Supporting Information

Conjugated microporous polymers with chiral BINAP ligand built in as efficient catalyst on asymmetric hydrogenation

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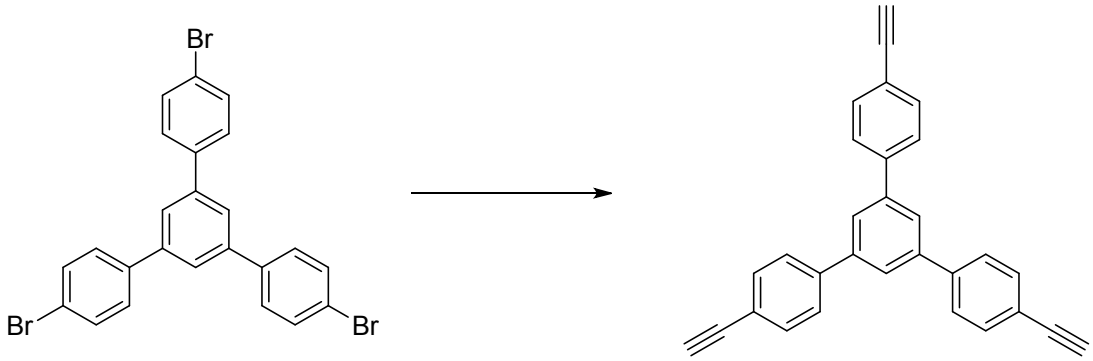
1. General information

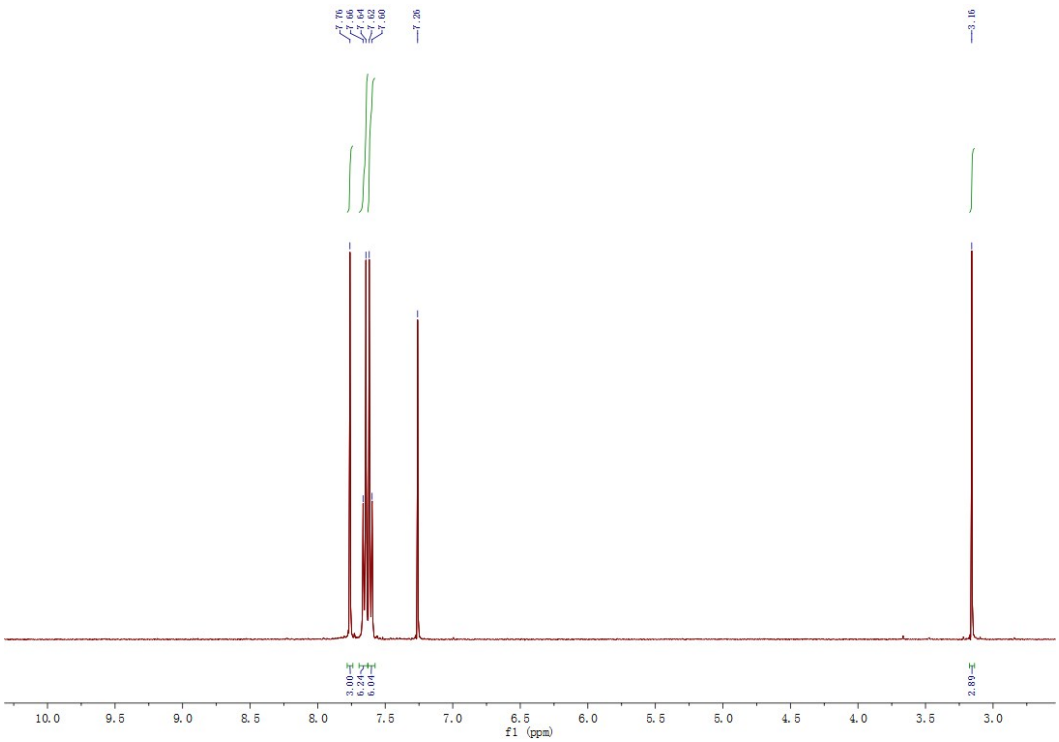
All the BINAPO-CMPs were synthesized through Sonogashira–Hagihara reaction. The raw material 1,3,5-triethynyl benzene was achieved from Acros agent, 1,3,5-Tris(4-bromophenyl)benzene ,trimethylsilylacetylene, phenylsilane, chlorotriphenylmethane, 1-bromoadamantane from JK without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer (101 MHz for ^{13}C NMR). Nitrogen sorption isotherms were measured at 77K with a AUTOSORB-1-MP analyzer. The Nonlocal Density Functional Theory (NLDFT) method was utilized to calculate the specific surface areas and the nonlocal density function theory was applied for the estimation of pore size, pore volume and pore distribution. Infrared spectra were recorded on a NEXUS 470 transform infrared spectrophotometer. TGA curves were measured on a Diamond TG/TGA analyzer. SEM image acquired on Quanta 200F analyzer.

2. Synthesis of raw materials used to build BINAPO-CMPs

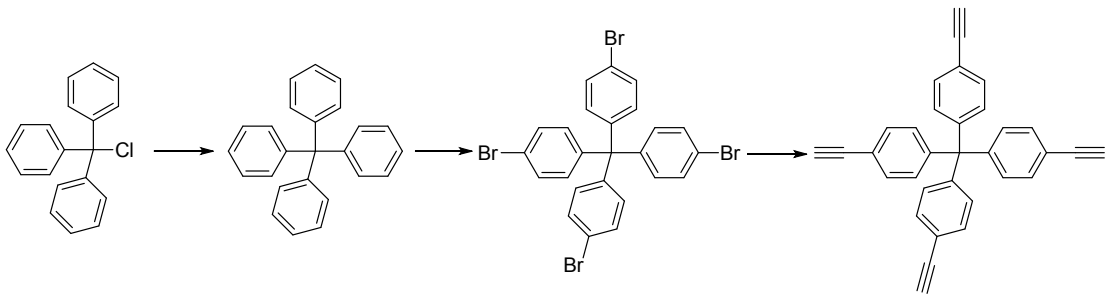
2.1 Synthesis of 1,3,5-Tris-(4-ethynyl-phenyl)-benzene)[1]



To a degassed solution of 1,3,5-Tris(4-bromophenyl)benzene (0.79 g, 1.46 mmol) in THF (50 mL) and Et_3N (50 mL) were added $Pd(PPh3)_2Cl_2$ (154 mg, 220 mol), PPh_3 (116 mg, 440 mol) and CuI (84 mg, 440 mol). Trimethylsilylacetylene (0.7 mL, 4.8 mmol) was slowly added and the reaction mixture was stirred for 5 hours at room temperature. Then the solution was partitioned between CH_2Cl_2 (300 mL) and 1 M HCl (200 mL). The organic phase was separated, washed with saturated NH_4Cl and dried over Na_2SO_4. After evaporation of CH_2Cl_2, the crude product was dissolved in THF (20 mL) and MeOH (80 mL), then K_2CO_3 (1.4 g, 10.13 mmol) was added. The reaction mixture was stirred for 3 hours. CH_2Cl_2 was added and the organic phase was washed with water, separated, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography (hexane/CH_2Cl_2; 10:3) to afford 5 (0.54 g, 85%) as colorless solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (s, 3H), 7.65 (d, J = 8.4 Hz, 6H), 7.61 (d, J = 8.4 Hz, 6H), 3.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.7,141.1, 132.7, 127.2, 125.3, 121.6, 83.4, 78.1.



2.2 Synthesis of Tetrakis(4-ethynylphenyl)methane[2]



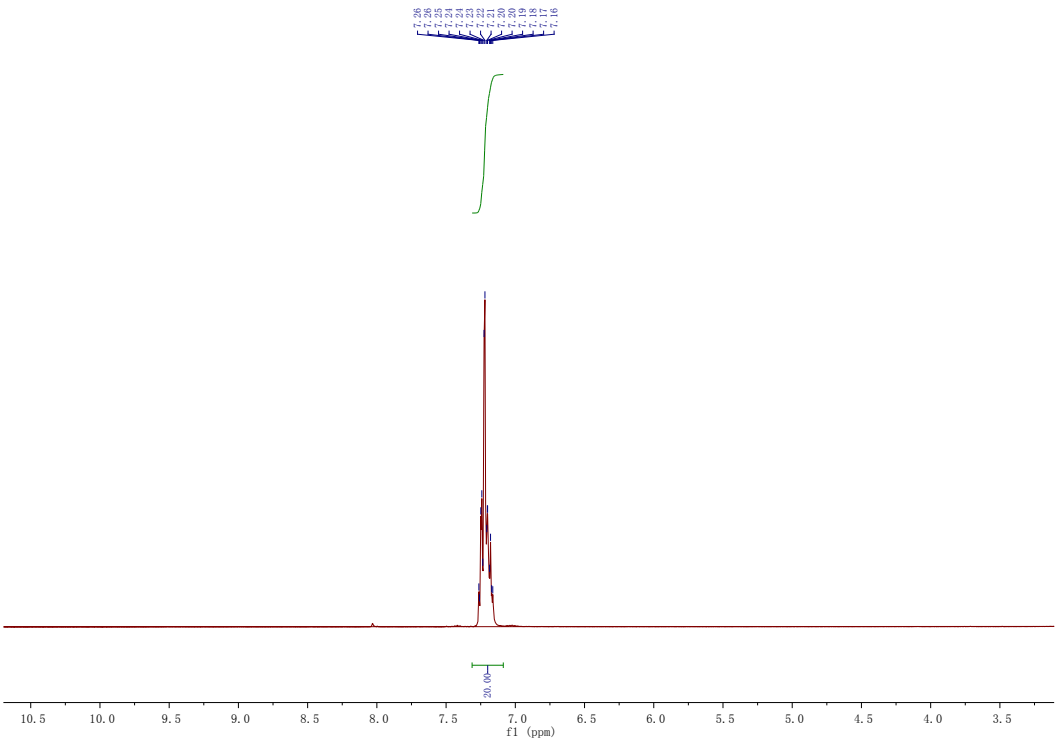
1 2 3 4

2.2.1 Tetraphenylmethane (2)

In a round bottomed flask chlorotriphenylmethane (25.0 g, 89.7 mmol, 1.0 equiv.) and aniline (22.0 mL, 22.5 g, 231.9 mmol, 2.6 equiv.) were heated at 190 °C under vigorous stirring. After 15 min, the reaction mixture was allowed to cool to room temperature. Then, a solution of aqueous HCl (2M, 100 mL) and methanol (150 mL) were added to the

pulverized solid and the reaction mixture was heated for 30 min at 80 °C. After cooling to room temperature, the resulting solid was filtered off, washed with water (250 mL) and dried in vacuo (70 °C, 16 h).

The dry solid was suspended in DMF (250 mL) and cooled to –15 °C. At this temperature sulfuric acid (96%, 27.5 mL) and isoamylnitrite (19.9 mL) were added slowly and the suspension was stirred for 1 h. After this, hypophosphorous acid (30%, 75 mL) was added dropwise. Once the addition was completed, the reaction mixture was heated at 50 °C until the evolution of gas has ceased. Then, the solid was filtered off and washed subsequently with DMF (250 mL), water (250 mL) and ethanol (250 mL). This washing procedure was repeated twice. After drying in vacuum (70 °C, 18 h), tetraphenylmethane (26.7 g, 83.3 mmol, 93%) was obtained as a brownish powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16–7.26 (m, 20 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.8, 131.1, 127.4, 125.9, 65.0.

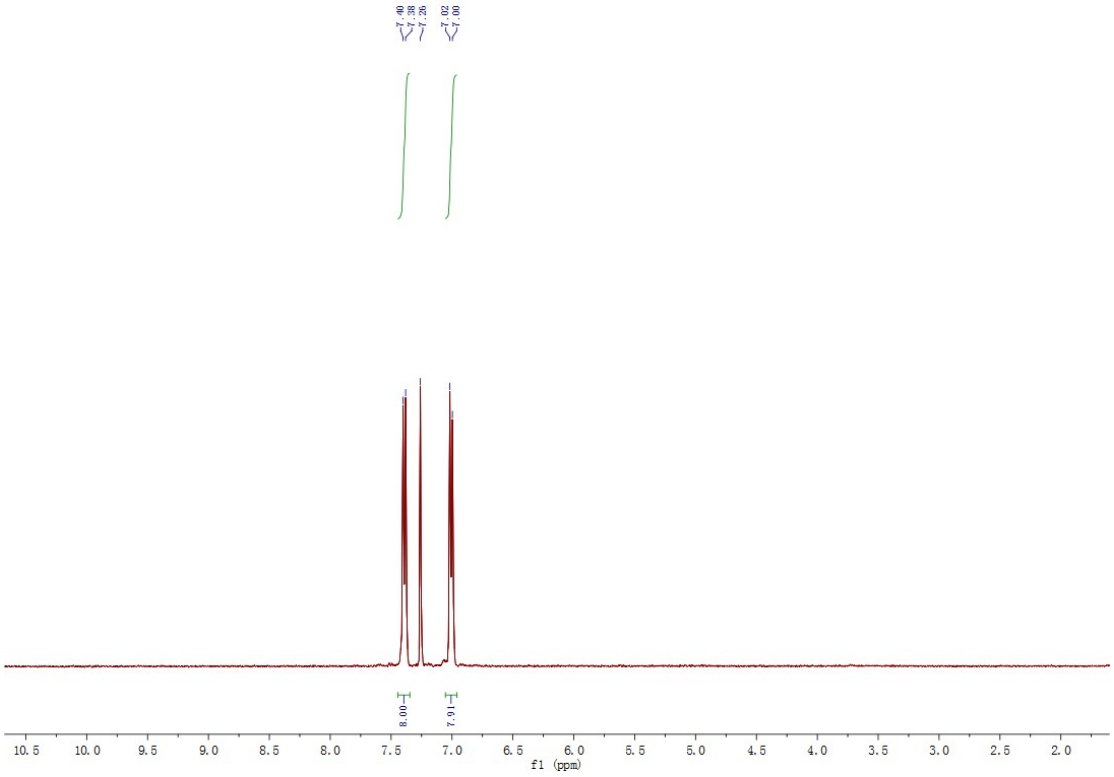


2.2.2 Tetrakis(4-bromophenyl)methane (3)

To a three necked round bottomed flask containing bromine (64.0 mL, 199 g, 1.25 mol, 20 equiv.), tetraphenylmethane (20.0 g, 62.4 mmol, 1 equiv.) was added in small portions under vigorous stirring at room temperature. After the addition was completed, the resulting solution was stirred for 20 min and then cooled down to

–78 °C. At this temperature, ethanol (150 mL) was added slowly and the formed suspension was allowed to warm to room temperature under stirring overnight. After this, the precipitate was filtered off and washed subsequently with an aqueous sodium hydrogensulfite solution (100 mL) and water (100 mL). After drying in vacuo, tetrakis(4-bromophenyl)methane (38.0 g, 59.7 mmol, 96%) was obtained as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, *J*= 8.3 Hz, 8 H),

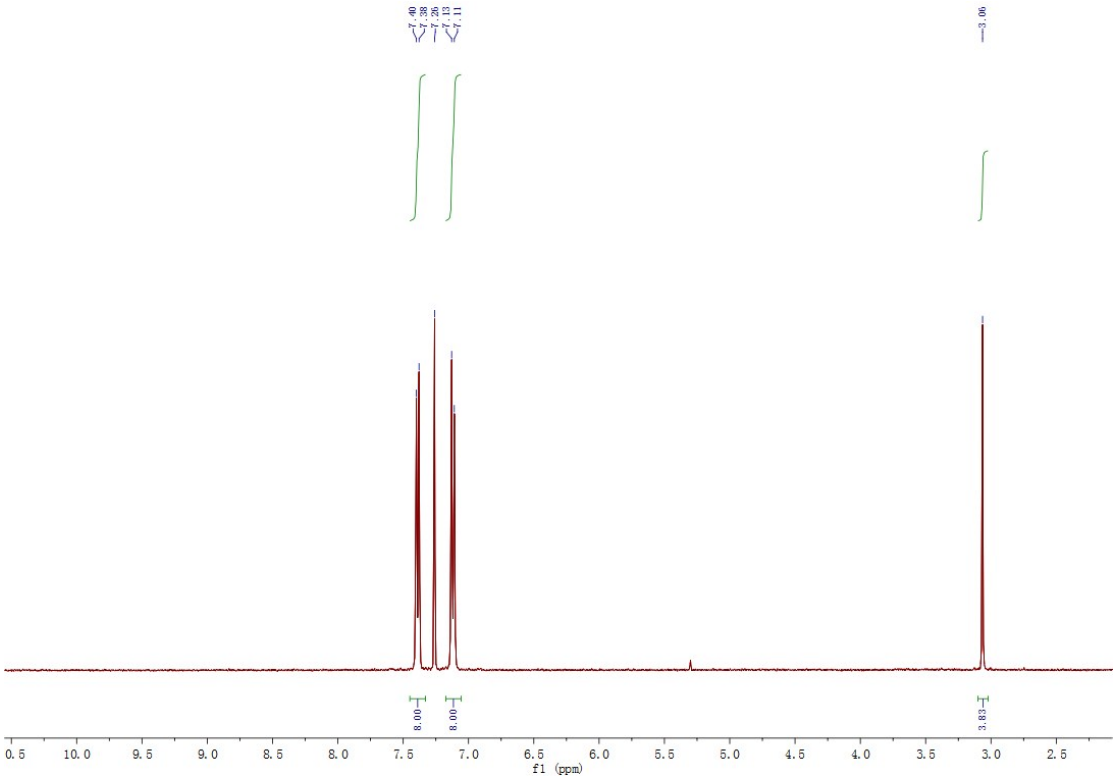
7.01 (d, *J*= 8.4 Hz, 8 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.4, 132.3, 131.1, 120.8, 63.6.



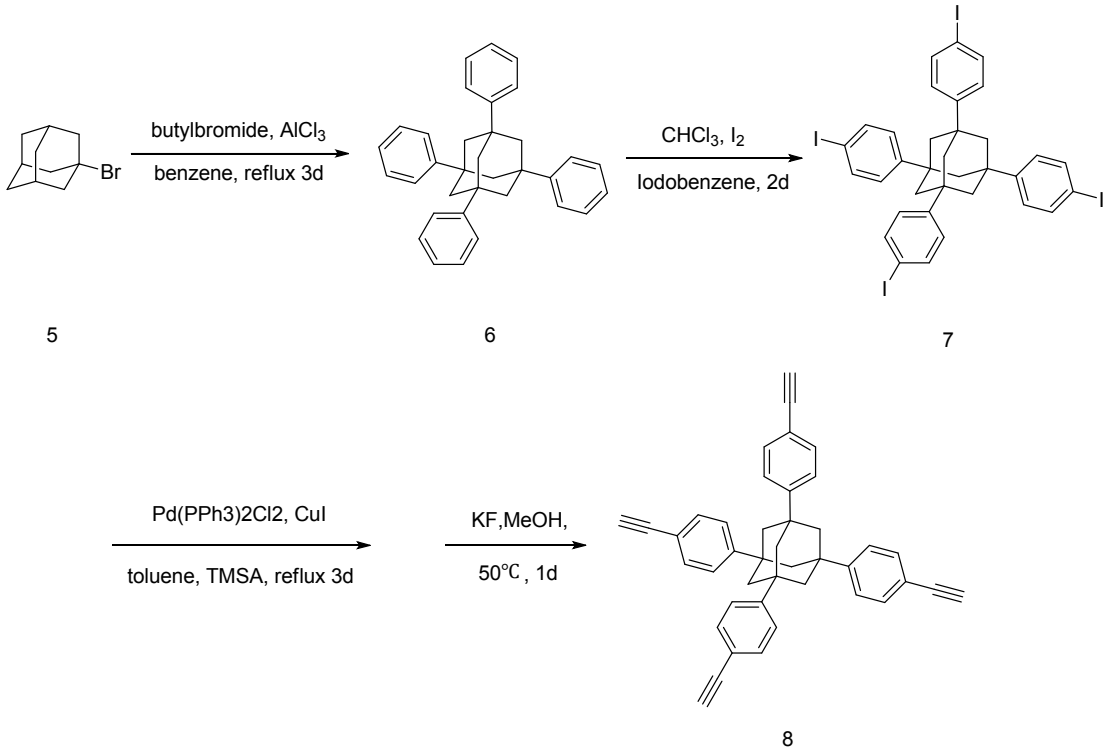
2.2.3 Tetrakis(4-ethynylphenyl)methane(4)

In a round bottomed Schlenk flask tetrakis(4-bromophenyl)methane (0.51 g, 0.82 mmol, 1.0 equiv.) was dissolved in dry benzene (3.5 mL) under argon atmosphere. To this solution, triethylamine (9.0 mL), trimethylsilylacetylene (0.7 mL, 0.48 g, 4.92 mmol, 6.0 equiv.), bis(triphenylphosphine)palladium chloride (0.03 g, 0.03 mmol, 0.04 equiv.) and copper(I)bromide (0.01 g, 0.03 mmol, 0.04 equiv.) were added subsequently. The resulting suspension was heated at 80 °C for 24 h. Then, the volatiles were removed under reduced pressure. The residue was taken up in diethylether (50 mL) and an aqueous solution of HCl

(1M, 20 mL). The organic phase was separated, washed with water (20 mL) and dried over magnesium sulfate. After removing of the solvent under reduced pressure, the crude product was deprotected without further purification. In a round bottomed flask tetrakis(4-(trimethylsilylethynyl)phenyl)methane (0.54 g, 0.75 mmol, 1.0 equiv.) was dissolved in dry benzene (10 mL) and dry acetonitrile (15 mL). To this solution a 1M solution in THF of tetrabutylammonium fluoride (4.5 mL, 4.51 mmol, 6.0 equiv.) was added and stirred for 2 h at room temperature. The reaction mixture was poured in water (25 mL). The organic phase was separated and the aqueous phase was extracted with dichloromethane (2 x 50 mL). The combined organic phases were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, pentane/toluene 1:1). The pure product was obtained (0.26 g, 0.63 mmol, 77% yield over two steps) as a yellow solid. Rf 0.30 (pentane/toluene 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.39 (d, *J*= 8.2 Hz, 8 H), 7.12 (d, *J*= 8.2 Hz, 8 H), 3.06 (s, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.2, 131.6, 130.7, 120.3, 83.1, 81.5, 64.8.



2.3 Synthesis of 1,3,5,7-Tetrakis(4-ethynylphenyl) adamantine(8)[3]



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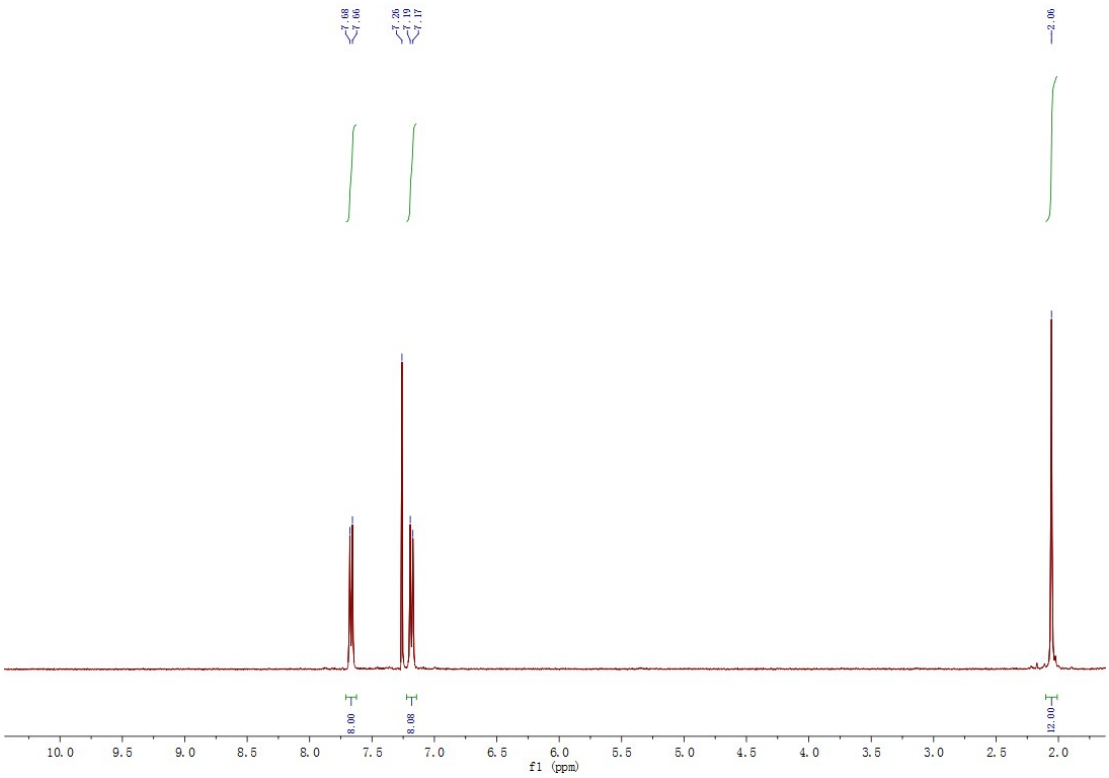
2.3.1 1,3,5,7-Tetrakisphenyladamantane(6)

1-Bromoadamantane (6.00 g, 27.9 mmol, 1.0 equiv.) was dissolved in benzene (60 mL) under argon atmosphere. t-Butylbromide (6.30 mL, 55.8 mmol, 2 equiv.) and $AlCl_3$ (320 mg, 2.40 mmol, 0.1 equiv.) was added to the suspension which was heated under reflux for 2 h. The reaction mixture was cooled to room temperature; the solid was filtered off and washed with chloroform (50 mL), water (30 mL) and chloroform (50 mL). The product was dried under reduced pressure (8.15 g, 18.5 mmol, 66%).

2.3.2 1,3,5,7-Tetrakis(4-iodophenyl)adamantane (7)

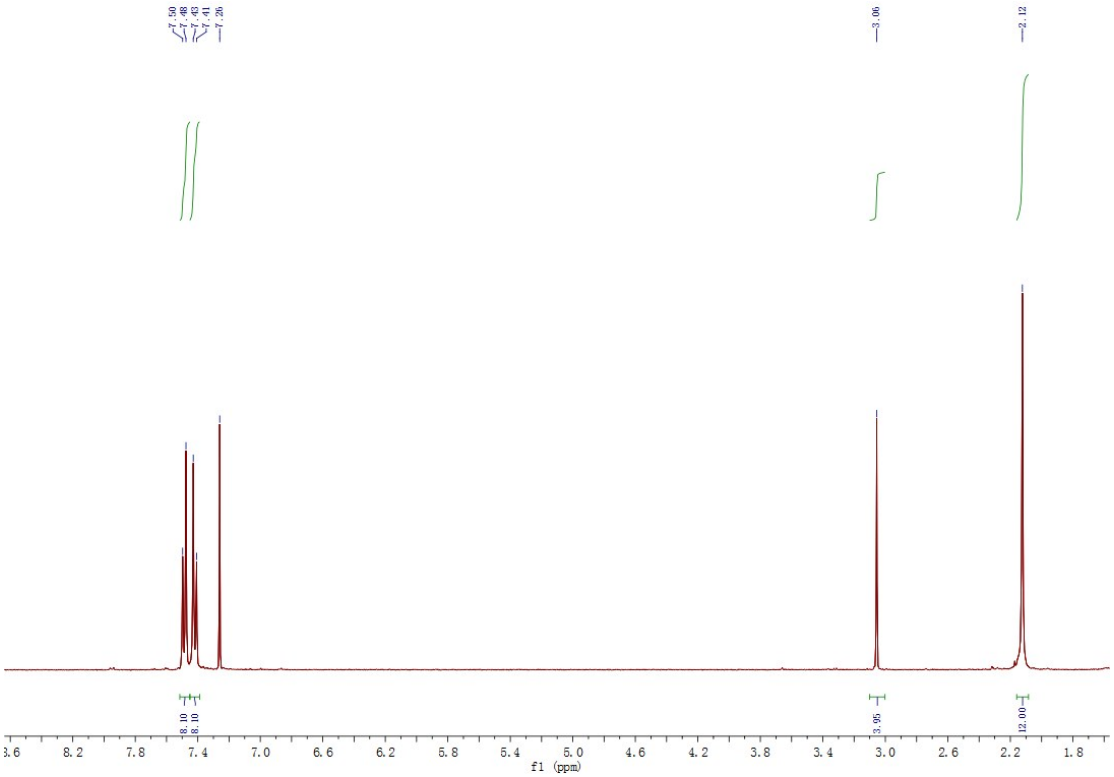
Iodine (2.36 g, 9.06 mmol, 2.0 equiv.) was added to a suspension of 1,3,5,7-tetraphenyladamantan (2.00 g, 4.54mmol, 1.0 equiv.) in chloroform (50 mL) and stirred until the iodine had dissolved. Then, (bis(trifluoroacetoxy)iodo)benzene (3.90 g, 9.06 mmol, 2.0 equiv.) was added an the suspension was stirred for 24 h at room temperature. The mixture was filtered to remove a purple solid. The organic layer was washed with a NaHSO3-solution (5%, 50 mL), water (50 mL), brine (50 mL) and dried over $MgSO_4$. The product was crystallized in a chloroform/methanol mixture (9:1) to isolate colorless crystals of 1,3,5,7-tetrakis(4-iodophenyl)- adamantane (1.90 g, 2.01 mmol, 44%). Rf 0.31 (cyclohexane/CH2Cl2, 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.67 (d, *J*= 8.4 Hz, 8 H), 7.18 (d, *J*= 8.4 Hz 8 H), 2.06 (s, 12 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 148.4, 137.5, 127.1, 91.7, 46.7, 39.1.



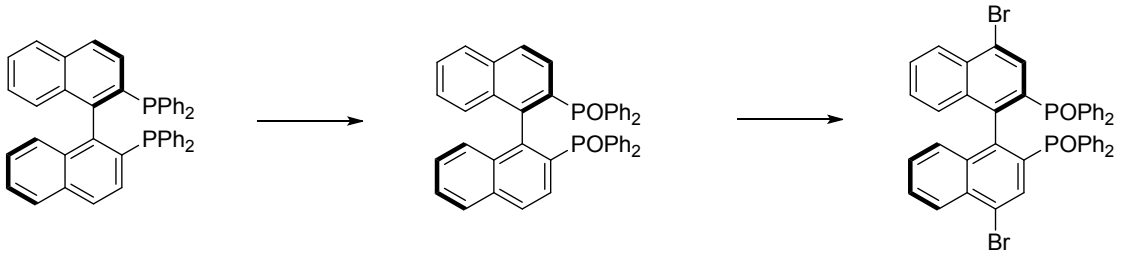
2.3.3 1,3,5,7-Tetrakis(4-ethynylphenyl)adamantine(8)

1,3,5,7-Tetrakis(4-iodophenyl)adamantane (7) (4.00 g, 4.25 mmol, 1.0 equiv.) was dissolved in dry toluene (83 mL) and dry Et3N (35 mL) was added under argon atmosphere. The flask was degassed several times after the addition of trimethylsilylacetylene (12.7 mL, 8.75 g, 89.2 mmol, 21equiv.), then $Pd(PPh3)_2Cl_2$ (213 mg, 0.3 mmol, 7 mol%) and CuI (57 mg, 0.3 mmol, 7 mol%) were added and the reaction became black within minutes. The mixture was stirred under reflux for 72 h, cooled to room temperature and the solvent removed under reduced pressure. The residue was then taken-up in chloroform (200 mL), washed with an aqueous solution of HCl (10%), water and dried over $MgSO_4$. The crude 1,3,5,7-tetrakis(4-trimethylsilyl-ethynylphenyl)adamantane was used for the next reaction (deprotection) without further purification. KF (2.47 g, 42.5

mmol, 10 equiv.) was added to a suspension of the silylated product (3.50 g, 4.25 mmol) in methanol (60 mL) and stirred overnight at 50 °C. The reaction mixture was poured into water (60 mL), extracted with chloroform (100 mL), washed with water (2 × 100 mL) and brine (2 × 100 mL). The organic layer was dried over $MgSO_4$. 1,3,5,7-Tetrakis(4-ethynylphenyl)adamantane (1.68 g, 74% yield over two steps) was isolated as a white solid after purification by flash chromatography on silica gel using cyclohexane/CH_2Cl_2 (gradient 2:1–1:1) as eluent. Rf 0.27 (cyclohexane/ CH_2Cl_2 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.49 (d, *J* = 8.5 Hz, 8H), 7.42 (d, *J* = 8.6 Hz, 8H), 3.06 (s, 4H), 2.12 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 149.6, 132.2, 125.0, 120.1, 83.5, 76.7, 46.7, 39.3.



2.4 (R)-4,4-DibromoBINAPO[4]



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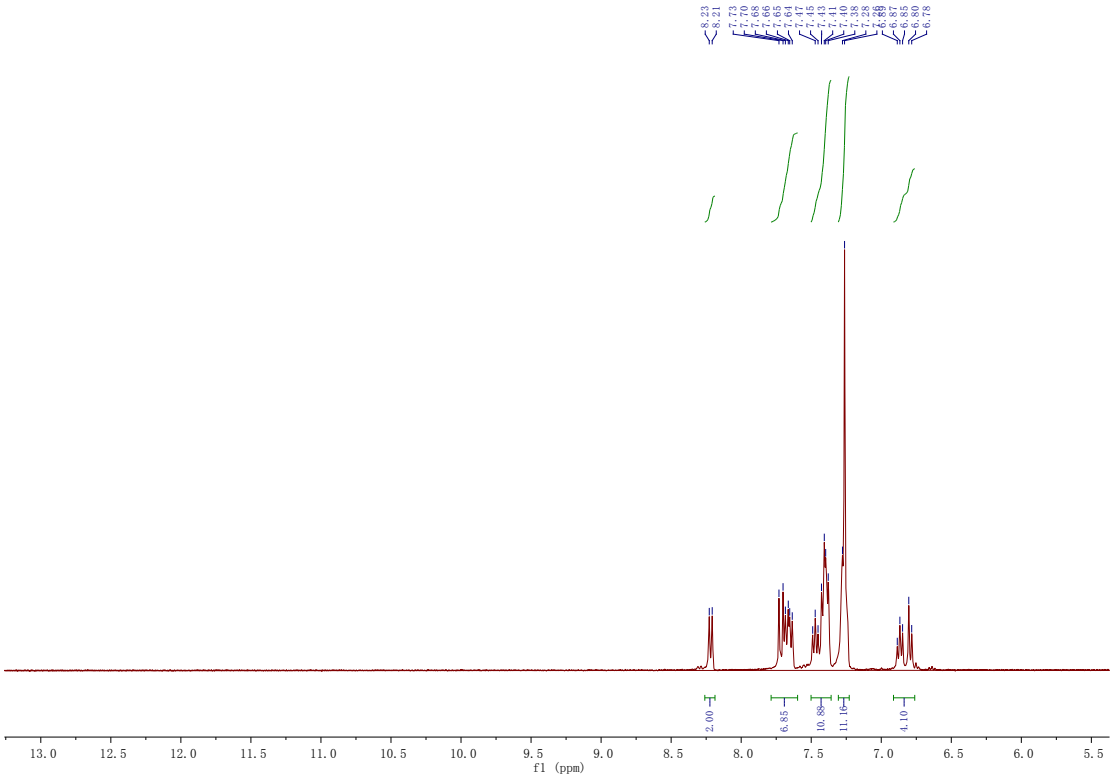
2.4.1(R)- BINAPO

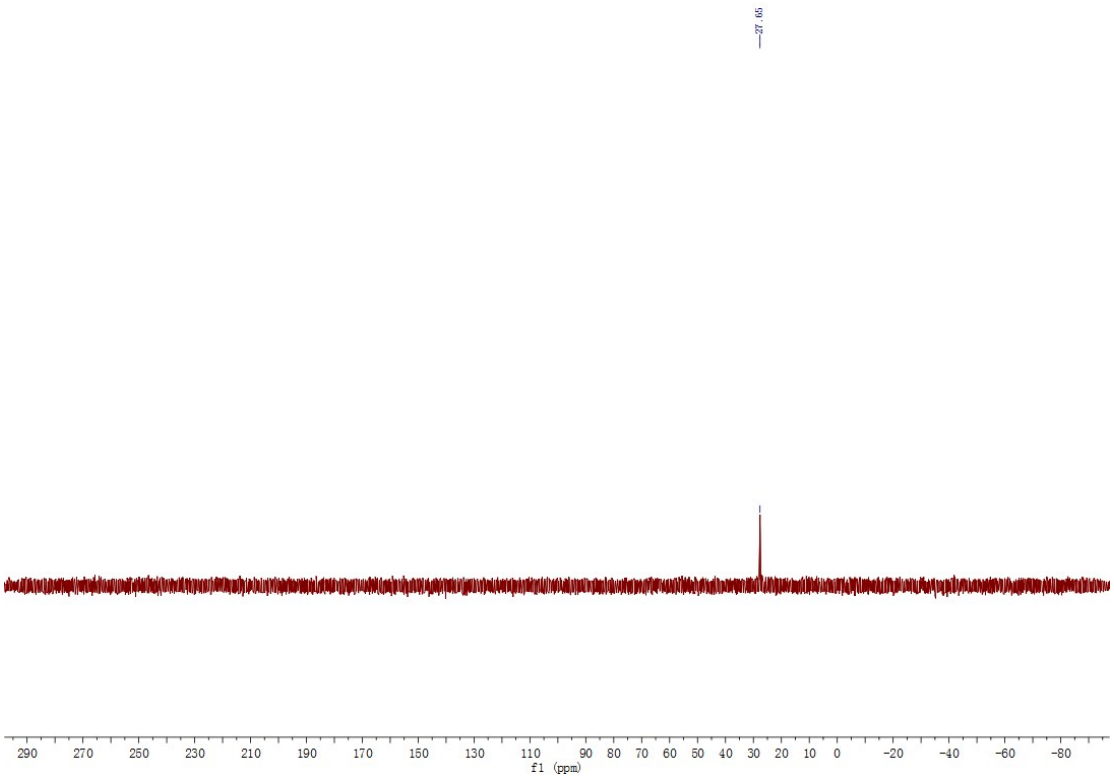
In a 250mL round-bottomed flask were placed either (R)-BINAP (5.6 g, 9mmol) and 100mL of CH_2Cl_2. The mixture was cooled to 0℃ and 10mL of hydrogen peroxide (35%) then added. The mixture was stirred for 4 h. Then 100mL of water was added. Aqueous phases were extracted with 50mL of CH_2Cl_2. The organics phases were washed with 50mL of aqueous sodium hydrogen sulfite solution, dried over Na_2SO_4 and evaporated to obtained a white solid(5.9 g, 9mmol, quantitative yield). ^1H NMR (400MHz, $CDCl_3$) δ= 7.8–7.9 (m, 4H), 7.6–7.7 (m, 4H), 7.3–7.5 (m, 12H), 7.2–7.3 (m, 8H), 6.80 (d, 4H).

2.4.2 (R)-4,4-DibromoBINAPO

To a 250 mL round bottom flask was added (R)-BINAPO(5.9g, 9 mmol), anhydrous CH_2Cl_2 (135 mL) and pyridine (0.9 mL, 9 mmol). With vigorous stirring, Bromine (1.8 mL, 35 mmol) was carefully added via a syringe. After stirring at room temperature for 20h, 1M aqueous sodium bisulfite was carefully added. This mixture was stirred for one hour until the organic layer turn from dark red to light yellow. The

organic layer was separated and washed three times with brine, dried over anhydrous magnesium sulfate. After all volatile component were removed, the product was obtained as light brown solid. This bromination procedure was repeated three times and the crude products were used as starting materials, giving 6.6g light brown solid product. ^{1}H NMR (400MHz, $CDCl_3$) δ= 8.22 (d, 4H), 7.64–7.73 (m, 6H), 7.38–7.49 (m, 10H), 7.20–7.30 (m, 8H), 6.78-6.89 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 141.9, 141.8, 134.4, 134.3, 134.0, 132.9, 132.6, 132.5, 132.3, 132.0, 131.9, 131.6, 131.5, 131.4, 131.2, 129.9, 128.6, 128.3, 128.1, 128.0, 127.4, 127.1, 126.7, 123.1, 122.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ= 27.65(s).





3. Synthesis of BINAPO-CMPs and deoxygenated procedure

The BINAPO-CMPs Networks were synthesized at a fixed overall solvent volume of 10 mL, a fixed reaction temperature of 80 °C, and a constant molar ratio of ethynyl to halogen functionalities of 1.5 : 1.

3.1 BINAPO-CMP-S

1,3,5-triethynylbenzene (75 mg, 0.5 mmol), (R)-4,4-DibromoBINAPO (406 mg, 0.5 mmol), tetrakis-(triphenylphosphine)palladium (23 mg), and copper iodide (16 mg) were dissolved in the mixture of dioxane (8 ml) and Et_3N (2 ml). The reaction mixture was heated to 80 °C, stirred for 72 h under a nitrogen atmosphere in order to rigorously exclude oxygen and to prevent homocoupling of the alkyne monomers.

The mixture was cooled to room temperature and the precipitated

network polymer was filtered and washed four times with chloroform, water, methanol, and acetone to remove any

unreacted monomer or catalyst residues. The further purification of the polymers was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 50 °C. (Yield, 53 %)

3.2 BINAPO-CMP -M

This network was synthesized by the same method as CMP-S. 1,3,5-Tris-(4-ethynyl-phenyl)-benzene) (150 mg, 0.4 mmol), (R)-4,4-DibromoBINAPO (325 mg, 0.4 mmol), tetrakis-(triphenylphosphine)palladium (23 mg), and copper iodide (16 mg) were dissolved in the mixture of dioxane (8 ml) and Et_3N (2 ml) were used in this case.(Yield, 70 %)

3.3 BINAPO-CMP -3D-1

This network was synthesized from Tetrakis(4-ethynylphenyl)-methane (160 mg, 0.375 mmol), (R)-4,4-DibromoBINAPO (406 mg, 0.5 mmol), tetrakis-(triphenylphosphine)palladium (23 mg), and copper iodide (16 mg) were dissolved in the mixture of THF (8 ml) and Et_3N (2 ml).(Yield, 88 %)

3.4 BINAPO-CMP -3D-2

1,3,5,7-Tetrakis(4-ethynylphenyl) adamantine (204 mg, 0.375 mmol), (R)-4,4-DibromoBINAPO (406 mg, 0.5 mmol), tetrakis-(triphenylphosphine)palladium (23 mg), and copper iodide (16 mg) were

dissolved in the mixture of dioxane (8 ml) and Et_3N (2 ml).(Yield, 99 %)

3.5 Deoxygenated procedure of the synthesized BINAPO-CMPs

The experiments were taken out using the Schlenk technique. As a typical run, 0.3 g of BINAPO-CMPs was suspended in 40 mL of dry toluene containing 1 mL of $HSiCl_3$, then 1g of triphenylphosphine used as oxygen acceptor was added. After that, with further addition of $HSiCl_3$ (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 toulene and CH_2Cl_2

yielded a yellow-brown powder.

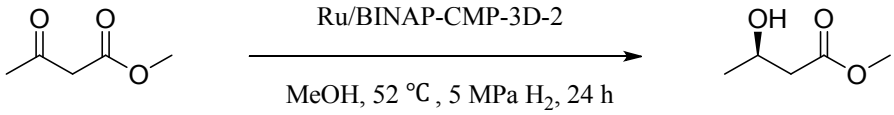
4. Asymmetric hydrogenation of β-keto esters and recycling experiments

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 BINAPO-CMPs(with BINAP/Ru 2:1) and dichloro(benzene) ruthenium(II)dimmer (1.25 mg, 0.0025 mmol) were added to anhydrous methanol in a test tube and stirred for 3 h at room temperature, then desired amount of substrates(5 mmol) was added. After that, the test tube was transferred into a stainless steel autoclave, sealed, and purged with H_2 for 4 times. Finally, the pressure of H_2 was adjusted to 5 MPa and the

autoclave was placed to a preheated 52℃ water bath, stirred for 24 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 methanol (5×5mL) under N_2 and dried under vacuum (using standard Schlenk-type techniques), after that the catalyst was used directly for the next catalytic reaction. According to ICP examination, no Ru element was found in the reaction solution after the hydrogenation reaction.

Table S1. Recycling experiment of β-keto esters catalyzed by Ru/BINAP-CMP-3D-2 catalyst [a]



Recycle	Conversion (%)[b]	E.e. (%)[b]
0	99	94
1	99	93
2	99	92
3	99	90
4	77	82

[a] Reaction conditions: 5 mmol of β-keto esters in 2 mL of MeOH, 0.0025 mmol [Ru(benzene)Cl2]2, 5 MPa H_2, 52°C for 24 h; [b] The conversion and *ee* values were determined by GC on a Supelco γ-DEX 225 capillary column;

5. General procedure for the asymmetric hydrogenation of

quinaldine

A mixture of [Ir(COD)Cl]2(0.85 mg, 0.00125 mmol) and BINAP-CMP-3D-2 (5.95 mg, 0.005 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 3 h in glovebox, the mixture was then transferred to a stainless steel autoclave, in which I_2(3.2 mg, 0.0125 mmol) and quinaldine (36 mg, 0.25 mmol) were charged beforehand. The hydrogenation was performed at room temperature under H_2(4 MPa) for 2 h. After carefully releasing of the hydrogen, the reaction mixture was diluted with dichloromethane (5 mL) and saturated sodium carbonate aqueous solution (2 mL), then stirred for 15 min and separated. The aqueous layer was extracted with dichloromethane (3 x 5 mL),and the combined organic layer was dried over sodium sulfate and concentrated to afford the crude product. Purification was performed by a silica gel column eluted with petroleum ether / dichloromethane to give pure product. The enantiomeric excesses were determined by chiral HPLC with OJ-H chiral columns (hexanes: *i*-PrOH 95: 5 at 0.5 mL / min 254nm).

6. BET data of the BINAPO/BINAP-CMPs

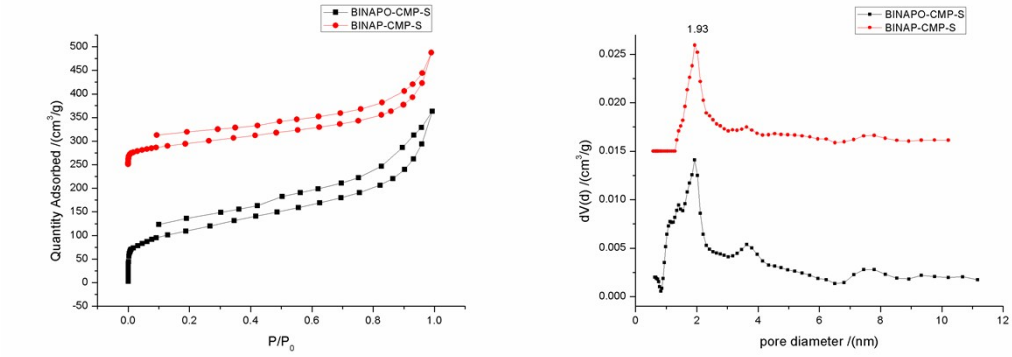


Fig. S1 (**left**) Nitrogen adsorption isotherms measured at 77 K of the BINAPO-CMP-S. (**right**) Pore size distribution (PSD) for the BINAPO-CMP-S, calculated with non-local density functional theory (NLDFT)

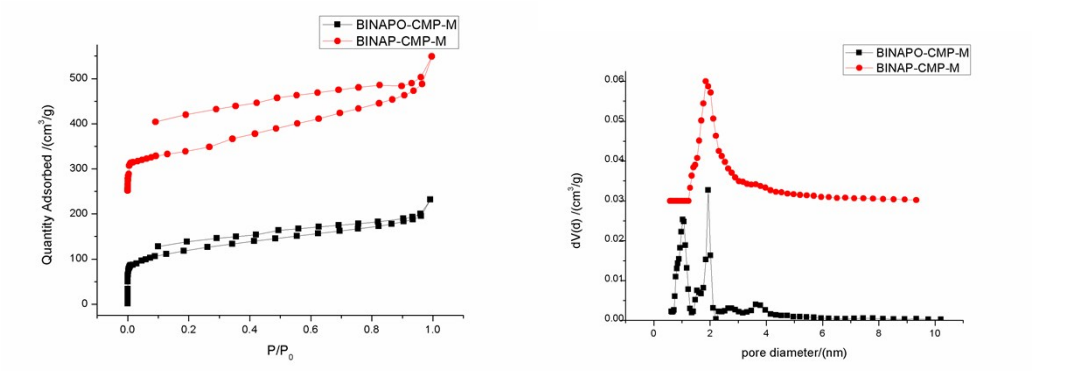


Fig. S2 (**left**) Nitrogen adsorption isotherms measured at 77 K of the BINAPO-CMP-M. (**right**) Pore size distribution (PSD) for the BINAPO-CMP-M, calculated with non-local density functional theory (NLDFT)

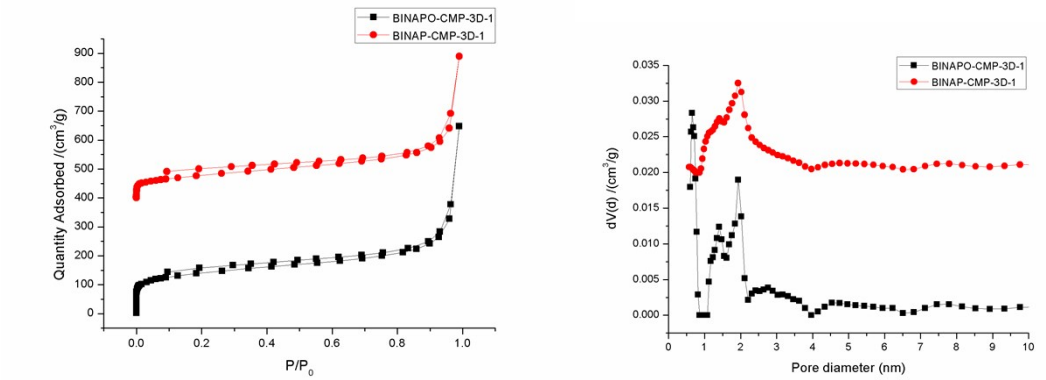


Fig. S3 (**left**) Nitrogen adsorption isotherms measured at 77 K of the BINAPO-CMP-3D-1. (**right**) Pore size distribution (PSD) for the BINAPO-CMP-3D-1, calculated with non-local density functional theory (NLDFT)

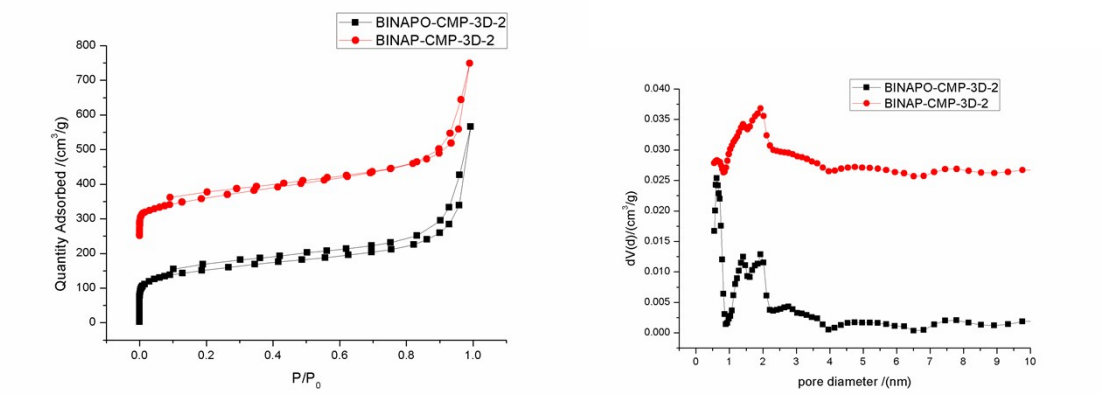


Fig. S4 (**left**) Nitrogen adsorption isotherms measured at 77 K of the BINAPO-CMP-3D-2. (**right**) Pore size distribution (PSD) for the BINAPO-CMP-3D-2, calculated with non-local density functional theory (NLDFT)

Table S2. Surface properties and gas uptake for CMPs before and after reduction

polymer	S_{BET}[a] (m^2/g)	S_{micro}[b] (m^2/g)	V_{total}[c] (cm^3/g)	V_{micro}[b] (cm^3/g)
BINAPO-CMP-S	391	146	0.56	0.07
BINAP-CMP -S	170	21	0.37	0.01
BIANPO-CMP -M	407	261	0.36	0.13
BINAP-CMP -M	318	175	0.46	0.02
BINAPO-CMP -3D-1	474	298	1.00	0.15
BINAP-CMP -3D-1	279	104	0.76	0.05
BINAPO-CMP -3D-2	509	334	0.88	0.17
BINAP-CMP -3D-2	398	137	0.77	0.07
Ru/BINAP-CMP-3D-2[d]	329	139	1.18	0.09

Ru/BINAP-CMP-3D-2[e]	301	131	1.16	0.09

[a] Surface area calculated from the N_2 adsorption isotherm using the Brunauer–Emmett–Teller method. [b] Micropore surface area and micropore volume calculated using the t-plot method based on the Halsey thickness equation.[c] Total pore volume at P/P0 = 0.99.[d] The in situ formed Ru/BINAP-CMP-3D-2; [e] After 3 times recycle experiment.

7.TGA analysis

As shown in the TGA test, all the synthesized CCMPs were stable under 300℃.

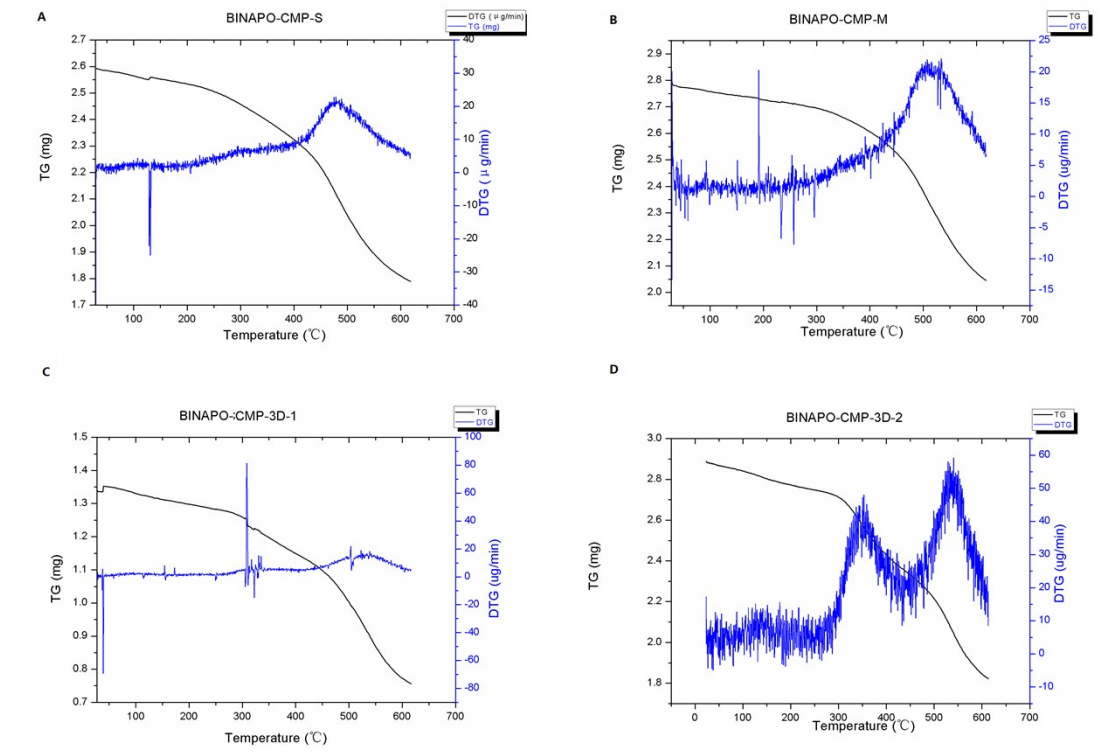


Fig. S5 TGA data of (**A**) BINAPO-CMP-S (**B**) BINAPO-CMP-M (**C**) BINAPO-CMP-3D-1 (**D**) BINAPO-CMP-3D-2

8. SEM image of the BINAPO-CMPs

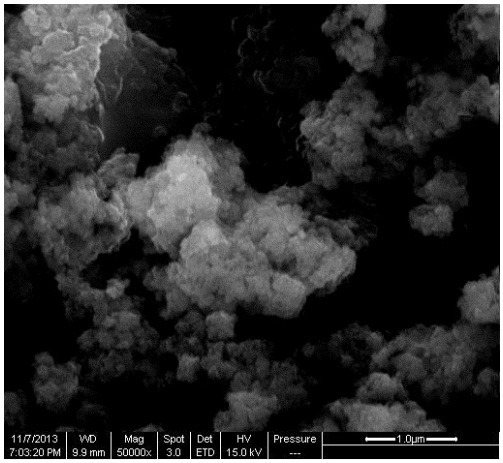


Fig. S6 SEM image of BINAPO-CMP-S

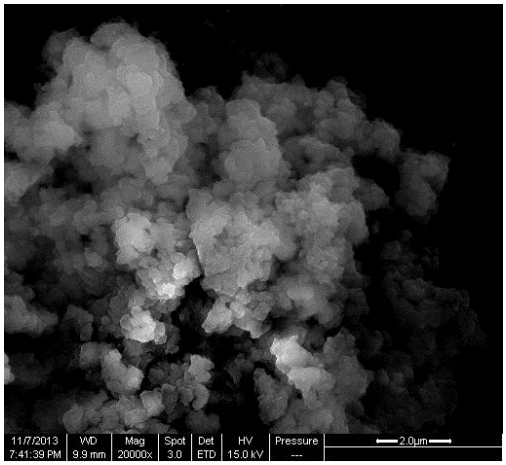


Fig. S7 SEM image of BINAPO-CMP-S

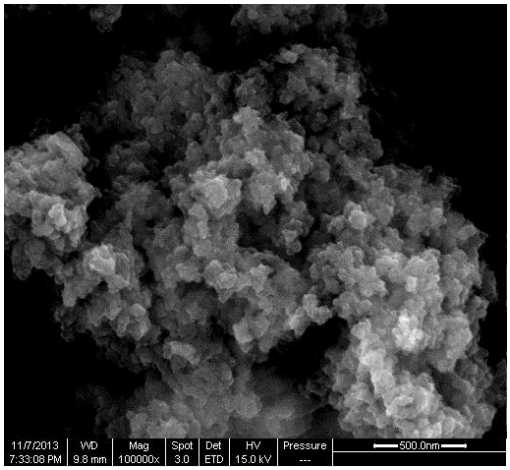


Fig. S8 SEM image of BINAPO-CMP-3D-1

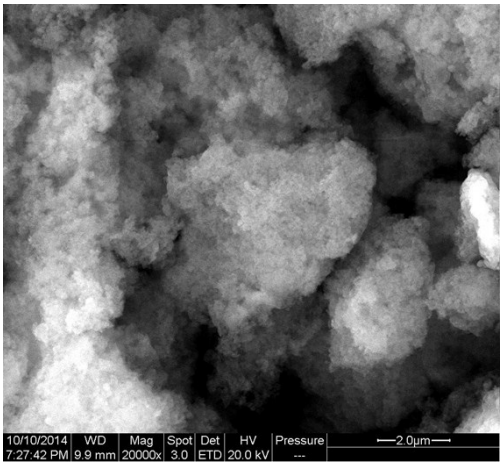


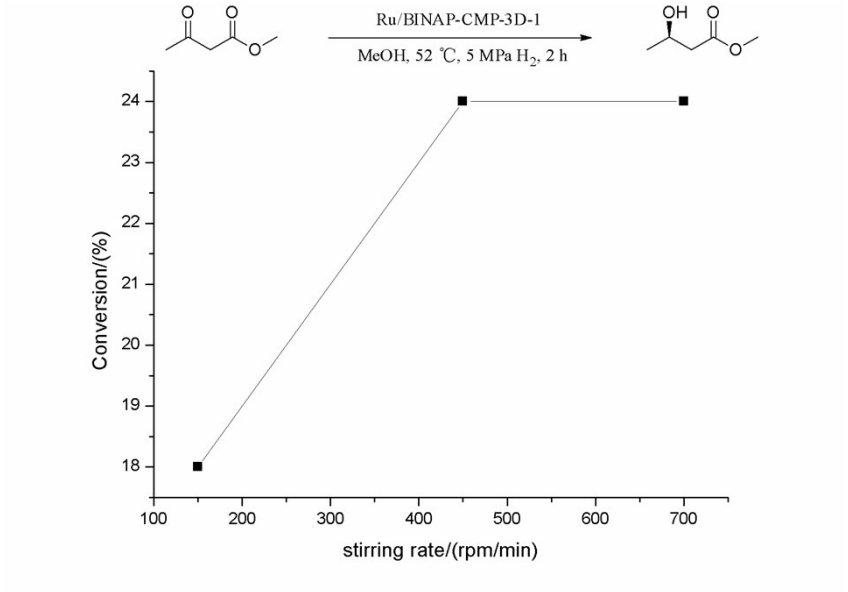
Fig. S9 SEM image of BINAPO-CMP-3D-2

9. Elemental Analysis

BINAPO-CMP-S: C 72.69%, H 3.47%, P 4.01%;
BINAPO-CMP-M: C 78.8%, H 5.27%, P 2.45%;
BINAPO-CMP-3D-1: C 82.20%, H 4.55%, P 4.66%
BINAPO-CMP-3D-2: C 85.57%, H 5.28%, P 5.21%

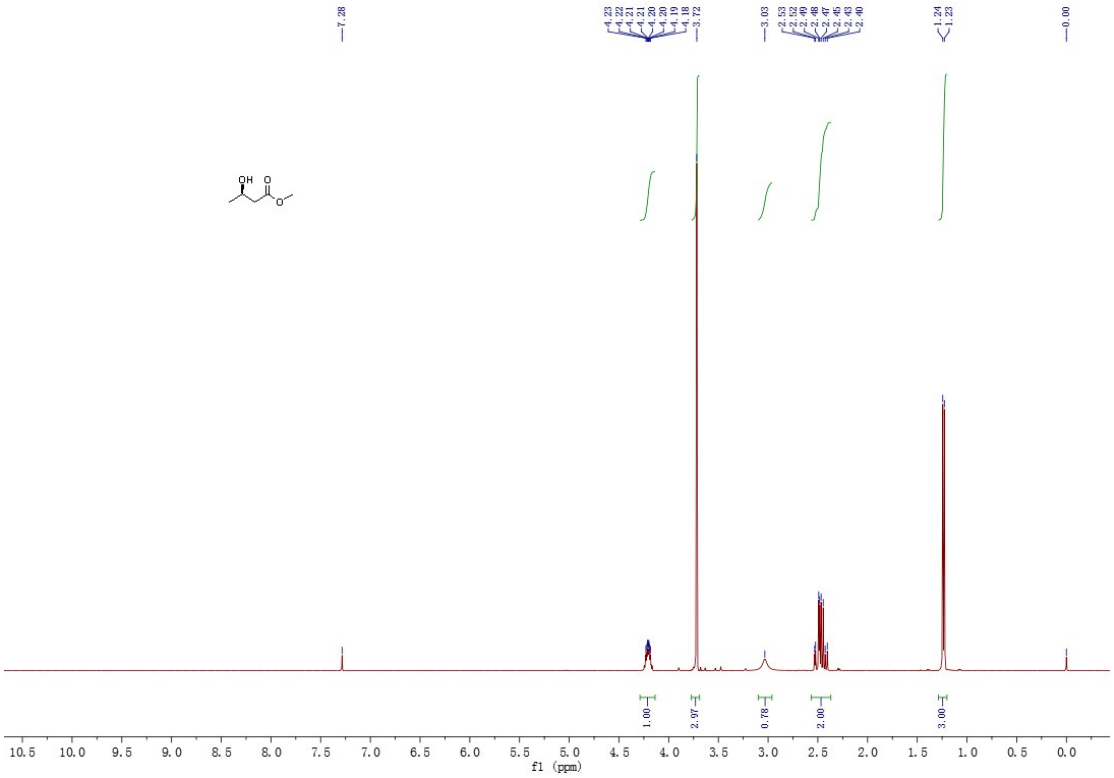
10. Stirring rate effect:

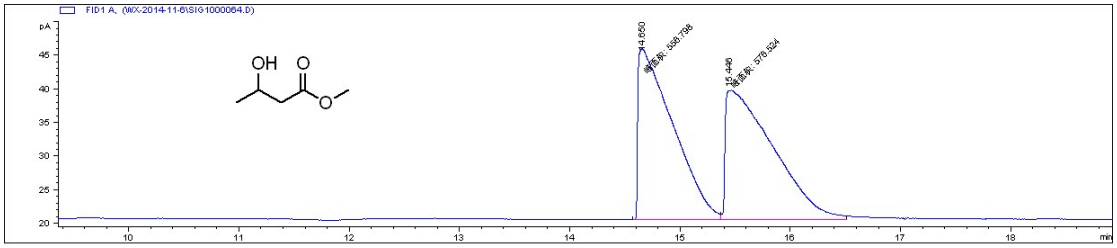
Three sample were examined with the same reaction conditions except for the stirring rate.

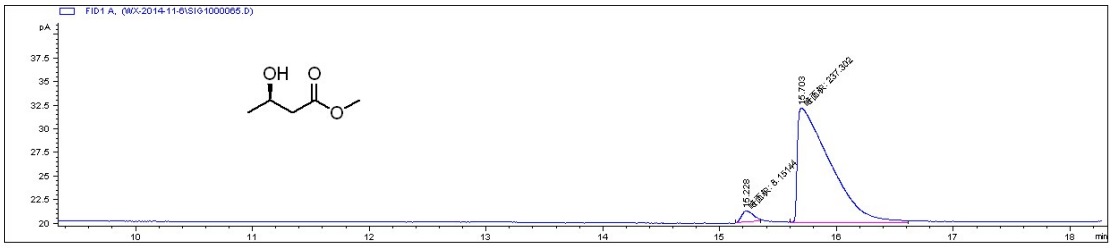


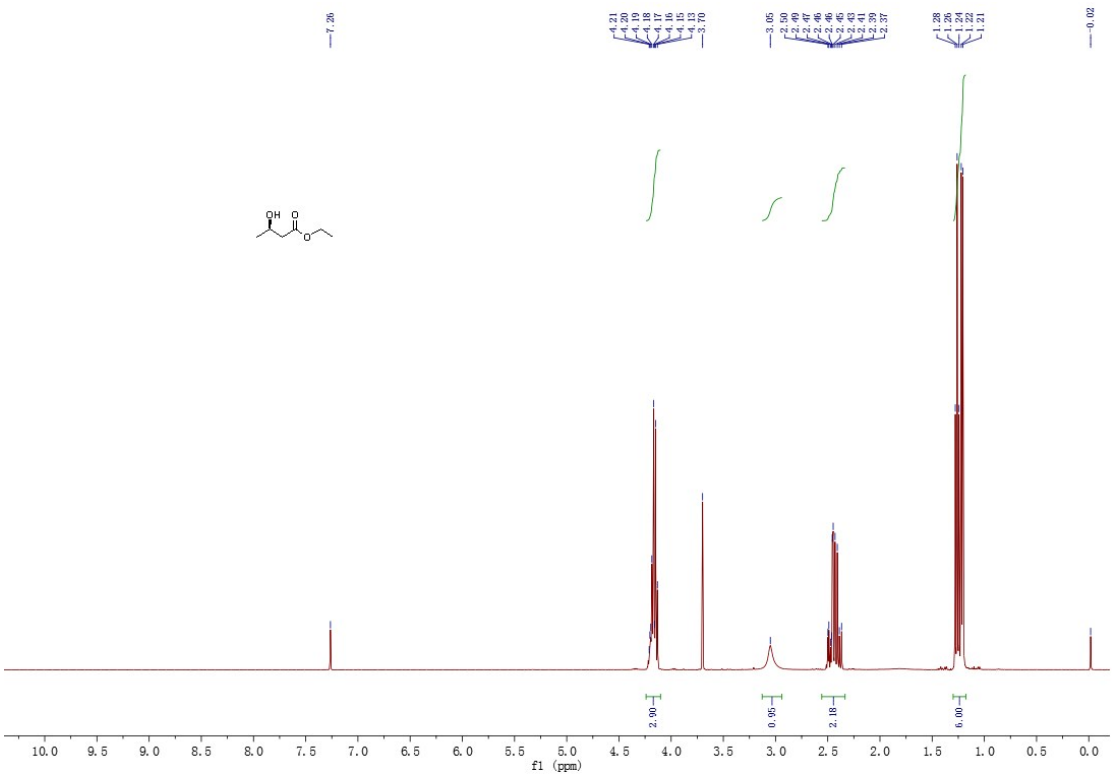
As shown in the figure, After reaction for 2 hours, when the stirring rate is lower than 450 rpm/min, the conversion increases with the accelerating of stirring rate ; When the stirring rate is over 450 rpm/min, the conversion does not changed significantly. So we choose to carry out the reaction under the stirring rate of 450 rpm/min to reduce the influence of diffusion.

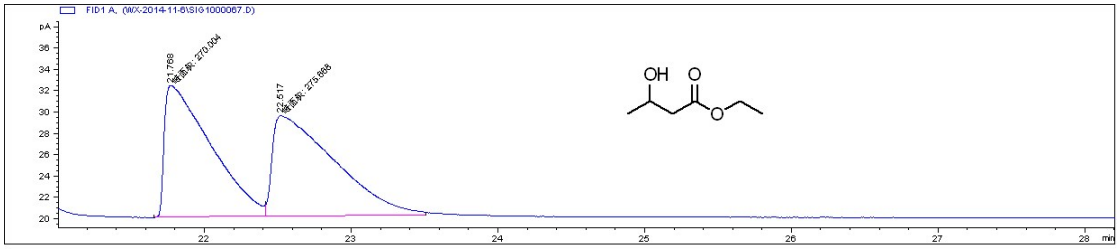
11.GC

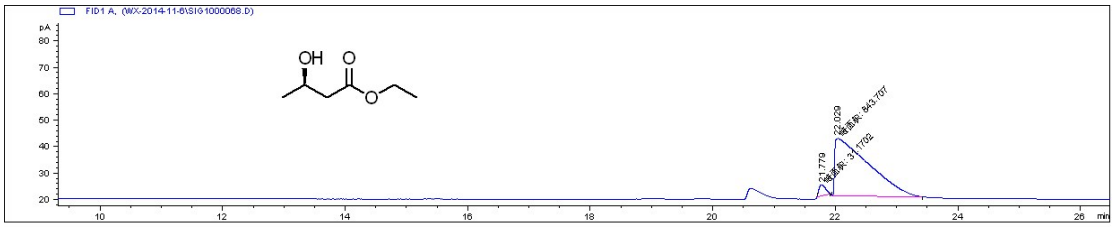

7.28
4.23
4.22
4.21
4.20
4.19
4.18
3.72
3.03
2.53
2.52
2.49
2.48
2.47
2.45
2.43
2.40
1.24
1.23
0.00
1.00
2.97
0.78
2.00
3.00
f1 (ppm)

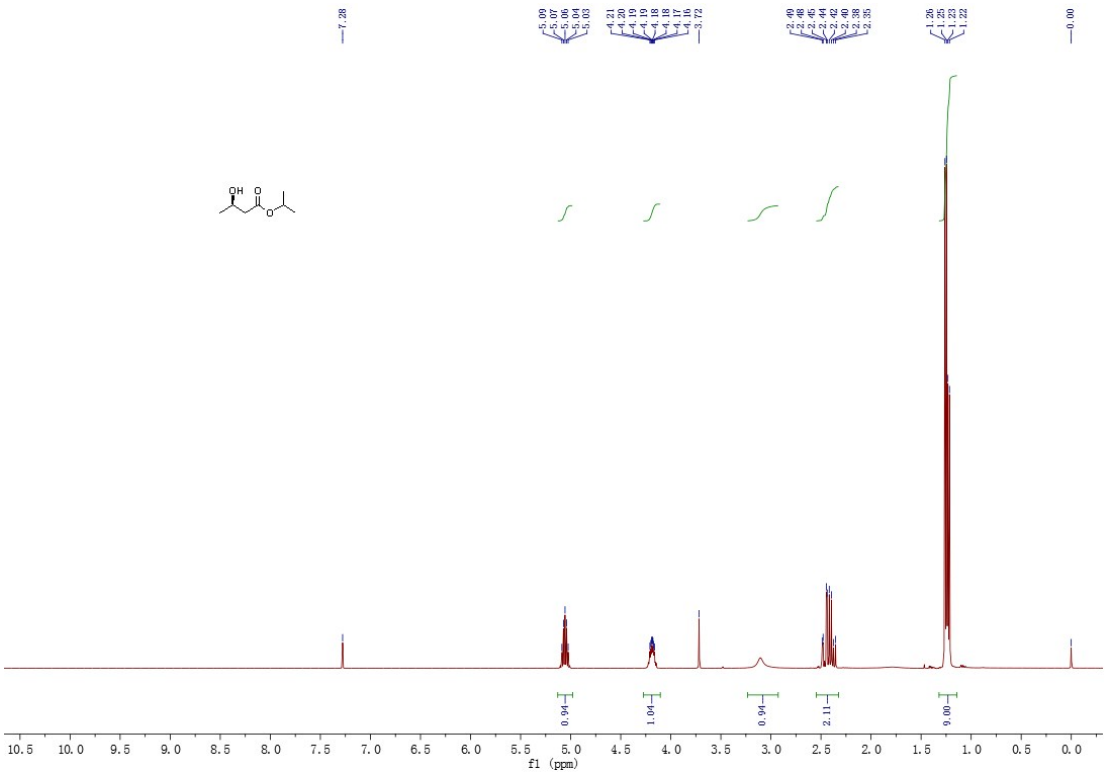

FID1 A, (WX-2014-11-6\SIG1000064.D)
pA
14.650
15.449
min

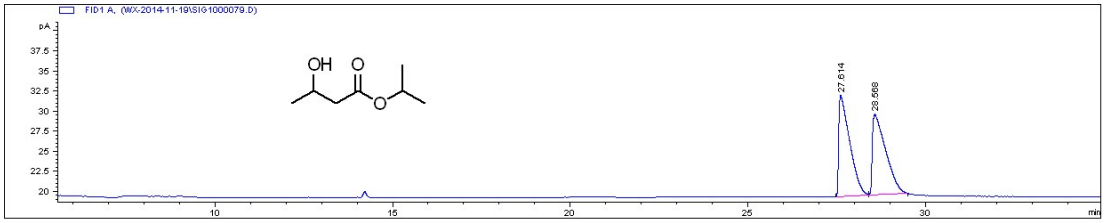

FID1 A, (WX-2014-11-6\SIG1000065.D)
pA
15.228
15.703
min

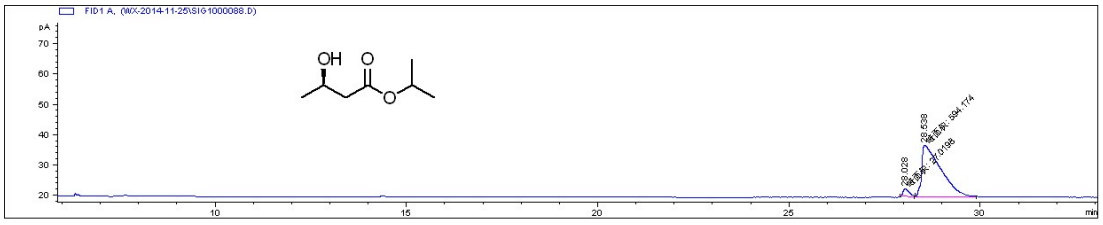

7.26
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.13
3.70
3.05
2.50
2.49
2.47
2.46
2.46
2.46
2.43
2.41
2.39
2.37
1.28
1.26
1.24
1.22
1.21
0.02
OH
O
O
2.90
0.95
2.18
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

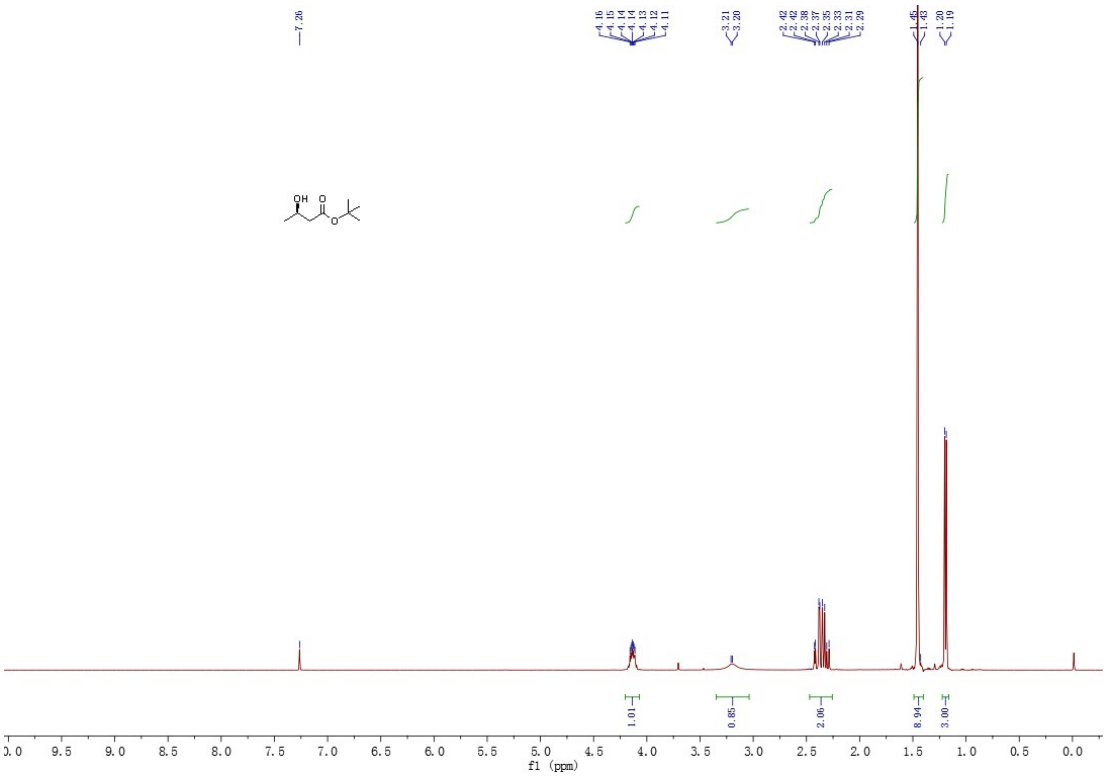

FID1 A, (WX-2014-11-6\SIG1000067.D)
pA
21.768
22.517
OH
O
O
min

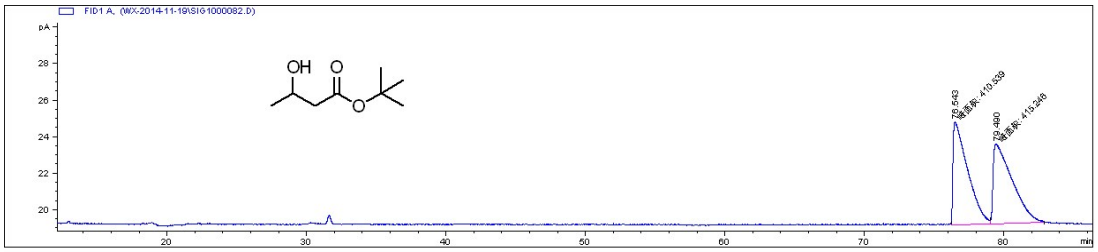

FID1 A, (WX-2014-11-6\SIG1000068.D)
pA
OH
O
O
21.779
22.029
min

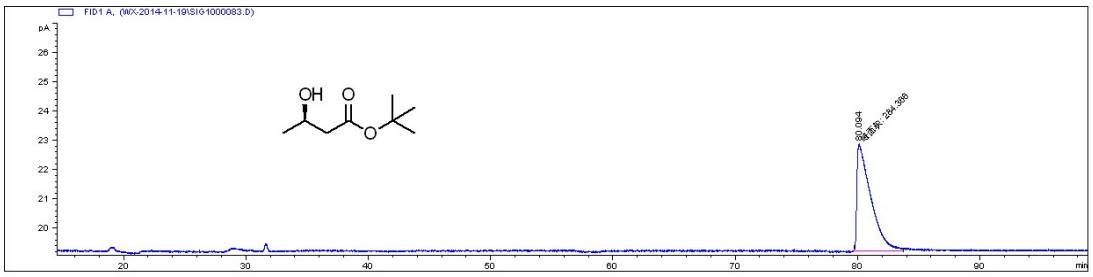

7.28
5.09
5.07
5.06
5.04
5.03
4.21
4.20
4.19
4.18
4.18
4.17
4.16
3.72
2.49
2.48
2.46
2.44
2.42
2.40
2.38
2.35
1.26
1.25
1.23
1.22
0.00
OH
O
O
0.94
1.04
0.94
2.11
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

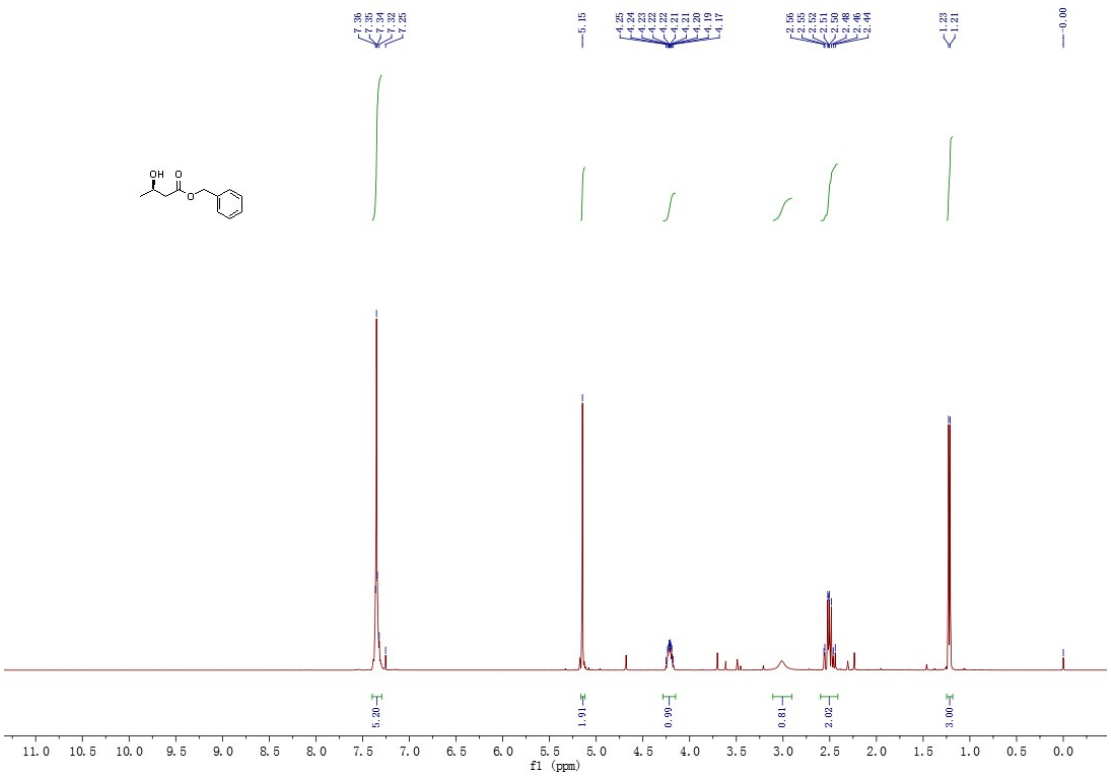

FID1 A, (WX-2014-11-19\SIG1000079.D)
pA
37.5
35
32.5
30
27.5
25
22.5
20
OH
O
O
27.614
28.568
10
15
20
25
30
min

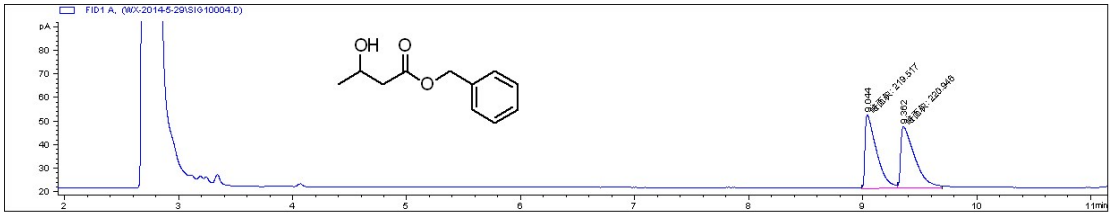

FID1 A, (WX-2014-11-25\SIG1000088.D)
pA
70
60
50
40
30
20
OH
O
O
28.028
28.538
27.198
10
15
20
25
30
min

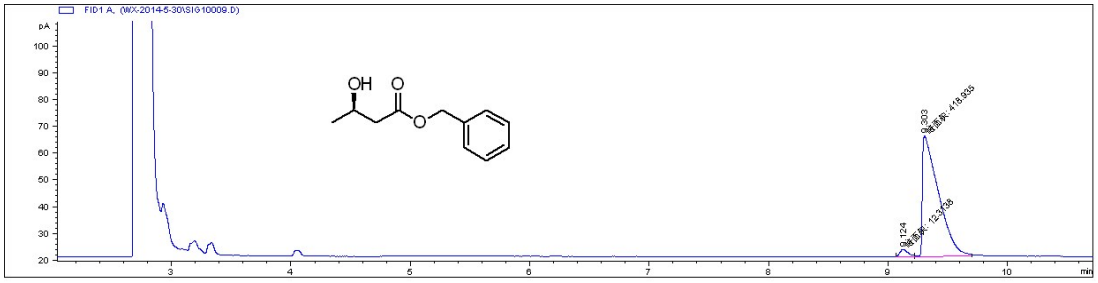

7.26
4.16
4.15
4.14
4.13
4.12
4.11
3.21
3.20
2.42
2.38
2.37
2.35
2.33
2.31
2.29
1.45
1.20
1.19
1.01
0.85
2.06
8.94
3.00
f1 (ppm)

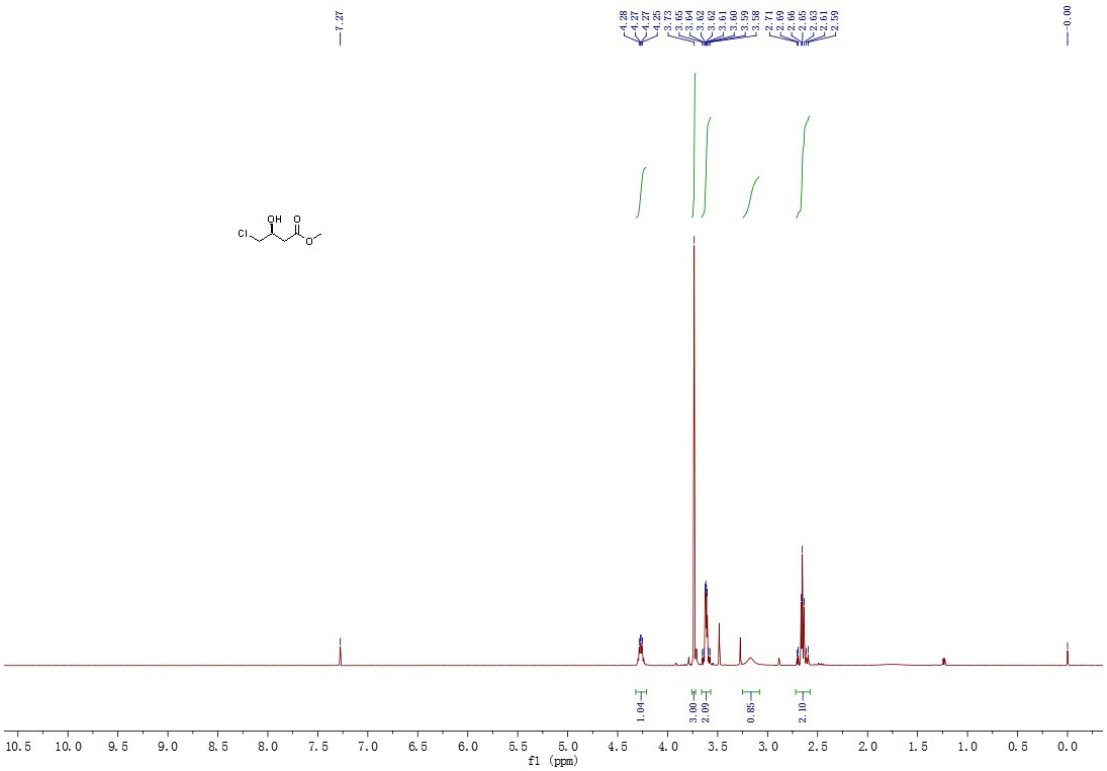

FID1 A, (WX-2014-11-19\SIG1000082.D)
pA
OH
O
O
79.543
峰面积: 410.559
79.990
峰面积: 415.248
min

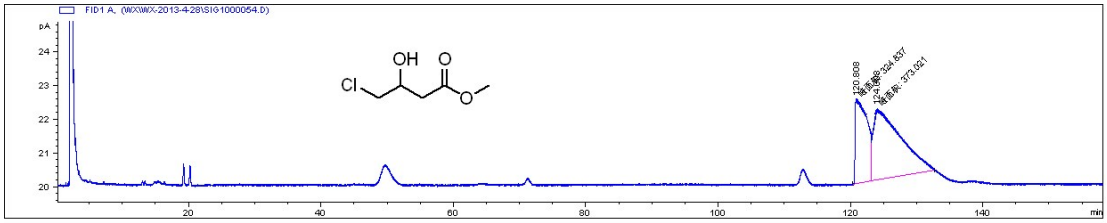

FID1 A, (WX-2014-11-19\SIG1000083.D)
pA
OH
O
O
80.084
峰面积: 284.386
min

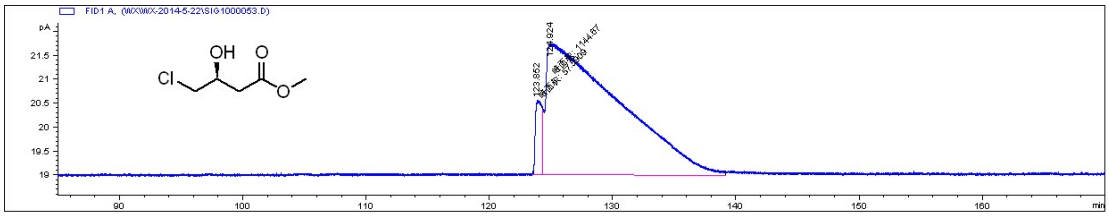

7.36
7.35
7.34
7.32
7.25
5.15
4.25
4.24
4.23
4.22
4.22
4.21
4.21
4.20
4.19
4.17
2.56
2.55
2.52
2.51
2.50
2.48
2.46
2.44
1.23
1.21
0.00
OH
O
O
5.20
1.91
0.99
0.81
2.02
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

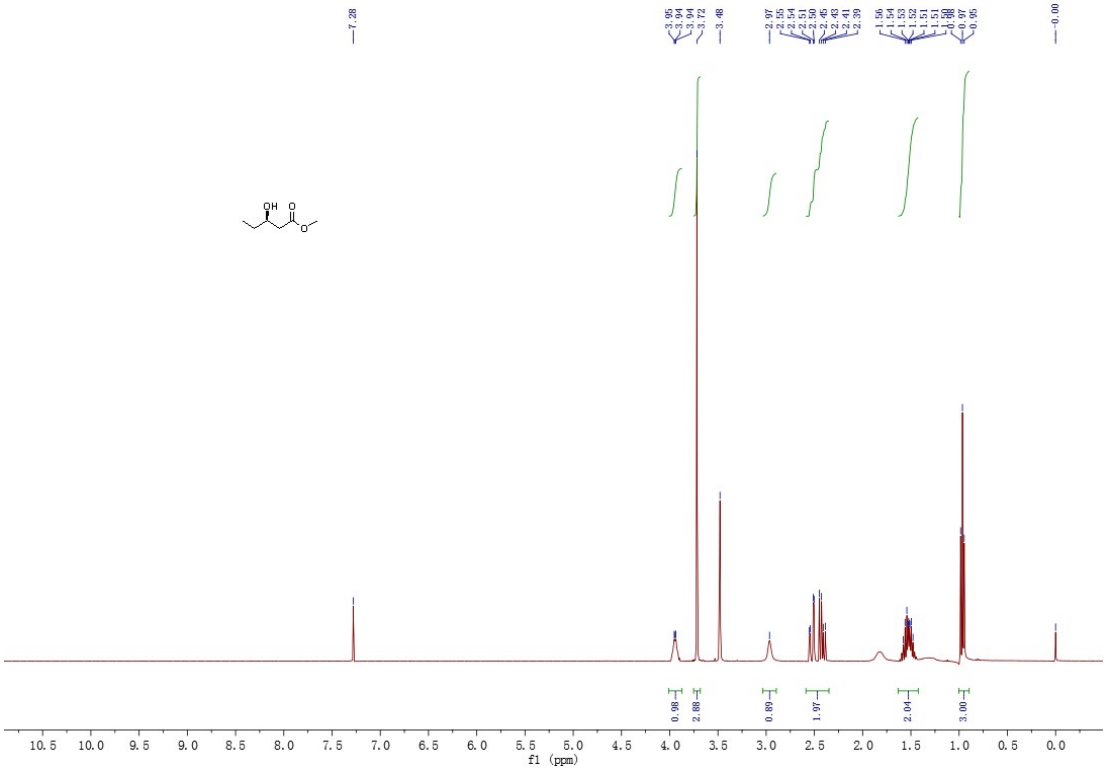

FID1 A, (WX-2014-5-29\SIG10004.D)
pA
OH
O
O
9.044
9.362
2
3
4
5
6
7
8
9
10
11min

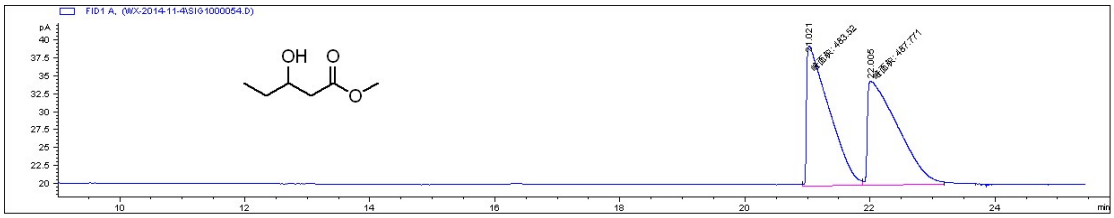

FID1 A, (WX-2014-5-30\SIG10009.D)
pA
OH
O
O
9.303
9.124
3
4
5
6
7
8
9
10
min

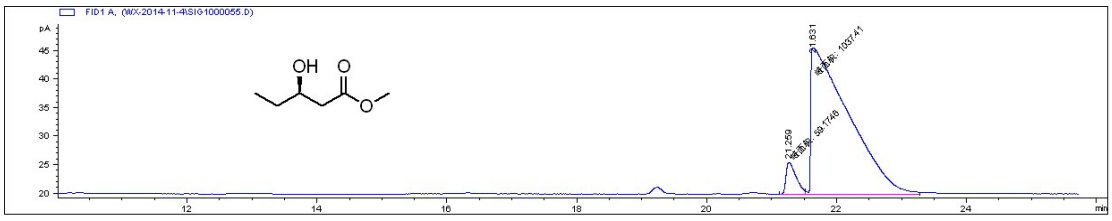

7.27
4.28
4.27
4.27
4.25
3.73
3.65
3.64
3.62
3.62
3.61
3.60
3.59
3.58
2.71
2.69
2.66
2.65
2.63
2.61
2.59
0.00
OH
O
Cl
O
1.04
3.00
2.09
0.85
2.10
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

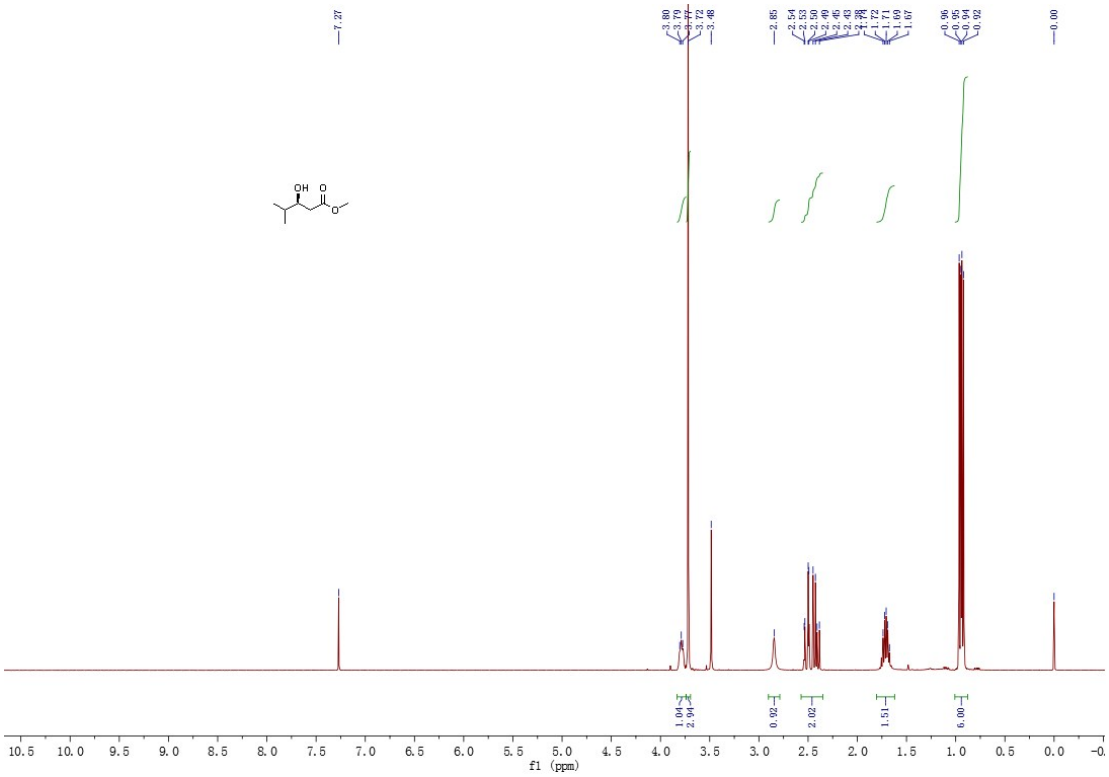

FID1 A, (WCX\WCX-2013-4-28\SIG1000054.D)
pA
24
23
22
21
20
OH
O
Cl
O
120.608
124.637
373.021
20
40
60
80
100
120
140
min

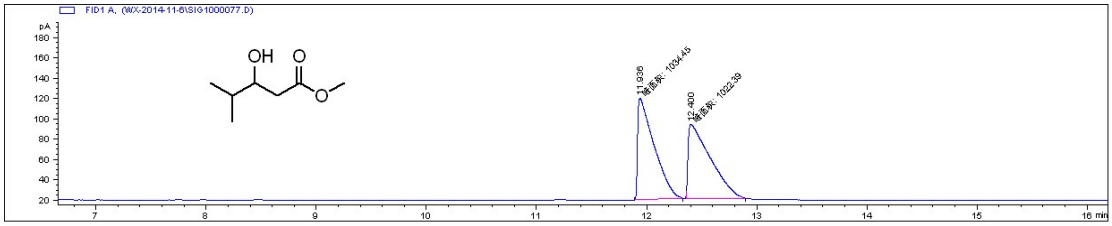

FID1 A, (WCX\WCX-2014-5-22\SIG1000053.D)
pA
21.5
21
20.5
20
19.5
19
OH
O
Cl
O
123.852
124.824
144.67
90
100
110
120
130
140
150
160
min

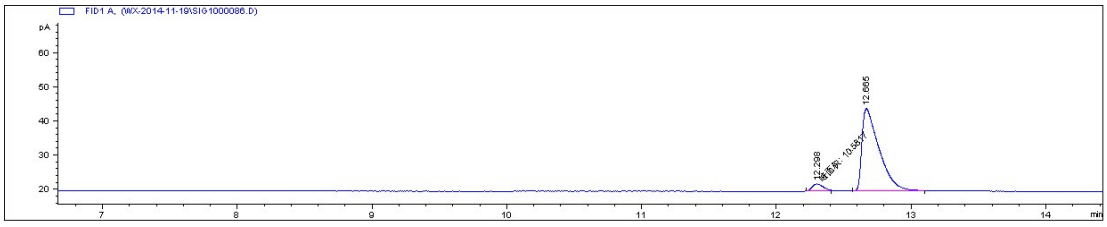

7.28
3.95
3.94
3.94
3.72
3.48
2.97
2.55
2.54
2.51
2.50
2.45
2.43
2.41
2.39
1.56
1.54
1.53
1.52
1.51
1.51
0.98
0.97
0.95
0.00
OH
O
O
0.98
2.88
0.89
1.97
2.04
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


FID1 A, (WX-2014-11-4\SIG1000054.D)
pA
OH
O
O
21.021
22.005
min

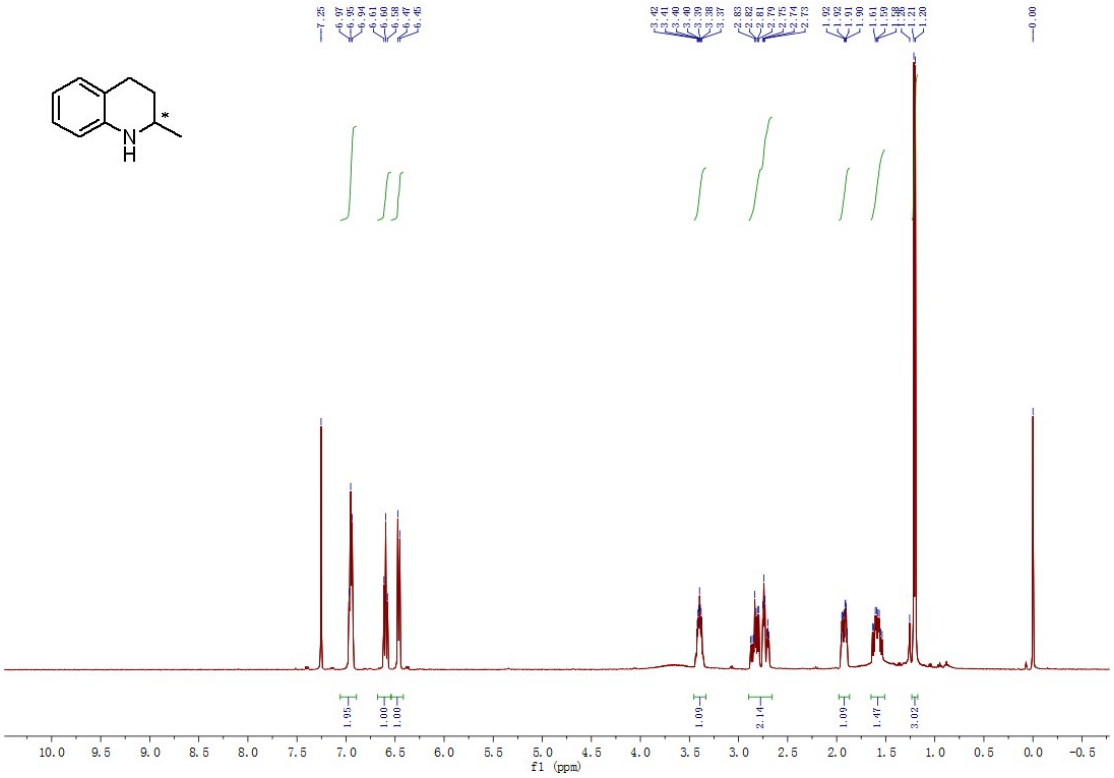

FID1 A, (WX-2014-11-4\SIG1000055.D)
pA
OH
O
O
21.631
1.259
min


7.27
3.80
3.79
3.77
3.72
3.48
2.85
2.54
2.53
2.50
2.49
2.46
2.43
1.72
1.71
1.69
1.67
0.96
0.95
0.94
0.92
0.00
OH
O
O
1.04
2.94
0.92
2.02
1.51
6.00
f1 (ppm)

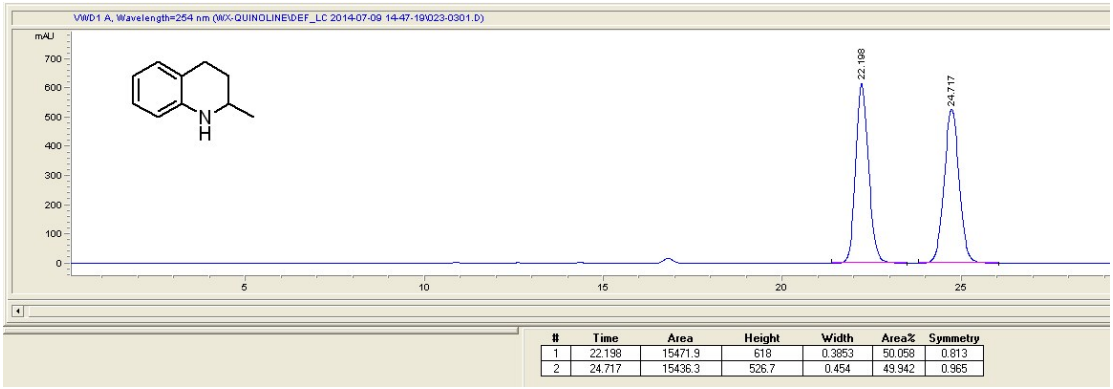

FID1 A, (WX-2014-11-6\SIG1000077.D)
pA
OH
O
O
11.936
峰面积: 1004.45
12.490
峰面积: 1022.59
min


FID1 A, (WX-2014-11-19\SIG1000086.D)
pA
12.685
12.298
峰面积: 10.5837
min

12. HPLC

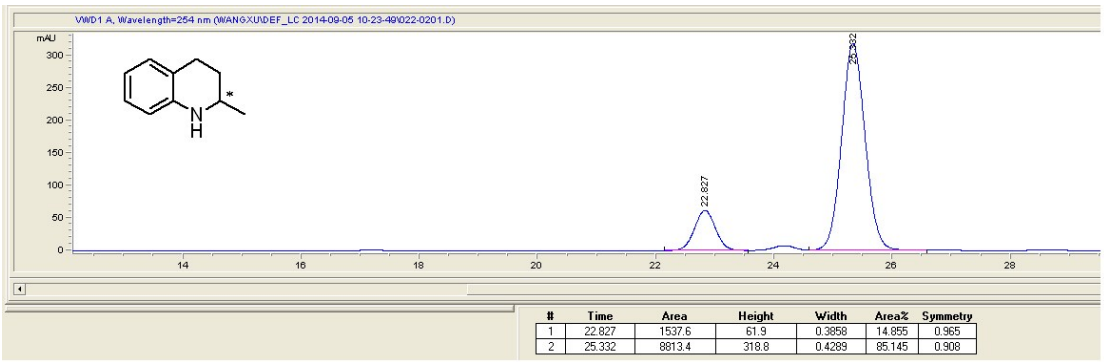


Racamic:



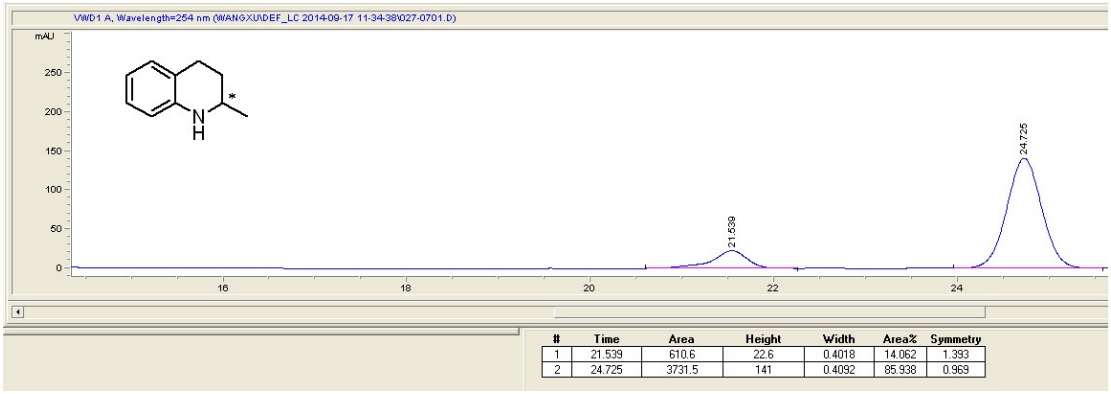
#	Time	Area	Height	Width	Area%	Symmetry
1	22.198	15471.9	618	0.3853	50.058	0.813
2	24.717	15436.3	526.7	0.454	49.942	0.965

Catalyst by Ir/BINAP-CMP-3D-2:



#	Time	Area	Height	Width	Area%	Symmetry
1	22.827	1537.6	61.9	0.3858	14.855	0.965
2	25.332	8813.4	318.8	0.4289	85.145	0.908

Catalyst by Ir/(R)-BINAP:



#	Time	Area	Height	Width	Area%	Symmetry
1	21.539	610.6	22.6	0.4018	14.062	1.393
2	24.725	3731.5	141	0.4092	85.938	0.969

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