

Mesoporous Cross-Linked Polymer Copolymerized with Chiral BINAP Ligands Coordinated to Ruthenium Species as an Efficient Heterogeneous Catalyst for Asymmetric Hydrogenation

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Catalysts Preparation

Synthesis of BINAP dioxide

5 g of (R)- or (S)-BINAP were dissolved in 50 mL of tetrahydrofuran (THF) and cooled down to 0°C, followed by addition of 30 mL of H₂O₂ for lasting 30 min. After stirring at room temperature for 4 h, THF was removed from the mixture under vacuum condition. Then, 50 mL of CH₂Cl₂ was added to the residue and the aqueous phases were extracted with 3×30 mL of CH₂Cl₂. The collected organic phase was combined and evaporated to obtain a white solid (5.25 g, quantitative yield), which was denoted as BINAPO.

Synthesis of 5,5'-dinitro BINAP dioxide

5,5'-dinitro BINAP dioxide was synthesized according to the literature.¹ As a typical run, 90 mL of acetic anhydride was cooled down to -10 °C, followed by addition of 15 mL of concentrated nitric (69%) in 30 minutes under stirring. After addition of 1.5 mL sulfuric acid (98%) to the resulting solution, 4.9 g of BINAPO were introduced. After the mixture was stirred at -5 °C for 5 h, NaOH solution (30%) was slowly added to adjust the pH=8-9. Finally, 3×50 mL of CH₂Cl₂ were added to extract the product. The combined organic phase was washed thoroughly with water and dried over with MgSO₄. The solvent was removed under vacuum and a yellow solid (5.13 g, 92% yield) was obtained, which was denoted as NO₂-BINAPO. ¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ 8.63-8.66 (m, 2H), 8.10 (d, 2H, *J*=7.2Hz), 7.67-7.74 (m, 6H), 7.29-7.47 (m, 16H), 7.07 (d, 2H, *J*=8.4Hz), 6.84 (t, 2H, *J*=8.0Hz)

ppm.

Synthesis of 5,5'-diamino BINAP dioxide

5,5'-diamino BINAP dioxide was synthesized as follows: 5 g of 5,5'-dinitro BINAP dioxide was dissolved in 50 mL of THF containing 1 g of 10% Pd/C as catalyst. Then, 5 mL of hydrazine monohydrate in 50 mL of ethanol was added dropwise over a period of 1 h. After the mixture was stirred at 80 °C for 12 h, the catalyst was filtered and all the volatile components were removed under vacuum to give a yellow-brown solid. The obtained solid was dissolved in CH₂Cl₂ and washed with water for several times. The combined organic phase was washed thoroughly with water and dried over with MgSO₄. The solvent was removed under vacuum and a brown solid (3.86 g, 84% yield) was obtained, which was denoted as NH₂-BINAPO. ¹H NMR (400MHz, CDCl₃, 298K, TMS): δ 7.68-7.79 (m, 6H), 7.22-7.47 (m, 16H), 6.53-6.63 (m, 4H), 6.23 (d, 2H, *J*=8.4Hz), 3.59-4.26 (m, 4H) ppm.

Synthesis of 5,5'-diacryloylamino BINAP dioxide

5,5'-diacryloylamino BINAP dioxide was synthesized as follows: NH₂-BINAPO (5 g, 7.46 mmol) was dissolved in 100 mL of CH₂Cl₂ in the presence of excessive of K₂CO₃ and cooled down to 0-5 °C. Then, a solution of acrylyl chloride (0.8 g, 8.95 mmol) in 30 mL of CH₂Cl₂ was slowly added and stirred at room temperature for 12 h. The resulting solution was filtered and washed with NaHCO₃ solution (5%) and water in turn. The combined organic phase was washed thoroughly with water and dried over with MgSO₄. The solvent was removed under vacuum and a brown solid (5.10 g, 88% yield) was obtained. ¹H NMR (400MHz, DMSO-d₆, 298K, TMS): δ 10.24 (s, 2H), 8.13 (d, 2H, *J*=8.4Hz), 7.59-7.72 (m, 6H), 7.72-7.53 (m, 18H), 6.64-6.79 (m, 4H), 6.30-6.42 (m, 4H), 5.80-5.83 (m, 2H) ppm.

Synthesis of Porous Cross-linked Polymer (PCP) with BINAPO (PCP-BINAPO)

PCP-BINAPO was synthesized *via* solvothermal synthesis according to literature.² As a typical run, 2 g of divinylbenzene and 0.5 g of 5,5'-diacryloylamino

BINAP dioxide were dissolved in 20 mL of DMF, followed by addition of 0.05 g of azobisisobutyronitrile (AIBN). After stirring for 3 h at room temperature, the mixture was transferred into an autoclave at 100 °C for 24 h. After extraction of solvent with ethanol, a brown solid product was obtained, which was designated as PCP-BINAPO.

Synthesis of PCP with BINAP (PCP-BINAP)

PCP-BINAP was synthesized by the reduction of PCP-BINAPO, and these experiments were taken out using the Schlenk technique. As a typical run, 1 g of PCP-BINAPO was suspended in 40 mL of dry toluene containing 1 mL of HSiCl₃, then 1g of triphenylphosphine used as oxygen acceptor was added³. After that, with further addition of HSiCl₃ (0.5 mL) for three time at 1, 3, and 10 h, the mixture was refluxed for 24 h. Hot filtration and subsequent washing with toluene and CH₂Cl₂ yielded a yellow-brown powder, which was denoted as PCP-BINAP.

Characterization

Nitrogen isotherms at the temperature of liquid nitrogen were measured using Micromeritics ASAP 3020M and Tristar system. The samples were outgassed for 10 h at 100 °C before the measurements. Pore diameters were determined from the adsorption branch using the Barrett-Joyner-Halenda (BJH) method. Scanning electron microscopy (SEM) was performed using a Hitachi SU 1510. ¹³C (100.5 MHz) cross-polarization magic-angle spinning (CP-MAS), and ³¹P (161.8 MHz) MAS solid-state NMR experiments were recorded on a Varian infinity plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO₂ rotor. All the solid-state NMR measurements were performed on the Varian Infinityplus-400 spectrometer. H→¹³C CP/MAS NMR spectra were recorded at 100.5 MHz using 5-mm MAS probe with a spinning rate of 8kHz, 4096 scans, a contact time of 6 ms, and a recycle delay of 2 s. The chemical shifts were referenced to the adamantane with the upfield methine peak at 29.5 ppm. ³¹P MAS NMR experiments were conducted at 161.8 MHz using 4-mm MAS probe with a spinning rate of 10 kHz, 1024scans, and a 2 s recycle delay. The ³¹P NMR chemical shifts were referenced to

the 85% H₃PO₄. FTIR spectra were performed on IFS 66 V (Bruker) IR spectrometer in the range 400-4000 cm⁻¹. Diffuse reflectance ultraviolet-visible (UV-vis) spectra were measured with spectrometer of PE Lambda 20, and BaSO₄ was an internal standard sample. CD spectra were performed on MOS-450. The leaching of Ru was detected by inductively coupled plasma (ICP) with a Perkin-Elmer plasma 40 emission spectrometer.

Catalytic tests

In the asymmetric hydrogenation, all experiments were carried out under a nitrogen atmosphere by using standard Schlenk-type techniques or performed in a glovebox unless otherwise stated. As a typical run for asymmetric hydrogenation of β -keto esters, a desired amount of PCP-BINAP and dichloro(benzene)ruthenium(II)dimer were added to anhydrous methanol in a test tube and stirred for 2 h at room temperature, then desired amount of substrates was added. After that, the test tube was transferred into a stainless steel autoclave, sealed, and purged with H₂ for 4 times. Finally, the pressure of H₂ was adjusted to desired value and the autoclave was placed to a preheated water bath, stirred for 20 h. After the reaction, the catalyst was taken out from the system by centrifugation and the liquid was passed through a short column before analyzed by gas chromatography (Agilent 6890 gas chromatography equipped with a flame ionization detector and a Supelco γ -DEX 225 capillary column).

For recycling the catalyst, the catalyst was separated by centrifugation (performed in a glovebox), washed with ethyl ether (5×5mL) under N₂ (ethyl ether was dried and deoxidized by standard methods) and dried under vacuum (using standard Schlenk-type techniques), after that the catalyst was used directly for the next catalytic reaction.

In asymmetric transfer hydrogenation of 1-phenyl-ethanone, the reaction was carried out using 0.5 mmol of 1-phenyl-ethanone, 2.5 mmol of HCOONa, and an S/C ratio of 100 in 5 mL of water at 40°C for 1.5 h.

Supporting Figure Captions

Figure S1. Photographs of (A) as-synthesized PCP-BINAPO, (B) PCP-BINAP before (a) and after (b) addition of methanol.

Figure S2. (A) N₂ sorption isotherms and (B) pore size distributions of the samples with various DVB/BINAPO weight ratios at (a) 8, (b) 4, (c) 2, (d) 1.3, and (e) 1, respectively. Isotherms of (a)-(c) have been offset by 500, 300, and 100 cm³/g, respectively, along the vertical axis for clarity. Pore size distributions of (a)-(d) have been offset by 1.0, 0.6, 0.4, and 0.2 cm³/g respectively, and each of them was estimated by BJH model from adsorption branch of the isotherms.

Figure S3. Pore size distributions of PCP-BINAPO and PCP-BINAP.

Figure S4. SEM image of PCP-BINAP.

Figure S5. (A) SEM image and (B) corresponding P element mapping for PCP-BINAP (Scale bar: 60 μm).

Figure S6. UV-Vis spectrum of PCP-BINAP.

Figure S7. (A) CD spectra of BINAP enantiomers and (B) UV-Vis spectrum of (*R*)-BINAP.

Figure S8. (A) CD and (B) UV-Vis spectra of PDVB.

Figure S9. UV-Vis spectra of (A) BINAP liquid sample and (B) PCP-BINAP solid sample before (a) and after coordination with Ru species (b).

Figure S10. The effect of BINAP/Ru molar ratios on the *ee* values in hydrogenation

of methyl acetoacetate. All the reactions were carried out under a H₂ pressure of 4 MPa in 2 mL methanol as a solvent and 1 mmol of methyl acetoacetate as a substrate at 50°C for 20 h with S/C=2000 (0.005 mmol of Ru was used).

Figure S11. The effect of the amount of solvent on the *ee* values in hydrogenation of methyl acetoacetate. All the reactions were carried out under a H₂ pressure of 4 MPa, methanol as a solvent and 10 mmol of methyl acetoacetate as a substrate at 50°C for 20 h with S/C=2000 (0.005 mmol of Ru was used).

Figure S12. The effect of H₂ pressure on the *ee* values in hydrogenation of methyl acetoacetate. All the reactions were carried out with S/C=2000 (0.005 mmol of Ru was used), 2 mL methanol as a solvent and 10 mmol of methyl acetoacetate as a substrate at 50°C for 20 h under various H₂ pressure.

Figure S13. The effect of S/C molar ratios on the *ee* values in hydrogenation of methyl acetoacetate. All the reactions were carried out under a H₂ pressure of 4 MPa in 2 mL methanol as a solvent and 10 mmol of methyl acetoacetate as a substrate at 50°C for 20 h with various catalyst amounts (0.002-0.1 mmol).

Figure S14. Photographs of the catalyst (a) after reaction and (b) after centrifugation.

Figure S15. The structure of functionalized chiral monomers of (a) N-4-vinyl-benzensulfonyl-1,2-diphenylethylenediamine (V-TsDPEN), (b) N,N-4-vinyl-benzensulfonyl-1,2-cyclohexane-1,2-diamine, and (c) N-(2-acryloylamino-cyclohexyl)-acrylamide.

Figure S16. (A) N₂ adsorption-desorption isotherms and (B) pore size distribution of chiral mesoporous polymers with DVB/V-TsDPEN weight ratio at 4.

Table S1. Textural Parameters for PCP-BINAPO with various weight ratios of DVB to BINAPO

Sample DVB/BINAPO ratio	S_{BET} (m ² /g)	Pore size distribution (nm)	Pore volume (cm ³ /g)
8/1	654	18.1	0.78
4/1	585	13.8	0.63
2/1	518	8.1	0.42
4/3	379	3.4	0.21
1/1	5	--	0.0035

Notably, the ratios of DVB/BINAP in the synthesis could be rationally adjusted (Fig. S2 and Table S1). When DVB/BINAPO ratio was 4, the sample showed high surface area, large pore volume, and large mesopore sizes. Therefore, in this work, the PCP-BINAP with DVB/BINAP at 4 was selected as a model catalyst for characterization and catalytic tests.

Table S2. Textural Parameters for PCP-BINAPO and PCP-BINAP

Sample	S_{BET} (m ² /g)	Pore size distribution (nm)	Pore volume (cm ³ /g)
PCP-BINAPO	585	13.8	0.63
PCP-BINAP	524	19.8	0.65

Table S3. Recycling test of Ru/PCP-BINAP in asymmetric hydrogenation of methyl methacrylate.^a

Recycles	Conversions (%) ^b	Selectivity (%) ^b	ee(%) ^b
0	>99.5	>99.5	94.6
1	>99.5	>99.5	95.3
2	>99.5	>99.5	95.4
3	>99.5	>99.5	95.1
4	>99.5	>99.5	94.5
5	>99.5	>99.5	92.7
6	>99.5	>99.5	94.3

^aThe reaction was carried out under a hydrogen pressure of 2 MPa in 2.0 mL methanol at 50 °C for 20 h with S/C ratio at 2000. ^bDetermined by GC on a Supelco γ -DEX 225 capillary column.

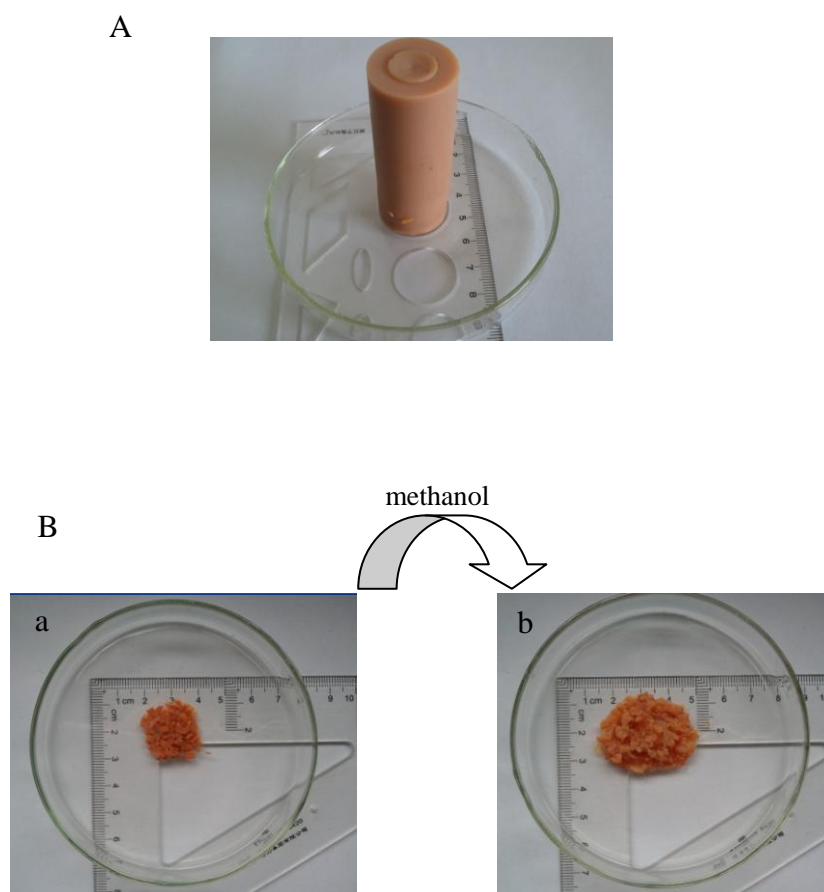


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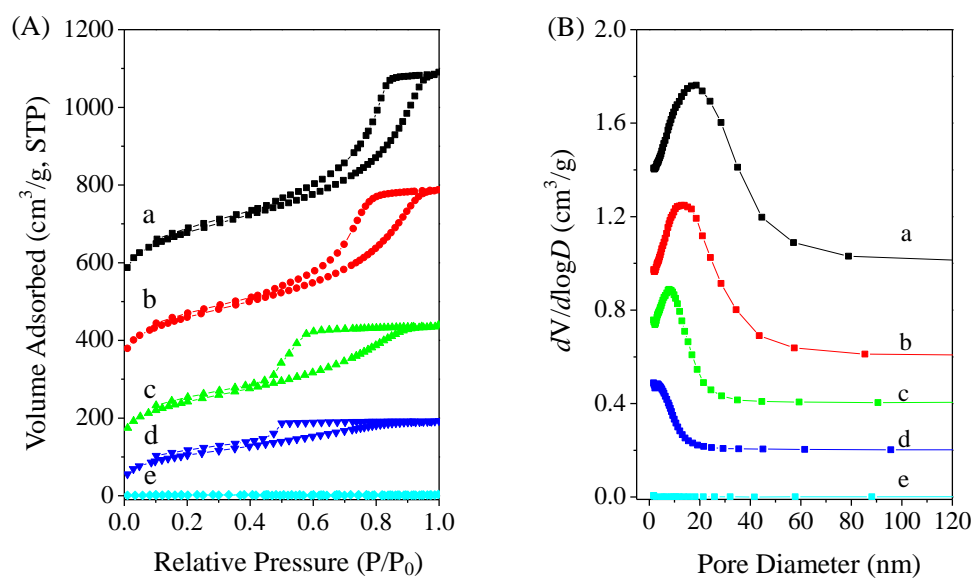


Figure S2.

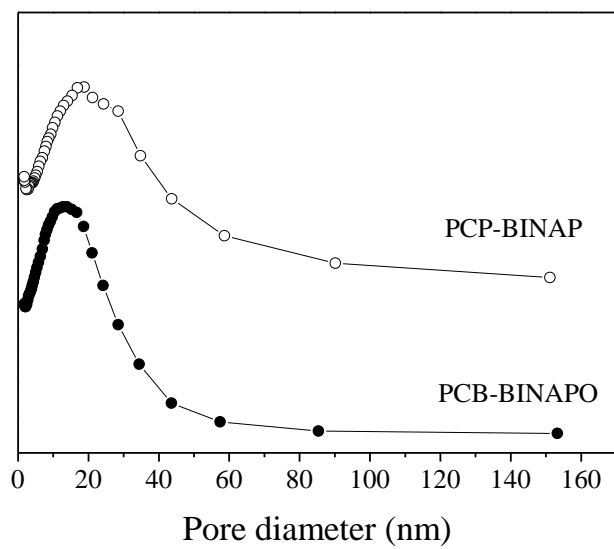


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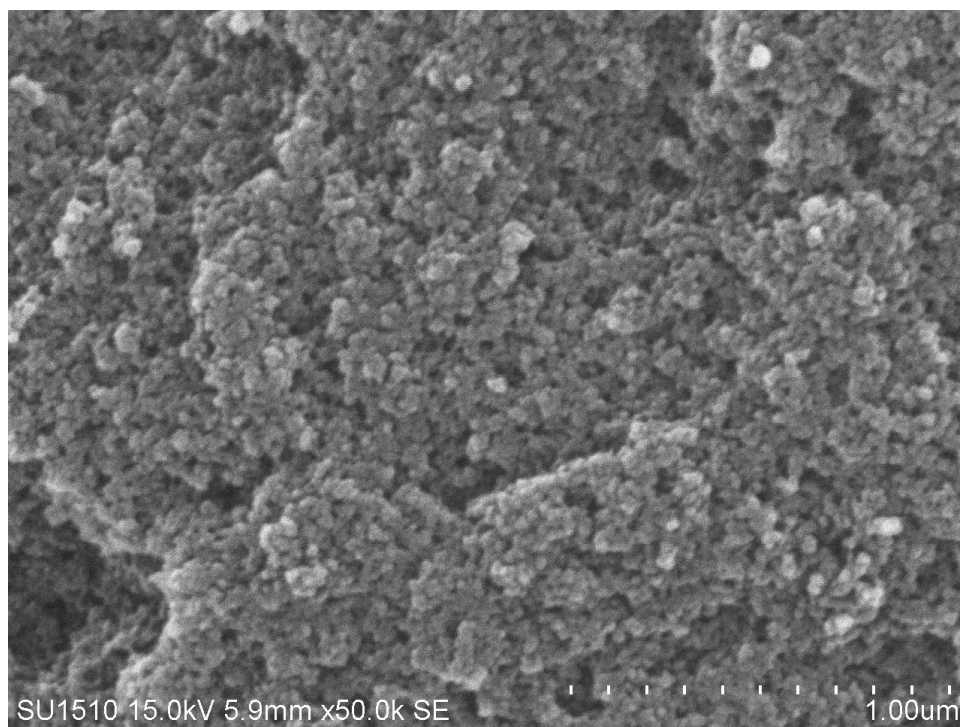


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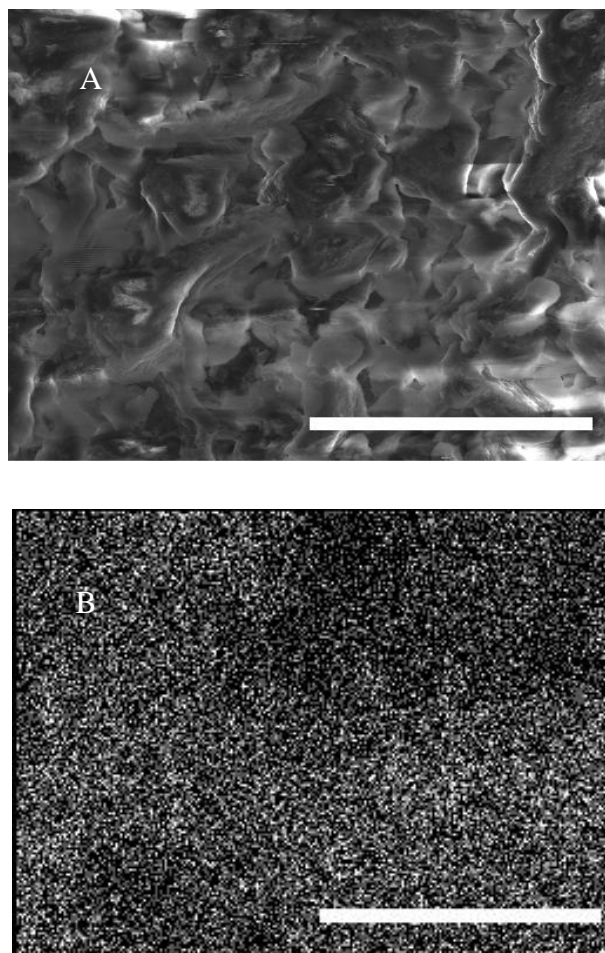


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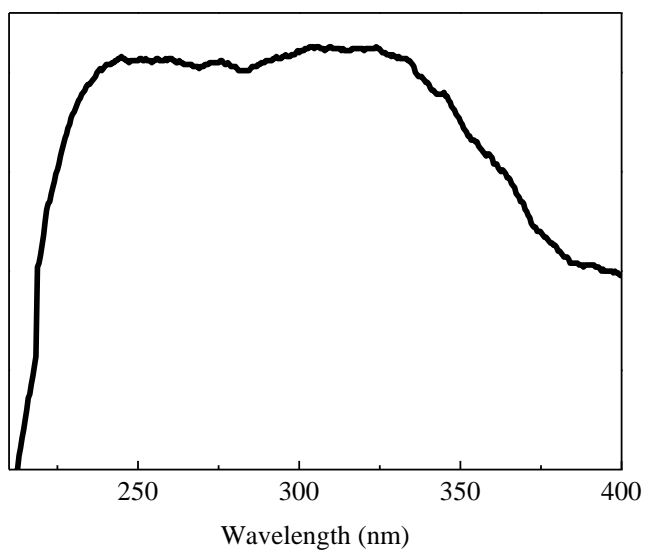


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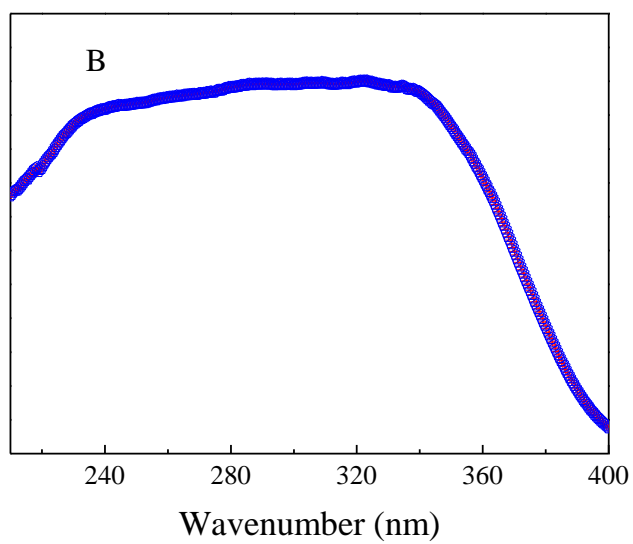
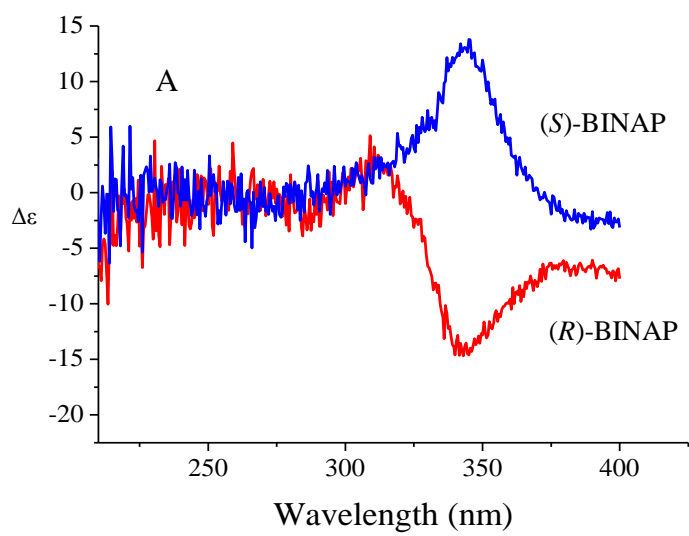


Figure. S7.

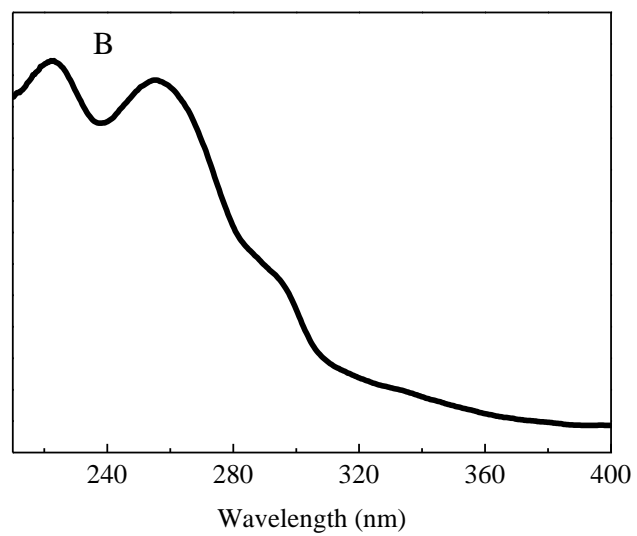
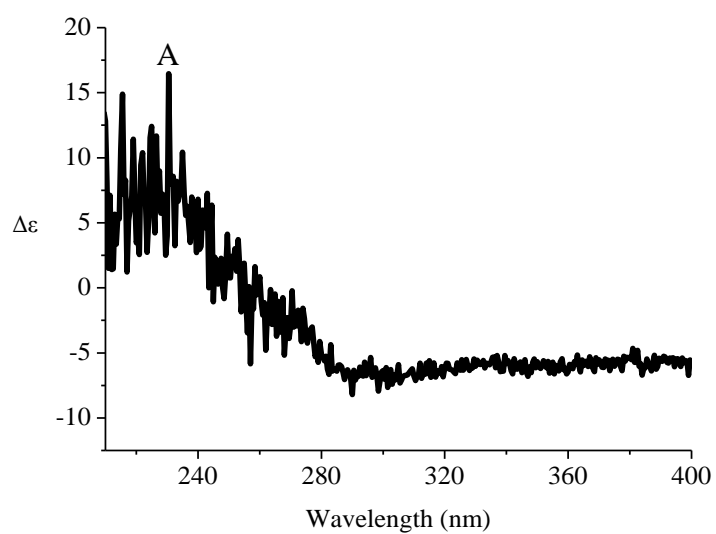


Figure S8.

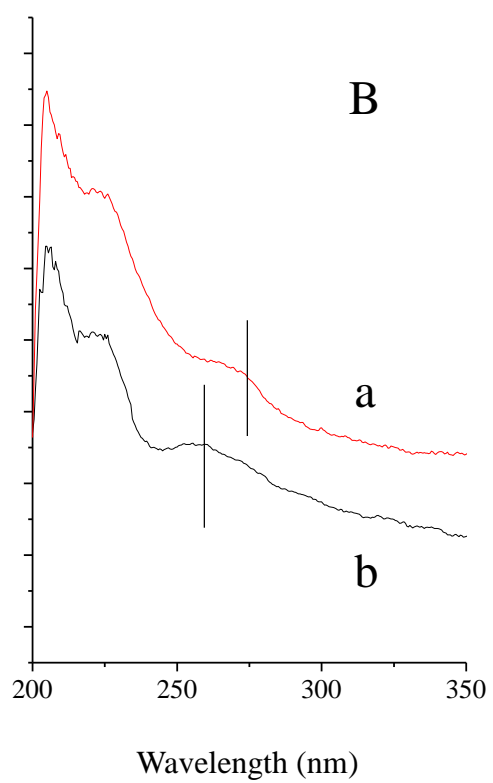
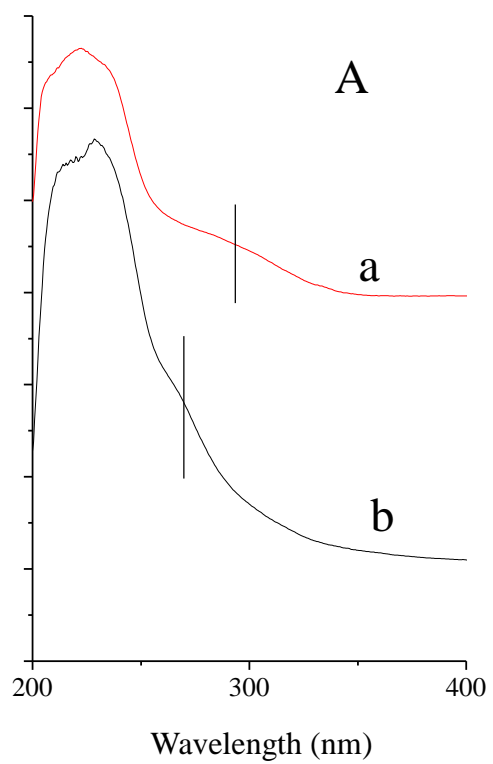


Figure S9.

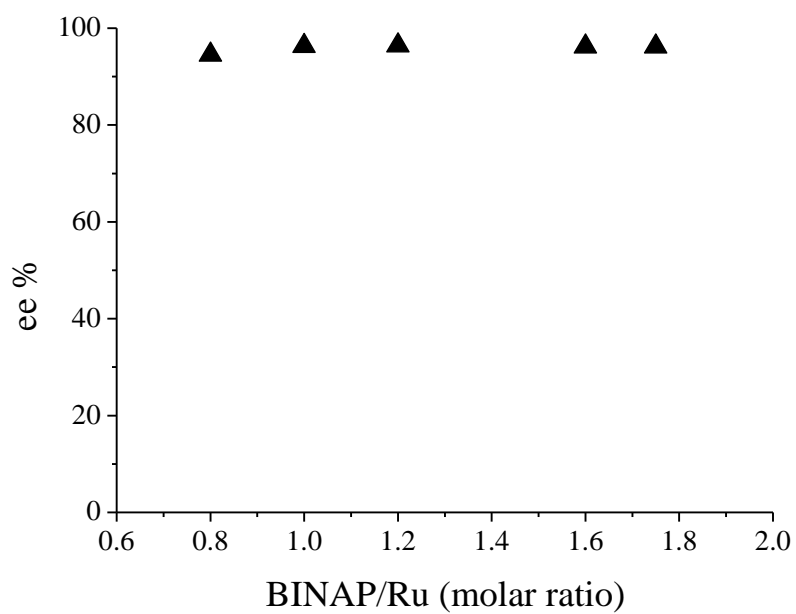


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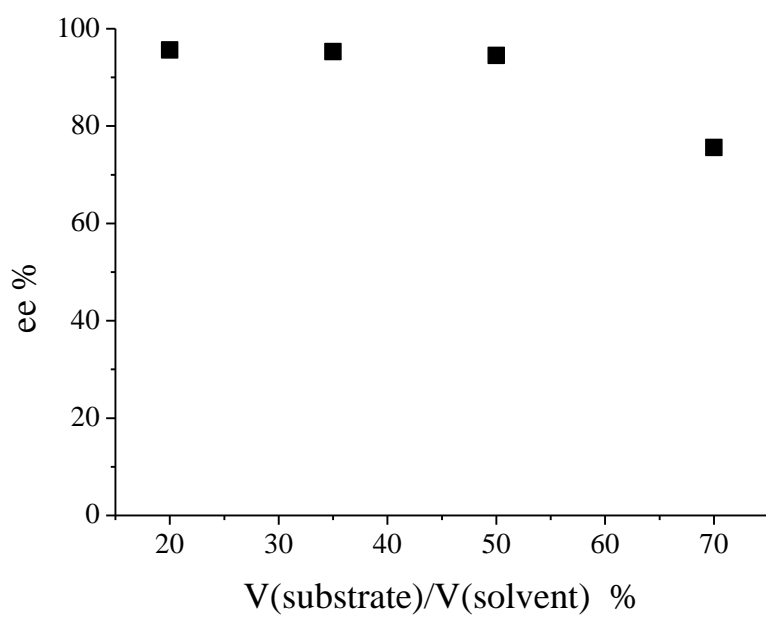


Figure S11.

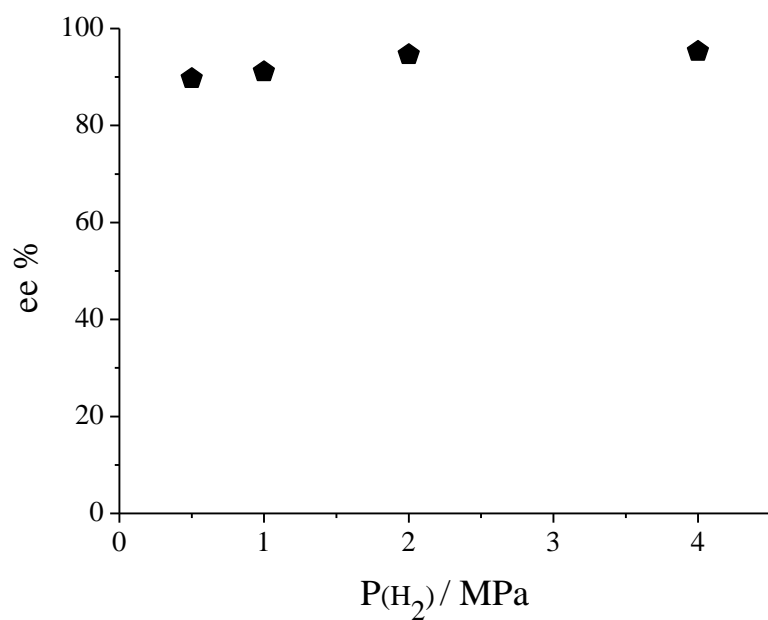


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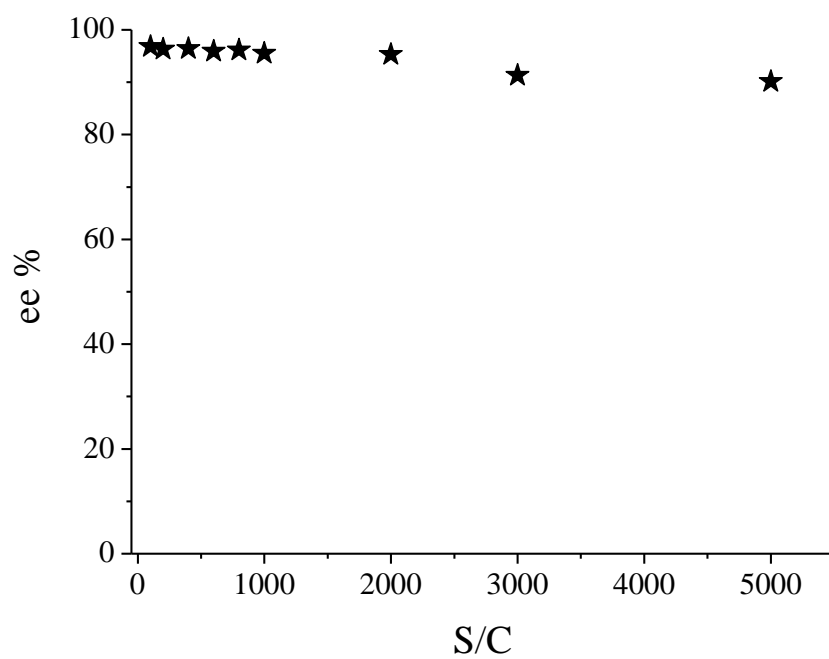


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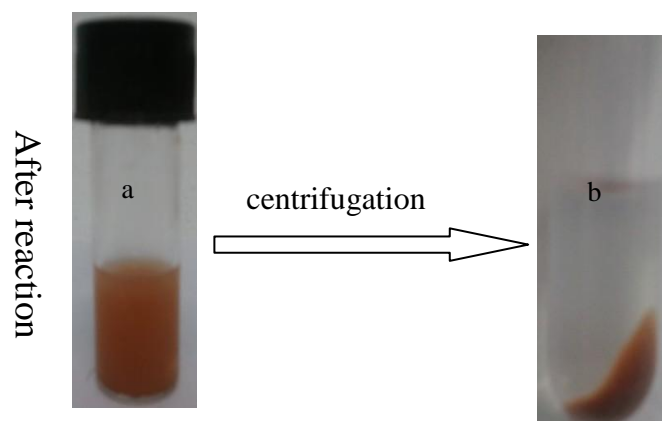
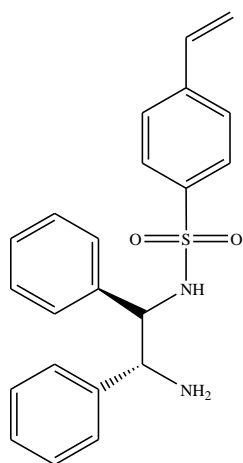
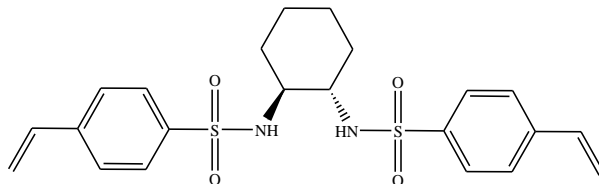


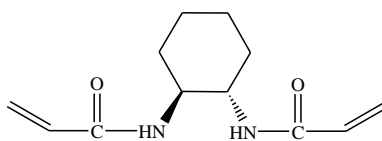
Figure S14.



a



b



c

Figure S15

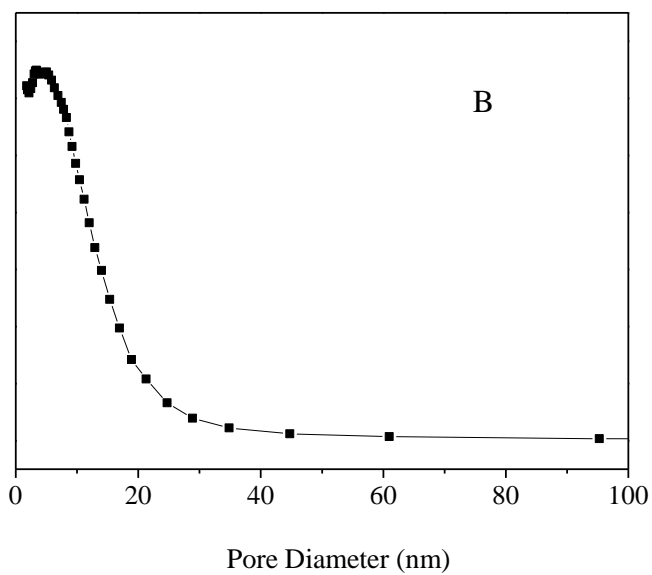
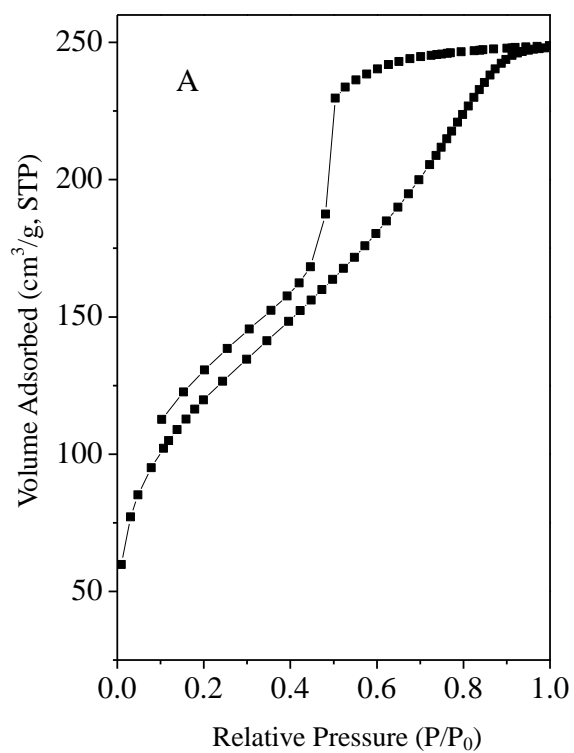
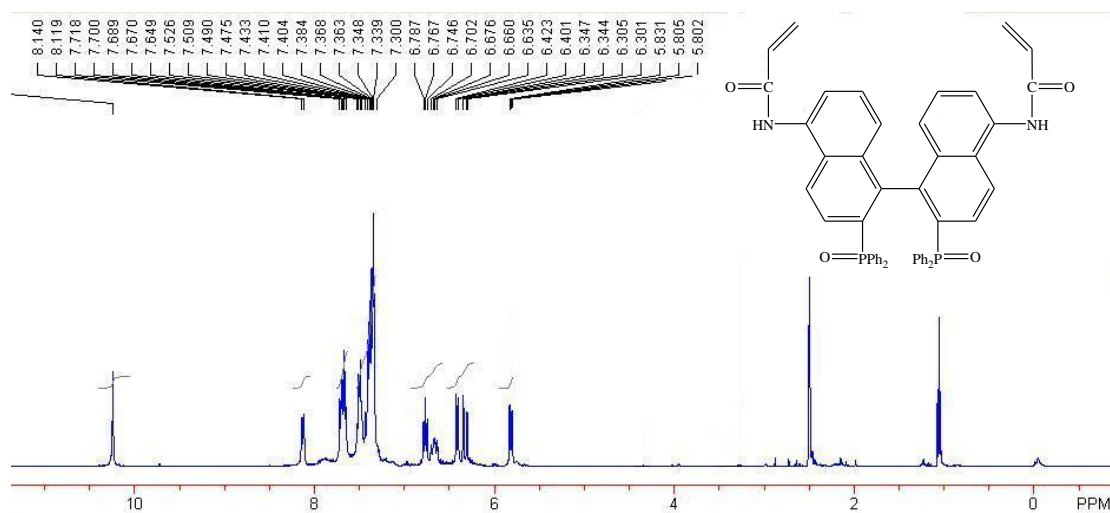
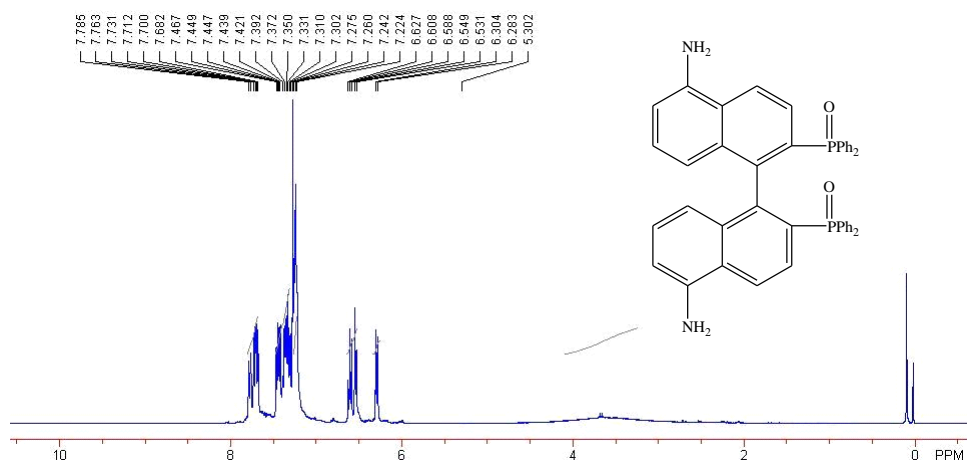
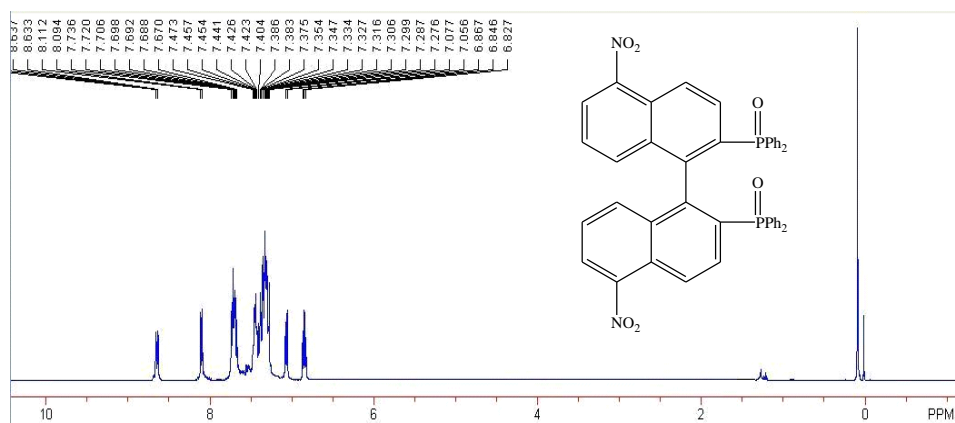
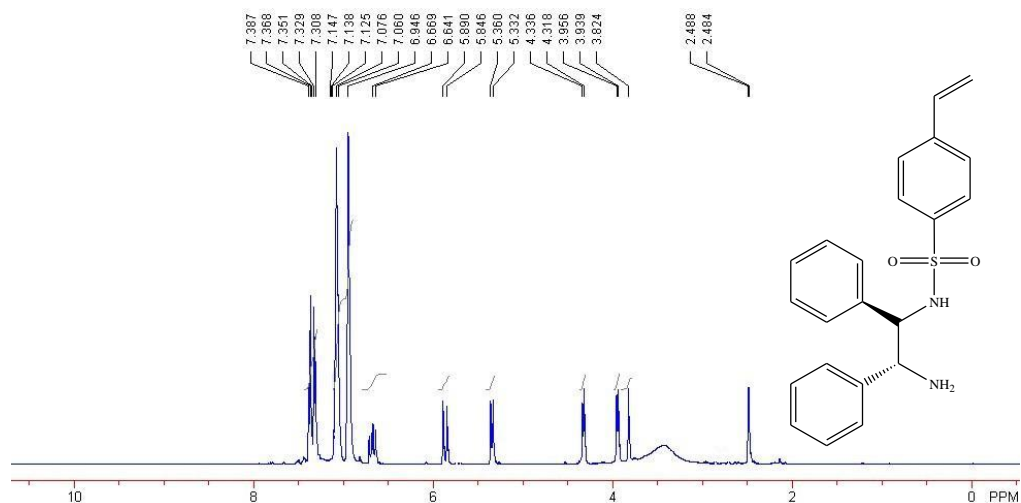


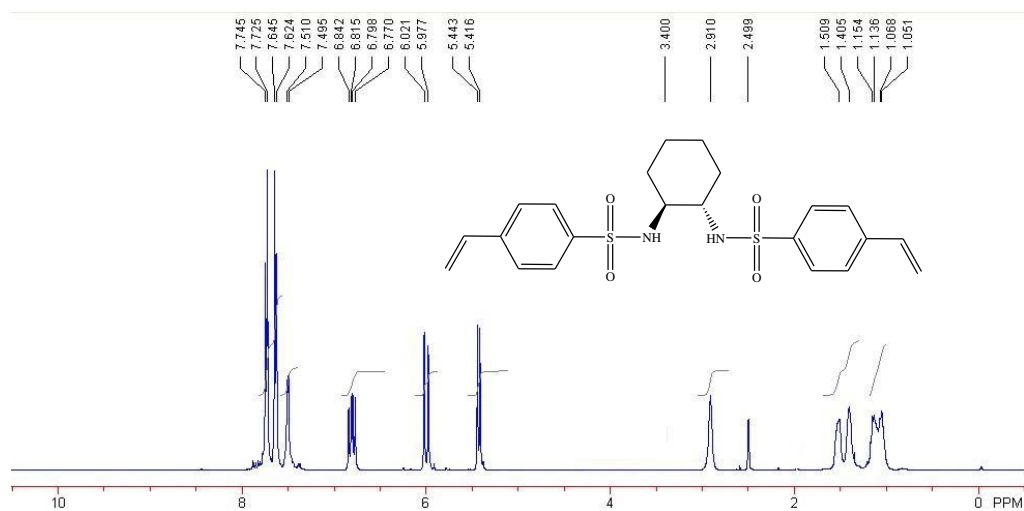
Figure S16

3. Corresponding ^1H NMR and GC spectra

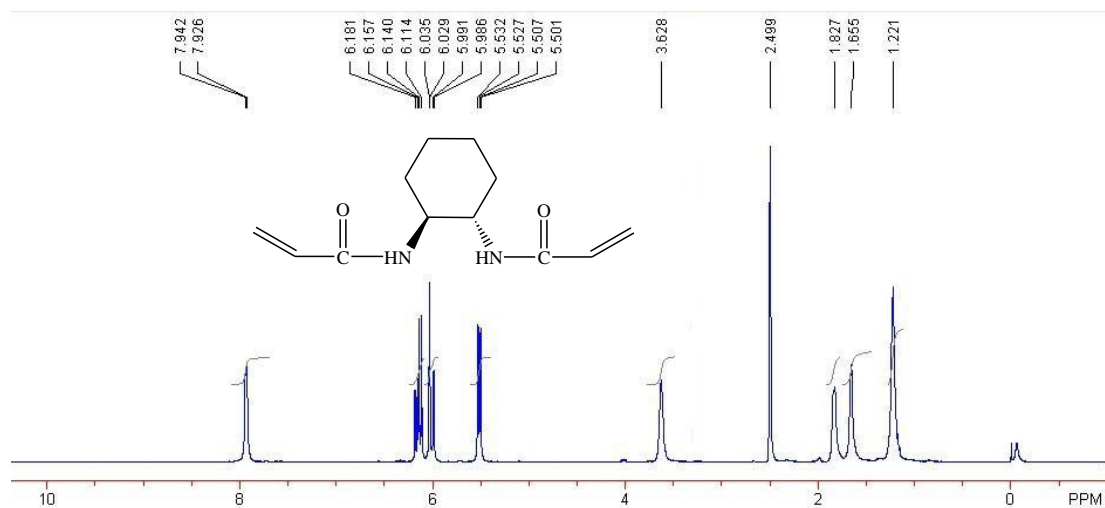




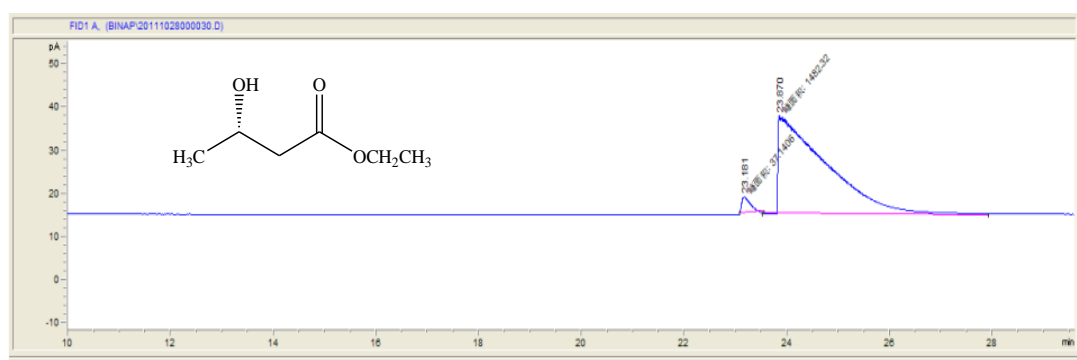
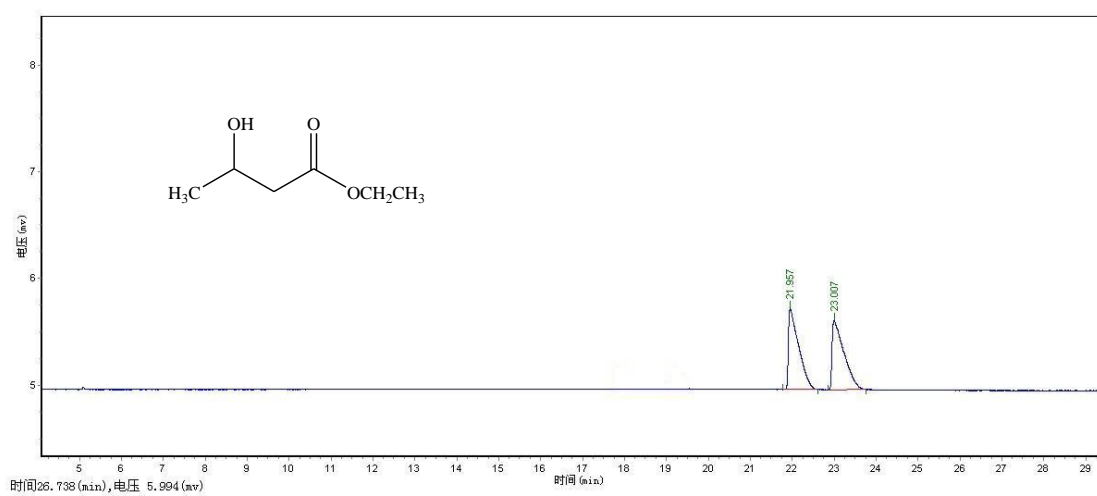
^1H NMR (400 MHz, DMSO- d_6 , 298K, TMS): δ 6.64-7.38 (m, 14H), 6.64-6.67 (m, 1H), 5.87 (d, 1H, $J=16.8\text{Hz}$), 5.35 (d, 1H, $J=11.2\text{Hz}$), 4.33 (d, 1H, $J=7.2\text{Hz}$), 3.95 (d, 1H, $J=6.6\text{Hz}$) ppm.

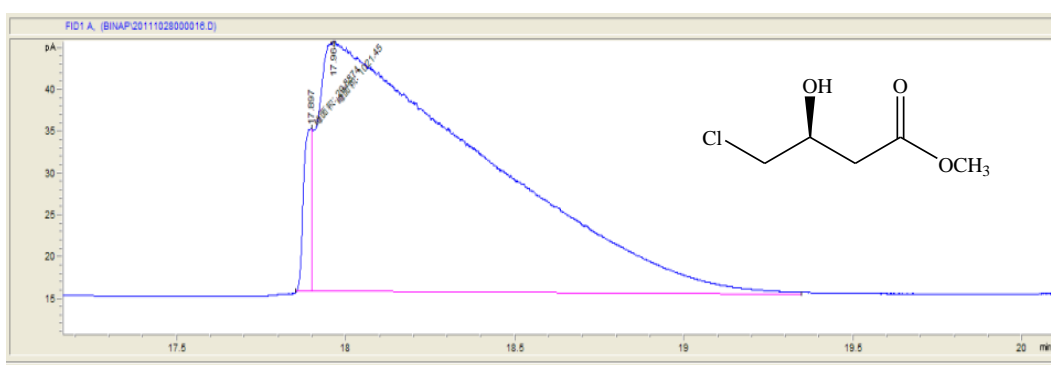
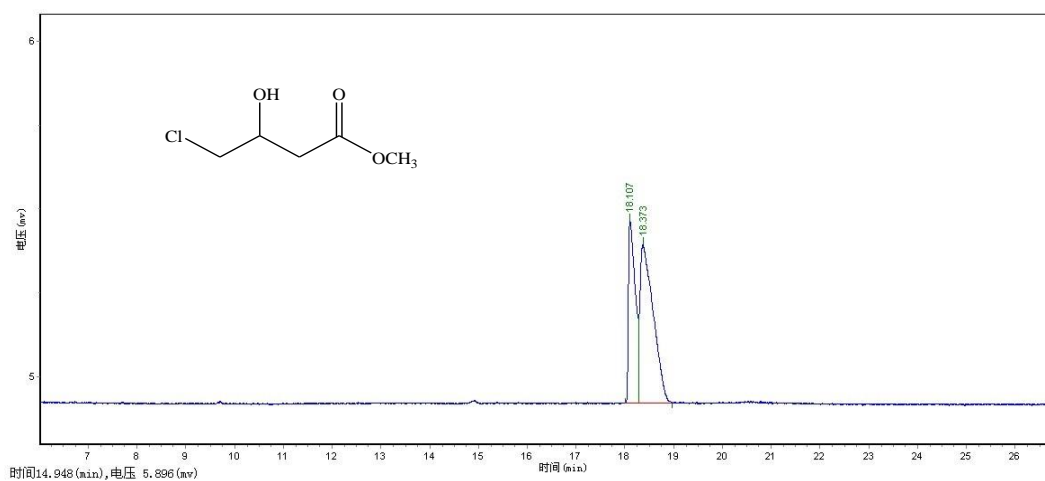


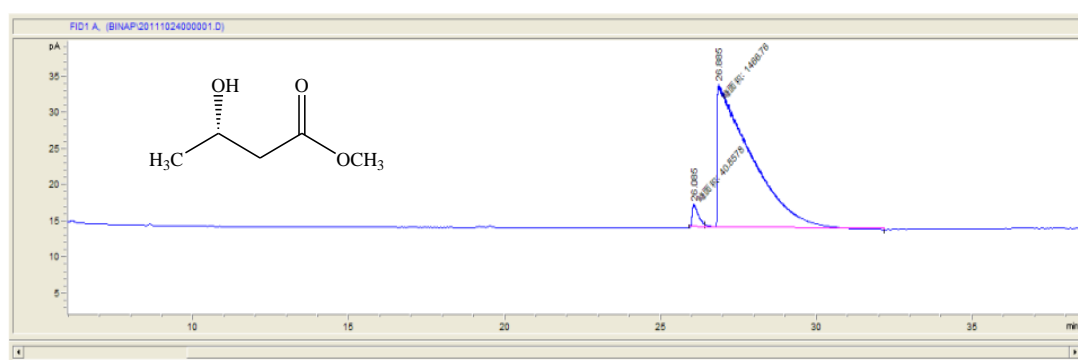
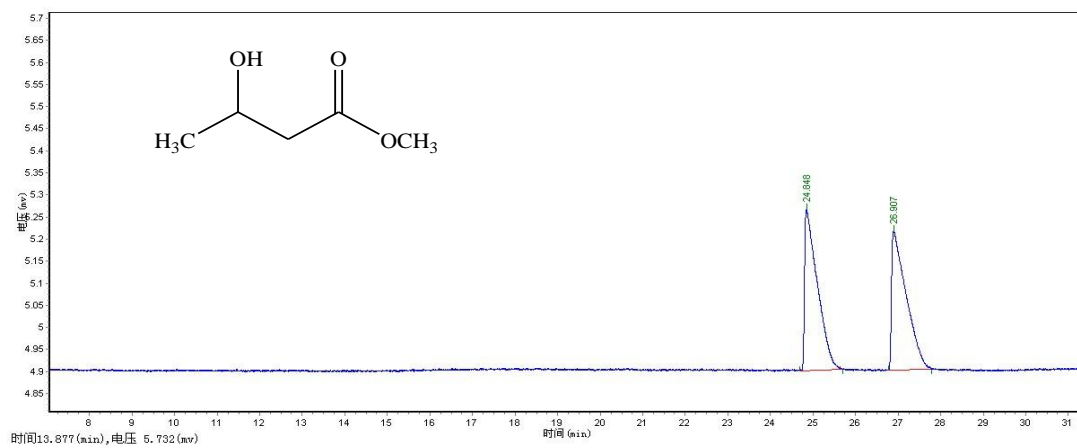
^1H NMR (400 MHz, DMSO- d_6 , 298K, TMS): δ 7.62-7.75 (m, 8H), 7.5 (m, 2H, $J=6\text{Hz}$), 6.77-6.84 (m, 2H), 6 (d, 2H, $J=17.6\text{Hz}$), 5.43 (d, 2H, $J=10.8\text{Hz}$), 2.91 (s, 2H), 1.05-1.51 (m, 8H) ppm.

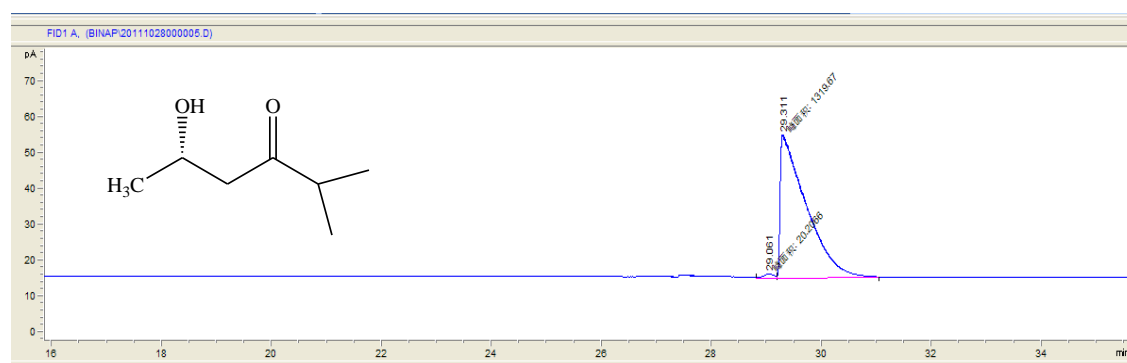
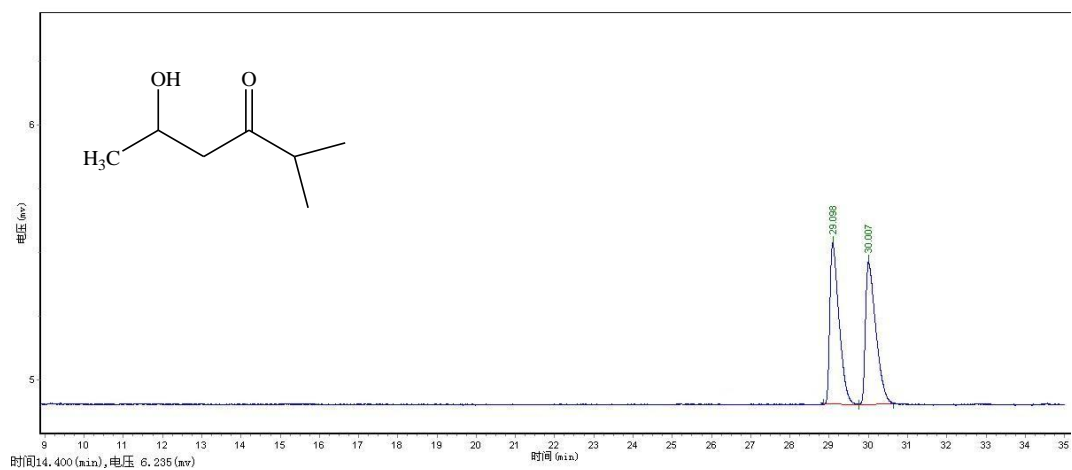


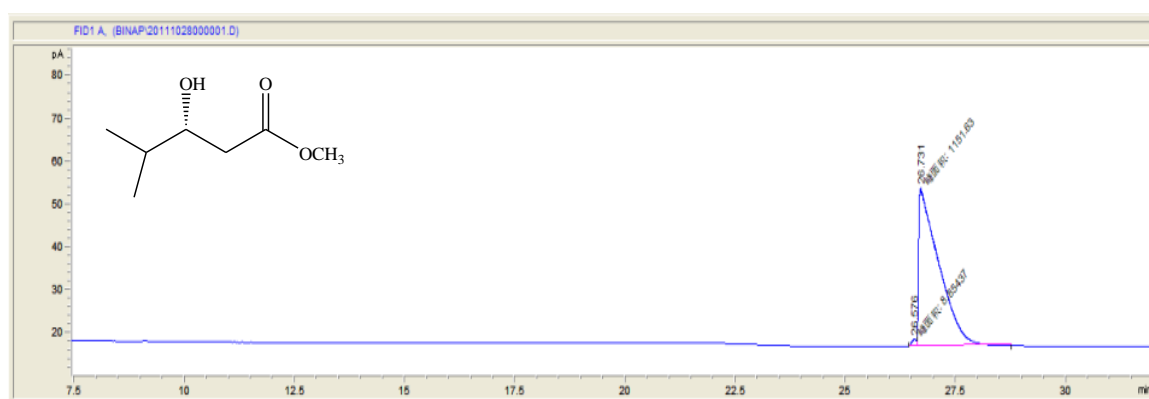
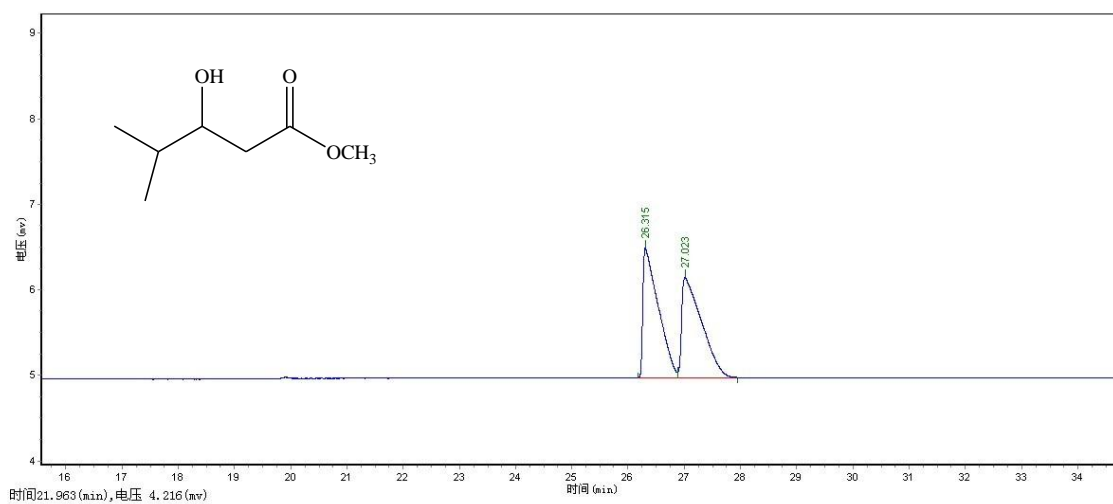
¹H NMR (400 MHz, DMSO-d₆, 298K, TMS): δ 7.93 (d, 2H, J=6.4Hz), 6.11-6.18 (m, 2H), 5.99-6.04 (m, 2H), 5.50-5.53 (m, 2H), 3.63 (s, 2H), 1.83 (s, 2H), 1.66 (s, 2H), 1.22 (s, 4H) ppm.

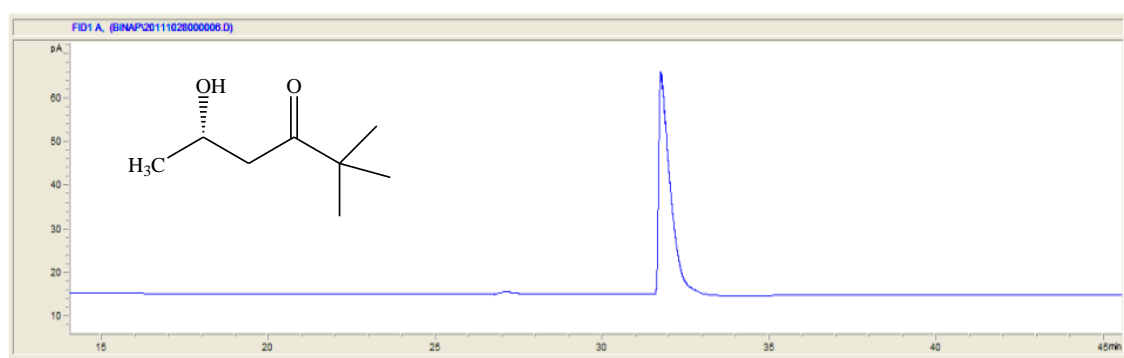
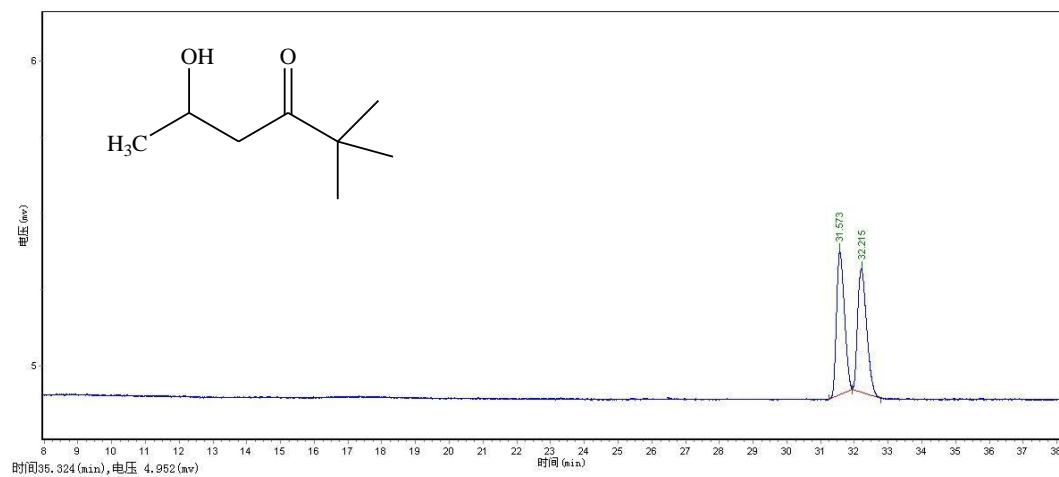


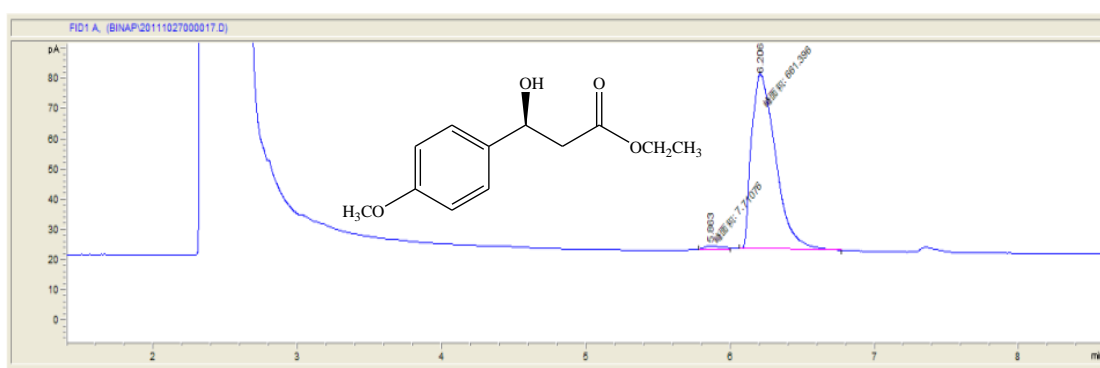
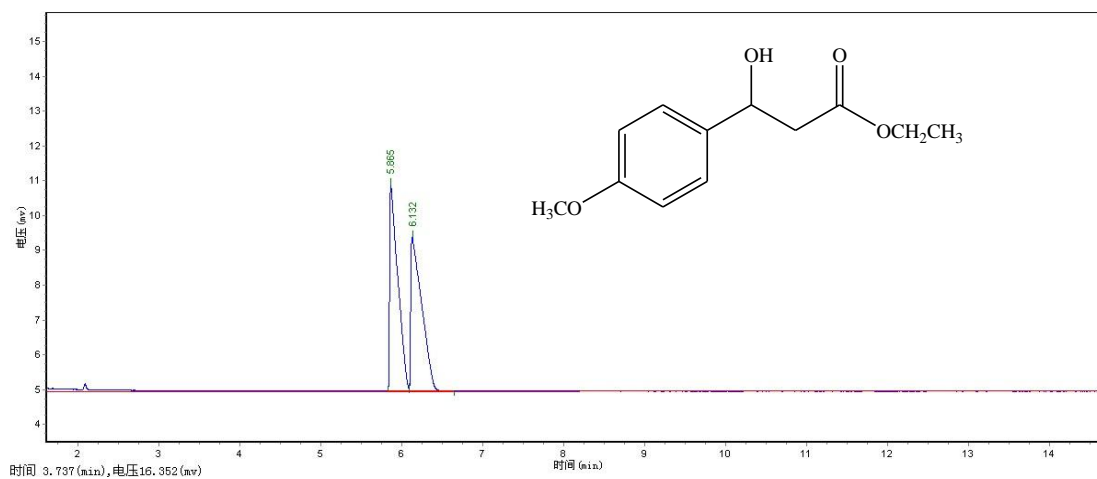


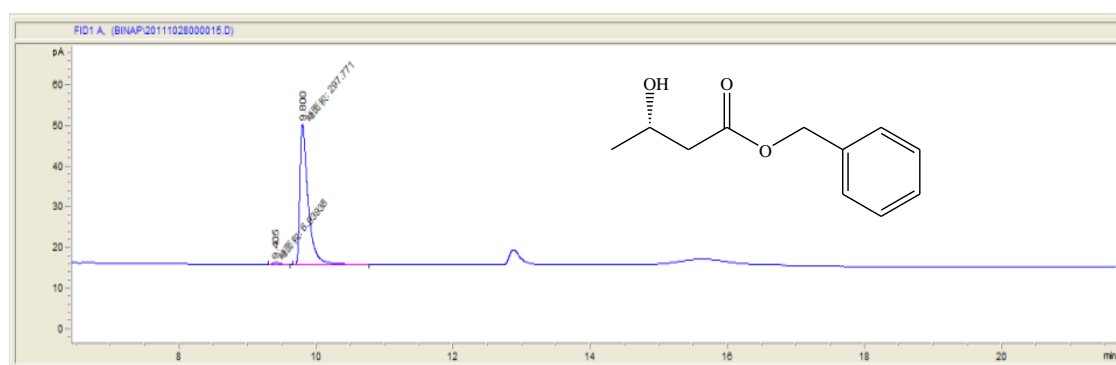
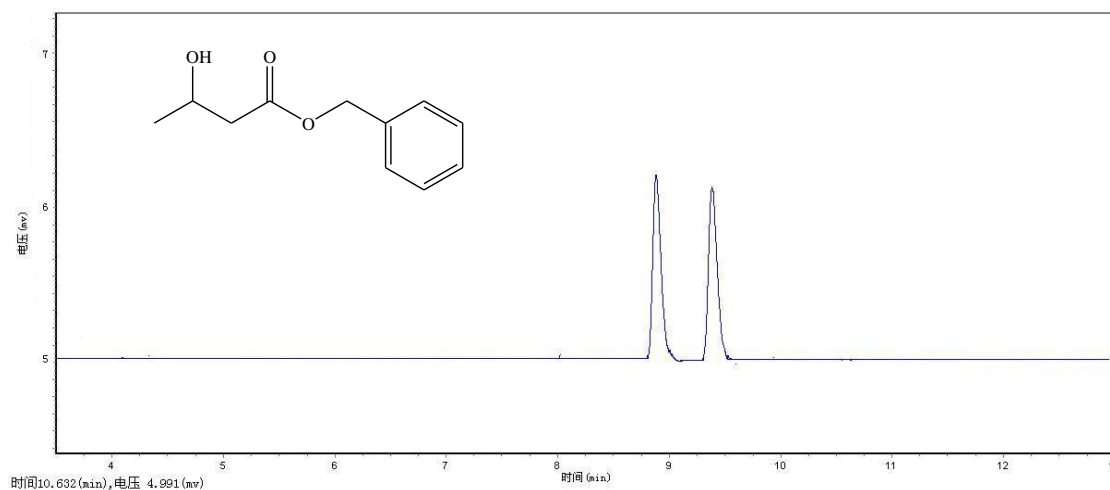












Supporting References

1. K. Jitsuo, K. Hisatoshi, F. Keiichi, S. Yasunobu, US Pat. NO 4,705,895, 1987.
2. Y. Zhang, S. Wei, Y. He, F. Nawaz, S. Liu, H. Zhang, F.-S. Xiao, *J. Mater. Chem.*, 2010, **20**, 4609-4614.
3. H.-C. Wu, J.-Q. Yu, J. B. Spencer, *Org. Lett.*, 2004, **25**, 4675-4678.