Supporting Information for:

A Remote Nonconjugated Electron Effect in Insertion Polymerization with α-Diimine Nickel and Palladium Species

Shuaikang Li, Guoyong Xu, Shengyu Dai*

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.

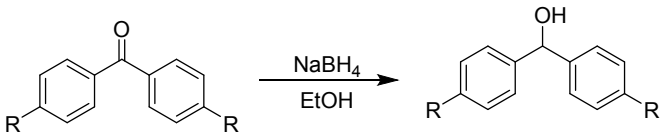
1. Experimental sections

1.1 General Considerations

All experiments were carried out under a dry Nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Solvent including dichloromethane, n-hexane and toluene were dried and distillated before. Other reagents were obtained from commercial sources and used without purification. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded by JNM-ECZ600R 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. Elemental analysis was performed by the Analytical Center of the Anhui University. 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. 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 were determined by gel permeation chromatography (GPC) with a PL 210 equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 160 ^{o}C using 1, 2, 4-trichlorobenzene as a solvent and calibrated with polystyrene standards.

Stress/strain experiments were performed at 10 mm/min by means of a Universal Test Machine (SUST-CMT5305) at room temperature. At least three specimens of each polymer were tested. Polymers were melt-pressed at 30 to 35^{o}C above their melting point to obtain the test specimens. The test specimens had 14-mm gauge length, 2-mm width, and thickness of 0.5 mm. 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 40°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).

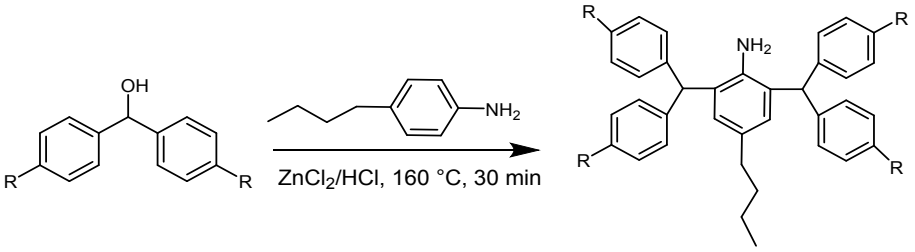
1.2 Procedure for the Synthesis of Diarylmethanols.



R = OMe (88%), Me (90%), F (93%)

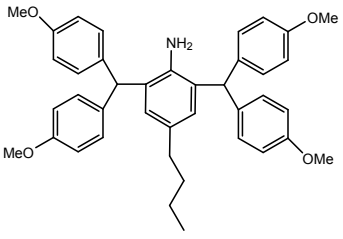
Diarylmethyl ketone (100 mmol, 1.0 equiv.) was dissolved in EtOH (300 mL), $NaBH_4$ (3.78g, 100 mmol, 1.0 equiv.) was then slowly added over a period of 10 min, and the mixture was stirred at room temperature overnight. 1 M HCl (aqueous, 1 mL) was added to quench the reaction, then the mixture was separated by filtration, the obtained solvent was evaporated at reduced pressure. The solid was dissolved with DCM (100 mL), then washed with water (100 mL×3). The organic layers were dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. These three compounds are known.[1]

1.3 Procedure for the Synthesis of Anilines.

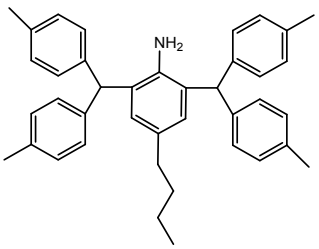


R = OMe, Me, H, F

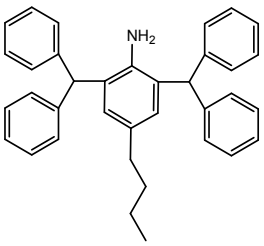
A mixture of diarylmethanol (40.0 mmol, 2.0 equiv.) and *p*-butylaniline (2.98 g, 20 mmol, 1.0 equiv.) was heated to 120 °C. A solution of anhydrous zinc chloride (1.36 g, 10 mmol, 0.5 equiv.) in concentrated hydrochloric acid (1.2 mL, 37% in H_2O, 1.0 equiv.) was added to the mixture (exothermic + intense bubbling), and the temperature was raised to 160 °C. After 30 min at 160 °C, the reaction mixture was cooled to room temperature and dissolved in CH_2Cl_2 (200 mL). The CH_2Cl_2 layer was washed with water (3 × 100 mL) and dried over anhydrous magnesium sulfate. The solution was concentrated to 20 mL. The product was crashed out with 200 ml EtOH and washed with EtOH (3 × 20 mL).



A1 (8.42 g, 70%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.6 Hz, 8H, Ar-*H*), 6.82 (d, *J* = 8.6 Hz, 8H, Ar-*H*), 6.37 (s, 2H, Ar-*H*), 5.35 (s, 2H, C*H*Ar_2), 3.79 (s, 12H, OC*H*$_3$), 3.32 (s, *br*, 2H, N*H*$_2$), 2.32 – 2.24 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.35 – 1.27 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.19 (dq, *J* = 14.5, 7.2 Hz, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.81 (t, *J* = 7.3 Hz, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.19, 139.74, 135.36, 131.83, 130.43, 129.70, 128.16, 113.86, 55.29 (OCH_3), 50.84 (*C*HAr_2), 35.09 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.89 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.25 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.98 (CH$_2$CH$_2$CH$_2$*C*H$_3$). ESI-MS (m/z): calcd for $C_{40}H_{44}NO_4$: 602.3270, Found, 602.3278, $[M+H]^+$.

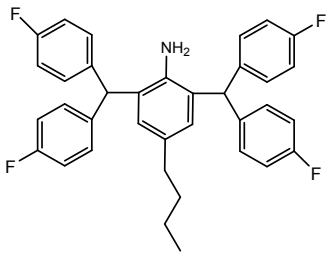


A2 (10.03 g, 93%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.8 Hz, 8H, Ar-*H*), 6.99 (d, *J* = 7.9 Hz, 8H, Ar-*H*), 6.41 (s, 2H, Ar-*H*), 5.39 (s, 2H, C*H*Ar_2), 3.31 (s, *br*, 2H, N*H*$_2$), 2.34 (s, 12H, Ar-C*H*$_3$), 2.32 – 2.28 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.33 (dt, *J* = 15.2, 7.5 Hz, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.23 – 1.14 (m, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.81 (t, *J* = 7.3 Hz, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.16, 139.88, 135.97, 131.73, 129.44, 129.39, 129.19, 128.28, 51.76 (*C*HAr_2), 35.02 (*C*H$_2$CH$_2$CH$_2$*C*H$_3$), 33.83 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.22 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 21.16 (Ar-*C*H$_3$), 13.98 (CH$_2$CH$_2$CH$_2$*C*H$_3$). ESI-MS (m/z): calcd for $C_{40}H_{44}N$: 538.3474, Found, 538.3474, $[M+H]^+$.



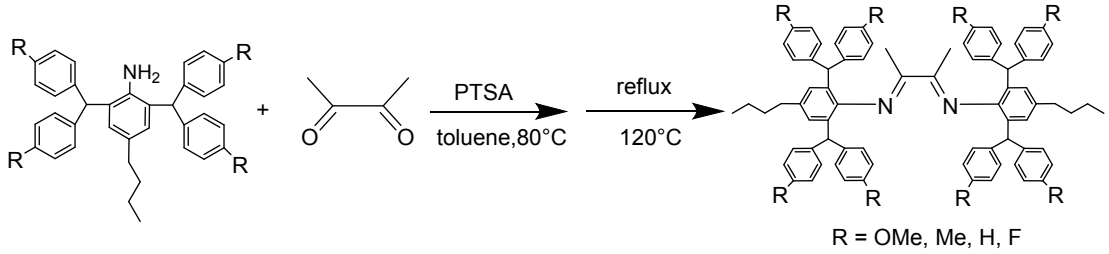
A3 (8.66 g, 90%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 8H, Ar-*H*), 7.23 (t, *J* = 7.3 Hz, 4H, Ar-*H*), 7.11 (d, *J* = 7.3 Hz, 8H, Ar-*H*), 6.40 (s, 2H, Ar-*H*), 5.48 (s, 2H, C*H*Ar_2), 3.30 (s, *br*, 2H, N*H*$_2$), 2.33 – 2.25 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.32 (dt, *J* = 12.8, 7.5 Hz, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.23 – 1.13 (m, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.80 (t, *J* = 7.3 Hz, 3H,

$CH_2CH_2CH_2CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.93, 139.88, 131.91, 129.63, 129.20, 128.52, 126.64, 52.52 ($CHAr_2$), 34.99 ($CH_2CH_2CH_2CH_3$), 33.75 ($CH_2CH_2CH_2CH_3$), 22.17 ($CH_2CH_2CH_2CH_3$), 13.95 ($CH_2CH_2CH_2CH_3$). ESI-MS (m/z): calcd for $C_{36}H_{36}N$: 482.2848, Found, 482.2849, $[M+H]^+$.



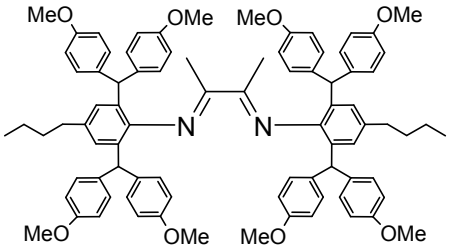
A4 (8.20 g, 74%), ^1H NMR (600 MHz, $CDCl_3$) δ 7.03 (tt, J = 4.7, 2.3 Hz, 8H, Ar-*H*), 7.01 – 6.96 (m, 8H, Ar-*H*), 6.34 (s, 2H, Ar-*H*), 5.41 (s, 2H, $CHAr_2$), 3.25 (s, *br*, 2H, NH_2), 2.31 – 2.26 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.35 – 1.27 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.22 – 1.15 (m, 2H, $CH_2CH_2CH_2CH_3$), 0.81 (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_2CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.56, 160.93, 139.49, 138.32, 138.31, 132.31, 130.91, 130.86, 129.01, 128.44, 115.59, 115.44, 50.91 ($CHAr_2$), 34.97 ($CH_2CH_2CH_2CH_3$), 33.76 ($CH_2CH_2CH_2CH_3$), 22.17 ($CH_2CH_2CH_2CH_3$), 13.91 ($CH_2CH_2CH_2CH_3$). ^{19}F NMR (565 MHz, $CDCl_3$) δ -115.56. ESI-MS (m/z): calcd for $C_{36}H_{32}F_4N$: 554.2471, Found, 554.2474, $[M+H]^+$.

1.4 Procedure for the Synthesis of Ligands L1-L4.

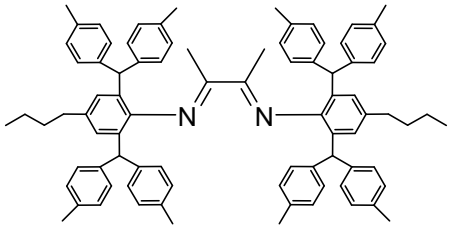


The ligand **L1-L4** were prepared as follows: a solution of anilines (8 mmol), 2, 3-butadione (344 mg, 4 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (50 mL) was stirred at 80 °C for 24 h, then the reactions were refluxed with Dean-stark trap at 120 °C for 3 days until there was one main point on the TLC plate. The solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in EtOH

(300 mL). The yellow solid was isolated by filtration, washed three times by 20 mL EtOH and dried under high vacuum.

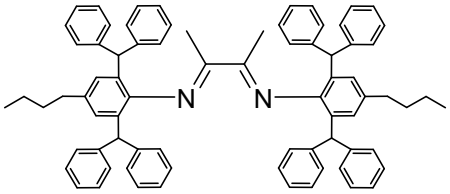


L1 (2.70 g, 54%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.5 Hz, 8H, Ar-*H*), 6.87 (d, *J* = 8.5 Hz, 8H, Ar-*H*), 6.75 (d, *J* = 8.6 Hz, 8H, Ar-*H*), 6.72 (d, *J* = 8.5 Hz, 8H, Ar-*H*), 6.65 (s, 4H, Ar-*H*), 5.08 (s, 4H, C*H*Ar_2), 3.76 (s, 12H, OC*H*$_3$), 3.71 (s, 12H, OC*H*$_3$), 2.47 – 2.34 (m, 4H, C*H*$_2$$CH_2CH_2CH_3$), 1.47 – 1.36 (m, 4H, CH_2C*H*$_2$$CH_2CH_3$), 1.29 – 1.18 (m, 10H, CH_2CH_2C*H*$_2$$CH_3$, C*H*$_3$), 0.85 (t, *J* = 7.3 Hz, 6H, $CH_2CH_2CH_2$C*H*$_3$).^{13}C NMR (151 MHz, $CDCl_3$) δ 169.82 (*C*=N), 157.98, 157.81, 145.64, 136.86, 136.50, 135.67, 131.35, 130.54, 130.31, 128.03, 113.72, 113.44, 55.25 (OC*H*$_3$), 55.23 (OC*H*$_3$), 50.00 (*C*HAr_2), 35.31 (*C*$H_2CH_2CH_2CH_3$), 33.81 (CH_2C*H*$_2$$CH_2CH_3$), 22.29 ($CH_2CH_2$C*H*$_2$$CH_3$), 17.02 (*C*H$_3$), 14.00 ($CH_2CH_2CH_2$C*H*$_3$). ESI-MS (m/z): calcd for $C_{84}H_{89}N_2O_8$: 1253.6619, Found, 1253.6644, $[M+H]^+$.

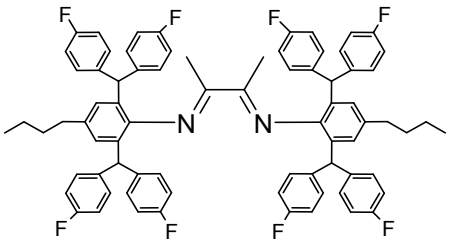


L2 (2.29 g, 51%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.9 Hz, 8H, Ar-*H*), 6.97 (d, *J* = 7.9 Hz, 8H, Ar-*H*), 6.93 (d, *J* = 7.9 Hz, 8H, Ar-*H*), 6.85 (d, *J* = 7.9 Hz, 8H, Ar-*H*), 6.69 (s, 4H, Ar-*H*), 5.08 (s, 4H, C*H*Ar_2), 2.43 – 2.38 (m, 4H, CH_2C*H*$_2$$CH_2CH_3$), 2.29 (s, 12H, Ar-C*H*$_3$), 2.27 (s, 12H, Ar-C*H*$_3$), 1.46 – 1.37 (m, 4H, CH_2C*H*$_2$$CH_2CH_3$), 1.26 – 1.22 (m, 4H, CH_2CH_2C*H*$_2$$CH_3$), 1.21 (s, 6H, C*H*$_3$), 0.84 (t, *J* = 7.3 Hz, 6H, $CH_2CH_2CH_2$C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.82 (*C*=N), 145.83, 141.35, 140.38, 136.71, 135.57, 135.28, 131.05, 129.52, 129.32, 129.02, 128.74, 128.10, 50.83 (*C*HAr_2), 35.25 (*C*$H_2CH_2CH_2CH_3$), 33.77 (CH_2*C*$H_2CH_2CH_3$), 22.24 (CH_2CH_2*C*H_2CH_3), 21.09 (Ar-*C*H$_3$), 16.85 (*C*H$_3$), 13.98

($CH_2CH_2CH_2CH_3$). ESI-MS (m/z): calcd for $C_{84}H_{89}N_2$: 1125.7026, Found,1125.7052, $[M+H]^+$.

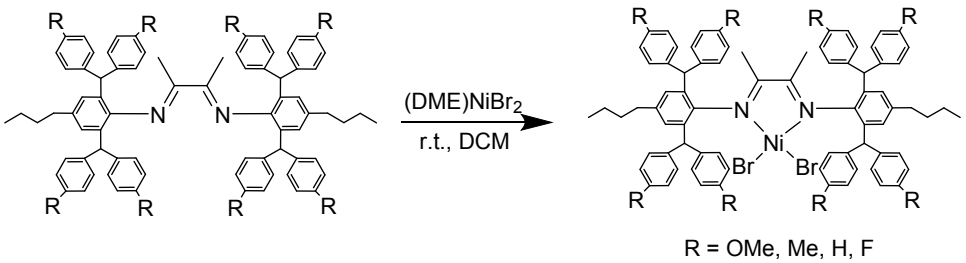


L3 (2.96 g, 65%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.5 Hz, 8H, Ar-*H*), 7.18 (dt, *J* = 14.1, 6.0 Hz, 16H, Ar-*H*), 7.10 (d, *J* = 7.3 Hz, 8H, Ar-*H*), 7.01 (d, *J* = 7.1 Hz, 8H, Ar-*H*), 6.70 (s, 4H, Ar-*H*), 5.21 (s, 4H, C*H*Ar_2), 2.42 (t, *J* = 7.6 Hz, 4H, C*H*$_2CH_2CH_2CH_3$), 1.43 (dt, *J* = 15.1, 7.5 Hz, 4H, CH_2C*H*$_2CH_2CH_3$), 1.24 (dt, *J* = 18.6, 5.5 Hz, 4H, CH_2CH_2C*H*$_2CH_3$), 1.21 (s, 6H, C*H*$_3$), 0.85 (t, *J* = 7.3 Hz, 6H, $CH_2CH_2CH_2$C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.89 (*C*=N), 145.81, 143.96, 143.19, 136.94, 130.83, 129.78, 129.52, 128.45, 128.13, 126.42, 126.13, 51.76 (*C*HAr_2), 35.25 (*C*$H_2CH_2CH_2CH_3$), 33.72 (CH_2*C*$H_2CH_2CH_3$), 22.23 (CH_2CH_2*C*H_2CH_3), 16.81 (*C*H_3), 14.00 ($CH_2CH_2CH_2$*C*H_3). ESI-MS (m/z): calcd for $C_{76}H_{73}N_2$: 1013.5774, Found, 1013.5758, $[M+H]^+$.

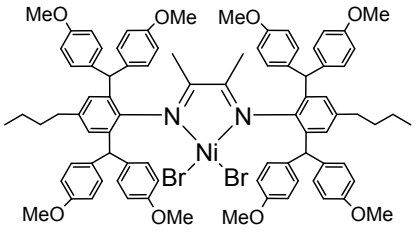


L4 (2.81g, 62%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 – 6.90 (m, 16H, Ar-*H*), 6.90 – 6.84 (m, 16H, Ar-*H*), 6.59 (s, 4H, Ar-*H*), 5.08 (s, 4H, C*H*Ar_2), 2.44 – 2.37 (m, 4H, C*H*$_2CH_2CH_2CH_3$), 1.43 – 1.37 (m, 4H, CH_2C*H*$_2CH_2CH_3$), 1.23 (dt, *J* = 14.7, 7.4 Hz, 4H, CH_2CH_2C*H*$_2CH_3$), 1.18 (s, 6H, C*H*$_3$), 0.84 (t, *J* = 7.3 Hz, 6H, $CH_2CH_2CH_2$C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.73 (*C*=N), 162.36, 162.29, 160.73, 160.67, 145.14, 139.10, 138.54, 137.71, 130.96, 130.91, 130.70, 130.65, 130.60, 128.43, 115.51, 115.37, 115.17, 115.03, 50.21 (*C*HAr_2), 35.17 (*C*$H_2CH_2CH_2CH_3$), 33.63 (CH_2*C*$H_2CH_2CH_3$), 22.20 (CH_2CH_2*C*H_2CH_3), 17.00 (*C*H_3), 13.91 ($CH_2CH_2CH_2$*C*H_3).^{19}F NMR (565 MHz, $CDCl_3$) δ -115.72, -116.41. ESI-MS (m/z): calcd for $C_{76}H_{65}F_8N_2$: 1157.5020, Found, 1157.5043, $[M+H]^+$.

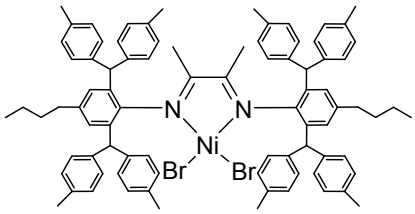
1.5 Procedure for the Synthesis of Nickel Complexes Ni1-Ni4.



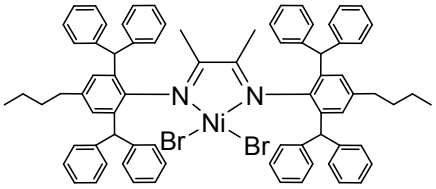
Complexes **Ni1-Ni4** were synthesized by the reaction of 1 equiv. of (DME)$NiBr_2$ with the corresponding ligands in methylene chloride. The corresponding ligand (0.2 mmol) was added in 5 mL of methylene chloride in a Schlenk tube under a nitrogen atmosphere. (DME)$NiBr_2$ (0.2 mmol, 62 mg) was added to the above solution. The resulting mixture was stirred at room temperature overnight. The solvent was evaporated under reduced pressure to afford a solid. The product was washed with 4 × 5 mL diethyl ether and dried under vacuum. The single crystal can be obtained by diffusion from layering hexane on to the CH_2Cl_2 solution at room temperature.



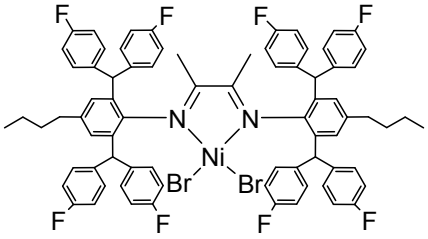
Ni1 (0.22 g, 74%), red solid, MALDI-TOF-MS (m/z): calcd for $C_{84}H_{88}BrN_2NiO_8$: 1391.51, Found, 1391.55, $[M-Br]^+$. Anal. Calcd for $C_{84}H_{88}Br_2N_2NiO_8$: C, 68.53; H, 6.03; N, 1.90; Found, C, 68.45; H, 6.16; N, 1.97.



Ni2 (0.22 g, 82%), red solid, MALDI-TOF-MS (m/z): calcd for $C_{84}H_{88}BrN_2Ni$: 1261.55, Found, 1261.35, [M-Br]+ Anal. Calcd for C84H88Br2N2Ni: C, 75.06; H, 6.60; N, 2.08; Found, C, 75.24; H, 6.46; N, 2.24.

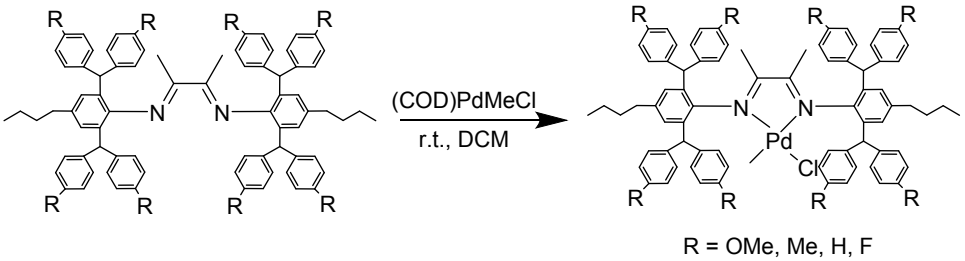


Ni3 (0.21 g, 84%), red solid, MALDI-TOF-MS (m/z): calcd for $C_{76}H_{72}BrN_2Ni$: 1151.42, Found, 1151.31, [M-Br]+. Anal. Calcd for C76H72Br2N2Ni: C, 74.10; H, 5.89; N, 2.27; Found, C, 74.31; H, 6.01; N, 2.14.

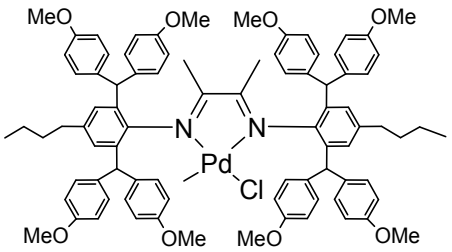


Ni4 (0.21 g, 77%), red solid, MALDI-TOF-MS (m/z): calcd for $C_{76}H_{64}F_8BrN_2Ni$: 1295.35, Found, 1295.21, $[M-Br]^+$. Anal. Calcd for $C_{76}H_{64}F_8Br_2N_2Ni$: C, 66.35; H, 4.69; N, 2.04; Found, C, 66.61; H, 4.78; N, 2.31.

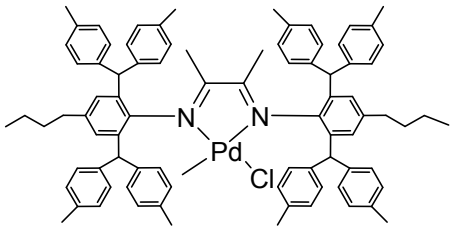
1.6 Procedure for the Synthesis of Palladium Complexes Pd1-Pd4.



A mixture of the ligand (1 mmol), Pd(COD)MeCl (265 mg, 1 mmol) in CH_2Cl_2 (20 mL) was stirred for 3 days at room temperature. During stirring, the color of the solution was deepening. At the end of the reaction, the desired compound was isolated using column chromatography. The pure compound was obtained as an orange or red solid.

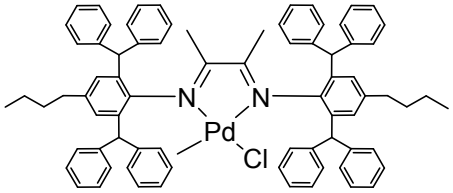


Pd1 (1.01 g, 72%),[1]H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 4H, Ar-*H*), 7.29 – 7.24 (m, 4H, Ar-*H*), 7.01 (d, *J* = 8.5 Hz, 4H, Ar-*H*), 6.97 (s, 2H, Ar-*H*), 6.92 (d, *J* = 8.6 Hz, 4H, Ar-*H*), 6.79 (dd, *J* = 16.0, 8.7 Hz, 8H, Ar-*H*), 6.73 (s, 2H, Ar-*H*), 6.63 (d, *J* = 8.7 Hz, 4H, Ar-*H*), 6.57 (d, *J* = 8.6 Hz, 4H, Ar-*H*), 5.90 (s, 2H, C*H*Ar_2), 5.63 (s, 2H, C*H*Ar_2), 3.77 (s, 6H, OC*H*$_3$), 3.76 (s, 6H, OC*H*$_3$), 3.68 (s, 6H, OC*H*$_3$), 3.65 (s, 6H, OC*H*$_3$), 2.54 – 2.47 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.46 – 2.40 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.48 (tt, *J* = 15.2, 7.6 Hz, 4H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.32 – 1.25 (m, 4H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.88 (tt, *J* = 7.7, 3.9 Hz, 6H, CH$_2$CH$_2$CH$_2$C*H*$_3$), 0.69 (s, 3H, Pd-C*H*$_3$), 0.44 (s, 3H, C*H*$_3$), 0.26 (s, 3H, C*H*$_3$) ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.55 (*C*=N), 172.95 (*C*=N), 158.37, 158.19, 158.06, 158.03, 141.29, 141.19, 141.02, 136.96, 135.18, 134.94, 134.77, 134.44, 131.04, 130.86, 130.76, 130.65, 128.84, 128.74, 113.96, 113.90, 113.86, 113.51, 55.34 (O*C*H$_3$), 55.29 (O*C*H$_3$), 55.24 (O*C*H$_3$), 55.18 (O*C*H$_3$), 50.09 (*C*HAr_2), 49.78 (*C*HAr_2), 35.39 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 35.34 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.54 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 33.44 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.46 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 22.36 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 20.70 (*C*H$_3$), 19.82 (*C*H$_3$), 14.04 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 13.97 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 5.70 (Pd-*C*H$_3$). MALDI-TOF-MS (m/z): calcd for $C_{84}H_{88}ClN_2O_8Pd$: 1394.53, Found, 1394.49, $[M\text{-}CH_3]^+$. Anal. Calcd for $C_{85}H_{91}ClN_2O_8Pd$: C, 72.38; H, 6.50; N, 1.99; Found, C, 72.41; H, 6.24; N, 2.21.

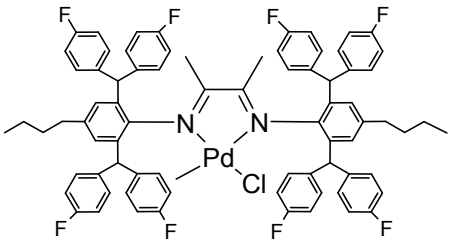


Pd2 (0.35 g, 27%), [1]H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 4H, Ar-*H*), 7.24 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 7.05 (dd, *J* = 7.8, 4.4 Hz, 8H, Ar-*H*), 7.01 (s, 2H, Ar-*H*), 6.98 (d, *J* = 7.9 Hz, 4H, Ar-*H*), 6.93 – 6.87 (m, 8H, Ar-*H*), 6.81 (d, *J* = 7.9 Hz, 4H, Ar-*H*), 6.77 (s, 2H, Ar-*H*), 5.90 (s, 2H, C*H*Ar_2), 5.67 (s, 2H, C*H*Ar_2), 2.56 – 2.47 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.48 – 2.41 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.30 (s, 6H, Ar-C*H*$_3$), 2.29 (s, 6H, Ar-C*H*$_3$), 2.25 (s, 6H, Ar-C*H*$_3$), 2.22 (s, 6H, Ar-C*H*$_3$), 1.55 – 1.44 (m, 4H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.34 – 1.24 (m, 4H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.88 (tt, *J* = 9.9, 4.9 Hz, 6H, CH$_2$CH$_2$CH$_2$C*H*$_3$), 0.72 (s, 3H, Pd-C*H*$_3$), 0.35 (s, 3H, C*H*$_3$), 0.20 (s, 3H, C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.54 (*C*=N), 172.91 (*C*=N),

141.47, 141.19, 140.93, 140.13, 139.99, 139.84, 139.75, 136.17, 135.90, 135.63, 135.53, 134.88, 134.20, 130.01, 129.90, 129.72, 129.65, 129.26, 129.21, 129.12, 128.92, 128.80, 50.99 (*C*HAr$_2$), 50.63 (*C*HAr$_2$), 35.34 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 35.29 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.50 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 33.41 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.40 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 22.32 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 21.13 (Ar-*C*H$_3$), 21.11 (Ar-*C*H$_3$), 21.03 (Ar-*C*H$_3$), 20.58 (*C*H$_3$), 19.69 (*C*H$_3$), 14.05 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 13.98 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 5.70 (Pd-*C*H$_3$). MALDI-TOF-MS (m/z): calcd for $C_{84}H_{88}ClN_2Pd$: 1266.57, Found, 1266.49, $[M\text{-}CH_3]^+$. Anal. Calcd for $C_{85}H_{91}ClN_2Pd$: C, 79.60; H, 7.15; N, 2.18; Found, C, 79.47; H, 6.91; N, 2.31.



Pd3 (0.79g, 68%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.1 Hz, 4H, Ar-*H*), 7.39 (d, *J* = 6.9 Hz, 4H, Ar-*H*), 7.27 (d, *J* = 7.5 Hz, 8H, Ar-*H*), 7.21 (d, *J* = 6.9 Hz, 2H, Ar-*H*), 7.15 (d, *J* = 4.9 Hz, 12H, Ar-*H*), 7.11 (d, *J* = 6.9 Hz, 2H, Ar-*H*), 7.08 – 7.03 (m, 10H, Ar-*H*), 6.79 (s, 2H, Ar-*H*), 6.03 (s, 2H, C*H*Ar$_2$), 5.76 (s, 2H, C*H*Ar$_2$), 2.53 (t, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.48 – 2.41 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.49 (dd, *J* = 16.3, 7.8 Hz, 4H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.24 (d, *J* = 56.1 Hz, 4H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.83 (t, *J* = 56.0 Hz, 6H, CH$_2$CH$_2$CH$_2$C*H*$_3$), 0.65 (s, 3H, Pd-C*H*$_3$), 0.42 (s, 3H, C*H*$_3$), 0.17 (s, 3H, C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.62 (*C*=N), 173.06 (*C*=N), 144.14, 142.61, 142.47, 142.44, 141.59, 141.22, 141.20, 140.26, 134.65, 134.03, 130.21, 129.95, 129.69, 129.25, 129.23, 128.77, 128.72, 128.56, 128.20, 126.94, 126.71, 126.57, 126.36, 51.80 (*C*HAr$_2$), 51.46 (*C*HAr$_2$), 35.35 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 35.30 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.46 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 33.37 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.41 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 22.31 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 20.43 (*C*H$_3$), 19.44 (*C*H$_3$), 14.04 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 13.97 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 5.74 (Pd-*C*H$_3$). MALDI-TOF-MS (m/z): calcd for $C_{76}H_{72}ClN_2Pd$: 1155.44, Found, 1155.46, $[M\text{-}CH_3]^+$. Anal. Calcd for $C_{77}H_{75}ClN_2Pd$: C, 79.02; H, 6.46; N, 2.39; Found, C, 79.16; H, 6.41; N, 2.25.



Pd4 (1.04g, 80%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.6, 5.4 Hz, 4H, Ar-*H*), 7.22 (dd, *J* = 8.6, 5.2 Hz, 4H, Ar-*H*, 7.04 (dd, *J* = 8.4, 5.3 Hz, 4H, Ar-*H*), 6.95 (dd, *J* = 9.1, 5.6 Hz, 12H, Ar-*H*), 6.93 (s, 2H, Ar-*H*), 6.88 (t, *J* = 7.2 Hz, 4H, Ar-*H*), 6.80 (t, *J* = 8.5 Hz, 4H, Ar-*H*), 6.71 (s, 2H, Ar-*H*), 5.88 (s, 2H, C*H*Ar_2), 5.61 (s, 2H, C*H*Ar_2), 2.58 – 2.49 (m, 2H, C*H*$_2$$CH_2CH_2CH_3$), 2.49 – 2.41 (m, 2H, C*H*$_2$$CH_2CH_2CH_3$), 1.52 – 1.41 (m, 4H, CH_2C*H*$_2$$CH_2CH_3$), 1.29 – 1.25 (m, 4H, CH_2CH_2C*H*$_2$$CH_3$), 0.91 – 0.84 (m, 6H, $CH_2CH_2CH_2$C*H*$_3$), 0.61 (s, 3H, Pd-C*H*$_3$), 0.51 (s, 3H, C*H*$_3$), 0.33 (s, 3H, C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.19 (*C*=N), 172.63 (*C*=N), 162.73, 162.57, 162.47, 162.37, 161.09, 160.94, 160.82, 160.73, 142.04, 141.11, 140.75, 139.29, 137.95, 137.93, 137.90, 137.77, 137.76, 134.48, 133.87, 131.49, 131.44, 131.15, 131.10, 130.92, 130.87, 129.28, 129.24, 115.94, 115.85, 115.80, 115.71, 115.66, 115.52, 115.21, 115.07, 50.25 (*C*HAr_2), 49.91 (*C*HAr_2), 35.24 (*C*$H_2CH_2CH_2CH_3$), 33.32 (CH_2*C*$H_2CH_2CH_3$), 33.30 (CH_2*C*$H_2CH_2CH_3$), 22.31 (CH_2CH_2*C*H_2CH_3), 22.25 (CH_2CH_2*C*H_2CH_3), 20.79 (*C*H_3), 19.84 (*C*H_3), 13.94 ($CH_2CH_2CH_2$*C*H_3), 13.89 ($CH_2CH_2CH_2$*C*H_3), 6.12 (Pd-*C*H_3). ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.08, -114.31, -114.99, -116.19. MALDI-TOF-MS (m/z): calcd for $C_{76}H_{64}ClF_8N_2Pd$: 1297.37, Found, 1297.36, $[M+H]^+$. Anal. Calcd for $C_{77}H_{67}ClF_8N_2Pd$: C, 70.37; H, 5.14; N, 2.13; Found, C, 70.14; H, 5.24; N, 2.05.

1.7 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.

1.8 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 4 atm of ethylene. After 12 h, the pressure reactor was vented and the polymer was dried under vacuum overnight.

1.9 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. 38 mL of DCM with the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the desired polar monomer and 4 atm 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 4 atm of ethylene. After 12 h, the pressure reactor was vented and the copolymer was dried under vacuum overnight.

2. Spectra Data

2.1 ^{1}H, ^{13}C and ^{19}F NMR of the Synthetic Compounds.

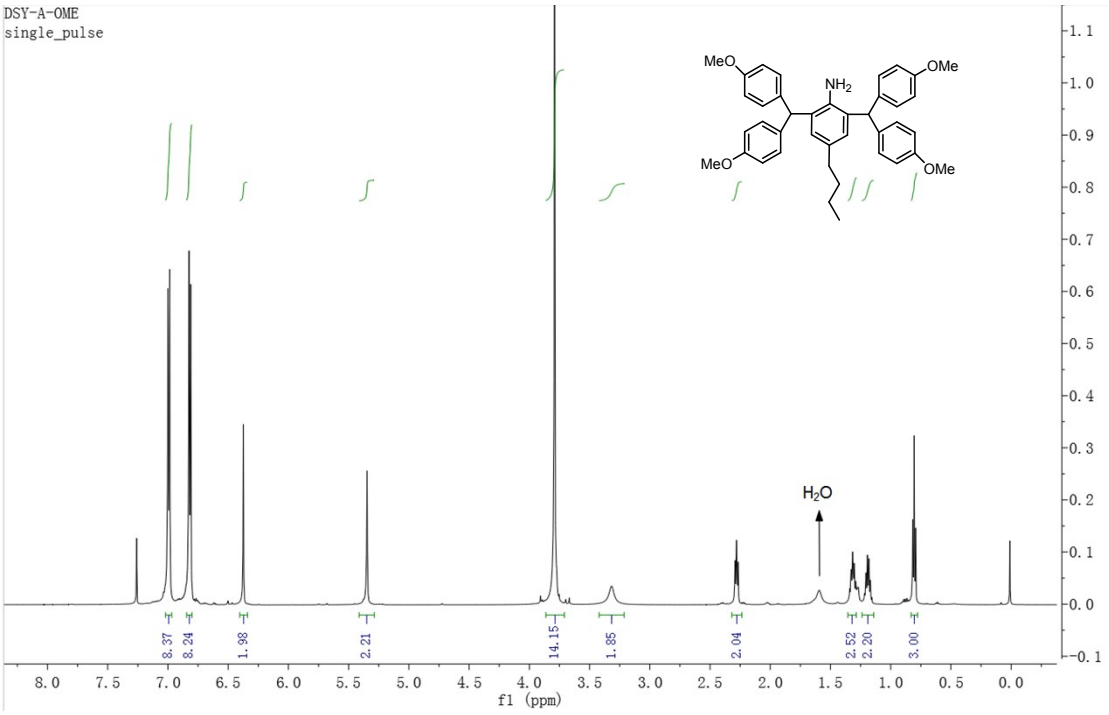


Figure S1. ^{1}H NMR spectrum of **A1** in $CDCl_3$.

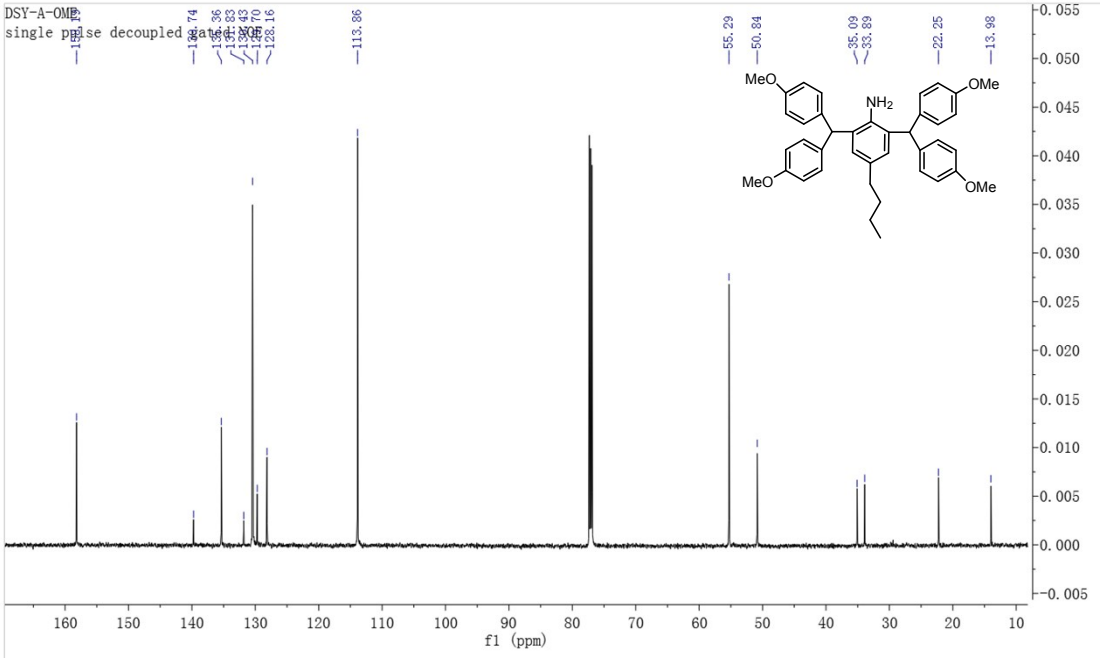


Figure S2. ^{13}C NMR spectrum of **A1** in $CDCl_3$.

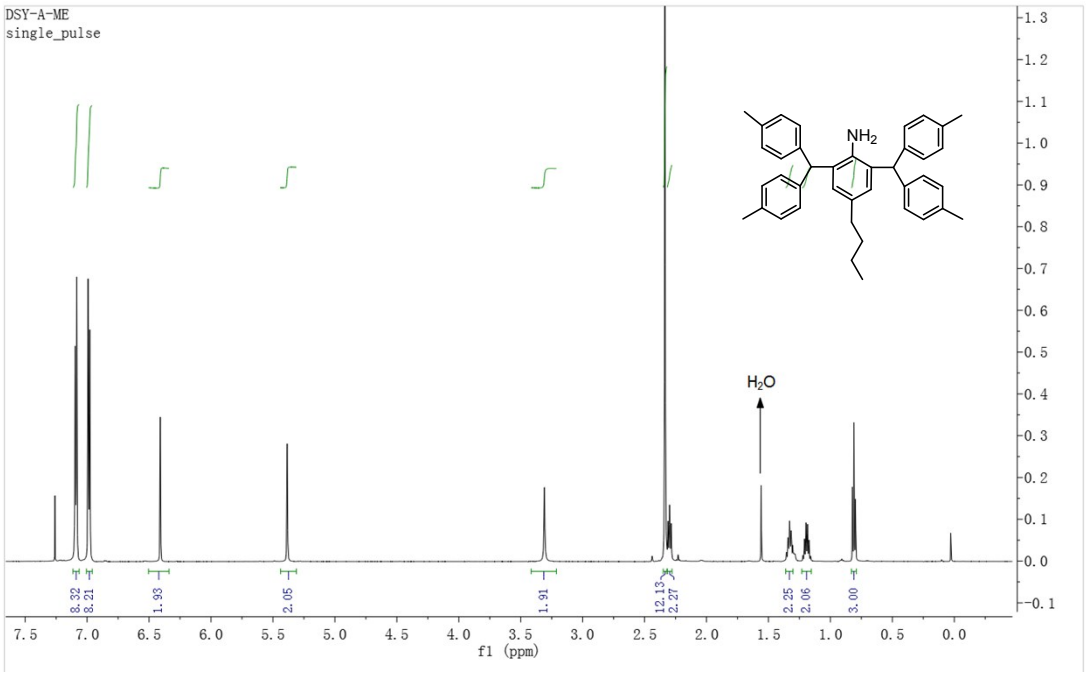


Figure S3. ^{1}H NMR spectrum of **A2** in $CDCl_3$.

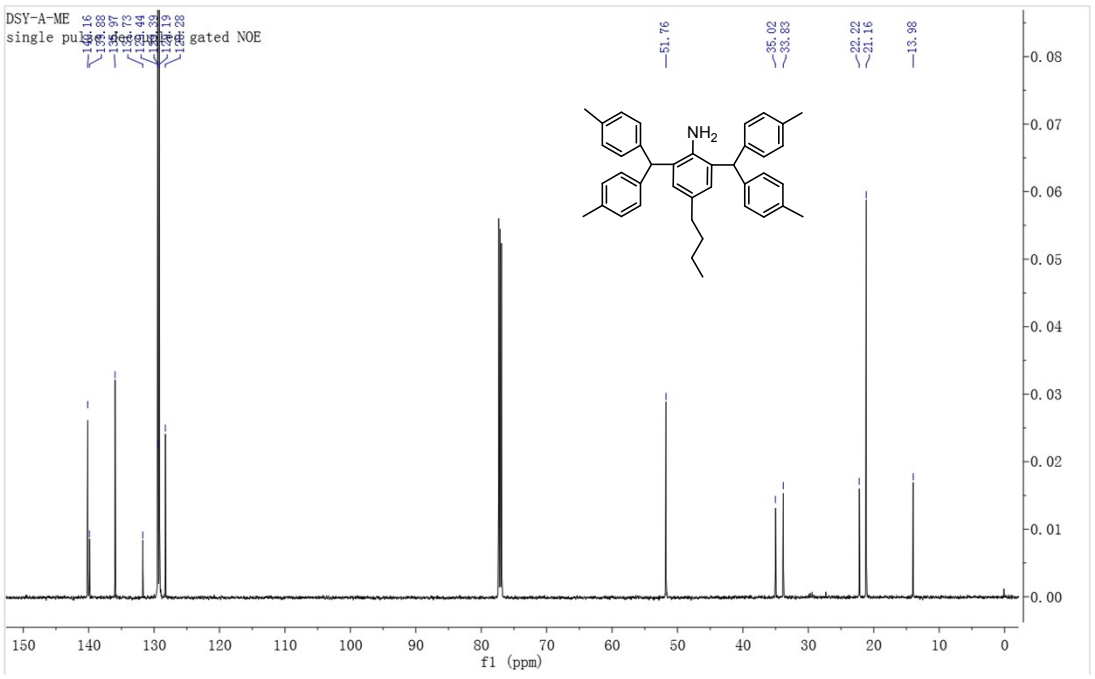


Figure S4. ^{13}C NMR spectrum of **A2** in $CDCl_3$.

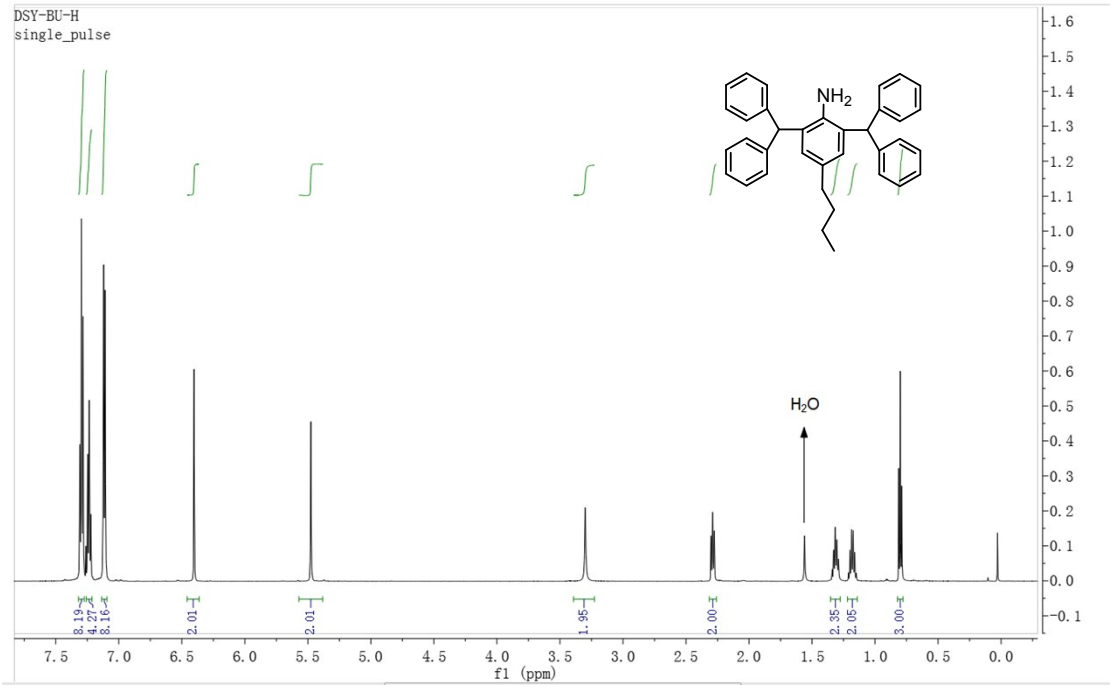


Figure S5. ^{1}H NMR spectrum of **A3** in $CDCl_3$.

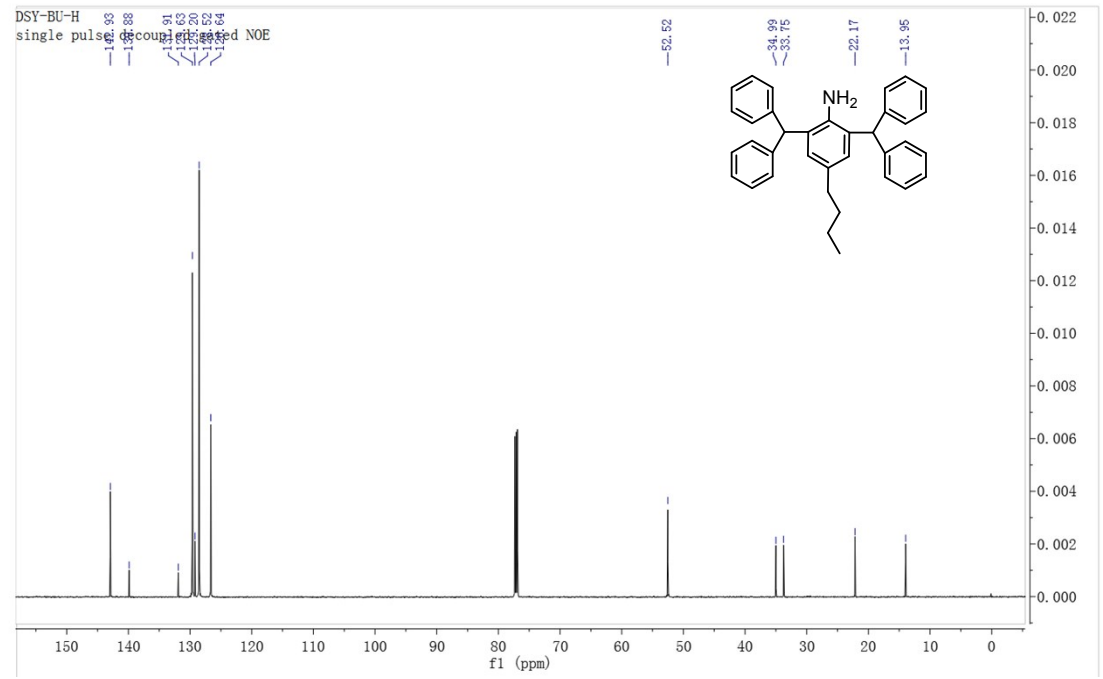


Figure S6. ^{13}C NMR spectrum of **A3** in $CDCl_3$.

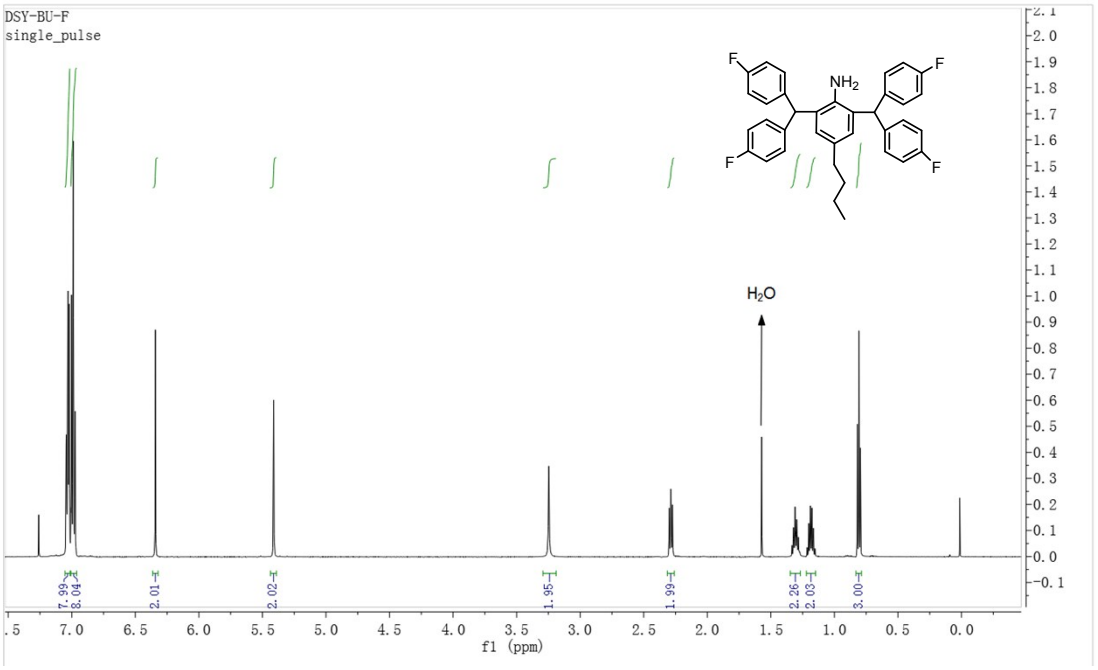


Figure S7. ^{1}H NMR spectrum of **A4** in $CDCl_3$.

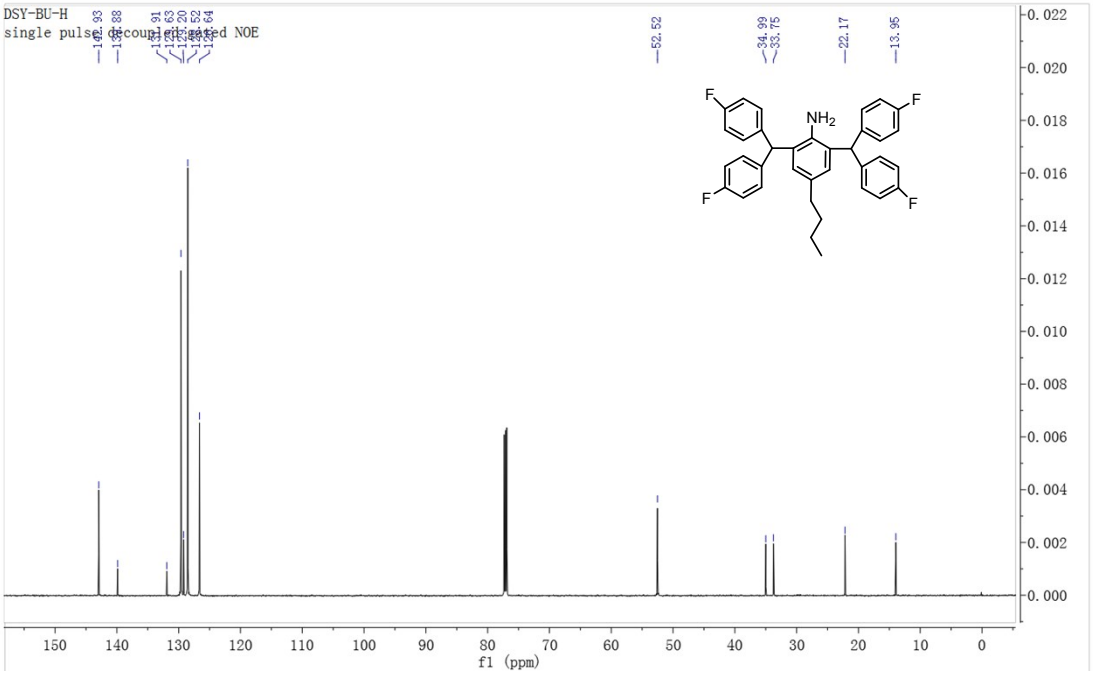


Figure S8. ^{13}C NMR spectrum of **A4** in $CDCl_3$.

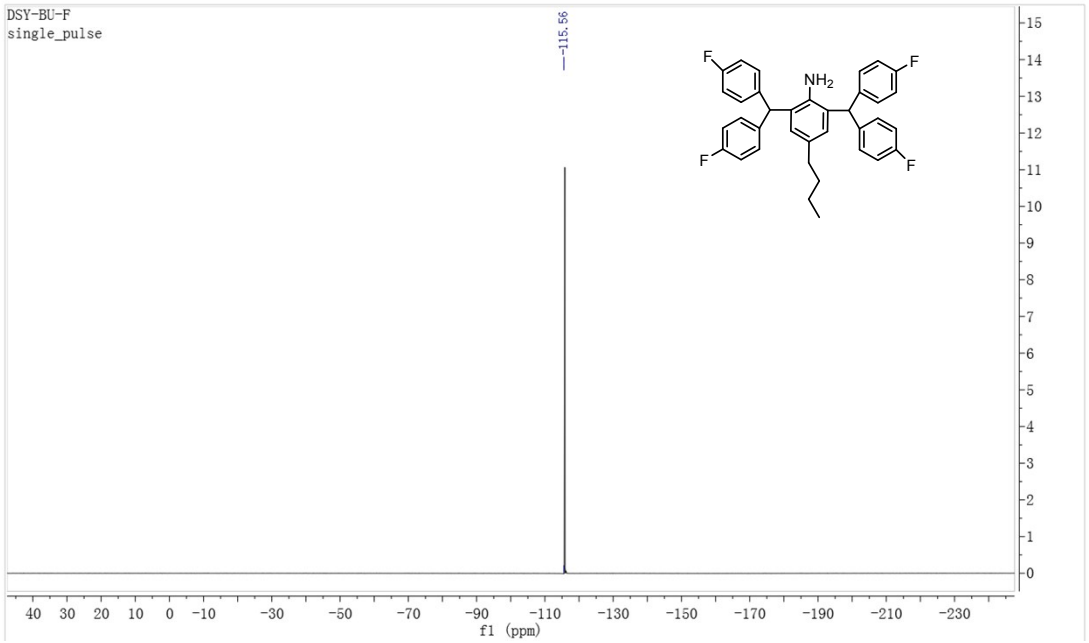


Figure S9. ^{19}F NMR spectrum of **A4** in $CDCl_3$.

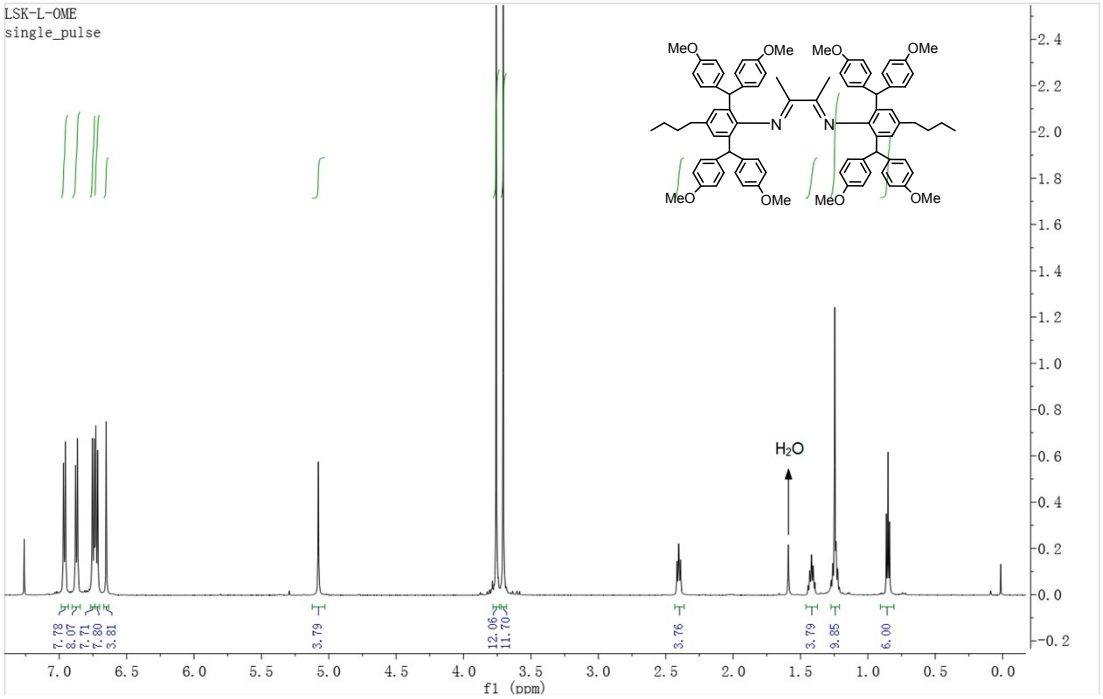


Figure S10. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

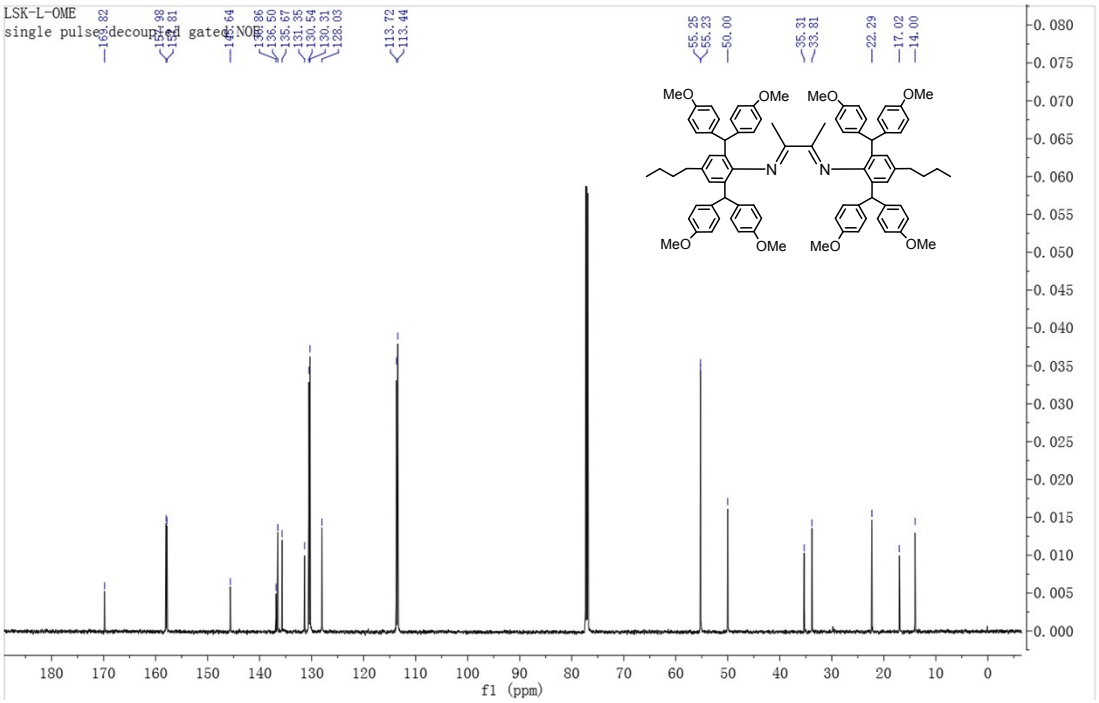


Figure S11. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

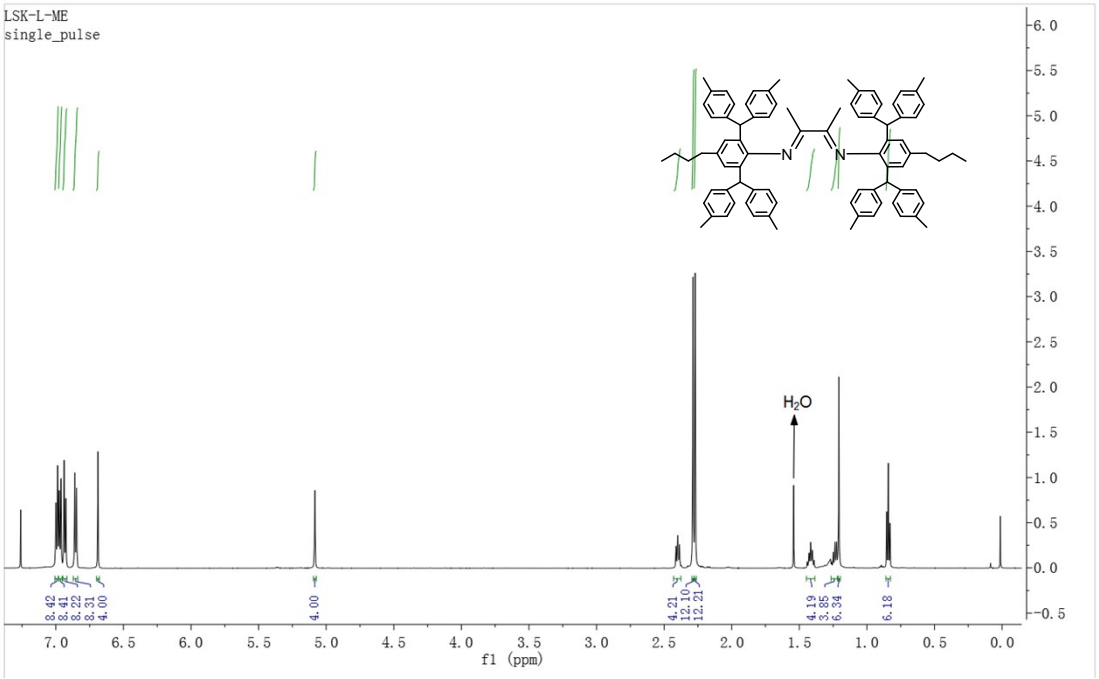


Figure S12. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

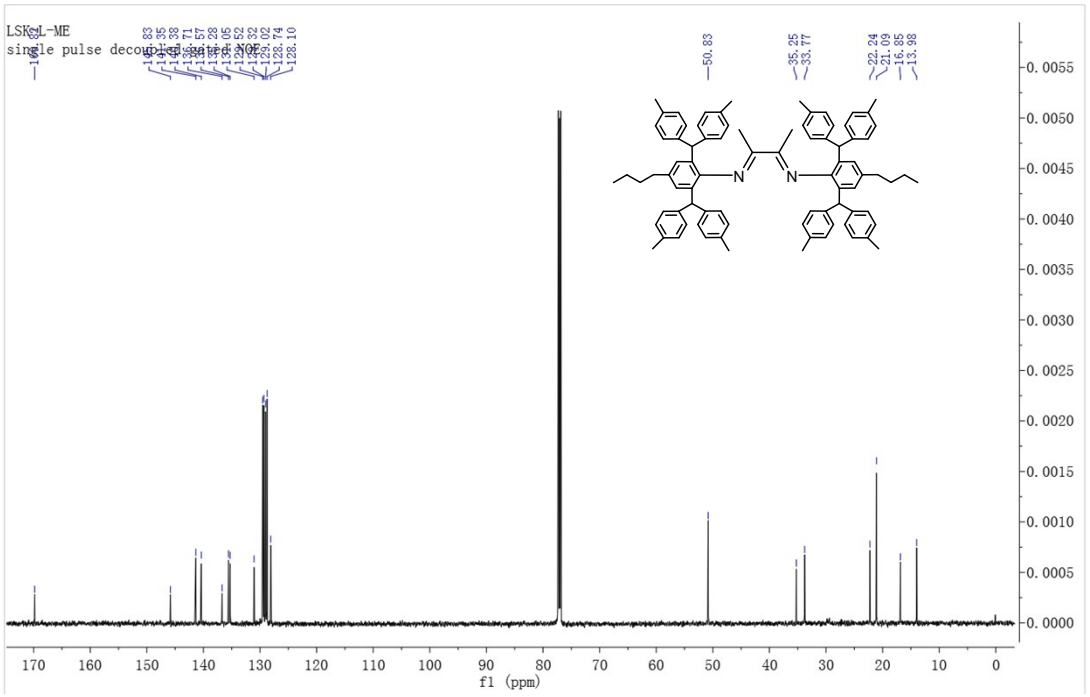


Figure S13. ^{13}C NMR spectrum of **L2** in $CDCl_3$.

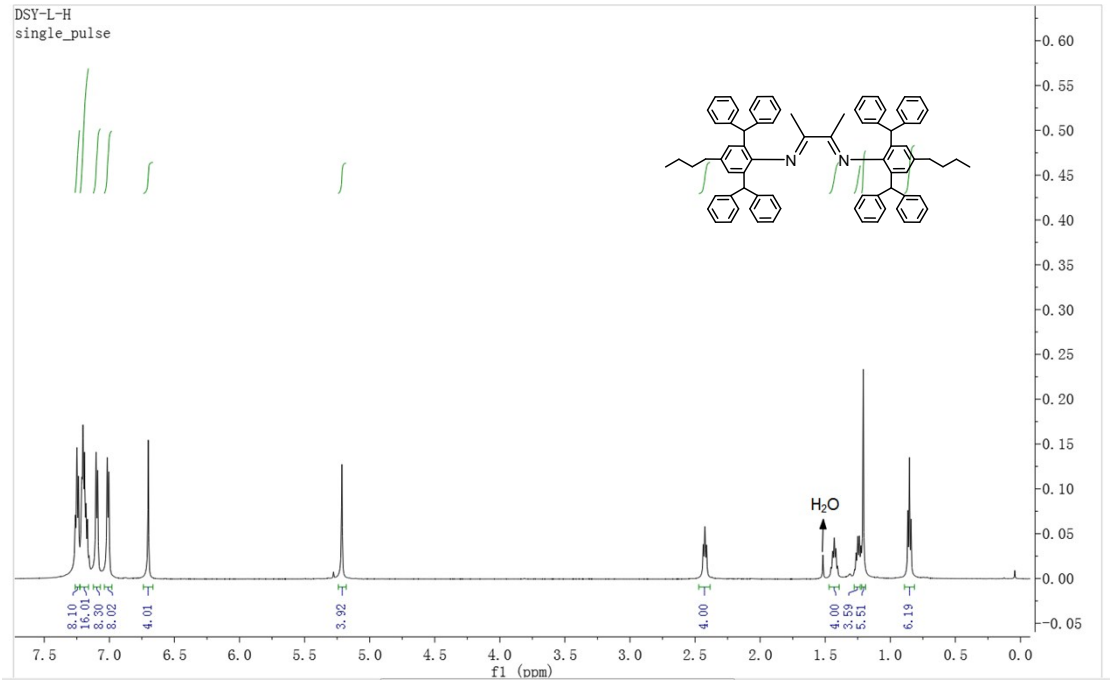


Figure S14. ^{1}H NMR spectrum of **L3** in $CDCl_3$.

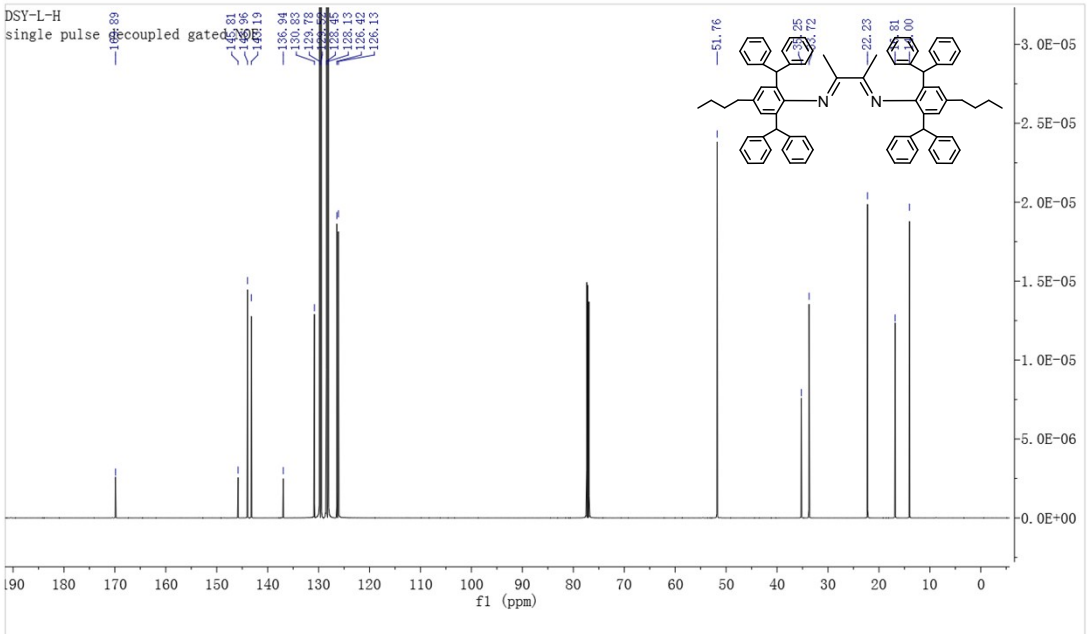


Figure S15. ^{13}C NMR spectrum of **L3** in $CDCl_3$.

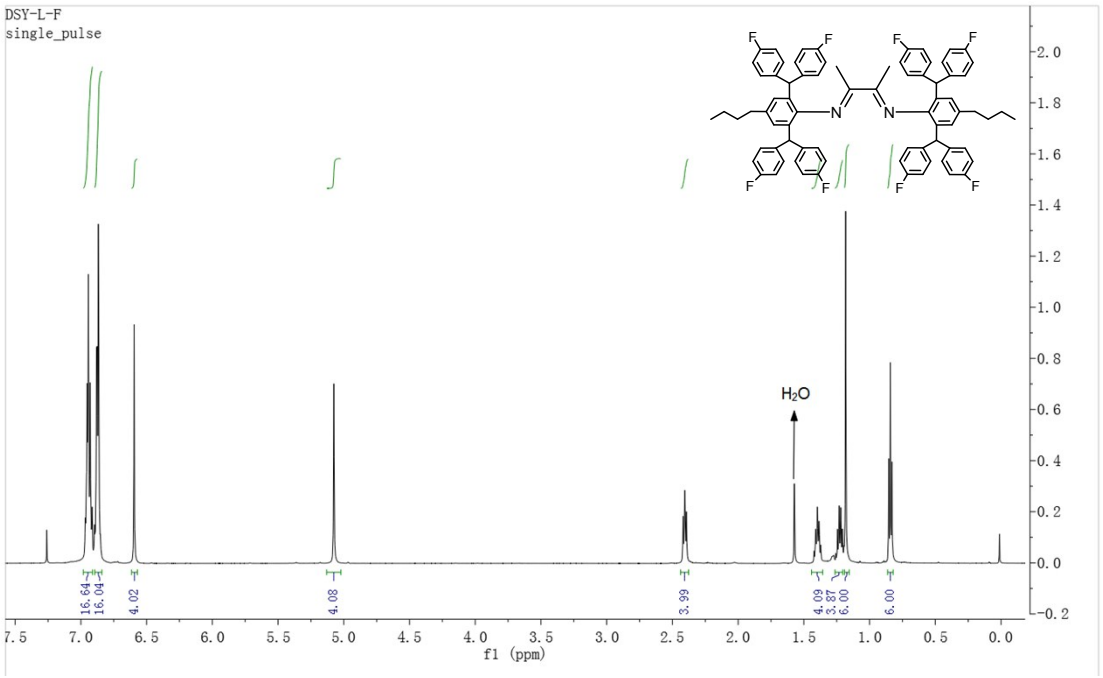


Figure S16. ^{1}H NMR spectrum of **L4** in $CDCl_3$.

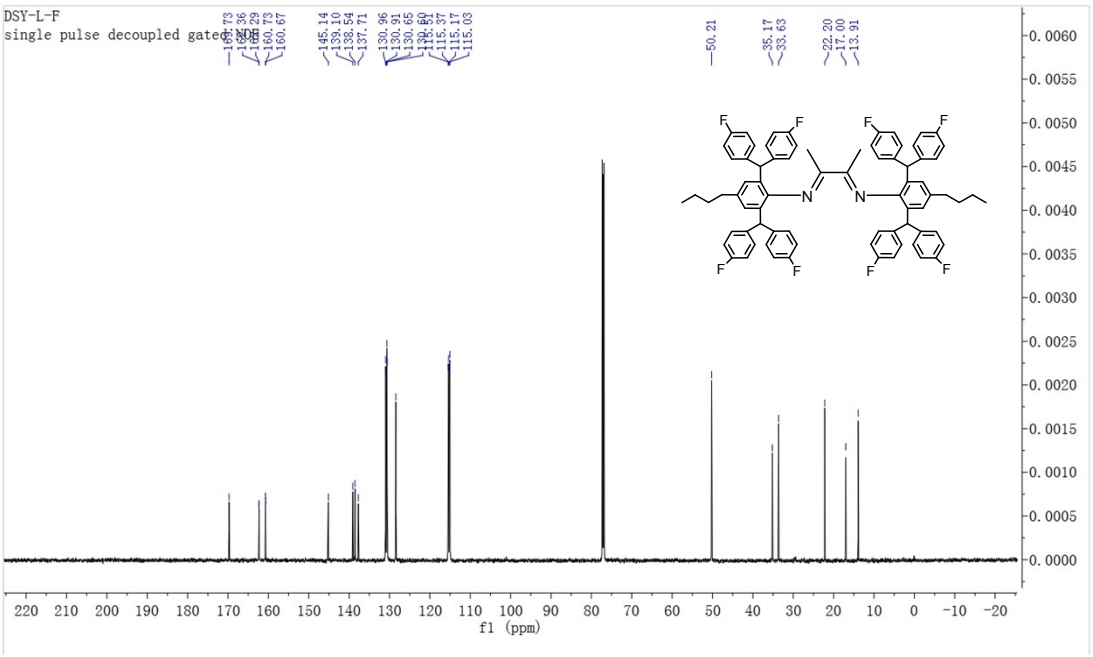


Figure S17. ^{13}C NMR spectrum of **L4** in $CDCl_3$.

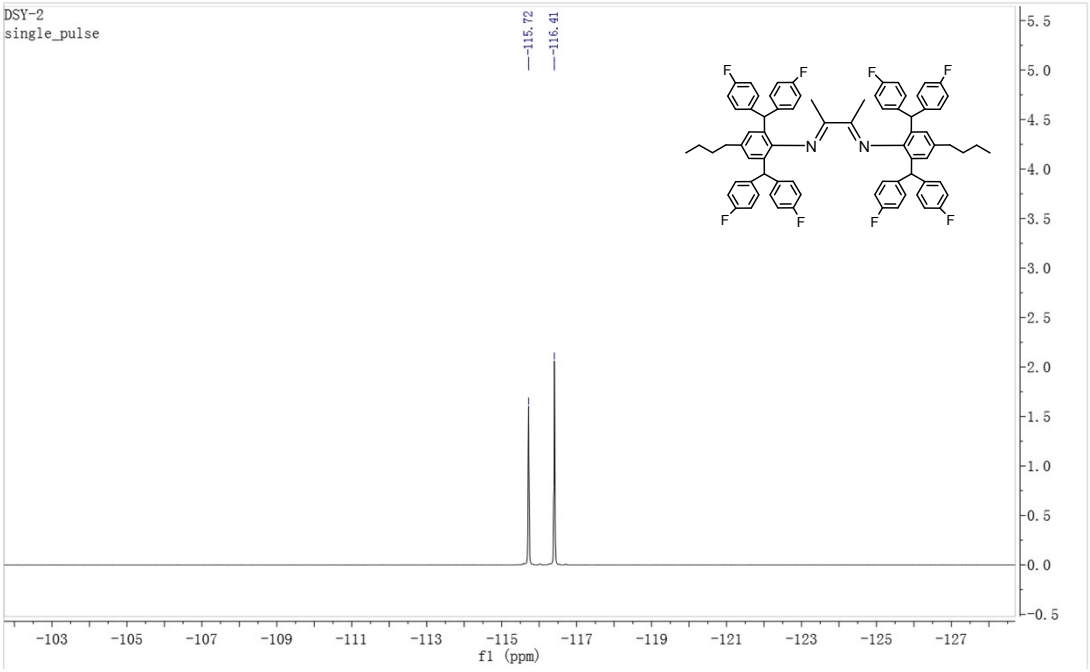


Figure S18. ^{19}F NMR spectrum of **L4** in $CDCl_3$.

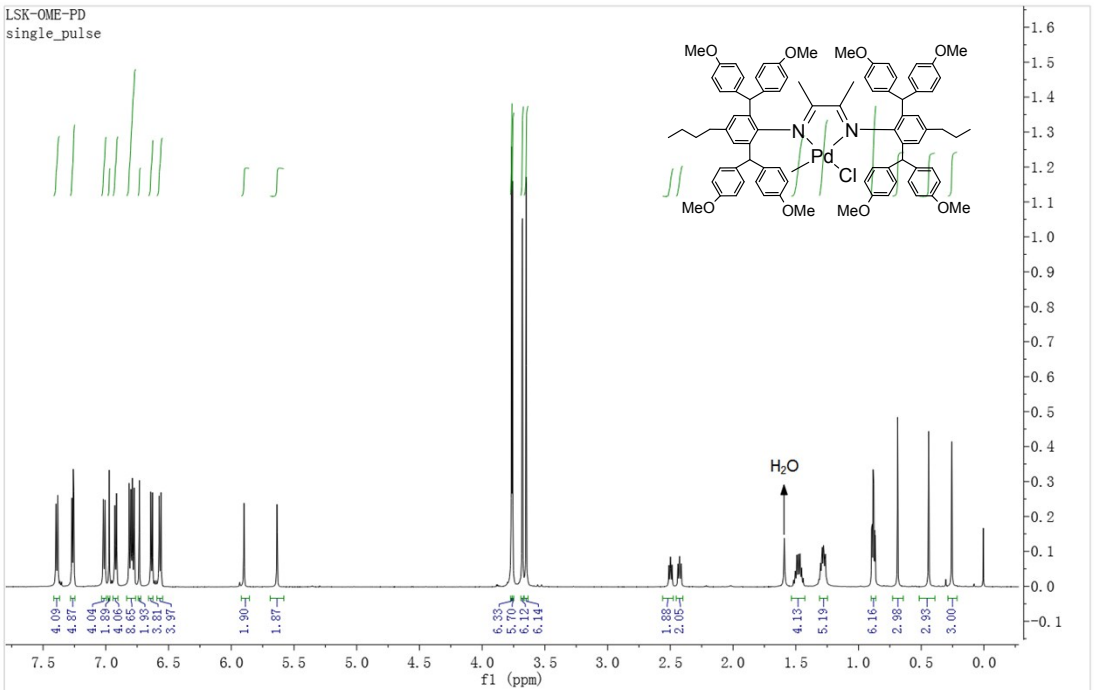


Figure S19. ^{1}H NMR spectrum of **Pd1** in $CDCl_3$.

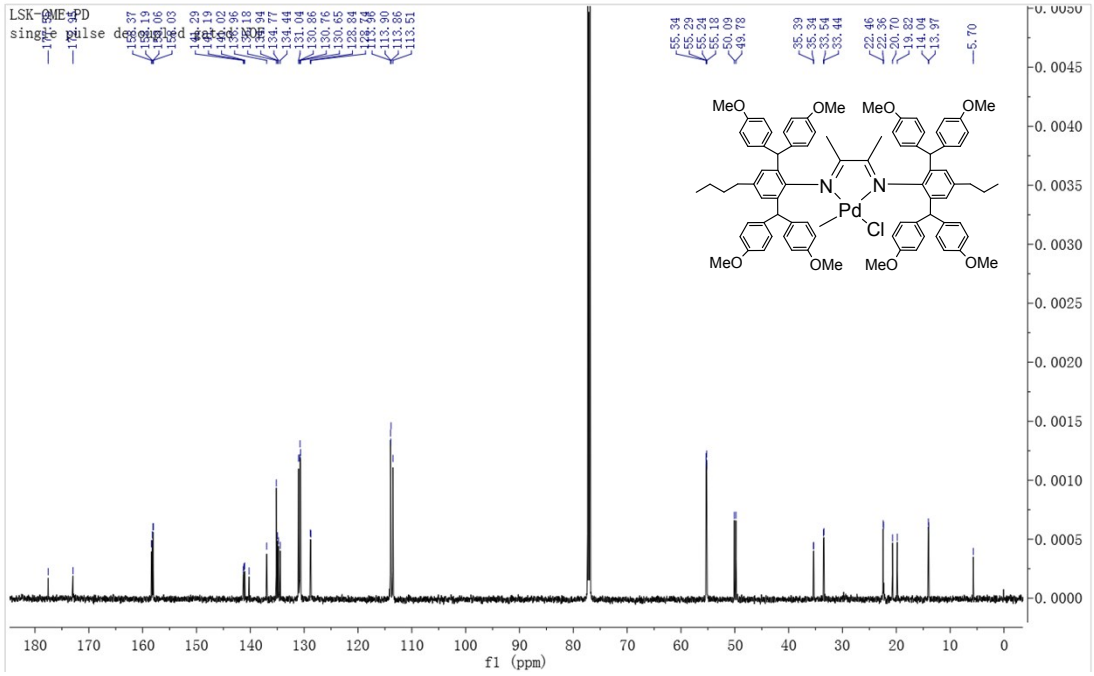


Figure S20. ^{13}C NMR spectrum of **Pd1** in $CDCl_3$.

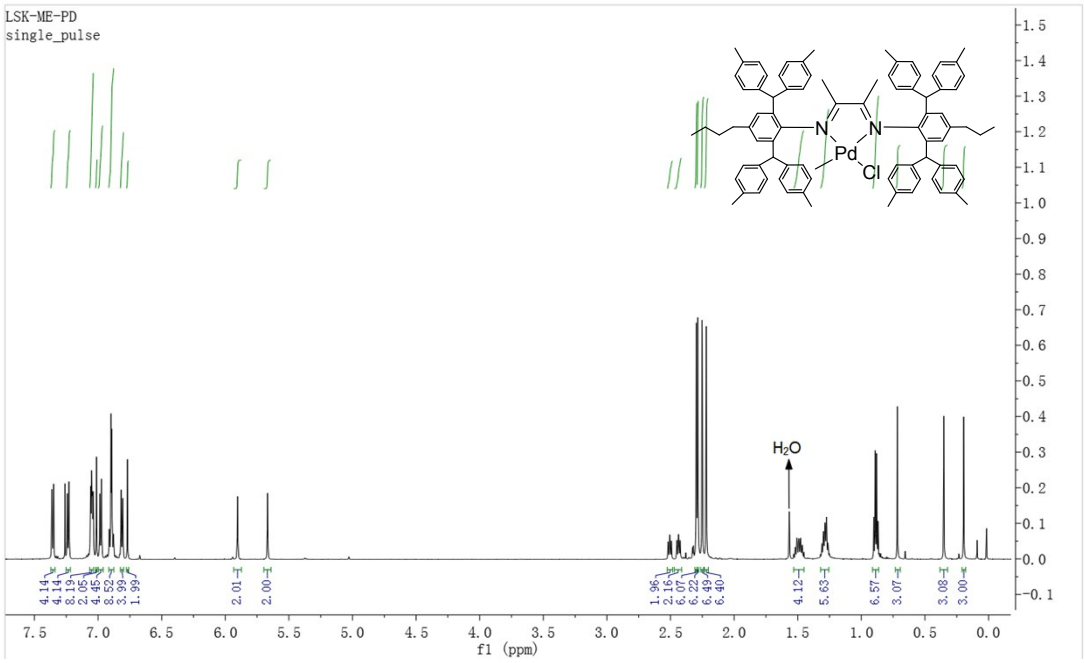


Figure S21. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

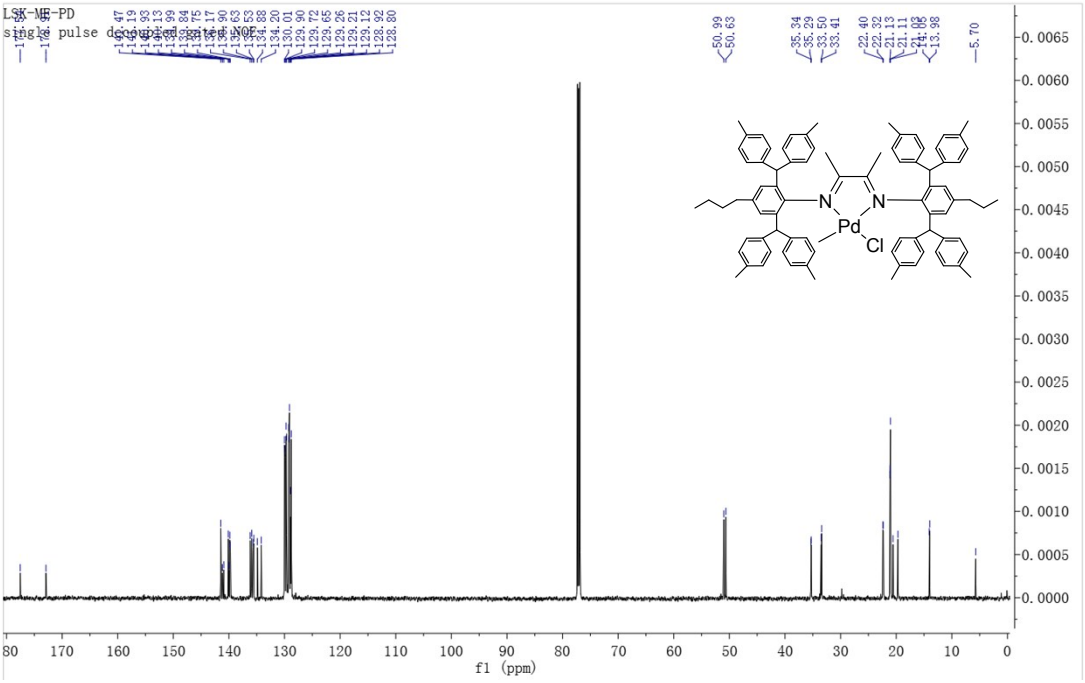


Figure S22. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

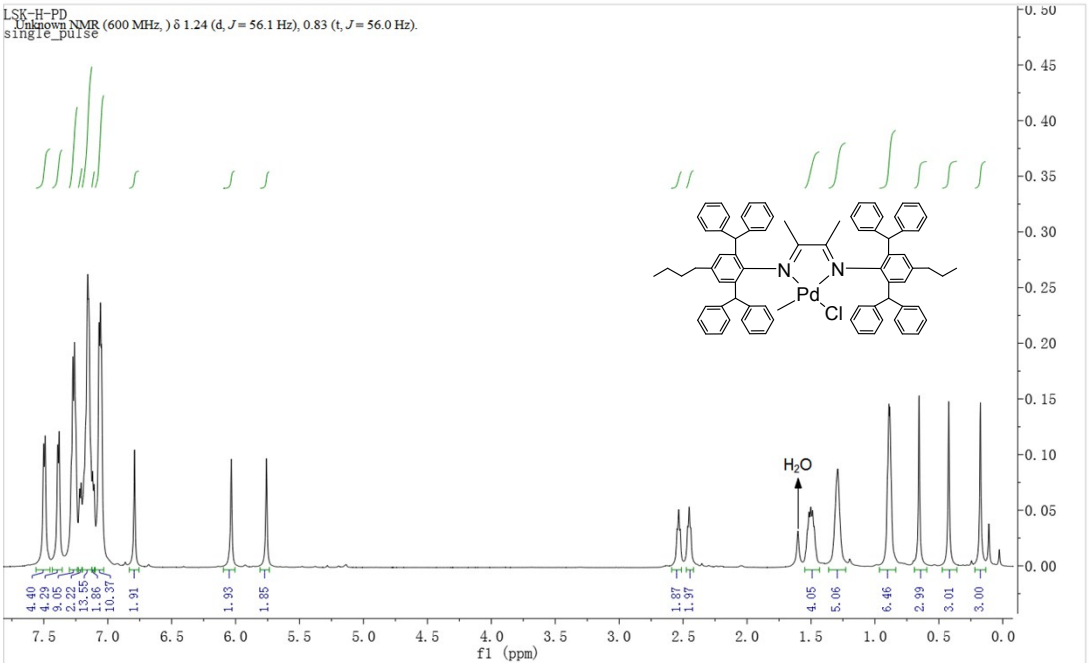


Figure S23. ^{1}H NMR spectrum of **Pd3** in $CDCl_3$.

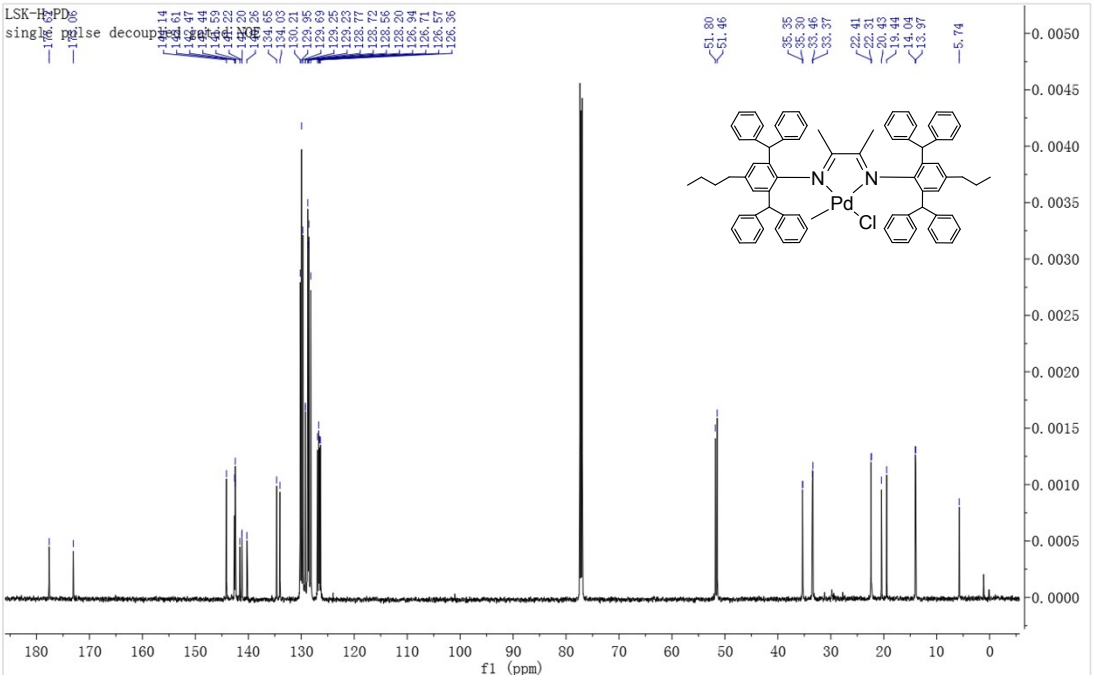


Figure S24. ^{13}C NMR spectrum of **Pd3** in $CDCl_3$.

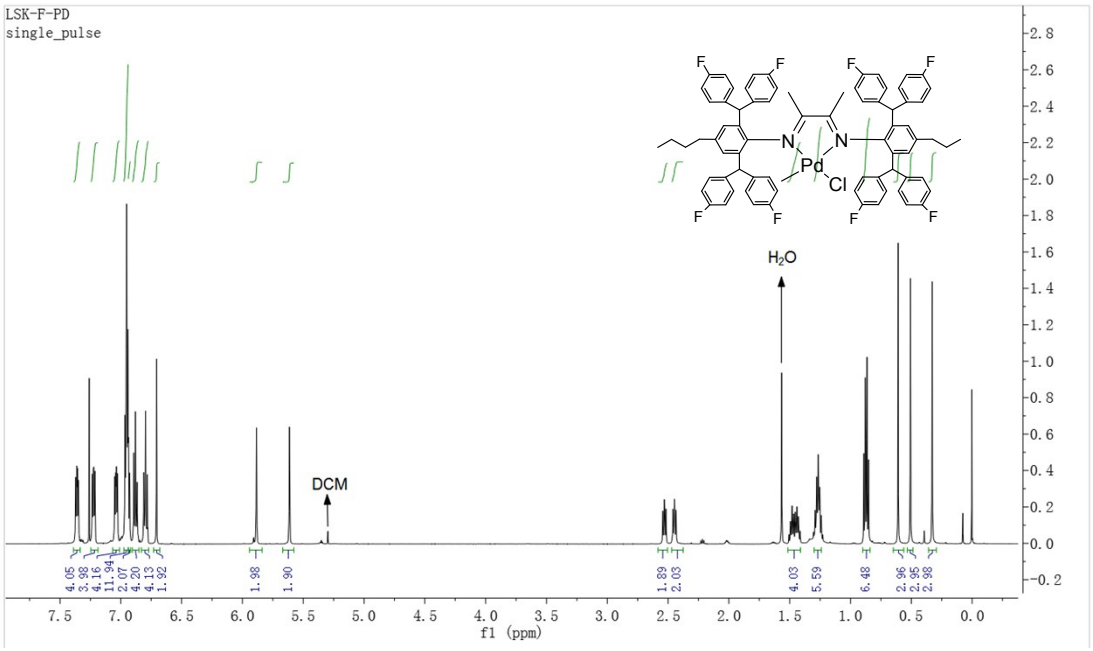


Figure S25. ^{1}H NMR spectrum of **Pd4** in $CDCl_3$.

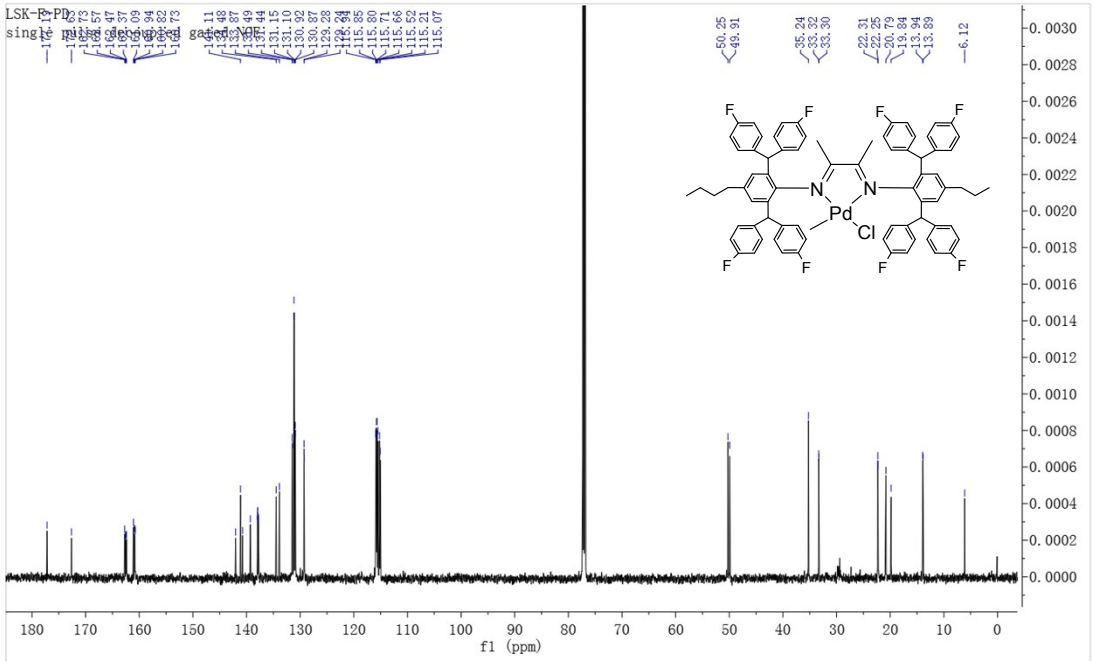


Figure S26. ^{13}C NMR spectrum of **Pd4** in $CDCl_3$.

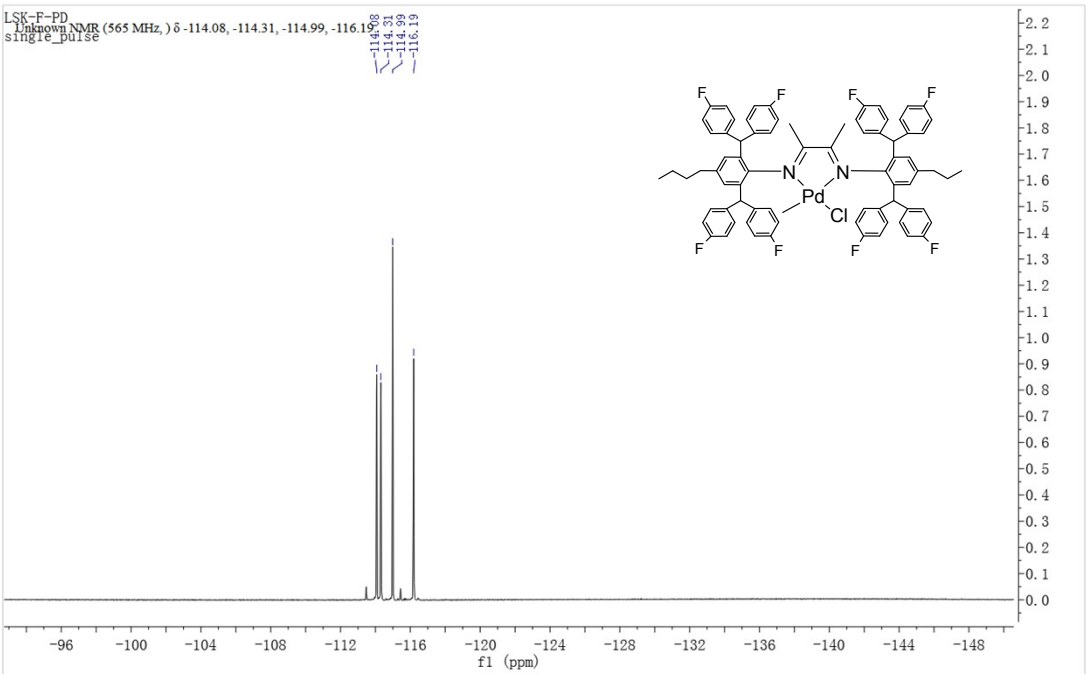


Figure S27. ^{19}F NMR spectrum of **Pd4** in $CDCl_3$.

2.2 ESI-MS and MALDI-TOF-MS Data.

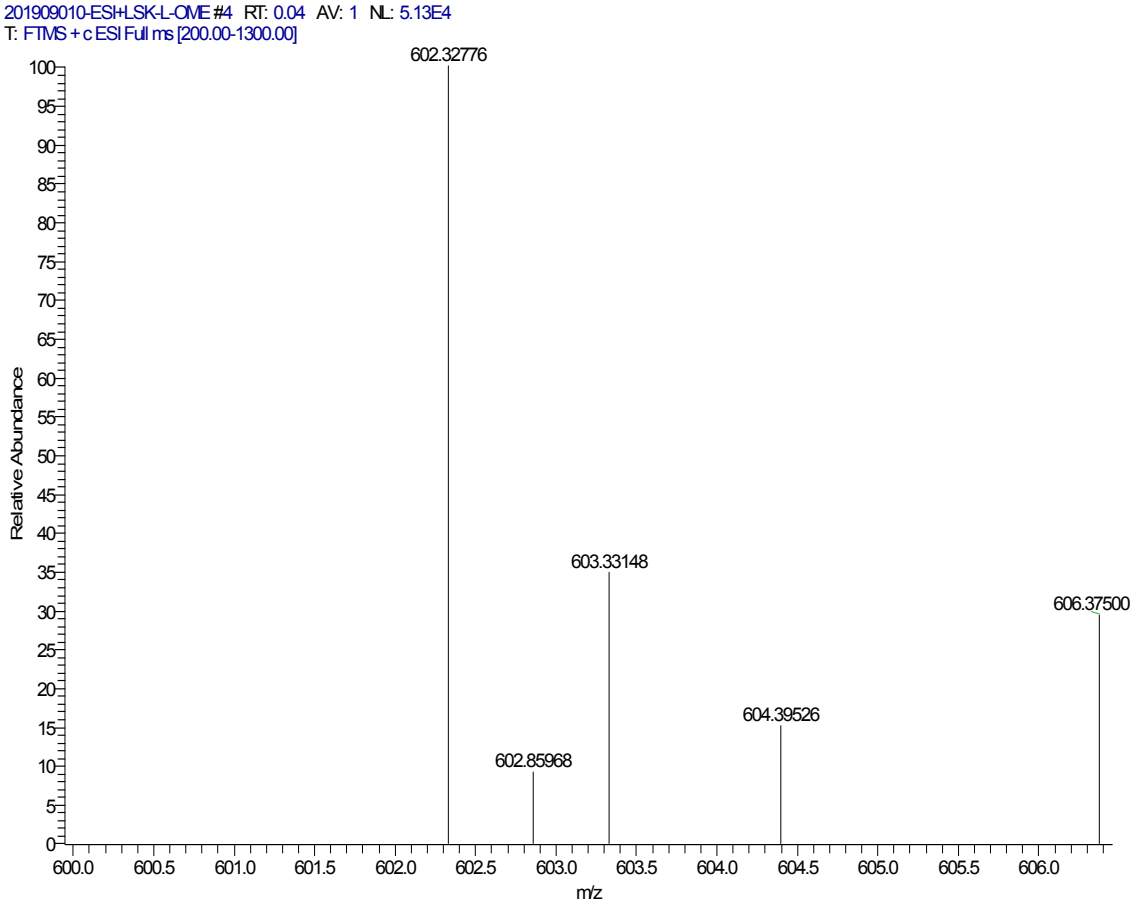


Figure S28. ESI-MS of **A1.**

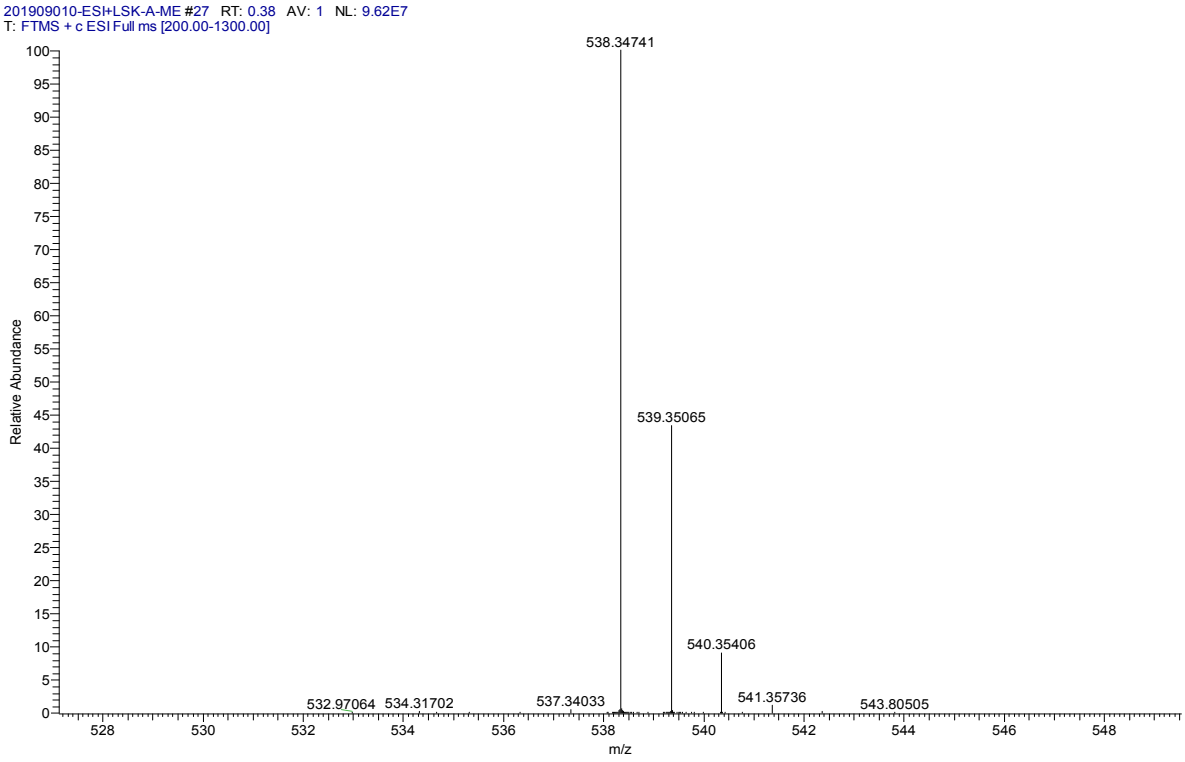


Figure S29. ESI-MS of **A2.**

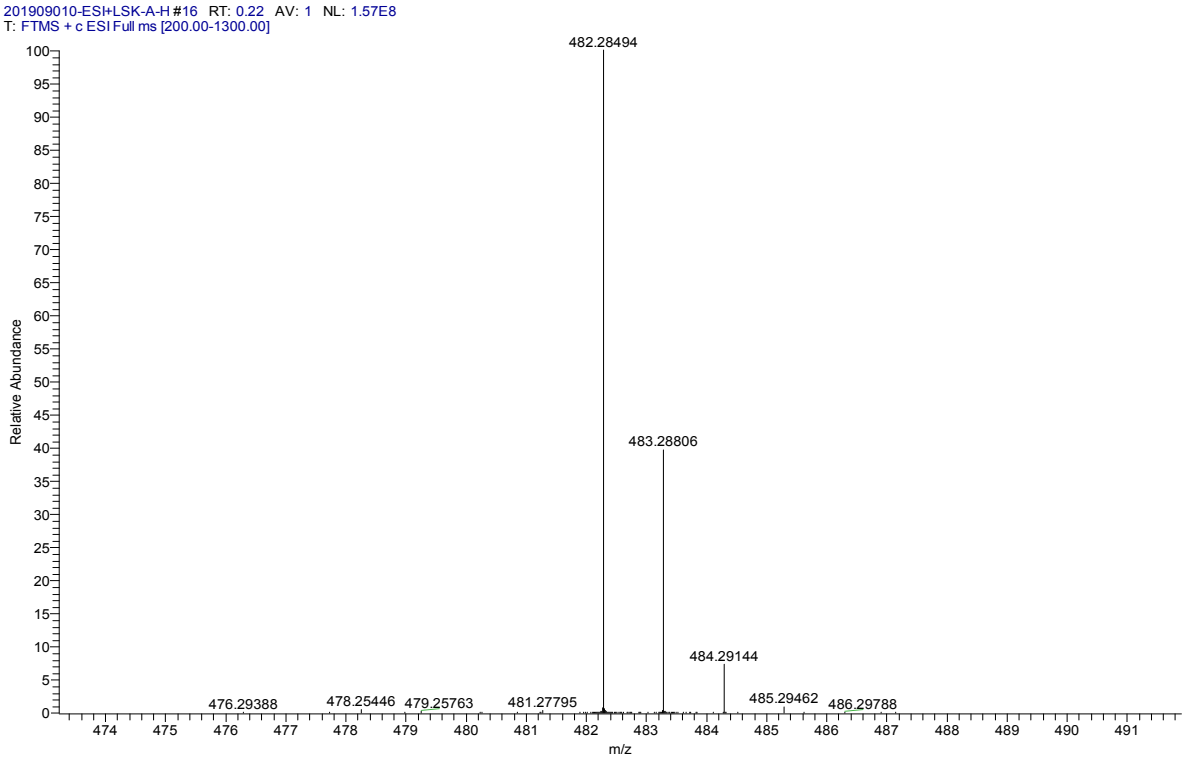


Figure S30. ESI-MS of **A3.**

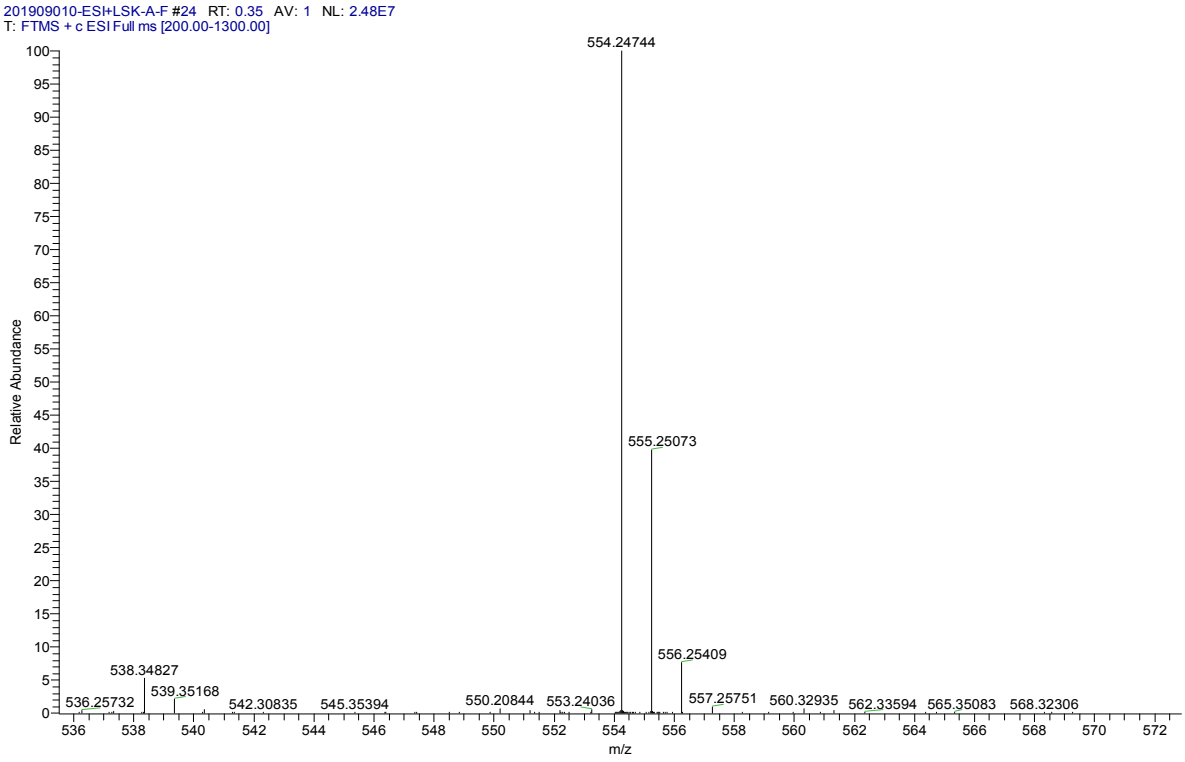


Figure S31. ESI-MS of **A4.**

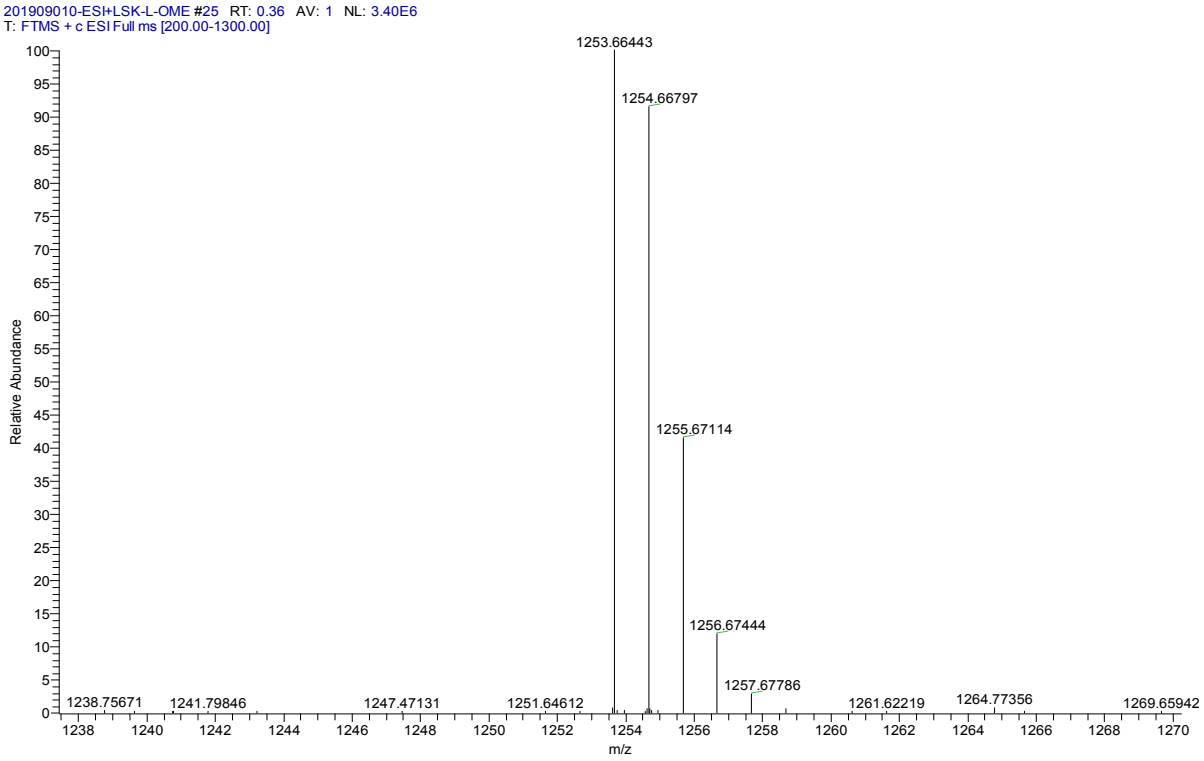


Figure S32. ESI-MS of **L1.**

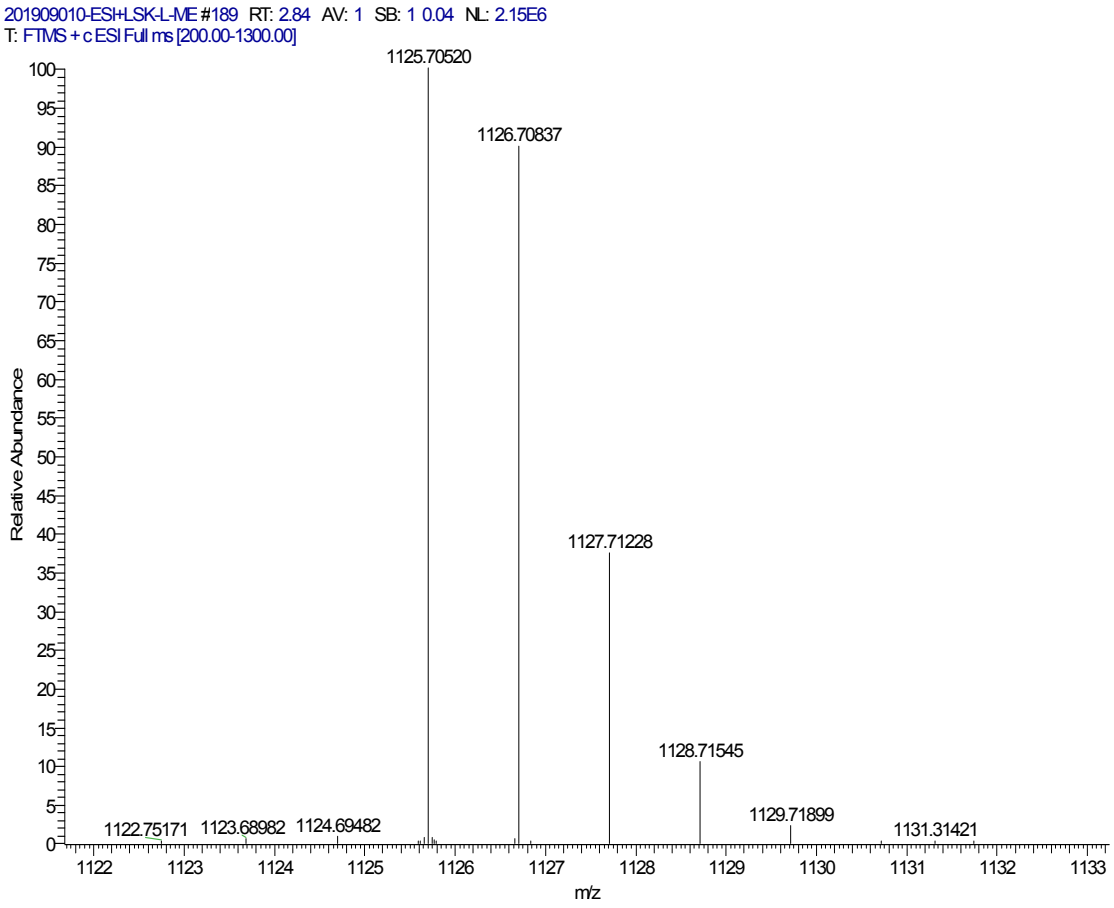


Figure S33. ESI-MS of **L2.**

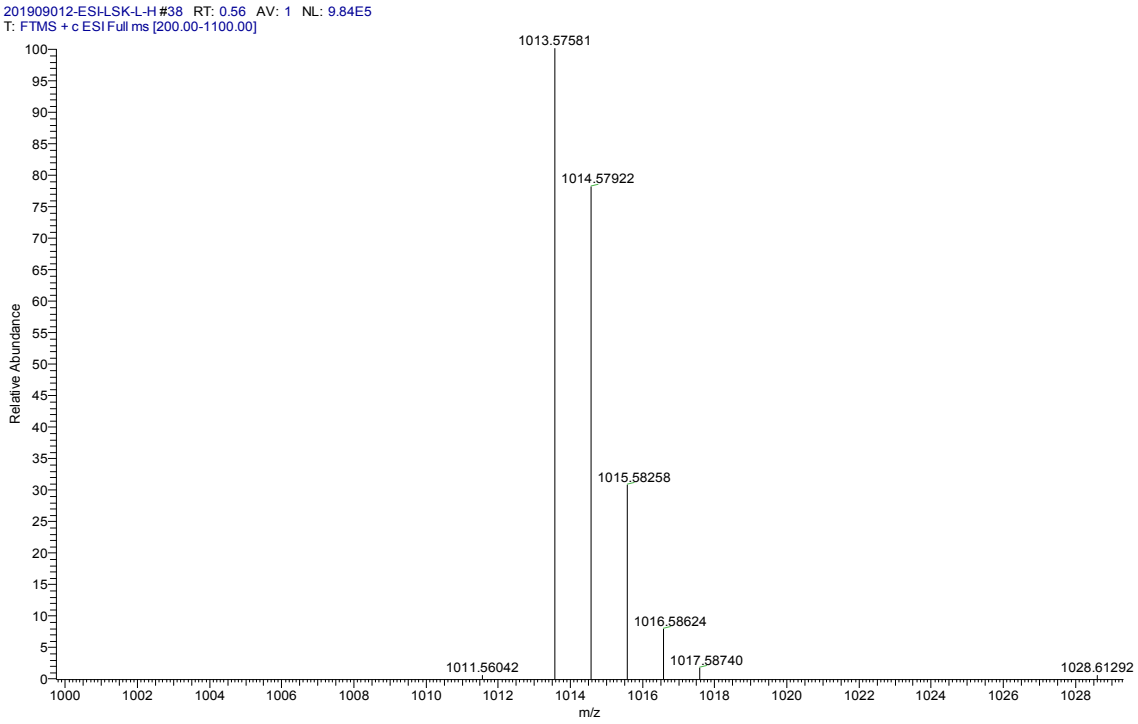


Figure S34. ESI-MS of **L3.**

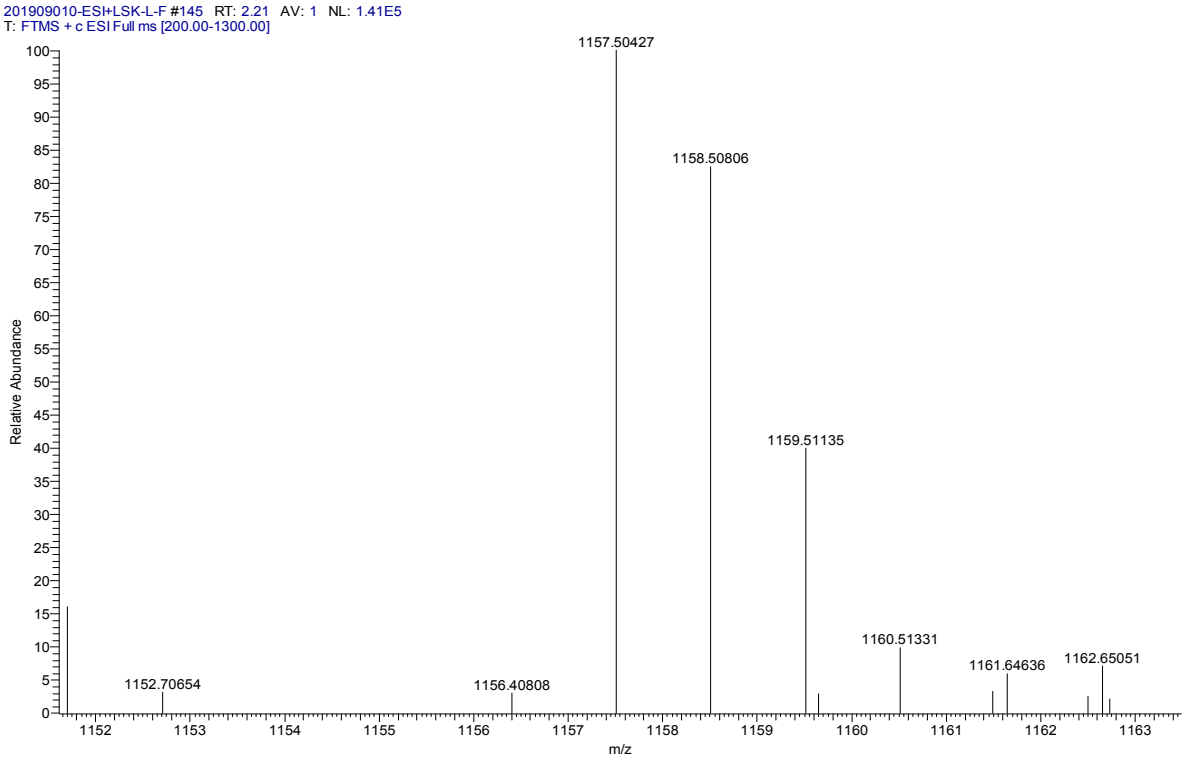


Figure S35. ESI-MS of **L4.**

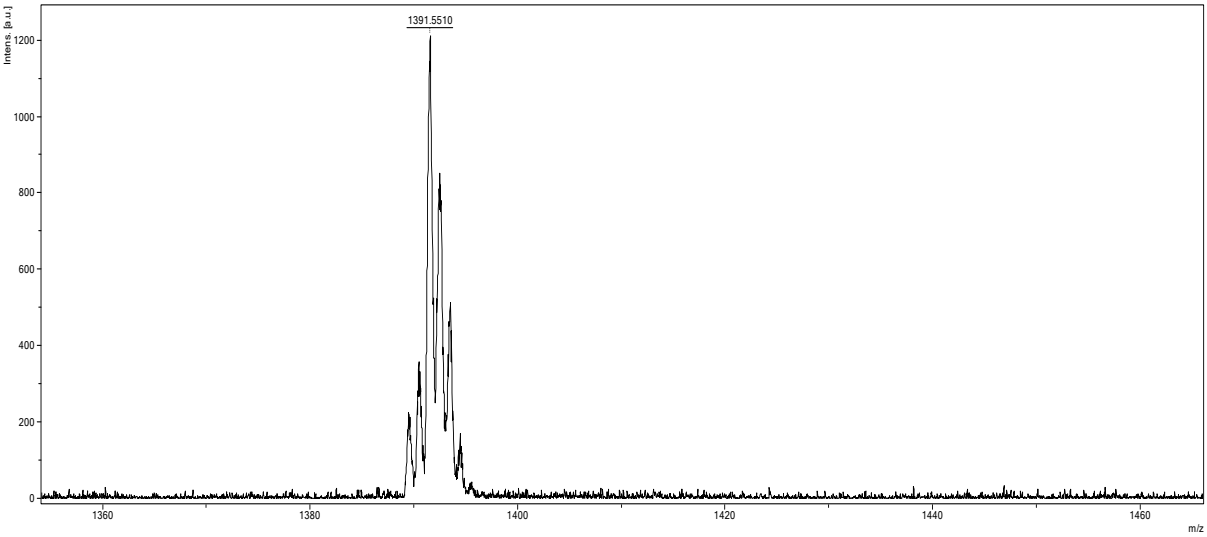


Figure S36. MALDI-TOF-MS of complex **Ni1**.

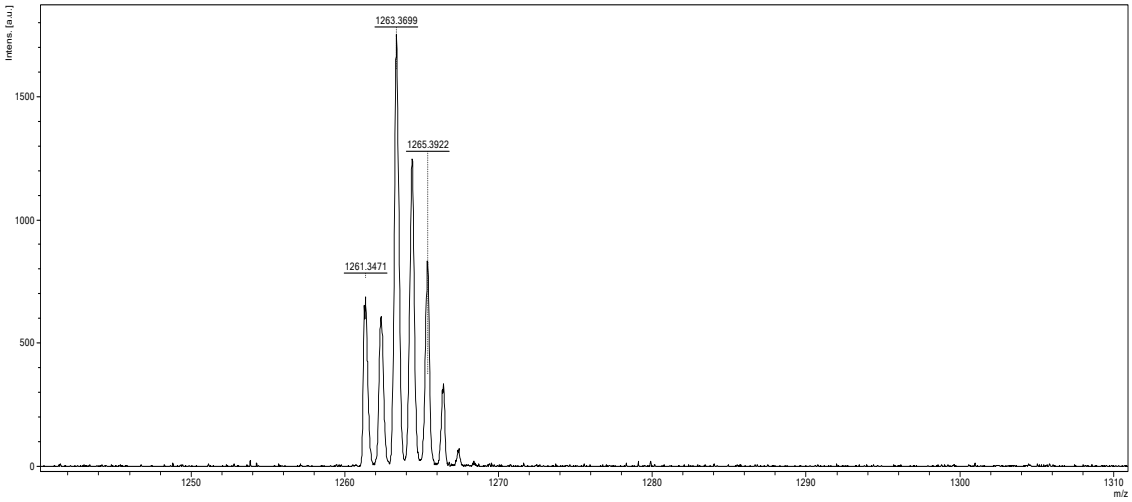


Figure S37. MALDI-TOF-MS of complex **Ni2**.

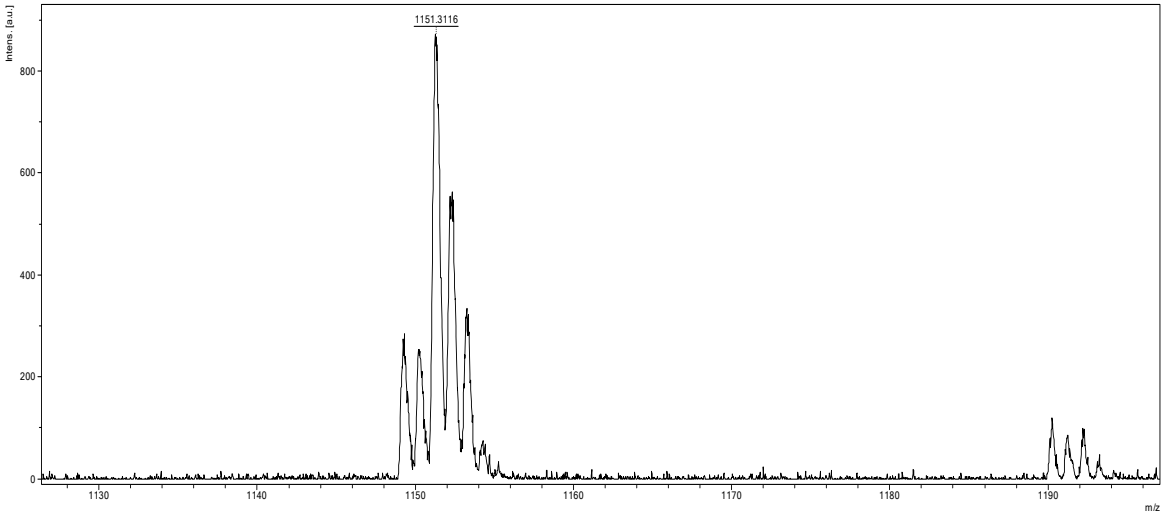
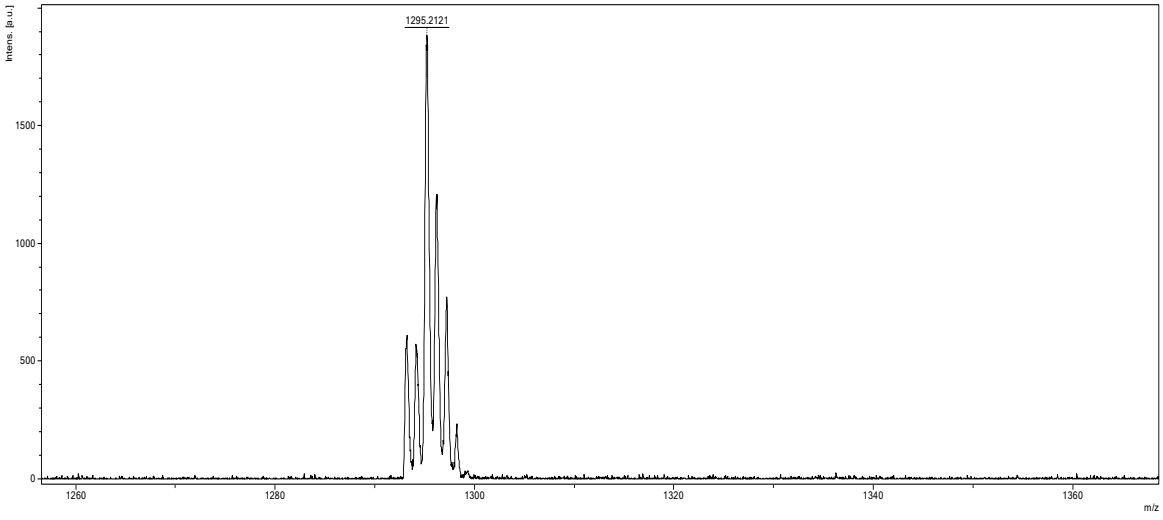


Figure S38. MALDI-TOF-MS of complex **Ni3**.



. **Figure S39.** MALDI-TOF-MS of complex **Ni4**.

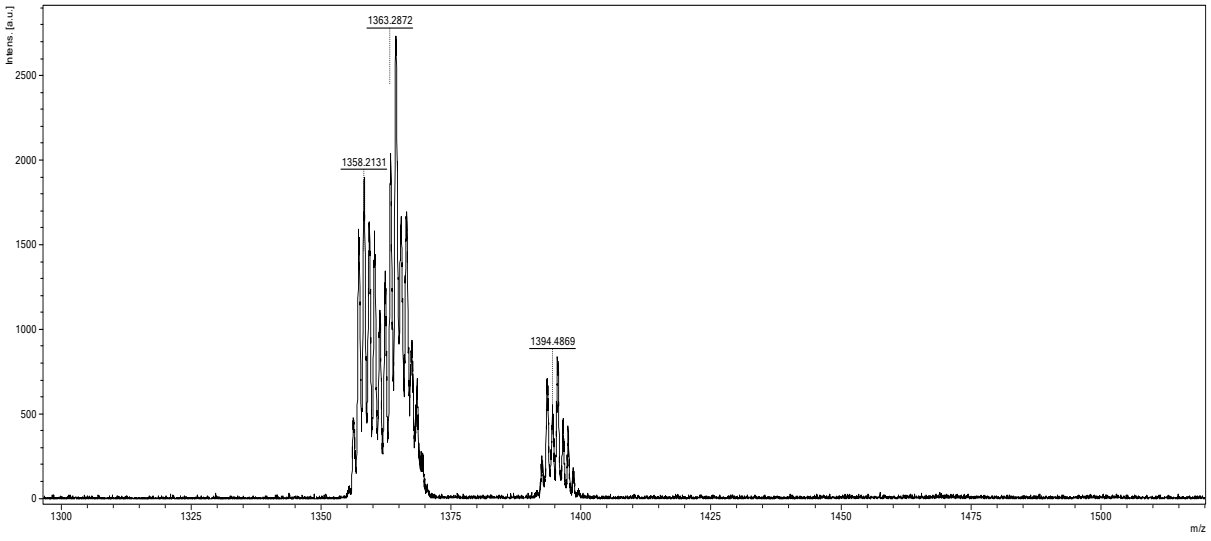


Figure S40. MALDI-TOF-MS of complex **Pd1**.

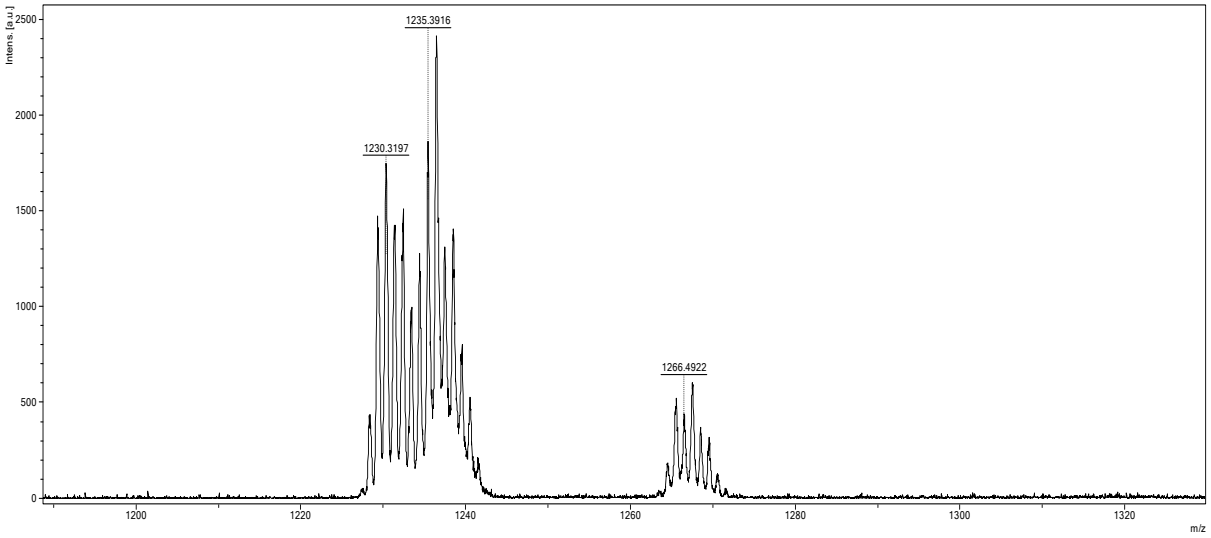


Figure S41. MALDI-TOF-MS of complex **Pd2**.

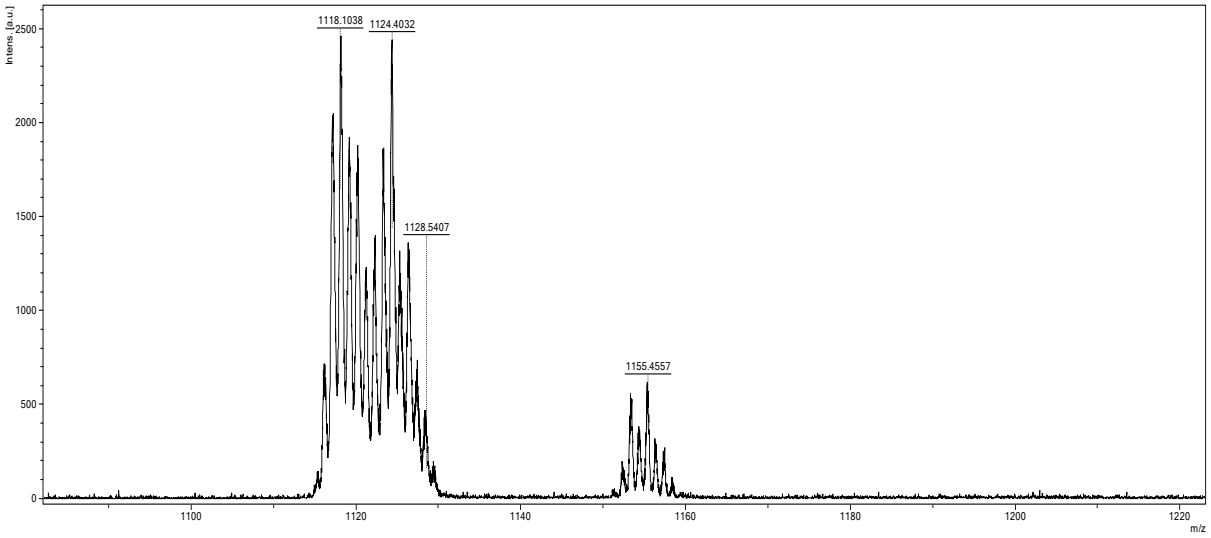


Figure S42. MALDI-TOF-MS of complex **Pd3**.

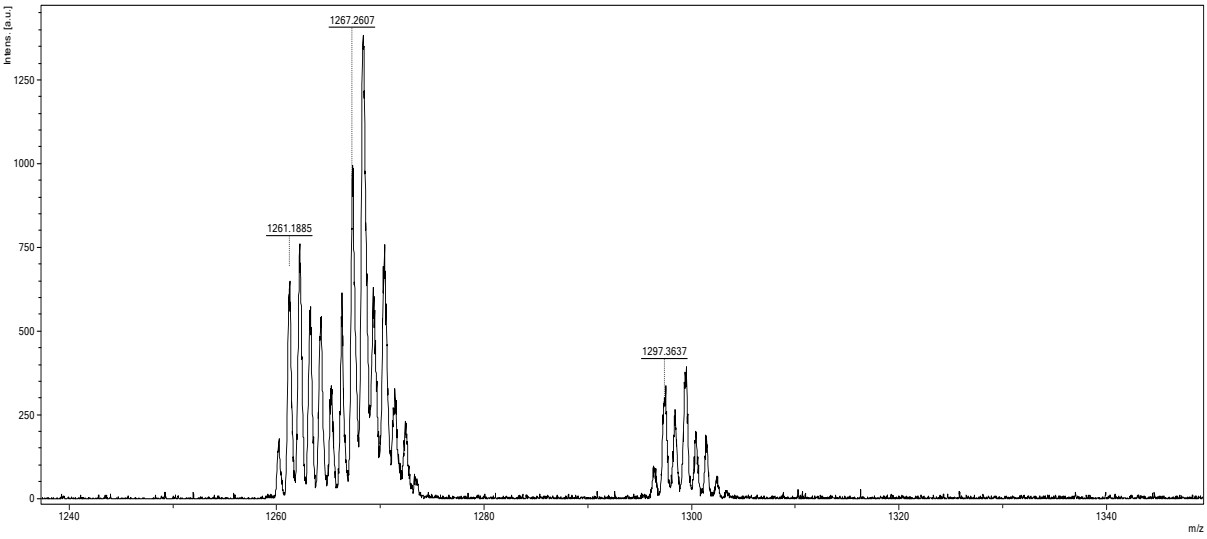


Figure S43. MALDI-TOF-MS of complex **Pd4**.

2.3 ^{1}H NMR of Polymers.

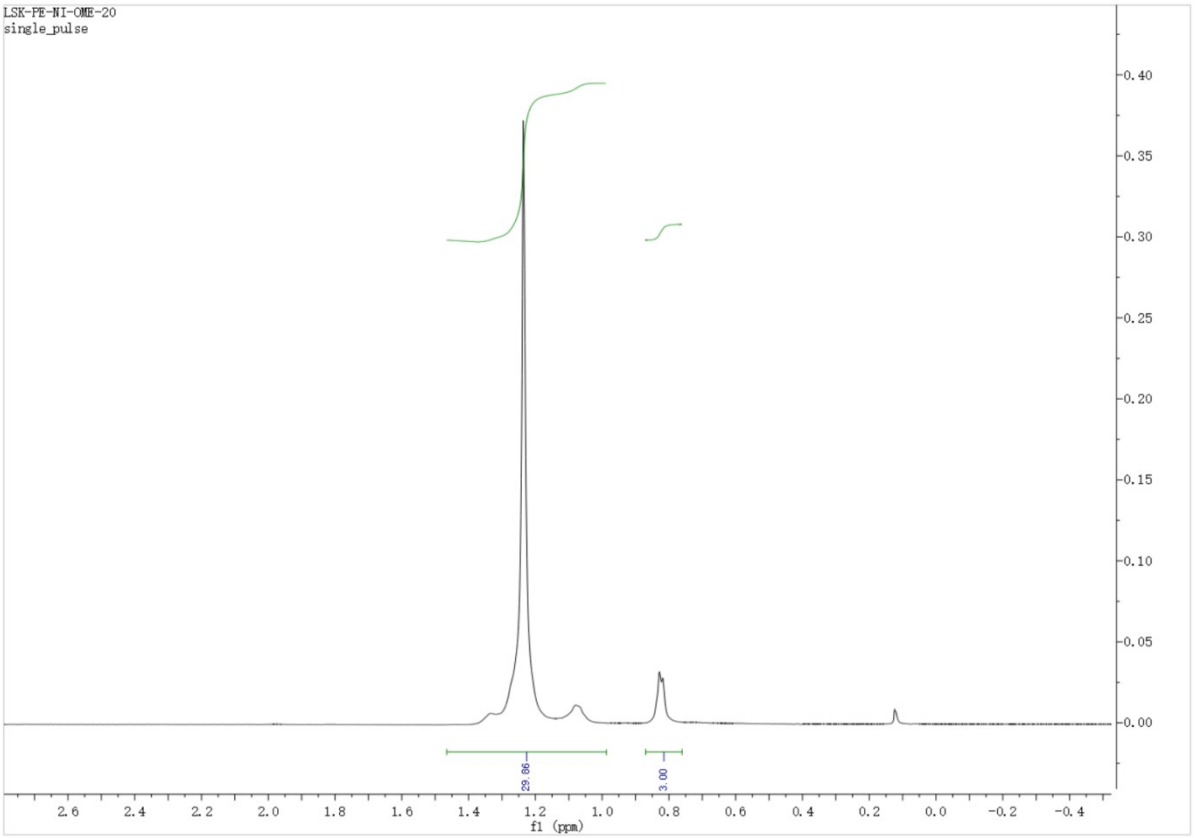


Figure S44. ^{1}H NMR spectrum of the polymer from table 1, entry 1 (d^{8}-toluene, 100 ^{o}C).

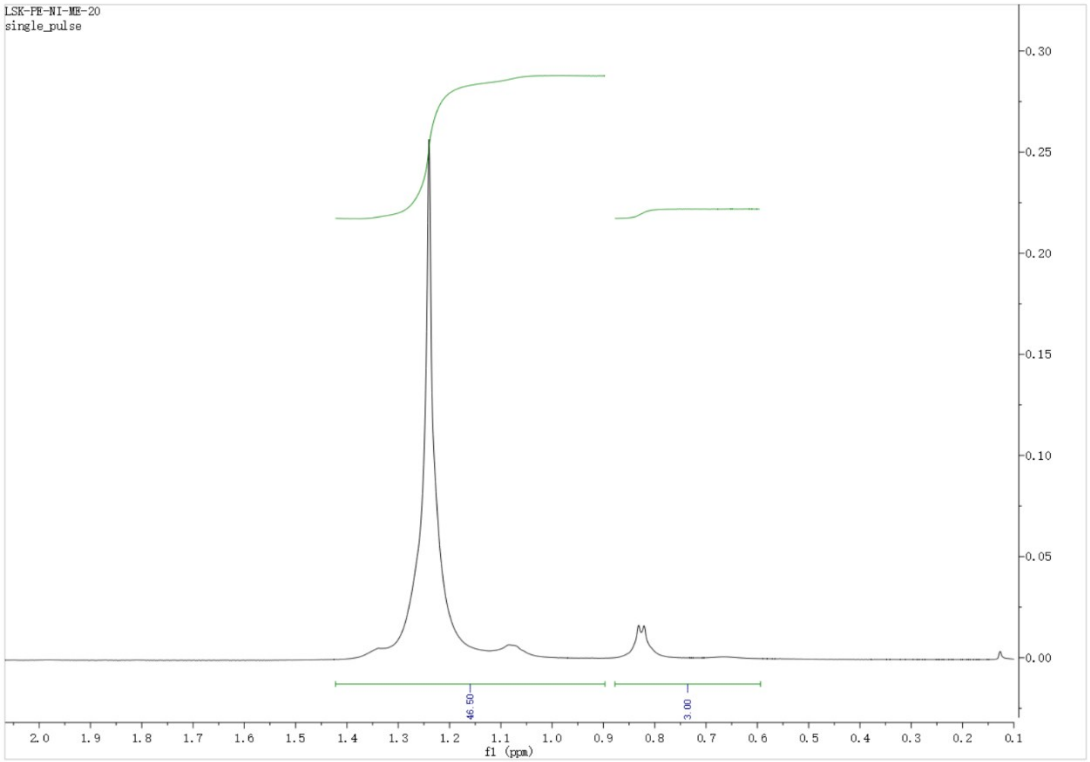


Figure S45. ^{1}H NMR spectrum of the polymer from table 1, entry 4 (d^{8}-toluene, 100 ^{o}C).

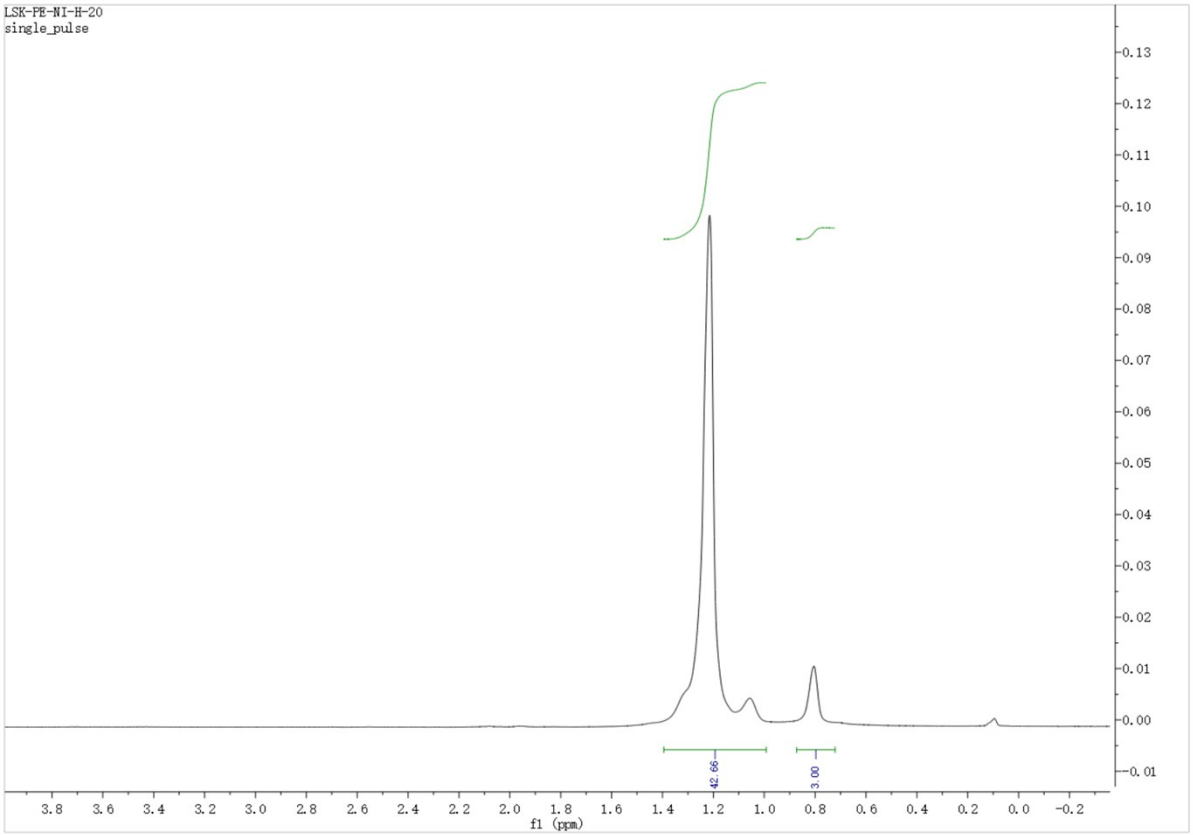


Figure S46. ^{1}H NMR spectrum of the polymer from table 1, entry 7 (d^{8}-toluene, 100 ^{o}C).

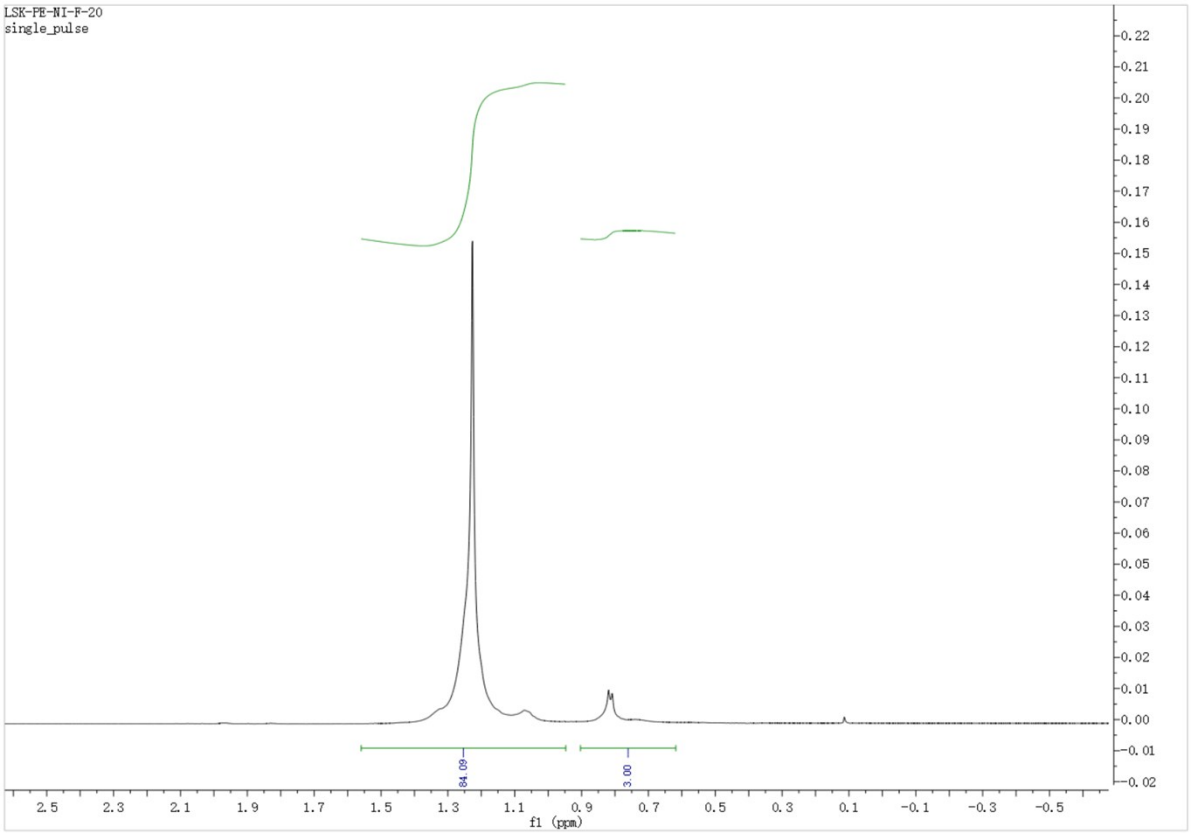


Figure S47. ^{1}H NMR spectrum of the polymer from table 1, entry 10 (d^{8}-toluene, 100 ^{o}C).

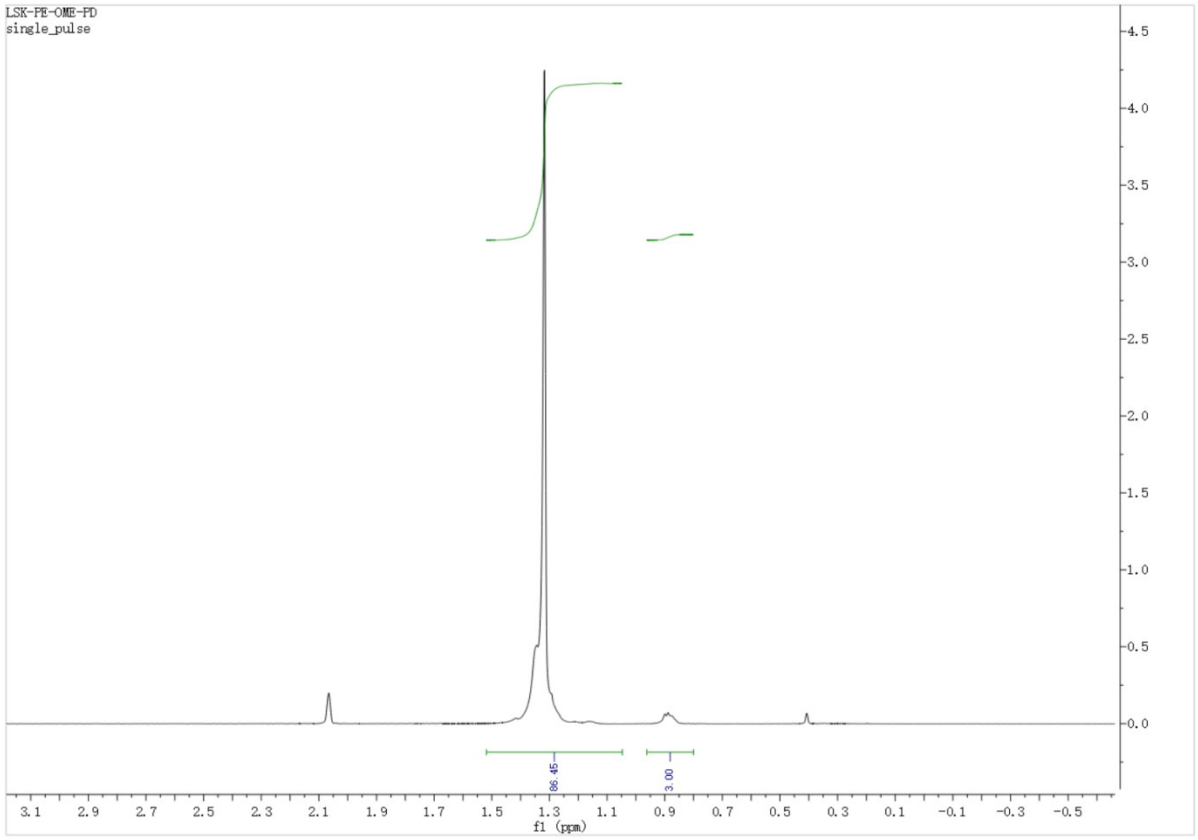


Figure S48. ^{1}H NMR spectrum of the polymer from table 2, entry 1 (d^{8}-toluene, 100 ^{o}C).

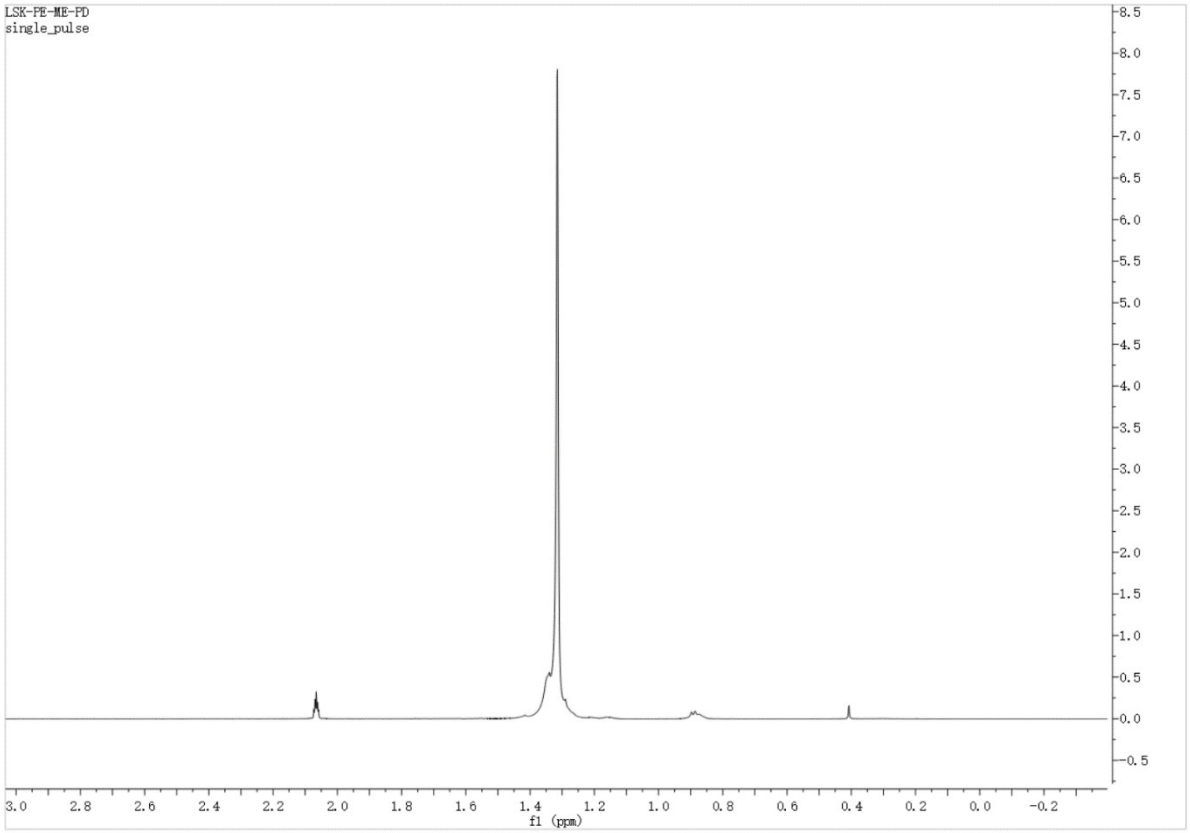


Figure S49. ^{1}H NMR spectrum of the polymer from table 2, entry 2 (d^{8}-toluene, 100 ^{o}C).

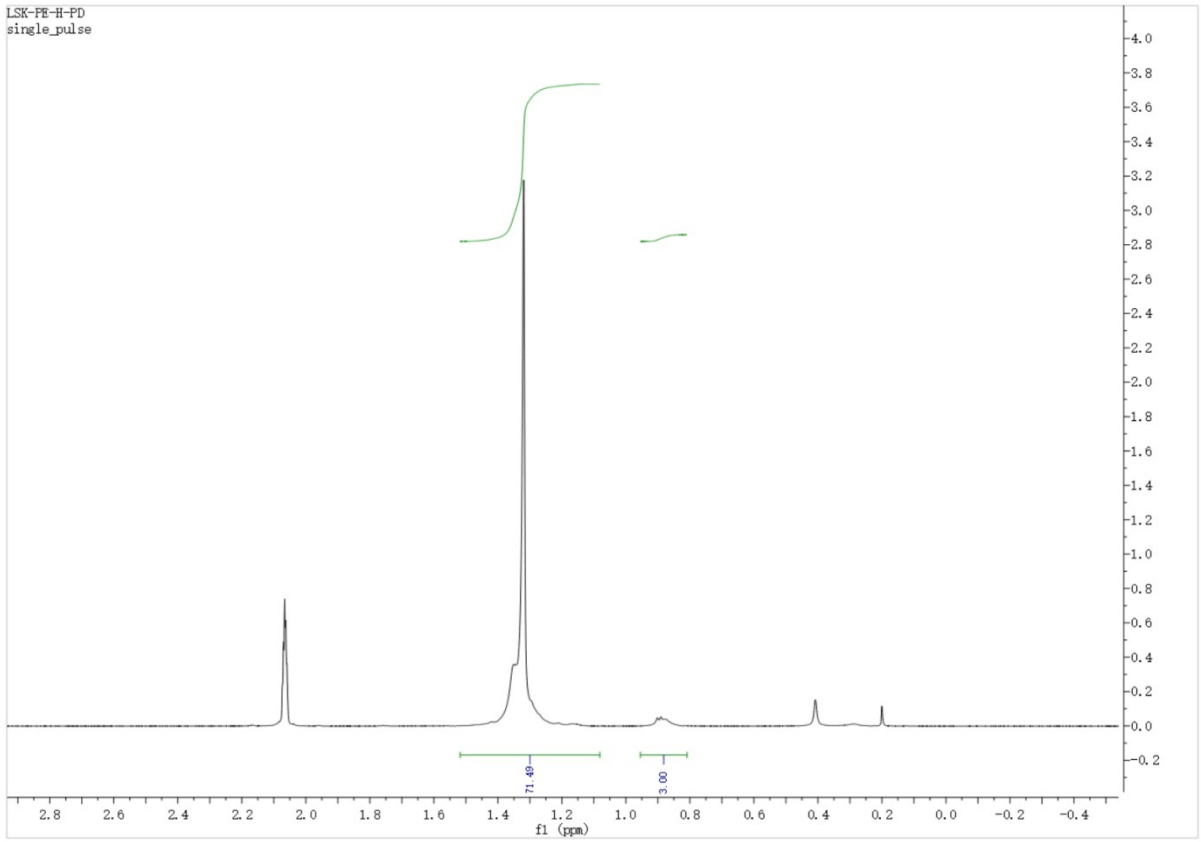


Figure S50. ^{1}H NMR spectrum of the polymer from table 2, entry 3 (d^{8}-toluene, 100 ^{o}C).

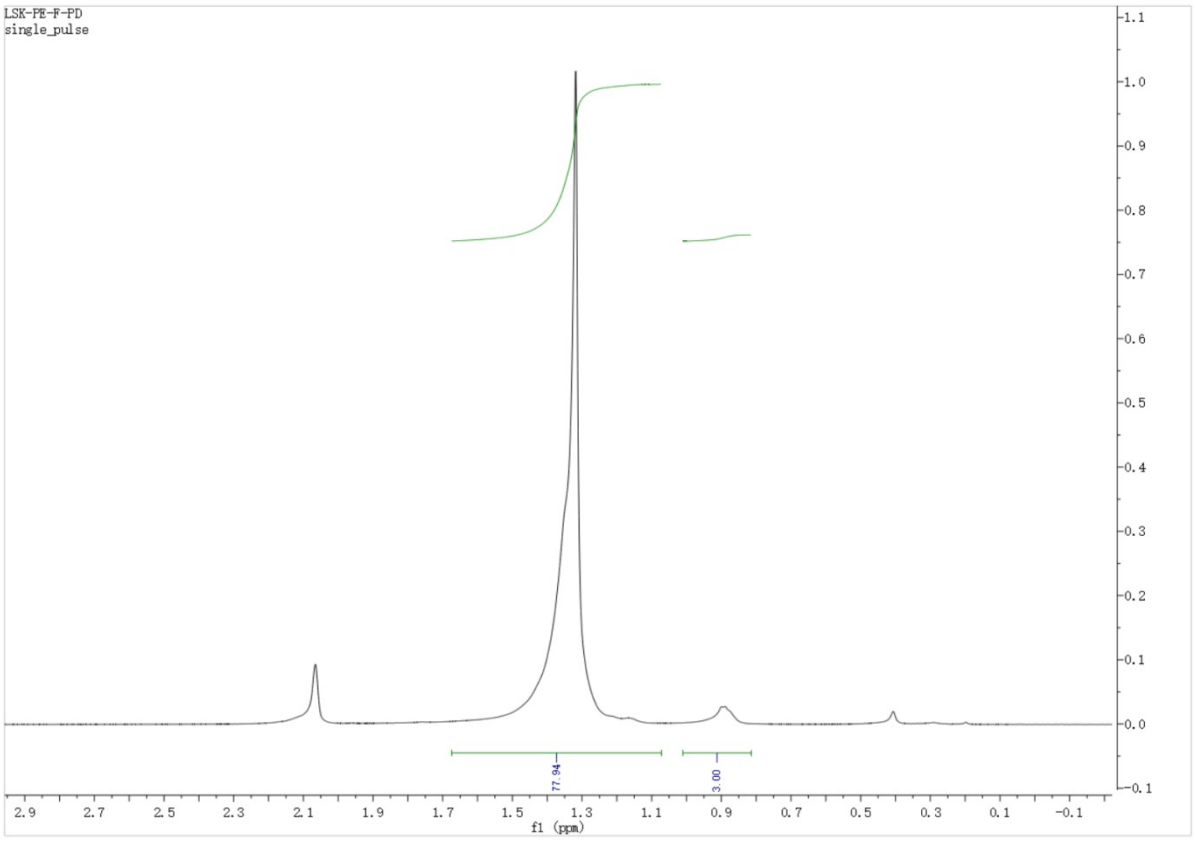


Figure S51. ^{1}H NMR spectrum of the polymer from table 2, entry 4 (d^{8}-toluene, 100 ^{o}C).

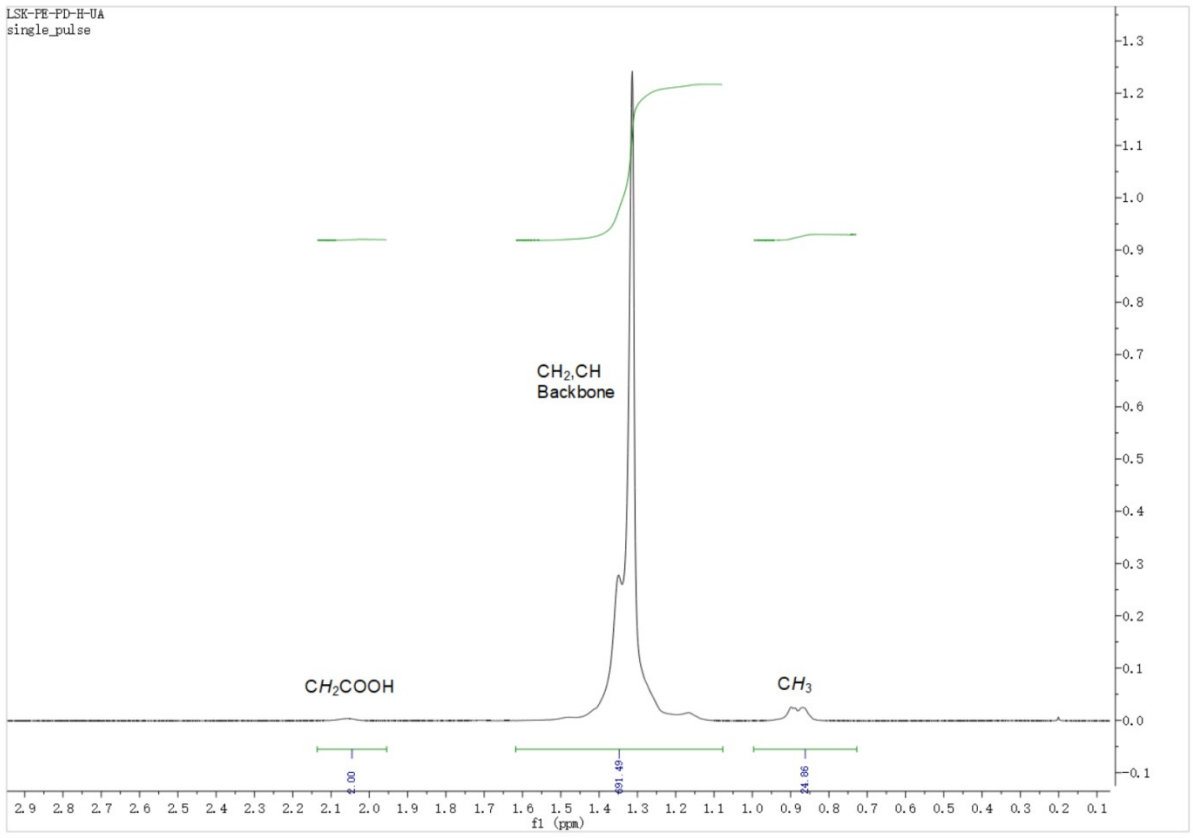


Figure S52. ^{1}H NMR spectrum of the polymer from table 3, entry 3 (C_6D_6, 70^{o}C).

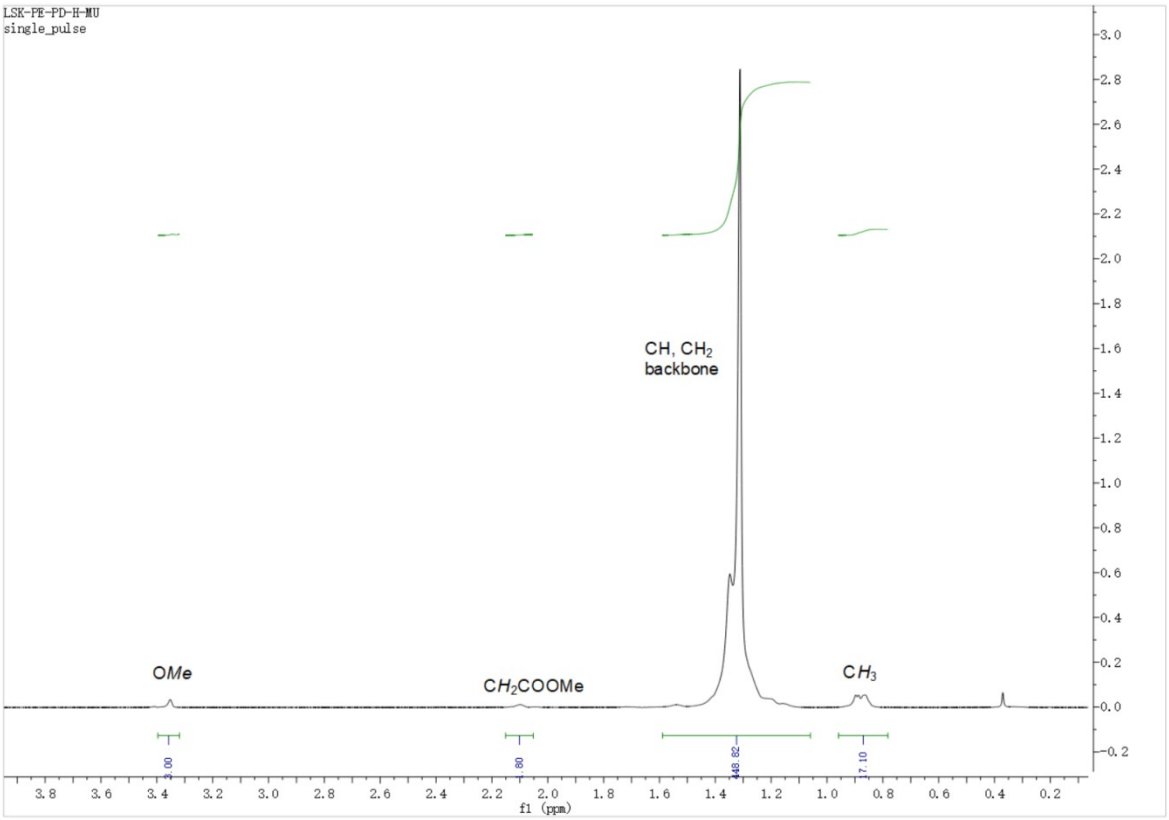


Figure S53. ^{1}H NMR spectrum of the polymer from table 3, entry 7 (C_6D_6, 70^{o}C).

2.4 DSC, DMA and GPC of Polymers.

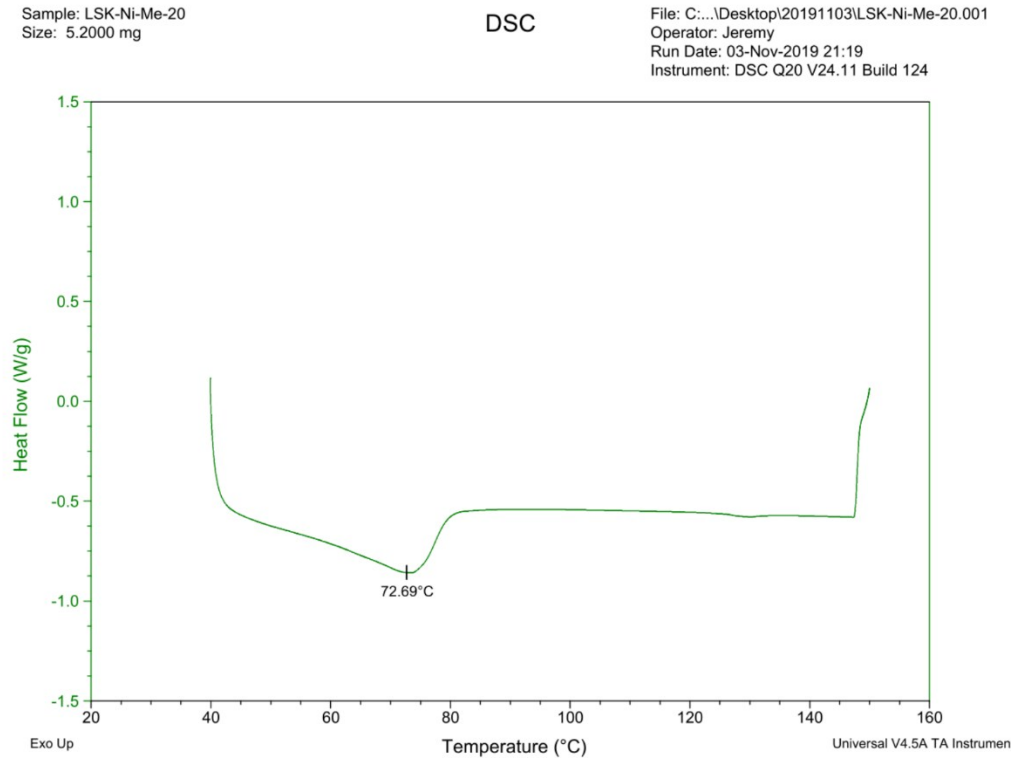


Figure S54. DSC of the polymer from table 1, entry 4.

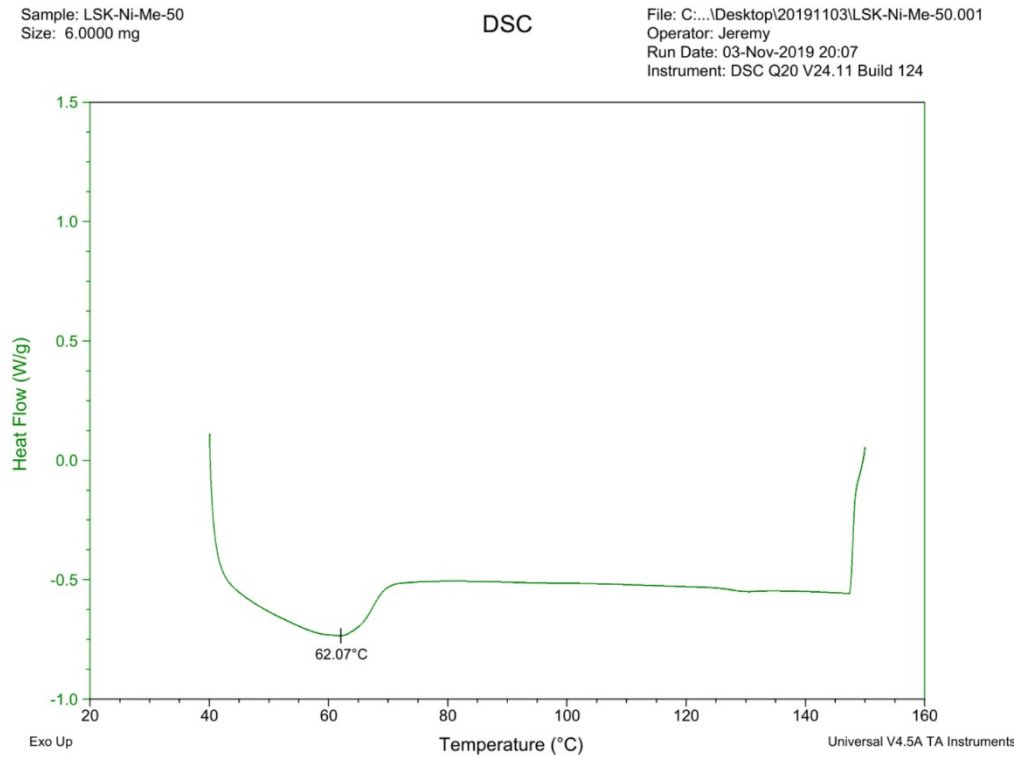


Figure S55. DSC of the polymer from table 1, entry 5.

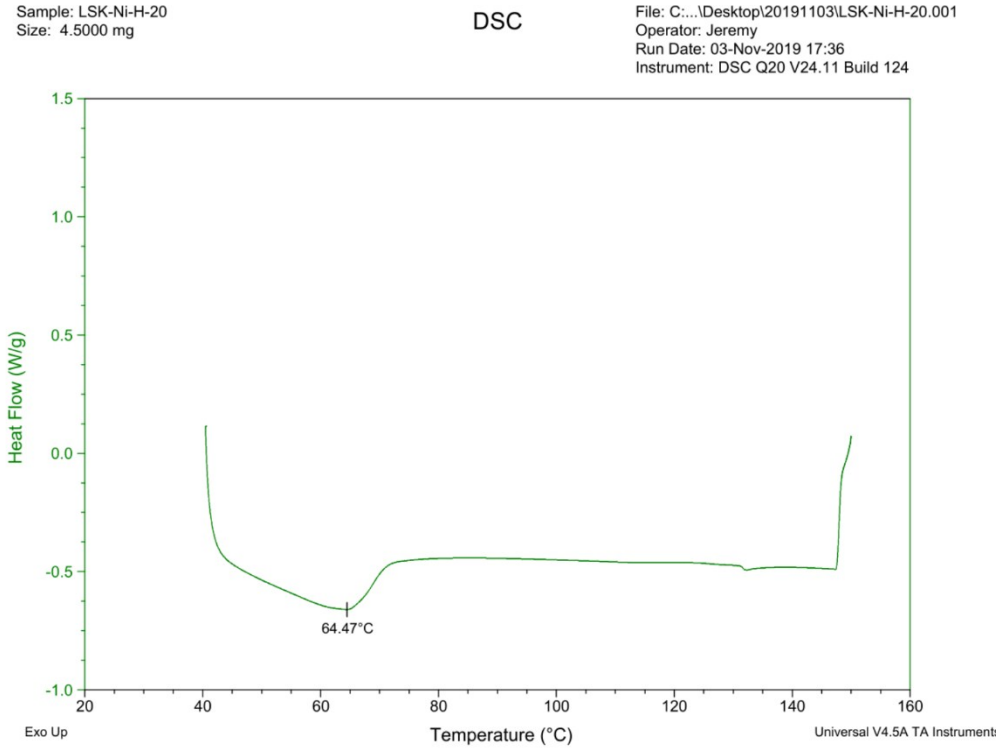


Figure S56. DSC of the polymer from table 1, entry 7.

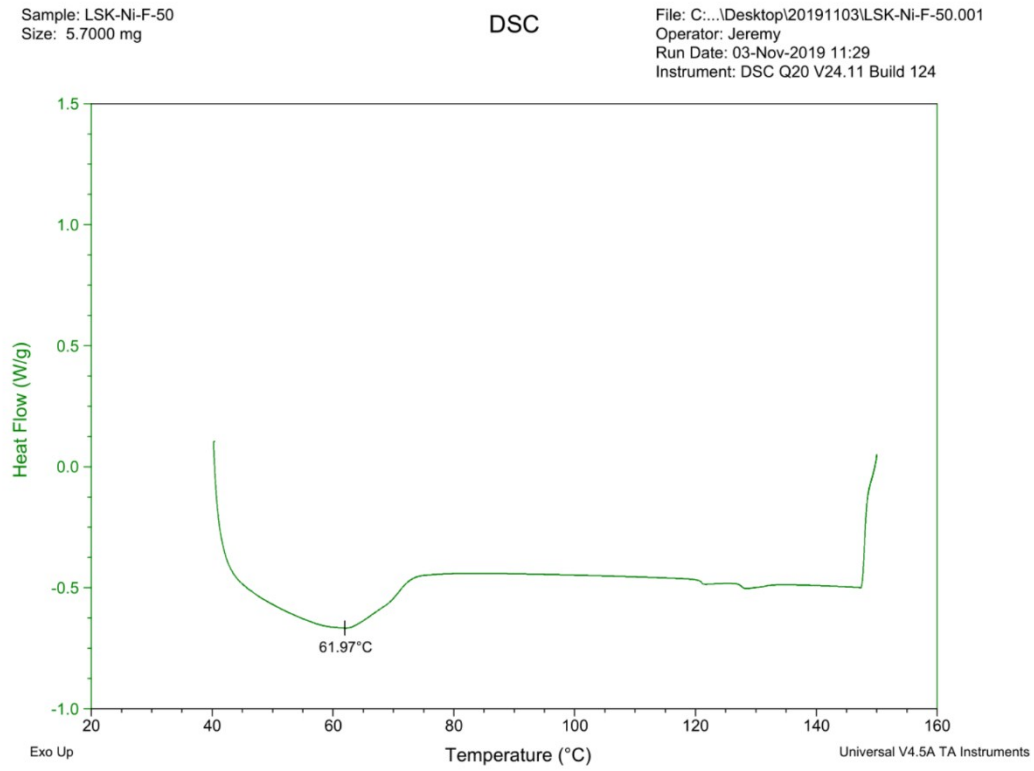


Figure S57. DSC of the polymer from table 1, entry 11.

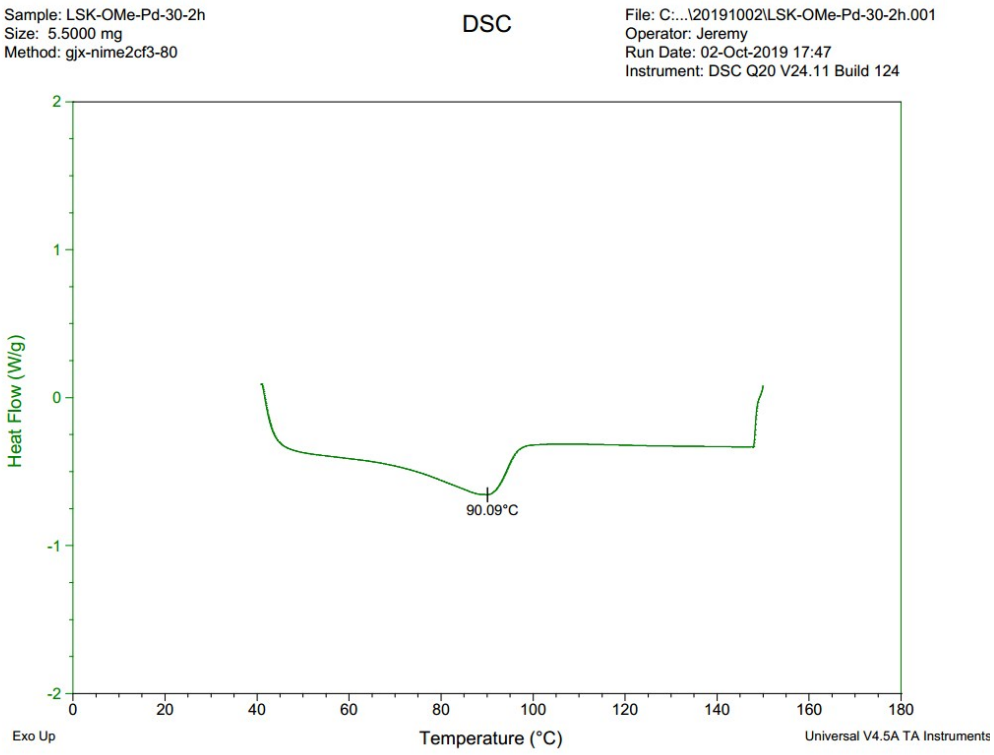


Figure S58. DSC of the polymer from table 2, entry 1.

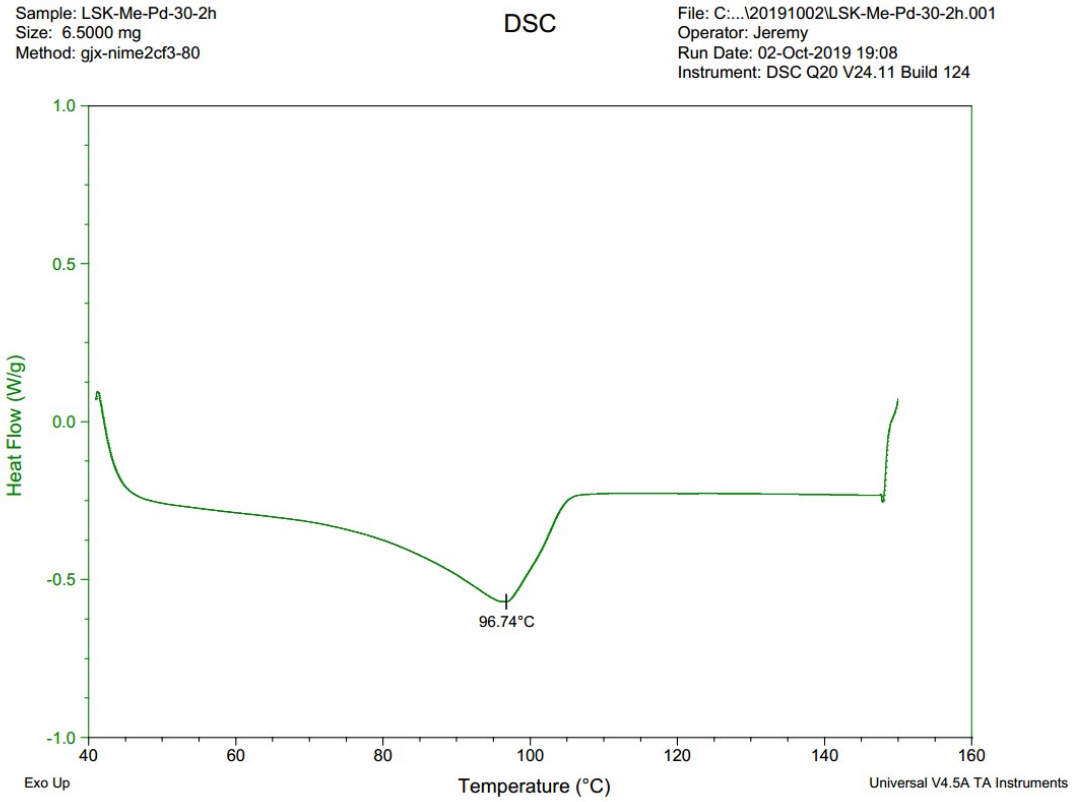


Figure S59. DSC of the polymer from table 2, entry 2.

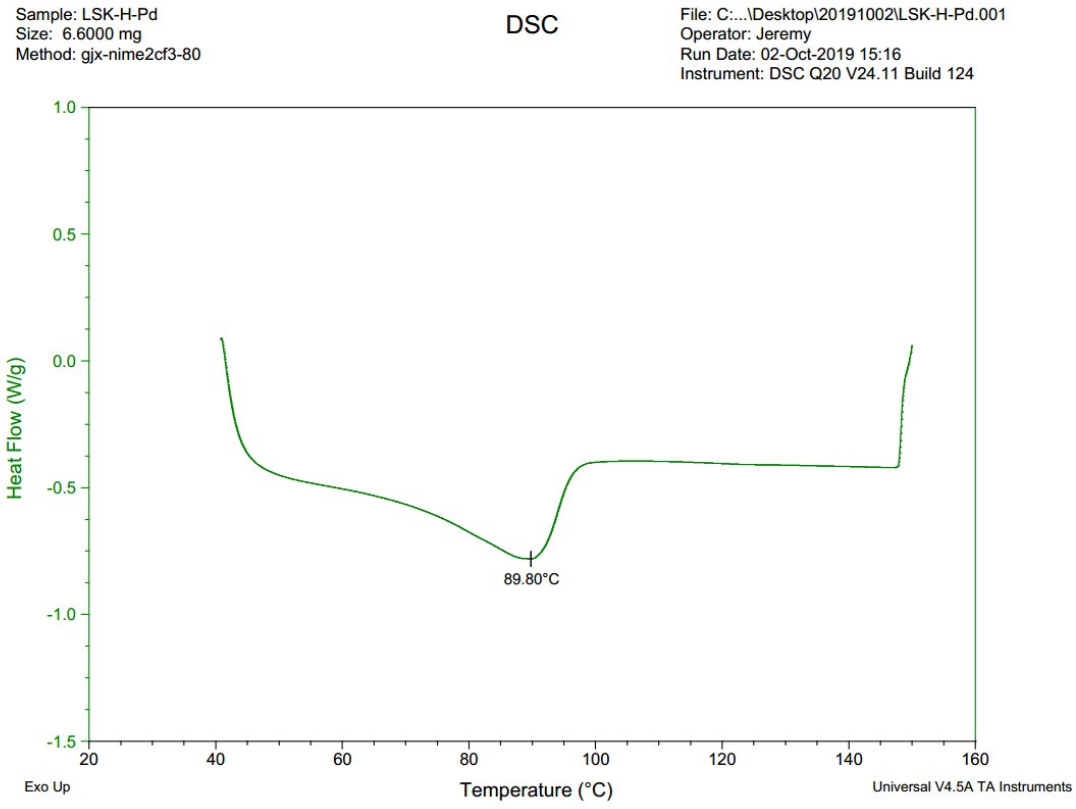


Figure S60. DSC of the polymer from table 1, entry 3.

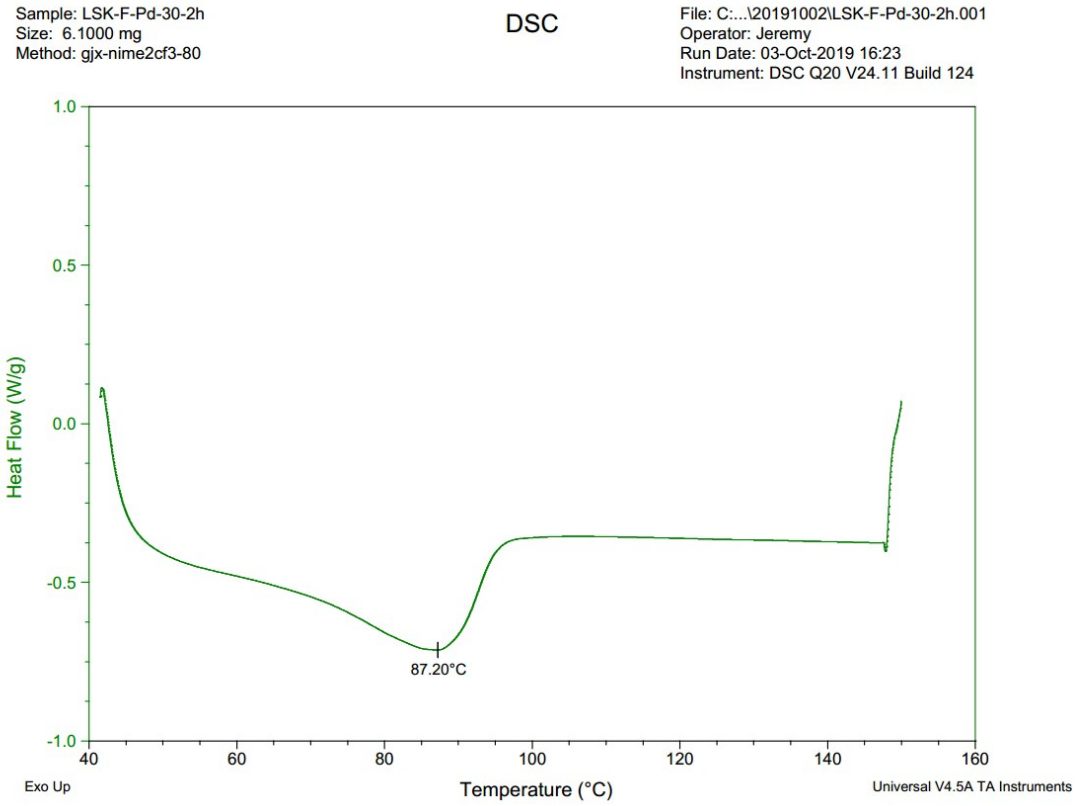


Figure S61. DSC of the polymer from table 1, entry 4.

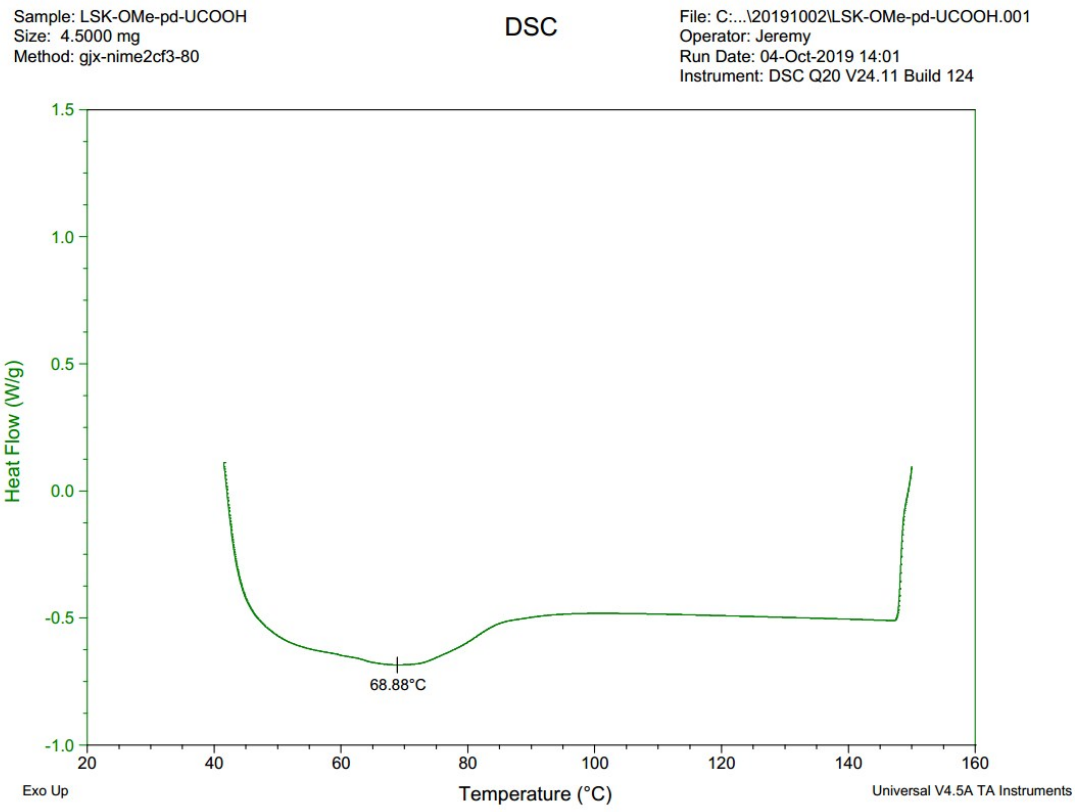


Figure S62. DSC of the polymer from table 3, entry 1.

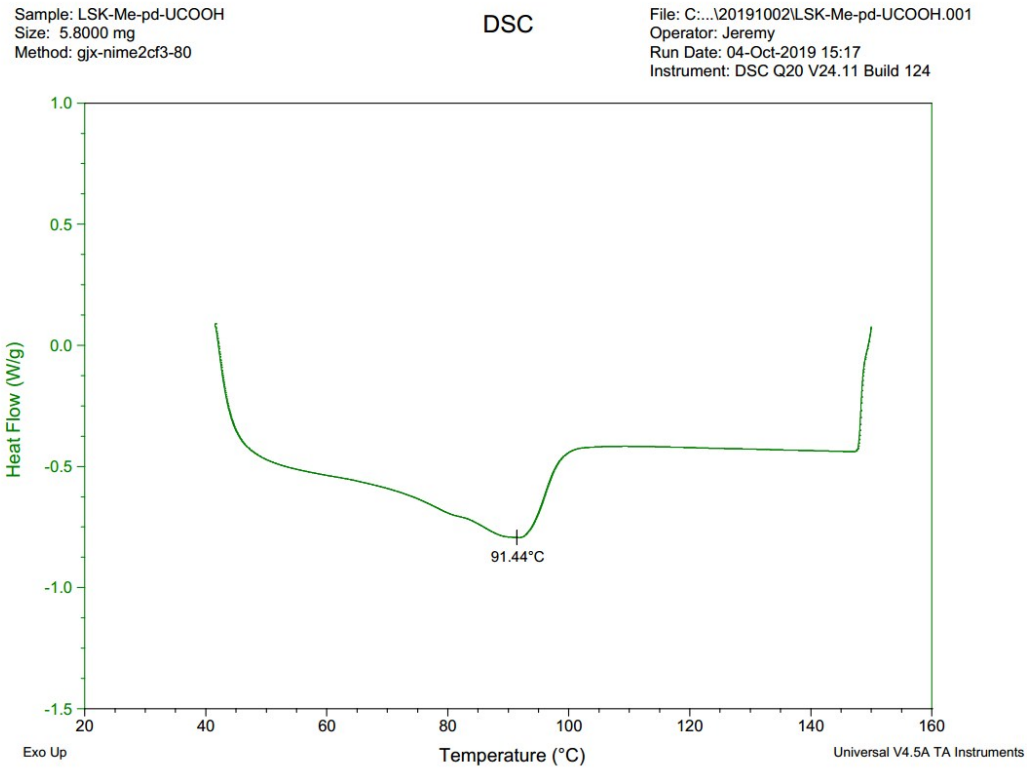


Figure S63. DSC of the polymer from table 3, entry 2.

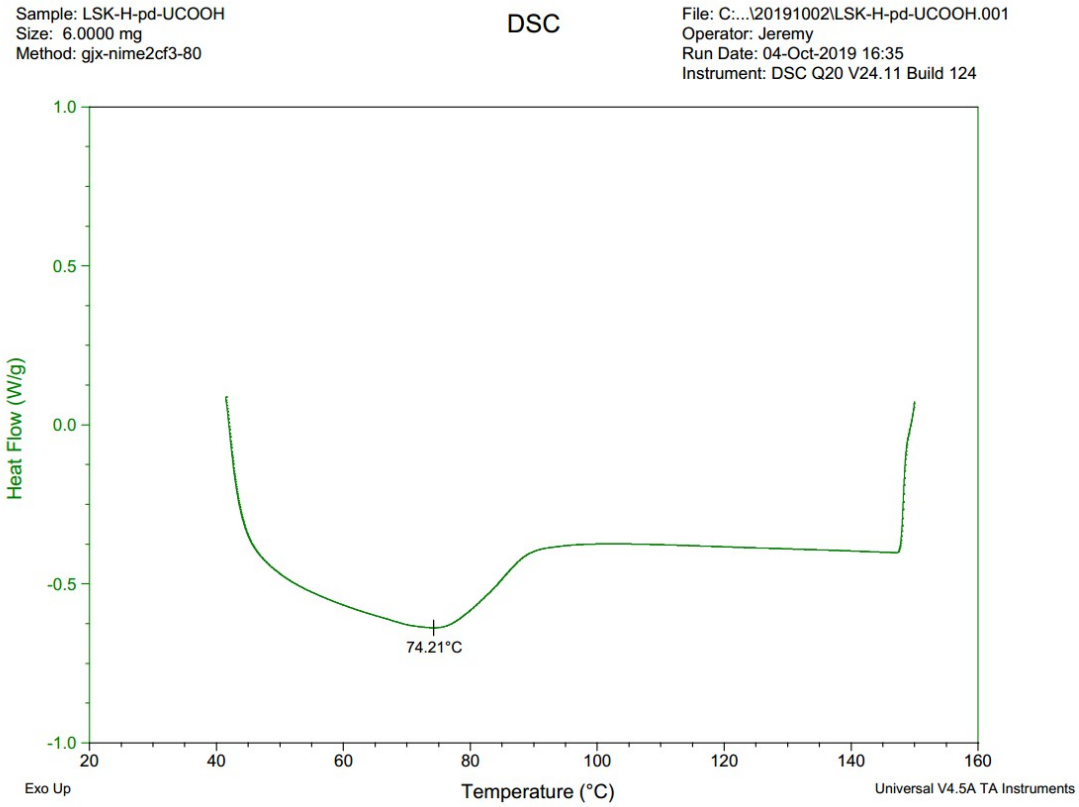


Figure S64. DSC of the polymer from table 3, entry 3.

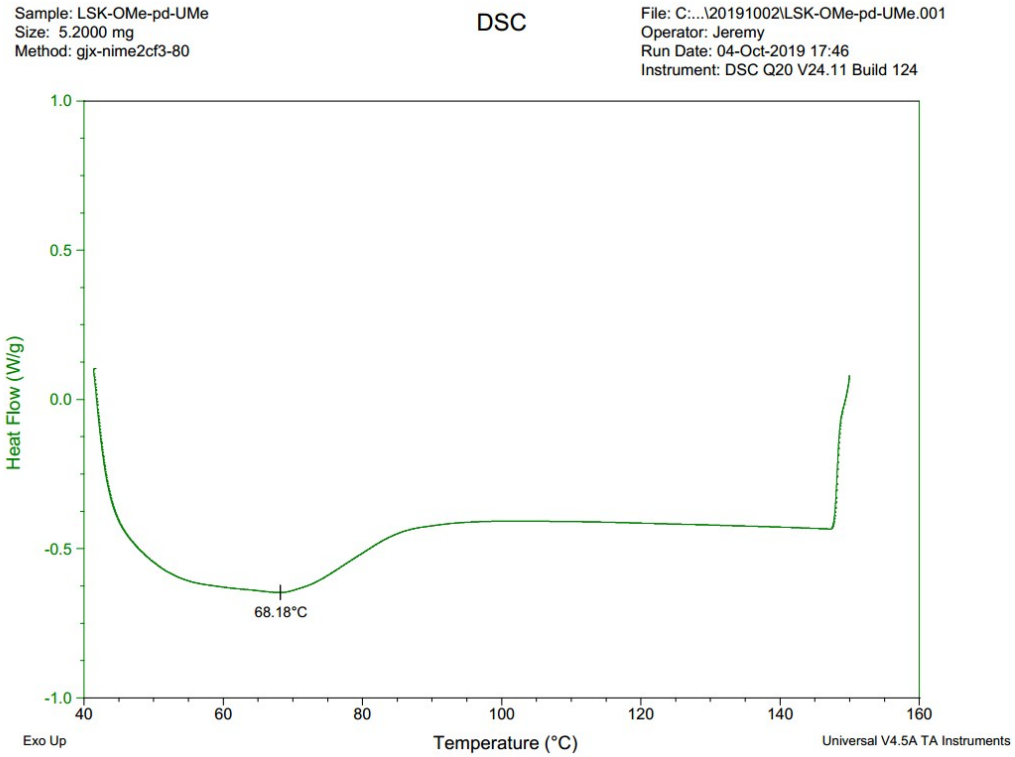


Figure S65. DSC of the polymer from table 3, entry 5.

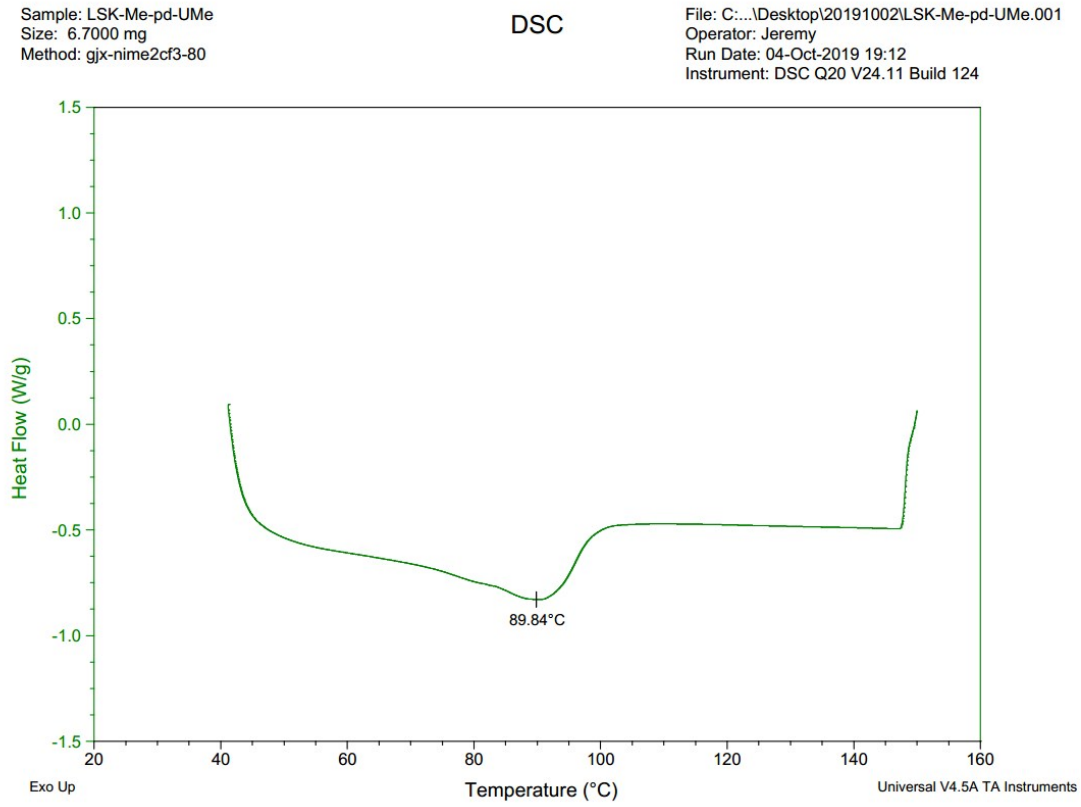


Figure S66. DSC of the polymer from table 3, entry 6.

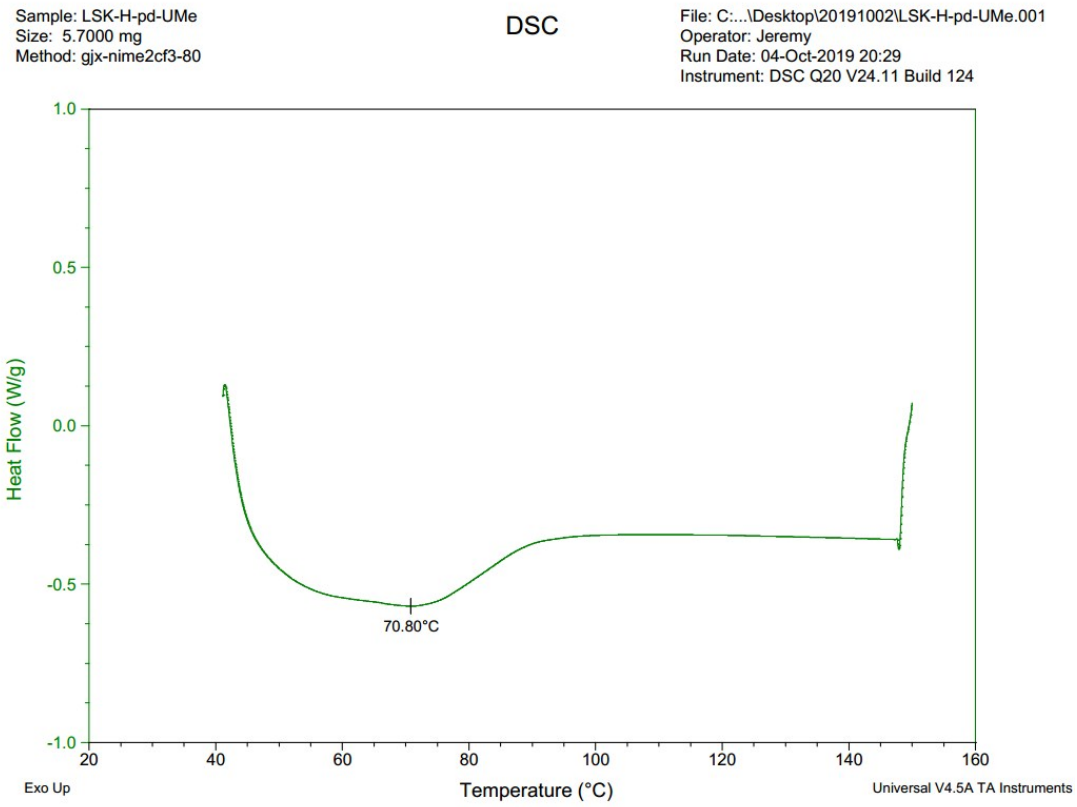


Figure S67. DSC of the polymer from table 3, entry 7.

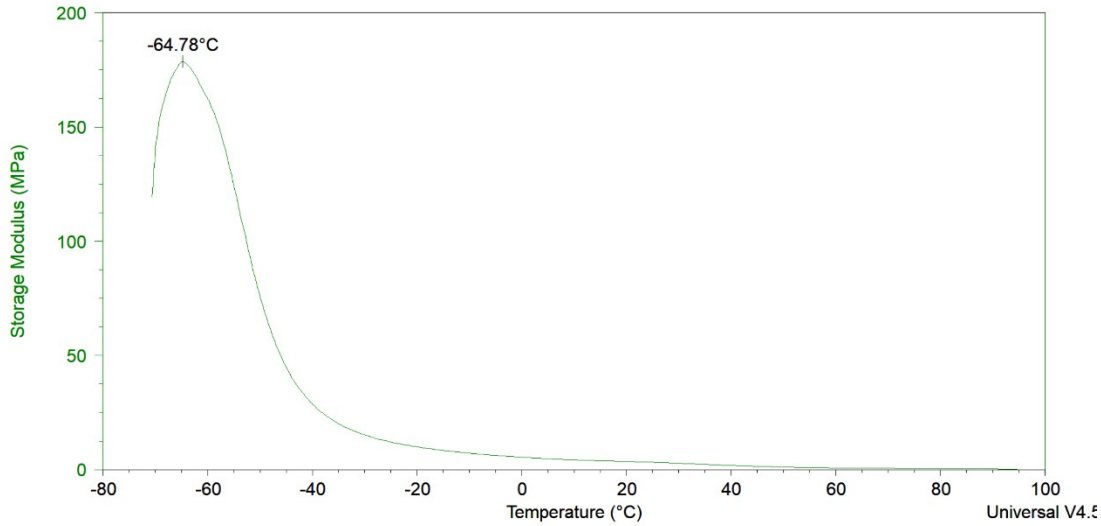


Figure S68. DMA of the polymer from table 1, entry 3.

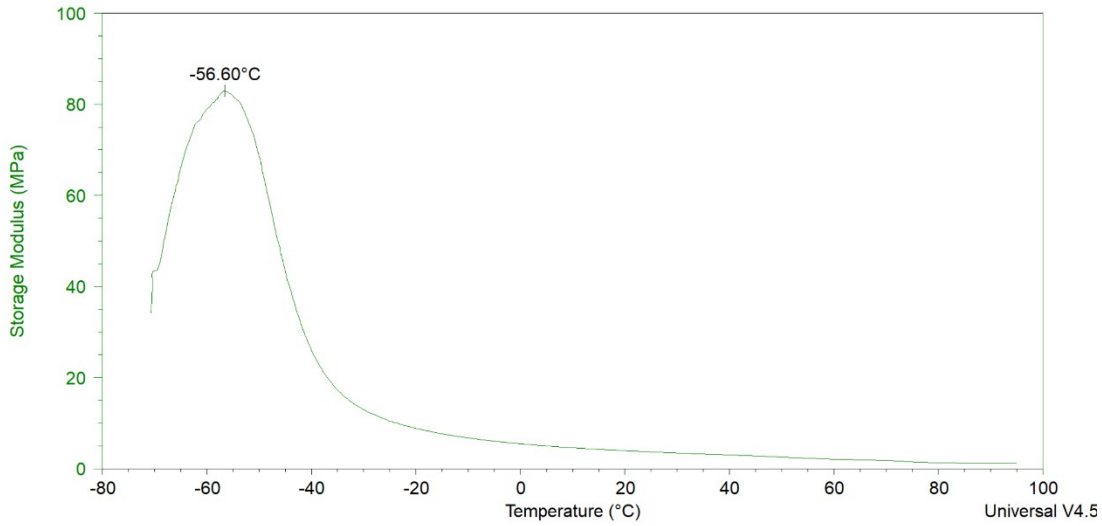


Figure S69. DMA of the polymer from table 1, entry 5.

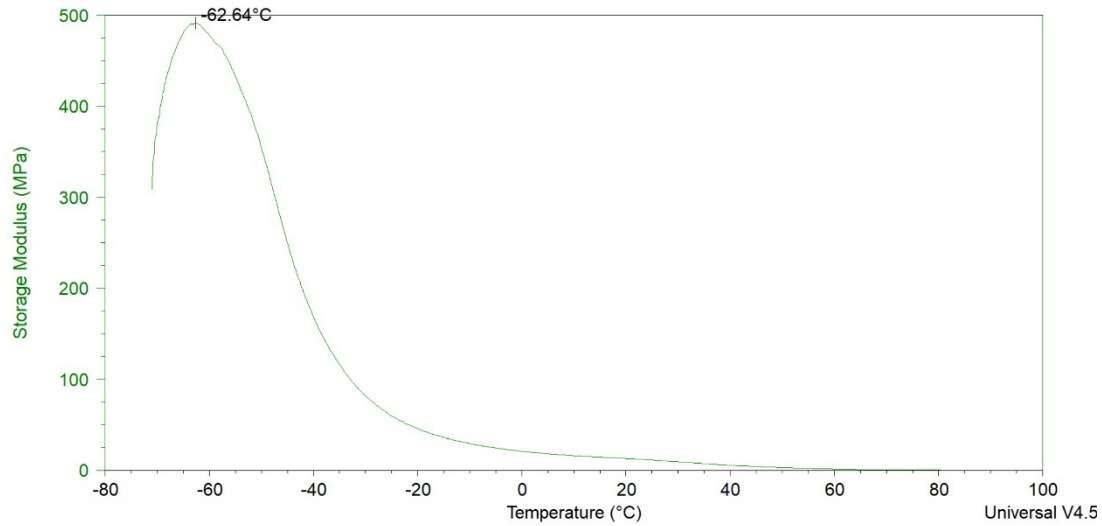
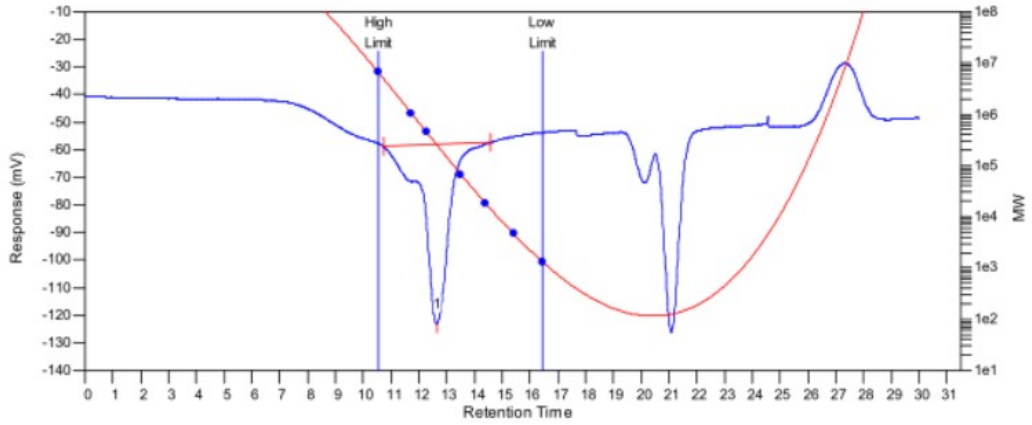
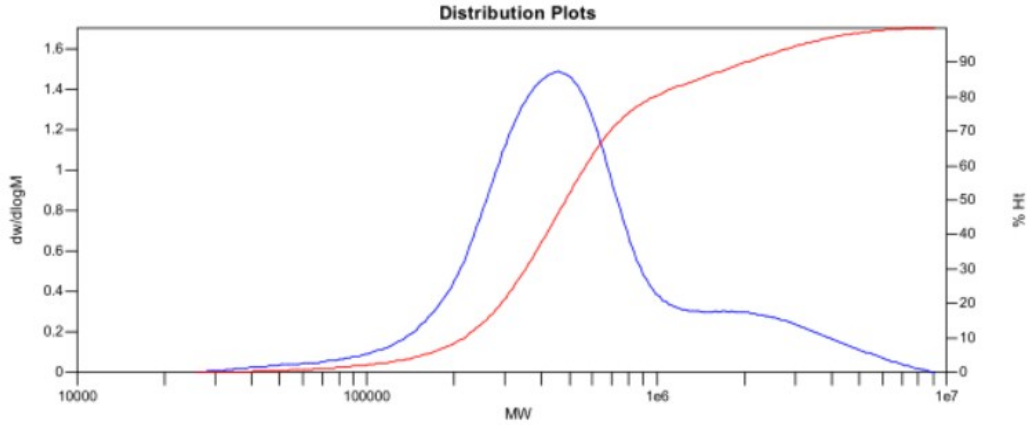


Figure S70. DMA of the polymer from table 2, entry 7.





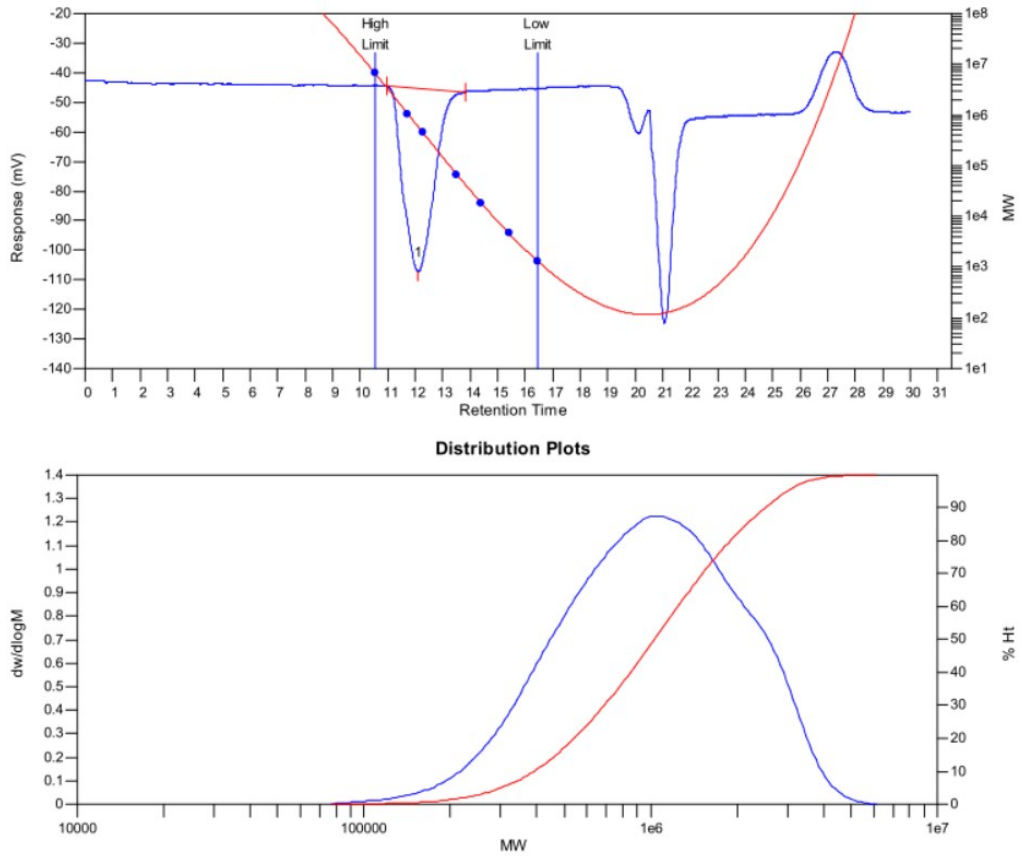
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	455621	374175	825647	2094286	3758656	712615	2.20658

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.73	12.65	14.57	-64.8908	100	3876.48	100

Figure S71. GPC of the polymer from table 1, entry 1.



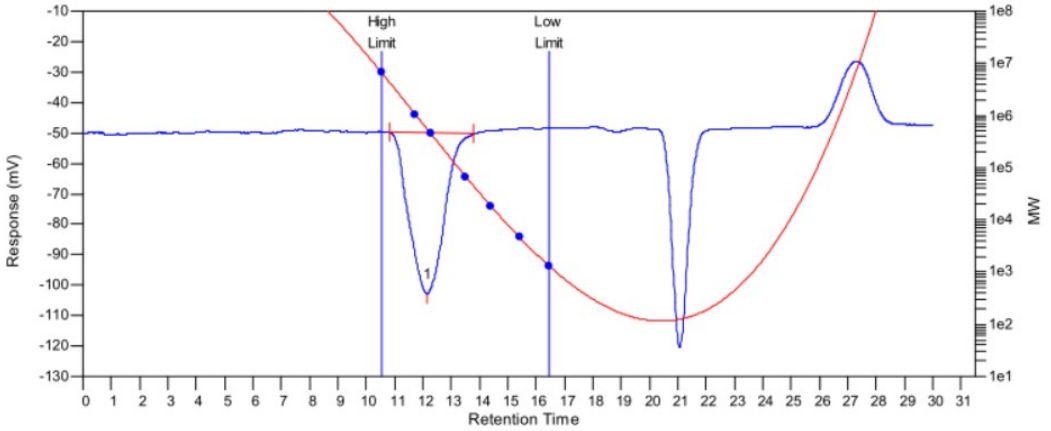
MW Averages

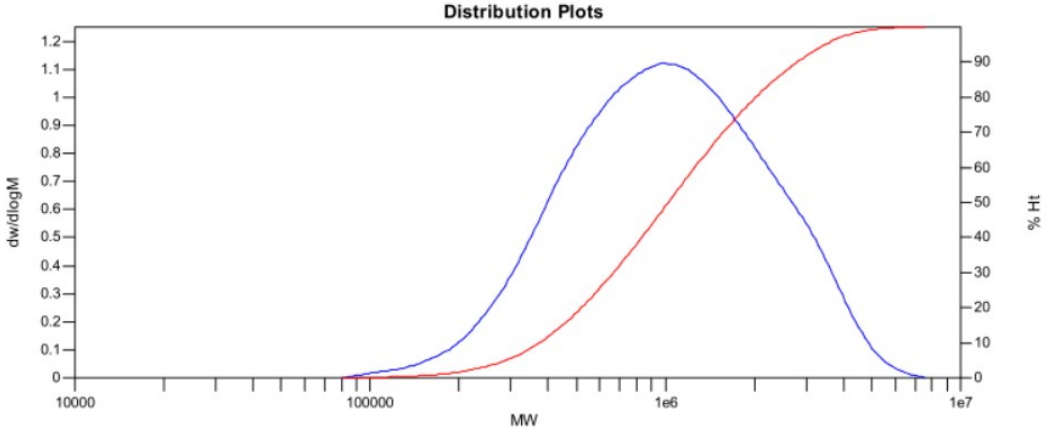
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1049134	758054	1238038	1807416	2343617	1157430	1.63318

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	12.12	13.82	-61.8734	100	4445.85	100

Figure S72. GPC of the polymer from table 1, entry 6.





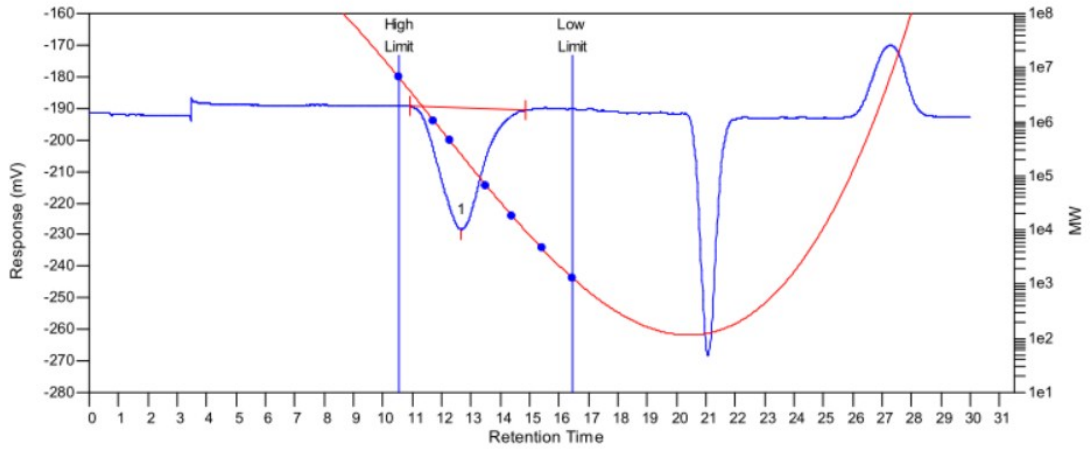
MW Averages

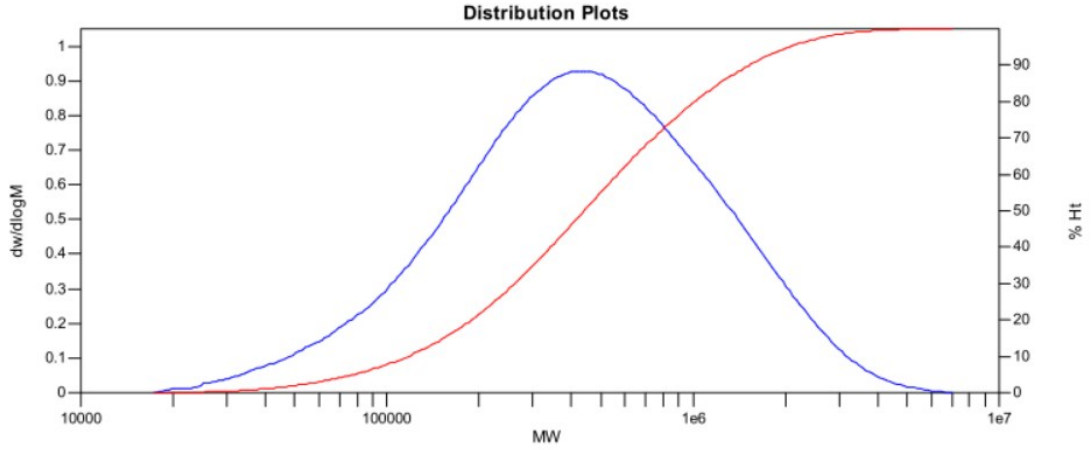
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	995707	743335	1316570	2096425	2881041	1212958	1.77117

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.85	12.15	13.78	-52.7688	100	4147.71	100

Figure S73. GPC of the polymer from table 1, entry 11.





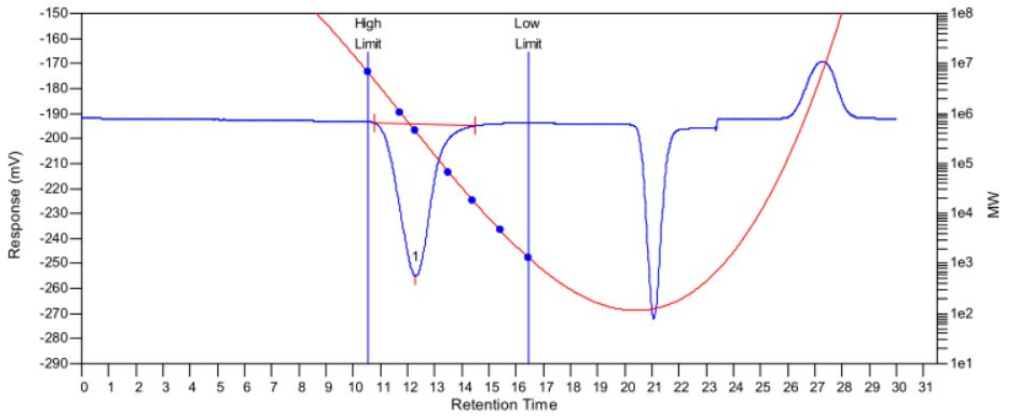
MW Averages

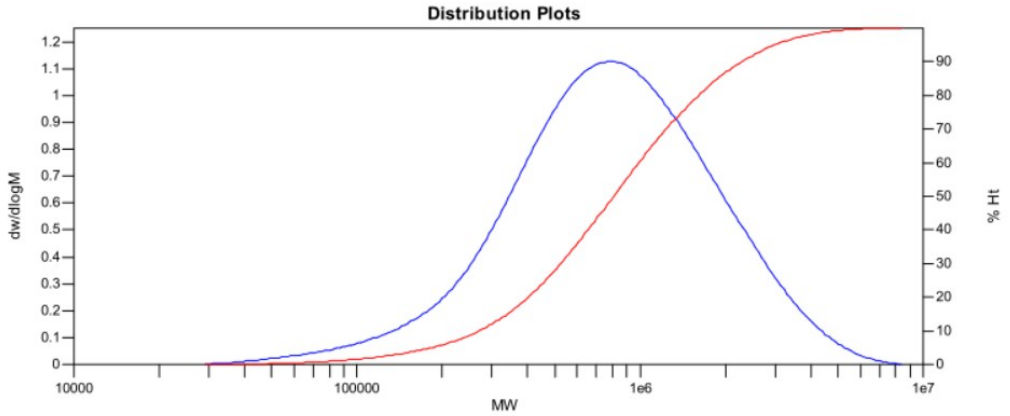
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	443948	250218	654679	1352760	2179142	574316	2.61643

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.90	12.67	14.85	-38.5186	100	3682.98	100

Figure S74. GPC of the polymer from table 2, entry 1.





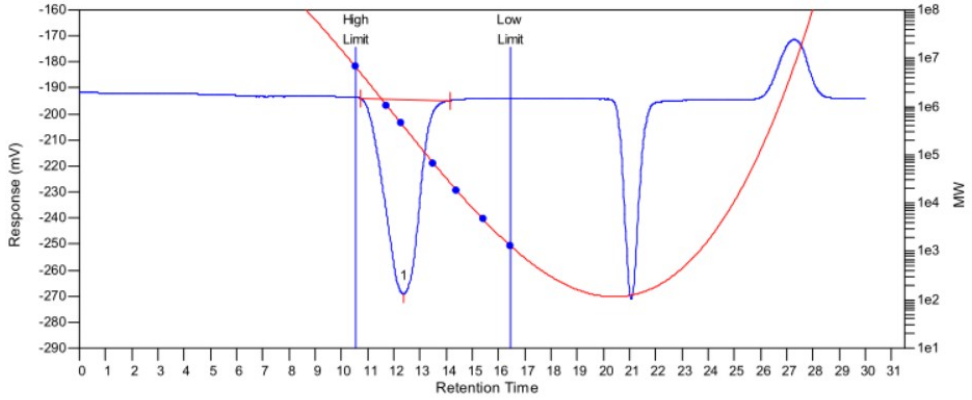
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	787143	517240	1071677	1873643	2818450	972767	2.07191

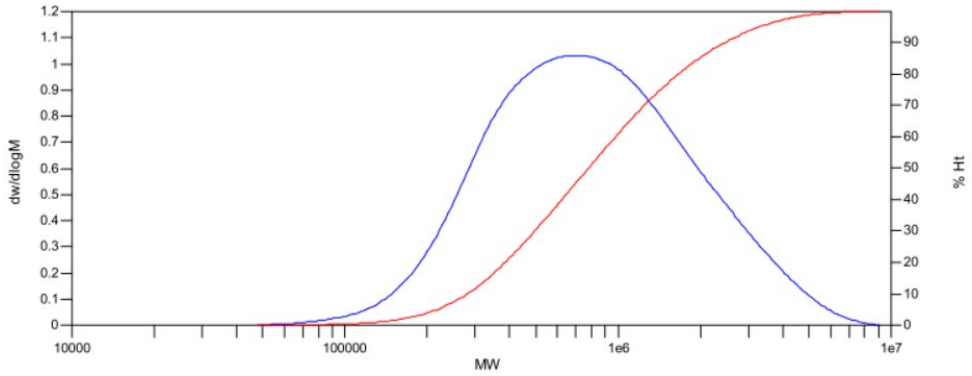
Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.78	12.30	14.48	-60.6634	100	4750.69	100

Figure S75. GPC of the polymer from table 2, entry 2.



Distribution Plots



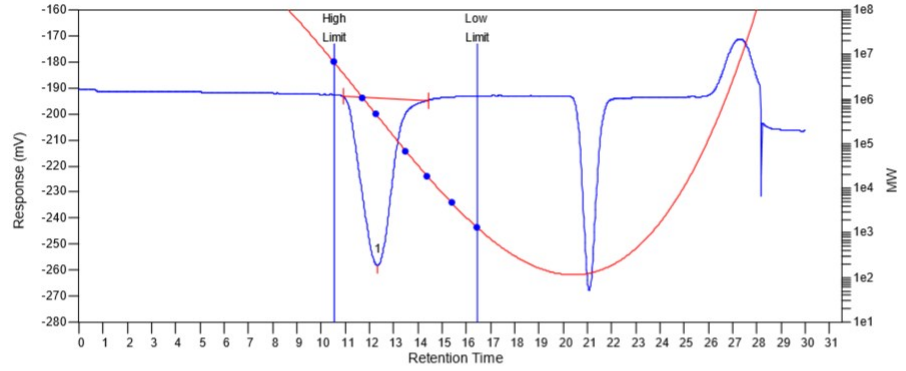
MW Averages

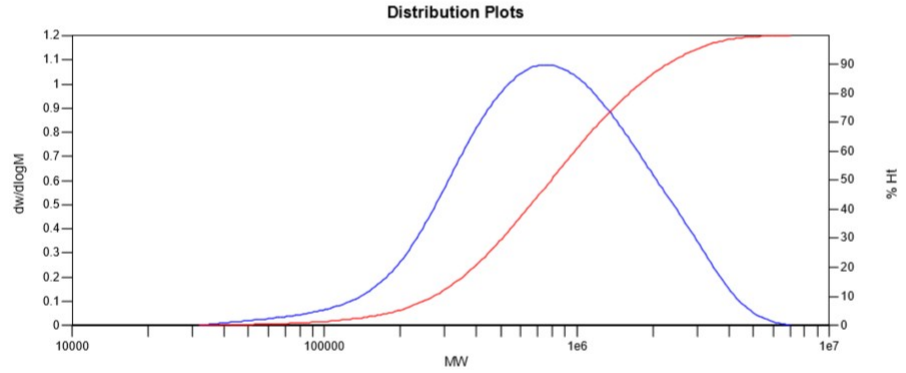
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	690889	564381	1106519	2049379	3159409	996327	1.96059

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.73	12.38	14.13	-74.725	100	6389	100

Figure S76. GPC of the polymer from table 2, entry 3.





MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	747117	523565	1048476	1778270	2548013	954697	2.00257

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.90	12.33	14.42	-64.374	100	5267.19	100

Figure S77. GPC of the polymer from table 2, entry 5.

2.5 Mechanical Properties of Copolymers.

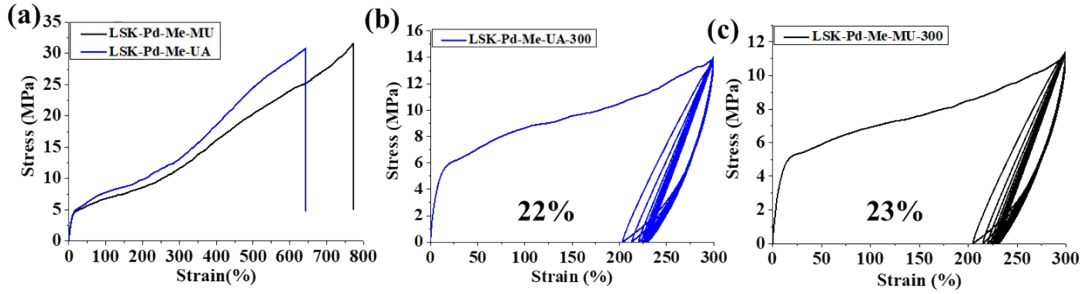


Figure S78. Stress-strain curves for E-UA and E-MU generated by **Pd2** (**Table 3**, entries 2 and 6) (**a**); Plots of hysteresis experiments of ten cycles at a strain of 300% for samples generated by **Pd2** (**b-c**) (**Table 3,** entries 2, 6)

3. References

1. L. Guo, W. Kong, Y. Xu, Y. Yang, R. Ma, L. Cong, S. Dai and Z. Liu, *J. Organometal. Chem.*, 2018, **859**, 58–67.

4. X-ray Crystallography

CCDC numbers of **Pd3-Pd4** are 1979307-1979308. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

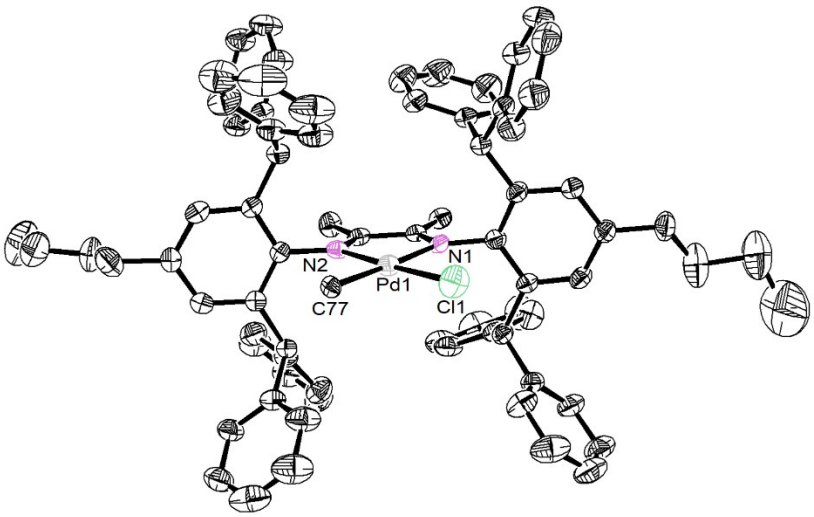


Table S1 Crystal data and structure refinement for **Pd3**.	
Identification code	**Pd3**
Empirical formula	C77 H75 Cl N2 Pd
Formula weight	1170.24
Temperature/K	293(2) K
Crystal system	Monoclinic
Space group	P2(1)/c
a/Å	13.1908(6)
b/Å	27.7405(13)
c/Å	18.6474(7)
α /°	90.00
β /°	92.509(2)
γ /°	90.00
Volume/Å^3	6816.9(5)
Z	4
ρ_{calc}g/cm^3	1.140
μ /mm^{-1}	2.861
F(000)	2456
Crystal size/mm^3	0.30 x 0.06 x 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.86 to 66.04

Index ranges	-15<=h<=12, -16<=k<=32, -19<=l<=22
Reflections collected	23809
Independent reflections	11887 [R(int) = 0.0508]
Data/restraints/parameters	11887 / 87 / 740
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ(I)]	R1 = 0.0602, wR2 = 0.1260
Final R indexes [all data]	R1 = 0.1050, wR2 = 0.1425
Largest diff. peak/hole / e $Å^{-3}$	0.613 and -0.651

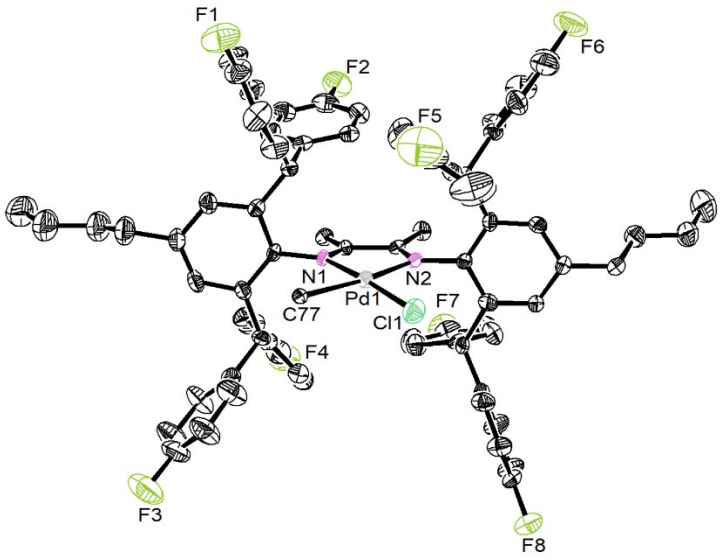


Table S2 Crystal data and structure refinement for Pd4.	
Identification code	Pd4
Empirical formula	C77 H67 Cl F8 N2 Pd
Formula weight	1314.18
Temperature/K	298(2) K
Crystal system	Monoclinic
Space group	P2(1)/c
a/Å	15.3320(14)
b/Å	36.690(3)
c/Å	14.7501(13) A
α/°	90
β/°	114.377(5)

γ/°	90
Volume/Å^3	7557.7(11)
Z	4
ρ_{calc}g/cm^3	1.155
μ/mm^{-1}	0.340
F(000)	2712
Crystal size/mm^3	0.30 x 0.10 x 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.22 to 25.02
Index ranges	-18<=h<=15, -36<=k<=43, -17<=l<=17
Reflections collected	38325
Independent reflections	13322 [R(int) = 0.1609
Data/restraints/parameters	13322 / 85 / 819
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ(I)]	R1 = 0.1150, wR2 = 0.2754
Final R indexes [all data]	R1 = 0.1876, wR2 = 0.3074
Largest diff. peak/hole / e Å^{-3}	0.819 and -1.131