Electronic Supplementary Material (ESI) for ChemComm.

The first porphyrin-salen based chiral metal-organic framework for asymmetric cyanosilylation of aldehydes

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Contents

1. Materials and methods

All of the reagents were commercially available and were used without further purification. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 powder diffractometer at 40 kV, 40 mA with Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 17.7 s/step and a step size of 0.01995^{o} (2θ). Solid-state circular dichroism (CD) spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). Thermogravimetric analyses (TGA) were performed on a Q600 SDT instrument under a flow of N_2 at a heating rate of 10^{o}C/min. ^{1}H NMR and ^{13}C NMR were done on a Bruker Model AM-400 (400 MHz) spectrometer. Elemental analyses (EA) for C, H and N were carried out using a Vario EL III Elemental Analyzer. Infrared (IR) spectra were measured from a KBr pellets on a Nicolet Model Nexus 470 FT-IR spectrometer in the range of 4000-400 cm^{-1}. Gas chromatography-mass spectroscopy (GC-MS) spectrometry was recorded on Shimadzu Model GCMS-QP5050A system that was equipped with a 0.25mm×30m DB-WAX capillary column. The content of metal ions was determined by Atomic Absorption Spectrometer (Z-2000, HITACHI). The gas adsorption measurement was performed on a MicroActive ASAP 2460 systems under N_2 (77 K) and CO_2 (273 K). HPLC was recorded on Agilent 1200 series system with a Analytical CHIRALCEL OD-H chiral column from Daicel for enantiomeric excess determination.

Single-crystal XRD analyses of **1** was performed on an Xcalibur Onyx Nova four-circle diffractometer using CuKα radiation (λ =1.54184 Å) at 100 K. The empirical absorption correction was performed using the CrystalClear program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares technique using the SHELX-97 program package.[1] The Cd and Ni atoms in the asymmetric unit were located firstly from the difference Fourier map and refined anisotropically. The other atoms (O, C and N) in the salen and porphyrin rings were then located from the difference Fourier map and partly refined isotropically, as a result of the relatively weak diffraction, (which is not uncommon for this kind of framework with large solvent accessible void space). Restraints (DELU and SIMU) on displacement parameters, and DFIX for bond lengths of salen framework were applied, and all phenyl rings of 1,2-diphenylethylenediimine on salen ligand were constrained to ideal six-member rings. SQUEEZE subroutine of the PLATON software suite[2] was applied to remove the scattering from the highly disordered guest molecules. The resulting new HKL file was used to further refine the structure. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined

using a riding model. The final values of refinement parameters are listed in Table S1. Note that the contributions of guest molecules have been included in the overall formula, formula weight, density, F(000) calculations reported in Table S1 and in the CIF. CCDC 1537778 contains the supplementary crystallographic data for this paper.

2. Synthesis

CdL^2 was synthesized according to the literature.[3]

2.1 Synthesis of L^1

A mixture of compound 3-tert-butyl-5-(4-pyridyl)salicylaldehyde (510.8 mg, 2 mmol), (R, R)-1,2-diphenylethylenediamine (212 mg, 1 mmol, 0.5 equiv), in EtOH (15 mL) was heated to reflux for 8 h before being allowed to cool to room temperature. The solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel with EtOAc to get a yellow solid. Yield: 629 mg (91 %). Melt Point: 132.5-133.2 ^{o}C. IR (ν/cm^{-1}): 3399.7, 3028.7, 2955.7, 2911.2, 2871.2, 1625.9, 1594.7, 1445.7, 1391.6, 1265.9, 1170.4, 1056.2, 990.5, 890.4, 821.3, 773.2, 703.6, 623.7, 545.6, 511.3. Elemental analysis, calcd. for $C_{46}H_{46}N_4O_2$: C, 80.43; H, 6.75; N, 8.16; found: C, 80.39; H, 6.78; N, 8.13. ^{1}H NMR ($CDCl_3$): δ 14.08(s, 2H), 8.57(s,4H), 8.42(s, 2H), 7.51(s, 2H), 7.33(s, 4H), 7.24(s, 12H), 4.79(s,2H), 1.44(s, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 166.84, 161.34, 150.03, 147.95, 138.93, 138.39, 128.54, 128.46, 128.30, 127.98, 127.85, 127.58, 120.87, 118.82, 80.06, 35.05, 29.24.

2.2 Synthesis of NiL^1

A solution of above metal-free salen ligand (0.365 g, 0.5 mmol) in MeOH (30 mL) was added dropwise to $Ni(OAc)_2{\cdot}4H_2O$ (0.125 g, 0.5 mmol) in MeOH (30 mL). The reaction mixture was stirred at room temperature for 2 h, and then reflux for 3 h. The resulted red powder was collected by filtration, washed with MeOH and dried under reduced pressure. Yield: 717 mg (96 %). Melt Point: 401.8-402.3 ^{o}C. IR: 3028.5, 2949.2, 2908.7, 1611.8, 1588.3, 1548.5, 1496.5, 1438.5, 1398.4, 1331.6, 1287.7, 1263.9, 1233.5, 1174.1, 1080.5, 991.6, 900.2, 860.9, 824.4, 788.2, 763.2, 698.7, 637.9, 619.6, 575.3, 520.5. EA, calcd. for $C_{46}H_{44}N_4NiO_2$: C, 74.30; H, 5.96; N, 7.53; found: C, 74.26; H, 6.01; N, 7.47. HR-MS: m/z, 743.2914 ($M+H^+$).

2.3 Synthesis of 1

Solvothermal reaction of $Cd(NO_3)_2{\cdot}6H_2O$ (30.8 mg, 0.1 mmol), L^1 (3.7 mg, 0.005 mmol) and L^2 (4 mg, 0.005 mmol) was performed in a mixture solvent of N,N-dimethylformamide and

methanol (DMF/CH_3OH, 3mL/1.5mL) in a 10 mL vial and heated at 60 °C for three days, then the reaction was cooled to room temperature at a rate of 5 °C/h. The product was isolated by decanting the mother liquor and washing with DMF. Yield: 16 mg (76 %). IR: 3770, 3480, 3400, 3114, 2943, 2385, 1671, 1602, 1536, 1410, 1097, 974, 859, 791, 723, 490. EA, calcd. for $C_{211}H_{200}Cd_5N_{22}Ni_2O_{31}$: C, 60.06; H, 4.78; N, 7.3; found: C, 59.77; H, 4.92; N, 7.12.

3. Catalytic Experiments

3.1 Asymmetric cyanosilylation of aldehydes

A mixture of catalyst **1** (1 mol%) and aldehyde (1 mmol) in 1 mL dichloromethane was stirred at room temperature for 0.5 h. Another mixture of TMSCN (1.2 mmol) and PPh_3O (1 mmol) was also stirred in 1mL dichloromethane at room temperature for 0.5 h. These two batches of mixtures were then combined at -20 °C and proceeded for 48 h. After completion of the reaction, the mixture was centrifuged for 5 min to remove the solid phrase and the filtrate was analyzed by GC-MS to determine the conversion.

After that, the filtrates were extracted with ethyl acetate (3 × 15 mL) and washed with water (20 mL), dried over anhydrous $MgSO_4$ and evaporated under vacuum to give the crude cyanohydrins. A mixture of crude cyanohydrins, pyridine (4 mmol) and acetic anhydride (3 mmol) was immersed in 2 mL dichloromethane and stirred at room temperature for 1 h. After that, the mixture was extracted by ethyl acetate (20 mL) and 1 M HCl (10 mL). Then, the organic layer was washed with water (3 × 20 mL), dried over anhydrous $MgSO_4$ and evaporated under vacuum to give the *o*-acetyl cyanohydirn. The ee value of the *o*-acetyl cyanohydirn was then determined by CHIRALCEL OD-H chiral column.

3.2 Recyclability tests

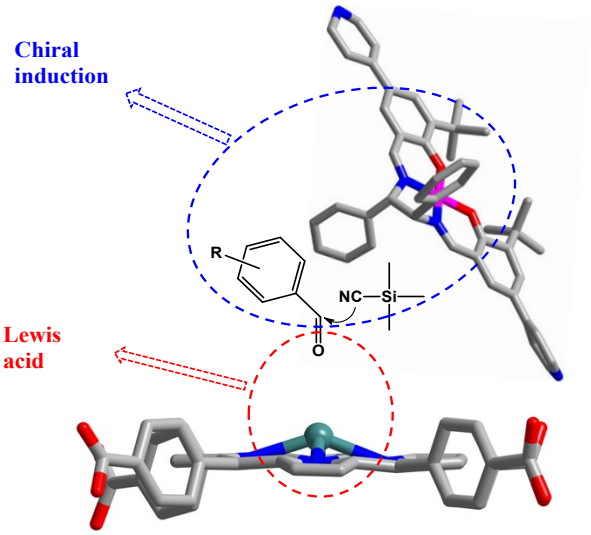
Upon completion of the reaction, the solid phrase was collected after centrifugation. After washing the catalysts with DMF three times, **1** was dried at 150 °C for 4 h under reduced pressure. Then it was ready for the next run.

4. Table 1. Crystallographic data and structure refinement for 1.

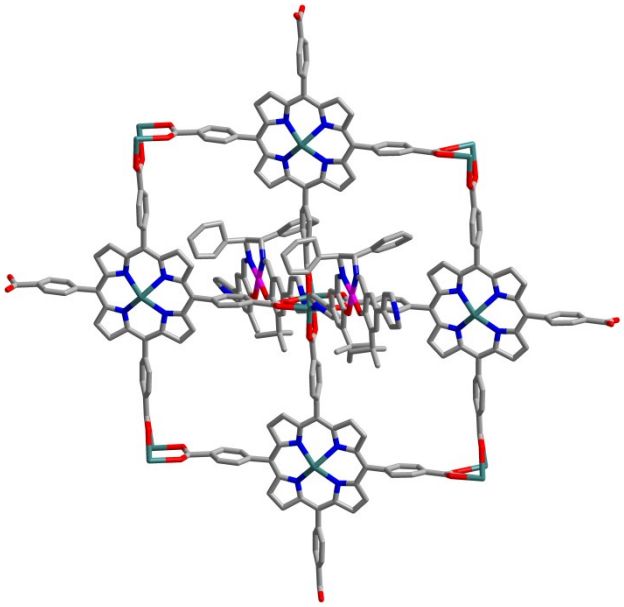
MOFs	**1**
Empirical formula	$C_{211}H_{200}Cd_5N_{22}Ni_2O_{31}$
Formula weight	4219.42
T (K)	100(2)
Wavelength (Å)	1.54178
Crystal system	Triclinic
Space group	*P1*
a /Å	16.3993(4)
b/Å	17.3042(3)
c/Å	24.3278(10)
α/°	85.324(2)
β/°	78.917(3)
γ/°	89.496(2)
V/Å^3	6752.2(3)
Z	1
ρ/ g·cm^{-3})	1.038
μ/mm^{-1}	3.597
F(000)	2159
θ range data collection	2.56-66.47
Reflections collected	28338
Unique	28338
Data/restraints/parameters	28338/130/1938
GOF on F^2	1.119
R_1, wR_2 [I>2σ(I)]	0.1026, 0.2682
R_1, wR_2 (all data)	0.1289, 0.2951

5. Additional X-ray crystallographic structures.

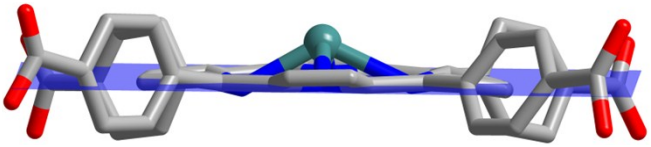
5.1 Fig. S1. The chiral induction of NiL^1 and Lewis acid activation of CdL^2 for cyanosilylation of aldehyde.



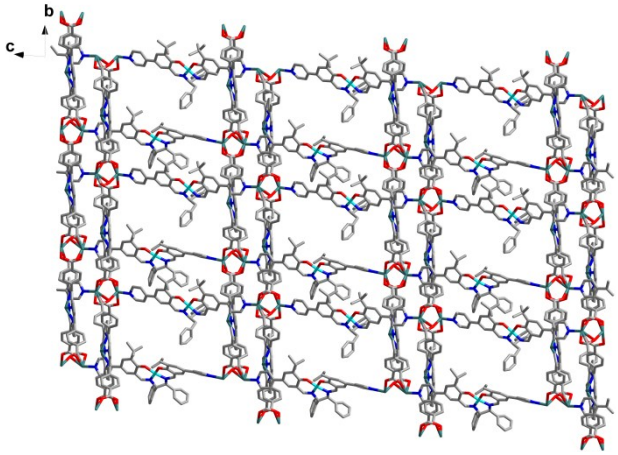
5.2 Fig. S2. The coordination environment of Cd-paddlewheel.



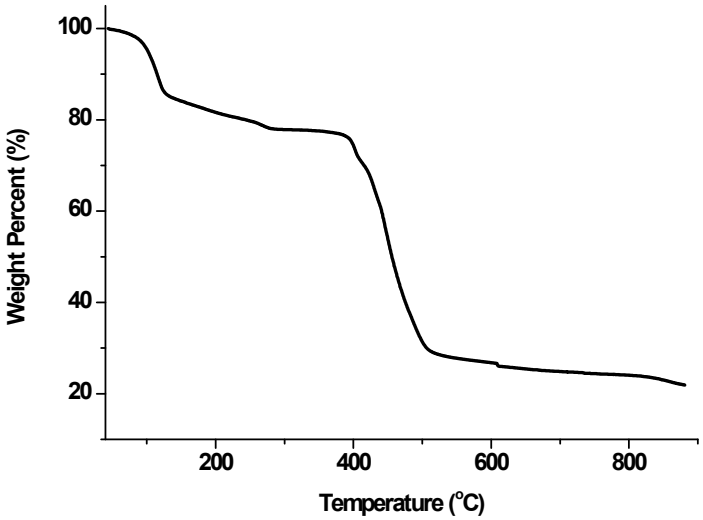
5.3 Fig. S3. The structure of Cd cation in L^2.



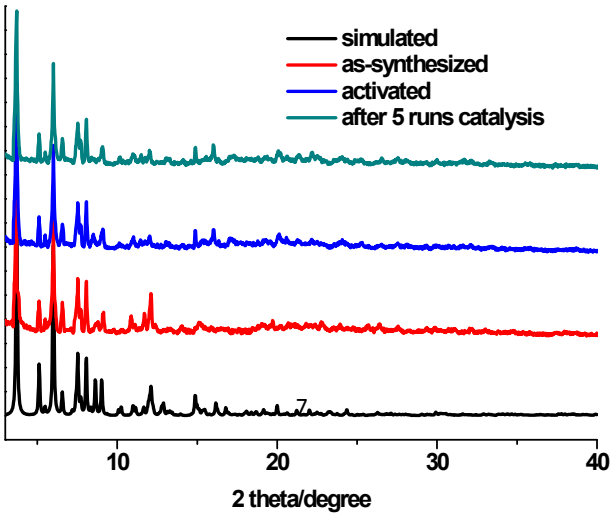
5.4 Fig. S4. View of the framework of 1 along *a* axis.



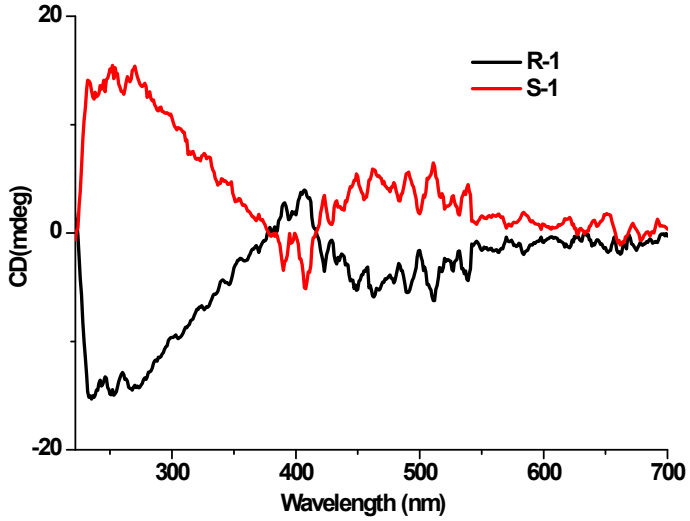
6. Fig. S5. TGA curve of 1.



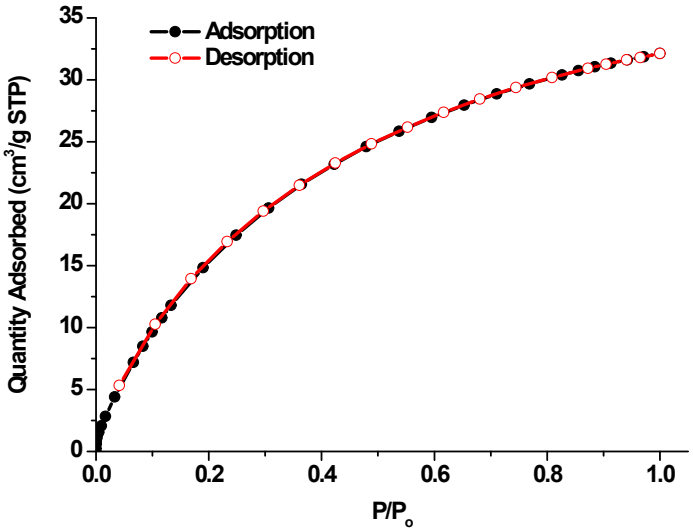
7. Fig. S6. PXRD patterns of 1.



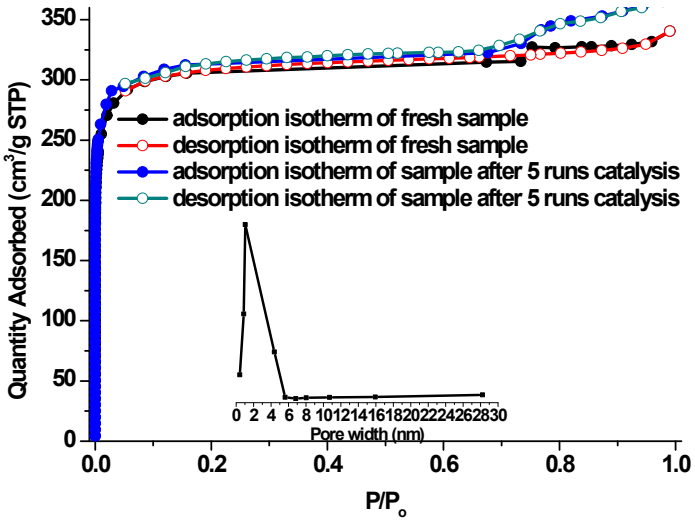
8. **Fig. S7. Solid state CD spectra of (R)-1 and (S)-1.**



9. **Fig. S8. CO_2 adsorption and desorption curves of 1 at 273 K.**



10. Fig. S9. N_2 adsorption and desorption curves at 77 K and pore distribution curve.

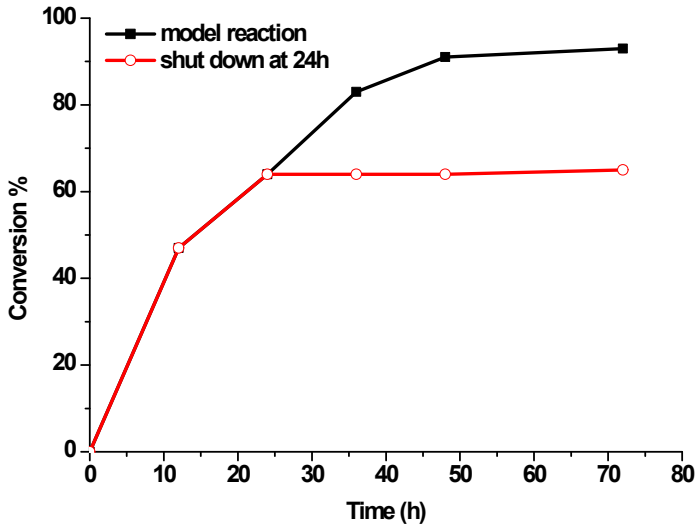


BET plots :

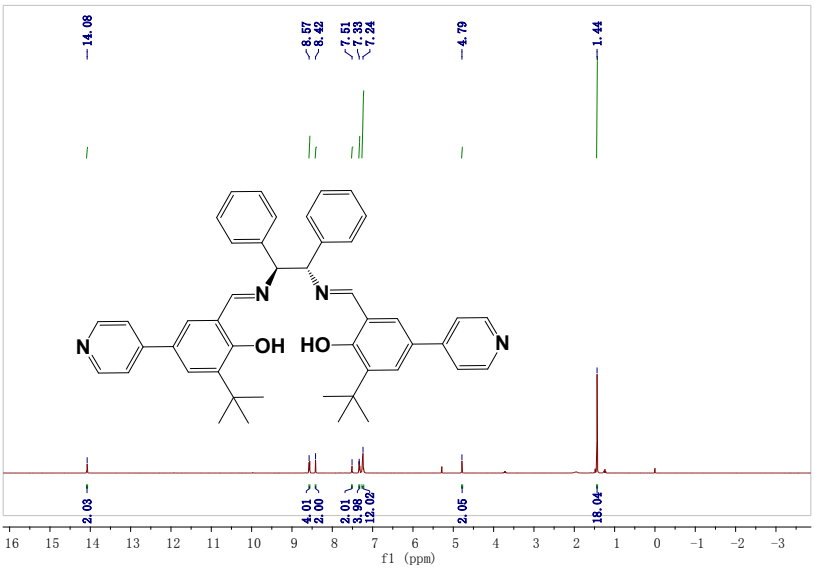
BET Surface Area:	1087.5918 ± 24.1450 m^2/g
Slope:	0.004029 ± 0.000088 g/cm^3 STP
Y-Intercept:	-0.000027 ±0.000010 g/cm^3 STP
C:	-146.904832
Qm:	249.8730 cm^3/g STP
Correlation Coefficient:	0.9995202
Molecular Cross-Sectional Area:	0.1620 nm^2

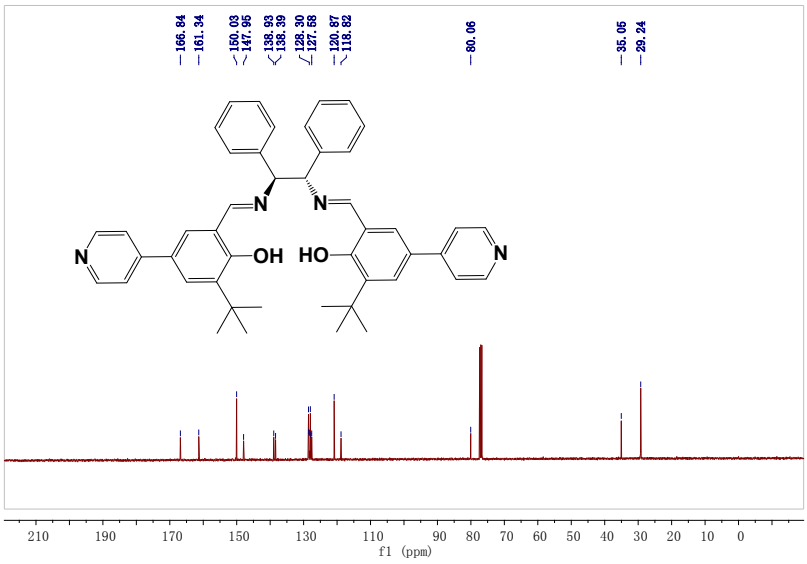
Relative Pressure (P/Po)	**Quantity Adsorbed (cm^3/g STP)**	**$1/[Q(P_o/P- 1)]$**
0.055937842	291.959	0.000203
0.085523411	298.526893	0.000313
0.12210618	302.818691	0.000459
0.157826347	305.516041	0.000613

11. **Fig. S10. Hot filtrate experiment of cyanosilylation of *para*-methoxybenzaldehyde.**

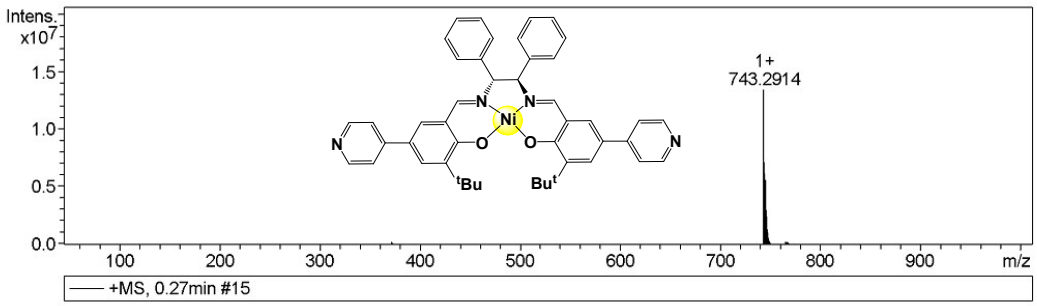


12. **Fig. S11. ^{1}HNMR and ^{13}CNMR of L^{1}.**



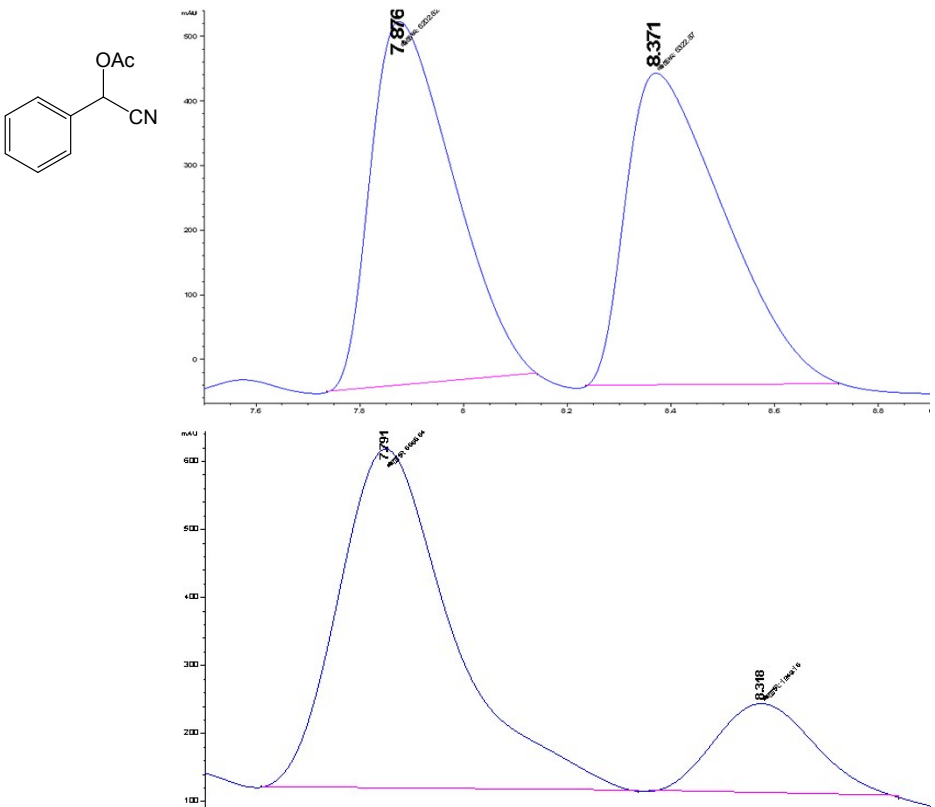


13. Fig. S12. HR-MS of NiL[1].



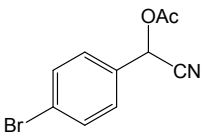
14. Fig. S13. HPLC of cyanosilylation products.

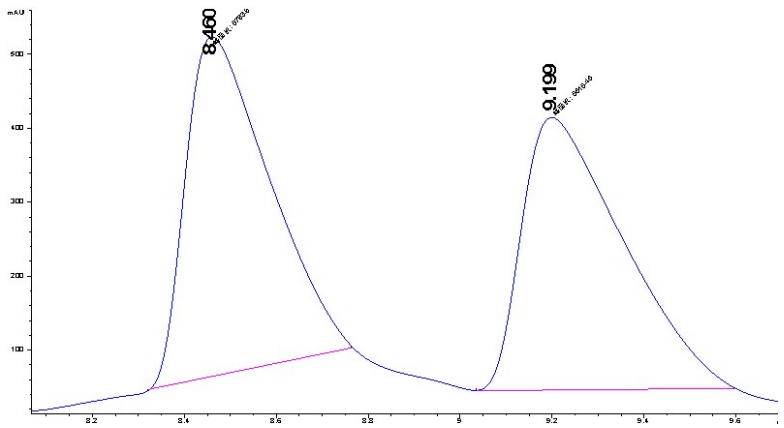
Cyano(phenyl)methyl acetate: chiralcel OD-H column (hexane/i-PrOH = 92/8, 1.0 mL/min, 60 bar), t_{major} = 7.791 min, t_{minor} = 8.318 min; ee = 63%.

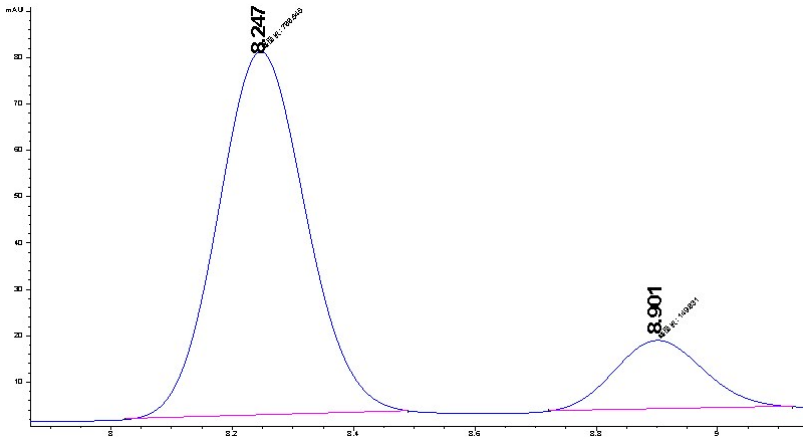


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.791	MM	0.1851	5535.64453	498.31860	81.5888
2	8.318	MM	0.1593	1249.16418	130.70985	18.4112

(4-Bromophenyl)(cyano)methyl acetate: chiralcel OD-H column (hexane/i-PrOH = 92/8, 1.0 mL/min, 60 bar), t_{major} = 8.247 min, t_{minor} = 8.901 min; ee = 68%.

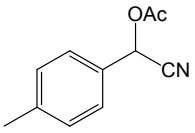


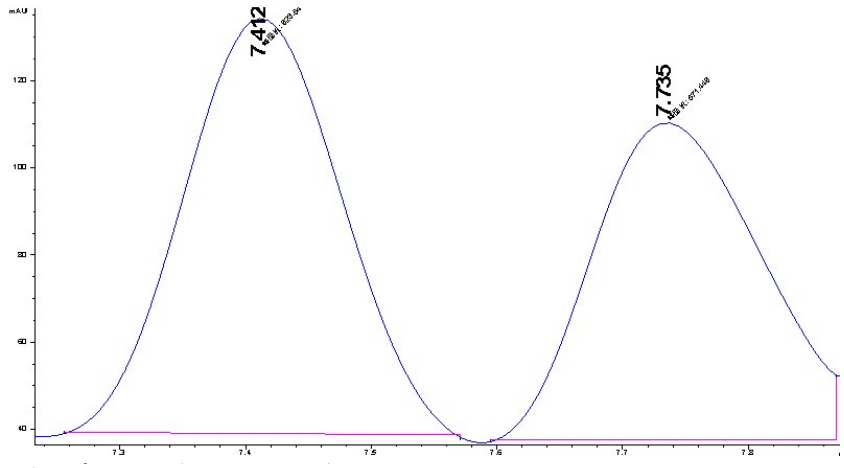


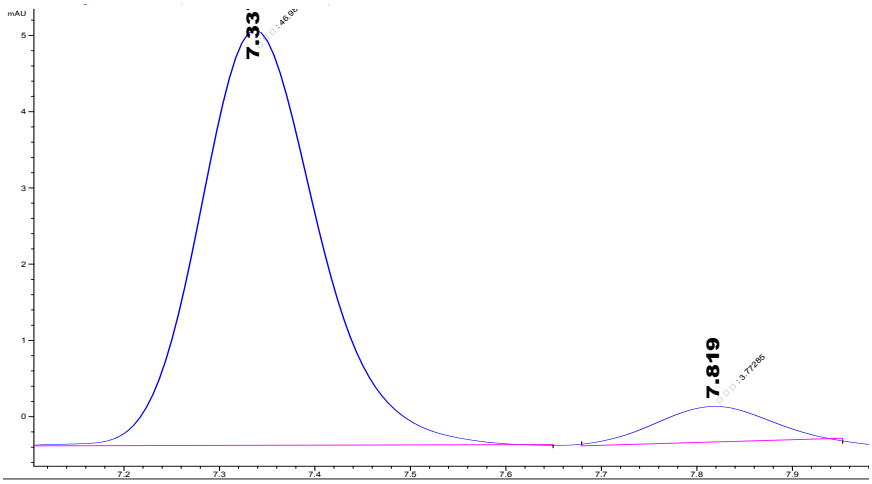


#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.247	MM	0.1686	796.74048	78.75406	84.2664
2	8.901	MM	0.1687	148.76169	14.70005	15.7336

Cyano(4-methyl)methyl acetate: chiralcel OD-H column (hexane/i-PrOH = 92/8, 1.0 mL/min, 60 bar), t_{major} = 7.337 min, t_{minor} = 7.819 min; ee = 85%.

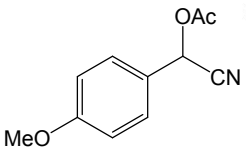


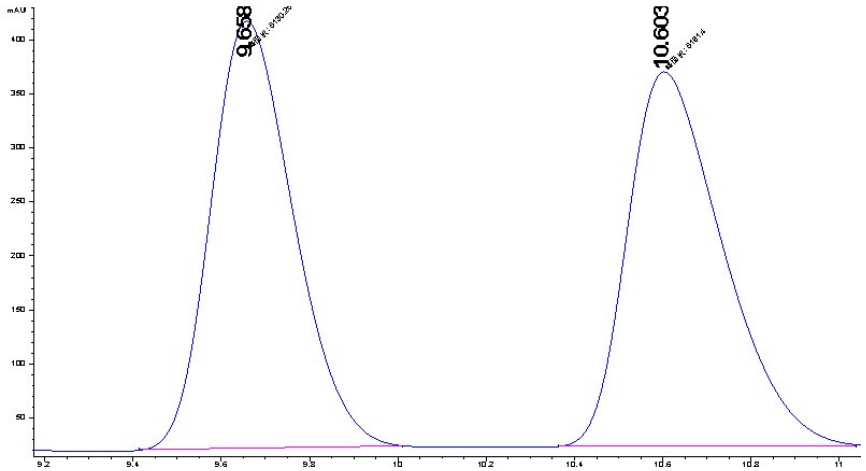


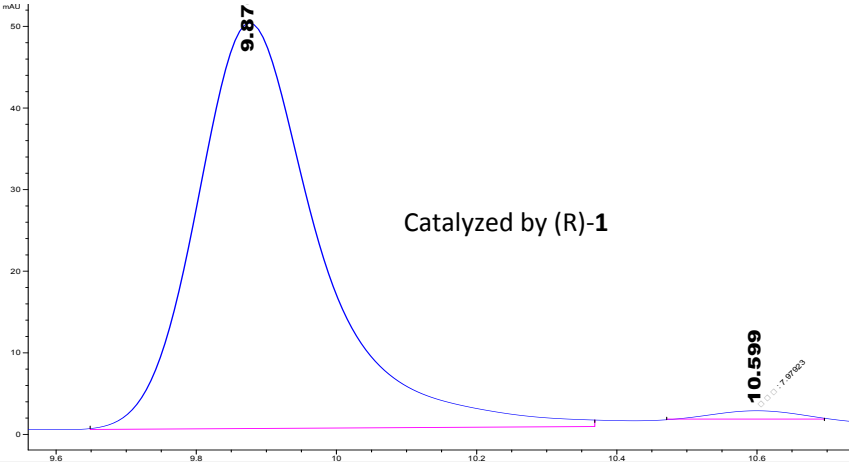


#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.337	MM	0.1436	46.98497	5.45190	92.5670
2	7.819	MM	0.1343	3.77285	4.68116e-1	7.4330

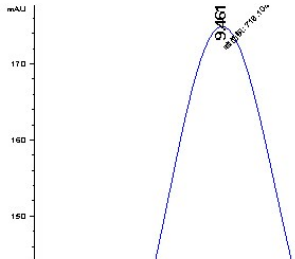
Cyano(4-methoxyphenyl)methyl acetate: chiralcel OD-H column (hexane/i-PrOH = 92/8, 1.0 mL/min, 60 bar), t_{major} = 9.876 min, t_{minor} = 10.599 min; ee = 98%.







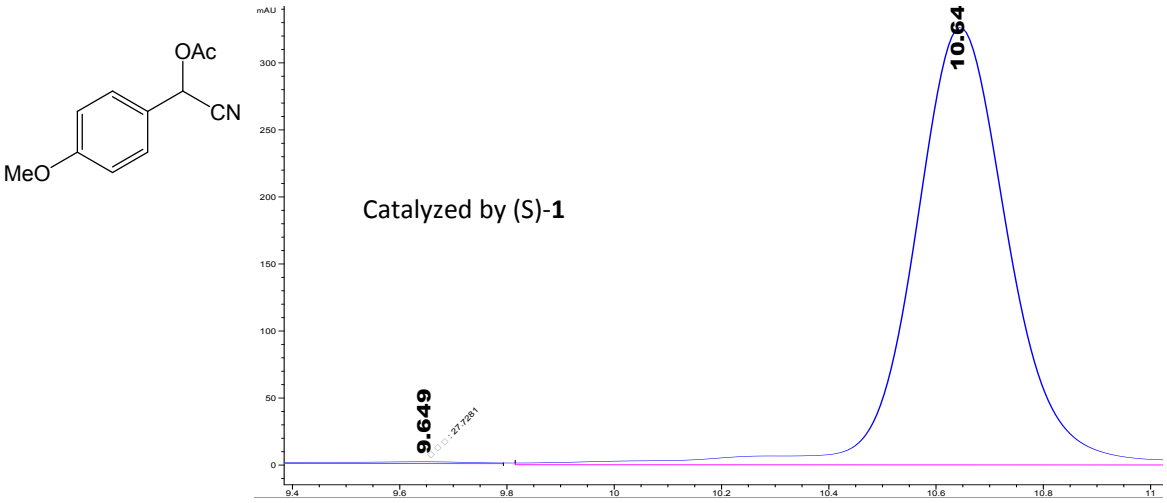
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.876	BB	0.1817	603.74823	49.70300	98.6956
2	10.599	MM	0.1297	7.97923	1.02510	1.3044



Catalyzed by NiL[1]

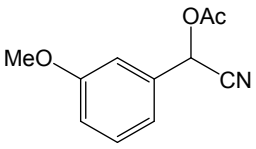
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.461	MM	0.2187	718.10394	54.72545	83.0411
2	10.225	MM	0.2004	146.65306	12.19853	16.9589

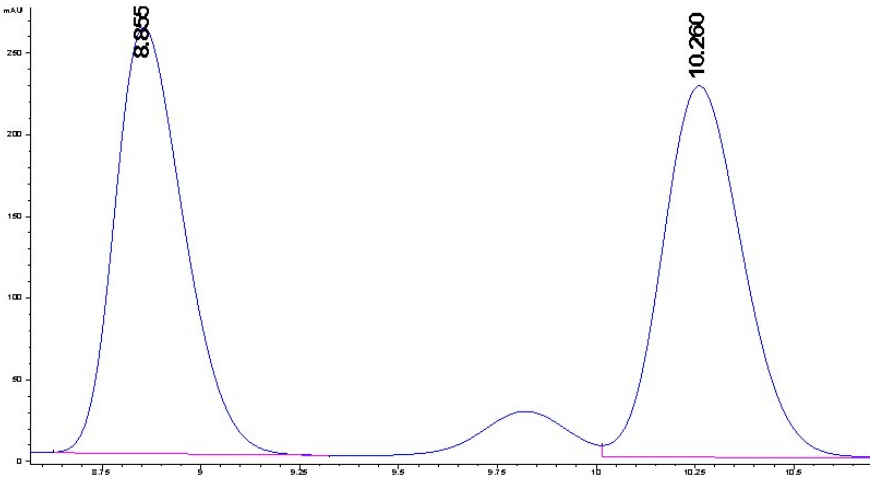
Cyano(4-methoxyphenyl)methyl acetate: chiralcel OD-H column (hexane/i-PrOH = 92/8, 1.0 mL/min, 60 bar), t_{minor} = 9.649 min, t_{major} = 10.645 min; ee = 98%.

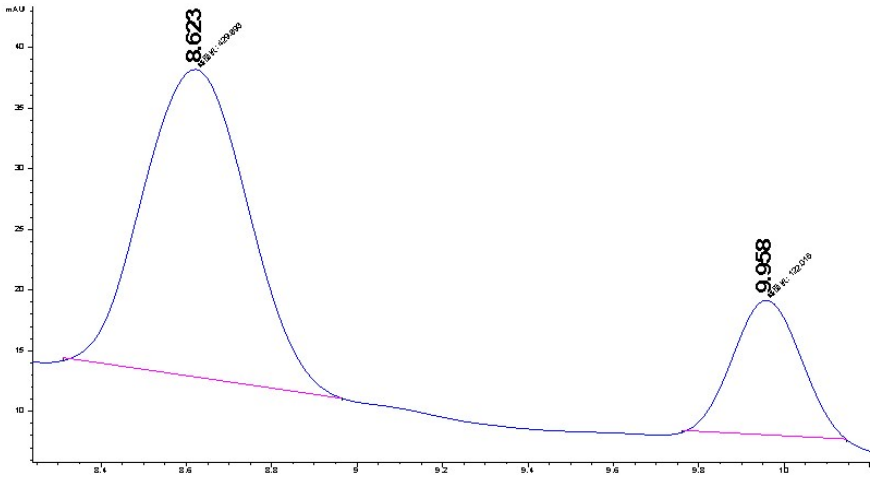


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.649	MM	0.3351	27.72813	1.37925	0.6833
2	10.645	VV	0.1881	4030.17920	326.30746	99.3167

Cyano(3-methoxyphenyl)methyl acetate: chiralcel OD-H column (hexane/i-PrOH = 92/8, 1.0 mL/min, 60 bar), t_{major} = 8.623 min, t_{minor} = 9.958 min; ee = 55%.

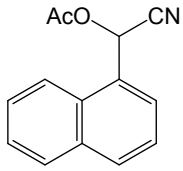


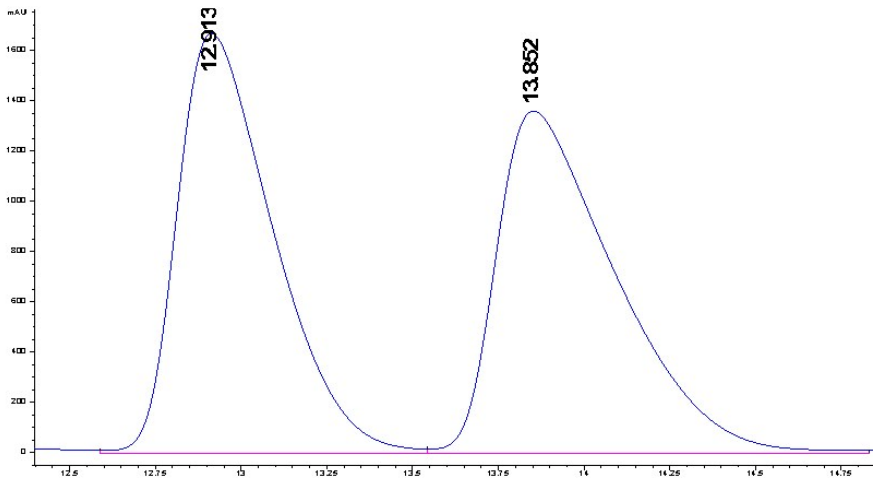


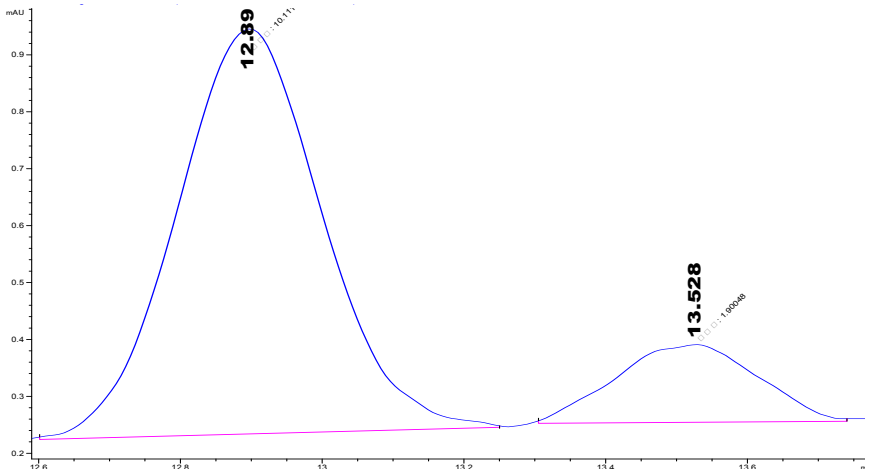


#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.623	MM	0.2887	446.19678	25.75970	77.4364
2	9.958	MM	0.1896	130.01378	11.43161	22.5636

Cyano(α-naphthyl)methyl acetate: chiralcel OD-H column (hexane/i-PrOH = 92/8, 1.0 mL/min, 60 bar), t_{major} = 12.898 min, t_{minor} = 13.528 min; ee = 68%.

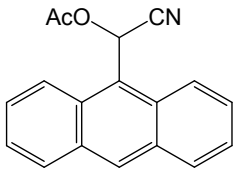


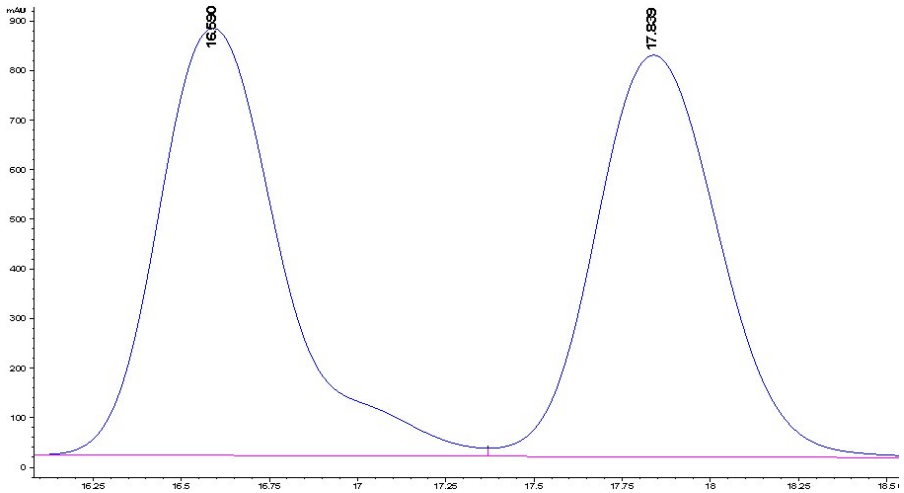


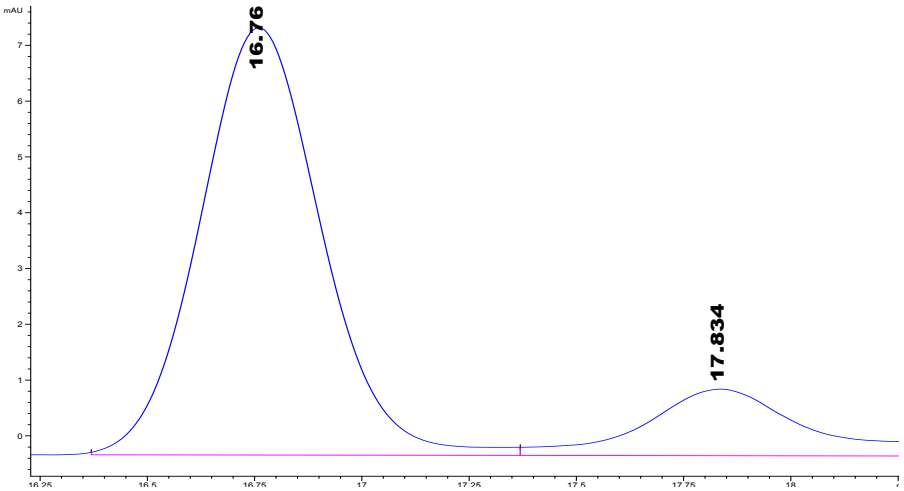


#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.898	MM	0.2367	10.11120	7.11929e-1	84.1781
2	13.528	MM	0.2319	1.90048	1.36594e-1	15.8219

(9-Anthral)(cyano)methyl acetate: chiralcel OD-H column (hexane/i-PrOH = 92/8, 1.0 mL/min, 60 bar), t_{major} = 16.760 min, t_{minor} = 17.834 min; ee = 83%.







#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.759	MM	0.3235	148.66743	7.65841	91.4914
2	17.836	MM	0.2698	13.82594	8.54106e-1	8.5086

References

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3. R. F. Pasternack, L. Francesconi, D. Raff and E. Spiro, *Inorg. Chem.*, 1973, **12**, 2609.