Zn-TPyP, and (c) Fe-TPyP.

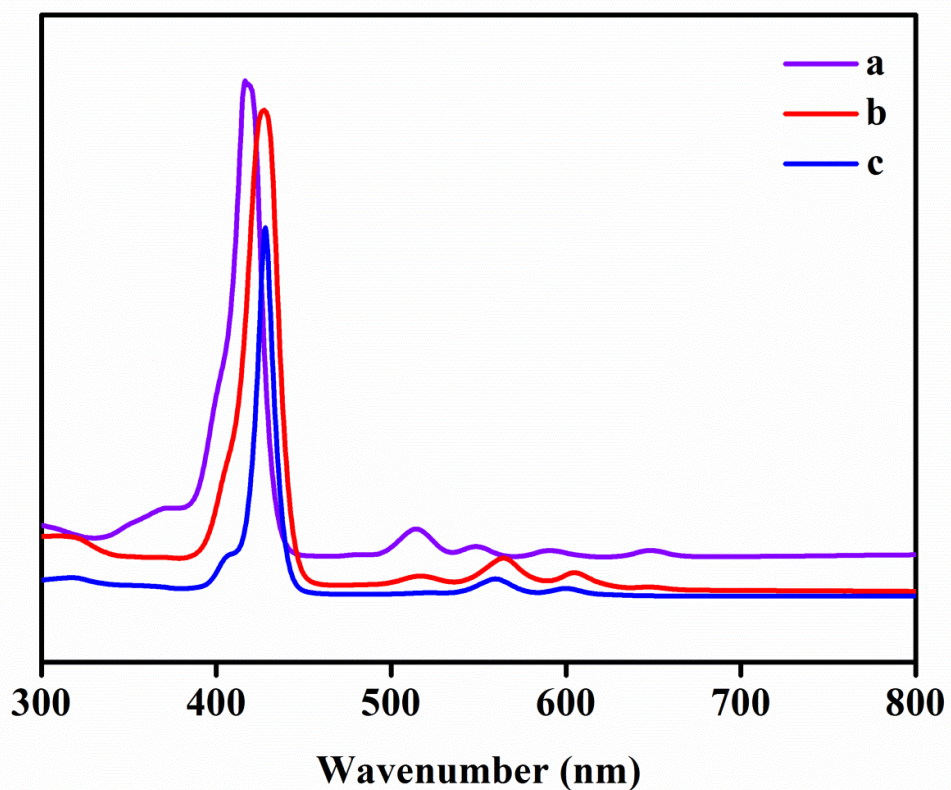


Fig. S4 UV-Visible absorption spectra (DMF (3 mL), 1 mg sample, 25 °C) of (a) TPyP, (b) Zn-TPyP, and (c) Fe-TPyP.

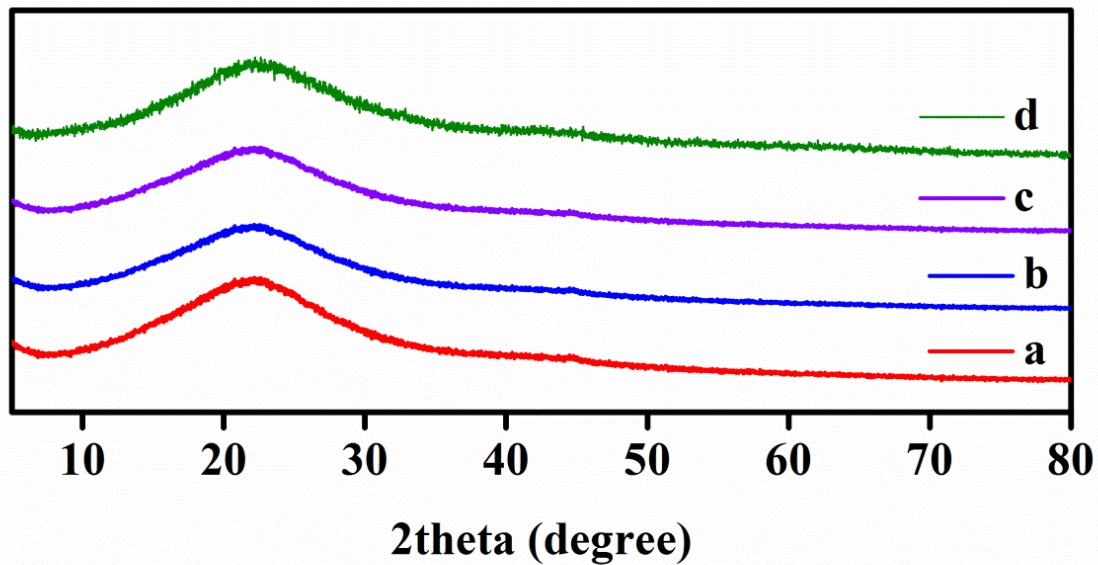


Fig. S5 PXR D plots of as-synthesized (a) Zn-IPOP1, (b) Fe-IPOP1, (c) Fe-IPOP2, and (d) recycled Fe-POP1.

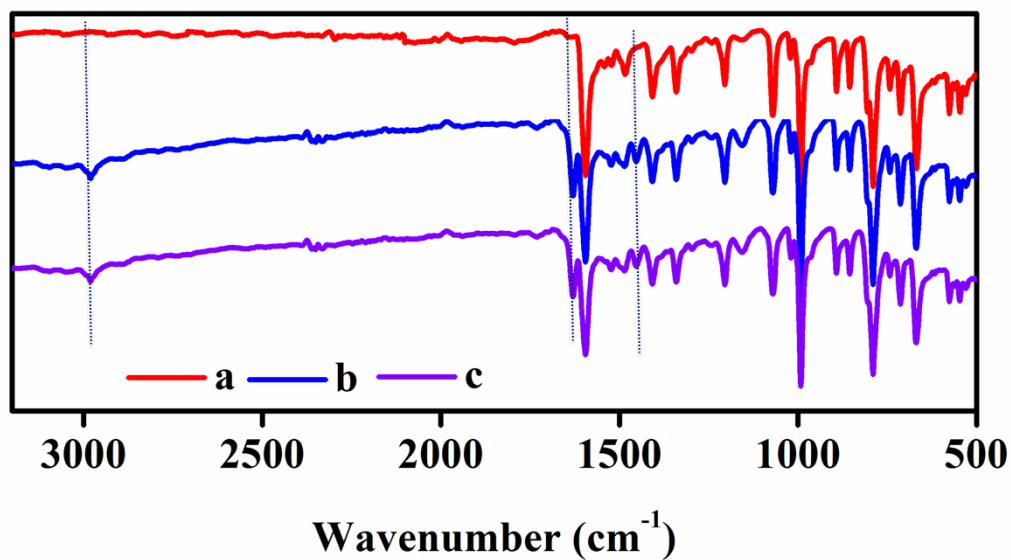


Fig. S6 FT-IR spectra (solid, 1 mg sample, 25 °C) of (a) Fe-TPyP, (b) Zn-IPOP1, and (c) Fe-IPOP1.

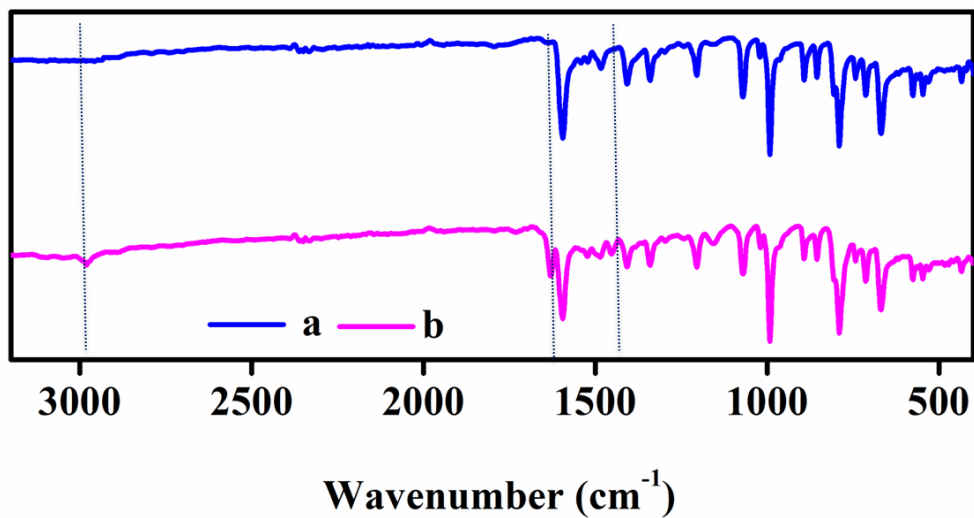


Fig. S7 FT-IR spectra (solid, 1 mg sample, 25 °C) of (a) Fe-TPyP, and (b) Fe-IPOP2.

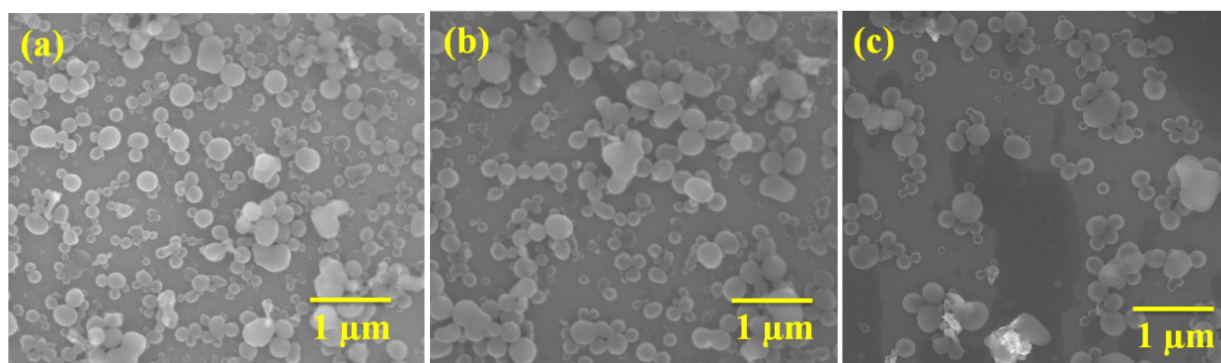


Fig. S8 FE-SEM images of (a) Fe-IPOP1, (b) Fe-IPOP2, and recycled Fe-POP1.

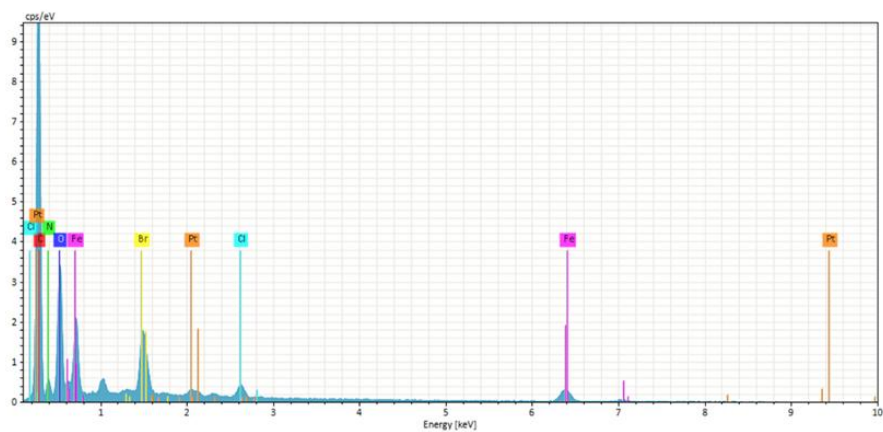


Fig. S9 EDX spectra of Fe-IPOP1.

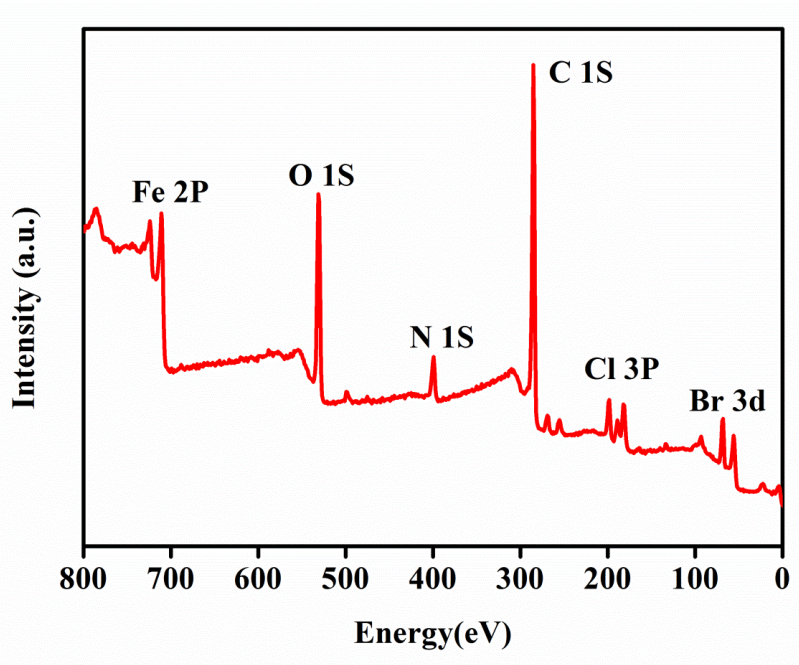


Fig. S10 XPS survey spectra for Fe-IPOP1.

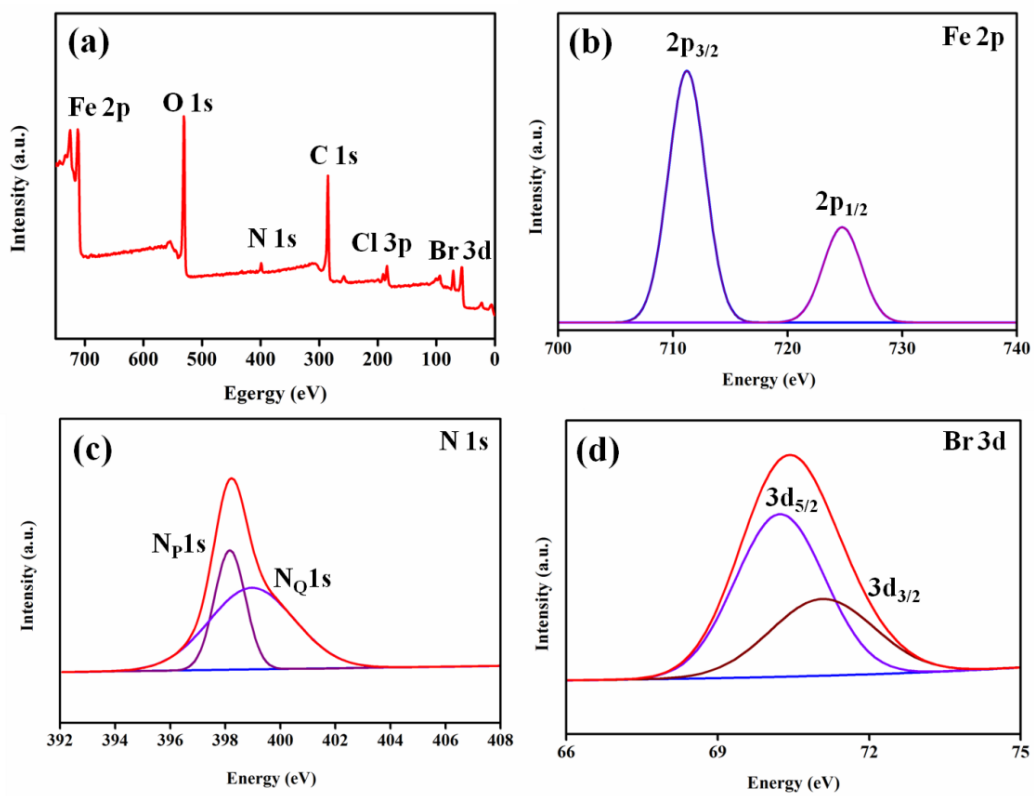


Fig. S11 XPS for Fe-POP2 (a) survey scan, (b) Fe 2p, (c) N 1s, and (d) Br 3d.

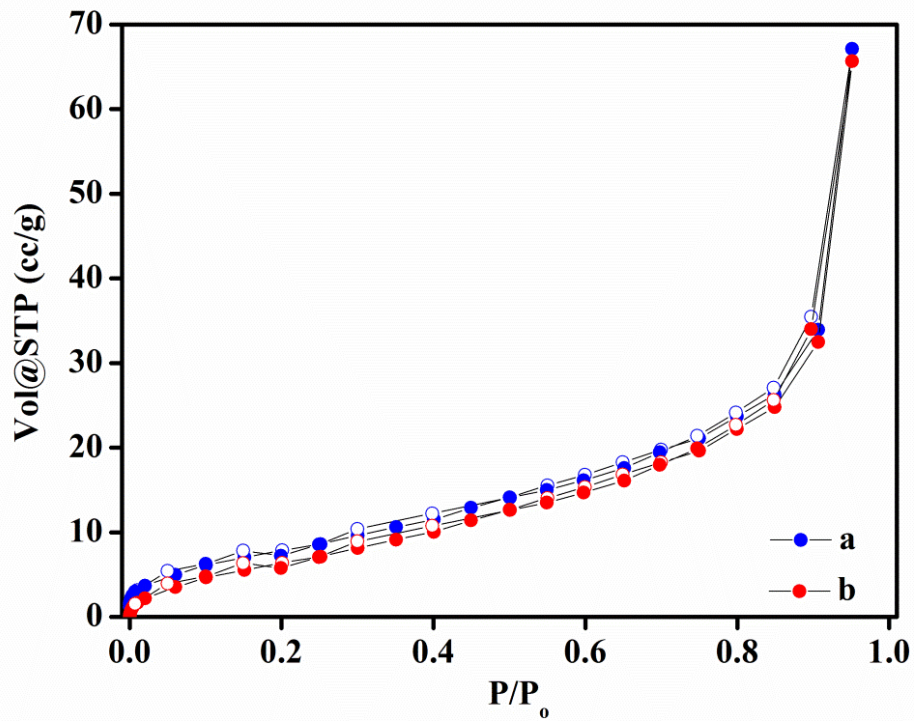


Fig. S12 N₂ adsorption isotherm of (a) as-synthesized Fe-IPOP1, and (b) recycled Fe-IPOP1.

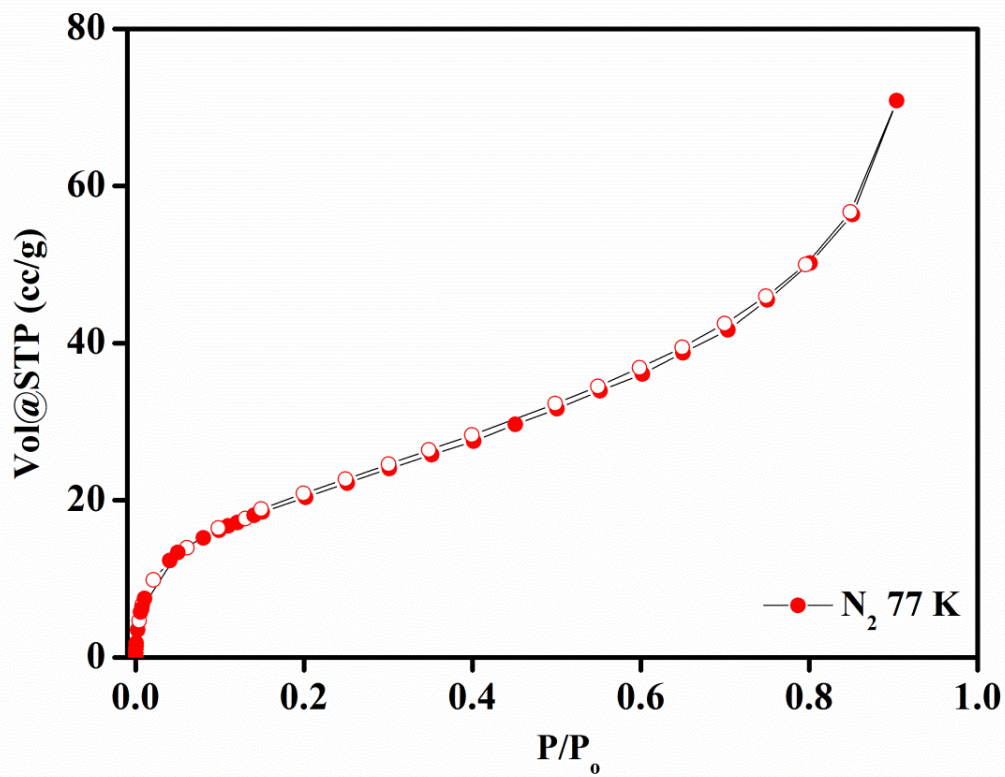


Fig. S13 N₂ adsorption isotherm of Fe-IPOP2.

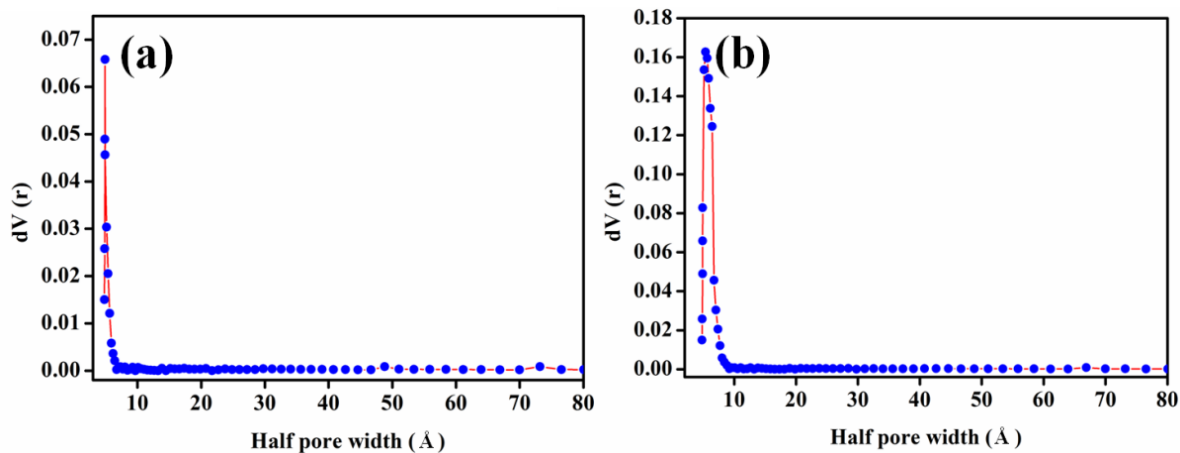


Fig. S14 Pore size distribution plots for (a) Fe-IPOP1, and (b) Fe-IPOP2.

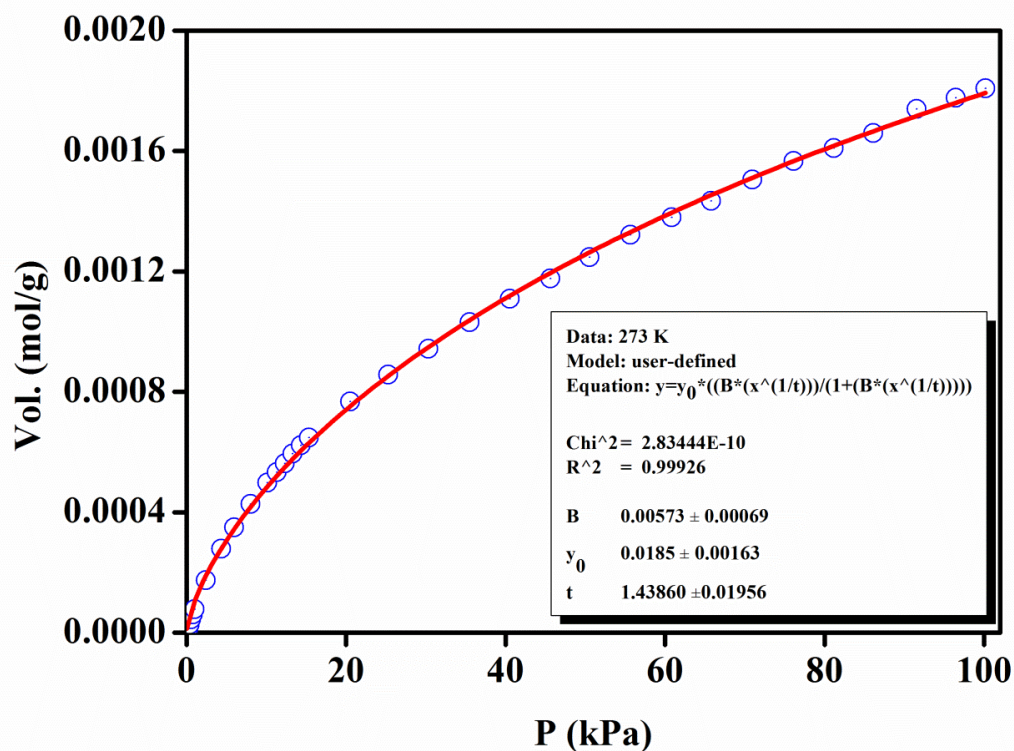


Fig. S15 Carbon dioxide adsorption isotherm of Fe-IPOP1 carried out at 273 K. The solid line shows the best fit to the data using the Langmuir-Freundlich equation.

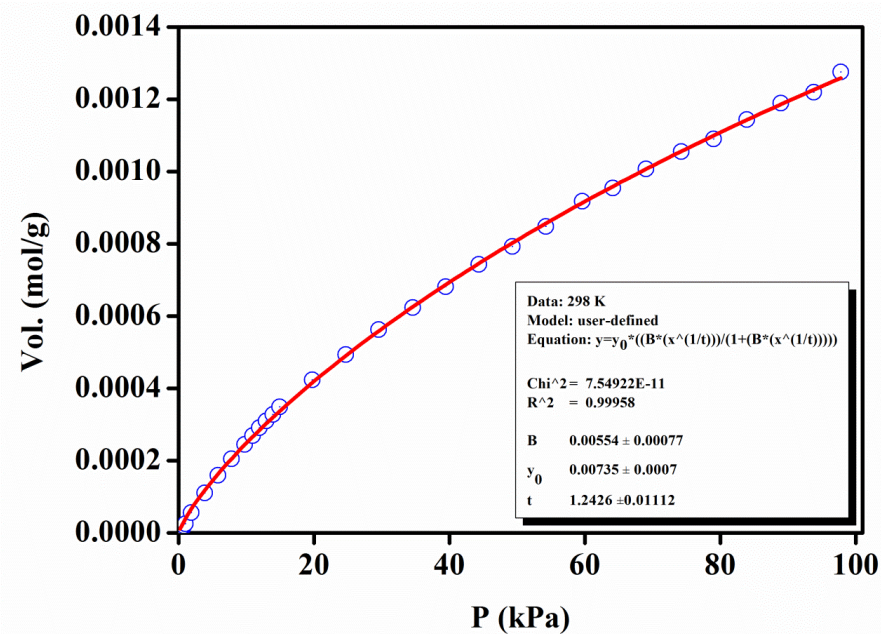


Fig. S16 Carbon dioxide adsorption isotherm of Fe-IPOP1 carried out at 298 K. The solid line shows the best fit to the data using the Langmuir-Freundlich equation.

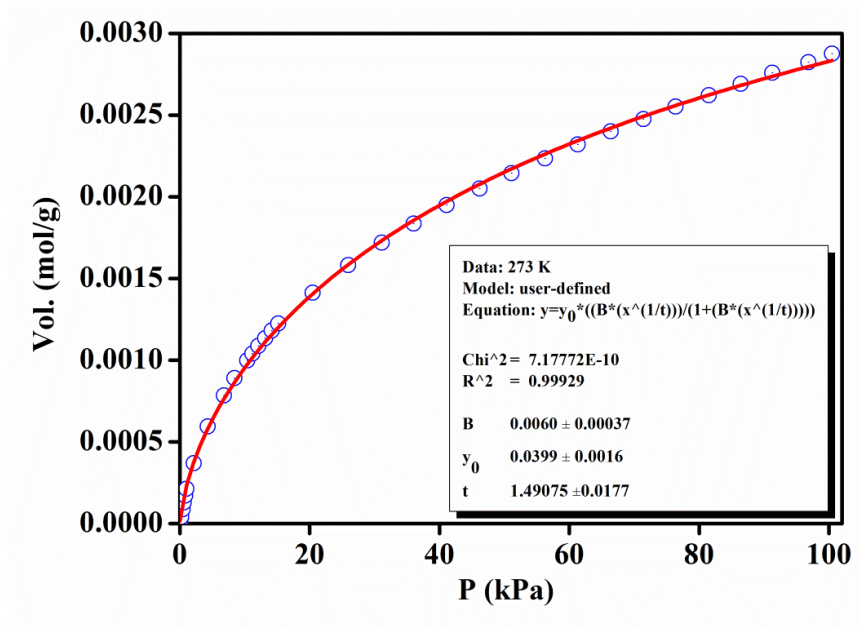


Fig. S17 Carbon dioxide adsorption isotherm of Fe-IPOP2 carried out at 273 K. The solid line shows the best fit to the data using the Langmuir-Freundlich equation.

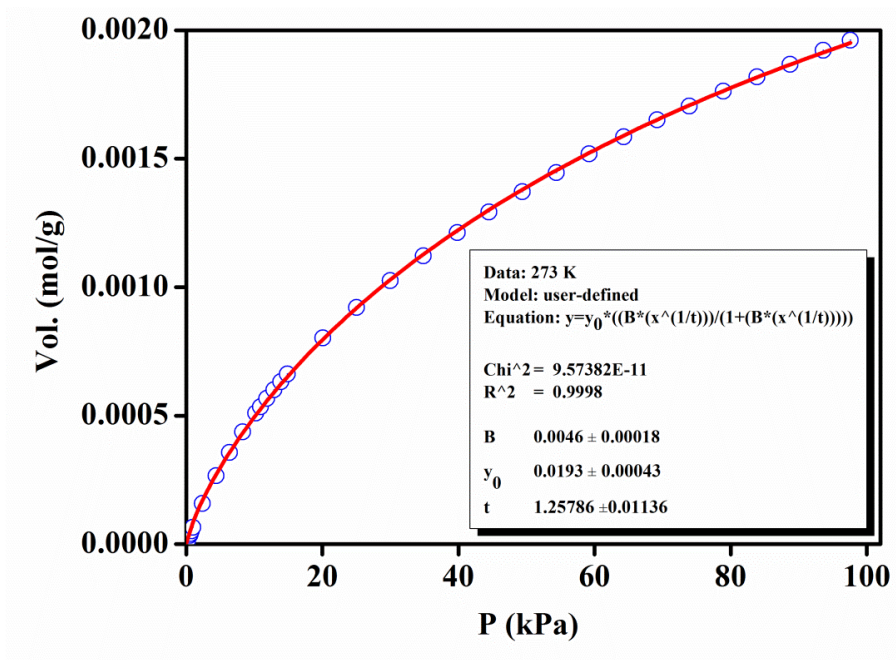


Fig. S18 Carbon dioxide adsorption isotherm of Fe-IPOP2 carried out at 298 K. The solid line shows the best fit to the data using the Langmuir-Freundlich equation.

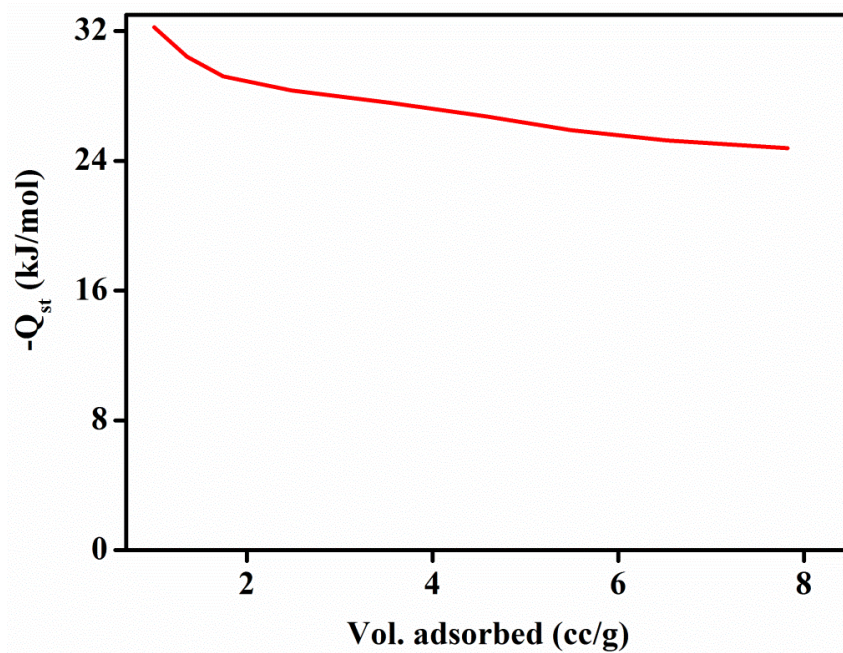


Fig. S19 Enthalpy of carbon dioxide adsorption for Fe-IPOP1 determined using the Clausius-Clapeyron equation.

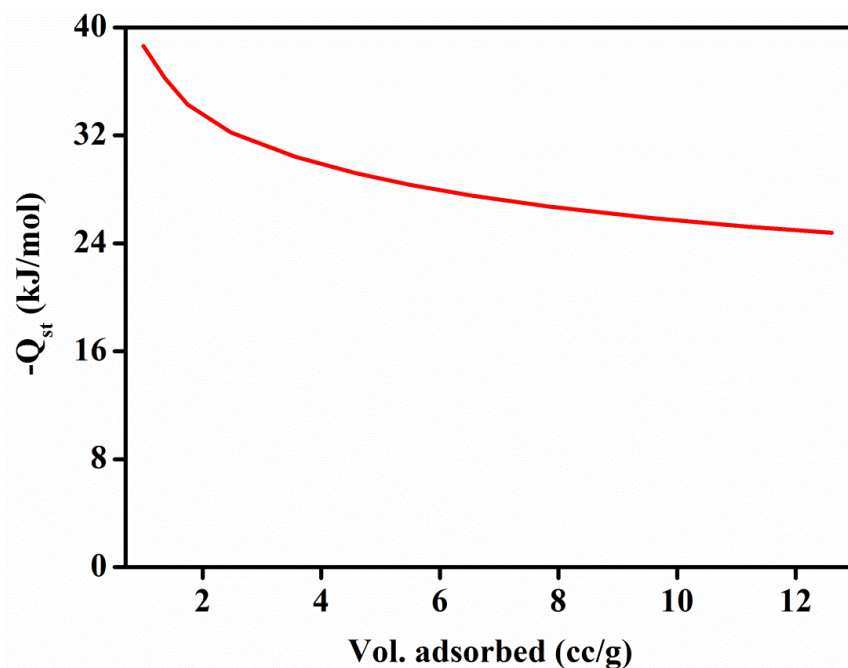


Fig. S20 Enthalpy of carbon dioxide adsorption for Fe-IPOP2 determined using the Clausius-Clapeyron equation.

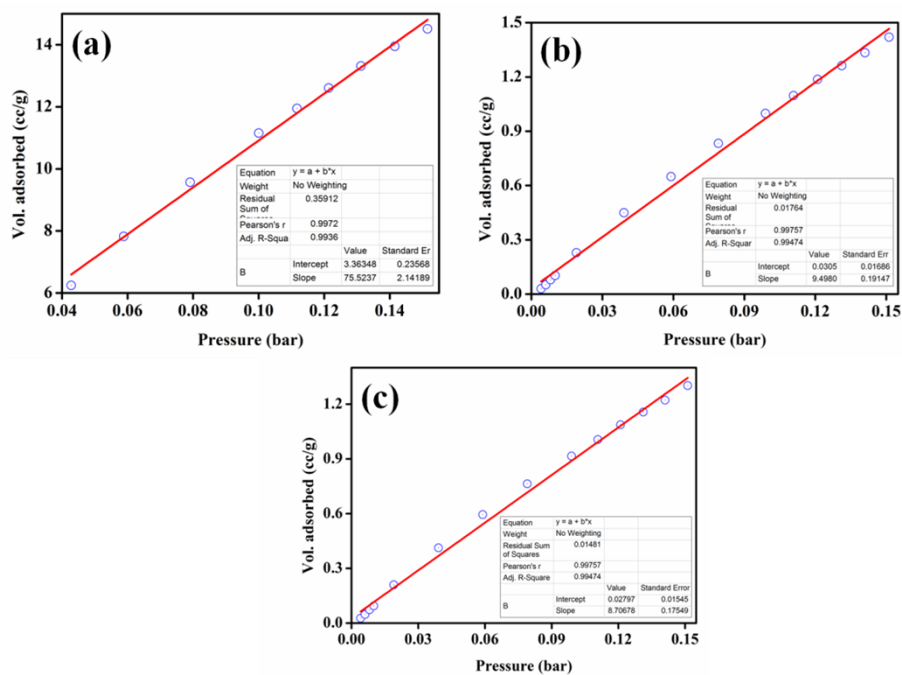


Fig. S21 Calculation of Henry gas selectivity constants for gases (a) CO₂, (b) N₂, and (c) CH₄.

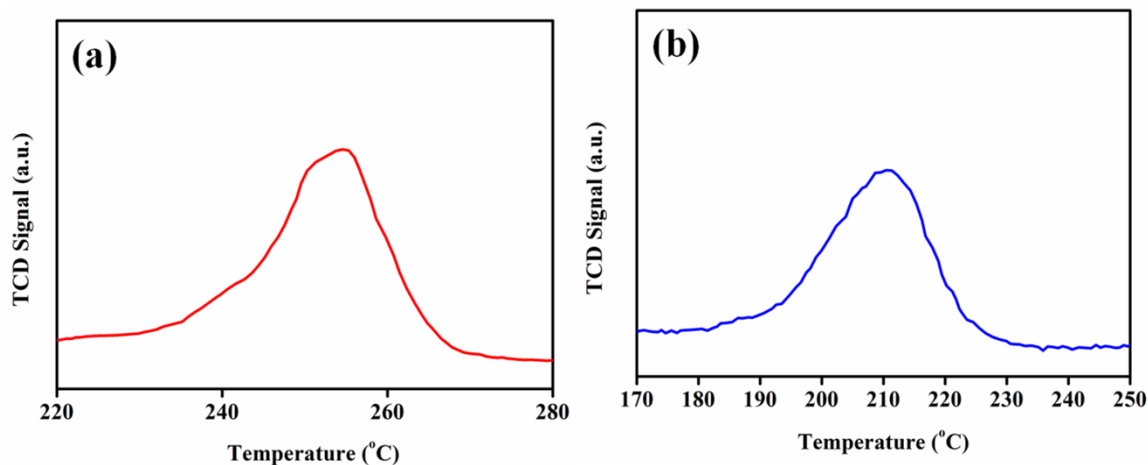


Fig. S22 Temperature-programmed desorption (TPD) profile for Fe-IPOP1 (a) NH_3 -TPD, and (b) CO_2 -TPD.

Table S1. Catalytic optimization for epoxidation of styrene.

SL. No.	Catalyst	Oxidizing agent	Time (h)	Conversion (%)
01	-	-	18	-
02	-	PhIO	18	02
03	FeCl_3	PhIO	18	12
04	Fe-TPy	PhIO	18	16
05	Fe-IPOP1	-	18	-
06	Zn-IPOP1	PhIO	18	-
07	Fe-IPOP1	PhIO	06	42
08	Fe-IPOP1	PhIO	12	78
09	Fe-IPOP1	PhIO	18	>99

^a Reaction conditions: Styrene (1 mmol), catalyst (20 mg), PhIO (1.5 mmol), DCM (2 mL),

Temperature (30 °C). ^b The catalytic conversions were determined by ^1H NMR analysis.

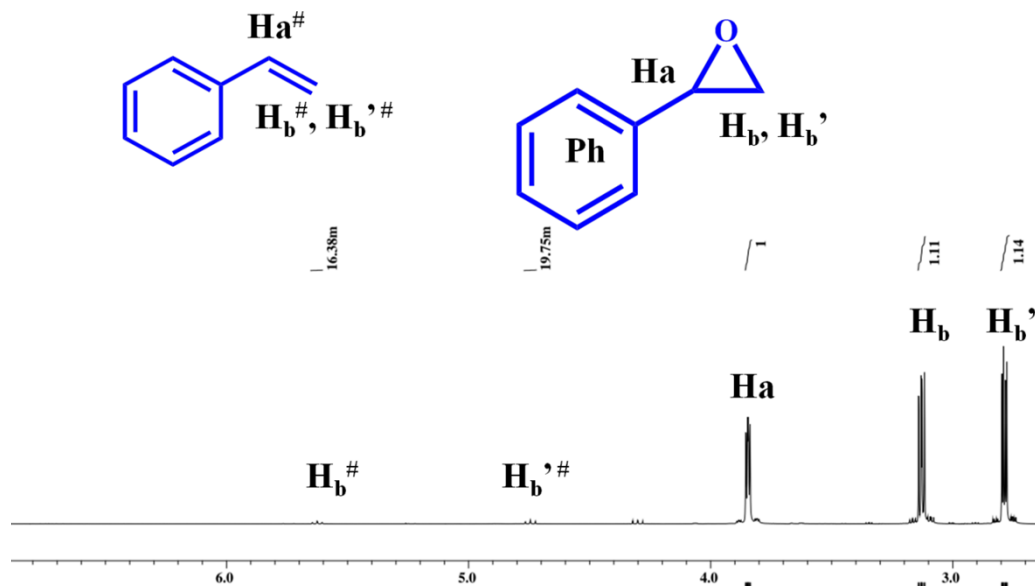


Fig. S23 ^1H NMR (400MHz, CDCl_3 , 20 $^\circ\text{C}$) spectrum for the epoxidation reaction of styrene catalyzed by Fe-IPOP1.

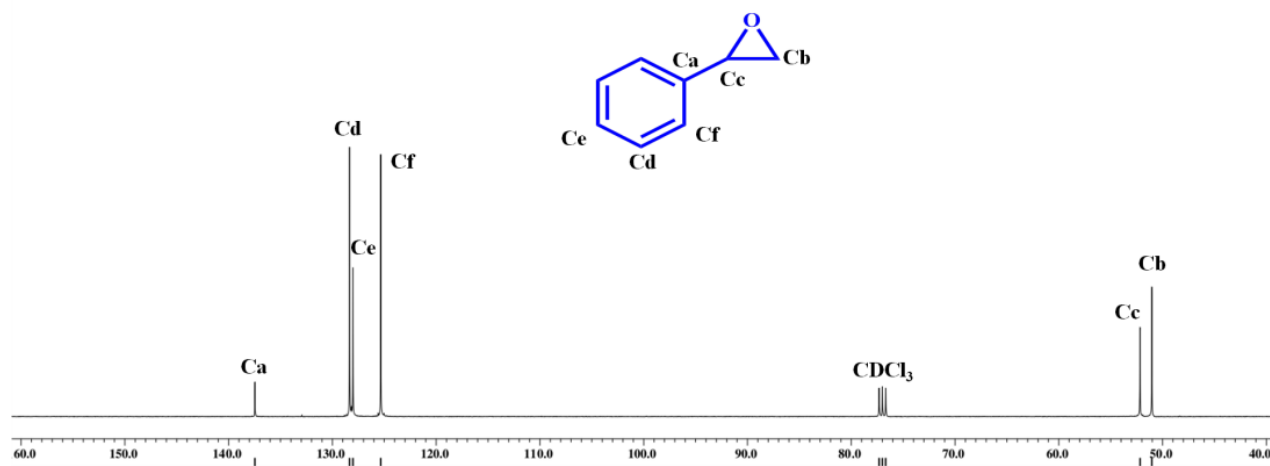


Fig. S24 ^{13}C NMR (400MHz, CDCl_3 , 20 $^\circ\text{C}$) spectrum for the epoxidation reaction of styrene catalyzed by Fe-IPOP1.

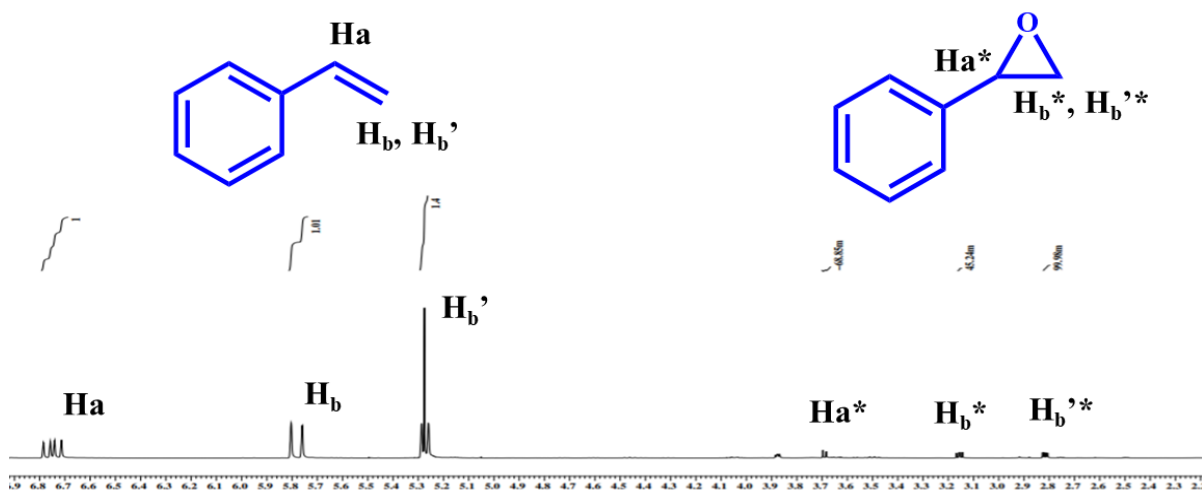
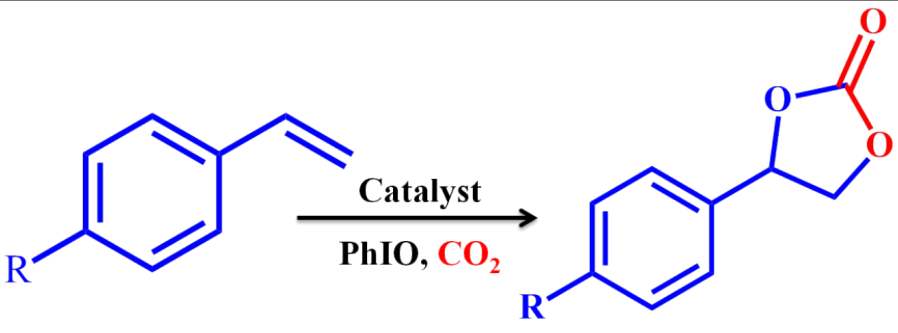


Fig. S25 ^1H NMR (400MHz, CDCl_3 , 20 °C) spectrum for the epoxidation reaction of styrene catalyzed by Zn-IPOP1.

Table S2. Catalytic optimization for the one-pot reaction of CO₂ with styrene.



SL. No.	Catalyst	Oxidizing agent	Time (h)	Temperature (°C)	Conversion (%)
01	-	-	24	80	-
02	Fe-TPyP	PhIO	24	80	03
03	Xylene dibromide	PhIO	24	80	-
04	Zn-IPOP1	PhIO	24	80	-
05	Fe-IPOP1	PhIO	08	80	49
06	Fe-IPOP1	PhIO	16	80	76
07	Fe-IPOP1	PhIO	24	30	32
08	Fe-IPOP1	PhIO	24	60	79
09	Fe-IPOP1	PhIO	24	80	>99

^a Reaction conditions: Styrene (1 mmol), catalyst (20 mg), PhIO (1.5 mmol), Pressure (1 bar), DCM (2 mL), Temperature (80 °C), time (24 h). ^b The catalytic conversions were determined by ¹H NMR analysis.

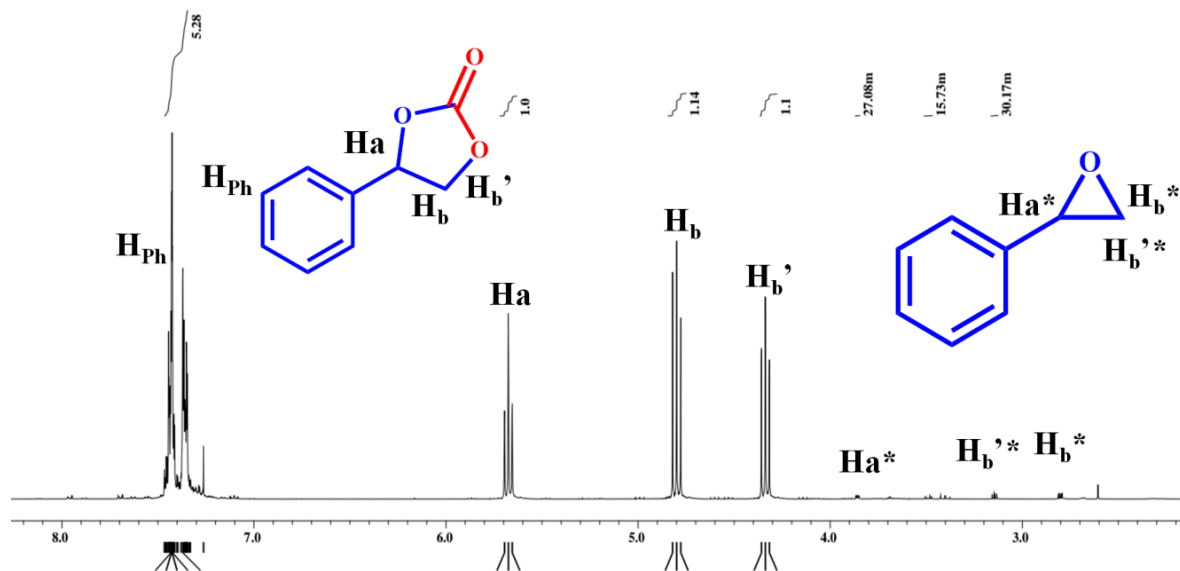


Fig. S26 ^1H NMR (400MHz, CDCl_3 , 20 °C) spectrum for the one-pot cyclic carboxylation of styrene with CO_2 catalyzed by Fe-IPOP1.

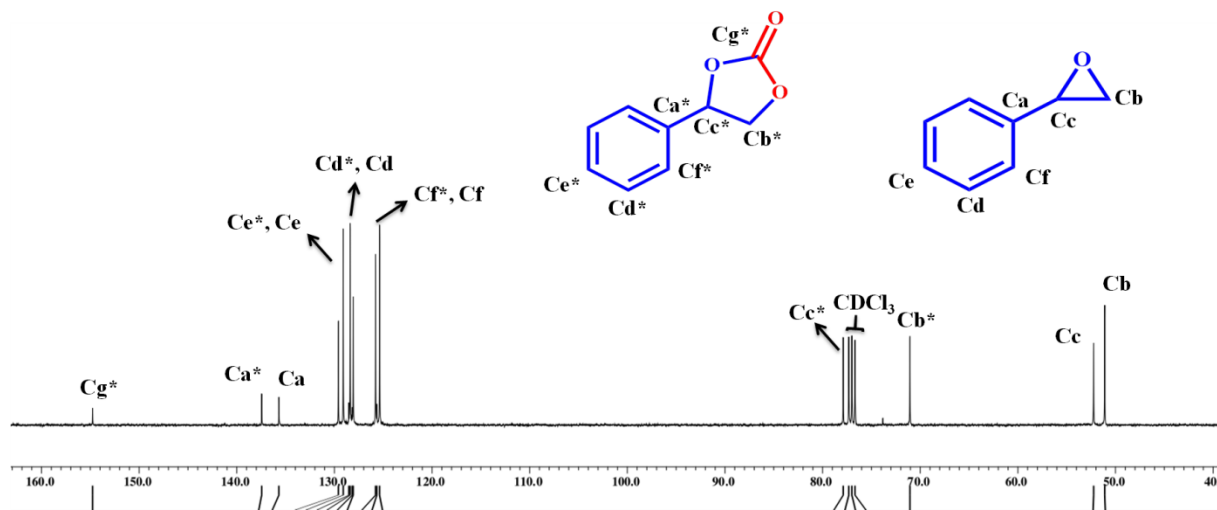


Fig. S27 ^{13}C NMR (400MHz, CDCl_3 , 20 °C) spectrum for the one-pot cyclic carboxylation of styrene with CO_2 catalyzed by Fe-IPOP2 in 12h.

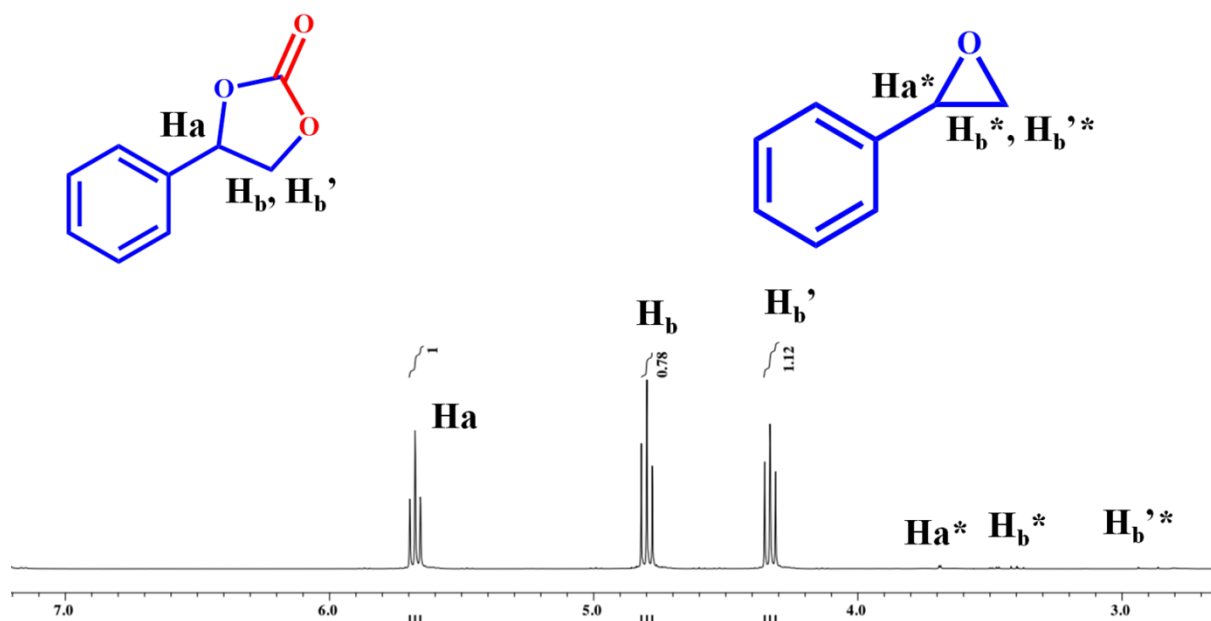


Fig. S28 ^1H NMR (400MHz, CDCl_3 , 20 $^\circ\text{C}$) spectrum for the one-pot cyclic carboxylation of styrene with CO_2 catalyzed by Fe-IPOP2.

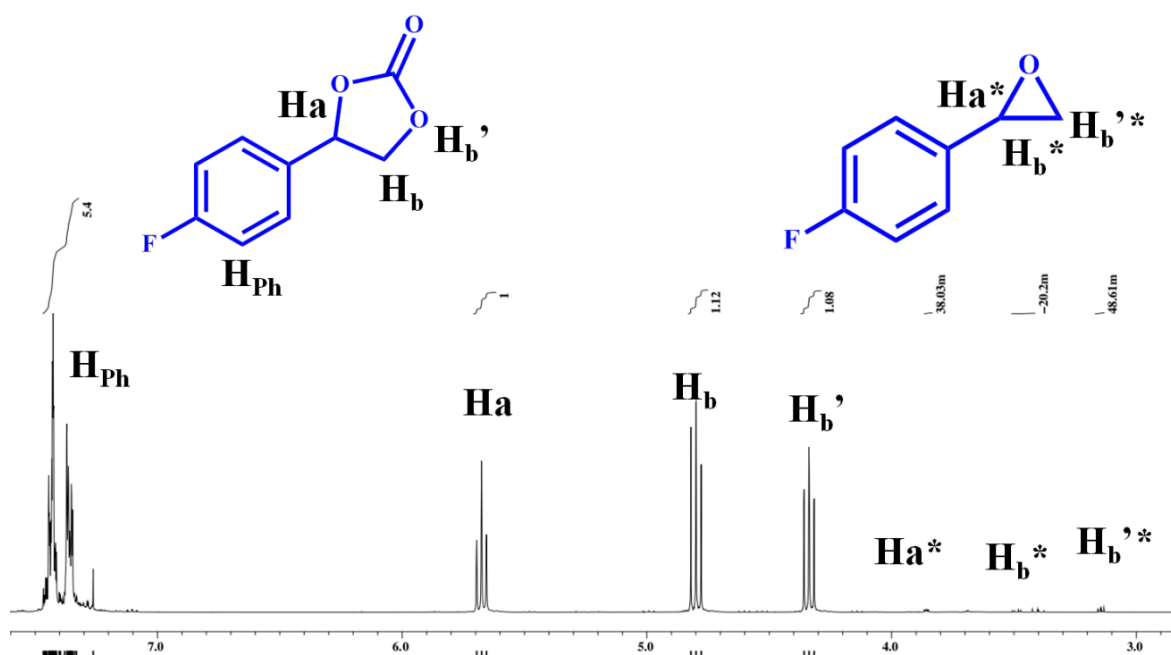


Fig. S29 ^1H NMR (400MHz, CDCl_3 , 20 $^\circ\text{C}$) spectrum for the one-pot cyclic carboxylation of 4-fluorostyrene with CO_2 catalyzed by Fe-IPOP1.

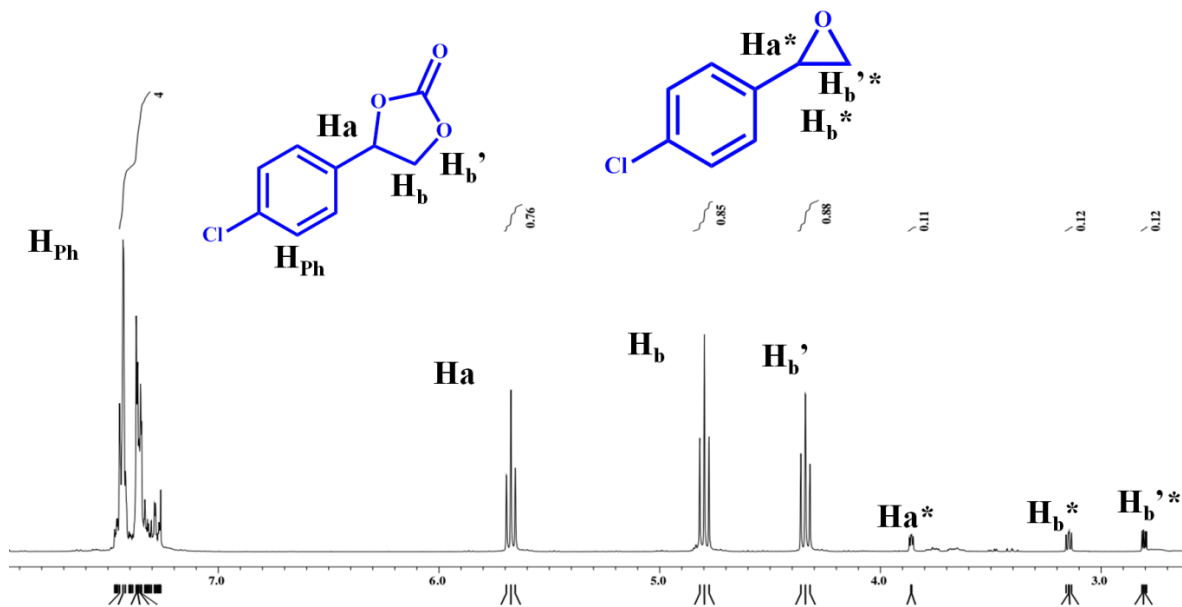


Fig. S30 ^1H NMR (400MHz, CDCl_3 , 20 $^\circ\text{C}$) spectrum for the one-pot cyclic carboxylation of 4-chlorostyrene with CO_2 catalyzed by Fe-IPOP1.

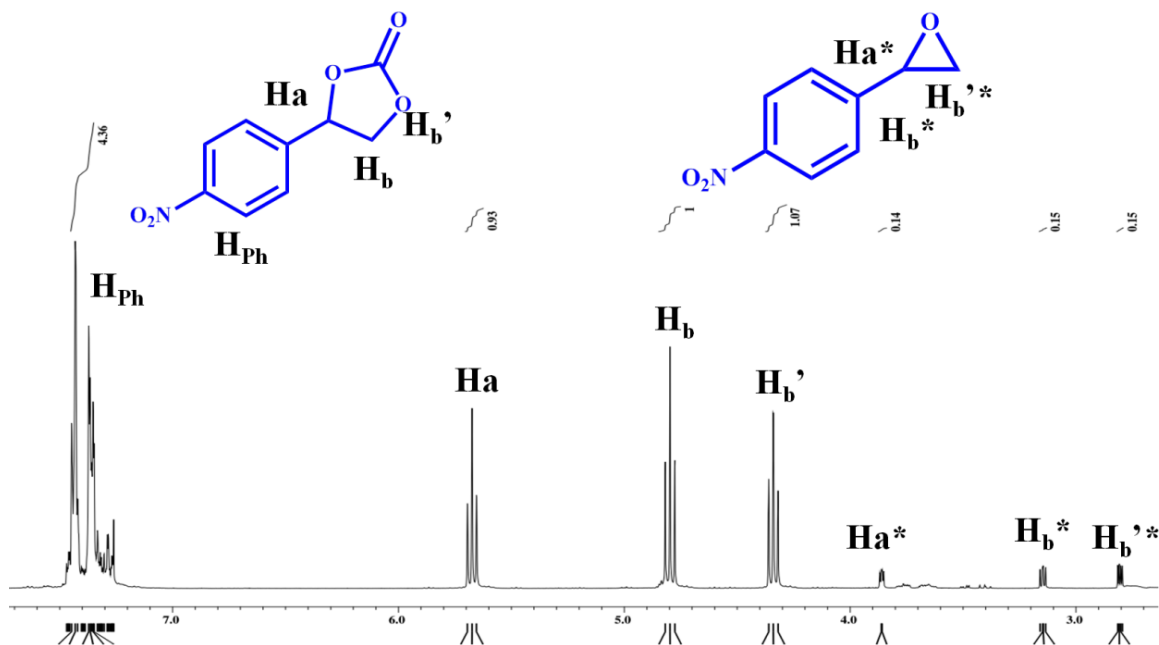


Fig. S31 ^1H NMR (400MHz, CDCl_3 , 20 $^\circ\text{C}$) spectrum for the one-pot cyclic carboxylation of 4-nitrostyrene with CO_2 catalyzed by Fe-IPOP1.

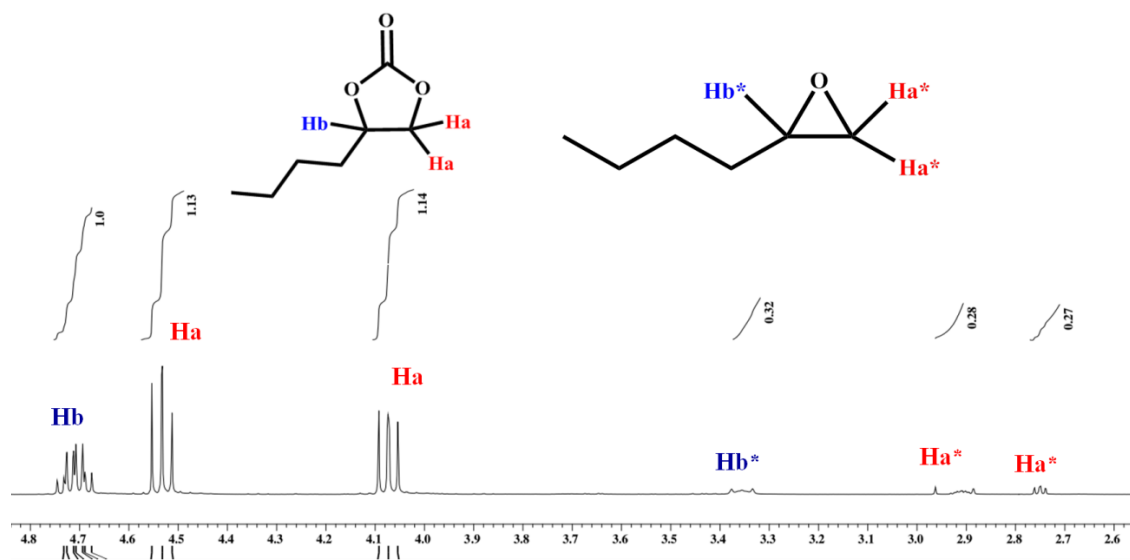


Fig. S32 ^1H NMR (400MHz, CDCl_3 , 20 $^\circ\text{C}$) spectrum for the one-pot cyclic carboxylation of 1-hexene with CO_2 catalyzed by Fe-IPOP1.

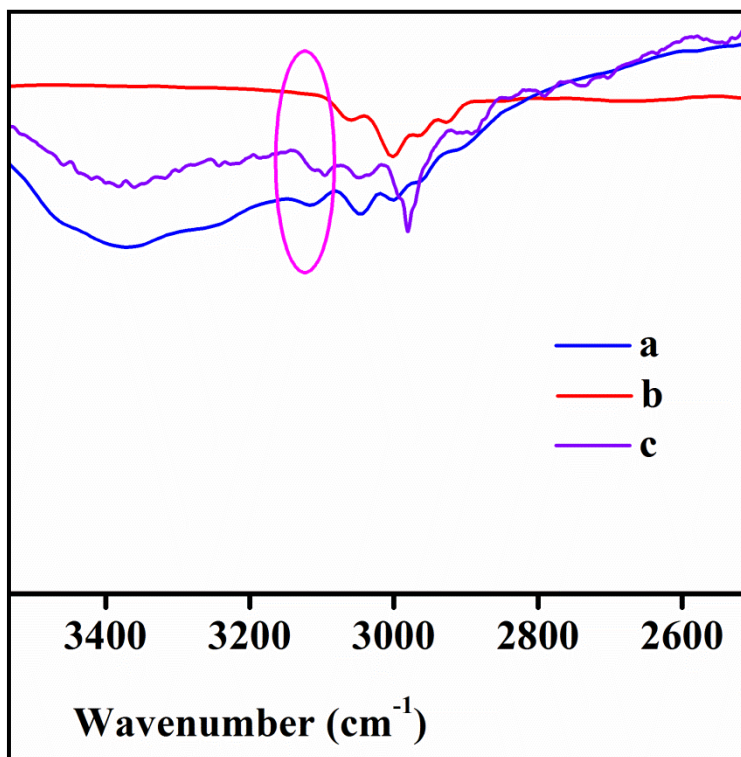


Fig. S33 FT-IR spectra (solid, 1 mg sample, 25 $^\circ\text{C}$) of (a) styrene oxide, (b) Fe-IPOP1, and (c) Fe-IPOP1 treated with styrene oxide.

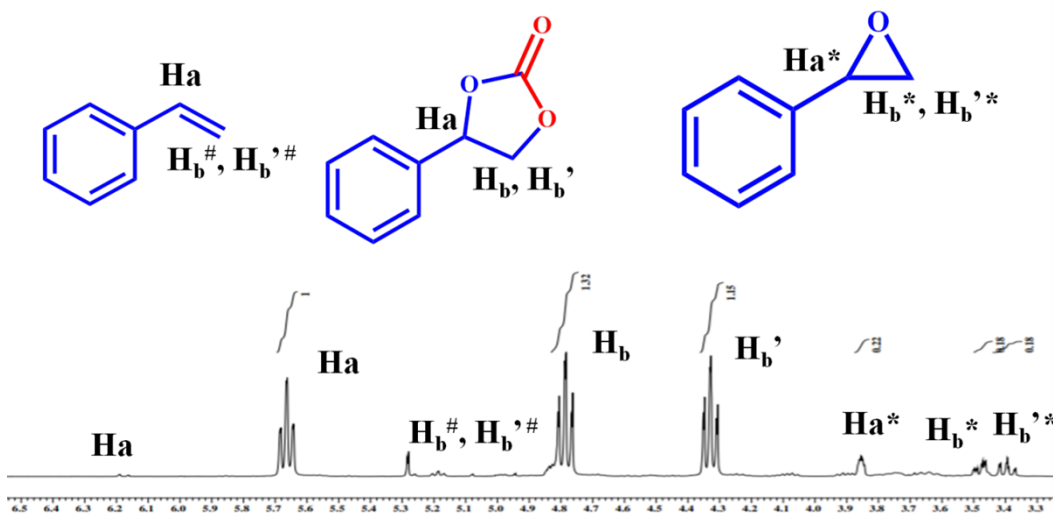


Fig. S34 ¹H NMR (400MHz, CDCl₃, 20 °C) spectrum for the one-pot cyclic carboxylation of styrene with CO₂ catalyzed by Fe-IPOP1 after eight catalytic cycles.

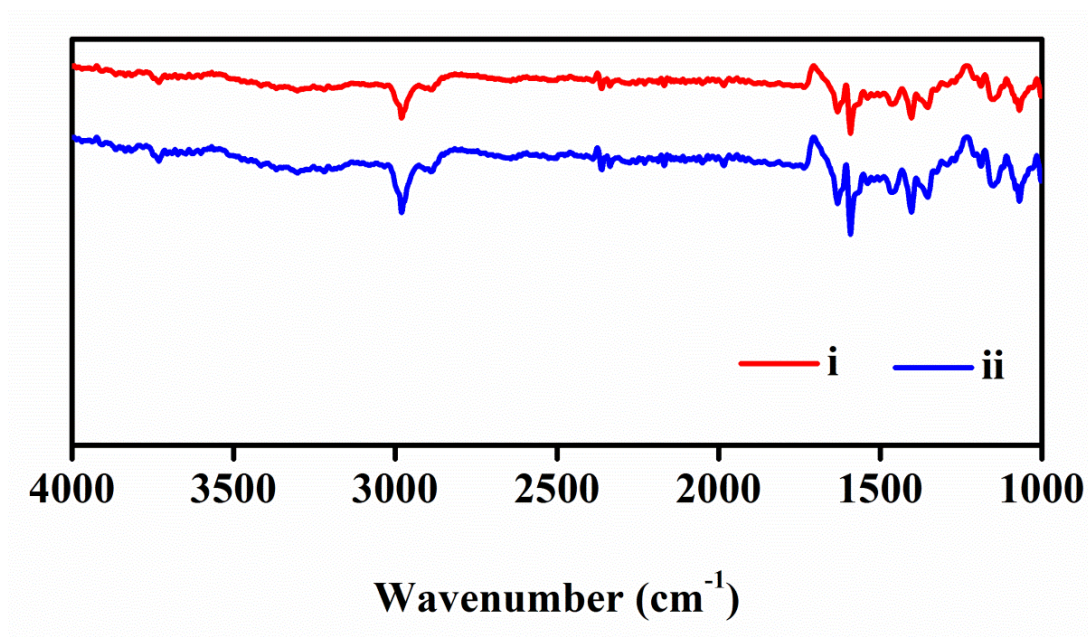


Fig. S35 FT-IR spectra (solid, 1 mg sample, 25 °C) of (i) as-synthesized and (ii) recycled Fe-IPOP1 after eight catalytic cycles.

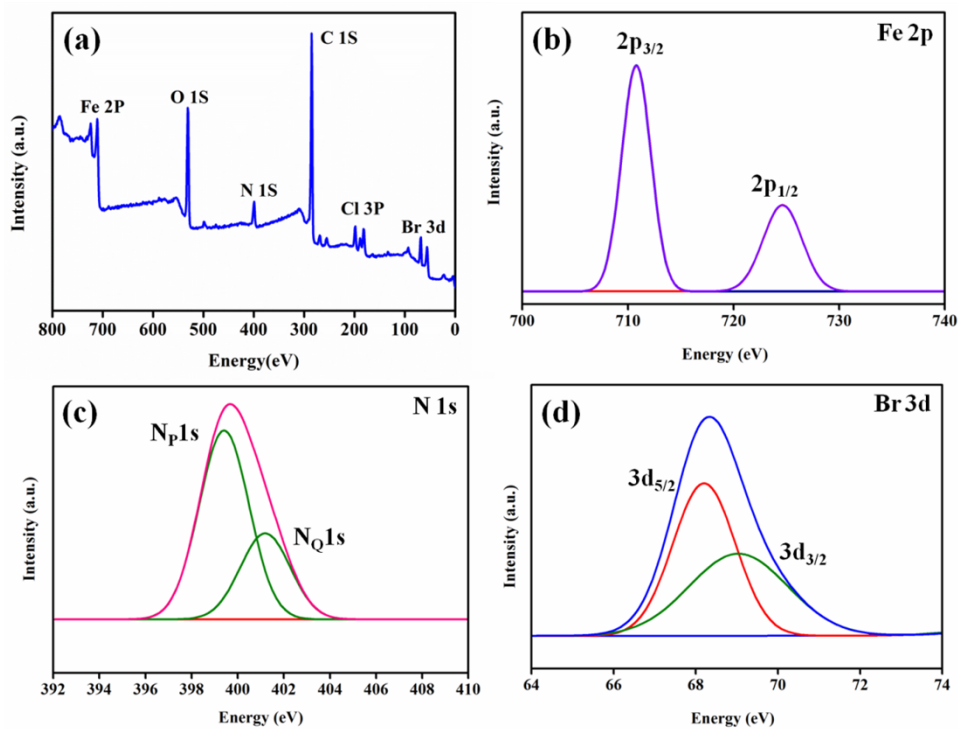


Fig. S36 XPS for recycled Fe-IPOP1 (a) survey scan, (b) Fe 2p, (c) N 1s, and (d) Br 3d.

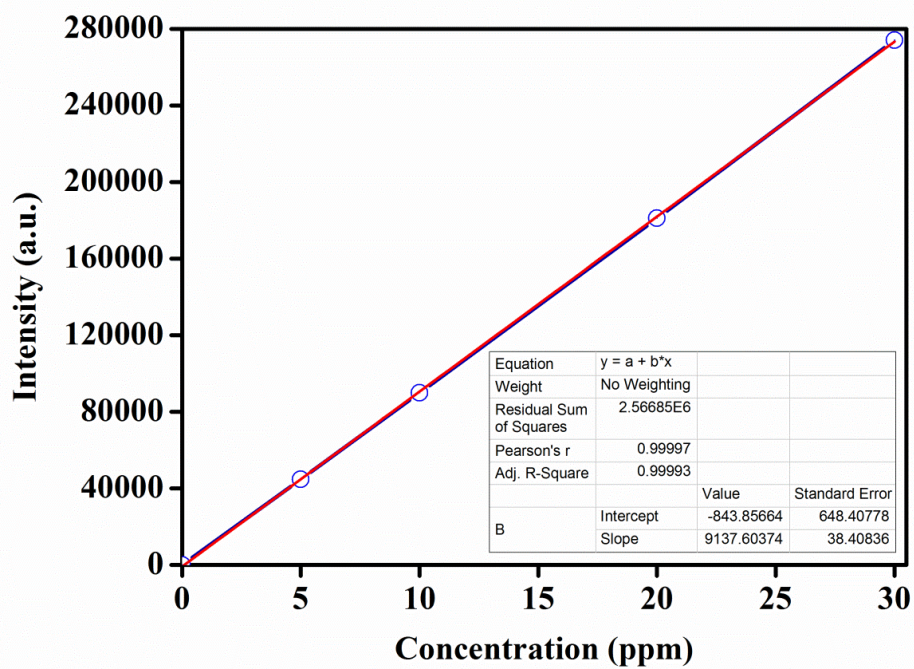


Fig. S37 MP-AES calibration plot for the filtrate of catalytic reaction with Fe-POP1.

References

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