

Supporting Information for

Chiral Covalent Organic Frameworks with High Chemical Stability for Heterogeneous Asymmetric Catalysis

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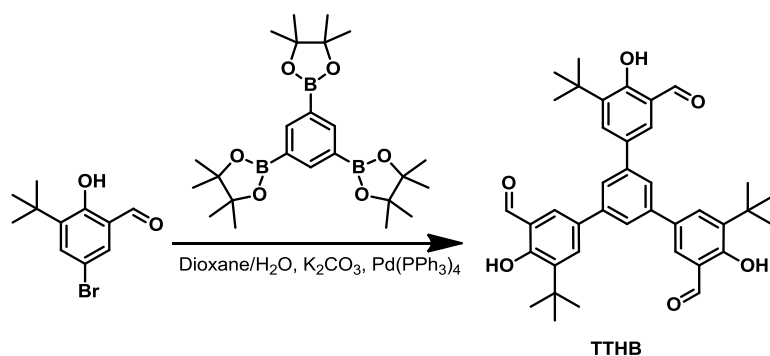
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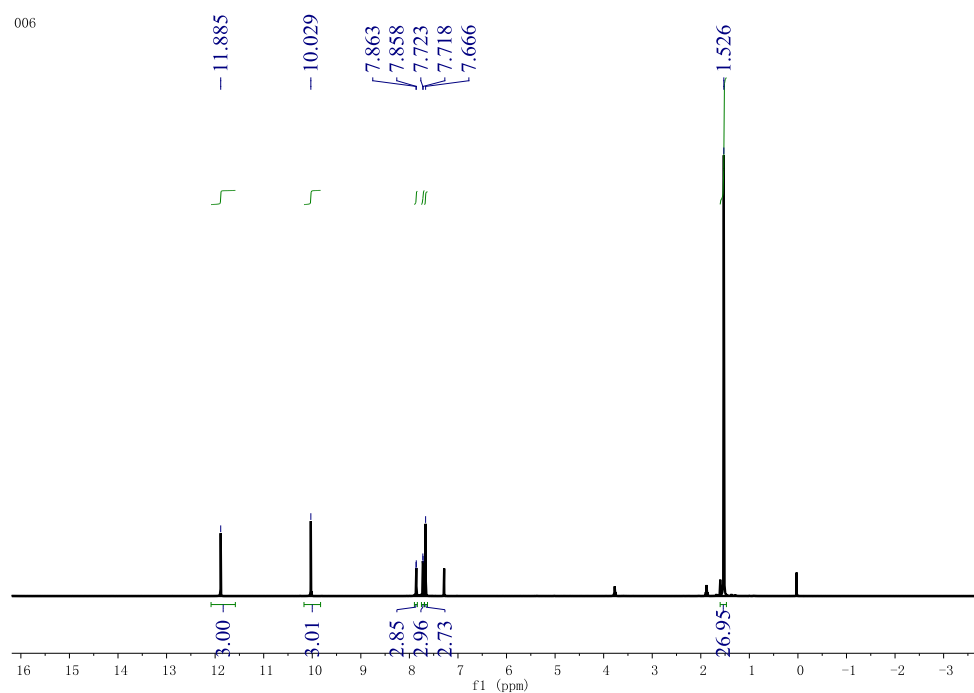
1. Materials and general procedures

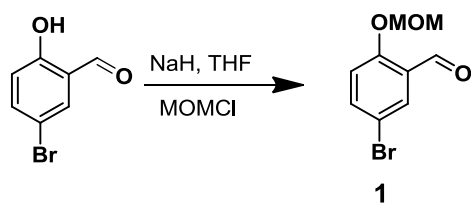
All the chemicals are commercial available, and used without further purification. All solvents were dried and distilled according to conventional methods. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. The CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). The solid state UV spectra were recorded by using pressed BaSO_4 matrix in the range of 200-800 nm at room temperature with a UV/Vis/NIR Spectrometer Lambda 750S (Perkin Elmer, Inc., USA). Powder X-ray diffraction data (PXRD) were collected on a Bruker D8 Advance diffractometer using $\text{Cu K}\alpha$ radiation. Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 5 $^\circ\text{C}/\text{min}$ on a STA449C integration thermal analyzer. Scanning Electron Microscopy (SEM) images were performed on a NOVA NanoSEM NPE218 and NanoSEM 230 instrument equipped with an energy dispersive spectroscopy (EDS) detector. Transmission electron microscopy (TEM) images were performed on a Talos F200X/TALOS F200X instrument. ICP-OES was performed on Optima 7300DV ICP-OES (Perkin Elmer Corporation, USA). ^1H and ^{13}C NMR experiments were carried out on a MERCURY plus 400 spectrometer operating at resonance frequencies of 400 MHz. Solid ^{13}C NMR experiments were carried out on a Bruker Avance III 400 MHz. Analytical high performance liquid chromatography (HPLC) was performed on a LC-2010HAT HPLC with UV detection at 200 or 254 nm. Analytical CHIRALCEL OD-H and AD-H columns (4.6 mm \times 25 cm) from Daicel were used. Absolute stereochemistry was assigned by comparison of optical rotation with reported values. The porous properties of the covalent organic frameworks (COFs) were investigated by nitrogen adsorption and desorption at 77.3 K using ASAP 2020 V4.00 (V4.00 H) Serial #: 1674 from USA. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. X-ray photoelectron spectroscopy (XPS) was recorded on an AXIS Ultra DLD electron spectrometer. The solid state UV spectra were recorded by using pressed BaSO_4 matrix in the range of 200-800 nm at room temperature with a UV/Vis/NIR Spectrometer Lambda 750S (Perkin Elmer, Inc., USA).

2. Synthesis

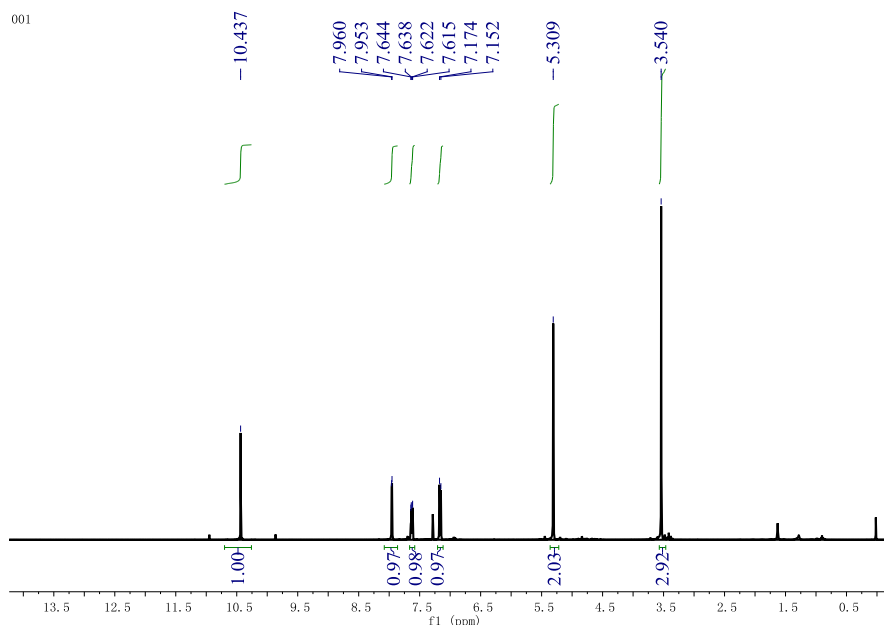


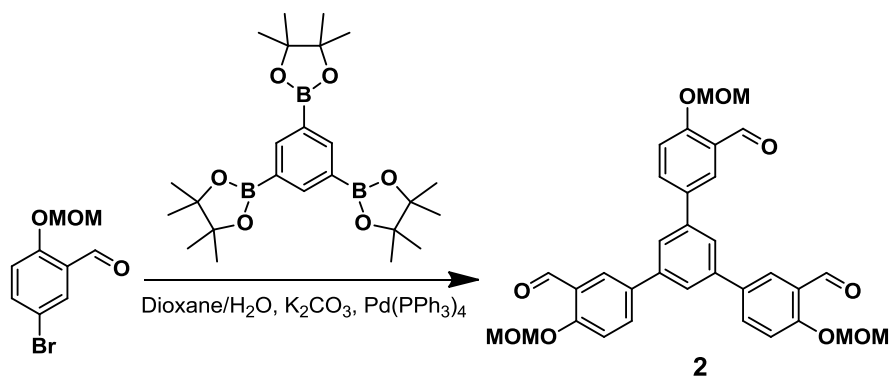
2.1 Synthesis of 1,3,5-tris(3'-tert-butyl-4'-hydroxy-5'-formylphenyl)benzene (TTHB): 5-bromo-3-(tert-butyl)-2-hydroxybenzaldehyde (2.57 g, 10 mmol), 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1.50 g, 3.33 mmol), K_2CO_3 (3.3 g, 24 mmol) and $Pd(PPh_3)_4$ (230 mg, 0.2 mmol) in dioxane/ H_2O (3/1 v/v, 80 mL) were degassed for 10 min. The suspension was stirred under N_2 at 100 °C for 24 h. After cooling to room temperature, the mixture was concentrated and then extracted with EtOAc. The organic phase was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure to remove the solvent. The crude product was purified by silica gel column chromatography (hexanes/ethyl acetate (3:1 v/v) to afford **TTHB**. Yield: (1.5 g, 74%). 1H NMR (400MHz, $CDCl_3$) δ : 11.89 (s, 3H), 10.03 (s, 3H), 7.86 (d, $J = 2.2$ Hz, 3H), 7.72 (d, $J = 2.3$ Hz, 3H), 7.67 (s, 3H), 1.53 (s, 27H).



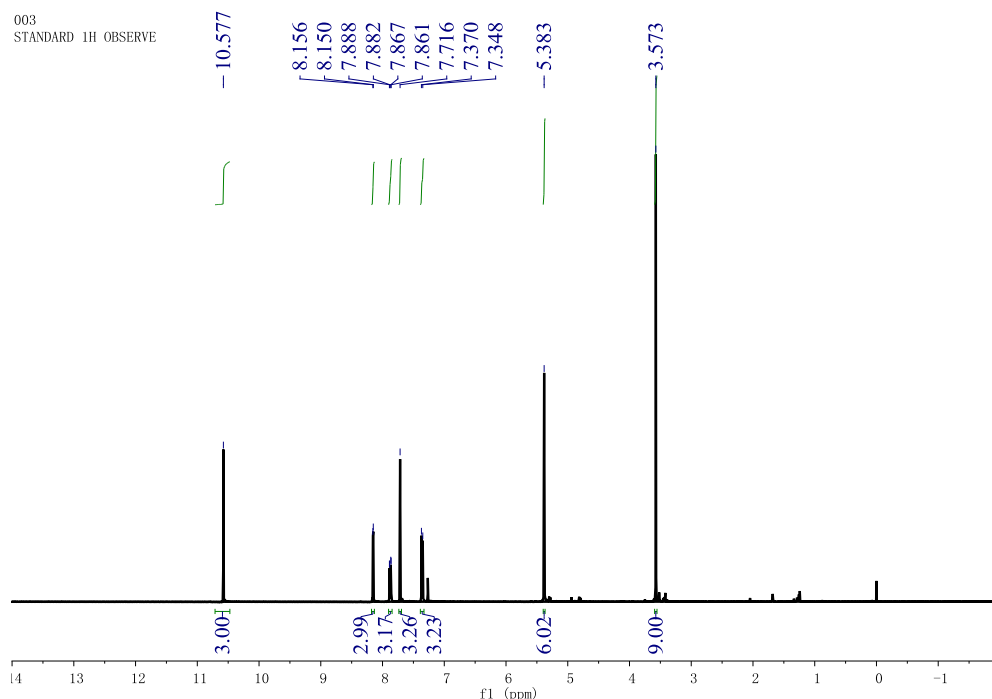


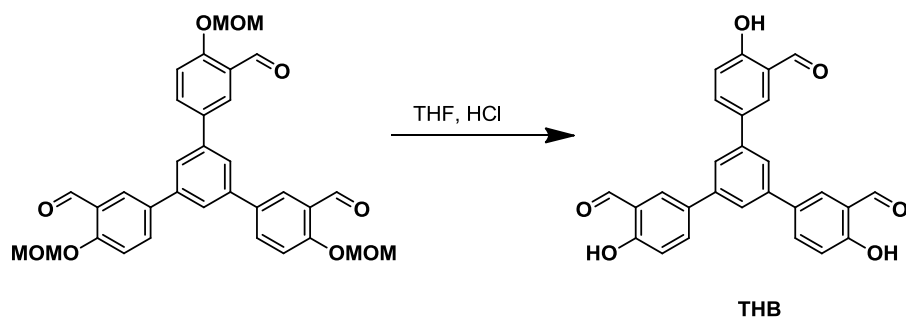
2.2 Synthesis of 5-bromo-3-(tert-butyl)-2-(methoxymethoxy)benzaldehyde(1): To a solution of NaH (6g, 60% dispersion in oil, 150 mmol) in anhydrous THF (30 mL) was added slowly 5-bromo-2-hydroxybenzaldehyde (20.1 g, 100 mmol) in 150 mL anhydrous THF at 0 °C. After 2 hours, chloromethyl methyl ether (12 g, 150 mmol) was then added dropwise to the solution at 0 °C. The mixture was stirred for another 5 hours at room temperature. The saturated Na₂CO₃ solution was added carefully to quench the reaction at 0 °C until the pH value reached to ~8. The organic layer was separated, and the aqueous phase was extracted with diethyl ether (3×100 mL). The combined organic phase was then dried over Na₂SO₄ and concentrated. The crude material was purified by flash chromatography on silica gel (hexanes/ethyl acetate (100:1 v/v) to give product (21 g, 86% yield) as colorless oil. ¹H NMR (CDCl₃) δ:10.44 (s, 1H), 7.96 (d, J = 2.6 Hz, 1H), 7.63 (dd, J = 8.9, 2.6 Hz, 1H), 7.16 (d, J = 8.9 Hz, 1H), 5.31 (s, 2H), 3.54 (s, 3H).



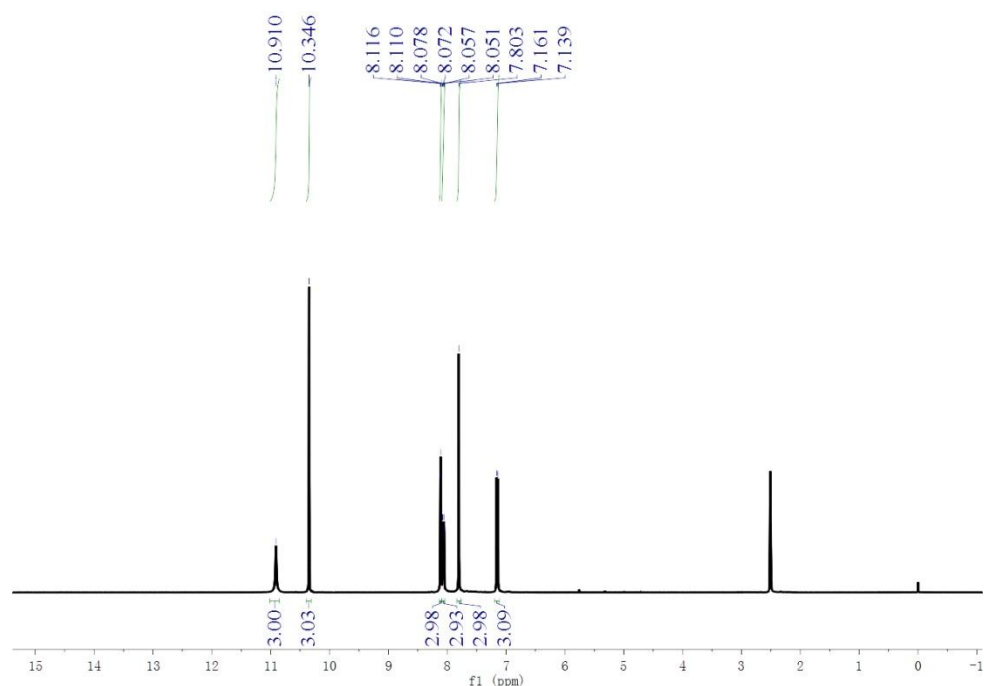


2.3 Synthesis of 1,3,5-tris(4'-methoxymethoxy-5'-formylphenyl) benzene(2): 1 (2.45 g, 10 mmol), 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1.50 g, 3.33 mmol), K_3PO_4 (3.3 g, 24 mmol) and $Pd(PPh_3)_4$ (230 mg, 0.2 mmol) in dioxane/ H_2O (3/1 v/v, 80 mL) were degassed for 10 mins. The suspension was stirred under N_2 at 100 °C for 24 hours. After cooling to room temperature, the mixture was concentrated and extracted with EtOAc. The organic phase was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure to remove the solvent. The crude product was purified by silica gel column chromatography (hexanes/ethyl acetate (3:1 v/v) to afford **2**. Yield: (1.7 g, 90%). 1H NMR (400 MHz, $CDCl_3$) δ : 10.58 (s, 3H), 8.15 (d, $J = 2.5$ Hz, 3H), 7.87 (dd, $J = 8.7, 2.5$ Hz, 3H), 7.72 (s, 3H), 7.36 (d, $J = 8.7$ Hz, 3H), 5.38 (s, 6H), 3.57 (s, 9H).





2.4 Synthesis of 1,3,5-tris(4'-hydroxy-5'-formylphenyl)benzene (THB): To a solution of **2** (1.7 g, 2.7 mmol) in anhydrous THF (30 mL) was added slowly 10% HCl (10 mL) solution at 50 °C. After 2 hours, 50 mL H₂O was then added to the solution. The precipitate was filtered and washed with a large amount of water. The gray powder was collected and dried in an oven to yield the target compound. Yield: (1.25 g, 96%). ¹H NMR (400 MHz, DMSO) δ: 10.91 (s, 3H), 10.35 (s, 3H), 8.11 (d, *J* = 2.4 Hz, 3H), 8.06 (dd, *J* = 8.6, 2.5 Hz, 3H), 7.80 (s, 3H), 7.15 (d, *J* = 8.6 Hz, 3H).



2.5 Synthesis of CCOF 3: A mixture of THB (29 mg, 0.067 mmol) and Zn(OAc)₂ · 2H₂O (33 mg, 0.15 mmol) in 3 mL of mesitylene/EtOH (1:1 v/v) in a small vial was sonicated for 15 mins and then the (1*R*, 2*R*)-(-)-1,2-diaminocyclohexane (11.4 mg, 0.1mmol) was added. After 0.3 mL aqueous acetic acid (6 mol/L) was added, and the mixture was sonicated to afford a homogeneous dispersion. The

solution was transferred into a pyrex tube and degassed by three freeze-pump-thaw cycles. The tube was sealed off and heated at 120 °C for 3 days. The solid was collected by filtration and washed with anhydrous THF (6 × 4 mL) and acetone (3 × 4 mL). The powder was dried at 80 °C under vacuum overnight to afford the CCOF in 70% isolated yield (31 mg). Attempts to make the CCOF without zinc(II) acetate have failed.

Table S1. Screening of the solvents for the synthesis of CCOF 3.

Entry	Solvents	metal salts	results
1	0.75 mL Mestylene, 0.75 mL EtOH	Zn(OAc) ₂	CCOF-3
2	0.75 mL Mestylene, 0.75 mL EtOH	-	amorphous solid
3	0.75 mL Mestylene, 0.75 mL Dioxane	-	Liquid
4	1.5 mL Dioxane	-	Liquid
5	0.75 mL Mestylene, 0.75 mL DMF	-	Liquid
6	0.75 mL EtOH, 0.75 mL DMF	-	amorphous solid

General conditions: THB (0.067 mmol), (1*R*, 2*R*)-(-)-1,2-diaminocyclohexane (0.1mmol), solvent (1.5 mL), 6 M HOAc (0.3 mL), 120 °C, 3 d.

2.6 Synthesis of CCOF 4: A mixture of TTHB (40 mg, 0.067 mmol) and Zn(OAc)₂ · 2H₂O (33 mg, 0.15 mmol) in 1.5 mL DMF/EtOH (2:1 v/v) in a small vial was sonicated for 15 mins to give a clear solution and then the (1*R*, 2*R*)-(-)-1,2-diaminocyclohexane(11.4 mg, 0.1 mmol) was added. The solution was transferred into a pyrex tube and degassed by three freeze-pump-thaw cycles. The tube was sealed off and heated at 120 °C for 3 days. The solid was collected by centrifugation and washed with anhydrous THF (6 × 4 mL) and acetone (3 × 4 mL). The powder was dried at 80 °C under vacuum overnight to afford the CCOF in 71% isolated yield (39 mg). Attempts to synthesize the CCOF without zinc(II) acetate have been unsuccessful.

Table S2. Screening of the solvents for the synthesis of CCOF 4.

Entry	Solvents	metal salts	results
1	1.0 mL DMF, 0.5 mL EtOH	Zn(OAc) ₂	CCOF-4
2	1.0 mL DMF, 0.5 mL EtOH	-	amorphous solid
3	0.75 mL Mestylene, 0.75 mL Dioxane	-	amorphous solid
4	1.5 mL Dioxane	-	amorphous solid
5	0.75 mL Mestylene, 0.75 mL DMF	-	amorphous solid
6	0.75 mL EtOH, 0.75 mL Mestylene	-	Liquid

General conditions: TTHB (0.067 mmol), (1*R*, 2*R*)-(-)-1,2-diaminocyclohexane (0.1mmol),

solvent (1.5 mL), 120 °C, 3 d.

2.7 Metal exchange of CCOF 4:

CCOF 4-Cr: To a mixture of **CCOF 4** (273 mg, 0.5 mmol) and CrCl₂ (246 mg, 2.0 mmol), was added dry THF (60 mL) under N₂ and stirred at room temperature for 24 hours. After that the mixture was exposed to air, and stirred overnight. The precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone to afford the product as dark yellow solid.

CCOF 4-Fe: To a mixture of **CCOF 4** (273 mg, 0.5 mmol) and Fe(OAc)₂ 4H₂O (492 mg, 2.0 mmol), was added dry MeOH (60 mL) under N₂ and stirred at room temperature for 24 hours with refreshment of the solutions three times. After that the mixture was exposed to air, and stirred overnight. The precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone to afford the product as black solid.

CCOF 4-Mn: To a mixture of **CCOF 4** (273 mg, 0.5 mmol) and Mn(OAc)₂ 4H₂O (490 mg, 2.0 mmol), was added dry MeOH (60 mL) under N₂ and stirred at room temperature for 24 hours with refreshment of the solutions three times. After that the mixture was exposed to air, added anhydrous LiCl (84 mg, 2.0 mmol) and stirred overnight. The precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone to afford the product as brown solid.

CCOF 4-V: A mixture of **CCOF 4** (273 mg, 0.5 mmol) in MeOH (10 mL) was added dropwise to VO(acac)₂ (530 mg, 2.0 mmol) in MeOH (10 mL) and stirred at room temperature for 48 hours with refreshment of the solutions three times. After that the precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone to afford the product as green solid.

CCOF 4-Co: A mixture of **CCOF 4** (273 mg, 0.5 mmol) in MeOH (10 mL) was added dropwise to Co(OAc)₂ 4H₂O (498 mg, 2.0 mmol) in MeOH (10 mL) and stirred at room temperature for 48 hours with refreshment of the solutions three times.

After that the precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone to afford the product as brown solid.

CCOF 4-Cr-Mn: To a mixture of **CCOF 4** (273 mg, 0.5 mmol) and CrCl_2 (36 mg, 0.3 mmol), was added dry THF (40 mL) under N_2 and stirred at room temperature for 24 hours. After that the mixture was exposed to air, and stirred overnight. The precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone and can get the **CCOF 4-Cr_{0.6}**. Then, to a mixture of **CCOF 4-Cr_{0.6}** and $\text{Mn(OAc)}_2 \cdot 4\text{H}_2\text{O}$ (73 mg, 0.3 mmol), was added dry MeOH (30 mL) under N_2 and stirred at room temperature for 24 hours. After that the mixture was exposed to air, and added anhydrous LiCl (42 mg, 1.0 mmol) and stirred overnight. The precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone to afford the product as brown solid.

CCOF 4-Cr-Co: To a mixture of **CCOF 4** (273 mg, 0.5 mmol) and CrCl_2 (36 mg, 0.3 mmol), was added dry THF (40 mL) under N_2 and stirred at room temperature for 24 hours. After that the mixture was exposed to air, and stirred overnight. The precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone and can get the **CCOF 4-Cr_{0.6}**. Then, the **CCOF 4-Cr_{0.6}** in MeOH (10 mL) was added dropwise to $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$ (249 mg, 1.0 mmol) in MeOH (10 mL) and stirred at room temperature for 48 hours. After that the precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone to afford the product as brown solid.

CCOF 4-Cr-Fe: To a mixture of **CCOF 4** (273 mg, 0.5 mmol) and CrCl_2 (36 mg, 0.3 mmol), was added dry THF (40 mL) under N_2 and stirred at room temperature for 24 hours. After that the mixture was exposed to air, and stirred overnight. The precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone and can get the **CCOF 4-Cr_{0.6}**. Then, to a mixture of **CCOF 4-Cr_{0.6}** and $\text{Fe(OAc)}_2 \cdot 4\text{H}_2\text{O}$ (246 mg, 1.0 mmol), was added dry MeOH (40 mL) under N_2 and stirred at room temperature for 24 hours. After that the mixture was exposed to air, and stirred

overnight. The precipitate was collected by filtration and washed with deionized water, THF, DMF, acetone to afford the product as black solid.

3. General procedure for asymmetric catalysis

3.1 Asymmetric Epoxidation Reaction of Alkene Catalyzed by CCOF 4-Mn

To a suspension of CCOF 4-Mn (1 mol%) in dry chloroform (1.0 mL), alkene (0.1 mmol) and 2-(tert-butylsulfonyl)iodosylbenzene (2 mg, 0.006 mmol) were added. The same amount of oxidant was added 18 more times at 15 mins intervals. The reaction was carried out overnight at 0 °C. After that, the mixture was centrifuged at 9000 rpm for 5 mins, and the supernatant was concentrated under vacuum. The concentrate was analyzed by ¹H NMR to give the conversion and by HPLC to give the ee value.

3.2 Asymmetric Epoxidation Reaction of Alkene Catalyzed by CCOF 4-Mn and NaClO as oxidant.

To a suspension of CCOF 4-Mn (1 mol%) in CH₂Cl₂ (1.0 mL), alkene (0.1 mmol) and sodium hypochlorite solution (14.5% available chlorine, 0.19 mL, 0.2 mmol) were added. The reaction was carried out at 0 °C for 24 hours. After that, the mixture was centrifuged at 9000 rpm for 5 mins, and the supernatant was diluted with diethyl ether (5 mL) and H₂O (5 mL). The organic layer was then separated and washed with water (5 mL) and brine (5 mL), dried over Na₂SO₄ and evaporated under reduced pressure. The concentrate was analyzed by ¹H NMR to give the conversion and by HPLC to give the ee value.

3.3 Asymmetric Epoxidation Reaction of Alkene Catalyzed by CCOF 4-Fe

To a suspension of CCOF 4-Fe (1 mol%) and alkene (0.1 mmol) in dry chloroform (1.0 mL), PhIO (0.2 mmol) was added at -20 °C, and then the reaction was allowed to proceed at -20 °C for 48 hours. After that, the mixture was centrifuged at 9000 rpm for 5 mins, and the supernatant was concentrated under vacuum. The concentrate was analyzed by ¹H NMR to give the conversion and by HPLC to give the ee value.

3.4 Asymmetric Aminolysis of Epoxide with Anilines Catalyzed by CCOF 4-Cr

To a suspension of CCOF 4-Cr (5.0 mol%) in chloroform (1.0 mL) was added epoxide (0.2 mmol) at room temperature under N₂. After stirring for 15 mins, aniline (0.1 mmol) was added and the reaction mixture was stirred for 48 hours. After that,

the mixture was centrifuged at 9000 rpm for 5 mins, and the supernatant was concentrated under vacuum. The concentrate was analyzed by ^1H NMR to give the conversion and by HPLC to give the ee value.

3.5 Asymmetric Diels-Alder Reactions Catalyzed by CCOF 4-Co

To a suspension of **CCOF 4-Co** (5.0 mol%), MS 4Å (30 mg) in dry chloroform (1.0 mL), AgNO_3 (5.0 mol%) was added at room temperature under N_2 , the mixture was stirred for 1 hour, then a solution of diene (0.1 mmol) and olefine aldehyde (0.2 mmol) in dry chloroform (0.5 mL) was added by cannula. The reaction mixture was stirred for 48 hours. After that, the mixture was centrifuged at 9000 rpm for 5 mins, and the supernatant was concentrated under vacuum. The concentrate was analyzed by ^1H NMR to give the conversion and by HPLC to give the ee value.

3.6 Asymmetric cyanosilylation Catalyzed by CCOF 4-V

To a suspension of **CCOF 4-V** (54 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) was added a CH_2Cl_2 solution (30 mL) of 3-chloroperoxybenzoic acid (41 mg, 0.24 mmol) with stirring for 4 hours. The resulting mixture was filtered, washed with CH_2Cl_2 (3×8 mL) and dried at 80 °C under vacuum. After that, TMSCN (0.6 mmol) was added dropwise to a mixture of catalyst **CCOF 4-VO** (1.0 mol%) and triphenylphosphine oxide (0.5 mmol) in THF (2.0 mL). The mixture was stirred at room temperature for 0.5 hour and then aldehyde (0.5 mmol) was added dropwise, and the reaction was allowed to proceed at 0 °C for 36 hours. After that, the mixture was centrifuged at 9000 rpm for 5 mins, and the supernatant was concentrated under vacuum. The concentrate was analyzed by ^1H NMR to give the conversion. The corresponding trimethylsilyl ether was purified by flash chromatography over silica gel and then acidized with 10 w/w% HCl/MeOH (0.2 mL) at room temperature for 10 mins. The filtrate was extracted with diethyl ether (10 mL \times 3) and washed with brine (20 mL), dried over MgSO_4 and evaporated under reduced pressure to give the cyanohydrin.

To a solution of the crude cyanohydrin in CH_2Cl_2 (2 mL) was added pyridine (0.16 mL, 2 mmol) and acetic anhydride (0.14 mL, 1.5 mmol). The mixture was stirred at room temperature for 45 mins, diluted with diethyl ether (20 mL) and 1M HCl (10 mL). The organic layer was then separated and washed with water (10 mL), NaHCO_3 solution (10 mL) and brine (10 mL), dried over Na_2SO_4 and evaporated under reduced pressure to give a o-acetyl cyanohydrin. The ee of resulted product was determined by HPLC using Chiralcel OD-H column.

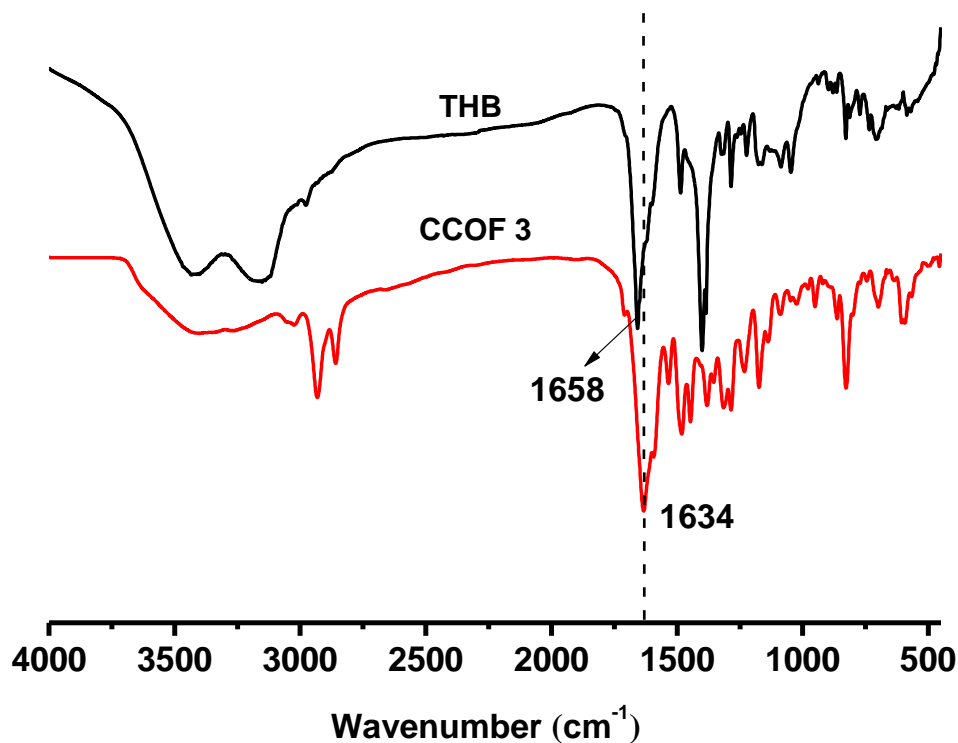
3.7 Asymmetric Alkene Epoxidation/Epoxide Aminolysis Catalyzed by CCOF 4-Cr-Mn

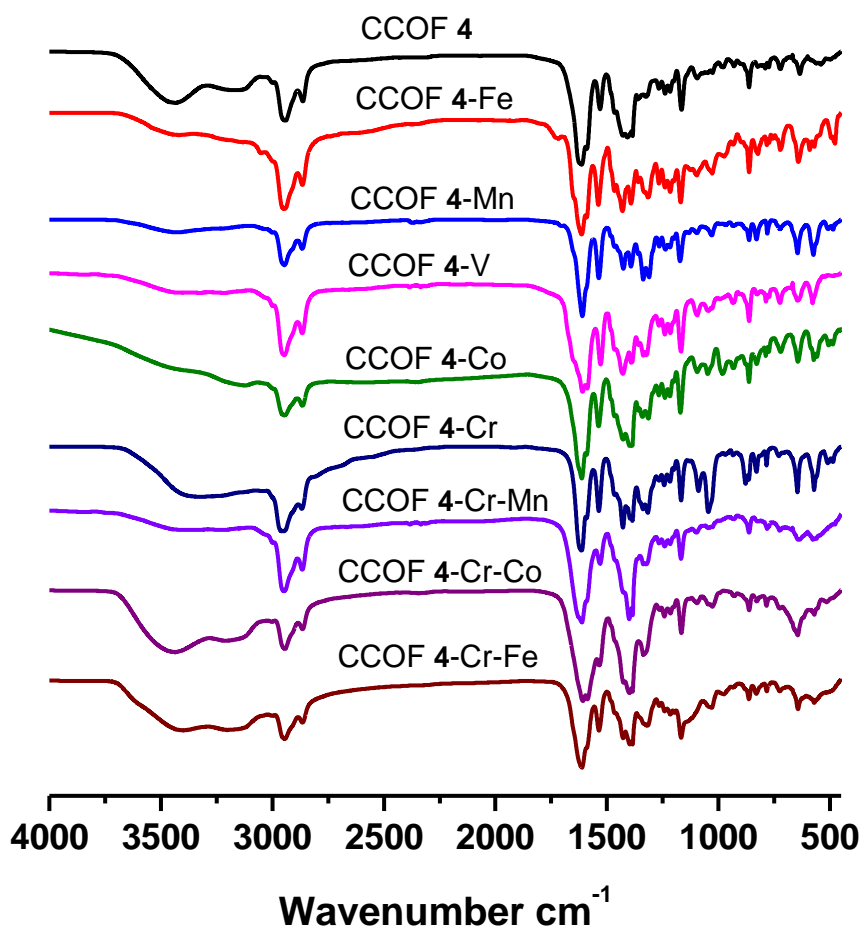
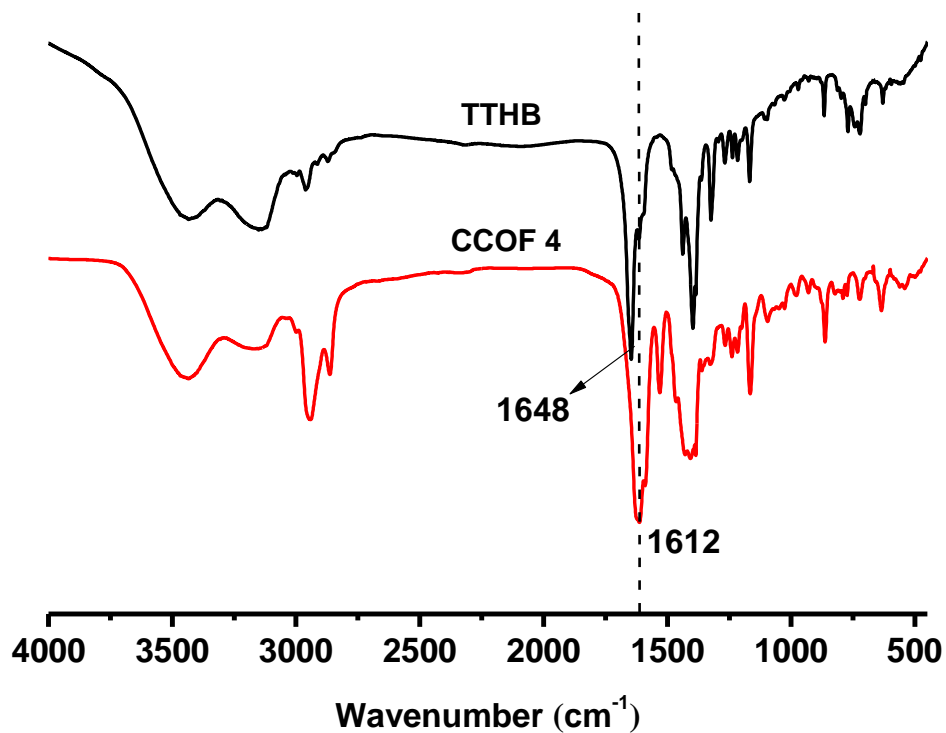
To a suspension of CCOF 4-Cr-Mn (1 mol%) in dry chloroform (1.0 mL), alkene (0.5 mmol) and 2-(tert-butylsulfonyl)iodosylbenzene (0.010 g, 0.03 mmol) were added. The same amount of oxidant was added 18 more times at 15 mins intervals. The reaction was carried out overnight at 0 °C. After that, aniline (0.12 mmol) was added and the reaction mixture was stirred until the disappearance of the epoxide at 0 °C. Then the mixture was centrifuged at 9000 rpm for 5 mins, and the supernatant was concentrated under vacuum. The concentrate was analyzed by ¹H NMR to give the conversion and by HPLC to give the ee value.

3.8 Recycling Experiments: (using Alkene Epoxidation/Epoxide Aminolysis as an example)

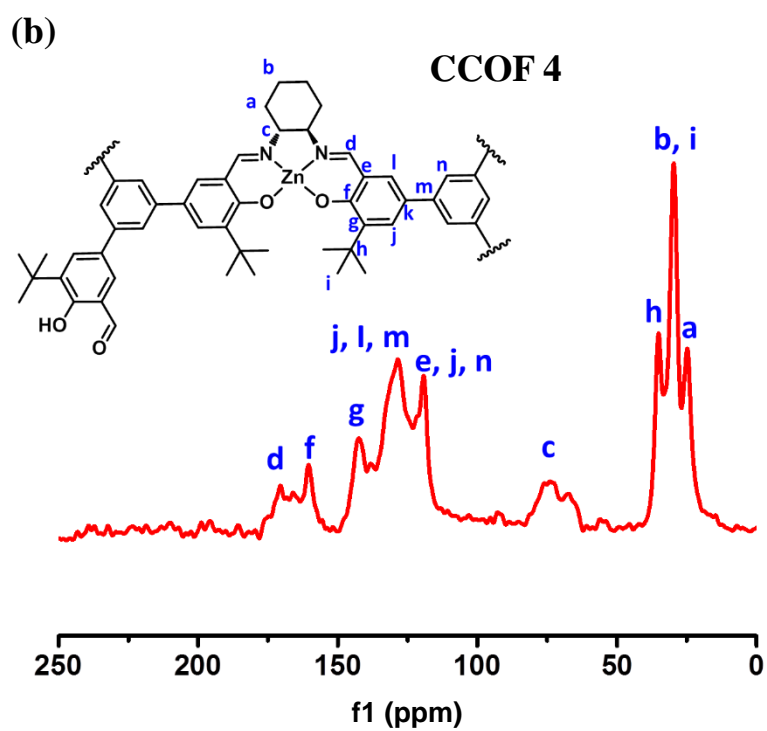
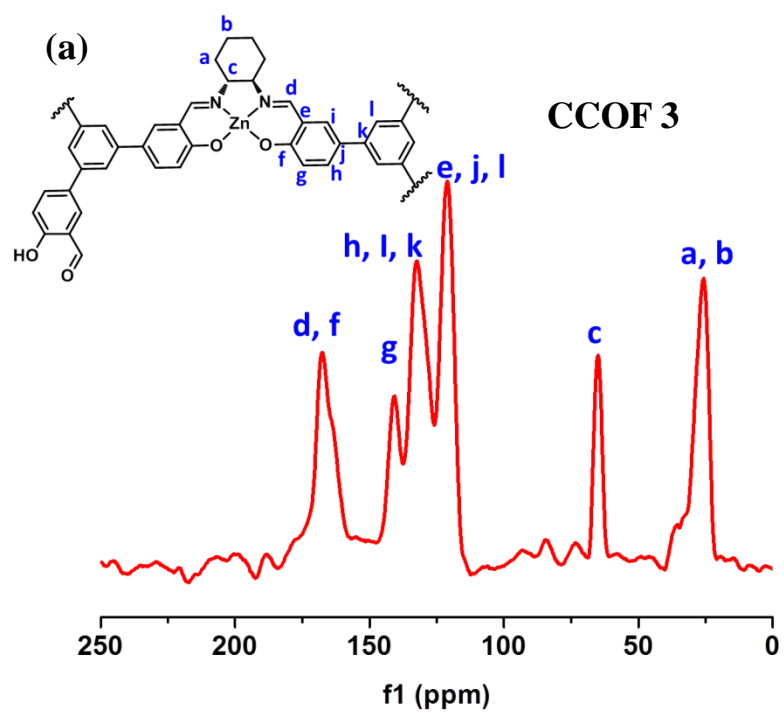
After the centrifugation, the precipitate was washed with CH₂Cl₂ for 3 times and sonicated for 10 mins dry under pressure. Then used for the next run. The recycled experimental of other four catalytic reactions were performed in a similar procedure.

4. Figure S1. FT-IR spectra

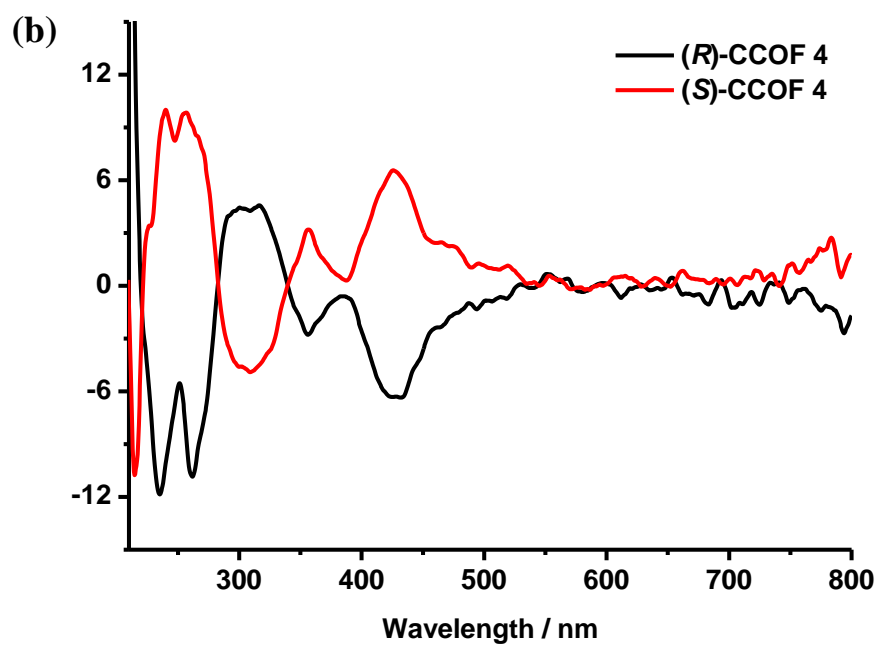
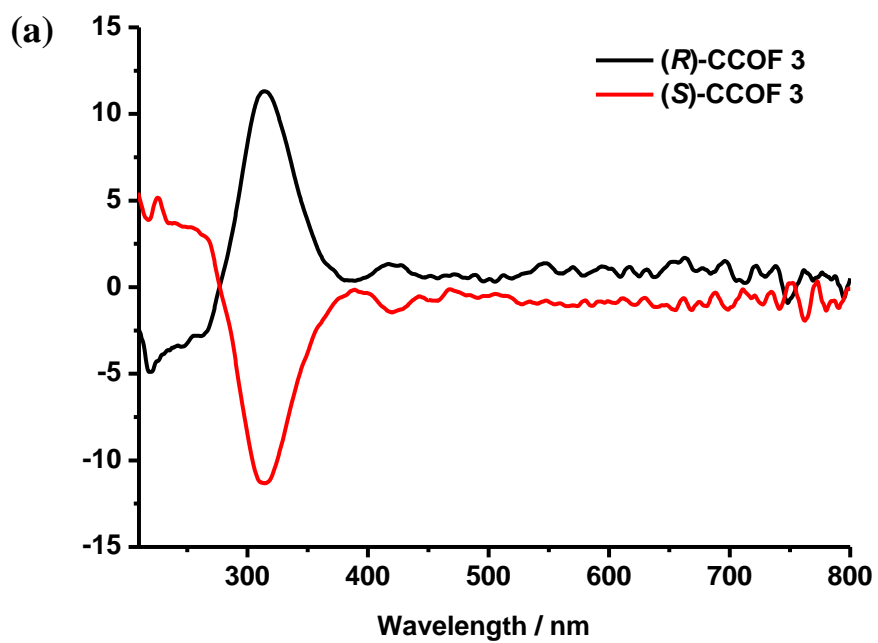




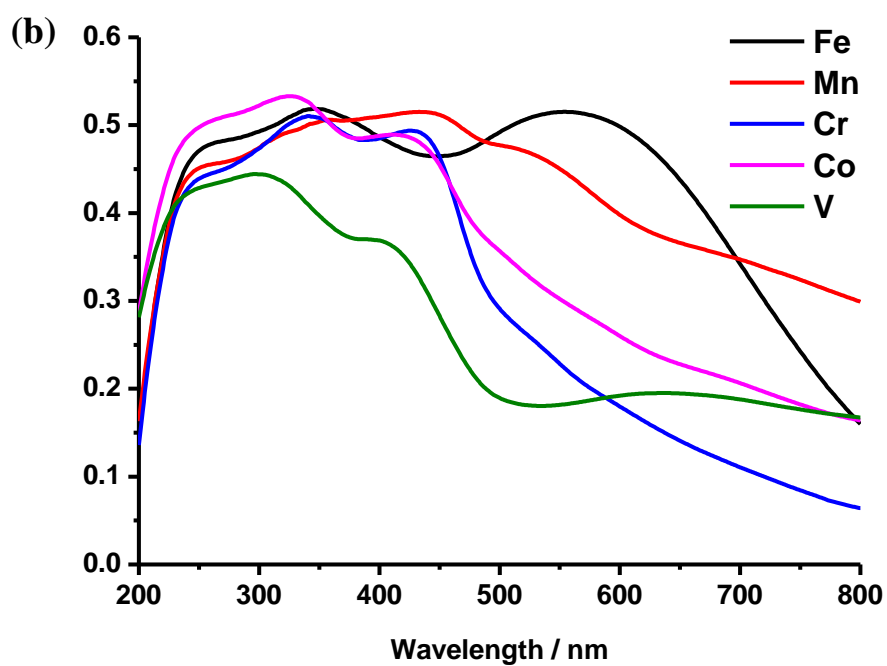
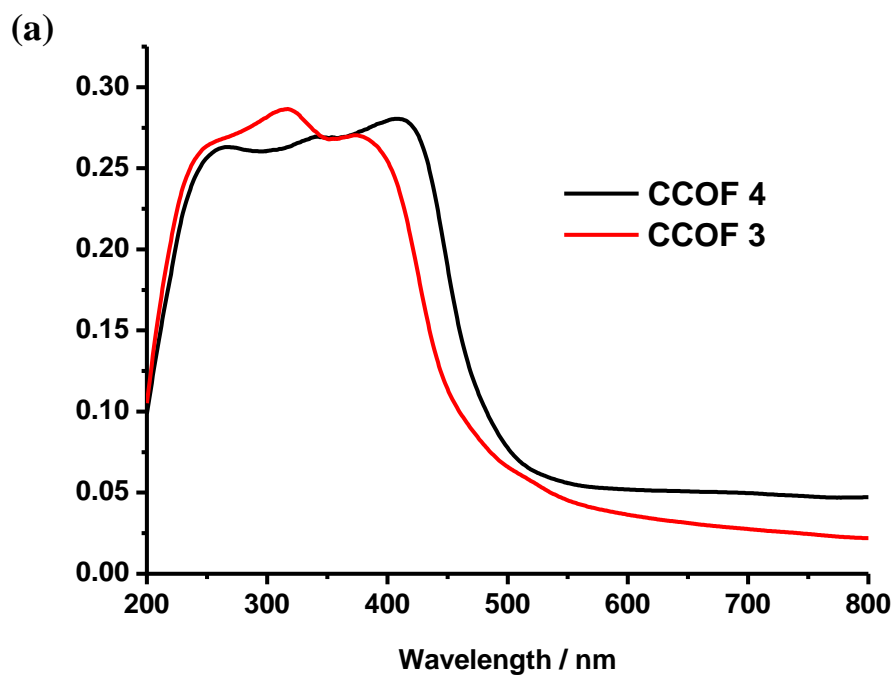
5. Figure S2. Solid-state ^{13}C NMR spectra.

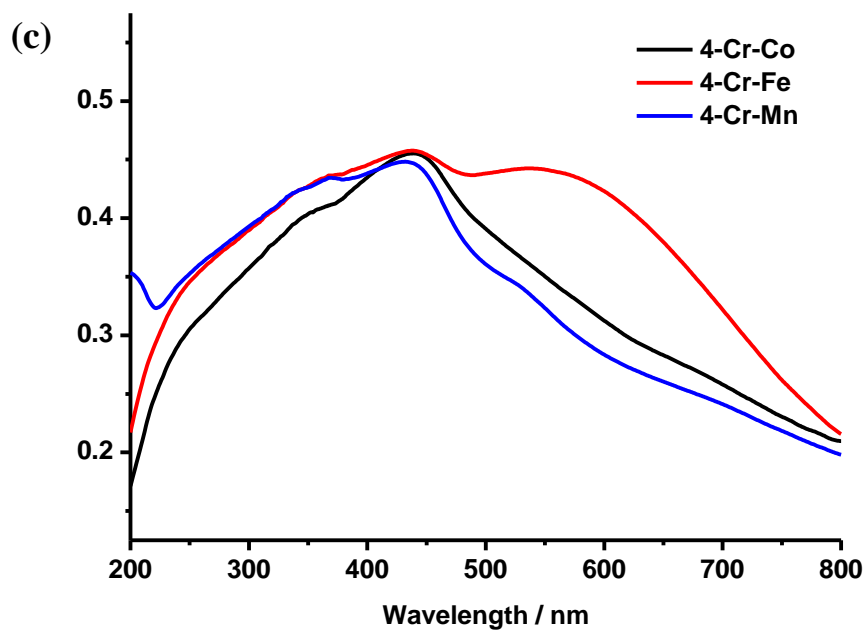


6. Figure S3. The CD spectra.

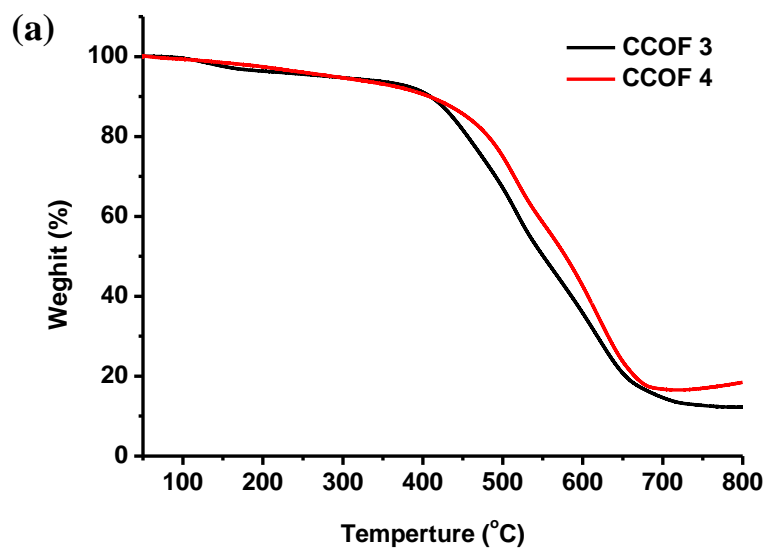


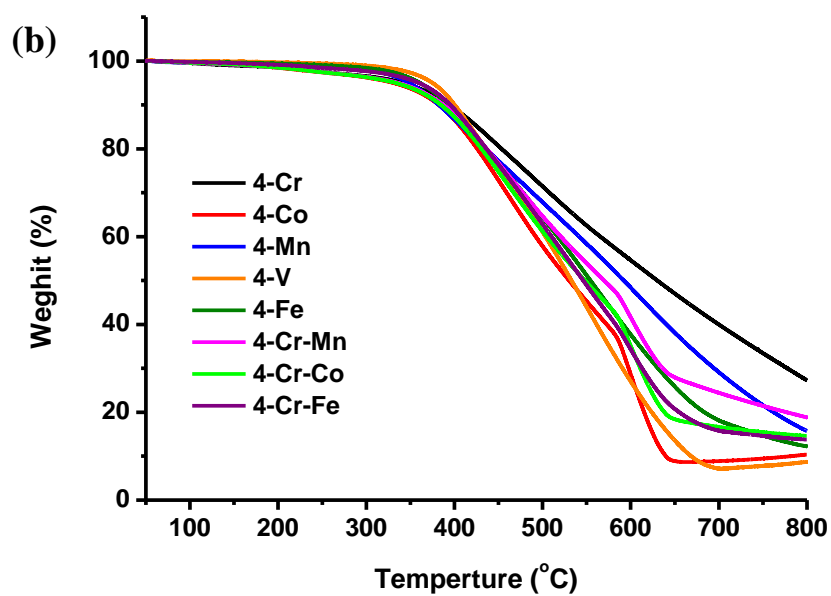
7. Figure S4. The Solid-UV spectra.





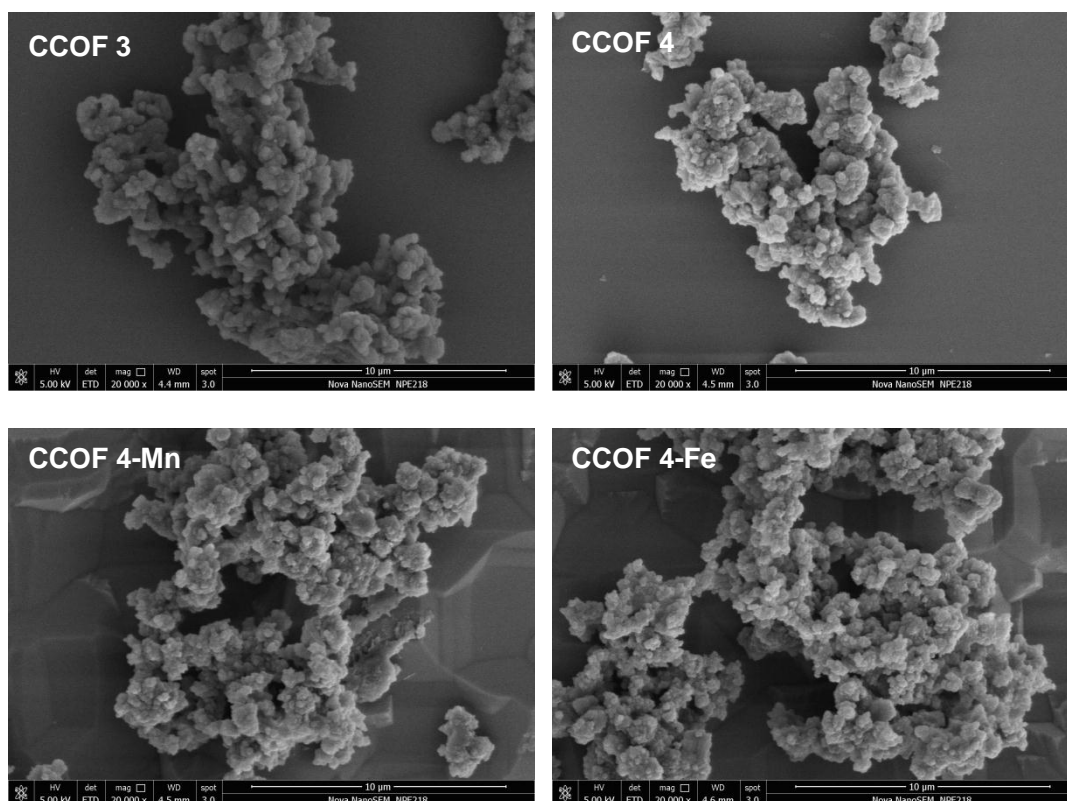
8. Figure S5. TGA curves





9. Figures S6& S7. SEM and EDS mapping images

Figure S6. SEM images



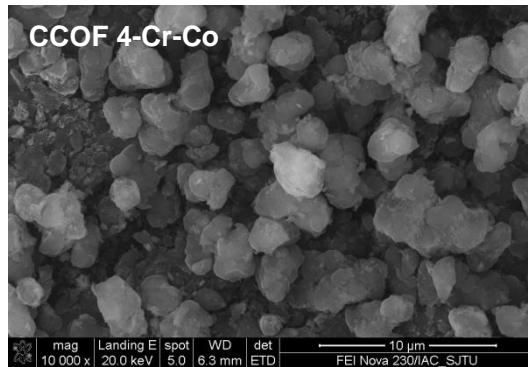
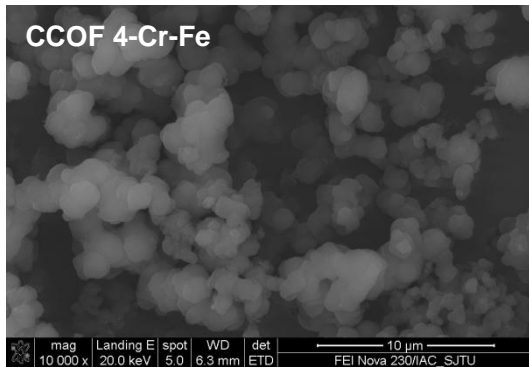
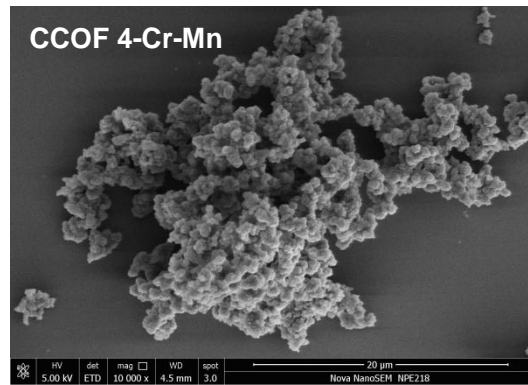
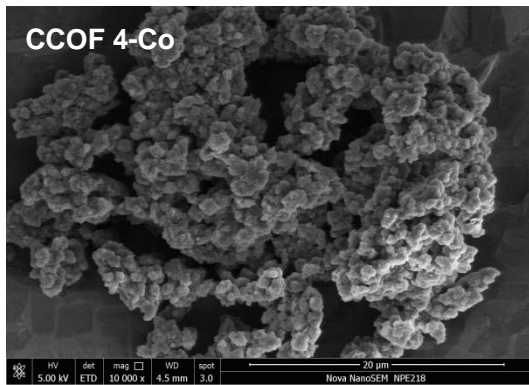
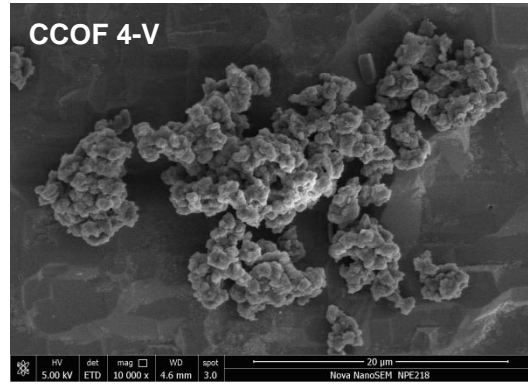
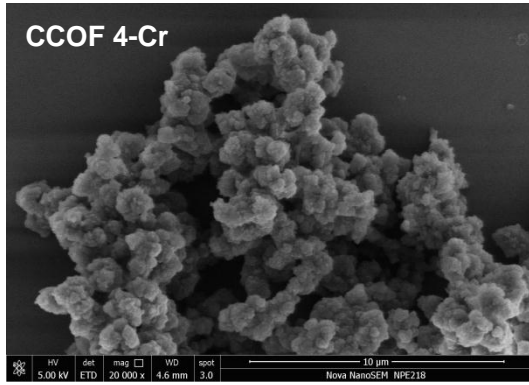
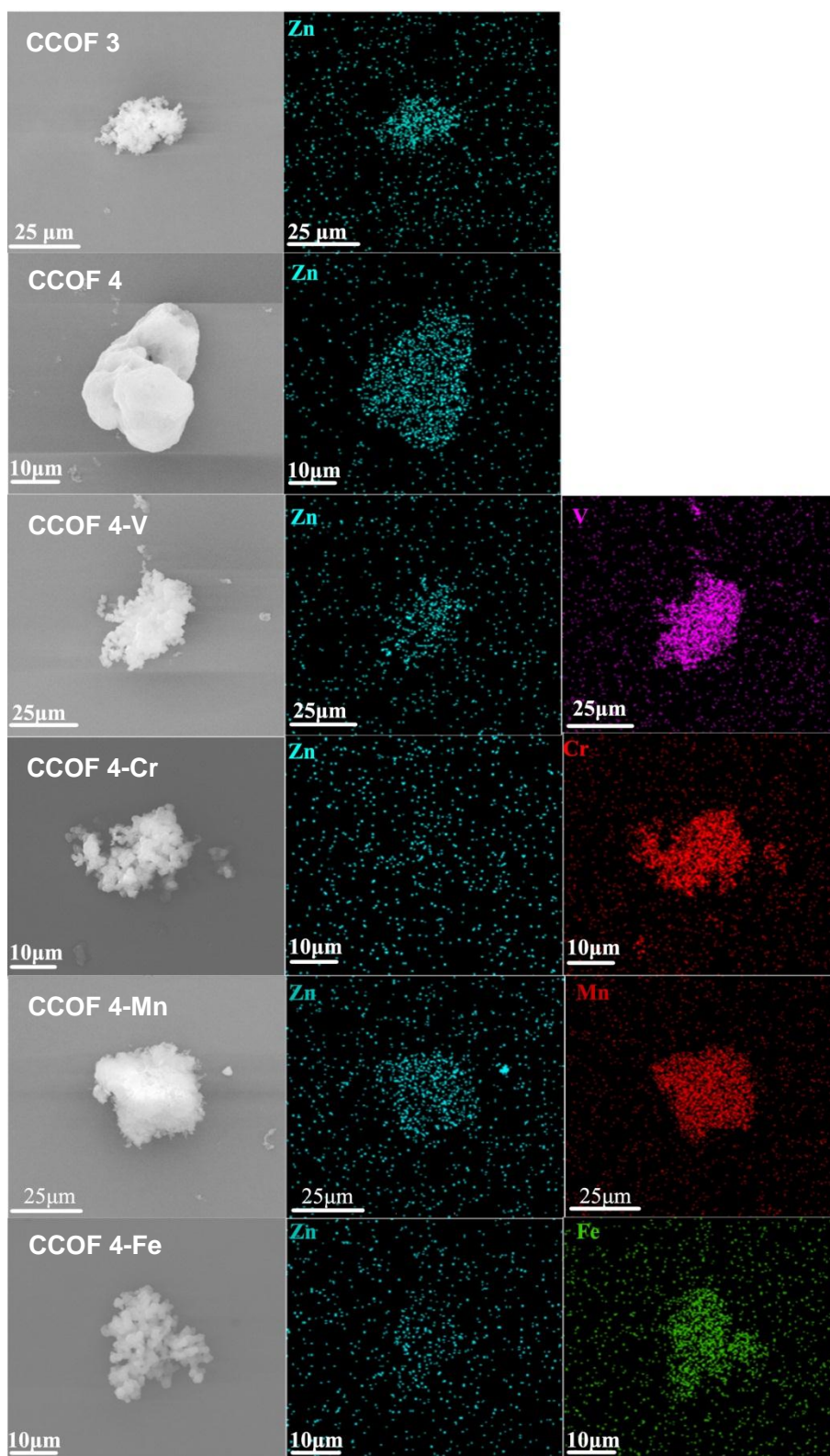
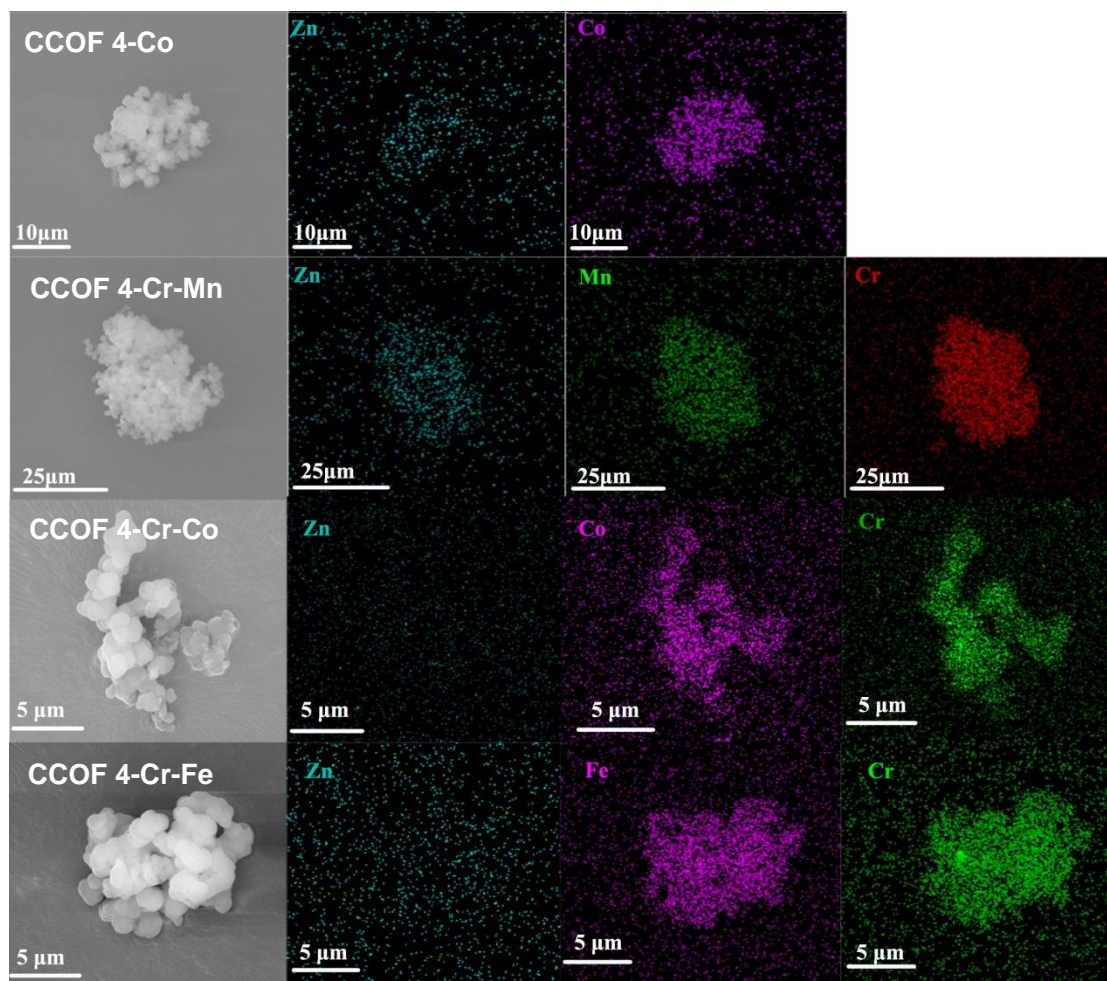
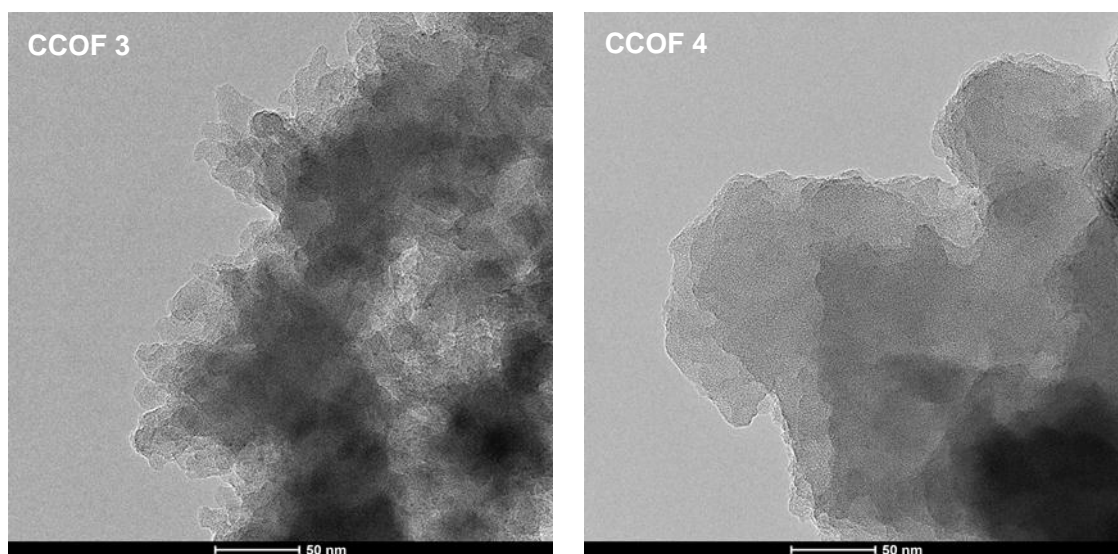


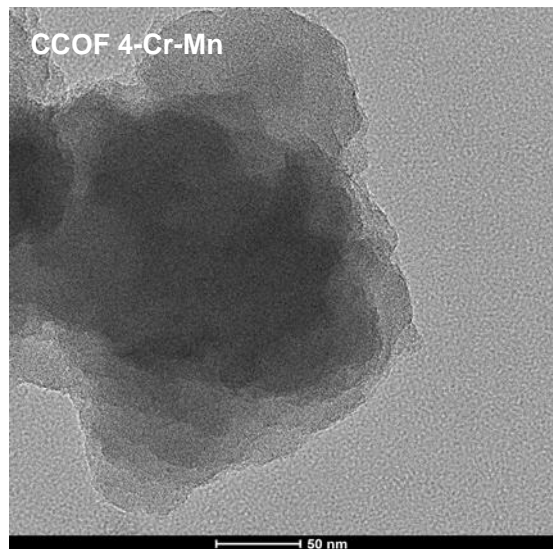
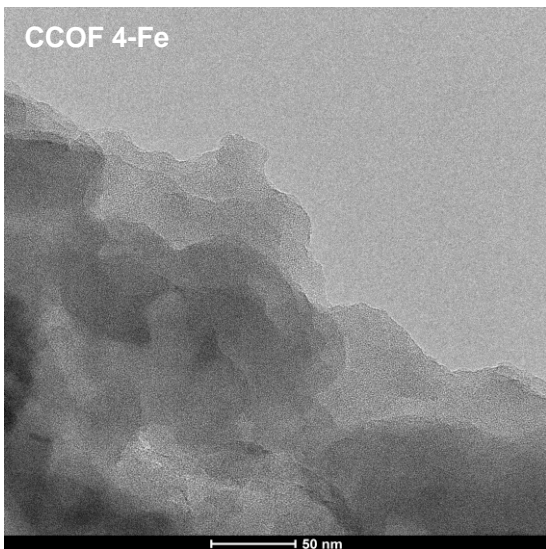
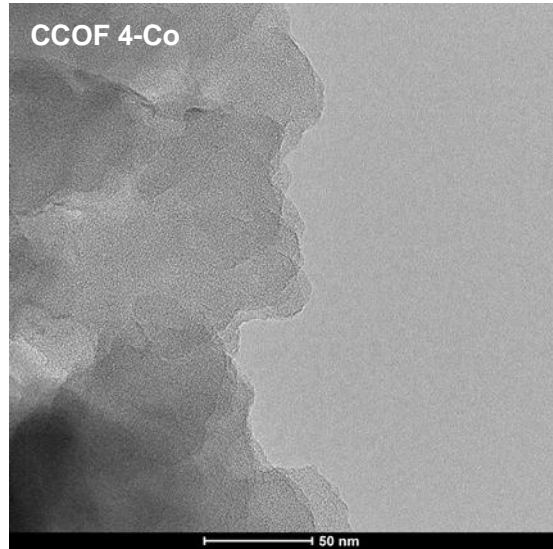
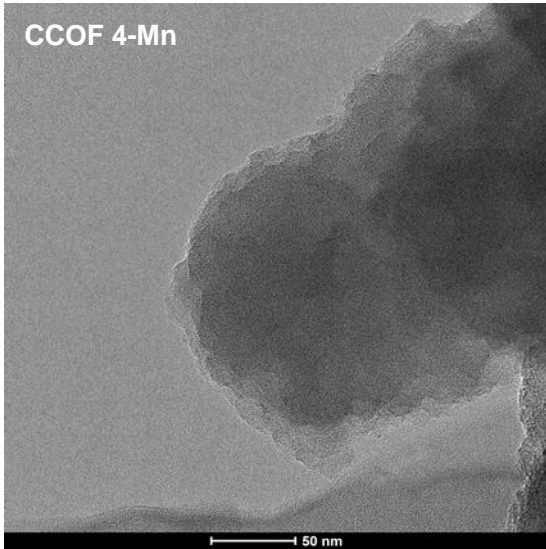
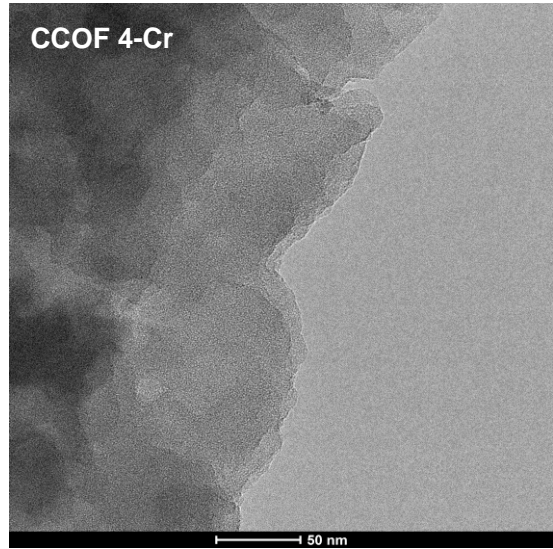
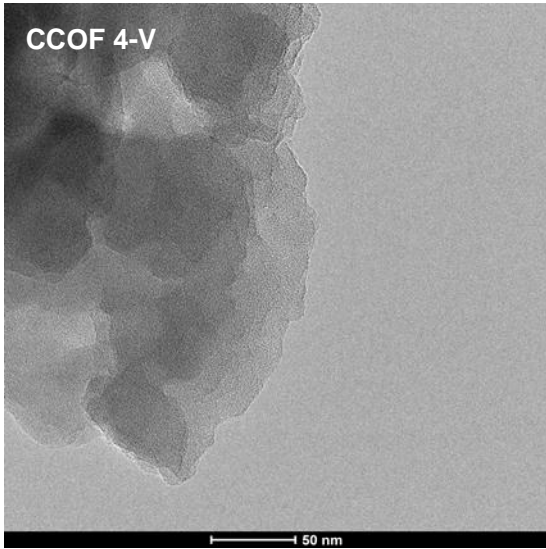
Figure S7. EDS mapping images.

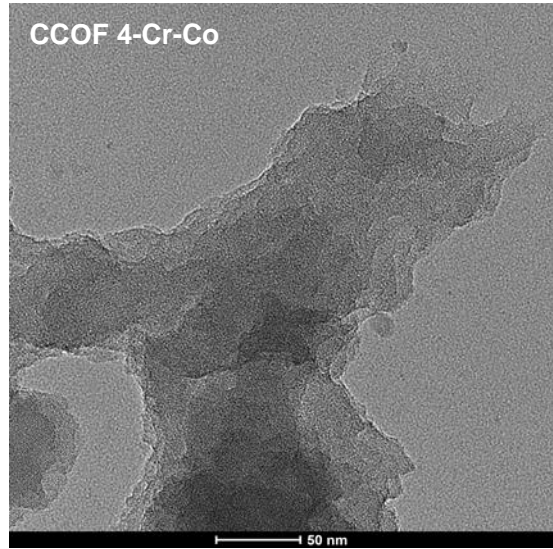
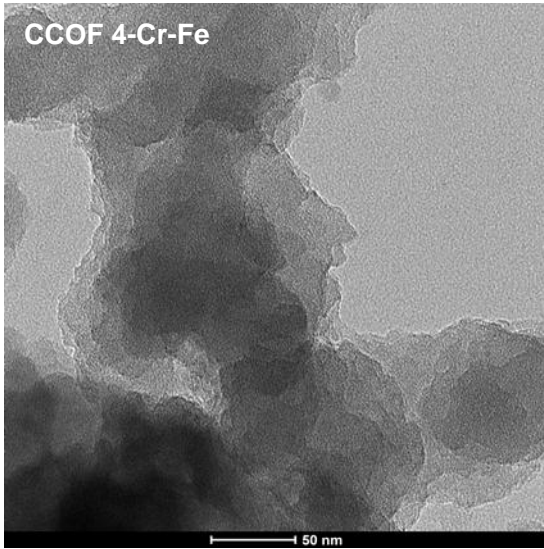




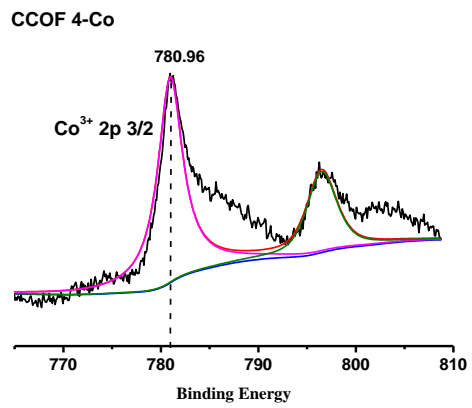
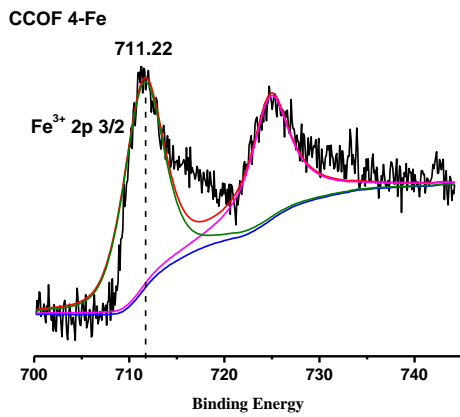
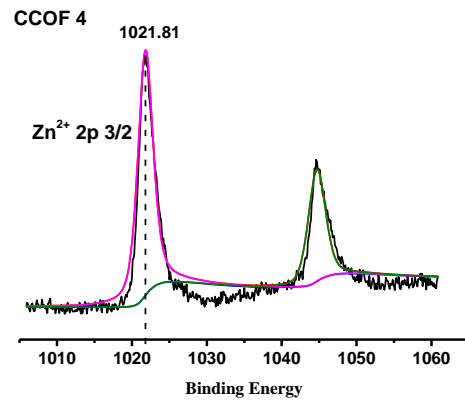
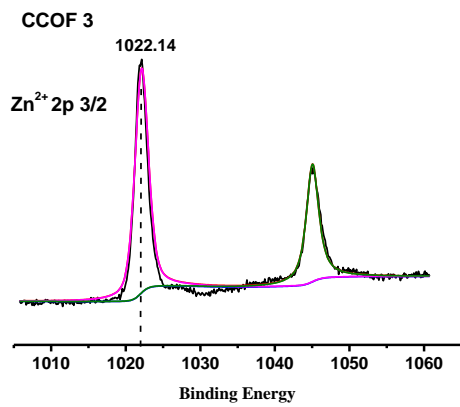
10. Figure S8. TEM images.

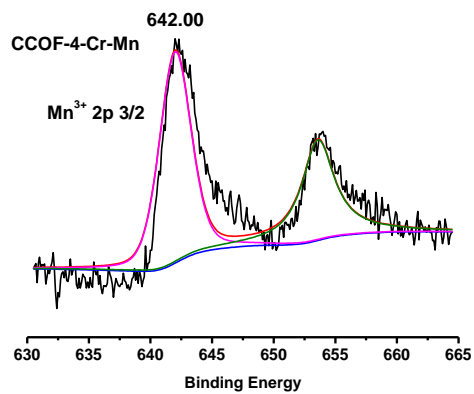
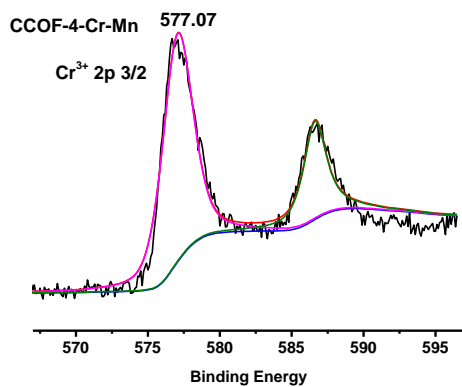
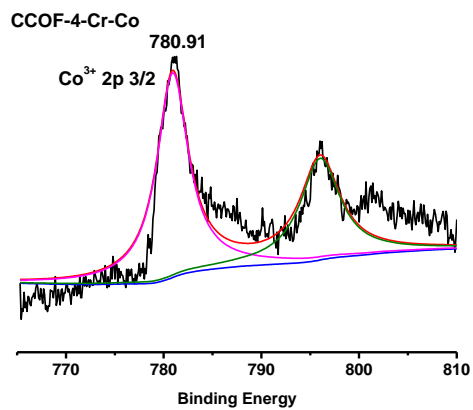
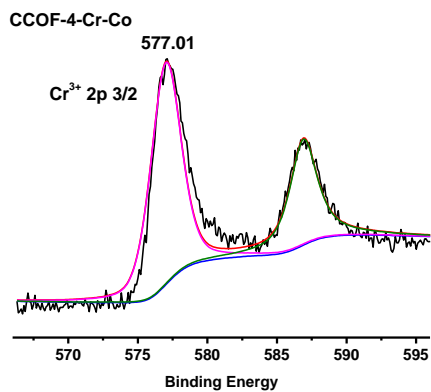
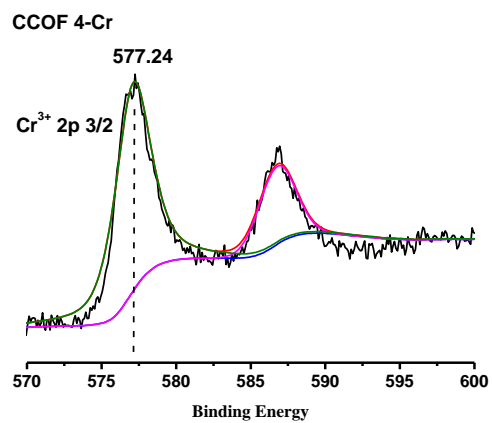
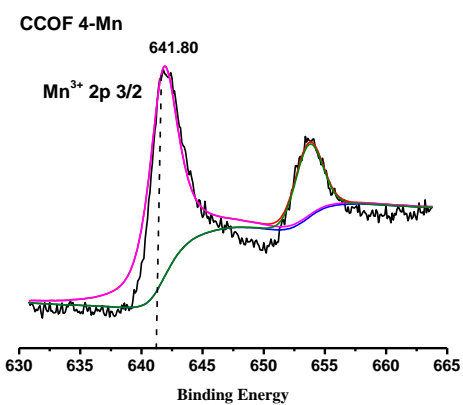
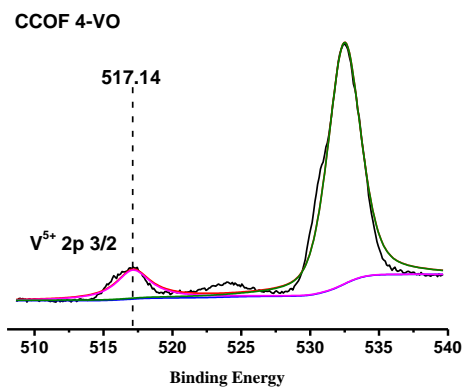
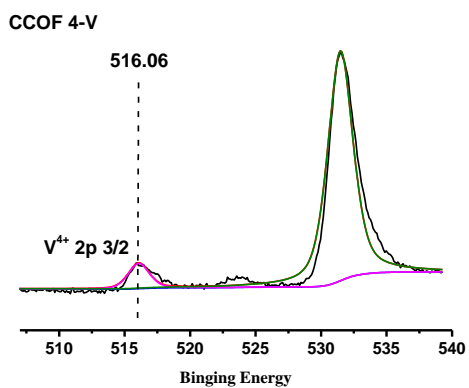


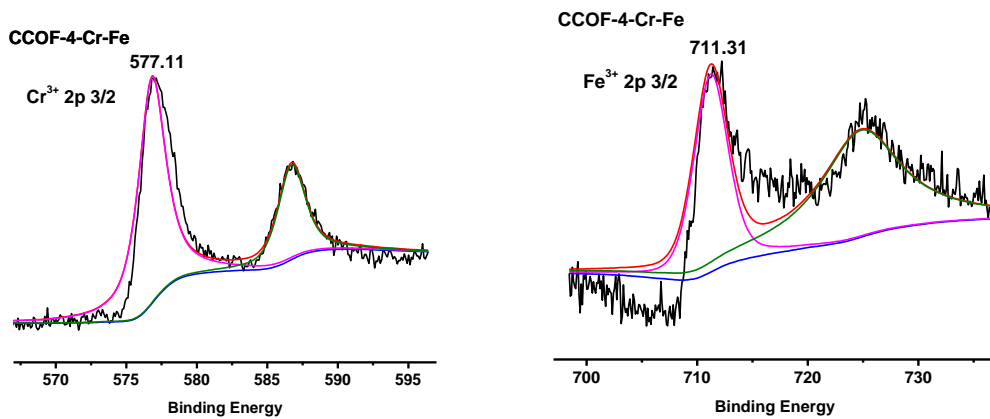




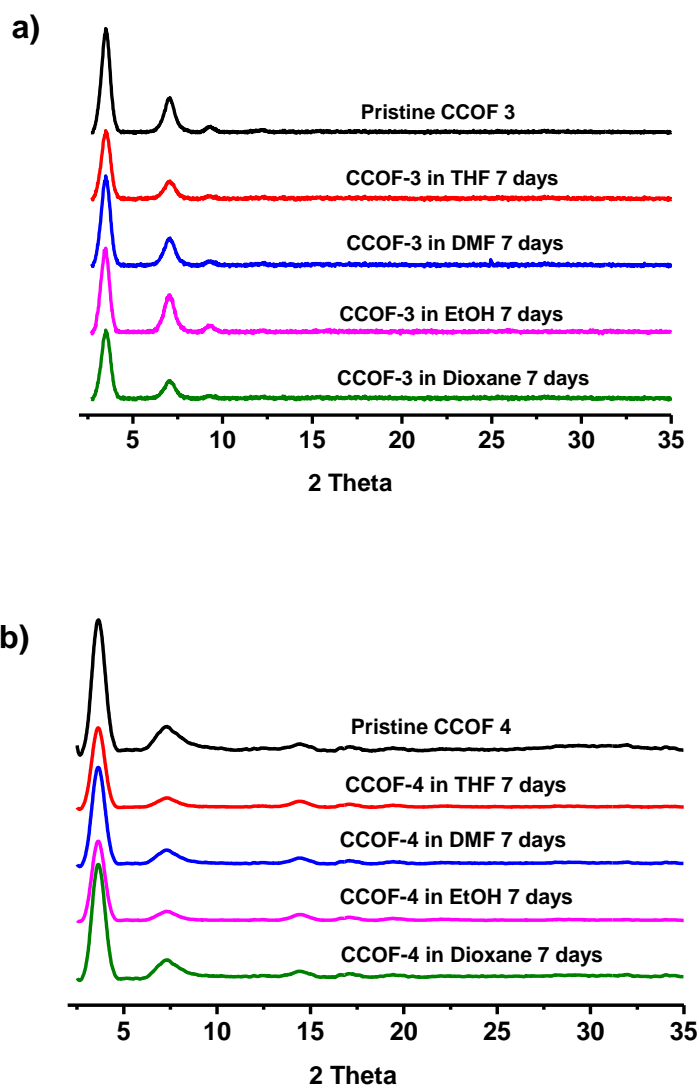
11. Figure S9. X-ray photoelectron spectroscopy analysis.

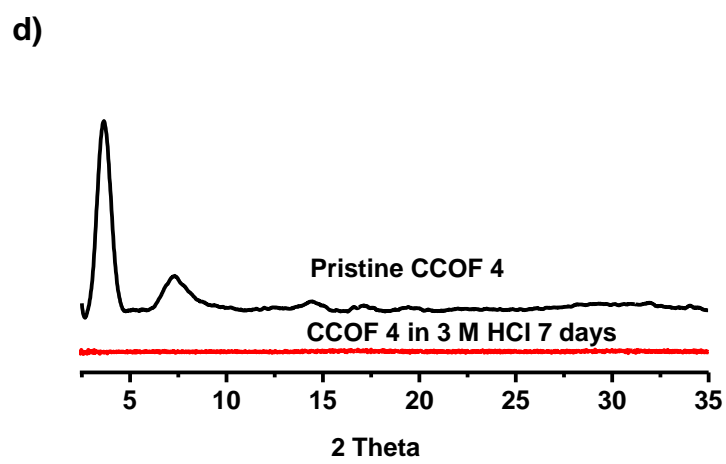
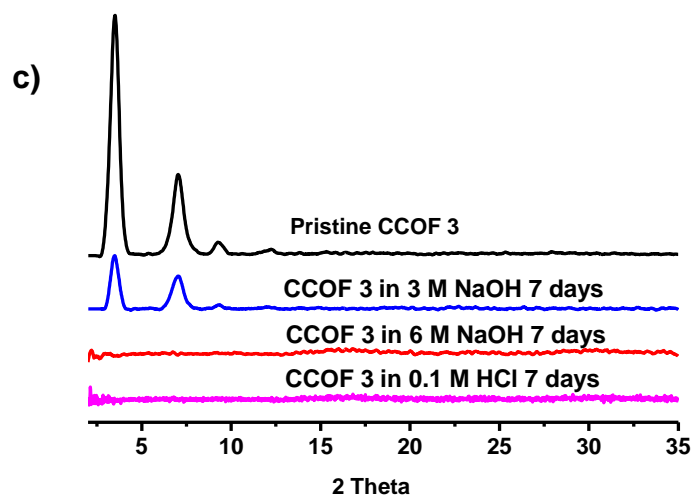






12. Figure S10. PXRD patterns.





13. Figure S11. N₂ adsorption.

Figure S11a. N₂ adsorption-desorption isotherms (77 K) of CCOFs-M.

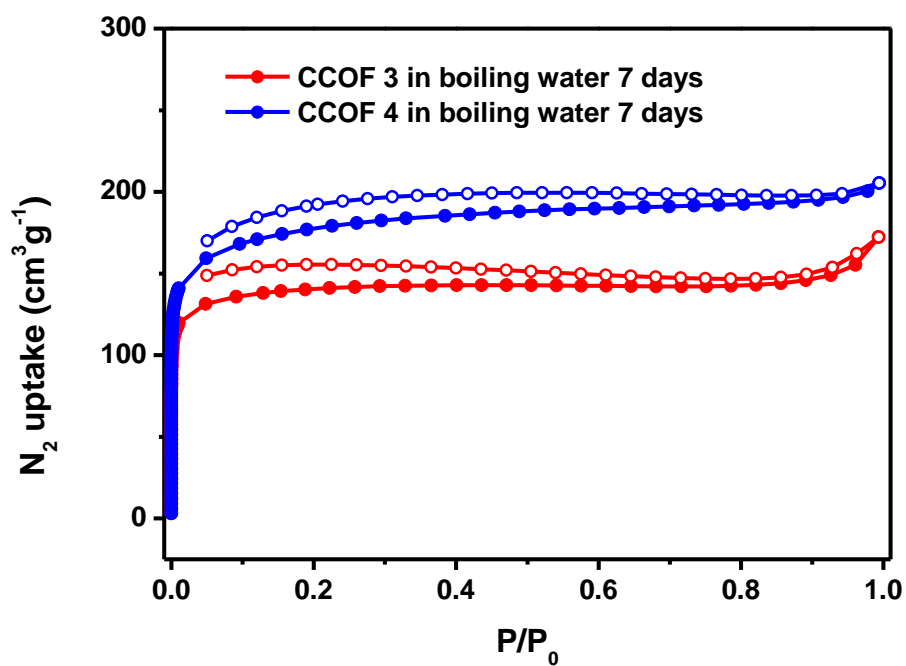
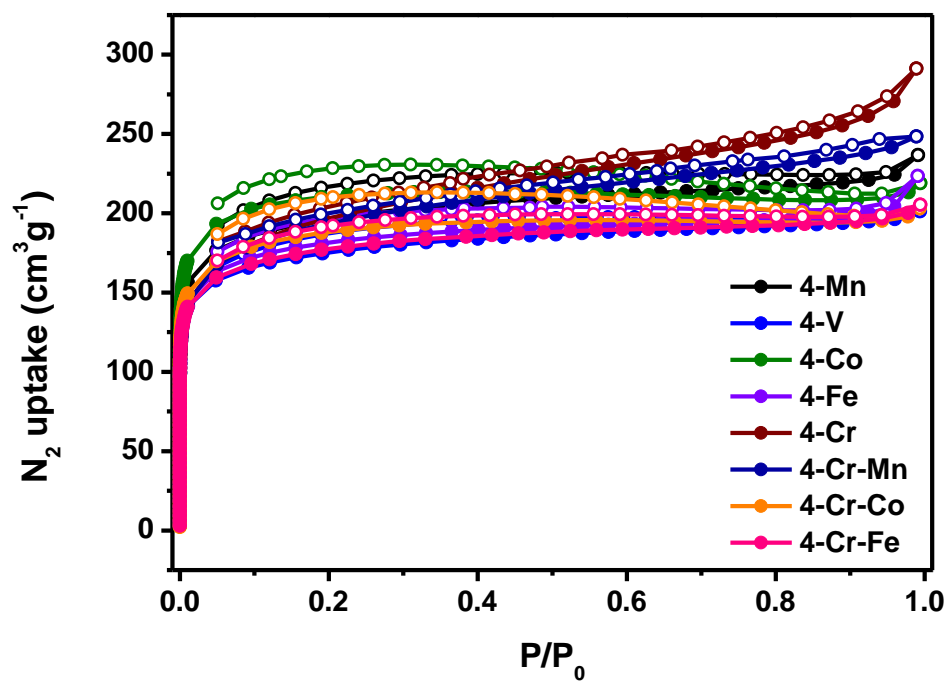
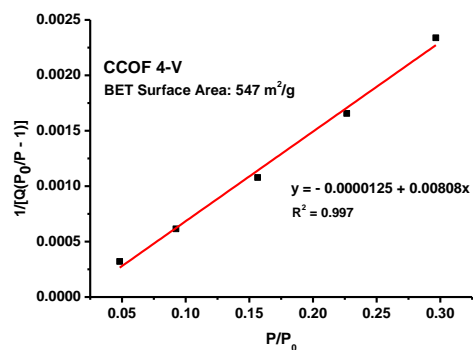
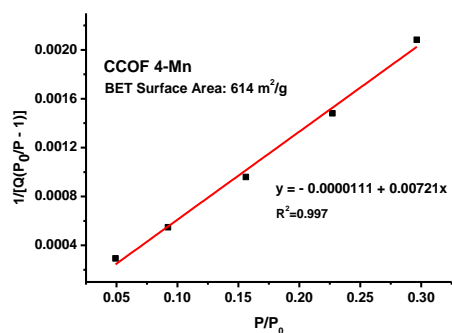
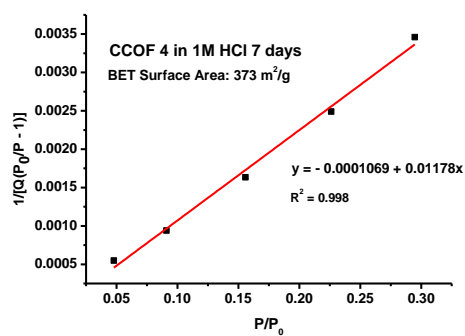
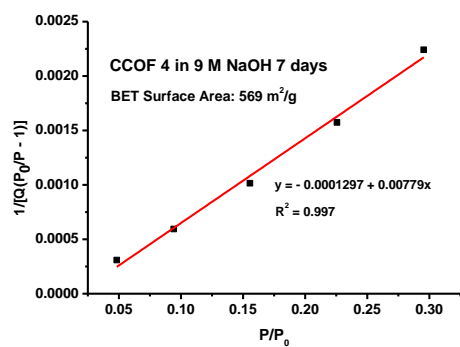
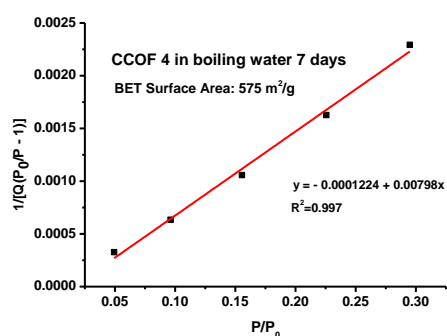
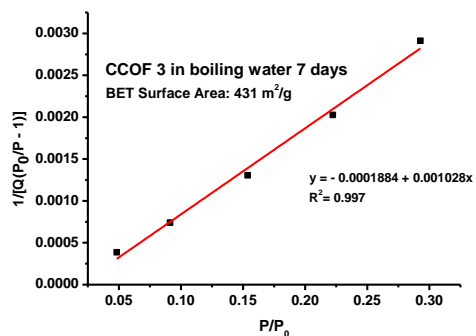
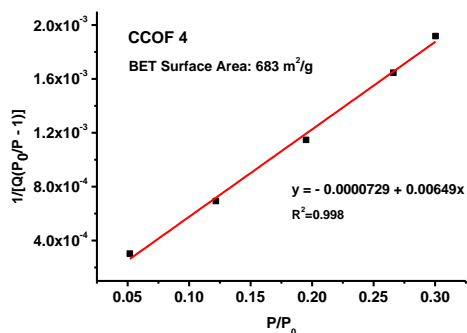
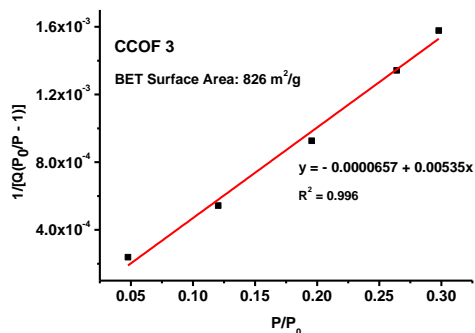


Figure S11b. BET plots of CCOFs.



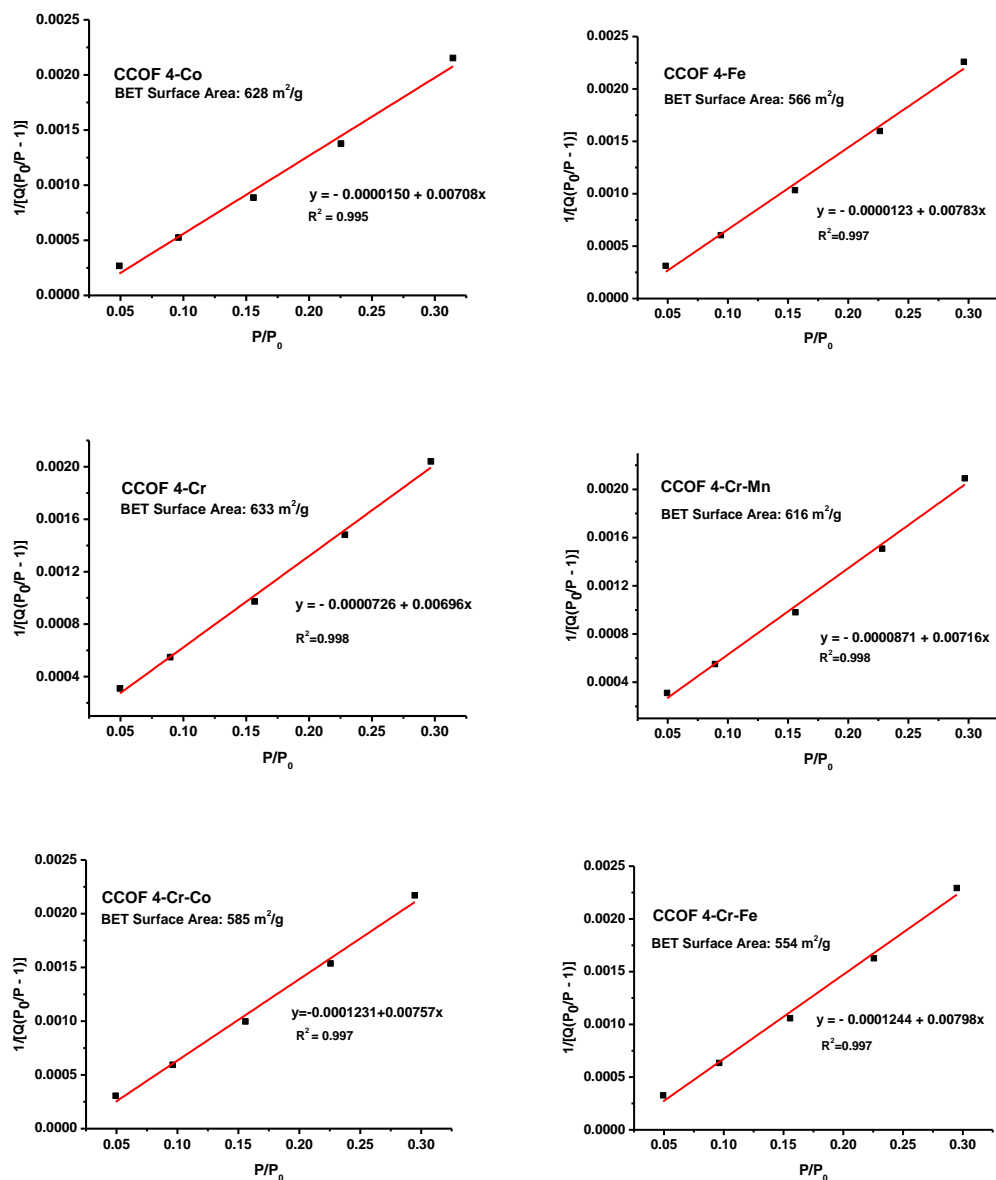
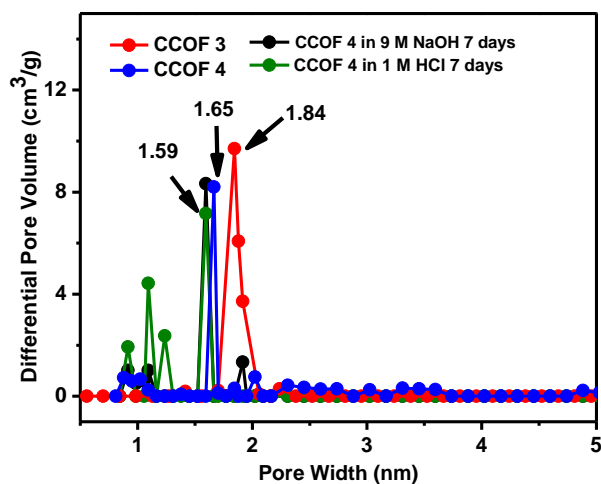
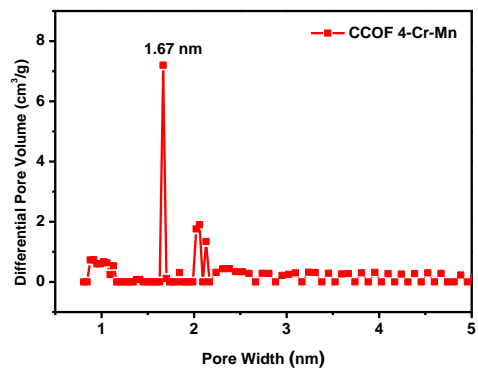
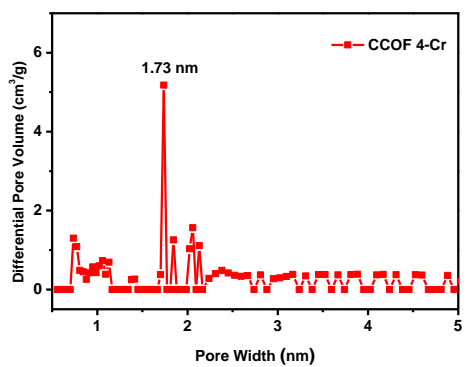
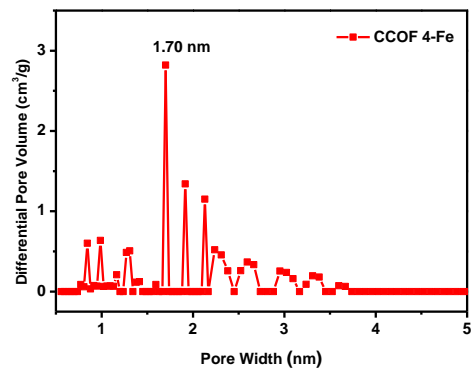
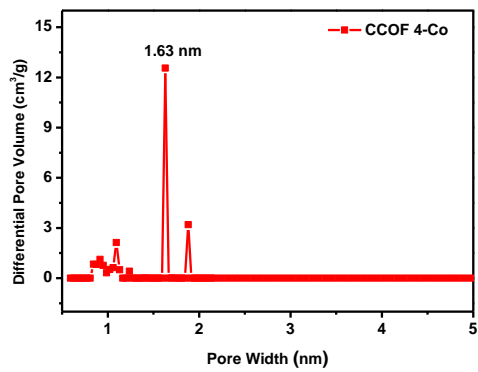
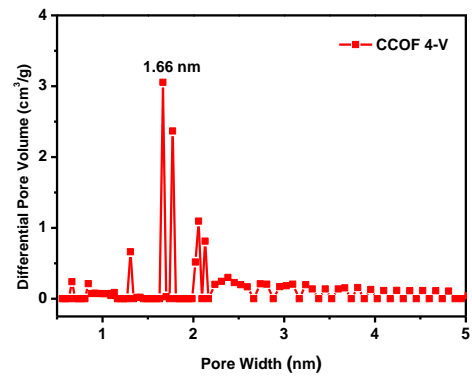
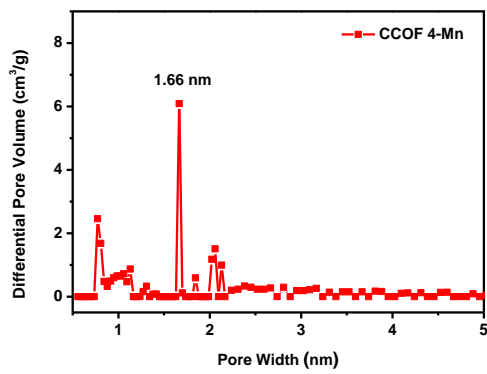
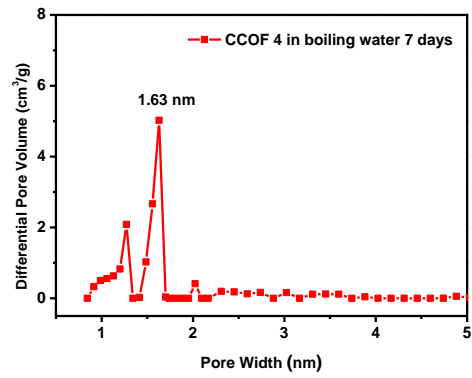
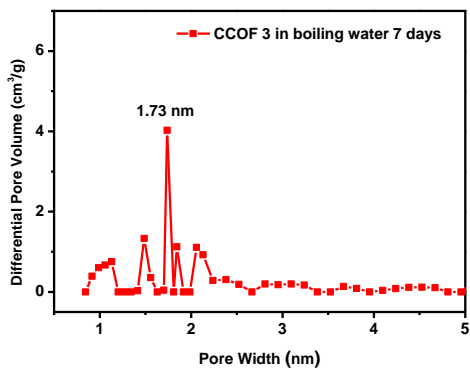
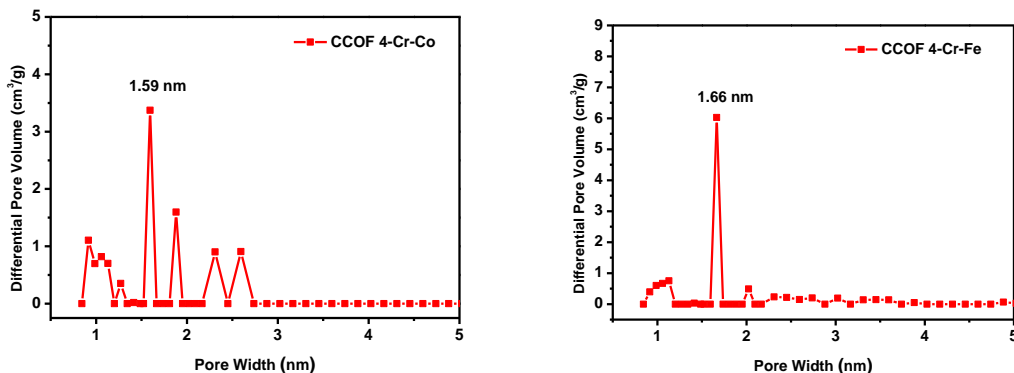


Figure S11c. Pore-size distribution.







14. Structural modeling and PXRD analysis of the CCOFs.

Structure Simulation: Molecular modeling of these COFs was generated with the Materials Studio (ver. 7.0) suite of programs. In Forcite tools geometry optimization program, we change the Zn to a heavy atom like La, so that the PXRD pattern can be dominated by the contribution of heavy metals and mathematically simpler to derive the topology. Pawley refinement was carried out using Reflex, a software package for crystal determination from PXRD pattern. Unit cell dimension was set to the theoretical parameters. The Pawley refinement was performed to optimize the lattice parameters iteratively until the R_{wp} value converges and the overlay of the observed with refined profiles shows good agreement. The lattice models (e.g., cell parameters, atomic positions, and total energies) were then fully optimized using MS Forcite molecular dynamics module (universal force fields, Ewald summations) method.

For CCOF-3 and CCOF 4, considering the geometry of the precursors and the connection patterns, only a few topologies are reasonable.

Figure S12a Space-filling models of CCOF-3 with different stacking and the calculated PXRD profiles. C, gray; N, blue; O, red; H, white.

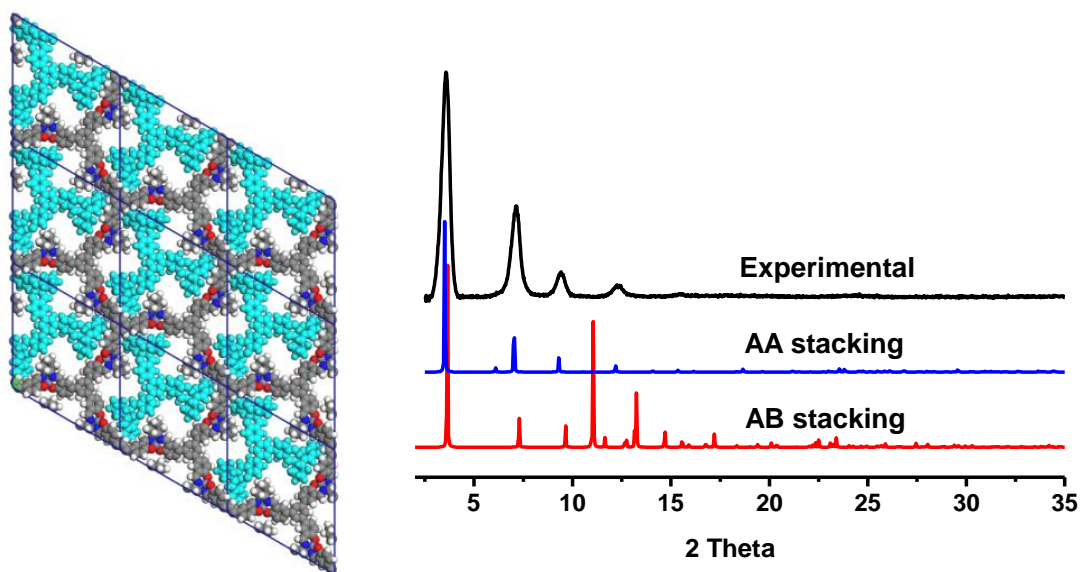
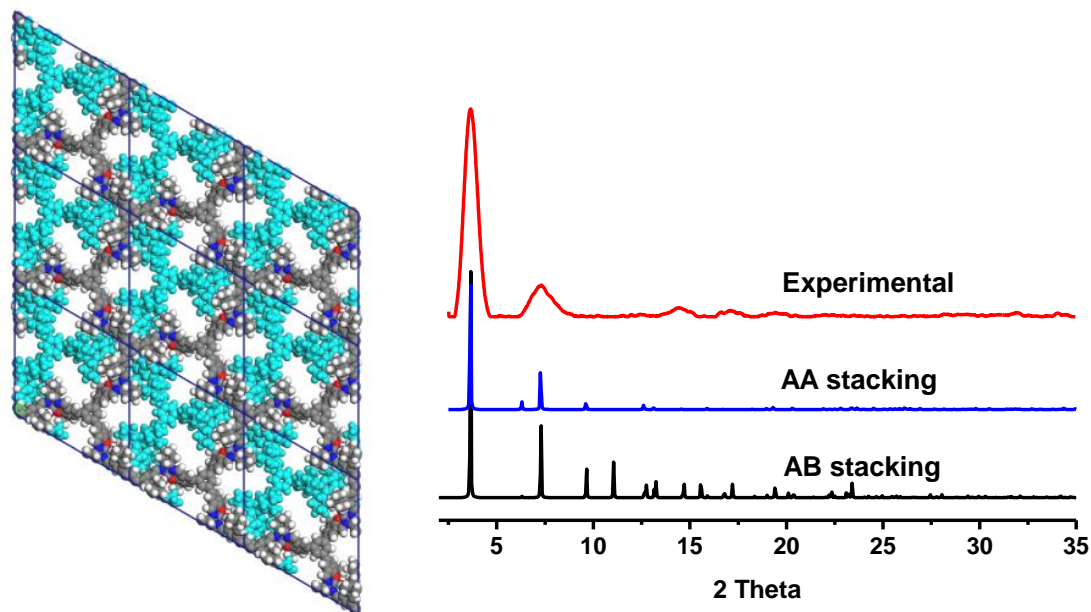


Figure S12b Space-filling models of CCOF 4 with different stacking and the calculated PXRD profiles. Carbon, gray; Nitrogen, blue; Oxygen, red; Hydrogen, white.



For CCOFs **3** and **4** AB stacking, the calculated PXRD patterns (Figure S11) have shown several peaks above 10 degrees that disagree with the experimental data. For AA stacking (*P321* space group, also see Figure S11), the calculated patterns were in agreement with experimental data.

15. Fractional atomic coordinates and unit cell parameters.

Table S3. Fractional atomic coordinates for the unit cell of CCOF 3 with *P321* space group.

CCOF 3: Space group: <i>P321</i>			
$a = 29.05 \text{ \AA}, b = 29.05 \text{ \AA}, c = 3.91 \text{ \AA}$			
$\alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ$			
Atom	x	y	z
C1	-0.4729	-0.58207	0.89988
C2	-0.41992	-0.55076	0.76572
C3	-0.38696	-0.57298	0.76802
C4	-0.40437	-0.62457	0.88434
C5	-0.45614	-0.65485	1.0078
C6	-0.48958	-0.63349	1.01802
O7	-0.50972	-0.56504	0.94385

C8	-0.36806	-0.64615	0.88193
C9	-0.38813	-0.7011	0.88206
C10	-0.39124	-0.49481	0.64186
N11	-0.46874	-0.41237	0.48903
C12	-0.41192	-0.38345	0.57653
C13	1.06021	0.3843	2.47784
C14	1.02528	0.32522	2.39305
H15	-0.34426	-0.54884	0.67274
H16	-0.47111	-0.69721	1.10058
H17	-0.53157	-0.65801	1.12434
H18	-0.4329	-0.72952	0.88228
H19	-0.34603	-0.47056	0.65769
H20	-0.40913	-0.38524	0.86657
H21	1.08603	0.40547	2.24622
H22	1.08718	0.38906	2.70298
H23	1.04852	0.30392	2.44605
H24	1.0138	0.32055	2.11113
Zn25	-0.50797	-0.50797	0.5

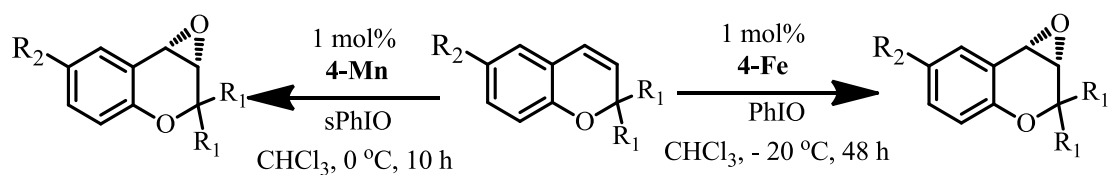
Table S4. Fractional atomic coordinates for the unit cell of CCOF 4 with *P321* space group.

CCOF 4: Space group: <i>P321</i>			
$a = 28.09 \text{ \AA}, b = 28.09 \text{ \AA}, c = 3.95 \text{ \AA}$			
$\alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ$			
Atom	x	y	z
C1	-0.44938	0.4448	0.91115
C2	-0.39599	0.47341	0.75483
C3	-0.36937	0.44441	0.69002
C4	-0.39347	0.38901	0.76458
C5	-0.44445	0.36175	0.9214
C6	-0.47384	0.38814	0.99852
O7	-0.47966	0.46995	0.97607
C8	-0.52955	0.35471	1.18404
C9	-0.54199	0.39141	1.40108
C10	-0.52958	0.30897	1.38974
C11	-0.57999	0.32439	0.96563
C12	-0.36309	0.36067	0.70927
C13	-0.39035	0.30362	0.71028
C14	-0.36147	0.53252	0.66129

N15	-0.43814	0.61938	0.46718
C16	-0.37981	0.65043	0.56084
C17	1.05973	1.35015	0.4291
C18	1.03008	1.29083	0.55653
H19	-0.32656	0.46605	0.57253
H20	-0.46337	0.31646	0.99074
H21	-0.56802	0.36706	1.62709
H22	-0.56548	0.4071	1.24525
H23	-0.50185	0.42777	1.49475
H24	-0.50742	0.32632	1.64003
H25	-0.50757	0.29079	1.24192
H26	-0.57378	0.2755	1.44157
H27	-0.59281	0.27897	0.9559
H28	-0.57044	0.34221	0.6988
H29	-0.61488	0.32907	1.07694
H30	-0.4372	0.27916	0.71196
H31	-0.31509	0.55457	0.70216
H32	-0.37746	0.65234	0.84894
H33	1.05958	1.35034	0.14059
H34	1.10397	1.3721	0.5244
H35	1.03194	1.29081	0.84474
H36	1.05113	1.26829	0.45062
Zn37	-0.47858	0.52142	0.5

16. The catalysis result.^{S1,S2}

16.1 Table S5. Alkene epoxidation catalyzed by CCOF 4-Mn and CCOF 4-Fe.

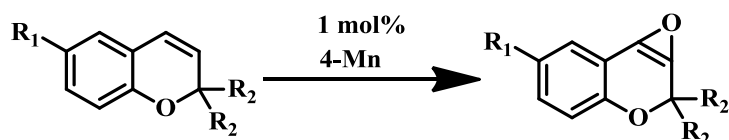


entry	R ₁	R ₂	CCOF 4-Mn		CCOF 4-Fe	
			Conv. (%) ^a	ee (%) ^b	Conv. (%) ^a	ee (%) ^b
1	Me	H	85	77	76	90
2	Me	Me	83	86	74	84
3	Me	NO ₂	79	97	71	92
4	-(CH ₂) ₅ -	H	83	87	84	94

^a Determined using ¹H NMR. ^b Determined by HPLC.

(S1). Xia, Q., Li, Z., Tan, C., Liu, Y., Gong, W., Cui, Y. *J. Am. Chem. Soc.* **2017**. DOI: 10.1021/jacs.7b03113. (S2) Xia, Q.; Liu, Y.; Li, Z.; Gong, W.; Cui, Y. *Chem. Commun.* **2016**, 52, 13167.

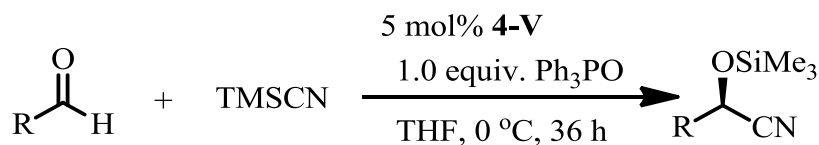
Table S6. Alkene epoxidation catalyzed by CCOF 4-Mn and NaClO as oxidant.



Entry	Temp.	Solvent	Oxidant	R1	R2	conversion ^a	ee
1	0 °C	CH ₂ Cl ₂	NaOCl	H	Me	trace	-
2	0 °C	CH ₂ Cl ₂	NaOCl	H	Me	trace	-
3	0 °C	CHCl ₃	NaOCl	H	Me	trace	-
4	0 °C	CHCl ₃	NaOCl	H	Me	trace	-
5	R.T.	CH ₂ Cl ₂	NaOCl	H	Me	trace	-
6	R.T.	CH ₂ Cl ₂	NaOCl	H	Me	trace	-
7	0 °C	CH ₂ Cl ₂	NaOCl	NO ₂	Me	trace	-
8	0 °C	CH ₂ Cl ₂	NaOCl	Me	Me	trace	-
9	0 °C	CH ₂ Cl ₂	NaOCl	H	-(CH ₂) ₅ -	trace	-

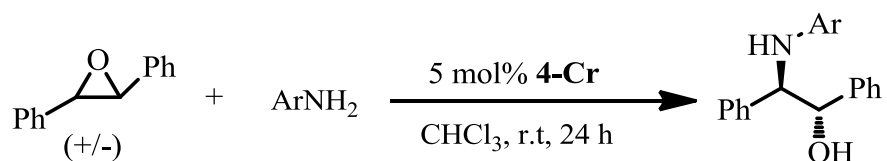
^a Determined using ¹H NMR.

Table S7. Asymmetric cyanosilylation catalyzed by CCOF 4-V.



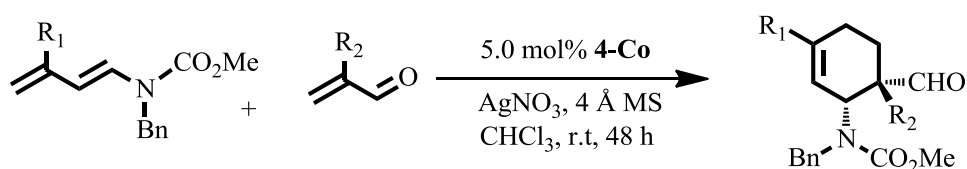
entry	substrate	Conv. (%) ^a	ee (%) ^b
1	4-BrC ₆ H ₄ CHO	77	89
2	4-MeC ₆ H ₄ CHO	79	89
3	4-MeOC ₆ H ₄ CHO	77	94
4	2-ThiopheneCHO	75	83

^a Determined using ¹H NMR. ^b Determined by HPLC.

Table S8. Aminolysis reaction of trans-stilbene oxide catalyzed by CCOF 4-Cr.

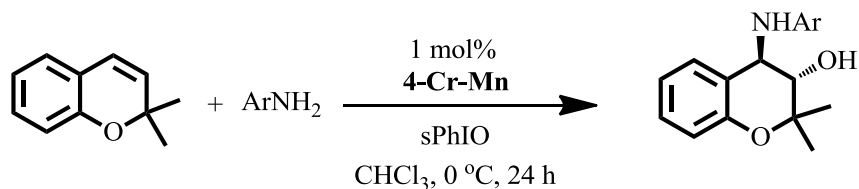
entry	Ar	Conv. (%) ^a	ee (%) ^b
1	Ph	81	82
2	<i>o</i> -MeC ₆ H ₄	76	86
3	<i>p</i> -MeC ₆ H ₄	72	79
4	<i>p</i> -IC ₆ H ₄	79	96

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

Table S9. Diels-Alder reaction catalyzed by CCOF 4-Co.

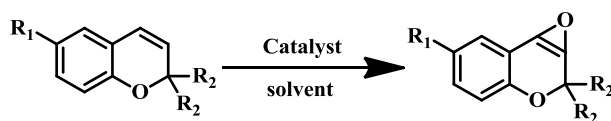
entry	R ₁	R ₂	Conv. (%) ^a	ee (%) ^b
1	Me	Me	83	95
2	Me	Et	86	96
3	H	Me	88	86
4	H	Et	87	89

^a Determined using ¹H NMR. ^b Determined by HPLC.

Table S10. Alkene epoxidation/epoxide aminolysis catalyzed by CCOF 4-Cr-Mn.

entry	Ar	Conv. (%) ^a	ee (%) ^b
1	C ₆ H ₅	84	91
2	<i>o</i> -MeC ₆ H ₄	73	86
3	<i>p</i> -MeC ₆ H ₄	81	90

^a Determined using ¹H NMR. ^b Determined by HPLC.

Table S11. Reported results of related asymmetric epoxidation of alkenes.**Heterogeneous**

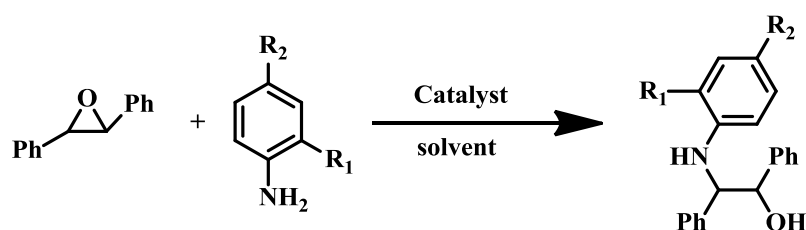
Entry	Catalyst	Oxidant	R1	R2	conversion	ee
1	Mn(salen)-polymer ^{S3}	sPhIO	H	Me	79	76
2	Mn(salen)-polymer ^{S4}	NaOCl	H	Me	90	95
3	Mn(salen)-Zn ₂ -MOF ^{S5}	sPhIO	H	Me	45	82
4	Mn(salen)-Zn ₄ O-MOF-4 ^{S6}	sPhIO	H	Me	87	85
5	Mn(salen)-Zn ₄ O-MOF-4 ^{S6}	sPhIO	NO ₂	Me	93	81
6	Mn(salen)-Zn ₄ O-MOF-4 ^{S6}	sPhIO	Me	Me	79	75
7	Mn(salen)-Zn ₄ O-MOF-5 ^{S6}	sPhIO	H	Me	82	92
8	Mn(salen)-Zn ₄ O-MOF-1 ^{S7}	sPhIO	H	Me	71	84
9	Mn(salen)-Zn ₄ O-MOF-1 ^{S7}	sPhIO	NO ₂	Me	76	77
10	Mn(salen)-Zn ₄ O-MOF-1 ^{S7}	sPhIO	Me	Me	64	72
11	Mn(salen)-MCM-41 ^{S8}	NaOCl	H	Me	94	95
12	Mn(salen)-SBA-15 ^{S8}	NaOCl	H	Me	96	96
13	Mn(salen)-MCM-41 ^{S9}	NaOCl	H	Me	86-98	82-92
14	Mn(salen)-MCM-41 ^{S9}	NaOCl	H	Me	98	94
15	Mn(salen)-SBA-15 ^{S10}	NaOCl	H	Me	99	96
16	Mn(salen)-MCM-41 ^{S10}	NaOCl	H	—(C ₅ H ₁₀)	90	78
17	Mn(salen)-SBA-15 ^{S10}	NaOCl	H	—(C ₅ H ₁₀)	92	77

Homogeneous

Entry	Catalyst	Oxidant	R1	R2	conversion	ee
1	Mn(salen)-2 ^{S11}	n-Bu ₄ NIO ₄	H	Me	64	84
2	Mn(salen)-5 ^{S12}	NaOCl	H	Me	72	98
3	Mn(salen)-6c ^{S13}	NaOCl	H	Me	78	55
4	Mn(salen)-L ^{S5}	sPhIO	H	Me		88
5	Mn(salen)-2 ^{S3}	sPhIO	H	Me	87	86
6	Mn(salen)-L ₃ -Me ₂ ^{S6}	sPhIO	H	Me	90	92
7	Mn(salen)-L ₃ -Me ₂ ^{S6}	sPhIO	NO ₂	Me	97	88
8	Mn(salen)-L ₃ -Me ₂ ^{S6}	sPhIO	Me	Me	81	88

(S3) Cho, S. H.; Gadzikwa, T.; Afshari, M.; Nguyen, S. T.; Hupp, J. T. *Eur. J. Inorg. Chem.* **2007**, 4863. (S4) Song, C. E.; Roh, E. J.; Yu, B. M.; Chi, D. Y.; Kim, S. C.; Lee, K.-J. *Chem. Commun.* **2000**, 615. (S5) Cho, S.-H.; Ma, B.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. commun.* **2006**, 2563. (S6) Song, F.; Wang, C.; Falkowski, J. M.; Ma, L.; Lin, W. *J. Am. Chem. Soc.* **2010**, *132*, 15390. (S7) Song, F.; Wang, C.; Lin, W. *Chem. Commun.* **2011**, *47*, 8256. (S8) Kureshy, R. I.; Ahmad, I.; Khan, N.-u. H.; Abdi, S. H. R.; Pathak, K.; Jasra, R. V. *J. Catal.* **2006**, *238*, 134. (S9) Kureshy, R. I.; Ahmad, I.; Khan, N.-u. H.; Abdi, S. H. R.; Singh, S.; Pandia, P. H.; Jasra, R. V. *J. Catal.* **2005**, *235*, 28. (S10) Kureshy, R. I.; Ahmad, I.; Khan, N.-u. H.; Abdi, S. H. R.; Pathak, K.; Jasra, R. V. *Tetrahedron: Asymmetry* **2005**, *16*, 3562. (S11) Pietikänen, P. *Tetrahedron lett.* **1995**, *36*, 319. (S12) Jacobsen, E. N., Zhang, W., Muci, A. R., Ecker, J. R., Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063. (S13) Scheurer, A., Mosset, P., Spiegel, M., Saalfrank, R. W. *Tetrahedron*, **1999**, *55*, 1063.

Table S12. Reported results of related asymmetric aminolysis of *trans*-stilbene oxide with anilines.



Heterogeneous

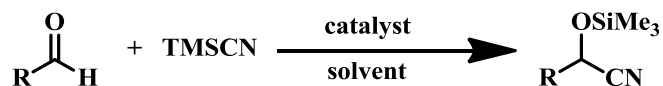
Entry	Catalyst	R1	R2	yield	conversion	ee
1	Cr(salen)-polymer ^{S14}	H	H	49		99
2	Cr(salen)-Zn ₂ -MOF ^{S2}	H	H		92	82
3	Cr(salen)-Zn ₂ -MOF ^{S2}	Me	H		93	94
4	Cr(salen)-Zn ₂ -MOF ^{S2}	H	Me		97	93
5	Cr(salen)-Zn ₂ -MOF ^{S2}	H	I		91	99

Homogeneous

Entry	Catalyst	R1	R2	yield	conversion	ee
1	Cr(salen)-Cr(Me ₂ L)Cl ^{S2}	H	H		97	74
2	Cr(salen)-Cr(Me ₂ L)Cl ^{S2}	H	I		96	89
3	Cr(salen)- 1 ^{S15}	Me	H	91		86

(S14) Kureshy, R. I.; Singh, S.; Khan, N.-u. H.; Abdi, S. H. R.; Agrawal, S.; Jasra, R. V. *Tetrahedron: Asymmetry* **2006**, *17*, 1638. (S15) Bartoli, G., Bosco, M., Carlone, A., Locatelli, M., Massaccesi, M., Melchiorre, P., Sambri, L. *Org. let.* **2004**, *6*, 2173.

Table S13. Reported results of related asymmetric cyanosilylation of aldehydes.



Heterogeneous

Entry	Catalyst	R	conversion	ee
1	VO(salen)-Cd-MOF ^{S16}	<i>p</i> -BrC ₆ H ₅	94	92
2	VO(salen)-Cd-MOF ^{S16}	<i>p</i> -MeC ₆ H ₅	90	92
3	VO(salen)-Cd-MOF ^{S16}	<i>p</i> -MeOC ₆ H ₅	90	94
4	VO(salen)-Cd-MOF ^{S16}	2-thiophenyl	92	92
5	VO(salen)-Cd-MOF ^{S17}	<i>p</i> -BrC ₆ H ₅	98	82
6	VO(salen)-Cd-MOF ^{S17}	<i>p</i> -MeC ₆ H ₅	97	95
7	VO(salen)-Cd-MOF ^{S17}	<i>p</i> -MeOC ₆ H ₅	96	96
11	VO(Salen)/SBA-16-C8 ^{S18}	<i>p</i> -BrC ₆ H ₅	85	87
12	VO(Salen)/SBA-16-C8 ^{S18}	<i>p</i> -MeC ₆ H ₅	67	84
13	VO(Salen)/SBA-16-C8 ^{S18}	<i>p</i> -MeOC ₆ H ₅	60	84

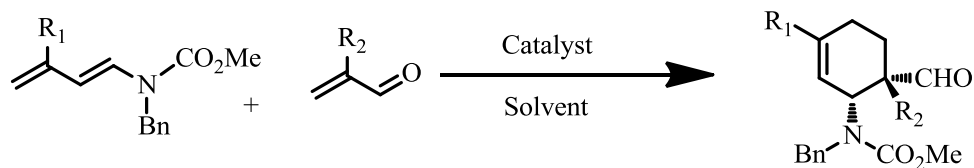
Homogeneous

Entry	Catalyst	R	conversion	ee
1	VO(salen)-Me ₂ L ^{S16}	<i>p</i> -BrC ₆ H ₅	93	63
2	VO(salen)-Me ₂ L ^{S16}	<i>p</i> -MeOC ₆ H ₅	91	89
3	VO(salen)-Me ₂ L ^{S17}	C ₆ H ₅	99	78
4	VO(salen)-Me ₂ L ^{S17}	<i>p</i> -MeOC ₆ H ₅	97	81
5	VO(salen)-Me ₂ L ^{S17}	<i>p</i> -BrC ₆ H ₅	99	73

(S16) Xi, W.; Liu, Y.; Xia, Q.; Li, Z.; Cui, Y. *Chem. - Eur. J.* **2015**, *21*, 12581 (S17) Zhu, C.; Xia, Q.; Chen, X.; Liu, Y.; Du, X.; Cui, Y. *ACS Catal.* **2016**, *6*, 7590. (S18) Yang, H.; Zhang, L.; Wang, P.; Yang, Q.; Li, C. *Green Chem.* **2009**, *11*, 257.

Table S14. Reported results of related asymmetric Diels-Alder reaction.

Homogeneous

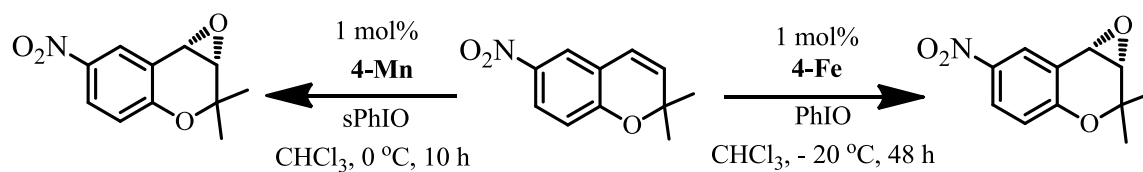


Entry	Catalyst	R1	R2	yield	ee
1	Co(salen)-4a ^{S19}	H	Me	98	98
2	Co(salen)-4a ^{S19}	H	Et	93	97

(S19) Hutson, G. E., Türkmen, Y. E., Rawal, V. H. *J. Am. Chem. Soc.* **2013**, *135*, 4988.

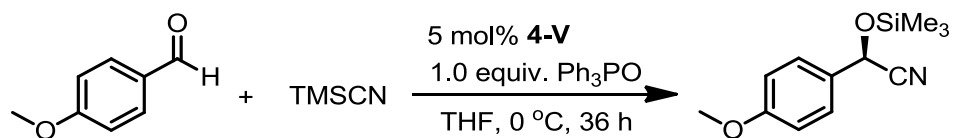
16.2 Recycled experiments.

Table S15. Alkene epoxidation.



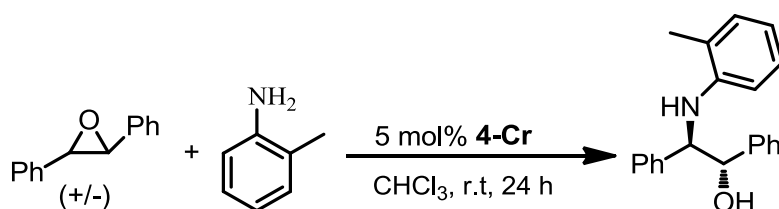
run	4-Mn		4-Fe	
	Conv. (%) ^a	ee (%) ^b	Conv. (%) ^a	ee (%) ^b
1	79	97	71	92
2	79	97	71	90
3	78	95	70	90
4	77	95	71	90
5	77	93	69	90

^a Determined using 1H NMR. ^b Determined by HPLC.

Table S16. Cyanohydrins reaction catalyzed by CCOF 4-V

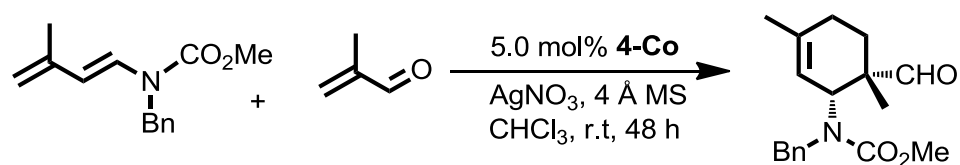
^a Determined using ¹H NMR. ^b Determined by HPLC.

Run	Conv. (%) ^a	ee (%) ^b
1	77	94
2	77	94
3	76	93
4	76	93
5	75	92

Table S17. Aminolysis of trans-stilbene oxide with anilines.

Run	Conv. (%) ^a	ee (%) ^b
1	76	86
2	76	85
3	75	83
4	76	82
5	74	81

^a Determined using ¹H NMR. ^b Determined by HPLC.

Table S18. Diels-Alder reaction.

Run	Conv. (%) ^a	ee (%) ^b
1	83	95
2	83	94
3	83	93
4	82	91
5	82	90

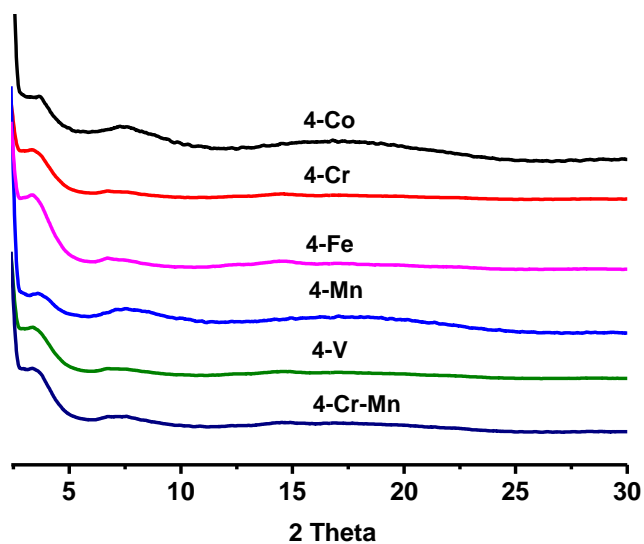
Table S19. Recycled experiments of alkene epoxidation/epoxide aminolysis.

Run	Conv. (%) ^a	ee (%) ^b
1	84	91
2	83	90
3	81	88
4	78	88
5	76	85

Table S20. ICP-OES of CCOF 3, CCOF 4 and CCOFs 4-M.

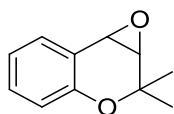
	Measured (wt%)	molar ratios
CCOF 3	(Zn) 9.45	1
CCOF 4	(Zn) 9.11	1
CCOF 4-Mn	(Zn) 0.61 : (Mn) 8.85	1 : 17
CCOF 4-Fe	(Zn) 0.41 : (Fe) 10.05	1 : 29
CCOF 4-V	(Zn) 0.87 : (V) 7.98	1 : 12
CCOF 4-Cr	(Zn) 0.21 : (Cr) 9.05	1 : 54
CCOF 4-Co	(Zn) 0.62 : (Co) 8.14	1 : 15
CCOF 4-Cr-Mn	(Zn) 0.39 : (Cr) 4.93 : (Mn) 3.28	1 : 16 : 10
CCOF 4-Cr-Co	(Zn) 0.17 : (Cr) 4.86 : (Co) 3.11	1 : 36 : 20
CCOF 4-Cr-Fe	(Zn) 0.13 : (Cr) 4.77 : (Fe) 4.96	1 : 46 : 45

Figure S13. PXRD of CCOFs 4-M after five catalytic runs.



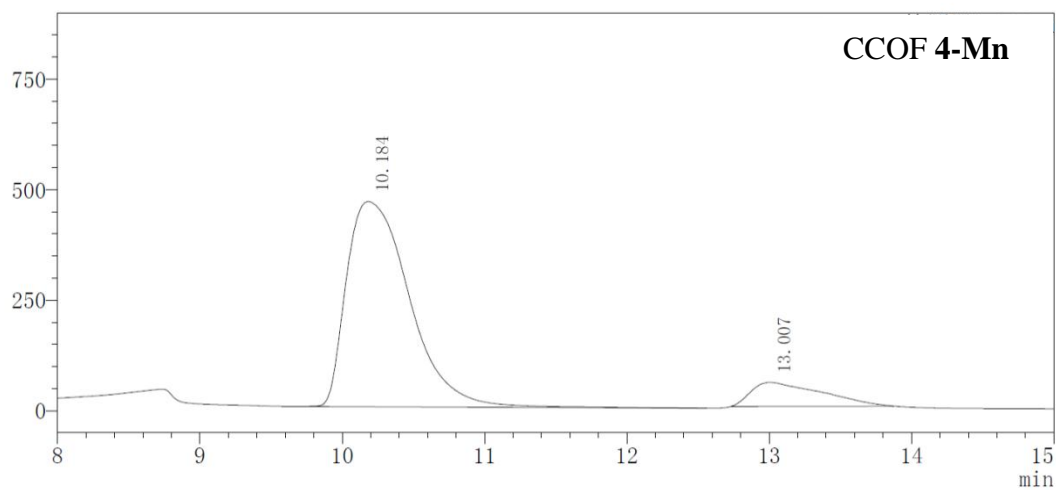
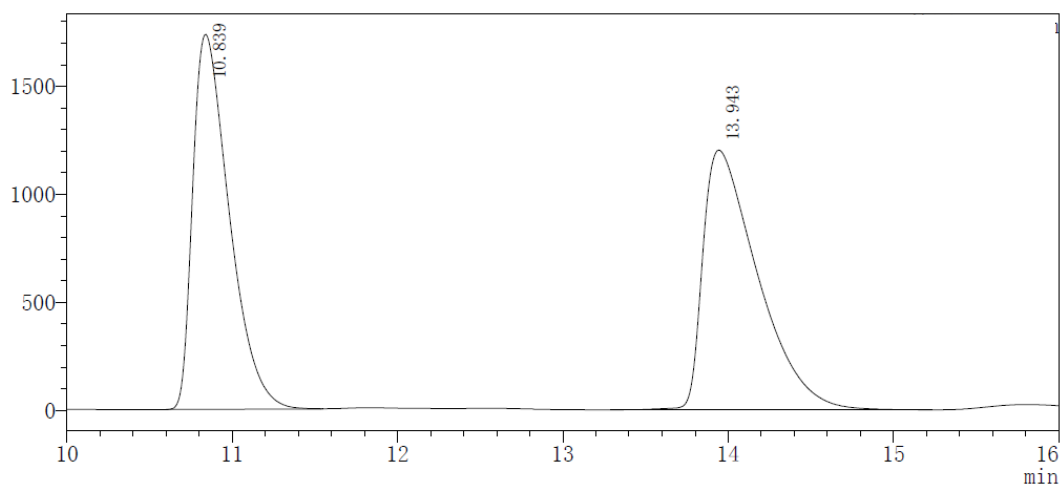
16.3 HPLC result.

16.3.1 Alkene epoxidation.

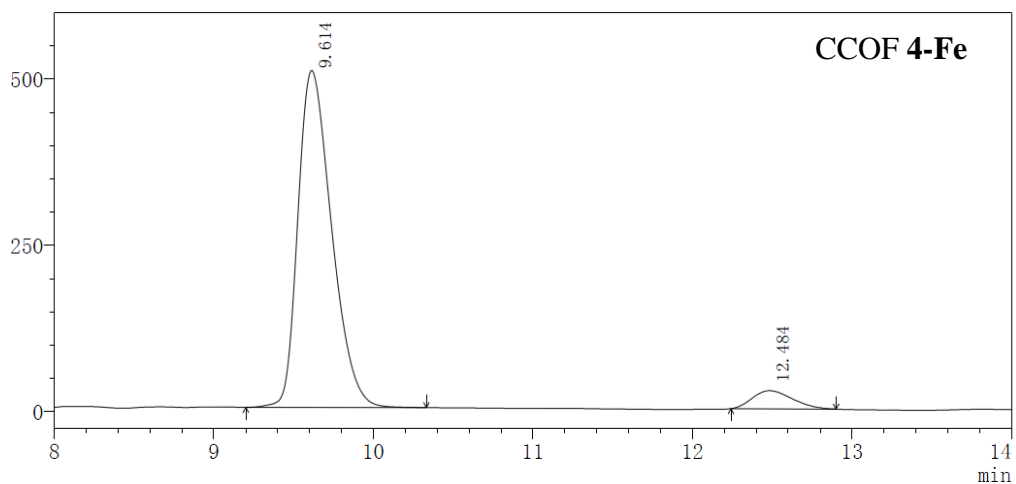


2,2-dimethyl-2,7b-dihydro-1aH-oxireno[2,3-c]chromene: Chiralcel OD-H column

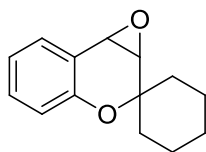
(hexane/*i*-PrOH = 99/1, 1.0 mL/min, 230 nm), $t_{major} = 10.184$ min, $t_{minor} = 13.007$ min for CCOF **4-Mn**, ee = 77%; $t_{major} = 9.614$ min, $t_{minor} = 12.484$ min for CCOF **4-Fe**, ee = 88%.



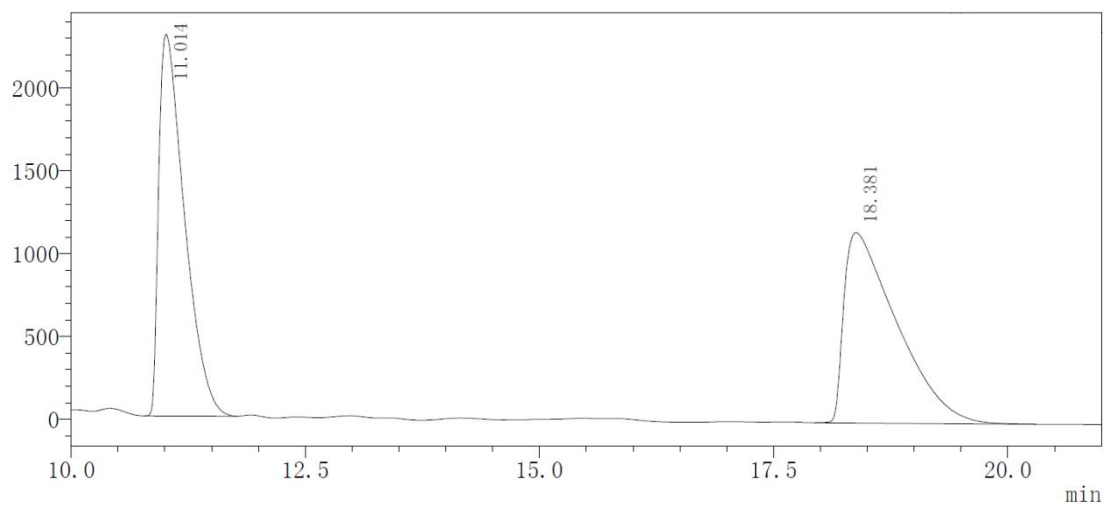
Serial Number	Retention Time [min]	Area	Area %
1	10.184	14334802	88.498
2	13.007	1863035	11.502

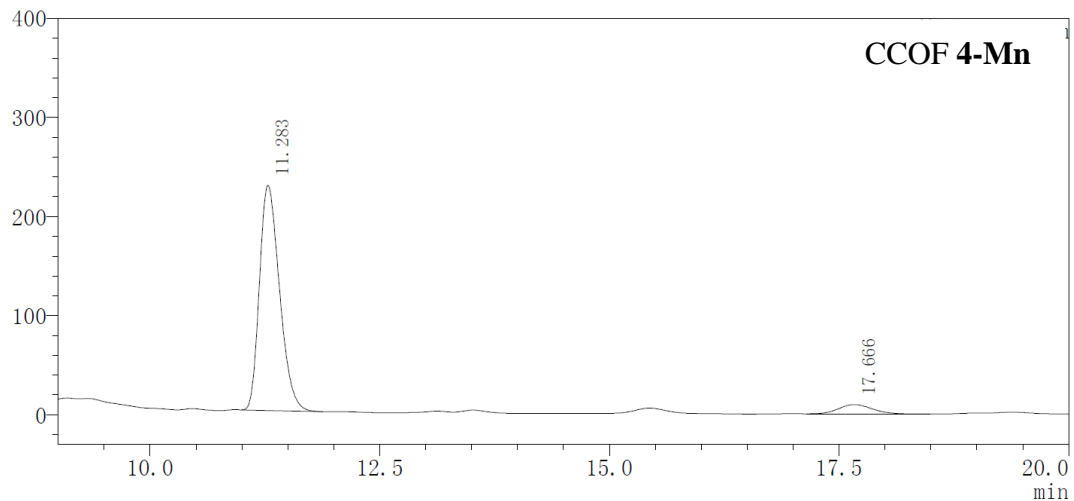


Serial Number	Retention Time [min]	Area [mAbs*s]	Area %
1	9.614	7442180	93.984
2	12.484	476351	6.016

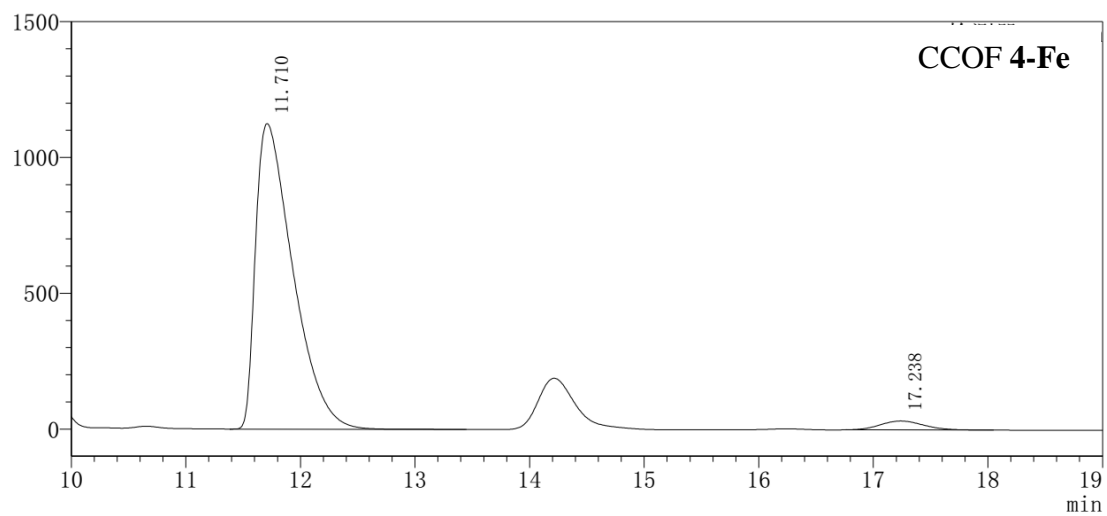


1a',7b'-dihydrospiro[cyclohexane-1,2'-oxireno[2,3-c]chromene]: Chiralcel OD-H column (hexane/i-PrOH = 99/1, 1.0 mL/min, 230 nm), $t_{major} = 11.283$ min, $t_{minor} = 17.666$ min for CCOF **4-Mn**, ee = 86%; $t_{major} = 11.710$ min, $t_{minor} = 17.238$ min for CCOF **4-Fe**, ee = 94%.

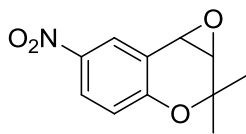




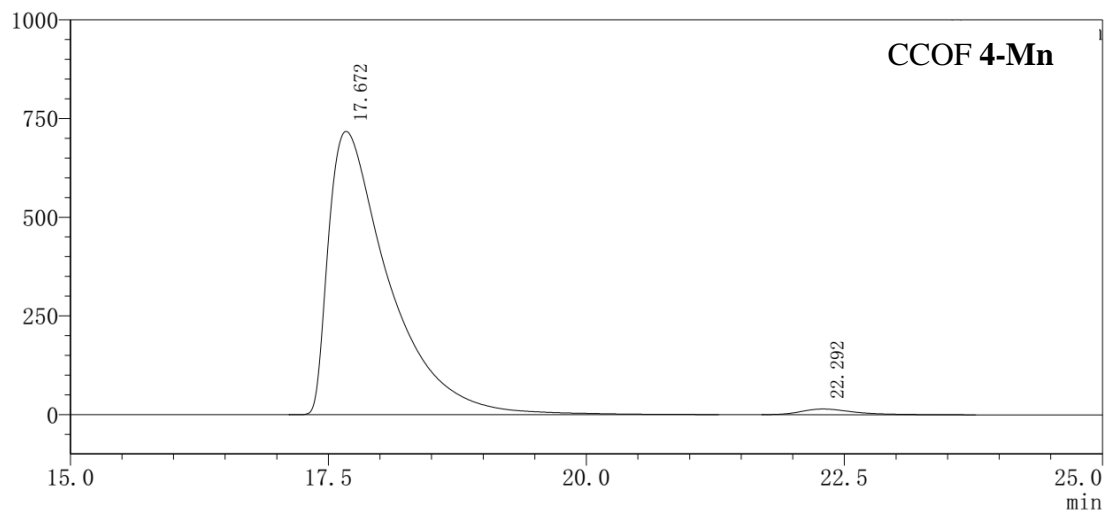
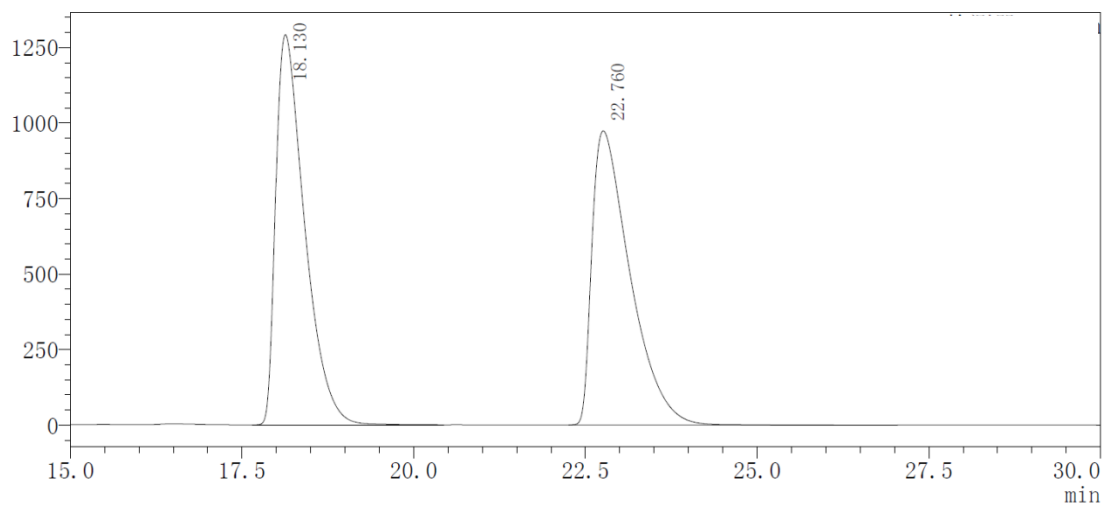
Serial Number	Retention Time [min]	Area	Area %
1	11.283	3461829	93.560
2	17.666	238285	6.440



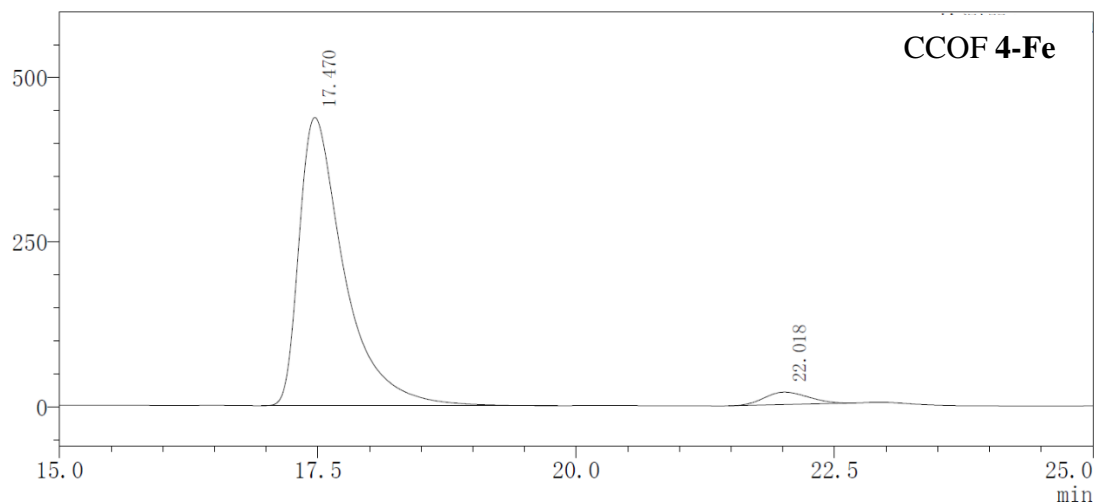
Serial Number	Retention Time [min]	Area	Area %
1	11.710	25482342	96.704
2	17.238	868427	3.296



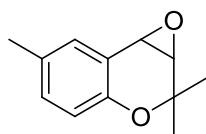
2,2-dimethyl-6-nitro-2,7b-dihydro-1aH-oxireno[2,3-c]chromene: Chiralcel OD-H column (hexane/*i*-PrOH = 98/2, 1.0 mL/min, 230 nm), $t_{major} = 17.672$ min, $t_{minor} = 22.292$ min for CCOF **4-Mn**, ee = 96%; $t_{major} = 17.410$ min, $t_{minor} = 22.018$ min for CCOF **4-Fe**, ee = 92%.



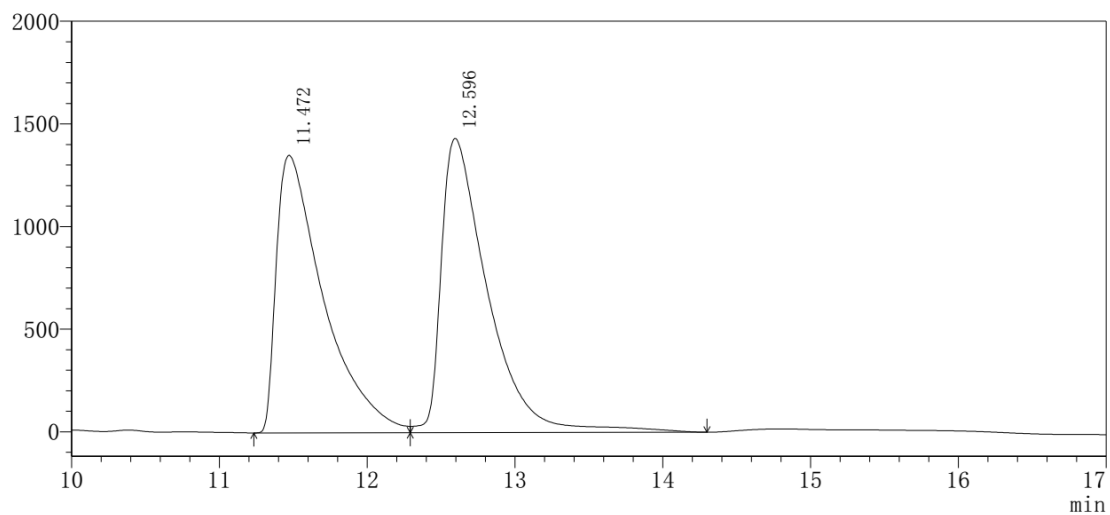
Serial Number	Retention Time [min]	Area	Area %
1	17.672	29341461	98.312
2	22.292	503858	1.688

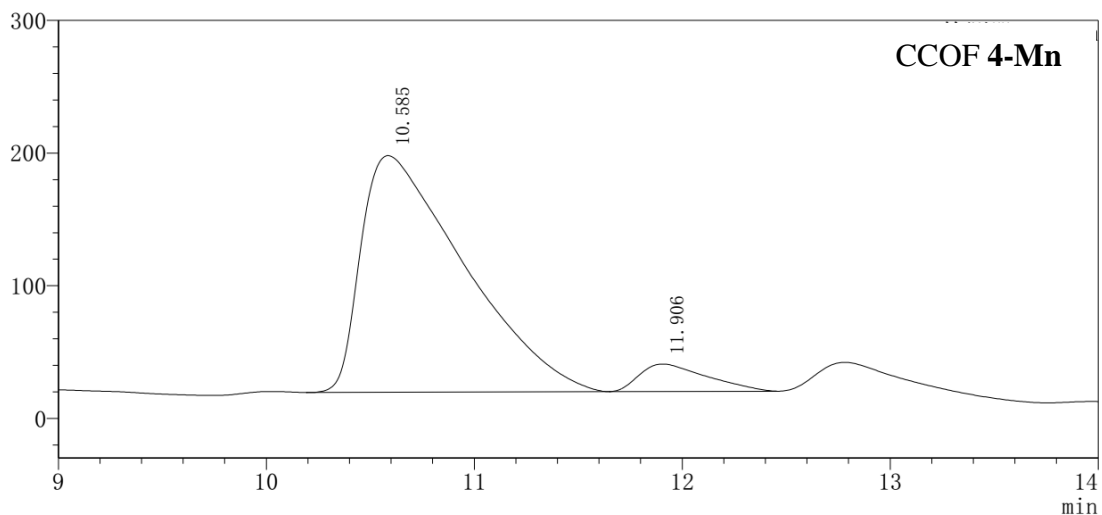


Serial Number	Retention Time [min]	Area	Area %
1	17.470	13326929	95.953
2	22.018	562082	4.047

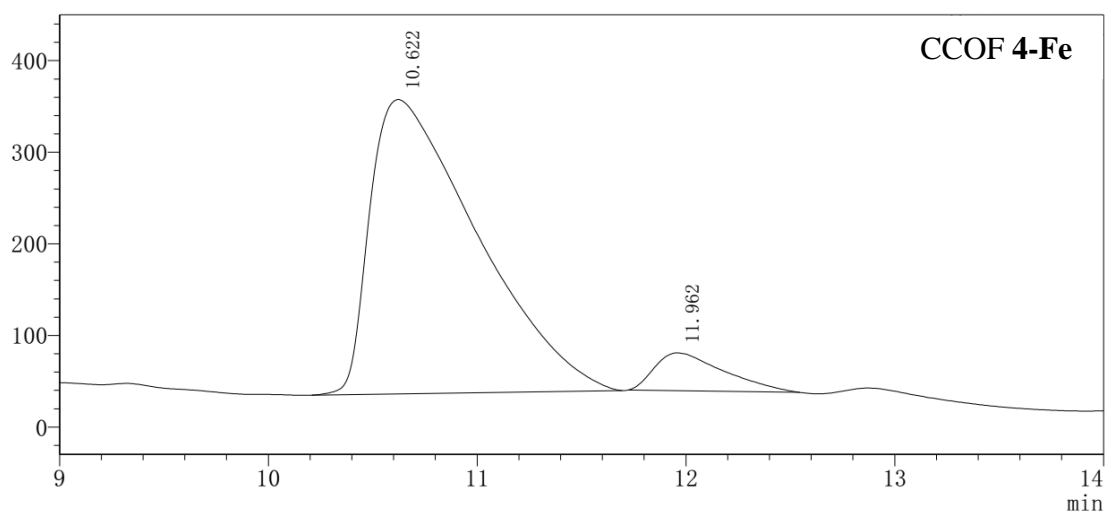


2,2-dimethyl-6-methyl-2,7b-dihydro-1aH-oxireno[2,3-c]chromene: Chiralcel OD-H column (hexane/*i*-PrOH = 99/1, 1.0 mL/min, 230 nm), $t_{major} = 10.585$ min, $t_{minor} = 11.906$ min for CCOF **4-Mn**, ee = 86%; $t_{major} = 10.622$ min, $t_{minor} = 11.962$ min for CCOF **4-Fe**, ee = 85%.



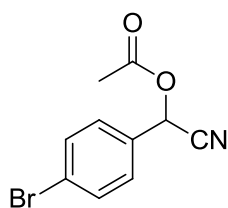


Serial Number	Retention Time [min]	Area	Area %
1	10.585	6148781	92.955
2	11.906	466045	7.045

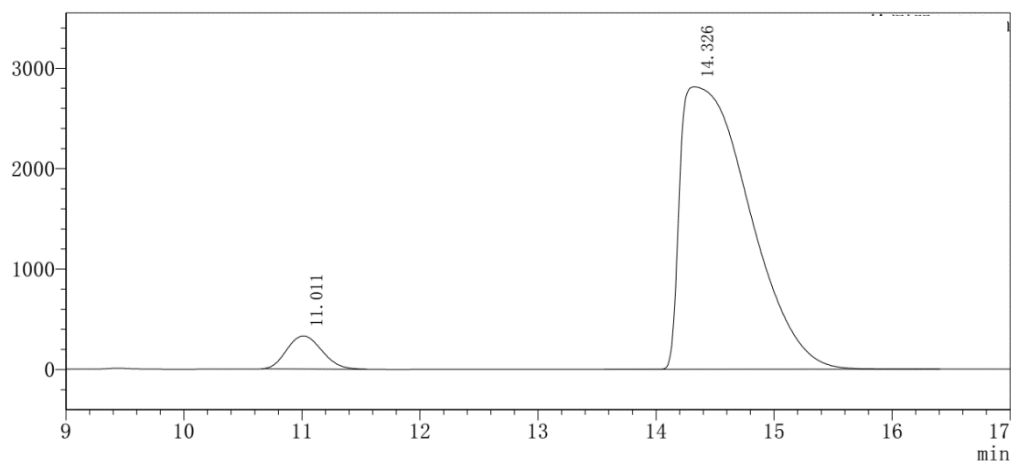
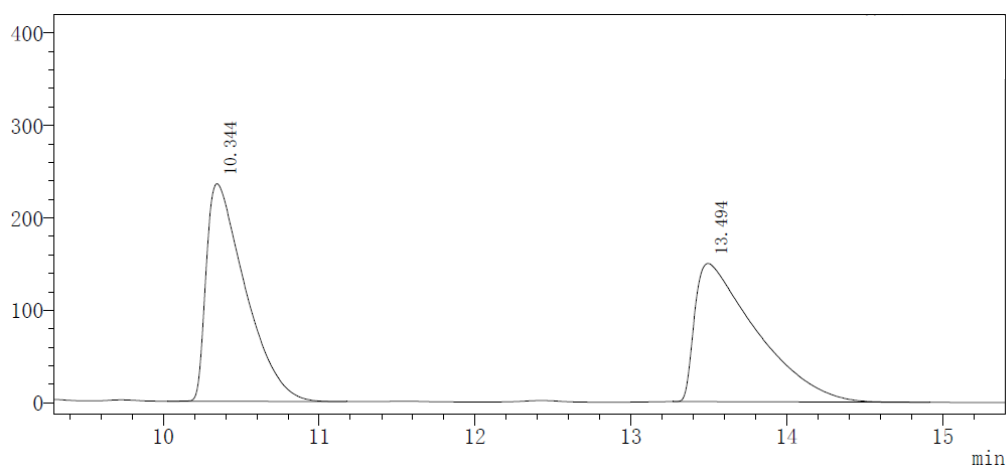


Serial Number	Retention Time [min]	Area	Area %
1	10.622	11435069	92.344
2	11.962	948055	7.656

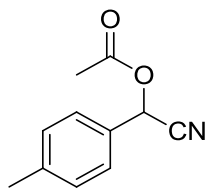
16.3.2 Cyanohydrins Reaction



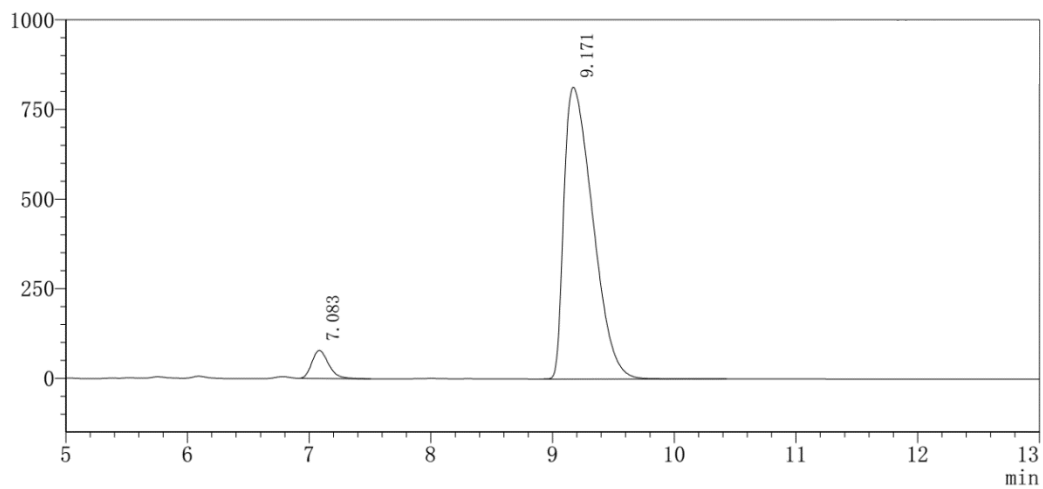
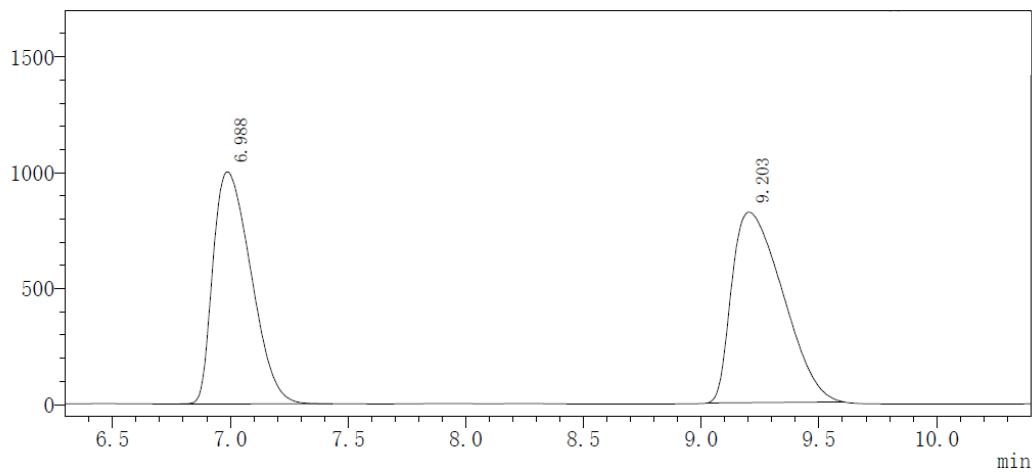
Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 230 nm), $t_{major} = 14.326$ min, $t_{minor} = 11.011$ min; ee= 89 %.



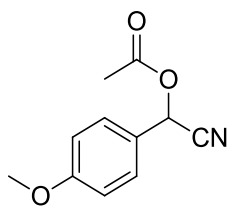
Serial Number	Retention Time [min]	Area	Area %
1	11.011	6769676	5.593
2	14.326	114279154	94.407



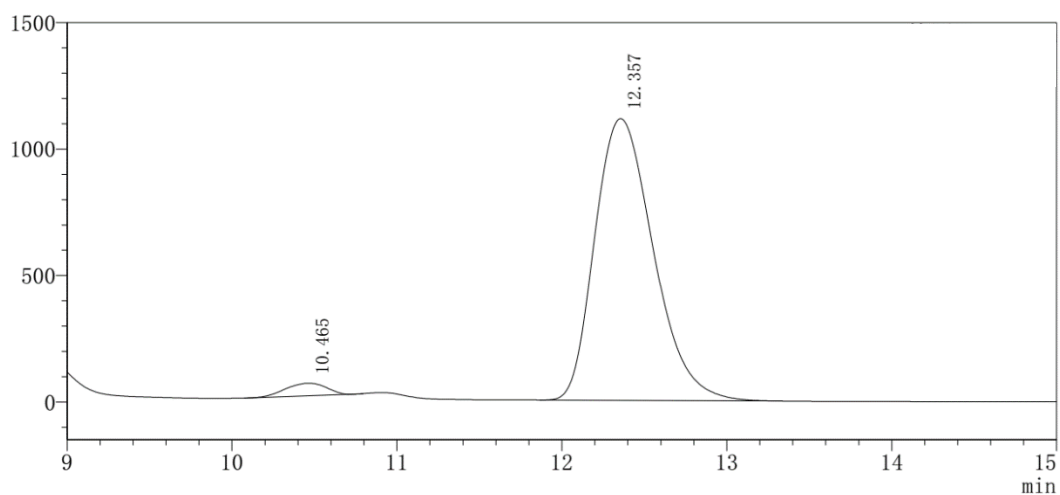
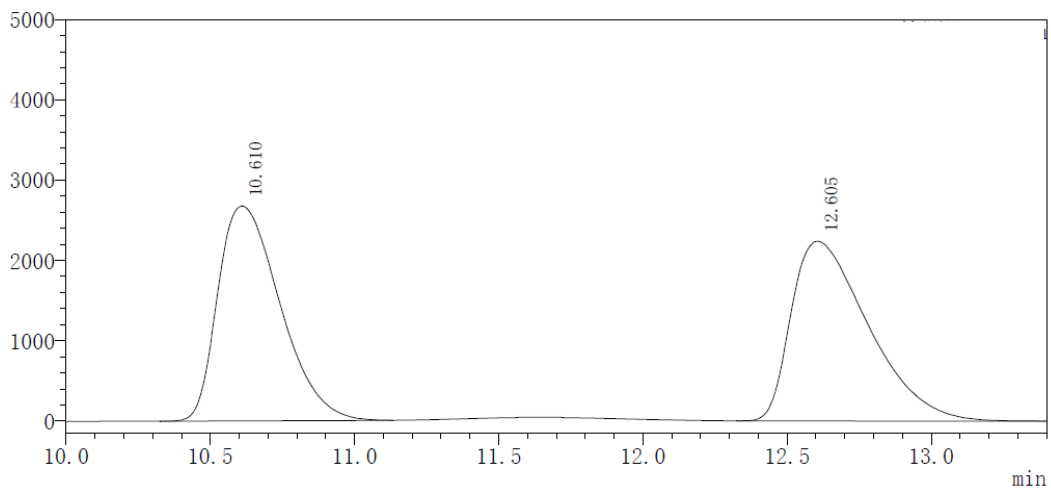
Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 230 nm), $t_{major} = 9.171$ min, $t_{minor} = 7.083$ min; ee= 89 %.



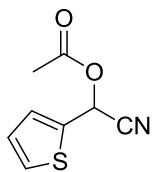
Serial Number	Retention Time [min]	Area	Area %
1	7.083	746815	5.282
2	9.171	13390884	94.718



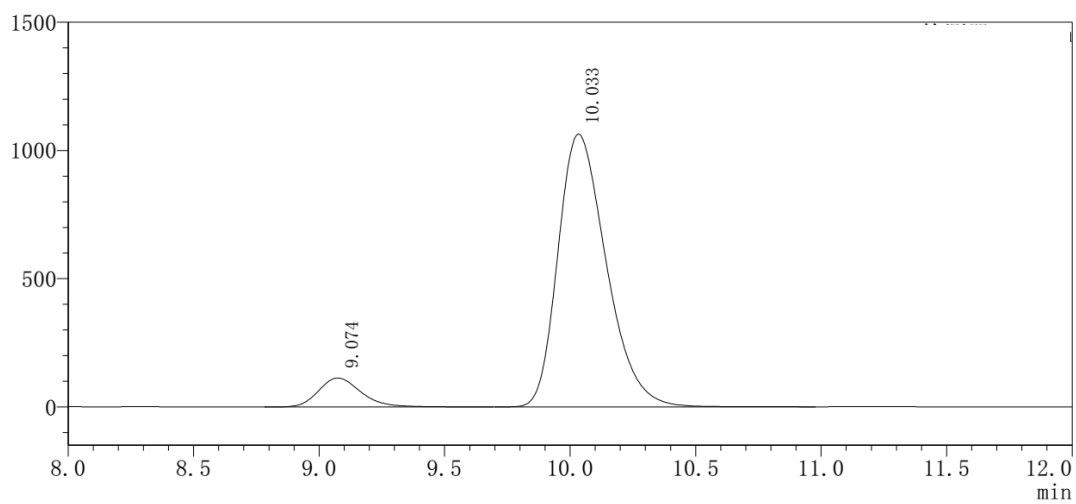
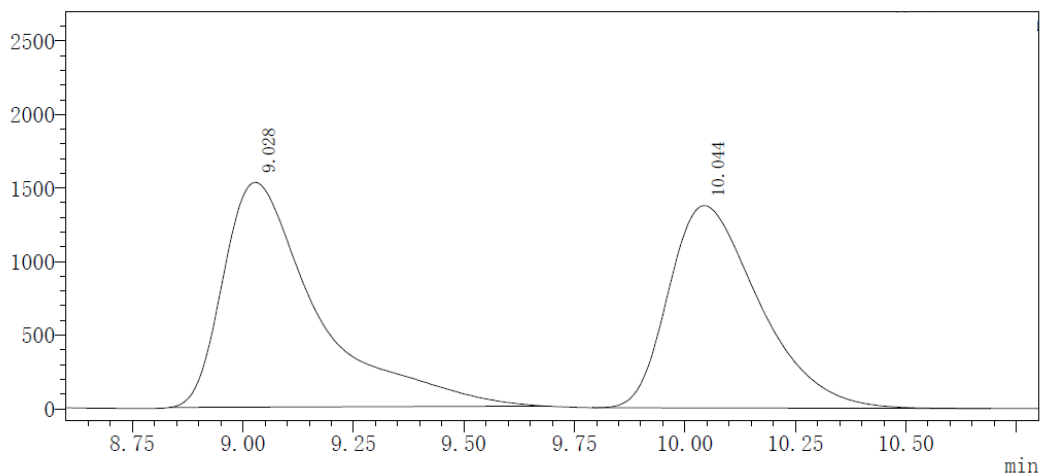
Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 12.357$ min, $t_{minor} = 10.465$ min; ee = 94 %.



Serial Number	Retention Time [min]	Area	Area %
1	10.456	851170	3.008
2	12.357	27446925	96.992

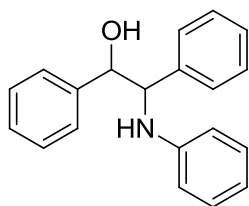


Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 230 nm), $t_{major} = 10.033$ min, $t_{minor} = 9.074$ min; ee= 83 %.



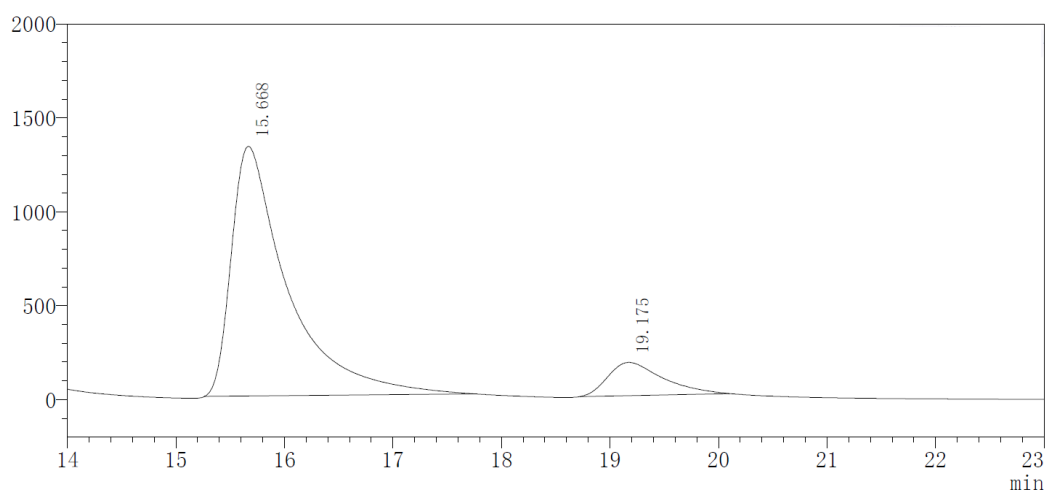
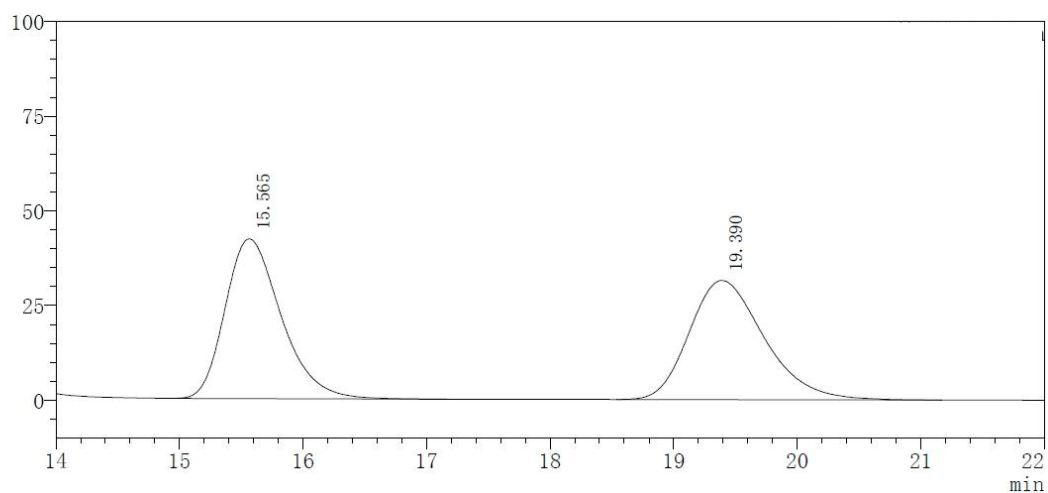
Serial Number	Retention Time [min]	Area	Area %
1	9.074	1333276	8.561
2	10.033	14241195	91.439

16.3.3 Aminolysis of trans-Stilbene Oxide

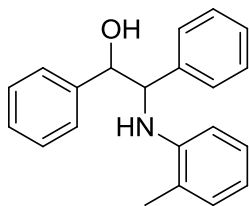


1,2-diphenyl-2-(phenylamino)ethanol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 90/10, 0.75 mL/min, 250 nm), $t_{major} = 15.668$ min, $t_{minor} = 19.175$ min; ee = 82 %.

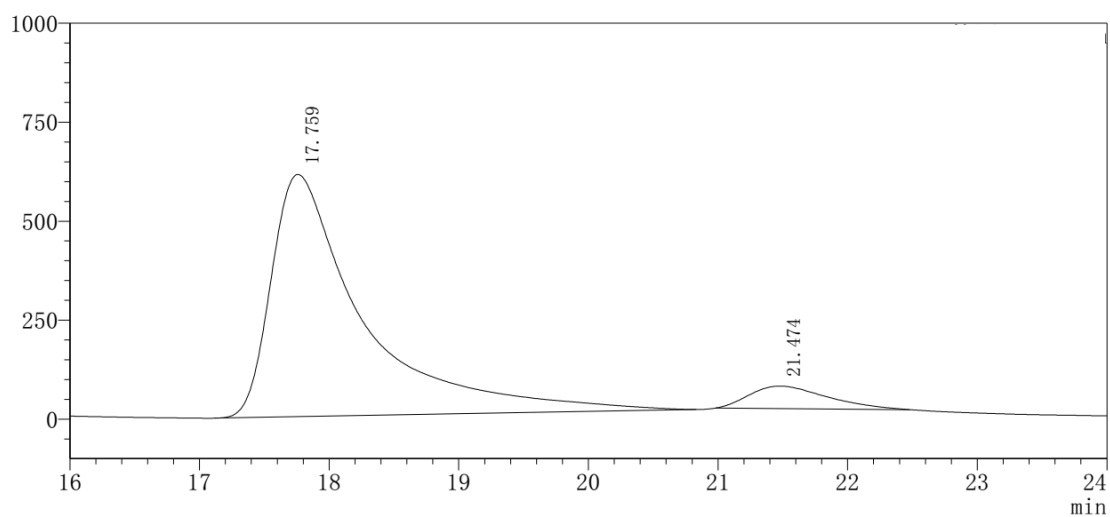
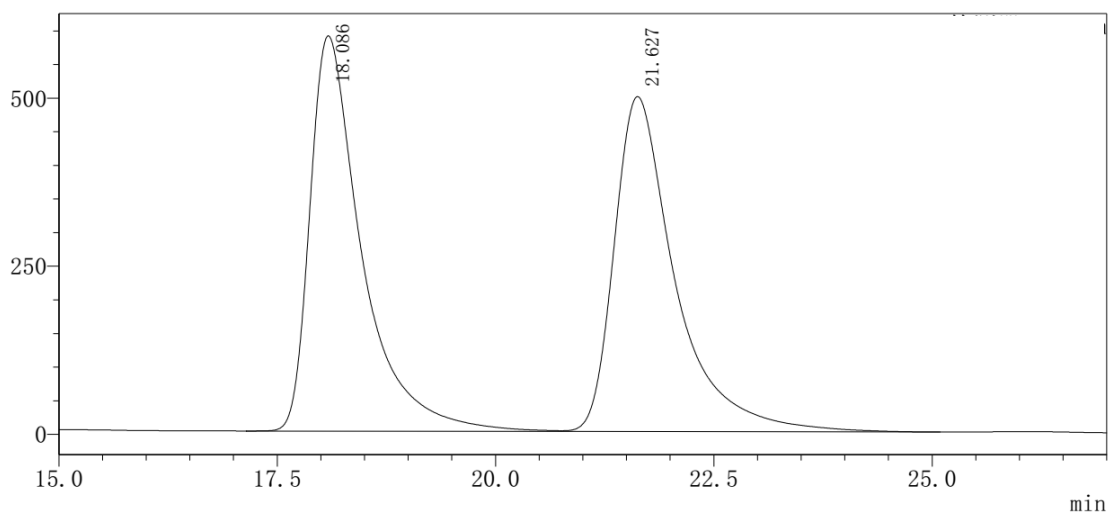


Serial Number	Retention Time [min]	Area	Area %
1	15.668	49286644	91.02
2	19.175	4862602	8.98

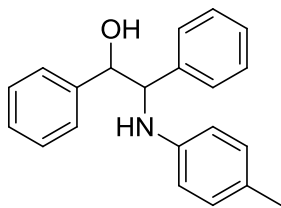


2-((2-methylphenyl)amino)-1,2-diphenylethanol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 17.759$ min, $t_{minor} = 21.474$ min; ee = 86 %.

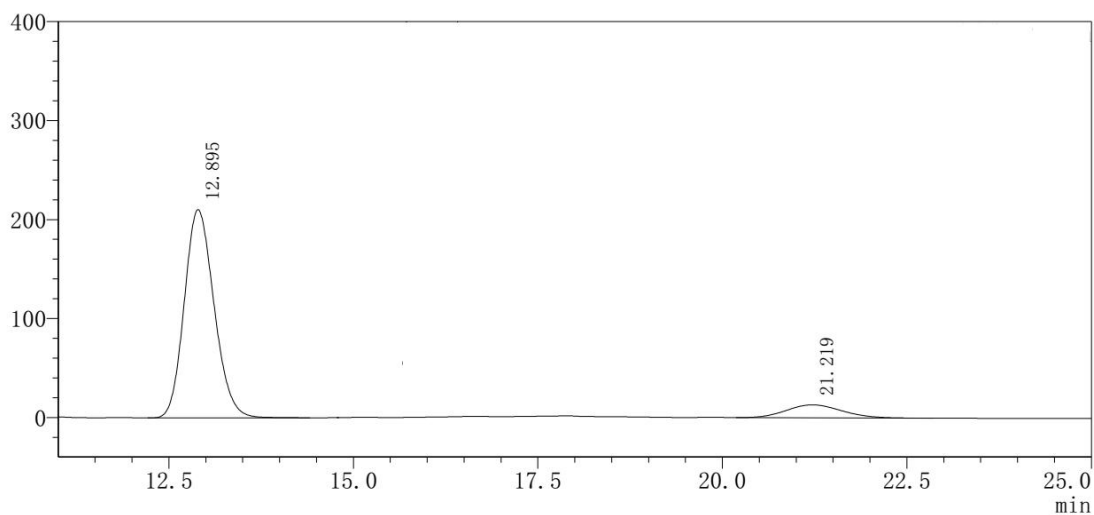
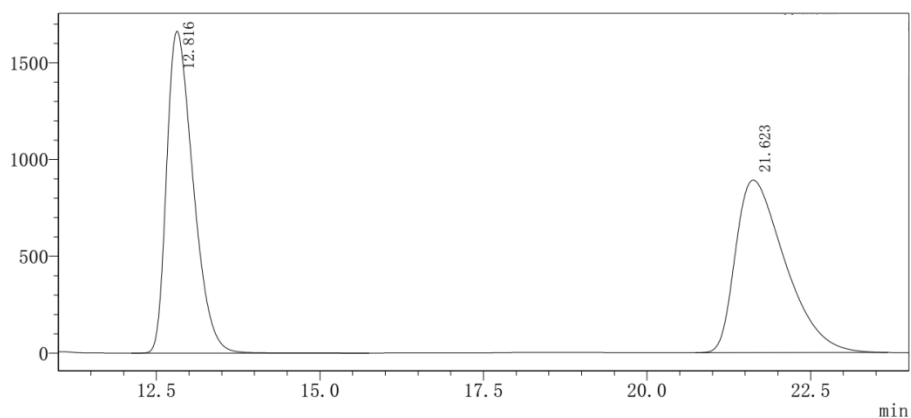


Serial Number	Retention Time [min]	Area	Area %
1	17.759	30244024	92.752
2	21.474	2363268	7.248

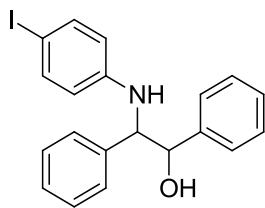


2-((4-methylphenyl)amino)-1,2-diphenylethanol

Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/*i*-PrOH = 90/10, 1.0 mL/min, 250 nm), $t_{major} = 12.895$ min, $t_{minor} = 21.219$ min; ee = 79%.

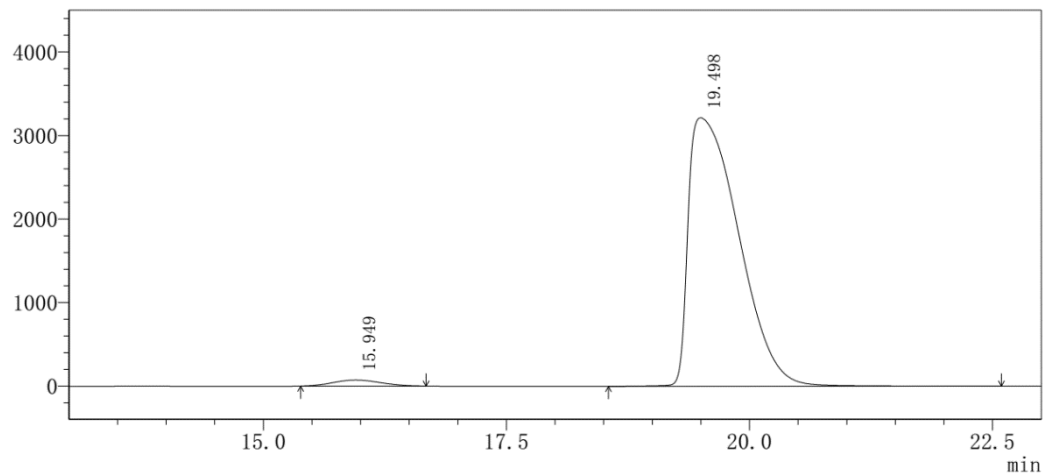
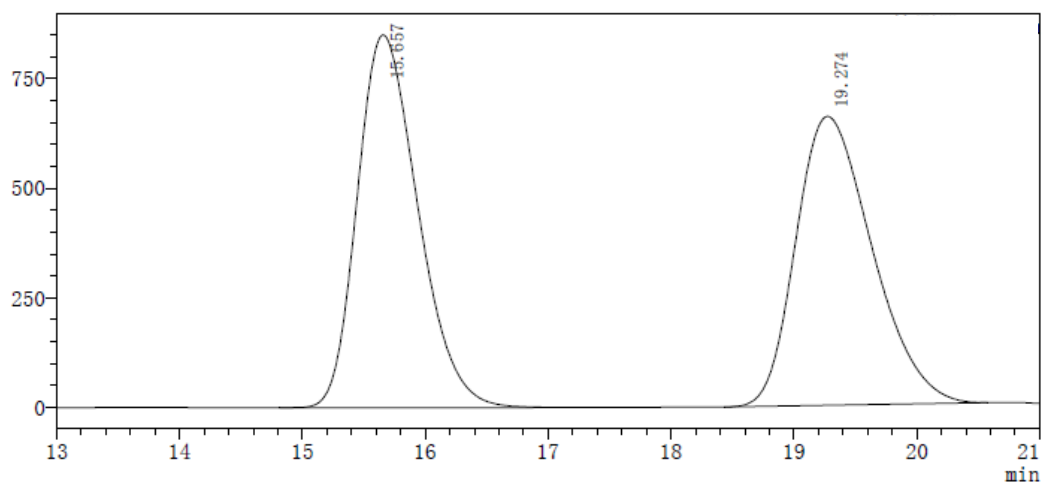


Serial Number	Retention Time [min]	Area	Area %
1	12.895	5924223	89.546
2	21.219	691590	10.454



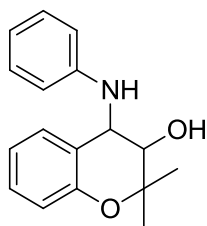
2-((4-iodophenyl)amino)-1,2-diphenylethanol

Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/*i*-PrOH = 90/10, 1.0 mL/min, 250 nm), $t_{major} = 19.498$ min, $t_{minor} = 15.949$ min; ee = 96%.



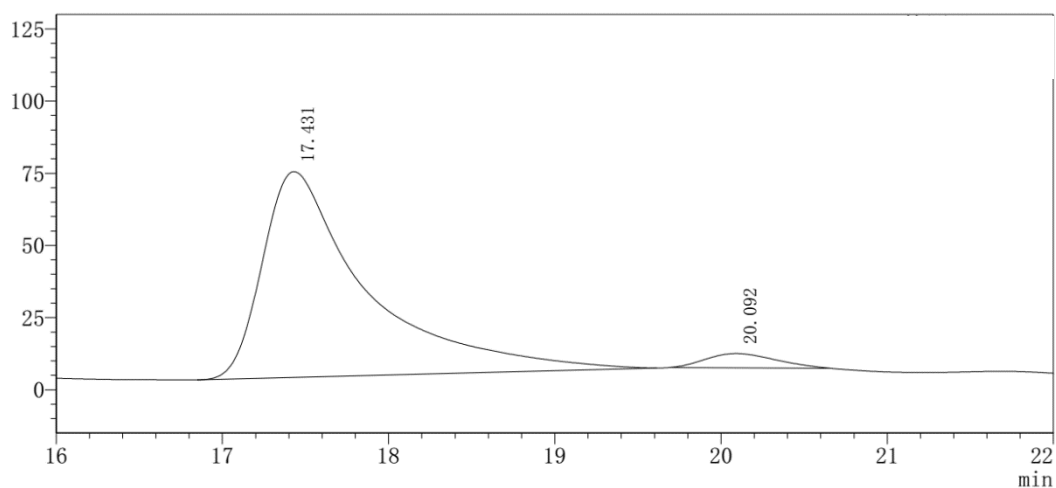
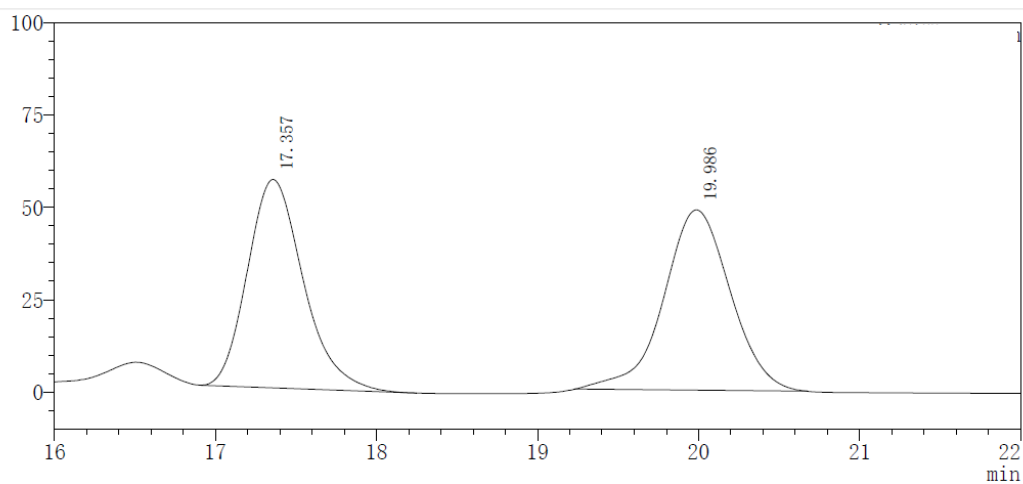
Serial Number	Retention Time [min]	Area	Area %
1	15.949	2517266	2.125
2	19.498	115948811	97.875

16.3.4 Alkene epoxidation/epoxide aminolysis

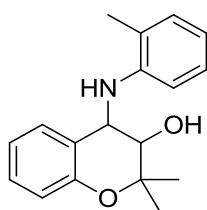


2,2-dimethyl-4-(phenylamino)chroman-3-ol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 17.431$ min, $t_{minor} = 20.092$ min; ee = 91%.

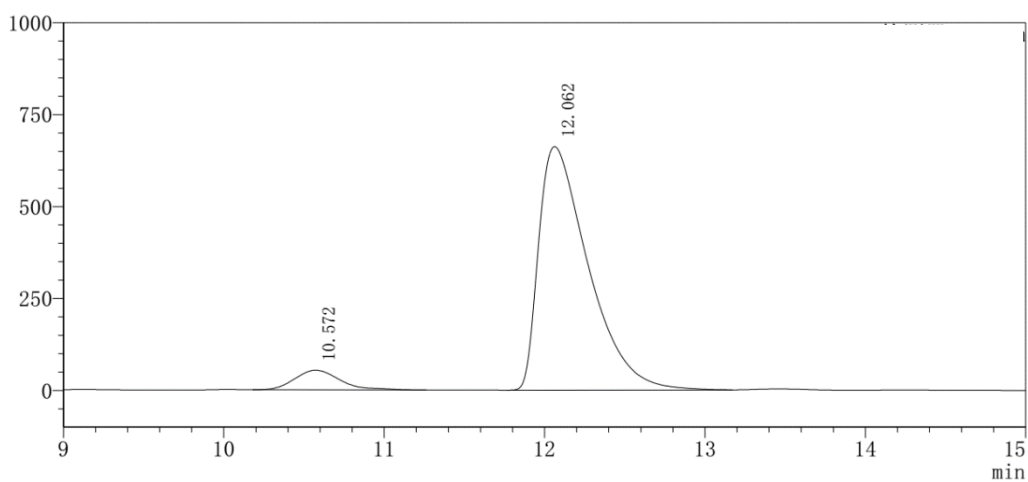
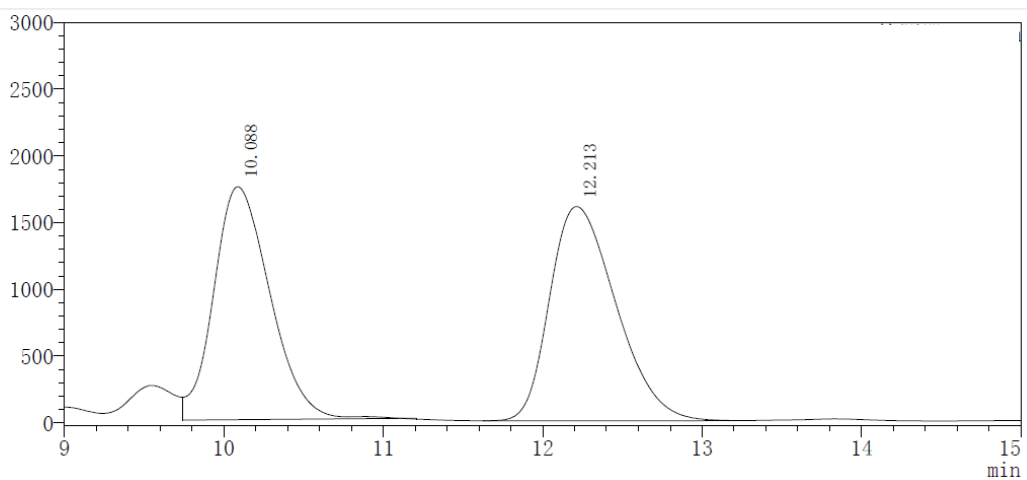


Serial Number	Retention Time [min]	Area	Area %
1	17.431	3117608	95.522
2	20.092	146168	4.478

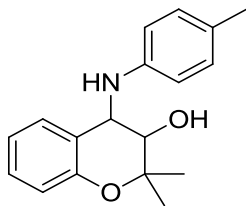


2,2-dimethyl-4-(o-tolylamino)chroman-3-ol

Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 220 nm), $t_{major} = 12.062$ min, $t_{minor} = 10.572$ min; ee = 86%.

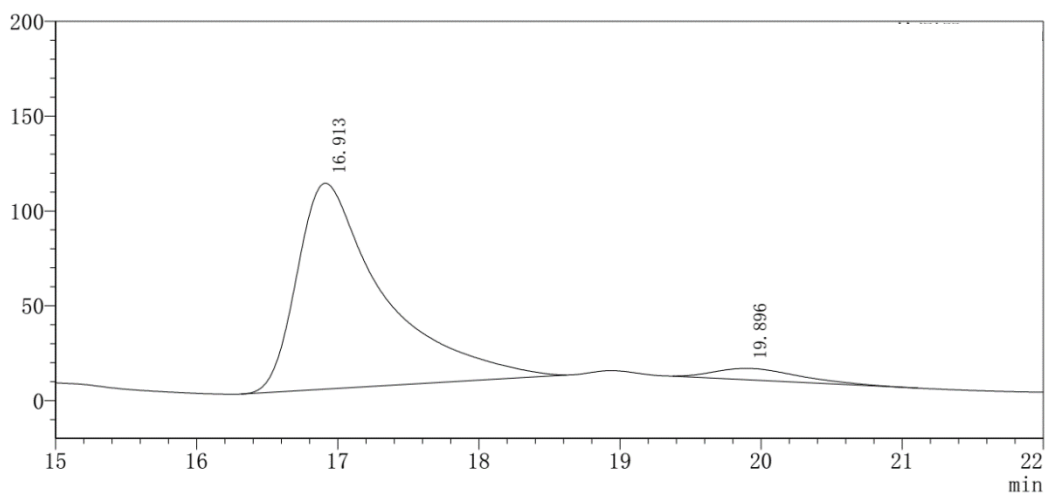
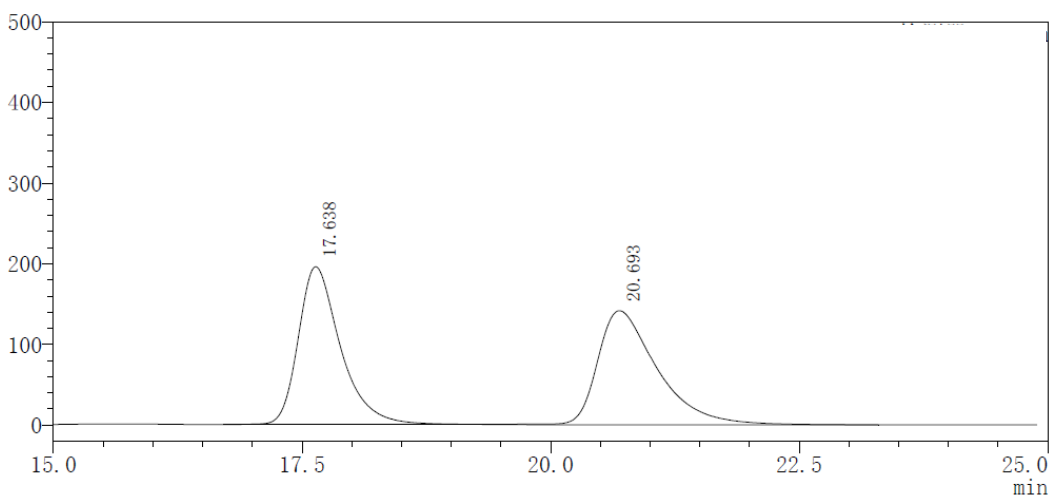


Serial Number	Retention Time [min]	Area	Area %
1	10.572	1047406	6.838
2	12.062	14270007	93.162



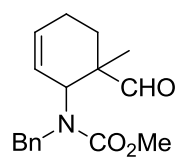
2,2-dimethyl-4-(p-tolylamino)chroman-3-ol

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL/min, 250 nm), $t_{major} = 16.913$ min, $t_{minor} = 19.896$ min; ee = 90%.



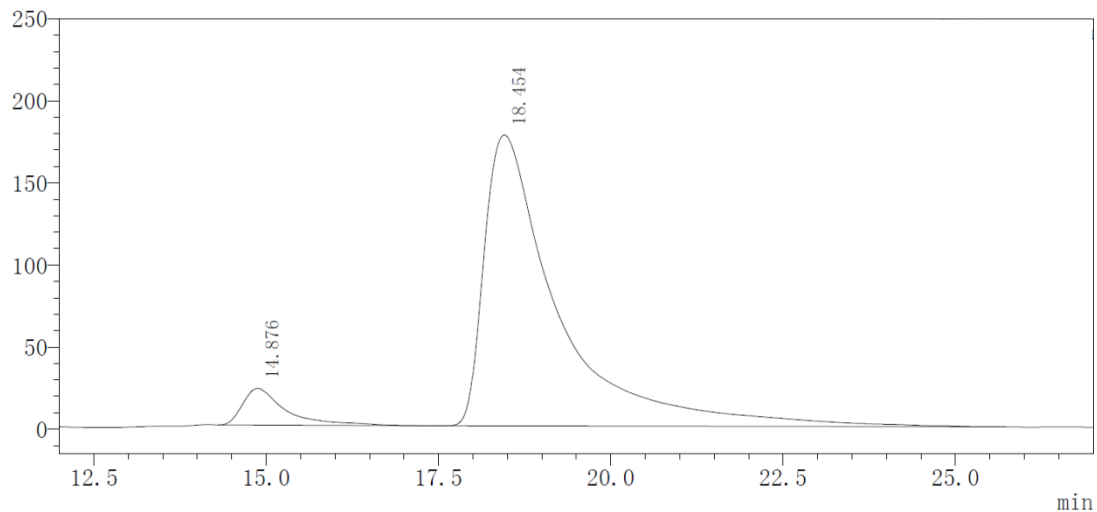
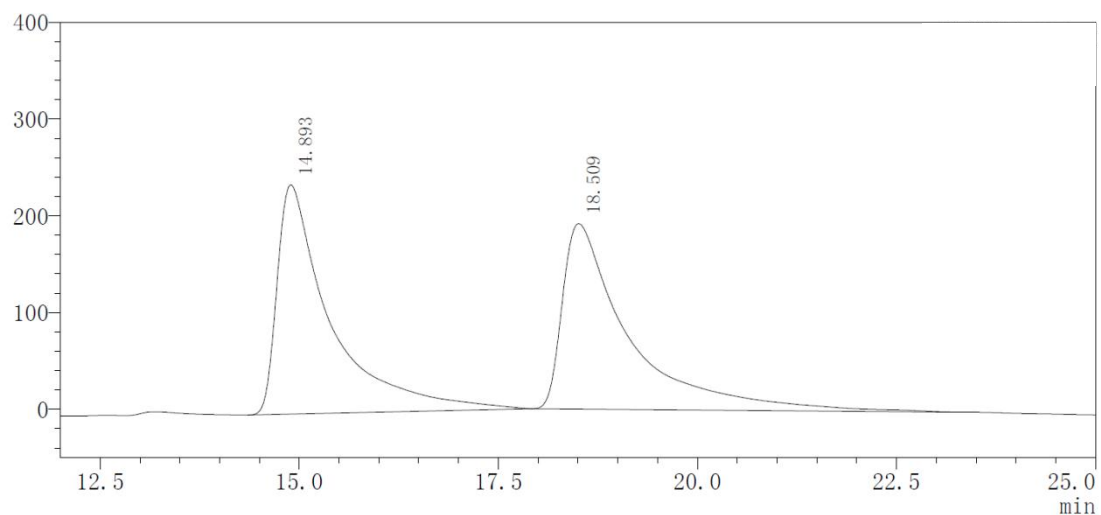
Serial Number	Retention Time [min]	Area	Area %
1	16.913	4646058	94.821
2	19.896	253777	5.179

16.3.5 Diels-Alder reactions

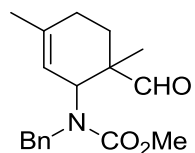


N-Benzyl-N-(6-formyl-6-methyl-2-cyclohexen-1-yl)carbamic Acid Methyl Ester

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 98/2, 1.0 mL/min, 220 nm), $t_{major} = 18.454$ min, $t_{minor} = 14.875$ min; ee = 86%.

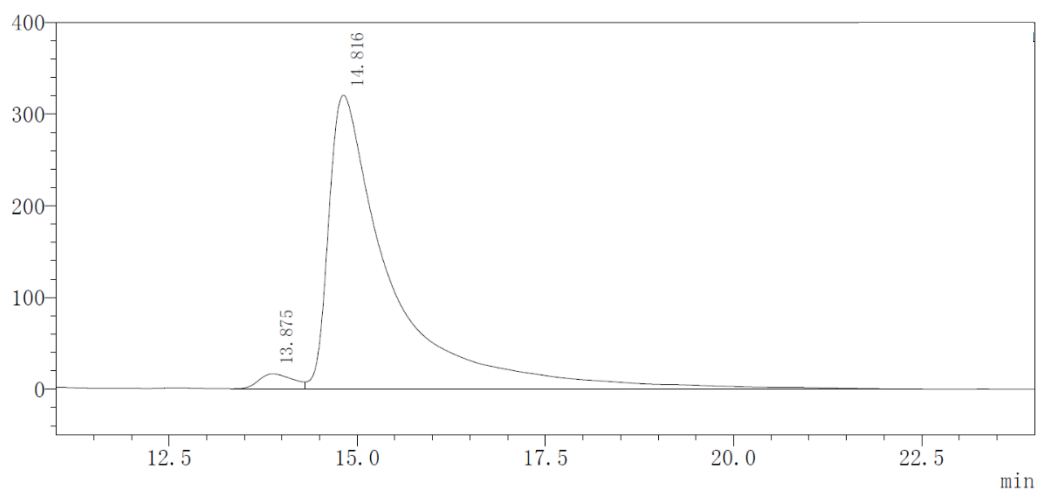
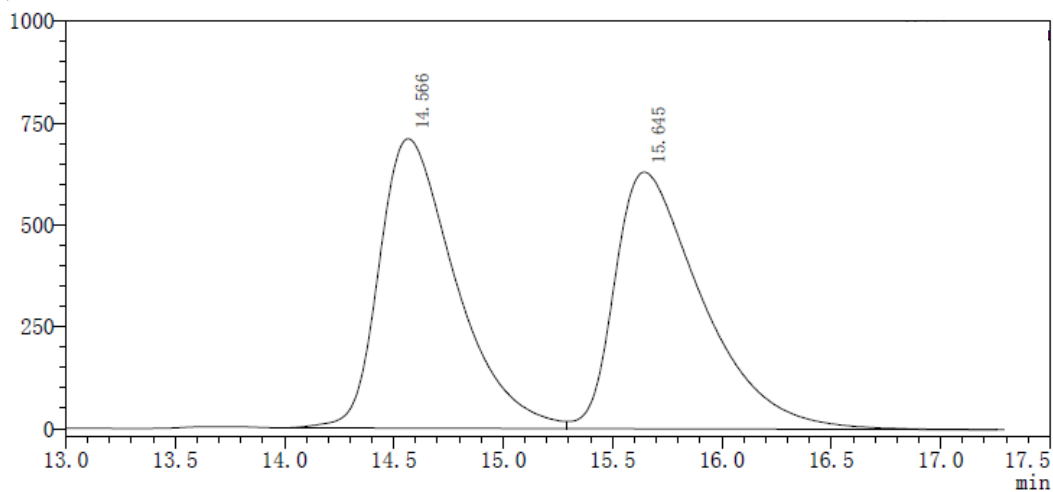


Serial Number	Retention Time [min]	Area	Area %
1	14.876	971658	6.795
2	18.454	13327397	93.205

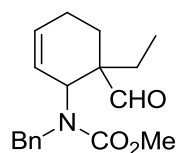


N-Benzyl-N-(6-formyl-3,6-dimethyl-2-cyclohexen-1-yl)carbamic Acid Methyl Ester

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 98/2, 1.0 mL/min, 220 nm), $t_{major} = 14.816$ min, $t_{minor} = 13.875$ min; ee = 95%.

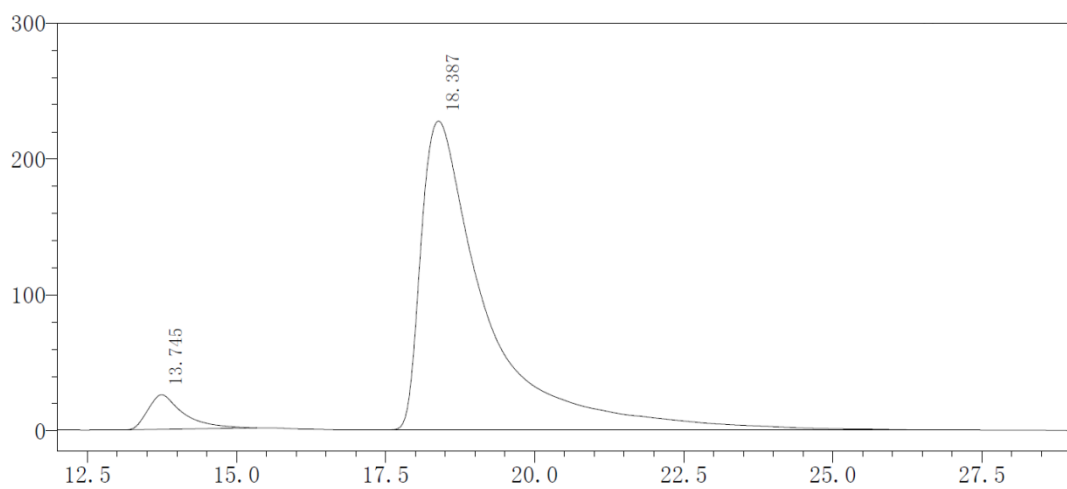
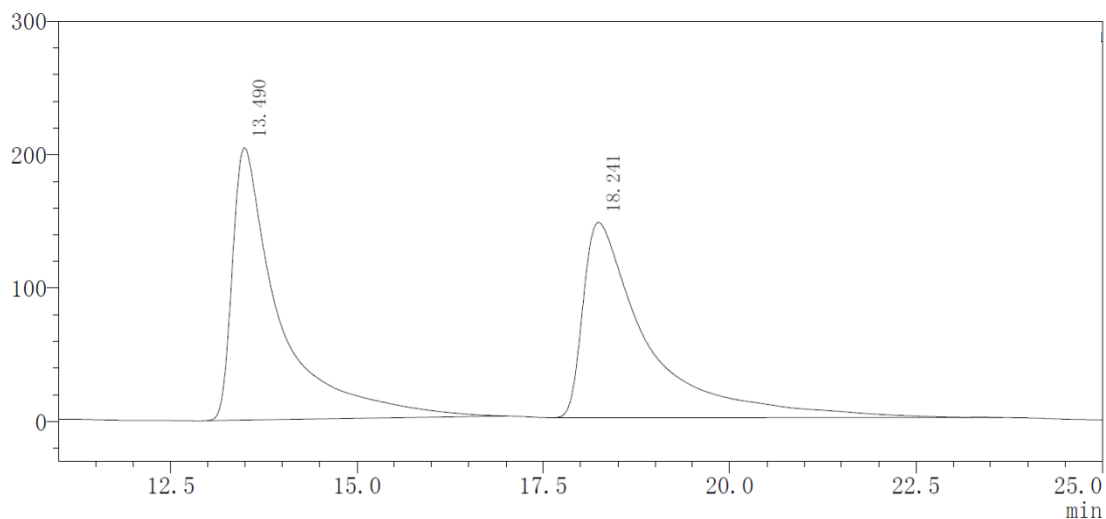


Serial Number	Retention Time [min]	Area	Area %
1	13.875	507485	2.655
2	14.816	18606624	97.345

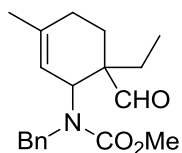


N-Benzyl-N-(6-formyl-6-ethyl-2-cyclohexen-1-yl)carbamic Acid Methyl Ester

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 98/2, 1.0 mL/min, 220 nm), $t_{major} = 18.387$ min, $t_{minor} = 13.490$ min; ee = 89%.

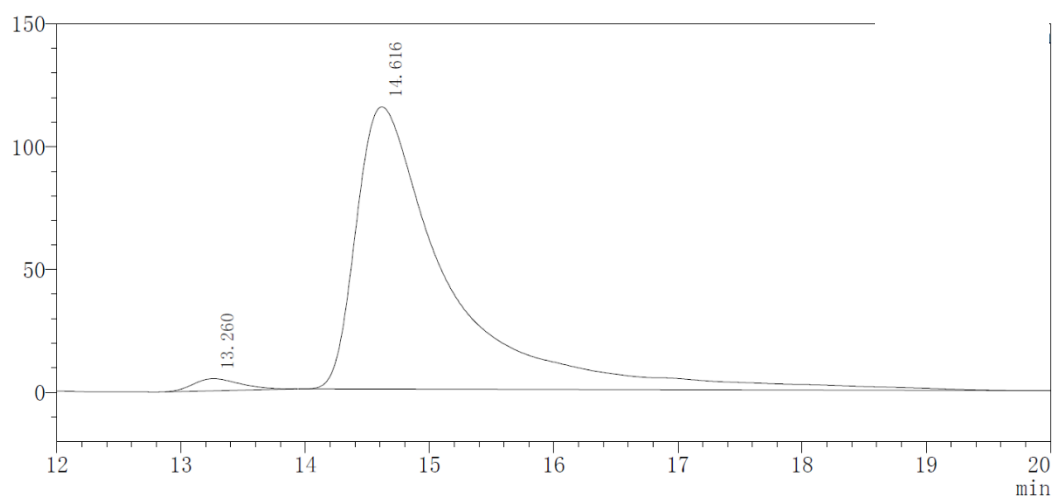
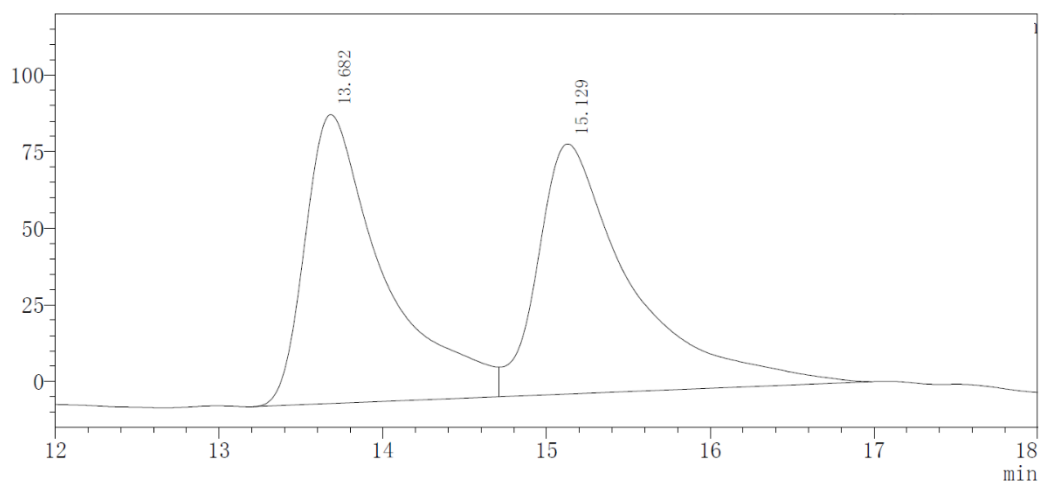


Serial Number	Retention Time [min]	Area	Area %
1	13.745	1053398	5.697
2	18.387	17437363	94.303



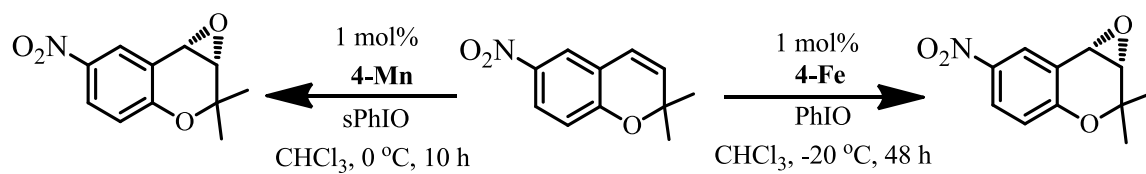
N-Benzyl-N-(6-formyl-3-ethyl-6-methyl-2-cyclohexen-1-yl)carbamic Acid Methyl Ester

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/*i*-PrOH = 98/2, 1.0 mL/min, 220 nm), $t_{major} = 14.616$ min, $t_{minor} = 13.260$ min; ee = 96%.

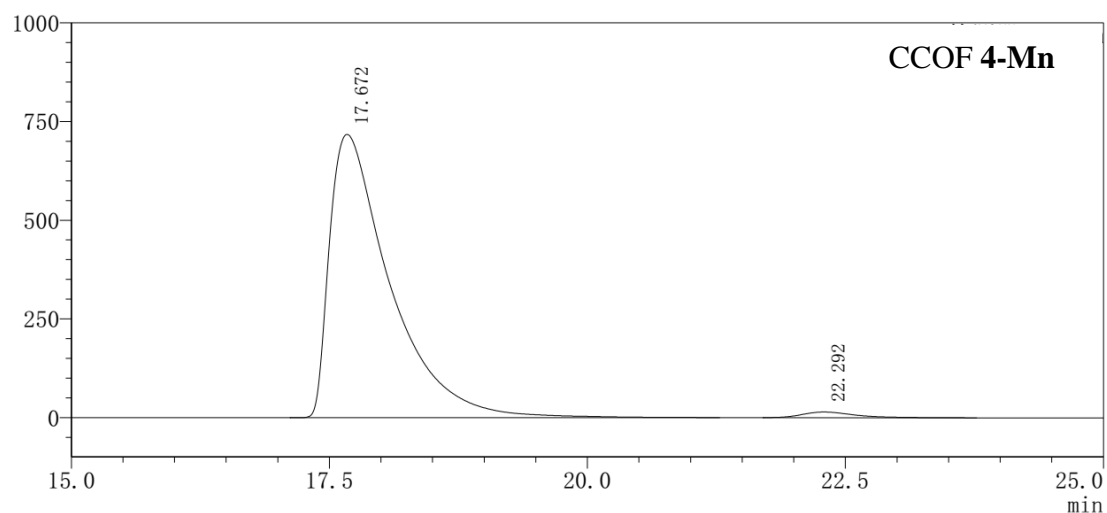


Serial Number	Retention Time [min]	Area	Area %
1	13.260	129685	2.122
2	14.616	5982988	97.878

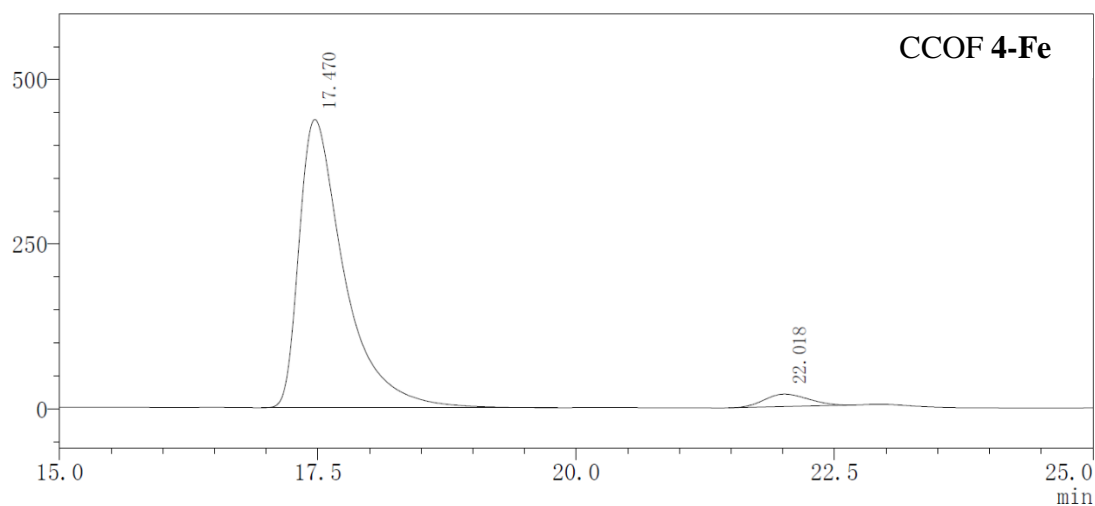
16.3.6 Recycled experiments of alkene epoxidation



Run 1

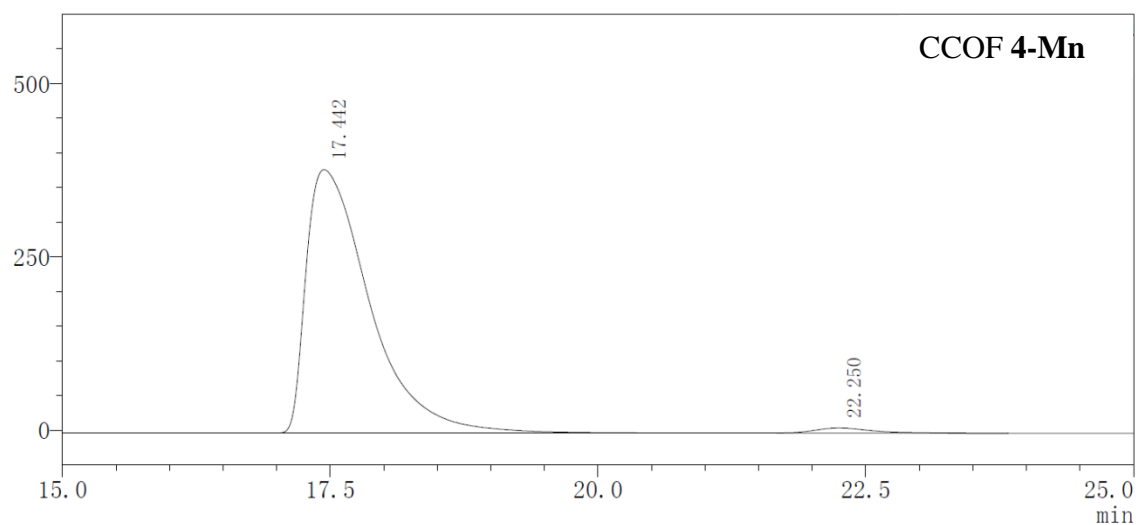


Serial Number	Retention Time [min]	Area	Area %
1	17.672	29341461	98.312
2	22.292	503858	1.688

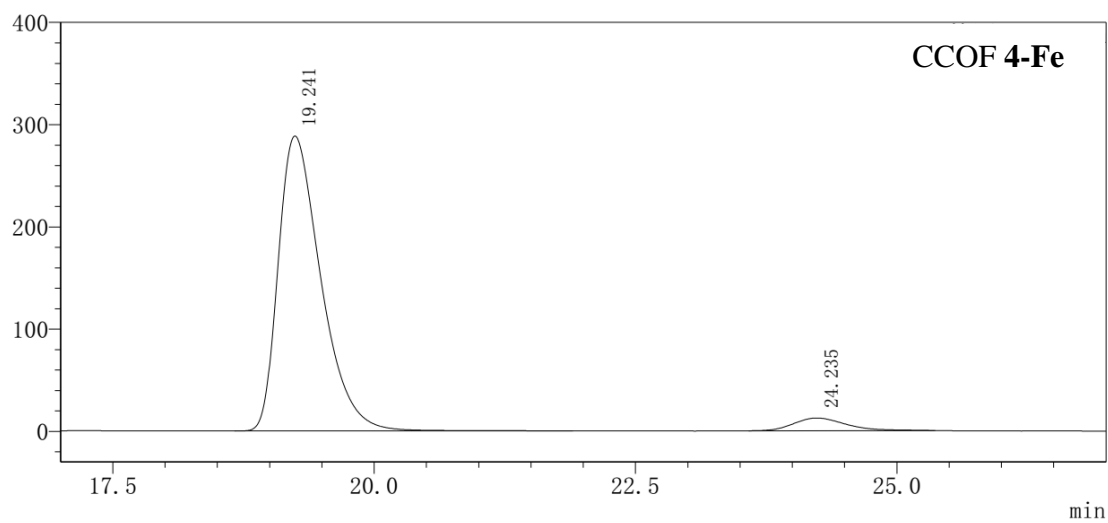


Serial Number	Retention Time [min]	Area	Area %
1	17.470	13326929	95.953
2	22.018	562082	4.047

Run 2

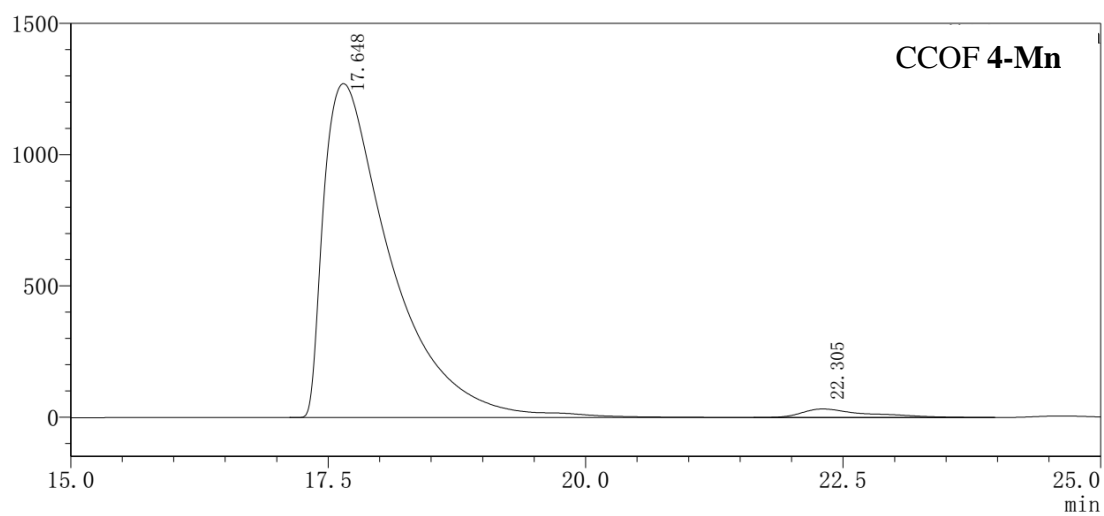


Serial Number	Retention Time [min]	Area	Area %
1	17.442	15725645	98.292
2	22.250	273185	1.708

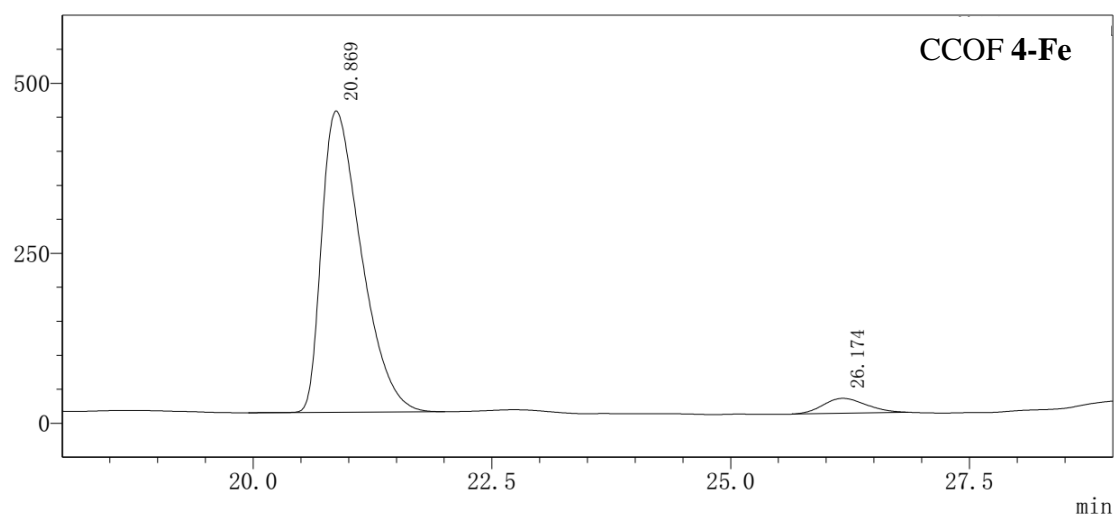


Serial Number	Retention Time [min]	Area	Area %
1	19.241	8194359	95.019
2	24.235	429525	4.981

Run 3

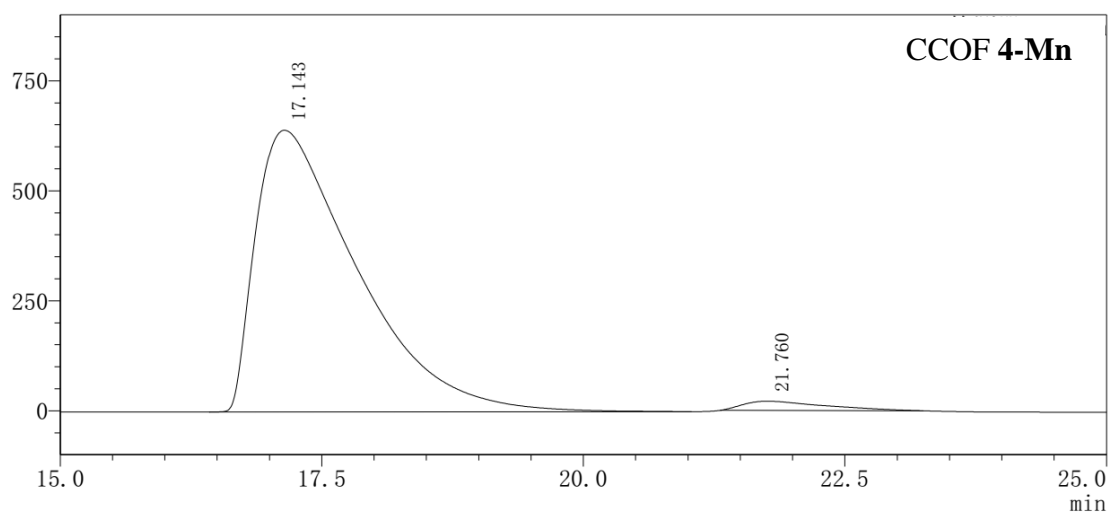


Serial Number	Retention Time [min]	Area	Area %
1	17.648	58140284	97.599
2	22.305	1430215	2.401

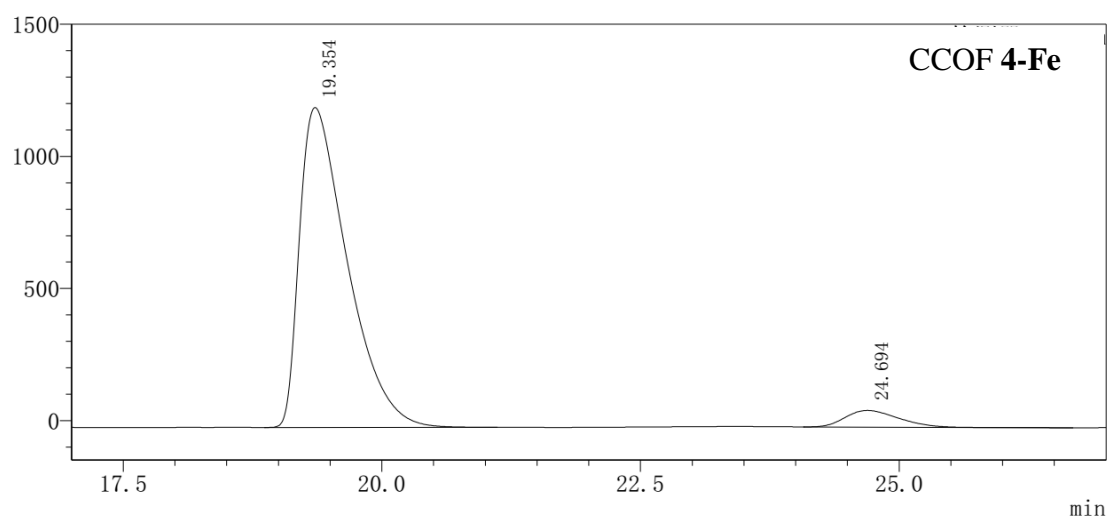


Serial Number	Retention Time [min]	Area	Area %
1	20.869	12806038	94.881
2	26.174	690968	5.119

Run 4

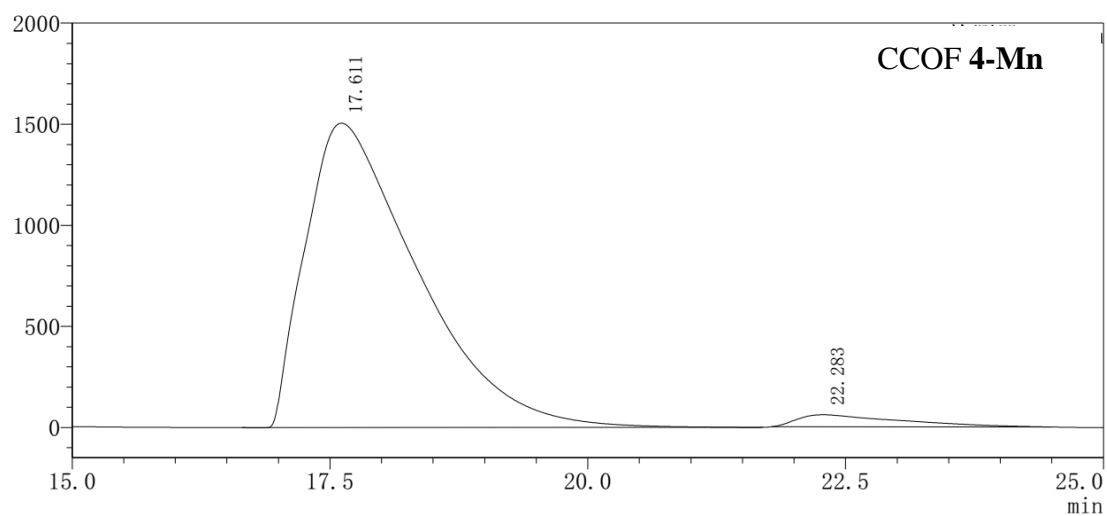


Serial Number	Retention Time [min]	Area	Area %
1	17.143	43226473	97.423
2	21.760	1143360	2.577

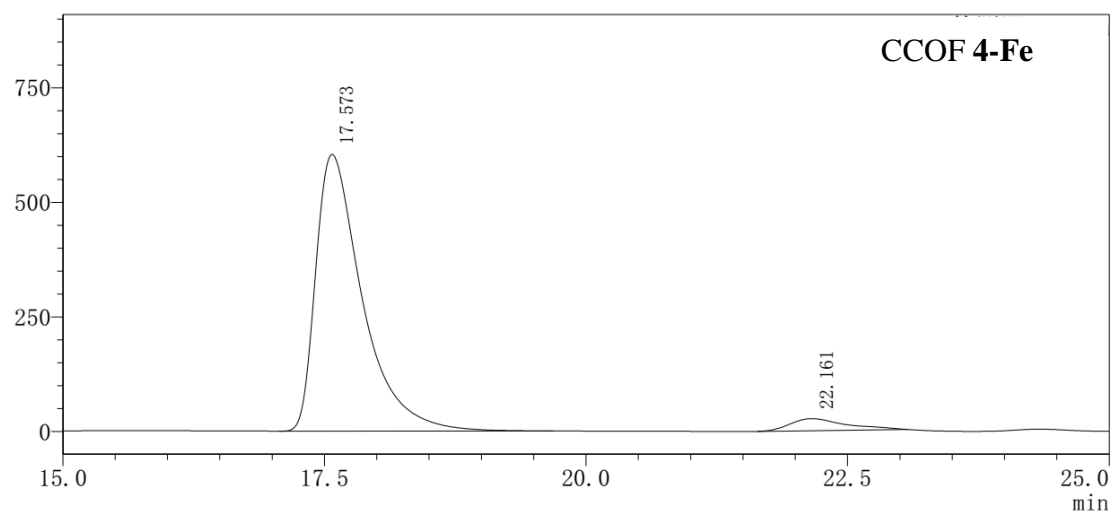


Serial Number	Retention Time [min]	Area	Area %
1	19.354	38958119	94.481
2	24.694	2275818	5.519

Run 5

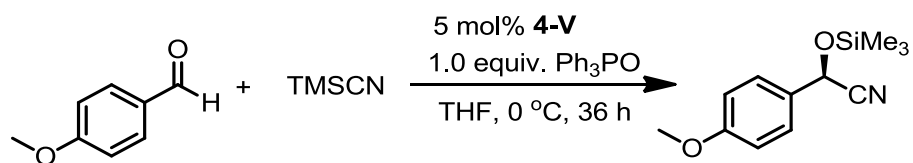


Serial Number	Retention Time [min]	Area	Area %
1	17.611	114127723	96.499
2	22.283	4140176	3.501

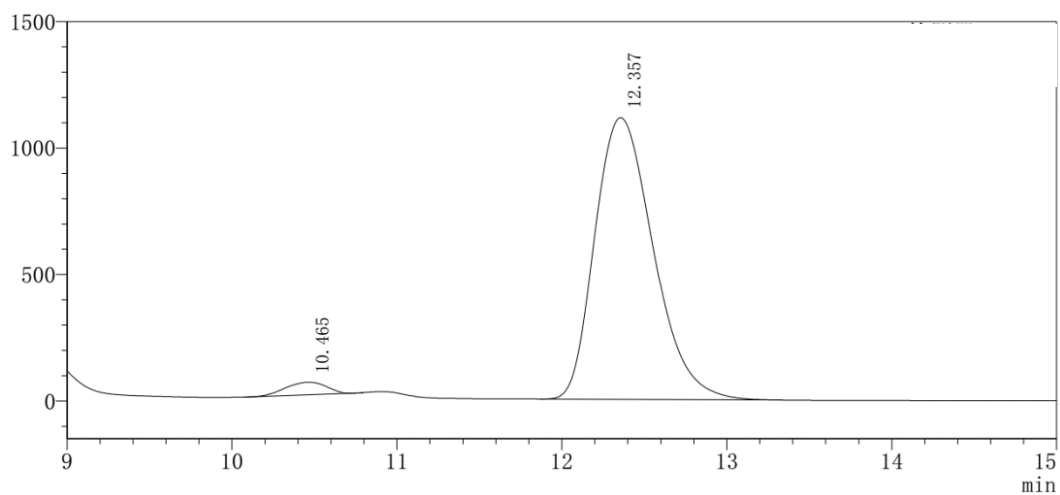


Serial Number	Retention Time [min]	Area	Area %
1	17.573	18733520	95.053
2	22.161	974981	4.947

16.3.7 Recycled experiments of cyanohydrins reaction

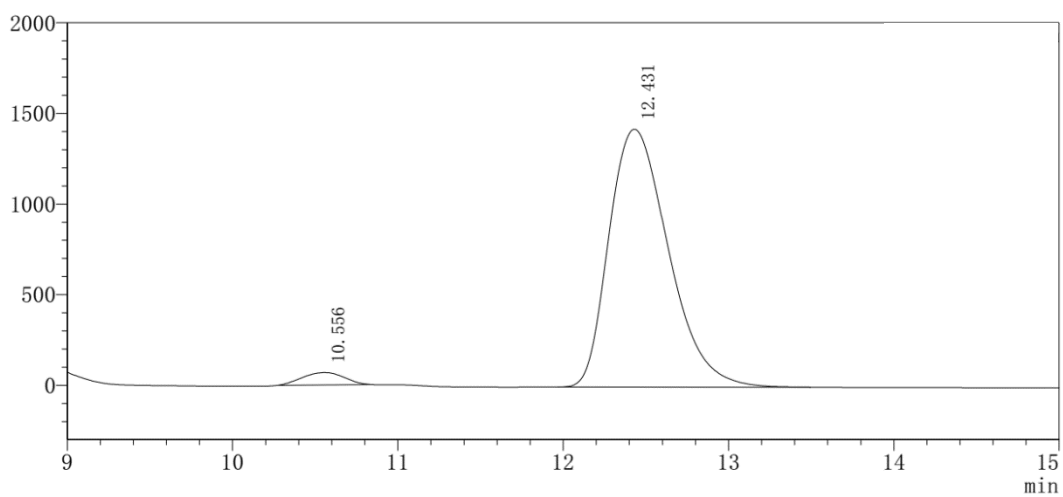


Run 1



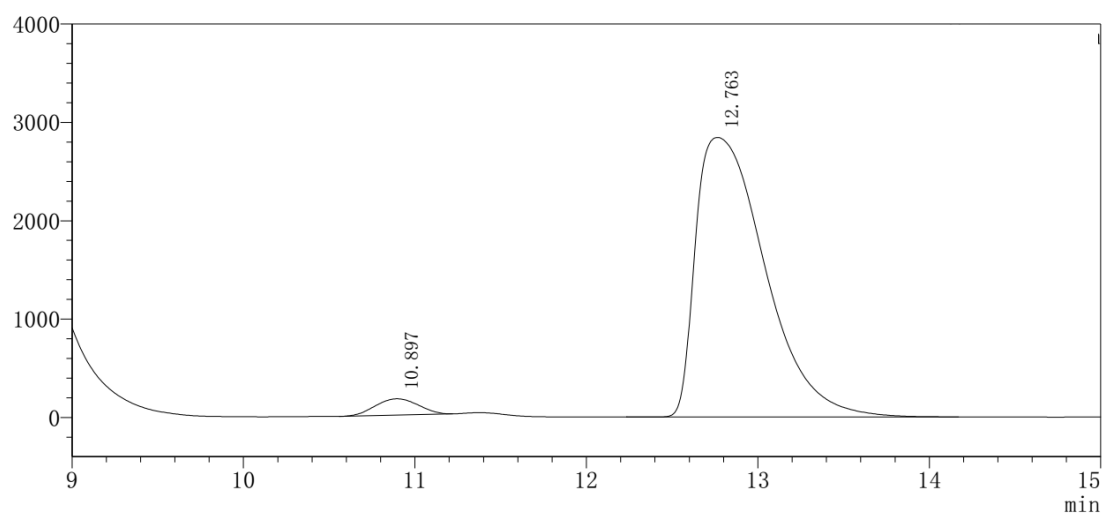
Serial Number	Retention Time [min]	Area	Area %
1	10.456	851170	3.008
2	12.357	27446925	96.992

Run 2



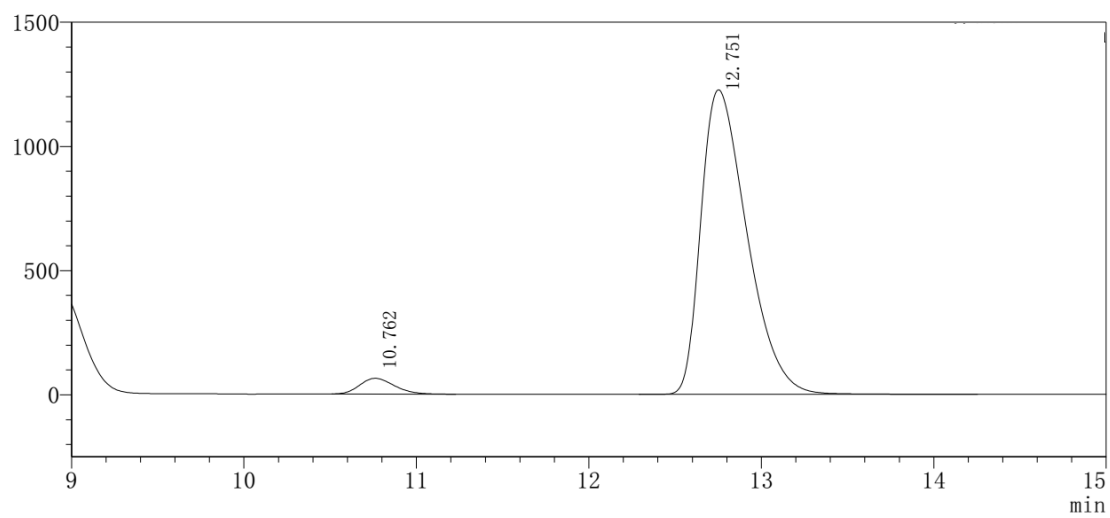
Serial Number	Retention Time [min]	Area	Area %
1	10.556	1205908	3.281
2	12.431	35547845	96.719

Run 3



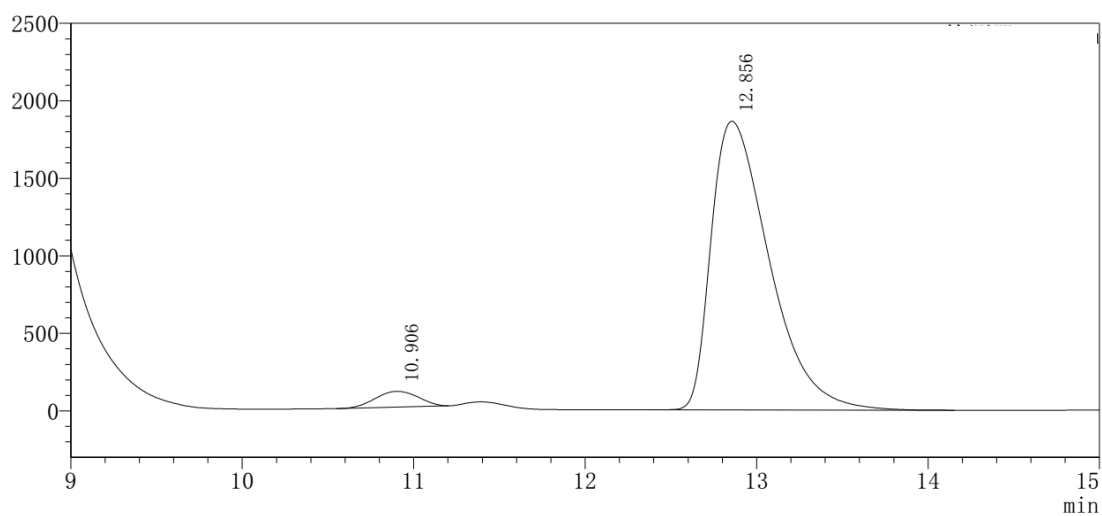
Serial Number	Retention Time [min]	Area	Area %
1	10.897	2908891	3.507
2	12.763	80036399	96.493

Run 4



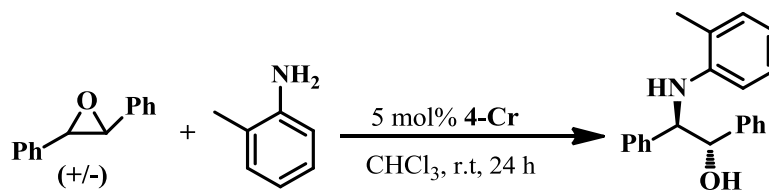
Serial Number	Retention Time [min]	Area	Area %
1	10.762	891370	3.774
2	12.751	22724399	96.226

Run 5

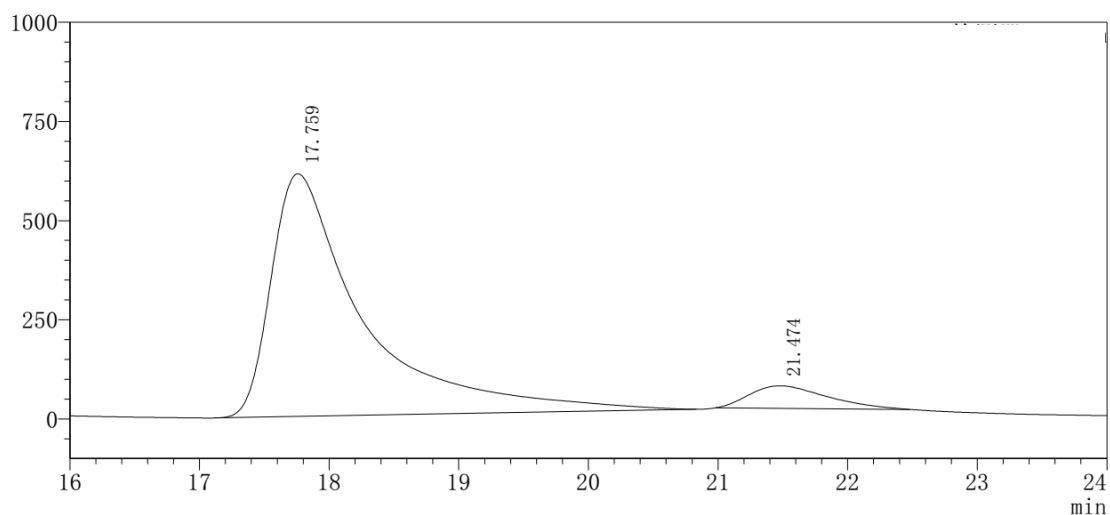


Serial Number	Retention Time [min]	Area	Area %
1	10.906	1777553	3.882
2	12.856	44103283	96.118

16.3.8 Recycled experiments of Aminolysis of trans-Stilbene Oxide with Anilines.

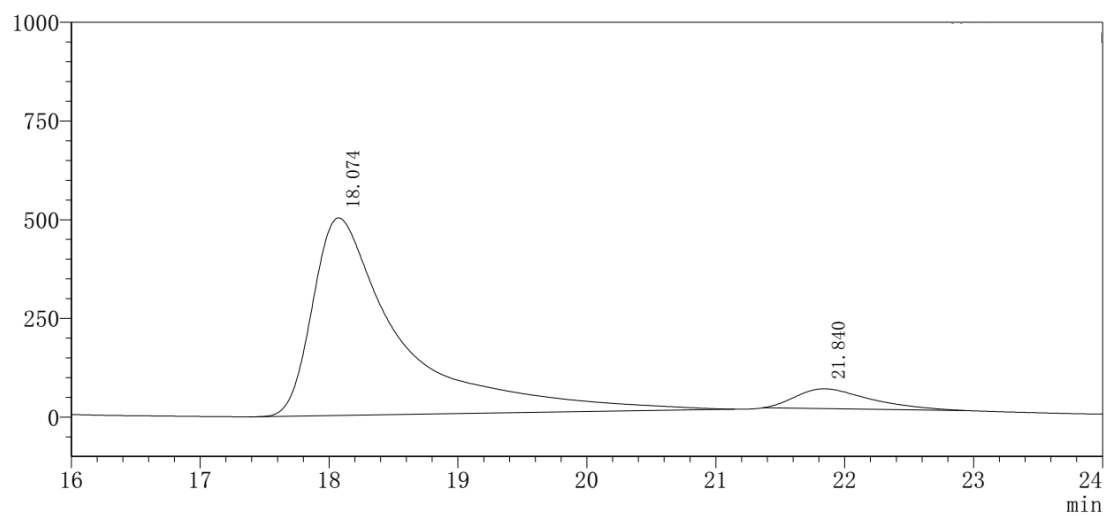


Run 1



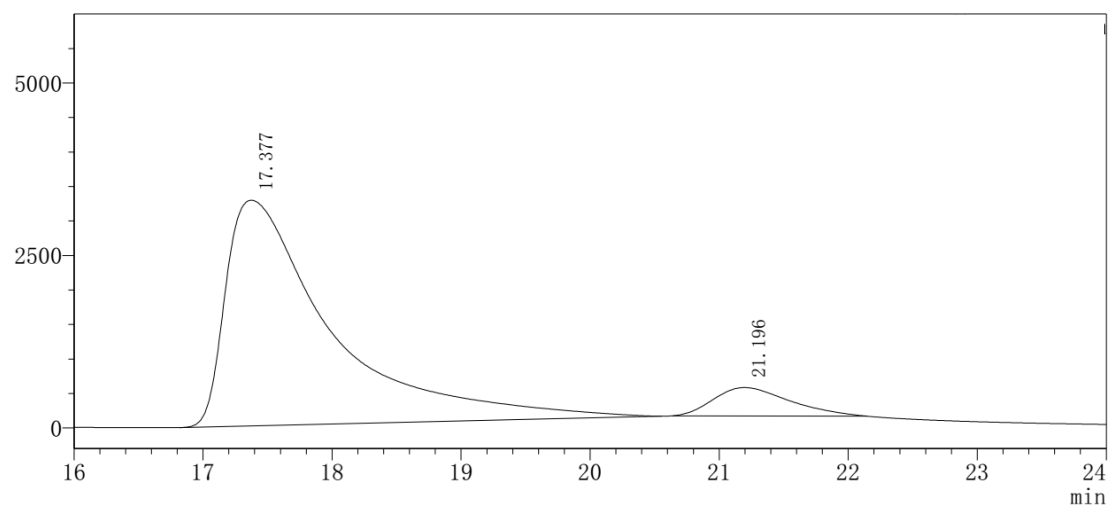
Serial Number	Retention Time [min]	Area	Area %
1	17.759	30244024	92.752
2	21.474	2363268	7.248

Run 2



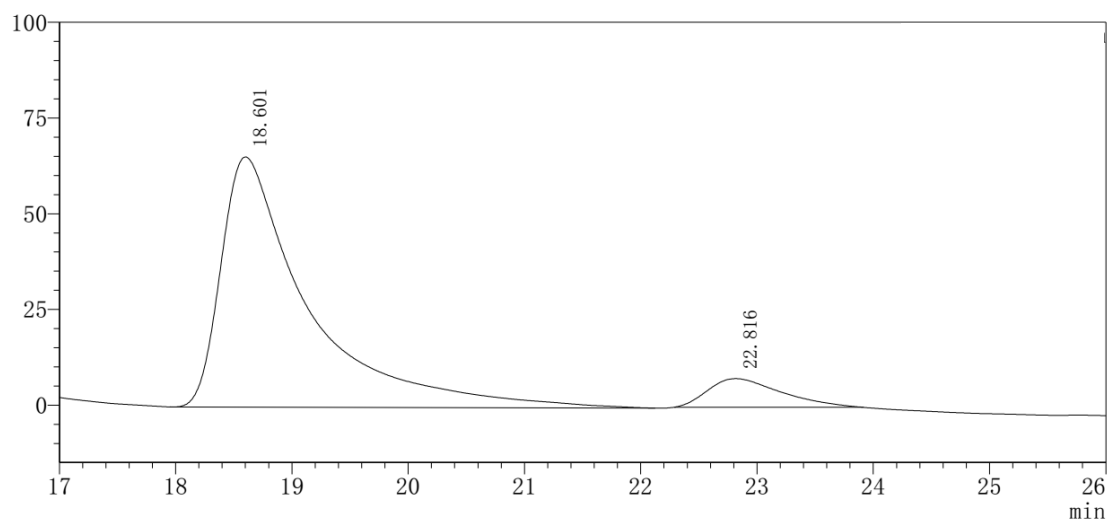
Serial Number	Retention Time [min]	Area	Area %
1	18.074	23944152	92.238
2	21.840	2015047	7.762

Run 3



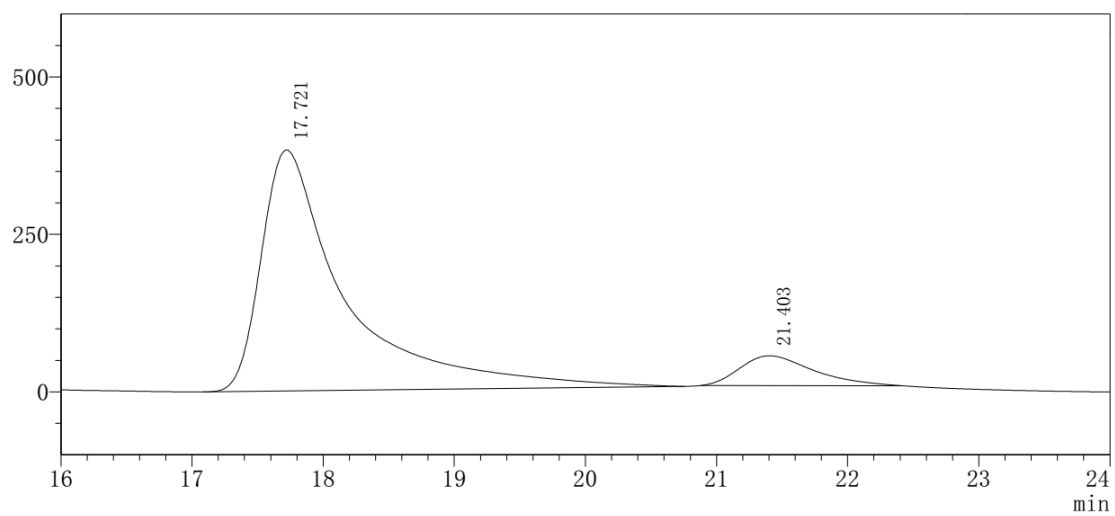
Serial Number	Retention Time [min]	Area	Area %
1	17.377	186201087	91.706
2	21.196	16840463	8.294

Run 4



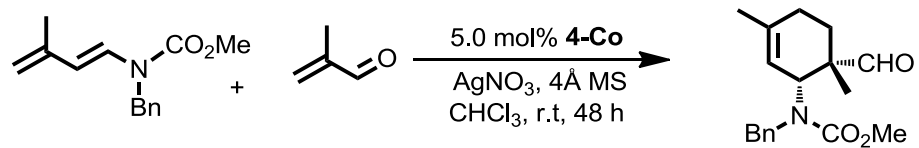
Serial Number	Retention Time [min]	Area	Area %
1	18.601	3402529	91.233
2	22.816	326947	8.767

Run 5

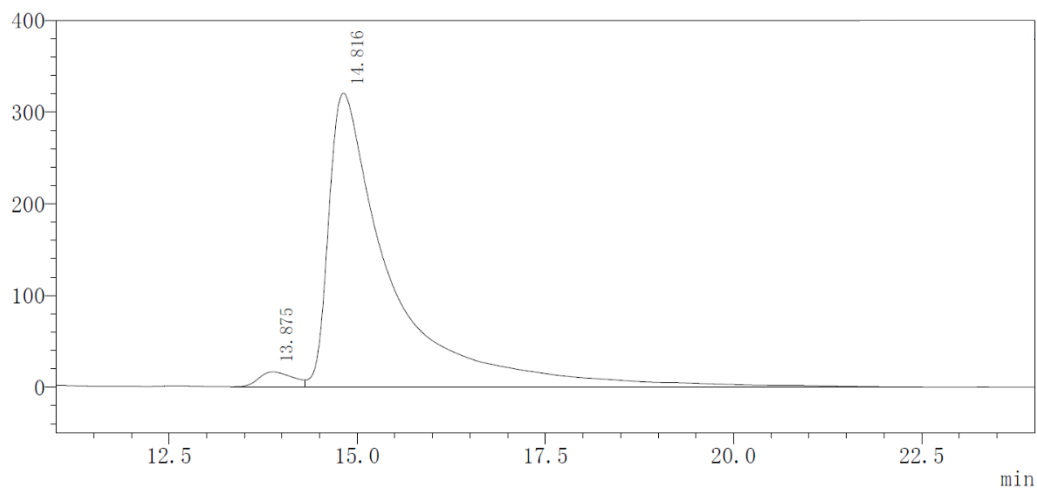


Serial Number	Retention Time [min]	Area	Area %
1	17.721	17137506	90.317
2	21.403	1837395	9.683

16.3.9 Recycled experiments of Diels-Alder reaction

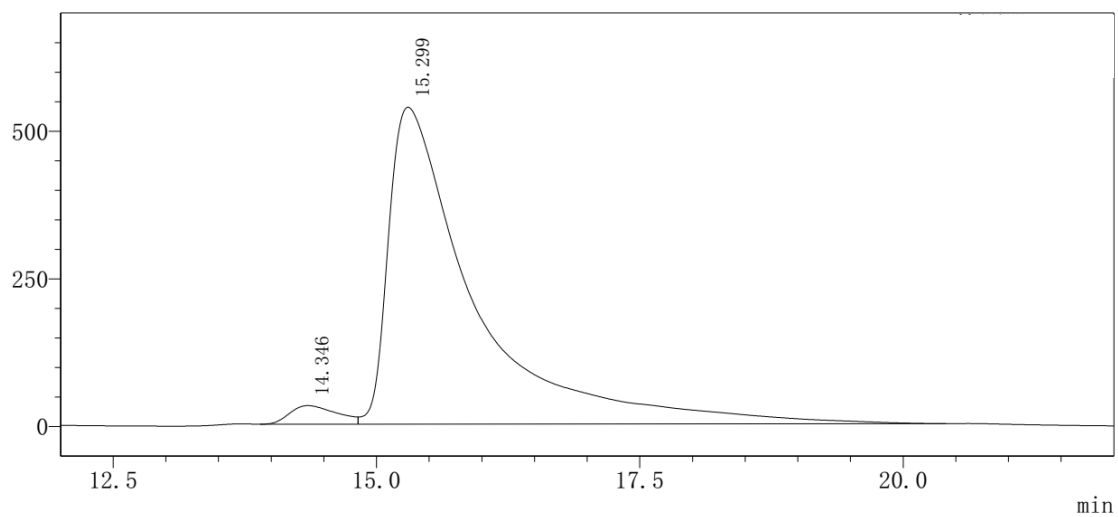


Run 1



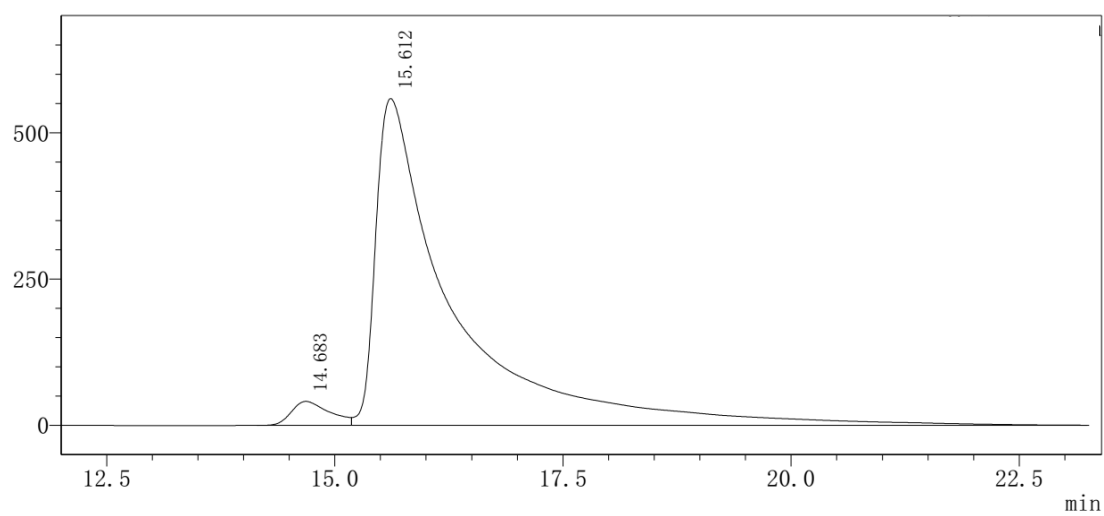
Serial Number	Retention Time [min]	Area	Area %
1	13.875	507485	2.655
2	14.816	18606624	97.345

Run 2



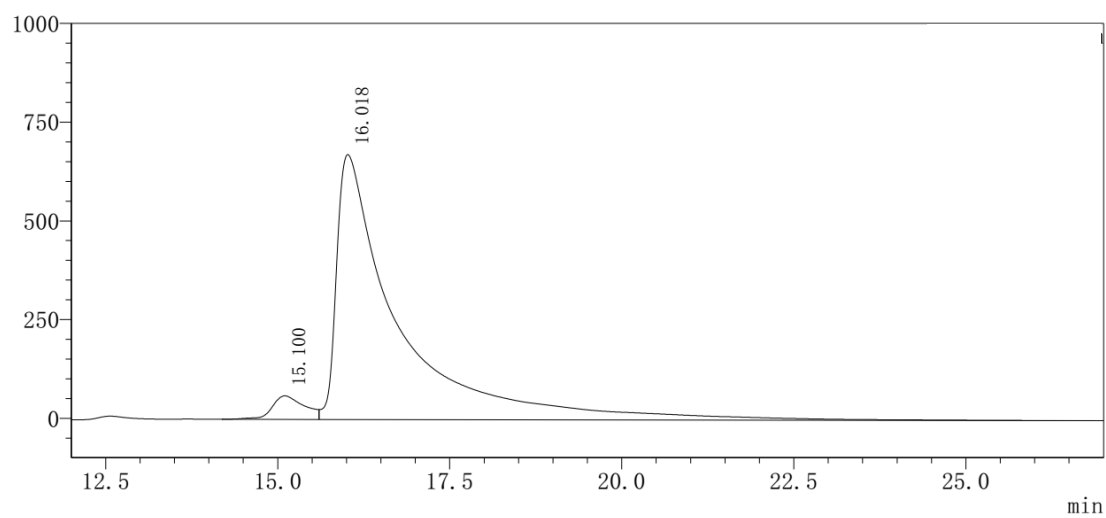
Serial Number	Retention Time [min]	Area	Area %
1	14.346	985920	3.121
2	15.299	30606937	96.879

Run 3



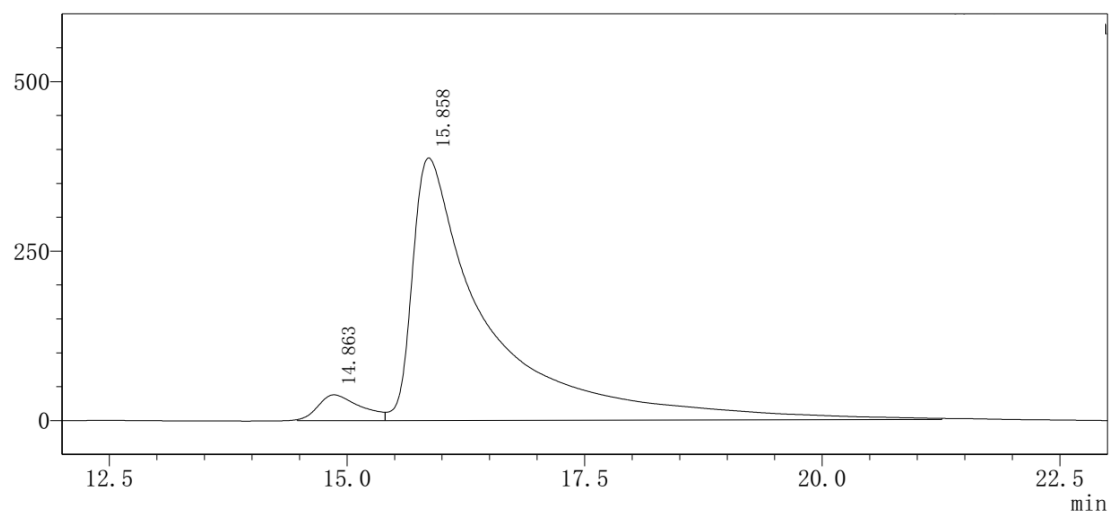
Serial Number	Retention Time [min]	Area	Area %
1	14.683	1201350	3.504
2	15.612	33085205	96.496

Run 4



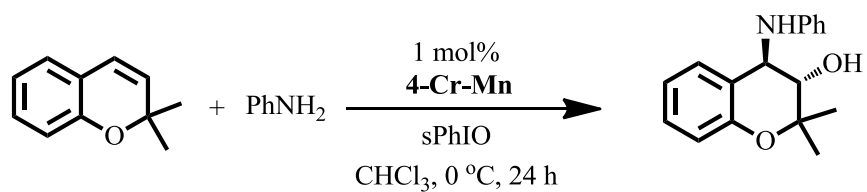
Serial Number	Retention Time [min]	Area	Area %
1	15.100	1945096	4.386
2	16.018	42404997	95.614

Run 5

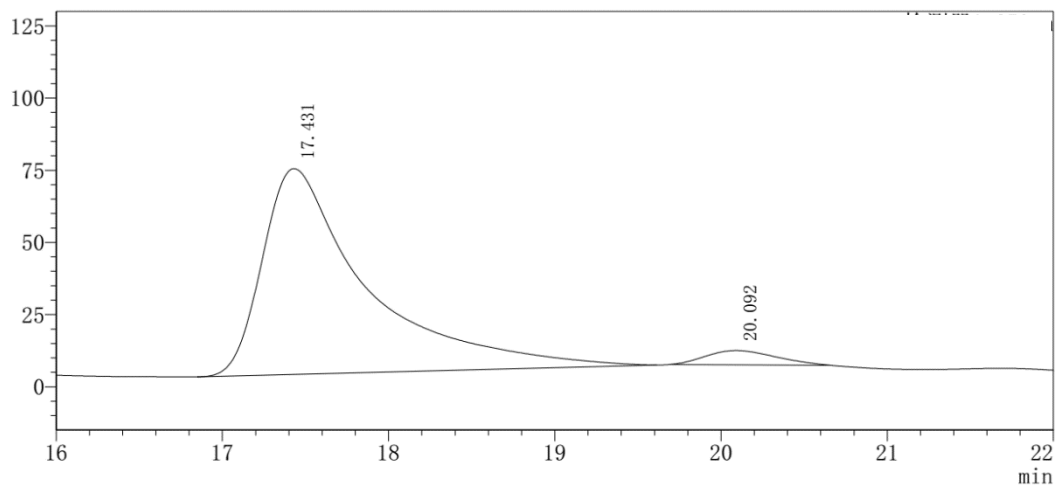


Serial Number	Retention Time [min]	Area	Area %
1	14.863	1205816	5.198
2	15.858	21992391	94.802

16.3.10 Recycled experiments of alkene epoxidation/epoxide aminolysis

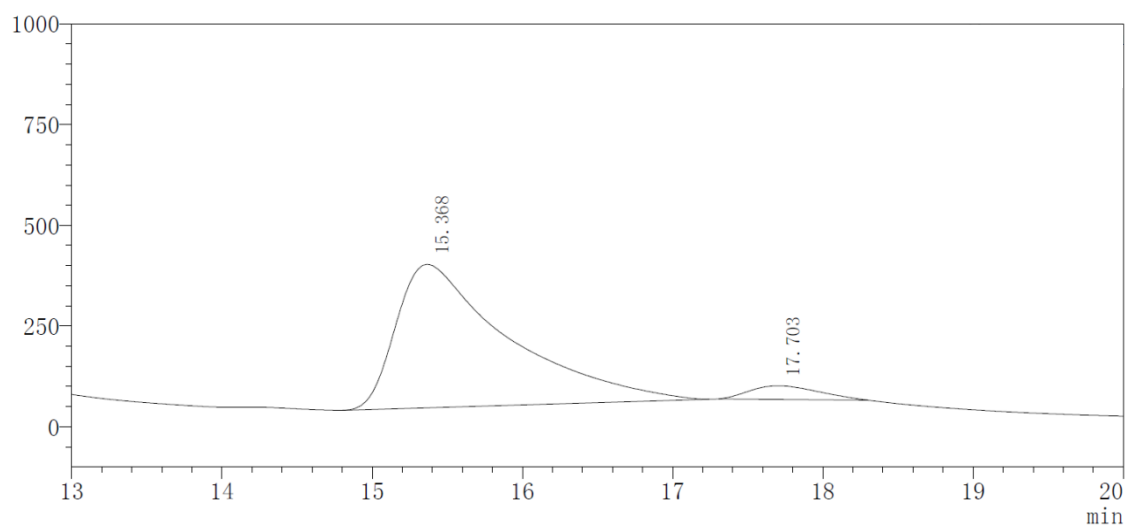


Run 1



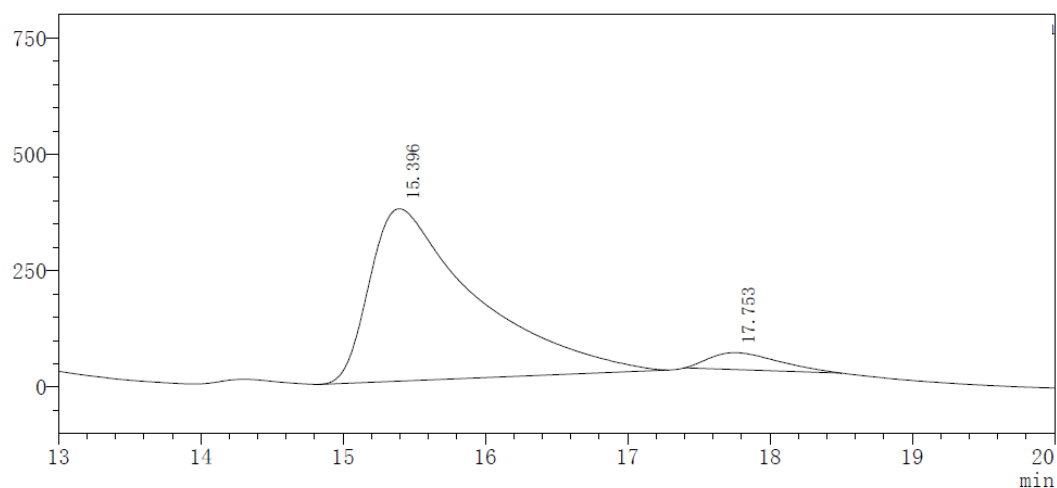
Serial Number	Retention Time [min]	Area	Area %
1	17.431	3117608	95.522
2	20.092	146168	4.478

Run 2



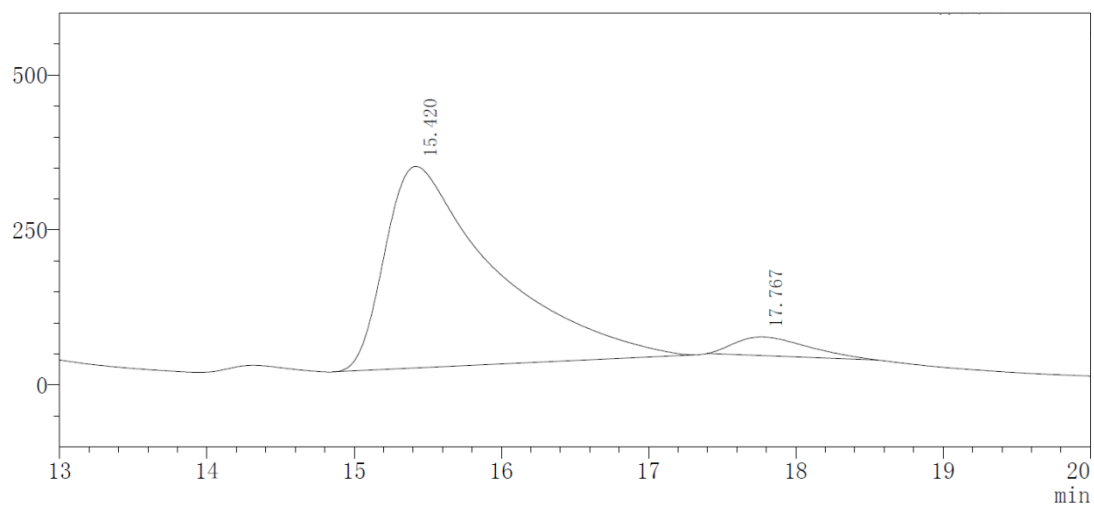
Serial Number	Retention Time [min]	Area	Area %
1	15.368	18429288	94.467
2	17.703	33852	5.553

Run 3



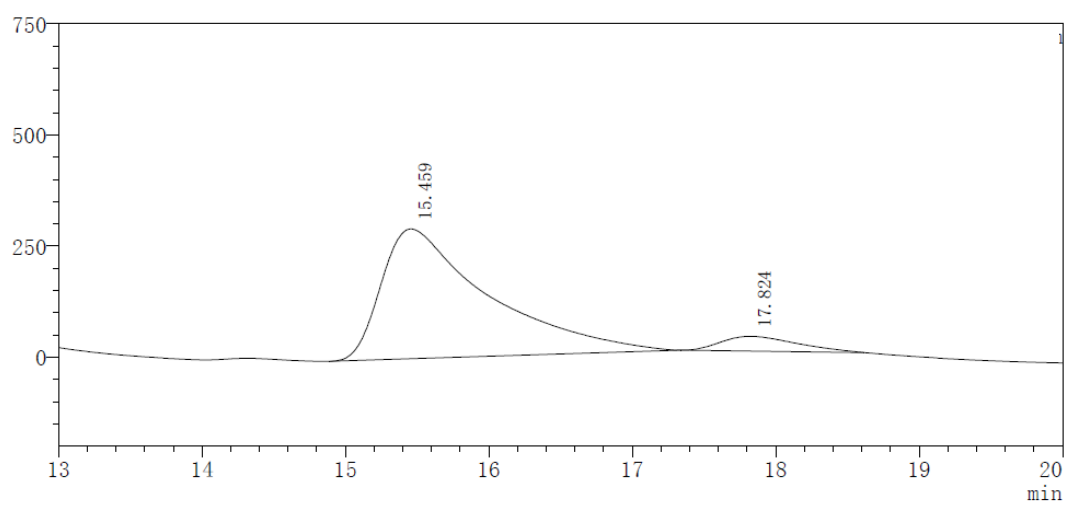
Serial Number	Retention Time [min]	Area	Area %
1	15.396	370466	93.931
2	17.753	36409	6.096

Run 4



Serial Number	Retention Time [min]	Area	Area %
1	15.420	325088	94.127
2	17.767	30066	5.873

Run 5



Serial Number	Retention Time [min]	Area	Area %
1	15.459	292126	92.503
2	17.824	33180	7.497