Supporting Information for

Controlled Structures of a 1D Chiral Metallosalen Polymer by Photo- and Solvent-Induced Partial Depolymerization

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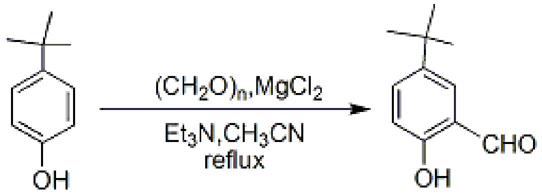
1. Materials and General Procedures.

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) spectrum was recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer.. ^{1}H and ^{13}C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 100.63 MHz. Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 ^{o}C min^{-1} 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. Electrospray ionization mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase. UV-vis spectra were obtained using a Varian Cary 500 spectrophotometer. Fluorescent spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. CD spectra were measured using a Jasco J-725 spectropolarimeter. Gel permeation chromatography (GPC) analyses of polymer samples were carried at 30°C using $CHCl_3$ as eluent on a Shimadzu LC-20AD instrument and calibrated using monodispersedpolystyrene standards at a flow rate of 1.0 mL/min. Number-average molecular weights and polydispersities of polymers are given relative to PS standards.

X-ray Crystallography. Single-crystal XRD data for the compounds was collected on on a Bruker Smart 1000 CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at room temperature. 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). The teritiary carbons of the t-butyl groups of the ligand and the CH_3 group of methanol were found to be disordered or seriously disordered, however, we failed to model the disordered sites by using different occupancies, all of which led to extremely high thermal parameters and/or unreasonable bond lengths. So, the bond lengths involving C14, C32, C56 and C74 in **1** and **2**, as well as those of guest MeOH molecules in **2** were constrained to be reasonable values. In both complexes, the guest molecules and H-atoms were refined isotropically, while all other atoms were refined anisotropically. Crystal data and details of the data collection are given in **Table S1**. The selected bond distances and angles are presented in **Tables S2**-**S3**.

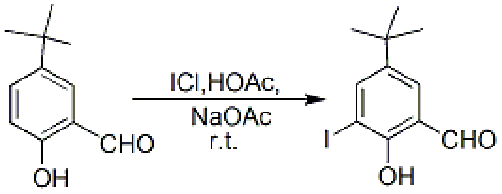
2. Synthesis of H_2L

5-tert-Butylsalicylaldehyde:



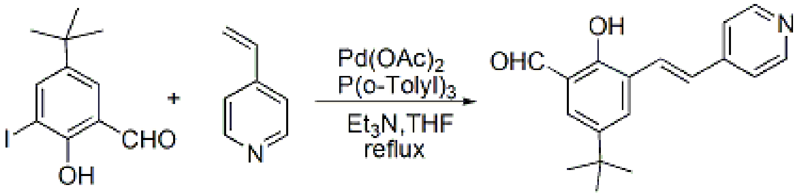
A 500ml side arm round bottom flask was placed under a nitrogen atmosphere and charged with the appropriate phenol (100 mmol) and dry acetonitrile (200ml). Dry triethylamine (52.2 ml, 375mmol), anhydrous $MgCl_2$ (14.28 g, 150 mmol) was added and the solution was stirred for 15 min. Dry paraformaldehyde (20.25 g, 675 mmol) was added. The solution was heated at reflux temperature under nitrogen overnight. The solution was allowed to cool to room temperature and added to 5% aq. HCl (800 ml) followed by stirring for 30 min. This was extracted with diethyl ether (7*50 ml) and the ether fractions collected together and washed with saturated NaCl(aq) (3*50ml). The ether layer was dried over anhydrous $MgSO_4$ followed by filtration. Volatiles were removed under reduced pressure to yield the corresponding salicylaldehydes (17.47 g, 106mmol,98%).^{1}HNMR ($CDCl_3$) δ : 10.86 (s, 1H, ArOH), 9.87 (s, 1H, HC=O), 7.57 (dd, 1H, ArH), 7.50 (d, 1H, ArH), 6.92 (d, 1H, ArH), 1.31 (s, 9H,CMe_3).

5-*tert*-Butyl-3-iodosalicylaldehyde



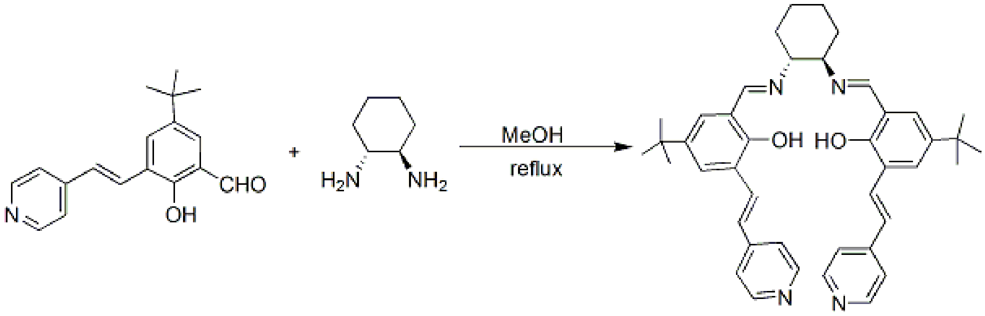
5-*tert*-Butylsalicylaldehyde (1.63 g, 9.92 mmol) and NaOAc (0.813 g, 9.92 mmol)was dissolved in glacial acetic acid (10 mL) in a 100 ml round bottomed flask. Iodine monochloride (2.26 g, 13.9 mmol), dissolved in glacial acetic acid (15 mL), was added dropwise to the solution and the reaction mixture was stirred overnight.,then poured into water (100 mL). The crude reaction mixture was extracted with CH_2Cl_2 (3 × 25 mL), the organic layers were washed with sodium thiosulfate, dried over $MgSO_4$ and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (silica gel, hexane) to yield the product (2.85 g, 9.22 mmol, 92%) as a pale yellow solid after evaporation of the solvent; ^{1}HNMR ($CDCl_3$) δ:11.63 (s, 1H, ArOH), 9.75 (s, 1H, HC=O), 8.00 (d, 1H, ArH), 7.53 (d, 1H, ArH), 1.32 (s, 9H,CMe_3).

5-*tert*-butyl-3-(4-vinyl-pyridyl) salicylaldehyde:



A 250mL round bottom flask was placed under a nitrogen atmosphere and charged with the 5-*tert*-Butyl-3-iodosalicylaldehyde(6.08g, 20mmol), 4-vinyl pyridine(2.63g, 25mmol), Tris(2-methylphenyl)phosphine (608mg, 2mmol), Pd(OAc)$_2$ (224mg,1mmol), Et$_3$N(30ml) and THF(80ml), the reaction mixture was refluxed and stirred 24h. Then the solvent was evaporated in vacuo and extracted with CH$_2$Cl$_2$ (3 × 50 mL), washed with saturated NaCl(aq). Dried over MgSO$_4$ and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (silica gel, hexane: ethyl acetate=10:1) to yield the product (4.33g, 15.4 mmol, 77%) as a yellow solid after evaporation of the solvent; ^{1}HNMR (CDCl$_3$) δ:11.52 (s, 1H, ArOH) , 9.91 (s, 1H, HC=O) , 8.58 (d, 2H, pyridylH) , 7.83 (d, 1H, ArH) , 7.60 (d, 1H, vinylH) , 7.51 (d, 1H, ArH) , 7.41 (d, 2H, pyridylH), 7.20 (d, 1H, vinylH) ,1.37 (s, 9H, CMe$_3$). ^{13}CNMR (CDCl$_3$) δ:197.23, 157.76, 150.37, 145.16, 142.91, 132.29, 130.77, 127.99, 127.06, 124.84, 121.17, 120.61, 34.20, 31.51. ESI-MS: m/z 280.6 (Calcd *m/z* 280.14 for [**L**+H]$^+$) (see Figure S6a).

(*R,R*)-(-)-*N,N*'-Bis(3-*tert*-butyl-5-(E)-(4-vinyl-pyridyl) salicylidene)-1,2-diamino-cyclohexane:



(R,R)- 1, 2-diamino-cyclohexane (74.3mg, 0.65 mmol) was slowly added, under stirring, to a warm solution of 5-*tert*-butyl-3-(4-vinyl-pyridyl) salicylaldehyde(0.371 g, 1.32 mmol) in EtOH (20 ml). The reaction mixture was refluxed for 24 h, then it was allowed to cool to room temperature. extracted with dichloromethane, The organic layer was collected, dried over Na$_2$SO$_4$, then evaporated to dryness give the product as a yellow solid (0.354 g, 85%);^{1}HNMR (CDCl$_3$) δ:8.54 (d, 4H, pyridylH) , 8.31 (s, 2H, HC=N) ,7.63 (d, 2H, vinylH) , 7.55 (d, 2H, ArH) , 7.38 (d, 4H, pyridylH) , 7.16 (d, 2H, vinylH) , 7.14 (d, 2H, ArH), 3.36 (d, 2H, cyclohexadecylH), 2.14-1.47 (m, 8H, cyclohexadecylH) ,1.26 (s, 18H, CMe$_3$). ^{13}CNMR (CDCl$_3$) δ:166.39, 157.73, 150.23, 145.66, 141.34, 129.11, 128.56, 127.68, 125.63, 123.89, 121.07, 118.48,72.78, 34.22, 33.36, 31.56, 24.40. ESI-MS: m/z 641.4 (Calcd *m/z* 640.38 for [**L**+H]$^+$) (see **Figure S6b**).

3. Synthesis of compounds 1 and 2

Synthesis of [Zn**L**] **1:** A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (7.3mg, 0.04 mmol) and H_2**L** (25.6mg, 0.04 mmol) was placed in a small vial containing DMF (1 mL), H_2O (0.1 mL) and i-BuOH (1 mL). The vial was sealed, heated at 80 ºC for one days, and allowed to cool to room temperature, and light yellow strip-like crystal was collected, washed with ether, and dried in air. Yield: 13.5 mg, 63 % based on Zn. Elemental analysis (%) Calcd for $C_{42}H_{46}N_4O_2Zn$: C, 71.63; H, 6.58; N, 7.96; Found: C 71.43, H 6.53, N 7.88. IR (KBr, cm^{-1}): 2949.92(m), 2860.45((m), 1626.02(s), 1603.86(s), 1523.83(s), 1498.08(w), 1445.22(m), 1389.15(m), 1361.30(m), 1289.09(m), 1217.53(m), 1132.27(w), 1021.40(m), 977.81(m), 871.51(m), 779.09(m), 728.01(w), 566.30(w), 542.92(m).

Synthesis of [Zn**L**]·MeOH **2:** A mixture of $Zn(NO)_3 \cdot 6H_2O$ (11.9mg, 0.04 mmol) and H_2**L** (25.6mg, 0.04 mmol) was placed in a small vial containing DMF (1 mL), H_2O (0.1 mL) and MeOH (1 mL). The vial was sealed, heated at 80 ºC for one days, and allowed to cool to room temperature, and light yellow strip-like crystal was collected, washed with ether, and dried in air. Yield: 16.0 mg, 57 % based on Zn. Elemental analysis (%) Calcd for $C_{43}H_{50}N_4O_3Zn$: C, 70.15; H, 6.84; N, 7.61; Found: C 70.00, H 6.78, N 7.56. IR (KBr, cm^{-1}): 3418.56(w), 2949.85(m), 2861.53(w), 2364.83(w), 1626.75(s), 1598.78(s), 1524.76(m), 1443.36(m), 1389.88(w), 1361.58(m). 1289.02(w), 1218.16(m), 1134.24(w), 1020.48(w), 973.28(w), 864.36 (w), 777.93(w), 728.59(w), 524.37(w).

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

Identification code	**1**	**2**
Empirical formula	C84H92N8O4Zn2	C86H100N8O6Zn2
Formula weight	1408.40	1472.48
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
Unit cell dimensions	a = 12.616(3) Å b = 25.145(5) Å c = 12.892(3) Å beta = 108.88(3) º	17.428(4) 13.517(3) 17.588(4) 100.24(3)
Volume (Å^3), Z	3869.6(13), 2	4077.5(14), 2
Density (calculated) (mg/m^3)	1.209	1.199
Absorption coefficient (mm^{-1})	0.673	0.644
F(000)	1488	1560
Theta range for data collection (º)	3.12 to 25.00	3.01 to 25.00
Limiting indices	$-14\leq h\leq 14$, $-29\leq k\leq 29$, $-15\leq l\leq 15$	$-20\leq h\leq 20$, $-16\leq k\leq 14$, $-20\leq l\leq 20$
Reflections collected	21525	31370
Independent reflections	11968 (Rint = 0.0649)	12720 (Rint = 0.0650)
Completeness to theta	25.00º, 95.7 %	25.00º, 99.6 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	11968/ 8 / 787	12720 / 20 / 796
Goodness-of-fit on F^2	1.019	1.065
Final R indices [I>2sigma(I)]	R1=0.0744, wR2=0.1250	R1=0.0720 wR2=0.1859
R indices (all data)	R1=0.1458, wR2=0.1501	R1=0.1286, wR2=0.2292
Absolute structure parameter	0.025(18)	0.03(2)
Largest diff. peak and hole (e.Å^{-3})	0.303 and -0.331	0.539 and -0.511

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

Zn(1)-O(4)	1.946(5)
Zn(1)-O(3)	1.946(5)
Zn(1)-N(3)	2.055(7)
Zn(1)-N(5)#1	2.088(4)
Zn(1)-N(2)	2.096(6)
Zn(2)-O(2)	1.950(5)
Zn(2)-O(1)	1.958(5)
Zn(2)-N(7)	2.063(6)
Zn(2)-N(6)	2.074(6)
Zn(2)-N(1)	2.088(4)
O(4)-Zn(1)-O(3)	92.2(2)
O(4)-Zn(1)-N(3)	88.0(3)
O(3)-Zn(1)-N(3)	160.4(3)
O(4)-Zn(1)-N(5)#1	110.5(2)
O(3)-Zn(1)-N(5)#1	98.2(2)
N(3)-Zn(1)-N(5)#1	100.1(2)
O(4)-Zn(1)-N(2)	140.2(2)
O(3)-Zn(1)-N(2)	87.4(2)
N(3)-Zn(1)-N(2)	80.1(3)
N(5)#1-Zn(1)-N(2)	108.9(2)
O(2)-Zn(2)-O(1)	91.6(2)
O(2)-Zn(2)-N(7)	150.9(3)
O(1)-Zn(2)-N(7)	87.7(3)
O(2)-Zn(2)-N(6)	87.3(3)
O(1)-Zn(2)-N(6)	152.9(2)
N(7)-Zn(2)-N(6)	80.4(3)
O(2)-Zn(2)-N(1)	102.9(2)
O(1)-Zn(2)-N(1)	106.8(2)
N(7)-Zn(2)-N(1)	105.1(2)
N(6)-Zn(2)-N(1)	99.8(2)

Symmetry transformations used to generate equivalent atoms:

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

6. **Table S3**. Selected bond lengths [Å] and angles [º] for **2**

Zn(1)-O(1)	1.964(2)
Zn(1)-O(2)	1.993(2)
Zn(1)-N(2)	2.057(3)
Zn(1)-N(3)	2.081(2)
Zn(1)-N(1)#1	2.1058(15)
Zn(2)-O(4)	1.960(2)
Zn(2)-O(3)	1.972(2)
Zn(2)-N(7)	2.054(2)
Zn(2)-N(5)#2	2.0697(15)
Zn(2)-N(6)	2.090(2)
O(1)-Zn(1)-O(2)	97.57(9)
O(1)-Zn(1)-N(2)	87.54(9)
O(2)-Zn(1)-N(2)	165.93(9)
O(1)-Zn(1)-N(3)	145.04(9)
O(2)-Zn(1)-N(3)	88.38(9)
N(2)-Zn(1)-N(3)	80.09(9)
O(1)-Zn(1)-N(1)#1	101.94(7)
O(2)-Zn(1)-N(1)#1	93.51(7)
N(2)-Zn(1)-N(1)#1	98.26(8)
N(3)-Zn(1)-N(1)#1	112.08(8)
O(4)-Zn(2)-O(3)	93.58(8)
O(4)-Zn(2)-N(7)	90.97(9)
O(3)-Zn(2)-N(7)	151.69(9)
O(4)-Zn(2)-N(5)#2	95.11(7)
O(3)-Zn(2)-N(5)#2	100.73(7)
N(7)-Zn(2)-N(5)#2	106.67(8)
O(4)-Zn(2)-N(6)	156.44(9)
O(3)-Zn(2)-N(6)	86.64(9)
N(7)-Zn(2)-N(6)	78.37(9)
N(5)#2-Zn(2)-N(6)	108.01(8)

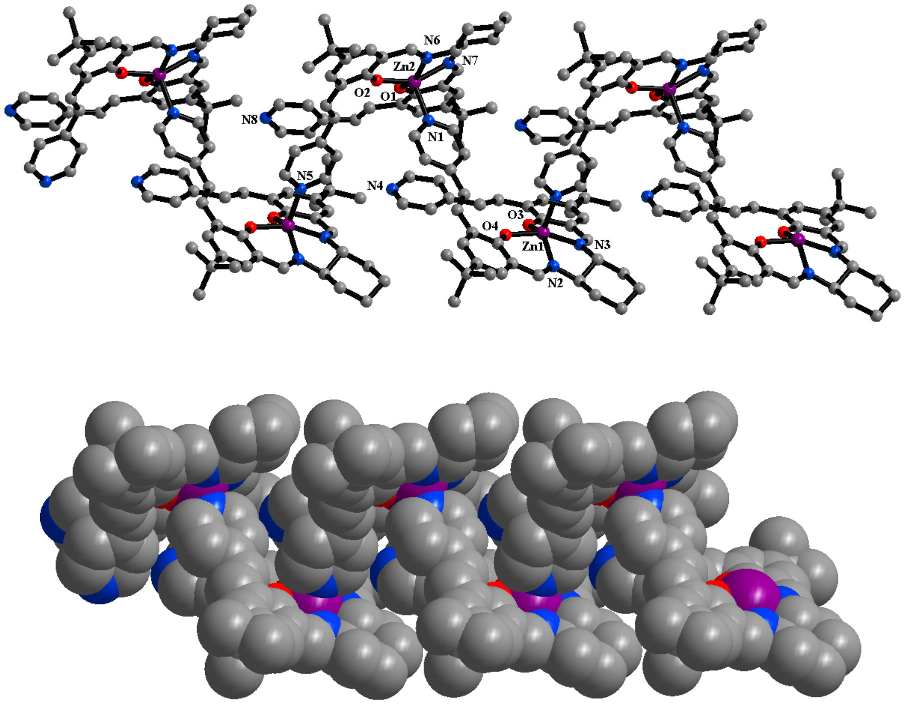
Hydrogen bonds

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5)...N(8)#5	0.82	2.03	2.732(10)	143.9
O(6)-H(6)...N(4)#6	0.82	2.06	2.869(6)	166.7

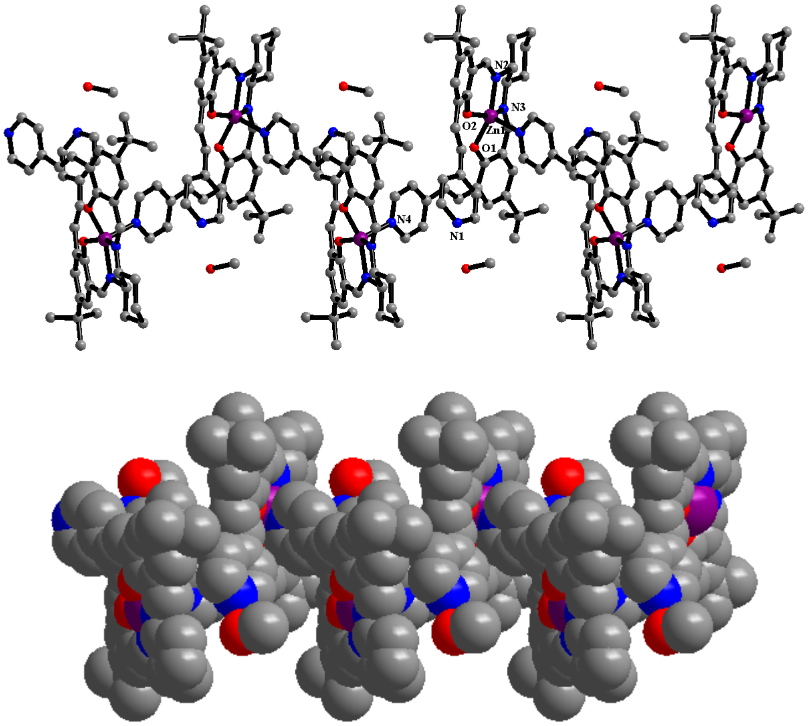
Symmetry transformations used to generate equivalent atoms:

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

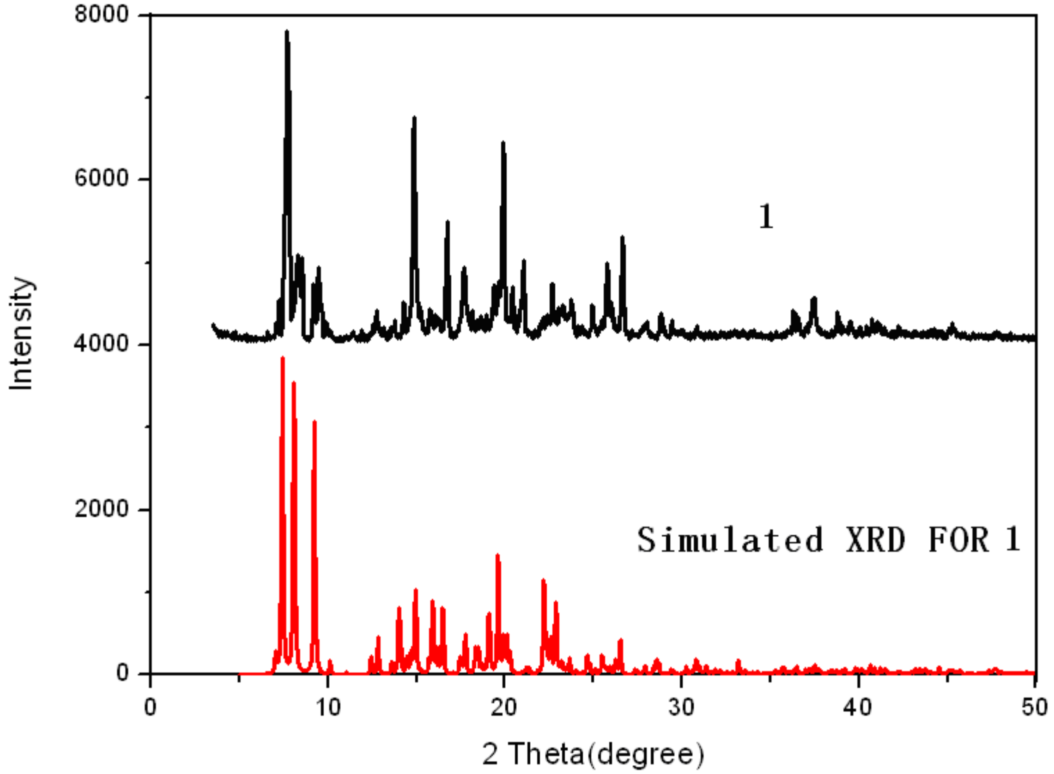
7. Figure S1. Ball-and-stick (top) and space-filling (bottom) representations of a 1D zigzag chain of **1**.



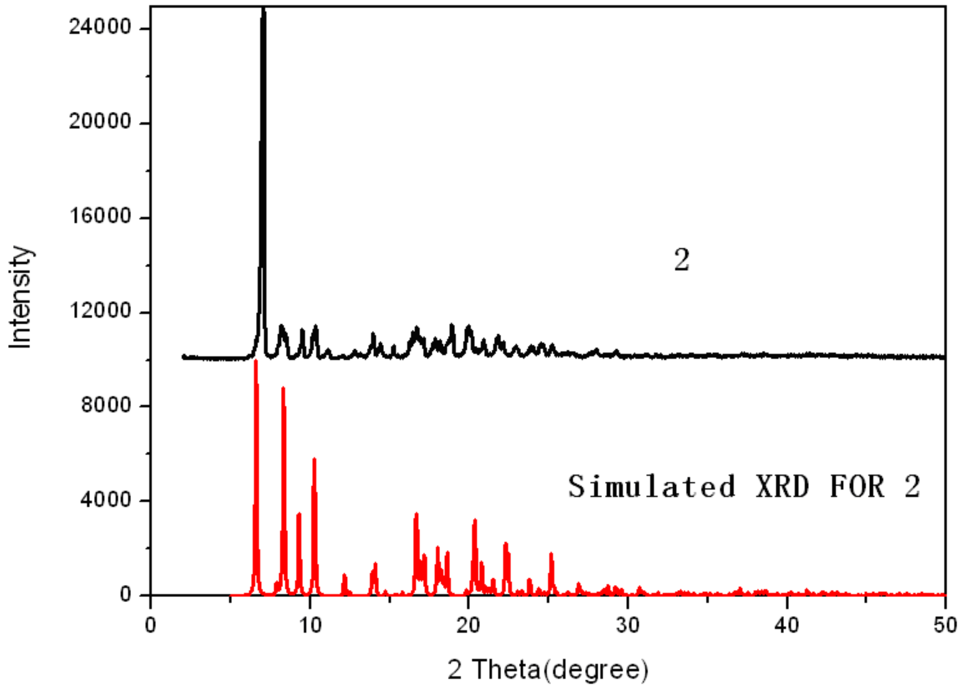
8. Figure S2. Ball-and-stick (top) and space-filling (bottom) representations of a 1D helix chain of **2**-MeOH.



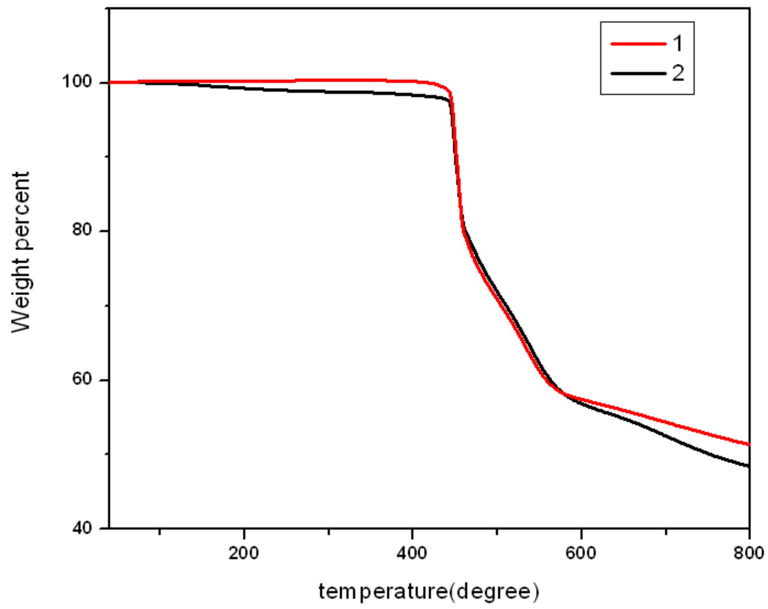
9**. Figure S3**. The PXRD patterns of **1** and the simulated PXRD pattern of **1**.



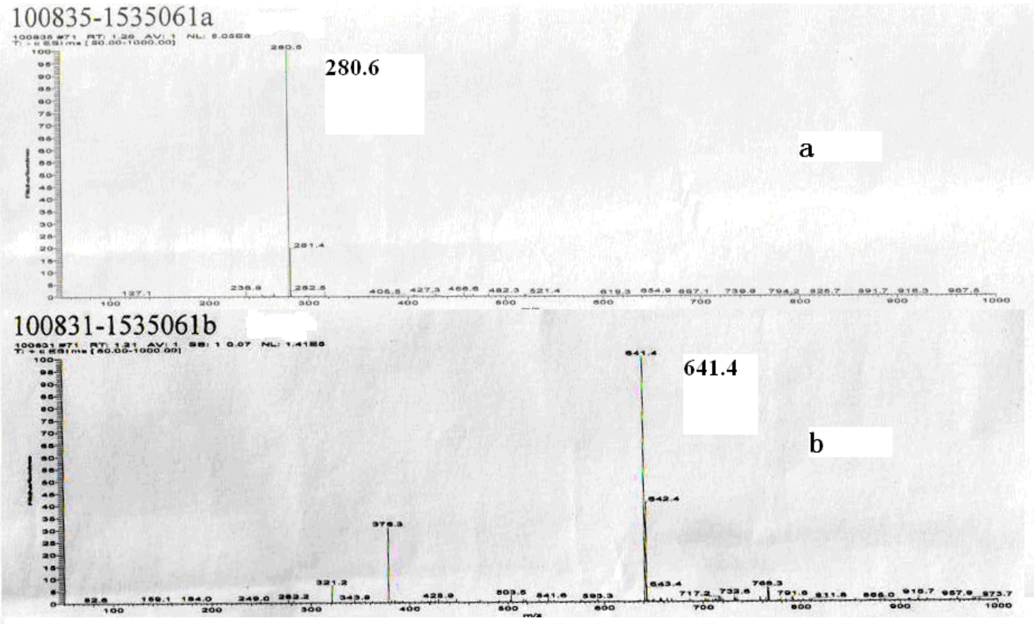
10**. Figure S4**. The PXRD patterns of **2** and the simulated XRD of **2**.



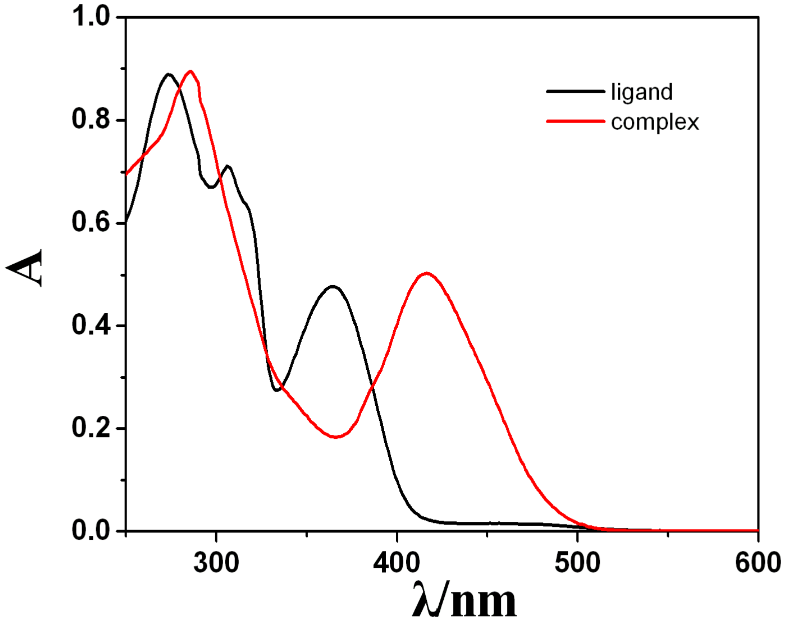
11. **Figure S5.** TGA curves of **1 and 2**



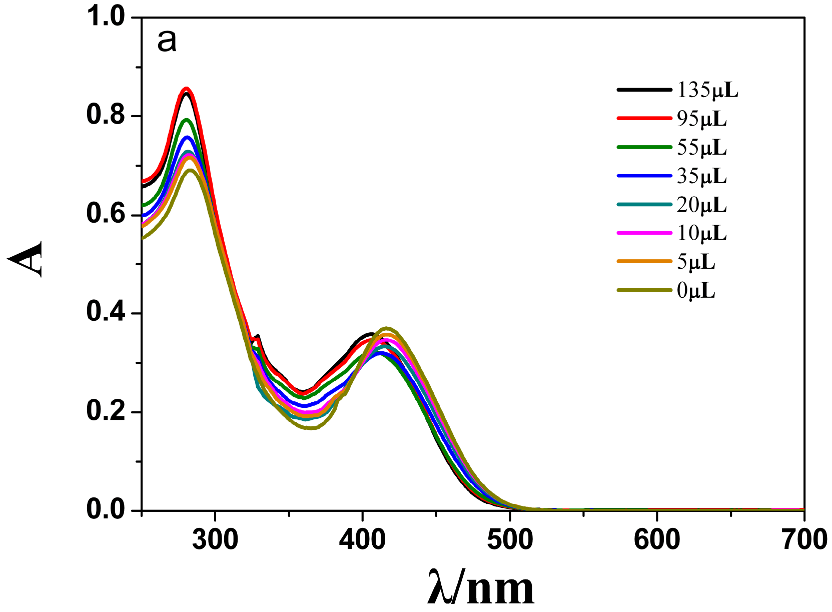
12. Figure S6. ESI-MS of (a) 5-*tert*-butyl-3-(4-vinyl-pyridyl) salicylaldehyde and (b) H_2**L**.

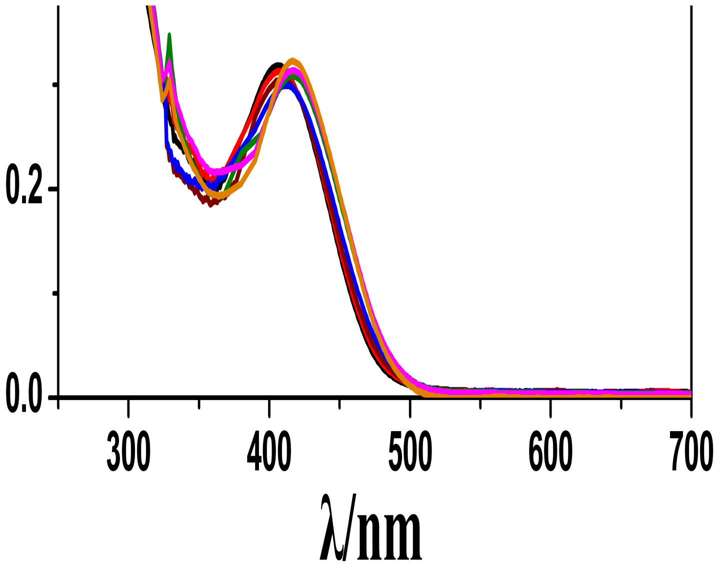


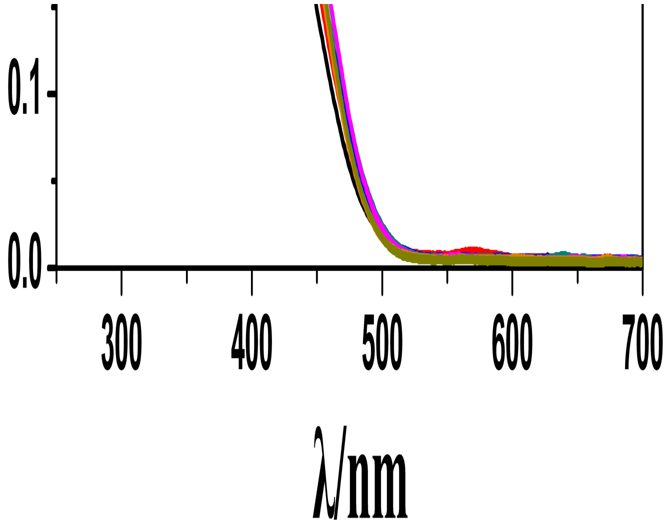
13．Figure S7. The UV-vis spectra of polymer **1** and H_2**L** (The spectra were measured in a 1 cm quartz cell at room temperature).



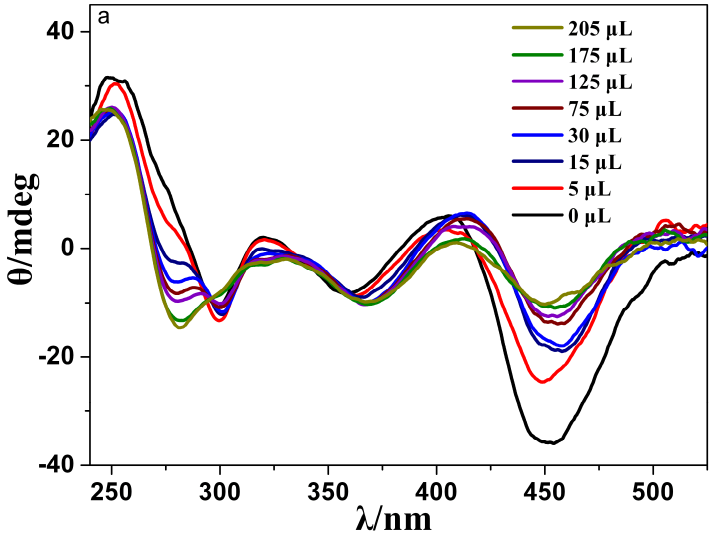
14. Figure S8. The changes in UV-Vis spectra of polymer **1** in $CHCl_3$ upon continuous addition of (a) methanol, (b) ethanol and (c) isopropyl alcohol. The spectra were measured in a 1 cm quartz cell at room temperature [1.4×10^{-4} M for (a) and 4.6×10^{-4} M for (b) and (c)].

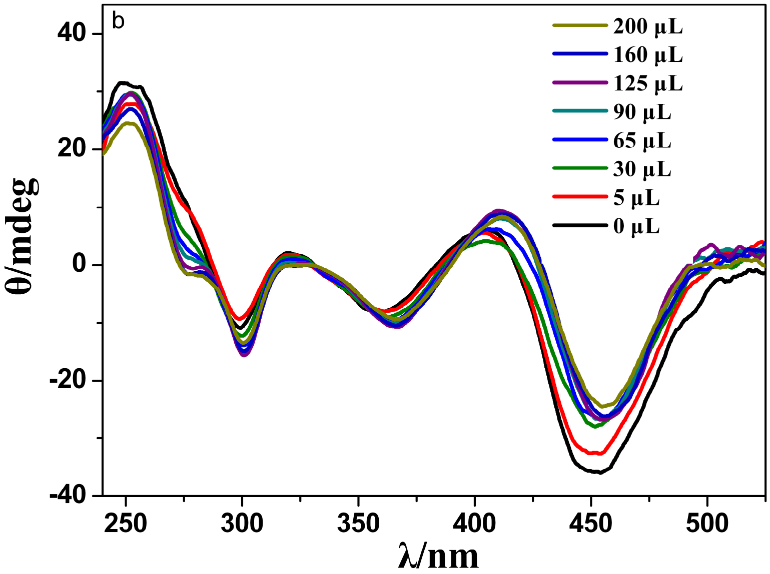



0.2
0.0
300
400
500
600
700
λ/nm


0.1
0.0
300
400
500
600
700
λ/nm

15. Figure S9. The changes in CD spectra of polymer **1** in $CHCl_3$ upon continuous addition of (a) methanol, (b) ethanol and (c) isopropyl alcohol. The spectra were measured in a 0.1 cm quartz cell at room temperature [1.4×10^{-4} M for (a) and 4.6×10^{-4} M for (b) and (c)].





16. Figure S10. The changes in fluorescence spectra of polymer **1** in $CHCl_3$ upon continuous addition of (a) methanol, (b) ethanol and (c) isopropyl alcohol. The spectra were measured in a 0.1 cm quartz cell at room temperature [1.4×10^{-4} M for (a) and 4.6×10^{-4} M for (b) and (c)].

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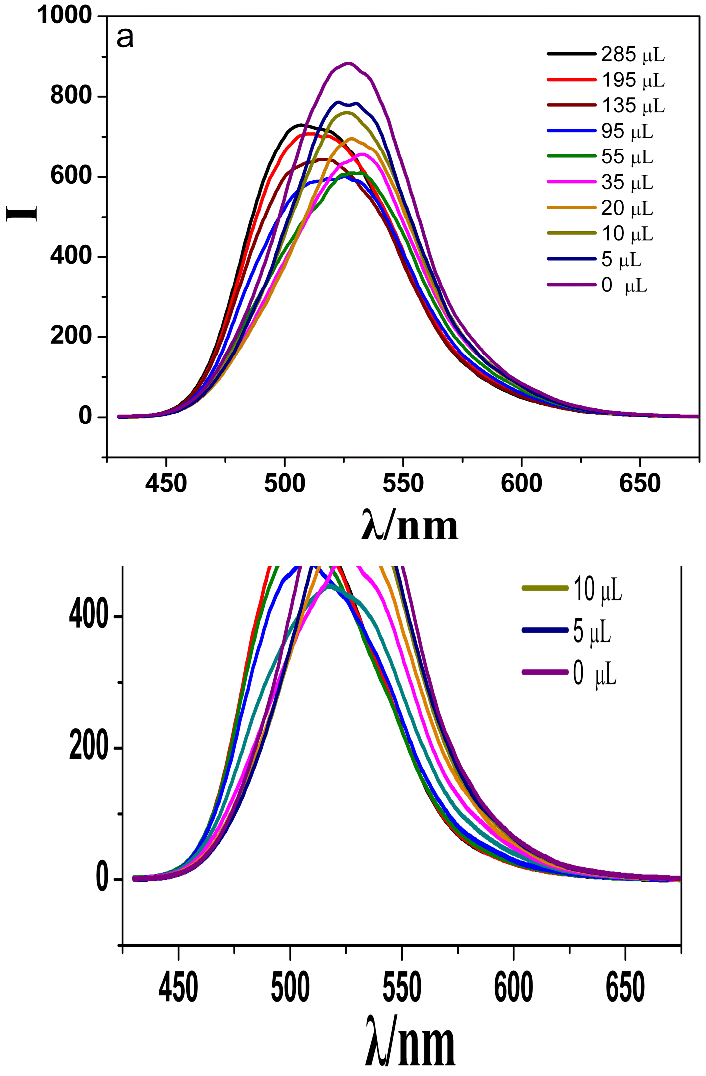
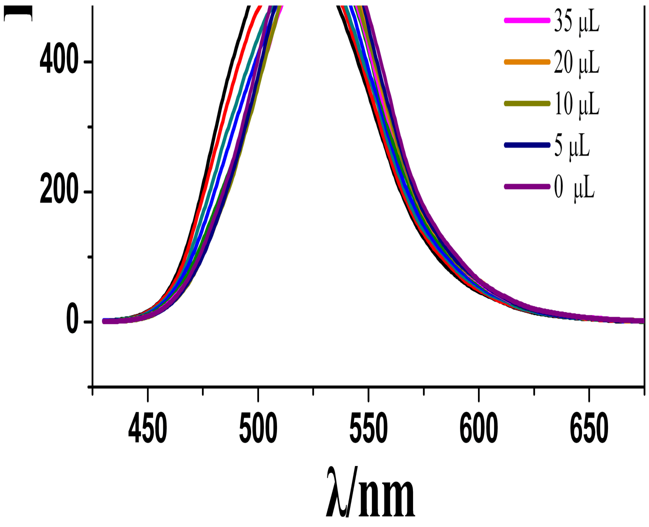
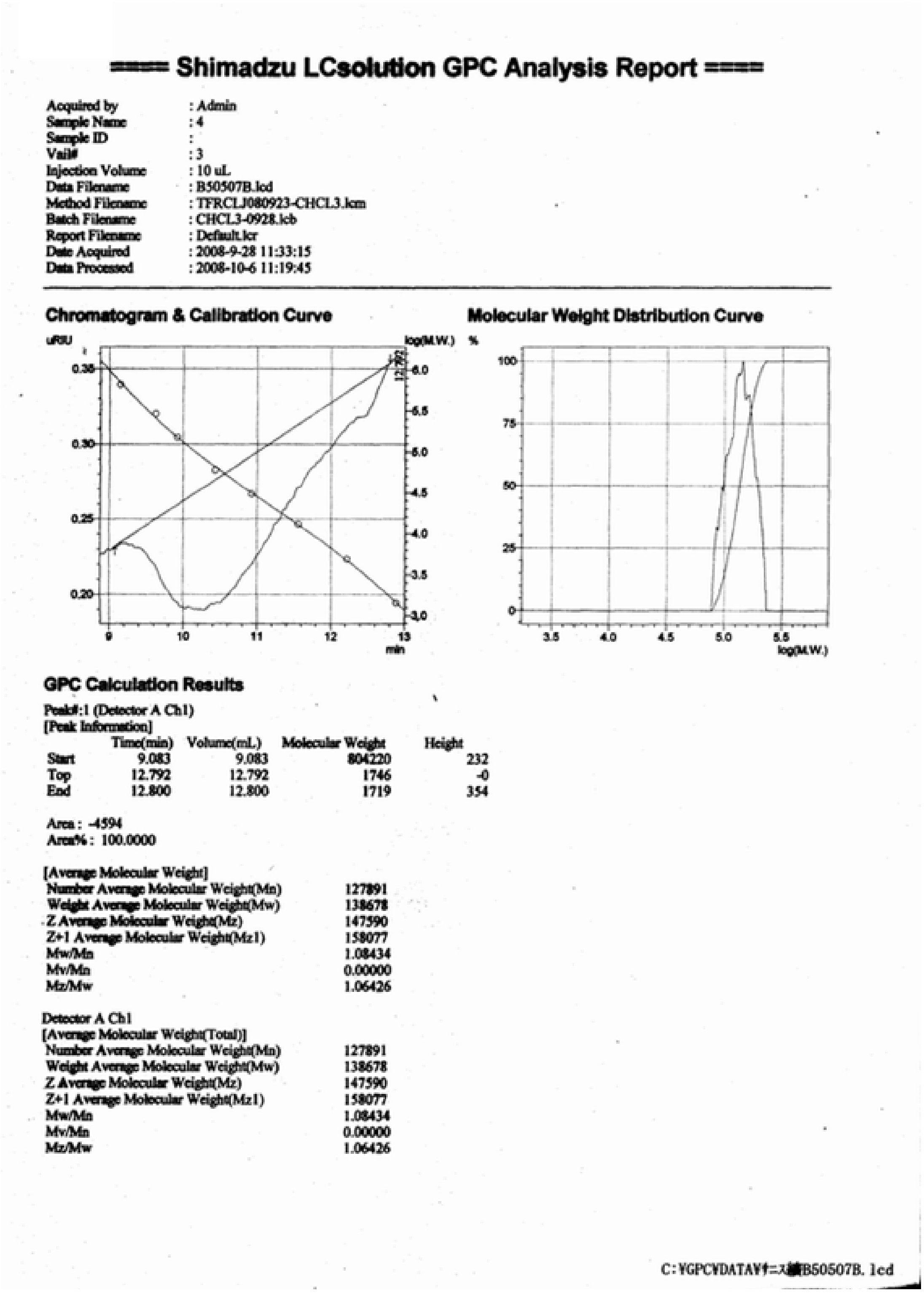




17. Figure S11. GPC of **1** before and after sunlight irradiation.



==== Shimadzu LCsolution GPC Analysis Report ====

Acquired by : Admin
Sample Name : 4
Sample ID :
Vail# : 3
Injection Volume : 10 uL
Data Filename : B50507B.lcd
Method Filename : TFRCLJ080923-CHCL3.lcm
Batch Filename : CHCL3-0928.lcb
Report Filename : Default.lcr
Date Acquired : 2008-9-28 11:33:15
Data Processed : 2008-10-6 11:19:45

Chromatogram & Calibration Curve

Molecular Weight Distribution Curve

GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	9.083	9.083	804220	232
Top	12.792	12.792	1746	-0
End	12.800	12.800	1719	354

Area : -4594
Area% : 100.0000

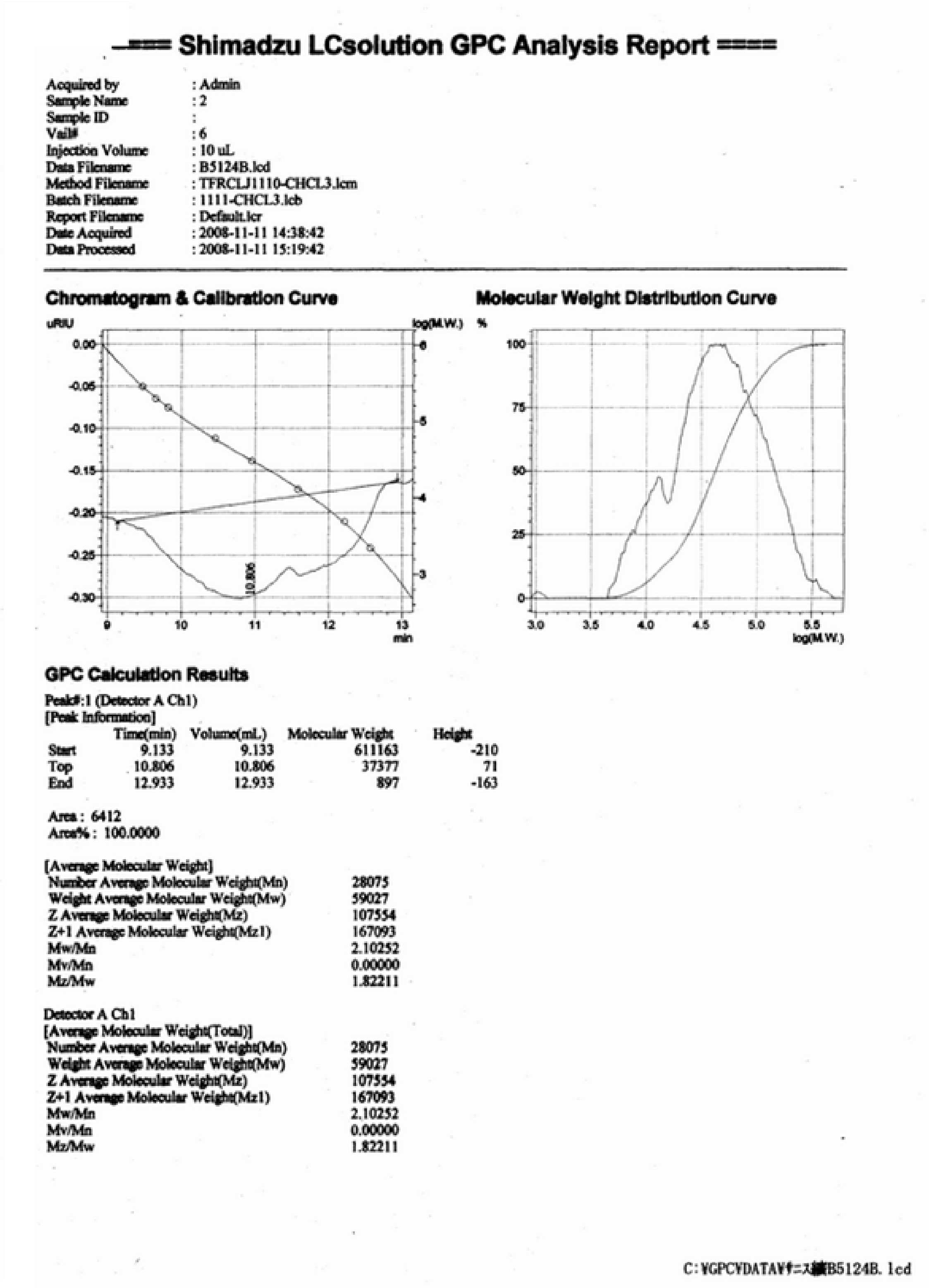
[Average Molecular Weight]

Number Average Molecular Weight(Mn)	127891
Weight Average Molecular Weight(Mw)	138678
Z Average Molecular Weight(Mz)	147590
Z+1 Average Molecular Weight(Mz1)	158077
Mw/Mn	1.08434
Mv/Mn	0.00000
Mz/Mw	1.06426

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	127891
Weight Average Molecular Weight(Mw)	138678
Z Average Molecular Weight(Mz)	147590
Z+1 Average Molecular Weight(Mz1)	158077
Mw/Mn	1.08434
Mv/Mn	0.00000
Mz/Mw	1.06426

C:¥GPC¥DATA¥[illegible]B50507B. lcd



=== Shimadzu LCsolution GPC Analysis Report ====

Acquired by : Admin
Sample Name : 2
Sample ID :
Vail# : 6
Injection Volume : 10 uL
Data Filename : B5124B.lcd
Method Filename : TFRCLJ1110-CHCL3.lcm
Batch Filename : 1111-CHCL3.lcb
Report Filename : Default.lcr
Date Acquired : 2008-11-11 14:38:42
Data Processed : 2008-11-11 15:19:42

Chromatogram & Calibration Curve

Molecular Weight Distribution Curve

GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	9.133	9.133	611163	-210
Top	10.806	10.806	37377	71
End	12.933	12.933	897	-163

Area : 6412
Area% : 100.0000

[Average Molecular Weight]

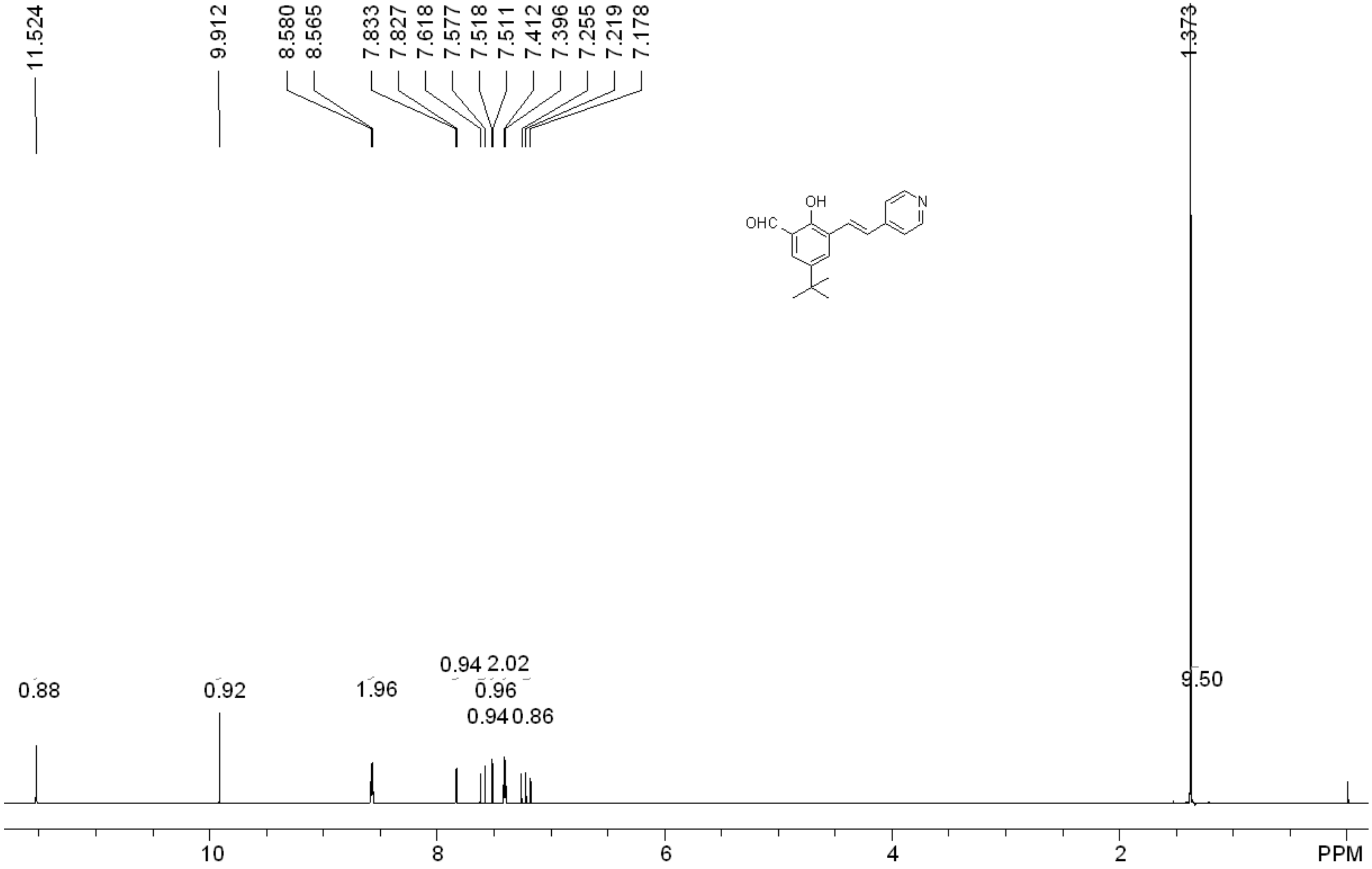
Number Average Molecular Weight(Mn)	28075
Weight Average Molecular Weight(Mw)	59027
Z Average Molecular Weight(Mz)	107554
Z+1 Average Molecular Weight(Mz1)	167093
Mw/Mn	2.10252
Mv/Mn	0.00000
Mz/Mw	1.82211

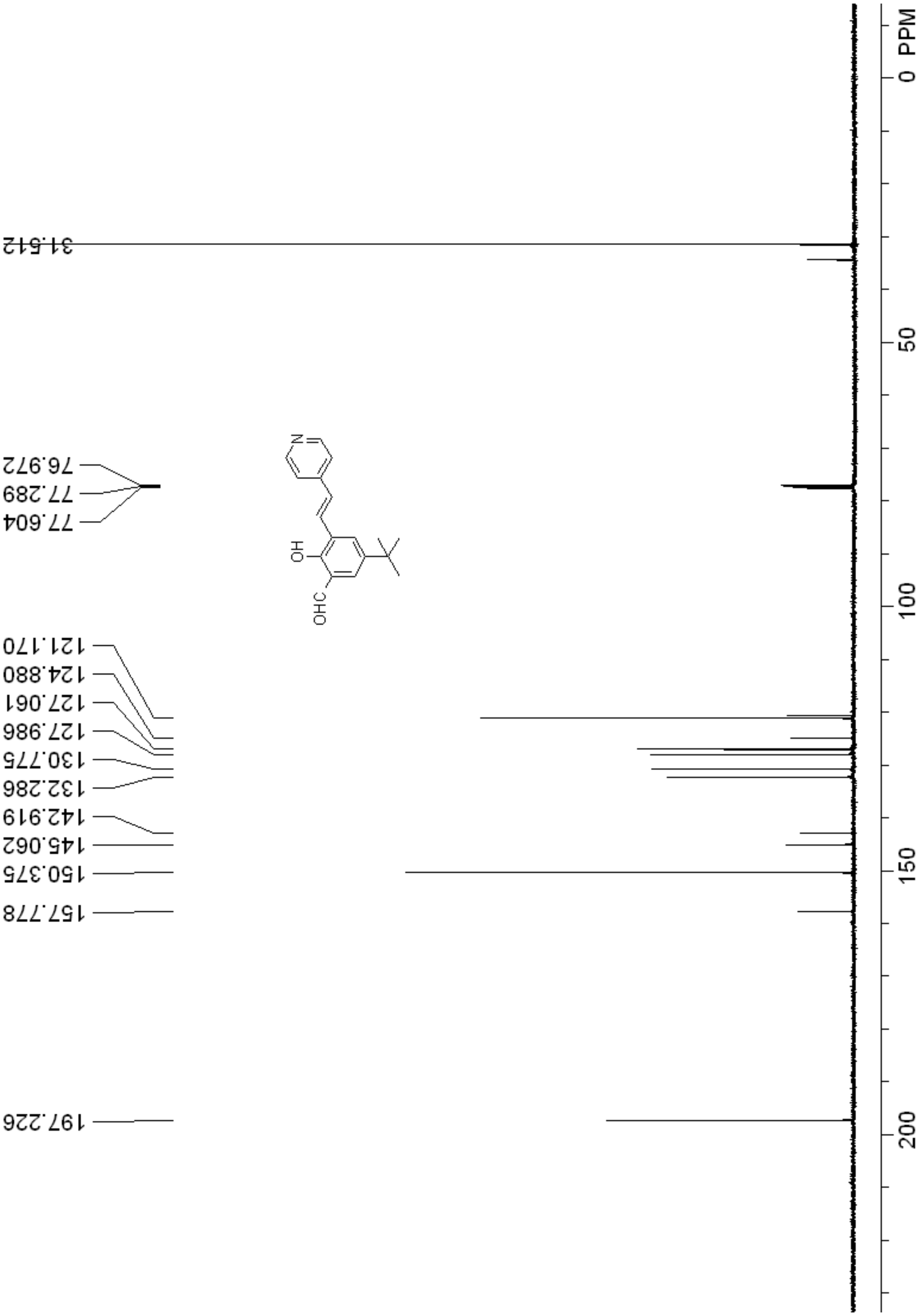
Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	28075
Weight Average Molecular Weight(Mw)	59027
Z Average Molecular Weight(Mz)	107554
Z+1 Average Molecular Weight(Mz1)	167093
Mw/Mn	2.10252
Mv/Mn	0.00000
Mz/Mw	1.82211

C:¥GPC¥DATA¥ｷ=ス[illegible]B5124B. lcd

18. Figure S12. H^1NMR,C^{13}NMR spectra of 5-tert-butyl-3-(4-vinyl-pyridyl) salicylaldehyde and the ligand **H_2L.**

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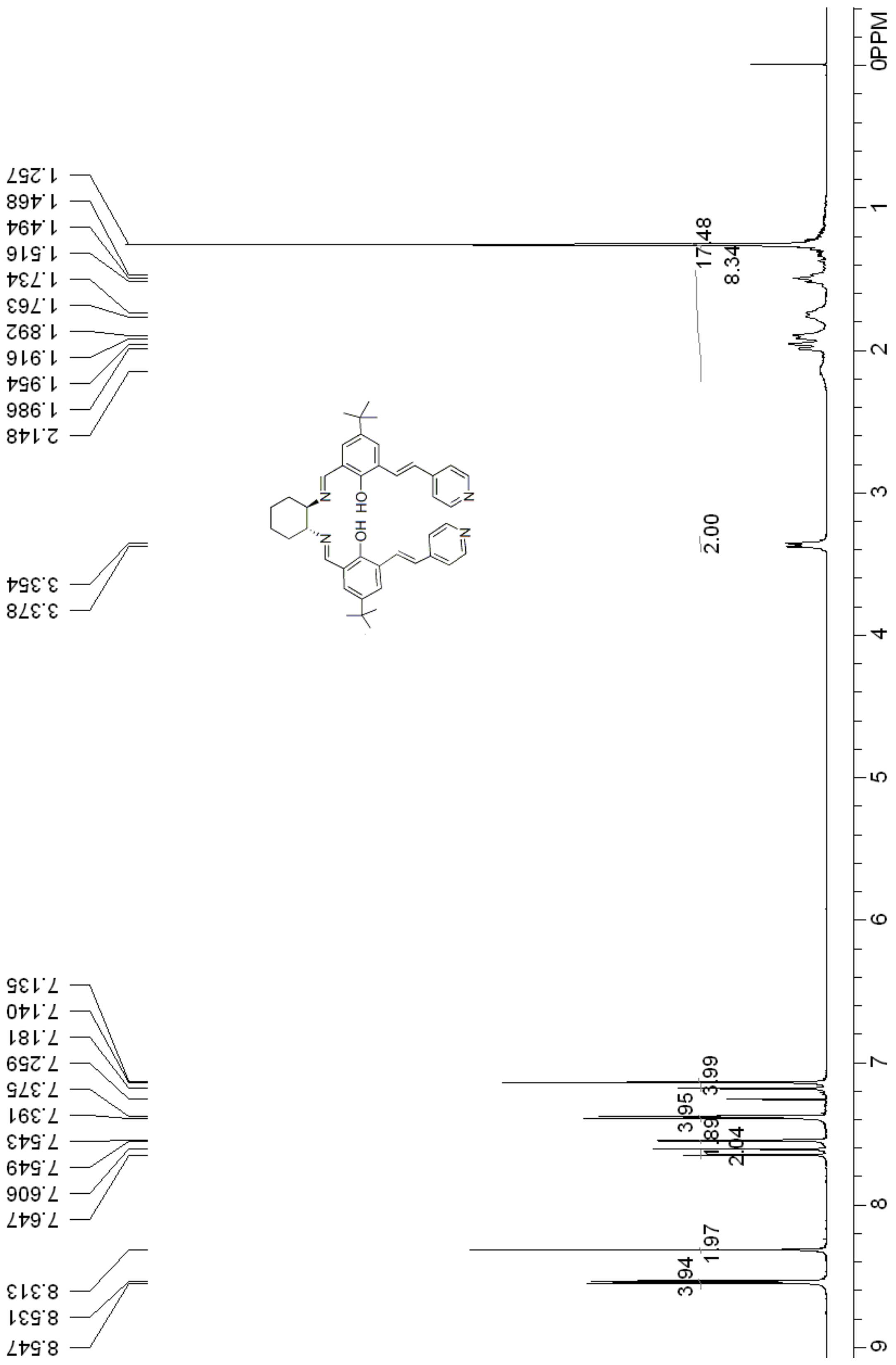
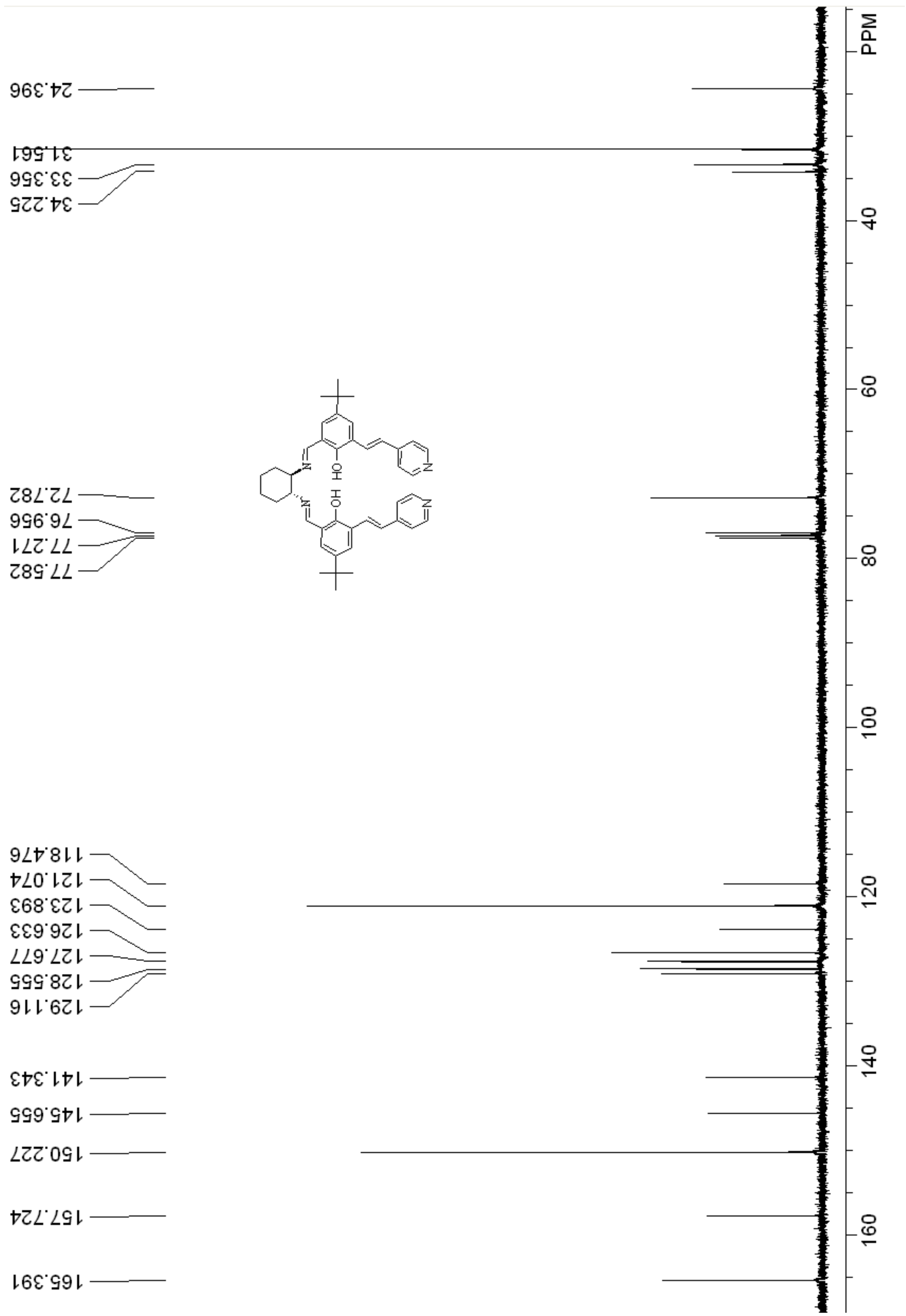
76.972
77.289
77.604
121.170
124.880
127.061
127.986
130.775
132.286
142.919
145.062
150.375
157.778
197.226
N
OH
OHC
0 PPM
50
100
150
200


1.257
1.468
1.494
1.516
1.734
1.763
1.892
1.916
1.954
1.986
2.148
3.354
3.378
7.135
7.140
7.181
7.259
7.375
7.391
7.543
7.549
7.606
7.647
8.313
8.531
8.547
17.48
8.34
2.00
3.99
3.95
1.89
2.04
1.97
3.94
0PPM
1
2
3
4
5
6
7
8
9
N
N
OH
HO
N
N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31.561
33.356
34.225
72.782
76.956
77.271
77.582
118.476
121.074
123.893
126.633
127.677
128.555
129.116
141.343
145.655
150.227
157.724
165.391
PPM
40
60
80
100
120
140
160
OH
OH
N
N
N
N