Supporting Information for:

Suppression of Chain Transfer via Restricted Rotation Effect of Dibenzosuberyl Substituents in Polymerization Catalysis

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1. Figures, Tables.

Table S1. Mechanical properties.[a]

Ent.	Precat.	*T*/°C	Strain at break (%)	Stress at break (MPa)
1	**Ni1**	20	590	29
2	**Ni1**	40	465	17
3	**Ni1**	60	1006	30
4	**Ni1**	80	1190	19
5	**Ni2**	20	658	18
6	**Ni2**	40	572	12
7	**Ni2**	60	516	3
8	**Ni2**	80	1317	4
9	**Ni3**	20	520	13
10	**Ni3**	40	612	9
11	**Ni3**	60	787	6
12	**Ni3**	80	799	3
13	**Ni4**	20	418	28
14	**Ni4**	40	374	18
15	**Ni4**	60	314	12
16	**Ni4**	80	550	14
17	**Ni5**	20	671	15
18	**Ni5**	40	909	12
19	**Ni5**	60	973	7
20	**Ni5**	80	2439	1

[a]Conditions: performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature.

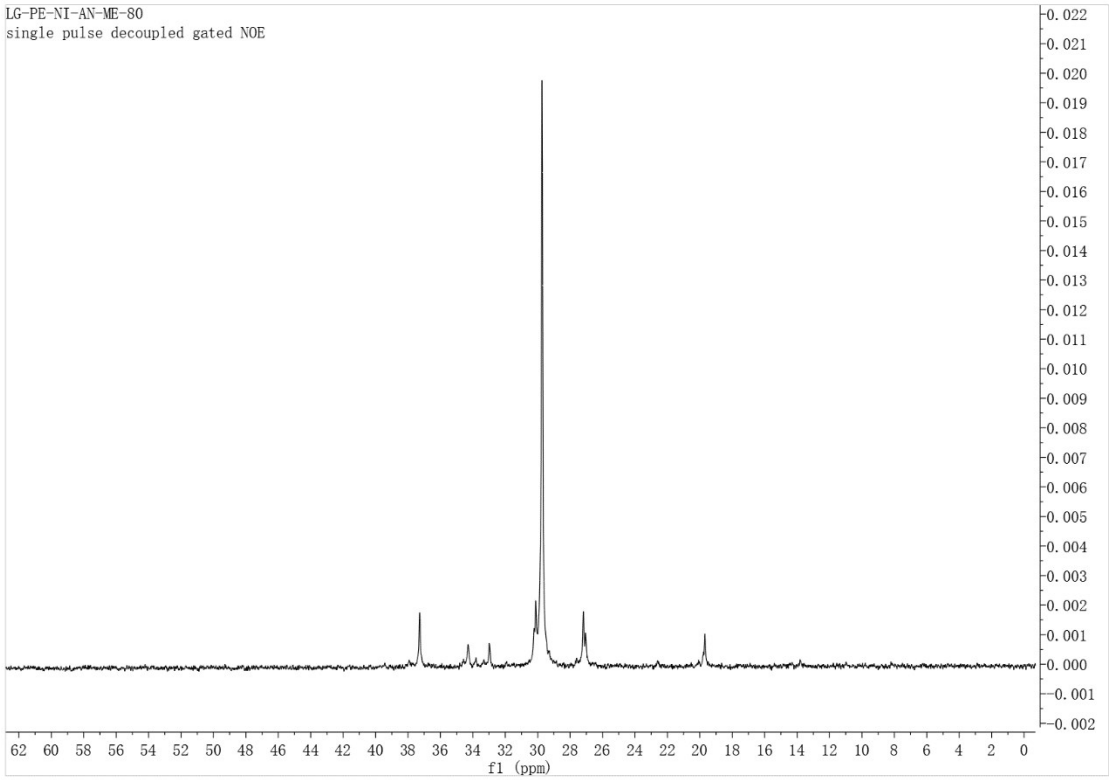


Figure S1. ^{13}C NMR spectrum of the polymer from table 1, entry 8 (d^4-*o*-dichlorobenzene, 120 ^oC).

2. Experimental sections

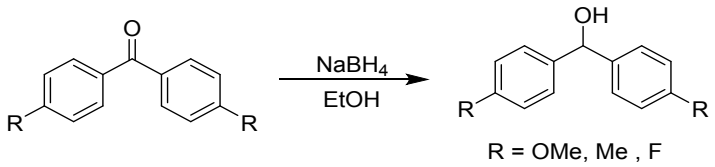
2.1 General Considerations

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. ^1H, ^{13}C, ^{19}F NMR spectra were recorded by JNM-ECZ600R at ambient temperature unless otherwise stated. The chemical shifts of the ^1H 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 **A1~A5** and **L1~L5**. Mass spectra of **Ni1~Ni5** and **Pd1~Pd5** 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 150 ^{o}C using 1, 2, 4-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.

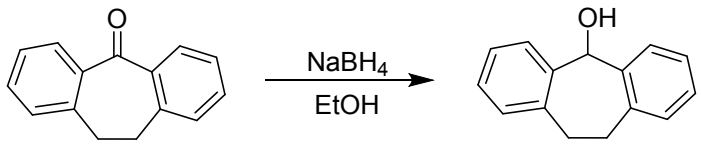
Stress/strain experiments were performed at 10 mm/min by means of a Universal Test Machine (SUST-CMT5305) at room temperature. At least three specimens of each polymer were tested. Polymers were melt-pressed at 30 to 35^{o}C above their melting point to obtain the test specimens. The test specimens had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

2.2 Procedure for the Synthesis of Diarylmethanols.



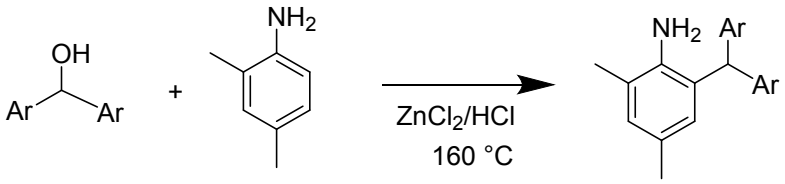
R = OMe, Me , F

Diarylmethyl ketone (100 mmol, 1.0 equiv.) was dissolved in EtOH (300 mL), $NaBH_4$ (3.78 g, 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].

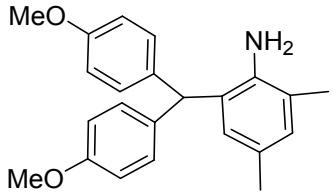


Dibenzosuberol can be obtained using the same procedure as for the synthesis of the first three alcohols. This compound is also known[2]. Dinaphthylmethyl alcohol was prepared by the method previously reported by our group.[3]

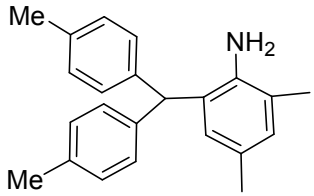
2.3 Procedure for the Synthesis of Anilines A1-A5.



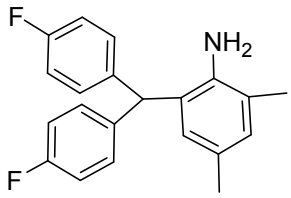
A mixture of diarylmethanol (20.0 mmol, 1.0 equiv.) and 2,4-dimethyl aniline (2.42 g, 20 mmol, 1.0 equiv.) was heated to 120 °C. A solution of anhydrous zinc chloride (1.36 g, 10 mmol, 0.5 equiv.) in concentrated hydrochloric acid (1.2 mL, 37% in H_2O, 1.0 equiv.) was added to the mixture (exothermic + 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 **A2, A3, A5** were crashed out with 100 ml EtOH and washed with EtOH (3 × 10 mL), **A5** needs long time for crystallization and precipitation. **A1** and **A4** were purification by column chromatography.



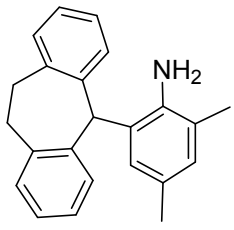
A1 (6.13 g, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 – 7.01 (m, 4H, Ar-*H*), 6.85 – 6.83 (m, 4H, Ar-*H*), 6.81 (s, 1H, Ar-*H*), 6.35 (d, *J* = 1.3 Hz, 1H, Ar-*H*), 5.37 (s, 1H, C*H*Ar$_2$), 3.81 (s, 6H, OC*H*$_3$), 3.37 (s, *br*, 2H, N*H*$_2$), 2.14 (s, 3H, C*H*$_3$), 2.13 (s, 3H, C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.25, 139.90, 135.28, 130.48, 129.45, 129.30, 128.34, 126.90, 122.61, 113.94, 55.31 (O*C*H$_3$), 50.87 (*C*HAr$_2$), 20.80 (*C*H$_3$), 17.77 (*C*H$_3$). ESI-MS (m/z): calcd for $C_{23}H_{26}NO_2$: 348.1964, Found, 348.1959, $[M+H]^+$.



A2 (4.01 g, 64%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.8 Hz, 4H, Ar-*H*), 7.07 – 7.02 (m, 4H, Ar-*H*), 6.85 (s, 1H, Ar-*H*), 6.41 (s, 1H, Ar-*H*), 5.43 (s, 1H, C*H*Ar_2), 3.39 (s, *br*, 2H, NH_2), 2.37 (s, 6H, CH_3), 2.17 (s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.06, 139.97, 136.06, 129.48, 129.29, 129.07, 128.44, 126.89, 122.59, 51.83 (*C*HAr_2), 21.18 (*C*H_3), 20.81(*C*H_3), 17.79 (*C*H_3). ESI-MS (m/z): calcd for $C_{23}H_{26}N$: 316.2065, Found, 316.2063, $[M+H]^+$.

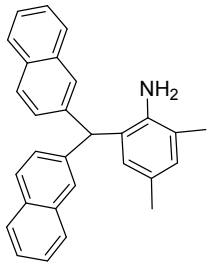


A3 (5.76g, 89%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09-7.01 (m, 4H, Ar-*H*), 7.01 – 6.95 (m, 4H, Ar-*H*), 6.84 (d, *J* = 13.4 Hz, 1H, Ar-*H*), 6.27 (s, 1H, Ar-*H*), 5.43 (s, 1H, C*H*Ar_2), 3.32 (s, *br*, 2H, NH_2), 2.14 (s, 3H, CH_3), 2.12 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.53, 160.91, 139.75, 138.45, 138.43, 133.83, 130.98, 130.93, 129.83, 128.71, 128.26, 128.21, 127.18, 122.92, 115.56, 115.42, 50.87 (*C*HAr_2), 20.73 (*C*H_3), 17.75 (*C*H_3). ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.03. ESI-MS (m/z): calcd for $C_{21}H_{19}F_2N$: 324.1564, Found, 324.1564, $[M+H]^+$.



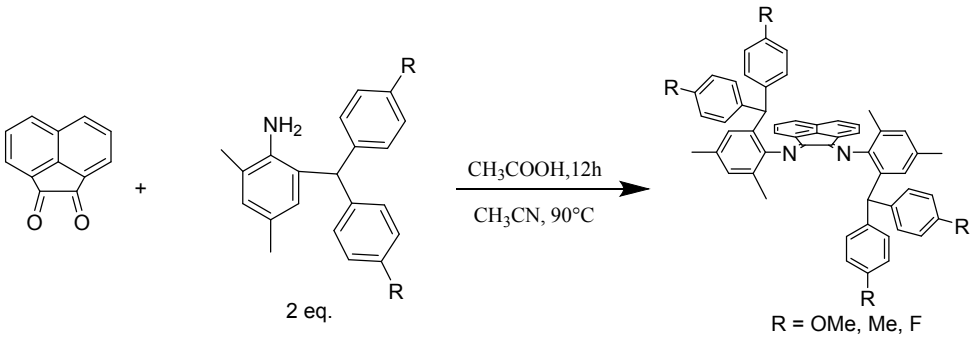
A4 (5.58 g, 89%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H, Ar-*H*), 7.22 – 7.11 (m, 6H, Ar-*H*), 6.79 (s, 1H, Ar-*H*), 6.49 (s, 1H, Ar-*H*), 5.15 (s, 1H, C*H*Ar_2), 3.60 (s, *br*, 2H, NH_2), 3.51 – 3.32 (m, 2H, ArC$H_2$$CH_2$Ar), 2.79 – 2.69 (m, 2H, ArCH_2CH_2Ar), 2.13 (s, 3H, CH_3), 2.10 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.36, 140.22, 140.06,

130.99, 130.58, 129.55, 129.14, 128.03, 127.41, 126.54, 126.37, 123.13, 56.63 (*C*HAr$_2$), 31.81 (Ar*C*H$_2$CH$_2$Ar), 20.93 (*C*H$_3$), 17.82 (*C*H$_3$). ESI-MS (m/z): calcd for $C_{23}H_{24}N$: 314.1903, Found, 314.1889, $[M+H]^+$.

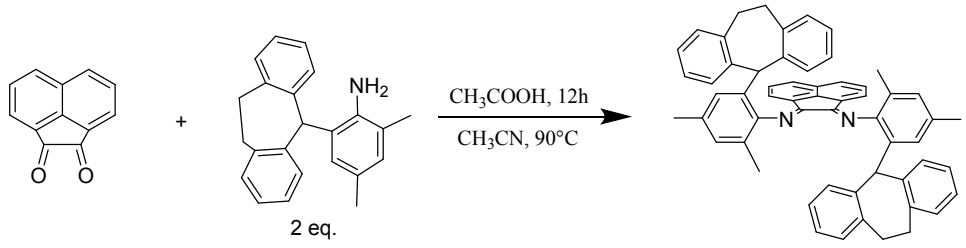


A5 (4.6 g, 59%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 21.2, 7.9 Hz, 4H, Ar-*H*), 7.76 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.60 (s, 2H, Ar-*H*), 7.54 – 7.45 (m, 4H, Ar-*H*), 7.42 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 6.92 (s, 1H, Ar-*H*), 6.50 (s, 1H, Ar-*H*), 5.86 (s, 1H, C*H*Ar$_2$), 3.37 (s, *br*, 2H, N*H*$_2$), 2.21 (s, 3H, C*H*$_3$), 2.17 (s, 3H, C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.43, 140.19, 133.66, 132.55, 129.86, 128.85, 128.51, 128.41, 128.32, 128.08, 128.06, 127.76, 127.18, 126.17, 125.87, 122.87, 52.79 (*C*HAr$_2$), 20.82 (*C*H$_3$), 17.86 (*C*H$_3$). ESI-MS (m/z): calcd for $C_{29}H_{25}N$: 388.2065, Found, 388.2061, [M+H]+.

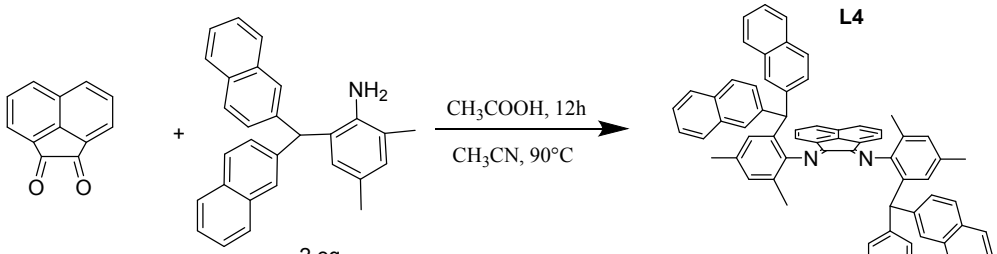
2.4 Procedure for the Synthesis of Ligands L1-L5.



L1-L3

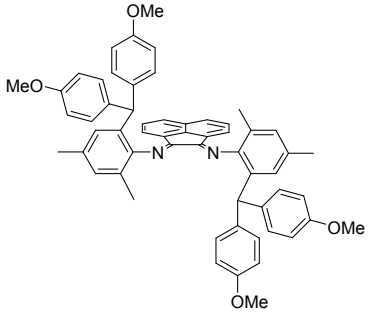


L4



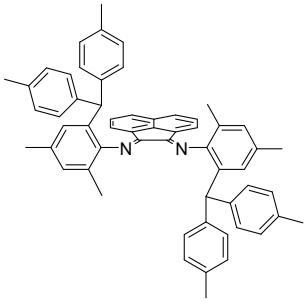
L5

The ligands **L1-L5** can be obtained as follows: acenaphthylene-1,2-dione (0.36 g, 2 mmol, 1.0 equiv) and anilines (4.0 mmol, 2 equiv) was suspended in acetonitrile (20 mL) and acetic acid (10 mL). The mixture was allowed to stir vigorously at 90 °C for 12 hours and became reddish-brown solution. Subsequently, the solution was cooled down to room temperate and a yellow precipitate was collected by filtration. After washing the solid with 15 ml EtOH and drying in vacuum, the desired products **L1~L5** were obtained.

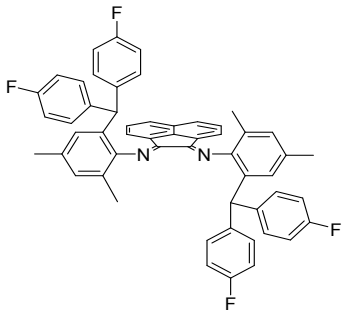


L1 (1.23 g, 73%). The ratio of cis to trans isomers is 1:2. ^{1}H NMR (600 MHz, $CDCl_3$)

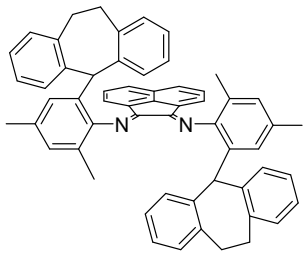
δ 7.72, 7.62 (d, *J* = 8.2 Hz, d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.23 – 7.17, 7.14 – 7.09 (m, m, 2H, Ar-*H*), 7.07 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.02 – 6.99 (m, 3H, Ar-*H*), 6.96, 6.68 (s, s, 2H, Ar-*H*), 6.83, 6.74 – 6.71 (t, *J* = 5.7 Hz, m, 4H, Ar-*H*), 6.80 – 6.74 (m, 5H, Ar-*H*), 6.51 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 6.11 (d, *J* = 8.5 Hz, 3H, Ar-*H*), 6.29, 5.80 – 5.77 (d, *J* = 7.2 Hz, m, 2H, Ar-*H*), 5.66, 5.58 (s, s, 2H, C*H*Ar_2), 3.77, 3.75 (s, s, 6H, OCH_3), 3.30, 3.02 (s, s, 6H, OCH_3), 2.33, 2.32 (s, s, 6H, CH_3), 2.29, 2.03 (s, s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.10 (*C*=N), 162.43 (*C*=N), 157.85, 157.14, 156.50, 146.47, 140.08, 139.72, 136.54, 136.10, 135.35, 134.32, 133.49, 132.93, 132.90, 132.74, 130.83, 130.50, 130.27, 129.69, 129.54, 129.16, 129.08, 128.31, 128.18, 127.87, 127.45, 127.08, 124.96, 124.60, 122.83, 122.57, 113.53, 113.46, 113.15, 112.66, 55.28 (O*C*H_3), 54.74 (O*C*H_3), 54.47 (O*C*H_3), 50.96 (O*C*H_3), 50.23 (O*C*H_3), 21.33 (Ar*C*H_3), 17.94 (Ar*C*H_3), 17.91 (Ar*C*H_3). ESI-MS (m/z): calcd for $C_{58}H_{53}N_2O_4$: 841.3993, Found, 841.3994, $[M+H]^+$.



L2 (1.34 g, 86%). The ratio of cis to trans isomers is 1:50. The minor isomer can be negligible. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.11 – 6.97 (m, 12H, Ar-*H*), 6.72 – 6.66 (m, 6H, Ar-*H*), 6.29 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 6.02 (d, *J* = 7.8 Hz, 4H, Ar-*H*), 5.60 (s, 2H, C*H*Ar_2), 2.33 (s, 6H, CH_3), 2.31 (s, 6H, CH_3), 2.30 (s, 6H, CH_3), 1.40 (s, 6H, CH_3).^{13}C NMR (151 MHz, $CDCl_3$) δ 163.23 (*C*=N), 146.57, 140.75, 139.81, 138.92, 135.38, 134.10, 133.30, 132.64, 130.76, 129.86, 129.70, 129.56, 129.08, 129.04, 128.89, 128.77, 128.03, 127.91, 127.52, 127.05, 125.08, 122.56, 51.88 (*C*HAr_2), 21.35 (Ar*C*H_3), 21.07 (Ar*C*H_3), 20.15 (Ar*C*H_3), 17.92 (Ar*C*H_3). ESI-MS (m/z): calcd for $C_{58}H_{53}N_2$: 777.4209, Found, 773.3893, $[M+H]^+$.

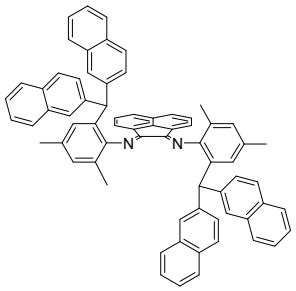


L3 (1.20 g, 76%) The ratio of cis to trans isomers is 1:7. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78, 7.69 (d, d, *J* = 8.3 Hz, *J* = 8.2 Hz, 2H, Ar-*H*), 7.23 – 7.17, 7.16 – 7.10 (m, m, 2H, Ar-*H*), 7.07 – 6.73 (m, 14H, Ar-*H*), 6.69, 6.60 (s, 2H, Ar-*H*), 6.50, 6.30 (d, d, *J* = 7.2 Hz, *J* = 7.1 Hz, 2H, Ar-*H*), 6.33, 5.99 (t, t, *J* = 8.6 Hz, *J* = 8.6 Hz, 4H, Ar-*H*), 5.63, 5.62 (s, s, 2H, C*H*Ar_2), 2.32, 2.31 (s, s, 6H, CH_3), 2.23, 2.03 (s, s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.18 (*C*=N), 161.07 (*C*=N), 160.61 (*C*=N), 159.44 (*C*=N), 146.30, 139.68, 139.03, 137.57, 133.17, 132.61, 131.21, 131.16, 130.96, 130.91, 129.58, 128.75, 128.66, 127.88, 127.16, 125.16, 122.53, 114.99, 114.85, 114.23, 114.08, 51.00 (*C*HAr_2), 21.30 (Ar*C*H_3), 17.87 (Ar*C*H_3). ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.94, -117.00, -117.09, -117.72. ESI-MS (m/z): calcd for $C_{54}H_{41}F_4N_2$: 793.3206, Found, 793.3189, $[M+H]^+$.



L4 (0.23 g, 15%). Only trans isomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.17 – 7.03 (m, 14H, Ar-*H*), 6.85 (s, 2H, Ar-*H*), 6.47 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 6.23 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 5.86 (t, *J* = 7.1 Hz, 2H, Ar-*H*), 5.82 (t, *J* = 7.1 Hz, 2H, Ar-*H*), 5.33 (s, 2H, C*H*Ar_2),), 3.64 (td, *J* = 13.7, 4.4 Hz, 2H, ArCH_2), 3.35 (dt, *J* = 17.2, 4.3 Hz, 2H, ArCH_2), 2.85 (ddd, *J* = 17.6, 13.4, 4.7 Hz, 2H, ArCH_2), 2.40 (s, 6H, CH_3), 2.31 (s, 6H, CH_3), 2.27 (dt, *J* = 15.0, 4.8 Hz, 2H, ArCH_2). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.33 (*C*=N), 146.16, 141.56, 140.31, 140.10, 139.30, 138.80, 131.67, 131.59, 131.36, 130.32, 129.84, 129.69, 128.49, 128.14, 126.90, 126.79, 126.36,

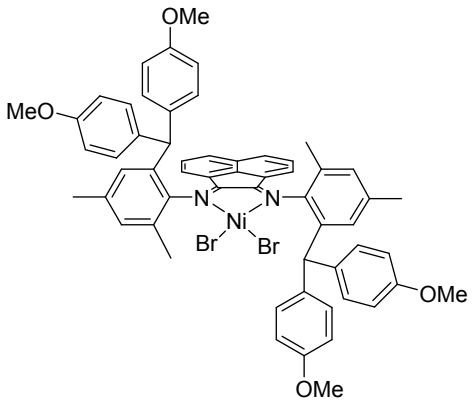
125.24, 125.05, 124.80, 121.62, 56.28 (Ar_2CH), 33.45 ($ArCH_2$), 30.44 ($ArCH_2$), 21.40 ($ArCH_3$), 18.43 ($ArCH_3$). ESI-MS (m/z): calcd for $C_{58}H_{49}N_2$: 773.3890, Found, 773.3893, $[M+H]^+$.



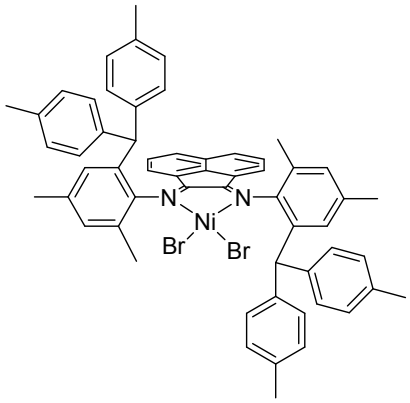
L5 (1.43 g, 77%). The ratio of cis to trans isomers is 1:60. ^1H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 4H, Ar-*H*), 7.55 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.44 (dd, *J* = 8.5, 1.2 Hz, 2H, Ar-*H*), 7.40 (dd, *J* = 11.0, 4.0 Hz, 2H, Ar-*H*), 7.37 – 7.33 (m, 4H, Ar-*H*), 7.15 (s, 2H, Ar-*H*), 7.09 (dt, *J* = 14.5, 4.5 Hz, 4H, Ar-*H*), 7.00 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 6.96 – 6.90 (m, 4H, Ar-*H*), 6.85 – 6.75 (m, 8H, Ar-*H*), 6.62 – 6.58 (m, 2H, Ar-*H*), 6.09 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 5.94 (s, 2H, $CHAr_2$), 2.41 (s, 6H, CH_3), 2.32 (s, 6H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.43 (*C*=N), 146.81, 141.41, 139.14, 138.88, 133.25, 132.86, 132.60, 132.55, 132.15, 131.08, 129.50, 128.78, 128.67, 128.21, 128.05, 127.95, 127.80, 127.71, 127.63, 127.60, 127.54, 126.72, 126.68, 126.13, 125.81, 125.54, 125.14, 124.55, 121.73, 52.73 (Ar_2CH), 21.34 ($ArCH_3$), 18.31 ($ArCH_3$). ESI-MS (m/z): calcd for $C_{70}H_{53}N_2$: 921.4203, Found, 921.4207, $[M+H]^+$.

2.5 Procedure for the Synthesis of Nickel Complexes Ni1-Ni5

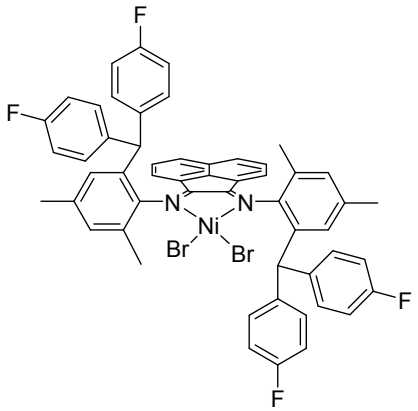
Ligand (0.30 mmol) and $(DME)NiBr_2$ (93 mg, 0.3 mmol) was added to 10 mL of CH_2Cl_2 in a Schlenk tube under a nitrogen atmosphere. The resulting mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, resulting in a red solid which was washed with 3×10 mL of n-hexane and dried under vacuum. The product was isolated as red powder.



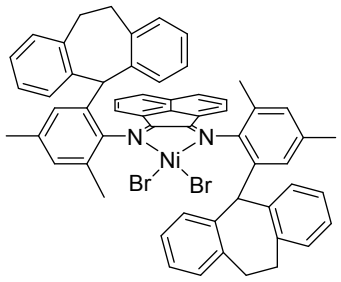
Ni1: (0.28 g, 88%). Anal. Calcd for ($C_{58}H_{52}Br_2N_2NiO_4$): C, 65.75; H, 4.95; N, 2.64. Found: C, 65.68; H, 5.03; N, 2.56. MALDI-TOF-MS (m/z): calcd for $C_{58}H_{52}BrN_2NiO_4$:979.21, Found, 979.24, $[M\text{-}Br]^+$.



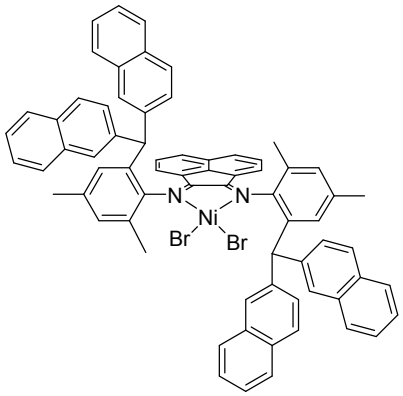
Ni2: (0.27 g, 91%). Anal. Calcd for ($C_{58}H_{52}Br_2N_2Ni$): C, 69.97; H, 5.26; N, 2.81. Found: C, 69.78; H, 5.12; N, 2.73. MALDI-TOF-MS (m/z): calcd for $C_{58}H_{52}BrN_2Ni$: 915.38, Found, 915.27, $[M\text{-}Br]^+$.



Ni3: (0.21 g, 69%). Anal. Calcd for ($C_{54}H_{40}Br_2F_4N_2Ni$): C, 64.13; H, 3.99; N, 2.77. Found: C, 64.34; H, 4.16; N, 2.84. MALDI-TOF-MS (m/z): calcd for $C_{54}H_{40}BrF_4N_2Ni$: 929.20, Found, 929.17, $[M-Br]^+$.



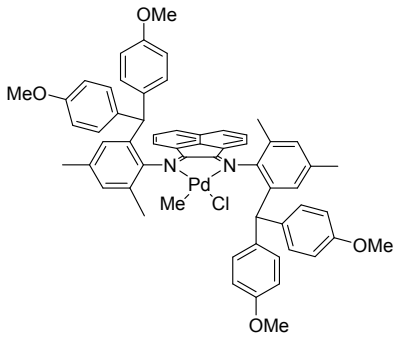
Ni4: (0.25 g, 85%). Anal. Calcd for ($C_{58}H_{48}Br_2N_2Ni$): C, 70.26; H, 4.88; N, 2.83. Found: C, 70.34; H, 4.81; N, 2.72. MALDI-TOF-MS (m/z): calcd for $C_{58}H_{48}BrN_2Ni$: 909.34, Found, 909.24, $[M-Br]^+$.



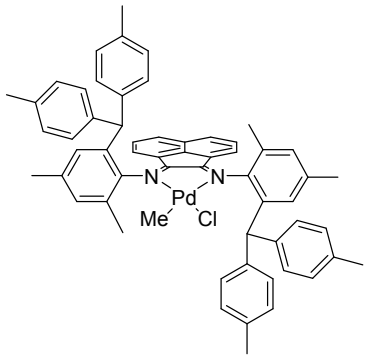
Ni5: (0.26 g, 75%). Anal. Calcd for ($C_{70}H_{52}Br_2N_2Ni$): C, 73.77; H, 4.68; N, 2.46. Found: C, 73.87; H, 4.76; N, 2.54. MALDI-TOF-MS (m/z): calcd for $C_{70}H_{52}BrN_2Ni$: 1059.26, Found, 1059.26, $[M-Br]^+$.

2.6 Procedure for the Synthesis of Palladium Complexes Pd1-5

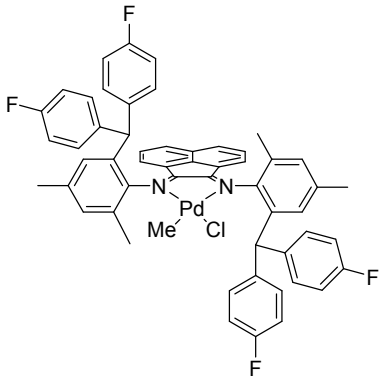
A mixture of the ligand (1 mmol), Pd(COD)MeCl (265 mg, 1 mmol) in CH_2Cl_2 (20 mL) was stirred for 1 day at room temperature. During stirring, the color of the solution was deepening. At the end of the reaction, the solution was concentrated to 5 mL. The product was crashed out with 20 ml ether and washed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



Pd1: (0.86 g, 86%), The ratio of cis to trans isomers is 1:7. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 5.9 Hz, 1H, Ar-*H*), 7.75 (d, *J* = 9.8 Hz, 1H, Ar-*H*), 7.40 – 7.38, 7.29 – 7.28 (m, 2H, Ar-*H*), 7.21 – 7.15 (m, 2H, Ar-*H*), 7.12 (s, 1H, Ar-*H*), 7.06 (s, 1H, Ar-*H*), 7.00 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 6.87 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 6.83 – 6.78 (m, 6H, Ar-*H*), 6.73 – 6.69 (m, 2H, Ar-*H*), 6.35 (s, 1H, C*H*Ar_2), 6.30 (d, *J* = 3.2 Hz, 1H, Ar-*H*), 6.13 (d, *J* = 3.2 Hz, 1H, Ar-*H*), 6.08 (s, 1H, C*H*Ar_2), 5.92 – 5.75 (m, 4H, Ar-*H*), 3.78, 3.77, 3.76, 3.32, 3.16, 3.11, 2.99, 2.97, 2.96 (s, 12H, OCH_3), 2.48, 2.45, 2.44, 2.37, 2.33, 2.31, 2.19, 2.18 (s, 12H, CH_3), 1.26, 1.02 (s, 3H, Pd-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.67 (*C*=N), 168.98 (*C*=N), 158.18, 157.96, 156.77, 156.61, 143.06, 141.31, 140.51, 137.02, 136.98, 136.51, 135.91, 135.61, 134.62, 134.30, 133.40, 131.21, 131.00, 130.98, 130.91, 130.51, 129.94, 129.77, 129.74, 129.47, 129.40, 129.07, 128.72, 128.24, 127.80, 127.73, 127.35, 126.17, 125.73, 124.12, 124.07, 113.60, 113.41, 113.03, 112.82, 55.32 (O*C*H_3), 54.45 (O*C*H_3), 51.05 (*C*HAr_2), 50.76 (*C*HAr_2), 21.53 (*C*H_3), 21.50 (*C*H_3), 18.31 (*C*H_3), 18.09 (*C*H_3), 3.55 (Pd-*C*H_3). Anal. Calcd for ($C_{59}H_{55}ClN_2O_4Pd$): C, 71.01; H, 5.56; N, 2.81. Found: C, 70.86; H, 5.47; N, 2.66. MALDI-TOF-MS (m/z): calcd for $C_{58}H_{52}N_2O_4Pd$: 946.30, found: 946.07 [M-Me-Cl]$^{+}$.

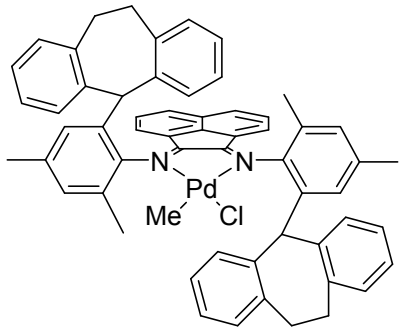


Pd2: (0.85 g, 91%), The ratio of cis to trans isomers is 1:50. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 7.73 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 7.25 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.19 – 7.11 (m, 3H, Ar-*H*), 7.05 (d, *J* = 8.2 Hz, 5H, Ar-*H*), 6.98 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.82 (d, *J* = 8.1 Hz, 3H, Ar-*H*), 6.78 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 6.72 (s, 1H, Ar-*H*), 6.35 (s, 1H, C*H*Ar_2), 6.29 (d, *J* = 7.1 Hz, 1H, Ar-*H*), 6.12 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 6.09 (s, 1H, C*H*Ar_2), 6.02 (dd, *J* = 7.5, 4.7 Hz, 4H, Ar-*H*), 2.46 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.01 (s, 3H, Pd-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.80 (*C*=N), 169.10 (*C*=N), 143.13, 141.42, 140.58, 140.12, 139.25, 139.01, 138.14, 136.91, 136.75, 136.24, 135.97, 135.80, 135.47, 134.68, 134.26, 130.07, 129.93, 129.73, 129.49, 129.47, 129.36, 129.17, 129.05, 128.92, 128.79, 128.71, 128.43, 128.28, 128.19, 127.80, 127.71, 127.49, 126.18, 125.73, 124.10, 51.94 (*C*HAr_2), 51.67 (*C*HAr_2), 21.52 (*C*H_3), 21.48 (*C*H_3), 21.14 (*C*H_3), 21.10 (*C*H_3), 20.06 (*C*H_3), 18.29 (*C*H_3), 18.07 (*C*H_3), 3.41 (Pd-*C*H_3). Anal. Calcd for ($C_{59}H_{55}ClN_2Pd$): C, 75.87; H, 5.94; N, 3.00. Found: C, 75.69; H, 5.91; N, 2.94. MALDI-TOF-MS (m/z): calcd for $C_{58}H_{52}N_2Pd$: 882.32, found: 882.13 $[M\text{-}Me\text{-}Cl]^+$.



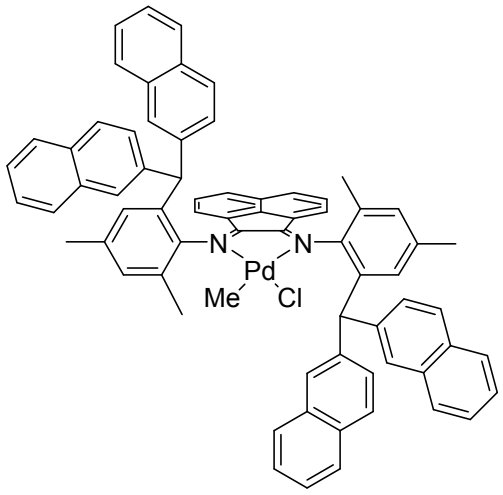
Pd3: (0.74 g, 78%), The ratio of cis to trans isomers is 1:3. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99, 7.87 (d, d, *J* = 8.4 Hz, *J* = 8.3 Hz, 1H, Ar-*H*), 7.85 – 7.30 (m, 8H, Ar-*H*), 7.30 – 6.56 (m, 14H, Ar-*H*, 1H, C*H*Ar_2), 6.49, 6.40 (s, s, 1H, C*H*Ar_2), 6.38 – 5.79 (m, 3H, Ar-*H*), 2.63, 2.61, 2.42, 2.41, 2.39, 2.38, 2.34, 2.34 (s, s, s, s, s, s, s, s, 12H, CH_3), 1.16, 1.04 (s, s, 3H, Pd-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.96 (*C*=N), 173.65 (*C*=N), 169.34 (*C*=N), 168.94 (*C*=N), 163.45, 162.59, 162.48, 161.21, 161.13, 161.10, 160.90, 160.10, 160.07, 159.58, 159.47, 146.82, 145.00, 143.06, 142.14, 141.64, 141.07,

140.86, 139.92, 139.22, 138.38, 137.67, 137.49, 137.14, 136.68, 136.22, 135.82, 135.52, 133.25, 133.11, 132.57, 132.51, 132.39, 132.36, 132.16, 131.50, 131.45, 131.41, 131.35, 131.08, 131.02, 130.99, 130.95, 130.50, 130.31, 130.18, 129.90, 129.82, 129.77, 129.49, 129.34, 129.24, 129.07, 129.01, 128.76, 128.71, 128.65, 128.62, 128.55, 128.43, 128.36, 128.23, 127.99, 127.97, 127.87, 127.65, 127.54, 127.50, 126.80, 126.76, 126.73, 126.67, 126.47, 126.13, 125.99, 125.83, 125.70, 125.59, 125.55, 125.44, 125.37, 125.26, 125.15, 124.98, 124.72, 124.53, 124.09, 123.13, 123.09, 115.28, 115.14, 114.95, 114.81, 114.72, 114.58, 114.43, 114.29, 52.91 (*C*HAr$_2$), 52.74 (*C*HAr$_2$), 52.53 (*C*HAr$_2$), 51.08 (*C*HAr$_2$), 50.78 (*C*HAr$_2$), 21.54 (*C*H$_3$), 21.50 (*C*H$_3$), 21.34 (*C*H$_3$), 18.74 (*C*H$_3$), 18.51 (*C*H$_3$), 18.31 (*C*H$_3$), 18.26 (*C*H$_3$), 18.02 (*C*H$_3$), 3.89 (Pd-*C*H$_3$), 3.84 (Pd-*C*H$_3$). Anal. Calcd for ($C_{55}H_{43}ClF_4N_2Pd$): C, 69.55; H, 4.56; N, 2.95. Found: C, 69.34; H, 4.71; N, 2.81. MALDI-TOF-MS (m/z): calcd for $C_{58}H_{52}N_2Pd$: 1024.14, found: 1024.49 $[M\text{-}Cl+Ag]^+$.



Pd4: (0.78 g, 84%), only trans isomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 3.7 Hz, 1H, Ar-*H*), 7.73 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.69 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.50 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 7.40 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 7.35 (d, *J* = 7.0 Hz, 1H, Ar-*H*), 7.22 – 7.03 (m, 10H, Ar-*H*), 7.01 (s, 1H, Ar-*H*), 6.94 (s, 1H, Ar-*H*), 6.44 (d, *J* = 7.1 Hz, 1H, Ar-*H*), 6.38 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 6.28 – 6.18 (m, 2H, Ar-*H*), 5.96 (s, 1H, C*H*Ar$_2$), 5.91 – 5.70 (m, 4H, Ar-*H*), 5.65 (s, 1H, C*H*Ar$_2$), 3.82 – 3.57 (m, 2H, ArC*H*$_2$), 3.43 – 3.23 (m, 2H, ArC*H*$_2$), 3.00 – 2.82 (m, 2H, ArC*H*$_2$), 2.64 (s, 3H, C*H*$_3$), 2.63 (s, 3H, C*H*$_3$), 2.36 (s, 3H, C*H*$_3$), 2.33 (s, 3H, C*H*$_3$), 2.32 – 2.17 (m, 2H, ArC*H*$_2$), 0.88 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.08 (*C*=N), 170.50 (*C*=N), 143.51, 141.92, 141.37, 141.25, 140.75, 140.57, 138.81, 138.58, 137.84, 137.27, 135.77,

134.70, 133.67, 133.02, 131.92, 131.61, 131.10, 130.72, 130.52, 130.41, 130.20, 130.16, 129.98, 129.87, 129.74, 129.63, 129.48, 129.29, 129.04, 128.97, 128.76, 127.69, 127.65, 127.48, 127.30, 126.89, 126.85, 126.74, 126.28, 125.80, 125.38, 125.22, 124.62, 123.05, 122.94, 56.11 (*C*HAr$_2$), 55.87 (*C*HAr$_2$), 33.72 (Ar*C*H$_2$), 33.48 (Ar*C*H$_2$), 30.30 (Ar*C*H$_2$), 30.17 (Ar*C*H$_2$), 21.60 (*C*H$_3$), 21.54 (*C*H$_3$), 18.96 (*C*H$_3$), 18.67 (*C*H$_3$), 3.18 (Pd-*C*H$_3$). Anal. Calcd for ($C_{59}H_{51}ClN_2Pd$): C, 76.20; H, 5.53; N, 3.01. Found: C, 76.35; H, 5.46; N, 2.98. MALDI-TOF-MS (m/z): calcd for $C_{58}H_{52}N_2Pd$: 878.29, found: 878.21 $[M\text{-}Me\text{-}Cl]^+$.



Pd5: (0.74 g, 79%), The ratio of cis to trans isomers is 1:60. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 7.87 – 7.77 (m, 4H, Ar-*H*), 7.58 (dd, *J* = 8.0, 4.1 Hz, 2H, Ar-*H*), 7.54 – 7.32 (m, 7H, Ar-*H*), 7.30 – 7.18 (m, 5H, Ar-*H*), 7.15 (s, 1H, Ar-*H*), 6.96 – 6.75 (m, 14H, Ar-*H*), 6.70 – 6.60 (m, 3H, , C*H*Ar$_2$, Ar-*H*), 6.41 (s, 1H, C*H*Ar$_2$), 6.07 (d, *J* = 7.0 Hz, 1H, Ar-*H*), 5.94 (d, *J* = 7.1 Hz, 1H, Ar-*H*), 2.63 (s, 3H, C*H*$_3$), 2.61 (s, 3H, C*H*$_3$), 2.38 (s, 3H, C*H*$_3$), 2.34 (s, 3H, C*H*$_3$), 1.16 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.96 (*C*=N), 169.33 (*C*=N), 142.14, 141.65, 141.08, 140.87, 139.92, 139.23, 138.38, 137.14, 136.22, 136.04, 135.52, 133.19, 133.12, 132.58, 132.51, 132.40, 132.37, 131.03, 130.96, 130.18, 129.82, 129.77, 129.49, 129.34, 129.07, 129.02, 128.71, 128.64, 128.56, 128.43, 128.37, 128.23, 128.06, 127.97, 127.87, 127.65, 126.80, 126.76, 126.74, 126.72, 126.47, 125.99, 125.83, 125.59, 125.55, 125.44, 125.37, 124.98, 124.72, 124.55, 123.13, 123.09, 52.91 (*C*HAr$_2$), 52.54 (*C*HAr$_2$), 21.54 (*C*H$_3$), 21.50 (*C*H$_3$), 18.74 (*C*H$_3$), 18.50 (*C*H$_3$), 3.83

(Pd-CH_3). Anal. Calcd for ($C_{71}H_{55}ClN_2Pd$): C, 79.10; H, 5.14; N, 2.60. Found: C, 79.21; H, 5.32; N, 2.50. MALDI-TOF-MS (m/z): calcd for $C_{58}H_{52}N_2Pd$: 1026.32, found: 1026.06 $[M\text{-}Me\text{-}Cl]^+$.

3. Spectra Data

3.1 ^1H, ^{13}C and ^{19}F NMR of the Synthetic Compounds.

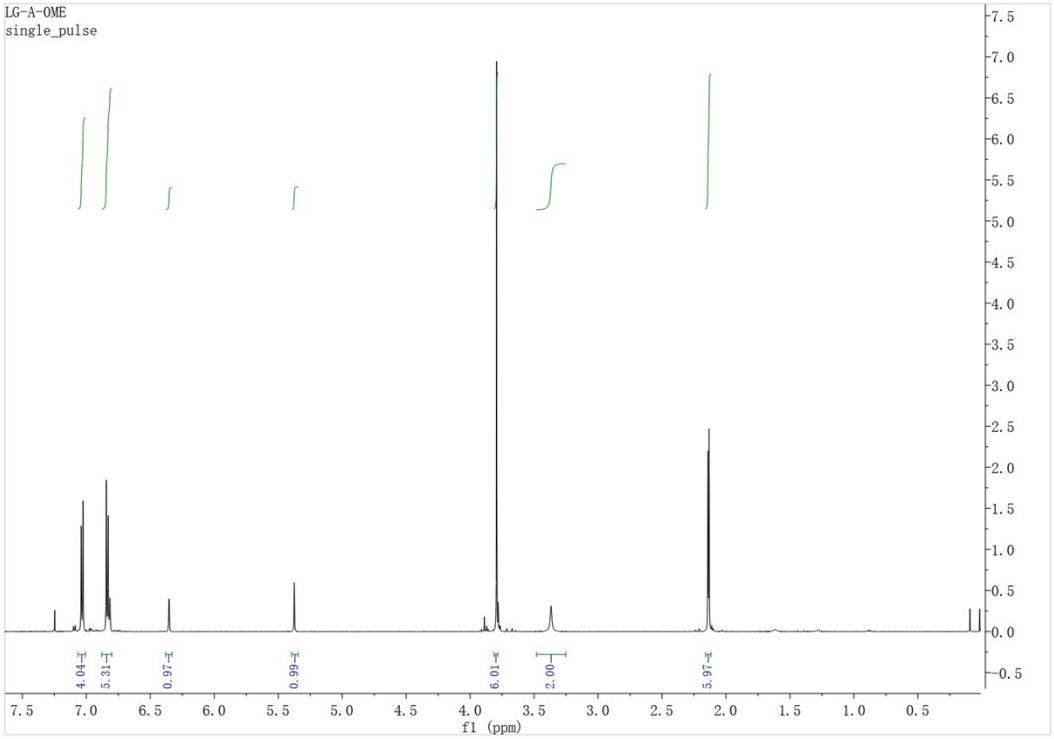


Figure S2. ^1H NMR spectrum of **A1** in $CDCl_3$.

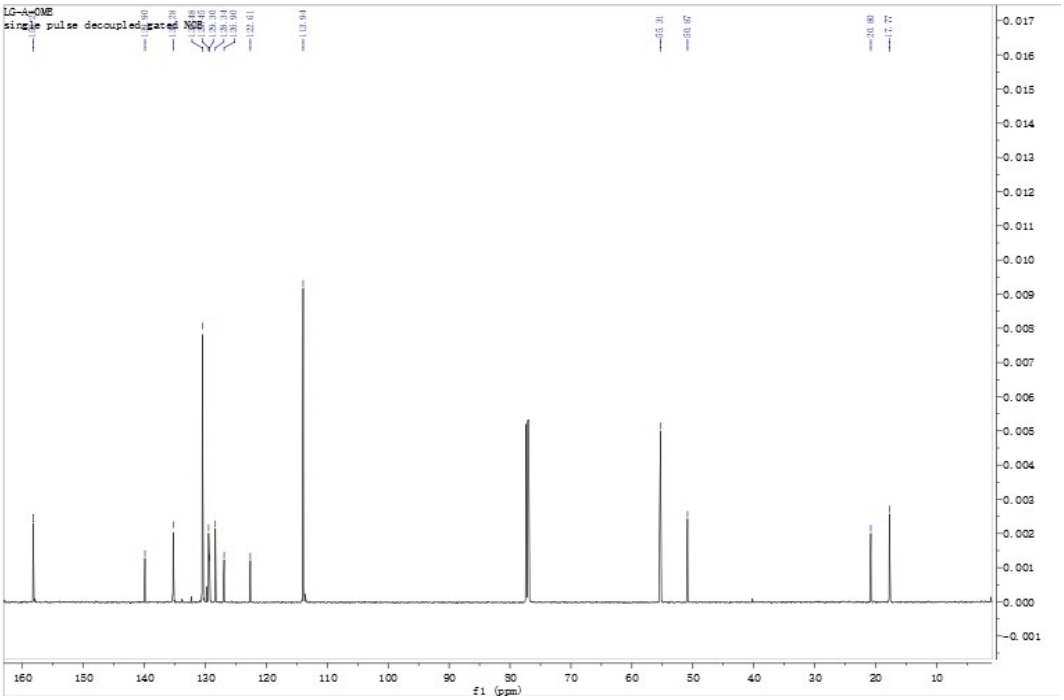


Figure S3. ^{13}C NMR spectrum of **A1** in $CDCl_3$.

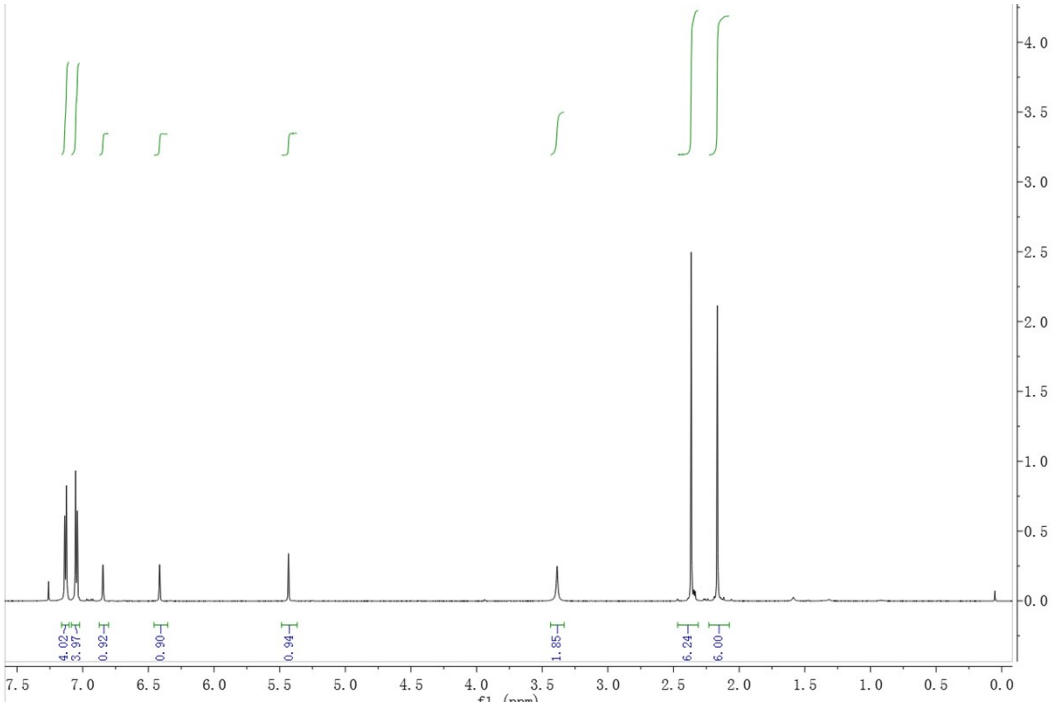


Figure S4. ^{1}H NMR spectrum of **A2** in $CDCl_3$.

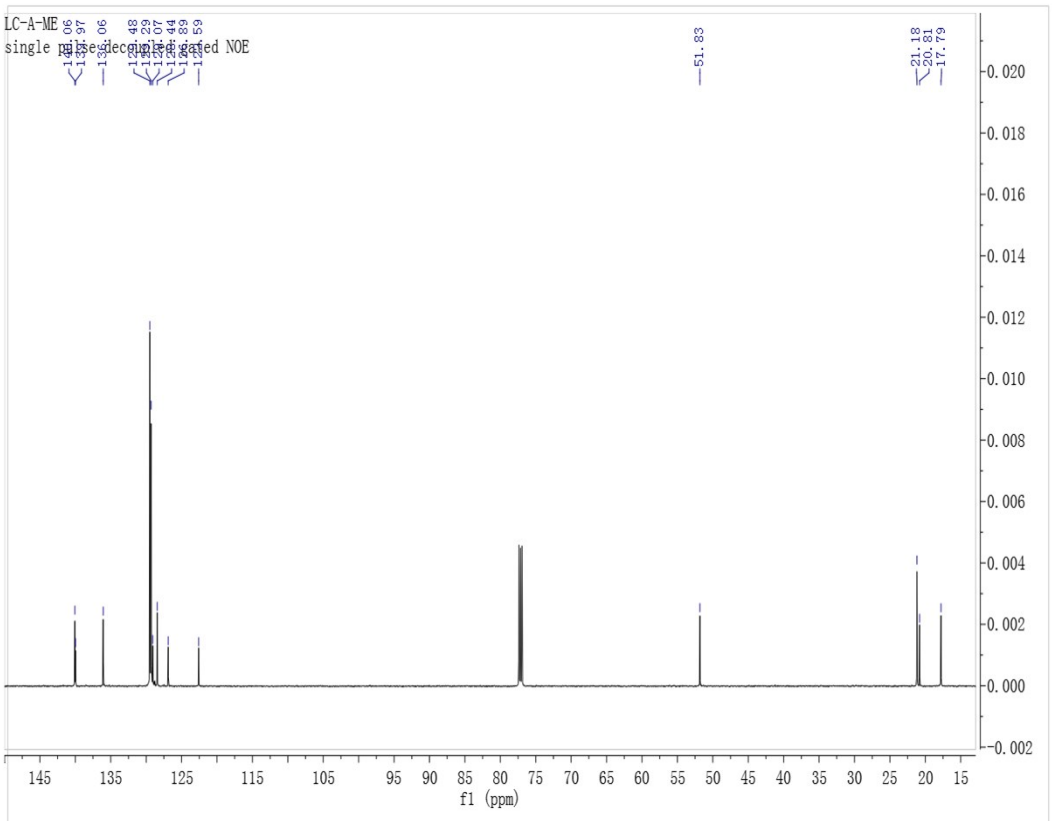


Figure S5. ^{13}C NMR spectrum of **A2** in $CDCl_3$.

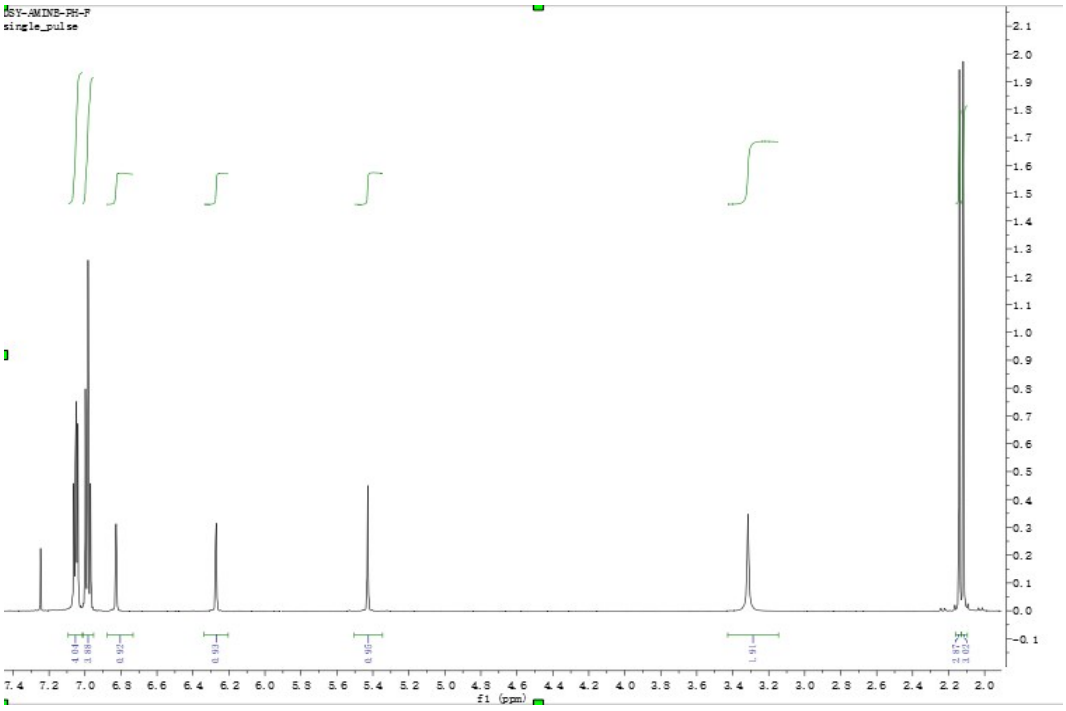


Figure S6. ^{1}H NMR spectrum of **A3** in $CDCl_3$.

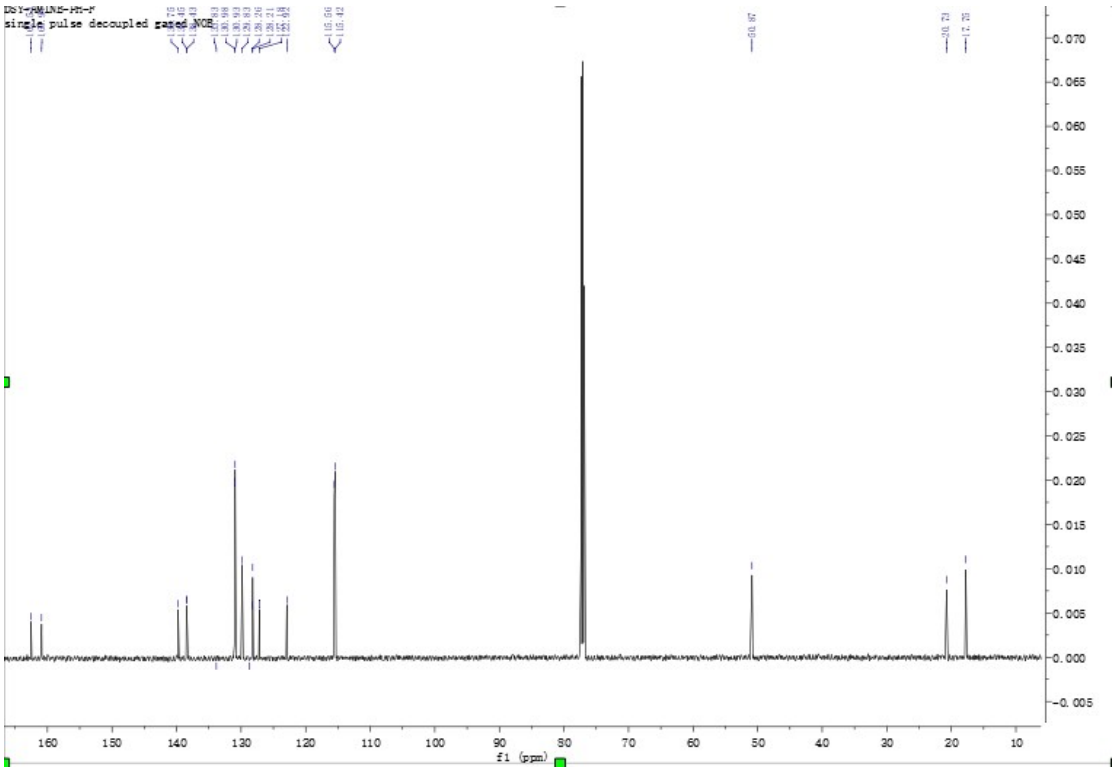


Figure S7. ^{13}C NMR spectrum of **A3** in $CDCl_3$.

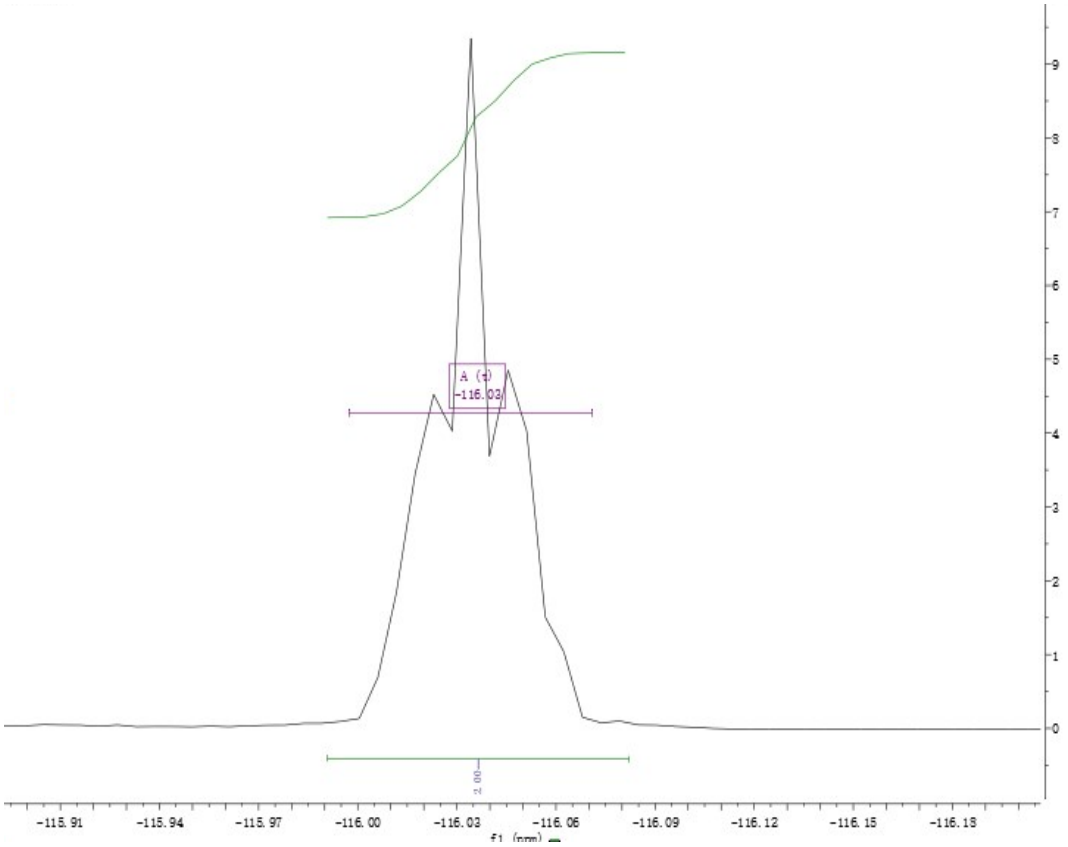


Figure S8. ^{19}F NMR spectrum of **A3** in $CDCl_3$.

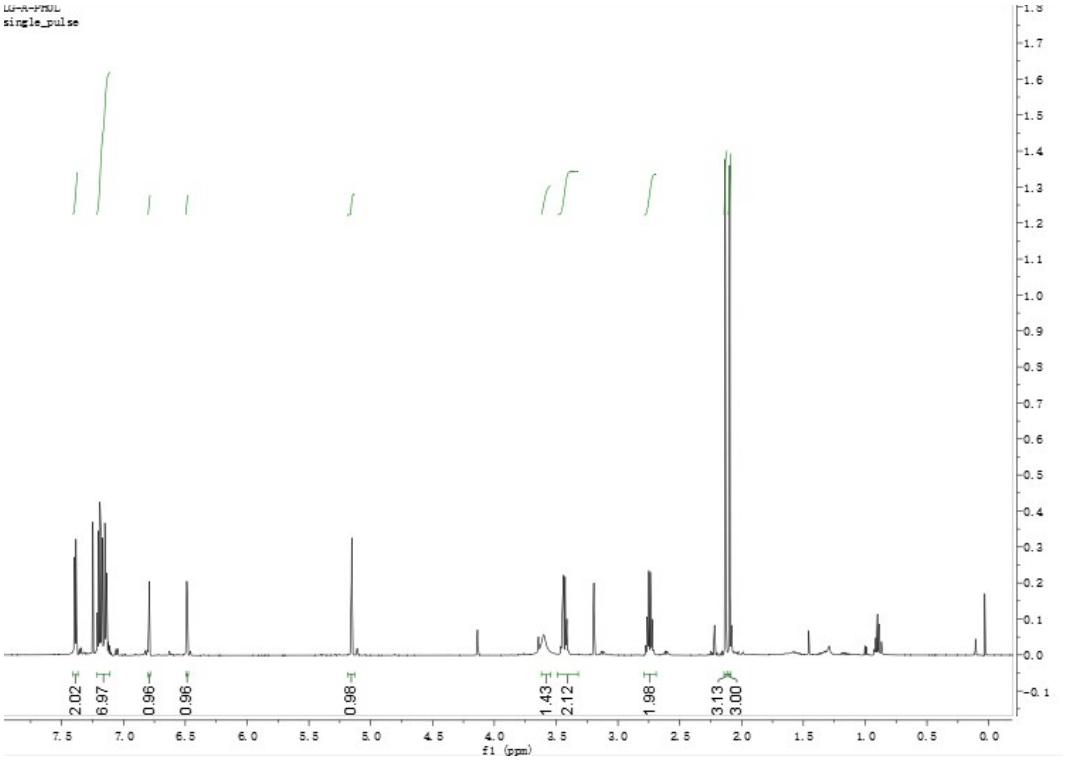


Figure S9. ^{1}H NMR spectrum of **A4** in $CDCl_3$.

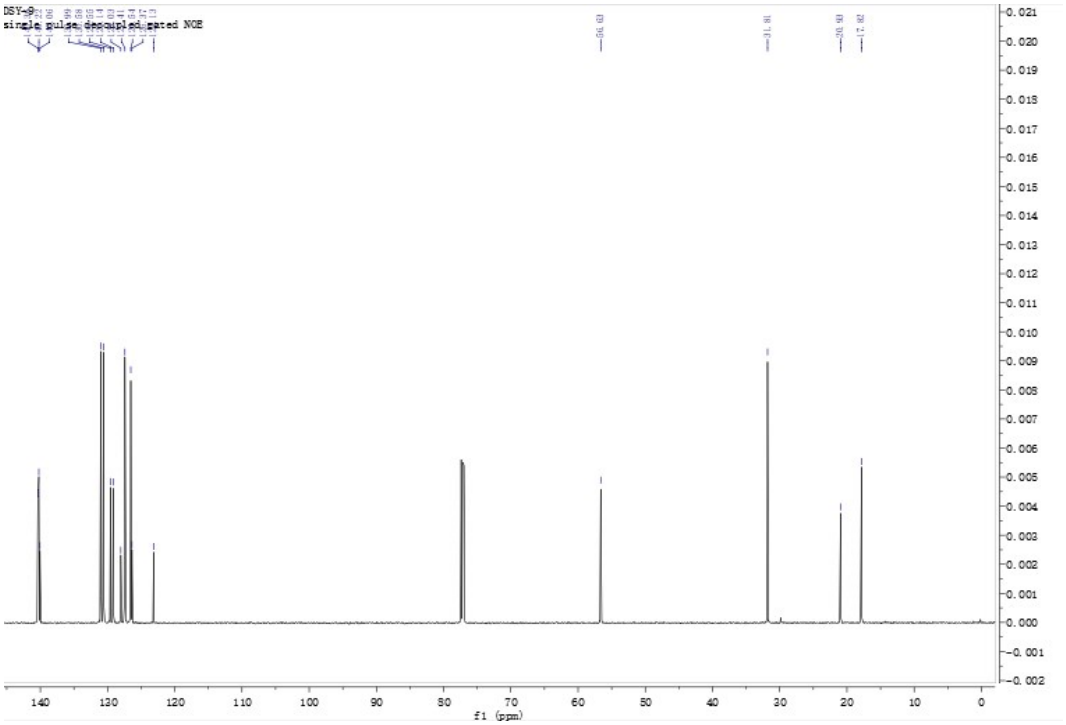


Figure S10. ^{13}C NMR spectrum of **A4** in $CDCl_3$.

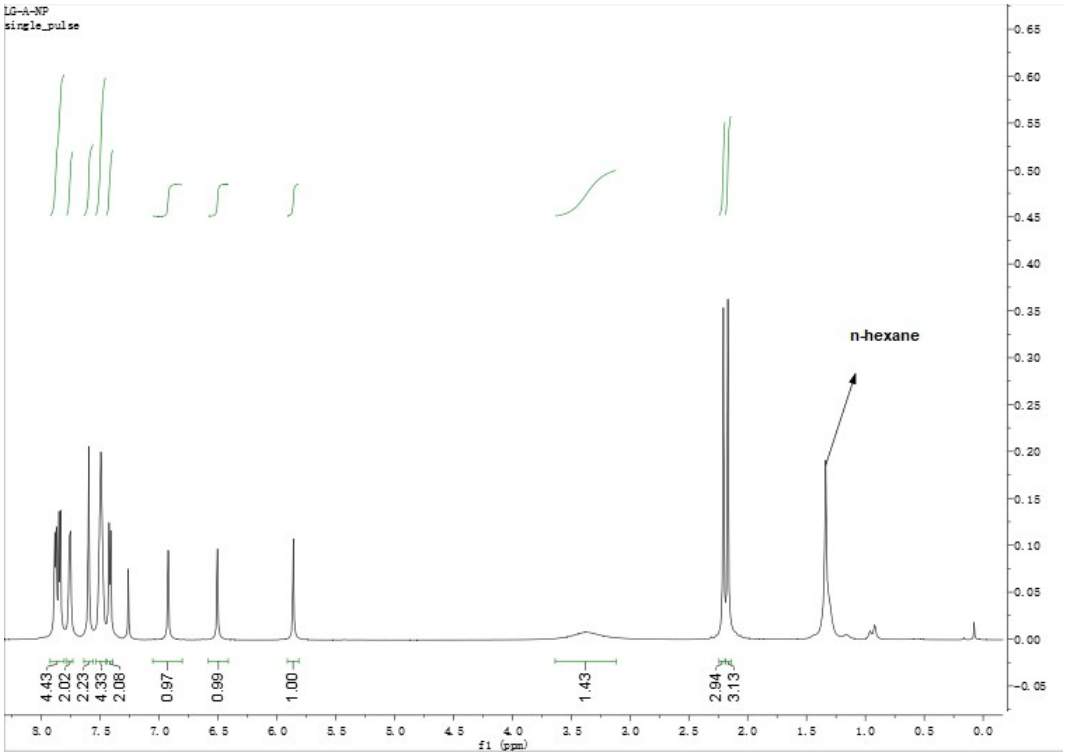


Figure S11. ^{1}H NMR spectrum of **A5** in $CDCl_3$.

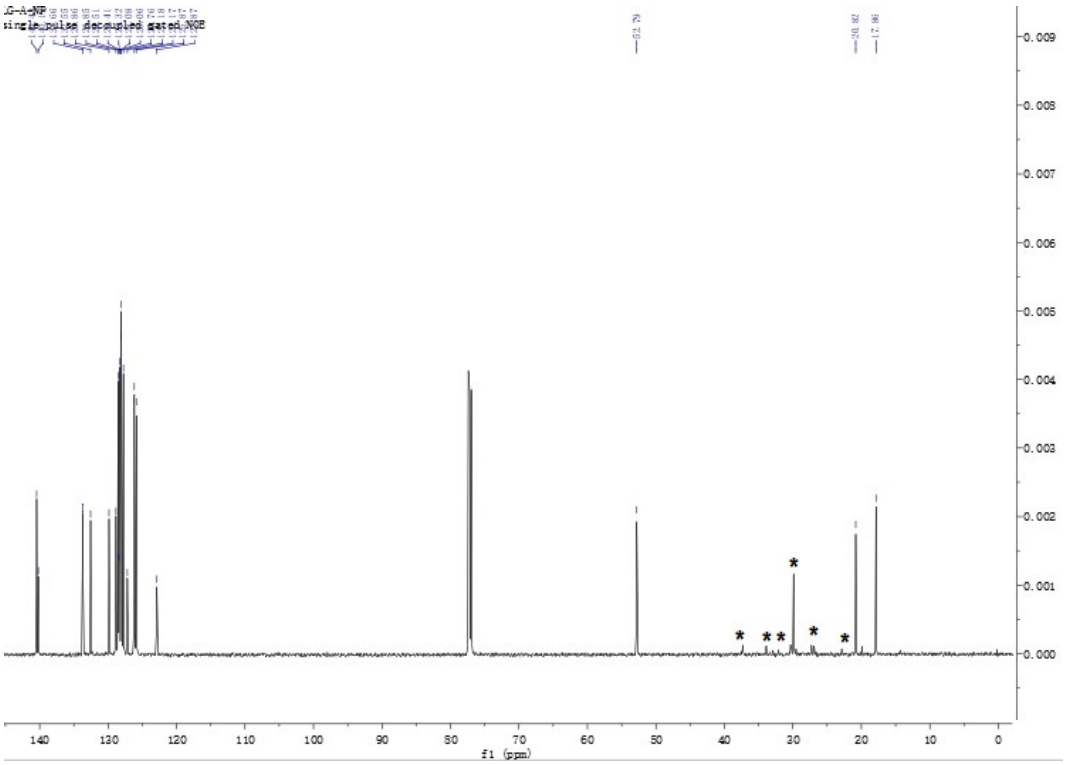


Figure S12. ^{13}C NMR spectrum of **A5** in $CDCl_3$.*Hexanes

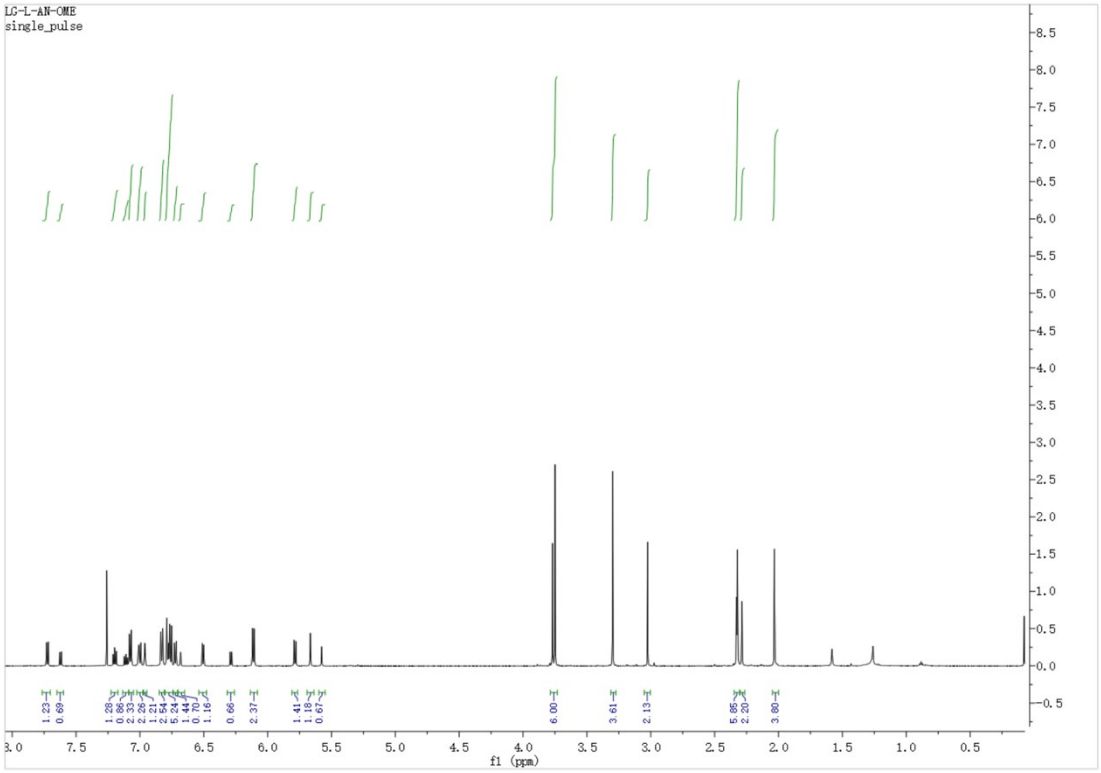


Figure S13. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

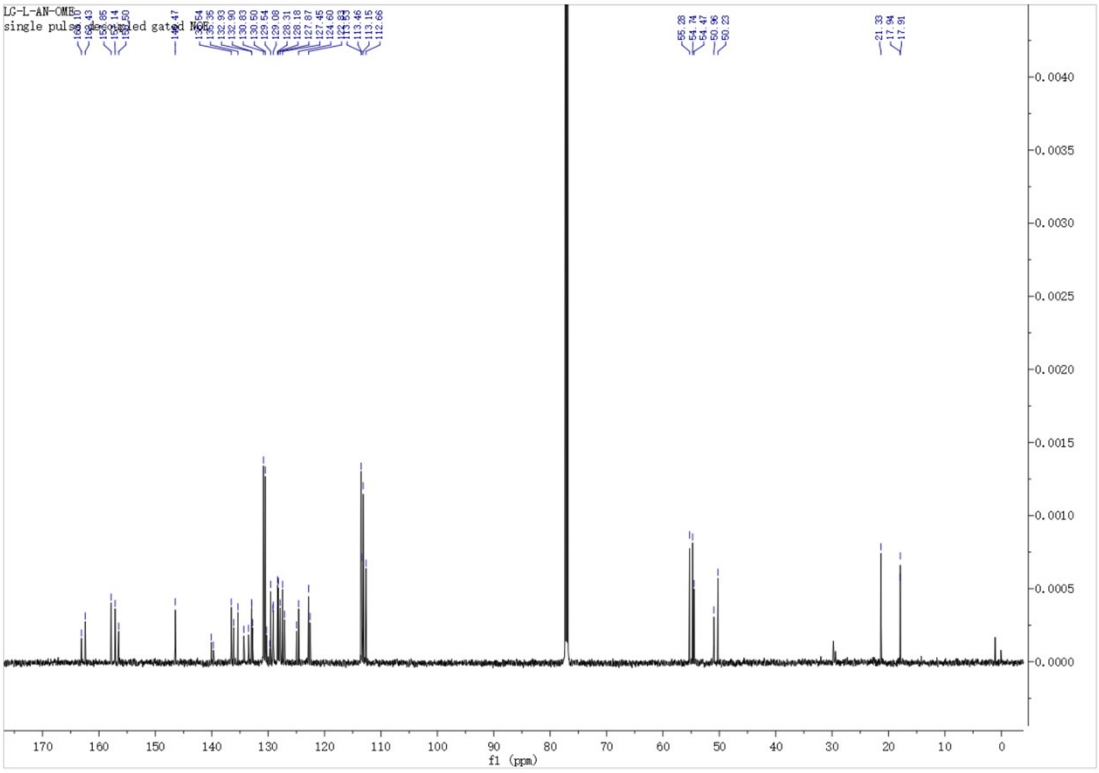


Figure S14. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

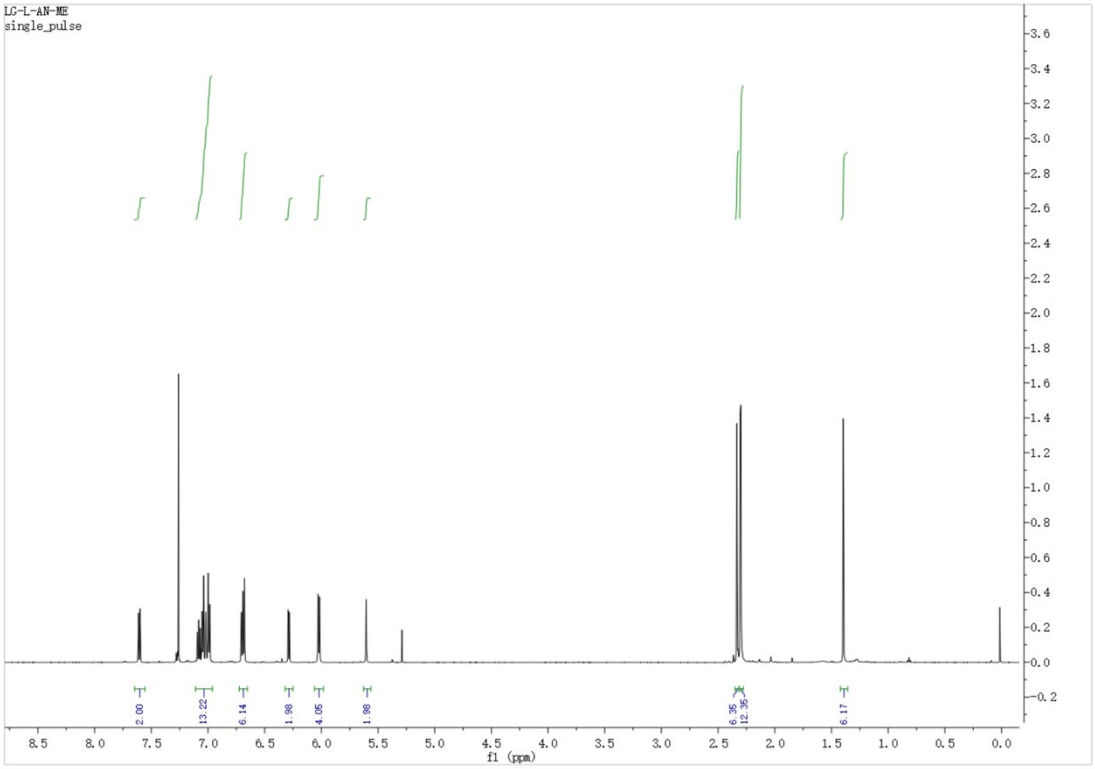


Figure S15. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

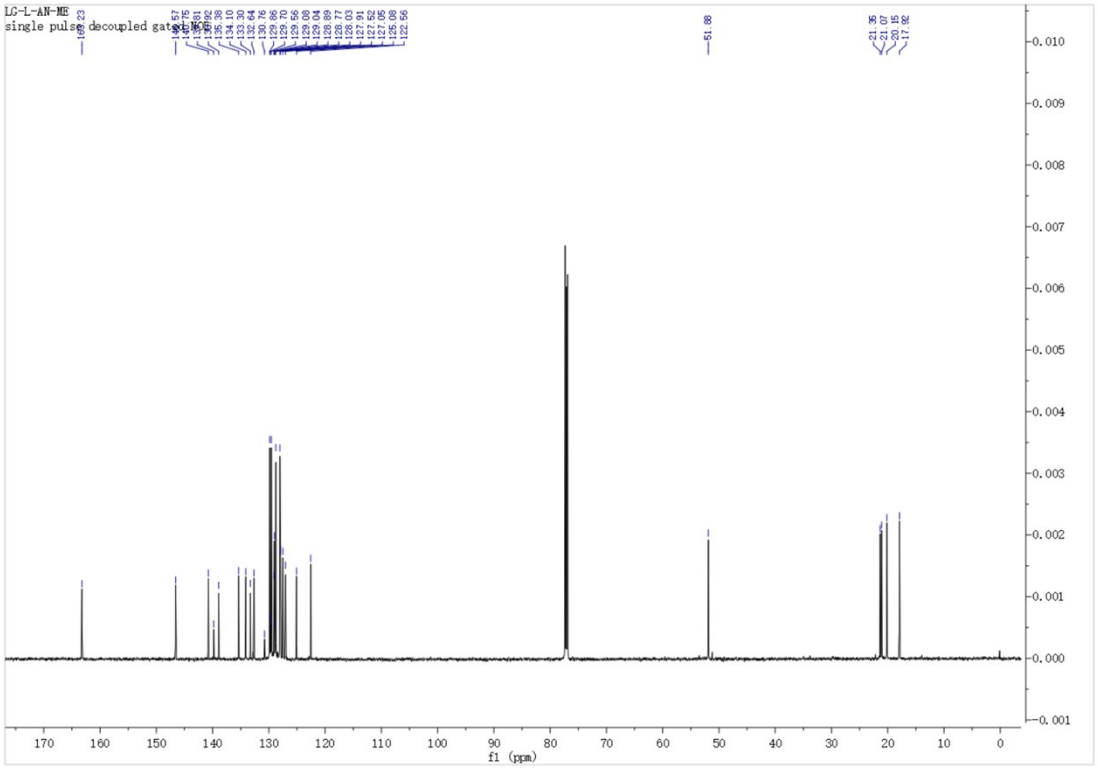


Figure S16. ^{13}C NMR spectrum of **L2** in $CDCl_3$.

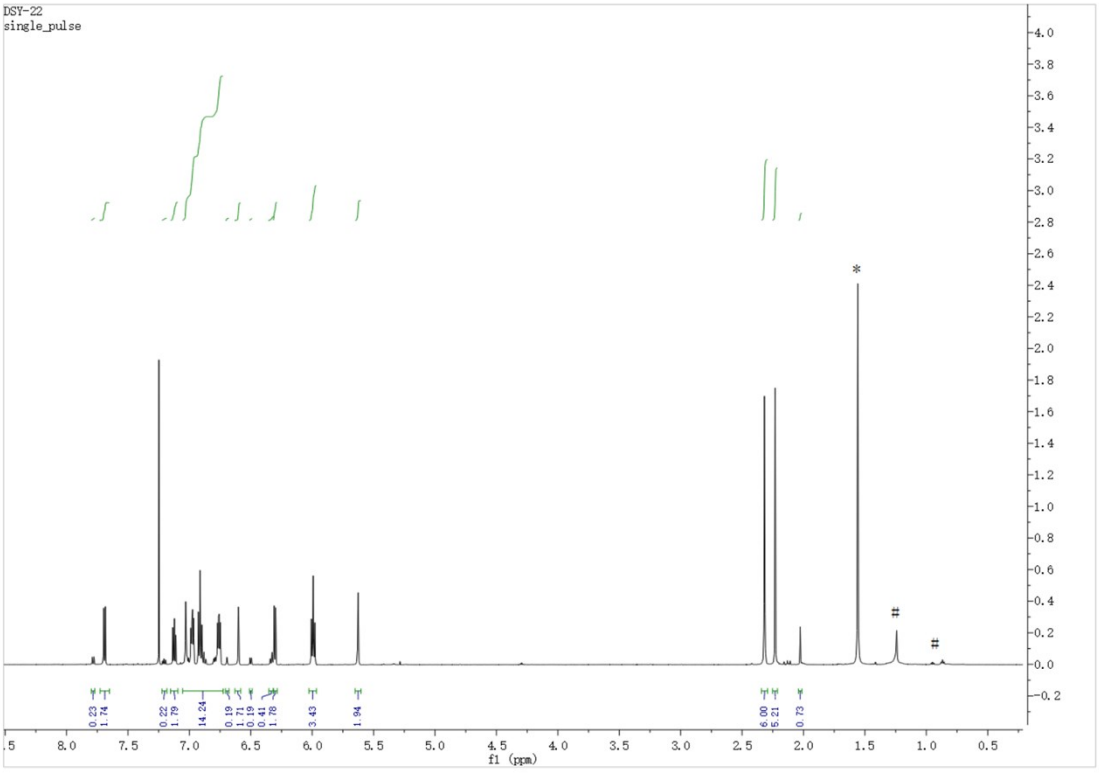


Figure S17. ^{1}H NMR spectrum of **L3** in $CDCl_3$. *H_2O, #Hexanes.

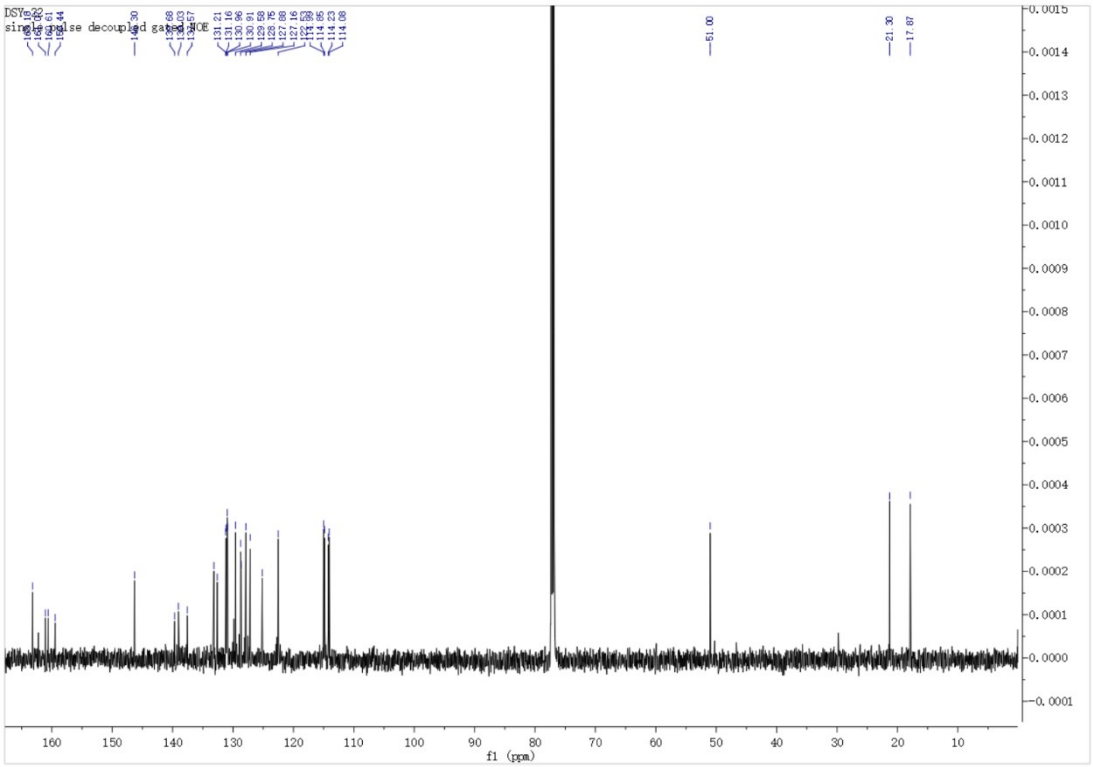


Figure S18. ^{13}C NMR spectrum of **L3** in $CDCl_3$.

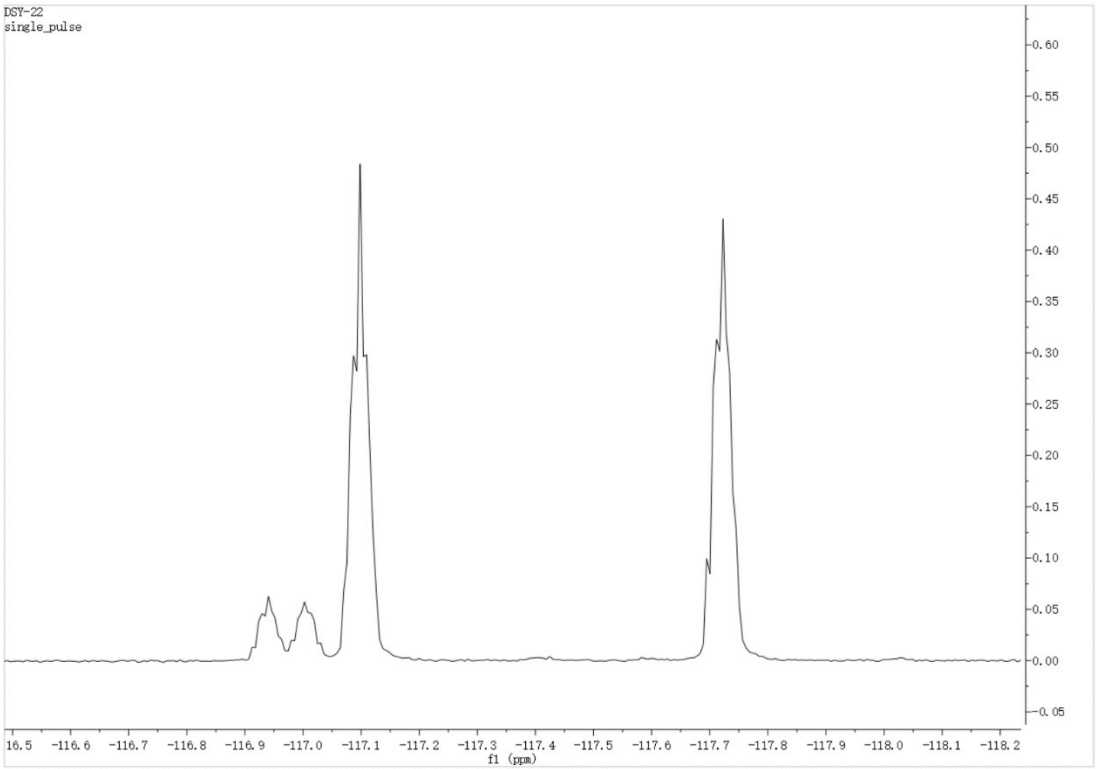


Figure S19. ^{19}F NMR spectrum of **L3** in $CDCl_3$.

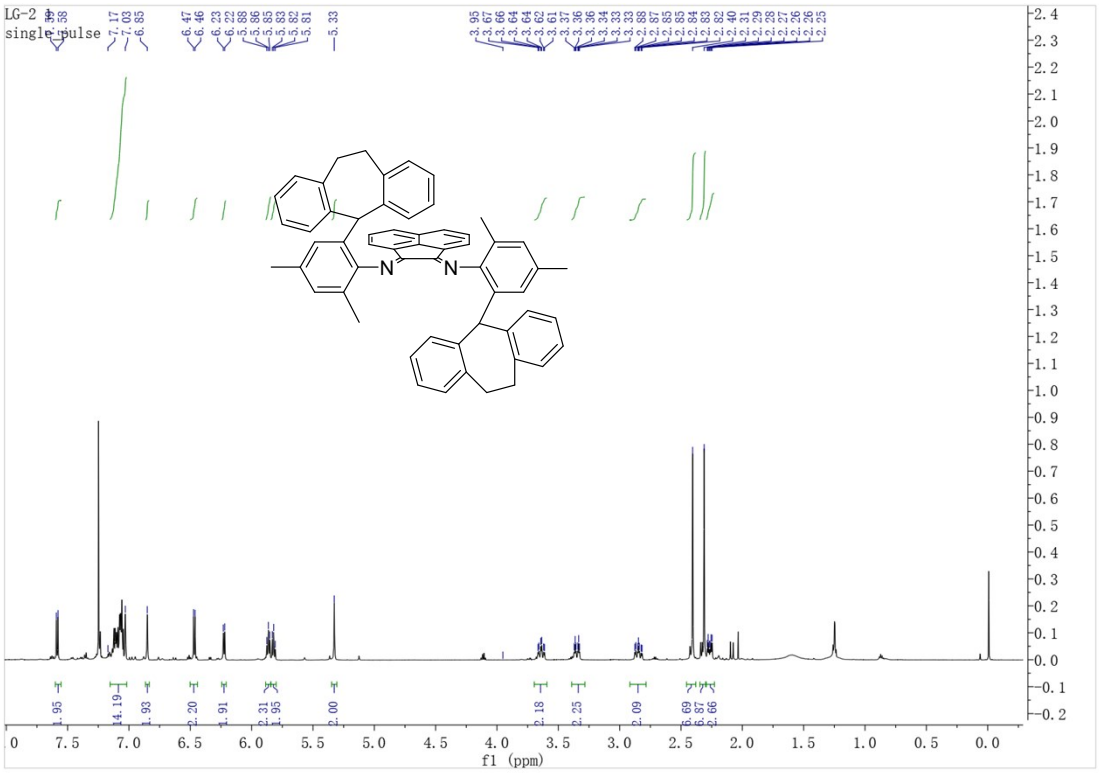


Figure S20. ^{1}H NMR spectrum of **L4** in $CDCl_3$.

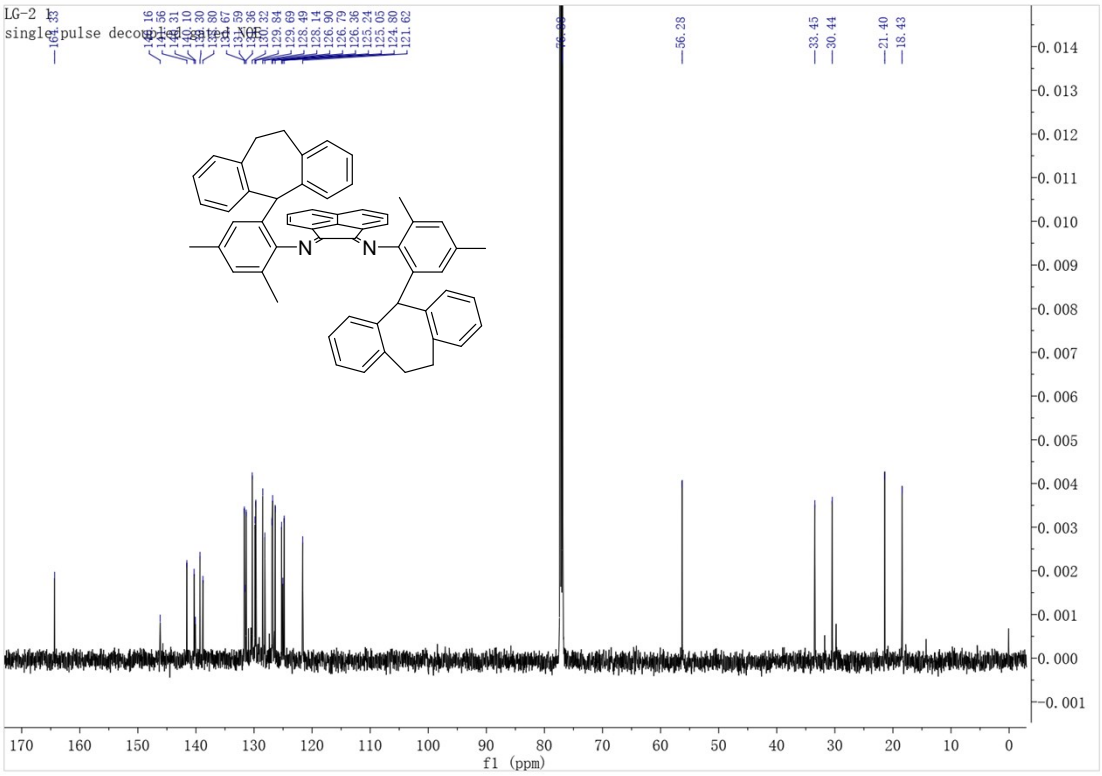


Figure S21. ^{13}C NMR spectrum of **L4** in $CDCl_3$.

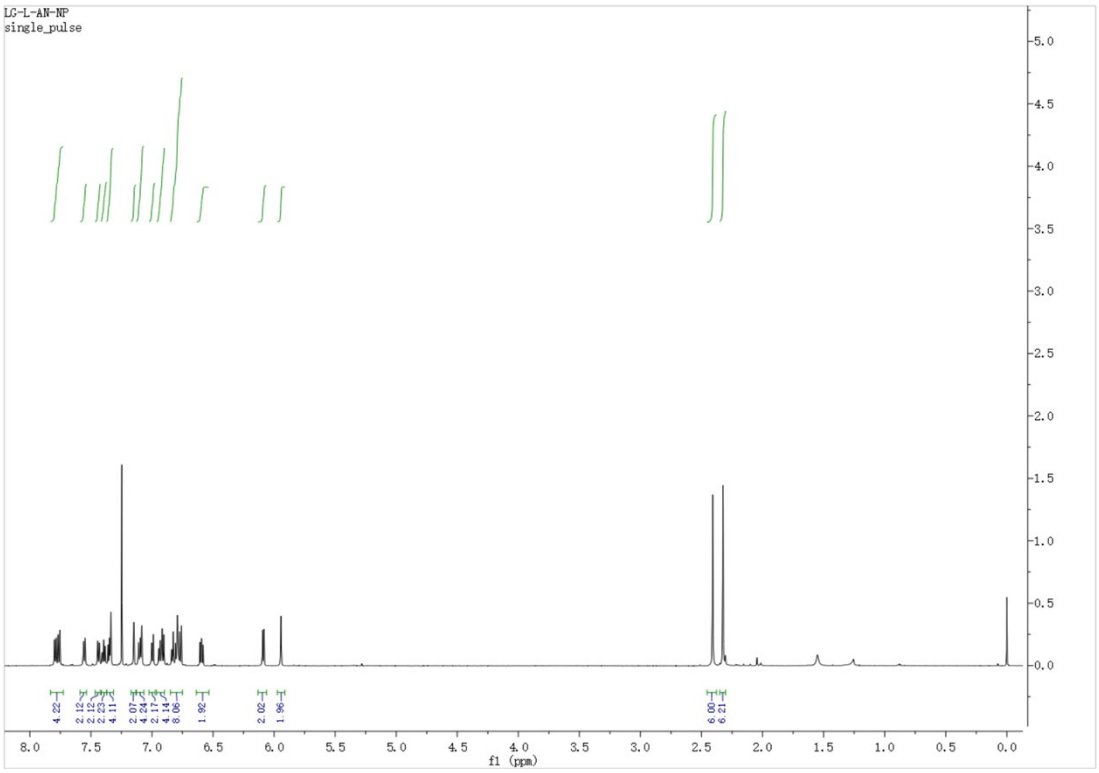


Figure S22. ^{1}H NMR spectrum of **L5** in $CDCl_3$.

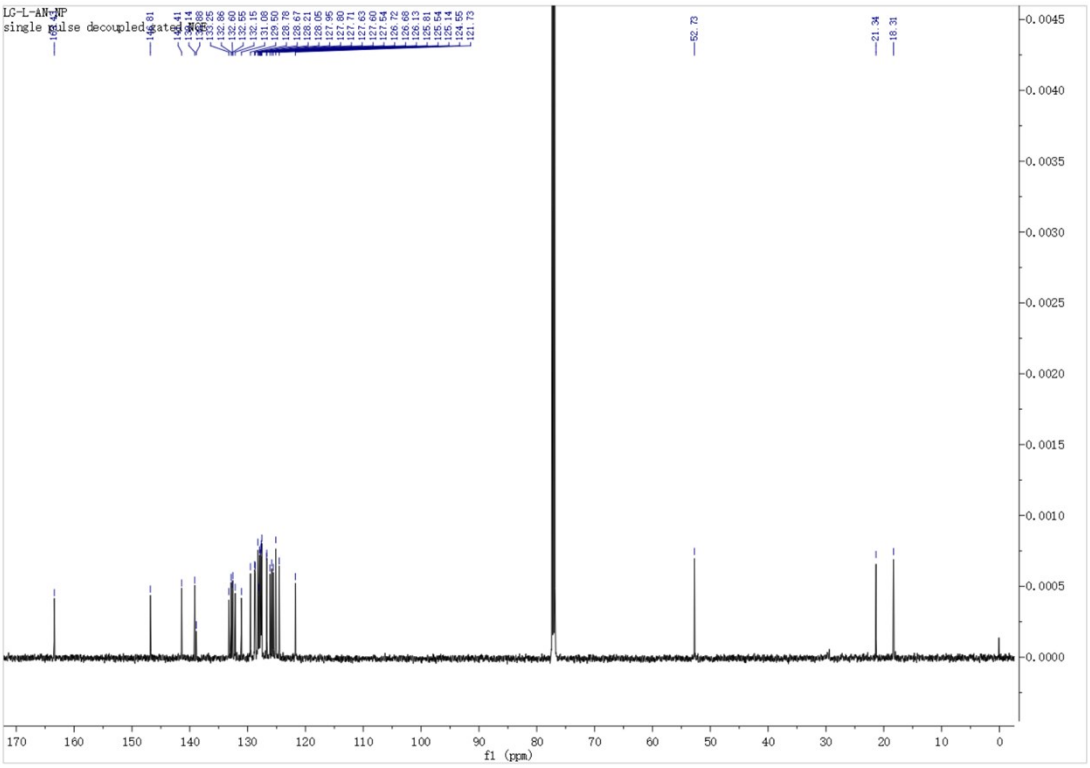


Figure S23. ^{13}C NMR spectrum of **L5** in $CDCl_3$.

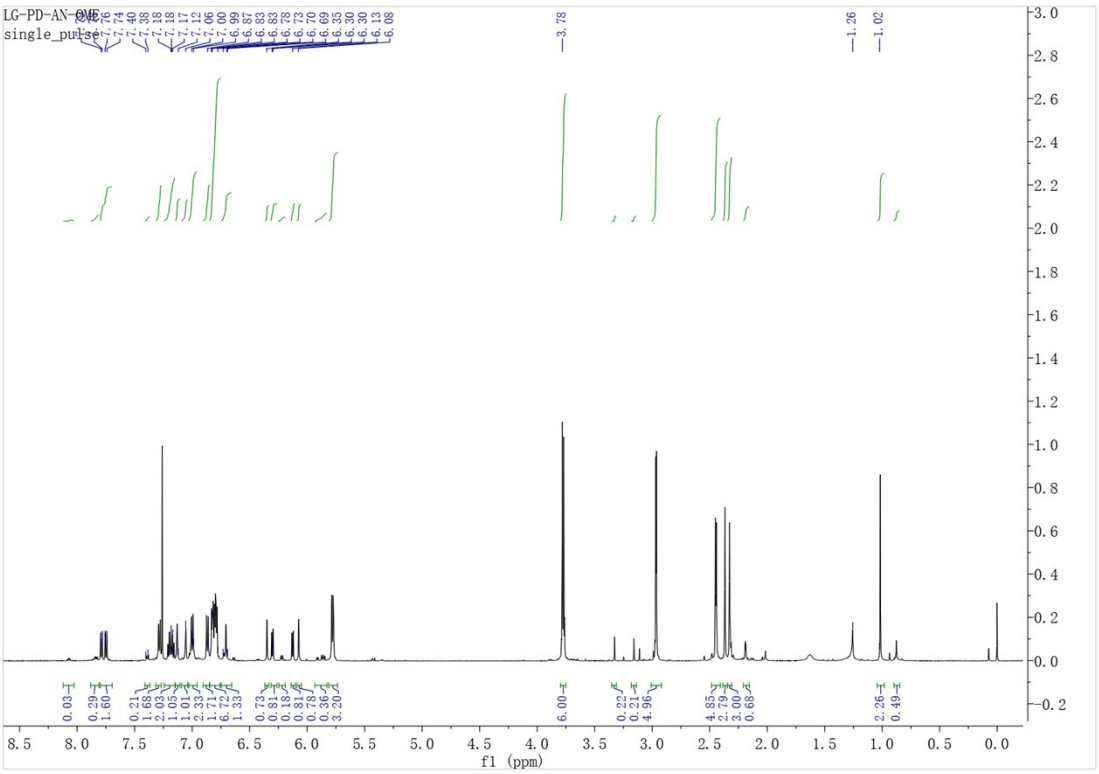


Figure S24. ^{1}H NMR spectrum of **Pd1** in $CDCl_3$.

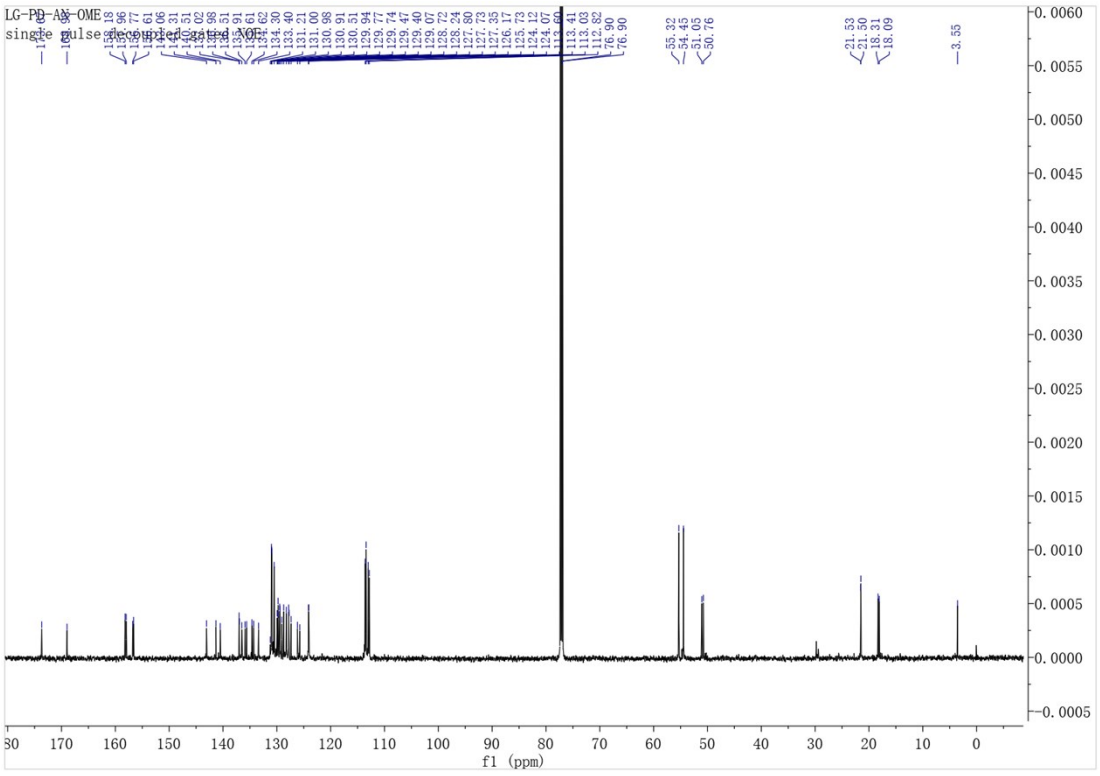


Figure S25. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

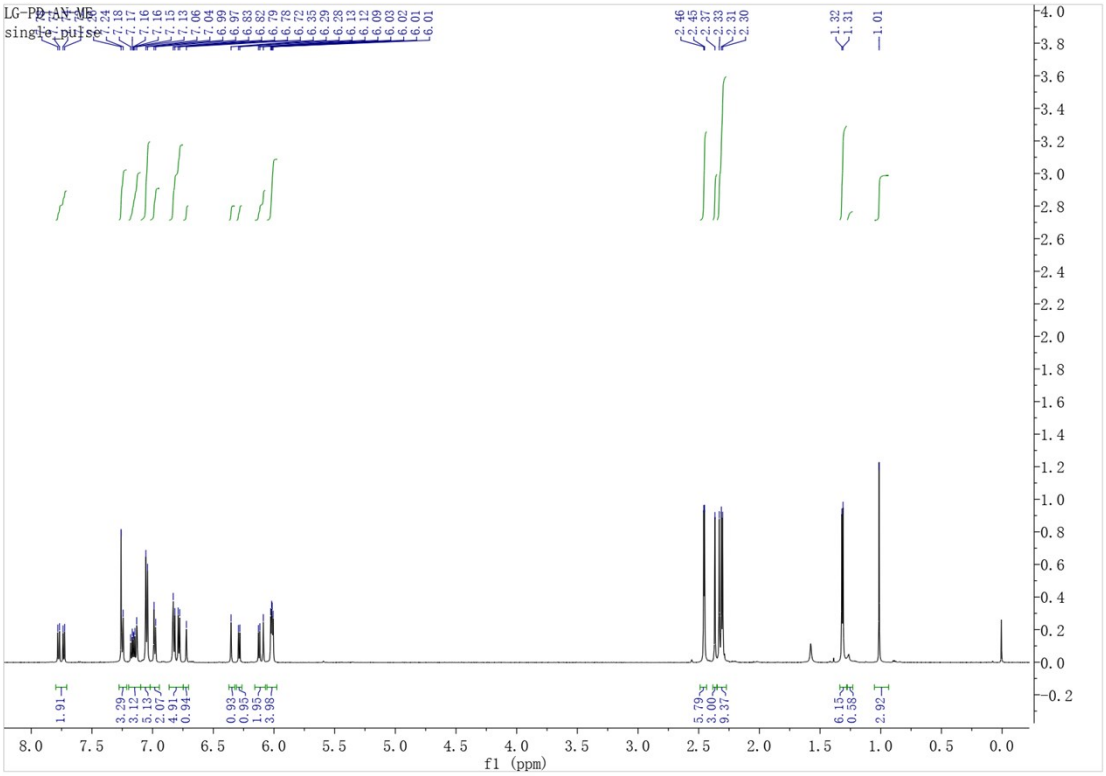


Figure S26. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

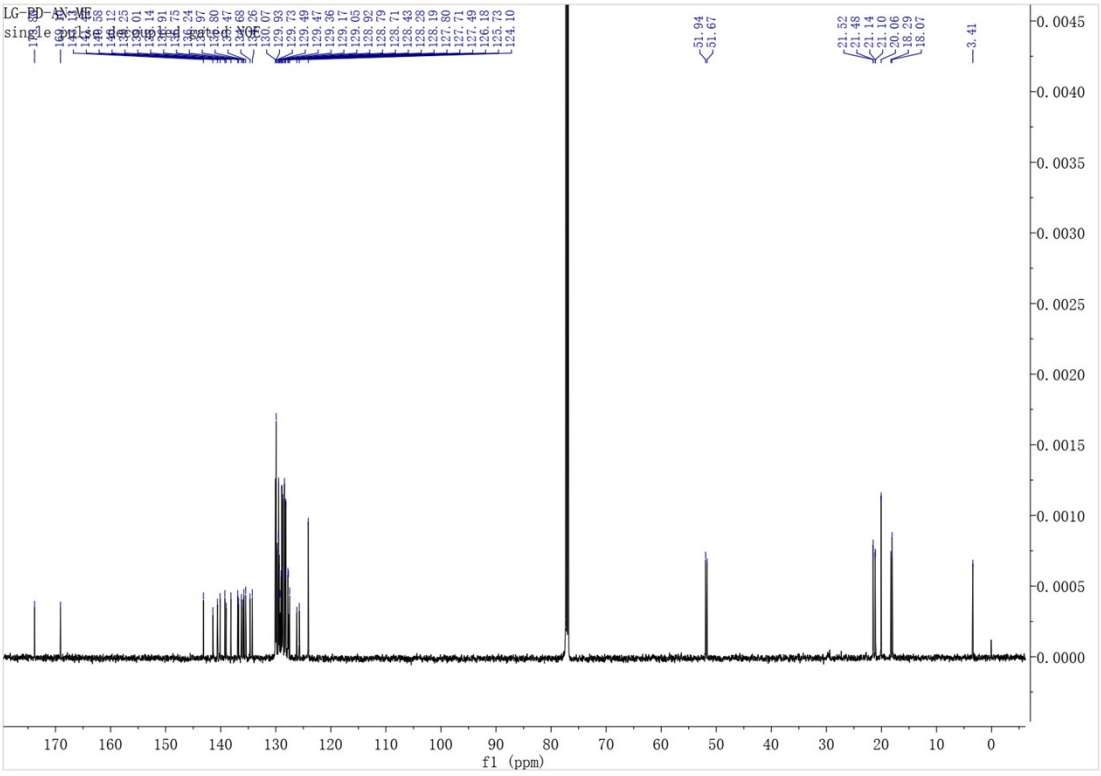


Figure S27. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

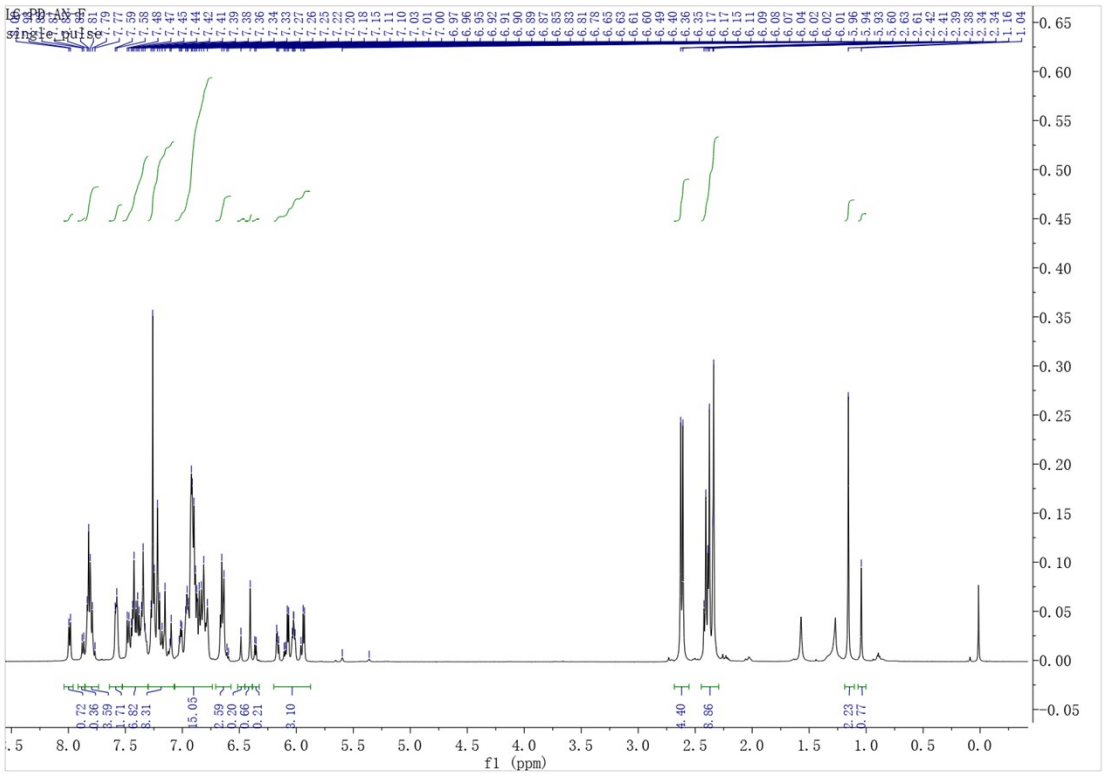


Figure S28. ^{1}H NMR spectrum of **Pd3** in $CDCl_3$.

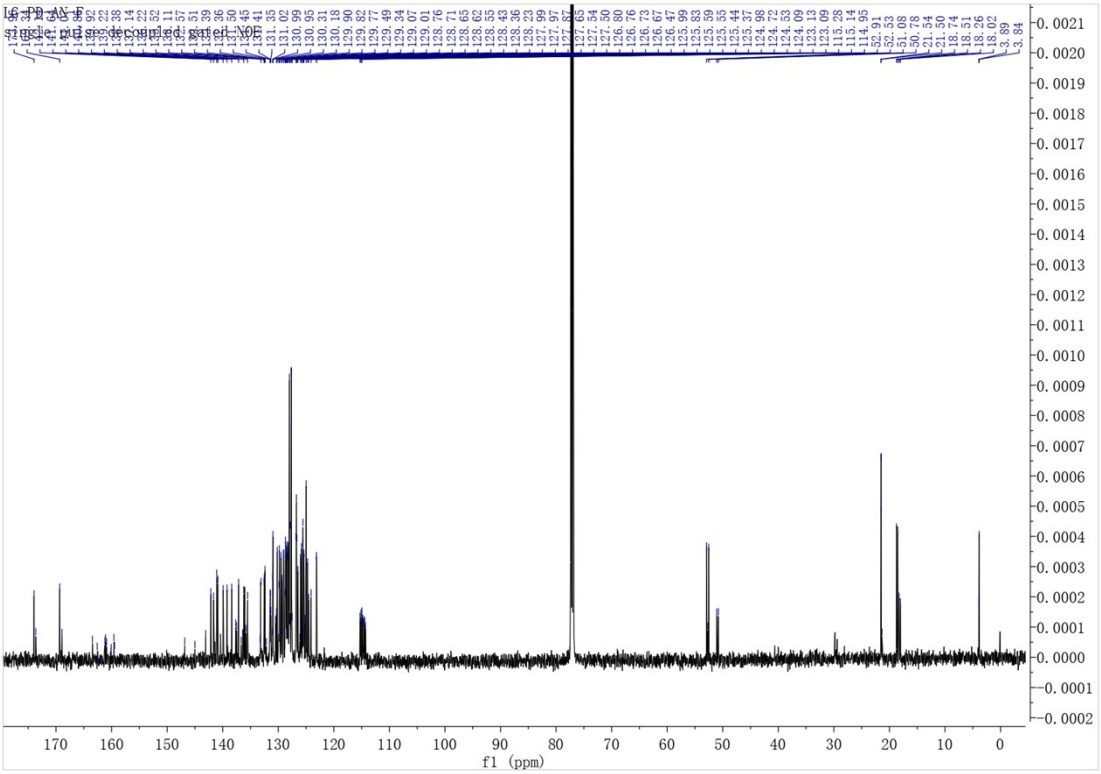


Figure S29. ^{13}C NMR spectrum of **Pd3** in $CDCl_3$.

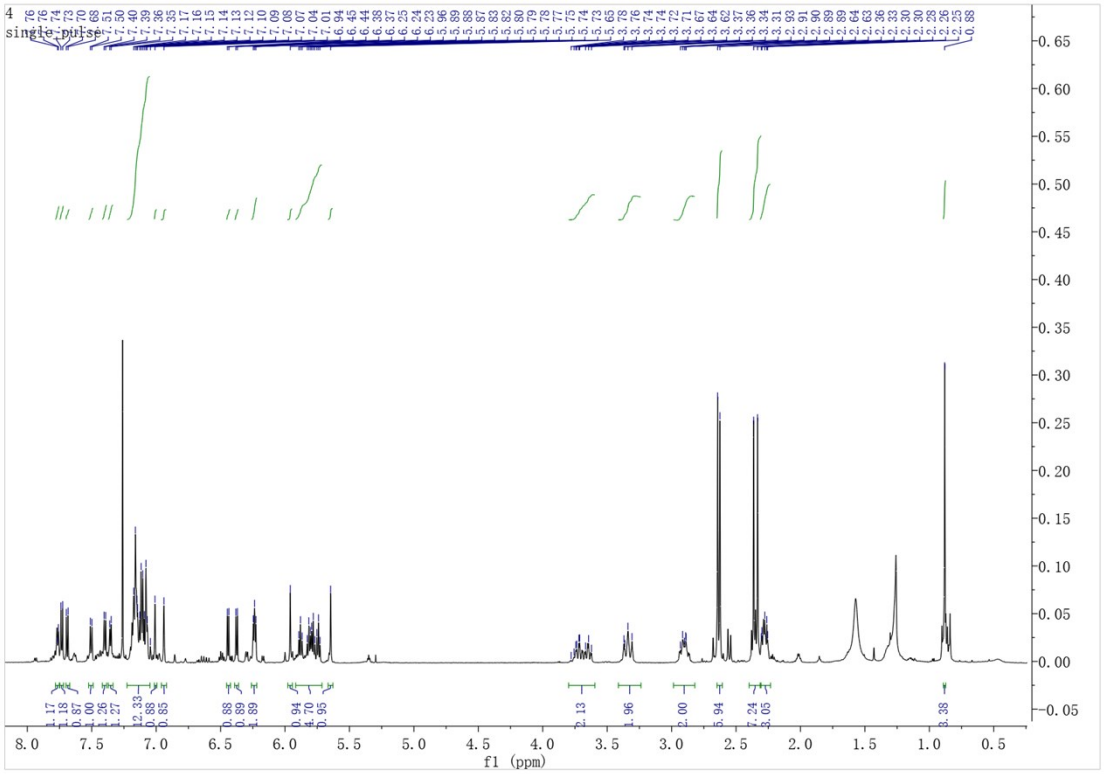


Figure S30. ^{1}H NMR spectrum of **Pd4** in $CDCl_3$.

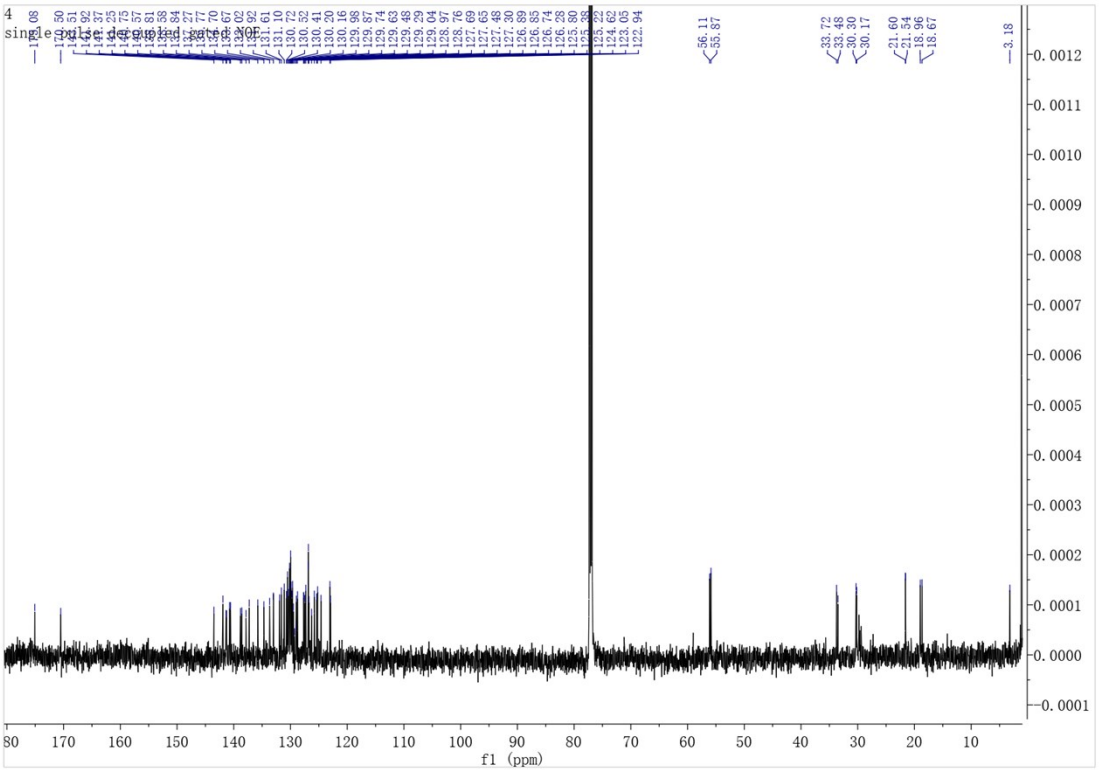


Figure S31. ^{13}C NMR spectrum of **Pd4** in $CDCl_3$.

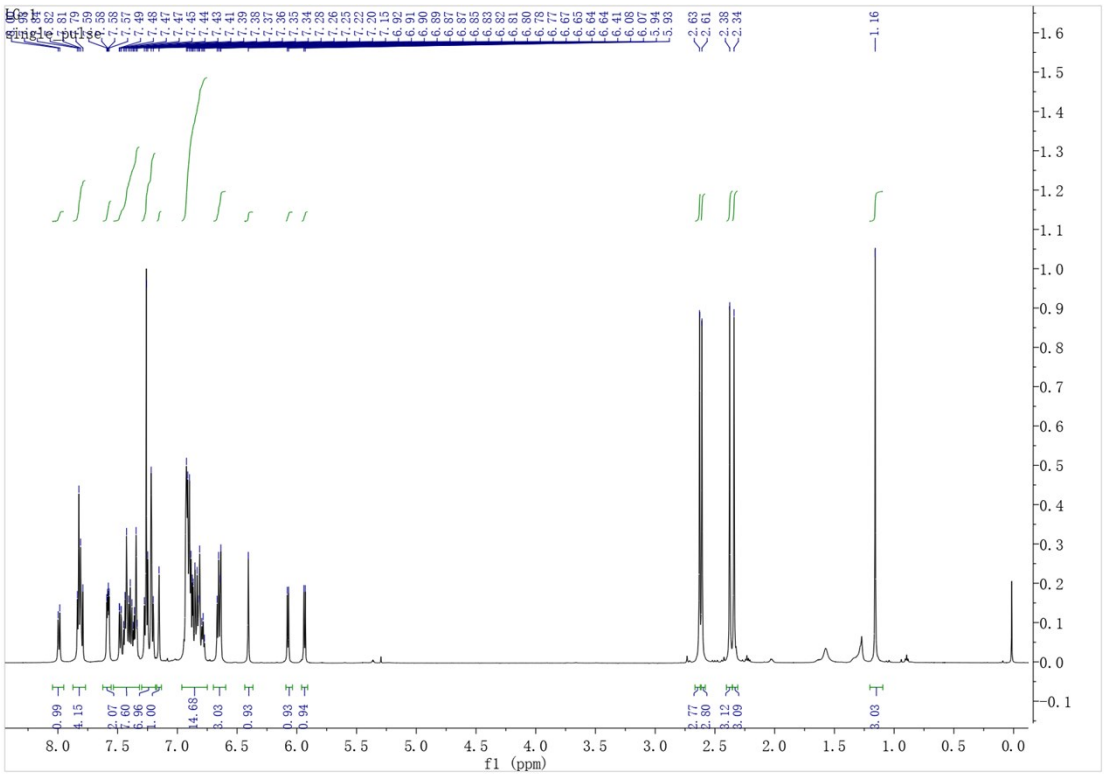


Figure S32. ^{1}H NMR spectrum of **Pd5** in $CDCl_3$.

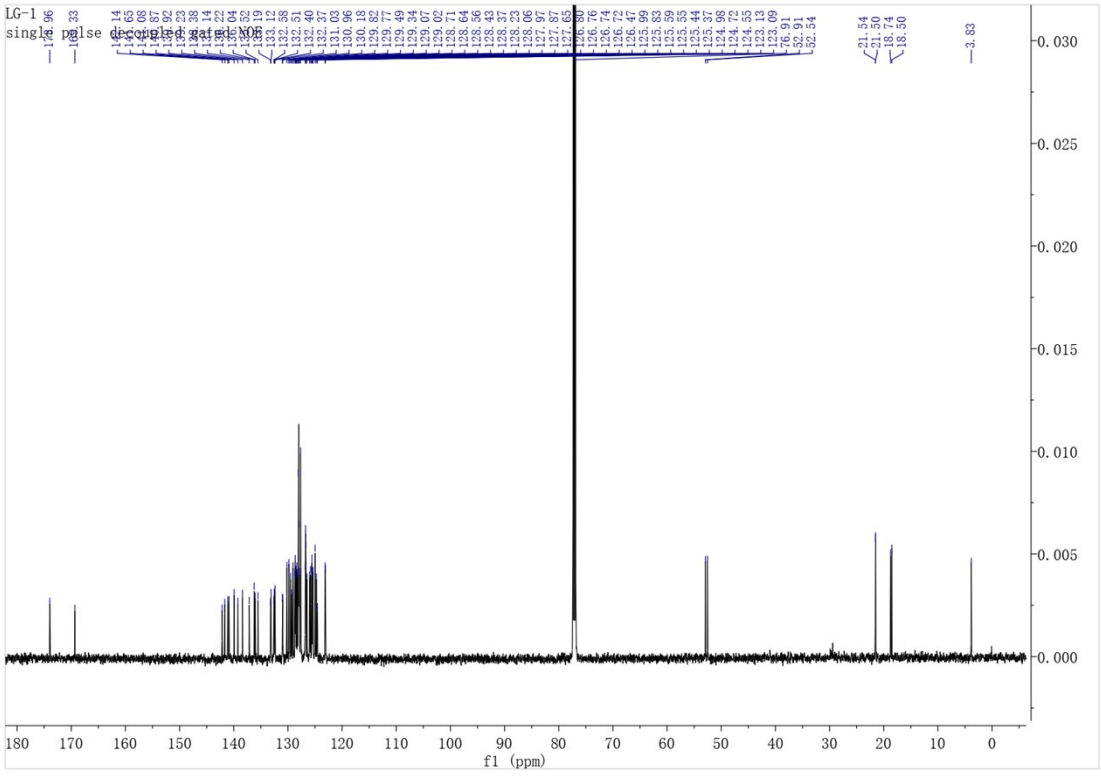


Figure S33. ^{13}C NMR spectrum of **Pd5** in $CDCl_3$.

3.2 ESI-MS and MALDI-TOF-MS Data

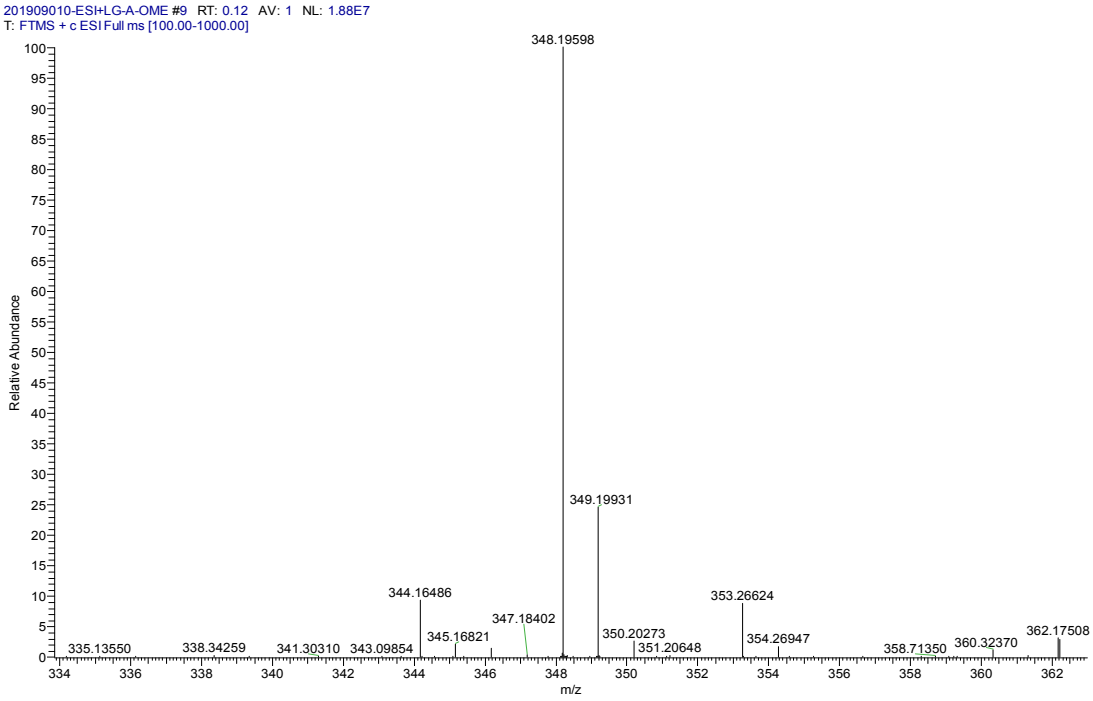


Figure S34. ESI-MS of **A1**.

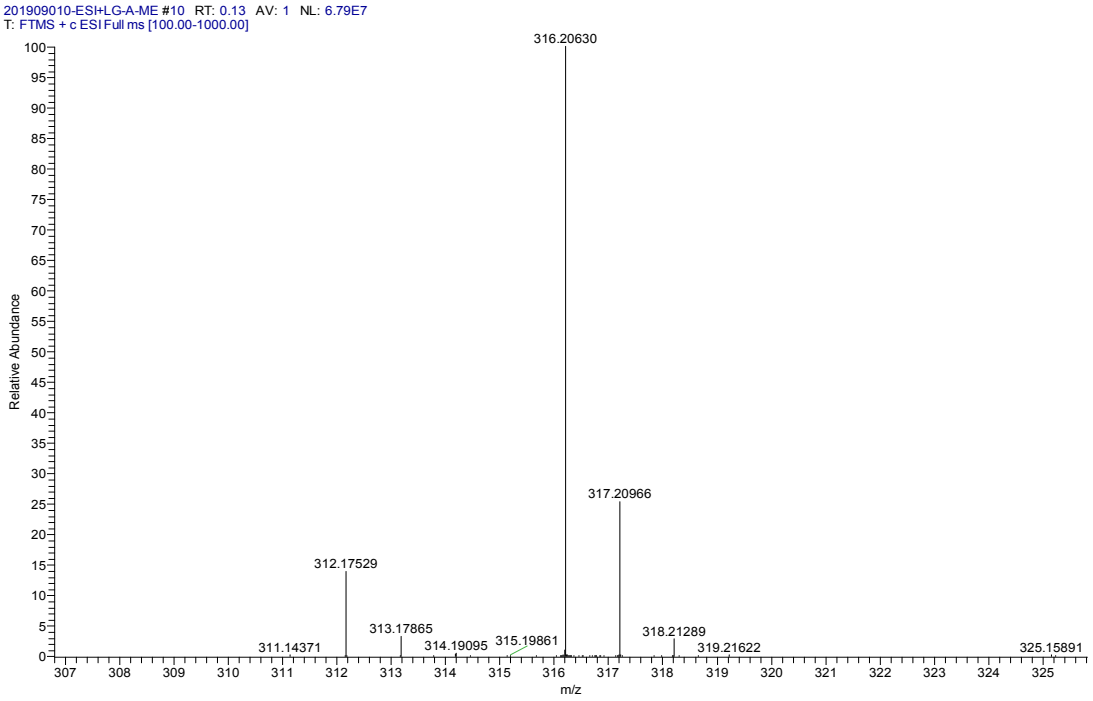


Figure S35. ESI-MS of **A2**.

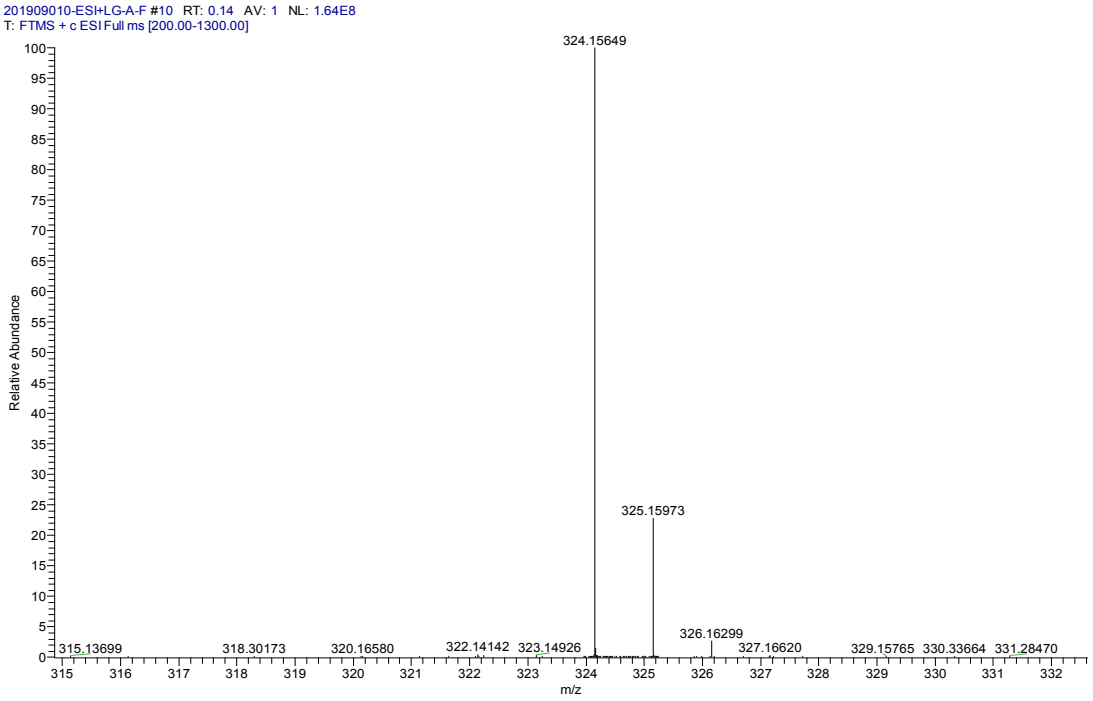


Figure S36. ESI-MS of **A3**.

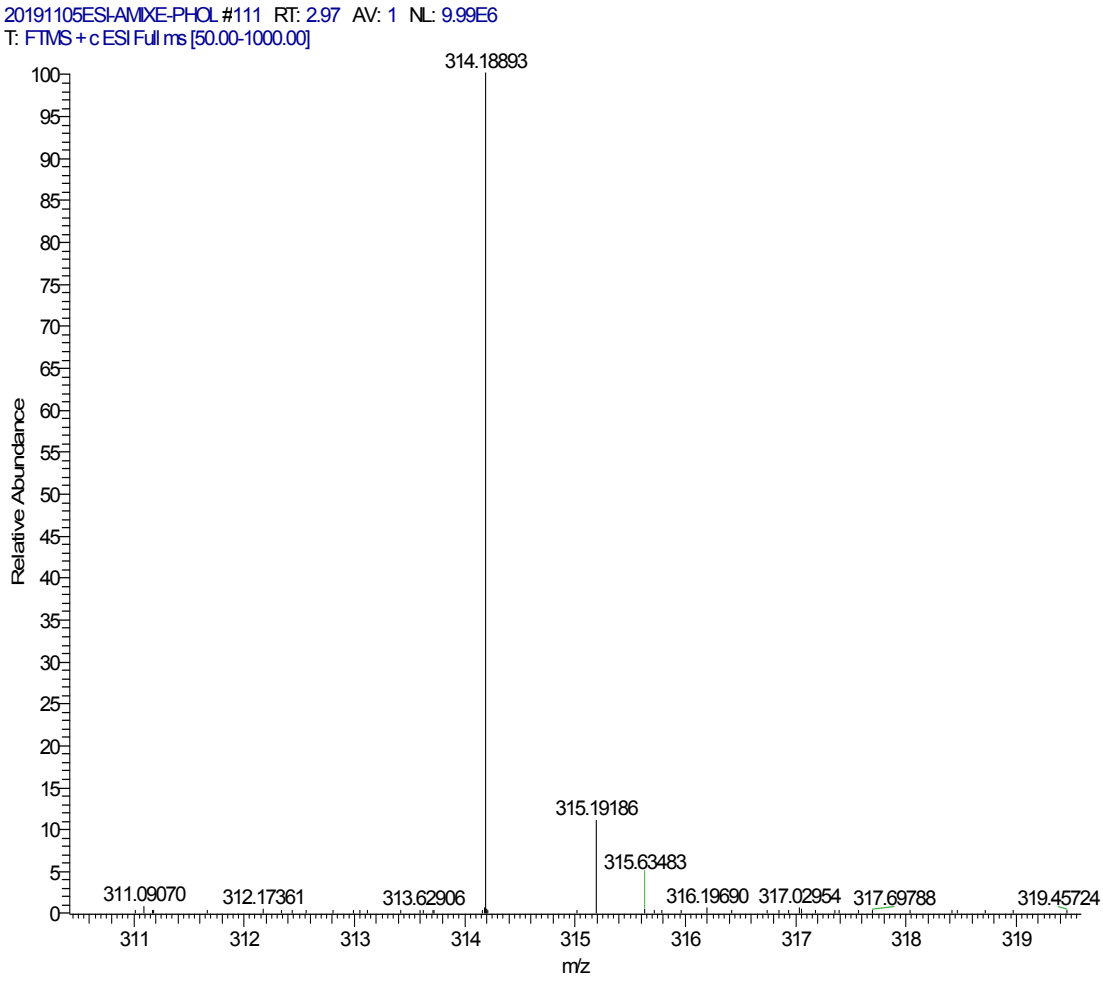


Figure S37. ESI-MS of **A4**.

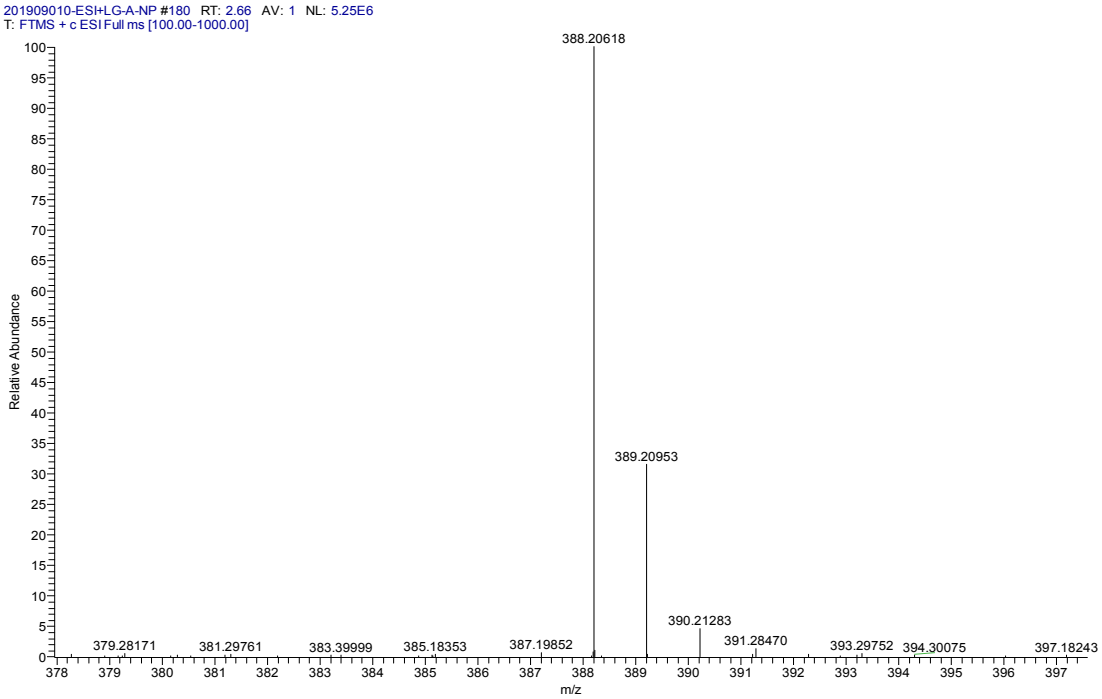


Figure S38. ESI-MS of **A5**.

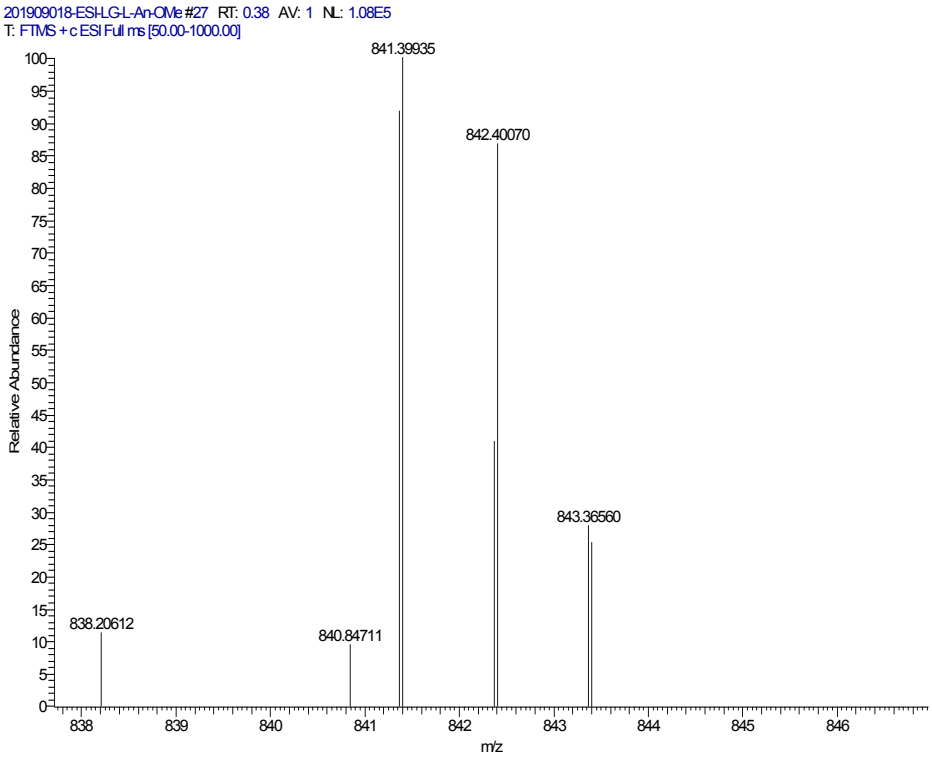


Figure S39. ESI-MS of **L1**.

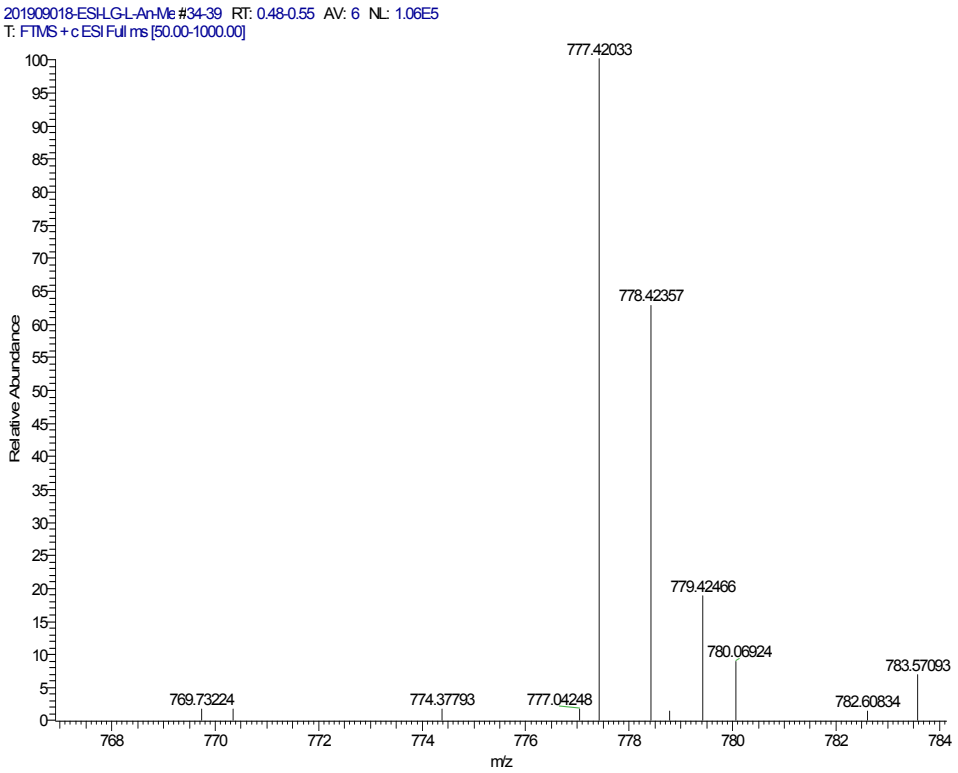


Figure S40. ESI-MS of **L2**.

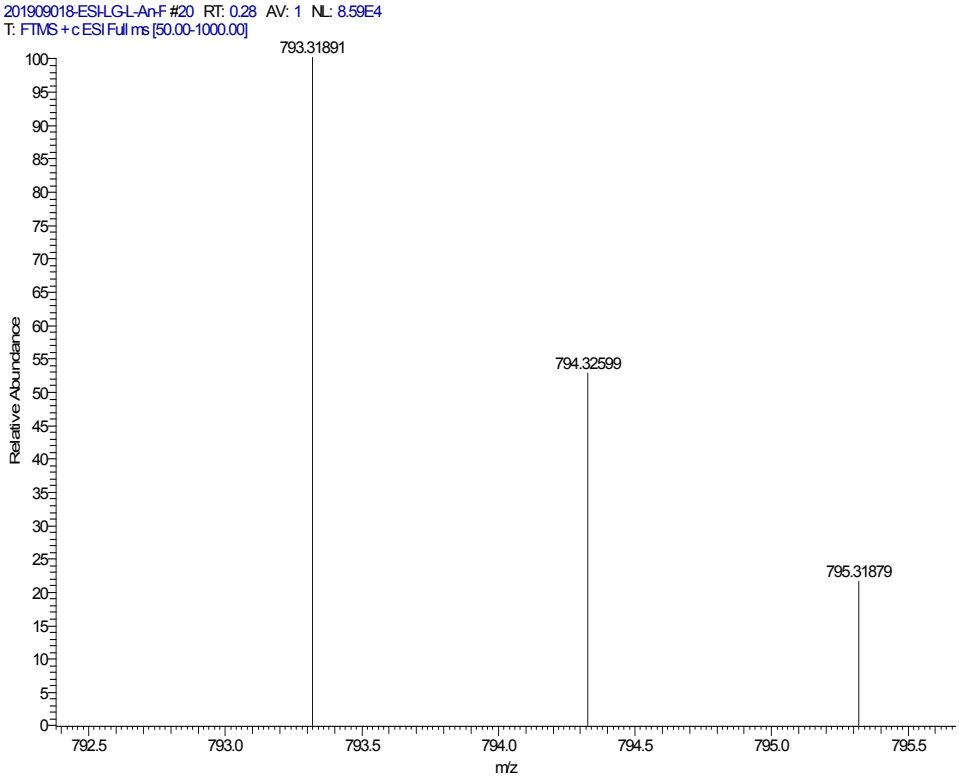


Figure S41. ESI-MS of **L3**.

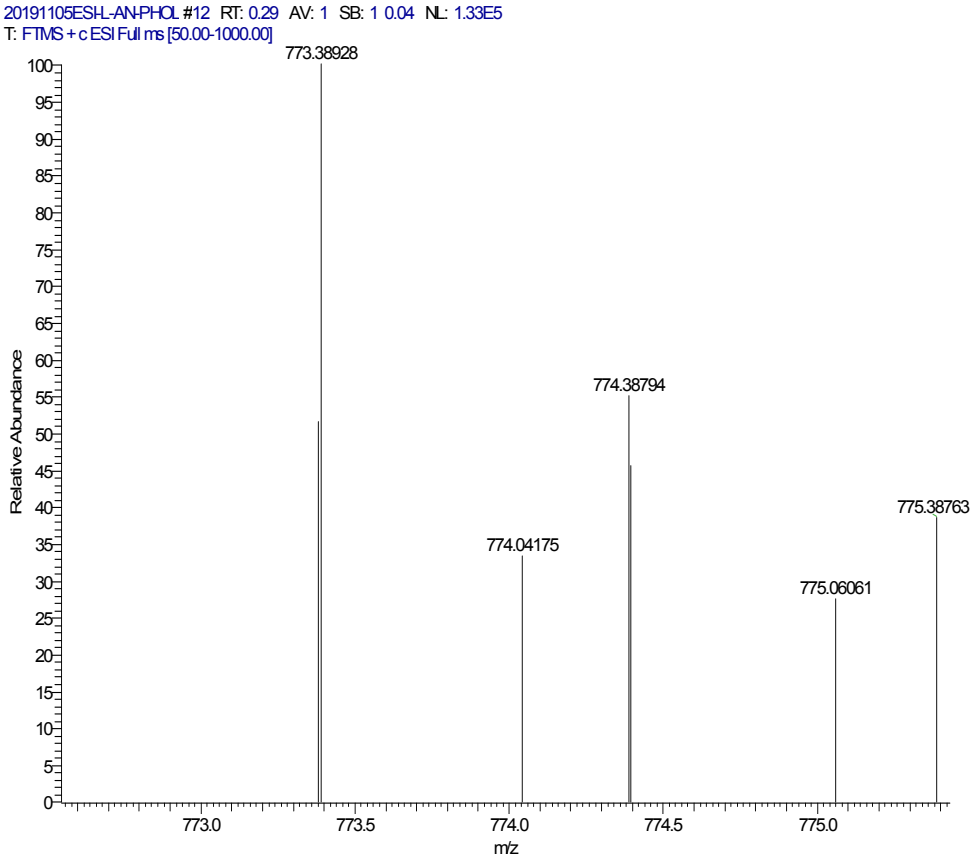


Figure S42. ESI-MS of **L4**.

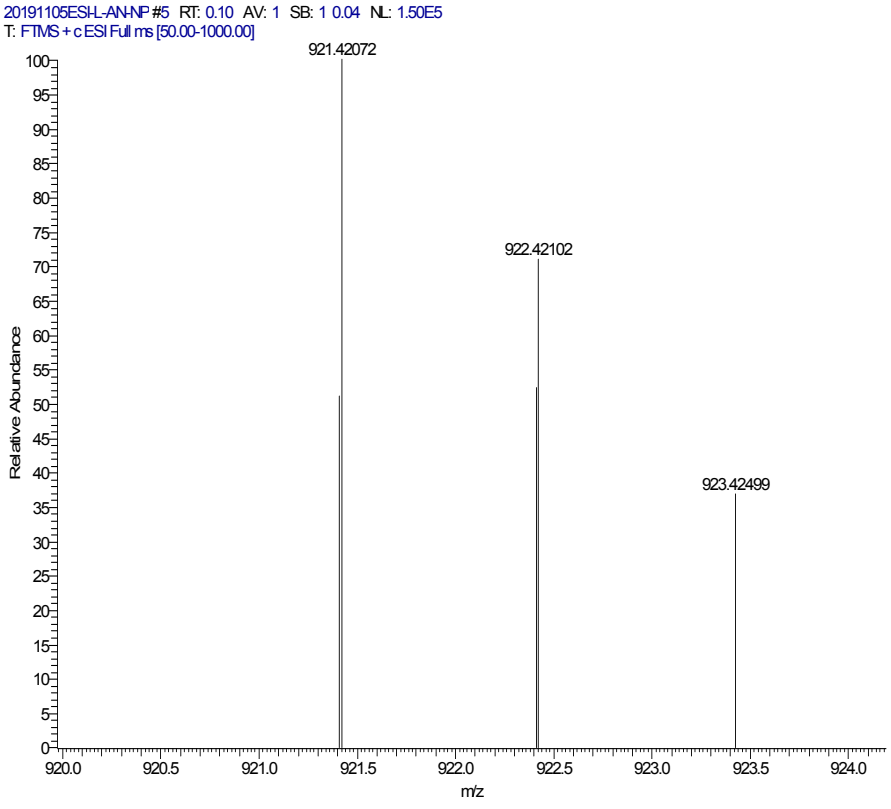


Figure S43. ESI-MS of **L5**.

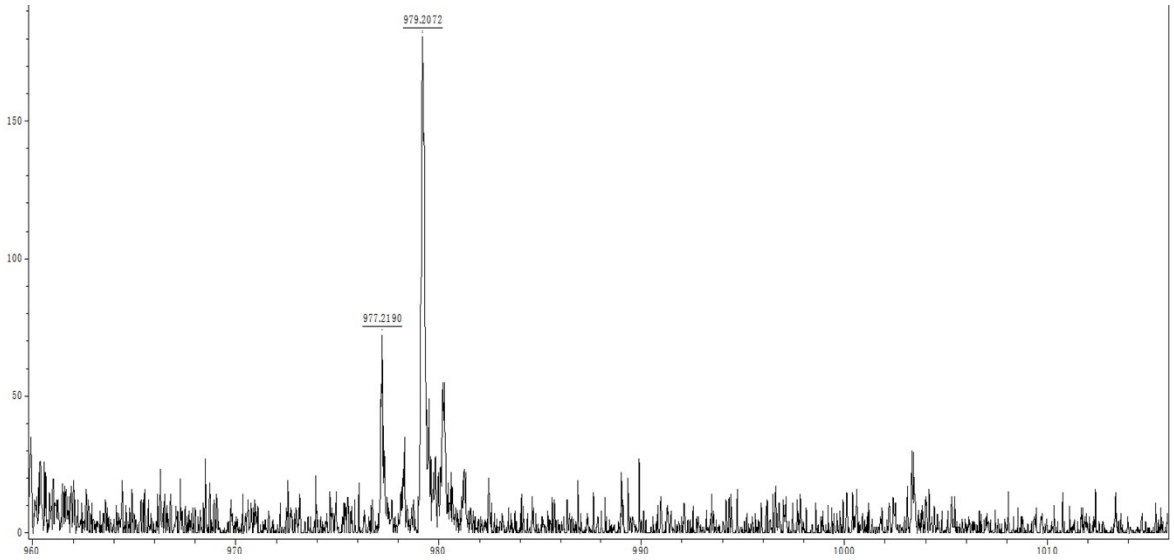


Figure S44. MALDI-TOF-MS of **Ni1.**

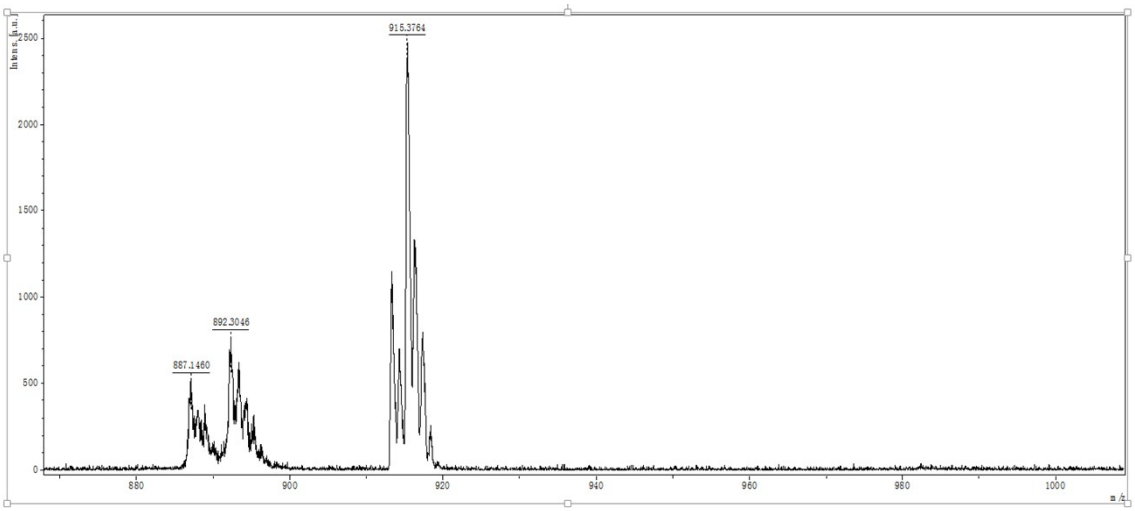


Figure S45. MALDI-TOF-MS of **Ni2.**

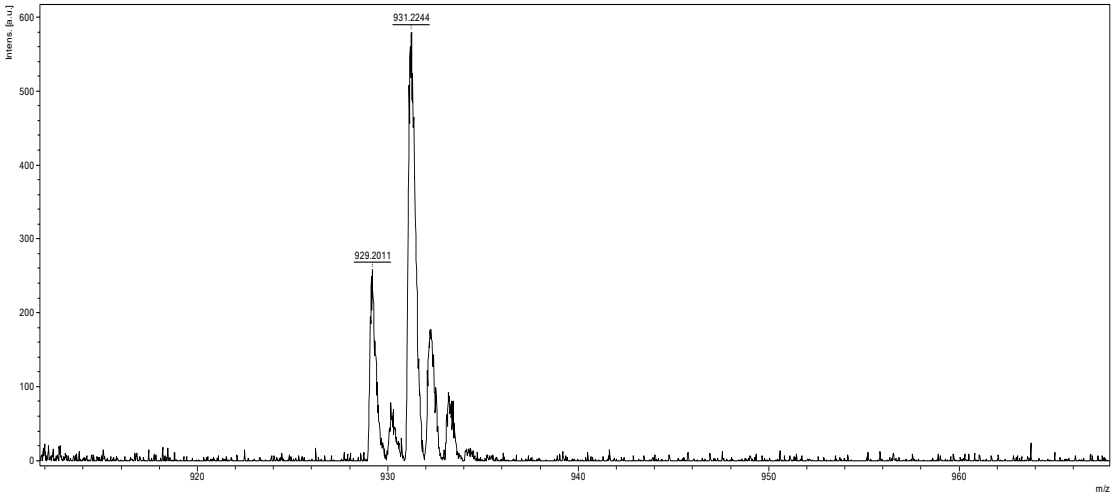


Figure S46. MALDI-TOF-MS of **Ni3.**

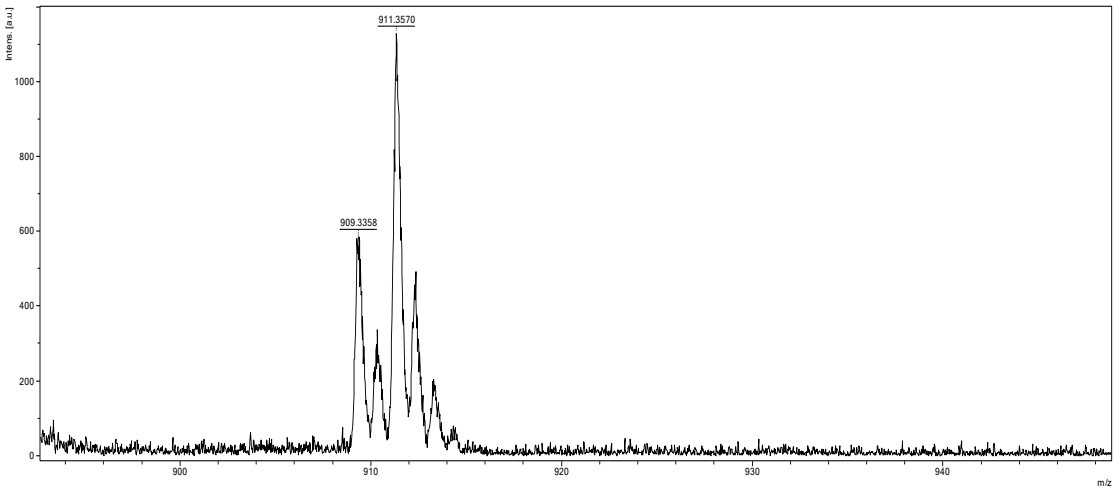


Figure S47. MALDI-TOF-MS of **Ni4.**

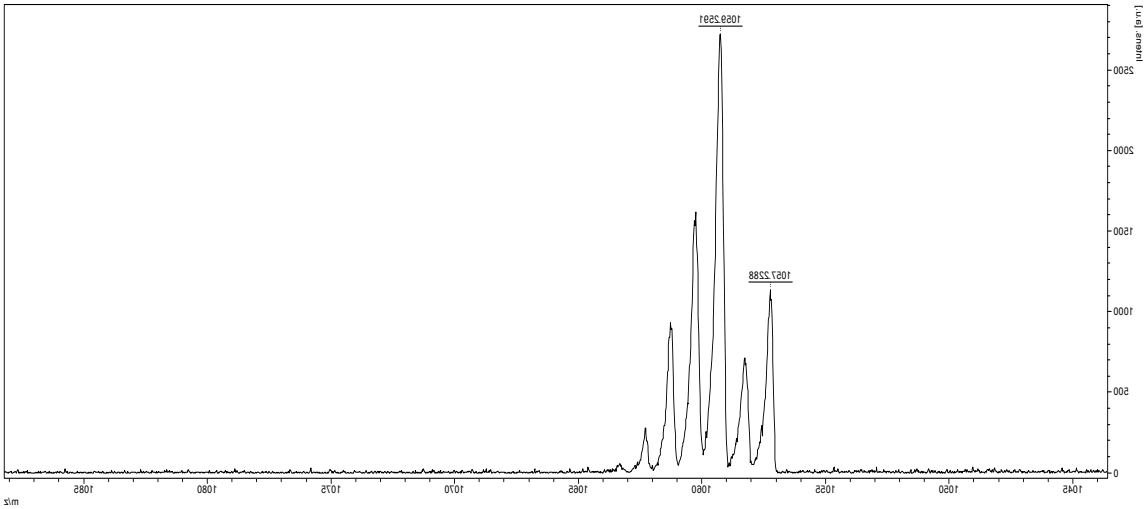


Figure S48. MALDI-TOF-MS of **Ni5.**

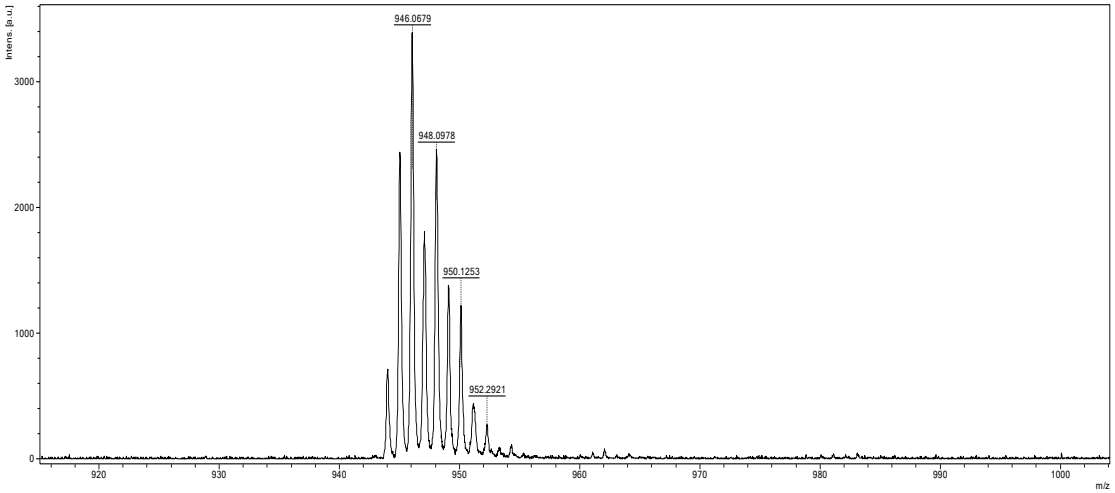


Figure S49. MALDI-TOF-MS of **Pd1.**

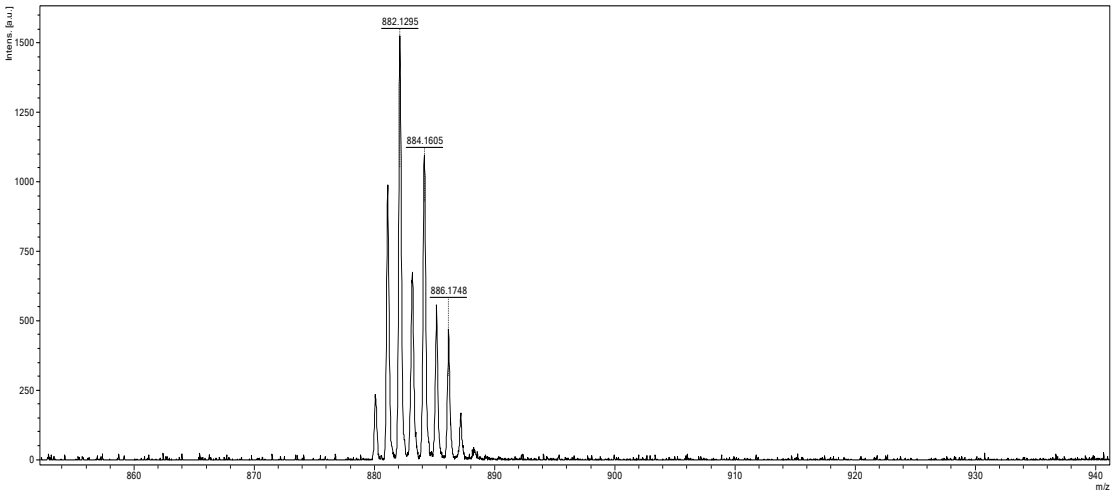


Figure S50. MALDI-TOF-MS of **Pd2.**

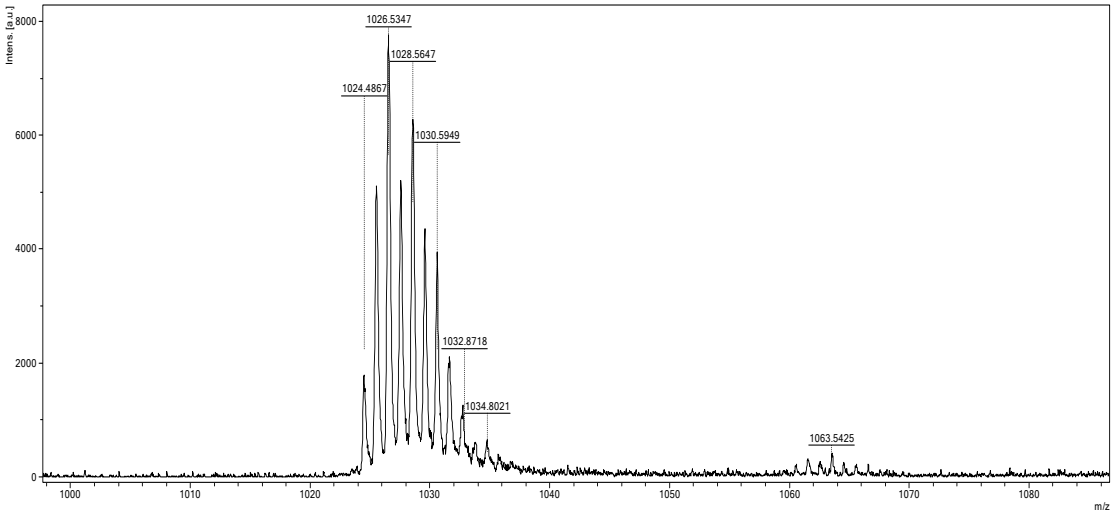


Figure S51. MALDI-TOF-MS of **Pd3.**

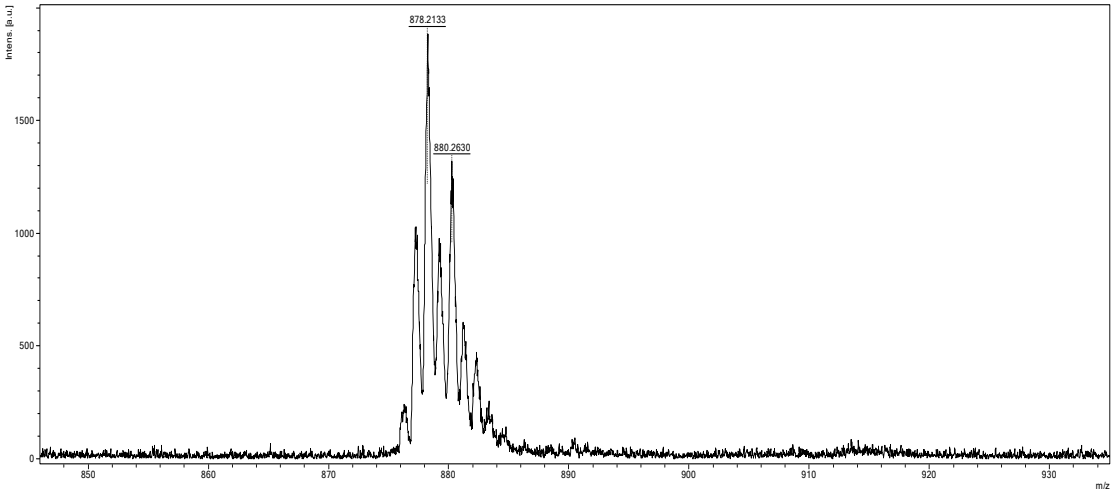


Figure S52. MALDI-TOF-MS of **Pd4.**

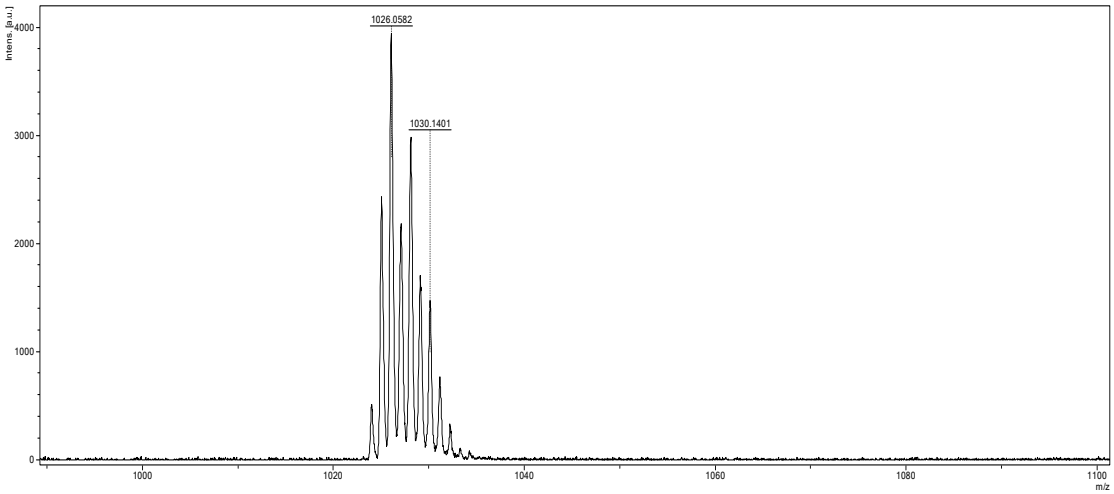


Figure S53. MALDI-TOF-MS of **Pd5.**

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

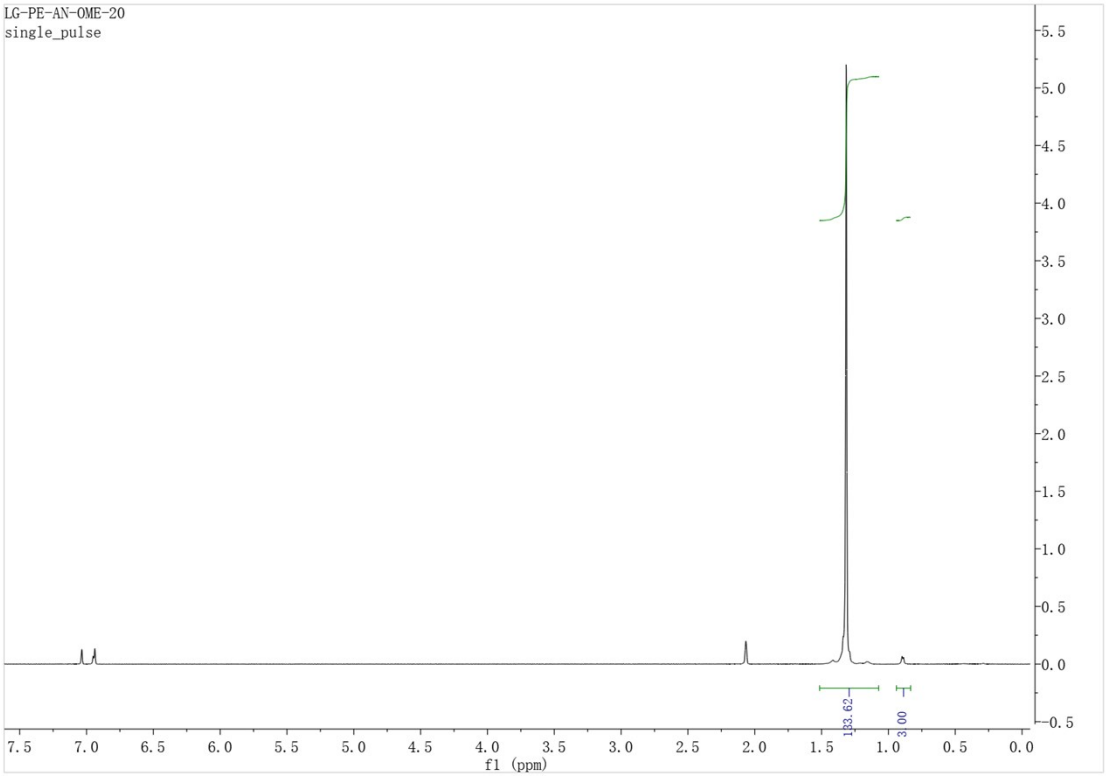


Figure S54. ^{1}H NMR spectrum of the polymer from table 1, entry 1 (d^{8}-toluene, 100 ^{o}C).

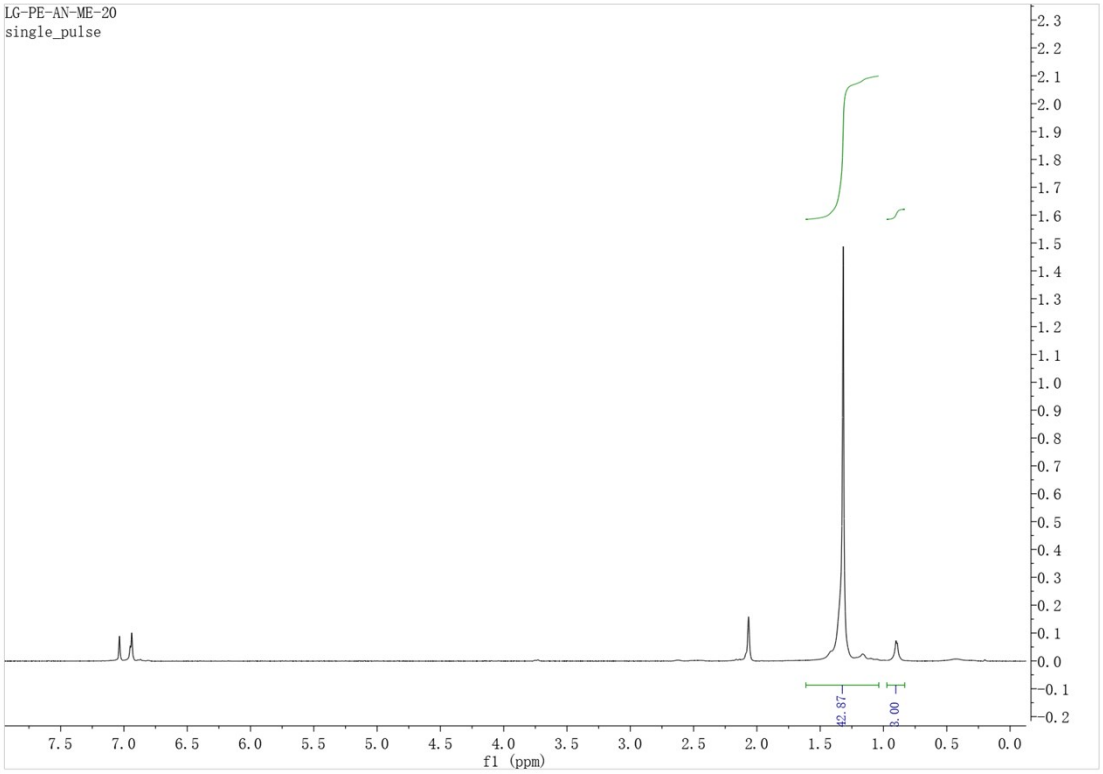


Figure S55. ^{1}H NMR spectrum of the polymer from table 1, entry 5 (d^{8}-toluene, 100 ^{o}C).

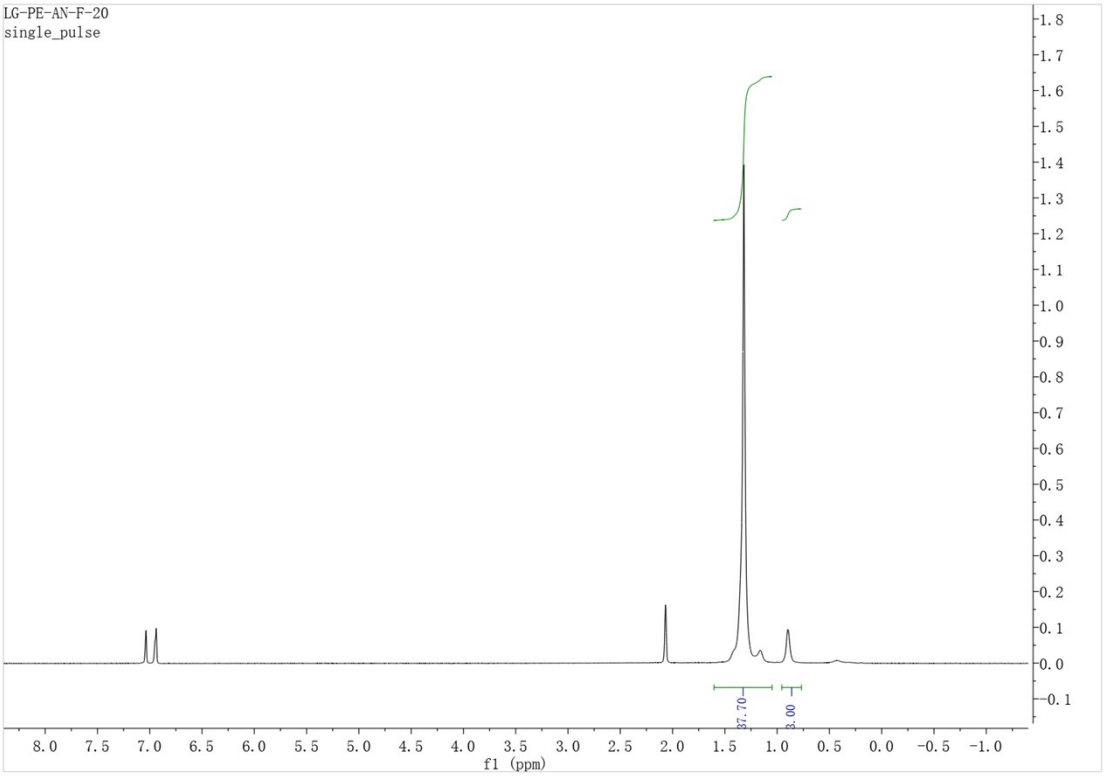


Figure S56. ^{1}H NMR spectrum of the polymer from table 1, entry 9 (d^{8}-toluene, 100 ^{o}C).

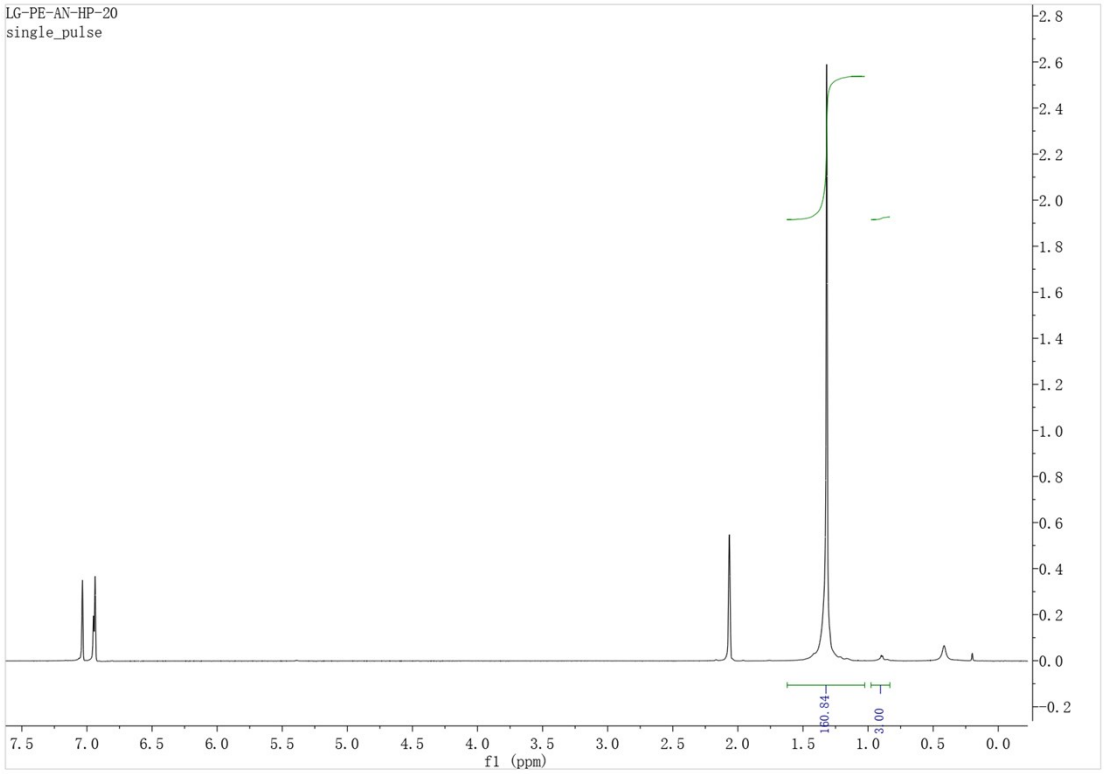


Figure S57. ^{1}H NMR spectrum of the polymer from table 1, entry 13 (d^{8}-toluene, 100 ^{o}C).

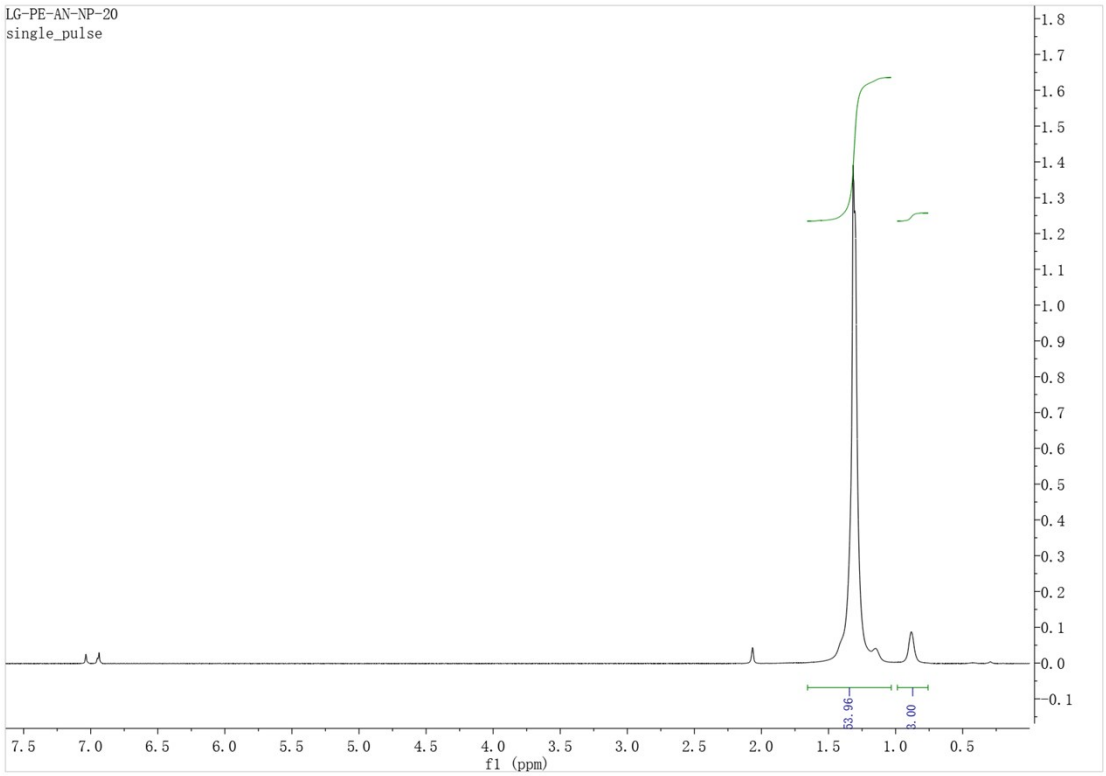


Figure S58. ^{1}H NMR spectrum of the polymer from table 1, entry 17 (d^{8}-toluene, 100 ^{o}C).

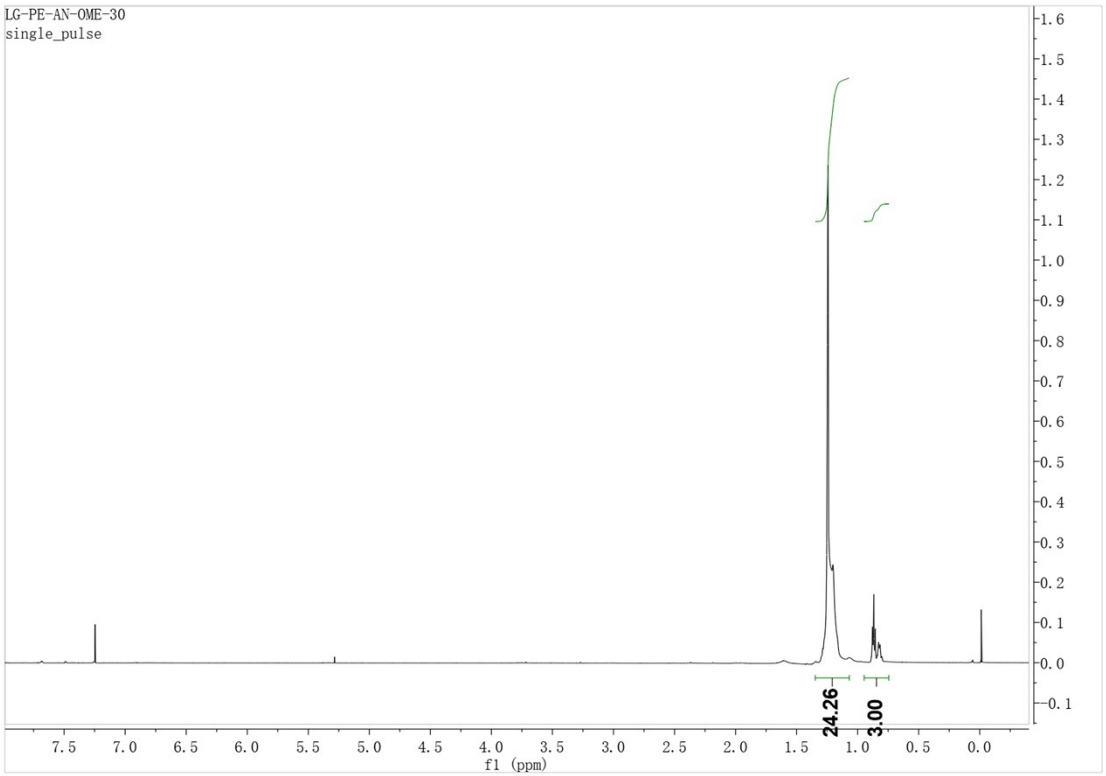


Figure S59. ^{1}H NMR spectrum of the polymer from table 2, entry 1 ($CDCl_3$, 20 ^{o}C).

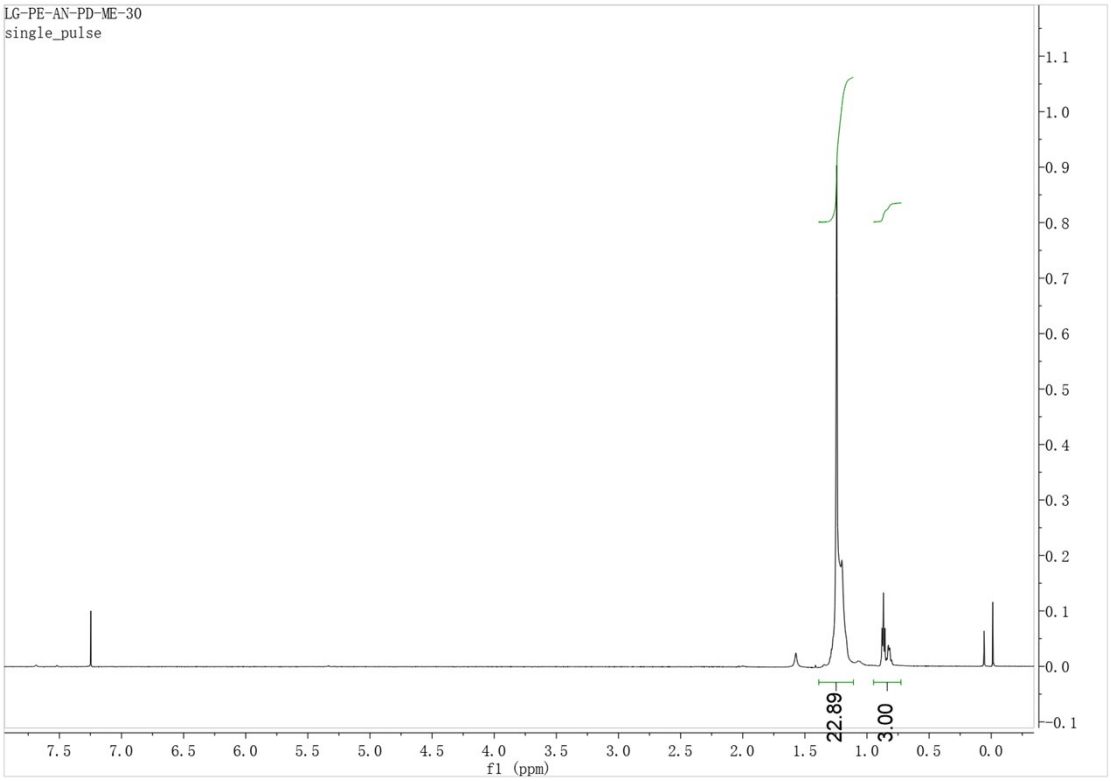


Figure S60. ^{1}H NMR spectrum of the polymer from table 2, entry 4 ($CDCl_3$, 20 ^{o}C).

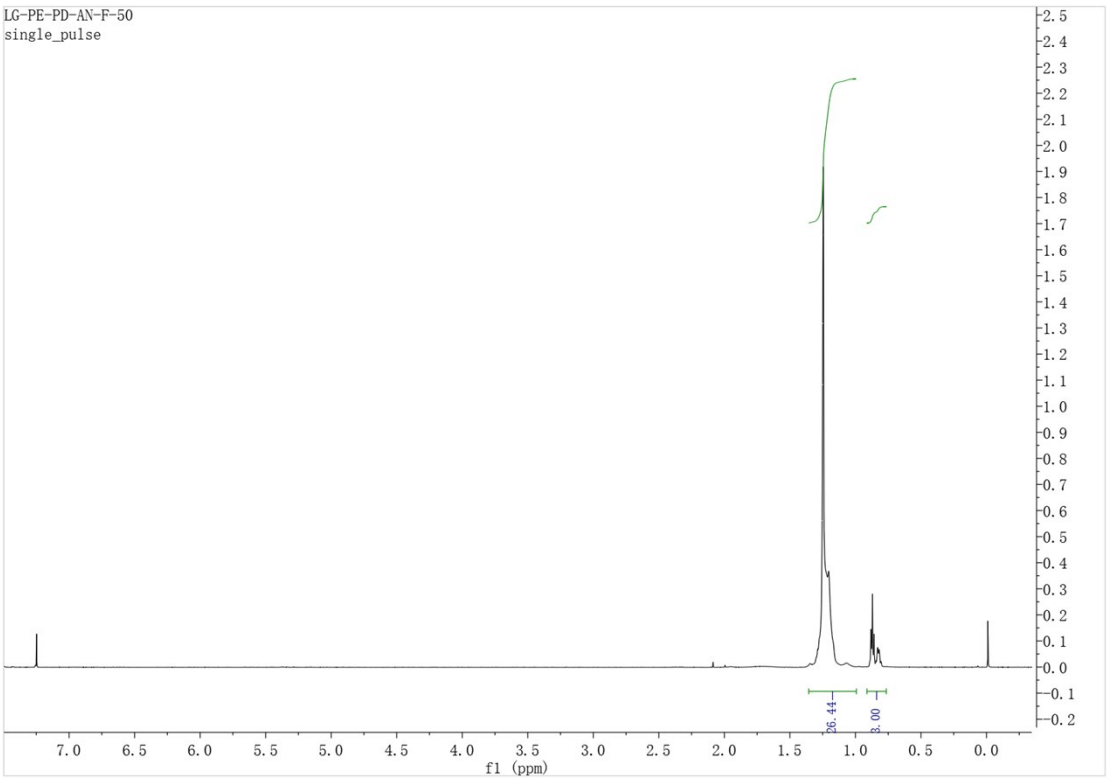


Figure S61. ^{1}H NMR spectrum of the polymer from table 2, entry 7 ($CDCl_3$, 20 ^{o}C).

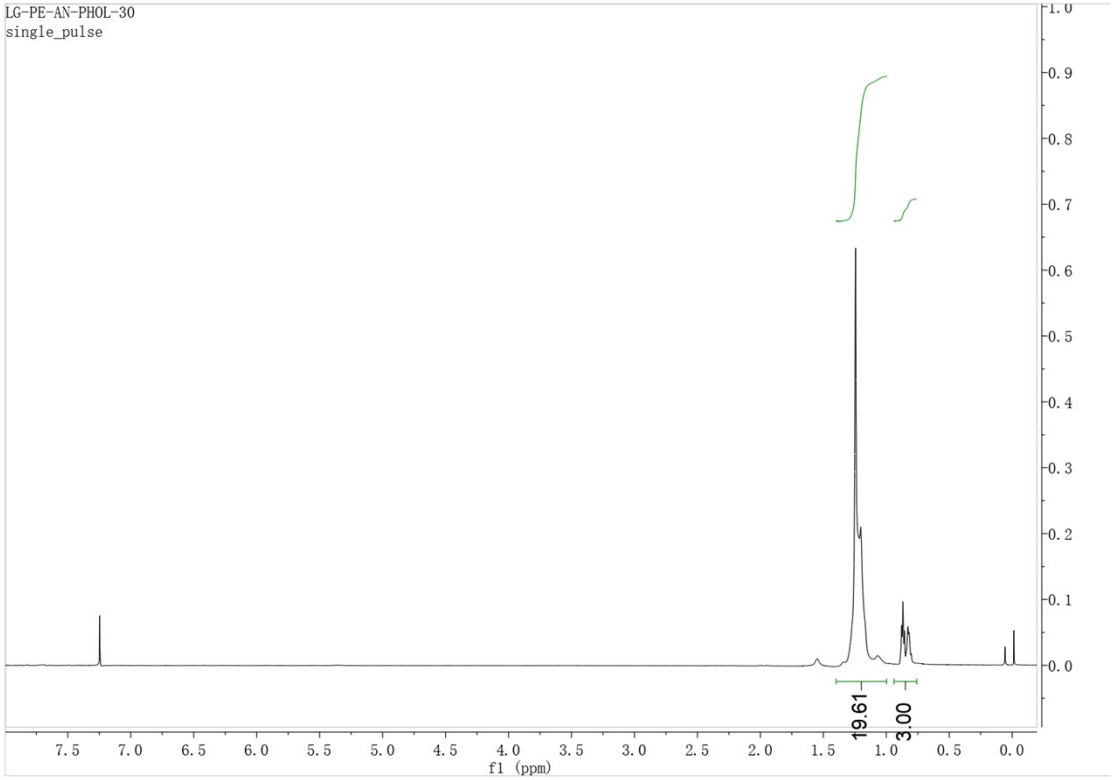


Figure S62. ^{1}H NMR spectrum of the polymer from table 2, entry 10 ($CDCl_3$, 20 ^{o}C).

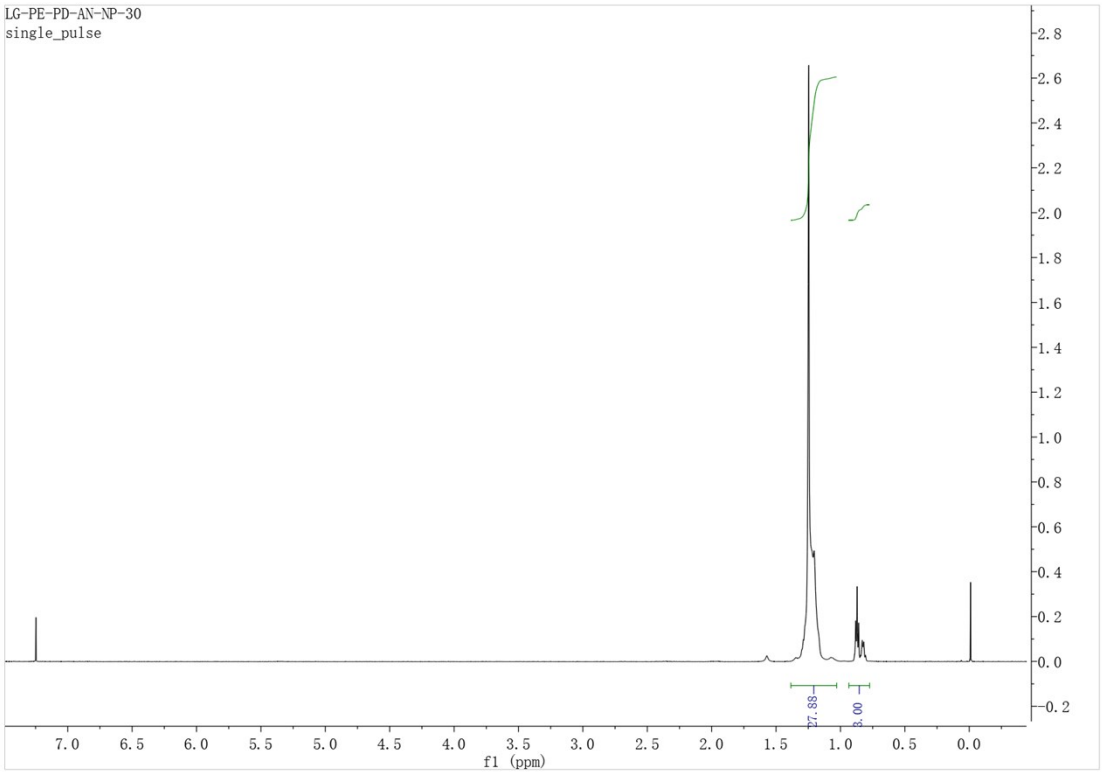


Figure S63. ^{1}H NMR spectrum of the polymer from table 2, entry 13 ($CDCl_3$, 20 ^{o}C).

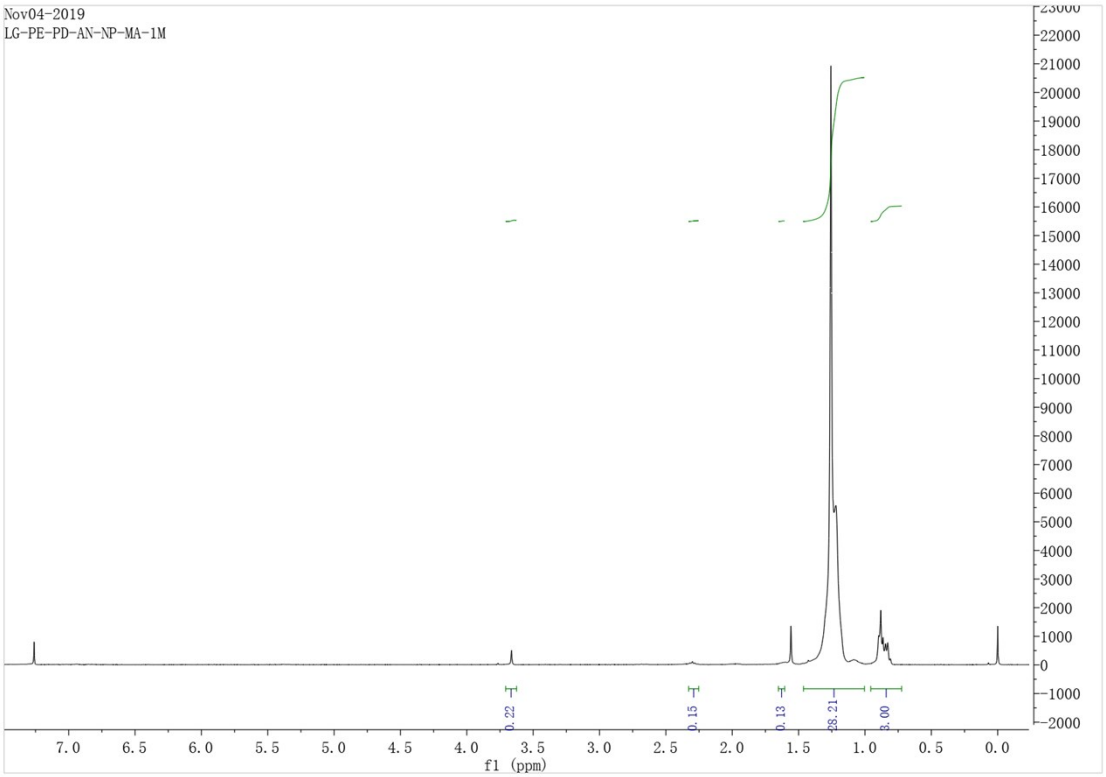


Figure S64. ^{1}H NMR spectrum of the polymer from table 3, entry 10 ($CDCl_3$, 20 ^{o}C).

3.4 DSC, GPC of Polymers and Copolymers.

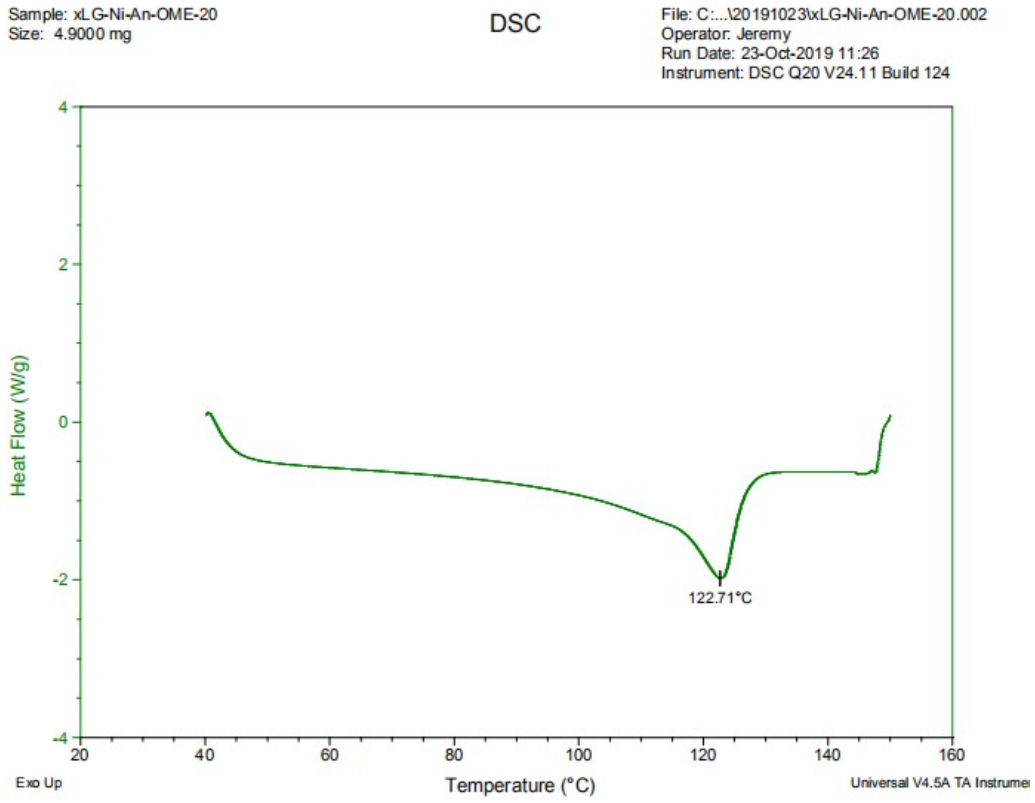


Figure S65. DSC of the polymer from table 1, entry 1.

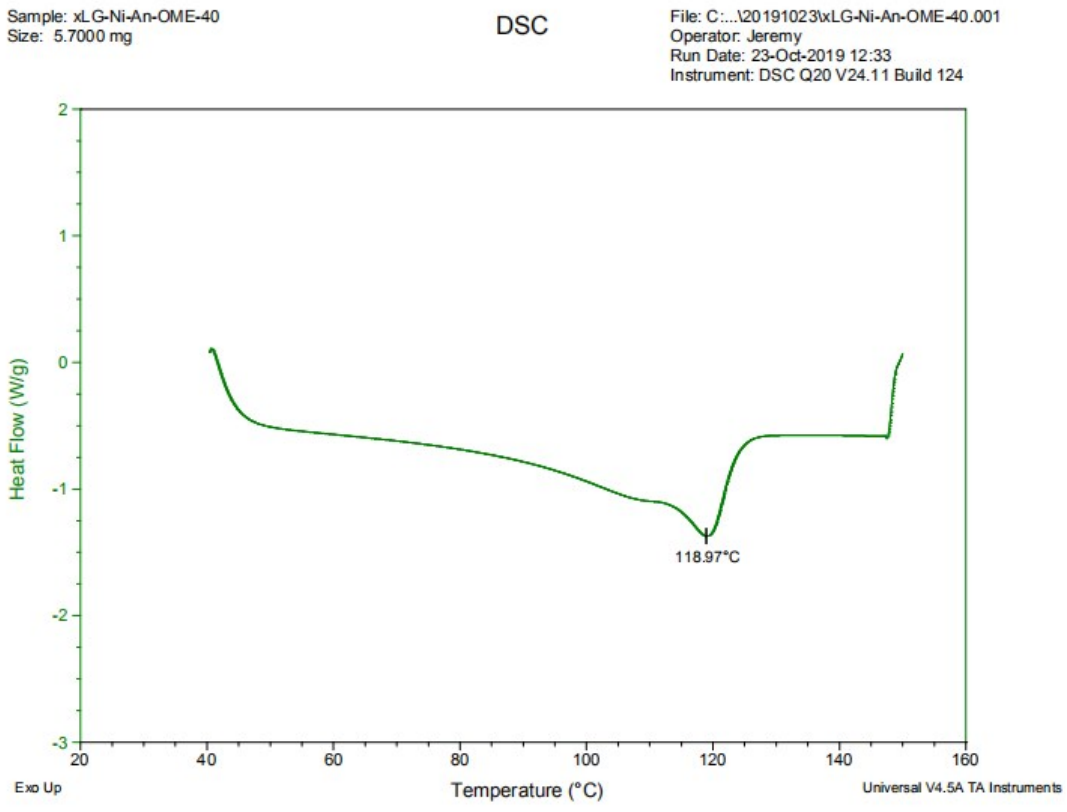


Figure S66. DSC of the polymer from table 1, entry 2.

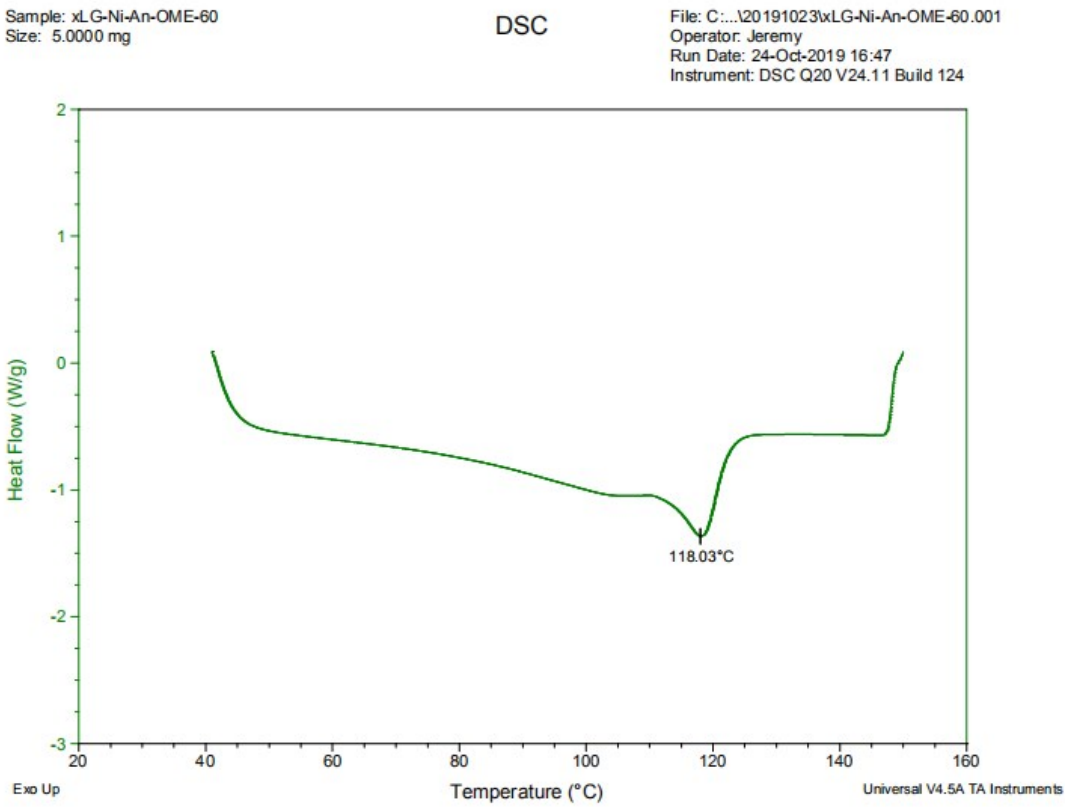


Figure S67. DSC of the polymer from table 1, entry 3.

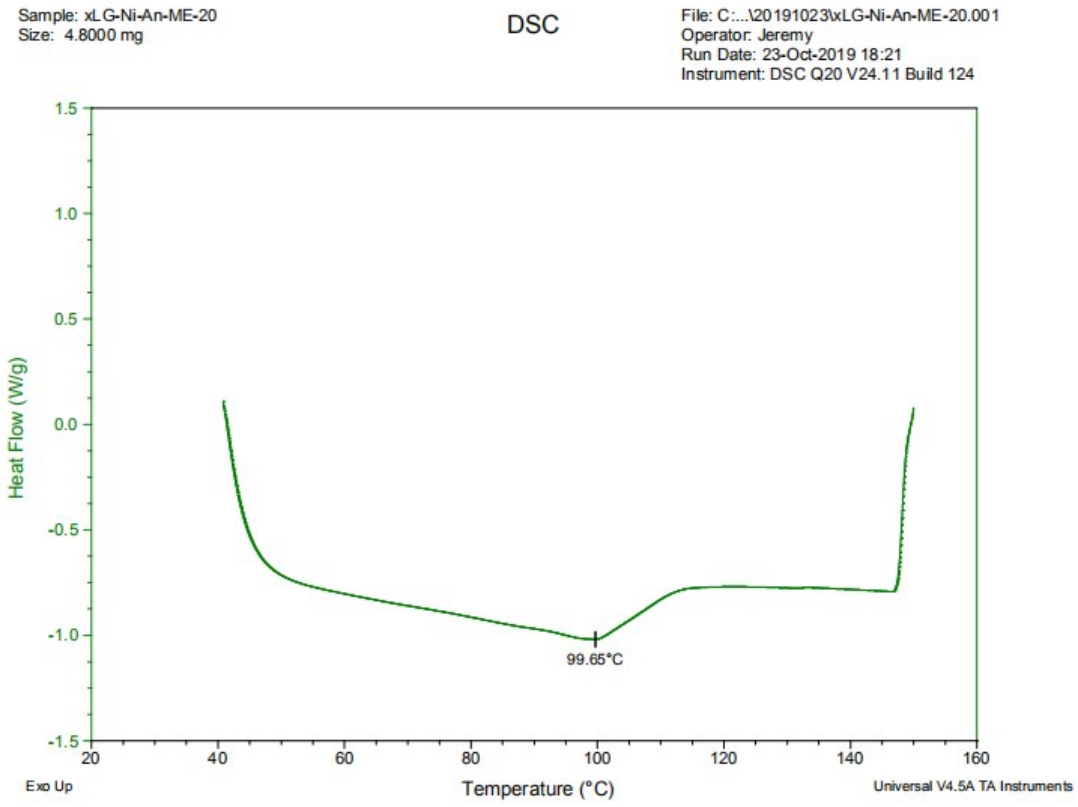


Figure S68. DSC of the polymer from table 1, entry 5.

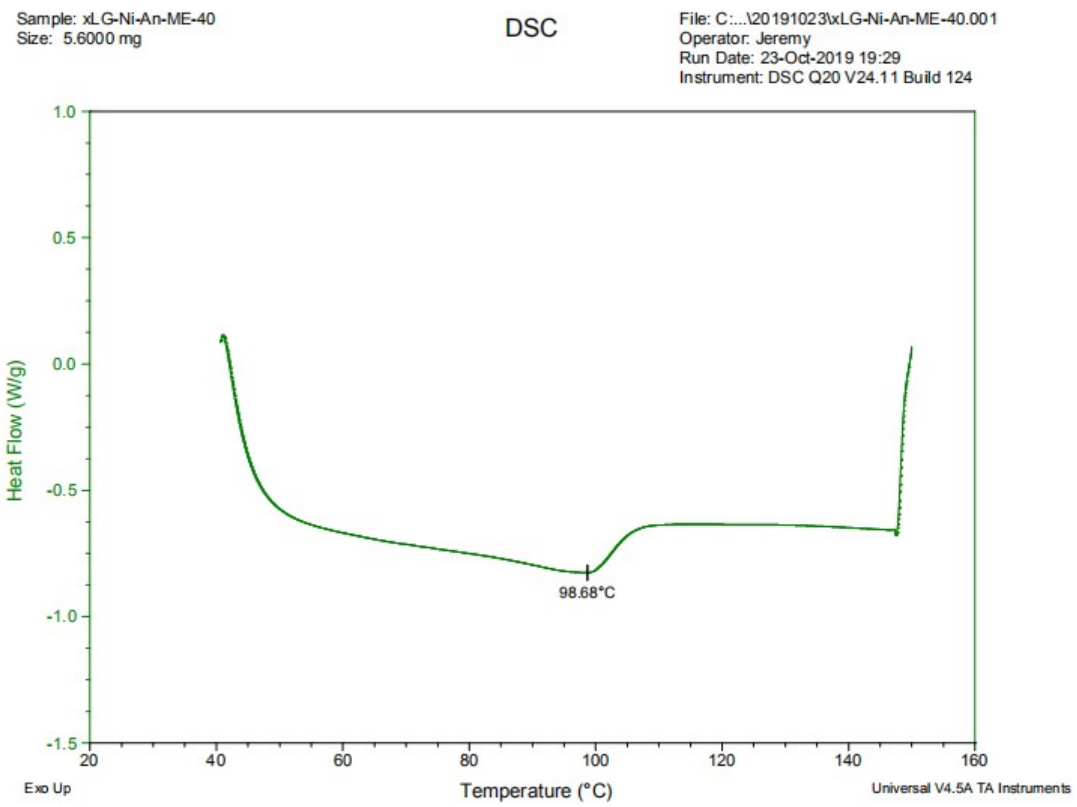


Figure S69. DSC of the polymer from table 1, entry 6.

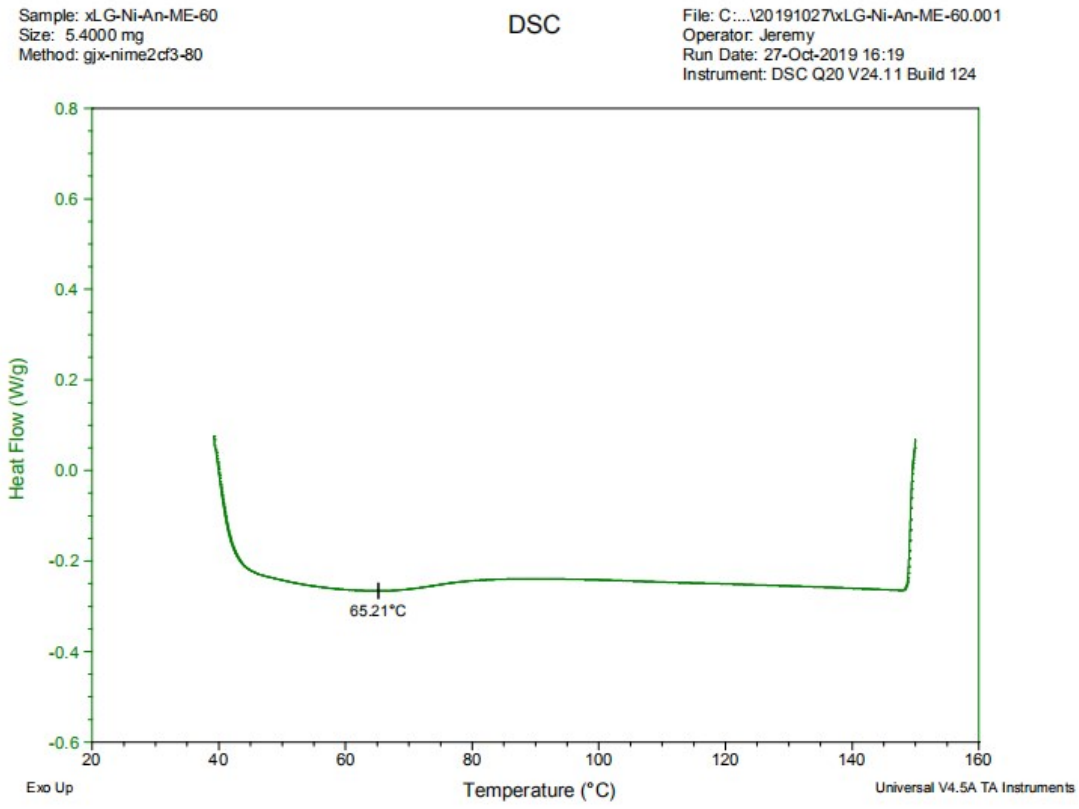


Figure S70. DSC of the polymer from table 1, entry 7.

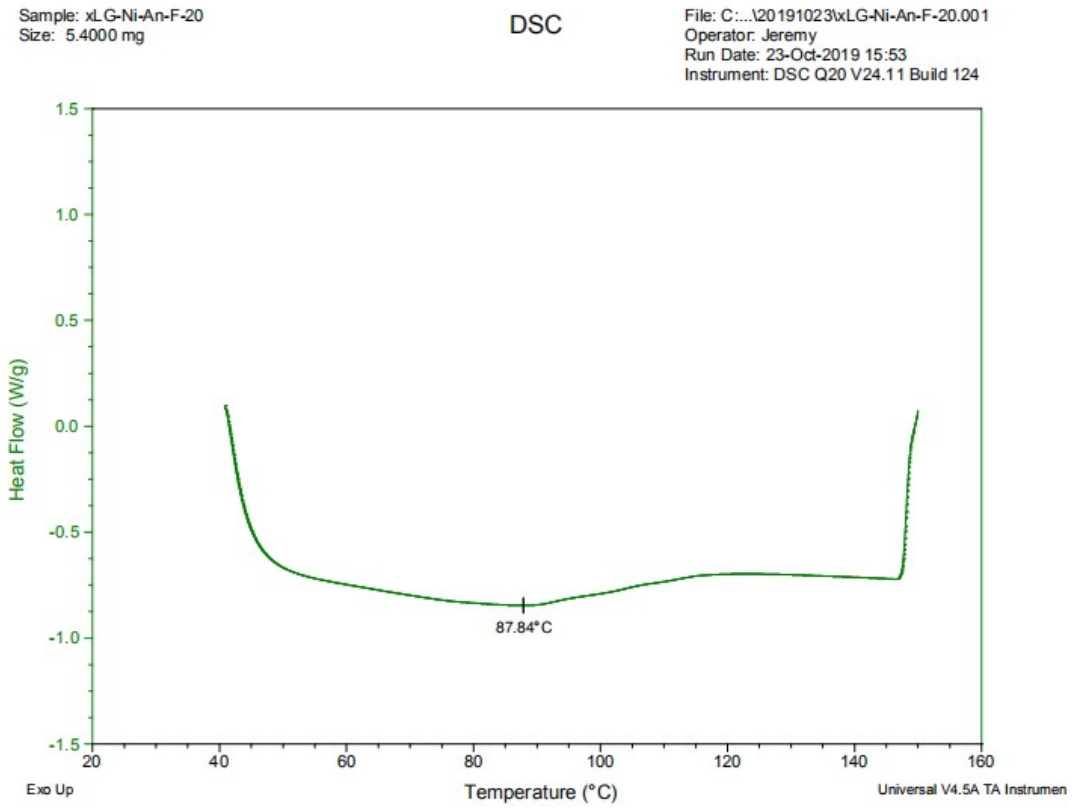


Figure S71. DSC of the polymer from table 1, entry 9.

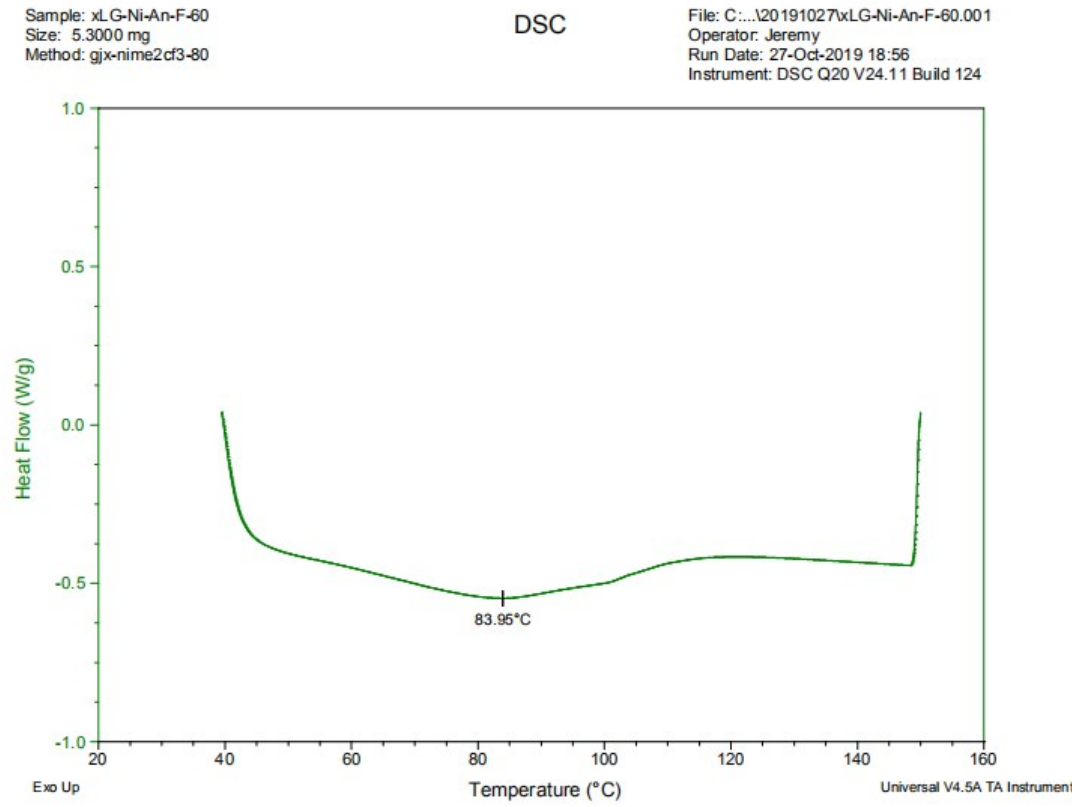


Figure S72. DSC of the polymer from table 1, entry 10.

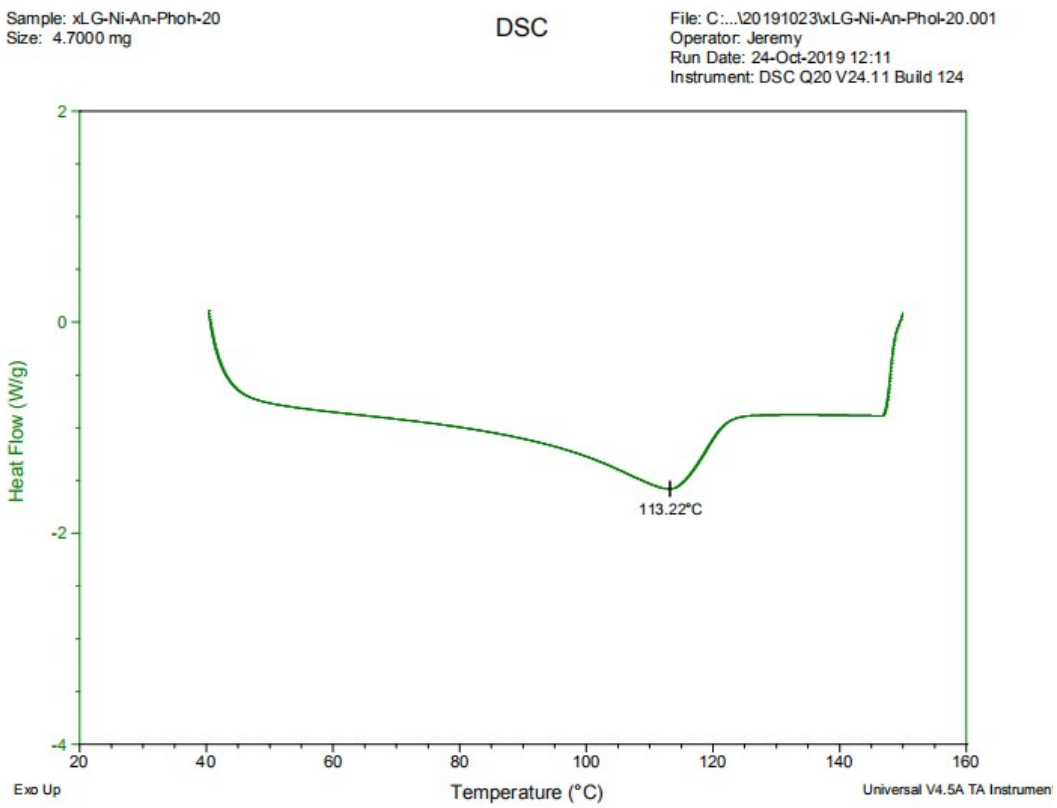


Figure S73. DSC of the polymer from table 1, entry 13.

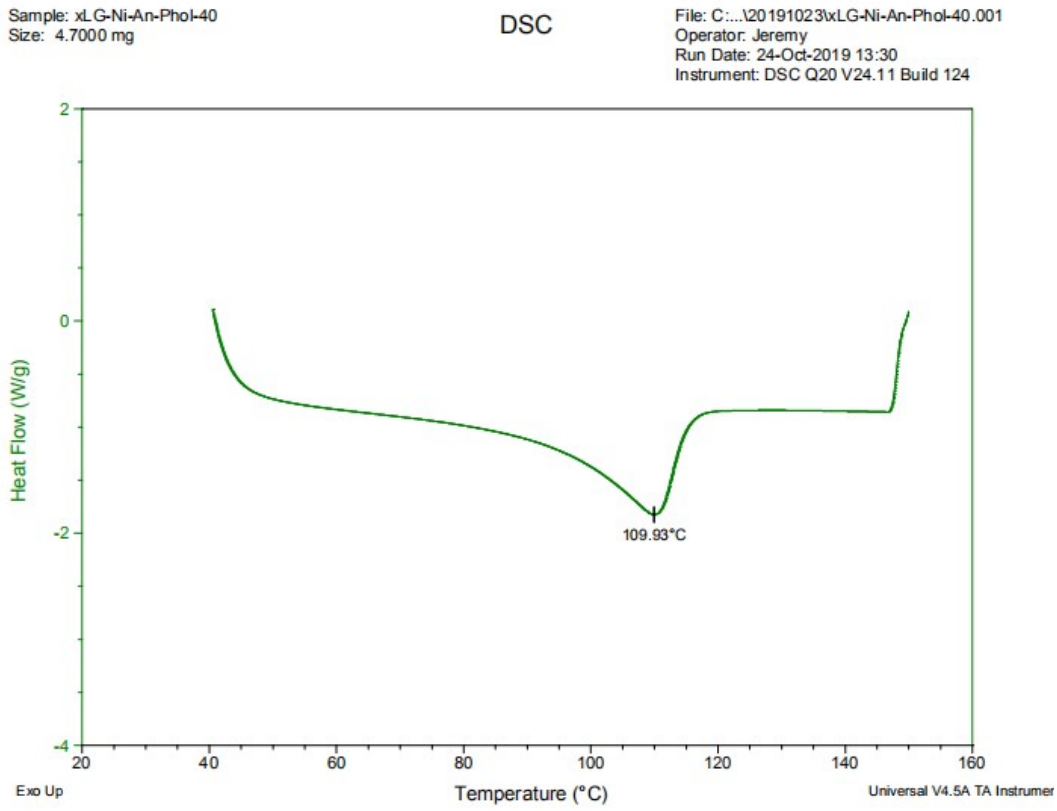


Figure S74. DSC of the polymer from table 1, entry 14.

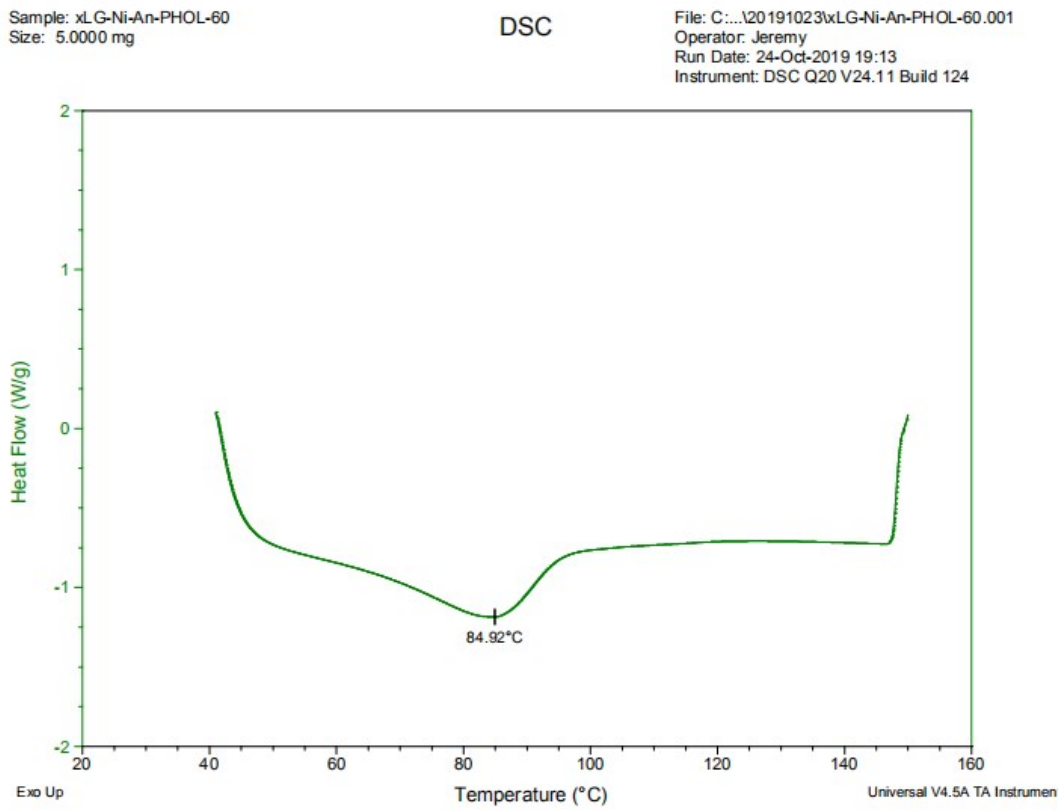


Figure S75. DSC of the polymer from table 1, entry 15.

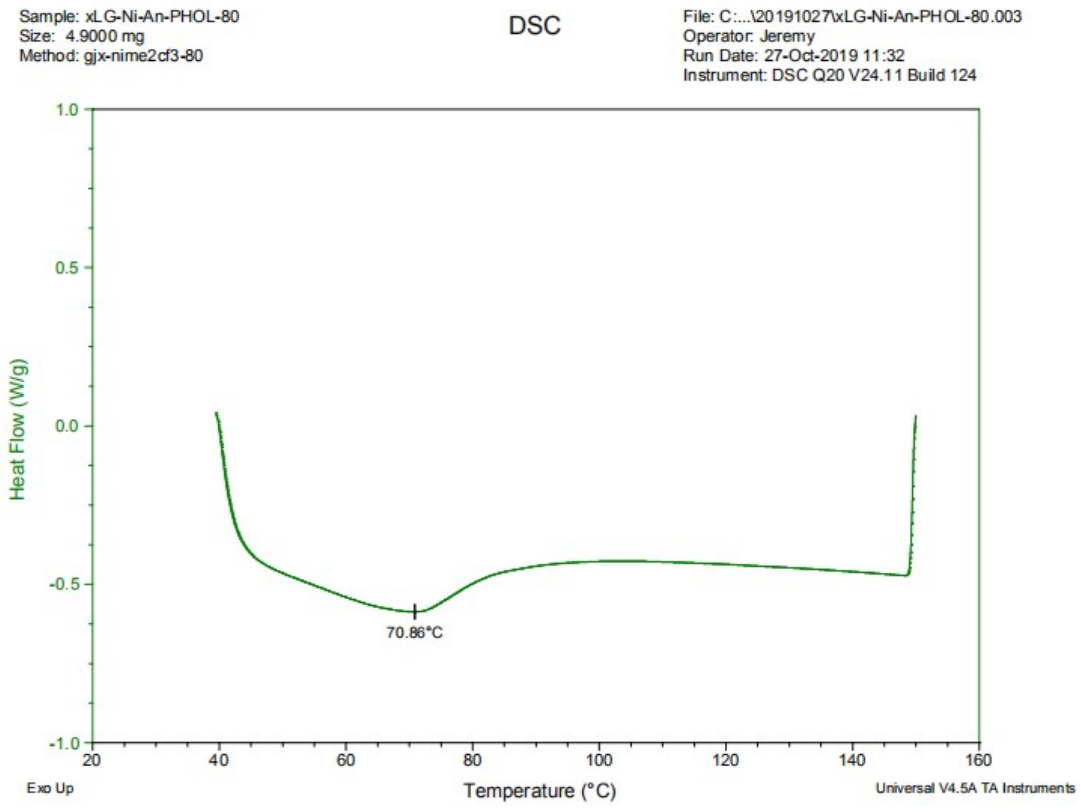


Figure S76. DSC of the polymer from table 1, entry 16.

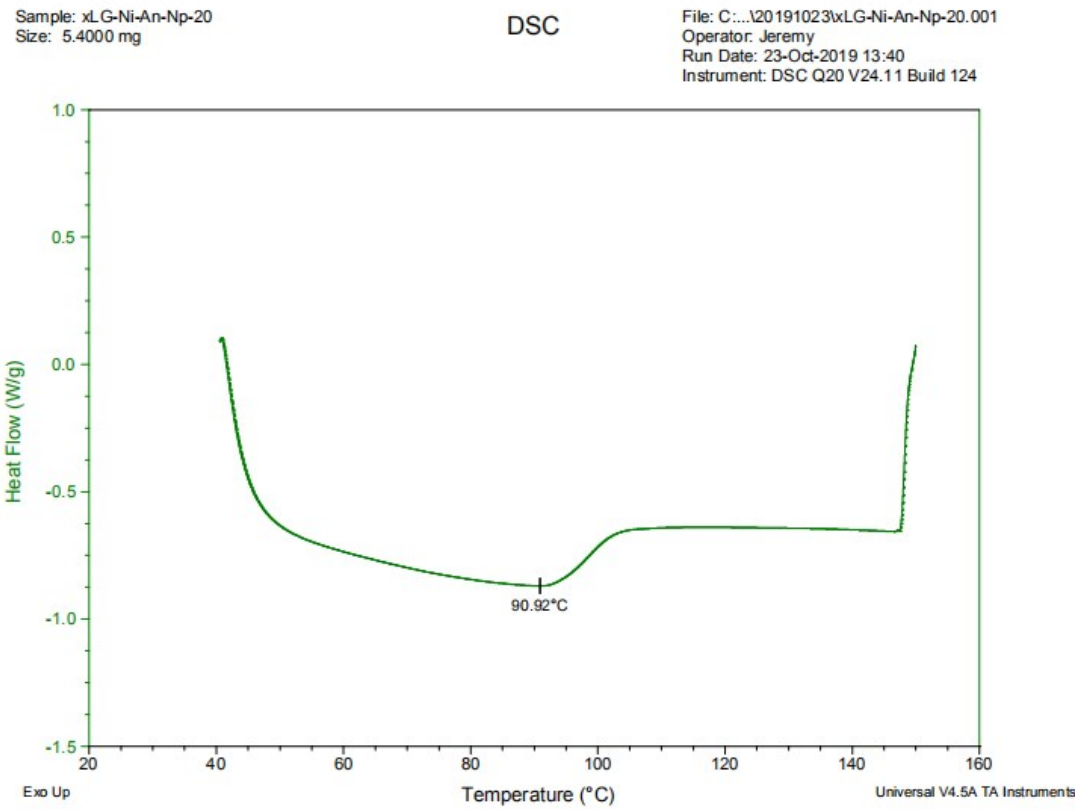


Figure S77. DSC of the polymer from table 1, entry 17.

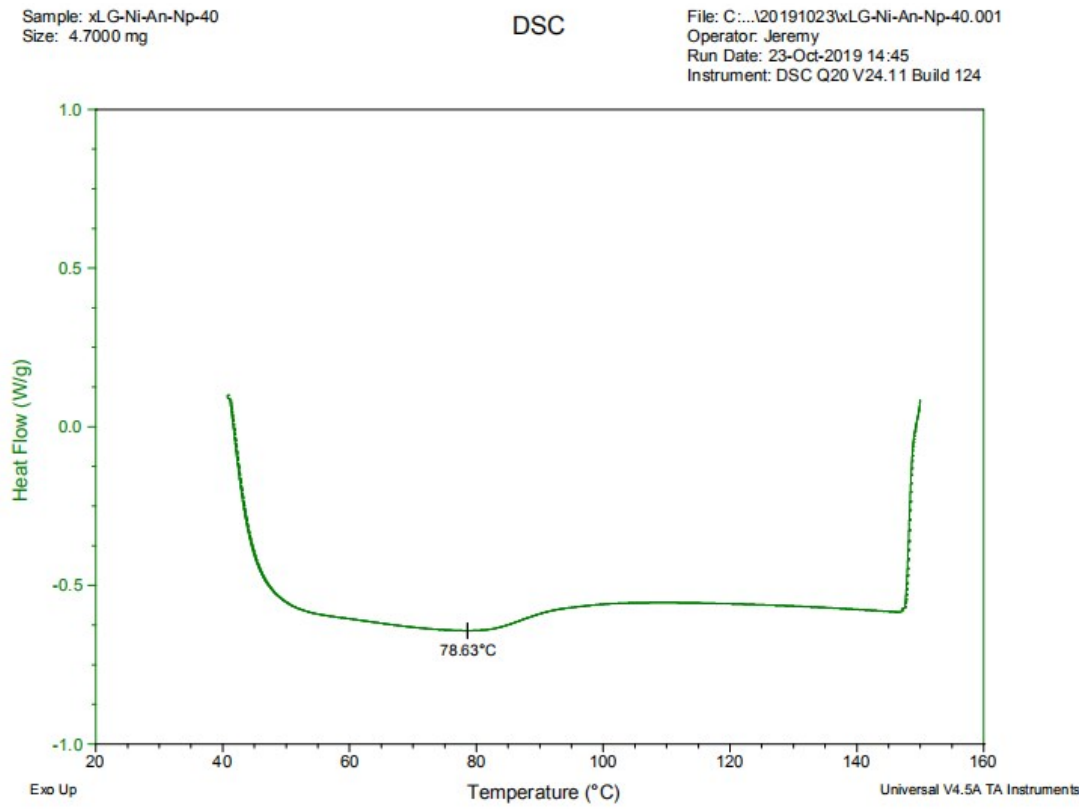
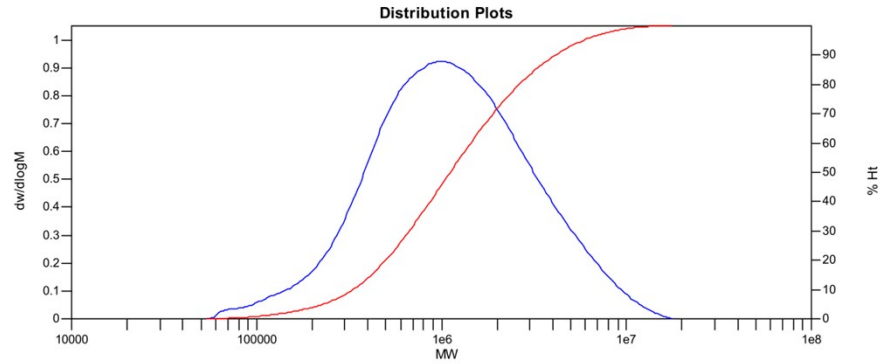


Figure S78. DSC of the polymer from table 1, entry 18.



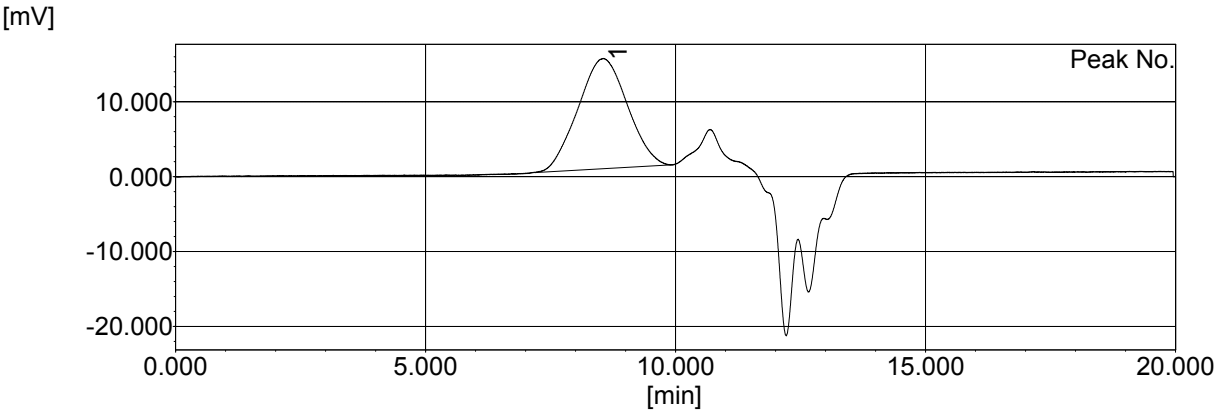
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	970027	686954	1771735	3903645	6463523	1541234	2.57912

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.30	12.13	14.05	-36.7364	100	3506.59	100

Figure S79. GPC of the polymer from table 1, entry 16.



Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	7.192	0.536		Mn	12,420
			117,871	Mw	19,346
Peak top	8.552	15.792	15,451	Mz	28,897
Peak end	9.937	1.587	1,951	Mz+1	39,946
				Mv	19,346
Height [mV]			14.735	Mp	15,451
Area [mV*sec]			1012.552	Mz/Mw	1.494
Area% [%]			100.000	Mw/Mn	1.558
[eta]			19345.92047	Mz+1/Mw	2.065

Figure S80. GPC of the polymer from table 1, entry 6.

4. References

1, Guo, L. H.; Kong, W. Y.; Xu, Y. J.; Yang, Y. L.; Ma, R.; Cong, L.; Dai, S. Y.; Liu, Z. Large-scale synthesis of novel sterically hindered acenaphthene-based α-diimine ligands and their application in coordination chemistry. *J. Organomet. Chem.* **2018**, *859*, 58-67.

2, Young, M. C.; Johnson, A. M.; Hooley, R. J. Self-promoted post-synthetic modification of metal–ligand M_2L_3 mesocates. *Chemical Communications* **2014**, *50*, 1378-1380.

3, Dai, S. Y.; Chen, C. L. Direct synthesis of functionalized high-molecular-weight polyethylene by copolymerization of ethylene with polar monomers. *Angew. Chem. Int. Ed.* **2016**, *55*, 13281-13285.

5. X-ray Crystallography

CCDC number of **Ni2**, **Ni5**, **Pd4** and **Pd5** are 2062231-2062234. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

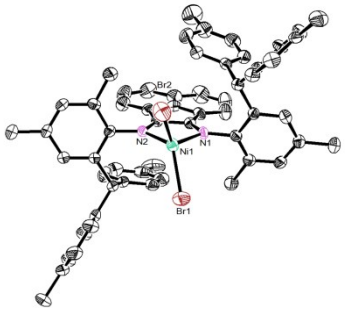


Table S2. Crystal data and structure refinement for Ni2.	
Identification code	**Ni2**
Empirical formula	C59.25 H54.50 Br2 Cl2.50 N2 Ni
Formula weight	1101.70
Temperature/K	298(2) K
Crystal system	Monoclinic
Space group	P2(1)/n
a/Å	15.1086(14)
b/Å	19.8115(17)
c/Å	19.2127(16)
α/°	90

β/°	93.602(2)
γ/°	90
Volume/Å^3	5739.5(9)
Z	4
ρ_{calc}g/cm^3	1.275
μ/mm^{-1}	1.883
F(000)	2258
Crystal size/mm^3	0.42 x 0.40 x 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.31 to 25.02
Index ranges	-17<=h<=17, -23<=k<=22, -22<=l<=12
Reflections collected	28553
Independent reflections	10081 [R(int) = 0.0781]
Data/restraints/parameters	10081 / 60 / 654
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R1 = 0.0697, wR2 = 0.2153
Final R indexes [all data]	R1 = 0.1506, wR2 = 0.2354
Largest diff. peak/hole / e Å^{-3}	1.005 and -0.462

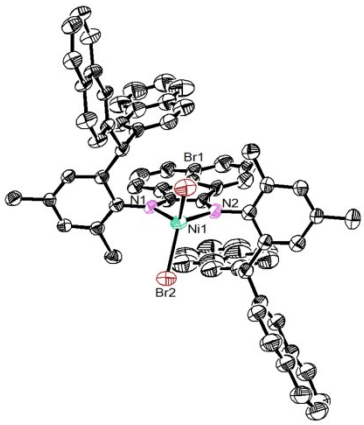


Table S3. Crystal data and structure refinement for Ni5.	
Identification code	**Ni5**
Empirical formula	C70 H52 Br2 N2 Ni
Formula weight	1139.67
Temperature/K	298(2) K
Crystal system	Triclinic
Space group	P-1
a/Å	17.6855(16)
b/Å	19.5147(18)

c/Å	21.7741(19)
α/°	66.1380(10)
β/°	87.031(3)
γ/°	70.111(2)
Volume/Å^3	6430.3(10)
Z	4
ρ_{calc}g/cm^3	1.177
μ/mm^{-1}	1.583
F(000)	2336
Crystal size/mm^3	0.20 x 0.17 x 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.15 to 25.02
Index ranges	-21<=h<=19, -20<=k<=23, -24<=l<=25
Reflections collected	33040
Independent reflections	22376 [R(int) = 0.0997]
Data/restraints/parameters	22376 / 0 / 1359
Goodness-of-fit on F^2	1.165
Final R indexes [I>=2σ (I)]	R1 = 0.1169, wR2 = 0.2321
Final R indexes [all data]	R1 = 0.2212, wR2 = 0.2475
Largest diff. peak/hole / e Å^{-3}	0.697 and -0.566

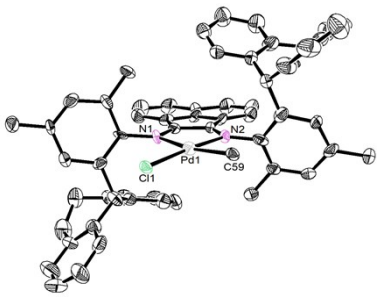


Table S4. Crystal data and structure refinement for Pd4.	
Identification code	**Pd4**
Empirical formula	C59 H51 Cl N2 Pd
Formula weight	929.87
Temperature/K	293(2) K
Crystal system	Monoclinic
Space group	P 21/c
a/Å	15.8600(16)
b/Å	16.3701(17)
c/Å	18.8102(19)
α/°	90

β/°	106.030(4)
γ/°	90
Volume/Å^3	4693.8(8)
Z	4
ρ_{calc}g/cm^3	1.316
μ/mm^{-1}	0.493
F(000)	1928
Crystal size/mm^3	0.170 x 0.080 x 0.030
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.825 to 25.020
Index ranges	-18<=h<=18, 0<=k<=19, 0<=l<=22
Reflections collected	8226
Independent reflections	8226 [R(int) = ?]
Data/restraints/parameters	8226 / 14 / 576
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R1 = 0.1034, wR2 = 0.1724
Final R indexes [all data]	R1 = 0.2442, wR2 = 0.2036
Largest diff. peak/hole / e Å^{-3}	0.895 and -1.412

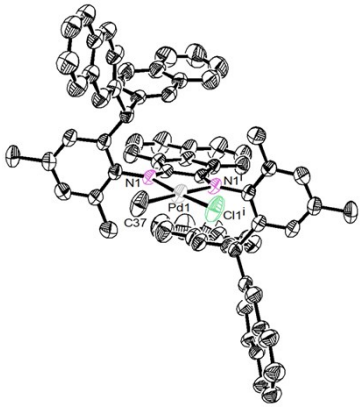


Table S5. Crystal data and structure refinement for Pd5.	
Identification code	**Pd5**
Empirical formula	C71 H53 Cl N2 Pd
Formula weight	1076.00
Temperature/K	298(2) K
Crystal system	Monoclinic
Space group	C2/c
a/Å	12.9760(11)
b/Å	19.5971(17)
c/Å	23.930(2)

α/°	90
β/°	96.867(2)
γ/°	90
Volume/Å^3	6041.6(9)
Z	4
ρ_{calc}g/cm^3	1.183
μ/mm^{-1}	0.392
F(000)	2224
Crystal size/mm^3	0.32 x 0.20 x 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.25 to 25.02
Index ranges	-15<=h<=15, -23<=k<=23, -15<=l<=28
Reflections collected	15259
Independent reflections	5317 [R(int) = 0.0890]
Data/restraints/parameters	5317 / 246 / 371
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R1 = 0.0674, wR2 = 0.1670
Final R indexes [all data]	R1 = 0.1074, wR2 = 0.1812
Largest diff. peak/hole / e Å^{-3}	0.555 and -0.927