Supporting Information

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1. Figures and Tables

Ent. a	Cat.	[cat]	Т	t	Yield	Act. ^b
		(µmol)	(°C)	(h)	(g)	
1	Ni3	1	70	0.25	2.0	8.0
2	Ni3	1	70	0.5	4.2	8.4
3	Ni3	1	70	1	5.2	5.2
4	Ni3	1	70	2	6.4	3.2
5	Ni3	1	70	4	6.8	1.7

Table S1. Ethylene homopolymerization with the nickel complexes at 9 atm.

^{*a*}General conditions: Al/Ni = 600, CH₂Cl₂ = 2 ml, toluene = 48 ml, ethylene = 8 atm. ^{*b*}10⁶ g of PE (mol of Ni)⁻¹ h⁻¹.



Figure S1. Productivity versus time for complexes Ni3 at 70 °C.

polymer	methyl	ethyl	propyl	butyl	butyl+	$Total(^{13}C)^a$	Total(¹ H) ^a
3	52	0	3	10	0	65	68
7	59	5	0	10	0	74	70
11	56	5	7	12	0	80	76

 Table S2. Polymer Chain Branching Distribution (%) and Number of Branches per 1000 Carbons.*

*polymer from table 1, entry 3, 7, 11.

^a Measured by ¹³C NMR and ¹H NMR in CDCl₂CDCl₂ at 120 °C



S2. ¹³C NMR spectrum of the polyethylene generated by **Ni1** from table 1, entry 3. (in CDCl₂CDCl₂ at 120 °C)



Figure S3. ¹³C NMR spectrum of the polyethylene generated by **Ni2** from table 1, entry 7. (in CDCl₂CDCl₂ at 120 °C)



(in CDCl₂CDCl₂ at 120 °C)

Table S3. Polymer Chain Branching Distribution (%) and Number of Branches per 1000 Carbons.*

polymer	methyl	ethyl	propyl	butyl	butyl+	$Total(^{13}C)^a$	Total(¹ H) ^a
9	40	0	0	8	0	48	53
18	46	0	0	0	0	46	52

*polymer from table 1, entry 9, 18.

^a Measured by ¹³C NMR and ¹H NMR in CDCl₂CDCl₂ at 120 °C



Figure S5. ¹³C NMR spectrum of the polyethylene generated by **Ni3** from table 1, entry 9. (in CDCl₂CDCl₂ at 120 °C)



Figure S6. ¹³C NMR spectrum of the polyethylene generated by **Ni-Me** from table 1, entry 18. (in CDCl₂CDCl₂ at 120 °C)

2. Experimental sections

2.1 General Considerations

All experiments were carried out under a dry Nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ¹H, ¹³C NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ¹H and ¹³C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Quantitative ¹³C NMR analysis of the polymer samples were obtained on 10-20 wt % solutions of the polymers and 0.05 M CrAcAc in 1,2,4-trichlorobenzene (TCB) unlocked at 120-140 °C using a 90° pulse of 17.8 µs, a spectral width of 35 kHz, a relaxation delay of 5 s, an acquisition time of 0.64 s, and inverse gated decoupling. Samples were preheated for at least 30 min before acquiring data. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K^{α} radiation ($\lambda = 0.71073$ Å). Molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 150 °C using o-dichlorobenzene as a solvent, and the calibration was made using polystyrene standard and are corrected for linear polyethylene by universal calibration using the Mark–Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ cm³/g and R = 0.67 for polystyrene and K = 5.90×10^{-2} cm³/g and R = 0.69 for polyethylene. Dichloromethane, toluene and hexanes were purified by solvent purification systems. 2arylamine were prepared by literature procedure.^{1,2} All other reagents were purchased from commercial sources and used without purification.

Differential scanning calorimetry (DSC). DSC was performed by a DSC Q20 from TA Instruments. Samples were quickly heated to 130°C and kept for 5 min to remove thermal history, then cooled to 30°C at a rate of 10 K/min, and finally reheated to 130°C at the same rate under a nitrogen flow (50 mL/min). The maximum points endotherm (heating scan) were taken as the melting temperature (T_m).

Stress/strain experiments were performed at 10 mm/min by means of a Universal Test

Machine (UTM2502) at room temperature. At least three specimens of each polymer were tested. Polymers were melt-pressed at 150°C to obtain the test specimens. The test specimens have 25-mm gauge length, 2-mm width, and thickness of 0.5 mm.

2.2 Standard Procedure for the Synthesis of 2-bisphenylarylanilines.

A 150 mL thick wall pressure bottle was charged with 2-arylamine (20.0 mmol, 1.0 equiv.) and diphenylmethanol (20 mmol, 1.0 equiv.), and heated to 120 °C. A solution of anhydrous zinc chloride (5 mmol, 0.4 equiv.) in concentrated hydrochloric acid (37% in H₂O, 0.8 equiv.) was added to the mixture (exothermic + intense bubbling), and the temperature was raised to 160 °C. After 60 min at 160 °C, the reaction mixture was cooled down to room temperature and dissolved in CH₂Cl₂ (200 mL). The CH₂Cl₂ layer was washed with water (3 × 100 mL) and dried over anhydrous magnesium sulfate. The solution was concentrated to 20 mL. The products were crashed out with 200 ml methanol and washed with methanol (3 × 100 mL). The desired anilines were obtained at 51-70 % yields.



3-benzhydryl-5-methyl-[1,1'-biphenyl]-2-amine

Yield 67 % (4.69 g). $R_f = 0.32$ (hexanes/EtOAc, 1:20). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, J = 4.1 Hz, 4H, aryl-*H*), 7.31 (t, J = 7.2 Hz, 5H, aryl-*H*), 7.26 – 7.23 (m, 2H, aryl-*H*), 7.17 (d, J = 7.2 Hz, 4H, aryl-*H*), 6.89 (s, 1H, aryl-*H*), 6.47 (s, 1H, aryl-*H*), 5.53 (s, 1H, C*H*Ph₂), 3.47 (s, 2H, N*H*₂), 2.17 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 142.78 (s), 139.99 (s), 138.98 (s), 129.94 (s), 129.70 (s), 129.45 (s), 129.40 (s), 128.91 (s), 128.81 (s), 128.65 (s), 127.16 (s), 127.13 (s), 126.73 (s), 52.66 (s, CHPh₂), 20.82 (s, CH₃). HRMS (m/z): calcd for C₂₆H₂₄N: 350.1909, found: 350.1905[M + H]⁺.



3-benzhydryl-4',5-dimethyl-[1,1'-biphenyl]-2-amine

Yield 63 % (4.57 g). $R_f = 0.3$ (hexanes/EtOAc, 1:20). ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 1.2 Hz, 2H, aryl-*H*), 7.32 – 7.27 (d, 4H, aryl-*H*), 7.26 (d, J = 1.2 Hz, 2H, aryl-*H*), 7.22 (t, J = 7.6 Hz, 2H, aryl-*H*), 7.17 (d, J = 7.8 Hz, 4H, aryl-*H*), 6.87 (s, 1H, aryl-*H*), 6.46 (s, 1H, aryl-*H*), 5.53 (s, 1H, CHPh₂), 3.47 (s, 2H, NH₂), 2.37 (s, 3H, CH₃), 2.16 (s, 1H, CH₃).¹³C NMR (101 MHz, CDCl₃) δ 141.66 (s), 137.88 (s), 135.82 (s), 135.62 (s), 128.59 (s), 128.55 (s), 128.48 (s), 128.34 (s), 128.26 (s), 128.13 (s), 127.74 (s), 127.47 (s), 125.94 (s), 125.53 (s), 51.49 (s, CHPh₂), 20.10 (s, CH₃), 19.66 (s, CH₃). HRMS (m/z): calcd for C₂₇H₂₆N: 364.2065 , found: 364.2062 [M + H]⁺.



3-benzhydryl-4'-(tert-butyl)-5-methyl-[1,1'-biphenyl]-2-amine

Yield 70 % (5.68 g). $R_f = 0.25$ (hexanes/EtOAc, 1:20). ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.38 (m, 2H, aryl-*H*), 7.34 (d, *J* = 8.7 Hz, 2H, aryl-*H*), 7.30 (d, *J* = 6.6 Hz, 4H, aryl-*H*), 7.23 (d, *J* = 6.7 Hz, 2H, aryl-*H*), 7.17 (d, *J* = 7.1 Hz, 4H, aryl-*H*), 6.90 (s, 1H, aryl-*H*), 6.46 (s, 1H, aryl-*H*), 5.53 (s, 1H, C*H*Ph₂), 3.49 (s, 2H, N*H*₂), 2.16 (s, 3H, C*H*₃), 1.33 (s, 9H, C(C*H*₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 148.82 (s), 141.65 (s), 137.97 (s), 135.79 (s), 128.54 (s), 128.45 (s), 128.27 (s), 127.92 (s), 127.69 (s), 127.46 (s), 125.88 (s), 125.52 (s), 124.52 (s), 51.52 (s, CHPh₂), 33.47 (s, *C*(CH₃)₃), 30.32 (s, C(CH₃)₃), 19.66 (s, *C*H₃). HRMS (m/z): calcd for C₃₀H₃₂N: 406.2535 , found: 406.2530 [M + H]⁺.



2-benzhydryl-4-methyl-6-(naphthalen-2-yl)aniline

Yield 51 % (4.08 g). $R_f = 0.35$ (hexanes/EtOAc, 1:20). ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.86 (m, 2H, aryl-*H*), 7.84 (dd, J = 7.9, 4.2 Hz, 1H, aryl-*H*), 7.55 (dd, J = 8.5, 1.4 Hz, 1H,

aryl-*H*), 7.49 (dd, J = 5.8, 3.5 Hz, 2H, aryl-*H*), 7.33 (t, J = 7.3 Hz, 1H, aryl-*H*), 7.26 (dd, J = 10.9, 3.6 Hz, 4H, aryl-*H*), 7.19 (d, J = 7.2 Hz, 6H, aryl-*H*), 6.98 (s, 1H, aryl-*H*), 6.51 (s, 1H, aryl-*H*), 5.57 (s, 1H, C*H*Ph₂), 3.54 (s, 2H, N*H*₂), 2.20 (s, 3H, C*H*₃).¹³C NMR (101 MHz, CDCl₃) δ 142.75 (s), 139.13 (s), 137.42 (s), 133.67 (s), 132.47 (s), 130.06 (s), 129.78 (s), 129.70 (s), 129.60 (s), 128.75 (s), 128.67 (s), 128.41 (s), 128.11 (s), 128.00 (s), 127.76 (s), 127.28 (s), 126.74 (s), 126.34 (s), 126.04 (s), 52.64 (s, CHPh₂), 20.84 (s, CH₃). HRMS (m/z): calcd for C₃₀H₂₆N: 400.2065, found: 400.2058 [M + H]⁺.

2.3 Standard Procedure for the Synthesis of Ligand L1-L4.

In a 100 mL round-bottom flask, $ZnCl_2$ (0.86 g, 6.25 mmol) and acenaphthenequinone (1 g, 5.5 mmol) were suspended in glacial acetic acid (10 mL). 2-bisphenylarylaniline (12.5 mmol) was added, and the reaction mixture was refluxed under stirring for 30 min. The solution was allowed to cool to room temperature, and a bright orange-red solid precipitated. The solid was separated by filtration and washed with acetic acid (3 × 10 mL) and diethyl ether (8 × 15 mL), to remove remaining acetic acid. The obtained solid was suspended in methylene chloride (200 mL), and a solution of potassium oxalate (1.84 g, 10 mmol) in water (10 mL) was added. The reaction mixture was stirred vigorously for 15 min. A white precipitate of zinc oxalate was generated in the aqueous phase. The two phases were separated, and the organic layer was washed with water (3 × 20 mL) and dried with MgSO₄. After filtration, the solvent was removed under vacuum to afford the desired product as a yellow or orange powder.



Yield 70 % (2.95 g). $R_f = 0.35$ (hexanes/EtOAc, 1:20). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 7.7 Hz, 4H, aryl-*H*), 7.36 (d, J = 8.2 Hz, 2H, aryl-*H*), 7.29 (d, J = 7.2 Hz, 2H, aryl-*H*), 7.25 (s, 1H, aryl-*H*), 7.24 – 7.18 (m, 2H, aryl-*H*), 7.12 (d, J = 10.2 Hz, 6H, aryl-*H*), 7.08 (d, J = 6.2 Hz, 3H, aryl-*H*), 6.97 – 6.83 (m, 6H, aryl-*H*), 6.22 – 6.02 (m, 6H, aryl-*H*), 5.95 – 5.75

(m, 6H, aryl-*H*), 5.46 (s, 2H, C*H*Ph₂), 2.38 (s, 1H, C*H*₃). ¹³C NMR (101 MHz, CDCl₃) δ 162.69 (s, N=*C*), 145.57 (s), 143.99 (s), 140.71 (s), 140.33 (s), 139.94 (s), 133.65 (s), 133.27 (s), 131.34 (s), 129.76 (s), 129.70 (s), 129.57 (s), 129.47 (s), 129.45 (s), 129.29 (s), 129.17 (s), 128.10 (s), 127.94 (s), 127.47 (s), 127.09 (s), 127.05 (s), 126.63 (s), 125.84 (s), 124.71 (s), 122.58 (s), 51.78 (s, CHPh₂), 21.27 (s, CH₃, CH₃). HRMS (m/z): calcd for C₆₄H₄₉N₂: 845.3896, found: 845.3890 [M + H]⁺.



Yield 63 % (2.75 g). $R_f = 0.32$ (hexanes/EtOAc, 1:20). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 8.0 Hz, 4H, aryl-H), 7.35 (d, J = 8.2 Hz, 2H, aryl-H), 7.29 (d, J = 7.2 Hz, 3H, aryl-H), 7.24 – 7.16 (m, 2H, aryl-H), 7.12 (d, J = 7.5 Hz, 3H, aryl-H), 7.07 (s, 2H, aryl-H), 6.92 (d, J = 6.8 Hz, 4H, aryl-H), 6.90 – 6.84 (m, 2H, aryl-H), 6.12 (d, J = 7.1 Hz, 4H, aryl-H), 6.07 (d, J = 7.1 Hz, 2H, aryl-H), 5.90 (dq, J = 14.1, 6.9 Hz, 5H, aryl-H), 5.48 (s, 2H, CHPh₂), 2.38 (s, 6H, C H_3), 1.81 (s, 6H, C H_3). ¹³C NMR (101 MHz, CDCl₃) δ 162.50 (s, N=C), 145.70 (s), 144.14 (s), 140.85 (s), 139.86 (s), 137.30 (s), 136.70 (s), 133.67 (s), 133.18 (s), 131.33 (s), 129.55 (s), 129.50 (s), 129.36 (s), 129.20 (s), 128.78 (s), 127.90 (s), 127.36 (s), 126.98 (s), 126.60 (s), 125.80 (s), 124.73 (s), 122.53 (s), 51.72 (s, CHPh₂), 21.28 (s, CH₃), 20.71 (s, CH₃). HRMS (m/z): calcd for C₆₆H₅₃N₂: 873.4209 , found: 873.4202 [M + H]⁺.



R₃=p-tBuPh

Yield 71 % (3.40 g). $R_f = 0.28$ (hexanes/EtOAc, 1:20). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 8.5 Hz, 4H, aryl-H), 7.32 (d, J = 8.1 Hz, 3H, aryl-H), 7.25 – 7.14 (m, 9H, aryl-H), 7.09 (d, J = 7.5 Hz, 6H, aryl-H), 6.88 (t, J = 7.7 Hz, 4H, aryl-H), 6.12 (d, J = 7.1 Hz, 2H, aryl-H), 6.06 – 5.97 (m, 3H, aryl-H), 5.75 (d, J = 3.5 Hz, 5H, aryl-H), 5.46 (s, 2H, $CHPh_2$), 2.37 (s, 6H, CH_3), 0.78 (s, 18H, $C(CH_3)_3$). ¹³C NMR (101 MHz, CDCl₃) δ 162.45 (s, N=C), 149.70 (s), 145.57 (s), 143.71 (s), 140.46 (s), 137.35 (s), 133.56 (s), 133.03 (s), 131.35 (s), 129.74 (s), 129.56 (s), 129.23 (s), 129.04 (s), 127.88 (s), 127.22 (s), 127.06 (s), 126.52 (s), 125.76 (s), 125.13 (s), 124.45 (s), 122.45 (s), 52.02 (s, $CHPh_2$), 34.06 (s, $C(CH_3)_3$), 30.86 (s, $C(CH_3)_3$), 21.27 (s, CH_3). HRMS (m/z): calcd for $C_{72}H_{65}N_2$: 957.5148 , found: 957.5142 [M + H]⁺.



Yield 10 % (0.47 g). $R_f = 0.18$ (hexanes/EtOAc, 1:20). ¹H NMR (400 MHz, CDCl₃) δ 8.11 – 7.93 (m, 6H, aryl-*H*), 7.80 (d, J = 8.7 Hz, 2H, aryl-*H*), 7.75 – 7.62 (m, 6H, aryl-*H*), 7.54 (s, 2H, aryl-*H*), 7.28 (t, J = 7.6 Hz, 2H, aryl-*H*), 7.12 (t, J = 7.3 Hz, 2H, aryl-*H*), 7.03 – 6.92 (m, 8H, aryl-*H*), 6.83 (d, J = 7.1 Hz, 4H, aryl-*H*), 6.75 (d, J = 7.7 Hz, 6H, aryl-*H*), 6.72 – 6.64 (m, 6H, aryl-*H*), 6.52 (d, J = 8.6 Hz, 2H, aryl-*H*), 6.39 (s, 2H, aryl-*H*), 5.10 (s, 2H, CHPh₂), 2.21 (s, 6H, CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 201.14 (s, N=C), 140.53 (s), 140.22 (s), 140.08 (s), 137.86 (s), 136.87 (s), 132.40 (s), 131.01 (s), 130.77 (s), 130.07 (s), 129.79 (s), 129.58 (s), 128.55 (s), 128.32 (s), 128.15 (s), 128.07 (s), 127.95 (s), 127.78 (s), 127.70 (s), 127.25 (s), 122.50 (s), 122.40 (s), 121.35 (s), 120.90 (s), 119.96 (s), 51.26 (s, CHPh₂), 20.25 (s, CH₃). HRMS (m/z): calcd for C₇₂H₅₃N₂: 945.4209, found: 945.4205[M + H]⁺.

2.4 Standard Procedure for the Synthesis of Complex 1-4.

A 50 mL Schlenk flask was charged with ligand (1.0 mmol), dry CH_2Cl_2 (20 mL) and 308 mg (1.0 mmol) of (DME)NiBr₂. During stirring, the color of the solution was changed from

yellow to red and some solid precipitated. After stirring overnight at room temperature, the desired compound can be isolated from filtration. After repeated recrystallization from Et_2O and CH_2Cl_2 , the pure compound was obtained as a dark red solid.



Yield 78 % (0.83 g). Anal. Calcd for C₆₄H₄₈Br₂N₂Ni: C, 72.27; H, 4.55; N, 2.63; Found: C, 72.21; H, 4.59; N, 2.28. MALDI-TOF-MS (m/z): calcd for C₆₄H₄₈BrN₂Ni: 981.2354, found: 981.2040 [M-Br]⁺.



R₂=p-MePh

Yield 76 % (0.84 g). Anal. Calcd for C₆₆H₅₂Br₂N₂Ni: C, 72.62; H, 4.80; N, 2.57; Found: C, 72.41; H, 4.69; N, 2.18. MALDI-TOF-MS (m/z): calcd for C₆₆H₅₂BrN₂Ni: 1009.2667, found: 1009.2381 [M-Br]⁺.



R₃=p-tBuPh

Yield 81 % (0.95g). Anal. Calcd for C₇₂H₆₄Br₂N₂Ni: C, 73.55; H, 5.49; N, 2.38; Found: C, 73.21; H, 4.98; N, 2.42. MALDI-TOF-MS (m/z): calcd for C₇₂H₆₄BrN₂Ni: 1093.3606, found: 1093.3084 [M-Br]⁺.



Yield 45 % (0.53 g). Anal. Calcd for C₇₂H₅₂Br₂N₂Ni: C, 74.31; H, 4.50; N, 2.41; Found: C, 74.27; H, 4.41; N, 2.43. MALDI-TOF-MS (m/z): calcd for C₇₂H₅₂BrN₂Ni: 1081.2667, found: 1081.2284 [M-Br]⁺.

2.5 Procedure for ethylene polymerization by nickel complexes.

In a typical experiment, a 350 mL thick-walled glass pressure vessel was charged with the required amount of MAO (600 eq), toluene (48 mL) and a magnetic stirrer bar in the glovebox. The pressure vessel was connected to a high pressure polymerization line and the solution was degassed. The vessel was warmed to 30 °C by using an oil bath and allowed to equilibrate for 5 min. The nickel complex (1 μ mol) in CH₂Cl₂ (2 mL) was injected into the vessel with a syringe. With rapid stirring, the reactor was pressurized and maintained at 9.0 atm of ethylene. After 0.5 h, the vessel was vented and the polymer was precipitated in acidified methanol (methanol/HCl = 50:1) and dried at 50 °C for 24 h under vacuum. Polymer branching density was determined by ¹H NMR.³ B = 1000×2(I_{CH3})/3(I_{CH2+CH}+I_{CH3}). CH₃ (m, 0.77-0.95 ppm); CH₂ and CH (m, ca. 1.0-1.45 ppm).

2.6 Procedure for α-olefin polymerization by nickel complexes.

In a typical experiment, a 50 mL glass tube was charged with the required amount of MAO (600 eq) and a magnetic stirrer bar in the glovebox. Then toluene and α -olefin (18 mL) was added in tube. The tube was warmed to 30 °C by using an oil bath with rapid stirring and allowed to equilibrate for 5 min. The nickel complex (3 µmol) in CH₂Cl₂ (2 mL) was injected into the tube with a syringe. After 12 h, the vessel was vented and the polymer was precipitated in acidified methanol (methanol/HCl = 50:1) and dried at 50 °C for 24 h under vacuum. B = $1000 \times 2(I_{CH3})/3(I_{CH2+CH}+I_{CH3})$. CH₃ (m, 0.77-0.95 ppm); CH₂ and CH (m, ca. 1.0-1.45 ppm).

2.7 Procedure for propene homopolymerization and copolymerization with the nickel complexes.

In a typical procedure, a 350 mL thick-walled glass pressure vessel with a stirring bar was heated for 3 h to 150 °C under vacuum and then cooled to room temperature. The appropriate toluene solvent, MAO and other additives (like polar-monomer in copolymerization) were introduced into the glass reactor under an propene atmosphere, then a 2 mL solution of the nickel catalyst (5 µmol) in CH₂Cl₂ was syringed into the well-stirred solution and the total reaction volume was kept at 20 mL. The propene pressure was kept at a constant value of 6atm by continuous feeding of gaseous propene for 15 min. The polymerizations were terminated by the addition of a large amount of methanol after continuous stirring for desirable time. The resulting precipitated polymers were collected and treated by concentration and drying under vacuum at 40 °C to a constant weight. The polar-monomer incorporation (mol %) was calculated from ¹H NMR analysis, as was done before in previous studies of copolymers. B = $1000 \times 2(I_{CH3})/3(I_{CH2+CH}+I_{CH3})$. CH₃ (m, 0.77-0.95 ppm); CH₂ and CH (m, ca. 1.0-1.45 ppm). %3,1-insertions = $[(1-R)/(1+R)] \times 100$, where R= $(I_{CH3})/(I_{CH2})$. UA% $= 6I_{OMe}/[3(I_{CH2+CH}+I_{CH3})-12I_{OMe}] \times 100\%$. OMe (s, ca. 3.78-4.21 ppm); CH2 and CH (m, ca. 1.0-1.65 ppm); CH3 (m, 0.77-0.95 ppm). U-ol% = $6I_{CH2OH}/[2(I_{CH2+CH}+I_{CH3})-12]$ I_{CH2OH}]×100%. CH₂OH (t, ca. 3.36-3.73 ppm); CH₃ (m, 0.77-0.95 ppm); CH₂ and CH (m, ca. 1.0-1.65 ppm).

3.Spectra Data

3.1¹H, ¹³C NMR of Amine



Fig

ure S7.¹H NMR spectrum of Amine-Ph in CDCl₃.



Figure S8.¹³C NMR spectrum of Amine-Ph in CDCl₃.



Fi

gure **S9.**¹H NMR spectrum of **Amine-Tol** in CDCl₃.



Figure S10.¹³C NMR spectrum of Amine-Tol in CDCl₃.



ure S11.¹H NMR spectrum of Amine-TBu in CDCl₃.



Figure S12.¹³C NMR spectrum of Amine-TBu in CDCl₃.



re S13.¹H NMR spectrum of Amine-Np in CDCl₃.



Figure S14.¹³C NMR spectrum of Amine-Np in CDCl₃.

3.2 ¹H, ¹³C NMR of Ligand



Fig

ure S15. ¹H NMR spectrum of Ligand-1 in CDCl₃.



Figure S16. ¹³C NMR spectrum of Ligand-1 in CDCl₃.



Figure S17. ¹H NMR spectrum of Ligand-2 in CDCl₃.(*: H₂O)



Figure S18. ¹³C NMR spectrum of Ligand-2 in CDCl₃.



re S19. ¹H NMR spectrum of Ligand-3 in CDCl₃. (*: H₂O)



Figure S20. ¹³C NMR spectrum of Ligand-3 in CDCl₃.



Figure S21. ¹H NMR spectrum of Ligand-4 in CDCl₃. (*: CH₃OH)



Figure S22. ¹³C NMR spectrum of Ligand-4 in CDCl₃. (*: CH₃OH)

3.3 ¹H NMR of polymer and copolymer



re S23.¹H NMR spectrum of the polyethylene generated by complex Ni1 from table 1, entry 1. (in CDCl₂CDCl₂ at 120 °C)



Figure S24.¹H NMR spectrum of the polyethylene generated by complex **Ni1** from table 1, entry 3. (in CDCl₂CDCl₂ at 120 °C)



S25.¹H NMR spectrum of the polyethylene generated by complex Ni2 from table 1, entry 5. (in $CDCl_2CDCl_2$ at 120 °C)



Figure S26.¹H NMR spectrum of the polyethylene generated by complex **Ni3** from table 1, entry 9. (in CDCl₂CDCl₂ at 120 °C)



Figure S27.¹H NMR spectrum of the polyethylene generated by complex **Ni3** from table 1, entry 11. (in CDCl₂CDCl₂ at 120 °C)



Figure S28.¹H NMR spectrum of the polyethylene generated by complex **Ni4** from table 1, entry 14. (in CDCl₂CDCl₂ at 120 °C)



Figure S29.¹H NMR spectrum of the polyethylene generated by complex **Ni-Me** from table 1, entry 19. (in Tol-d⁸)



Figure S30.¹H NMR spectrum of the polyethylene generated by complex **Ni-1** from table 1, entry 4. (in Tol-d⁸)



Figure S31.¹H NMR spectrum of the polyethylene generated by complex **Ni-3** from table 1, entry 12. (in Tol-d⁸)



Figure S32.¹H NMR spectrum of copolymer generated by complex **Ni4** from table 2, entry 6. (in Tol-d⁸ at 100 °C)



Figure S33.¹H NMR spectrum of copolymer generated by complex **Ni4** from table 3, entry 8. (in CDCl₂CDCl₂ at 120 °C)





Figure S34. DSC of the polymer from table 1, entry 9.



Figure S35. DSC of the polymer from table 1, entry 10.



Figure S36. DSC of the polymer from table 1, entry 16.



Figure S37. DSC of the polymer from table 1, entry 17.



Figure S38. DSC of the polymer from table 1, entry 19.



Figure S39. DSC of the polymer from table 1, entry 6.



Figure S40. DSC of the polymer from table 1, entry 2.



Figure S41. DSC of the polymer from table 1, entry 4.



Figure S42. DSC of the polymer from table 1, entry 10.



Figure S43. DSC of the copolymer from table 3, entry 4.



Figure S44. DSC of the copolymer from table 3, entry 6.



Figure S45. DSC of the copolymer from table 3, entry 7.



Figure S46. DSC of the copolymer from table 3, entry 5.

3.5 GPC of polymer and copolymer



Generated by: GPC Thursday, November 10, 2016 12:58 PM Workbook: C:\Cirrus Workbooks\GPC20160331\GPC20160331.plw

Sample Details

 Sample Name: S-Ni-2
 Acquired: 11/10/2016 5:45:10 AM
 By Analyst: GPC
 Batch Name: 20161108-2

 Concentration: 0.10 mg/mllnjection Volume: 200.0 ul K of Sample: 14.1000
 Alpha of Sample: 0.7000

 Analysis Using Method: PS20160331
 0.7000

Calibration Used: 8/18/2016 4:29:40 PM

Calibration Type: Narrow StandardCurve Fit Used: 1K: 14.1000Alpha: 0.7000Calibration Curve: y = 13.094584 - 0.612462x^1High Limit MW RT: 10.50 minsLow Limit MW RT: 16.92 minsFlow Marker RT: 0.00 minsFRCF: 1.0000FRM Name:



Figure S47. GPC of the polymer from table 1, entry 7.



Figure S48. GPC of the polymer from table 1, entry 15.



Figure S49. GPC of the polymer from table 1, entry 14.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Thursday, October 26, 2017 9:09 AM Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

Sample Name: S-2

Acquired: 10/23/2017 10:18:08 PM By Analyst: HTGPC Batch Name: SXL Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000 Analysis Using Method: PS2016113001

FRM Name:

Calibration Used: 8/12/2017 3:25:40 PM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000 Calibration Curve: y = 13.269036 - 0.643042x^1 High Limit MW RT: 10.27 mins Low Limit MW RT: 16.37 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000



Cirrus GPC Version 3.4

10/26/2017 9:09 AM

Figure S50. GPC of the polymer from table 1, entry 16.



Figure S51. GPC of the polymer from table 2, entry 3.

Cirrus GPC Sample Injection Report Generated by: HTGPC Wednesday, January 18, 2017 9:25 AM Workbook: E:\Cirrus Workbooks\20161130\20161130.plw Sample Details Sample Name: S-PP-2 Acquired: 1/13/2017 7:19:47 AM By Analyst: HTGPC Batch Name: WZX Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000 Analysis Using Method: PS2016113001 Calibration Used: 11/30/2016 3:39:51 PM Alpha: 0.7000 Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Calibration Curve: y = 13.153976 - 0.624162x^1 High Limit MW RT: 10.47 mins Low Limit MW RT: 16.68 mins Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name: -35 1eB Hgh wما 40-Linit Linit -45--50--55-Response (mV) -60--65-4 -70-163 -75--80-1e2 -85 -00 1 4 10 14 15 16 17 2 3 19 20 21 22 23 24 27 28 29 30 31 25 28 12 9 ntion Time Distribution Plots 1.1 100 -90 09-- 80 08-70 ۵7--60 Mpolb/wb 06-% Ht -50 05-40 04--30 0.3-20 0.2 10 01 0-1110 100000 1-11-11-11-11-0 10000 MW MW Averages Peak No Mp Mn Mw Mz Mz+1 Mv PD 1 439769 220115 476188 788684 1075397 434160 2.16336 Processed Peaks

Peak No Name Start RT Max RT End RT Pk Height % Height Area % Area (mins) (mins) (mV) (mV.secs) (mins) 891.81 100 1 12.03 14.30 9.24567 10.73 100

Figure S52. GPC of the polymer from table 2, entry 4.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Wednesday, January 18, 2017 9:25 AM Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

Sample Name: S-PP-3

Acquired: 1/13/2017 7:52:39 AM By Analyst: HTGPC Batch Name: WZX Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000 Analysis Using Method: PS2016113001

Calibration Used: 11/30/2016 3:39:51 PM

K: 14.1000 Alpha: 0.7000 Calibration Type: Narrow Standard Curve Fit Used: 1 Calibration Curve: y = 13.153976 - 0.624162x^1 Low Limit MW RT: 16.68 mins High Limit MW RT: 10.47 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Figure S53. GPC of the copolymer from table 2, entry 5.



Figure S54. GPC of the copolymer from table 2, entry 6.



Figure S55. GPC of the copolymer from table 2, entry 7.

Figure S56. GPC of the copolymer from table 2, entry 8.

4. Stress-strain Curves of polyethylene

Figure S57. Stress-strain curves of polyethylene generated using complexes Ni1-4 at 30°C.

Figure S58. Stress-strain curves of polyethylene generated using complexes Ni1-4 at 50°C.

Figure S59. Stress-strain curves of polyethylene generated using complexes Ni1-4 at 70°C.

Figure S60. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni-Me** at 50°C. (sample was cyclically tested for 10 cycles with a maximum strain of 300 %)

Figure S61. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni-Me** at 70°C. (sample was cyclically tested for 10 cycles with a maximum strain of 300 %)

Figure S62. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni1** at 30°C. (sample was cyclically tested for 10 cycles with a maximum strain of 300 %)

Figure S63. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni1** at 50°C. (sample was cyclically tested for 10 cycles with a maximum strain of 300 %)

Figure S64. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni1** at 70°C. (sample was cyclically tested for 10 cycles with a maximum strain of 300 %)

Figure S65. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni2** at 30°C. (sample was cyclically tested for 10 cycles with a maximum strain of 300 %)

Figure S66. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni2** at 50°C. (sample was cyclically tested for 10 cycles with a maximum strain of 300 %)

Figure S67. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni2** at 70°C. (sample was cyclically tested for 10 cycles with a maximum strain of 300 %)

Figure S68. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni3** at 30°C. (sample was cyclically tested for 10 cycles with a maximum strain of 300 %)

Figure S69. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni3** at 50°C. (sample was cyclically tested for 10 cycles with a maximum strain of 300 %)

Figure S70. Cyclic Stress–strain curves of polyethylene generated using complexes **Ni3** at 70°C. (sample was cyclically tested for 3 cycles with a maximum strain of 300 %)

5. X-Ray Crystallography of complex Ni2.

Entry	Ni2
Formula	C67 H54 Br2 Cl2 N2 Ni
Formula weight	1176.51
Temperature[K]	298(2)
λ (Mo-K α)[Å]	0.71073
Crystal system	Monoclinic
Space group	P21/c
a[Å]	17.9769(15)
b[Å]	12.1378(11)
c[Å]	29.0552(18)
$\alpha[^{\circ}]$	90.00
β[°]	116.588(4)
γ[°]	90.00
Volume[Å ³]	5669.4(8)
Z	4
$D(calc)[g \cdot cm^{-3}]$	1.378
μ[mm ⁻¹]	1.889
F(000)	2408
θ min-max (°)	2.699 -23.876
h	-21
k	-14
l	-34→34
Reflections collected	28258
Reflections unique	10011
R(int)	0.0551
Data / restraints / parameters	10011 /0 / 699
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0450$
	$wR_2 = 0.0921$
R indices (all data)	$R_1 = 0.1038$
it malees (un autu)	$wR_2 = 0.1073$
GOF on F ²	0.935

6. X-Ray Crystallography of complex Ni1.

Selected bond distances (Å) and angles (deg): Ni1-Br1 2.3339(16), Ni1-Br2 2.3174(17), Ni1-N1 2.059(7), Ni1-N2 2.032(7), Br1-Ni1-Br2 110.79(6), N2-Ni1-Br2 106.8(2), N1-Ni1-Br1 103.77(19), N1-Ni1-N2 82.9(3).

Entry	Ni1
Formula	C64 H48 Br2 N2 Ni
Formula weight	1063.54
Temperature[K]	298(2)
λ (Mo-K α)[Å]	0.71073
Crystal system	Rhombohedral
Space group	R3c
a[Å]	33.739(3)
b[Å]	33.739(3)
c[Å]	26.116(5)
α[°]	90.00
β[°]	90.00
γ[°]	120.00
Volume[Å ³]	25746(8)
Z	18
$D(calc)[g \cdot cm^{-3}]$	1.235
$\mu[mm^{-1}]$	1.774
F(000)	9792
θ min-max (°)	2.415 -17.479
h	- 36→40
k	-40→22
l	- 30→30
Reflections collected	40142
Reflections unique	10061
R(int)	0.1092
Data / restraints / parameters	10061 /1 / 670
Final R indices [I>2o(I)]	$R_1 = 0.0711$
	$wR_2 = 0.1487$
D indians (all data)	$R_1 = 0.1487$
it indices (an data)	$wR_2 = 0.1702$
GOF on F ²	1.036

7. Reference

1. Wang, Q.; Dong, X.; Xiao, T.; Zhou, Lei. PhI(OAc)₂-Mediated Synthesis of 6-(Trifluoromethyl)phenanthridines by Oxidative Cyclization of 2-Isocyanobiphenyls with CF₃SiMe₃ under Metal-Free Conditions. *Org. Lett.* **2013**, *15*, 4846-4849.

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3. Daugulis, O.; Brookhart, M.; White, P. S. Phosphinidine-Palladium Complexes for the Polymerization and Oligomerization of Ethylene. *Organometallics* **2002**, *21*, 5935.