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A Chiral Porous Metallosalan-Organic Framework Containing Titanium-Oxo Clusters for Enantioselective Catalytic Sulfoxidation

Weimin Xuan, Chengcheng Ye, Mengni Zhang, Zhijie Chen and Yong Cui*
School of Chemistry and Chemical Technology and State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University,
Shanghai 200240, China;
Email: yongcui@sjtu.edu.cn

Table of Content

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 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. All UV/Vis absorption spectrum were recorded on a Lambda 20 UV/Vis Spectrometer (Perkin Elmer, Inc., USA). Fluorescence spectra were performed on LS 50B Fluorescence Spectrometer (Perkin Elmer, Inc., USA). ^{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. Analytical high performance liquid chromatography (HPLC) was performed on a YL-9100 HPLC with UV detection at 254 nm. Analytical CHIRALCEL OD-H columns (4.6 mm × 25 cm) from Daicel were used.

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X-ray Crystallography. Single-crystal XRD data for the compound was collected on a Bruker Smart 1000 CCD diffractometer with Cu-Kα radiation (λ = 1.54178 Å) at 123K. 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 F2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997).

The structure was solved using direct method, and refined by full-matrix least-squares on $F2$ (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 water 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*; structures were then refined again using the data generated. Elemental analysis showed that the formula unit of compound **1** includes about 16 water guest molecules. Crystal data and details of the data collection are given in Table S1. Selected bond distances are presented in Tables S2.

2. Synthesis of the ligand and MOF 1

The salen precursor of H_2**L** was synthesized according to the literature (*J. Am. Chem. Soc.*, 2004, **126**, 6314).

2.1 Synthesis of the ligand H_2L. The precursor (295 mg, 0.5 mmol) was dissolved in MeOH (25 mL), and 6 equiv of $NaBH_4$ (220 mg, 3 mmol) were added portion-wise with stirring. The reaction mixture was stirred overnight at RT, during which time its color turned light yellow. The reaction mixture was poured into 100 mL of water, and the desired product was isolated by vacuum filtration (0.272 g, 92% yield).

^1H NMR ($CDCl_3$) δ: 8.55-8.57 (dd, 4H, pyridyl-H), 7.47-7.47 (d, 2H, Ar-H), 7.43-7.44 (dd, 4H, pyridyl-H), 7.37-7.39 (d, 4H, pyridyl-H), 7.16-7.17 (d, 2H, ArH), 4.00-4.17 (dd, 4H, Methylene-H), 2.46 (d, 2H, cyclohexadecyl-H), 2.24 (d, 2H, cyclohexadecyl-H), 1.73 (d, 2H, cyclohexadecyl-H), 1.38 (s, 18H, cyclohexadecyl-H/CMe_3), 1.23 (d, 4H, cyclohexadecyl-H). ^{13}C NMR ($CDCl_3$) δ: 158.55, 150.15, 148.90, 137.93, 128.12, 125.20, 125.12, 123.83, 121.23, 60.19, 50.54, 35.06, 31.15, 29.60, 24.54.

ESI-MS: m/z 593.3 (Calcd *m/z* 593.4 for $[H_2\mathbf{L}+H]^+$).

FTIR (KBr pellet, □/cm^{-1}): 3368(m), 3221(m), 2954(s), 2860(s), 1605(m), 1570(w), 1482(s), 1445(w), 1391(w), 1358(w), 1250(w), 1232(w), 1155(w), 1084(w), 1024(w), 993(m), 947(w), 880(m), 807(m), 755(w), 713(m), 646(w), 617(w).

2.2 Synthesis of TiL

The complex was prepared according to a published procedure (Tshuva et al., *J. Am. Chem. Soc.* **2011**, *133*, 16812–16814). A solution of tetrabutyl titanate (340 mg, 1mmol) in anhydrous THF (10 mL) was added dropwise to H_2**L** (590 mg, 1 mmol) in anhydrous THF (30 mL). The reaction mixture immediately change into bright yellow and stirred at room temperature for 2 h, after which the solvent was evaporated under vacuum, The yellow powder of Ti**L** was collected and dried under reduced pressure (665 mg, 85%). Anal (%). Calcd for $C_{46}H_{62}N_4O_4Ti$: C, 70.57; H, 7.98; N, 7.16. Found: C, 70.06; H, 7.94; N, 7.13. FTIR (KBr pellet): 3433(m), 3209(m), 2954(s), 2861(s), 1630(m), 1590(w), 1478(s), 1415(w), 1393(w), 1362(w), 1249(w), 1213(w), 1113(w), 1095(w), 991(m), 970(m), 865(w), 805(w), 750(w), 672(w), 549(w), 507(w).

2.3 Synthesis of MOF 1

A mixture of $CdI_2\cdot 4H_2O$ (0.03 mmol), Ti**L** (0.04 mmol), biphenyl-4,4'-dicarboxylic acid (H_2BPDC, 0.03 mmol) and DMF (1.0 mL) in a capped vial was heated at 80 °C. After for 4 days, yellow rod-like crystals of **1** were filtered, washed with THF, and dried at room temperature. Yield: 5.41 mg (42.1%). Elemental analysis showed **1** has the formula $[H_2NMe_2]_2[Cd_3\{TiO_6(Ti\mathbf{L})_3\}(BPDC)_3(H_2O)_3]\cdot 16H_2O]$, which was also supported by TGA and IR. Anal (%). Calcd for $C_{160}H_{210}Cd_3N_{14}O_{43}Ti_4$: C, 54.19; H, 5.97; N, 5.53. Found: C, 53.98; H, 5.91; N, 5.50. FTIR (KBr pellet): 3448(m), 3200(m), 2955(s), 2861(s), 1604(m), 1545(w), 1500(w), 1446(s), 1364(w), 1323(w), 1286(m), 1249(w) 1203(w), 1067(w), 1026(w), 980(m), 9 877(w), 827(w), 774(w), 700(w), 563(w), 539(w). Ti exhibiting +4 oxidation state was confirmed by XPS spectrum (see Figure S14).

3. The MO (Methyl Orange) dye inclusion experiment

Fresh crystal **1** (3 mg, 0.661 μmol) was briefly dried on a filter paper, and then soaked in a methanol solution of Methyl Orange (60 mM) overnight. The resulting red crystals were washed with water thoroughly until the washings become colorless. The washed samples were digested by Na_2EDTA (0.05 M, 2 mL) and NaOH (6 M, 0.1 mL), the resultant clear solution with light red color was diluted to 100 mL. Absorption experiments were performed on Lambda 20 UV/Vis Spectrometer(Perkin Elmer, Inc., USA)**.** The experimental showed that MOF **1** could adsorb 1.6 methyl orange (MO) per formula unit in solution (51.9%).

4. Experimental procedure for photocatalytic degradation of Methyl Orange

Photocatalytic reactions for decomposition of MO were carried out in a 25 mL vial. An UV LED Spot Light Source curing device equipped with 450 nm pure UV light source was used, which was placed over the vial with the height of 8 cm. The Powerful intensity was determined as 8000mW/cm^2 by energy meter. Typically, 0.025 mmol **1,** Ti**L** or $CdSO_4$ was dispersed into 20 ml of 20 mg/L MO aqueous solution. The suspensions were then magnetically stirred for 30 min in the dark. At regular irradiation time intervals, 1 ml solution was sampled, filtered and diluted to 3 times volume. The photographs were then taken accordingly and the UV-Vis absorption spectra of methyl orange aqueous solutions were measured by Lambda 20 UV/Vis Spectrometer (Perkin Elmer, Inc., USA). The relationship between A and C: $A=0.0027+0.076C$ (A: absorbance, for methyl orange, A (464 nm) is used in this relationship; C: mg/L; this relationship stands when C below or equals to 20 mg/L).

5. Experimental procedure for oxidation of sulfides

Methyl phenyl sulfide, methyl p-tolyl sulfide, methyl 4-nitrophenyl sulfide, isopropyl phenyl sulfide, benzyl phenyl sulfide and 2-naphthyl methyl sulfide were commercially available from J&K, while benzyl 2-naphthyl sulfide, naphthyl 2-methylenenaphthyl sulfide and dendritic sulfide were synthesized according to literature method (Bryliakov K. and Tals E. *Eur. J. Org. Chem.* **2011**, 4693–4698).

***General Procedur for* oxidation of sulfides.** The catalyst **1** (16 mg, 0.020 mmol) and the related sulfide (0.25 mmol) were combined in CH_2Cl_2 (1 mL) and stirred for 20 min at 25 °C, followed by adding an 1.2 equiv. 30 % H_2O_2 (or urea-H_2O_2). The mixture was further stirred for 48 h–72 h at 25 °C. The reaction progress was monitored by TLC (eluent: EtOAc/hexane). The ee of the resulted sulfoxide was determined by HPLC using Chiralcel OD-H, Chiralcel AD-H or Chiralcel OJ-H, and the conversion was determined by ^1H NMR. The recycling study was performed similarly.

6. Table S1. Crystal data and structure refinement for **1**

Identification code	**1**
Empirical formula	C_{160} H_{178} N_{14} O_9 Ti_4Cd3
Formula weight	3257.96
Temperature (K)	123(2)
Wavelength (Å)	1.54178
Crystal system	Hexagonal
Space group	P622
Unit cell dimensions	a = 32.0273(3), α = 90 ° b = 32.0273(3), β = 90 ° c = 29.1427(7), γ = 120°
Volume (Å^3), Z	25888.1(7) , 4
Density (calculated) (mg/m^3)	0.836
Absorption coefficient (mm^{-1})	3.295
F(000)	6736
θ range for data collection (°)	1.59 to 53.99
Limiting indices	$-33 \leqslant h \leqslant 33$, $-31 \leqslant k \leqslant 32$, $-30 \leqslant I \leqslant 28$
Reflections collected	68827
Independent reflections	10155 (Rint = 0.2486)
Completeness to theta	53.99/ 97 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10155 /1208 / 563
Goodness-of-fit on F^2	1.246
Final R indices [I>2sigma(I)]	R1 = 0.0966, wR2 = 0.2253
R indices (all data)	R1 = 0.1267, wR2 = 0.2452
Absolute structure parameter	0.122(18)
Largest diff. peak and hole (e.Å^{-3})	1.354 and -0.568

7. **Table S2.** Selected Bond lengths [Å] and angles [º] for **1**

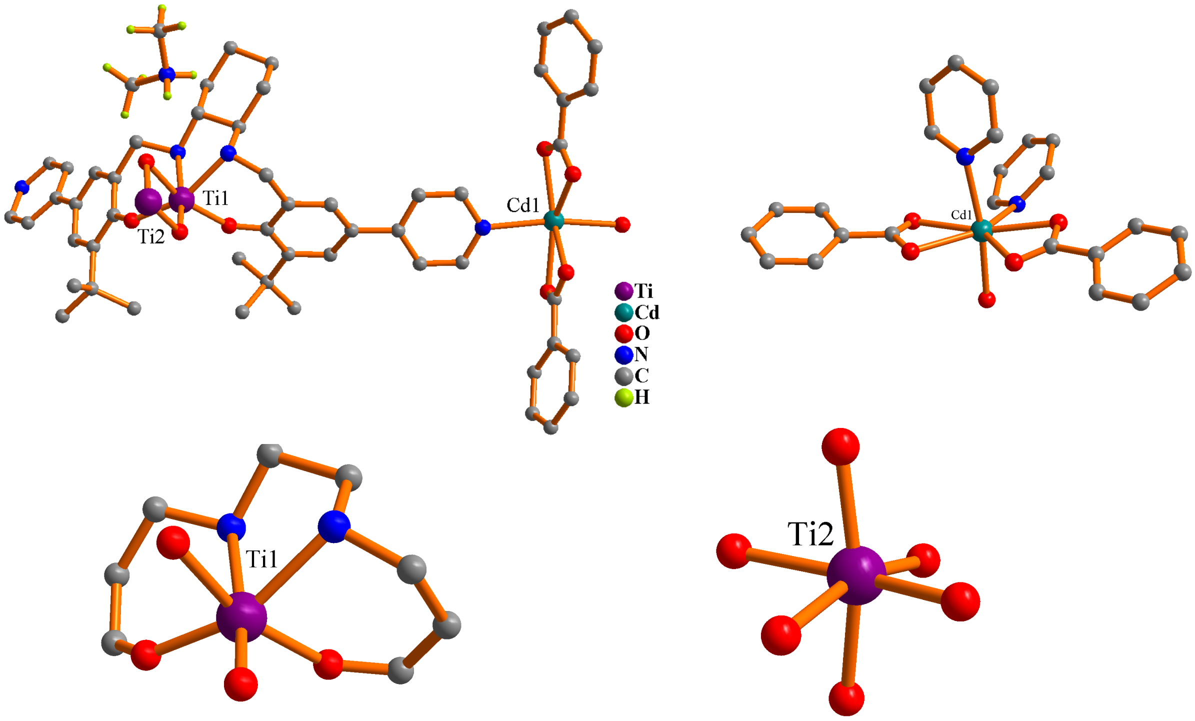
Ti(1)-O(8)	184.3(9)
Ti(1)-O(2)	194.1(7)
Ti(1)-O(1)	194.4(8)
Ti(1)-O(9)	200.1(9)
Ti(1)-N(1)	216.6(10)
Ti(1)-N(3)	231.2(11)
Ti(1)-Ti(2)	294.37(19)
Ti(2)-O(8)	189.6(9)
Ti(2)-O(9)	207.2(9)
Ti(2)-Ti(1)#1	294.4(2)
Ti(2)-Ti(1)#2	294.37(19)
Cd(1)-O(7)	227.9(7)
Cd(1)-O(5)	234.9(8)
Cd(1)-O(3)	235.3(8)
Cd(1)-N(2)	240.0(5)
Cd(1)-O(6)	243.7(8)
Cd(1)-O(4)	244.5(7)
Cd(1)-N(4)#3	247.6(7)
O(8)-Ti(1)-O(2)	101.0(3)
O(8)-Ti(1)-O(1)	97.2(4)
O(2)-Ti(1)-O(1)	107.7(3)
O(8)-Ti(1)-O(9)	83.4(4)
O(2)-Ti(1)-O(9)	90.0(3)
O(1)-Ti(1)-O(9)	161.7(3)
O(8)-Ti(1)-N(1)	98.2(4)
O(2)-Ti(1)-N(1)	158.1(4)
O(1)-Ti(1)-N(1)	80.2(3)
O(9)-Ti(1)-N(1)	81.5(3)
O(8)-Ti(1)-N(3)	169.2(4)
O(2)-Ti(1)-N(3)	82.0(3)
O(1)-Ti(1)-N(3)	91.7(4)
O(9)-Ti(1)-N(3)	86.2(4)
N(1)-Ti(1)-N(3)	77.3(3)
O(8)-Ti(1)-Ti(2)	38.7(3)
O(2)-Ti(1)-Ti(2)	97.3(2)
O(1)-Ti(1)-Ti(2)	133.6(3)
O(9)-Ti(1)-Ti(2)	44.7(3)
N(1)-Ti(1)-Ti(2)	90.9(3)
N(3)-Ti(1)-Ti(2)	130.9(3)
O(8)#1-Ti(2)-O(8)	97.2(4)
O(8)#1-Ti(2)-O(9)	96.2(3)
O(8)-Ti(2)-O(9)	80.2(4)
O(8)#2-Ti(2)-O(9)	166.6(4)
O(8)#1-Ti(2)-O(9)#1	80.2(4)
O(8)-Ti(2)-O(9)#1	166.6(4)
O(8)#2-Ti(2)-O(9)#1	96.2(3)
O(9)-Ti(2)-O(9)#1	87.0(4)
O(8)#1-Ti(2)-O(9)#2	166.6(4)
O(8)-Ti(2)-O(9)#2	96.2(3)
O(8)#2-Ti(2)-O(9)#2	80.2(4)

O(9)-Ti(2)-O(9)#2	87.0(4)
O(8)#1-Ti(2)-Ti(1)	98.3(2)
O(8)-Ti(2)-Ti(1)	37.4(3)
O(8)#2-Ti(2)-Ti(1)	133.4(3)
O(9)-Ti(2)-Ti(1)	42.8(2)
O(9)#1-Ti(2)-Ti(1)	129.6(3)
O(9)#2-Ti(2)-Ti(1)	92.9(2)
O(8)#1-Ti(2)-Ti(1)#1	37.4(3)
O(8)-Ti(2)-Ti(1)#1	133.4(3)
O(8)#2-Ti(2)-Ti(1)#1	98.3(2)
O(9)-Ti(2)-Ti(1)#1	92.9(2)
O(9)#1-Ti(2)-Ti(1)#1	42.8(2)
O(9)#2-Ti(2)-Ti(1)#1	129.6(3)
Ti(1)-Ti(2)-Ti(1)#1	119.935(12)
O(8)#1-Ti(2)-Ti(1)#2	133.4(3)
O(8)-Ti(2)-Ti(1)#2	98.3(2)
O(8)#2-Ti(2)-Ti(1)#2	37.4(3)
O(9)-Ti(2)-Ti(1)#2	129.6(3)
O(9)#1-Ti(2)-Ti(1)#2	92.9(2)
O(9)#2-Ti(2)-Ti(1)#2	42.8(2)
Ti(1)-Ti(2)-Ti(1)#2	119.935(12)
Ti(1)#1-Ti(2)-Ti(1)#2	119.935(12)
O(7)-Cd(1)-O(5)	89.3(4)
O(7)-Cd(1)-O(3)	89.8(4)
O(5)-Cd(1)-O(3)	86.8(2)
O(7)-Cd(1)-N(2)	172.5(4)
O(5)-Cd(1)-N(2)	97.5(4)
O(3)-Cd(1)-N(2)	87.4(3)
O(7)-Cd(1)-O(6)	99.5(4)
O(5)-Cd(1)-O(6)	53.4(3)
O(3)-Cd(1)-O(6)	138.7(3)
N(2)-Cd(1)-O(6)	87.2(3)
O(7)-Cd(1)-O(4)	89.2(4)
O(5)-Cd(1)-O(4)	141.9(3)
O(3)-Cd(1)-O(4)	55.1(3)
N(2)-Cd(1)-O(4)	83.4(3)
O(6)-Cd(1)-O(4)	163.0(3)
O(7)-Cd(1)-N(4)#3	84.2(3)
O(5)-Cd(1)-N(4)#3	130.0(3)
O(3)-Cd(1)-N(4)#3	142.4(3)
N(2)-Cd(1)-N(4)#3	93.8(3)
O(6)-Cd(1)-N(4)#3	78.8(3)
O(4)-Cd(1)-N(4)#3	87.7(3)
Ti(1)-O(8)-Ti(2)	103.9(5)
Ti(1)-O(9)-Ti(2)	92.5(4)

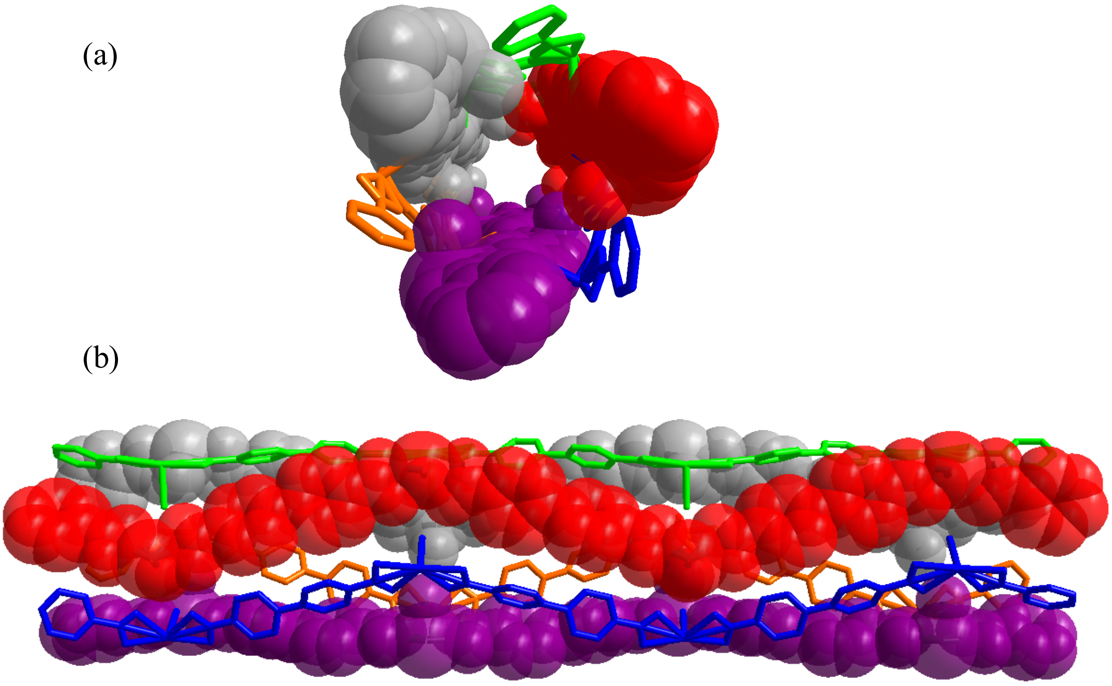
Symmetry transformations used to generate equivalent atoms: #1 -y+1,x-y,z #2 -x+y+1,-x+1,z #3 -x+1,-y,z #4 x,x-y,-z #5 x,x-y,-z+1

8. Additional X-ray crystallographic structures of reported compounds.

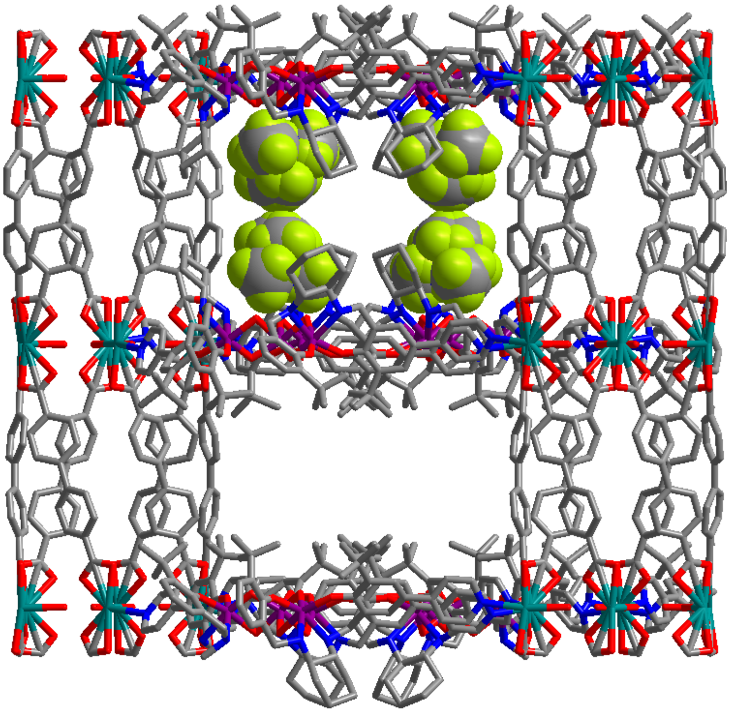
8.1 Figure S1. (a) The molecular structure of **1** and coordination environments of Cd1, Ti1 and Ti2.



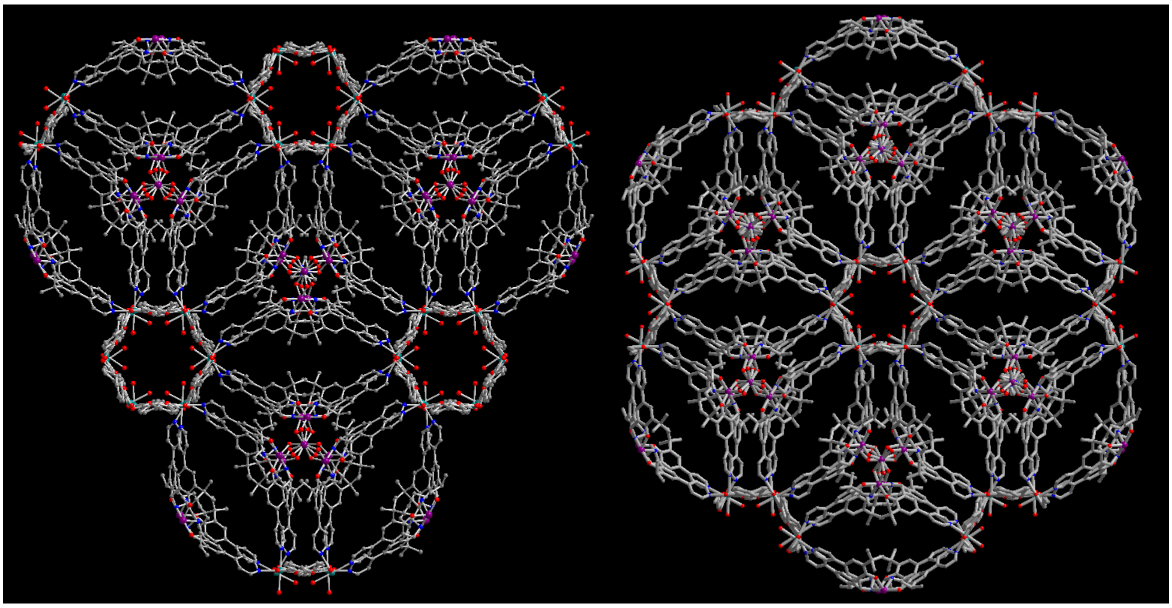
8.2 Figure S2. View of six zigzag chains constructed from Cd centers and BPDC along *c* (a) and *b* (b) direction.



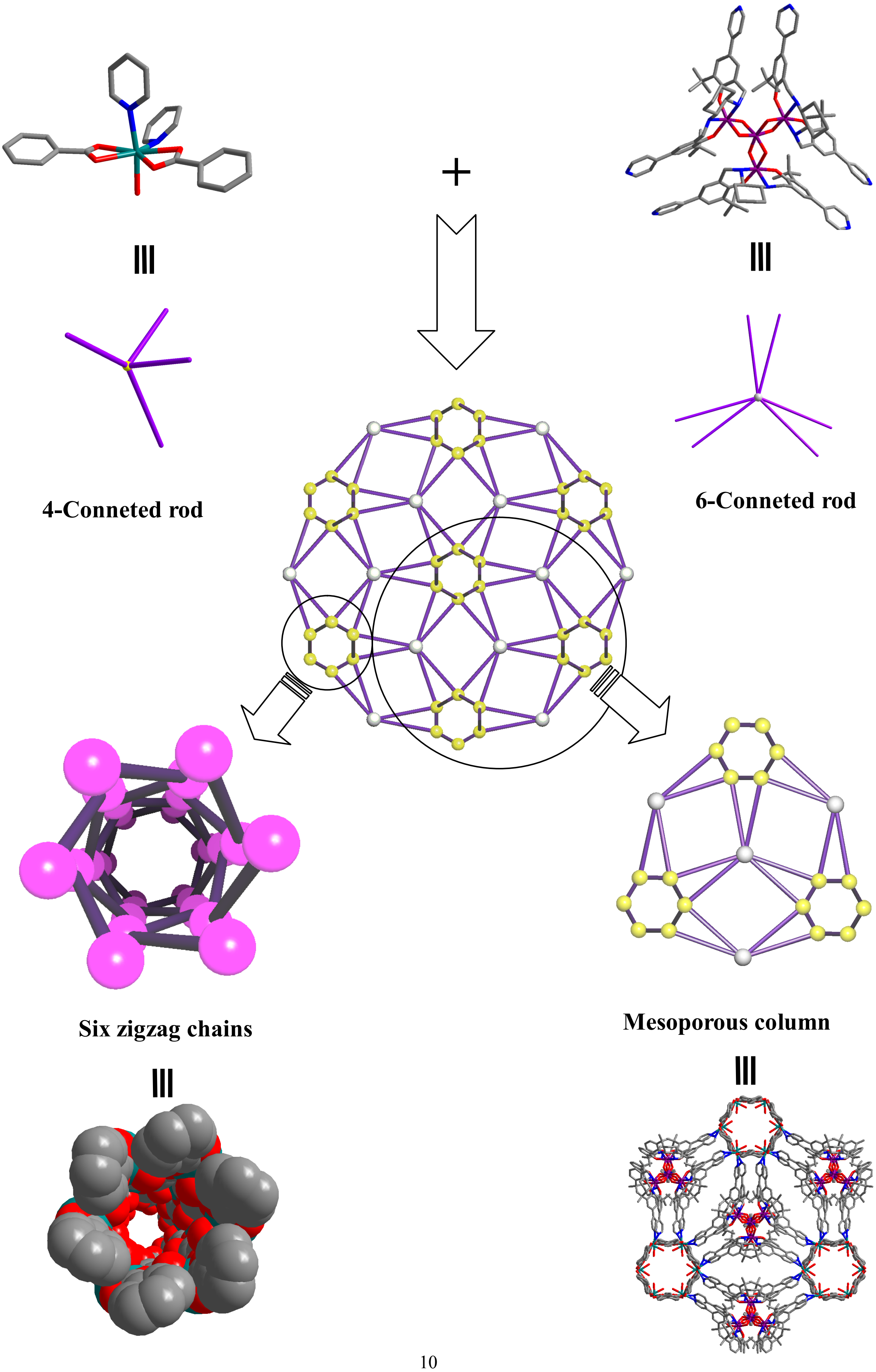
8.3 Figure S3. View of two kinds of open channels along *c* direction. One is filled by counterion $H_2N(Me)_2$ and lined with hexane groups, another is lined with ter-butyl groups.



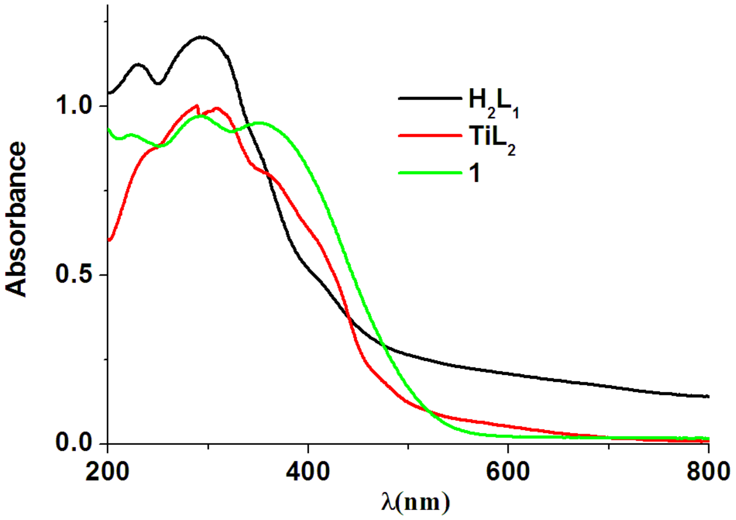
8.4. Figure S4. View of packing mode showing that one mesoporous column is interlocked by there other columns and three sets of six zigzag chains along the *c*-direction (left), and one set of six zigzag chains is surrounded by six interlocked mesoporous columns (right).



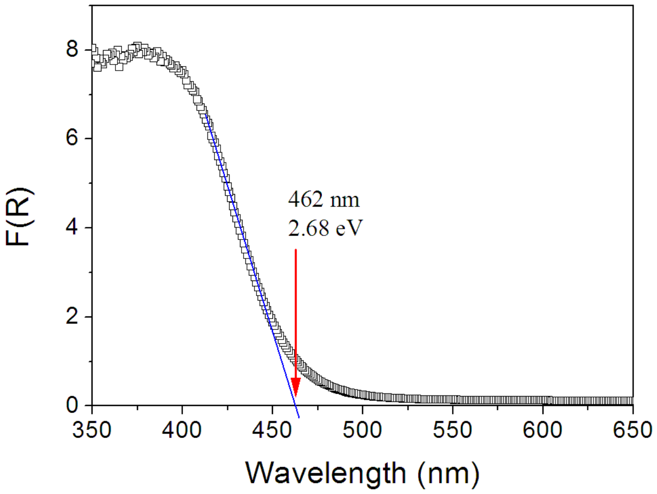
8.5. Figure S5. Topologic representation of **1** constructed from 4-conneted Cd centers and 6-connected tetranuclear Ti cluster.



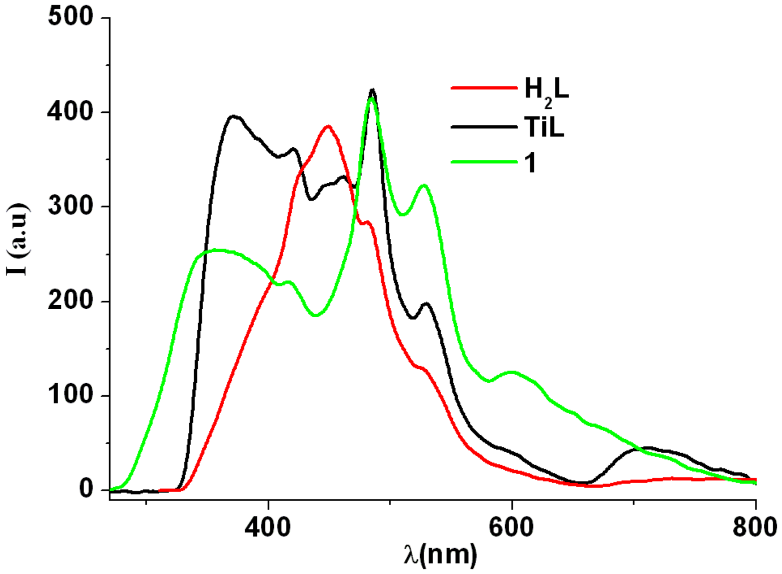
9. Figure S6. UV/Vis absorption spectra of H_2**L,** (Ti**L**) and **1** in the solid state.



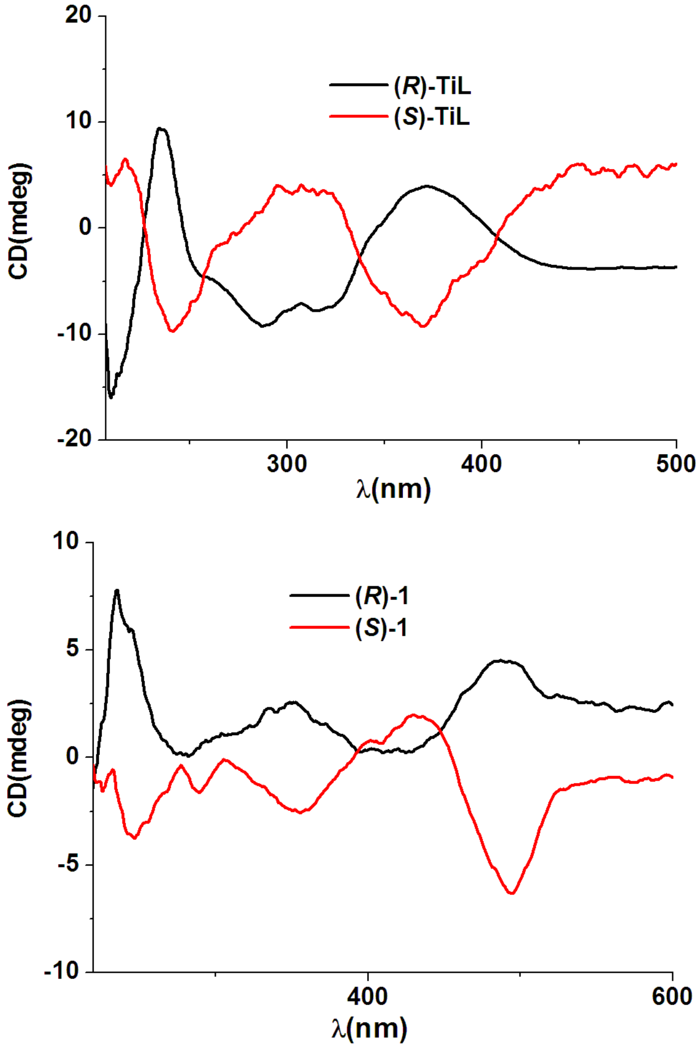
10. Figures S7. Calculation of band gap in complex **1** (2.68 eV).



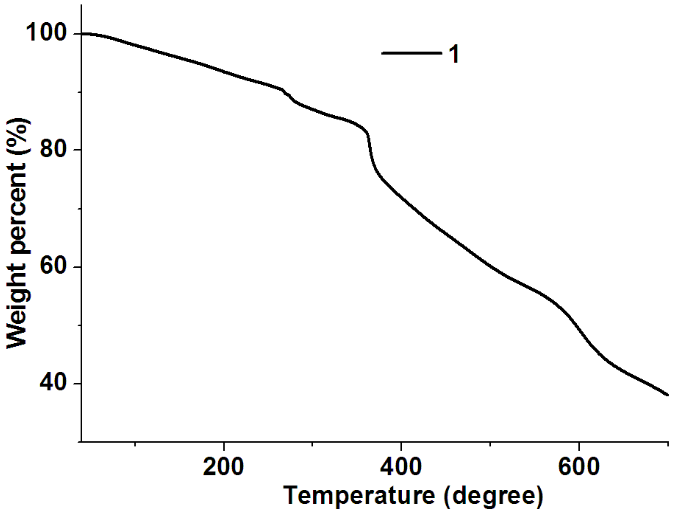
11. Figure S8. Fluorescence spectra for H_2**L,** Ti**L** and **1** in the solid state.



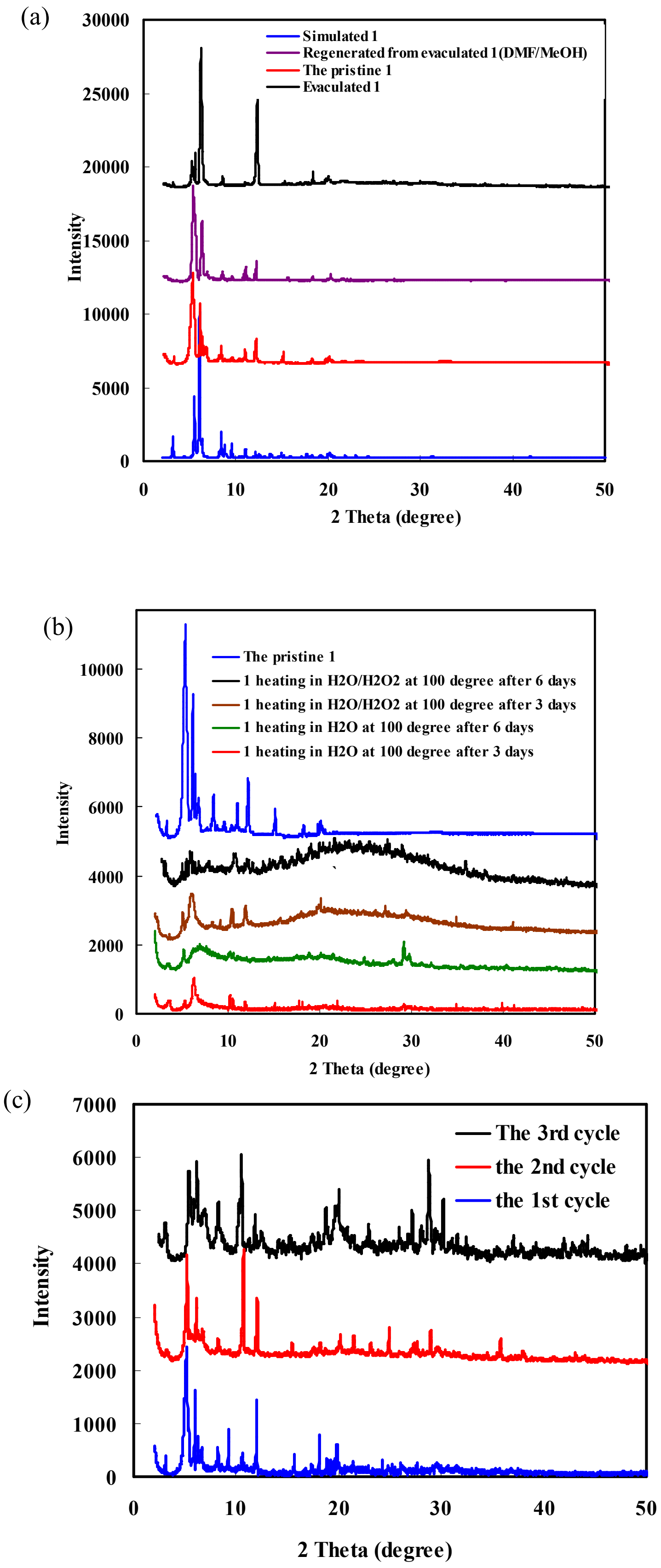
12. Figure S9. CD spectra of (*R*)- and (*S*)-Ti**L** and (*R*)- and (*S*)-**1** in the solid state.



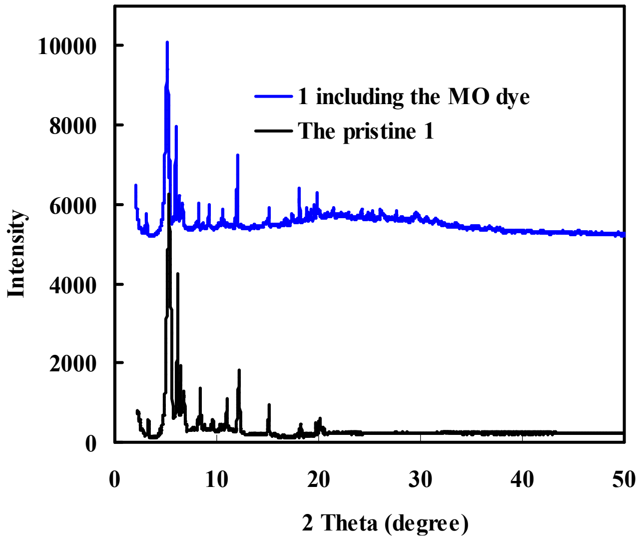
13. Figure S10. TGA curve of **1**.



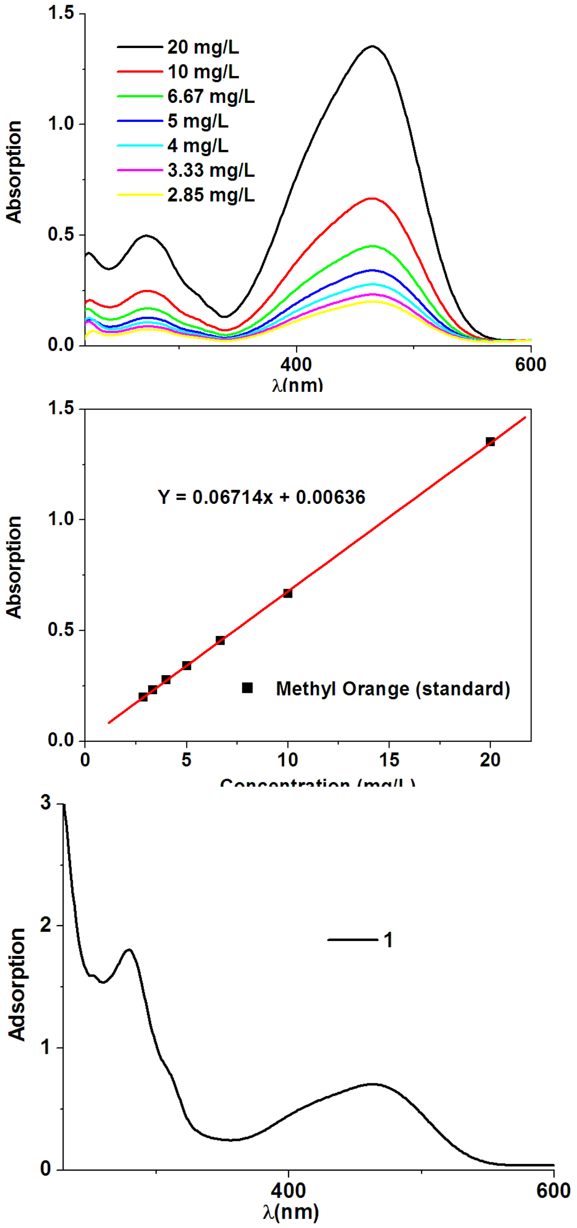
14. Figure S11. PXRD patterns of the pristine, evacuated (regenerated), the samples of **1** after including the MO dye and after heating in H2O and H2O/H2O2.



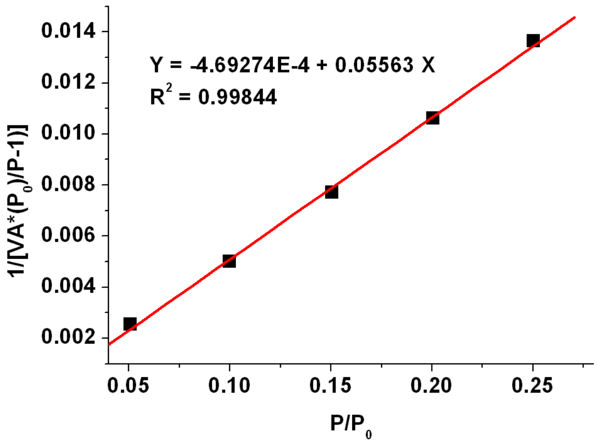
(d)

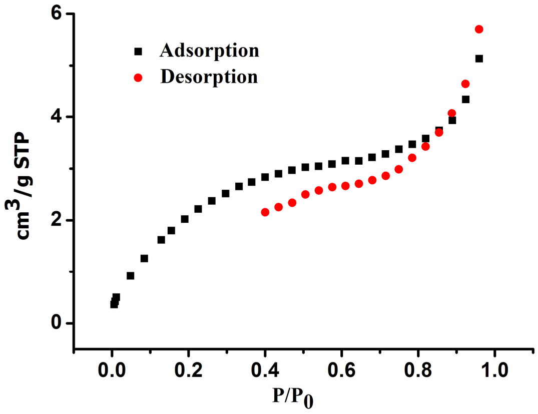


15. Figure S12. UV-Vis Absorption spectra of digested frameworks **1** loaded with MO (Methyl Orange).

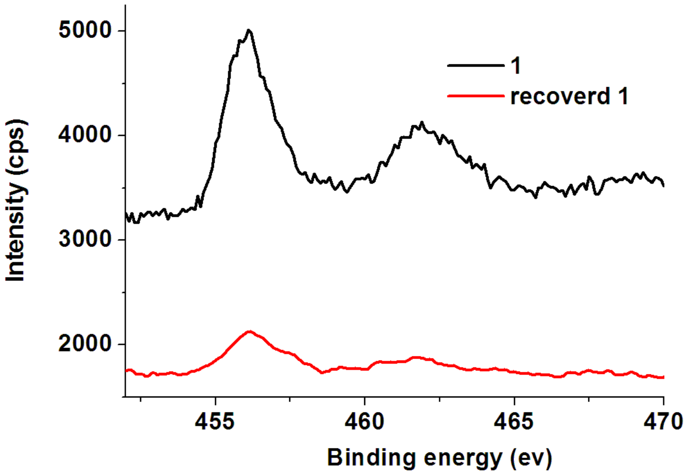


16. Figures S13. Bet plot and N_2 adsorption of **1**.

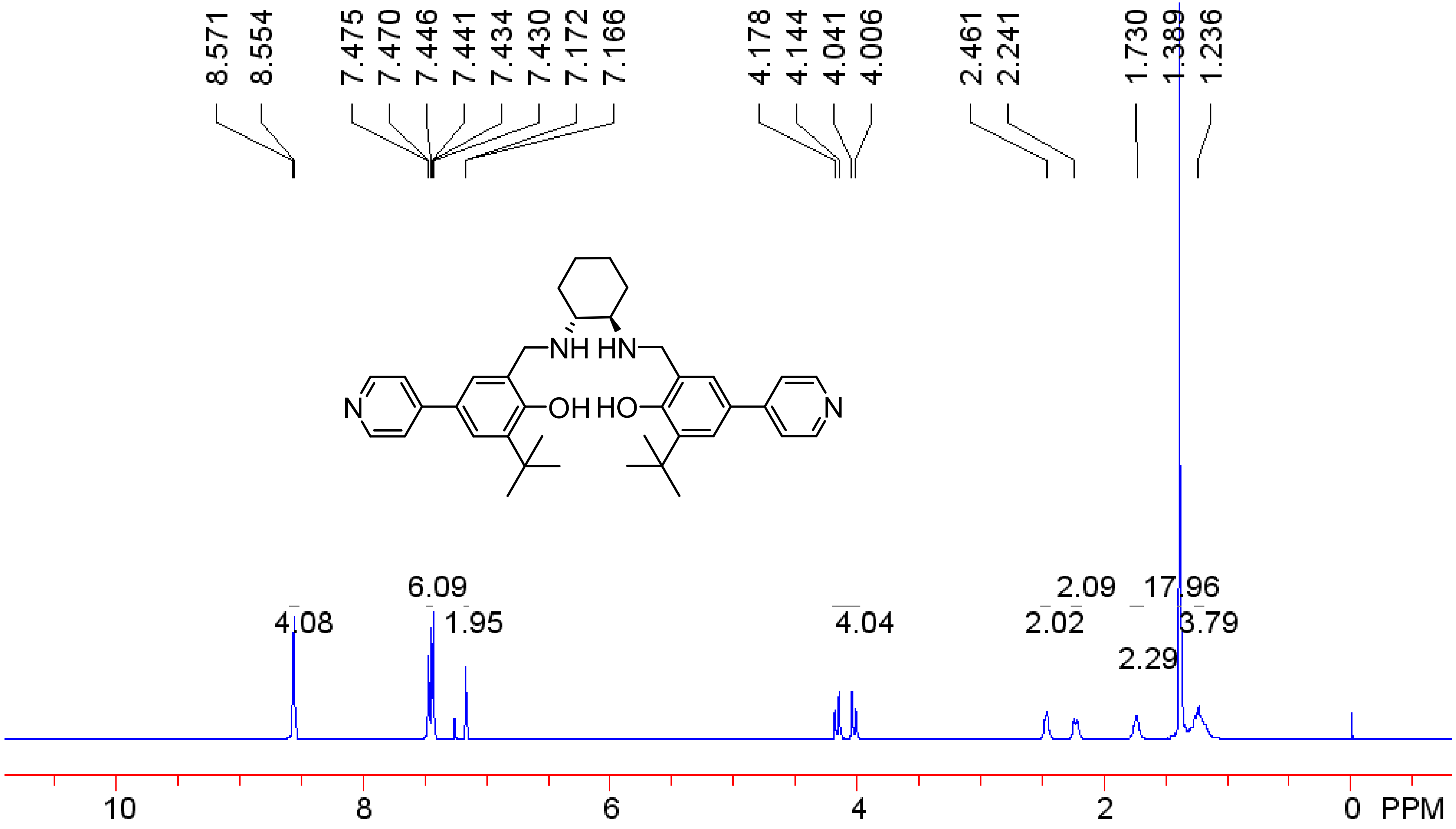


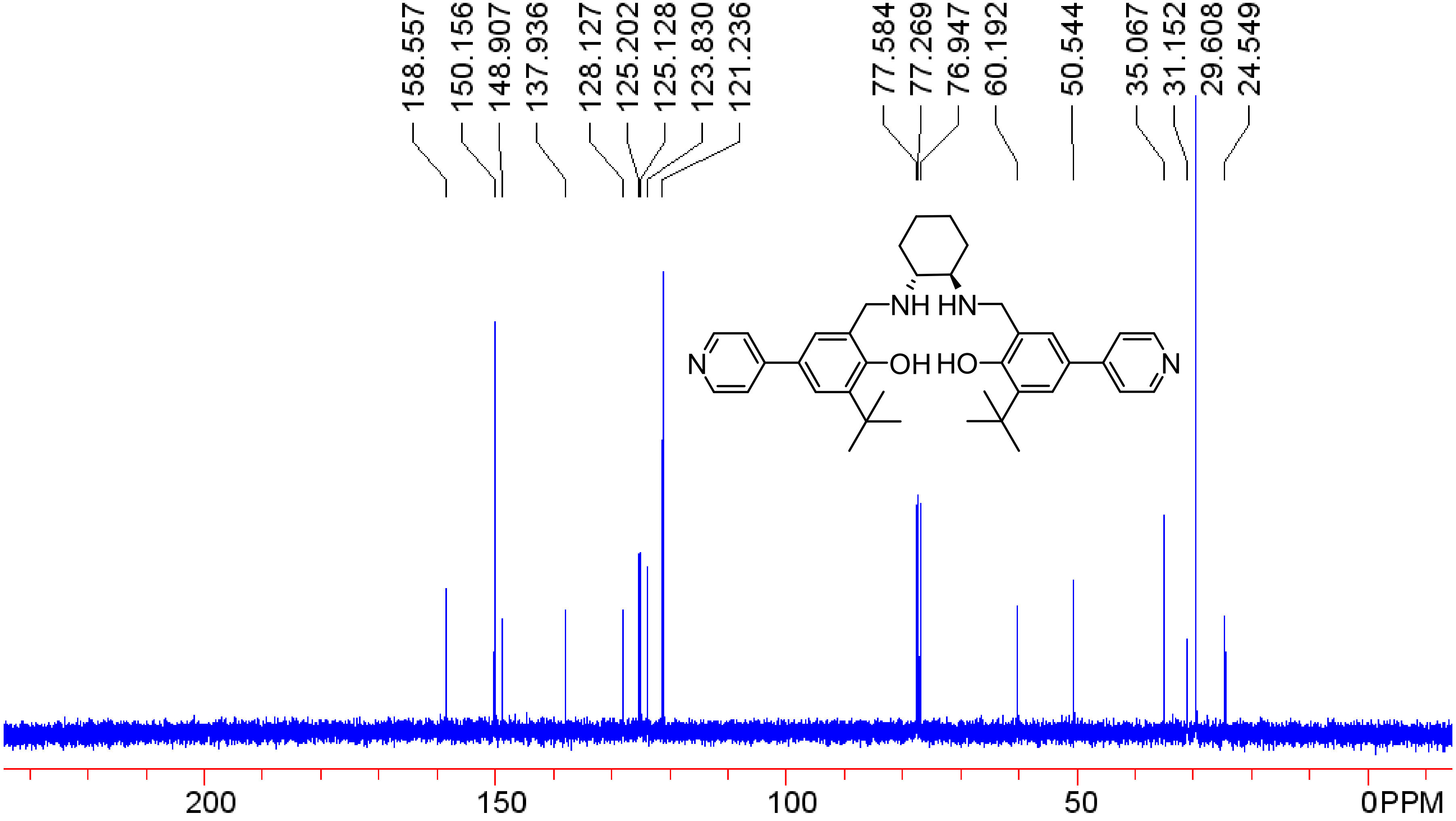


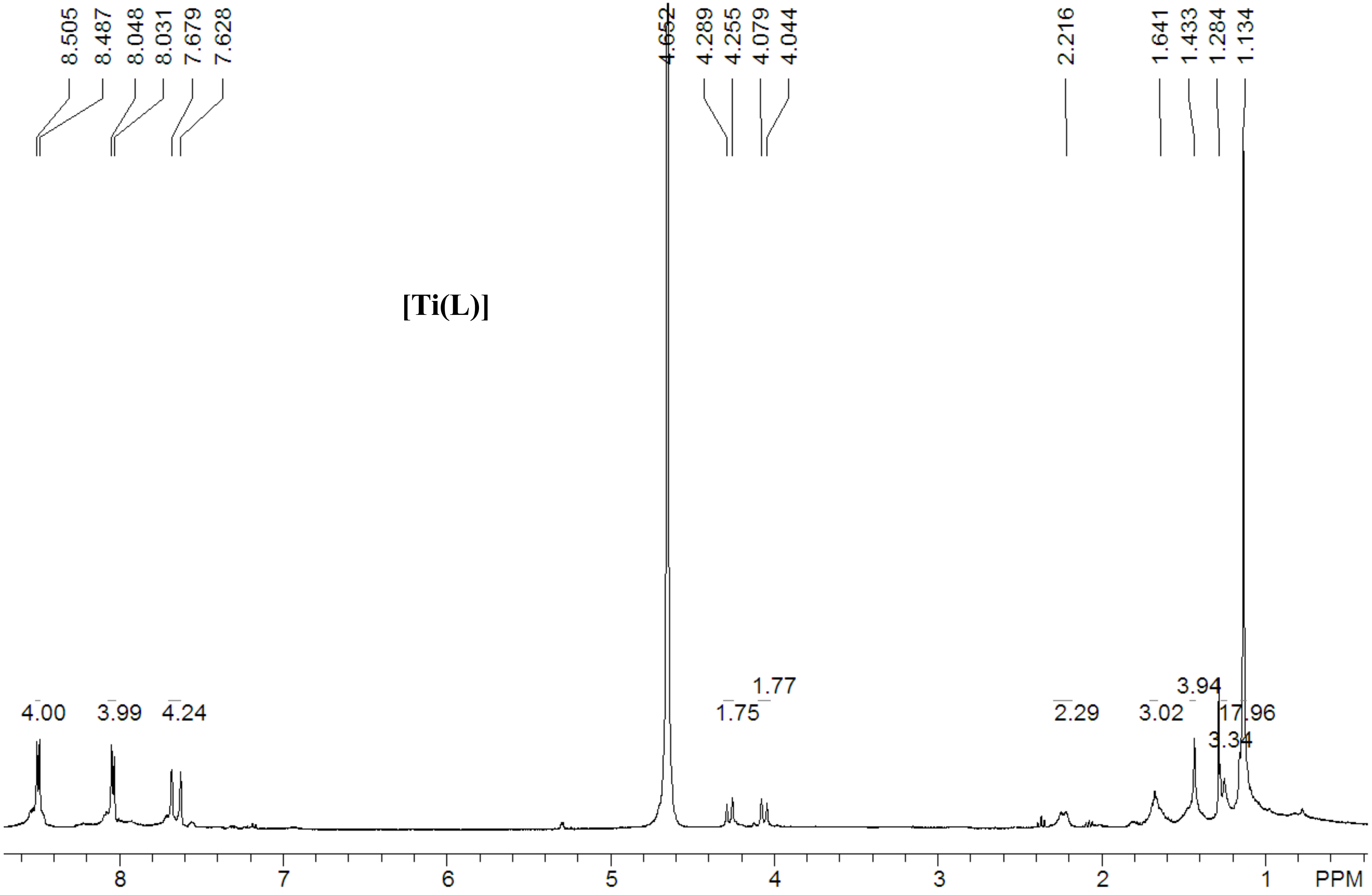
17. Figures S14. XPS of complex **1** and recovered complex **1**



18. Figure S15. ^{1}H and ^{13}C NMR for the ligand (*R*)-H_2**L** , (*R*)-**TiL** , sulfides, sulfoxides and sulfone in $CDCl_3$.




158.557
150.156
148.907
137.936
128.127
125.202
125.128
123.830
121.236
77.584
77.269
76.947
60.192
50.544
35.067
31.152
29.608
24.549
N
NH
HN
OH
HO
N
200
150
100
50
0PPM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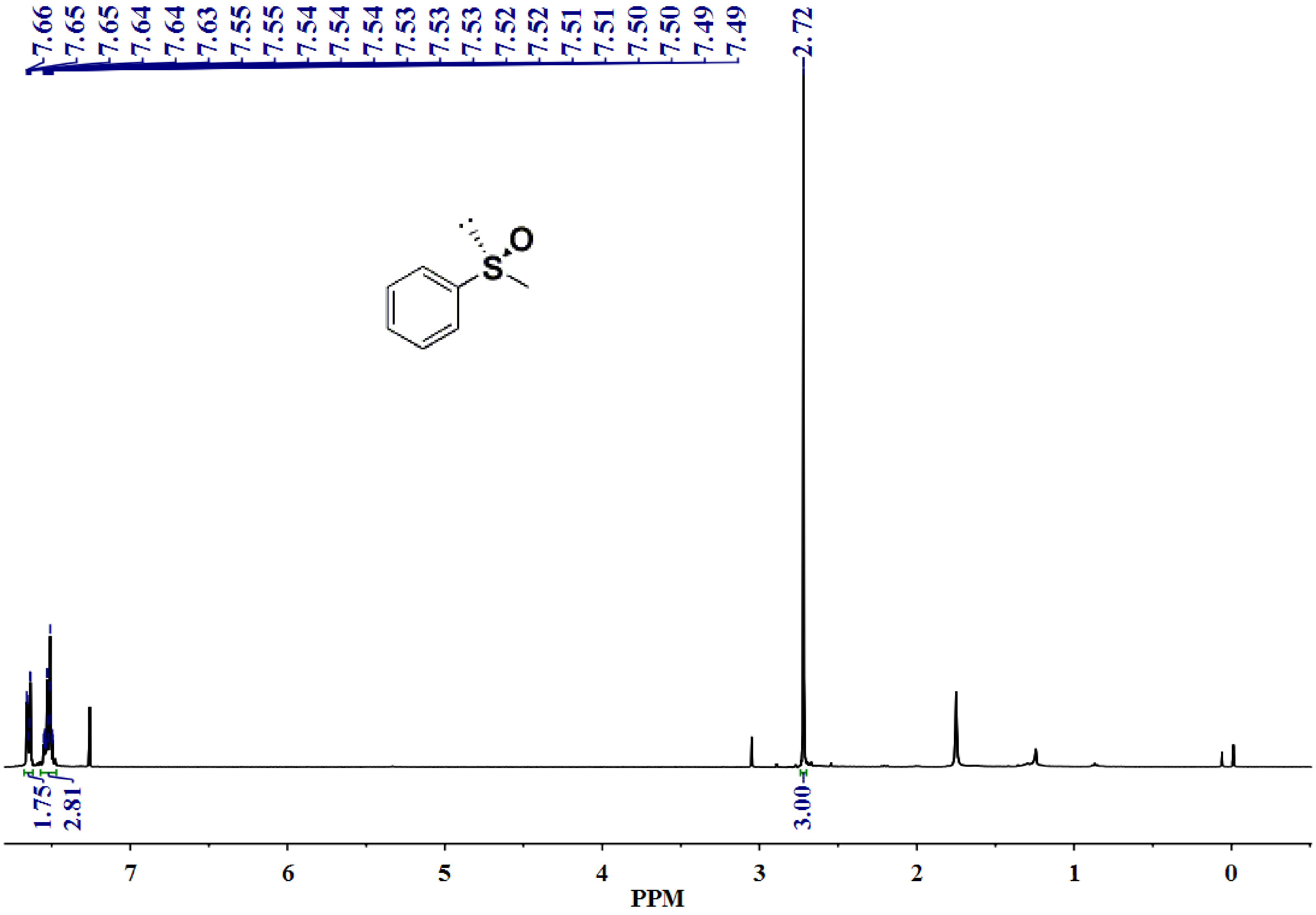
8.048
8.031
7.679
7.628
4.652
4.289
4.255
4.079
4.044
2.216
1.641
1.433
1.284
1.134
[Ti(L)]
4.00
3.99
4.24
1.75
1.77
2.29
3.02
3.94
3.34
17.96
8
7
6
5
4
3
2
1
PPM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7.65
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7.64
7.63
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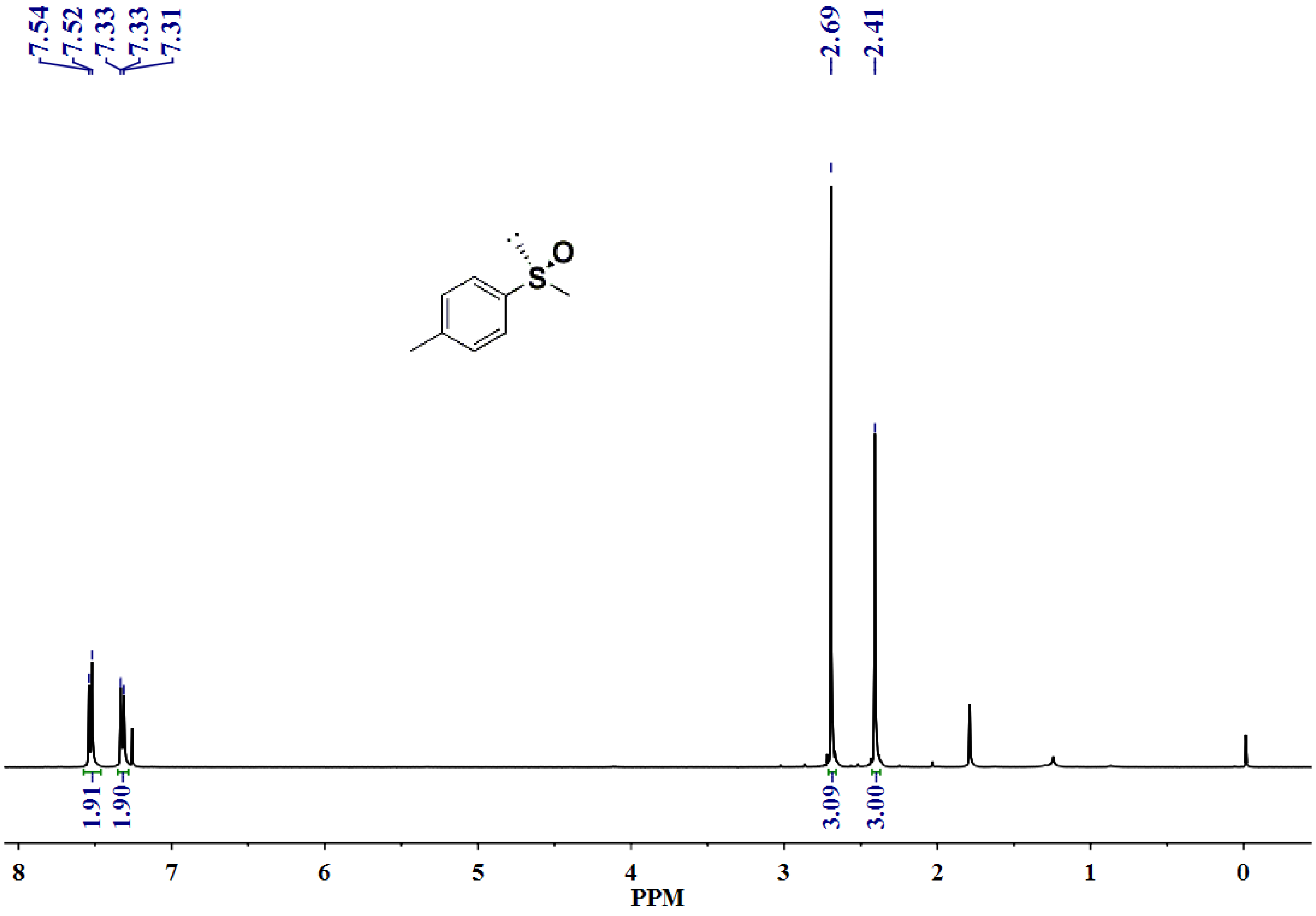
7.55
7.54
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.49
2.72
S
O
1.75
2.81
3.00
7
6
5
4
3
2
1
0
PPM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7.52
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7.33
7.31
2.69
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O
S
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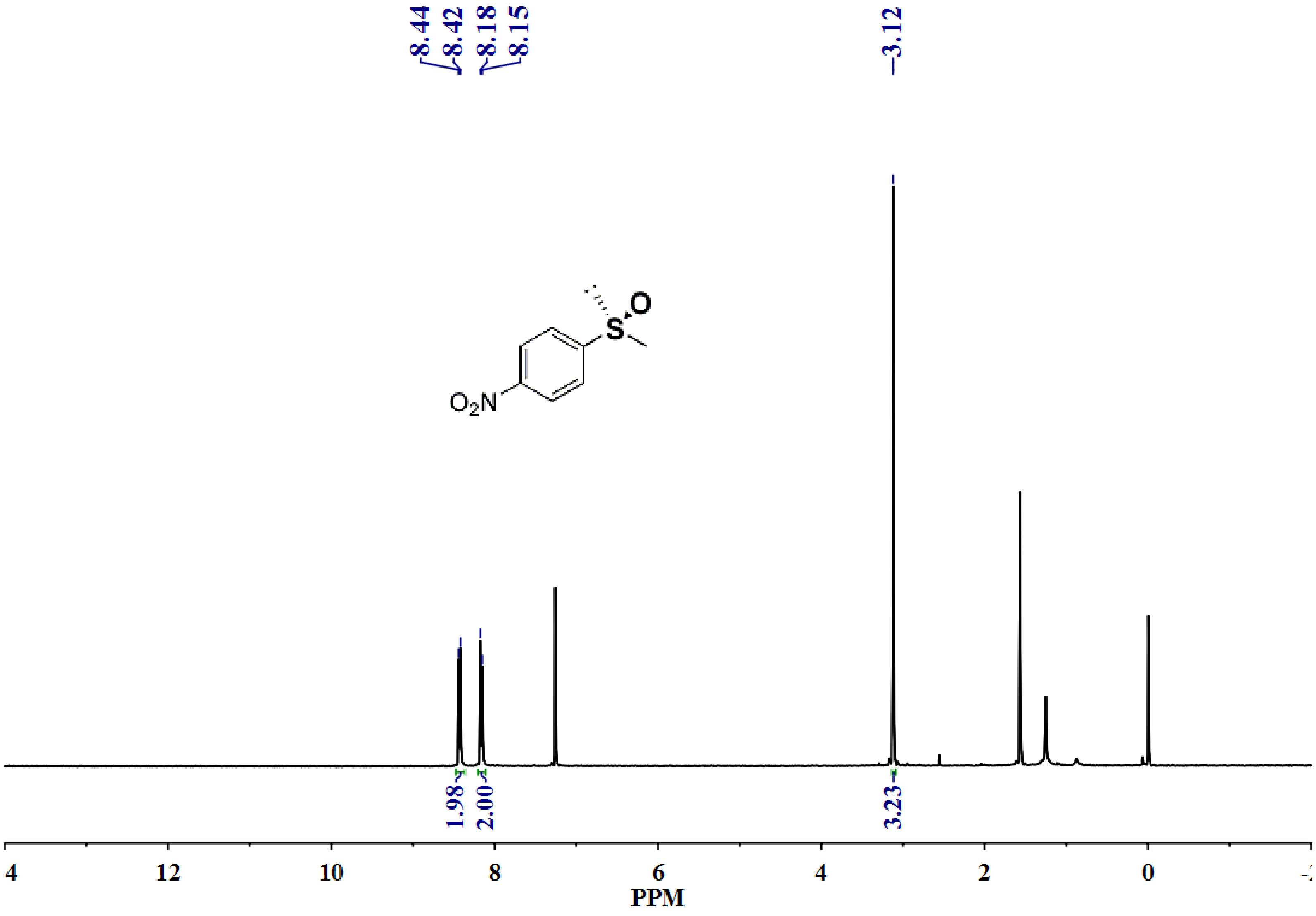
1.90
3.09
3.00
8
7
6
5
4
3
2
1
0
PPM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8.42
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8.15
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S
O
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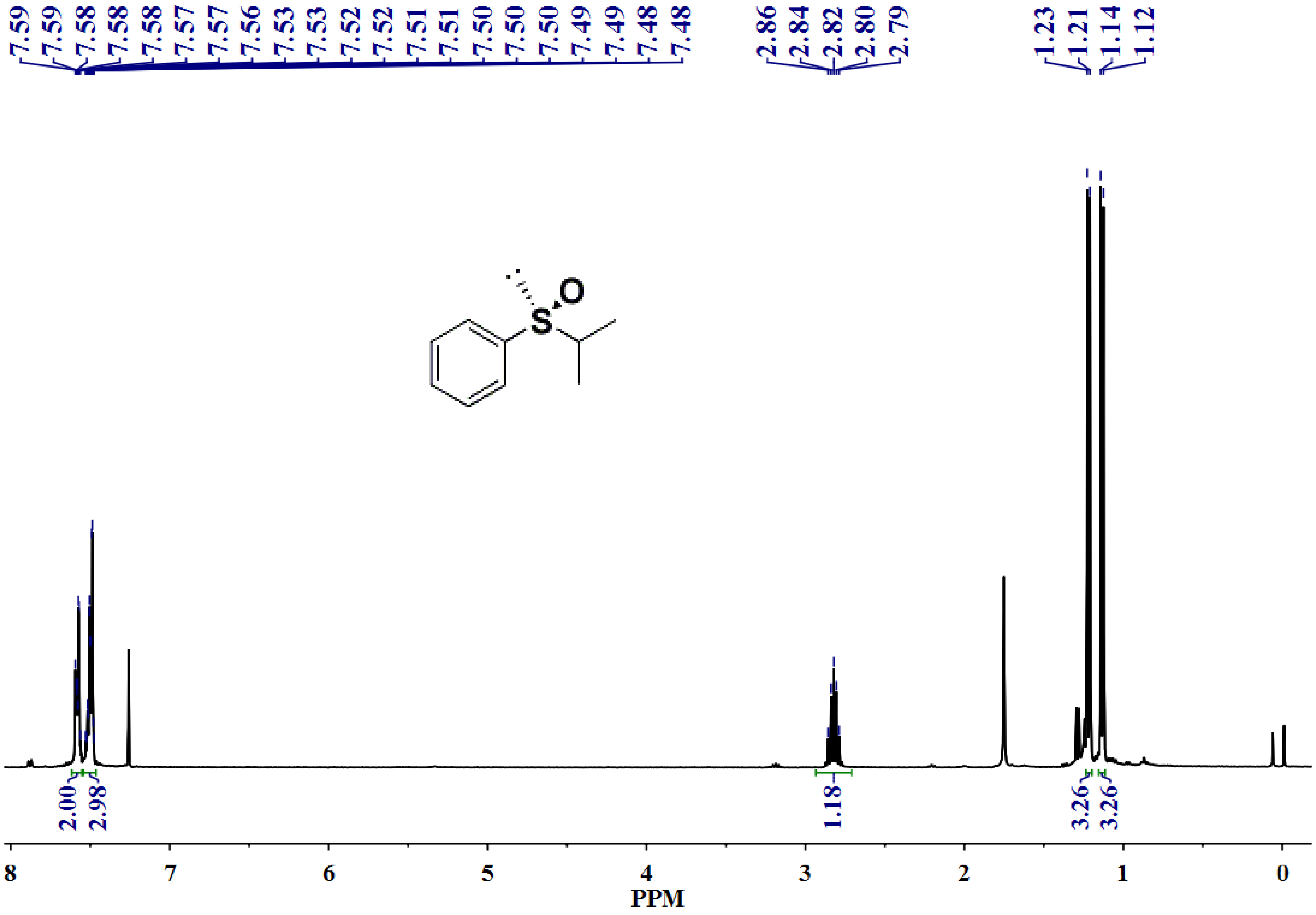
2.00
3.23
4
12
10
8
6
4
2
0
PPM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7.57
7.56
7.53
7.53
7.52
7.52
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7.51
7.50
7.50
7.50
7.49
7.49
7.48
7.48
2.86
2.84
2.82
2.80
2.79
1.23
1.21
1.14
1.12
S
O
2.00
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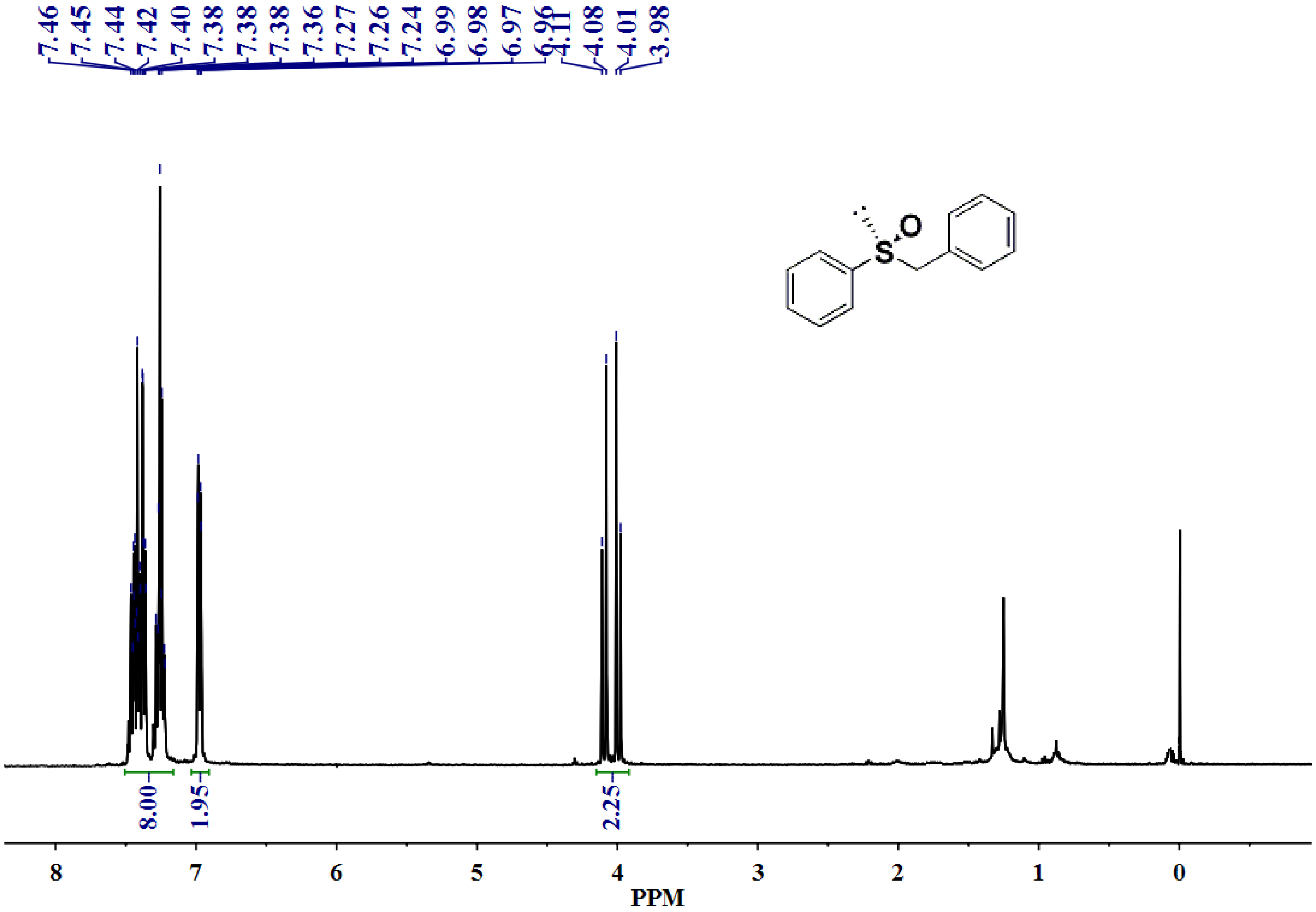
1.18
3.26
3.26
8
7
6
5
4
3
2
1
0
PPM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7.42
7.40
7.38
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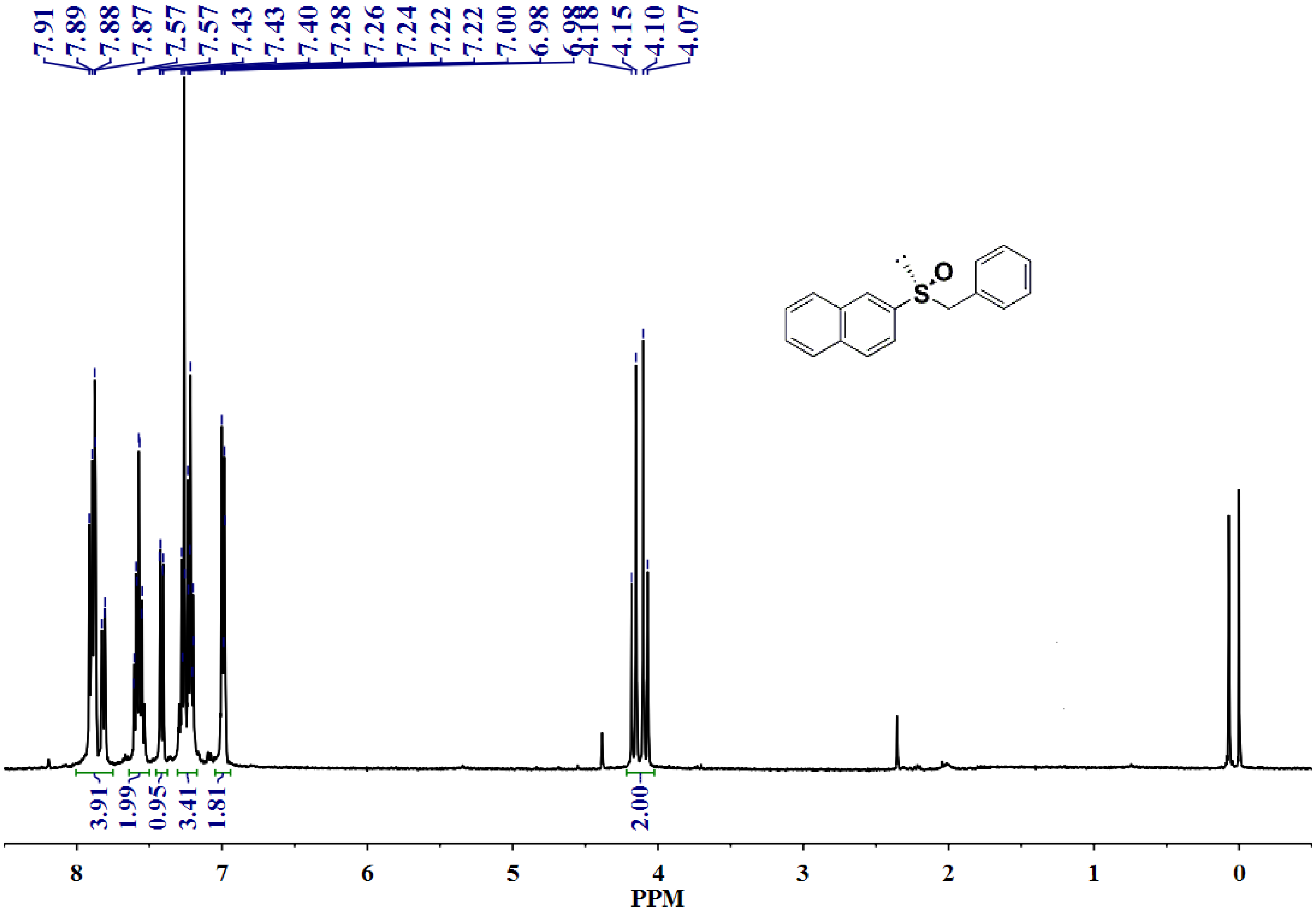
7.38
7.36
7.27
7.26
7.24
6.99
6.98
6.97
6.96
4.11
4.08
4.01
3.98
8.00
1.95
2.25
8
7
6
5
4
3
2
1
0
PPM
S
O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7.88
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7.57
7.43
7.43
7.40
7.28
7.26
7.24
7.22
7.22
7.00
6.98
6.98
4.18
4.15
4.10
4.07
3.91
1.99
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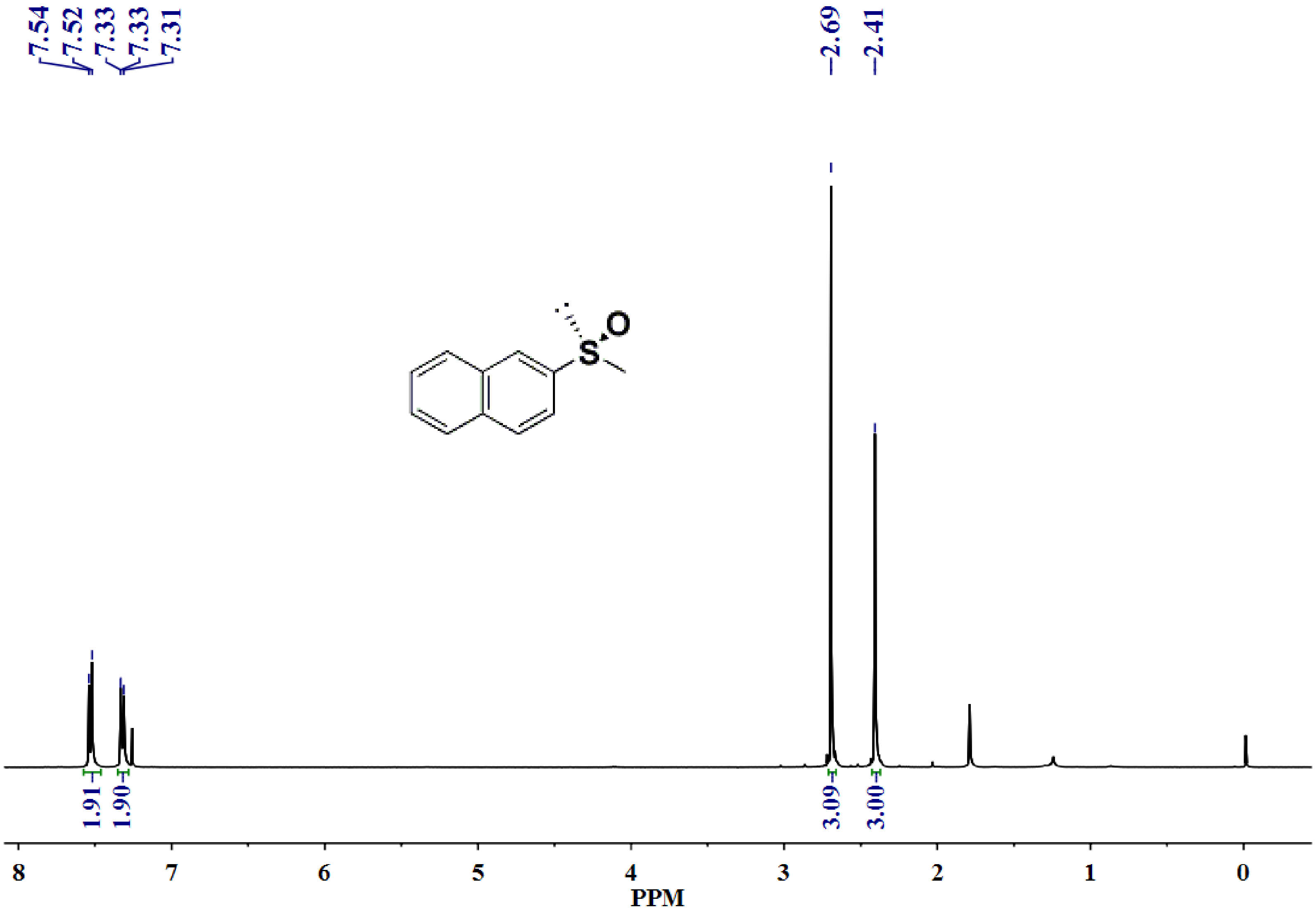
3.41
1.81
2.00
8
7
6
5
4
3
2
1
0
PPM
S
O


7.54
7.52
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2.69
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3.00
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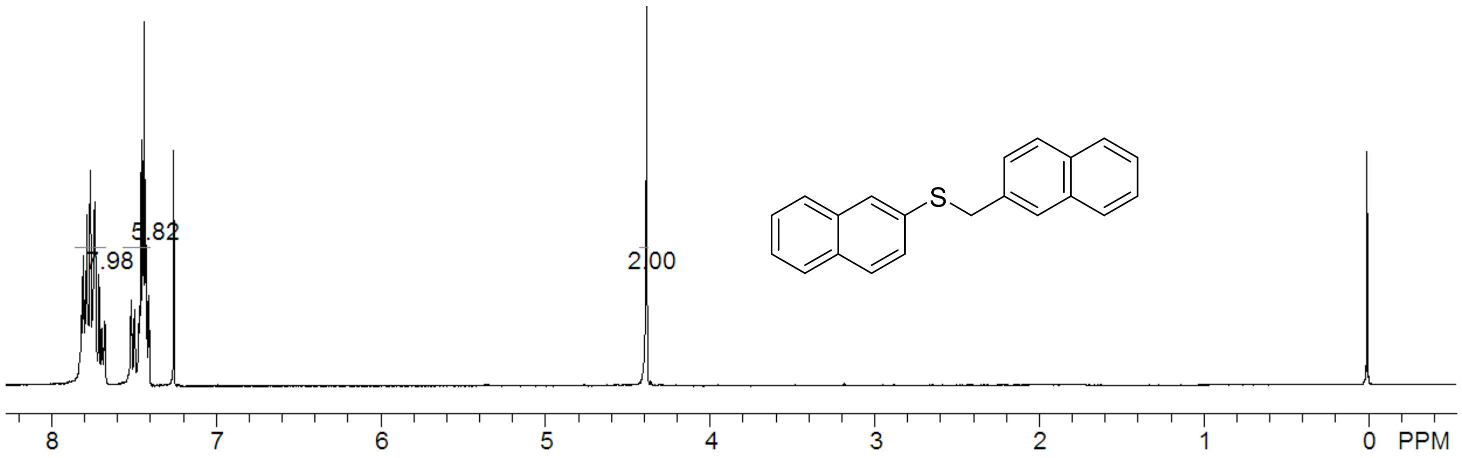
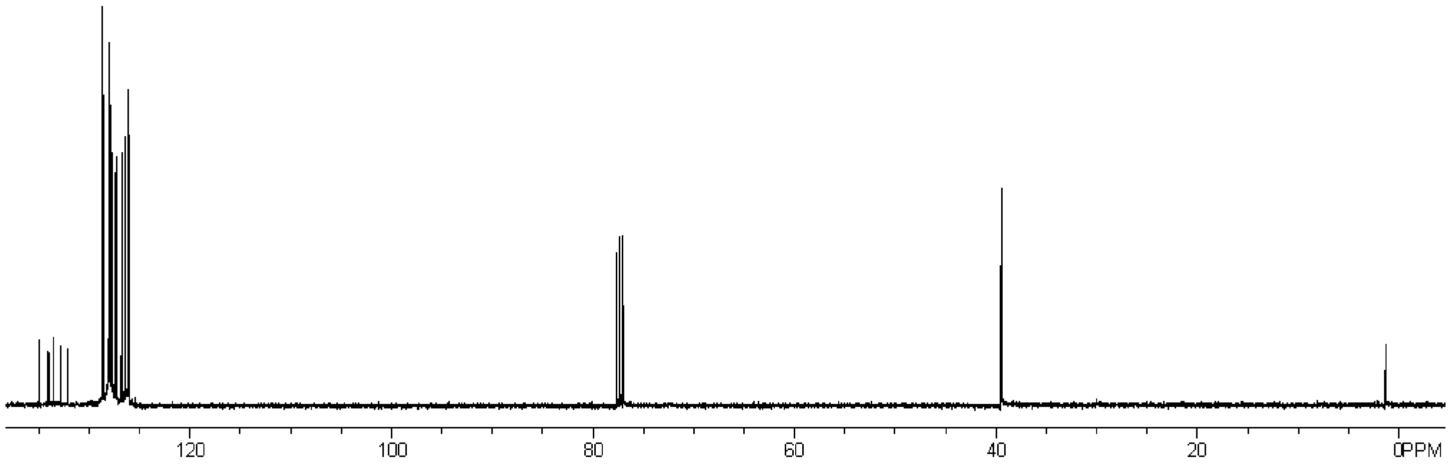
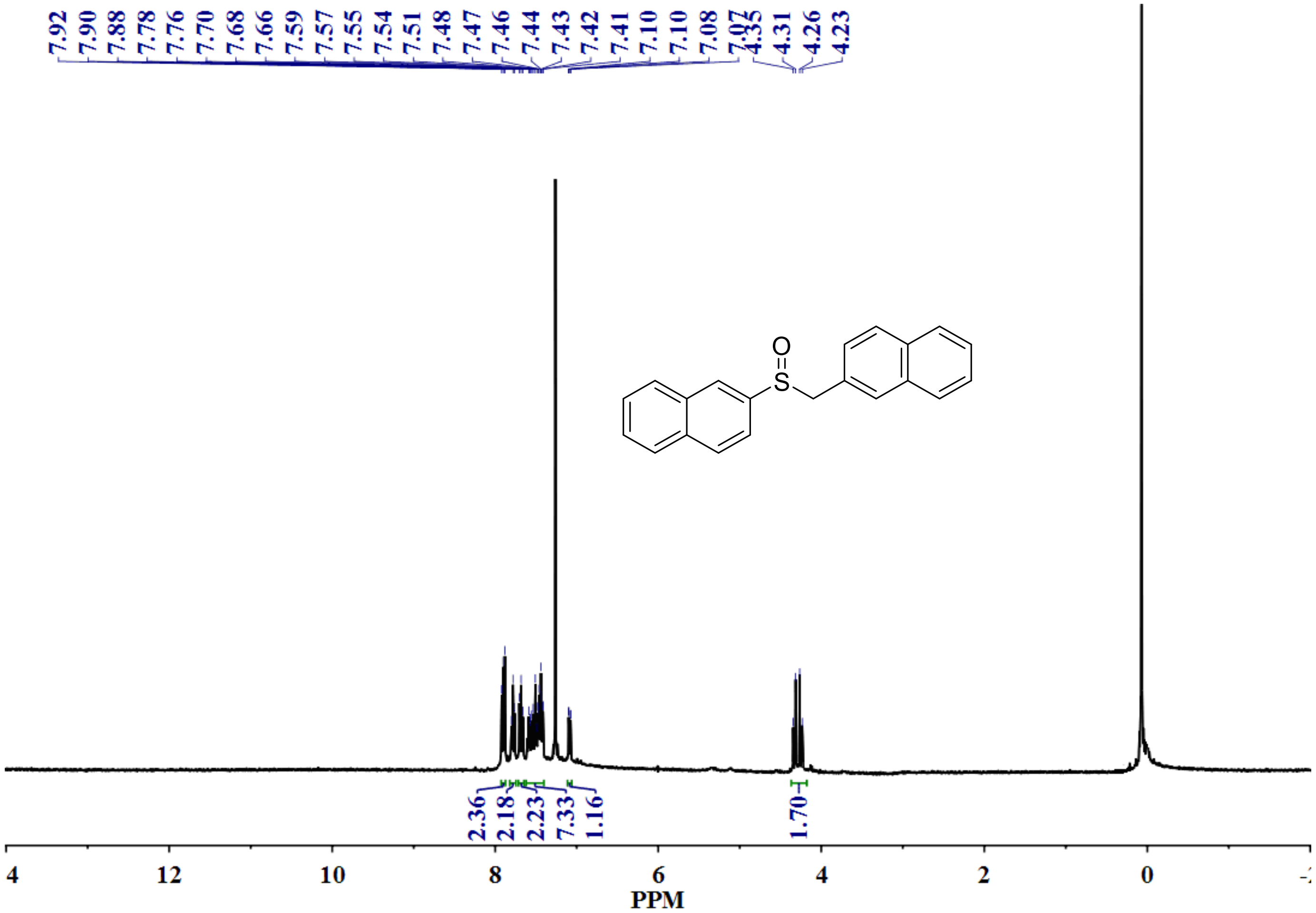
4
3
2
1
0
PPM
S
O

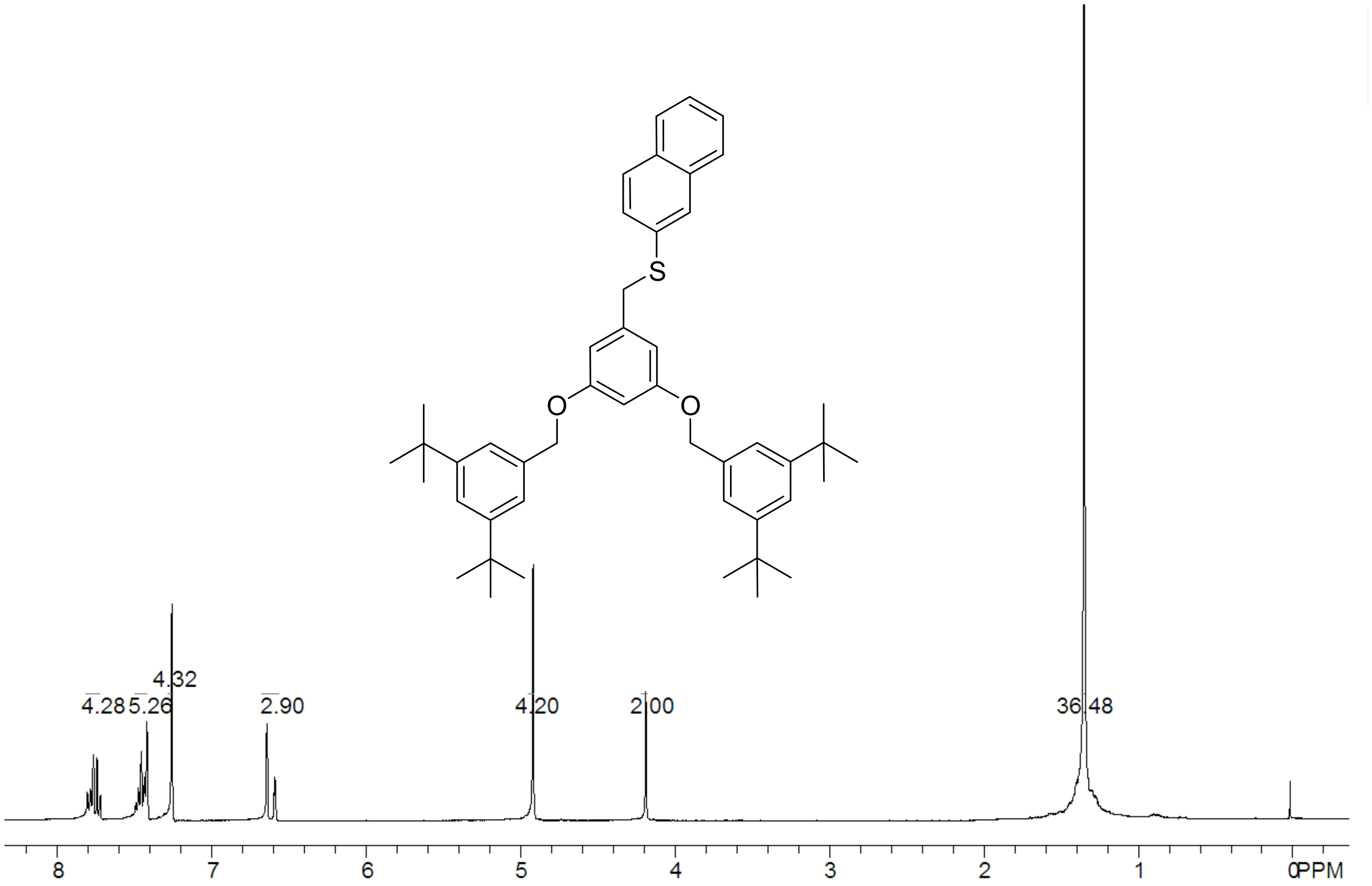




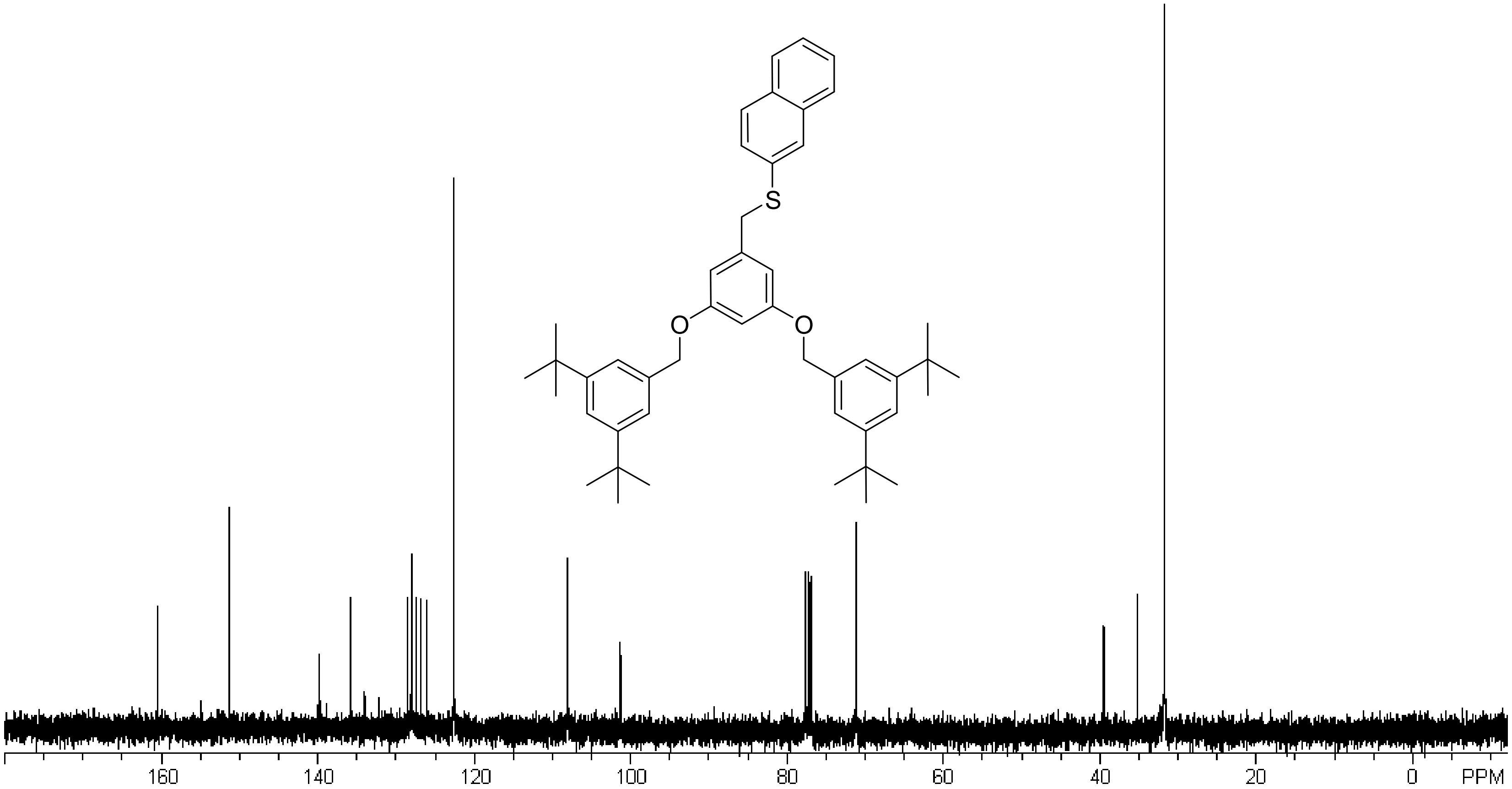
^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.60-7.90 (m,8H), 7.30-7.60 (m, 6H), 4.39 (s, 2H). ^{13}C NMR (400 MHz, CDCl$_3$, δ):139.984, 134.136, 133.951, 133.559, 132.850, 132.131, 128..635, 127.985, 127.963, 127.938, 127.924, 127.753, 127.433, 127.259, 126.765, 126.440, 126.397, 126.170, 126.135, 126.025, 39.457.



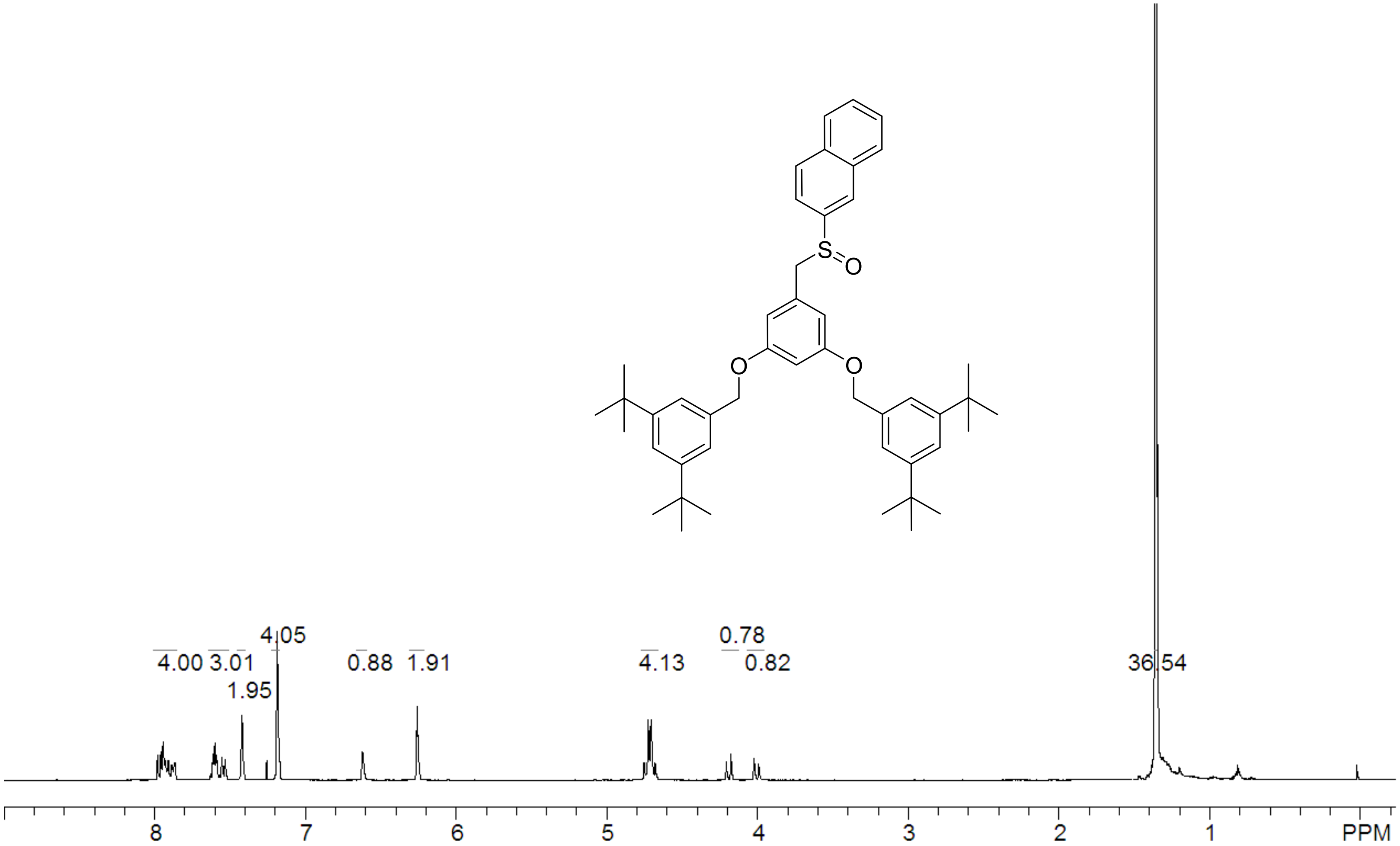
^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.41-7.92 (m, 13H), 7.07-7.10 (dd, 1H), 4.23-4.35 (s, 2H)



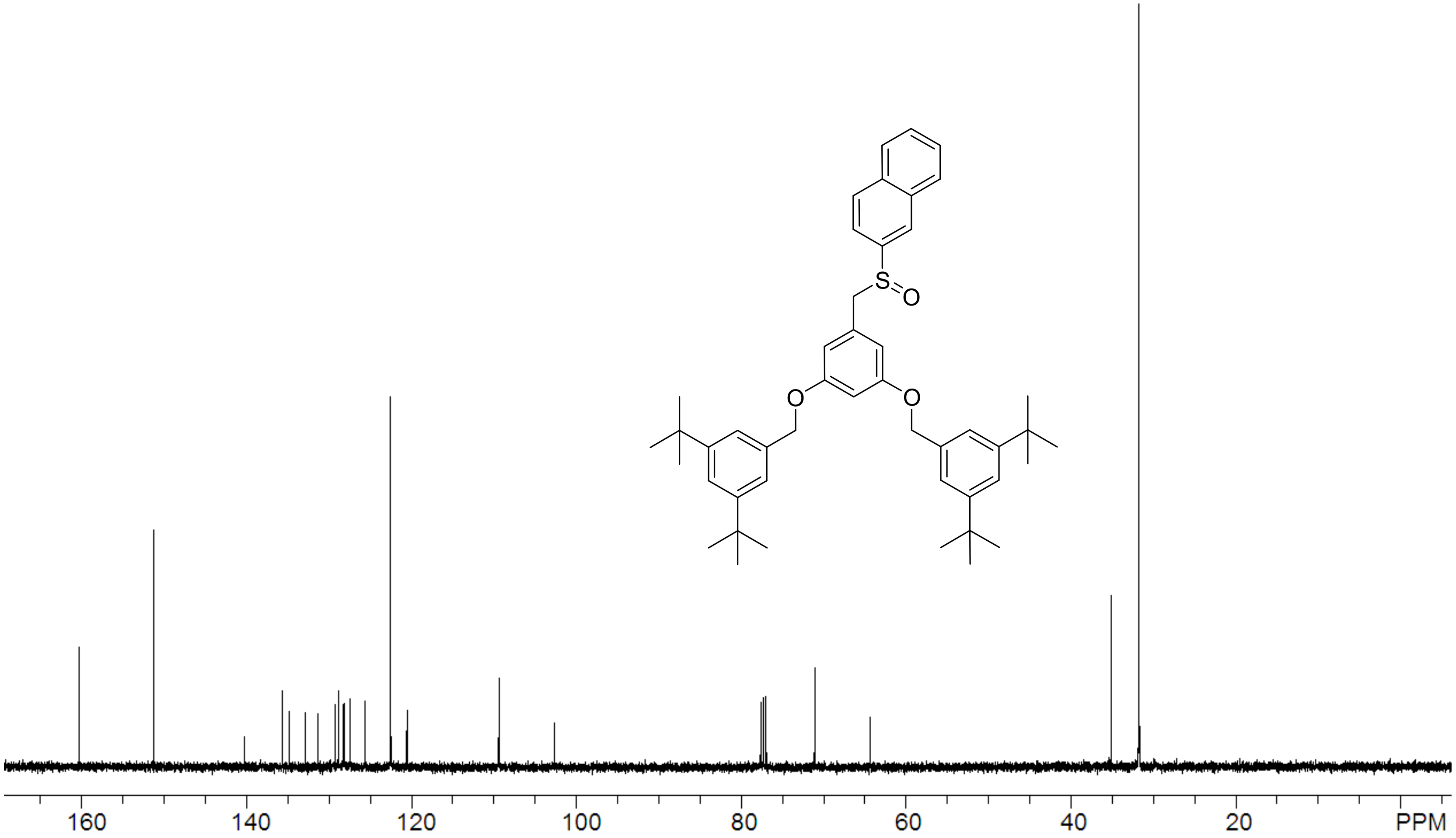
^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.70-7.85 (m, 4H), 7.40-7.50 (m, 5H), 4.18 (s, 2H), 6.50-6.70 (m, 3H), 4.91 (s, 4H), 4.18 (s, 2H), 1.35 (s, 36H).



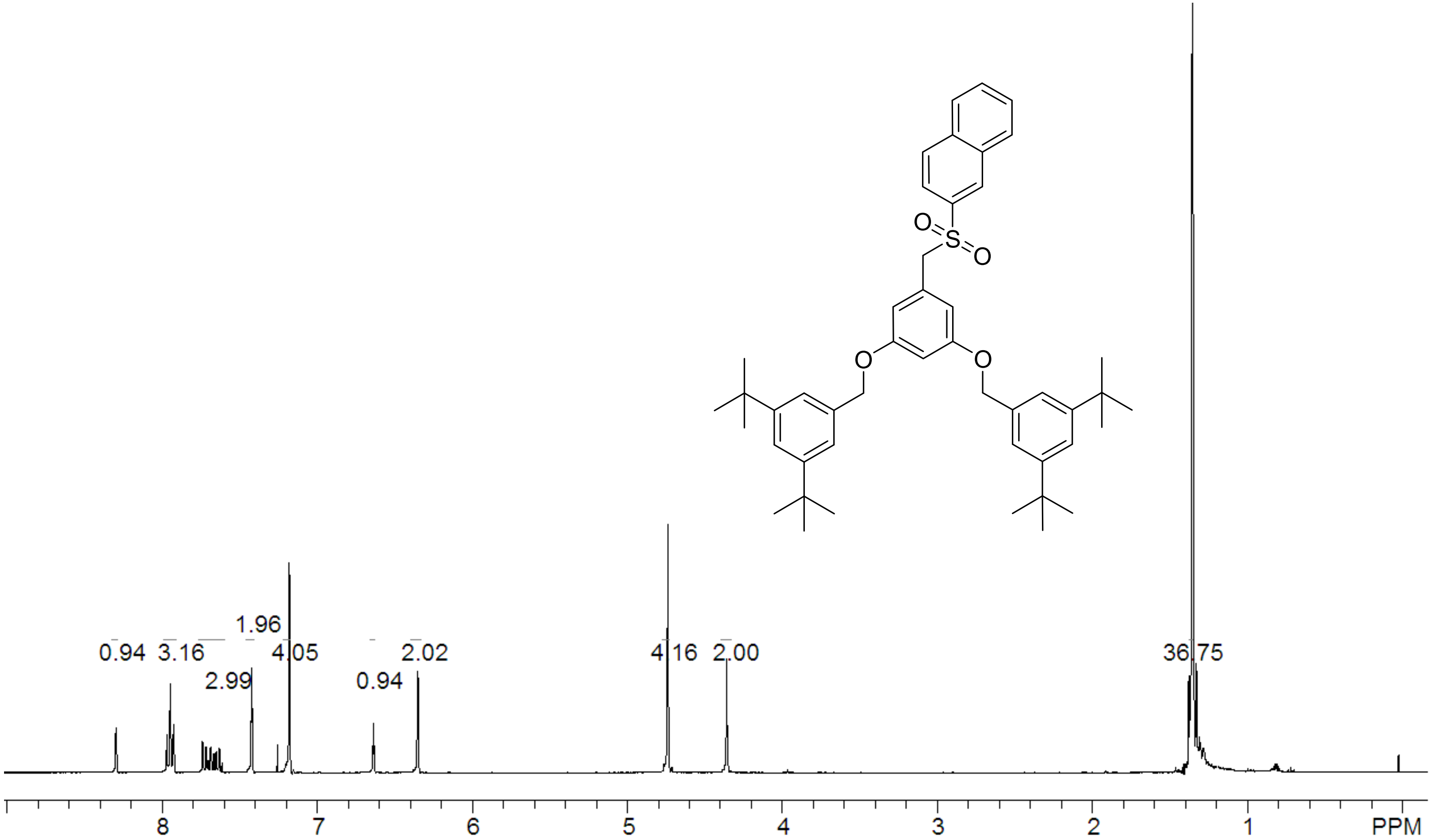
^{13}C NMR(400 MHz, CDCl$_3$, δ):160.434, 151.246, 139.75, 135.877, 134.170, 133.938, 132.112, 128.597, 128.021, 127.941, 127.437, 126.745, 126.024, 122.615, 122.541, 108.032, 101.290, 71.140, 39.494, 35.131, 31.741.



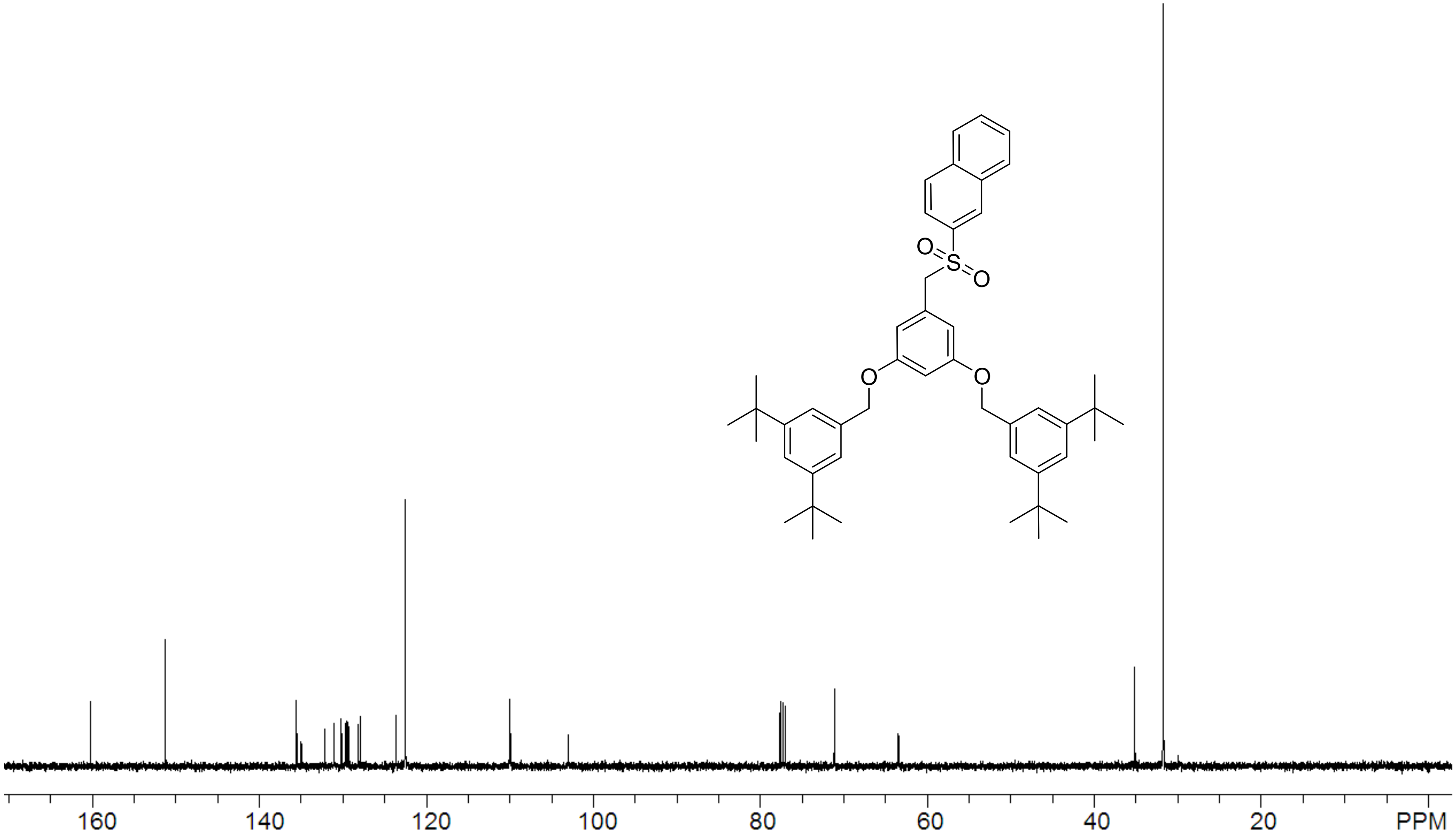
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.87-7.98 (m, 4H), 7.53-7.63 (m, 3H), 7.42 (d, 2H), 7.19 (s, 4H), 6.62 (d, 1H), 6.26 (s, 2H), 4.68-4.75 (dd, 4H), 3.99-4.21 (dd, 2H), 1.36 (s, 36H).



^{13}C NMR (400 MHz, CDCl$_3$, δ):160.280, 151.243, 140.279, 135.665, 134.810, 132.874, 131.326, 129.297, 128.822, 128.240, 128.118, 127.495, 125.684, 122.538, 120.557, 109.406, 102.678, 71.087, 64.354, 35.135, 31.746.



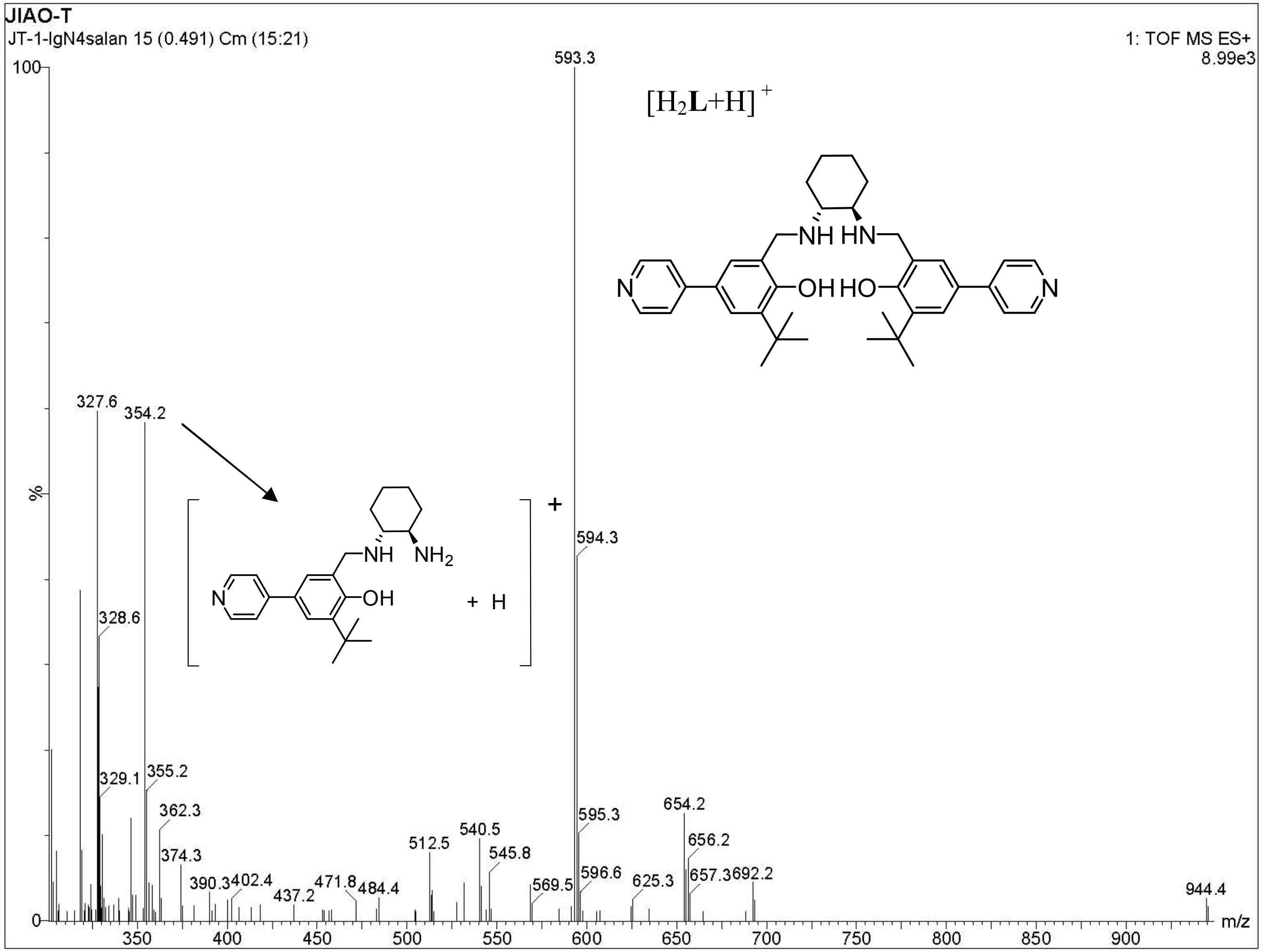
^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.30 (s, 1H), 7.93-7.97 (m, 3H), 7.61-7.74 (m, 3H), 7.18 (d, 4H), 6.63-6.64 (m, 1H), 6.35 (d, 2H), 4.74 (s, 4H), 4.36 (s, 2H), 1.36 (s, 36H).

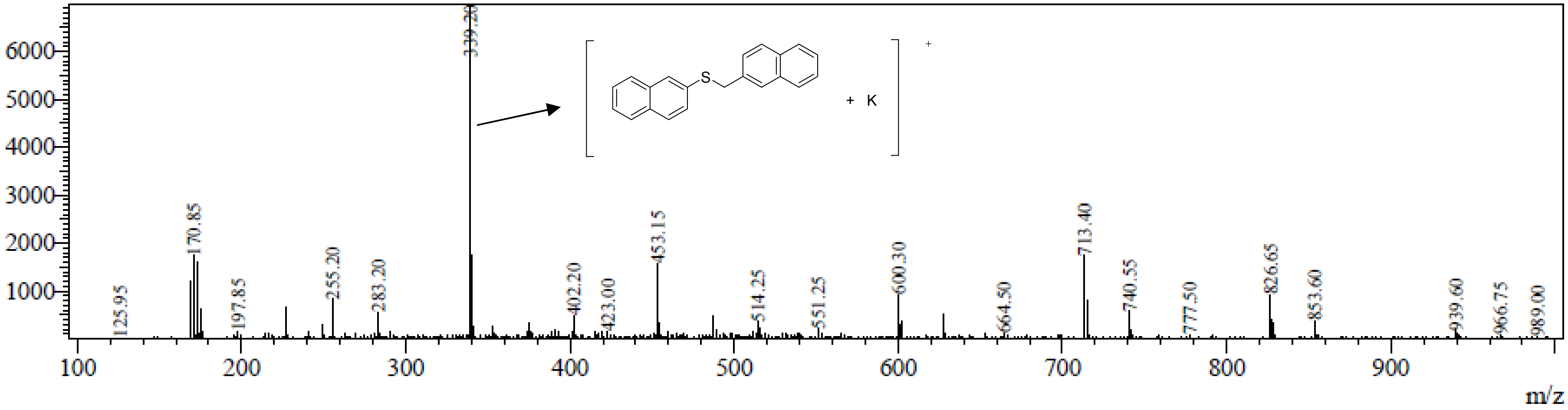


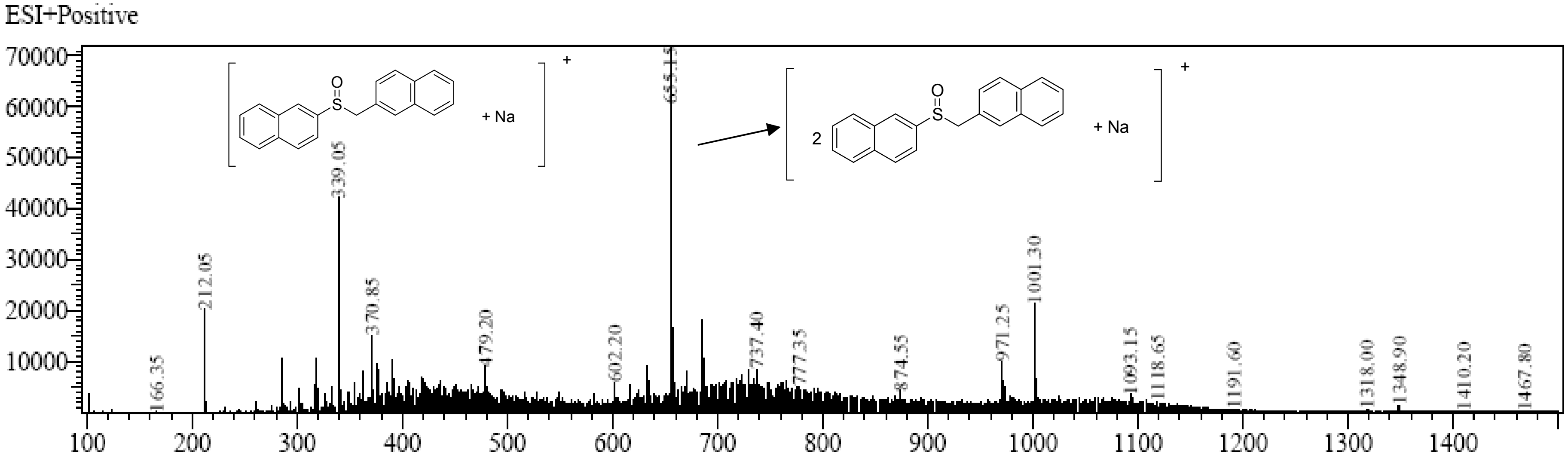
^{13}C NMR (400 MHz, $CDCl_3$, δ):160.269, 151.263, 135.565, 134.998, 131.036, 130.188, 129.729, 129.618, 129.359, 128.164, 127.899, 123.644, 122.586, 122.527, 109.979, 103.058, 71.139, 63.469, 35.131, 31.738.

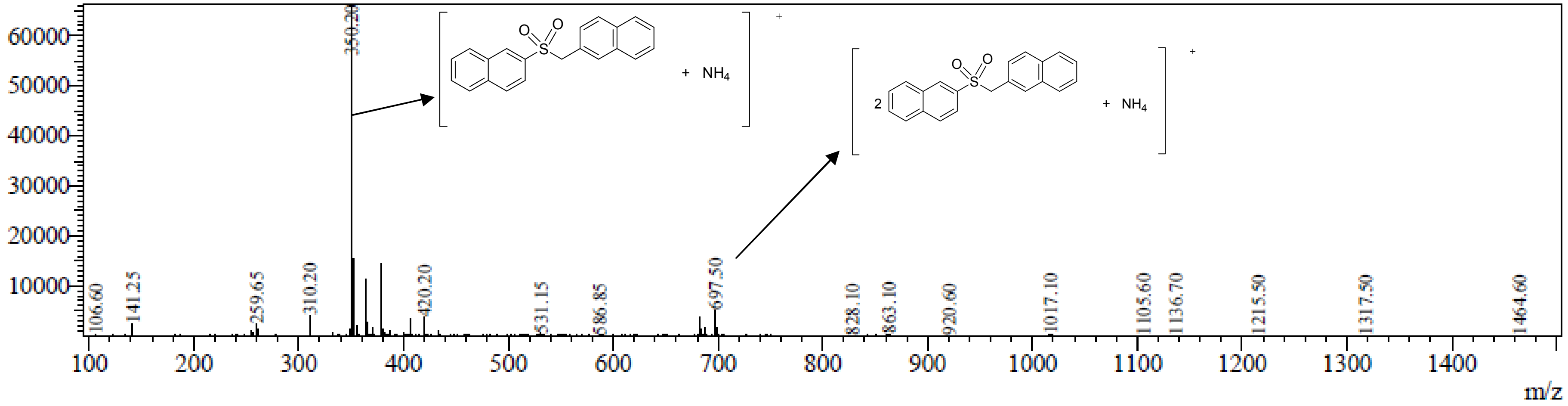
►

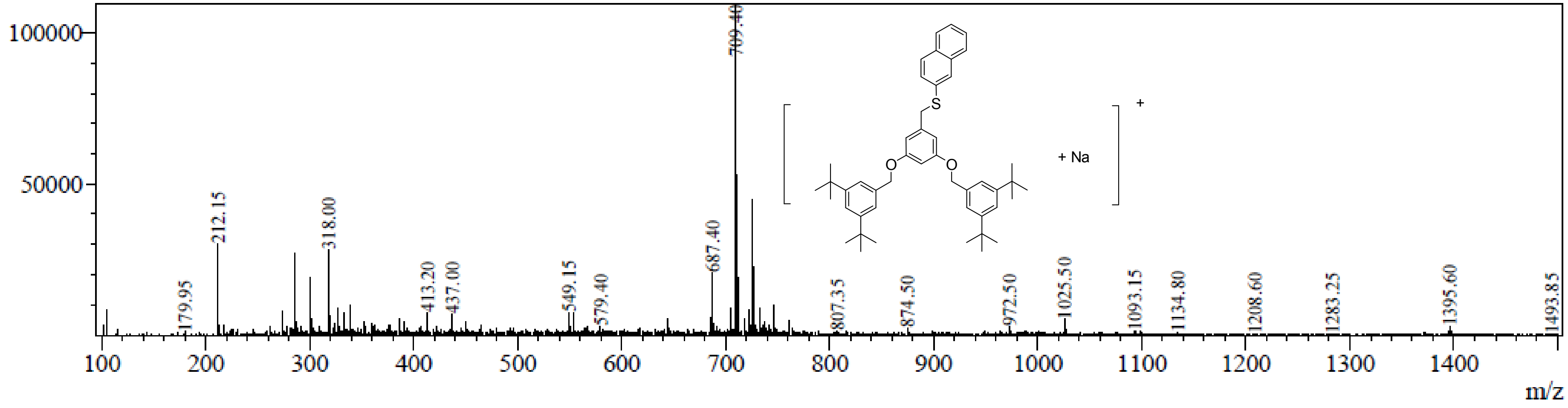
19. Figure S16. ESI-Mass of (*R*)-H_2**L**, (*R*)-**TiL** and some sulfides and sulfoxides.

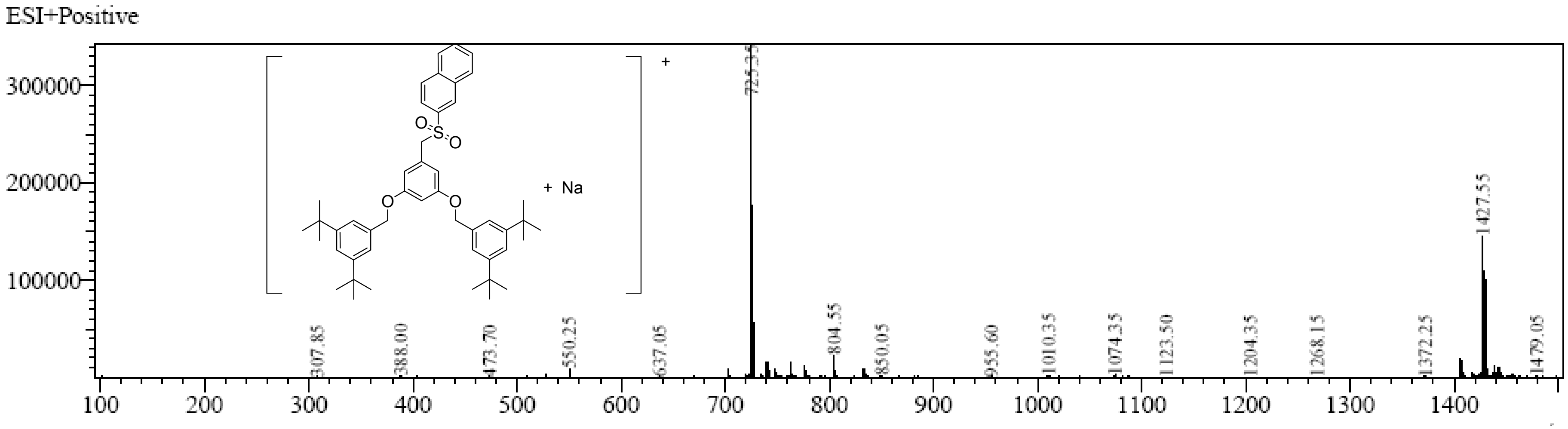



6000
5000
4000
3000
2000
1000
125.95
170.85
197.85
255.20
283.20
339.20
402.20
423.00
453.15
514.25
551.25
600.30
664.50
713.40
740.55
777.50
826.65
853.60
939.60
966.75
989.00
S
+ K
+
100
200
300
400
500
600
700
800
900
m/z


ESI+Positive
70000
60000
50000
40000
30000
20000
10000
O
S
+ Na
+
2
O
S
+ Na
+
166.35
212.05
339.05
370.85
479.20
602.20
655.15
737.40
777.35
874.55
971.25
1001.30
1093.15
1118.65
1191.60
1318.00
1348.90
1410.20
1467.80
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400


60000
50000
40000
30000
20000
10000
106.60
141.25
259.65
310.20
350.20
420.20
531.15
586.85
697.50
828.10
863.10
920.60
1017.10
1105.60
1136.70
1215.50
1317.50
1464.60
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
m/z
O
O
S
+ NH4
+
2
+ NH4


100000
50000
179.95
212.15
318.00
413.20
437.00
549.15
579.40
687.40
709.40
807.35
874.50
972.50
1025.50
1093.15
1134.80
1208.60
1283.25
1395.60
1493.85
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
m/z
S
O
O
+ Na
+


ESI+Positive
O
S
O
O
O
+ Na
+
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1427.55
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388.00
473.70
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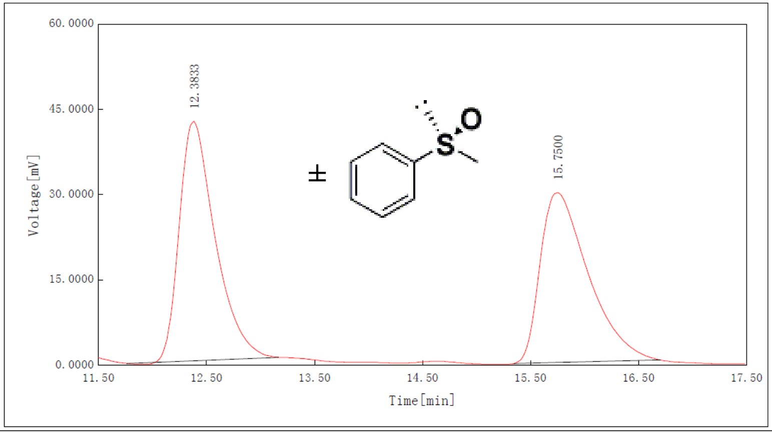
637.05
804.55
850.05
955.60
1010.35
1074.35
1123.50
1204.35
1268.15
1372.25
1479.05
300000
200000
100000
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400

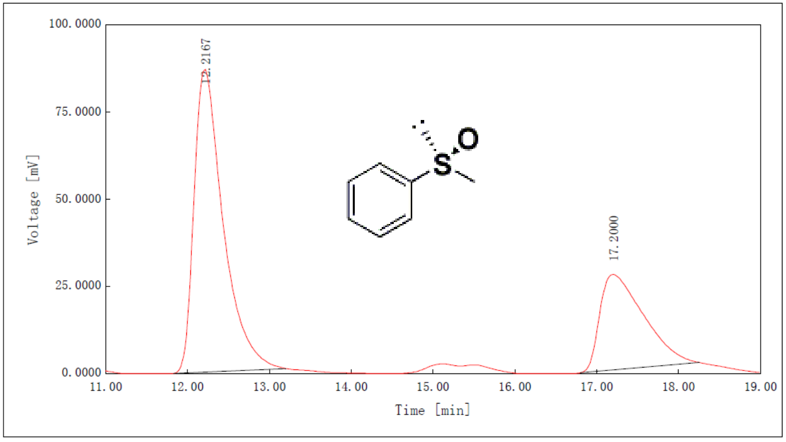
20. The HPLC and ^{1}H NMR analyses of sulfoxides.

20.1 The oxidation catalyzed by 8 mol % MOF 1.

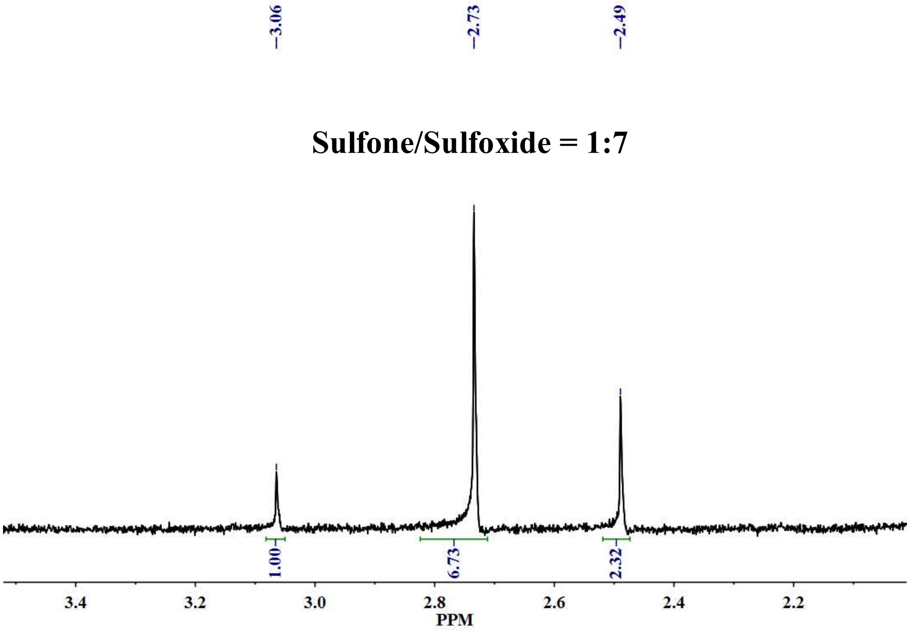
(*R*)-Methyl phenyl sulfoxide (catalyzed by 8 mol % (*R*)-1)

Chiralcel OD-H column: 90/10 hexane/i-PrOH; flow rate 1.0 mL/min; t_R = 12.21 min; t_R = 17.203 min;



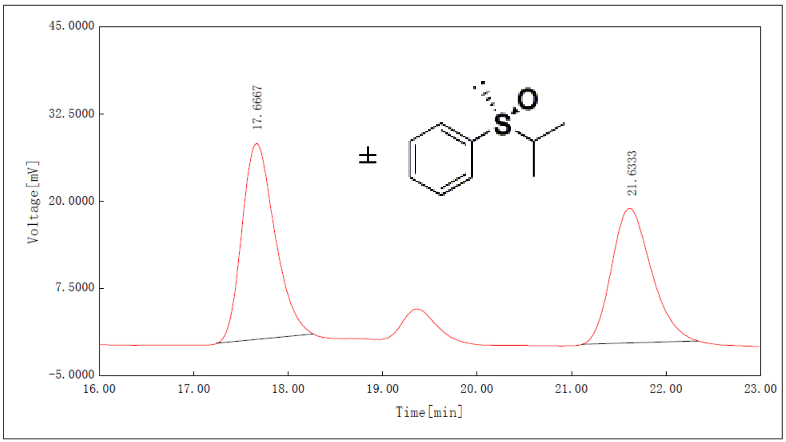


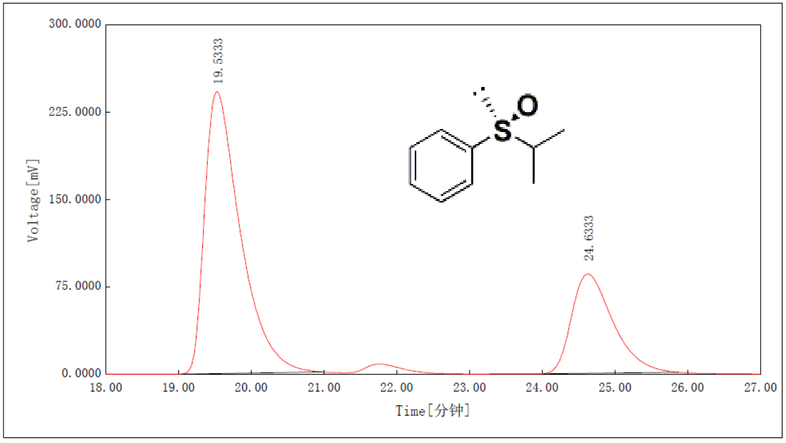
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	12.2167	2149.0591	BB	67.8512
2	17.2000	1018.2519	BB	32.1488
The Total		3167.3110		



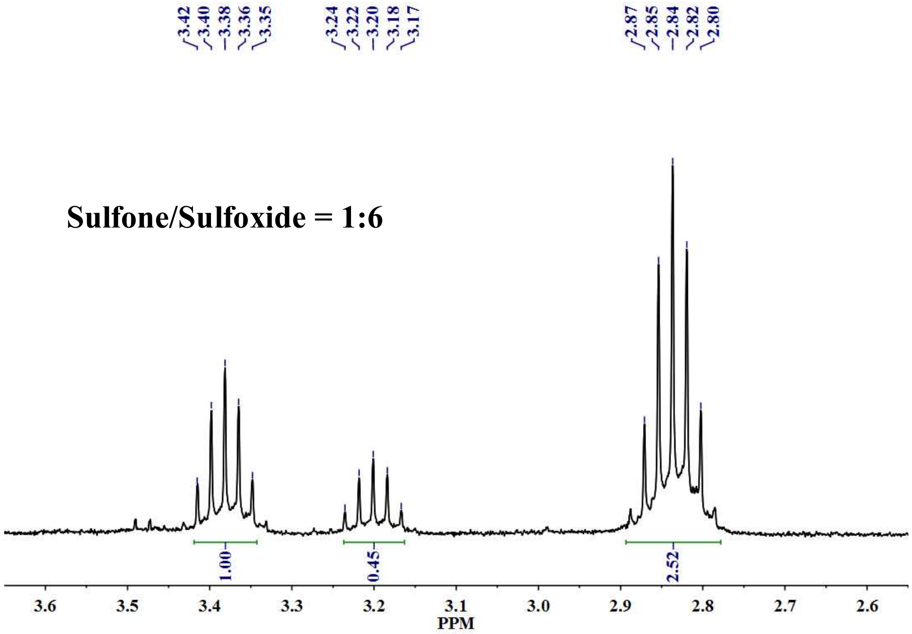
(*R*)- Isopropyl phenyl sulfoxide (catalyzed by 8 mol % (*R*)-1)

Chiralcel OD-H column: 93/7 hexane/i-PrOH; flow rate 0.5 mL/min; t_R = 19.53 min; t_R = 24.63 min;



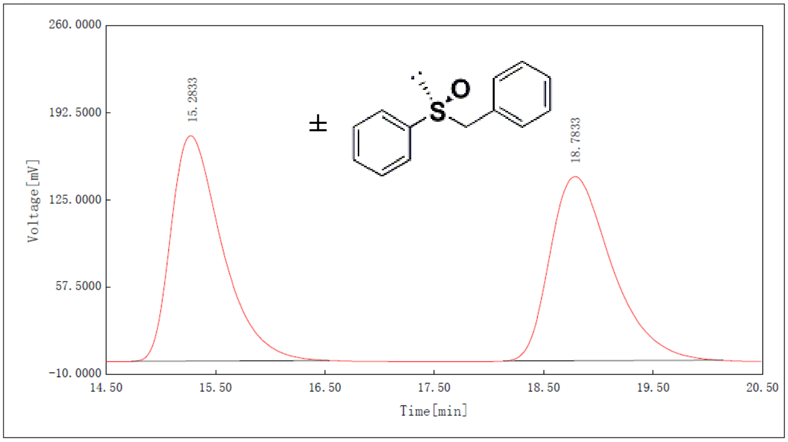


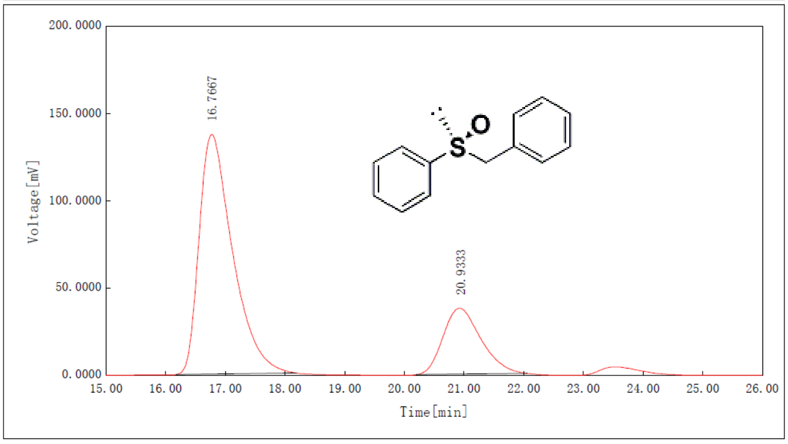
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	19.5333	8257.8054	BB	71.0559
2	24.6333	3363.7540	BB	28.9441
The Total		11621.5594		



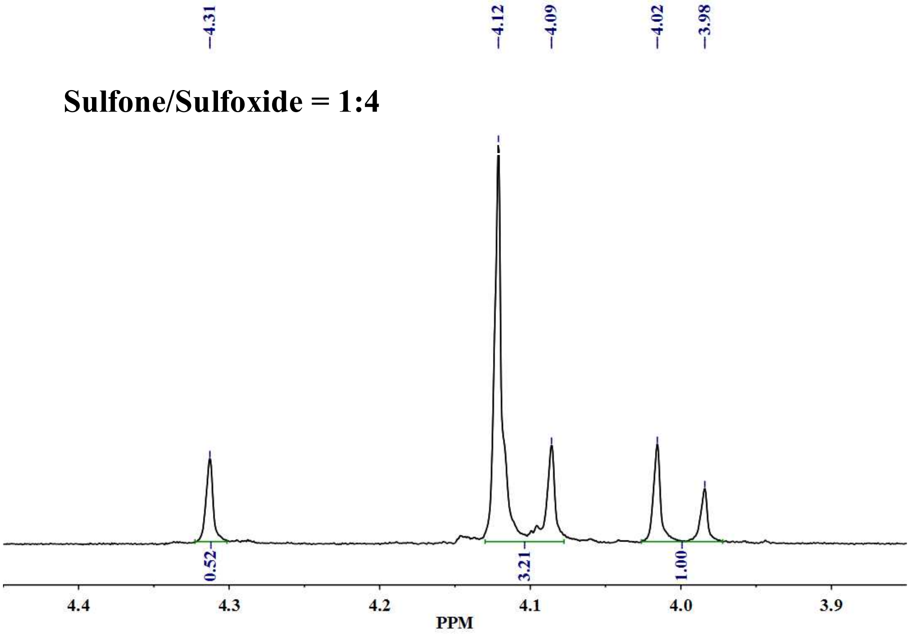
(*R*)- Benzyl phenyl sulfoxide (catalyzed by 8 mol % (*R*)-1)

Chiralcel OD-H column: 90/10 hexane/i-PrOH; flow rate 1.0 mL/min; t_R = 16.76 min; t_R = 20.93 min;

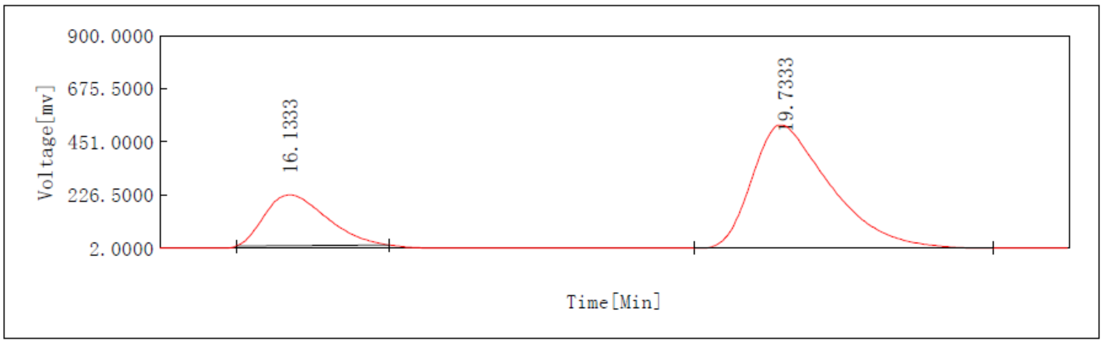




Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	16.7667	5355.5805	BB	76.3067
2	20.9333	1662.9132	BB	23.6933
The Total		7018.4937		



(*S*)- Benzyl phenyl sulfoxide (catalyzed by 8 mol % (*S*)-1)

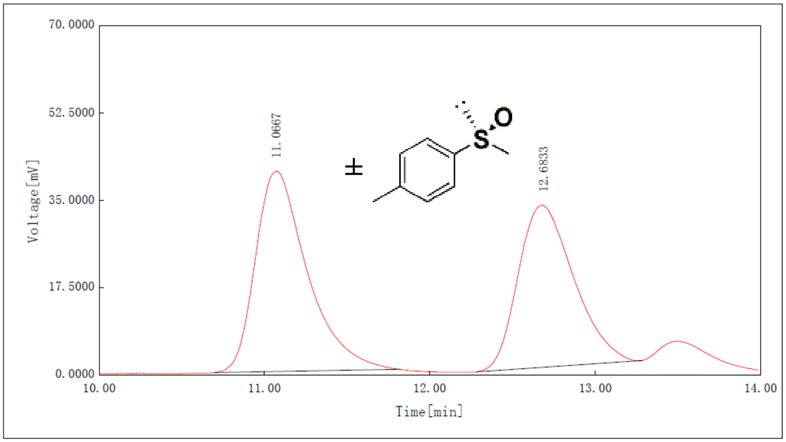


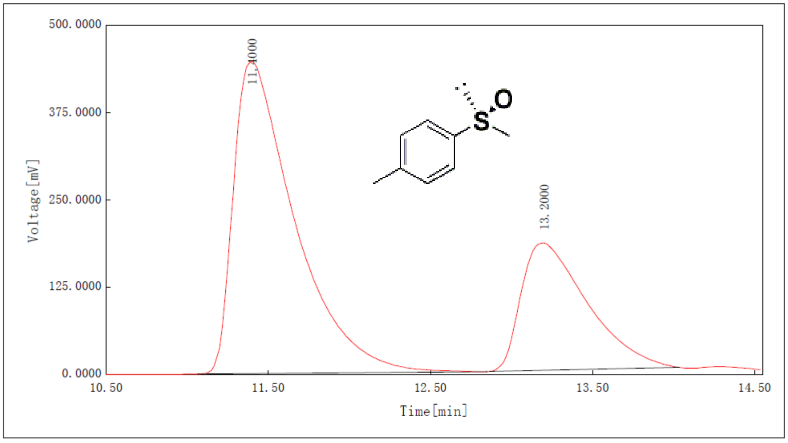
分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	16.1333	6720.0431	BB	67.0000	24.3456
2	19.7333	20882.6249	BB	130.0000	75.6544
和		27602.6680			

(*R*)-Methyl p-toyl sulfoxide (catalyzed by 8 mol % (*R*)-1)

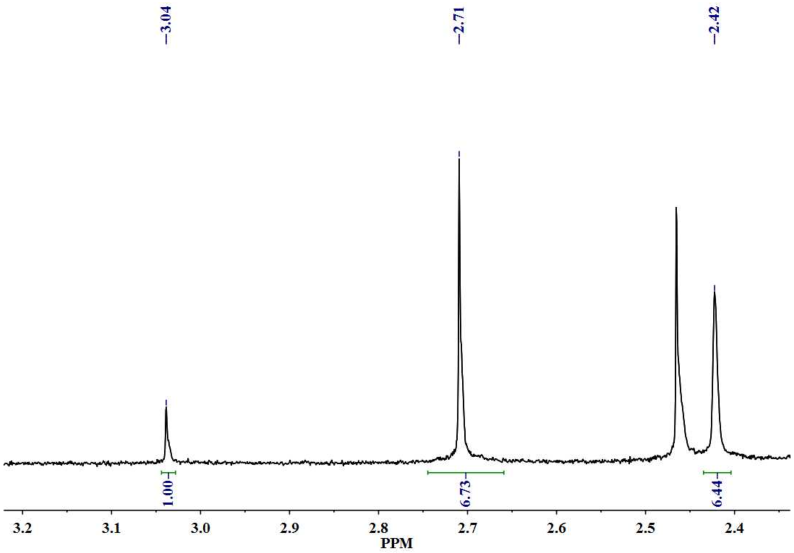
Chiralcel OD-H column: 90/10 hexane/i-PrOH; flow rate 1.0 mL/min; t_R = 11.40 min; t_R = 13.20 min;





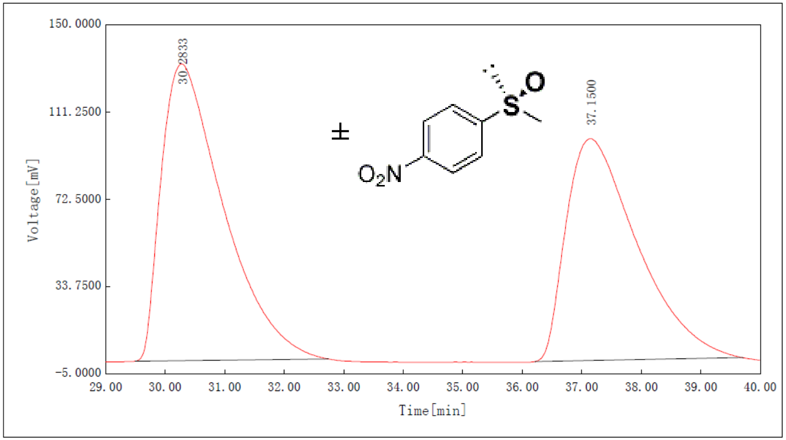
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11.4000	11770.3305	BB	69.4964
2	13.2000	5166.2758	BB	30.5036
The Total		16936.6063		

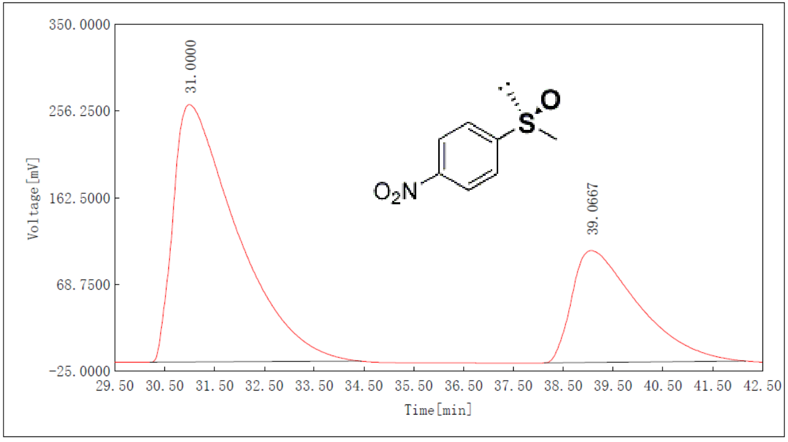
Sulfone/Sulfoxide = 1:6.73



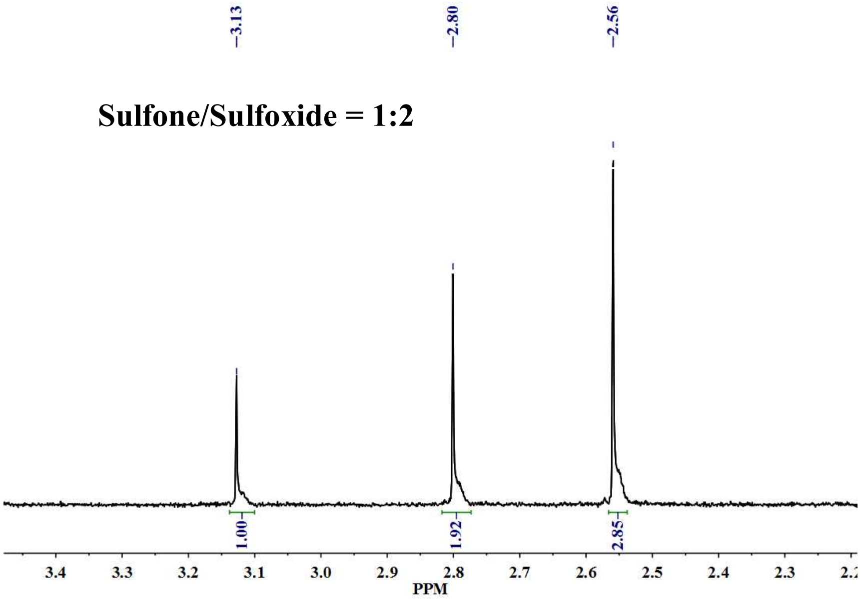
(*R*)-Methyl

(*R*)-**14-nitrophenyl sulfoxide oxidized by 30% H_2O_2 (catalyzed by 8 mol %** (*R*)-**1)**
Chiralcel OJ-H column: 80/20 hexane/i-PrOH; flow rate 1.0 mL/min; t_R = 31.00 min; t_R = 39.06 min;





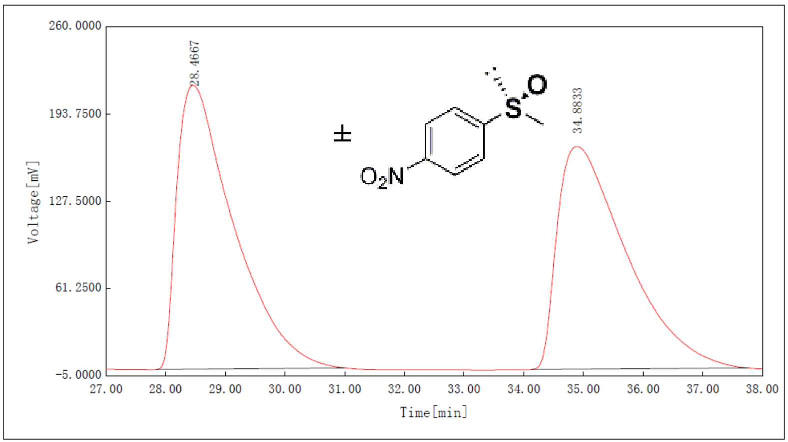
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	31.0000	24780.8786	BB	68.8408
2	39.0667	11216.4759	BB	31.1592
The Total		35997.3545		

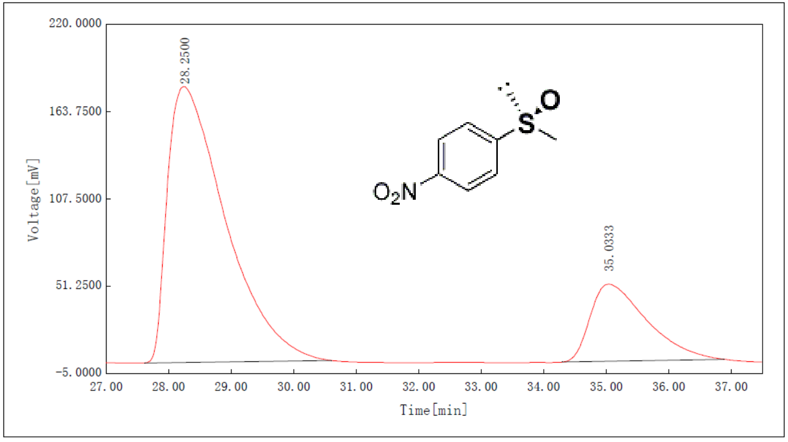


(*R*)-Methyl 4-nitrophenyl sulfoxide oxidized by 30% H_2O_2-Urea (catalyzed by 8 mol % (*R*)-1).

Chiralcel OJ-H column: 80/20 hexane/i-PrOH; flow rate 1.0 mL/min; t_R = 28.25 min; t_R = 35.03 min;

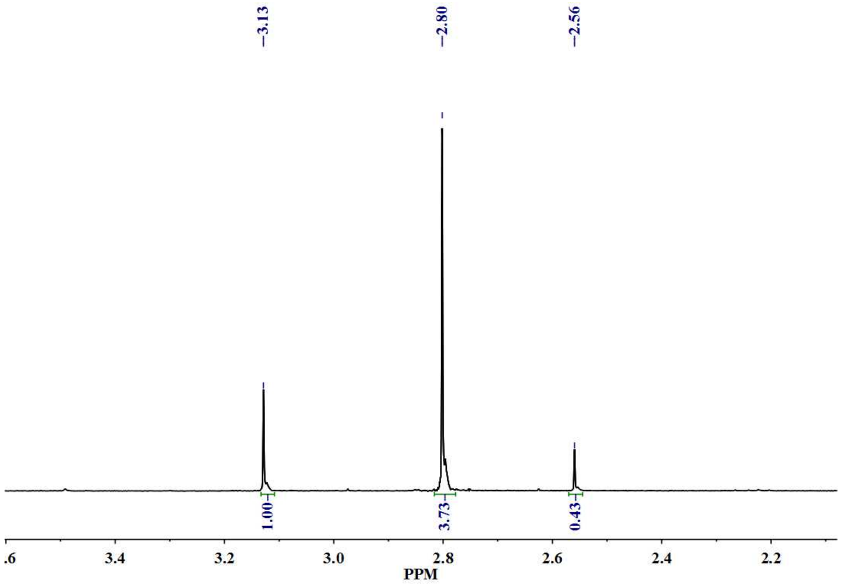
±





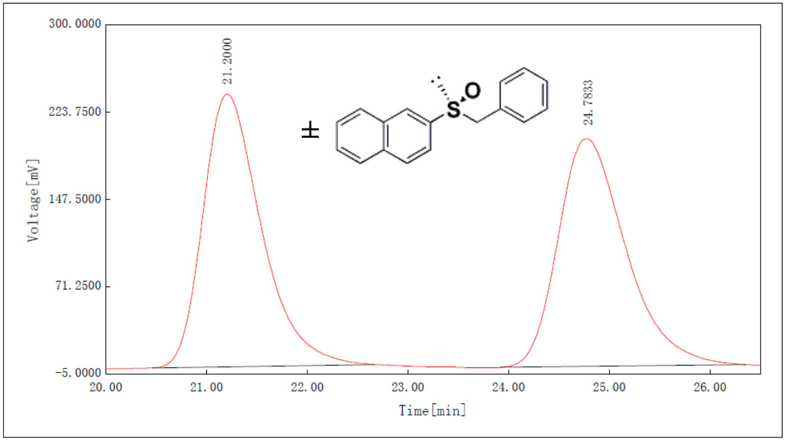
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	28.2500	11496.7565	BB	78.6729
2	35.0333	3116.6112	BB	21.3271
The Total		14613.3678		

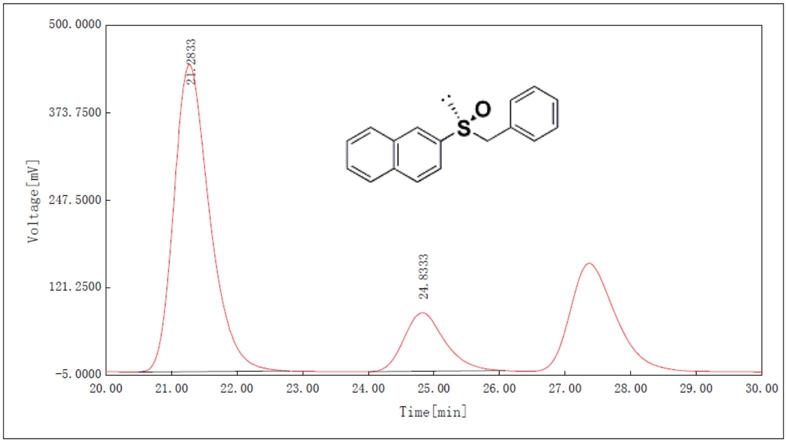
Sulfone/Sulfoxide = 1:4



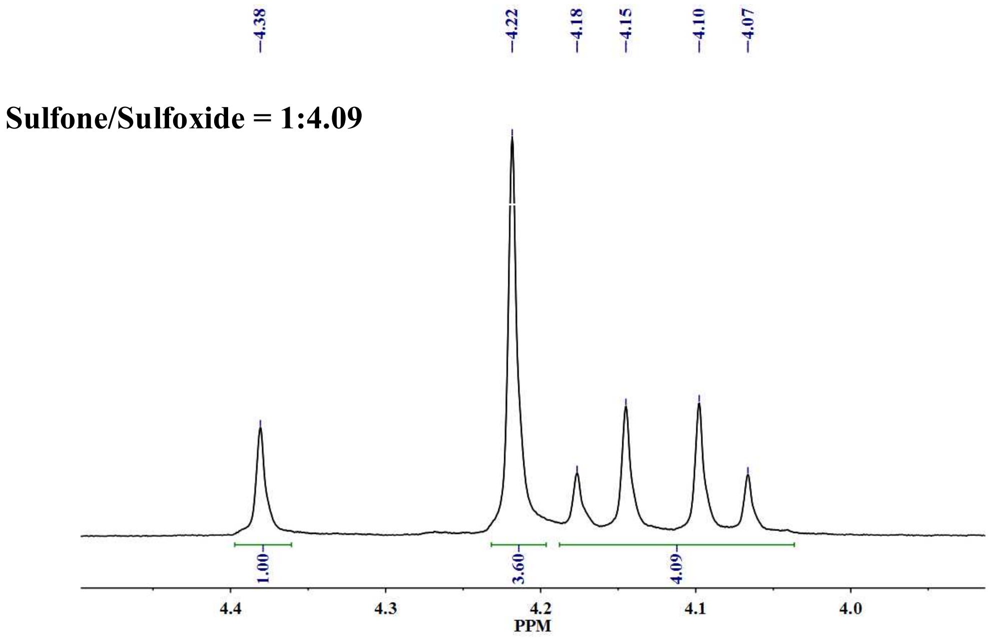
(*R*)-2-naphthyl Benzyl sulfoxide (catalyzed by 8 mol % (*R*)-1)

Chiralcel AD-H column: 85/15 hexane/i-PrOH; flow rate 1.2 mL/min; t_R = 21.28 min; t_R = 24.83 min;

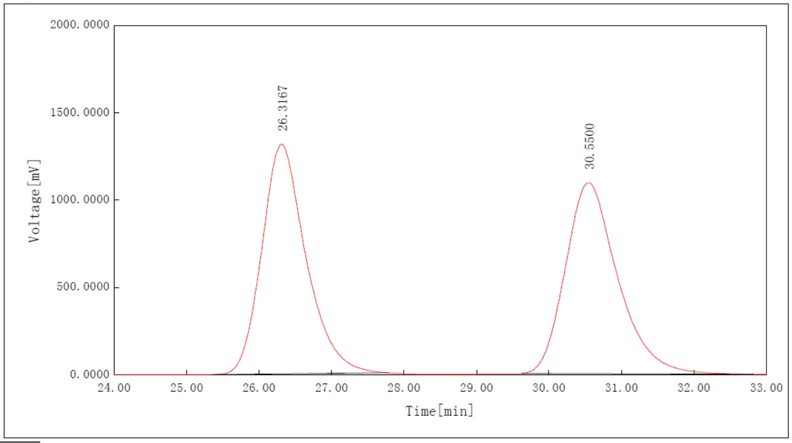


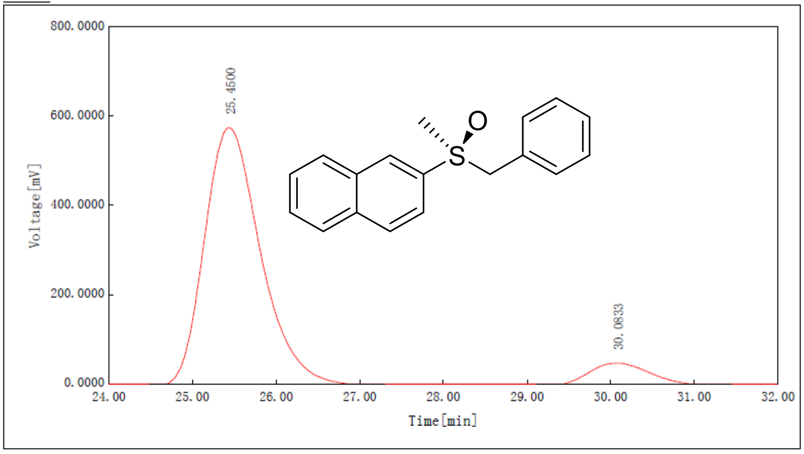


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	21.2833	16808.5943	BB	82.1663
2	24.8333	3648.2022	BB	17.8337
The Total		20456.7966		

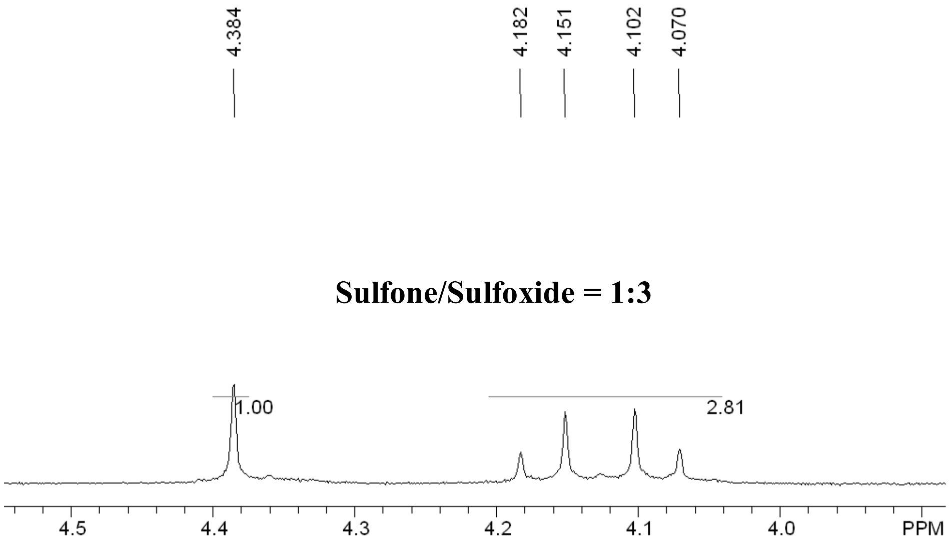


(*R*)- 2-Naphthyl benzyl sulfoxide (catalyzed by 8 mol% (*R*)-1)
Chiralcel AD-H column: 85/15 hexane/i-PrOH; flow rate 1.0 mL/min; t_R = 21.28 min; t_R = 24.83 min;





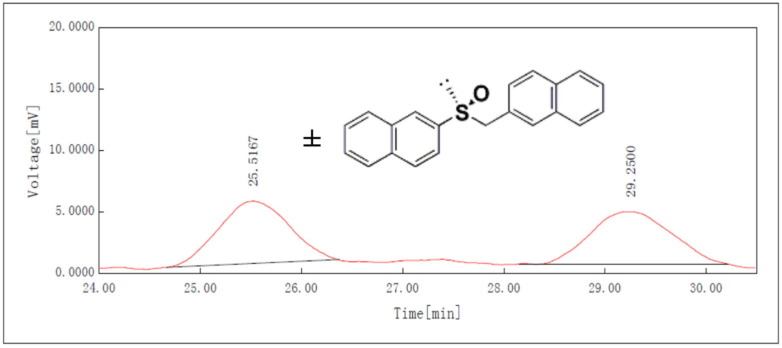
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	25.4500	27282.0755	BB	90.4708
2	30.0833	2873.5907	BB	8.5292
The Total		3015.6662		

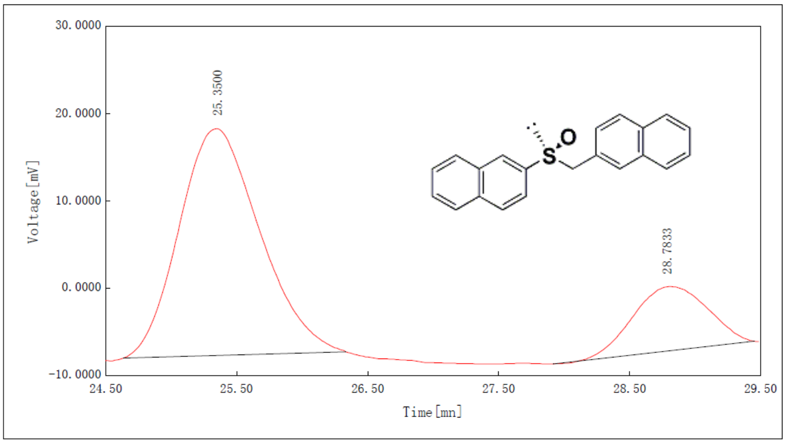


Sulfone/Sulfoxide = 1:3

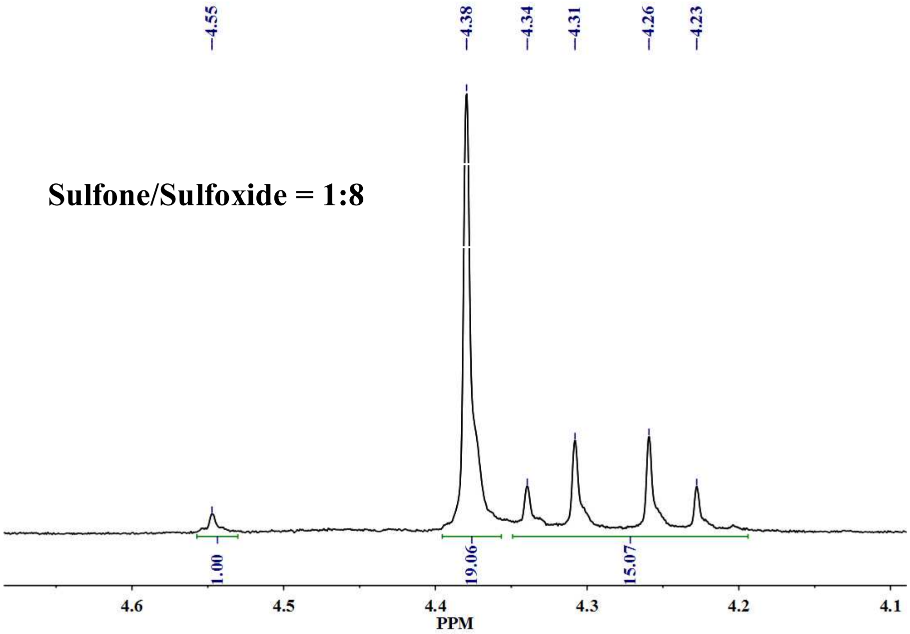
(*R*)- Naphthyl 2-methylenenaphthyl sulfoxide (catalyzed by 8 mol % (*R*)-1)

Chiralcel AD-H column: 85/15 hexane/i-PrOH; flow rate 1.0 mL/min; t_R = 25.35 min; t_R = 28.78 min;





Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	25.3500	1110.6274	BB	79.2573
2	28.7833	1290.6662	BB	20.7427
The Total		1401.2936		



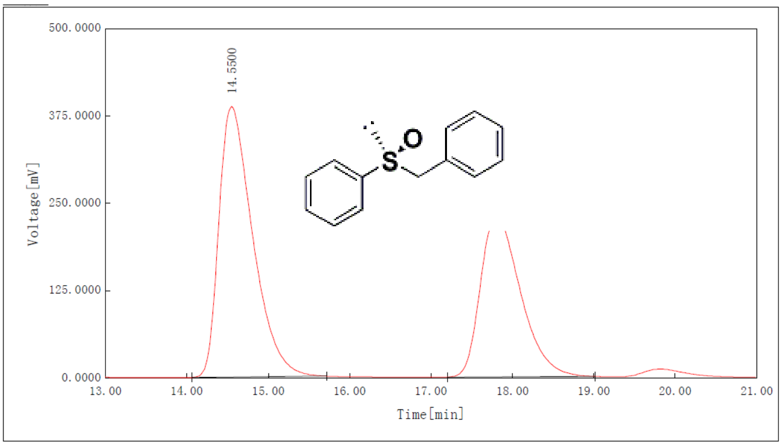
20.2 Oxidation of $PhSCH_2Ph$ by 1 mol% and 0.1 mol % of MOF 1

The catalytic reaction with low catalyst loading was carried out in the same way as described above (72 h) and the results were summarized as following:

Table S3 Comparison of the catalytic performance at different catalyst loading

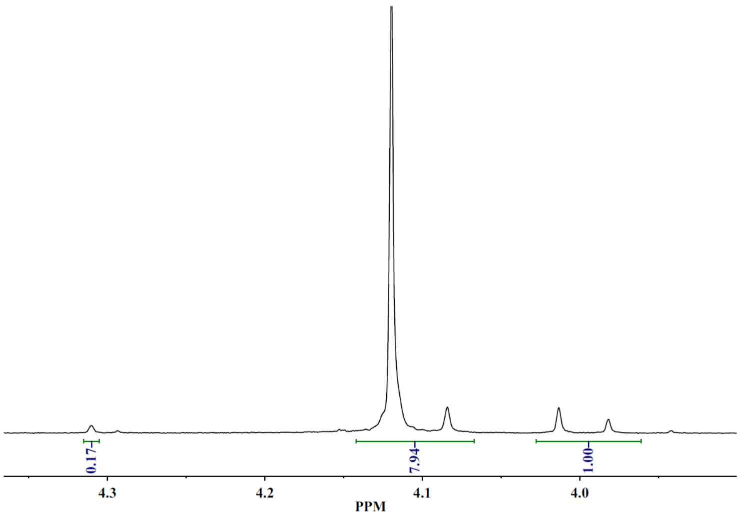
Catalyst loading (%) of **1**	Conv. (%)	ee (%)	Select. (%)
1	24	17	92
0.1	18	7	94

1% catalyst loading

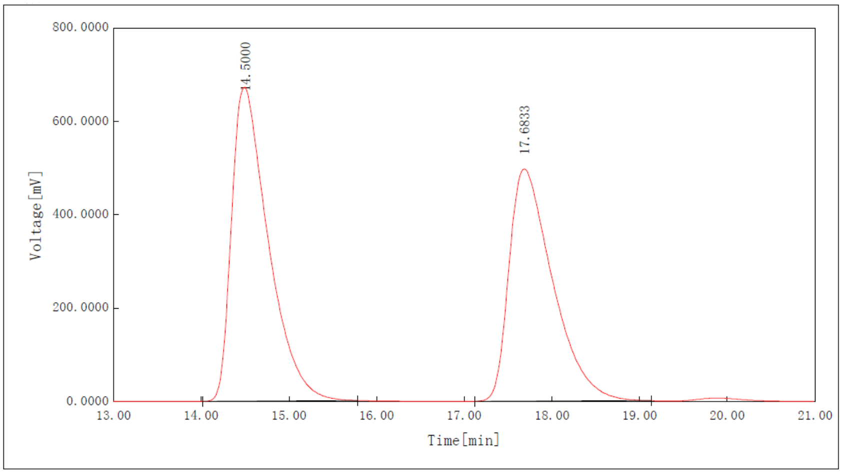


分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.5500	11180.4508	BB	99.0000	58.6475
2	17.8167	7883.3611	BB	109.0000	41.3525
和		19063.8119			

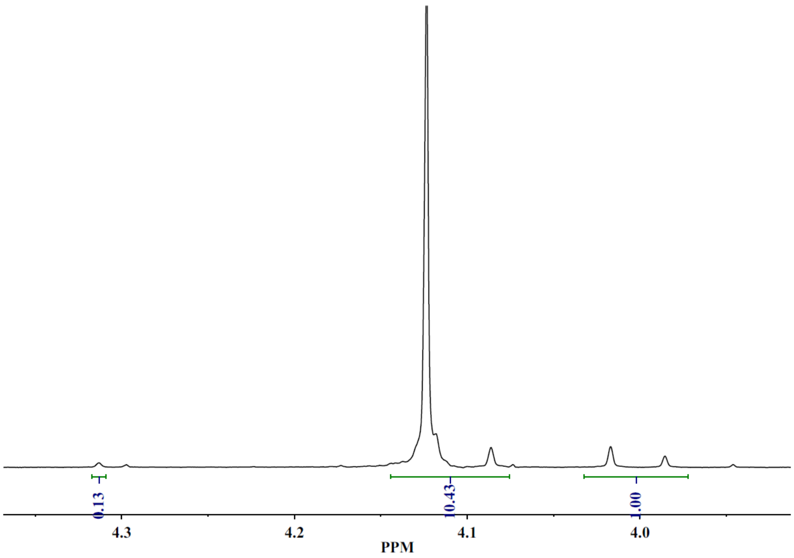


0.1% catalyst loading



分析结果

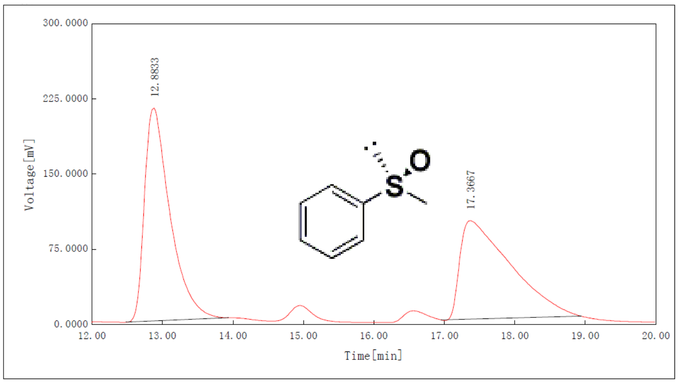
编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.5000	19572.3311	BB	106.0000	53.2596
2	17.6833	17176.5893	BB	121.0000	46.7404
和		36748.9204			



20.3 The oxidation catalyzed by 24 mol% TiL.

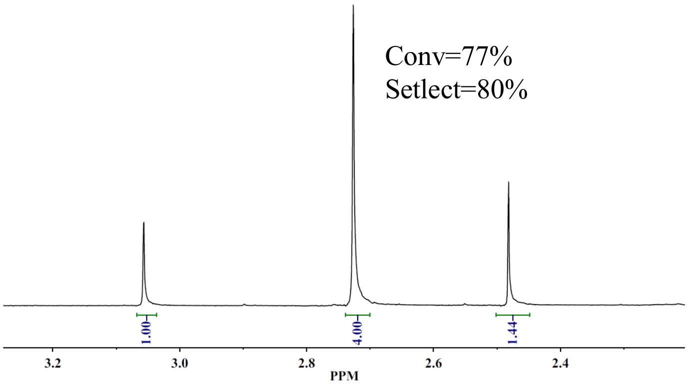
The reactions were carried out in the same way as described above and stopped at the conversions close to those of corresponding heterogeneous reactions catalyzed by **1**.

(*R*)-Methyl phenyl sulfoxide (catalyzed by 24 mol% TiL, 24h)



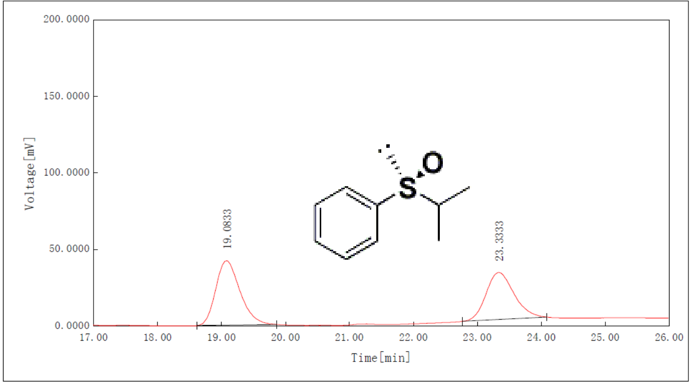
分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	12.8833	5372.1721	BB	87.0000	52.2977
2	17.3667	4900.1167	FF	119.0000	47.7023
和		10272.2888			



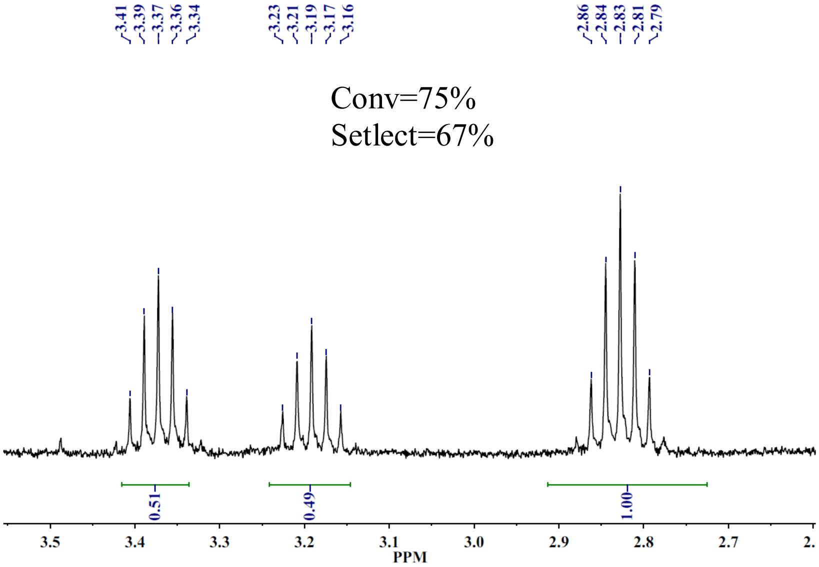
Conv=77%
Setlect=80%

(*R*)-Isopropyl phenyl sulfoxide (catalyzed by 24 mol%TiL, 24h)



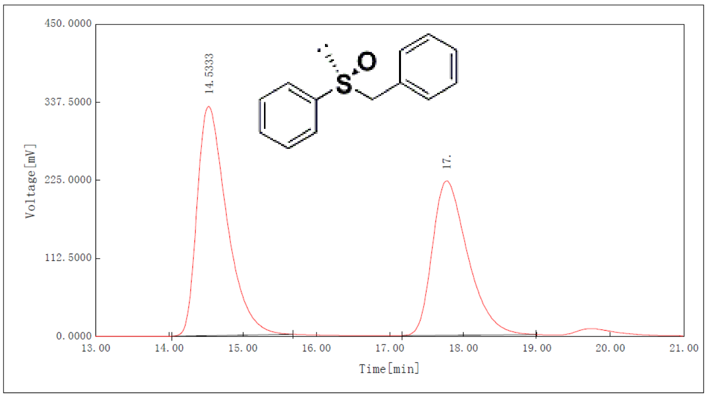
分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	19.0833	1108.2551	BB	75.0000	54.2621
2	23.3333	934.1568	BB	79.0000	45.7379
和		2042.4119			



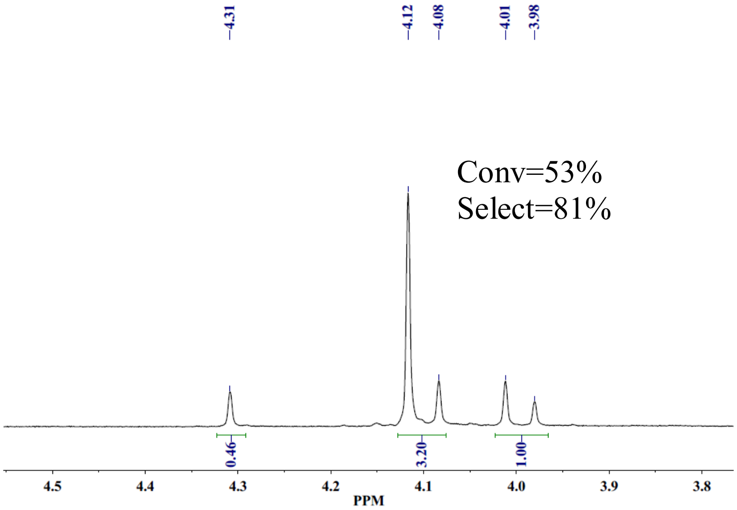
Conv=75%
Setlect=67%

(*R*)-Benzyl phenyl sulfoxide (catalyzed by 24 mol % TiL, 28h)



分析结果

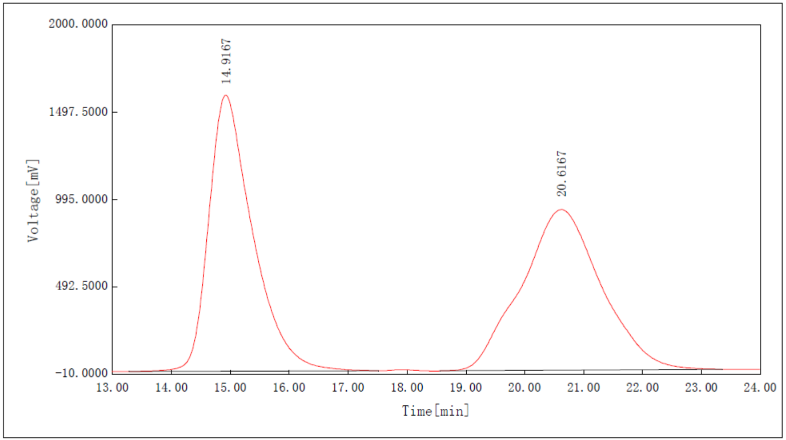
编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.5333	9320.1887	BB	99.0000	55.6064
2	17.7667	7440.8149	BB	109.0000	44.3936
和		16761.0035			

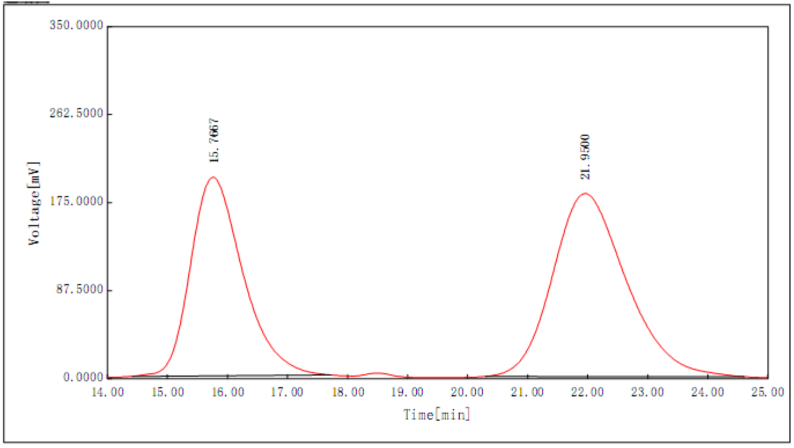


Conv=53%
Select=81%

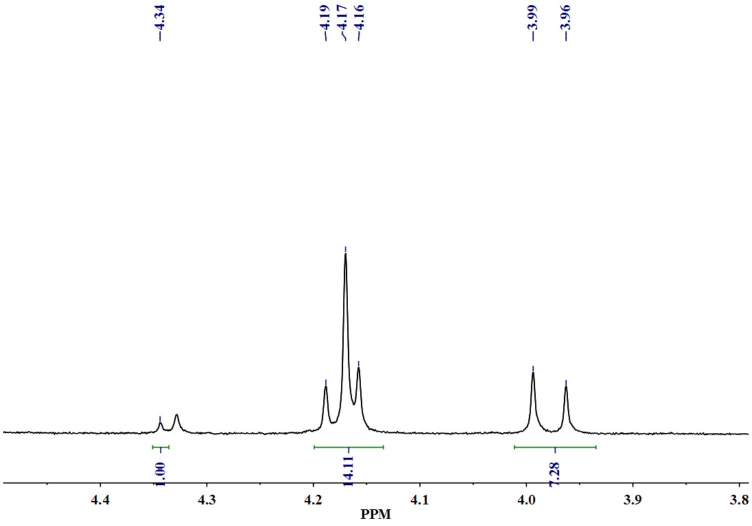
(*R*)-Naphthyl dendritic sulfoxide (catalyzed by 24% mol TiL, 72h)

Chiralcel OD-H column: 90/10 hexane/i-PrOH; flow rate 0.5 mL/min; t_R = 15.76 min; t_R = 21.95 min;





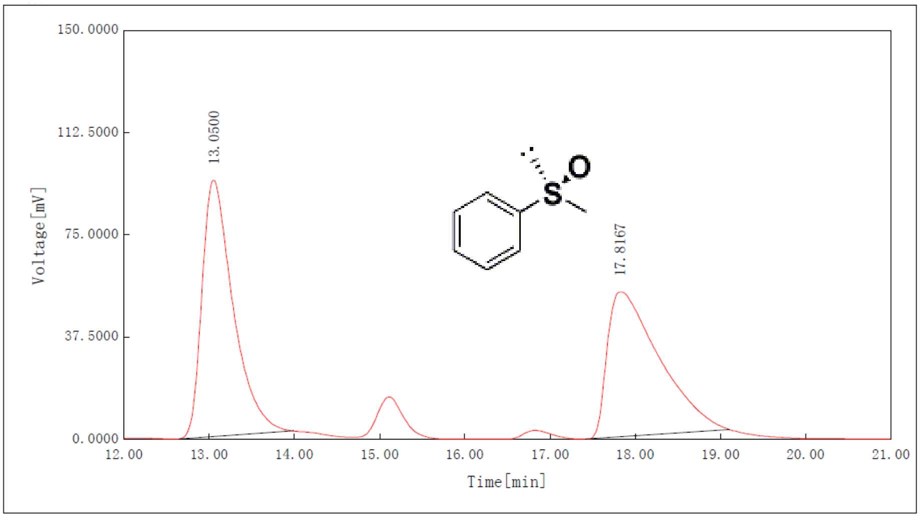
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	15.7667	11948.5556	BB	43.5221
2	21.9500	15505.4555	BB	56.4779
The Total		27454.0114		



20.4 Oxidation of sulfides catalyzed by 8 mol% TiL.

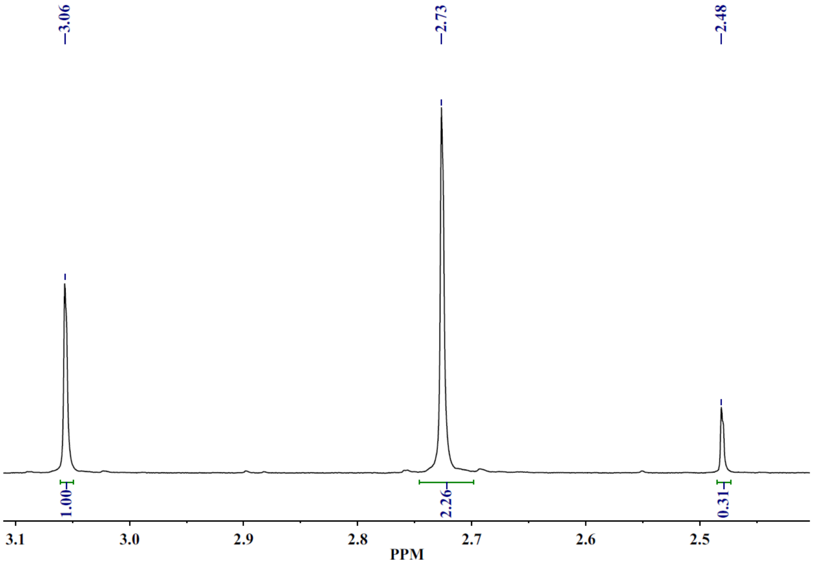
Table S4 Summary of the catalytic results with 8 mol% TiL

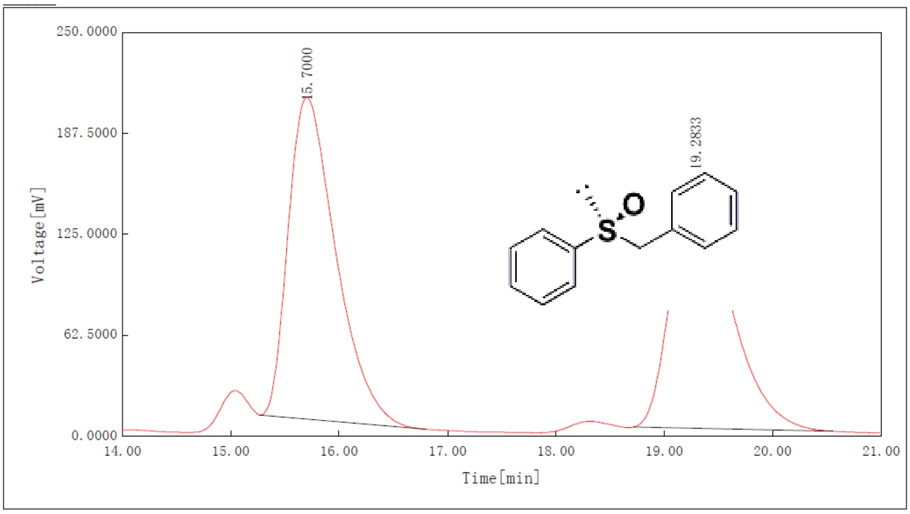
	Conv. (%)	ee (%)	Select. (%)
Methyl phenyl sulfide	91	3	69
Benzyl phenyl sulfide	71	3	73



分析结果

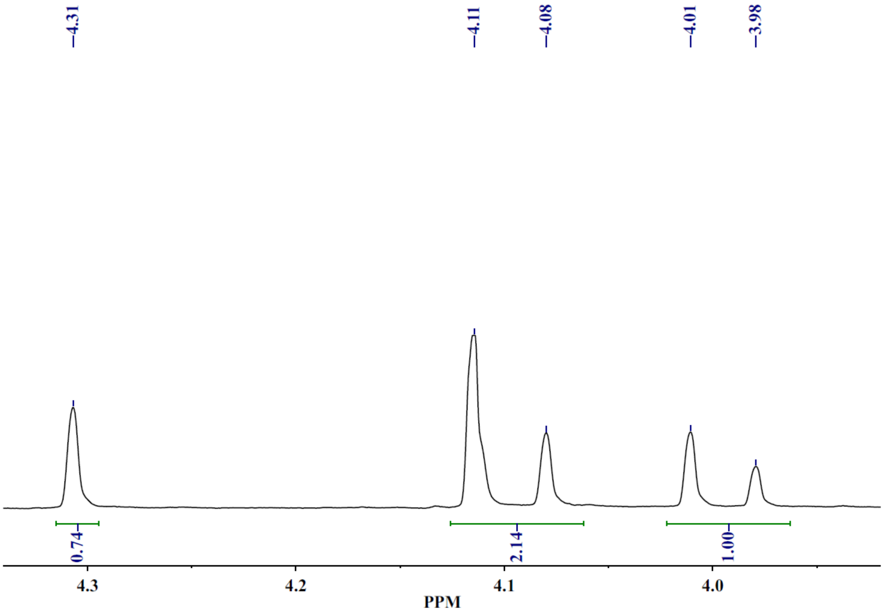
编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	13. 0500	2392. 1845	BB	80. 0000	51. 4686
2	17. 8167	2255. 6634	FF	101. 0000	48. 5314
和		4647. 8479			





分析结果

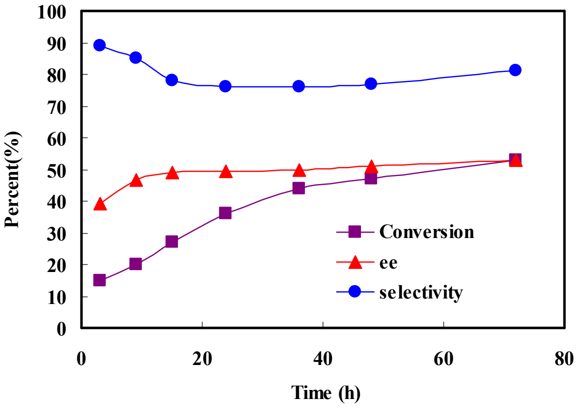
编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	15.7000	6093.4088	BB	91.0000	51.6754
2	19.2833	5698.2960	BB	110.0000	48.3246
和		11791.7047			



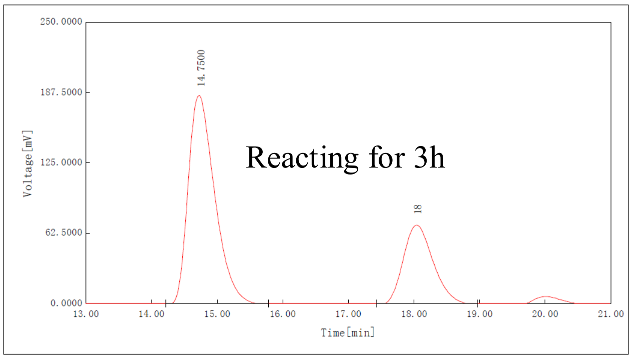
21. The result of recycling study of **1** in the oxidation benzyl phenyl sulfide with 1.2 equiv H_2O_2. (All reactions were run for 72 h at r.t unless noted otherwise).

21.1. Study of conversion, selectivity and enantiomeric excess *vs* time in the catalytic oxidation of $PhSCH_2Ph$ by MOF **1** in the 1st cycle.

Figure S17 Sulfide conversion, selectivity of sulfoxide and enantiomeric excess vs time for the 1st cycle.

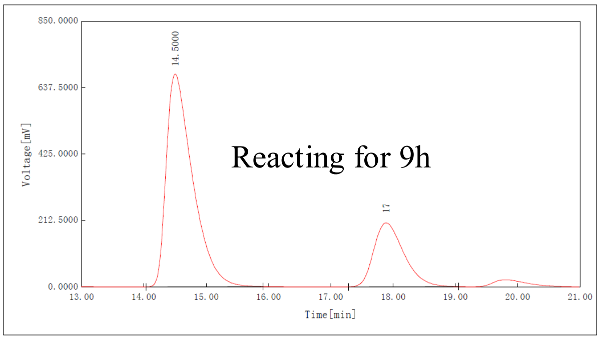


HPLC data



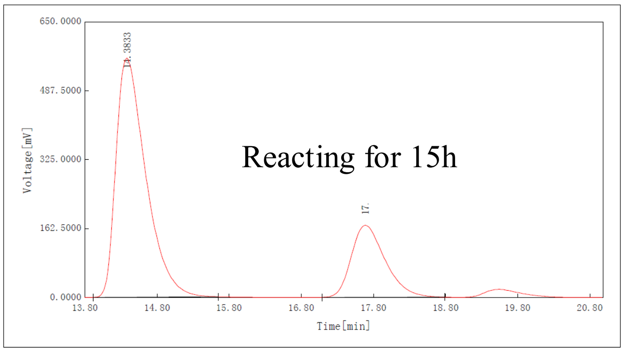
<u>分析结果</u>

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.7500	5313.4376	BB	94.0000	69.6176
2	18.0500	2318.8802	BB	92.0000	30.3824
和		7632.3178			



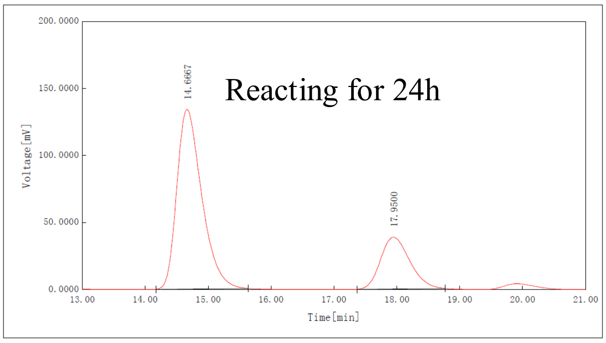
<u>分析结果</u>

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.5000	20012.8722	BB	113.0000	74.4885
2	17.8833	6854.1729	BB	106.0000	25.5115
和		26867.0451			



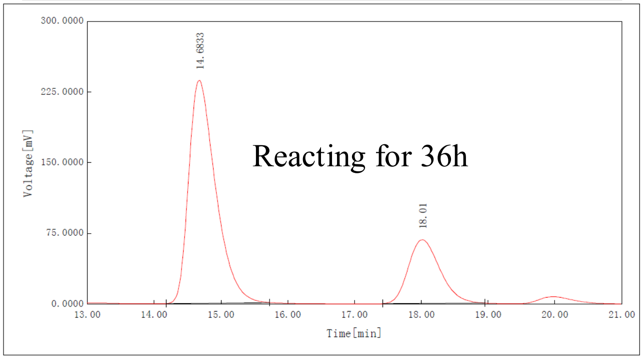
分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.3833	16175.2127	BB	104.0000	74.5957
2	17.6833	5508.6360	BB	102.0000	25.4043
和		21683.8487			



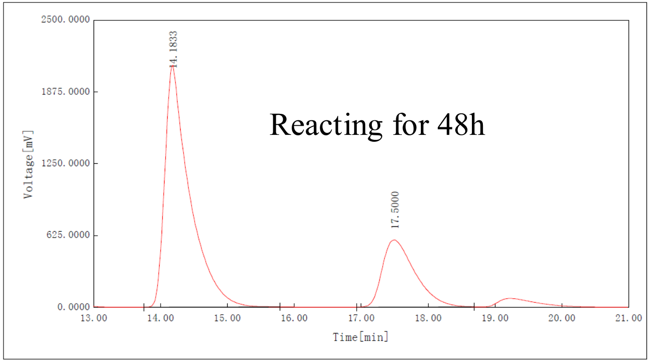
分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.6667	3694.1170	BB	88.0000	74.7843
2	17.9500	1245.5797	BB	84.0000	25.2157
和		4939.6967			



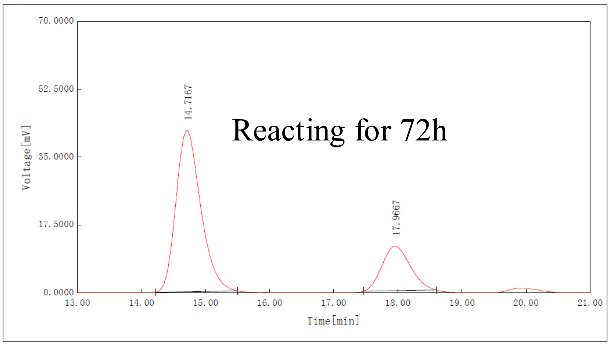
分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.6833	6642.1278	BB	93.0000	74.9710
2	18.0167	2217.4734	BB	92.0000	25.0290
和		8859.6012			



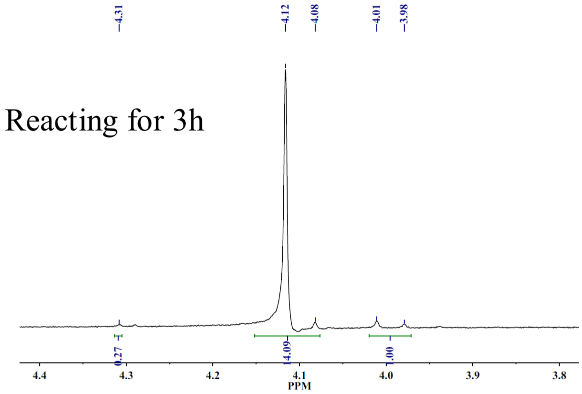
分析结果

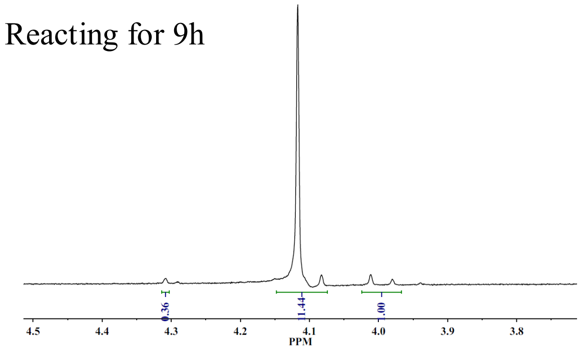
编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.1833	54177.0133	BB	122.0000	73.3318
2	17.5000	19702.3267	BB	105.0000	26.6682
和		73879.3399			

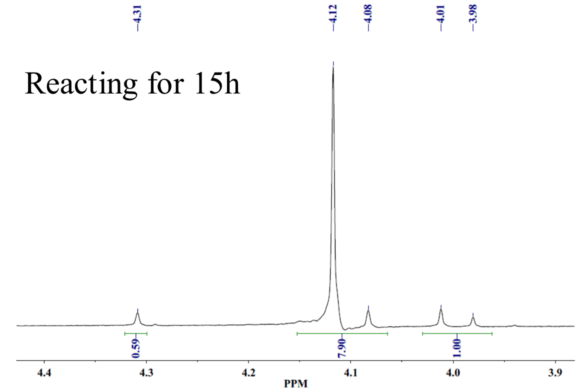


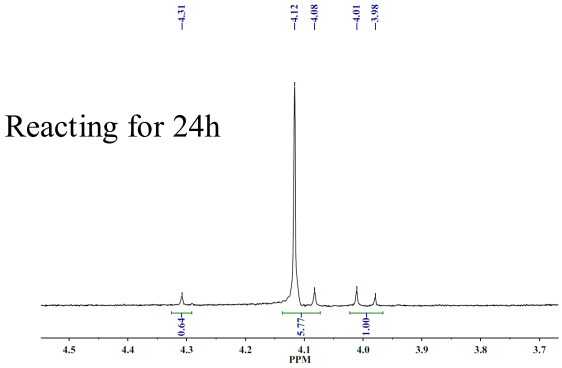
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	14.7167	1120.4145	BB	76.1088
2	17.9667	351.7086	BB	23.8912
The Total		8379.1334		

^{1}H NMR data

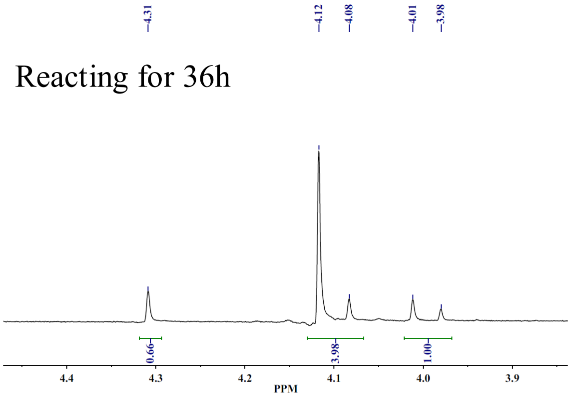




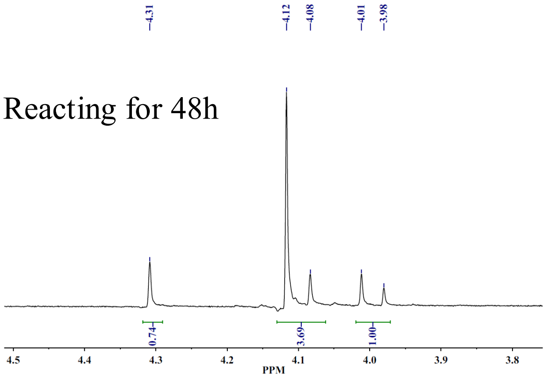




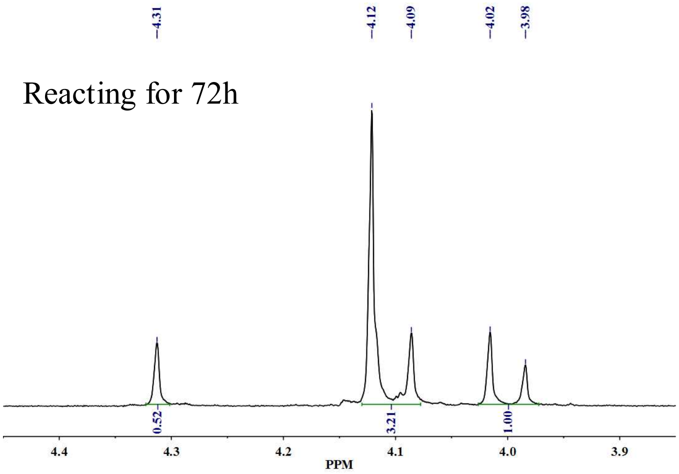
Reacting for 24h



Reacting for 36h

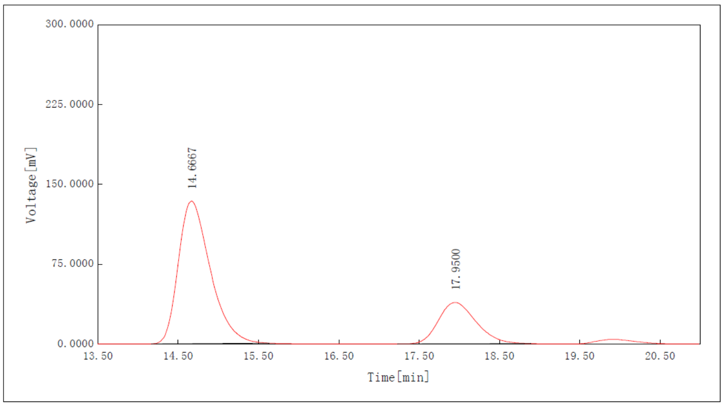


Reacting for 48h

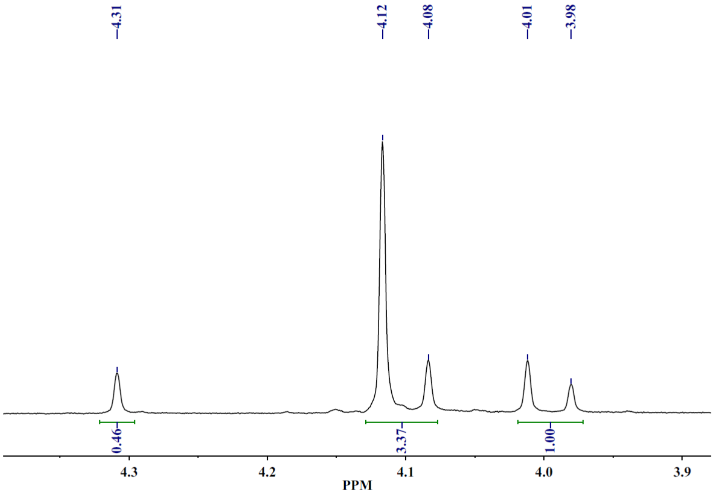


Reacting for 72h

21.2. The result of the 2nd cycle

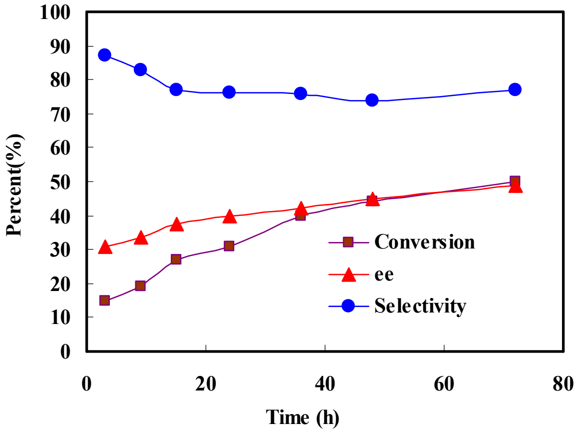


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	14.6667	3704.1061	BB	74.8019
2	17.9500	1247.7801	BB	25.1981
The Total		4951.8861		

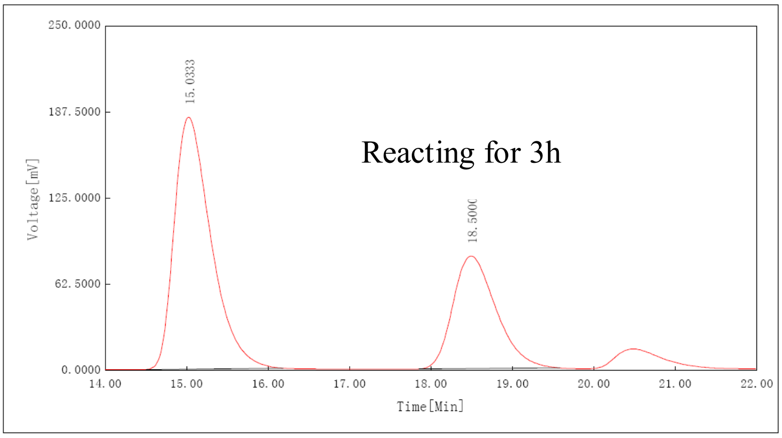


21.3 Kinetic study of conversion, selectivity and enantiomeric excess *vs* time in the catalytic oxidation of $PhSCH_2Ph$ by MOF **1** in the 3rd cycle.

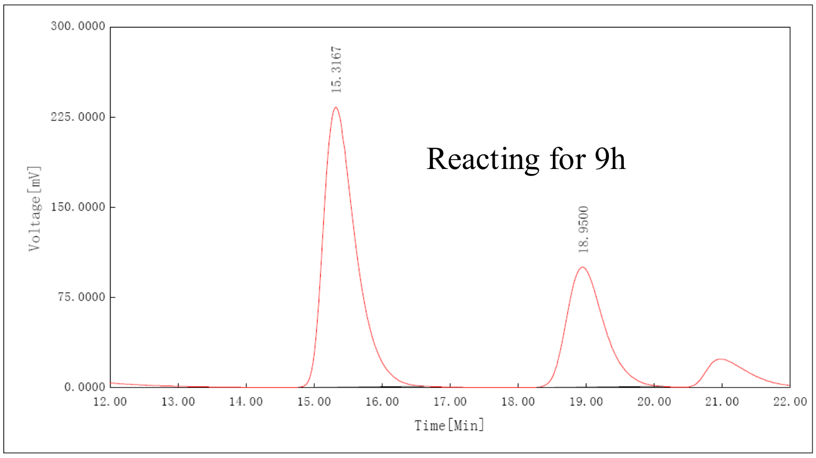
Figure S18. Plots of sulfide conversion, selectivity of sulfoxide and enantiomeric excess vs time for the 3rd cycle .



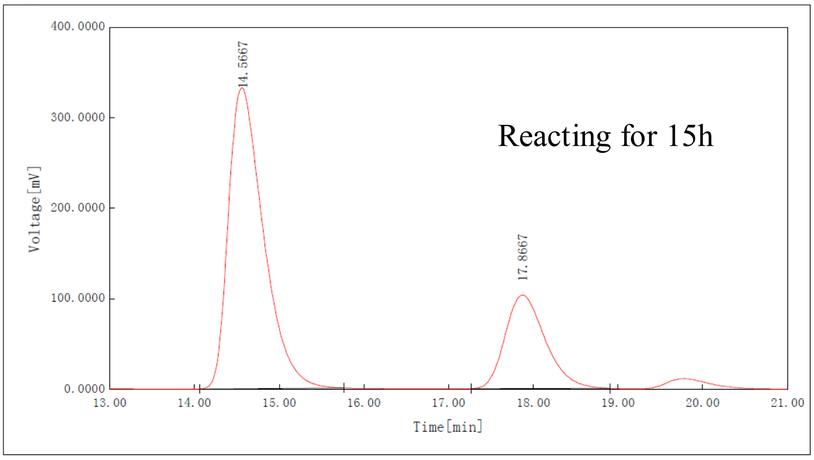
HPLC data



Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	15.0333	5759.8054	BB	65.6434
2	18.5000	2998.8751	BB	34.3566
The Total		8728.6806		

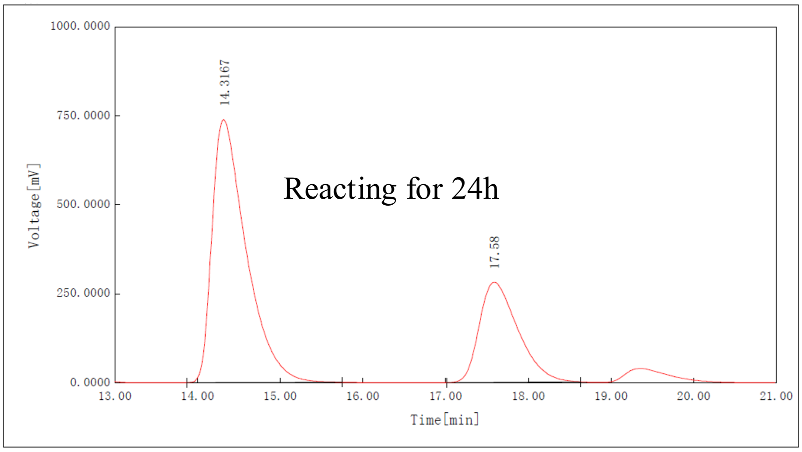


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	15.3167	7697.3323	BB	66.8660
2	18.9500	3814.2539	BB	33.1340
The Total		11511.5862		



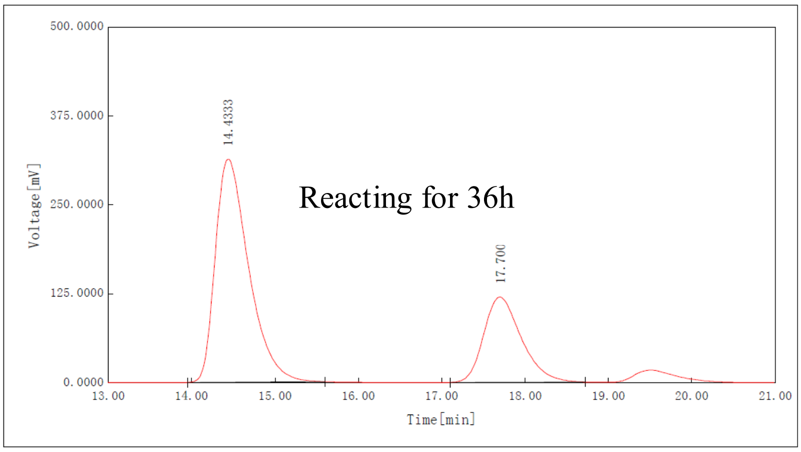
分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.5667	9553.1026	BB	102.0000	73.8023
2	17.8667	3391.0697	BB	98.0000	26.1977
和		12944.1723			



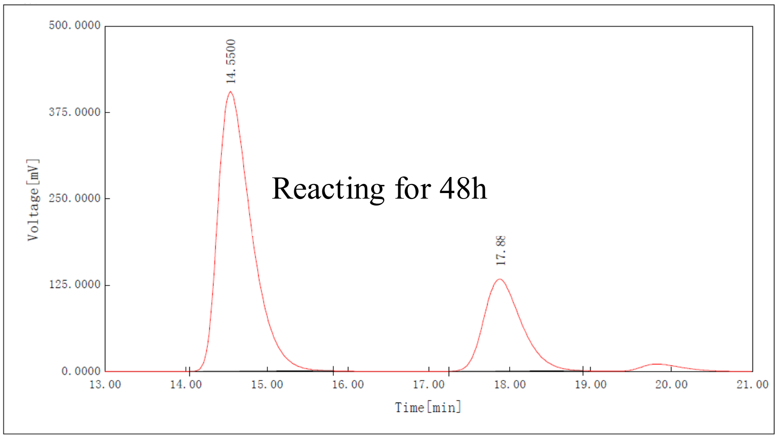
分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.3167	21189.3367	BB	113.0000	69.8947
2	17.5833	9126.7545	BB	97.0000	30.1053
和		30316.0912			



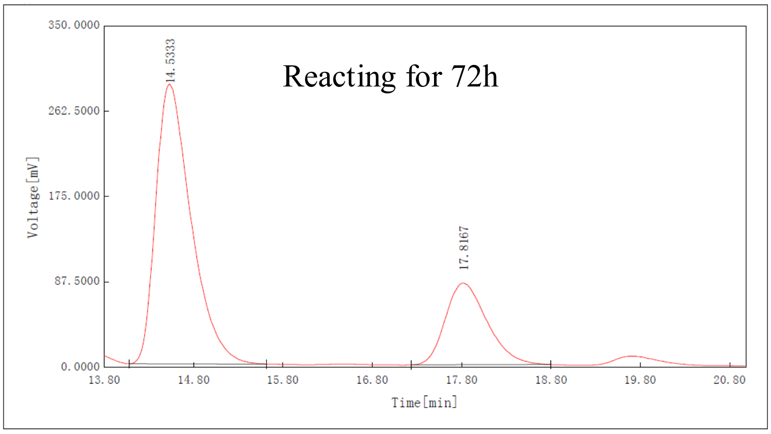
分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.4333	8731.2078	BB	99.0000	69.9934
2	17.7000	3743.1145	BB	97.0000	30.0066
和		12474.3223			



分析结果

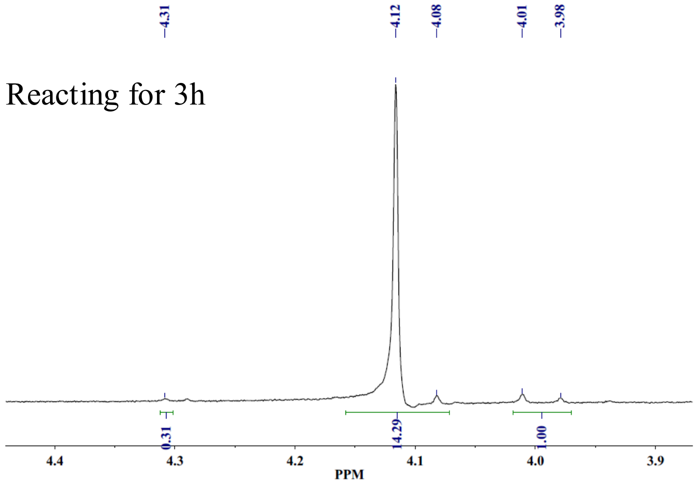
编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.5500	11659.5205	BB	106.0000	72.9569
2	17.8833	4321.8624	BB	99.0000	27.0431
和		15981.3828			



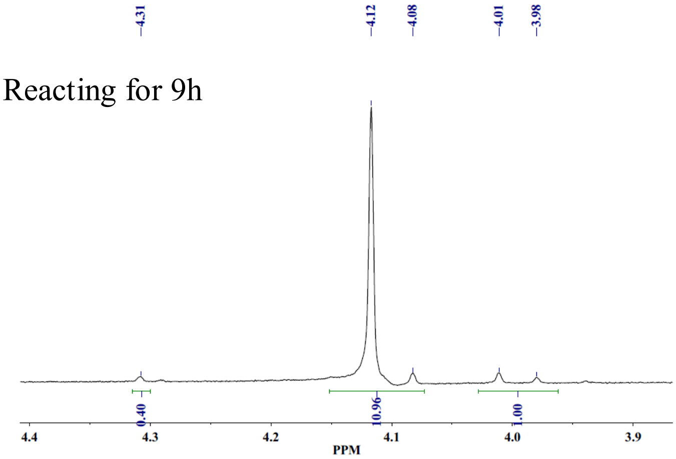
分析结果

编号	RT[分钟]	面积[mAbs*s]	类型	峰宽[秒]	面积%
1	14.5333	7893.7467	BB	92.0000	74.3927
2	17.8167	2717.1711	BB	94.0000	25.6073
和		10610.9178			

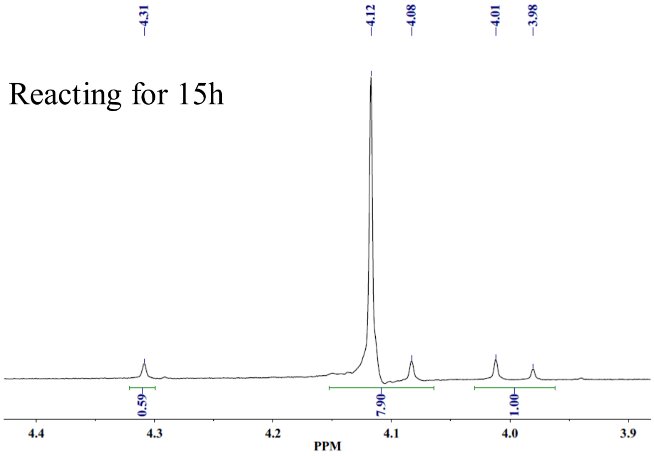
^{1}H NMR data



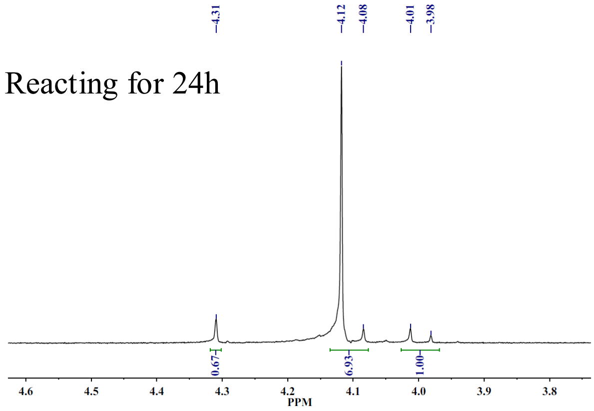
Reacting for 3h

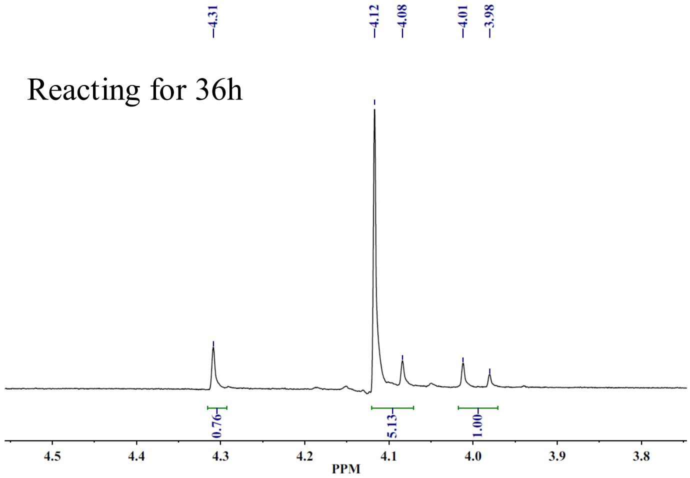


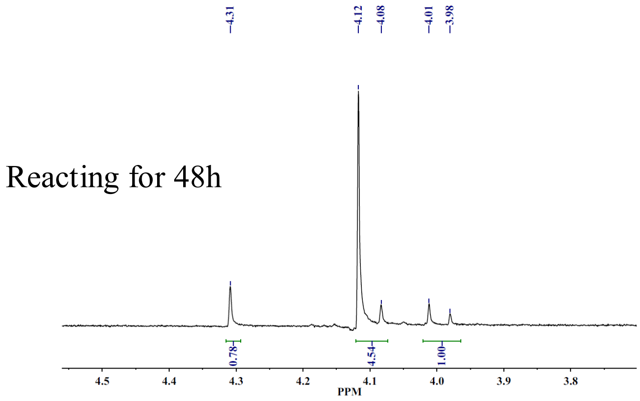
Reacting for 9h

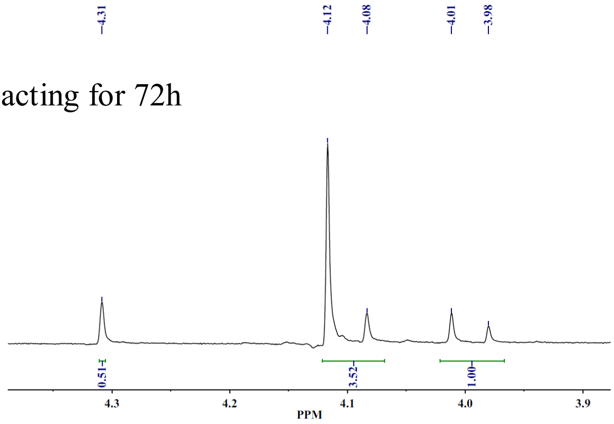


Reacting for 15h


Reacting for 24h


Reacting for 36h


Reacting for 48h


Reacting for 72h