Supporting Information

Novel zirconium complexes with constrained cyclic β-enaminoketonato ligands: Improved catalytic capability toward ethylene polymerization

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†Electronic supplementary information (ESI) available: molecular structure of constrained geometry bulky β-enaminoketonato ligands-based zirconium complex **6b** and hafnium complex **7c**, crystal data and structure refinements of complexes **5a**, **5b**, **6b**, and **7b**, and crystallographic data in CIF format. CCDC 1419051–1419054. For ESI and crystallographic data in CIF or other electronic format see DOI: ××××××

Fig. S6. Typical DSC curves of the ethylene polymers

EXPERIMENTAL SECTION

General Methods and Materials.

All air- and moisture sensitive compounds were manipulated using standard Schlenk techniques or in an MBraun glove-box under a dry nitrogen atmosphere. All solvents used were purified from an MBraun SPS system. The NMR data of ligands and complexes were obtained through a Bruker 400 MHz spectrometer at ambient temperature with $CDCl_3$ or C_6D_6 as a solvent. Elemental analysis were performed using an Elemental Vario EL spectrometer. Single crystal X-ray analysis were operated with a ω scan mode (185K) on a Bruker Smart APEX diffractometer with CCD detector using Mo Kα radiation (λ = 0.71073Å). The NMR spectra of polymers and oligomers were recorded by a Bruker400 MHz spectrometer at 120 °C with *o*-$C_6D_4Cl_2$ as a solvent. The molecular weights and the polydispersities of the polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three PL gel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by the polystyrene standard Easi Cal PS-1 (PL Ltd.). The DSC measurements were performed with a Q2000 V24.10 Build 122 DSC differential scanning calorimeter at a rate of 10 °C/min. Zirconium (IV) chloride, hafnium (IV) chloride and aniline derivatives were charged from Aldrich Chemical and used without any further purification. 7-bromoindan-1-one was synthesized according to the literature[1]. Dried MAO was prepared from commercial MAO by removal of the volatile under vacuo at 50 °C. Commercial ethylene was directly used for polymerization without further purification. The other reagents and solvents were commercially available.

Synthesis of Tetrabenzylzirconium

A suspension of zirconium (IV) chloride (2.3 g, 10 mmol) in 20.0 mL of toluene was added slowly to 50 mL of ethyl ether solution of benzyl(chloro)magnesium (1M) under 78 °C, and an aluminized paper was employed to avoid light. The mixture was stirred for another 1 hour, then warmed to room temperature. and stirred overnight. The reaction mixture was filtered, and the solvent of the obtained dark filtrate was removed under reduced pressure. The residue was resolved in toluene, filtered, concentrated and recrystallized from toluene/hexane to give tetrabenzylzirconium as an orange crystal (3.6 g, 78.3%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.05 (t, J_{HH}= 7.5 Hz, 8H, *m*-Ar-*H*), 6.95 (t, J_{HH}= 7.3 Hz, 4H, *p*-Ar-*H*), 6.37 (d, J_{HH}= 7.5 Hz, 8H, *o*-Ar-*H*), 1.53 (s, 8H, CH_2).

Synthesis of Tetrabenzylhafnium

Tetrabenzylhafnium was prepared in a similar way to Tetrabenzylzirconium, and hafnium(IV) chloride was added instead of zirconium(IV) chloride. The operation for avoiding light is unnecessary. Tetrabenzylhafnium was obtained as a yellow crystal (4.1 g, 75.9%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.08 (t, J_{HH}= 7.6 Hz, 8H, *m*-Ar-*H*), 6.94 (t, J_{HH}= 7.4 Hz, 4H, *p*-Ar-*H*), 6.53 (d, J_{HH}= 7.4 Hz, 8H, *o*-Ar-*H*), 1.49 (s, 8H, CH_2).

Synthesis of compounds A, B, D and E

***o*-phenylacetophnones (A).** The synthesis method of **A** is similar to the literature procedure[2]. In glove box, 1.4 mL (10 mmol) of *o*-bromoacetophnones, 1.70 g (3 equiv., 30 mmol) of KF, 1.80 g (1.5 equiv.,15 mmol) of phenylboronic acid, 0.09 g (4 mol%, 0.4 mmol) of $Pd(OAc)_2$, 0.24 g (8 mol%, 0.8 mmol) of biphP (t-Bu)$_2$, and 20 mL of THF were added to a Schlenk flask. The flask was sealed and the solution was stirred at 80 °C over 14 h. The reaction solution was cooled to room temperature, filtered, and concentrated under reduced pressure. The crude material was chromatographed on silica gel to afford **A** as a colorless oil (1.8 g, 89.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, J_{HH} = 7.6 Hz, 1.3 Hz, 1H, Ar-*H*), 7.50 (t, J_{HH} = 7.5 Hz, 1H, Ar-*H*), 7.44-7.36 (m, 5H, Ar-*H*), 7.34 (D, J_{HH} = 1.9 Hz, 1H, Ar-*H*), 7.33-7.32 (m, 1H, Ar-*H*), 2.03, 1.99 (s, 1H, CH_3).

7-Phenyl-1-Indanone (B). B was prepared in a similar method to **A**, and 7-bromoindan-1-one was added instead of *o*-bromoacetophnones. **B** was obtained as a white solid after purification by chromatography on silica gel (1.7 g, 81.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (t, J_{HH} = 7.5 Hz, 1H, Ar-*H*), 7.46-7.36 (m, 6H, Ar-*H*), 7.25 (d, J_{HH} = 4.4 Hz, 1H, Ar-*H*), 3.16 (m, 2H, CH_2), 2.69 (m, 2H, CH_2).

8-Phenyl-1-Tetralone (D). The synthesis method of **D** is similar to the literature procedure[3]. 1.4 mL (10 mmol) of 1-tetralone, 2.90 g (30 mmol) of phenylboricneopentyl glycol ester, 0.50 g of $RuH_2(CO)(PPh_3)_3$ as the catalyst, 10 mL of pinacolone and 10 mL of toluene were added to a 100 mL Schlenk flask under dry N_2 atmosphere. Subsequently, the flask was sealed and heated to 140 °C for 4 h. The reaction mixture was filtered and the filtrate was concentrated. After purification by chromatography on silica gel, **D** was obtained as a white solid (1.76 g, 74.3%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (t, J_{HH} = 7.6 Hz, 1H, Ar-H), 7.39-7.29 (m, 3H, Ar-H), 7.24 (d, J_{HH} = 3.3 Hz, 1H, Ar-*H*), 7.23-7.18 (m, 2H, Ar-*H*), 7.13 (d, J_{HH} = 7.5 Hz, 1H, Ar-*H*), 3.01 (t, J_{HH} = 6.1 Hz, 2H, CH_2), 2.62 (t, J_{HH} = 6.6 Hz, 2H, CH_2), 2.14 (m, 2H, CH_2).

9-Phenyl-1-Benzosuberone (E). E was prepared in a similar method to **D**, and 1-benzosuberone was added instead of 1-tetralone. **E** was obtained as a white solid after purification by

chromatography on silica gel (1.20 g，49.3%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.12 (m, 8H, Ar-*H*), 2.80 (m, 2H, CH_2), 2.66(m, 2H, CH_2), 1.90 (m, 4H, CH_2).

Synthesis of Ligands

[C_6H_5N=CH-C_9H_5(C_6H_5)OH] (1b). 1.0 g (5 mmol) of 7-phenyl-1-indanone and 0.8 mL of ethyl formate (2.0 equiv.) were added into a slurry of ^{t}BuOK (0.90 g, 1.5 equiv.) in anhydrous diethyl ether (10 mL) at 0 °C, a large amount of white precipitate appeared immediately. The mixture was kept stirring at 0°C for 30 min, then warmed to room temperature and stirred overnight. The obtained suspension was dealt by Formic acid in ethanol to pH < 7. Subsequently, 0.5 mL (5 mmol) of aniline was added to the resultant solution of β-diketone in ethanol and the condensation reaction was carried out for another 24 h at room temperature. Ligand **1b** was obtained as yellow solid after filtered without any further purification (1.10 g, 72.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.23 (d, J_{HH} = 11.9 Hz, 1H, O-*H*), 7.56-7.39 (m, 8H, Ar-*H*), 7.30 (d, J_{HH} = 7.8 Hz, 2H, Ar-*H*), 7.26 (d, J_{HH} = 7.6 Hz, 1H, Ar-*H*), 7.03 (d, J_{HH} = 8.0 Hz, 2H, Ar-*H*), 6.99 (d, J_{HH} = 7.5 Hz, 1H, N=C-*H*), 3.70 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.96 (N=*C*H), 149.94 (C=*C*-OH), 140.83, 140.53, 138.90, 138.31, 136.71, 131.59, 127.60, 124.76, 122.85, 115.63 (-Ar), 108.28 (C=*C*-CH=N), 30.45 (*C*H_2). Anal. Calcd. for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.84; H, 5.44; N, 4.46.

Ligands **1c**, **2a-c**, **3b-c and I** were prepared in similar method.

[C_6F_5N=CH-C_9H_5(C_6H_5)OH] (1c). In a similar way described above, pentafluoroaniline was added instead of aniline to give **1c** as an orange solid (1.0 g, 50.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.13 (d, J_{HH} = 11.1 Hz, 1H, O*H*,), 7.60-7.39 (m, 8H, Ar-H), 7.29 (d, J_{HH} = 7.4 Hz, 1H, N=CH), 3.71 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.37 (N=*C*H), 150.43 (C=*C*-OH), 141.40, 138.40, 135.87, 132.61, 129.67, 129.49, 127.79, 127.72, 124.92 (Ar), 111.51 (C=*C*-CH=N), 30.15 (*C*H_2); ^{19}F NMR (376 MHz, $CDCl_3$): δ -155.24 (2F, *m*-Ar-F), -162.32 (2F, *o*-Ar-F), -164.77 (1F, *p*-Ar-F). Anal. Calcd. for $C_{22}H_{12}F_5NO$: C, 65.84; H, 3.01; N, 3.49. Found: C, 65.85; H, 2.99; N, 3.48.

[C_6H_5N=CH-$C_{10}H_8$OH] (2a). In a similar way described above, 1-tetralone was added instead of 7-phenyl-1-indanone to give **2a** as a yellow solid after filtered without any further purification (1.10 g, 85.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.88 (d, J_{HH} = 11.3 Hz, 1H, O-*H*), 7.97 (d, J_{HH} = 7.7 Hz, 1H, N=C-*H*), 7.38-7.22 (m, 5H, Ar-*H*), 7.19-7.13 (m, 1H, Ar-*H*), 7.01 (d, J_{HH} = 8.0 Hz, 2H, Ar-*H*), 6.96 (t, J_{HH} = 7.4 Hz, 1H, Ar-*H*), 2.86 (m, 2H, CH_2), 2.62 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.62 (N=*C*H), 140.59 (C=*C*-OH), 140.55, 140.49, 139.54, 134.04, 130.82, 128.62, 126.83, 125.75, 125.54, 121.86, 114.81 (-Ar), 104.17 (C=*C*-CH=N), 28.74, 26.71 (*C*H_2). Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.93; H, 6.04; N, 5.60.

[C_6H_5N=CH-$C_{10}H_7$(C_6H_5)OH] (2b). In a similar way described above, 8-phenyl-1-tetralone

was added instead of 7-phenyl-1-indanone to give yellow solid **2b** (1.5 g, 89.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.45 (d, J_{HH} = 11.6 Hz,1H, O-*H*), 7.41-7.22 (m, 11H, Ar-*H*), 7.17 (d, J_{HH} = 7.5 Hz, 1H, Ar-*H*), 7.00 (d, J_{HH} = 7.8 Hz, 2H, Ar-*H*), 6.97 (d, J_{HH} = 7.4 Hz, 1H, N=C-*H*), 2.95 (m, 2H, CH_2), 2.68 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.01 (N=*C*H), 143.76 (C=*C*-OH), 143.17, 140.97, 133.63, 130.60, 129.53, 128.45, 127.24, 126.43, 122.70, 116.06 (-Ar), 106.76 (C=*C*-CH=N), 31.38, 28.25 (*C*H_2). Anal. Calcd. for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 84.92; H, 5.88; N, 4.31.

[C_6F_5N=CH-$C_{10}H_7$(C_6H_5)OH] (2c). In a similar way described above, 8-phenyl-1-tetralone and pentafluoroaniline was added instead of 7-phenyl-1-indanone and aniline to give **2c** as a yellow solid (1.4 g, 67.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.39 (d, J_{HH} = 11.1 Hz, 1H, O*H*,), 7.42-7.23 (m, 8H, Ar-*H*), 7.19 (d, J_{HH} = 7.5 Hz, 1H, N=C*H*), 2.97 (m, 2H, CH_2), 2.66 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.57 (N=*C*H), 143.97 (C=*C*-OH), 143.67, 142.84, 141.55, 133.03, 131.26, 130.69, 128.48, 127.91, 127.35, 126.61 (Ar), 109.91 (C=*C*-CH=N), 31.02, 28.14 (*C*H_2). ^{19}F NMR (376 MHz, $CDCl_3$): δ -154.82 (2F, *m*-Ar-*F*), -162.58 (2F, *o*-Ar-*F*), -164.70 (1F, *p*-Ar-*F*). Anal. Calcd. for $C_{23}H_{14}F_5NO$: C, 66.51; H, 3.40; N, 3.37. Found: C, 66.53; H, 3.42; N, 3.37.

[C_6H_5N=CH-$C_{11}H_9$(C_6H_5)OH] (3b). In a similar way described above, 9-phenyl-1-benzosuberone was added instead of 7-phenyl-1-indanone and yellow solid **3b** was obtained (1.2 g, 70.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.62 (d, J_{HH} = 12.0 Hz, 1H, O-*H*), 7.38-7.25 (m, 10H, Ar-*H*), 7.14 (d, J_{HH} = 7.4 Hz, 1H, N=C-*H*), 7.05-6.97 (m, 3H, Ar-*H*), 2.74 (m, 2H, CH_2), 2.37 (m, 2H, CH_2), 1.92 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.48 (N=*C*H), 141.57 (C=*C*-OH), 140.85, 140.62, 138.53, 129.63, 129.19, 128.29, 127.48, 126.79, 123.02, 116.06 (-Ar), 109.01 (C=*C*-CH=N), 30.99, 30.14, 27.77 (*C*H_2). Anal. Calcd. for $C_{24}H_{21}NO$: C, 84.92; H, 6.24; N, 4.13. Found: C, 84.95; H, 6.22; N, 4.14.

[C_6F_5N=CH-$C_{11}H_9$(C_6H_5)OH] (3c). In a similar way described above, 9-phenyl-1-benzosuberone and pentafluoroaniline was added instead of 7-phenyl-1-indanone and aniline to give **3c** as a white-yellow solid (0.9 g, 42.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.53 (d, J_{HH} = 11.1 Hz, 1H, O*H*,), 7.41-7.27 (m, 8H, Ar-*H*), 7.15 (d, J_{HH} = 7.4 Hz, 1H, N=C*H*), 2.76 (t, J_{HH} = 6.6 Hz, 2H, CH_2), 2.39 (m, 2H, CH_2); 1.92 (p, J_{HH} = 6.7 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.60 (N=*C*H), 141.30 (C=*C*-OH), 141.10, 139.11, 138.38, 130.10, 129.26, 128.71, 128.25, 127.50, 126.88 (-Ar), 112.14 (C=*C*-CH=N), 30.80, 29.39, 27.63 (*C*H_2). ^{19}F NMR (376 MHz, $CDCl_3$): δ -154.77 (2F, *m*-Ar-*F*), -162.41 (2F, *o*-Ar-*F*), -164.44 (1F, *p*-Ar-*F*). Anal. Calcd. for $C_{24}H_{16}F_5NO$: C, 67.13; H, 3.76; N, 3.26. Found: C, 67.12; H, 3.74; N, 3.25.

[C_6H_5N=CH-CH=C(OH)C_6H_4(*o*-C_6H_5)] (I). In a similar way described above, *o*-phenylacetophnones was added instead of 7-phenyl-1-indanone give **I** as a yellow solid (1.0 g,

66.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.74 (d, J_{HH} = 12.1 Hz, 1H, O*H*), 7.65 (d, J_{HH} = 7.5 Hz, 1H, N=C*H*), 7.51-7.27 (m, 10H, Ar-*H*), 7.15 (dd, J_{HH} = 12.4 Hz, 7.8 Hz, 1H, Ar-*H*), 7.03 (dd, J_{HH} = 14.1 Hz, 7.6 Hz, 3H, Ar-*H*), 5.13 (d, J_{HH} = 7.8 Hz, 1H, C=C*H*-C). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.61 (N=*C*H), 143.12 (C=*C*-OH), 141.17, 141.08, 140.19, 140.10, 130.36, 129.81, 129.63, 129.13, 128.40, 128.27, 127.27, 127.25, 123.45 (-Ar), 116.14 (C=*C*-CH=N), 99.20 (C=*C*H-C). Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.22; H, 5.74; N,4.65.

Density Functional Theory Calculations

Density functional theory (DFT) calculations were used for the structure of active species generated by complexes **4b-c**, **5b-c** and **6b-c** by using the Amsterdam Density Functional program package. Geometry optimizations and energy calculations were performed using the local density approximation augmented with Becke's nonlocal exchange corrections and Perdew's nonlocal correction. A triple STO basis set was used for Zr, whereas all other atoms were described by a double-f plus polarization STO basis. The 1s electrons of the C, N, O and F atoms, as well as the 1s-2p electrons of Zr atom, were treated as frozen core.

Table S1 Crystal Data and Structure Refinements for complex **5a, 5b, 6b** and **7b**

	5a	5b	6b	7b
Foemula	$C_{48}H_{42}N_2O_2Zr$	$C_{60}H_{50}N_2O_2Zr$	$C_{62}H_{54}N_2O_2Zr$	$C_{60}H_{50}N_2O_2Hf$
Fw	770.06	922.24	950.29	1009.51
Cryst. System	monoclinic	monoclinic	monoclinic	triclinic
Space group	P2(1)/n	P2(1)/n	P2(1)/c	P-1
A (Å)	15.1215(11)	11.2590(10)	22.6289(19)	17.8992(11)
B (Å)	9.6375(7)	24.229(2)	15.0048(13)	19.3310(12)
C (Å)	26.4463(18)	17.8544(15)	18.0332(16)	20.5734(13)
α (deg)	90.00	90.00	90.00	97.5330(10)
β (deg)	97.815(2)	91.370(2)	101.611(2)	94.4190(10)
γ (deg)	90.00	90.00	90.00	116.1370(10)
V ($Å^3$), Z	3818.3(5), 4	4869.3(7), 4	5997.7(9), 4	6262.4(7), 4
density ($Mg \cdot cm^{-3}$)	1.340	1.258	1.052	1.071
absorpcoeff (mm^{-1})	0.330	0.271	0.221	1.701
F(000)	1600	1920	1984	2048
Cryst. Size (mm)	0.35×0.22×0.18	0.39×0.18×0.07	0.38×0.23×0.16	0.42×0.24×0.11
θ range (deg)	1.66-26.05	1.42-25.06	1.64-26.05	1.28-25.06
no. of rflnscollected	7530	8618	11795	21784
no. of indeprflns	4365 (R_{int}= 0.0966)	5461 (R_{int}= 0.0000)	6961 (R_{int}= 0.0000)	15061 (R_{int}= 0.0000)
max. and min. transmn	0.917 and 0.942	0.931 and 0.952	0.961 and 0.943	0.5875 and 0.7845
no. of data/restraints/params	4365/0/478	5461/0/586	6961/0/604	15061/0/1171
goodness-of-fit on F^2	0.945	1.010	0.932	1.028
final *R* indices [$I > 2\sigma(I)$]: R_1, wR_2	0.0526, 01254	0.0711, 0.1363	0.0657, 0.1575	0.0518, 0.1579
largest diff peak and hole ($e \cdot Å^{-3}$)	0.454 and -0.497	0.502 and -0.399	0.553 and -0.391	1.668 and -0.761

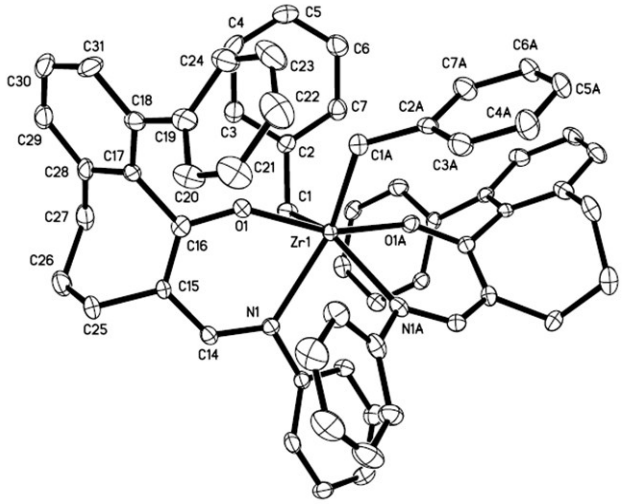

Fig. S1. Molecular structure of Complex **6b**. Ellipsoids are shown with 30% probability. The H atoms are omitted for clarity.

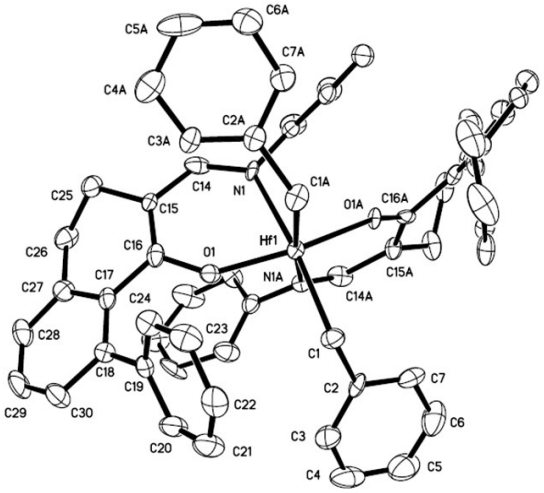

Fig. S2. Molecular structure of Complex **7b**. Ellipsoids are shown with 30% probability. The H atoms are omitted for clarity.

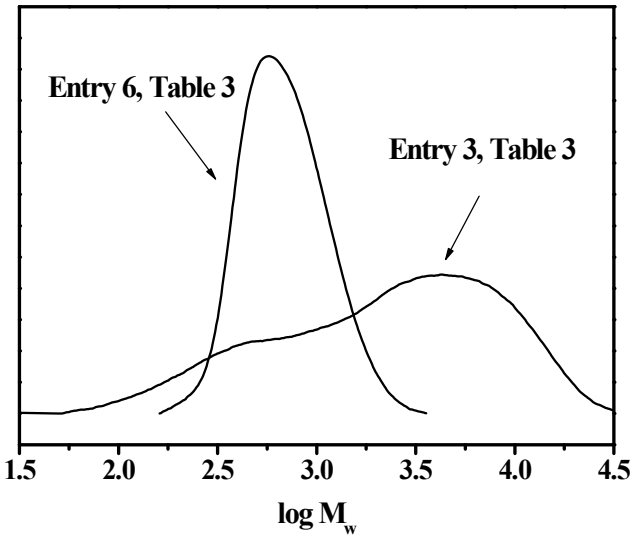

Fig. S3. Typical GPC results of the ethylene oligomers

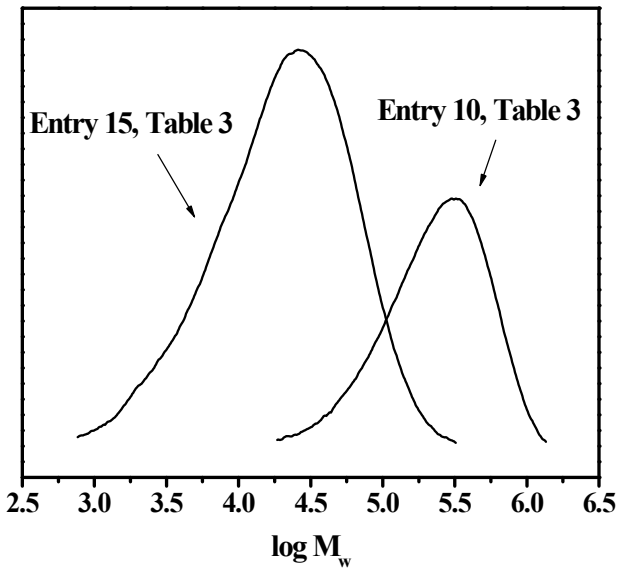

Fig. S4.GPC results of the ethylene polymers

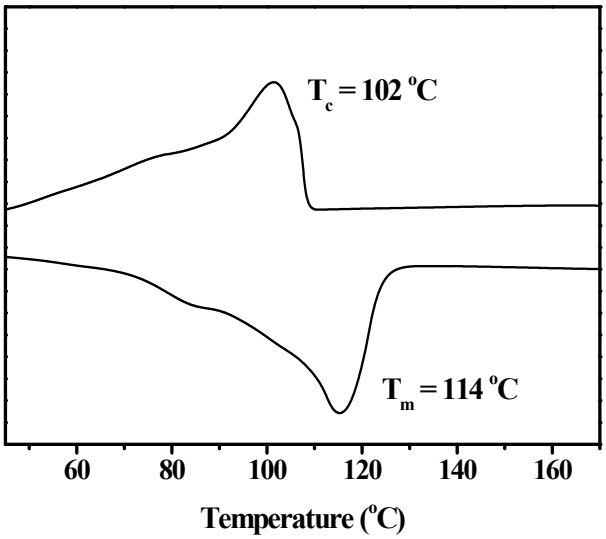

Fig. S5. Typical DSC curves of the ethylene oligomers (Entry 6)

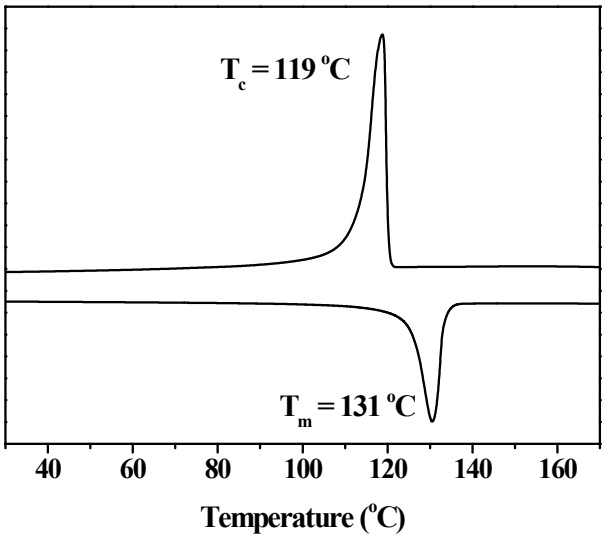

Fig. S6. Typical DSC curves of the ethylene polymers (Entry 15)

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