Supporting information

Thermostability promotion of α-diimine nickel precatalysts tailored with 2,6-bis(bis(4-fluorophenyl)methyl)-3,4,5-trimethoxyaniline for PE elastomer synthesis

Zexu Hu,[a,b] Geng Ren,[b] Qaiser Mahmood,[b,*] Zhixin Yu,[a,*] Yizhou Wang,[c] Kainat Fatima Tahir,[b,c] Song Zou,[c] Tongling Liang,[c] Wen-Hua Sun [b,c,*]

[a] School of Pharmaceutical Sciences, Changchun University of Chinese Medicine, Changchun 130117, China
[b] Chemistry and Chemical Engineering Guangdong Laboratory, Shantou 515031, China
[c] Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Contents

1. General considerations

All manipulations involving air and/or moisture sensitive compounds were performed under an atmosphere of nitrogen using standard Schlenk techniques. Toluene was dried over sodium and distilled under nitrogen atmosphere prior to use. Methylaluminoxane (MAO, 1.67 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Anhui Botai Electronic Materials Co. Dimethylaluminum chloride (Me$_2$AlCl, 0.9 M in heptane) and diethylaluminum chloride (Et$_2$AlCl, 2.0 M in hexane) were supplied from Shanghai Macklin Biochemical Co., Ltd. Ethylaluminium sesquichloride (EASC, 0.87 M in n-hexane) were purchased from Acros Chemicals. High-purity ethylene was purchased from Guangdong Jieyang Petrochemical Company and used as received. Acenaphthylene-1,2-dione was bought from Macklin with 98% purity, 3,4,5-Trimethoxyaniline was bought from Leyan with purity ≥ 97%. Bis(4-fluorophenyl)methanol for the synthesis of bulky aniline was also obtained from Leyan with 99.68% purity. All common anilines (Ar = 2,6-Me$_2$C$_6$H$_3$, 2,6-Et$_2$C$_6$H$_3$, 2,6-iPr$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$ and 2,6-Et$_2$-4-MeC$_6$H$_2$) were obtained from, Heowns and Macklin with 98% purity. ZnCl$_2$ used as catalyst during the synthesis of bulky aniline was obtained from Macklin with 98% purity. (DME)NiBr$_2$ with 97% purity was obtained from Leyan. *p*-Toluenesulfonic acid monohydrate used as catalysts during synthesis of ligands was obtained from Dingjiuding Chemicals with 98% purity. Toluene was obtained from Xihua, with purity ≥ 99.5 with H$_2$O% ≤ 0.03% which was distilled over sodium before use. Other reagents were purchased from Aldrich, Acros or local suppliers. 2,6-bis(bis(4-fluorophenyl)methyl)-3,4,5-trimethoxyaniline was prepared using the literature route [1]. ^{1}H, ^{13}C and ^{19}F NMR spectroscopic measurements for the organic compounds were performed using a Bruker AVANCE III 600WB spectrometer at 599.92 MHz with 1024 and 16 scans respectively. Operating conditions used for ^{13}C and ^{1}H spectra: spectral width 15.0 kHz; acquisition time 2.1845 s; relaxation delay 2.0 s. Chemical shifts are measured in ppm for the ^{1}H, ^{13}C and ^{19}F NMR spectra and are relative to TMS as an internal standard. Elemental analyses were conducted on a Flash EA 1112 microanalyzer. FT-IR spectra were carried out using a PerkinElmer System 2000 FT-IR spectrometer. The sample is grinded with KBr to prepare a homogeneous KBr pellet for scanning. The concentration of the sample in KBr was maintained in the range of 0.2% to 1%. The frequency ranges were measured as wave numbers typically over the range 4000–400 cm^{-1} using, OMNIC software. Molecular weights

(M_w) and molecular weight distributions ($Đ$) of the polyethylenes were determined using a PL-GPC220 instrument at 150 °C with 1,2,4-trichlorobenzene as the solvent. The flow rate of TCB was kept at 1.00 ml/min with injection volume 200.0 μl and column length was settled at 650 mm. The columns used has specifications 2 × PLgel MIXED-B 10μm 300 × 7.5 mm. Sample concentration was kept at 0.1 mg/ml. Narrow standards for calibration were used. The melting temperatures of the polyethylenes were measured from the second scanning run on a PerkinElmer TA-Q2000 DSC analyzer under a nitrogen atmosphere. In the procedure, a sample of about 4.0–6.0 mg was heated to 150 °C at a heating rate of 20 °C min^{-1} and kept for 5 min at 150 °C to remove the thermal history and then cooled at a rate of 20 °C min^{-1} to 25 °C. The ^{1}H NMR spectra of the polyethylenes were recorded on a Bruker DMX 300 MHz instrument at 110 °C and ^{13}C at 110 °C in deuterated tetrachloroethane with TMS as an internal standard and peaks were integrated using deconvolution method. Operating conditions used for ^{1}H spectra: spectral width 15 kHz; acquisition time 2.1889 s; relaxation delay 2.0 s. Operating conditions used for ^{13}C spectra: spectral frequency 125.70 MHz; pulse width 10.0 Ms; spectral width 21.3675 kHz; acquisition time 0.7668 s; relaxation delay 5.0 s; number of scans 2048.The chemical shift values (δ) are reported in parts per million (ppm), while the coupling constants (J) are expressed in Hertz(Hz). The stress–strain curves were obtained using a universal tester (Instron 1122, UK). Polyethylene samples for stress-strain and strain recovery tests were prepared as thin films (1 mm thick) by melting polyethylene at 200 °C under constant pressure. For stress-strain measurements, the films were cut into rectangular shapes with dimensions of 5 mm in width, 1 mm in thickness, and 30 mm in length. For strain recovery tests, the samples measured 2.5 mm in width, 1 mm in thickness, and 15 mm in length. In the stress-strain test, the stress was applied at a constant rate of 50 mm/min until the sample broke at maximum stress and elongation. For stress-strain hysteresis experiments, the stress was applied at a constant rate of 50 mm/min for ten cycles at a fixed strain of 300%. All tests were performed at room temperature. Each stress-strain measurement was repeated three times, and each strain recovery test was repeated twice.

2. X-ray crystallographic studies

The single-crystal X-ray diffraction analysis of **Ni-Me$_2$** and **Ni-Et$_2$Me** complexes were conducted using a Rigaku Sealed Tube CCD (Saturn 724+) diffractometer, Japan. The diffractometer employed graphite-monochromated Cu-Kα radiation with a

wavelength (λ) of 0.71073 Å. The measurements were performed at a temperature of 170 ($\pm$10) K. The cell parameters were determined by globally refining the positions of all collected reflections. The intensities obtained from the X-ray diffraction analysis were corrected for Lorentz and polymerization effects; an empirical absorption correction was carried out as well. The structures of complexes **Ni-Me$_2$** and **Ni-Et$_2$Me** were identified via direct methods and further refined via full-matrix least squares fitting on F2. The non-hydrogen atoms in each complex were refined anisotropically. The positions of all hydrogen atoms were determined based on calculated positions. The structural solution and refinement for each complex were carried out using SHELXT (Sheldrick) software.[2] The crystal data and processing parameters for **Ni-Me$_2$** and **Ni-Et$_2$Me** are presented in Table S2.

3. Typical procedure for ethylene polymerization

The polymerization process at 1MPa ethylene pressure was conducted in a 250 mL stainless steel autoclave equipped with an ethylene pressure control system, a mechanical stirrer, and a temperature controller. Initially, the autoclave was dried, then purged twice with nitrogen and once with ethylene under reduced pressure to ensure an inert environment. Then, the complex (2.0 μmol) was dissolved in 30 mL of toluene and injected into the autoclave at the required reaction temperature. An additional 30 mL of toluene was added for washing purposes. Next, the appropriate amount of co-catalyst (MAO, MMAO, Me$_2$AlCl, Et$_2$AlCl, EASC) and more toluene were added successively to reach a total volume of 100 mL. The autoclave was immediately pressurized with 1 MPa of ethylene, and stirring was initiated. After the desired reaction time, the ethylene pressure was released, and the reaction was quenched by adding 10% hydrochloric acid in ethanol. The resulting polymer was collected, washed with ethanol, dried under reduced pressure at room temperature, and then weighed.

4. Effect of Al/Ni, temperature, time, ethylene pressure using Ni-Me$_2$/MMAO catalytic system

In order to find the optimal Al/Ni ratio, polymerization tests were conducted using MMAO as a cocatalyst at varying Al/Ni ratios of 1000, 1250, 1500, 1750, 2000, 2250 and 2500 under otherwise identical reaction conditions (temperature = 30 °C, time = 30 min, pressure = 1 MPa). According to the polymerization results in entries 1-6 (Table S1), it was found that the maximum activity of 5.9×10^6 g mol^{-1} h^{-1} was achieved at an Al/Ni molar ratio of 1750 (Table S1, entry 4). Deviation from this

concentration led to lower catalytic activities.[3,4] In addition, the molecular weight of the polymer decreases with the increase of the Al/Ni molar ratio, which may be due to the increased chain transfer from active species to aluminum compounds, resulting in the production of short-chain polymers (Table S1, entries 1-6).[5] After selecting the optimal amount of cocatalyst using **Ni-Me$_2$**, the effect of temperature on the polymerization reaction was studied, as shown in Table S1 (entries 4, 7-10). For this, polymerization reactions were conducted at 40 °C, 60 °C, 80 °C, and 100 °C using the optimal cocatalyst amount of 1750 (time = 30 min, pressure = 1 MPa). The experimental results showed that catalytic activity and polymer molecular weights both gradually decreased with the rise in temperature. The decrease in activity may be due to the gradual deactivation of active species under the influence of high temperature, leading to decreased activity.[5] On the other hand, high temperature may reduce the solubility of ethylene monomers in the solvent.[6] It is worth mentioning that even when the polymerization reaction was carried out at the high temperature of 100 °C, the active species of **Ni-Me$_2$** still exhibited an activity of 0.5 × 10^6 g mol^{-1} h^{-1} (Table S1, entry 10). In addition, the gradual decrease in molecular weights with temperature may be due to the higher temperature causing a high rate of chain transfer reactions, leading to a consistent decrease in polymer molecular weights.[7] To examine the lifetime of active species, polymerization tests were conducted for 5 min, 10 min, 15 min, 45 min, and 60 min under fixed optimal conditions (Al/Ni = 1750, temperature = 30 °C, pressure = 1 MPa), as shown in Table S1 (entries 4, 11-15). For 5 min of reaction, the polymer activity reached its maximum value of 21.96 × 10^6 g mol^{-1} h^{-1} (Table S1, entry 11), indicating a short induction period.[8] As the reaction time prolonged, the catalytic activity gradually decreased. When the polymerization time reached 60 min, the activity of the polymer dropped to its minimum value of 4.79 × 10^6 g mol^{-1} h^{-1} (Table S1, entry 15), which is the result of the gradual decomposition of the nickel metal catalyst over time. However, the polymer still possesses high activity, indicating that this catalytic system has high stability at the optimal Al/Ni molar ratio and temperature. Additionally, the molecular weight of the polymer increases with the prolongation of polymerization time due to lower chain transfer reactions at extended reaction times. Next, the effect of ethylene pressure was studied (Al/Ni = 1750, temperature = 30 °C, time = 30 min). Ethylene polymerization experiments were conducted using pressures of 0.1 MPa, 0.5 MPa and 1 MPA (entries 4, 16-17). When the ethylene pressure

increased from 0.1 MPa to 0.5 MPa, the activity increased from 2.89×10^6 g mol^{-1} h^{-1} to 4.18×10^6 g mol^{-1} h^{-1} and then to 5.9×10^6 g mol^{-1} h^{-1} at 1 MPa. This is due to the high rate of monomer insertion leading to high activity.[9] The polymer molecular weights gradually improve with ethylene pressure. The mass distributions under all reaction conditions were narrow, ranging from 1.7 to 2.6 (Figure S1). Moreover, polymer melt temperatures decreased with an increase in cocatalyst concentration and reaction temperature, while melt temperatures increased with prolonged time and ethylene pressure.
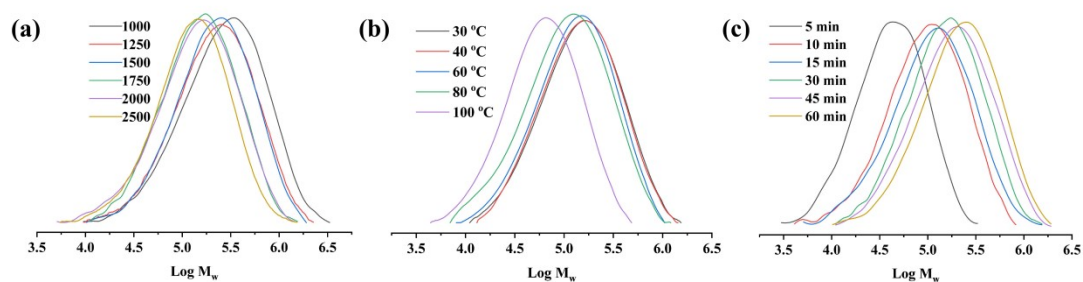
Figure S1: GPC curves (a) at different ratio (b) at different temperatures (c) at different times (entries 1-15 in Table S1).

Table S1. Effect of co-catalyst amount, temperature, time, ethylene pressure, ligand structure on ethylene polymerization using MMAO cocatalyst.[a]

Entry	T (ºC)	t (min)	Al/Ni	PE (g)	Act $(10^6)^b$	$M_w (10^5)^c$	$Đ^c$	T_m^d (°C)
1	30	30	1000	4.8	4.8	4.0	2.5	106.9
2	30	30	1250	5.0	5.0	3.2	2.3	106.6
3	30	30	1500	5.7	5.7	3.0	2.2	105.2
4	30	30	1750	5.9	5.9	2.1	2.1	94.4
5	30	30	2000	4.9	4.9	2.1	2.3	82.7
6	30	30	2500	4.3	4.3	1.8	2.1	81.6
7	40	30	1750	4.6	4.6	2.1	2.2	86.5
8	60	30	1750	3.1	3.1	1.8	2.0	76.7
9	80	30	1750	2.1	2.1	1.6	2.3	76.4
10	100	30	1750	0.5	0.5	0.8	1.9	72.9
11	30	5	1750	3.7	22.0	0.6	1.9	78.0
12	30	10	1750	5.1	15.4	1.4	2.3	80.6

13	30	15	1750	5.5	10.9	1.7	2.4	82.3
14	30	45	1750	8.2	5.0	2.6	2.2	94.4
15	30	60	1750	9.6	4.8	3.0	2.2	96.0
16[e]	30	30	1750	2.9	2.9	1.4	2.6	80.0
17[f]	30	30	1750	4.2	4.2	1.7	1.7	81.7

[a]Conditions: cat. = 2.0 μmol; solvent = toluene; total volume = 100 mL; ethylene = 1 MPa; [b]activity unit = g mol^{-1} h^{-1}; [c]GPC results; M_w unit = g mol^{-1}; [d] DSC results; [e] ethylene: 0.1 MPa. [f] ethylene: 0.5 MPa.

5. ^{1}H/^{19}F/^{13}C NMR spectra of organic compounds
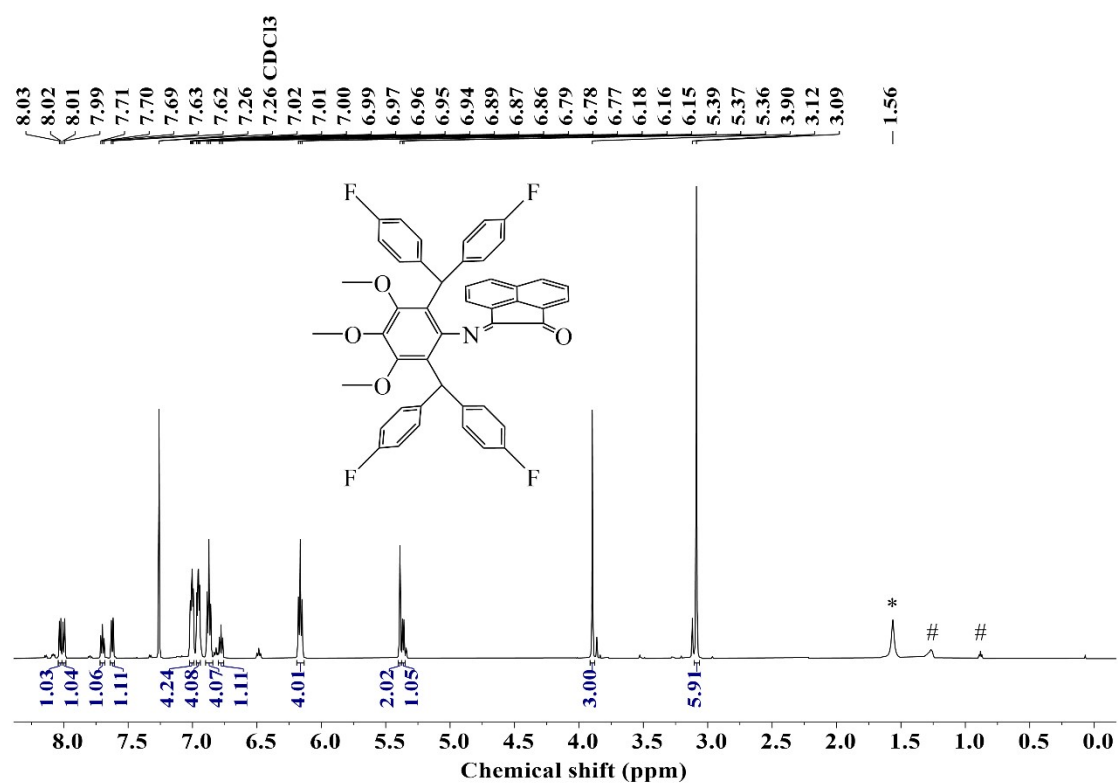
Figure S2. ^{1}H NMR spectrum (in CDCl$_3$) of imino-ketone [* is water and # is hexane].
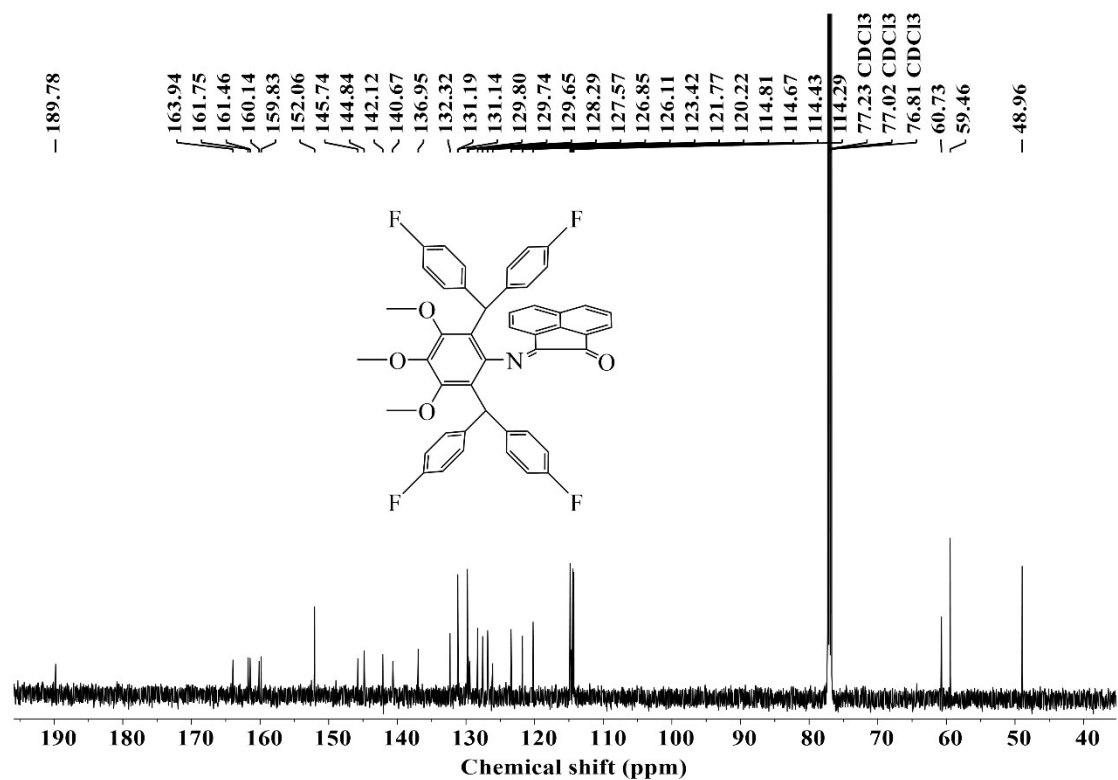
Figure S3. ^{13}C NMR spectrum (in $CDCl_3$) of imino-ketone.
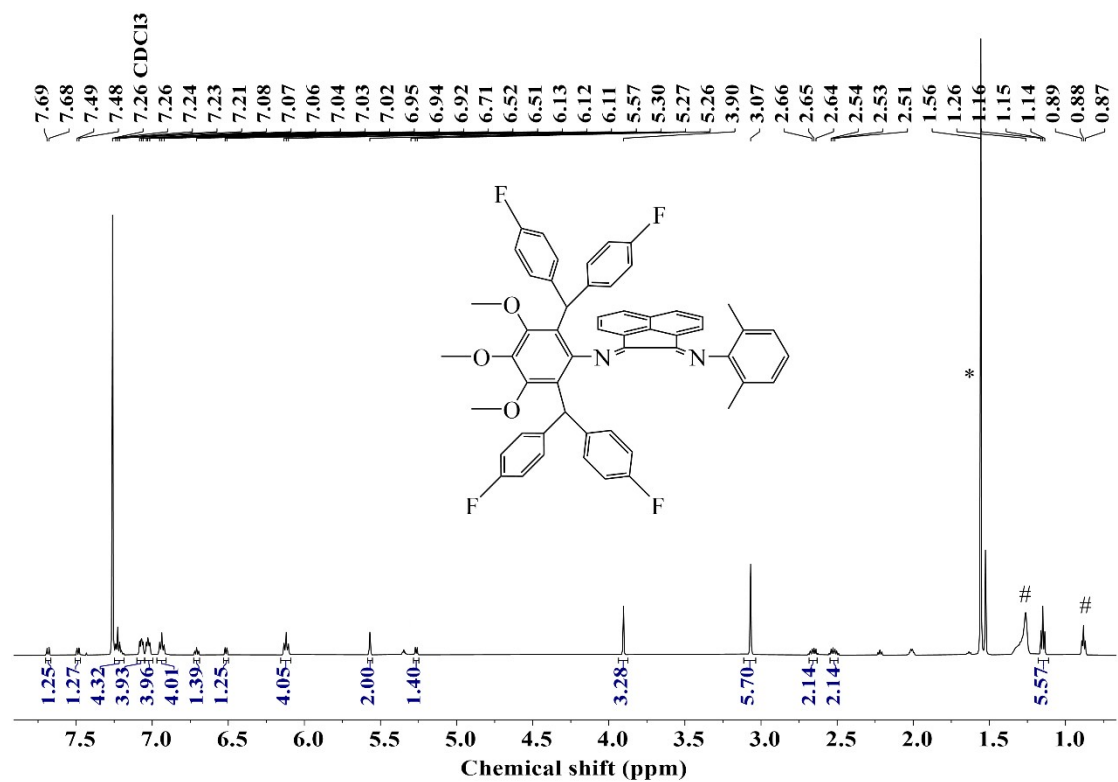
Figure S4. ^1H NMR spectrum (in $CDCl_3$) of **L-Me₂** [* is water and # is hexane].
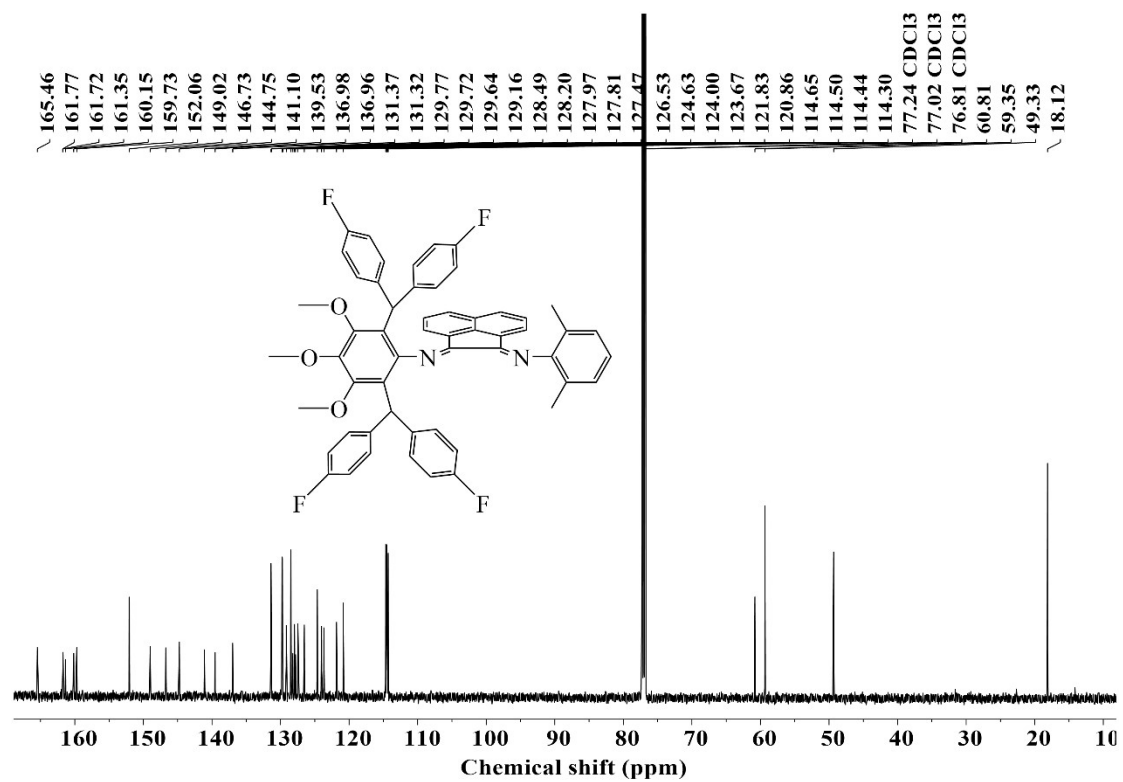
Figure S5. ^{13}C NMR spectrum (in CDCl$_3$) of **L-Me$_2$.**
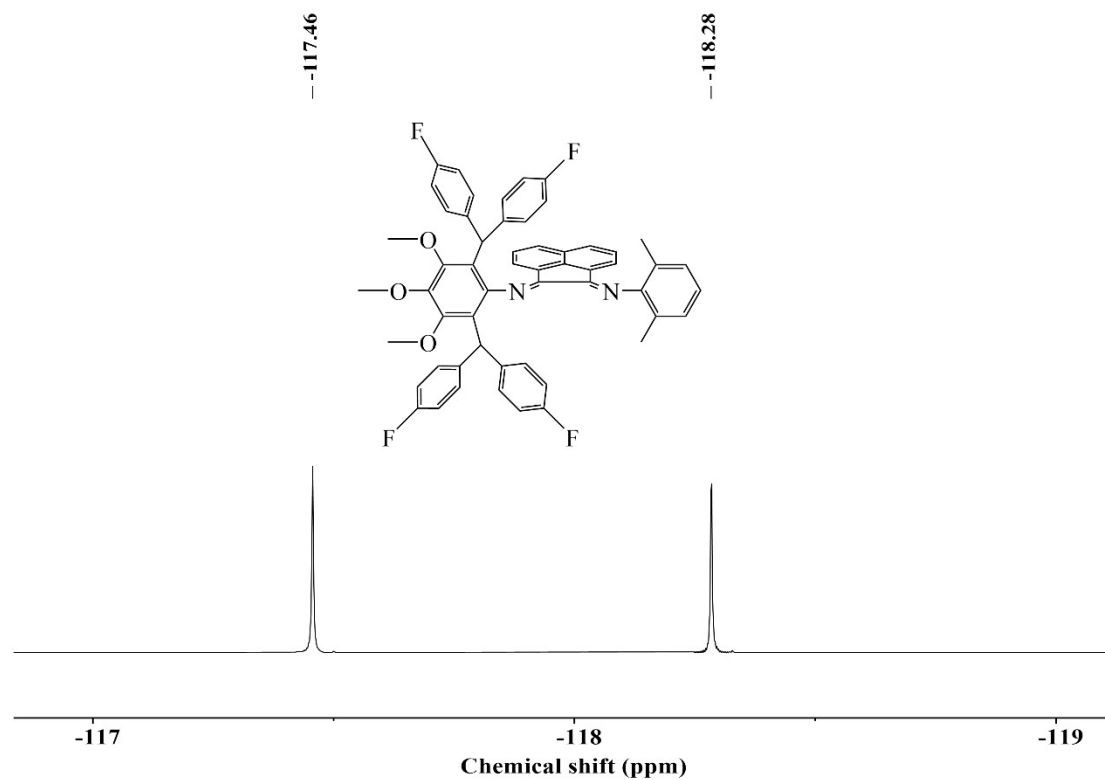
Figure S6. ^{19}F NMR spectrum (in CDCl$_3$) of **L-Me$_2$.**
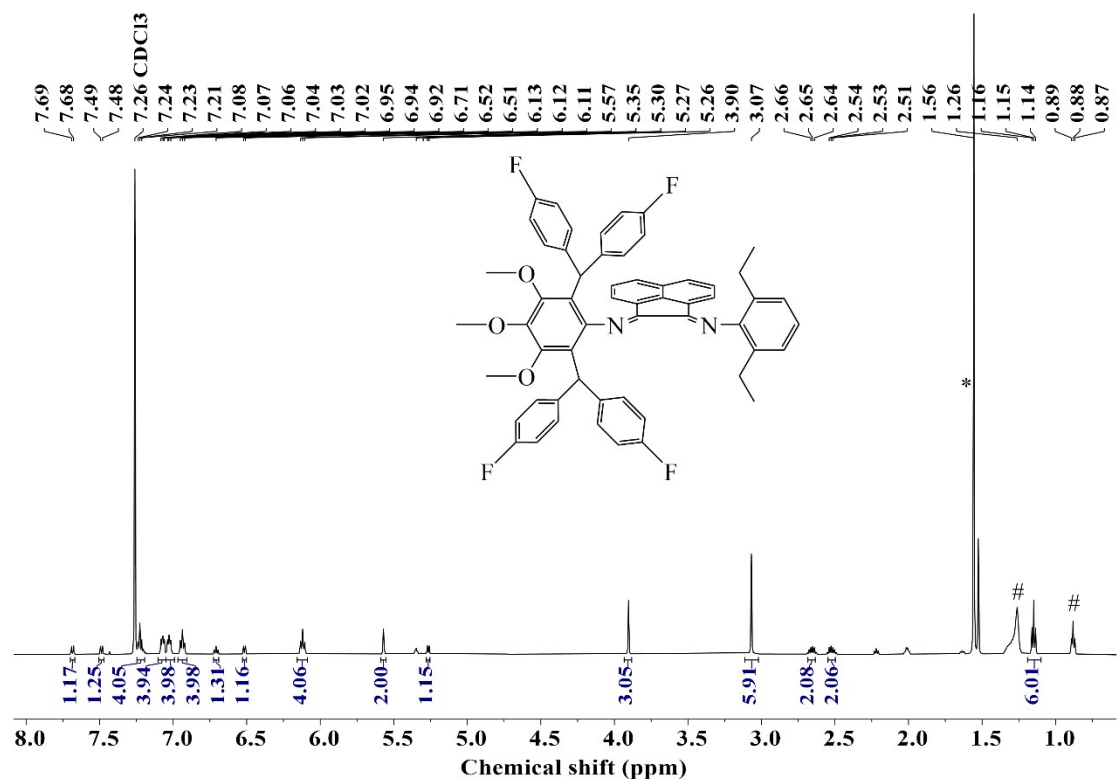
Figure S7 . ^{1}H NMR spectrum (in CDCl$_3$) of **L-Et$_2$** [* is water and # is hexane].
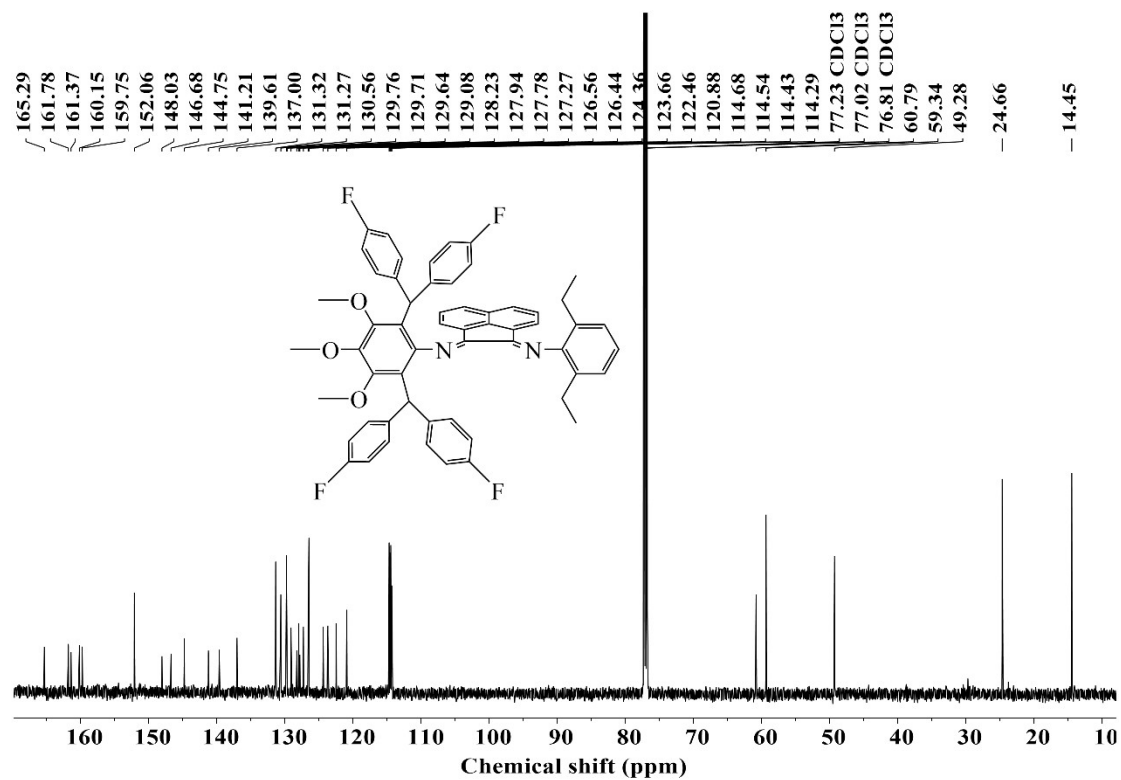
Figure S8. ^{13}C NMR spectrum (in CDCl$_3$) of **L-Et$_2$.**
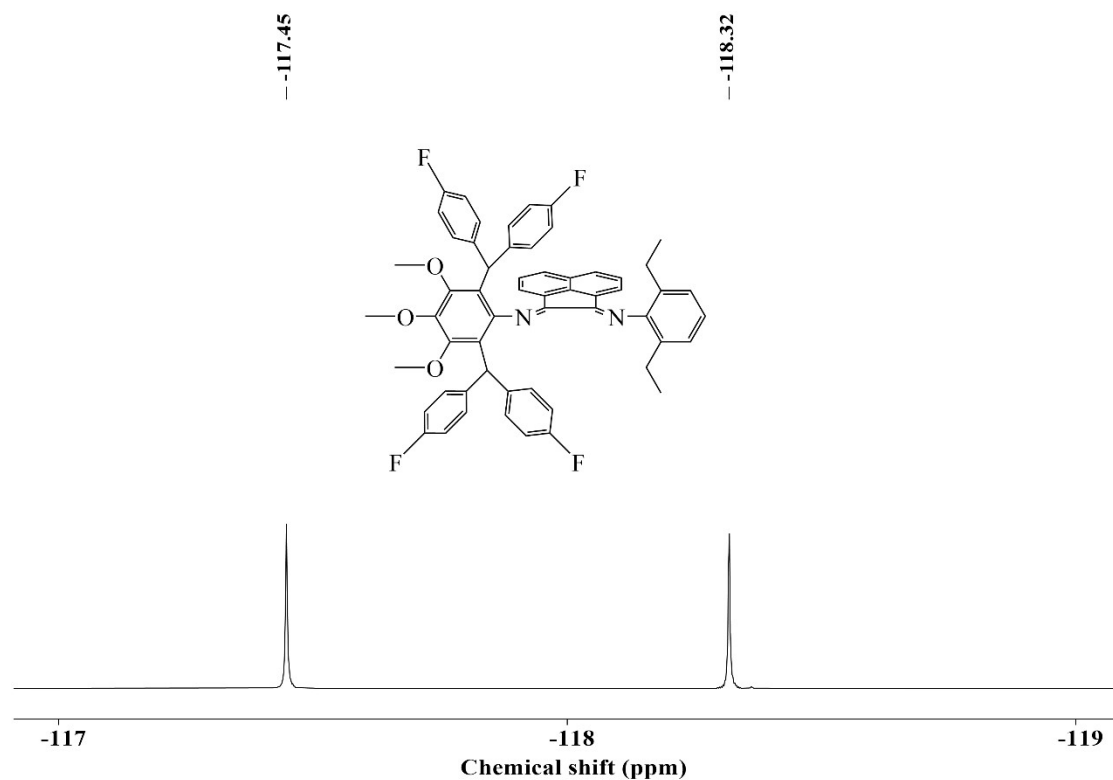
Figure S9. ^{19}F NMR spectrum (in CDCl$_3$) of **L-Et$_2$.**
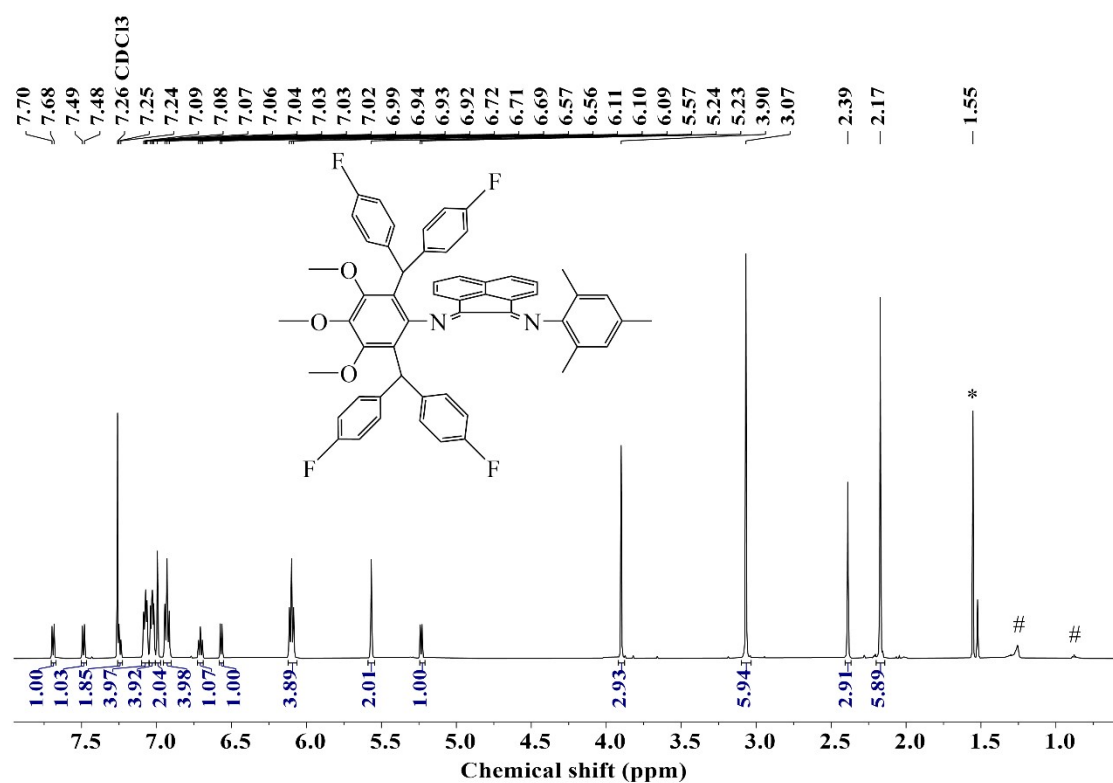
Figure S10. ^{1}H NMR spectrum (in CDCl$_3$) of **L-iPr$_2$** [* is water and # is hexane].
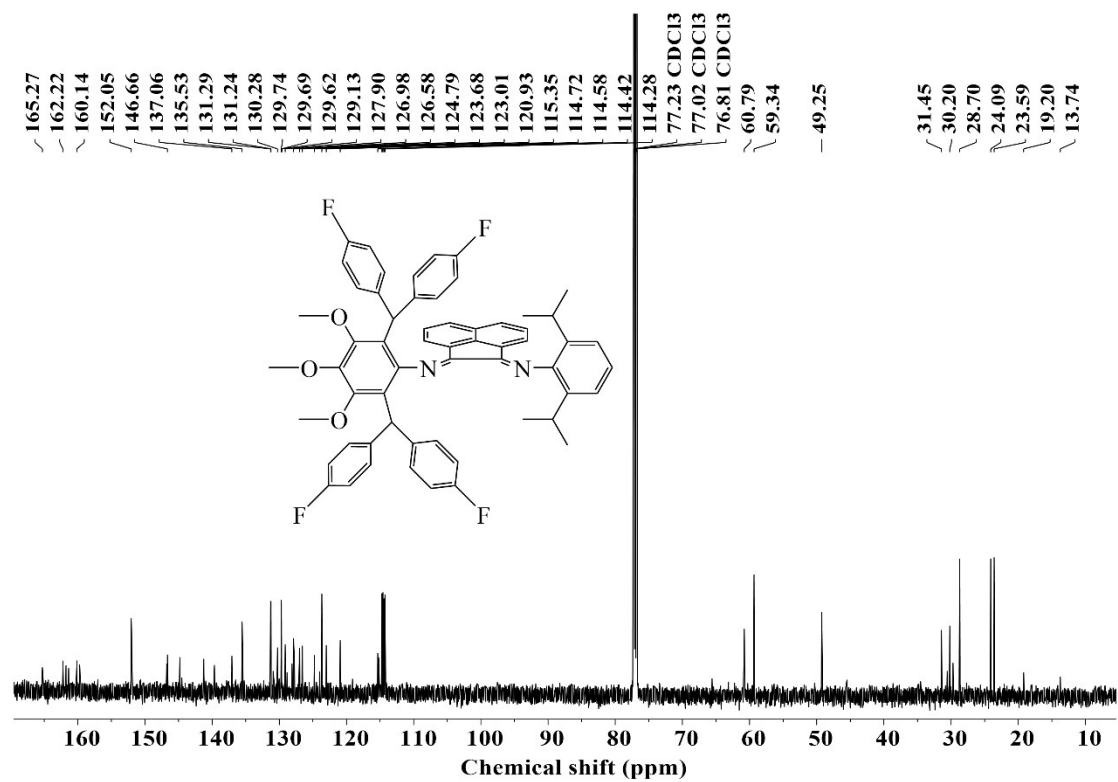
Figure S11. ^{13}C NMR spectrum (in CDCl$_3$) of L-iPr$_2$.
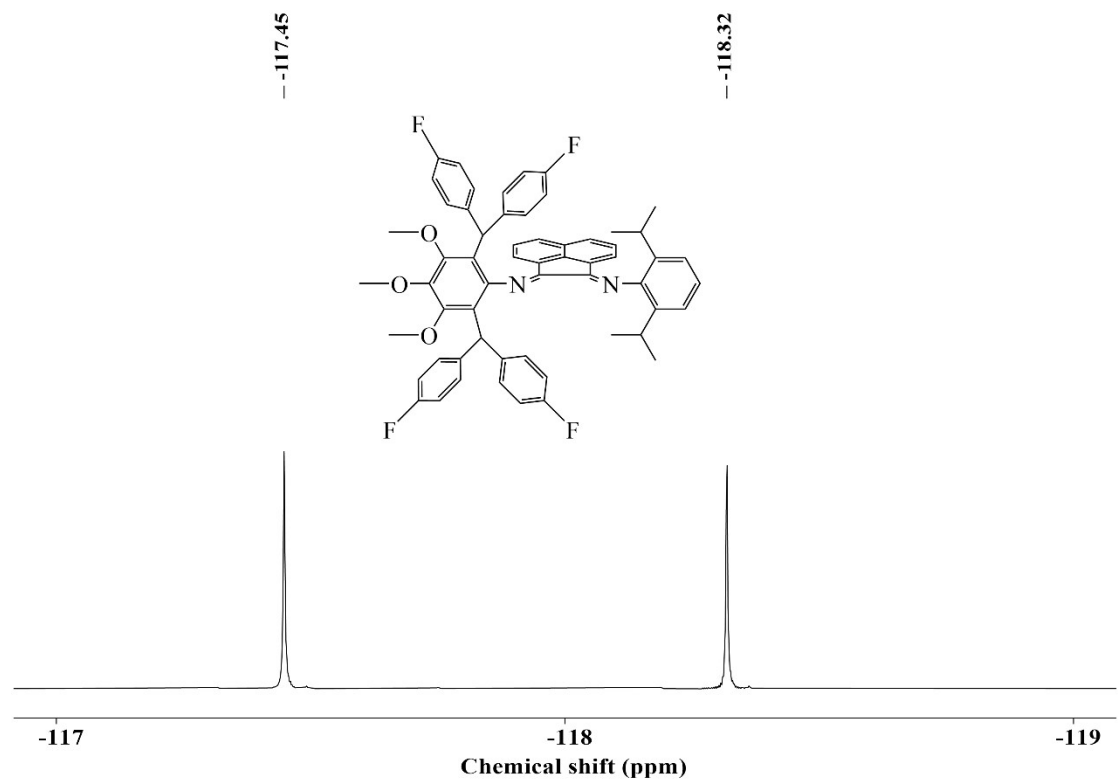
Figure S12. ^{19}F NMR spectrum (in CDCl$_3$) of L-iPr$_2$.
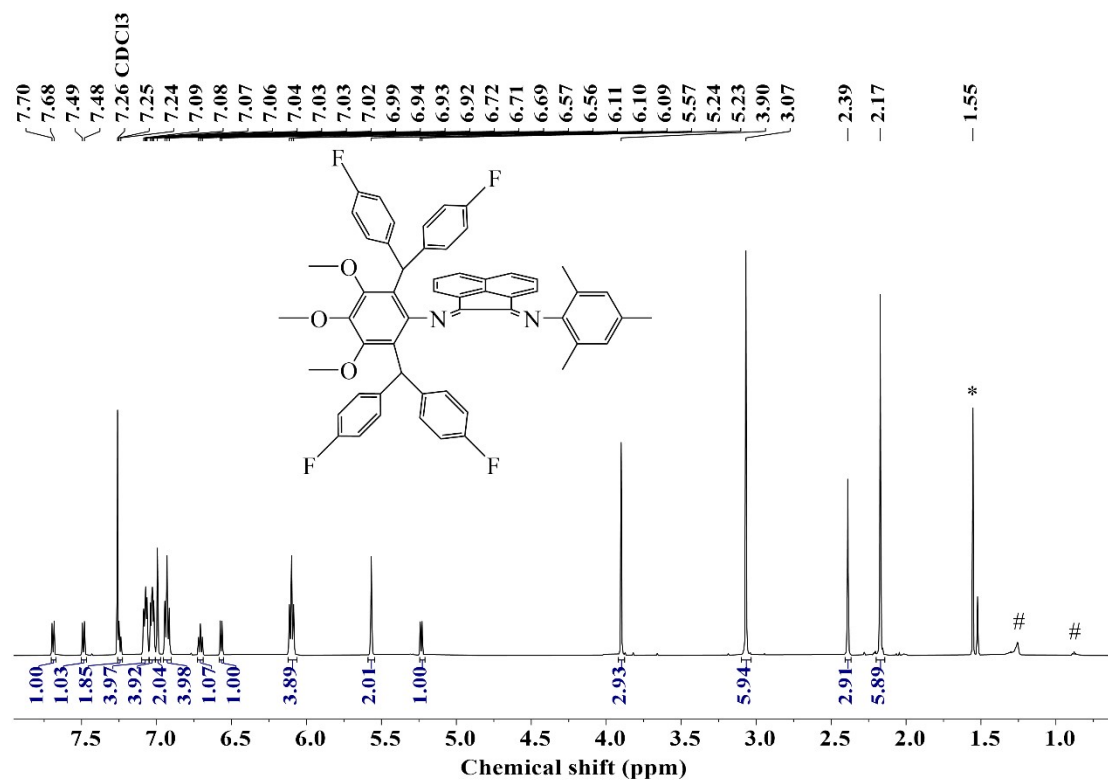
Figure S13. ^1H NMR spectrum (in CDCl$_3$) of **L-Me$_3$** [* is water and # is hexane].
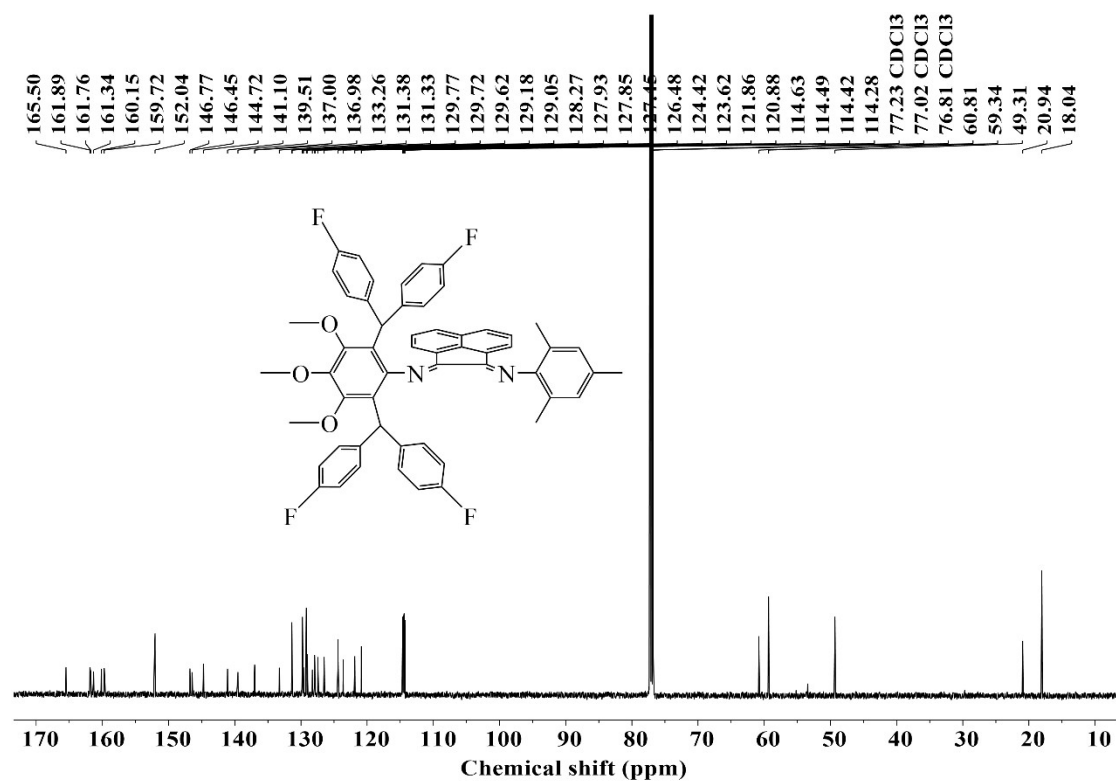
Figure S14. ^{13}C NMR spectrum (in CDCl$_3$) of **L-Me$_3$.**

Figure S15. ^{19}F NMR spectrum (in CDCl$_3$) of **L-Me$_3$.**

Figure S16. ^{1}H NMR spectrum (in CDCl$_3$) of **L-Et$_2$Me** [* is water and # is hexane].
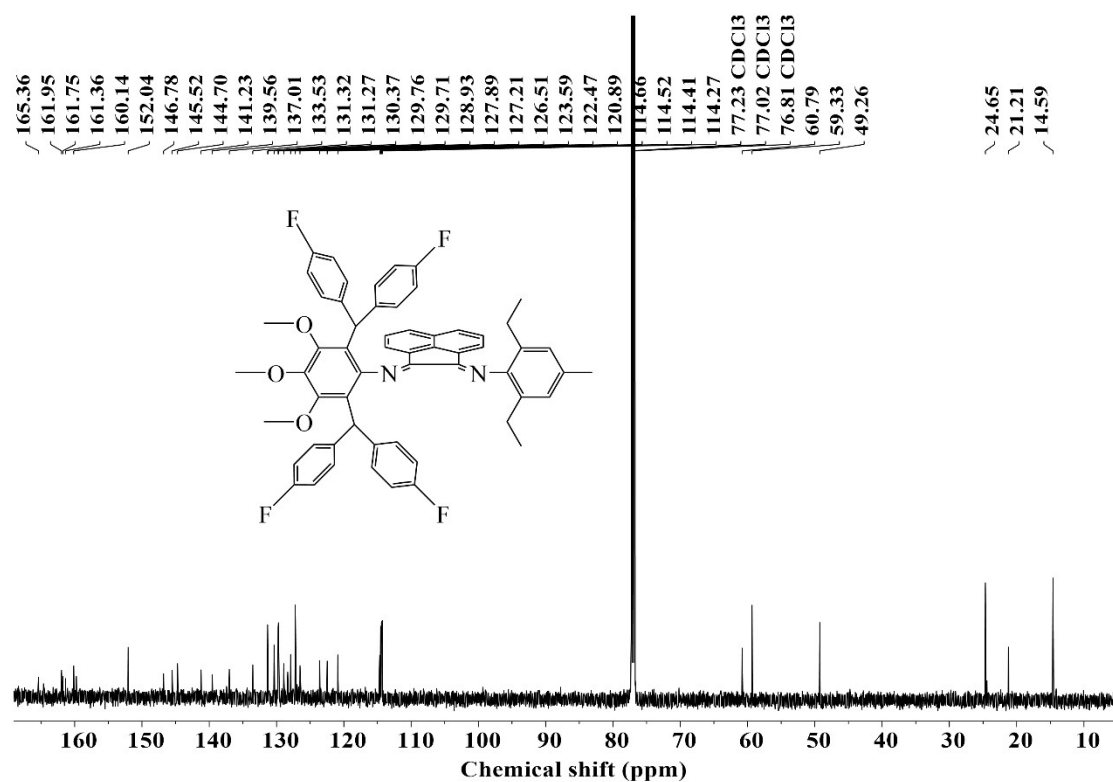
Figure S17. ^{13}C NMR spectrum (in CDCl$_3$) of **L-Et$_2$Me.**
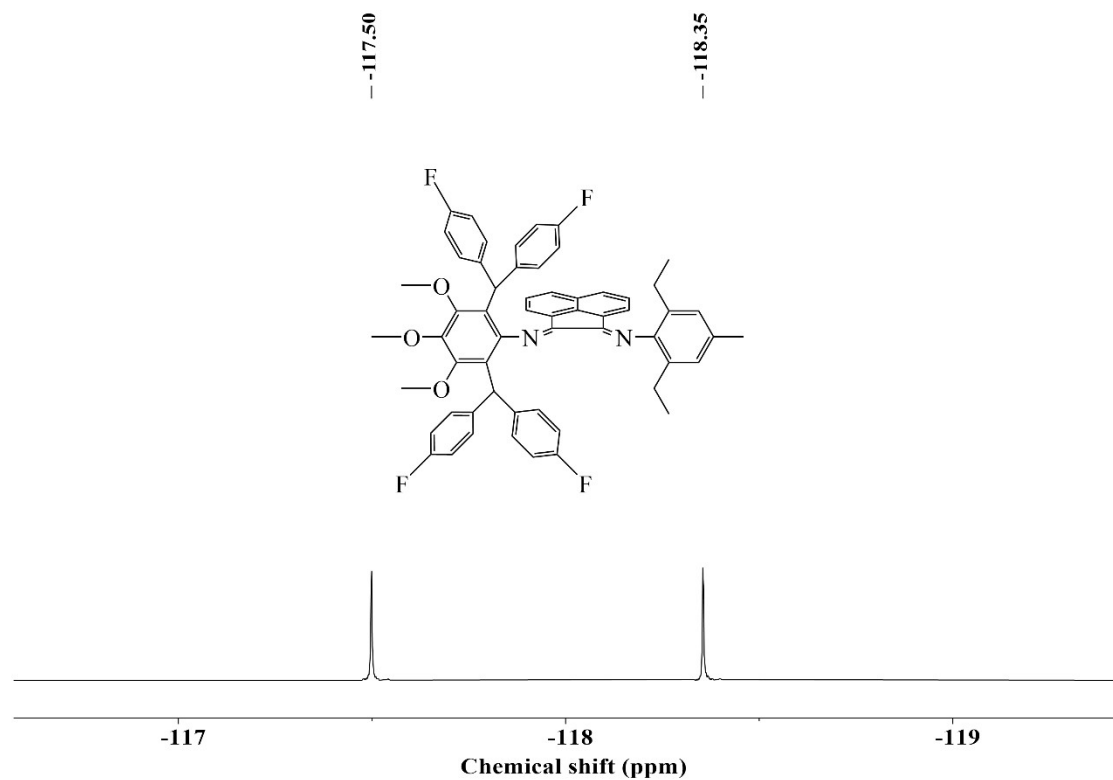
Figure S18. ^{19}F NMR spectrum (in CDCl$_3$) of **L-Et$_2$Me.**

6. ¹H NMR spectra of obtained polyethylene using different nickel complexes and different temperatures.
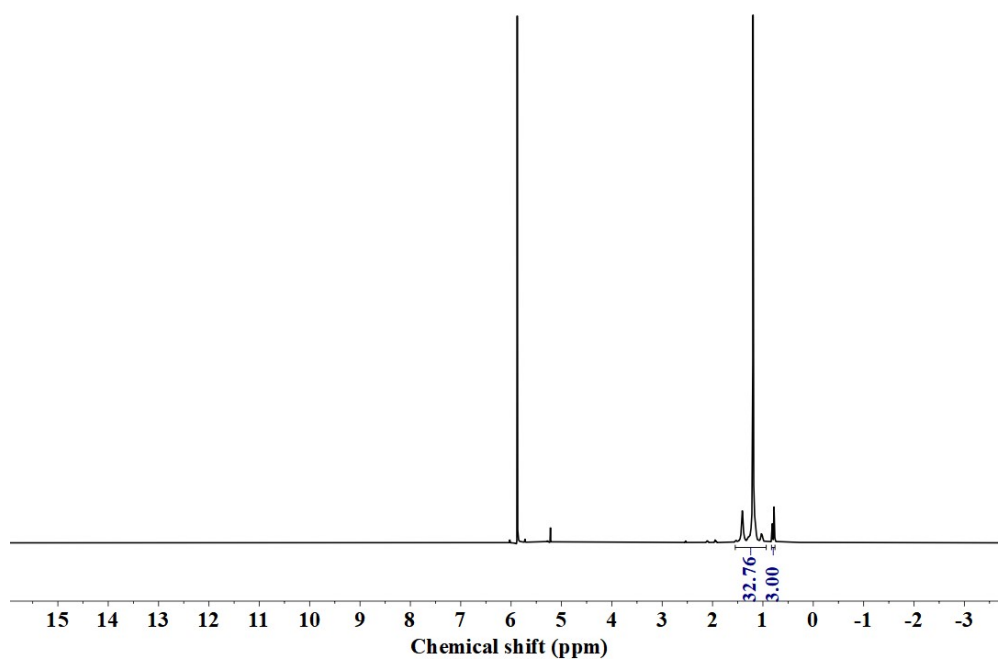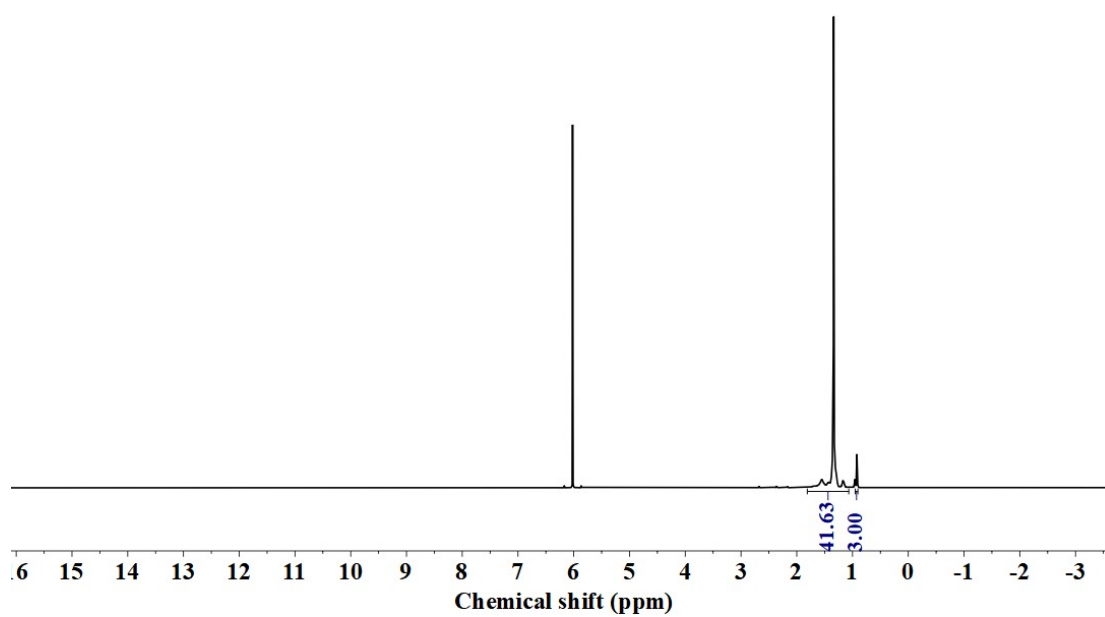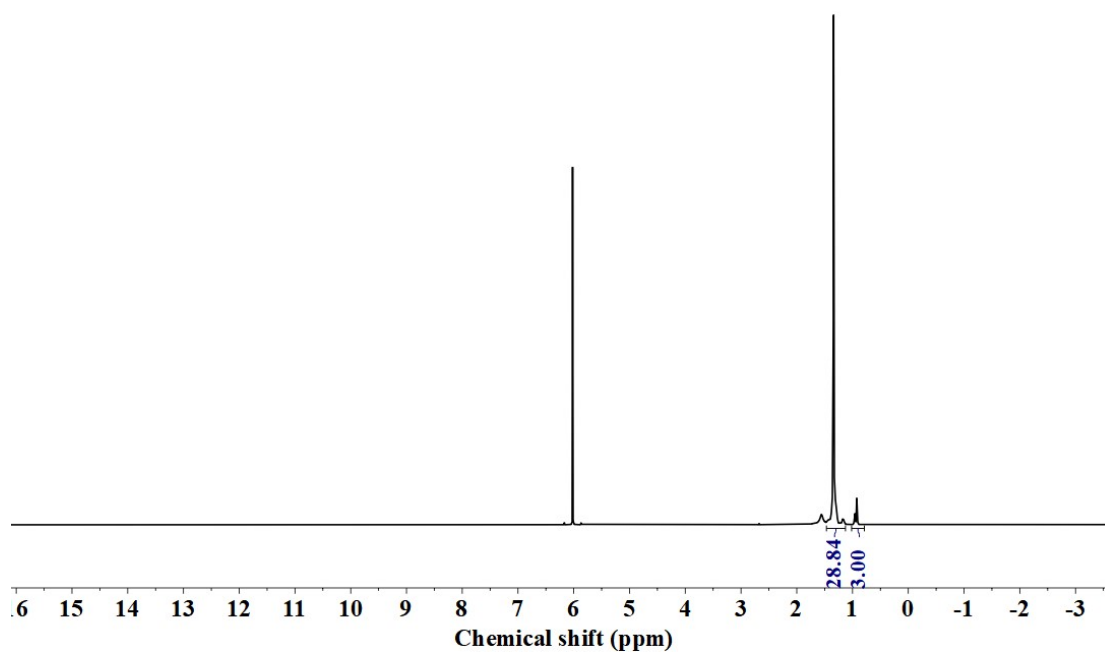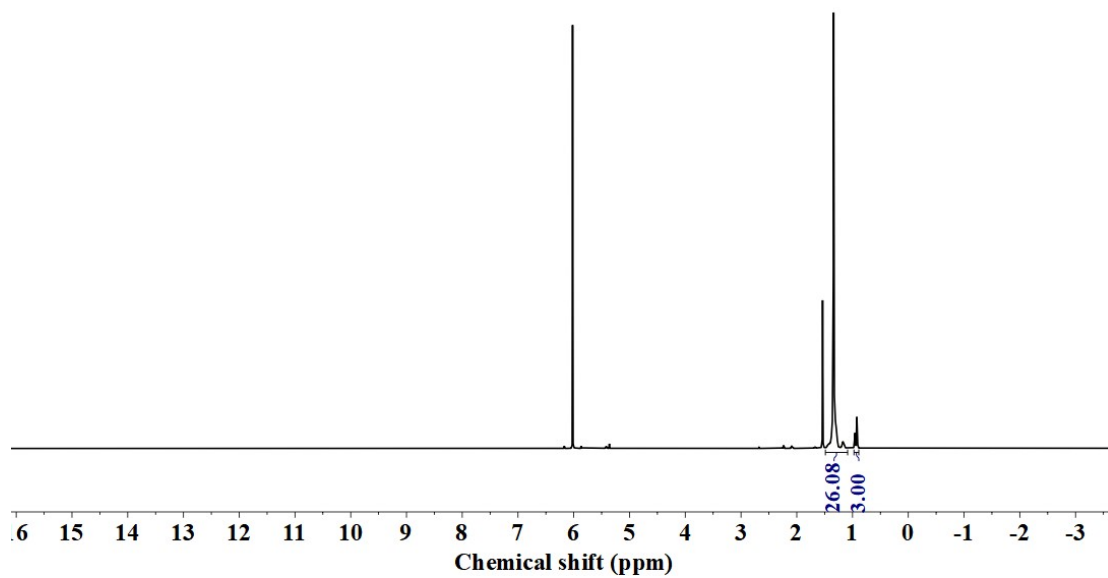

Figure S19. ¹H NMR spectrum of polyethylene produced using **Ni-Me₂/Et₂AlCl** (entry 1, Table 3).
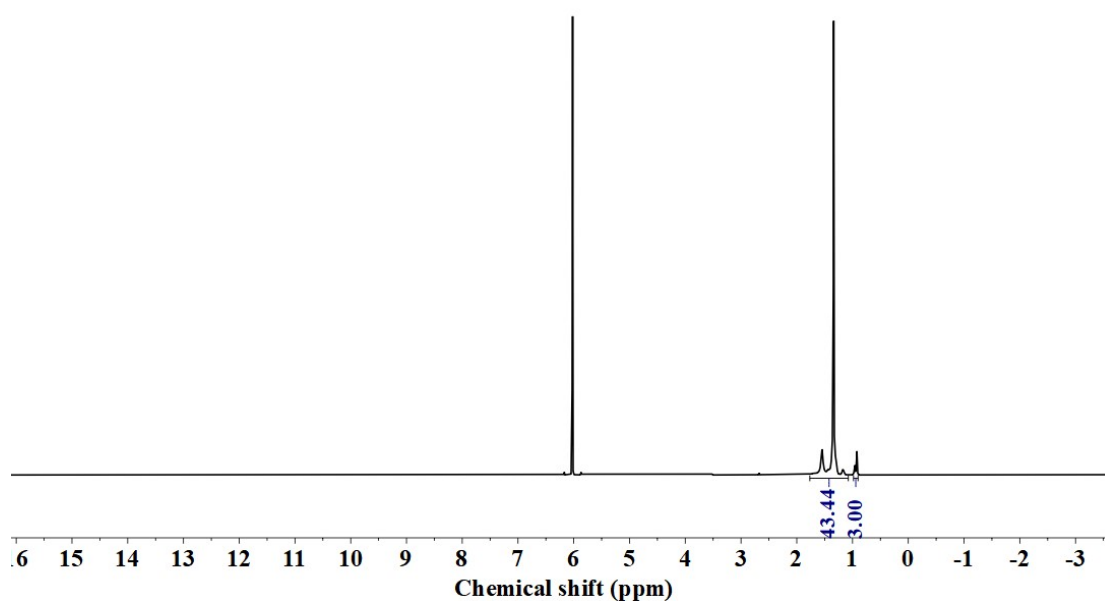
Figure S20. ¹H NMR spectrum of polyethylene produced using **Ni-Et₂/Et₂AlCl** (entry 2, Table 3).
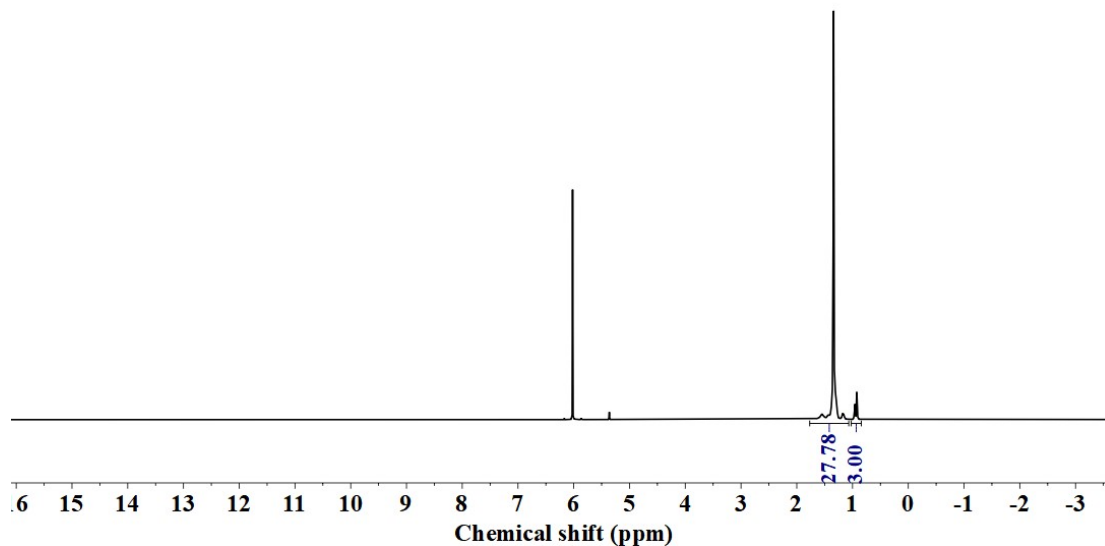
Figure S21. ^{1}H NMR spectrum of polyethylene produced using **Ni-iPr$_2$/Et$_2$AlCl** (entry 3, Table 3).
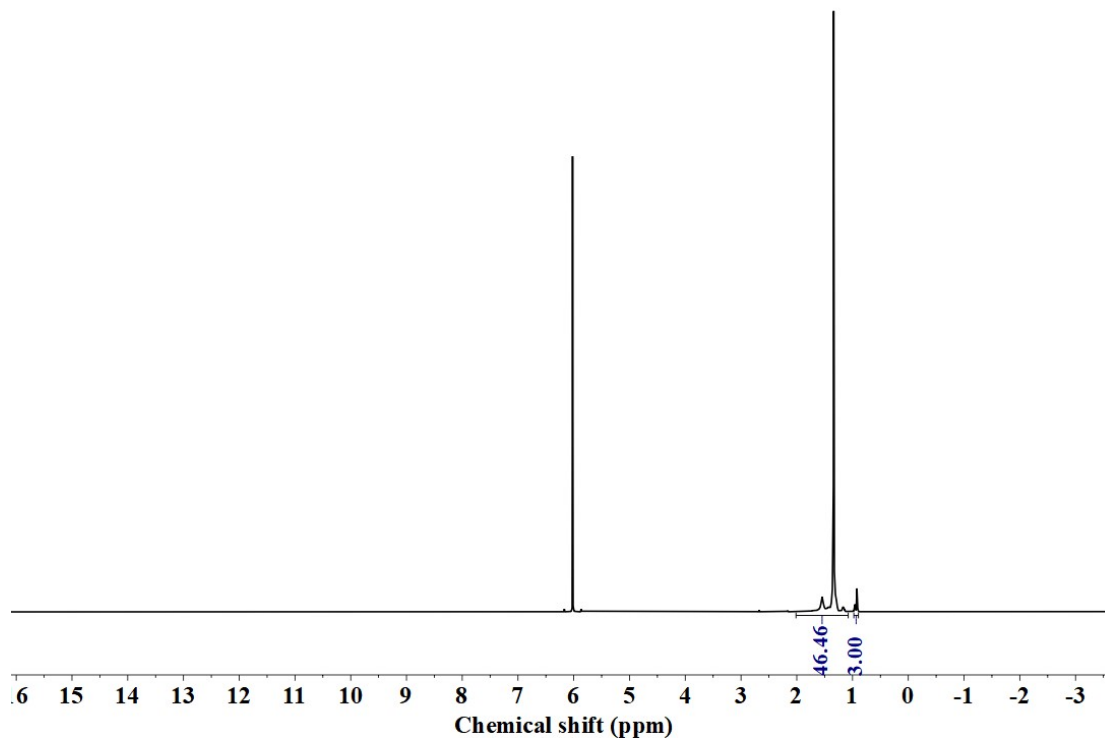
Figure S22. ^{1}H NMR spectrum of polyethylene produced using **Ni-Me$_3$/Et$_2$AlCl** (entry 4, Table 3).

Figure S23. ^{1}H NMR spectrum of polyethylene produced using **Ni-Et$_2$Me/Et$_2$AlCl** (entry 5, Table 3).
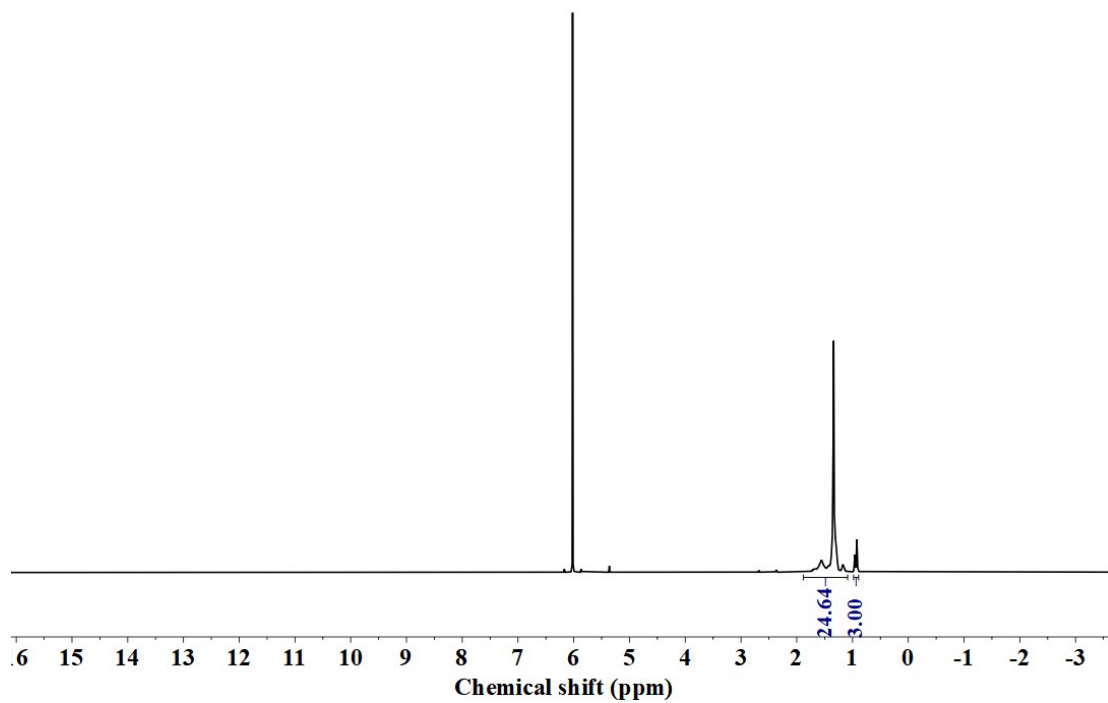

Figure S24. ^{1}H NMR spectrum of polyethylene produced using **Ni-Me$_2$/Et$_2$AlCl** at 40°C (entry 6, Table 5).

Figure S25. ^{1}H NMR spectrum of polyethylene produced using **Ni-Me$_2$/Et$_2$AlCl** at 60°C (entry 7, Table 5).

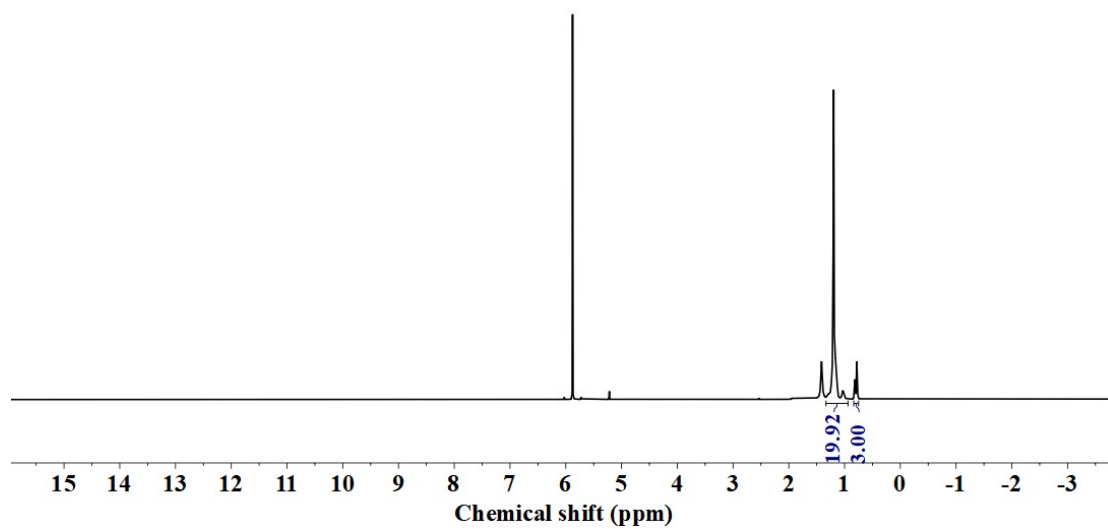**Figure S26.** ^{1}H NMR spectrum of polyethylene produced using **Ni-Me$_2$/Et$_2$AlCl** at 80°C (entry 8, Table 5).

Figure S27. ^{1}H NMR spectrum of polyethylene produced using **Ni-Me₂/Et₂AlCl** at 100°C (entry 9, Table 2).
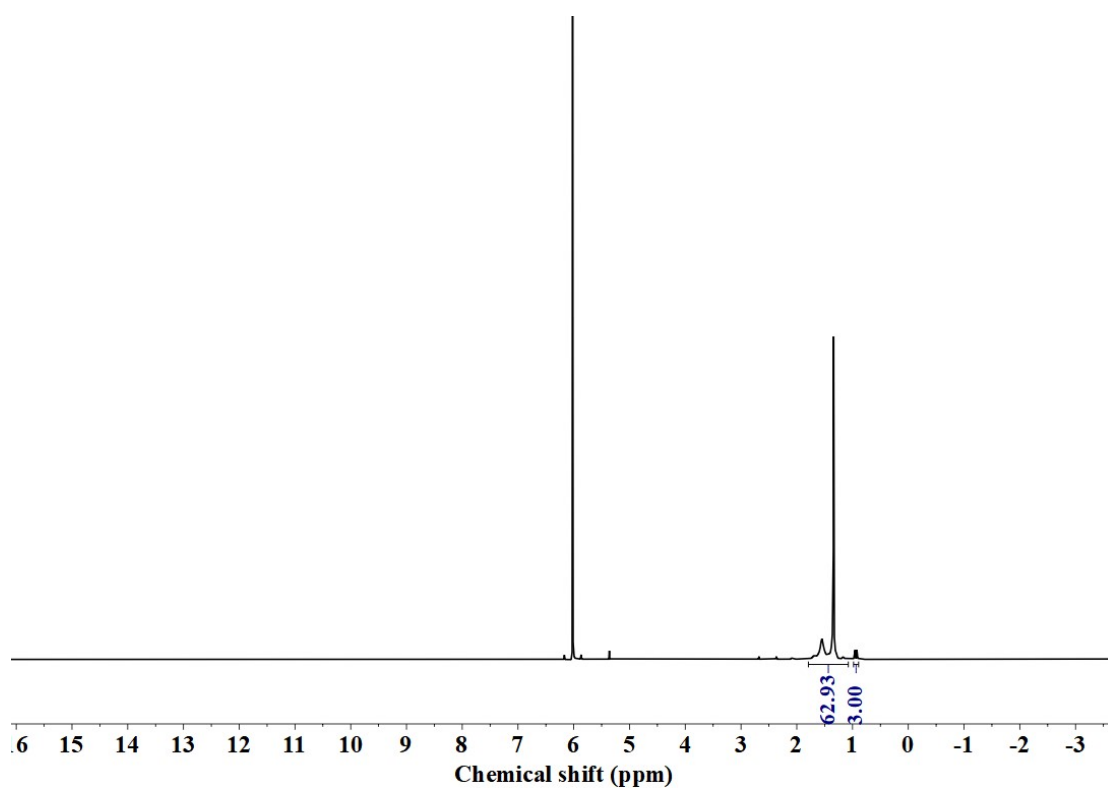

Figure S28. ^{1}H NMR spectrum of polyethylene produced using **Ni-Me₂/MMAO** (entry 1, Table 4).
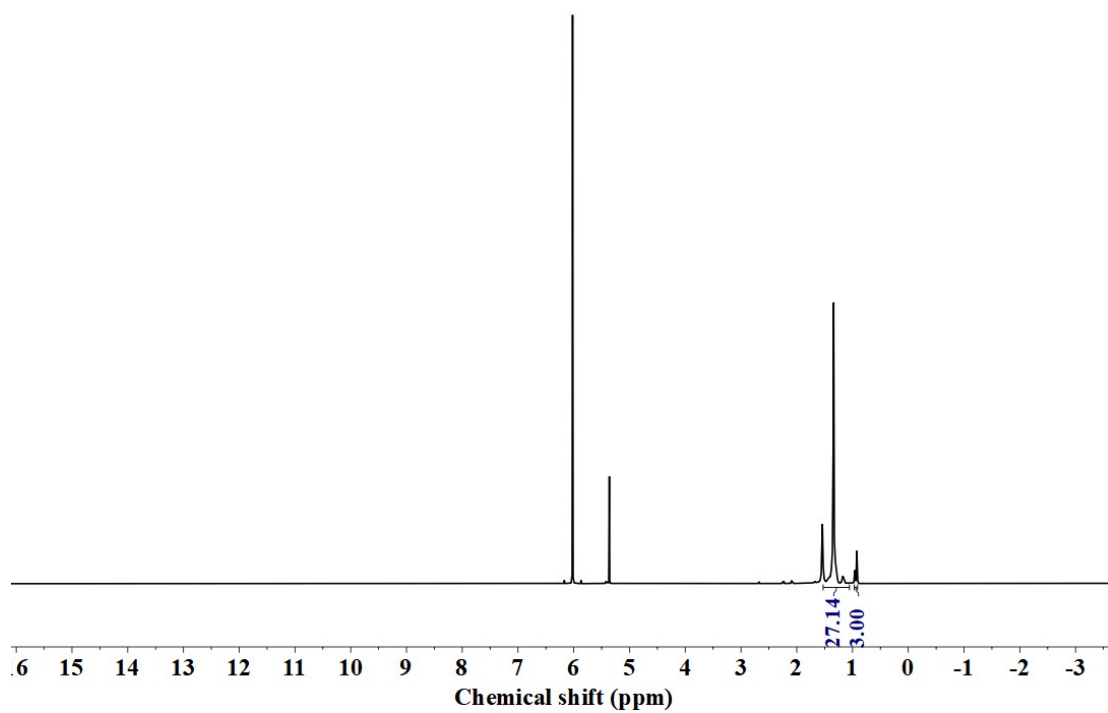
Figure S29. ^{1}H NMR spectrum of polyethylene produced using **Ni-Et$_2$/MMAO** (entry 2, Table 4).
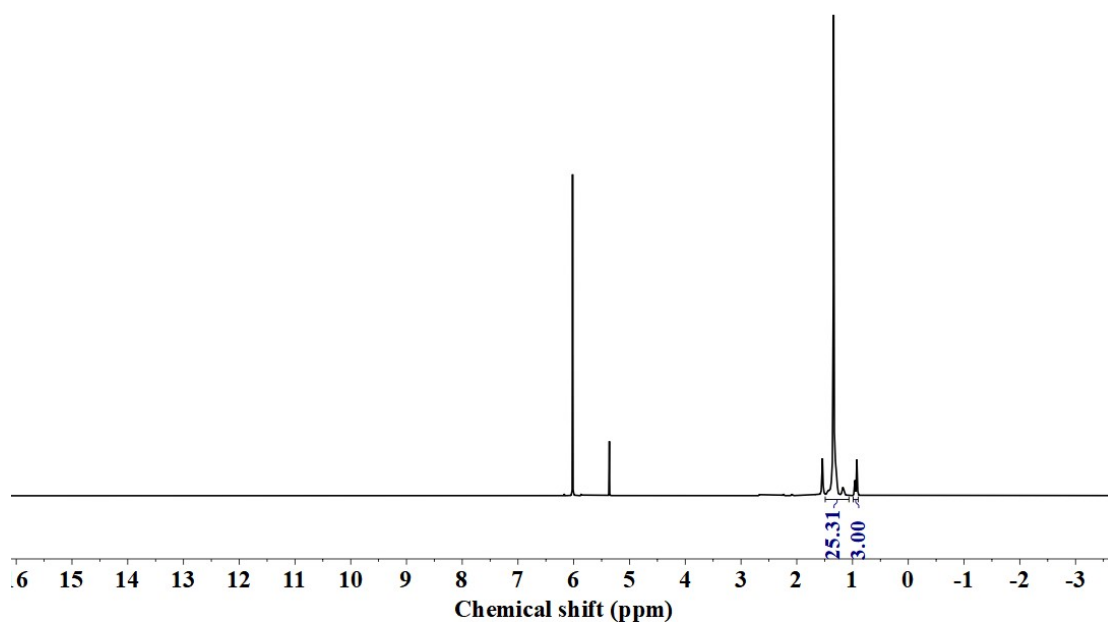

Figure S30. ^{1}H NMR spectrum of polyethylene produced using **Ni-iPr$_2$/MMAO** (entry 3, Table 4).
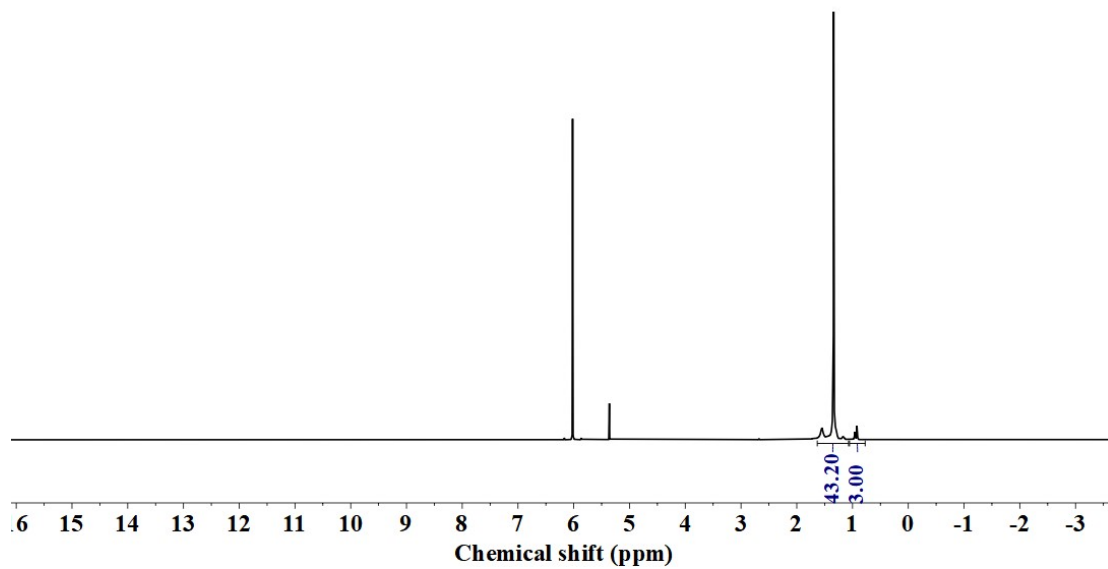
Figure S31. ^{1}H NMR spectrum of polyethylene produced using **Ni-Me$_3$/MMAO** (entry 4, Table 4).
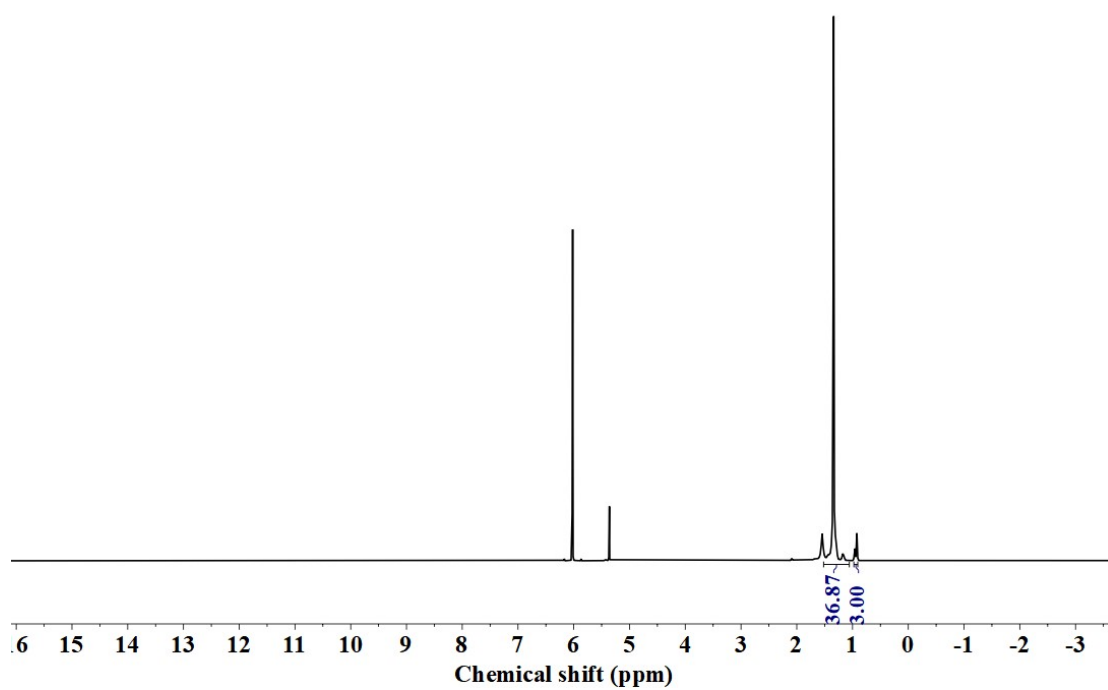

Figure S32. ^{1}H NMR spectrum of polyethylene produced using **Ni-Et$_2$Me/MMAO** (entry 5, Table 4).

Figure S33. ^{1}H NMR spectrum of polyethylene produced using **Ni-Me$_2$/MMAO** at 40°C (entry 7, Table S1).

Figure S34. ^{1}H NMR spectrum of polyethylene produced using **Ni-Me$_2$/MMAO** at 60°C (entry 8, Table S1).
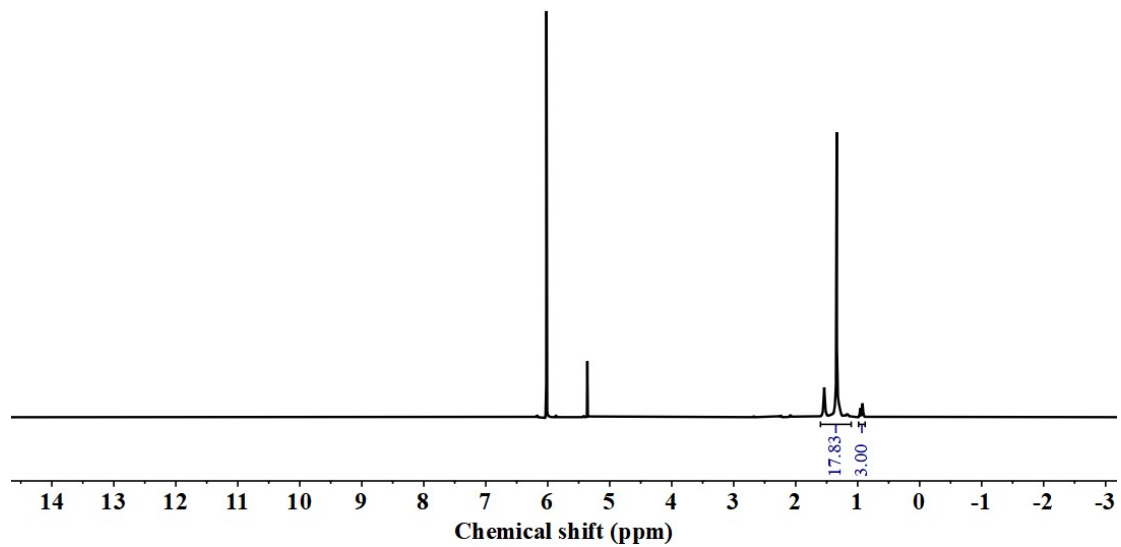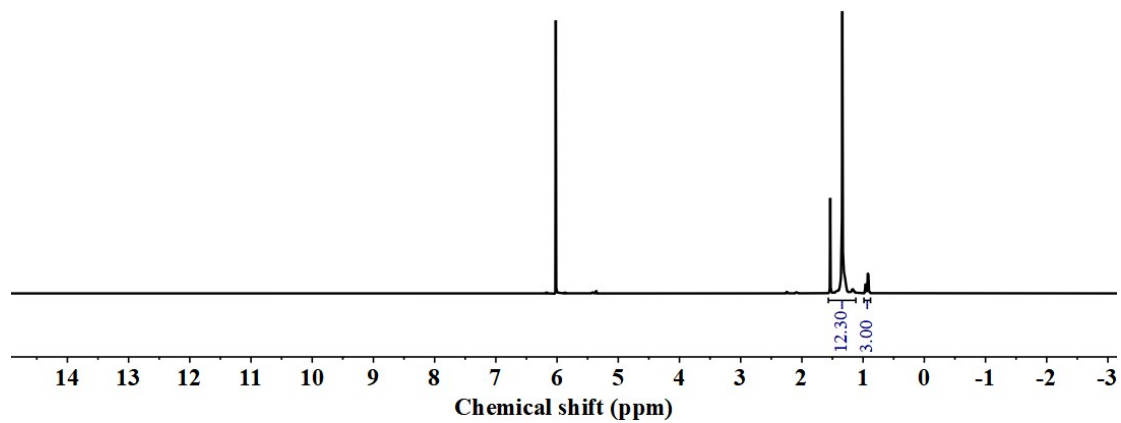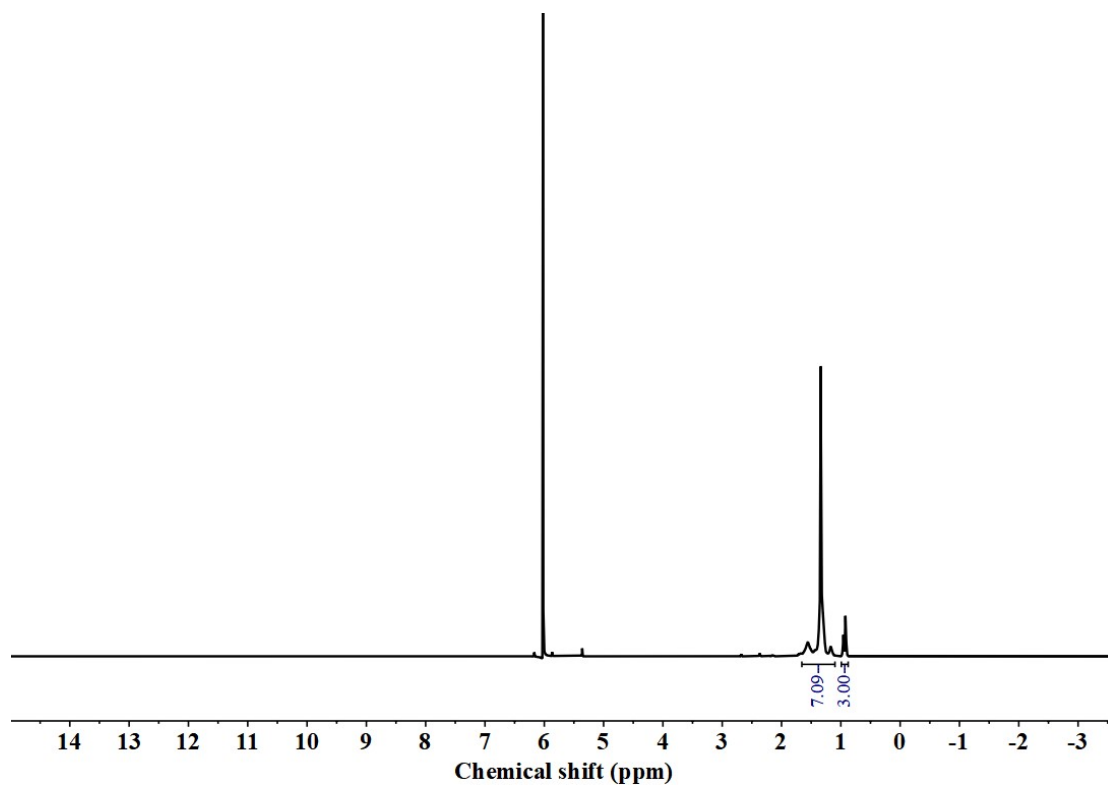
Figure S35. ^{1}H NMR spectrum of polyethylene produced using **Ni-Me$_2$/MMAO** at 80°C (entry 9, Table S1).
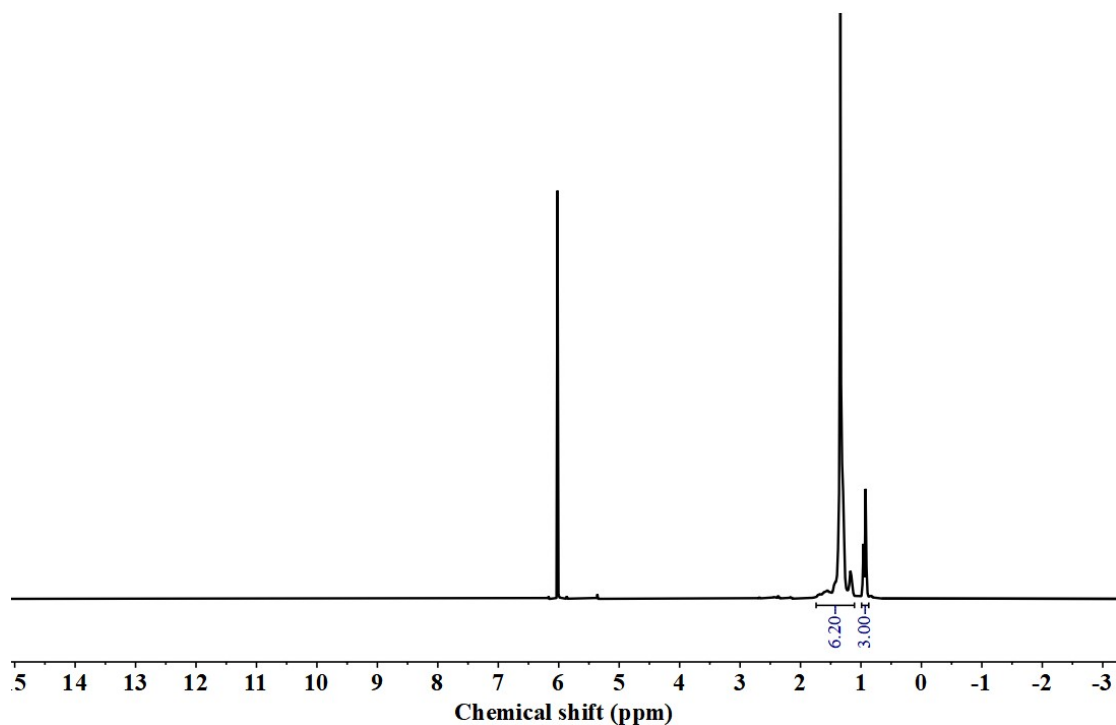

Figure S36. ^{1}H NMR spectrum of polyethylene produced using **Ni-Me$_2$/MMAO** at 100°C (entry 10, Table S1).

7.   Crystal data and structural refinements for complexes

Table S2. Crystal data and structural refinements for **Ni-Me₂** and **Ni-Et₂Me**

	Ni-Me₂	Ni-Et₂Me
Bond precision	C-C = 0.0051 A	C-C = 0.0047 A
	Wavelength = 1.54184	Wavelength = 1.54184
Empirical formula	$C_{55}H_{42}Br_2F_4N_2NiO_3$	$C_{58}H_{48}Br_2F_4N_2NiO_3$
Formula weight	1073.43	1115.48
Temperature/K	170(2)	170(2)
Crystal system	monoclinic	triclinic
Space group	$P2_{1/c}$	P-1
a/Å	16.4700(2)	15.9280(2)
b/Å	15.97260(10)	17.20886(19)
c/Å	21.2499(2)	22.3881(4)
α/°	90	74.9860(12)
β/°	105.4430(10)	77.6538(13)
γ/°	90	89.1093(10)
Volume/Å³	5388.35(9)	5784.92(15)
Z	4	2
ρ_{calc}g/cm³	1.323	1.281
μ/mm⁻¹	2.716	2.548
F(000)	2176.0	2272.0
F000'	2164.27	2260.47
Crystal size/mm³	0.22 × 0.15 × 0.12	0.1 × 0.08 × 0.06
Radiation	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
θ range	5.566 to 155.59	4.186 to 155.696
h,k,lmax	20,20,26	20,21,28
Index ranges	-20≤ h ≤ 20, -19 ≤ k ≤ 17, -26 ≤ l ≤ 26	-20 ≤ h ≤ 19, -19 ≤ k ≤ 21, -27 ≤ l ≤ 27
Reflections collected	42037	91159
Independent reflections	11062 [R_{int} = 0.0524, R_{sigma} = 0.0427]	23695 [R_{int} = 0.0398, R_{sigma} = 0.0374]
Data/restraints/parameters	11062/0/610	23695/2/1293
Goodness-of-fit on F²	1.047	1.043
Data completeness	1.000	1.000

Theta(max)	77.795	77.848
Final R indexes [I>=2σ(I)]	$R_1 = 0.0504$,	$R_1 = 0.0493$,
	$wR_2 = 0.1200$	$wR_2 = 0.1400$
Final R indexes [all data]	$R_1 = 0.0573$,	$R_1 = 0.0568$,
	$wR_2 = 0.1229$	$wR_2 = 0.1450$
Largest diff. peak/hole/e Å^{-3}	1.43/-0.83	1.39/-0.58
S	1.052	1.043
Npar	610	1293

8. ^{13}C NMR spectra with peak assignment and microstructure of polyethylene produced at 100 ºC (entry 9, Table 2).
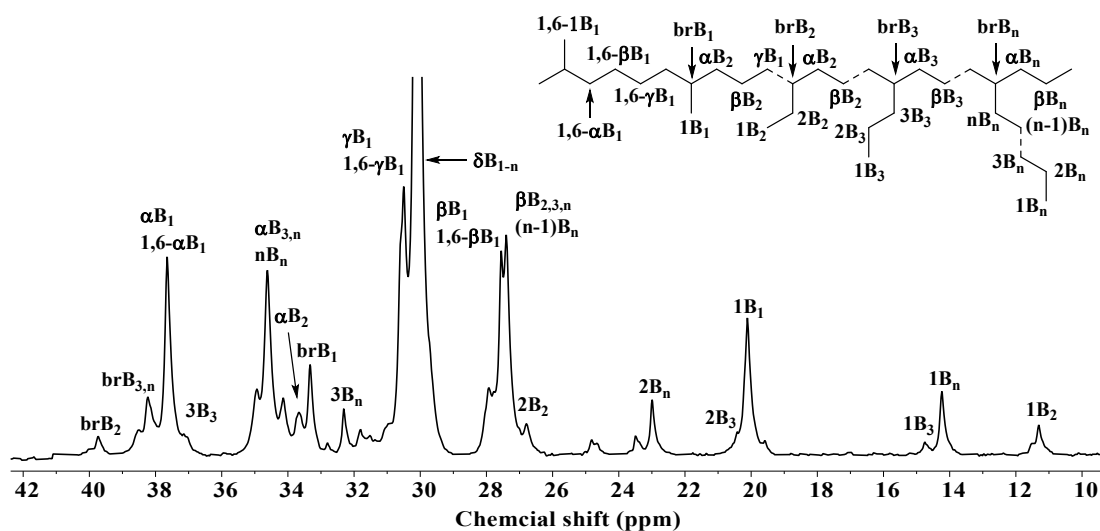

Figure S37. ^{13}C NMR spectrum with peak assignment and microstructure of polyethylene produced at 100 ºC (entry 9, Table 2).

9. Elastic recovery behaviour of polyethylene obtained by using different nickel precatalysts
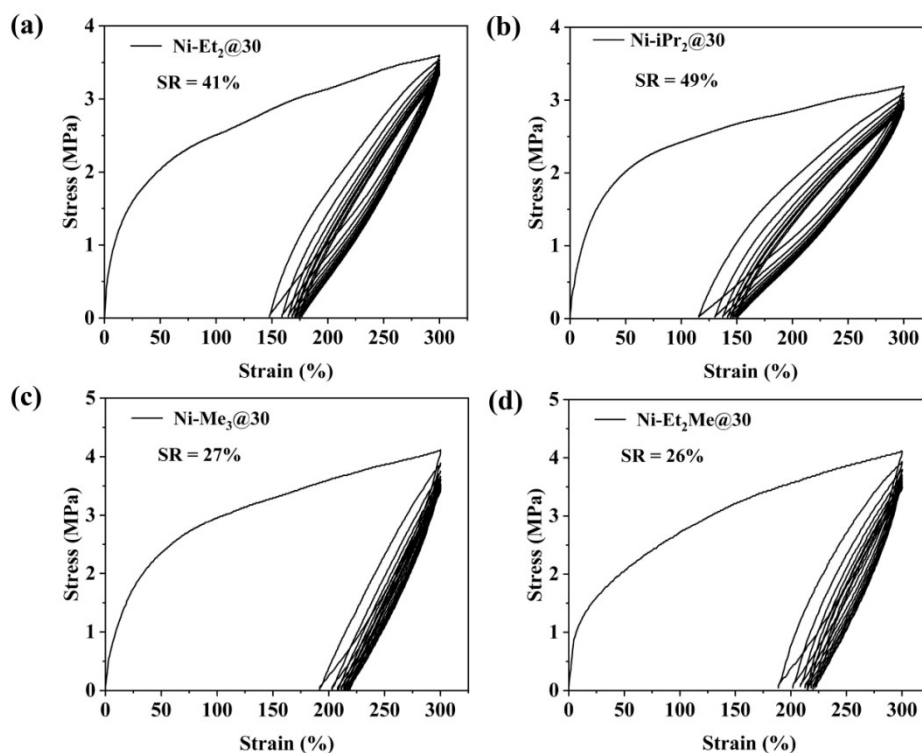

Figure S38. Elastic recovery of different catalyst by using Et_2AlCl.

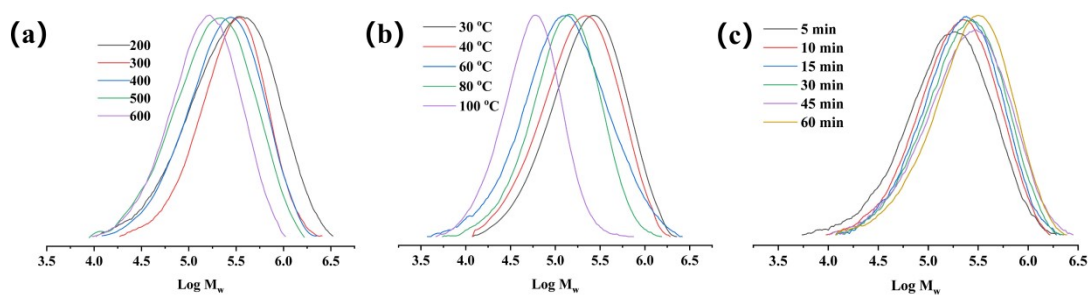## 10. Polymer molecular weights and their GPC curves by using Et_2AlCl.

Figure S39: GPC curves (a) at different ratio (b) at different temperatures (c) at different times (entries 1-14 in Table 2).

Reference

1 R. Yuan, Y. Wang, Q. Mahmood, Y. Zeng, L. Qin, S. Zou, T. Liang, W. H. Sun, "Synergistic influence of methoxy and benzhydryl groups in α-diimine nickel precatalysts for facile synthesizing UHMW PE elastomers." *Polymer*, **293**, 126690 (2024).

2   G. M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.

3   J. Wang, L. Wang, H. Yu, R. S. Ullah, M. Haroon, A. Zain ul, X. Xia, R. U. Khan, "Recent Progress in Ethylene Polymerization Catalyzed by Ni and Pd Catalysts." *Eur. J. Inorg. Chem.*, **2018**, 1450 (2018).

4   C. G. de Souza, R. F. de Souza, K. Bernardo-Gusmão, "Effect of alkylaluminum cocatalyst on ethylene polymerization with nickel-α-diimine complex." *Appl. Catal. A-Gen.*, **325**, 87 (2007).

5   A. Valente, A. Mortreux, M. Visseaux, P. Zinck, "Coordinative Chain Transfer Polymerization." *Chem. Rev.*, **113**, 3836 (2013).

6   X. Li, L. Qin, Q. Mahmood, Z. Yu, S. Zou, Y. Wang, T. Liang, W. H. Sun, "Thermally stable unsymmetrical 2,3-diiminobutane-nickel pre-catalysts for synthesis of high molecular weight polyethylene elastomers." *Eur. Polym. J.*, **200**, 112520 (2023).

7   L. D. Qin, X.Y. Wang, Q. Mahmood, Z. X. Yu, Y. Z. Wang, S. Zou, T. L. Liang, W. H. Sun, "High-Performance α-Diimine Nickel Complexes for Facile Access of PE Elastomers with Exceptional Material Properties." *Chinese J. Polym. Sci.*, (2023).

8   Q. Mahmood, Y. Zeng, X. Wang, Y. Sun, W. H. Sun, "Advancing polyethylene properties by incorporating NO_2 moiety in 1,2-bis(arylimino)acenaphthylnickel precatalysts: synthesis, characterization and ethylene polymerization." *Dalton Trans.*, **46**, 6934 (2017).

9   M. Liu, R. Zhang, Y. Ma, M. Han, G. A. Solan, W. Yang, T. Liang, W. H. Sun, "Trifluoromethoxy-substituted nickel catalysts for producing highly branched polyethylenes: impact of solvent, activator and N,N′-ligand on polymer properties." *Polym. Chem.*, **13**,1040 (2022).