Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Ligand Steric Effects on *α*-Diimine Nickel Catalyzed Ethylene and 1-Hexene Polymerization

Jinlong Sun,[a] Fuzhou Wang,*[ab] Weimin Li[a] and Min Chen*[a]

[a] Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, School of Pertrochemical Engineering, Changzhou University, Changzhou 213164, China.

[b] Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739-8527, Japan.

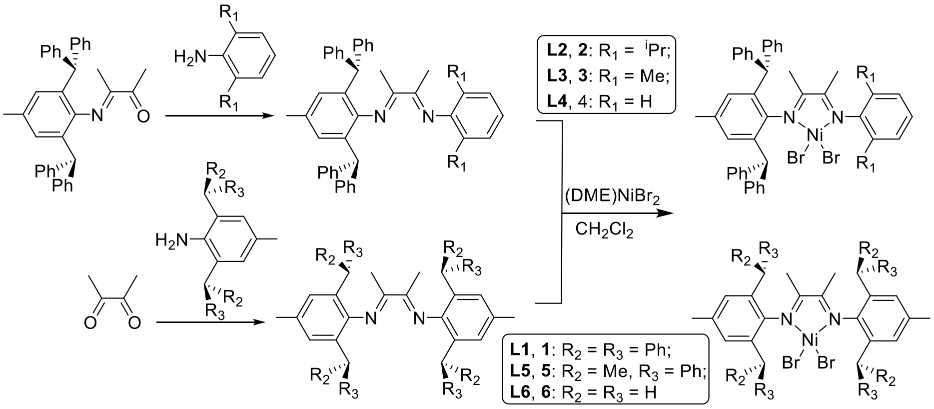
*Correspondence to: F. Z. Wang (E-mail: wangfuzhou1718@126.com)
M. Chen (E-mail: misschen@ustc.edu.cn)

Contents

1. Synthesis and Characterization

1.1. Synthesis of *α*-diimine ligands L1–L6 and complexes 1–6

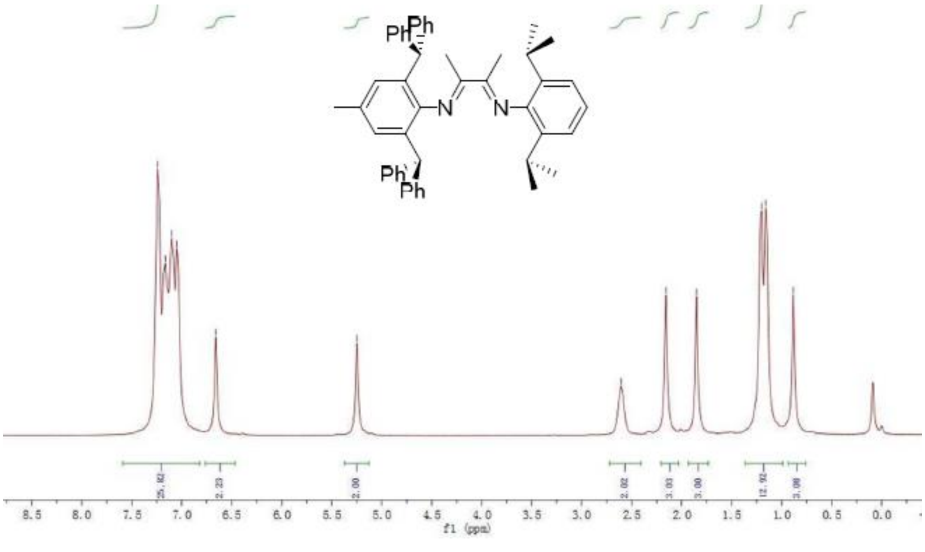
The desired ligands were prepared by the the Schiff base condensation using *p*-toluenesulfonic acid (*p*-TsOH) as catalyst in high yields (**Scheme S1**). All *α*-diimine ligands **L1–L6** were characterized by elemental analysis, ^{1}H NMR and ^{13}C NMR. Complexes **1–6** were synthesized from the reactions of the corresponding ligand with (DME)NiBr$_2$ in high yields. These complexes were characterized by IR spectroscopy and elemental analysis.



Scheme S1. Synthesis of *α*-diimine ligands **L1–L6** and their complexes **1–6**.

All *α*-diimine ligands **L1–L6**[1–4], {bis[*N*,*N′*-(4-methyl-2,6-dibenzhydrylphenyl)imino]-2,3-butadiene}dibromidonickel **1**[2], {bis[*N*,*N′*-(4-methyl-2,6-di-*sec*-phenylethylphenyl)imino]-2,3-butadiene}dibromidonickel **5**[4] and {bis[*N*,*N′*-(2,4,6-trimethylphenyl)imino]-2,3-butadiene}dibromidonickel **6**[4] were synthesized according to the literature.

1.2. NMR spectrum of the ligands L2–L6



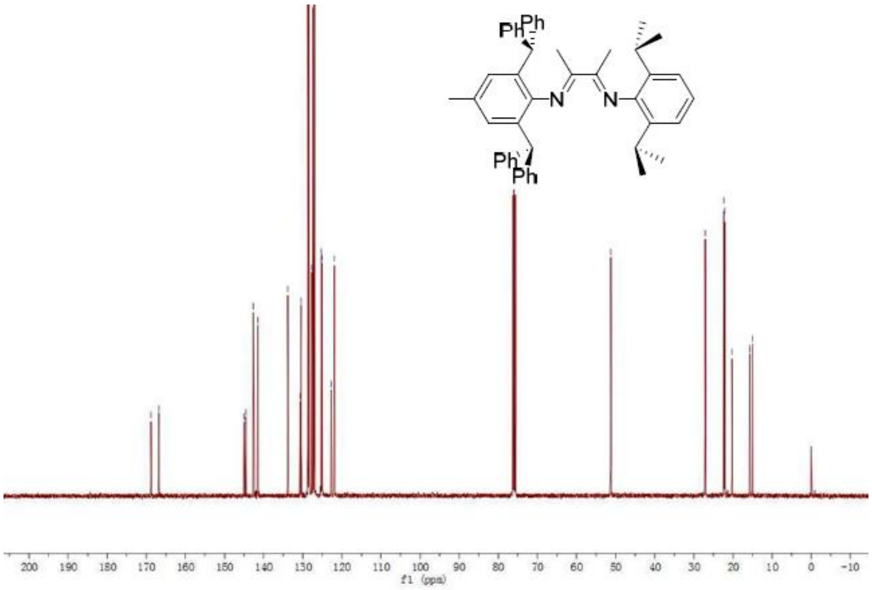


Fig. S1. ^{1}H and ^{13}C NMR spectrum of ligand **L2**.

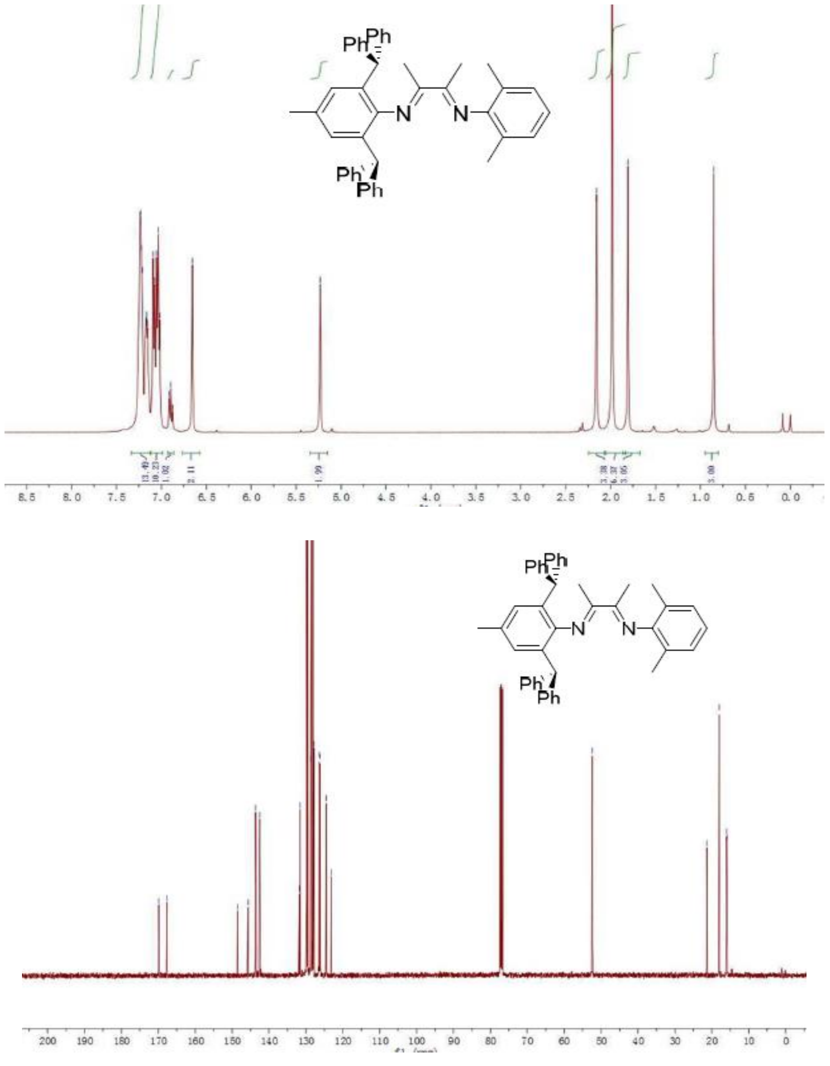


Fig. S2. ^{1}H and ^{13}C NMR spectrum of ligand **L3**.

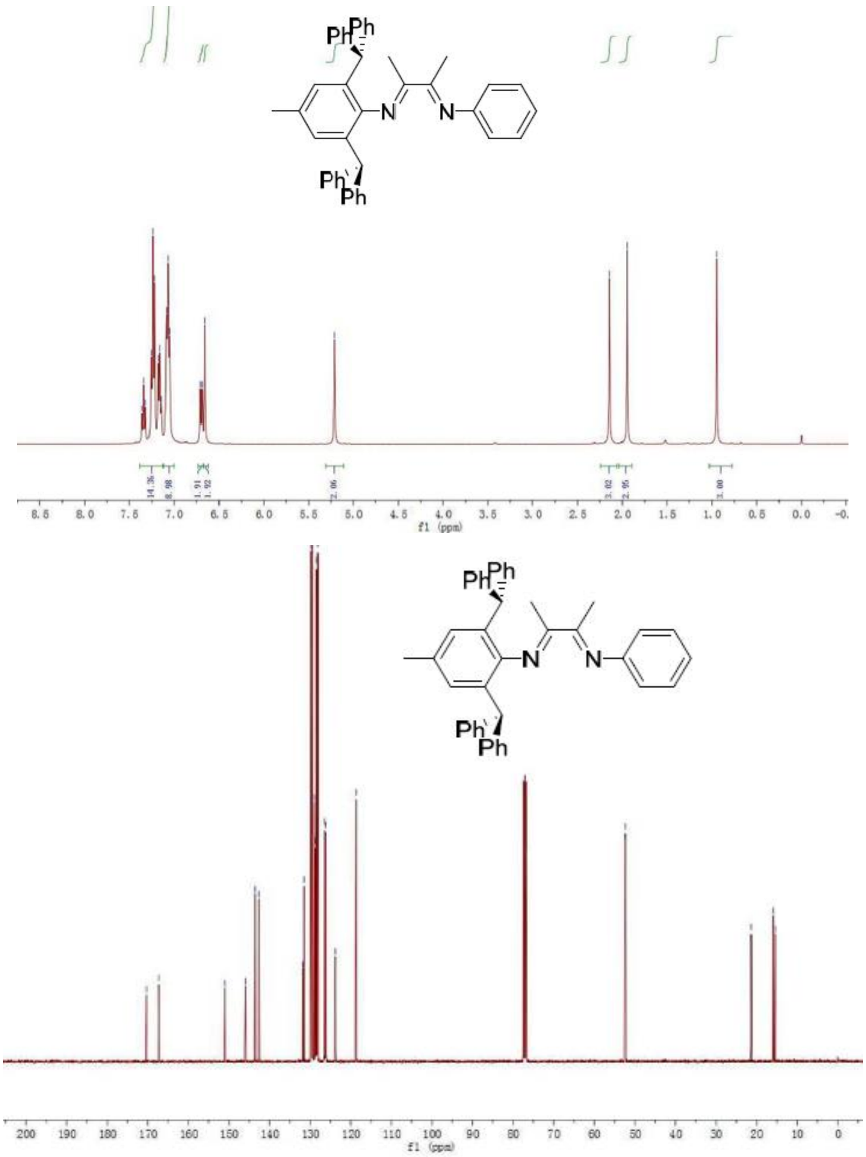
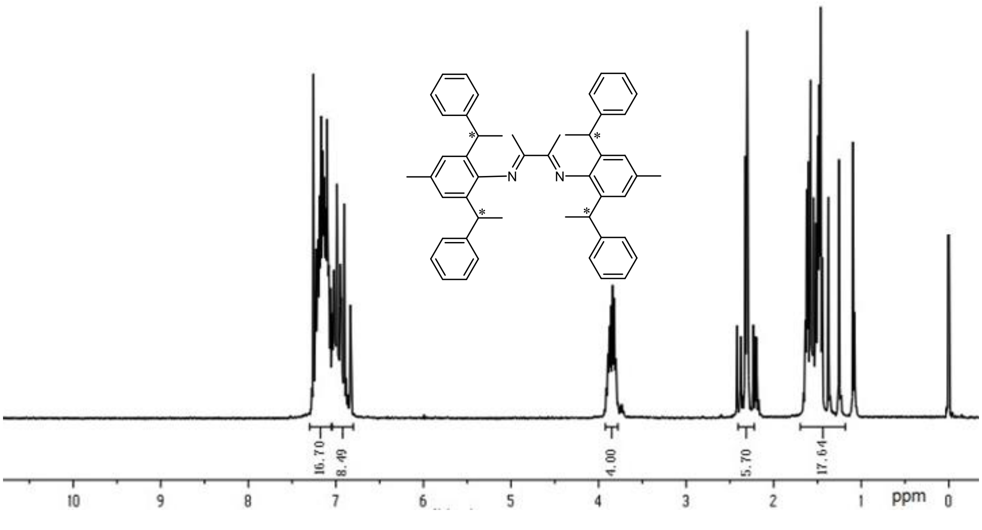


Fig. S3. ^{1}H and ^{13}C NMR spectrum of ligand **L4**.



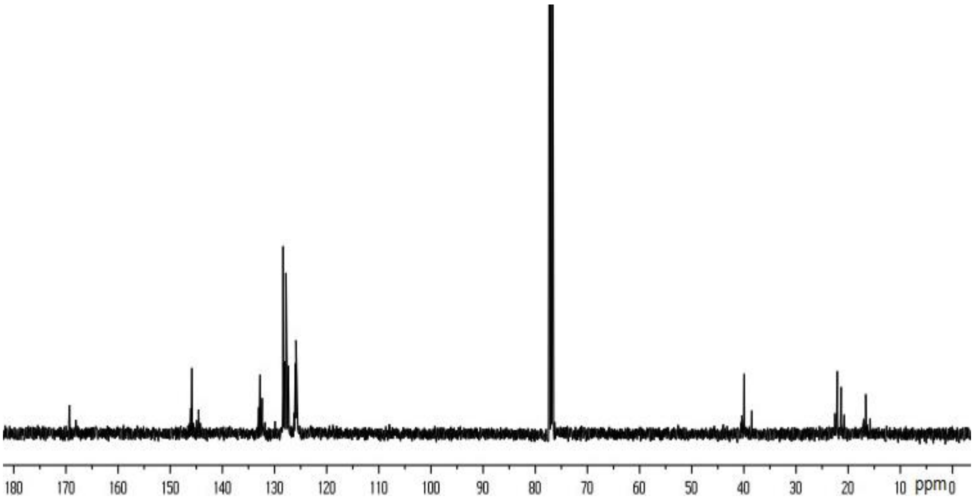


Fig. S4. ^{1}H and ^{13}C NMR spectrum of ligand **L5**.

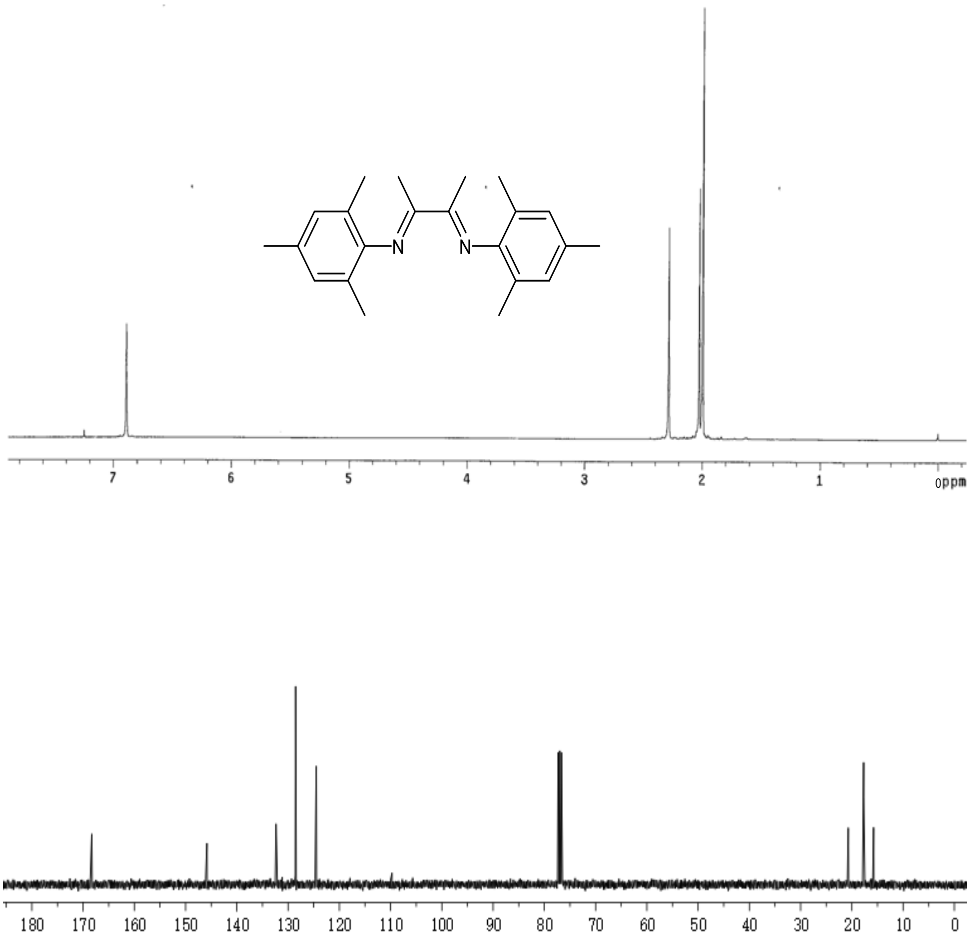


Fig. S5. ^{1}H and ^{13}C NMR spectrum of ligand **L6**.

2. X-ray structure determination

Table S1 Crystal Data and Structure Refinement for complexes **2**, **3** and **5**

Complex	**2**	**3**	**5**
Empirical Formula	$C_{49}H_{49}Br_2N_2Ni$	$C_{45}H_{42}Br_2N_2Ni$	$C_{50}H_{42}Br_2N_2Ni_2$
Formula mass	884.43	829.34	899.47
Temperature (*K*)	298	298	293
Wavelength (*Å*)	0.71073	0.71073	0.71073
Crystal size (mm^3)	0.26 × 0.15 × 0.12	0.27 × 0.10 × 0.05	0.24 × 0.21 × 0.06
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	P2/a
a (Å)	25.465 (2)	9.1819 (9)	22.4157 (8)
b (Å)	17.0368 (17)	23.1568 (19)	8.5771 (3)
c (Å)	22.342 (2)	19.0157 (16)	24.0509 (8)
V ($Å^3$)	8716.6 (14)	3962.1 (6)	4215.0 (2)
Z	8	4	4
Density (calcd.) (mg/cm^3)	1.348	1.390	1.417
Absorption coefficient (mm^{-1})	2.31	2.539	3.15
$F(000)$	3640	1696	1856
Theta range for data collec. (°)	2.4–23.9	2.4–28.8	3.7–72.7
Limiting indices	$-30 \leq h \leq 30$	$-10 \leq h \leq 10$	$-27 \leq h \leq 16$
	$-20 \leq k \leq 20$	$-27 \leq k \leq 27$	$-10 \leq k \leq 10$
	$-26 \leq l \leq 26$	$-11 \leq l \leq 22$	$-28 \leq l \leq 29$
No. of rflns collected	15356	18723	14743
No. unique rflns [R(int)]	7209	6939	7775
R_{int}	0.000	0.155	0.029
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1324$	$R_1 = 0.1136$	$R_1 = 0.0823$
	$wR_2 = 0.3405$	$wR_2 = 0.2199$	$wR_2 = 0.1875$
R indices (all data)	$R_1 = 0.1844$	$R_1 = 0.2249$	$R_1 = 0.1146$,
	$wR_2 = 0.3770$	$wR_2 = 0.2418$	$wR_2 = 0.2022$
Goodness-of-fit on F^2	1.132	1.098	1.26
Max. and min. transmission	0.7688 and 0.5846	0.8835 and 0.5472	1.000 and 0.644
Largest diff. peak and hole ($e.Å^{-3}$)	2.87 and –3.64	0.89 and −1.34	0.62 and –0.71

3. Microstructure Analysis of Polymer

3.1. Equations for the microstructure analysis of the polymers

Calculation of the degree of branching

The degree of branching was estimated by ^{1}H NMR spectroscopy and was corrected for end groups as follows [5]:

$$B = \frac{2(I_{CH_3})}{3(I_{CH}+I_{CH_2}+I_{CH_3})}\times 1000 \qquad \mathbf{S1}$$

Branching degree, the number of methyl carbon in every 1000 carbons, CH_3, CH_2, CH refer to the intensities of the methyl, methylene and methine resonances in ^{1}H NMR spectra. CH_3 (alkyl methyl, alk-CH_3, m, 0.70–0.95 ppm), CH_2 and CH (alk-CH and alk-CH_2, m, ca. 1.00–1.45 ppm) refer to the intensities of the methyl, methylene and methine resonances in ^{1}H NMR spectra.

Assignments of the ^{13}CNMR spectra and equations for the quantitative analysis of the polyolefins under investigation, according to **equation S2** reported by Azoulay et al. [6]. Chemical shift and assignment of the peak listed in the **Table S2** are marked in the spectrum (**Fig. S6**).

$\mathbf{CH_3} = (I_2 + I_5)/2 + I_1 + I_3 + I_6$

Methyl branch, **Me** = $I_6 - I_4 + I_7$; Ethyl branch, **Et** = $(I_1 + I_{10})/2$

Propyl branch, **Pr** = $(I_4 + I_{23})/2$; Butyl branch, **Bu** = $I_3 - I_8$ **S2**

sec-Butyl branch, ***s*Bu** = $(I_2 + I_5)/2$; Longer branch, **Lg** = $(I_8 + I_{17})/2$

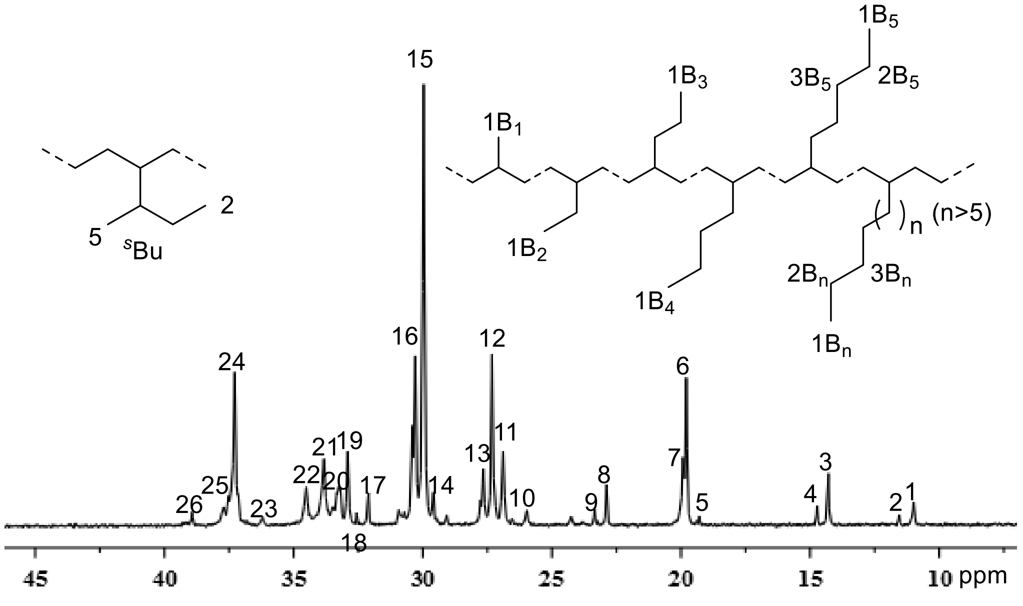


Fig. S6. ^{13}C NMR spectrum of the polyethylene obtained by complex **1** at 80 °C (entry 15, **Table 2**).

Table S2. Chemical shift and assignment of peaks.[a]

Peak No.	Chemical shift (ppm)	Assignment	Peak No.	Chemical shift (ppm)	Assignment
1	11.09	$1B_2$	14	29.61	$4B_n$
2	11.53	^{s}Bu	15	29.95	CH_2
3	14.25	$1B_4$, $1B_n$	16	30.36	γB_1, γB_{2+}
4	14.66	$1B_3$	17	32.09	$3B_n$
5	19.33	^{s}Bu	18	32.57	$3B_5$
6	19.81	$1B_1$	19	32.94	brB_1
7	19.98	$2B_3$	20	33.34	αB_2
8	22.85	$2B_n$	21	33.91	αB_{3+}
9	23.24	$2B_4$	22	34.56	nB_n
10	26.03	$2B_2$	23	36.84	$3B_3$
11	26.95	$(n\text{-}1)B_n$	24	37.33	αB_1
12	27.30	βB_{2+}	25	37.77	brB_n
13	27.66	βB_1	26	39.03	brB_2

[a] ^{13}C NMR ($CDCl_3$ δ: 77.16 ppm) measurements of the polyethylene are marked in **Fig. S6**; Note on labels: for xB_n B_n is a branch of length n carbons, x is the carbon being discussed, and the methyl at the end of the branch is numbered 1. Thus, the second carbon from the end of a butyl branch is $2B_4$. xB_{n+} refers to branches of length n and longer.

3.2. ^{1}H and ^{13}C NMR spectrum of polyethylenes

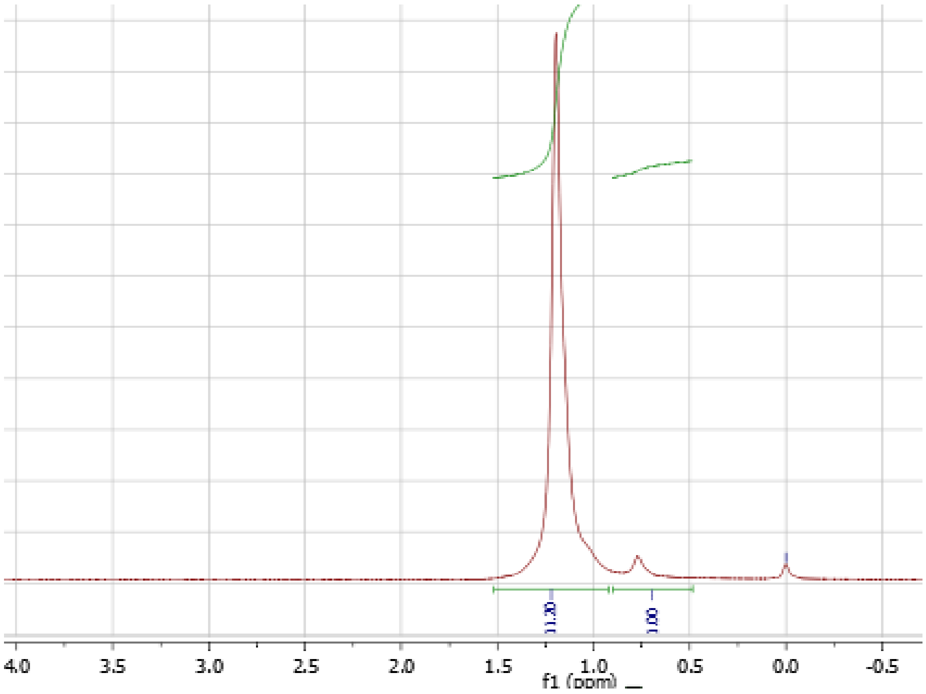


Fig. S7. ^{1}H NMR spectrum of polyethylene obtained by complex **1** at 20 °C from **Table 1**, entry 1 (d^6-benzene, 60 °C, B = 55).

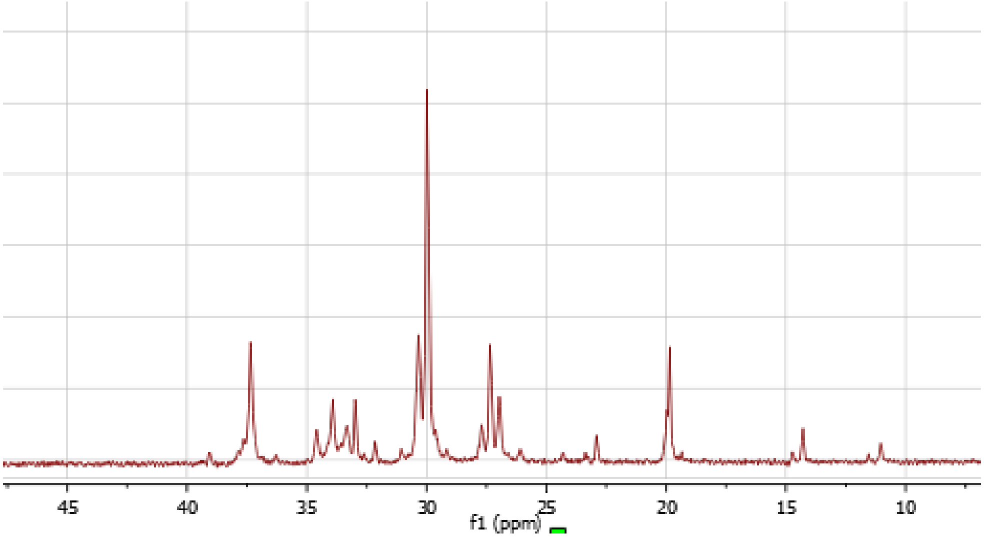


Fig. S8. ^{13}C NMR spectrum of polyethylene obtained by complex **5** at 50 °C from **Table 1**, entry 11 (d^6-benzene, 60 ^{o}C).

3.3. ^{1}H and ^{13}C NMR spectrum of poly(1-hexene)s

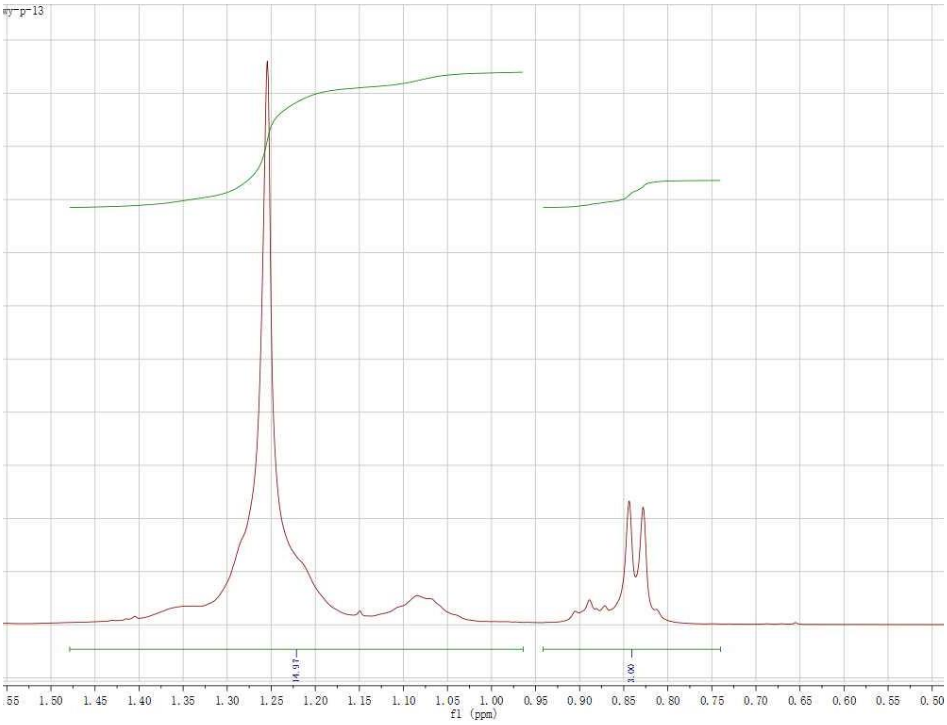


Fig. S9. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **1** at 40 °C from **Table 2**, entry 2 (d^6-benzene, 60 ^{o}C, B = 111.3).

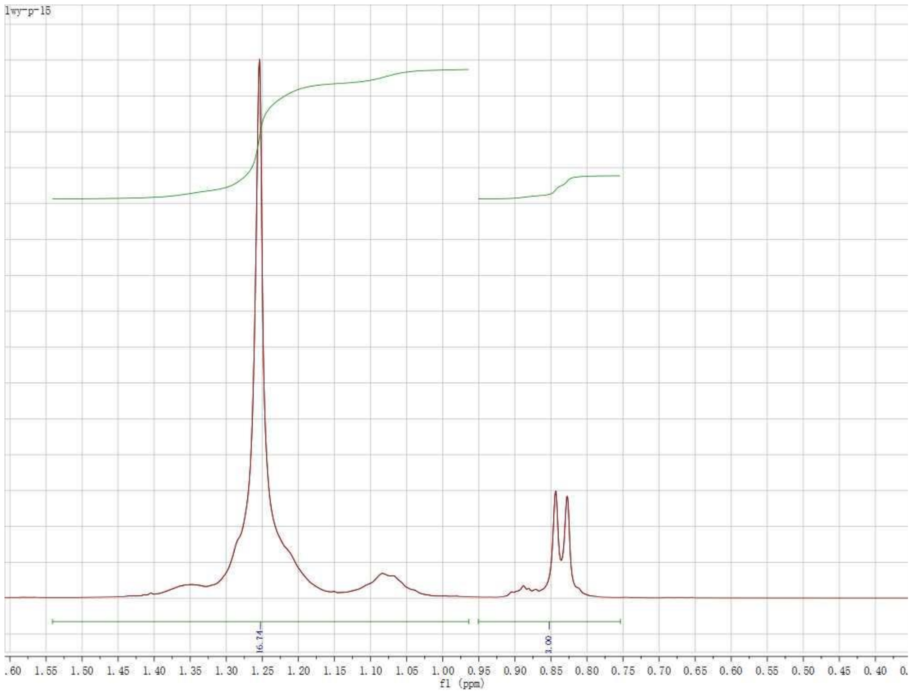


Fig. S10. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **1** at 60 °C from **Table 2**, entry 3 (d^6-benzene, 60 ^{o}C, B = 106.7).

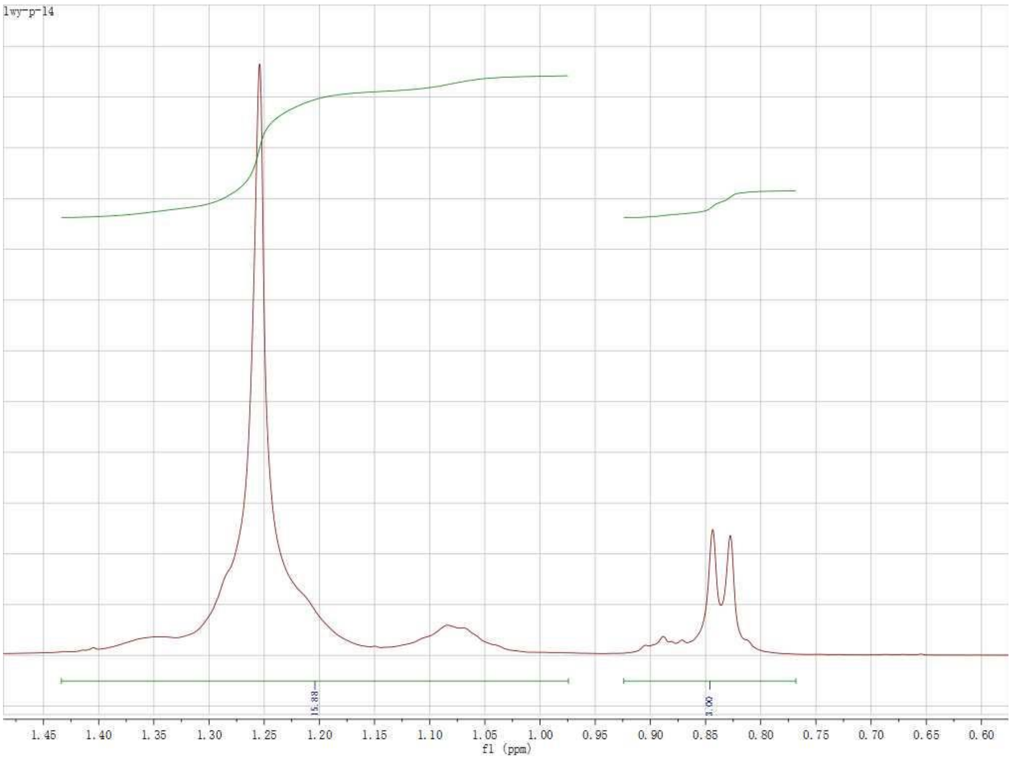


Fig. S11. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **1** at 80 °C from **Table 2**, entry 4 (d^6-benzene, 60 ^{o}C, B = 105.9).

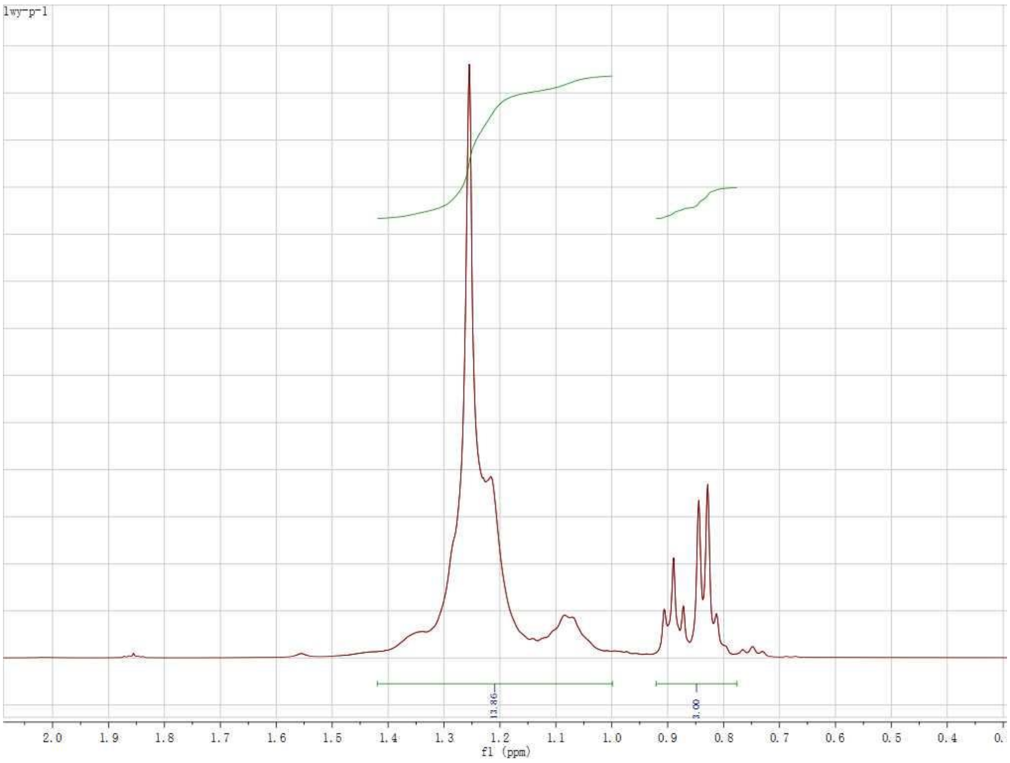


Fig. S12. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **2** at 20 °C from **Table 2**, entry 5 (d^{6}-benzene, 60 ^{o}C, B = 118.6).

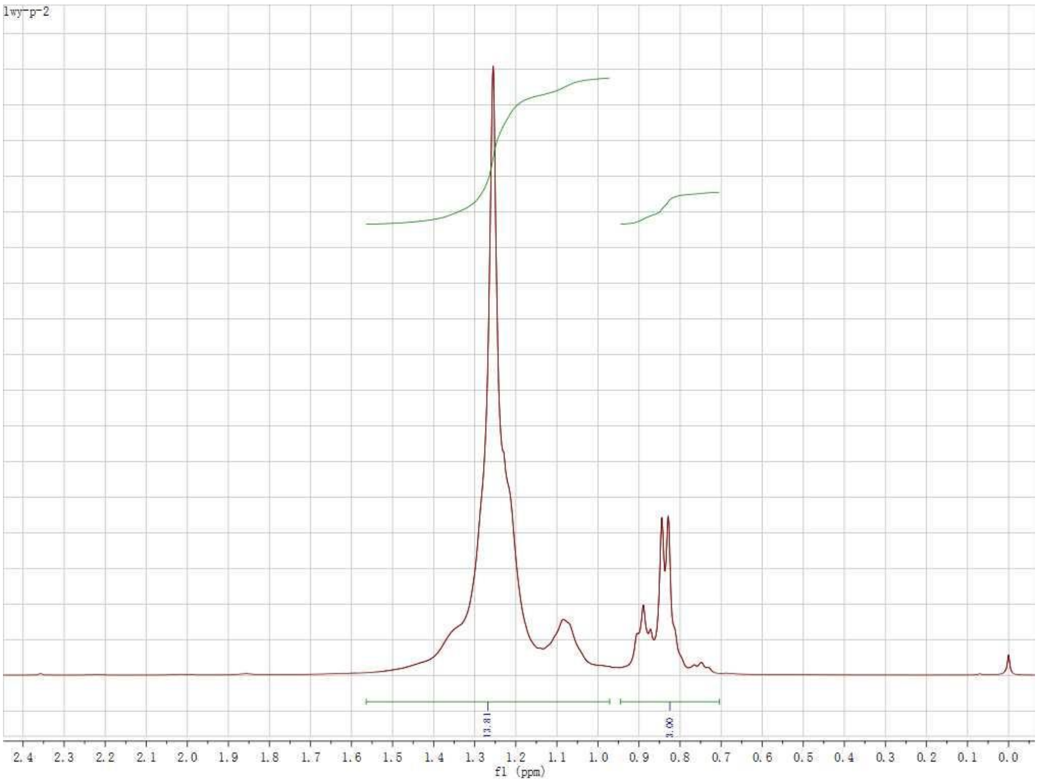


Fig. S13. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **2** at 40 °C from **Table 2**, entry 6 (d^{6}-benzene, 60 ^{o}C, B = 119.0).

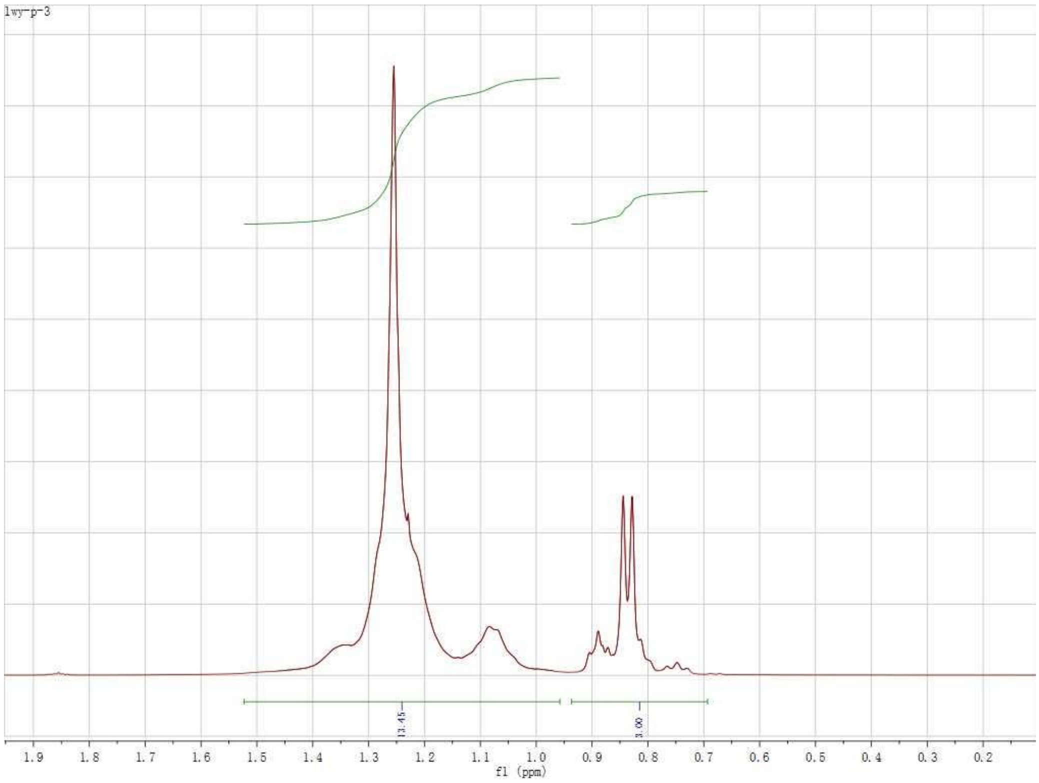


Fig. S14. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **2** at 60 °C from **Table 2**, entry 7 (d^6-benzene, 60 ^{o}C, B = 121.6).

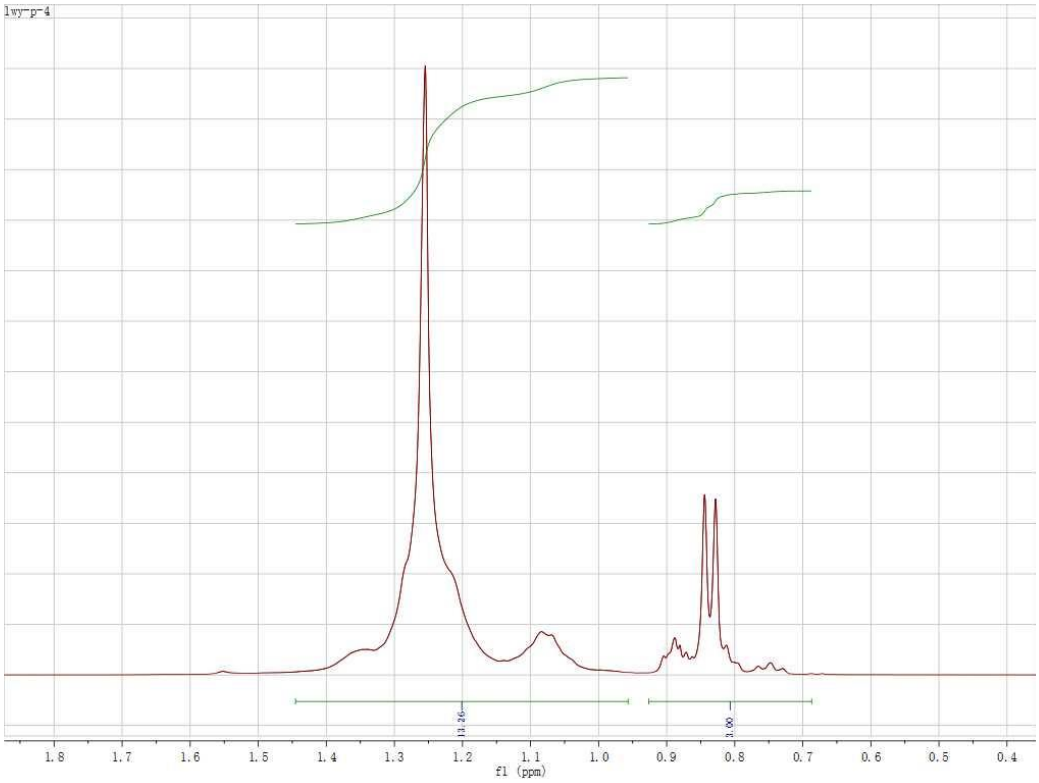


Fig. S15. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **2** at 80 °C from **Table 2**, entry 8 (d^6-benzene, 60 ^{o}C, B = 123.0).

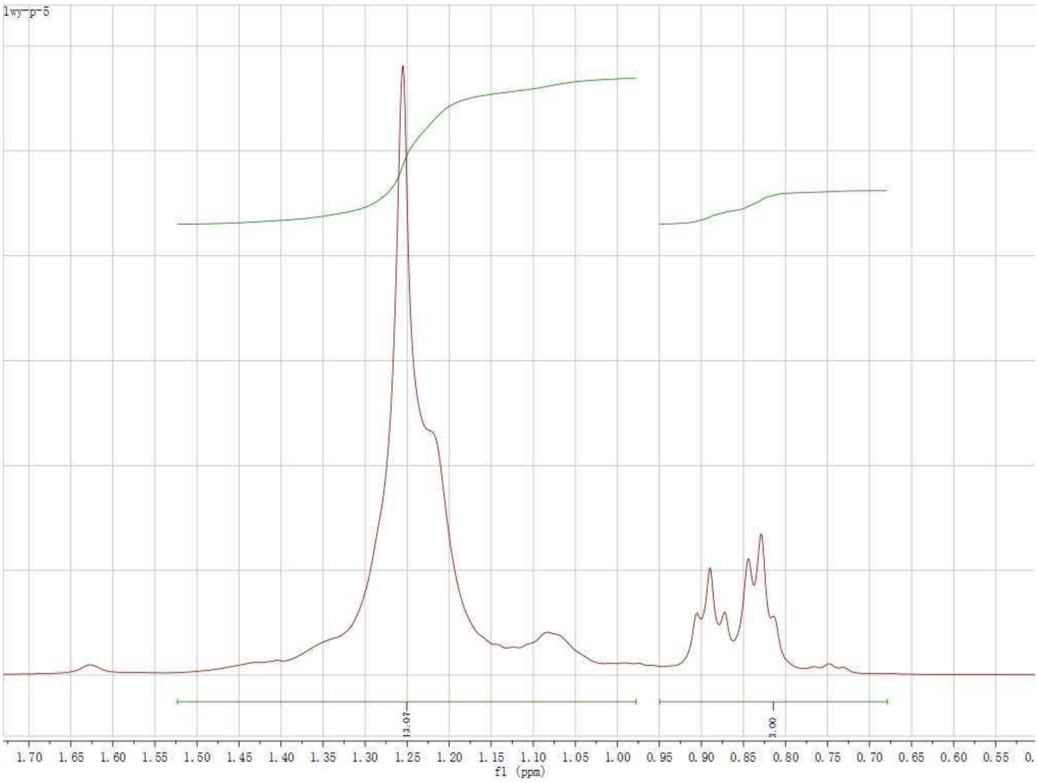


Fig. S16. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **3** at 20 °C from **Table 2**, entry 9 (d^6-benzene, 60 ^{o}C, B = 124.5).

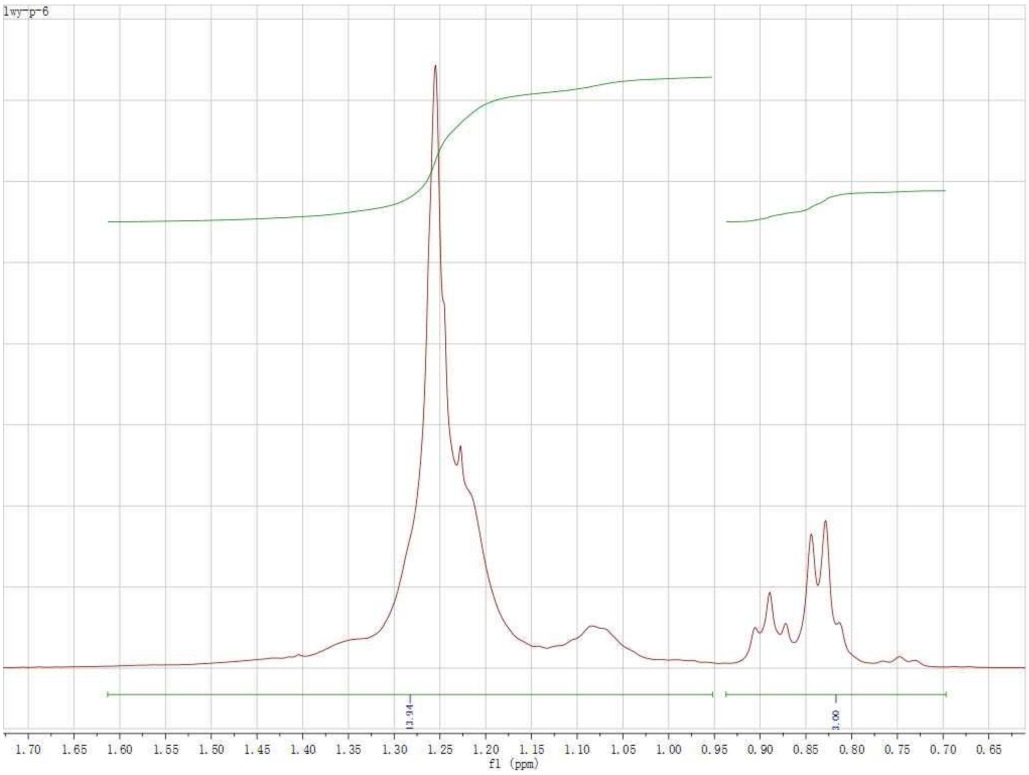


Fig. S17. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **3** at 40 °C from **Table 2**, entry 10 (d^6-benzene, 60 ^{o}C, B = 118.1).

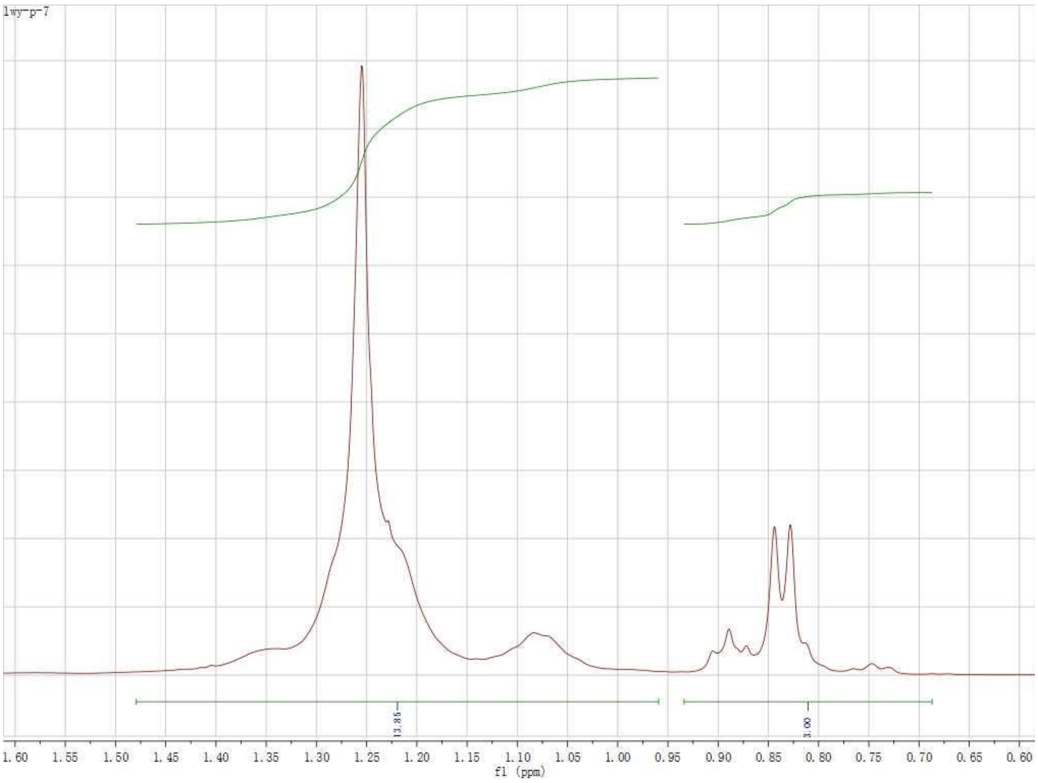


Fig. S18. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **3** at 60 °C from **Table 2**, entry 11 (d^6-benzene, 60 ^{o}C, B = 118.7).

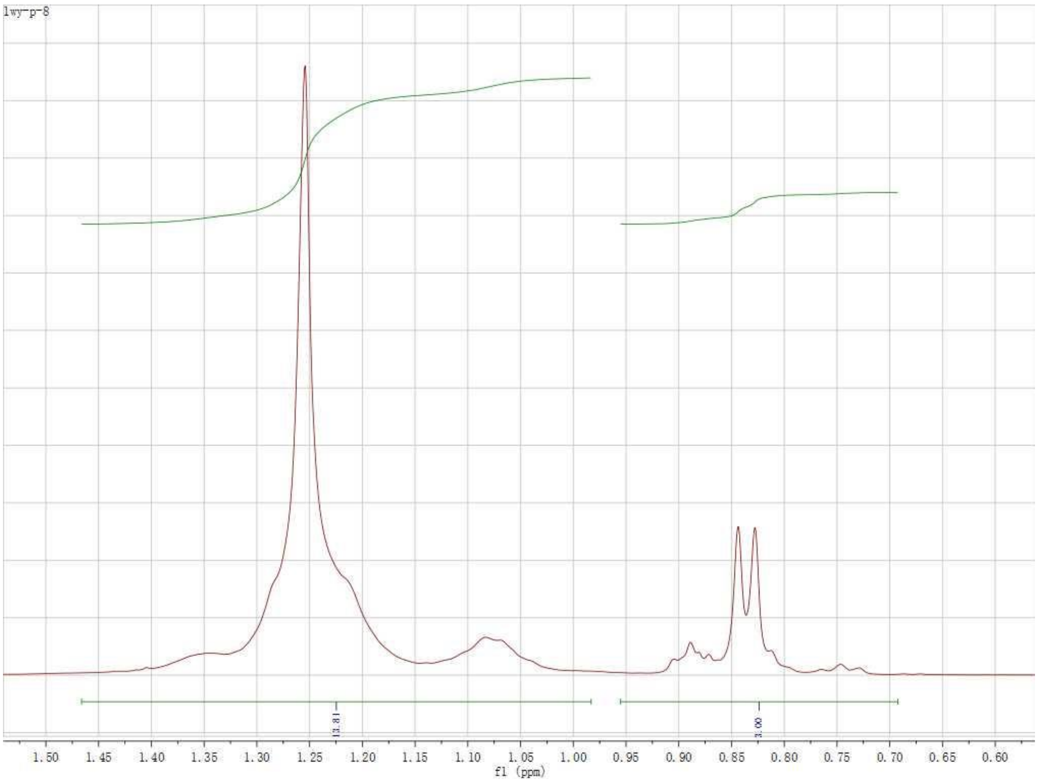


Fig. S19. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **3** at 80 °C from **Table 2**, entry 12 (d^6-benzene, 60 ^{o}C, B = 119.0).

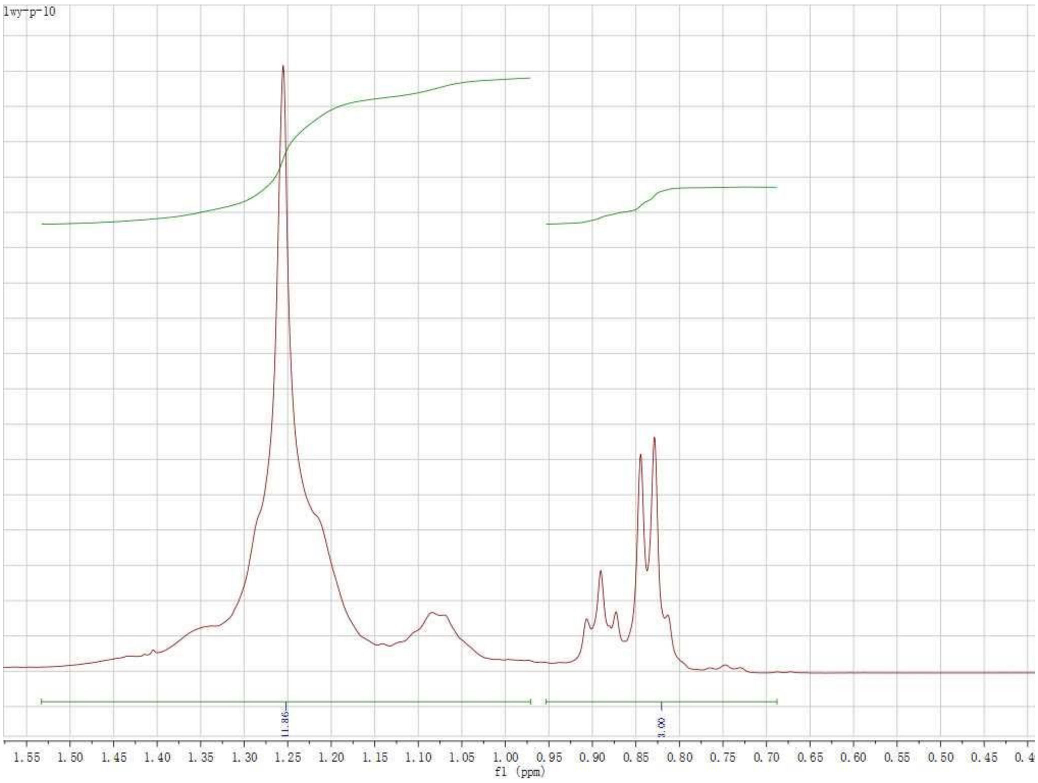


Fig. S20. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **4** at 40 °C from **Table 2**, entry 14 (d^6-benzene, 60 ^{o}C, B = 134.6).

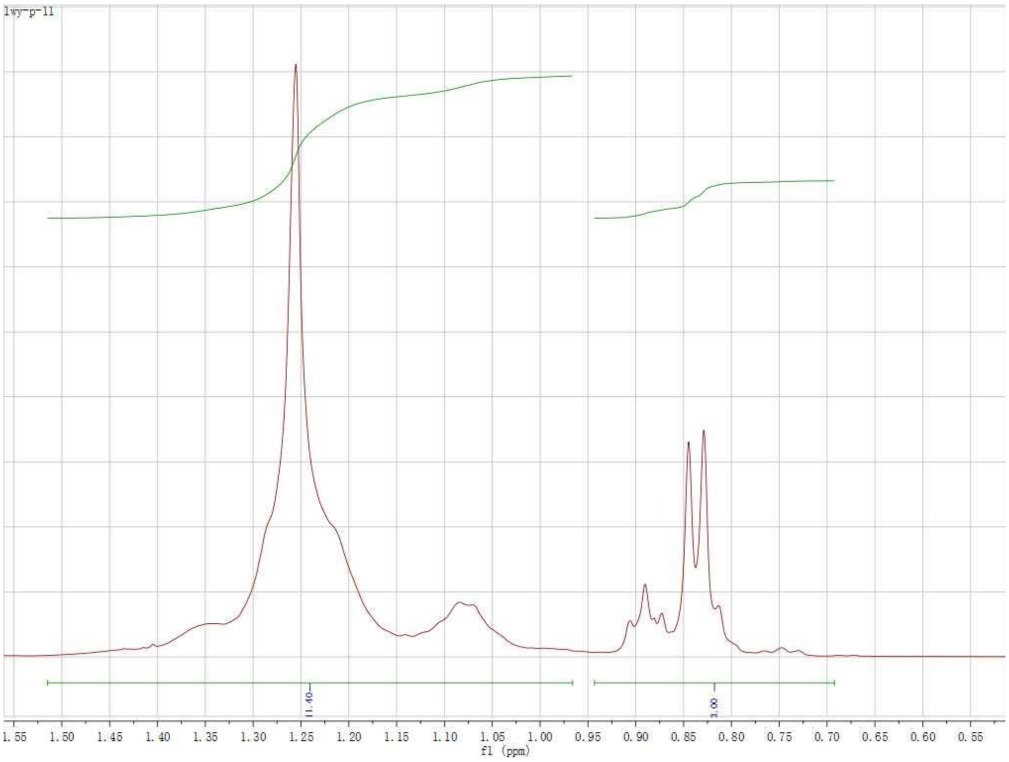


Fig. S21. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **4** at 60 °C from **Table 2**, entry 15 (d^6-benzene, 60 ^{o}C, B = 138.9).

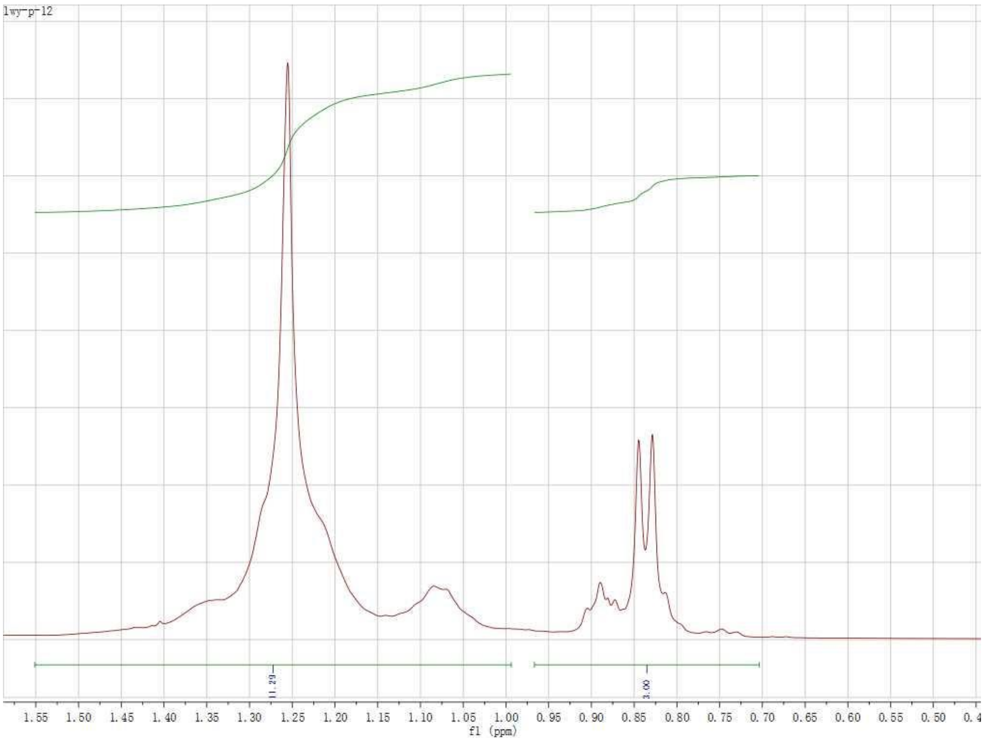
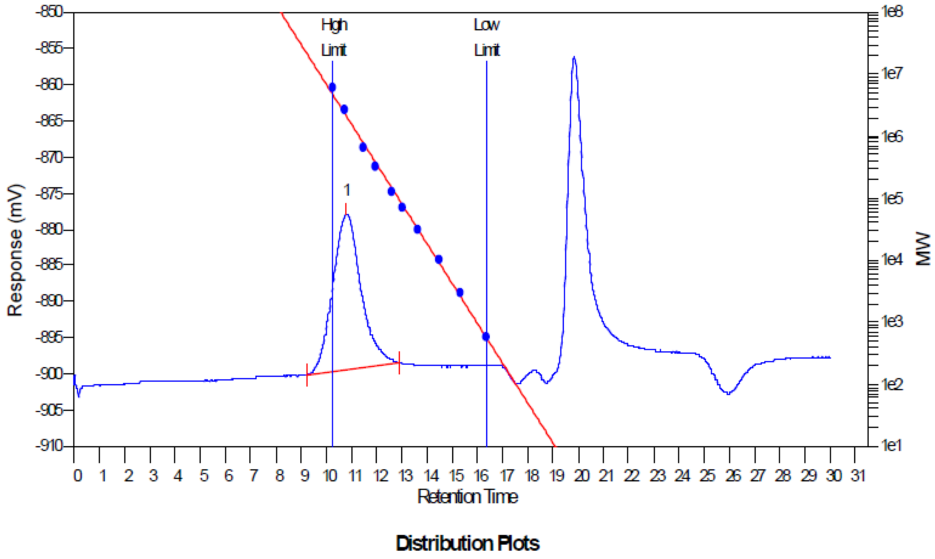


Fig. S22. ^{1}H NMR spectrum of poly(1-hexene) obtained by complex **4** at 80 °C from **Table 2**, entry 16 (d^6-benzene, 60 ºC, B = 140.0).

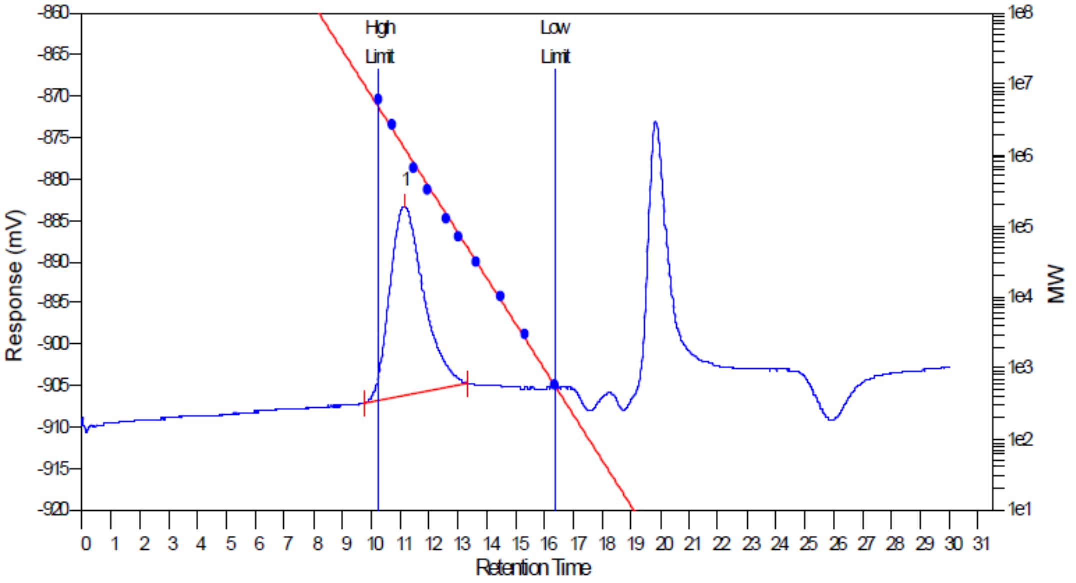
4. GPC Curves for the Polyethylenes



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2109509	1314118	2618119	4442255	6697287	2398256	1.9923

Fig. S23. GPC curve for the polyethylene obtained by complex **1** at 50 °C from **Table 1**, entry 2.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1256367	651571	1342822	2182754	3080823	1232669	2.0609

Fig. S24. GPC curve for the polyethylene obtained by complex **3** at 50 °C from **Table 1**, entry 8.

5. References

[1] J. L. Rhinehart, L. A. Brown and B. K. Long, A robust Ni(II) α-diimine catalyst for high temperature ethylene polymerization. *J. Am. Chem. Soc.* **2013**, *135*, 16316–16319.

[2] L. H. Guo, S. Y. Dai, C. L. Chen, Investigations of the ligand electronic effects on α-diimine nickel(II) catalyzed ethylene polymerization. *Polymers* **2016**, *8*, 37.

[3] F. Z. Wang, J. C. Yuan, F. Y. Song, J. Li, Z. Jia and B. N. Yuan, New chiral-diimine nickel(II) complexes bearing *ortho*-*sec*-phenethyl groups for ethylene polymerization. *Appl. Organomet. Chem.* **2013**, *27*, 319–327.

[4] S. Y. Dai, S. X. Zhou, W. Zhang and C. L. Chen, Systematic investigations of ligand steric effects on α-diimine palladium catalyzed olefin polymerization and copolymerization. *Macromolecules* **2016**, *49*, 8855–8862.

[5] J. C. Jenkins and M. Brookhart, A highly active anilinoperinaphthenone-based neutral nickel(II) catalyst for ethylene polymerization. *Organometallics* **2003**, *22*, 250–256.

[6] J. D. Azoulay, G. C. Bazan and G. B. Galland, Microstructural characterization of poly(1-hexene) obtained using a nickel α-Keto-β-diimine initiator. *Macromolecules* **2010**, *43*, 2794–2800.