8Synthesis, Characterization and Efficient Catalytic Ethylene Polymerization Reactions of Phenylphosphine Half-metallocene Zirconium Complexes

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1. Experiment

1.1 General Producer and materials

All compounds sensitive to moisture and oxygen were handled in a Vigor glovebox or under nitrogen protection using standard Schlenk techniques. Anhydrous and oxygen-free solvents such as toluene, tetrahydrofuran (THF), dichloromethane, and n-hexane were prepared using a Vigor solvent purification system. Norbornene (NBE) and 1-hexene (HE) were purified under an inert atmosphere by stirring with CaH_2 at 60 °C or room temperature for two days to remove trace amounts of water, followed by distillation under reduced pressure into Schlenk bottles containing 4Å molecular sieves, and stored in the glovebox for future use. The ethylene gas used in the homopolymerization and copolymerization experiments was further purified through a purification column before use. $^{i}Bu_3Al$ and $[Ph_3C][B(C_6F_5)_4]$ were purchased from Anagene Chemical Reagents Inc. Methylaluminoxane (MAO) and modified methylaluminoxane (MMAO) were procured from Nouryon Chemical Inc. All other reagents, unless otherwise specified, were used as received without further purification.

All new compounds in this study were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy using a Bruker-500 NMR spectrometer at room temperature, with TMS as the internal standard and deuterated chloroform as the solvent. The ^{13}C NMR spectra of the polymers were recorded on a Bruker-400 NMR spectrometer at 120 °C, with TMS as the internal standard and 1,2-dichlorobenzene-d_4 as the solvent. The molecular weight and molecular weight distribution of polyethylene and ethylene copolymers were determined on a PL-GPC 220 at 150 °C, using polystyrene as the standard, with 1,2,4-trichlorobenzene as the mobile phase, to which 0.05 wt% of Butylated hydroxytoluene (BHT) was added as an antioxidant.

1.2 Polymerzation

Initially, the reaction vessel was heated to 150 °C and subjected to vacuum treatment for 5 h. The temperature was then adjusted to the desired polymerization temperature. Once the system cooled and stabilized, the feeding process began. In a 500 mL high-pressure reaction vessel, an appropriate amount of xylene solution was added

to maintain a total polymerization volume of 200 mL. Ethylene gas (1 bar) was introduced at the target temperature until saturation was achieved. An alkyl aluminum reagent was then added, followed by stirring for 5 minutes. Next, a xylene solution containing the catalyst was introduced. After sealing the feeding port, ethylene gas was continuously fed into the reactor at a pressure of 4 bar to initiate the polymerization reaction. The reaction mixture was stirred for 10 minutes at the specified temperature. To quench the reaction, the mixture was poured into ethanol acidified with HCl. The resulting polymer was collected via filtration, washed with ethanol, and dried under vacuum until a constant weight was obtained. For E/NBE and E/HE copolymerization experiments, the required amount of norbornene or 1-hexene was added to the xylene solution in advance, and the remaining experimental procedures followed the same steps as those used for ethylene polymerization.

1.3 Density functional theory calculations

Density Functional Theory (DFT) calculations were performed to optimize the structures of two active species $\{CpZr[O\text{-}2\text{-}^{t}Bu\text{-}4\text{-}^{t}Bu\text{-}6\text{-}(PPh_2)C_6H_2]Et\}^+$ and $\{CpZr[O\text{-}2\text{-}^{t}Bu\text{-}4\text{-}OCH_3\text{-}6\text{-}(PPh_2)C_6H_2]Et\}^+$ (Et = CH_2CH_3). All calculations were conducted using the Gaussian 16, C01 software package[1]. For these calculations, the Becke three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional[2] were employed, combined with the D3 version of Grimme's dispersion[3] (including Becke-Johnson damping for D3BJ dispersion correction[4]). The SDD[5] basis set was utilized for Zr during geometry optimization and frequency calculations, while the 6-31G+(d,p)[6-7] basis set was applied for other elements. The integral-equation-formalism polarizable continuum model (IEF-PCM) was used for solvation modeling related to histological grade. Singlet point energy calculations were executed with the SDD basis for Zr and the 6-311+G(d,p)[8] basis for other elements, and the Solvation Model Density (SMD) implicit solvation model[9] accounted for the solvation effects related to histological grade.

2. Synthesis and characterization of ligands

2.1 Synthesis of ligand 2,4-^{t}Bu$_2$-6-PPh$_2$-C$_6$H$_2$OH (1a)

Under a nitrogen atmosphere, the ligand intermediate (3.56 g, 20 mmol) was dissolved in 30 mL of anhydrous ether. The solution was cooled to -30 °C, and then a solution of *n*-BuLi (10 mL, 22 mmol) was added slowly. The reaction mixture was gradually warmed to room temperature and stirred for 8 h, resulting in a large amount of white precipitate. The mixture was then cooled again to -30 °C, and PPh_2Cl (4.3 mL, 28 mmol) was added slowly. The reaction was allowed to return to room temperature and stirred overnight. The reaction was terminated by the addition of water. Following extraction and concentration with diethyl ether, the residue was dissolved in 40 mL of dichloromethane. Subsequently, 2 mL of concentrated hydrochloric acid was added, and the mixture was allowed to react for 4 hours to remove the hydroxyl protecting group, with thin layer chromatography (TLC) used to monitor the reaction progress. Upon completion of the reaction, most of the solvent was removed under reduced pressure, and the mixture was extracted again with dichloromethane. The resulting solution was adjusted to pH 7 using a sodium bicarbonate ($NaHCO_3$) solution, then washed with water (2 × 40 mL) and dried with anhydrous sodium sulfate (Na_2SO_4). After concentration, column chromatography was performed, yielding a white solid with a 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.37 – 7.31 (m, 10H, Ar-H), 6.88 (dt, J = 5.7, 1.9 Hz, 1H, Ar-H), 6.66 (dd, J = 10.0, 1.3 Hz, 1H, Ar-H), 1.41 (d, J = 1.5 Hz, 9H, ^{t}Bu), 1.15 (d, J = 1.4 Hz, 9H, ^{t}Bu). ^{13}C NMR (126 MHz, $CDCl_3$, 298K): δ 156.07, 155.92, 142.29, 142.27, 135.53, 135.50, 135.30, 135.29, 133.45, 133.30, 129.29, 129.26, 128.86, 128.63, 128.57, 126.28, 119.96, 35.14, 35.12, 34.42, 31.46, 29.68. ^{31}P NMR (202 MHz, $CDCl_3$, 298K): δ -30.08.

2.2 Synthesis of ligand 2,4-C(CH$_3$)$_2$CH$_2$CH$_3$-6-PPh$_2$-C$_6$H$_2$OH (1b)

The preparation method was similar to **1a**, obtaining a transparent oily substance with a yield of 53%. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.34 – 7.27 (m, 10H, Ar-H), 7.21 (d, J = 2.5 Hz, 1H, Ar-H), 6.78 (dd, J = 5.8, 2.4 Hz, 1H, Ar-H), 6.59 (d, J = 10.0 Hz, 1H, Ar-H), 1.85 (q, J = 7.5 Hz, 3H, CH_3), 1.44 (q, J = 7.4 Hz, 3H, CH_3), 1.37 (s, 5H, CH_2CH_3), 1.10 (s, 5H, CH_2CH_3), 0.64 (t, J = 7.5 Hz, 3H, CH_3), 0.57 (t, J = 7.4

Hz, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298K): δ 155.92, 155.77, 140.35, 140.33, 135.68, 135.65, 133.53, 133.52, 133.38, 133.24, 130.01, 129.98, 128.82, 128.61, 128.55, 128.35, 119.61, 38.69, 38.68, 37.54, 37.03, 33.07, 28.41, 27.79, 9.57, 9.07. ^{31}P NMR (202 MHz, $CDCl_3$, 298K): δ -30.05.

2.3 Synthesis of ligand 2-^{t}Bu-4-OCH_3-C_6H_2OH (1c)

The preparation method was similar to **1a**, obtaining a transparent oily substance with a yield of 65%. ^1H NMR (500 MHz, $CDCl_3$, 298K): δ 7.32 (d, J = 5.4 Hz, 9H, Ar-H), 6.93 (d, J = 3.3 Hz, 1H, Ar-H), 6.43 (dt, J = 10.5, 2.4 Hz, 1H, Ar-H), 6.35 (dq, J = 5.2, 3.1, 2.4 Hz, 1H, Ar-H), 3.56 (d, J = 1.7 Hz, 3H, OCH_3), 1.40 (s, 9H, ^{t}Bu). ^{13}C NMR (126 MHz, $CDCl_3$, 298K): δ 152.89, 152.86, 152.63, 152.48, 137.86, 137.84, 135.13, 135.10, 133.50, 133.36, 129.06, 128.77, 128.71, 121.41, 121.39, 116.67, 115.23, 115.20, 55.54, 35.14, 35.13, 29.55. ^{31}P NMR (202 MHz, $CDCl_3$, 298K): δ -29.32.

2.4 Synthesis of ligand 2-Cumenyl-4-OCH_3-C_6H_2OH (1d)

The preparation method was similar to 1a, obtaining a white crystalline substance with a yield of 68%. ^1H NMR (500 MHz, $CDCl_3$, 298K) δ 7.33 – 7.07 (m, 15H, Ar-H), 3.58 (s, 3H, OCH_3), 1.68 (s, 9H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298K): δ 153.39, 153.38, 150.11, 149.98, 148.34, 137.03, 137.02, 136.20, 136.13, 133.76, 133.60, 128.96, 128.75, 128.48, 128.43, 126.71, 125.88, 125.58, 125.50, 115.66, 115.64, 114.95, 55.41, 42.14, 42.12, 29.49. ^{31}P NMR (202 MHz, $CDCl_3$, 298K): δ -18.49.

3. Synthesis and characterization of complexes

3.1 Synthesis of complex $CpZr(thf)Cl_2$[O-2,4-^{t}Bu-6-(PPh_2)C_6H_2] (2a)

Under a nitrogen atmosphere, ligand A (0.278 g, 1 mmol) was dissolved in 15 mL of anhydrous THF and cooled to -30 °C. NaH (0.048 g, 2 mmol) was then added, and the mixture was allowed to warm to room temperature and stirred for 6 hours. After the reaction, the excess NaH was filtered off, resulting in a golden-yellow filtrate. At -30 °C, this filtrate was slowly added to a THF solution (15 mL) of $CpZrCl_3$ (0.219 g, 1 mmol). The mixture was then gradually warmed to room temperature and stirred overnight, yielding a white suspension. The solvent was removed under vacuum, and

the residue was dissolved in 20 mL of dichloromethane. The solution was filtered, and the filter cake was washed with additional dichloromethane. The filtrate was concentrated to approximately 5 mL, and then 20 mL of n-hexane was slowly added to induce phase separation. The mixture was allowed to diffuse slowly, resulting in the recrystallization of a white powder, with a yield of 50.0%. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.73 – 7.66 (m, 4H, Ar-H), 7.42 (dt, J = 13.9, 3.5 Hz, 6H, Ar-H), 7.35 – 7.26 (m, 1H, Ar-H), 7.12 (s, 1H, Ar-H), 6.49 (s, 5H, C_5H_5), 3.74 (s, 4H, -OCH_2-), 1.49 (s, 9H, ^{t}Bu-H), 1.30 – 1.17 (m, 9H, ^{t}Bu-H + -CH_2-). ^{13}C NMR (126 MHz, $CDCl_3$, 298K): δ 25.07, 29.89, 31.49, 31.60, 34.68, 35.19, 35.32, 116.01, 127.68, 128.43, 128.60, 128.84, 128.91, 129.81, 130.47, 132.77, 133.24, 134.10, 134.22, 137.34, 137.62, 164.69. ^{31}P NMR (202 MHz,$CDCl_3$, 298K): δ -2.37. Anal. Calc. For $C_{36}H_{46}Cl_2O_2PZr$: C, 61.03; H, 6.29. Found: C, 61.42; H, 6.59.

3.2 Synthesis of complex CpZr(thf)Cl_2[O-2,4-C$(CH_3)_2CH_2CH_3$-6-$(PPh_2)C_6H_2$] (2b)

The preparation method was similar to **2a**, obtaining a white substance with a yield of 68%. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.31 (dd, J = 23.4, 2.8 Hz, 6H, Ar-H), 7.12 – 7.09 (m, 6H, Ar-H), 6.49 (d, J = 0.9 Hz, 5H, C_5H_5), 1.48 (d, J = 7.9 Hz, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.13 – 0.63 (s, 6H, CH_3), 0.58 (dd, 6H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298K): δ 142.16, 135.40, 133.81, 133.34, 133.27, 133.17, 129.80, 129.18, 128.79, 128.57, 128.52, 128.43, 128.36, 116.02, 38.68, 37.69, 36.96, 33.18, 33.03, 28.48, 28.36, 27.34, 9.60, 8.99. ^{31}P NMR (202 MHz,$CDCl_3$, 298K): δ -1.19, -4.70, -7.98. Anal. Calc. For $C_{38}H_{50}Cl_2O_2PZr$: C, 61.99; H, 6.81. Found: C, 62.36; H, 6.86.

3.3 Synthesis of complex CpZr(thf)Cl_2[O-2-^{t}Bu-4-OCH_3-6-$(PPh_2)C_6H_2$] (2c)

The preparation method was similar to **2a**, obtaining a yellow powdery substance with a yield of 48%. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.34 - 7.28 (m, 4H, Ar-H), 7.27 (m, 7H, Ar-H), 6.98 (dd, 1H, Ar-H), 6.49 (s, 5H, C_5H_5), 3.62 (s, 3H, OCH_3), 1.33 – 1.26 (s, 6H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298K): δ 154.07, 139.22, 133.93, 133.33, 133.23, 130.03, 129.80, 128.52, 128.13, 128.06, 118.09, 116.03, 114.61, 55.51, 53.45, 35.20, 31.60, 29.32, 22.67, 14.14. ^{31}P NMR (202 MHz,$CDCl_3$, 298K): δ -1.33, -

4.42, -8.02. Anal. Calc. For $C_{33}H_{40}Cl_2O_3PZr$: C, 57.99; H, 5.63. Found: C, 58.48; H, 5.95.

3.4 Synthesis of complex $CpZr(thf)Cl_2[O\text{-}2\text{-}Cumenyl\text{-}4\text{-}OCH_3\text{-}6\text{-}(PPh_2)C_6H_2]$ (2d)

The preparation method was similar to **2a**, obtaining a light yellow powdery substance with a yield of 61%. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 7.62 (t, J = 8.7 Hz, 1H, Ar-H), 7.58 – 7.37 (m, 3H, Ar-H), 7.40 – 7.34 (m, 4H, Ar-H), 7.30 (d, J = 3.0 Hz, 1H, Ar-H), 7.28 (s, 2H), 7.26 (s, 1H, Ar-H), 7.21 (q, J = 7.6, 6.9 Hz, 2H, Ar-H), 7.02 (t, J = 7.3 Hz, 1H, Ar-H), 6.58 (dd, J = 6.5, 2.9 Hz, 1H, Ar-H), 6.49 (s, 5H, C_5H_5), 3.11 - 2.97 (d, 4H, -OCH_2-), 3.74 (d, J = 6.1 Hz, 3H, OCH_3), 1.85 (s, 3H, CH_3), 1.26 (s, 2H, -CH_2-), 1.60 (s, 2H, -CH_2-), 1.12 (s, 3H，CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 298K): δ 160.59, 154.58, 154.53, 150.12, 139.36, 128.90, 127.89, 126.59, 125.83, 124.99, 122.08, 121.80, 118.38, 116.00, 114.58, 74.29, 55.80, 42.21, 42.19, 31.59, 29.71, 25.61, 24.62, 22.66, 14.12. ^{31}P NMR (202 MHz,$CDCl_3$, 298K): δ -2.58. Anal. Calc. For $C_{38}H_{42}Cl_2O_3PZr$: C, C, 61.31; H, 5.42. Found: C, 61.69; H, 5.72.

4. The ^{1}H NMR spectrum of complexes

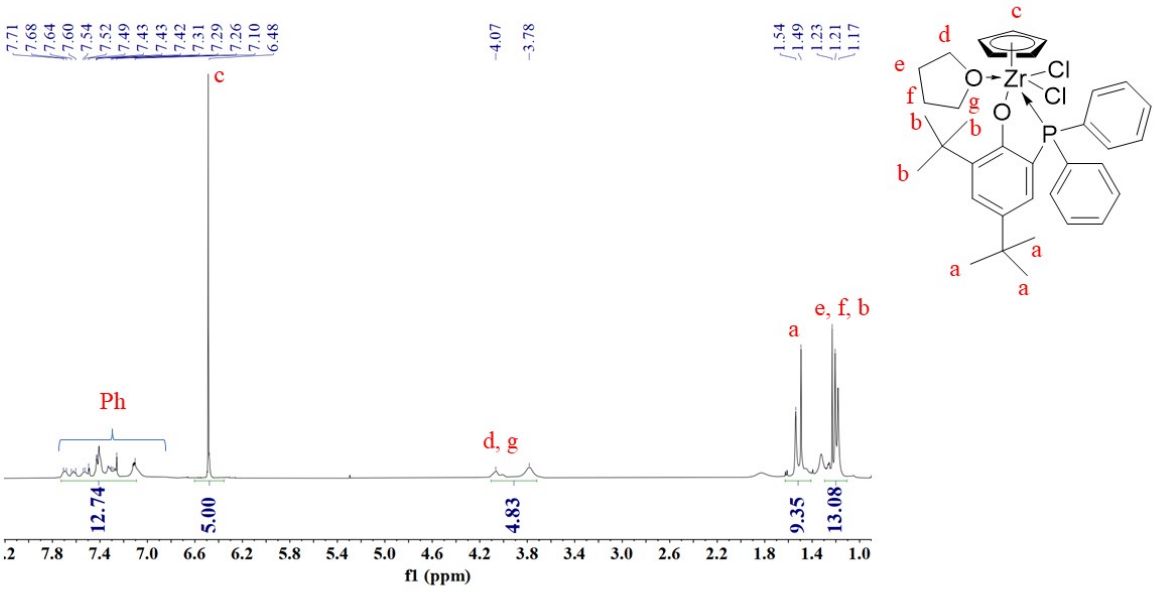


Figure S1 The ^{1}H NMR spectrum of complex **2a**

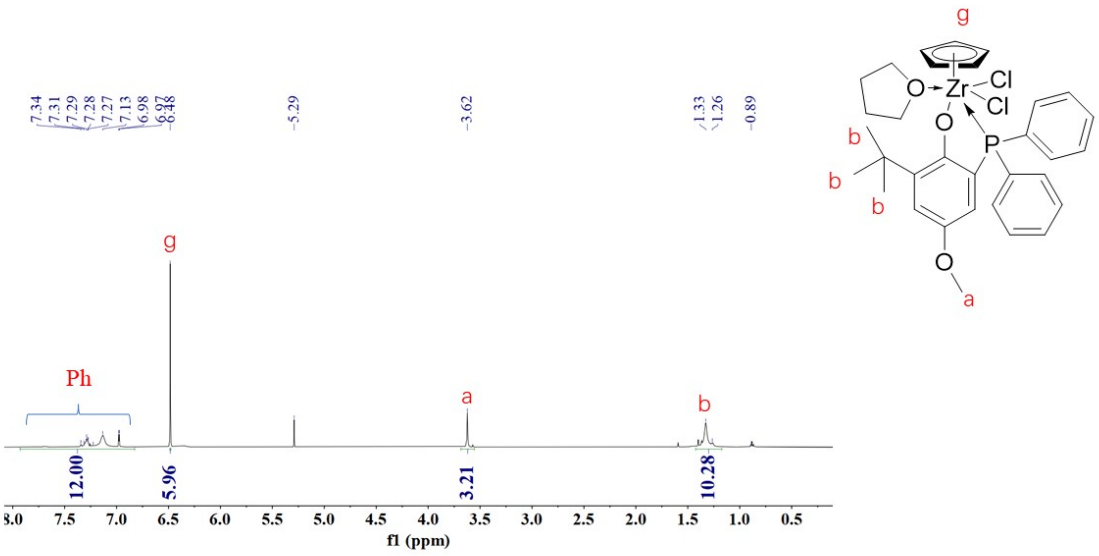


Figure S2 The ^{1}H NMR spectrum of complex **2b**

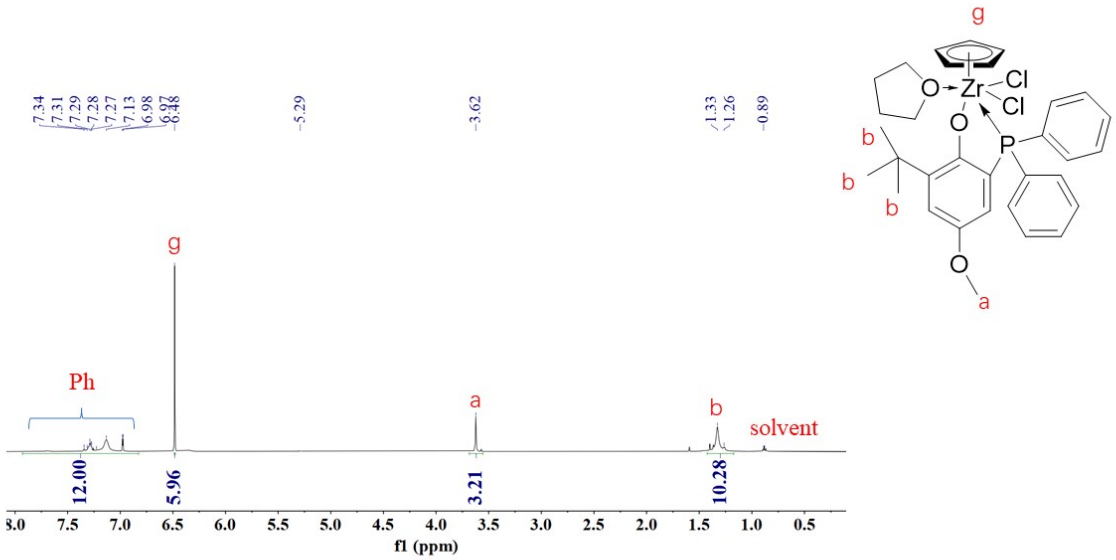


Figure S3 The ^{1}H NMR spectrum of complex **2C**

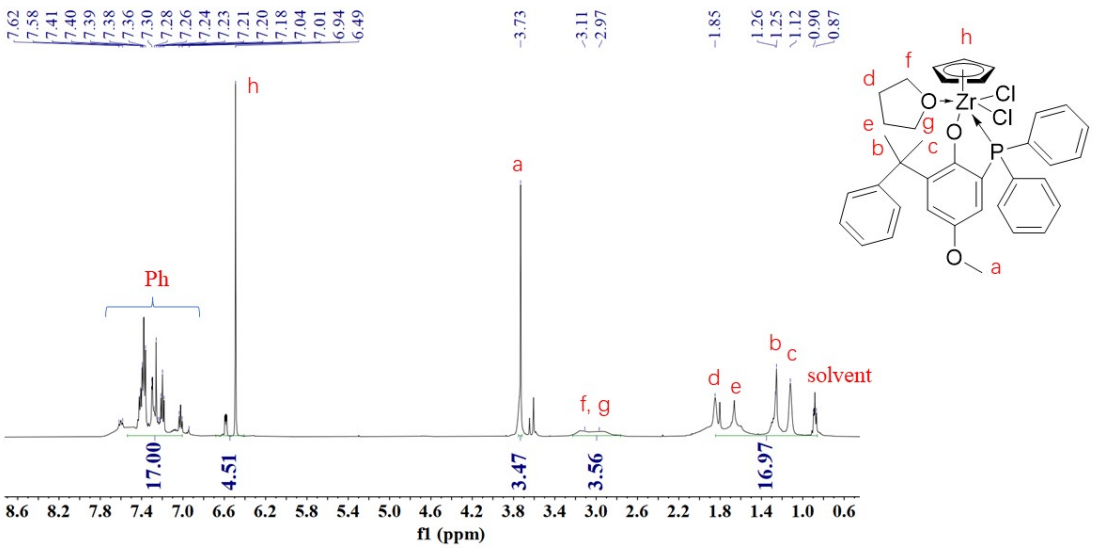


Figure S4 The ^{1}H NMR spectrum of complex **2d**

5. The ^{13}C NMR spectrum of complexs

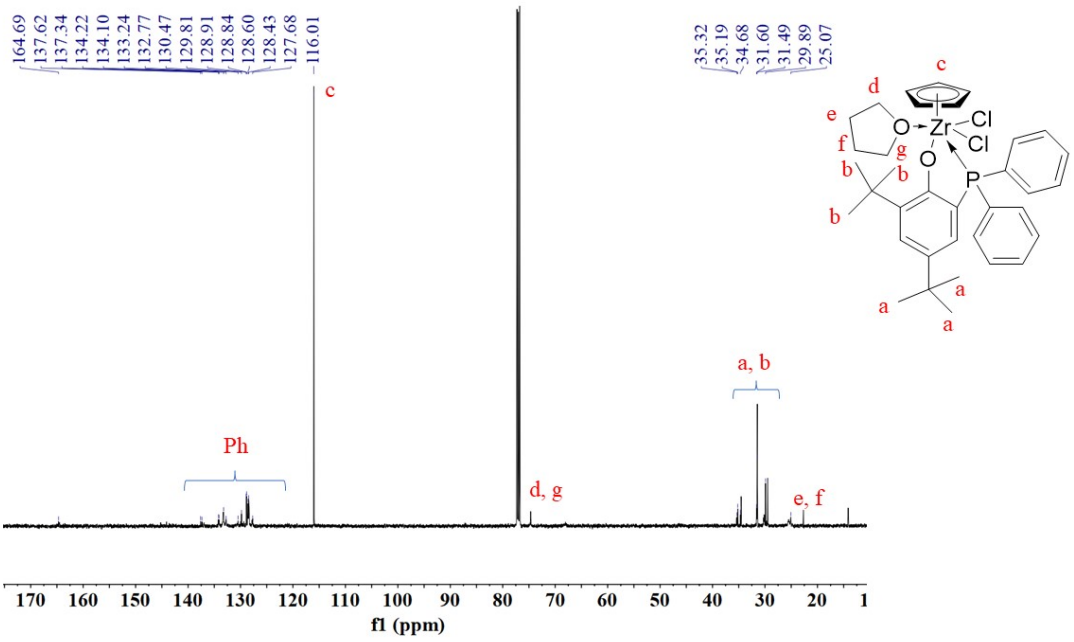


Figure S5 The ^{13}C NMR spectrum of complex **2a**

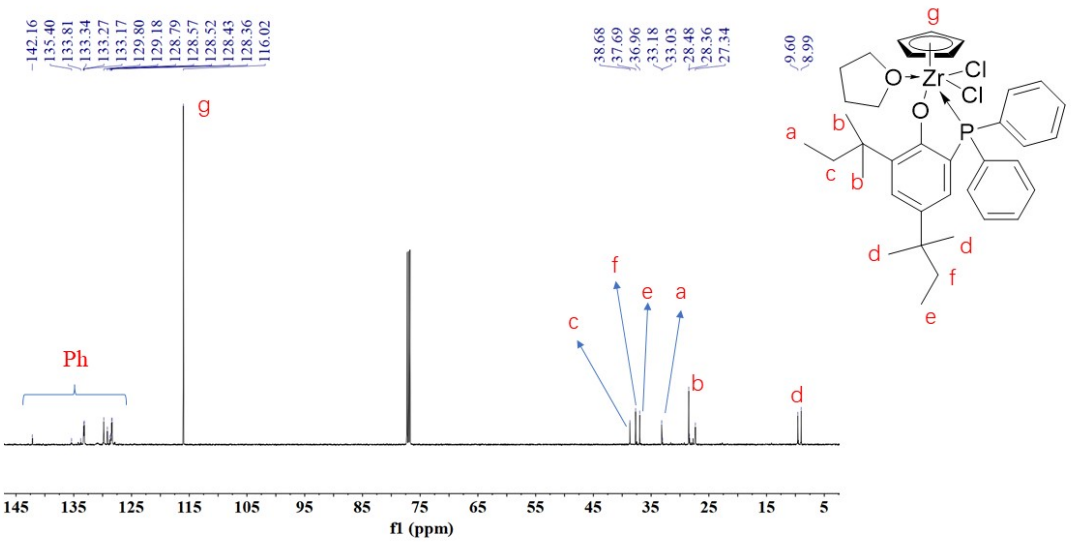


Figure S6 The ^{13}C NMR spectrum of complex **2b**

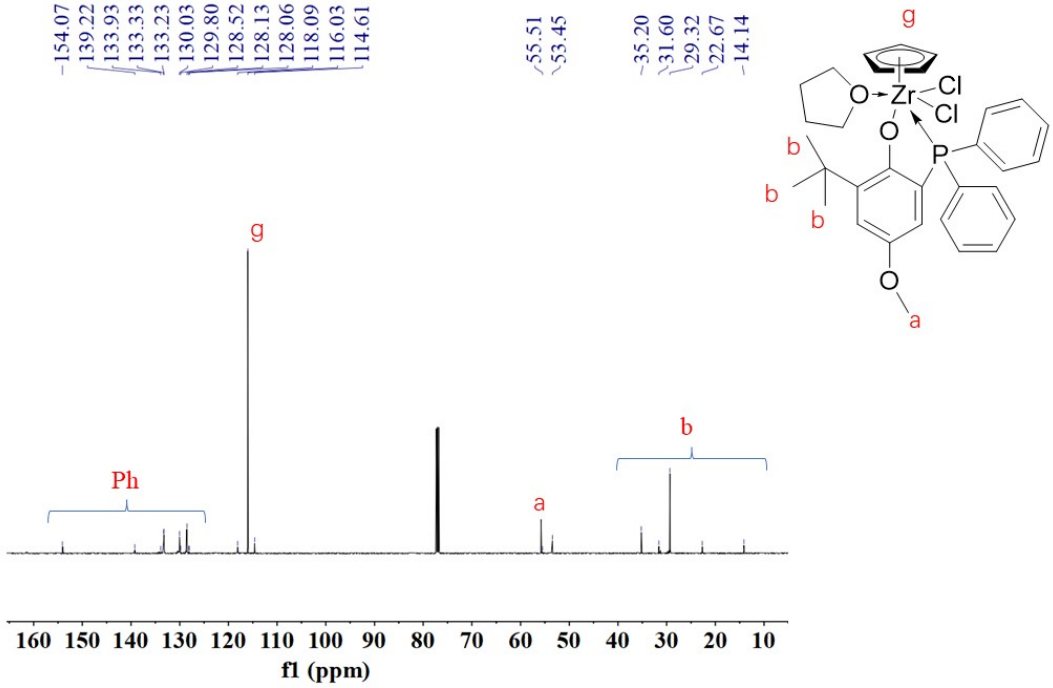


Figure S7 The ^{13}C NMR spectrum of complex **2c**

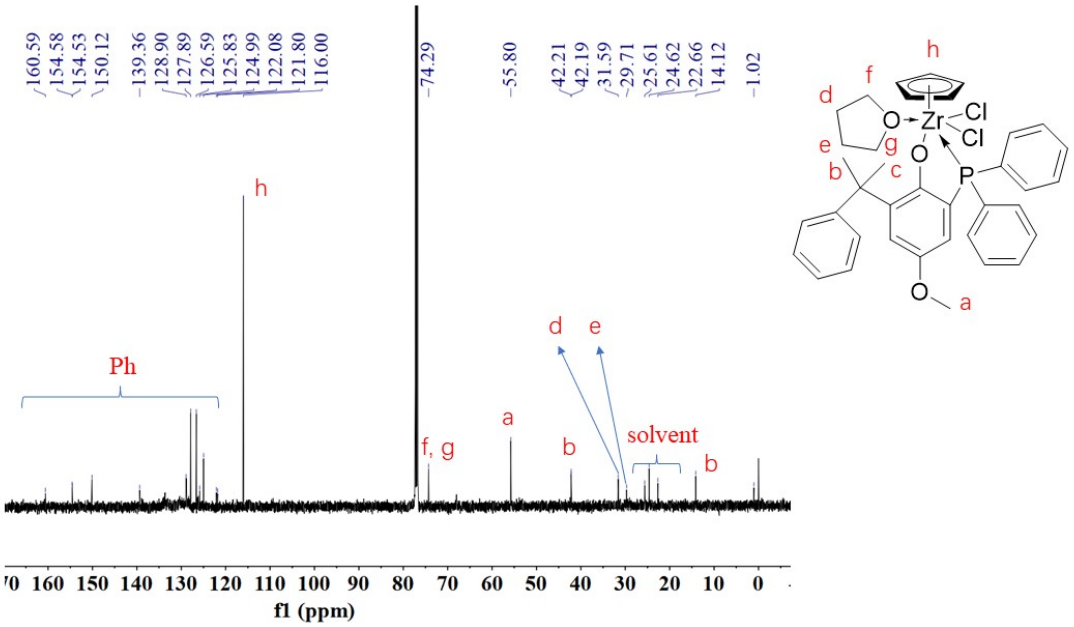


Figure S8 The ^{13}C NMR spectrum of complex **2d**

6. The ^{31}P NMR spectrum of complexes

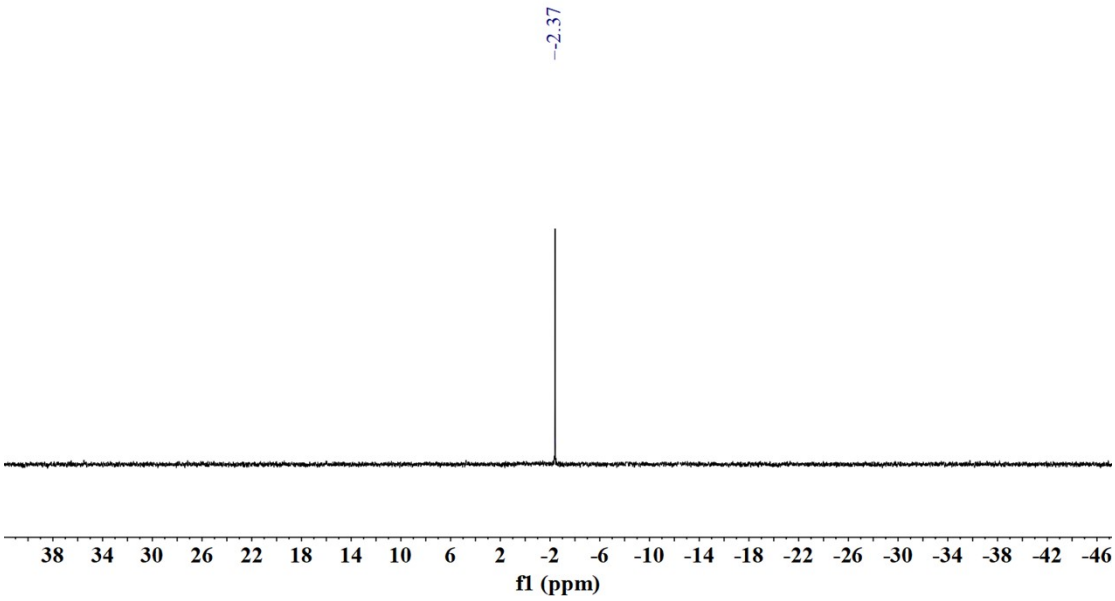


Figure S9 The ^{31}P NMR spectrum of complex **2a**

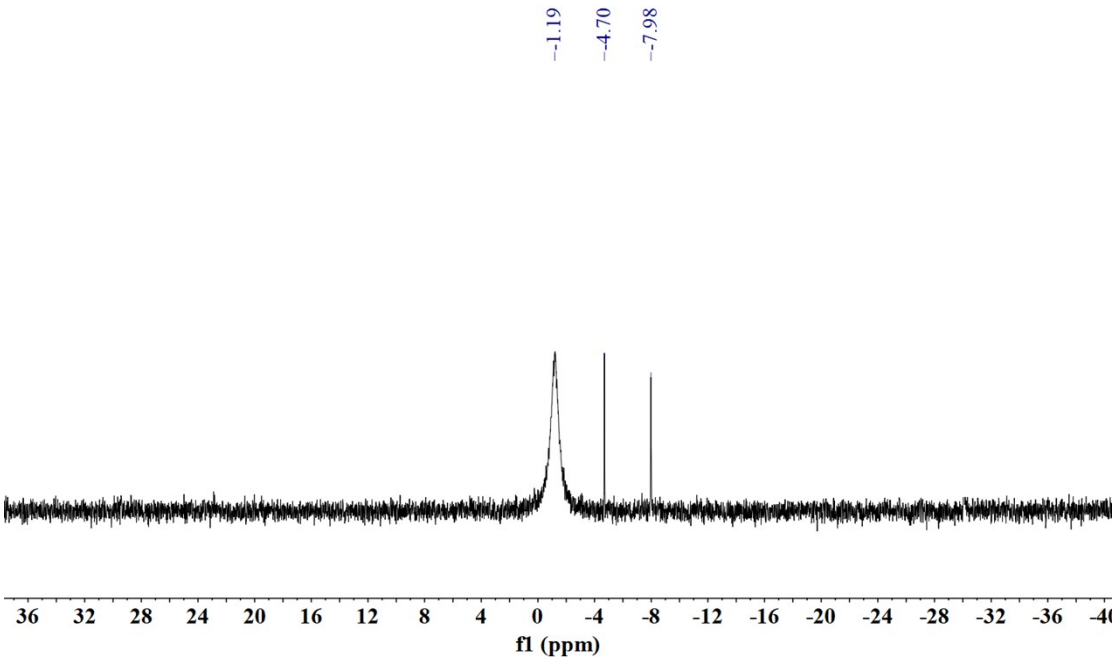


Figure S10 The ^{31}P NMR spectrum of complex **2b**

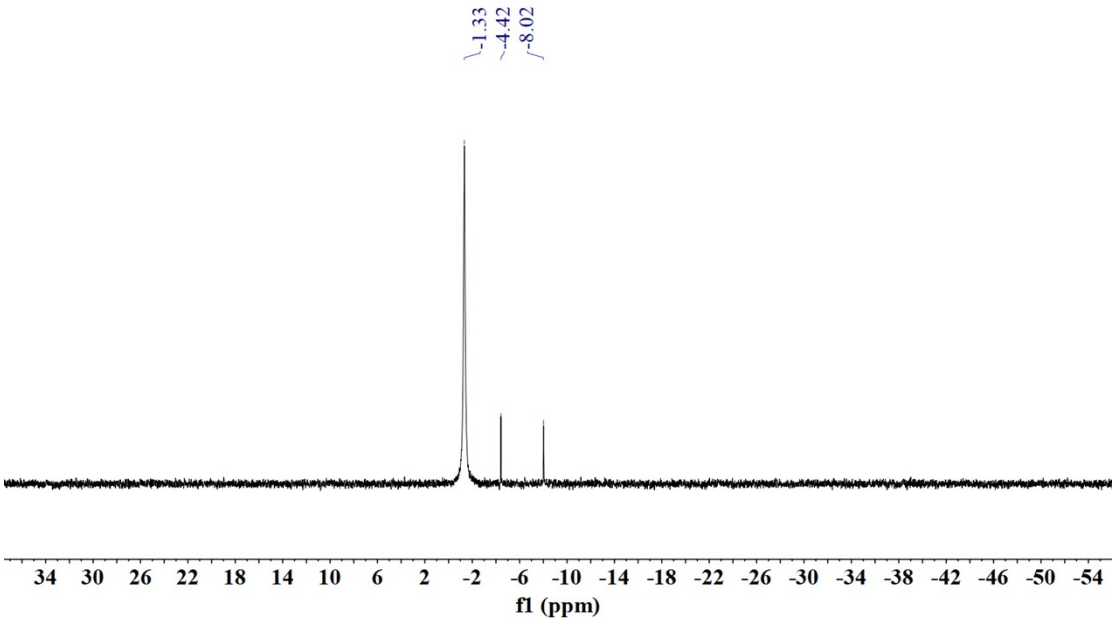


Figure S11 The ^{31}P NMR spectrum of complex **2c**

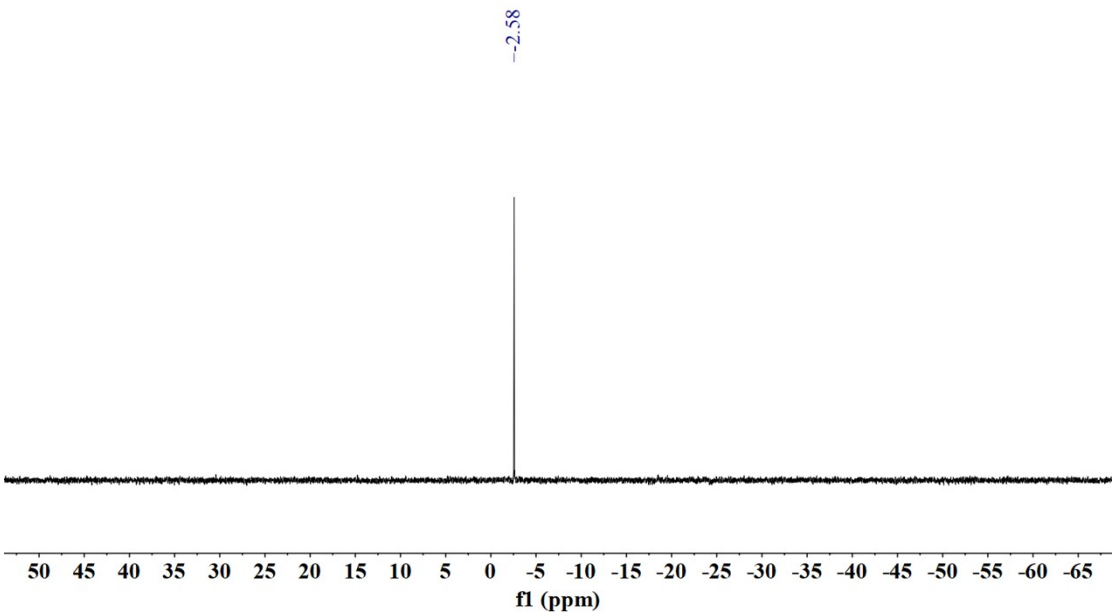
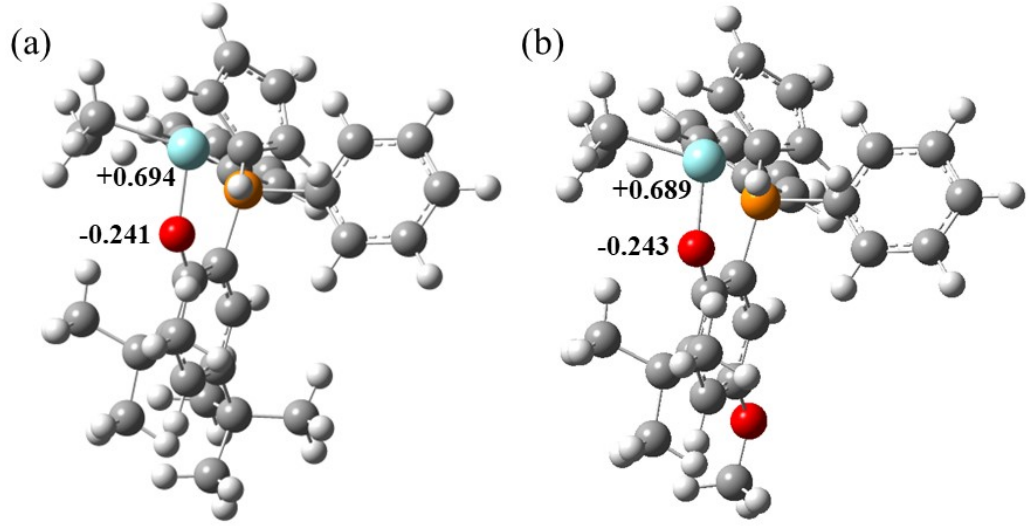


Figure S12 The ^{31}P NMR spectrum of complex **2d**

6. Density functional theory calculations



{CpZr[O-2-^{t}Bu-4-^{t}Bu-6-(PPh$_2$)C$_6$H$_2$]Et}$^+$ {CpZr[O-2-^{t}Bu-4-OCH$_3$-6-(PPh$_2$)C$_6$H$_2$]Et}$^+$

Figure S13 Geometrical parameters and Hishfeld charges for optimized geometries of activity centers at B3LYP level. Bule, orange, red, gray, and white spheres represent the zirconium, phosphorus, oxygen, carbon, and hydrogen atoms, respectively.

(a)

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	2.32604	0.50044	0.01989
C	3.38432	-0.40311	0.15548
C	3.06607	-1.77036	0.18284

C	1.76156	-2.27905	0.08324
C	0.72124	-1.33565	-0.04921
C	1.01111	0.04587	-0.07896
H	2.51723	1.56776	-0.00549
H	3.87432	-2.47893	0.28528
O	-0.57621	-1.71502	-0.1686
C	1.47133	-3.78833	0.10672
C	0.80172	-4.20919	-1.22285
H	1.45963	-3.98791	-2.07054
H	0.6077	-5.28771	-1.21548
H	-0.14565	-3.69051	-1.37567
C	2.75631	-4.62058	0.26834
H	2.49271	-5.68285	0.28329
H	3.45359	-4.46379	-0.56133
H	3.27596	-4.39411	1.20529
C	0.54072	-4.12146	1.29646
H	1.01844	-3.84931	2.24414
H	-0.40881	-3.5895	1.22206
H	0.33483	-5.19761	1.31646
P	-0.43427	1.1536	-0.19341
C	0.00316	2.52577	-1.31099
C	0.79745	3.59711	-0.87066
C	-0.44282	2.49387	-2.64046
C	1.15354	4.61355	-1.75784
H	1.1276	3.64388	0.16185
C	-0.08362	3.51305	-3.5258
H	-1.07332	1.68164	-2.98601
C	0.71624	4.57164	-3.08629
H	1.76903	5.43795	-1.41151
H	-0.43442	3.48233	-4.55249
H	0.99223	5.36552	-3.7733
C	-0.5819	1.91687	1.46274
C	-1.46938	2.99063	1.63978
C	0.08901	1.38269	2.57153
C	-1.67583	3.527	2.91106
H	-1.99441	3.41141	0.7873
C	-0.12539	1.91961	3.84411
H	0.77277	0.5507	2.44429
C	-1.00662	2.99019	4.01675
H	-2.36096	4.35934	3.03823
H	0.39793	1.50016	4.69776
H	-1.17222	3.40484	5.00622
Zr	-2.33396	-0.8496	-0.5573
C	-2.97409	-1.89893	-2.41482

H	-3.94434	-1.56409	-2.78981
C	-3.92172	0.39274	1.02645
C	-4.76838	-0.44068	0.25008
H	-5.49855	-0.10559	-0.47497
C	-4.43825	-1.79074	0.53141
H	-4.89675	-2.66505	0.0904
C	-3.08067	-0.44256	1.81713
H	-2.32308	-0.10606	2.51123
C	-3.39869	-1.78935	1.51249
H	-2.92371	-2.6657	1.93427
H	-3.91028	1.4744	1.01982
H	-2.95421	-2.98861	-2.33858
C	-1.78518	-1.31137	-3.17266
H	-1.02796	-2.05891	-3.41943
H	-2.07288	-0.76137	-4.07234
H	-1.19749	-0.5384	-2.5932
C	4.82124	0.12394	0.28007
C	5.16901	0.96482	-0.96953
C	4.92536	1.01379	1.53987
C	5.85271	-1.01069	0.40193
H	5.10316	0.35543	-1.87726
H	4.49346	1.81782	-1.08439
H	6.19022	1.35367	-0.89021
H	4.68239	0.44008	2.44078
H	5.94407	1.4033	1.64528
H	4.24281	1.86755	1.48849
H	6.85609	-0.58128	0.48672
H	5.67802	-1.62517	1.29139
H	5.84305	-1.66441	-0.47665

Hishfeld Charges：

Atom	1(C):	-0.03453934
Atom	2(C):	0.00428771
Atom	3(C):	-0.03560948
Atom	4(C):	-0.00084217
Atom	5(C):	0.07702031
Atom	6(C):	-0.06895214
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Atom	10(C):	0.03122524
Atom	11(C):	-0.08880369
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Atom 19(C): -0.08945574
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Atom 22(H): 0.03132022
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Atom 24(C): -0.04948994
Atom 25(C): -0.02637058
Atom 26(C): -0.03467882
Atom 27(C): -0.02617249
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Atom 29(C): -0.02937734
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Atom 31(C): -0.02026260
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Atom 38(C): -0.02734732
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Atom 40(C): -0.02738906
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Atom 42(C): -0.02446682
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Atom 46(Zr): 0.69473471
Atom 47(C): -0.18564057
Atom 48(H): 0.03676891
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Atom	76(H):	0.03176602

(b)

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	1.63445	2.15674	0.02759
C	3.02466	2.14488	0.14813
C	3.70993	0.92253	0.20039
C	3.04945	-0.31383	0.12524
C	1.64422	-0.2874	-0.0073
C	0.95256	0.94325	-0.04706
H	1.10902	3.10486	-0.00547
H	4.78501	0.93075	0.2978
O	0.91487	-1.4274	-0.12295
C	3.82255	-1.64133	0.17724
C	3.59847	-2.42431	-1.13784
H	3.95474	-1.84318	-1.99545
H	4.15947	-3.36509	-1.10779
H	2.54389	-2.65614	-1.29086
C	5.33776	-1.4225	0.34051
H	5.83521	-2.3965	0.38018
H	5.76513	-0.86703	-0.50095
H	5.57761	-0.89006	1.2669
C	3.33384	-2.47765	1.38305
H	3.51249	-1.93884	2.3201
H	2.26857	-2.70138	1.30941

H	3.88523	-3.42368	1.42467
P	-0.86511	0.80873	-0.13482
C	-1.47753	2.08508	-1.28108
C	-1.58941	3.43103	-0.89642
C	-1.83009	1.70431	-2.58454
C	-2.03458	4.384	-1.81359
H	-1.34351	3.73313	0.1162
C	-2.27389	2.66125	-3.49995
H	-1.76519	0.66364	-2.88414
C	-2.37482	4.00136	-3.11574
H	-2.11878	5.42293	-1.51055
H	-2.5468	2.35838	-4.50588
H	-2.72455	4.7446	-3.82547
C	-1.45392	1.31158	1.52078
C	-2.8058	1.64679	1.70003
C	-0.60109	1.25551	2.63225
C	-3.2945	1.92856	2.97615
H	-3.47415	1.69832	0.84582
C	-1.09641	1.5336	3.90897
H	0.44402	0.99547	2.50327
C	-2.4417	1.86916	4.08387
H	-4.33974	2.19176	3.10468
H	-0.42916	1.4889	4.76405
H	-2.82443	2.0849	5.07646
Zr	-0.97814	-1.95863	-0.51645
C	-0.81531	-3.14244	-2.40806
H	-1.78161	-3.42951	-2.83031
C	-3.11657	-1.80144	0.89858
C	-3.33436	-2.94477	0.08555
H	-4.07873	-3.03497	-0.69481
C	-2.35422	-3.91399	0.41172
H	-2.24221	-4.88809	-0.04401
C	-2.02064	-2.07881	1.76784
H	-1.61447	-1.4078	2.51222
C	-1.54697	-3.3802	1.46418
H	-0.71059	-3.87867	1.93807
H	-3.69098	-0.88593	0.87829
H	-0.17982	-4.02629	-2.30423
C	-0.14229	-1.98446	-3.14958
H	0.90596	-2.18701	-3.38215
H	-0.67184	-1.69068	-4.05941
H	-0.09128	-1.03122	-2.55743
O	3.63382	3.36905	0.21169
C	5.05473	3.41217	0.35102

H	5.31707	4.46957	0.38469
H	5.37561	2.92521	1.27906
H	5.55062	2.93864	-0.50406

Hishfeld Charges：

Atom	1(C):	-0.05110543
Atom	2(C):	0.06701879
Atom	3(C):	-0.05452864
Atom	4(C):	0.00378017
Atom	5(C):	0.06858239
Atom	6(C):	-0.06400932
Atom	7(H):	0.04804365
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Atom	9(O):	-0.24366232
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Atom	23(P):	0.24680755
Atom	24(C):	-0.04910004
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Atom	36(C):	-0.02729053
Atom	37(C):	-0.02891729
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Atom	40(C):	-0.02736484
Atom	41(H):	0.04340469
Atom	42(C):	-0.02449344
Atom	43(H):	0.05436424
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Atom	46(Zr):	0.68994103
Atom	47(C):	-0.18641797
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Atom	64(O):	-0.13953685
Atom	65(C):	0.00879653
Atom	66(H):	0.05478549
Atom	67(H):	0.04337997
Atom	68(H):	0.04379541

7. Ethylene polymerization

Table S1 Results of ethylene polymerization catalyzed by **2c**[a]

Run	Cat.	Temp. (°C)	Product (g)	Activity ($kg \cdot mol_{Zr}^{-1} \cdot h^{-1}$)	M_w[f] (kDa)	PDI	T_m[g] (°C)
1[b]	2c	75	8.35	16700	323	2.46	143.3
2[c]	2c	75	2.40	4800	1013	2.31	137.1
3[d]	2c	75	4.80	9600	412	2.21	142.6
4[e]	2c	75	13.80	27600	93	2.11	134.5
5	2c	120	13.25	26500	86	1.66	130.2

[a] Conditions: catalyst 3 μmol, ethylene pressure 4 bar, total polymerization volume 200 mL, polymerization time 10 min. [b] MAO 3 mmol. [c] *d*-MAO 3 mmol. [d] $^{i}Bu_3Al$ 3 mmol, $[Ph_3C][B(C_6F_5)_4]$ 6 μmol. [e] MMAO 6 mmol. [f] Weight-average molecular weights and polydispersity indexes determined by high temperature GPC at 150 °C in 1,2,4-$C_6Cl_3H_3$ *vs.* narrow polystyrene standards. [g] The melting temperature of the polymer was measured by DSC, with a heating rate of 10 °C/min.

8. Ethylene and norbornene copolymerization

Table S2 Results of E/NBE copolymerization catalyzed by **2a**, **2b**, and **2d**[a]

Run	Cat.	Temp. (°C)	NBE (mol/L)	Product (g)	Activity ($kg \cdot mol_{Zr}^{-1} \cdot h^{-1}$)	Incrop.[b] (mol%)	M_w[c] (kDa)	PDI	T_g[d] (°C)
1	2a	50	1.0	3.80	3800	26.8	106	1.65	77.3
2	2a	100	1.0	4.43	4430	33.5	73	2.01	92.1
3	2a	75	0.5	3.75	3750	17.4	128	1.98	49.1
4	2b	50	1.0	4.57	4570	26.2	155	1.76	75.4
5	2b	100	1.0	3.00	3000	31.6	102	2.01	87.7
6	2b	75	0.5	7.61	7610	15.4	184	1.51	34.2
7	2d	50	1.0	7.28	7275	22.5	306	1.55	63.4
8	2d	100	1.0	3.30	3300	26.3	135	1.96	77.3
9	2d	75	0.5	2.00	2000	16.6	245	1.50	31.5

[a] Conditions: catalyst 6 μmol, $^{i}Bu_3Al$ 3 mmol, $[Ph_3C][B(C_6F_5)_4]$ 12 μmol, ethylene pressure 4 bar, total polymerization volume 200mL, polymerization time 10 min. [b] NBE content (mol%) estimated by ^{13}C NMR spectra. [c] Weight-average molecular weights and polydispersity indexes determined by high temperature GPC at 150 °C in 1,2,4-$C_6Cl_3H_3$ *vs.* narrow polystyrene standards. [d] The melting temperature of the polymer was measured by DSC, with a heating rate of 10 °C/min.

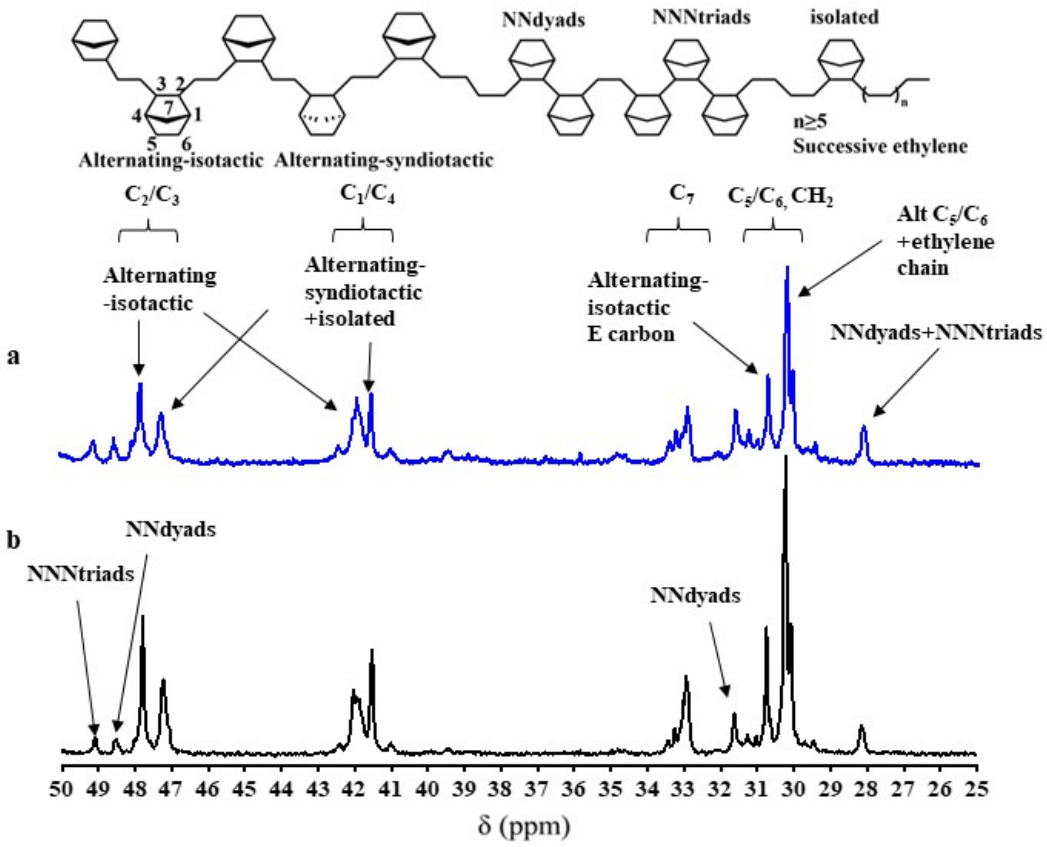

Figure S14 ^{13}C NMR spectra of E/NBE copolymers (a, Table 2, Run 11, 52.4 % ; b, Table 2, Run 11, 56.2%)

9. Ethylene and 1-hexene copolymerization

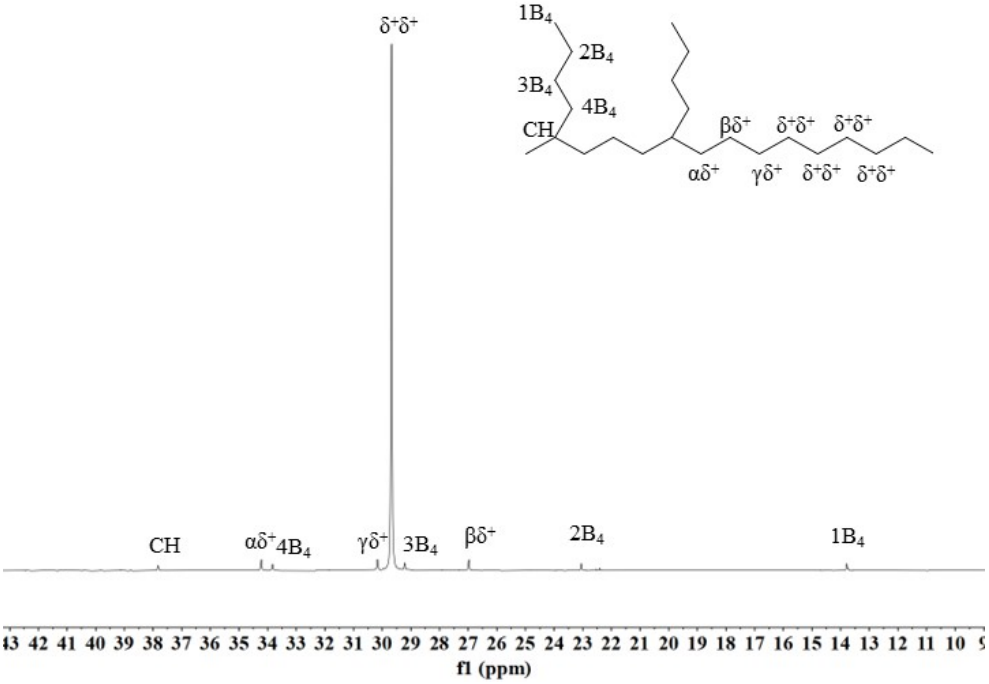

Figure S15 ^{13}C NMR spectra of E/HE copolymers from Table 3, Run 1

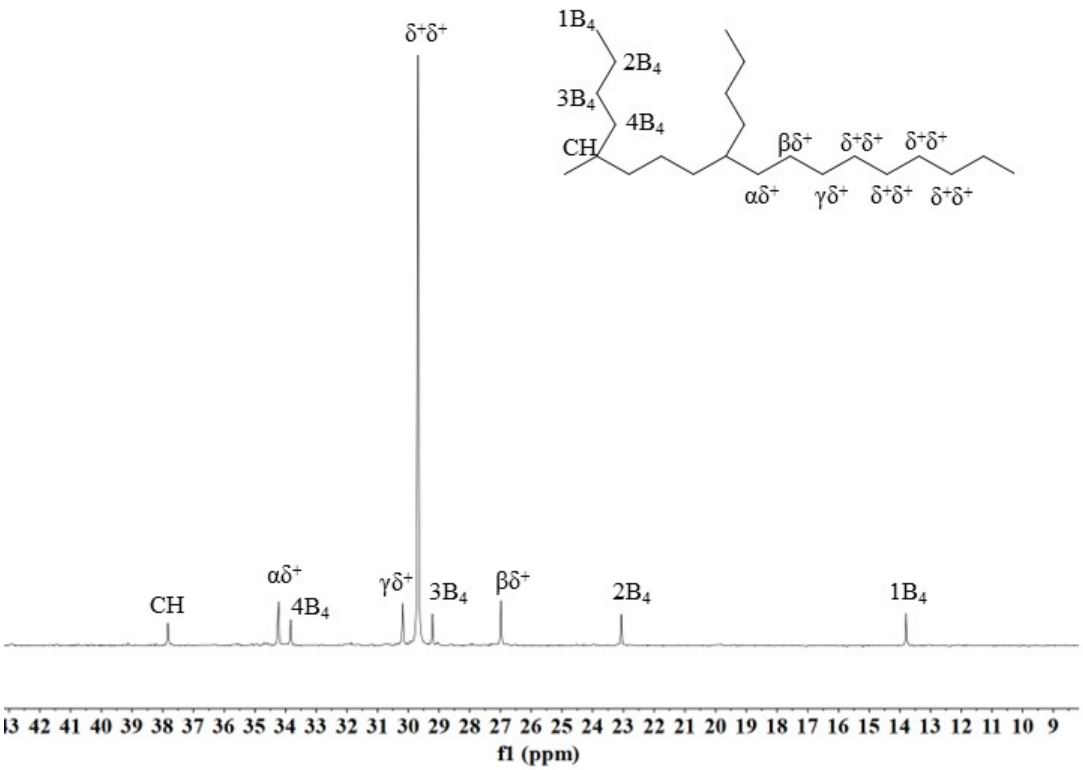

Figure S16 ^{13}C NMR spectra of E/HE copolymers from Table 3, Run 3

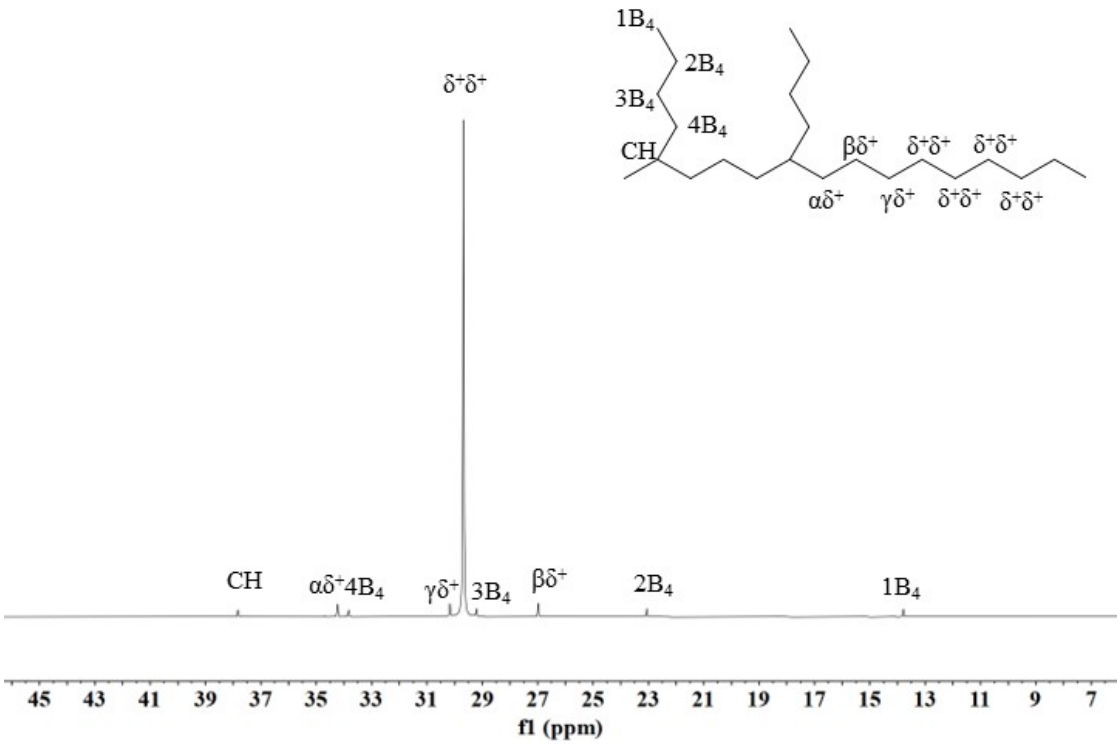

Figure S17 ^{13}C NMR spectra of E/HE copolymers from Table 3, Run 4

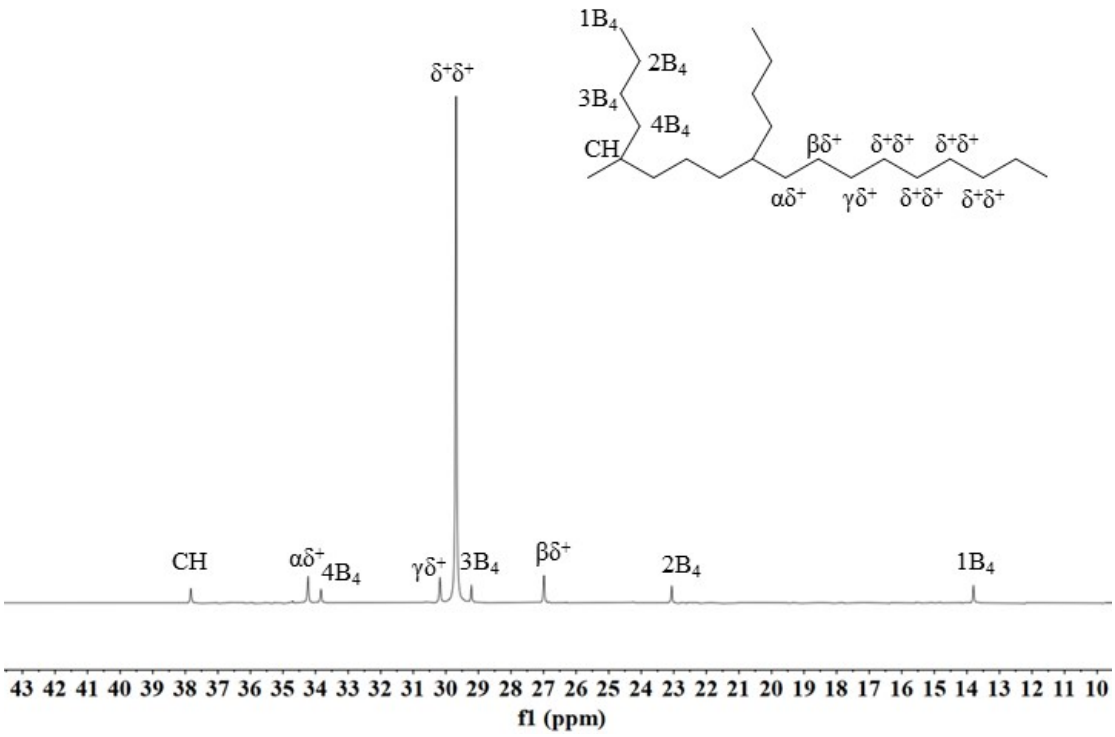

Figure S18 ^{13}C NMR spectra of E/HE copolymers from Table 3, Run 6

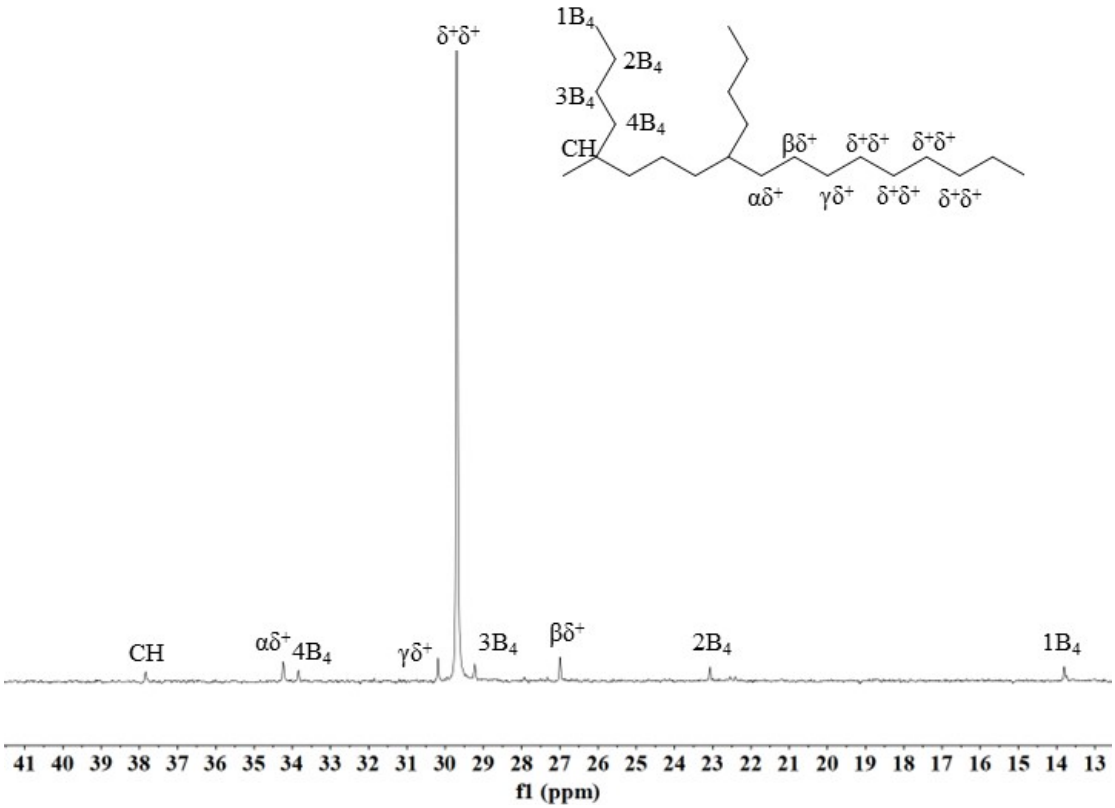

Figure S19 ^{13}C NMR spectra of E/HE copolymers from Table 3, Run 7

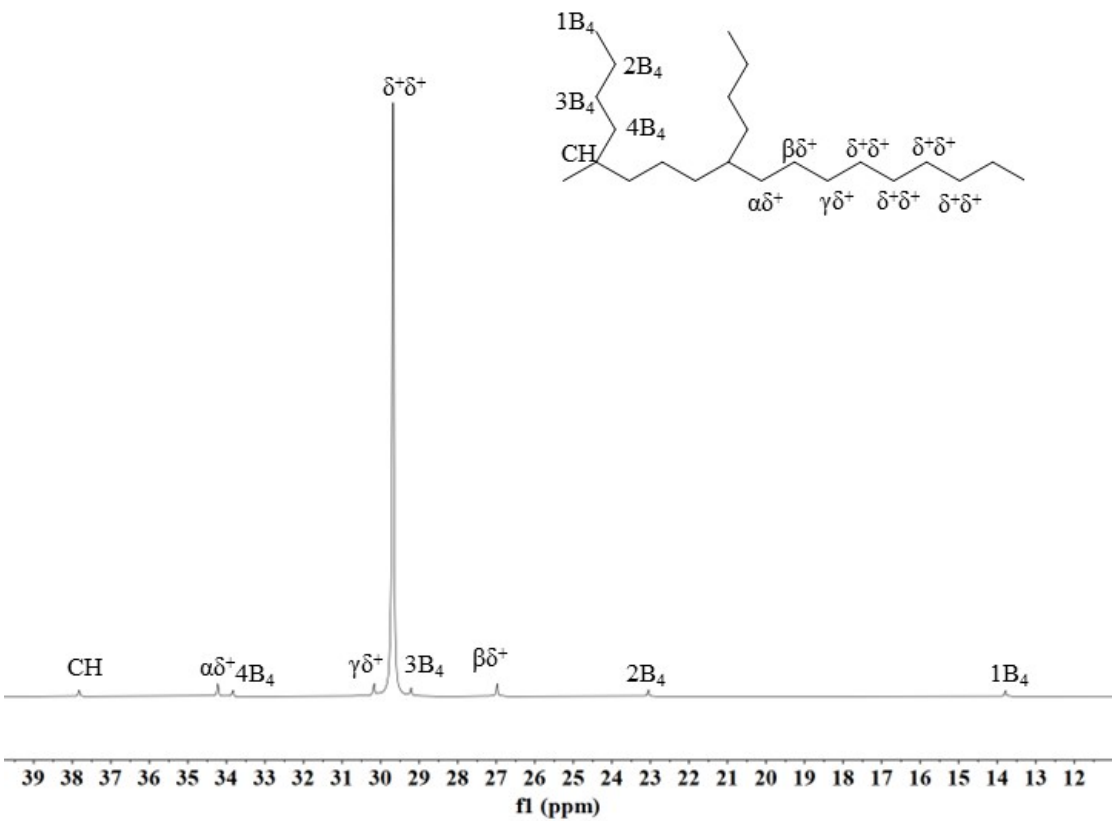

Figure S20 ^{13}C NMR spectra of E/HE copolymers from Table 3, Run 10

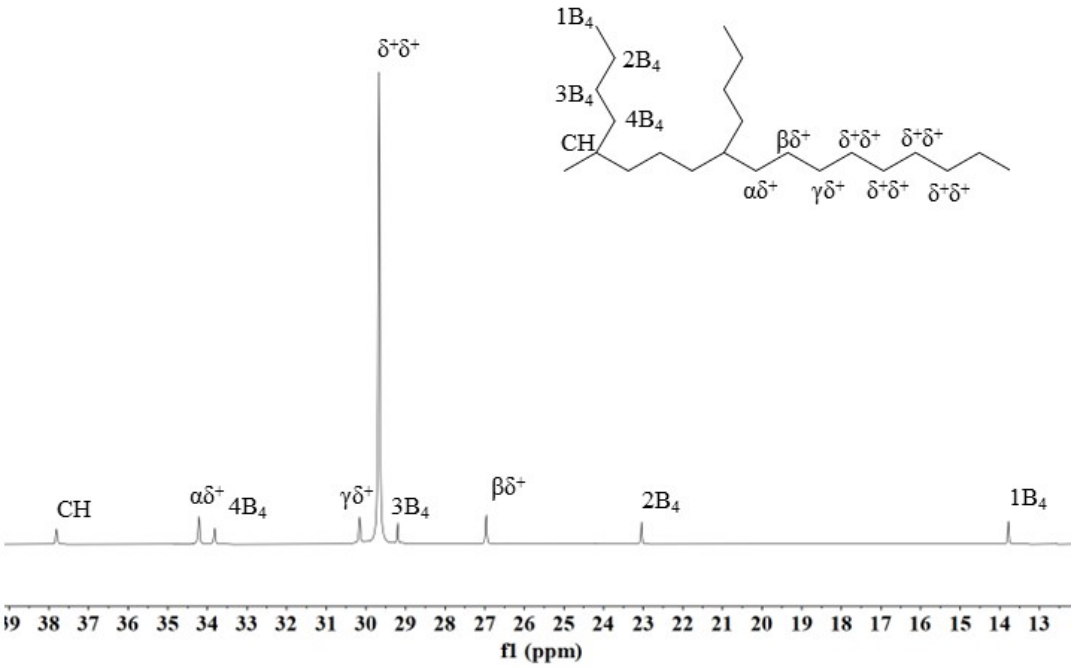

Figure S21 ^{13}C NMR spectra of E/HE copolymers from Table 3, Run 12

10. GPC curves of Polymers

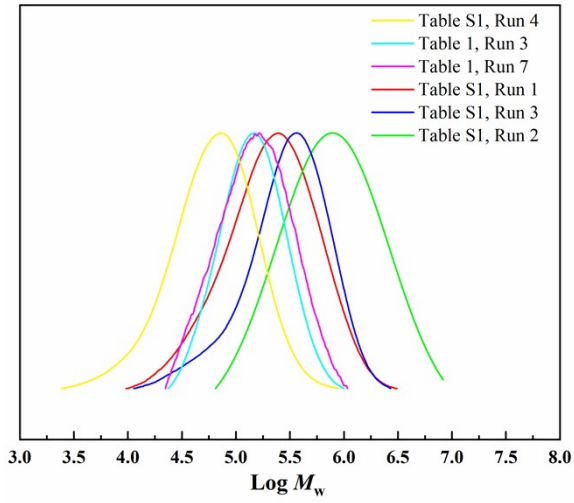

Figure S22 GPC curve of ethylene polymers

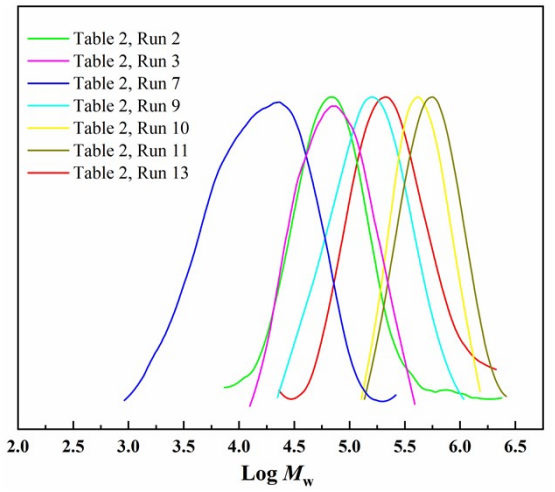

Figure S23 GPC curve of E/NBE copolymers

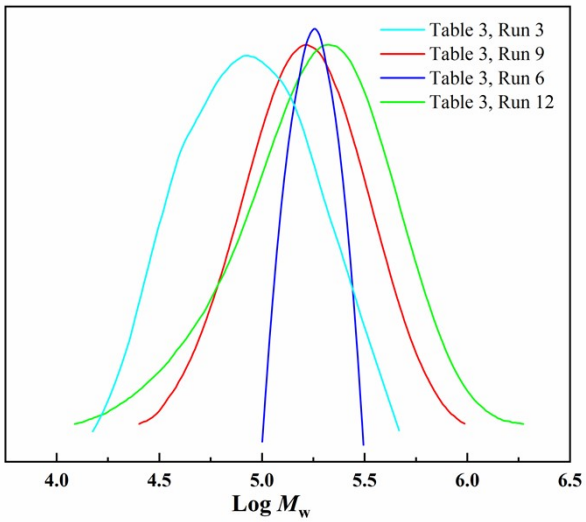

Figure S24 GPC curve of E/HE copolymers

11. DSC curves of Polymers

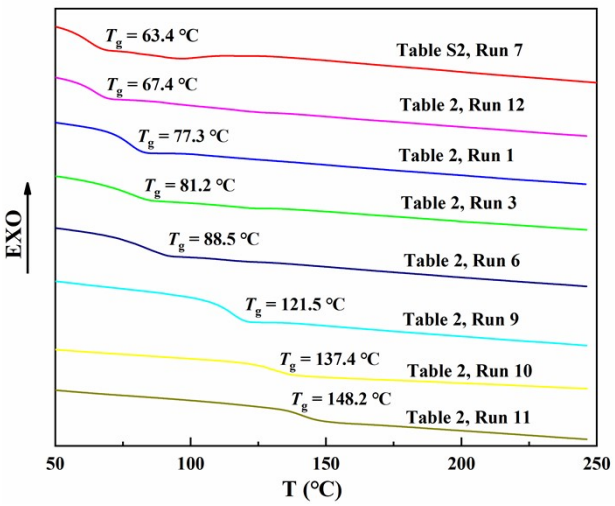

Figure S25 DSC curve of E/NBE copolymers

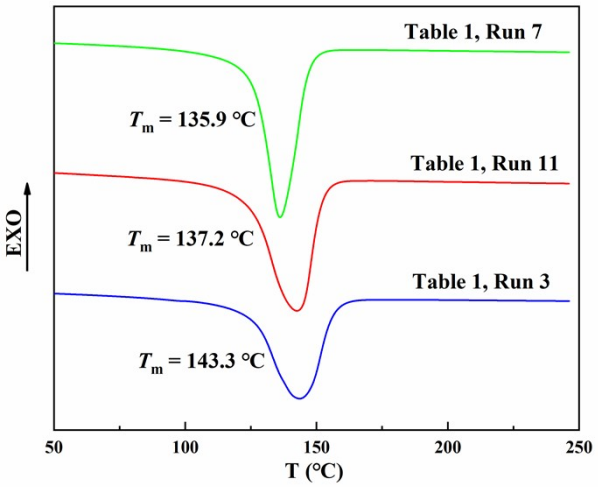

Figure S26 DSC curve of ethylene polymers

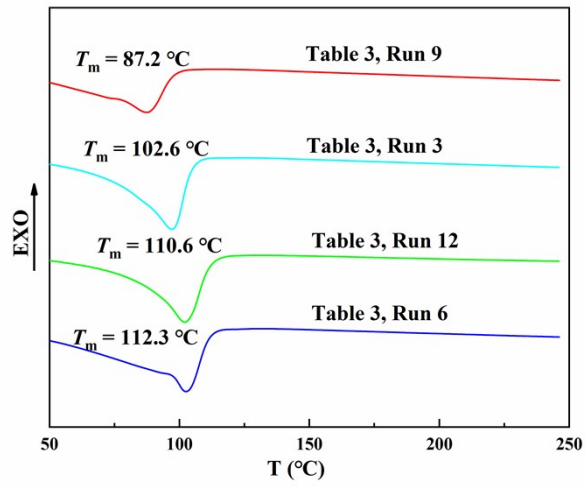

Figure S27 DSC curve of E-HE copolymers

Reference

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4. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem. 2011,* ***32****, 1456.*
5. P. P. Fuentealba, H.; Stoll, H.; Szentpaly, L. v., *Chem. Phys. Lett. 1982,* ***89****, 418.*
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8. R. B. Krishnan, J. S.; Seeger, R.; Pople, J. A., *J. Chem. Phys. 1980,* ***72****, 652.*
9. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B 2009,* ***113****, 6378.*