

Supporting Information for

Design and Assembly of a Chiral Composite Metal–Organic Framework for Efficient Asymmetric Sequential Transformation of Alkene to Amino Alcohol

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1. Materials and general procedures

All reagents and solvents used in these studies are commercially available and used without further purification. Elemental analyses were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. The CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using $\text{Cu-K}\alpha$ radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. The NMR experiments were carried out on a MERCURY plus 400 spectrometer operating at resonance frequencies of 400 MHz. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase. ICP-OES was performed on Optima 7300DV ICP-OES (Perkin Elmer Corporation, USA). Analytical high performance liquid chromatography (HPLC) was performed on a LC-2010HAT HPLC with UV detection at 200 or 254nm. Analytical CHIRALCEL OD-H, AD-H, AS-H and OJ-H column (4.6 mm \times 25 cm) from Daicel were used. The CO_2 adsorption isotherms were recorded at 273K by using a micromeritics ASAP 2020 surface area and porosity analyzer. Before the adsorption measurement, the samples were activated at 80 $^{\circ}\text{C}$ under vacuum ($< 10^{-3}$ torr) for 4 h. Scanning Electron Microscopy (SEM) images were performed on a NOVA NanoSEM 230 instrument equipped with an energy dispersive spectroscopy (EDS) detector. X-ray photoelectron spectroscopy (XPS) were recorded on a AXIS Ultra DLD surface analysis instrument.

Single-Crystal X-ray Diffraction. Single-crystal XRD data for compound **1** was collected on a Bruker SMART Apex II CCD-based X-ray diffractometer with $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 150 K. We have collected about several datasets for **1** using $\text{Mo-K}\alpha$ radiation. Among the several datasets, the best dataset was used for structure solution and refinement. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996).

The structure was solved by direct methods with SHELXS-2018 and refined with SHELXL-2018 using OLEX 1.2. In the structure, all the non-hydrogen atoms except guest molecules were refined by full-matrix least-squares techniques with anisotropic displacement parameters, and the hydrogen atoms were geometrically fixed at the calculated positions attached to their parent atoms, treated as riding atoms. Contributions to scattering due to these highly disordered solvent molecules were removed using the *SQUEEZE* routine of *PLATON*; structures were then refined again using the data generated. We have also tried our best to re-growing an ideal single crystal, and got several other sets of data. Both of them had weak diffractions even with a very long exposure time, especially at higher Bragg angles. Among the several date sets for **1**, we

choose the best one for structure solution and refinement, but there were still two B level alerts about the problem that coordination water molecules do not form hydrogen bonds in checkcif, that maybe due to the absence of hydrogen bonding interactions between the coordination water molecule and the solvent molecules. The heavily disordered co-crystalizing solvent which were removed from the unit-cell presumably was DMF. The CIF format output from PLATON (generated as platon.sqf) to the CIF from which the contributions of some 822 electrons removed from the unit-cell contents of compound **1**, the disordered co-crystalizing solvent was in the structure presumably it was DMF which has 40 electrons and implies that SQUEEZE removed the contributions of some $822/40 = 20.6$ molecules of DMF from the unit-cell contents. In this C2 space group with $Z = 4$ this then implies that some $20.6/4 = 5$ disordered DMF molecules would be associated with the formula unit. Thus, $(C_{68}H_{70}AlCd_3N_7O_{20}) \cdot 5(C_3H_7NO)$ would be better for the Empirical formula.

The structure was then refined again using the data generated. Crystal data and details of the data collection are given in **Table S1**. CCDC 153348 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

2. Synthesis

The ligands H₂L and [MnLCl] were synthesized according to the literatures 1 and 2 respectively.

2.1 Synthesis of [AlLCl]

A solution of H₂L (0.588 g, 1 mmol) in dry toluene (50 mL) was degassed for 20 minutes. AlEt₂Cl (1.22 mL, 0.9 M in toluene, 1.1 mmol) was then added to the solution and the reaction mixture was stirred at room temperature for 10 h. The yellow solid was collected by filtration, washed with ether and dried under reduced pressure (0.603 g, 93%). ESI-MS m/z : 632.3 (Calcd m/z 632.3 for [M-Cl+H₂O]⁺). IR (KBr pellet, ν/cm^{-1}): 3436 (w), 2946 (s), 1635 (s), 1600 (s), 1557 (s), 1463 (s), 1444 (s), 1410 (s), 1386 (s), 1354 (s), 1326 (s), 1284 (m), 1172 (m), 1088 (m), 824 (m), 624 (m), 595 (m).

2.2 Synthesis of **1**

[AlLCl] (187 mg, 0.288 mmol), AgNO₃ (49 mg, 0.288 mmol) and DMF (10 mL) were mixed with together and stirred at room temperature for 20 min. After that, the mixture was centrifuged at 9400 rpm for 5 min, and the supernatant was collected. Then, CdI₂ (106 mg, 0.288 mmol), H₂BDC (48 mg, 0.288 mmol), DMF (5 mL) and MeOH (13 mL) were added. The mixture was heated at 80 °C for 12 h. The mixture was then cooled to room temperature. Colorless needle-like crystals of **1** were collected, washed with MeOH and Et₂O, and dried in air. Yield: 243 mg, 51%. The products can be best formulated as [Cd₃AlLNO₃(BDC)₃]•2DMF on the basis of

microanalysis, TGA, ICP, elemental analysis, IR and single-crystal diffraction. Elemental analysis and IR for **1**: Anal (%). Calcd for $C_{68}H_{70}AlCd_3N_7O_{20}$: C, 49.44; H, 3.20; N, 5.94. Found: C, 48.87; H, 3.44; N, 6.12. ICP measurement indicated the ratio of Al: Cd is 1:3. IR (KBr, cm^{-1}): 3421 (w), 2927 (s), 2855 (w), 1635 (s), 1595 (s), 1556(s), 1462 (m), 1443 (m), 1410 (m), 1383 (m), 1354 (m), 1283 (m), 1244 (m), 1172 (m), 1088 (s), 1049 (m), 824 (m), 790 (m), 644 (w), 593(w).

2.3 Synthesis of **2**

[MnLCl] (194.5 mg, 0.288 mmol), $Cd(NO_3)_2 \cdot 4H_2O$ (88 mg, 0.288 mmol), H_2BDC (48 mg, 0.288 mmol), DMF (15 mL), MeOH (15 mL) were added together. The mixture was heated at 80 °C for 12 h. Brown needle-like crystals of **2** were collected, washed with MeOH and Et_2O , and dried in air. Yield: 304 mg, 64%. The products can be best formulated as $[Cd_3MnLCl(BDC)_3] \cdot 2DMF$ on the basis of microanalysis, TGA, ICP, elemental analysis, IR and powder X-ray diffraction. Elemental analysis and IR for **2**: Anal (%). Calcd for $C_{68}H_{70}MnClCd_3N_6O_{17}$; C, 49.40; H, 3.20; N, 5.08. Found: C, 48.91; H, 3.50; N, 4.89. ICP measurement indicated the ratio of Mn: Cd is 1:3. IR (KBr, cm^{-1}): 3448 (w), 2924 (s), 2846 (w), 16334 (s), 1597 (s), 1503(s), 1437 (m), 1380 (m), 1311 (m), 1266 (m), 1225 (m), 1171 (m), 1105 (m), 827 (s), 839 (m), 749 (m), 573(w).

2.4 Synthesis of **3**

After experimental section **2.2**, the solvent in the vial was removed, then $Cd(NO_3)_2 \cdot 4H_2O$ (88 mg, 0.288 mmol), [MnLCl] (194.5 mg, 0.288 mmol), H_2BDC (48 mg, 0.288 mmol), DMF (15 mL), MeOH (15 mL) were added together. The mixture was continued to heat at 80 °C for 12 h. Brown needle-like crystals of **3** were collected, washed with MeOH and Et_2O , and dried in air. Yield: 542 mg. The products can be best formulated as $[Cd_3(AlLNO_3)_{0.44}(MnLCl)_{0.56}(BDC)_3] \cdot 2DMF$ on the basis of microanalysis, TGA, ICP, elemental analysis, IR and powder X-ray diffraction. Elemental analysis and IR for **3**: Anal (%). Calcd for $C_{68}H_{70}Mn_{0.56}Cl_{0.56}Al_{0.44}Cd_3N_{6.44}O_{18.32}$; C, 49.42; H, 3.20; N, 5.46. Found: C, 49.12; H, 3.35; N, 5.58. ICP measurement indicated the ratio of Mn:Al: Cd is 1:0.75:5.44. IR (KBr, cm^{-1}): 3440 (w), 2943 (s), 2863 (w), 1601 (s), 1563 (s), 1503(s), 1435 (m), 1387 (m), 1315 (m), 1273 (m), 1225 (m), 1173 (m), 1087 (m), 1014 (m), 897 (s), 839 (m), 828 (m), 785 (m), 745 (w), 643(w), 573(w), 519(w).

3. Experimental

3.1 Aminolysis of *trans*-Stilbene Oxide Catalyzed by **1**

To a suspension of **1** (10 mg, 3.0 mol%) in DCM (1.0 mL), *trans*-stilbene oxide (39.2 mg, 0.2 mmol) and aniline (0.1 mmol) was added. The reaction was carried out at 60 °C until the

disappearance of the amine. After that, the mixture was centrifuged at 9000 rpm for 5 min, the supernatant was concentrated under vacuum, the concentrate was analyzed by ^1H NMR to give the conversion and by HPLC to give the ee value. The precipitate was washed with CH_2Cl_2 for 3 times and dried under pressure, then used for the next run. After the fifth run, the precipitate was washed with CH_2Cl_2 for 3 times, dried under pressure, immersed in DMF and heated at 80 °C for 12 h, then used for PXRD and BET analysis.

$$m = \text{MS(MOF)} \times n(\text{sub.}) \times \text{molar \%}$$

3.2 Asymmetric Epoxidation Reaction of Alkene Catalyzed by 2

To a suspension of **2** (1.6 mg, 0.5 mol%) in dry DCM (1.0 mL), alkene (0.2 mmol) and 2-(tert-butylsulfonyl)iodosylbenzene (4 mg, 0.012 mmol) were added. The same amount of oxidant was added 18 more times at 15 min intervals. The reaction was carried out overnight at 0 °C. After that, the mixture was centrifuged at 9000 rpm for 5 min, the supernatant was concentrated under vacuum, the concentrate was analyzed by ^1H NMR to give the conversion and by HPLC to give the ee value. The precipitate was washed with CH_2Cl_2 for 3 times and sonicated for 10 min dry under pressure, then used for the next run. After the fifth run, the precipitate was washed with CH_2Cl_2 for 3 times, dried under pressure, immersed in DMF and heated at 80 °C for 12 h, then used for PXRD and BET analysis.

3.3 Alkene Epoxidation/Epoxide Aminolysis Catalyzed by 3

To a suspension of **3** (1.6 mg, 0.5 mol%) in dry DCM (1.0 mL), alkene (0.2 mmol) and 2-(tert-butylsulfonyl)iodosylbenzene (4 mg, 0.012 mmol) were added. The same amount of oxidant was added 18 more times at 15 min intervals. The reaction was carried out overnight at 0 °C. After that aniline (0.24 mmol) was added and the reaction mixture was stirred at 0 °C until the disappearance of the epoxide. The mixture was centrifuged at 9000 rpm for 5 min, the supernatant was concentrated under vacuum, the concentrate was analyzed by ^1H NMR to give the conversion and by HPLC to give the ee value. The precipitate was washed with CH_2Cl_2 for 3 times and sonicated for 10 min dry under pressure, then used for the next run, after the fifth run, the precipitate was washed with CH_2Cl_2 for 3 times, dried under pressure, immersed in DMF and heated at 80 °C for 12 h, then used for PXRD and BET analysis. The supernatant was concentrated under vacuum then used for ICP-MS analysis.

4. Representative procedure for dye uptake measurements

Fresh crystals of **1** (2.50 mg) were briefly dried and then soaked in an aqueous solution of methyl orange (60 mg) overnight. The resulted samples were washed with MeOH thoroughly until the washings became colorless. The washed samples were digested by Na_2EDTA (0.05 M, 2 mL) and NaOH (6 M, 0.1 mL), the clear solution with light orange color was diluted to 50 mL. Absorption experiments were performed on Lambda 20 UV/Vis Spectrometer.

Creation of a standard curve: (1) The methyl orange (32.7 mg) was added to a flask and diluted to 1000 mL. The solution of methyl orange is stock solution, and 2.5, 5, 10 and 25 mL stock solution were diluted to 50 mL, respectively. (2) The absorbance of different concentrations of methyl orange was determined by UV/Vis Spectrometer. Data for known concentrations of methyl orange were used to make the standard curve, plotting concentration on the X axis, and the assay measurement of absorbance on the Y axis. According to the Beer-Lambert law, the standard curve can be calculated by linear fitting of the data.

$$A = \log_{10} \frac{I_0}{I_t} = \log_{10} \frac{1}{T} = K \cdot l \cdot c$$

Crystal	1	2	3
The number of dye uptake (per formula)	1.53	1.64	1.47

The uptake of bulky dye molecules by MOFs has recently been utilized to assess their substrate-accessible pore volumes in solution. **1-3** could adsorb 1.53 methyl orange molecules (MO, ca. 1.47 nm × 0.53 nm × 0.53 nm in size) per formula unit in solution and the inclusion crystal displayed almost the same PXRD pattern as the pristine sample, indicating the maintenance of porosity and structural integrity of them in solution, revealing the retention of the framework structure in solution.

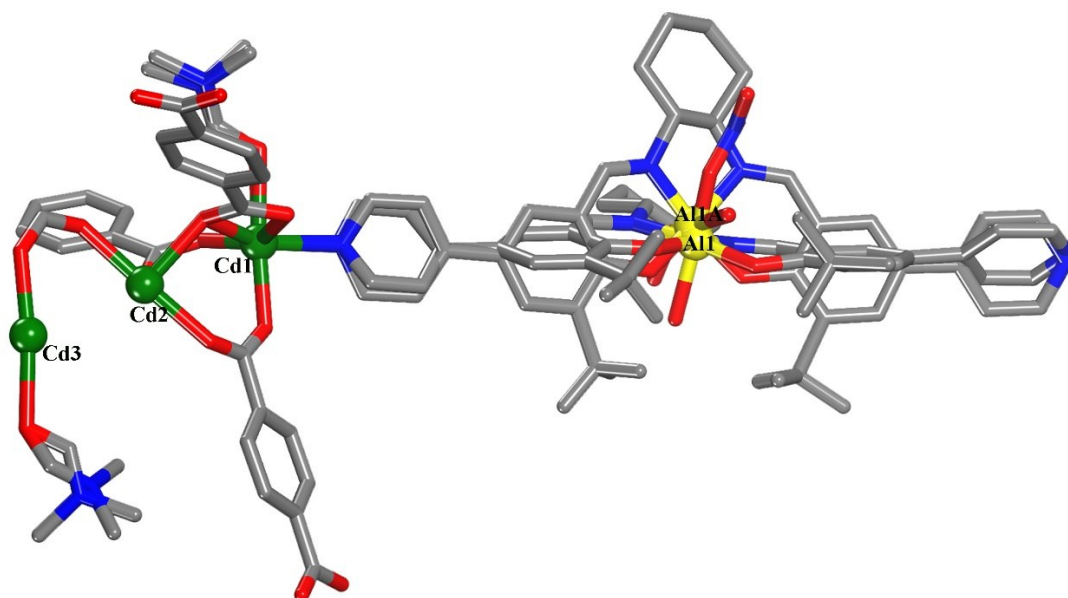
5. Table S1. Crystal data and structure refinement for **1**

Identification code	1
Empirical formula	C ₈₃ H ₁₀₅ Al Cd ₃ N ₁₂ O ₂₅
Formula weight	2034.96
Temperature (K)	120(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2
Unit cell dimensions	a = 59.112(15) Å b = 9.934(3) Å c = 18.475(5) Å α = γ = 90; β = 106.229(5)°
Volume (Å ³), Z	10416(5), 4
Density (calculated) (mg/m ³)	1.298
Absorption coefficient (mm ⁻¹)	0.685
F(000)	4176
θ range for data collection (°)	1.435 to 27.640
Limiting indices	-72 ≤ h ≤ 76 -12 ≤ k ≤ 12 -23 ≤ l ≤ 23
Reflections collected	52364
Independent reflections	23700 [R(int) = 0.0959]
Completeness to theta	99.9 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	23700 / 4015 / 1315
Goodness-of-fit on F ²	0.986
Final R indices [I > 2σ(I)]	R1 = 0.0710, wR2 = 0.1684

R indices (all data)	R1 = 0.1082, wR2 = 0.1856
Absolute structure parameter	0.05(5)
Largest diff. peak and hole (e.Å ⁻³)	1.502 and -2.287 e.Å ⁻³

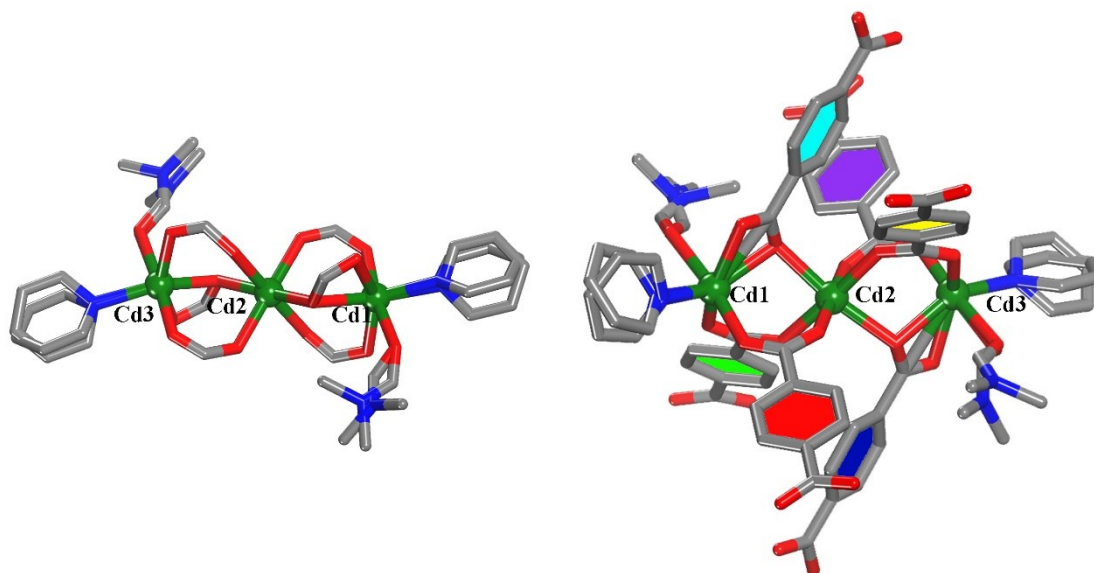
6. Figure S1~S3. Additional X-ray crystallographic structures

6.1 Figure S1.



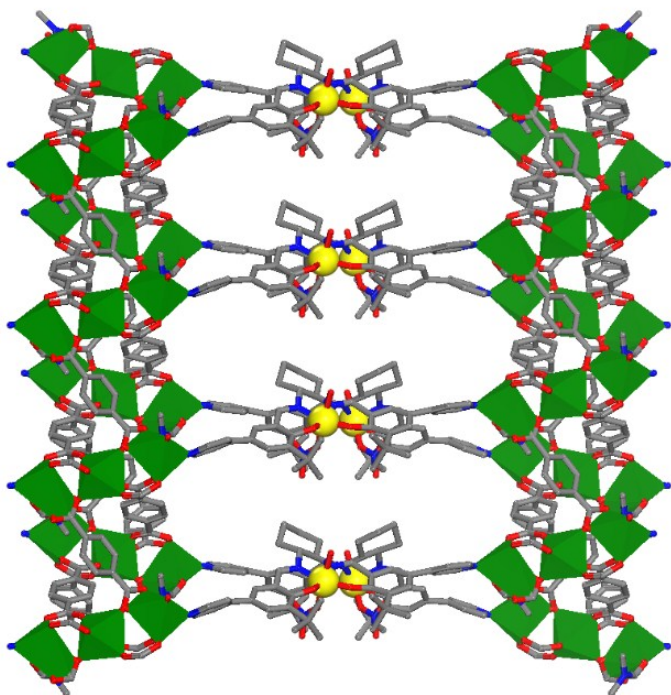
The asymmetric unit of **1** (yellow Al, green Cd, red O, blue N, gray C)

6.2 Figure S2.



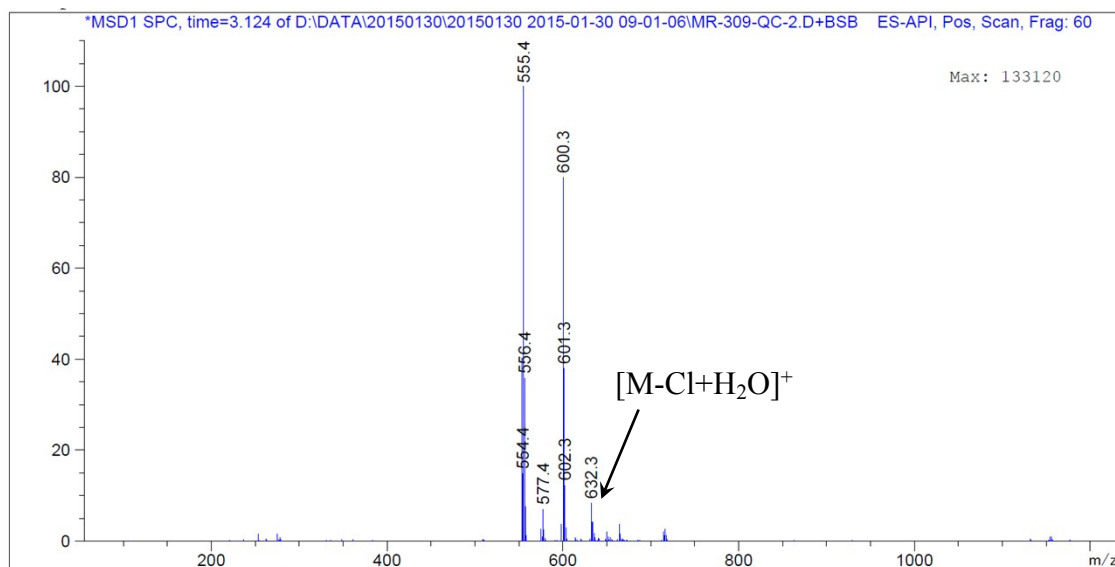
The structure of $[Cd_3(CO_2)_6]$ clusters (green Cd, red O, blue N, gray C)

6.3 Figure S3.



View of the interpenetrated 3D framework of **1** along the *c*-axis (yellow Al, green Cd, red O, blue N, gray C; the metal centers are shown as polyhedra)

7. Figure S4. ESI-MS

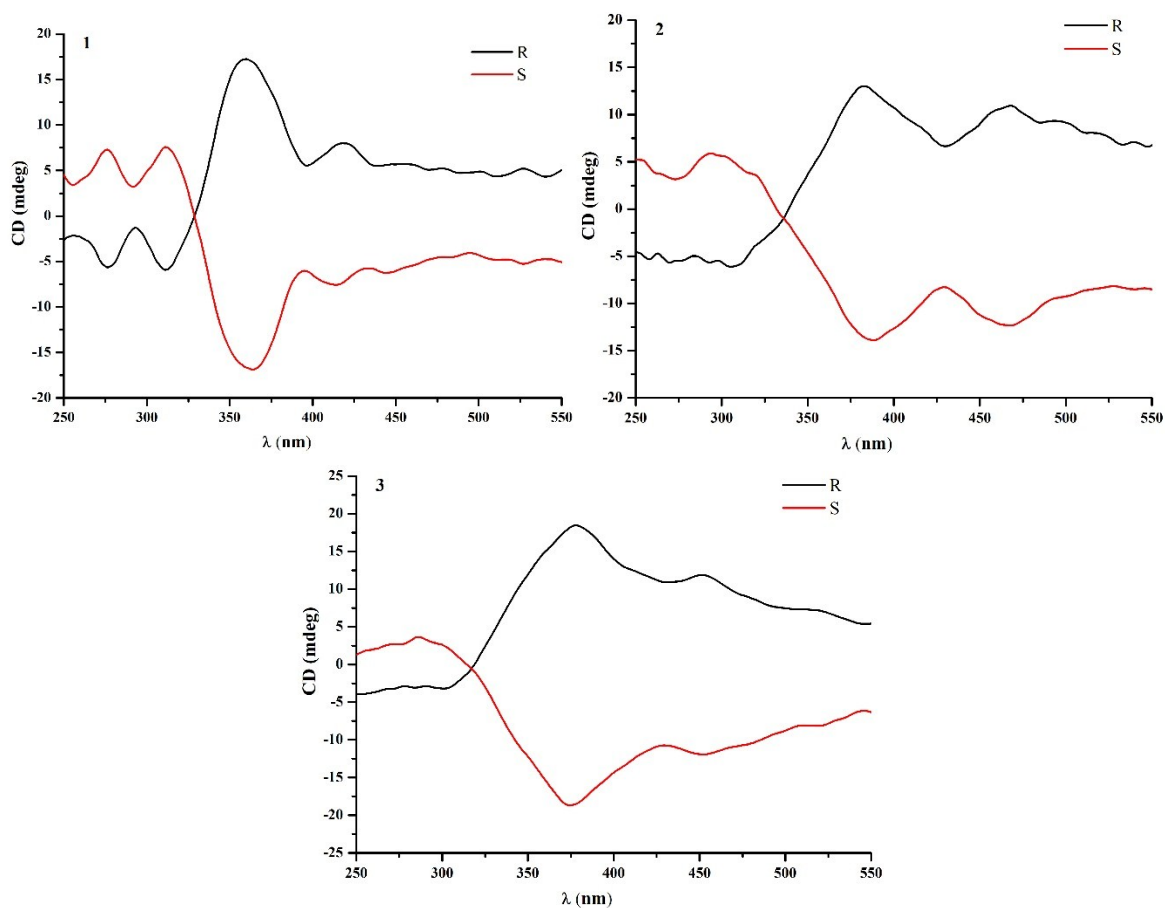


MS (Al-salen): 649.2

ESI-MS m/z: 632.3

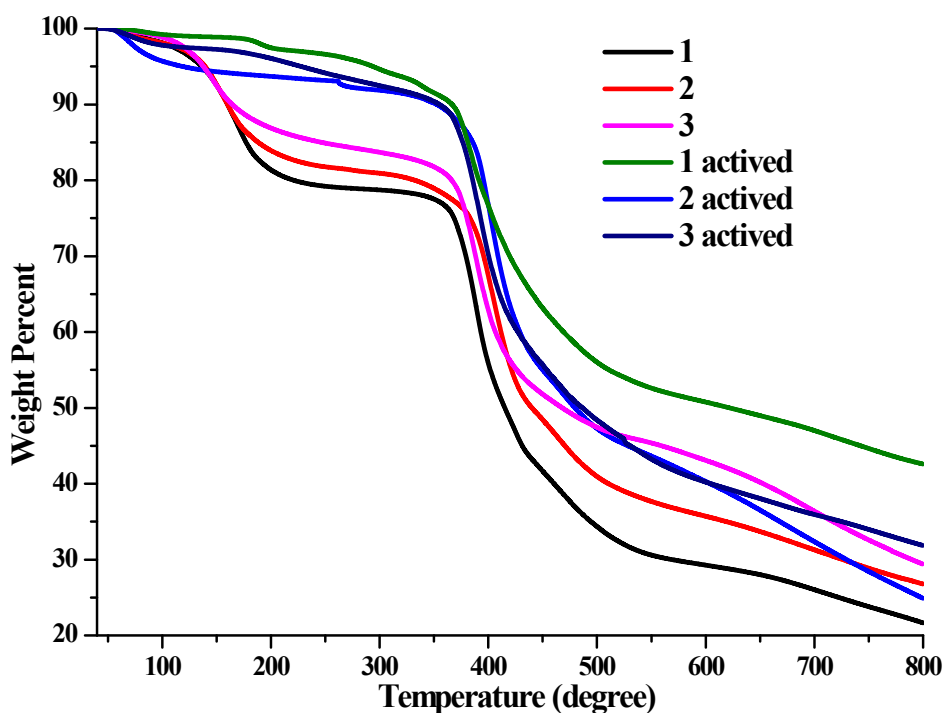
Calcd m/z 632.3 for $[M-Cl+H_2O]^+$

8. Figure S5. CD spectra of (R)/(S)



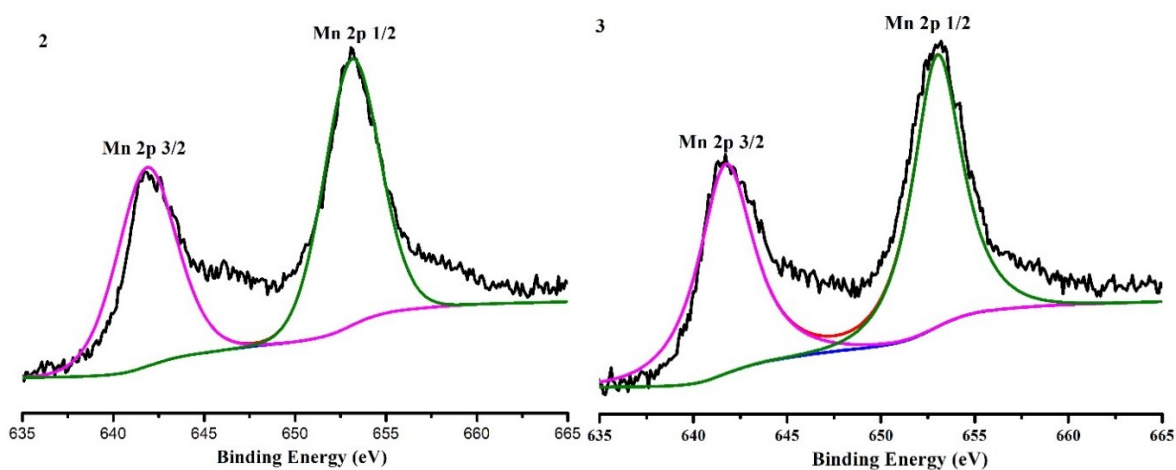
CD spectra of **1**, **2** and **3**, showing almost the mirror images of each other, demonstrated their enantiomeric nature.

9. Figure S6. TGA curve



The TGA curve of **1**, **2** and **3** before and after activities. All the samples were activated under vacuum at 100 °C.

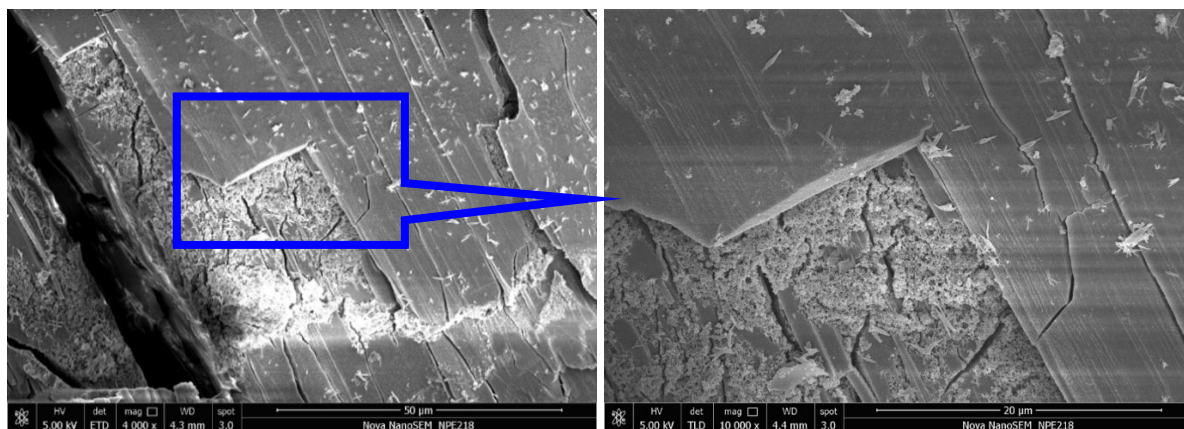
10. Figure S7. XPS spectra



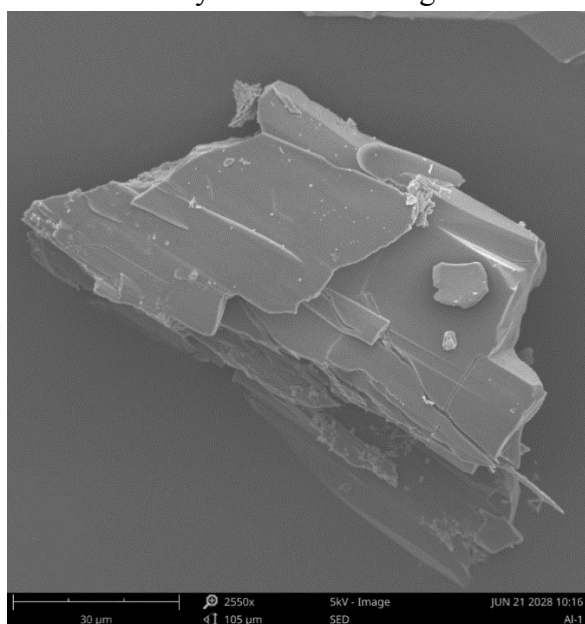
The XPS spectra of Mn 2p_{3/2} and 2p_{1/2} peaks in **2** (left) and **3** (right), the Mn 2p_{3/2} and 2p_{1/2} peaks around 641.9 and 653.3 eV corresponds to +3 oxidation state.

11. Figure S8~S10. SEM, EDS and Microscope images

11.1 Figure S8. SEM image of **3**

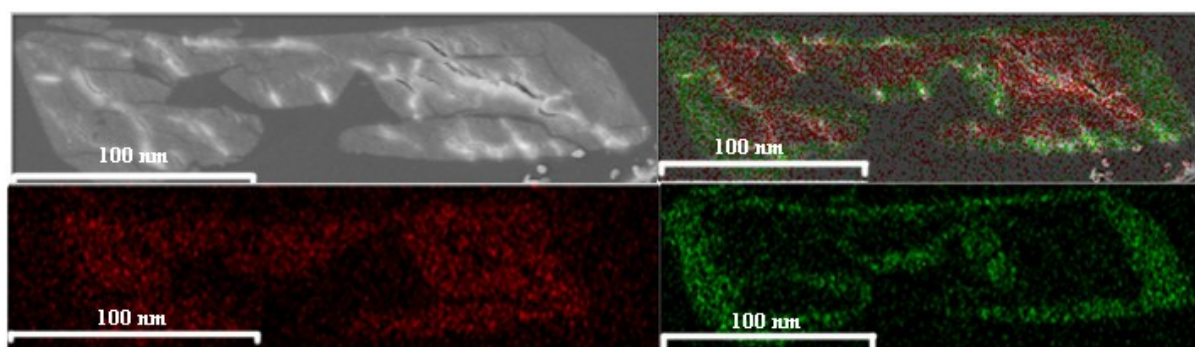


As synthesized of **3**, the SEM image revealed **2** were coating outside **1** and the cracks, observed on the crystals appeared after drying, has been observed previously and crystals **3** still retain their overall crystal habit. The right is the enlargement of the left.



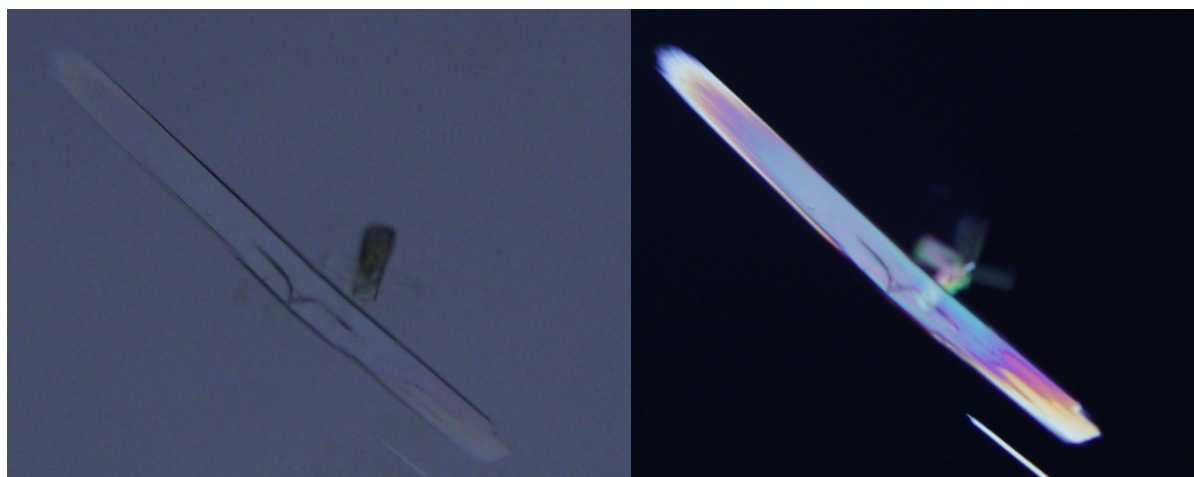
The SEM image of **3** after catalysis revealed that the cracks was still observed and crystals **3** still retain their overall crystal habit

11.3 Figure S9. SEM-EDS of **3**

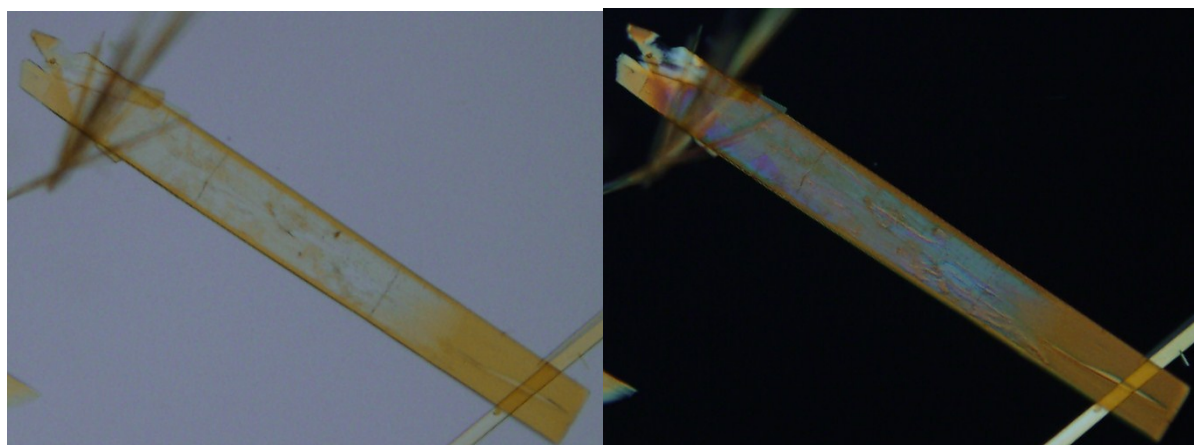


SEM and image of elemental mapping for **3** with energy dispersive X-ray spectroscopy (EDS). Corresponding EDS elemental mapping for green Mn, red Al, respectively.

11.4 Figure S10 Microscope images and fluorescent photographs

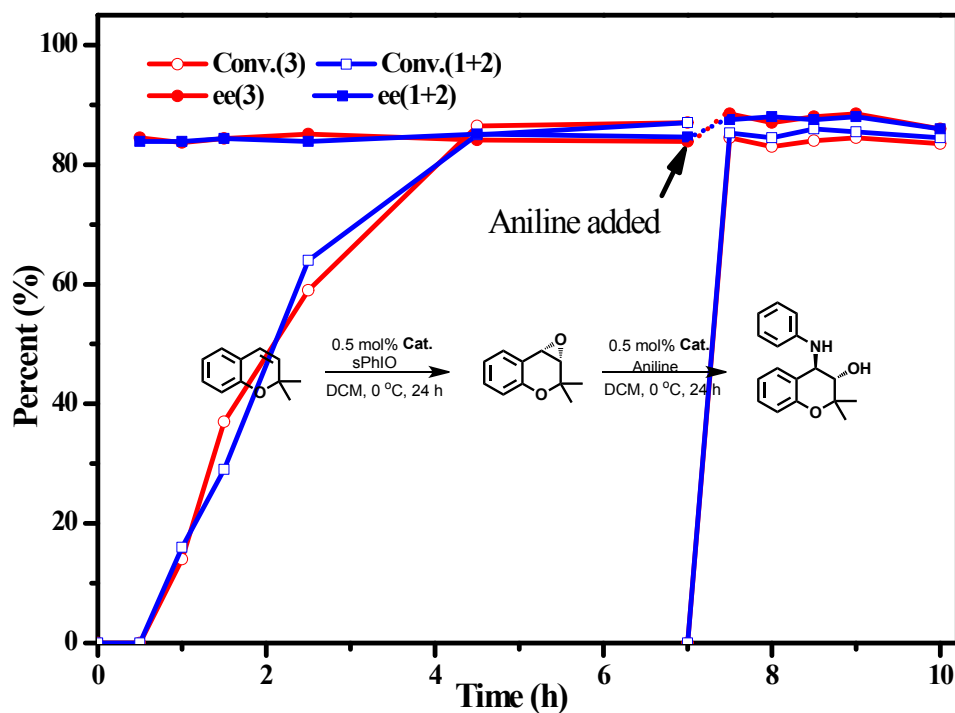


The Microscope images (left) and fluorescent photographs (right) of **1**.



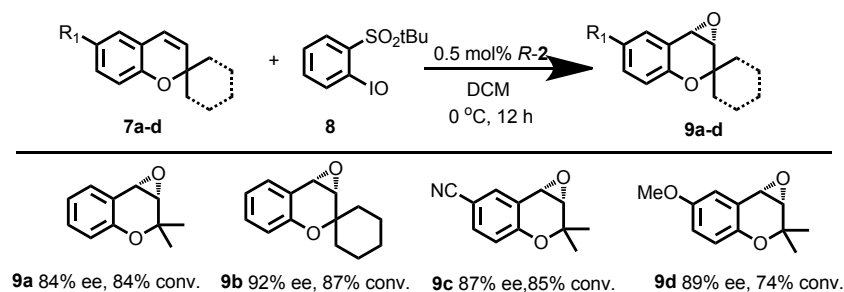
The Microscope images (left) and fluorescent photographs (right) of **3** revealed **2** (yellow part) were coating outside **1**.

12. Figure S11. The kinetics curve



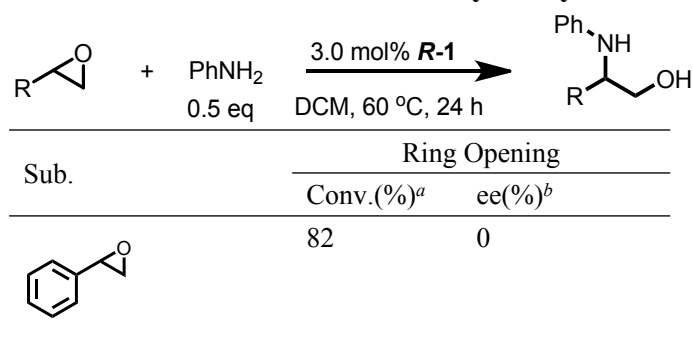
Kinetic curve of (*R*)-**3** and mixture of (*R*)-**1** and (*R*)-**2**. The kinetics revealed that the chromene was smoothly oxidized in after 4.5 h with 86% conversion and 84% ee, and the amino alcohol was got in after 0.5 h with almost quantitative yield; Comparing with (*R*)-**3**, the mixture of (*R*)-**1** and (*R*)-**2** (the same M(salen) loading as (*R*)-**3**) can also catalyze the sequential reactions efficiently with almost the same conversions and ee values.

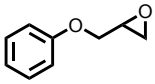
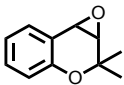
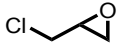
13. Figure S12. Alkene epoxidation catalyzed by *R*-2



Conversions were calculated by ^1H NMR. ee values were determined by HPLC.

14. Table S2. Other substrates catalyzed by *R*-1

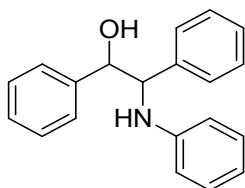


	76	0
	93	0
	95	0

^a Determined using ¹H NMR base on anilines. ^b ee values determined by HPLC.

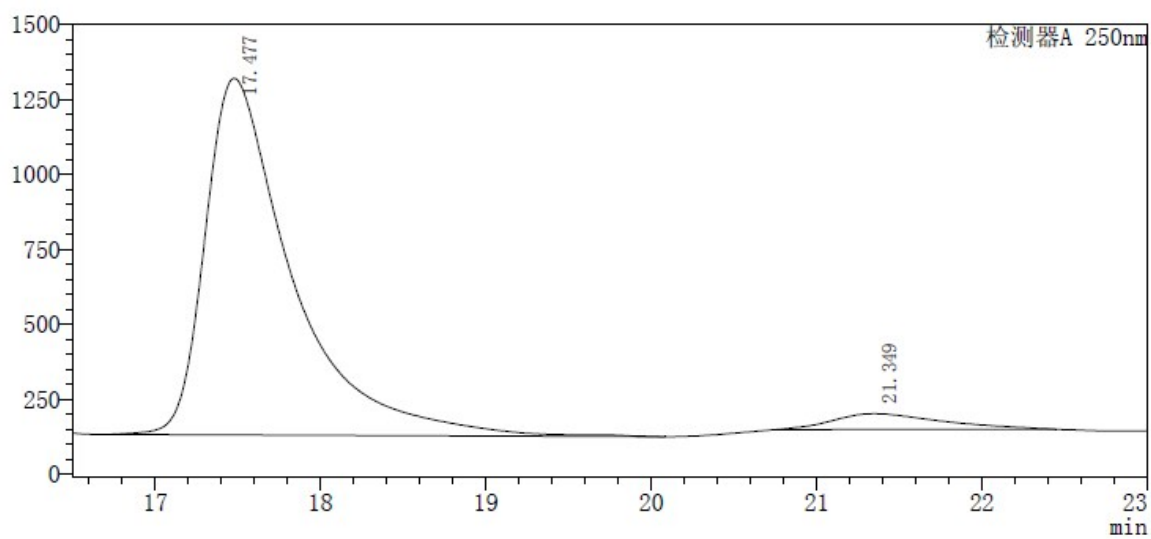
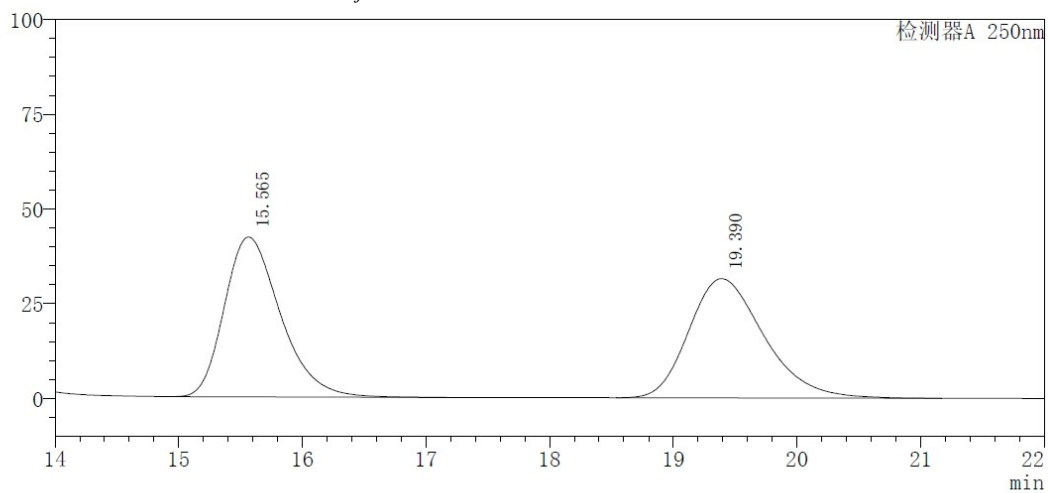
15. HPLC

15.1 Aminolysis of trans-Stilbene Oxide with Anilines

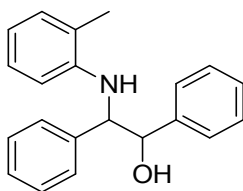


1,2-diphenyl-2-(phenylamino)ethanol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 90/10, 0.75 mL/min, 250 nm), $t_{major} = 17.477$ min, $t_{minor} = 21.349$ min; ee=90%.

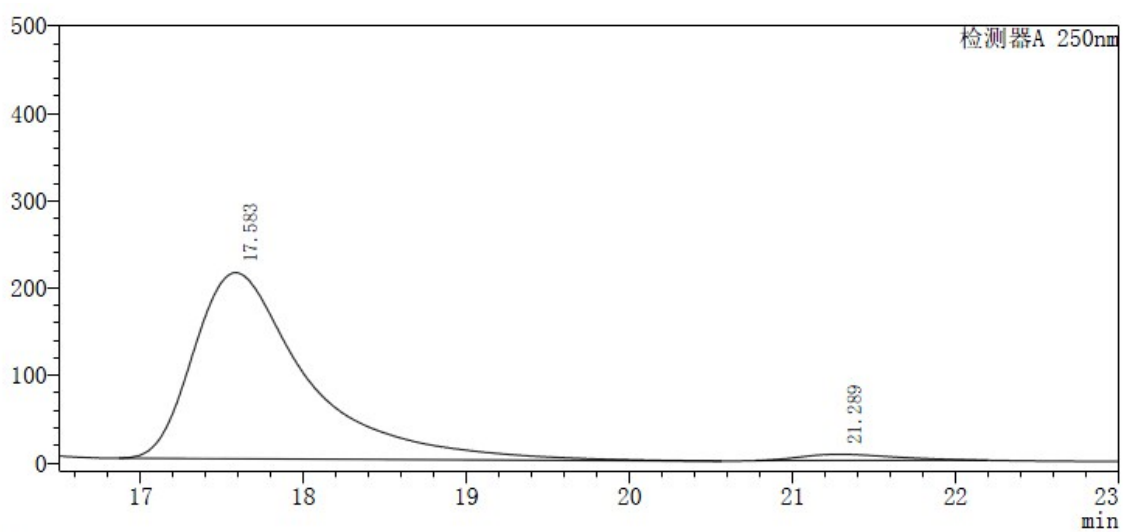
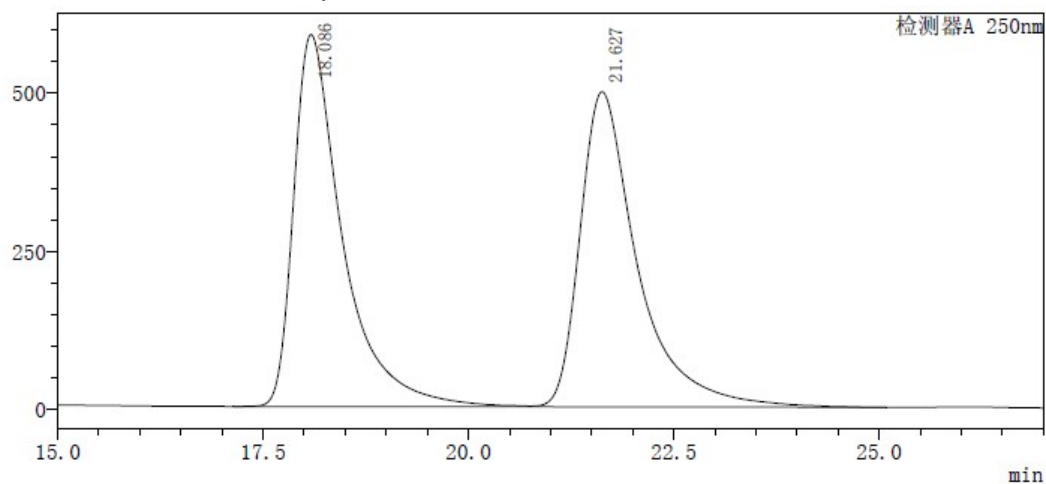


Serial Number	Retention Time [min]	Area %
1	17.477	94.720
2	21.349	5.280

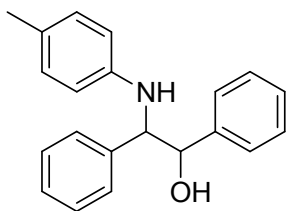


2-((*o*-methylphenyl)amino)-1,2-diphenylethanol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 17.583$ min, $t_{minor} = 21.289$ min; ee=94.5%.

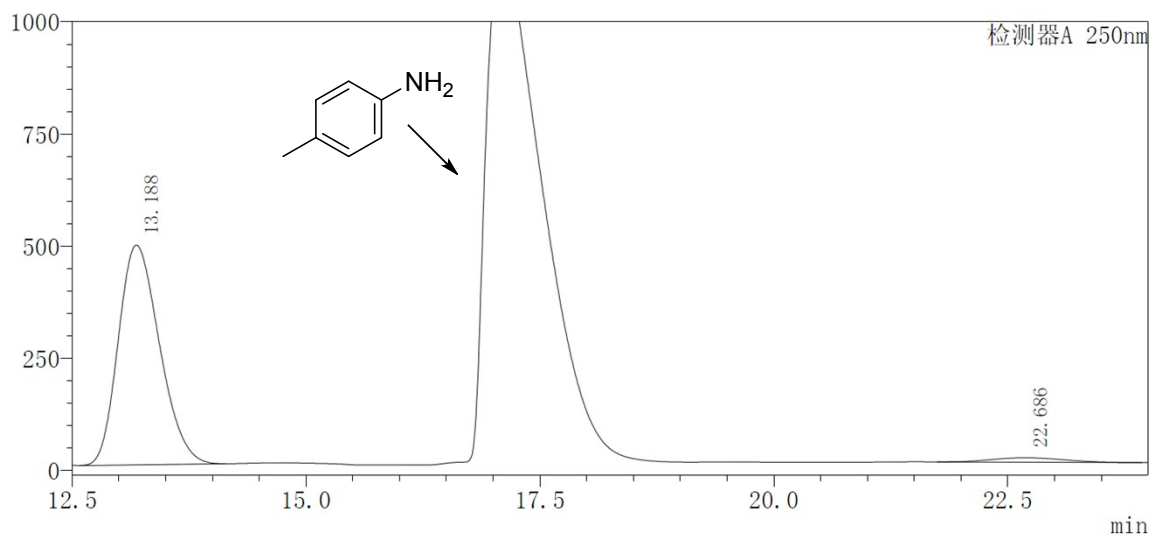
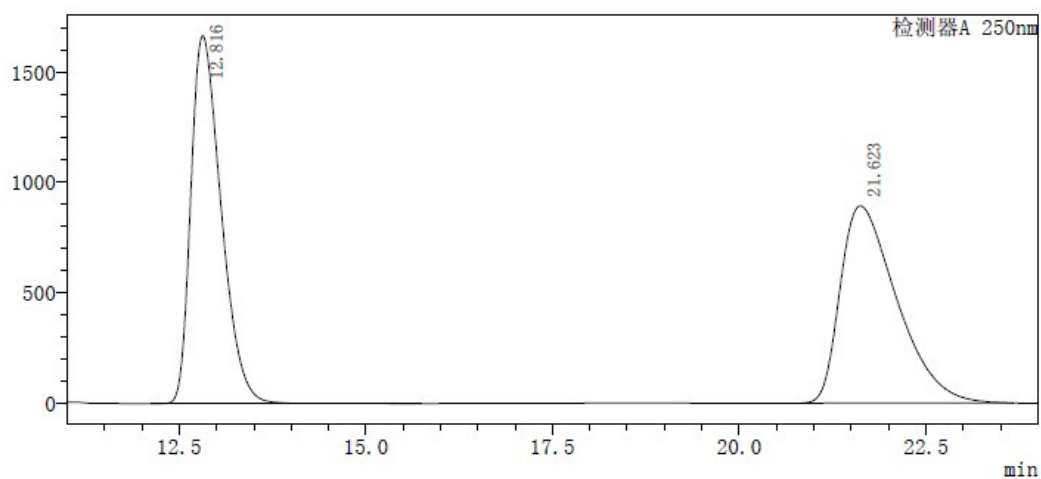


Serial Number	Retention Time [min]	Area %
1	17.583	97.259
2	21.289	2.741

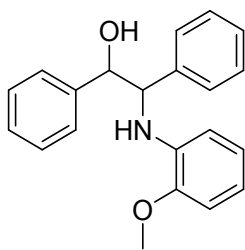


2-((*p*-methylphenyl)amino)-1,2-diphenylethanol

Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/*i*-PrOH = 90/10, 1.0 mL/min, 250 nm), $t_{major} = 13.188$ min, $t_{minor} = 22.686$ min; ee=93%.

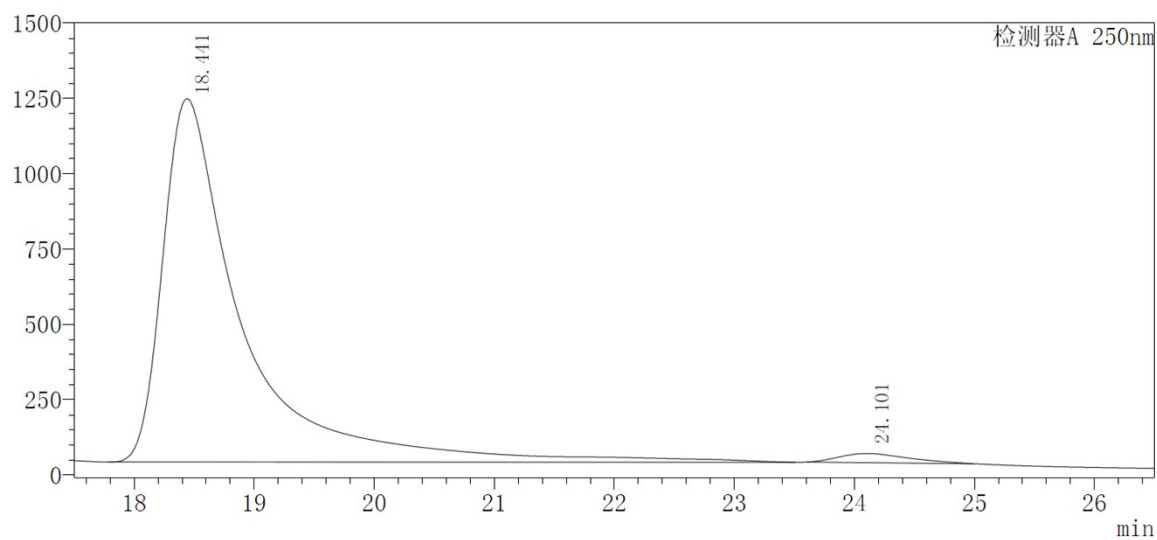
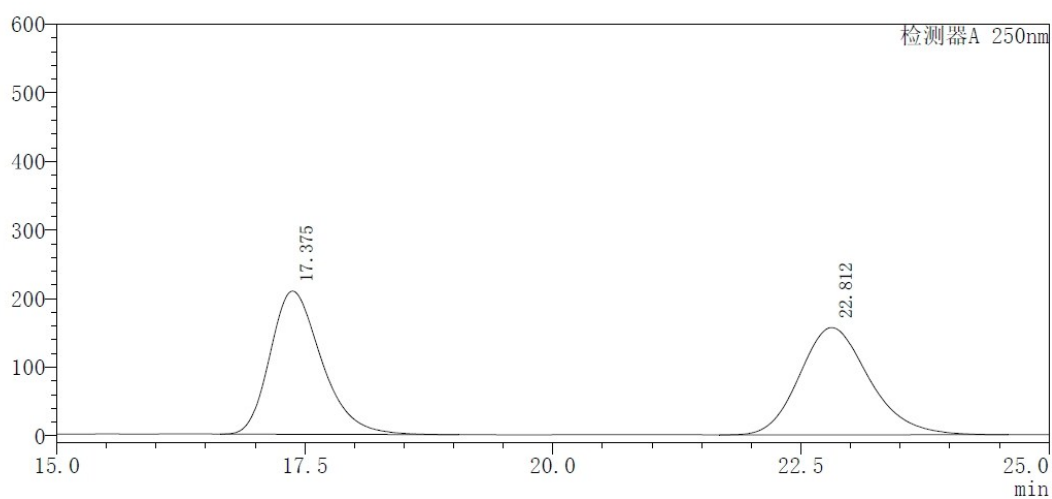


Serial Number	Retention Time [min]	Area %
1	13.188	96.542
2	22.686	3.458

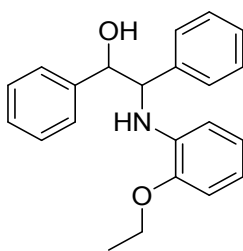


2-((2-methoxyphenyl)amino)-1,2-diphenylethanol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 90/10, 0.75 mL/min, 250 nm), $t_{major} = 18.441$ min, $t_{minor} = 24.101$ min; ee = 96%.

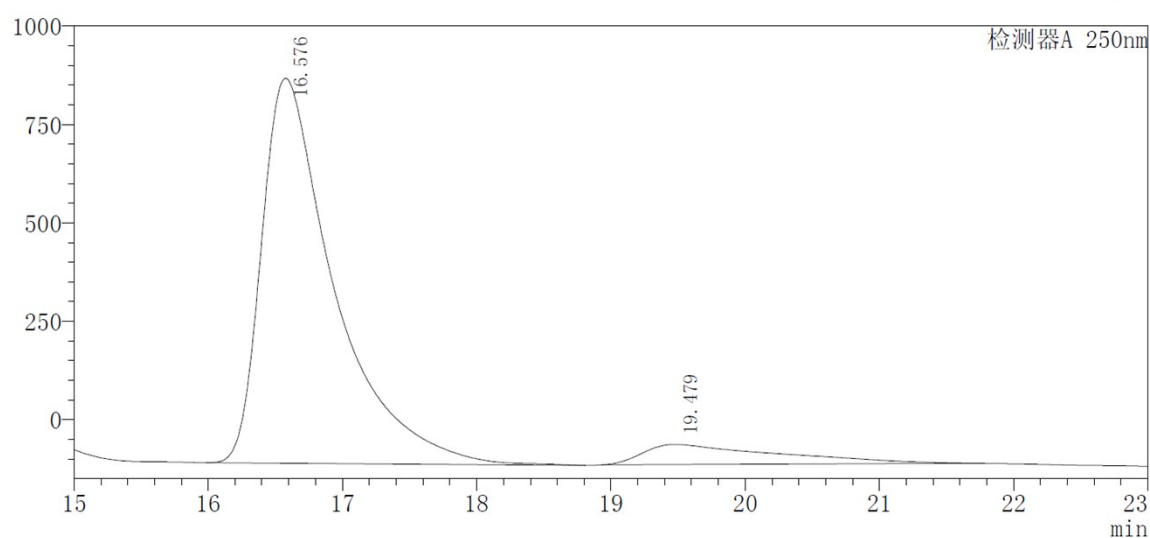
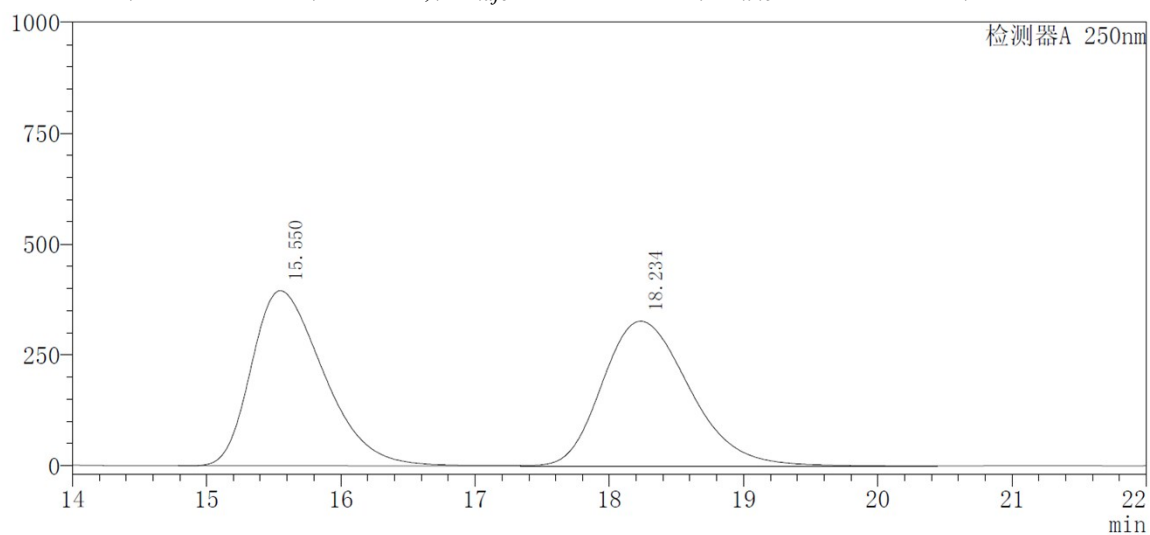


Serial Number	Retention Time [min]	Area %
1	18.441	97.879
2	24.101	2.121

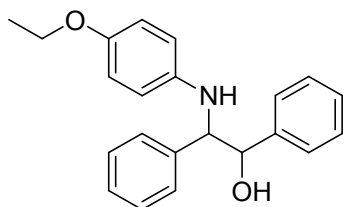


2-((2-ethoxyphenyl)amino)-1,2-diphenylethanol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 90/10, 0.75 mL/min, 250 nm), $t_{major} = 16.576$ min, $t_{minor} = 19.479$ min; ee = 82%.

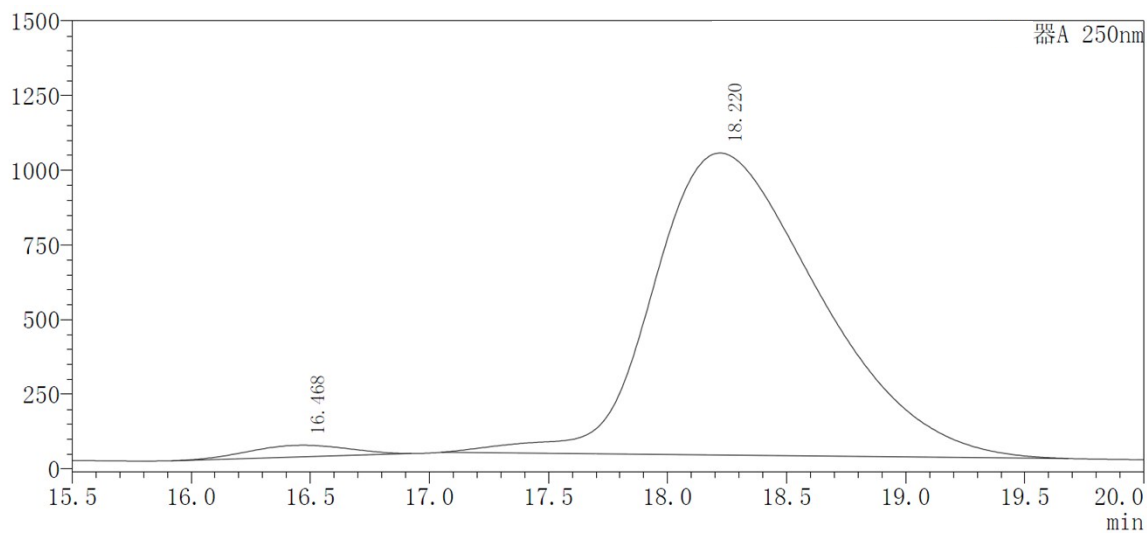
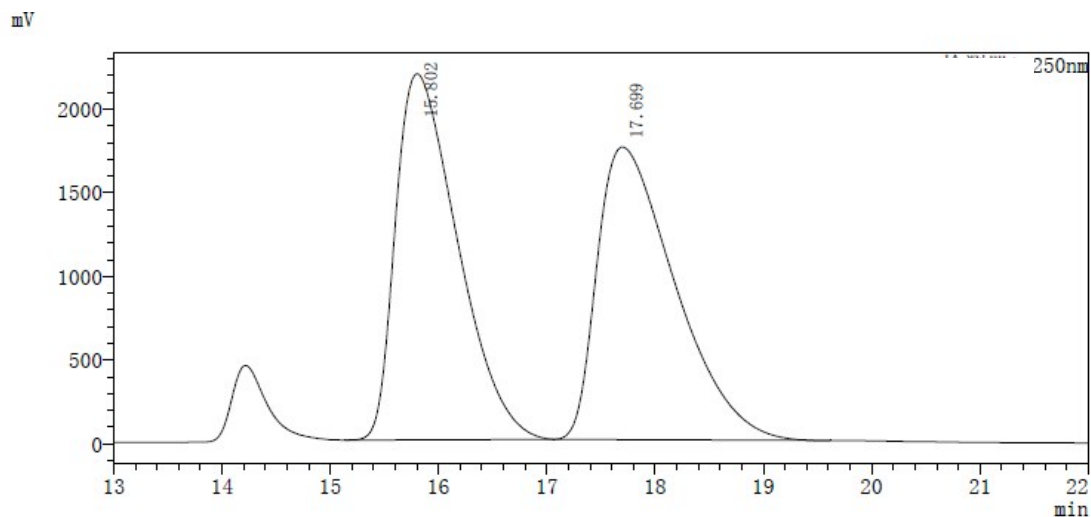


Serial Number	Retention Time [min]	Area %
1	16.576	91.245
2	19.479	8.755



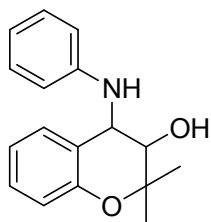
2-((4-ethoxyphenyl)amino)-1,2-diphenylethanol

Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/*i*-PrOH = 90/10, 1.0 mL/min, 250 nm), $t_{major} = 18.220$ min, $t_{minor} = 16.468$ min; ee = 96%.



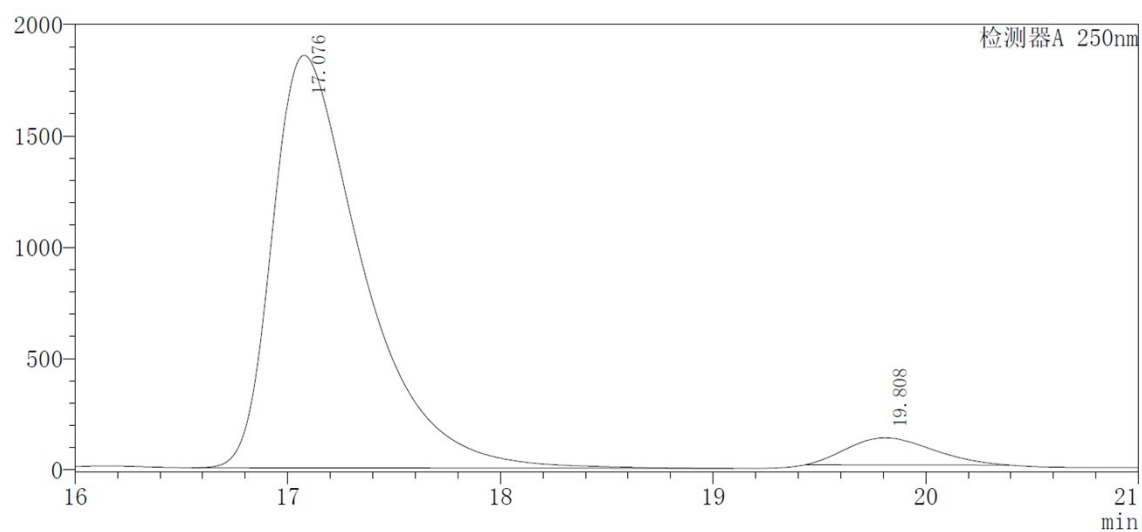
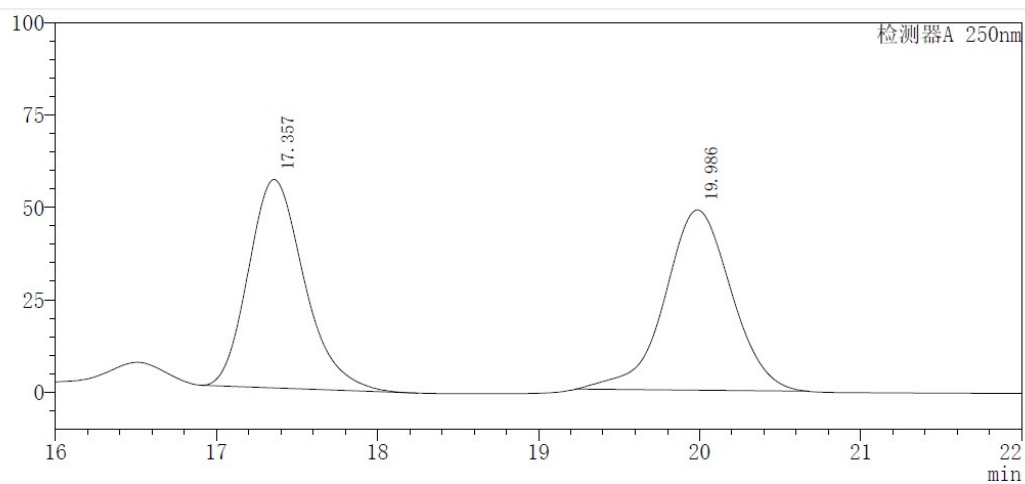
Serial Number	Retention Time [min]	Area %
1	16.468	2.261
2	18.220	97.739

15.2 Alkene Epoxidation/Epoxide Aminolysis

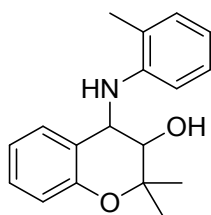


2,2-dimethyl-4-(phenylamino)chroman-3-ol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 17.076$ min, $t_{minor} = 19.808$ min; ee = 88%.

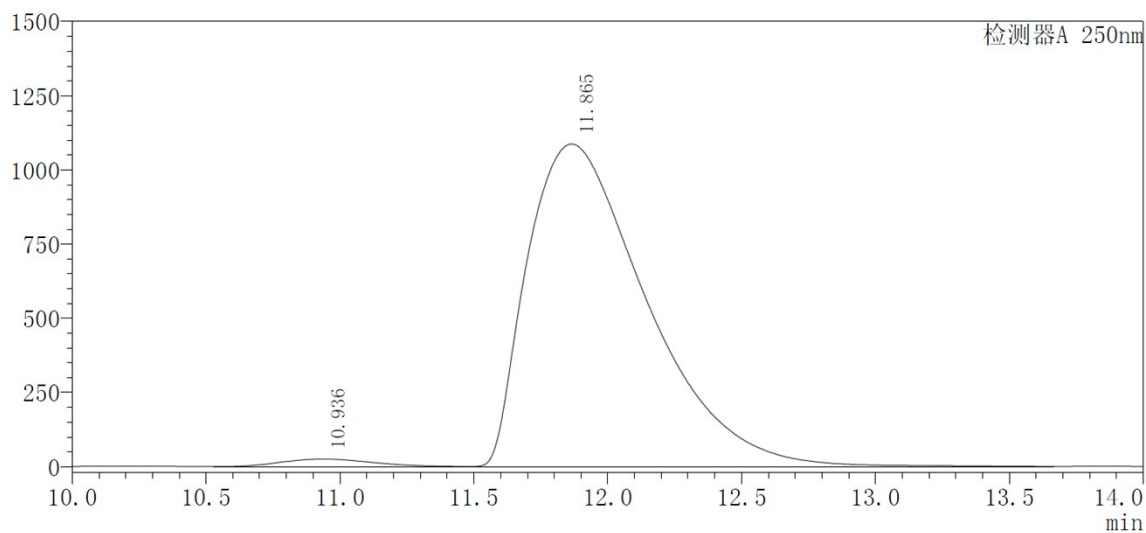
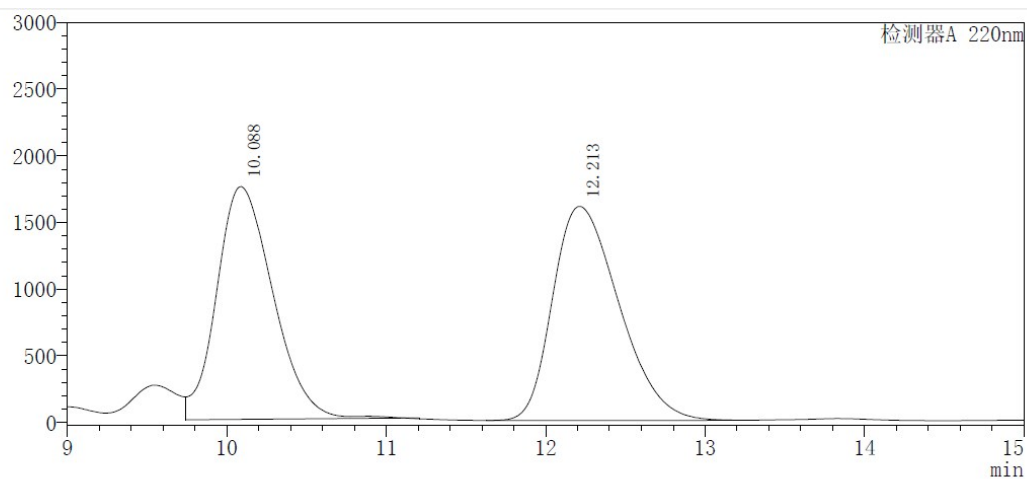


Serial Number	Retention Time [min]	Area %
1	17.076	94.132
2	19.808	5.868

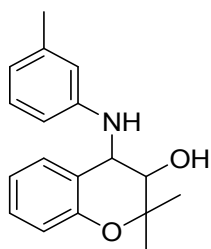


2,2-dimethyl-4-(o-tolylamino)chroman-3-ol

Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 11.865$ min, $t_{minor} = 10.936$ min; ee = 97%.

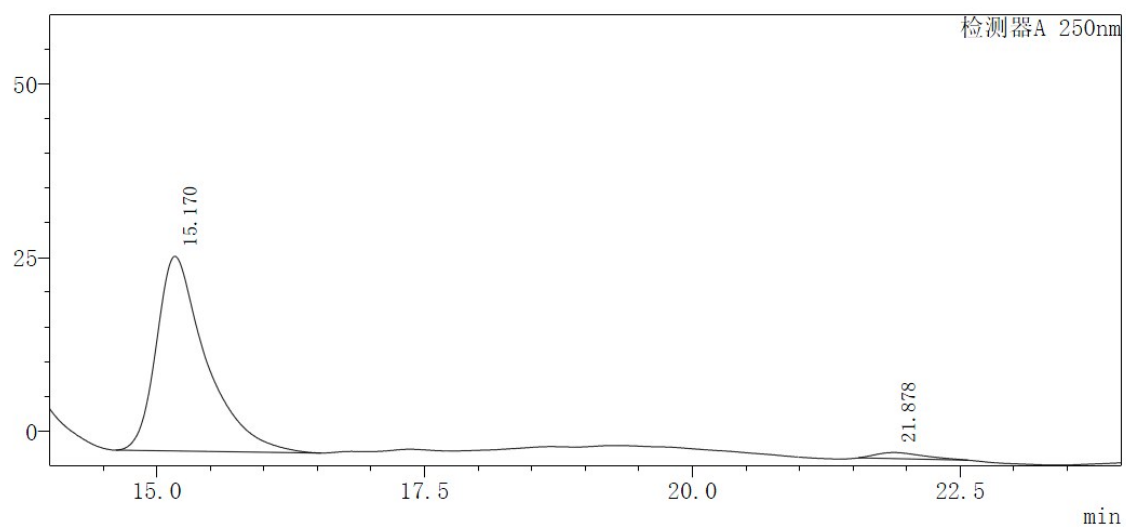
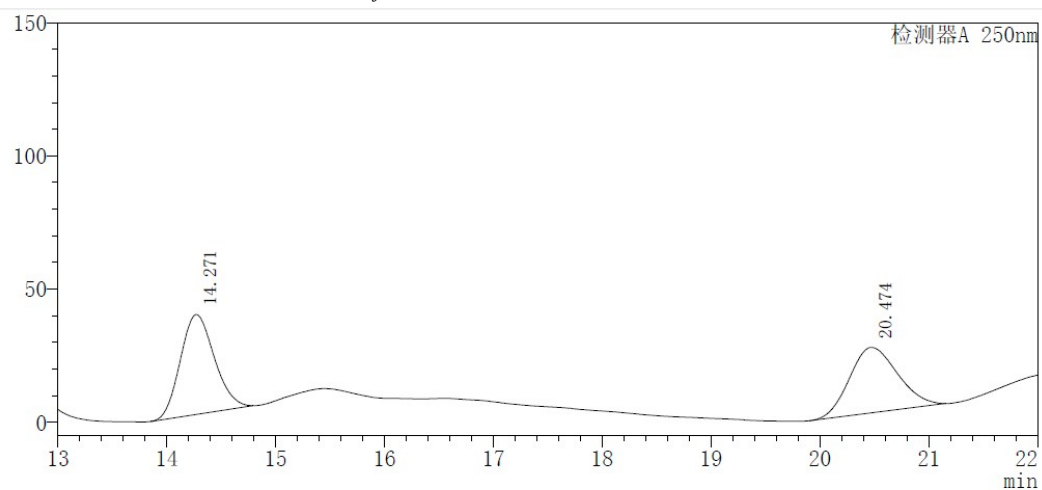


Serial Number	Retention Time [min]	Area %
1	10.936	1.750
2	11.865	98.250

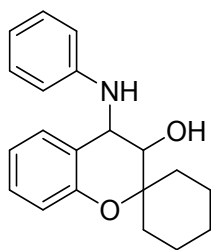


2,2-dimethyl-4-(m-tolylamino)chroman-3-ol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 15.170$ min, $t_{minor} = 21.878$ min; ee = 94%.

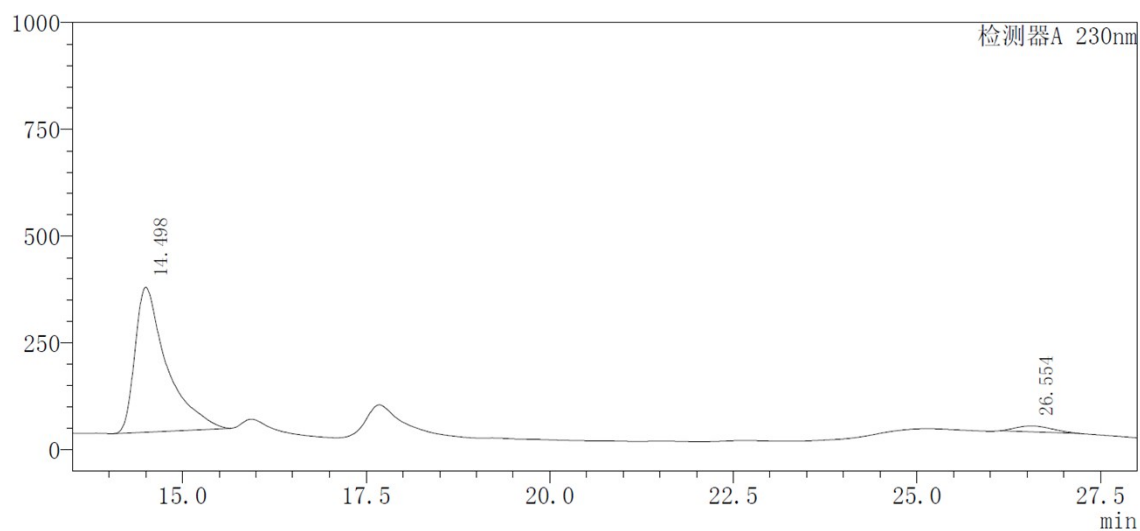
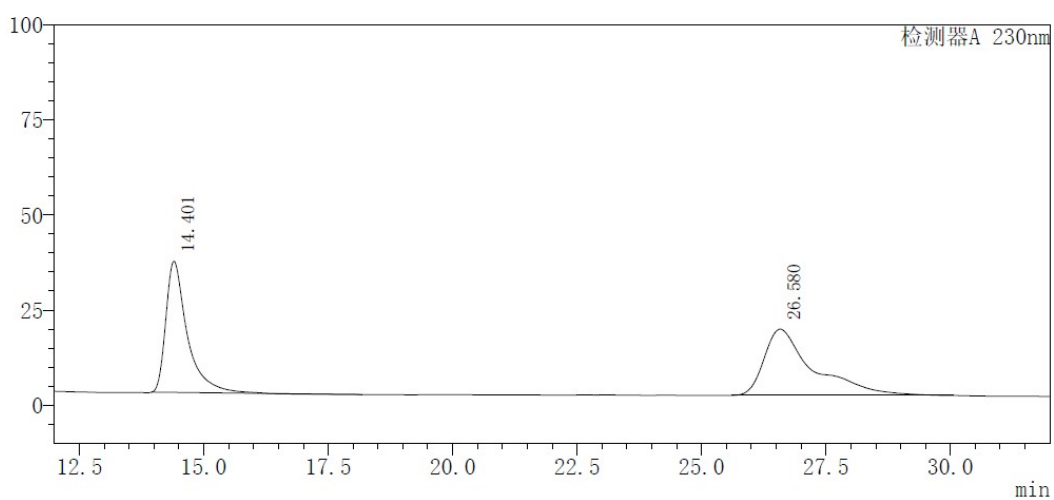


Serial Number	Retention Time [min]	Area %
1	15.170	97.065
2	21.878	2.935

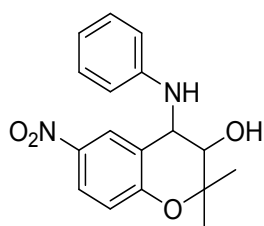


4-(phenylamino)spiro[chroman-2,1'-cyclohexan]-3-ol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 14.498$ min, $t_{minor} = 26.554$ min; ee = 91%.

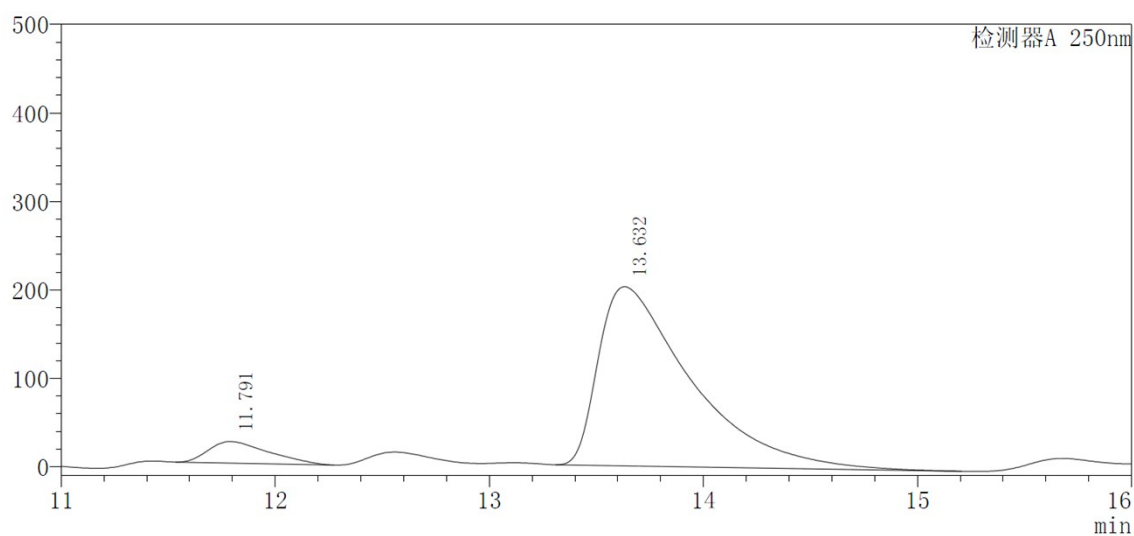
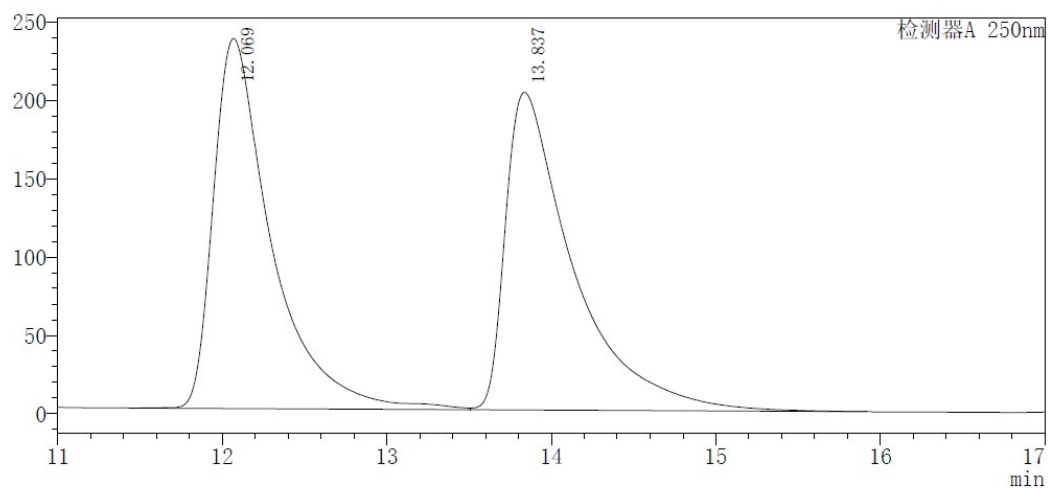


Serial Number	Retention Time [min]	Area %
1	14.498	95.687
2	26.554	4.313

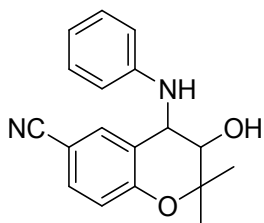


2,2-dimethyl-6-nitro-4-(phenylamino)chroman-3-ol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 13.632$ min, $t_{minor} = 11.791$ min; ee = 86%.

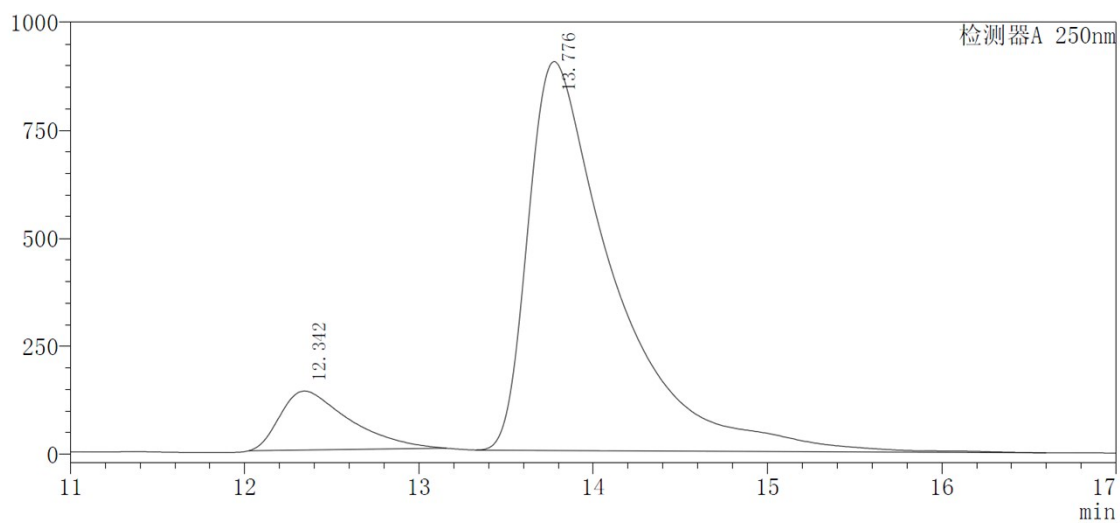
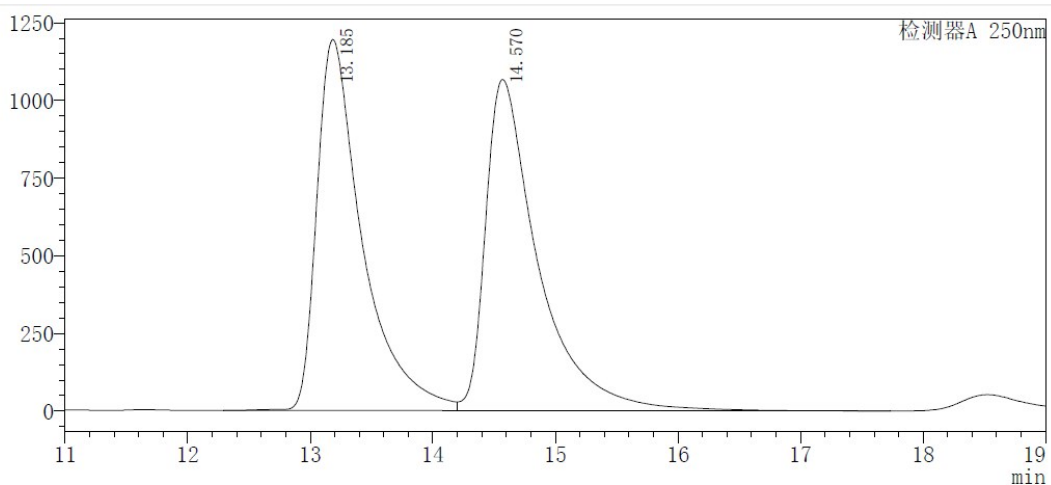


Serial Number	Retention Time [min]	Area %
1	11.791	7.271
2	13.632	92.729

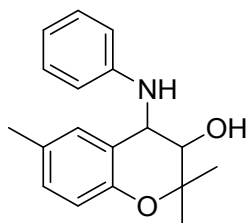


3-hydroxy-2,2-dimethyl-4-(phenylamino)chroman-6-carbonitrile

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 11.776$ min, $t_{minor} = 12.342$ min; ee = 80%.

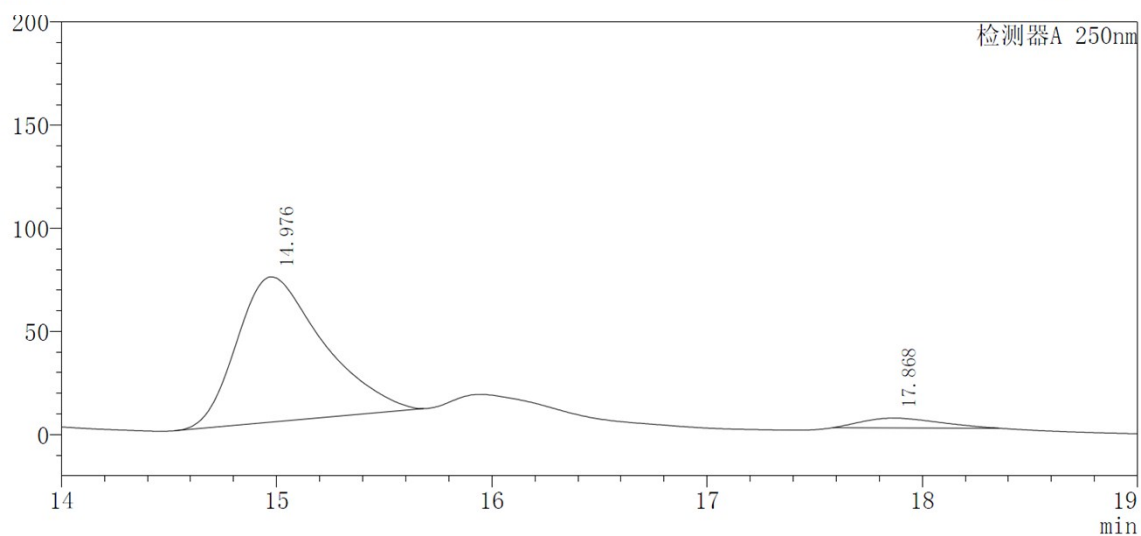
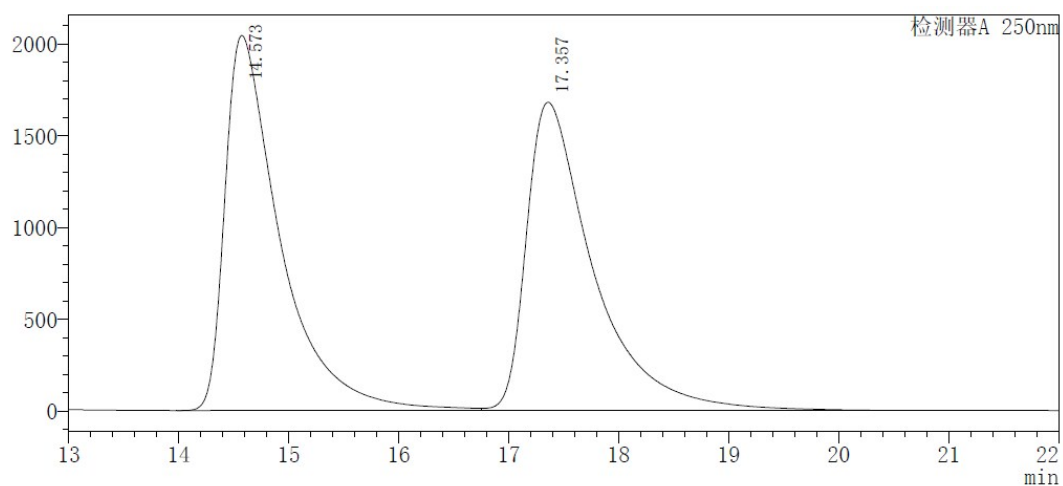


Serial Number	Retention Time [min]	Area %
1	12.342	10.034
2	13.776	89.966



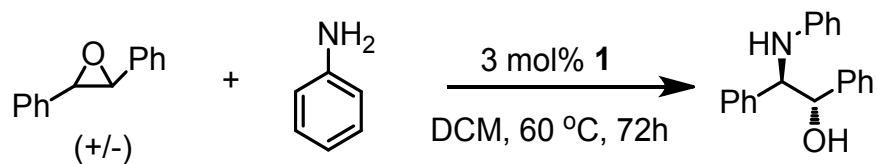
6-methyl-2,2-dimethyl-4-(phenylamino)chroman-3-ol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 14.976$ min, $t_{minor} = 17.868$ min; ee=89%.



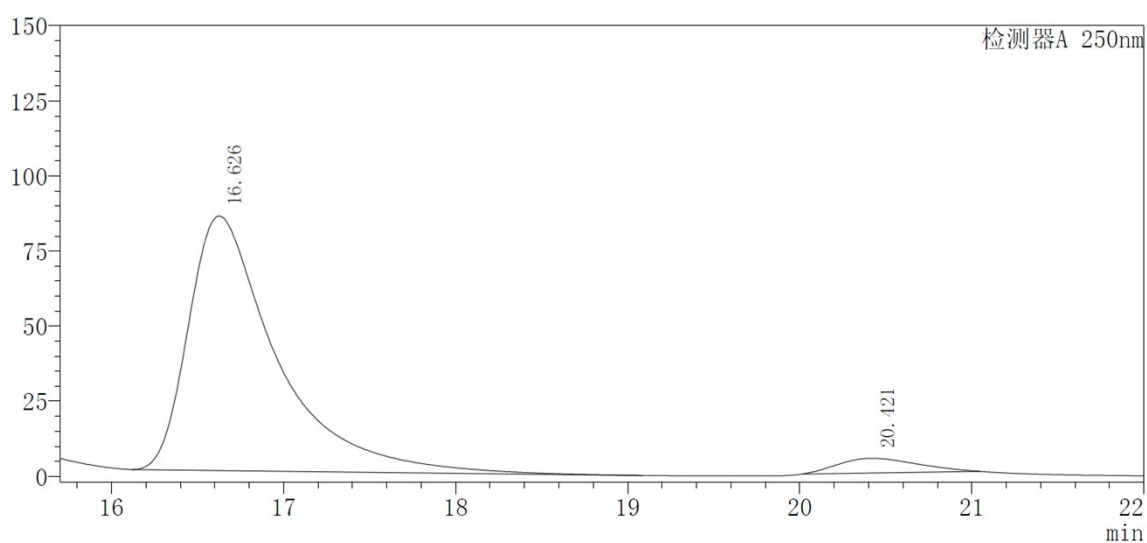
Serial Number	Retention Time [min]	Area %
1	14.976	94.316
2	17.868	5.684

15.3 Recycle Experiments



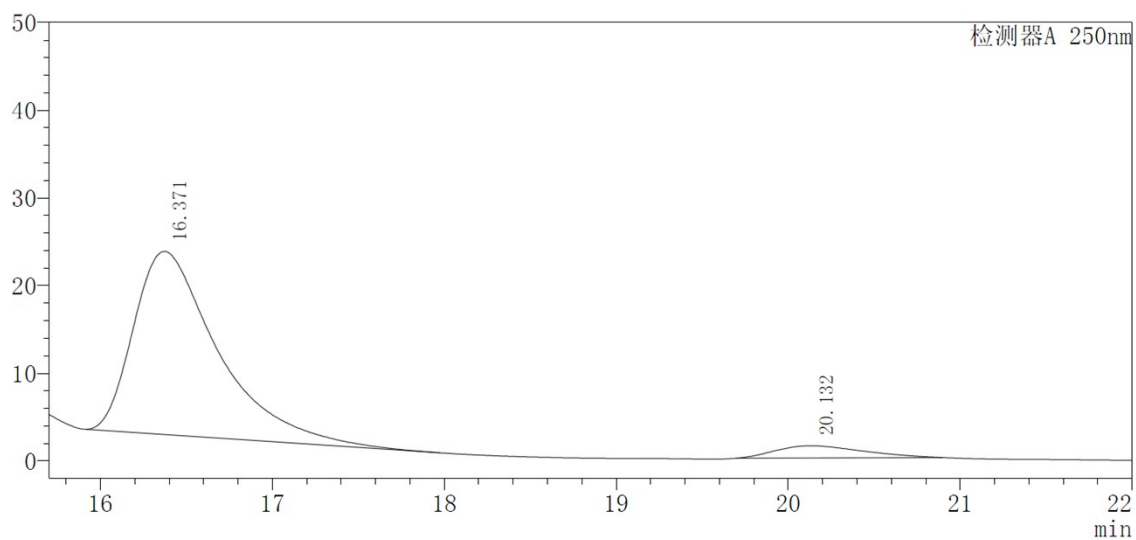
Run	conv.(%)	ee (%)
1	88	90
2	84	87
3	85	87
4	84	82
5	83	83

Run 1



Serial Number	Retention Time [min]	Area %
1	16.626	95.044
2	20.421	4.956

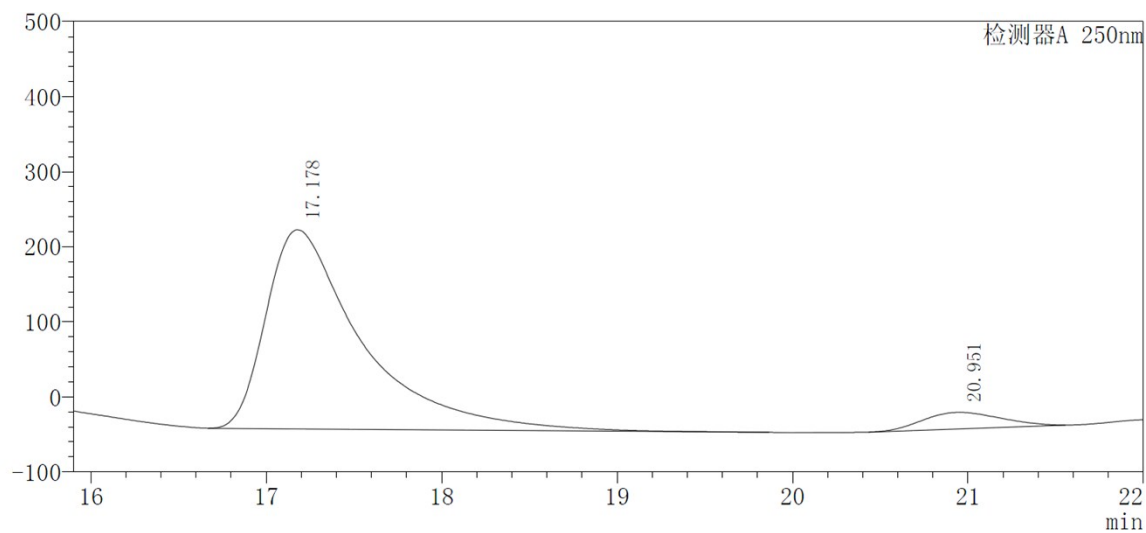
Run 2



Serial Number	Retention Time [min]	Area %
1	16.371	
2	20.132	

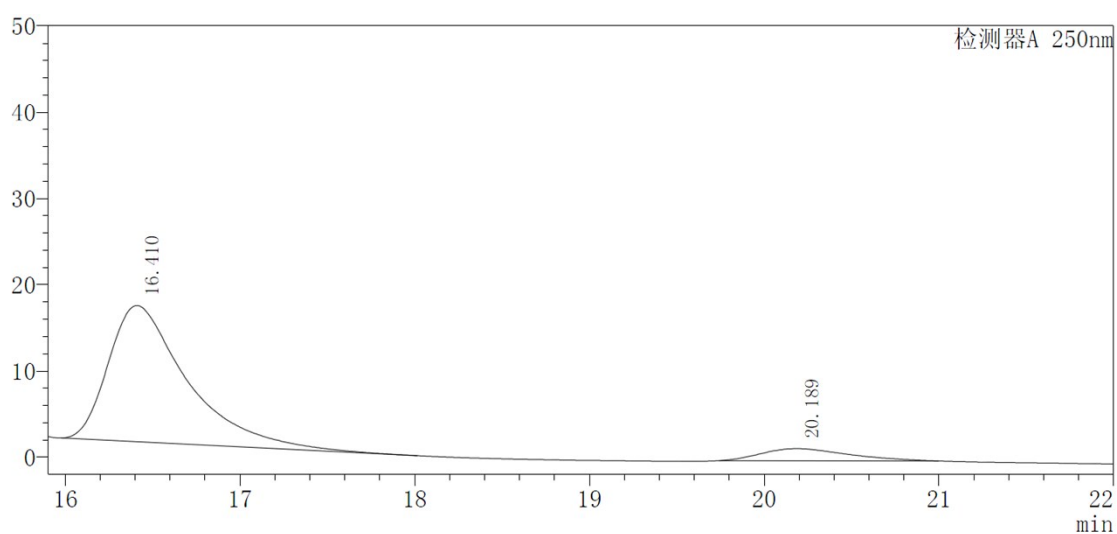
1	16.371	93.478
2	20.132	6.522

Run 3



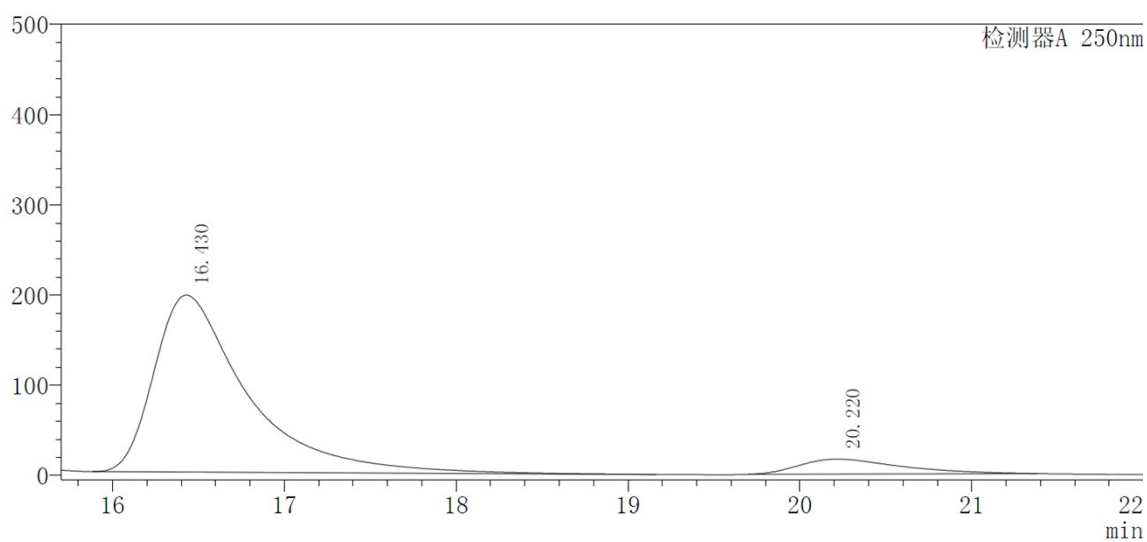
Serial Number	Retention Time [min]	Area %
1	17.178	93.663
2	20.951	6.337

Run 4



Serial Number	Retention Time [min]	Area %
1	16.410	91.045
2	20.189	8.955

Run 5

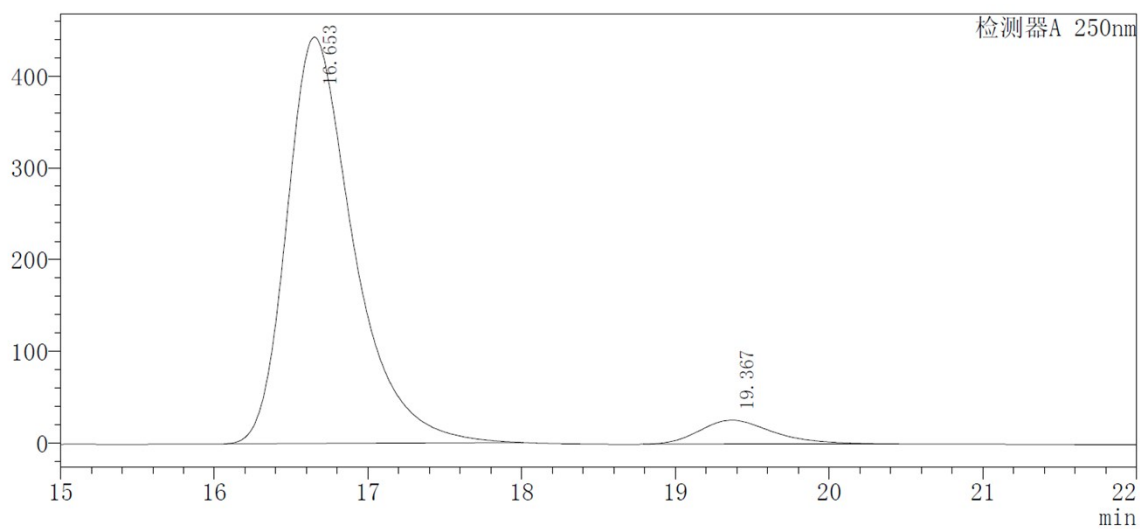


Serial Number	Retention Time [min]	Area %
1	16.430	91.503
2	20.220	8.479



Run	conv (%)	ee (%)
1	89	88
2	87	86
3	84	87
4	83	84
5	79	86

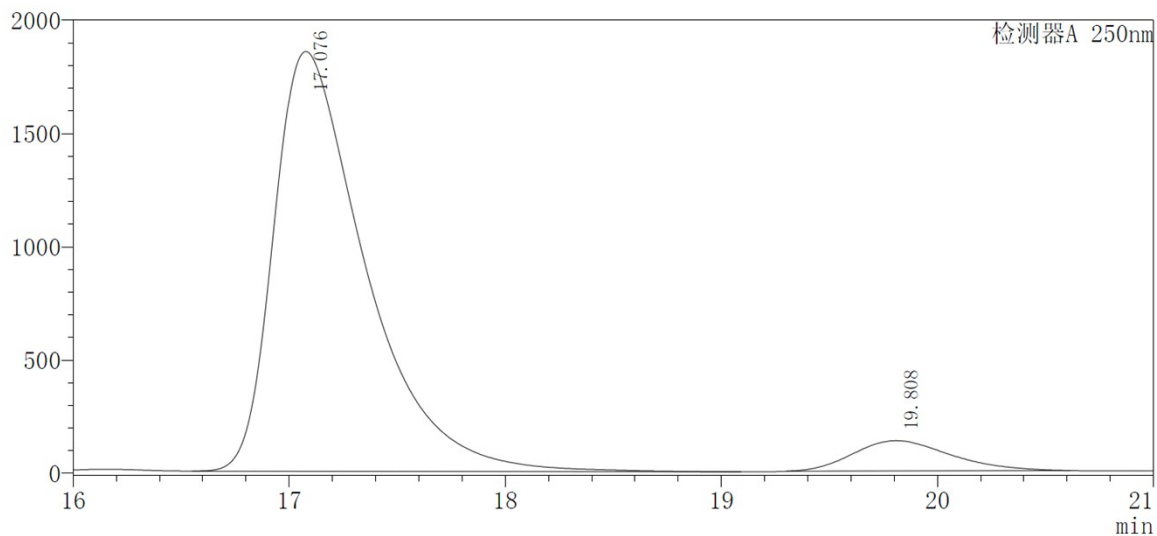
Run 1



Serial Number	Retention Time [min]	Area %
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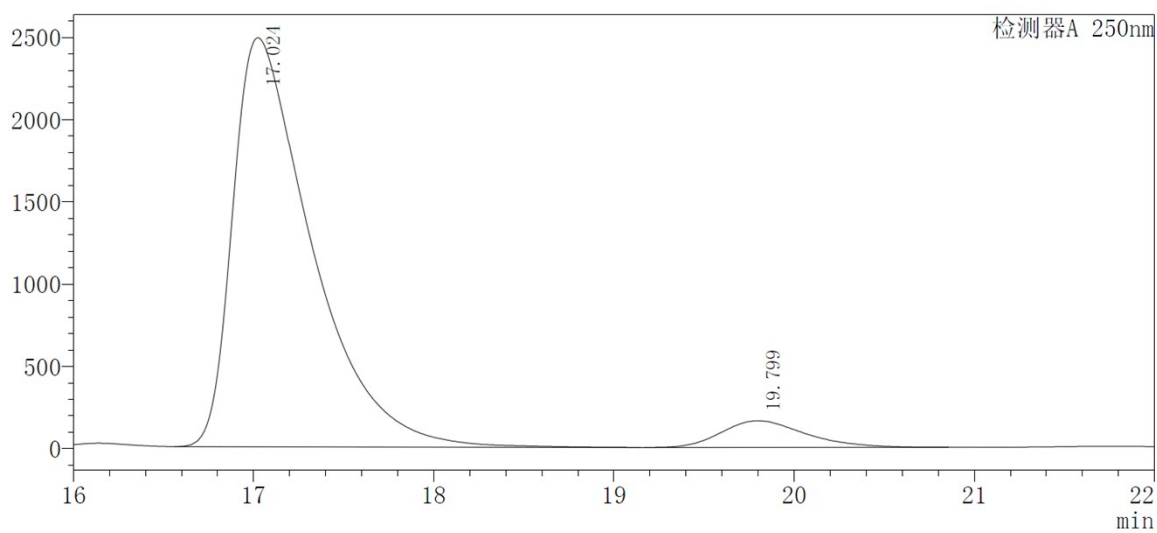
1	16.653	93.951
2	19.367	6.049

Run 2



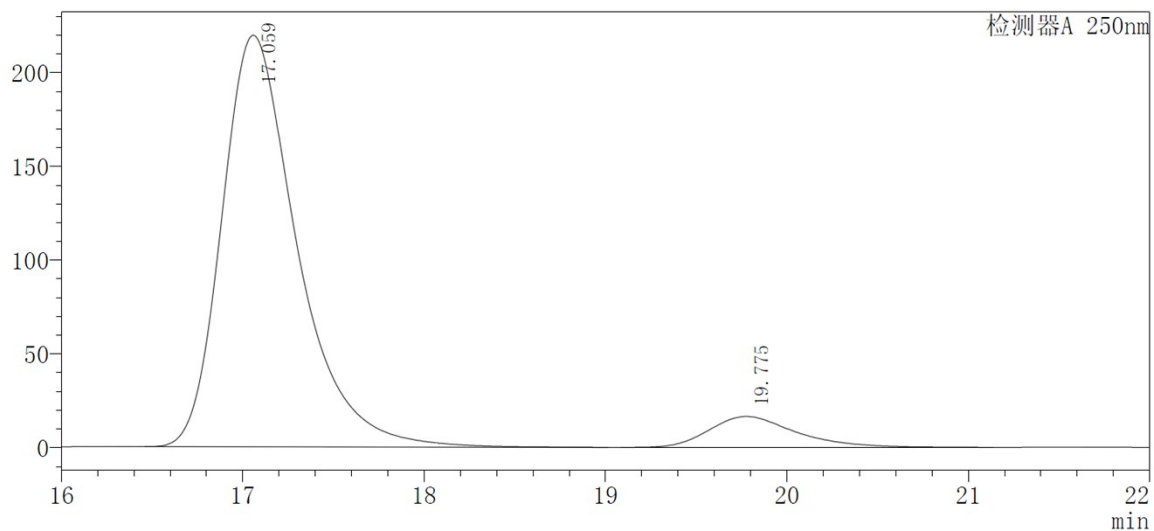
Serial Number	Retention Time [min]	Area %
1	17.076	92.864
2	19.808	7.136

Run 3



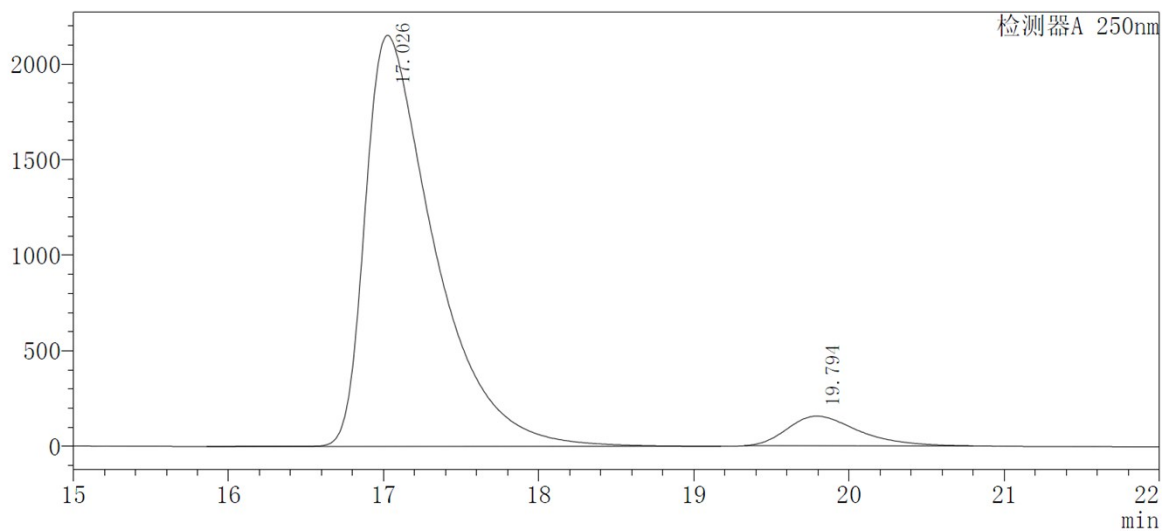
Serial Number	Retention Time [min]	Area %
1	17.024	93.508
2	19.799	6.492

Run 4



Serial Number	Retention Time [min]	Area %
1	17.059	91.981
2	19.775	8.019

Run 5



Serial Number	Retention Time [min]	Area %
1	17.026	93.108
2	19.794	6.892

Reference

1. Yang, Z.; Zhu, C.; Li, Z.; Liu, Y.; Liu, G.; Cui, Y. *Chem. Commun.*, **2014**, *50*, 8775-8778.
2. Cho, S. H.; Ma, B. Q.; Nguyen, S. B. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.*, **2006**, 2563-2565