Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

for

8-(2-Cycloalkylphenylimino)-5,6,7-trihydro-quinolylnickel halides: Polymerizing ethylene to highly branched and lower molecular weight polyethylenes

Zelin Sun,[a,b] Erlin Yue,[b] Mengnan Qu,*[a] Irina V. Oleynik,[c] Ivan I. Oleynik,[c] Kanshe Li,[a] Tongling Liang,[b] Wenjuan Zhang[b] and Wen-Hua Sun*[b]

[a] College of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an 710054, China.
[b] Key laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
[c] N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Pr. Lavrentjeva 9, Novosibirsk 630090, Russia.

General considerations

All manipulations involving air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene), modified methylaluminoxane (MMAO, 1.93 M in heptane) and dimethylaluminium chloride (Me$_2$AlCl, 1.0 M solution in toluene) were purchased from Akzo Nobel Corp. Diethylaluminium chloride (Et$_2$AlCl, 1.17 M in toluene) was purchased from Acros Chemicals. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard; IR spectra were recorded using a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 micro-analyzer. Molecular weights and molecular weight distribution (MWD) of polyethylene were determined by PL-GPC220 at 150 °C, with 1,2,4-trichlorobenzene as the solvent. The melting points of polyethylene were measured from the second scanning run using a Perkin-Elmer TA-Q2000 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere. In the procedure, a sample of about 4.0 mg was heated to 140 °C at the rate of 20 °C min^{-1} and kept for 2 min at 140 °C to remove the thermal history and then cooled at the rate of 20 °C min^{-1} to −40 °C. ^{13}C NMR spectra of the polyethylenes were recorded using a Bruker DMX 400 MHz instrument at ambient temperature in deuterated 1,2-dichlorobenzene with TMS as an internal standard.

8-(2,6-Dicyclohexylphenylimino)-5,6,7-trihydroquinoline (L1) and 8-(2,6-Dicyclohexylphenylamino)-5,6-dihydroquinoline (L1′). 5,6,7-Trihydroquinolin-8-one (0.37 g, 2.5 mmol) and 2,6-dicyclohexyl aniline (0.51 g, 2 mmol) were mixed with a catalytic amount of *p*-toluenesulfonic acid dissolved in 25 mL toluene. The solution was heated to reflux and remaining 4 hours, the color of the solution gradually darkened. After solvent was evaporated under reduced pressure, silica gel column chromatography ($V_{\text{petroleum ether}}$: $V_{\text{triethylamine}}$ = 250 : 1) was used to quickly purify the crude product to obtain yellow oil (**L1** : **L1′** = 36 : 64, 0.25 g, 32% yield). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 8.75 (d, J = 1.2 Hz, 1H, **L1**-Py H), 8.44 (d, J = 4.0 Hz, **L1′**-Py H), 7.58 (d, J = 7.2 Hz, 1H, **L1**-Py H), 7.46 (d, J = 7.2 Hz, **L1′**-Py H), 7.32–7.29 (m, 1H, **L1**-Py H), 7.23–7.21 (m, **L1′**-Py H), 7.18–7.16 (m, 1H, **L1**-Ar H and **L1′**-Ar H), 7,14–7.11 (m, **L1′**-Ar H), 7.08–7.04 (m, 2H, **L1**-Ar H), 6.64 (s, **L1′**-NH), 4.54 (t, J = 4.8 Hz **L1′**-CH), 2.97 (t, J = 6.0 Hz, 2H, **L1**-CH$_2$), 2.83 (t, J = 7.8 Hz, **L1′**-CH$_2$), 2.44–2.39 (m, 2H, **L1**-CH$_2$ and **L1′**-CH$_2$), 2.29–2.24 (m, 2H, **L1**-CH$_2$), 1.82–1.75 (m, **L1′**-CH$_2$), 1.69–1.61 (m, 10H, **L1**-5 × CH$_2$), 1.48–1.38 (m, 10H, **L1**-5 × CH$_2$), 1.34–1.22 (m, **L1′**-10 × CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 164.69, 150.01, 148.90, 147.04, 146.10, 146.00, 140.50, 137.51, 137.30, 136.86, 135.26, 134.69, 132.30, 126.17, 124.81, 124.19, 123.68, 123.23, 122.08, 98.54, 39.10, 39.00, 34.01, 33.83,31.01, 29.61, 28.17, 27.30, 27.23, 26.97, 26.50, 26.42. FT-IR (KBr, cm^{-1}): 3503, 3314, 2921, 2848, 1642, 1570, 1445, 1346, 1261, 1084, 816, 789. Anal. calcd for C$_{27}$H$_{34}$N$_2$ (387): C, 83.89; H, 8.87; N, 7.25. Found: C, 84.24; H, 8.60; N, 7.13%.

8-(2,6-Dicyclopentylphenylimino)-5,6,7-trihydroquinoline (L2) and 8-(2,6-Dicyclopentylphenylamino)-5,6-dihydroquinoline (L2′). This compound was synthesized in the same procedure as described for **L1**. **L2** and **L2′** were obtained concurrently (yellow oil, **L2** : **L2′** = 17 : 83, 0.27 g, 38% yield). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 8.74 (d, J = 4.0 Hz, 1H, **L2**-Py H), 8.41 (d, J = 4.8 Hz, **L2′**-Py H), 7.57 (d, J = 7.6 Hz, 1H, **L2**-Py H), 7.43 (d, J = 7.6 Hz, **L2′**-Py H), 7.44–7.28 (m, 1H, **L2**-Py H and **L2′**-Py H), 7.19 (s, **L2′**-Ar H), 7.13 (d, J = 7.6 Hz, 2H, **L2**-Ar H), 7,06–7.02 (m, 1H, **L2**-Ar H and **L2′**-Ar H), 6.59 (s, **L2′**-NH), 4.54 (t, J = 4.0 Hz **L2′**-CH), 3.31–3.27 (m, **L2′**-CH$_2$), 2.94 (t, J = 6.0 Hz, 2H, **L2**-CH$_2$), 2.88 (t, J = 8.2 Hz, 2H, **L2**-CH$_2$), 2.84–2.79 (m, **L2′**-CH$_2$), 2.39 (t, J = 6.1 Hz, 2H, **L2**-CH$_2$), 2.28–2.23 (m, **L2′**-CH$_2$), 2.06–2.03 (m, 4H, **L2**-2 × CH$_2$ and **L2′**-2 × CH$_2$), 1.94–1.88 (m, **L2′**-3 × CH$_2$), 1.81–1.68 (m, 6H, **L2**-3 × CH$_2$), 1.59–1.48 (m, 6H, **L2**-3 × CH$_2$ and **L2′**-3 × CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 164.64, 150.01, 148.88, 148.41, 137.26, 137.00, 134.17, 124.77, 123.93, 123.44, 123.23, 40.22, 39.99, 34.57, 34.32, 32.32, 30.99, 29.53, 26.02, 25.94, 25.87, 22.29. FT-IR (KBr, cm^{-1}): 3503, 3322, 2951, 2862, 1639, 1571, 1473, 1345, 1260, 1166, 1081, 1017, 815, 785. Anal. calcd for C$_{25}$H$_{30}$N$_2$ (359): C, 83.75; H, 8.43; N, 7.81 Found: C, 83.97; H, 8.37; N, 7.72%.

8-(2,4-Dimethyl-6-cyclohexylphenylimino)-5,6,7-trihydroquinoline (L3) and 8-(2,4-Dimethyl-6-cyclohexylphenylamino)-5,6-dihydroquinoline (L3′). This compound was synthesized in the same procedure as described for **L1**. **L3** and **L3′** were obtained concurrently (yellow oil, **L3** : **L3'** = 60 : 40, 0.2 g, 30 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.74 (d, *J* = 4.4 Hz, 1H, **L3**-Py H), 8.42 (d, *J* = 4.8 Hz, **L3'**-Py H), 7.56 (d, *J* = 7.6 Hz, 1H, **L3**-Py H), 7.44 (d, *J* = 7.2 Hz, **L3'**-Py H), 7.30–7.26 (m, 1H, **L3**-Py H), 7.11–7.08 (m, **L3'**-Py H), 6.97 (s, **L3'**-Ar H), 6.92 (s, 2H, **L3**-Ar H), 6.84 (s, **L3'**-Ar H), 6.55 (s, **L3'**-NH), 4.51 (t, *J* = 4.6 Hz **L3'**-CH), 2.94 (t, *J* = 6.2 Hz, 2H, **L3**-CH_2), 2.82 (t, *J* = 7.8 Hz, 2H, **L3**-CH_2), 2.47–2.41 (m, **L3'**-2 × CH_2), 2.32 (s, **L3'**-CH_3), 2.30 (s, 3H, **L3**-CH_3), 2.23 (s, **L3'**-CH_3), 1.99 (s, 3H, **L3**-CH_3), 1.93–1.89 (m, **L3'**-3 × CH_2), 1.80–1.71 (m, 6H, **L3**-3 × CH_2), 1.41–1.18 (m, 6H, **L3**-3 × CH_2 and **L3'**-3 × CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 164.82, 150.22, 150.12, 148.92, 146.12, 145.70, 145.40, 139.18, 137.28, 136.85, 136.03, 135.84, 135.49, 135.03, 134.67, 132.36, 131.91, 128.81, 128.31, 125.04, 124.91, 124.78, 124.60, 122.02, 98.01, 77.52, 77.20, 76.89, 38.82, 38.70, 34.46, 33.45, 30.76, 29.61, 28.13, 27.24, 27.18, 26.88, 26.49, 26.43, 22.40, 21.56, 21.36, 21.17, 18.55, 18.44. FT-IR (KBr, cm^{-1}): 3503, 3322, 2951, 2862, 1639, 1571, 1473, 1345, 1260, 1166, 1081, 1017, 815, 785. Anal. calcd for $C_{23}H_{28}N_2$ (332): C, 83.09; H, 8.49; N, 8.43. Found: C, 83.51; H, 9.33; N, 8.31%.

Synthesis of nickel complexes

General procedure: $NiCl_2{\cdot}6H_2O$ or DME·$NiBr_2$ (0.5 mmol) was dissolved in 10 mL CH_2Cl_2 and added dropwise to the corresponding ligand (0.5 mmol) which dissolved in 5 mL CH_2Cl_2. The mixture was stirred for 12 h at room temperature, and then diethyl ether was added to the mixture to precipitate the complex. The precipitant was collected by filtration, washed with diethyl ether, and dried under vacuum.

8-(2,6-Dicyclohexylphenylimino)-5,6,7-trihydroquinolylnickel dibromide (Ni1). (Green, 0.29 g, 95% yield): FT-IR (KBr, cm^{-1}): 3342, 2922, 2848, 1619, 1580, 1447, 1348, 1220, 1083, 882, 774. Anal. calcd for $C_{27}H_{34}Br_2N_2Ni$ (605): C, 53.59; H, 5.66; N, 4.67. Found: C, 53.18; H, 5.51; N, 4.52%.

8-(2,6-Dicyclopentylphenylimino)-5,6,7-trihydroquinolylnickel dibromide (Ni2). (Green, 0.19 g, 66% yield): FT-IR (KBr, cm^{-1}): 2946, 2861, 1619, 1583, 1450, 1337, 1215, 1085, 1045, 773. Anal. calcd for $C_{25}H_{30}Br_2N_2Ni$ (577): C, 52.04; H, 5.24; N, 4.85. Found: C, 51.87; H, 5.12; N, 4.81%.

8-(2,4-Dimethyl-6-cyclohexylphenylimino)-5,6,7- trihydroquinolylnickel dibromide (Ni3). (Green, 0.20 g, 72% yield) FT-IR (KBr, cm^{-1}): 3098, 2917, 2846, 1618, 1579, 1453, 1327, 1219, 1196, 1142, 1040, 852, 796. Anal. calcd for $C_{23}H_{28}Br_2N_2Ni$ (551): C, 50.14; H, 5.12; N, 5.08. Found: C, 49.87; H, 5.02; N, 4.98%.

8-(2,4-Dimethyl-6-cyclohexylphenylimino)-trihydroquinolylnickel dichloride (Ni4). (Green, 0.17 g, 72% yield): FT-IR (KBr, cm^{-1}): 2921, 2849, 1624, 1583,1450, 1174, 1118, 1032, 1006, 853, 796, 677. Anal. calcd for $C_{23}H_{28}C_{l2}N_2Ni_2$ (462): C, 59.78; H, 6.11; N, 6.06. Found: C, 59.56; H, 6.02; N, 5.93%.

X-ray crystallographic studies

A single crystal of the nickel complex **Ni1**·H2O suitable for X-ray diffraction was obtained by layering diethyl ether onto the mixed solution of dichloromethane and methanol at room temperature. X-ray studies were carried out using a Rigaku Saturn724+CCD diffractometer with MoKα radiation (λ = 0.71073 Å) at 173(2) K (**Ni1**), cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by fullmatrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[1] Details of the X-ray structure determinations and refinements are provided in Table S1. The molecular structure is shown in Figure S1, and the bond lengths and angles are tabulated in Table S1'.

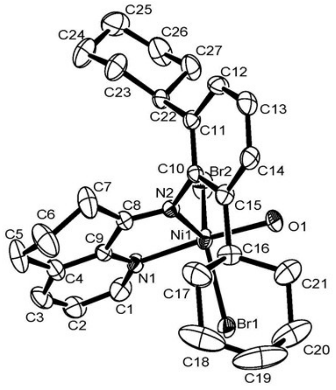

Figure S1. ORTEP drawing of the molecular structure of **Ni1**·H_2O**.** Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms were omitted for clarity.

Table S1 Crystal data and structure refinement for **Ni1**·H_2O

	Ni1·H2O
Crystal color	yellow
Empirical formula	$C_{27}H_{36}Br_{2}N_{2}Ni\ O$
Formula weight	623.07
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	10.197(2)
b (Å)	10.504(2)
c (Å)	14.735(3)
α (°)	89.36(3)
β (°)	79.33(3)
γ (°)	64.21(3)
Volume ($Å^3$)	1392.2(5)
Z	2
D calcd (mg m^{-3})	1.486
μ (mm^{-1})	3.588
F (000)	636
Crystal size (mm)	0.74 x 0.44 x 0.14
θ range(°)	2.26 - 27.50
Limiting indices	$-13 \leq h \leq 13$
	$-13 \leq k \leq 13$
	$-19 \leq l \leq 18$
No. of rflns collected	12586
No. of unique rflns	6356
R_{int}	0.0413
Completeness to θ (%)	99.2 ($\theta = 27.50$)
Goodness-of-fit on F^2	1.003
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0503
	wR2 = 0.1402
R indices (all data)	R1 = 0.0590
	wR2 = 0.1478
Largest diff. Peak and hole(e $Å^{-3}$)	1.089 and -0.982

Table S1' Bond lengths (Å) for **Ni1**·H_2O

Br(1)–Ni(1)	2.4642(9)	C(17)–C(18)	1.547(8)
Ni(1)–O(1)	2.035(3)	C(17)–H(17A)	0.9900
Ni(1)–N(2)	2.044(3)	C(17)–H(17B)	0.9900
Ni(1)–N(1)	2.045(3)	C(21)–C(20)	1.528(8)
Ni(1)–Br(2)	2.4079(9)	C(21)–H(21A)	0.9900
N(1)–C(1)	1.324(5)	C(21)–H(21B)	0.9900
N(1)–C(9)	1.351(5)	C(23)–C(24)	1.530(6)
N(2)–C(8)	1.276(5)	C(23)–H(23A)	0.9900
N(2)–C(10)	1.445(4)	C(23)–H(23B)	0.9900
C(8)–C(9)	1.474(5)	C(7)–C(6)	1.467(7)
C(8)–C(7)	1.505(6)	C(7)–H(7A)	0.9900
C(11)–C(12)	1.391(5)	C(7)–H(7B)	0.9900
C(11)–C(10)	1.409(5)	C(5)–C(6)	1.520(7)
C(11)–C(22)	1.523(5)	C(5)–H(5A)	0.9900
C(22)–C(27)	1.528(6)	C(5)–H(5B)	0.9900
C(22)–C(23)	1.533(6)	C(25)–C(24)	1.533(9)
C(22)–H(22)	1.0000	C(25)–H(25A)	0.9900
C(10)–C(15)	1.411(5)	C(25)–H(25B)	0.9900
C(15)–C(14)	1.394(5)	C(18)–C(19)	1.508(12)
C(15)–C(16)	1.517(5)	C(18)–H(18A)	0.9900
C(13)–C(14)	1.370(6)	C(18)–H(18B)	0.9900
C(13)–C(12)	1.388(6)	C(27)–H(27A)	0.9900
C(13)–H(13)	0.9500	C(27)–H(27B)	0.9900
C(9)–C(4)	1.379(5)	C(6)–H(6A)	0.9900
C(26)–C(27)	1.514(6)	C(6)–H(6B)	0.9900
C(26)–C(25)	1.515(9)	C(20)–C(19)	1.487(11)
C(26)–H(26A)	0.9900	C(20)–H(20A)	0.9900
C(26)–H(26B)	0.9900	C(20)–H(20B)	0.9900
C(4)–C(3)	1.386(6)	C(2)–H(2)	0.9500
C(4)–C(5)	1.510(7)	C(24)–H(24A)	0.9900
C(12)–H(12)	0.9500	C(24)–H(24B)	0.9900
C(16)–C(17)	1.515(7)	C(19)–H(19A)	0.9900
C(16)–C(21)	1.546(7)	C(19)–H(19B)	0.9900
C(16)–H(16)	1.0000	C(14)–H(14)	0.9500
C(1)–C(2)	1.385(7)	O(1)–H(1A)	0.8516
C(1)–H(1)	0.9500	O(1)–H(1B)	0.8517
C(3)–C(2)	1.362(8)		
C(3)–H(3)	0.9500		

Table S1’ Bond angles (°) for **Ni1**·H_2O

O(1)–Ni(1)–N(2)	94.96(13)	C(20)–C(21)–H(21B)	109.6	C(13)–C(12)–C(11)	121.3(4)
O(1)–Ni(1)–N(1)	170.68(14)	C(16)–C(21)–H(21B)	109.6	C(13)–C(12)–H(12)	119.3
N(2)–Ni(1)–N(1)	80.05(13)	H(21A)–C(21)–H(21B)	108.2	C(19)–C(20)–H(20B)	109.1
O(1)–Ni(1)–Br(2)	95.52(10)	C(24)–C(23)–C(22)	110.6(4)	C(21)–C(20)–H(20B)	109.1
N(2)–Ni(1)–Br(2)	112.91(9)	C(24)–C(23)–H(23A)	109.5	H(20A)–C(20)–H(20B)	107.9
N(1)–Ni(1)–Br(2)	93.68(10)	C(22)–C(23)–H(23A)	109.5	C(11)–C(12)–H(12)	119.3
O(1)–Ni(1)–Br(1)	87.06(10)	C(24)–C(23)–H(23B)	109.5	C(17)–C(16)–C(15)	111.5(4)
N(2)–Ni(1)–Br(1)	108.64(9)	C(22)–C(23)–H(23B)	109.5	C(17)–C(16)–C(21)	110.2(4)
N(1)–Ni(1)–Br(1)	87.11(10)	H(23A)–C(23)–H(23B)	108.1	C(15)–C(16)–C(21)	111.5(4)
Br(2)–Ni(1)–Br(1)	137.94(3)	C(6)–C(7)–C(8)	113.1(4)	C(17)–C(16)–H(16)	107.8
C(1)–N(1)–C(9)	119.1(4)	C(6)–C(7)–H(7A)	109.0	C(15)–C(16)–H(16)	107.8
C(1)–N(1)–Ni(1)	127.5(3)	C(8)–C(7)–H(7A)	109.0	C(21)–C(16)–H(16)	107.8
C(9)–N(1)–Ni(1)	113.2(2)	C(6)–C(7)–H(7B)	109.0	N(1)–C(1)–C(2)	121.4(4)
C(8)–N(2)–C(10)	121.3(3)	C(8)–C(7)–H(7B)	109.0	N(1)–C(1)–H(1)	119.3
C(8)–N(2)–Ni(1)	114.2(2)	H(7A)–C(7)–H(7B)	107.8	C(2)–C(1)–H(1)	119.3
C(10)–N(2)–Ni(1)	124.4(2)	C(4)–C(5)–C(6)	112.0(4)	C(2)–C(3)–C(4)	119.2(4)
N(2)–C(8)–C(9)	117.9(3)	C(4)–C(5)–H(5A)	109.2	C(2)–C(3)–H(3)	120.4
N(2)–C(8)–C(7)	125.9(4)	C(6)–C(5)–H(5A)	109.2	C(4)–C(3)–H(3)	120.4
C(9)–C(8)–C(7)	116.2(3)	C(4)–C(5)–H(5B)	109.2	C(16)–C(17)–C(18)	109.3(5)
C(12)–C(11)–C(10)	117.3(3)	C(6)–C(5)–H(5B)	109.2	C(16)–C(17)–H(17A)	109.8
C(12)–C(11)–C(22)	120.0(3)	H(5A)–C(5)–H(5B)	107.9	C(18)–C(17)–H(17A)	109.8
C(10)–C(11)–C(22)	122.7(3)	C(26)–C(25)–C(24)	111.8(4)	C(16)–C(17)–H(17B)	109.8
C(11)–C(22)–C(27)	113.7(3)	C(26)–C(25)–H(25A)	109.3	C(18)–C(17)–H(17B)	109.8
C(11)–C(22)–C(23)	111.3(3)	C(24)–C(25)–H(25A)	109.3	H(17A)–C(17)–H(17B)	108.3
C(27)–C(22)–C(23)	108.6(4)	C(26)–C(25)–H(25B)	109.3	C(3)–C(2)–C(1)	119.9(4)
C(11)–C(22)–H(22)	107.7	C(24)–C(25)–H(25B)	109.3	C(3)–C(2)–H(2)	120.1
C(27)–C(22)–H(22)	107.7	H(25A)–C(25)–H(25B)	107.9	C(1)–C(2)–H(2)	120.1
C(23)–C(22)–H(22)	107.7	C(19)–C(18)–C(17)	112.5(6)	C(23)–C(24)–C(25)	109.7(4)
C(11)–C(10)–C(15)	122.3(3)	C(19)–C(18)–H(18A)	109.1	C(23)–C(24)–H(24A)	109.7
C(11)–C(10)–N(2)	118.5(3)	C(17)–C(18)–H(18A)	109.1	C(25)–C(24)–H(24A)	109.7
C(15)–C(10)–N(2)	119.1(3)	C(19)–C(18)–H(18B)	109.1	C(23)–C(24)–H(24B)	109.7
C(14)–C(15)–C(10)	117.2(3)	C(17)–C(18)–H(18B)	109.1	C(25)–C(24)–H(24B)	109.7
C(14)–C(15)–C(16)	120.7(3)	H(18A)–C(18)–H(18B)	107.8	H(24A)–C(24)–H(24B)	108.2
C(10)–C(15)–C(16)	122.1(3)	C(26)–C(27)–C(22)	111.1(4)	C(20)–C(19)–C(18)	111.6(5)
C(14)–C(13)–C(12)	120.2(4)	C(26)–C(27)–H(27A)	109.4	C(20)–C(19)–H(19A)	109.3
C(14)–C(13)–H(13)	119.9	C(22)–C(27)–H(27A)	109.4	C(18)–C(19)–H(19A)	109.3
C(12)–C(13)–H(13)	119.9	C(26)–C(27)–H(27B)	109.4	C(20)–C(19)–H(19B)	109.3
N(1)–C(9)–C(4)	122.2(3)	C(22)–C(27)–H(27B)	109.4	C(18)–C(19)–H(19B)	109.3
N(1)–C(9)–C(8)	114.3(3)	H(27A)–C(27)–H(27B)	108.0	H(19A)–C(19)–H(19B)	108.0
C(4)–C(9)–C(8)	123.5(4)	C(7)–C(6)–C(5)	114.3(5)	C(13)–C(14)–C(15)	121.7(4)
C(27)–C(26)–C(25)	112.2(5)	C(7)–C(6)–H(6A)	108.7	C(13)–C(14)–H(14)	119.2
C(27)–C(26)–H(26A)	109.2	C(5)–C(6)–H(6A)	108.7	C(15)–C(14)–H(14)	119.2
C(25)–C(26)–H(26A)	109.2	C(7)–C(6)–H(6B)	108.7	Ni(1)–O(1)–H(1A)	109.3
C(27)–C(26)–H(26B)	109.2	C(5)–C(6)–H(6B)	108.7	C(20)–C(21)–C(16)	110.1(5)
C(25)–C(26)–H(26B)	109.2	H(6A)–C(6)–H(6B)	107.6	C(20)–C(21)–H(21A)	109.6
H(26A)–C(26)–H(26B)	107.9	C(19)–C(20)–C(21)	112.3(5)	C(16)–C(21)–H(21A)	109.6
C(9)–C(4)–C(3)	118.2(4)	C(19)–C(20)–H(20A)	109.1	Ni(1)–O(1)–H(1B)	109.9
C(9)–C(4)–C(5)	120.0(4)	C(21)–C(20)–H(20A)	109.1	H(1A)–O(1)–H(1B)	109.4
C(3)–C(4)–C(5)	121.8(4)				

General procedure for ethylene polymerization

Ethylene polymerizations were carried out in a 250 mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller. And the clave was evacuated by a vacuum pump and back–filled three times with N_2 and once with ethylene. When the required temperature was reached, 30 mL toluene (freshly distilled) was added under ethylene atmosphere, and another 20 mL toluene which dissolved the nickel pre–catalyst was injected. The required amount of co–catalyst (MAO or Et_2AlCl) and additional toluene (maintaining total volume as 100 mL in reactor) were added by syringe. The reaction mixture was intensively stirred for the desired time under 10 atm of ethylene and maintained at this level by constant feeding of ethylene. The reaction was quenched by addition of acidic ethanol. The precipitated polymer was washed with ethanol several times and dried in vacuum until of constant weight.

Similar to **Ni1**/MAO system(Figure S2) (Table S2), the **Ni**/Et$_2$AlCl system also produced highly branched polyethylenes, which were indicated by the ^{13}C NMR spectra of the polyethylene by **Ni1**/Et$_2$AlCl at 30 (Figure S3) (Table S3) or 50 ºC (Figure S4) (Table S4). The **Ni2**/MAO and **Ni3**/MAO system were also tested at the best condition (Figure S5) (Table S5) and (Figure S6) (Table S6).

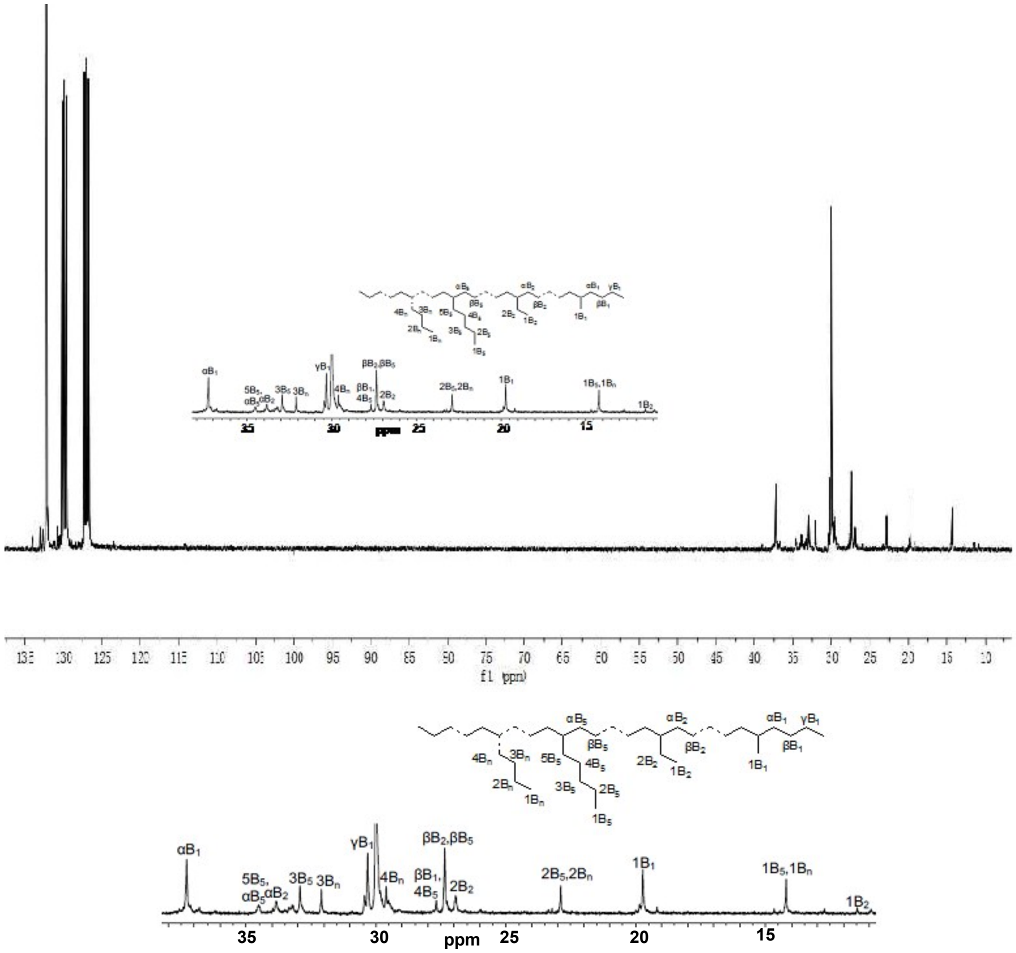

Figure S2. ^{13}C NMR spectrum of the polyethylene by **Ni1**/MAO at 50 ºC (entry 9, Table 2).

Table S2 Experimental integrals, percentage of branching for the polyethylene by **Ni1**/MAO at 50 °C (entry 9, Table 2) [a]

Peak no.	assignments	Chem. Shifts /ppm	Integral exp.	Branch content		Percentage over total branching	Percentage of branching
1	$1B_2$	11.46	0.02	N_m	1.51	39.74 %	14.09 %
2	1B*n*, $1B_5$	14.21	1	$N_{m(1,4)}$	0	0.00 %	0.00 %
4	$1B_1$	19.73	1.97	$N_{m(1,5)}$	0	0.00 %	0.00 %
7	$2B_5$, 2B*n*	22.89	0.81	$N_{m(1,6)}$	0	0.00 %	0.00 %
10	$2B_2$	26.95	1.17	N_e	0.52	13.68 %	4.85 %
11	βB_2, βB_5	27.36	2.96	N_p	0	0.00 %	0.00 %
12	βB_1, $4B_5$	27.68	0.47	N_b	0	0.00 %	0.00 %
15	4B*n*	29.61	0.58	N_a	1.19	31.32 %	11.10 %
16		30	14.41	N_l	0.58	15.26 %	5.41 %
17	γB_1	30.32	2.91	$N_{l(1,4)}$	0	0.00 %	0.00 %
20	3B*n*	32.11	0.58	δδCH2	13.83		
21	$3B_5$	32.93	1.19	[E]	6.92		
24	αB_2	33.84	0.76	[R]	3.8	100.00 %	
26	$5B_5$, αB_5	34.52	0.38	Total branching = 35.4 %			
29	αB_1	37.3	3.02	177 Branches/1000C			
				Methyl branches		14.09 %	
				Ethyl branches		4.85 %	
				Propyl branches		0.00 %	
				Butyl branches		0.00 %	
				Amyl branches		11.10 %	
				Long branches		5.41 %	

[a] Branches per 1000 C atoms determined by ^{13}C NMR spectroscopy.[2]

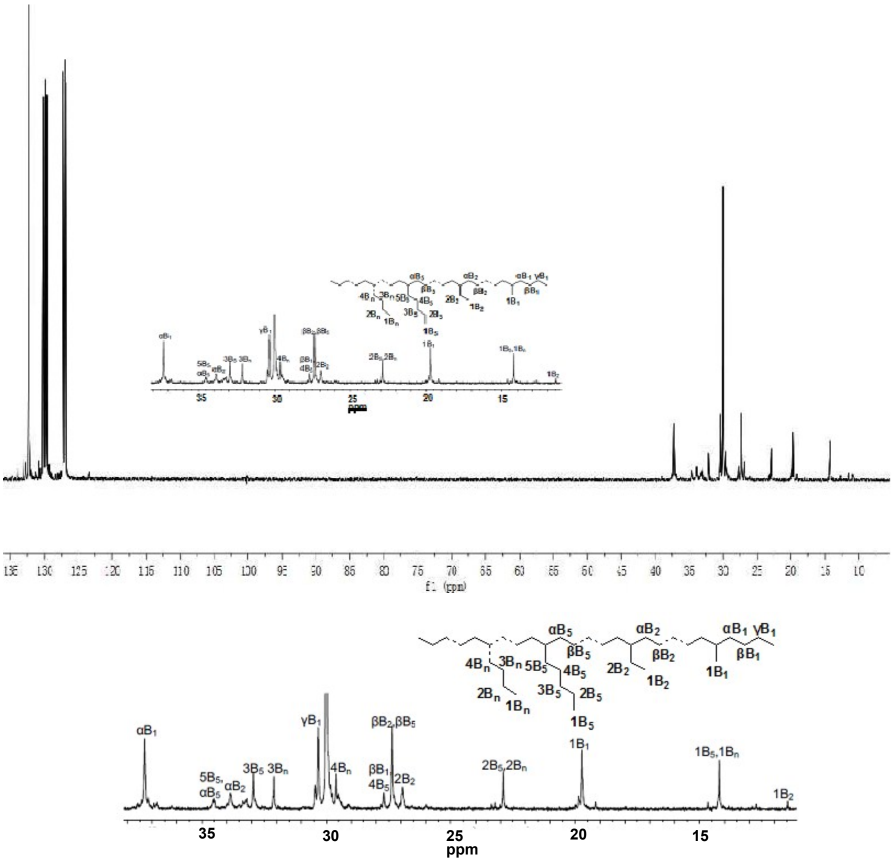

Figure S3. ^{13}C NMR spectrum of the polyethylene by **Ni1**/Et_2AlCl at 30 ºC (entry 2, Table 3).

Table S3 Experimental integrals, percentage of branching for the polyethylene by **Ni1**/Et_2AlCl at 30 °C (entry 2, Table 3)[a]

Peak no.	assignments	Chem. Shifts /ppm	Integral exp.	Branch content		Percentage over total branching	Percentage of branching
1	$1B_2$	11.46	0.07	N_m	1.985	40.47 %	14.21 %
2	$1B_n$, $1B_5$	14.21	1.28	$N_{m(1,4)}$	0	0.00 %	0.00 %
4	$1B_1$	19.73	2.62	$N_{m(1,5)}$	0	0.00 %	0.00 %
7	$2B_5$, $2B_n$	22.89	1	$N_{m(1,6)}$	0	0.00 %	0.00 %
10	$2B_2$	26.95	1.35	N_e	0.63	12.84 %	4.51 %
11	βB_2, βB_5	27.36	3.85	N_p	0	0.00 %	0.00 %
12	βB_1, $4B_5$	27.68	0.58	N_b	0	0.00 %	0.00 %
15	$4B_n$	29.61	0.83	N_a	1.46	29.77 %	10.45 %
16		30	18.96	N_l	0.83	16.92 %	5.94 %
17	γB_1	30.32	4.39	$N_{l(1,4)}$	0	0.00 %	0.00 %
20	$3B_n$	32.11	0.83	δδCH2	18.13		
21	$3B_5$	32.93	1.46	[E]	9.065		
24	αB_2	33.85	1.09	[R]	4.905	100.00 %	
26	$5B_5$, αB_5	34.49	0.47	Total branching = 35.1 %			
29	αB_1	37.3	3.97	176 Branches/1000C			
				Methyl branches		14.21 %	
				Ethyl branches		4.51 %	
				Propyl branches		0.00 %	
				Butyl branches		0.00 %	
				Amyl branches		10.45 %	
				Long branches		5.94 %	

[a] Branches per 1000 C atoms determined by ^{13}C NMR spectroscopy.[2]

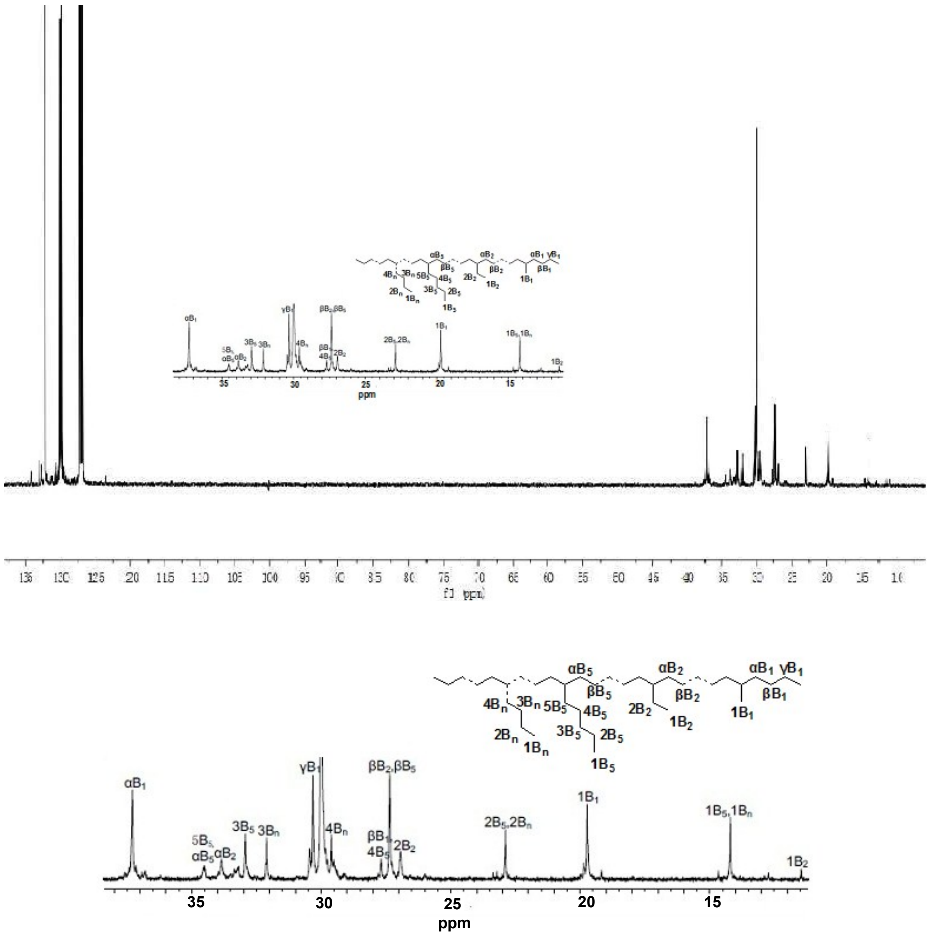

Figure S4. ^{13}C NMR spectrum of the polyethylene by **Ni1**/Et_2AlCl at 50 ºC (entry 8, Table 3).

Table S4 Experimental integrals, percentage of branching for the polyethylene by **Ni1**/Et$_2$AlCl at 50 °C (entry 8, Table 3) [a]

Peak no.	assignments	Chem. Shifts /ppm	Integral exp.	Branch content		Percentage over total branching	Percentage of branching
1	$1B_2$	11.49	0.02	N_m	0.5	30.67 %	12.99 %
2	$1B_n$, $1B_5$	14.21	0.33	$N_{m(1,4)}$	0	0.00 %	0.00 %
4	$1B_1$	19.73	0.7	$N_{m(1,5)}$	0	0.00 %	0.00 %
7	$2B_5$, $2B_n$	22.89	0.18	$N_{m(1,6)}$	0	0.00 %	0.00 %
10	$2B_2$	26.93	0.36	N_e	0.17	10.43 %	4.42 %
11	βB_2, βB_5	27.36	1.02	N_p	0	0.00 %	0.00 %
12	βB_1, $4B_5$	27.68	0.15	N_b	0	0.00 %	0.00 %
15	$4B_n$	29.61	0.56	N_a	0.4	24.54 %	10.39 %
16		30	5	N_l	0.56	34.36 %	14.55 %
17	γB_1	30.32	1.13	$N_{l(1,4)}$	0	0.00 %	0.00 %
20	$3B_n$	32.11	0.56	δδCH2	4.44		
21	$3B_5$	32.93	0.4	[E]	2.22		
24	αB_2	33.83	0.29	[R]	1.63	100.00 %	
26	$5B_5$, αB_5	34.55	0.15	Total branching = 42.3 %			
29	αB_1	37.3	1	212 Branches/1000C			
				Methyl branches		12.99 %	
				Ethyl branches		4.42 %	
				Propyl branches		0.00 %	
				Butyl branches		0.00 %	
				Amyl branches		10.39 %	
				Long branches		14.55 %	

[a] Branches per 1000 C atoms determined by ^{13}C NMR spectroscopy.[2]

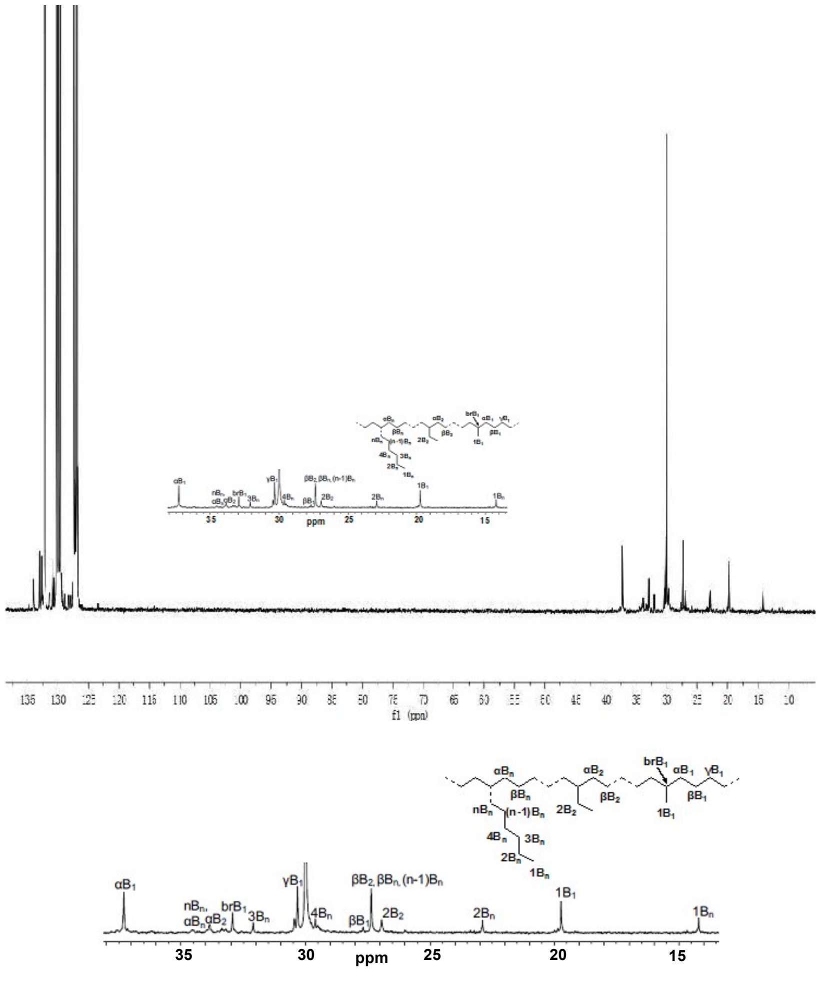

Figure S5. ^{13}C NMR spectrum of the polyethylene by **Ni2**/MAO at 30 ºC (entry 13, Table 2).

Table S5 Experimental integrals, percentage of branching for the polyethylene by **Ni2**/MAO at 30 °C (entry 13, Table 2) [a]

Peak no.	assignments	Chem. Shifts /ppm	Integral exp.	Branch content		Percentage over total branching	Percentage of branching
2	$1Bn$	14.2	0.28	N_m	0.43	53.09 %	8.60 %
4	$1B_1$	19.73	0.62	$N_{m(1,4)}$	0	0.00 %	0.00 %
7	$2Bn$	22.89	0.23	$N_{m(1,5)}$	0	0.00 %	0.00 %
10	$2B_2$	26.94	0.47	$N_{m(1,6)}$	0	0.00 %	0.00 %
11	βB_2, βBn, (n-1)Bn	27.36	1.18	N_e	0.2	24.69 %	4.00 %
12	βB_1	27.69	0.1	N_p	0	0.00 %	0.00 %
15	$4Bn$	29.61	0.18	N_b	0	0.00 %	0.00 %
16		30	8.56	N_a	0	0.00 %	0.00 %
17	γB_1	30.32	1.09	N_l	0.18	22.22 %	3.60 %
20	$3Bn$	32.1	0.18	$N_{l(1,4)}$	0	0.00 %	0.00 %
22	brB_1	32.93	0.43	δδCH2	8.38		
24	αB_2	33.85	0.28	[E]	4.19		
26	nBn, αBn	34.52	0.11	[R]	0.81	100.00 %	
29	αB_1	37.3	1	Total branching = 16.2 %			
				81 Branches/1000C			
				Methyl branches	8.60 %		
				Ethyl branches	4.00 %		
				Propyl branches	0.00 %		
				Butyl branches	0.00 %		
				Amyl branches	0.00 %		
				Long branches	3.60 %		

[a] Branches per 1000 C atoms determined by ^{13}C NMR spectroscopy.[2]

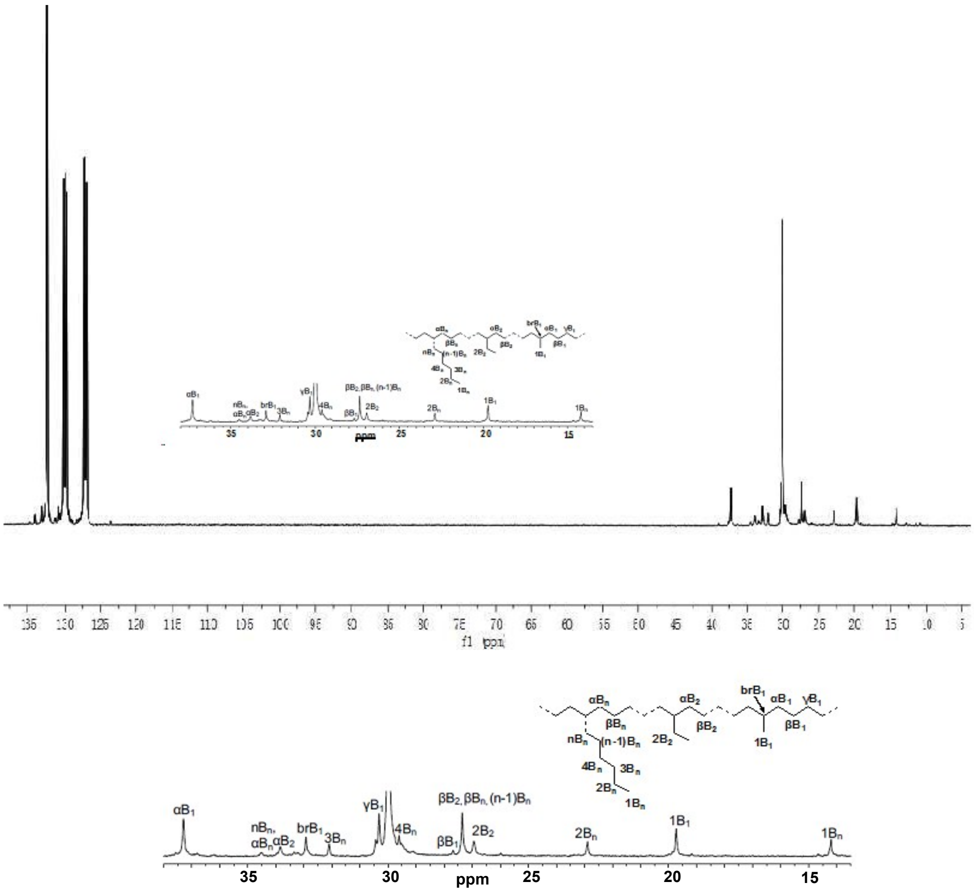

Figure S6. ^{13}C NMR spectrum of the polyethylene by **Ni3**/MAO at 30 ºC (entry 14, Table 2).

Table S6 Experimental integrals, percentage of branching for the polyethylene by **Ni3**/MAO at 30 °C (entry 14, Table 2) [a]

Peak no.	assignments	Chem. Shifts /ppm	Integral exp.	Branch content		Percentage over total branching	Percentage of branching
2	1B*n*	14.2	0.29	N_m	0.5	52.91 %	9.74 %
4	1B$_1$	19.73	0.56	$N_{m(1,4)}$	0	0.00 %	0.00 %
7	2B*n*	22.89	0.23	$N_{m(1,5)}$	0	0.00 %	0.00 %
10	2B$_2$	26.94	0.37	$N_{m(1,6)}$	0	0.00 %	0.00 %
11	*β*B$_2$, *β*B*n*, (n-1)B*n*	27.35	1.05	N_e	0.175	18.52 %	3.41 %
12	*β*B$_1$	27.68	0.1	N_p	0	0.00 %	0.00 %
15	4B*n*	29.61	0.27	N_b	0	0.00 %	0.00 %
16		30	8.65	N_a	0	0.00 %	0.00 %
17	γB$_1$	30.32	1.52	N_l	0.27	28.57 %	5.26 %
20	3B*n*	32.1	0.27	$N_{l(1,4)}$	0	0.00 %	0.00 %
22	brB$_1$	32.93	0.5	δδCH2	8.38		
24	αB$_2$	33.85	0.31	[E]	4.19		
26	nB*n*, αB*n*	34.51	0.09	[R]	0.945	100.00 %	
29	αB$_1$	37.3	1	Total branching = 18.4 %			
				92 Branches/1000C			
				Methyl branches		9.74 %	
				Ethyl branches		3.41 %	
				Propyl branches		0.00 %	
				Butyl branches		0.00 %	
				Amyl branches		0.00 %	
				Long branches		5.26 %	

[a] Branches per 1000 C atoms determined by ^{13}C NMR spectroscopy.[2]

We have provided the DSC curves at different conditions (Figure S7 – Figure S40).

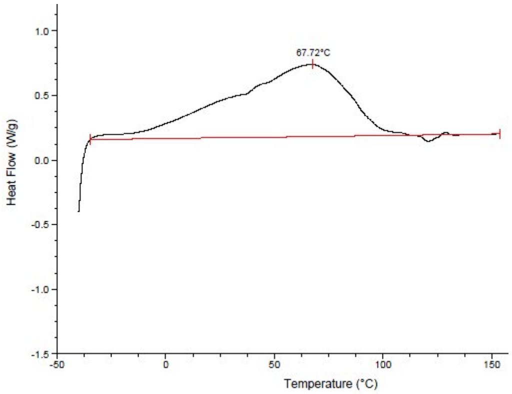

Figure S7. DSC spectrum of the polyethylene by **Ni1**/MMAO at 30 ºC (entry 2, Table 1)

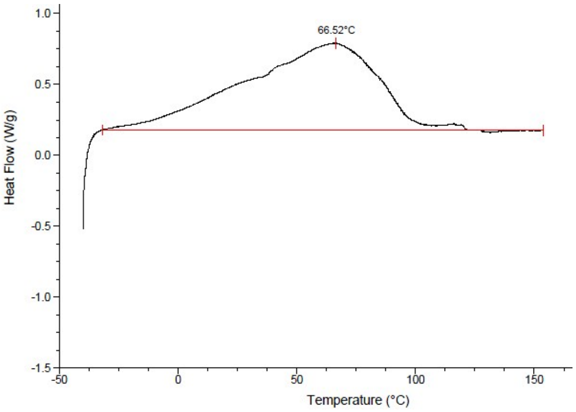

Figure S8. DSC spectrum of the polyethylene by **Ni1**/MAO at 30 ºC and the Al/Ni ratio is 1000 (entry 1, Table 2)

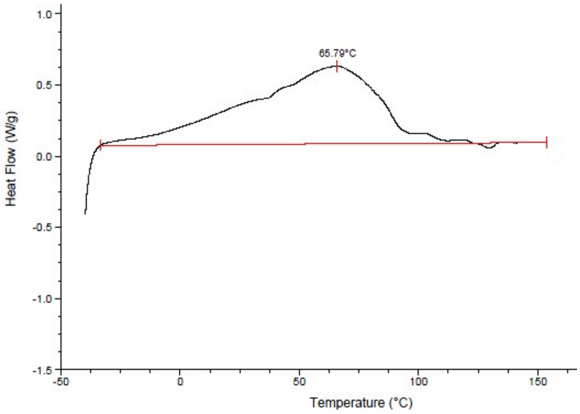

Figure S9. DSC spectrum of the polyethylene by **Ni1**/MAO at 30 ºC and the Al/Ni ratio is 1500 (entry 2, Table 2)

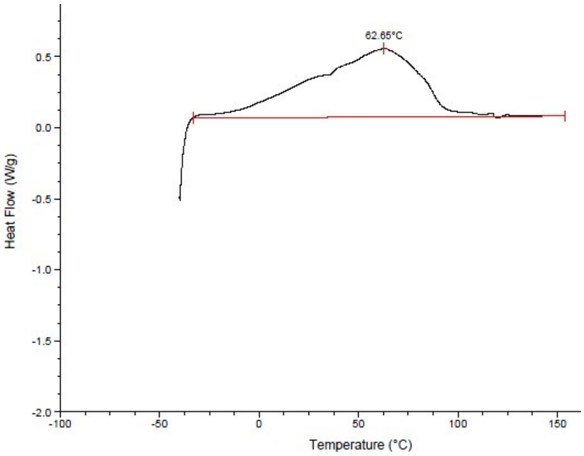

Figure S10. DSC spectrum of the polyethylene by **Ni1**/MAO at 30 ºC and the Al/Ni ratio is 2000 (entry 3, Table 2)

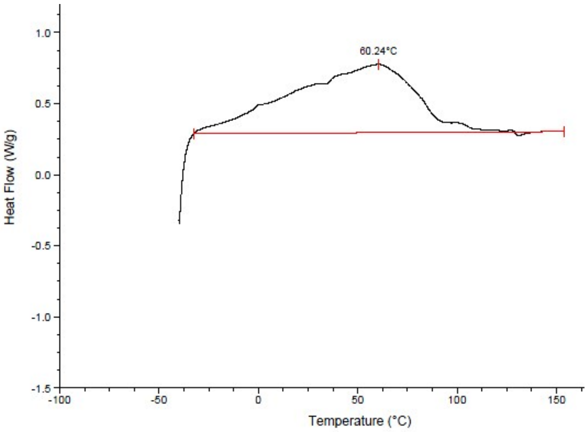

Figure S11. DSC spectrum of the polyethylene by **Ni1**/MAO at 30 ºC and the Al/Ni ratio is 2500 (entry 4, Table 2)

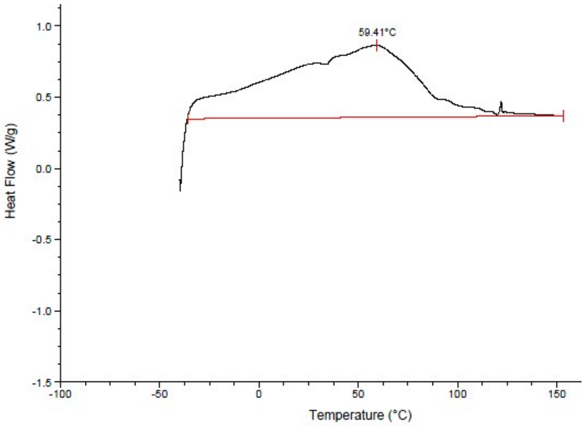

Figure S12. DSC spectrum of the polyethylene by **Ni1**/MAO at 30 ºC and the Al/Ni ratio is 3000 (entry 5, Table 2)

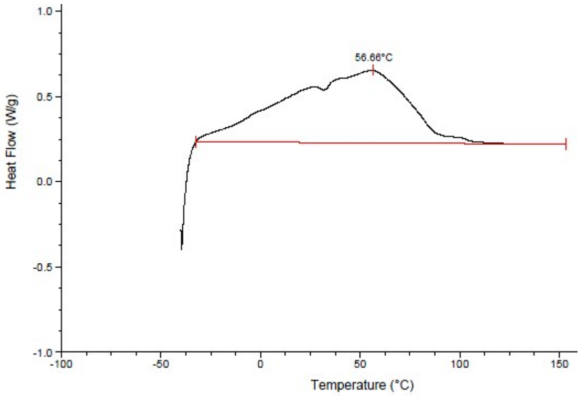

Figure S13. DSC spectrum of the polyethylene by **Ni1**/MAO at 30 ºC and the Al/Ni ratio is 3500 (entry 6, Table 2)

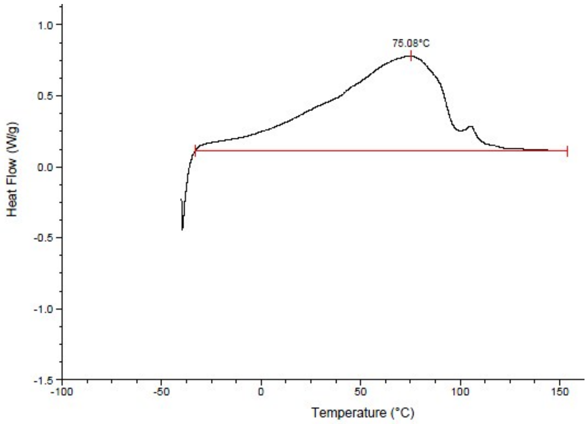

Figure S14. DSC spectrum of the polyethylene by **Ni1**/MAO at 20 ºC and the Al/Ni ratio is 2500 (entry 7, Table 2)

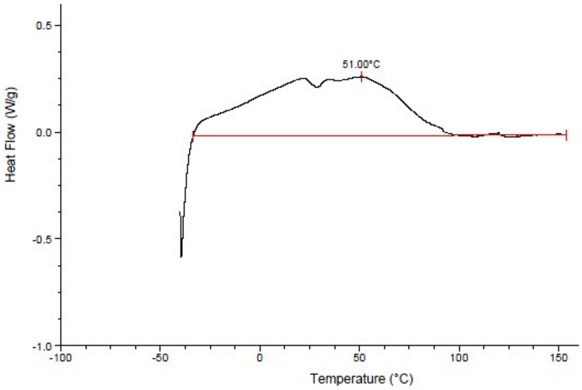

Figure S15. DSC spectrum of the polyethylene by **Ni1**/MAO at 40 ºC and the Al/Ni ratio is 2500 (entry 8, Table 2)

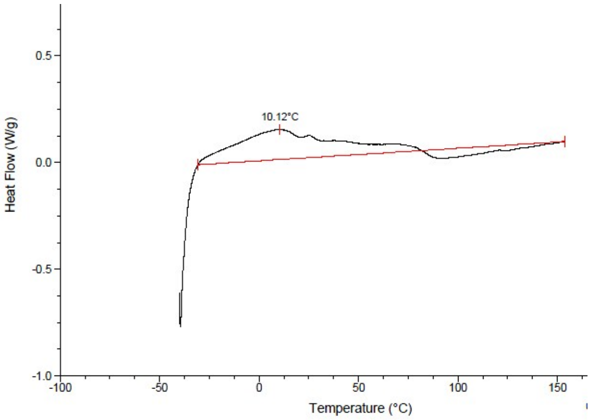

Figure S16. DSC spectrum of the polyethylene by **Ni1**/MAO at 50 ºC and the Al/Ni ratio is 2500 (entry 9, Table 2)

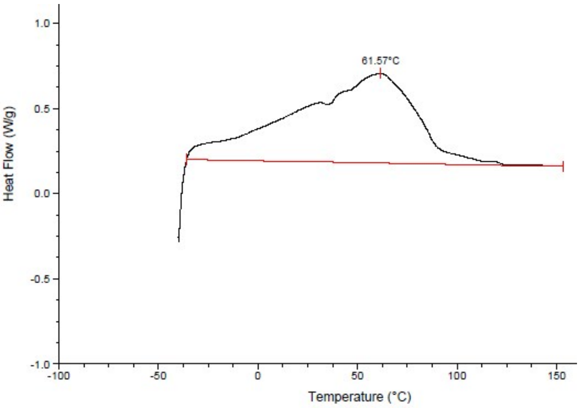

Figure S17. DSC spectrum of the polyethylene by **Ni1**/MAO at 30 ºC and the time is 15 min (entry 10, Table 2)

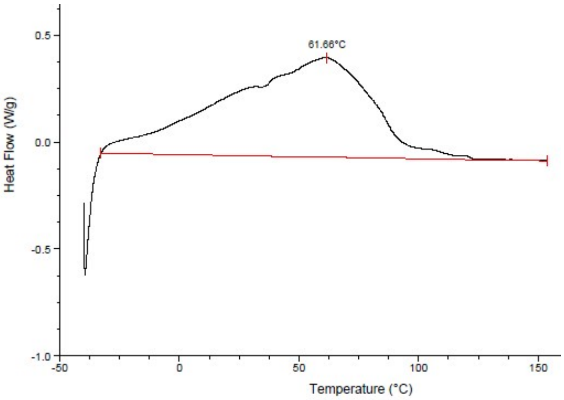

Figure S18. DSC spectrum of the polyethylene by **Ni1**/MAO at 30 ºC and the time is 45 min (entry 11, Table 2)

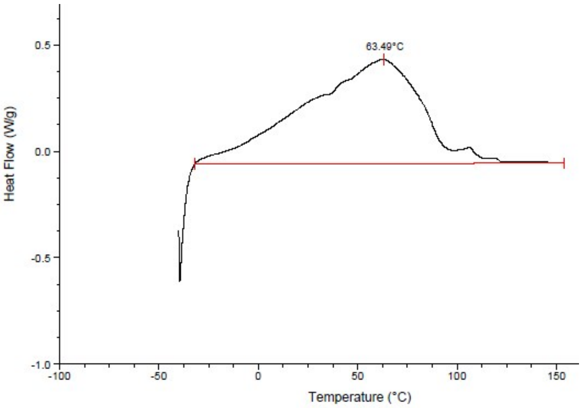

Figure S19. DSC spectrum of the polyethylene by **Ni1**/MAO at 30 ºC and the time is 60 min (entry 12, Table 2)

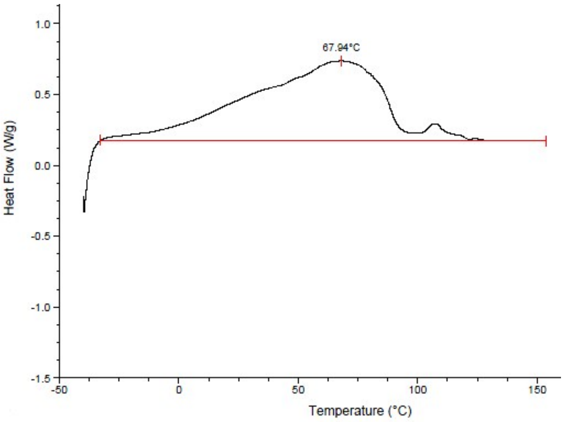

Figure S20. DSC spectrum of the polyethylene by **Ni2**/MAO at 30 ºC (entry 13, Table 2)

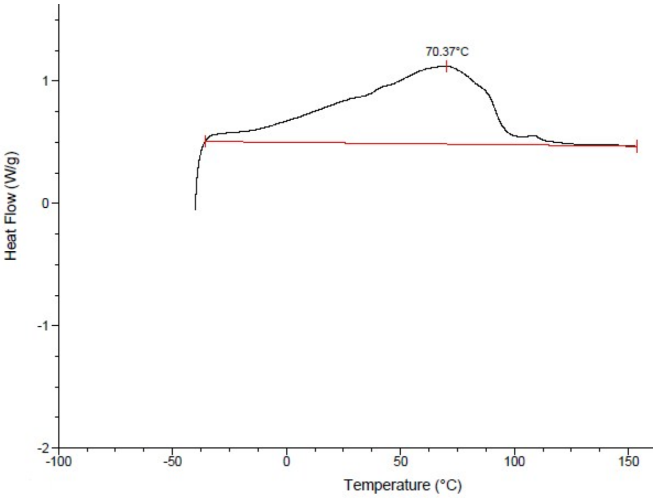

Figure S21. DSC spectrum of the polyethylene by **Ni3**/MAO at 30 ºC (entry 14, Table 2)

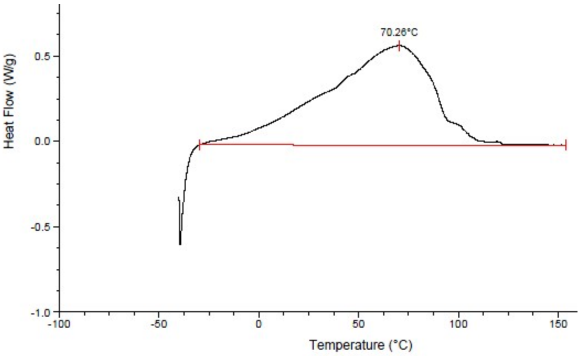

Figure S22. DSC spectrum of the polyethylene by **Ni4**/MAO at 30 ºC (entry 15, Table 2)

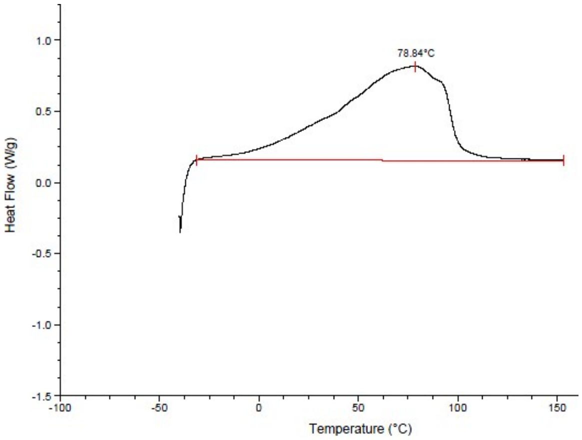

Figure S23. DSC spectrum of the polyethylene by **Ni5**/MAO at 30 ºC (entry 16, Table 2)

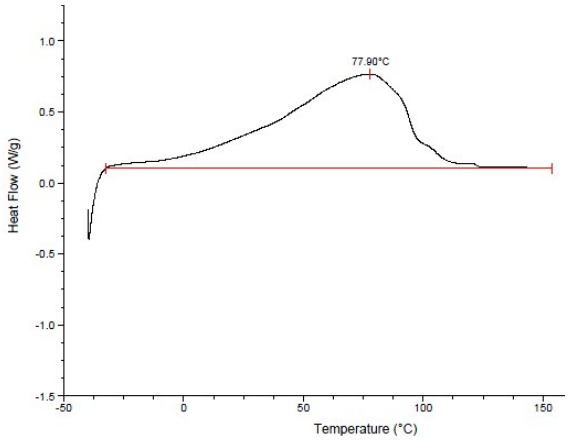

Figure S24. DSC spectrum of the polyethylene by **Ni6**/MAO at 30 ºC (entry 17, Table 2)

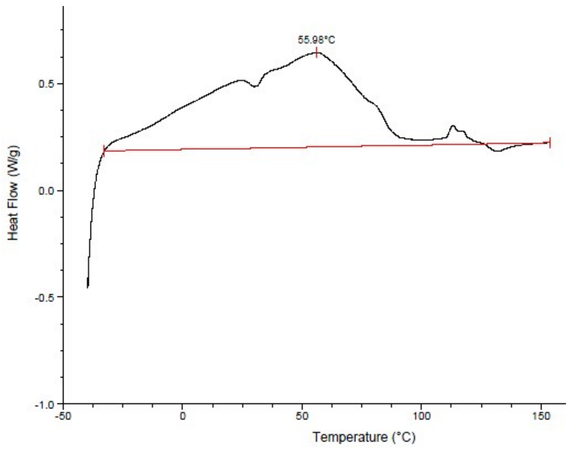

Figure S25. DSC spectrum of the polyethylene by **Ni1**/Et$_2$AlCl at 30 ºC and the Al/Ni ratio is 200 (entry 1, Table 3)

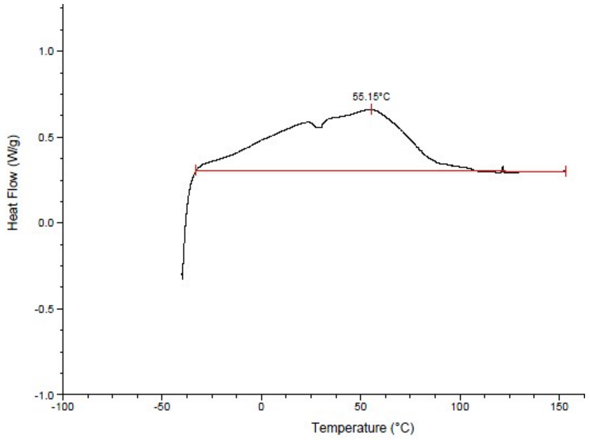

Figure S26. DSC spectrum of the polyethylene by **Ni1**/Et$_2$AlCl at 30 ºC and the Al/Ni ratio is 300 (entry 2, Table 3)

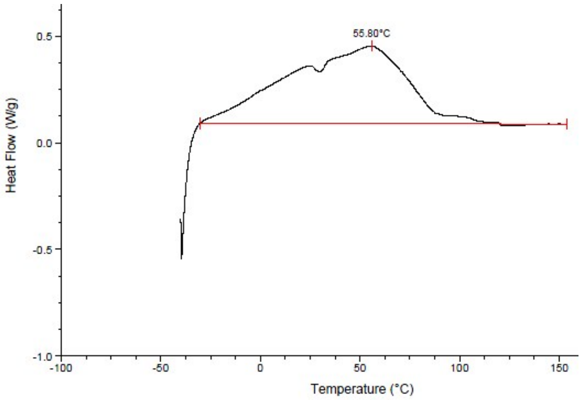

Figure S27. DSC spectrum of the polyethylene by **Ni1**/Et_2AlCl at 30 ºC and the Al/Ni ratio is 400 (entry 3, Table 3)

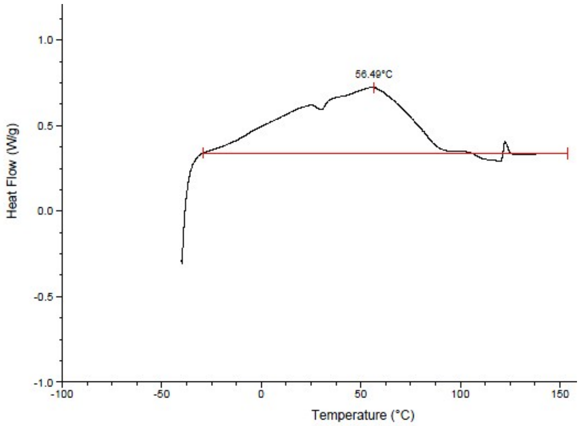

Figure S28. DSC spectrum of the polyethylene by **Ni1**/Et_2AlCl at 30 ºC and the Al/Ni ratio is 500 (entry 4, Table 3)

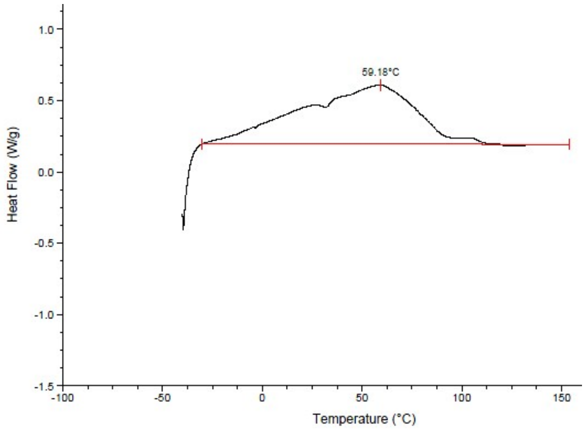

Figure S29. DSC spectrum of the polyethylene by **Ni1**/Et_2AlCl at 30 ºC and the Al/Ni ratio is 600 (entry 5, Table 3)

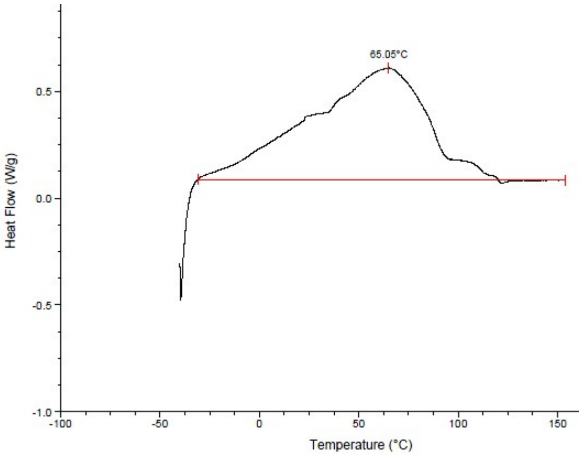

Figure S30. DSC spectrum of the polyethylene by **Ni1**/Et$_2$AlCl at 20 ºC and the Al/Ni ratio is 300 (entry 6, Table 3)

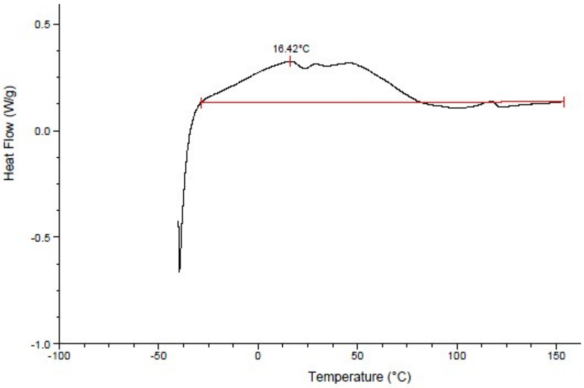

Figure S31. DSC spectrum of the polyethylene by **Ni1**/Et$_2$AlCl at 40 ºC and the Al/Ni ratio is 300 (entry 7, Table 3)

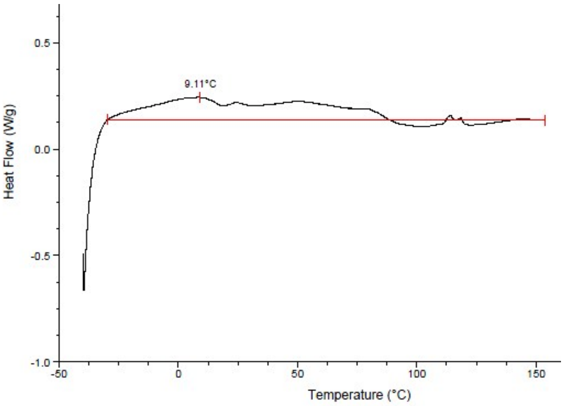

Figure S32. DSC spectrum of the polyethylene by **Ni1**/Et$_2$AlCl at 50 ºC and the Al/Ni ratio is 300 (entry 8, Table 3)

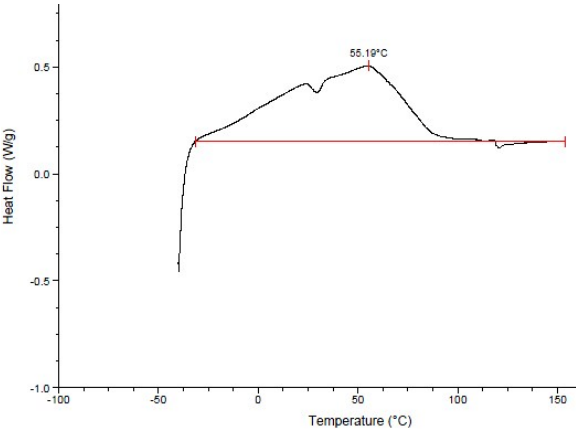

Figure S33. DSC spectrum of the polyethylene by **Ni1**/Et$_2$AlCl at 30 ºC and the time is 15 min (entry 9, Table 3)

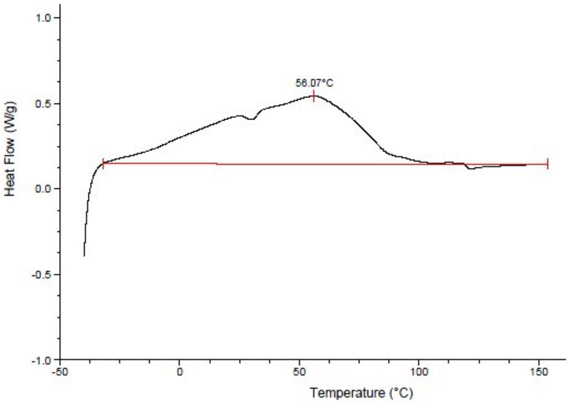

Figure S34. DSC spectrum of the polyethylene by **Ni1**/Et$_2$AlCl at 30 ºC and the time is 45 min (entry 10, Table 3)

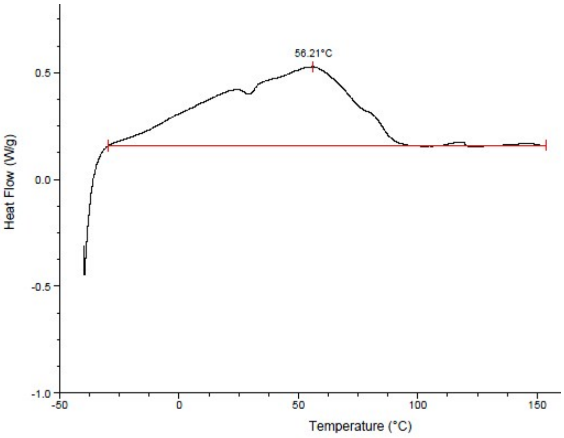

Figure S35. DSC spectrum of the polyethylene by **Ni1**/Et$_2$AlCl at 30 ºC and the time is 60 min (entry 11, Table 3)

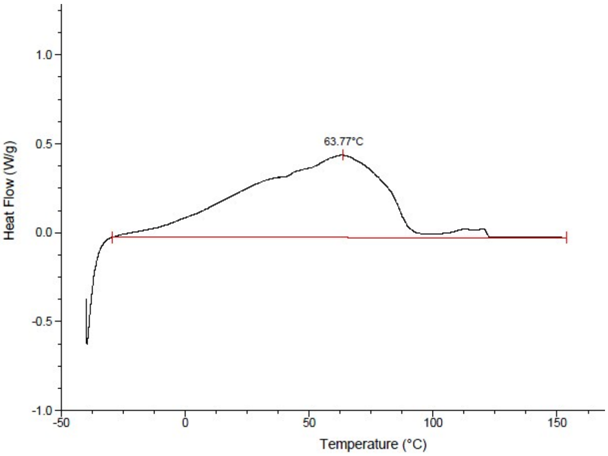

Figure S36. DSC spectrum of the polyethylene by **Ni2**/Et_2AlCl at 30 ºC (entry 12, Table 3)

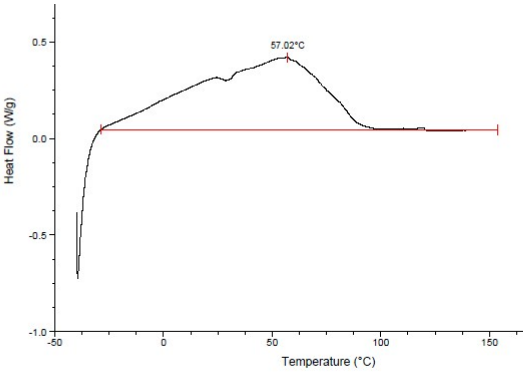

Figure S37. DSC spectrum of the polyethylene by **Ni3**/Et_2AlCl at 30 ºC (entry 13, Table 3)

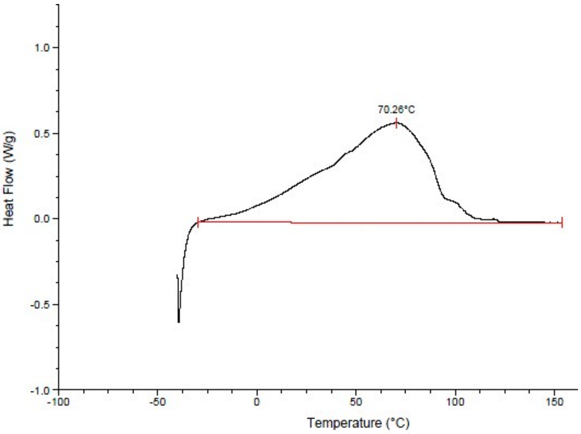

Figure S38. DSC spectrum of the polyethylene by **Ni4**/Et_2AlCl at 30 ºC (entry 14, Table 3)

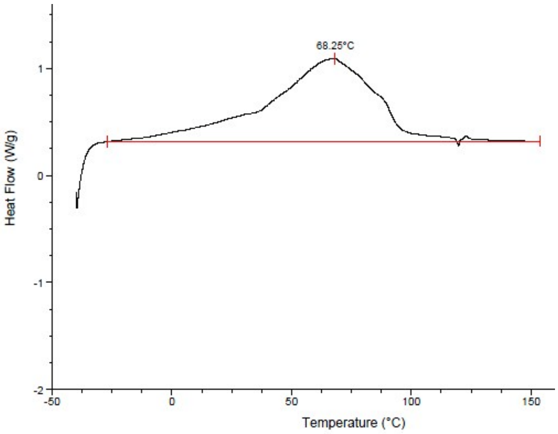

Figure S39. DSC spectrum of the polyethylene by **Ni5**/Et$_2$AlCl at 30 ºC (entry 15, Table 3)

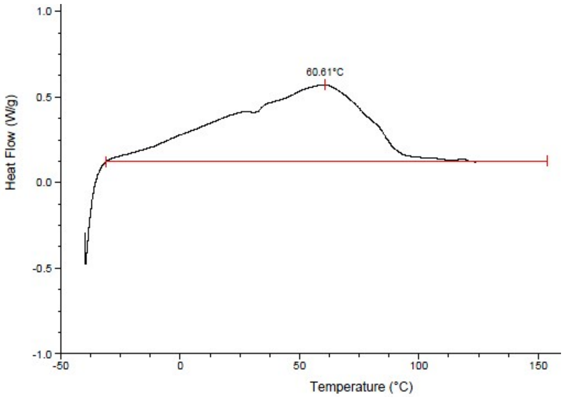

Figure S40. DSC spectrum of the polyethylene by **Ni6**/Et$_2$AlCl at 30 ºC (entry 16, Table 3)

Conducting the polymerization between 20 to 50 °C, it was still approved as the best activity achieved at 30 °C; higher reaction temperature, the activities were significantly decreased. The obtained polyethylenes showed gradually lower molecular weights regarding the higher temperature used (Figure S41).

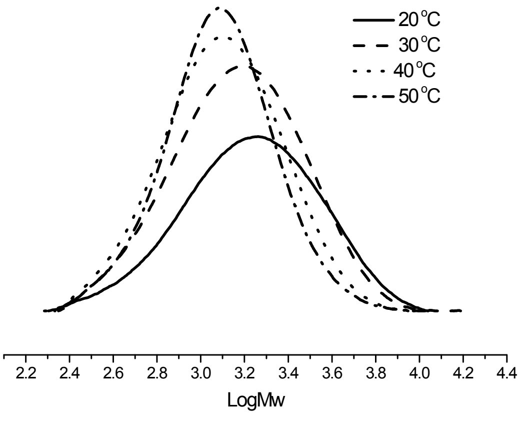

Figure S41. GPC traces of PE produced by **Ni1**/Et$_2$AlCl catalytic system at different reaction temperature (entries 2, 6–8, Table 3)

Reference

1 G. M. Sheldrick, *SHELXTL–97 Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.

2 G. B. Galland, R. F. de Souza, R. S. Mauler and F. F. Nunes, *Macromolecules*, 1999, **32**, 1620–1625.