catalysts

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Supplementary Information
for

LLDPE-like Polymers Accessible via Ethylene Homopolymerization using Nitro-Appended 2-(Arylimino)Pyridine-Nickel Catalysts

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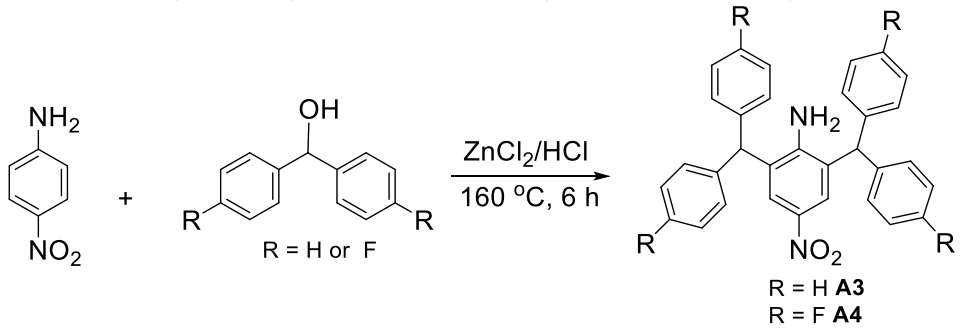
Preparative details for the anilines (A3 – A5)

As **A1** and **A2** were commercially available (**A1**: CAS number #163704-72-1 and **A2**: CAS number # PH008328), they were used directly for ligand synthesis. The other anilines, 2,6-{$CH(C_6H_5)_2$}$_2$-4-$NO_2C_6H_2NH_2$ (**A3**) 2,6-{$CH(4\text{-}F\text{-}C_6H_4)_2$}$_2$-4-$NO_2C_6H_2NH_2$ (**A4**) and 2,6-*i*-Pr_2-3-NO_2-4-$(4\text{-}FPh)_2C_6HNH_2$ (**A5**), were prepared using routes described below and illustrated in Schemes S1 and S2 below, respectively.

(i) Preparation of 2,6-{$CH(4\text{-}R\text{-}C_6H_4)_2$}$_2$-4-$NO_2C_6H_2NH_2$ (R = H **A3**, R = F **A4**).



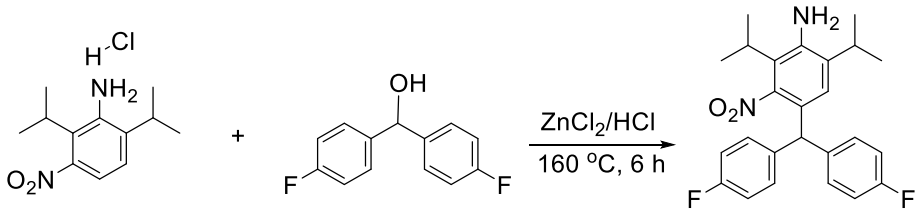
Scheme S1 Synthetic route to anilines **A3** and **A4**.

Based on procedures described in the literature [S1-S4], a mixture of 4-nitroaniline (4.0 g, 29 mmol) and diphenylmethanol (10.7 g, 59.9 mmol) was stirred and heated at 160 °C for 20 min to form a homogeneous melt. Then a solution of $ZnCl_2$ (15%) in conc. HCl (5 mL) was added dropwise to the melt at a stirring speed of 800 rpm. The reaction mixture was further stirred and heated at 160 °C for a further 7 h. Upon cooling to room temperature, the resulting solid was dissolved in dichloromethane (500 mL).

The solution was washed firstly with aqueous solution of NH_4Cl (3 × 200 mL) and then secondly with an aqueous solution of NaCl (2 × 250 mL). The organic phase was dried over anhydrous $MgSO_4$ and filtered. After evaporation of the majority of the solvent under reduced pressure, the viscous syrup was dissolved in a minimum amount of dichloromethane and recrystallized from excess methanol to afford the desired product **A3** as a yellow crystalline powder (7.6 g, 56%)
Compound **A3**: ^{1}H NMR (400 Hz, $CDCl_3$, TMS): δ 7.03-6.93 (m, 13H, Ph-H), 6.79-6.78 (m, 8H, Ph-H), 5.05 (s, 2H, -CH-), 3.88 (s, 2H, NH_2).

Similarly, a mixture of 4-nitroaniline (4.0 g, 29 mmol) and bis-(4-fluorophenyl)methanol (12.75 g, 59 mmol) was stirred and heated at 160 °C for 20 min to form a homogeneous melt. Then a solution of $ZnCl_2$ (15%) in conc. HCl (5 mL) was added dropwise to the melt at a stirring speed of 800 rpm. The reaction mixture was further stirred and heated at 160 °C for a further 7 h. Upon cooling to room temperature, the resulting solid was dissolved in dichloromethane (500 mL). The solution was washed with an aqueous solution of NH_4Cl (3 × 200 mL) and then an aqueous solution of NaCl (2 × 250 mL). The organic phase was dried over anhydrous $MgSO_4$ and filtered. After evaporation of the majority of the solvent under reduced pressure, the viscous syrup was dissolved in a minimum amount of dichloromethane and recrystallized from excess methanol to afford the desired product **A4** as a yellow powder (6.8 g, 43%).
Compound **A4**: ^{1}H NMR (400 Hz, $CDCl_3$, TMS): δ7.52 (s, 2H), 7.04–7.03 (m, 16H, $CH(F\text{-}Ph)_2$, 5.33 (s, 2H, -CH-), 4.15 (s, 2H, NH_2).
Additionally, the complete characterization data of **A3** and **A4** could be found in references S3 and S4.

(ii) Preparation of 2,6-diisopropyl-3-nitro-4-(4,4-difluorobenzhydryl)aniline (**A5**)



Scheme S2 Synthetic route to 2,6-diisopropyl-3-nitro-4-(4,4-difluorobenzhydryl)aniline (**A5**)

A mixture of 2,6-diisopropyl-3-nitroaniline hydrochloride (11.7 g, 45.2 mmol) and bis(4-fluorophenyl)methanol (10.15 g, 46.1 mmol) was stirred at 155 °C for 20 min to form a homogeneous melt. Then a solution of $ZnCl_2$ (2.35 g, 20%) in conc. HCl (5 mL) was added dropwise at a stirring speed of 800 rpm. The reaction mixture was further stirred and heated at 160 °C for further 6 h and then allowed to cool to room temperature. The resulting solid was dissolved in dichloromethane (400 mL) by using an ultra-sonic water bath and washed with aqueous solution of NH_4Cl (3 × 200 mL) and then an aqueous solution of NaCl (2 × 200 mL). The organic phase was dried with anhydrous $MgSO_4$, filtered and then evaporated under reduced pressure to give a brown viscous residue. This residue was recrystallized by dissolving in a minimum amount of dichloromethane, followed by the addition of excess methanol to afford the desired product as a yellow powder (16.26 g, 85%).

A5: ^{1}H NMR (400 Hz, $CDCl_3$, TMS): δ7.01–6.93 (m, 8H, $CH(F–Ph)_2$), 6.64 (s, 1H), 5.32 (s, 1H, –CH–), 3.95 (s, 2H, NH_2), 2.98–2.90 (m, 1H, –CH–), 2.86–2.79 (m, 1H, –CH–), 1.38-1.36 (d, J = 8.0, 6H, $–CH_3$), 1.12–1.10 (d, *J* = 8.0, 6H, $–CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 162.8, 160.4, 150.4, 141.3, 138.4, 138.3, 134.4, 130.6, 130.5, 125.2, 122.9, 121.2, 115.3, 115.1, 49.5, 49.5, 28.6, 27.8, 22.0, 19.8.

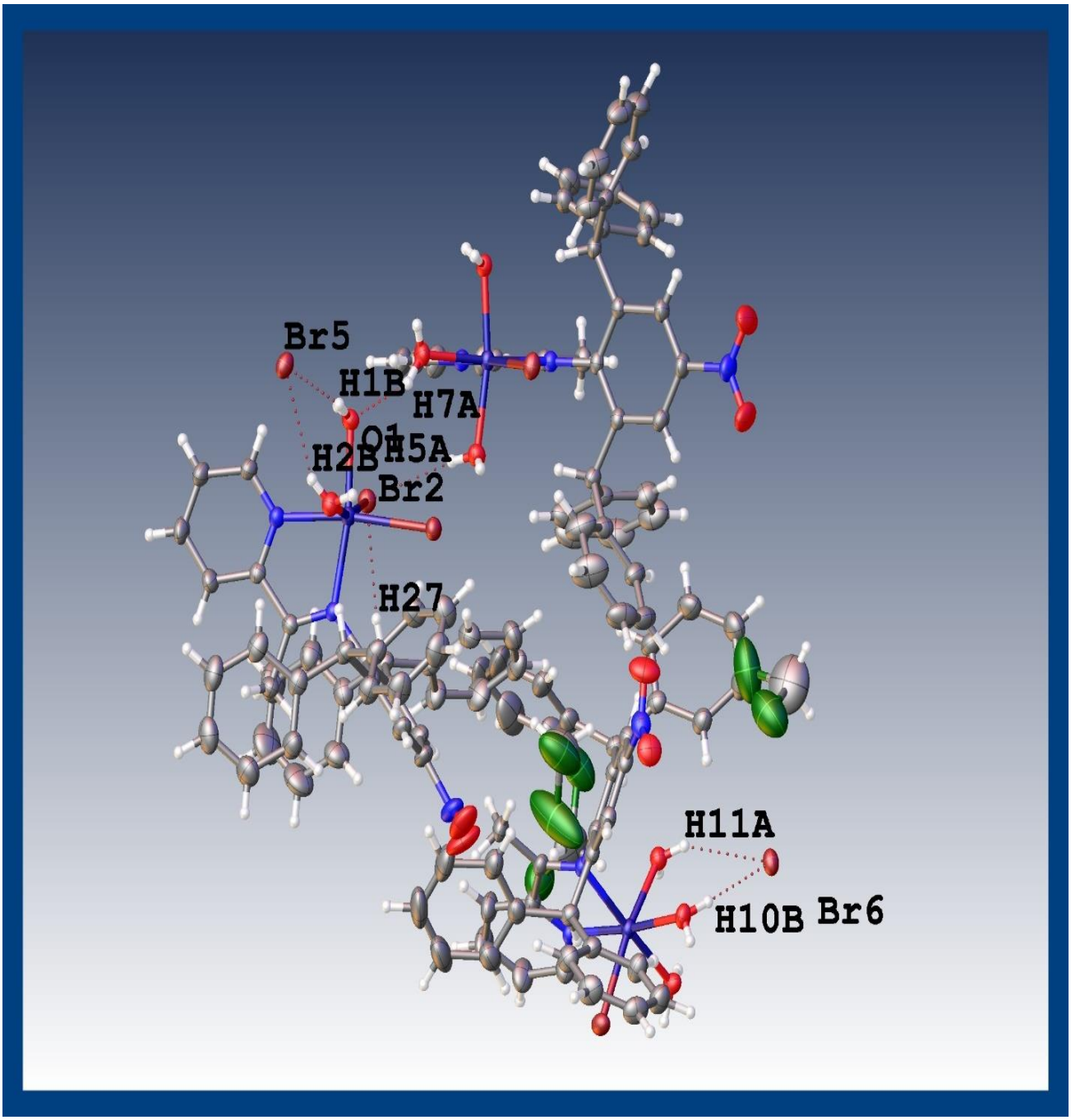


Figure S1 The three independent molecules (A, B and C) present in the unit cell of **Ni3**·xH_2O (x = 2,3) including three molecules of dichloromethane. Thermal ellipsoids are shown at the 30% probability level while OH···Br hydrogen bonding interactions between the coordinated water molecules and free bromide ions are shown with dotted lines.

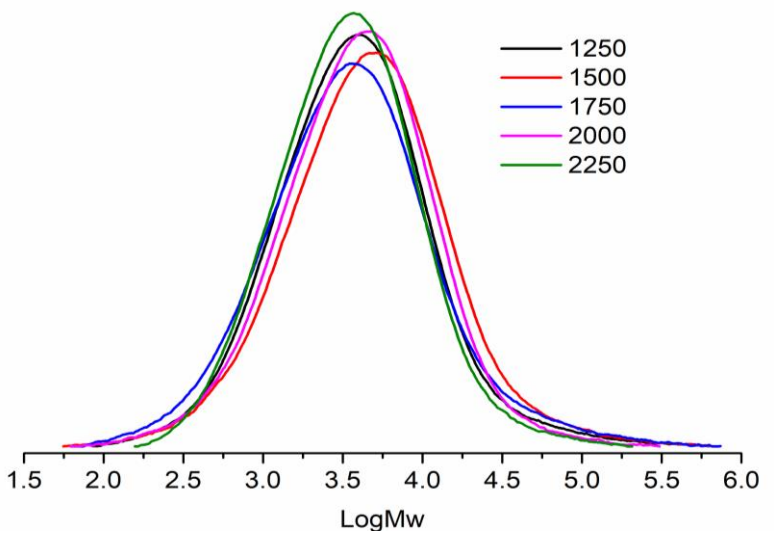


Figure S2 GPC curves of the polyethylene produced using **Ni4**/MMAO at different molar ratios (runs 1 – 5, Table 4).

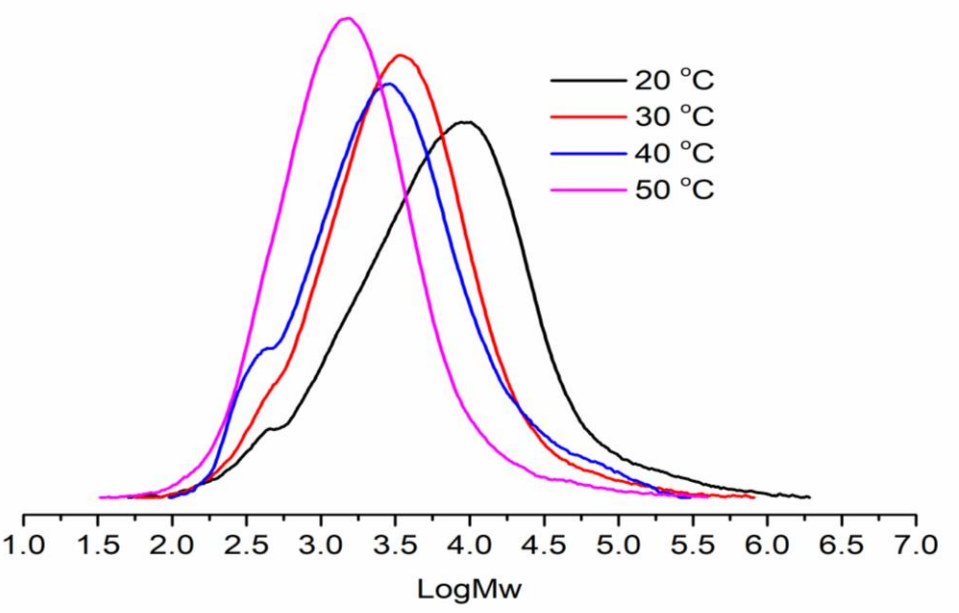


Figure S3 GPC curves of the polyethylene produced using **Ni4**/MMAO at different run temperatures (runs 3, 6 – 8, Table 4).

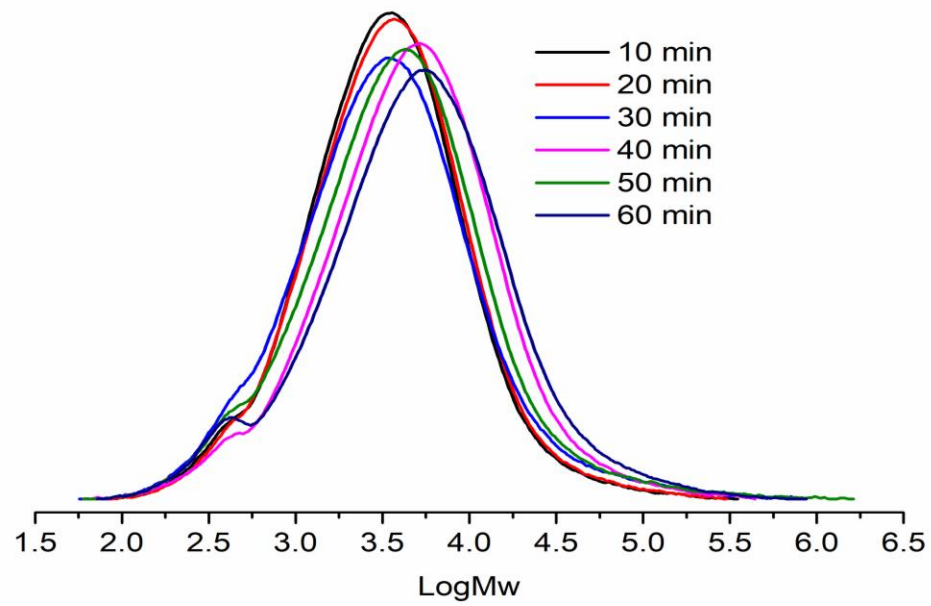


Figure S4 GPC curves of the polyethylene produced using **Ni4**/MMAO over different run times (runs 3, 9 – 13, Table 4).

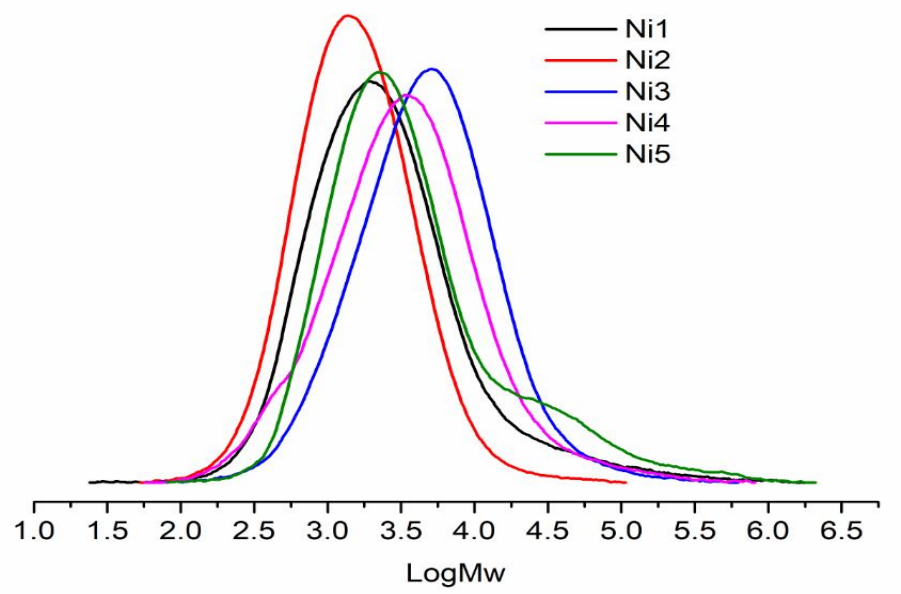


Figure S5 GPC curves of the polyethylene produced using **Ni1** – **Ni5**/MMAO under optimum conditions (runs 3, 16 – 19, Table 4).

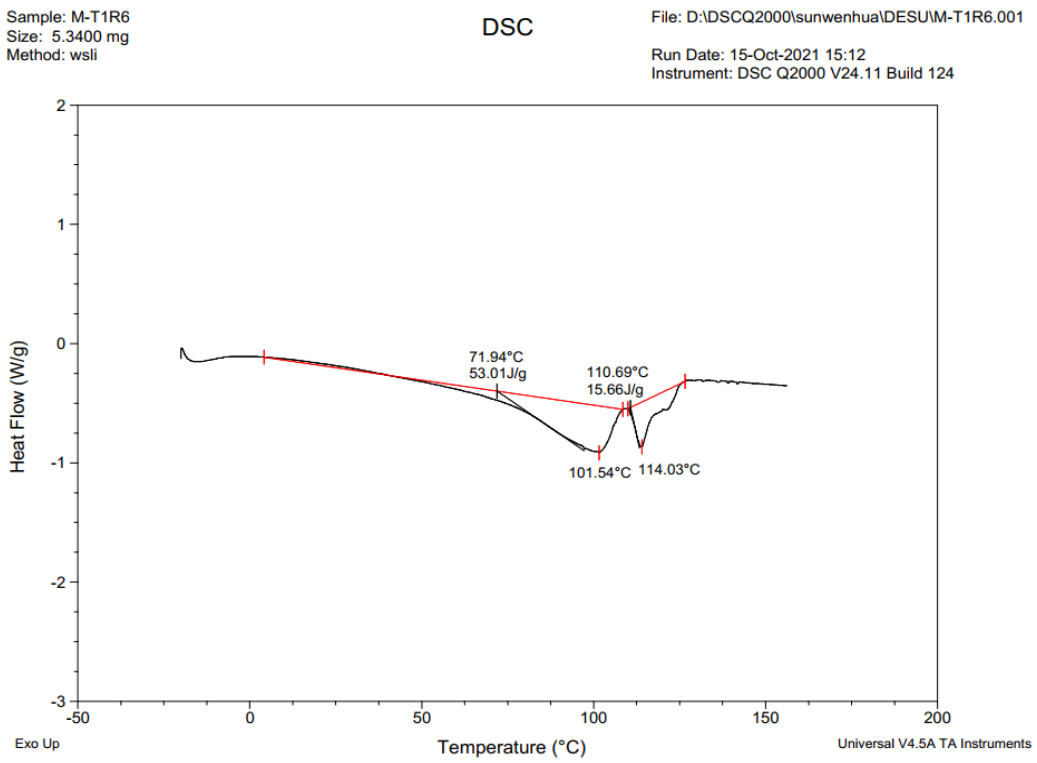


Figure S6 DSC thermogram of the polyethylene produced using **Ni4**/MMAO (run 4, Table 4).

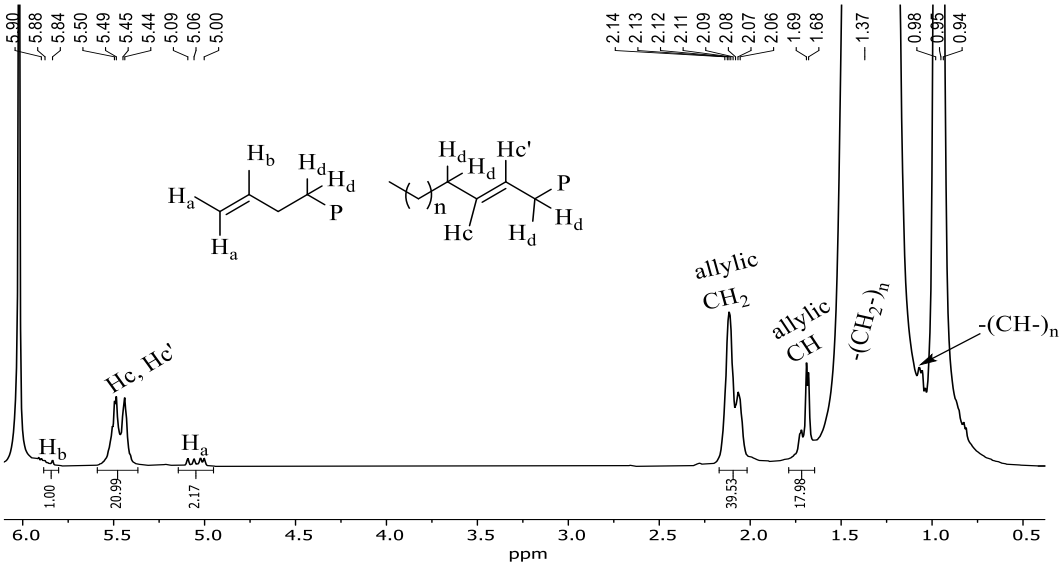


Figure S7 ^{1}H NMR spectrum of the polyethylene sample produced using **Ni4**/MMAO at 30 °C (run 3, Table 4); recorded at 100 °C in *d*-$C_2D_2Cl_4$.

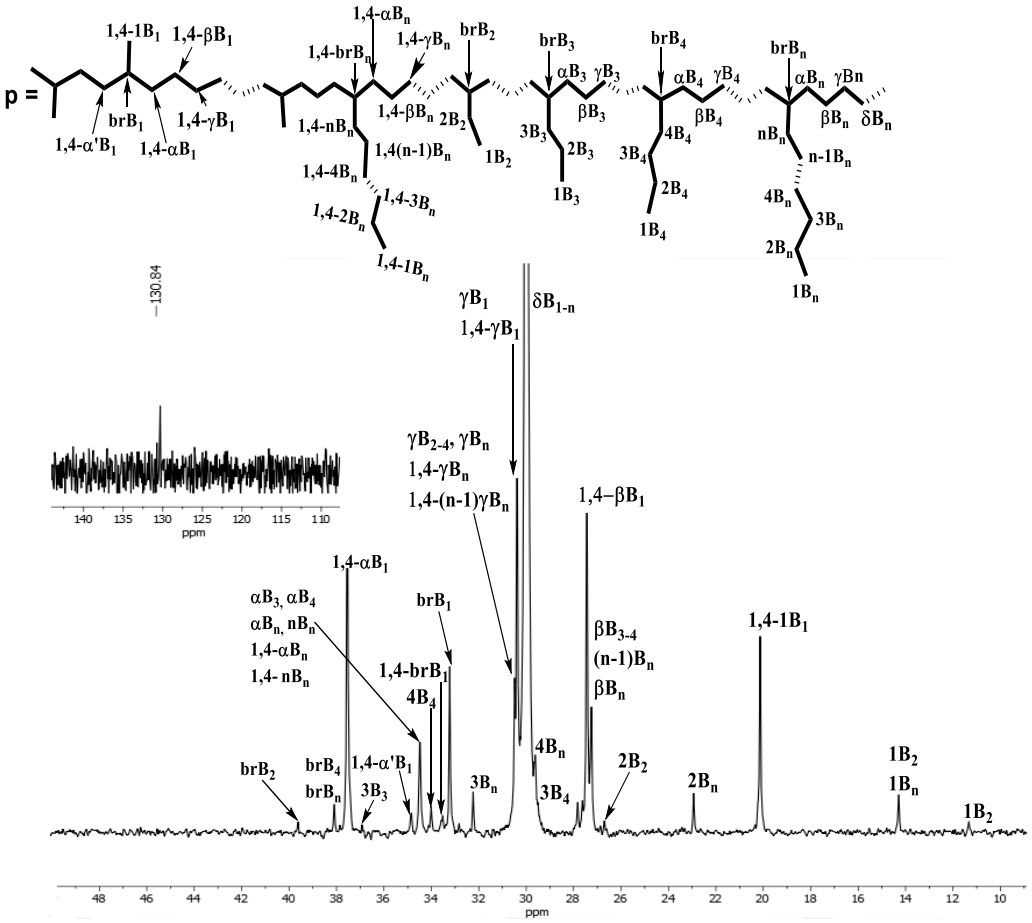


Figure S8 ^{13}C NMR spectrum of the polyethylene sample produced using **Ni4**/MMAO at 30 °C, including an inset of the δ 110–150 ppm region and a segment of the assigned polymer backbone (run 3, Table 4); recorded at 100 °C in *d*-$C_2D_2Cl_4$.

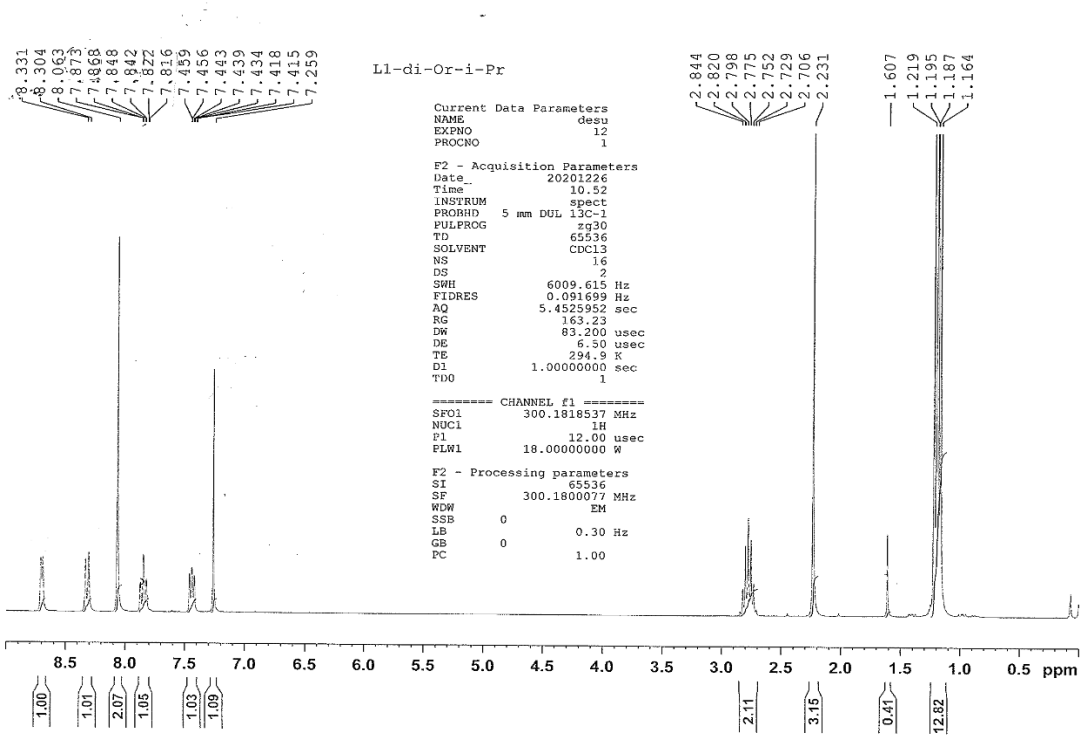


Figure S9a ^{1}H NMR spectrum of ligand **L1**; recorded in $CDCl_3$ at ambient temperature.

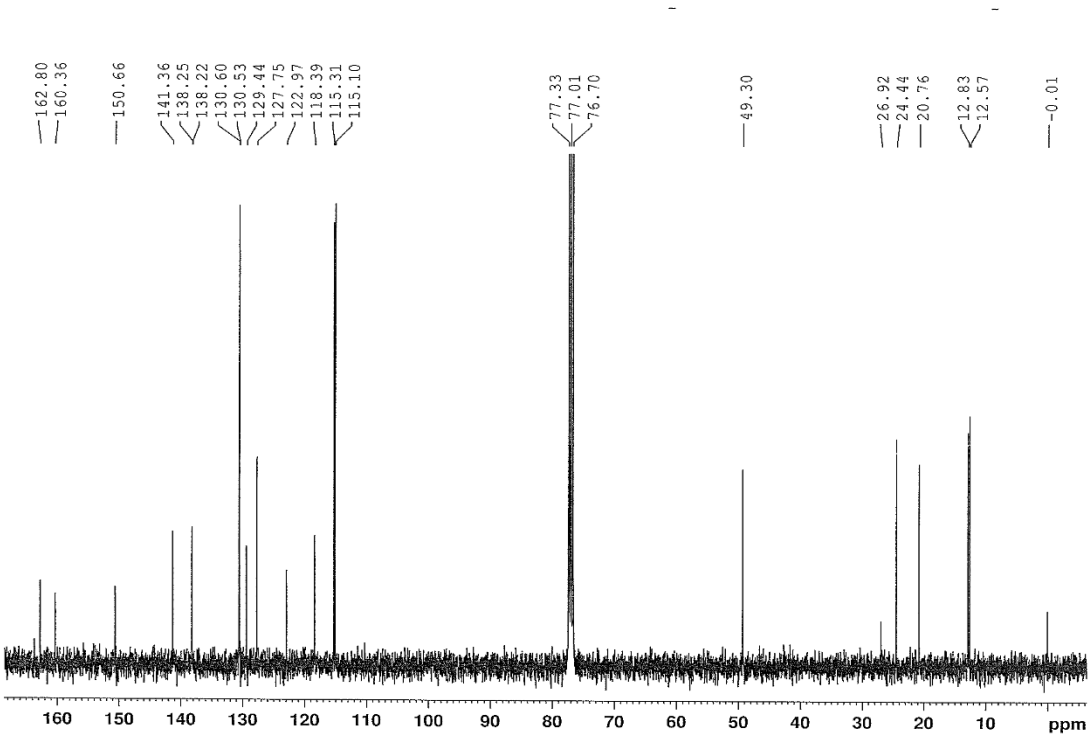


Figure S9b ^{13}C NMR spectrum of ligand **L1**; recorded in $CDCl_3$ at ambient temperature.

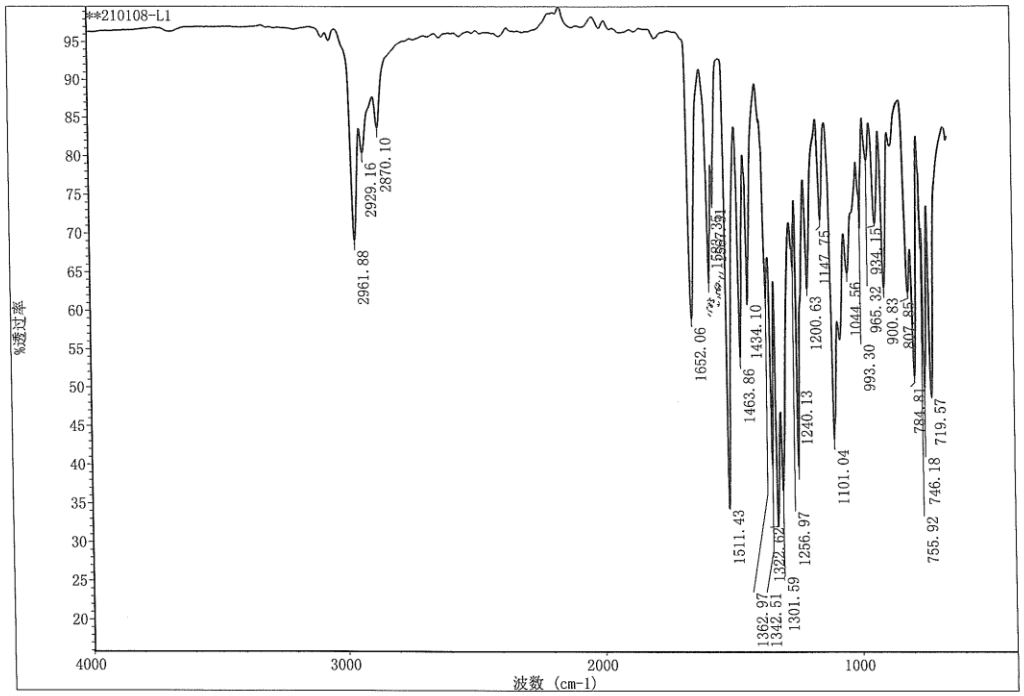


Figure S10a FTIR spectrum of ligand **L1**.

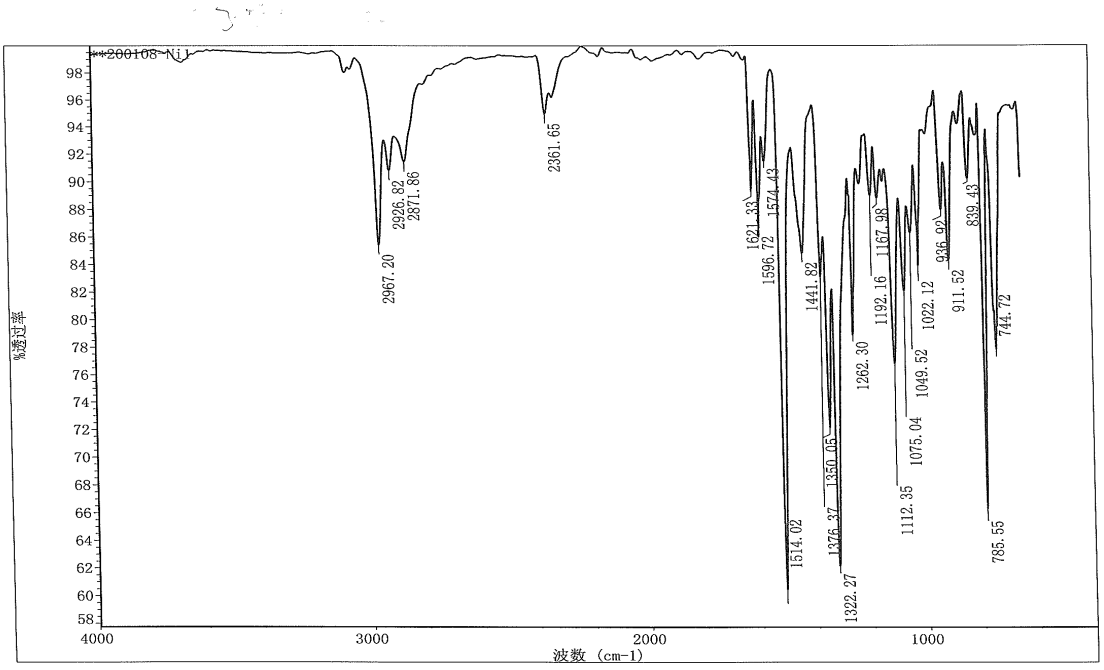


Figure S10b FTIR spectrum of complex **Ni1**.

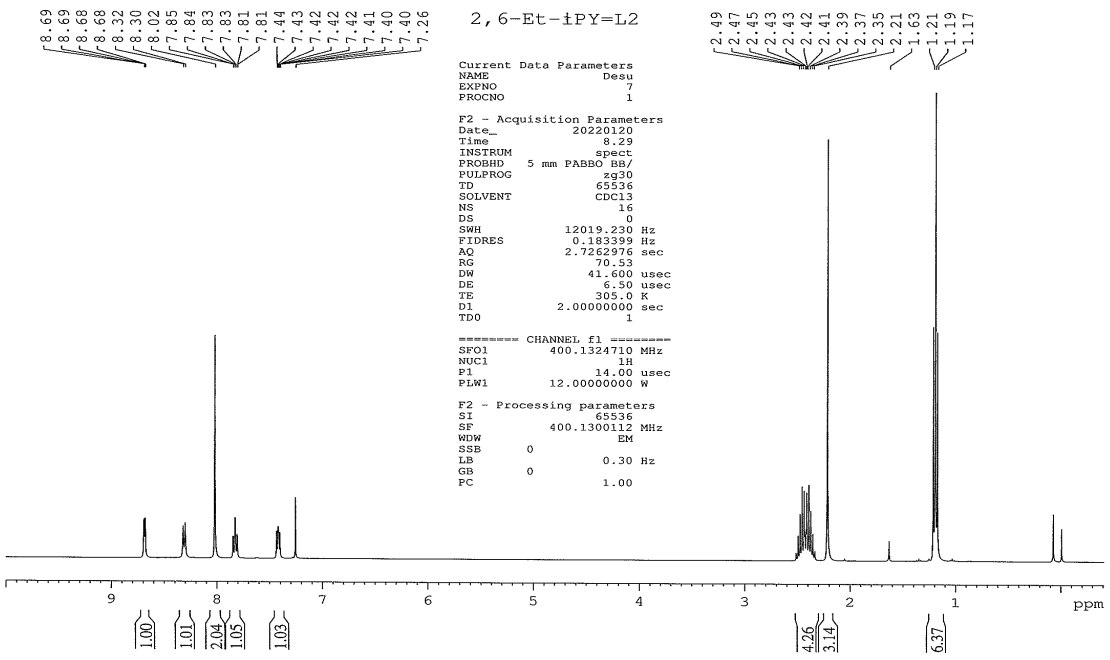


Figure S11a ^{1}H NMR spectrum of ligand **L2**; recorded in $CDCl_3$ at ambient temperature.

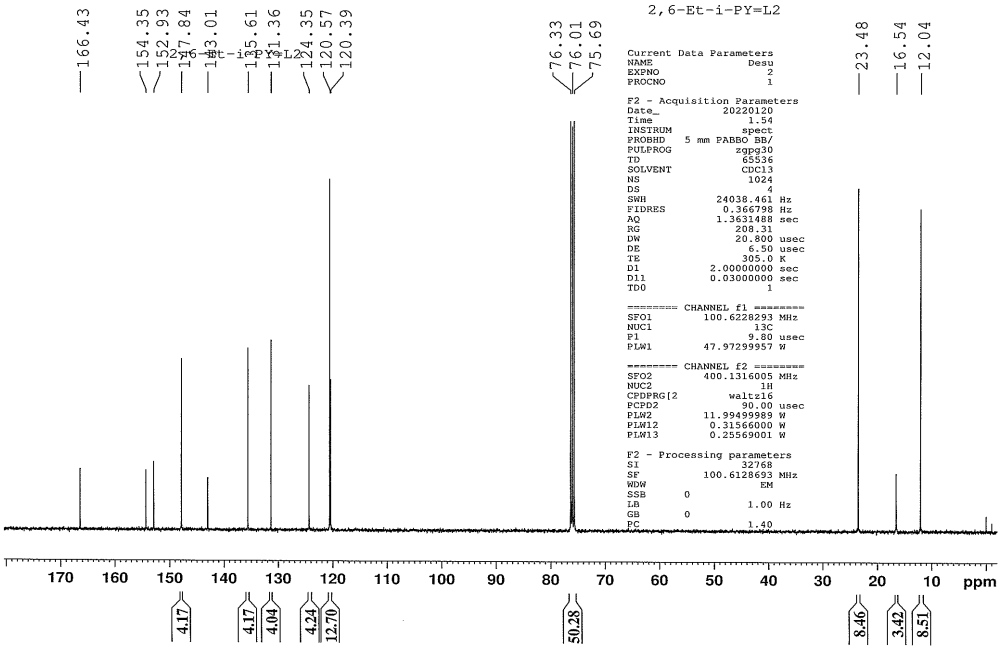


Figure S11b ^{13}C NMR spectrum of ligand **L2**; recorded in $CDCl_3$ at ambient temperature.

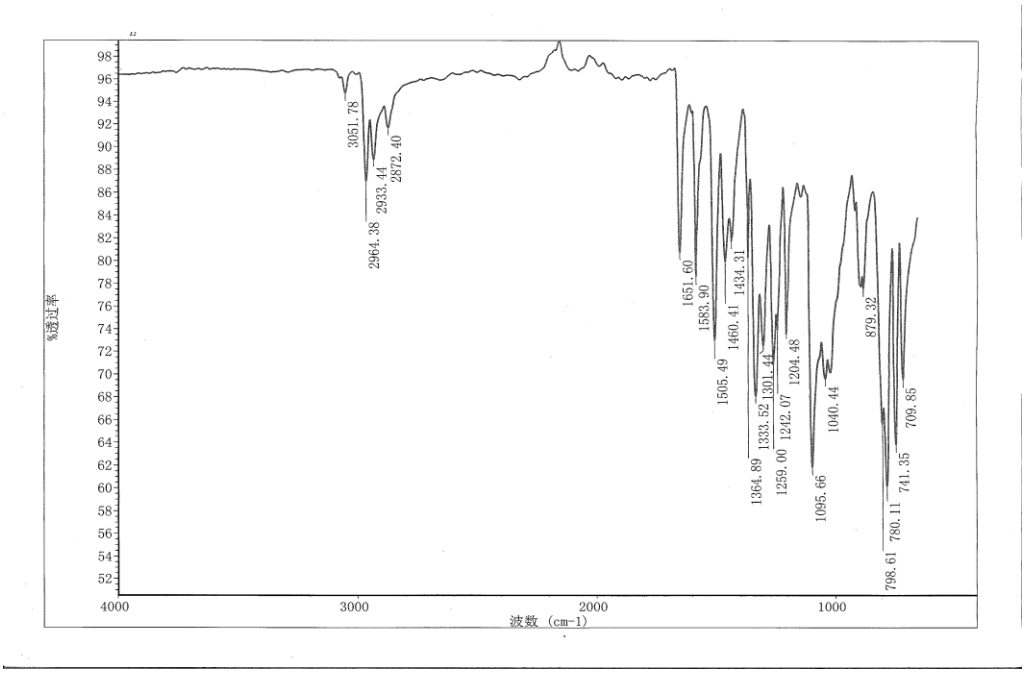


Figure S12a FTIR spectrum of ligand **L2**.

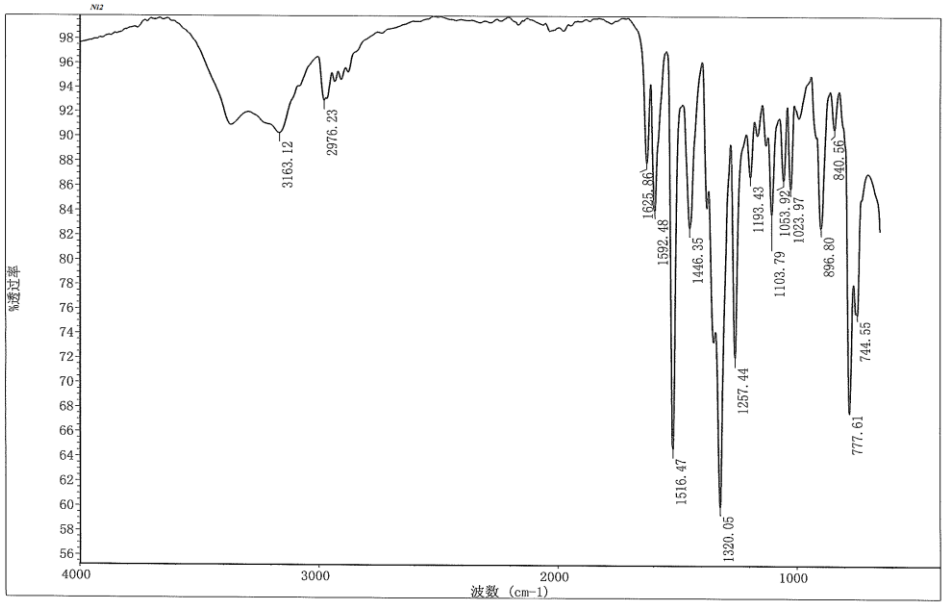


Figure S12b FTIR spectrum of complex **Ni2**.

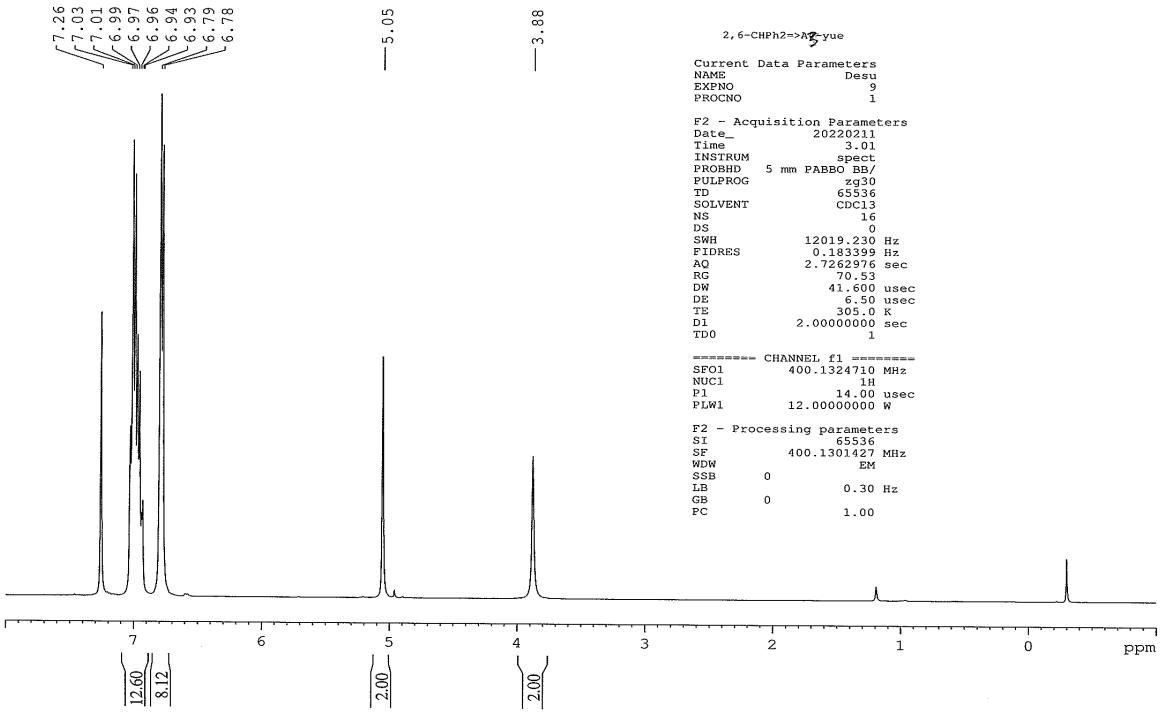


Figure S13 ^{1}H NMR spectrum of aniline **A3**; recorded in $CDCl_3$ at ambient temperature.

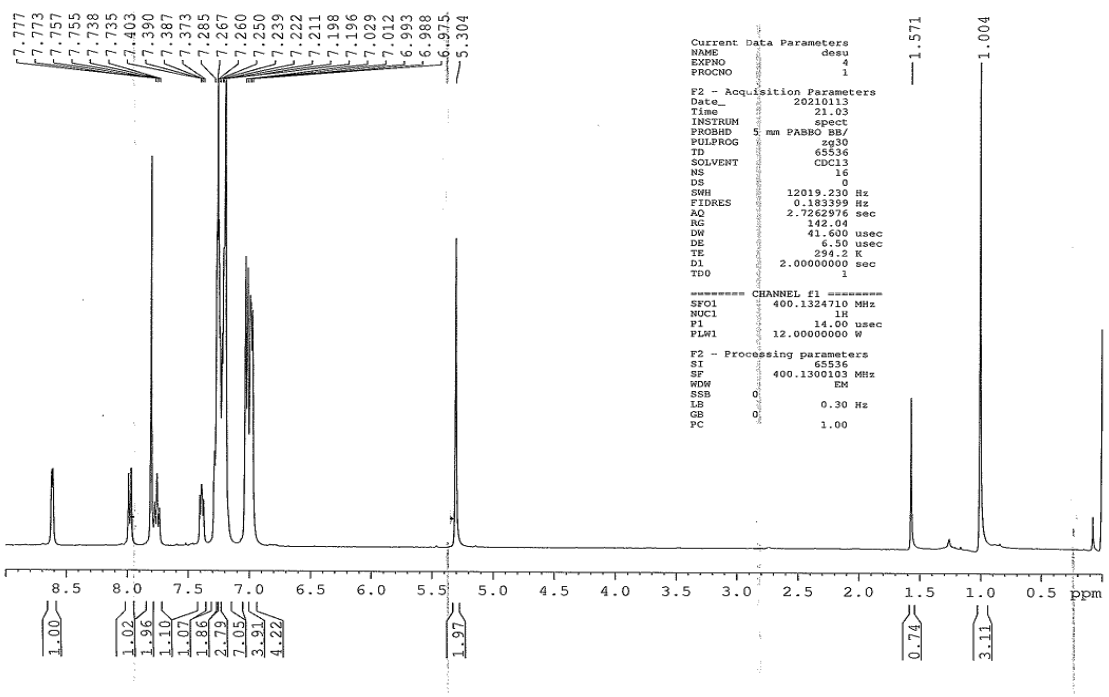


Figure S14a ^{1}H NMR spectrum of ligand **L3**; recorded in $CDCl_3$ at ambient temperature.

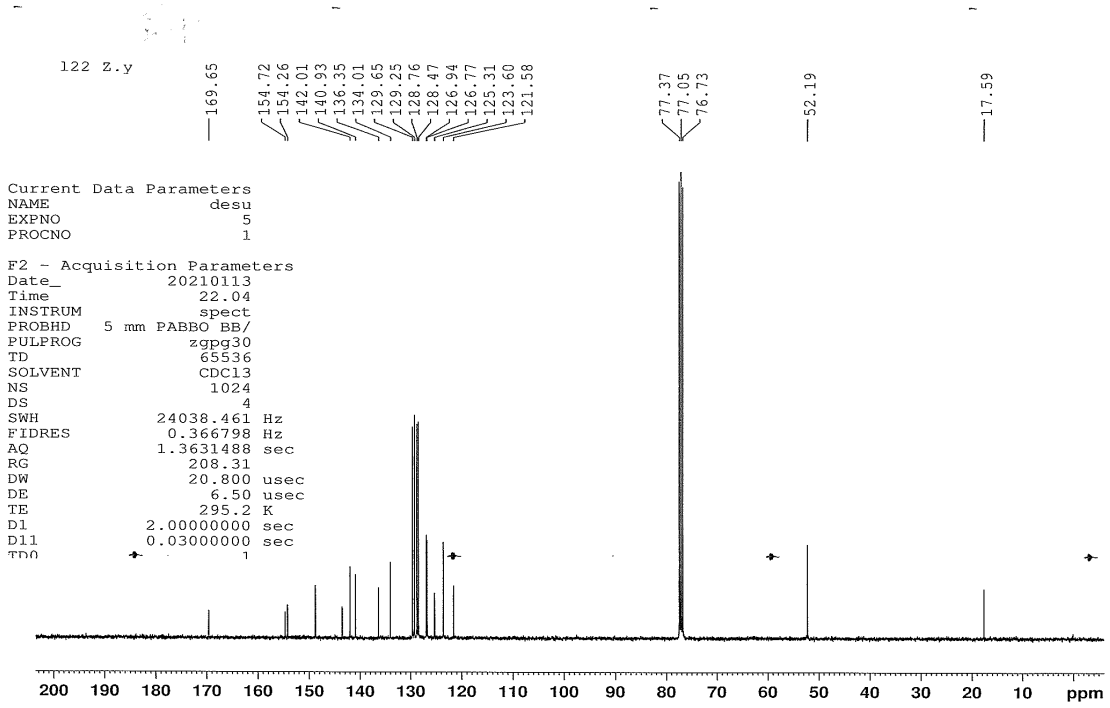


Figure S14b ^{13}C NMR spectrum of ligand **L3**; recorded in $CDCl_3$ at ambient temperature.

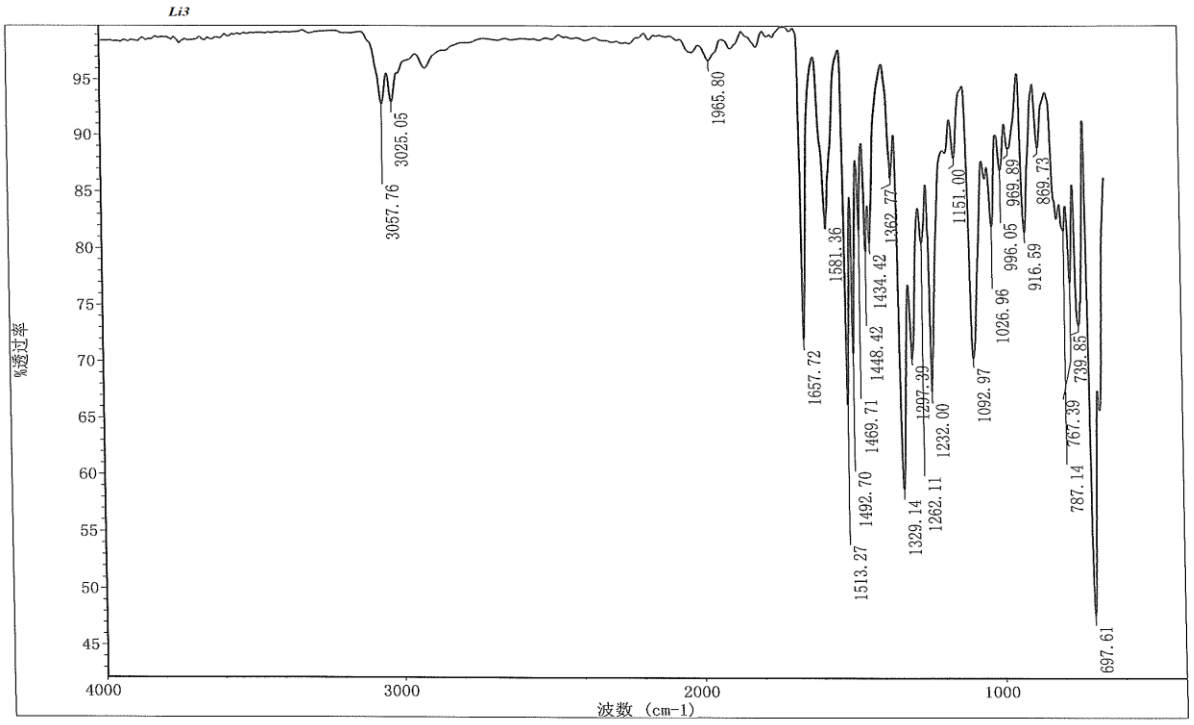


Figure S15a FTIR spectrum of ligand **L3**.

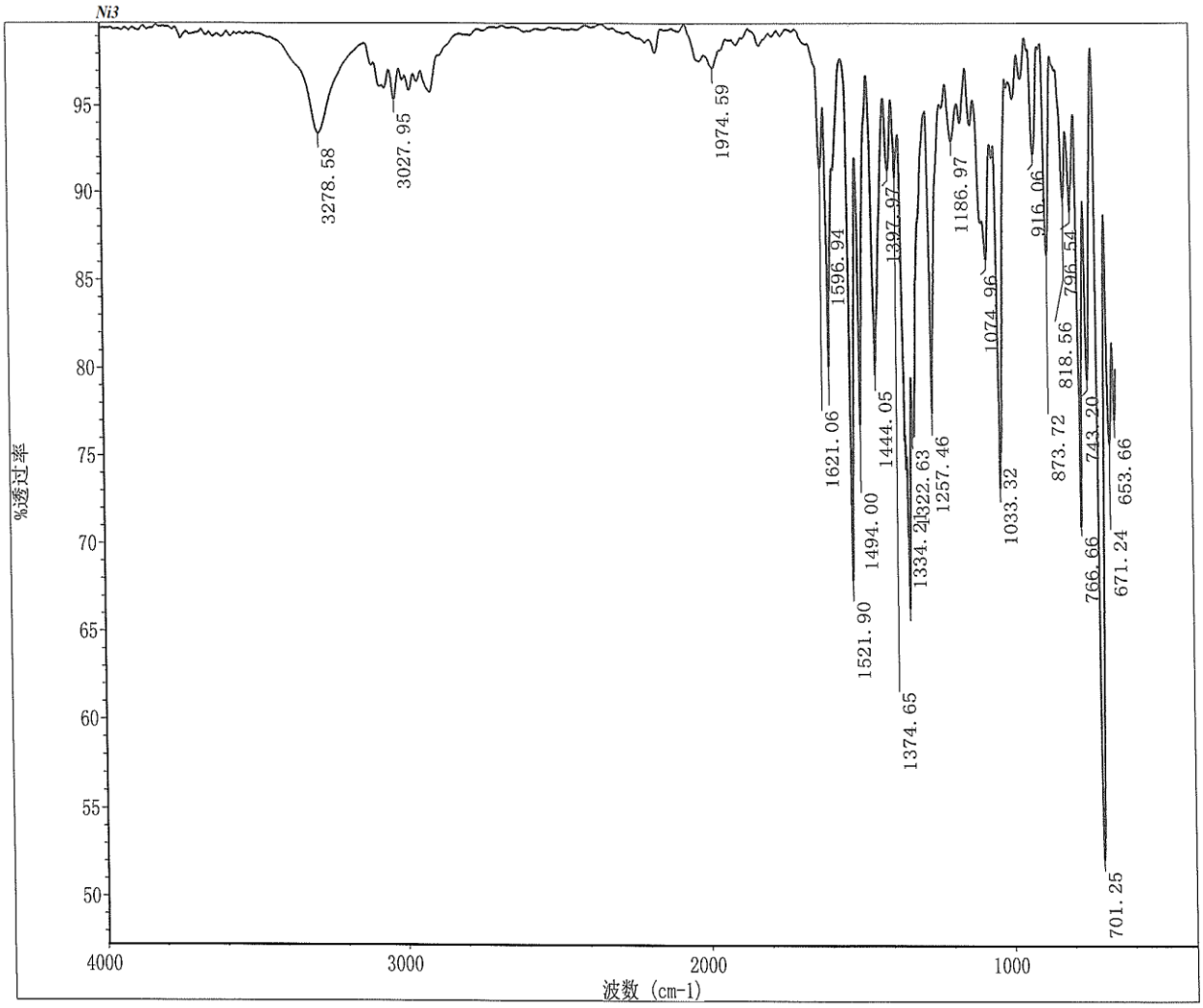


Figure S15b FTIR spectrum of complex **Ni3**.

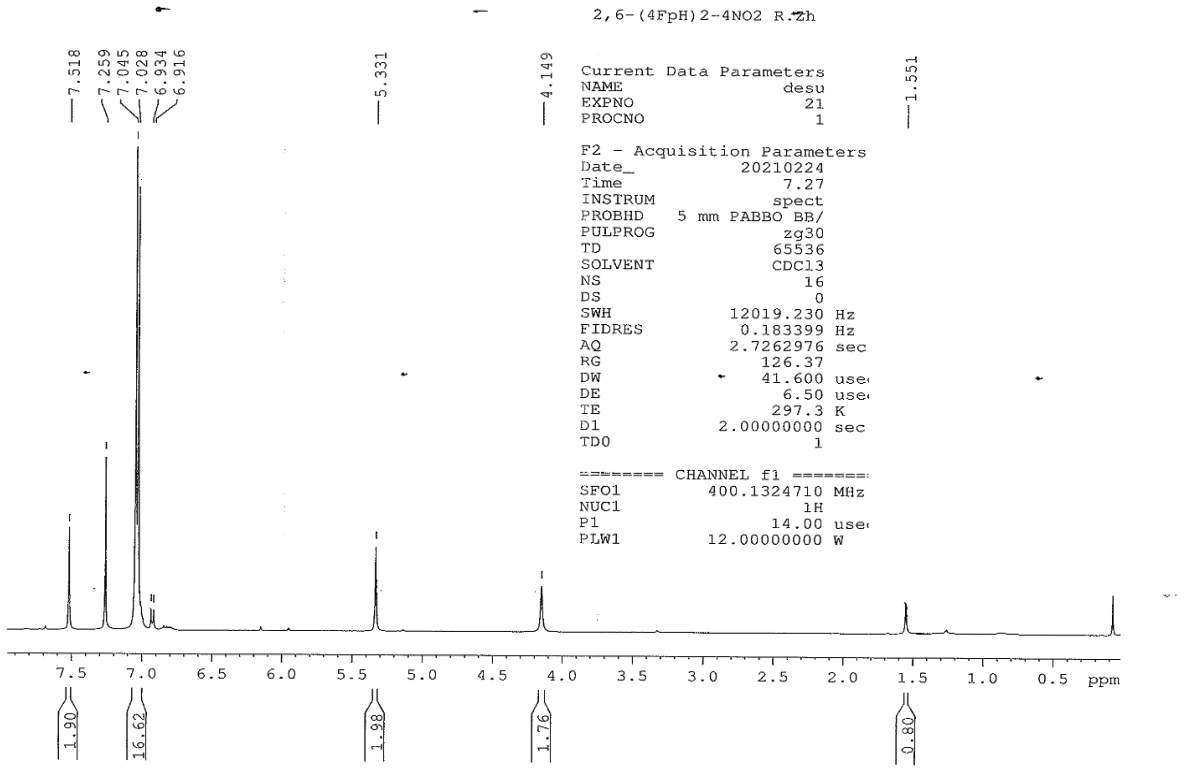


Figure S16 ^{1}H NMR spectrum of aniline **A4**; recorded in $CDCl_3$ at ambient temperature.

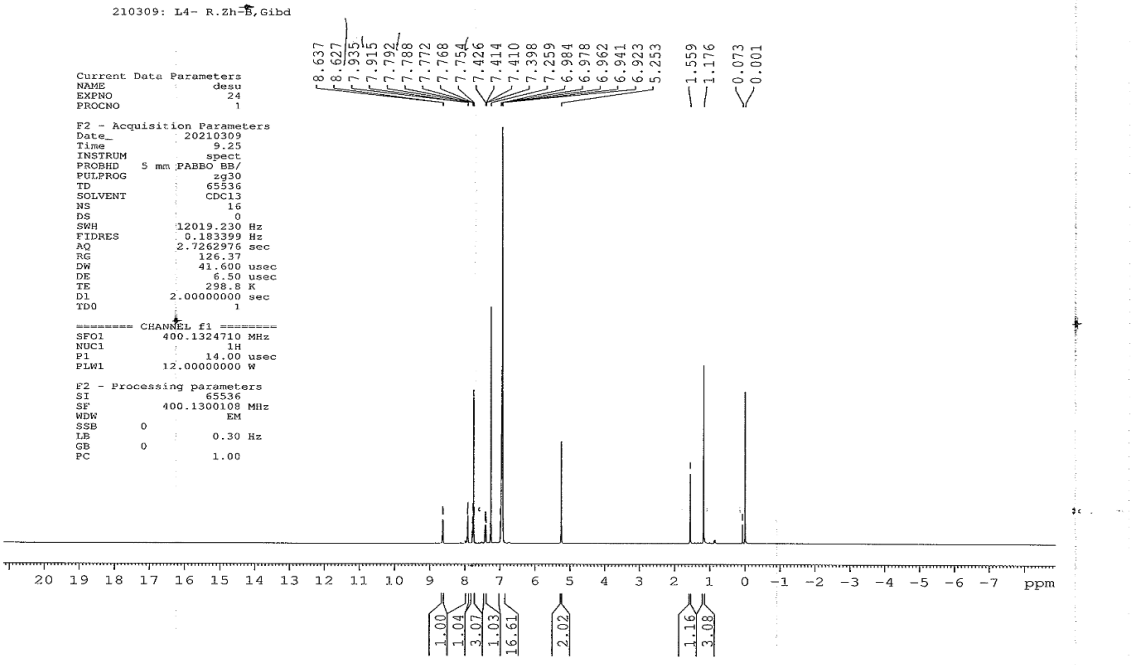


Figure S17a ^{1}H NMR spectrum of ligand **L4**; recorded in $CDCl_3$ at ambient temperature.

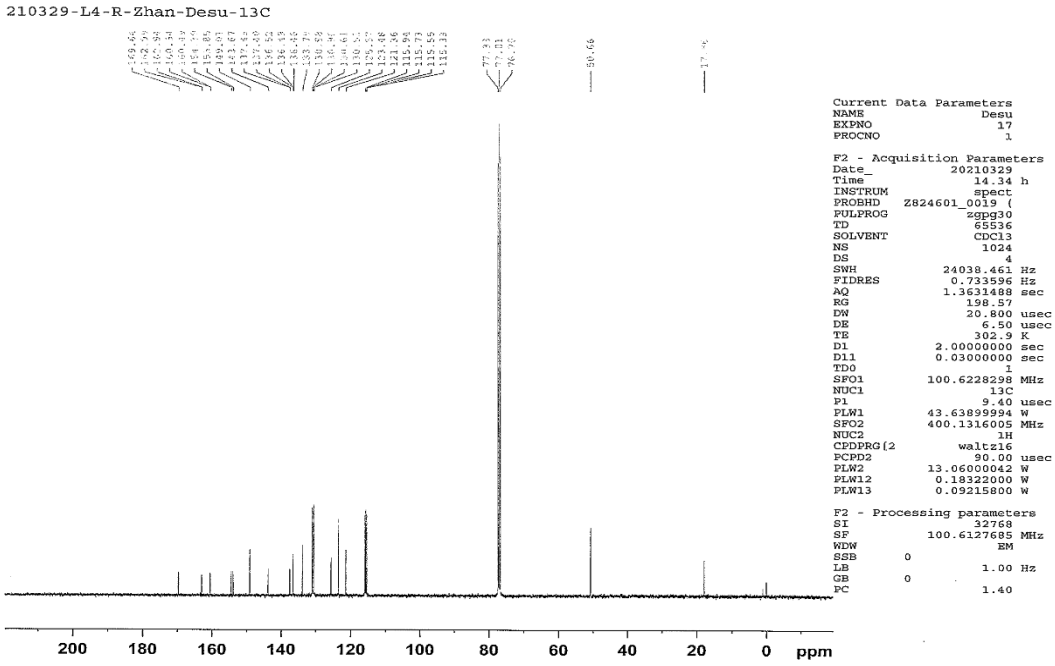


Figure S17b ^{13}C NMR spectrum of ligand **L4**; recorded in $CDCl_3$ at ambient temperature.

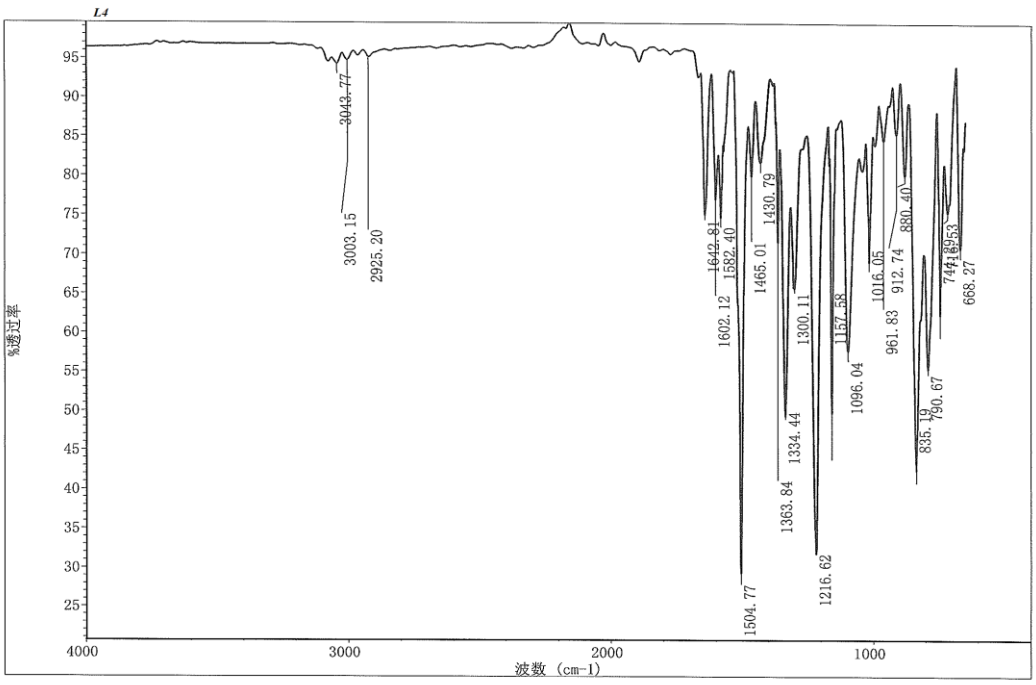


Figure S18a FTIR spectrum of ligand **L4**.

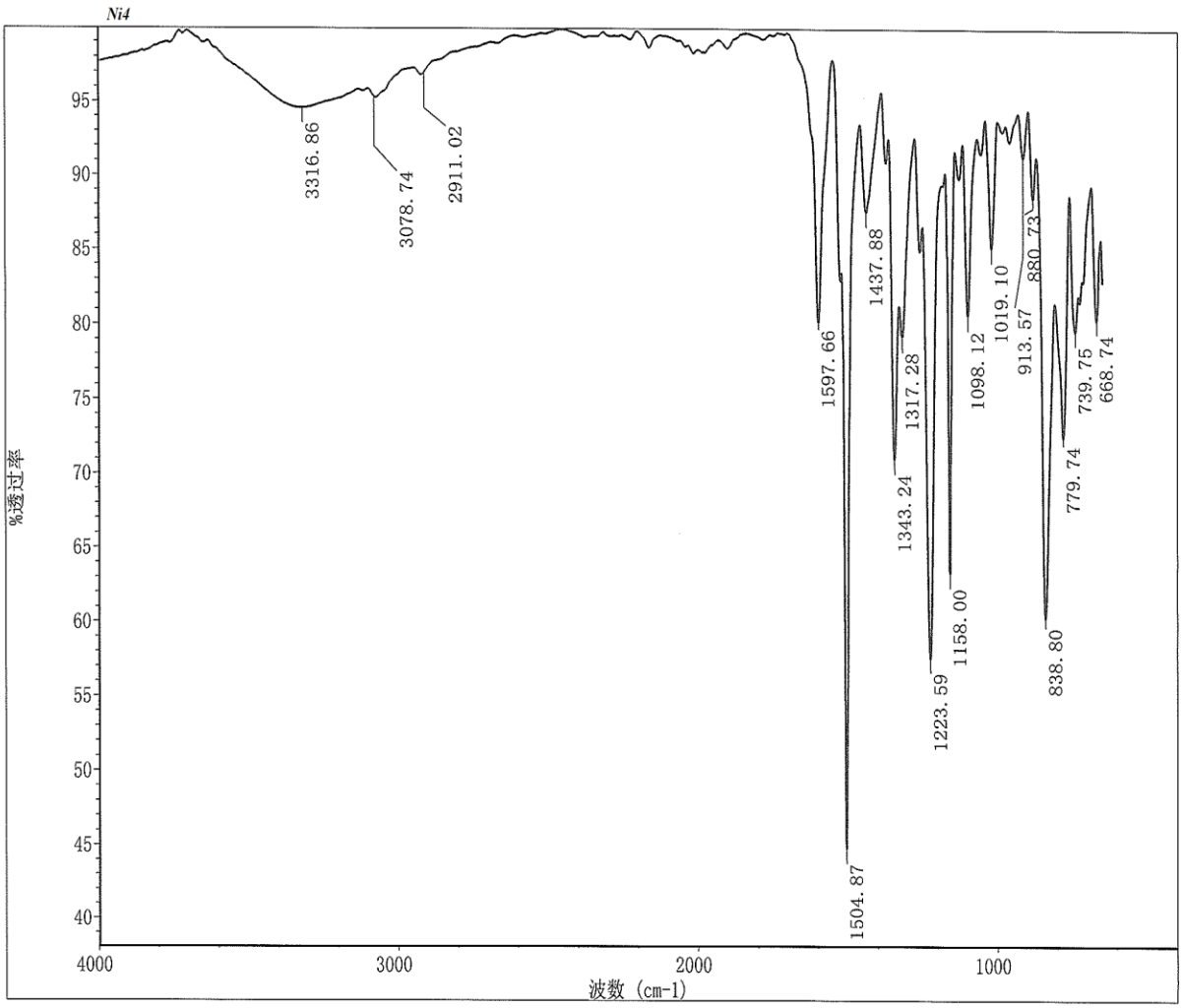


Figure S18b FTIR spectrum of complex **Ni4**.

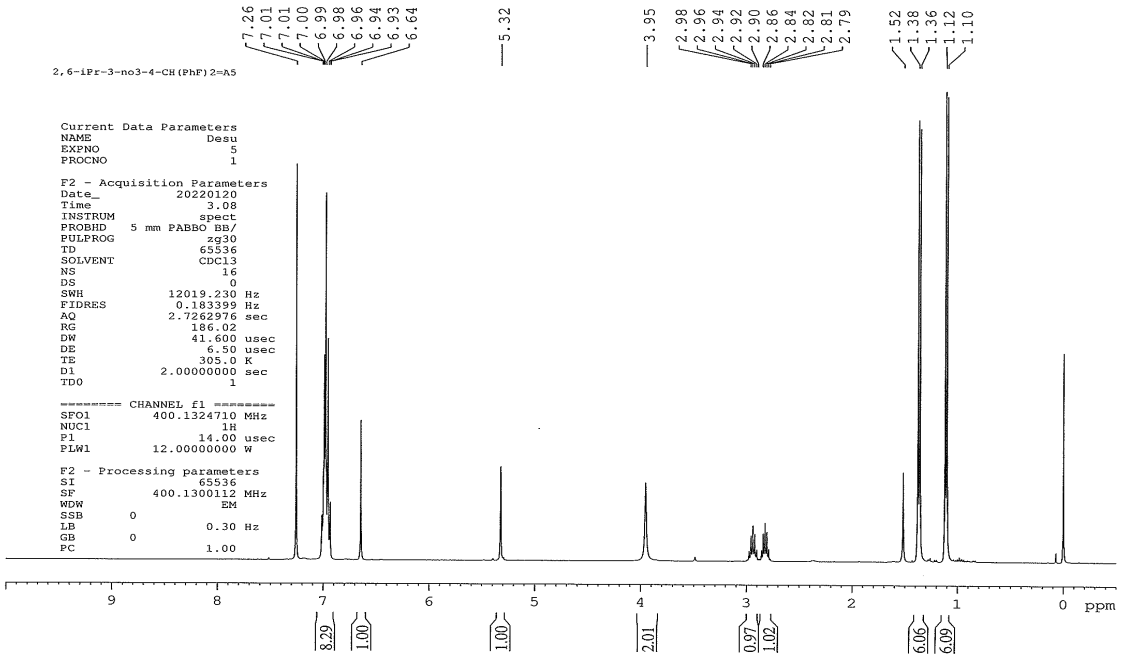


Figure S19a ^{1}H NMR spectrum of aniline **A5**; recorded in $CDCl_3$ at ambient temperature.

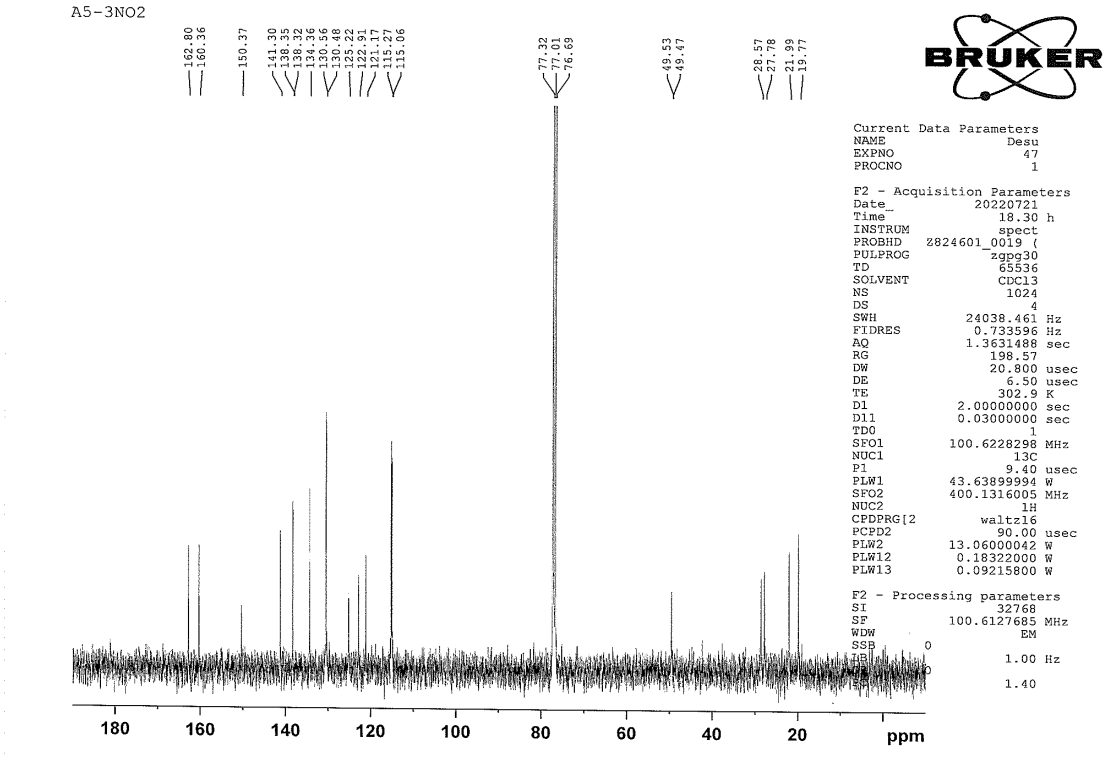


Figure S19b ^{13}C NMR spectrum of aniline **A5**; recorded in $CDCl_3$ at ambient temperature.

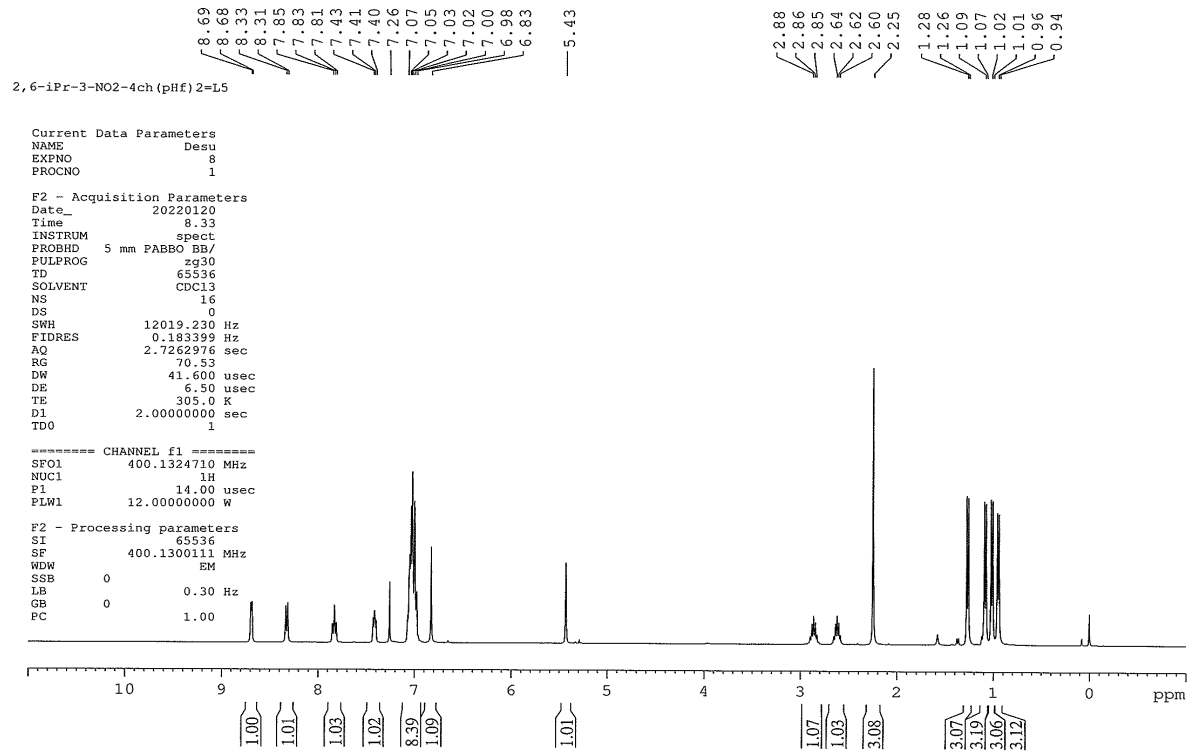


Figure S20a ^{1}H NMR spectrum of ligand **L5**; recorded in $CDCl_3$ at ambient temperature.

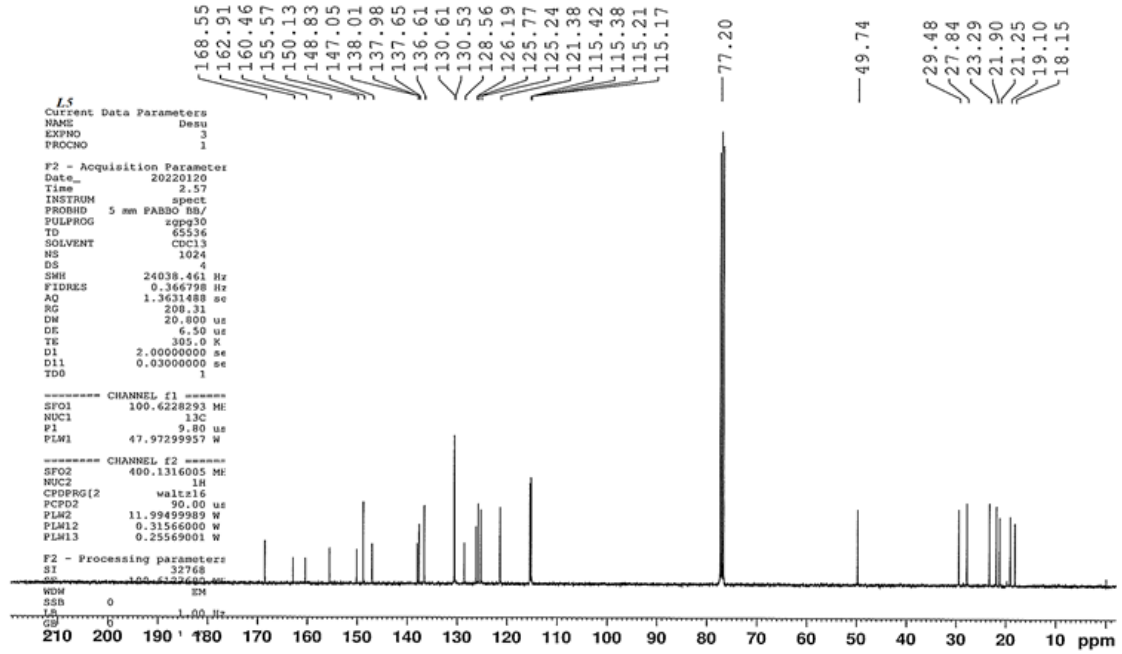


Figure S20b ^{13}C NMR spectrum of ligand **L5**; recorded in $CDCl_3$ at ambient temperature.

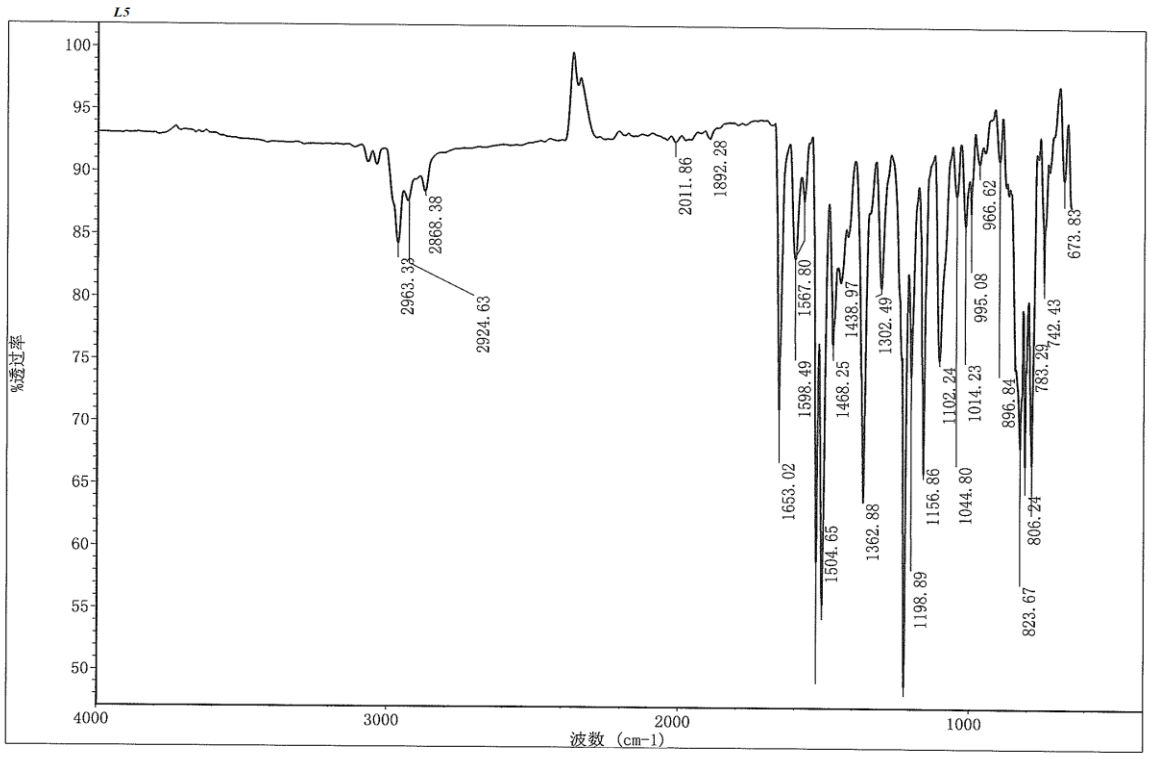


Figure S21a FTIR spectrum of ligand **L5**.

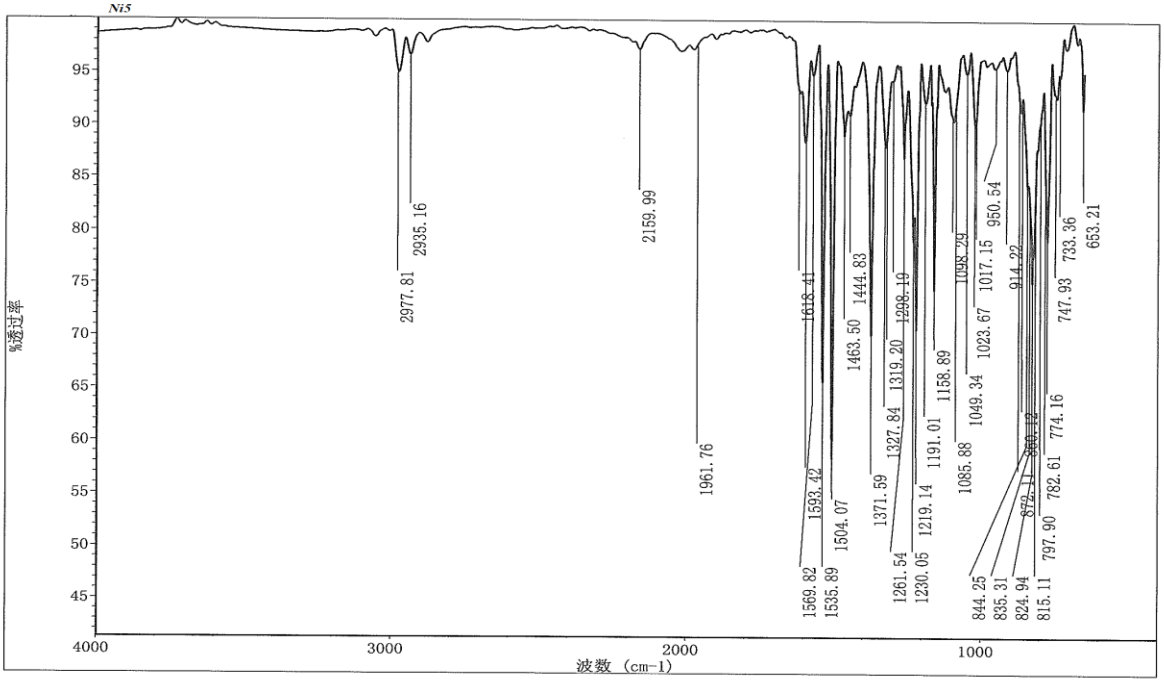


Figure S21b FTIR spectrum of complex **Ni5**.

Table S1 Crystallographic data for **Ni3**·xH_2O (x = 2,3), **Ni4** and **Ni5**.

Identification code	**Ni3**·xH_2O (x = 2,3)	**Ni4**	**Ni5**
CCDC No.	2195148	2195149	2195150
Empirical formula	$C_{117}H_{109}Br_6N_9Ni_3O_{14}\cdot 3CH_2Cl_2$	$C_{39}H_{27}N_3Br_2O_2F_4Ni$	$C_{32}H_{31}N_3Br_2O_2F_2Ni$
Formula weight	2775.49	864.16	746.13
Temperature/K	170.00(12)	170.00(13)	170.00(11)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	P-1	P-1
a/Å	17.20860(10)	11.9377(4)	10.7461(2)
b/Å	21.93390(10)	12.5497(4)	11.2319(2)
c/Å	35.0020(2)	16.0360(4)	13.9891(2)
α/°	90	78.123(2)	102.7970(10)
β/°	94.9920(10)	71.397(3)	105.9090(10)
γ/°	90	75.959(3)	96.0270(10)
Volume/$Å^3$	13161.45(12)	2187.23(12)	1558.55(5)
Z	4	2	2
$\rho_{calc}g/cm^3$	1.401	1.312	1.590
μ/mm^{-1}	4.230	3.201	4.283
F(000)	5624.0	864.0	752.0
Crystal size/mm^3	0.15 × 0.06 × 0.05	0.15 × 0.1 × 0.06	0.4 × 0.3 × 0.2
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.542 to 150.778	5.872 to 151.358	6.808 to 150.482
Index ranges	$-21 \le h \le 21$, $-22 \le k \le 27$, $-43 \le l \le 42$	$-14 \le h \le 14$, $-14 \le k \le 15$, $-15 \le l \le 19$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-16 \le l \le 17$
Reflections collected	103711	27525	18282
Independent reflections	26087 [R_{int} = 0.0355, R_{sigma} = 0.0301]	8656 [R_{int} = 0.0577, R_{sigma} = 0.0445]	6159 [R_{int} = 0.0209, R_{sigma} = 0.0161]
Data/restraints/parameters	26087/132/1525	8656/0/461	6159/0/384
Goodness-of-fit on F^2	1.019	1.073	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0397, wR_2 = 0.1028	R_1 = 0.0745, wR_2 = 0.2096	R_1 = 0.0325, wR_2 = 0.0850
Final R indexes [all data]	R_1 = 0.0445, wR_2 = 0.1059	R_1 = 0.0813, wR_2 = 0.2177	R_1 = 0.0331, wR_2 = 0.0855
Largest diff. peak/hole / e $Å^{-3}$	1.53/-1.94	2.06/-1.74	0.76/-0.89

Table S2 ^{13}C NMR data of the polyethylene sample produced using **Ni4**/$EtAlCl_2$ at 30 °C (run 3, Table 3).

Peak no.	Chemical shift (ppm)	Experimental integration	Peak no.	Chemical shift (ppm)	Experimental integration
1	11.31	0.1	18	30.48	1.4
2	14.27	1	19	31.68	0
3	14.77	0.54	20	32.23	0.97
4	19.86	0.12	21	32.72	0.44
5	20.12	3.29	22	33.22	2.4
6	20.33	0	23	33.57	0.42
7	22.93	0.77	24	33.83	0
8	23.42	0	25	34.01	0.63
9	24.67	0	26	34.5	0.97
10	26.72	0.3	27	34.87	0.5
11	27.26	1.72	28	36.94	0
12	27.44	5.74	29	37.55	6.8
13	27.83	0.73	30	37.86	0
14	29.53	1.24	31	38.11	0.42
15	29.61	2.62	32	38.37	0
16	30	126.51	33	39.62	0
17	30.38	6.68			

Table S3 Branching analysis for the polyethylene sample produced using **Ni4**/$EtAlCl_2$ at 30 °C (run 3, Table 3) [S5].

Branching content		Relative percentage (%)
N_M	7.715	67.97
N_E	0.33	2.90
N_P	0.64	5.64
N_B	0.5	4.40
N_A	0	0
$N_{M(1,4)}$	0.75	6.61
$N_{M(1,5)}$	0	0
$N_{M(1,6)}$	0.435	3.83
N_L	0.98	8.63
$N_{L(1,4)}$	0	0
[E]	105.475	
[R]	11.35	100 %
Total branches		**48/1000 Cs %**
Methyl branches		78.41
Ethyl branches		2.91
Propyl branches		5.64
Butyl branches		4.41
Amyl branches		0
Longer branches		8.63

Table S4 ^{13}C NMR data of the polyethylene sample with **Ni4**/MMAO at 30 °C (run 3, Table 4).

Peak no.	Chemical shift (ppm)	Experimental integration	Peak no.	Chemical shift (ppm)	Experimental integration
1	11.34	0.23	18	30.49	4.06
2	14.29	1	19	31.68	0
3	14.77	0	20	32.24	0.9
4	19.86	0	21	32.72	0
5	20.13	5.46	22	33.22	4.29
6	20.33	0	23	33.52	0.68
7	22.94	0.94	24	33.83	0
8	23.42	0	25	34.01	0.79
9	24.67	0	26	34.49	3.32
10	26.7	0.21	27	34.85	0.63
11	27.25	3.98	28	36.94	0.85
12	27.44	10.81	29	37.54	11.22
13	27.83	0.94	30	37.86	0
14	29.53	1.3	31	38.1	0.68
15	29.62	2.77	32	38.37	0
16	30	174.11	33	39.62	0.18
17	30.38	10.66		-	-

Table S5 Branching analysis for the polyethylene sample produced using **Ni4**/MMAO at 30 °C (run 3, Table 4) [S5].

Branching content		Relative percentage (%)
N_M	10.0125	75.61
N_E	0.13	0.98
N_P	0.85	6.42
N_B	0.395	2.98
NA	0	0
$N_{M(1,4)}$	0.485	3.66
$N_{M(1,5)}$	0	0
$N_{M(1,6)}$	0.47	3.55
N_L	0.9	6.80
$N_{L(1,4)}$	0	0
[E]	86.6	
[R]	13.2425	100%
Total branches		**66/1000 Cs**
Methyl branches		82.82
Ethyl branches		0.98
Propyl branches		6.42
Butyl branches		2.98
Amyl branches		0
Longer branches		6.80

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