Supporting Information for:

Synergistic Effect of Rigid and Flexible Substituents in Insertion Polymerization with α-Diimine Nickel and Palladium Catalysts

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1. Figures, Tables.

Table S1. Mechanical properties.[a]

Ent.	Precat.	*T*/°C	Strain at break (%)	Stress at break (MPa)	SR (%)[b]	Young's modulus[c]
1	**Ni1**	30	762	4.7	82	0.62
2	**Ni1**	50	1153	2.6	70	0.23
3	**Ni1**	70	863	1.8	69	0.21
4	**Ni2**	30	651	8.5	69	1.31
5	**Ni2**	50	998	10.3	75	1.03
6	**Ni2**	70	532	2.1	83	0.39
7	**Ni3**	30	592	5.9	76	1.00
8	**Ni3**	50	599	2.2	80	0.37
9	**Ni3**	70	2062	0.3	35	0.01
10	**Ni4**	30	695	4.9	76	0.71
11	**Ni4**	50	547	1.0	69	0.18
12	**Ni4**	70	2385	0.2	20	0.01
13	**Ni5**	30	565	13.1	29	2.32

[a]Conditions: Samples from Table 1, entries 1-13 were 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]Young's modulus refers to the average modulus during tension.

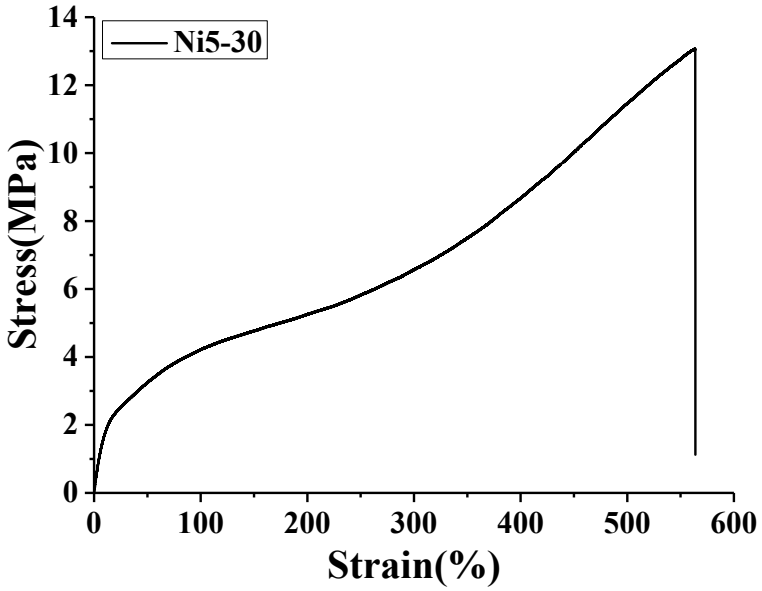


Figure S1. Stress-strain curves for polyethylene generated by **Ni5** at 30 °C.

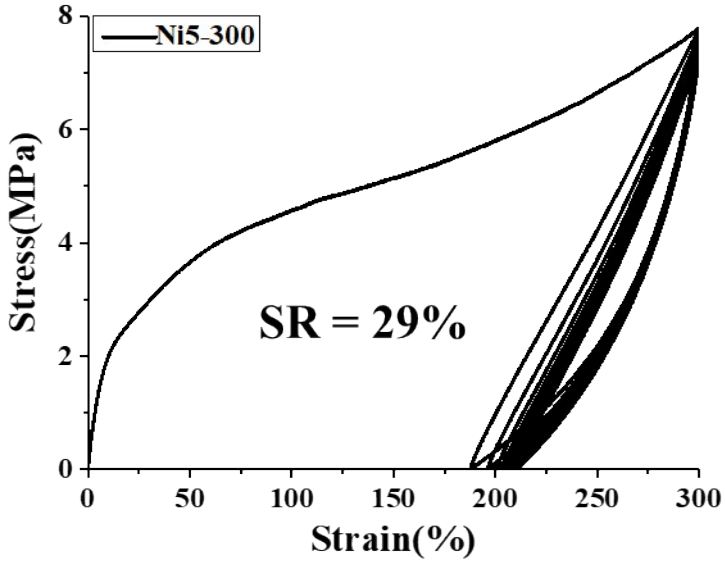


Figure S2. Plot of hysteresis experiment of ten cycles at a strain of 300% for sample generated by **Ni5** at 30 ^{o}C.

2. Experimental Sections

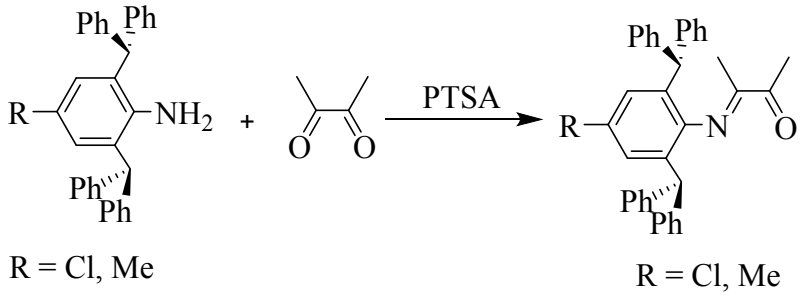
2.1 General Considerations

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 JEOL JNM-ECZ600R 400 or 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$^{\alpha}$ 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 ^{o}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.

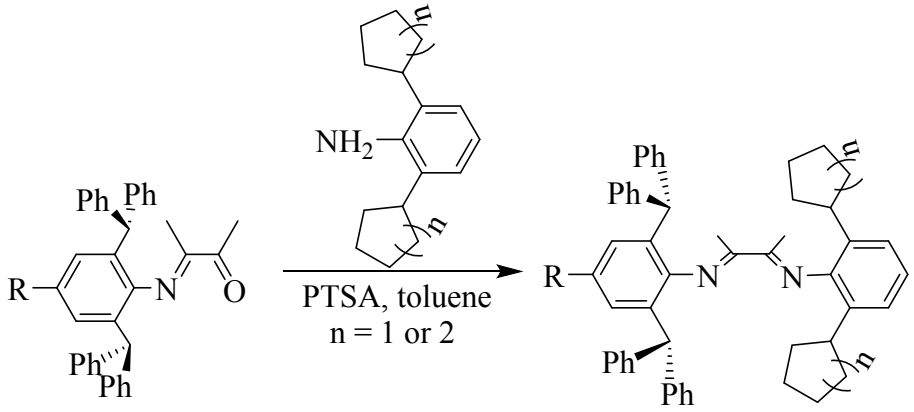
Stress/strain experiments were performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature. At least three specimens of each polymer were tested. Polymers were melt-pressed at 50 ^{o}C above their melting point to obtain the test specimens. The test specimens have 14-mm 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-L4.

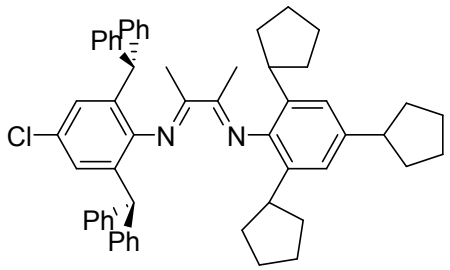


R = Cl, Me R = Cl, Me

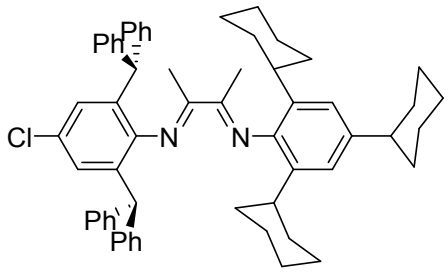
A solution of arylamine (10 mmol), 2, 3-butadione (30 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (100 mL) was stirred at 80 °C for 24 h, until there was one main point on the TLC plate. The solvent was partially evaporated under reduced pressure until the formation of a light yellow solid. The remaining solution was diluted in methanol (100 mL). The yellow solid was isolated by filtration, dried by vacuum. The two compounds are known.[1-2]



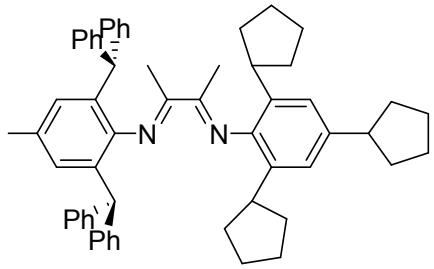
A mixture of α-imino-ketones (2 mmol) and cycloalkyl arylamines (4.0 mmol) in toluene (40 mL) was stirred at 120 °C for 24 h. The solvent was evaporated under reduced pressure. The remaining mixture was diluted with methanol (100 mL). The resulting yellow solid was collected by filtration and recrystallized from CH_2Cl_2 and hexanes to afford the desired product.



L1 (1.26 g, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 12.9, 5.5 Hz, 8H, Ar-*H*), 7.20 (d, *J* = 5.3 Hz, 4H, Ar-*H*), 7.07 (d, *J* = 6.9 Hz, 4H, Ar-*H*), 7.03 (d, *J* = 7.1 Hz, 4H, Ar-*H*), 6.99 (s, 2H, Ar-*H*), 6.85 (s, 2H, Ar-*H*), 5.23 (s, 2H, C*H*Ph_2), 3.00 – 2.90 (m, 1H, *p*-Cp-C*H*), 2.69 (p, *J* = 7.8 Hz, 2H, *o*-Cp-C*H*), 2.05 (s, 2H, Cp-CH_2), 1.98 (d, *J* = 5.0 Hz, 2H, Cp-CH_2), 1.93 – 1.75 (m, 11H, Cp-CH_2, N=C-CH_3), 1.74 – 1.50 (m, 12H, Cp-CH_2), 0.94 (s, 3H, N=C-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.74 (*C*=N), 168.04 (*C*=N), 146.57, 145.21, 142.89, 141.77, 141.55, 133.61, 132.90, 129.73, 129.38, 128.70, 128.39, 128.27, 126.79, 126.57, 122.26, 52.25 (*C*HPh_2), 46.05 (*p*-Cp-*C*H), 40.08 (*o*-Cp-*C*H), 34.85 (Cp-*C*H_2), 34.49 (Cp-*C*H_2), 34.24 (Cp-*C*H_2), 26.29 (Cp-*C*H_2), 26.17 (Cp-*C*H_2), 25.57 (Cp-*C*H_2), 16.97 (N=C-*C*H_3), 16.35 (N=C-*C*H_3). HRMS (m/z): calcd for $C_{57}H_{60}ClN_2$: 807.4440, found: 807.4435 $[M+H]^+$.

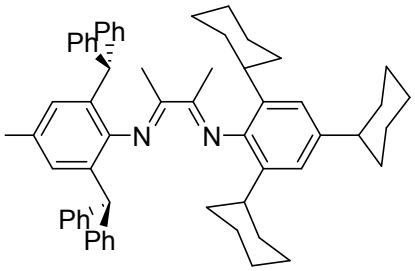


L2 (1.41 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.18 (m, 12H, Ar-*H*), 7.13 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 7.07 (d, *J* = 7.9 Hz, 4H, Ar-*H*), 6.96 (s, 2H, Ar-*H*), 6.90 (s, 2H, Ar-*H*), 5.28 (s, 2H, C*H*Ph_2), 2.49 (d, *J* = 8.1 Hz, 1H, Cy-C*H*), 2.20 (t, *J* = 11.2 Hz, 2H, Cy-C*H*), 1.89 (dd, *J* = 20.0, 7.2 Hz, 8H, Cy-CH_2), 1.72 (q, *J* = 13.4 Hz, 9H, Cy-CH_2, N=C-CH_3), 1.56 – 1.20 (m, 19H, Cy-CH_2, N=C-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.68 (*C*=N), 167.72 (*C*=N), 146.52, 143.81, 143.23, 142.98, 141.98, 133.86, 133.46, 129.76, 129.37, 128.80, 128.75, 128.40, 128.37, 126.82, 126.58, 122.15, 52.17 (*C*HPh_2), 44.58 (*p*-Cy-*C*H), 39.26 (*o*-Cy-*C*H), 34.86 (Cy-*C*H_2), 33.70 (Cy-*C*H_2), 33.55 (Cy-*C*H_2), 28.16 (Cy-*C*H_2), 27.52 (Cy-*C*H_2), 27.21 (Cy-*C*H_2), 27.18 (Cy-*C*H_2), 26.37 (Cy-*C*H_2), 16.91(N=C-*C*H_3), 16.72 (N=C-*C*H_3). HRMS (m/z): calcd for $C_{60}H_{66}ClN_2$: 849.4909, found: 849.4903 $[M+H]^+$.



L3 (1.27 g, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.2 Hz, 8H, Ar-*H*), 7.20 (dd, *J* = 11.2, 7.1 Hz, 4H, Ar-*H*), 7.11 (d, *J* = 7.7 Hz, 4H, Ar-*H*), 7.07 (d, *J* = 7.7 Hz, 4H, Ar-*H*), 7.02 (s, 2H, Ar-*H*), 6.70 (s, 2H, Ar-*H*), 5.27 (s, 2H, C*H*Ph_2), 3.02 – 2.93 (m, 1H, *p*-Cp-C*H*), 2.74 (p, *J* = 8.4 Hz, 2H, *o*-Cp-C*H*), 2.20 (s, 3H, Ar-CH_3), 2.09 (dd, *J* = 15.7, 11.5 Hz, 2H, Cp-CH_2), 2.04 – 1.97 (m, 2H, Cp-CH_2), 1.97 – 1.89 (m, 2H, Cp-CH_2), 1.87 (s, 3H, N=C-CH_3) 1.87 – 1.78 (m, 6H, Cp-CH_2), 1.75 – 1.53 (m, 12H, Cp-CH_2), 0.98 (s, 3H, N=C-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.29 (*C*=N), 168.38 (*C*=N), 145.72, 145.41, 143.91, 142.71, 141.41, 132.98, 131.78, 131.42, 129.86, 129.52, 128.92, 128.51, 128.19, 126.45, 126.20, 122.24, 52.26 (*C*HPh_2), 46.08 (*p*-Cp-*C*H), 40.11 (*o*-Cp-*C*H), 34.87 (Cp-*C*H_2), 34.51 (Cp-*C*H_2), 34.25 (Cp-

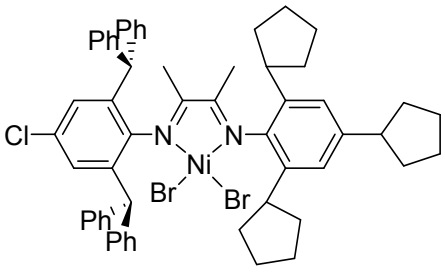
CH_2), 26.31 (Cp-*C*H_2), 26.20 (Cp-*C*H_2), 25.60 (Cp-*C*H_2), 21.43 (Ar-*C*H_3), 17.04 (N=C-*C*H_3), 16.20 (N=C-*C*H_3). HRMS (m/z): calcd for $C_{58}H_{63}N_2$: 787.4986, found: 787.4966 $[M+H]^+$.



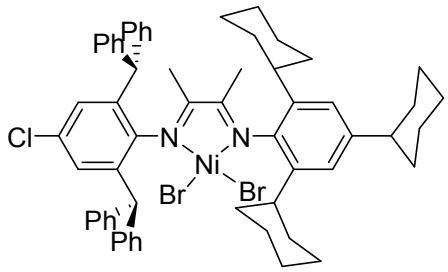
L4 (1.23 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 8H, Ar-*H*), 7.25 (dt, *J* = 8.7, 7.4 Hz, 8H, Ar-*H*), 7.17 (d, *J* = 7.4 Hz, 4H, Ar-*H*), 7.04 (s, 2H, Ar-*H*), 6.81 (s, 2H, Ar-*H*), 5.38 (s, 2H, C*H*Ph_2), 2.56 (dd, *J* = 11.0, 8.3 Hz, 1H, Cy-C*H*), 2.36 – 2.19 (m, 5H, Cy-CH_2, Ar-CH_3), 2.05 – 1.70 (m, 18H, Cy-CH_2, N=C-CH_3), 1.63 – 1.23 (m, 18H, Cy-CH_2, N=C-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.28 (*C*=N), 168.12 (*C*=N), 145.73, 144.08, 144.05, 143.14, 142.98, 133.99, 131.93, 131.31, 129.96, 129.57, 129.07, 128.60, 128.26, 126.53, 126.27, 122.18, 52.22 (*C*HPh_2), 44.67 (*p*-Cy-*C*H), 39.31 (*o*-Cy-*C*H), 34.96 (Cy-*C*H_2), 33.78 (Cy-*C*H_2), 33.66 (Cy-*C*H_2), 27.58 (Cy-*C*H_2), 27.28 (Cy-*C*H_2), 26.49 (Cy-*C*H_2), 21.52 (Ar-*C*H_3), 17.04 (N=C-*C*H_3), 16.64 (N=C-*C*H_3). HRMS (m/z): calcd for $C_{61}H_{69}N_2$: 829.5455, found: 829.5453 $[M+H]^+$.

2.3 Procedure for the Synthesis of Nickel Complexes Ni1-4:

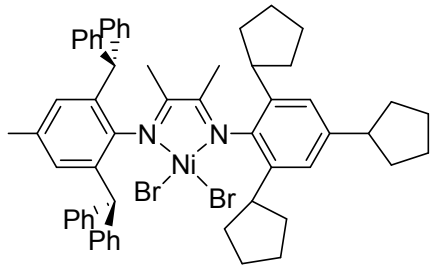
The nickel complexes were prepared in a similar manner by the reaction of 0.2 mmol ligand with 1 equivalent (DME)$NiBr_2$ in dichloromethane. After stirring overnight, the solvent was removed, and the brown solid powder was washed with ether (10 mL × 2) and dried under vacuum to give the corresponding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



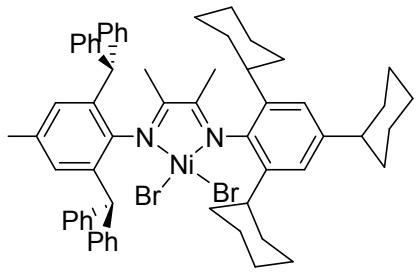
Ni1: (191 mg, 93%). Elemental analysis: calc. for $C_{57}H_{59}Br_2ClN_2Ni$: C, 66.72; H, 5.80; N, 2.73. Found: C, 66.38; H, 5.62; N, 2.57. MALDI-TOF-MS (m/z): calcd for $C_{57}H_{59}BrClN_2Ni$: 943.2898, found: 943.2863 $[M-Br]^+$.



Ni2: (194 mg, 91%). Elemental analysis: calc. for $C_{60}H_{65}Br_2ClN_2Ni$: C, 67.47; H, 6.13; N, 2.62. Found: C, 67.30; H, 6.36; N, 2.51. MALDI-TOF-MS (m/z): calcd for $C_{60}H_{65}BrClN_2Ni$: 985.3368, found: 985.3348 $[M-Br]^+$.



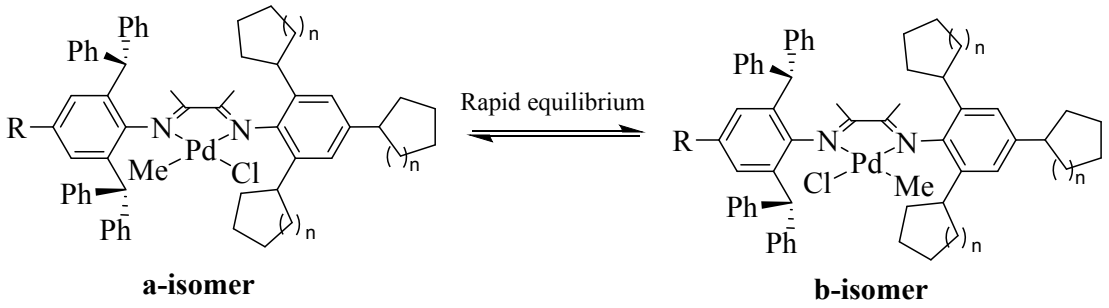
Ni3: (171 mg, 85%). Elemental analysis: calc. for $C_{58}H_{62}Br_2N_2Ni$: C, 69.27; H, 6.21; N, 2.79. Found: C, 69.46; H, 6.33; N, 2.86. MALDI-TOF-MS (m/z): calc. for $C_{58}H_{62}BrN_2Ni$: 923.3444, found: 923.3396 $[M-Br]^+$.



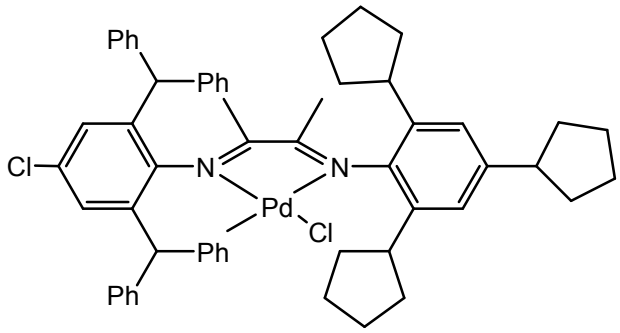
Ni4: (182 mg, 87%). Elemental analysis: calc. for $C_{61}H_{68}Br_2N_2Ni$: C, 69.93; H, 6.54; N, 2.67. Found: C, 69.78; H, 6.38; N, 2.81. MALDI-TOF-MS (m/z): calc. for $C_{61}H_{68}BrN_2Ni$: 965.3914, found: 965.3886 $[M-Br]^+$.

2.4 Procedure for the Synthesis of Palladium Complexes Pd1-4:

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. Interconversion of two isomers in palladium complexes:

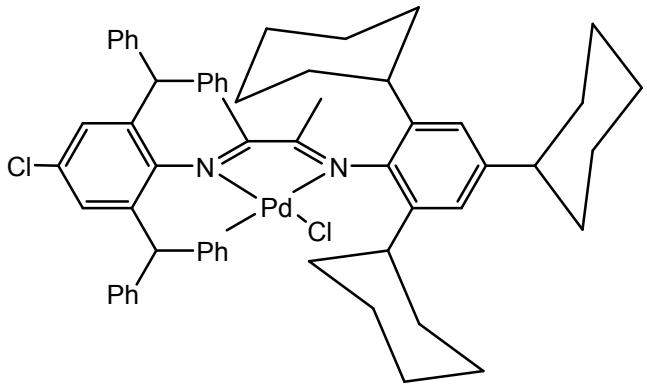


a-isomer **b-isomer**

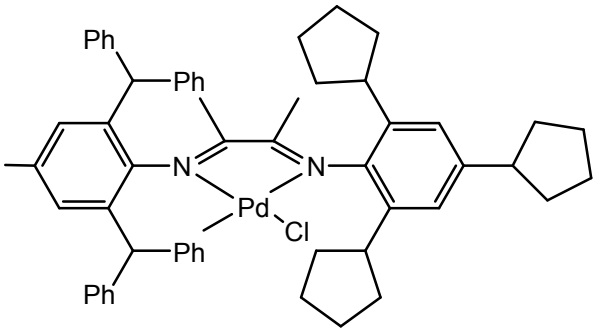


Pd1: (0.68 g, 71%). a-isomer: b-isomer = 12:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H, Ar-*H*), 7.29 – 7.22 (m, 8H, Ar-*H*), 7.18 (dt, *J* = 24.5, 8.2 Hz, 8H, Ar-*H*), 7.10, 7.07 – 6.97 (s, m, 2H, Ar-*H*), 6.86 – 6.81 (m, 2H, Ar-*H*), 5.97, 5.94, 5.90 (s, 2H, C*H*Ph$_2$), 3.22 – 3.12, 2.50 – 2.41 (m, 3H, Cp-C*H*, Cp-C*H*$_2$), 3.06 – 2.94 (m, 1H, Cp-C*H*), 2.09 (ddd, *J* = 10.2, 9.6, 4.0 Hz, 2H, Cp-C*H*$_2$), 1.97 – 1.50 (m, 21H, Cp-C*H*$_2$), 1.42, 1.40, 1.37 (s, 3H, N=C-C*H*$_3$), 0.80, 0.72 (s, 3H, Pd-C*H*$_3$), -0.30, -0.36 (d, *J* = 5.4 Hz, 3H, N=C-C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.13 (*C*=N), 173.83 (*C*=N), 170.79 (*C*=N), 145.88, 142.38, 142.07, 141.76, 141.29, 140.56, 137.03, 136.77, 131.61, 130.07, 129.78, 129.37, 129.11, 128.89, 128.70, 128.46, 128.38, 127.09, 126.72, 125.64, 123.14, 122.18, 118.11, 52.39 (*C*HPh$_2$), 45.93 (*p*-Cp-*C*H), 41.12 (*p*-Cp-*C*H), 40.29 (*o*-Cp-*C*H), 40.13 (*o*-Cp-*C*H), 39.96 (*o*-Cp-*C*H), 38.10 (*o*-Cp-*C*H), 35.73 (Cp-*C*H$_2$), 35.53 (Cp-*C*H$_2$), 35.17 (Cp-*C*H$_2$), 35.03 (Cp-*C*H$_2$), 34.66 (Cp-*C*H$_2$), 34.48 (Cp-*C*H$_2$), 32.36 (Cp-*C*H$_2$), 32.28 (Cp-*C*H$_2$), 29.41 (Cp-*C*H$_2$), 29.06 (Cp-*C*H$_2$), 28.46 (Cp-*C*H$_2$), 27.80 (Cp-

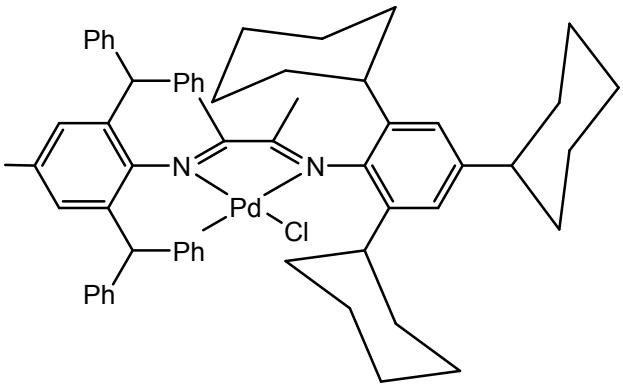
CH_2), 27.68 (Cp-CH_2), 26.61 (Cp-CH_2), 26.52 (Cp-CH_2), 26.35 (Cp-CH_2), 26.15 (Cp-CH_2), 25.57 (Cp-CH_2), 25.24 (Cp-CH_2), 20.10 (N=C-CH_3), 19.94 (N=C-CH_3), 18.68 (N=C-CH_3), 4.70 (Pd-CH_3), 4.51 (Pd-CH_3). Anal. Calcd for ($C_{58}H_{62}Cl_2N_2Pd$): C, 72.23; H, 6.48; N, 2.90. Found: C, 72.12; H, 6.57; N, 2.76. MALDI-TOF-MS (m/z): calcd for $C_{57}H_{59}ClN_2Pd$: 914.3406, found: 914.4093 $[M\text{-}Me\text{-}Cl]^+$.



Pd2: (0.74 g, 74%). a-isomer: b-isomer = 8:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.7 Hz, 4H, Ar-*H*), 7.30 – 7.22 (m, 12H, Ar-*H*), 7.21 – 7.15 (m, 4H, Ar-*H*), 7.08 (d, *J* = 2.1 Hz, 2H, Ar-*H*), 7.05, 6.89 (s, 2H, Ar-*H*), 5.91, 5.87 (s, 2H, C*H*Ph_2), 2.65 (ddd, *J* = 15.2, 11.2, 3.6 Hz, 2H, Cy-C*H*), 2.49 (tt, *J* = 13.9, 7.0 Hz, 1H, Cy-C*H*), 2.24 (d, *J* = 12.6 Hz, 2H, Cy-CH_2), 2.02 – 1.58 (m, 14H, Cy-CH_2), 1.48 – 1.20 (m, 17H, Cy-CH_2, N=C-CH_3), 0.89, 0.73 (s, 3H, Pd-CH_3), -0.26, -0.33 (s, 3H, N=C-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.02 (*C*=N), 173.70 (*C*=N), 147.05, 143.41, 142.31, 141.78, 141.70, 141.45, 140.24, 139.57, 138.09, 137.14, 136.97, 133.16, 131.67, 130.71, 130.17, 130.01, 129.68, 129.32, 129.04, 128.83, 128.75, 128.46, 128.39, 127.37, 127.08, 126.70, 125.27, 123.62, 52.24 (*C*HPh_2), 44.45 (*p*-Cy-*C*H), 39.53 (*o*-Cy-*C*H), 38.95 (*o*-Cy-*C*H), 34.55 (Cy-*C*H_2), 34.39 (Cy-*C*H_2), 33.89 (Cy-*C*H_2), 27.07 (Cy-*C*H_2), 26.97 (Cy-*C*H_2), 26.82 (Cy-*C*H_2), 26.23 (Cy-*C*H_2), 25.97 (Cy-*C*H_2), 20.09 (N=C-*C*H_3), 18.44 (N=C-*C*H_3), 5.12 (Pd-*C*H_3). Anal. Calcd for ($C_{61}H_{68}Cl_2N_2Pd$): C, 72.79; H, 6.81; N, 2.78. Found: C, 72.87; H, 6.64; N, 2.64. MALDI-TOF-MS (m/z): calcd for $C_{60}H_{65}ClN_2Pd$: 954.3871, found: 954.3022 $[M\text{-}Me\text{-}Cl]^+$.



Pd3: (0.72 g, 76%). a-isomer: b-isomer = 6:1. ^{1}H NMR (600 MHz, $CDCl_3$) 7.35 (t, *J* = 7.7 Hz, 4H, Ar-*H*), 7.30 – 7.20 (m, 8H, Ar-*H*), 7.20 – 7.12 (m, 8H, Ar-*H*), 7.09, 7.07, 7.05 (s, 2H, Ar-*H*), 6.83, 6.66 (s, 2H, Ar-*H*), 5.96, 5.93, 5.88 (s, 2H, C*H*Ph_2), 3.23 – 3.15, 2.52 – 2.40 (m, 3H, Cp-C*H*, Cp-CH_2), 3.02 – 2.92, 2.68 – 2.60 (m, 1H, Cp-C*H*), 2.12, 2.16 (s, 3H, Ar-CH_3), 2.13 – 2.06 (m, 2H, Cp-CH_2), 1.97 – 1.53 (m, 21H, Cp-CH_2), 1.42, 1.40, 1.39 (s, 3H, N=C-CH_3), 0.97, 0.76, 0.69 (s, 3H, Pd-CH_3), -0.29, -0.35 (s, 3H, N=C-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.26 (*C*=N), 173.45 (*C*=N), 145.70, 143.33, 142.43, 142.14, 141.54, 141.25, 140.68, 136.86, 135.61, 135.30, 135.18, 134.67, 130.16, 130.08, 129.90, 129.51, 129.38, 129.10, 128.90, 128.69, 128.42, 128.20, 127.04, 126.75, 126.26, 123.07, 122.51, 52.41 (*C*HPh_2), 52.23 (*C*HPh_2), 45.94 (*p*-Cp-*C*H), 41.07 (*p*-Cp-*C*H), 40.25 (*o*-Cp-*C*H), 40.14 (*o*-Cp-*C*H), 39.93 (*o*-Cp-*C*H), 35.72 (Cp-*C*H_2), 35.58 (Cp-*C*H_2), 35.14 (Cp-*C*H_2), 35.01 (Cp-*C*H_2), 34.85 (Cp-*C*H_2), 34.66 (Cp-*C*H_2), 34.47 (Cp-*C*H_2), 32.38 (Cp-*C*H_2), 32.29 (Cp-*C*H_2), 27.80 (Cp-*C*H_2), 27.68 (Cp-*C*H_2), 26.61 (Cp-*C*H_2), 26.36 (Cp-*C*H_2), 26.23 (Cp-*C*H_2), 26.15 (Cp-*C*H_2), 25.57 (Cp-*C*H_2), 25.25 (Cp-*C*H_2), 21.60 (Ar-*C*H_3), 20.10 (N=C-*C*H_3), 19.94 (N=C-*C*H_3), 19.74 (N=C-*C*H_3), 18.76 (N=C-*C*H_3), 18.53 (N=C-*C*H_3), 4.14 (Pd-*C*H_3), 3.96 (Pd-*C*H_3). Anal. Calcd for ($C_{59}H_{65}ClN_2Pd$): C, 75.06; H, 6.94; N, 2.97. Found: C, 75.21; H, 6.78; N, 2.79. MALDI-TOF-MS (m/z): calcd for $C_{58}H_{62}N_2Pd$: 892.3948, found: 892.2830 $[M\text{-}Me\text{-}Cl]^+$.



Pd4: (0.67 g, 68%). a-isomer: b-isomer = 3:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38, 7.33 (d, *J* = 7.7 Hz, 4H, Ar-*H*), 7.30 – 7.13 (m, 16H, Ar-*H*), 7.08, 7.04 (s, 2H, Ar-*H*), 6.88, 6.71 (s, 2H, Ar-*H*), 5.91, 5.87 (s, 2H, C*H*Ph_2), 2.68 (dd, *J* = 11.3, 8.0 Hz, 2H, Cy-C*H*), 2.50 (dd, *J* = 11.2, 8.2 Hz, 1H, Cy-C*H*), 2.30 – 2.23 (m, 2H, Cy-CH_2), 2.23, 2.17 (s, 3H, Ar-CH_3), 2.03 – 1.55 (m, 14H, Cy-CH_2), 1.53 – 1.20 (m, 17H, Cy-CH_2, N=C-CH_3), 0.91, 0.70 (s, 3H, Pd-CH_3), -0.23, -0.31 (s, 3H, N=C-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.19 (*C*=N), 175.15 (*C*=N), 173.33 (*C*=N), 170.42 (*C*=N), 146.89, 144.35, 143.28, 142.98, 142.37, 142.28, 141.86, 141.78, 141.13, 140.99, 139.95, 139.69, 137.83, 137.22, 136.95, 136.68, 136.46, 136.31, 136.03, 135.22, 135.16, 135.10, 134.60, 130.78, 130.25, 130.10, 129.80, 129.46, 129.22, 129.05, 128.83, 128.64, 128.46, 128.21, 127.78, 127.03, 126.74, 126.24, 125.38, 123.54, 123.08, 122.92, 52.24 (*C*HPh_2), 52.13 (*C*HPh_2), 44.45 (*p*-Cy-*C*H), 44.27 (*p*-Cy-*C*H), 39.47 (*o*-Cy-*C*H), 38.91 (*o*-Cy-*C*H), 34.57 (Cy-*C*H_2), 34.41 (Cy-*C*H_2), 34.02 (Cy-*C*H_2), 33.89 (Cy-*C*H_2), 27.23 (Cy-*C*H_2), 27.08 (Cy-*C*H_2), 26.98 (Cy-*C*H_2), 26.82 (Cy-*C*H_2), 26.36 (Cy-*C*H_2), 26.24 (Cy-*C*H_2), 26.20 (Cy-*C*H_2), 26.01 (Cy-*C*H_2), 21.65 (Ar-*C*H_3), 21.61 (Ar-*C*H_3), 20.10 (N=C-*C*H_3), 19.45 (N=C-*C*H_3), 18.69 (N=C-*C*H_3), 18.32 (N=C-*C*H_3), 4.60 (Pd-*C*H_3), 4.51 (Pd-*C*H_3). Anal. Calcd for ($C_{62}H_{71}ClN_2Pd$): C, 75.52; H, 7.26; N, 2.84. Found: C, 75.81; H, 7.54; N, 2.71. MALDI-TOF-MS (m/z): calcd for $C_{61}H_{68}N_2Pd$: 934.4417, found: 934.3491 $[M\text{-}Me\text{-}Cl]^+$.

2.5 A General Procedure for the Homopolymerization of Ethylene Using Ni Complexes.

In a typical experiment, a 350 mL thick wall pressure glass 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 10 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 350 mL thick wall pressure glass 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 NaBArF 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 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 350 mL thick wall pressure glass 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 amount of 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.

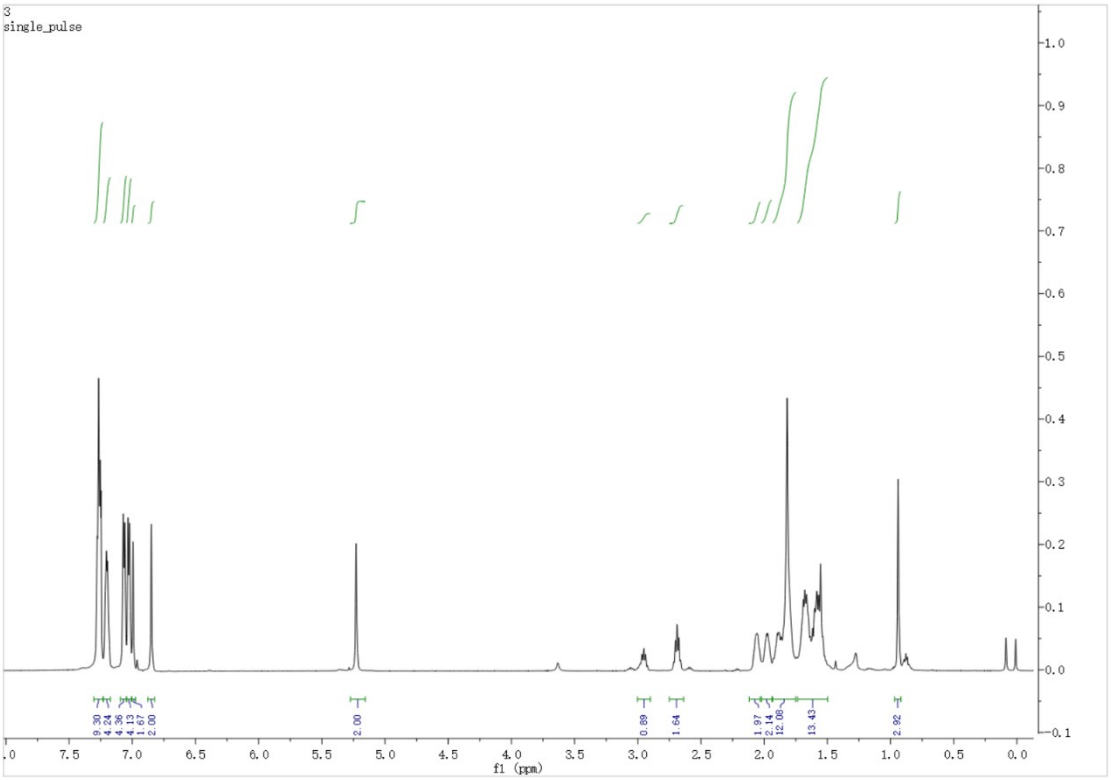


Figure S3. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

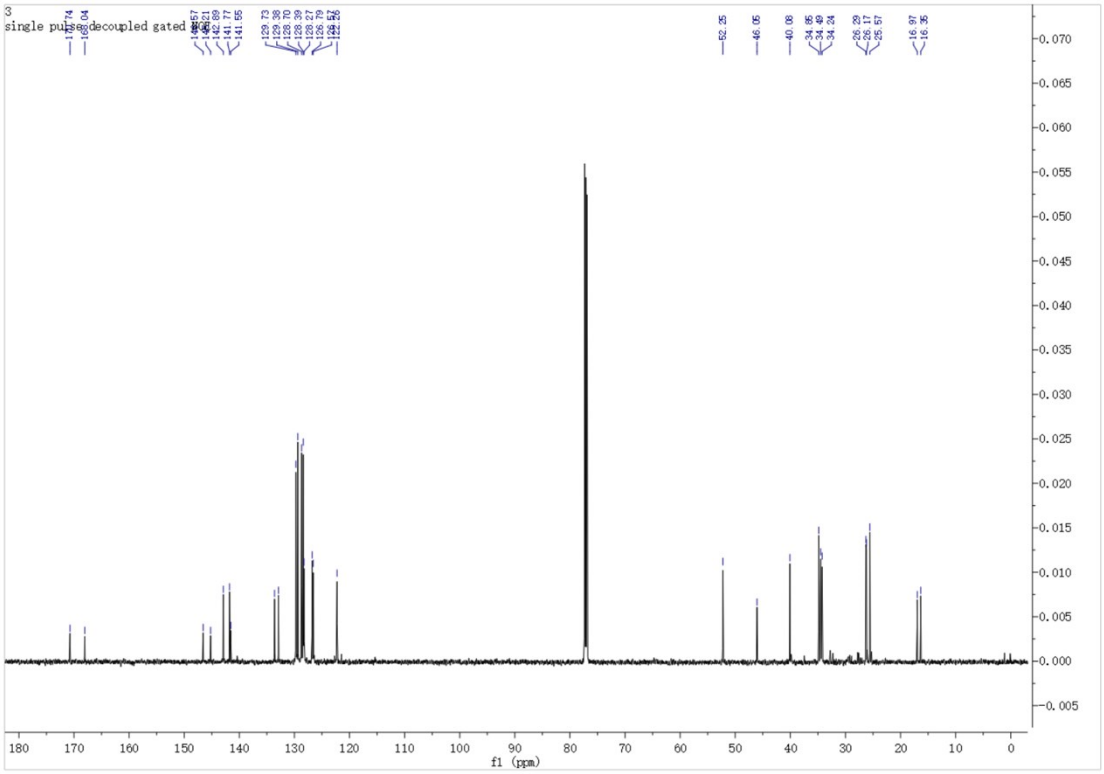


Figure S4. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

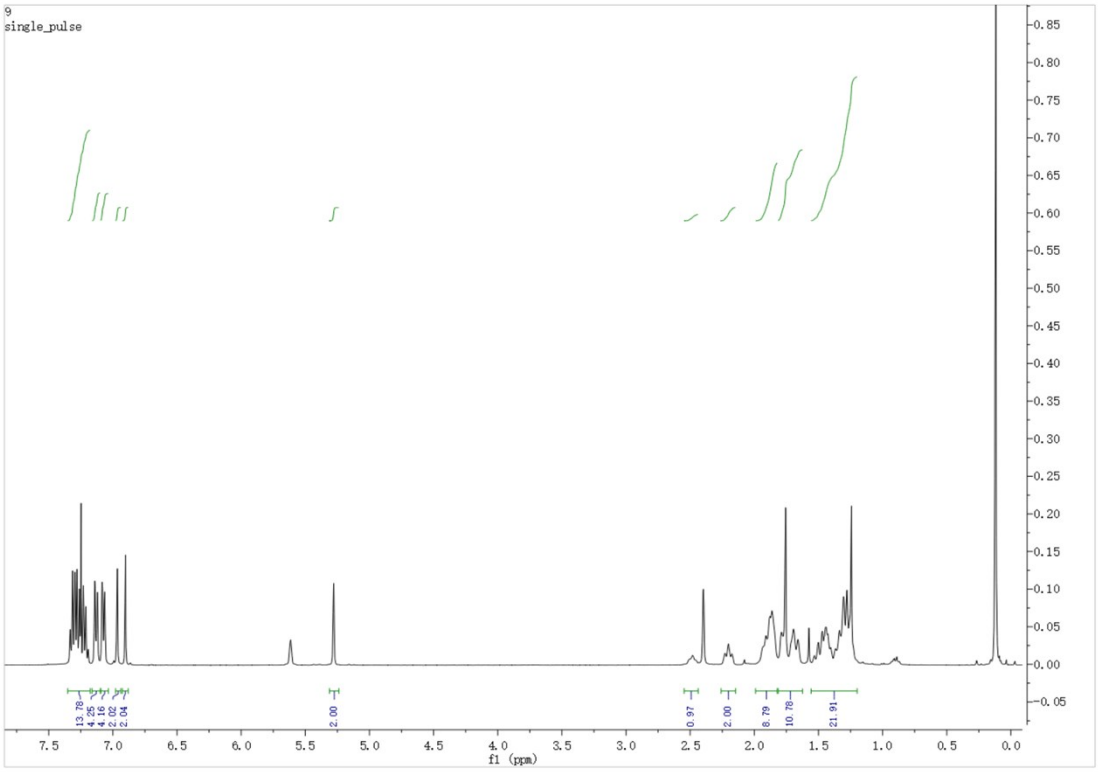


Figure S5. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

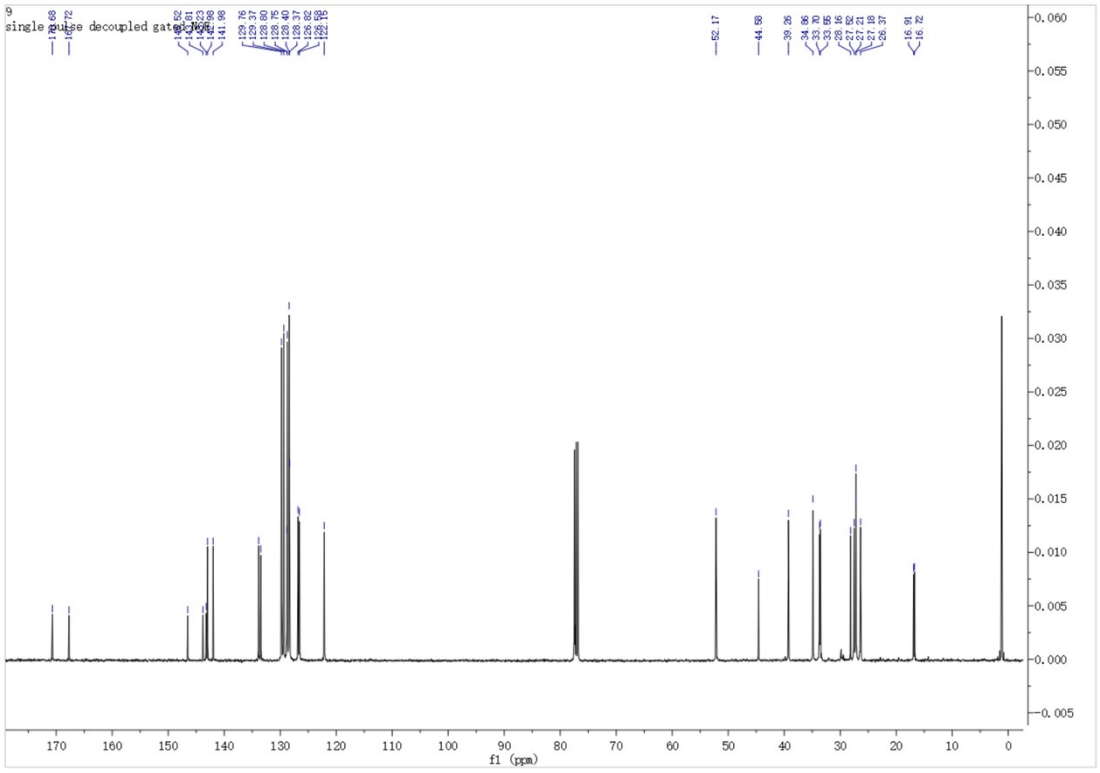


Figure S6. ^{13}C NMR spectrum of **L2** in $CDCl_3$.

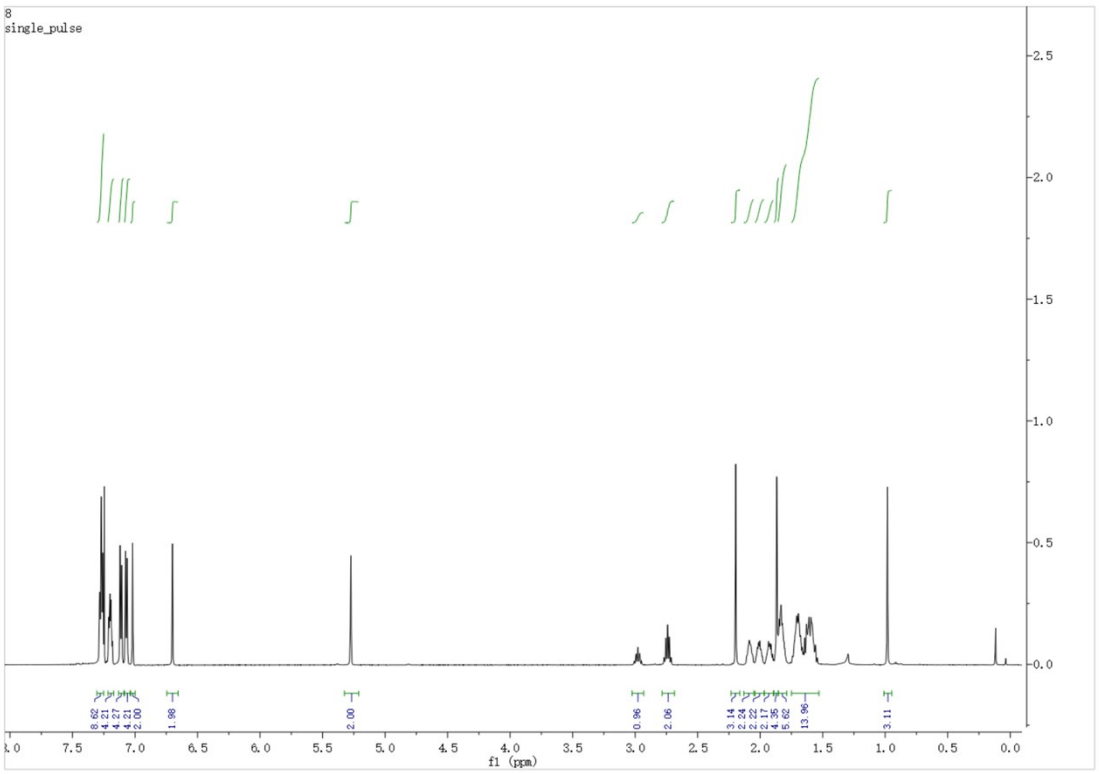


Figure S7. ^{1}H NMR spectrum of **L3** in $CDCl_3$.

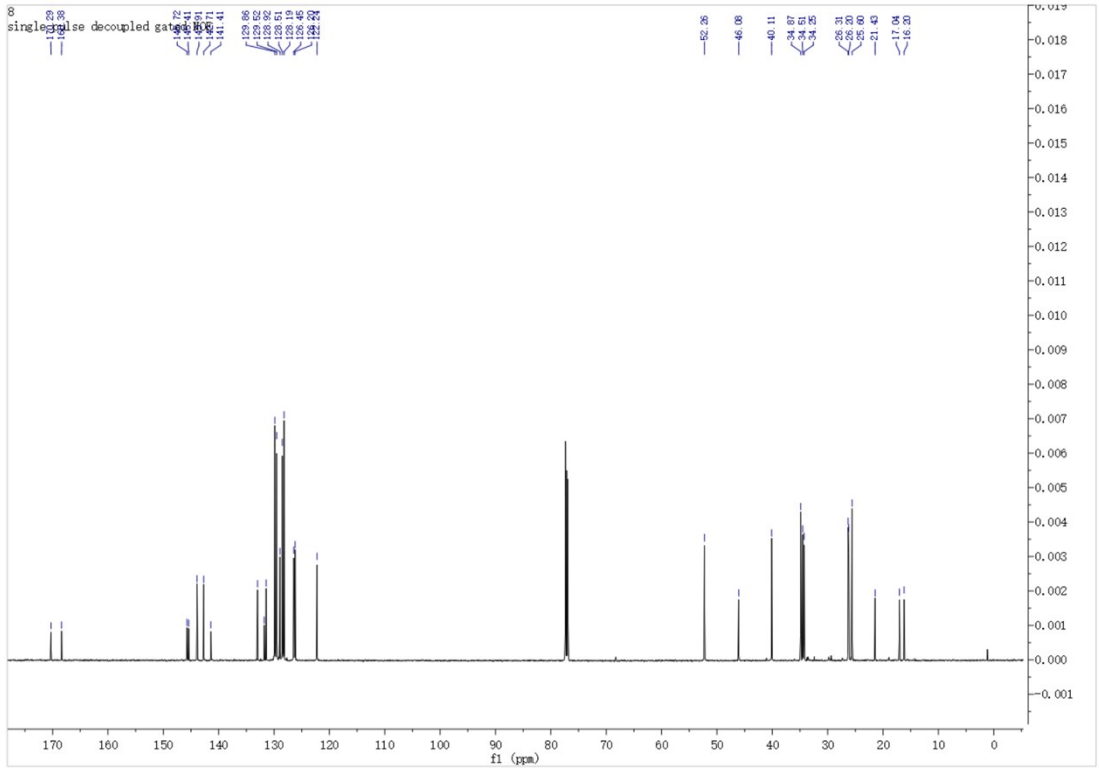


Figure S8. ^{13}C NMR spectrum of **L3** in $CDCl_3$.

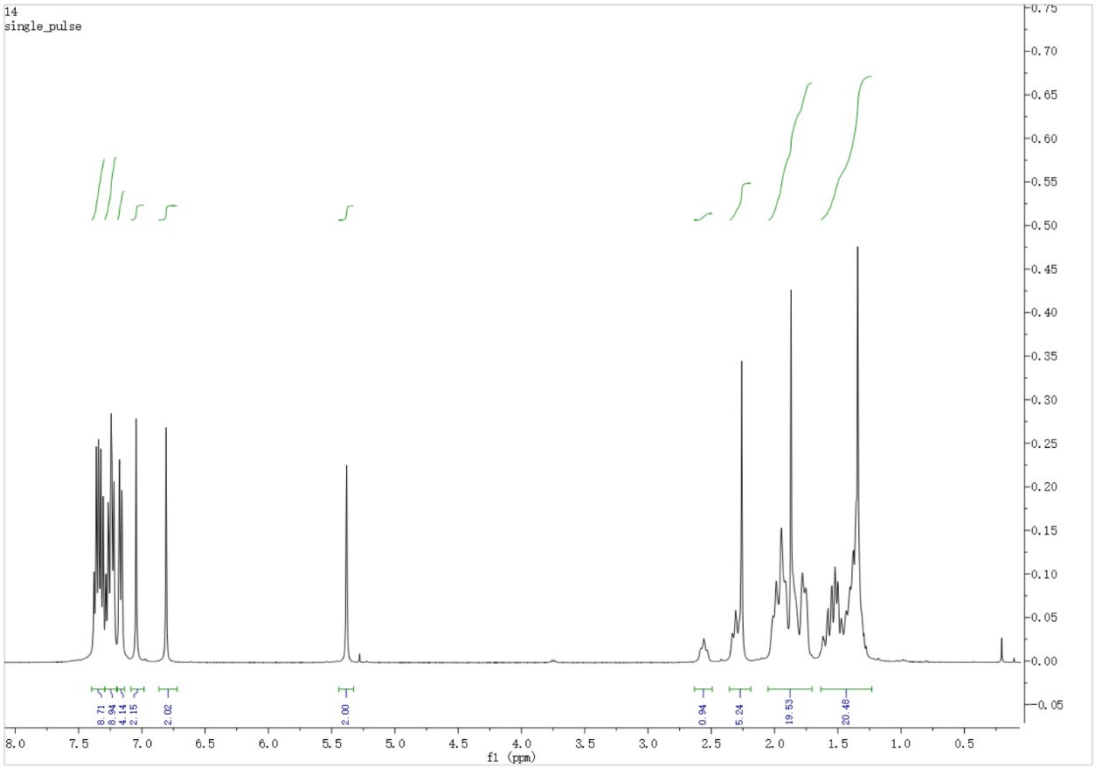


Figure S9. ^{1}H NMR spectrum of **L4** in $CDCl_3$.

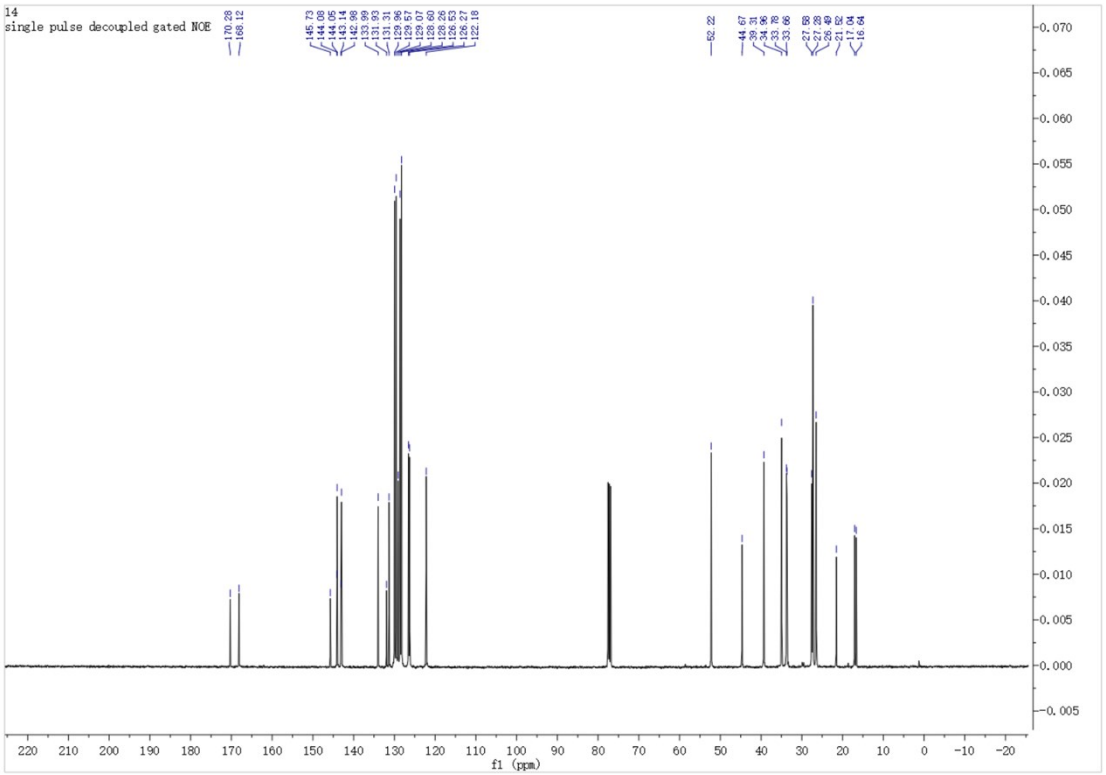


Figure S10. ^{13}C NMR spectrum of **L4** in $CDCl_3$.

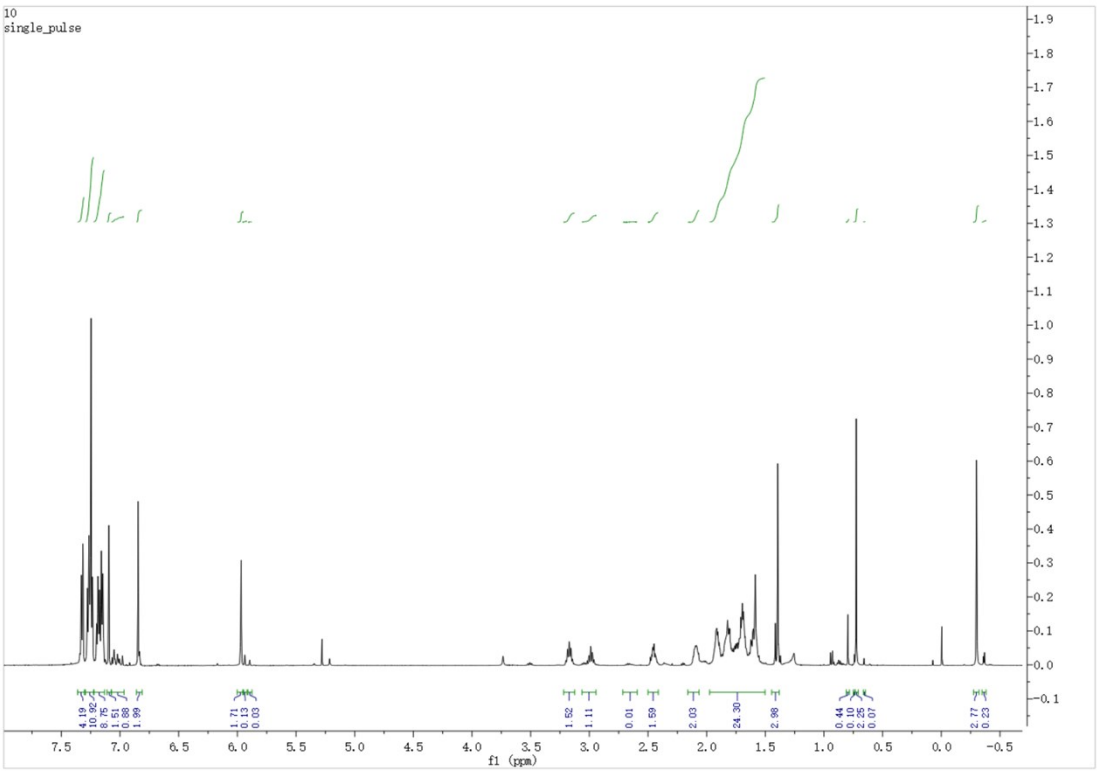


Figure S11. ^{1}H NMR spectrum of **Pd1** in $CDCl_3$.

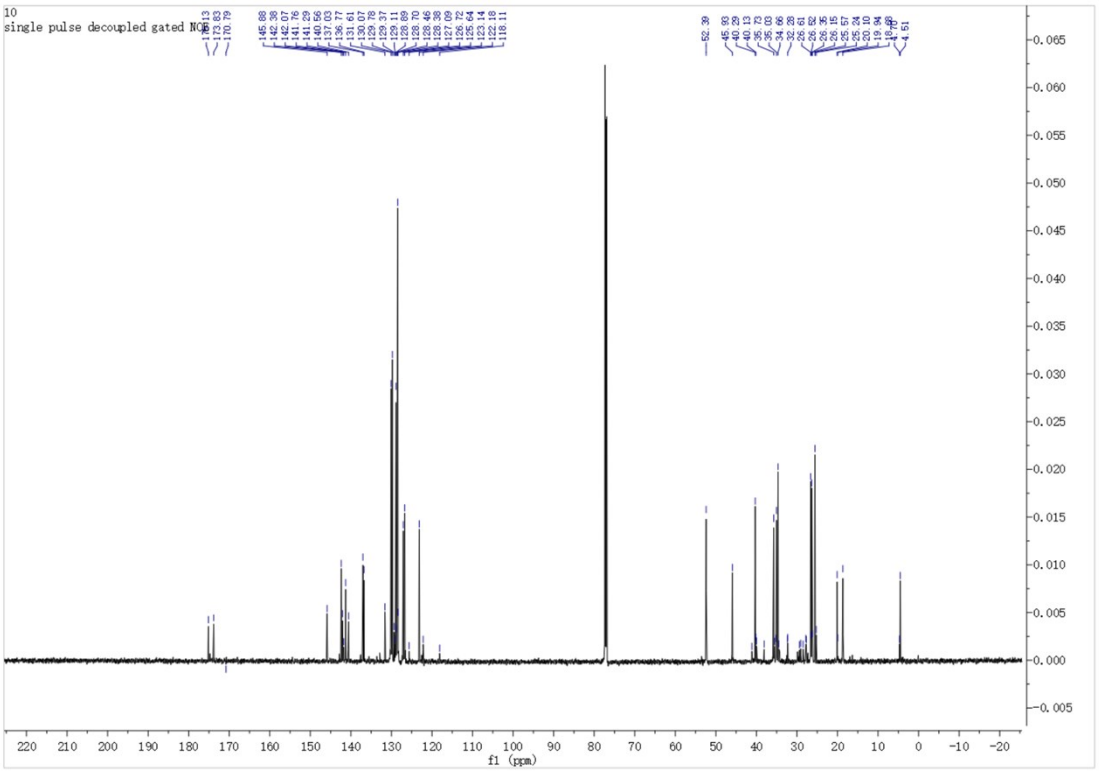


Figure S12. ^{13}C NMR spectrum of **Pd1** in $CDCl_3$.

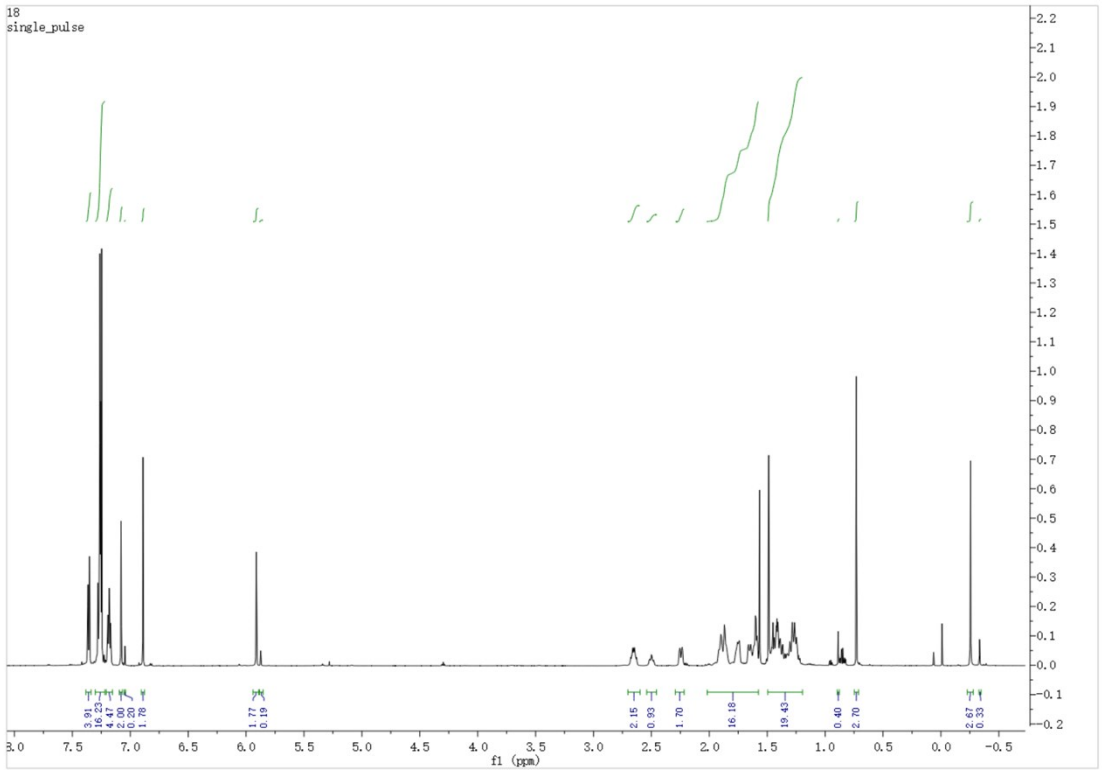


Figure S13. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

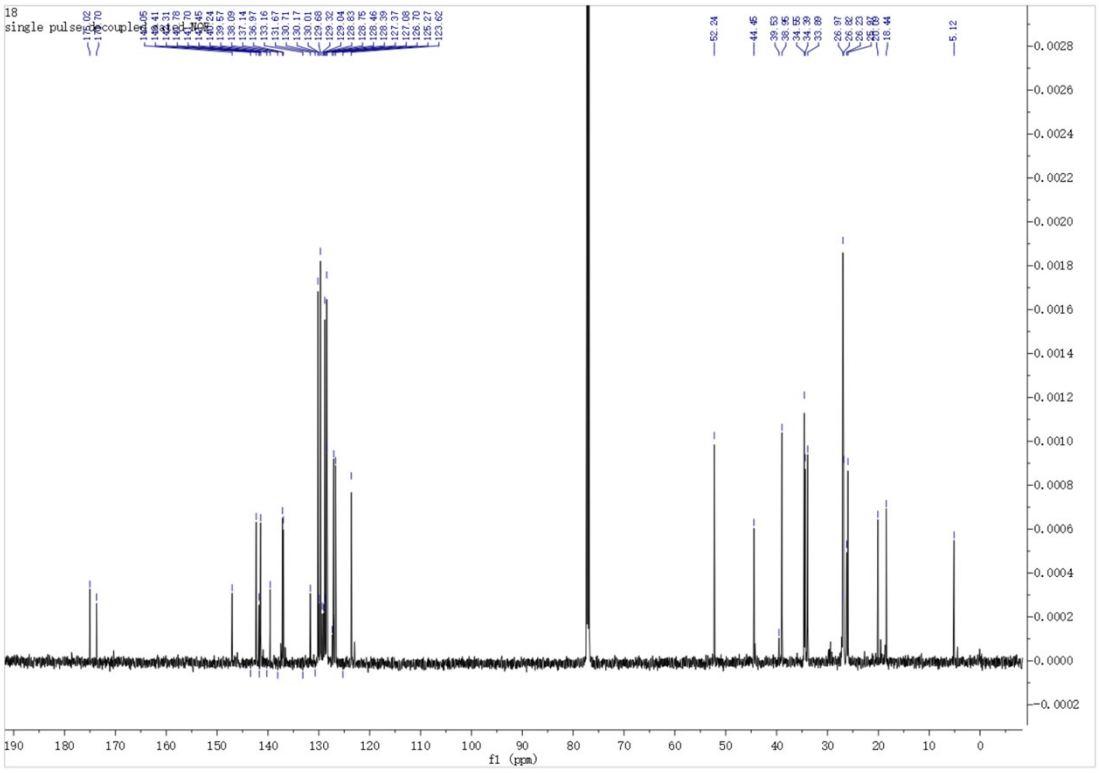


Figure S14. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

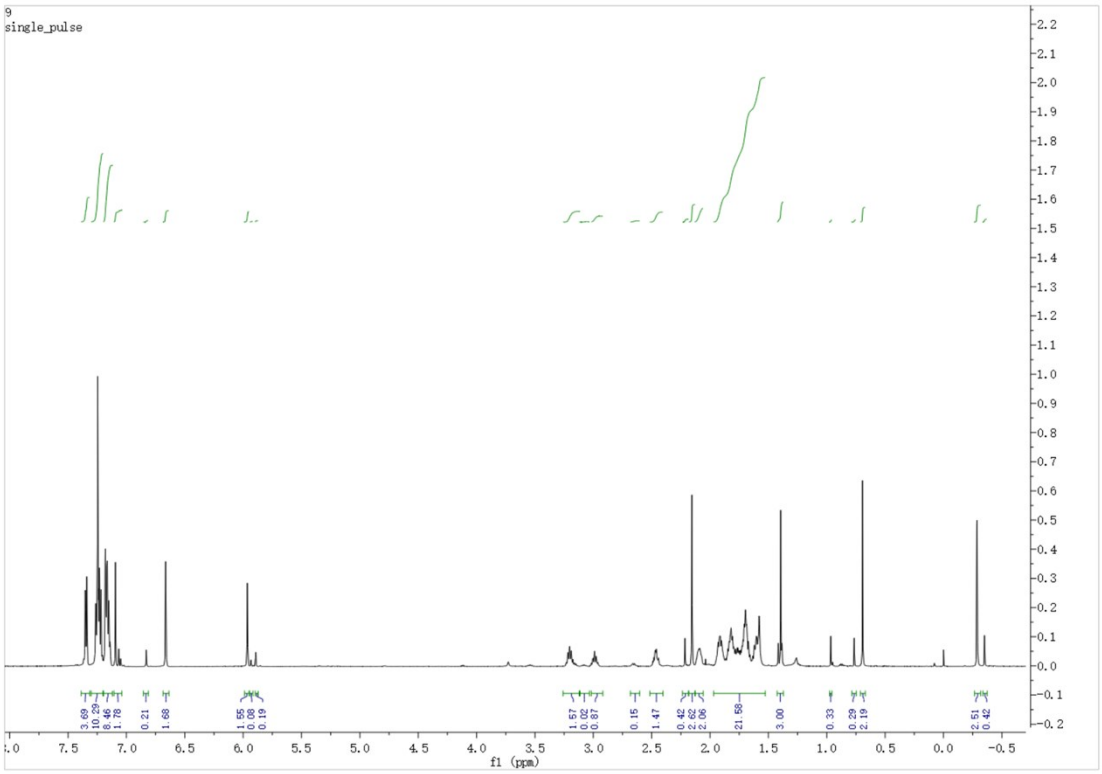


Figure S15. ^{1}H NMR spectrum of **Pd3** in $CDCl_3$.

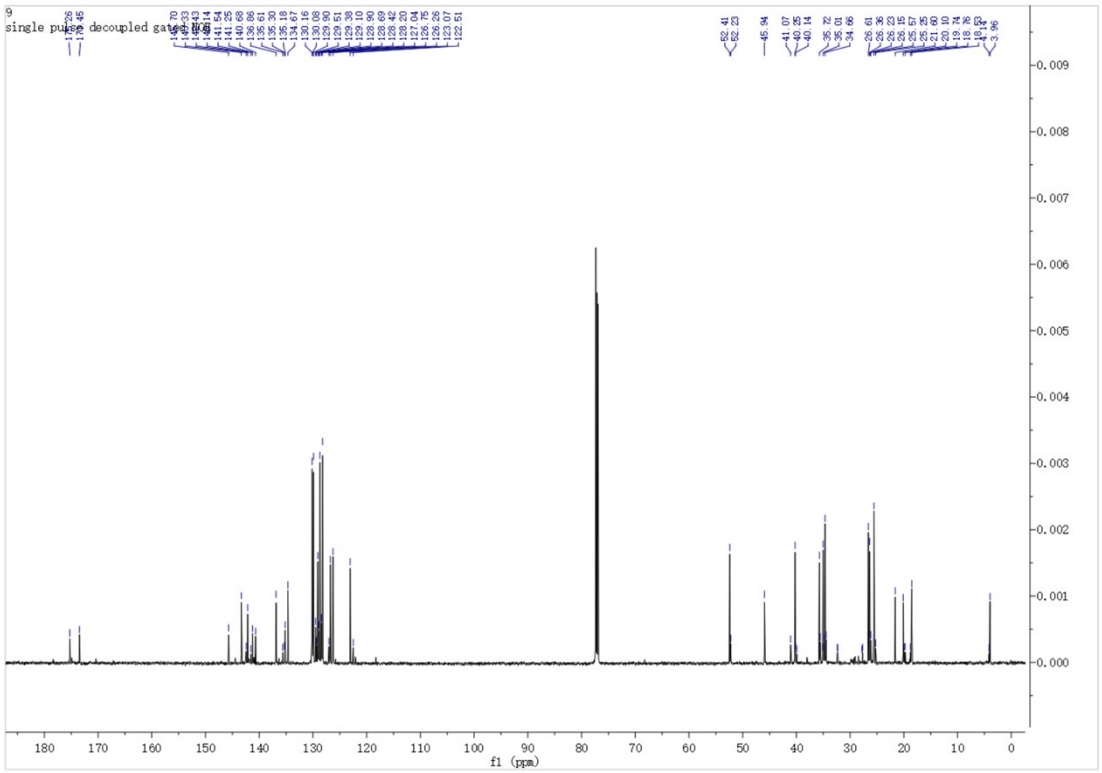


Figure S16. ^{13}C NMR spectrum of **Pd3** in $CDCl_3$.

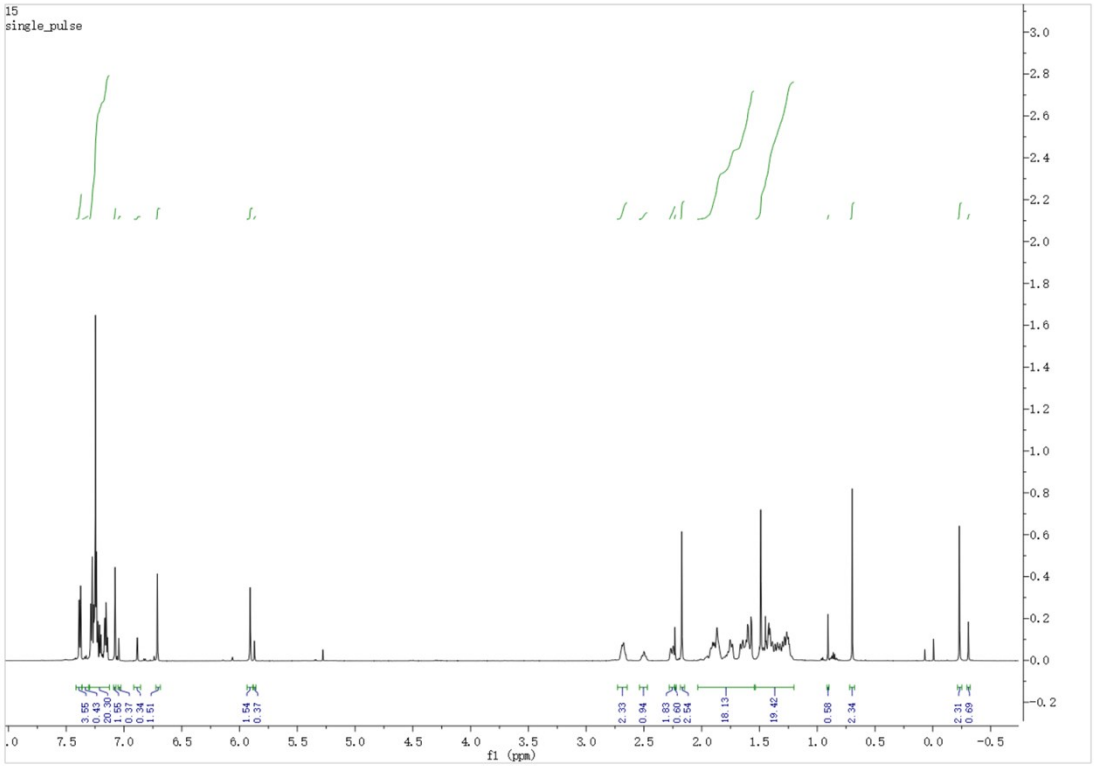


Figure S17. ^{1}H NMR spectrum of **Pd4** in $CDCl_3$.

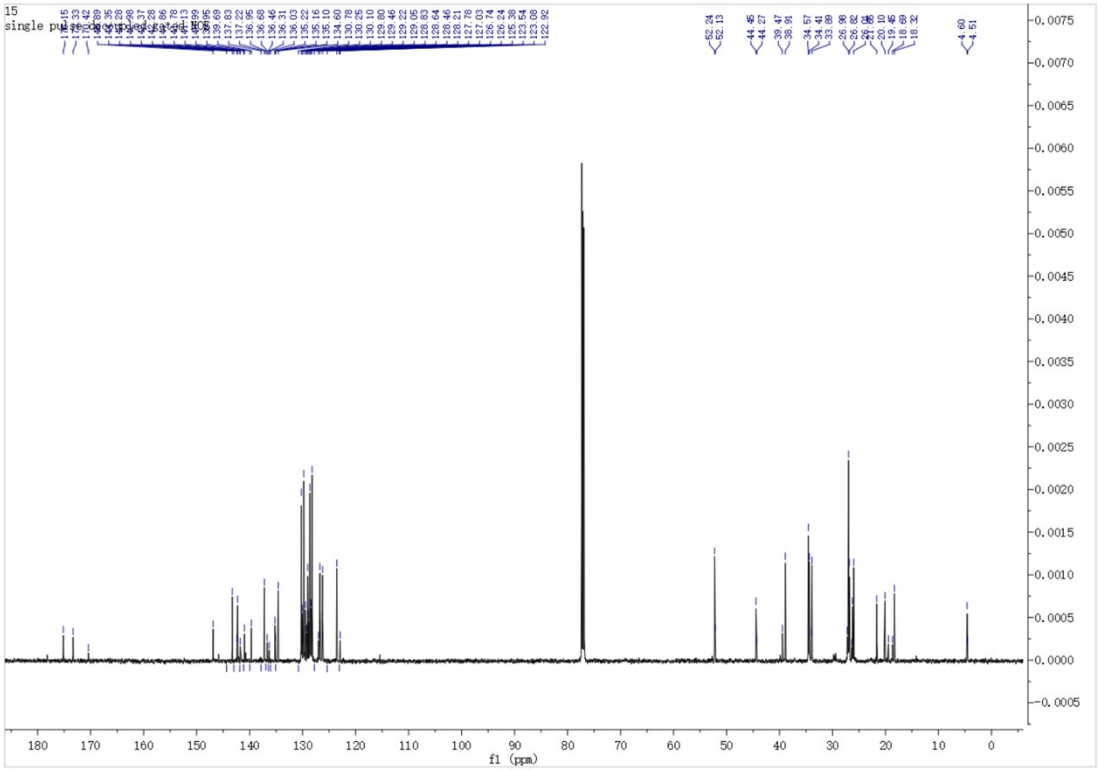


Figure S18. ^{13}C NMR spectrum of **Pd4** in $CDCl_3$.

3.2 HRMS and MALDI-TOF-MS Data.

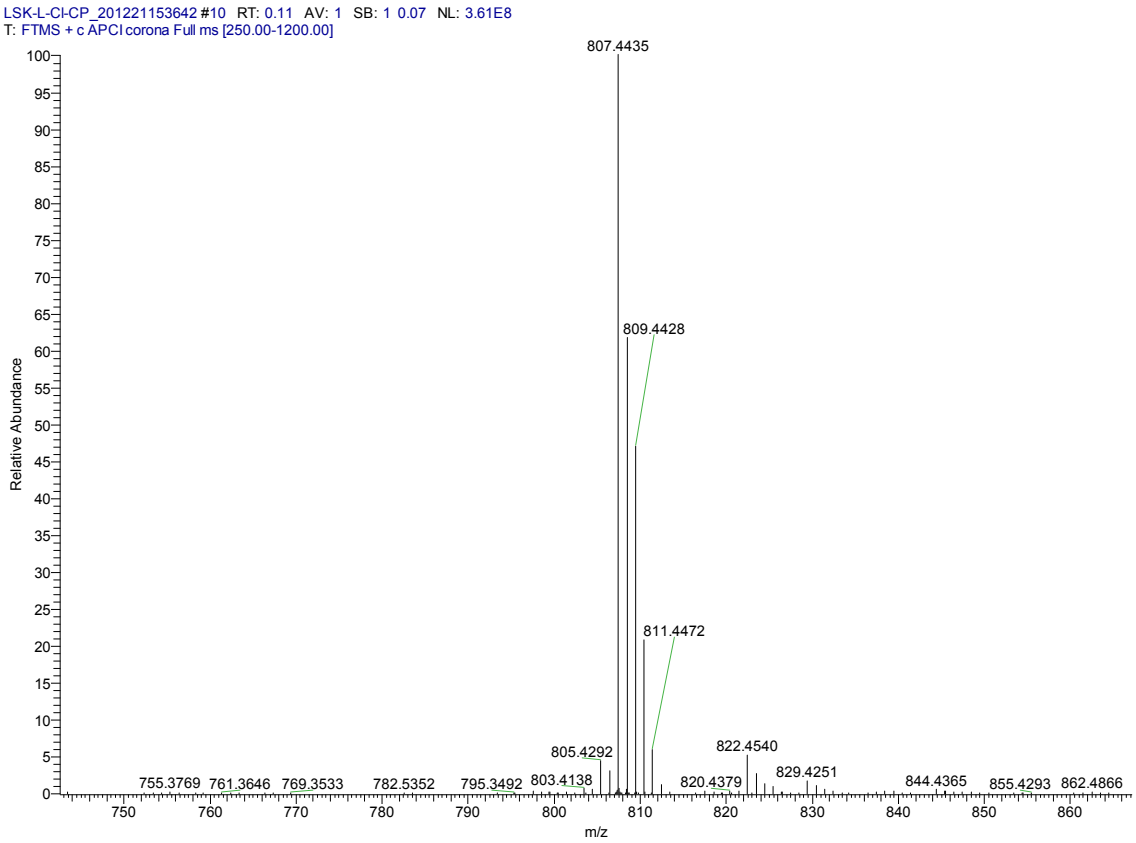


Figure S19. HRMS of **L1.**

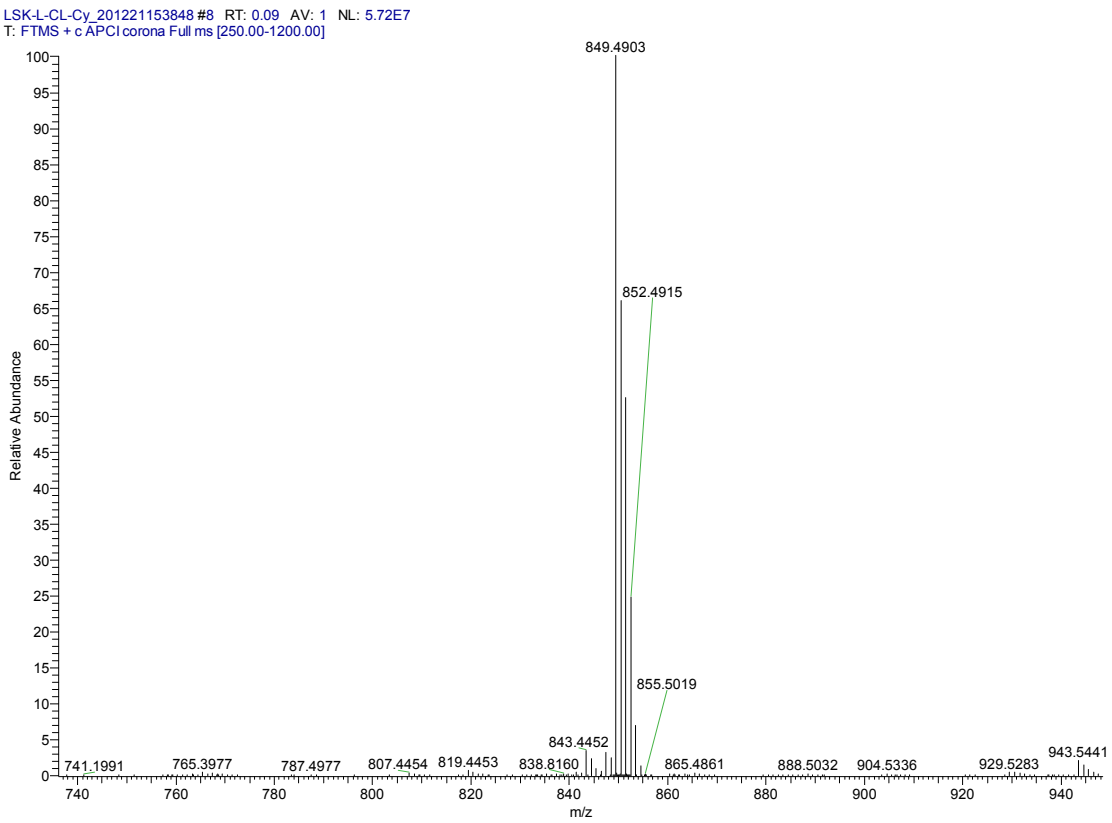


Figure S20. HRMS of **L2.**

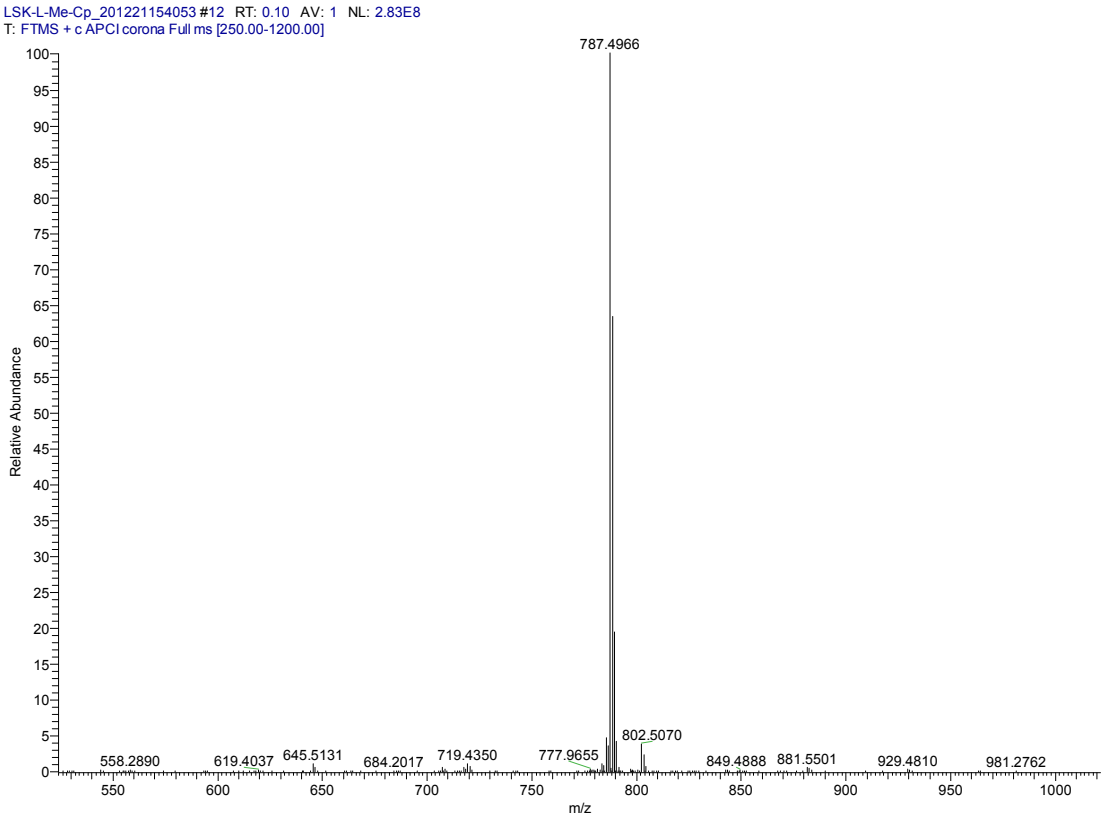


Figure S21. HRMS of **L3.**

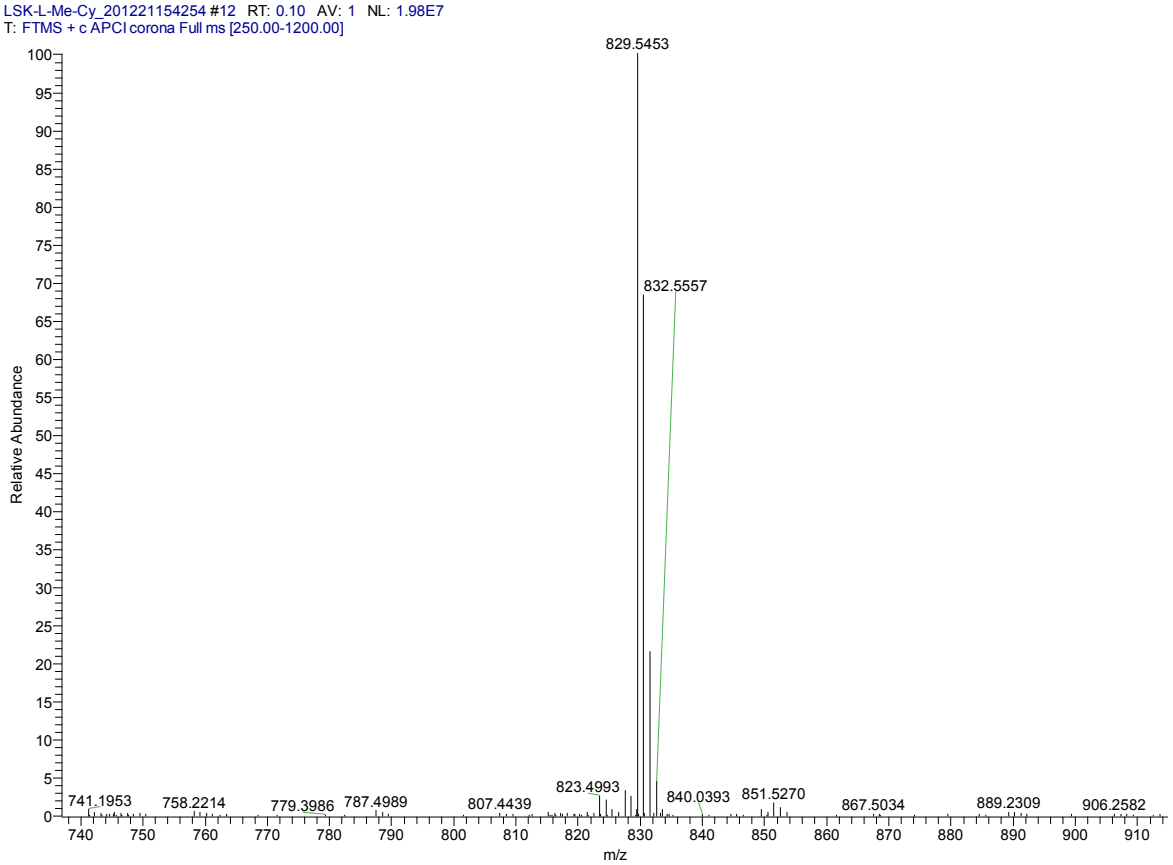


Figure S22. HRMS of **L4.**

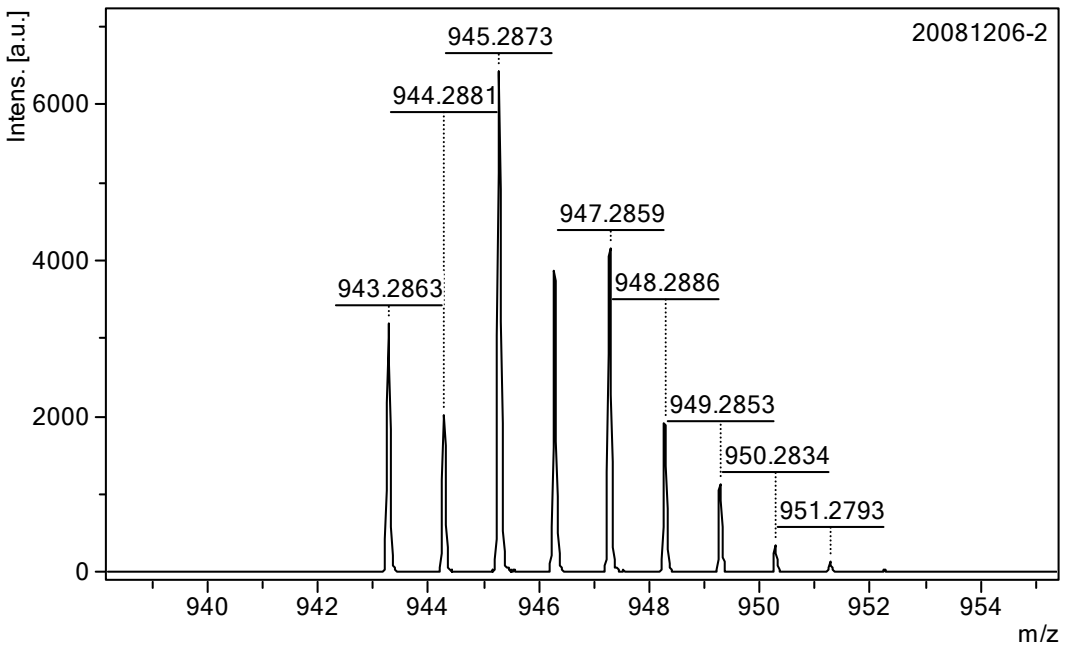


Figure S23. MALDI-TOF-MS of complex **Ni1**.

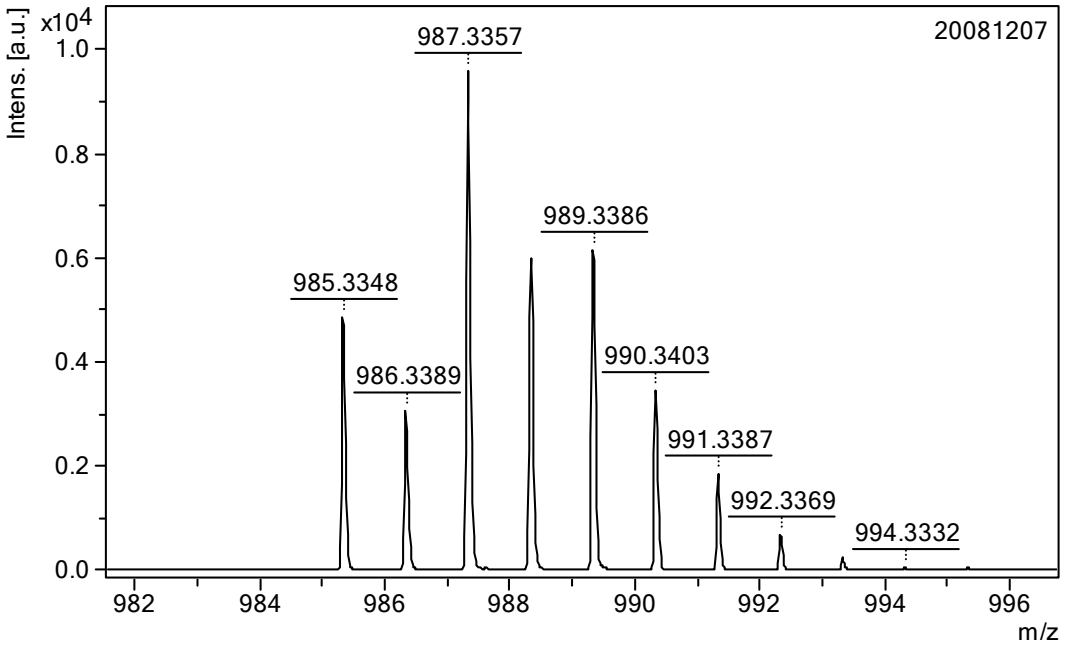


Figure S24. MALDI-TOF-MS of complex **Ni2**.

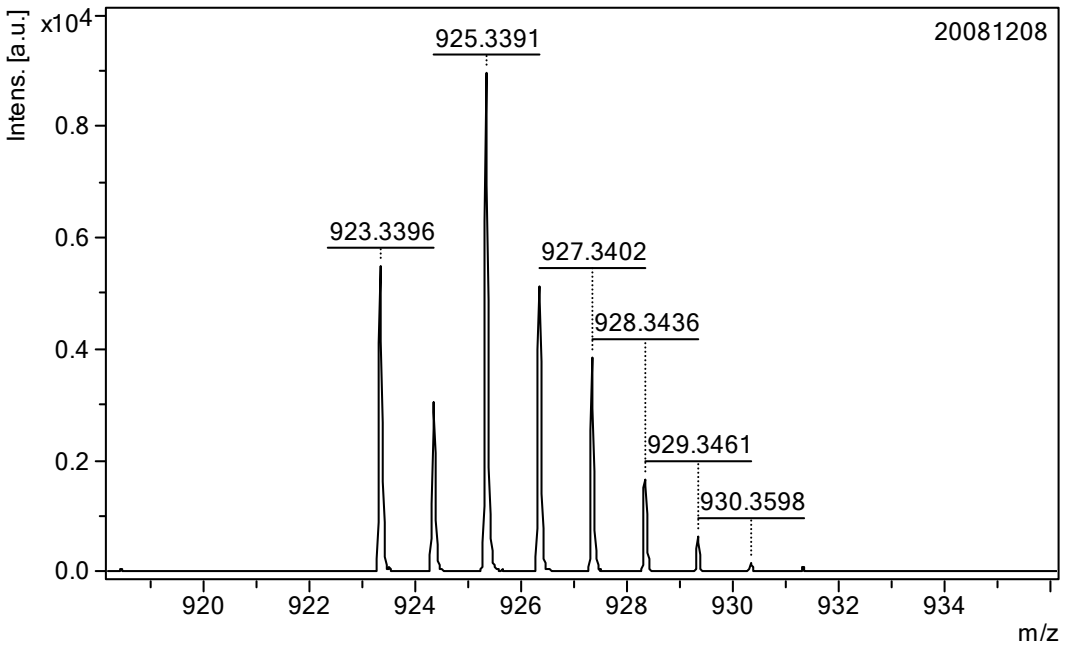
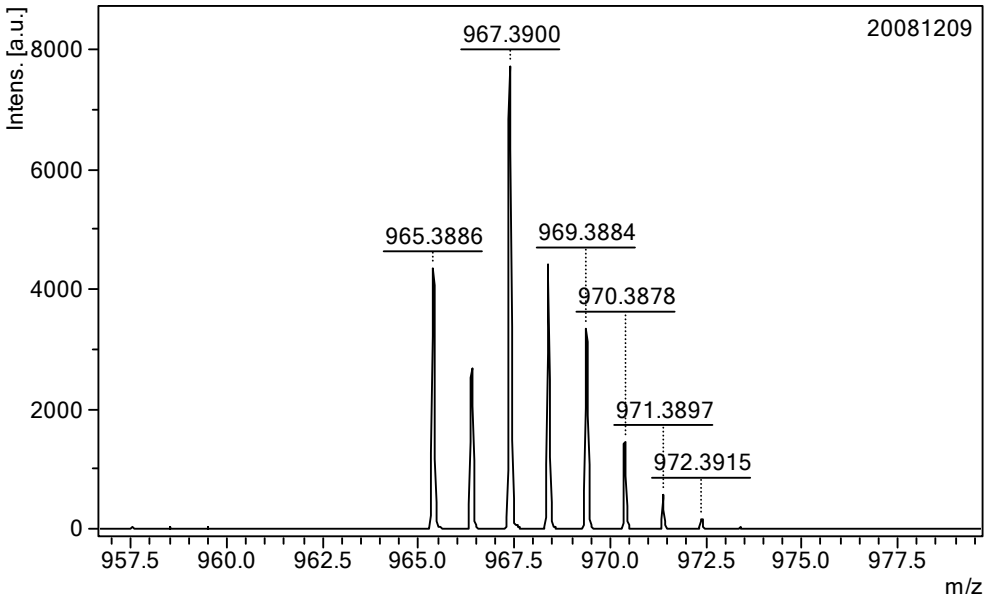


Figure S25. MALDI-TOF-MS of complex **Ni3**.



. **Figure S26.** MALDI-TOF-MS of complex **Ni4**.

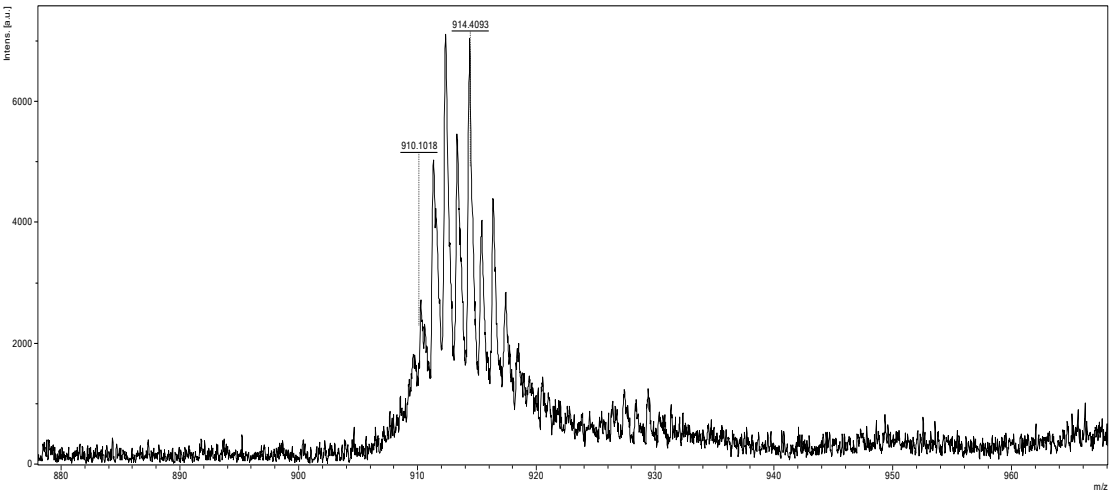


Figure S27. MALDI-TOF-MS of complex **Pd1**.

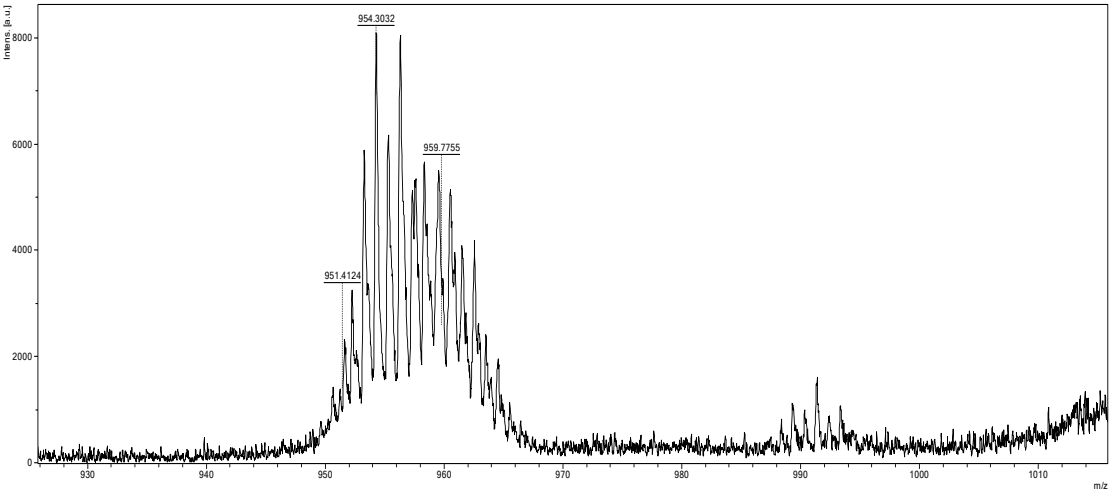


Figure S28. MALDI-TOF-MS of complex **Pd2**.

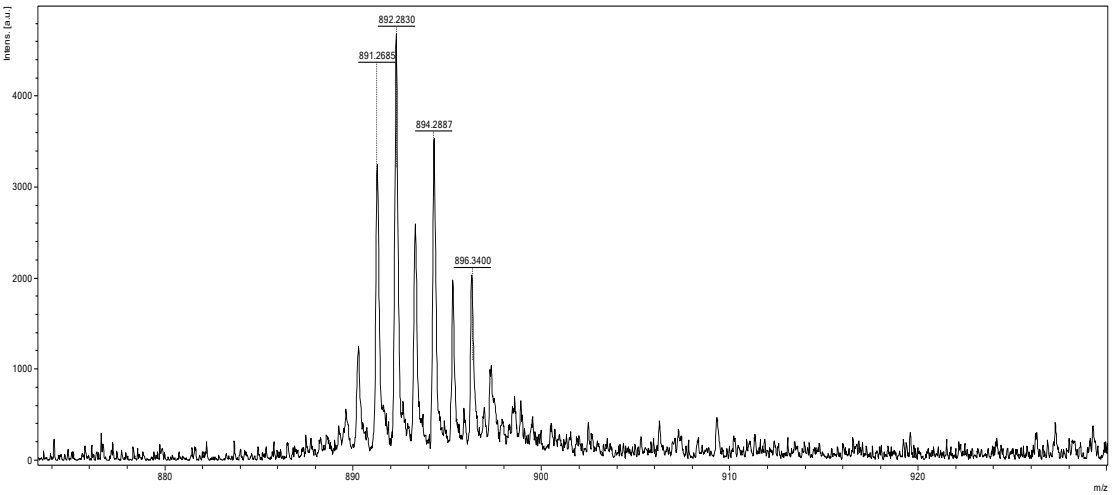


Figure S29. MALDI-TOF-MS of complex **Pd3**.

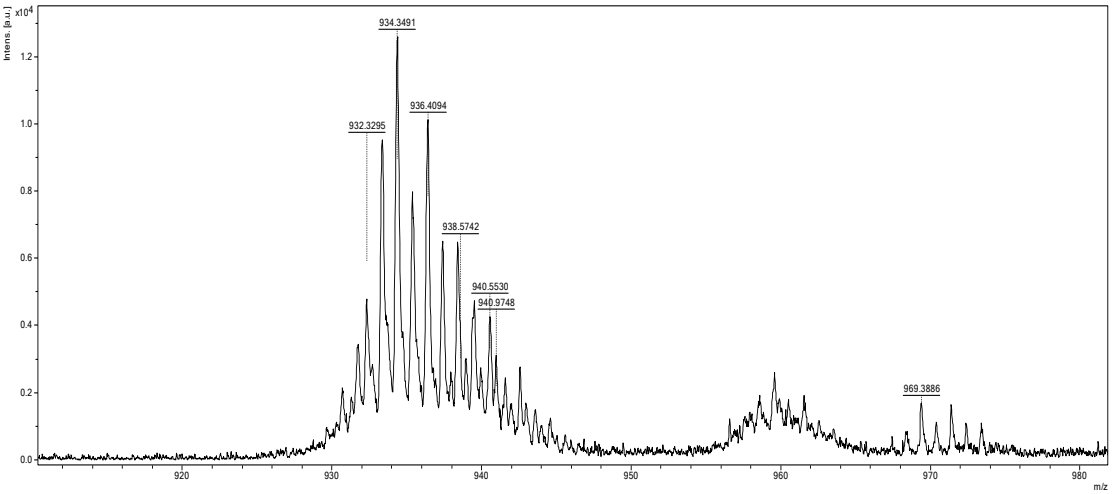


Figure S30. MALDI-TOF-MS of complex **Pd4**.

3.3 ^{1}H and ^{13}C NMR of Polymers.

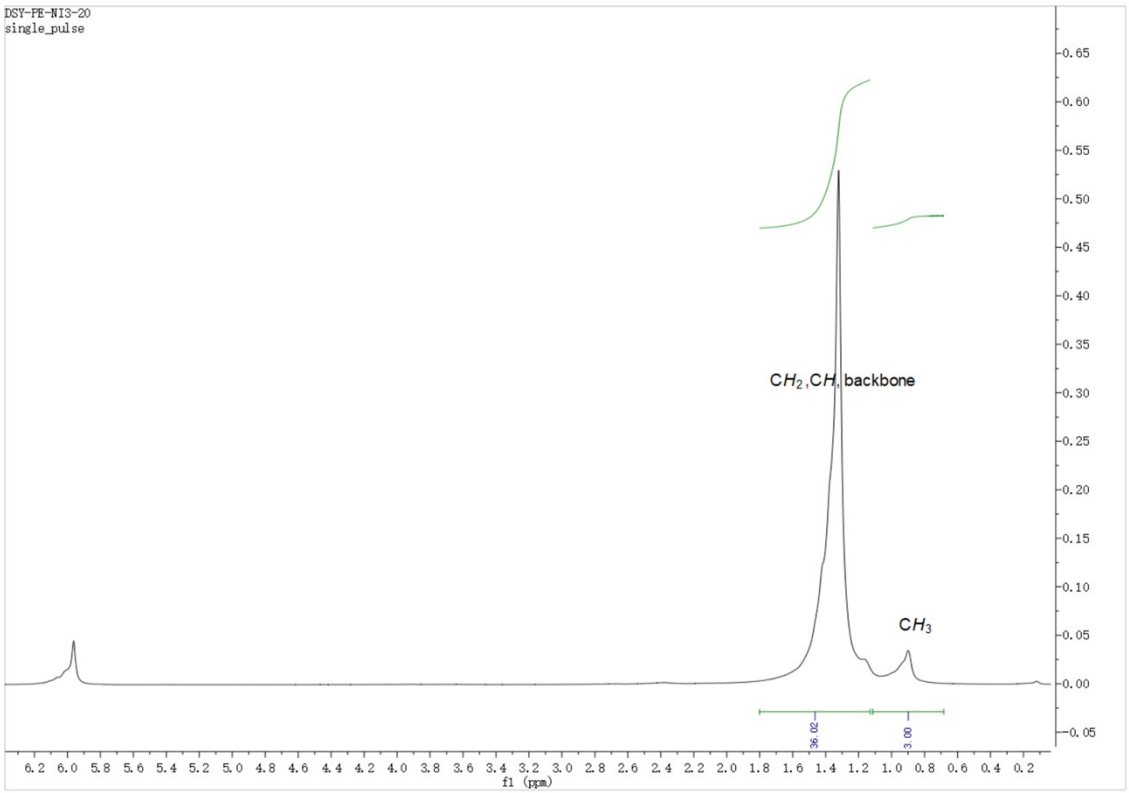


Figure S31. ^{1}H NMR spectrum of the polymer from table 1, entry 7 ($CDCl_2CDCl_2$, 120 ^{o}C).

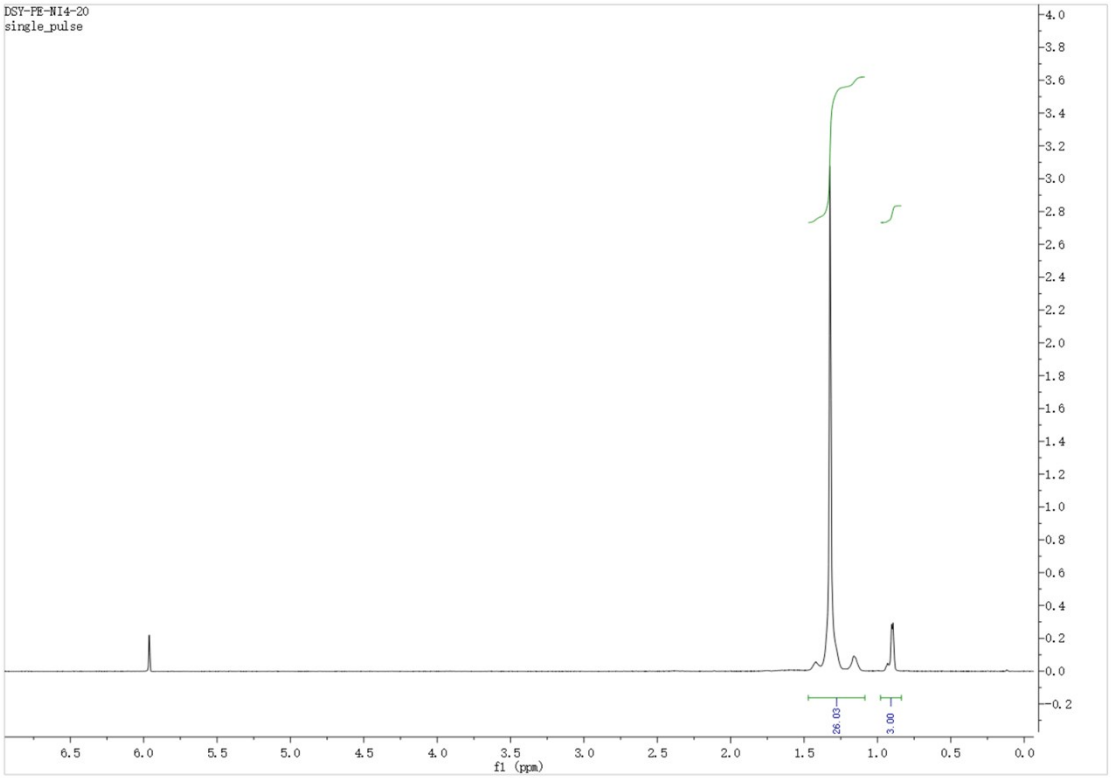


Figure S32. ^{1}H NMR spectrum of the polymer from table 1, entry 10 ($CDCl_2CDCl_2$, 120 °C).

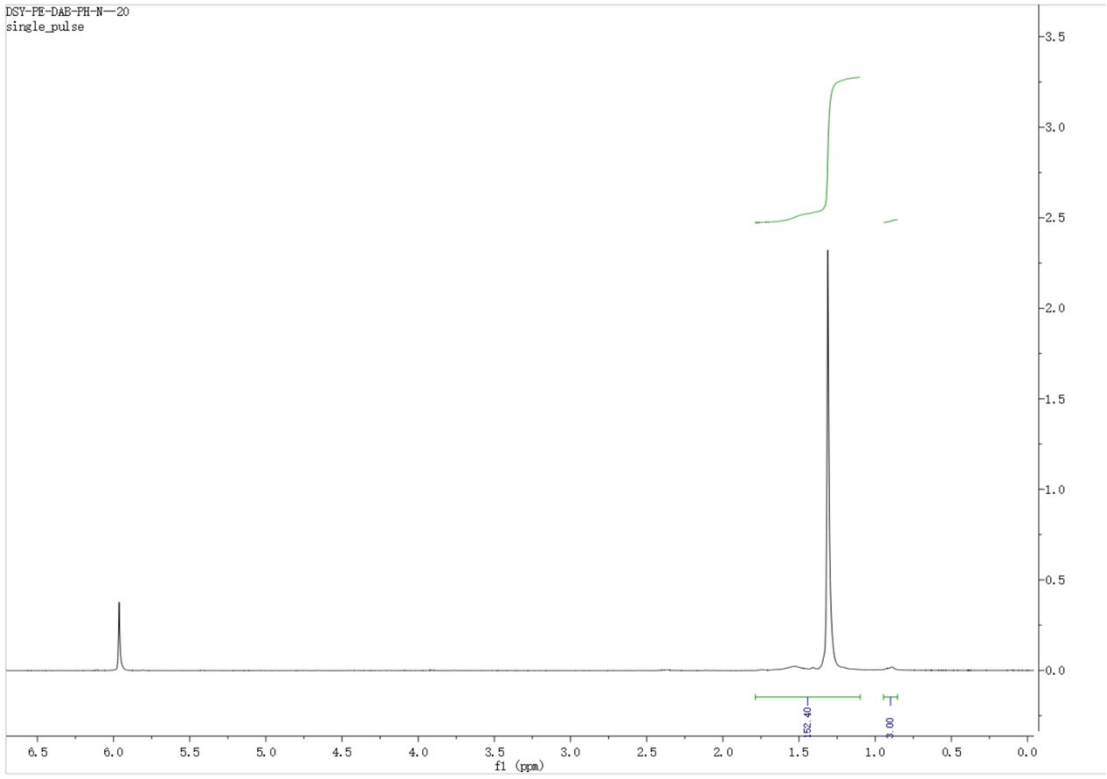


Figure S33. ^{1}H NMR spectrum of the polymer from table 1, entry 13 ($CDCl_2CDCl_2$, 120 °C).

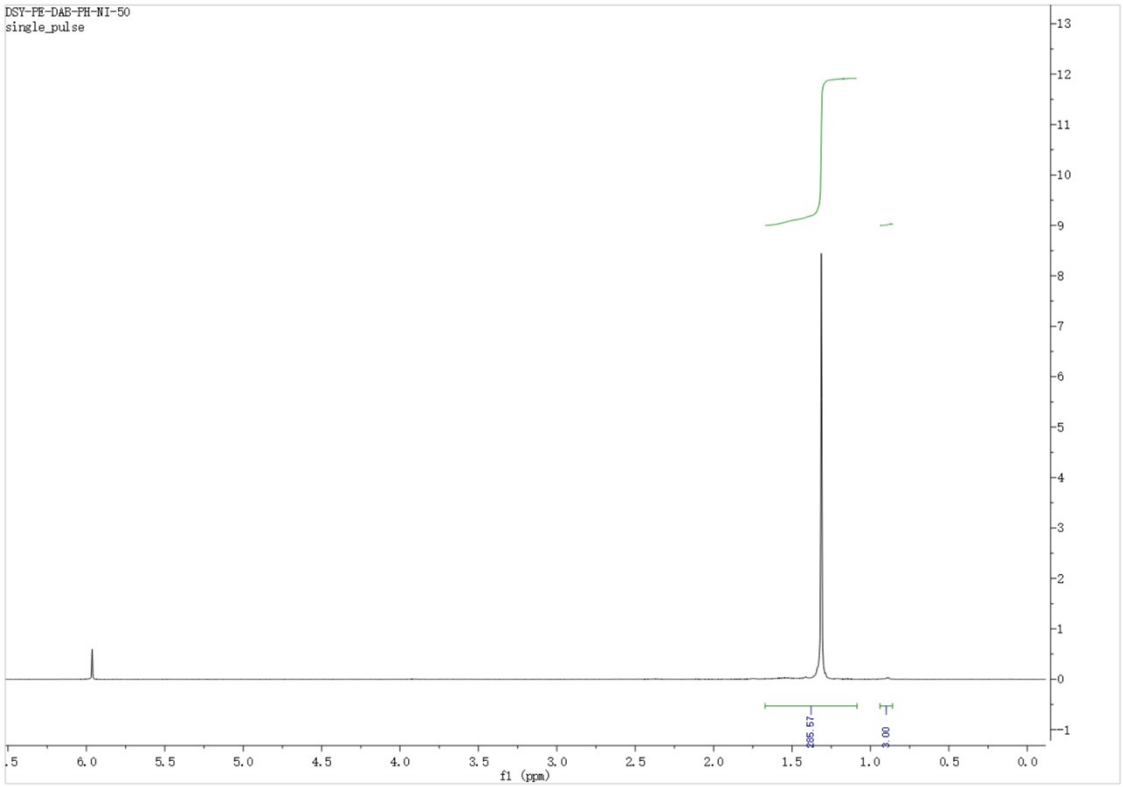


Figure S34. ^{1}H NMR spectrum of the polymer from table 1, entry 14 ($CDCl_2CDCl_2$, 120 ^{o}C).

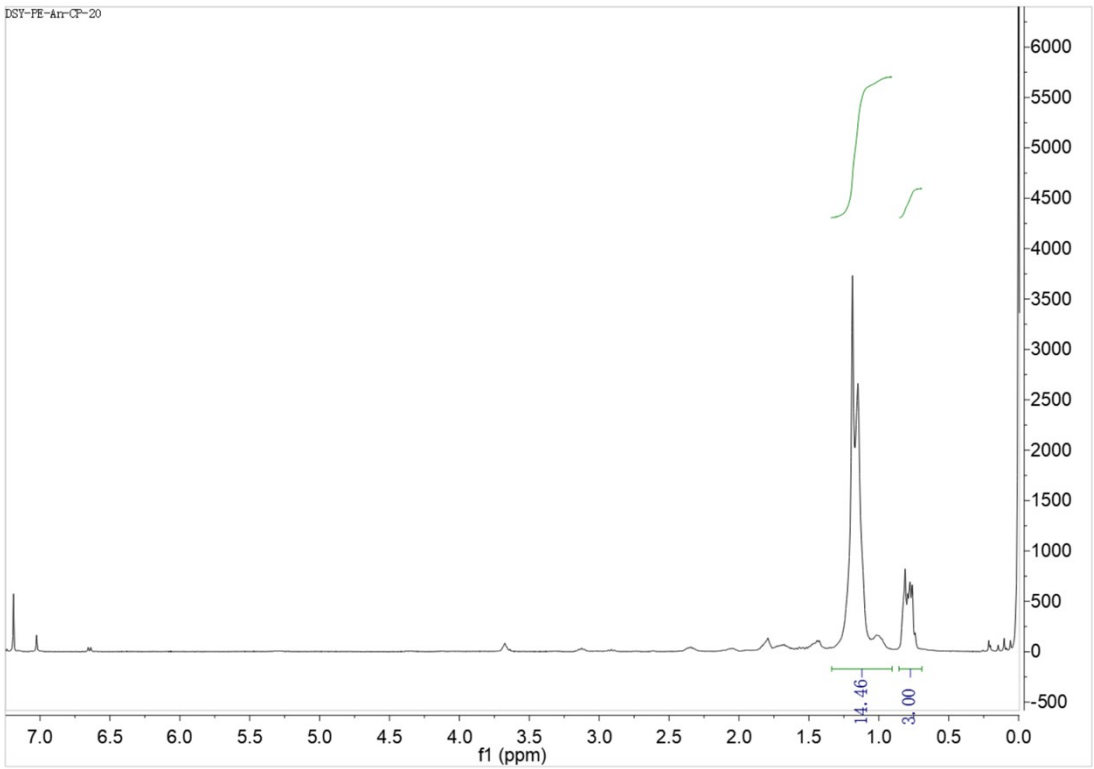


Figure S35. ^{1}H NMR spectrum of the polymer from table 2, entry 1 ($CDCl_3$, 20 ^{o}C).

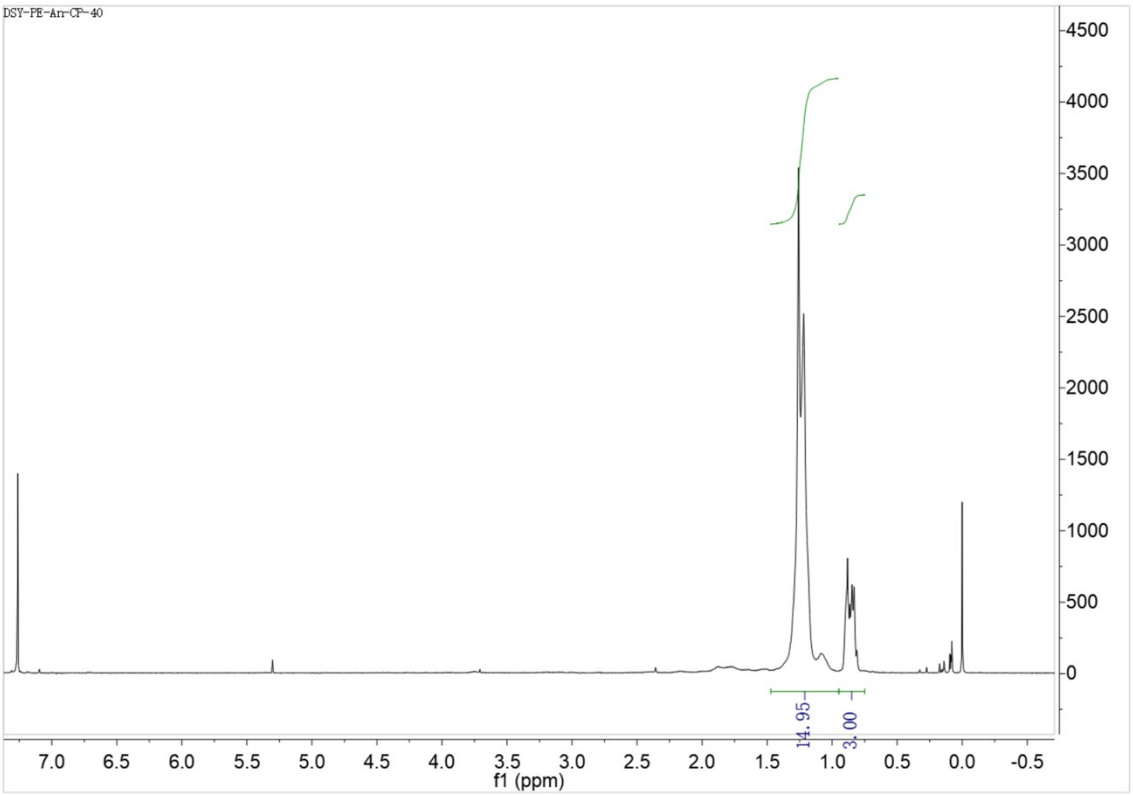


Figure S36. ^{1}H NMR spectrum of the polymer from table 2, entry 2 ($CDCl_3$, 20 ^{o}C).

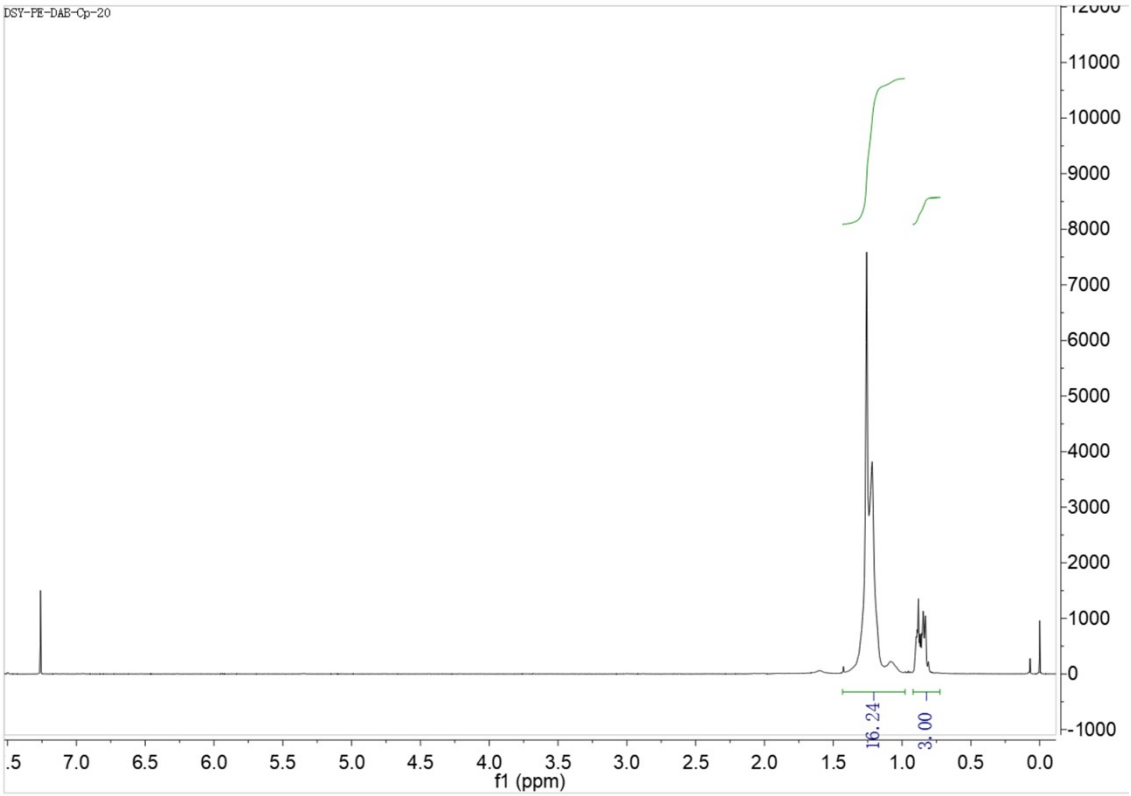


Figure S37. ^{1}H NMR spectrum of the polymer from table 2, entry 5 ($CDCl_3$, 20 ^{o}C).

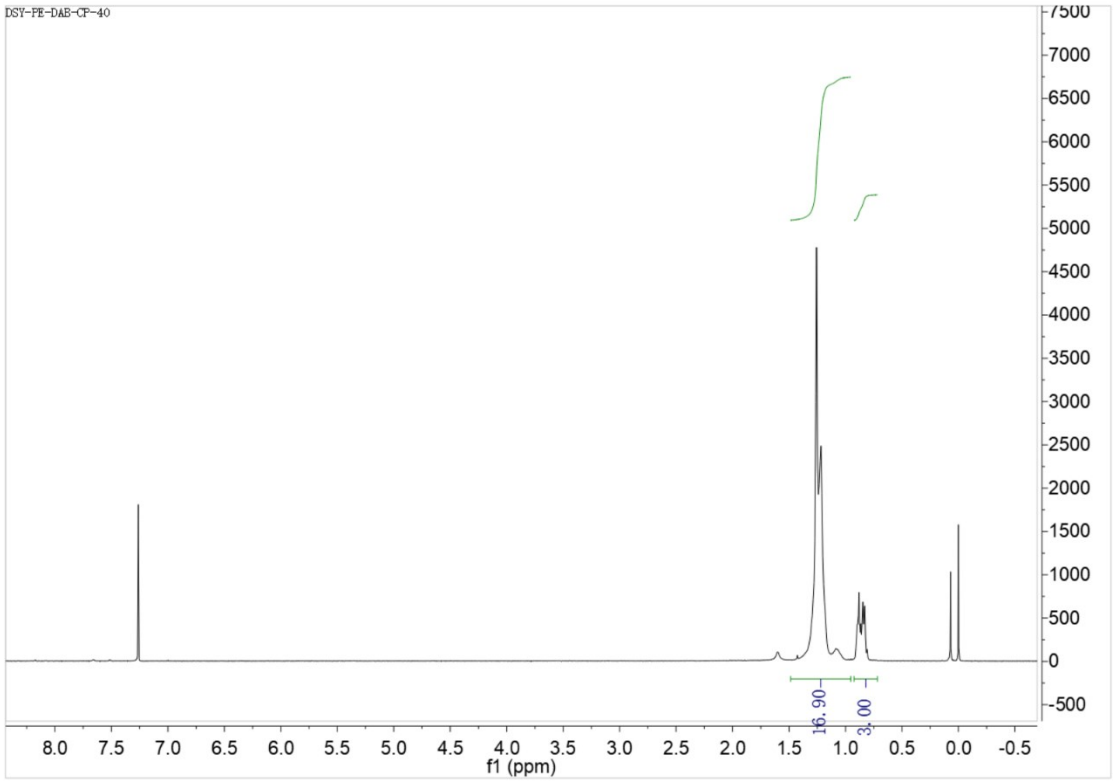


Figure S38. ^{1}H NMR spectrum of the polymer from table 2, entry 6 ($CDCl_3$, 20 ^{o}C).

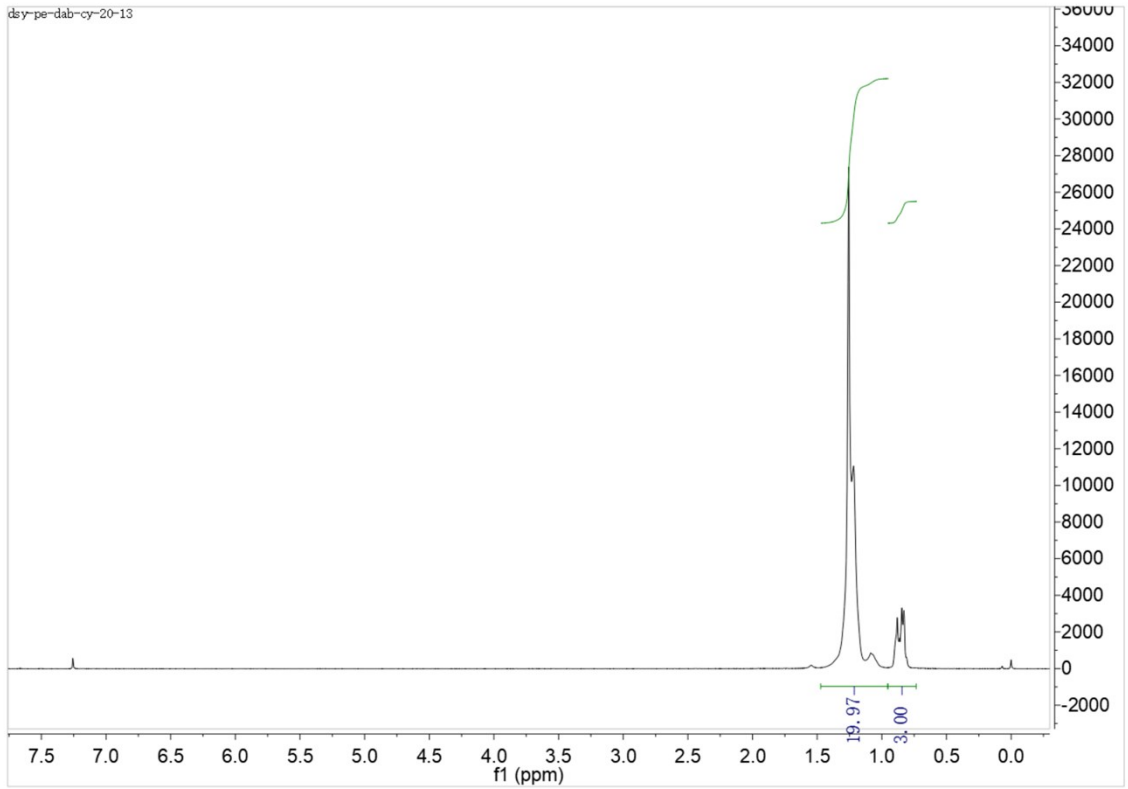


Figure S39. ^{1}H NMR spectrum of the polymer from table 2, entry 7 ($CDCl_3$, 20 ^{o}C).

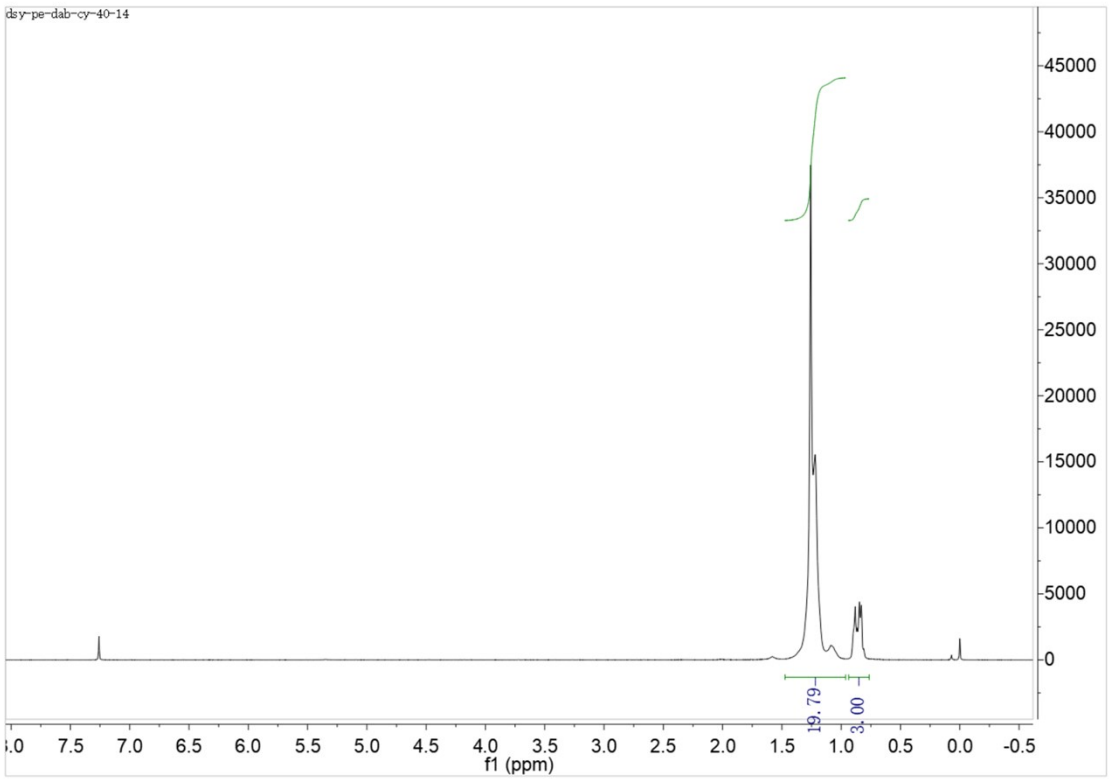


Figure S40. ^{1}H NMR spectrum of the polymer from table 2, entry 8 ($CDCl_3$, 20 ^{o}C).

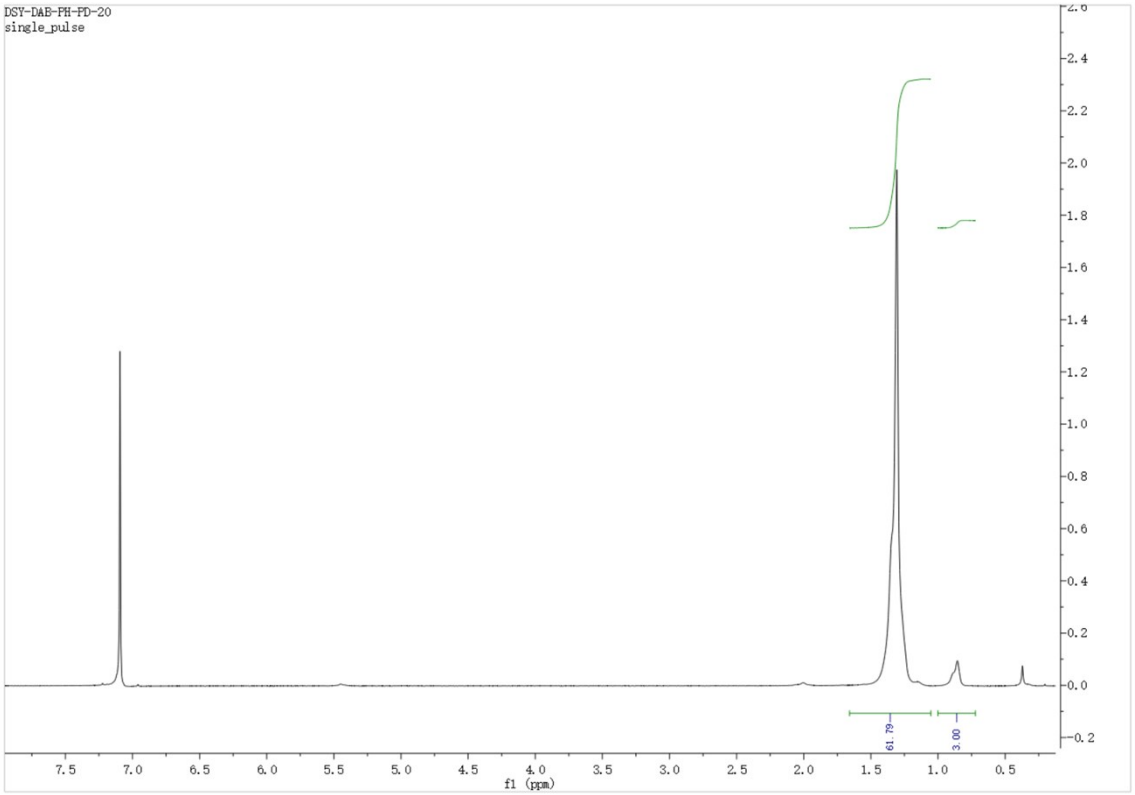


Figure S41. ^{1}H NMR spectrum of the polymer from table 2, entry 9 ($CDCl_3$, 20 ^{o}C).

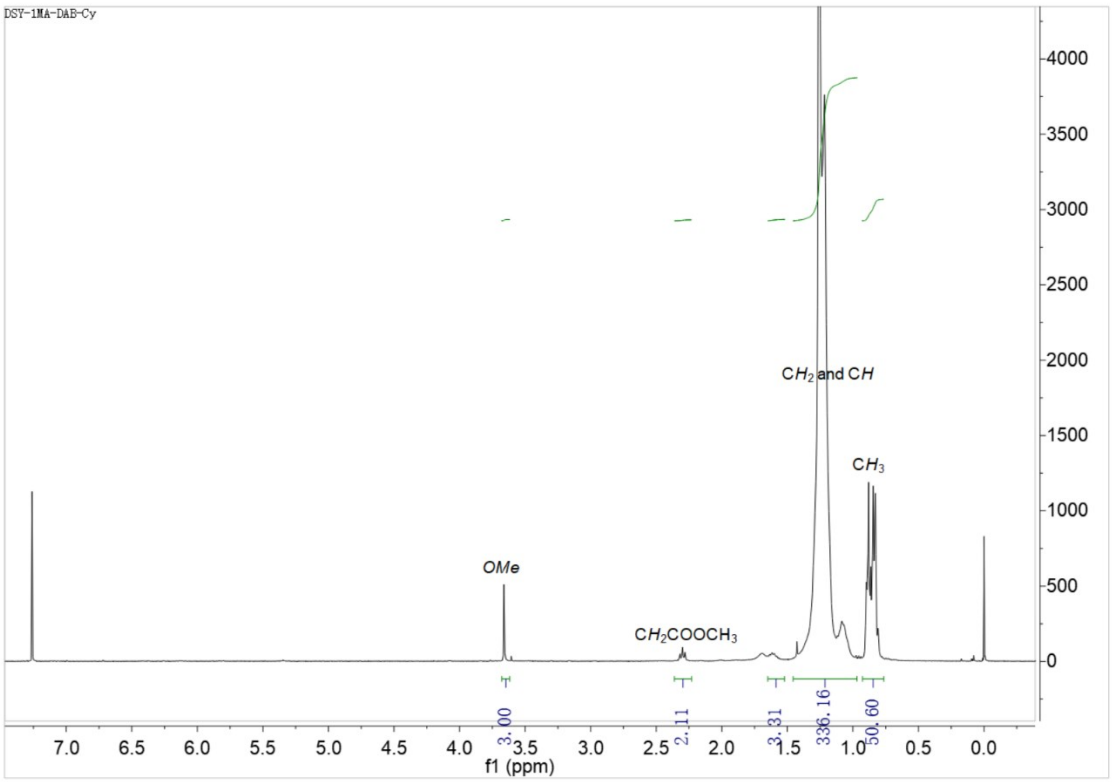


Figure S42. ^{1}H NMR spectrum of the polymer from table 3, entry 11 ($CDCl_3$, 20 ^{o}C).

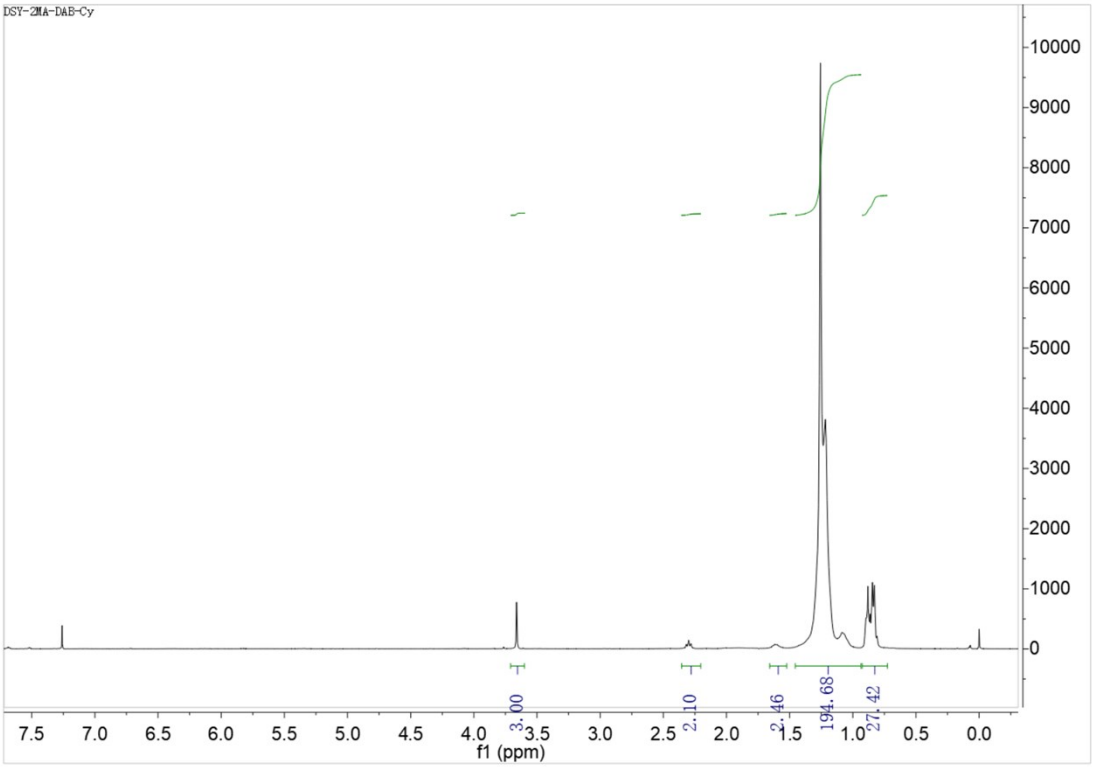


Figure S43. ^{1}H NMR spectrum of the polymer from table 3, entry 12 ($CDCl_3$, 20 ^{o}C).

3.4 DSC and GPC of Polymers.

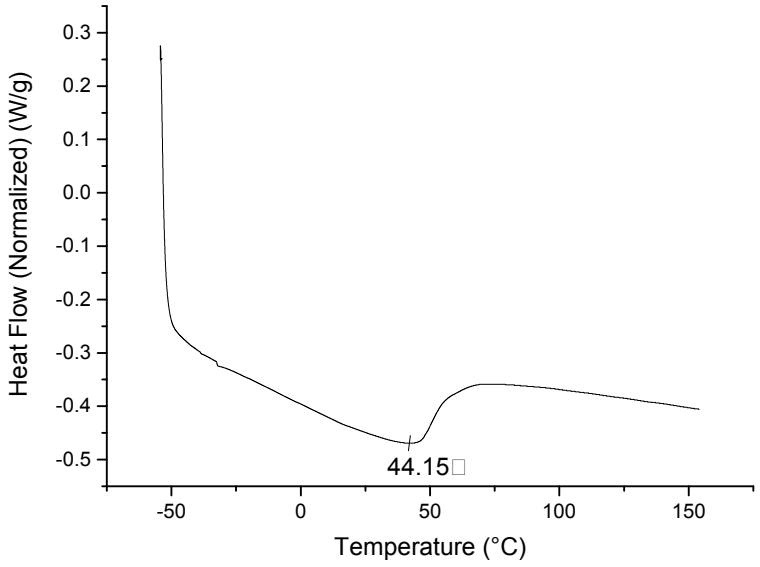


Figure S44. DSC of the polymer from table 1, entry 1.

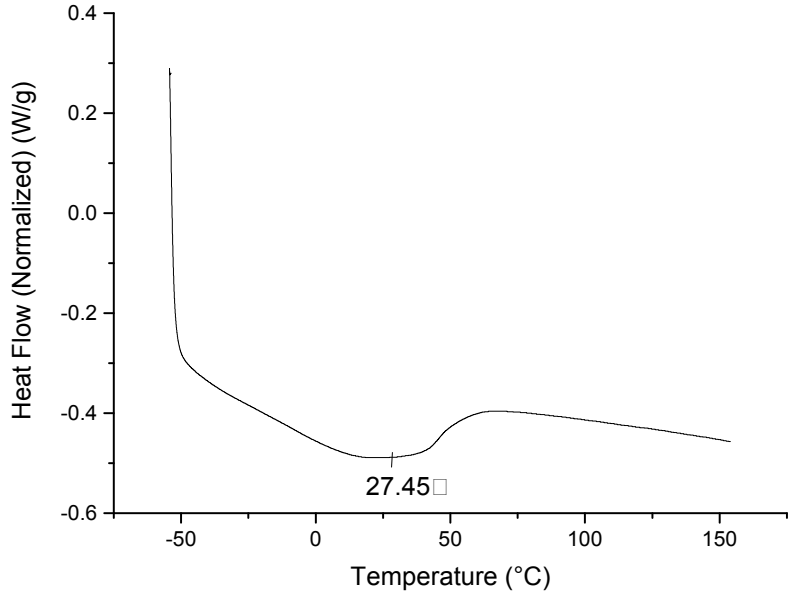


Figure S45. DSC of the polymer from table 1, entry 6.

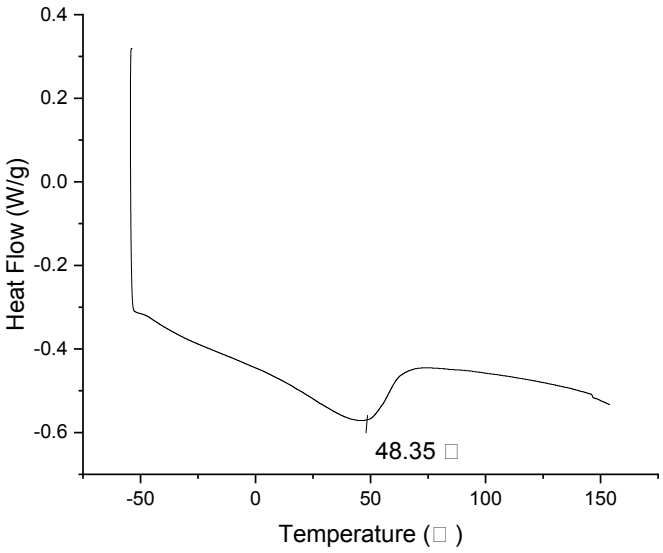


Figure S46. DSC of the polymer from table 1, entry 7.

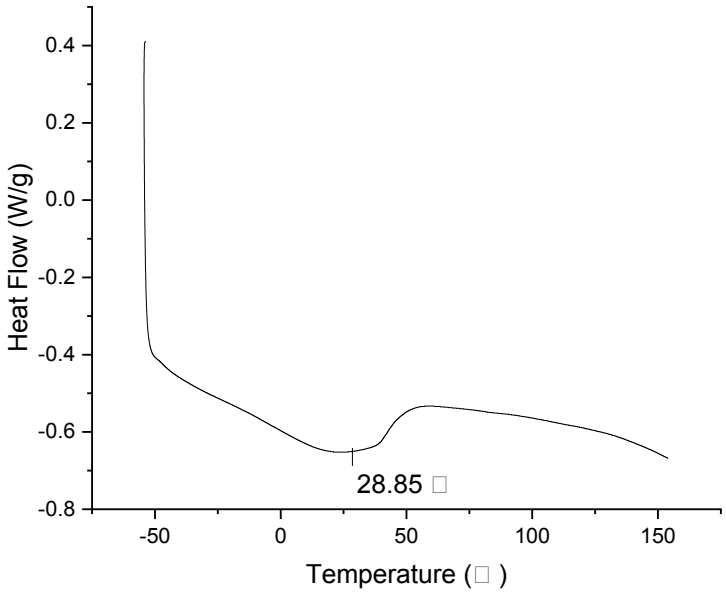


Figure S47. DSC of the polymer from table 1, entry 11.

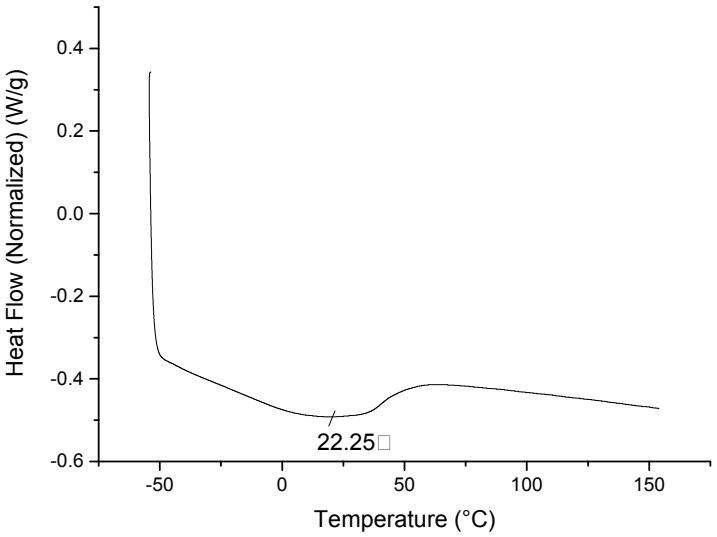
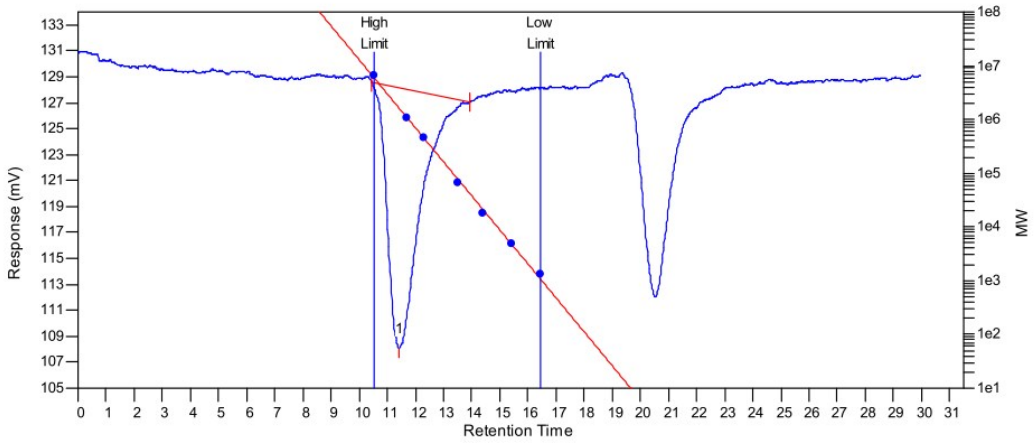
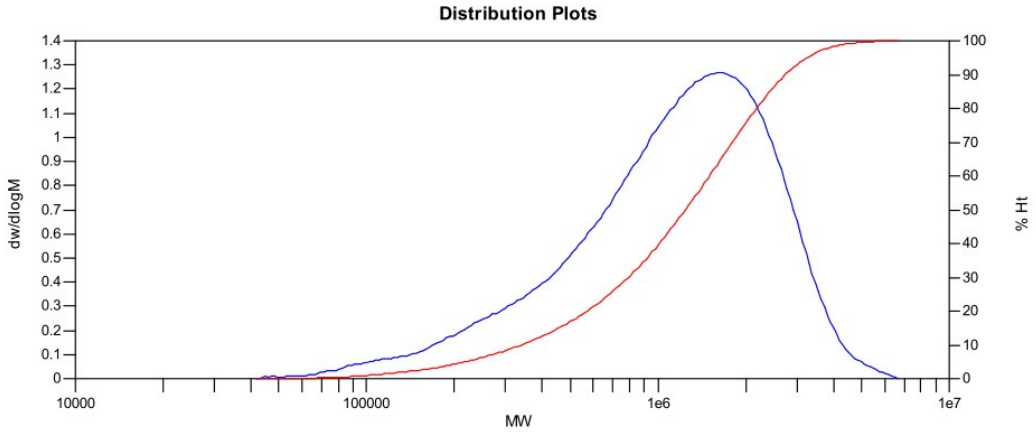


Figure S48. DSC of the polymer from table 1, entry 12.





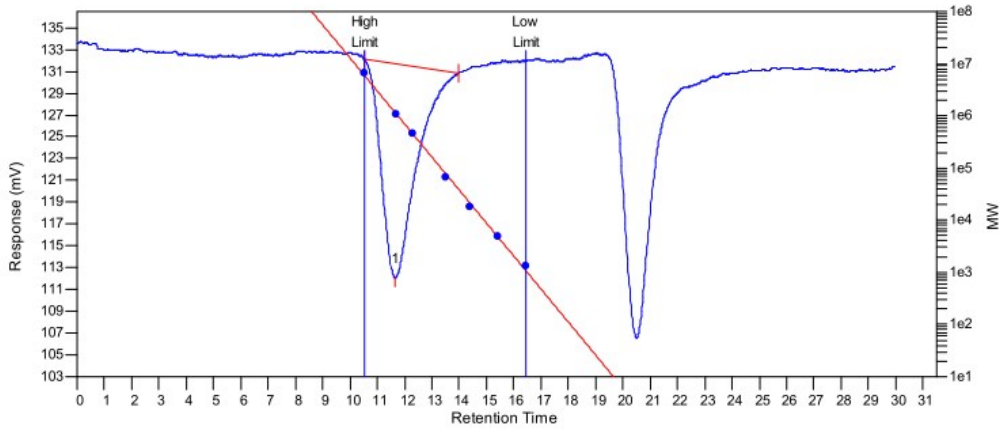
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1631216	707407	1408769	2057334	2618705	1312319	1.99145

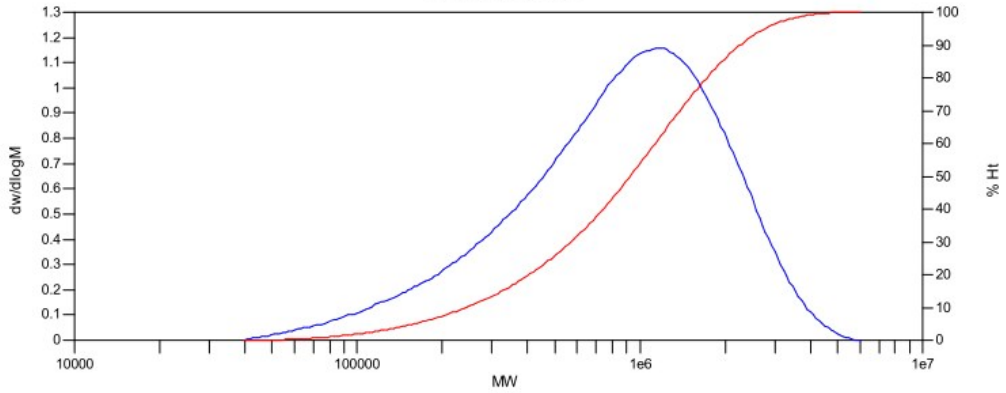
Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.45	11.42	13.93	-20.0765	100	1501.34	100

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



Distribution Plots



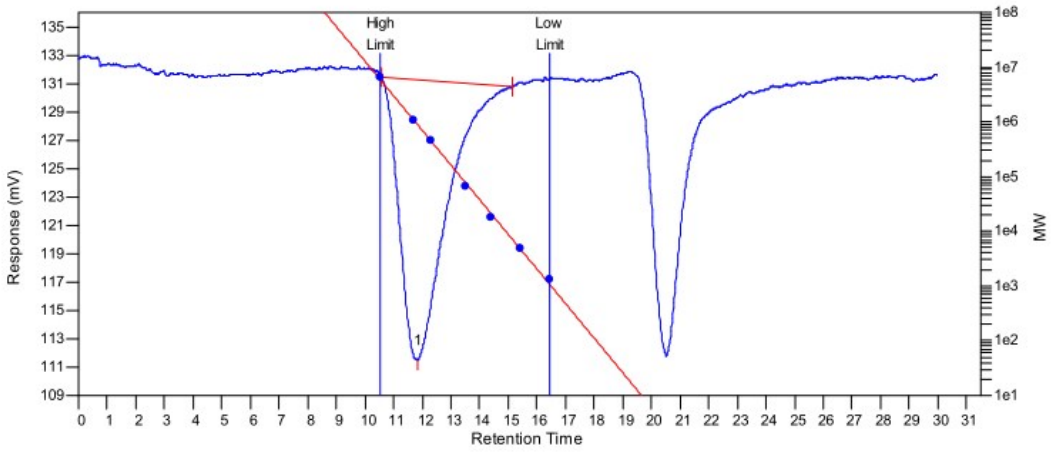
MW Averages

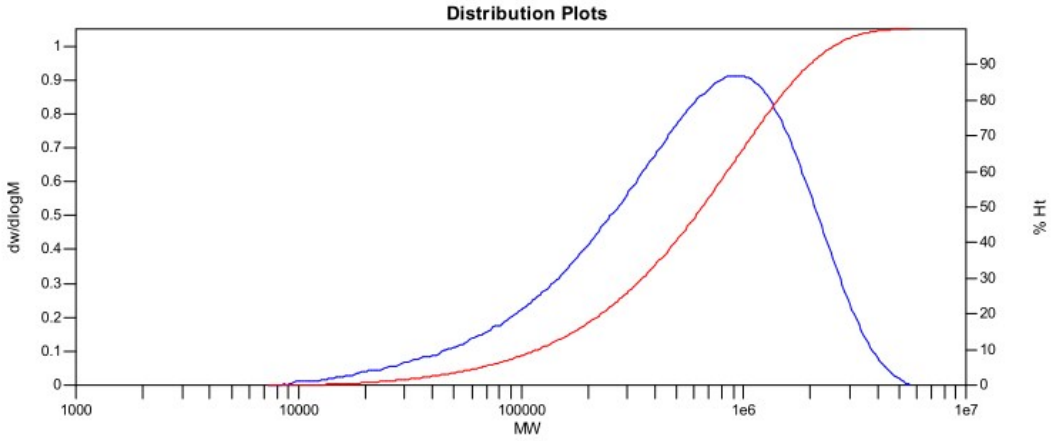
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1161277	525518	1105525	1721725	2280341	1018596	2.10369

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.52	11.65	13.97	-19.6208	100	1607.71	100

Figure S50. GPC of the polymer from table 1, entry 2.





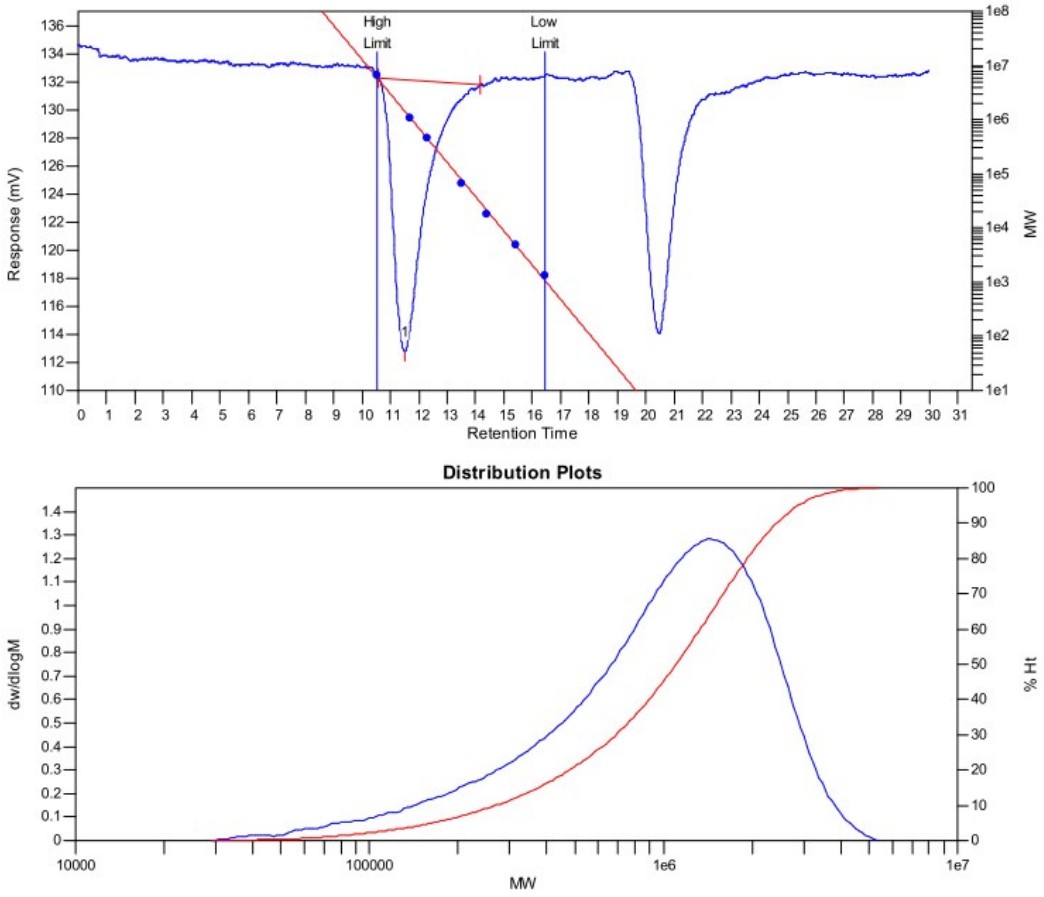
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	867846	252027	872311	1583419	2207444	775719	3.46118

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.57	11.85	15.13	-19.7679	100	2054.53	100

Figure S51. GPC of the polymer from table 1, entry 3.



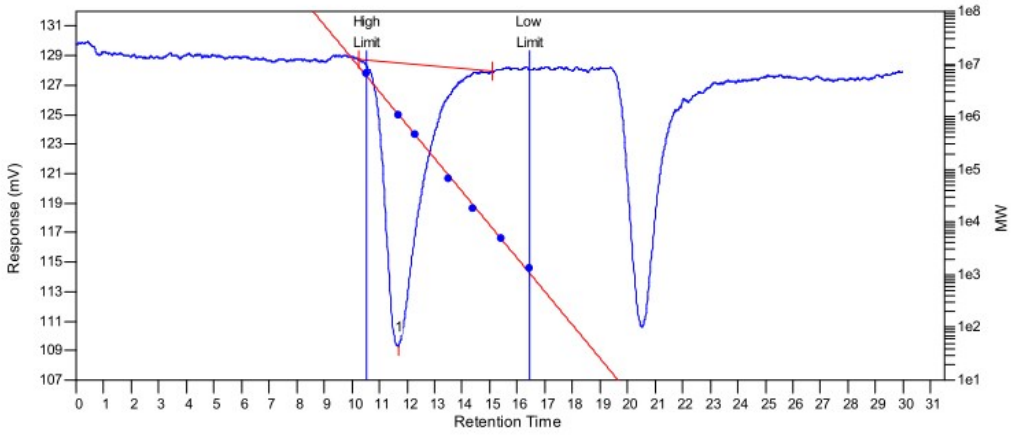
MW Averages

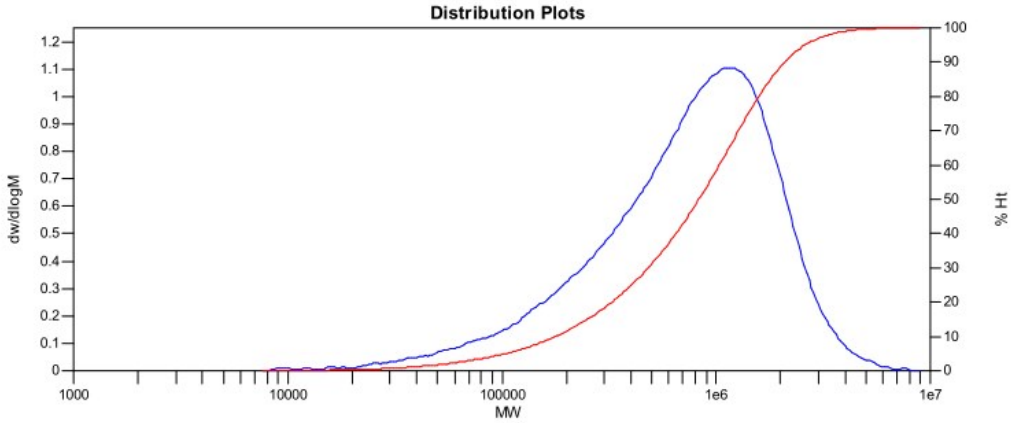
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1444794	562564	1235303	1808934	2267738	1147147	2.19584

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.60	11.50	14.18	-19.3749	100	1430.48	100

Figure S52. GPC of the polymer from table 1, entry 4.





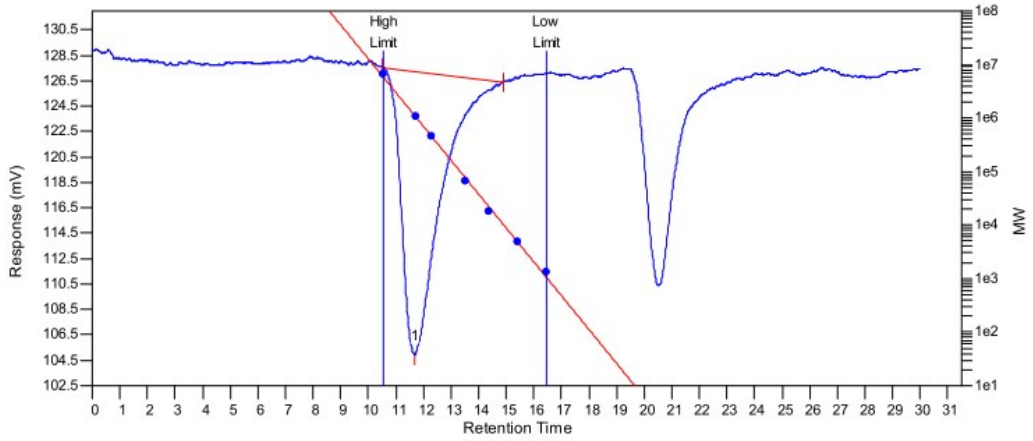
MW Averages

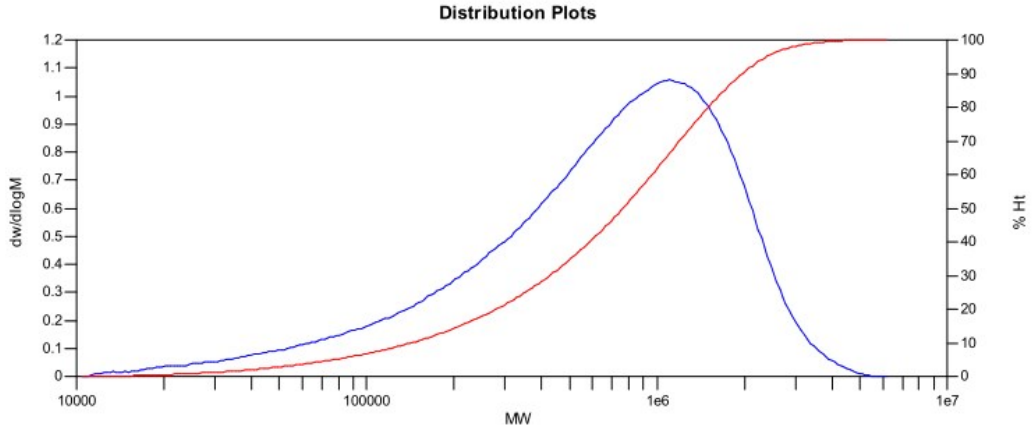
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1106251	353522	1011120	1700566	2435853	917737	2.86013

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.25	11.68	15.10	-19.1587	100	1646.43	100

Figure S53. GPC of the polymer from table 1, entry 5.





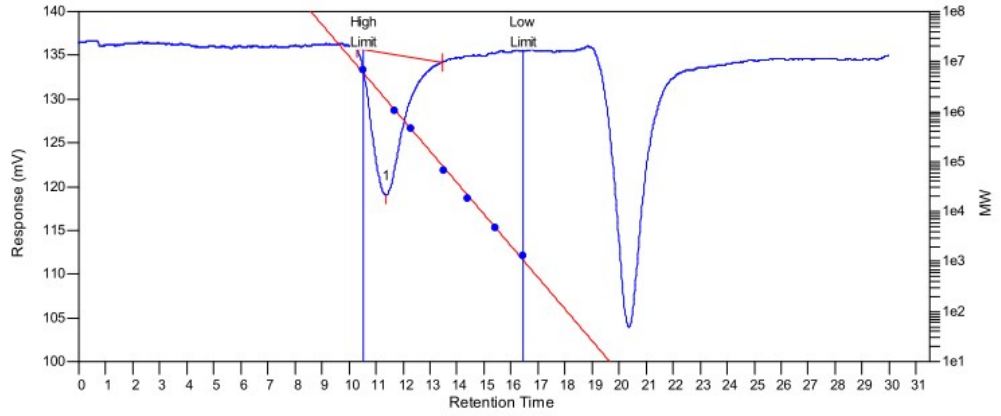
MW Averages

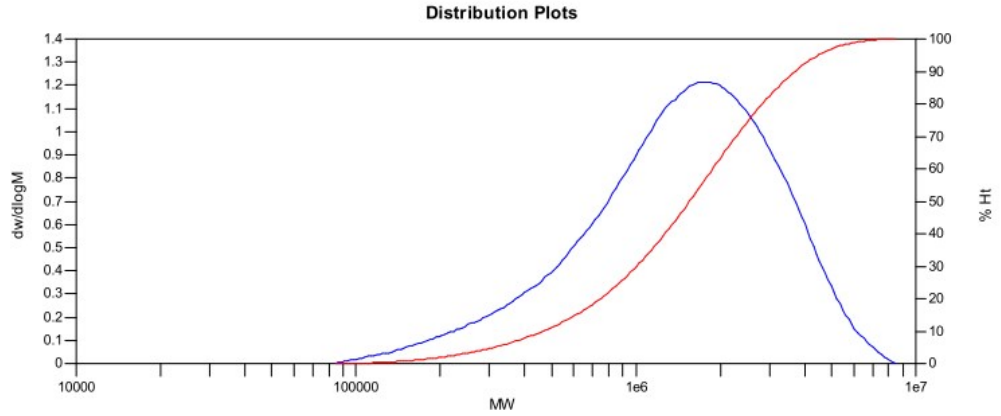
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1106251	295480	926645	1530575	2046498	838733	3.13607

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.50	11.68	14.88	-22.3331	100	2004.76	100

Figure S54. GPC of the polymer from table 1, entry 6.





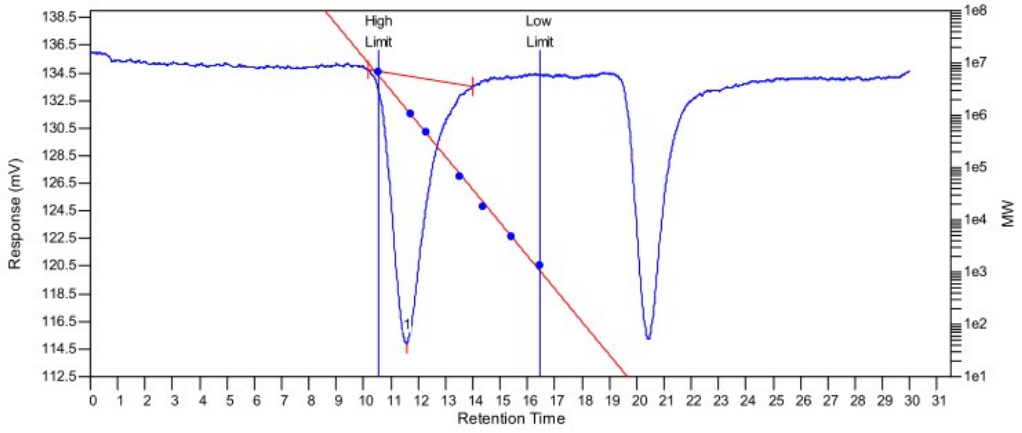
MW Averages

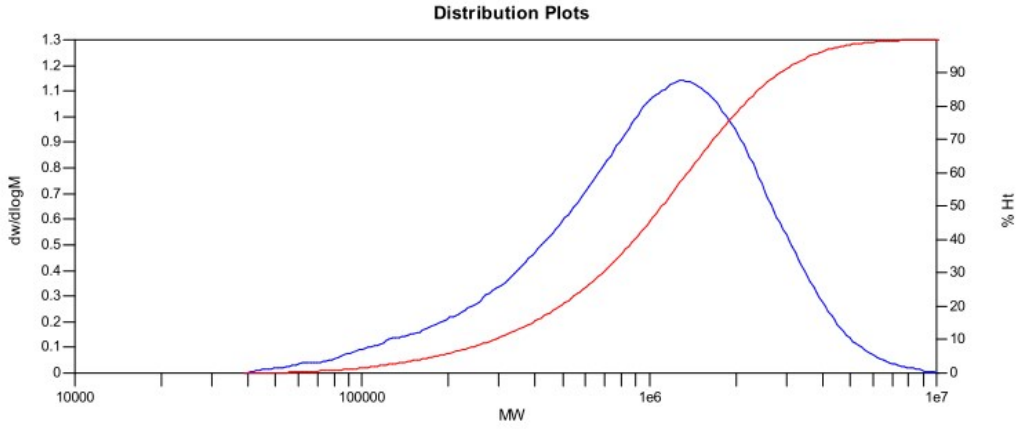
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1754425	967228	1838779	2757726	3592573	1708674	1.90108

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.28	11.37	13.45	-16.2391	100	1268.76	100

Figure S55. GPC of the polymer from table 1, entry 7.





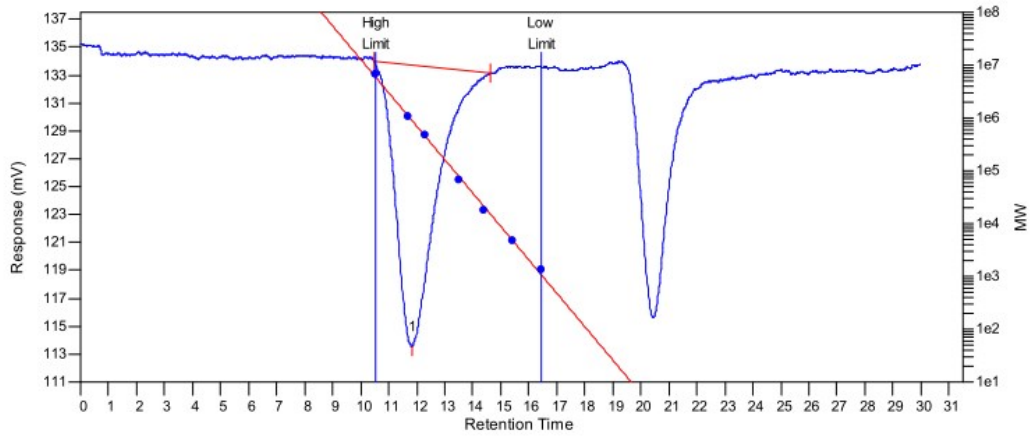
MW Averages

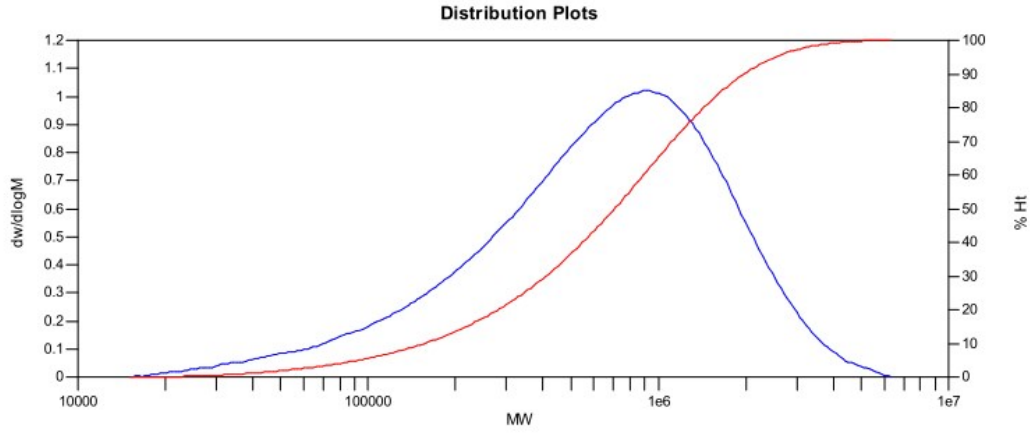
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1279677	609753	1376117	2298519	3310364	1256271	2.25684

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.15	11.58	13.98	-19.4339	100	1613.34	100

Figure S56. GPC of the polymer from table 1, entry 8.





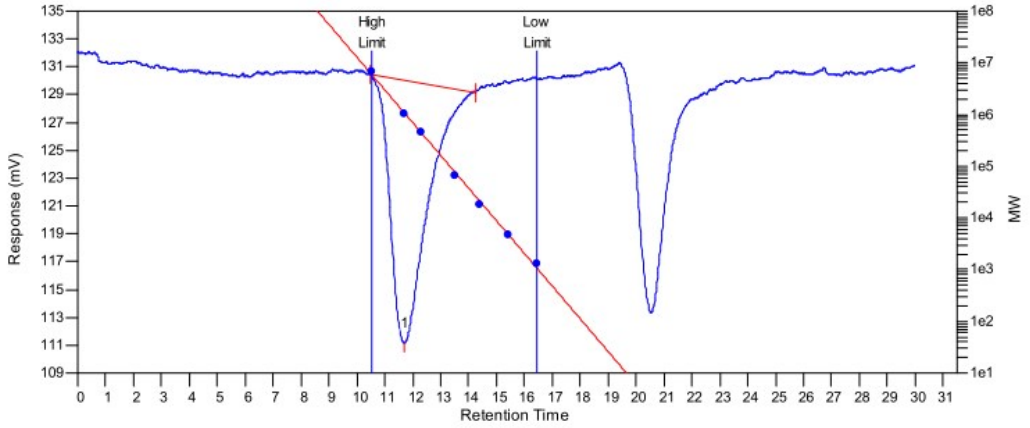
MW Averages

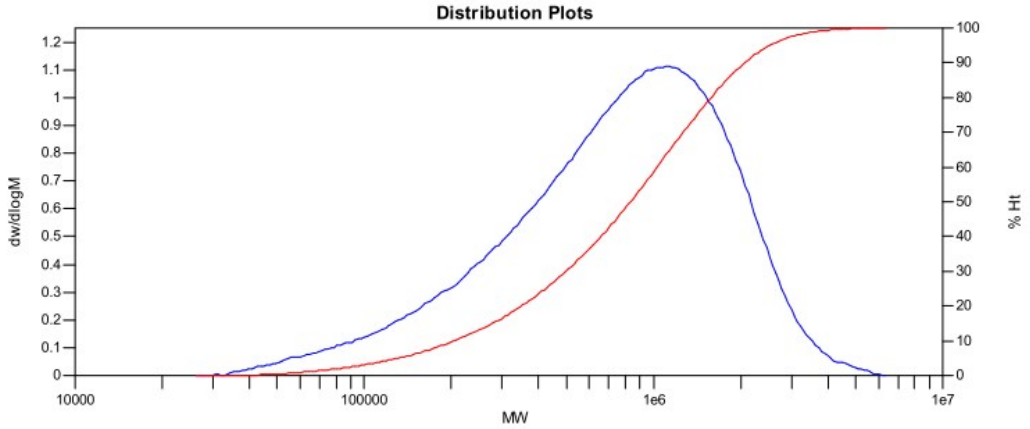
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	889168	333770	913432	1609440	2315114	822425	2.73671

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.48	11.83	14.63	-20.1457	100	1872.33	100

Figure S57. GPC of the polymer from table 1, entry 9.





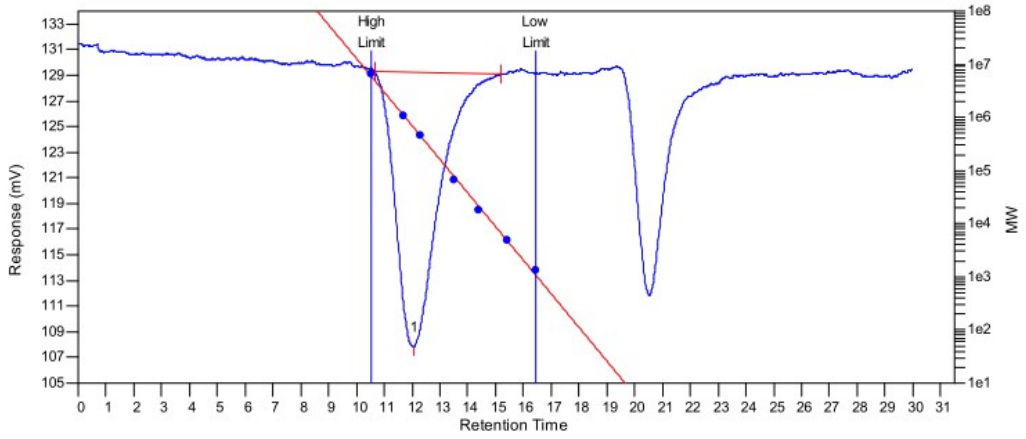
MW Averages

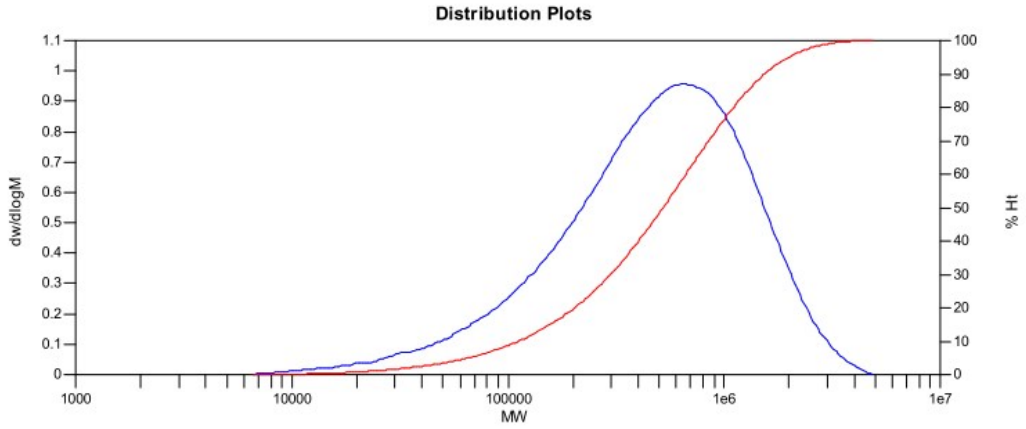
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1106251	446815	1003970	1606117	2180820	920180	2.24695

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.48	11.68	14.25	-18.9043	100	1612.56	100

Figure S58. GPC of the polymer from table 1, entry 10.





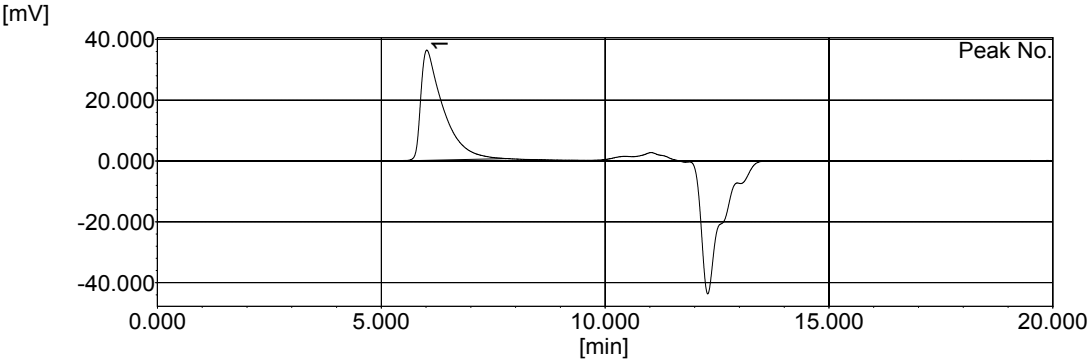
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	648559	228100	696067	1259598	1813524	622716	3.05159

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.67	12.05	15.20	-21.3702	100	2120.78	100

Figure S59. GPC of the polymer from table 1, entry 12.

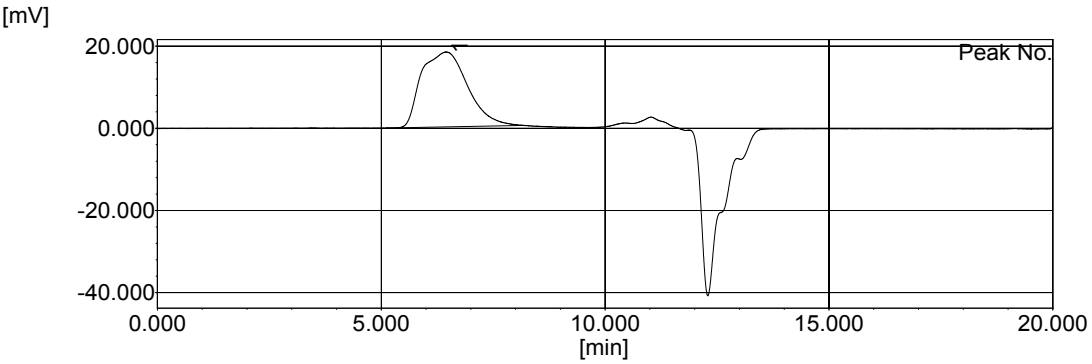


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.192	-0.029		Mn	422,216
			2,308,111	Mw	534,456
Peak top	6.013	36.485	682,468	Mz	614,371
Peak end	7.767	0.784	50,686	Mz+1	676,840
				Mv	534,456
Height [mV]			36.255	Mp	682,469
Area [mV*sec]			1257.610	Mz/Mw	1.150
Area% [%]			100.000	Mw/Mn	1.266
[eta]			534456.28047	Mz+1/Mw	1.266

Figure S60. GPC of the polymer from table 2, entry 1.

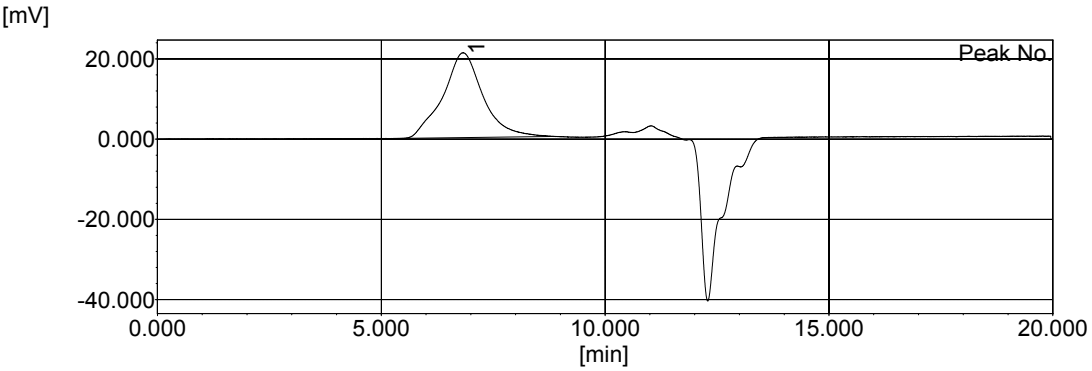


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.107	0.074	2,618,176	Mn	279,569
Peak top	6.453	18.598	355,395	Mw	435,731
Peak end	8.170	0.715	27,869	Mz	597,551
				Mz+1	742,609
Height [mV]			18.242	Mv	435,731
Area [mV*sec]			1308.353	Mp	355,395
Area% [%]			100.000	Mz/Mw	1.371
[eta]			435730.55993	Mw/Mn	1.559
				Mz+1/Mw	1.704

Figure S61. GPC of the polymer from table 2, entry 2.

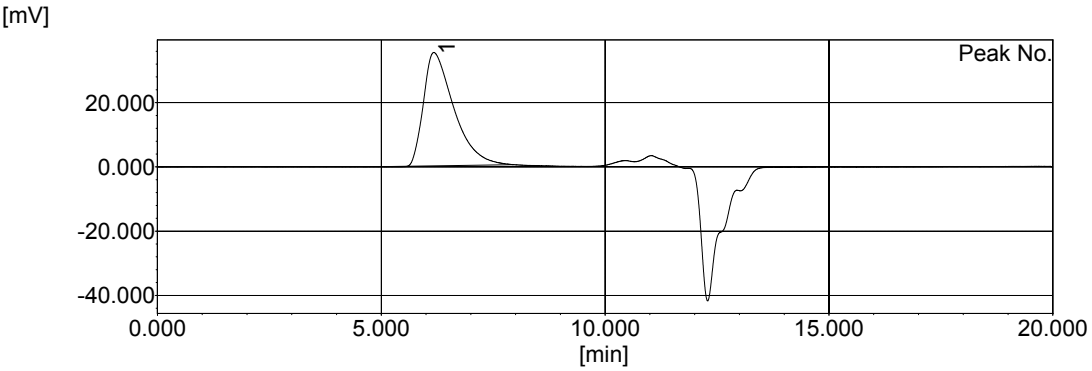


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.255	0.167	2,101,205	Mn	147,244
Peak top	6.830	21.571	203,296	Mw	250,548
Peak end	8.852	0.649	10,142	Mz	381,303
				Mz+1	535,619
				Mv	250,548
Height [mV]			21.193	Mp	203,296
Area [mV*sec]			1319.175	Mz/Mw	1.522
Area% [%]			100.000	Mw/Mn	1.702
[eta]			250548.29829	Mz+1/Mw	2.138

Figure S62. GPC of the polymer from table 2, entry 3.

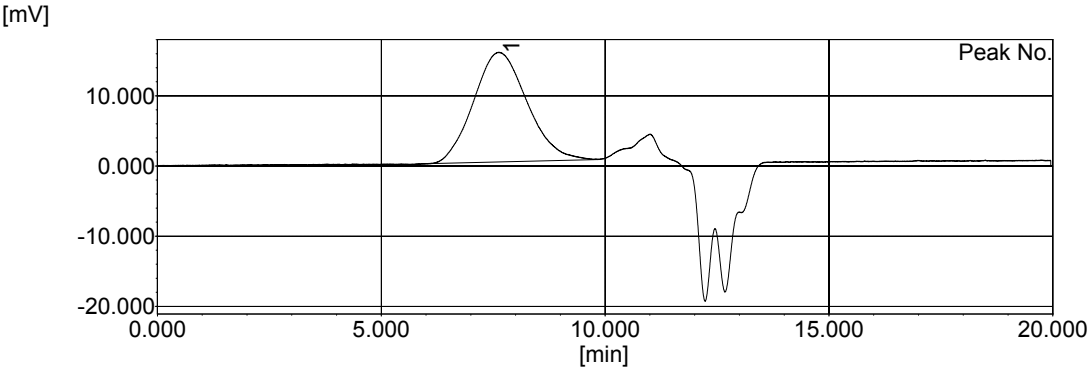


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.063	0.096	2,791,943	Mn	342,850
Peak top	6.165	35.629	545,011	Mw	460,531
Peak end	7.937	0.690	39,391	Mz	563,094
				Mz+1	664,795
				Mv	460,531
Height [mV]			35.305	Mp	545,011
Area [mV*sec]			1668.594	Mz/Mw	1.223
Area% [%]			100.000	Mw/Mn	1.343
[eta]			460531.13084	Mz+1/Mw	1.444

Figure S63. GPC of the polymer from table 2, entry 4.

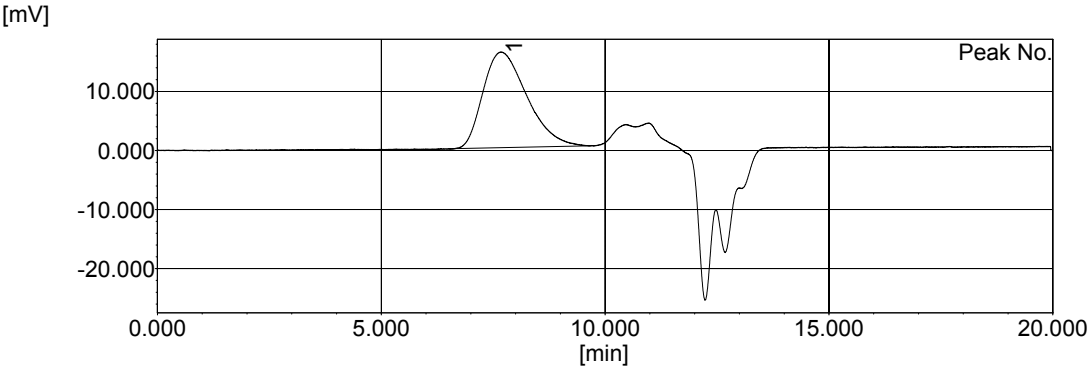


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.828	0.300	923,849	Mn	39,198
Peak top	7.613	16.226	65,128	Mw	79,595
Peak end	9.827	0.915	2,429	Mz	138,323
				Mz+1	212,290
				Mv	79,595
Height [mV]			15.651	Mp	65,128
Area [mV*sec]			1301.582	Mz/Mw	1.738
Area% [%]			100.000	Mw/Mn	2.031
[eta]			79595.15437	Mz+1/Mw	2.667

Figure S64. GPC of the polymer from table 3, entry 1.



Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	6.505	0.299	338,033	Mn	35,877
Peak top	7.668	16.710	60,017	Mw	58,136
Peak end	9.637	0.786	3,222	Mz	81,311
				Mz+1	103,611
				Mv	58,136
Height [mV]			16.230	Mp	60,018
Area [mV*sec]			1103.632	Mz/Mw	1.399
Area% [%]			100.000	Mw/Mn	1.620
[eta]			58135.53859	Mz+1/Mw	1.782

Figure S65. GPC of the polymer from table 3, entry 3.

4. References

(1) Dai, S.; Zhou, S.; Zhang, W.; Chen, C. Systematic Investigations of Ligand Steric Effects on α-diimine Palladium Catalyzed Olefin Polymerization and Copolymerization. *Macromolecules* **2016**, *49*, 8855-8862.

(2) Luo, B.; Liu, H.; Lin, Z.; Jiang, J.; Shen, D.; Liu, R.; Ke, Z.; Liu, F. Aerobic and Efficient Direct Arylation of Five-Membered Heteroarenes and Their Benzocondensed Derivatives with Aryl Bromides by Bulky α-Hydroxyimine Palladium Complexes. *Organometallics* **2015**, *34*, 4881-4894.

5. X-ray Crystallography

CCDC number of **Pd1** is 2052788. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

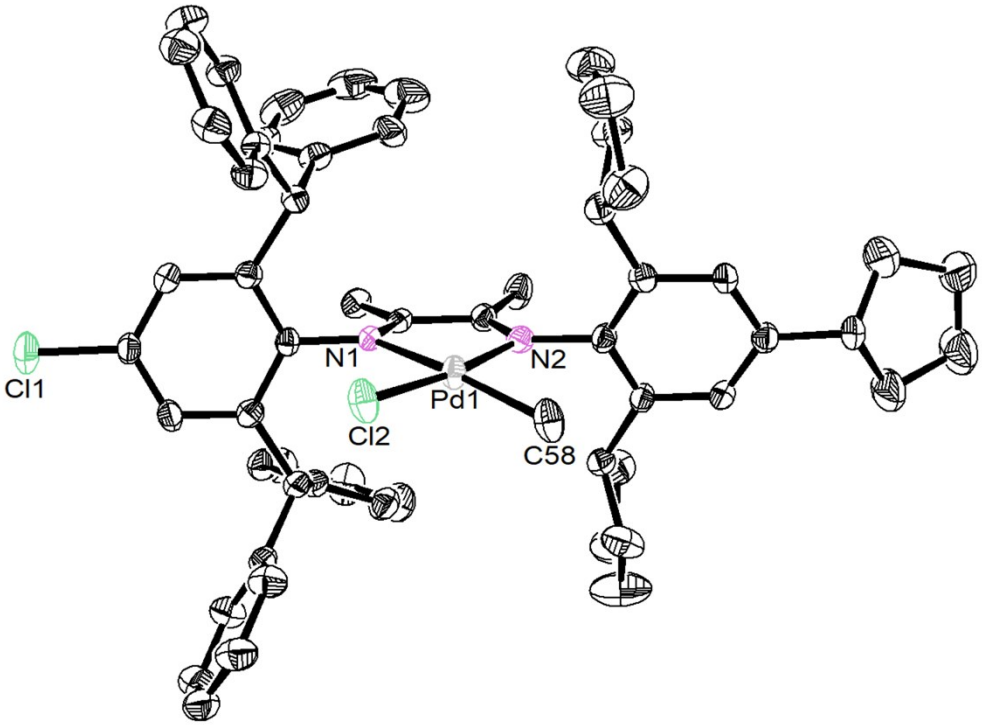


Table S2 Crystal data and structure refinement for Pd1.	
Identification code	Pd1
Empirical formula	C58 H62 Cl2 N2 Pd
Formula weight	964.40
Temperature/K	298(2) K
Crystal system	Monoclinic
Space group	P2(1)
a/Å	11.0865(11)
b/Å	24.739(2)
c/Å	18.0106(17)
α /°	90
β /°	100.813(2)
γ /°	90
Volume/Å^3	4852.1(8)
Z	4
ρ_{calc}g/cm^3	1.320

μ/mm^{-1}	0.533
F(000)	2016
Crystal size/mm^3	0.35 x 0.23 x 0.20
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.01 to 25.02
Index ranges	-13<=h<=13, -29<=k<=24, -21<=l<=20
Reflections collected	24137
Independent reflections	8558 [R(int) = 0.0638]
Data/restraints/parameters	8558 / 185 / 571
Goodness-of-fit on F^2	1.109
Final R indexes [I>=2σ (I)]	R1 = 0.0749, wR2 = 0.2027
Final R indexes [all data]	R1 = 0.1101, wR2 = 0.2311
Largest diff. peak/hole / e Å^{-3}	0.687 and -1.798