Electronic Supporting Information

for

Highly Active Self-immobilized FI-Zr Catalysts in a PCP Framework for Ethylene Polymerization

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Contents

Section 1. Materials and methods.

All manipulations involving air and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere (ultra-high purity) using either standard Schlenk techniques or glove box techniques. Solvents were dried and distilled using standard procedures. Reagents were purchased and used as received without further purification. $ZrCl_4(THF)_2$[S1], $Ph_3CB(C_6F_5)_4$[S2], 2-*tert*-butyl-4-acetylphenol[S3] and complex **3** bis[*N*-(3-*tert*-butylsalicylidene)-cyclohexylaminato]zirconium (IV) dichloride [S4] were prepared according to literature procedures. Polymerization grade ethylene was further purified by passage through columns of 5 A molecular sieves. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-300 NMR spectrometer, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Solid-state ^{13}C CP/MAS NMR measurements were recorded on a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 KHz and a CP contact time of 2 ms. Infrared spectra were recorded from 400 to 4000 cm^{-1} on a Nicolet FT-IR 360 spectrometer by using KBr pellets. ESI-MS was carried out on a Thermo Fisher ITQ1100 ion trap gas chromatography-mass spectrometry. Elemental analyses were carried out on an Elementar model vario EL cube analyzer. Field emission scanning electron microscopy was performed on a SU8020 model HITACHI microscope. The Zirconium contents in polymer frameworks were determined by Perkin-Elmer ICP-OES Optima 3300DV spectroscopy. Powder X-ray diffraction data were recorded on a PANalytical BV Empyrean diffractometer by depositing powder on glass substrate, from $2\theta = 4.0°$ to 40° with 0.02° increment at 25 °C. Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimeter by measuring the weight loss while heating at a rate of 10 °C min^{-1} from 25 to 800 °C under nitrogen. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume, the Saito-Foley (SF) method was applied for the estimation of pore size distribution. The molecular weight and molecular weight distribution of the polymer samples were measured on a PL-GPC 220 at 140 °C with 1,2,4-trichlorobenzene as the solvent. The melting points of the polymer were measured by differential scanning calorimetry (DSC) on a NETZSCH DSC 204 at a heating/cooling rate of 10 °C min^{-1} from 35 to 180 °C and the data from the second heating scan were used.

Section 2. Synthetic procedures.

Synthesis of 1,3,5-Tris(3’-tert-butyl-4’-hydroxyphenyl)benzene

2-*tert*-butyl-4-acetylphenol (2.3 g，12 mmol) was dissolved in 25 mL dry ethanol. Then $SiCl_4$ (6.9 mL, 60 mmol) was added to it at 0 °C. The mixture was stirred at 0 °C for 30 min and at room temperature overnight. The reaction mixture was quenched with water and extracted 3 times with

CH_2Cl_2. The combined organic layer was dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel column chromatography (CH_2Cl_2/petroleum 1:1) to give the title compound as a colorless solid 1.45 g, yield 70%. Melting point: 112.3~114.5 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.61(s, 3H, Ar-H), 7.58 (d, 3H, J =3.0 Hz, Ar-H), 7.39 (dd, 3H, J =8.1 Hz, Ar-H), 6.77 (d, 3H, J =8.1 Hz, Ar-H), 4.84 (s, 3H, OH), 1.46 (s, 27H, t-Bu).^{13}C NMR ($CDCl_3$, 75MHz): δ 148.7, 137.2, 131.2, 128.8, 121.2, 120.7, 118.9, 111.7, 29.5, 24.4. ESI-MS (m/z): 522.85 [M^+]. IR (KBr pellet): 3540, 2960, 1605, 1500, 1255, 1080, 815, 735 cm^{-1}. Anal. Calcd for $C_{36}H_{42}O_3$: C 82.7, H 8.10. Found: C 82.8, H 8.06.

Synthesis of 1,3,5-Tris(3'-tert-butyl-4'-hydroxy-5'-formylphenyl)benzene (TBHFPB)

To a stirred mixture of anhydrous magnesium dichloride (2.0 g, 21 mmol) and solid paraformaldehyde (0.96 g, 31 mmol) in dried THF was added 3 mL of triethylamine dropwise and the mixture was stirred at room temperature for 10 min. A solution of 1,3,5-Tris(3'-tert-butyl-4'-hydroxyphenyl)benzene (1.85 g, 3.5 mmol) in THF was added dropwise. Then the mixture was heated to reflux for 4h. After the reaction mixture was cooled to room temperature, 50 mL of ethyl acetate and 50 mL of 1N HCl were added. The organic phase was separated and washed with 1 N HCl (2×100 mL) and water (3 × 100 mL), dried over $MgSO_4$, and filtered. The solvent was removed by rotatory evaporation to leave the crude product which was purified by column chromatography on silica gel using petroleum ether/CH_2Cl_2(3: 1) mixture as the eluent to give the title compound 1.33 g, yield 62%. Melting point: 174.1~176.5 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): ^{1}H NMR ($CDCl_3$, 300 MHz): 11.85(s, 3H, OH), 10.00(s, 3H, CHO), 7.82 (d, 3H, J =2.4 Hz, Ar-H), 7.68 (d, 3H, J =2.4 Hz, Ar-H), 7.63 (s, 3H, Ar-H), 1.49 (s, 27H, t-Bu).^{13}C NMR ($CDCl_3$, 75MHz): δ 197.1, 160.9, 141.8, 139.1, 133.2, 132.1, 130.3, 124.4, 120.7, 35.1, 29.2. ESI-MS (m/z): 606.85 [M^+]. IR (KBr pellet): 2958, 1650, 1433, 1393, 1318, 1162, 770, 720 cm^{-1}. Anal. Calcd for $C_{39}H_{42}O_6$: C 77.2, H 6.98. Found: C 77.0, H 7.02.

Synthesis of L_1H_3

Cyclohexylamine (0.43 g, 4.0 mmol) and 1,3,5-Tris(3'-tert-butyl-4'-hydroxy-5'-formyl phenyl)benzene (0.4 g, 0.66mmol) were dissolved in 20 mL THF ,then one drop of formic acid was added and the mixture was refluxed for 12 h, the solvent was evaporated under reduced pressure. Recrystallization of the residue in ethanol gave L_1H_3 as a yellow solid 0.45 g, 80% yield. Melting point: 187.8~189.2 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 14.44(s, 3H, OH), 8.46(s, 3H, CH=N), 7.62(d, 3H, J =1.8 Hz, Ar-H), 7.60(s, 3H, Ar-H), 7.40(d, 3H, J =1.8 Hz, Ar-H), 3.22-3.33 (m, 3H, cyclohexyl-CH) 1.51 (s, 27H, t-Bu), 1.29-1.92 (m, 30H, cyclohexyl-CH_2). ^{13}C NMR ($CDCl_3$, 75MHz): δ 162.9, 160.6, 142.4, 137.9, 130.7, 128.4, 128.0, 123.7, 118.8, 67.6, 35.0, 34.3, 29.4, 25.5, 24.4. ESI-MS (m/z): 850.42 [M^+]. IR (KBr pellet): 3450, 2930, 2865, 1640, 1450, 1385, 1180, 870 cm^{-1}. Anal. Calcd for $C_{57}H_{75}N_3O_3$: C 80.5, H 8.89, N 4.94. Found: C 80.3, H 8.85, N 4.97.

Synthesis of L_2H_3

The procedure described for the synthesis of **L_1H_3** was used with phenylamine (0.95 g, 10 mmol) and 1,3,5-Tris(3'-tert-butyl-4'-hydroxy-5'-formylphenyl)benzene (0.6 g, 1.0 mmol) as starting materials. L_2H_3 was obtained as a yellow solid (0.68 g, 82% yield). Melting point: 289.2~291.5 °C. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ 14.07(s, 3H, OH), 8.76(s, 3H, CH=N), 7.73 (d, 3H, J =2.4 Hz, Ar-H),7.68 (s, 3H, Ar-H), 7.59 (d, 3H, J =2.4 Hz, Ar-H), 7.29-7.47 (m, 15H, Ar-H), 1.55 (s, 27H, t-Bu).^{13}C NMR ($CDCl_3$, 75MHz): δ 163.2, 160.4, 148.2, 142.3, 138.3, 129.4, 129.2, 126.9, 124.0, 121.2, 119.3, 35.2, 29.4. ESI-MS (m/z): 831.83 [M^+]. IR (KBr pellet): 3440, 2965, 1618, 1585, 1435, 1165, 855, 752 cm^{-1}. Anal. Calcd for $C_{57}H_{57}N_3O_3$: C 82.3, H 6.90, N 5.05. Found: C 82.2, H 6.95, N 5.09.

General procedure for synthesis of Cat 1a-c and Cat 2a-b

In a typical procedure, NaH (40 mg, 1.7 mmol) was added to a THF (CH_2Cl_2 or dioxane) solution of 0.5 mmol of L_1H_3 (or L_2H_3) . The solution was vigorously stirring at room temperature for 12 h. Then $ZrCl_4(THF)_2$ (0.75 mmol) was added, and the reaction mixture was refluxed for 3 days. The precipitate was collected by filteration, washed and dried under vacuum for 12 h. The self-immobilized catalysts **1a-c** and **2a-b** were obtained in 70~85% yields.

Ethylene polymerization experiments

A dry 250 mL steel autoclave with a magnetic stirrer was charged with 50 mL of toluene, and saturated with ethylene (1.0 bar). The autoclave was kept in a water bath at a corresponding temperature. The polymerization reaction was started by injection of a mixture of AlR_3, $Ph_3CB(C_6F_5)_4$ and a catalyst suspended in toluene (10 mL). The vessel was repressurized to the needed pressure with ethylene immediately, and the pressure was kept by continuously feeding of ethylene. After a certain period of time, the polymerization was quenched by injecting acidified methanol (HCl (3 M)/methanol 1/1). The polymer was collected by filtration, washed with water and methanol, and dried at 60 °C in vacuo to a constant weight. Most of the PCP catalyst should be retained in the polymer due to its insolubility in water and common organic solvents.

Section 3. TGA profiles.

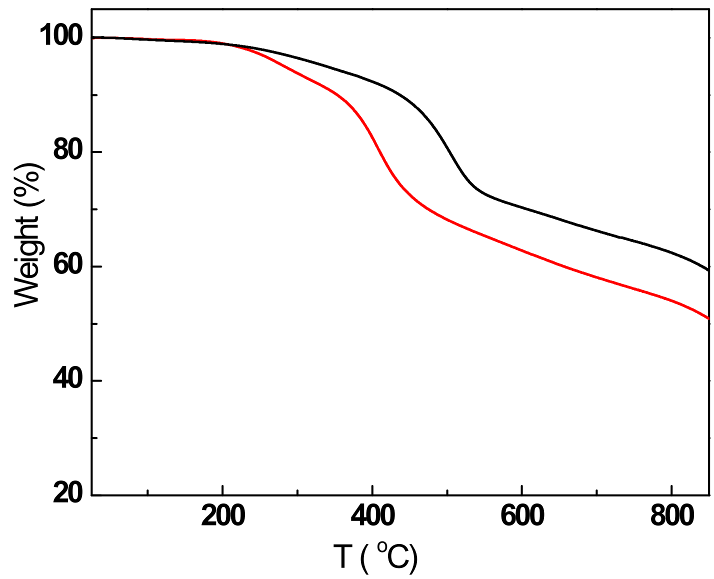


Figure S1. TGA profiles of **1a** (red) and **2a** (black).

Section 4. Solid-state ^{13}C NMR spectra.

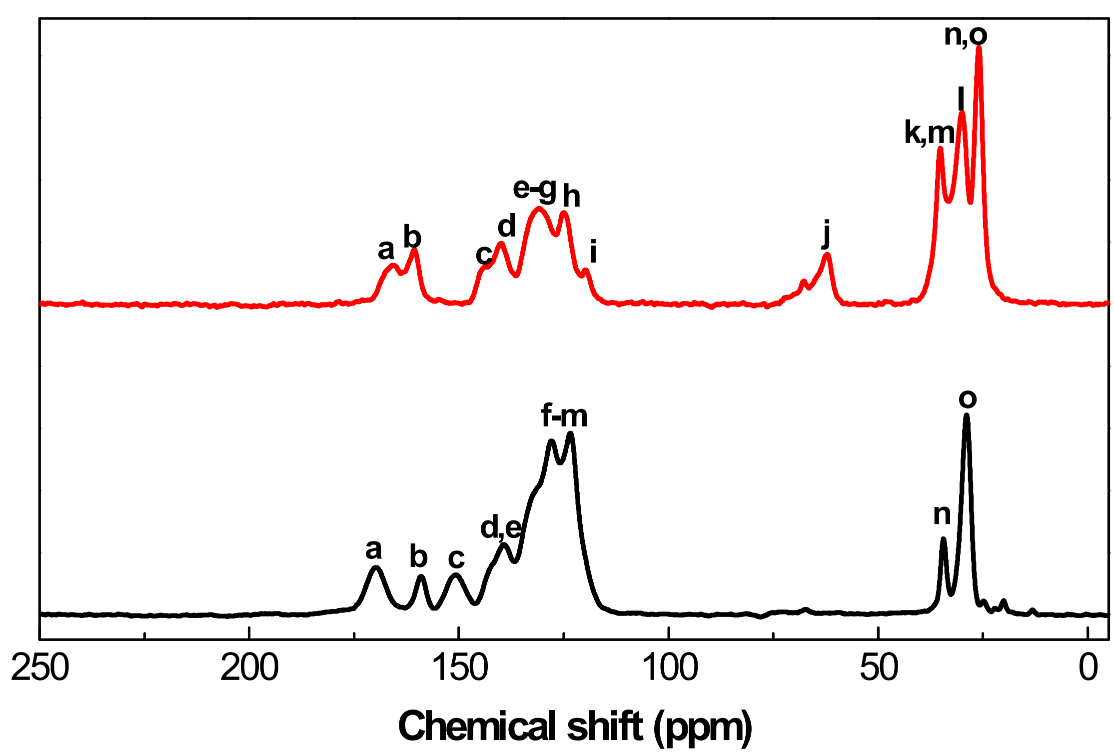


Figure S2. ^{13}C CP/MAS NMR spectroscopy of **1a** (red) and **2a** (black).

Section 5. FT-IR spectra of the ligands (L_1H_3 and L_2H_3) and the catalysts (1a-c and 2a-b).

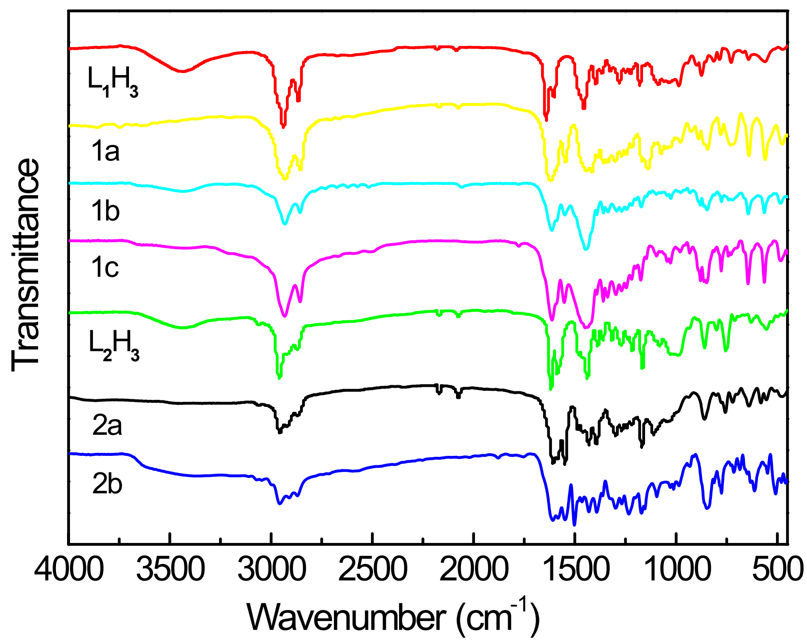


Figure S3. FTIR spectra of the ligands (L_1H_3 and L_2H_3) and the catalysts (1a-c and 2a-b).

Section 6. Elemental and ICP-OES analyses.

Table S1. Results of elemental and ICP-OES analyses, and estimated formulae of the PCP catalysts.

Sample	C [wt %]	H [wt %]	N [wt %]	Na [wt %]	Zr [wt %]	Estimated formula
1a	55.55	6.05	3.29	4.9	10.6	$C_{57}H_{72}N_3O_3(ZrCl_2)_{1.5}(NaCl)_{2.7}(C_4H_8O)_{0.4}$
1b	54.00	6.07	3.07	5.1	9.4	$C_{57}H_{72}N_3O_3(ZrCl_2)_{1.4}(NaCl)_3(C_4H_8O_2)_{1.2}$
1c	54.08	5.75	3.33	5.1	10.5	$C_{57}H_{72}N_3O_3(ZrCl_2)_{1.5}(NaCl)_{2.8}$
2a	56.57	4.72	3.28	4.8	10.0	$C_{57}H_{54}N_3O_3(ZrCl_2)_{1.4}(NaCl)_{2.7}(C_4H_8O)_{0.6}$
2b	56.17	5.54	3.13	4.5	9.0	$C_{57}H_{54}N_3O_3(ZrCl_2)_{1.4}(NaCl)_{2.7}(C_4H_8O_2)_2$

Section 7. Powder X-ray diffraction patterns.

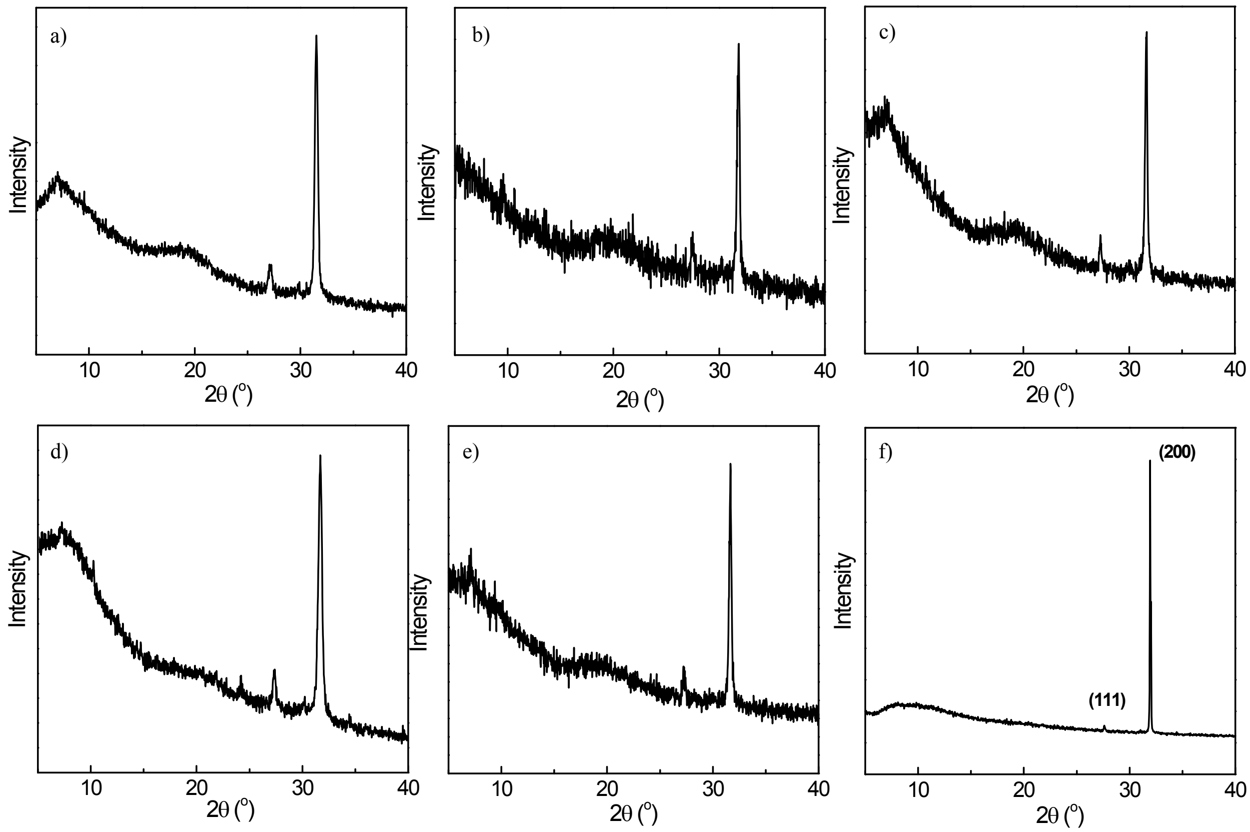


Figure S4. Powder X-ray diffraction profiles of (a) 1a, (b) 1b, (c) 1c, (d) 2a, (e) 2b, (f) NaCl powder. The peaks at 27.3 and 31.7° are from NaCl (111 and 200, respectively).

Section 8. SEM images of the catalysts.

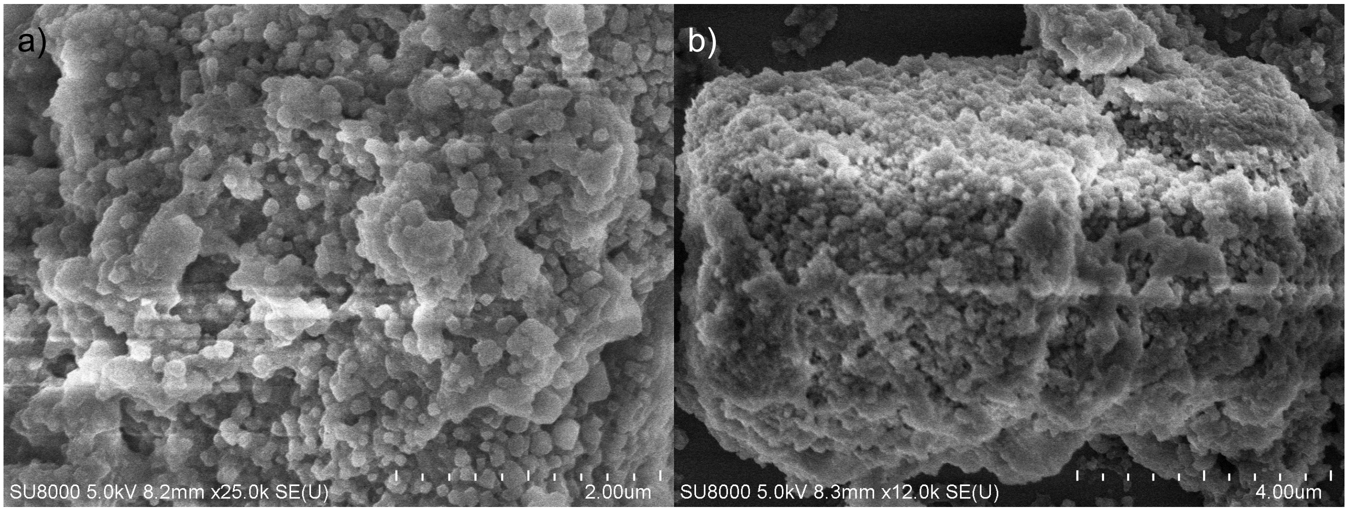


Figure S5. SEM images of the catalysts **1a** (a) and **2a** (b).

Section 9. Pore structure parameters of the samples.

Table S2. Pore structure parameters of the samples[a]

Sample	S_{BET}[m^2g^{-1}]	$S_{Langmuir}$[m^2g^{-1}]	V_{micro}[cm^3g^{-1}]	V_{total}[cm^3g^{-1}]
1a	479	535	0.186	0.31
1b	71	83	0.027	0.10
1c	41	47	0.016	0.09
2a	230	258	0.087	0.17
2b	54	62	0.021	0.11
1a-1[b]	455	514	0.178	0.29
2a-1[b]	166	193	0.059	0.17

[a] V_{micro}= micropore volume calculated by Saito-Flory method and V_{total}= total pore volume at P/P_0=0.99. [b] Samples **1a-1** and **2a-1** were obtained from the repeated experiments under the same conditions as for the preparation of **1a** and **2a**.

Section 10. N_2 sorption isotherms and pore size distribution.

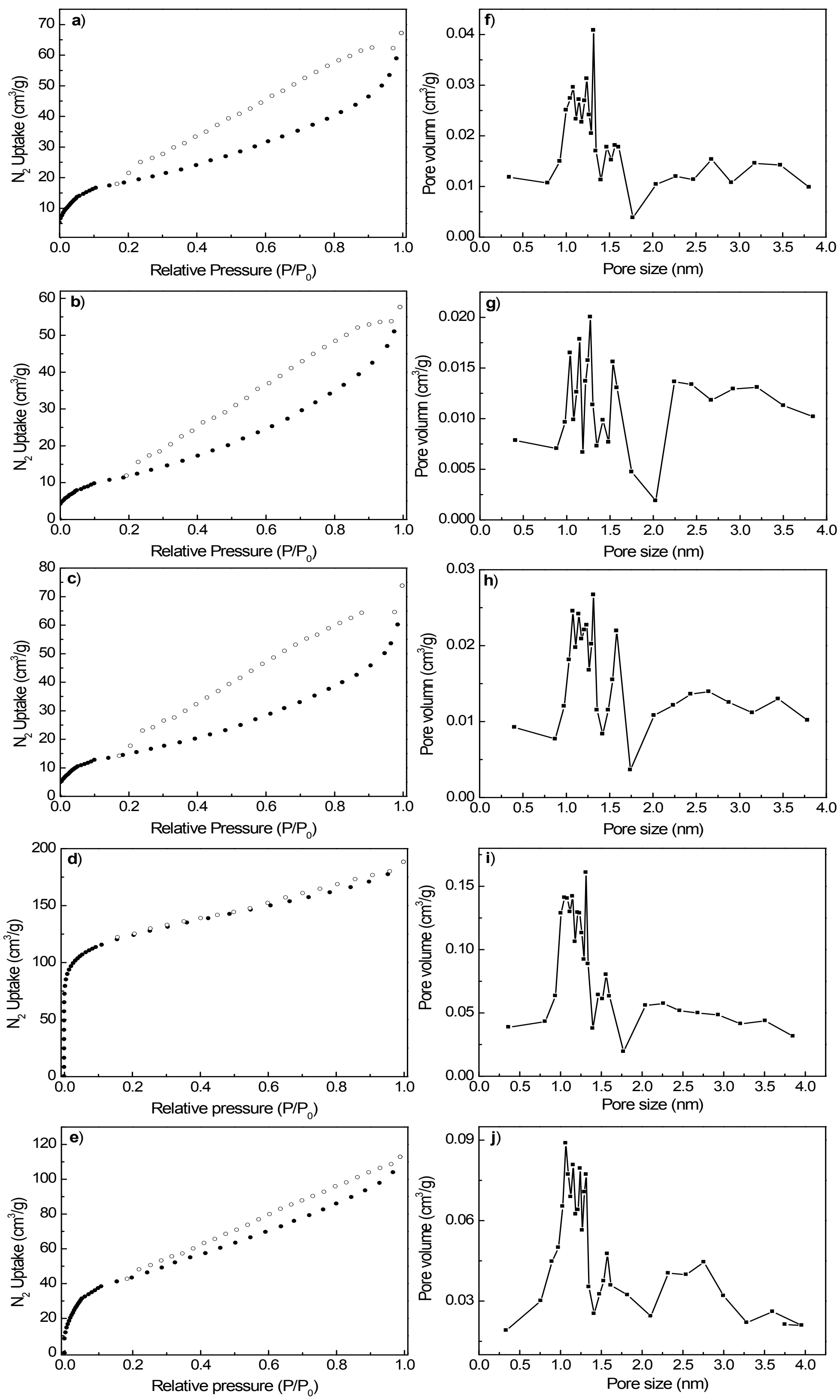


Figure S6. (a-e) Nitrogen adsorption (●) and desorption (○) isotherm profiles of (a) **1b**, (b) **1c**, (c) **2b**, (d) **1a-1**, (e) **2a-1**. (f-j) Pore size distribution of (f) **1b**, (g) **1c**, (h) **2b**, (i) **1a-1**, (j) **2a-1** by SF modeling on the N_2 adsorption isotherms .

Section 11. Ethylene polymerization results.

Table S3. Summary of ethylene polymerization catalyzed by 1a-c, 2a-b and the model catalyst 3.[a]

Entry	Cat	Cocat	Al/Zr	T (°C)	Activity [b]	M_w[c] (×10^4) (av.)	M_w/M_n (av.)	Peak 1			Peak 2		
								%	Mw[c] (×10^4)	M_w/M_n	%	Mw[c] (×10^4)	M_w/M_n
1	**1a**	$AlMe_3$	50	50	0.92	9.35	6.1	72	11.0	1.90	28	0.92	1.34
2	**1a**	$AlEt_3$	50	50	1.21	11.9	6.4	70	14.1	1.94	30	1.12	1.29
3	**1a**	Al^iBu_3	50	50	1.38	15.1	12.2	75	20.0	2.78	25	0.65	1.76
4	**1a**	Al^iBu_3	25	50	0.72	17.2	10.1	79	21.1	2.56	21	0.78	1.84
5	**1a**	Al^iBu_3	75	50	1.32	11.9	10.2	78	17.0	1.89	22	1.19	1.90
6	**1a**	Al^iBu_3	50	0	0.30	37.5	14.0	86	53.7	2.26	14	3.88	1.63
7	**1a**	Al^iBu_3	50	25	0.69	17.6	11.6	72	22.5	2.37	28	0.92	2.27
8	**1a**	Al^iBu_3	50	75	1.28	11.6	10.7	78	14.9	3.01	22	0.46	1.52
9[d]	**1a**	Al^iBu_3	50	50	1.17	16.4	14.9	82	20.2	3.36	18	0.31	1.88
10	**2a**	$AlMe_3$	50	50	0.18	20.4	14.2	78	25.4	2.97	22	0.78	1.65
11	**2a**	$AlEt_3$	50	50	0.21	40.4	13.7	77	51.8	3.89	23	1.31	1.84
12	**2a**	Al^iBu_3	50	50	0.39	36.4	20.9	87	42.2	5.73	13	0.44	1.46
13	**2a**	Al^iBu_3	50	25	0.05	45.6	16.5	71	54.5	4.05	29	1.64	1.16
14	**2a**	Al^iBu_3	50	75	0.10	27.7	17.7	77	37.0	2.53	23	1.10	2.43
15	**1a**	MAO	500	50	0.14	10.0	6.26	70	12.3	2.61	30	0.61	1.59
16	**2a**	MAO	500	50	0.04	13.8	4.13	71	17.4	1.75	29	1.62	1.47
17	**1b**	Al^iBu_3	50	50	1.20	7.27	6.64	70	8.93	2.00	30	0.50	1.45
18	**1c**	Al^iBu_3	50	50	1.25	12.7	8.15	65	15.5	2.74	35	0.62	1.57
19	**2b**	Al^iBu_3	50	50	0.23	15.8	9.13	70	19.2	2.73	30	0.67	1.73
20	**3**	Al^iBu_3	50	50	2.16	1.52	2.76						
21[d]	**3**	Al^iBu_3	50	50	1.15	1.58	2.85						

[a] Polymerization conditions: precatalyst = 5 μmol; solvent: 60 mL of toluene; $Ph_3CB(C_6F_5)_4$= 6 μmol; ethylene pressure 5 bar; polymerization time, 30 min. [b] In units of kg·PE(mmol Zr)$^{-1}$h^{-1}. [c] Determined by GPC with polystyrene standards. [d] polymerization time, 60 min.

Section 12. Gel Permeation Chromatography (GPC) curves and the resolution results.

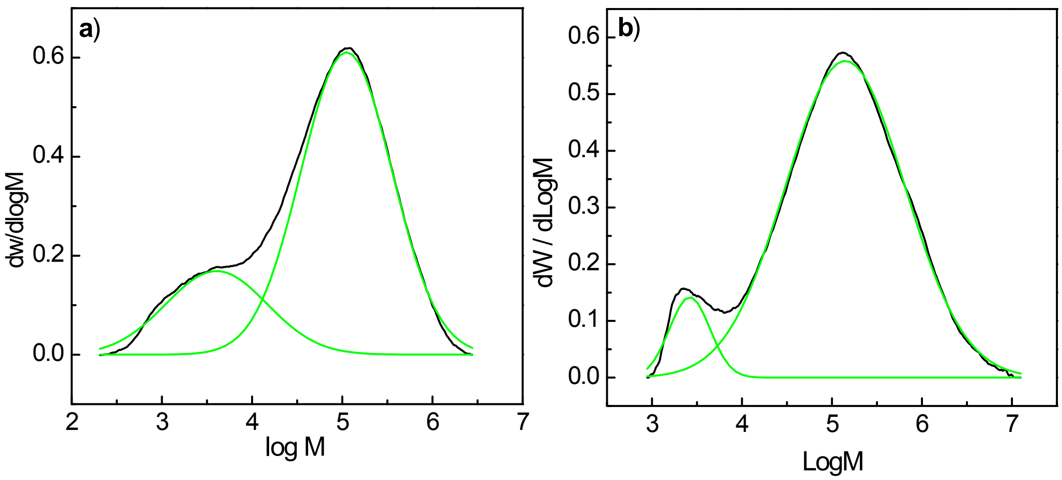
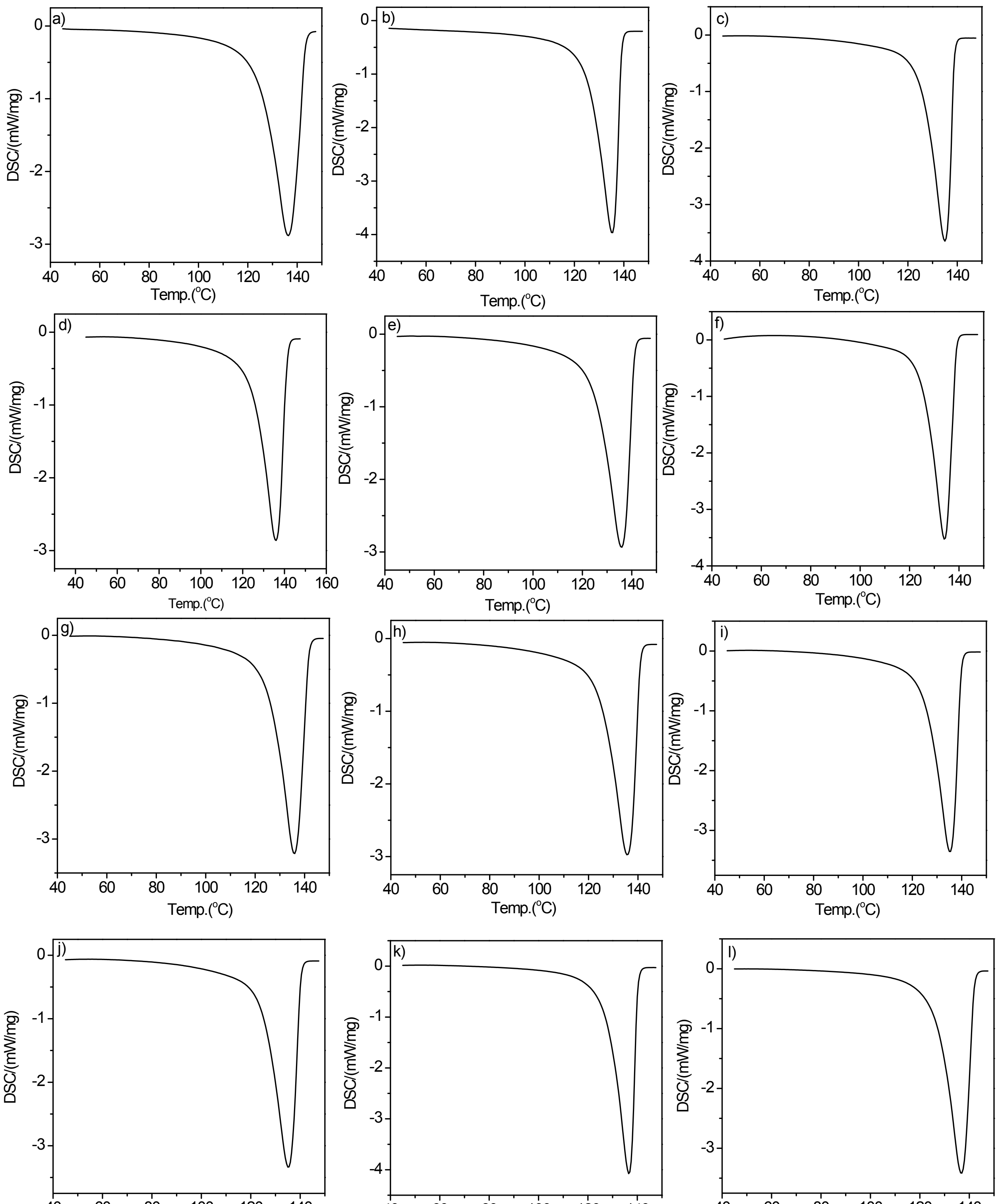


Figure S7. Typical GPC curves of polymers obtained with (a) Cat **1a** in entry 3 of Table S3 and (b) Cat **2a** in entry 11 of Table S3. The black line is the GPC curve, and the green lines are the resolution curves.

Section 13. DSC profiles of the polyethylene samples.


a)
b)
c)
d)
e)
f)
g)
h)
i)
j)
k)
l)
DSC/(mW/mg)
Temp.(°C)

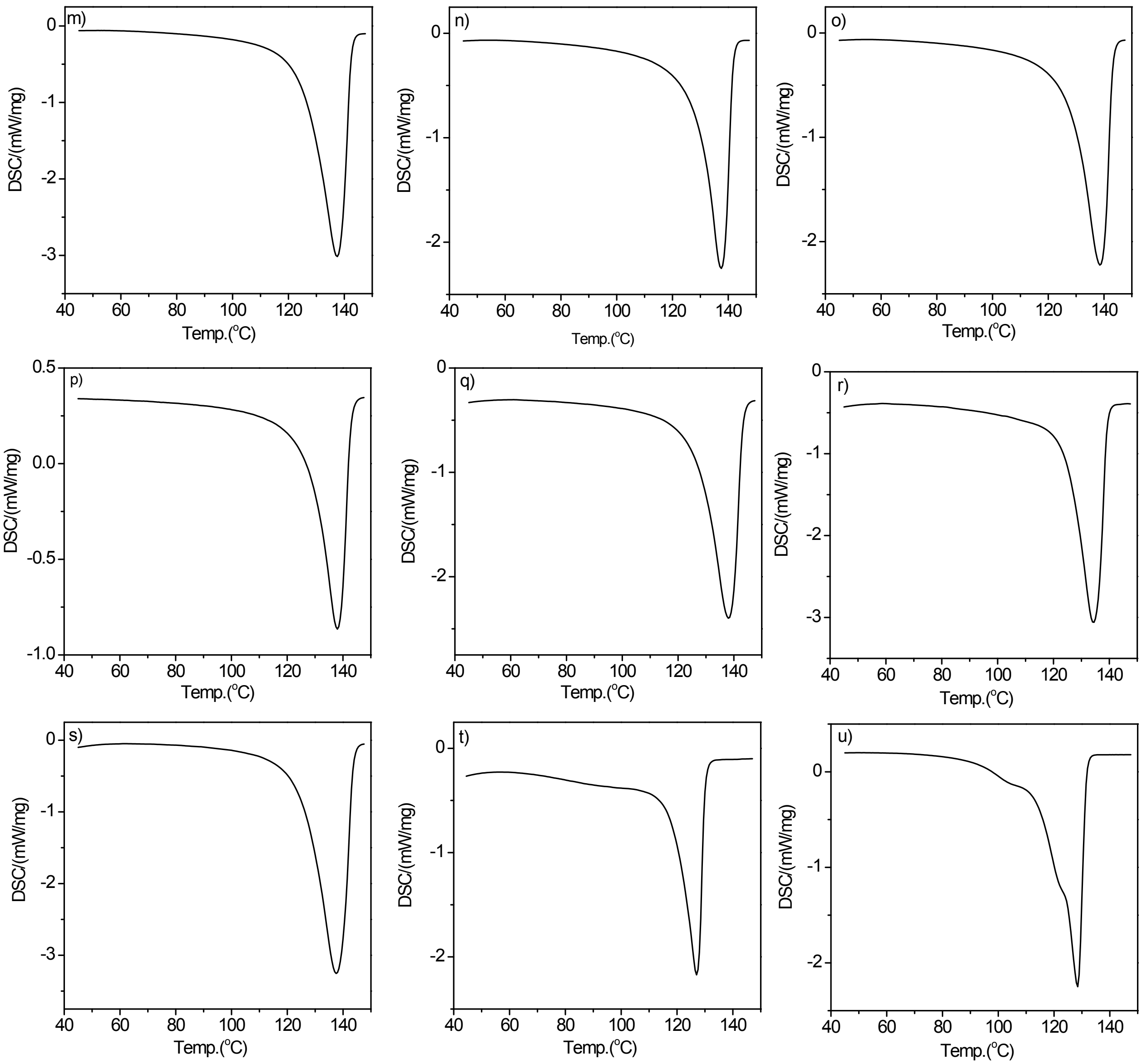


Figure S8. DSC profiles of the polyethylene samples, figures a to u correspond to the polyethylene samples from entry 1 to entry 21 in Table S3.

Section 14. ^{13}C NMR spectra of the polyethylene samples.

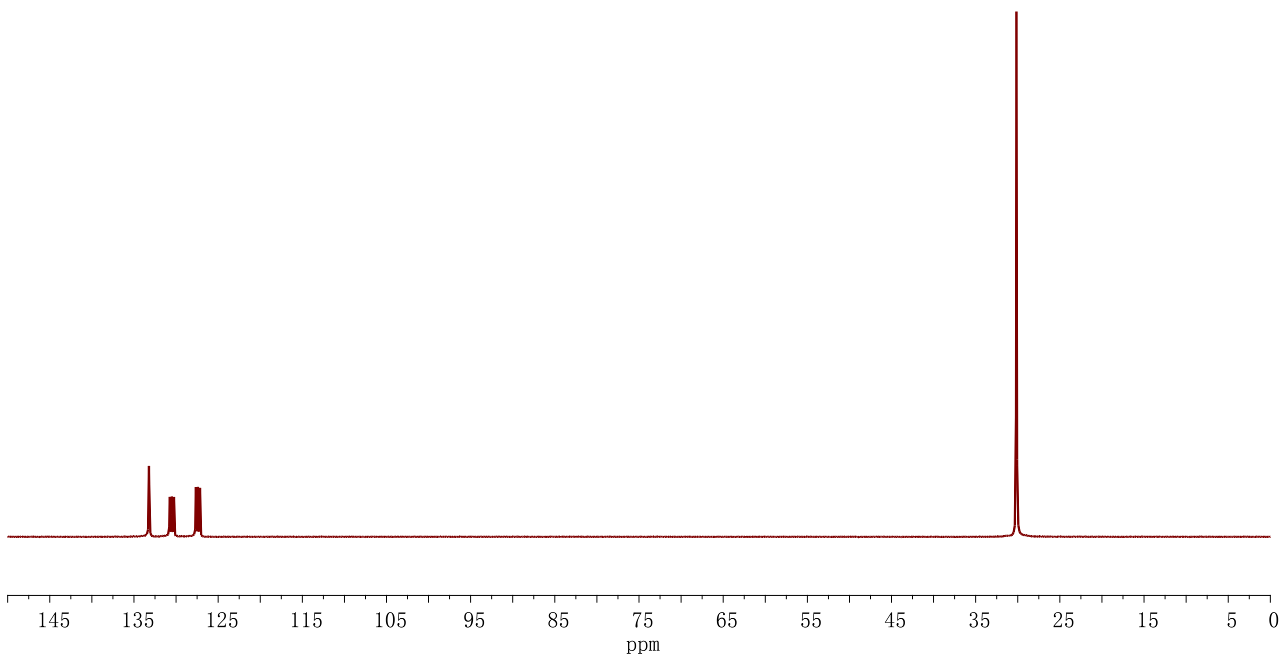
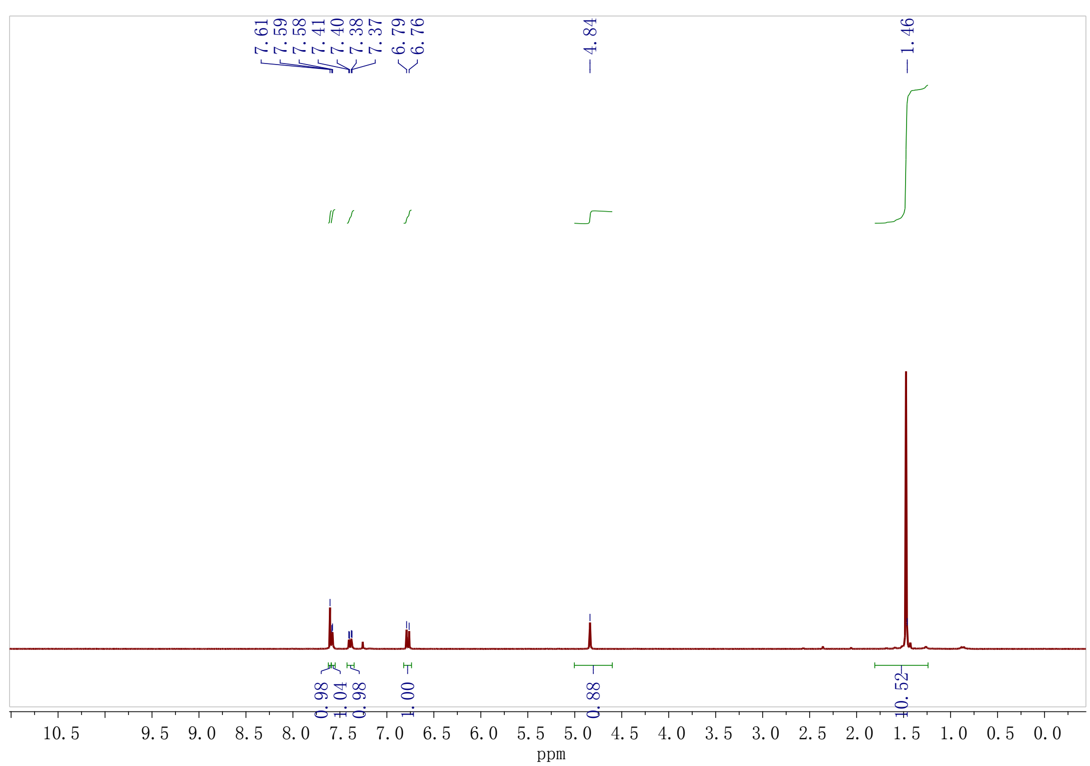
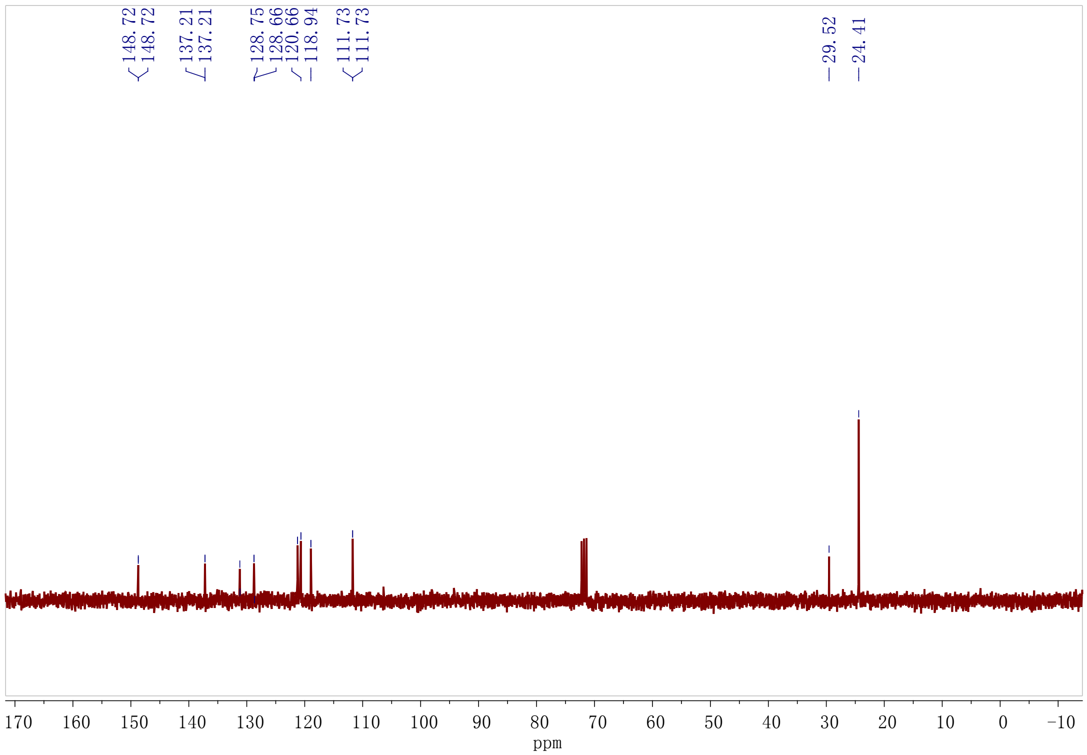


Figure S9. ^{13}C NMR spectra of the polyethylene sample (entry 3 in Table S3).

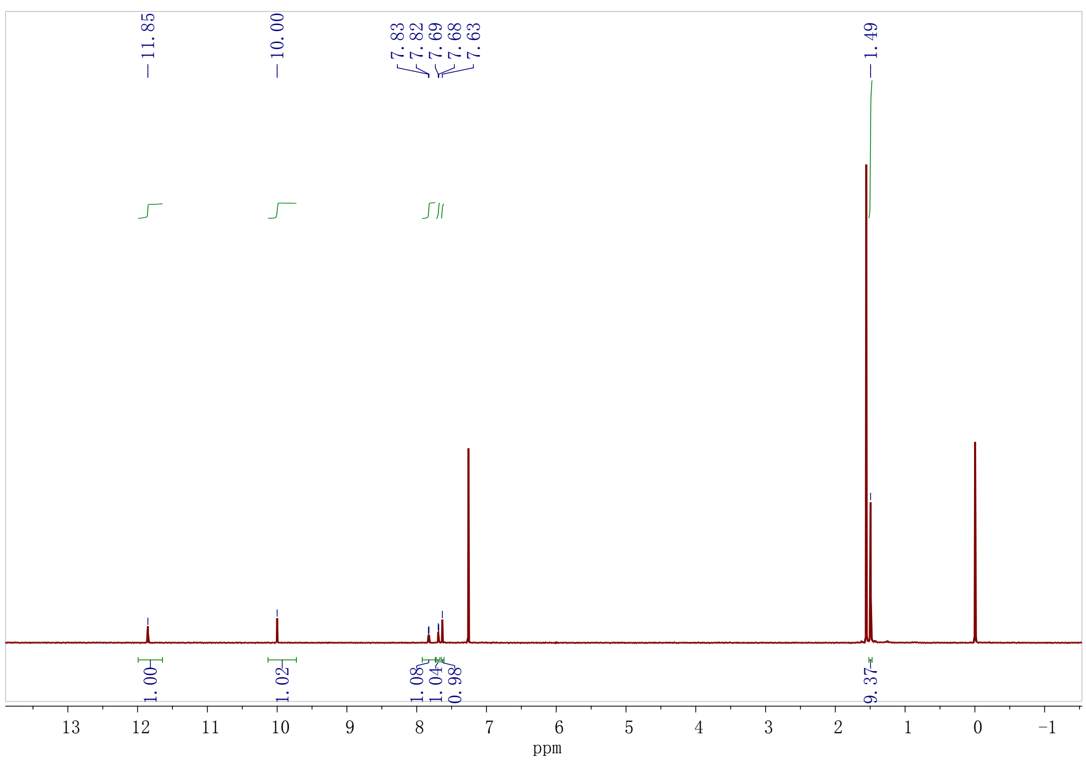
Section 15. ^{1}H and ^{13}C NMR spectra of ligands and pre-ligands.



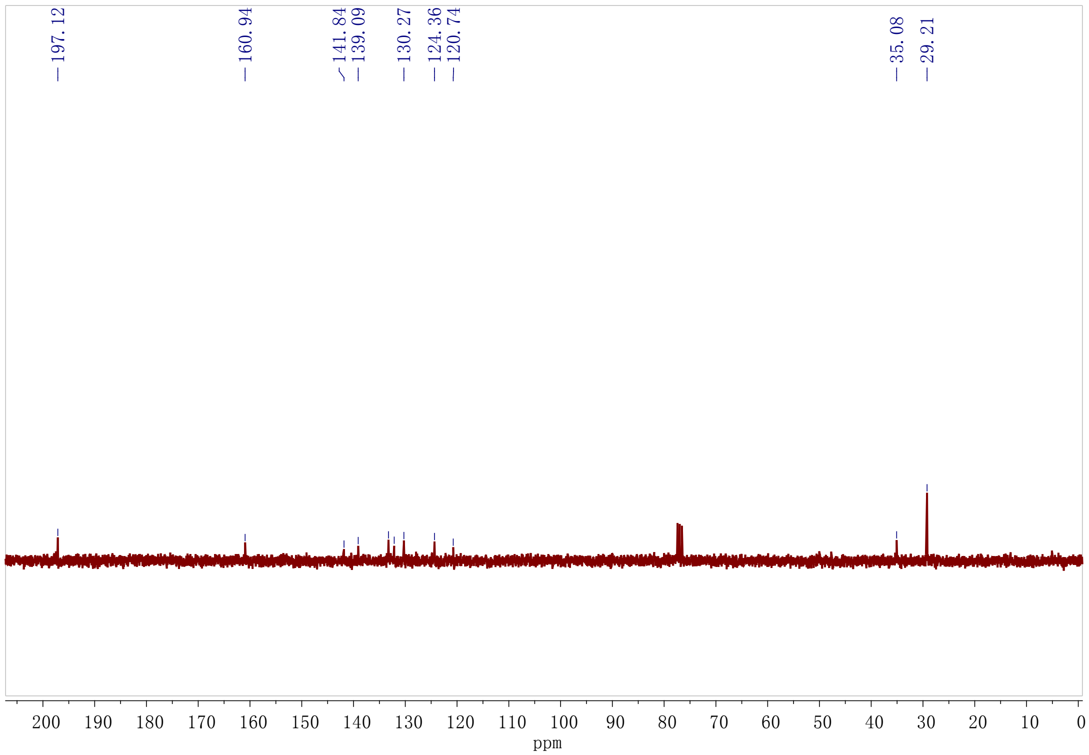
^{1}H NMR spectra of 1,3,5-Tris(3'-tert-butyl-4'-hydroxyphenyl)benzene



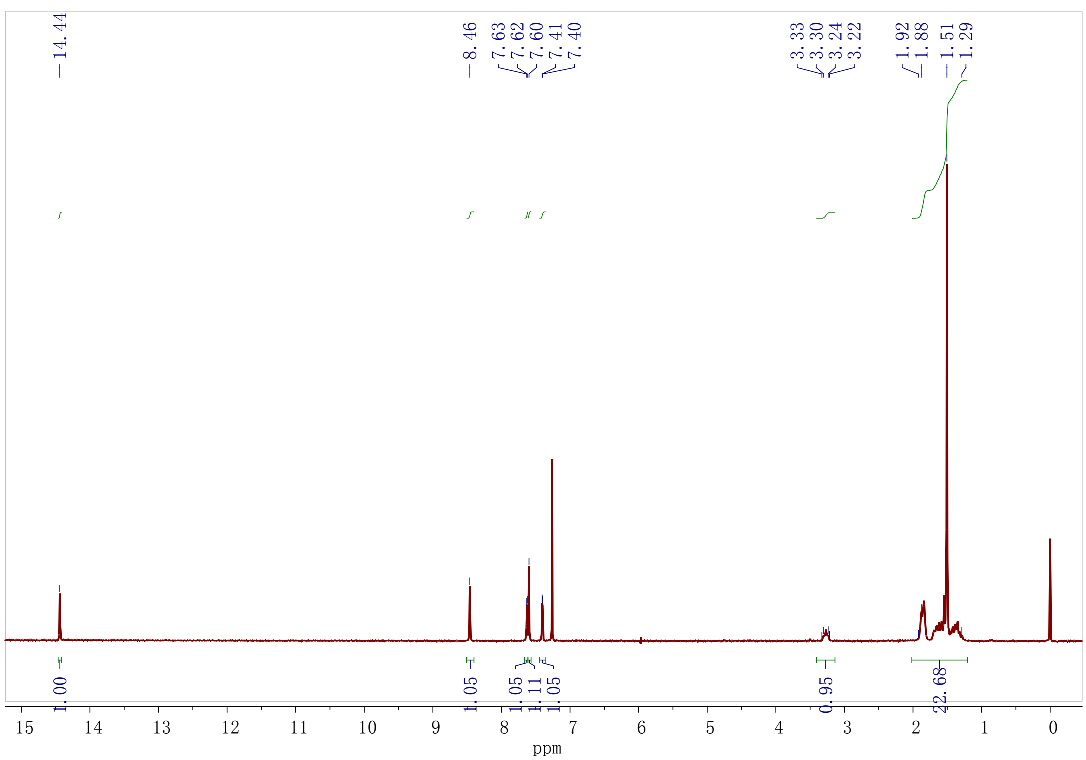
[13]C NMR spectra of 1,3,5-Tris(3’-tert-butyl-4’-hydroxyphenyl)benzene



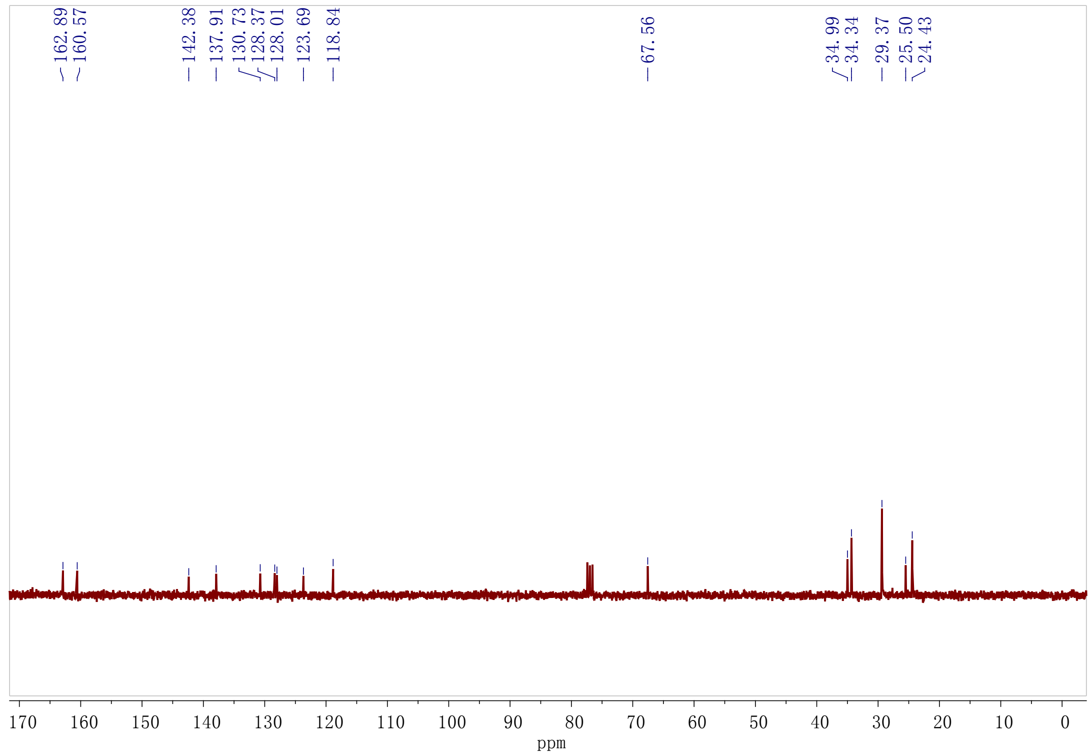
[1]H NMR spectra of 1,3,5-Tris(3’-tert-butyl-4’-hydroxy-5’-formylphenyl)benzene (TBHFPB)



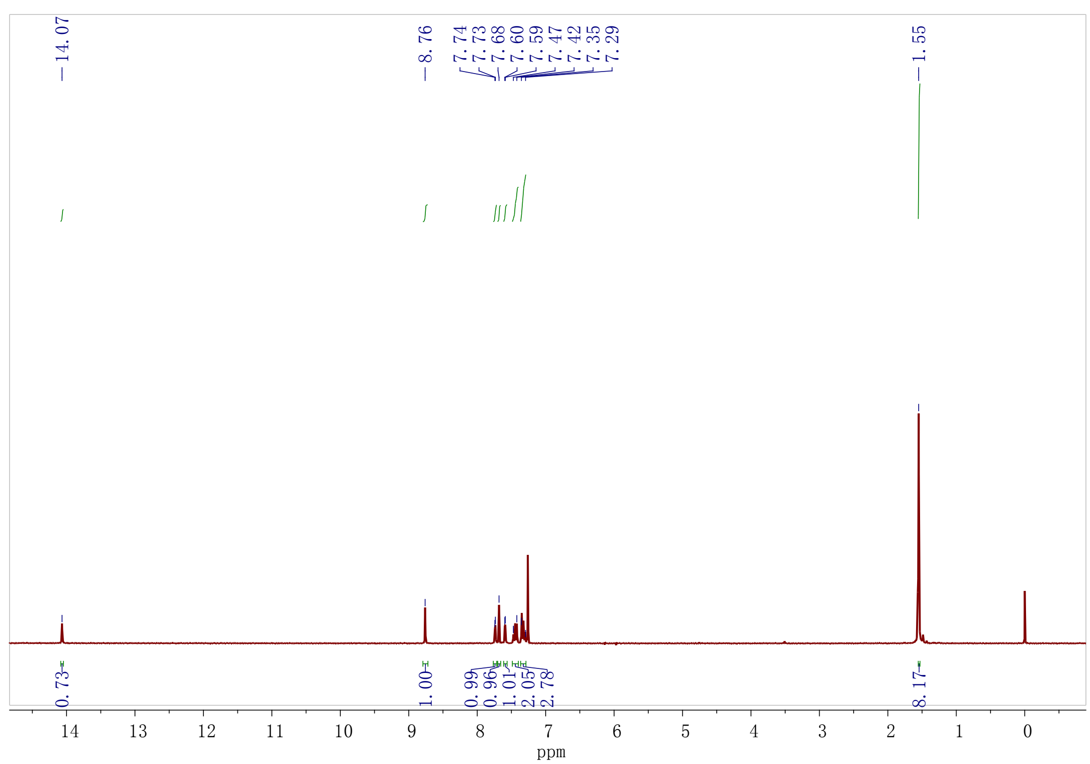
^{13}C NMR spectra of 1,3,5-Tris(3'-tert-butyl-4'-hydroxy-5'-formylphenyl)benzene (TBHFPB)



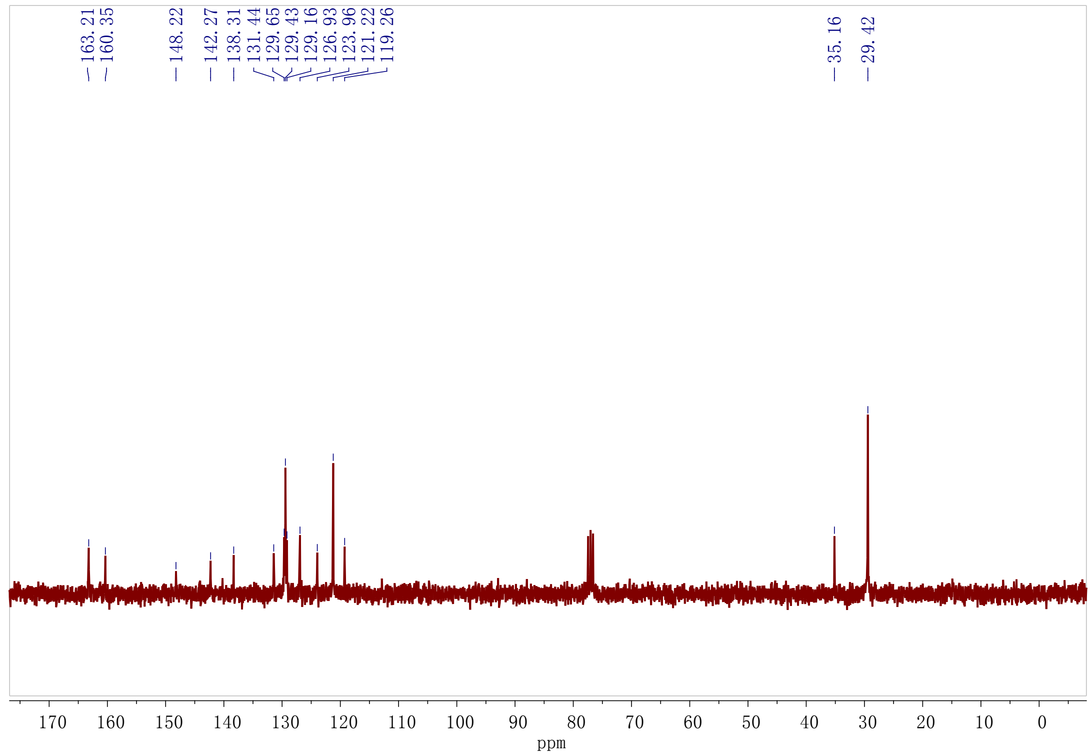
^{1}H NMR spectra of L_1H_3



^{13}C NMR spectra of L_1H_3

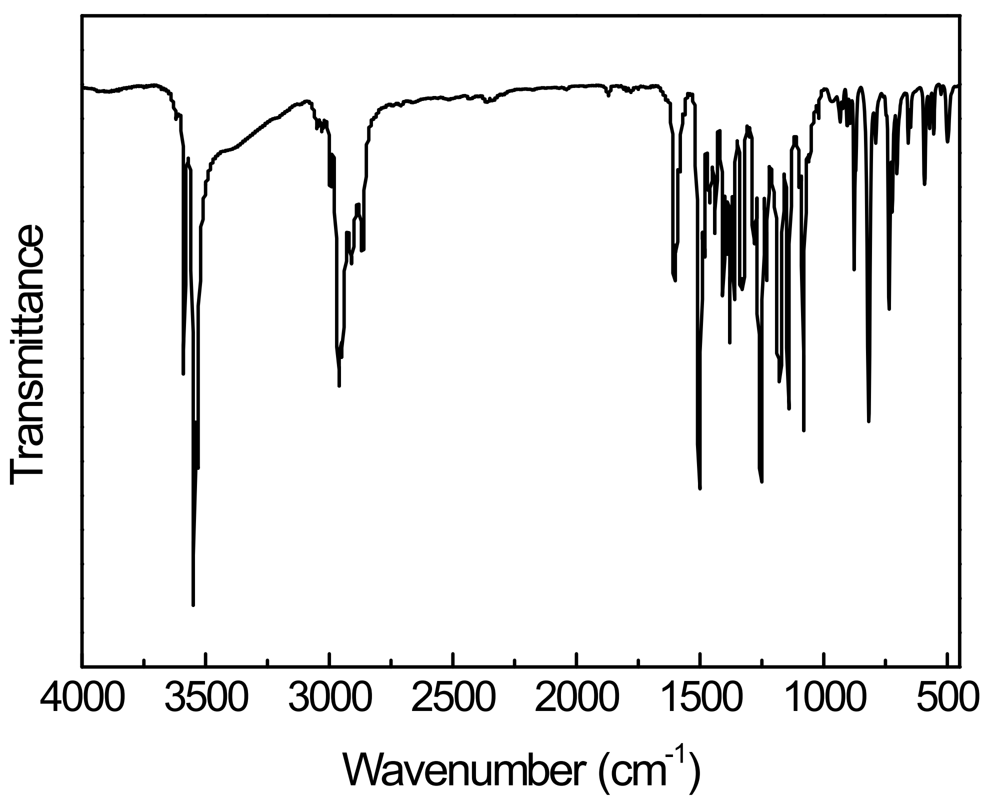


^{1}H NMR spectra of L_2H_3

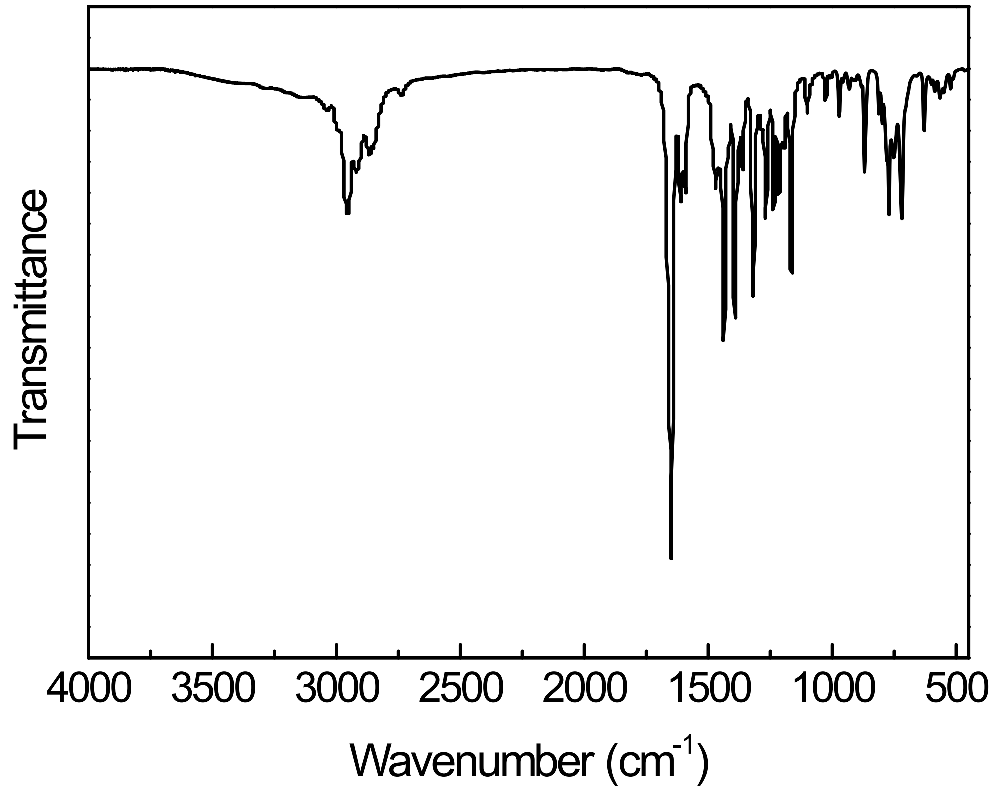


^{13}C NMR spectra of L_2H_3

Section 16. FT-IR spectra of 1,3,5-Tris(3'-tert-butyl-4'-hydroxyphenyl)benzene and TBHFPB.

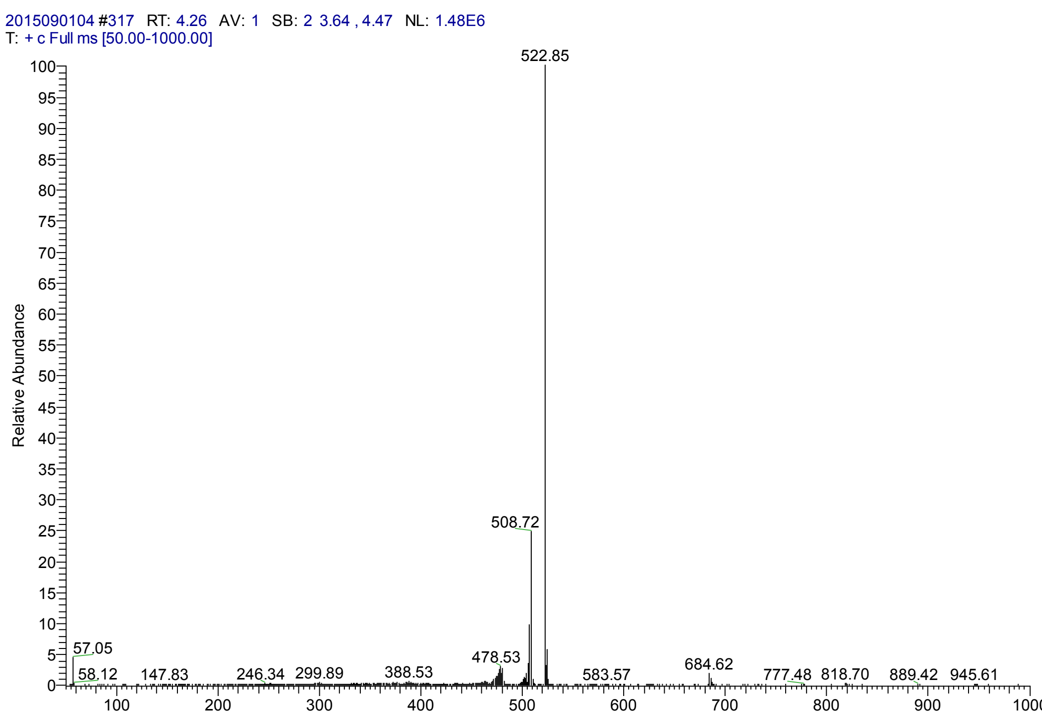


FT-IR spectra of 1,3,5-Tris(3'-tert-butyl-4'-hydroxyphenyl)benzene

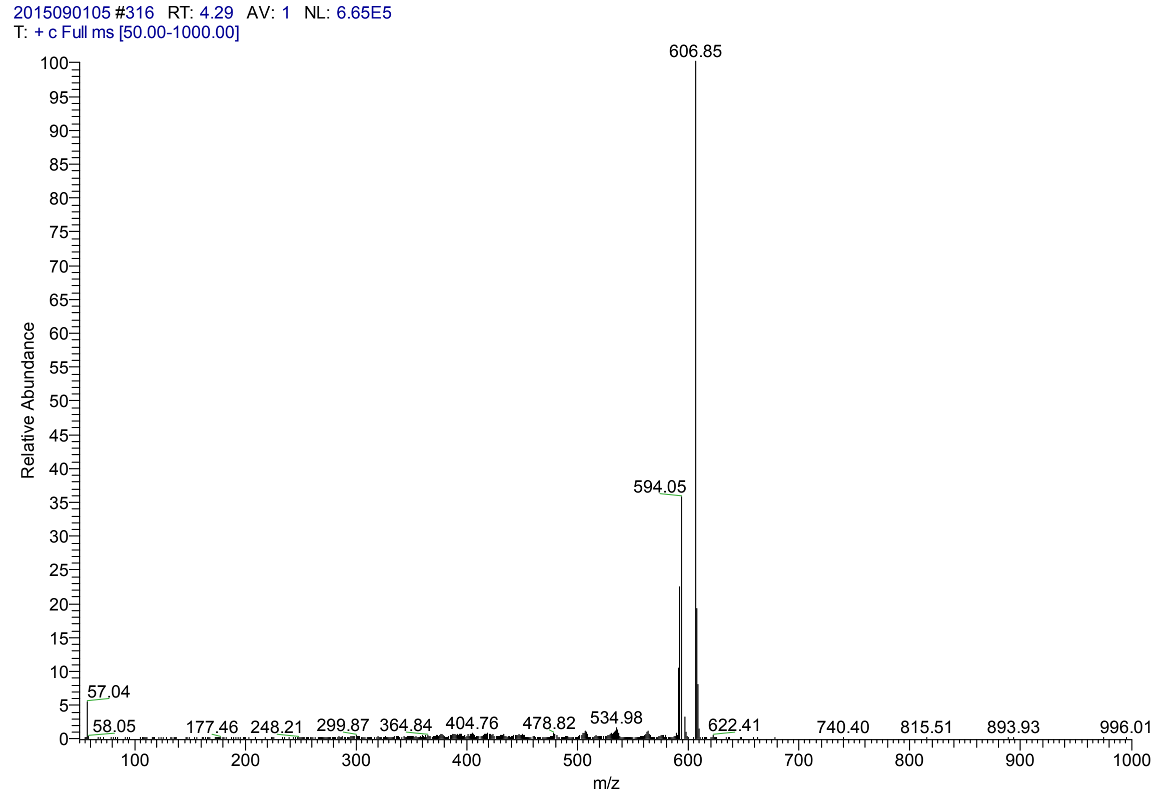


FT-IR spectra of 1,3,5-Tris(3’-tert-butyl-4’-hydroxy-5’-formylphenyl)benzene (TBHFPB)

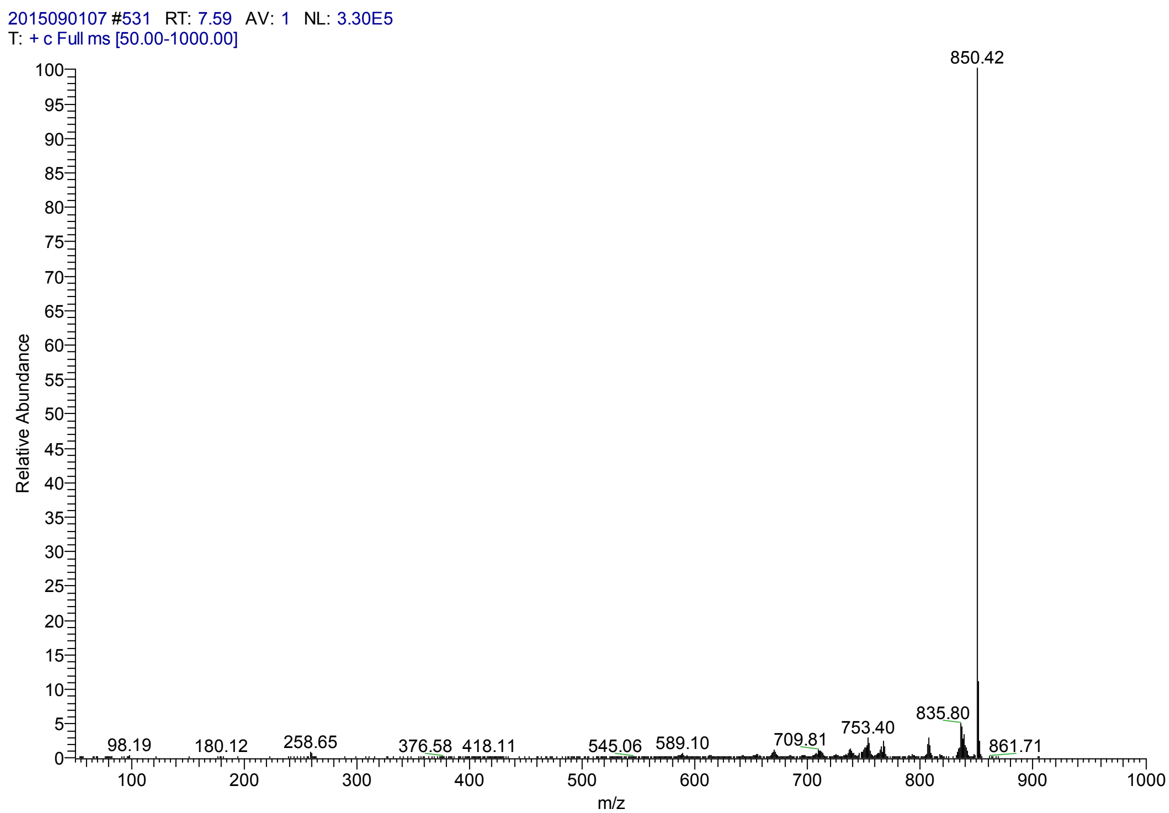
Section 17. ESI-MS spectra of ligands and pre-ligands.



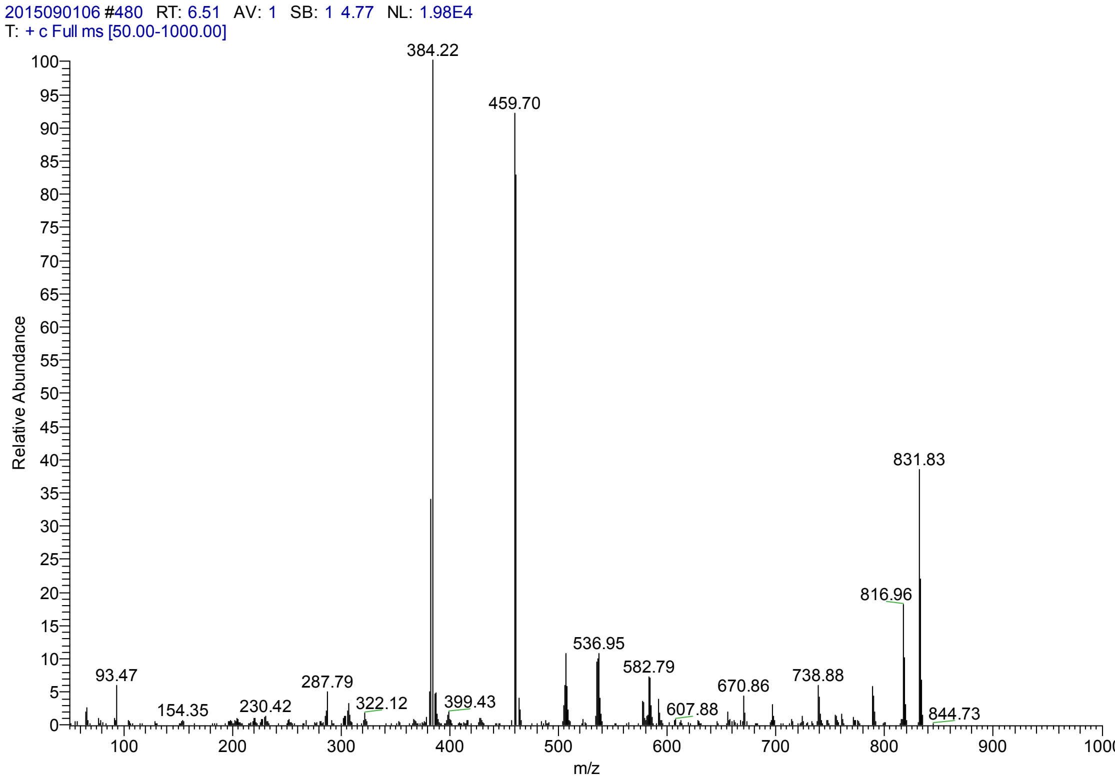
ESI-MS spectra of 1,3,5-Tris(3’-tert-butyl-4’-hydroxyphenyl)benzene



ESI-MS spectra of 1,3,5-Tris(3’-tert-butyl-4’-hydroxy-5’-formylphenyl)benzene (TBHFPB)



ESI-MS spectra of L_1H_3



ESI-MS spectra of L_2H_3

Section 18. References of Electronic Supporting Information.

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