Supporting Information

High performance polyethylene elastomer using a hybrid steric approach in α-diimine nickel precatalysts

Hassan Saeed[a,b,c], Qaiser Mahmood[b,*], Rongyan Yuan[b], Yizhou Wang[a,c], Song Zou[a], Kainat Fatima Tahir[b,c], Yanping Ma[a,c,*], Tongling Liang[a], Wen-Hua Sun[a,b,c,*]

[a]Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: whsun@iccas.ac.cn; [b]Chemistry and Chemical Engineering Guangdong Laboratory, Shantou 515031, China. E-mail: qaiser@ccelab.com.cn

[c]CAS Research/Education Center for Excellence in Molecular Sciences and International School, University of Chinese Academy of Sciences, Beijing 100049, China

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1. General Considerations

Compounds that exhibit sensitivity to air and humidity are commonly employed inside a controlled nitrogen environment, employing established Schlenk procedures. Prior to the commencement of the polymerization reaction, it is imperative to ensure the removal of moisture from toluene through the introduction of metallic sodium in a nitrogen-rich environment. The following catalysts were procured from Macklin Corp: MAO (10 wt%), MMAO (Al = 4.5%), EASC (0.4M in hexane), and Et_2AlCl (2.0M in hexane). Additional chemical reagents were procured from reputable providers such as Synthware, Macklin, and Aladdin. ^{1}H and ^{13}C NMR spectroscopic measurements for the organic compounds were performed on a Bruker DMX 600 MHz instrument at room temperature. Chemical shifts are measured in ppm for the ^{1}H and ^{13}C 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. 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 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 160 °C to remove the thermal history and then cooled at a rate of 20 °C min^{-1} to 25 °C. The ^{1}H and ^{13}C NMR spectra of the polyethylenes were recorded on a Bruker DMX 300 MHz instrument at 120 °C in deuterated tetrachloroethane with TMS as an internal standard. The stress–strain curves were obtained using a universal tester (Instron 1122, UK).

2. General procedure of ethylene polymerization

The polymerization process was conducted using a 250 mL stainless steel autoclave that was equipped with an ethylene pressure control system, a mechanical stirrer, and a temperature controller. The reaction was performed under a pressure of 10 atm. The compound (2.0 μmol) was initially dissolved in 30 mL of toluene at the designated reaction temperature. Subsequently, the aforementioned solution was introduced into the autoclave, and a supplementary quantity of 30 mL of toluene was added for the purpose of rinsing. Afterwards, the necessary amount of co-catalyst (such as MAO, MMAO, EASC, Et_2AlCl) and additional toluene were consecutively introduced to achieve a final volume of 100 mL. The autoclave was rapidly pressurized with a

pressure of 10 atmospheres of ethylene, and agitation was initiated.Following the designated duration for reaction time, the pressure of ethylene was alleviated, and the reaction was brought to a halt by employing a solution consisting of 10% hydrochloric acid in ethanol. The polymer obtained was gathered, subjected to ethanol washing, dried under decreased pressure at a temperature of 50 °C, and subsequently weighed.

3. X-ray crystallographic studies

Crystals of **Ni^{C5}** and **Ni^{C6}** and **Ni^{C12}** were produced as single entities, suitable for X-ray measurements, using the process of layering hexane onto their respective dichloromethane solutions at room temperature. X-ray analysis were conducted using a Rigaku Saturn 724+ CCD instrument equipped with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 173(2) K. The cell characteristics were determined using a comprehensive refinement process that involved analysing the positions of all acquired reflections. The intensities were adjusted to account for the influence of Lorentz and polarisation effects, as well as empirical absorption. The structures were determined using direct methods and subsequently refined using complete matrix least squares on the squared structure factor amplitudes (F2). The hydrogen atoms were positioned in accordance with calculated coordinates. The process of structure solution and refinement was conducted using the Olex2 1.2 software programme.The structural solution and refinement for each complex were carried out using SHELXT (Sheldrick) software. The solvent molecules, which do not influence the geometry of the main compound, were also processed using SHELXT [1]. The crystal data and processing parameters for **Ni^{C5}**, **Ni^{C6}** and **Ni^{C12}** are presented in Table S1.

4. Table S1. Crystal data and structural refinements for **Ni^{C5}**, **Ni^{C6}** and **Ni^{C12}**

	Ni^{C5}	**Ni^{C6}**	**Ni^{C12}**
Empirical formula	$C_{86}H_{72}N_2Br_2Ni$	$C_{88}H_{76}Br_2N_2Ni$	$C_{100}H_{100}Br_2N_2Ni$
Formula weight	1349.93	1380.03	1548.34
Temperature/K	169.99(10)	169.99(10)	170.00(10)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	21.2365(3)	21.2367(2)	28.8212(18)
b/Å	17.3426(3)	17.34528(14)	10.4943(4)
c/Å	20.7677(3)	20.7624(2)	30.215(2)
α/°	90	90	90
β/°	109.509(2)	109.5382(11)	118.380(8)
γ/°	90	90	90

Volume/Å^3	7209.5(2)	7207.58(13)	8040.6(10)
Z	4	4	4
ρ_{calc}g/cm^3	1.350	1.272	1.279
μ/mm^{-1}	2.732	2.035	1.285
F(000)	90.6	2864.0	3248.0
Crystal size/mm^3	0.2 × 0.15 × 0.05	0.2 × 0.15 × 0.05	0.35 × 0.25 ×0.15
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.42 to 151.14	4.416 to 151.108	3.064 to 62.056
Index ranges	-26 ≤ h ≤ 26, -19 ≤ k ≤ 21, -26 ≤ l ≤ 25	-26 ≤ h ≤ 26, -19 ≤ k ≤ 21, -26 ≤ l ≤ 25	-37 ≤ h ≤ 37, -11 ≤ k ≤ 14, -34 ≤ l ≤ 43
Reflections collected	56887	56887	81936
Independent reflections	14533 [R_{int} = 0.0315, R_{sigma} = 0.0268]	14533 [R_{int} = 0.0315, R_{sigma} = 0.0268]	22073 [R_{int} = 0.1511, R_{sigma} = 0.1744]
Data/restraints/parameters	14533/0/865	14533/0/838	22073/234/1001
Goodness-of-fit on F^2	1.040	1.029	1.167
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1536	R_1 = 0.0505, wR_2 = 0.1491	R_1 = 0.1353, wR_2 = 0.2532
Final R indexes [all data]	R_1 = 0.0575, wR_2 = 0.1569	R_1 = 0.0545, wR_2 = 0.1521	R_1 = 0.2209, wR_2 = 0.2861
Largest diff. peak/hole / e Å^{-3}	0.60/-1.24	0.54/-1.16	1.20/-1.32

5. ^{1}H and ^{13}C NMR spectra of ligands

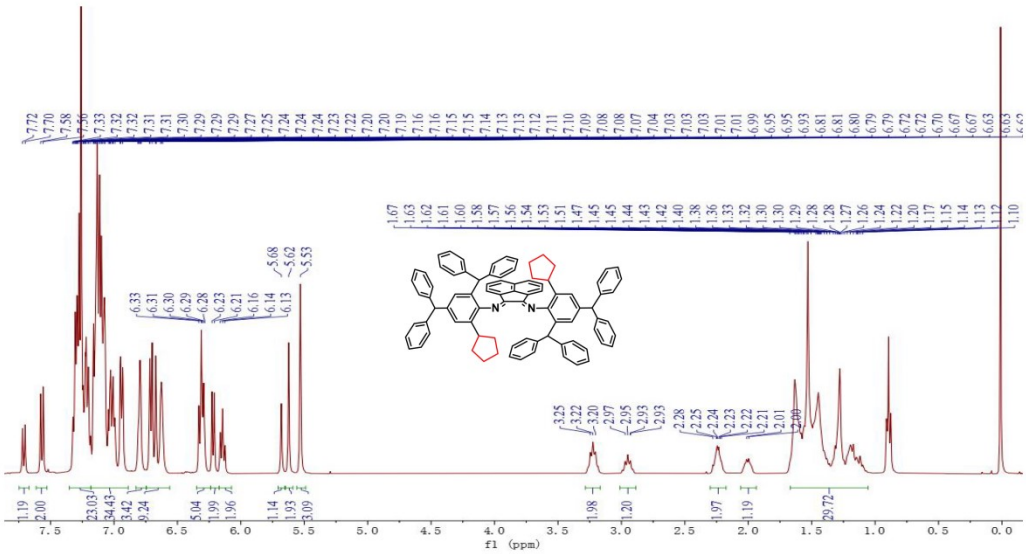

Figure S1 ^{1}H NMR spectra (in $CDCl_3$) of $\mathbf{L^{C5}}$

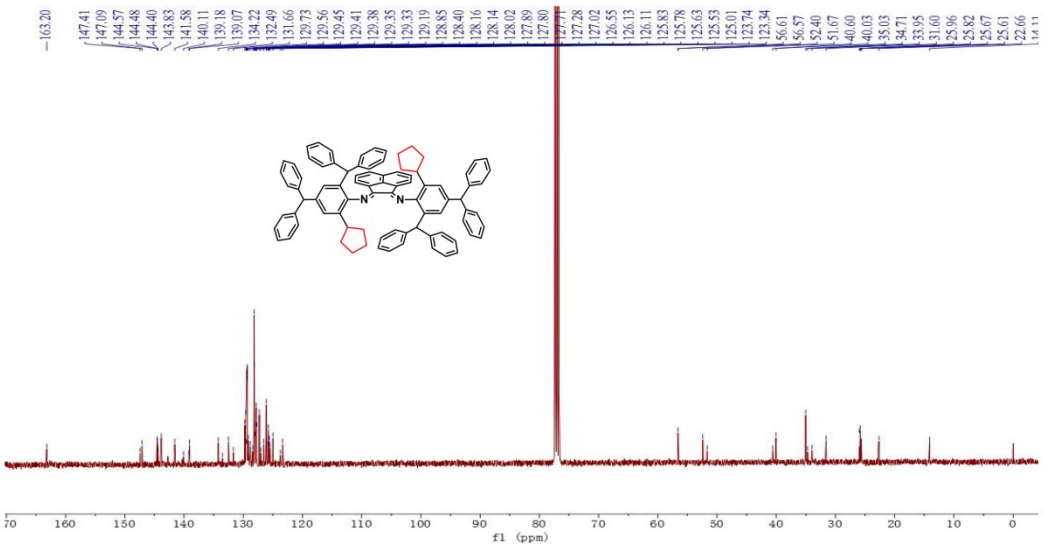

Figure S2 ^{13}C NMR spectra (in $CDCl_3$) of $\mathbf{L^{C5}}$

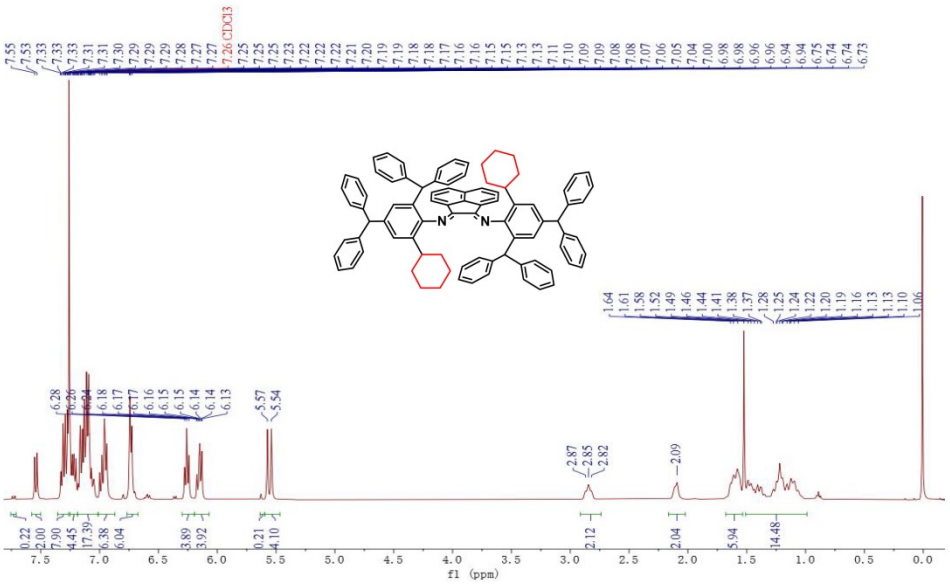

Figure S3 ^{1}H NMR spectra (in $CDCl_3$) of $\mathbf{L^{C6}}$

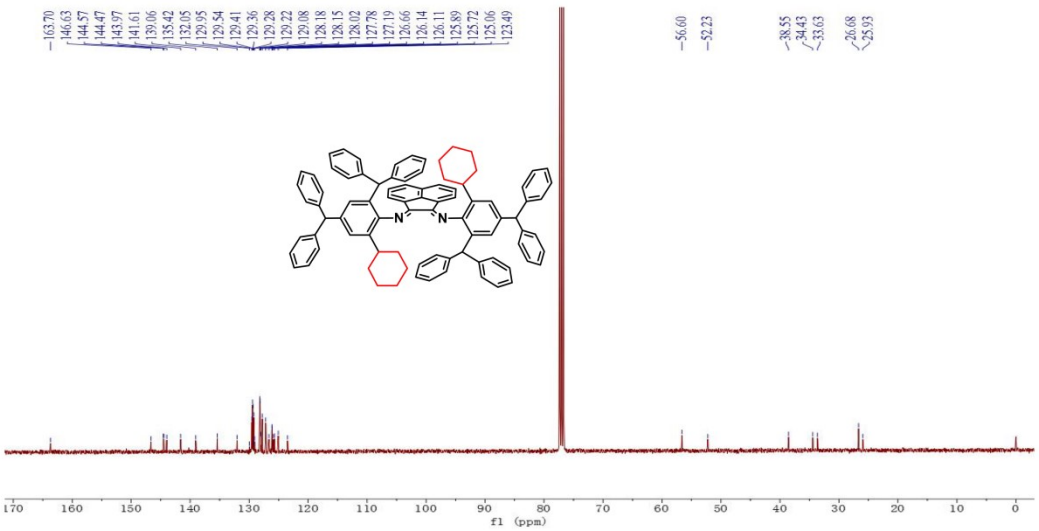

Figure S4 ^{13}C NMR spectra (in $CDCl_3$) of $\mathbf{L^{C6}}$

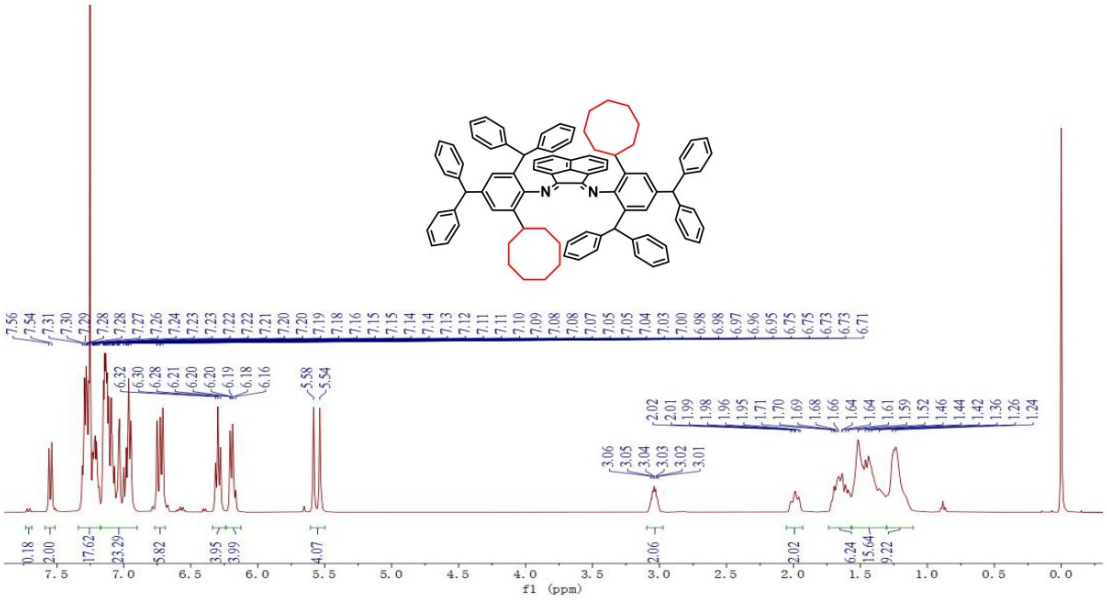

Figure S5 ^{1}H NMR spectra (in $CDCl_3$) of $\mathbf{L^{C8}}$

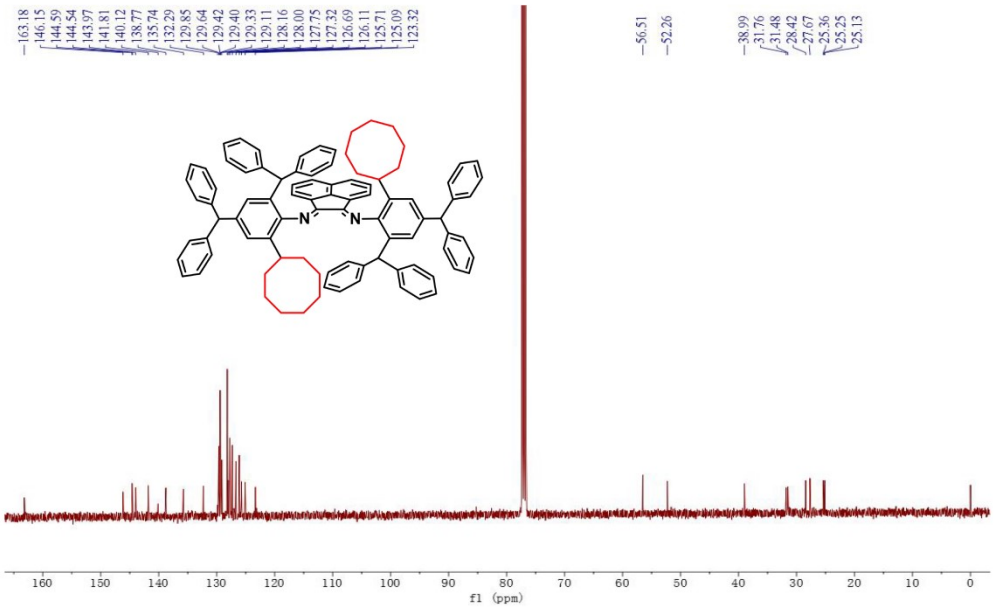

Figure S6 ^{13}C NMR spectra (in $CDCl_3$) of $\mathbf{L^{C8}}$

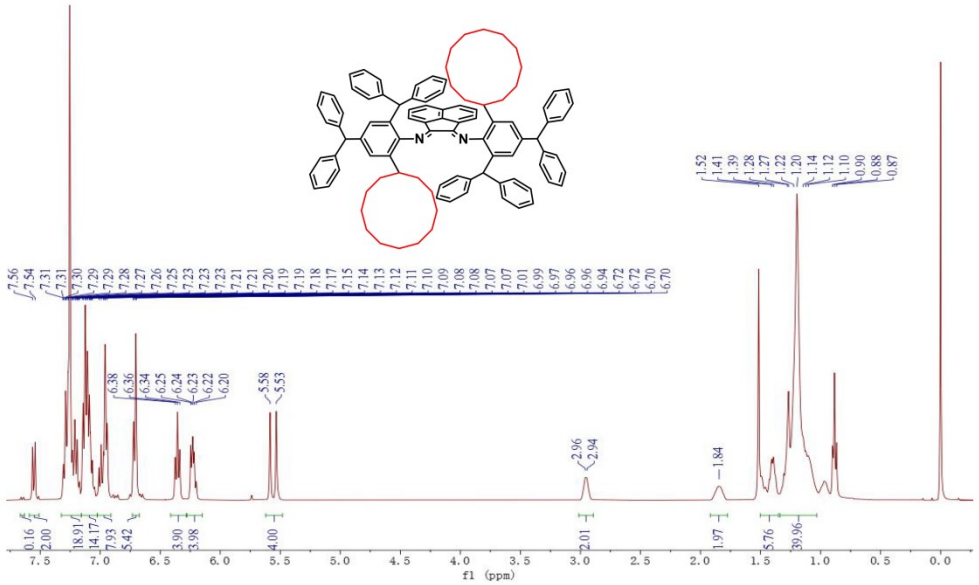

Figure S7 ^{1}H NMR spectra (in $CDCl_3$) of $\mathbf{L^{C12}}$

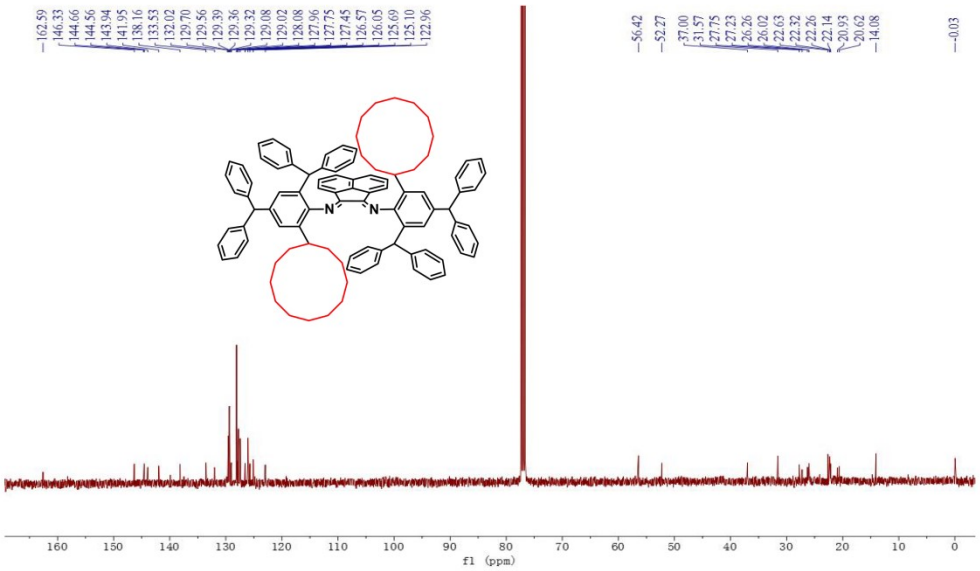

Figure S8 ^{13}C NMR spectra (in $CDCl_3$) of $\mathbf{L^{C12}}$

6. ^{1}H NMR spectra of polyethylene at different conditions

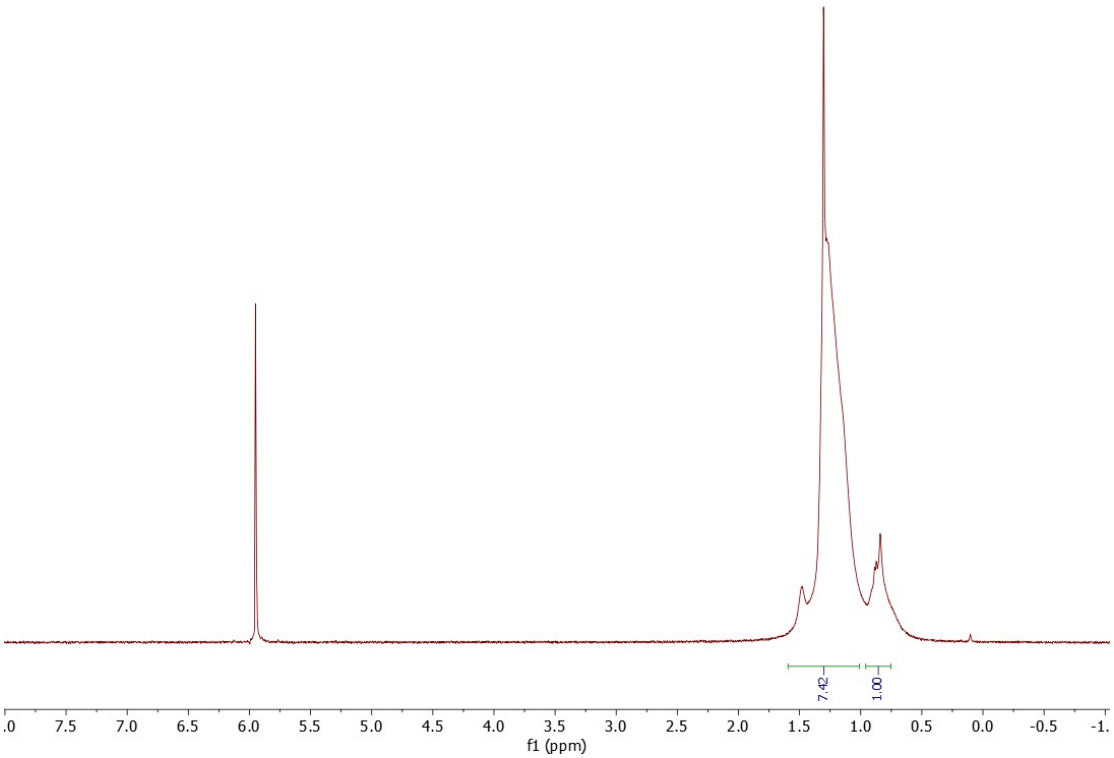

Figure S9 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C5}** at 30 °C

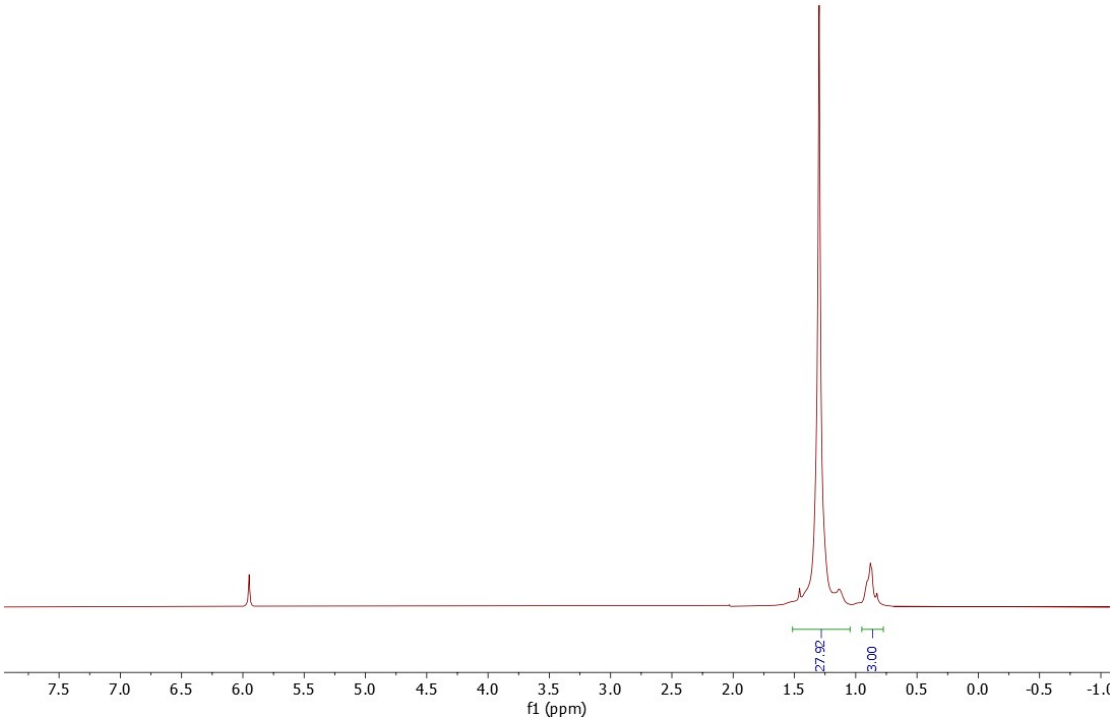

Figure S10 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C5}** at 40 °C

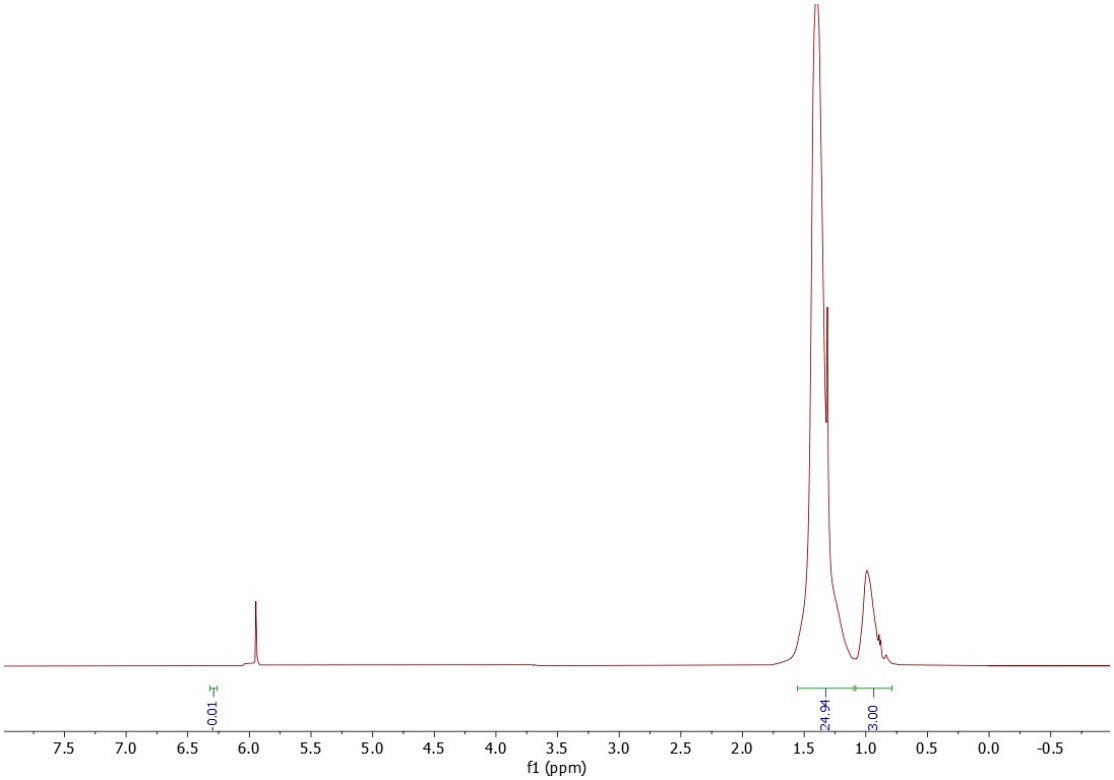

Figure S11 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C5}** at 60 °C

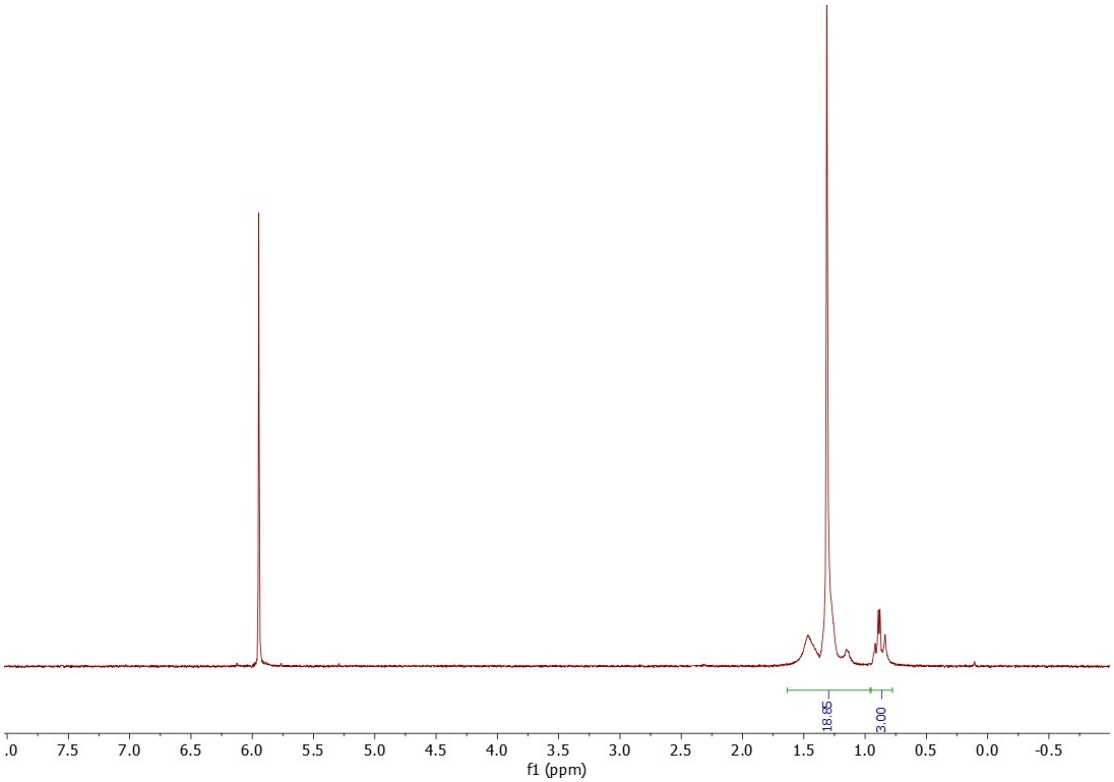

Figure S12 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C5}** at 80 °C

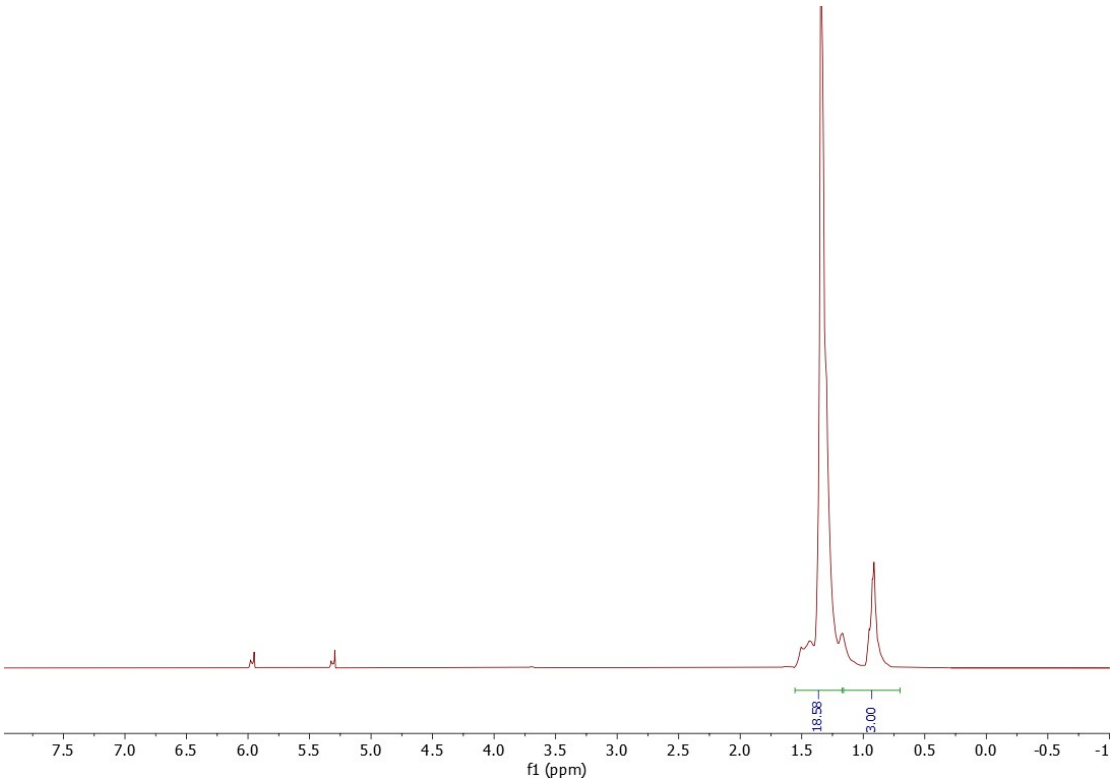

Figure S13 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C5}** at 100 °C

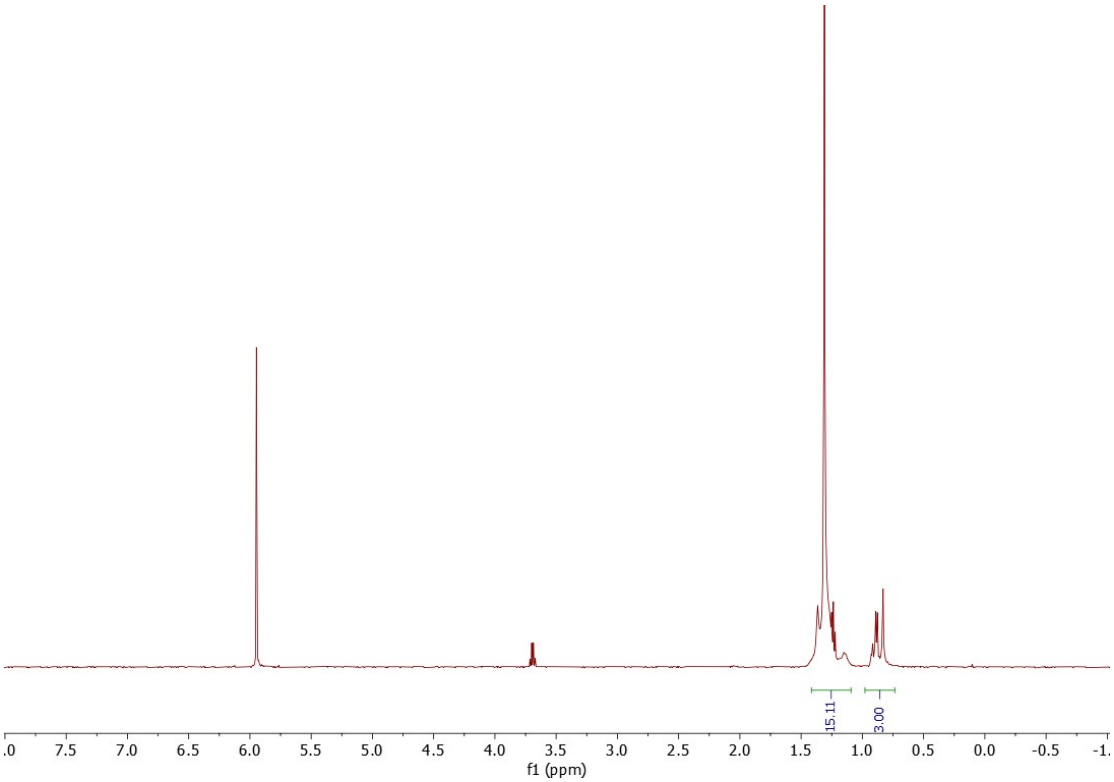

Figure S14 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C5}** at 110 °C

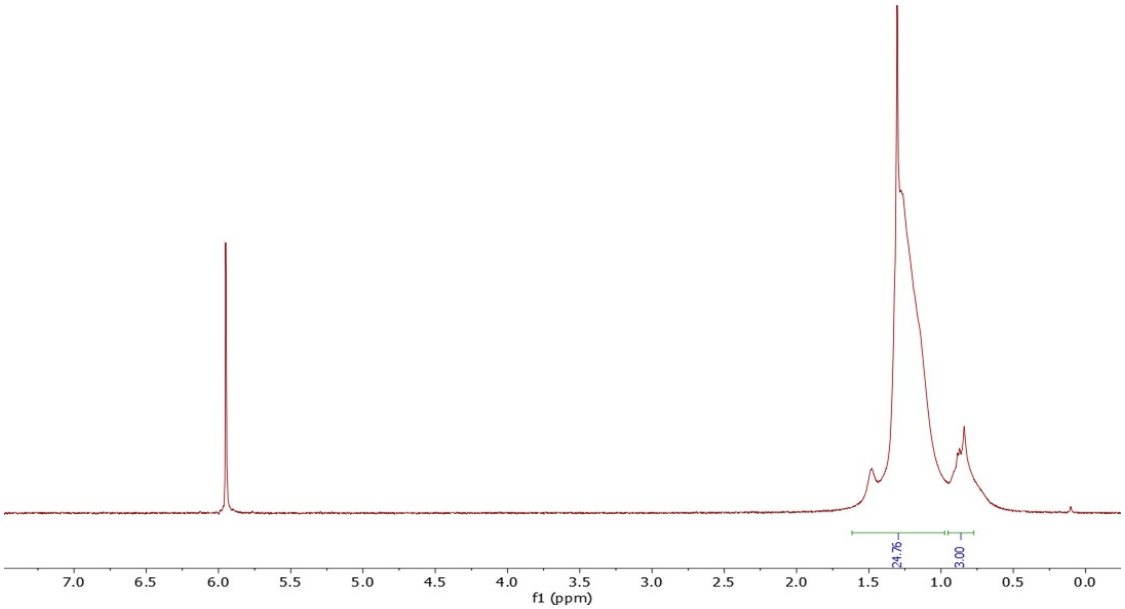

Figure S15 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C6}** at 30 °C

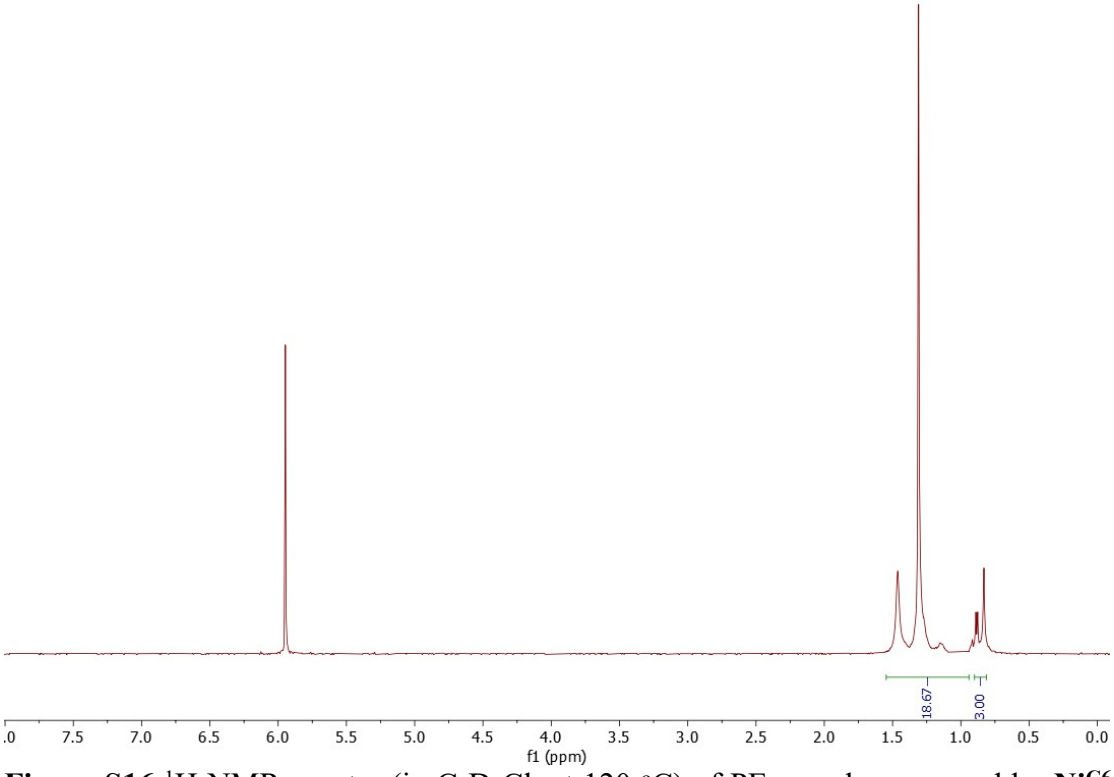

Figure S16 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C6}** at 40 °C

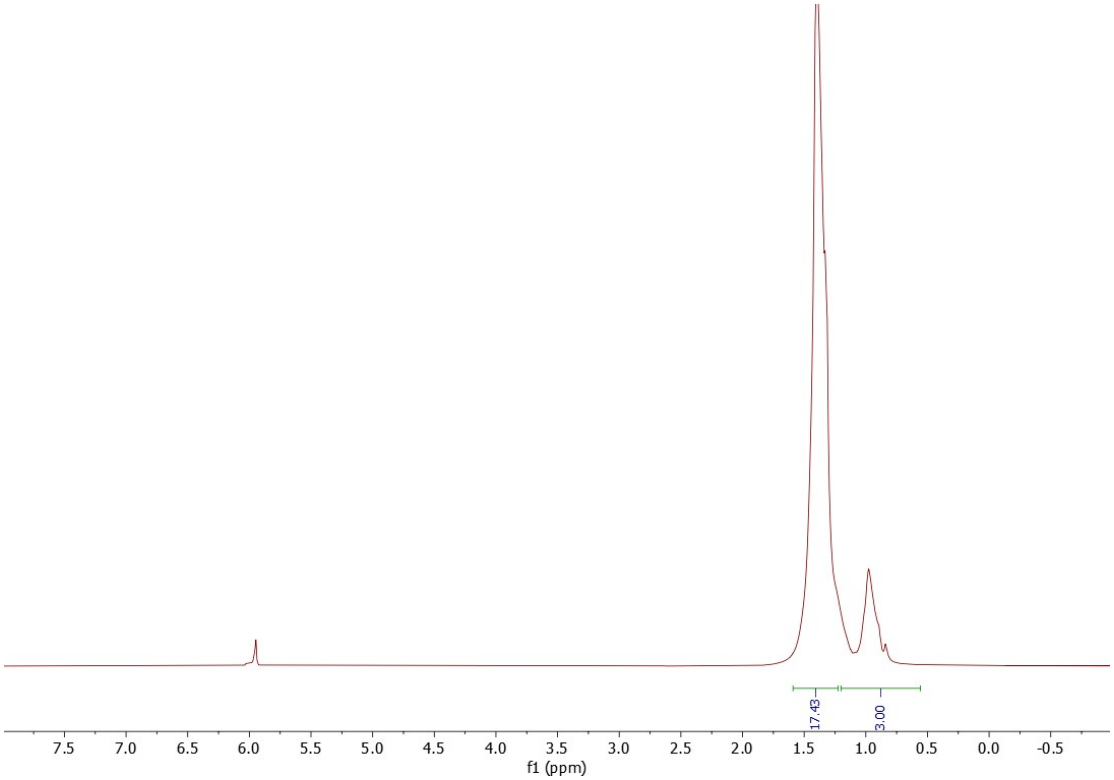

Figure S17 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C6}** at 60 °C

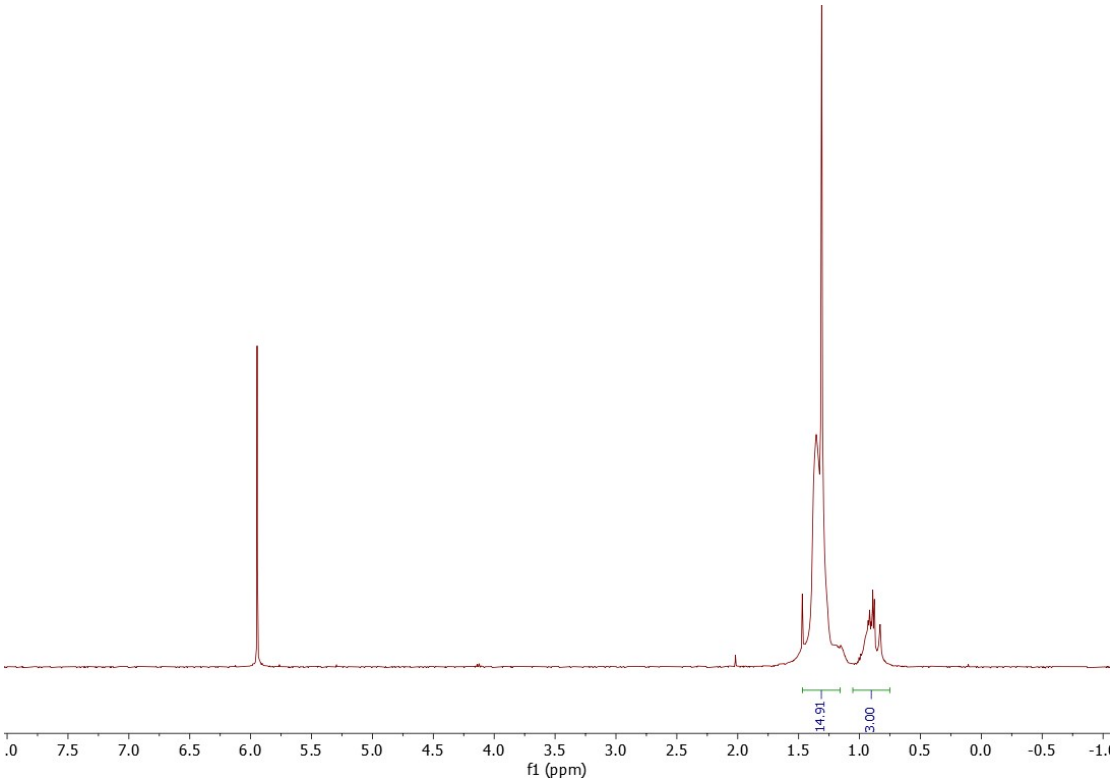

Figure S18 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C6}** at 80 °C.

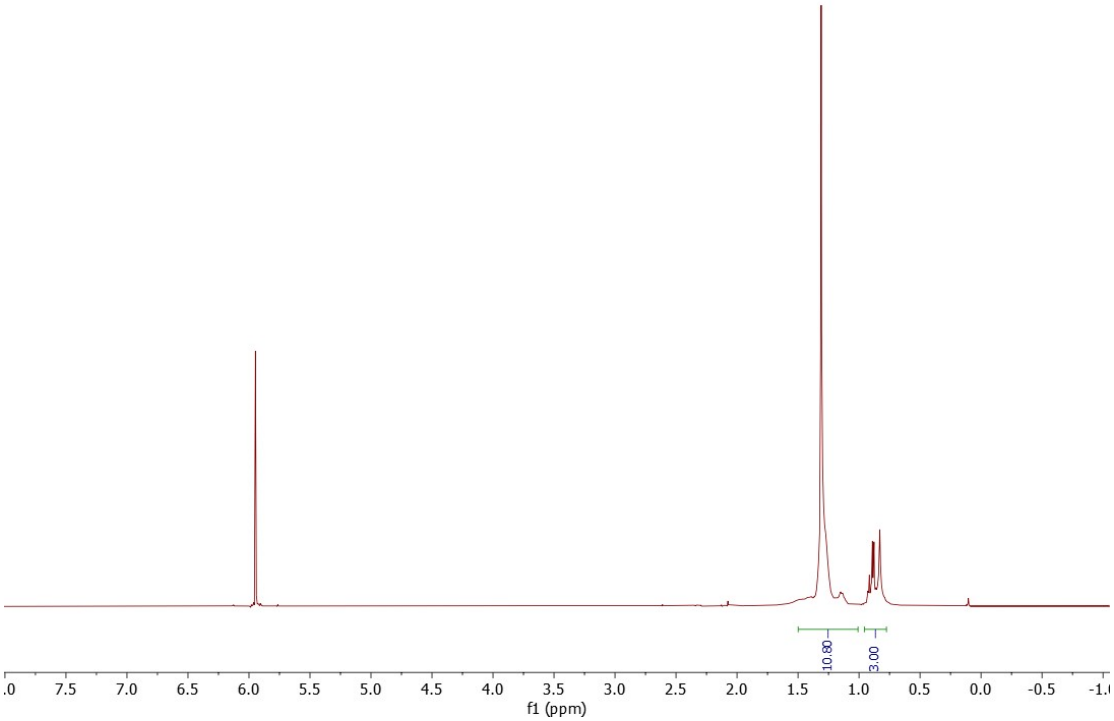

Figure S19 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C6}** at 100 °C

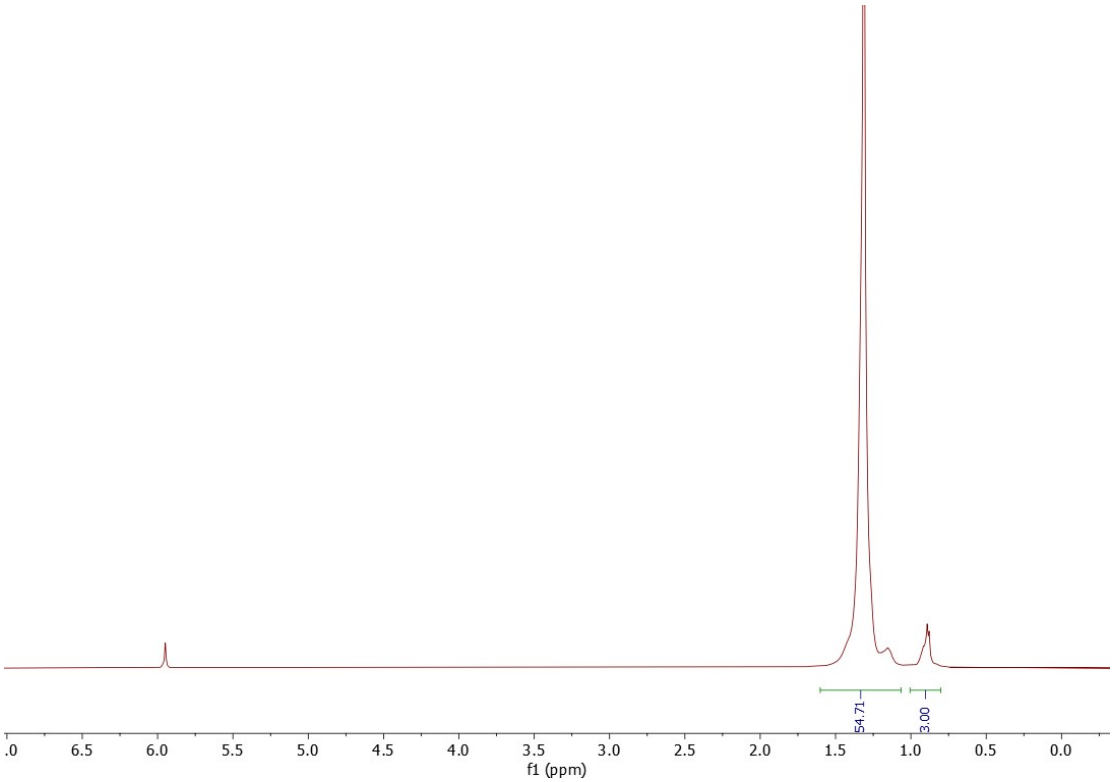

Figure S20 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C8}** at 30 °C

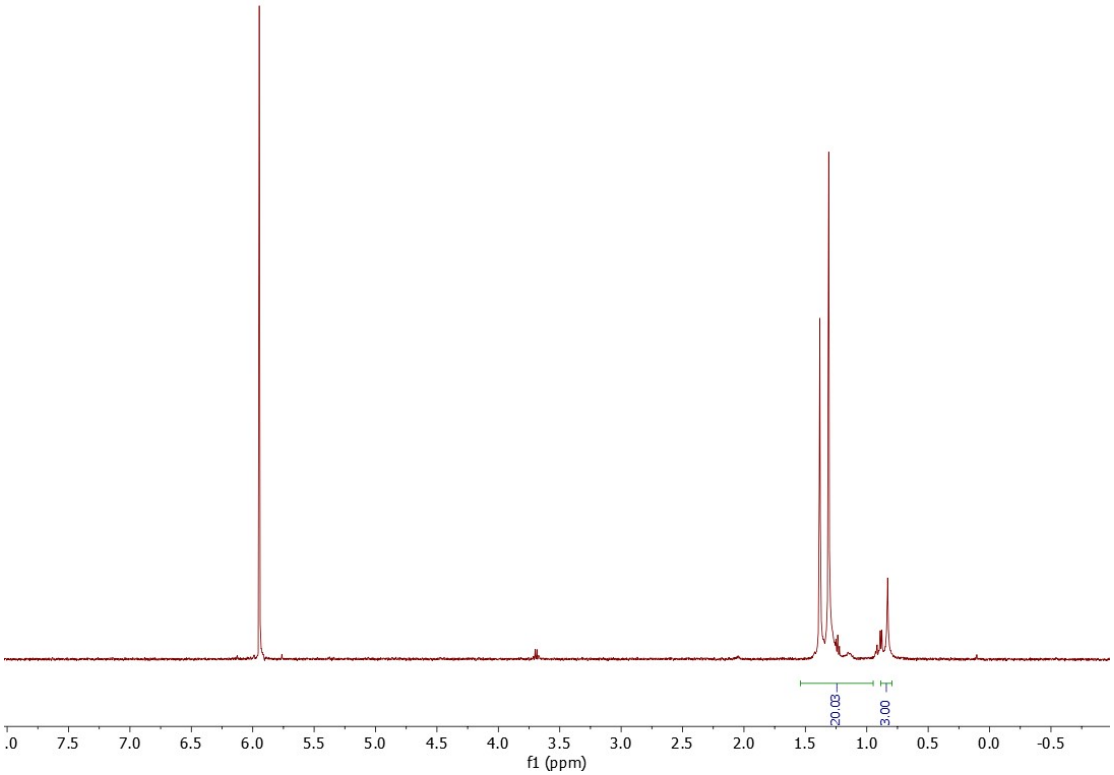

Figure S21 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C8}** at 60 °C

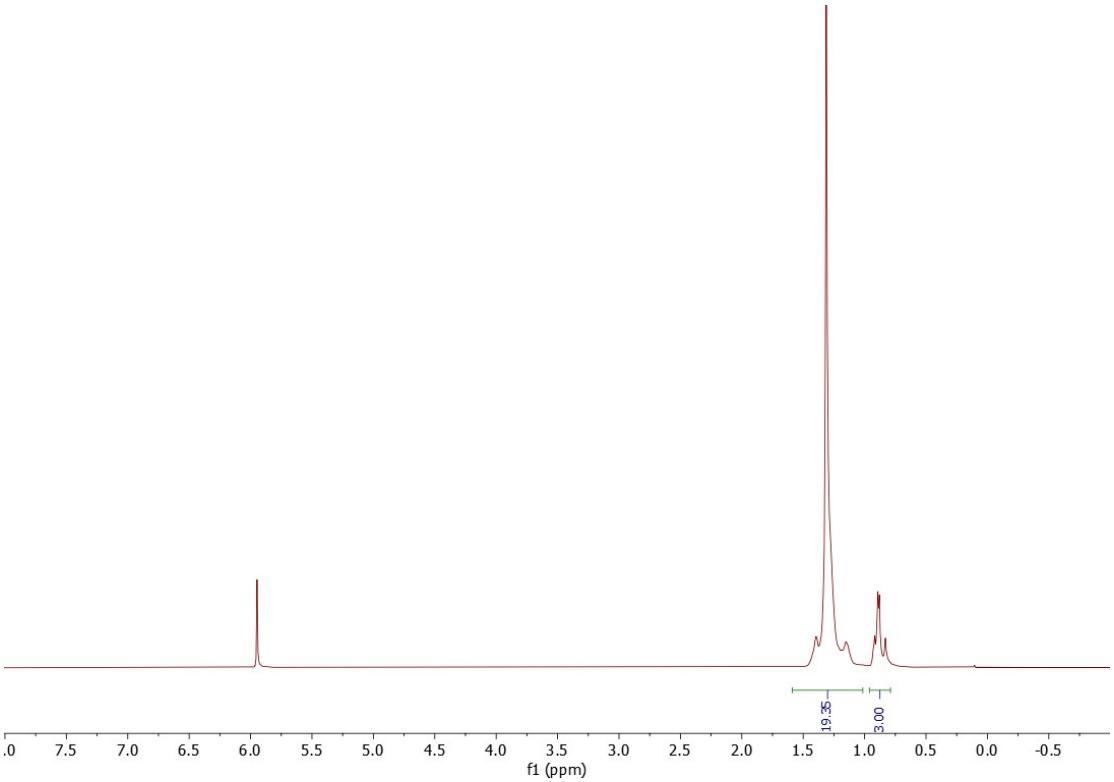

Figure S22 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C8}** at 80 °C

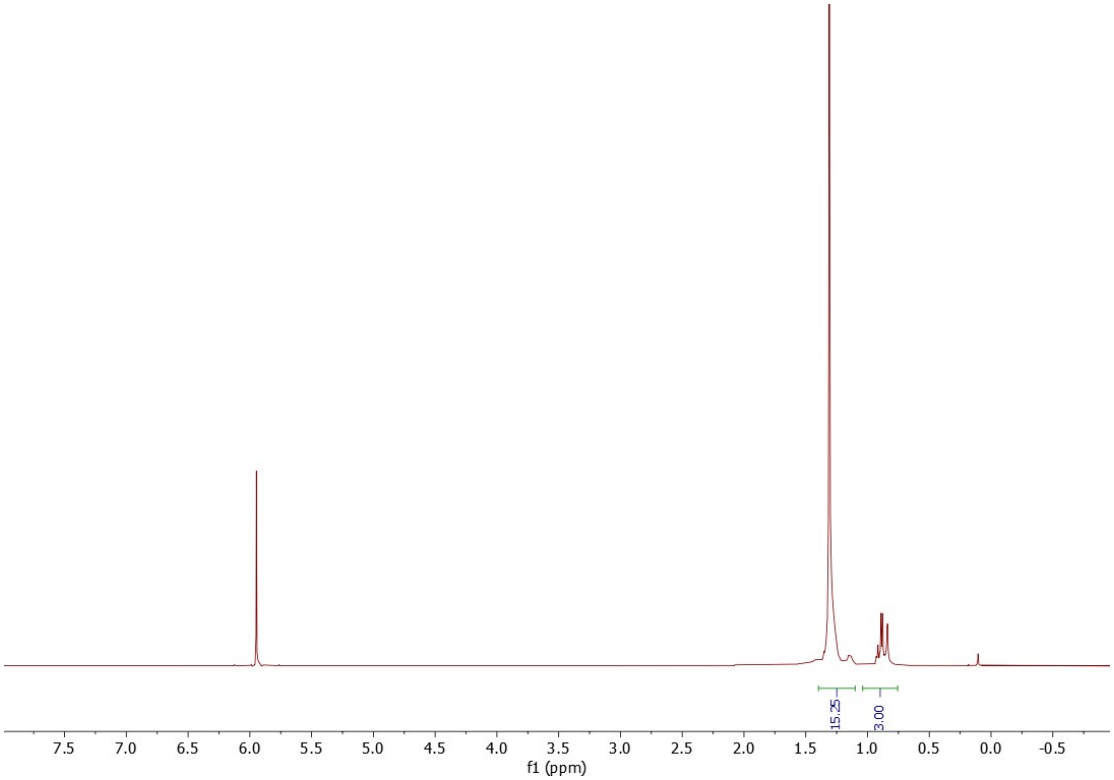

Figure S23 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C8}** at 100 °C

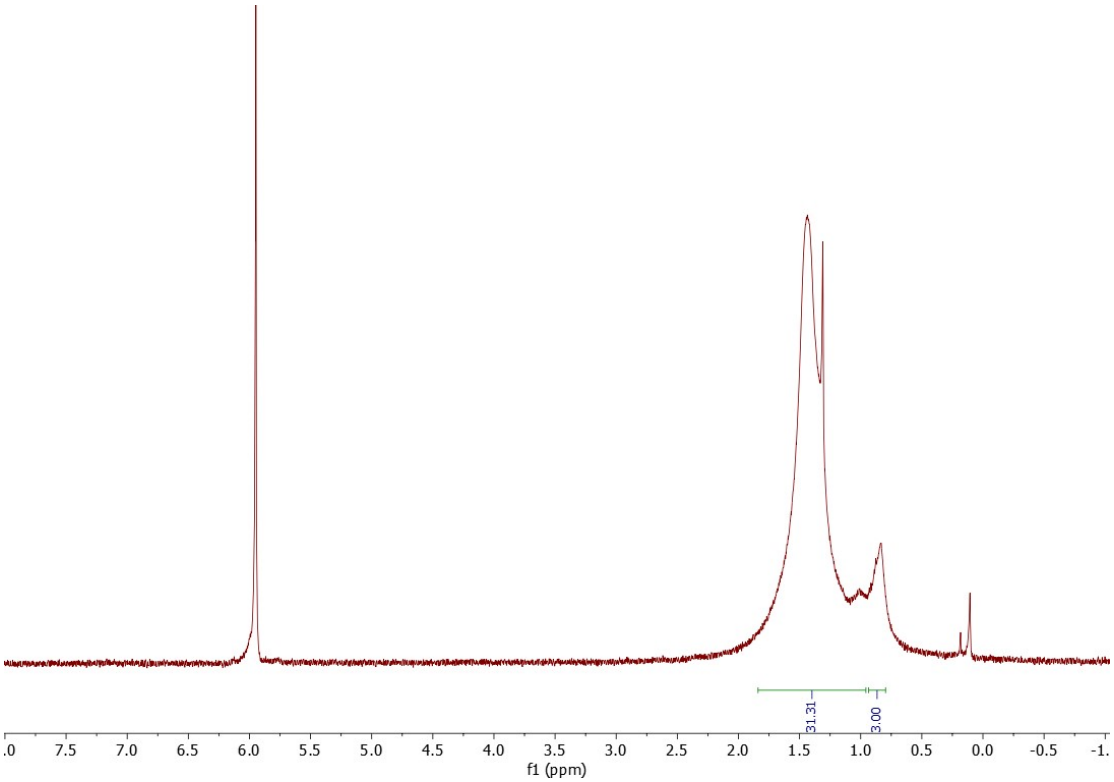

Figure S24 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C12}** at 30 °C

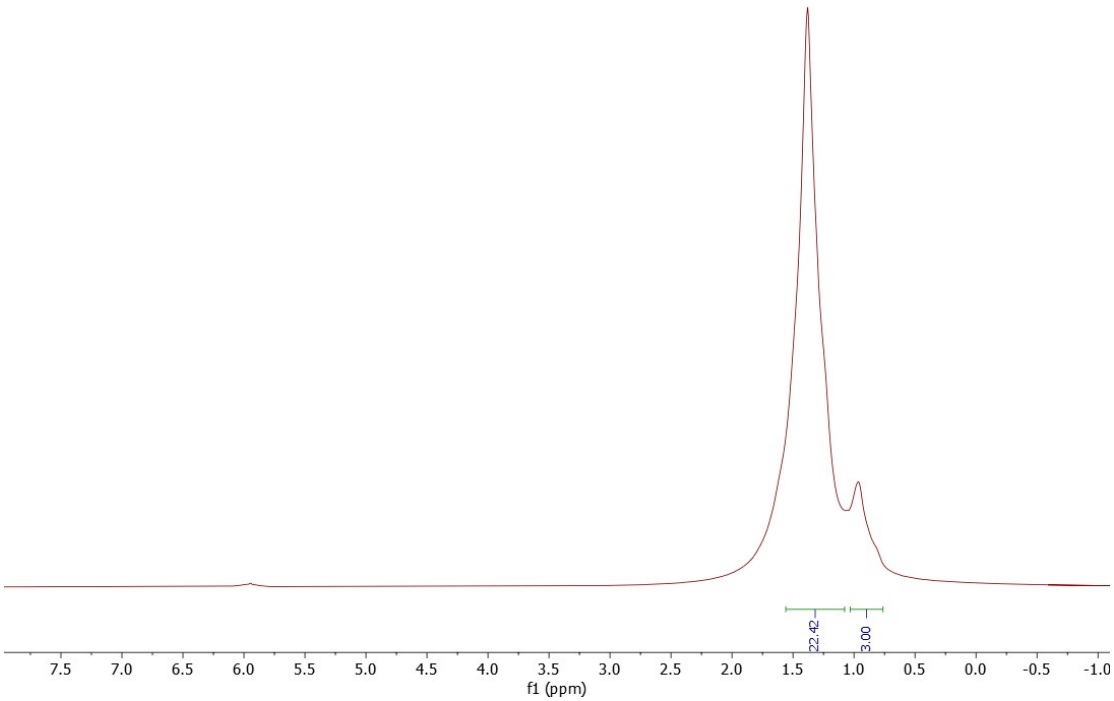

Figure S25 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C12}** at 80 °C

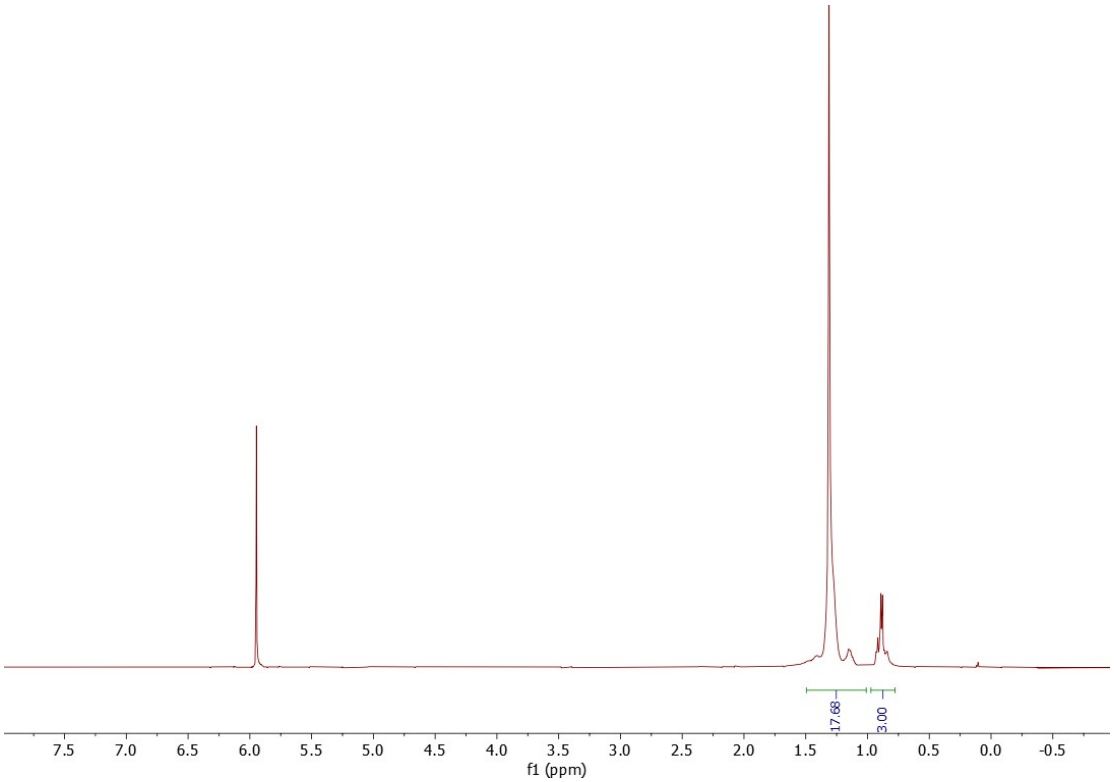

Figure S26 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C12}** at 100 °C

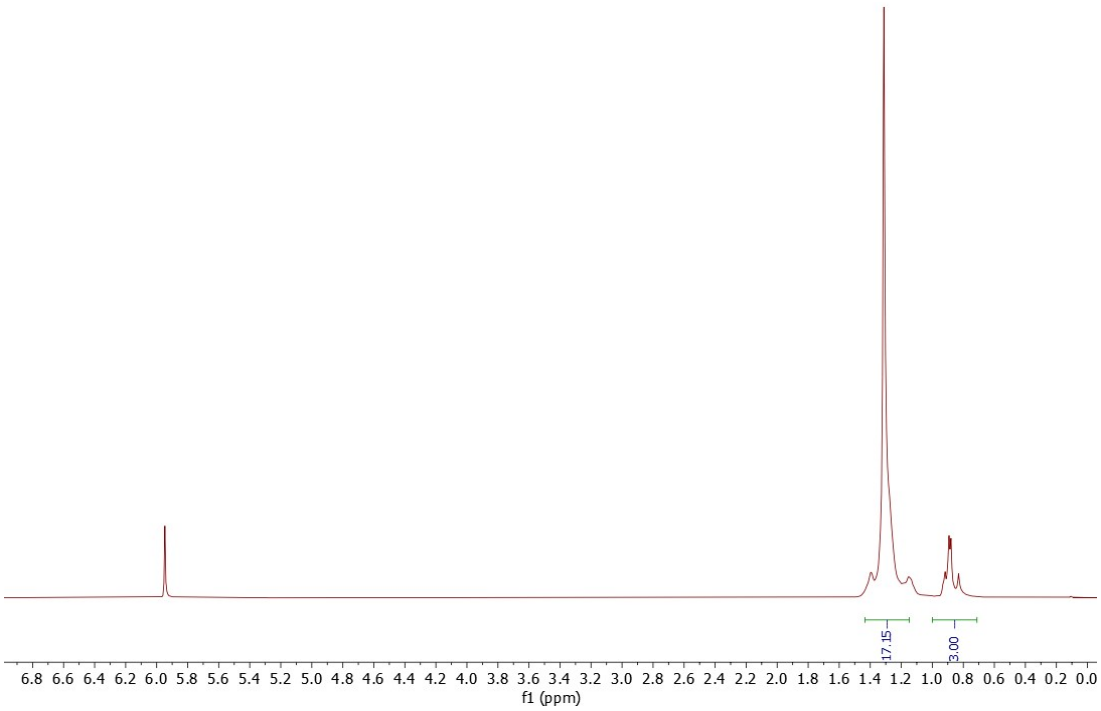

Figure S27 ^{1}H NMR spectra (in $C_2D_2Cl_4$ at 120 °C) of PE samples prepared by **Ni^{C12}** at 110 °C

7. Elastic recovery measurement of different polyethylene samples

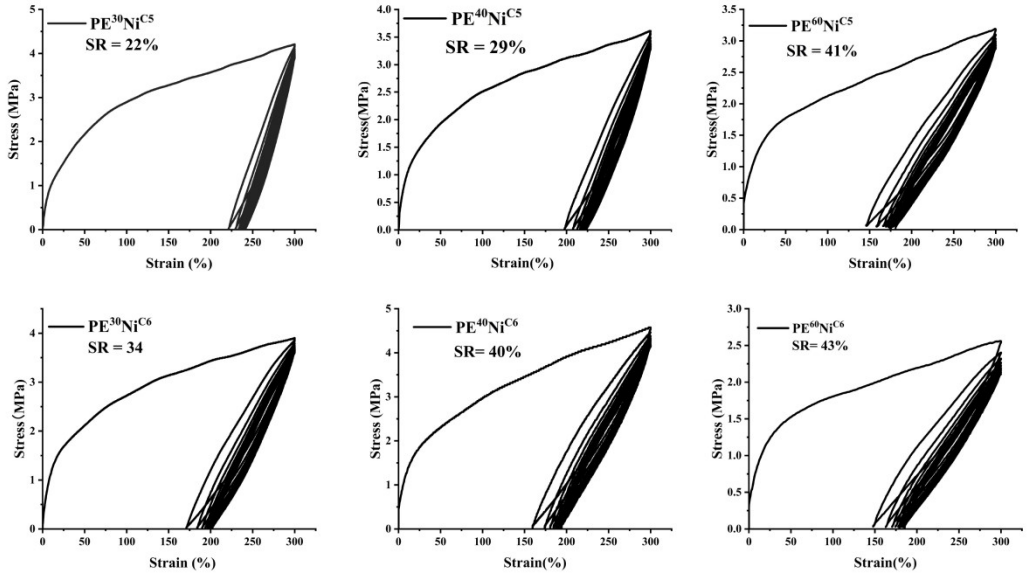

Figure S28 Strain recovery measurements of PE samples prepared by **Ni^{C5}** and **Ni^{C6}** at 30 °C, 40 °C and 60 °C.

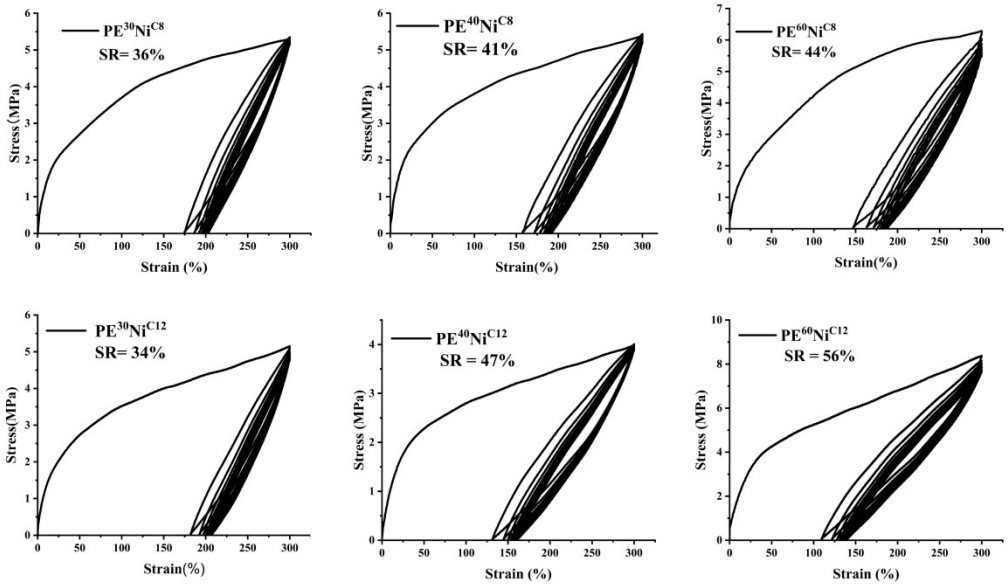

Figure S29 Strain recovery measurements of PE samples prepared by **Ni^{C8}** and **Ni^{C12}** at 30 °C, 40 °C and 60 °C.

8. GPC curves of different polyethylene samples

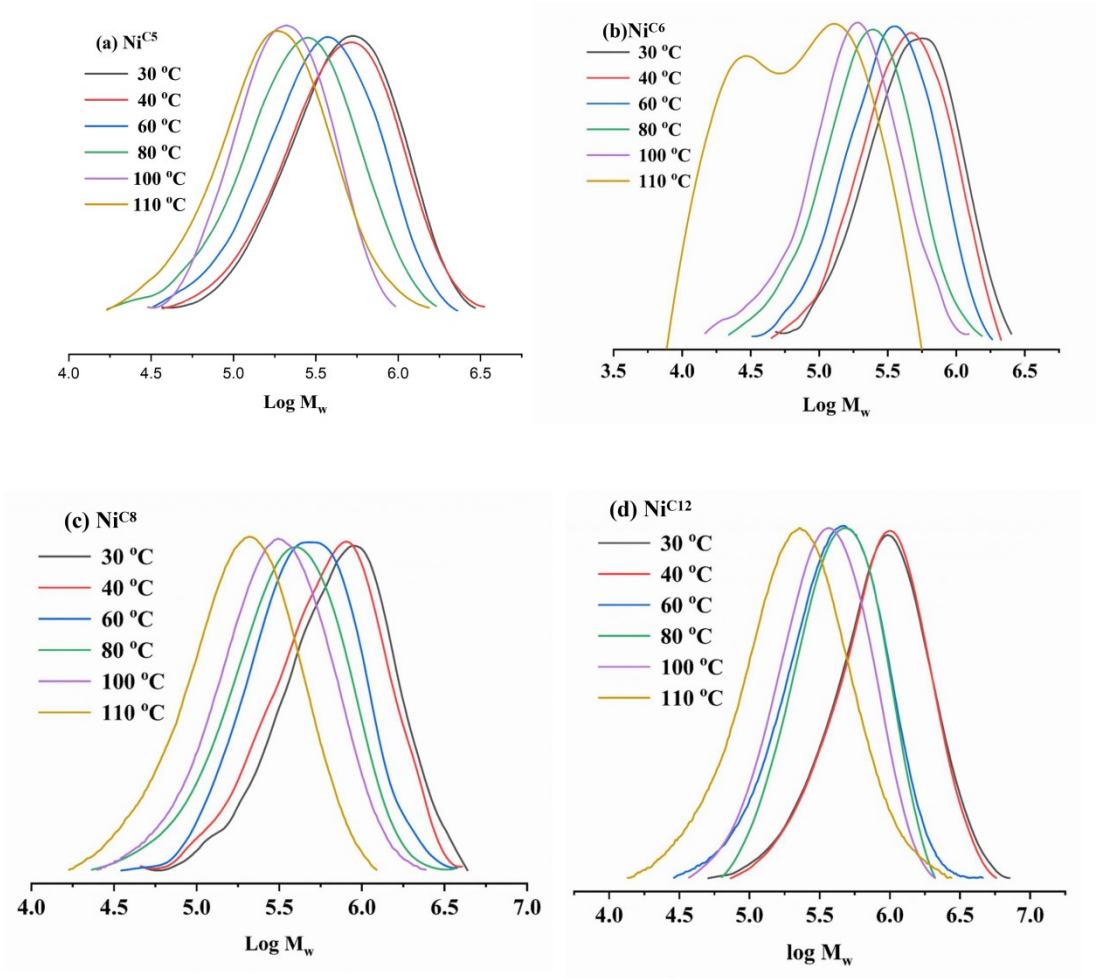

Figure S30 GPC curves of PE samples prepared by $\mathbf{Ni^{C5}}$, $\mathbf{Ni^{C6}}$, $\mathbf{Ni^{C8}}$ and $\mathbf{Ni^{C12}}$ at various reaction temperatures.

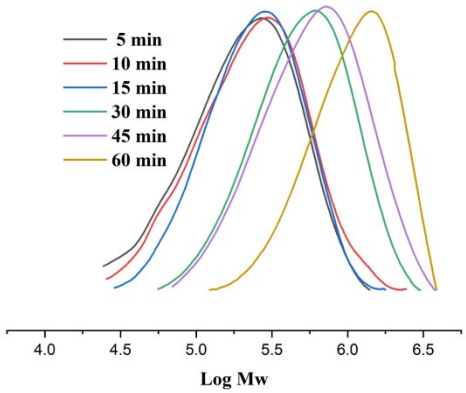

Figure S31 GPC curves of PE samples prepared by $\mathbf{Ni^{C5}}$ at various reaction times.

9. References

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