Electronic Supplementary Material (ESI) for Chemical Communications

Chiral Microporous Ti(salan)-Based Metal-Organic Frameworks for Asymmetric Sulfoxidation

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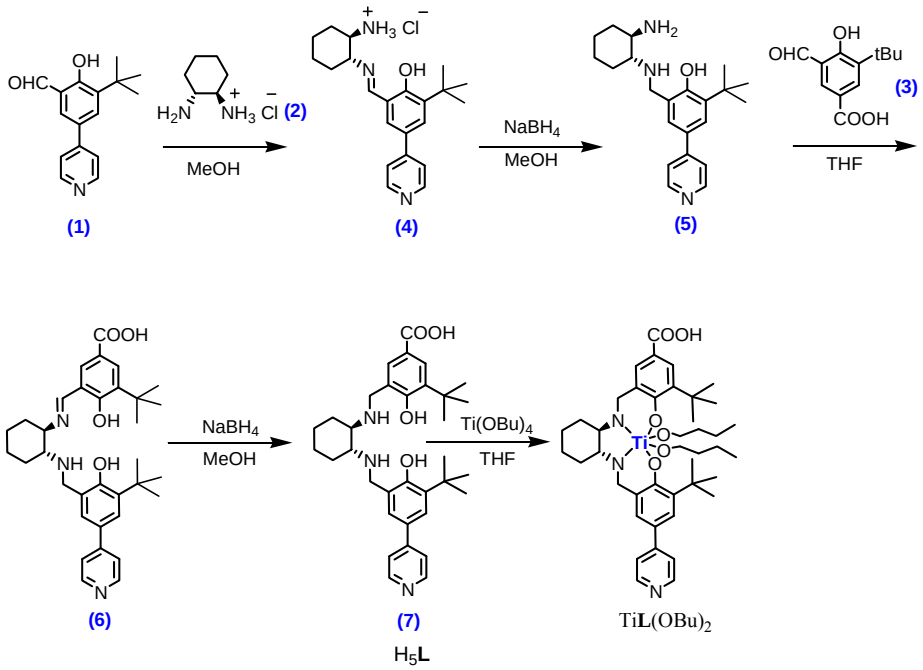
1. Materials and General Procedures.

All of the chemicals are commercial available, and used without further purification. Elemental analyses of C, H and N were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. The solid state CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). Thermogravimetric analyses (TGA) were carried out in an nitrogen 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. Electrospray ionization mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase. A iCAP6300 inductively coupled plasma optical emission spectrometer(ICP-OES) was used to measure Ti and Cd concentrations. Analytical high performance liquid chromatography (HPLC) was performed on a YL-9100 HPLC with UV detection at 254 nm. Analytical CHIRALCEL OD-H and OD-H columns (4.6 mm × 25 cm) from Daicel were used.

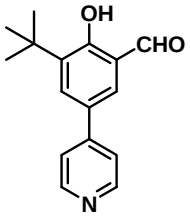
X-ray Crystallography. Single-crystal XRD data for the compounds **1** and **2** were collected on a Bruker Smart 1000 CCD diffractometer with Cu-*K*α radiation (λ = 1.54178 Å) at 100 K. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). The structure was solved using direct method, and refined by full-matrix least-squares on F^2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). In all compounds, the guest molecules and H-atoms were refined isotropically, while all other atoms were refined anisotropically. Crystal data and details of the data collection are given in Tables S1, while the selected bond distances and angles are presented in Tables S2-S3.

2. Synthetic Procedures of the ligand H_5L, $TiL(OBu)_2$, 1 and 2.



The synthetic routes of H_5L and $TiL(OBu)_2$.

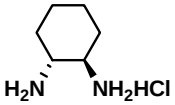
2.1 Preparation of compound (1)



（1）

3-tert-butyl-2-hydroxy-5-(pyridin-4-yl)benzaldehyde was synthesized according the the literature (Morris, G. A.; Nguyen, S. T. *Tetrahedron Letters*. **2001**, *42*, 2093-2096.)

2.2 Preparation of compound (2)

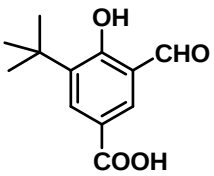


（2）

(1R,2R)-cyclohexane-1,2-diamine hydrochloride was synthesized according the

the literature (Holbach, M.; Zheng, X.; Burd, C.; Jones, C. W.; Weck, M. *J. Org. Chem.* **2006**, *71*, 2903-2906.)

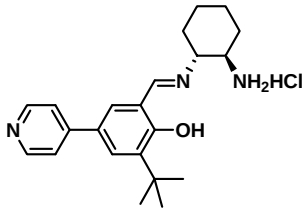
2.3 Preparation of compound (3)



（3）

3-tert-butyl-5-formyl-4-hydroxybenzoic acid was synthesized according the the literature(Yuan, G.; Zhu, C.; Liu, Y.; Cui, Y. *Chem. Commun*. **2010**, *47*, 3180-3182).

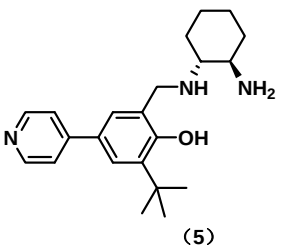
2.4 Preparation of compound (4)



（4）

A solution of 3-tert-butyl-2-hydroxy-5-(pyridin-4-yl)benzaldehyde(2.55 g, 10 mmol) in MeOH (25 ml) was added dropwise to (1*R*,2*R*)-cyclohexane-1,2-diamine hydrochloride(1.8 g, 10.2 mmol) in MeOH (10 ml) at 60 °C. The reaction mixture was stirred at 60 °C for 4 h. Then, the light yellow precipitate of compound **4** was produced during the reaction and the precipitate were collected by filtration and washed with hot methanol (50°C), which in that case gave quantitative pure compound of **4**.

2.5 Preparation of compound (5)

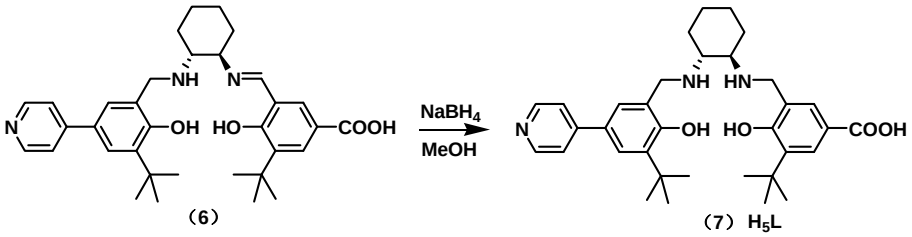


（5）

A slurry of compound **4** (774 mg, 2 mmol) in methanol (10 mL) and 3 equiv of

$NaBH_4$ (227 mg, 6 mmol) were added portion-wise with stirring. The reaction mixture was stirred 6 h at RT, during which time its color turned light yellow. The solvent was evaporated under vacuum and the reaction mixture was poured into 50 mL of water. Then the desired product was extracted with ethyl acetate (3×50 ml). The combined organic layers were washed with brine till the pH reached 7 and then dried over Na_2SO_4. After removal of the solvent, the pure product compound **5** was obtained in a 96% yield.

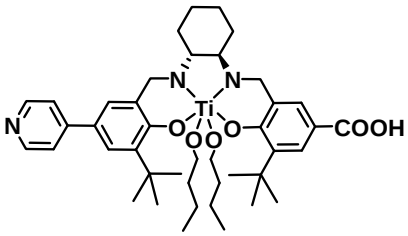
2.6 Preparation of compound (7)



(6) (7) H_5L

A solution of compound **5** (0.706 g, 2 mmol) in THF (5 ml) was added dropwise to 3-tert-butyl-5-formyl-4-hydroxybenzoic acid **3** (0.457 g, 2.06 mmol) in THF (5 ml) at 60 °C. The reaction mixture was stirred at 60 °C for 5 h and the solvent was removed in vacuo and the crude product of **6** was obtained as yellow power, which was proceed directly to the next step of the reduction reaction. The crude product of **6** in methanol (25 mL) and 3 equiv of $NaBH_4$ (227 mg, 6 mmol) were added portion-wise with stirring. The reaction mixture was stirred 6 h at RT. The solvent was evaporated under vacuum and the reaction mixture was poured into 50 mL of water. Then the desired product was extracted with ethyl acetate (3×50 ml). The combined organic layers were washed with brine till the pH reached 7 and then dried over Na_2SO_4. After removal of the solvent and washed with Et_2O (2×5 ml). the pure product compound **7** was obtained in a total yield of 76% (849 mg).

2.7 Synthesis of [TiL(OBu)$_2$]



A solution of tetrabutyl titanate (340 mg, 1mmol) in anhydrous THF (10 mL) was added dropwise to H_3**L** (559 mg, 1 mmol) in anhydrous THF (30 mL). The reaction mixture immediately change into bright yellow and stirred at room temperature for 8 h, after which the solvent was evaporated under vacuum, The yellow powder of [Ti**L**$(OBu)_2$] was collected, washed with MeOH and Et_2O,respectively, then dried under reduced pressure (637 mg, 85%). MS (ESI) for $[M+H]^+$: calcd 749.3,found 750.0.

2.8 Synthesis of 1.

A mixture of $CdBr_2{\cdot}4H_2O$ (2.75 mg, 0.008 mmol), [Ti**L**$(OBu)_2$] (2.99 mg, 0.004 mmol), DMF (1 mL) and MeOH (0.3 ml) in a capped vial was heated at 100 °C for one day. Yellow block-like crystals of **1** were filtered, washed with DMF and MeOH, respectively, and dried at room temperature. Yield: 5.26 mg (76.0%). Elemental Analysis an IR data of $Cd_3(\mu_3\text{-OH})Br[(Ti\mathbf{L}OMe)_2O]_2{\cdot}3DMF{\cdot}H_2O$: Anal (%). Calcd for C158H172BrCd3N18O31Ti4: C, 55.36; H, 5.06; N, 7.36. Found: C, 54.91; H, 5.83; N, 7.30. FTIR (KBr pellet): 3434 (m), 3081 (w), 2938 (s), 2861 (m), 2804 (w),1663 (m), 1598 (s), 1537 (m), 1524 (m), 1465 (s), 1444 (s), 1384 (s), 1320 (m), 1275 (s), 1226 (m), 1163 (w), 1074 (m), 1015 (w), 974 (w), 947 (w), 902(w), 827 (m), 805 (w), 794 (w), 703 (s), 606(w), 570 (m), 551 (w), 485 (w) cm^{-1}.

2.9 Synthesis of 2.

A mixture of $Zn(OAc)_2{\cdot}2H_2O$ (1.76 mg, 0.008 mmol), [Ti**L**$(OBu)_2$] (2.99 mg, 0.004 mmol), DMF (1 mL) and EtOH (0.5 ml) in a capped vial was heated at 100 °C for one day. Yellow block-like crystals of **2** were filtered, washed with DMF and

MeOH, respectively, and dried at room temperature. Yield: 4.31 mg (66%). Elemental Analysis an IR data of $Zn_3(\mu_3$-OH)(OH)[(Ti**L**OEt)$_2$O]$_2$·3DMF: Anal (%). Calcd for C162H180N18O30Ti4Zn3: C, 59.93; H, 5.59; N, 7.76. Found: C, 59.46; H, 6.31; N, 7.71. FTIR (KBr pellet): 3426 (m), 3090 (w), 2936 (s), 2857 (m), 2808 (w),1670 (m), 1597 (s), 1541 (m), 1466 (s), 1443 (s), 1385 (s), 1322 (m), 1273 (s), 1224 (m), 1163 (w), 1121 (w), 1075 (m), 1026 (w), 1002 (w), 974 (w), 946 (w), 919 (w), 902 (w), 827 (m), 792 (w), 703 (s), 680 (s), 647 (w), 606 (w), 569 (m), 551 (w), 488 (w) cm^{-1}.

3. Experimental procedure and determination of enantiomeric purity for sulfoxides

Typical catalytic process

The catalyst (*R*,*R*)-**1** (9.8 mg, 2.8 μmol, 0.0112 equiv) and sulfide (0.25 mmol) were combined in acetone (1 mL) and stirred for 20 min at 25 °C, followed by adding an 1.15 eq oxidant (30 % aqueous hydroperoxide) in one portion. Stirring was continued at 0°C for 16 h. The ee of resulted sulfoxides was determined by HPLC using Chiralcel OD-H and Chiralcel OJ-H columns, and conversion was determined by ^{1}H NMR.

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

Identification code	**1**	**2**
Empirical formula	$C_{158}H_{172}BrCd_3N_{18}O_{31}Ti_4$	$C_{162}H_{180}N_{18}O_{30}Ti_4Zn_3$
Formula weight	3427.85	3246.95
Temperature (K)	100(2) K	100(2) K
Wavelength (Å)	1.54178	1.54178
Crystal system	orthorhombic	orthorhombic
Space group	P 2_12_12	P 2_12_12
Unit cell dimensions	a =34.4419(13) Å b = 16.7622(8) Å c = 18.4473(8)Å $\alpha = \beta = \gamma = 90°$	a = 34.0597(5) Å b = 16.9014(2) Å c = 18.3315(3) Å $\alpha = \beta = \gamma = 90°$
Volume ($Å^3$), Z	10650.0(8), 2	10552.6(3), 2
Density (calculated) (mg/m^3)	1.069	1.022
Absorption coefficient (mm^{-1})	4.258	2.073
F(000)	3522	3392
θ range for data collection (º)	3.51 to 55	2.92 to 55.00
Limiting indices	-36≤ h≤ 32, -13≤ k≤ 17, -16≤ l≤19	-35≤ h≤ 35, -17≤ k≤ 13, -17≤ l≤ 19
Reflections collected	26815	25138
Independent reflections	11722 [R(int) = 0.0894]	12261 [R(int) = 0.0377]
Completeness to theta	55.00/96.1 %	55.00/96.9 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	11722 / 14 / 783	12261 / 102 / 821
Goodness-of-fit on F^2	1.074	1.084
Final R indices [I>2sigma(I)]	R_1= 0.0794, wR_2= 0.1873	R_1 = 0.0984, wR_2 = 0.2573
R indices (all data)	R_1= 0.1197, wR_2= 0.2054	R_1 = 0.1145, wR_2 = 0.2757
Absolute structure parameter	0.005(12)	0.031(13)
Largest diff. peak and hole ($e.Å^{-3}$)	0.672 and -0.492	1.202 and -0.579

5. Table S2. Selected Bond lengths and angles for 1.

Ti(1)-O(6)	1.832(8)
Ti(1)-O(4)	1.859(7)
Ti(1)-O(5)	1.864(8)
Ti(1)-O(3)	1.921(8)
Ti(1)-N(1)	2.200(9)
Ti(1)-N(2)	2.284(10)
Ti(2)-O(6)	1.829(8)
Ti(2)-O(12)	1.864(7)
Ti(2)-O(11)	1.874(7)
Ti(2)-O(10)	1.936(7)
Ti(2)-N(4)	2.211(9)
Ti(2)-N(5)	2.252(9)
Cd(1)-O(7)	2.319(9)
Cd(1)-O(7)#1	2.319(9)
Cd(1)-N(6)#2	2.348(5)
Cd(1)-N(6)#3	2.348(5)
Cd(1)-O(9)	2.377(15)
Cd(1)-Br(1)	2.582(2)
Cd(2)-O(9)	2.147(4)
Cd(2)-N(3)#2	2.199(7)
Cd(2)-O(8)	2.242(12)
Cd(2)-O(2)#4	2.298(10)
Cd(2)-O(1)#4	2.327(9)
Cd(2)-O(7)	2.477(9)
O(2)-Cd(2)#5	2.298(10)
O(9)-Cd(2)#1	2.147(4)
N(3)-Cd(2)#6	2.199(7)
N(6)-Cd(1)#6	2.348(5)

O(6)-Ti(1)-O(4)	99.4(3)
O(6)-Ti(1)-O(5)	90.8(3)
O(4)-Ti(1)-O(5)	103.6(3)
O(6)-Ti(1)-O(3)	167.4(3)
O(4)-Ti(1)-O(3)	91.8(3)
O(5)-Ti(1)-O(3)	92.2(4)
O(6)-Ti(1)-N(1)	86.1(3)
O(4)-Ti(1)-N(1)	157.3(4)
O(5)-Ti(1)-N(1)	98.3(4)
O(3)-Ti(1)-N(1)	81.3(3)
O(6)-Ti(1)-N(2)	84.2(4)
O(4)-Ti(1)-N(2)	81.8(3)
O(5)-Ti(1)-N(2)	173.2(4)
O(3)-Ti(1)-N(2)	91.8(4)

N(1)-Ti(1)-N(2)	76.8(3)
O(6)-Ti(2)-O(12)	90.2(3)
O(6)-Ti(2)-O(11)	98.9(3)
O(12)-Ti(2)-O(11)	103.9(4)
O(6)-Ti(2)-O(10)	164.5(3)
O(12)-Ti(2)-O(10)	92.2(3)
O(11)-Ti(2)-O(10)	95.4(3)
O(6)-Ti(2)-N(4)	83.6(3)
O(12)-Ti(2)-N(4)	97.2(4)
O(11)-Ti(2)-N(4)	158.7(3)
O(10)-Ti(2)-N(4)	80.9(3)
O(6)-Ti(2)-N(5)	86.3(3)
O(12)-Ti(2)-N(5)	173.4(4)
O(11)-Ti(2)-N(5)	82.2(3)
O(10)-Ti(2)-N(5)	89.8(3)
N(4)-Ti(2)-N(5)	76.8(3)
O(7)-Cd(1)-O(7)#1	155.1(4)
O(7)-Cd(1)-N(6)#2	86.8(3)
O(7)#1-Cd(1)-N(6)#2	89.6(3)
O(7)-Cd(1)-N(6)#3	89.6(3)
O(7)#1-Cd(1)-N(6)#3	86.8(3)
N(6)#2-Cd(1)-N(6)#3	163.3(4)
O(7)-Cd(1)-O(9)	77.5(2)
O(7)#1-Cd(1)-O(9)	77.5(2)
N(6)#2-Cd(1)-O(9)	81.7(2)
N(6)#3-Cd(1)-O(9)	81.7(2)
O(7)-Cd(1)-Br(1)	102.5(2)
O(7)#1-Cd(1)-Br(1)	102.5(2)
N(6)#2-Cd(1)-Br(1)	98.3(2)
N(6)#3-Cd(1)-Br(1)	98.3(2)
O(9)-Cd(1)-Br(1)	180.000(1)
O(9)-Cd(2)-N(3)#2	108.3(3)
O(9)-Cd(2)-O(8)	130.3(4)
N(3)#2-Cd(2)-O(8)	100.1(4)
O(9)-Cd(2)-O(2)#4	113.9(5)
N(3)#2-Cd(2)-O(2)#4	94.5(4)
O(8)-Cd(2)-O(2)#4	103.2(3)
O(9)-Cd(2)-O(1)#4	83.8(4)
N(3)#2-Cd(2)-O(1)#4	149.2(4)
O(8)-Cd(2)-O(1)#4	92.1(5)
O(2)#4-Cd(2)-O(1)#4	55.0(3)
O(9)-Cd(2)-O(7)	78.6(4)
N(3)#2-Cd(2)-O(7)	101.7(4)
O(8)-Cd(2)-O(7)	55.9(3)

O(2)#4-Cd(2)-O(7)	155.3(3)
O(1)#4-Cd(2)-O(7)	108.5(4)
Ti(2)-O(6)-Ti(1)	159.5(4)
Cd(1)-O(7)-Cd(2)	97.6(3)
C(35)-O(8)-Cd(2)	95.5(9)
Cd(2)-O(9)-Cd(2)#1	148.5(8)
Cd(2)-O(9)-Cd(1)	105.8(4)
Cd(2)#1-O(9)-Cd(1)	105.8(4)

Symmetry transformations used to generate equivalent atoms:

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

#3 -x+3/2,y-1/2,-z+1 #4 x,y,z+1 #5 x,y,z-1

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

Table S3. Selected Bond lengths and angles for 2.

Zn(1)-N(6)#1	2.021(4)
Zn(1)-O(8)#2	2.032(10)
Zn(1)-O(3)	2.042(9)
Zn(1)-O(2)	2.093(13)
Zn(1)-O(7)#2	2.323(14)
Zn(2)-O(3)	1.929(19)
Zn(2)-N(3)#4	2.048(8)
Zn(2)-O(1)	2.050(12)
Zn(2)-O(1)#3	2.140(14)
Zn(2)-O(13)	2.386(11)
Ti(1)-O(12)	1.836(5)
Ti(1)-O(5)	1.845(6)
Ti(1)-O(6)	1.857(8)
Ti(1)-O(4)	1.938(7)
Ti(1)-N(1)	2.217(8)
Ti(1)-N(2)	2.254(9)
Ti(2)-O(12)	1.829(5)
Ti(2)-O(11)	1.868(5)

Ti(2)-O(10)	1.874(5)
Ti(2)-O(9)	1.923(5)
Ti(2)-N(4)	2.203(7)
Ti(2)-N(5)	2.275(6)
O(1)-Zn(2)#3	2.140(14)
O(3)-Zn(2)#3	1.929(19)
O(3)-Zn(1)#3	2.042(9)
O(7)-Zn(1)#5	2.323(14)
O(8)-Zn(1)#5	2.032(10)
O(13)-Zn(2)#3	2.386(11)
N(6)-Zn(1)#7	2.021(4)

N(6)#1-Zn(1)-O(8)#2	142.5(5)
N(6)#1-Zn(1)-O(3)	108.4(2)
O(8)#2-Zn(1)-O(3)	93.7(4)
N(6)#1-Zn(1)-O(2)	99.7(3)
O(8)#2-Zn(1)-O(2)	95.2(5)
O(3)-Zn(1)-O(2)	118.9(6)
N(6)#1-Zn(1)-O(7)#2	89.3(5)
O(8)#2-Zn(1)-O(7)#2	53.8(5)
O(3)-Zn(1)-O(7)#2	129.7(7)
O(2)-Zn(1)-O(7)#2	103.0(6)
O(3)-Zn(2)-N(3)#4	91.4(4)
O(3)-Zn(2)-O(1)	86.2(4)
N(3)#4-Zn(2)-O(1)	106.0(6)
Zn(2)#3-Zn(2)-O(1)#3	71.7(6)
O(3)-Zn(2)-O(1)#3	83.8(5)
N(3)#4-Zn(2)-O(1)#3	98.8(5)
O(1)-Zn(2)-O(1)#3	153.5(2)
Zn(2)#3-Zn(2)-O(13)	78.44(8)

O(3)-Zn(2)-O(13)	154.1(2)
N(3)#4-Zn(2)-O(13)	114.1(4)
O(1)-Zn(2)-O(13)	90.2(5)
O(1)#3-Zn(2)-O(13)	88.1(4)
O(12)-Ti(1)-O(5)	99.0(3)
O(12)-Ti(1)-O(6)	91.8(3)
O(5)-Ti(1)-O(6)	103.6(3)
O(12)-Ti(1)-O(4)	165.5(3)
O(5)-Ti(1)-O(4)	93.4(3)
O(6)-Ti(1)-O(4)	92.5(3)
O(12)-Ti(1)-N(1)	84.0(3)
O(5)-Ti(1)-N(1)	158.2(4)
O(6)-Ti(1)-N(1)	97.9(3)
O(4)-Ti(1)-N(1)	81.7(3)
O(12)-Ti(1)-N(2)	84.9(3)
O(5)-Ti(1)-N(2)	83.7(3)
O(6)-Ti(1)-N(2)	172.4(3)
O(4)-Ti(1)-N(2)	89.1(3)
N(1)-Ti(1)-N(2)	75.0(3)
O(12)-Ti(2)-O(11)	90.9(2)
O(12)-Ti(2)-O(10)	99.1(2)
O(11)-Ti(2)-O(10)	104.1(3)
O(12)-Ti(2)-O(9)	165.6(3)
O(11)-Ti(2)-O(9)	92.7(2)
O(10)-Ti(2)-O(9)	93.5(2)
O(12)-Ti(2)-N(4)	84.8(3)
O(11)-Ti(2)-N(4)	97.8(3)
O(10)-Ti(2)-N(4)	157.6(2)
O(9)-Ti(2)-N(4)	80.9(3)
O(12)-Ti(2)-N(5)	84.5(2)

O(11)-Ti(2)-N(5)	172.9(3)
O(10)-Ti(2)-N(5)	82.0(2)
O(9)-Ti(2)-N(5)	90.5(2)
N(4)-Ti(2)-N(5)	76.5(2)
Zn(2)#3-O(3)-Zn(1)	116.8(5)
Zn(2)-O(3)-Zn(1)	113.6(5)
Zn(2)#3-O(3)-Zn(1)#3	113.6(5)
Zn(2)-O(3)-Zn(1)#3	116.8(5)
Zn(1)-O(3)-Zn(1)#3	127.9(10)
Ti(2)-O(12)-Ti(1)	157.7(3)

Symmetry transformations used to generate equivalent atoms:

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

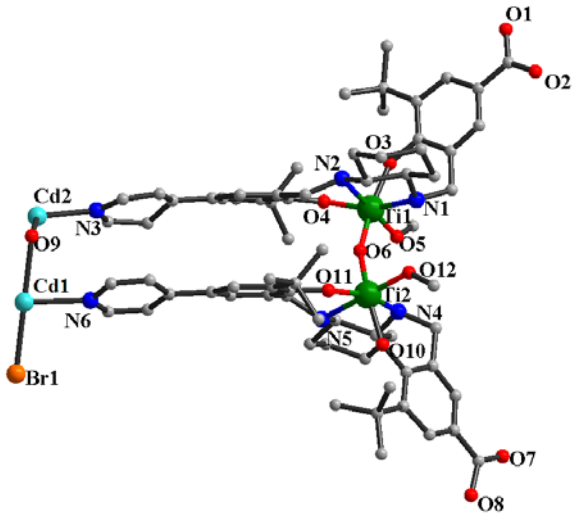
#4 -x+3/2,y+1/2,-z #5 x,y,z+1 #6 -x+3/2,y-1/2,-z

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

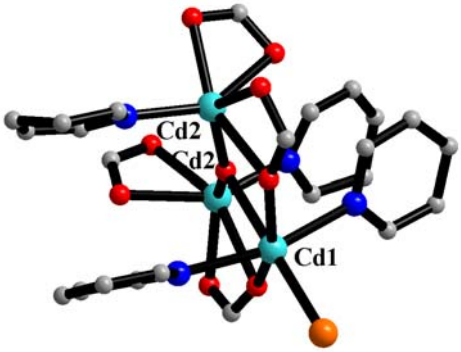
`

6. Figures S1-S5. Additional X-ray crystallographic structure of 1 and 2.

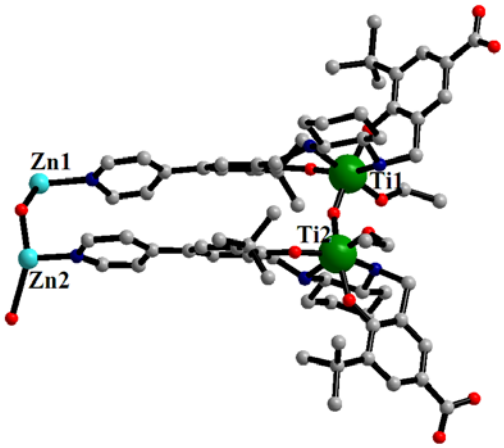
6.1 Figure S1. *Coordination environment of dinuclear TiL unit in* ***1****. For clarity, hydrogen atoms were deleted.*



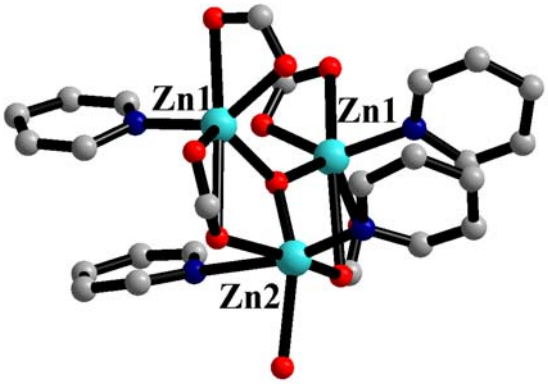
6.2 Figure S2. *The coordination environment of Cd centers in* ***1****.*



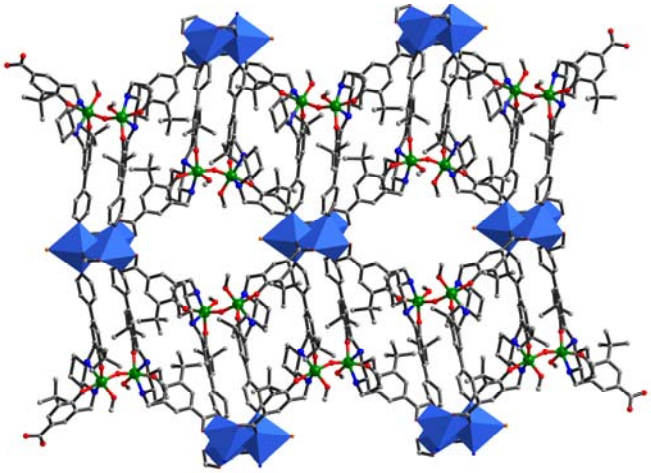
6.3 Figure S3. *Coordination environment of dinuclear TiL unit in* ***2****. For clarity, hydrogen atoms were deleted.*



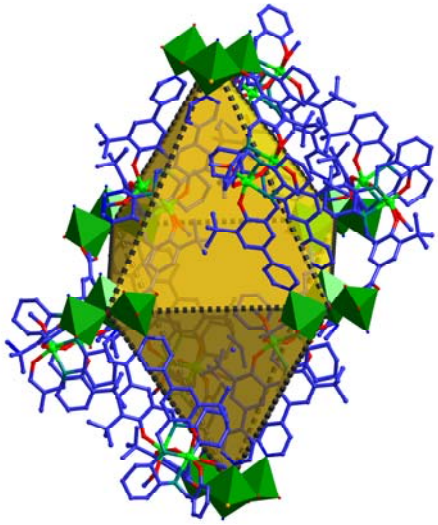
6.4 Figure S4. *The coordination environment of Zn centers in* ***2****.*



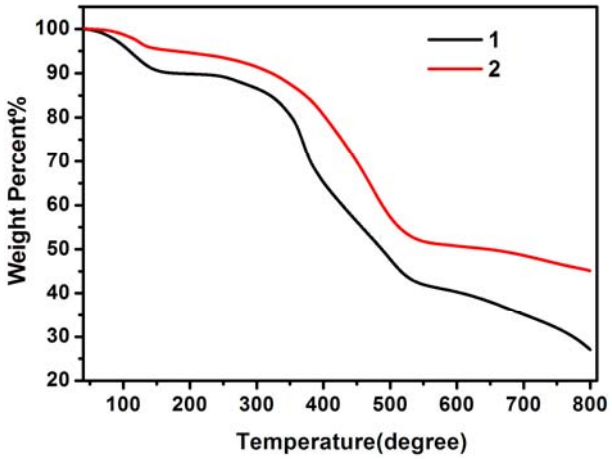
6.5 Figure S5. *View of 3D structures of* ***1*** *and* ***2*** *along b direction.*



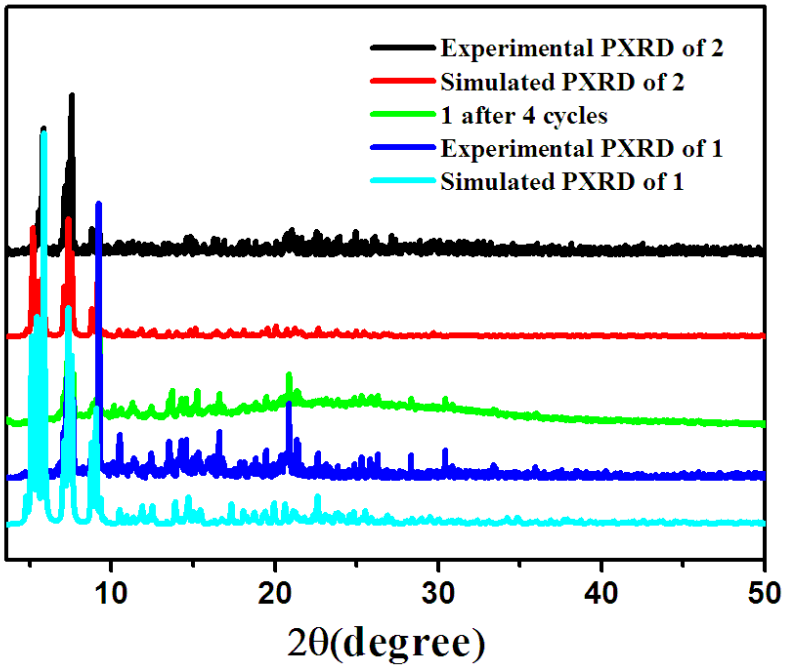
6.6 Figure S6. *View of the distorted octahedral cavity in* ***1*** *and* ***2****.*



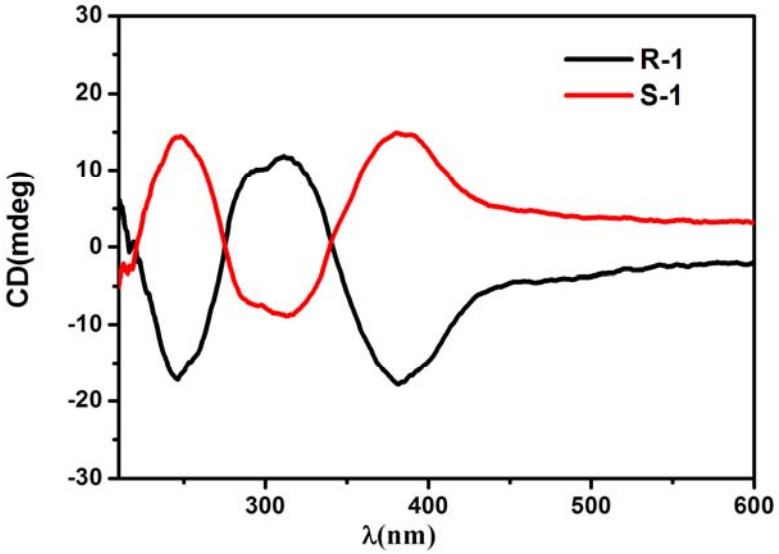
7. Figure S7. TGA curves of 1 and 2.

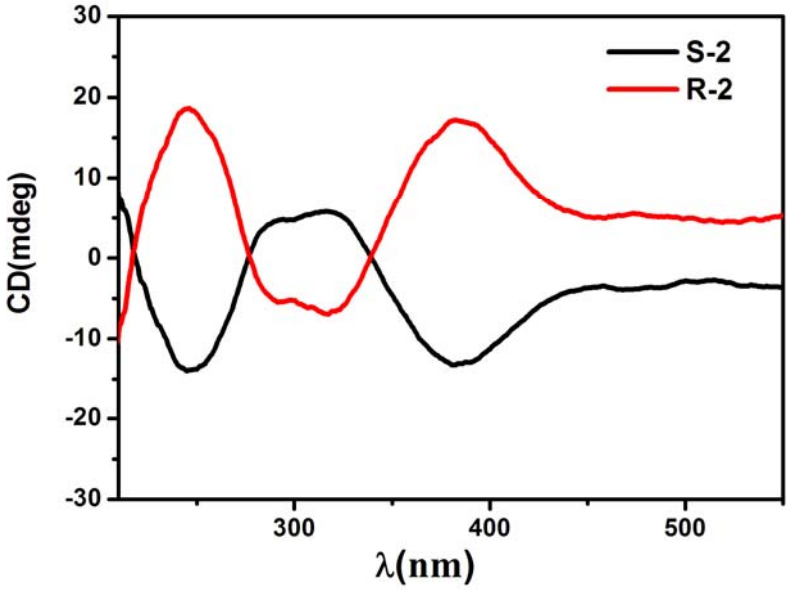


8. Figure S8. PXRD patterns of 1 and 2.

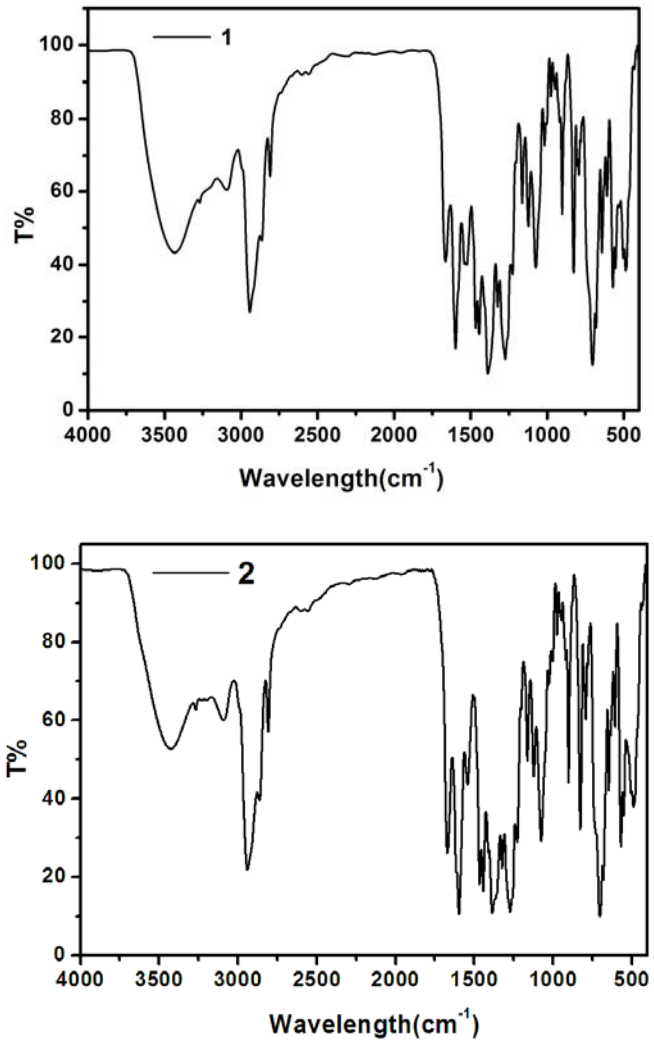


9. Figure S9. CD spectra of (R)/(S)-1 and (R)/(S)-2

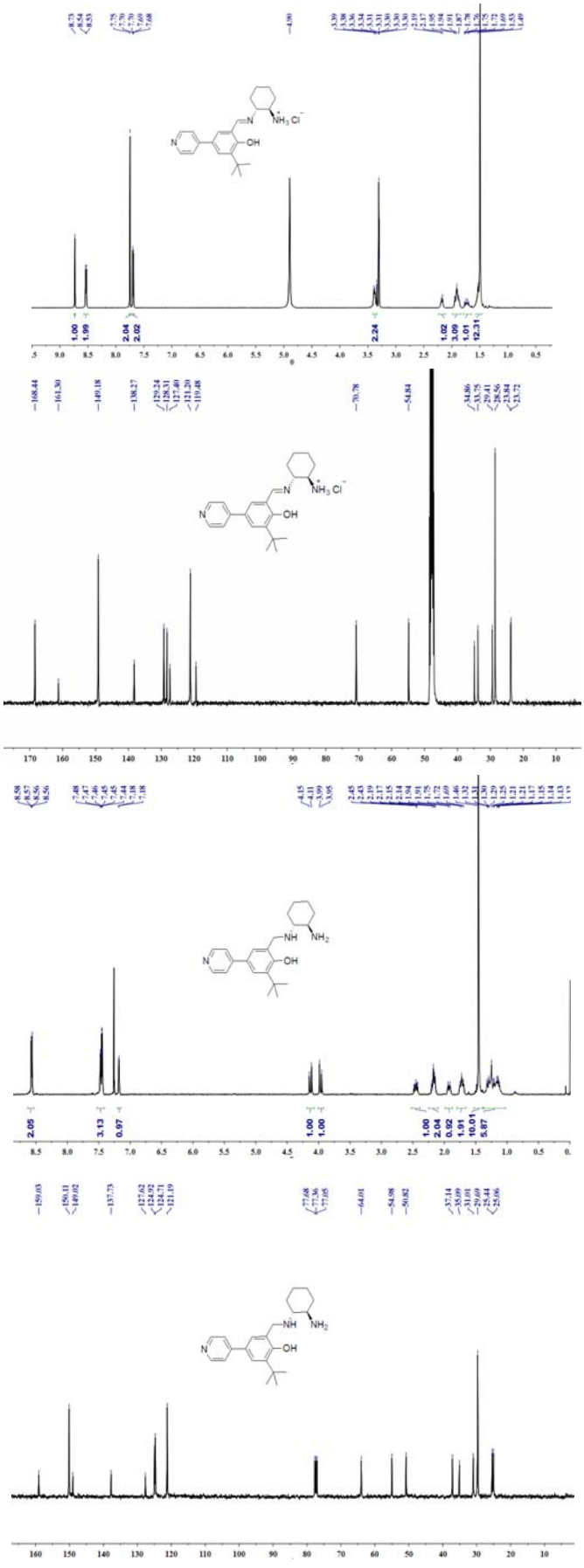


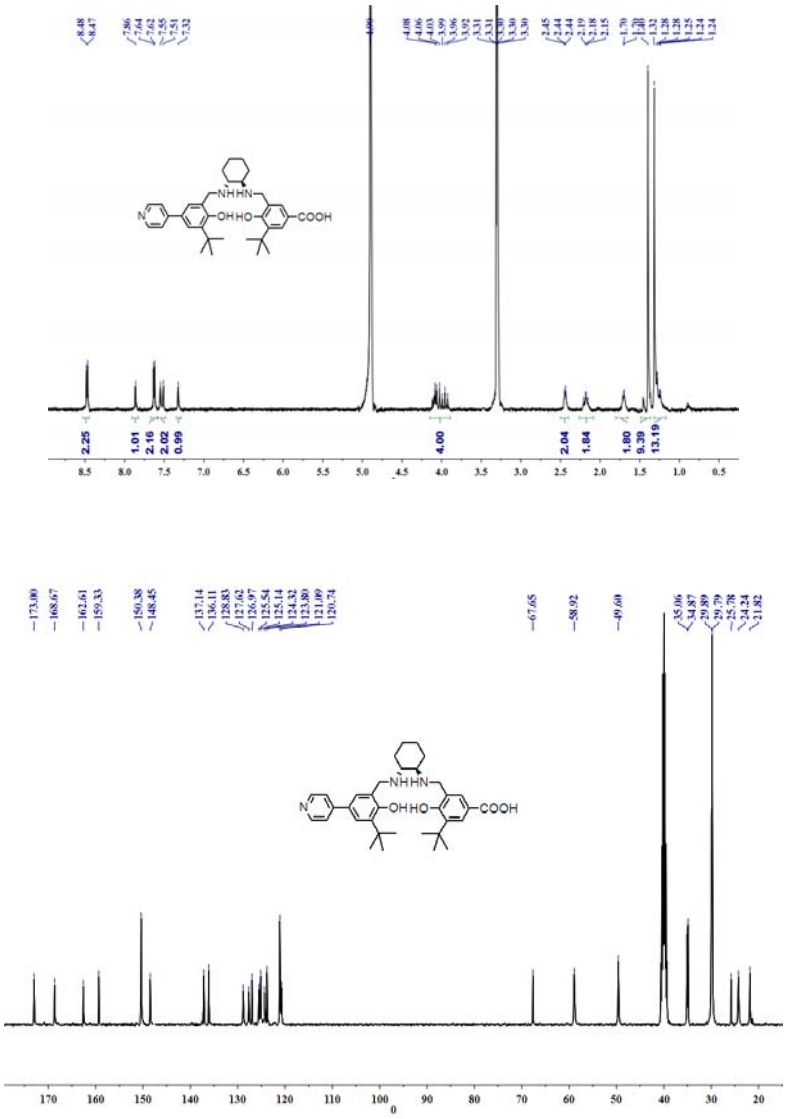


10. Figure S10. IR spectra of 1 and 2

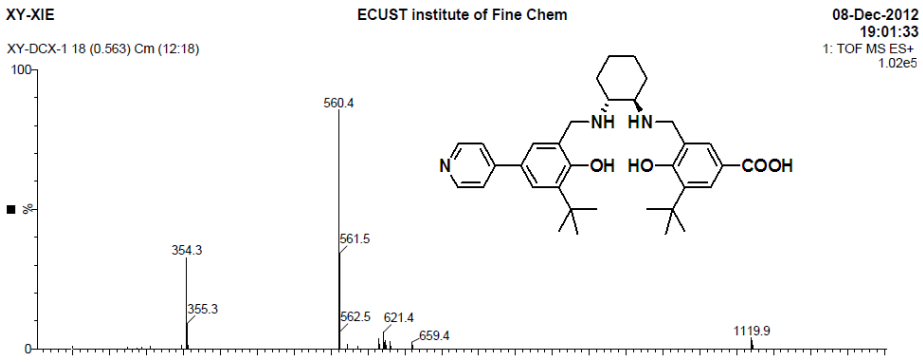


11. Figure S11. ^{1}H and ^{13}C NMR for the H_5L and related predecessors.

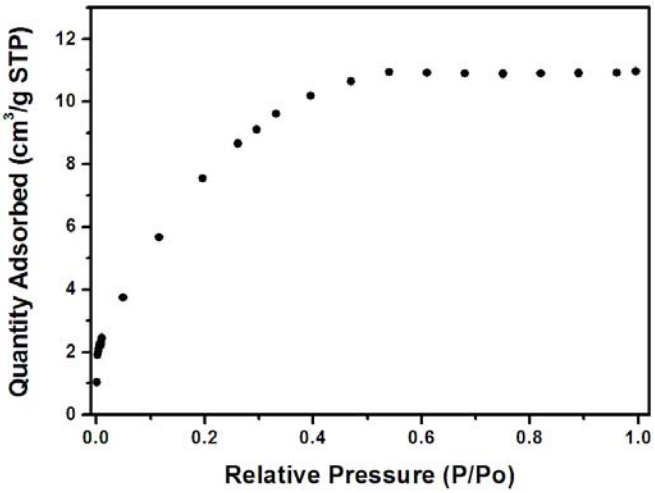




12. Figure S12. ESI-Mass of (*R*)-H_5L.



13. **Figure S13.** Nitrogen sorption isotherm (77 K) of activated **1**.

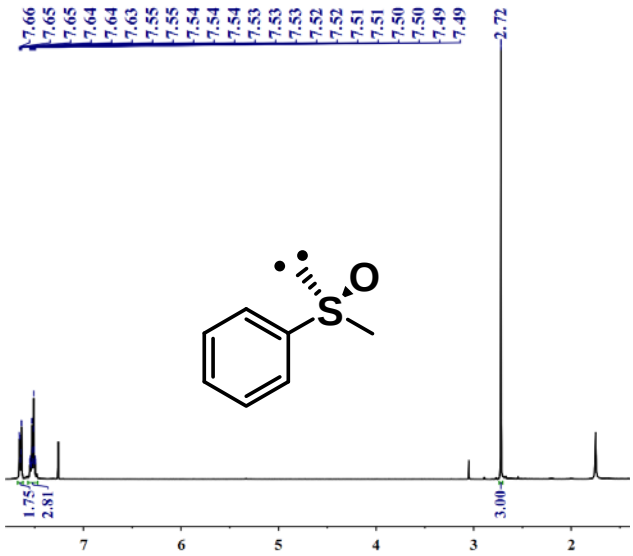


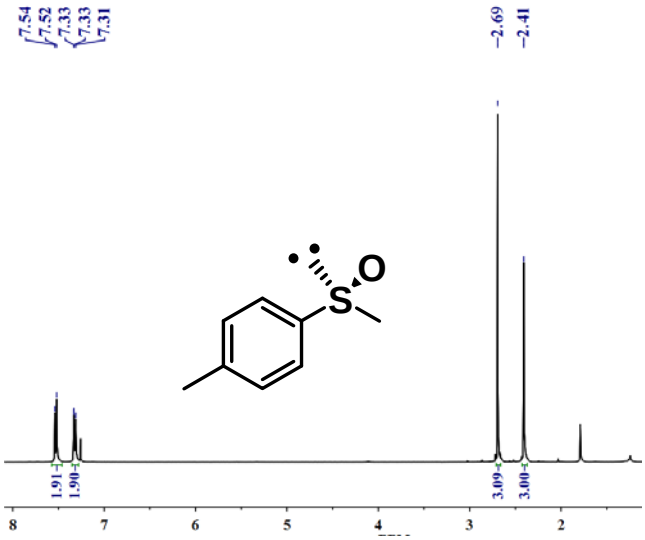
14. Figure S14. ICP-OES data obtained from the filtrate after asymmetric sulfoxidation of methyl *p*-toyl sulfide.

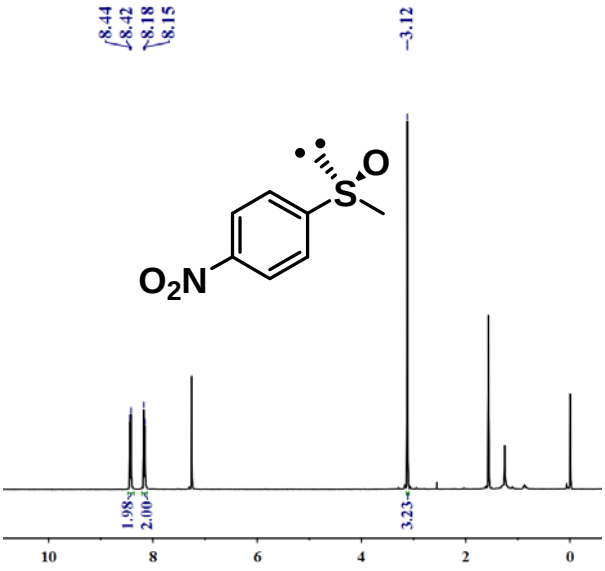
样品名:朱1　　获取: 2013-3-27 16:17:52　　类型: Unk
方法: quan10(v250)　　模式: CONC　　校正因子: 0.061616
用户: admin　　定制ID1:　　定制ID2:　　定制ID3:
备注:

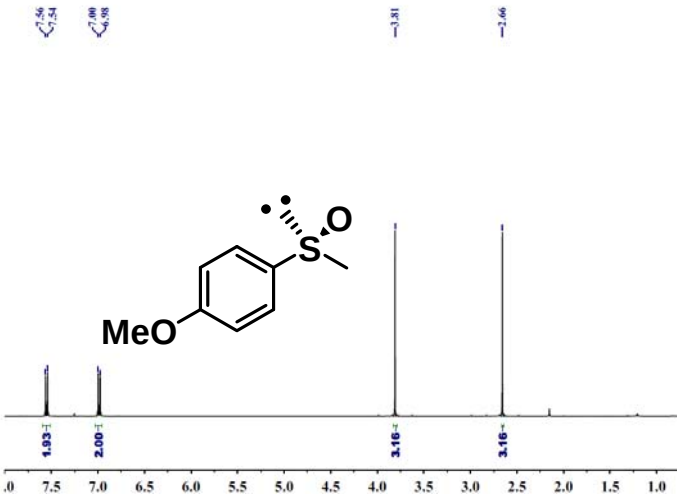
元素	Cd2144	Ti3361
单位	%	%
平均值	**.0002**	**.0006**
标准偏差	.0000	.0000
%RSD	4.597	.9533
#1	.0002	.0006
#2	.0002	.0006
#3	.0002	.0006

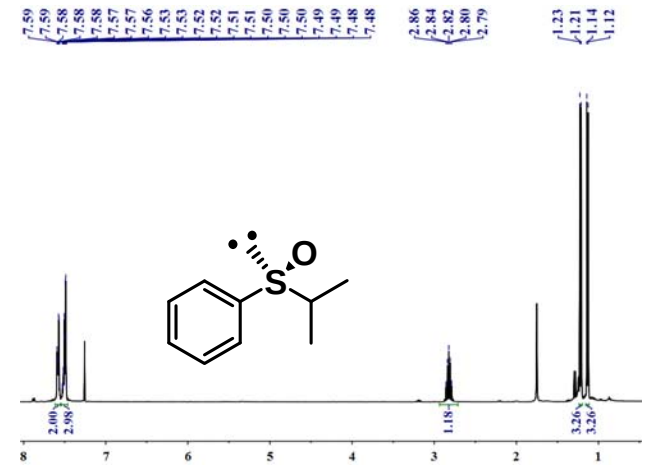
15. Figure S15. The HNMR spectra of sulfoxides.

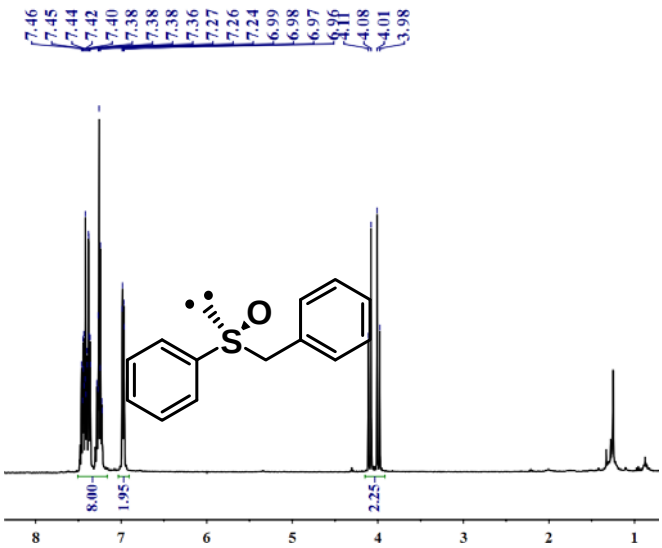


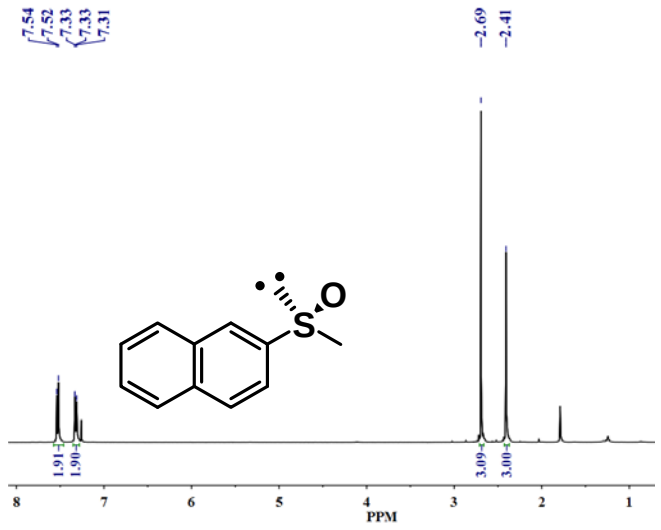


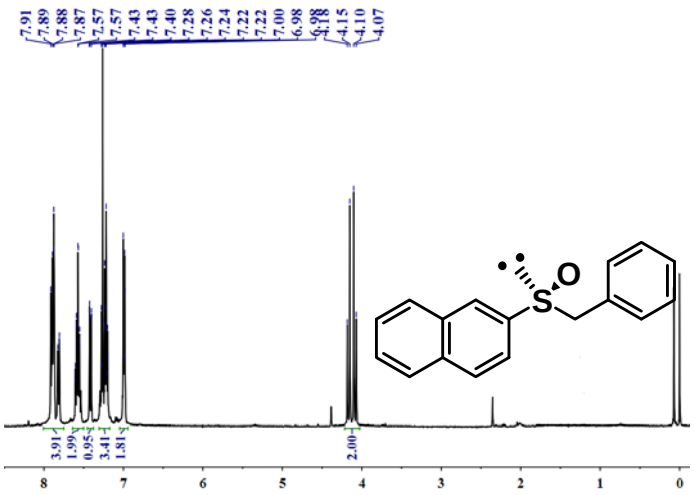






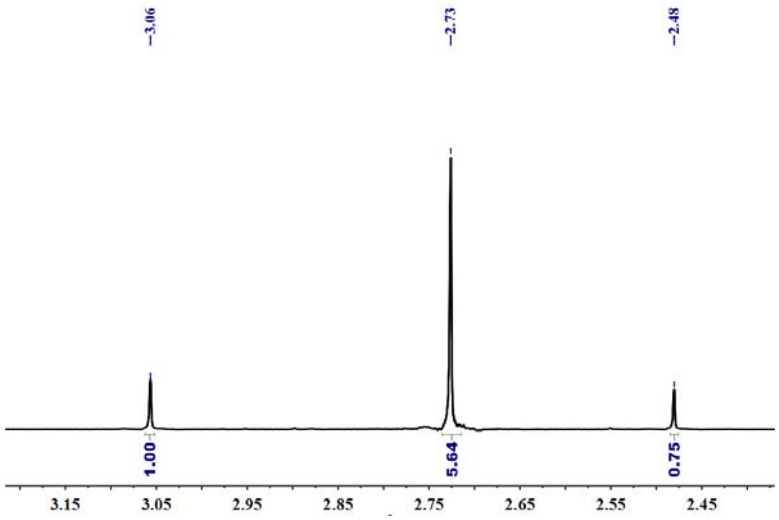




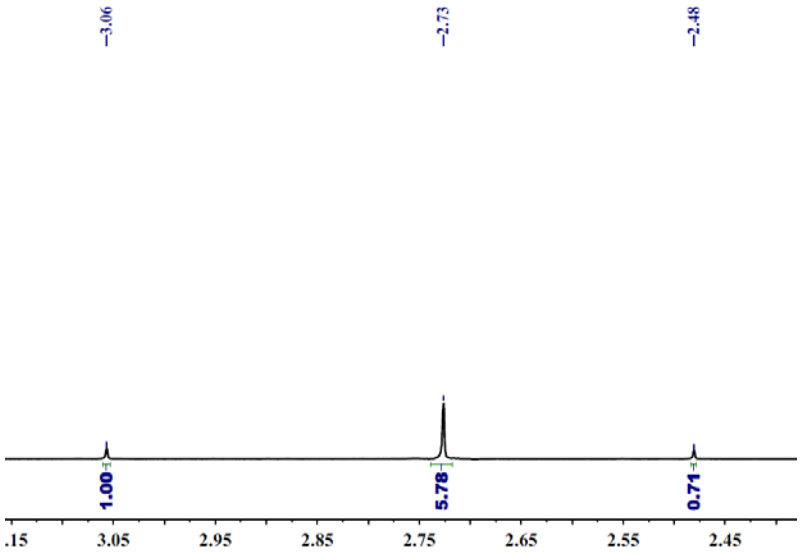


16. Figure S16. The HNMR analyses of conversion and selectivity in the oxidation reaction of sulfides. The conversion were calculated according to the equation: conversion = ([sulfone]+[sulfoxide])/([sulfide]+ [sulfoxide]+[sulfone])×100%; The selectivity were calculated according to the equation: selectivity = ([sulfoxide]/([sulfoxide]+[sulfone])×100%.

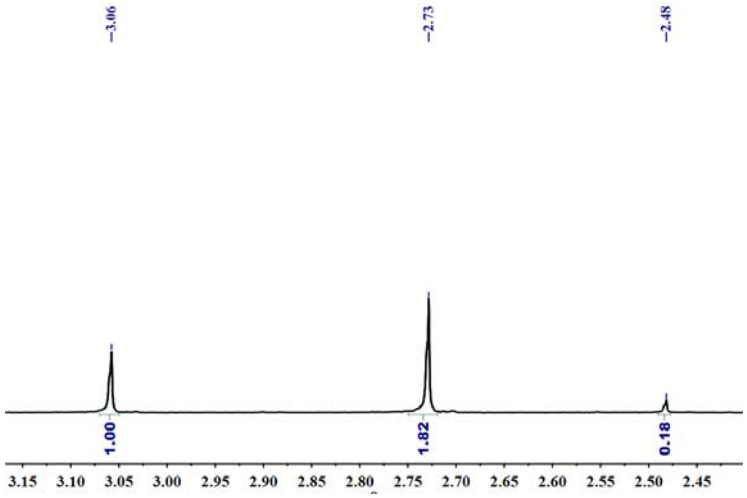
Entry 1:Methyl phenyl sulfide(conversion=89%; selectivity = 84%)



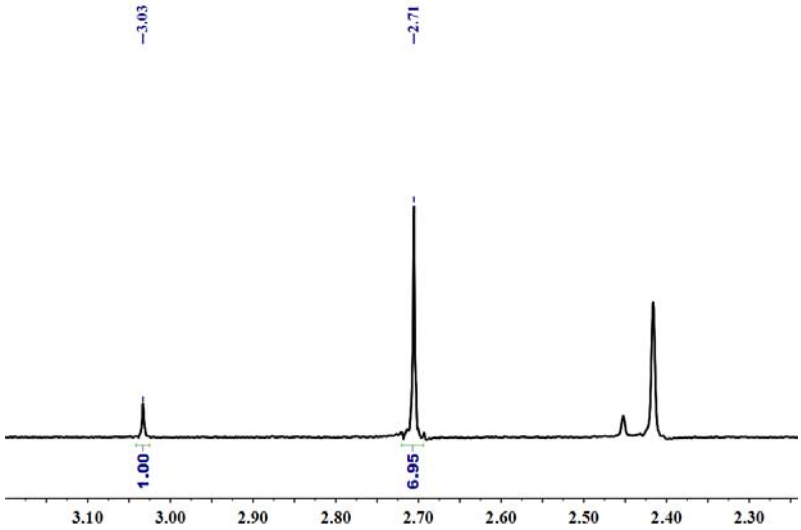
Entry 2:Methyl phenyl sulfide(conversion=90%; selectivity = 85%)



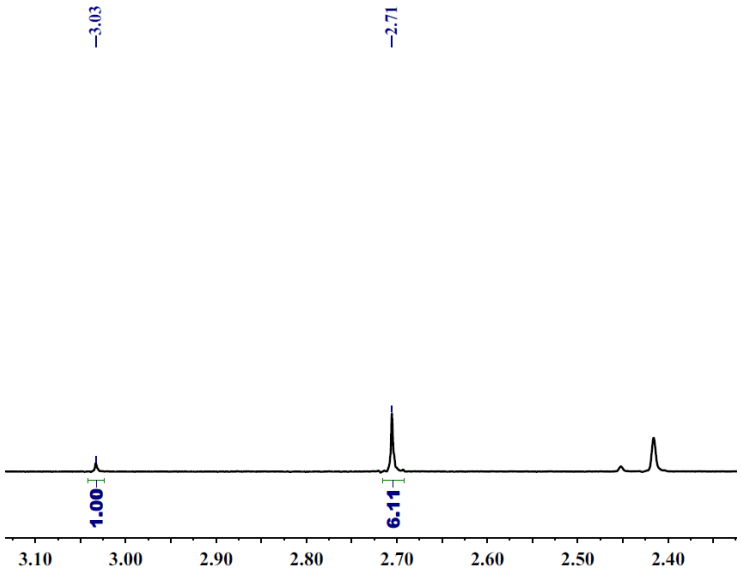
Entry 3:Methyl phenyl sulfide(conversion=94%; selectivity = 64%)



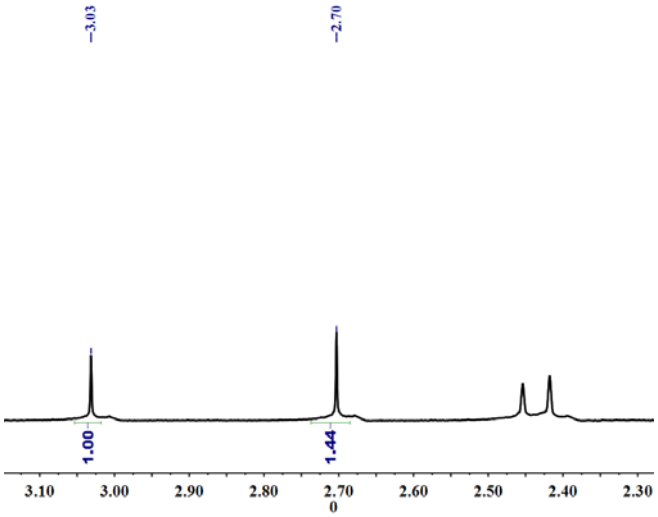
Entry 4: Methyl 4-methylphenyl sulfide (conversion=90%; selectivity = 87%)



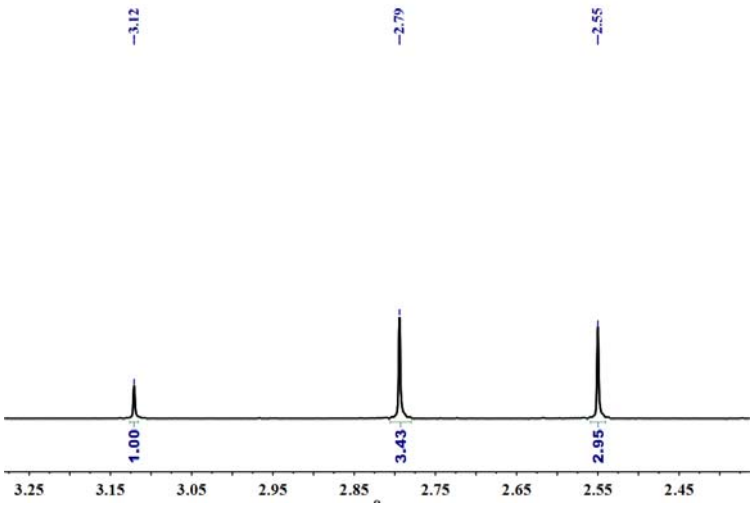
Entry 5: Methyl 4-methylphenyl sulfide (conversion=89%; selectivity = 86%)



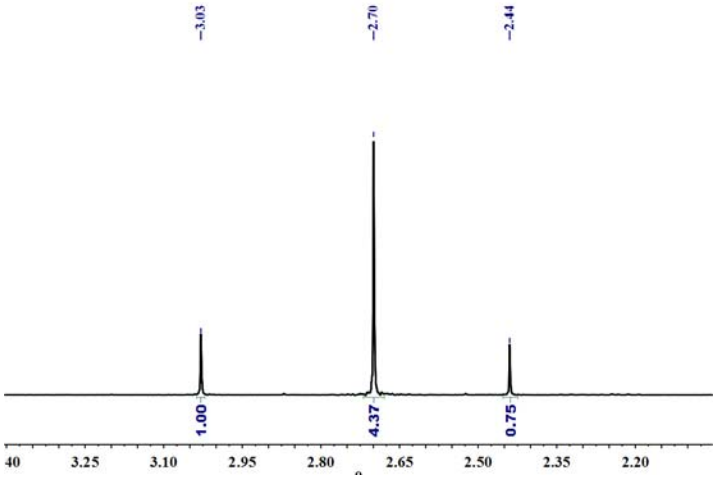
Entry 6: Methyl 4-methylphenyl sulfide (conversion=93%; selectivity = 59%)



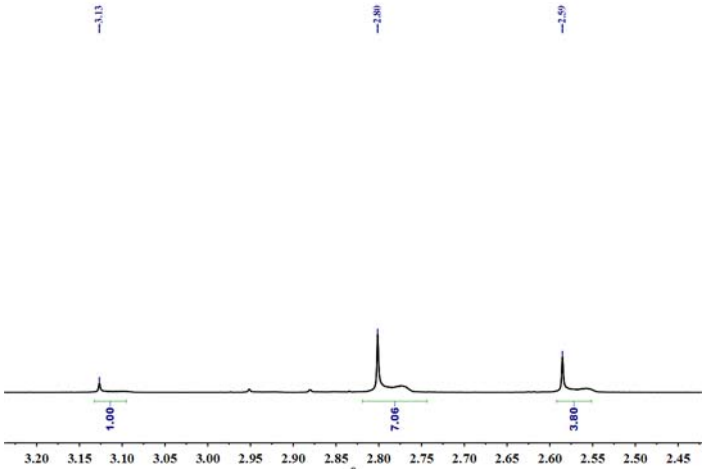
Entry 7: Methyl 4-nitrophenyl sulfide(conversion=60%; selectivity = 77%)



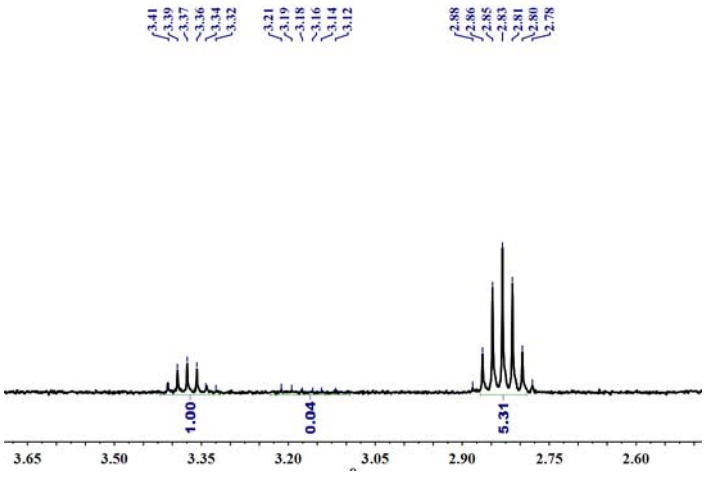
Entry 8: Methyl 4-methoxyphenyl sulfide(conversion=88%; selectivity = 81%)



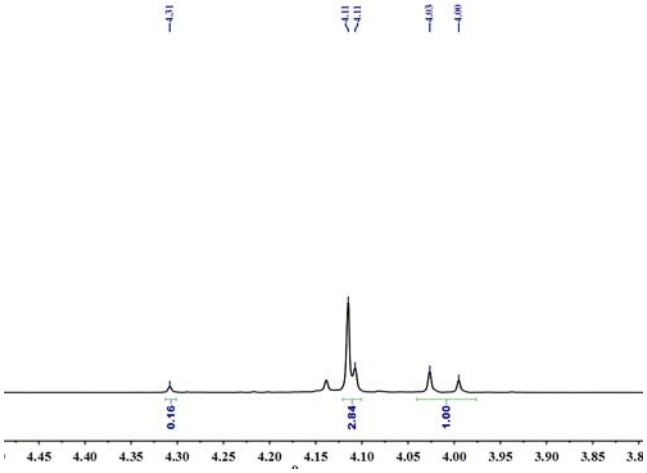
Entry 9: Methyl 2-naphthyl sulfide(conversion=68%; selectivity = 88%)



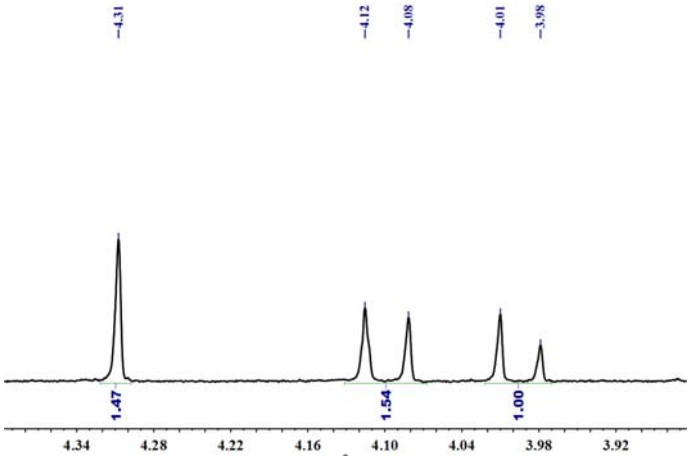
Entry 10: Isopropyl phenyl sulfide(conversion=84%; selectivity = 99%)



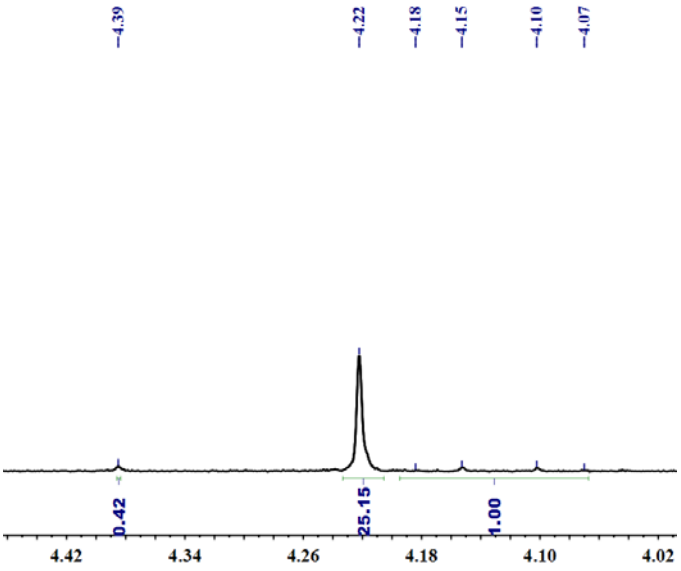
Entry 11: Benzyl phenyl sulfide(conversion=54%; selectivity = 93%)



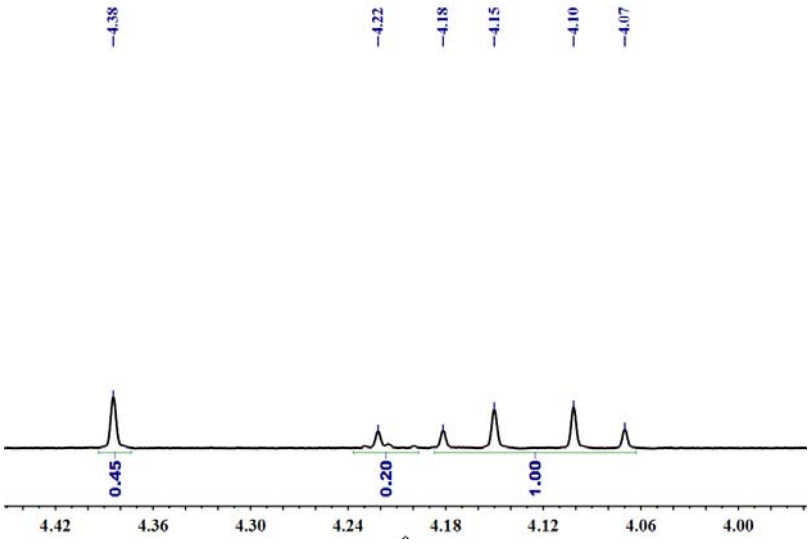
Entry 12: Benzyl phenyl sulfide(conversion=87%; selectivity = 58%)



Entry 13: Benzyl 2-naphthyl sulfide(conversion=5%； selectivity = 70%)

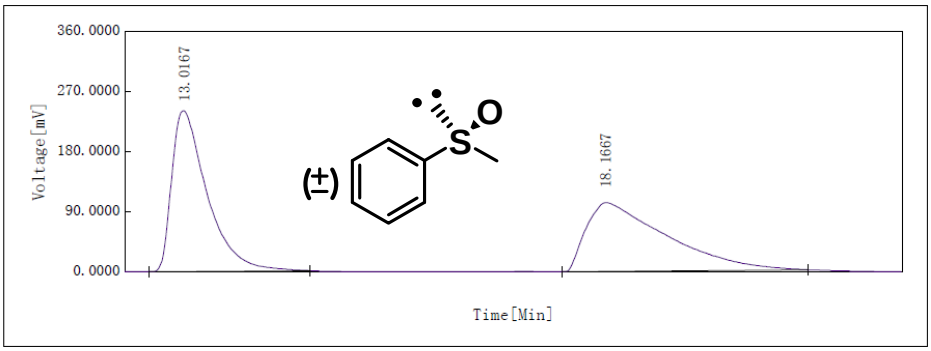


Entry 14: Benzyl 2-naphthyl sulfide (conversion=88%; selectivity = 68%)

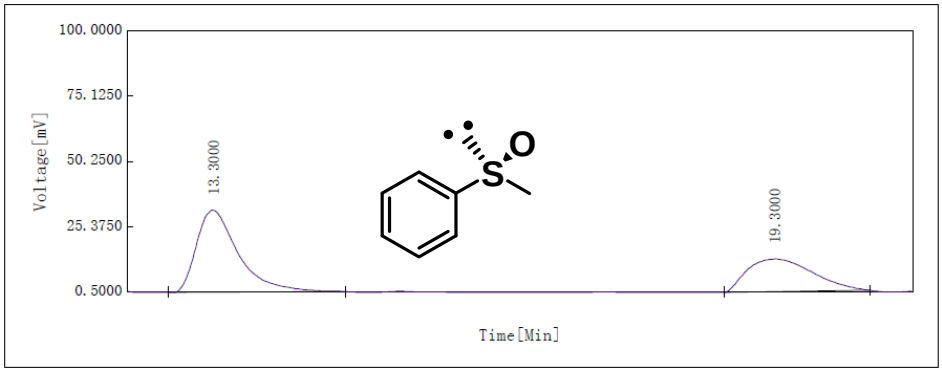


17. Figure S17. The HPLC analyses of sulfoxides.

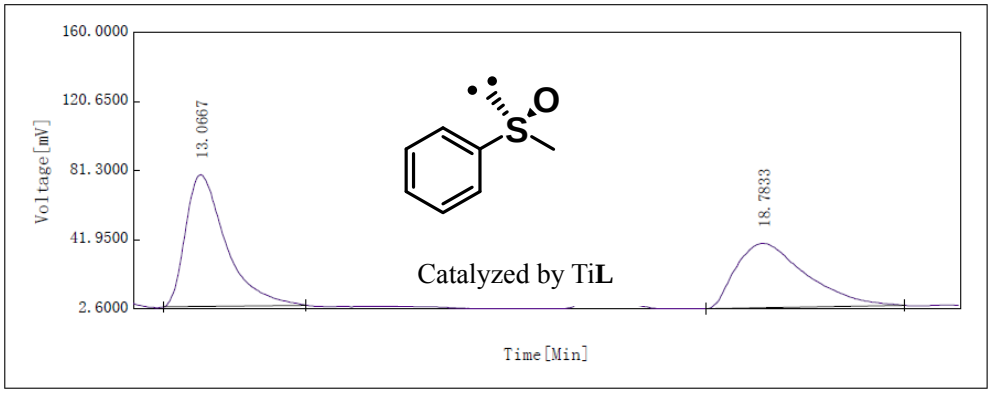
Methyl phenyl sulfoxide: Chiralcel OD-H column: 90/10 hexane/*i*-PrOH; flow rate 1.0 mL/min; t_R = 13.3 min; t_R = 19.3 min.



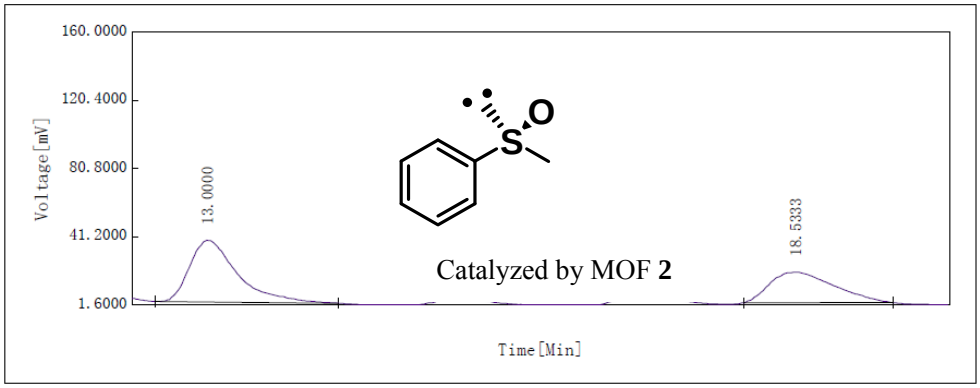
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	13.0167	7253.6035	BB	50.8064
2	18.1667	7023.3479	BB	49.1936
The Total		14276.9514		



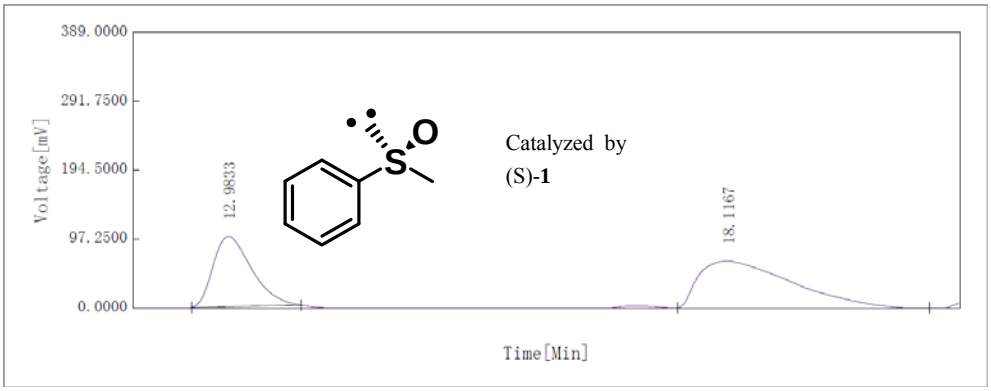
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	13.3000	998.3892	BB	61.5530
2	19.3000	623.6112	BB	38.4470
The Total		1622.0005		



Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	13.0667	2141.8732	BB	53.9128
2	18.7833	1830.9723	BB	46.0872
The Total		3972.8455		

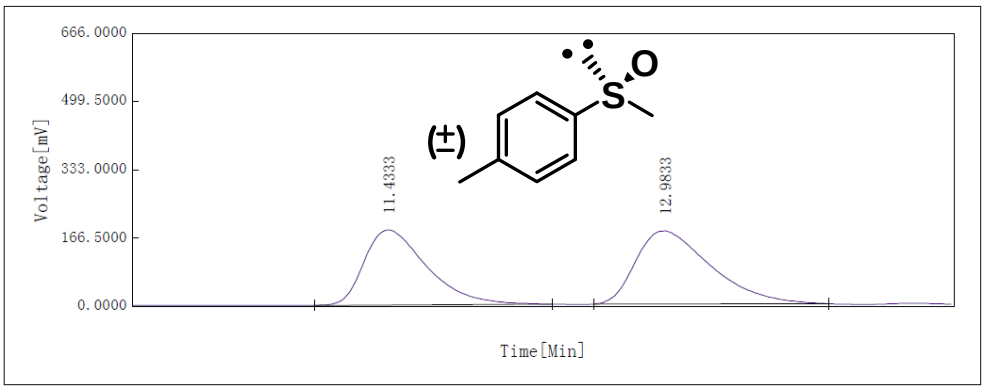


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	13.0000	1114.3944	BB	59.8709
2	18.5333	746.9358	BB	40.1291
The Total		1861.3302		



Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	12.9833	2740.8914	BB	37.8208
2	18.1167	4506.1579	BB	62.1792
The Total		7247.0493		

Methyl p-toyl sulfoxide: Chiralcel OD-H column: 90/10 hexane/*i*-PrOH; flow rate 1.0 mL/min; t_R = 11.0167 min; t_R = 12.2667 min.



Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
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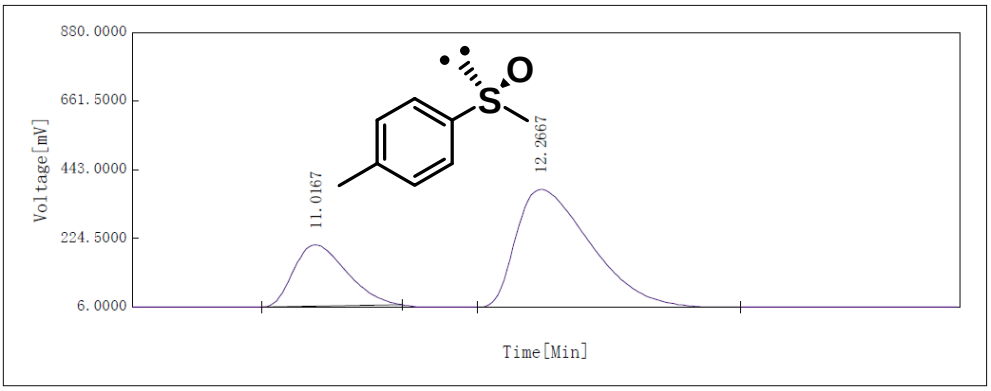
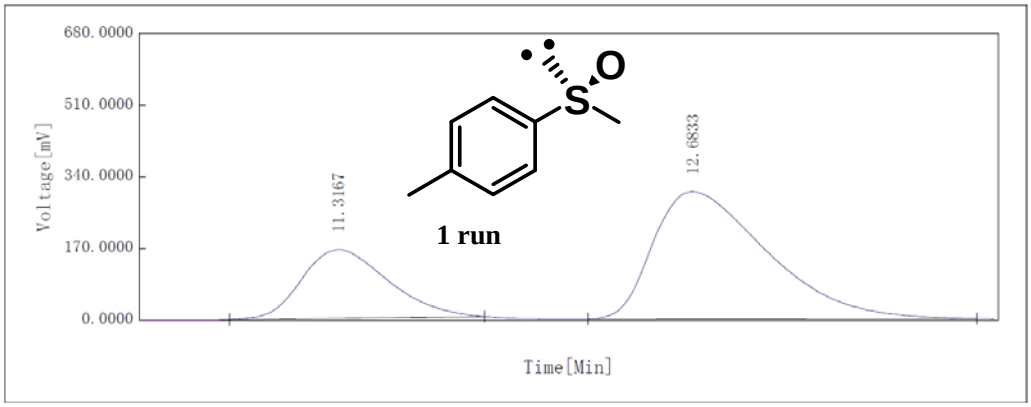
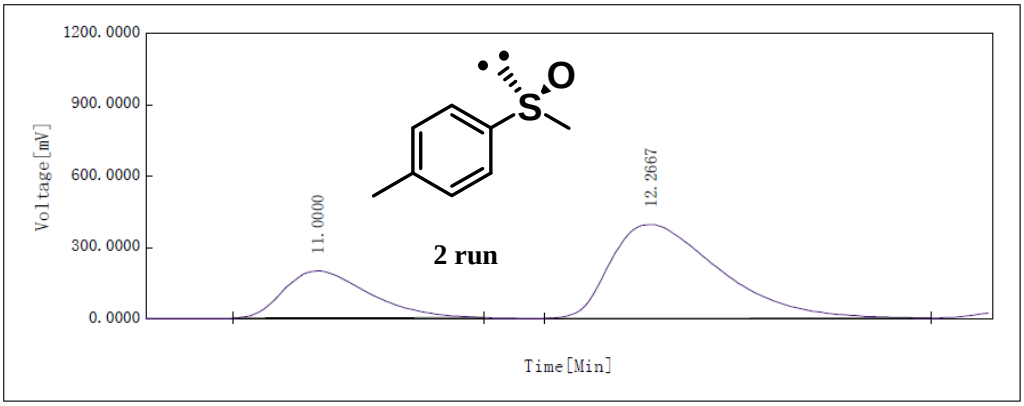
2	12.9833	4512.8149	BB	50.3296
The Total		8966.5111		



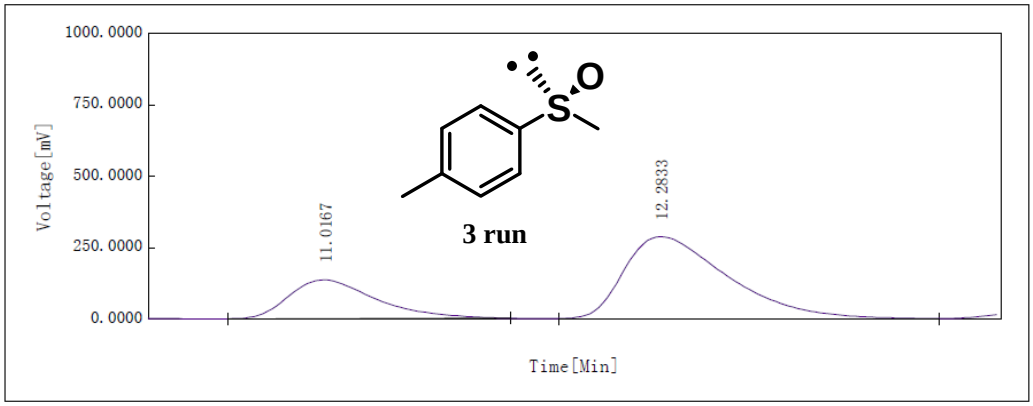
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11.0167	4092.1742	BB	27.1015
2	12.2667	11007.2847	BB	72.8985
The Total		15099.4589		



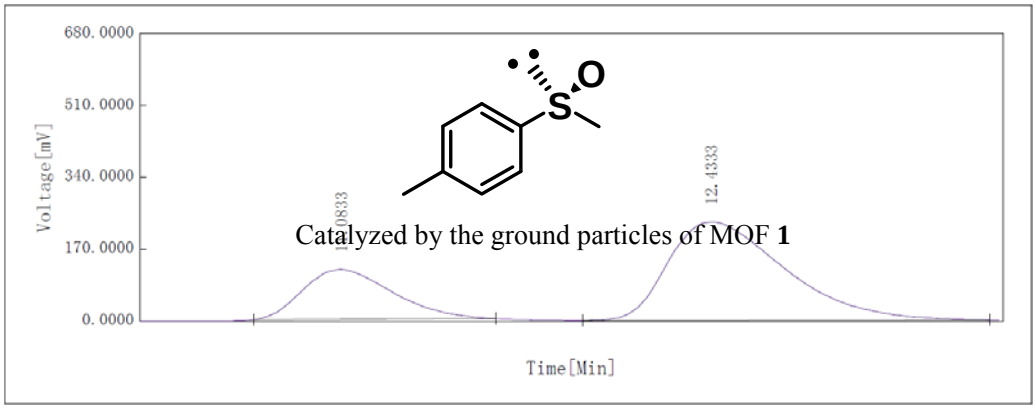
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11. 3167	3747.8805	BB	28.8863
2	12.6833	9226.7189	BB	71.1137
The Total		12974.5993		



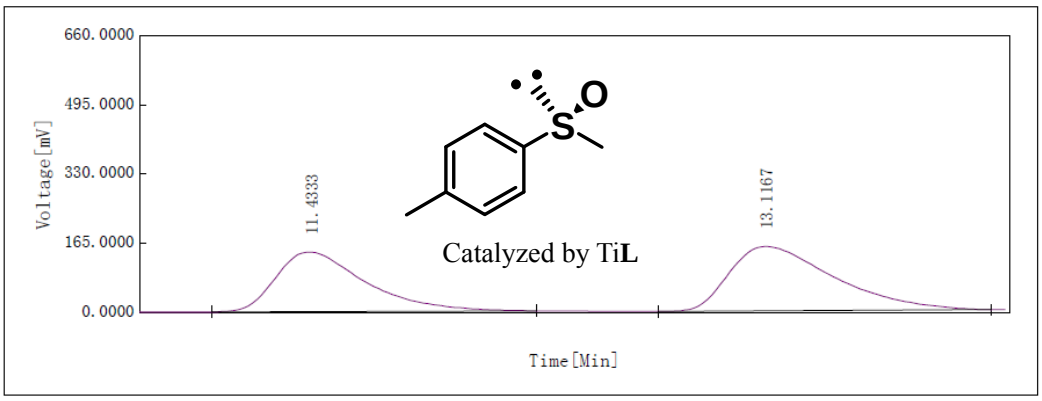
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11. 0167	4417.9786	BB	28.1926
2	12.2667	11252.7204	BB	71..8074
The Total		15670.6990		



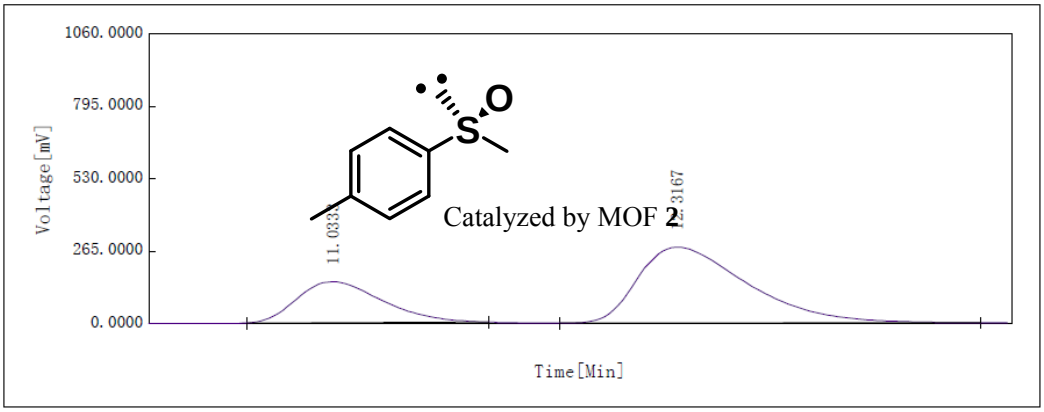
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11.0000	3088.6280	BB	28.4909
2	12.2833	7752.1067	BB	71.5091
The Total		15670.6990		



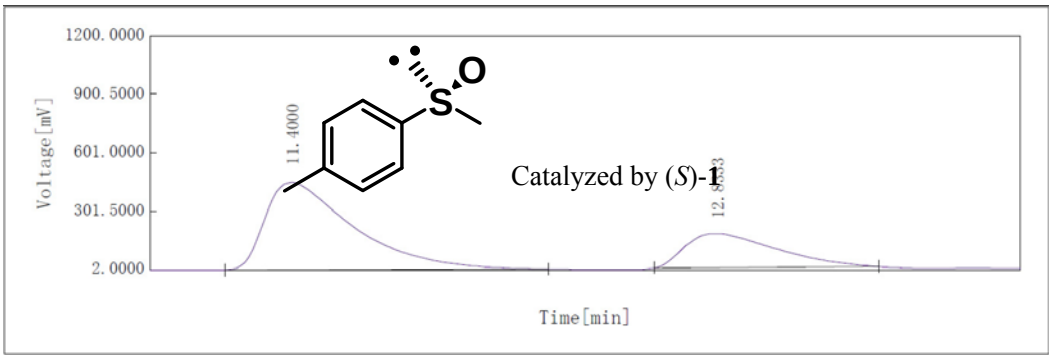
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11.0833	2663.2837	BB	28.0059
2	12.4333	6846.4338	BB	71.9941
The Total		9509.7175		



Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11.4333	3264.5932	BB	44.0554
2	13.1167	4145.6135	BB	55.9446
The Total		7410.2066		

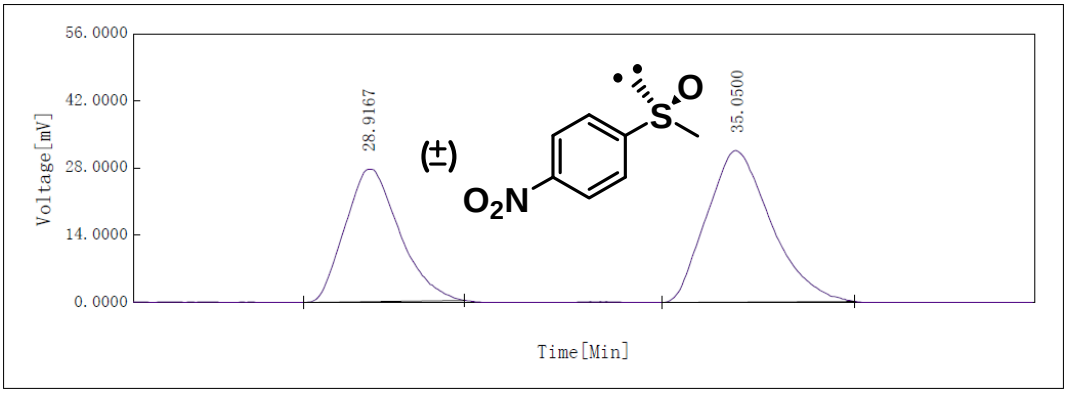


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11.0333	3302.5542	BB	29.5424
2	12.3167	7876.4923	BB	70.4576
The Total		11179.0465		

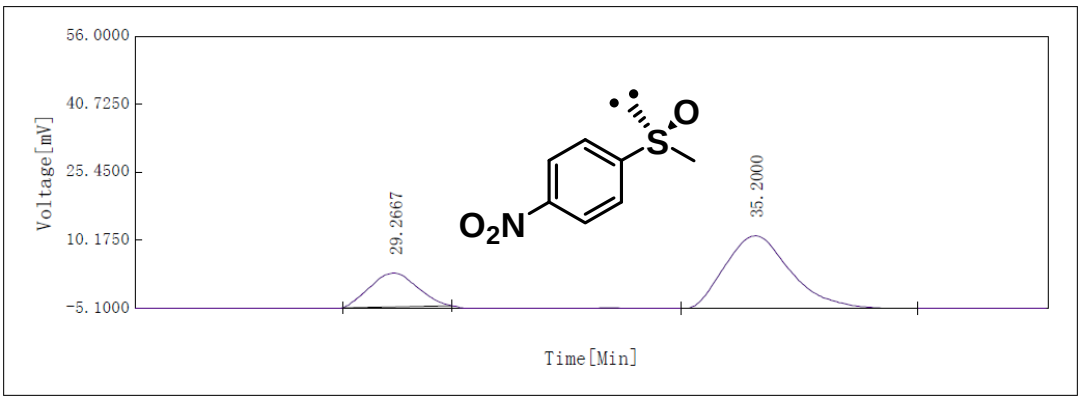


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11.4000	11562.8868	BB	71.4626
2	12.8333	4617.4400	BB	28.5374
The Total		16180.3268		

Methyl 4-nitrophenyl sulfoxide: Chiralcel OJ-H column: 80/20 hexane/i-PrOH; flow rate 1.0 mL/min; t_R = 29.2667 min; t_R = 35.2000 min.

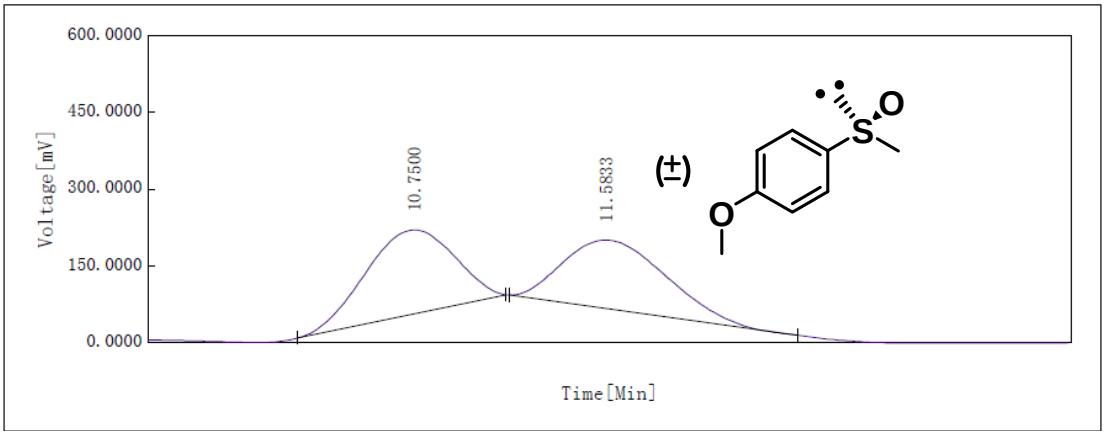


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	28.9167	1711.6341	BB	48.4220
2	35.0500	1823.1912	BB	51.5779
The Total		3534.8253		

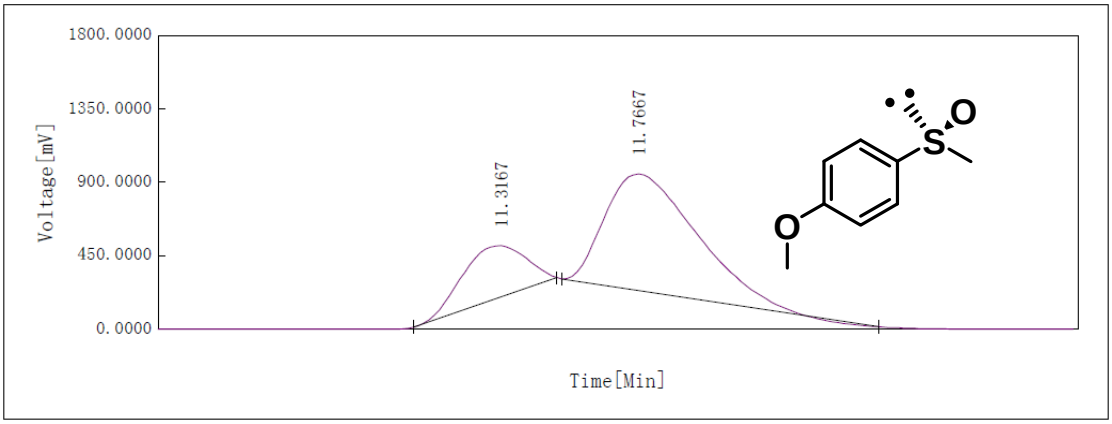


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	29.2667	406.4830	BB	24.4663
2	35.2000	1254.9162	BB	75.5337
The Total		1661.3992		

Methyl 4- methoxyphenyl sulfoxide: Chiralcel OD-H column: 90/10 hexane/*i*-PrOH; flow rate 1.0 mL/min; t_R = 11.3167 min; t_R = 11.7667 min.

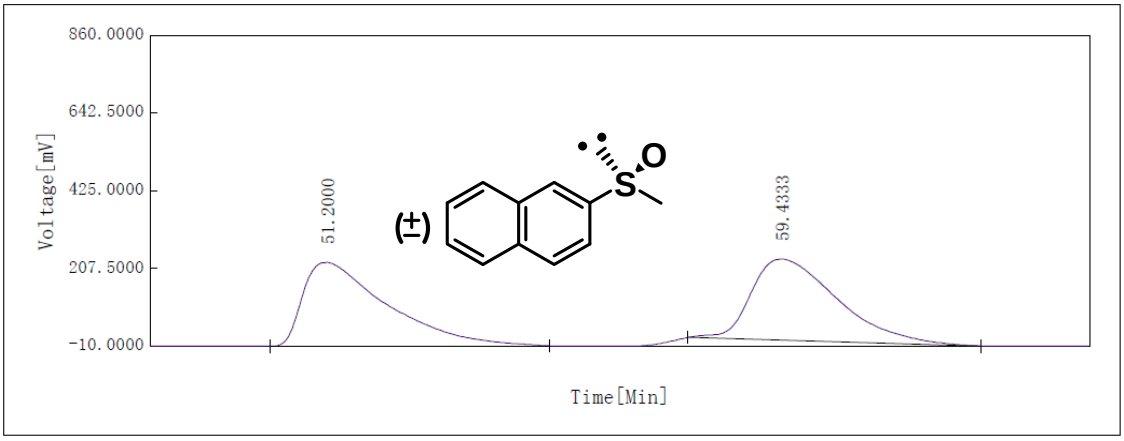


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	10.7500	4391.7692	FF	51.3452
2	11.5833	4161.6543	FF	48.6548
The Total		8553.4235		

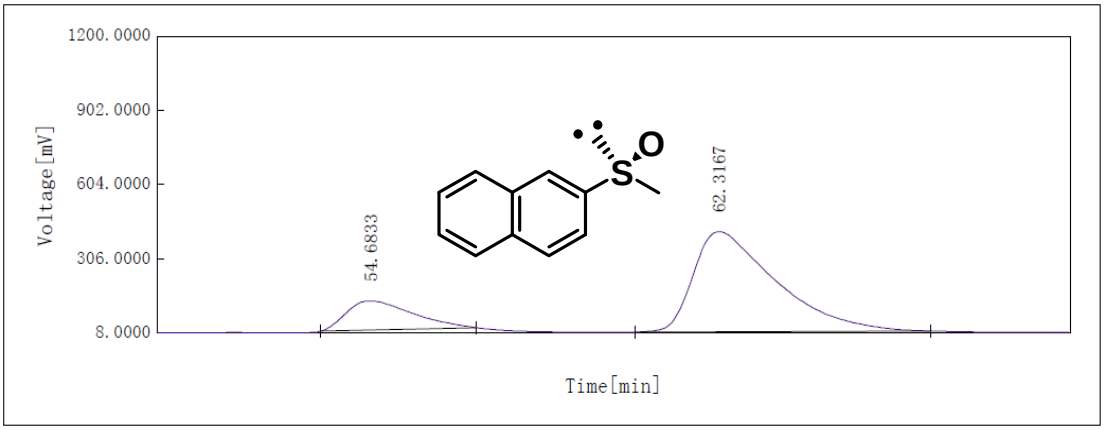


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11.3167	4659.0584	FF	23.7660
2	11.7667	14944.8227	FF	76.2340
The Total		19603.8811		

Methyl 2-naphthyl sulfoxide: Chiralcel OD-H column: 93/7 hexane/i-PrOH; flow rate 0.5 mL/min; t_R = 54.6833 min; t_R = 62.3167 min;

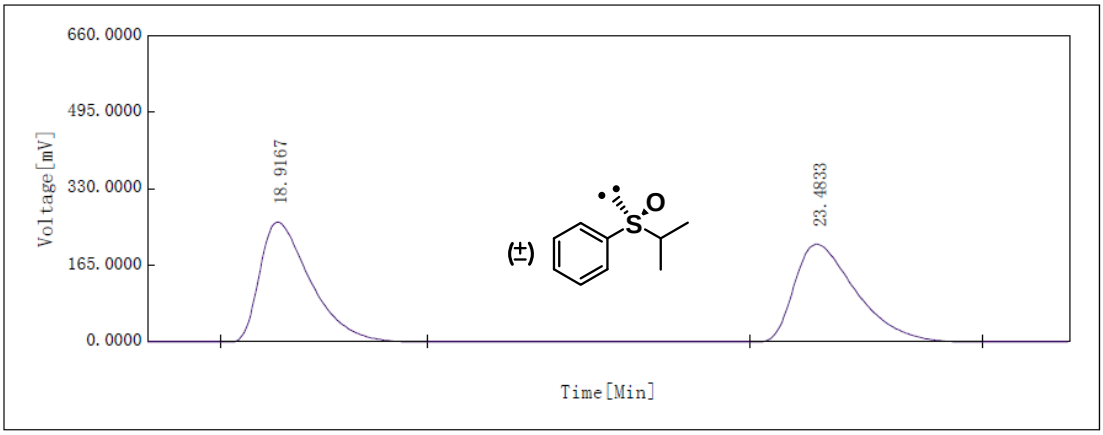


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	51.2000	24801.7832	BB	50.4157
2	59.4333	24392.8230	BB	49.5843
The Total		49194.6062		

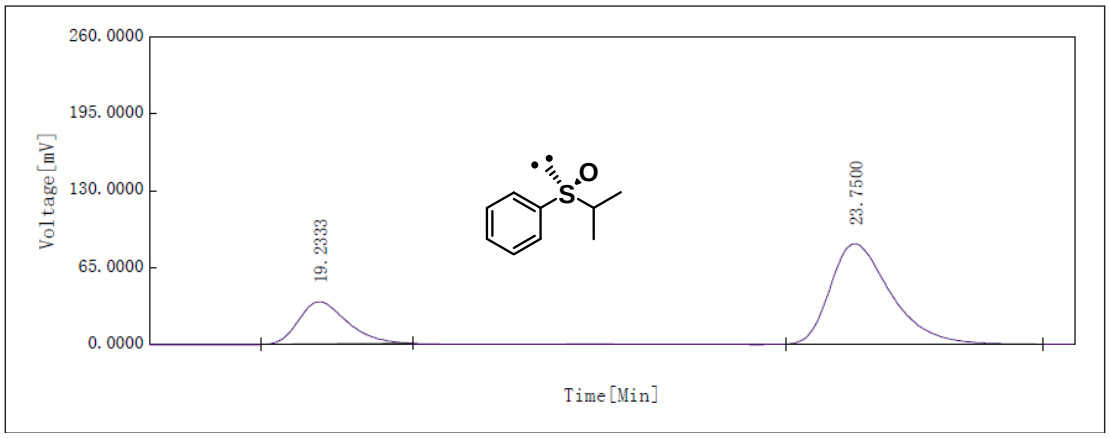


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	54.6833	11737.1926	BB	19.0593
2	62.3167	19845.4043	BB	80.9407
The Total		61582.5969		

Isopropyl phenyl sulfoxide: Chiralcel OD-H column: 93/7 hexane/i-PrOH; flow rate 0.5 mL/min; t_R = 19.2333 min; t_R = 23.7500 min

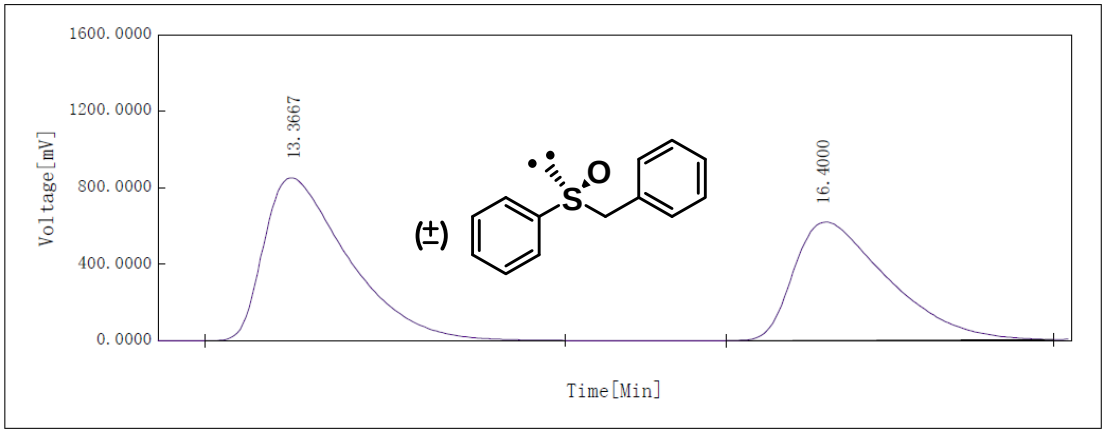


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.9167	7879.5464	BB	49.9985
2	23.4833	7880.0256	BB	50.0015
The Total		15759.5720		

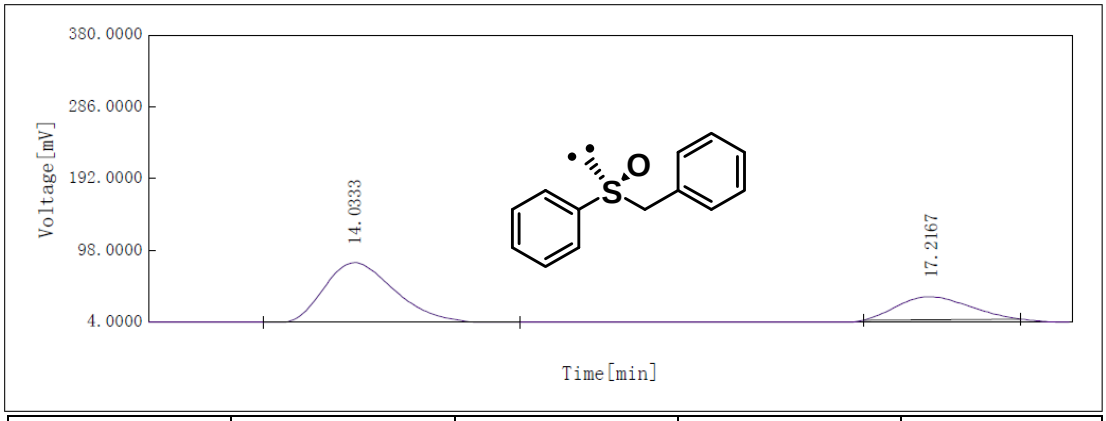


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	19.2333	1016.3851	BB	25.3129
2	23.7500	2998.9061	BB	74.6871
The Total		4015.2912		

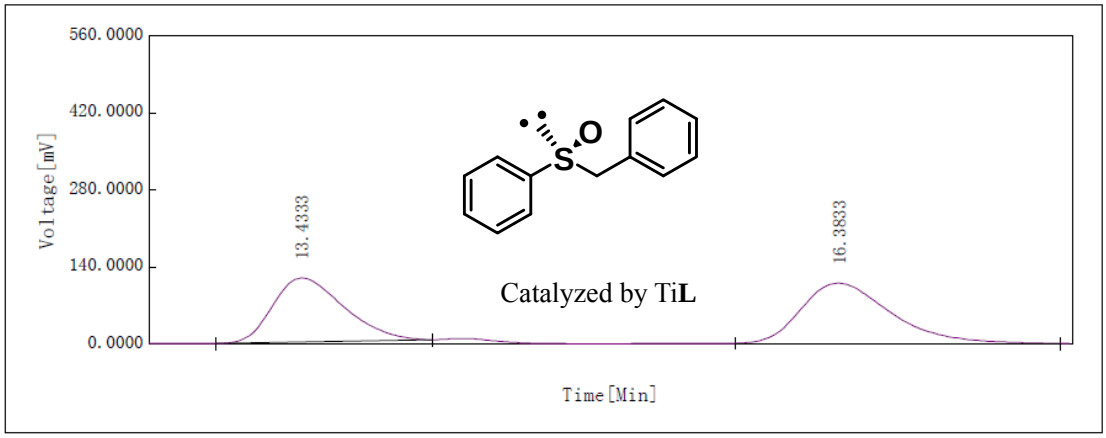
Benzyl phenyl sulfoxide: Chiralcel OD-H column: 90/10 hexane/i-PrOH; flow rate 1.0 mL/min; t_R = 24.0333 min; t_R = 17.2167 min



Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	13.3667	28413.0710	BB	52.0959
2	16.4000	26126.8469	BB	47.9041
The Total		54539.9179		



Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	14.0333	2298.1354	BB	73.8481
2	17.2167	813.8410	BB	26.1519
The Total		3111.9764		



Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	13.4333	3139.4160	BB	45.8599
2	16.3833	3706.2573	BB	54.1401
The Total		6845.6733		