Supporting Information for

A Cr(salen)-Based Metal-Organic Framework as Versatile Catalyst for Efficient Asymmetric Transformations

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1. Materials and general procedures

All of the chemicals are commercial available, and used without further purification. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. 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 ^{o}C/min on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. NMR experiments were carried out on a MERCURY plus 400 spectrometer operating at resonance frequencies of 400 M Hz. ESI-MS spectrum was recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase. ICP-OES was performed on Optima 7300DV ICP-OES (Perkin Elmer Coporation, USA). Analytical high performance liquid chromatography (HPLC) was performed on YL-9100 HPLC. Analytical CHIRALCEL OD-H, AD-H, AS-H or OJ-H column from Daicel was 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^{o}C under vacuum (< 10^{-3} torr) for 4h.

X-ray Crystallography. Single-crystal XRD data for **1** was collected on a Bruker SMART APEX II CCD-based X-ray diffractometer with Cu-Kα radiation (λ = 1.54178 Å) at 116 K. We have collected about several datasets for **1** using Cu-Kα radiation. Among the several datesets for **1**, 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 using direct method, and refined by full-matrix least-squares on F^2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). All non-H atoms (except water and methanol molecules), were refined anisotropically. Due to the relatively weak diffraction, only parts of the guest molecules could be found in difference Fourier maps and all the phenyl rings are constrained to ideal six-membered rings. Contributions to scattering due to these highly disordered solvent molecules were removed using the *SQUEEZE* routine of *PLATON*; the structures were then refined again using the data generated under *OLEX2-1.2* (Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl.Crystallogr.* **2009**, 42, 339-341). Crystal data and details of the data collection are given in **Table S1**, while the selected bond distances and angles are presented in **Table S2**. CCDC 1449027 (**1**)

contains the supplementary crystallographic data for this paper. The 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 H_4**L** and H_2**L**-Me_2 were synthesized according to the published procedures (Zhu, C.; Yuan, G.; Chen, X.; Yang, Z.; Cui, Y. *J. Am. Chem. Soc.*, **2012,** *134*, 8058–8061).

2.1 Synthesis of [Cr(H_2L)Cl]

A solution of (*R*,*R*)-(-)-N,N'-bis(3-carboxyl-5-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (0.25 g, 1 mmol) in dry THF (50 mL) was degassed for 20 minutes. $CrCl_2$ (0.134 g, 1.1 mmol) was then added to the solution and the reaction mixture was stirred at 55 ^oC for 2h. The mixture was then cooled to room temperature, exposed to air, and stirred overnight. The brown solid was collected by filtration, washed with MeOH and dried under reduced pressure to give [Cr(H_2**L**)Cl] in 83% yield. ESI-MS m/z: 572.2 (Calcd m/z 572.2 for $[M-Cl]^+$). IR (KBr pellet, ν/cm^{-1}): 3403 (w), 2949 (s), 2863 (w), 1674(s), 1624 (s), 1599 (s), 1540(s), 1468 (m), 1395 (m), 1384 (s), 1350 (s), 1297 (s), 1283 (s), 1253 (m), 1227 (m), 1177 (m), 1028 (w), 959(w), 921 (m), 810 (m), 793 (m), 696(m), 562 (w), 509 (m).

2.2 Synthesis of [Cr(Me_2L)Cl]

A mixture of H_2(Me_2**L**) (0.203 mmol), $CrCl_2$ (0.244 mmol), and dry THF (4 mL) was heated at 55 ^oC for 3h. The reaction was then cooled to room temperature, exposed to air, and stirred overnight. The mixture was diluted with DCM (20 mL), washed with saturated aqueous NH_4Cl and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the desired product as a brown solid in 93% yield. ESI-MS m/z: 600.2 (Calcd m/z 600.3 for $[M-Cl]^+$). IR (KBr, cm^{-1}): 3414 (w), 2948 (s), 2866 (m), 1694 (s), 1628 (s), 1621 (s), 1504 (s), 1466 (s), 1434 (s), 1417 (s), 1389 (s), 1350 (s), 1299 (s), 1284 (s), 1251(s), 1223 (s), 1171 (s), 1126 (m), 1028(w), 827(m), 792 (m), 769 (w), 714 (w), 560(w), 519(m).

2.3 Synthesis of MOF 1

A mixture of CdI_2 (14 mg, 0.04 mmol), [Cr(H_2**L**)Cl] (24 mg, 0.04 mmol), NaOAc (10 mg, 0.07 mmol), DMF (5 mL), THF (5 mL), MeOH (2 mL) and H_2O (1 mL) in a capped vial was heated at 100 ^oC for four days. The mixture was then cooled to room temperature. Red block-like crystals of **1** were collected, washed with

MeOH and Et_2O, and dried in air. Yield: 42mg, 35.4%. The products can be best formulated as $[Na_5Cd_2(Cr\mathbf{L})_4(OH)_2(O_2CCH_3)(O_2CH)_2(H_2O)_7(CH_3OH)_3]\cdot 12H_2O$ on the basis of microanalysis, IR, TGA and single-crystal diffraction.

Elemental Analysis and IR for **1**: Anal (%). Calcd for $C_{127}H_{193}Cd_2Cr_4N_8Na_5O_{54}$: C, 47.03; H, 6.00; N, 3.45. Found: C, 47.50; H, 5.89; N, 3.59. ICP measurement indicated the ratio of Na:Cd:Cr is 5:2:4

IR (KBr, cm^{-1}): 3434 (w), 2946 (s), 2856 (w), 1634 (s), 1596 (s), 1558(s), 1467 (m), 1384 (m), 1320 (s), 1223 (m), 1197 (m), 1133 (m), 1017 (w), 934(w), 786 (m), 716 (m), 586(m), 522 (w).

3. Experimental procedure for asymmetric catalysis

3.1 Nazarov Cyclization Reaction

A suspension of **1** (5.0 mol% equiv. based on Cr(salen)) and 4Å MS (30 mg) in dry CH_2Cl_2 (0.5 mL) was stirred under nitrogen at room temperature, and then a solution of divinyl ketone (0.1 mmol) in dry CH_2Cl_2 (0.5 mL) was added. After the reaction was completed, the mixture was centrifuged at 9000 rpm for 5min and the supernatant was concentrated under vacuum, and the crude product was purified by silica gel column chromatography to give the corresponding cyclopentenone. The conversion and diastereomer ratio were determined by ^1H NMR, and the ee value was determined by HPLC analysis.

3.2 Aminolysis of trans-Stilbene Oxide

To a suspension of **1** (5.0 mol% equiv. based on Cr(salen)) in CH_2Cl_2 (0.5 mL) was added the trans-stilbene oxide (0.2 mmol) at room temperature under nitrogen. After stirring for 15 min, the aniline (0.1 mmol) was added. After the reaction completed, the mixture was centrifuged at 9000 rpm for 5min, and the supernatant was concentrated under vacuum. The crude product was purified by silica gel column chromatography. The conversion and ee value were determined by ^1H NMR and HPLC analysis, respectively.

3.3 Diels-Alder Reaction

A suspension of **1** (5.0 mol% equiv. based on Cr(salen)) and 4Å MS (30 mg) in dry CH_2Cl_2 (0.5 mL) was stirred under nitrogen at room temperature, and the solutions of diene (0.1 mmol) and olefine aldehyde (0.2 mmol) in dry CH_2Cl_2 (0.5 mL) were then added. After the reaction completed, the mixture was centrifuged at 9000 rpm for 5min, and the supernatant was concentrated under vacuum. The crude product was purified by silica gel column chromatography. The conversion and ee value were

determined by ^{1}H NMR and HPLC analysis, respectively.

3.4 Hetero-Diels-Alder Reaction

To a suspension of **1** (5.0 mol% equiv. based on Cr(salen)) and 4Å MS (30 mg) in dry CH_2Cl_2 (0.5 mL) were added aldehyde (0.10 mmol) and 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (0.12 mmol) at -20 ^oC under nitrogen. After the reaction completed, the insoluble solids were removed by filtration. The filter liquor was treated with TFA and stirred for another 5 min. The mixture was concentrated, and the residue was purified by silica gel column chromatography to give the corresponding product. The conversion and ee value were determined by ^{1}H NMR and HPLC analysis, respectively.

The four catalytic reactions catalyzed by Cr(Me_2**L**)Cl were performed in a similar procedure.

3.5 The procedure for recycled experiments (using Nazarov cyclization as an example)

After experimental section **3.1**, the recycled catalyst which contained 4Å MS was washed with CH_2Cl_2 for 3 times, sonicated for 10 min and dried under pressure. To a stirred suspension of recycled **1** and 4Å MS (30 mg) in dry CH_2Cl_2 (0.5 mL) was added a CH_2Cl_2 (0.5 mL) solution of divinyl ketone (0.1 mmol) under nitrogen at room temperature. After the reaction completed, the following workup is identical to section **3.1**.

The recycled experimental of other three catalytic reactions were performed in a similar procedure.

4. Dye uptake measurements

Fresh crystals of **1** (2.50 mg) were briefly dried and then soaked in an aqueous solution of Rhodamine 6G (60 mg) overnight. The resulted samples were washed with water thoroughly until the washings became colorless (The channels of the MOF are hydrophobic so water cannot easily get in the channels to wash out the dye molecules inside the channels). 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 red color was diluted to 50 mL. Absorption experiments were performed on Lambda 20 UV/Vis Spectrometer.

Creation of a standard curve: (1) The Rhodamine 6G (32.7 mg) was added to a flask and diluted to 1000 mL. The solution of Rhodamine 6G 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 Rhodamine 6G was determined by UV/Vis

Spectrometer. Data for known concentrations of Rhodamine 6G 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.

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

The methyl orange (MO) uptake measurements were conducted in the same way.

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

Identification code	**1**
CCDC	1449027
Empirical formula	C127H139Cd2Cr4N8Na5O42
Formula weight	2997.20
Temperature (K)	116.15 K
Wavelength (Å)	1.54178
Crystal system	Orthorhombic
Space group	F222
Unit cell dimensions	a = 40.623(2) Å b = 41.321(2) Å c = 51.868(3) Å α = β = γ = 90°
Volume (Å^3), Z	87065(7), 16
Density (calculated) (mg/m^3)	0.915
Absorption coefficient (mm^{-1})	3.667
F(000)	24640
θ range for data collection (°)	1.747 to 55.013
Limiting indices	-43<=h<=40 -43<=k<=35 -54<=l<=52
Reflections collected	116878
Independent reflections	26170 [R(int) = 0.0585]
Completeness to theta	98.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	26170 / 2010 / 1606
Goodness-of-fit on F^2	1.010
Final R indices [I>2sigma(I)]	R1 = 0.0650, wR2 = 0.1767
R indices (all data)	R1 = 0.1186, wR2 = 0.2161
Absolute structure parameter	0.277(13)
Largest diff. peak and hole (e.Å^{-3})	0.773 and -0.327 e.A^-3

6. Table S2. Selected bond lengths [Å] and angles [°] for 1

Cd(1)-O(5)	2.437(11)	Na(1)-O(25)#5	2.473(15)
Cd(1)-O(6)	2.332(10)	Na(2)-O(5W)	2.52(2)
Cd(1)-O(11)	2.220(11)	Na(2)-O(6W)	2.68(2)

Cd(1)-O(12)	2.592(12)	Na(2)-O(12)	2.242(13)
Cd(1)-O(15)	2.230(11)	Na(2)-O(16)	2.235(16)
Cd(1)-O(23)#1	2.320(13)	Na(2)-O(23)#1	3.014(15)
Cd(1)-O(24)#1	2.548(14)	Na(2)-O(27H)	2.449(16)
Cd(2)-O(3)#2	2.280(11)	Na(3)-O(12)	2.524(15)
Cd(2)-O(9)#3	2.302(10)	Na(3)-O(23)#1	2.275(15)
Cd(2)-O(10)#3	2.544(12)	Na(3)-O(25)	2.265(13)
Cd(2)-O(17)	2.512(11)	Na(3)-O(27H)	2.403(14)
Cd(2)-O(18)	2.343(12)	Na(3)-O(31H)	2.673(18)
Cd(2)-O(21)	2.376(12)	Na(4)-O(7W)	2.69(2)
Cr(1)-O(1)	1.896(11)	Na(4)-O(9)#3	2.331(14)
Cr(1)-O(2)	1.907(11)	Na(4)-O(22)	2.471(14)
Cr(1)-O(29)	2.109(16)	Na(4)-O(26)#4	2.293(13)
Cr(1)-O(30)	2.031(16)	Na(4)-O(33)#4	2.361(15)
Cr(1)-N(1)	1.976(14)	Na(5)-O(3)#2	2.322(13)
Cr(1)-N(2)	1.991(13)	Na(5)-O(4W)	2.51(2)
Cr(2)-O(1W)	1.943(14)	Na(5)-O(18)	2.242(13)
Cr(2)-O(2W)	1.980(15)	Na(5)-O(28)	2.692(15)
Cr(2)-O(7)	1.854(12)	Na(5)-O(34)	2.280(16)
Cr(2)-O(8)	1.940(12)	Na(6)-O(17)	2.272(14)
Cr(2)-N(3)	2.010(14)	Na(6)-O(17)#4	2.272(14)
Cr(2)-N(4)	1.977(15)	Na(6)-O(21)#4	2.723(13)
Cr(3)-O(3W)	1.980(14)	Na(6)-O(21)	2.723(12)
Cr(3)-O(13)	1.936(12)	Na(6)-O(26)#4	2.414(15)
Cr(3)-O(14)	1.903(11)	Na(6)-O(26)	2.414(15)
Cr(3)-O(28)#4	2.029(13)	O(3)-Cd(2)#6	2.280(11)
Cr(3)-N(5)	1.980(13)	O(3)-Na(5)#6	2.322(13)
Cr(3)-N(6)	2.023(13)	O(9)-Cd(2)#7	2.301(10)
Cr(4)-O(19)	1.875(12)	O(9)-Na(4)#7	2.331(14)
Cr(4)-O(20)	1.977(12)	O(10)-Cd(2)#7	2.543(12)
Cr(4)-O(32)	2.10(2)	O(23)-Cd(1)#8	2.320(12)
Cr(4)-O(35)	1.975(19)	O(23)-Na(2)#8	3.014(15)
Cr(4)-N(7)	2.044(14)	O(23)-Na(3)#8	2.274(15)
Cr(4)-N(8)	1.979(15)	O(24)-Cd(1)#8	2.548(14)
Na(1)-O(5)#5	2.333(13)	O(26)-Na(4)#4	2.293(13)
Na(1)-O(5)	2.333(13)	O(28)-Cr(3)#4	2.029(13)
Na(1)-O(11)#5	2.732(11)	O(33)-Na(4)#4	2.361(15)
Na(1)-O(11)	2.732(11)	Na(1)-O(25)	2.473(15)

O(5)-Cd(1)-O(12)	110.6(4)	O(27H)-Na(2)-O(23)#1	80.4(4)
O(5)-Cd(1)-O(24)#1	98.3(4)	O(12)-Na(3)-O(31H)	169.4(5)
O(6)-Cd(1)-O(5)	55.3(4)	O(23)#1-Na(3)-O(12)	74.4(5)
O(6)-Cd(1)-O(12)	153.7(4)	O(23)#1-Na(3)-O(27H)	98.7(6)
O(6)-Cd(1)-O(24)#1	85.0(5)	O(23)#1-Na(3)-O(31H)	106.4(5)

O(11)-Cd(1)-O(5)	78.9(4)	O(25)-Na(3)-O(12)	86.0(5)
O(11)-Cd(1)-O(6)	101.5(4)	O(25)-Na(3)-O(23)#1	112.8(6)
O(11)-Cd(1)-O(12)	52.2(4)	O(25)-Na(3)-O(27H)	139.9(7)
O(11)-Cd(1)-O(15)	106.7(5)	O(25)-Na(3)-O(31H)	103.1(5)
O(11)-Cd(1)-O(23)#1	115.6(4)	O(27H)-Na(3)-O(12)	79.1(5)
O(11)-Cd(1)-O(24)#1	169.2(5)	O(27H)-Na(3)-O(31H)	90.3(5)
O(15)-Cd(1)-O(5)	129.1(4)	O(9)#3-Na(4)-O(7W)	95.5(5)
O(15)-Cd(1)-O(6)	74.4(4)	O(9)#3-Na(4)-O(22)	75.5(4)
O(15)-Cd(1)-O(12)	111.8(4)	O(9)#3-Na(4)-O(33)#4	109.5(5)
O(15)-Cd(1)-O(23)#1	124.0(4)	O(22)-Na(4)-O(7W)	82.2(6)
O(15)-Cd(1)-O(24)#1	83.2(5)	O(26)#4-Na(4)-O(7W)	144.6(6)
O(23)#1-Cd(1)-O(5)	94.7(5)	O(26)#4-Na(4)-O(9)#3	112.8(5)
O(23)#1-Cd(1)-O(6)	126.8(5)	O(26)#4-Na(4)-O(22)	84.6(5)
O(23)#1-Cd(1)-O(12)	72.4(4)	O(26)#4-Na(4)-O(33)#4	109.8(6)
O(23)#1-Cd(1)-O(24)#1	54.0(4)	O(33)#4-Na(4)-O(7W)	78.2(6)
O(24)#1-Cd(1)-O(12)	120.7(4)	O(33)#4-Na(4)-O(22)	160.1(6)
O(3)#2-Cd(2)-O(9)#3	121.1(4)	O(3)#2-Na(5)-O(4W)	88.8(7)
O(3)#2-Cd(2)-O(10)#3	82.7(4)	O(3)#2-Na(5)-O(28)	99.3(5)
O(3)#2-Cd(2)-O(17)	132.9(4)	O(4W)-Na(5)-O(28)	142.6(6)
O(3)#2-Cd(2)-O(18)	80.3(4)	O(18)-Na(5)-O(3)#2	81.5(4)
O(3)#2-Cd(2)-O(21)	105.9(4)	O(18)-Na(5)-O(4W)	90.4(7)
O(9)#3-Cd(2)-O(10)#3	52.5(4)	O(18)-Na(5)-O(28)	126.8(5)
O(9)#3-Cd(2)-O(17)	96.2(4)	O(18)-Na(5)-O(34)	146.2(5)
O(9)#3-Cd(2)-O(18)	128.1(4)	O(34)-Na(5)-O(3)#2	131.4(5)
O(9)#3-Cd(2)-O(21)	116.6(4)	O(34)-Na(5)-O(4W)	96.7(7)
O(17)-Cd(2)-O(10)#3	102.1(4)	O(34)-Na(5)-O(28)	51.3(4)
O(18)-Cd(2)-O(10)#3	90.2(5)	O(17)#4-Na(6)-O(17)	107.0(7)
O(18)-Cd(2)-O(17)	53.2(4)	O(17)-Na(6)-O(21)	74.6(4)
O(18)-Cd(2)-O(21)	97.7(4)	O(17)#4-Na(6)-O(21)#4	74.6(4)
O(21)-Cd(2)-O(10)#3	169.1(5)	O(17)-Na(6)-O(21)#4	96.1(4)
O(21)-Cd(2)-O(17)	77.1(4)	O(17)#4-Na(6)-O(21)	96.1(4)
O(1)-Cr(1)-O(2)	95.9(5)	O(17)-Na(6)-O(26)	151.2(5)
O(1)-Cr(1)-O(29)	91.3(6)	O(17)-Na(6)-O(26)#4	100.8(4)
O(1)-Cr(1)-O(30)	92.1(6)	O(17)#4-Na(6)-O(26)	100.9(4)
O(1)-Cr(1)-N(1)	172.9(6)	O(17)#4-Na(6)-O(26)#4	151.2(5)
O(1)-Cr(1)-N(2)	90.7(5)	O(21)#4-Na(6)-O(21)	164.5(6)
O(2)-Cr(1)-O(29)	90.5(6)	O(26)#4-Na(6)-O(21)#4	110.2(5)
O(2)-Cr(1)-O(30)	93.4(6)	O(26)-Na(6)-O(21)#4	84.0(4)
O(2)-Cr(1)-N(1)	91.1(5)	O(26)#4-Na(6)-O(21)	84.0(4)
O(2)-Cr(1)-N(2)	173.3(6)	O(26)-Na(6)-O(21)	110.2(5)
O(30)-Cr(1)-O(29)	174.5(6)	O(26)#4-Na(6)-O(26)	53.2(6)
N(1)-Cr(1)-O(29)	89.5(6)	C(13)-O(1)-Cr(1)	131.7(9)
N(1)-Cr(1)-O(30)	86.5(6)	C(25)-O(2)-Cr(1)	131.1(9)
N(1)-Cr(1)-N(2)	82.3(6)	Cd(2)#6-O(3)-Na(5)#6	98.5(4)

N(2)-Cr(1)-O(29)	90.7(6)	C(18)-O(3)-Cd(2)#6	107.7(12)
N(2)-Cr(1)-O(30)	85.0(6)	C(18)-O(3)-Na(5)#6	144.9(13)
O(1W)-Cr(2)-O(2W)	173.7(6)	Na(1)-O(5)-Cd(1)	105.2(5)
O(1W)-Cr(2)-N(3)	86.5(6)	C(26)-O(5)-Cd(1)	88.6(11)
O(1W)-Cr(2)-N(4)	91.6(6)	C(26)-O(5)-Na(1)	130.6(14)
O(2W)-Cr(2)-N(3)	87.8(6)	C(26)-O(6)-Cd(1)	91.1(11)
O(7)-Cr(2)-O(1W)	93.2(6)	C(43)-O(7)-Cr(2)	129.7(10)
O(7)-Cr(2)-O(2W)	92.1(7)	C(55)-O(8)-Cr(2)	133.8(10)
O(7)-Cr(2)-O(8)	96.5(5)	Cd(2)#7-O(9)-Na(4)#7	104.9(5)
O(7)-Cr(2)-N(3)	172.8(6)	C(44)-O(9)-Cd(2)#7	100.0(12)
O(7)-Cr(2)-N(4)	91.7(6)	C(44)-O(9)-Na(4)#7	155.1(13)
O(8)-Cr(2)-O(1W)	92.6(6)	C(44)-O(10)-Cd(2)#7	89.1(13)
O(8)-Cr(2)-O(2W)	90.2(6)	Cd(1)-O(11)-Na(1)	99.3(4)
O(8)-Cr(2)-N(3)	90.7(6)	C(56)-O(11)-Cd(1)	102.5(11)
O(8)-Cr(2)-N(4)	170.5(7)	C(56)-O(11)-Na(1)	106.2(11)
N(4)-Cr(2)-O(2W)	84.9(7)	Na(2)-O(12)-Cd(1)	94.1(4)
N(4)-Cr(2)-N(3)	81.1(6)	Na(2)-O(12)-Na(3)	87.5(5)
O(3W)-Cr(3)-O(28)#4	177.3(6)	Na(3)-O(12)-Cd(1)	91.2(5)
O(3W)-Cr(3)-N(5)	91.4(6)	C(56)-O(12)-Cd(1)	85.0(11)
O(3W)-Cr(3)-N(6)	90.7(6)	C(56)-O(12)-Na(2)	157.0(13)
O(13)-Cr(3)-O(3W)	90.4(6)	C(56)-O(12)-Na(3)	115.4(11)
O(13)-Cr(3)-O(28)#4	92.3(6)	C(73)-O(13)-Cr(3)	127.1(9)
O(13)-Cr(3)-N(5)	173.8(5)	C(81)-O(14)-Cr(3)	127.8(8)
O(13)-Cr(3)-N(6)	92.7(5)	C(74)-O(15)-Cd(1)	105.3(12)
O(14)-Cr(3)-O(3W)	89.5(6)	C(74)-O(16)-Na(2)	162.1(16)
O(14)-Cr(3)-O(13)	94.4(5)	Na(6)-O(17)-Cd(2)	105.0(4)
O(14)-Cr(3)-O(28)#4	90.5(5)	C(86)-O(17)-Cd(2)	91.3(10)
O(14)-Cr(3)-N(5)	91.5(5)	C(86)-O(17)-Na(6)	134.5(12)
O(14)-Cr(3)-N(6)	172.9(6)	Na(5)-O(18)-Cd(2)	99.0(5)
N(5)-Cr(3)-O(28)#4	85.9(6)	C(86)-O(18)-Cd(2)	100.6(11)
N(5)-Cr(3)-N(6)	81.4(6)	C(86)-O(18)-Na(5)	160.2(12)
N(6)-Cr(3)-O(28)#4	88.9(5)	C(103)-O(19)-Cr(4)	126.7(10)
O(19)-Cr(4)-O(20)	95.0(5)	C(115)-O(20)-Cr(4)	128.8(10)
O(19)-Cr(4)-O(32)	89.8(7)	Cd(2)-O(21)-Na(6)	96.0(4)
O(19)-Cr(4)-O(35)	91.4(7)	C(104)-O(21)-Cd(2)	100.2(12)
O(19)-Cr(4)-N(7)	176.4(6)	C(104)-O(21)-Na(6)	103.2(12)
O(19)-Cr(4)-N(8)	93.1(6)	C(104)-O(22)-Na(4)	116.8(12)
O(20)-Cr(4)-O(32)	92.3(7)	Cd(1)#8-O(23)-Na(2)#8	82.2(4)
O(20)-Cr(4)-N(7)	88.5(5)	Na(3)#8-O(23)-Cd(1)#8	105.4(5)
O(20)-Cr(4)-N(8)	171.5(6)	Na(3)#8-O(23)-Na(2)#8	75.8(4)
O(35)-Cr(4)-O(20)	92.1(7)	C(116)-O(23)-Cd(1)#8	96.6(12)
O(35)-Cr(4)-O(32)	175.4(7)	C(116)-O(23)-Na(2)#8	108.5(12)
O(35)-Cr(4)-N(7)	87.7(7)	C(116)-O(23)-Na(3)#8	157.9(14)
O(35)-Cr(4)-N(8)	85.2(7)	C(116)-O(24)-Cd(1)#8	85.6(13)

N(7)-Cr(4)-O(32)	90.8(7)	Na(3)-O(25)-Na(1)	126.4(6)
N(8)-Cr(4)-O(32)	90.3(7)	C(121)-O(25)-Na(1)	90.7(16)
N(8)-Cr(4)-N(7)	83.3(6)	C(121)-O(25)-Na(3)	139.5(16)
O(5)#5-Na(1)-O(5)	113.4(8)	Na(4)#4-O(26)-Na(6)	126.0(6)
O(5)-Na(1)-O(11)#5	100.7(4)	C(123)-O(26)-Na(4)#4	140.2(17)
O(5)#5-Na(1)-O(11)#5	71.2(4)	C(123)-O(26)-Na(6)	91.4(17)
O(5)#5-Na(1)-O(11)	100.7(4)	Na(3)-O(27H)-Na(2)	85.8(5)
O(5)-Na(1)-O(11)	71.2(4)	Cr(3)#4-O(28)-Na(5)	146.0(6)
O(5)#5-Na(1)-O(25)	148.9(5)	C(127)-O(28)-Cr(3)#4	128.7(16)
O(5)-Na(1)-O(25)	97.0(5)	C(127)-O(28)-Na(5)	82.1(15)
O(5)#5-Na(1)-O(25)#5	97.0(5)	C(125)-O(29)-Cr(1)	151.6(14)
O(5)-Na(1)-O(25)#5	148.9(5)	C(126)-O(30)-Cr(1)	134.7(17)
O(11)#5-Na(1)-O(11)	165.7(6)	C(0AA)-O(32)-Cr(4)	157(2)
O(25)-Na(1)-O(11)	82.5(4)	C(128)-O(33)-Na(4)#4	127.5(17)
O(25)#5-Na(1)-O(11)#5	82.5(4)	C(127)-O(34)-Na(5)	98.8(14)
O(25)-Na(1)-O(11)#5	110.6(4)	C(128)-O(35)-Cr(4)	133(2)
O(25)#5-Na(1)-O(11)	110.6(4)	C(1)-N(1)-Cr(1)	112.8(10)
O(25)-Na(1)-O(25)#5	54.0(6)	C(19)-N(1)-Cr(1)	129.8(13)
O(5W)-Na(2)-O(6W)	91.9(9)	C(2)-N(2)-Cr(1)	114.1(11)
O(5W)-Na(2)-O(23)#1	108.4(8)	C(7)-N(2)-Cr(1)	123.8(13)
O(6W)-Na(2)-O(23)#1	159.4(6)	C(31)-N(3)-Cr(2)	115.1(12)
O(12)-Na(2)-O(5W)	173.4(9)	C(49)-N(3)-Cr(2)	124.6(13)
O(12)-Na(2)-O(6W)	94.3(6)	C(32)-N(4)-Cr(2)	110.2(13)
O(12)-Na(2)-O(23)#1	65.3(4)	C(37)-N(4)-Cr(2)	126.1(14)
O(12)-Na(2)-O(27H)	83.9(5)	C(61)-N(5)-Cr(3)	112.3(10)
O(16)-Na(2)-O(5W)	89.6(7)	C(79)-N(5)-Cr(3)	121.0(12)
O(16)-Na(2)-O(6W)	105.2(7)	C(62)-N(6)-Cr(3)	112.2(10)
O(16)-Na(2)-O(12)	91.1(5)	C(67)-N(6)-Cr(3)	123.1(12)
O(16)-Na(2)-O(23)#1	79.0(5)	C(91)-N(7)-Cr(4)	108.9(11)
O(16)-Na(2)-O(27H)	159.0(6)	C(109)-N(7)-Cr(4)	125.9(13)
O(27H)-Na(2)-O(5W)	93.1(7)	C(92)-N(8)-Cr(4)	111.4(12)
O(27H)-Na(2)-O(6W)	95.6(6)	C(97)-N(8)-Cr(4)	125.3(13)

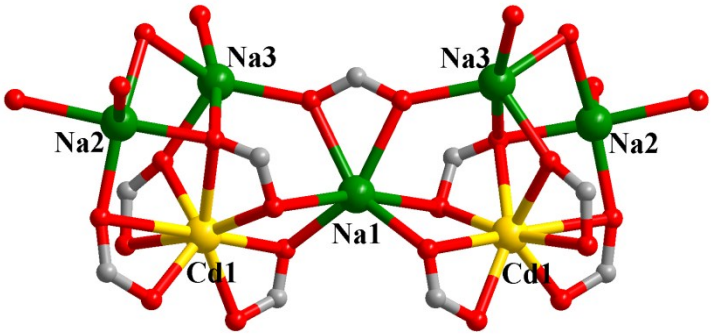
Symmetry transformations used to generate equivalent atoms:

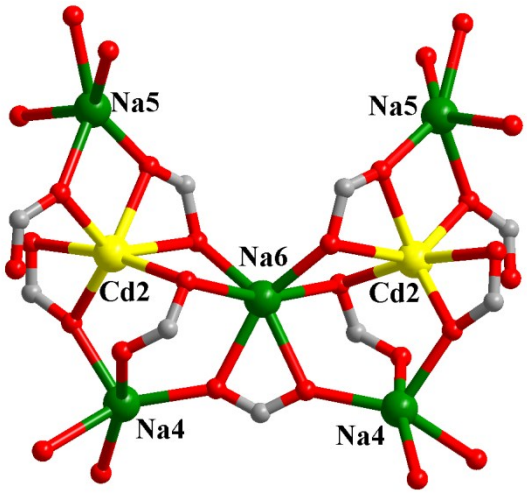
#1 x+1/2,y+1/2,z #2 x,y-1/2,z+1/2 #3 x-1/2,y,z+1/2 #4 x,-y+1,-z+1

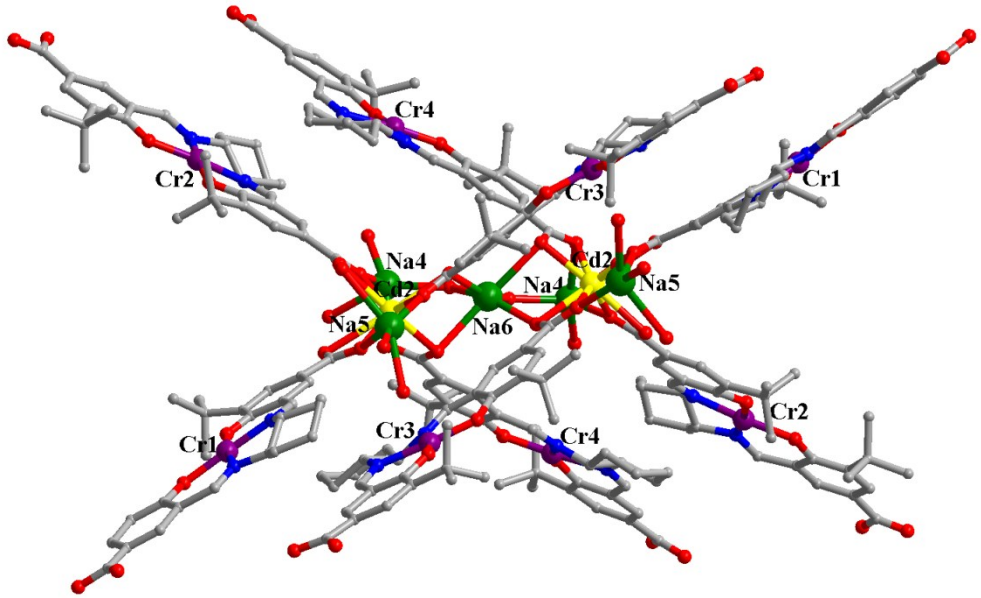
#5 x,-y+3/2,-z+1/2 #6 x,y+1/2,z-1/2 #7 x+1/2,y,z-1/2 #8 x-1/2,y-1/2,z

7. Figures S1-S3. Additional X-ray crystallographic structures

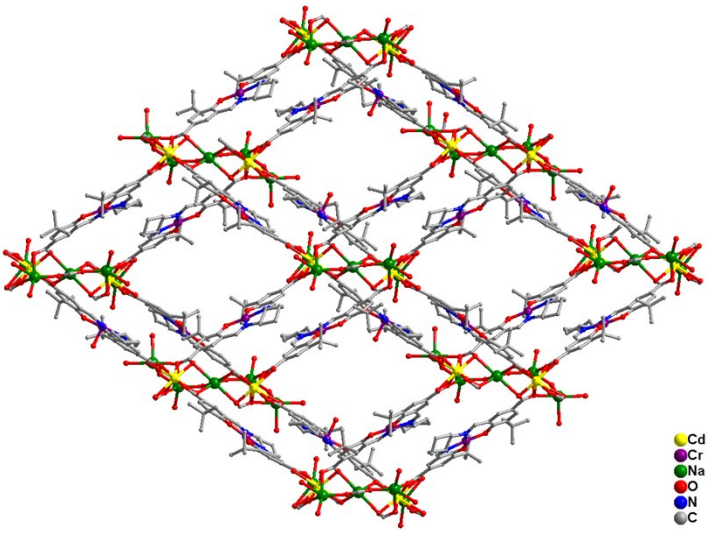
7.1 Figure S1. The structure of $[Cd_2Na_5(CO_2)_9]$ clusters





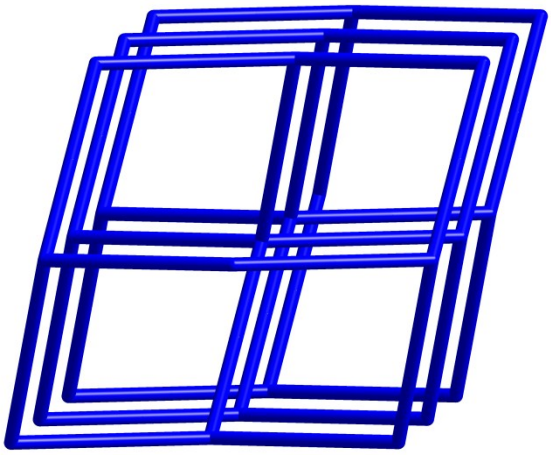


7.2 Figure S2. View of one independent network in 1 along the a-axis

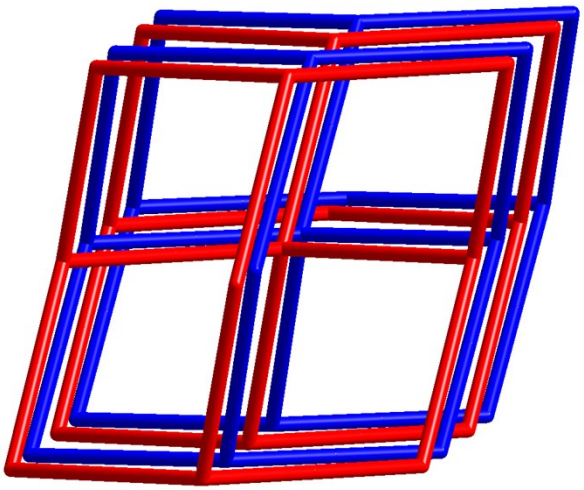


7.3 Figure S3. Scheme showing the independent network of 1 (a) and the two-fold interpenetrated nets in 1

(a)

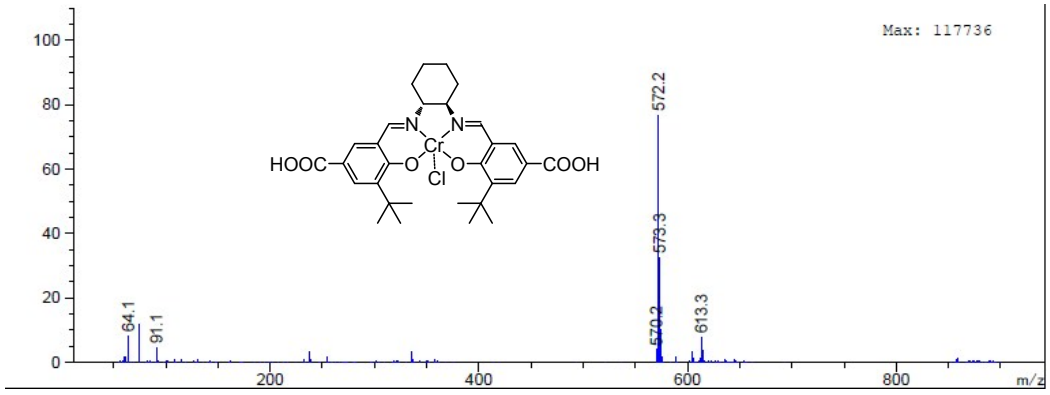


(b)

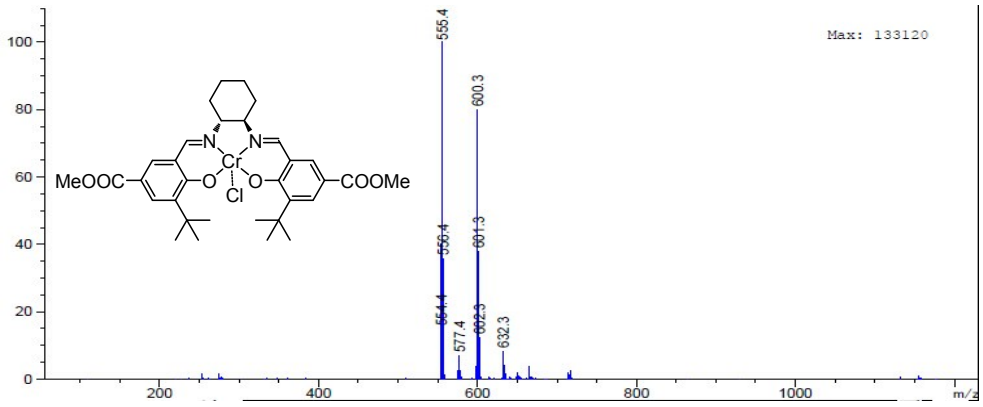


8. Figure S4. ESI-MS spectra of Cr(H_2L)Cl (a) and Cr(Me_2L)Cl (b)

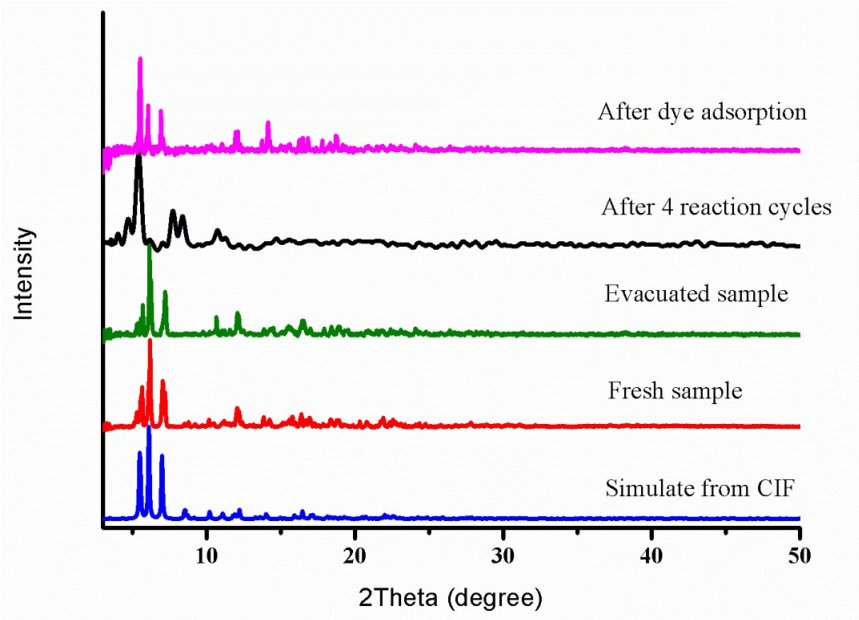
(a)



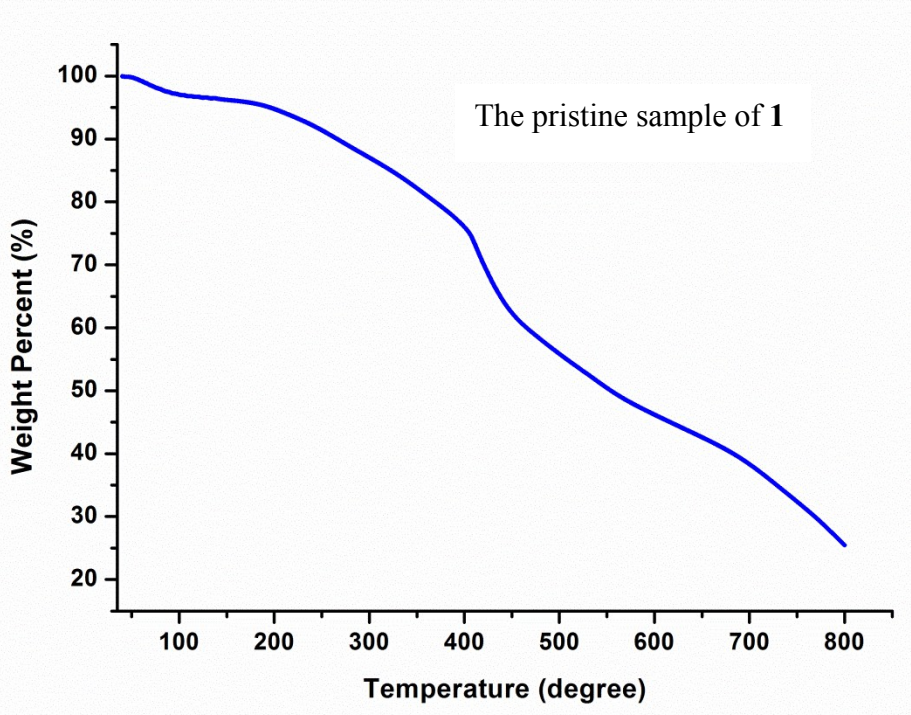
(b)



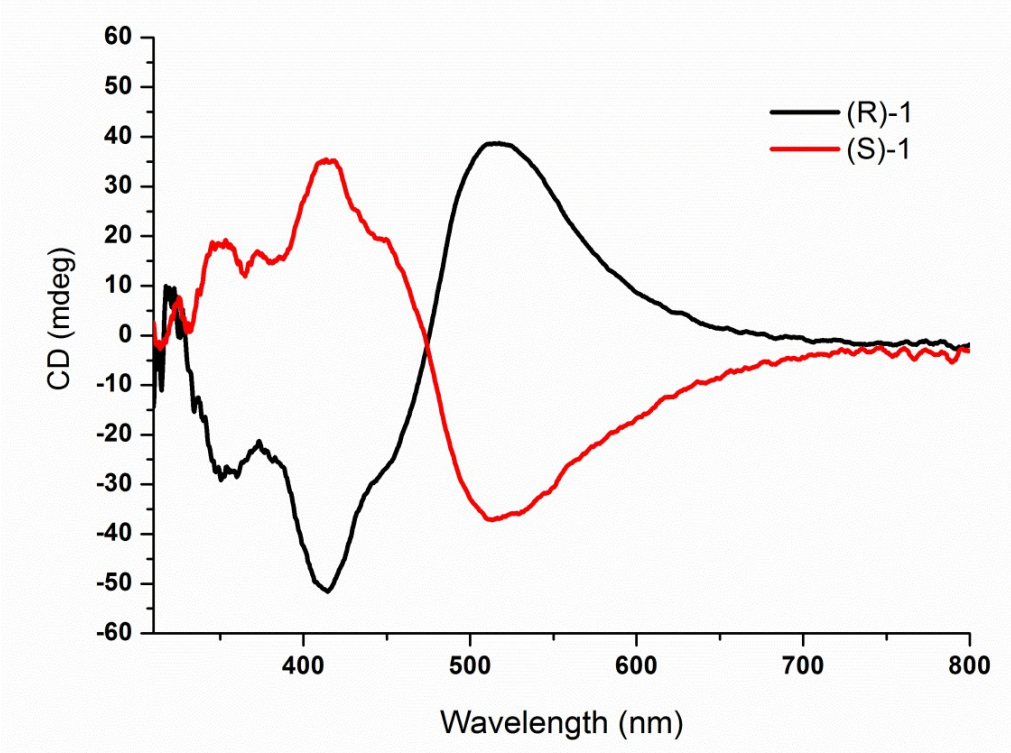
9. Figure S5. PXRD patterns (Catalytic reactions, including recycle experiments (with stirring operation) can distort the framework, thereby leading to shift of the PXRD peaks for the recovered sample)



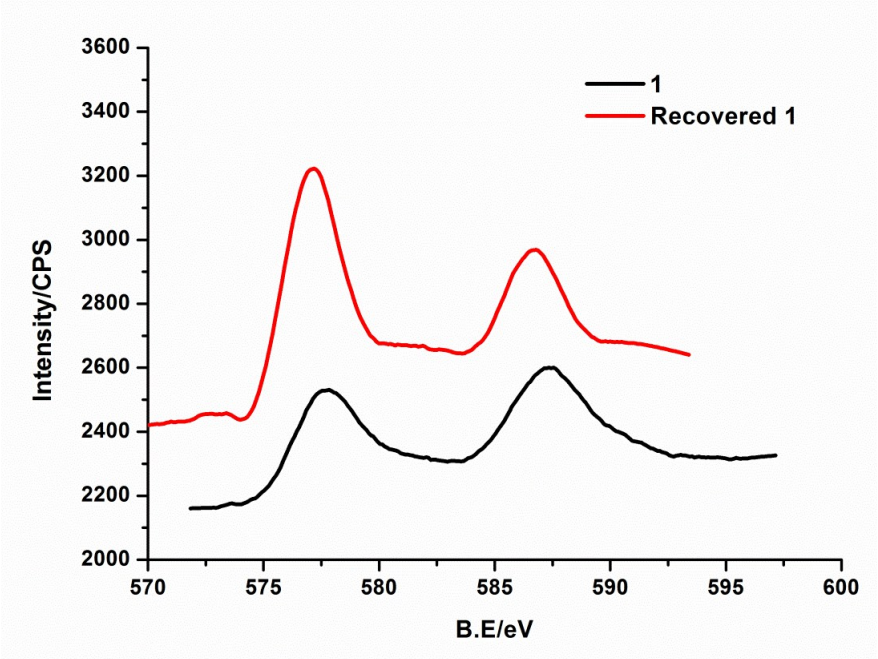
10. Figure S6. TGA curve of 1



11. Figure S7. Solid-state CD spectra

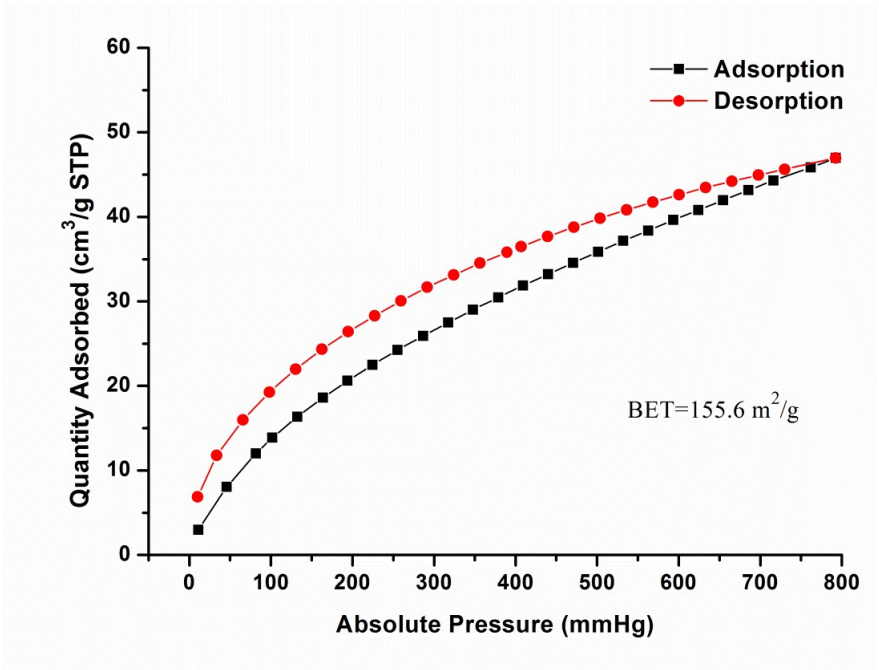


12. Figure S8. XPS spectra



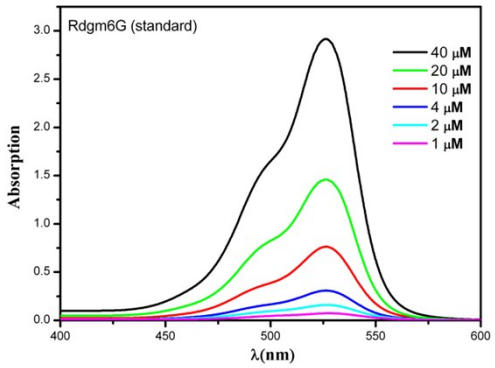
13. Figure S9. The CO_2 adsorption isotherms for 1 (The apparent adsorption-desorption hysteresis in **1** was observed, probably as a consequence of the framework flexibility. The theoretical surface area of MOF **1** was calculated to be 1975.6 m^2/g, according to the method described by Düren et al. (T. Düren, F. Millange, G. Férey, K.

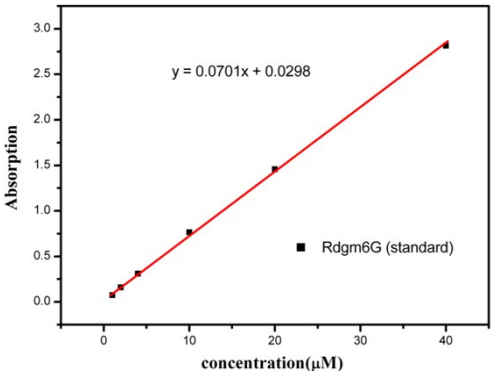
S. Walton, R. Q. Snurr, *J. Phys. Chem. C*., **2007**, *111*, 15350-15356). The observed surface area is obviously smaller probably due to the framework distortion upon removal of guest solvent molecules, which is often observed for porous MOFs.)

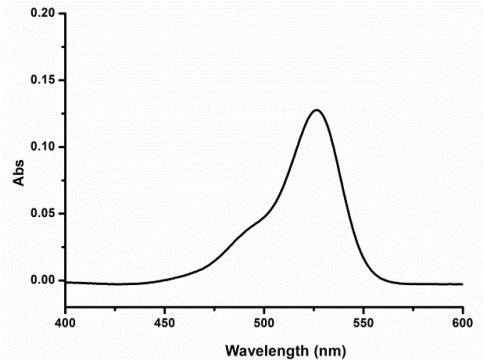


14. Figure S10. Dye adsorption (The concentration of the dye molecules was determined by comparing the UV-Vis absorption with a standard curve. The number of the dye molecules was calculated by dividing the amount of dye per unit cell by the void space inside the unit cell).

(a) Adsorption of Rhodamine 6G

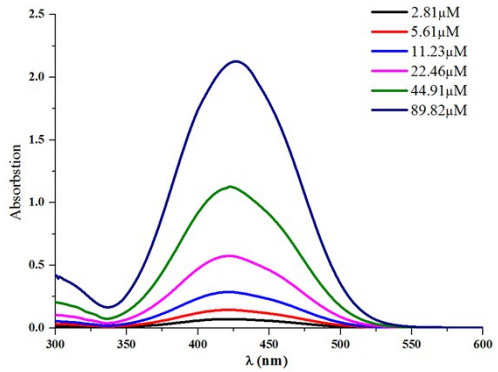


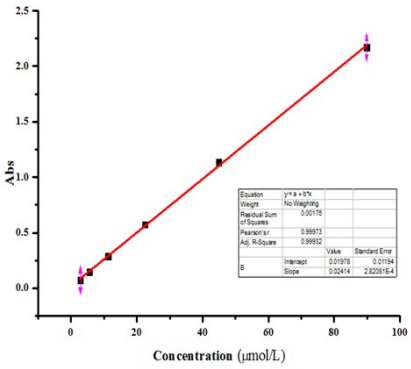


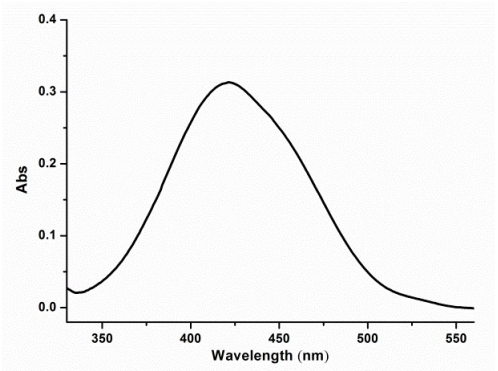


	The number of dye uptake (per formula)
Rhodamine 6G	1.7

(b) Adsorption of methyl orange(MO)



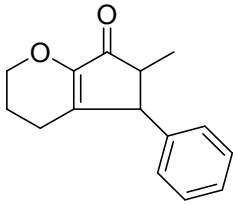




	The number of dye uptake (per formula)
Methyl Orange	2.3

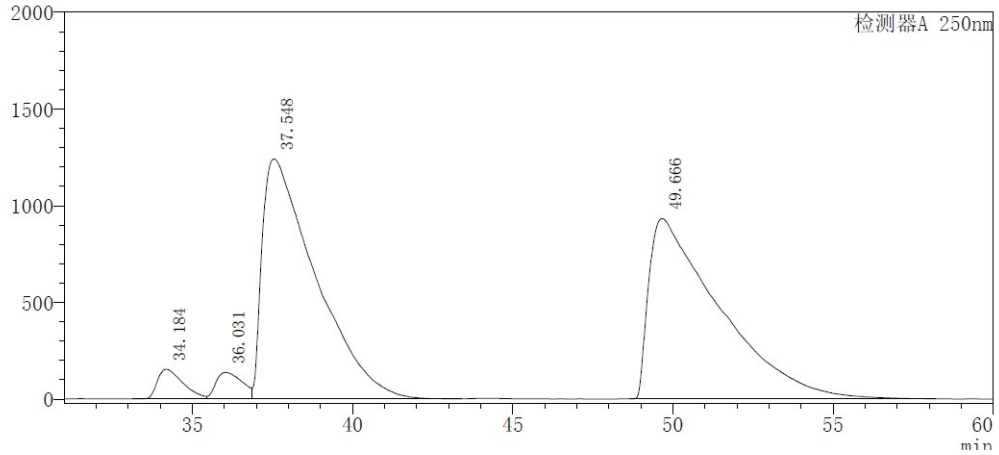
15. HPLC and ^{1}H NMR

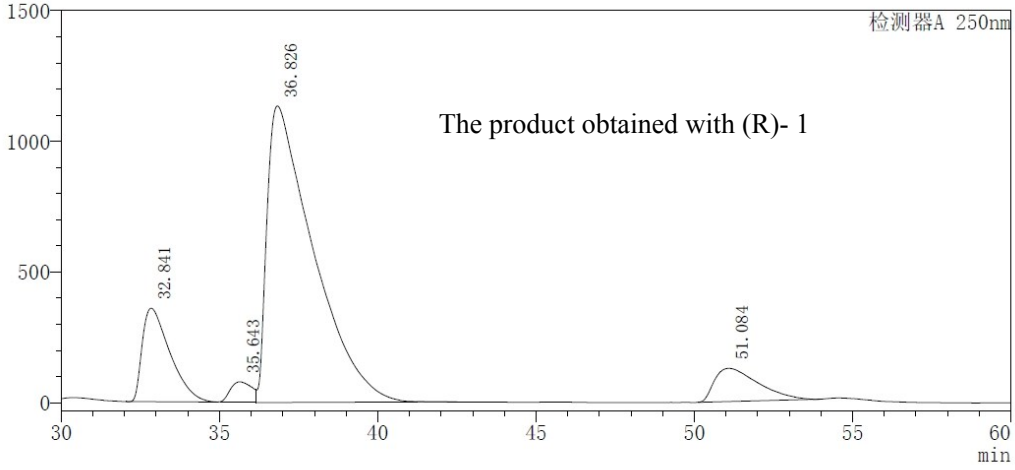
15.1 Nazarov Cyclization



6-methyl-5-phenyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

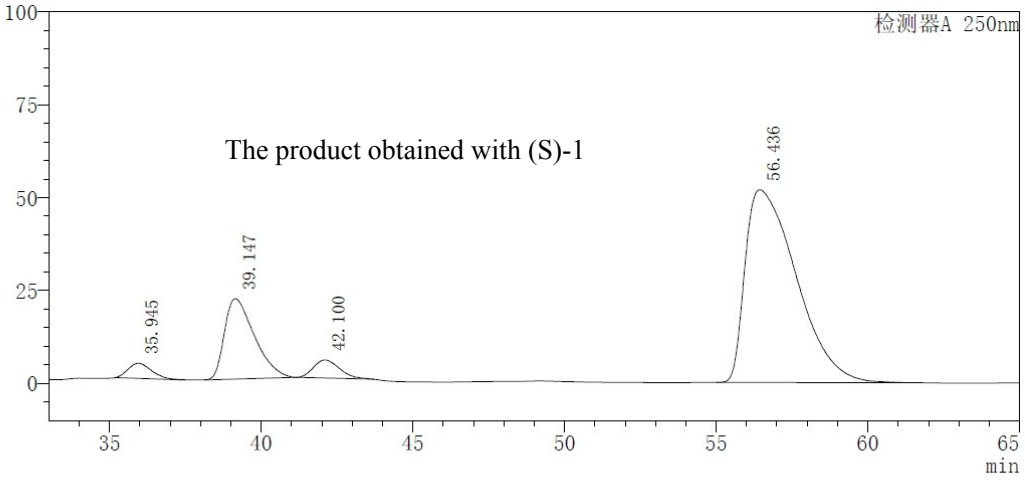
Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 98/2, 1.0 mL/min, 250 nm), t $_{major}$ = 36.83 min, t $_{minor}$ = 51.08 min; ee_{trans} =81%, ee_{cis} =84%. $Dr_{(trans/cis)}$=1:0.21. ^{1}H NMR ($CDCl_3$) δ: 0.86 (d, J = 7.6 Hz, 3H), 1.95 (m, 2H), 2.18 (m, 2H), 2.75 (m, 1H), 4.0 (d, J = 7.2 Hz, 1H), 4.20 (m, 2H), 7.0 (d, J=8Hz, 2H), 7.20~7.35 (m, 3H).



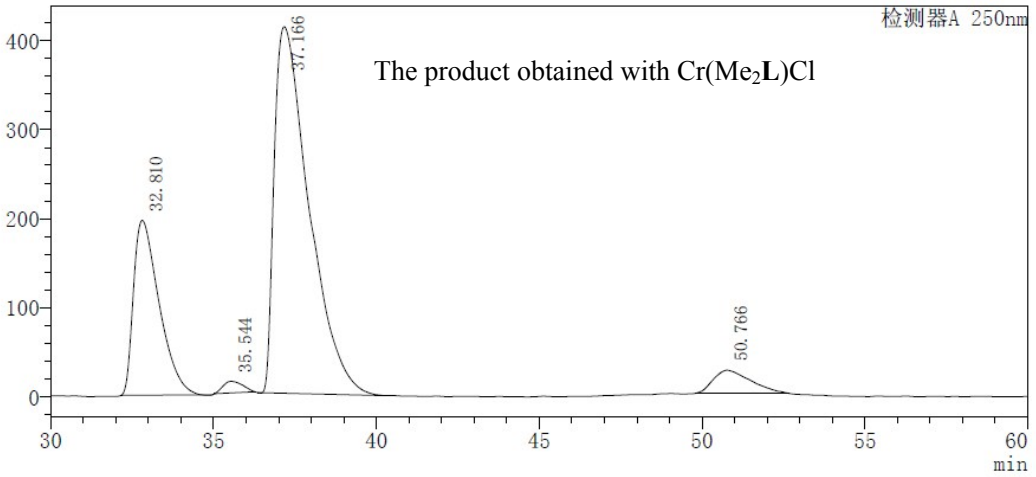


The product obtained with (R)- 1

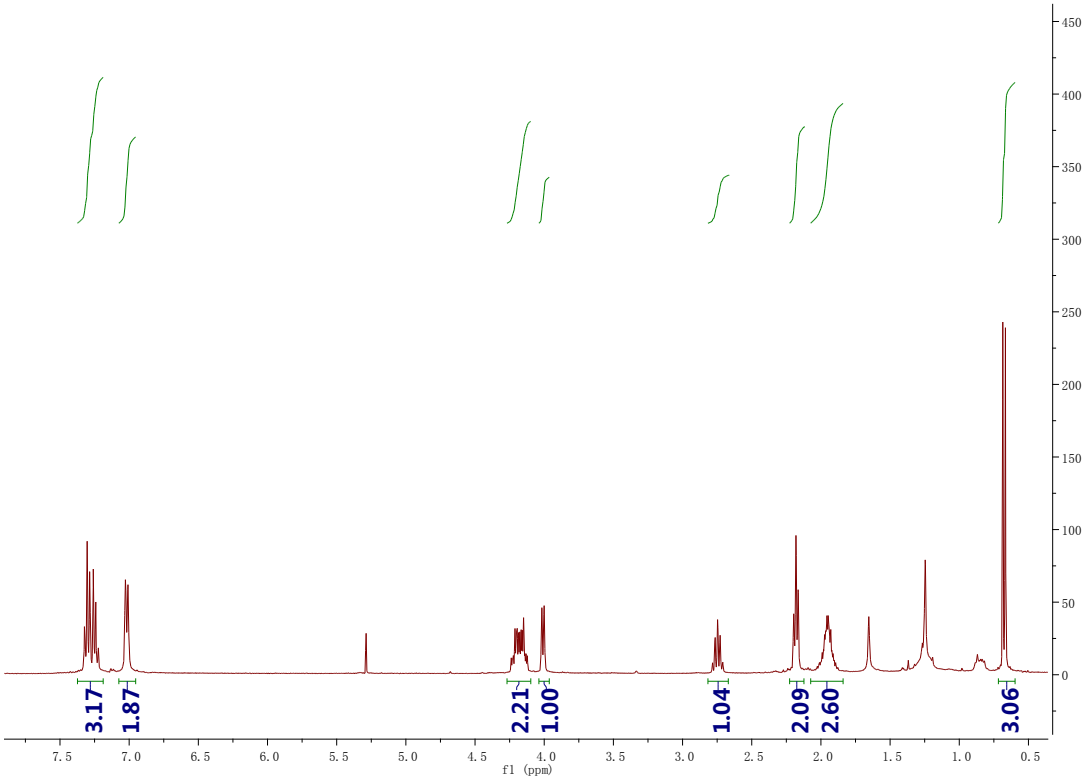
Serial Number	Retention Time [min]	Area	Area %
1	32.841	21766851	14.192
2	35.643	3462415	2.258
3	36.826	115889577	75.563
4	51.084	12249855	7.987

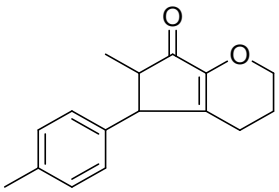


Serial Number	Retention Time [min]	Area	Area %
1	35.945	217219	2.689
2	39.147	1481109	18.332
3	42.100	292478	3.620
4	56.436	6088389	75.359



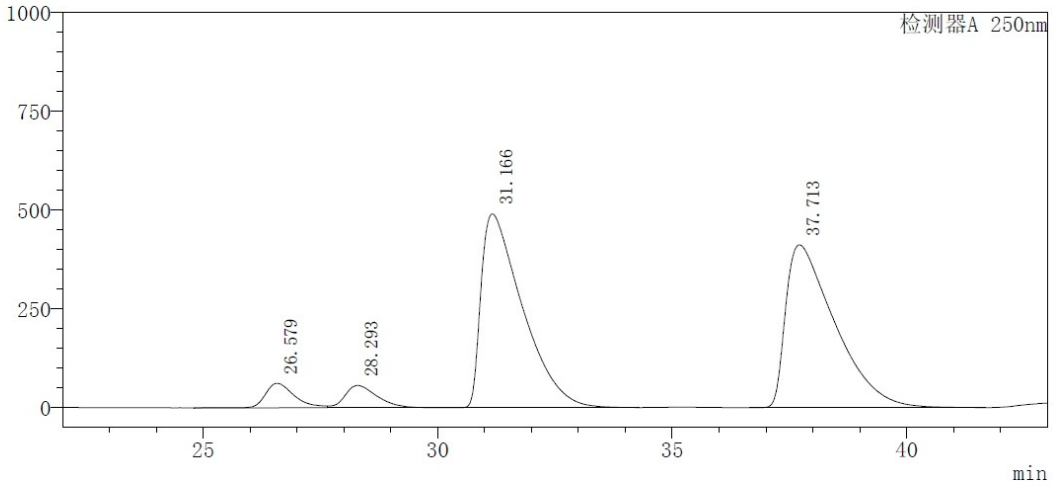
Serial Number	Retention Time [min]	Area	Area %
1	32.810	10731985	24.425
2	35.544	547015	1.245
3	37.166	30603122	69.650
4	50.766	2056434	4.680

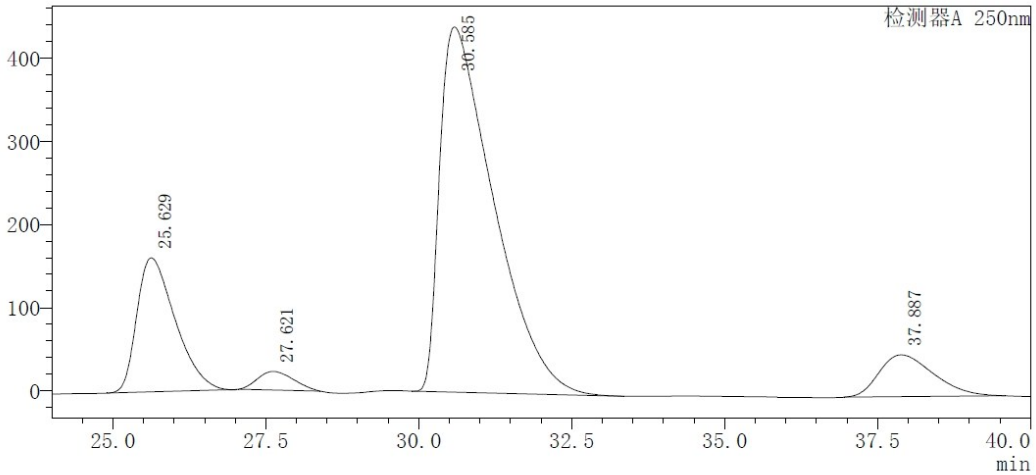

3.17
1.87
2.21
1.00
1.04
2.09
2.60
3.06
f1 (ppm)



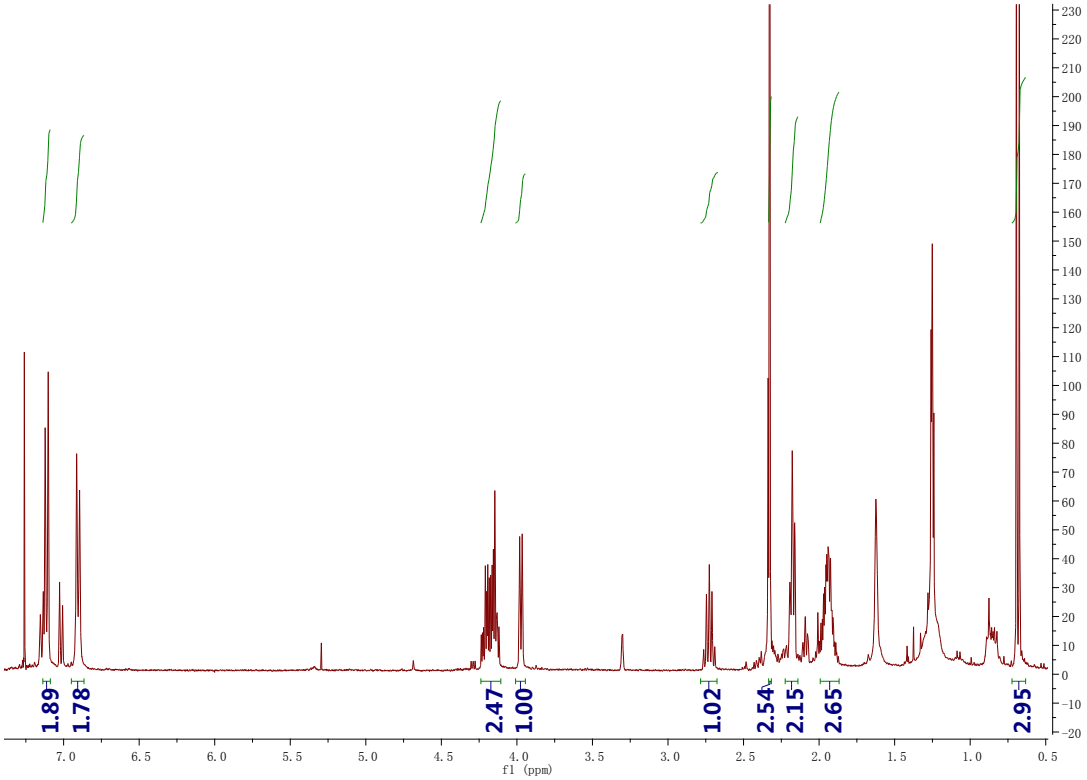
6-methyl-5-(p-tolyl)-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

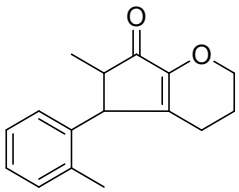
Enantiomeric excess was determined by HPLC with a chiralcel AS-H column (hexane/i-PrOH = 93/7, 1.0 mL/min, 250 nm), t_{major} = 30.58 min, t_{minor} = 37.87 min; ee_{trans} =75%, ee_{cis} =75%. $Dr_{(trans/cis)}$=1:0.20. ^1H NMR ($CDCl_3$) δ: 0.68 (d, J=7.6 Hz, 3H), 1.90 (m, 2H), 2.20 (m, 2H), 2.30 (s, 3H), 2.73(m, 1H), 3.97 (d, J=7.2 Hz, 1H), 4.15 (m, 2H), 6.9 (d, J=8 Hz, 2H), 7.10 (d, J=8 Hz, 2H).





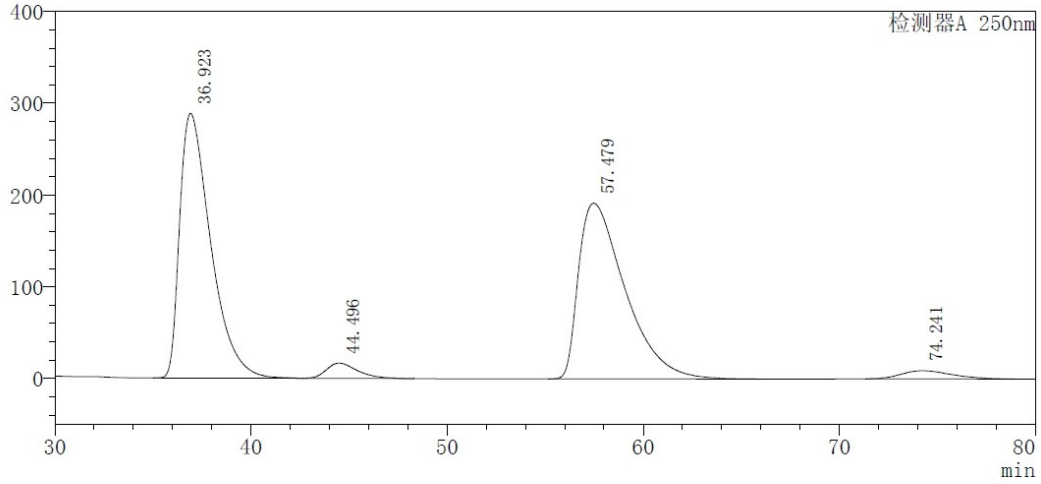
Serial Number	Retention Time [min]	Area	Area %
1	25.629	7034583	18.461
2	27.621	912923	2.396
3	30.585	27040792	70.965
4	37.887	3116326	8.178

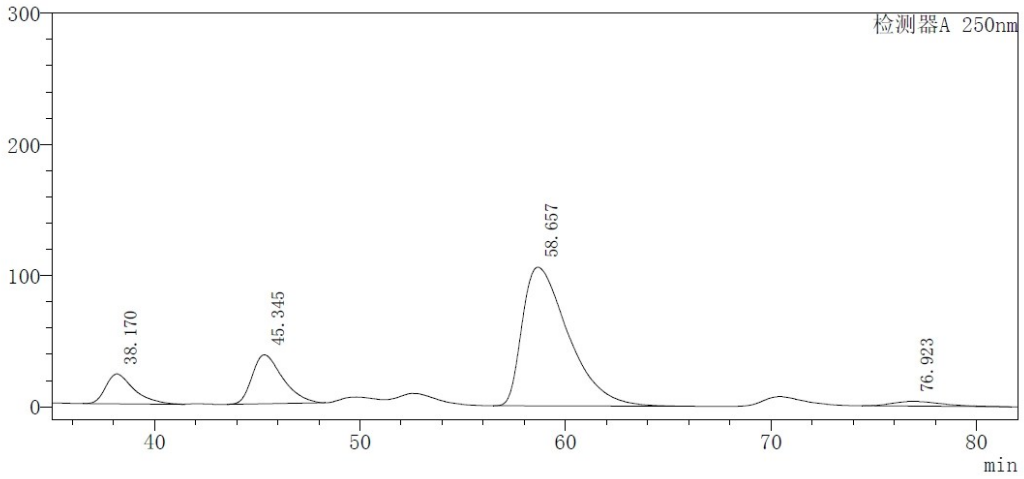

1.89
1.78
2.47
1.00
1.02
2.54
2.15
2.65
2.95
f1 (ppm)



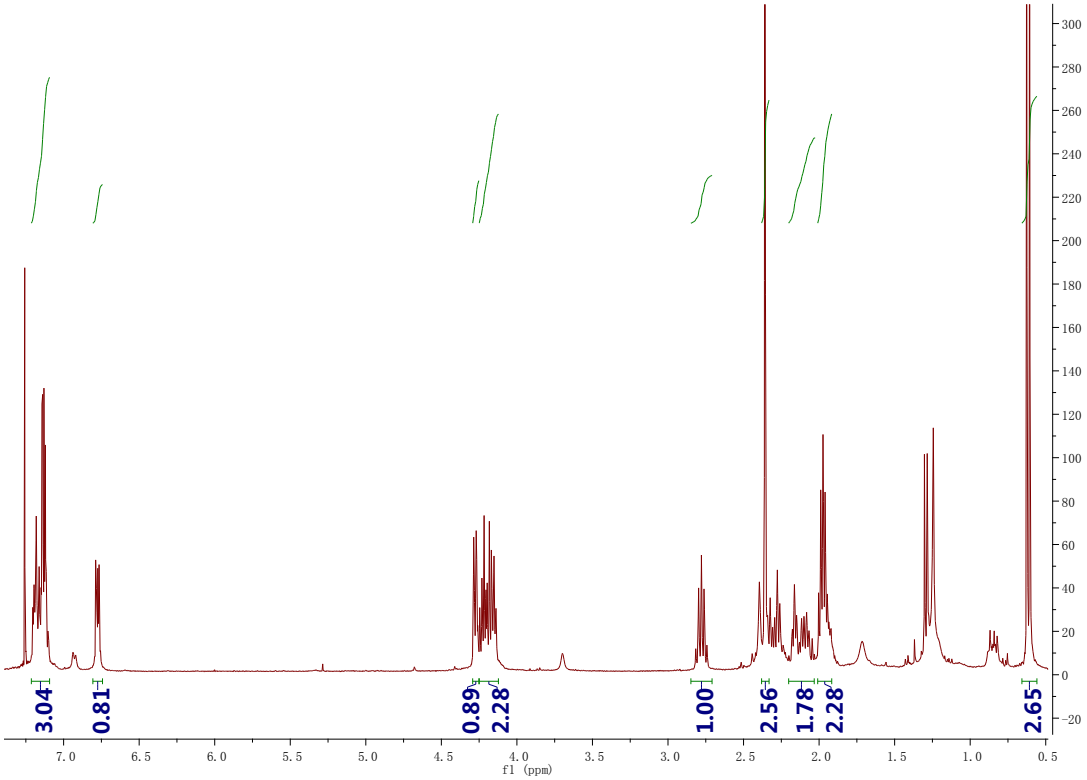
6-methyl-5-(o-tolyl)-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

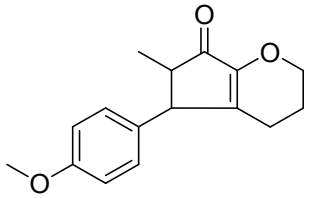
Enantiomeric excess was determined by HPLC with a chiralcel AS-H column (hexane/i-PrOH = 93/7, 1.0 mL/min, 250 nm), t $_{major}$ = 58.65 min, t $_{minor}$ = 38.17 min; ee_{trans} =77%, ee_{cis} =77%. $Dr_{(trans/cis)}$=1:0.24. ^{1}H NMR ($CDCl_3$) δ: 0.60 (d, J=8 Hz, 3H), 1.95 (m, 2H), 2.10 (m, 2H), 2.35 (s, 3H), 2.78 (m, 1H), 4.18 (m, 2H), 4.28 (d, J=8 Hz, 1H), 6.8 (m, 1H), 7.10~7.25 (m, 3H).





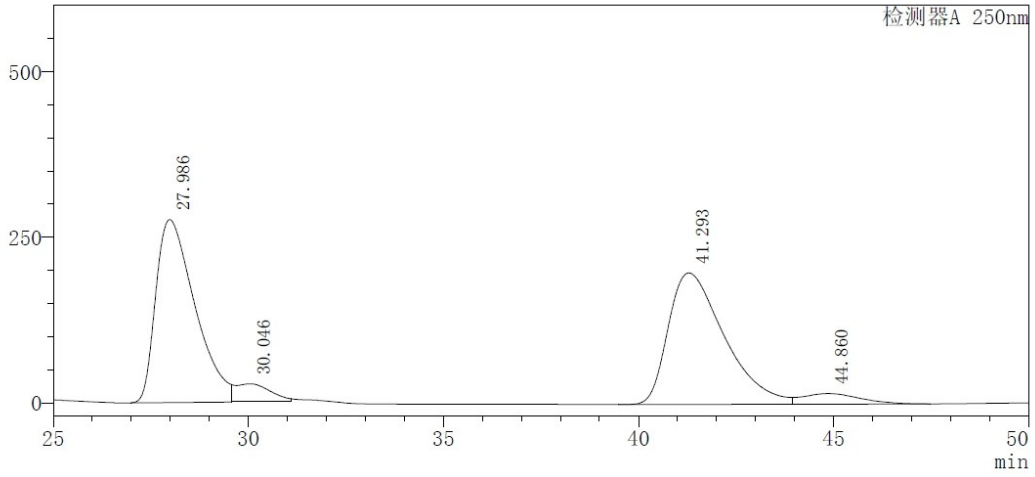
Serial Number	Retention Time [min]	Area	Area %
1	38.170	2185863	9.416
2	45.345	3860653	16.631
3	58.657	16556559	71.322
4	76.923	610581	2.630

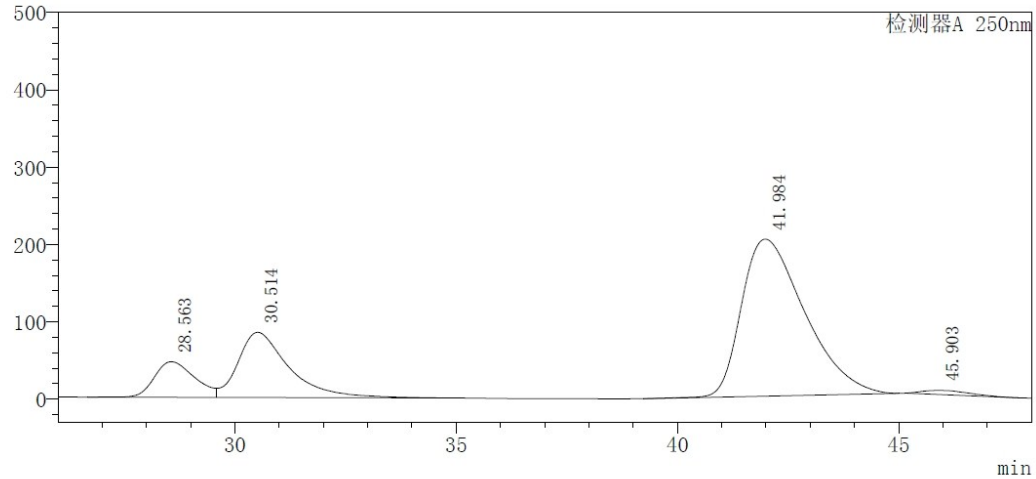

3.04
0.81
0.89
2.28
1.00
2.56
1.78
2.28
2.65
f1 (ppm)



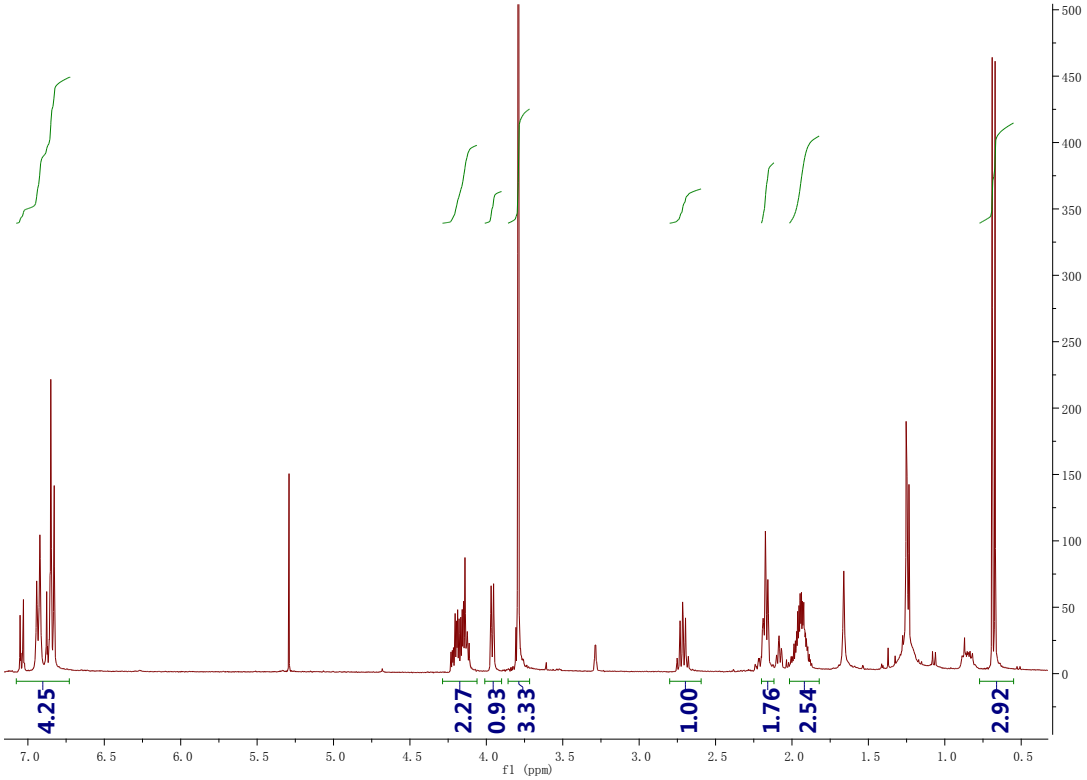
5-(4-methoxyphenyl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

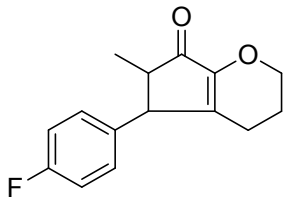
Enantiomeric excess was determined by HPLC with a chiralcel AS-H column (hexane/i-PrOH = 93/7, 1.0 mL/min, 250 nm), t_{major} = 41.84 min, t_{minor} = 28.53 min; ee_{trans} =81%, ee_{cis} =83%. $Dr_{(trans/cis)}$=1:0.23. ^1H NMR ($CDCl_3$) δ: 0.68 (d, J=8.4 Hz, 3H), 1.90 (m, 2H), 2.17 (m, 2H), 2.71 (m, 1H), 3.39 (s, 3H), 3.95 (d, J=7.2 Hz, 1H), 4.15 (m, 2H), 6.80~7.10 (m, 4H).





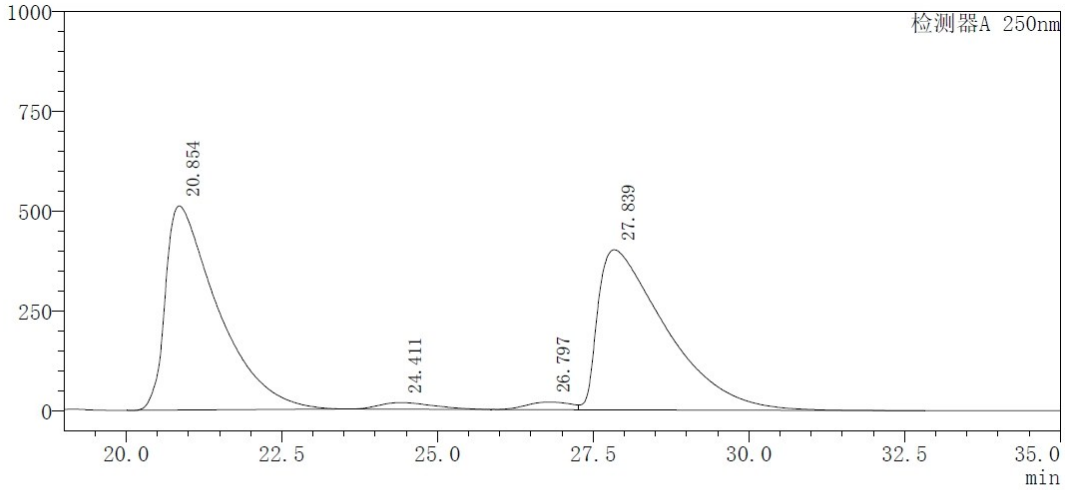
Serial Number	Retention Time [min]	Area	Area %
1	28.563	2919045	9.654
2	30.514	6732750	22.267
3	41.984	20175288	66.725
4	45.903	409200	1.353

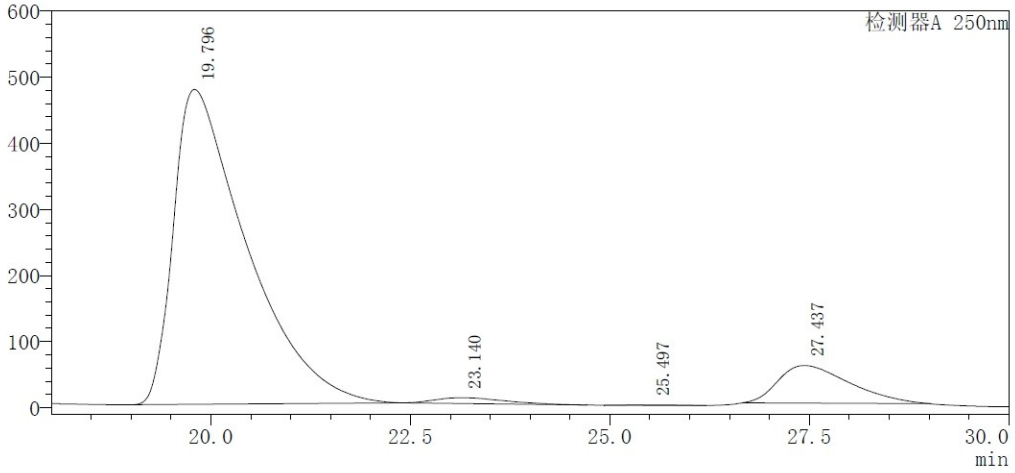

4.25
2.27
0.93
3.33
1.00
1.76
2.54
2.92
f1 (ppm)



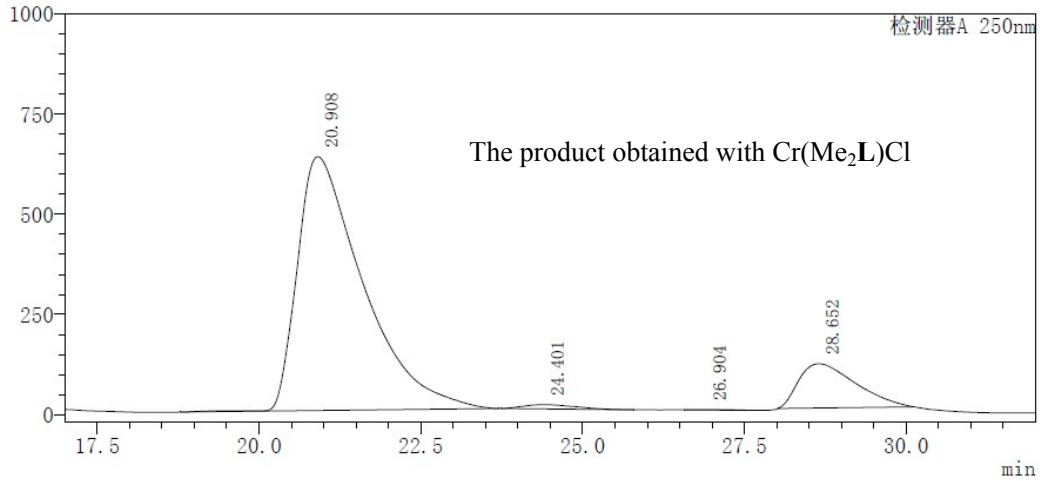
5-(4-fluorophenyl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

Enantiomeric excess was determined by HPLC with a chiralcel OJ-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t_{major} = 19.79 min, t_{minor} = 27.43 min; ee_{trans} =72%, ee_{cis} =95%. $Dr_{(trans/cis)}$=1:0.21. ^1H NMR ($CDCl_3$) δ: 0.66 (d, J=8 Hz, 3H), 1.95 (m, 2H), 2.17 (m, 2H), 2.75(m, 1H), 3.97 (d, J=7.2 Hz, 1H), 4.16 (m, 2H), 6.9~7.10 (m, 4H).

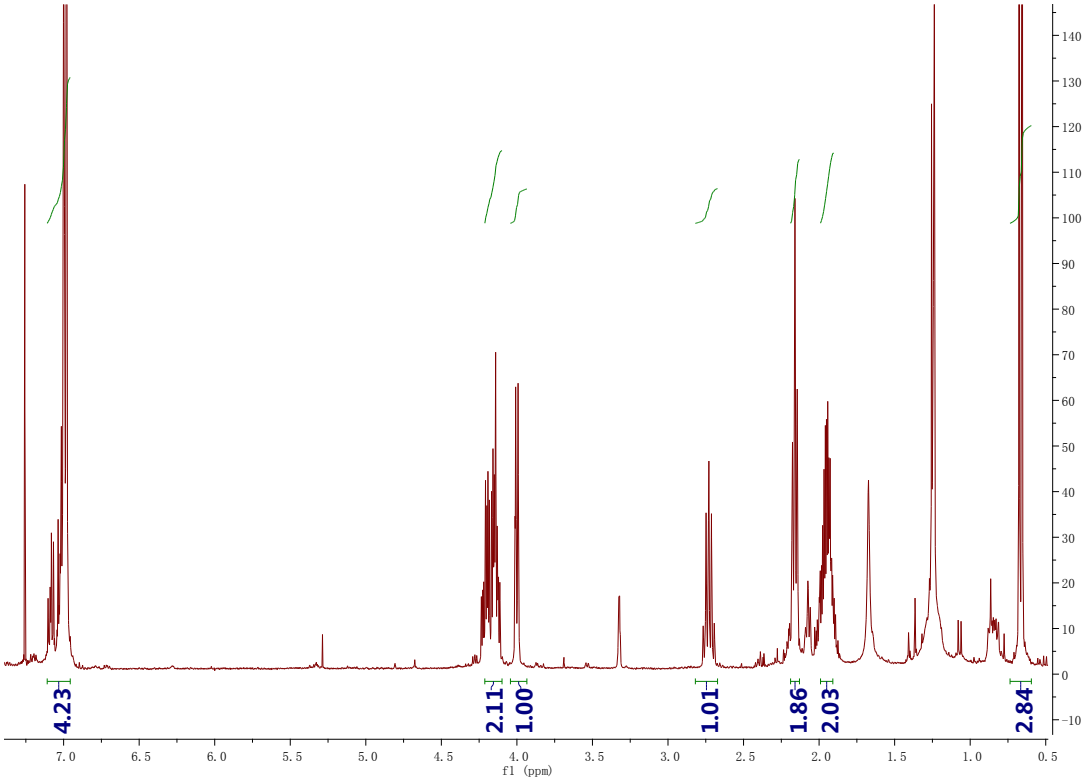


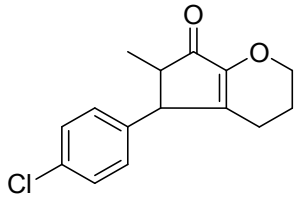


Serial Number	Retention Time [min]	Area	Area %
1	19.796	30466069	88.101
2	23.140	526241	1.522
3	25.497	24531	0.071
4	27.437	3563965	10.306



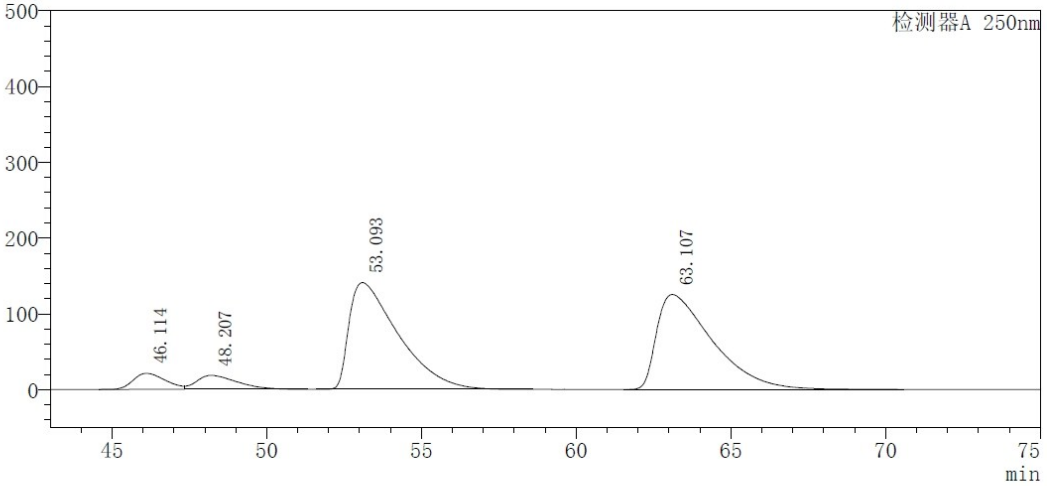
Serial Number	Retention Time [min]	Area	Area %
1	20.908	44784544	85.905
2	24.401	592671	1.137
3	26.904	35546	0.068
4	28.652	6719637	12.890

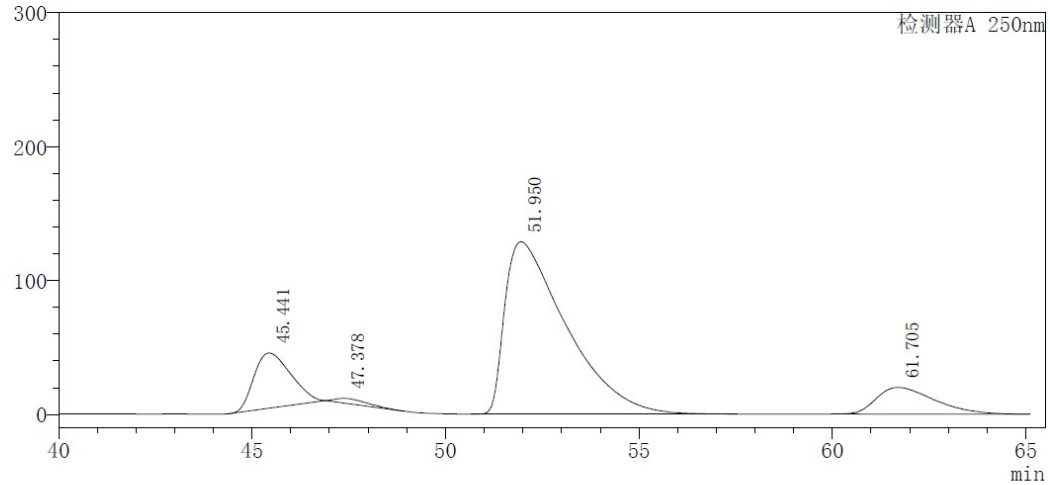




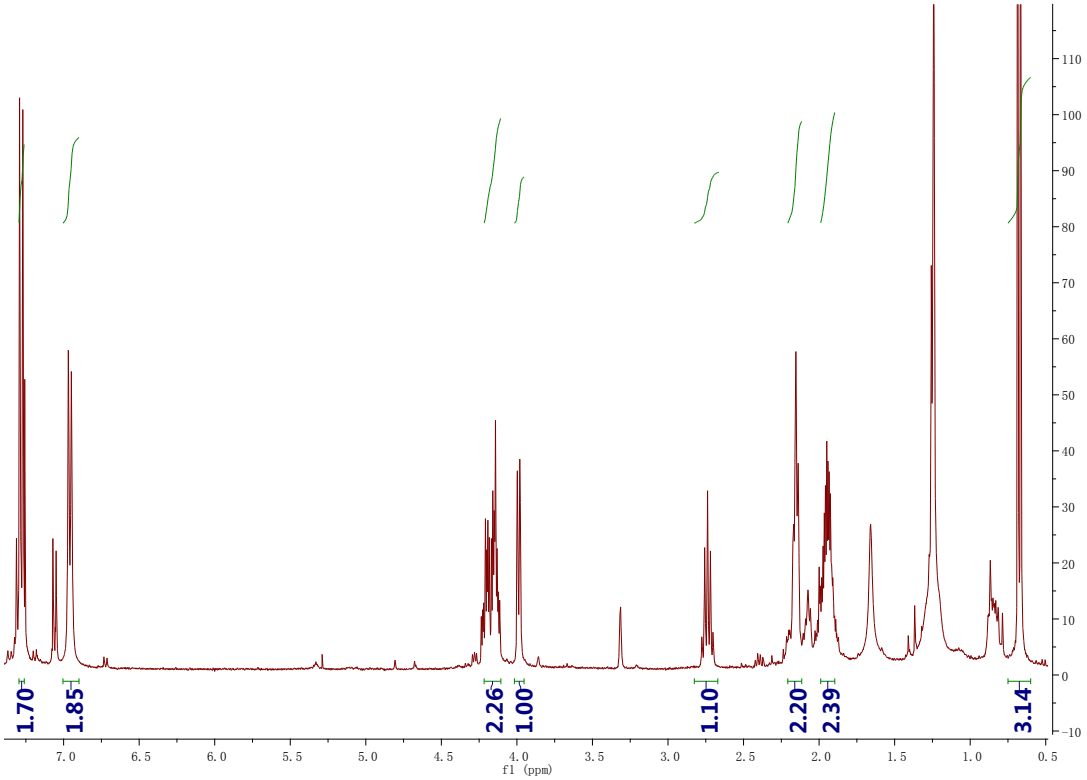
5-(4-chlorophenyl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

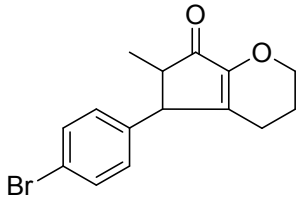
Enantiomeric excess was determined by HPLC with a chiralcel AS-H column (hexane/i-PrOH = 93/7, 1.0 mL/min, 250 nm), t $_{major}$ = 51.96 min, t $_{minor}$ = 61.70 min; ee_{trans} =78%, ee_{cis} =86%. $Dr_{(trans/cis)}$=1:0.21. ^{1}H NMR ($CDCl_3$) δ: 0.67 (d, J=8 Hz, 3H), 1.90 (m, 2H), 2.15 (m, 2H), 2.73(m, 1H), 3.97 (d, J=7.2 Hz, 1H), 4.15 (m, 2H), 6.95 (d, J=8 Hz, 2H), 7.30 (d, J=8 Hz, 2H).





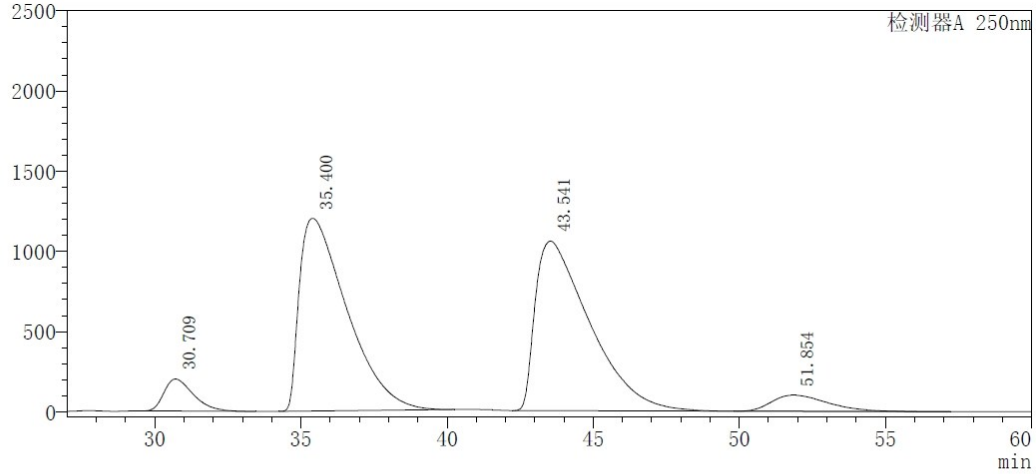
Serial Number	Retention Time [min]	Area	Area %
1	45.441	2720256	14.110
2	47.378	210895	1.094
3	51.950	14247018	73.897
4	61.705	2101317	10.899

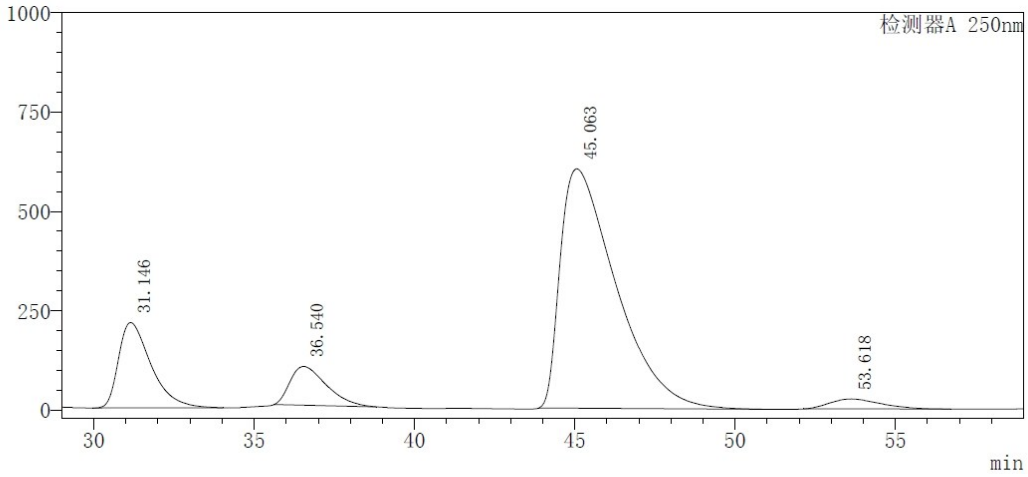

1.70
1.85
2.26
1.00
1.10
2.20
2.39
3.14
f1 (ppm)



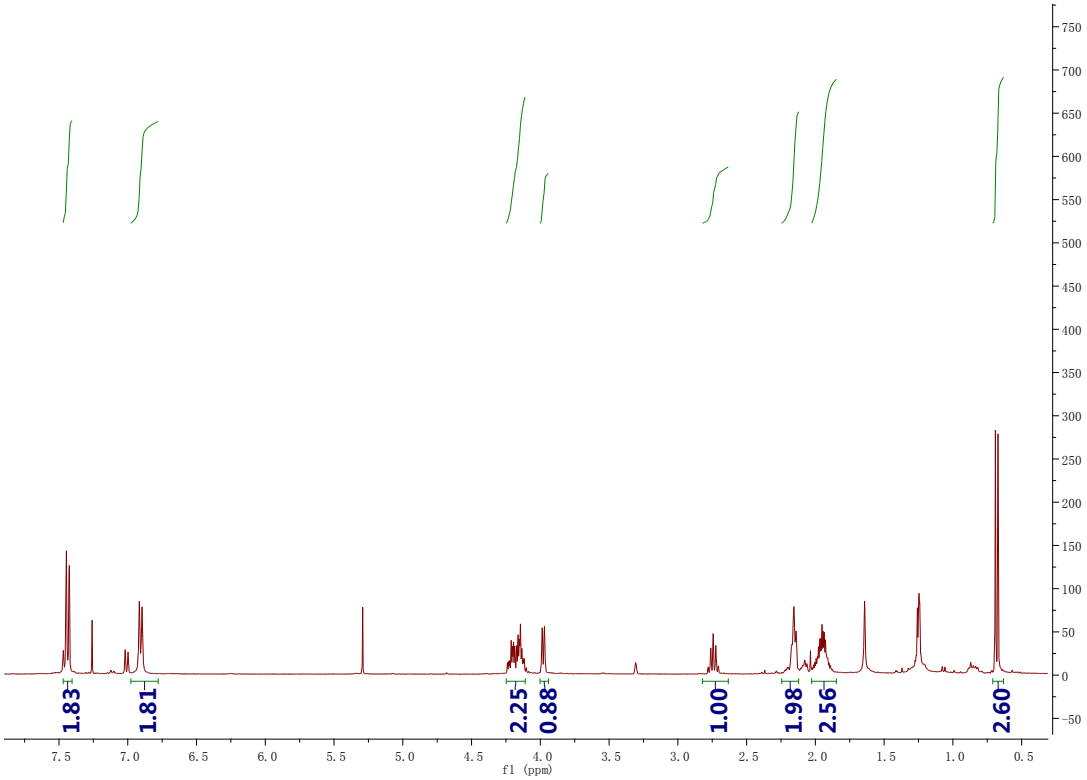
5-(4-bromophenyl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

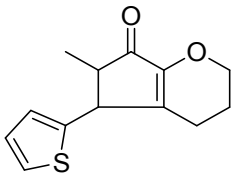
Enantiomeric excess was determined by HPLC with a chiralcel AS-H column (hexane/i-PrOH = 93/7, 1.0 mL/min, 250 nm), t $_{major}$ = 45.06 min, t $_{minor}$ = 36.54 min; ee_{trans} =81%, ee_{cis} =70%. $Dr_{(trans/cis)}$=1:0.18. ^{1}H NMR ($CDCl_3$) δ: 0.66 (d, J=8.4 Hz, 3H), 1.95 (m, 2H), 2.15 (m, 2H), 2.75 (m, 1H), 3.98 (d, J=7.2 Hz, 1H), 4.18 (m, 2H), 6.9 (d, J =8 Hz, 2H), 7.45 (d, J =8 Hz, 2H).





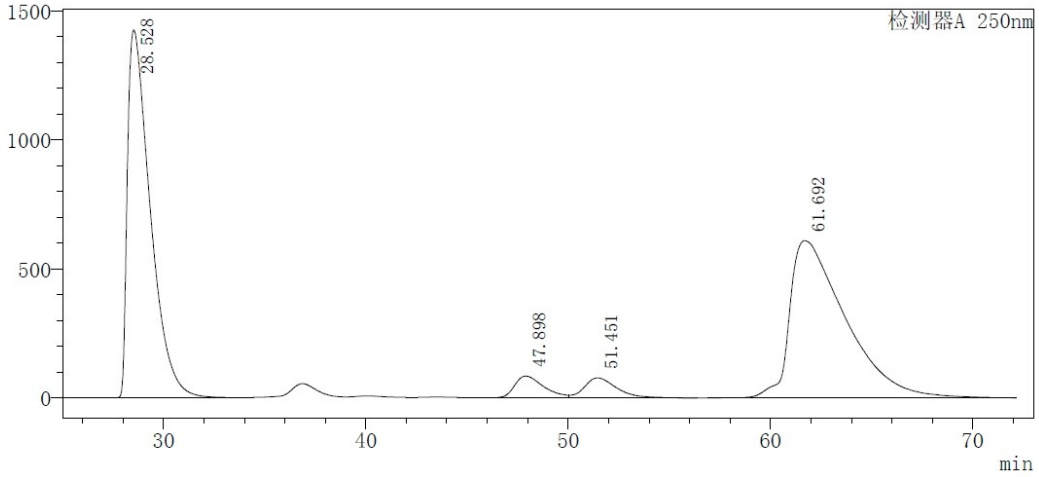
Serial Number	Retention Time [min]	Area	Area %
1	31.146	15126135	15.363
2	36.540	7704605	7.825
3	45.063	72883792	74.024
4	53.618	2745562	2.789

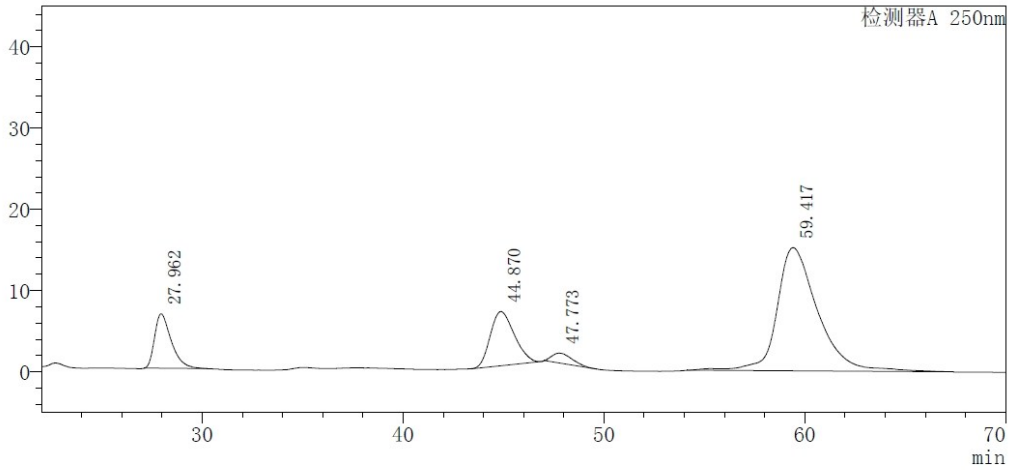

1.83
1.81
2.25
0.88
1.00
1.98
2.56
2.60
f1 (ppm)



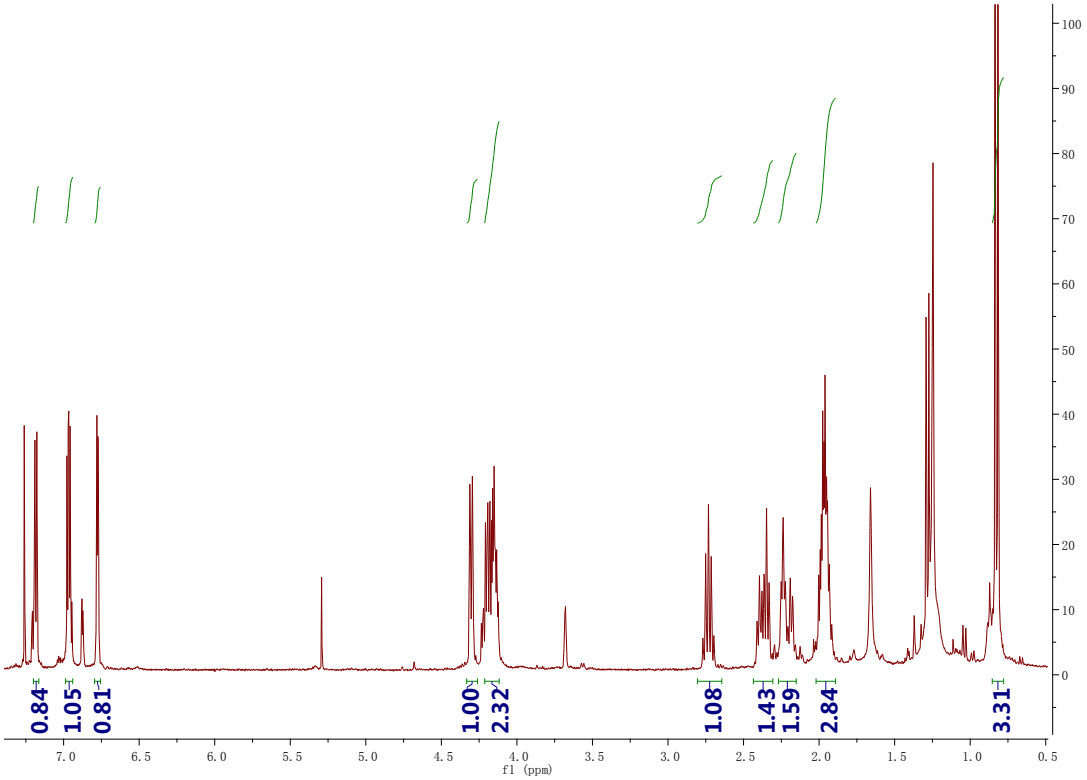
6-methyl-5-(thiophen-2-yl)-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

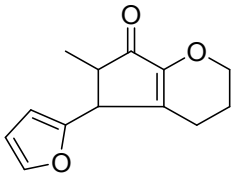
Enantiomeric excess was determined by HPLC with a chiralcel AS-H column (hexane/i-PrOH = 93/7, 1.0 mL/min, 250 nm), t $_{major}$ = 59.42 min, t $_{minor}$ = 27.96 min; ee_{trans} =70%, ee_{cis} =73%. $Dr_{(trans/cis)}$=1:0.25. ^{1}H NMR ($CDCl_3$) δ: 0.82 (d, J=7.6 Hz, 3H), 1.95 (m, 2H), 2.30 (m, 2H), 2.73 (m, 1H), 4.16 (m, 2H), 4.30 (d, J=6.4 Hz, 1H), 6.75 (m, 1H), 6.95 (m, 1H), 7.18 (m, 1H).





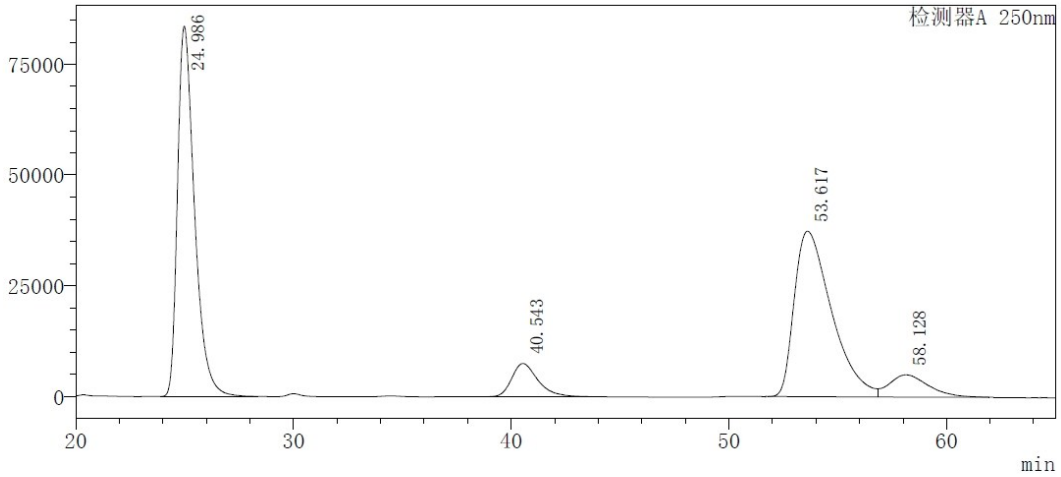
Serial Number	Retention Time [min]	Area	Area %
1	27.962	387212	12.206
2	44.870	552351	17.411
3	47.773	86955	2.741
4	59.417	2145823	67.642

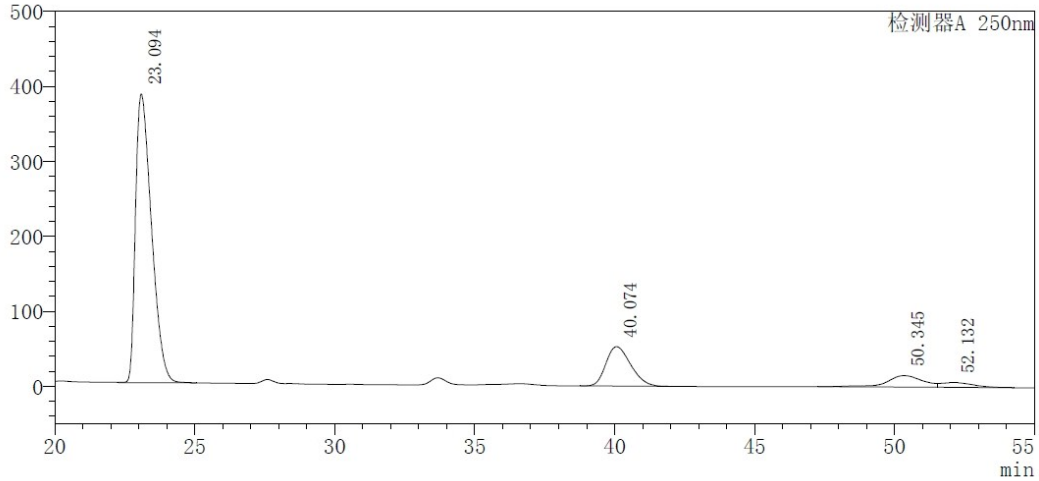

0.84
1.05
0.81
1.00
2.32
1.08
1.43
1.59
2.84
3.31
f1 (ppm)



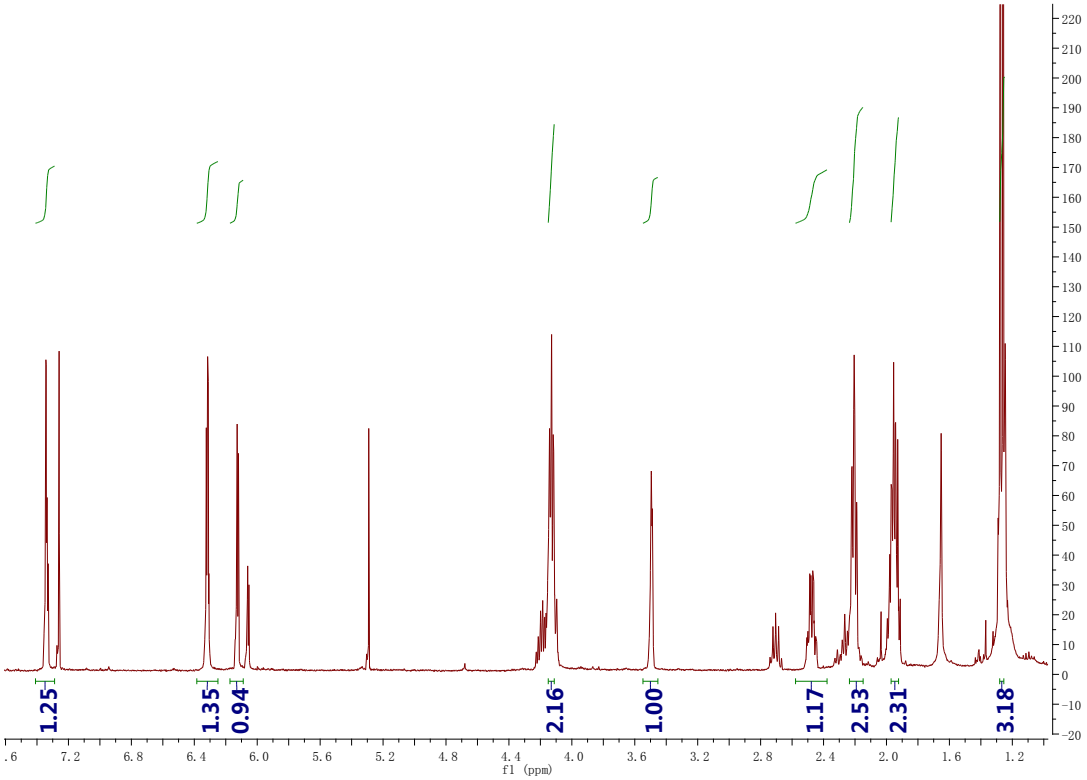
5-(furan-2-yl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

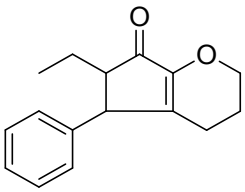
Enantiomeric excess was determined by HPLC with a chiralcel AS-H column (hexane/i-PrOH = 93/7, 1.0 mL/min, 250 nm), t $_{major}$ = 23.09 min, t $_{minor}$ = 50.34 min; ee_{trans} =90%, ee_{cis} =91%. $Dr_{(trans/cis)}$=1:1.67. ^{1}H NMR ($CDCl_3$) δ: 1.27 (d, J=7.6 Hz, 3H), 1.95 (m, 2H), 2.20 (m, 2H), 2.48 (m, 1H), 3.50 (m, 1H), 4.15 (m, 2H), 6.15 (m, 1H), 6.32 (m, 1H), 7.34 (m, 1H).





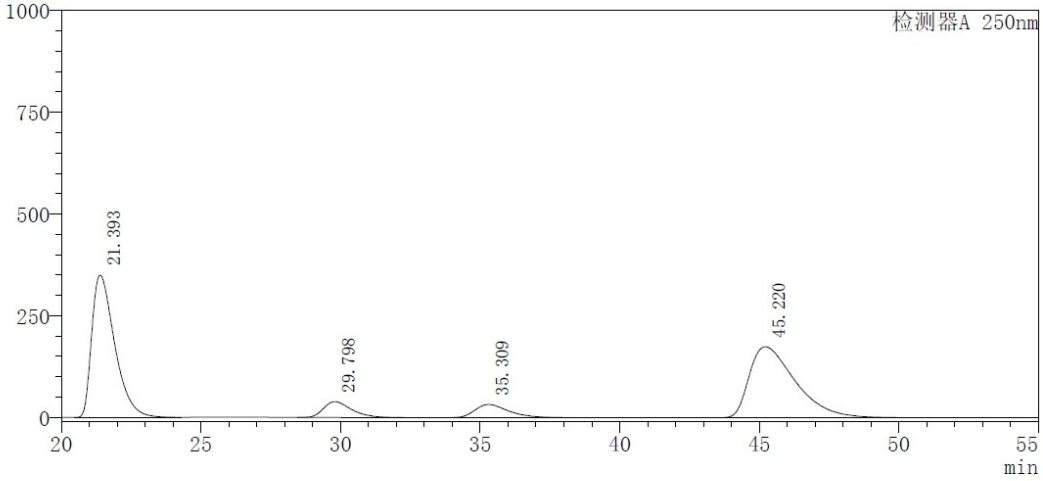
Serial Number	Retention Time [min]	Area	Area %
1	23.094	15231520	74.865
2	40.074	3240857	15.925
3	50.345	1370418	6.736
4	52.132	502391	2.469

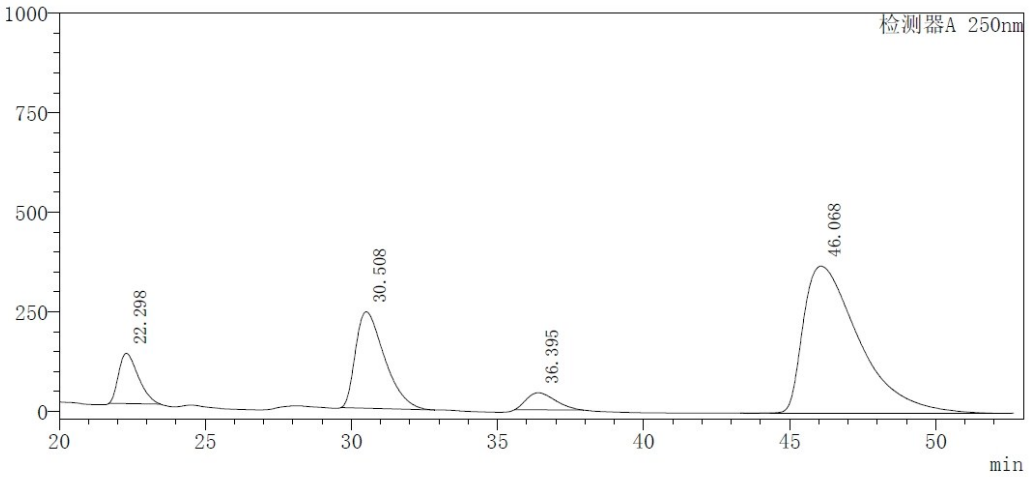

1.25
1.35
0.94
2.16
1.00
1.17
2.53
2.31
3.18
f1 (ppm)



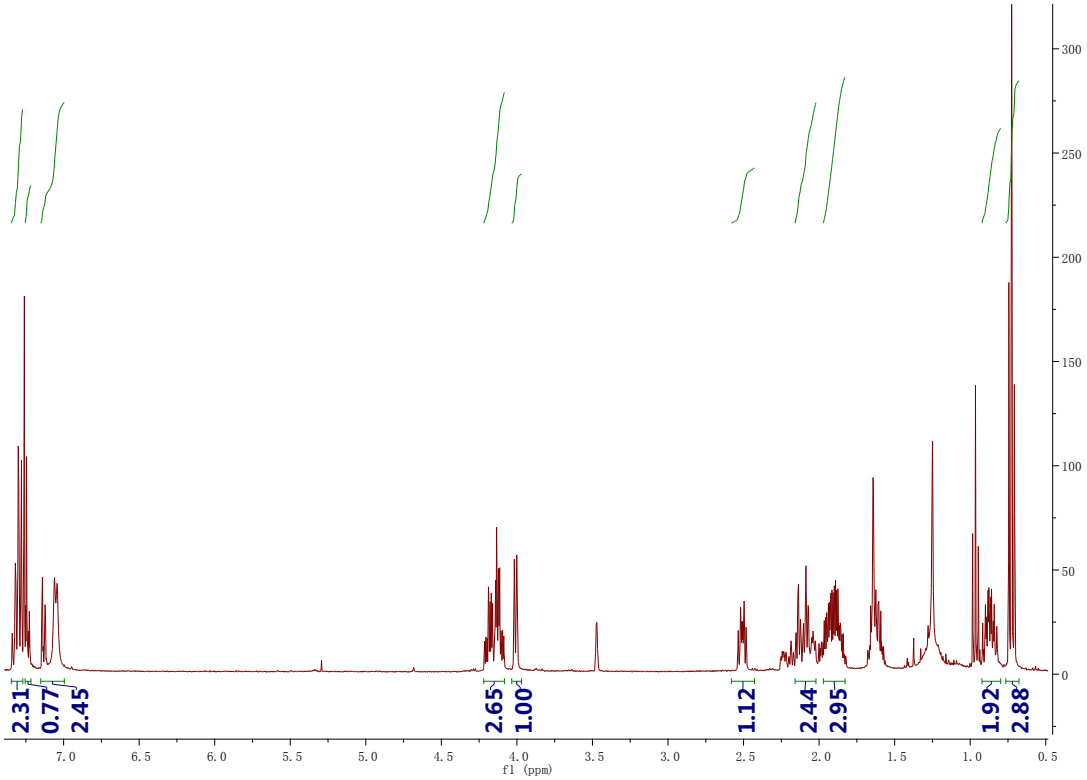
6-ethyl-5-phenyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

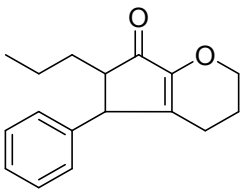
Enantiomeric excess was determined by HPLC with a chiralcel AS-H column (hexane/i-PrOH = 93/7, 1.0 mL/min, 250 nm), t_{major} = 46.09 min, t_{minor} = 22.29 min; ee_{trans} =80%, ee_{cis} =72%. $Dr_{(trans/cis)}$=1:0.29. ^1H NMR ($CDCl_3$) δ: 0.73 (t, 3H), 0.85 (m, 2H), 1.90 (m, 2H), 2.10 (m, 2H), 2.50 (m, 1H), 4.0 (d, J=6.8 Hz, 1H), 4.15 (m, 2H), 7.0~7.34 (m, 5H).





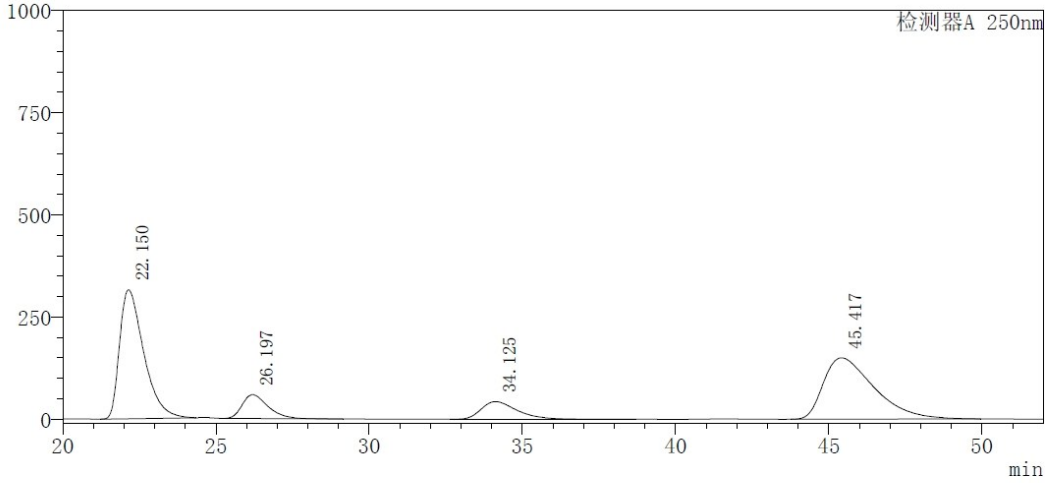
Serial Number	Retention Time [min]	Area	Area %
1	22.298	5888481	7.868
2	30.508	16757611	22.390
3	36.395	2951358	3.943
4	46.068	49247601	65.799

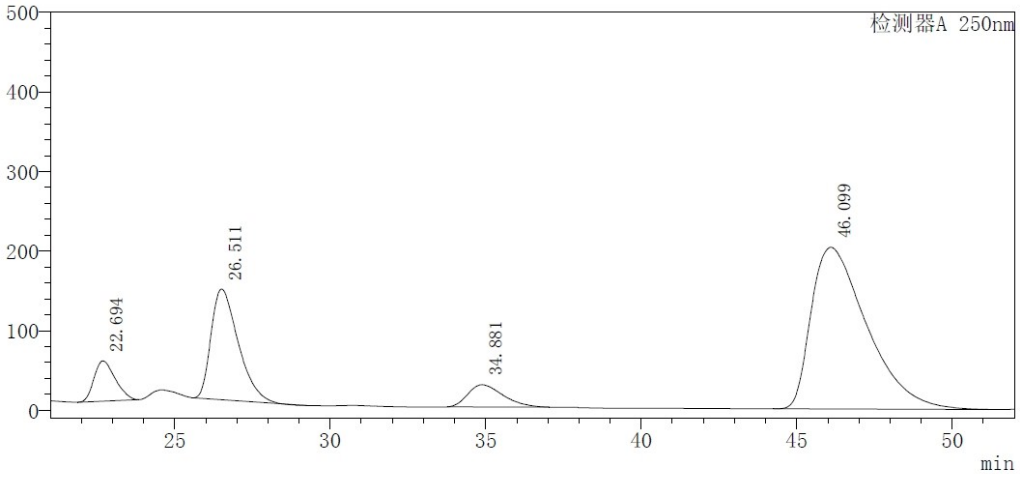

2.31
0.77
2.45
2.65
1.00
1.12
2.44
2.95
1.92
2.88
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
300
250
200
150
100
50
0



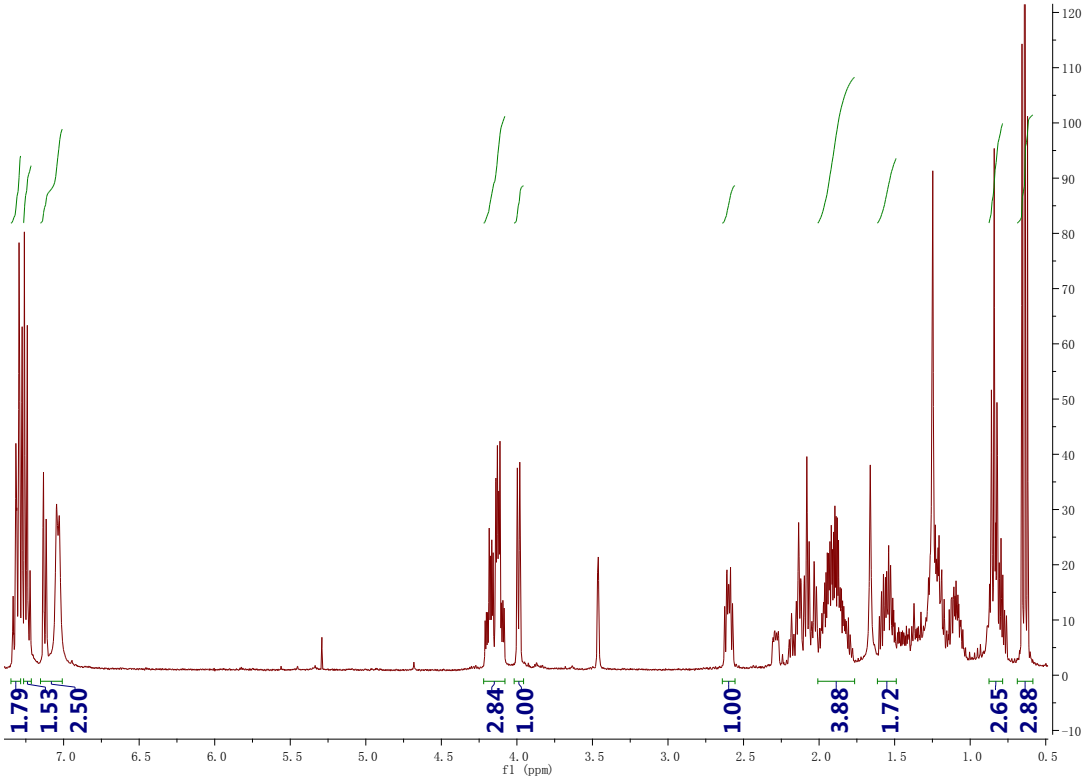
5-phenyl-6-propyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

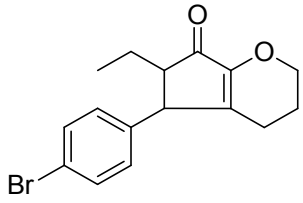
Enantiomeric excess was determined by HPLC with a chiralcel AS-H column (hexane/i-PrOH = 93/7, 1.0 mL/min, 250 nm), t $_{major}$ = 46.09 min, t $_{minor}$ = 22.69 min; ee_{trans} =79%, ee_{cis} =76%. $Dr_{(trans/cis)}$=1:0.37. ^{1}H NMR ($CDCl_3$) δ: 0.64 (t, 3H), 0.84 (m, 2H), 1.55 (m, 2H), 1.75~2.0 (m, 4H), 2.60 (m, 1H), 4.0 (d, J=6.8 Hz, 1H), 4.15 (m, 2H), 7.0~7.35 (m, 5H).





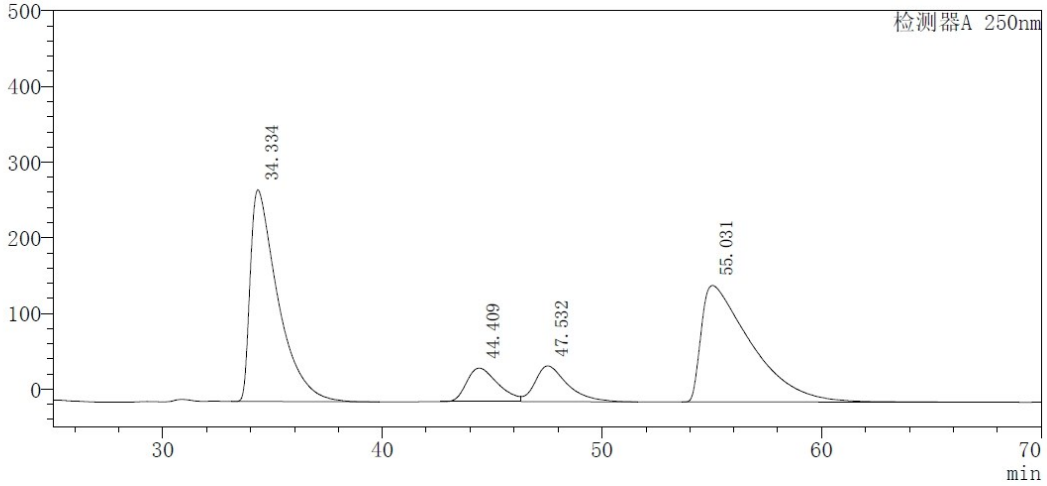
Serial Number	Retention Time [min]	Area	Area %
1	22.694	2399145	6.246
2	26.511	8436627	21.965
3	34.811	2207949	5.748
4	46.099	25366320	66.041

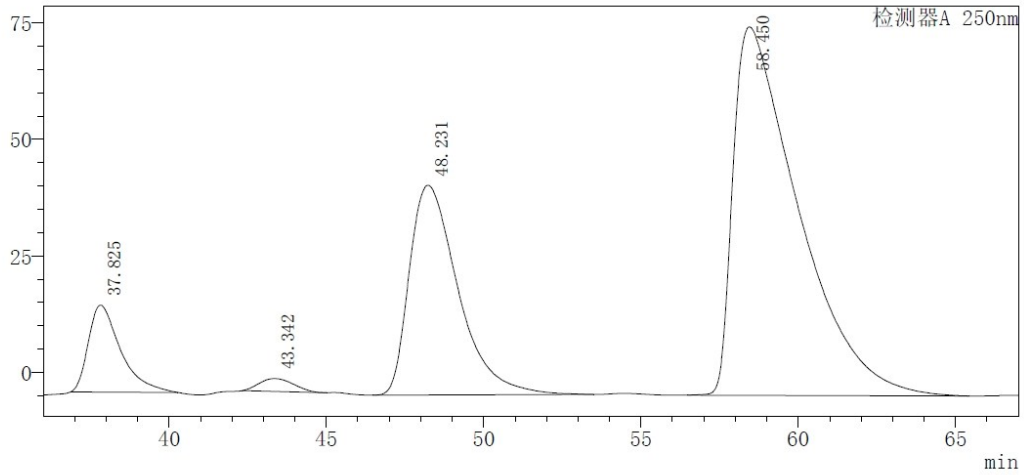

1.79
1.53
2.50
2.84
1.00
1.00
3.88
1.72
2.65
2.88
f1 (ppm)



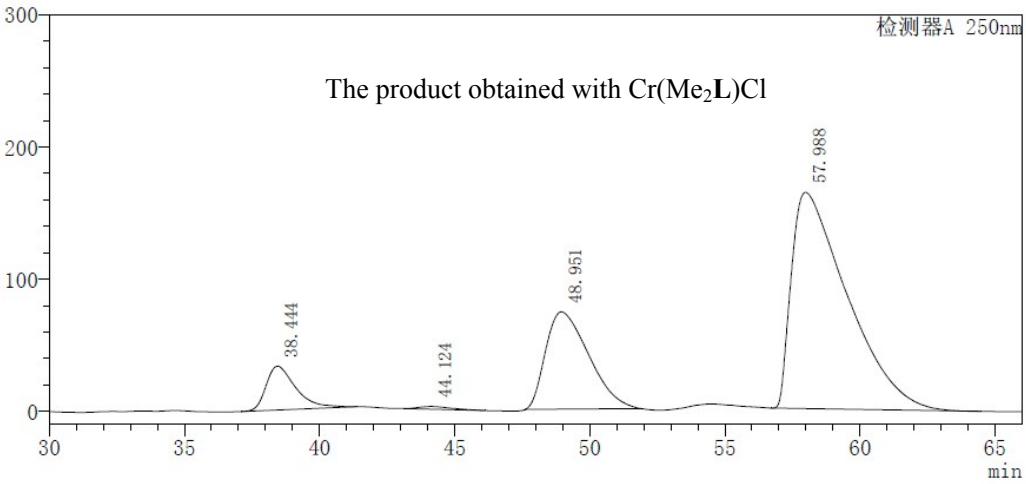
5-(4-bromophenyl)-6-ethyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one

Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 98.5/1.5, 1.2 mL/min, 250 nm), t_{major} = 58.45 min, t_{minor} = 37.82 min; ee_{trans} =84%, ee_{cis} =90%. $Dr_{(trans/cis)}$=1:0.30. ^1H NMR ($CDCl_3$) δ: 0.73 (t, 3H), 0.84 (m, 2H), 1.80~2.10 (m, 4H), 2.53(m, 1H), 3.98 (d, J=8 Hz, 1H), 4.15 (m, 2H), 6.9 (m, 2H), 7.45 (m, 2H).

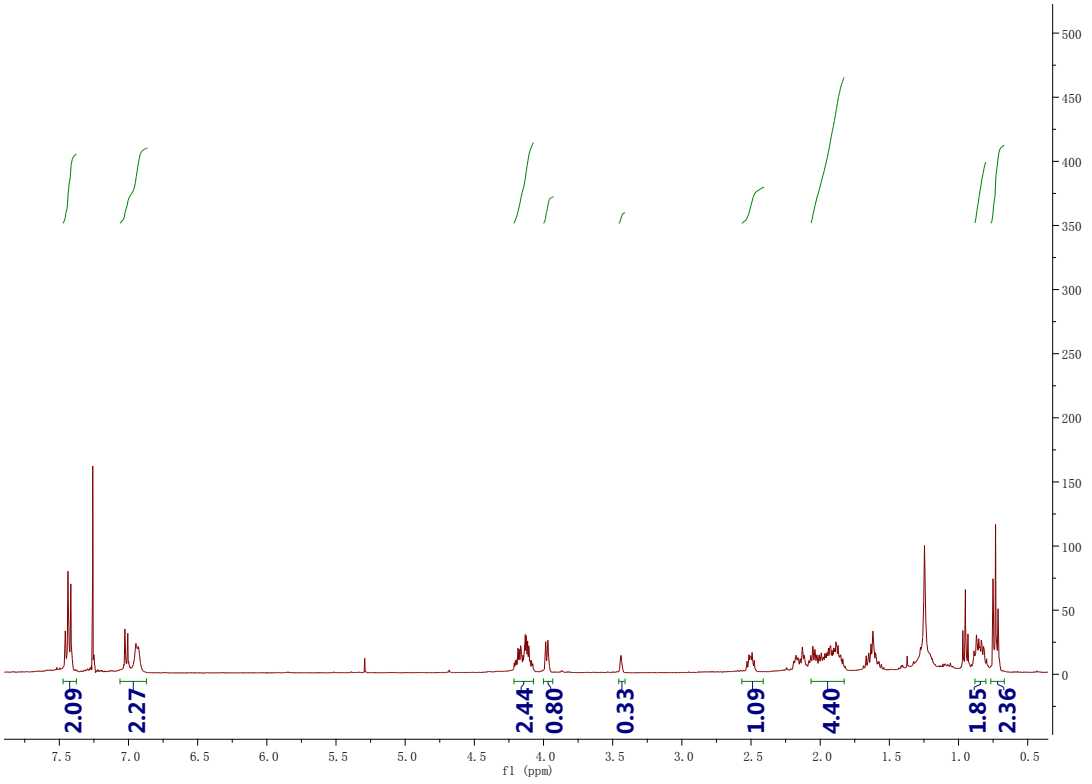




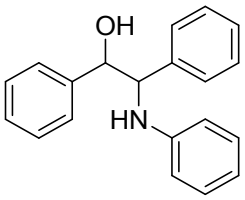
Serial Number	Retention Time [min]	Area	Area %
1	37.825	1327786	7.461
2	43.342	208567	1.172
3	48.231	4869997	27.365
4	58.450	11389785	64.001



Serial Number	Retention Time [min]	Area	Area %
1	38.444	2526043	7.340
2	44.124	168681	0.490
3	48.951	8163885	23.721
4	57.988	23558176	68.450

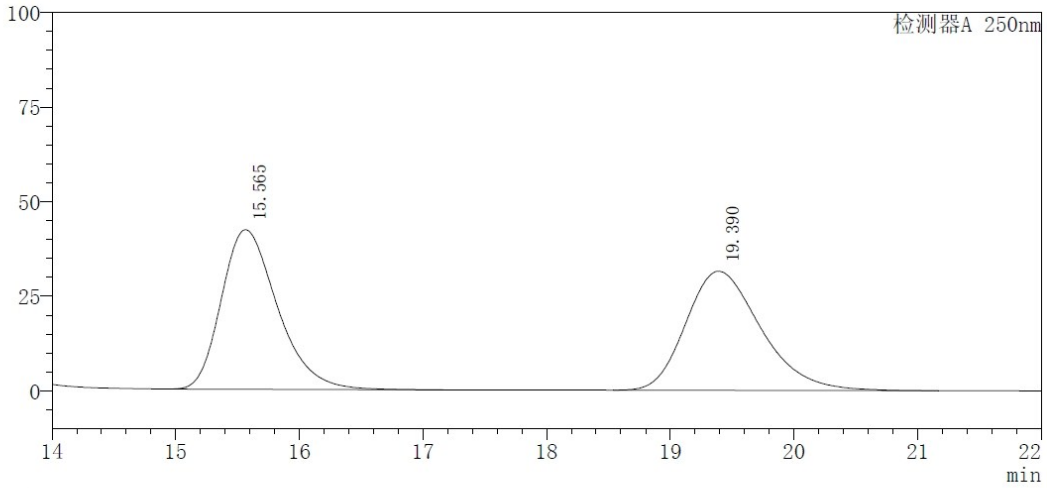


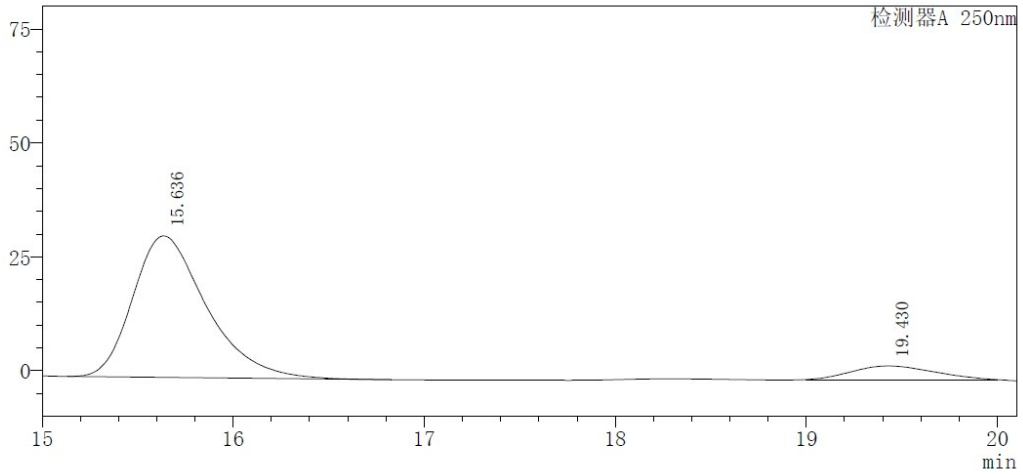
15.2 Aminolysis of trans-Stilbene Oxide with Anilines



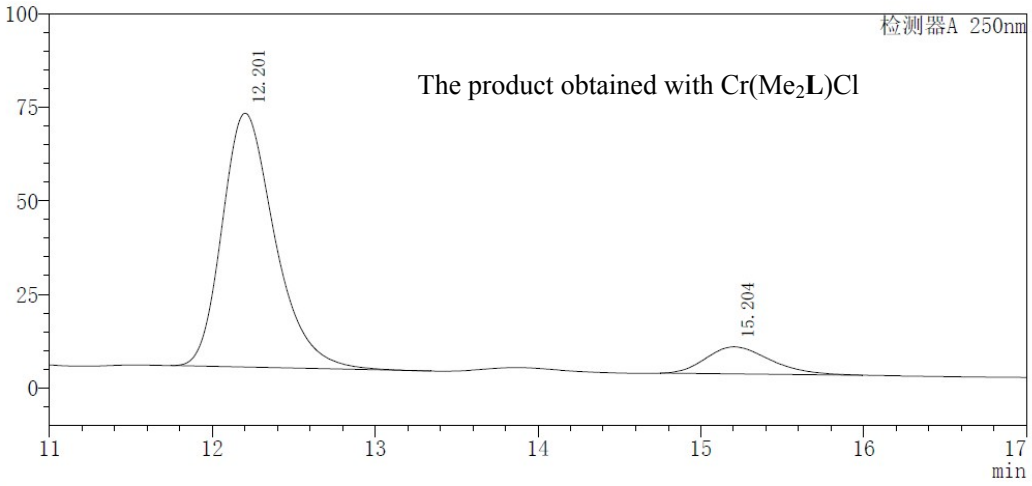
1,2-diphenyl-2-(phenylamino)ethanol

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} = 15.63 min, t_{minor} = 19.43 min; ee=82%. ^1H NMR ($CDCl_3$): δ: 2.29 (s, 1H), 4.44 (bs, 1H), 4.65 (d, J=4.8 Hz, 1H), 5.05 (d, J=4.8 Hz, 1H), 6.48~7.5 (m, 15H);

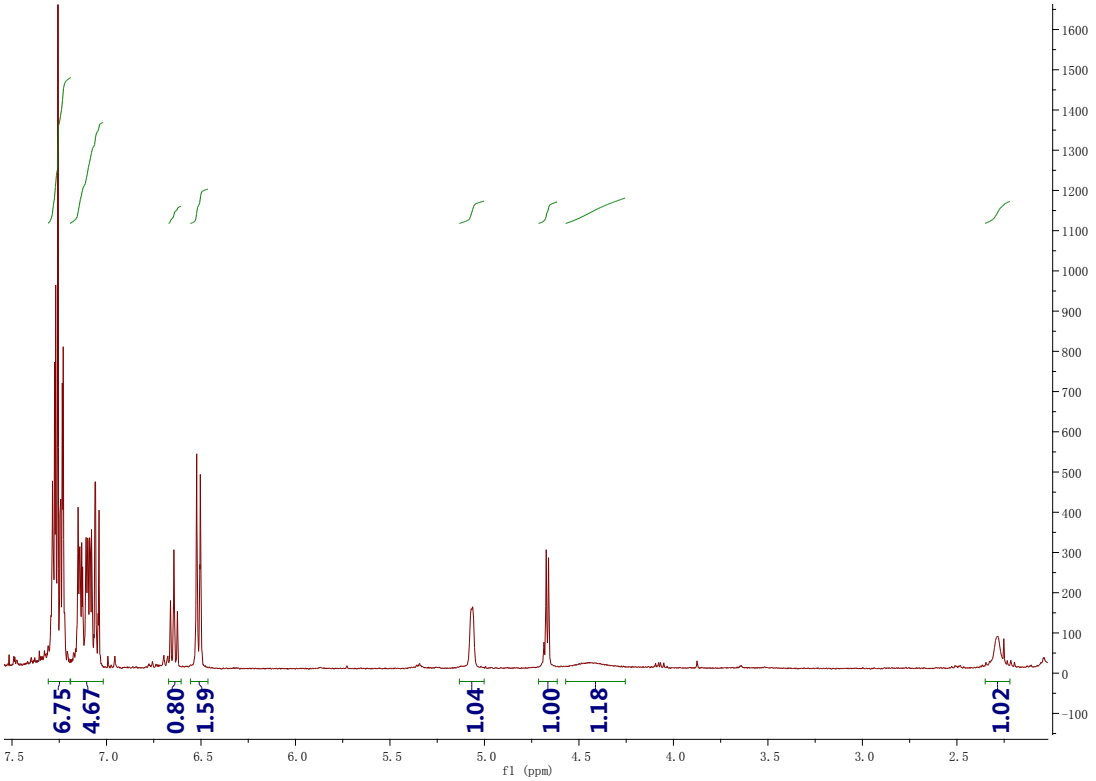


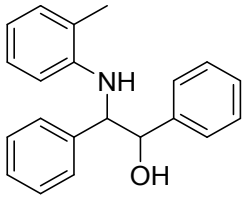


Serial Number	Retention Time [min]	Area	Area %
1	15.636	833496	90.326
2	19.430	89269	9.674



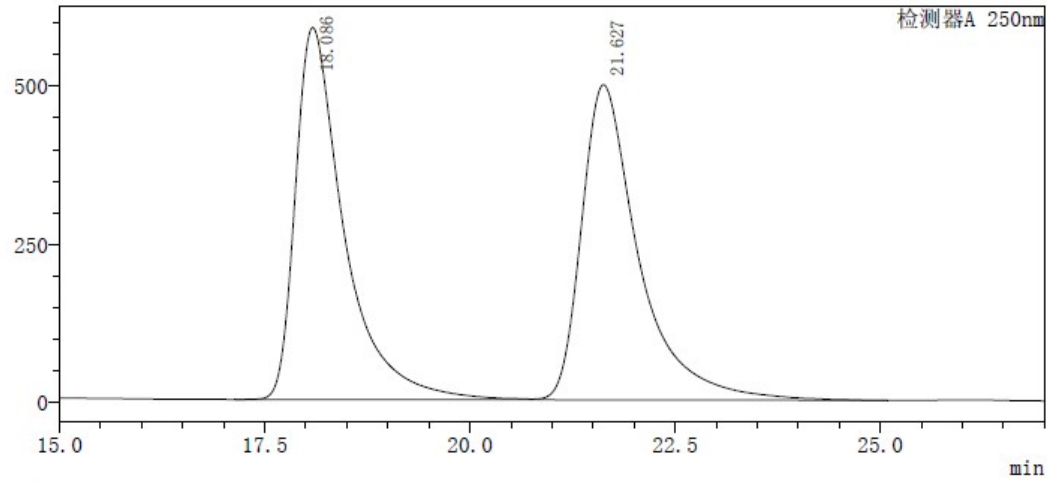
Serial Number	Retention Time [min]	Area	Area %
1	12.201	1524944	88.395
2	15.204	200201	11.605

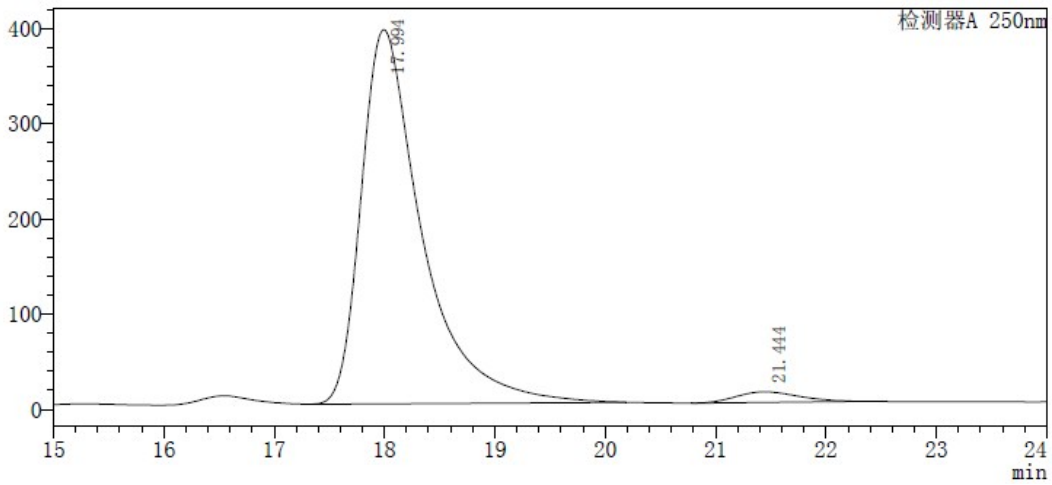




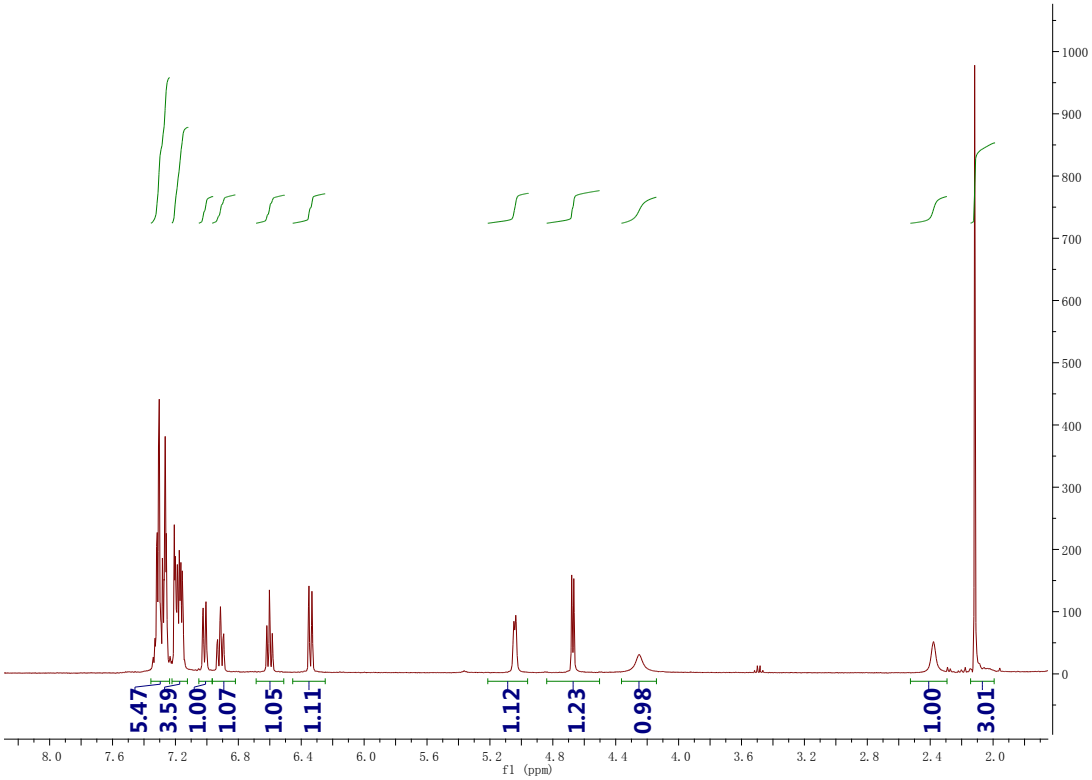
2-((*o*-methlyphenyl)amino)-1,2-diphenylethanol

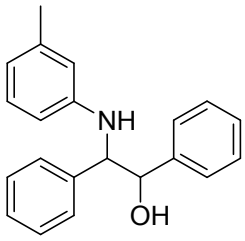
Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{major} = 17.99 min, t_{minor} = 21.44 min; ee=94.3%. ^{1}H NMR ($CDCl_3$): δ: 2.10 (s, 3H), 2.4 (s, 1H), 4.25 (s, 1H), 4.65 (d, J=5.2 Hz, 1H), 5.05 (d, J=5.2 Hz, 1H), 6.30~7.35 (m, 14H).





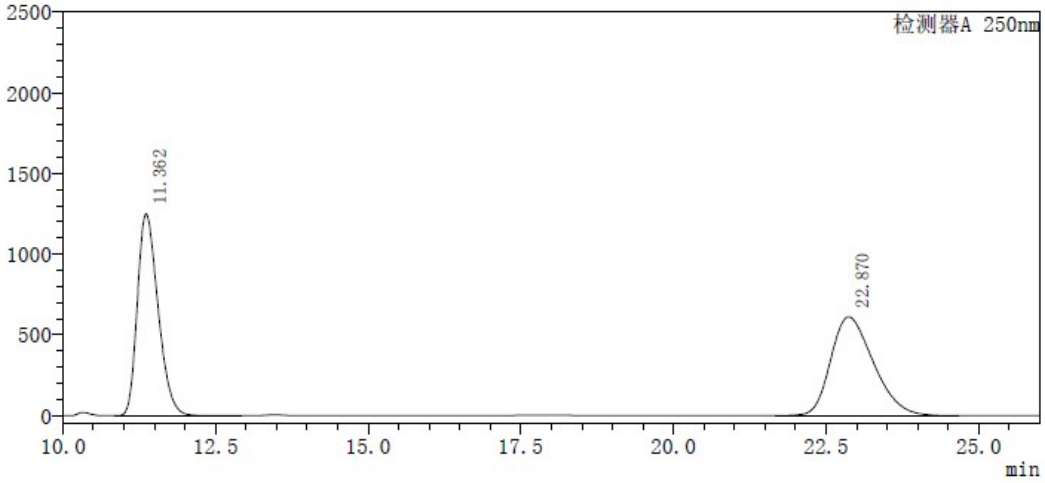
Serial Number	Retention Time [min]	Area	Area %
1	17.994	15009446	97.129
2	21.444	443707	2.871

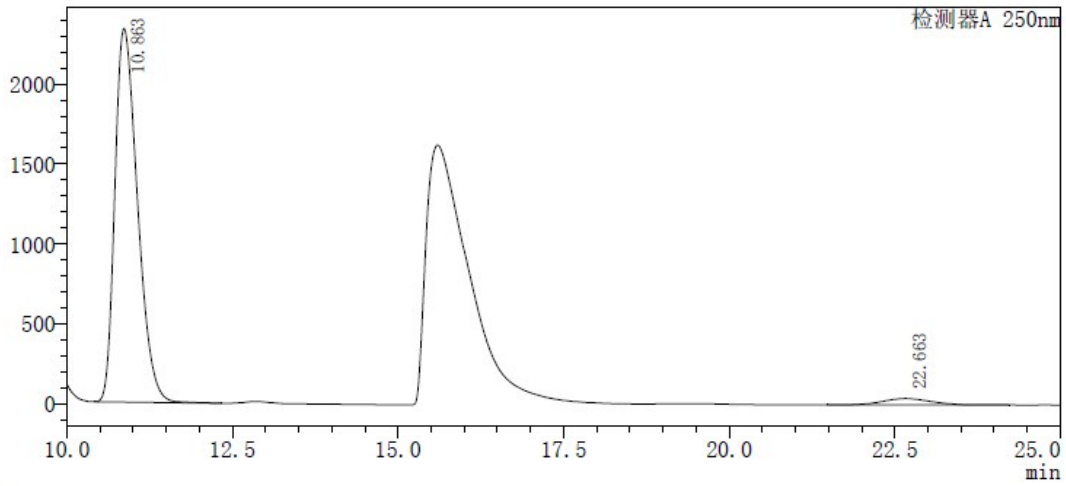

5.47
3.59
1.00
1.07
1.05
1.11
1.12
1.23
0.98
1.00
3.01
f1 (ppm)



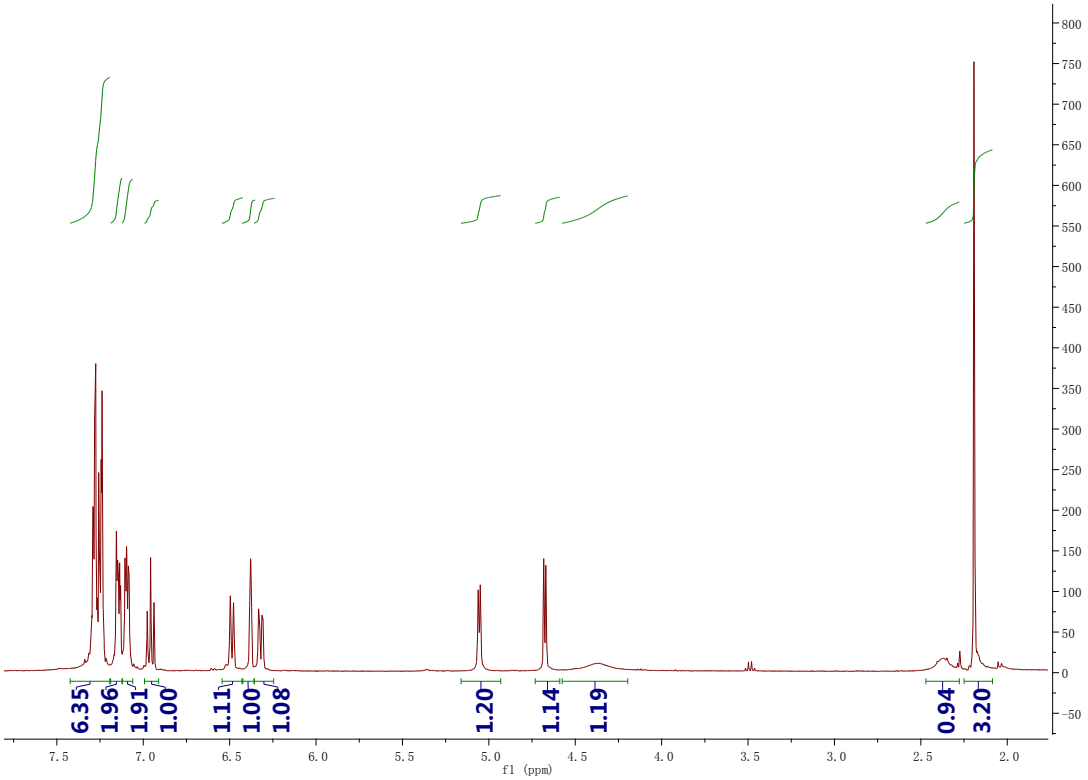
2-((*m*-methlyphenyl)amino)-1,2-diphenylethanol

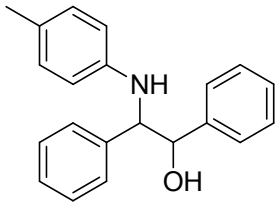
Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t_{major} = 10.86 min, t_{minor} = 22.66 min; ee=93%. ^{1}H NMR ($CDCl_3$): δ: 2.18 (s, 3H), 2.4 (s, 1H), 4.40 (s, 1H), 4.67 (d, J=5.6 Hz, 1H), 5.05 (d, J=5.6 Hz, 1H), 6.25~7.35 (m, 14H).





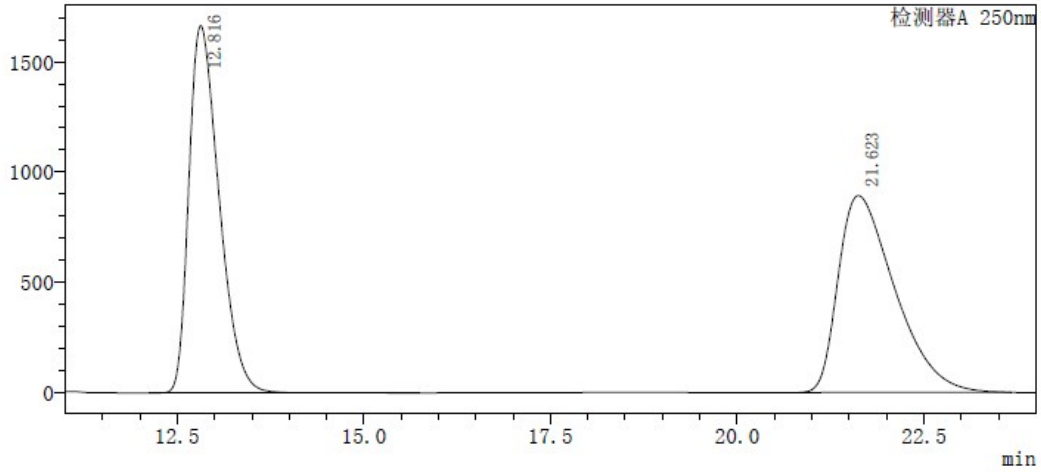
Serial Number	Retention Time [min]	Area	Area %
1	10.863	55586865	96.475
2	22.663	2031117	3.525

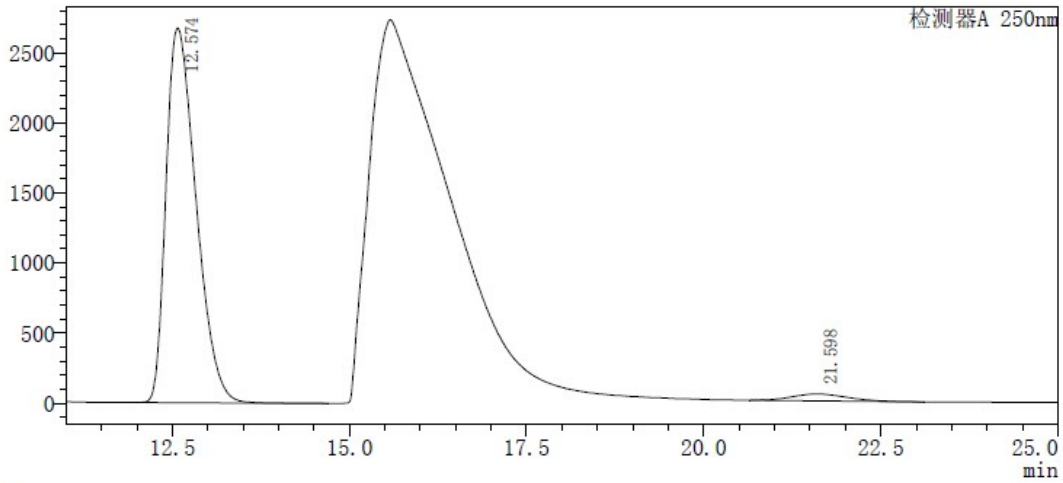

6.35
1.96
1.91
1.00
1.11
1.00
1.08
1.20
1.14
1.19
0.94
3.20
f1 (ppm)



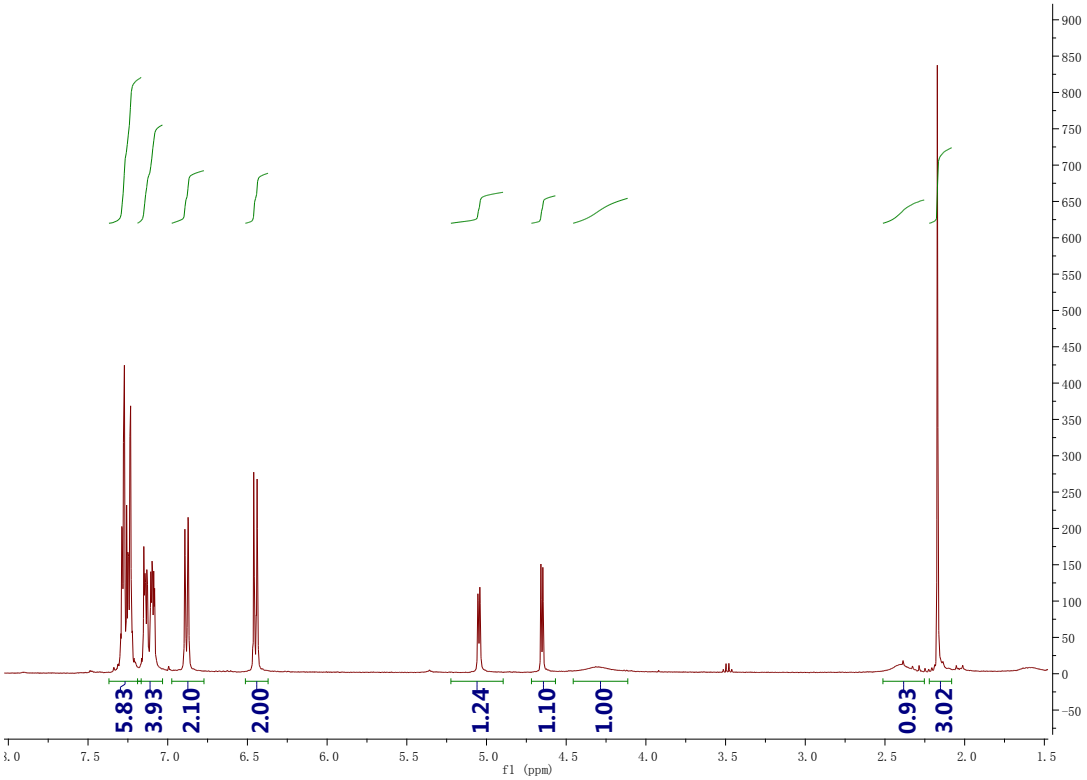
2-((*p*-methlyphenyl)amino)-1,2-diphenylethanol

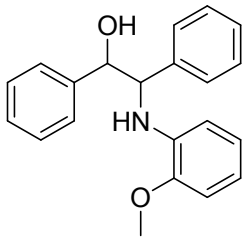
Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t_{major} = 12.57 min, t_{minor} = 21.59 min; ee=93.5%. ^{1}H NMR ($CDCl_3$): δ: 2.18 (s, 3H), 2.4 (s, 1H), 4.28 (s, 1H), 4.65 (d, J=5.6 Hz, 1H), 5.05 (d, J=5.6 Hz, 1H), 6.40~7.35 (m, 14H).





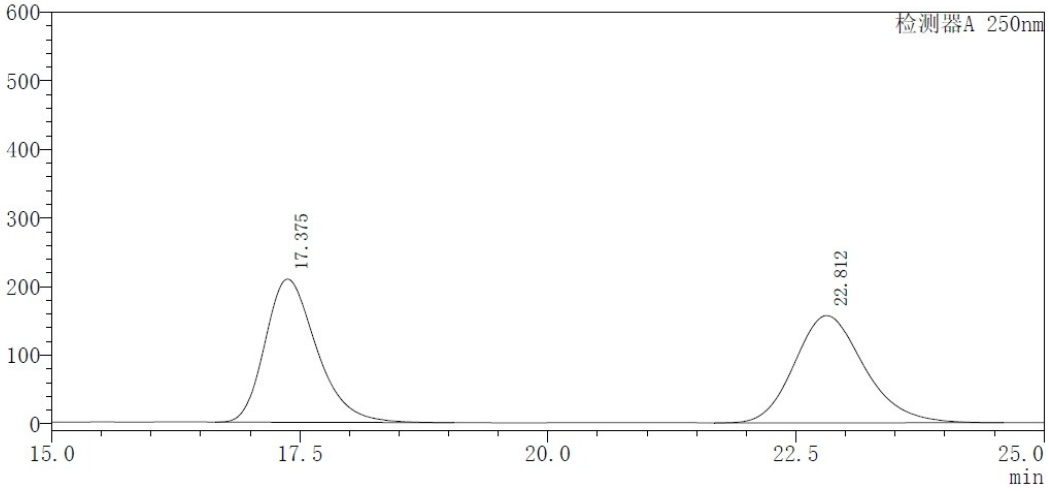
Serial Number	Retention Time [min]	Area	Area %
1	12.574	78842770	96.725
2	21.598	2669789	3.275

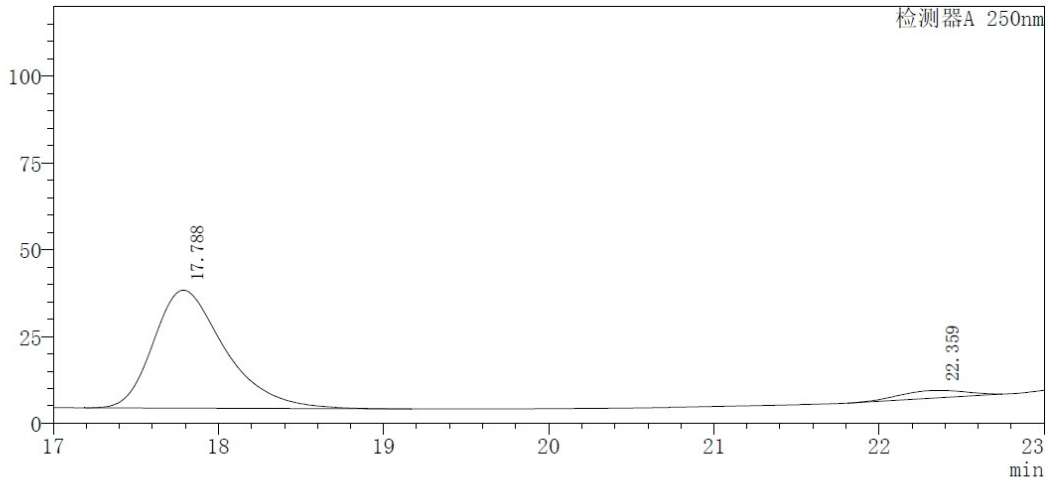

5.83
3.93
2.10
2.00
1.24
1.10
1.00
0.93
3.02
f1 (ppm)



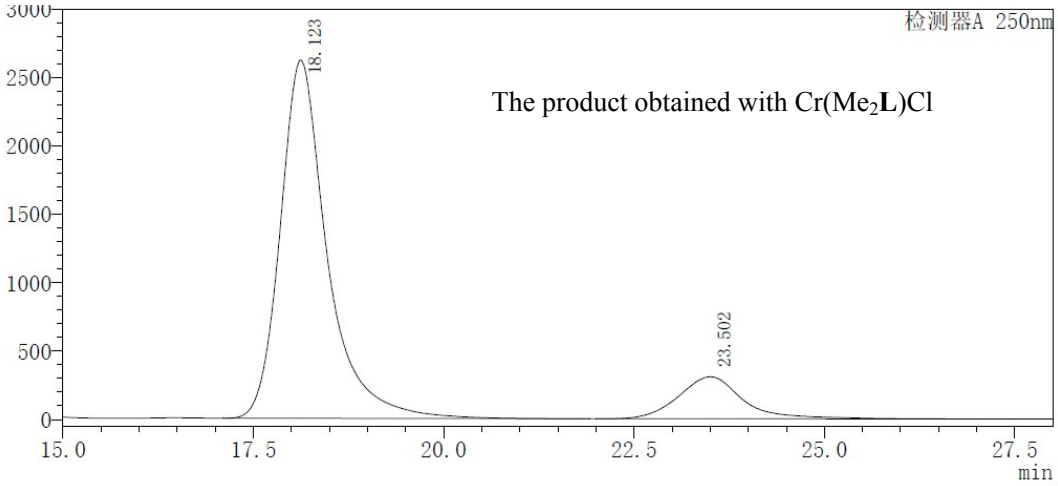
2-((2-methoxyphenyl)amino)-1,2-diphenylethanol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 90/10, 0.75 mL/min, 250 nm), t $_{major}$ = 17.78 min, t $_{minor}$ = 22.81 min; ee=84%. ^{1}H NMR ($CDCl_3$): δ: 3.83 (s, 3H), 4.66 (d, J=5.6 Hz, 1H), 5.10 (d, J=5.6 Hz, 1H), 6.35~7.44 (m, 14H).

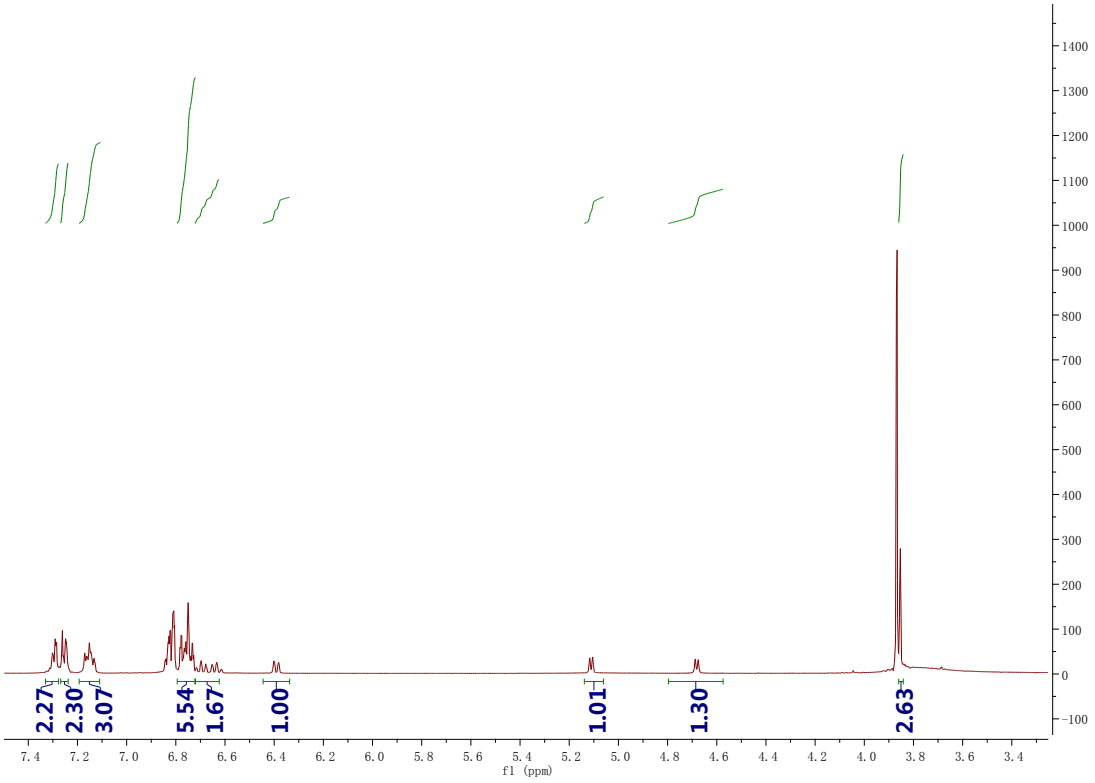


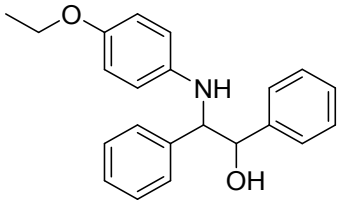


Serial Number	Retention Time [min]	Area	Area %
1	17.788	1024459	94.380
2	22.359	610001	5.620



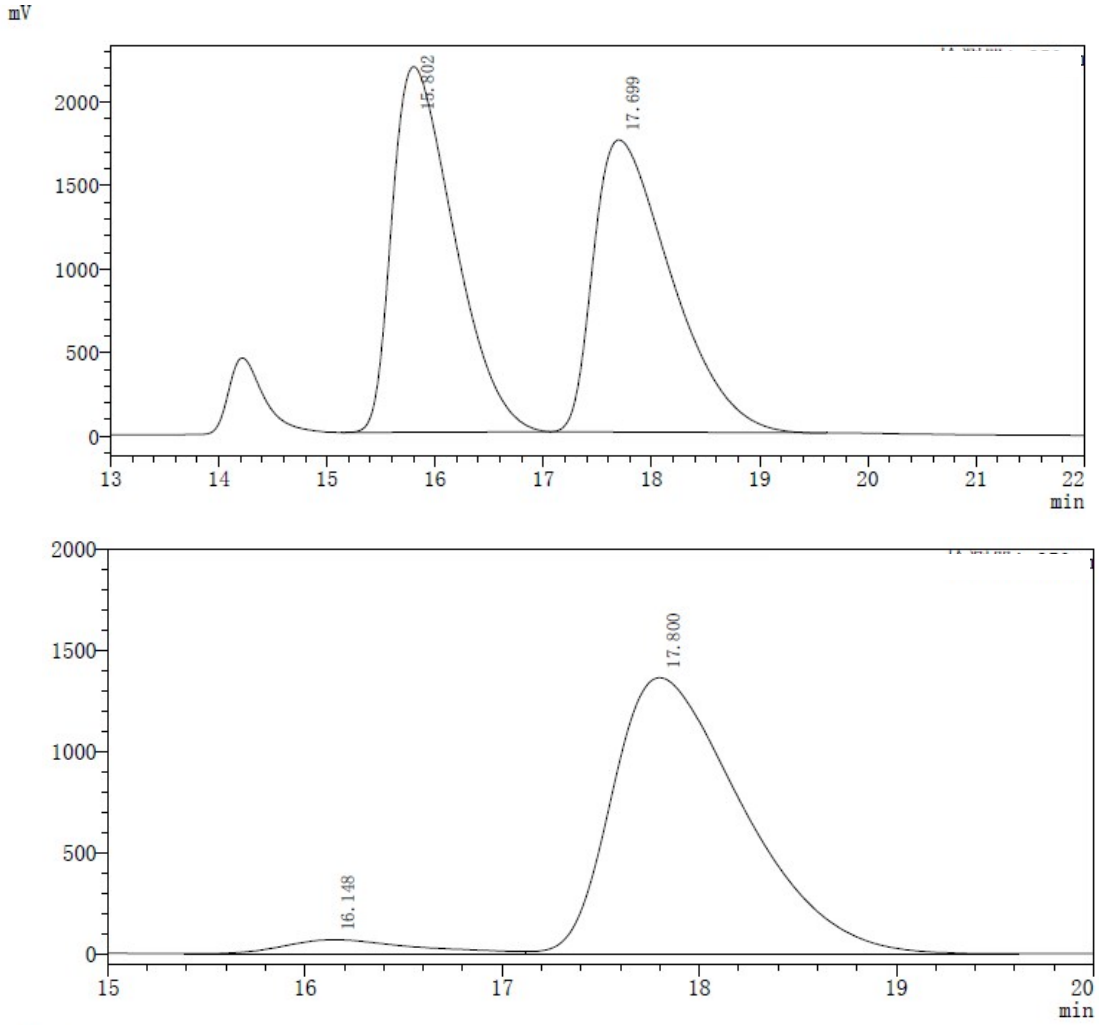
Serial Number	Retention Time [min]	Area	Area %
1	18.123	112345219	86.039
2	23.502	18229693	13.961



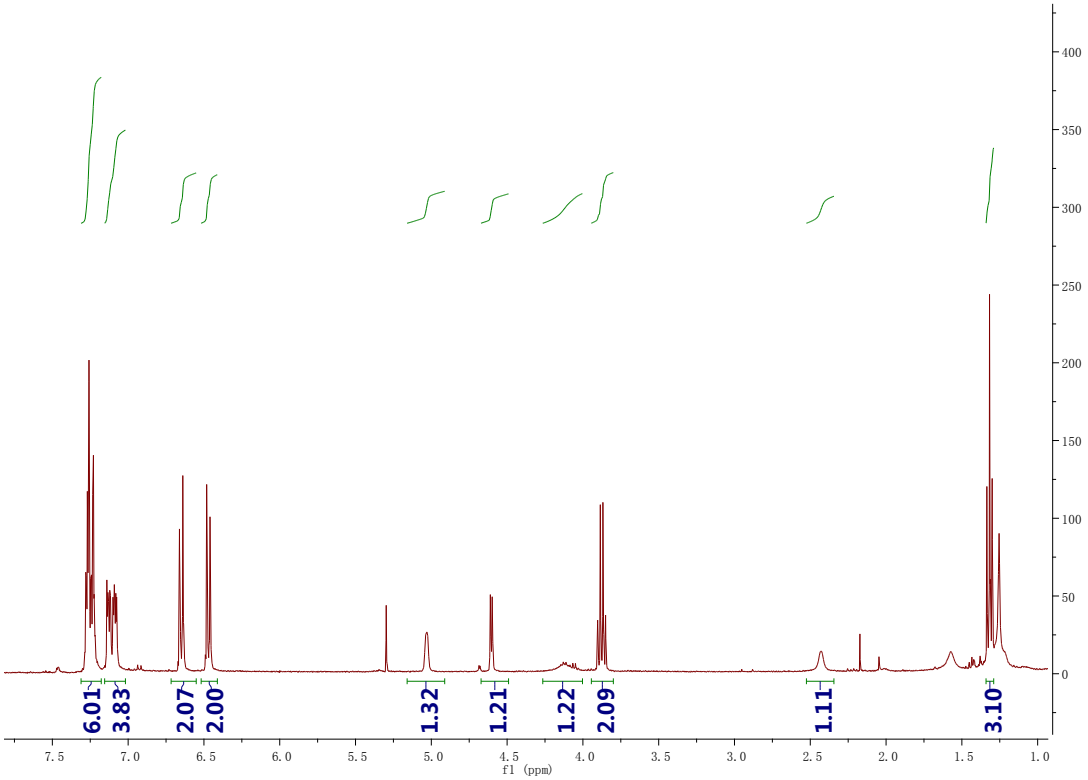


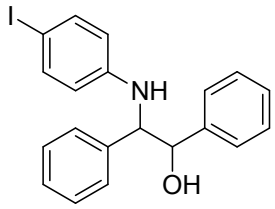
2-((4-ethoxyphenyl)amino)-1,2-diphenylethanol

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} = 17.80 min, t_{minor} = 16.14 min; ee=90%. ^{1}H NMR ($CDCl_3$): δ: 1.3 (t, 3H), 2.4 (s, 1H), 3.87 (q, 2H), 4.15 (s, 1H), 4.60 (d, J=5.6 Hz, 1H), 5.05 (m, 1H), 6.40~7.30 (m, 14H).



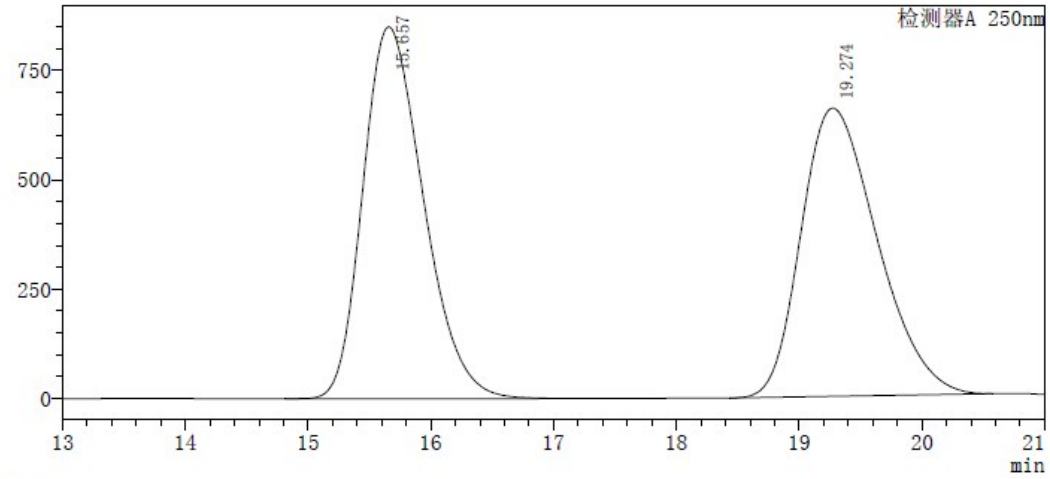
Serial Number	Retention Time [min]	Area	Area %
1	16.148	3141870	4.767
2	17.800	62760500	95.233

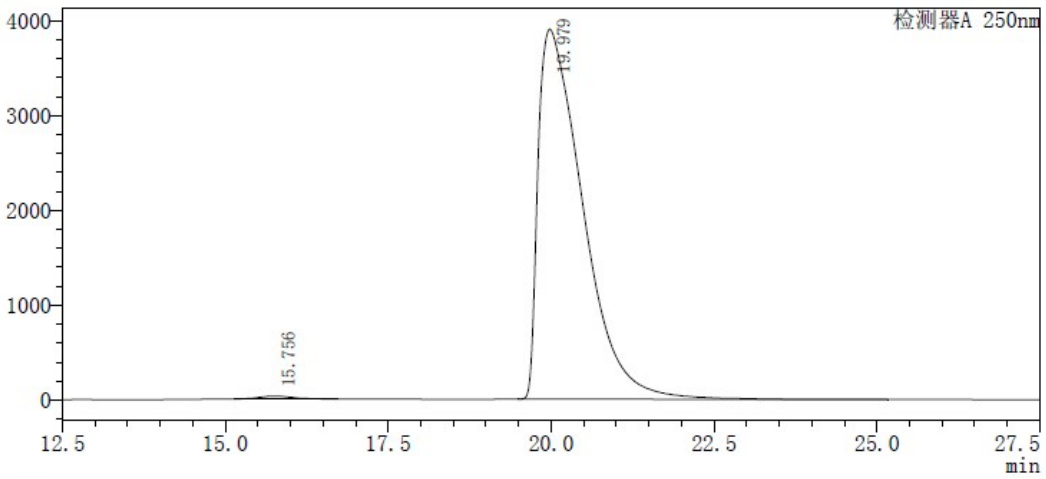

6.01
3.83
2.07
2.00
1.32
1.21
1.22
2.09
1.11
3.10
f1 (ppm)



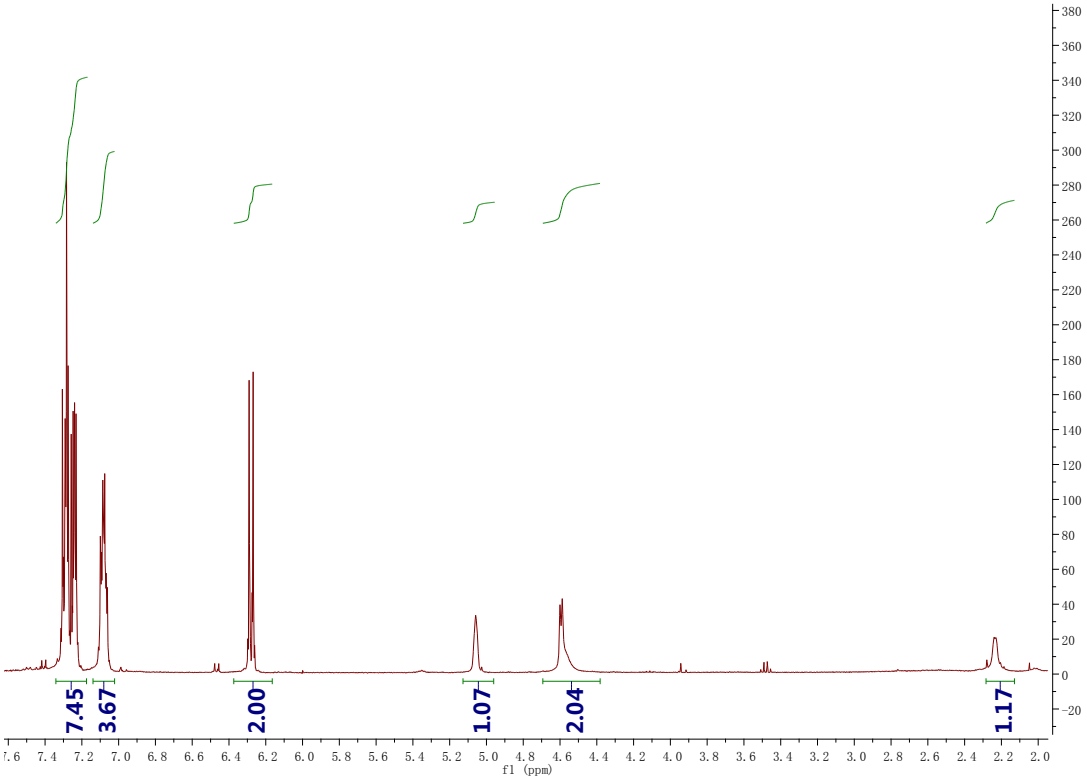
2-((4-iodophenyl)amino)-1,2-diphenylethanol

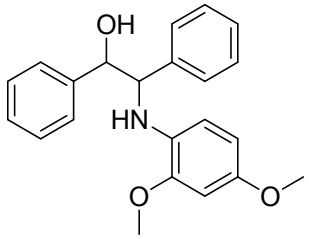
Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t_{major} = 19.97 min, t_{minor} = 15.75 min; ee=98.9%. ^{1}H NMR ($CDCl_3$): δ: 2.2 (s, 1H), 4.55 (m, 2H), 5.05 (m, 1H), 6.20~7.35 (m, 14H).





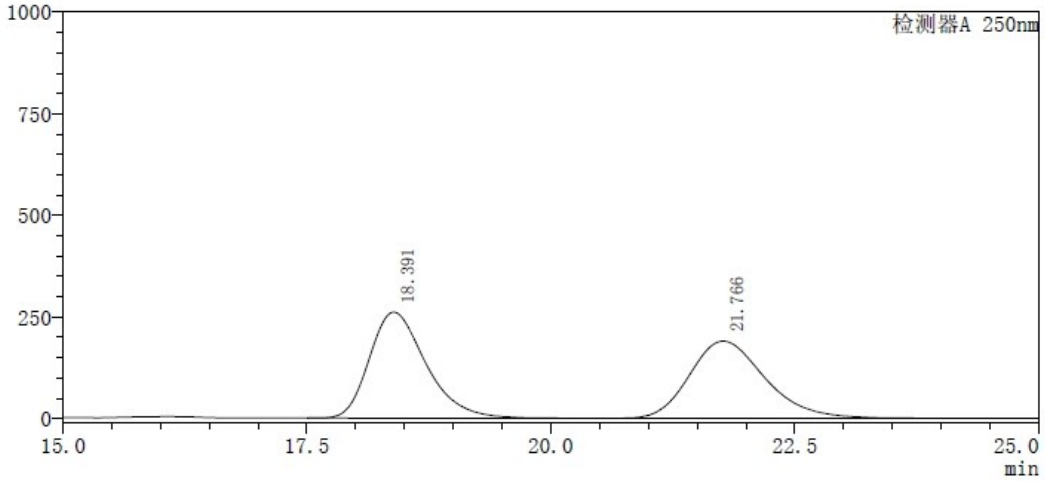
Serial Number	Retention Time [min]	Area	Area %
1	15.756	1072209	0.572
2	19.979	186528775	99.428

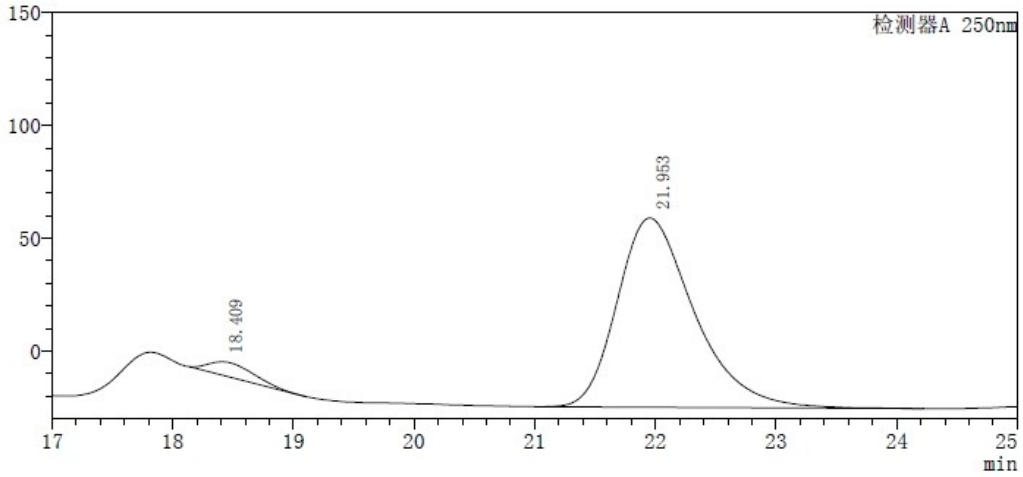

7.45
3.67
2.00
1.07
2.04
1.17
f1 (ppm)



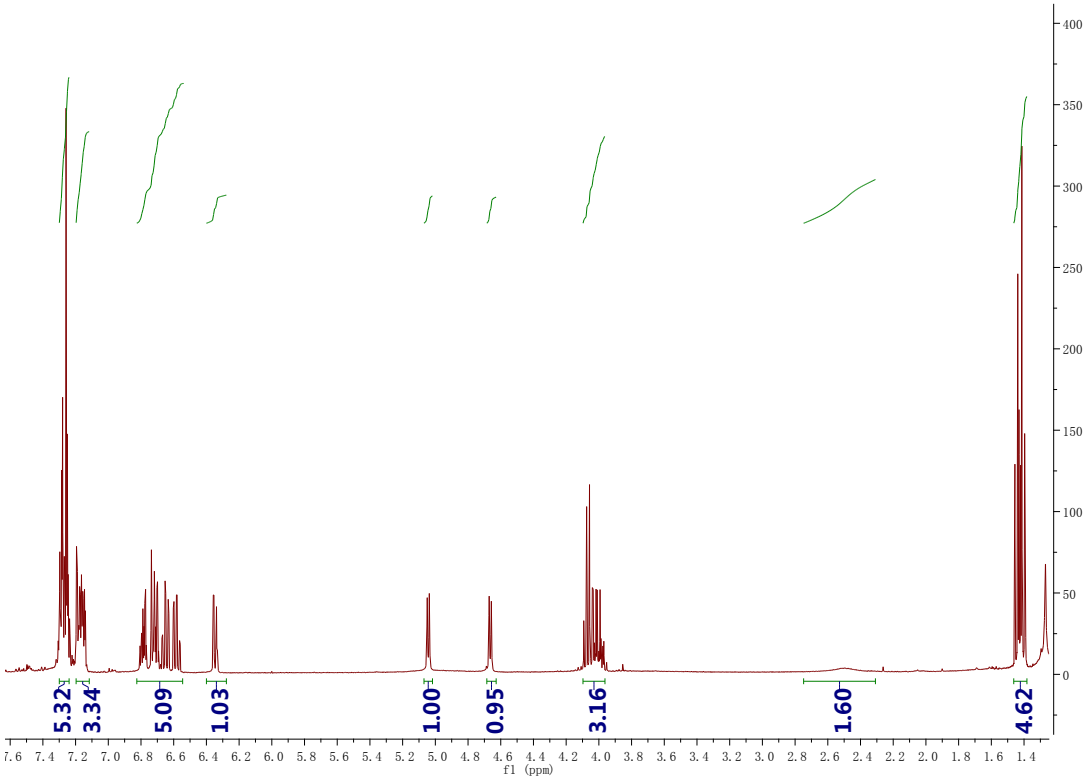
2-((2,4-dimethoxyphenyl)amino)-1,2-diphenylethanol

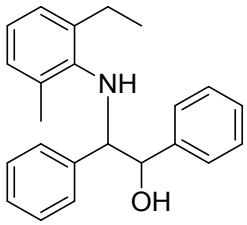
Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 90/10, 0.75 mL/min, 250 nm), t_{major} = 21.95 min, t_{minor} = 18.40 min; ee=92%. ^{1}H NMR ($CDCl_3$): δ: 2.49 (bs, 1H), 3.66 (s, 3H), 3.80 (s, 3H), 4.60 (d, J=5.6 Hz, 1H), 5.08 (d, J=5.6 Hz, 1H), 6.00~7.40 (m, 13H).





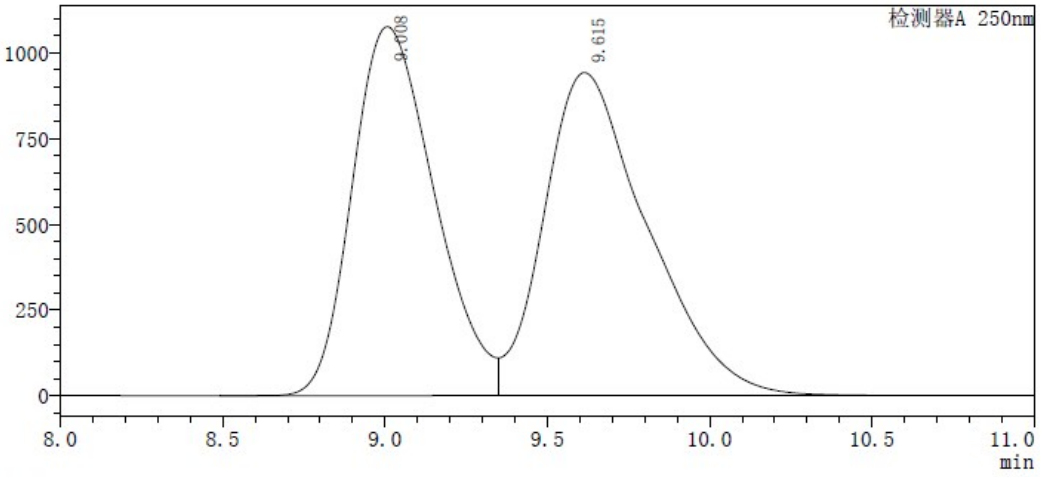
Serial Number	Retention Time [min]	Area	Area %
1	18.409	161194	4.155
2	21.953	3717959	95.845

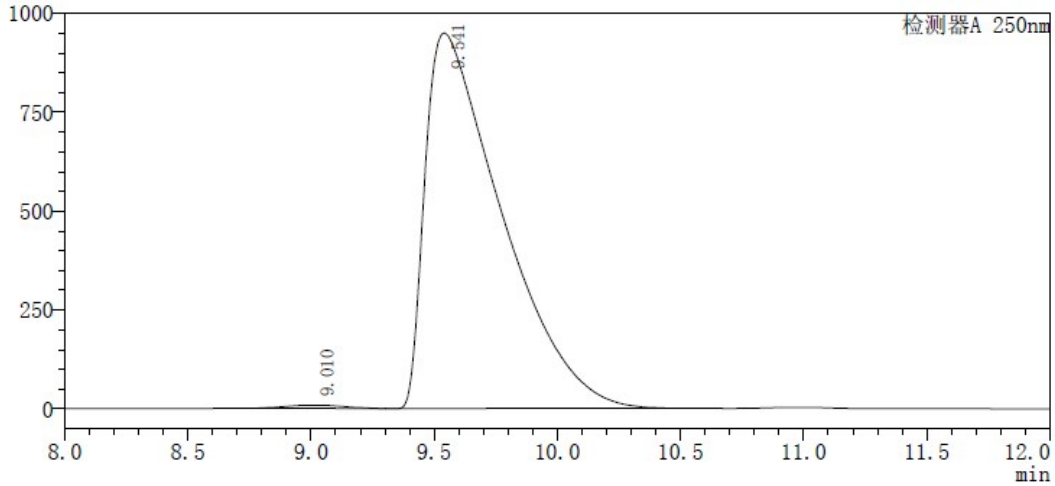

5.32
3.34
5.09
1.03
1.00
0.95
3.16
1.60
4.62
f1 (ppm)



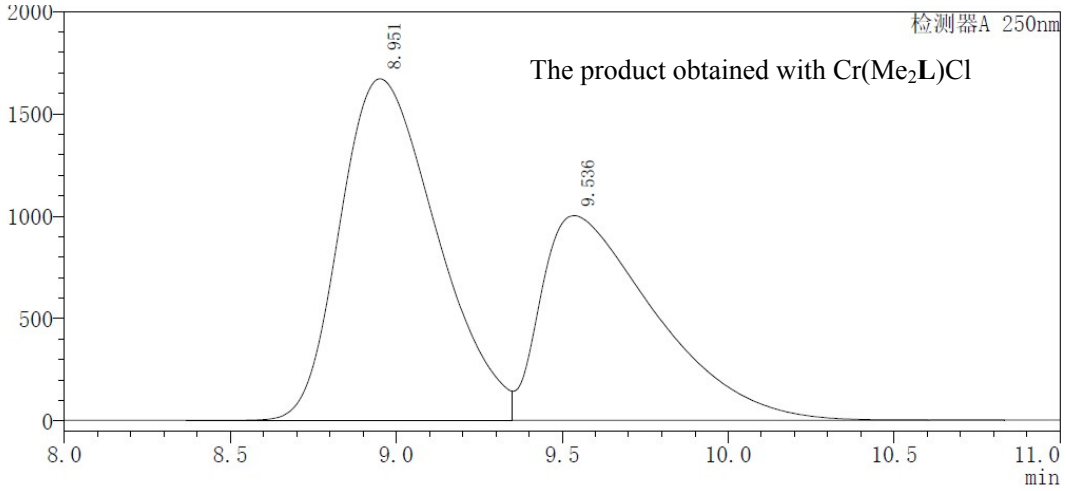
2-((2-ethly-6-methlyphenyl)amino)-1,2-diphenylethanol

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} = 9.54 min, t_{minor} = 9.01 min; ee=98.7 %. ^{1}H NMR ($CDCl_3$): δ: 1.20 (t, 3H), 2.20 (s, 3H), 2.3 (s, 1H), 2.55 (m, 2H), 4.45 (d, J=5.6 Hz, 1H), 5.10 (m, 1H), 6.80~7.25 (m, 14H).

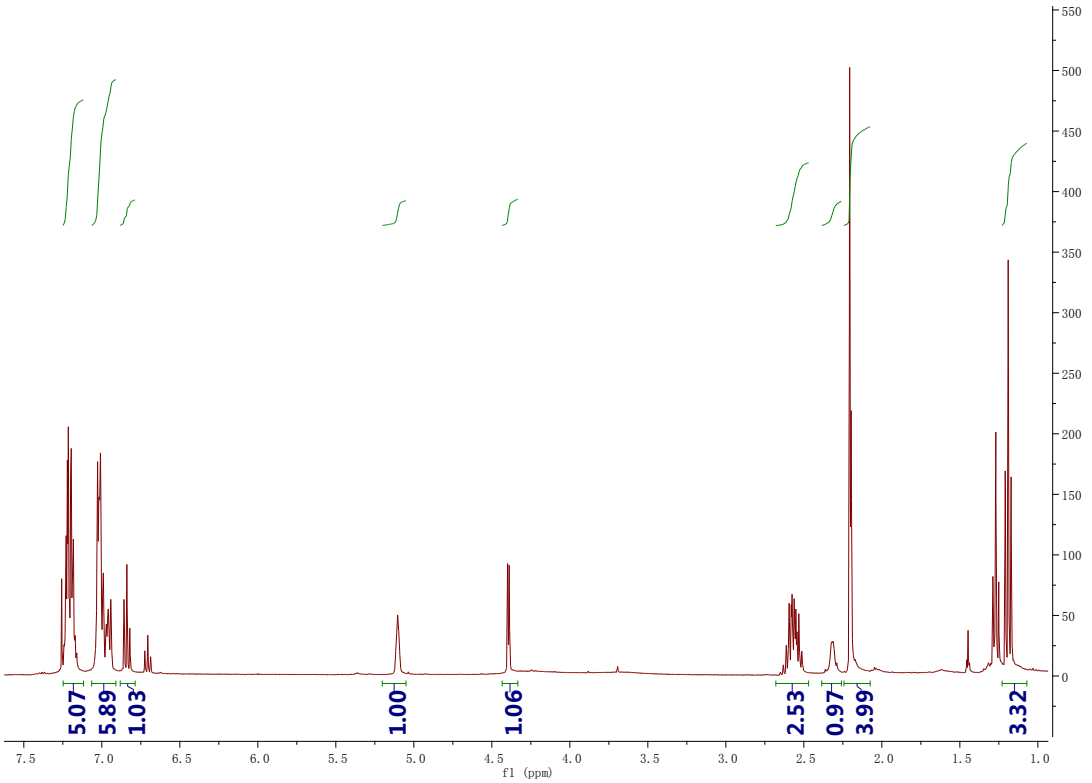




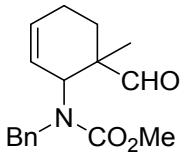
Serial Number	Retention Time [min]	Area	Area %
1	9.010	136731	0.661
2	9.541	20557909	99.339



Serial Number	Retention Time [min]	Area	Area %
1	8.951	33887931	58.542
2	9.536	23998732	41.458

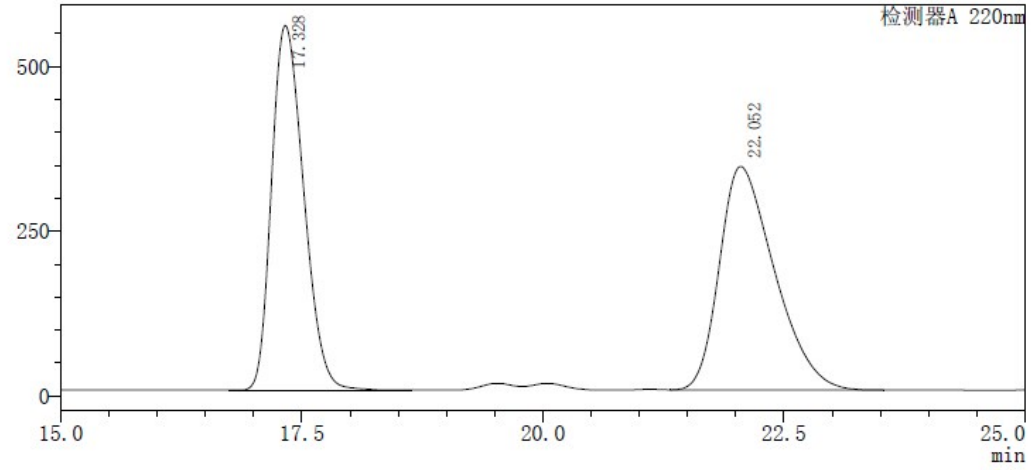


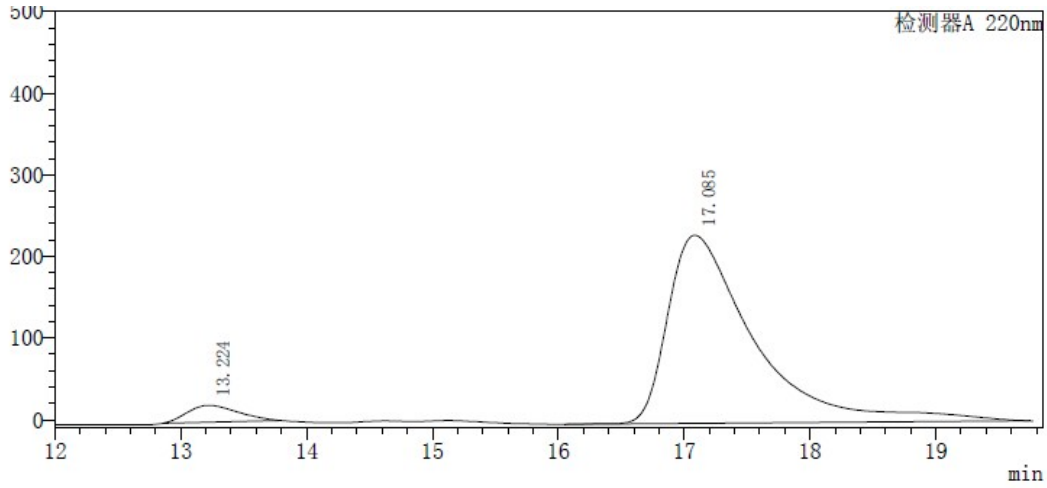
15.3 Diels-Alder Reactions



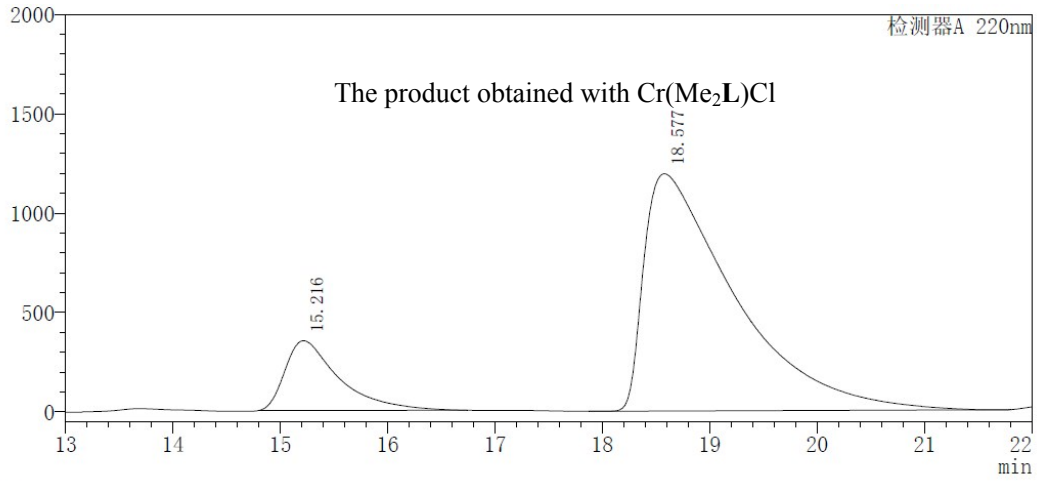
N-Benzyl-N-(6-formyl-6-methly-2-cyclohexen-1-yl)carbamic Acid Methly Ester

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 98/2, 1.0 mL/min, 220 nm), t_{major} = 17.08 min, t_{minor} = 13.24 min; ee=87.1%. ^{1}H NMR ($CDCl_3$): 1.18 (s, 3H), 1.48 (m, 1H), 1.85 (m, 1H), 2.06 (m, 1H), 2.22 (m, 1H), 3.60 (s, 3H), 4.44 (s, 2H), 4.77 (br s,1H), 5.50 (m,1H), 5.92(m, 1H), 7.10-7.25 (m, 5H), 9.75 (s, 1H).

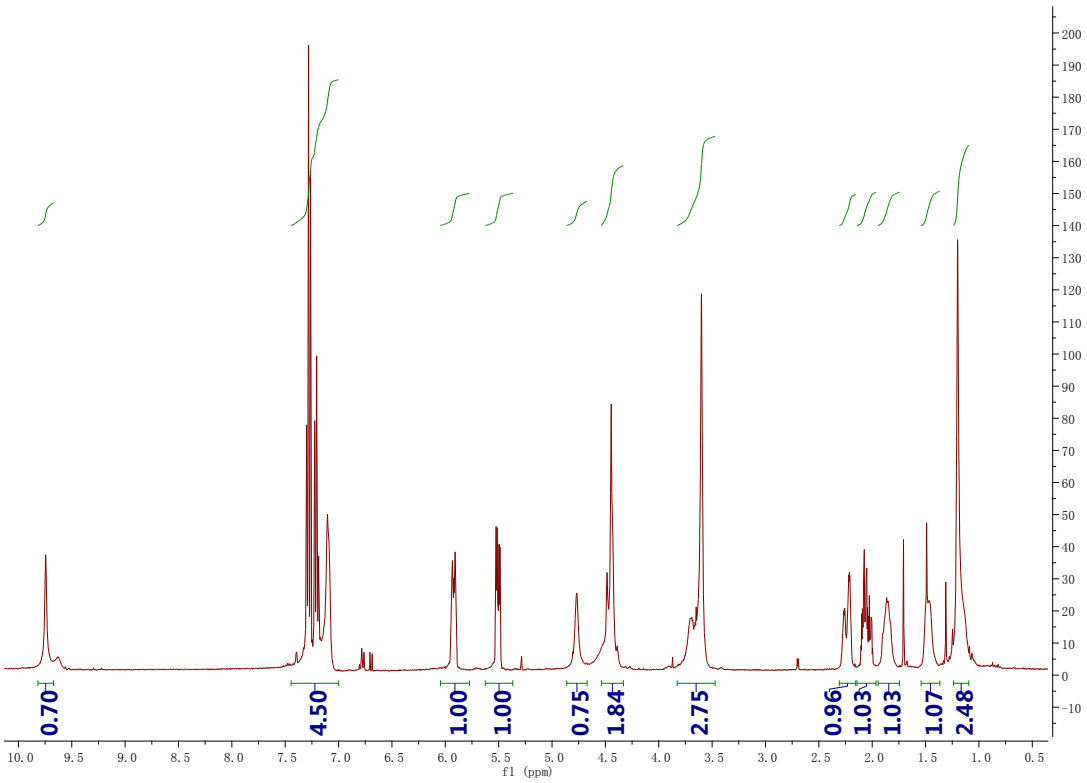


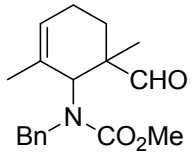


Serial Number	Retention Time [min]	Area	Area %
1	13.224	580461	5.021
2	17.085	10979331	94.979



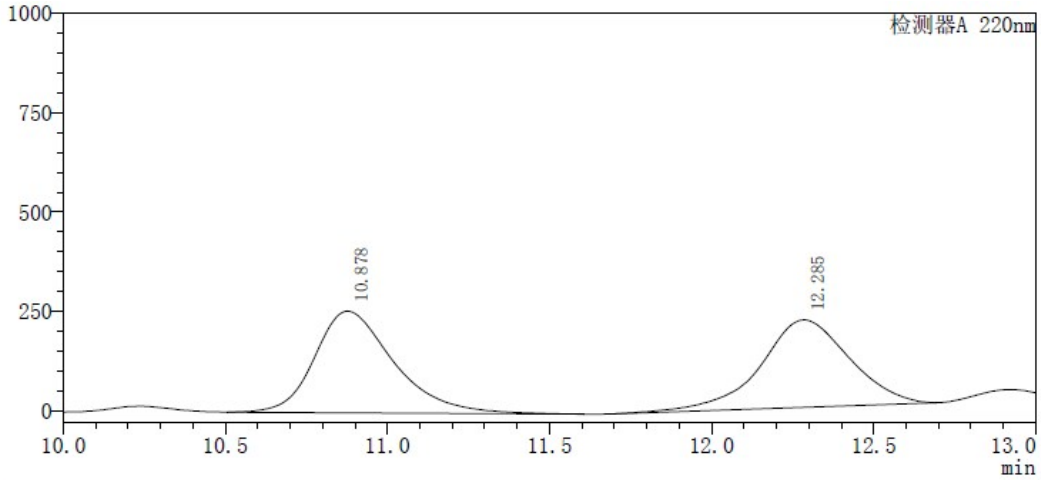
Serial Number	Retention Time [min]	Area	Area %
1	15.216	12246009	14.836
2	18.577	70295192	85.164

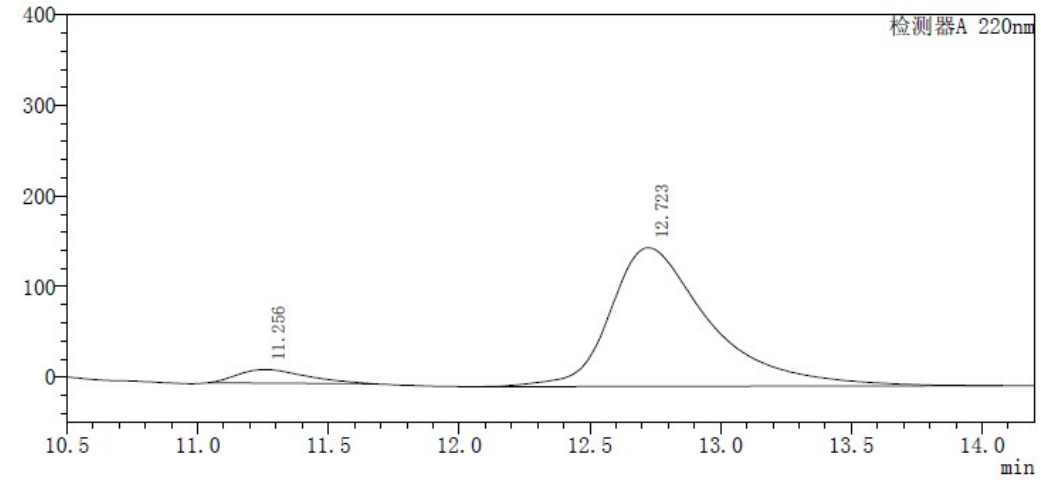




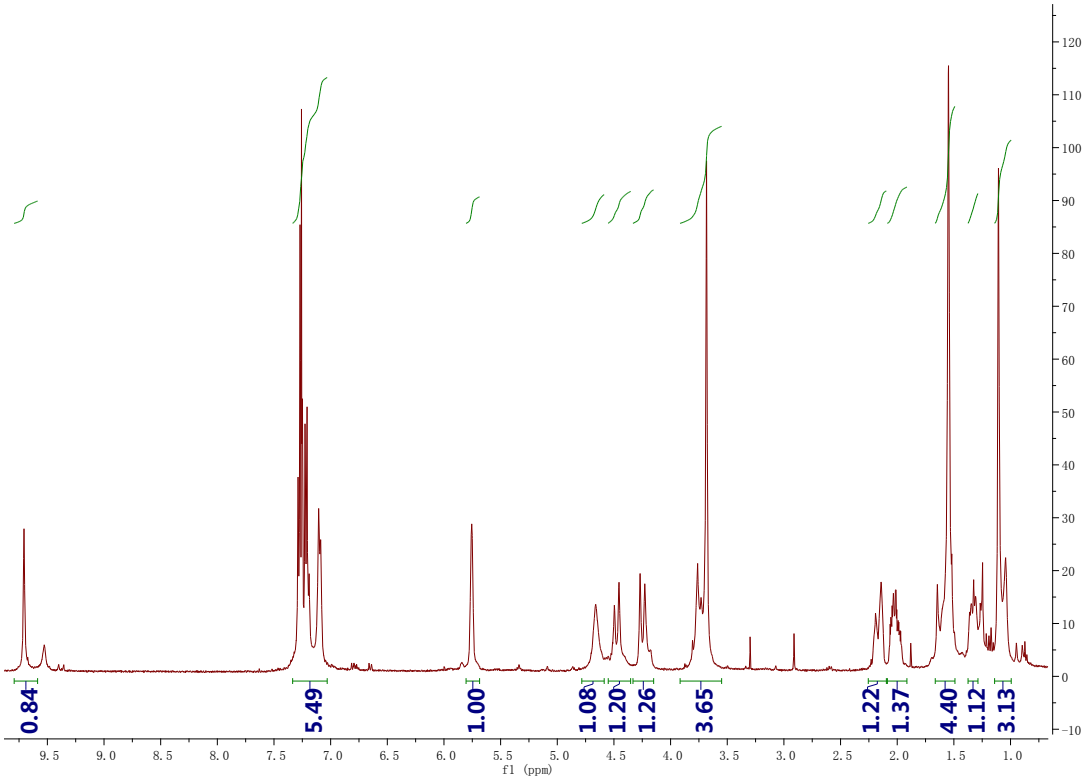
N-Benzyl-N-(6-formyl-2,6-dimethly-2-cyclohexen-1-yl)carbamic Acid Methly Ester

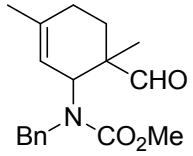
Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 98/2, 1.0 mL/min, 220 nm), t_{major} = 12.72 min, t_{minor} = 11.25 min; ee=86%.^{1}H NMR ($CDCl_3$): 1.10 (s, 3H), 1.33 (m, 1H), 1.55 (s,3H), 1.62 (m, 1H), 2.02 (s, 1H), 2.18 (s, 1H), 3.68 (s, 3H), 4.24 (d, J=17 Hz, 1H), 4.48 (d, J=17 Hz, 1H), 4.65 (br s, 1H), 4.75 (s, 1H), 7.10 (d, J=8Hz, 2H), 7.18~7.30 (m, 3H), 9.70 (s, 1H).





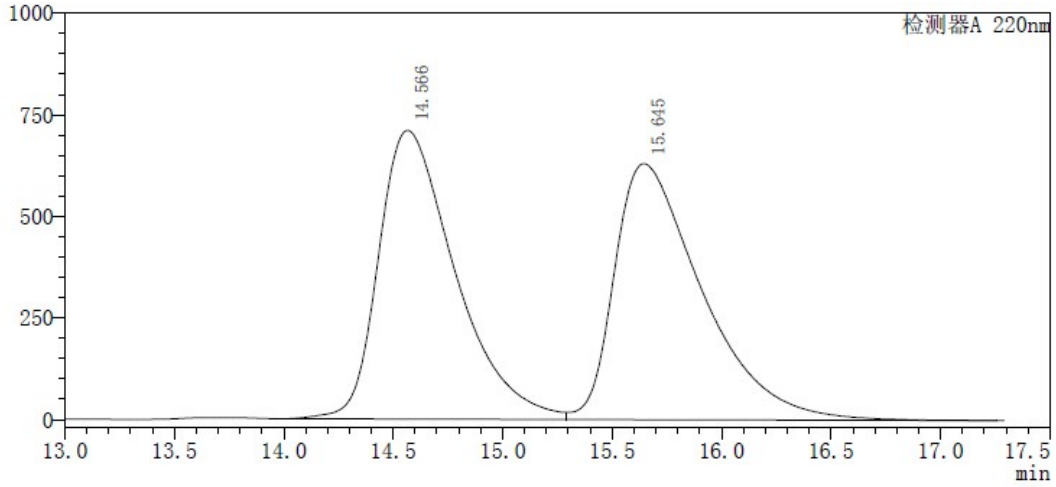
Serial Number	Retention Time [min]	Area	Area %
1	11.256	274499	6.316
2	12.723	4071773	93.648

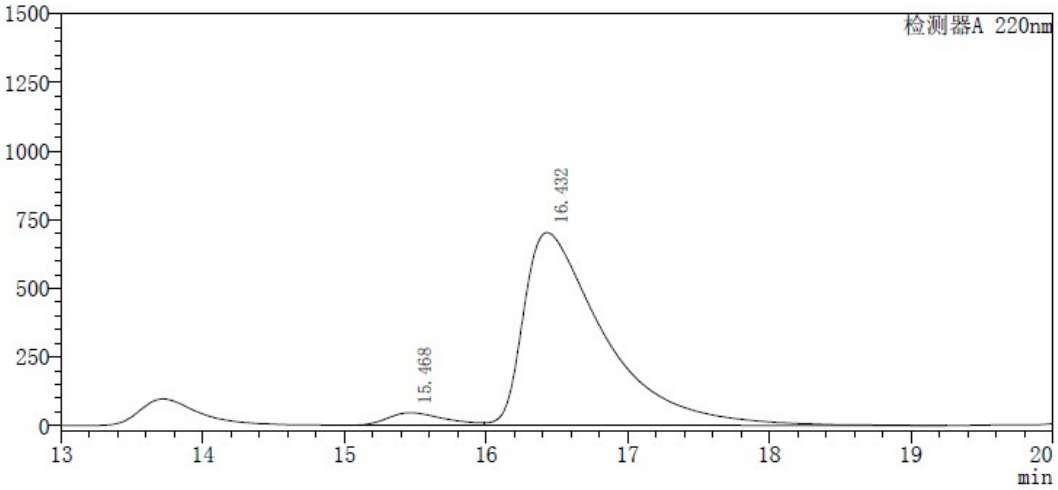

0.84
5.49
1.00
1.08
1.20
1.26
3.65
1.22
1.37
4.40
1.12
3.13
f1 (ppm)



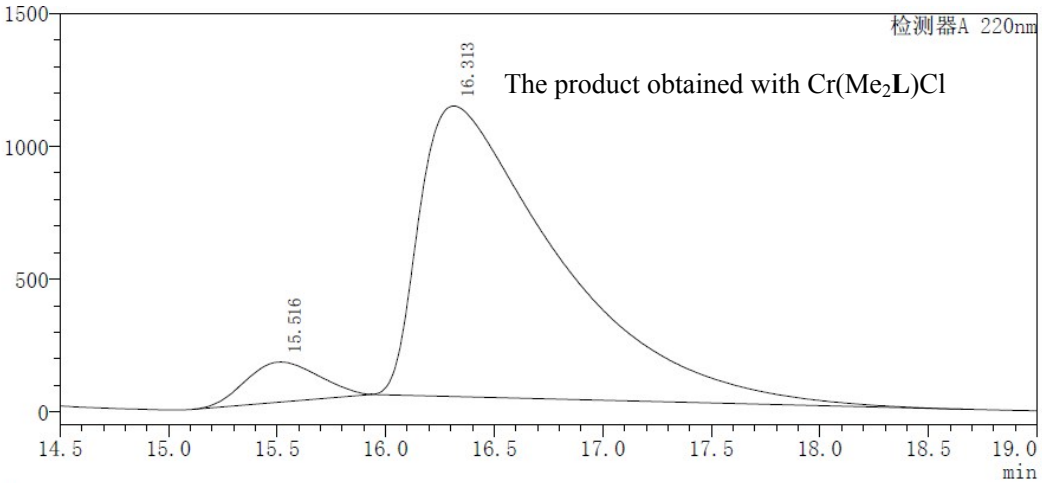
N-Benzyl-N-(6-formyl-3,6-dimethly-2-cyclohexen-1-yl)carbamic Acid Methly Ester

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 98/2, 1.0 mL/min, 220 nm), t_{major} = 16.43 min, t_{minor} = 15.46 min; ee=91.3%. ^{1}H NMR ($CDCl_3$): 1.16 (s, 3H), 1.45 (m, 1H), 1.63 (s,3H), 1.88 (m, 1H), 1.99 (s, 1H), 2.10 (s, 1H), 3.60 (s, 3H), 4.32 (d, J=17 Hz, 1H), 4.46 (d, J=17 Hz, 1H), 4.76 (br s, 1H), 5.16 (m, 1H), 7.08 (d, J=8Hz, 2H), 7.15~7.30 (m, 3H), 9.73 (s, 1H).

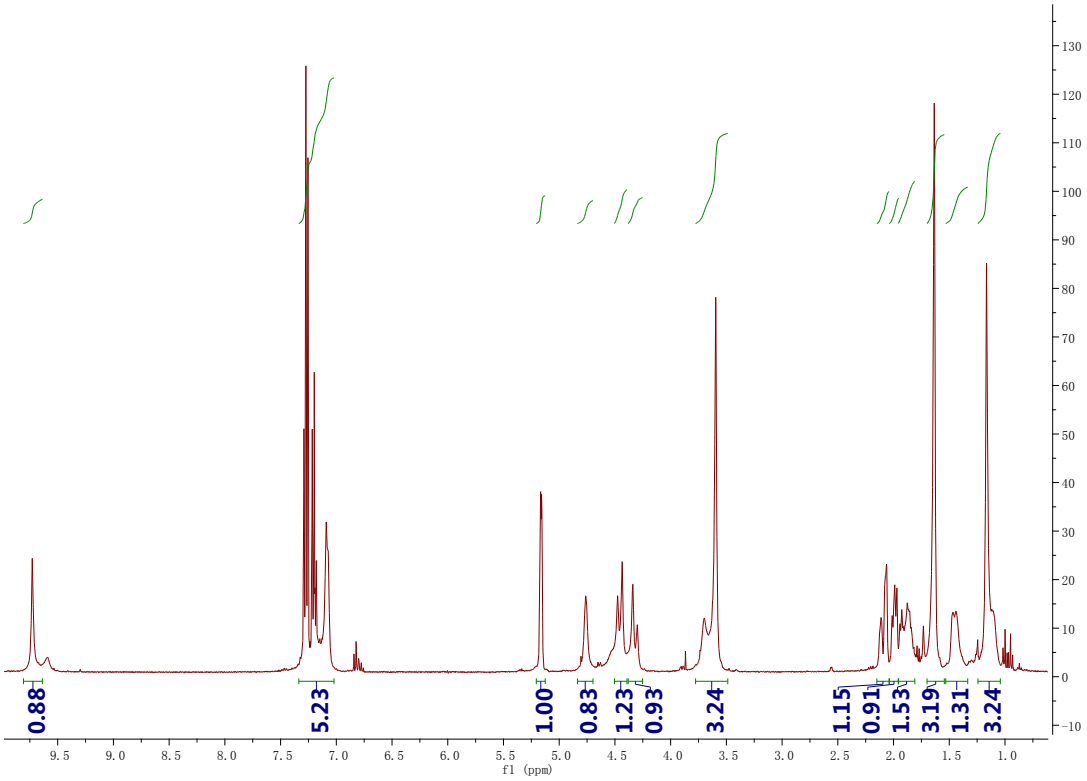


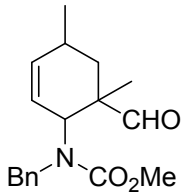


Serial Number	Retention Time [min]	Area	Area %
1	15.468	1278243	4.392
2	16.432	27823300	95.608



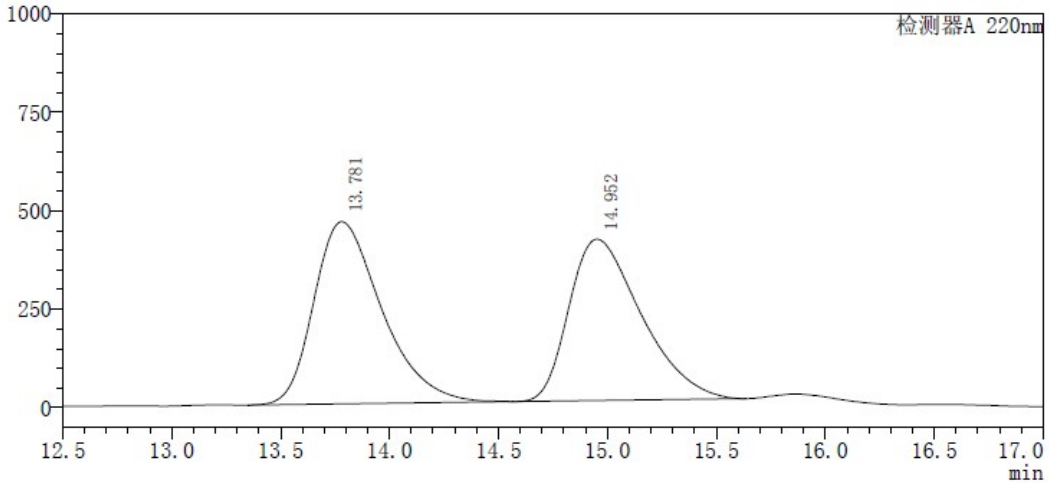
Serial Number	Retention Time [min]	Area	Area %
1	15.516	3536349	6.735
2	16.313	48974390	93.286

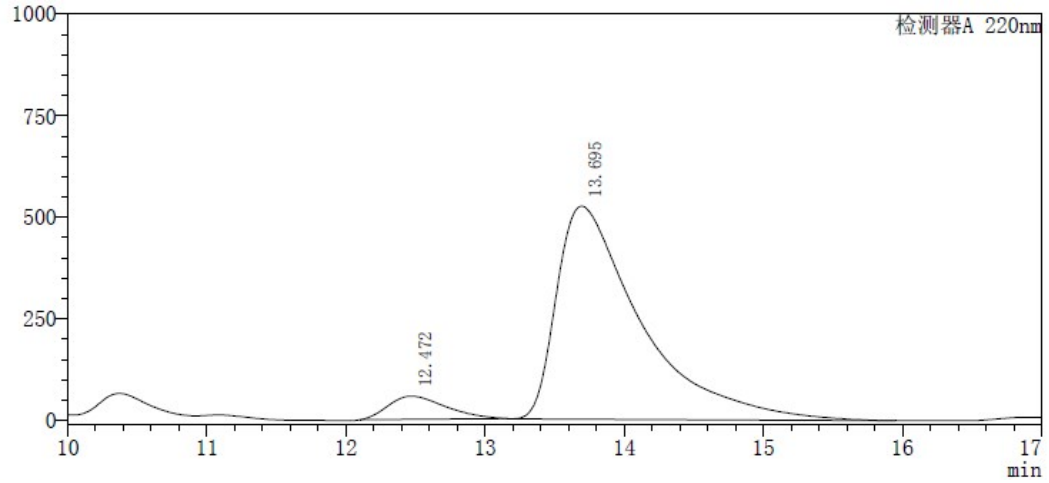




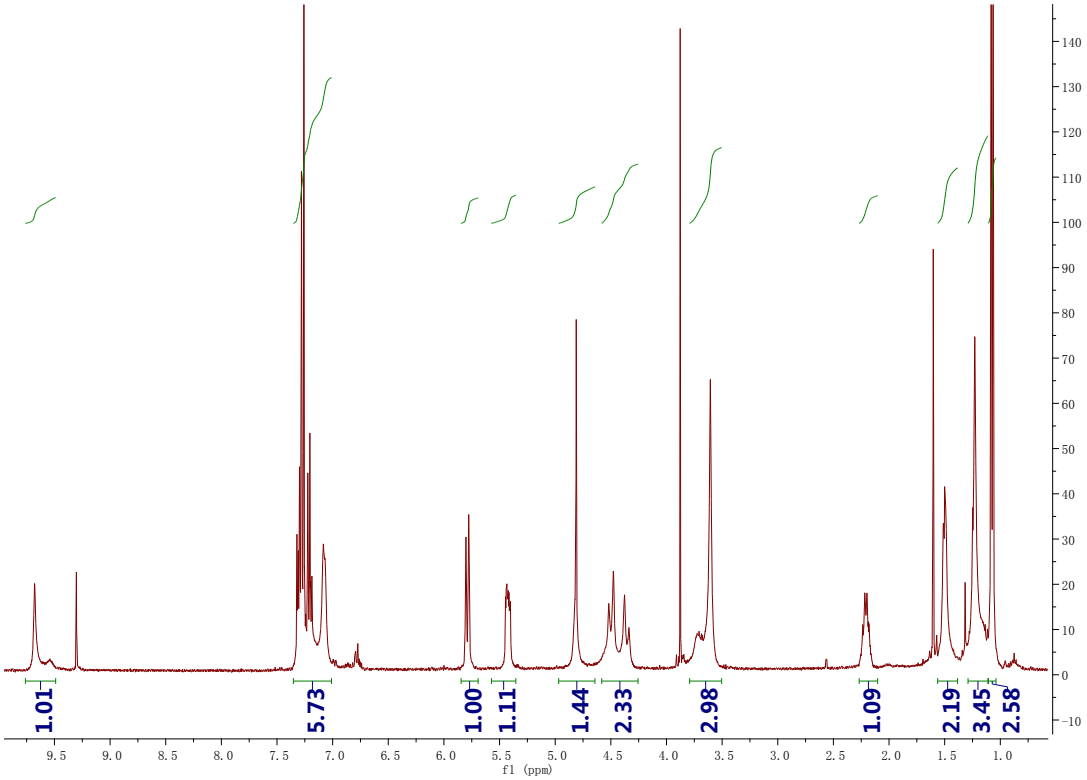
N-Benzyl-N-(6-formyl-4,6-dimethly-2-cyclohexen-1-yl)carbamic Acid Methly Ester

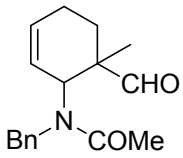
Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 98/2, 1.0 mL/min, 220 nm), t_{major} = 13.69 min, t_{minor} = 12.47 min; ee=87.3%. ^{1}H NMR ($CDCl_3$): 1.07 (d, J=4Hz, 3H), 1.25 (s, 3H), 1.50 (m, 2H), 2.21 (m, 1H), 1.87 (s, 3H), 3.61 (s, 3H), 4.35 (d, J=17 Hz, 1H), 4.50 (d, J=17 Hz, 1H),4.80 (br s, 1H), 5.42 (m, 1H), 5.80 (m, 1H), 7.08 (d, J=8Hz, 2H), 7.17~7.33 (m, 3H), 9.68 (s, 1H).





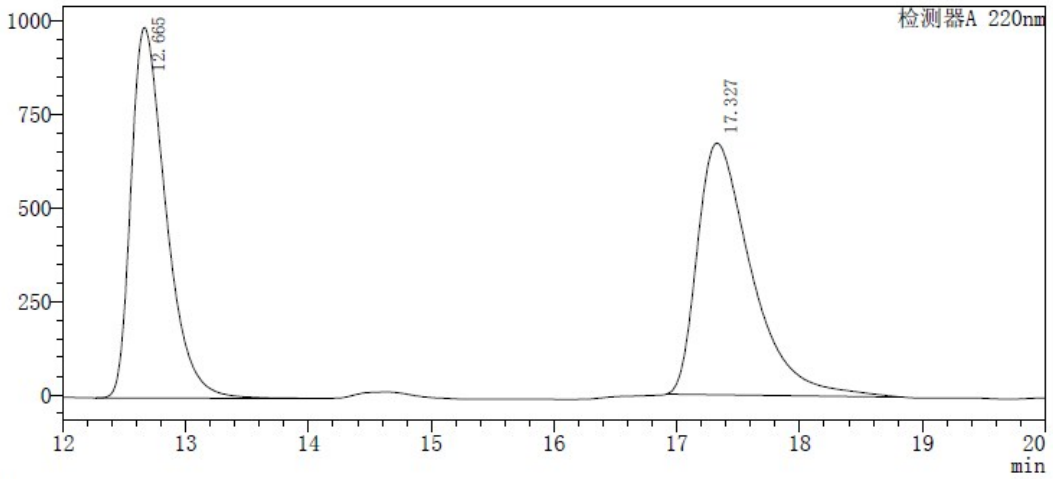
Serial Number	Retention Time [min]	Area	Area %
1	12.472	1625581	6.846
2	13.695	22120235	93.154

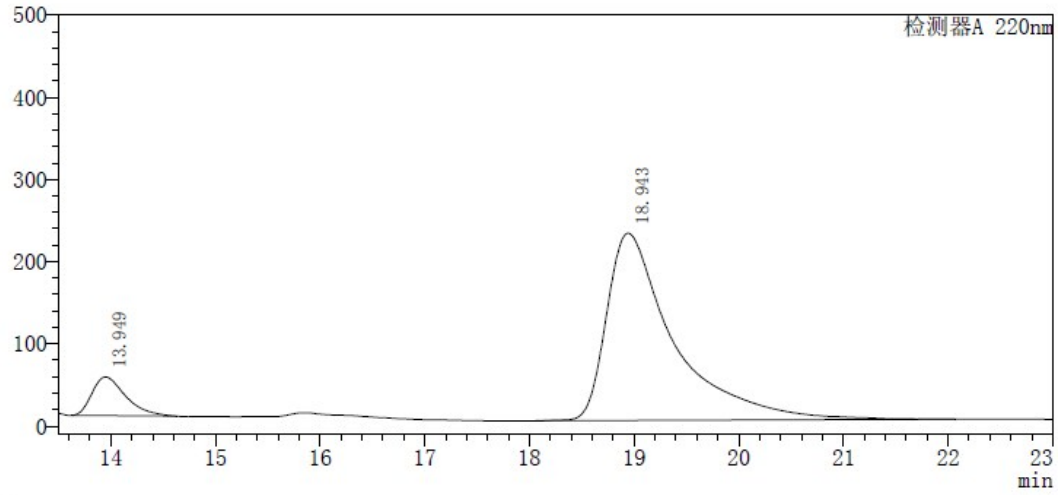

1.01
5.73
1.00
1.11
1.44
2.33
2.98
1.09
2.19
3.45
2.58
f1 (ppm)



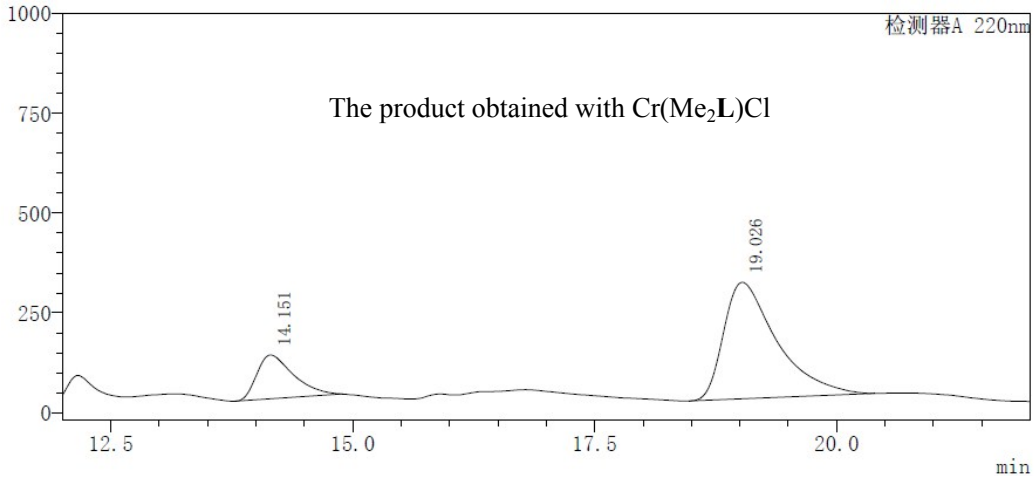
N-Acetyl-N-benzylamino-1-methyl-3-cyclohexenecarboxaldehyde

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 220 nm), t_{major} = 18.94 min, t_{minor} = 13.94 min; ee =81.3%. ^{1}H NMR ($CDCl_3$): 1.25 (s, 3H), 1.42 (m, 1H), 1.85 (m, 1H), 1.87 (s, 3H), 2.06 (m, 1H), 2.22 (m, 1H), 4.47 (d, J=17 Hz, 1H), 4.67 (d, J=17 Hz, 1H), 5.12 (br s, 1H), 5.20 (m, 1H), 5.95 (m, 1H), 7.10 (d, J=8Hz, 2H), 7.19~7.35 (m, 3H), 9.66 (s, 1H).

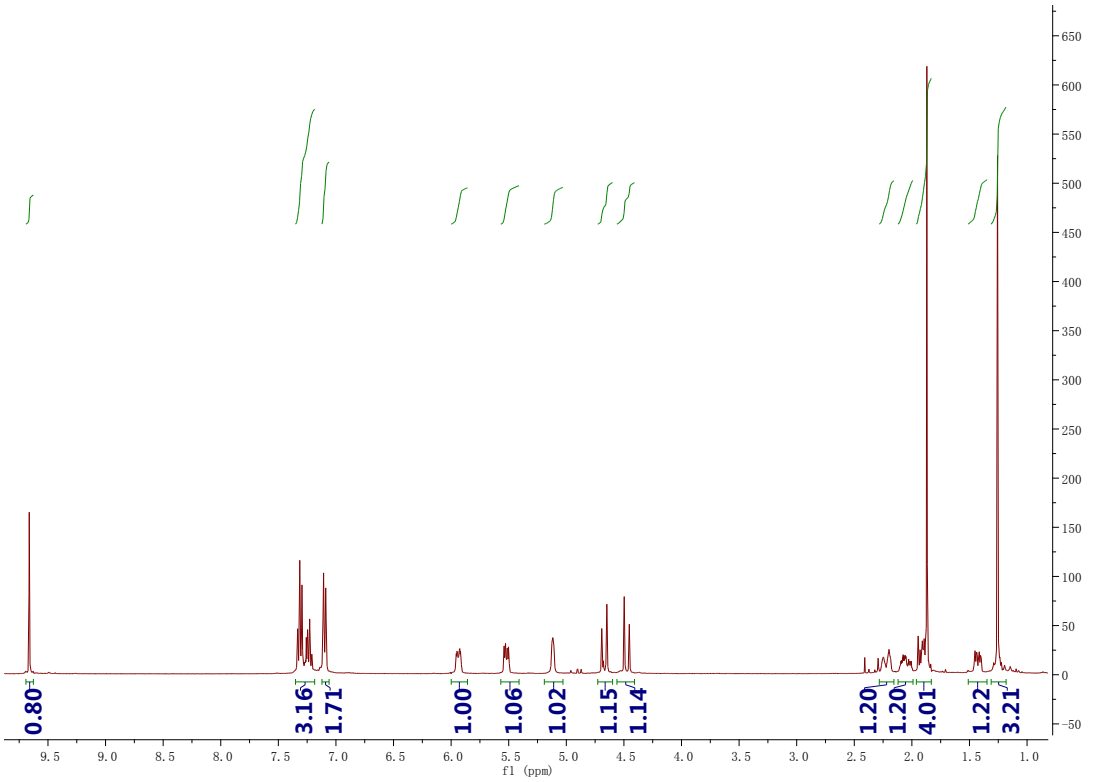


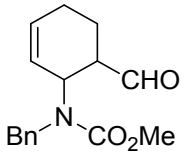


Serial Number	Retention Time [min]	Area	Area %
1	13.949	1047282	9.336
2	18.943	10170531	90.664



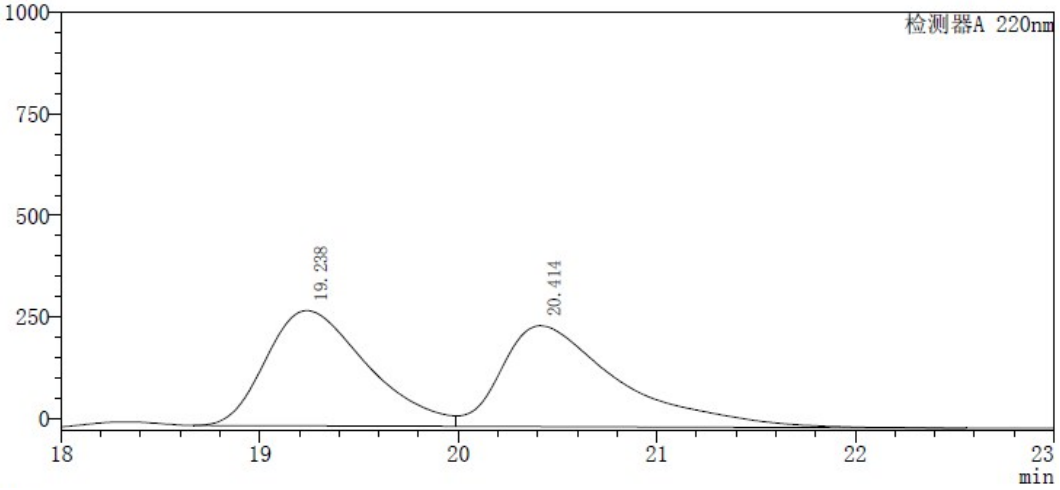
Serial Number	Retention Time [min]	Area	Area %
1	14.151	2887956	20.533
2	19.026	11176993	79.467

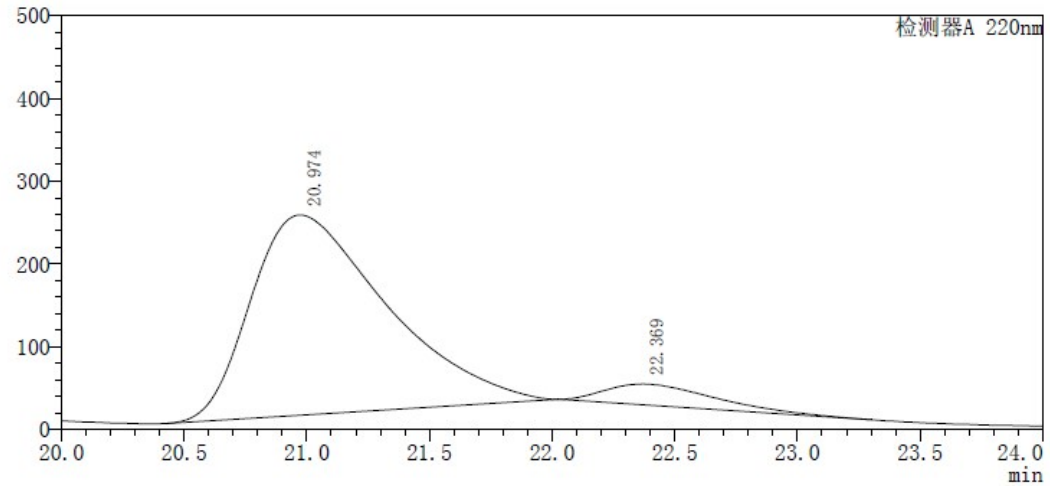




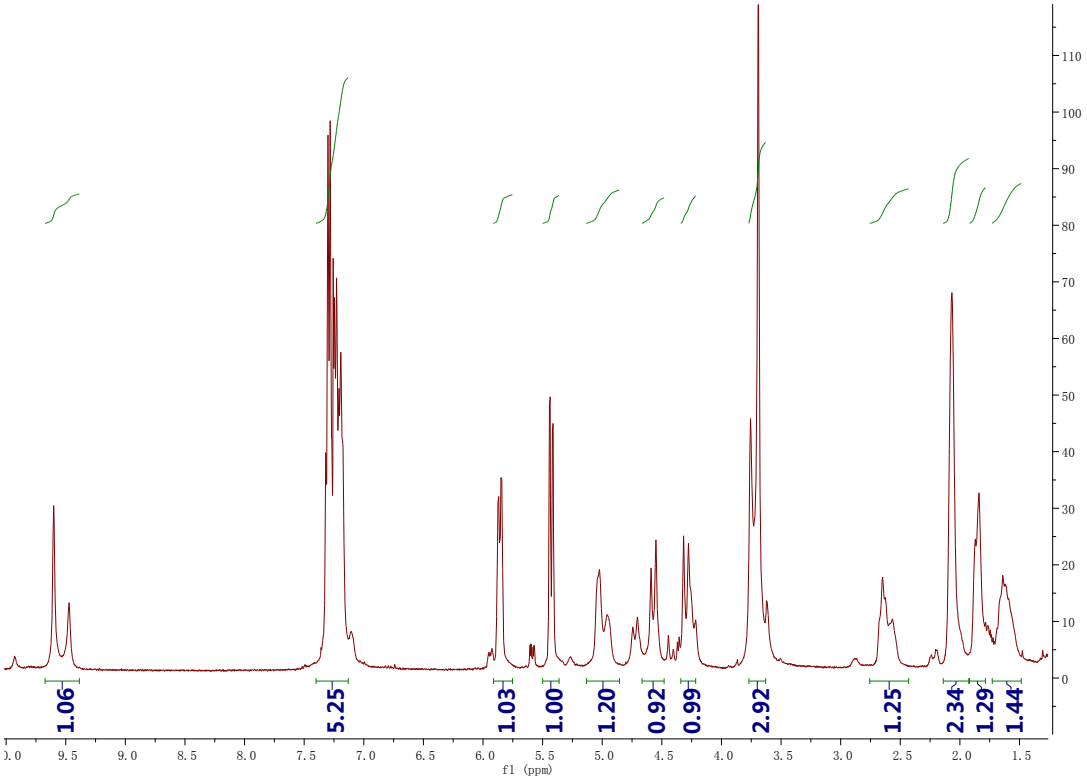
N-Benzyl-N-(6-formyl-2-cyclohexen-1-yl)carbamic Acid Methly Ester

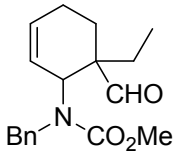
Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 98/2, 1.0 mL/min, 220 nm), t_{major} = 20.97 min, t_{minor} = 22.39 min; ee=84%. ^{1}H NMR ($CDCl_3$): 1.60 (m, 1H), 1.85 (m, 1H), 2.06 (m, 2H), 2.58 (s, 1H), 3.70 (s, 3H), 4.30 (d, J=17 Hz, 1H), 4.57 (d, J=17 Hz, 1H), 5.00 (m, 1H), 5.42 (m, 1H), 5.86 (m, 1H), 7.15~7.30 (m, 5H), 9.60 (s, 1H).





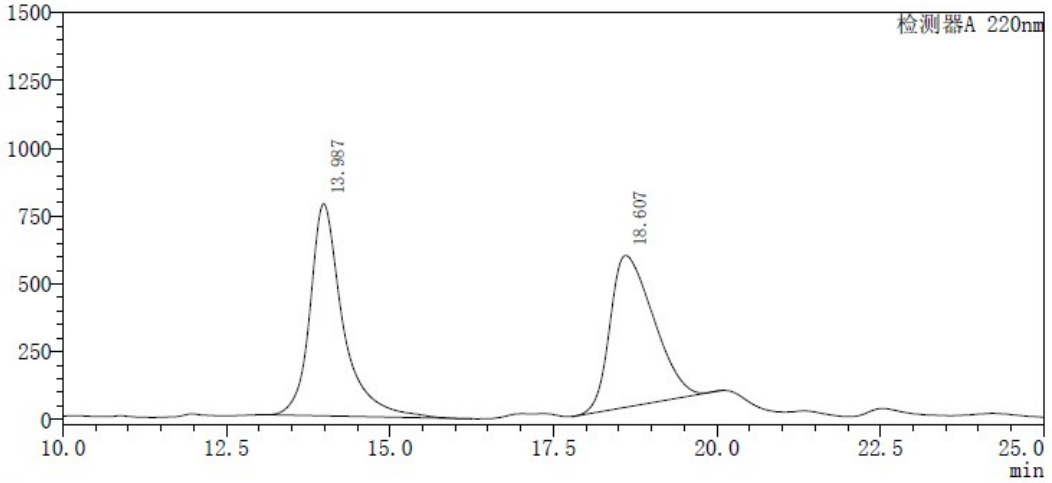
Serial Number	Retention Time [min]	Area	Area %
1	20.974	9313953	92.123
2	22.369	796393	7.877

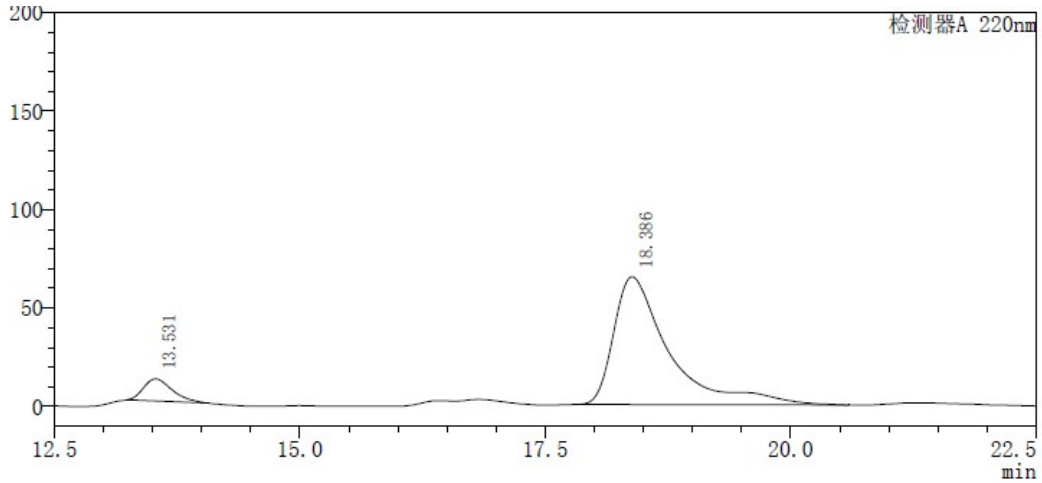

1.06
5.25
1.03
1.00
1.20
0.92
0.99
2.92
1.25
2.34
1.29
1.44
f1 (ppm)



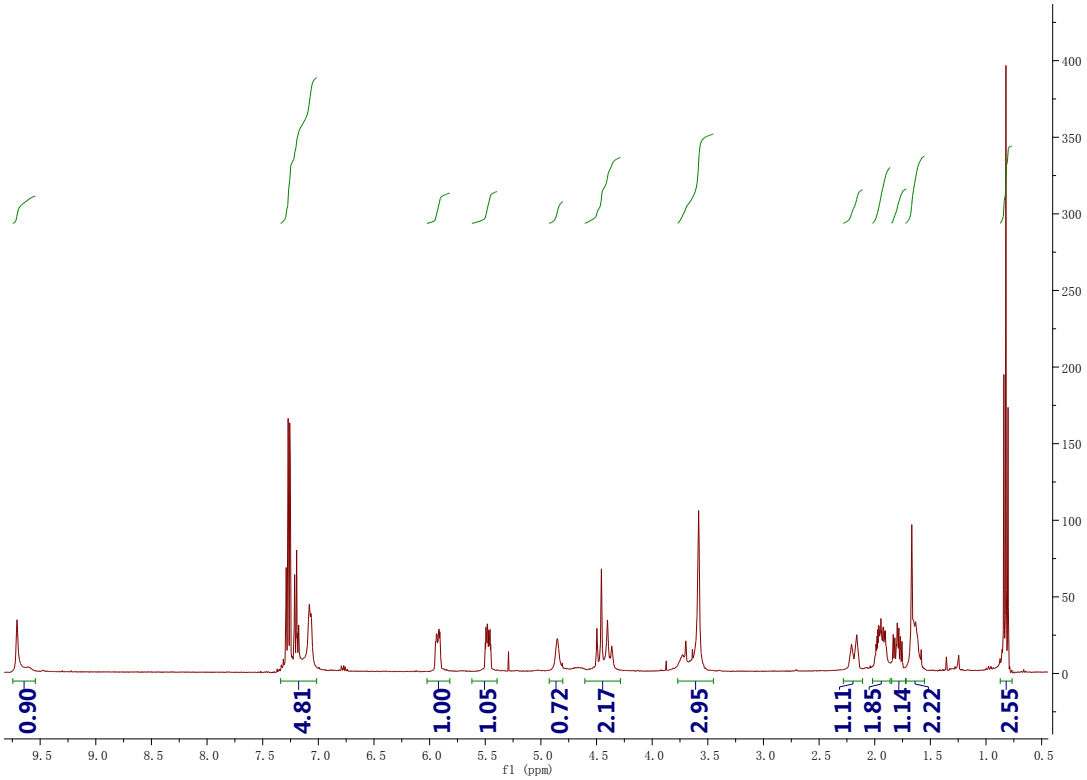
N-Benzyl-N-(6-formyl-6-ethly-2-cyclohexen-1-yl)carbamic Acid Methly Ester

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 98/2, 1.0 mL/min, 220 nm), t_{major} = 18.38 min, t_{minor} = 13.53 min; ee=83.5%. ^{1}H NMR ($CDCl_3$): 0.82 (t, 3H), 1.65 (m, 2H), 1.80 (m, 1H), 1.95 (m, 1H), 2.20 (m, 1H), 3.58 (s, 3H), 4.38 (d, J=17 Hz, 1H), 4.48 (d, J=17 Hz, 1H), 4.85 (s, 1H), 5.00 (m, 1H), 5.47 (m, 1H), 5.93 (m, 1H), 7.08 (d, J=8Hz, 2H), 7.16~7.30 (m, 3H), 9.71 (s, 1H).

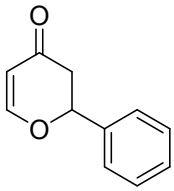




Serial Number	Retention Time [min]	Area	Area %
1	13.531	230144	8.268
2	18.386	2553437	91.732

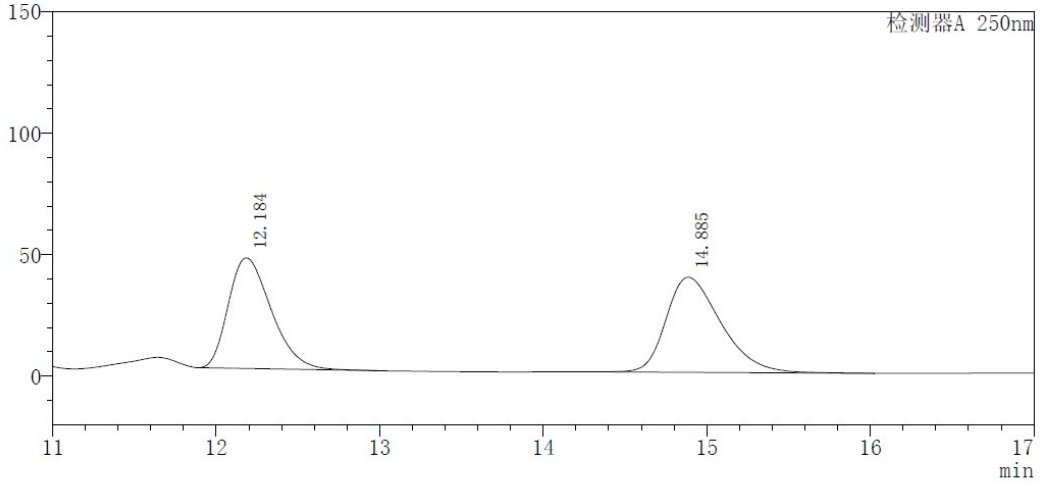

0.90
4.81
1.00
1.05
0.72
2.17
2.95
1.11
1.85
1.14
2.22
2.55
f1 (ppm)

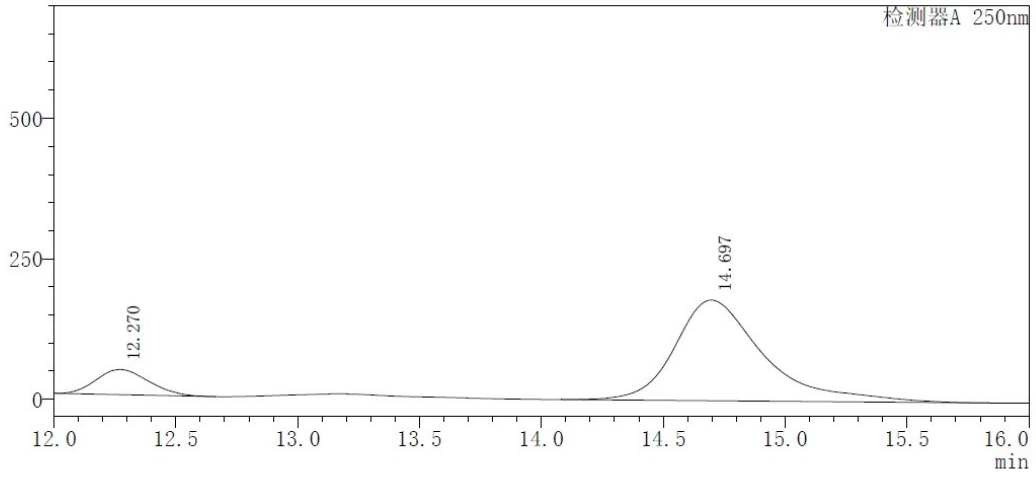
15.4 Hetero-Diels-Alder Reactions



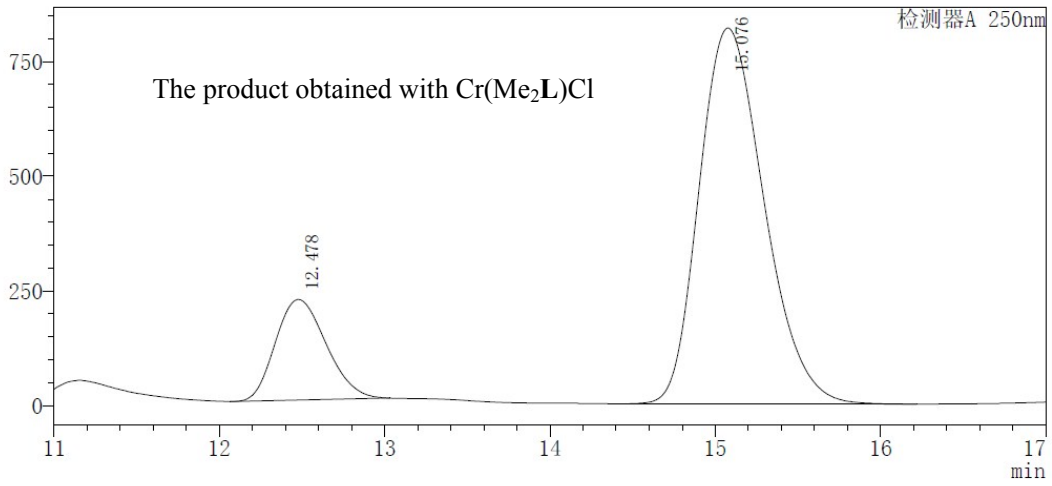
2-phenyl-2H-pyran-4(3H)-one

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} = 14.69 min, t_{minor} = 12.27 min; ee=78%. ^{1}H NMR ($CDCl_3$): 2.65~2.71 (ddd, 1H, J =15.0, 4.0, 1.0 Hz,), 2.88~2.97 (dd, 1H, J = 17.0, 13.5 Hz), 5.43 (dd, 1H, J = 13.5, 4.0Hz), 5.53 (dd, 1H, J = 6.0, 1.0 Hz,), 7.38~7.44 (m, 5H), 7.48 (d, 1H, J =6.0 Hz).

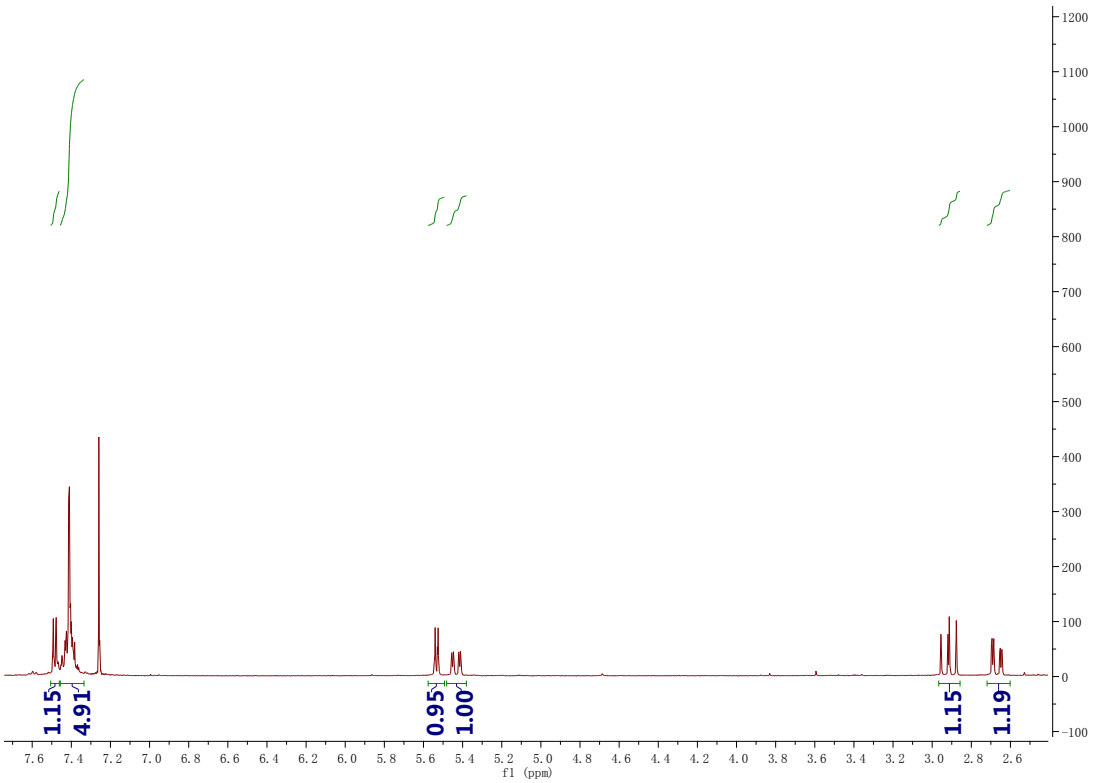


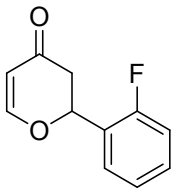


Serial Number	Retention Time [min]	Area	Area %
1	12.270	676177	12.984
2	14.697	4531617	87.016



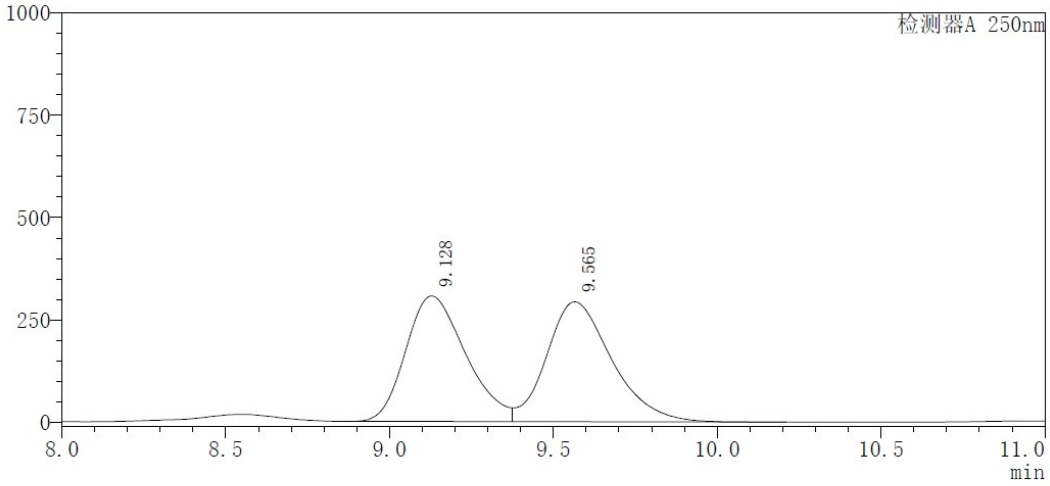
Serial Number	Retention Time [min]	Area	Area %
1	12.478	4682283	17.299
2	15.076	22384924	82.701

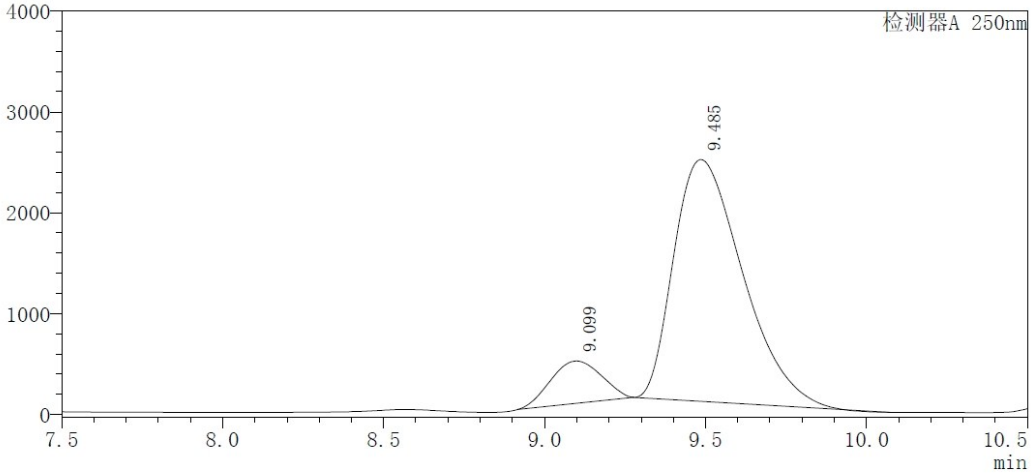




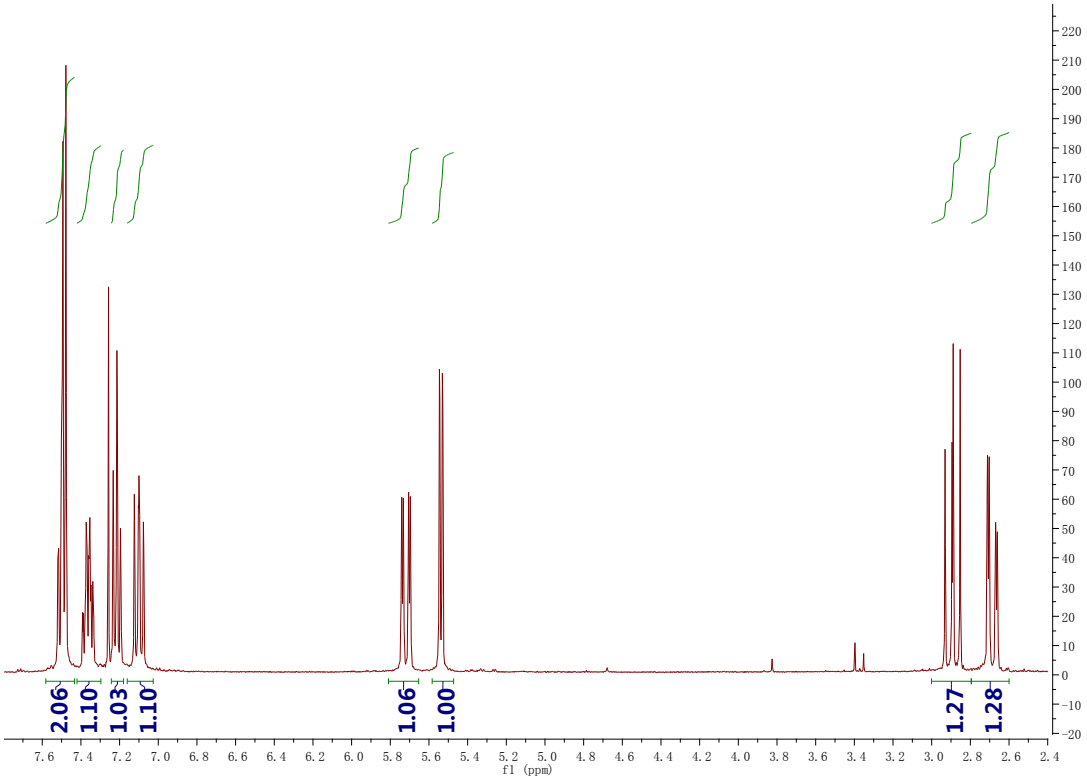
2-(2-fluorophenyl)-2H-pyran-4(3H)-one

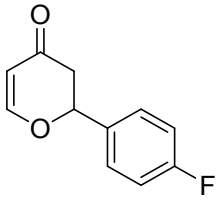
Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t_{major} = 9.48 min, t_{minor} = 9.09 min; ee=78%. ^{1}H NMR ($CDCl_3$): 2.64~2.72 (ddd, 1H, J =15.0, 4.0, 1.0 Hz,), 2.79~2.94 (dd, 1H, J = 17.0, 13.5 Hz), 5.54 (dd, 1H, J = 13.5, 4.0Hz), 5.73 (dd, 1H, J = 6.0, 1.0 Hz,), 7.06~7.54 (m, 5H).





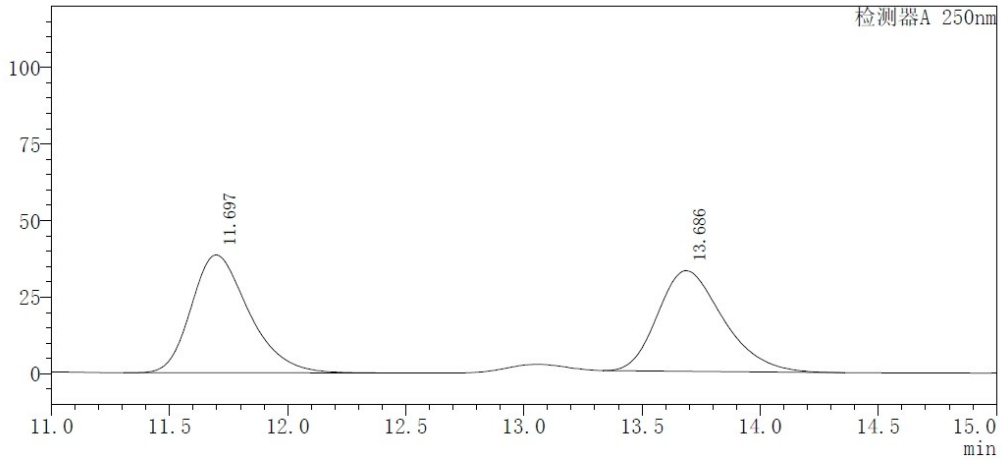
Serial Number	Retention Time [min]	Area	Area %
1	9.099	4666706	11.522
2	9.485	35836891	88.478

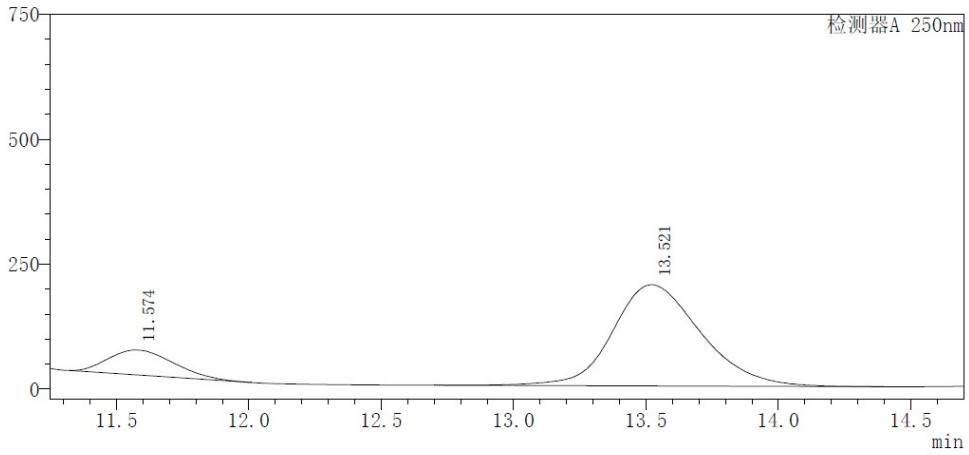

2.06
1.10
1.03
1.10
1.06
1.00
1.27
1.28
f1 (ppm)



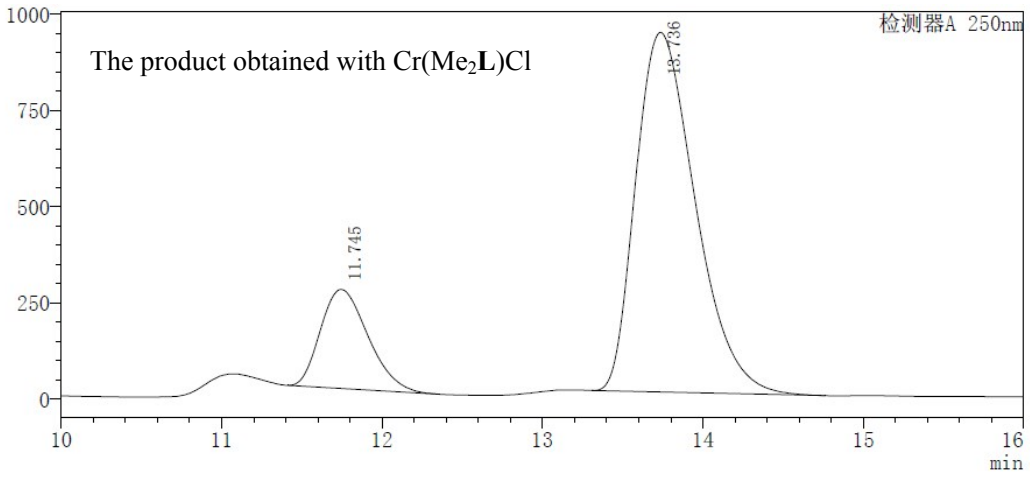
2-(4-fluorophenyl)-2H-pyran-4(3H)-one

Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t $_{major}$ = 13.52 min, t $_{minor}$ = 11.57 min; ee=79%. ^{1}H NMR ($CDCl_3$): 2.60~2.68 (ddd, 1H, J =15.0, 4.0, 1.0 Hz,), 2.82~2.94 (dd, 1H, J = 17.0, 13.5 Hz), 5.40 (dd, 1H, J = 13.5, 4.0Hz), 5.53 (dd, 1H, J = 6.0, 1.0 Hz,), 7.05~7.15 (m, 2H),7.35~ 7.41 (m, 2H), 7.46 (d, 1H, J =8.0 Hz).

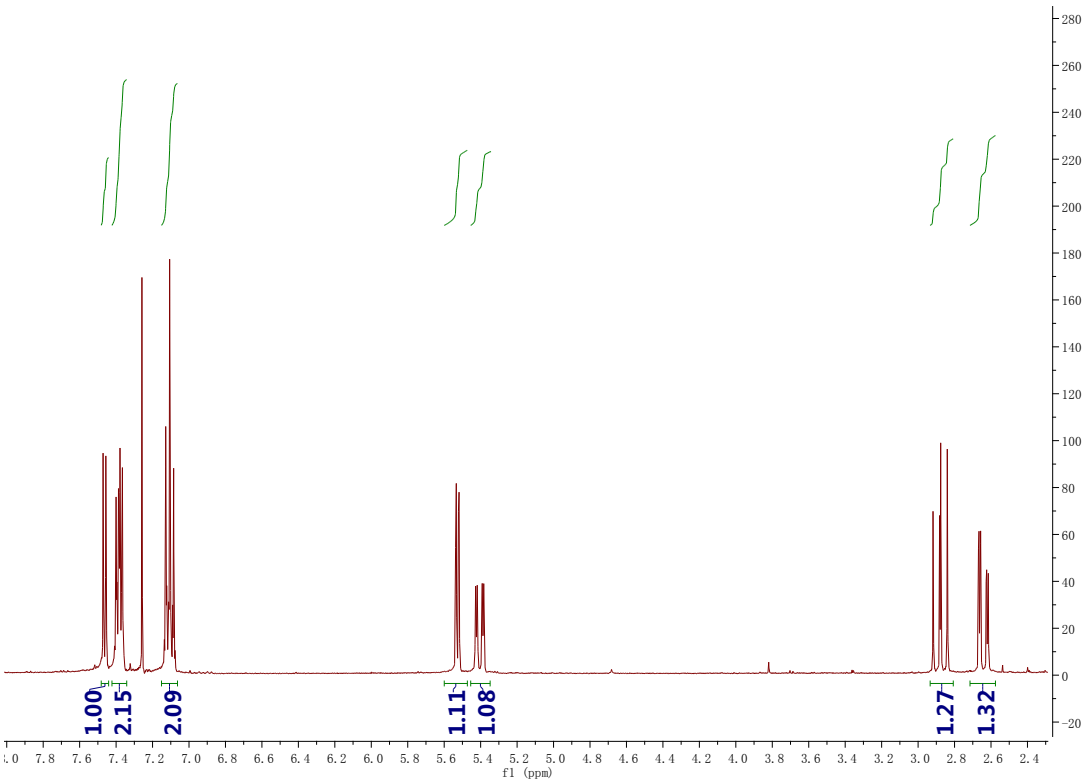


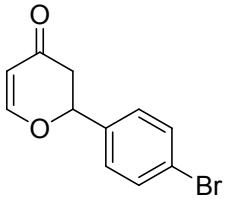


Serial Number	Retention Time [min]	Area	Area %
1	11.574	858148	15.406
2	13.521	4711936	84.594



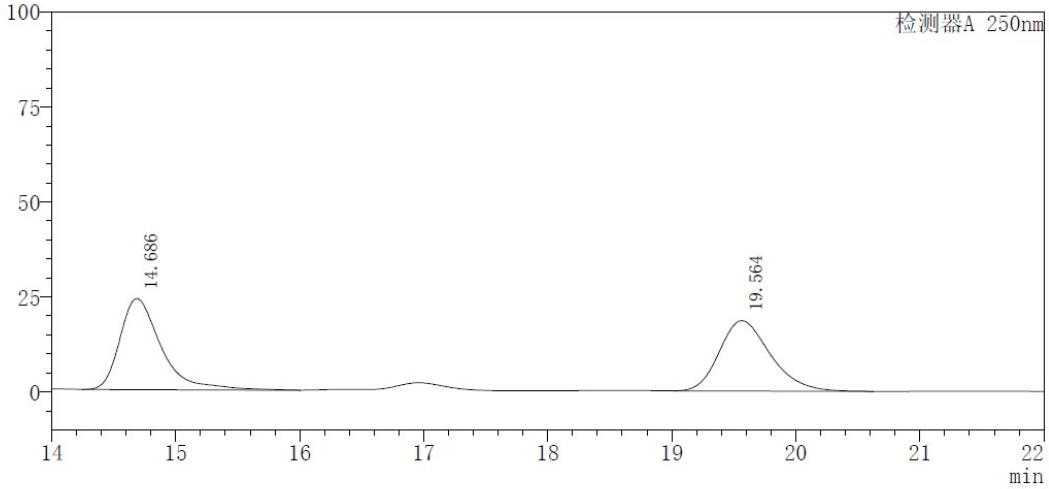
Serial Number	Retention Time [min]	Area	Area %
1	11.745	5304734	18.053
2	13.736	24080267	81.947

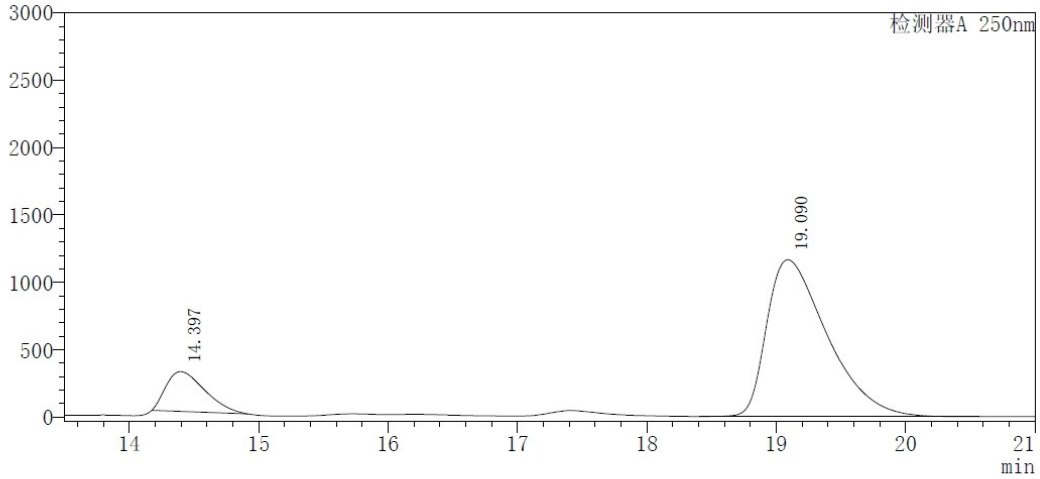




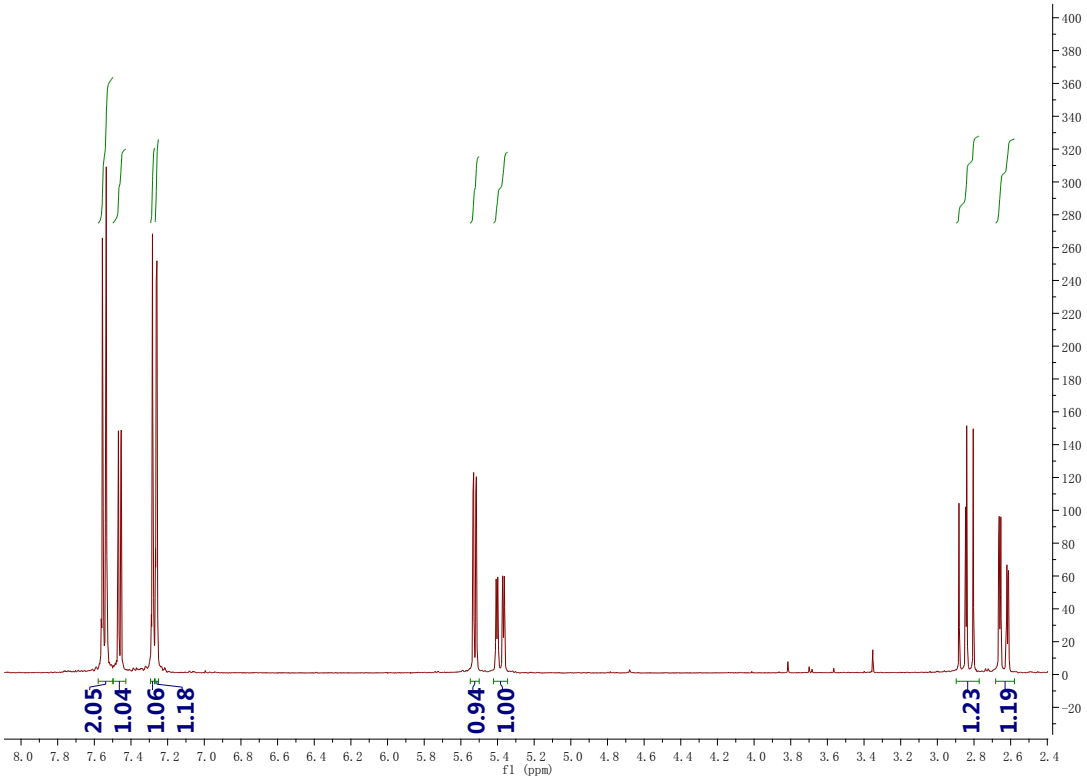
2-(4-bromophenyl)-2H-pyran-4(3H)-one

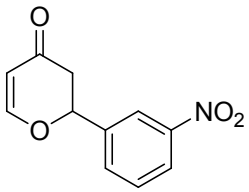
Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t_{major} = 14.39 min, t_{minor} = 19.09 min; ee=72%. ^{1}H NMR ($CDCl_3$): 2.60~2.68 (ddd, 1H, J =15.0, 4.0, 1.0 Hz,), 2.79~2.90 (dd, 1H, J = 17.0, 13.5 Hz), 5.40 (dd, 1H, J = 13.5, 4.0Hz), 5.53 (dd, 1H, J = 6.0, 1.0 Hz,), 7.24~7.36 (m, 2H), 7.46 (d, 1H, J =8.0 Hz), 7.52~ 7.58 (m, 2H).





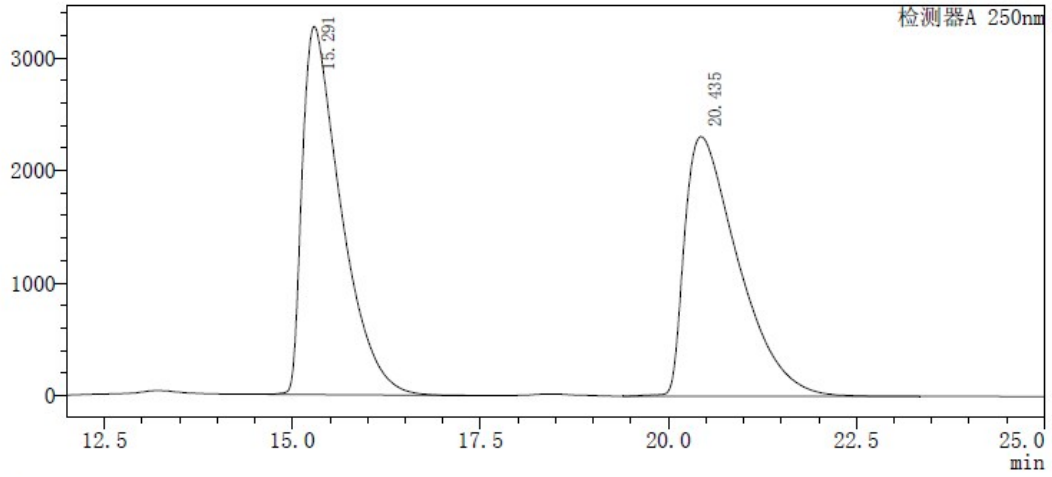
Serial Number	Retention Time [min]	Area	Area %
1	14.397	6138116	14.002
2	19.090	37699442	85.998

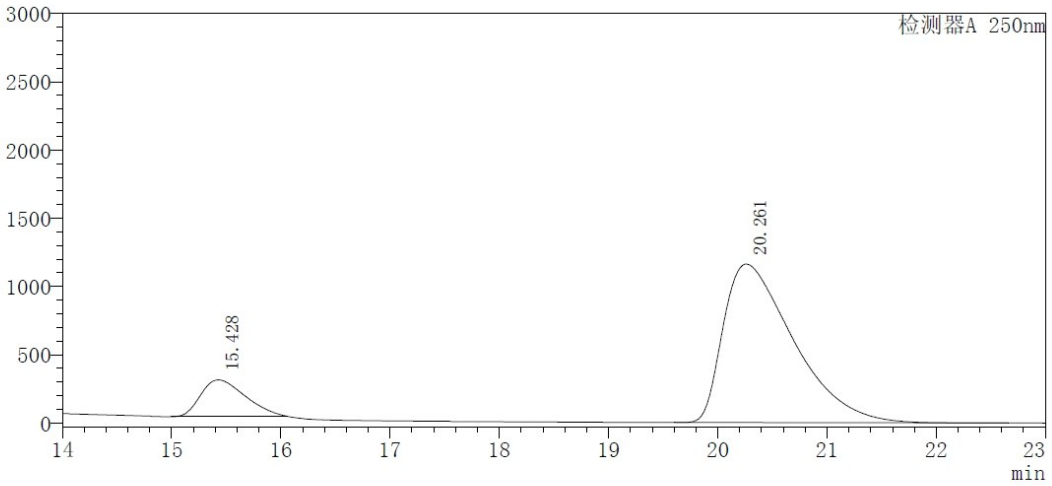

2.05
1.04
1.06
1.18
0.94
1.00
1.23
1.19
f1 (ppm)



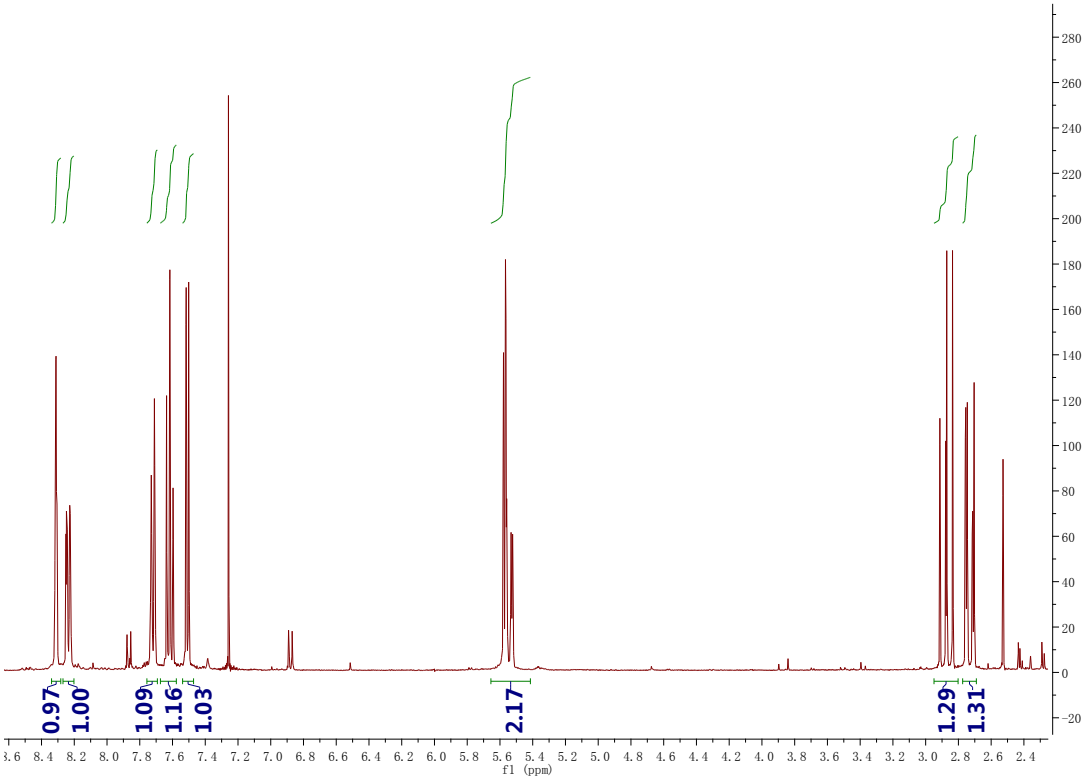
2-(3-nitrophenyl)-2H-pyran-4(3H)-one

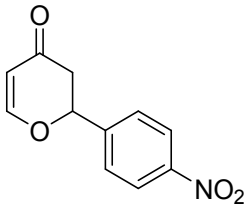
Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t $_{major}$ = 20.26 min, t $_{minor}$ = 15.42 min; ee=75%. ^{1}H NMR ($CDCl_3$): 2.68~2.78 (ddd, 1H, J =15.0, 4.0, 1.0 Hz,), 2.82~2.92 (dd, 1H, J = 17.0, 13.5 Hz), 5.52 (dd, 1H, J = 13.5, 4.0Hz), 5.57 (dd, 1H, J = 6.0, 1.0 Hz,), 7.50 (d, 1H, J =8.0 Hz), 7.55~7.75 (m, 2H), 8.20~ 8.35 (m, 2H).





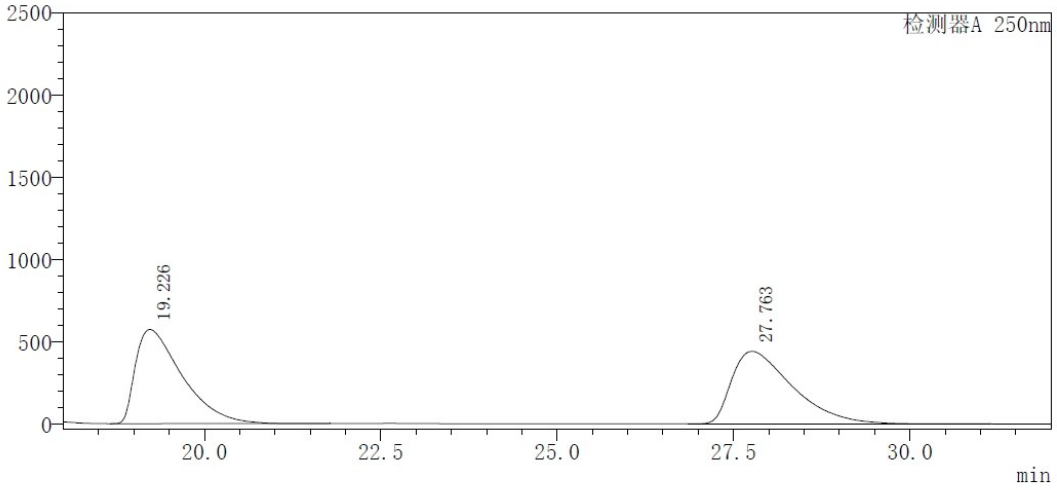
Serial Number	Retention Time [min]	Area	Area %
1	15.428	7586746	12.747
2	20.261	51930121	87.253

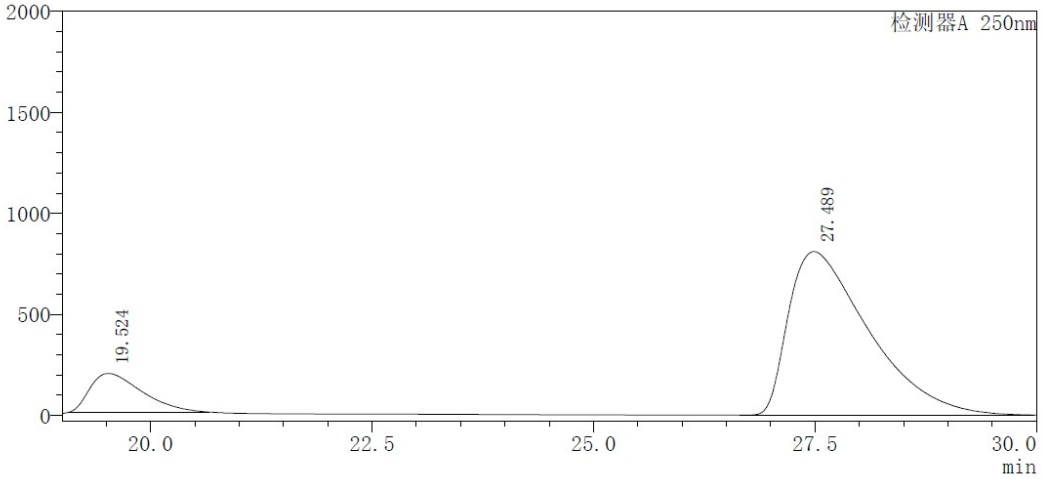

0.97
1.00
1.09
1.16
1.03
2.17
1.29
1.31
f1 (ppm)



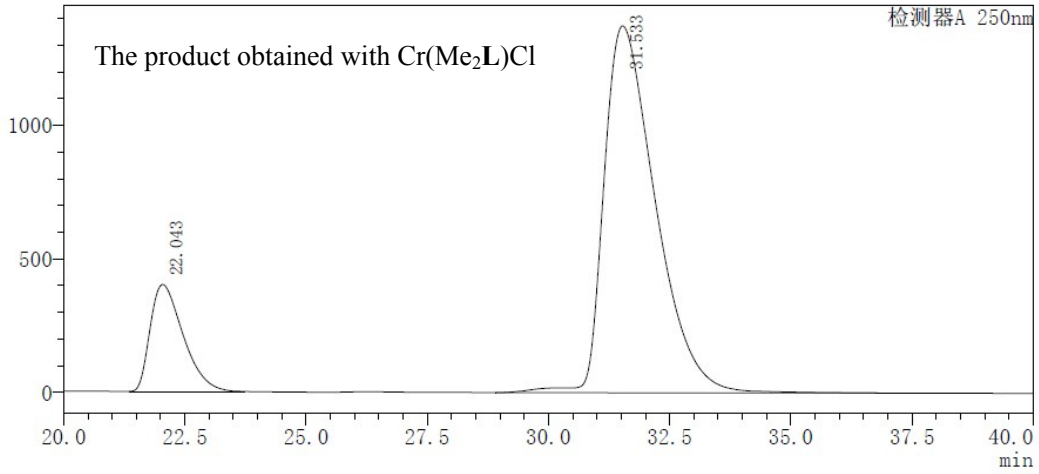
2-(4-nitrophenyl)-2H-pyran-4(3H)-one

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} = 27.48 min, t_{minor} = 19.52 min; ee=75%. ^{1}H NMR ($CDCl_3$): 2.66~2.76 (ddd, 1H, J =15.0, 4.0, 1.0 Hz,), 2.79~2.90 (dd, 1H, J = 17.0, 13.5 Hz), 5.49 (dd, 1H, J = 13.5, 4.0Hz), 5.57 (dd, 1H, J = 6.0, 1.0 Hz,), 7.50 (d, 1H, J =8.0 Hz), 7.55~7.65 (m, 2H), 8.20~8.30 (m, 2H).

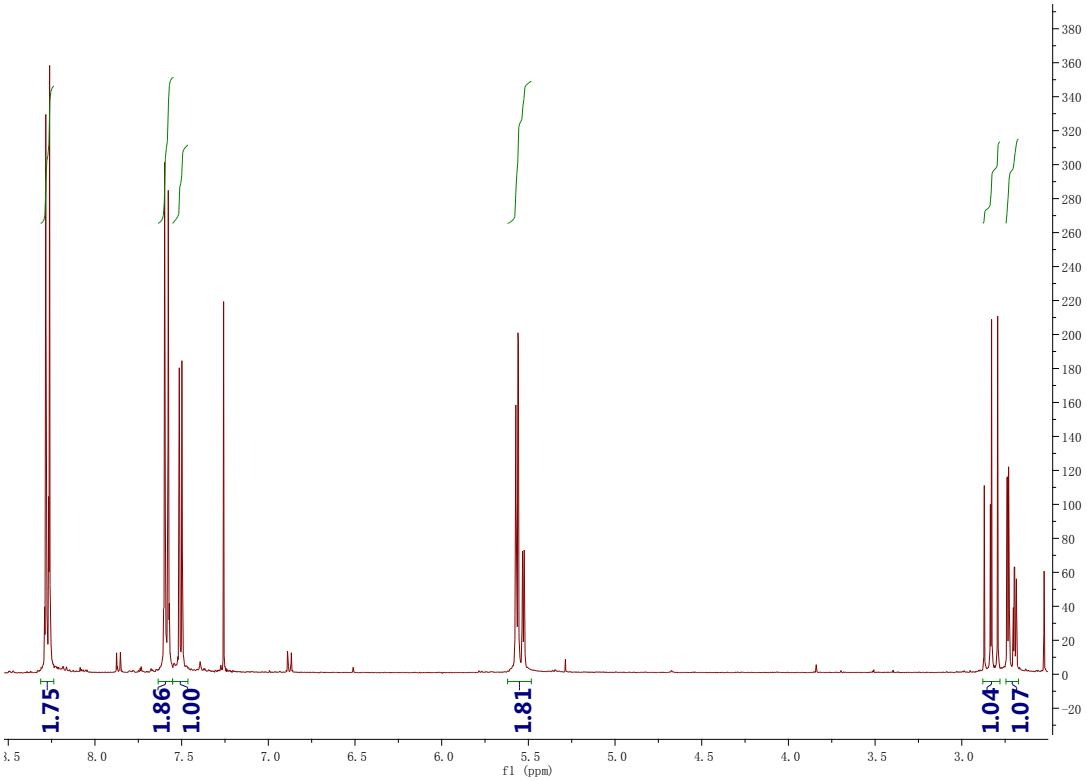


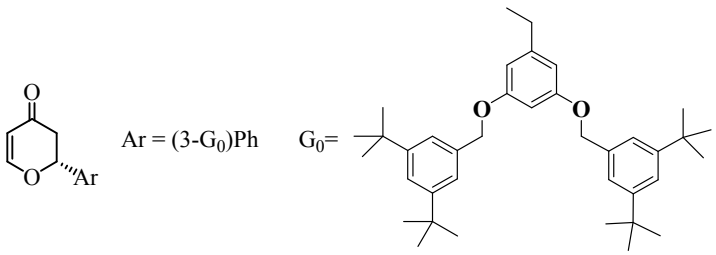


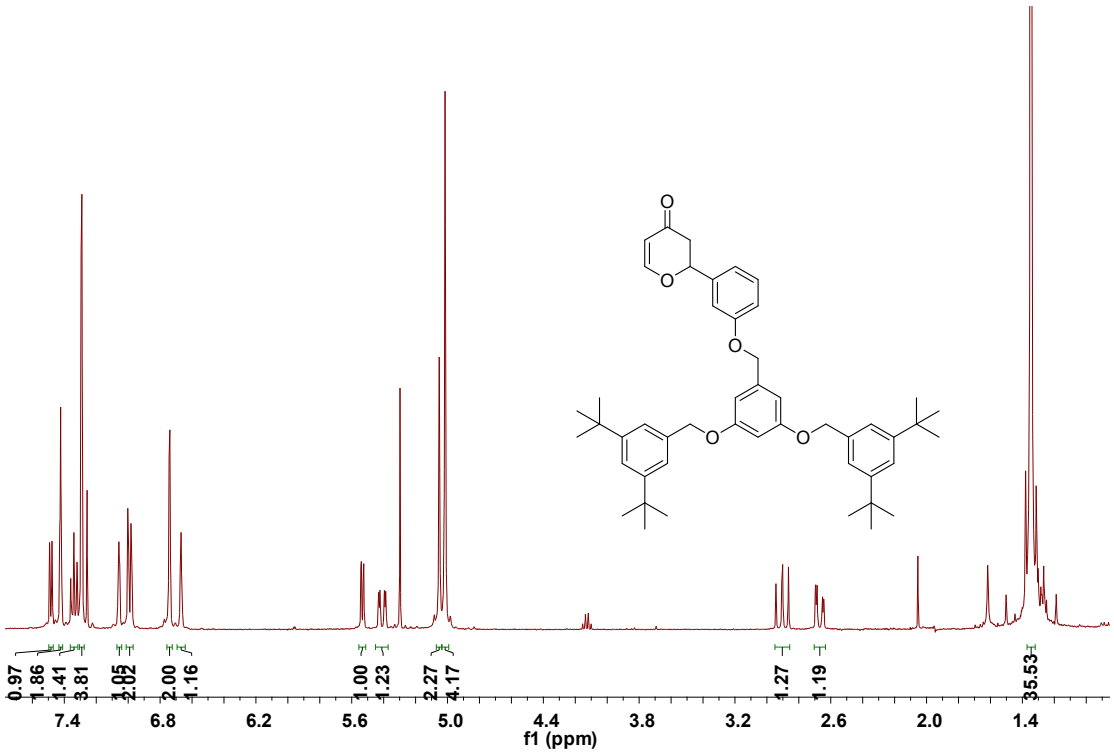
Serial Number	Retention Time [min]	Area	Area %
1	19.524	7845993	13.293
2	27.489	51177906	86.707

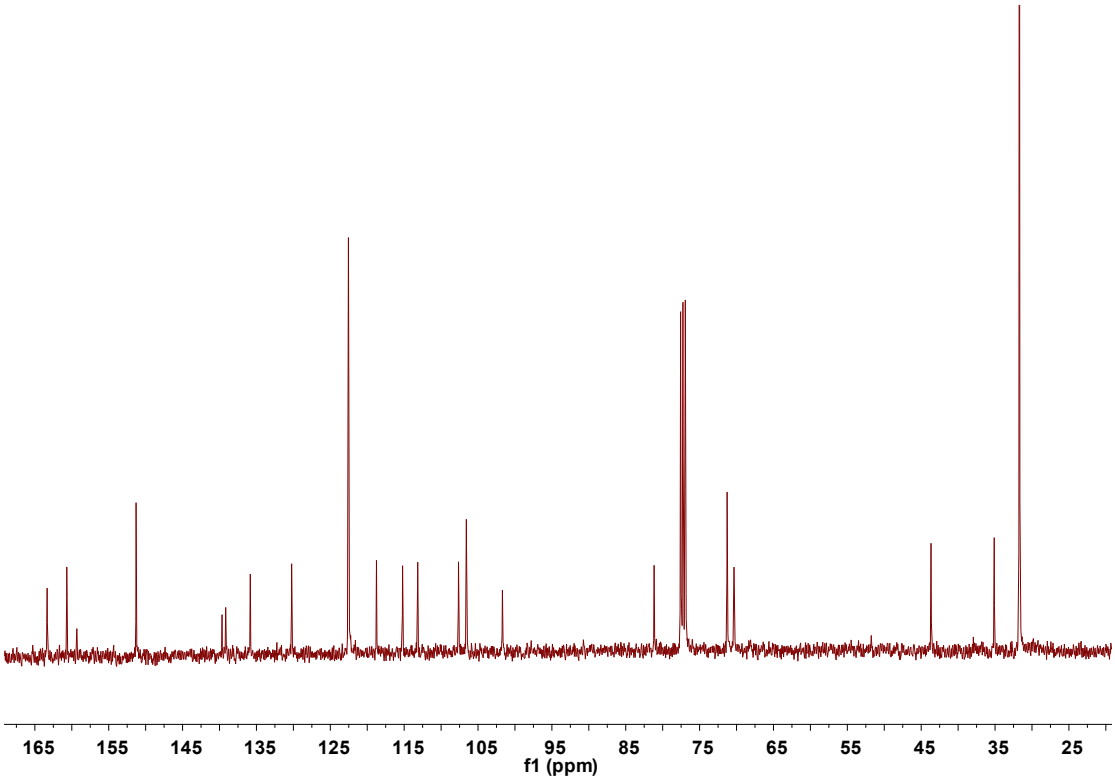


Serial Number	Retention Time [min]	Area	Area %
1	22.043	18918257	15.720
2	31.533	101426376	84.280



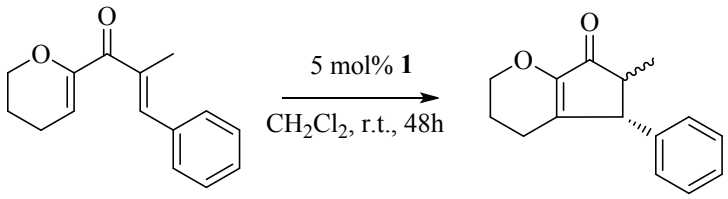

O
O
Ar
Ar = (3-G0)Ph
G0=
O
O


O
O
O
O
O
0.97
1.86
1.41
3.81
1.05
2.02
2.00
1.16
1.00
1.23
2.27
4.17
1.27
1.19
35.53
7.4
6.8
6.2
5.6
5.0
4.4
3.8
3.2
2.6
2.0
1.4
f1 (ppm)


165
155
145
135
125
115
105
95
85
75
65
55
45
35
25
f1 (ppm)

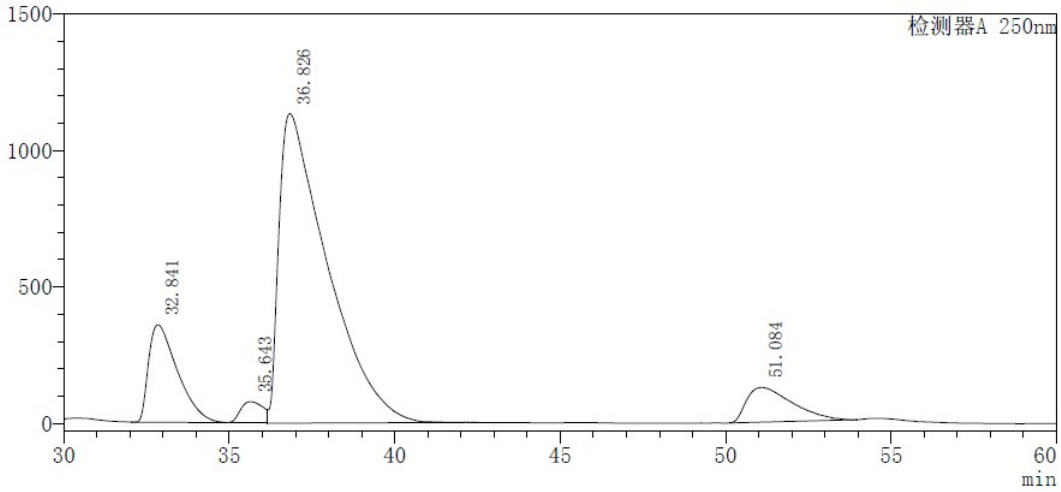
15.5. Recycle Experiments

15.5.1 Nazarov Cyclization



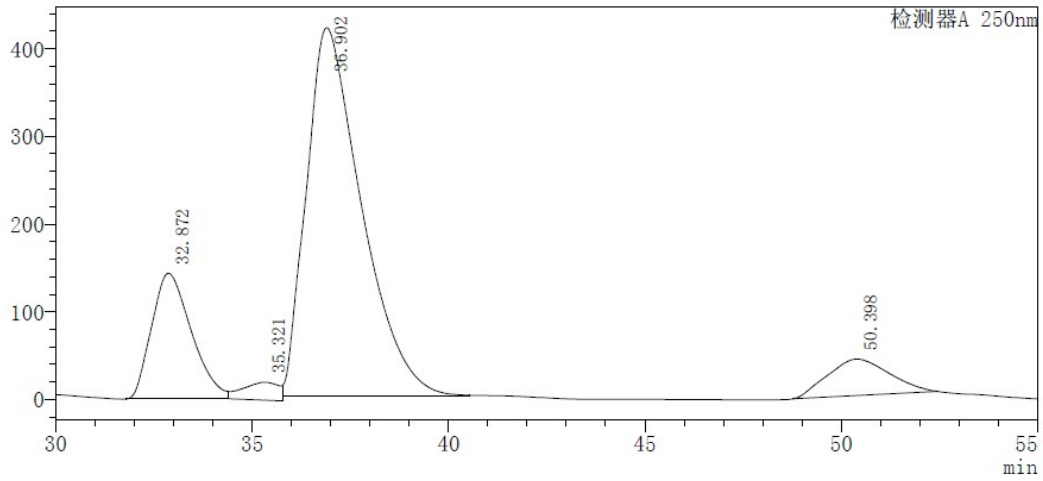
run	conv.(%)	dr	ee $_{trans}$(%)	ee $_{cis}$(%)
1	82	1:0.21	81	84
2	75	1:0.21	81	80
3	74	1:0.21	79	81
4	78	1:0.21	80	75

Run 1



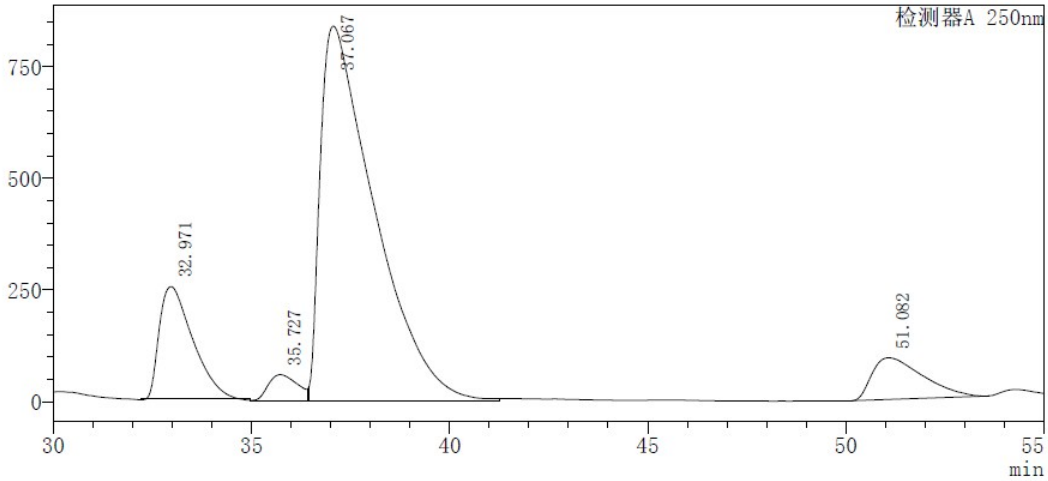
Serial Number	Retention Time [min]	Area	Area %
1	32.841	21766851	14.192
2	35.643	3462415	2.258
3	36.826	115889577	75.563
4	51.084	12249855	7.987

Run 2



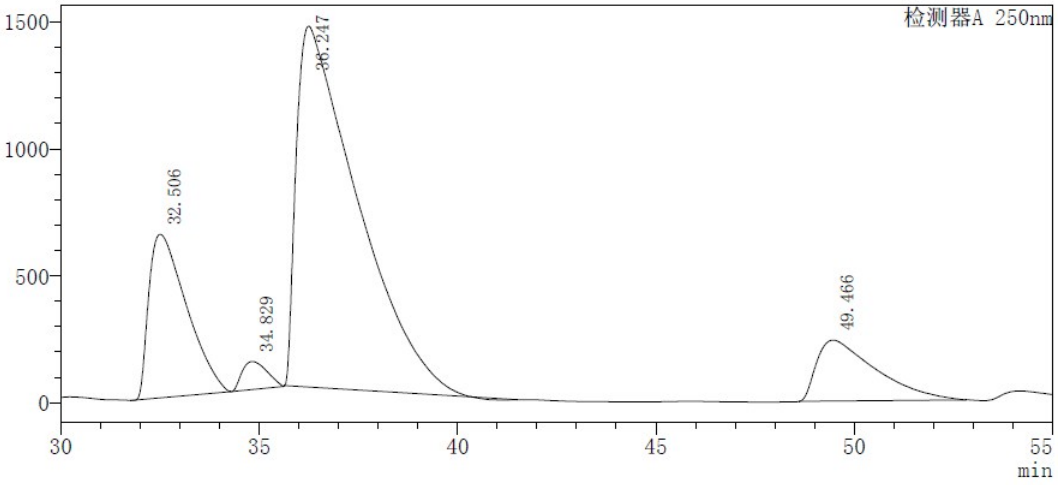
Serial Number	Retention Time [min]	Area	Area %
1	32.872	10082712	17.681
2	35.321	1301704	2.283
3	36.902	41078927	72.036
4	50.398	4562528	8.001

Run 3



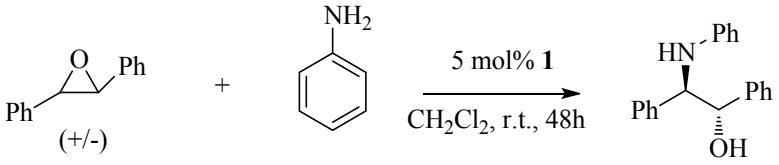
Serial Number	Retention Time [min]	Area	Area %
1	32.971	14787066	13.965
2	35.727	3031618	2.863
3	37.067	79763541	75.328
4	51.082	8306438	7.845

Run 4



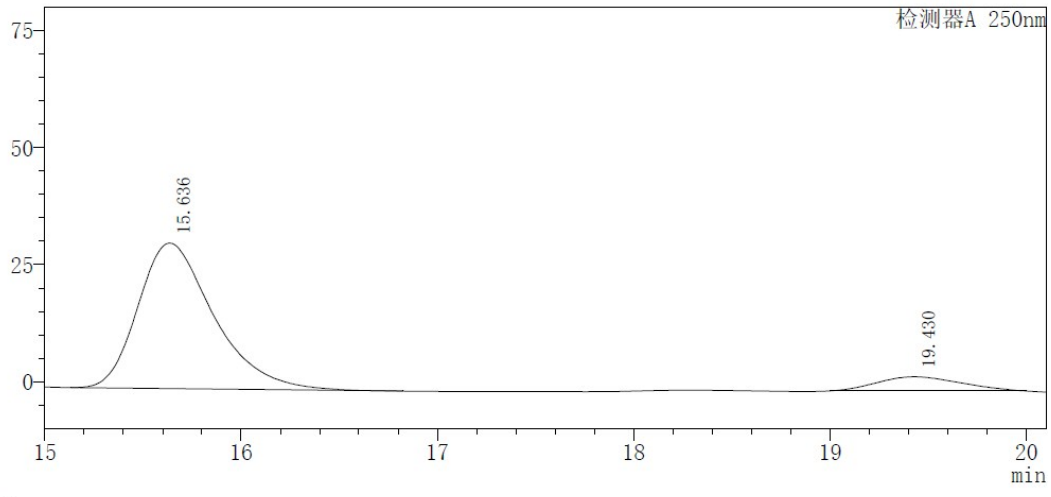
Serial Number	Retention Time [min]	Area	Area %
1	32.506	42617362	18.930
2	34.829	4816329	2.139
3	36.247	152892052	67.914
4	49.466	24799747	11.016

15.5.2 Aminolysis of trans-Stilbene Oxide with Anilines



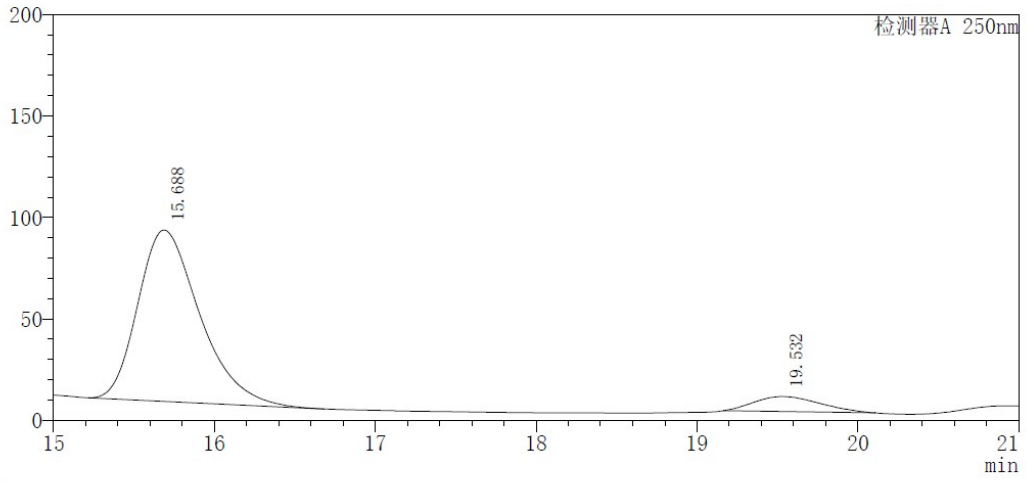
Run	conv.(%)	ee (%)
1	92	81
2	90	81
3	90	77
4	87	77

Run 1



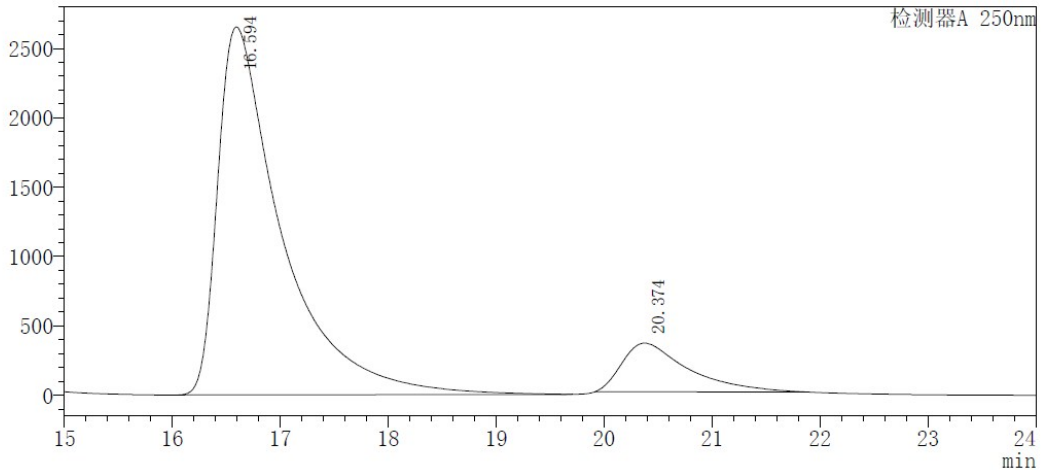
Serial Number	Retention Time [min]	Area	Area %
1	15.636	833496	90.326
2	19.430	89269	9.674

Run 2



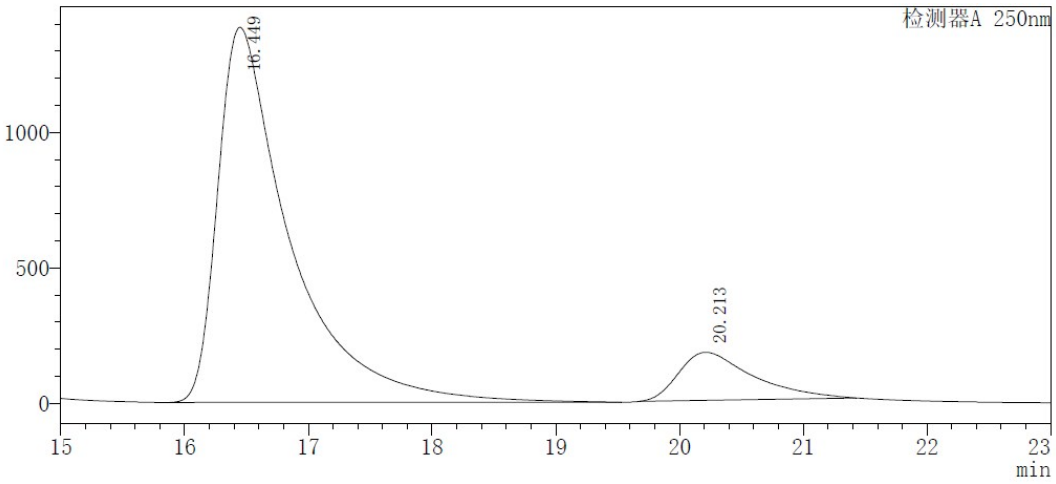
Serial Number	Retention Time [min]	Area	Area %
1	15.688	2259961	91.475
2	19.532	210608	8.525

Run 3



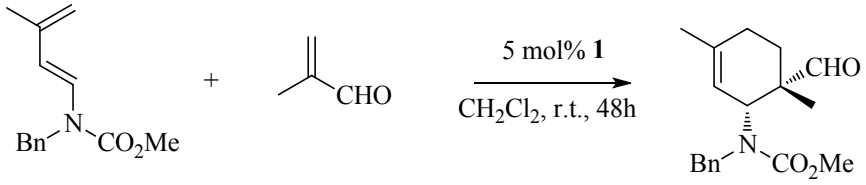
Serial Number	Retention Time [min]	Area	Area %
1	16.594	109322147	90.326
2	20.374	14842148	9.674

Run 4



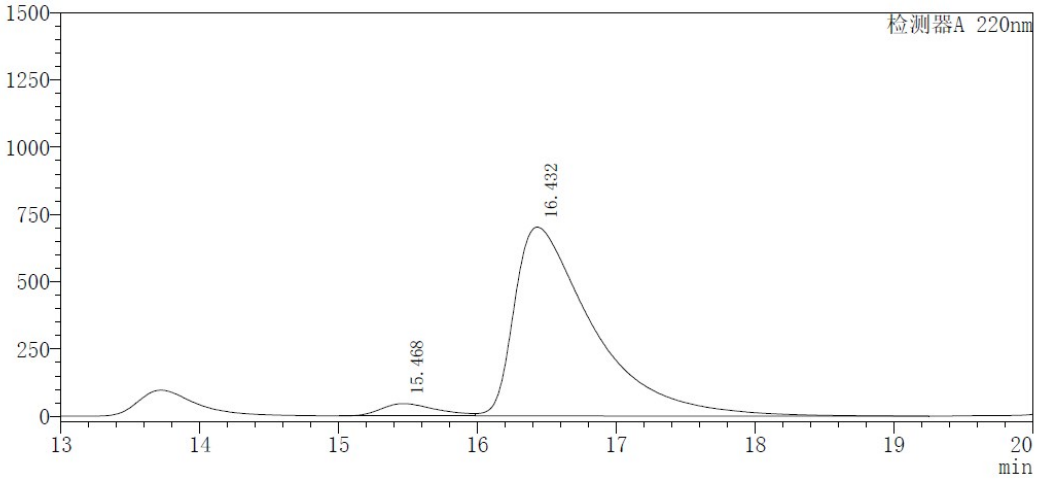
Serial Number	Retention Time [min]	Area	Area %
1	15.449	55955894	90.326
2	19.213	7357830	9.674

15.5.3 Diels-Alder Reactions



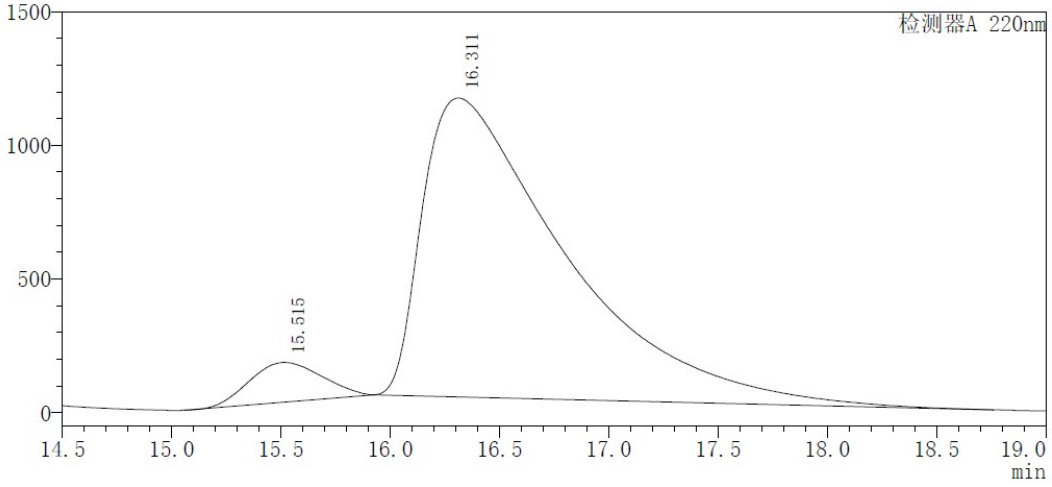
Run	Conv.(%)	ee(%)
1	79	91
2	74	86
3	75	86
4	74	80

Run 1



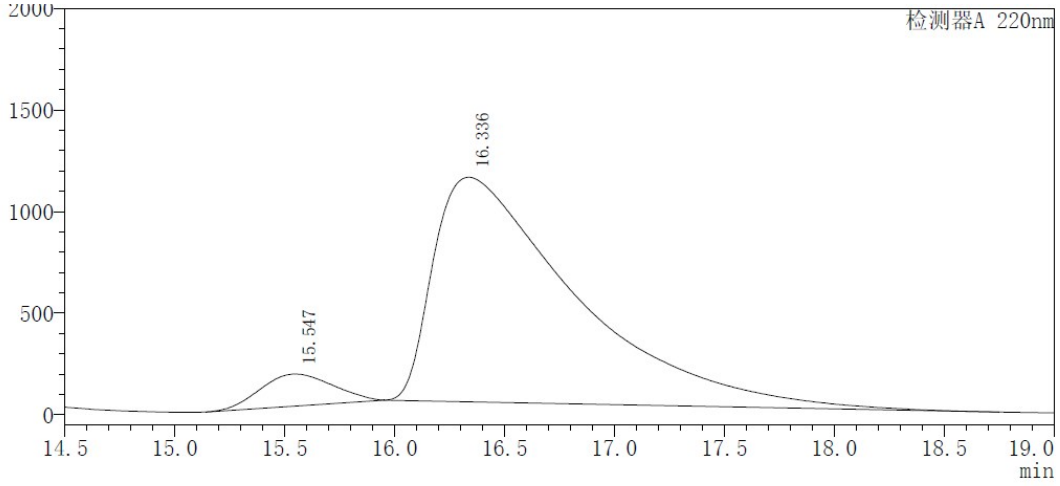
Serial Number	Retention Time [min]	Area	Area %
1	15.468	1278243	4.392
2	16.432	27823300	95.608

Run 2



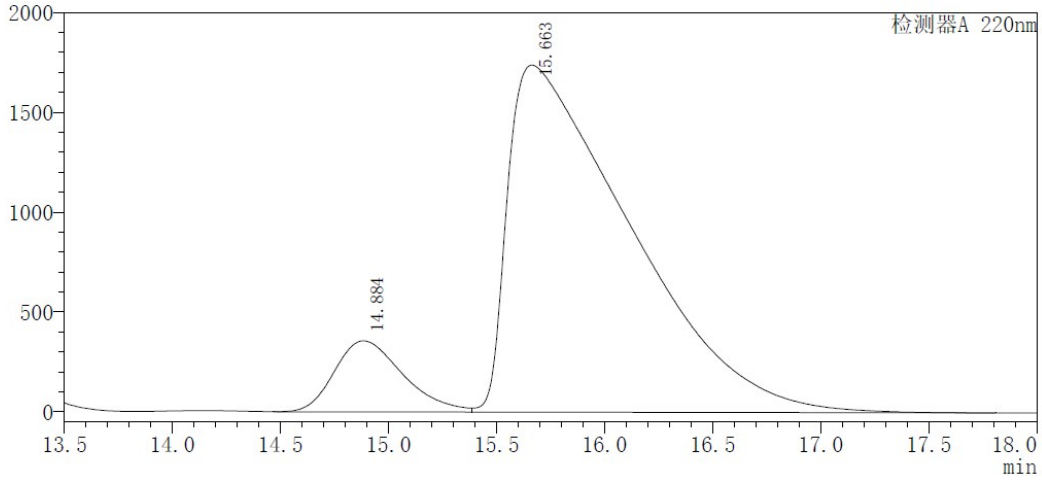
Serial Number	Retention Time [min]	Area	Area %
1	15.515	3435240	6.325
2	16.311	50874693	93.675

Run 3



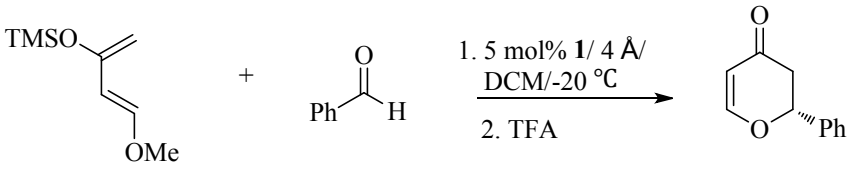
Serial Number	Retention Time [min]	Area	Area %
1	15.547	3611655	6.746
2	16.336	49925040	93.254

Run 4



Serial Number	Retention Time [min]	Area	Area %
1	14.884	7868440	10.269
2	15.663	68751540	89.731

15.5.4 Hetero-Diels-Alder Reactions

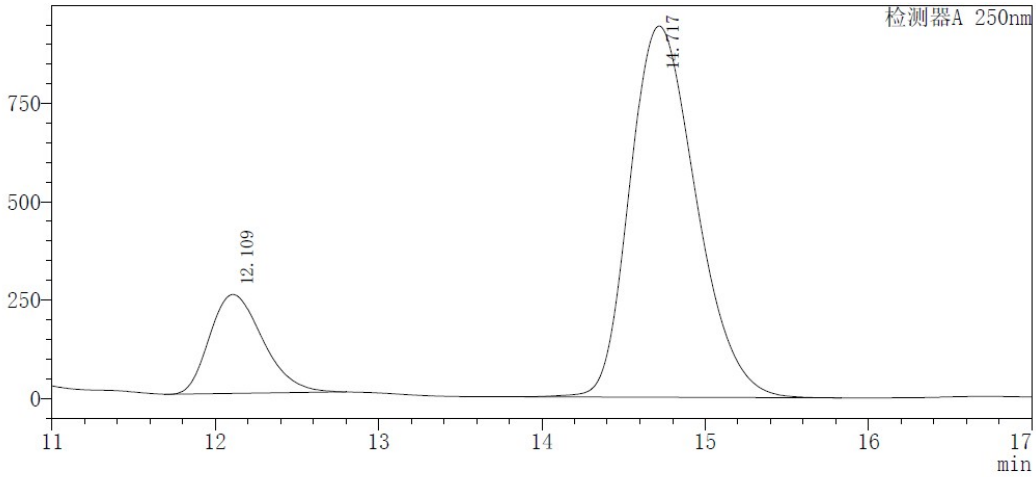


Run	Conv.(%)	ee(%)
1	87	78
2	84	74
3	80	65
4	81	66

Run 1

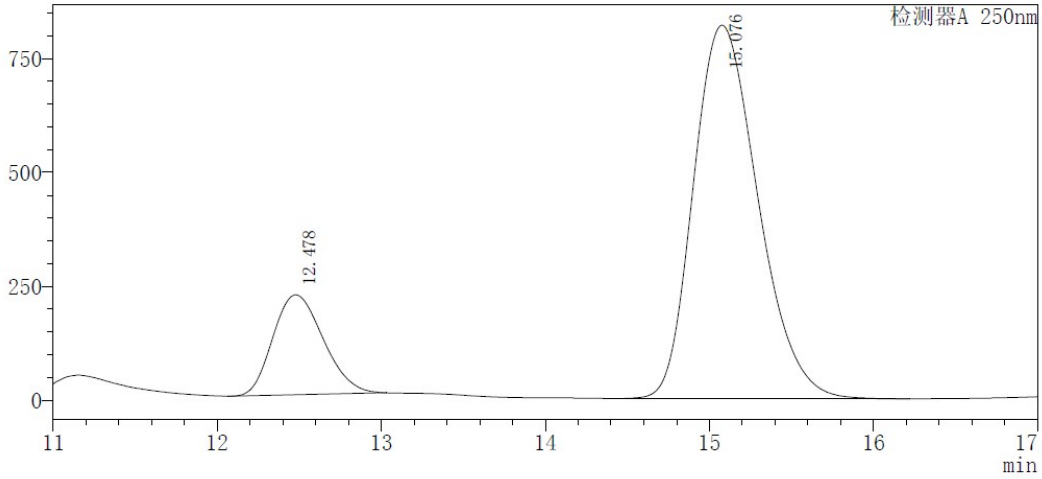
Serial Number	Retention Time [min]	Area	Area %
1	12.270	676177	12.984
2	14.697	4531617	87.016

Run 2



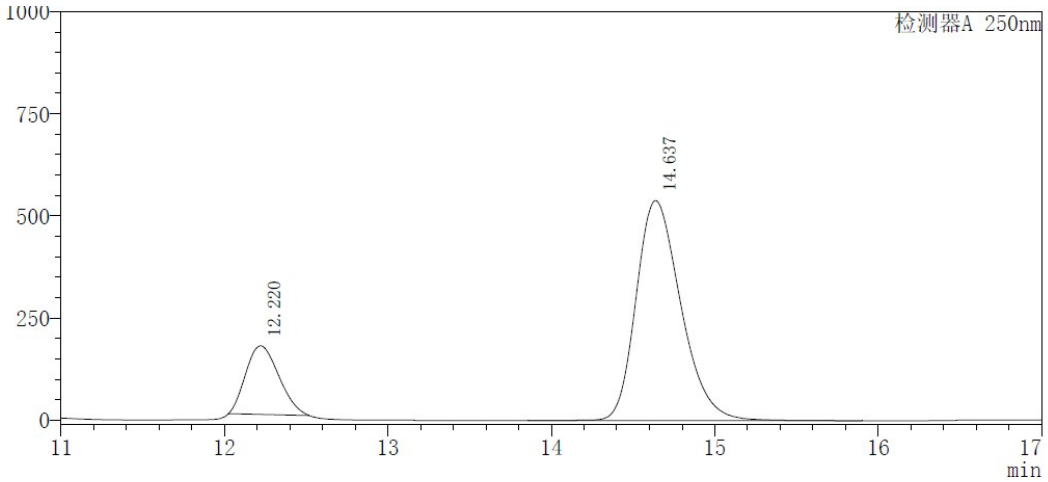
Serial Number	Retention Time [min]	Area	Area %
1	12.109	5675821	17.593
2	14.717	26586788	82.407

Run 3



Serial Number	Retention Time [min]	Area	Area %
1	12.478	4682283	17.299
2	15.076	22384924	82.701

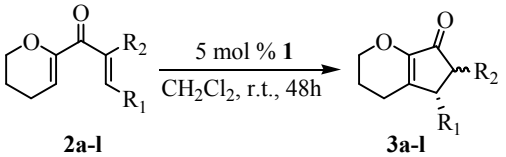
Run 4



Serial Number	Retention Time [min]	Area	Area %
1	12.220	2350789	18.746
2	14.637	10189396	81.254

16. Additional catalytic results

16.1 Table S3. Asymmetric Nazarov Cyclization Catalyzed by **1**.[a]

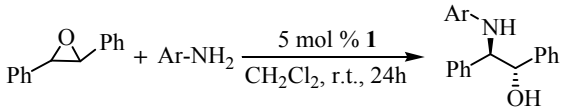


2a-l **3a-l**

Entry	R_1	R_2	**3**/Conv (%)[b]	dr[b]	ee_{trans} (%)[c]	ee_{cis} (%)[c]	TON
1	Ph	Me	**a**/86(95)	5.1(3.3)	81(86)	84(92)	68.8(19.0)
2[d]	Ph	Me	**a**/89	4.8	80	75	71.2
3	*p*-MeC_6H_4	Me	**b**/82	4	75	75	65.6
4	*o*-MeC_6H_4	Me	**c**/83	4.2	77	77	66.4
5	*p*-*Me*OC_6H_4	Me	**d**/79	3.7	81	83	63.2
6	*p*-FC_6H_4	Me	**e**/84(93)	4.8(3.6)	72(75)	95(87)	67.2(18.6)
7	*p*-ClC_6H_4	Me	**f**/85	4.8	78	86	68.0
8	*p*-BrC_6H_4	Me	**g**/89	4.8	81	70	71.2
9	Thiophene	Me	**h**/86	4.8	70	73	68.8
10	Furan	Me	**i**/86	2	90	91	68.8
11	Ph	Et	**j**/72	2.7	80	72	57.6
12	Ph	Pr	**k**/80	1.2	79	76	64.0
13	*p*-BrC_6H_4	Et	**l**/94(94)	3.3(2.6)	84(80)	90(92)	75.2(18.8)

[a]For reaction details see Experimental section in SI; the data in parentheses are results catalyzed by Cr(Me_2**L**)Cl. [b]Calculated by ^{1}H NMR. [c]Determined by HPLC. [d]Catalyzed by 1 mol% (S)-**1**, the configuration of products is opposite to above.

16.2 Table S4. Asymmetric Aminolysis Catalyzed by **1**.[a]

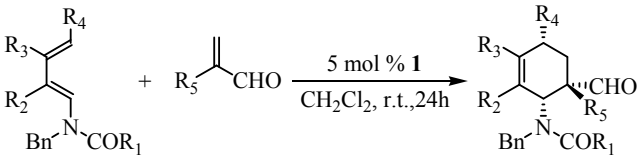


4a-i **5a-i**

Entry	Ar	**5**/Conv (%)[b]	ee (%)[c]	TON
1	Ph	**a**/92(97)	82(74)	73.6(19.4)
2	*o*-MeC_6H_4	**b**/93	94	74.4
3	*m*-MeC_6H_4	**c**/88	93	70.4
4	*p*-MeC_6H_4	**d**/97	93	77.6
5	*o*-$MeOC_6H_4$	**e**/93(97)	84(72)	74.4(19.4)
6	*p*-$EtOC_6H_4$	**f**/93	91	74.4
7	*p*-IC_6H_4	**g**/91(96)	99(89)	72.8(19.2)
8	(2,4-$(OMe)_2$)C_6H_4	**h**/92	92	73.6
9	(2-Et-6-Me)C_6H_4	**i**/76(97)	99(17)	60.8(19.4)

[a]For reaction details see Experimental section in SI; the data in parentheses are results catalyzed by Cr(Me_2**L**)Cl. [b]The conversions were determined by ^{1}H NMR analysis based on anilines **4a-i** (0.5 equiv). [c]Determined by HPLC.

16.3 Table S5. Asymmetric Diels-Alder Reactions Catalyzed by **1**.[a]

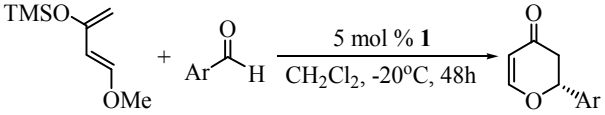


6a-g **7a-c** **8a-g**

Entry	Diene	R_1	R_2	R_3	R_4	R_5	**8**/Conv (%)[b]	ee (%)[c]	TON
1	**6a**	MeO	H	H	H	**7a**/Me	**a**/90(98)	87(70)	72.0(19.6)
2	**6b**	MeO	Me	H	H	**7a**/Me	**b**/32	86	25.6
3	**6c**	MeO	H	Me	H	**7a**/Me	**c**/79(98)	91(86)	63.2(19.6)
4	**6d**	MeO	H	H	Me	**7a**/Me	**d**/30	87	24.0
5	**6e**	Me	H	H	H	**7a**/Me	**e**/81(85)	81(58)	64.8(17.0)
6	**6f**	MeO	H	H	H	**7b**/H	**f**/88	84	70.4
7	**6g**	MeO	H	H	H	**7c**/Et	**g**/81	83	64.8

[a]For reaction details see Experimental section in SI; the data in parentheses are results catalyzed by Cr(Me_2**L**)Cl. [b]Calculated by ^{1}H NMR. [c]Determined by HPLC.

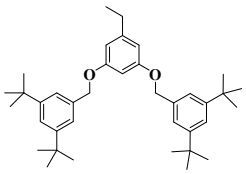
16.4 Table S6. Asymmetric Hetero-Diels-Alder Reactions Catalyzed by **1**.[a]



9a-h **10a-h**

Entry	Ar	**10**/Conv (%)[b]	ee (%)[c]	TON
1	Ph	**a**/87(92)	78(66)	69.6(18.4)
2	(2-F)Ph	**b**/89	78	71.2
3	(4-F)Ph	**c**/84(95)	79(64)	67.2(19.0)
4	(4-Br)Ph	**e**/86	72	68.8
5	(3-NO_2)Ph	**f**/83	75	66.4
6	(4-NO_2)Ph	**g**/77(89)	75(70)	61.6(17.8)
7	(3-G_0)Ph	**h**/<5(88)	n.d.(n.d.)	n.d.

G_0:



[a]For reaction details see Experimental section in SI; the data in parentheses are results catalyzed by Cr(Me_2**L**)Cl. [b]Calculated by ^{1}H NMR. [c]Determined by HPLC.