Supporting Information for

Chiral Porous Metal-Organic Frameworks Containing μ-oxo-bis[Ti(salan)] Units for Asymmetric Cyanation of Aldehydes

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1. Materials and general procedures

All of the chemicals are commercial available, and used without further purification. Elemental analyses of C and H were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 ^{o}C/min on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. ^{1}H and ^{13}C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 400 MHz. Analytical high performance liquid chromatography (HPLC) was performed on a YL-9100 HPLC with UV detection. Analytical CHIRALCEL OD-H column (4.6 mm × 25 cm) from Daicel was used. The N_2 adsorption isotherms were recorded at 77K by using a micromeritics ASAP 2020 surface area and porosity analyzer. Before the adsorption measurement, the samples were activated at 80 ^{o}C under vacuum (< 10^{-3} torr) for 4h. All UV/Vis absorption spectra were recorded on a Lambda 20 UV/Vis Spectrometer (Perkin Elmer, Inc., USA).

X-ray Crystallography. Single-crystal XRD data for the compound **1** and **2** were collected on a Bruker Smart Apex II CCD-based X-ray diffractometer with Cu-*K*α radiation (λ = 1.54178 Å) at 173 K. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). The structures were solved using direct method, and refined by full-matrix least-squares on F^2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). All non-hydrogen atoms are refined anisotropically, except the guest molecules. Due to the relatively weak diffraction, only parts of the guest molecules could be found in difference Fourier maps and all the phenyl rings are constrained to ideal six-membered rings. Contributions to scattering due to these highly disordered solvent molecules were removed using the *SQUEEZE* routine of *PLATON*; the structures were then refined again using the data generated. Crystal data and details of the data collection are given in **Table S1**, while the selected bond distances and angles are presented in **Table S2-S3**.

2. Synthesis

2.1 Synthesis of H_2**L** and Ti**L**$(OBu)_2$

The salan precursor of H_2**L** and Ti**L**$(OBu)_2$ were synthesized according to the literature (Chem. Sci, 2013, 4, 3154).

2.2 Synthesis of MOFs 1 and 2

2.2.1 Synthesis of 1: A mixture of $Cd(OAc)_2{\cdot}2H_2O$ (2.132 mg, 0.008 mmol), Ti**L**$(OBu)_2$ (2 mg, 0.002 mmol), THF (0.7 mL) and MeOH (0.3 mL) in a capped vial was heated at 80 °C for 12 hours. Yellow rod-like crystals of MOF **1** were filtered, washed with THF, and dried at room temperature. Yield: 67%. Elemental analysis showed **1** has the formula $[Cd_2(O_2CCH_3)_4][(Ti\mathbf{L})_2O(OMe)_2]{\cdot}2H_2O$, which was also supported by TGA and IR. Calcd for $C_{86}H_{114}Cd_2N_8O_{17}Ti_2$: C, 55.76; H, 6.20; N, 6.05;. Found: C, 56.01; H, 6.14; N, 5.98. FTIR (KBr pellet, ν/cm^{-1}): 3431 (w), 2924 (m), 1597 (m), 1512 (s), 1465 (w), 1443 (w), 1401 (w), 1382 (s), 1323 (w),1281 (w), 1242 (s),1242 (s), 1143 (s), 1044 (w), 1014 (w), 957 (s), 900 (w), 823 (w), 717 (m), 642 (w), 565 (m), 514 (w), 460 (w).

3.1 Synthesis of 2: A mixture of $Cd(OAc)_2{\cdot}2H_2O$ (1.066 mg, 0.004 mmol), $CdBr_2{\cdot}4H_2O$ (1.377 mg, 0.004 mmol), Ti**L**$(OBu)_2$ (2 mg, 0.002 mmol), THF (0.5 mL) and MeOH (0.5 mL) in a capped vial was heated at 65 °C for 24 hours. Yellow thin rod-like crystals of **2** were filtered, washed with THF, and dried at room temperature. Yield:52%. Elemental analysis showed **2** has the formula $[Cd_2Br_2(O_2CCH_3)_2][(Ti\mathbf{L})_2O(OMe)_2]{\cdot}2H_2O$, which was also supported by TGA and IR. Calcd for $C_{82}H_{108}Br_2Cd_2N_8O_{13}Ti_2$: C, 52.00; H, 5.75; N, 5.92;. Found: C, 51.67; H, 5.69; N, 5.87. FTIR (KBr pellet, ν/cm^{-1}): 3463 (m), 3084 (m), 2927 (s), 2858 (w), 2811 (w), 1610 (s), 1599 (s), 1573 (m), 1464 (s), 1443 (s), 1411 (m), 1387 (w),1356 (w), 1324 (s), 1280 (s), 1263 (s), 1239 (w), 1151 (w), 1089 (s), 1072 (s), 1017 (m), 973 (w), 957 (w), 937 (w), 921 (w), 900 (s), 830 (s), 823 (s), 816 (s), 774 (w), 718 (s), 693 (w), 684 (w), 642 (s), 625 (w), 607 (w), 570 (m), 550 (w) , 512 (m), 497 (m), 462 (m).

3. Experimental procedure for asymmetric cyanation reactions

***General Procedure*:** Catalyst (5.0 mol%) was added to a solution of indicated aldehyde (0.25 mmol) in CH_2Br_2 or CH_2Cl_2 (1.0 mL), the mixture was stirred at room temperature under N_2 atmosphere for 30 min. Then the mixture was cooled to -10 ^{o}C. TMSCN (2 equiv) was added dropwise. After stirring for 20 h the reaction mixture was centrifuged at 14000 rpm for 10 min, and the supernatant was concentrated under vacuum. The corresponding trimethylsilyl ethers were purified by flash chromatography over silica gel and then acidized by 10 w/w% HCl/MeOH at -78 ^{o}C. The filtrate was extracted with ethyl acetate and washed with brine, dried over Na_2SO_4 and evaporated, giving corresponding cyanohydrins.

To a solution of the crude cyanohydrins in CH_2Cl_2 (2 mL) were 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 min, 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 cyanohydirn. The ee of resulted product was determined by HPLC using Chiralcel OD-H column.

4. Dye inclusion

Fresh crystals of MOF **1** (10 mg) and MOF **2**(10 mg) were briefly dried on a filter paper and soaked in a solution of saturation methyl orange overnight. The resulted red samples were washed with water thoroughly until the washings became colorless. Then the washed samples were digested by Na_2EDTA (0.05 M, 2 mL) and NaOH (6 M, 0.1 mL), the clear solution with red color was diluted to 100 mL. Absorption experiments were performed on Lambda 20 UV/Vis Spectrometer.

The experimental showed that the fresh sample of **1** could adsorb ~0.67 MO per formula unit in solution, **2** could adsorb ~0.61 MO per formula unit in solution.

Creation of a standard curve: The MO(32.73 mg) was added to a flash and diluted to 1000 mL. The solution of MO is stock solution, and 5, 10, 25, 50 mL stock solution were diluted to 100 mL. The adsorbance of different concentration of MO was determined by UV/Vis Spectrometer. Data for known concentrations of MO were used to make the standard curve, plotting concentration on the X axis, and the assay measurement of absorbance on the Y axis. According to the Beer-Lambert law, the standard curve can be calculated by linear fitting of the data.

Calculation of the MO number: The samples solution were diluted to 100 mL to meet the needs of linear range of concentration. The absorbance of the samples solution were determined by the UV/Vis Spectrometer(Figure S13). The concentration of MO can be calculated by comparing the UV/Vis absorbance with a standard curve.

For example:

$Y=0.02279X-0.0089$($Y=0.8343$, $X=3.7*10^{-5}$ mol/L)

$n(MO)=V*c=0.1(L)*X=3.7*10^{-6}$ mol

$n(crystal)=m/M=10(mg)/M=5.5*10^{-6}$ mol

n(MO): n(crystal)=0.67

5. Table S1. Crystal data and structure refinement for 1 and 2

Identification code	**1**	**2**
Empirical formula	$C_{86}H_{110}Cd_2N_8O_{15}Ti_2$	$C_{41}H_{52}BrCdN_4O_{5.5}Ti$
Formula weight	1816.41	929.07
Temperature (K)	173.15 K	173.15 K
Wavelength (Å)	1.54178	1.54178
Crystal system	Orthorhombic	Tetragonal
Space group	$P2_12_12_1$	$P4_12_12$
Unit cell dimensions	a =13.9325(12) Å b = 26.873(2) Å c = 27.147(2)Å $\alpha = \beta = \gamma = 90°$	a = 26.8901(2) Å b =26.8901(2) Å c = 13.2591(3) Å $\alpha = \beta = \gamma = 90°$
Volume ($Å^3$), Z	10164.2(15),4	9587.4(3), 8
Density (calculated) (mg/m^3)	1.187	1.287
Absorption coefficient (mm^{-1})	5.059	6.282
F(000)	3768	3800
θ range for data collection (º)	3.256 to 66.593	3.287 to 59.728
Limiting indices	-13≤ h≤ 16, -31≤ k≤ 31, -32≤ l≤23	-30≤ h≤ 29, -23≤ k≤ 28, -14≤ l≤ 12
Reflections collected	28745	24662
Independent reflections	13756 [R(int) = 0.0812]	6936 [R(int) = 0.0486]
Completeness to theta	67.679/82.2 %	67.679/81.7%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	13756/ 17/ 988	6936/ 157 / 574
Goodness-of-fit on F^2	0.893	1.050
Final R indices [I>2sigma(I)]	R_1= 0.0511, wR_2= 0.1166	R_1 = 0.0672, wR_2 = 0.1965
R indices (all data)	R_1= 0.0770, wR_2= 0.1307	R_1 = 0.0775, wR_2 = 0.2117
Absolute structure parameter	0.025(6)	0.045(5)
Largest diff. peak and hole ($e.Å^{-3}$)	0.560 and -0.566	0.521 and -1.063

6.1 Table S2. Selected Bond lengths and angles for 1

Cd(1)-O(8)	2.322(10)
Cd(1)-O(9)	2.429(14)
Cd(1)-O(13)#1	2.430(11)
Cd(1)-O(14)#1	2.295(9)
Cd(1)-N(3)#2	2.281(7)
Cd(1)-N(4)	2.341(9)
Cd(2)-O(10)	2.260(11)
Cd(2)-O(11)	2.457(16)
Cd(2)-O(12)	2.421(12)
Cd(2)-O(13)	2.403(14)
Cd(2)-O(14)	2.370(9)
Cd(2)-N(7)#3	2.331(8)
Cd(2)-N(8)	2.363(9)
Ti(1)-O(2)	1.876(5)
Ti(1)-O(1)	1.922(7)
Ti(1)-O(5)	1.851(6)
Ti(1)-O(6)	1.865(7)
Ti(1)-N(1)	2.208(8)
Ti(1)-N(2)	2.262(9)
Ti(2)-O(3)	1.881(6)
Ti(2)-O(4)	1.959(6)
Ti(2)-O(5)	1.822(6)
Ti(2)-O(7)	1.861(6)
Ti(2)-N(5)	2.277(8)
Ti(2)-N(6)	2.216(8)
O(13)-Cd(1)#4	2.430(11)
O(14)-Cd(1)#4	2.295(9)
N(3)-Cd(1)#5	2.281(7)
N(7)-Cd(2)#6	2.331(8)
O(8)-Cd(1)-O(9)	55.6(4)
O(8)-Cd(1)-O(13)#1	90.3(4)
O(8)-Cd(1)-N(4)	85.7(3)
O(9)-Cd(1)-O(13)#1	86.8(4)
O(14)#1-Cd(1)-O(8)	102.2(4)
O(14)#1-Cd(1)-O(9)	151.8(4)
O(14)#1-Cd(1)-O(13)#1	75.4(4)
O(14)#1-Cd(1)-N(4)	118.5(4)
N(3)#2-Cd(1)-O(8)	148.2(5)
N(3)#2-Cd(1)-O(9)	92.8(4)
N(3)#2-Cd(1)-O(13)#1	85.4(4)
N(3)#2-Cd(1)-O(14)#1	107.1(3)

N(3)#2-Cd(1)-N(4)	91.0(3)
N(4)-Cd(1)-O(9)	79.9(4)
N(4)-Cd(1)-O(13)#1	166.1(4)
O(10)-Cd(2)-O(11)	54.3(5)
O(10)-Cd(2)-O(12)	93.8(6)
O(10)-Cd(2)-O(13)	134.2(5)
O(10)-Cd(2)-O(14)	90.2(4)
O(10)-Cd(2)-N(7)#3	141.0(5)
O(10)-Cd(2)-N(8)	86.3(4)
O(12)-Cd(2)-O(11)	146.1(5)
O(13)-Cd(2)-O(11)	162.5(5)
O(13)-Cd(2)-O(12)	49.5(4)
O(14)-Cd(2)-O(11)	91.4(4)
O(14)-Cd(2)-O(12)	100.8(4)
O(14)-Cd(2)-O(13)	74.5(3)
N(7)#3-Cd(2)-O(11)	86.7(4)
N(7)#3-Cd(2)-O(12)	124.1(5)
N(7)#3-Cd(2)-O(13)	83.3(4)
N(7)#3-Cd(2)-O(14)	91.2(3)
N(7)#3-Cd(2)-N(8)	89.7(3)
N(8)-Cd(2)-O(11)	84.2(5)
N(8)-Cd(2)-O(12)	82.4(4)
N(8)-Cd(2)-O(13)	110.1(4)
N(8)-Cd(2)-O(14)	175.4(4)
N(8)-Cd(2)-C(81)	83.4(5)
O(2)-Ti(1)-O(1)	92.6(3)
O(2)-Ti(1)-N(1)	158.1(3)
O(2)-Ti(1)-N(2)	82.3(3)
O(1)-Ti(1)-N(1)	80.0(3)
O(1)-Ti(1)-N(2)	87.2(3)
O(5)-Ti(1)-O(2)	99.9(3)
O(5)-Ti(1)-O(1)	165.1(3)
O(5)-Ti(1)-O(6)	92.1(3)
O(5)-Ti(1)-N(1)	85.5(3)
O(5)-Ti(1)-N(2)	86.5(3)
O(6)-Ti(1)-O(2)	102.5(3)
O(6)-Ti(1)-O(1)	93.1(3)
O(6)-Ti(1)-N(1)	98.5(3)
O(6)-Ti(1)-N(2)	175.2(3)
N(1)-Ti(1)-N(2)	76.8(3)
O(3)-Ti(2)-O(4)	95.3(3)
O(3)-Ti(2)-N(5)	82.2(3)

O(3)-Ti(2)-N(6)	157.4(3)
O(4)-Ti(2)-N(5)	87.7(3)
O(4)-Ti(2)-N(6)	79.8(3)
O(5)-Ti(2)-O(3)	100.1(3)
O(5)-Ti(2)-O(4)	163.0(3)
O(5)-Ti(2)-O(7)	91.8(3)
O(5)-Ti(2)-N(5)	87.3(3)
O(5)-Ti(2)-N(6)	83.2(3)
O(7)-Ti(2)-O(3)	101.3(3)
O(7)-Ti(2)-O(4)	92.2(3)
O(7)-Ti(2)-N(5)	176.5(3)
O(7)-Ti(2)-N(6)	101.0(3)
N(6)-Ti(2)-N(5)	75.6(3)
C(13)-O(2)-Ti(1)	138.7(5)
C(29)-O(1)-Ti(1)	140.5(4)
C(51)-O(3)-Ti(2)	140.9(5)
C(67)-O(4)-Ti(2)	139.5(4)
Ti(2)-O(5)-Ti(1)	155.5(3)
C(77)-O(6)-Ti(1)	132.8(9)
C(78)-O(7)-Ti(2)	131.6(8)
C(79)-O(8)-Cd(1)	94.6(10)
C(79)-O(9)-Cd(1)	88.0(12)
C(81)-O(10)-Cd(2)	93.9(12)
C(81)-O(11)-Cd(2)	85.5(14)
C(83)-O(12)-Cd(2)	96.9(10)
Cd(2)-O(13)-Cd(1)#4	102.4(5)
C(83)-O(13)-Cd(1)#4	126.8(10)
C(83)-O(13)-Cd(2)	99.9(13)
Cd(1)#4-O(14)-Cd(2)	107.6(4)
C(85)-O(14)-Cd(1)#4	105.3(8)
C(85)-O(14)-Cd(2)	133.1(8)
C(1)-N(1)-Ti(1)	112.2(6)
C(23)-N(1)-Ti(1)	109.7(6)
C(2)-N(2)-Ti(1)	110.7(6)
C(7)-N(2)-Ti(1)	112.1(6)
C(20)-N(3)-Cd(1)#5	124.5(8)
C(21)-N(3)-Cd(1)#5	122.0(8)
C(36)-N(4)-Cd(1)	120.4(8)
C(37)-N(4)-Cd(1)	123.7(7)
C(39)-N(5)-Ti(2)	112.3(6)
C(45)-N(5)-Ti(2)	110.6(6)
C(40)-N(6)-Ti(2)	111.4(6)
C(61)-N(6)-Ti(2)	108.9(6)
C(58)-N(7)-Cd(2)#6	118.3(8)

C(59)-N(7)-Cd(2)#6	126.1(8)
C(75)-N(8)-Cd(2)	125.5(8)
C(74)-N(8)-Cd(2)	117.5(7)
O(8)-C(79)-Cd(1)	58.5(8)
O(9)-C(79)-Cd(1)	63.3(9)
C(80)-C(79)-Cd(1)	177.0(13)
O(10)-C(81)-Cd(2)	58.5(11)
O(11)-C(81)-Cd(2)	67.8(13)
C(82)-C(81)-Cd(2)	171.8(18)

Symmetry transformations used to generate equivalent atoms:
#1 x+3/2,-y+3/2,-z+2 #2 -x+2,y+1/2,-z+3/2 #3 -x+1/2,-y+1,z+1/2
#4 x-3/2,-y+3/2,-z+2 #5 -x+2,y-1/2,-z+3/2 #6 -x+1/2,-y+1,z-1/2

6.2. Table S3. Selected Bond lengths and angles for 2

Ti(1)-O(4)	1.861(7)
Ti(1)-O(0AA)	1.949(6)
Ti(1)-N(0AA)	2.200(8)
Ti(1)-N(2)	2.263(8)
Ti(1)-O(3)	1.834(2)
Ti(1)-O(1AA)	1.860(6)
O(3)-Ti(1)#1	1.834(2)
Cd(1)-Br(1)	2.735(5)
Cd(1)-Br(1)#1	1.725(13)
Cd(1)-O(5)	2.29(2)
Cd(1)-C(40)	2.64(3)
Cd(1)-Br(1A)	3.002(6)
Cd(1)-Br(1A)#1	2.748(13)
Cd(1)-O(6)	2.41(2)
Cd(1)-N(4)	2.383(14)
Cd(1)-N(3)#2	2.44(2)
Br(1)-Cd(1)#1	1.725(13)
Br(1)-Cd(1A)#1	2.677(14)
Br(1)-Cd(1A)	2.776(6)
Cd(1A)-Br(1)#1	2.677(14)
Cd(1A)-Br(1A)	2.672(5)
Cd(1A)-O(6A)	2.47(3)
Cd(1A)-O(5A)	2.177(19)
Cd(1A)-C(40A)	2.54(3)
Cd(1A)-N(4A)	2.262(18)
Cd(1A)-N(3A)#2	2.37(18)

Br(1A)-Cd(1)#1	2.748(13)
N(3)-Cd(1)#3	2.44(2)
N(3A)-Cd(1A)#3	2.368(16)

O(4)-Ti(1)-O(0AA)	92.3(3)
O(4)-Ti(1)-N(0AA)	98.6(3)
O(4)-Ti(1)-N(2)	174.7(3)
O(0AA)-Ti(1)-N(0AA)	81.2(3)
O(0AA)-Ti(1)-N(2)	88.9(3)
N(0AA)-Ti(1)-N(2)	76.5(3)
O(3)-Ti(1)-O(4)	91.7(3)
O(3)-Ti(1)-O(0AA)	165.5(2)
O(3)-Ti(1)-N(0AA)	84.4(2)
O(3)-Ti(1)-N(2)	85.9(2)
O(3)-Ti(1)-O(1AA)	100.1(3)
O(1AA)-Ti(1)-O(4)	102.8(3)
O(1AA)-Ti(1)-O(0AA)	92.6(3)
O(1AA)-Ti(1)-N(0AA)	157.9(3)
O(1AA)-Ti(1)-N(2)	82.3(3)
C(39)-O(4)-Ti(1)	132.0(7)
C(9)-O(0AA)-Ti(1)	139.0(4)
C(1AA)-N(0AA)-Ti(1)	109.0(6)
C(2AA)-N(0AA)-Ti(1)	113.1(6)
C(3AA)-N(2)-Ti(1)	111.6(6)
C(23)-N(2)-Ti(1)	110.8(6)
Ti(1)-O(3)-Ti(1)#1	154.7(5)
C(24)-O(1AA)-Ti(1)	139.7(5)
Br(1)#1-Cd(1)-Br(1)	88.3(3)
Br(1)#1-Cd(1)-O(5)	104.0(6)
Br(1)#1-Cd(1)-Br(1A)#1	11.7(3)
Br(1)-Cd(1)-Br(1A)	21.78(15)
Br(1)#1-Cd(1)-Br(1A)	110.0(3)
Br(1)-Cd(1)-Br(1A)#1	91.9(2)
Br(1)#1-Cd(1)-O(6)	160.2(4)
Br(1)#1-Cd(1)-N(4)	105.9(5)
Br(1)#1-Cd(1)-N(3)#2	92.7(6)
O(5)-Cd(1)-Br(1)	90.8(6)
O(5)-Cd(1)-Br(1A)	86.9(6)
O(5)-Cd(1)-Br(1A)#1	115.0(6)
O(5)-Cd(1)-O(6)	56.3(6)
O(5)-Cd(1)-N(4)	149.4(7)
O(5)-Cd(1)-N(3)#2	82.5(8)
Br(1A)#1-Cd(1)-Br(1A)	112.92(18)
O(6)-Cd(1)-Br(1)	93.9(4)

O(6)-Cd(1)-C(40)	27.5(5)
O(6)-Cd(1)-Br(1A)	74.0(4)
O(6)-Cd(1)-Br(1A)#1	169.6(4)
O(6)-Cd(1)-N(3)#2	83.0(6)
N(4)-Cd(1)-Br(1)	96.6(5)
N(4)-Cd(1)-Br(1A)	89.0(5)
N(4)-Cd(1)-Br(1A)#1	94.5(5)
N(4)-Cd(1)-O(6)	93.4(6)
N(4)-Cd(1)-N(3)#2	89.6(8)
N(3)#2-Cd(1)-Br(1)	173.3(6)
N(3)#2-Cd(1)-Br(1A)	156.8(6)
N(3)#2-Cd(1)-Br(1A)#1	90.3(5)
Cd(1)#1-Br(1)-Cd(1)	87.9(2)
Cd(1A)#1-Br(1)-Cd(1A)	105.2(2)
C(40)-O(5)-Cd(1)	91.1(16)
Br(1)#1-Cd(1A)-Br(1)	71.5(2)
Br(1A)-Cd(1A)-Br(1)#1	94.9(2)
Br(1A)-Cd(1A)-Br(1)	23.53(16)
O(6A)-Cd(1A)-Br(1)	117.0(4)
O(6A)-Cd(1A)-Br(1)#1	164.2(4)
O(6A)-Cd(1A)-Br(1A)	94.9(5)
O(6A)-Cd(1A)-C(40A)	29.1(6)
O(5A)-Cd(1A)-Br(1)	100.0(5)
O(5A)-Cd(1A)-Br(1)#1	105.3(9)
O(5A)-Cd(1A)-Br(1A)	96.8(6)
O(5A)-Cd(1A)-O(6A)	61.1(9)
O(5A)-Cd(1A)-N(4A)	155.8(10)
O(5A)-Cd(1A)-N(3A)#2	83(7)
C(40A)-Cd(1A)-Br(1)	113.0(6)
C(40A)-Cd(1A)-Br(1)#1	136.6(6)
C(40A)-Cd(1A)-Br(1A)	98.0(7)
N(4A)-Cd(1A)-Br(1)#1	95.6(6)
N(4A)-Cd(1A)-Br(1)	98.1(6)
N(4A)-Cd(1A)-Br(1A)	93.3(6)
N(4A)-Cd(1A)-O(6A)	96.2(7)
N(4A)-Cd(1A)-N(3A)#2	86(7)
N(3A)#2-Cd(1A)-Br(1)	156(6)
N(3A)#2-Cd(1A)-Br(1)#1	85(6)
N(3A)#2-Cd(1A)-Br(1A)	180(7)
N(3A)#2-Cd(1A)-O(6A)	85(6)
O(5)-C(40)-Cd(1)	60.0(15)
O(6)-C(40)-Cd(1)	65.4(14)
Cd(1)#1-Br(1A)-Cd(1)	66.97(18)
C(40)-O(6)-Cd(1)	87.1(16)

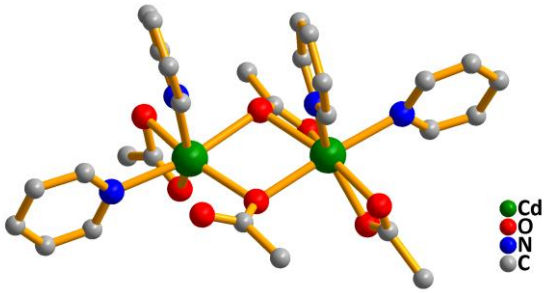
C(40A)-O(6A)-Cd(1A)	78.3(19)
C(40A)-O(5A)-Cd(1A)	88.8(15)
C(36)-N(4)-Cd(1)	120.8(9)
C(37)-N(4)-Cd(1)	118.4(9)
C(36A)-N(4A)-Cd(1A)	118.1(11)
C(37A)-N(4A)-Cd(1A)	121.5(11)
C(20)-N(3)-Cd(1)#3	118.2(19)
C(21)-N(3)-Cd(1)#3	123(2)
C(20A)-N(3A)-Cd(1A)#3	121.5(11)
C(21A)-N(3A)-Cd(1A)#3	117.6(11)

Symmetry transformations used to generate equivalent atoms:

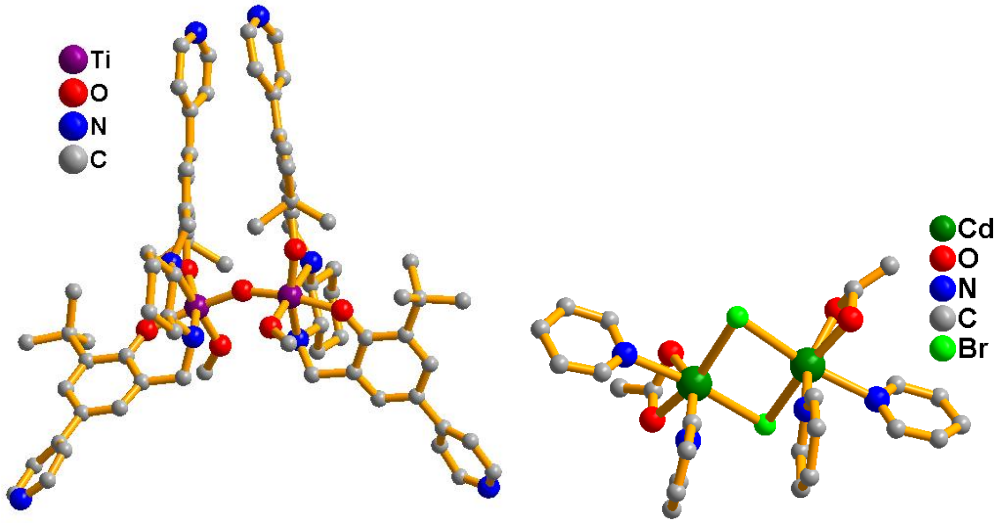
#1 -y+1,-x+1,-z+3/2 #2 x+1/2,-y+3/2,-z+3/4 #3 x-1/2,-y+3/2,-z+3/4

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

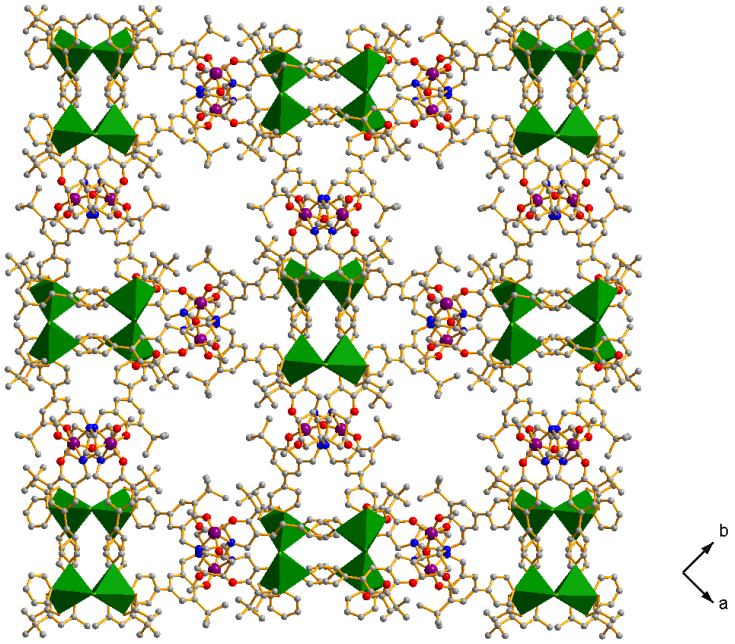
7.1 Figure S1. The structure of Cd_2 dimer in 1



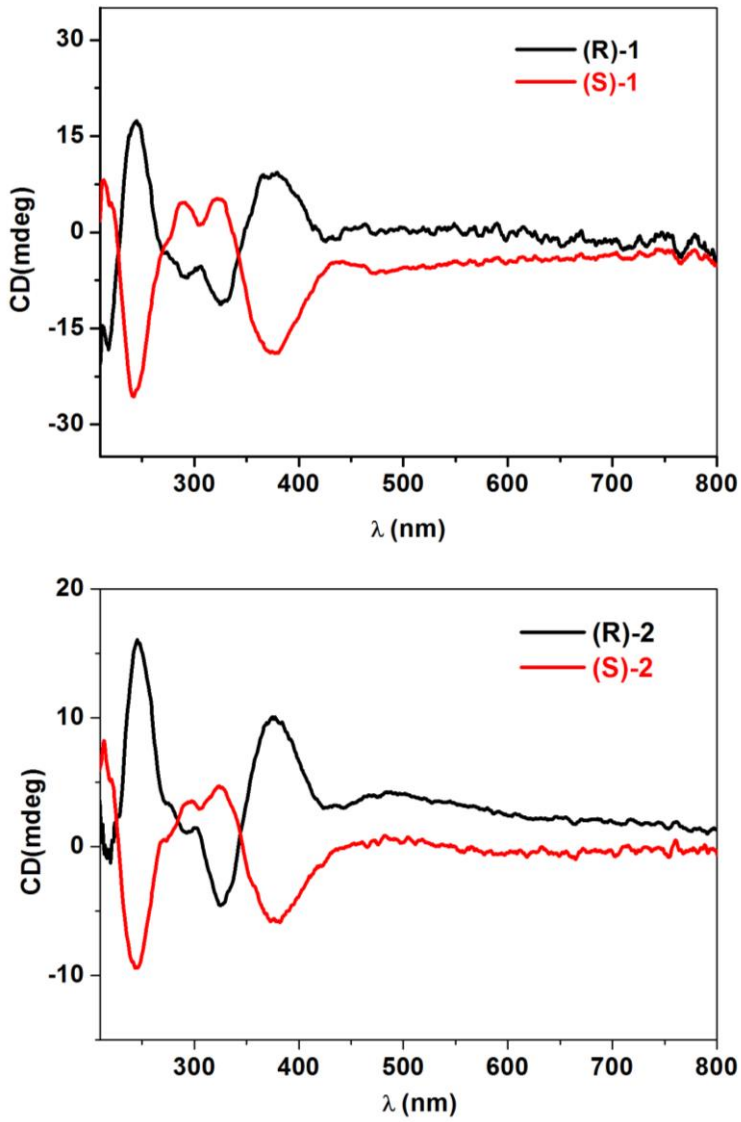
7.2 Figure S2. The structures of $(TiL)_2(\mu\text{-}O)$ unit and Cd_2 dimer in 2



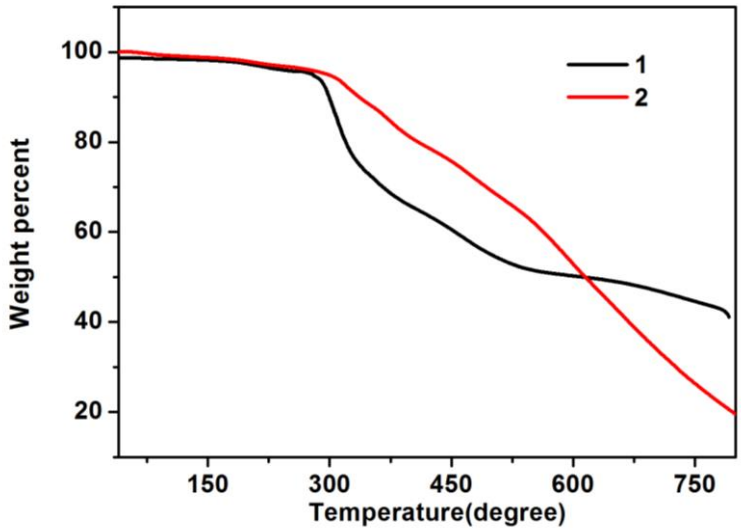
7.3 Figure S3. The 3D structure of 2



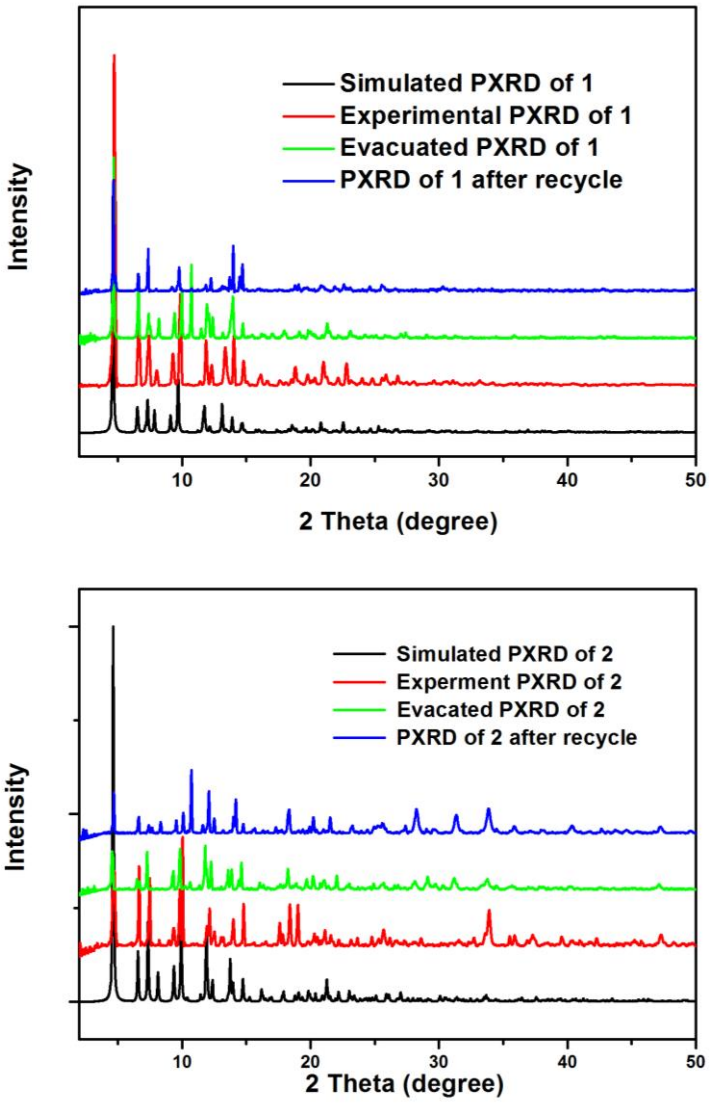
8.Figure S4. Solid-state CD spectra



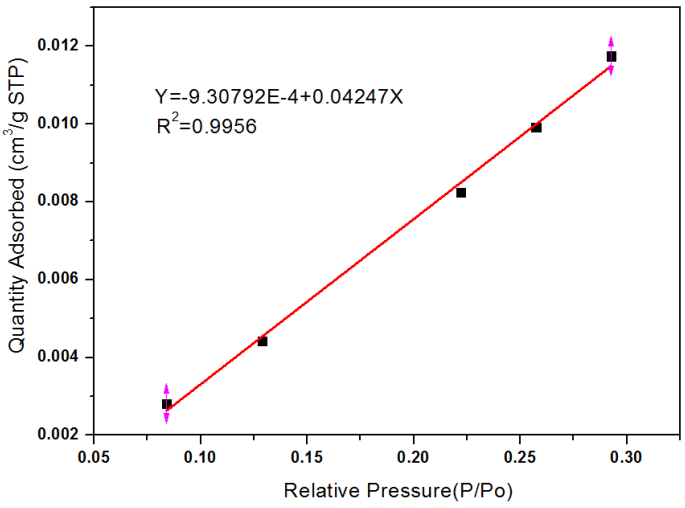
9. Figure S5. TGA curves

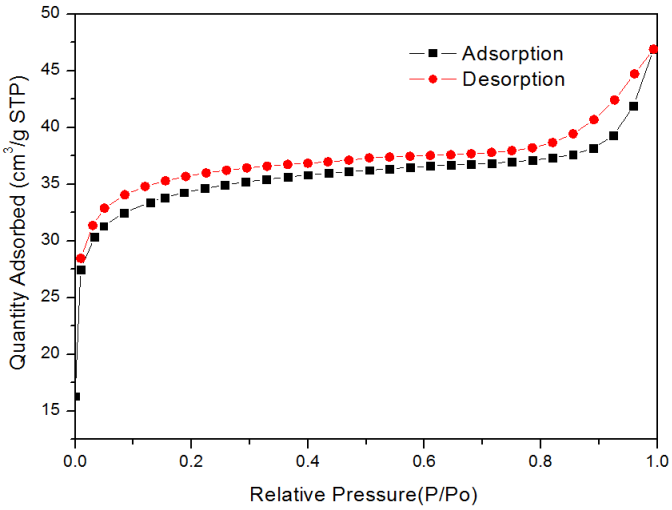


10. Figure S6. PXRD patterns

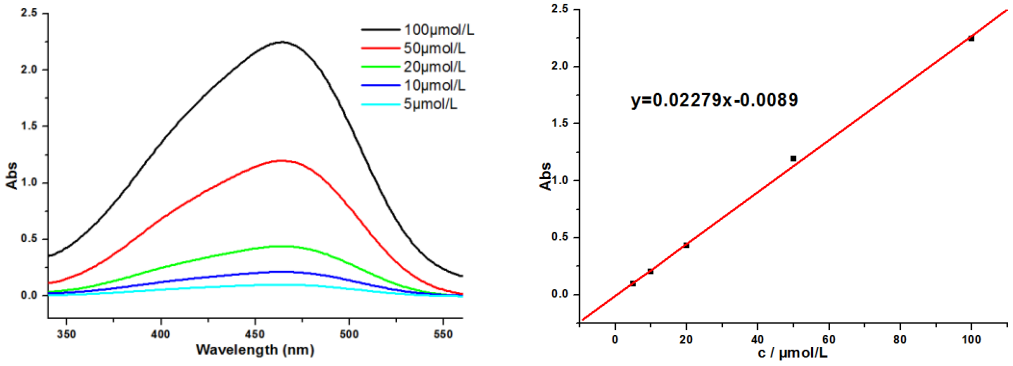


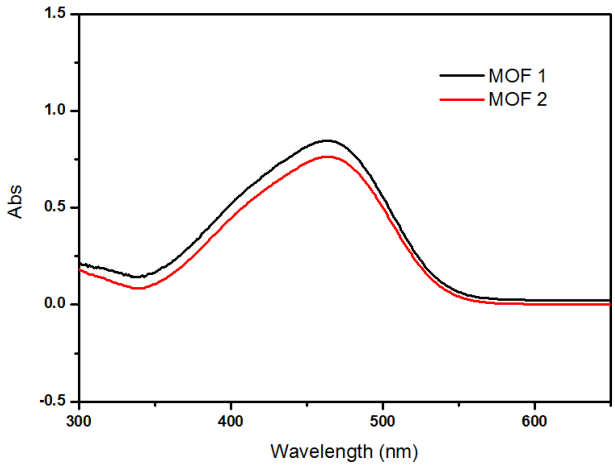
11. Figure S7. BET plot and N_2 adsorption isotherms of 1





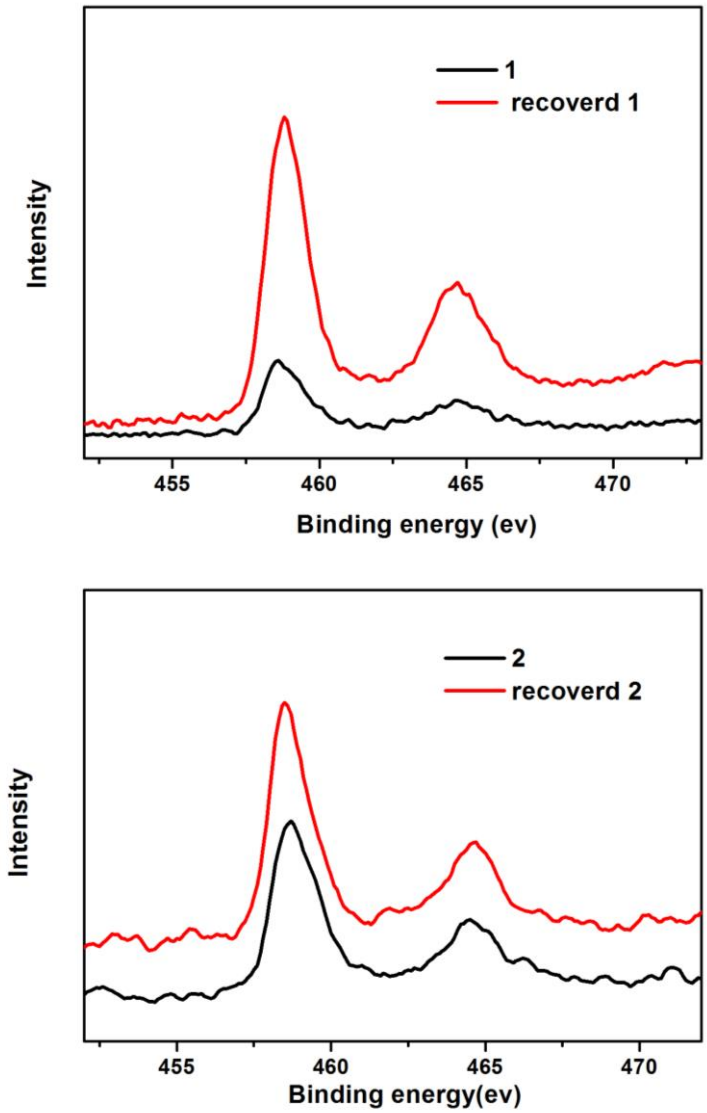
12. Figure S8.Dye adsorption





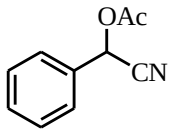
	1	2
The number of dye uptake (per formula)	0.67	0.61

13. Figure S9. XPS spectra

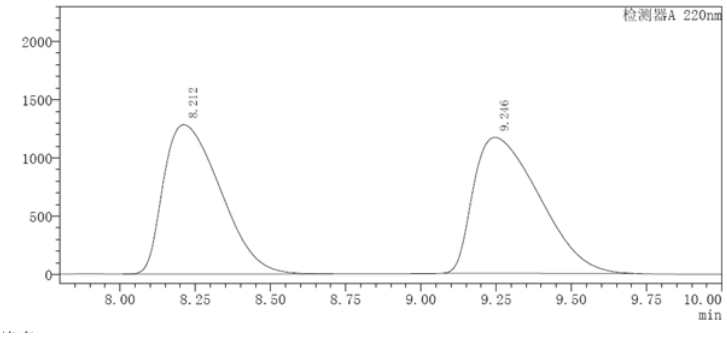


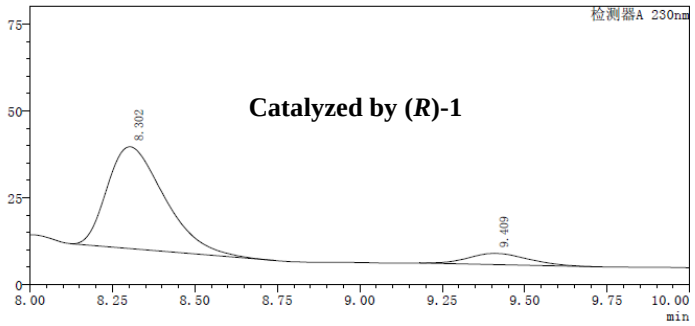
14. Asymmetric Cyanation Catalyzed by 1 and TiL(OBu)$_2$

14.1 HPLC of 1 catalyzed cyanation reaction



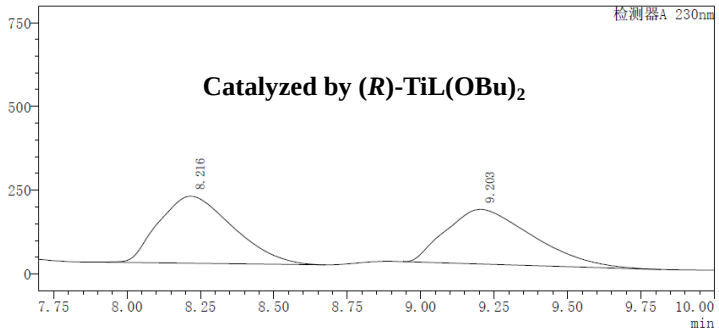
(*R*)-Cyano(phenyl)methyl acetate: Chiralcel OD-H column(hexane/*i*-PrOH 95/5,1.0 mL/min); (*R*)-**1**: t_{major}= 8.302 min; t_{minor} = 9.409 min; (*R*)-Ti**L**(OBu)$_2$: t_{major}= 8.216 min; t_{minor} = 9.203 min.





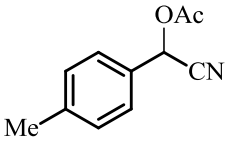
Catalyzed by (*R*)-1

Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	8.302	354827	29357	89.664
2	9.409	40902	3239	10.336
The Total		395729	32595	

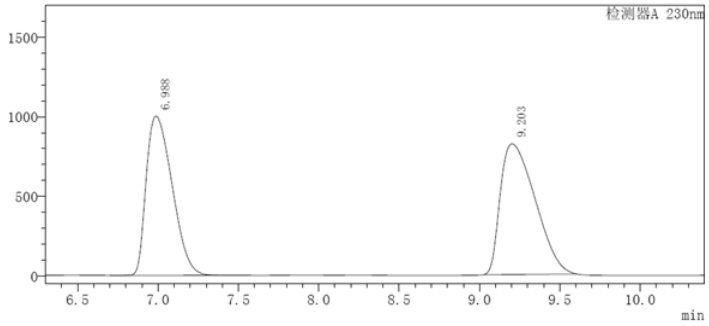


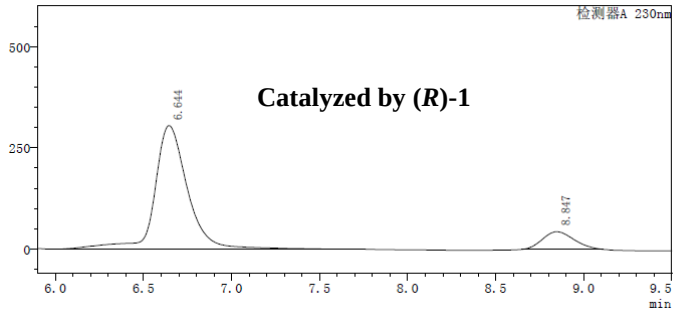
Catalyzed by (*R*)-TiL(OBu)$_2$

Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	8.216	3507716	199856	51.185
2	9.203	3345348	162770	48.815
The Total		6853063	362626	

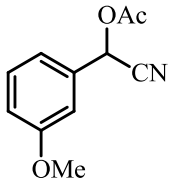


(*R*)-Cyano(4-methyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{major}= 6.644 min; t_{minor} = 8.847 min.

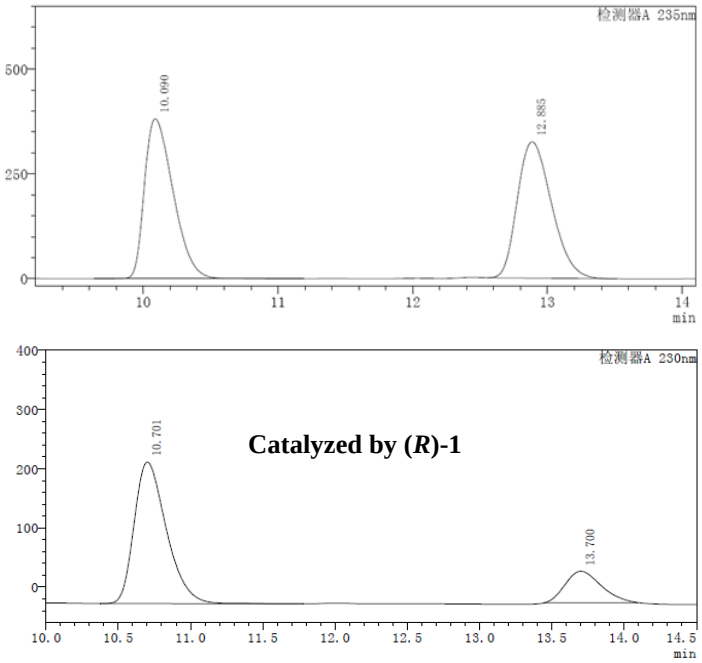




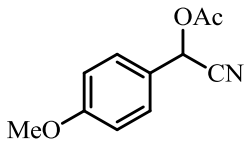
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	6.644	3943855	305220	87.907
2	8.847	542537	43579	12.093
The Total		4486391	348799	



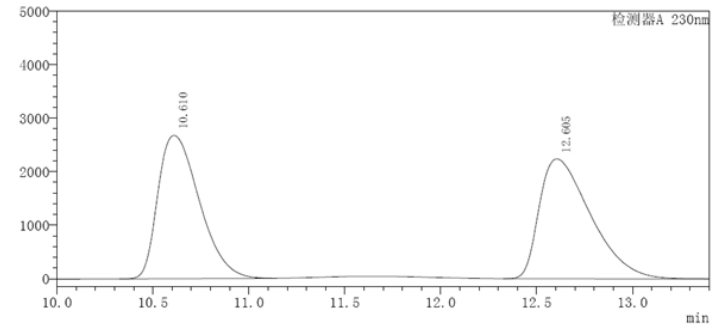
(*R*)-Cyano(3-methoxyphenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{major} = 10.701 min; t_{minor} = 13.700 min.

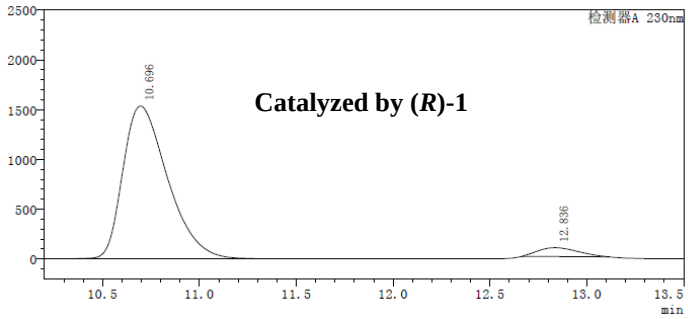


Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.701	3721175	239518	80.236
2	13.700	916596	53116	19.764
The Total		4637770	292634	



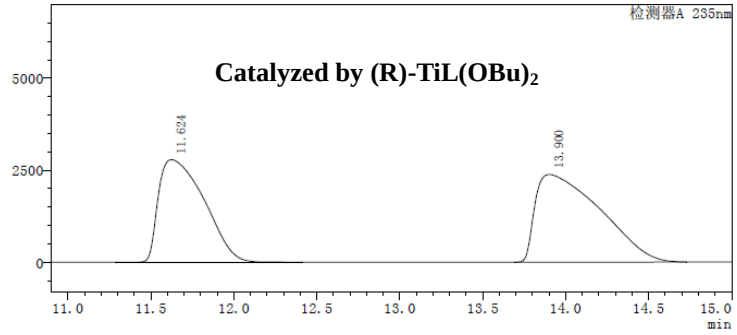
(*R*)-Cyano(4-methoxyphenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min); (*R*)-**1**: t_{major} = 10.696 min; t_{minor} = 12.836 min;



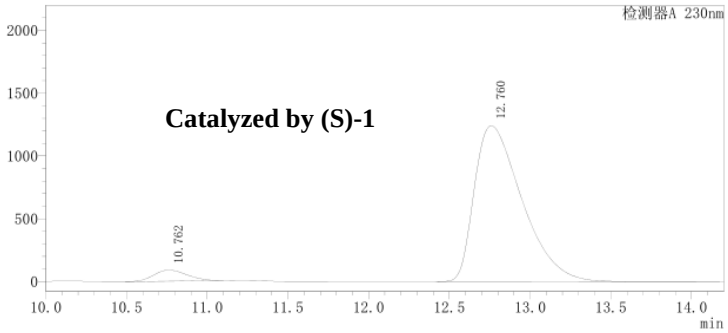


Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.696	24648473	1533978	95.085
2	12.836	1274171	88412	4.915
The Total		25922644	1622390	

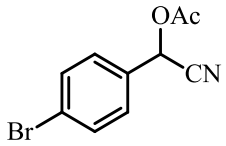
(*S*)-Cyano(4-methoxyphenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min). (*R*)-Ti**L**$(OBu)_2$: t_{minor}= 11.624 min; t_{major} = 13.900 min; (*S*)-**1**: t_{minor} = 10.762 min; t_{major} = 12.760 min.



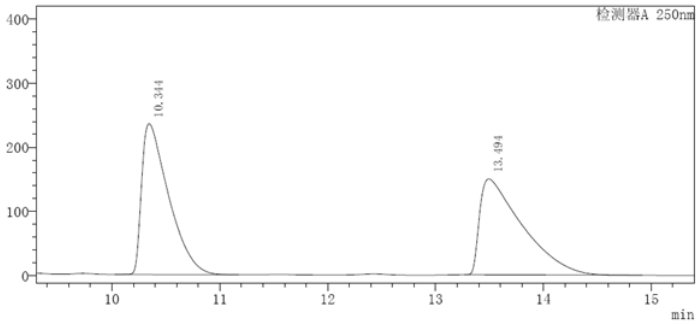
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	11.624	53225717	2782364	45.052
2	13.900	64915973	2380989	54.948
The Total		118141689	5163353	

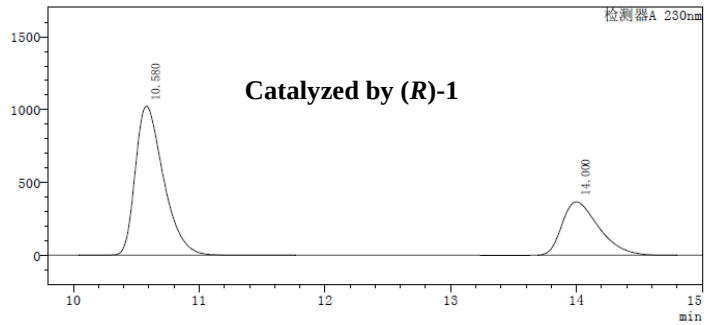


Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.762	1275944	89071	4.773
2	12.760	25458388	1241279	95.227
The Total		26734332	1330350	

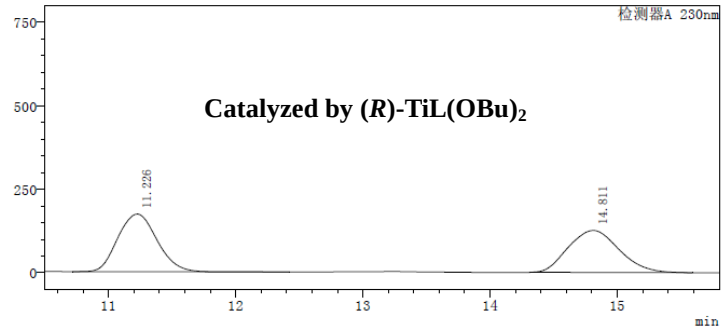


(*R*)-Cyano(4-bromophenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min); (*R*)-**1**: t_{major}= 10.580 min; t_{minor} = 14.000 min; (*R*)-Ti**L**$(OBu)_2$: t_{major}= 11.226 min; t_{minor} = 14.811 min.

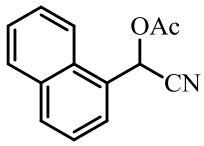




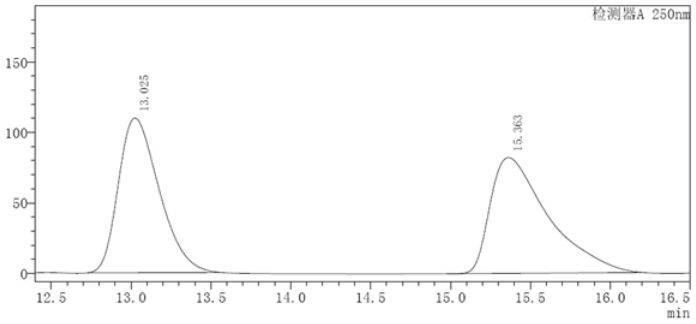
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.580	15911736	1022220	68.157
2	14.000	7434110	366038	31.843
The Total		23345846	1388258	

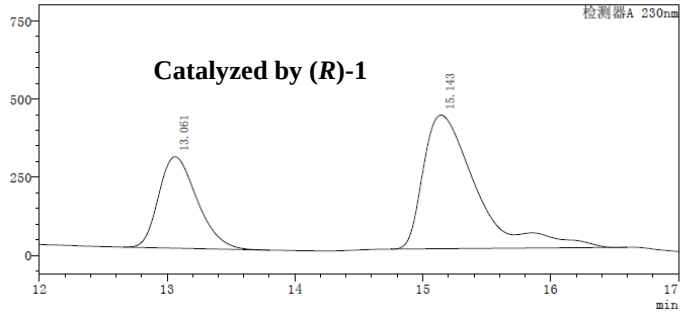


Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	11.226	3714217	172792	51.467
2	14.811	3502479	125810	48.533
The Total		7216695	298602	

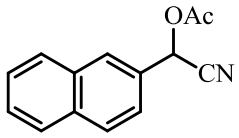


(*S*)-Cyano(α-naphthyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{minor} = 13.061 min; t_{major} = 15.143 min.

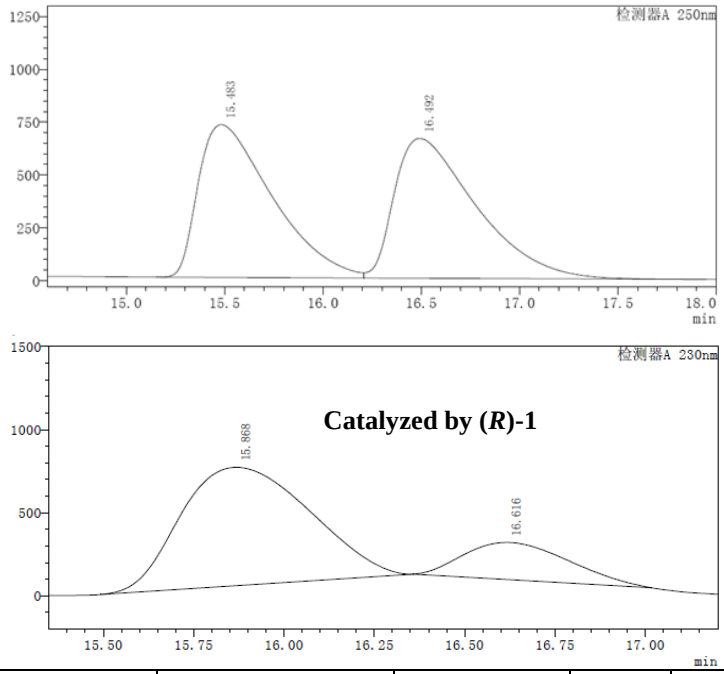




Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	13.061	6101816	292796	32.946
2	15.143	12418869	427965	67.054
The Total		18520686	720761	

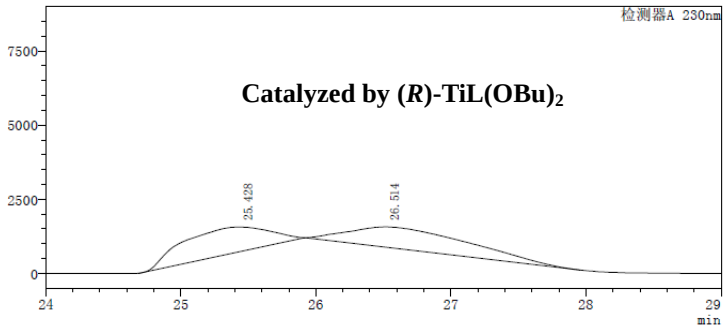


(*R*)-Cyano(β-naphthyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min); (*R*)-**1**: t_{major}= 15.868 min; t_{minor} = 16.616 min.

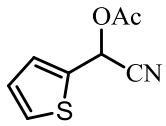


Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	15.868	17729863	713044	79.685
2	16.616	4520081	222986	20.315
The Total		22249944	936030	

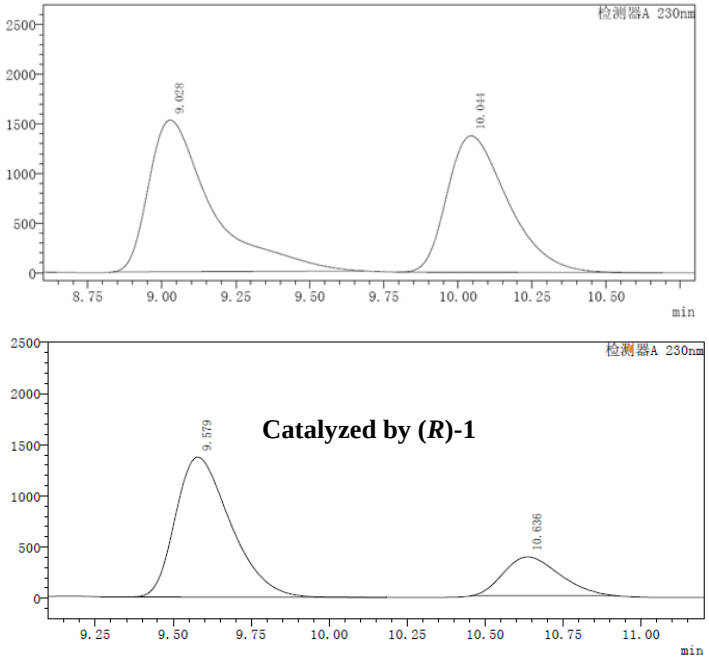
(*S*)-Cyano(β-naphthyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 99/1, 1.0 mL/min); (*R*)-Ti**L**$(OBu)_2$: t_{minor} = 25.428 min; t_{major}= 26.514 min;



Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	25.428	40419784	834253	47.214
2	26.514	45189640	679902	52.786
The Total		85609424	1514155	

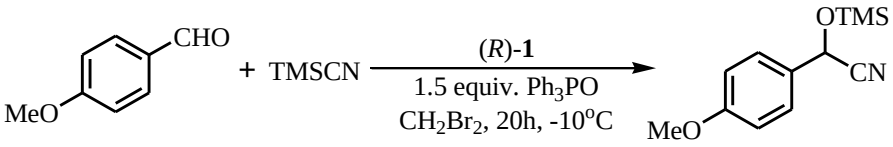


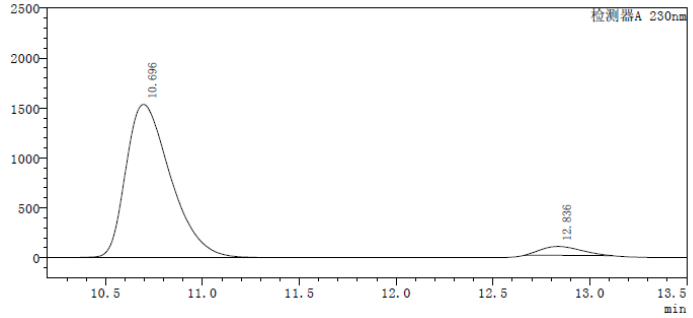
(*R*)-Cyano(2-thiophenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{major}= 9.579 min; t_{minor}= 10.636 min.

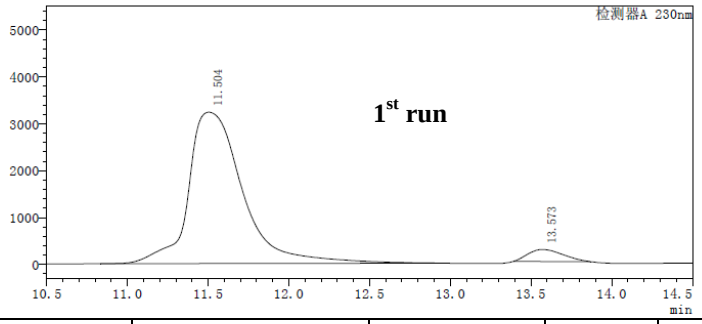


Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	9.579	16810350	1368656	78.072
2	10.636	4721484	378560	21.928
The Total		21531834	1747216	

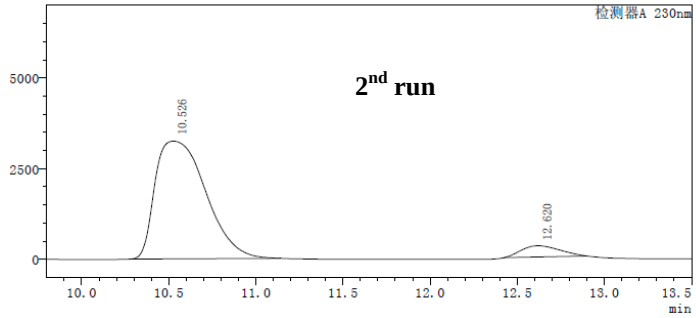
14.2. HPLC of recycling study



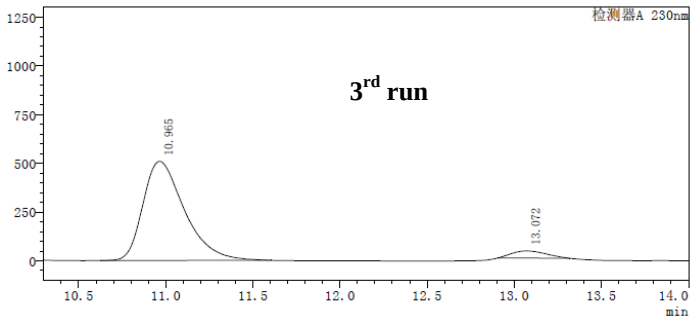




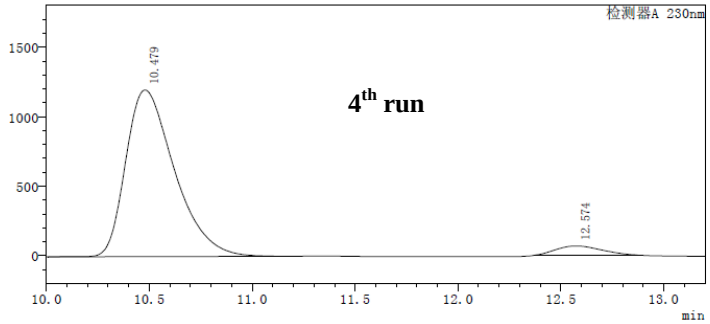
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	11.504	75763261	3228342	95.160
2	13.573	3853772	256447	4.840
The Total		79617034	3484789	



Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.526	65762730	3249766	93.269
2	12.620	4746242	308518	6.731
The Total		70508973	3558283	

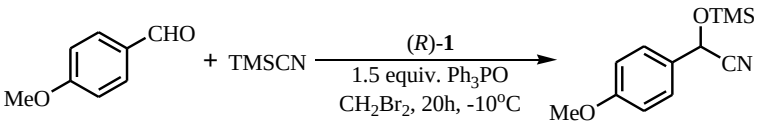


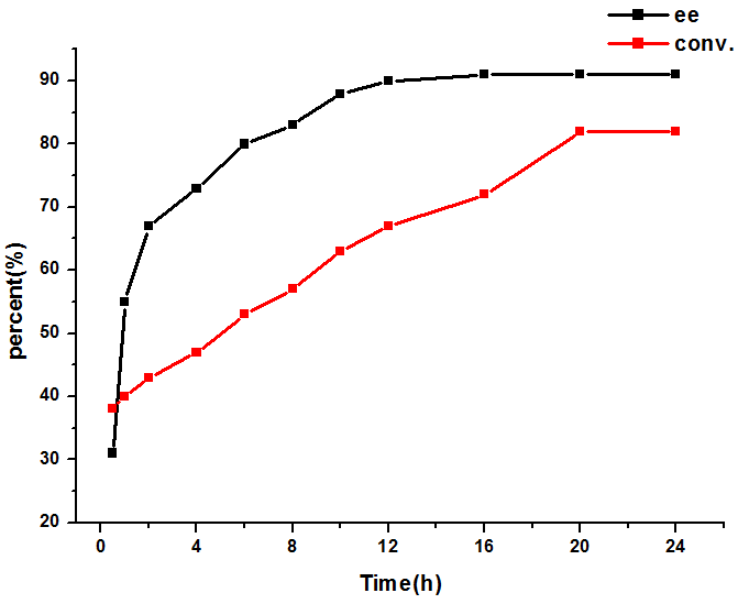
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.965	8429822	509186	94.429
2	13.072	497369	36442	5.571
The Total		8927191	545627	



Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.479	19751745	1198778	94.998
2	12.574	1040042	66991	5.002
The Total		20791788	1265768	

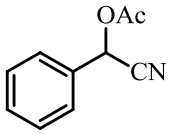
14.3. Kinetic study



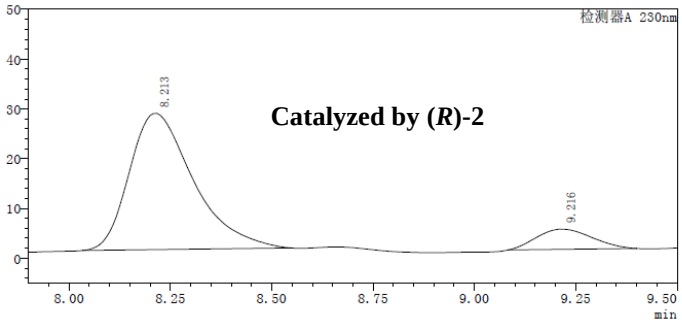


15. Asymmetric Cyanosilylation Catalyzed by 2

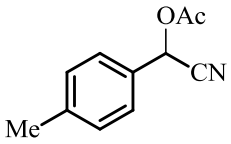
15.1. HPLC of 2 catalyzed cyanation reaction



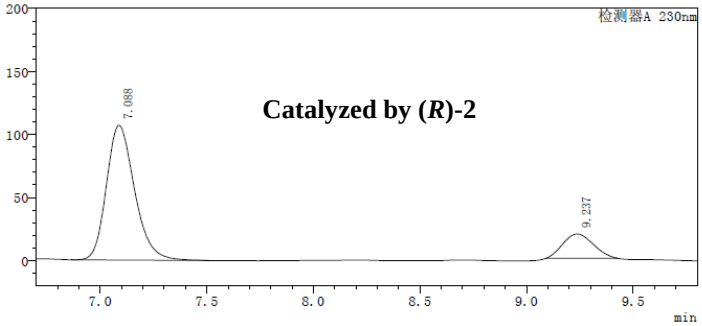
(*R*)-Cyano(phenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{major}= 8.213 min; t_{minor} = 9.216 min.



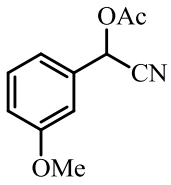
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	8.213	301637	27386	88.631
2	9.216	38692	4076	11.369
The Total		340329	31461	



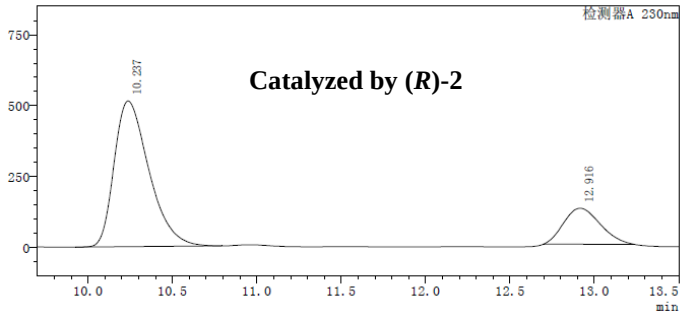
(*R*)-Cyano(4-methylphenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{major} = 7.088 min; t_{minor}= 9.237 min.



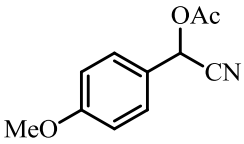
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	7.088	985996	106905	83.820
2	9.237	190332	19167	16.180
The Total		1176328	126073	



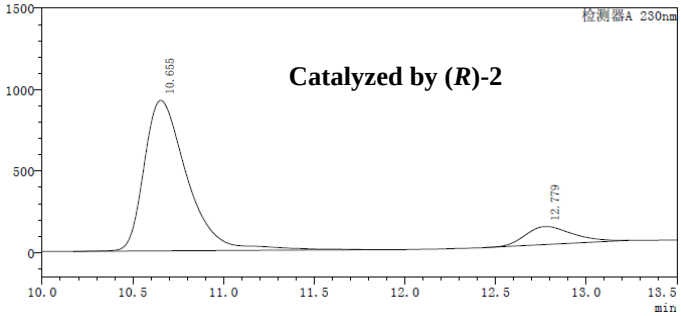
(*R*)-Cyano(3-methoxyphenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{major} = 10.237 min; t_{minor}= 12.916 min.



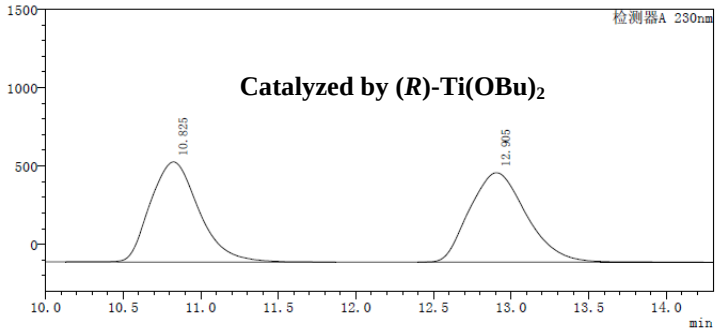
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.237	7380779	513624	79.318
2	12.916	1924554	127171	20.682
The Total		9305333	640794	



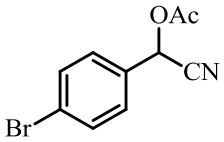
(*R*)-Cyano(4-methoxyphenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{major} = 10.655 min; t_{minor}= 12.779 min.



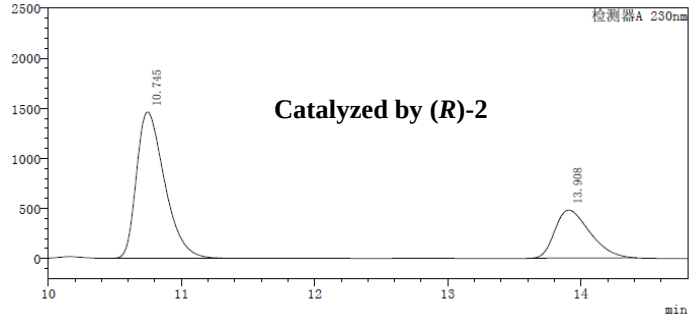
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.655	15271507	924285	88.246
2	12.779	2034066	110989	11.754
The Total		17305573	1035274	



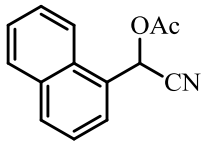
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.825	13899417	638457	48.875
2	12.905	14539569	570549	51.125
The Total		28438986	1209006	



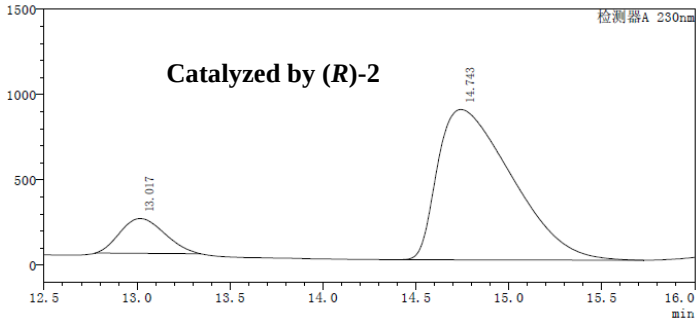
(*R*)-Cyano(4-bromophenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{major} = 10.745 min; t_{minor}= 13.908 min.



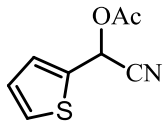
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.745	21522017	1462687	71.064
2	13.908	8763508	479608	28.936
The Total		30285525	1942296	



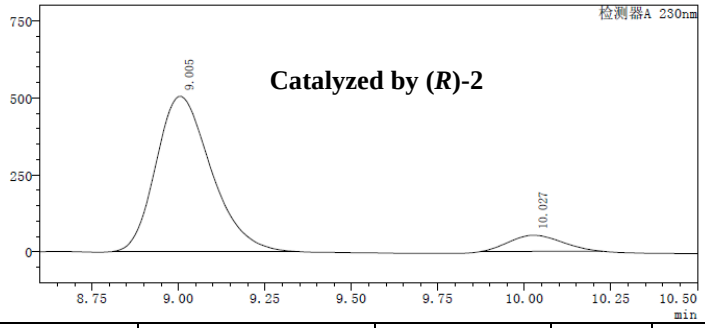
(*S*)-Cyano(α-naphthyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{minor} = 13.017 min; t_{major} = 14.743 min.



Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	13.017	3413819	204409	12.222
2	14.743	24517036	882379	87.778
The Total		27930854	1086788	

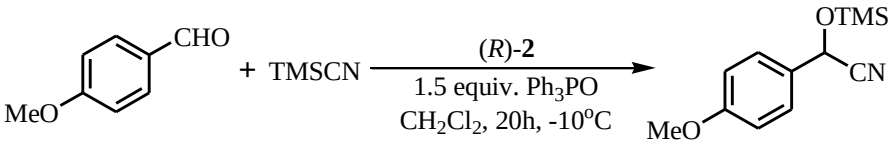


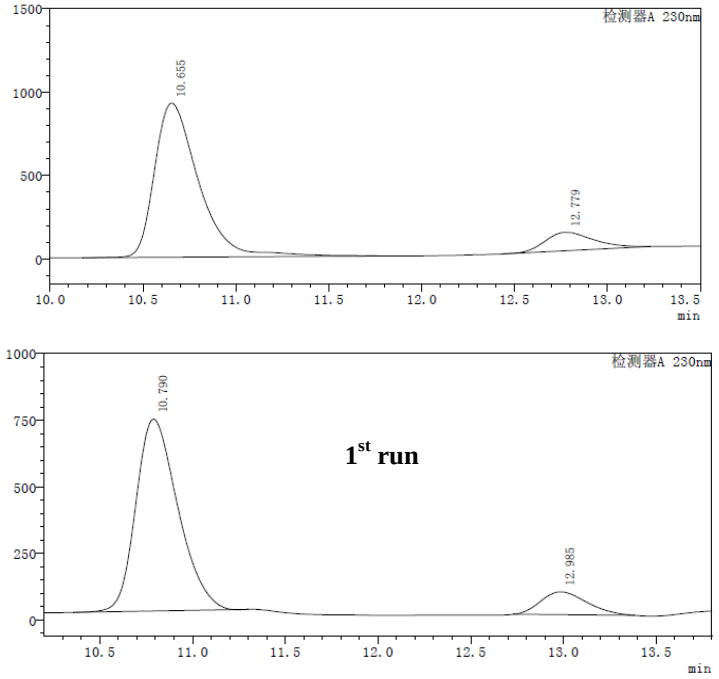
(*R*)-Cyano(2-thiophenyl)methyl acetate: chiralcel OD-H column (hexane/*i*-PrOH 95/5,1.0 mL/min), t_{major}= 9.005 min; t_{minor}= 10.027 min.



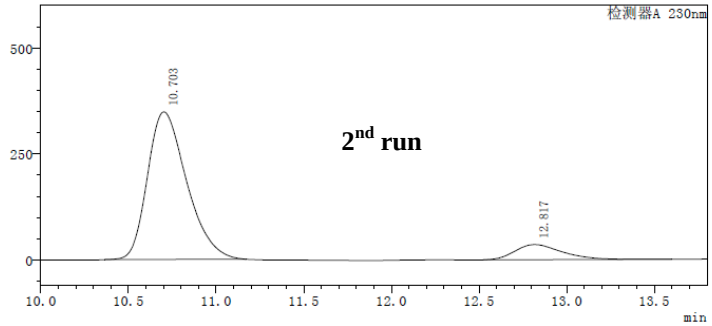
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	9.005	5596400	504417	90.971
2	10.027	555450	52305	9.029
The Total		6151850	556722	

15.2. HPLC of recycling study

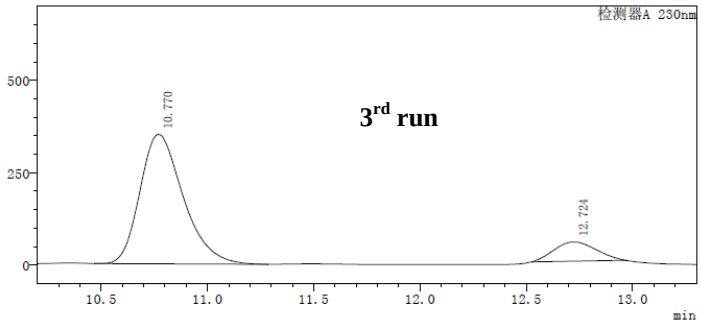




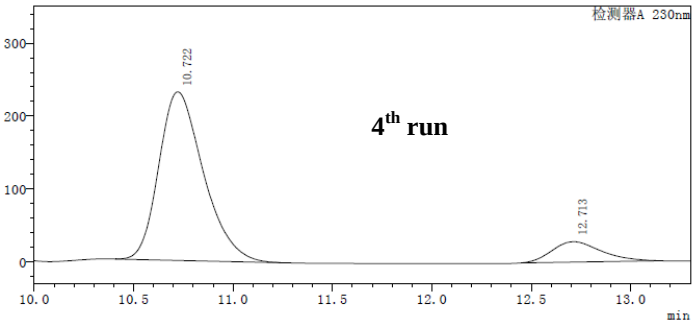
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.790	11376012	720825	88.402
2	12.985	1492468	85880	11.598
The Total		12868480	806704	



Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.703	5423421	348645	88.931
2	12.817	675055	35837	11.069
The Total		6098476	384482	

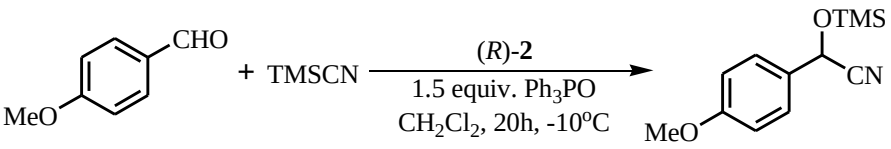


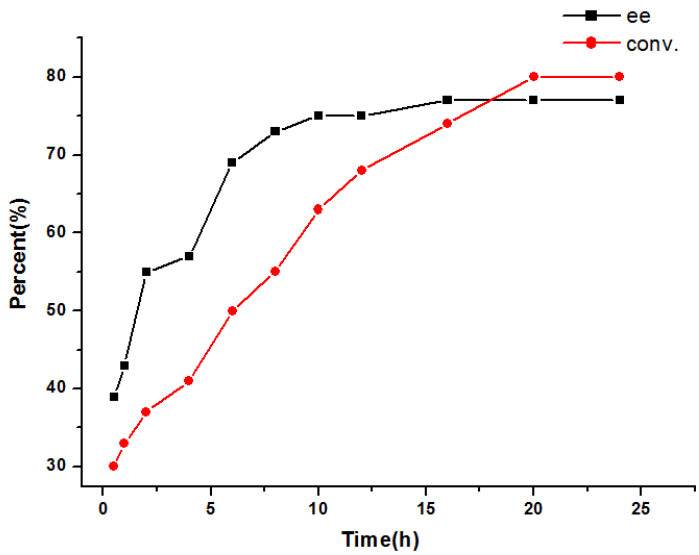
Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.770	4961818	350656	87.405
2	12.724	714975	52003	12.595
The Total		5676794	402659	



Serial Number	Retention Time [min]	Area [mAbs*s]	height	Area %
1	10.722	3610724	231243	88.128
2	12.713	486400	28045	11.872
The Total		4097124	259288	

15.3. Kinetic study





16. NMR spectra