Supporting Information for

Engineering Chiral Fe(salen)-Based Metal Organic Frameworks for Asymmetric Sulfide Oxidation

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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 a 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 (ESI-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase. An iCAP6300 inductively coupled plasma optical emission spectrometer (ICP-OES) was used to measure Fe, Zn 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. The X-ray photoelectron spectroscopy (XPS) measurement was carried out with an AXIS Ultra DLD electron spectrometer.

X-ray Crystallography. Single-crystal XRD data for the compounds **1** and **2** were collected on a Bruker Apex II CCD-based X-ray diffractometer with Mo- or /Cu-$K\alpha$ radiation (λ = 0.71073 or 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 F^2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). Due to the relatively weak diffraction, only parts of the guest molecules could be found in difference Fourier maps and all the phenyl rings are constrained to ideal six-membered rings. Contributions to scattering due to these highly disordered solvent molecules were removed using the *SQUEEZE* routine of *PLATON*; the structure was then refined again using the data generate. 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. Synthesis of the ligands and MOFs

The chiral ligands $H_2\mathbf{L_1}$ and $H_2\mathbf{L_2}$ were synthesized according to the published procedures (*J. Am. Chem. Soc*. **2008**, *130*, 4582; *CrystEngComm*. **2010**, *12*, 2424).

2.1 Synthesis of Fe$\mathbf{L_1}$(OAc)

A solution of $Fe(OAc)_2 \cdot 4H_2O$(246mg, 1mmol) in anhydrous MeOH (5mL) was added dropwise to $H_2\mathbf{L_1}$ (588 mg, 1 mmol) in anhydrous MeOH (50 mL) at 60 ºC. The reaction mixture immediately turned red and stirred at 60 ºC for 6 h, after which the solvent was evaporated under vacuum. The red powder was collected, washed with Et_2O, and then dried under reduced pressure to obtain pure Fe$\mathbf{L_1}$(OAc) (87.7%). ESI-MS m/z: 642.25 (Calcd m/z 642.27). Elemental analysis for Fe$\mathbf{L_1}$(OAc): Anal (%). Calcd for $C_{40}H_{45}FeN_4O_4$: C, 68.47; H, 6.46; N, 7.98. Found: C, 67.73; H, 6.39; N, 7.90. IR (KBr pellet, ν/cm^{-1}): 3431 (s), 2941 (s), 2864 (m), 1618 (s), 1592 (s), 1553 (m), 1510 (m), 1438 (s), 1386 (m), 1350 (m), 1298 (w), 1277 (m), 1240 (m), 1171 (m), 1111 (s), 1026 (w), 896 (w), 820 (s), 776 (w), 621 (w), 585 (w), 567 (w), 551 (w), 496 (w), 484 (w).

2.2 Synthesis of Fe$\mathbf{L_2}$(OAc)

A solution of $Fe(OAc)_2 \cdot 4H_2O$(246mg, 1mmol) in anhydrous MeOH (5mL) was added dropwise to $H_2\mathbf{L_2}$ (588 mg, 1 mmol) in anhydrous MeOH (50 mL) at 60 ºC. The reaction mixture immediately turned red and stirred at 60 ºC for 6 h, after which the solvent was evaporated under vacuum. The red powder was collected, washed with Et_2O, and then dried under reduced pressure to obtain pure Fe$\mathbf{L_2}$(OAc) (83.2%). ESI-MS m/z: 642.19 (Calcd m/z 642.27). Elemental analysis for Fe$\mathbf{L_2}$(OAc): Anal (%). Calcd for $C_{40}H_{45}FeN_4O_4$: C, 68.47; H, 6.46; N, 7.98. Found: C, 68.01; H, 6.41; N, 7.87. IR (KBr pellet, ν/cm^{-1}): 3416 (s), 2943 (s), 2864 (m), 1615 (s), 1543 (s), 1435 (m), 1397 (m), 1387 (m), 1349 (w), 1316 (m), 1273 (s), 1170 (m), 1118 (s), 1028 (m), 895 (w), 817 (m), 784 (w), 711 (w), 656 (w), 619 (w), 588 (w), 569 (w), 497 (w).

2.3 Synthesis of 1.

A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (1.76 mg, 0.008 mmol), Fe$\mathbf{L_1}$(OAc) (5.46 mg, 0.008mmol), biphenyl-4,4’-dicarboxylic acid (H_2BPDC, 1.936 mg, 0.008 mmol), DMA (1 mL) and MeOH (0.1 ml) in a capped vial was heated at 100 °C for 10 hours . Red block-like crystals of **1** were filtered, washed with DMA (N,N-Dimethylacetamide) and MeOH, respectively, and dried at room temperature. Yield: 4.63mg (90.1%). Elemental Analysis for **1**/$[Zn_2(Fe\mathbf{L_1})_2O(BPDC)_{1.5}] \cdot 4DMA \cdot 6H_2O$: Anal (%). Calcd for $C_{113}H_{145}Fe_2N_{12}O_{22}Zn_2$: C, 59.90; H, 6.45; N, 7.42. Found: C, 60.33; H, 6.40; N, 7.38. FTIR (KBr, cm^{-1}): 3423 (s), 2936 (s), 2862 (m), 1597 (s), 1551 (s), 1511 (m), 1435 (s), 1384 (s), 1350 (s), 1322 (s), 1301 (m), 1278 (m), 1262 (m), 1225 (m), 1195 (w), 1170 (m), 1085 (w), 1071 (w), 1024 (w), 959 (w), 897 (w), 856(w), 833 (w), 819 (w), 789 (w), 771 (s), 701 (w), 682 (w), 649 (m), 628 (w), 585 (w), 567 (w), 549 (w), 519 (w), 478 (w).

2.4 Synthesis of 2.

A mixture of $Cd(OAc)_2 \cdot 3H_2O$ (1.8036 mg, 0.008 mmol), Fe$\mathbf{L_2}$(OAc) (5.46mg, 0.008 mmol), H_2BPDC (1.936 mg, 0.008 mmol), DMA (1 mL) and MeOH (1ml) in a capped vial was heated at 80 °C for 16 hours. Red block-like crystals of **2** were filtered, washed with DMA and MeOH, respectively, and dried at room temperature. Yield: 4.35 mg (84.6%). Elemental Analysis for **2**/$[Cd_2(Fe\mathbf{L_2})_2O(BPDC)_2]\cdot 6DMA\cdot 8H_2O$: Anal (%). Calcd for $C_{128}H_{170}Cd_2Fe_2N_{14}O_{27}$: C, 57.51; H, 6.41; N, 7.34. Found: C, 57.40; H, 6.31; N, 7.28. FTIR (KBr, cm^{-1}): 3418 (s), 2939 (s), 2862 (m), 1615 (s), 1580 (s), 1533 (s), 1424 (m), 1386 (s), 1347 (s), 1319 (s), 1274 (s), 1258 (m), 1194 (w), 1167 (m), 1105 (w), 1027 (w), 1002 (w), 974 (w), 897 (w), 856 (m), 813 (m), 773 (m), 704 (m), 680 (w), 655 (m), 586 (w), 567 (w), 549 (w), 478 (w).

3. Experimental procedure for asymmetric sulfide oxidation

3.1 Typical catalytic process

The catalyst (*R*,*R)*-**1** or (*S*,*S*)-**1** (1.5 μmol, 0.015 equiv) and sulfide (0.1 mmol) were combined in CH_2Cl_2 (1 mL) and stirred for 20 min at 25 °C, followed by adding an 2.0 eq oxidant (MesIO, 0.2 mmol, 52.4 mg) in one portion. Stirring was continued at -20°C for indicated time. The ee of resulted sulfoxides was determined by HPLC using Chiralcel OD-H and Chiralcel AD-H columns, and conversion was determined by ^{1}H NMR. The catalyst (*R*,*R*)-**2** or (*S*,*S*)-**2** (1.5 μmol, 0.015 equiv) and catalyst (*R*,*R*)-Fe$\mathbf{L_1}$(OAc) or (*R*,*R*)-Fe$\mathbf{L_2}$(OAc) (3.0 μmol, 0.03 equiv) took the same procedure to catalyze the reaction.

3.2 Kinetic data collection

The catalytic reaction was carried out according to the above procedure, and a proper portion of reaction mixture was taken out at proper time interval and dried under N_2 flow. The ee value was determined by HPLC using Chiralcel OD-H, and conversion was determined by ^{1}H NMR.

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

Identification code	**1**	**2**
Empirical formula	$C_{97}H_{97}Zn_2N_8O_{12}Fe_2$	$C_{104}H_{100}Cd_2N_8O_{13}Fe_2$
Formula weight	1809.27	2006.41
Temperature (K)	123(2) K	123(2) K
Wavelength (Å)	0.71073	1.54178
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2	*F*222
Unit cell dimensions	a =14.400(3) Å b = 37.700(8) Å c = 27.200(5)Å $\alpha = \gamma = 90°$ β =100.00 (3)°	a = 19.2468(5) Å b = 54.9054(13) Å c = 64.1439(16) Å $\alpha = \beta = \gamma = 90°$
Volume (Å^3), Z	14542(5), 4	67784(3), 16
Density (calculated) (mg/m^3)	0.826	0.880
Absorption coefficient (mm^{-1})	0.562	3.629
F(000)	3772	16512
θ range for data collection (º)	0.760 to 24.39	1.609 to 67.893
Limiting indices	$-16\leq h\leq 16$, $-32\leq k\leq 43$, $-30\leq l\leq 30$	$-21\leq h\leq 23$, $-61\leq k\leq 63$, $-64\leq l\leq 74$
Reflections collected	23666	83697
Independent reflections	14901 [R(int) = 0.050]	28626 [R(int) = 0.0401]
Completeness to theta	24.39/82.6 %	67.679/94.4%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	14901/234/803	28626/10/1085
Goodness-of-fit on F^2	1.067	1.064
Final R indices [I>2sigma(I)]	R_1= 0.0721, wR_2= 0.1819	R_1 = 0.0773, wR_2 = 0.2475
R indices (all data)	R_1= 0.0953, wR_2= 0.1945	R_1 = 0.0891, wR_2 = 0.2613
Absolute structure parameter	0.22(2)	0.076(5)
Largest diff. peak and hole (e.Å^{-}	0.528 and -0.289	1.514 and -1.150

5. Table S2. Selected bond lengths [Å] and angles [º] for 1

Zn(1)-O(7)	1.901(8)
Zn(1)-O(10)	1.965(7)
Zn(1)-N(4)	2.017(4)
Zn(1)-N(3)#1	2.03(2)
Zn(1)-O(9)	2.413(7)
Zn(2)-O(12)	1.952(6)
Zn(2)-O(13)	2.037(10)
Zn(2)-N(8)	2.047(4)
Zn(2)-N(7)#2	2.057(11)
Fe(1)-O(3)	1.746(2)
Fe(1)-O(1)	1.944(7)
Fe(1)-O(2)	1.951(7)
Fe(1)-N(2)	2.104(7)
Fe(1)-N(1)	2.131(8)
Fe(2)-O(6)	1.7773(18)
Fe(2)-O(5)	1.874(8)
Fe(2)-O(4)	1.900(7)
Fe(2)-N(6)	2.034(9)
Fe(2)-N(5)	2.072(7)
O(7)-Zn(1)-O(10)	101.8(3)
O(7)-Zn(1)-N(4)	114.8(3)
O(10)-Zn(1)-N(4)	99.6(3)
O(7)-Zn(1)-N(3)#1	105.0(17)
O(10)-Zn(1)-N(3)#1	132(2)
N(4)-Zn(1)-N(3)#1	104.5(15)
O(7)-Zn(1)-O(9)	94.9(3)
O(10)-Zn(1)-O(9)	54.6(3)
N(4)-Zn(1)-O(9)	145.2(3)
N(3)#1-Zn(1)-O(9)	83.5(19)
O(7)-Zn(1)-C(91)	102.6(3)
O(10)-Zn(1)-C(91)	26.4(3)
N(4)-Zn(1)-C(91)	121.3(3)
N(3)#1-Zn(1)-C(91)	108(2)
O(9)-Zn(1)-C(91)	28.5(2)
O(12)-Zn(2)-O(13)	104.2(4)
O(12)-Zn(2)-N(8)	111.0(2)
O(13)-Zn(2)-N(8)	111.1(5)
O(12)-Zn(2)-N(7)#2	120(2)
O(13)-Zn(2)-N(7)#2	104(2)
N(8)-Zn(2)-N(7)#2	106(2)
O(3)-Fe(1)-O(1)	112.9(4)

O(3)-Fe(1)-O(2)	103.5(3)
O(1)-Fe(1)-O(2)	92.2(3)
O(3)-Fe(1)-N(2)	106.6(3)
O(1)-Fe(1)-N(2)	90.0(3)
O(2)-Fe(1)-N(2)	146.3(4)
O(3)-Fe(1)-N(1)	95.2(4)
O(1)-Fe(1)-N(1)	151.1(3)
O(2)-Fe(1)-N(1)	87.2(3)
N(2)-Fe(1)-N(1)	75.3(3)
O(6)-Fe(2)-O(5)	110.9(2)
O(6)-Fe(2)-O(4)	101.5(4)
O(5)-Fe(2)-O(4)	93.6(3)
O(6)-Fe(2)-N(6)	99.6(4)
O(5)-Fe(2)-N(6)	86.3(4)
O(4)-Fe(2)-N(6)	157.4(3)
O(6)-Fe(2)-N(5)	111.6(3)
O(5)-Fe(2)-N(5)	136.6(3)
O(4)-Fe(2)-N(5)	86.2(3)
N(6)-Fe(2)-N(5)	78.6(3)
Fe(1)#3-O(3)-Fe(1)	165.2(7)
Fe(2)#4-O(6)-Fe(2)	175.3(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,y+1/2,-z #2 -x-1/2,y+1/2,-z+1 #3 -x+1,y,-z #4 -x-1,y,-z+1
#5 -x+3/2,y-1/2,-z #6 -x-1/2,y-1/2,-z+1 #7 -x+2,y,-z+1

Table S3. Selected bond lengths [Å] and angle [º] for 2

Cd(1)-N(5)	2.297(8)
Cd(1)-O(8)#3	2.304(7)
Cd(1)-N(4)	2.320(8)
Cd(1)-O(7)	2.323(7)
Cd(1)-O(13)	2.357(10)
Cd(1)-O(14)	2.391(6)
Cd(1)-O(7)#3	2.603(7)
Cd(2)-N(8)#4	2.303(14)
Cd(2)-N(1)#5	2.304(11)
Cd(2)-O(11)	2.308(10)
Cd(2)-O(9)	2.317(8)
Cd(2)-O(10)#6	2.319(8)
Cd(2)-O(12)	2.409(9)
Cd(2)-O(10)	2.612(8)
Fe(1)-O(3)	1.775(3)
Fe(1)-O(2)	1.902(10)

Fe(1)-O(1)	1.941(10)
Fe(1)-N(2)	2.078(11)
Fe(1)-N(3)	2.115(10)
Fe(2)-O(6)	1.770(4)
Fe(2)-O(4)	1.912(10)
Fe(2)-O(5)	1.941(10)
Fe(2)-N(6)	2.108(10)
Fe(2)-N(7)	2.120(10)
N(1)-Cd(2)#7	2.303(11)
N(8)-Cd(2)#4	2.303(14)
O(3)-Fe(1)#8	1.775(3)
O(6)-Fe(2)#4	1.770(4)
O(7)-Cd(1)#3	2.603(7)
O(8)-Cd(1)#3	2.304(7)
O(10)-Cd(2)#6	2.319(8)

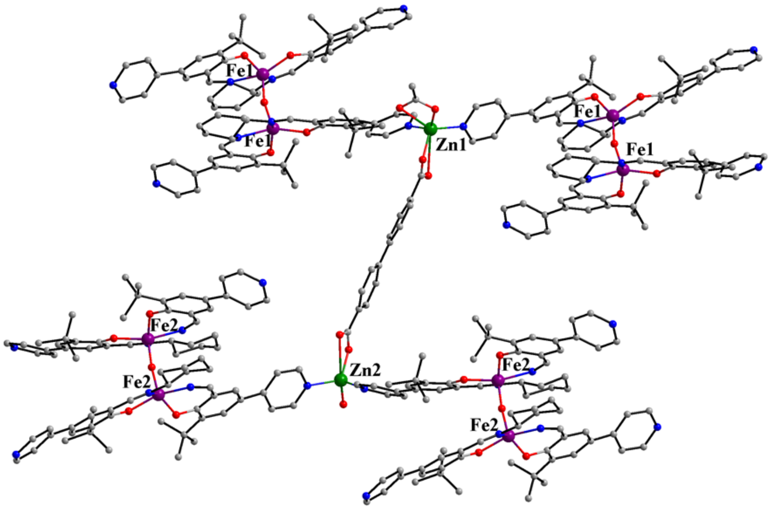
N(5)-Cd(1)-O(8)#3	94.4(3)
N(5)-Cd(1)-N(4)	174.5(3)
O(8)#3-Cd(1)-N(4)	88.6(3)
N(5)-Cd(1)-O(7)	87.2(3)
O(8)#3-Cd(1)-O(7)	127.6(3)
N(4)-Cd(1)-O(7)	87.4(3)
N(5)-Cd(1)-O(13)	93.1(4)
O(8)#3-Cd(1)-O(13)	81.1(3)
N(4)-Cd(1)-O(13)	91.9(4)
O(7)-Cd(1)-O(13)	151.2(3)
N(5)-Cd(1)-O(14)	91.3(3)
O(8)#3-Cd(1)-O(14)	136.5(3)
N(4)-Cd(1)-O(14)	89.6(3)
O(7)-Cd(1)-O(14)	95.7(2)
O(13)-Cd(1)-O(14)	55.5(3)
N(5)-Cd(1)-O(7)#3	83.4(3)
O(8)#3-Cd(1)-O(7)#3	52.3(2)
N(4)-Cd(1)-O(7)#3	94.9(3)
O(7)-Cd(1)-O(7)#3	76.0(2)
O(13)-Cd(1)-O(7)#3	132.6(3)
O(14)-Cd(1)-O(7)#3	170.4(2)
N(8)#4-Cd(2)-N(1)#5	172.5(5)
N(8)#4-Cd(2)-O(11)	92.2(6)
N(1)#5-Cd(2)-O(11)	94.7(5)
N(8)#4-Cd(2)-O(9)	89.9(4)
N(1)#5-Cd(2)-O(9)	94.3(3)
O(11)-Cd(2)-O(9)	79.2(3)
N(8)#4-Cd(2)-O(10)#6	85.3(4)

N(1)#5-Cd(2)-O(10)#6	87.2(3)
O(11)-Cd(2)-O(10)#6	152.1(3)
O(9)-Cd(2)-O(10)#6	128.5(3)
N(8)#4-Cd(2)-O(12)	91.3(5)
N(1)#5-Cd(2)-O(12)	90.1(4)
O(11)-Cd(2)-O(12)	56.0(3)
O(9)-Cd(2)-O(12)	135.2(3)
O(10)#6-Cd(2)-O(12)	96.2(3)
N(8)#4-Cd(2)-O(10)	92.8(4)
N(1)#5-Cd(2)-O(10)	84.8(3)
O(11)-Cd(2)-O(10)	131.8(3)
O(9)-Cd(2)-O(10)	52.9(3)
O(10)#6-Cd(2)-O(10)	76.1(3)
O(12)-Cd(2)-O(10)	170.9(3)
O(3)-Fe(1)-O(2)	114.6(6)
O(3)-Fe(1)-O(1)	107.9(5)
O(2)-Fe(1)-O(1)	91.2(4)
O(3)-Fe(1)-N(2)	105.1(6)
O(2)-Fe(1)-N(2)	139.0(6)
O(1)-Fe(1)-N(2)	86.1(4)
O(3)-Fe(1)-N(3)	101.2(4)
O(2)-Fe(1)-N(3)	85.7(4)
O(1)-Fe(1)-N(3)	149.2(6)
N(2)-Fe(1)-N(3)	76.7(4)
O(6)-Fe(2)-O(4)	111.1(5)
O(6)-Fe(2)-O(5)	107.1(6)
O(4)-Fe(2)-O(5)	90.9(4)
O(6)-Fe(2)-N(6)	100.6(6)
O(4)-Fe(2)-N(6)	86.5(4)
O(5)-Fe(2)-N(6)	151.2(6)
O(6)-Fe(2)-N(7)	112.9(4)
O(4)-Fe(2)-N(7)	135.1(6)
O(5)-Fe(2)-N(7)	84.3(4)
N(6)-Fe(2)-N(7)	77.6(4)
Fe(1)-O(3)-Fe(1)#8	174.2(9)
Fe(2)#4-O(6)-Fe(2)	157.3(8)
Cd(2)#6-O(10)-Cd(2)	103.7(3)

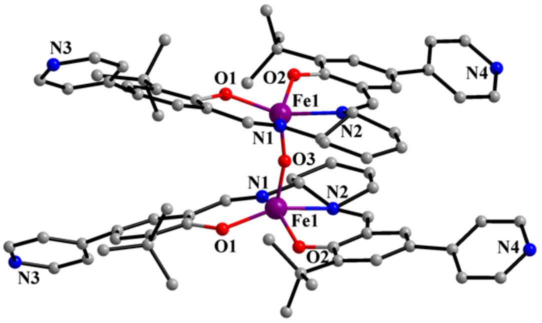
Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,z   #2 -x+1/2,-y+1/2,z   #3 -x+2,-y,z   #4 -x+3/2,y,-z+3/2
#5 -x+3/2,y+1/2,-z+2   #6 -x+3/2,-y+1/2,z   #7 -x+3/2,y-1/2,-z+2
#8 -x+2,y,-z+2

6. Figures S1-S6. Additional X-ray crystallographic structures

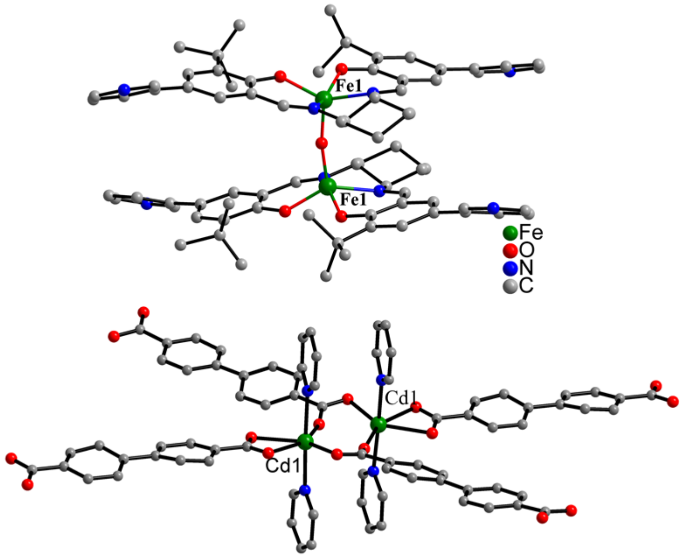
6.1 Figure S1. Coordination environments of Zn ions and [$Fe_2(\mathbf{L_1})_2(\mu_2\text{-O})$] units.



6.2 Figure S2. The structure of the $Fe_2(\mathbf{L_1})_2(\mu_2\text{-O})$ unit in 1.

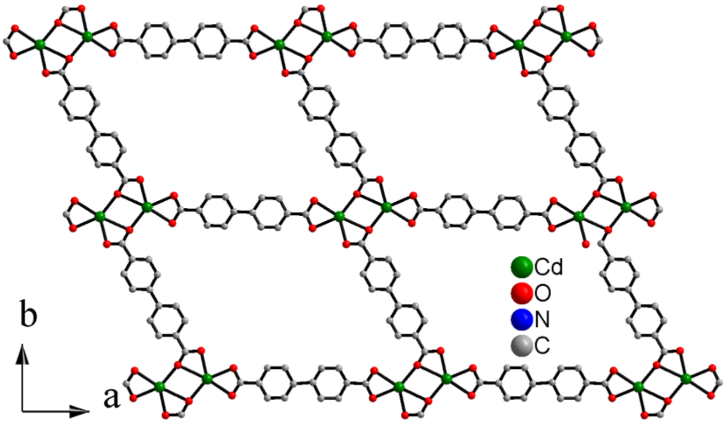


6.3 Figure S3. The structures of the $Fe_2(\mathbf{L_2})_2(\mu_2\text{-O})$ unit and Cd$_2$ dimer in 2.

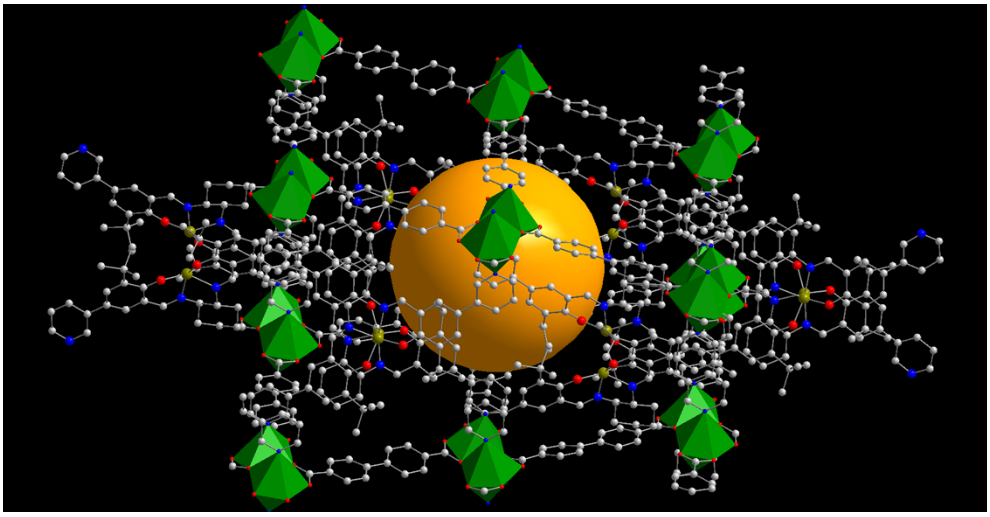


6.4 Figure S4. The 2D

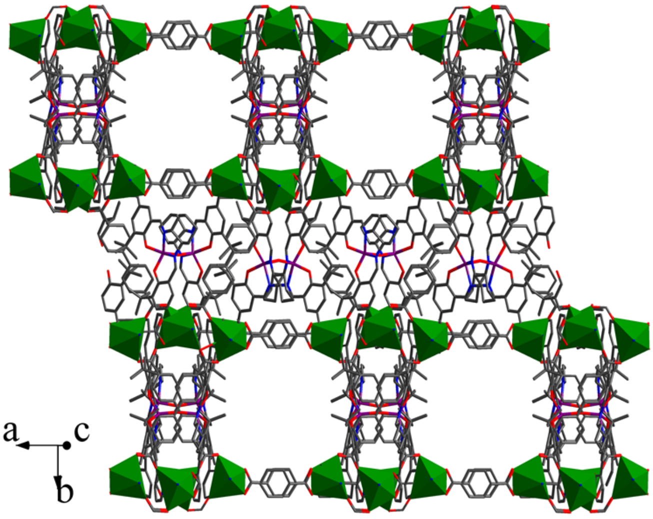
structure formed by Cd-BPDC in 2.



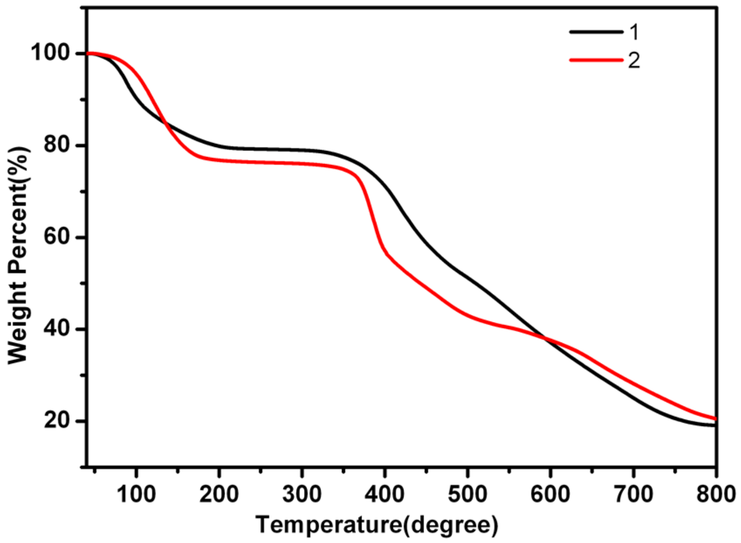
6.5 Figure S5. The Cage formed by Cd_2, BPDC and $Fe_2(L_2)_2(\mu_2\text{-}O)$ in 2.



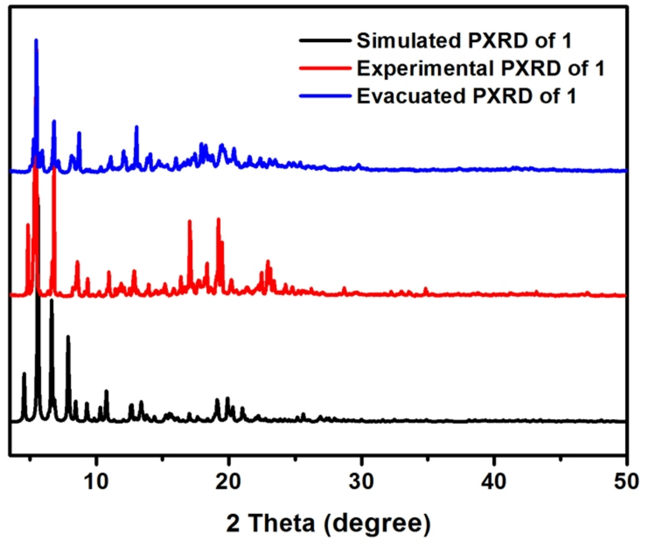
6.6 Figure S6. A view of the 3D structure of 2.

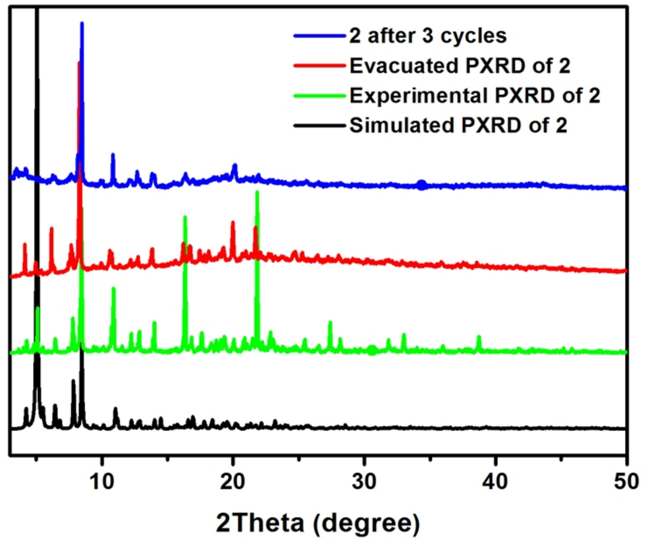


7. Figure S7. TGA curves of 1 and 2

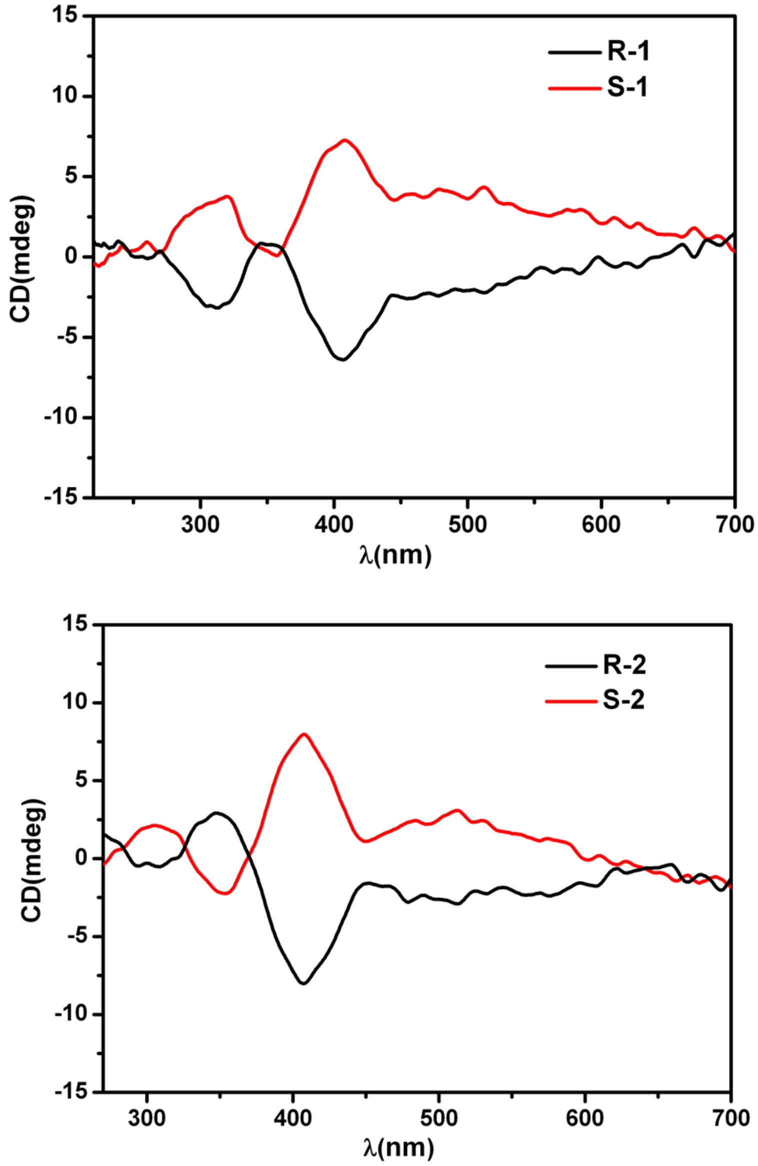


8. Figure S8. PXRD patterns of 1 and 2



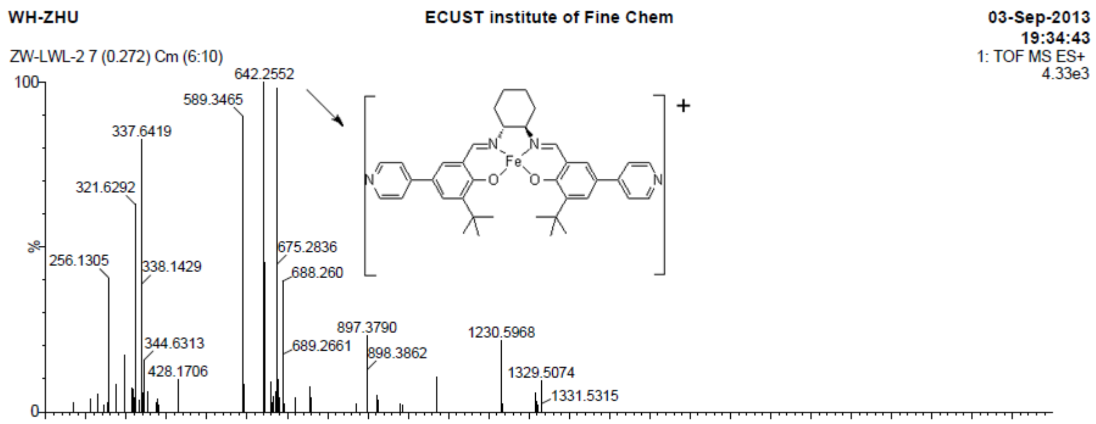


9. Figure S9. CD spectra of (*R*)/(*S*)-1 and (*R*)/(*S*)-2

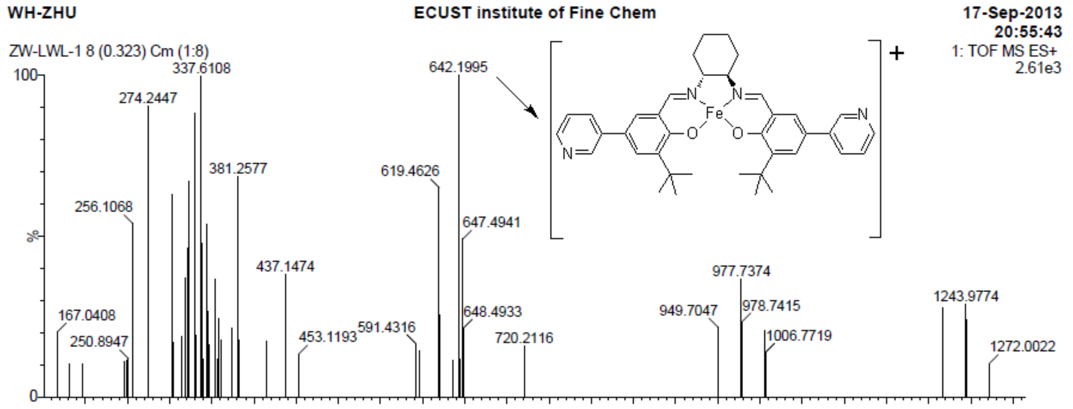


10. Figure S10. ESI-MS of $FeL_1(OAc)$ **(a) and** $FeL_2(OAc)$ **(b)**

(a)

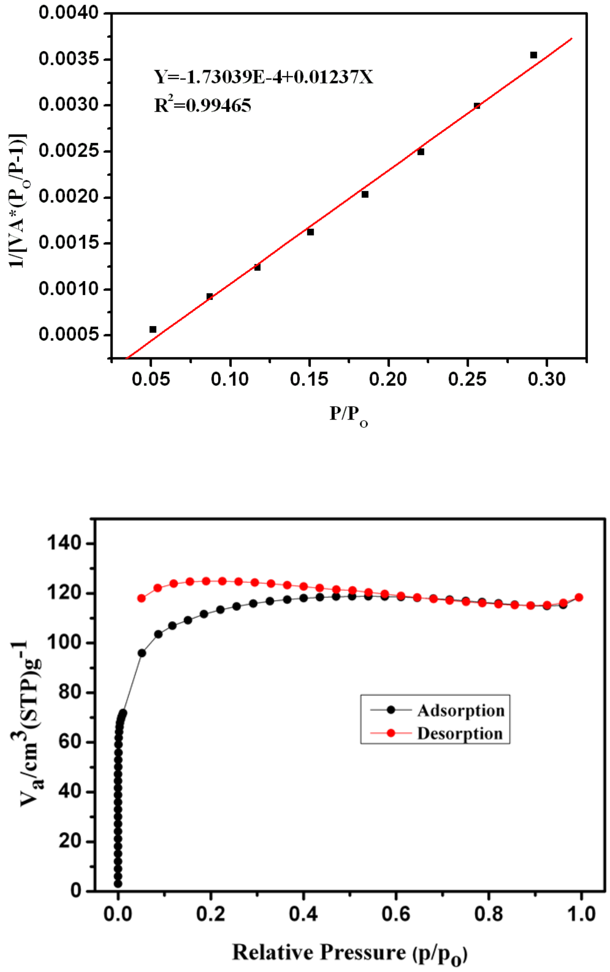


(b)

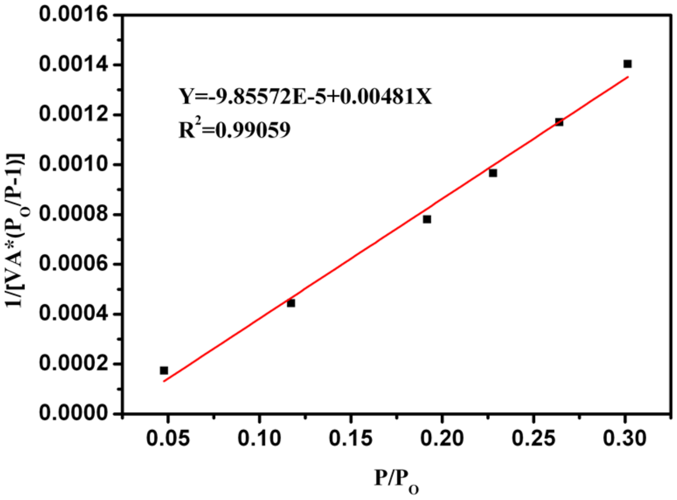


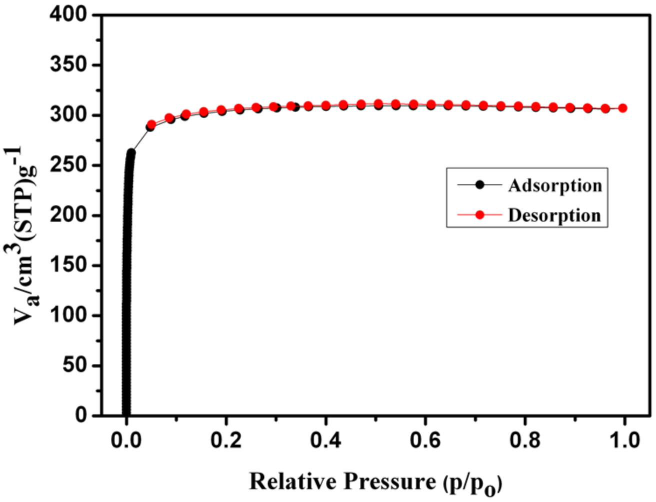
11. Figure S11. The BET plot and N_2 adsorption isotherm of 1 (a) and 2 (b) (The apparent adsorption-desorption hysteresis in **1** was observed, probably as a consequence of the framework flexibility)

(a)

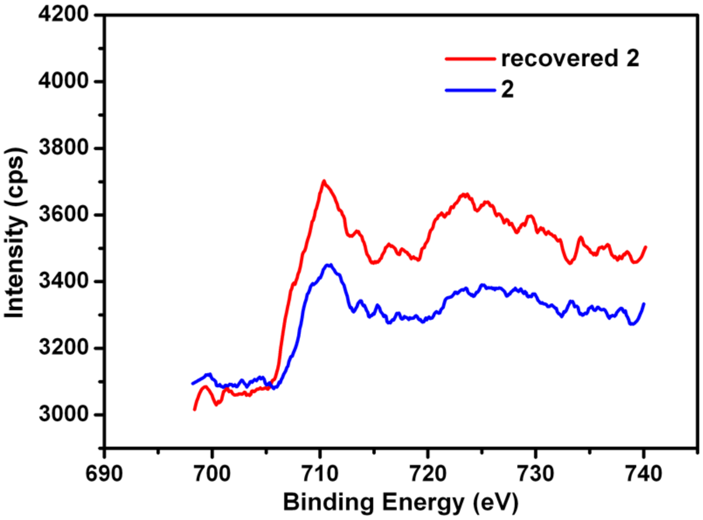


(b)

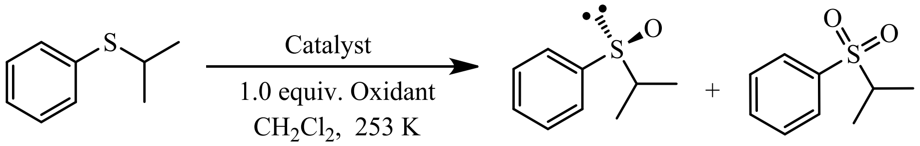




12. Figure S12. XPS of MOF 2



13. Table S4. Catalyzed asymmetric oxidation of isopropyl phenyl sulfide using various oxidants[a]

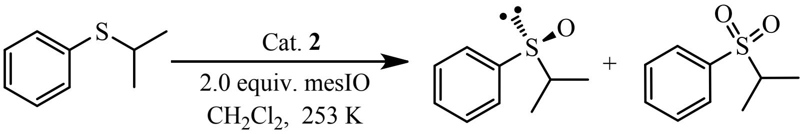


Entry	**Catalyst**	**Oxidant**	**Time (h)**	**Conv (%)[b]**	**Selec (%)[c]**	**ee (%)[d]**
1	**1**	MesIO	11	89	100	53
2	**2**	MesIO	8	93.5	100	60
3	**1**	PhIO	10	87.3	85	46
4	**2**	PhIO	7	91.2	87	54
5	**1**	H_2O_2	15	63.4	100	1
6	**2**	H_2O_2	13	64.8	100	1

[a]For reaction details see Experimental section **3**, except the oxidant amount decreased to 1.0 equivalent. [b]determined by ^{1}H NMR. Conversion is calculated as ([sulfone]+[sulfoxide])/([sulfide]+[sulfoxide]+[sulfone])×100%. [c]Selectivity is calculated as ([sulfoxide]/([sulfoxide]+[sulfone])×100. [d]determined by HPLC.

14. Kinetic study of 2 and $FeL_2(OAc)$ in asymmetric catalysis

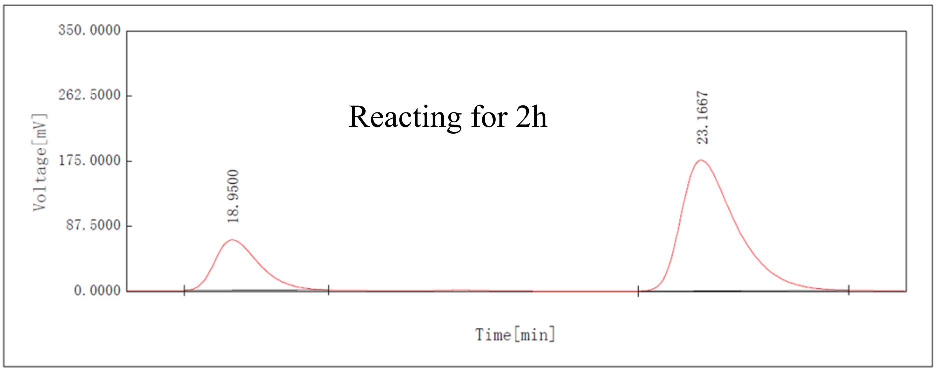
14.1 Table S5. Kinetic study of 2



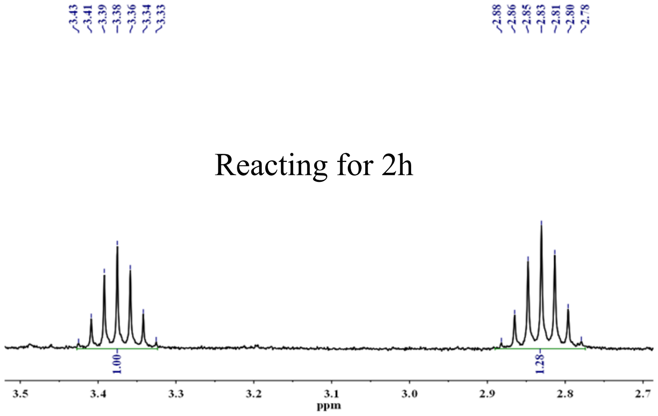
Entry	Time(h)	Conv.(%)[a]	Selec.(%)[b]	ee (%)[c]
1	2	58	100	52
2	4	64	100	55
3	6	77	100	57
4	8	94	100	60
5	11	100	85	67
6	14	100	65	74
7	18	100	45	86
8	22	100	32	91
9	26	100	29	93
10	30	100	27	96
11	32	100	26	95

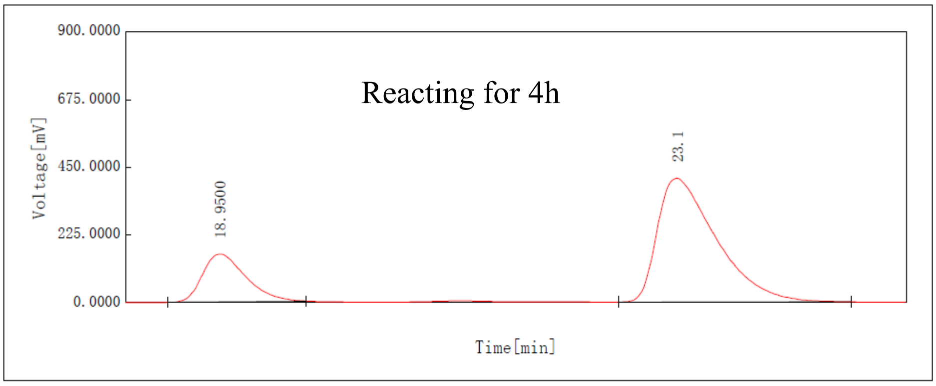
[ab]Calculated from ^{1}HNMR. [c]ee was determined by HPLC with Chiralcel OD-H column.

HPLC and ^{1}H NMR data:

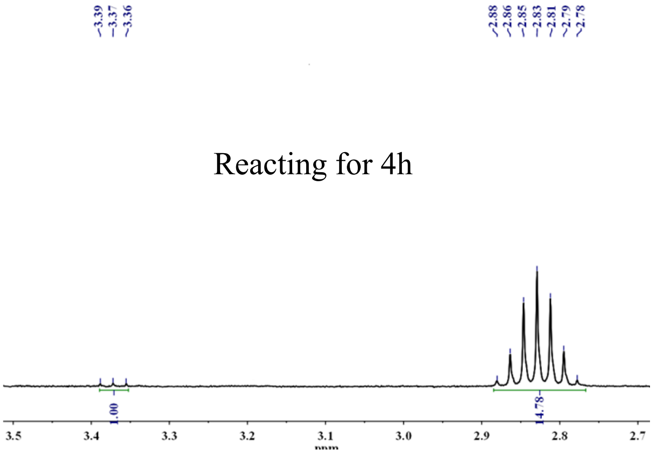


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.9500	1883.3077	BB	23.7774
2	23.1667	6037.2563	BB	76.2226
The Total		7920.5640		

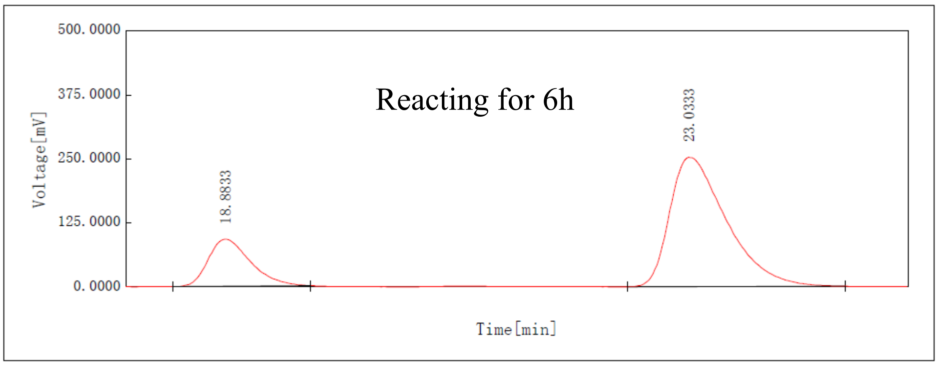




Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.9500	4323.7721	BB	22.1151
2	23.1000	15227.4828	BB	77.8849
The Total		19551.2548		

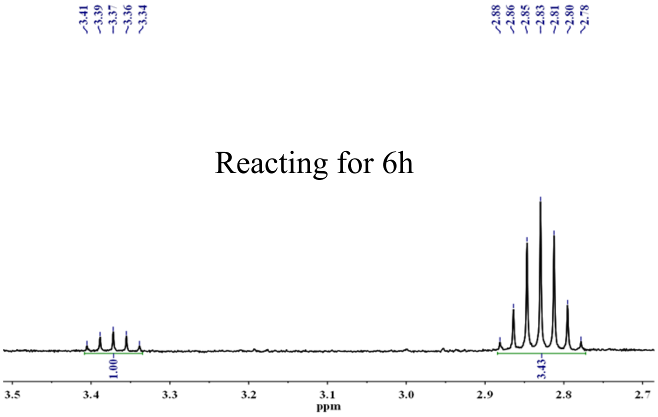


Reacting for 4h

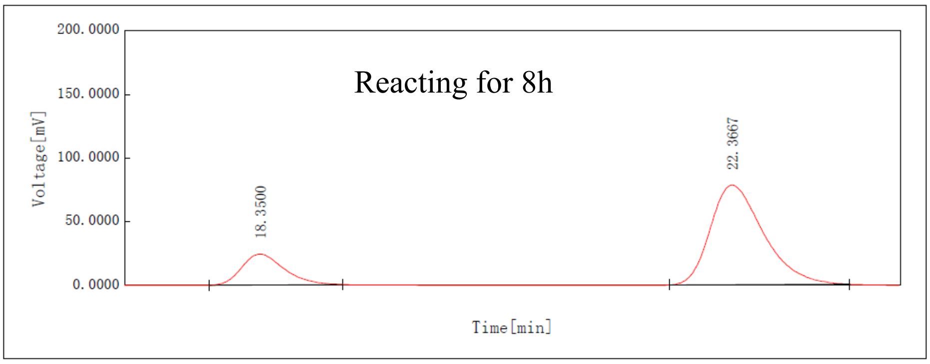


Reacting for 6h

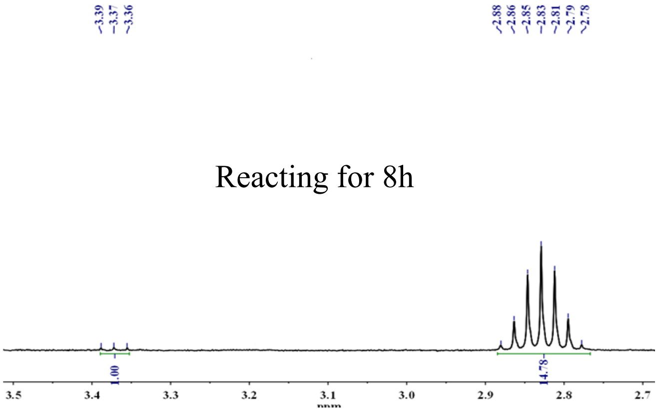
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.8833	2412.6385	BB	21.3523
2	23.0333	8886.5354	BB	78.6477
The Total		11299.1739		

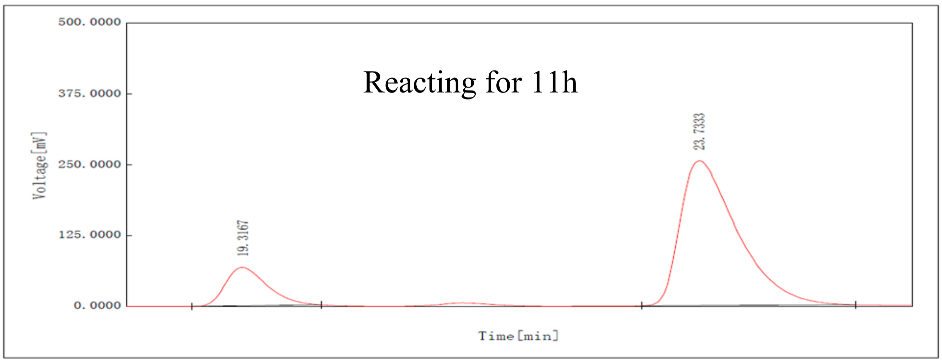


Reacting for 6h

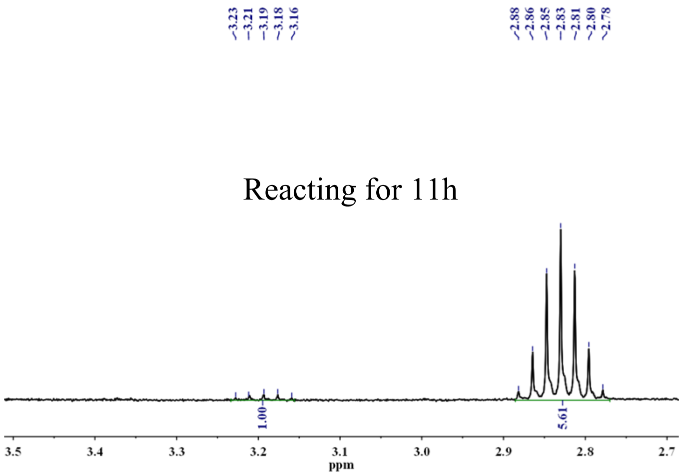


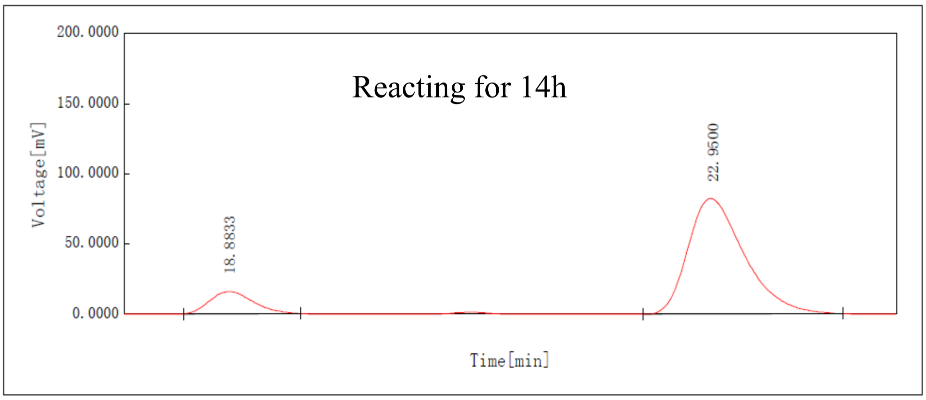
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.3500	613.0922	BB	19.9784
2	23.3667	2455.6851	BB	80.0216
The Total		3068.7772		



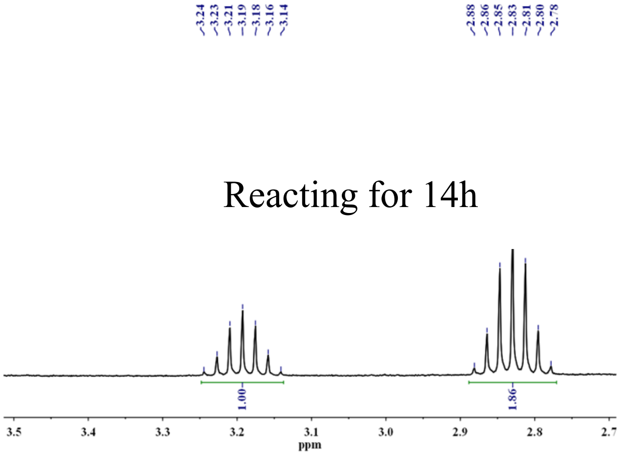


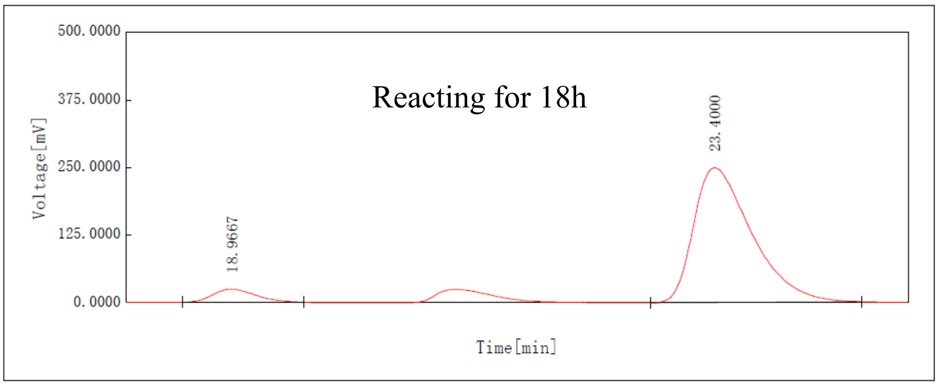
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	19.3167	1914.9674	BB	16.2596
2	23.7333	9862.5014	BB	83.7404
The Total		11777.4687		



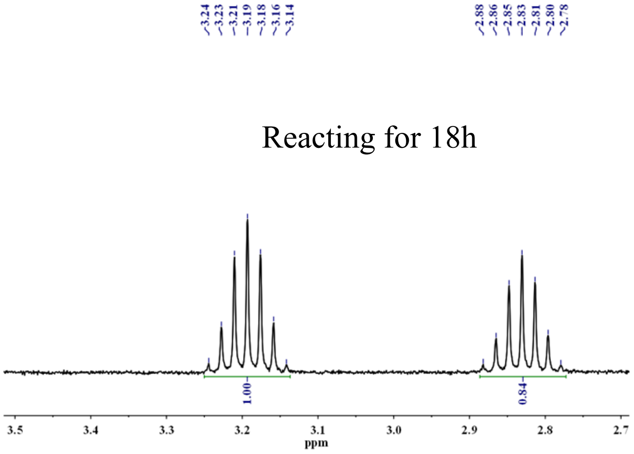


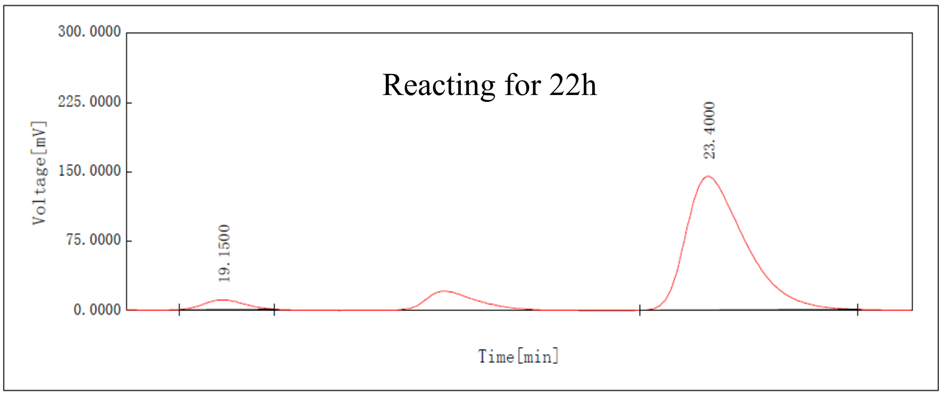
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.8833	405.0286	BB	12.8925
2	23.9500	2736.5522	BB	87.1075
The Total		3141.5809		



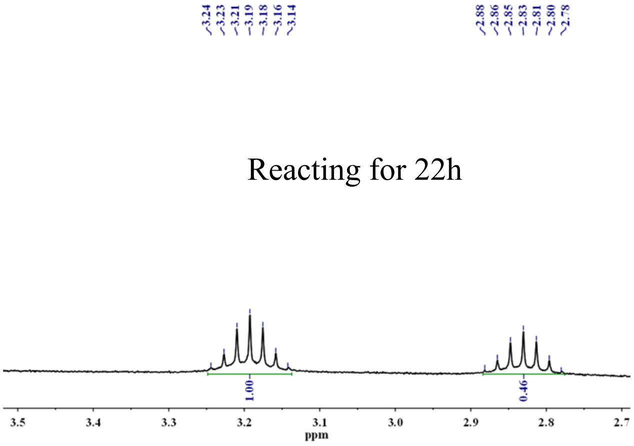


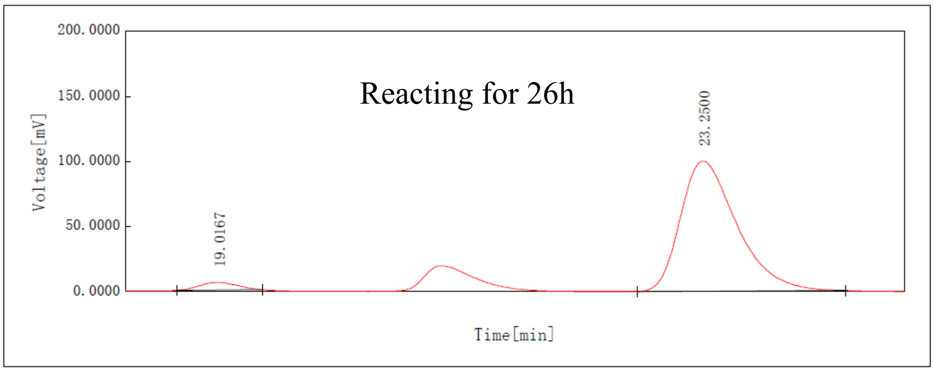
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.9667	668.5103	BB	6.7582
2	23.4000	9223.3762	BB	93.2418
The Total		9891.8865		



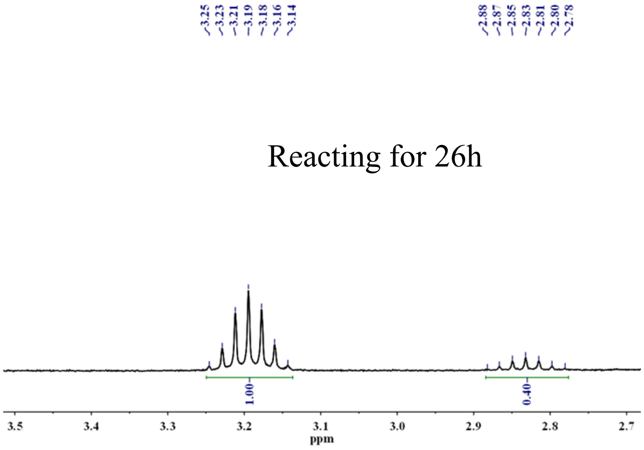


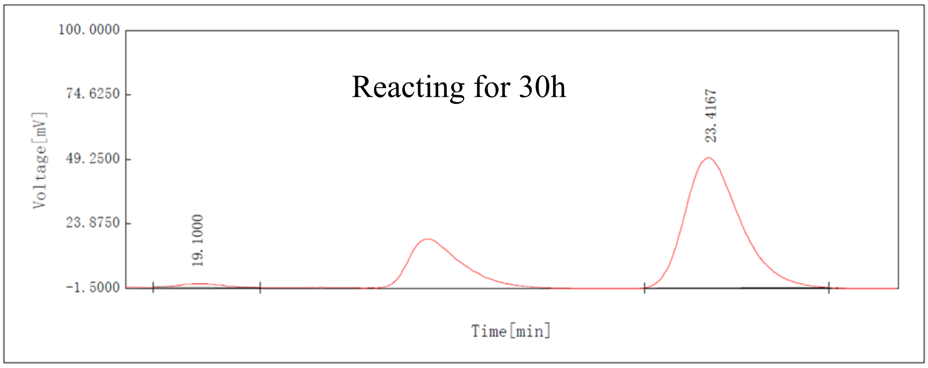
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	19.1500	247.7794	BB	4.5596
2	23.4000	5186.4818	BB	95.4404
The Total		5434.2612		


Reacting for 22h

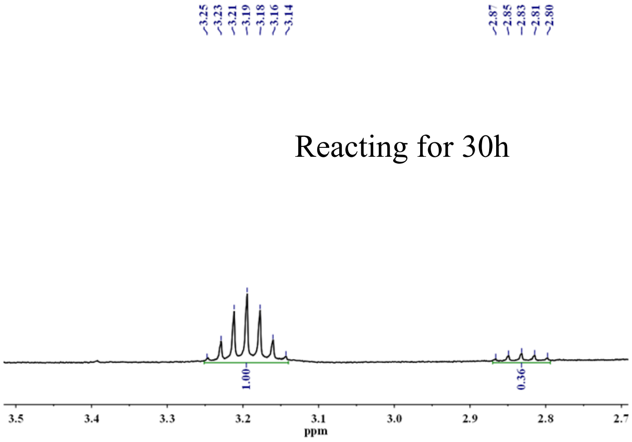

Reacting for 26h

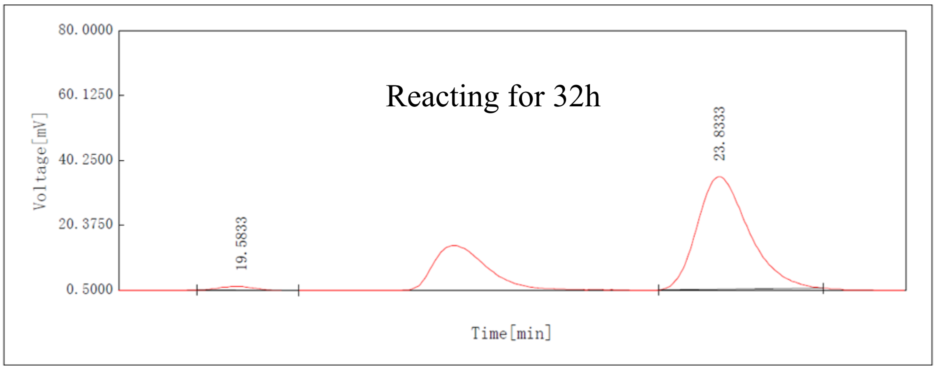
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	19.0167	131.1329	BB	3.6962
2	23.2500	3416.6687	BB	96.3038
The Total		3547.8016		


Reacting for 26h

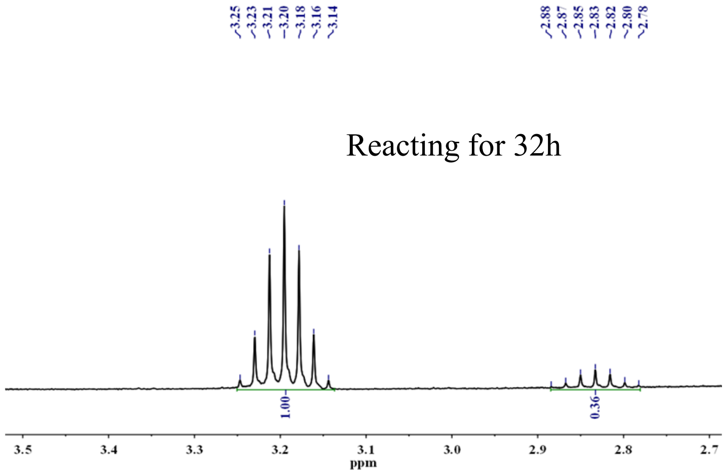


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	19.1000	35.9035	FF	2.1173
2	23.4167	1659.8542	BB	97.8827
The Total		1695.7578		



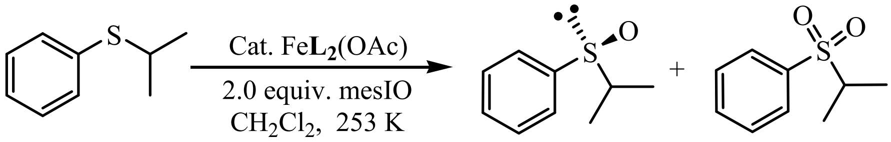


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	19.5833	29.8477	FF	2.6407
2	23.8333	1100.4374	BB	97.3593
The Total		1130.2850		



Reacting for 32h

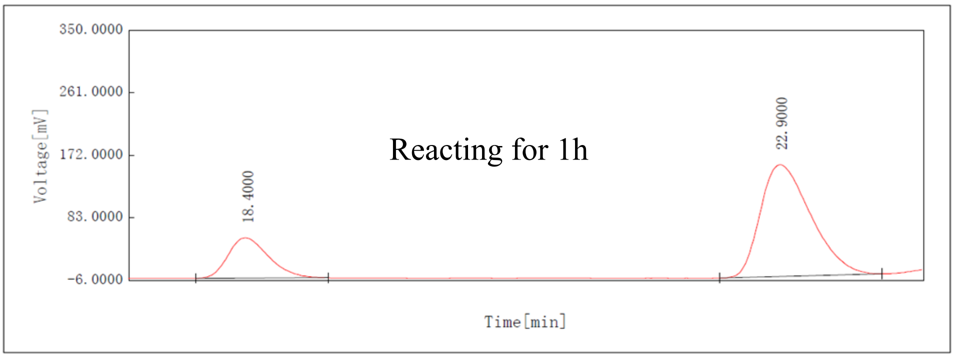
14.2 Table S6. Kinetic study of $FeL_2(OAc)$



Entry	Time(h)	Conv.(%)[a]	Selec.(%)[b]	ee (%)[c]
1	1	53.5	100	55
2	2	78	100	60
3	3	100	94.6	64
4	4	100	81.4	71
5	5	100	70.8	77
6	6	100	59.2	84
7	7	100	49	89
8	8	100	41.5	93
9	9	100	33	95
10	10	100	27	96

[ab] Calculated from ^1H NMR. [c]ee was determined by HPLC with Chiralcel OD-H column

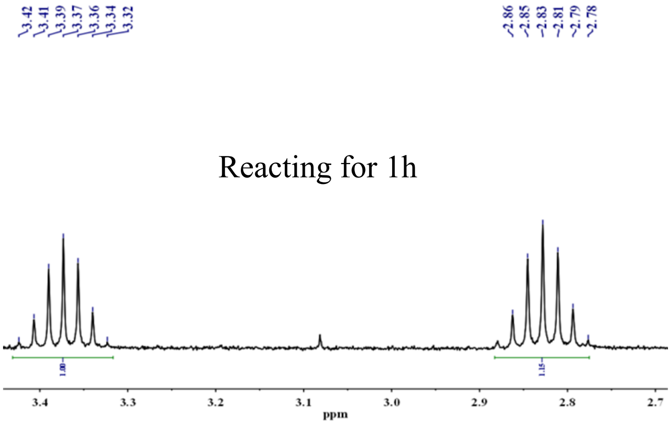
HPLC and ^1H NMR data:

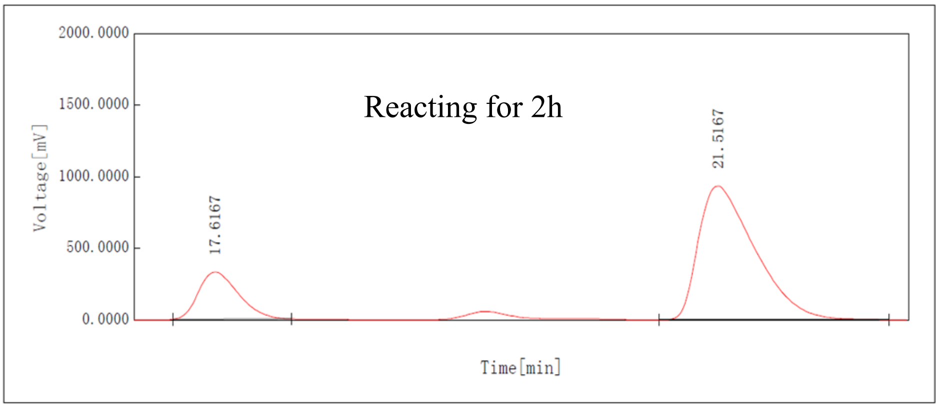


Reacting for 1h

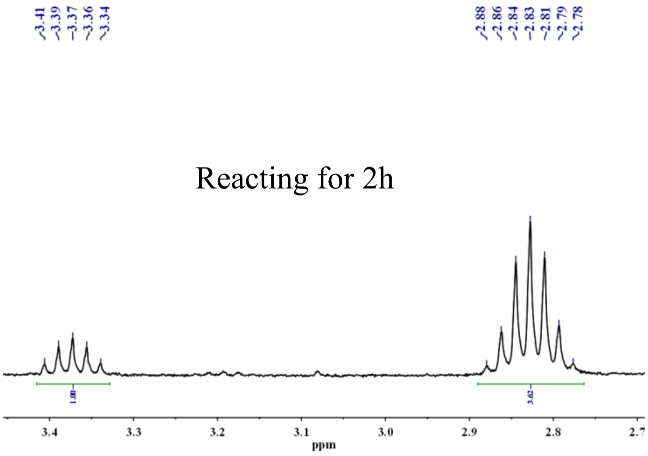
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.4000	1360.5001	BB	22.4163
2	22.9000	4708.7521	BB	77.5837
The Total		6069.2521		

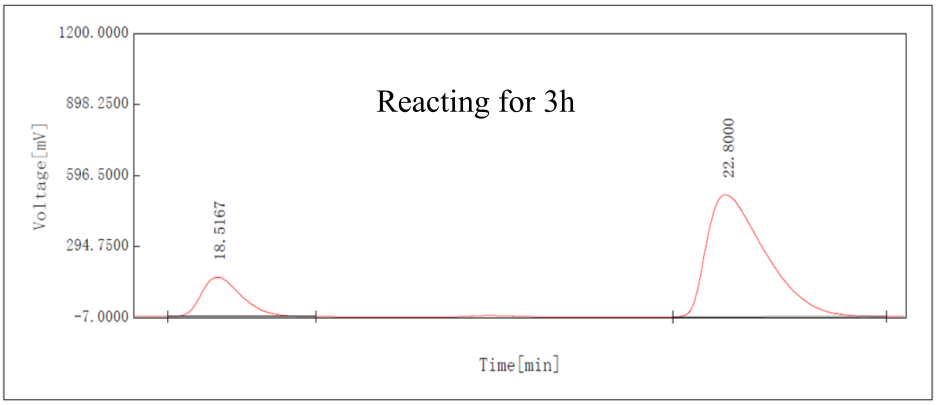
Reacting for 1h



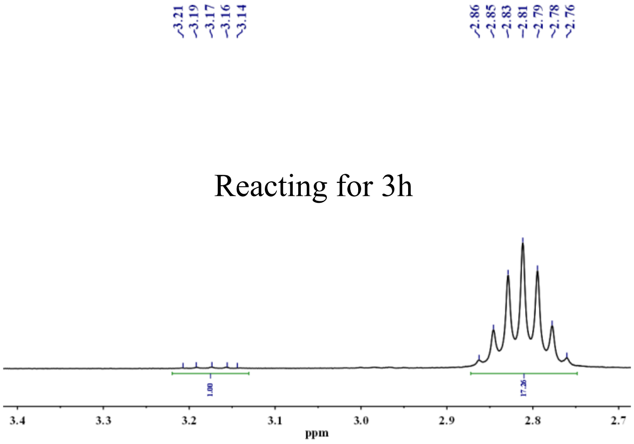

Reacting for 2h

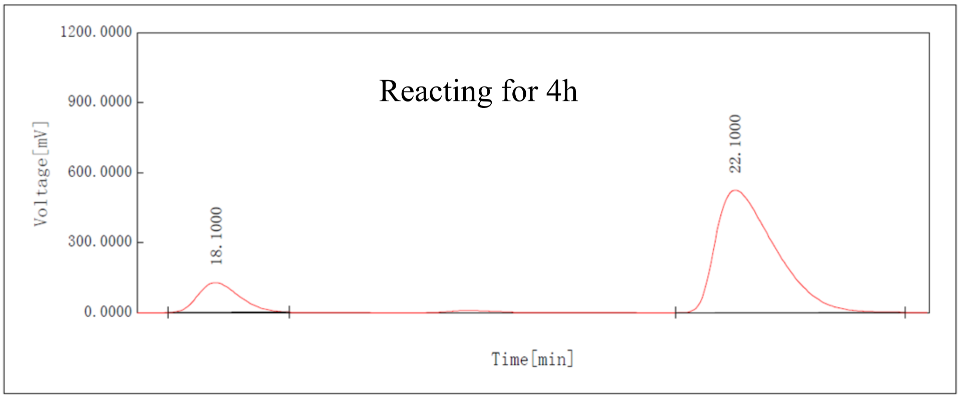
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	17.6167	7034.7682	FF	19.9188
2	21.5167	28282.5318	BB	80.0812
The Total		35317.3000		


Reacting for 2h

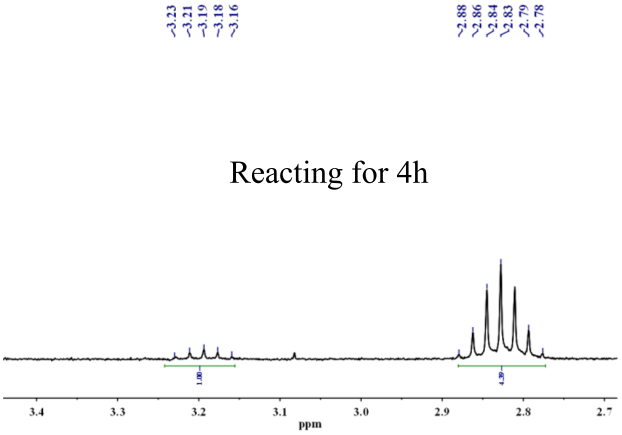

Reacting for 3h

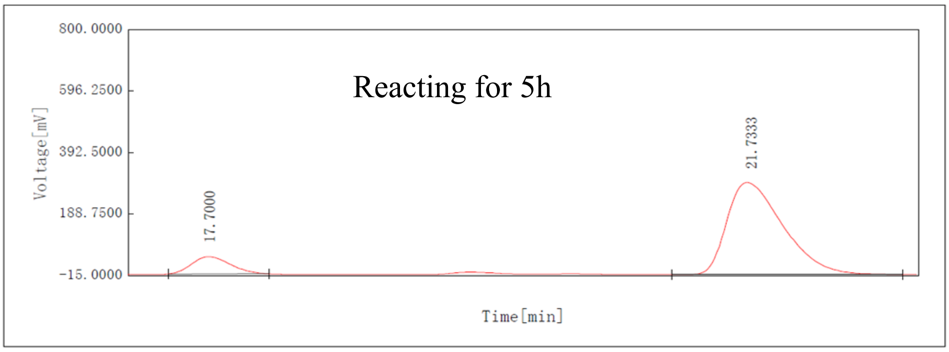
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.5167	3921.5544	BB	18.1547
2	22.8000	17679.2649	BB	81.8453
The Total		21600.8193		


Reacting for 3h



Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.1000	2806.7356	BB	14.4434
2	22.1000	16625.9105	BB	85.5566
The Total		19432.6461		

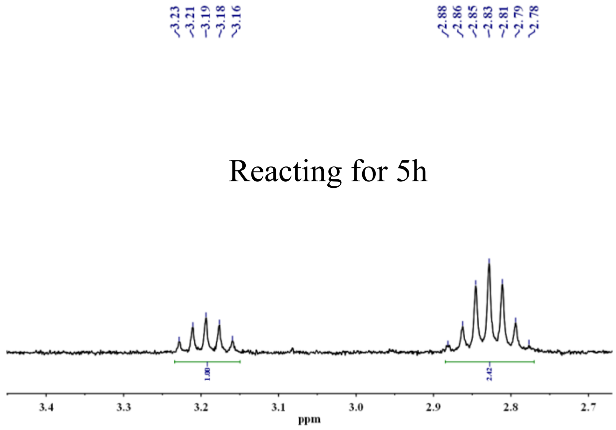


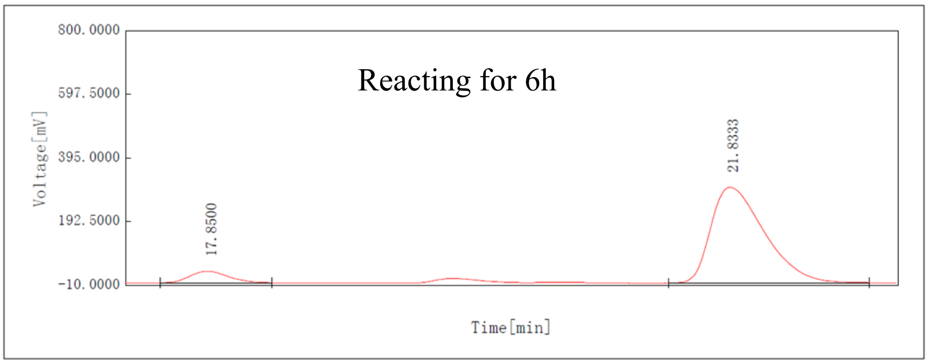


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	17.7000	1137.0347	FF	11.3834
2	21.7333	8851.5141	FF	88.6166

The Total		9988.5487		

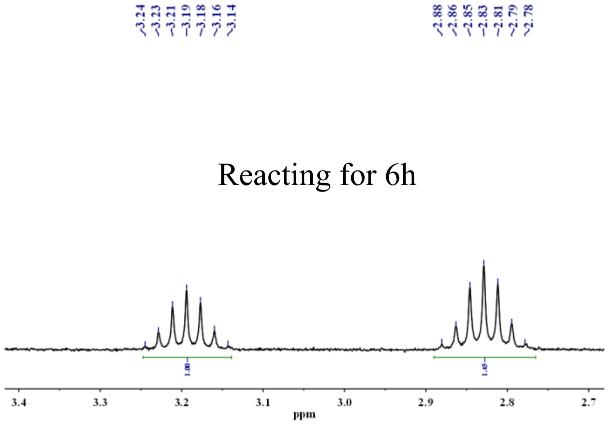
Reacting for 5h

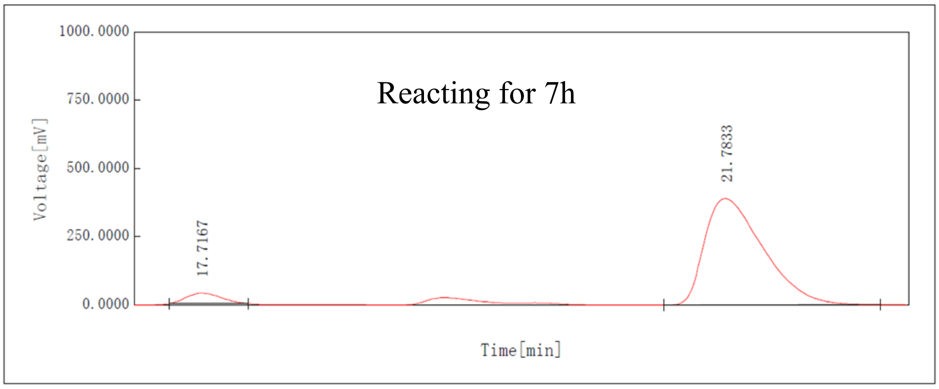




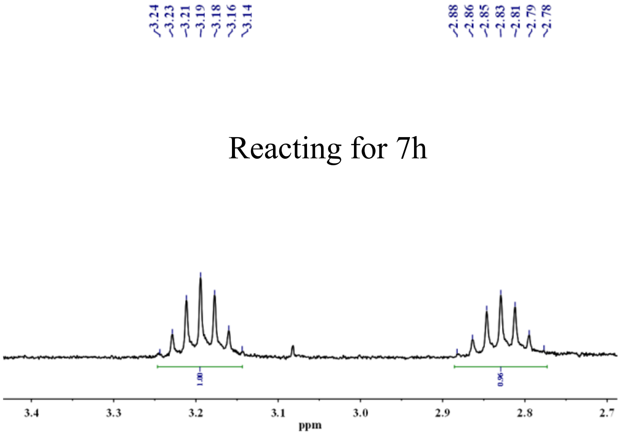
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	17.8500	746.4852	FF	7.9621
2	21.8333	8629.0286	BB	92.0379
The Total		9375.5138		

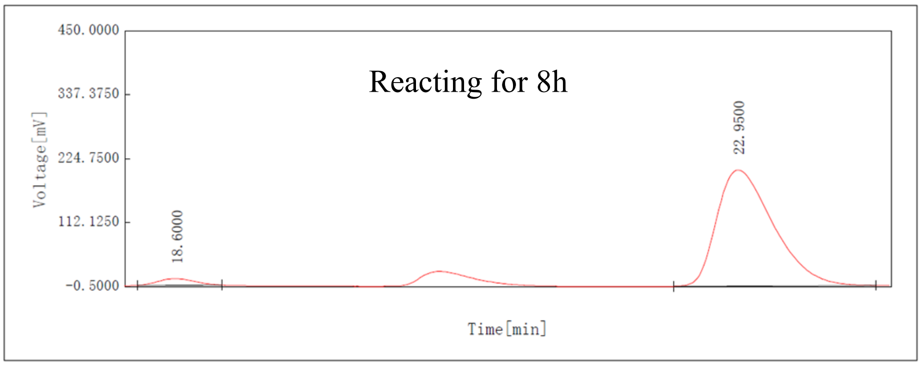
Reacting for 6h





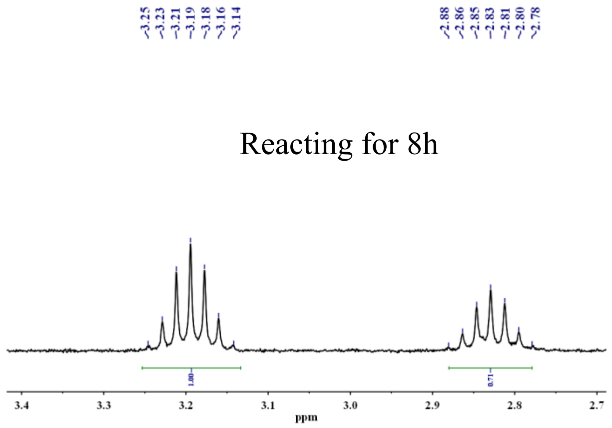
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	17.7167	719.9301	BB	5.5368
2	21.7833	12282.7359	BB	94.4632
The Total		13002.6660		

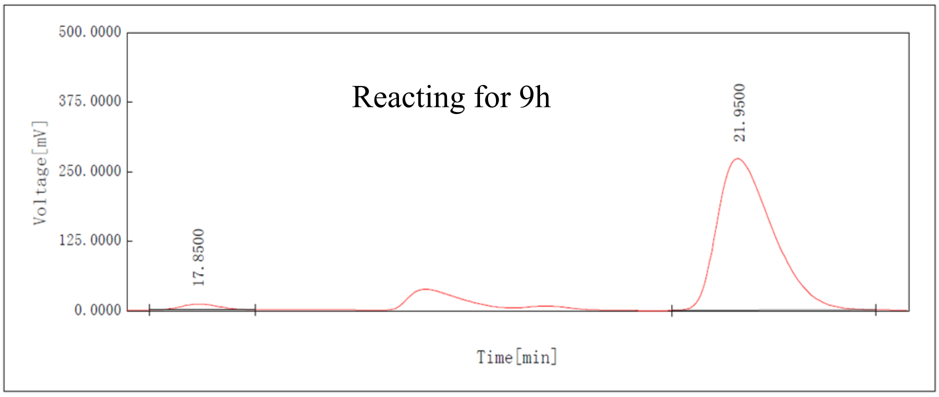




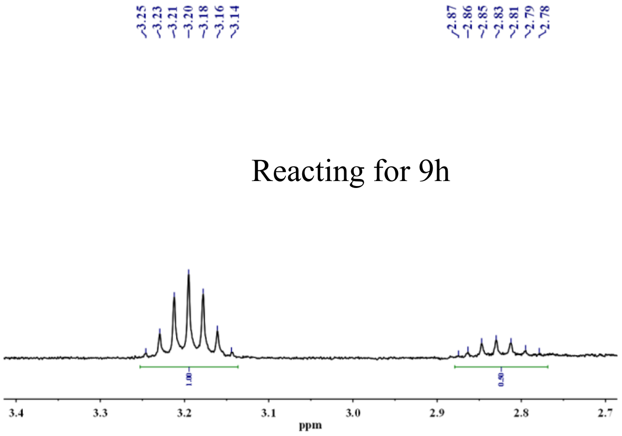
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.6000	225.2345	FF	3.5179

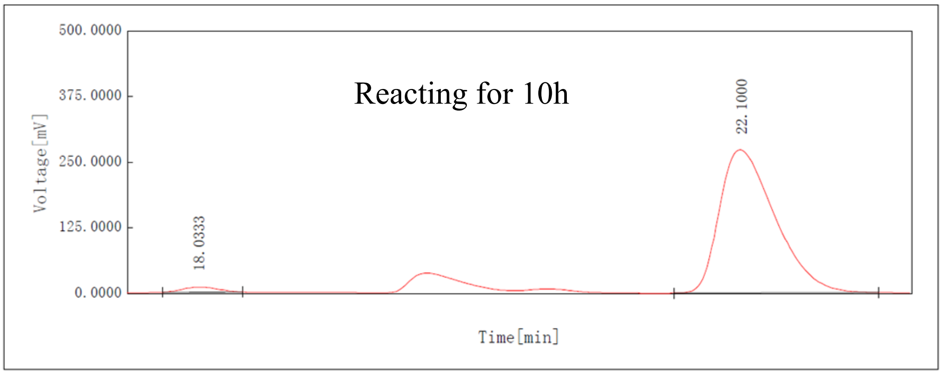
2	22.9500	6177.2560	BB	96.4821
The Total		6402.4904		



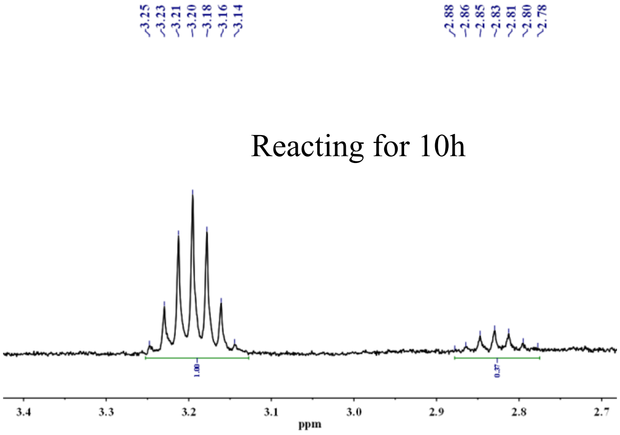


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	17.8500	208.9886	FF	2.5851
2	21.9500	7875.2191	BB	97.4149
The Total		8084.2077		

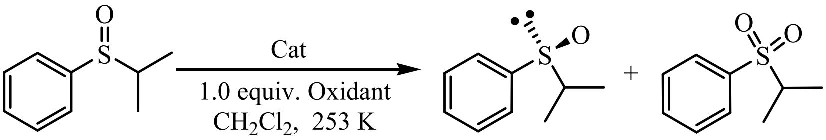




Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.0333	177.6961	FF	2.2066
2	22.1000	7875.21911	BB	97.7934
The Total		8052.9152		



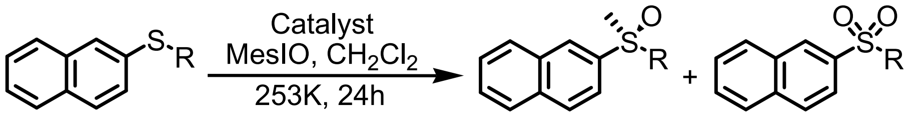
15. Table S7. Kinetic resolution of racemic sulfoxide



Entry	Catalyst	Oxidant	Solvent	Time(h)	ee(%)[b]
1	**2**	MesIO	CH_2Cl_2	23	60
2	**2**	MesIO	CH_3CN	30	31
3	**2**	MesIO	Toluene	30	8
4	**2**	PhIO	CH_2Cl_2	26	39
5	Fe**L**$_2$(OAc)	MesIO	CH_2Cl_2	8	60

[a]Calculated from ^1H NMR. [b]ee was determined by HPLC with Chiralcel OD-H column

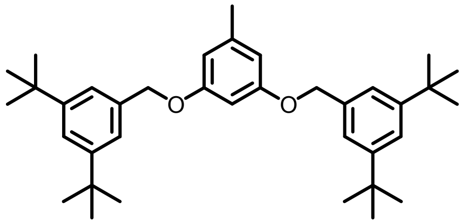
16. HPLC and ^1H NMR data for size-exclusion catalysis experiments

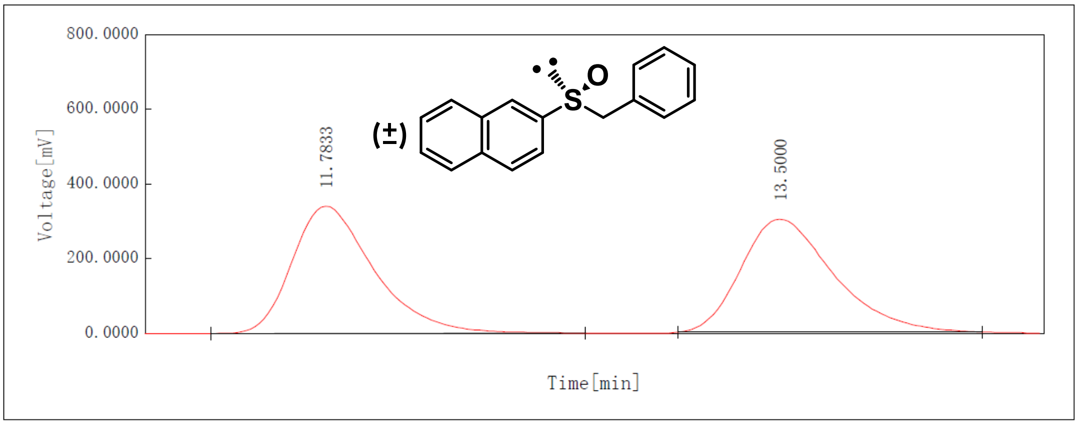


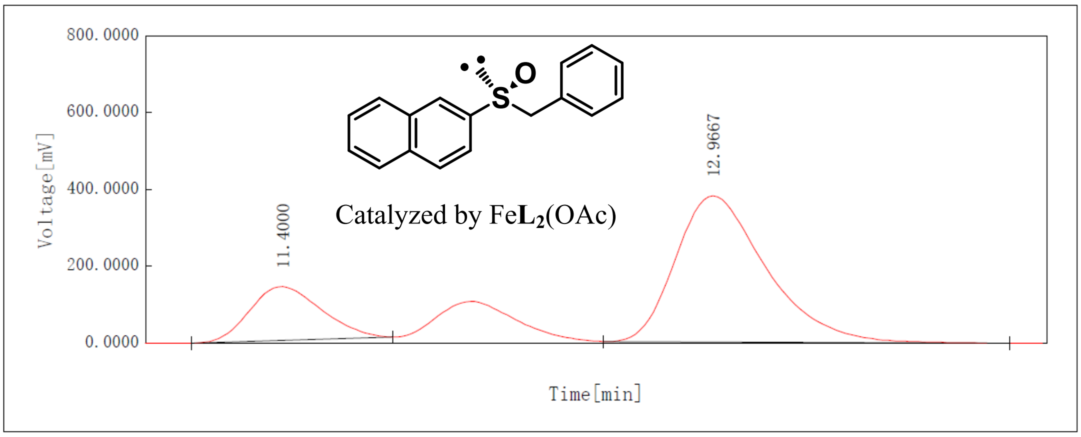
Entry	Catalyst	R	Conv.	Selec. (%)[b]	ee (%)[c]
1	**2**	benzyl	60	98	36
2	Fe**L**$_2$(OAc)	benzyl	100	47	54
3	**2**	naphthalene-2-ylmethyl	28	95	9
4	Fe**L**$_2$(OAc)	naphthalene-2-ylmethyl	95	81	21
5	**2**	R_0	n.d	—	—
6	Fe**L**$_2$(OAc)	R_0	77	94	11

[ab]Calculated from ^{1}HNMR. [c]ee was determined by HPLC with Chiralcel OD-H column.

R_0 :

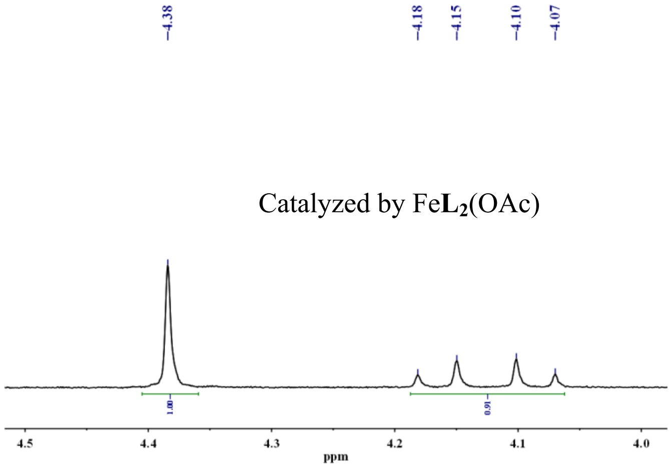




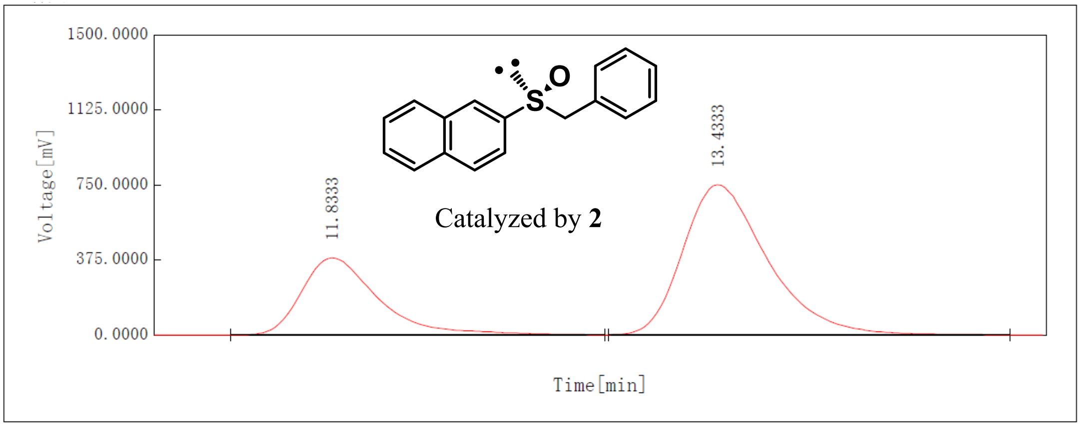


Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %

1	11.4000	2546.1412	BB	22.5668
2	12.9667	8736.5341	BB	77.4332
The Total		11282.6753		

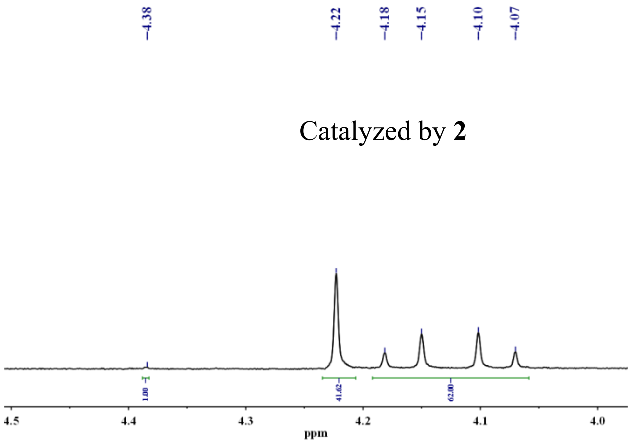


Catalyzed by Fe**L**$_2$(OAc)

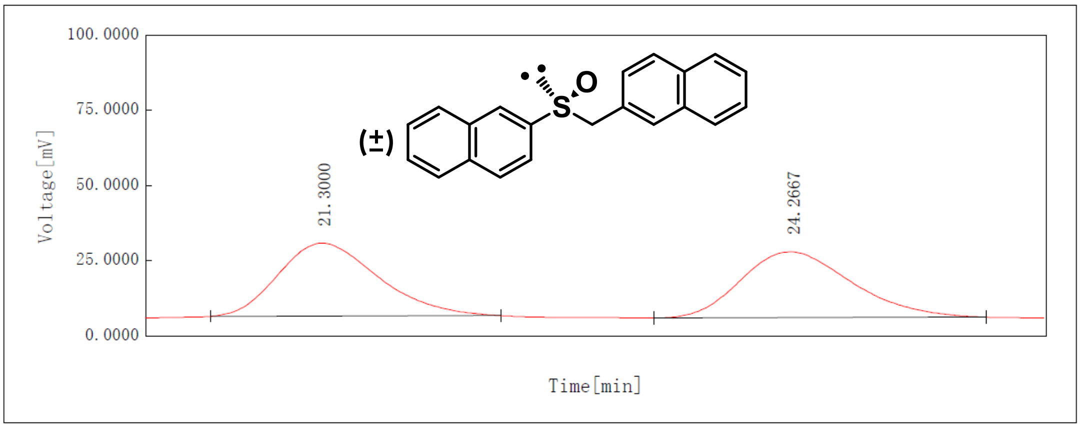


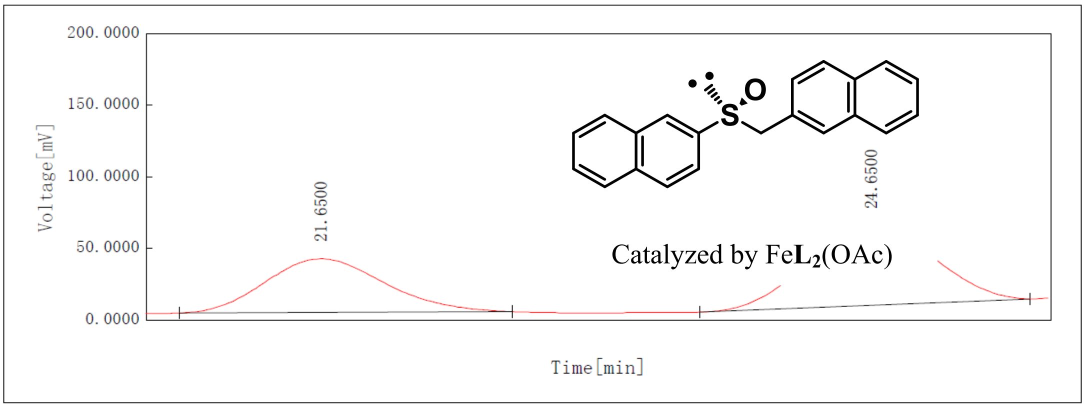
Catalyzed by **2**

Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	11.8333	8465.3229	BB	31.7509
2	13.4333	18196.3171	BB	68.2491
The Total		26661.6400		



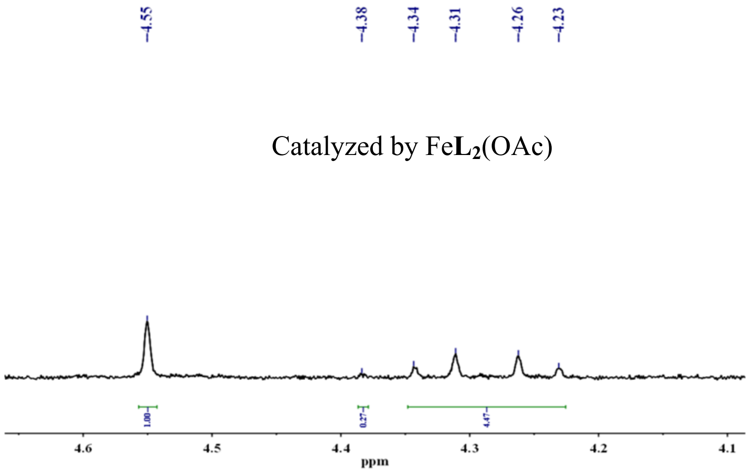
Catalyzed by **2**

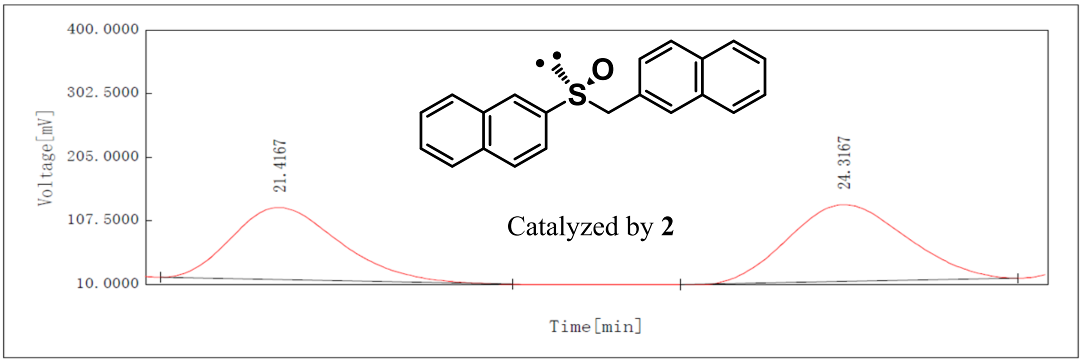




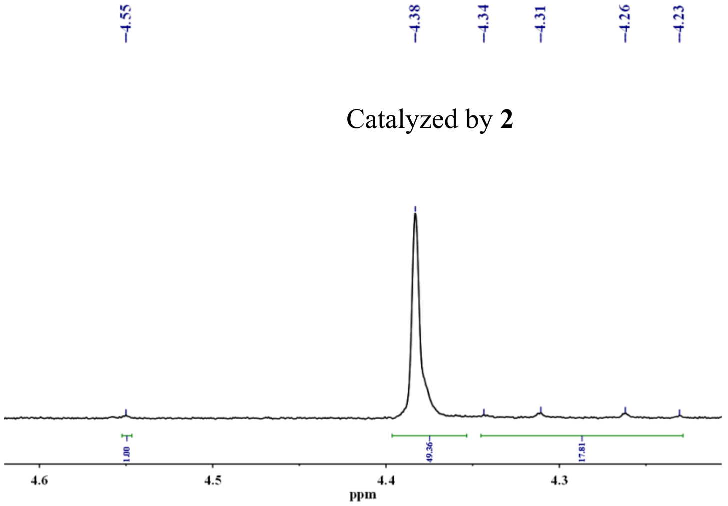
Catalyzed by $Fe\mathbf{L}_2(OAc)$

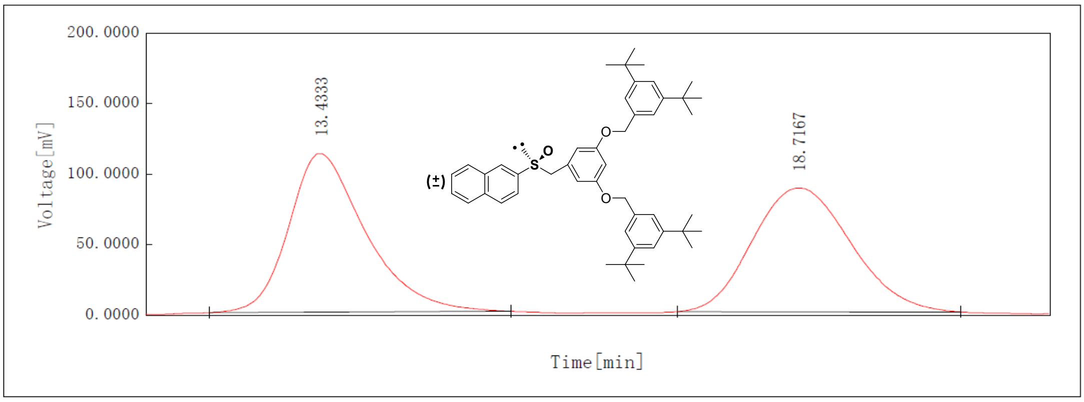
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	21.6500	1687.8589	BB	39.3128
2	24.6500	2605.5457	BB	60.6872
The Total		4293.4047		

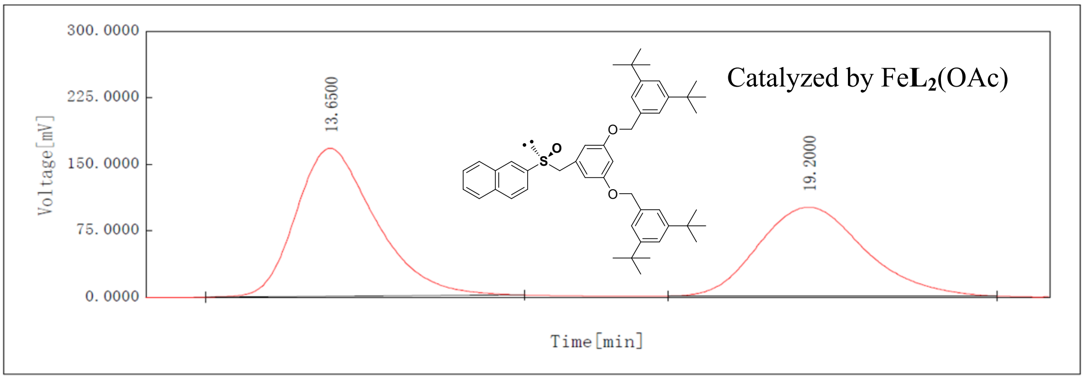

Catalyzed by Fe**L**$_2$(OAc)


Catalyzed by **2**

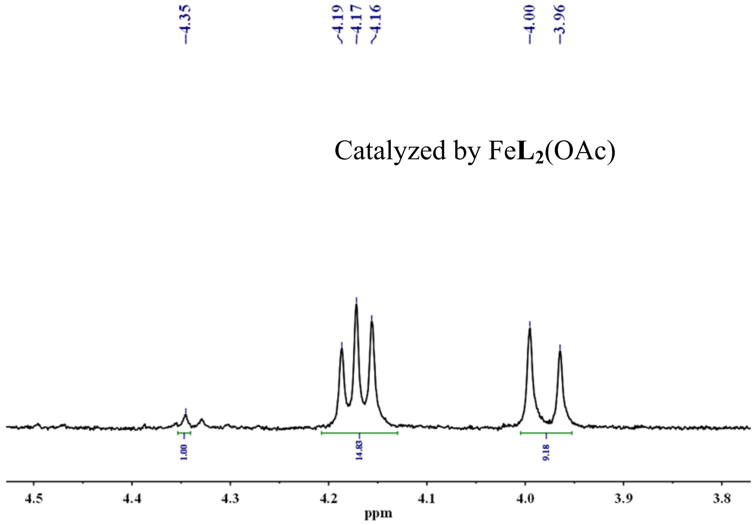
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	21.4167	4602.6508	BB	45.3768
2	24.3167	5540.5198	BB	54.6232
The Total		10143.1706		


Catalyzed by **2**





Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	13.6500	10725.6951	FF	55.6065
2	19.2000	8562.8577	FF	44.3935
The Total		19288.5528		



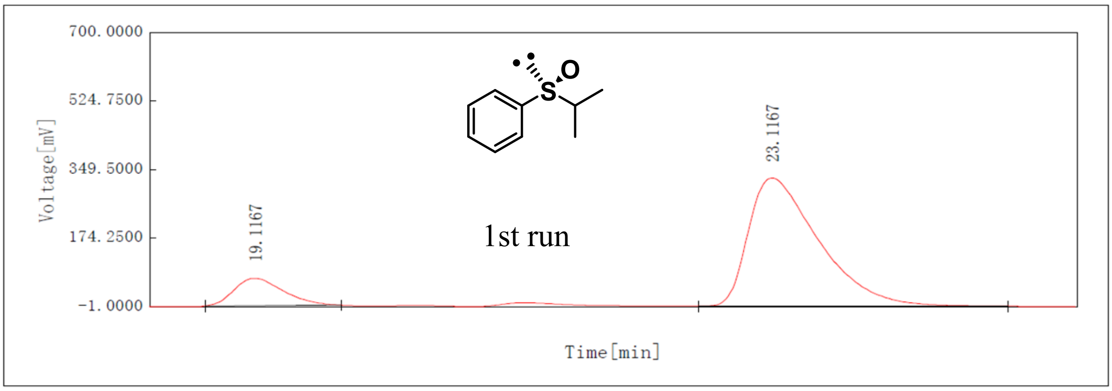
17. Table S8. Recycling study of 2 in catalysis

c

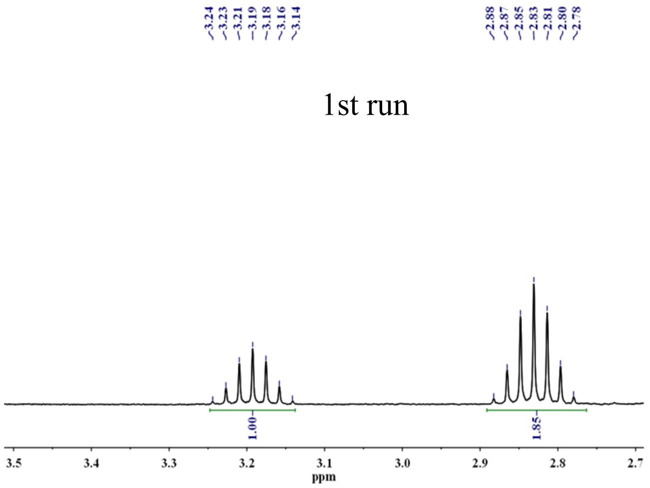
	Conv (%)	Selec (%)	ee (%)

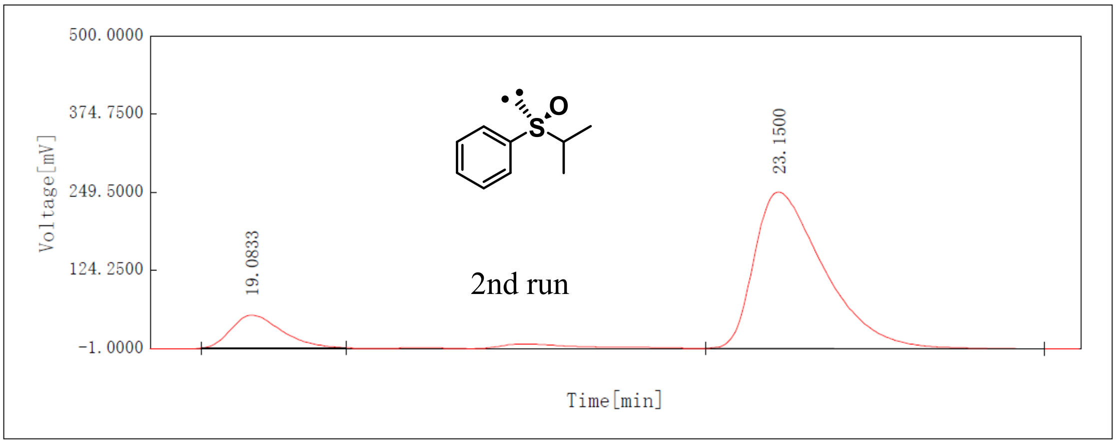
1st run	100	64.9	74
2nd run	100	65.4	73.7
3rd run	100	65.2	73.9

HPLC and ^{1}H NMR data

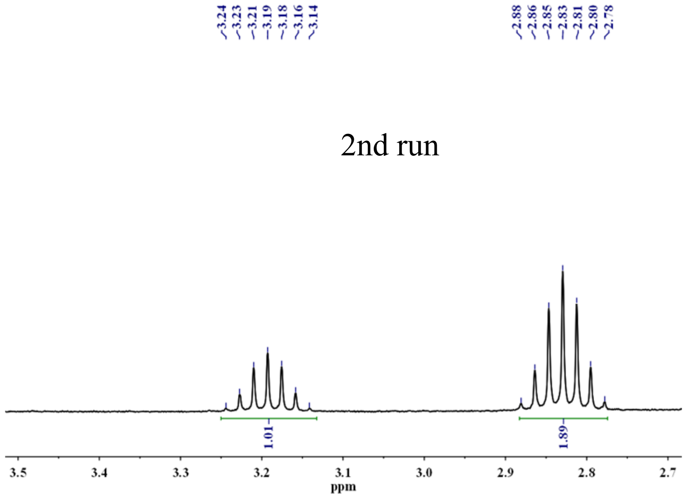


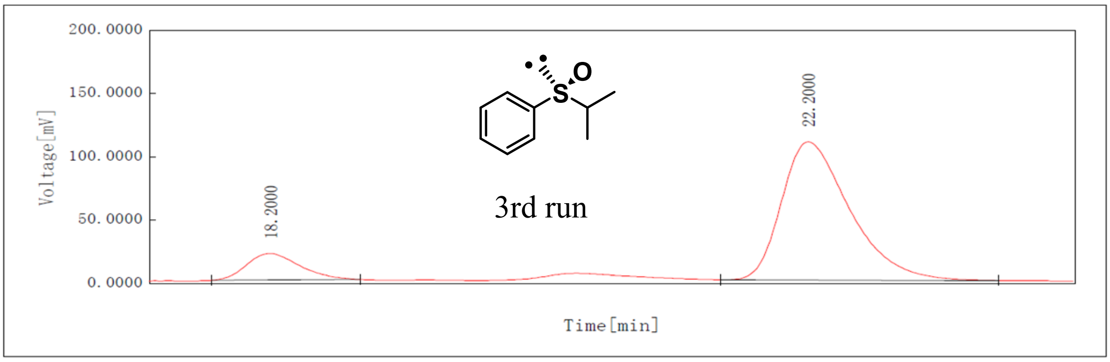
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	19.1167	1851.4549	FF	13.0226
2	23.1167	12365.8202	FF	86.9774
The Total		14217.2751		





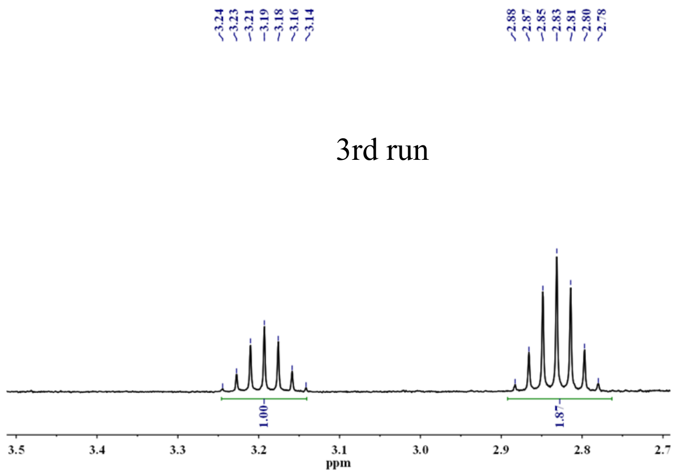
Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	19.0833	1412.9475	BB	13.1261
2	23.1500	9351.4621	FF	86.8739
The Total		10764.4096		





Serial Number	Retention Time [min]	Area [mAbs*s]	Type	Area %
1	18.2000	577.4867	BB	13.0627
2	22.2000	3843.4007	FF	86.9373

The Total		4420.8873		



3rd run