

## Supplementary Information

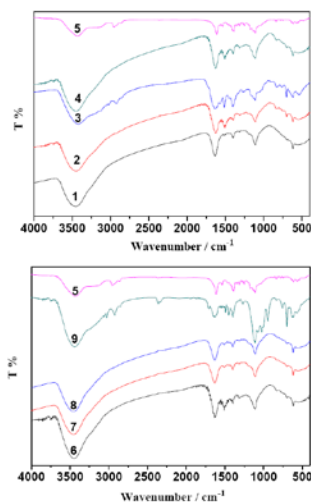


Fig. S1 FT-IR spectra of (1) 5a; (2) 5b; (3) 5c; (4) 5d; (5) the neat chiral salen Mn(III) complex 4; (6) 5e; (7) 5f; (8) 5g; (9) 5h.

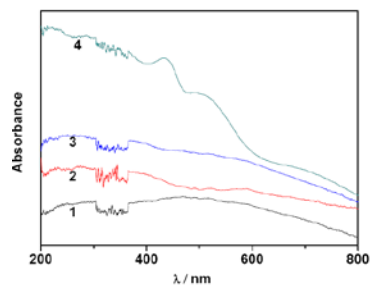


Fig. S2 UV-vis spectra of (1) 5a; (2) 5c; (3) 5g; (d) the neat chiral salen Mn(III) complex 4

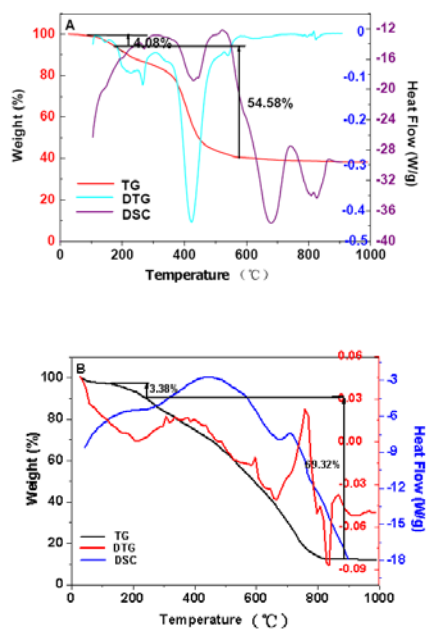
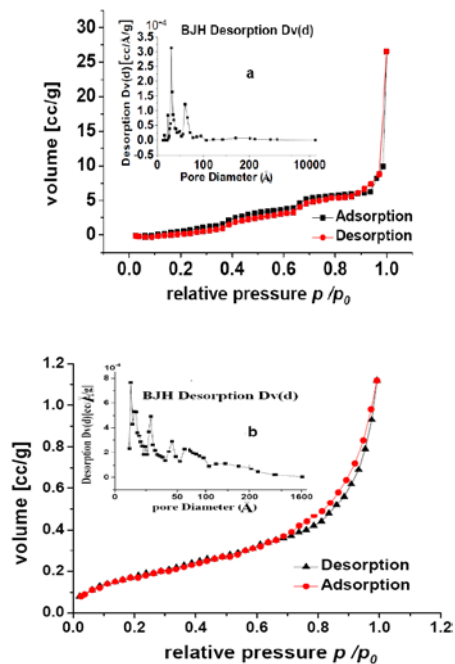


Fig. S3 TG curves of ZnPS-PVPA 1c(A) and 5c (B)



**Fig. S4** The nitrogen adsorption-desorption isotherm and pore distribution of (a) ZnPS-PVPA; (b) the supported catalyst **5c**.



**Fig. S5** Large-scale asymmetric epoxidation reaction of  $\alpha$ -methylstyrene (100 times as much as the experimental scale)

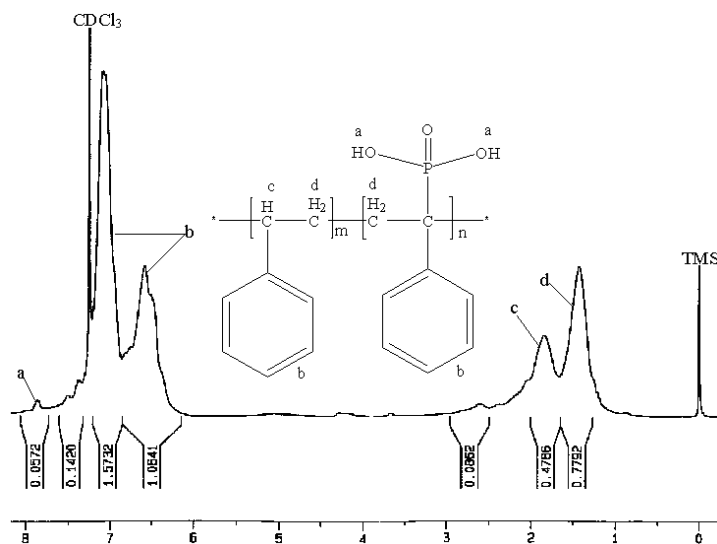


Fig. S6  $^1\text{H}$  NMR of copolymer

## Experimental section

### Characterization of copolymer PS-PVPA

To a solution of PS-PVPA (0.1g) in 20 ml of THF, sodium hydroxide standard solution in water was added titrated slowly with vigorous magnetic stirring. According to the consumed volume of sodium hydroxide standard solution corresponding to the place of sudden change of pH in pH-V NaOH titration curve.

### Chemical analysis

#### Na content of ZnPS-PVPA

In a white porcelain crucible, a sample of 50 mg ZnPS-PVPA was put in it and was heated up to 700°C for 5 h in Muffle furnace. Due to the high temperature, ZnPS-PVPA decomposed. Then 20 mL of hydrochloric acid (1:1) was added to the porcelain crucible and was heated to boiling for 30 min on the electric furnace. In the resulting solution, the sodium content was determined by AAS.

#### Cl content of ZnCMPS-PVPA

In every of three white porcelain crucibles chosen, 2 g sodium bicarbonate, 1 g sodium peroxide, 0.1000-0.1200 g ZnCMPS-PVPA (weighted accurately) were tiled in turn, and then heated up to 800-850 °C for 6 h in Muffle furnace. Then the residue was transferred into a beaker, dissolved with deionized water and filtrated. Subsequently, a proper amount of 1 g/L<sup>-1</sup> phenolphthalein indicator was added to the filtrate and neutralized with 1:1 nitric acid solution till the color was changed into achromatic color. Finally, using chromate potassium as indicator, 40 mmol/L AgNO<sub>3</sub> standard solution was titrated till brick-red was turned out. The same procedure was repeated for three times and the average value of three times testing was used as the ultimate data.

## Results and discussion

### Characterizations of the supports and the heterogeneous chiral catalysts

#### The copolymerization reaction of PVPA with styrene

To ascertain the structure of copolymer, PVPA and copolymer were investigated by  $^{31}\text{P}$  NMR and  $^1\text{H}$  NMR. The  $^{31}\text{P}$  NMR spectra of PVPA displayed one peak at 15.9 ppm and the copolymer showed only one peak at 36.2 ppm. Moreover, there was only one kind of configuration of phosphor atom, which demonstrated the successful copolymerization of PVPA with styrene. In addition, the structure of copolymer was also characterized by  $^1\text{H}$  NMR. A typical  $^1\text{H}$  NMR spectrum of copolymer was shown in Fig. S6, and the peaks were labeled to assign corresponding protons.

### The content of phosphonic acid in the copolymer PS-PVPA

As described in gel-permeation chromatography (GPC), copolymer PS-PVPA has average molecular weight ( $M_n$ ) = 38608,  $M_w/M_n = 2$ . The content of phosphonic acid in the copolymer could be calculated using the following formula:

$$\frac{W}{104n + 184} = C_0V$$

where  $W$  is the mass of the copolymer;  $n$  is the number of styrene in the unit of the copolymer;  $C_0$  is the concentration of sodium hydroxide standard solution and  $V$  is the consumed volume of sodium hydroxide standard solution corresponding to the place of sudden change of pH in pH-V NaOH titration curve.

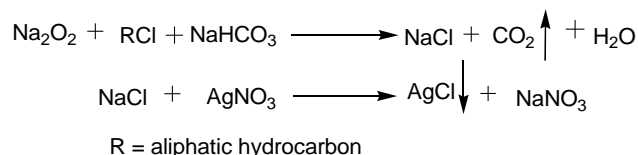
Using this formula, it could be inferred that average every segment of the molecule chain  $-(St)_{m1}-(PVPA)_n-(St)_{m2}-(PVPA)_n-(St)_{m3}-$  in the copolymer contained 8 organic phosphonates ( $n = 8$ ). Consequently, the result that the copolymer average was comprised in 38 units ( $m = 38$ ) could be deduced.

### Na content of ZnPS-PVPA

The sodium content in sample **1c** was 1.7%, which were 0.2% lower than that of theoretical values; this can probably be attributed to the surface-bound or intercalated water leading to the augment of the molecular weight.

### Cl content of ZnCMPS-PVPA

ZnCMPS-PVPA, sodium bicarbonate and sodium peroxide were together fused under high temperature and the Cl element in ZnCMPS-PVPA was conjugated with sodium to generate sodium chloride. Then the residue was dissolved with deionized water and titrated with standard  $AgNO_3$  solution to make chloridion combined with silver ions to produce silver chloride precipitation. The end point of titration was determined with chromate potassium as indicator. The chemical equations were shown below:



And the Cl content of ZnCMPS-PVPA could be reckoned on the following formula:

$$A = (CV \cdot 0.03546) / m \cdot 100\%$$

Where  $C$  is the concentration of  $AgNO_3$  standard solution;  $V$  is the used volume of  $AgNO_3$  standard solution;  $m$  is the mass of the sample;  $A$  is the Cl percent content of the sample; 0.03546 is the weight of 1mmol Cl atom. The Cl contents of the supports ZnCMPS-PVPA were displayed in Table 1, respectively.

**Table 1** The Cl content of ZnCMPS-PVPA

Sample (x)	2a (0.2)	2b (0.25)	2c (0.33)	2d (0.4)	2e (0.5)	2f (0.75)	2g (1)	2h (0.33)
Cl content (mmol/g)	1.6	2.1	2.5	2.9	3.3	3.7	4.1	2.6

Based on the results in Table 1, it could be deduced that the Cl content of ZnCMPS-PVPA decreased from 4.1 to 1.6 mmol/g, accompanied with the  $x$  values varied from 1 to 0.2. In essence, the  $x$  value denoted the distribution of active group in the interlayer or on the surface of the

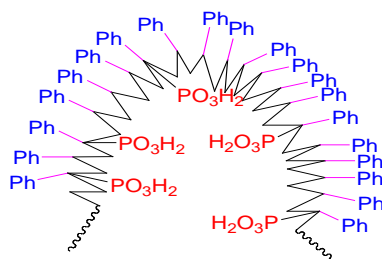
supports. In other words, the  $x$  value meant the density and the alignment of the active group in the interlayer or on the surface of the supports. Therefore, the least of  $x$  value was, the least content of polystyrene segment in the interlayer or on the surface of the supports were. That was to say that the  $x$  value could directly contributed to the quantity of chloromethylation, such as the quantity of chloromethylation at  $x = 0.33$  was lower 0.8 mmol/g than that at  $x = 0.5$  did. Simultaneously, the degree of chloromethylation of the supports would directly influence the final quantity of immobilization of salen Mn (III) that the least  $x$  value was, the lower quantity of immobilization of salen Mn (III) was.

Through the formula, it could be inferred that the conversions of chloromethylation of the supports were 98.2%, 96.1% and 93.3%, respectively, at  $x = 0.2, 0.33, 0.5$ . It was obvious that the extent of chloromethylation of the supports decreased with the increasing of  $x$  values. Meanwhile, it was also concluded that  $-CH_2Cl$  was introduced in equivalently 80-85% benzene rings in ZnPS-PVPA through chloromethylation. This demonstrated that 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 zinc phosphonate closely.

### Structure analysis of the supports

#### Structure of the copolymer

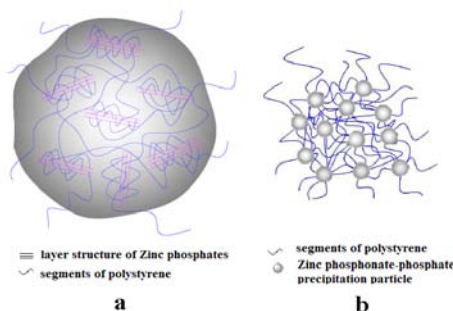
The potentiality for ZnPS-PVPA as excellent catalyst supports is correlated with the structure of the copolymer. The possible structure of copolymer is shown in Fig. S7. In the experiment, the content of PVPA in the copolymer was controlled by means of adjusting the amount of initiator and ratio of PVPA to St. Generally speaking, the main segments of the molecule chain are  $-(St)_{m1}-(PVPA)_n-(St)_{m2}-(PVPA)_n-(St)_{m3}-$  in the copolymer, here the  $n$  is usually 1 and seldom more than 2, because the ratio of PVPA to St in the experiment is 1:8 and the relative reactivities in the copolymerization for PVPA and St are comparable, thus the content ratio of PVPA to St in the copolymers prepared are found in the range of 1: 6-9. On the basis of the data, it can be deduced that a great number of hydrophobic segments of polystyrene can form half or part of holes and



**Fig. S7** possible ideal structure of copolymer.

cavums with different volume and shapes for that the content of hydrophobic segments of polystyrene in the copolymer is much more than that of hydrophilic segments of PVPA in the copolymer, thus many hydrophilic  $-PO_3H_2$  groups might gather together. The biggest surface area with the ratio of organic phosphonate to phosphate is 1:2<sup>1</sup>. When aqueous solution of hydrated zinc acetate is added, the phosphate, the phosphonic acid in the copolymer and water react with  $Zn^{2+}$  immediately to form white colloidal precipitation of ZnPS-PVPA. During the process, almost all phosphate in the reaction solution participate in forming the white colloidal precipitate of ZnPS-PVPA, while most of organic phosphoric acid in copolymer participate in forming or entering the white colloidal precipitation and little free phosphoric acid in the copolymer covers on the surface of white colloidal precipitation of ZnPS-PVPA. Simultaneously, hydrophobic segments of polystyrene in copolymer which exist half or part of holes and cavums with different volume and shapes are also covered on the surface of the white colloidal precipitation of ZnPS-PVPA. The two neighboring  $-PO_3H_2$  groups in the copolymer may be in same or in different white colloidal precipitation which will aggregate into bigger colloidal precipitation particles of ZnPS-PVPA. Therefore, it is the hydrophobic of polystyrene parts and the hydrophilic of phosphate parts in ZnPS-PVPA that make ZnPS-PVPA possess dual properties which are hydrophobic and hydrophilic. Meanwhile, ZnPS-PVPA could be reacted with other complexes either in aqueous solution or in organic solvent even in mixed solvent which is the character that many other materials couldn't compare with. According to the surface morphology, there are

probably two kinds of gathering model.

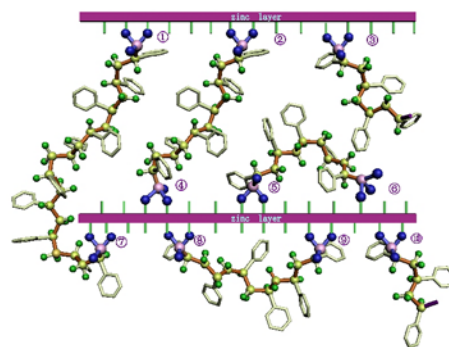


**Fig. S8** possible ideal structure of ZnPS-PVPA.

Fig. S8a, signifies that the two or more neighboring  $-\text{PO}_3\text{H}_2$  groups (there is a polystyrene chain between and connected them) are in same colloidal precipitation; while Fig. S8b, signifies that the two neighboring  $-\text{PO}_3\text{H}_2$  groups (there is a polystyrene segment between and linked them) are in different colloidal precipitation. In the aggregation process of the colloidal precipitation into bigger particles, many precipitation particles link each other to form even bigger hybrid ZnPS-PVPA precipitation particles, a great deal of channels, holes and cavums with different volume and shapes are gradually formed. Therefore, if precipitation particles link in the form of model b, different length and shape of channels, holes and cavums will come into being. And if the particles link in the form of model a, the channels, holes and cavums with smaller volume will be formed and cover on the surface of the small precipitation particle<sup>2</sup>.

### The hypothesized layered structure of ZnPS-PVPA

In the hypothesized models deduced for ZnPS-PVPA (Fig. S9), some oxygen atoms of the hydroxyl groups or hydroxy sodium in the segments of the inorganic phosphate groups were coordinated with zinc atoms, making the zinc atoms self-assemble in the same plane, while the other oxygen atoms of the portion of the inorganic phosphate groups in the ZnPS-PVPA stretched



**Fig. S9** The hypothesized layered structure of ZnPS-PVPA.

over the surface of the zinc layer. On the other side, there are several types of organic polymer phosphonate- $\text{PO}_3\text{H}_2$  (opp- $\text{PO}_3\text{H}_2$ ) formed in ZnPS-PVPA: opp- $\text{PO}_3\text{H}_2$  ③ was located on the interlayer surface of one zinc layer, and was connected to other particle of ZnPS-PVPA by polystyrene segment, in other words, opp- $\text{PO}_3\text{H}_2$  ③ and its one neighboring opp- $\text{PO}_3\text{H}_2$  were located not in same but in different particle of ZnPS-PVPA. The same to opp- $\text{PO}_3\text{H}_2$  group ⑩. Opp- $\text{PO}_3\text{H}_2$  group ② and ④ were linked each other by polystyrene chain and situated on the interlayer surface of the two adjacent zinc layers respectively. Opp- $\text{PO}_3\text{H}_2$  group ① was perched on the interlayer surface of one zinc layer and joined to opp- $\text{PO}_3\text{H}_2$  group ⑦ by polystyrene chain which lied on the surface of another contiguous zinc interlayer space. Both opp- $\text{PO}_3\text{H}_2$  group ⑤ and opp- $\text{PO}_3\text{H}_2$  group ⑥ which were conjunct to one another were located on the interlayer surface of the same zinc layer, similar to opp- $\text{PO}_3\text{H}_2$  group ⑧ and opp- $\text{PO}_3\text{H}_2$  group ⑨. In summary, there were at least three imaginable structures: (i) two adjacent opp- $\text{PO}_3\text{H}_2$  groups (there is a polystyrene chain between and connected them) were situated on the same layer in the same crystalline grain; (ii) two neighboring opp- $\text{PO}_3\text{H}_2$  groups (there is also a polystyrene chain among and linked them) were located on the different layer in the same crystalline grain; (iii) two

contiguous opp-PO<sub>3</sub>H<sub>2</sub> groups (there is a polystyrene segment between and jointed them) in the uniform particle were perched on diverse crystalline grain. So pores or channels of various sizes and shapes by appropriate modification of the styrene-phenylvinylphosphonic acid copolymer chain were formed that consequentially give birth to significant impact on the excellent catalytic activity<sup>2</sup>.

### The confinement effect originated in the x values of ZnPS-PVPA

As described in Table 5, the effect of the x value (ZnPS-PVPA) on the confinement effect of the heterogeneous chiral Mn (III) salen catalysts played vital impacts on the results of the enantioselective epoxidation of unfunctionalized alkenes. ZnPS-PVPA can be formed by coprecipitation of the zinc in the presence of styrene-phenylvinyl phosphonic acid copolymer (H<sub>2</sub>O<sub>3</sub>P-G) and phosphate (H<sub>2</sub>O<sub>3</sub>P-OH), leading to the formation of a porous zinc poly(styrene-phenylvinylphosphonate)-phosphate hybrid material. Because in the ZnPS-PVPA hybrid material, residue or side chain for opp-groups of P-G and inorganic phosphate P-OH are sufficiently different in size, obviously opp-groups of P-G are quite bulky and inorganic phosphate P-OH are relatively small. These hybrid compounds usually contain a random distribution of the organic groups such that all layers have identical stoichiometry. In such systems, the interlayer spacing (*d*-space) is a function of pendant group stoichiometry, and has a generally linear dependence on component mole fraction. Intermediate x values result in intermediate steric constraints, resulting in *d* values between the two organic groups<sup>2</sup>.

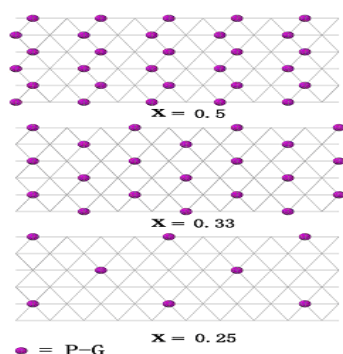
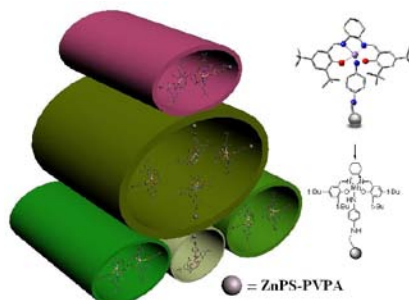


Fig. S10 The cross section of the x = 0.25, x = 0.33 and x = 0.5.

Then the models of Zn (NaPO<sub>4</sub>)<sub>1-x</sub> [PS-PVPA]<sub>x</sub>·yH<sub>2</sub>O series, viz. where x = 0.2, 0.25, 0.33, 0.4, 0.5, 0.75 and 1 were deduced. As we know, each zinc atom is bonded to six oxygen atoms, and every three of these oxygen atoms are bonded to one phosphorus atom. As a result, the layers of the ZnPS-PVPA are formed. A layer of ZnPS-PVPA **1e** (x = 0.5) presents that in order to exclude the higher-energy arrangement of pendant groups segregating on the interlayer, there is always a P-G (B) groups insert between two P-OH (A) or reverse. That is to say, the ideal model can be simply denoted as “ABABAB...”, and the scheme of the ideal cross section (Fig. S10) indicates that two bulky P-G (B) and four P-OH (A) groups are located around one P-G group, sterically directed energy allows bulky P-G groups to get out of the layers. Similarly, the ideal model for ZnPS-PVPA **1c** (x = 0.33) can also be denoted as “AABAABAAB...”, and the scheme of the ideal cross section (Fig. S10) suggests that six small P-OH (A) groups are located around one P-G group. The *d*-space is bigger than that of ZnPS-PVPA **1e** (x = 0.5), and it can offer enough space for some smaller substrates coordination to the active sites. Meanwhile, confinement effect generated for steric hindrance among the substrates and active sites. For ZnPS-PVPA **1b** (x = 0.25) the ideal model can also be denoted as “BAAABAAABAA...”, and the scheme of the ideal cross section (Fig. S10) suggests that the space of two neighboring P-G groups is much larger than the other two compounds. Although there is big room for catalytic reaction, the confinement effect and the content of the active sites always are decreased<sup>2</sup>.

Qualitatively, the changes in the *d* spacing with composition can be rationalized in terms of interrelated factors that pertain to the steric interactions of the bulkier styrene-phenylvinylphosphonic acid copolymer groups and the conformations of the organic groups. The styrene-phenylvinylphosphonic acid copolymer chains are located on the external surfaces or between the layers of ZnPS-PVPA. If the x values are big like ZnPS-PVPA **1e** (x = 0.5) or more the room between two styrene-phenylvinylphosphonic acid copolymer groups will be small, and in order to exclude the higher-energy arrangement of pendant groups segregating on the interlayer the most of the styrene-phenylvinylphosphonic acid copolymer groups are pushed out and located

on the external surface of ZnPS-PVPA. In contrast, if  $x$  values are relatively small like ZnPS-PVPA **1c** ( $x = 0.33$ ) and ZnPS-PVPA **1b** ( $x = 0.25$ ) or less the space between two styrene-phenylvinylphosphonic acid copolymer groups will be big which was in good according with the results obtained by XRD. And more part of the styrene-phenylvinylphosphonic acid copolymer groups are naturally located between the layers of ZnPS-PVPA. In conclusion, the frameworks of ZnPS-PVPA can be easily designed and assembled to generate pores or channels of various sizes and shapes by appropriate modification of the styrene-phenylvinylphosphonic acid copolymer chain (Fig. S11). The porous hosted materials affect catalytic performance due to a cooperative interaction among the nanoporous solid, immobilizing linker, and Mn-salen complex. Mesoporous materials are the most applicable supports for the immobilization of Mn-salen complexes<sup>3</sup>. Just as this special structures of ZnPS-PVPA contributed to the excellent catalytic effect.



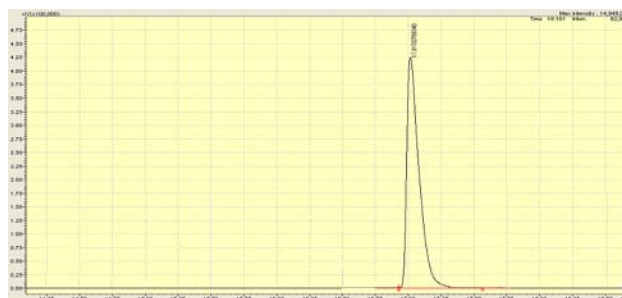
**Fig. S11** The hypothesized structure of the heterogeneous catalyst.

## References

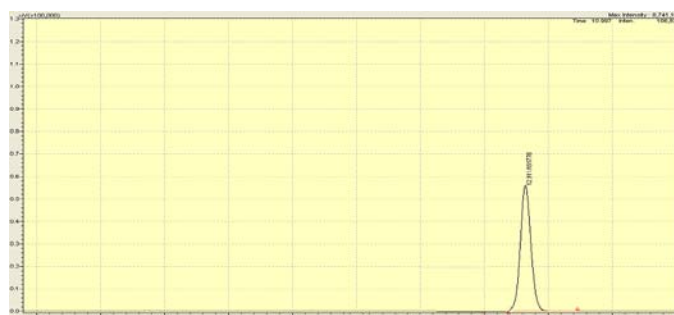
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GC chromatograms of standard racemic epoxide sample



Entry 20 in Table 6.



Entry 4 in Table 8.