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Supporting Information for:

Flexible Cycloalkyl Substituents in Insertion Polymerization with α-Diimine Nickel and Palladium Species

Shengyu Dai[a,*] Shuaikang Li[a], Guoyong Xu[a], Cheng Wu[c], Yudan Liao[c,*] Lihua Guo[b,*]

[a]Institutes of Physical Science and Information Technology, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Anhui University, Hefei, Anhui, 230601, China.
[b]Institute of Anticancer Agents Development and Theranostic Application, The Key Laboratory of Life-Organic Analysis and Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, Department of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, China.
[c]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renmin Street 5625, Changchun 130022, China

1. Figures, Tables.

Tables S1. Mechanical properties.[a]

Ent.	Precat.	*T*/°C	Strain at break (%)	Stress at break (MPa)	SR (%)[b]
1	**Ni1**	20	492	10.7	34
2	**Ni1**	50	970	9.5	52
3	**Ni1**	80	2784	1.1	58
4	**Ni2**	20	836	1.0	55
5	**Ni2**	50	863	0.1	44
6	**Ni2**	80	659	<0.1	-[c]
7	**Ni3**	20	331	9.4	31
8	**Ni3**	50	514	7.2	63
9	**Ni3**	80	472	3.2	74
10	**Ni4**	20	349	4.9	53
11	**Ni4**	50	1639	5.1	77
12	**Ni4**	80	1458	3.4	71
13	**Ni5**	20	38	14.3	-[d]
14	**Ni5**	50	321	32.5	20
15	**Ni5**	80	201	15.4	-[d]

[a]Conditions: performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature. [b]The strain recovery values (SR) can be calculated by SR = $100(\varepsilon_a - \varepsilon_r)/\varepsilon_a$, where ε_a is the applied strain and ε_r is the strain in the cycle at zero load after 10th cycle. [c]Too soft to be determined. [d]Strain is smaller than 300%.

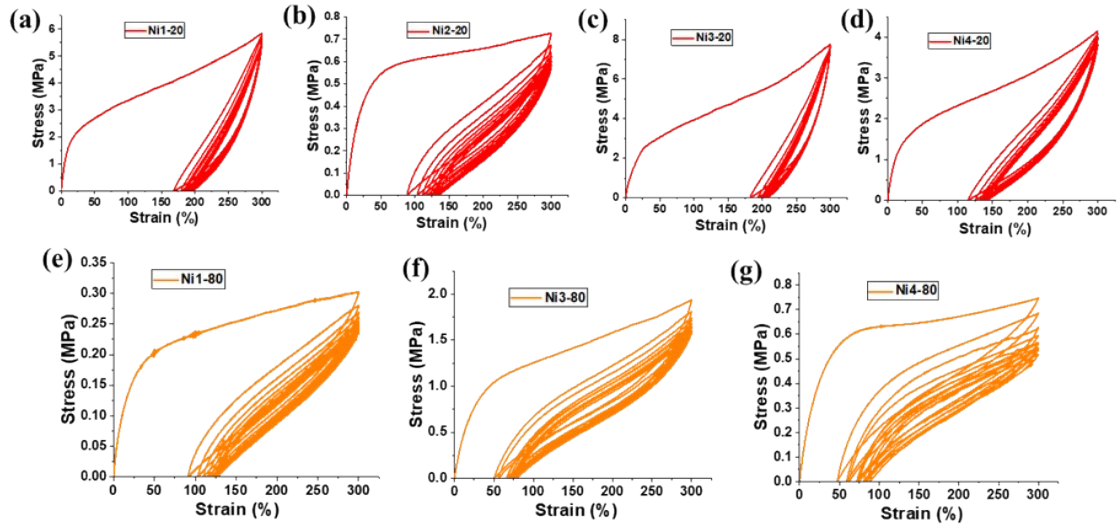


Figure S1. Plots of hysteresis experiments of ten cycles at a strain of 300% for samples generated by **Ni1** at 20 °C **(a)**, **Ni2** at 20 °C **(b)**, **Ni3** at 20 °C **(c)**, **Ni4** at 20 °C **(d)**, **Ni1** at 80 °C **(e)**, **Ni3** at 80 °C **(f)**, and **Ni4** at 80 °C **(g)**.

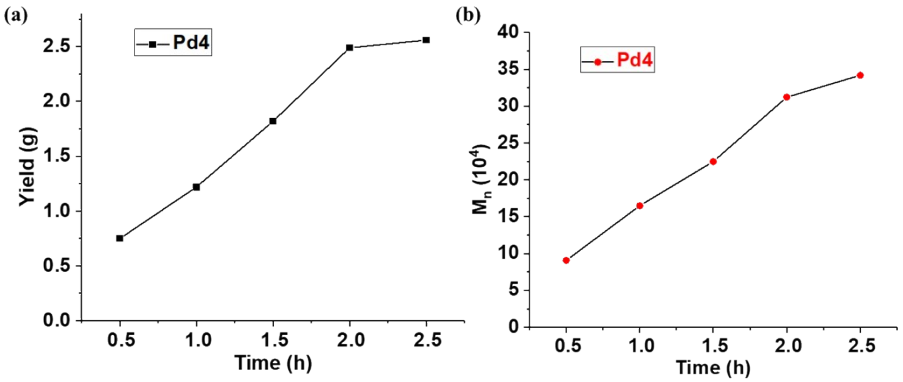


Figure S2. Plots of (a) yield versus time and (b) M_n versus time for **Pd4** at 20 °C.

Table S2. Effect of Time on Ethylene Polymerization at 80 °C using Ni4.[a]

Ent.	Precat.	Time (min)	Yield/g
1	**Ni4**	5	0.78
2	**Ni4**	10	1.47
3	**Ni4**	15	2.03
4	**Ni4**	30	3.06

[a]General conditions: Ni catalyst (2 μmol), MAO (500 equiv.), tolune (40 mL), ethylene (6 bar).

2. Experimental Sections

2.1 General Considerations

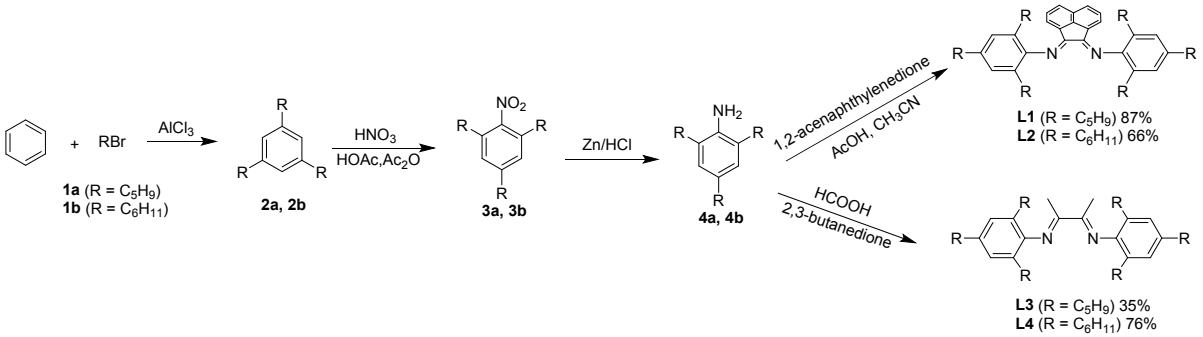
All chemicals were commercially sourced, except those whose synthesis is described. All experiments were carried out under a dry Nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H, ^{13}C NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer or a JEOL JNM-ECZ600R 600 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Mass spectra were obtained using electro spray ionization (ESI) LCMS-2010A for **L1**~**L4**. Mass spectra of **Ni1**~**Ni4** and **Pd1**~**Pd4** were determined on a Atouflex Speed MALDI-TOF MS. Elemental analysis was performed by the Analytical Center of the Anhui University. X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K^{α} radiation (λ = 0.71073 Å). Molecular weight and molecular weight distribution of the polymers with low solubility at room temperature were determined by gel permeation chromatography (GPC) with a PL 210 equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 150 °C using trichlorobenzene as a solvent and calibrated with polystyrene standards. The molecular weight and the molecular weight distribution of the polymers with good solubility at room temperature were determined by gel permeation chromatography (GPC) equipped with two linear Styragel columns (HR2 and HR4) at 40°C using THF as a solvent and

calibrated with polystyrene standards, and THF was employed as the eluent at a flow rate of 1.0 mL/min.

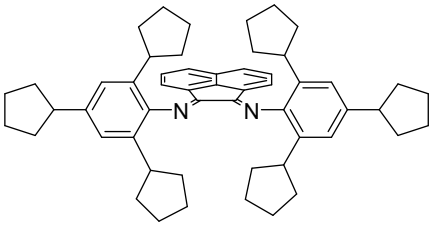
Stress/strain experiments were performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature. At least three specimens of each polymer were tested. Polymers were melt-pressed at 50 °C above their melting point to obtain the test specimens. The test specimens have 14-mm gauge length, 2-mm width, and thickness of 0.5 mm.

Differential scanning calorimetry (DSC). DSC was performed by a DSC Q2000 from TA Instruments. Samples were quickly heated to 150°C and kept for 5 min to remove thermal history, then cooled to -50°C at a rate of 10 K/min, and finally reheated to 150°C at the same rate under a nitrogen flow (50 mL/min). The maximum points endotherm (heating scan) were taken as the melting temperature (T_m).

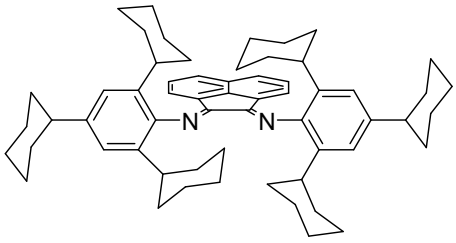
2.2 Procedure for the Synthesis of Ligands L1-L5.



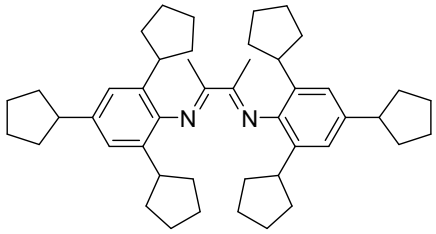
The arylamines with flexible cycloalkyl substituents were synthesized according to the literature procedure.[1]



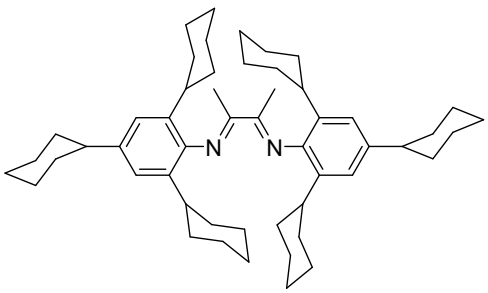
L1 (3.22 g, 87%). Under nitrogen atmosphere, acenaphthylene-1, 2-dione (0.91 g, 5 mmol, 1.0 equiv) and 2,4,6-cyclopentyl aniline **4a** (2.97 g, 10 mmol, 2.0 equiv) was suspended in acetonitrile (40 mL) and acetic acid (16 mL). The mixture was allowed to stir vigorously at 90 °C for 12 hours and became reddish-brown solution. Subsequently, the solution was cooled down to room temperate and a yellow precipitate was collected by filtration. After washing the solid with methanol and drying in vacuo, the desired product **L1** was obtained as yellow powders. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H, aryl-*H*), 7.33 (t, J = 7.7 Hz, 2H, aryl-*H*), 7.12 (s, 4H, aryl-*H*), 6.44 (s, 2H, d, J = 7.2 Hz, aryl-*H*), 3.12 – 2.98 (m, 6H, C*H*, cyclopentyl), 2.43 – 0.89 (m, 48H, CH_2, cyclopentyl). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.47 (*C*=N-Ar), 147.24, 141.90, 140.77, 132.61, 131.02, 129.88, 128.63, 127.97, 123.44, 122.54, 46.15, 41.16, 34.99, 34.34, 33.41, 25.69, 25.67. This compound is knwon.[1]



L2 (1.13 g, 66%). Using the same procedure as for the synthesis of **L1** except that 2,4,6-cyclohexyl aniline **4b** (3.39 g, 10 mmol, 2.0 equiv) was used, **L3** was obtained as a yellow powder. ^{1}H NMR (600 MHz,) δ 7.83 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 7.29 (t, *J* = 7.7 Hz, 2H, aryl-*H*), 7.05 (s, 4H, aryl-*H*), 6.36 (d, *J* = 7.2 Hz, 2H, aryl-*H*), 2.74 – 2.43 (m, 6H, C*H*, cyclohexyl), 2.05 – 1.85 (m, 12H, CH_2, cyclohexyl), 1.75 (dd, *J* = 28.3, 12.3 Hz, 6H, CH_2, cyclohexyl), 1.63 – 0.95 (m, 32H, CH_2, cyclohexyl). This compound is knwon.[1]

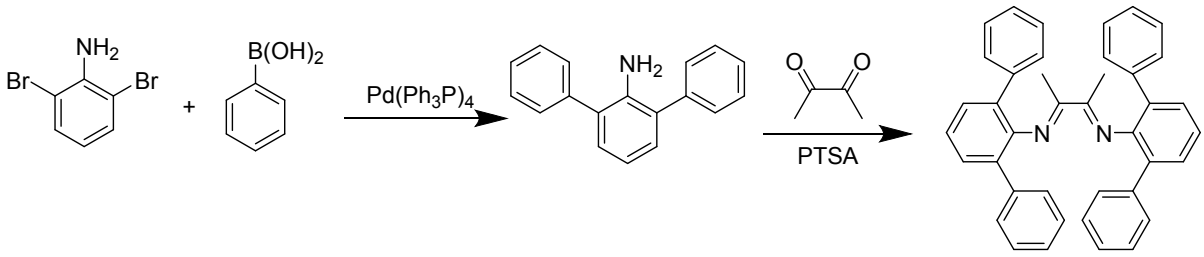


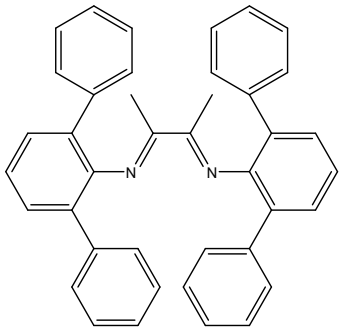
L3 (1.13 g, 35%). To the solution of 2,4,6-cyclopentyl aniline **4a** (2.97 g, 10 mmol) in EtOH (50 mL) were added diacetyl (435 μL, 5 mmol) and three drops of formic acid. The reaction mixture was stirred for 4 days at 80 °C. The formed yellow suspension was cooled to room temperature and concentrated to a half of its original volume. The yellow precipitate was collected by filtration, washed with EtOH and dried in vacuo. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 4H, aryl-*H*), 3.13 – 2.88 (m, 2H, *p*-C*H*, cyclopentyl), 2.81 – 2.71 (m, 4H, *o*-C*H*, cyclopentyl), 2.06 (s, 6H, N=C-CH_3), 2.00 – 1.45 (m, 48H, CH_2, cyclopentyl). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.55 (N=*C*-CH_3), 145.81, 141.24, 132.41, 122.34, 46.14, 41.05, 34.91, 33.74, 33.55, 25.81, 25.74, 25.62, 17.03 (N=C-*C*H_3). ESI-MS (m/z): calcd for $C_{46}H_{65}N_2$:645.5148, found: 645.5132 $[M+H]^+$.



L4 (2.77 g, 76%). Using the same procedure as for the synthesis of **L3** except that 2,4,6-cyclohexyl aniline **4b** (3.39 g, 10 mmol, 2.0 equiv) was used, **L4** was obtained as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 4H, aryl-*H*), 2.51 – 2.44 (m, 2H, *p*-C*H*, cyclohexyl), 2.29 – 2.23 (m, 4H, *o*-C*H*, cyclohexyl), 2.04 (s, 6H, N=C-CH_3), 1.97 – 1.57 (m, 30H, CH_2, cyclohexyl), 1.58 – 1.09 (m, 30H, CH_2, cyclohexyl). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.95 (N=*C*-CH_3), 144.35, 143.08, 133.74, 121.98, 44.63, 39.82, 34.91, 33.54, 33.39,

27.60, 27.50, 27.22, 26.52, 26.44, 16.68 (N=C-*C*H$_3$). ESI-MS (m/z): calcd for $C_{52}H_{77}N_2$: 729.6087, found: 729.6086 $[M+H]^+$.

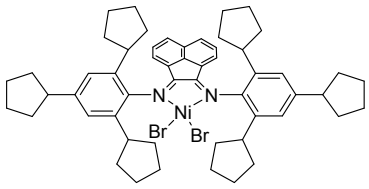




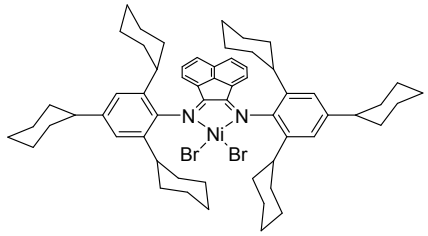
L5 (1.62 g, 60%). **L5** were synthesized according to the literature procedure.[2]

2.3 Procedure for the Synthesis of Nickel Complexes Ni1-5:

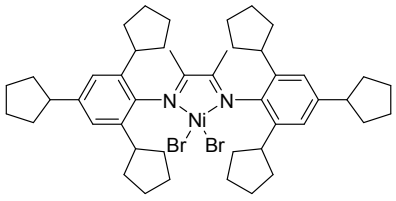
The nickel complexes were prepared in a similar manner by the reaction of 0.2 mmol ligand with 1 equivalent (DME)$NiBr_2$ in dichloromethane. After stirring overnight, the solvent was removed, and the brown solid powder was washed with ether (10 mL × 2) and dried under vacuum to give the corresponding nickel complexes.



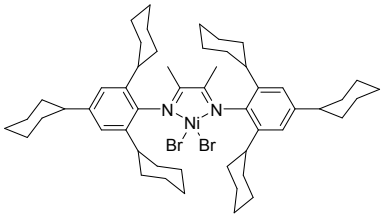
Ni1: (180 mg, 94%). Elemental analysis: calc. For $C_{54}H_{64}Br_2N_2Ni$: C, 67.59; H, 6.72; N, 2.92. Found: C, 67.35; H, 6.62; N, 2.87. MALDI-TOF-MS (m/z):877.14, $[M-Br]^+$



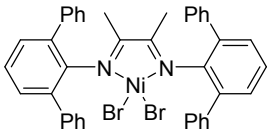
Ni2: (187 mg, 90%). Elemental analysis: calc. For $C_{60}H_{76}Br_2N_2Ni$: C, 69.04; H, 7.34; N, 2.68. Found: C, 69.21; H, 7.46; N, 2.53. MALDI-TOF-MS (m/z):963.18, $[M-Br]^+$



Ni3: (150 mg, 87%). Elemental analysis: calc. For $C_{46}H_{64}Br_2N_2Ni$: C, 63.98; H, 7.47; N, 3.24. Found: C, 63.76; H, 7.23; N, 2.06. MALDI-TOF-MS (m/z):781.17, $[M\text{-}Br]^+$



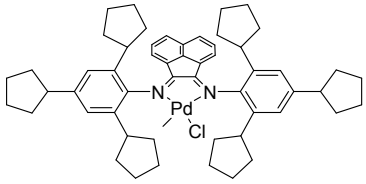
Ni4: (159 mg, 84%). Elemental analysis: calc. For $C_{52}H_{76}Br_2N_2Ni$: C, 65.90; H, 8.08.; N, 2.96. Found: C, 65.77; H, 8.34; N, 2.87. MALDI-TOF-MS (m/z):867.10, $[M\text{-}Br]^+$



Ni5: (136 mg, 89%). **Ni5** were synthesized according to the literature procedure.[2]

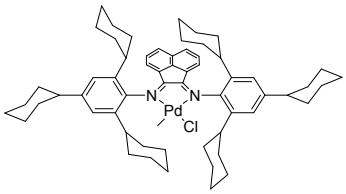
2.4 Procedure for the Synthesis of Palladium Complexes Pd1-5:

A mixture of the ligand (1 mmol), Pd(COD)MeCl (265 mg, 1 mmol) in CH_2Cl_2 (20 mL) was stirred for 1 day at room temperature. During stirring, the color of the solution was deepening. At the end of the reaction, the solution was concentrated to 5 mL. The product was crashed out with 20 ml ether and washed with ether (3 × 5 mL). Then dried under reduced pressure at room temperature for about 5 h. The pure compound was obtained as an orange or red solid.

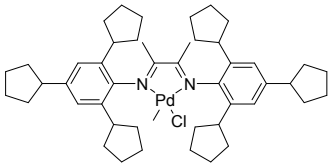


Pd1: (0.85 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 17.0, 8.2 Hz, 2H, aryl-*H*), 7.43 (ddd, *J* = 15.6, 15.1, 9.5 Hz, 2H, aryl-*H*), 7.22 (s, 2H, aryl-*H*), 7.17 (s, 2H, aryl-*H*), 6.45 (t, *J* = 8.3 Hz, 1H, aryl-*H*), 6.31 (d, *J* = 7.2 Hz, 1H, aryl-*H*), 3.45 – 3.32 (m, 4H, Cp-*H*), 3.19 – 2.96 (m, 2H, Cp-*H*), 2.54 – 2.38 (m, 2H, Cp-*H*), 2.26 (dt, *J* = 14.2, 9.4 Hz, 2H, Cp-*H*), 2.22 – 2.08 (m, 4H, Cp-*H*), 1.96 – 1.51 (m, 30H, Cp-*H*), 1.46 – 1.25 (m, 10H, Cp-*H*), 0.85 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.07 (*C*=N-Ar), 167.77 (*C*=N-Ar), 146.09, 144.68, 143.65, 141.95, 140.58, 136.79, 135.36, 131.17, 130.91, 130.46, 128.89, 128.69, 127.59, 126.89, 124.65, 124.55, 123.13, 122.67, 46.11, 46.10, 41.33, 40.76, 35.34, 34.83, 34.74, 34.30, 33.66, 33.56, 25.78, 25.75, 25.74, 25.64, 25.57, 25.55, 3.27 (Pd-*C*H_3). Elemental

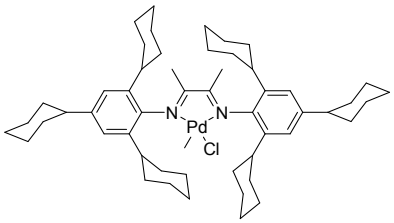
analysis: calc. For $C_{53}H_{79}ClN_2Pd$: C, 73.56; H, 7.52; N, 3.12. Found: C, 73.31; H, 7.81; N, 2.96. MALDI-TOF-MS (m/z): 845.33, $[M\text{-}Me\text{-}Cl]^+$.



Pd2: (0.92 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 16.9, 8.1 Hz, 2H, aryl-*H*), 7.41 (dd, *J* = 16.5, 8.4 Hz, 2H, aryl-*H*), 7.17 (s, 2H, aryl-*H*), 7.11 (s, 2H, aryl-*H*), 6.46 (d, *J* = 7.0 Hz, 1H, aryl-*H*), 6.32 (d, *J* = 6.9 Hz, 1H, aryl-*H*), 2.98 – 2.82 (m, 4H, Cy-*H*), 2.63 – 2.50 (m, 4H, Cy-*H*), 2.16 – 1.03 (m, 58H, Cy-*H*), 0.86 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.01 (*C*=N-Ar), 167.84 (*C*=N-Ar), 147.78, 146.52, 144.09, 140.19, 139.17, 138.13, 136.95, 131.42, 131.13, 130.67, 128.86, 128.67, 127.30, 126.50, 125.00, 124.80, 123.68, 122.96, 44.74, 44.64, 40.03, 39.49, 34.97, 34.85, 34.30, 33.93, 27.47, 27.43, 27.23, 27.17, 27.12, 27.07, 26.43, 26.33, 26.15, 3.38 (Pd-*C*H_3). Elemental analysis: calc. For $C_{61}H_{79}ClN_2Pd$: C, 74.60; H, 8.11; N, 2.85. Found: C, 74.91; H, 8.37; N, 2.99. MALDI-TOF-MS (m/z): 929.29, $[M\text{-}Me\text{-}Cl]^+$.

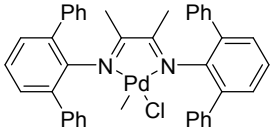


Pd3: (0.61 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 2H，aryl-*H*), 7.05 (s, 2H，aryl-*H*), 3.19 – 3.05 (m, 4H, Cp-*H*), 2.97 (dd, *J* = 17.1, 8.8 Hz, 2H, Cp-*H*), 2.47 – 2.35 (m, 2H, Cp-*H*), 2.30 – 2.20 (m, 2H, Cp-*H*), 2.11 – 2.05 (m, 4H, Cp-*H*), 1.99 (s, 3H, CH_3-C=N), 1.97 (s, 3H, CH_3-C=N), 1.92 – 1.44 (m, 40H, Cp-*H*), 0.50 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.06 (*C*=N-Ar), 169.32 (*C*=N-Ar), 145.25, 144.02, 141.53, 141.09, 135.91, 134.84, 122.67, 122.19, 48.81, 45.97, 45.93, 43.73, 41.37, 40.69, 35.61, 34.65, 34.44, 33.99, 33.81, 33.71, 31.44, 25.85, 25.79, 25.64, 25.49, 25.45, 21.75, 21.12, 20.26 (*C*H_3-C=N), 19.78 (*C*H_3-C=N), 2.76 (Pd-*C*H_3). Elemental analysis: calc. For $C_{53}H_{79}ClN_2Pd$: C, 70.39; H, 8.42; N, 3.49. Found: C, 70.23; H, 8.34; N, 3.29. MALDI-TOF-MS (m/z): 747.62, $[M\text{-}Me\text{-}Cl]^+$.



Pd4: (0.92 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 2H, aryl-*H*), 6.99 (s, 2H, aryl-*H*), 2.89 – 2.21 (m, 8H, Cp-*H*), 2.02 (s, 3H, CH_3-C=N), 2.01 (s, 3H, CH_3-C=N), 1.96 – 1.74 (m, 22H, Cy-*H*), 1.61 – 1.18 (m, 36H, Cy-*H*), 0.50 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.05 (*C*=N-Ar), 169.44 (*C*=N-Ar), 146.85, 145.73, 139.57, 139.46, 137.25, 136.50, 123.01, 122.41, 44.43, 44.20, 39.87, 39.28, 34.91, 34.53, 34.49, 33.86, 33.47, 27.54, 27.28,

27.03, 26.93, 26.31, 26.26, 26.18, 26.09, 21.38 (CH_3-C=N), 19.79 (CH_3-C=N), 2.71 (Pd-CH_3). Elemental analysis: calc. For $C_{53}H_{79}ClN_2Pd$: C, 71.84; H, 8.99; N, 3.16. Found: C, 71.71; H, 8.91; N, 3.17. MALDI-TOF-MS (m/z):831.68, $[M\text{-}Me\text{-}Cl]^+$.



Pd5: (0.49 g, 70%). **Pd5** were synthesized according to the literature procedure.[2]

2.5 A General Procedure for the Homopolymerization of Ethylene Using Ni Complexes.
In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 40 mL of toluene and the desired amount MAO was added to the reactor under N_2 atmosphere, then the desired amount of catalyst in 1 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 6 atm of ethylene. After 30 min, the pressure reactor was vented and the polymer was precipitated in ethanol, filtered and dried at 50 °C for at least 24 h under vacuum.

2.6 A General Procedure for the Homopolymerization of Ethylene Using Pd Complexes.
In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 38 mL of DCM and the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the desired amount of catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 6 atm of ethylene. After the desired time, the pressure reactor was vented and the polymer was dried under vacuum overnight.

2.7 A General Procedure for the Copolymerization of Polar Monomer with Ethylene using Pd Complexes.
In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 18 mL of DCM with the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the desired polar monomer and the desired amount of Pd catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at the desired pressure of ethylene. After 12 h, the pressure reactor was vented and the copolymer was dried under vacuum overnight.

3. Spectra Data

3.1 ^{1}H and ^{13}C NMR of the Synthetic Compounds.

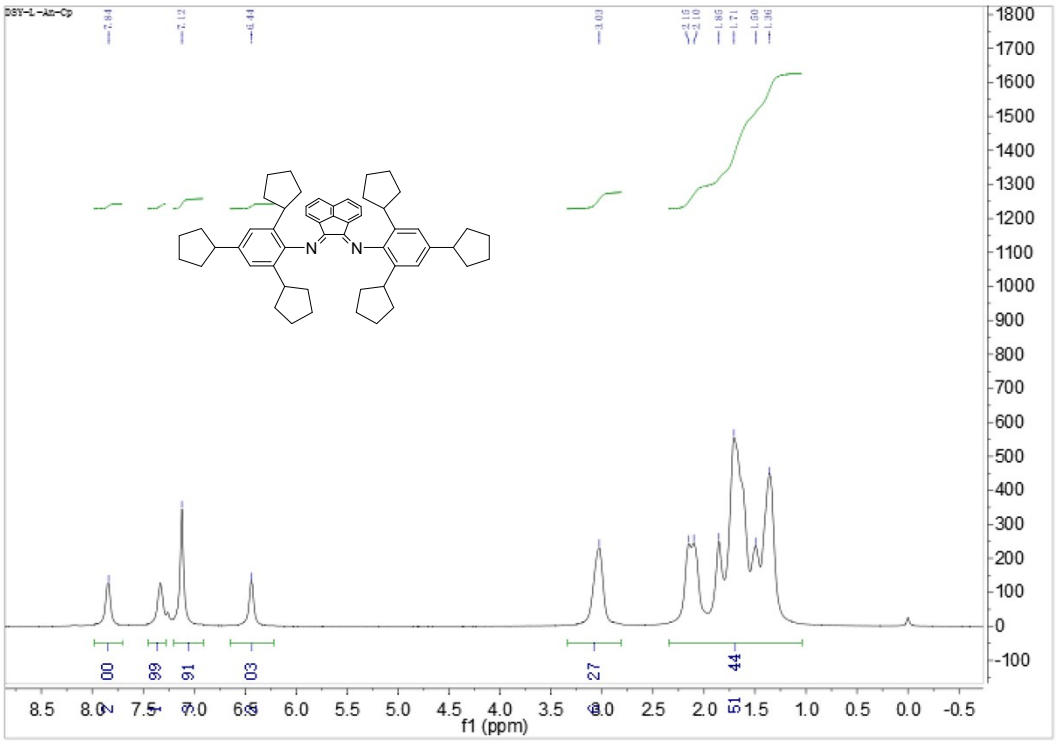


Figure S3. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

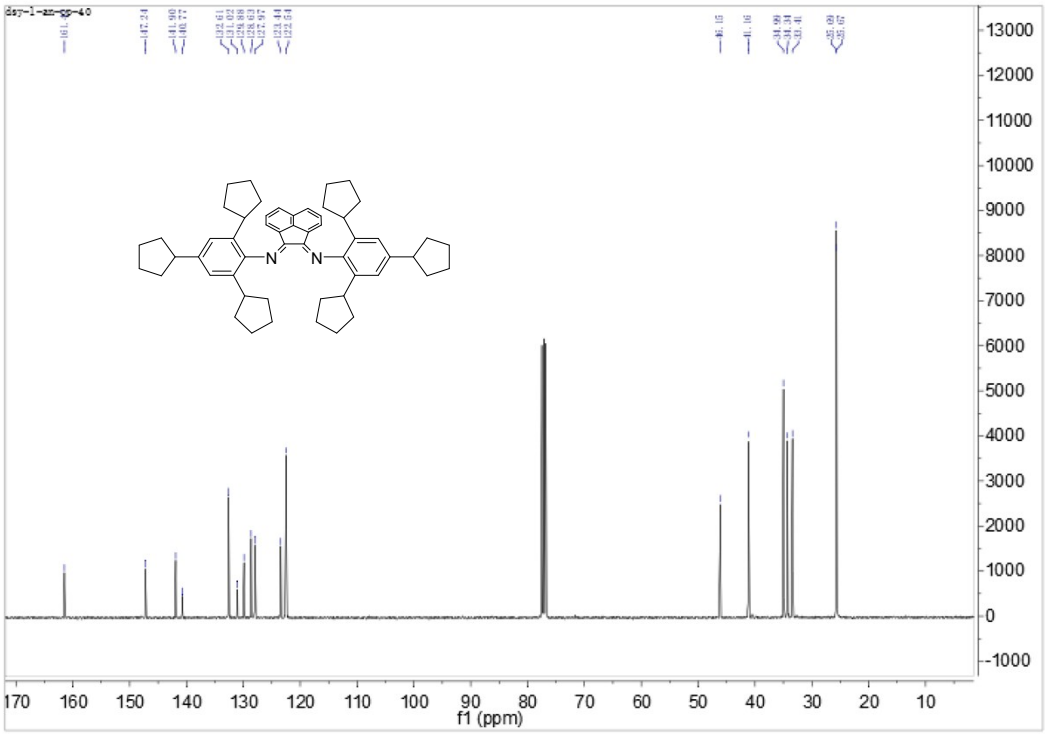


Figure S4. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

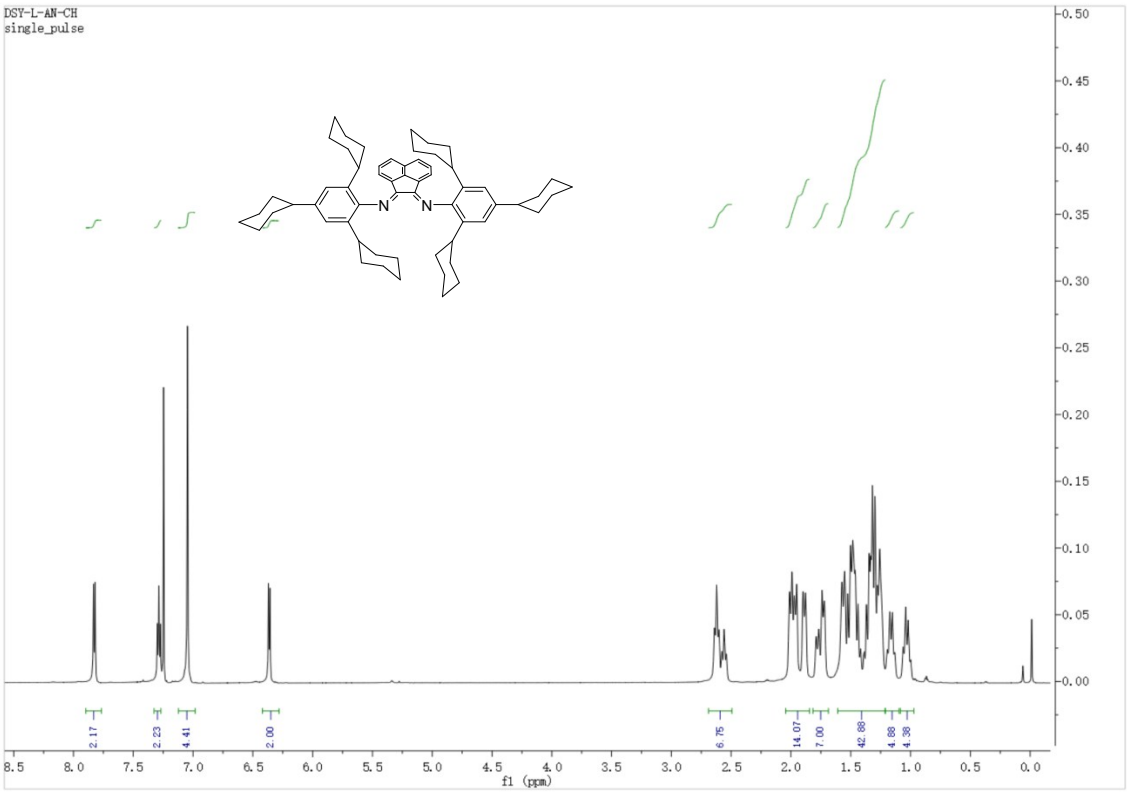


Figure S5. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

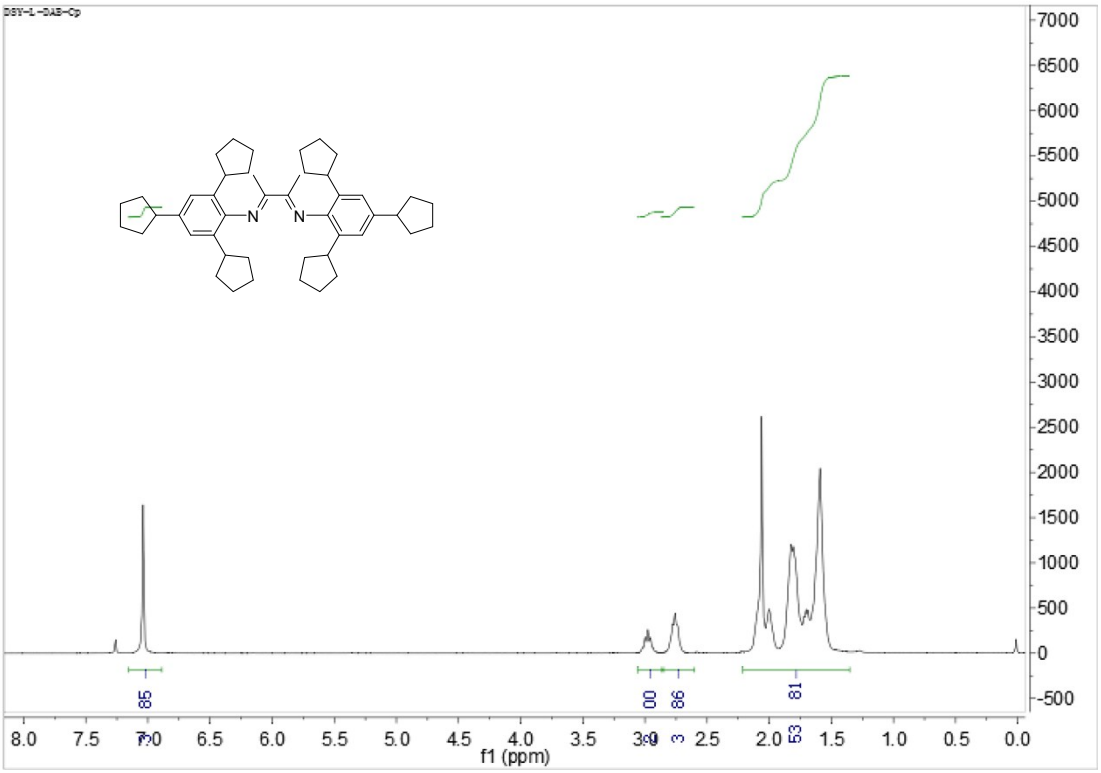


Figure S6. ^{1}H NMR spectrum of **L3** in $CDCl_3$.

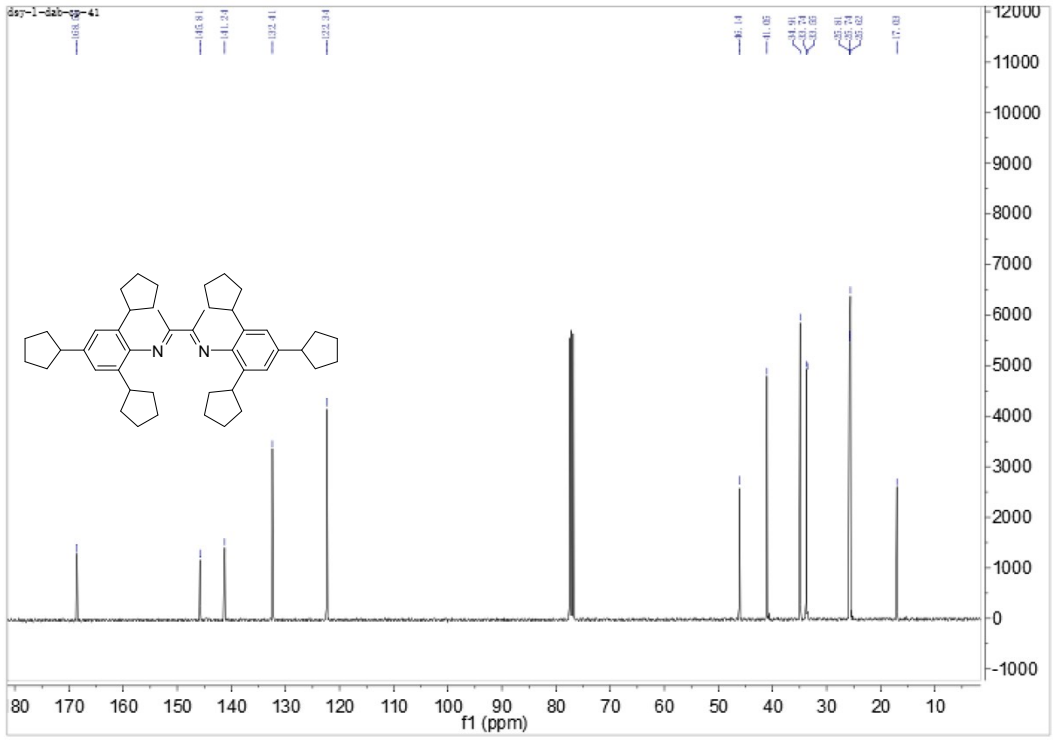


Figure S7. ^{13}C NMR spectrum of **L3** in $CDCl_3$.

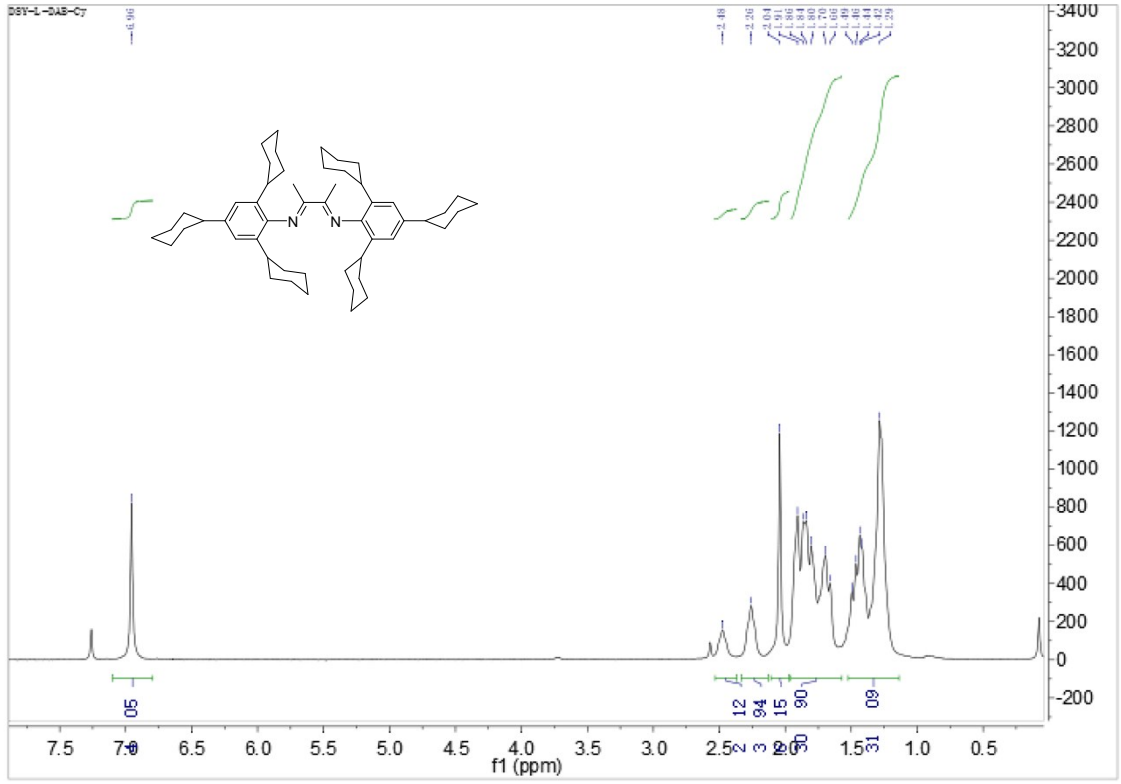


Figure S8. ^{1}H NMR spectrum of **L4** in $CDCl_3$.

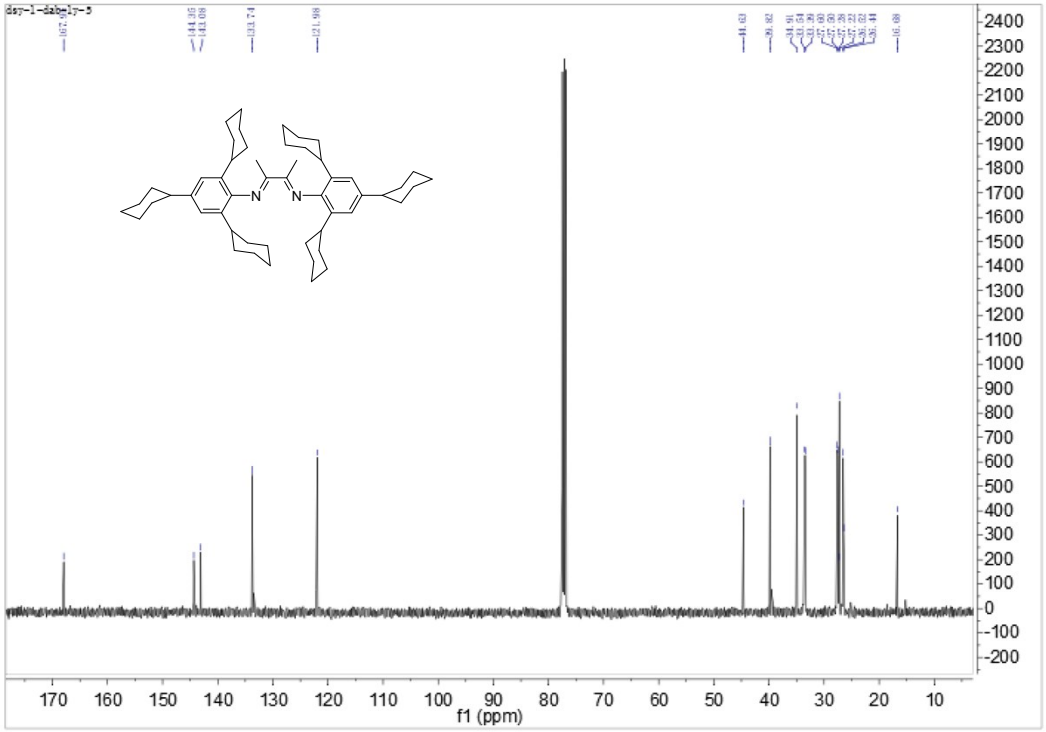


Figure S9. ^{13}C NMR spectrum of **L4** in $CDCl_3$.

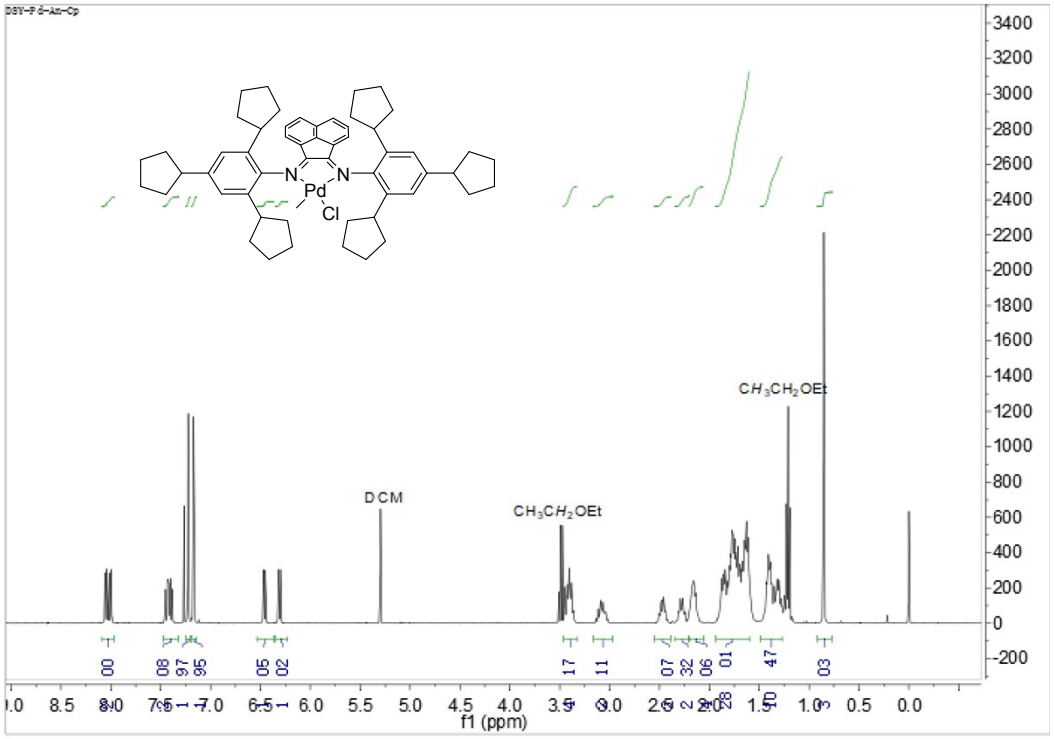


Figure S10. ^{1}H NMR spectrum of **Pd1** in $CDCl_3$.

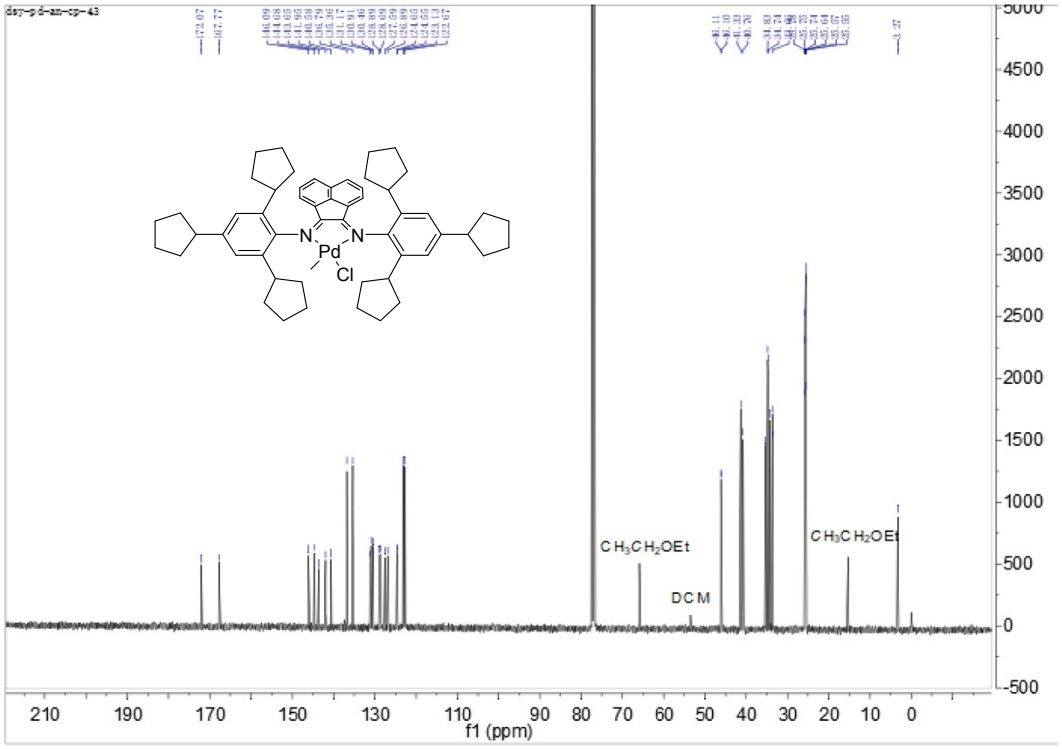


Figure S11. ^{13}C NMR spectrum of **Pd1** in $CDCl_3$.

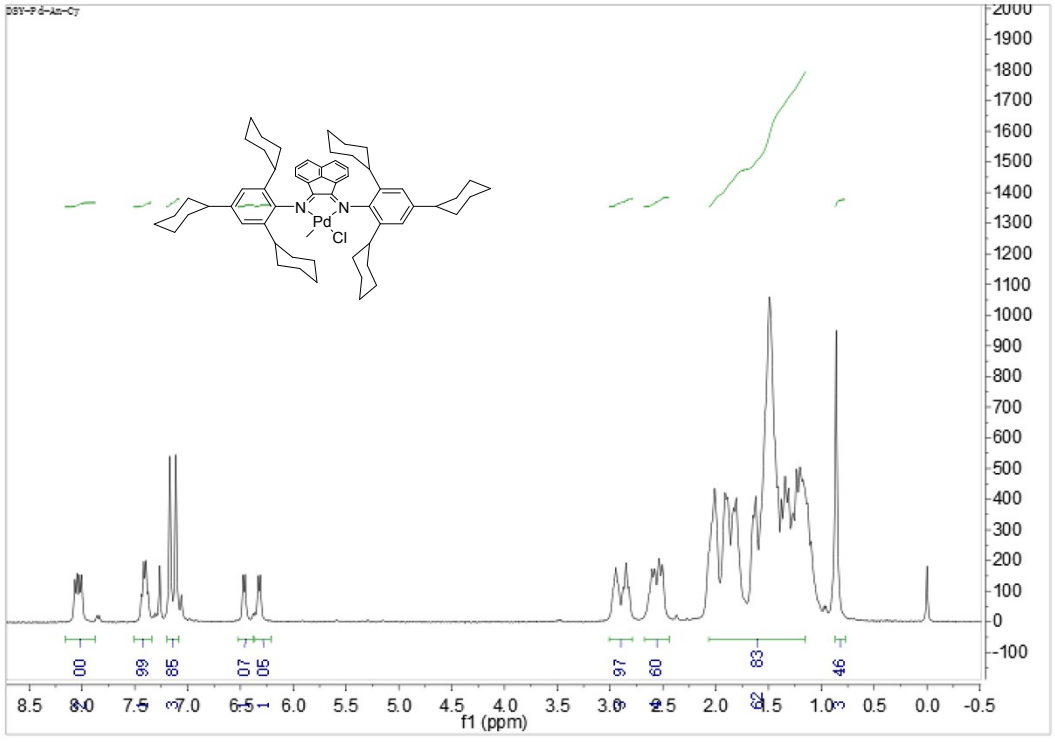


Figure S12. ^{1}H NMR spectrum of **Pd3** in $CDCl_3$.

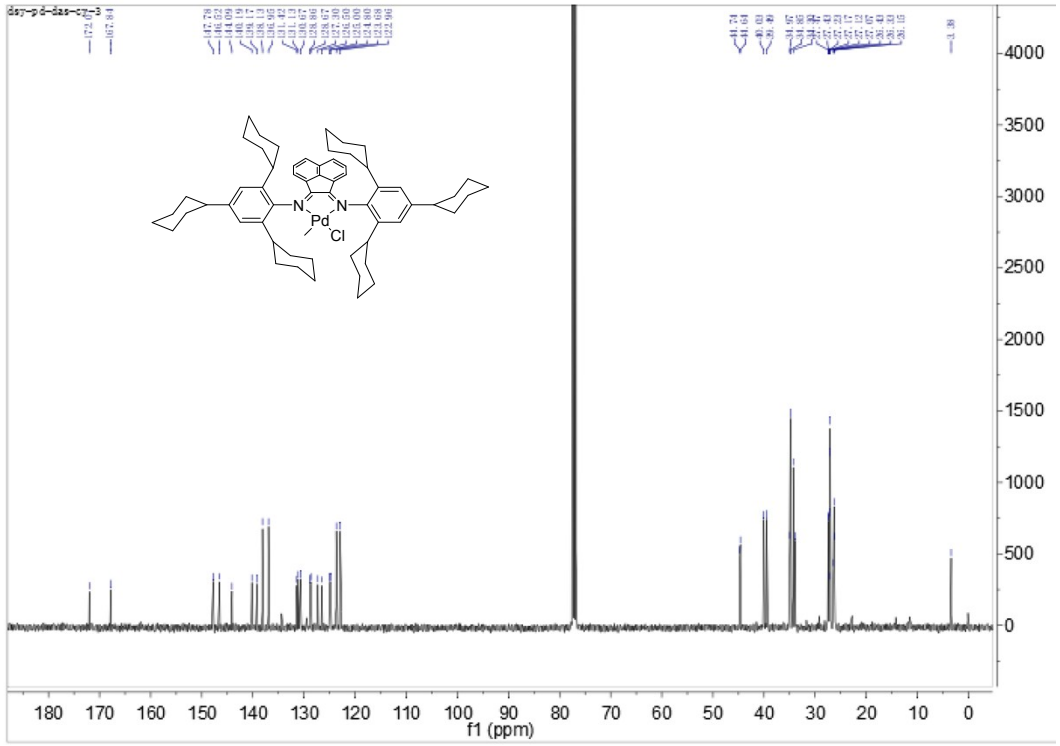


Figure S13. ^{13}C NMR spectrum of **Pd3** in $CDCl_3$.

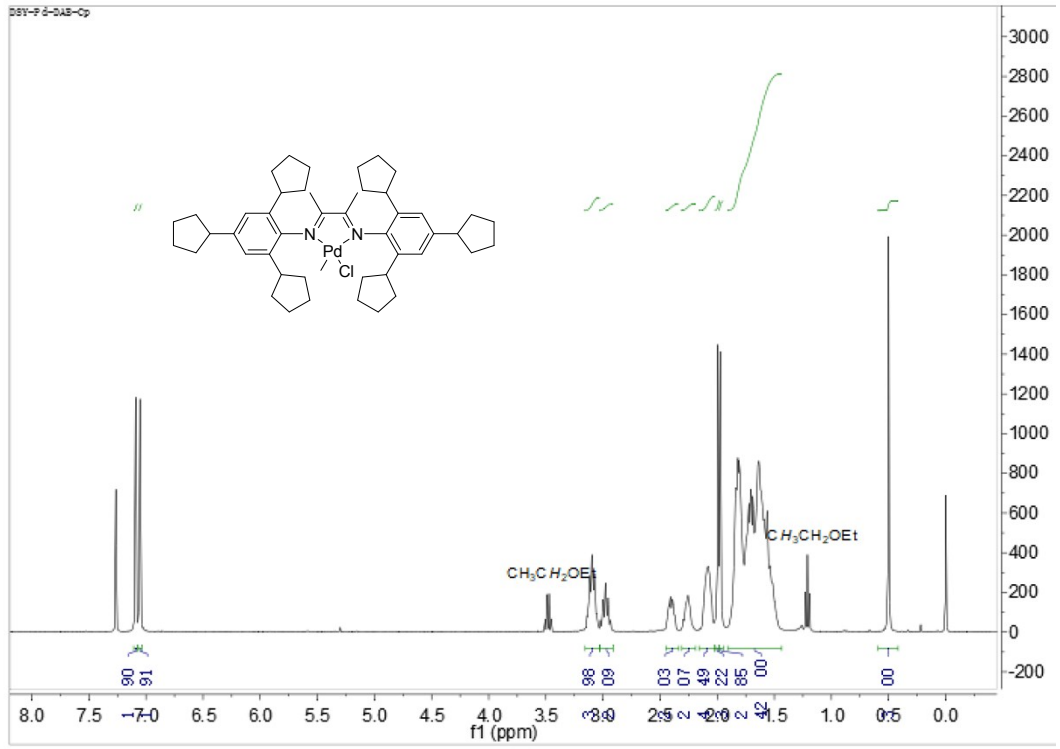


Figure S14. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

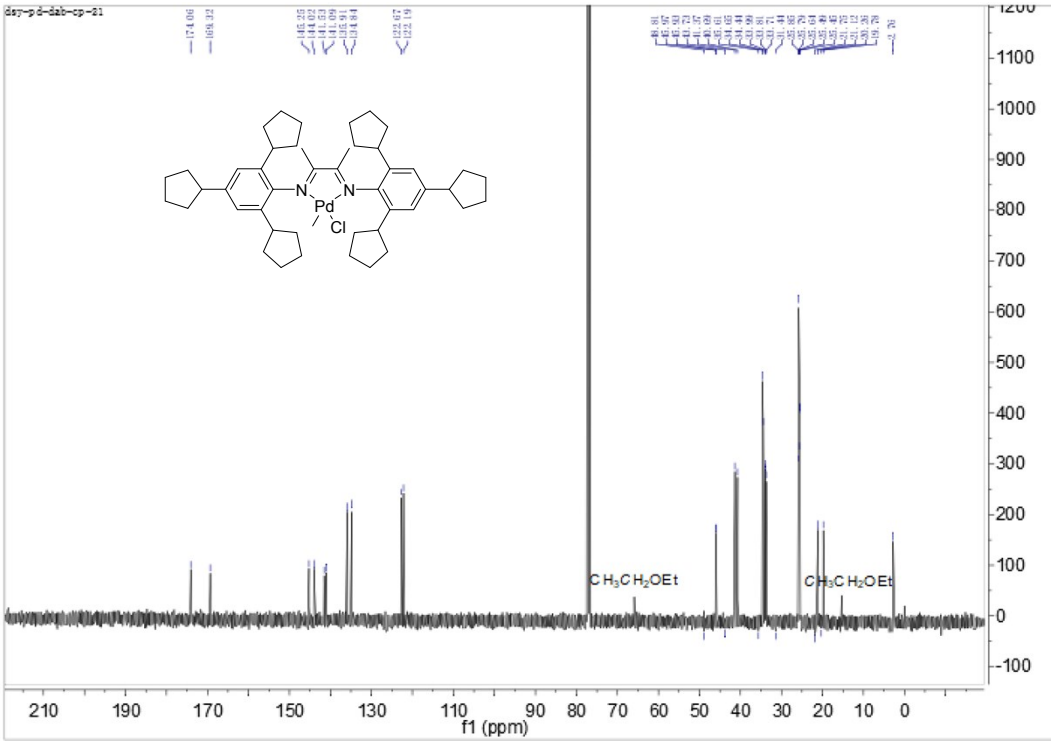


Figure S15. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

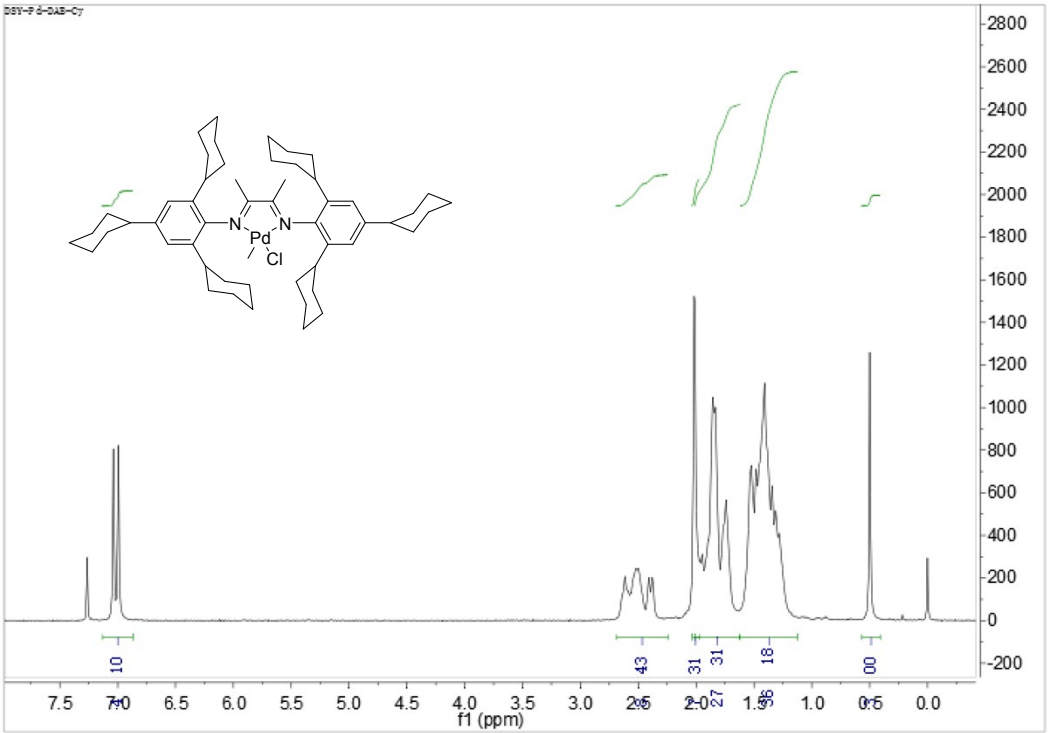


Figure S16. ^{1}H NMR spectrum of **Pd4** in $CDCl_3$.

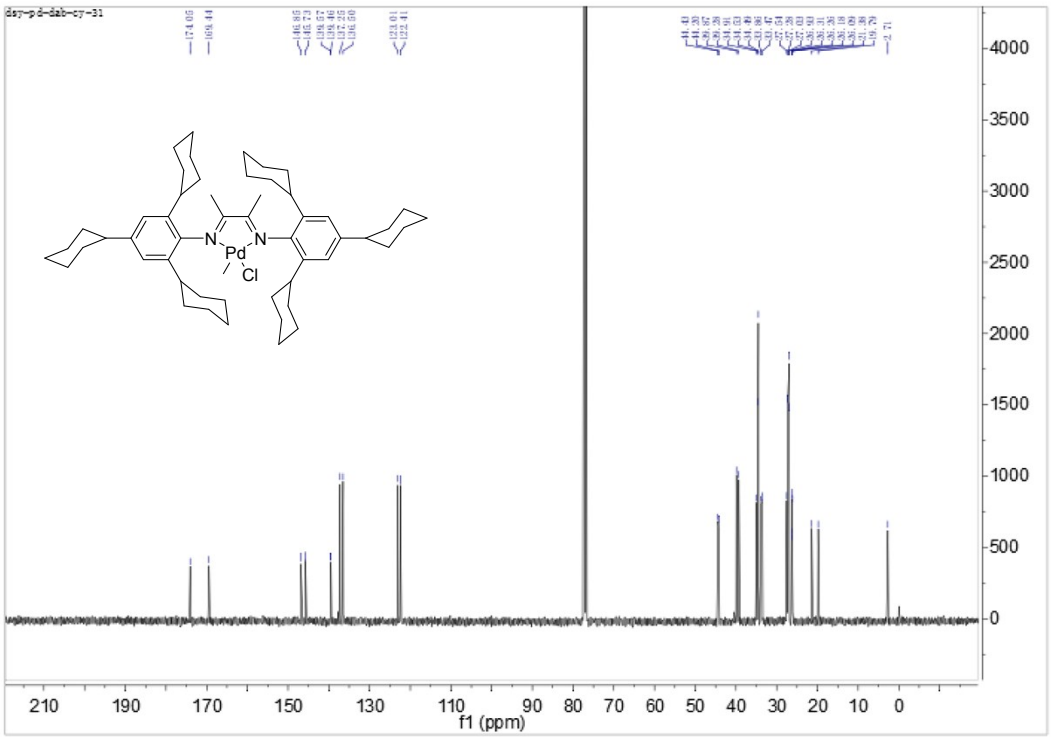


Figure S17. ^{13}C NMR spectrum of **Pd4** in $CDCl_3$.

3.2 ESI-MS of Ligand L2, L4.

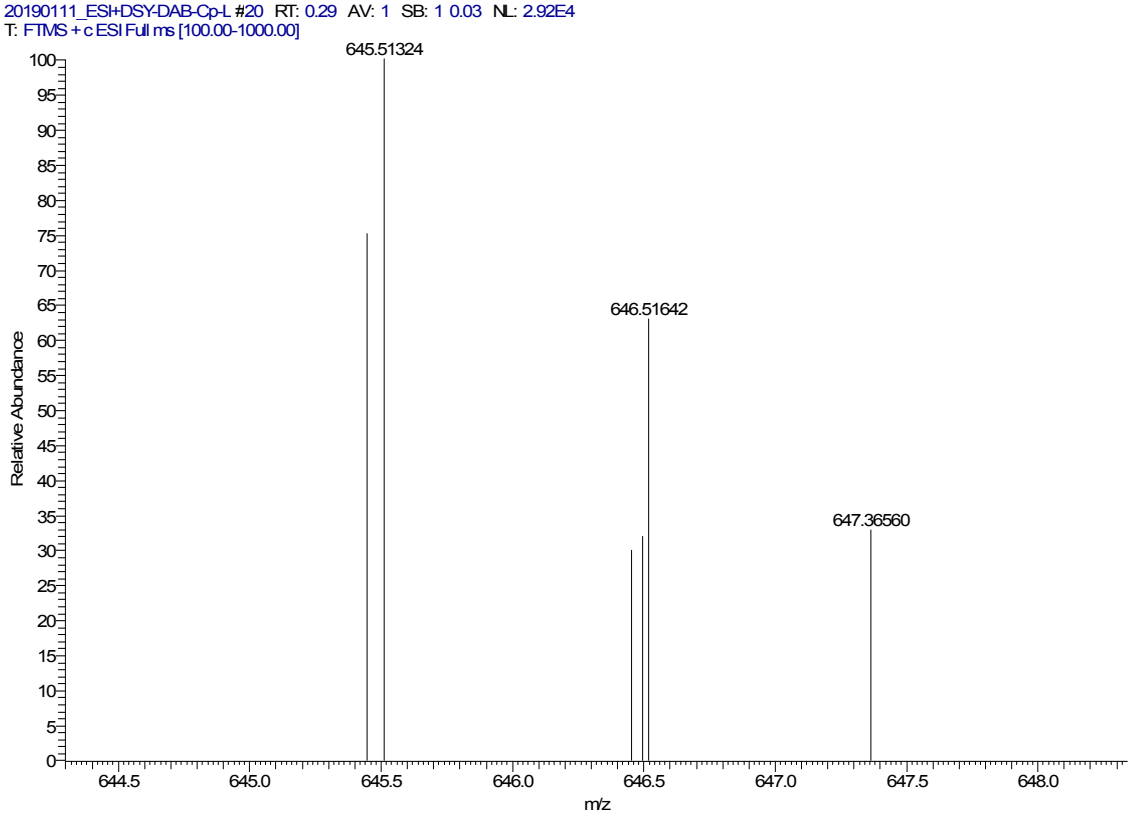


Figure S18. ESI-MS of **L2.**

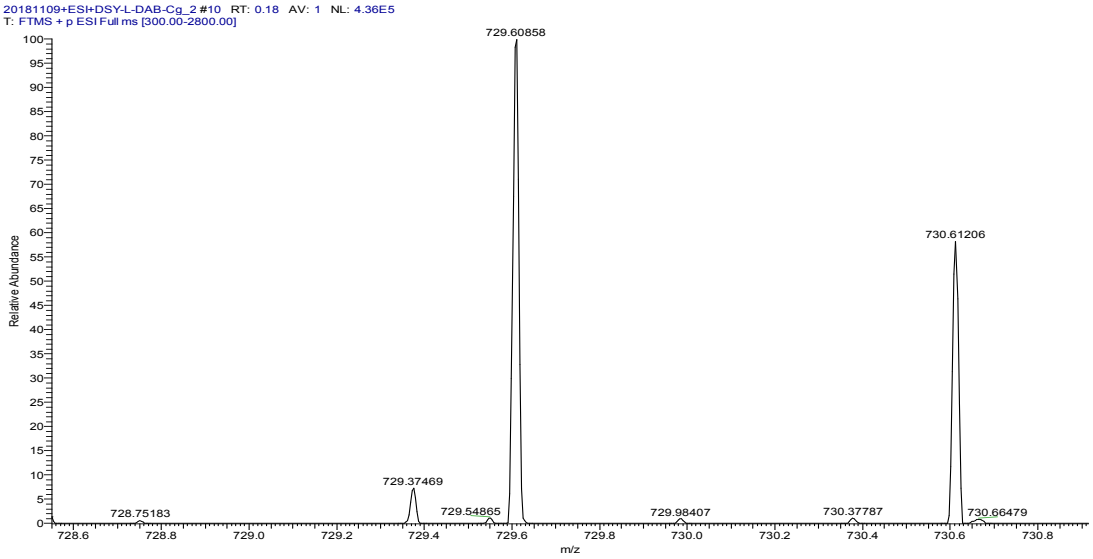


Figure S19. ESI-MS of **L4.**

3.3 MALDI-TOF of Complexes Ni1-Ni4, Pd1-Pd4.

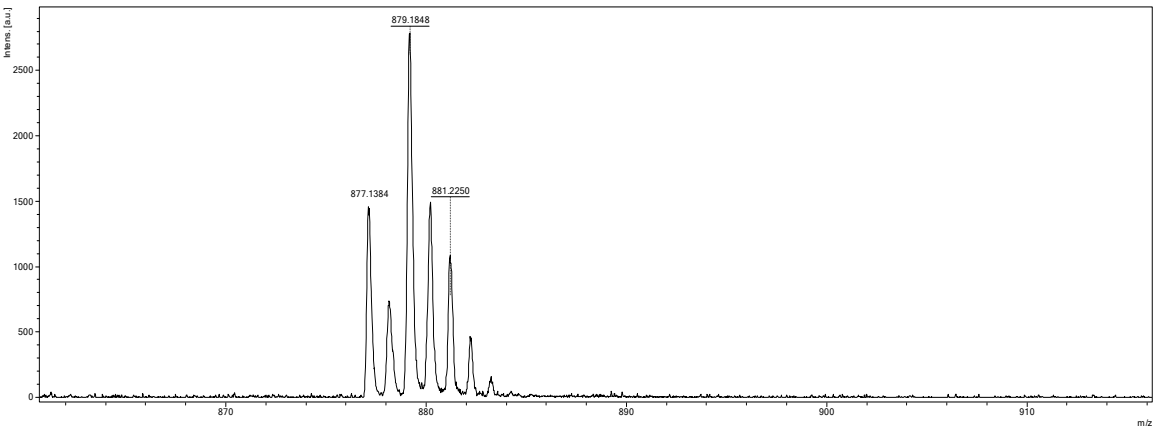


Figure S20. MALDI-TOF-MS of complex **Ni1**.

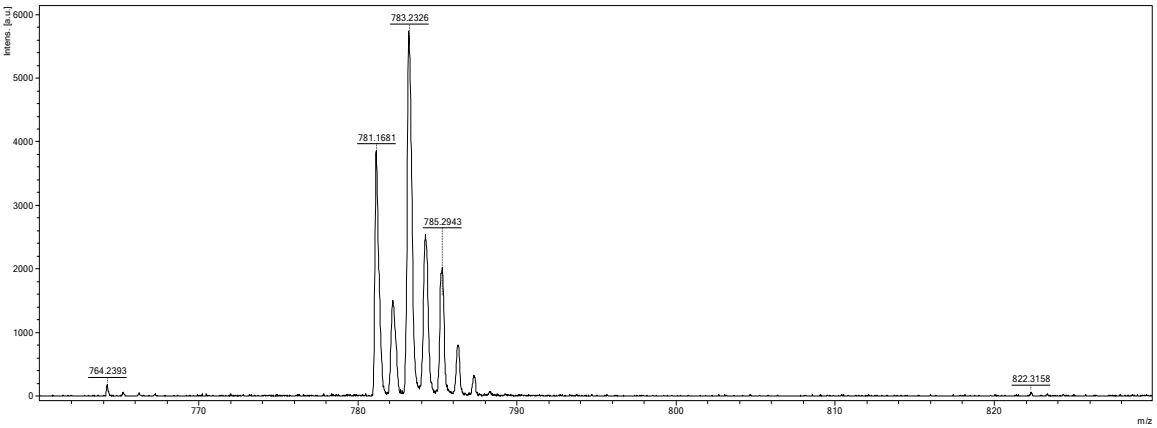


Figure S21. MALDI-TOF-MS of complex **Ni2**.

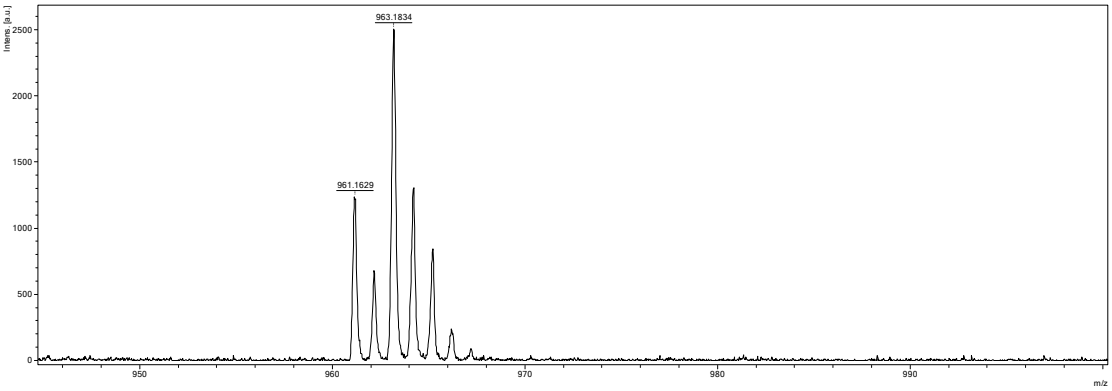
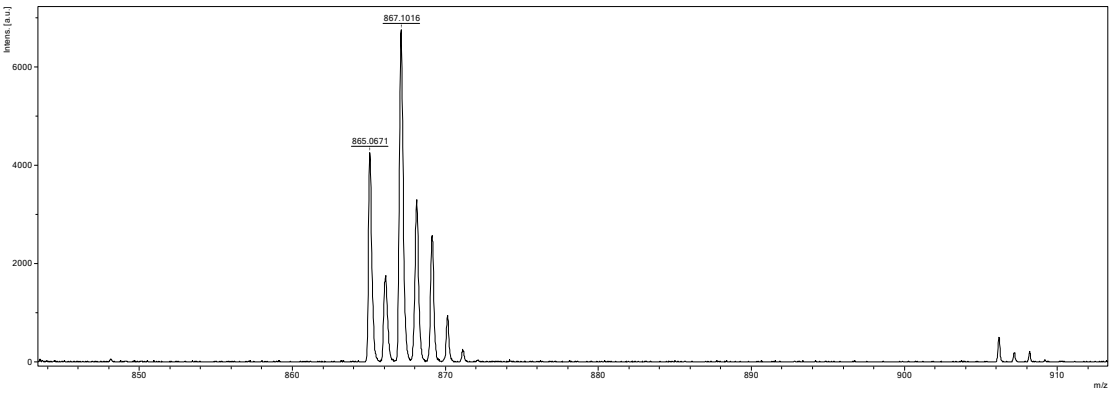


Figure S22. MALDI-TOF-MS of complex **Ni3**.



. **Figure S23.** MALDI-TOF-MS of complex **Ni4**.

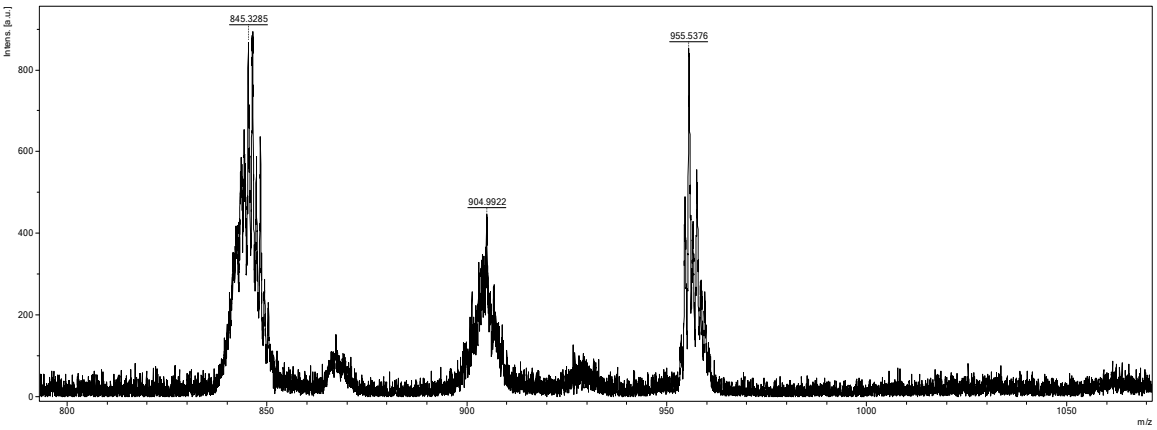


Figure S24. MALDI-TOF-MS of complex **Pd1**.

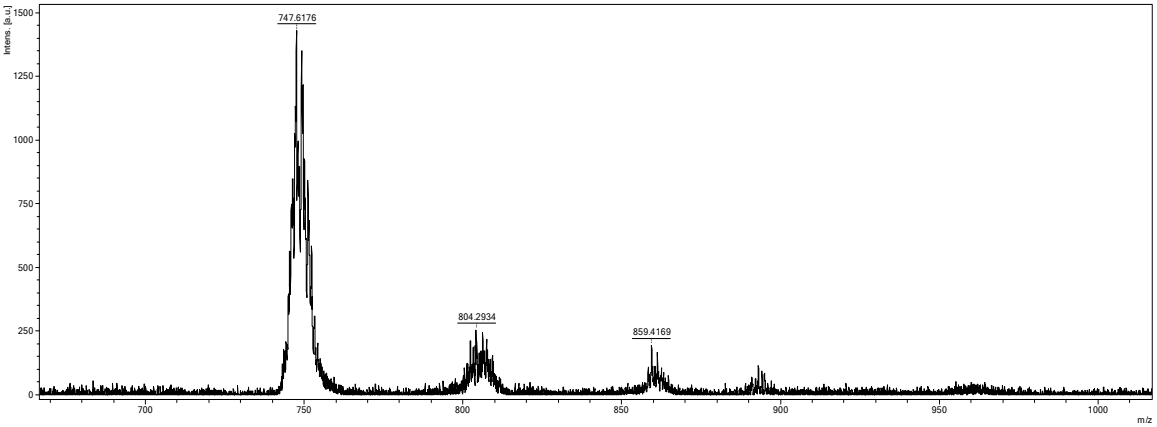


Figure S25. MALDI-TOF-MS of complex **Pd2**.

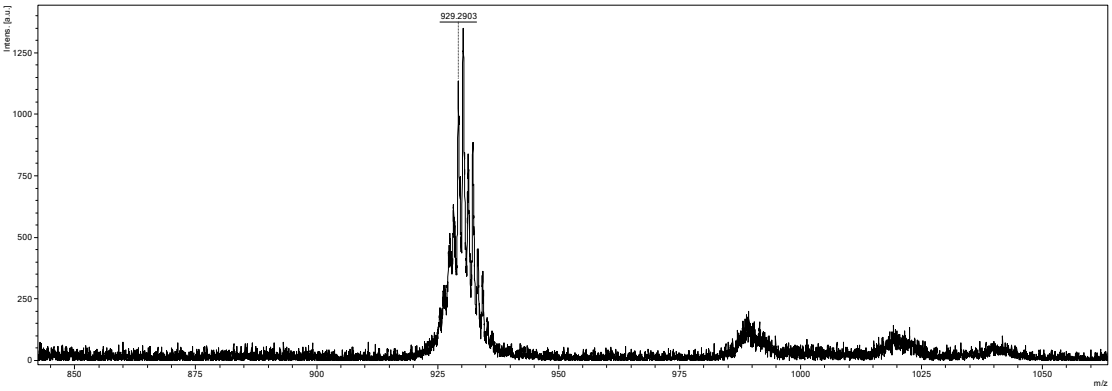


Figure S26. MALDI-TOF-MS of complex **Pd3**.

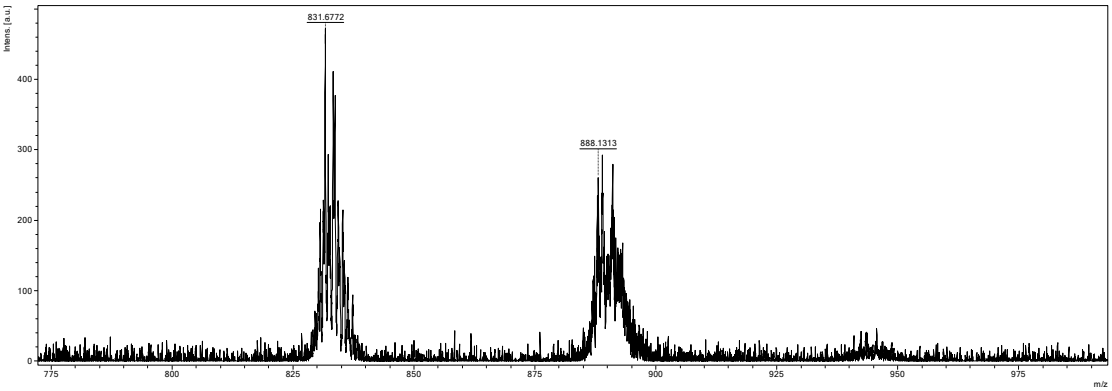


Figure S27. MALDI-TOF-MS of complex **Pd4**.

3.4 ^{1}H and ^{13}C NMR of polymer and copolymer.

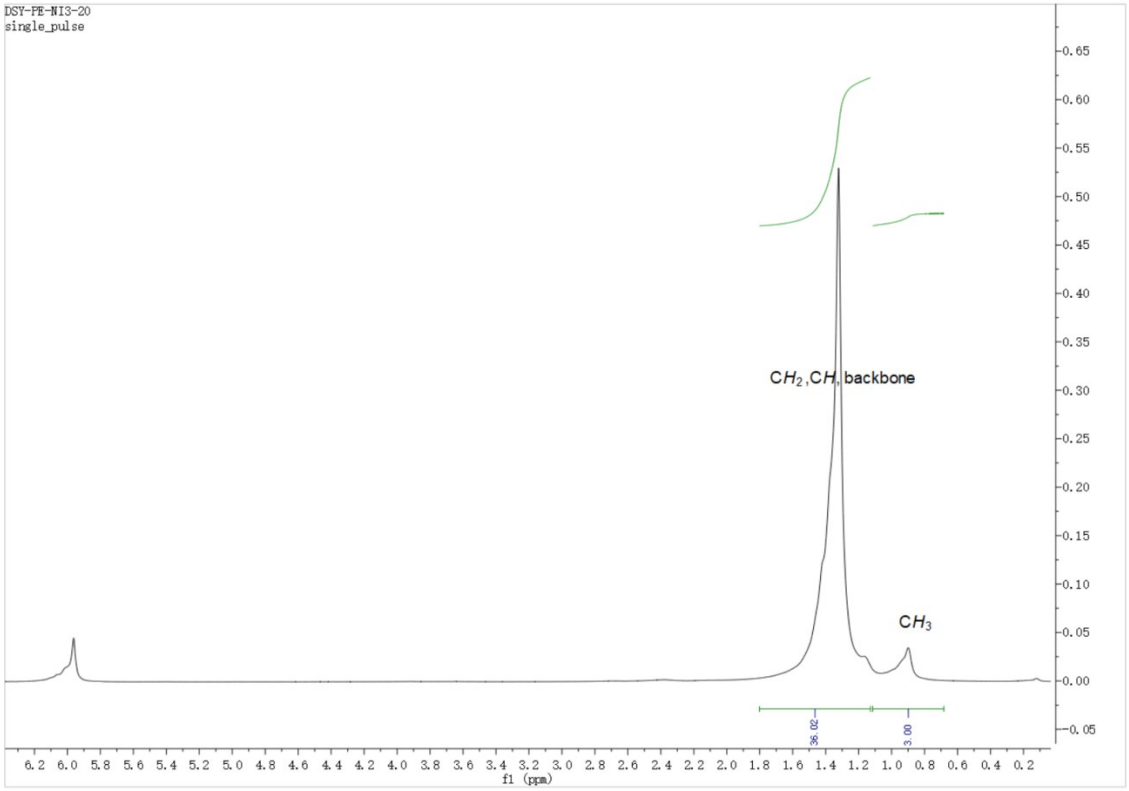


Figure S28. ^{1}H NMR spectrum of the polymer from table 1, entry 7 ($CDCl_2CDCl_2$, 120 °C).

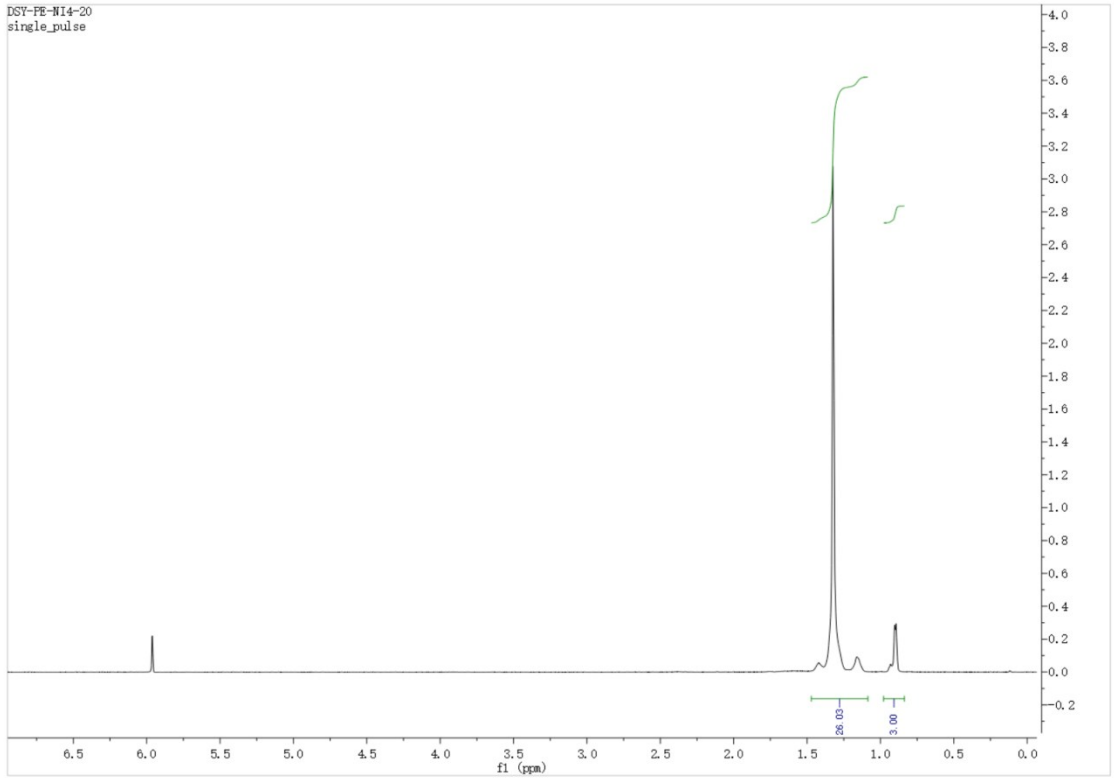


Figure S29. ^{1}H NMR spectrum of the polymer from table 1, entry 10 ($CDCl_2CDCl_2$, 120 °C).

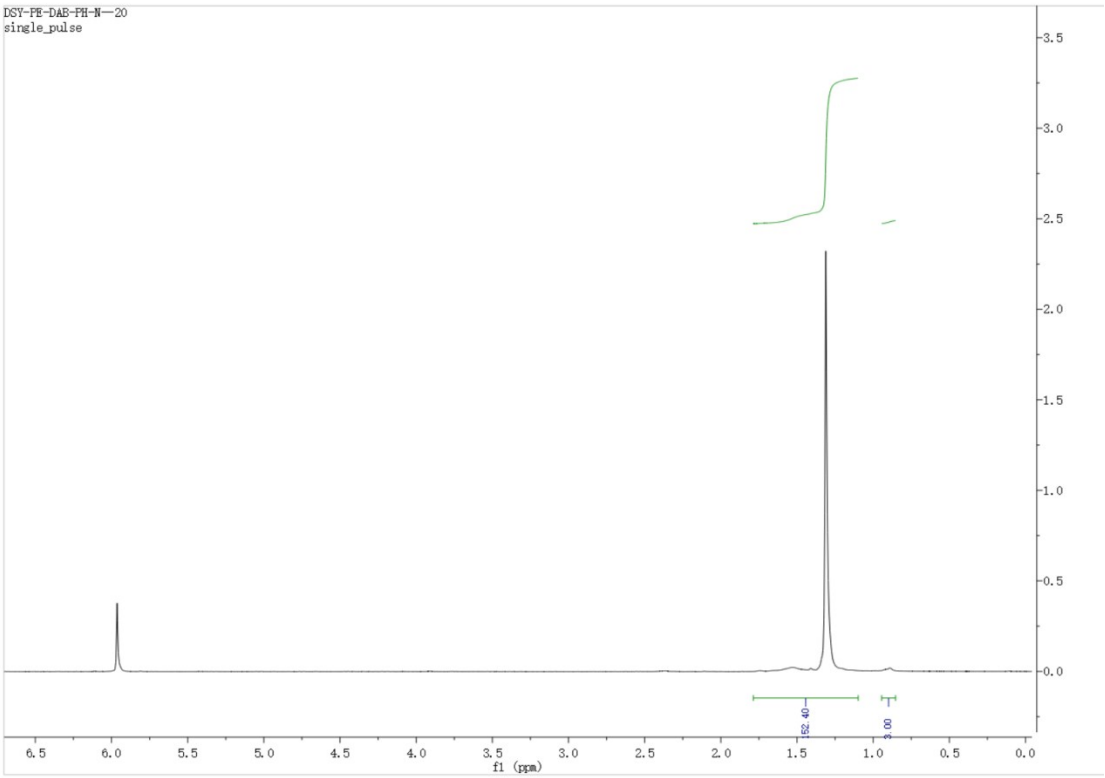


Figure S30. ^{1}H NMR spectrum of the polymer from table 1, entry 13 ($CDCl_2CDCl_2$, 120 °C).

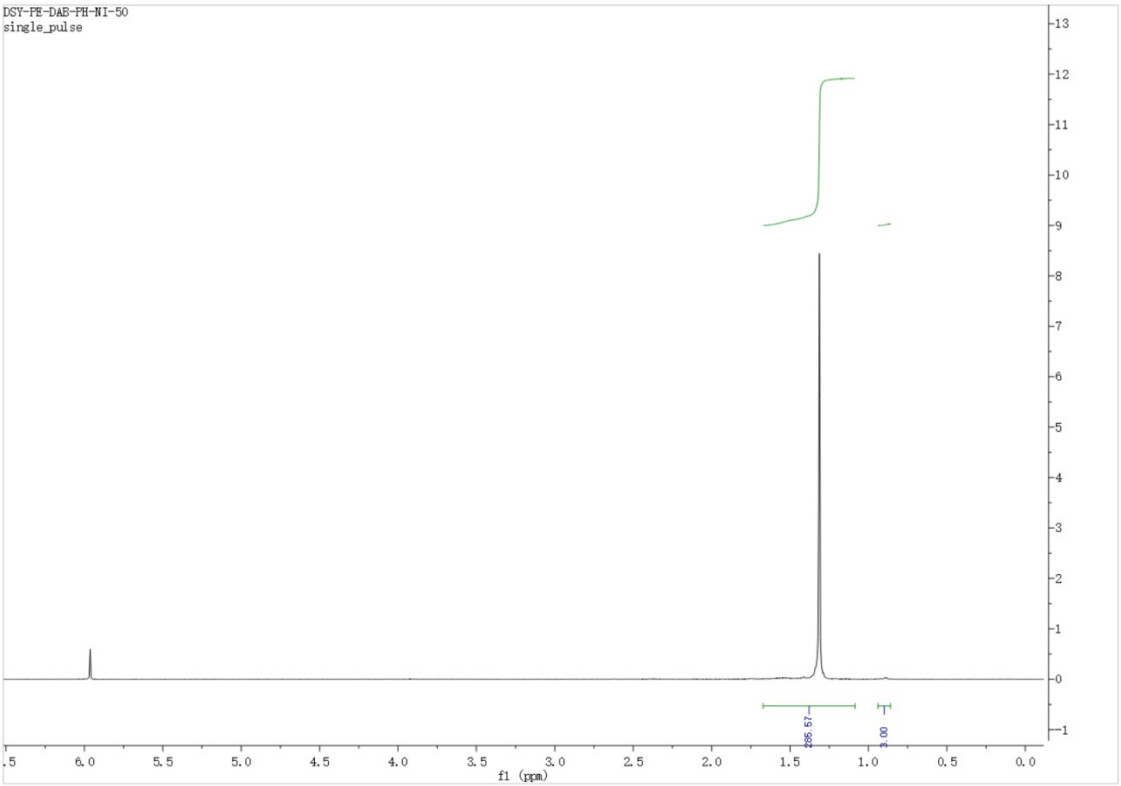


Figure S31. ^{1}H NMR spectrum of the polymer from table 1, entry 14 ($CDCl_2CDCl_2$, 120 °C).

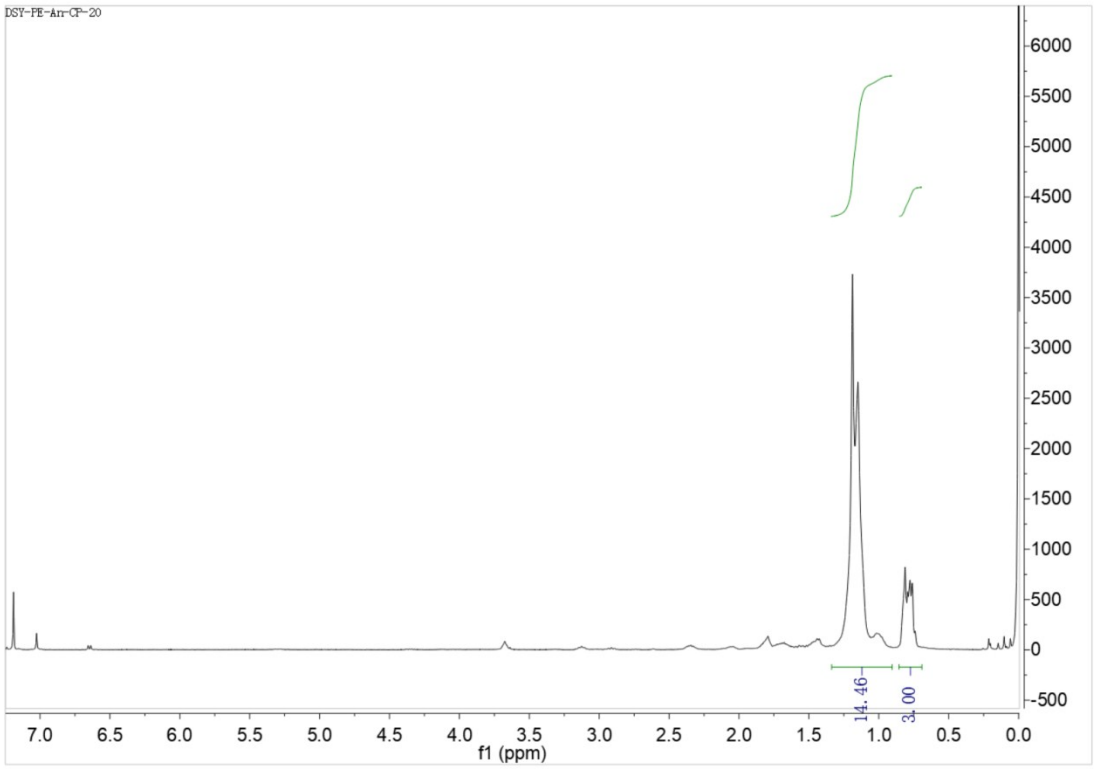


Figure S32. ^{1}H NMR spectrum of the polymer from table 2, entry 1 ($CDCl_3$, 20 ^{o}C).

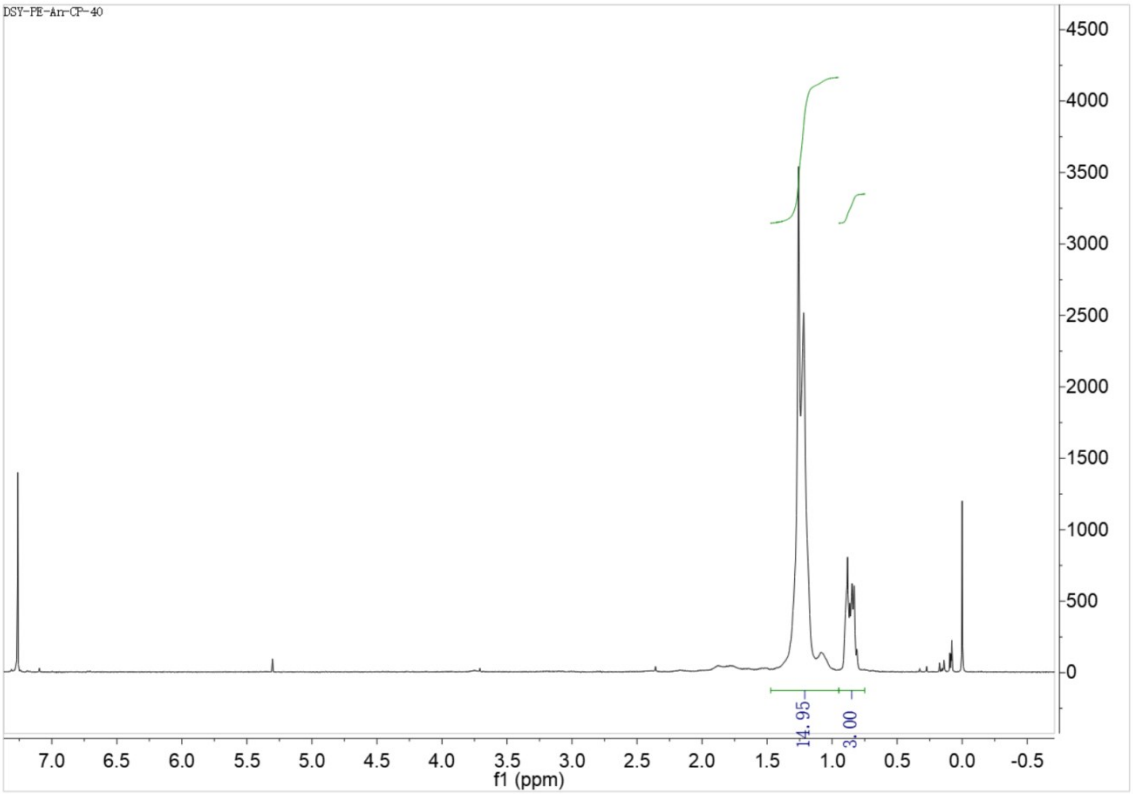


Figure S33. ^{1}H NMR spectrum of the polymer from table 2, entry 2 ($CDCl_3$, 20 ^{o}C).

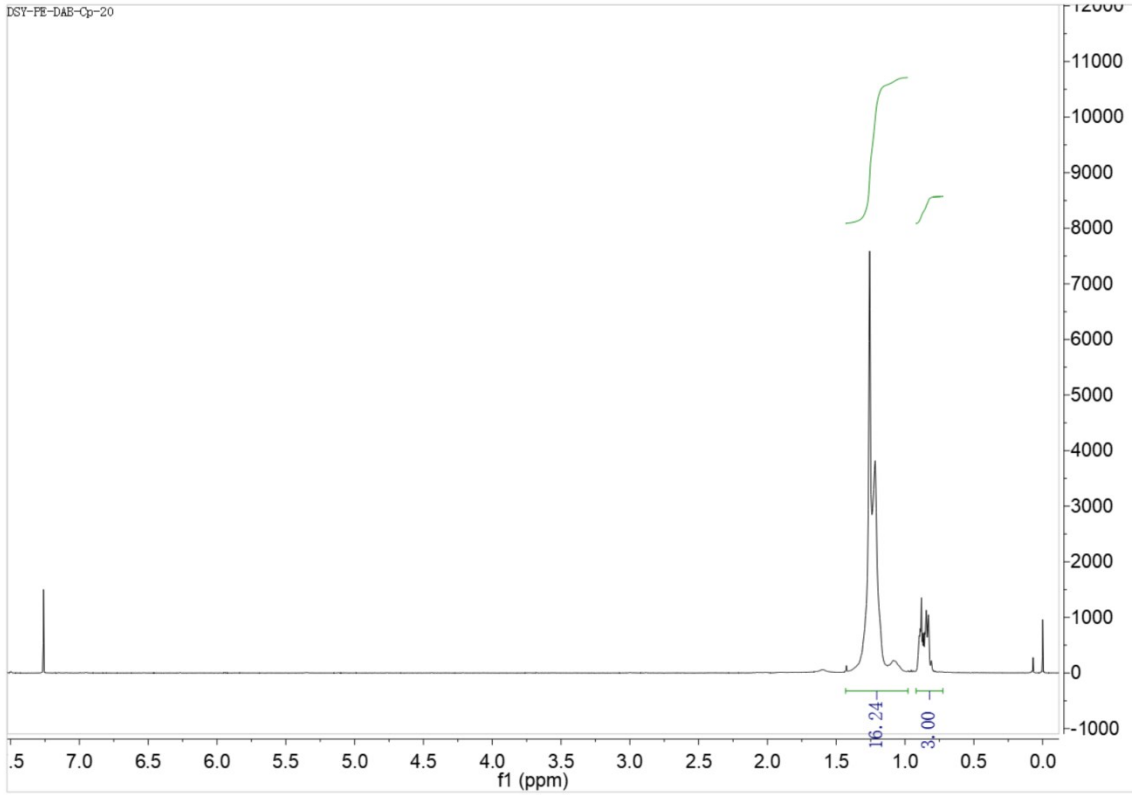


Figure S34. ^{1}H NMR spectrum of the polymer from table 2, entry 5 ($CDCl_3$, 20 ^{o}C).

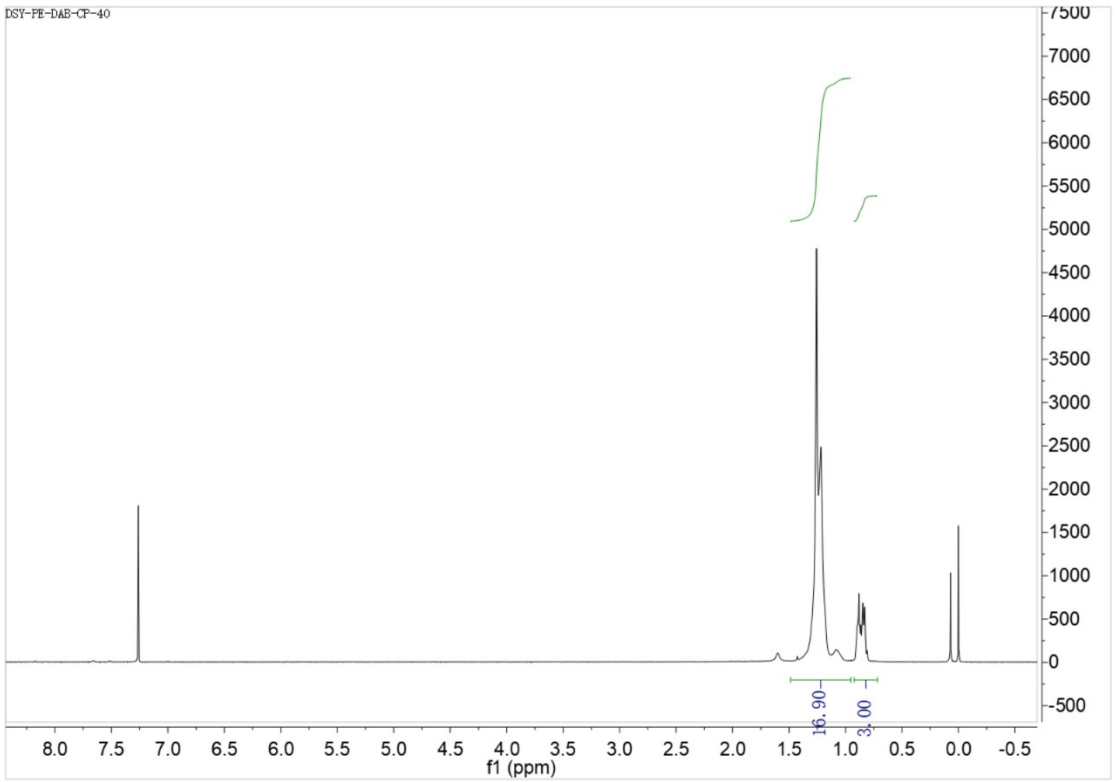


Figure S35. ^{1}H NMR spectrum of the polymer from table 2, entry 6 ($CDCl_3$, 20 ^{o}C).

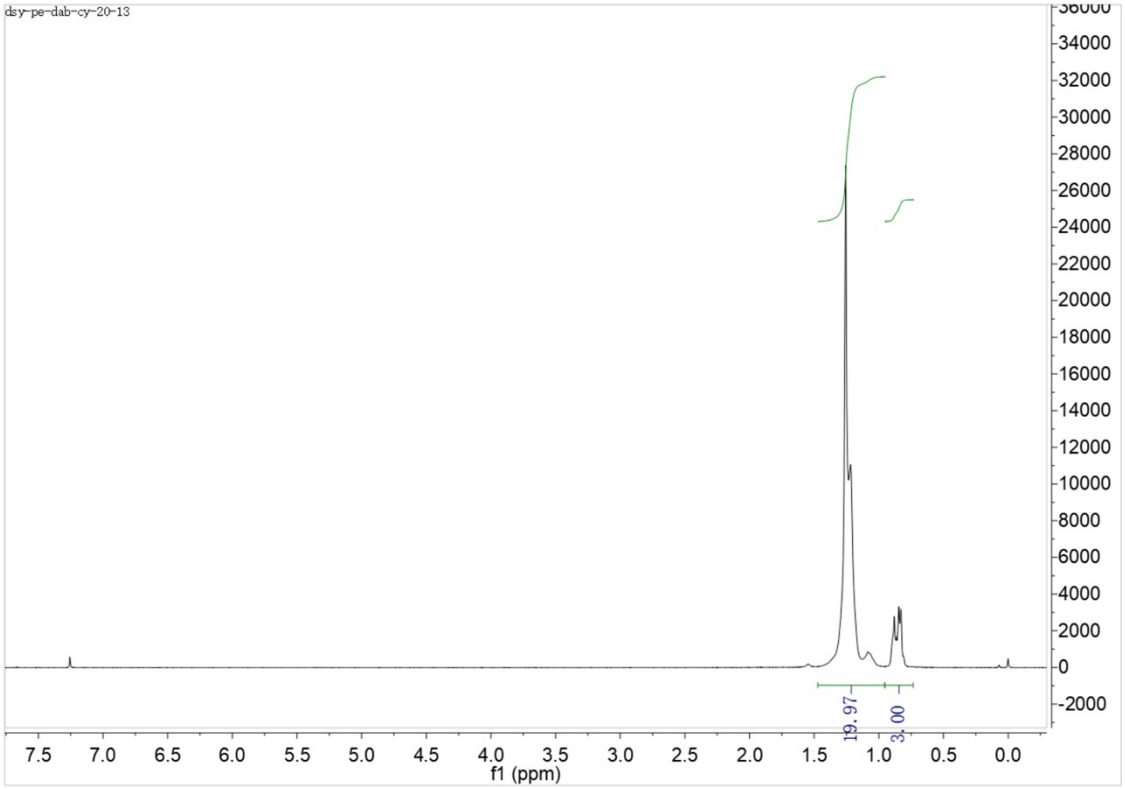


Figure S36. ^{1}H NMR spectrum of the polymer from table 2, entry 7 ($CDCl_3$, 20 ^{o}C).

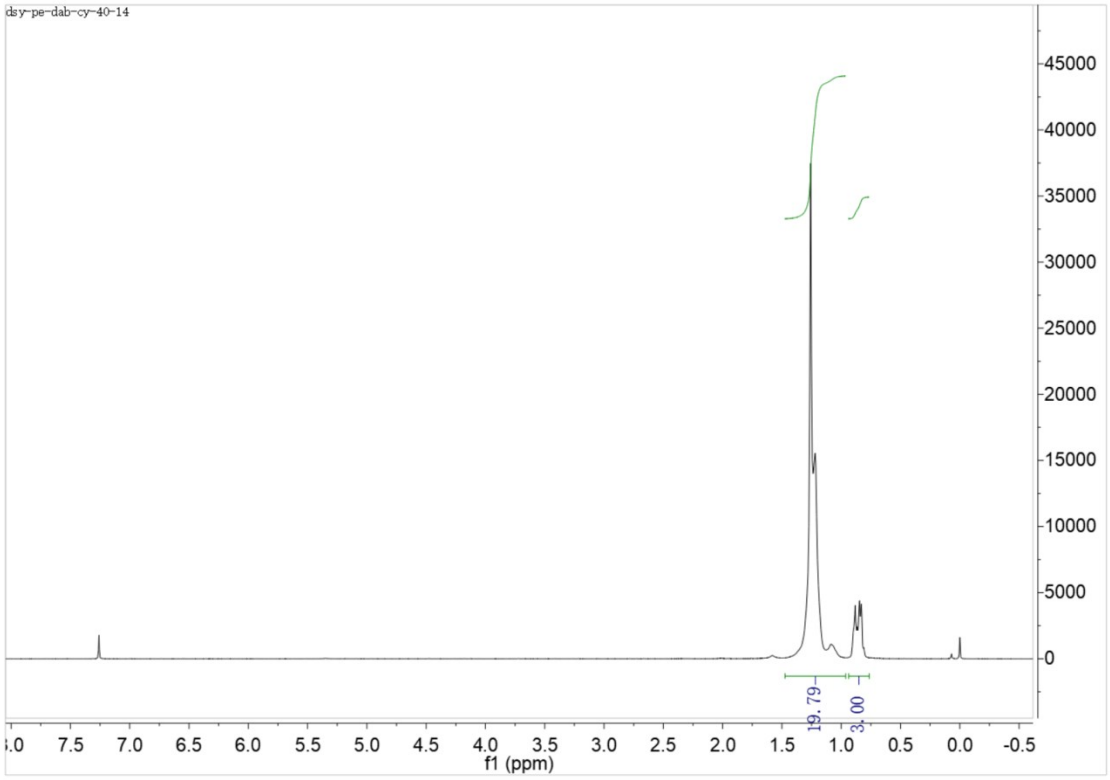


Figure S37. ^{1}H NMR spectrum of the polymer from table 2, entry 8 ($CDCl_3$, 20 ^{o}C).

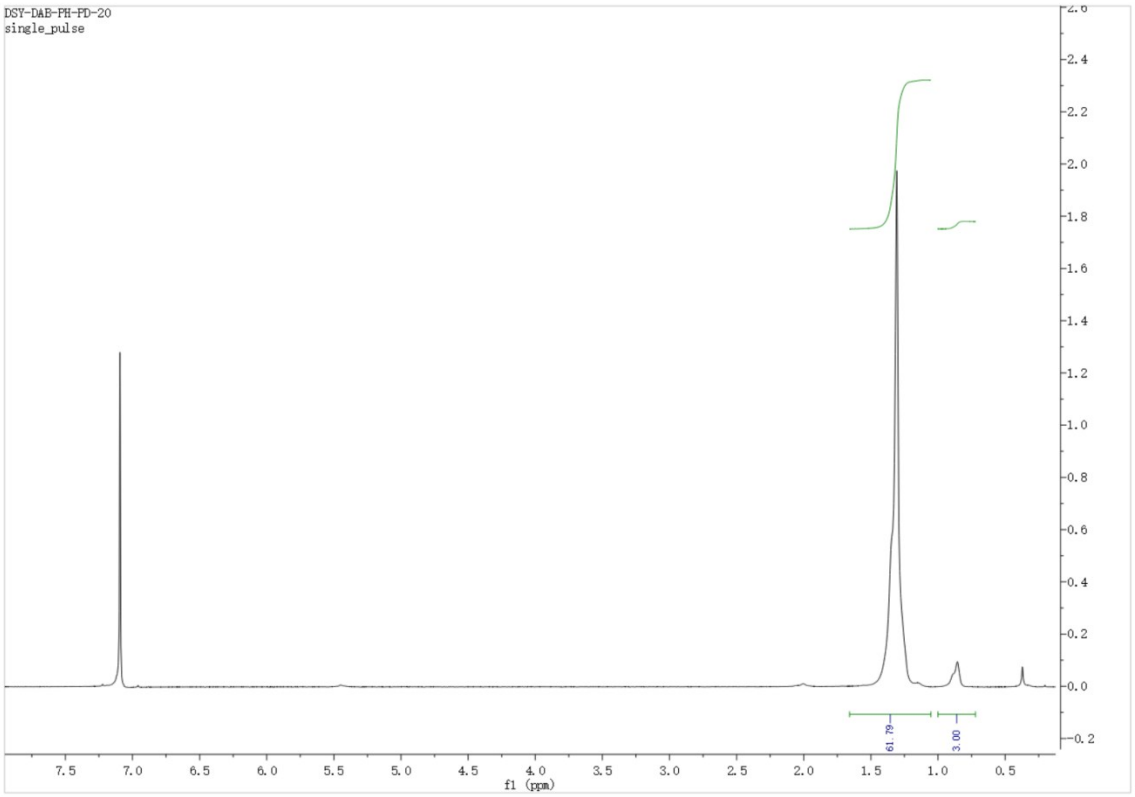


Figure S38. ^{1}H NMR spectrum of the polymer from table 2, entry 9 ($CDCl_3$, 20 ^{o}C).

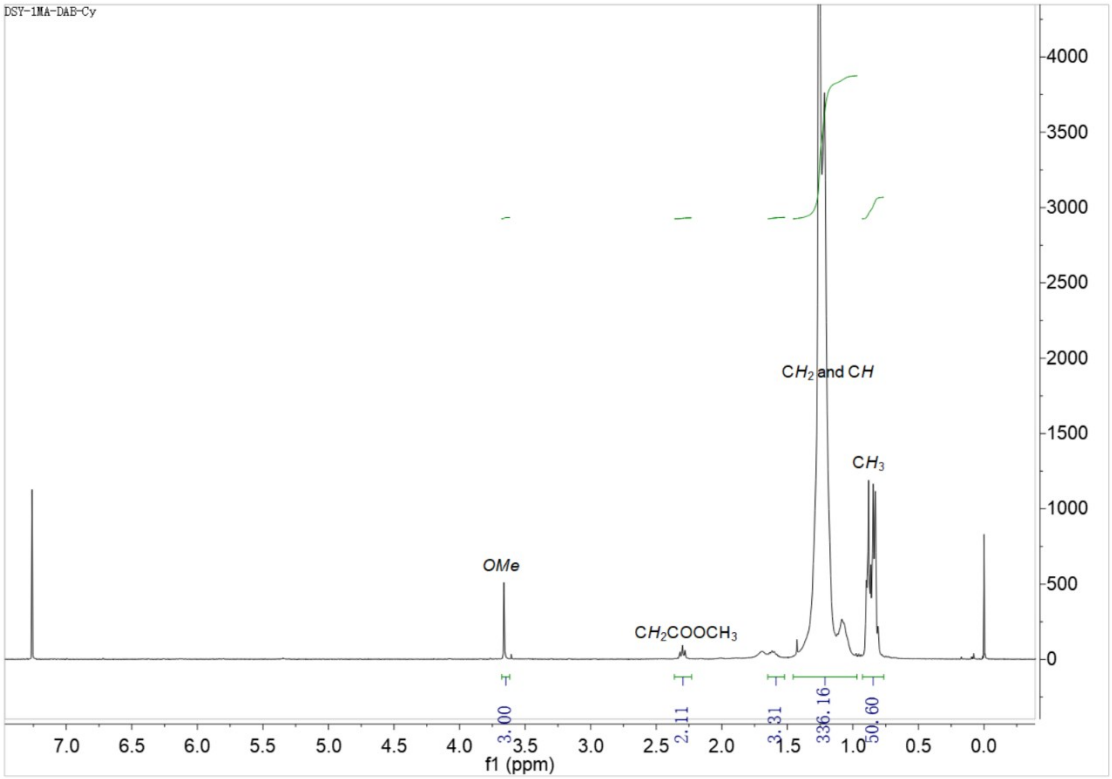


Figure S39. ^{1}H NMR spectrum of the polymer from table 3, entry 11 ($CDCl_3$, 20 ^{o}C).

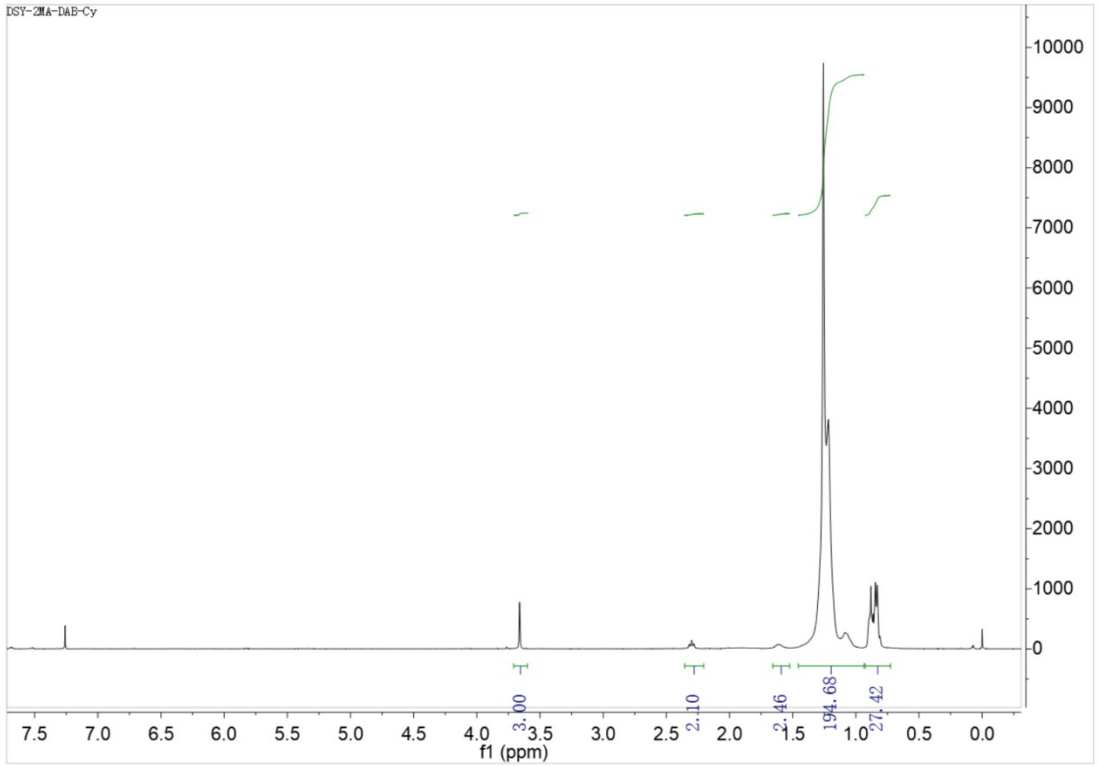


Figure S40. ^{1}H NMR spectrum of the polymer from table 3, entry 12 ($CDCl_3$, 20 ^{o}C).

3.5 DSC and GPC of polymer and copolymer.

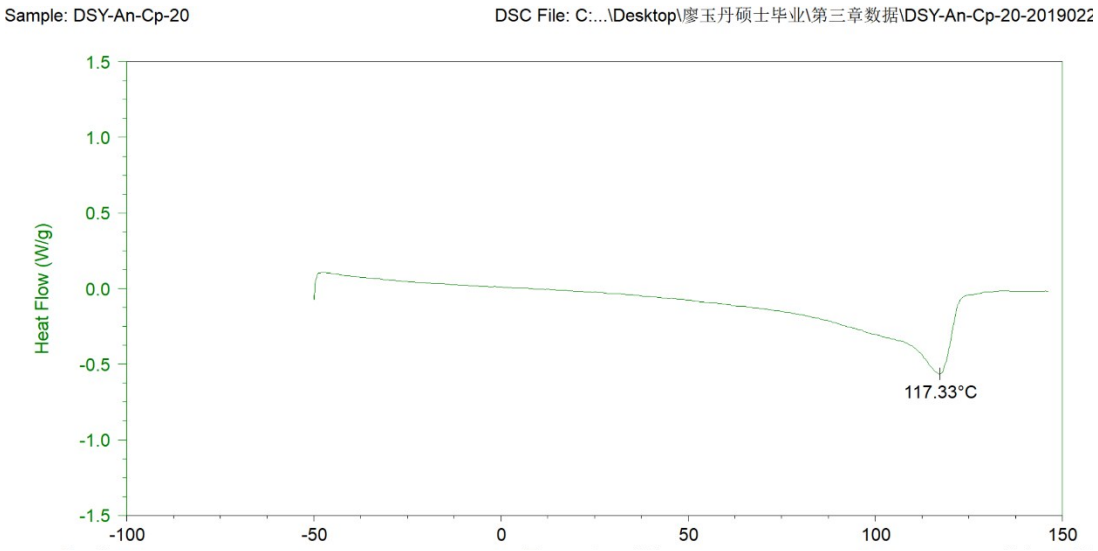


Figure S41. DSC of the polymer from table 1, entry 1.

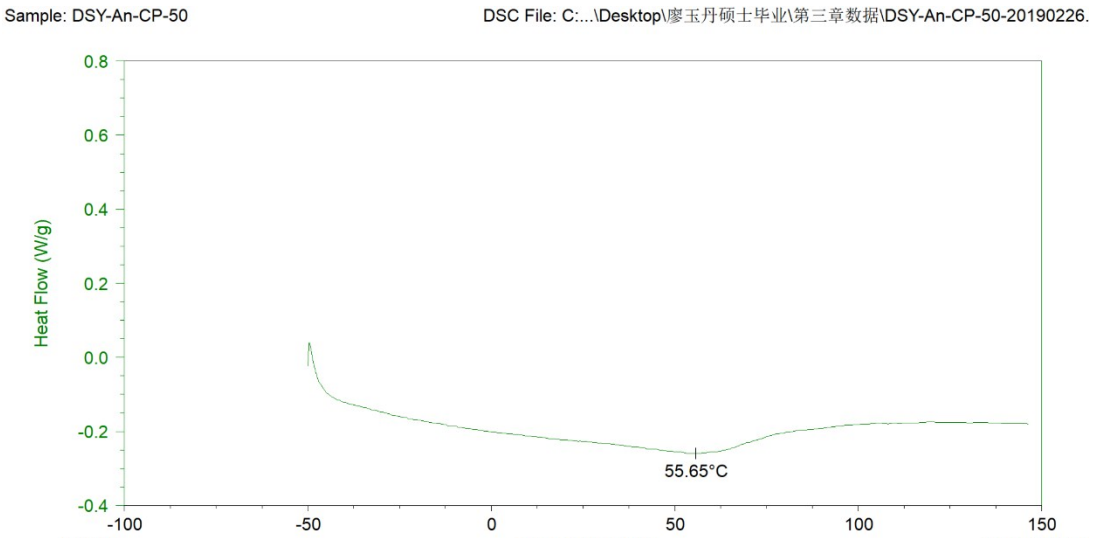


Figure S42. DSC of the polymer from table 1, entry 2.

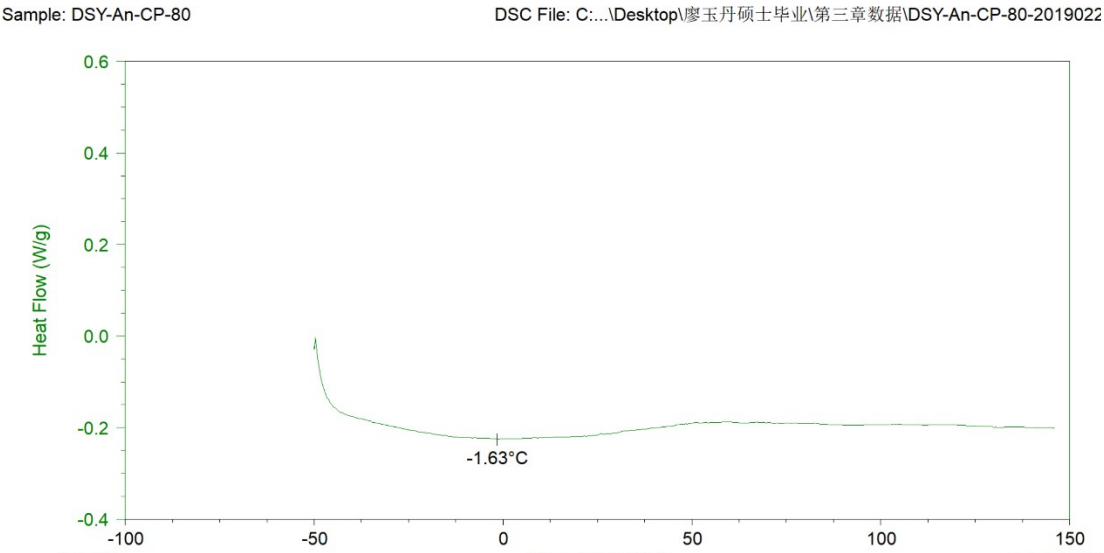


Figure S43. DSC of the polymer from table 1, entry 3.

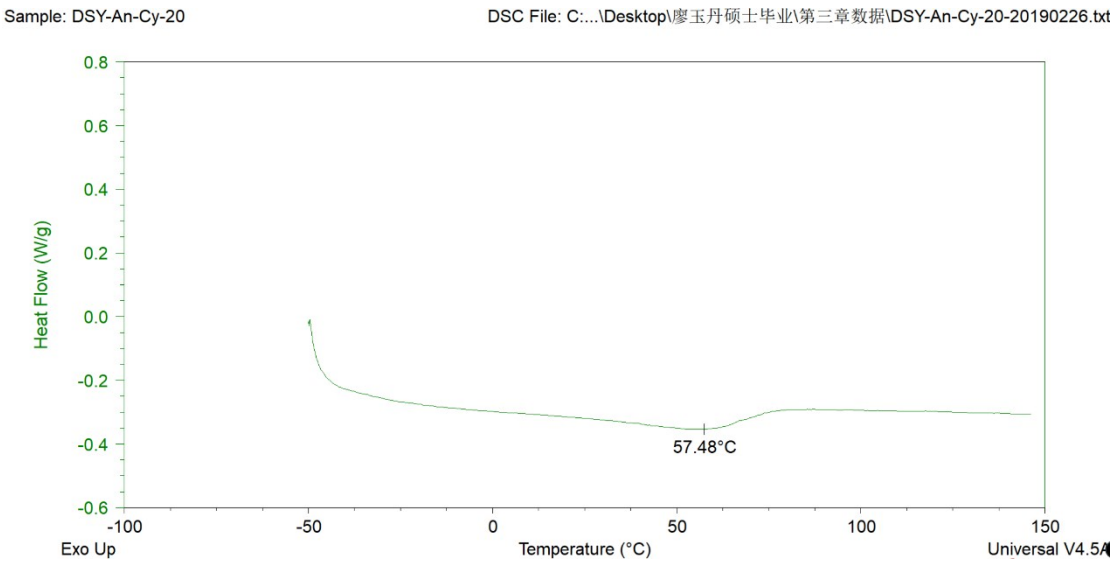


Figure S44. DSC of the polymer from table 1, entry 4.

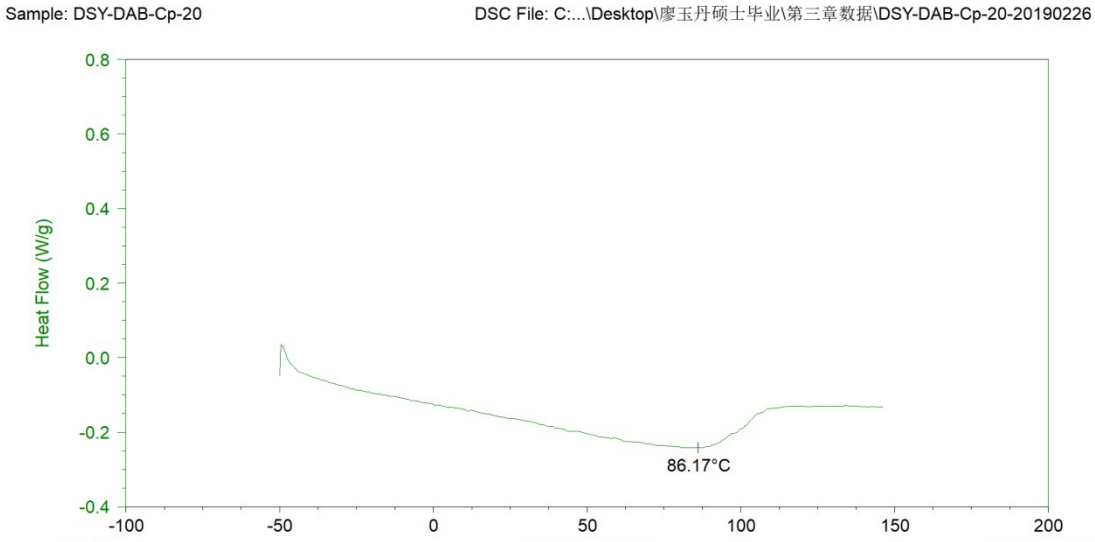


Figure S45. DSC of the polymer from table 1, entry 7.

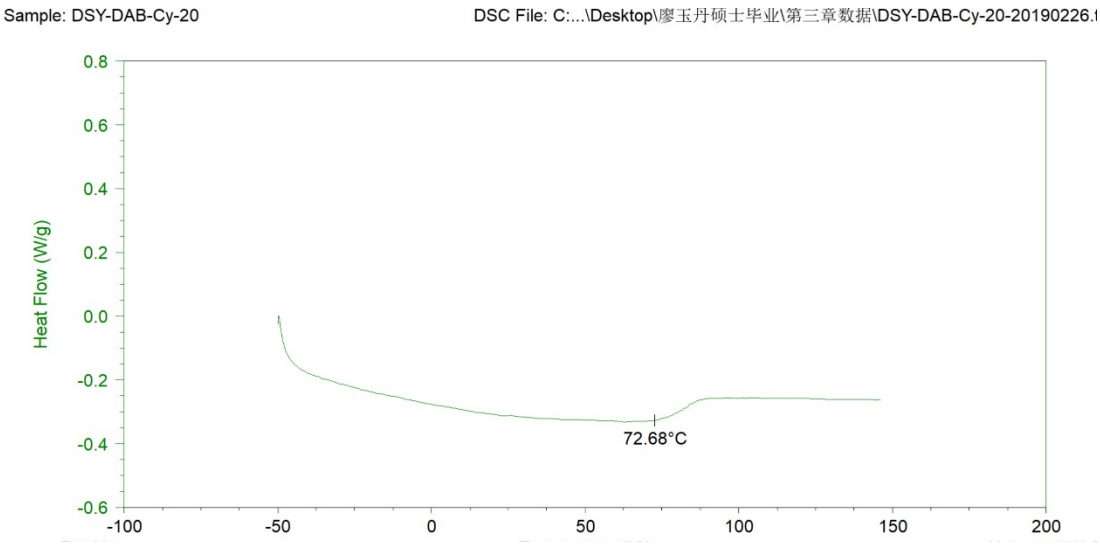


Figure S46. DSC of the polymer from table 1, entry 10.

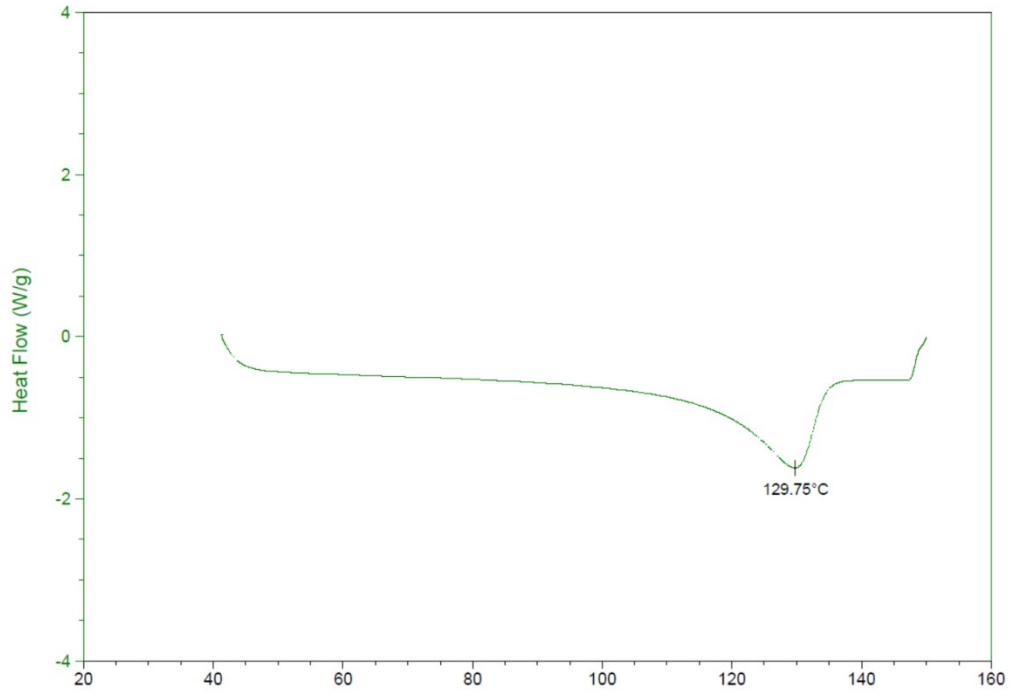
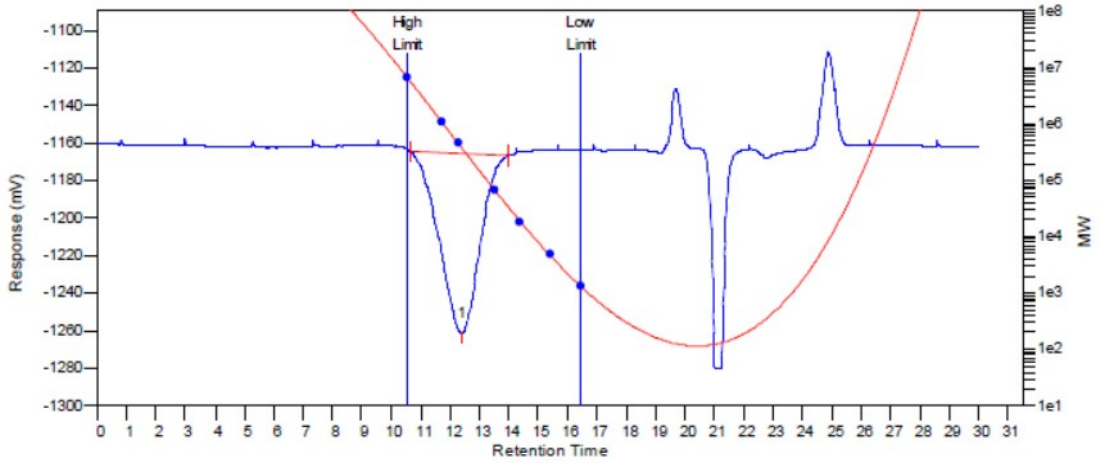
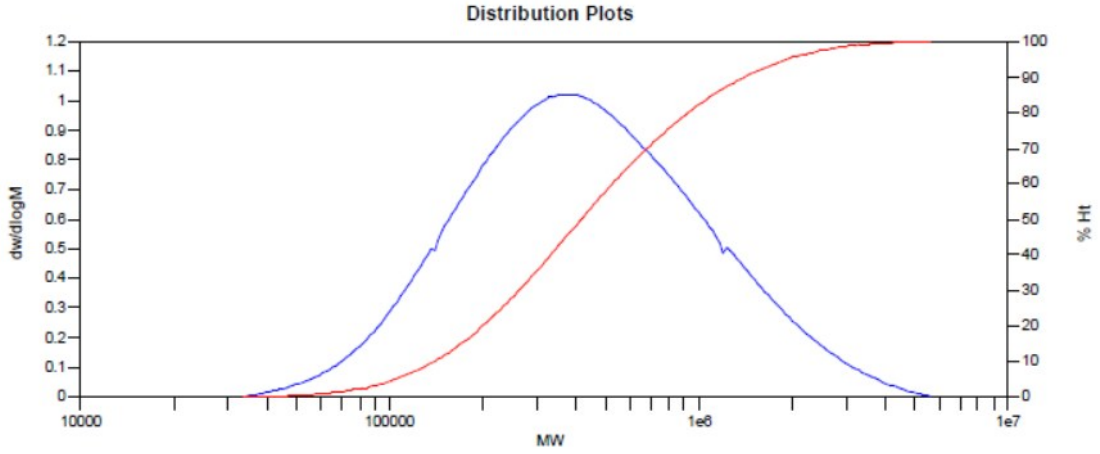


Figure S47. DSC of the polymer from table 1, entry 13.





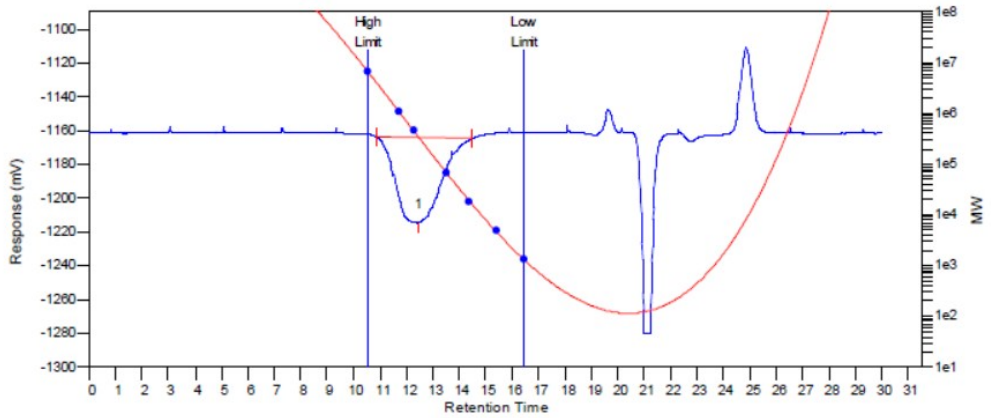
MW Averages

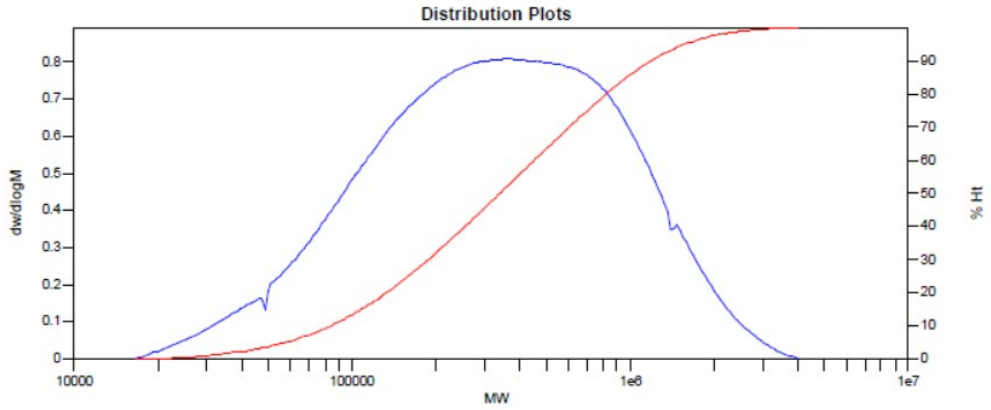
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	372593	293619	623719	1259319	2048699	555754	2.12425

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.65	12.40	13.98	-95.4282	100	8288.44	100

Figure S48. GPC of the polymer from table 1, entry 1.





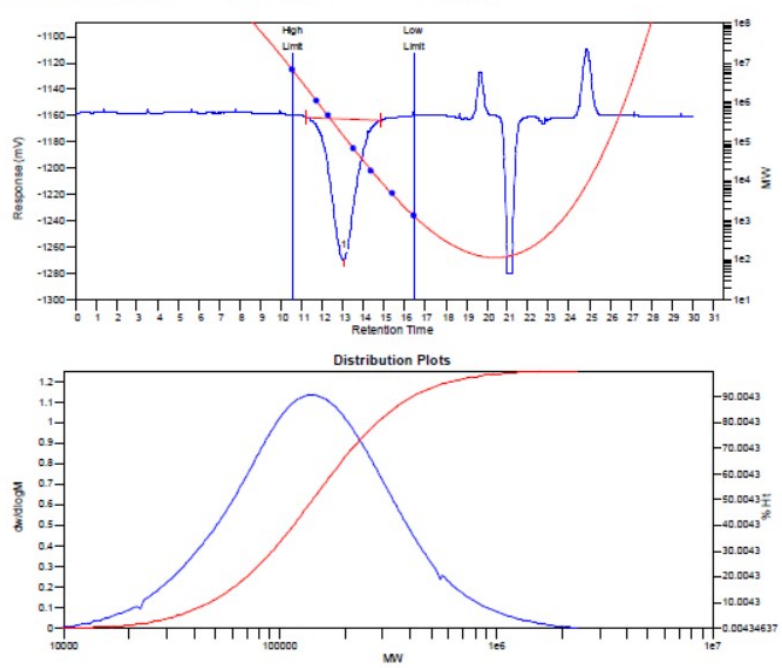
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	372593	189288	505292	1004037	1503740	445306	2.66943

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.87	12.42	14.47	-50.1643	100	5519.36	100

Figure S49. GPC of the polymer from table 1, entry 2.



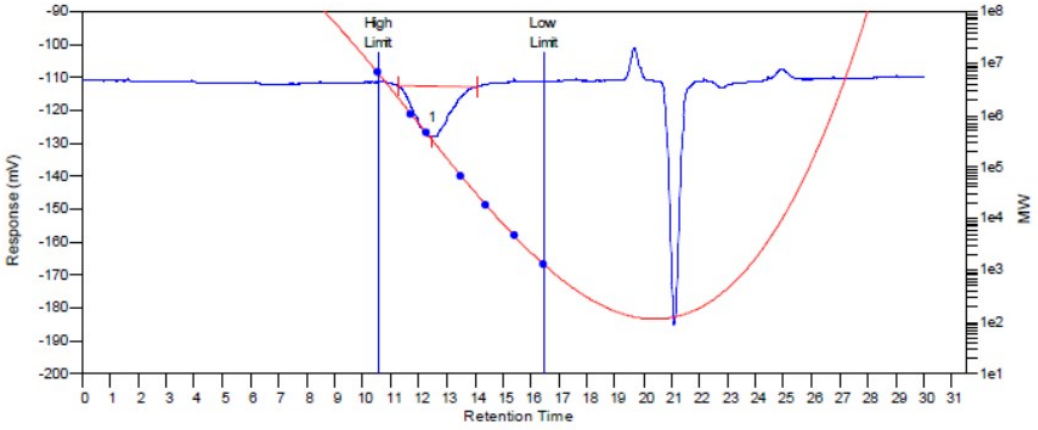
MW Averages

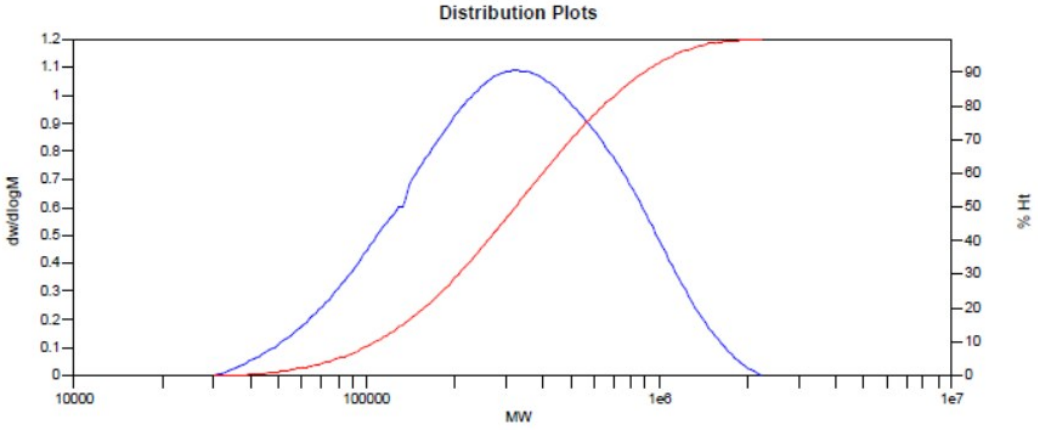
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	140011	96107	195734	392733	707110	175920	2.03663

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.22	13.03	14.87	-107.279	100	8519.35	100

Figure S50. GPC of the polymer from table 1, entry 3.





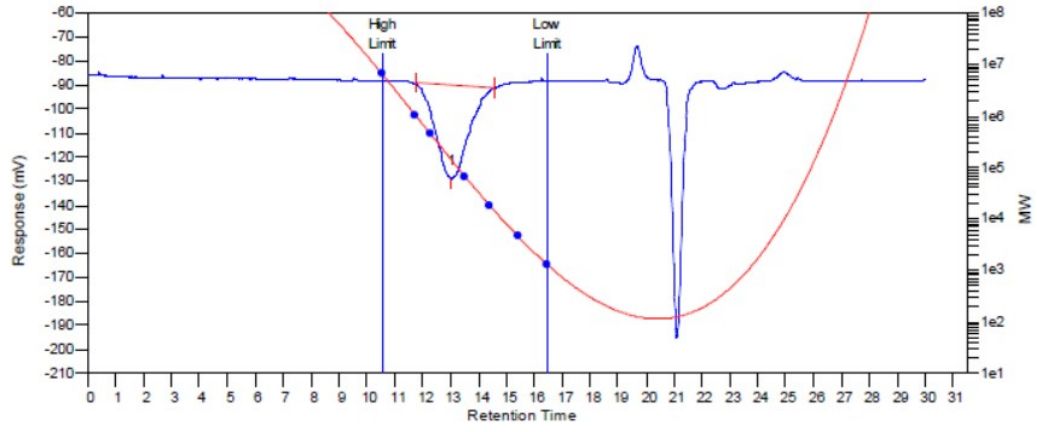
MW Averages

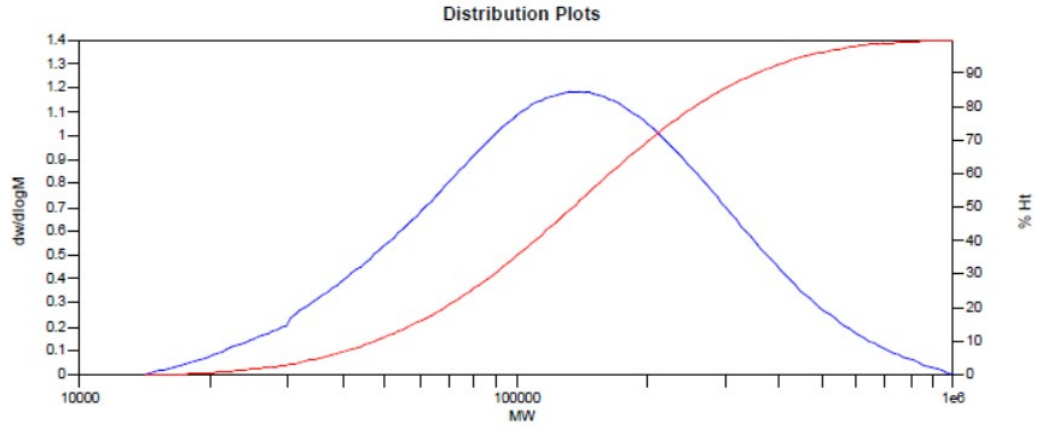
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	327338	223355	413404	669910	924812	380279	1.85088

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.25	12.48	14.05	-15.5436	100	1268.92	100

Figure S51. GPC of the polymer from table 1, entry 4.





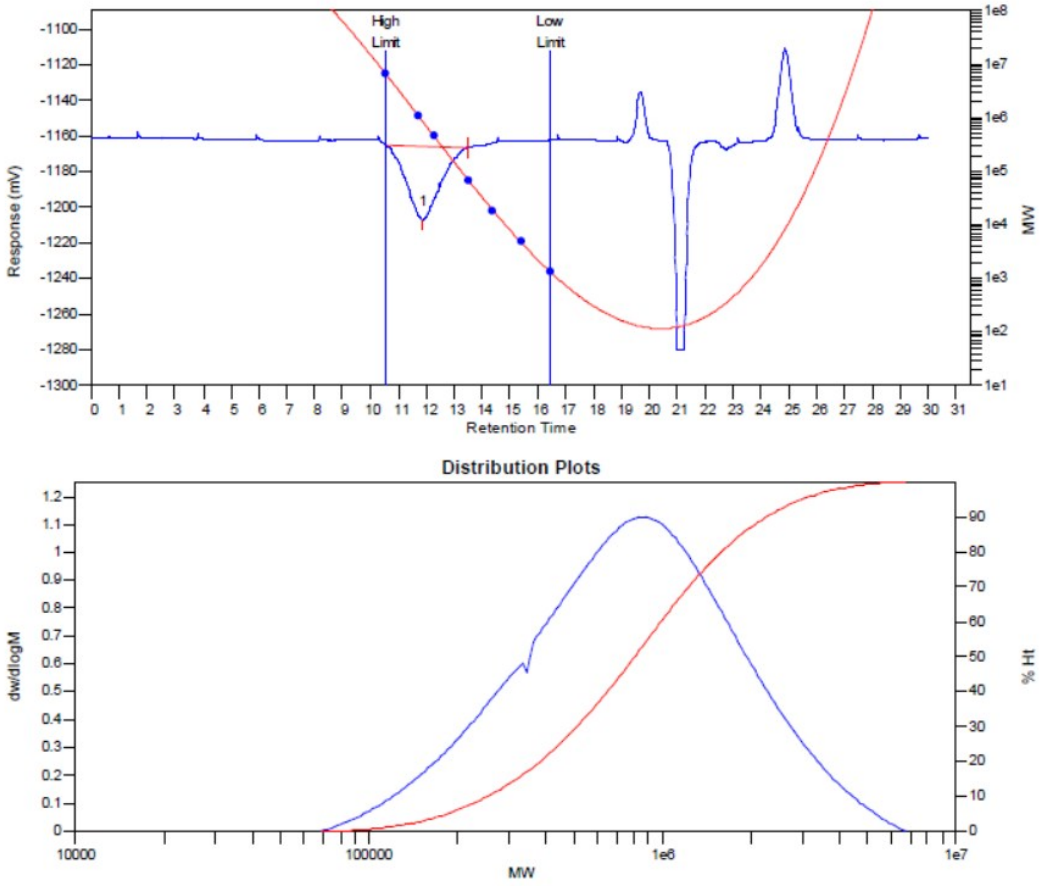
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	136480	95763	169725	275853	394767	156595	1.77234

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.77	13.05	14.58	-39.1522	100	2975.95	100

Figure S52. GPC of the polymer from table 1, entry 6.



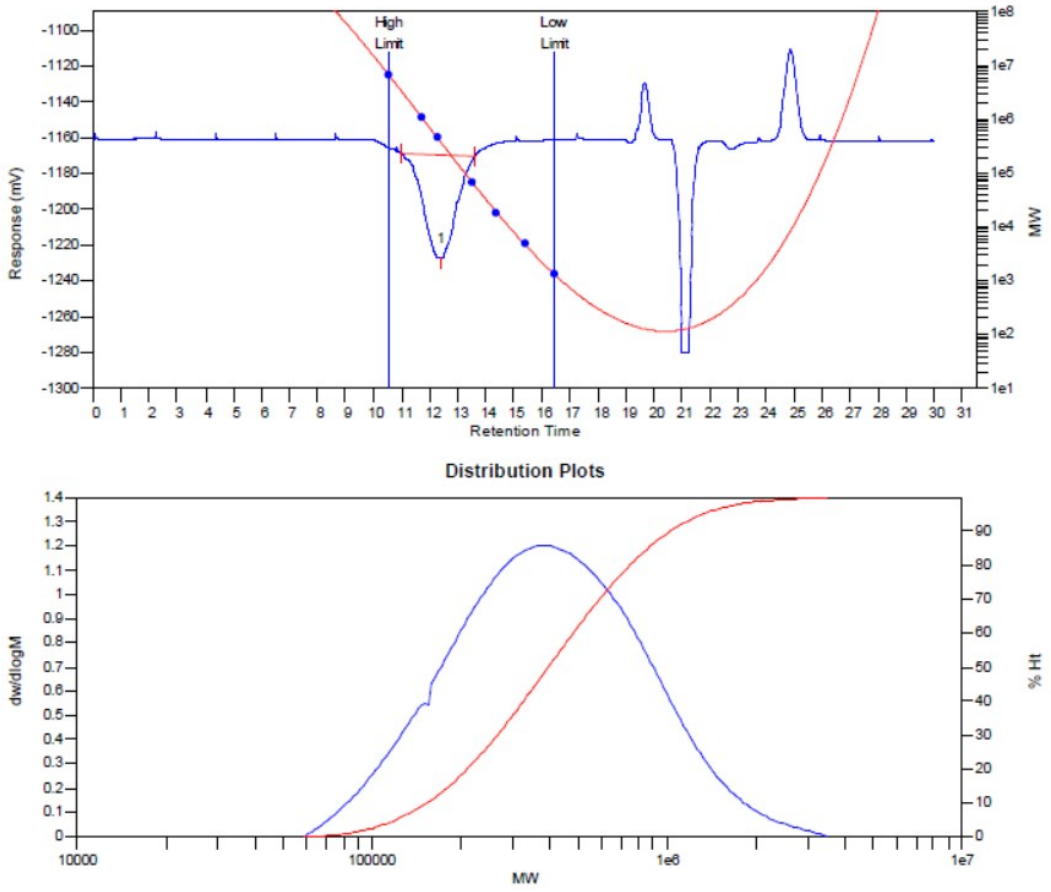
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	855400	543925	1062032	1831762	2683460	968532	1.95253

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.53	11.87	13.50	-41.524	100	3266.62	100

Figure S53. GPC of the polymer from table 1, entry 7.



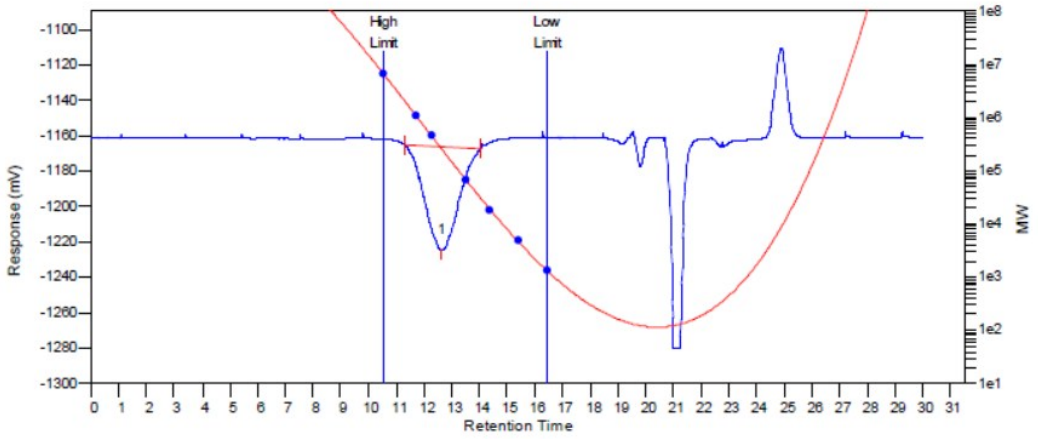
MW Averages

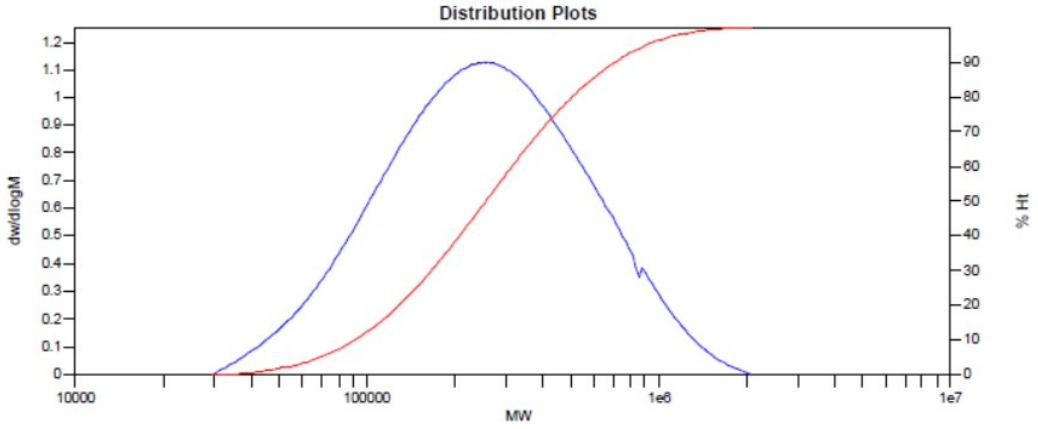
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	382375	304198	507189	824237	1222340	469617	1.6673

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.97	12.38	13.60	-57.7216	100	4260.86	100

Figure S54. GPC of the polymer from table 1, entry 8.





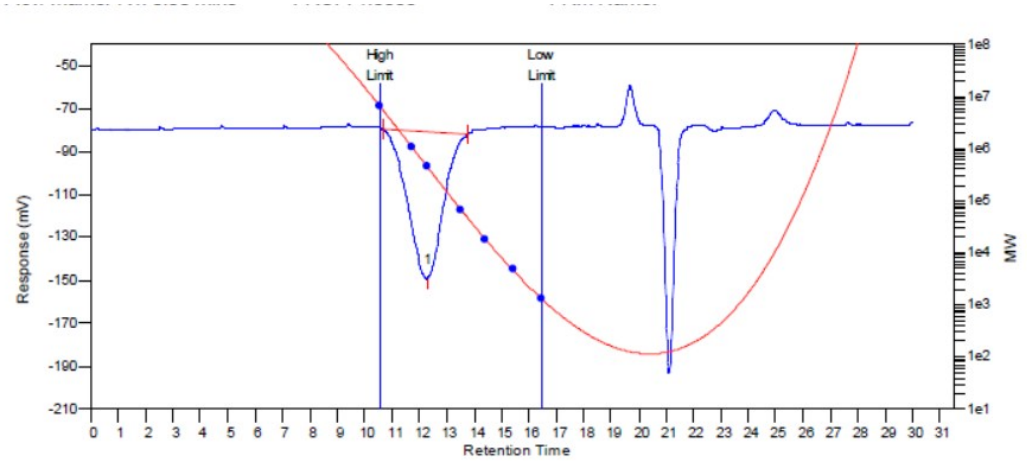
MW Averages

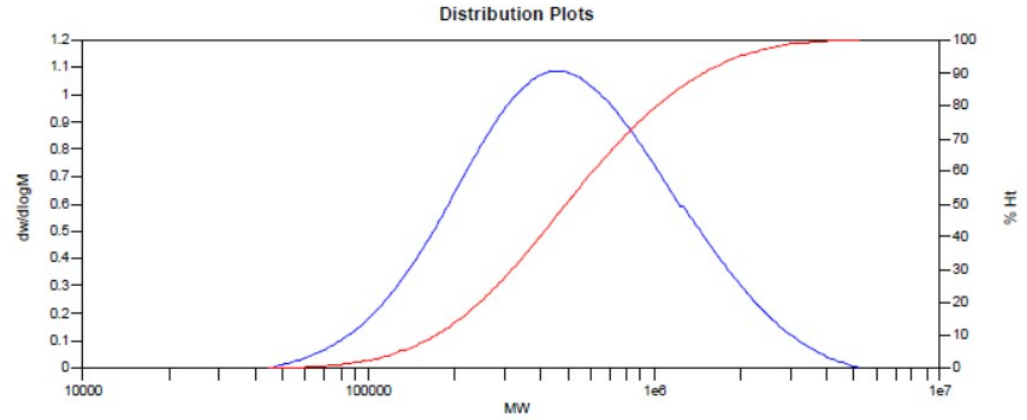
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	259393	185348	333024	551957	792515	306133	1.79675

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.30	12.65	14.07	-58.4118	100	4631.53	100

Figure S55. GPC of the polymer from table 1, entry 9.





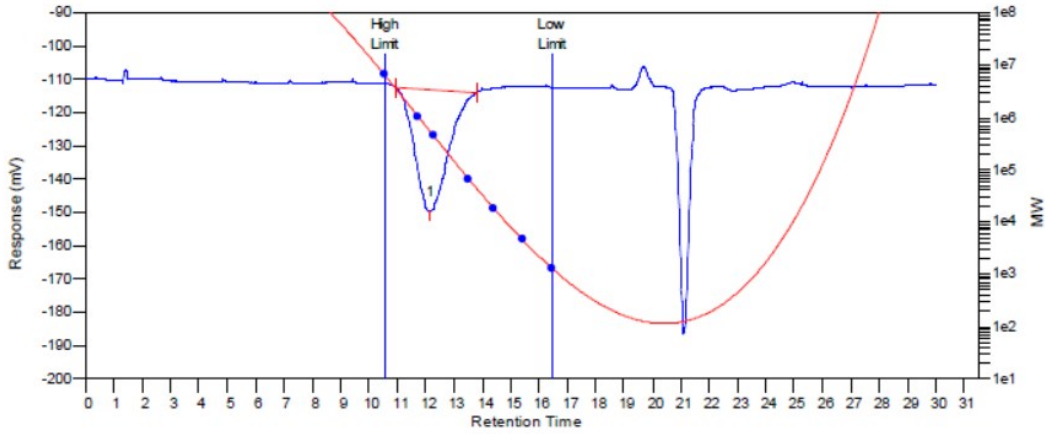
MW Averages

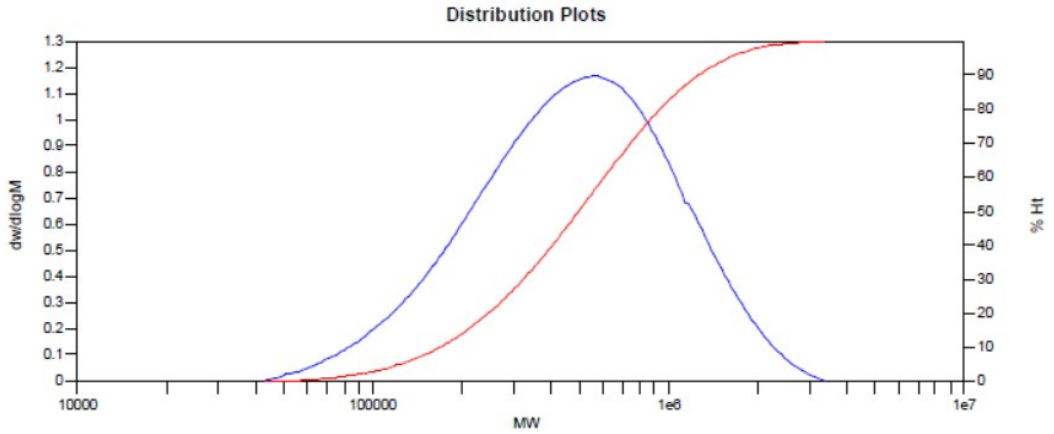
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	458501	354514	688251	1255879	1933200	623593	1.94139

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.70	12.27	13.78	-68.6451	100	5597.85	100

Figure S56. GPC of the polymer from table 1, entry 10.





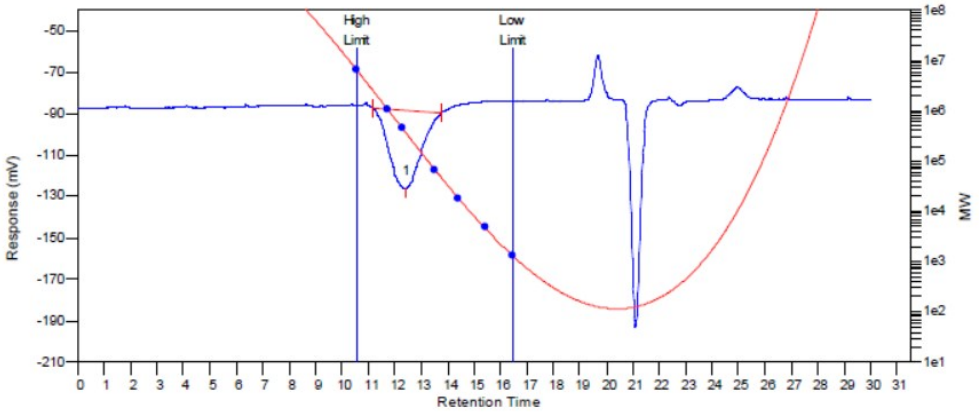
MW Averages

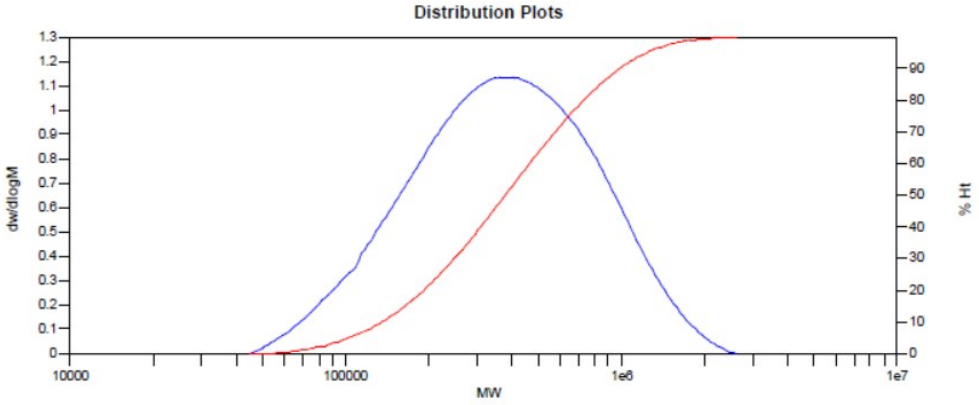
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	564367	345256	616836	968716	1331974	571025	1.7866

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.98	12.13	13.82	-36.5866	100	2779.19	100

Figure S57. GPC of the polymer from table 1, entry 11.





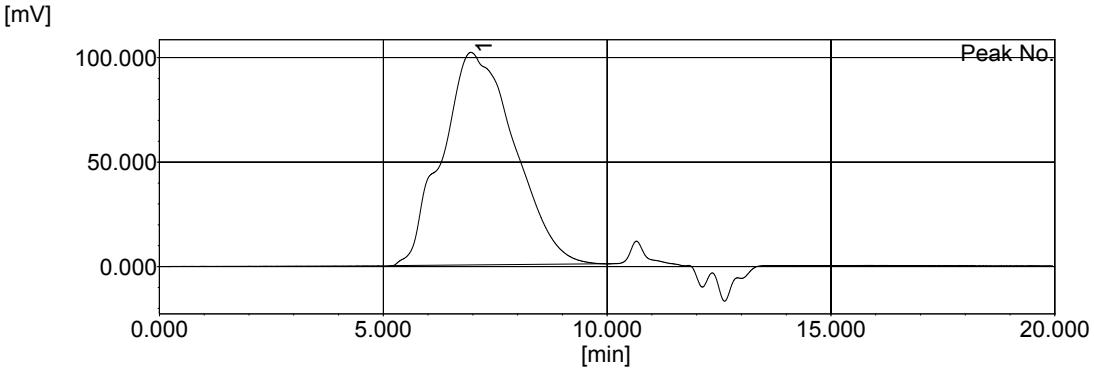
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	392417	275363	476355	747037	1025547	441389	1.72992

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.15	12.40	13.78	-37.9339	100	2962.84	100

Figure S58. GPC of the polymer from table 1, entry 12.

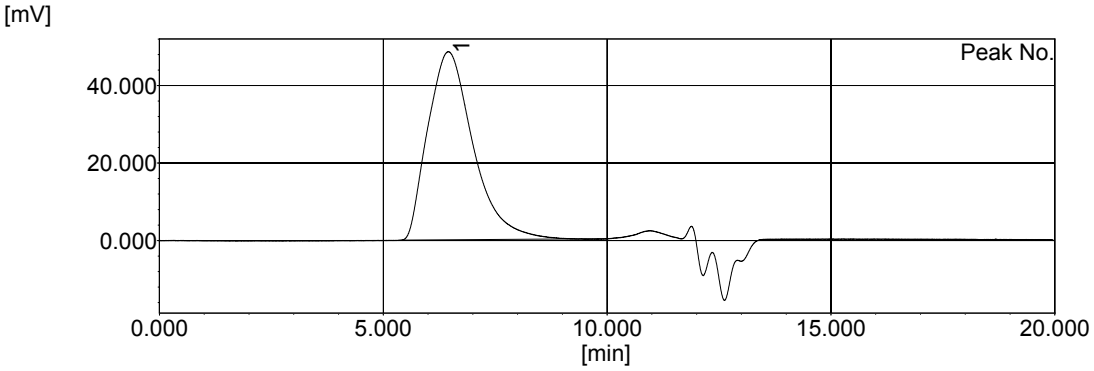


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.185	0.448	2,259,755	Mn	69,769
Peak top	6.948	102.569	178,029	Mw	213,692
Peak end	10.042	1.368	2,063	Mz	469,147
				Mz+1	743,589
				Mv	213,692
Height [mV]			101.787	Mp	178,029
Area [mV*sec]			11442.941	Mz/Mw	2.195
Area% [%]			100.000	Mw/Mn	3.063
[eta]			213692.20342	Mz+1/Mw	3.480

Figure S59. GPC of the polymer from table 2, entry 3.

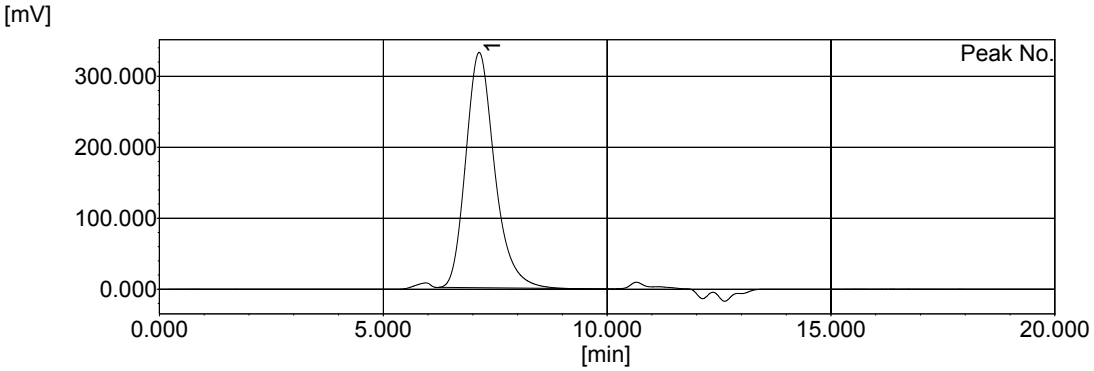


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.425	0.135	1,599,039	Mn	197,090
Peak top	6.448	48.787	365,942	Mw	379,580
Peak end	10.000	0.483	2,190	Mz	534,685
				Mz+1	670,878
				Mv	379,580
Height [mV]			48.574	Mp	365,943
Area [mV*sec]			3416.085	Mz/Mw	1.409
Area% [%]			100.000	Mw/Mn	1.926
[eta]			379579.88923	Mz+1/Mw	1.767

Figure S60. GPC of the polymer from table 2, entry 8.

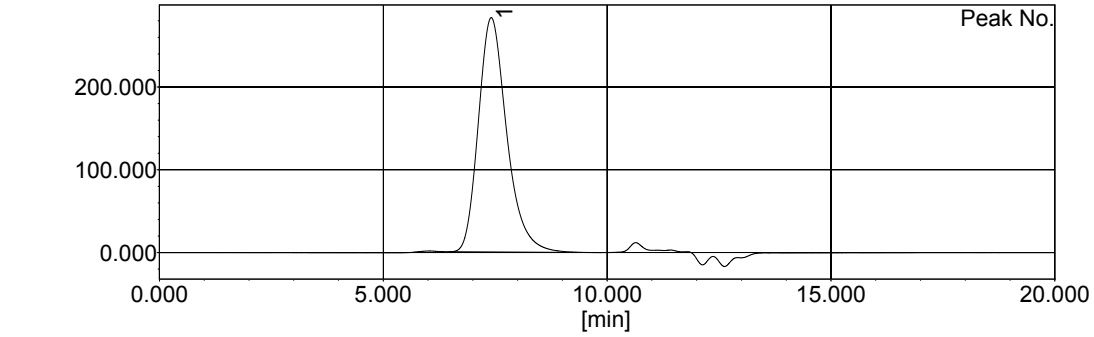


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	6.243	2.706	491,712	Mn	104,629
Peak top	7.138	333.805	135,388	Mw	135,583
Peak end	10.023	0.651	2,118	Mz	162,104
				Mz+1	187,785
				Mv	135,583
Height [mV]			331.586	Mp	135,389
Area [mV*sec]			14882.603	Mz/Mw	1.196
Area% [%]			100.000	Mw/Mn	1.296
[eta]			135582.87580	Mz+1/Mw	1.385

Figure S61. GPC of the polymer from table 3, entry 11.



Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	6.500	1.095	339,686	Mn	71,443
Peak top	7.410	283.959	91,529	Mw	90,544
Peak end	9.847	-0.053	2,732	Mz	107,347
				Mz+1	123,387
				Mv	90,544
Height [mV]			283.176	Mp	91,530
Area [mV*sec]			12483.053	Mz/Mw	1.186
Area% [%]			100.000	Mw/Mn	1.267
[eta]			90543.77534	Mz+1/Mw	1.363

Figure S62. GPC of the polymer from table 3, entry 12.

4. References

1. R. Savka, H. Plenio, *Eur. J. Inorg. Chem.* 2014, **36**, 6246–6253.

2. M. Schmid; R. Eberhardt, M. Klinga, M. Leskela, B. Rieger, *Organometallics* 2001, **20**, 2321-2330.

5. X-ray Crystallography

CCDC numbers of **Ni2** and **Pd2** are 1951644, 1951643, respectively. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

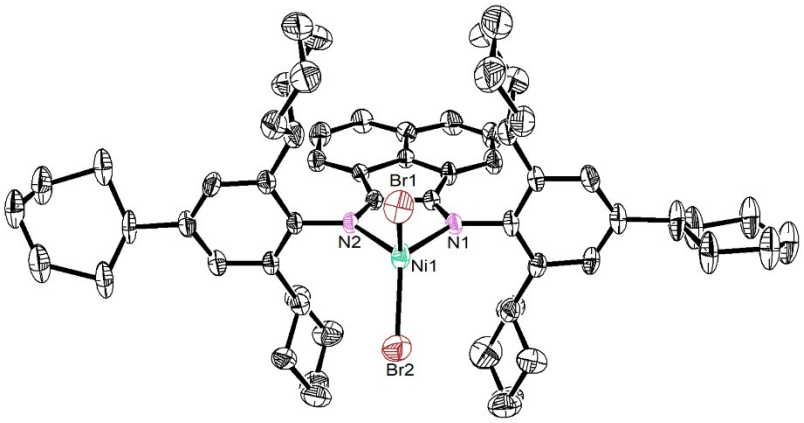


Table S3 Crystal data and structure refinement for **Ni2**.	
Identification code	**Ni2**
Empirical formula	C60 H76 Br2 N2 Ni
Formula weight	1043.76
Temperature/K	298(2)
Crystal system	Monoclinic
Space group	P2(1)/n
a/Å	16.6310(14)
b/Å	15.6730(13)
c/Å	22.5127(19)
α/°	90.00
β/°	99.756(2)
γ/°	90.00
Volume/Å^3	5783.2(8)
Z	4
ρ_{calc}g/cm^3	1.199
μ/mm^{-1}	1.753
F(000)	2192
Crystal size/mm^3	0.43 x 0.21 x 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.25 to 25.02
Index ranges	-10<=h<=19, -17<=k<=18, -26<=l<=23
Reflections collected	29124
Independent reflections	10198 [R(int) = 0.0832]
Data/restraints/parameters	10198 / 229 / 624

Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R1 = 0.0543, wR2 = 0.0789
Final R indexes [all data]	R1 = 0.1412, wR2 = 0.0848
Largest diff. peak/hole / e $Å^{-3}$	0.497 and -0.370

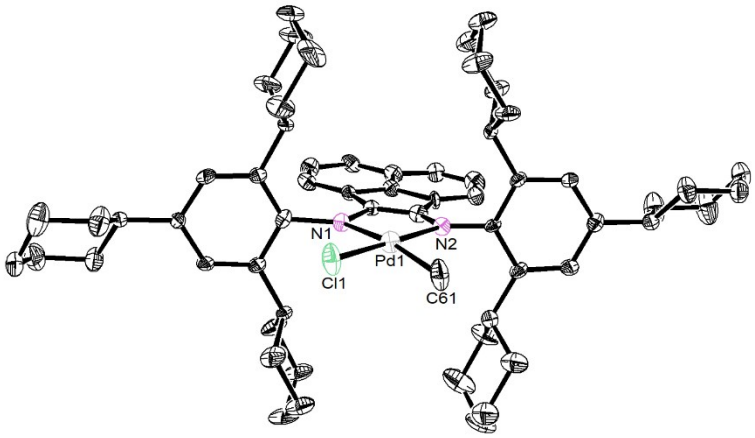


Table S4 Crystal data and structure refinement for Pd2.	
Identification code	Pd2
Empirical formula	C61 H79 Cl N2 Pd
Formula weight	982.11
Temperature/K	298(2) K
Crystal system	Triclinic
Space group	P1
a/Å	10.9521(9)
b/Å	12.1033(11)
c/Å	12.5780(11)
α /°	115.914(4)
β /°	92.6830(10)
γ /°	110.251(3)
Volume/$Å^3$	1367.6(2)
Z	1
ρ_{calc}g/cm^3	1.192
μ /mm^{-1}	0.426
F(000)	522
Crystal size/mm^3	0.35 x 0.26 x 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.22 to 25.02
Index ranges	-12<=h<=13, -14<=k<=14, -14<=l<=11
Reflections collected	6929

Independent reflections	5785 [R(int) = 0.0357]
Data/restraints/parameters	5785 / 3 / 608
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R1 = 0.0890, wR2 = 0.2086
Final R indexes [all data]	R1 = 0.0990, wR2 = 0.2179
Largest diff. peak/hole / e $Å^{-3}$	3.874 and -0.544