Supplementary Information

For

Axial-phenyl Constrained Bis(imino)acenaphthene-Nickel Precatalysts Enhancing Ethylene Polymerization

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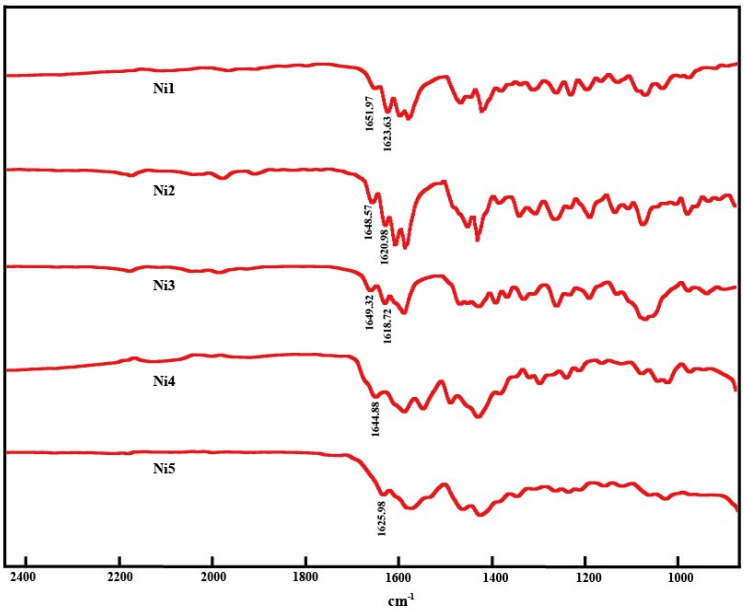


Figure S1. FT-IR spectrum of **Ni1**-**Ni5.**

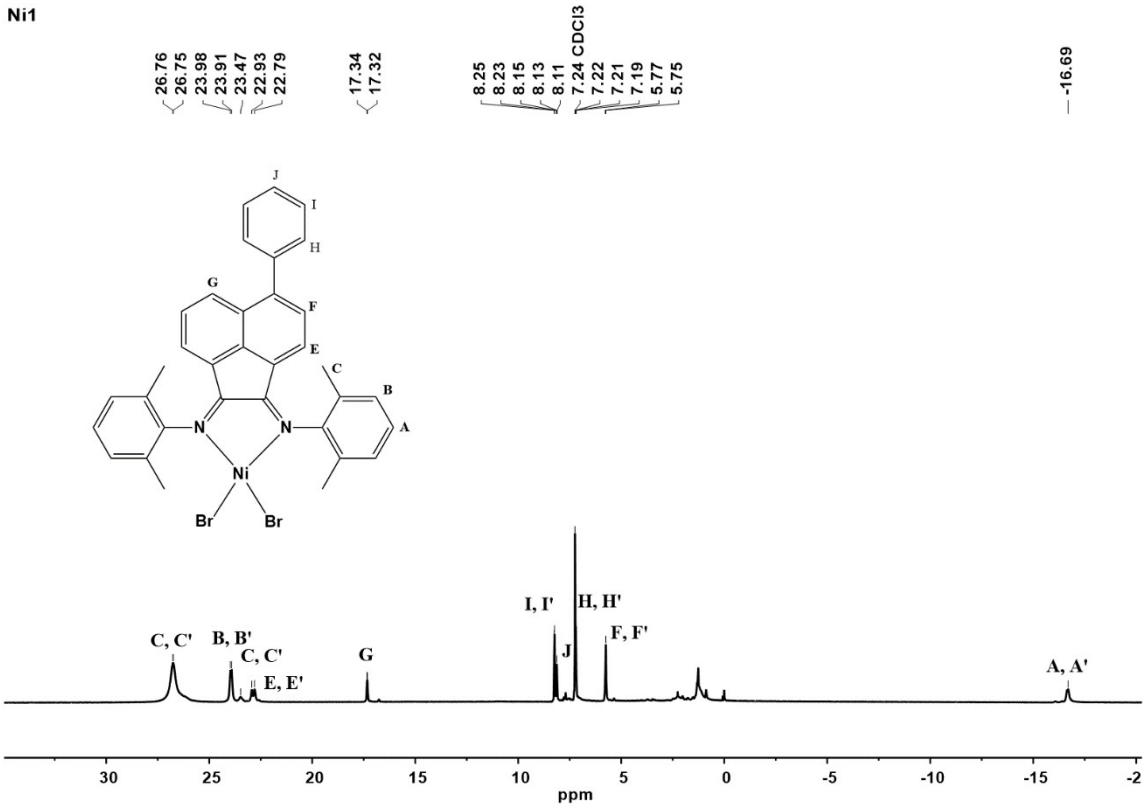


Figure S2. ^{1}H NMR (400 MPa) spectrum of **Ni1** (recorded in $CDCl_3$ at 25 °C).

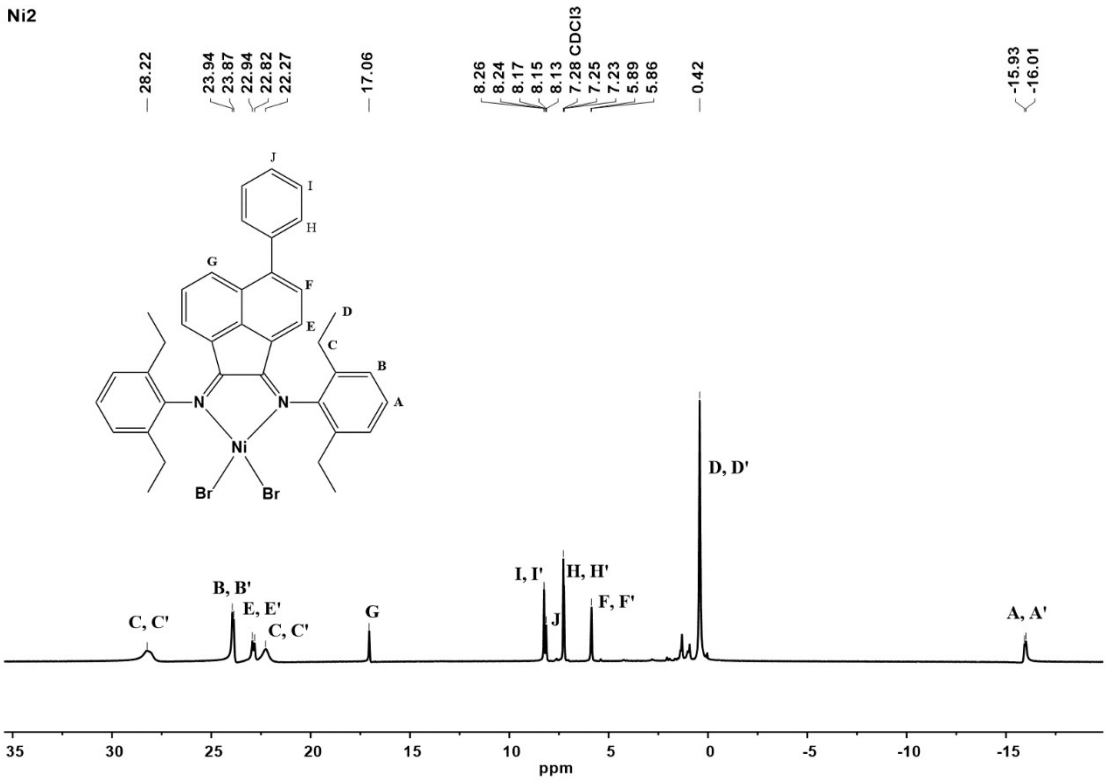


Figure S3. ^{1}H NMR (400 MPa) spectrum of **Ni2** (recorded in $CDCl_3$ at 25 °C).

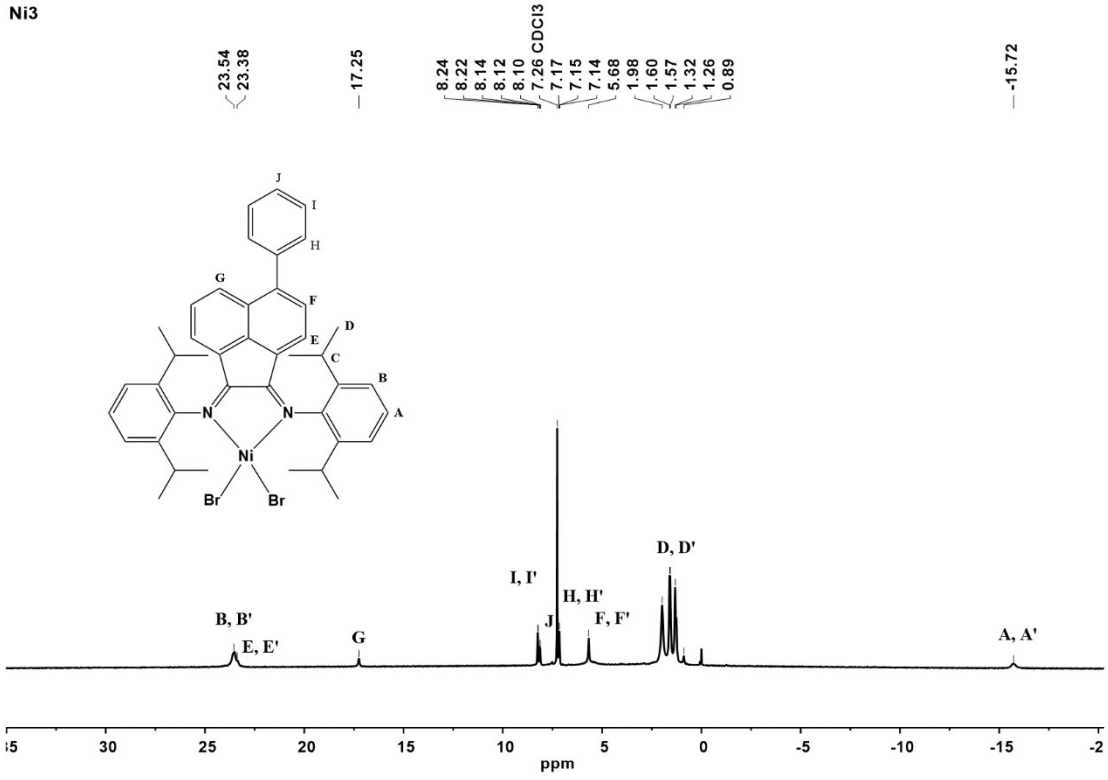


Figure S4. ^{1}H NMR (400 MPa) spectrum of **Ni3** (recorded in $CDCl_3$ at 25 °C).

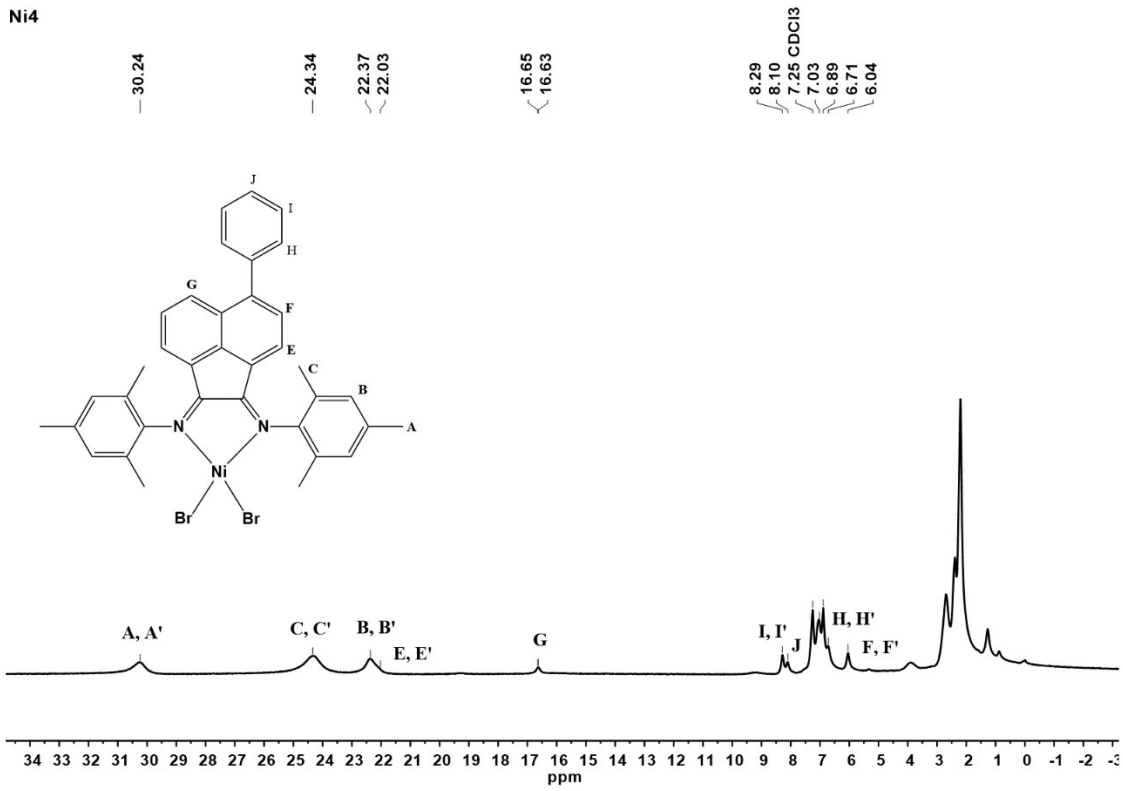


Figure S5. ^{1}H NMR (400 MPa) spectrum of **Ni4** (recorded in $CDCl_3$ at 25 °C).

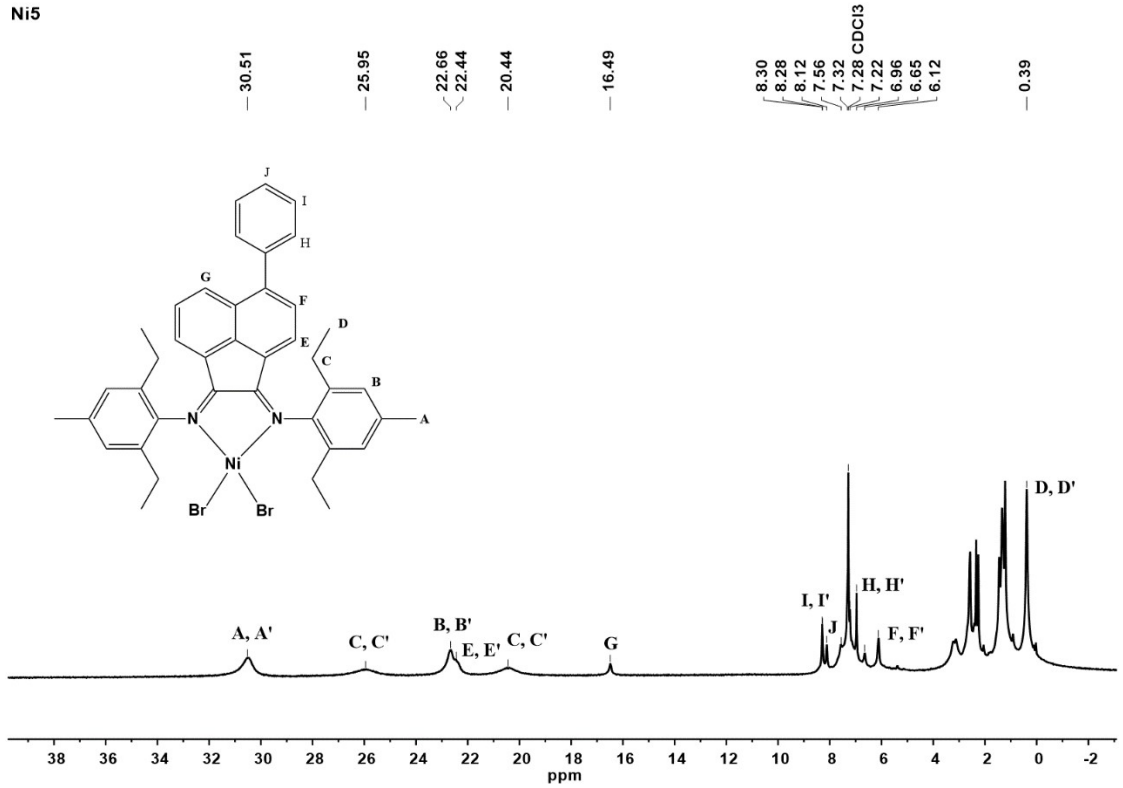


Figure S6. ^{1}H NMR (400 MPa) spectrum of **Ni5** (recorded in $CDCl_3$ at 25 °C).

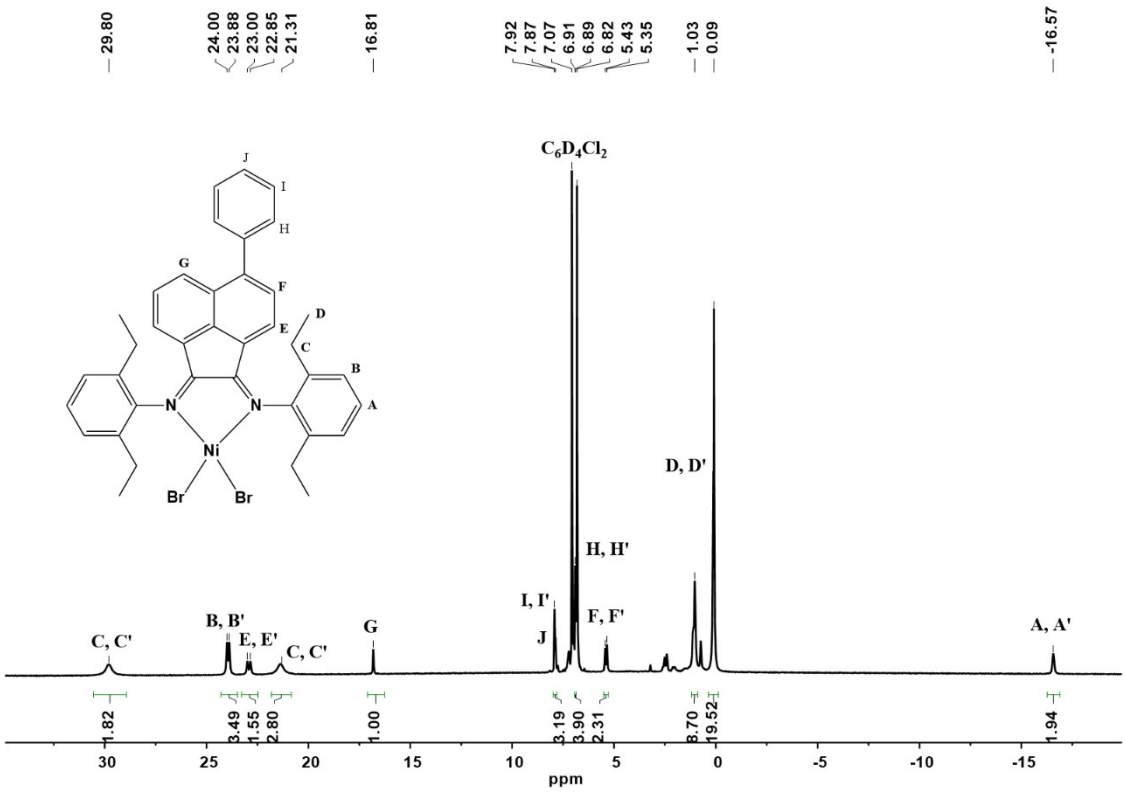


Figure S7. ^{1}H NMR (500 MPa) spectrum of **Ni2** (recorded in $C_6D_4Cl_2$ at 25 °C).

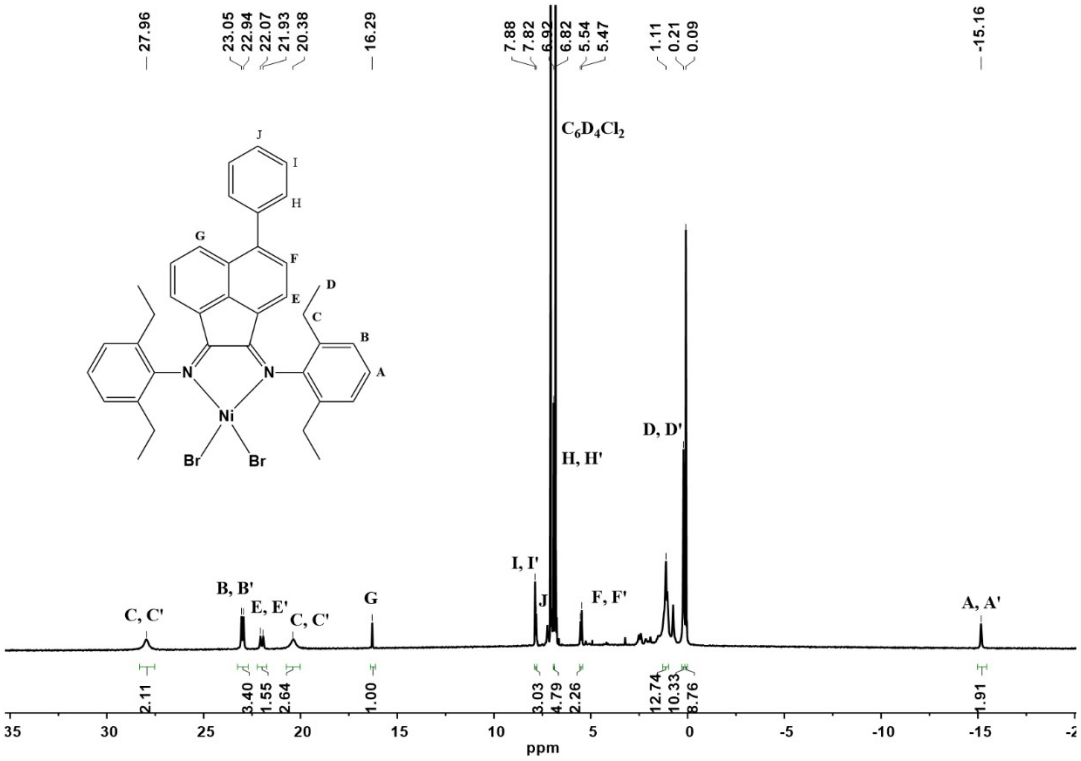


Figure S8. ^{1}H NMR (500 MPa) spectrum of **Ni2** (recorded in $C_6D_4Cl_2$ at 40 °C).

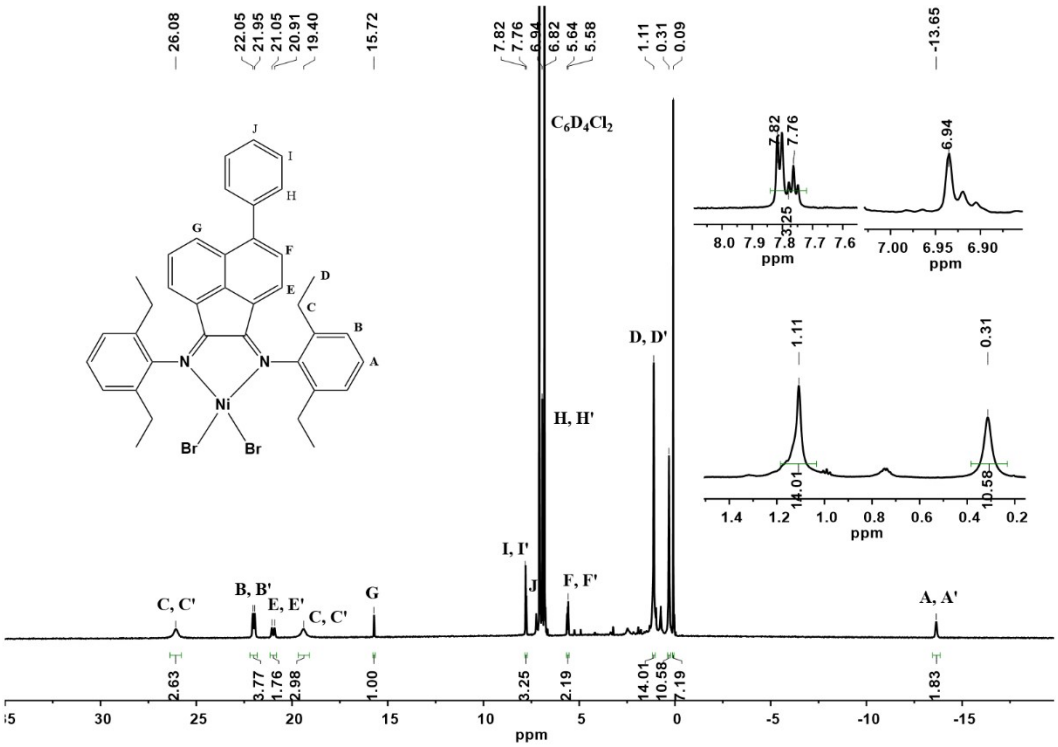


Figure S9. ^{1}H NMR (500 MPa) spectrum of **Ni2** (recorded in $C_6D_4Cl_2$ at 60 °C).

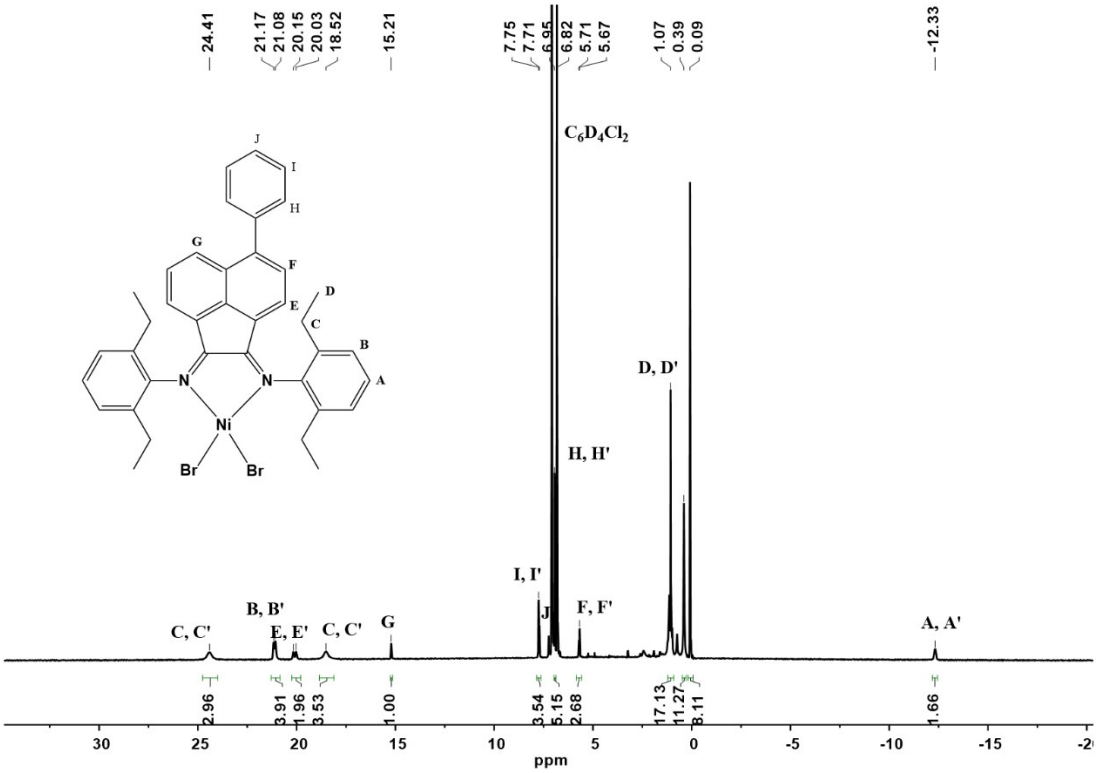


Figure S10. ^{1}H NMR (500 MPa) spectrum of **Ni2** (recorded in $C_6D_4Cl_2$ at 80 °C).

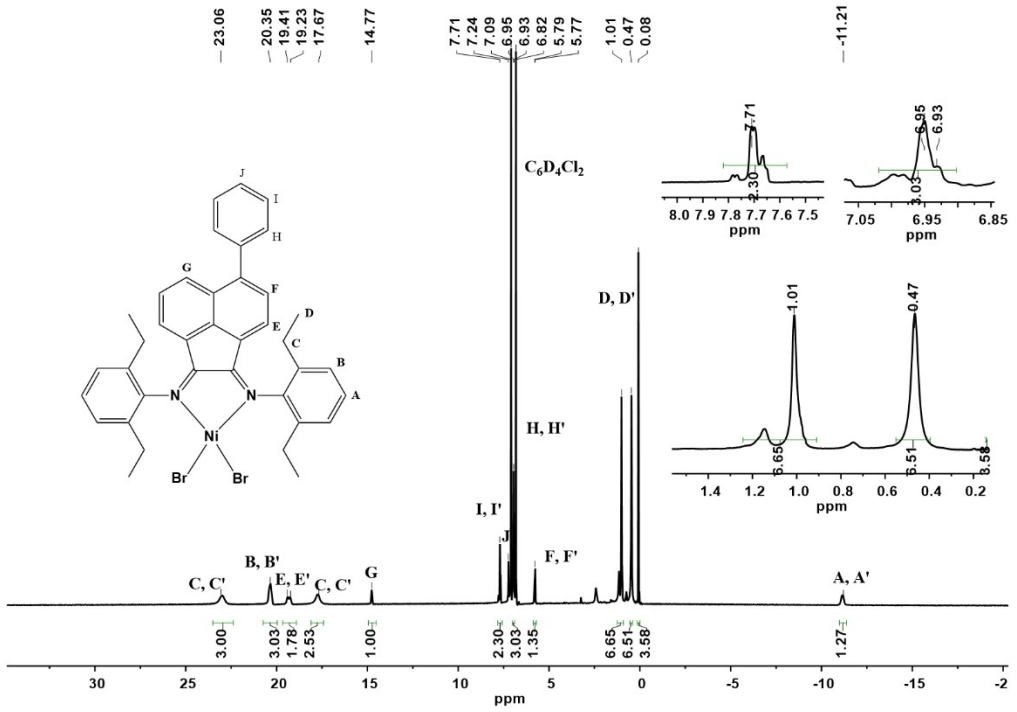


Figure S11. ^{1}H NMR (500 MPa) spectrum of **Ni2** (recorded in $C_6D_4Cl_2$ at 100 °C).

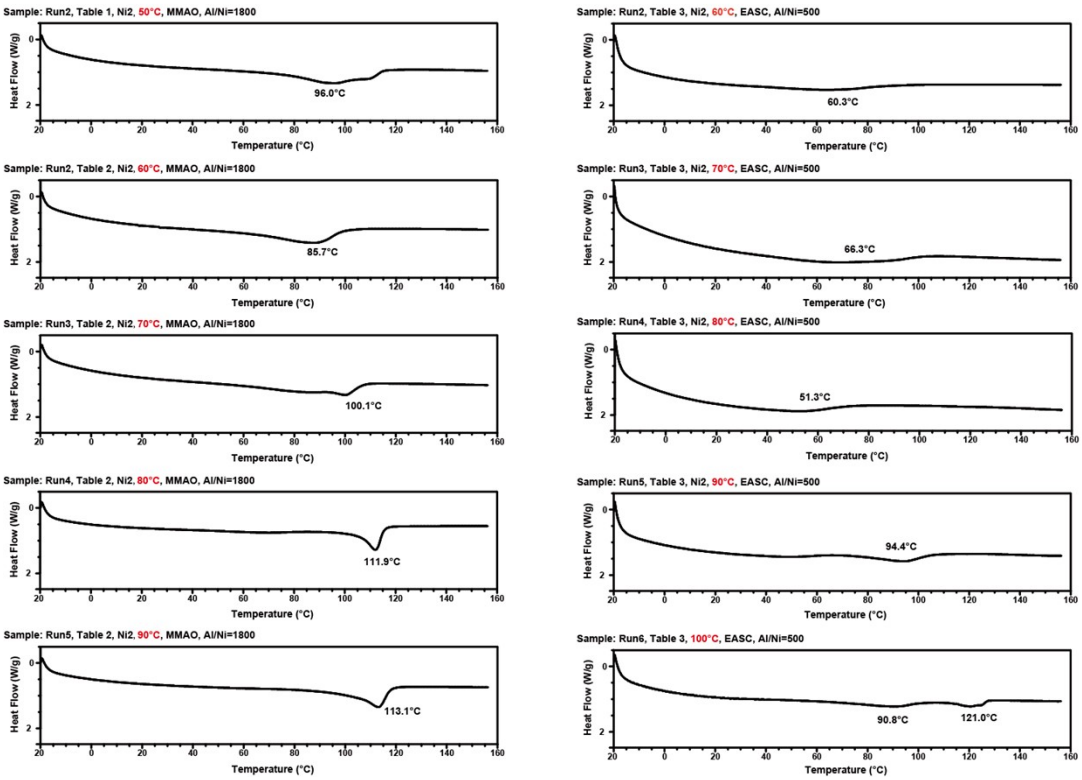


Figure S12. DSC spectrum of the polyethylenes obtained at different polymerization temperatures using MMAO or EASC as cocatalyst.

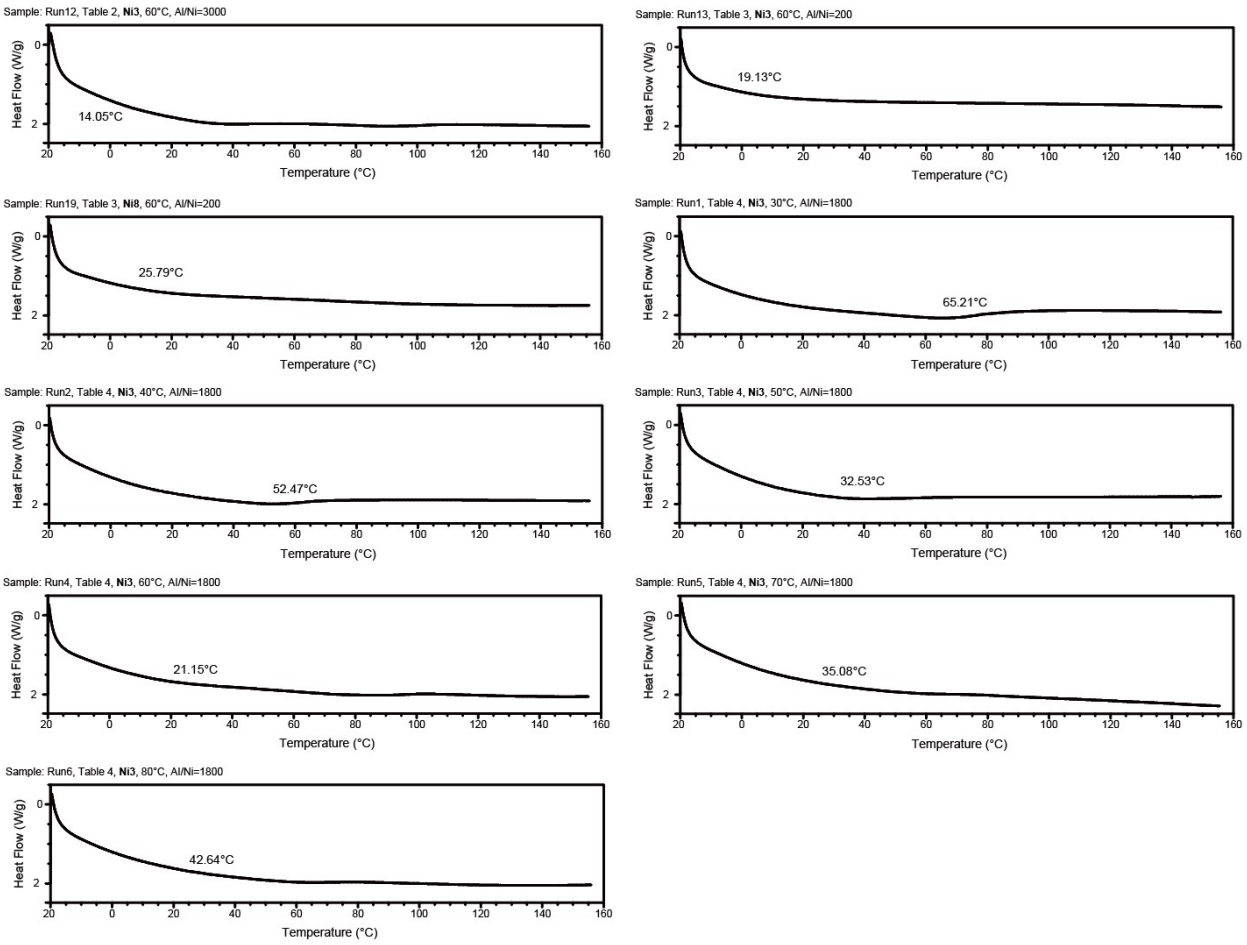


Figure S13. DSC spectrum of amorphous polyethylenes.

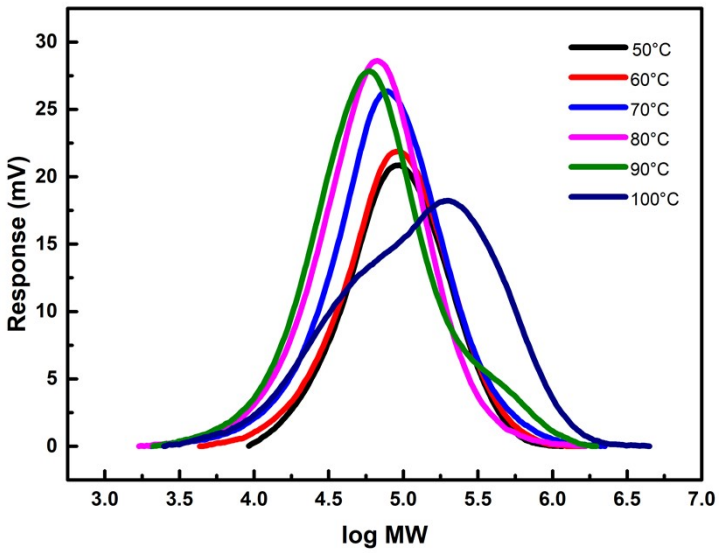
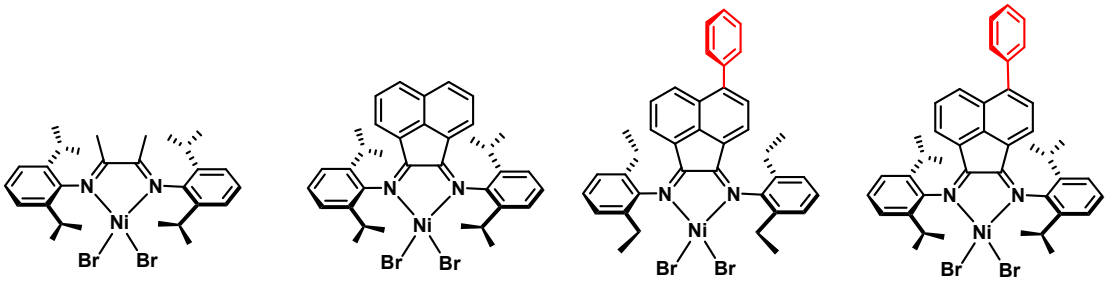


Figure S14. GPC traces of the polyethylenes produced by **Ni2**/EASC (Run 1-6, Table 3).



The stronger the skeleton rigidity, the lower the buried volume value

Rotation suppression of N-aryl group

Figure S15. The structures of **Ni9**, **Ni8**, **Ni2** and **Ni3** and their value of the buried volume ($\%V_{Bur}$).

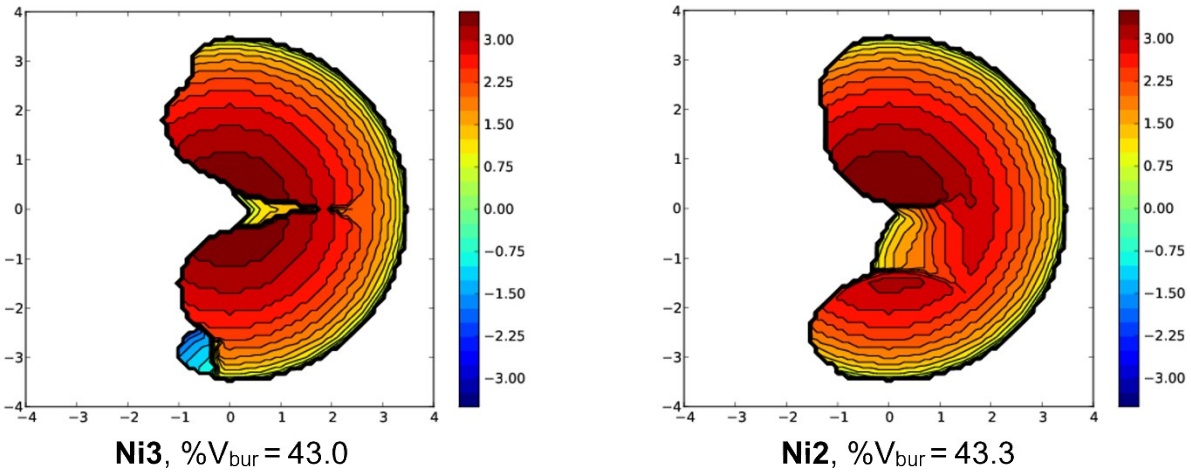


Figure S16. Topographical stereograms of **Ni3** and **Ni2**.

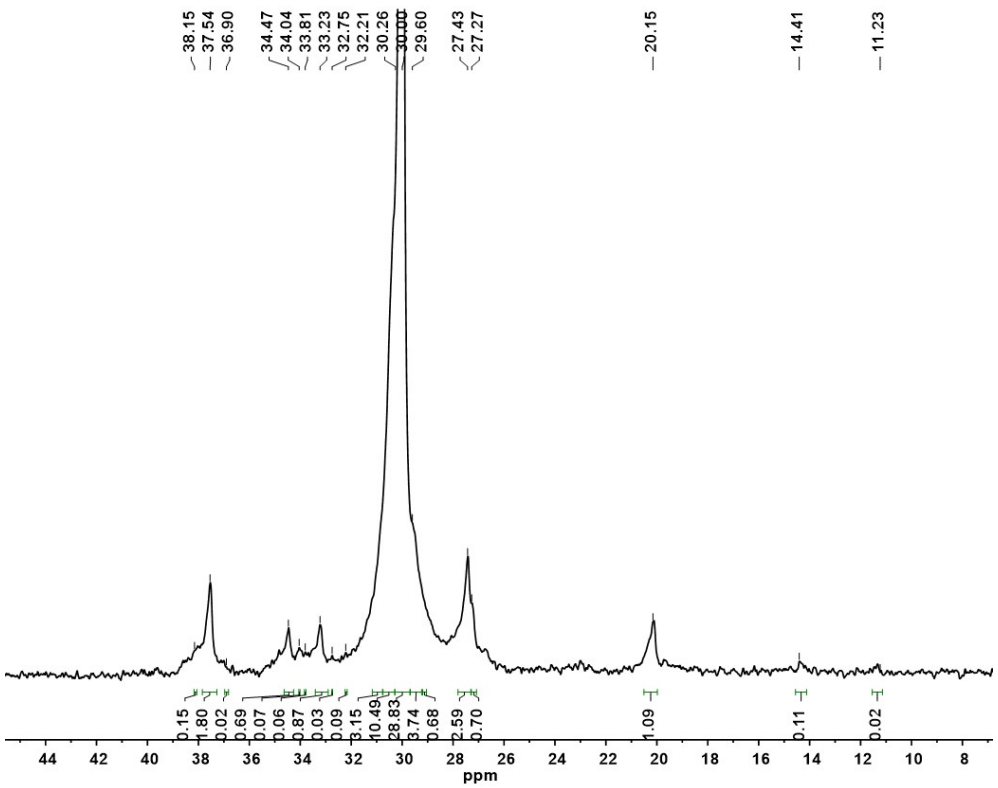


Figure S17. ^{13}C NMR (125 MPa) spectrum of **$PE_{Ni2\text{-}60\text{-}M1}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

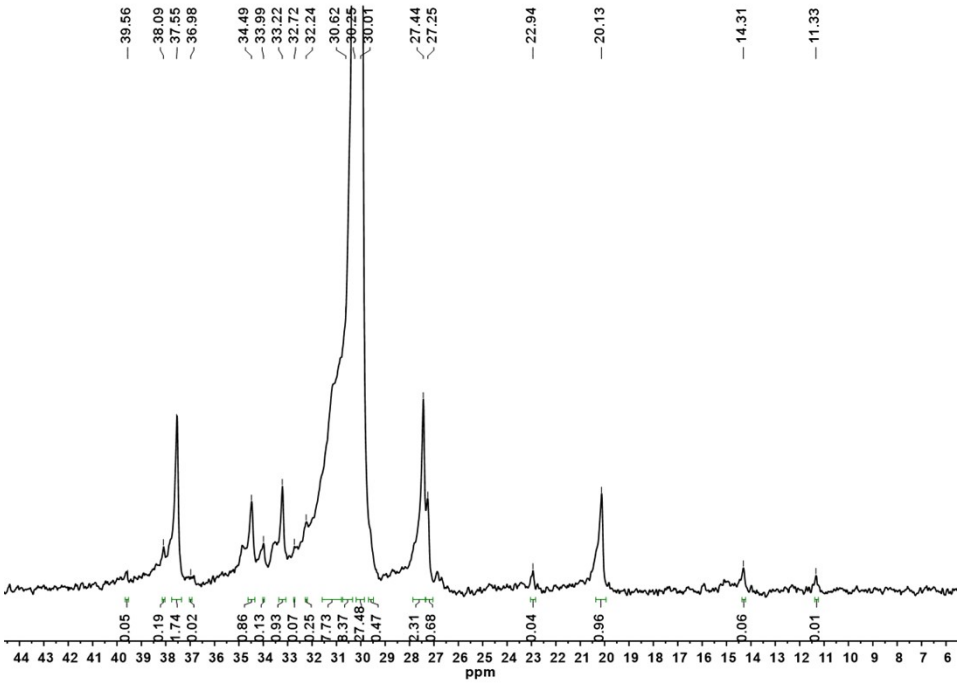


Figure S18. ^{13}C NMR (125 MPa) spectrum of **$PE_{Ni2\text{-}80\text{-}M1}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

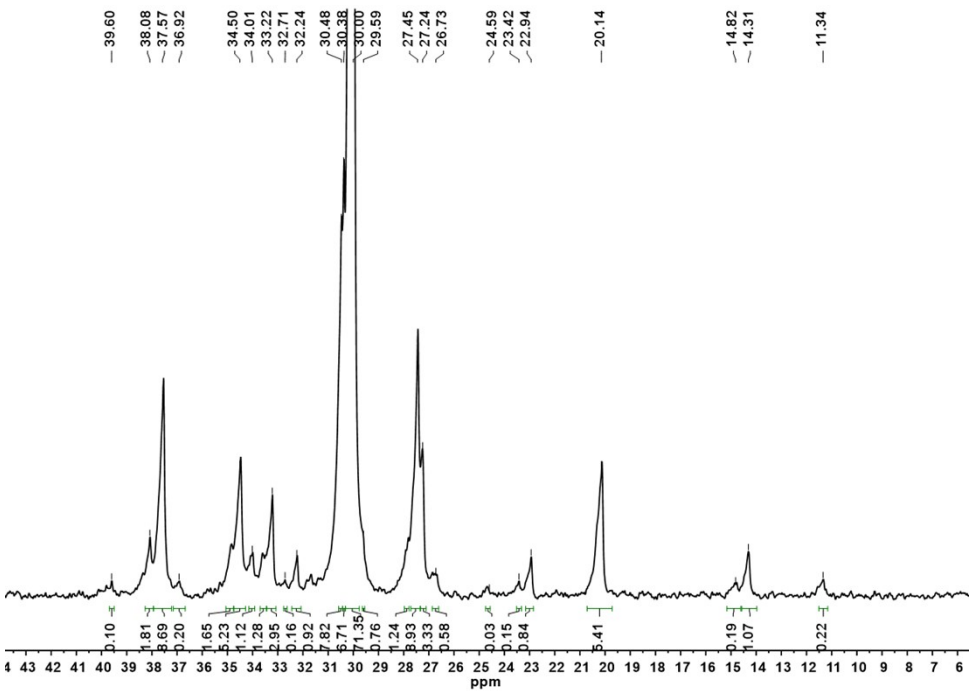


Figure S19. ^{13}C NMR (125 MPa) spectrum of **$PE_{Ni2\text{-}60\text{-}E5}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

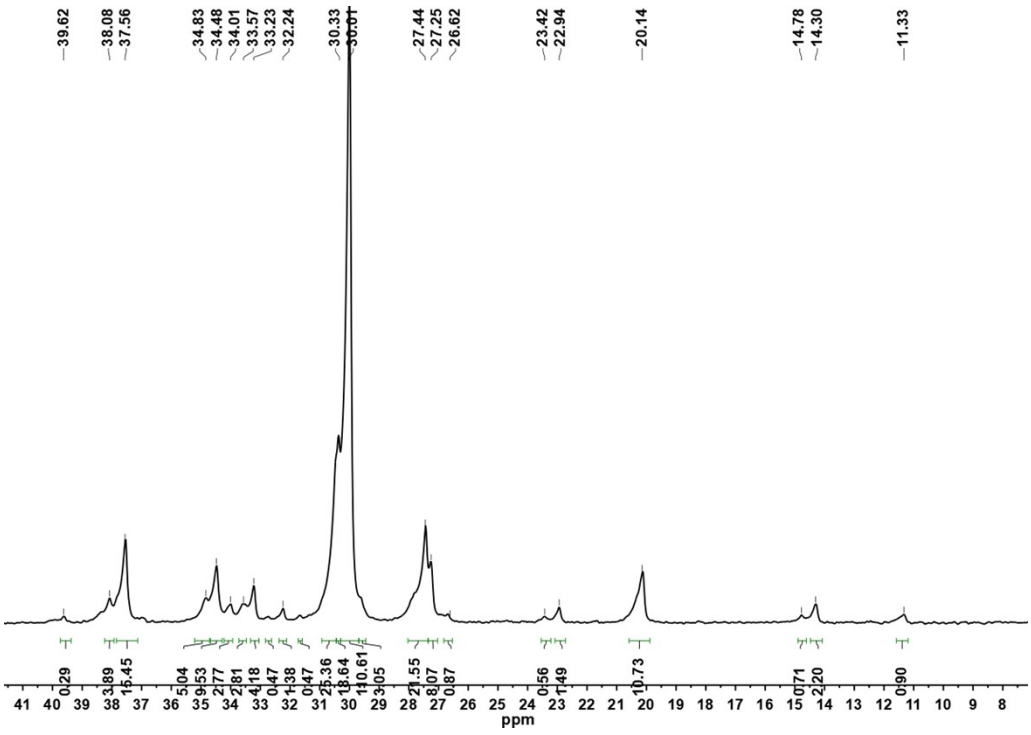


Figure S20. ^{13}C NMR (125 MPa) spectrum of **$PE_{Ni2\text{-}80\text{-}E5}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

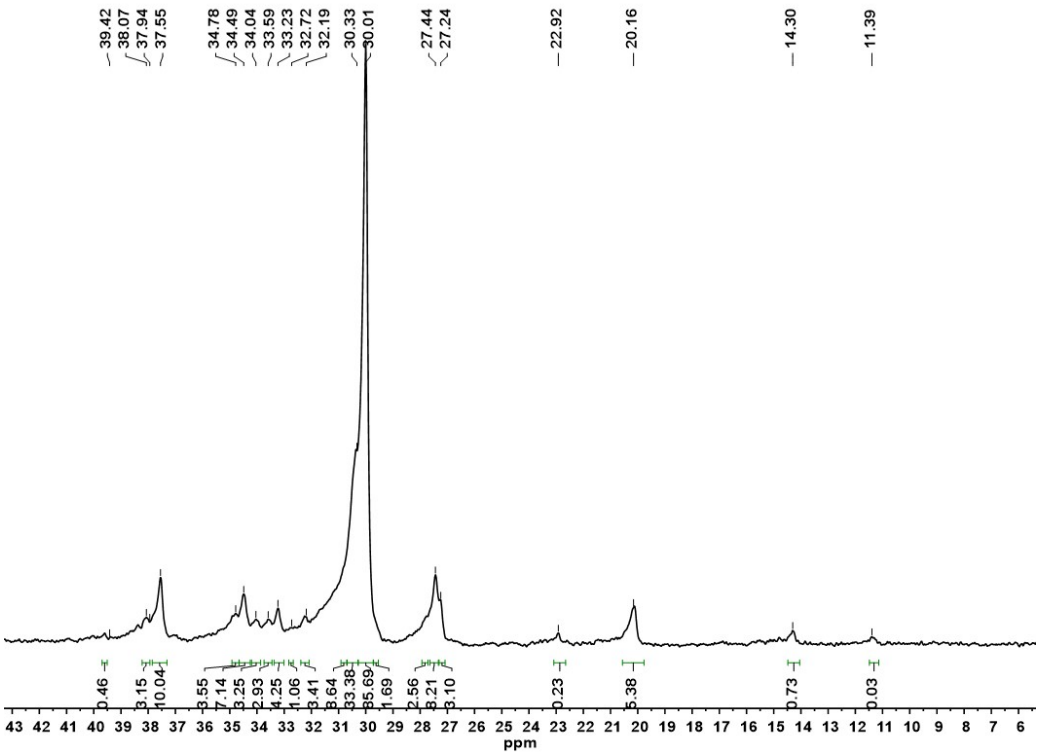


Figure S21. ^{13}C NMR (125 MPa) spectrum of **PE$_{Ni2\text{-}100\text{-}E5}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

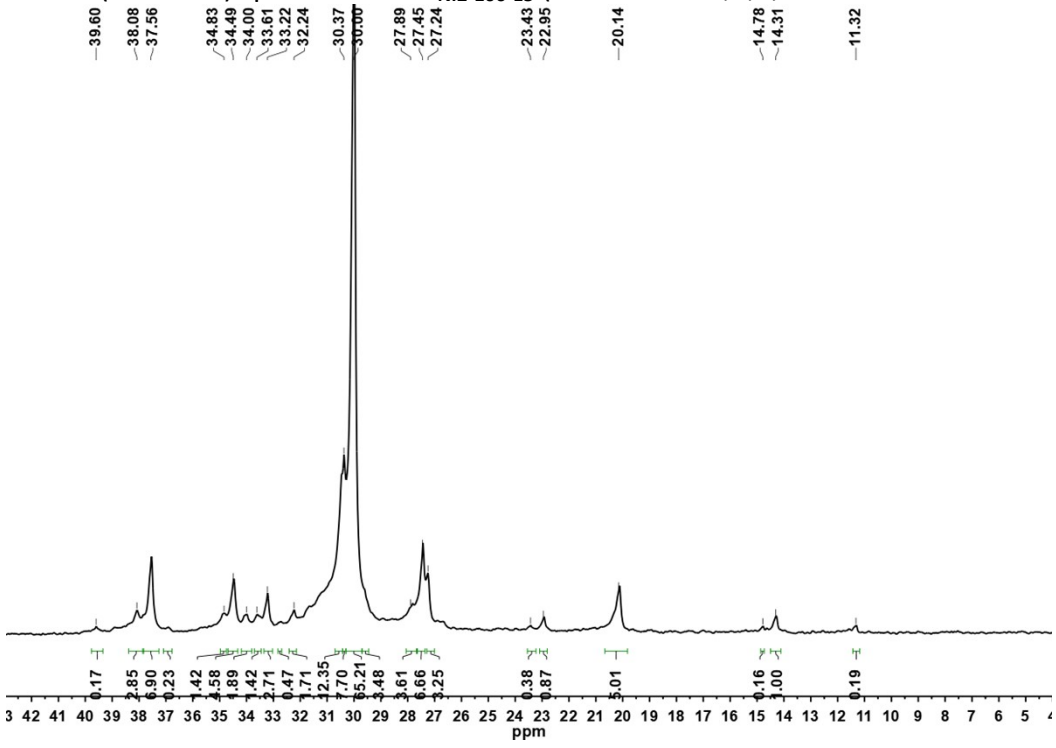


Figure S22. ^{13}C NMR (125 MPa) spectrum of **PE$_{Ni2\text{-}60\text{-}E2}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

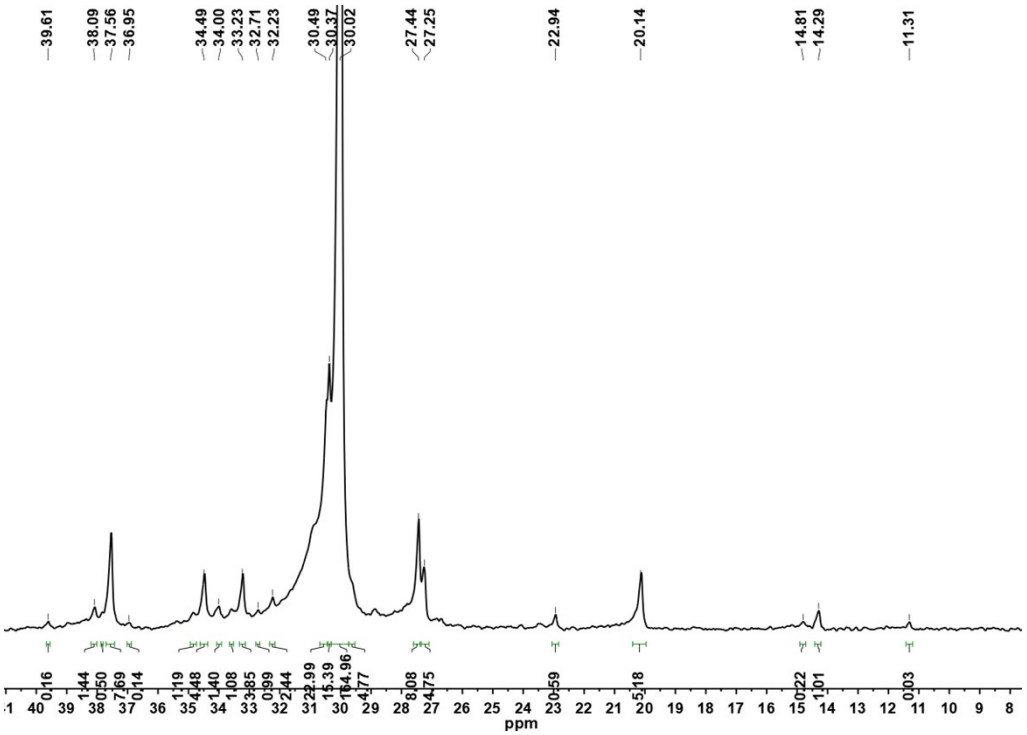


Figure S23. ^{13}C NMR (125 MPa) spectrum of **$PE_{Ni1\text{-}60\text{-}E2}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

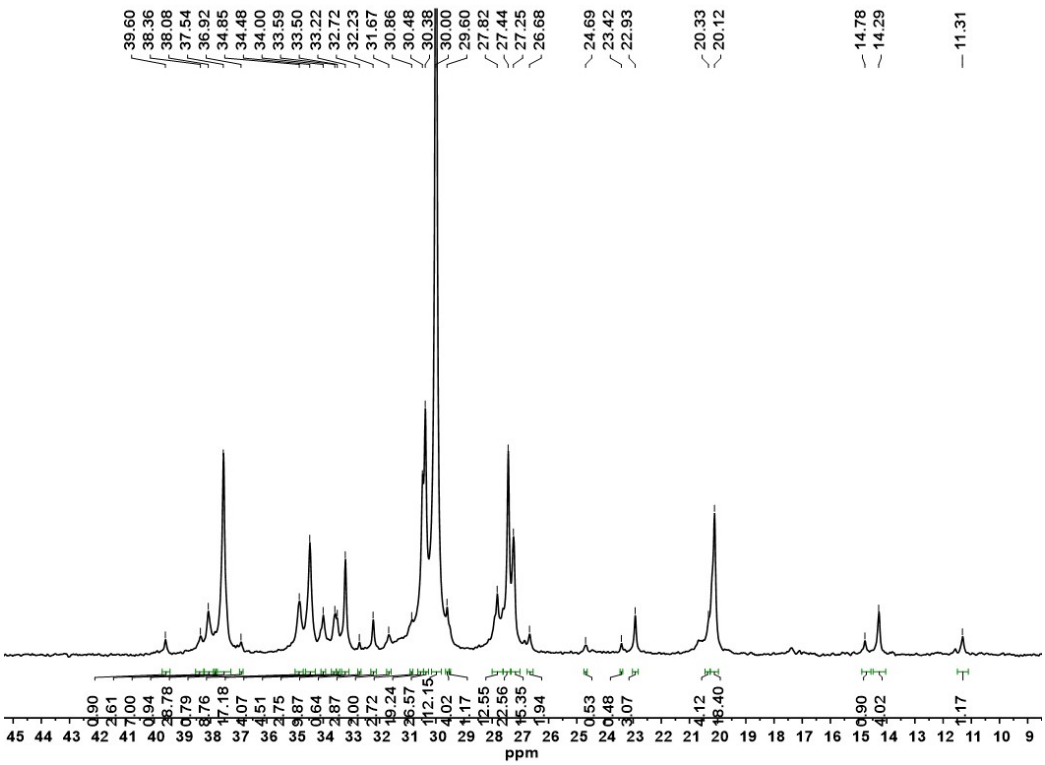


Figure S24. ^{13}C NMR (125 MPa) spectrum of **$PE_{Ni3\text{-}60\text{-}E2}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

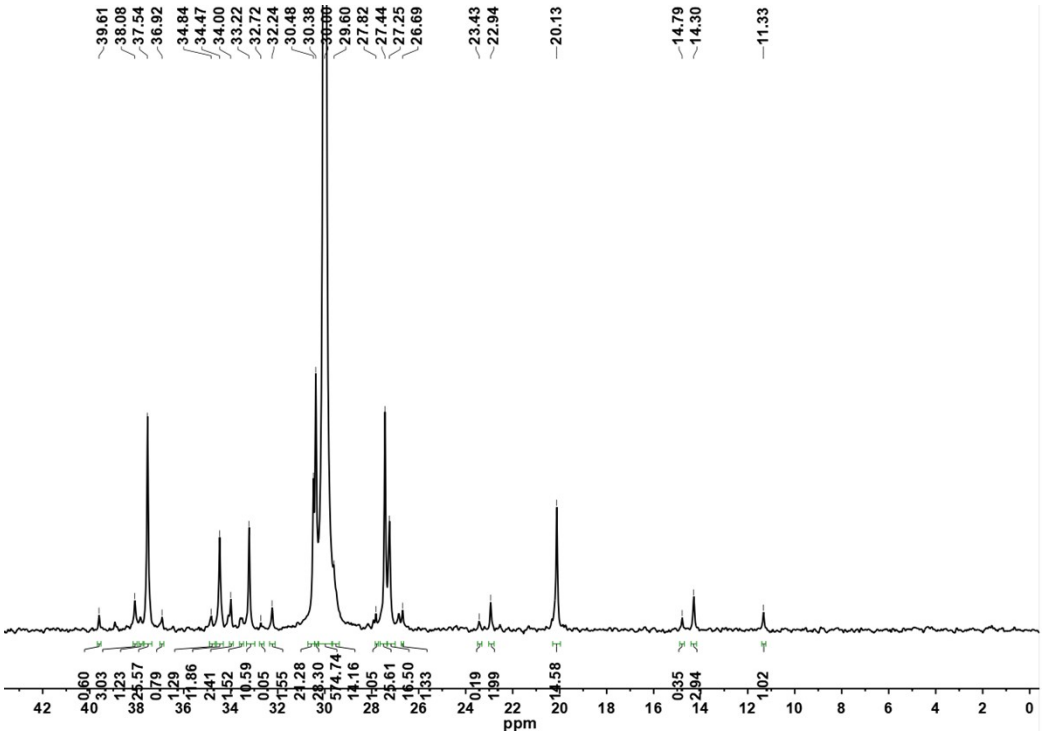


Figure S25. ^{13}C NMR (125 MPa) spectrum of **$PE_{Ni4\text{-}60\text{-}E2}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

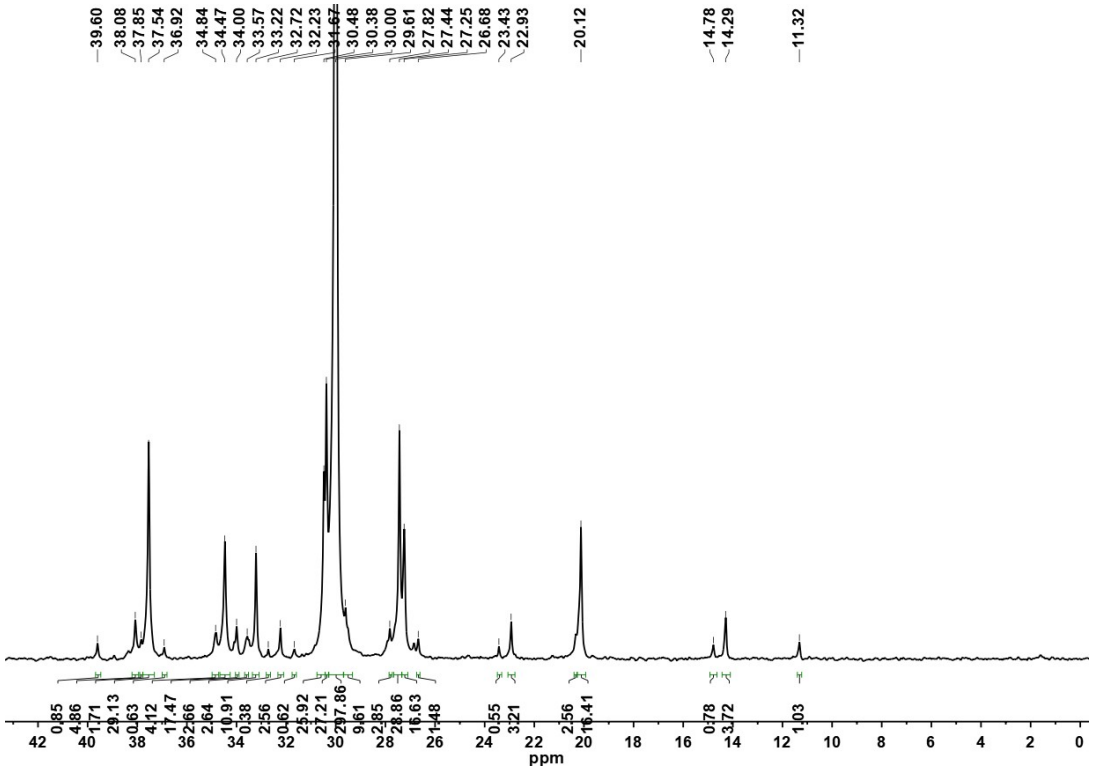


Figure S26. ^{13}C NMR (125 MPa) spectrum of **$PE_{Ni5\text{-}60\text{-}E2}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

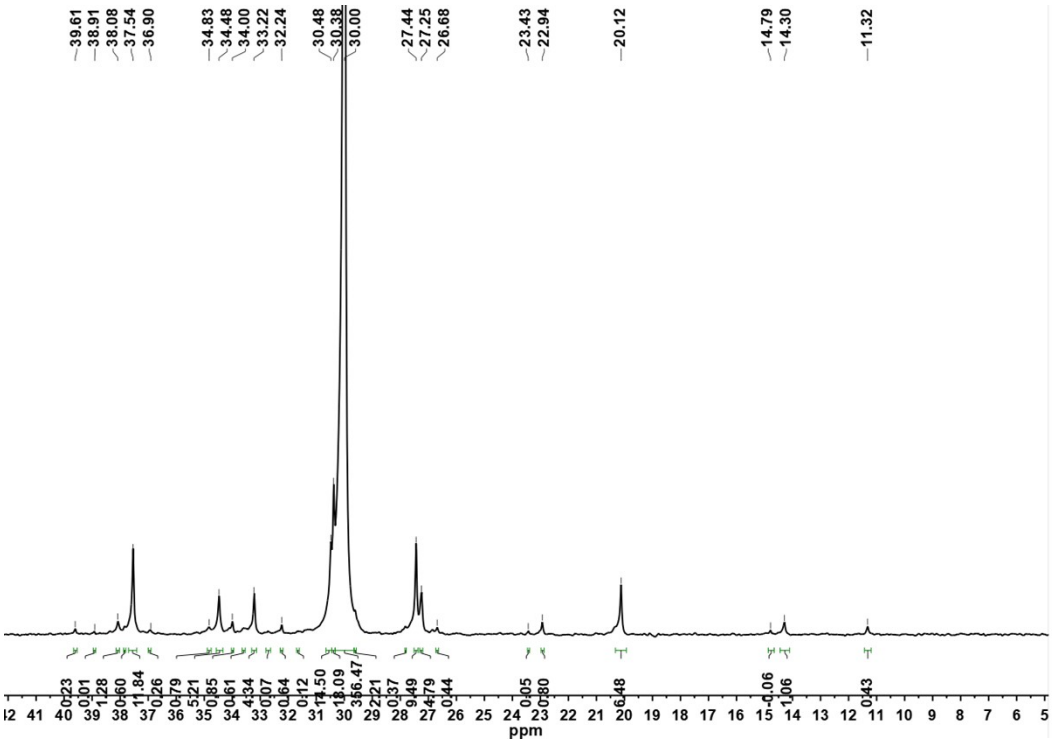


Figure S27. ^{13}C NMR (125 MPa) spectrum of **PE$_{Ni6\text{-}60\text{-}E2}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

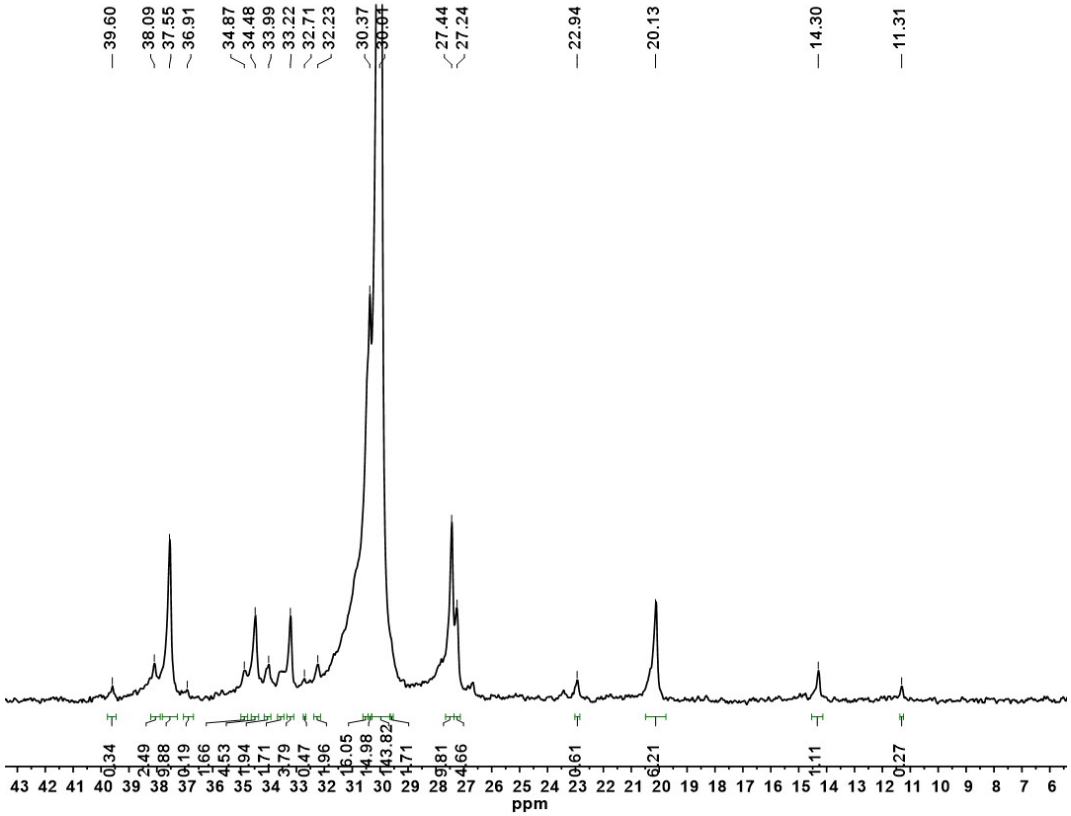


Figure S28. ^{13}C NMR (125 MPa) spectrum of **PE$_{Ni7\text{-}60\text{-}E2}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

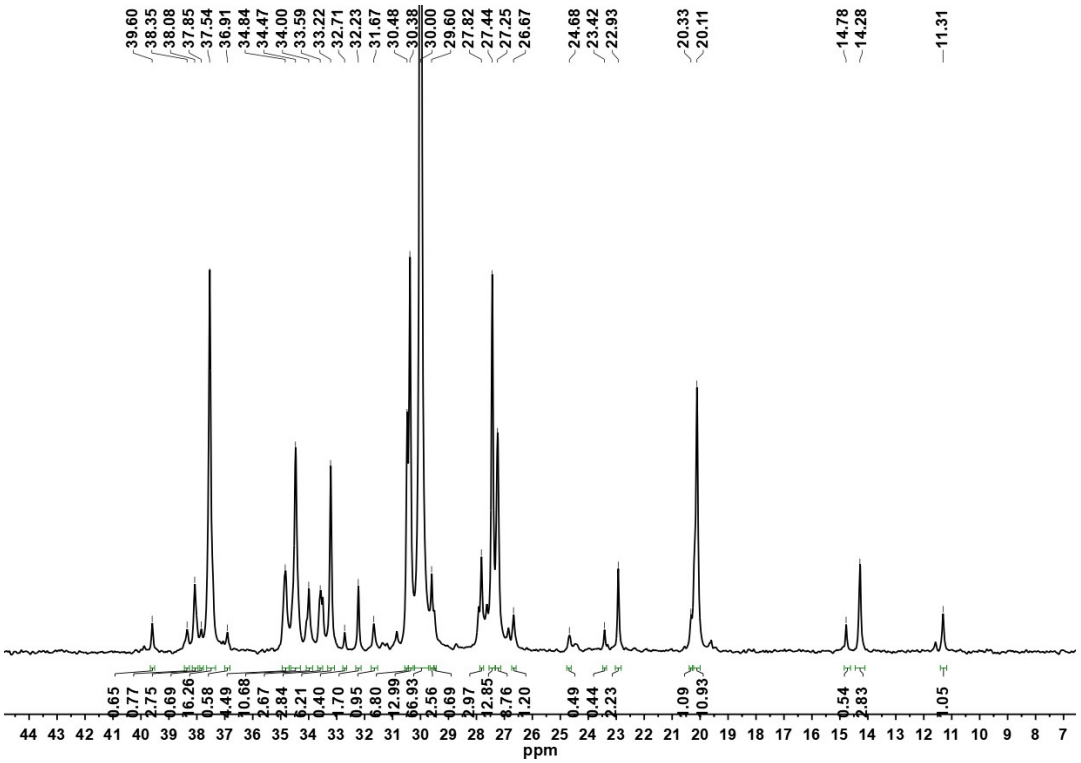


Figure S29. ^{13}C NMR (125 MPa) spectrum of **$PE_{Ni8\text{-}60\text{-}E2}$** (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C).

Table S1. Crystal data and structure refinement of **Ni2** and **Ni3**.

	Ni2	**Ni3**
CCDC number	2331173	2331174
Empirical formula	$C_{38}H_{36}Br_2N_2Ni$	$C_{84}H_{88}Br_4N_4Ni_2$
Formula weight	739.22	1590.64
Temperature/K	169.96(13)	169.98(11)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P-1
a/Å	12.9593(8)	10.1206(4)
b/Å	15.7707(6)	11.7415(6)
c/Å	17.4731(10)	18.2647(5)
α/°	90	100.897(3)
β/°	110.829(7)	90.722(3)
γ/°	90	104.200(4)
Volume/Å^3	3337.7(3)	2062.19(15)
Z	4	1
ρ_{calc} g/cm^3	1.471	1.281
μ/mm^{-1}	3.852	3.153
F(000)	1504.0	816.0
Crystal size/mm^3	0.1 × 0.06 × 0.05	0.15 × 0.08 × 0.05
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.794 to 152.49	7.924 to 151.494
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 19, -20 ≤ l ≤ 20	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	23084	24318
Independent reflections	6489 [R_{int} = 0.0513, R_{sigma} = 0.0368]	8177 [R_{int} = 0.0618, R_{sigma} = 0.0563]
Data/restraints/parameters	6489/751/578	8177/0/432
Goodness-of-fit on F^2	1.094	1.033
Final *R* indexes [I>=2σ (I)]	R_1 = 0.1258, wR_2 = 0.2328	R_1 = 0.0723, wR_2 = 0.1817
Final *R* indexes [all data]	R_1 = 0.1349, wR_2 = 0.2363	R_1 = 0.0866, wR_2 = 0.1975
Largest diff. peak/hole / e Å^{-3}	1.29/-0.90	1.89/-0.96

Table S2. Peak assignments of ^{13}C NMR spectrum of the polyethylenes [a]

Peak	Attribution	Peak	Attribution	Peak	Attribution
1	$1B_2$	12	βB_1 1,4-βB_1 1,5-βB_1 1,6-βB_1 $4B_5$	23	1,4-brB_1
2	$1B_4$ $1B_5$ $1B_n$	13	1,6-$\beta'B_1$	24	αB_2
3	$1B_3$	14	$3B_4$	25	$4B_4$
4	$1B_1$ 1,5-B_1 1,6-B_1	15	$4B_n$	26	$\alpha B_{3\text{-}5}$ $5B_5$ nB_n αB_n 1,4-αB_n 1,4-nB_n
5	1,4-$1B_1$	16	$\delta B_{1\text{-}n}$	27	1,4-$\alpha'B_1$
6	$2B_3$	17	γB_1 1,4-γB_1 1,5-γB_1 1,6-γB_1	28	$3B_3$
7	$2B_5$ $2B_n$ 1,4-$2B_n$	18	$\gamma B_{2\text{-}5}$ 1,4-γB_n 1,4-$(n\text{-}2)B_n$ γB_n	29	αB_1 1,4-αB_1 1,5-αB_1 1,6-αB_1 1,6-$a'B_1$
8	$2B_{4\text{-}8}$	19	1,4-$\alpha'B_n$	30	brB_3 1,5-$\alpha'B_1$
9	1,5-$\beta'B_1$	20	$3B_n$ 1,4-$3B_n$	31	$brB_{4,5,n}$
10	$2B_2$	21	$3B_5$	32	1,4-brB_n
11	$\beta B_{2\text{-}5}$ βB_n $(n\text{-}1)B_n$ 1,4-βB_n 1,4-$(n\text{-}1)B_n$	22	brB_1 1,5-brB_1 1,6-brB_1	33	brB_2

[a] ^{13}C NMR spectrum of the polyethylenes (**$PE_{Ni3\text{-}60\text{-}E2}$**) was shown in Figure 12 in manuscript.

Table S3. Branching analysis of selected samples of polyethylenes. [a]

Samples	Branches /1000 C's	Methyl branches/%	Ethyl branches/ %	Propyl branches/%	Butyl branches/ %	Amyl branches/ %	Long branches/ %	Details
$PE_{Ni2\text{-}60\text{-}M1}$	81	93.30	0.36	0.72	1.27	1.09	3.26	Run 2, Table 2
$PE_{Ni2\text{-}80\text{-}M1}$	83	84.36	0.62	0.74	2.41	2.60	9.27	Run 4, Table 2
$PE_{Ni2\text{-}60\text{-}E5}$	122	81.22	1.99	1.75	5.67	1.40	8.07	Run 2, Table 3
$PE_{Ni2\text{-}80\text{-}E5}$	167	83.12	1.41	3.10	6.06	1.71	4.60	Run 4, Table 3
$PE_{Ni2\text{-}100\text{-}E5}$	119	69.76	0.09	3.05	9.22	3.60	14.27	Run 6, Table 3
$PE_{Ni1\text{-}60\text{-}E2}$	65	64.58	0.44	1.15	5.73	8.11	20.00	Run 8, Table 3
$PE_{Ni2\text{-}60\text{-}E2}$	123	65.31	0.55	2.22	10.93	4.53	16.47	Run 12, Table 3
$PE_{Ni3\text{-}60\text{-}E2}$	185	76.22	4.83	2.46	7.10	2.00	7.39	Run 13, Table 3
$PE_{Ni4\text{-}60\text{-}E2}$	48	85.29	2.55	2.60	4.30	0.16	5.10	Run 14, Table 3
$PE_{Ni5\text{-}60\text{-}E2}$	97	83.67	2.19	1.77	4.52	1.07	6.78	Run15, Table 3
$PE_{Ni6\text{-}60\text{-}E2}$	30	85.68	1.98	2.31	3.99	0.62	5.41	Run16, Table 3
$PE_{Ni7\text{-}60\text{-}E2}$	74	82.47	0.32	0.82	5.81	1.72	8.85	Run17, Table 3
$PE_{Ni8\text{-}60\text{-}E2}$	180	74.89	3.37	3.15	8.46	2.18	7.95	Run19, Table 3

[a] Data determined from the ^{13}C NMR spectrum.

Table S4. Stress-strain properties of the selected polyethylene samples.

Samples	Maximum load /N	Modulus of elasticity /%	Rupture Stress /MPa	Rupture Strain /%
$\mathbf{PE_{Ni2\text{-}60\text{-}M1}}$	99.68566	31.16010	20.86127	989.17561
$\mathbf{PE_{Ni2\text{-}80\text{-}M1}}$	121.83333	25.94073	26.47687	1407.09152
$\mathbf{PE_{Ni1\text{-}60\text{-}M3}}$	35.26493	231.10084	5.11201	441.05134
$\mathbf{PE_{Ni3\text{-}60\text{-}M3}}$	34.90348	3.92895	7.15527	945.84150
$\mathbf{PE_{Ni4\text{-}60\text{-}M3}}$	63.21949	327.03846	10.63216	1357.50637
$\mathbf{PE_{Ni5\text{-}60\text{-}M3}}$	98.77724	25.40926	22.83357	1008.34370
$\mathbf{PE_{Ni2\text{-}60\text{-}E5}}$	55.29499	14.95573	12.10514	1189.17704
$\mathbf{PE_{Ni2\text{-}80\text{-}E5}}$	43.55141	9.05498	10.36686	2019.59190