Supporting Information:

A Thermally Robust Amine-Imine Nickel Catalyst Precursor for Living Polymerization of Ethylene above Room Temperature

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1. Experimental Section

General Procedures

All manipulations involving air- and moisture sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard vacuum-line, Schlenk, or glovebox techniques.

Materials

Dichloromethane was distilled from CaH_2 under nitrogen, and toluene and hexane from Na/K alloy. Butane-2,3-dione, aniline, 2,6-dimethylaniline, 2,6-diisopropylaniline, and $(DME)NiBr_2$ were purchased from Aldrich and used as received. MMAO (7 wt. % Al in heptane) was purchased from Akzo-Nobel and used as received. Diethylaluminium chloride (DEAC, 1.0 M in hexane), trimethylaluminium (TMA，2.0 M in toluene) were purchased from Acros. Ethylene (99.99%) was purified by passing through Agilent moisture and oxygen traps. Hexene was distilled from CaH_2 under nitrogen prior to use. Other commercially available reagents were purchased and used without purification.

Measurements

Elemental analyses were performed on a Vario EL microanalyzer. Mass spectra were obtained using electro spray ionization (ESI) LCMS-2010A (for ligands) or fast atom bombardment (FAB) LCQ DECA XP (for nickel complexes). NMR spectra of organic compounds were carried out on a Bruker 500 MHz instrument in $CDCl_3$ using TMS as a reference. ^{13}C NMR spectra of polymers were carried out on a Bruker 500

MHz at 120 °C *o*-$C_6D_4Cl_2$ solution using 30 ppm for main chain of PE (-$(CH_2)_n$-) as a reference. DSC analyses were conducted with a Perkin Elmer DCS-7 system. The DSC curves were recorded at second heating curves from -80 °C to 140 °C at a heating rate of 10 °C/min and a cooling rate of 10 °C/min. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution ($PDI = M_w/M_n$) of the polymers at 150 °C were performed on a high-temperature chromatography, PL-GPC 220 instrument equipped with a triple detection array, including a differential refractive index (RI) detector, a two-angle light scattering (LS) detector, and a four-bridge capillary viscometer. The detection angles of the LS detector were 15 and 90, and the laser wavelength was 658 nm. 1,2,4-Trichlorobenzene (TCB) was used as the eluent at a flow rate of 1.0 mL/min.

Crystal Structure Determination.

The crystals were mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer.[1] Data obtained with the ω-2θ scan mode was collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K_α radiation (λ= 0.71073 Å) at 293 K. The structures were solved using direct methods, while further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package.[2,3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

High pressure polymerization of ethylene

A mechanically stirred 100 mL Parr reactor was heated to 150 °C for 2h under vacuum and then cooled to room temperature. The autoclave was pressurized to 100 psi of ethylene and vented three times. The autoclave was then charged with 28 mL solution of MMAO in toluene under 150 psi of ethylene at initialization temperature. The system was maintained by continuously stirring for 5 min, and then 2 mL solution of nickel complex in CH_2Cl_2 was charged into the autoclave under 150 psi of ethylene. The ethylene pressure was raised to the specified value (300 psi), and the reaction was carried out for a certain time. Polymerization was terminated by addition of acidic methanol after releasing ethylene pressure. The resulting precipitated polymers were collected and treated by filtering, washing with methanol several times, and drying under vacuum at 40 °C to a constant weight.

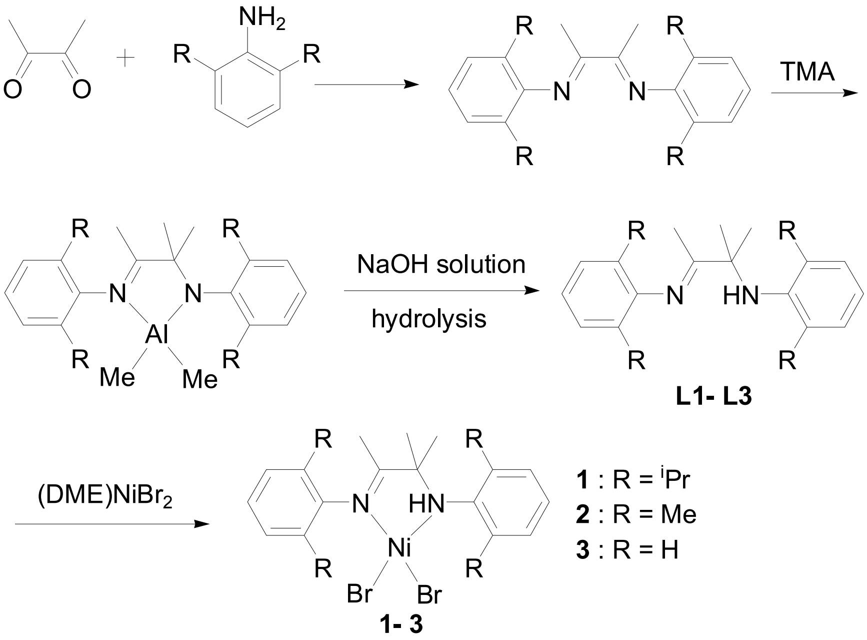
Atmosphere pressure polymerization of ethylene

In a typical procedure, a round-bottom Schlenk flask with stirring bar was heated 3h to 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 15 psi of ethylene and vented three times. The appropriate alkylaluminium compound as cocatalyst was introduced into the glass reactor under 3 psi of ethylene. The system was maintained by continuously stirring for 5 min, and then toluene and 2 mL solution of nickel complex in CH_2Cl_2 were syringed into the well-stirred solution in order, and the total reaction volume was kept at 30 mL. The ethylene pressure was kept constant value of 3 psi by continuous feeding of gaseous ethylene throughout the reaction. Except for 0 °C maintained with ice-water bath, the other reaction temperatures were controlled with an external oil bath in polymerization experiments. The polymerizations were terminated by the addition of 200 mL of acidic methanol (95:5 ethanol/HCl) after continuously stirring for an appropriate period. The resulting precipitated polymers were collected and treated by filtration, washing with methanol several times, and drying in vacuum at 40 °C to a constant weight.

Synthesis of PE-*b*-PH block copolymers

A round-bottom Schlenk flask with stirring bar was heated 3 h to 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 15 psi of ethylene and vented three times. The appropriate alkylaluminium compound as cocatalyst was introduced into the glass reactor under 3 psi of ethylene. The system was maintained by continuously stirring for 5 min, and then toluene and 2 mL solution of nickel complex in CH_2Cl_2 were syringed into the well-stirred solution in order, and the total reaction volume was kept at 30 mL. The ethylene pressure was kept constant value of 3 psi by continuous feeding of gaseous ethylene throughout the reaction. The reaction temperatures were controlled with an external oil bath in polymerization experiments. After ethylene polymerization of 15 minutes, the ethylene feed was stopped, and the reaction flask was charged with N_2 and vented for three times. Then 2 mL of freshly distilled 1-hexene was syringed into the reactor and the mixture was stirred for 6 h. The polymerizations were terminated by the addition of 200 mL of acidic methanol (95:5 ethanol/HCl) after continuously stirring for an appropriate period. The resulting precipitated polymers were collected and treated by filtration, washing with methanol several times, and drying in vacuum at 40 °C to a constant weight.

Scheme S1 Synthesis route of amine-imine nickel complexes



Synthesis of α-diimine compounds

α-Diimine compounds were prepared according to the reported procedure.[4,5] To a solution of butane-2,3-dione (1.72 g, 20 mmol) in 50 mL ethanol was added a solution of 2 equivalents substituted anilines in ethanol in the presence of formic acid. The solution was allowed to stir for 5h at 50 °C, and cooled to -20 °C overnight. The yellow crystalline solids were collected on a frit after washing with cool ethanol in good isolated yield.

Ar-N=C(Me)-(Me)C=N-Ar (Ar = 2,6-diisopropylphenyl): ^{1}H NMR (CDCl$_3$, 500 MHz): 7.19-7.10 (m, 6H, Ph), 2.72 (septet, 4H, CH), 2.10(s, 6H, CH$_3$), 1.19 (dd, 24H,

CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): 168.15, 146.16, 135.03, 123.73, 122.99, 28.51, 23.00, 22.68, 16.57. Anal. Calcd for $C_{28}H_{40}N_2$: C, 83.11; H, 9.97; N, 6.92. Found: C, 83.05; H, 9.93; N, 7.00.

Ar-N=C(Me)-(Me)C=N-Ar (Ar = 2,6-dimethylphenyl): ^1H NMR ($CDCl_3$, 500 MHz): 7.08 (d, 4H, Ph), 6.95 (t, 2H, Ph), 2.05 (s, 6H, CH_3), 2.04(s, 12H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): 167.96, 148.29, 127.86, 124.52, 123.18, 17.71, 15.73. Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 82.26; H, 8.20; N, 9.51.

Ar-N=C(Me)-(Me)C=N-Ar (Ar = phenyl): ^1H NMR ($CDCl_3$, 500 MHz): 7.37(t, 4H, Ph), 7.12(t, 2H, Ph), 6.79(d, 4H, Ph), 2.16(s, 6H, Me). ^{13}C NMR ($CDCl_3$, 125 MHz): 168.08, 150.85, 128.85, 123.68, 118.61, 15.23. Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.33; H, 6.82; N, 11.85. Found: C, 81.20; H, 6.83; N, 11.92.

Synthesis of amine-imine ligands

Ar-N=C(Me)-(Me)$_2$C-NH-Ar (Ar = 2,6-diisopropylphenyl) (L1): Under nitrogen atmosphere, the solution of α-diimine compounds Ar-N=C(Me)-(Me)C=N-Ar (Ar = 2,6-diisopropylphenyl) (4.04 g, 10 mmol) in toluene (50 mL) was introduced into a 100 mL Schlenk flask, and then trimethylaluminum (TMA) (8 mL, 2.0 M in toluene) was injected slowly through a syringe at room temperature. The reaction was heated to reflux overnight. After the solution was cooled to 0 °C using ice/water bath, the reaction mixture was carefully hydrolyzed with 5% aqueous NaOH solution. The organic layer was separated and dried over Na_2SO_4, and the solvent was evaporated off. The desired product was obtained as viscous oil. The resulting yellow oil was dissolved in hot toluene/hexane solvent and then cooled slowly to -20 °C to give white crystals in 95% yield (4.00 g). ^{1}H NMR (CDCl$_3$, 500 MHz): 7.16-7.06 (m, 6H, Ph), 4.34 (s, 1H, NH), 3.54 (septet, 2H, CH), 2.82 (septet, 2H, CH), 1.88 (s, 3H, CH$_3$), 1.36 (s, 6H, CH$_3$), 1.21-1.18 (m, 24H, CH$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): 176.46, 146.56, 145.96, 140.15, 136.25, 124.50, 123.08, 122.99, 61.73, 28.37, 27.85, 27.08, 24.18, 23.50, 23.19, 16.39. Anal. Calcd for $C_{29}H_{44}N_2$: C, 82.80; H, 10.54; N, 6.66. Found: C, 82.70; H, 10.44; N, 6.84. ESI-MS (*m/z*): 423, 422, 421 [M$^+$+1].

Ar-N=C(Me)-(Me)$_2$C-NH-Ar (Ar = 2,6-dimethylphenyl) (L2) Following the same procedure used for **L1**, the reaction of Ar-N=C(Me)-(Me)C=N-Ar (Ar = 2,6-dimethylphenyl) (2.92 g, 10 mmol) and TMA (8 mL, 2.0 M in toluene) gave ligand **L2** as white solid in 92% yield (2.82 g). ^{1}H NMR (CDCl$_3$, 500 MHz): 7.03 (t, 4H, Ph), 6.90 (t, 2H, Ph), 4.48 (s, 1H, NH), 2.37 (s, 6H, CH$_3$), 2.05 (s, 6H, CH$_3$), 1.87 (s, 3H, CH$_3$), 1.43 (s, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): 176.53, 148.28, 133.99, 128.46, 128.06, 125.69, 122.97, 122.67, 62.08, 27.22, 20.62, 18.18, 15.73. Anal. Calcd for $C_{21}H_{28}N_2$: C, 81.77; H, 9.15; N, 9.08. Found: C, 81.70; H, 9.23; N, 9.05 . ESI-MS (*m/z*): 311, 310, 309 [M$^+$+1].

Ar-N=C(Me)-(Me)$_2$C-NH-Ar (Ar = phenyl) (L3): Following the same procedure used for **L1**, the reaction of Ar-N=C(Me)-(Me)C=N-Ar (Ar = phenyl) (2.36 g, 10 mmol) and TMA (8 mL, 2.0 M in toluene) gave ligand **L3** as white solid in 94% yield (2.37 g). ^{1}H NMR (CDCl$_3$, 500 MHz): 7.32 (t, 2H, Ph), 7.18 (t, 2H, Ph), 7.05 (t, 1H, Ph), 6.73-6.67 (m, 5H, Ph), 4.12 (s, 1H, NH), 1.82 (s, 3H, CH$_3$), 1.58 (s, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): 176.95, 151.54, 146.18, 129.09, 128.96, 123.04, 118.73, 117.39, 114.14, 59.37, 26.32, 14.89. Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.96; H, 7.86; N, 11.25. ESI-MS (*m/z*): 255, 254, 253 [M^{+}+1].

Synthesis of amine-imine nickel complexes

[Ar-N=C(Me)-(Me)$_2$C-NH-Ar]NiBr$_2$ (Ar = 2,6-diisopropylphenyl) 1: To a stirring suspension of (DME)NiBr$_2$ (DME = 1,2-dimethoxyethane) (337 mg, 1.1 mmol) in 30 mL dichloromethane, ligand **L1** Ar-N=C(Me)-(Me)$_2$C-NH-Ar (Ar = 2,6-diisopropylphenyl) (420 mg, 1 mmol), in 10 mL dichloromethane, was added at room temperature. Shortly after the addition of the ligand, the solution began to turn brown. The suspension was allowed to stir for an additional 5 hours at room temperature. The solution was filtered through celite, and the solvent of the filtrate was removed in vacuum. The residue was recrystallized from CH_2Cl_2-hexane to give pure pale powder in 68% yield (432 mg). Single crystals were grown from a dichloromethane solution at -35 °C. Anal. Calcd for $C_{29}H_{44}Br_2N_2Ni$: C, 54.49; H, 6.94; N, 4.38. Found: C, 54.40; H, 6.78; N, 4.35. FAB-MS (*m/z*): 560, 559, 558 [M-2Br]$^{+}$; 422, 421 [ligand]$^{+}$. 219, 218 [NiBr$_2$]$^{+}$.

[Ar-N=C(Me)-(Me)$_2$C-NH-Ar]NiBr$_2$ (Ar = 2,6-methylphenyl) 2: Following the above procedure, the reaction of (DME)NiBr$_2$ (337 mg, 1.1 mmol) and **L2** (308 mg, 1mmol) gave 2 in 60% yield (314 mg). Anal. Calcd for $C_{21}H_{28}Br_2N_2Ni$: C, 47.86; H, 5.36; N, 5.32. Found: C, 47.90; H, 5.43; N, 5.12. FAB-MS (*m/z*): 367, 366, 365 [M-2Br]$^{+}$; 310, 309 [ligand]$^{+}$. 219, 217 [NiBr$_2$]$^{+}$.

[Ar-N=C(Me)-(Me)$_2$C-NH-Ar]NiBr$_2$ (Ar = phenyl) 3: Following the above procedure, the reaction of (DME)NiBr$_2$ (337 mg, 1.1 mmol) and **L3** (252mg, 1mmol) gave **3** in 54% yield (254 mg). Anal. Calcd for $C_{17}H_{20}Br_2N_2Ni$: C, 43.36; H, 4.28; N, 5.95. Found: C, 43.41; H, 4.37; N, 5.65. FAB-MS (*m*/*z*): 393, 391, 389 $[M\text{-}Br]^+$; 312, 310 $[M\text{-}2Br]^+$; 253 $[ligand]^+$; 219, 217 $[NiBr_2]^+$.

2. Crystallographic Data for Complexes 1, 2 and 3

Table S1. Crystal data and structure refinement for complexes **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{29}H_{44}Br_2N_2Ni$	$C_{21}H_{29}Br_2N_2Ni$	$C_{17}H_{20}Br_2N_2Ni$
Formula weight	639.19	527.99	470.88
Crystal system	Monoclinic	Orthorhombic	Monoclinic
space group	P2(1)/n	Pnma	P2(1)/c
a (Å)	10.803(2)	15.230(5)	12.487(4)
b (Å)	20.726(5)	17.385(5)	8.246(2)
c (Å)	13.844(3)	8.388(3)	18.729(6)
α (deg)	90	90	90
β (deg)	101.466(4)	90	101.359(5)
γ (deg)	90	90	90
Volume ($Å^3$)	3037.8(12)	2220.9(11)	1890.8(10)
Z	4	4	4
D(calc.) (g/cm^3)	1.398	1.579	1.654
F(000)	1320	1068	936
Crystal size (mm)	0.32 x 0.25 x 0.22	0.41 x 0.25 x 0.21	0.45 x 0.32 x 0.24
θ range (deg)	1.97 to 23.27	2.34 to 26.00	2.22 to 26.00
Index ranges	-11<=h<=11	-18<=h<=18	-15<=h<=15,
	-17<=k<=22	-21<=k<=14	-9<=k<=10
	-15<=l<=15	-10<=l<=10	-22<=l<=23
Reflections collected / unique	19080 / 4116	13452 / 2249	14392 / 3697
	$R_{int} = 0.0535$	$R_{int} = 0.0807$	$R_{int} = 0.0940$
Data completeness	94.4 %	99.5 %	99.3 %
Transmission (max/min)	0.5316 and 0.4193	0.4531 and 0.2610	0.3655 and 0.2010
Data / restraints / parameters	4116 / 1 / 335	2249 / 55 / 141	3697 / 0 / 207
Goodness-of-fit on F^2	1.016	0.986	0.932
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0417$;	$R_1 = 0.0408$	$R_1 = 0.0510$
	$wR_2 = 0.1039$	$wR_2 = 0.0988$	$wR_2 = 0.1235$
R indices (all data)	$R_1 = 0.0692$	$R_1 = 0.0765$	$R_1 = 0.1173$
	$wR_2 = 0.1188$	$wR_2 = 0.1113$	$wR_2 = 0.1470$
Largest diff. peak and hole (e A^{-3})	0.749 and -0.724	0.675 and -0.867	0.565 and -0.432

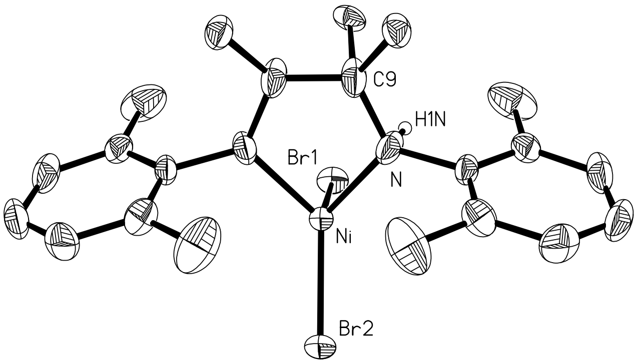


Figure S1. Crystal structure of complex **2** with the thermal ellipsoids shown at 30% probability level. The hydrogen atoms except H(1N) are omitted for clarity. (The structure is position disordered due to the existence of 2/m symmetry in the space group)

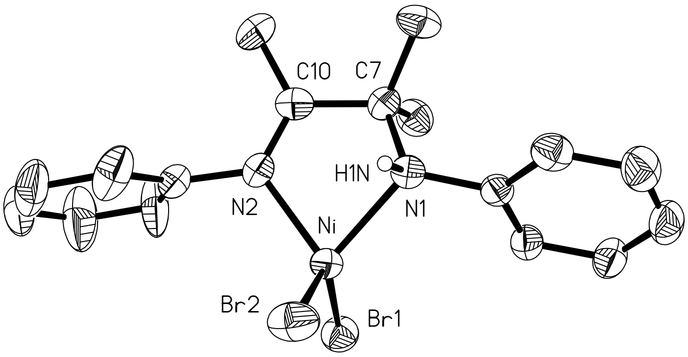


Figure S2. Crystal structure of complex **3** with the thermal ellipsoids shown at 30% probability level. The hydrogen atoms except H(1N) are omitted for clarity.

3. Characterization of Selected Polymer Samples

Table S2. Ethylene polymerization results at different Al/Ni ratios using **1**/Et_2AlCl system at 35 ˚C [a]

Al/Ni	Yield (g)	Activity (kg PE (mol Ni)$^{-1}$h^{-1})	M_n[b] (kg mol^{-1})	PDI[b]	Br[c] (/1000C)	T_g[d] (°C)
50	0.392	38.2	54	1.03	176	-54
100	0.377	37.7	52	1.04	178	-53
200	0.373	37.3	50	1.04	180	-55
500	0.360	36.8	50	1.02	182	-54

[a] Polymerization conditions: 10 µmol of nickel, 60 min, 3 psig, 28 mL toluene and 2 mL CH_2Cl_2, activators: Et_2AlCl, temperature: 35 ˚C. [b] M_n and PDI were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 ˚C using a light scattering detector. [c] Branching density, branches per 1000 carbon atoms determined by ^{13}C NMR spectroscopy. [d] Determined by DSC.

Table S3. Ethylene living polymerization results at different times

	1/MMAO at 20 ˚C			**1**/Et_2AlCl at 35 ˚C		
Reaction time (min)	Yield (g)	M_n-LS (kg/mol)	PDI-LS	Yield (g)	M_n-LS (kg/mol)	PDI-LS
8	0.063	14.8	1.08	0.050	7.2	1.05
15	0.145	28.6	1.04	0.094	14.0	1.03
30	0.302	50.2	1.03	0.194	28.9	1.02
60	0.582	106.9	1.02	0.373	50.4	1.04
120	1.117	200.8	1.04	0.747	95.5	1.05

To obtain absolute number-average molecular weights (M_n), a light scattering detector was used in GPC measurement.

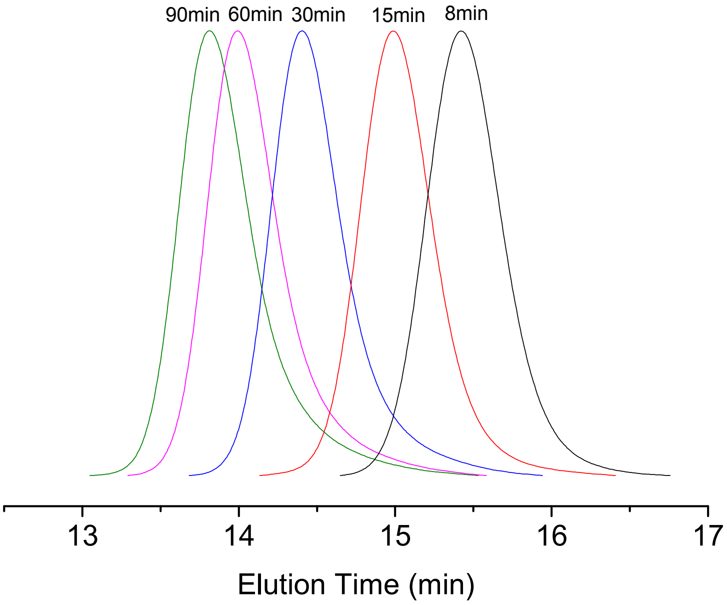


Figure S3. GPC traces of PE obtained by amine-imine nickel **1**/Et_2AlCl at different time intervals at 50 ˚C.

Table S4. GPC results

t(min)	M_n (kg/mol)	PDI
8	6.7	1.03
15	12.5	1.02
30	27.7	1.04
60	48.4	1.08
90	60.7	1.15

The GPC curves at 60min and 90 min exhibit the tail peaks in the low-molecular-weight region, indicating that a portion of deactivation of nickel species occurs at 50 ˚C.

Table S5. Synthesis and characterization of block copolymers (PE-*b*-PH)

Catalyst	t_1/Tp (ethylene)	t_2/Tp (1-hexene)	Yield (g)	M_n-LS (kg/mol)	PDI-LS
1/MMAO	15min/20 °C	-	0.145	28.6	1.04
1/MMAO	15min/20 °C	6h/20 °C	0.205	38.9	1.05
1/Et_2AlCl	15min/35 °C	-	0.094	14.0	1.03
1/Et_2AlCl	15min/35 °C	6h/35 °C	0.173	25.1	1.04

Polymerization conditions: 10 μmol of nickel, Al/Ni = 200, 3 psig of ethylene pressure, 28 mL toluene and 2 mL CH_2Cl_2

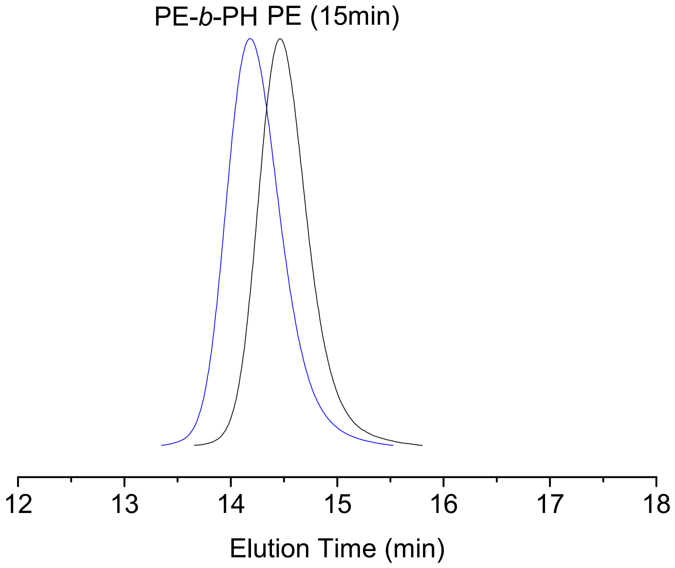


Figure S4. GPC traces of PE block and PE-*b*-PH block copolymer obtained by amine-imine nickel **1**/MMAO at 20 ˚C.

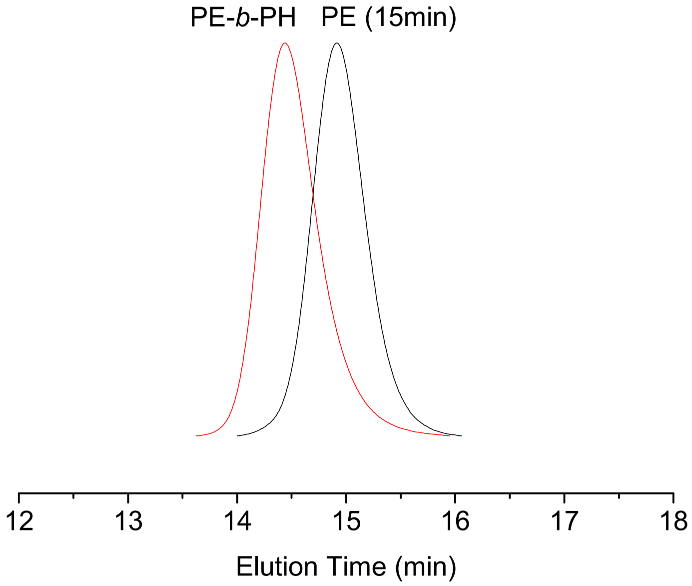


Figure S5. GPC traces of PE block and PE-*b*-PH block copolymer obtained by amine-imine nickel **1**/Et_2AlCl at 35 ˚C.

Table S6. Branched chain distributions of polyethylenes obtained with amine-imine nickel catalyst precursors

			Branched chain (/1000C)						Branches
entry	catalyst	T(°C)	Me	Et	Pr	Bu	Pe	Lg	(/1000C)
8	**1**/MMAO	0	104	5	2	2	2	8	123
1	**1**/MMAO	20	111	7	2	6	6	20	153
4	**1**/MMAO	20	108	2	1	3	3	2	119
9	**1**/MMAO	35	117	9	4	6	4	28	168
10	**1**/MMAO	50	108	11	5	7	5	39	175
5	Al/Ni=50	20	108	5	6	4	3	22	148
6	Al/Ni=100	20	112	5	2	5	5	23	152
7	Al/Ni=500	20	113	7	4	3	3	27	157
11	**1**/Et_2AlCl	20	133	8	1	5	2	22	171
12	**1**/Et_2AlCl	35	137	5	3	4	4	27	180
13	**1**/Et_2AlCl	50	134	8	4	6	5	28	185
14	**1**/Et_2AlCl	75	130	12	6	8	7	31	194
2	**2**/MMAO	20	138	15	7	10	6	37	213
3	**3**/MMAO	20	82	28	4	10	3	48	175

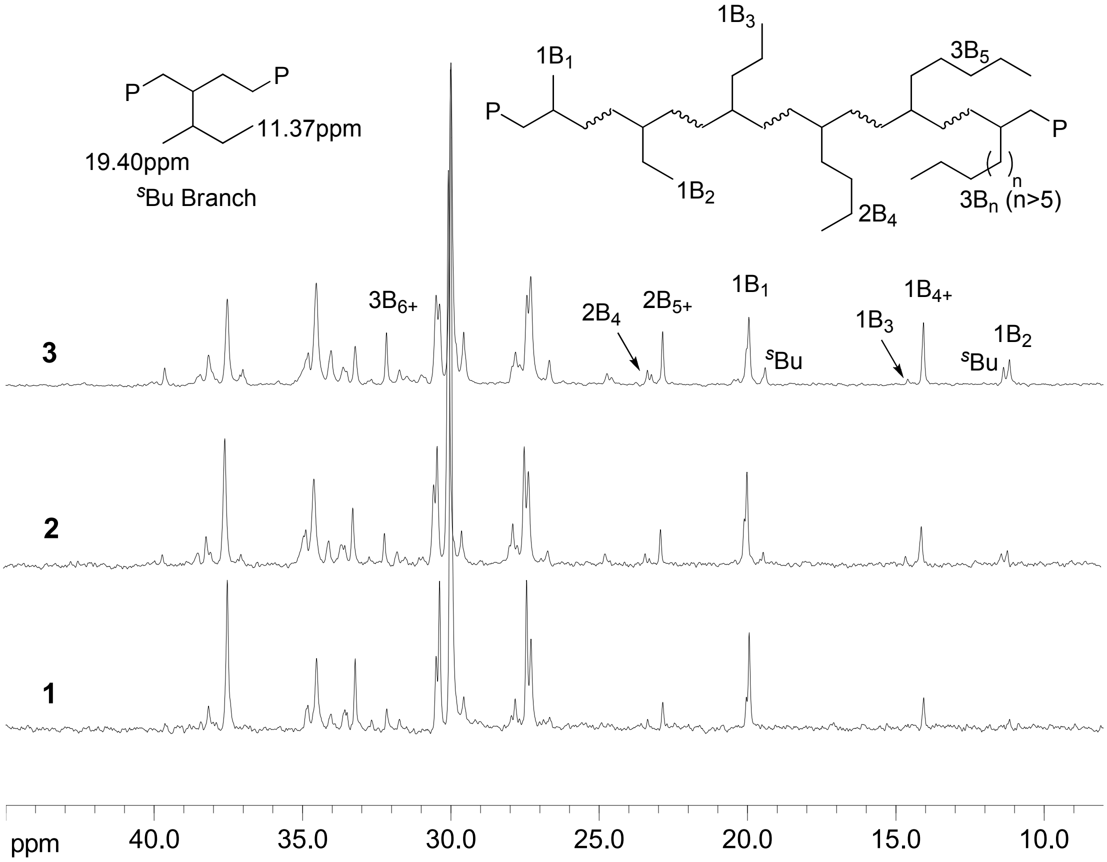


Figure S6. ^{13}C NMR spectra of the polyethylenes produced by **1-3**/MMAO at 20 ˚C (Table 1, entries 1-3)

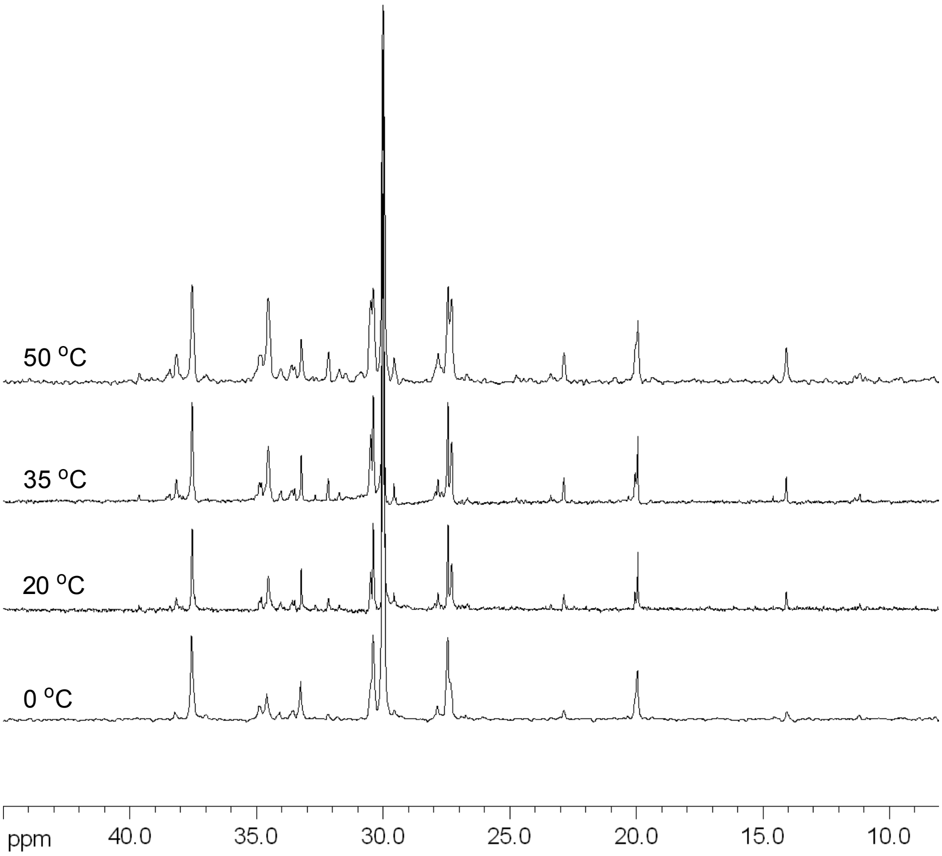


Figure S7. ^{13}C NMR spectra of the polyethylenes produced by **1**/MMAO at different temperatures (Table 1, entries 1, 8-10)

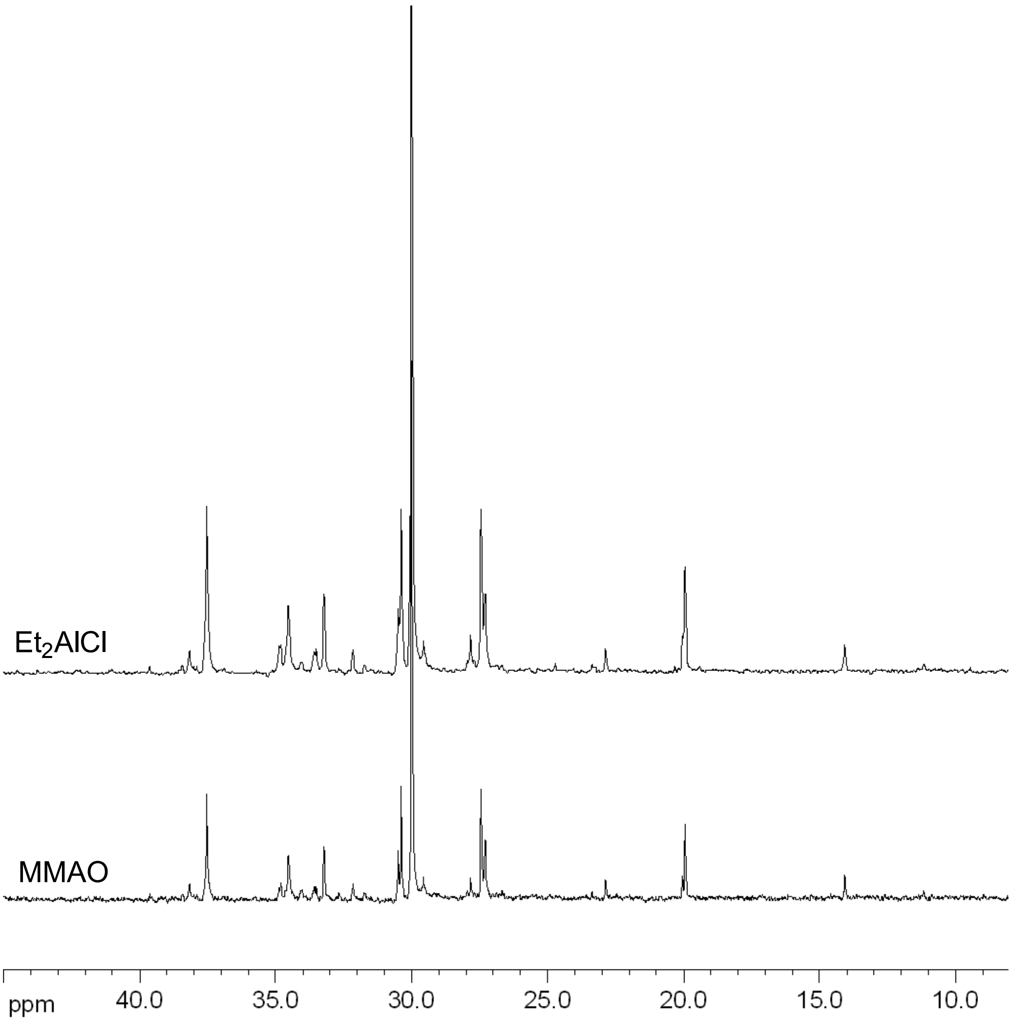


Figure S8. ^{13}C NMR spectra of the polyethylenes produced by **1**/MMAO and **1**/Et_2AlCl (Table 1, entries 1 and 11)

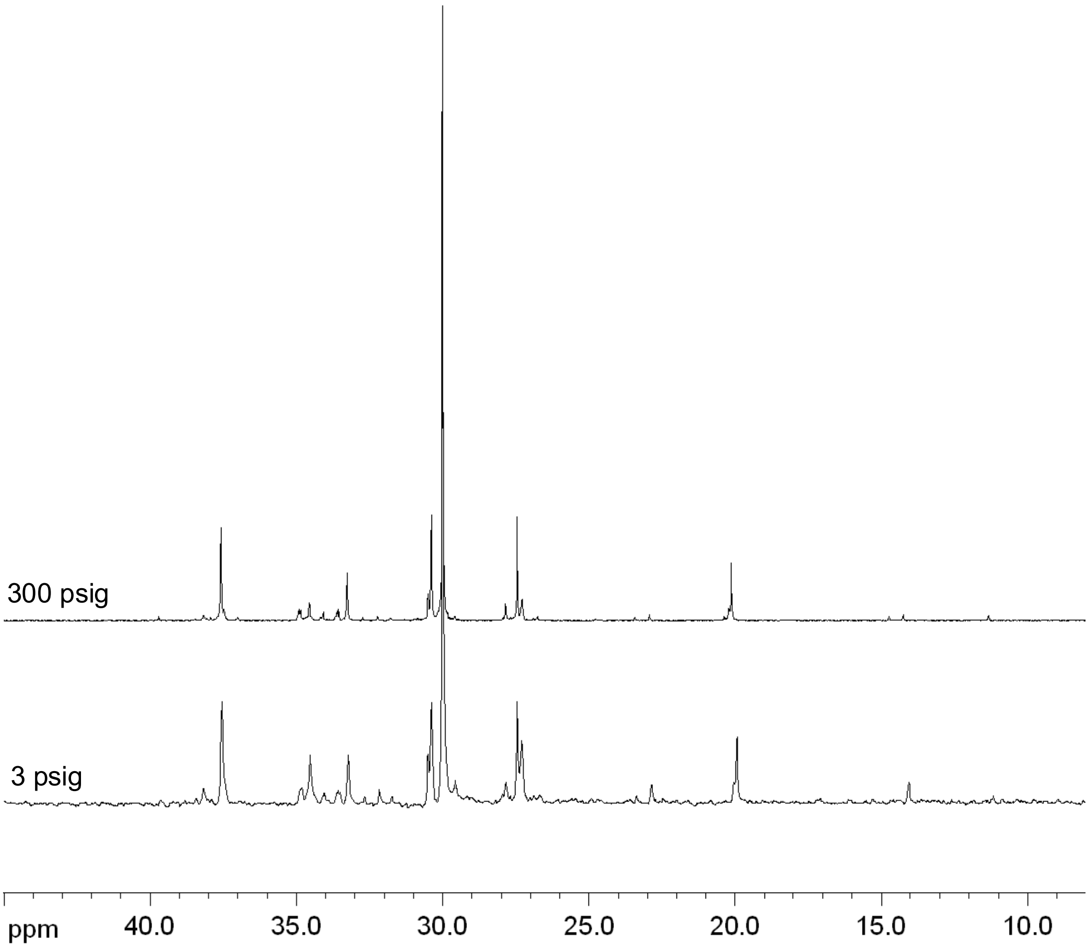


Figure S9. ^{13}C NMR spectra of the polyethylenes produced by **1**/MMAO at different ethylene pressures (Table 1, entries 1 and 4)

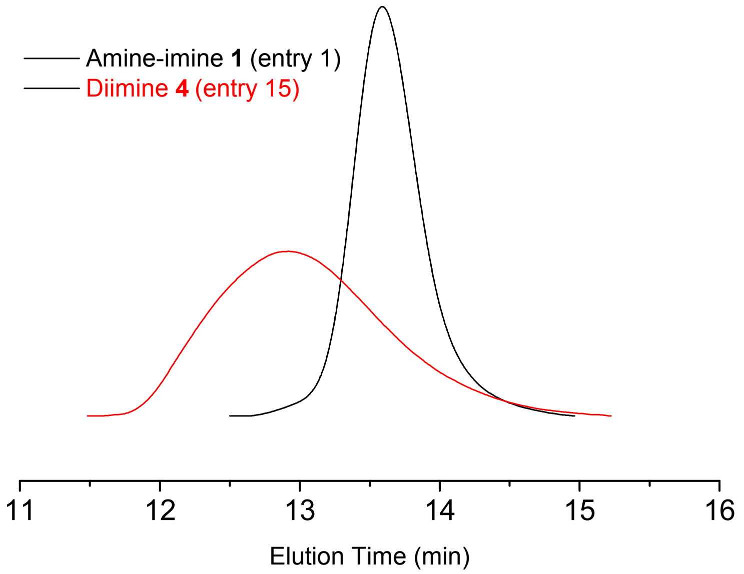


Figure S10. GPC traces of the polyethylenes obtained by amine-imine nickel **1**/MMAO and α-diimine nickel **4**/MMAO (Table 1, entries 1, 15).

4. ^{1}H NMR of Amine-Imine Ligands

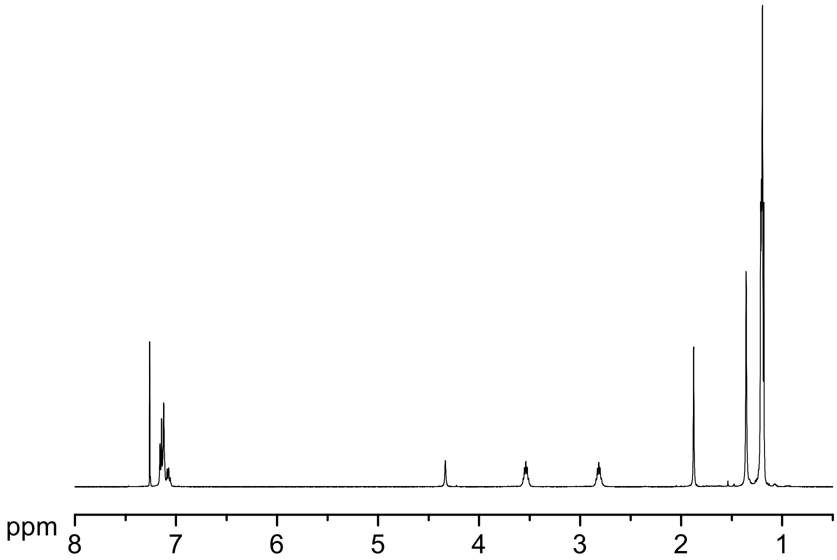


Figure S11. ^{1}H NMR of ligand **L1**

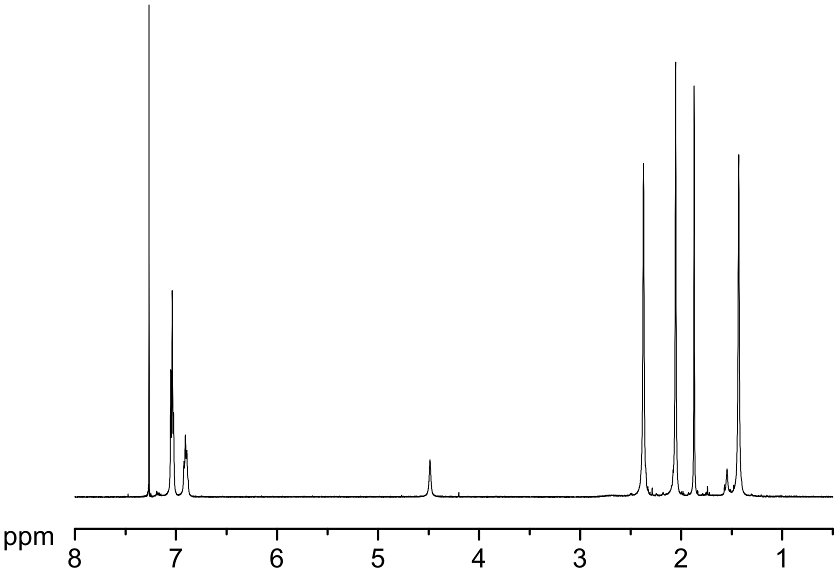


Figure S12. ^{1}H NMR of ligand **L2**

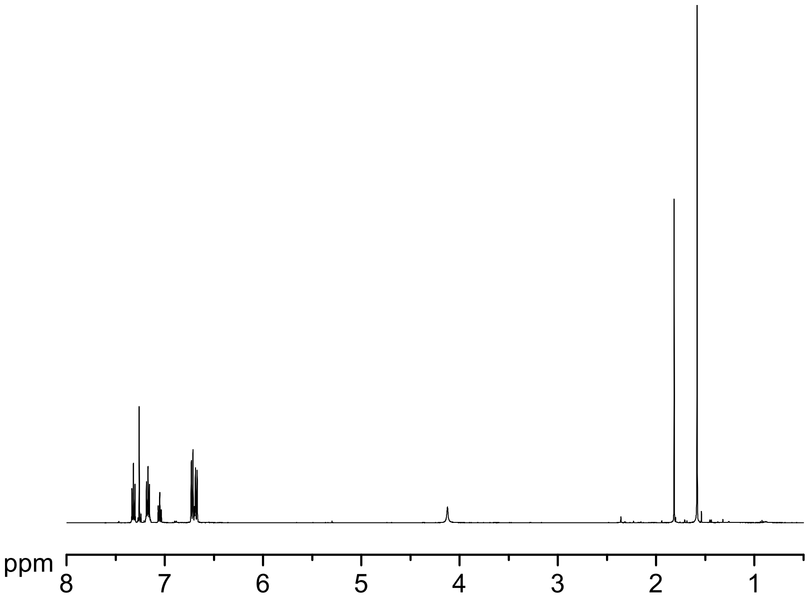


Figure S13. ^{1}H NMR of ligand **L3**

5. References

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