

## Supporting Information

### Experiment

#### Experiment instruments

FT-IR spectra were recorded from KBr pellets using a Bruker RFS100/S spectrophotometer (USA) and diffuse reflectance UV-vis spectra of the solid samples were recorded in the spectrophotometer with an integrating sphere using BaSO<sub>4</sub> as standard. <sup>1</sup>H NMR and <sup>31</sup>P NMR were performed on AV-300 NMR instrument at ambient temperature at 300 and 121 MHz, respectively. All of the chemical shifts were reported downfield in ppm relative to the hydrogen and phosphorus resonance of TMS and 85% H<sub>3</sub>PO<sub>4</sub>, respectively. Number- and weight-average molecular weights (M<sub>n</sub> and M<sub>w</sub>) and polydispersity (M<sub>w</sub>/M<sub>n</sub>) were estimated by Waters1515 gel permeation chromatograph (GPC; against polystyrene standards) using THF as an eluent (1.0 mLmin<sup>-1</sup>) at 35 °C. X-ray photoelectron spectrum was recorded on ESCALab250 instrument. The interlayer spacings were obtained on DX-1000 automated X-ray power diffractometer, using Cu K $\alpha$  radiation and internal silicon powder standard with all samples. The patterns were generally measured between 3.00° and 80.00° with a step size of 0.02° min<sup>-1</sup> and X-ray tube settings of 36 kV and 20 mA. C, H and N elemental analysis was obtained from an EATM 1112 automatic elemental analyzer instrument (Thermo, USA). TG analyses were performed on a SBTQ600 thermal analyzer (USA) with the heating rate of 20 °C min<sup>-1</sup> from 25 to 1000 °C under flowing N<sub>2</sub> (100 mL min<sup>-1</sup>). The Mn contents of the catalysts were determined by a TAS-986G (Pgeneral, China) atomic absorption spectroscopy. SEM were performed on KYKY-EM 3200 (KYKY, China) micrograph. TEM were obtained on a TECNAI10 (PHILIPS, Holland) apparatus. Nitrogen adsorption isotherms were measured at 77 K on a 3H-2000I (Huihaihong, China) volumetric adsorption analyzer with BET method. The racemic epoxides were prepared by epoxidation of the corresponding olefins by 3-chloroperbenzoic acid in CH<sub>2</sub>Cl<sub>2</sub> and confirmed by NMR (Bruker AV-300), and the gas chromatography (GC) was calibrated with the samples of n-nonane, olefins and corresponding racemic epoxides. The conversions (with n-nonane as internal standard) and the ee values were analyzed by gas chromatography (GC) with a Shimadzu GC2010 (Japan) instrument equipped using a chiral column (HP19091G-B213, 30 m  $\times$  30 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m) and FID detector, injector 230 °C, detector 230 °C. Ultrapure nitrogen was used as the carrier (rate 34 mL/min) with carrier pressure 39.1kPa and the injection pore temperature was set at 230°C. The column temperature for indene,  $\alpha$ -methylstyrene and styrene was programmed in the range of 80-180 °C.

#### Materials and instruments

All chemicals and reagents in this work were analytical grade and used as received. All the solvents were further purified before their being used. Chiral salen ligand and chiral homogeneous catalyst salen Mn(III) were synthesized according to the standard literature procedures,<sup>1</sup> and further identified by analysis and comparison of IR spectra with literature.<sup>2</sup>

### **Synthesis of styrene-phenylvinylphosphonic acid copolymer (PS-PVPA)**

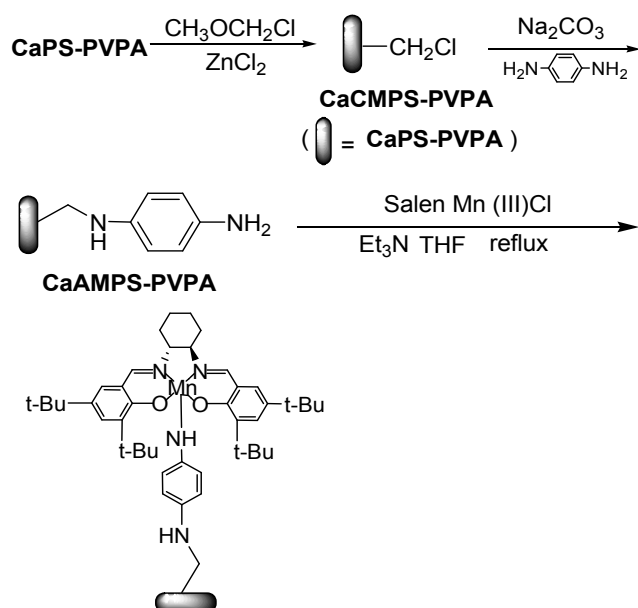
1-Phenylvinyl phosphonic acid (PVPA) was synthesized according to literature<sup>3</sup> and its structures were confirmed by <sup>1</sup>H NMR, <sup>31</sup>P NMR and FT-IR. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 6.06 (d, 1H), 6.23 (d, 1H), 7.26-7.33 (m, 3H), 7.48 (m, 2H). <sup>31</sup>P NMR (CD<sub>3</sub>OD): 15.9. IR (KBr): 2710, 2240, 1500, 1200, 1040, 950, 780, 720, 700 cm<sup>-1</sup>.

1-Phenylvinyl phosphonic acid (4 g, 21.7 mmol), styrene (20 mL, 173.9 mmol), ethyl acetate (150 mL) and dibenzoyl peroxide (BPO, 1.0g, 4.7 mmol) were used for preparation of PS-PVPA copolymer as literature<sup>4</sup>. GPC: Mn = 39729.43, m = 38.3, n = 8.2, Mw/Mn = 2.

### **Synthesis of calcium poly(styrene-phenylvinylphosphonate) -phosphate (CaPS-PVPA)**

Sodium dihydrogen phosphate dihydrate (0.62 g, 4 mmol) was added to poly(styrene-phenylvinylphosphonate) (PS-PVPA) solution (1.0 g, 1 mmol) for preswelling in 100 mL THF. Thereafter, calcium nitrate tetrahydrate (1.2 g, 5 mmol) was added in while the temperature gradually rising to 66°C and then retaining for 4 h, which was followed by evaporating. The ivory yellow solid CaPS-PVPA 1 was filtered, then washed with deionized water and dried. CaPS-PVPA 2-7 were prepared according to the similar procedure. IR (KBr): v<sub>max</sub>/cm<sup>-1</sup> 3059, 3025, 2922 (CH), 1601, 1493, 1452, 756, 698 (-C<sub>6</sub>H<sub>5</sub>), 1026 (P=O). CaPS-PVPA 3: Found: C, 62.8; H, 5.17. Calc. for C<sub>74</sub>H<sub>73</sub>O<sub>11</sub>P<sub>3</sub>Na<sub>2</sub>Ca<sub>3</sub>: C, 63.5; H, 5.22%.

### **Synthesis of the supported catalyst (Scheme S1)**



Scheme S1 synthesis of the supported catalyst

### Synthesis of chloromethyl-calcium poly(styrene-phenylvinylphosphonate)-phosphate (CaCMPS-PVPA)

Chloromethyl methyl ether (9.3 mL), anhydrous zinc chloride (3.23 g, 24.34 mmol) and CaPS-PVPA 3 (4.73 g, 3.4 mmol) were mixed in 40 mL chloroform and stirred at 40 °C for 10 h. After cooling down, sodium carbonate saturated solution was added to neutralize the mixture, and the solvent was evaporated under reduced pressure, filtered, washed with deionized water and dried in vacuo<sup>5-7</sup> to yield CaCMPS-PVPA (5.37 g, 92.4%). IR (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3031, 2924 (CH), 1645, 1554, 1516, 1494 ( $-\text{C}_6\text{H}_5$ ), 1256 (P=O), 702 (C-Cl). Found: C, 50.6; H, 3.62. Calc. for  $\text{C}_{74}\text{H}_{64}\text{O}_{11}\text{P}_3\text{Na}_2\text{Ca}_3\text{C}_{19}$ : C, 51.7; H, 3.71%.

### Synthesis of arylaminomethyl-calcium poly (styrene-phenylvinylphosphonate)- phosphate (CaAMPS-PVPA)

The corresponding ratio of aryl diamine p-phenyl-enediamine was blended with CaCMPS-PVPA (1 g),  $\text{Na}_2\text{CO}_3$  (1.06 g, 0.01 mol), CuI (0.2 g, 1 mmol) and alcohol 50 mL, while stirring and retaining at 70 °C for 12 h, followed by neutralizing and vaporizing. The product was filtered, washed and dried in vacuo. Found: C, 64.71; H, 5.24; N, 9.86. Calc. for  $\text{C}_{123}\text{H}_{121}\text{O}_{11}\text{P}_3\text{Na}_2\text{Ca}_3\text{N}_{16}$ : C, 65.23; H, 5.35; N, 10.16%.

### Synthesis of grafting chiral salen (III) onto CaAMPS-PVPA

Chiral salen Mn (III) (4 mmol) in 10 mL of THF was added to CaAMPS-PVPA (0.5 g) solution for preswelling in THF and  $\text{Et}_3\text{N}$  (5 mmol). The mixture was stirred for 10 h under

reflux, followed by neutralizing and evaporating. The amount of Mn (salen) anchored onto CaPS-PVPA was 0.76 mmol/g ascertained by AAS based on Mn element. Found: C, 69.1; H, 7.41; N, 6.26. Calc. for  $C_{418}H_{539}O_{27}P_3Na_2Ca_3N_{32}$ : C, 70.03; H, 7.52; N, 6.41%.

### Asymmetric epoxidation

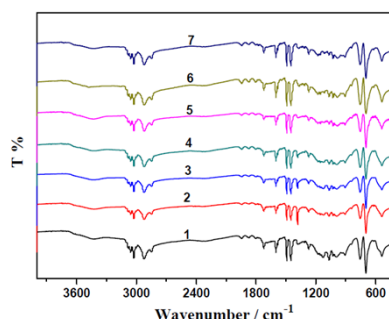
The activity of the supported catalysts are investigated for the epoxidation of non-functionalized olefins in  $CH_2Cl_2$  at  $-40\text{ }^\circ\text{C}$  for 5 h with *m*-CPBA/NMO. After reaction,  $Na_2CO_3$  (4 mL, 1.0 M) is added to quench the reaction.

### References

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### The mechanism of the transformation in the chloromethylation reaction

In the presence of zinc chloride, the group of  $-CH_2Cl$  was introduced in benzene rings in CaPS-PVPA through chloromethylation. And most of the benzene rings in poly(styrene-phenylvinylphosphonate) were chloromethylated, and the remaining benzene rings unchloromethylated may be ascribed to steric obstacle originated in approaching the calcium phosphonate closely.



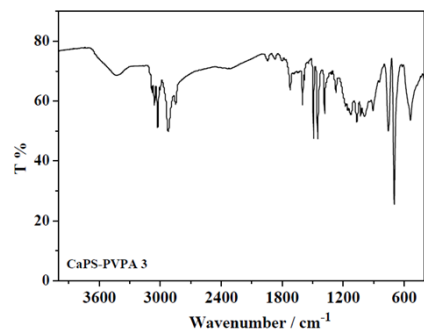


Fig. S1 FT-IR spectra of CaPS-PVPA 1-7

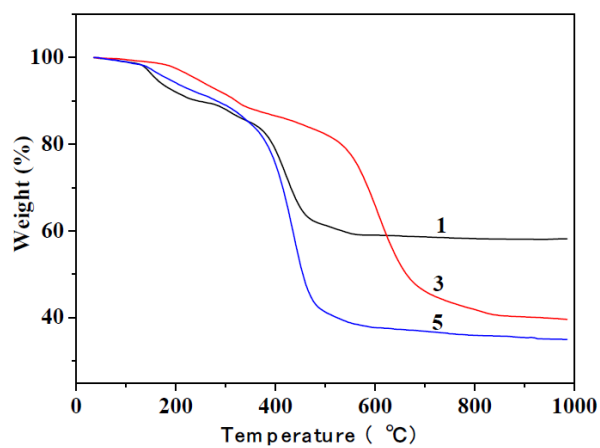
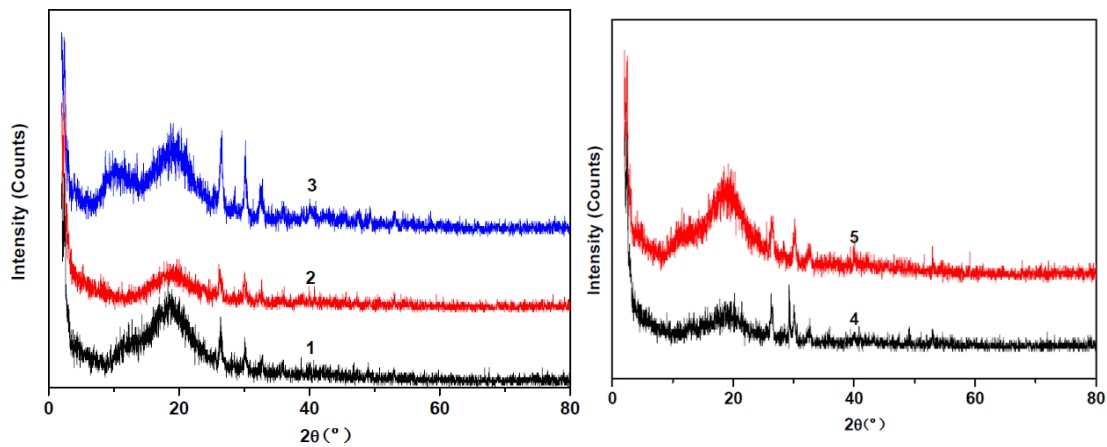


Fig. S2 TG curves of CaPS-PVPA 1, 3, 5.



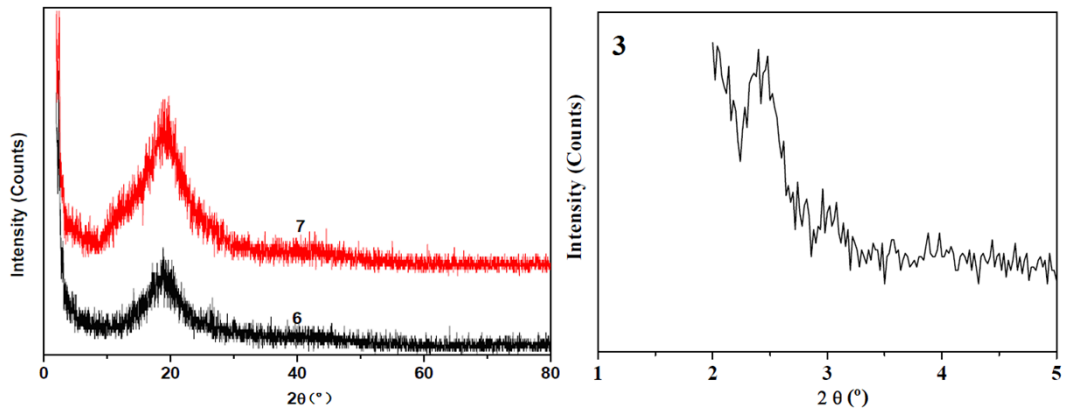


Fig. S3 XRD of CaPS-PVPA 1-7

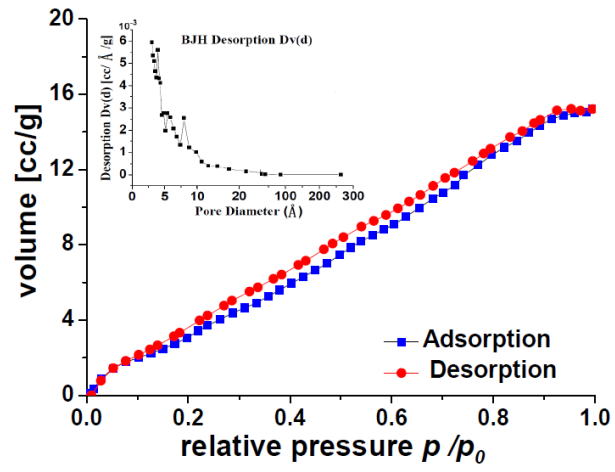


Fig. S4 The nitrogen adsorption-desorption isotherm CaPS- PVPA 3

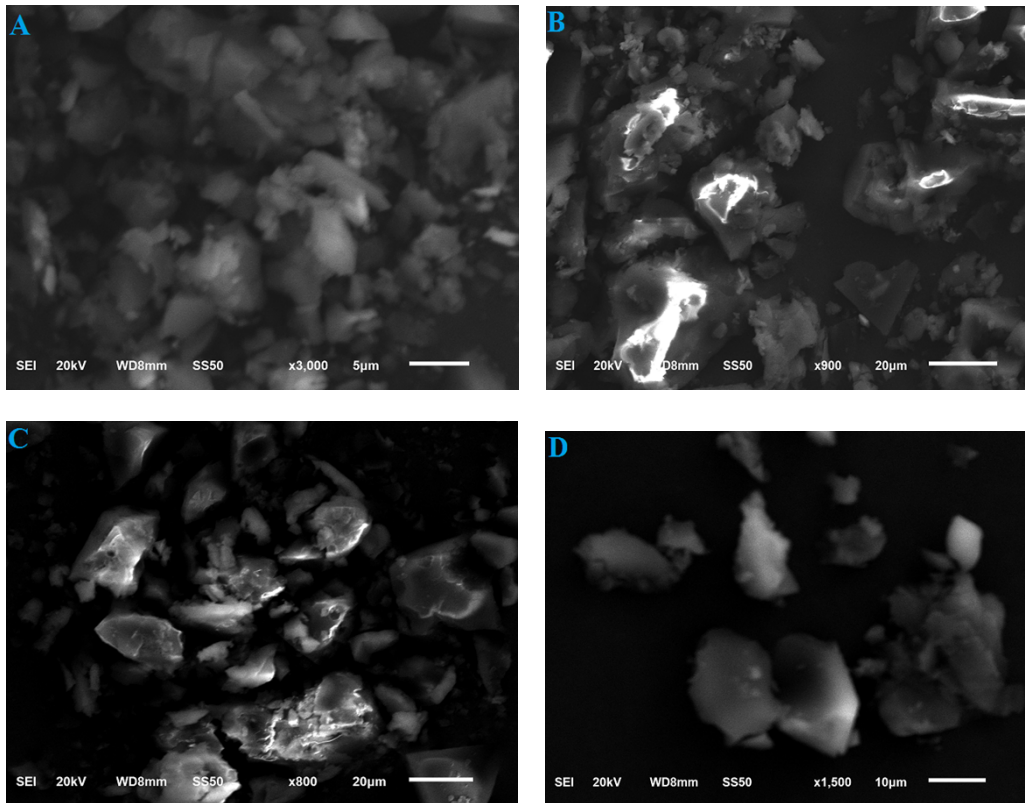


Fig. S5 SEM image of layered CaPS-PVPA 1 (A), 3 (B), 5 (C) and 7 (D).

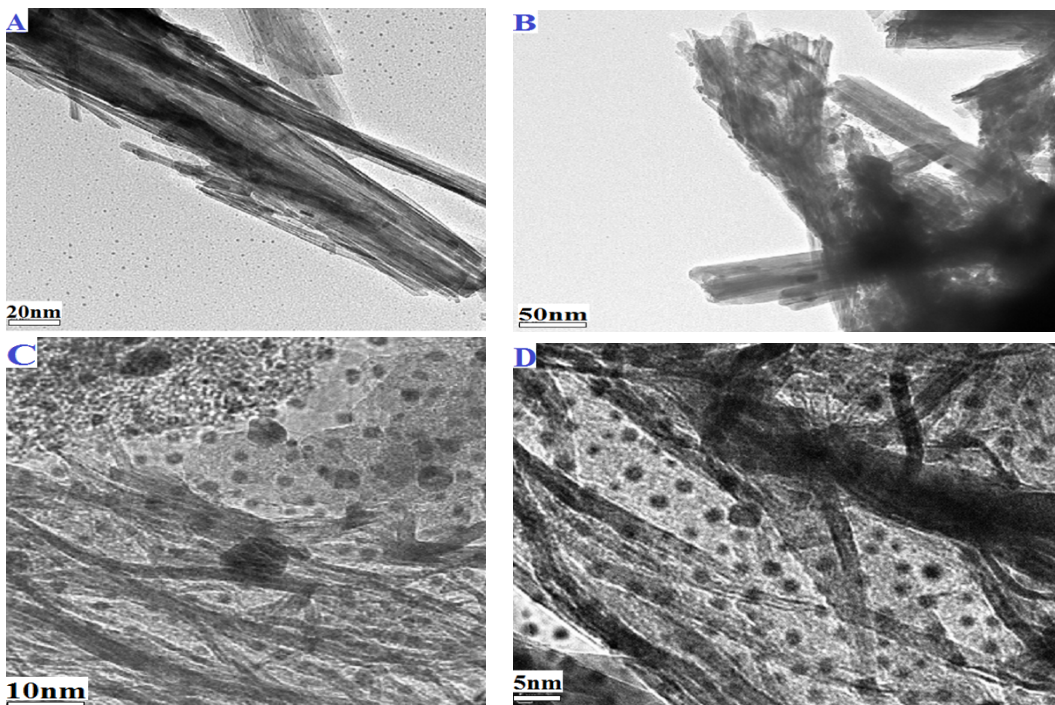
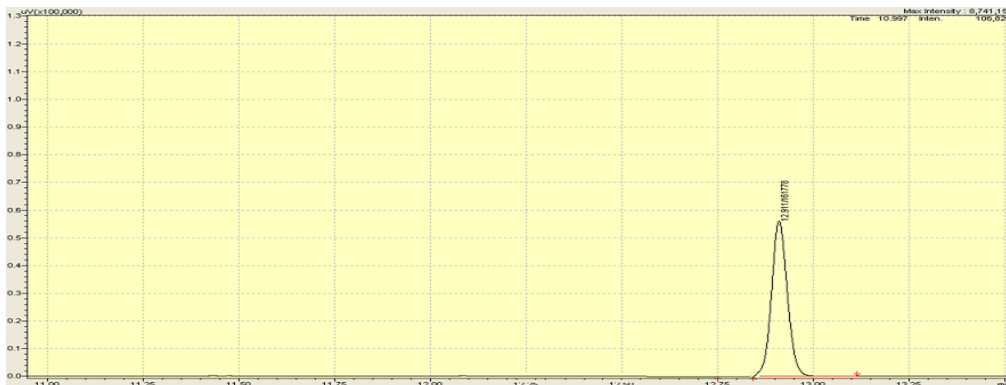
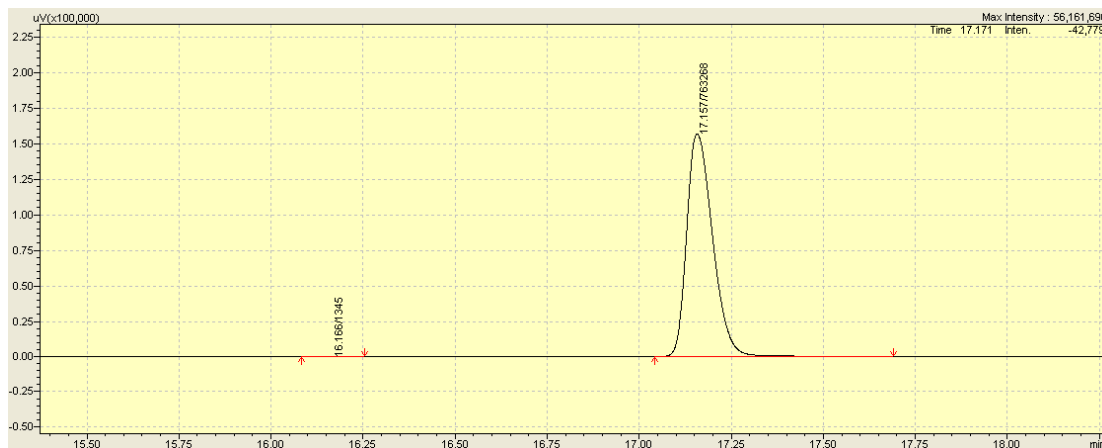


Fig. S6 TEM micrographs of CaPS-PVPA 3 (A-D).



**Entry 1 in Table 1**



**Entry 3 in Table 1**