Rigid-Flexible Double-Layer Steric Strategy Promoting Ethylene Polymerization and Copolymerization in Alkane Solvents

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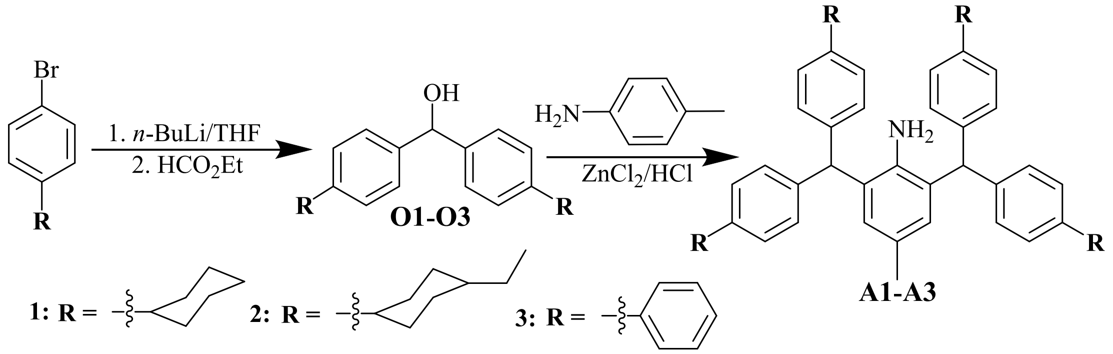
1. Experimental Sections

1.1 General Considerations

The chemicals (1-bromo-4-cyclohexylbenzene, 1-bromo-4-((1r, 4r)-4-ethylcyclohexyl)benzene, 4-bromobiphenyl, n-butyllithium, ethyl formate, benzhydrol, 2, 3-butanedione, p-TSA, (COD)PdMeCl and (DME)NiBr$_2$) including deuterated solvent (CDCl$_3$, C$_6$D$_6$, C$_7$D$_8$) were purchased from the company of Energy Chemical, except those synthetic compounds. The controlled substances like hydrochloric acid, toluene and diethyl ether were purchased from the company of Sinopharm Chemical Reagent Co.. And other common solvents (dichoromethane, hexanes and prtroleum ether) were purchased from the company of Yong Da Chemical. All those agents could be directly used.

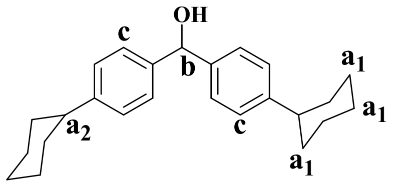
All experiments were carried out under dry nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded by a JEOL 400M or 600M spectrometer at ambient temperature unless otherwise stated. The chemical shifts of ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Mass spectra and elemental analysis were performed by the Analytical Center of the Anhui University. X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K$^\alpha$ radiation (λ = 0.71073 Å). Molecular weight and molecular weight distribution of the polymers were determined by size exclusion chromatography (SEC) with a PL 210 equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 150^{o}C using trichlorobenzene as a solvent and calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was performed by a DSC Q25 from TA Instruments. Samples were quickly heated to 150°C and kept for 5 min to remove thermal history, then cooled to -50°C at a rate of 10 K/min, and finally reheated to 150°C at the same rate under a nitrogen flow (50 mL/min). The maximum points endotherm (heating scan) were taken as the melting temperature (T_m). Stress/strain experiments were performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature. Polymers were melt-pressed at 150 °C to obtain the test specimens, which have 12-mm gauge length, 2-mm width, and thickness of 0.5 mm. At least three specimens of each polymer were tested.

1.2 Procedure for the Synthesis of O1-O3 and A1-A3

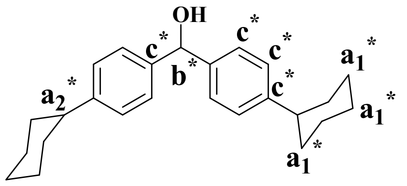


To a dried 500 mL Schlenk-flask was added 4-substituted bromobenzene (40 mmol) and anhydrous THF (100 mL) under nitrogenatmosphere. The solution was cooled to −78 °C and *n*-BuLi (2.5 mol/L, 20 mL) was added dropwise over 10 min. After stirring for 1 hour at −78 °C, ethyl formate (1.48 g, 20 mmol) was added dropwise to the mixture. The mixture was slowly warmed to room temperature and stirred for 3 hours. The reaction was quenched by addition of saturated ammonium chloride solution and extracted with dichloromethane. The organic phase was dried by anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to providecrude product. The crude product was purified by recrystallization from dichloromethane and petroleum ether, and then dried under vacuum to give diarylmethanol as a white solid.

A mixture of diarylmethanol (10 mmol) and *p*-toluidine (5 mmol) was heated to 120 °C. A solution of anhydrous zinc chloride (2.8 mmol) in concentrated hydrochloric acid (0.5 mL) 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 dichloromethane (200 mL). The dichloromethane layer was washed with water (3 × 100 mL) and dried over anhydrous magnesium sulfate. After filtered, the solution was concentrated to 20 mL. The crude diarylmethylaniline was purified by recrystallization from dichloromethane and EtOH, and then dried under vacuum to give a white solid.

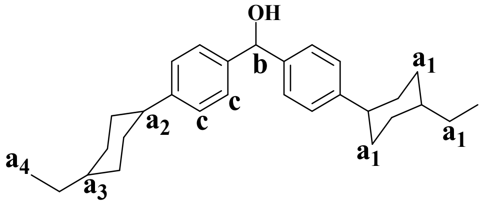


^{1}H NMR

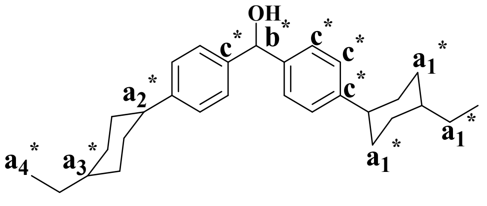


^{13}C NMR

O1 (5.49 g, 79%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 7.31 (d, *J* = 8.0 Hz, 4H, c, Ar-*H*), 7.19 (d, *J* = 8.0 Hz, 4H, c, Ar-*H*), 5.79 (s, 1H, b, C*H*Ar_2), 2.50 (t, *J* = 9.2 Hz, 2H, a_2, Ar-C*H*), 2.22 (s, 1H, O*H*), 1.90 – 1.83 (m, 8H, a_1, CH_2), 1.76 (d, *J* = 12.7 Hz, 2H, a_1, CH_2), 1.45 – 1.36 (m, 8H, a_1, CH_2), 1.30 – 1.24 (m, 2H, a_1, CH_2). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.4, 141.5, 127.0, 126.6, 76.2 (*C*HAr_2, b^*), 44.4 (Ar-*C*H, a_2^*), 34.6 (*C*H_2, a_1^*), 27.0 (*C*H_2, a_1^*), 26.3 (*C*H_2, a_1^*).

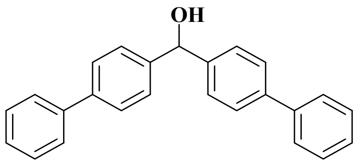


^{1}H NMR

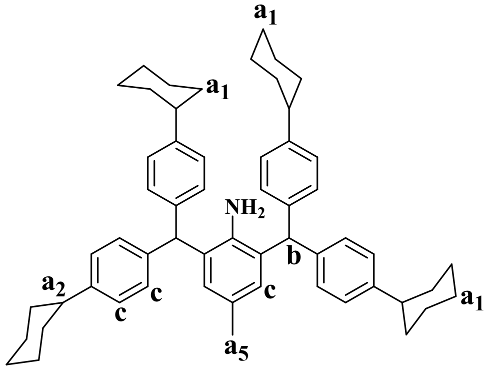


^{13}C NMR

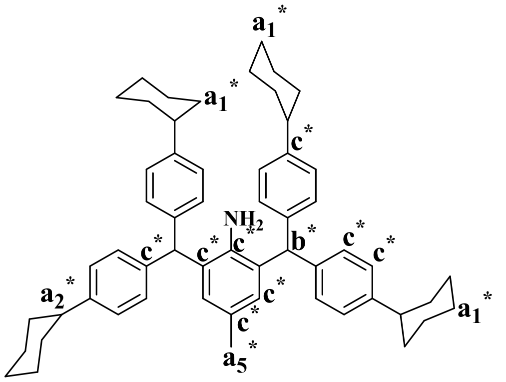
O2 (6.04 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.30 (t, *J* = 6.6 Hz, 4H, c, Ar-*H*), 7.19 (d, *J* = 8.1 Hz, 4H, c, Ar-*H*), 5.79 (s, 1H, b, C*H*Ar_2), 2.50 – 2.42 (m, 2H, a_2, Ar-C*H*), 2.20 (s, 1H, O*H*), 1.89 (d, *J* = 11.3 Hz, 8H, a_1, CH_2), 1.50 – 1.40 (m, 4H, a_1, CH_2), 1.28 (t, *J* = 7.2 Hz, 4H, a_1, CH_2), 1.24 – 1.14 (m, 2H, a_3, C*H*), 1.12 – 1.01 (m, 4H, a_1, CH_2), 0.94, 0.92, 0.91 (s, s, s, 6H, a_4, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 141.4, 126.9, 126.5, 76.1 (*C*HAr_2, b^*), 44.3 (Ar-*C*H, a_2^*), 39.1 (*C*H, a_3^*), 34.3 (*C*H_2, a_1^*), 33.2 (*C*H_2, a_1^*), 30.0 (*C*H_2, a_1^*), 11.6 (*C*H_3, a_4^*).



O3 (4.38 g, 65%). **O3** were prepared in the manner reported in the literature.[1]

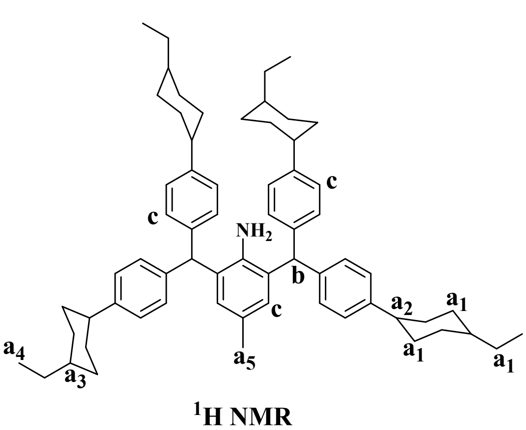


^{1}H NMR

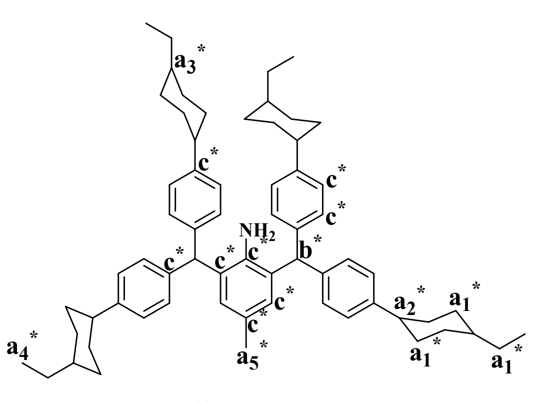


^{13}C NMR

A1 (5.04 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.09 (d, *J* = 8.0 Hz, 8H, c, Ar-*H*), 6.99 (d, *J* = 8.0 Hz, 8H, c, Ar-*H*), 6.39 (s, 2H, c, Ar-*H*), 5.37 (s, 2H, b, C*H*Ar$_2$), 3.28 (s, 2H, N*H*$_2$), 2.46 (s, 4H, a$_2$, Ar-C*H*), 2.03 (s, 3H, a$_5$, Ar-C*H*$_3$), 1.90 – 1.81 (m, 16H, a$_1$, C*H*$_2$), 1.74 (d, *J* = 12.3 Hz, 4H, a$_1$, CH$_2$), 1.47 – 1.34 (m, 16H, a$_1$, C*H*$_2$), 1.30 – 1.21 (m, 4H, a$_1$, C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 140.2, 139.7, 129.8, 129.3, 128.8, 126.7, 126.5, 51.7 (*C*HAr$_2$, b*), 44.1 (Ar-*C*H, a$_2^*$), 34.5 (*C*H$_2$, a$_1^*$), 27.0 (*C*H$_2$, a$_1^*$), 26.2 (*C*H$_2$, a$_1^*$), 21.1 (Ar-*C*H$_3$, a$_5^*$). ESI-MS (m/z): calcd for $C_{57}H_{70}N^+$: 768.5503, Found, 768.5532, [M+H]$^+$.

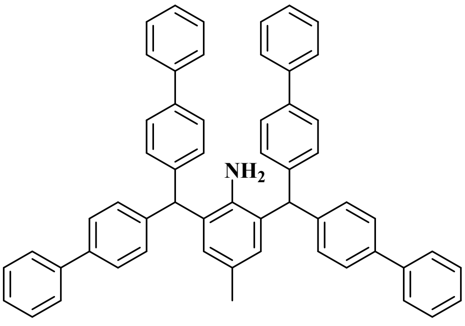


^{1}H NMR



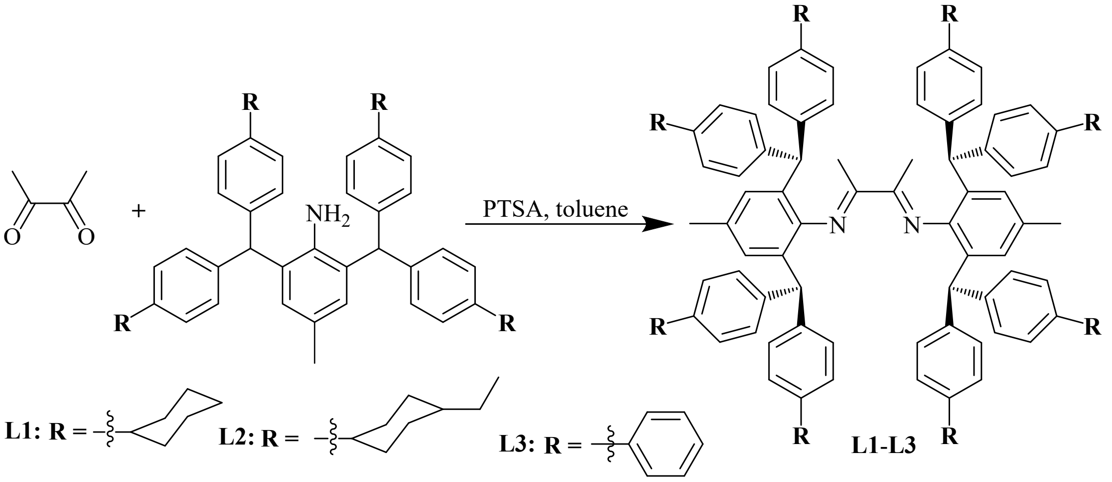
^{13}C NMR

A2 (6.47 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.11 (d, *J* = 8.0 Hz, 8H, c, Ar-*H*), 7.00 (d, *J* = 7.9 Hz, 8H, c, Ar-*H*), 6.41 (s, 2H, c, Ar-*H*), 5.38 (s, 2H, b, C*H*Ar$_2$), 3.28 (s, 2H, N*H*$_2$), 2.45 (t, *J* = 12.1 Hz, 4H, a$_2$, Ar-C*H*), 2.04 (s, 3H, a$_5$, Ar-C*H*$_3$), 1.97 – 1.82 (m, 16H, a$_1$, C*H*$_2$), 1.44 (dt, *J* = 22.6, 11.4 Hz, 8H, a$_1$, C*H*$_2$), 1.27 (dd, *J* = 14.0, 6.9 Hz, 8H, a$_1$, C*H*$_2$), 1.21 (d, *J* = 6.1 Hz, 4H, a$_3$, C*H*), 1.10 – 1.00 (m, 8H, a$_1$, C*H*$_2$), 0.93 (t, *J* = 7.3 Hz, 12H, a$_4$, C*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 145.8, 140.3, 139.72, 129.8, 129.3, 128.8, 126.8, 126.5, 51.7 (*C*HAr$_2$, b*), 44.2 (Ar-*C*H, a$_2^*$), 39.1 (*C*H, a$_3^*$), 34.4 (*C*H$_2$, a$_1^*$), 34.3 (*C*H$_2$, a$_1^*$), 33.3 (*C*H$_2$, a$_1^*$), 30.0 (*C*H$_2$, a$_1^*$), 21.1 (Ar-*C*H$_3$, a$_5^*$), 11.6 (*C*H$_3$, a$_4^*$). ESI-MS (m/z): calcd for $C_{65}H_{86}N^+$: 880.6755, Found, 880.6770, [M+H]$^+$.



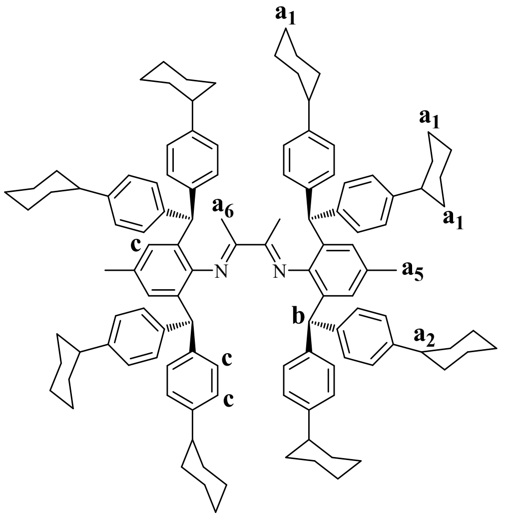
A3 (4.02 g, 54%). **A3** was prepared in the manner reported in the literature.[1]

1.3 Procedure for the Synthesis of L1-L3

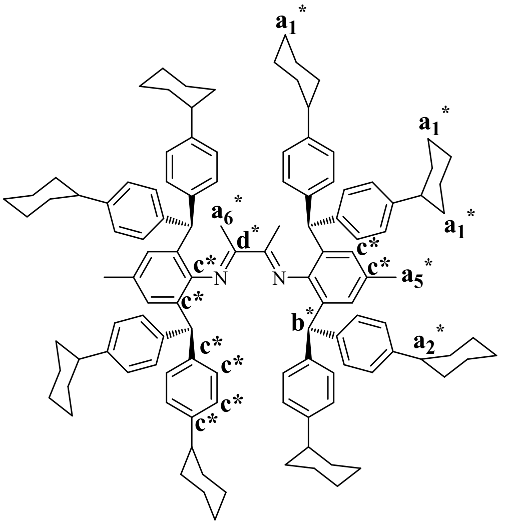


A solution of arylamine (2 mmol), 2, 3-butadione (1 mmol) and *p*-toluenesulfonic acid (10 mg) in toluene (20 mL) was stirred at 120 °C, until there was one main point on the TLC plate. The solvent was partially evaporated under reduced pressure until the formation of a light yellow solid. The remaining solution was diluted in ethanol

(30 mL). The yellow solid was isolated by filtration, dried by vacuum.

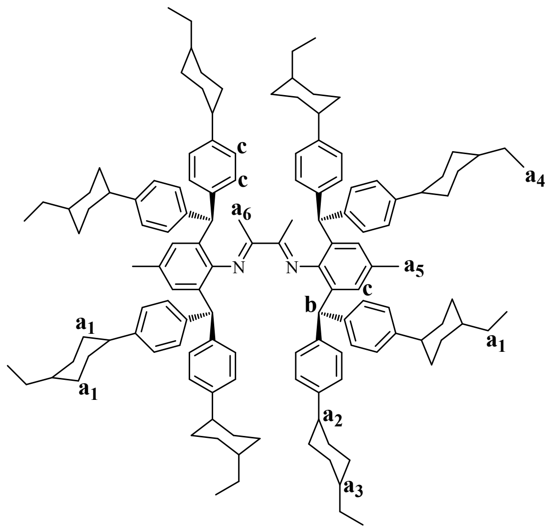


^{1}H NMR

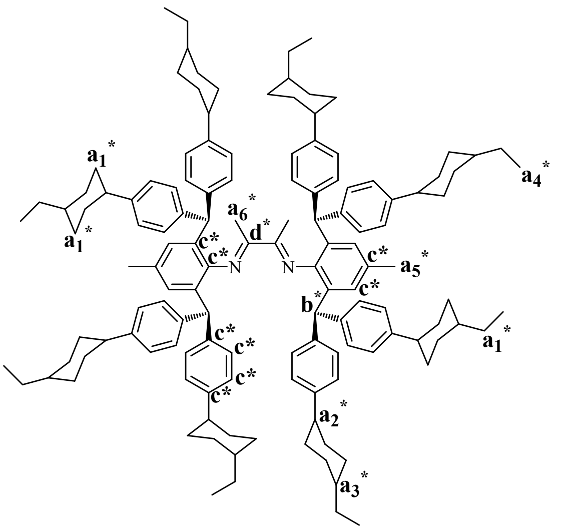


^{13}C NMR

L1 (1.21 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.03 (d, *J* = 8.0 Hz, 8H, c, Ar-*H*), 6.96 (t, *J* = 7.9 Hz, 16H, c, Ar-*H*), 6.91 (d, *J* = 8.1 Hz, 8H, c, Ar-*H*), 6.71 (s, 4H, c, Ar-*H*), 5.10 (s, 4H, b, C*H*Ar$_2$), 2.43 (s, 8H, a$_2$, Ar-C*H*), 2.17 (s, 6H, a$_5$, Ar-C*H*$_3$), 1.78 (d, *J* = 37.1 Hz, 40H, a$_1$, C*H*$_2$), 1.43 – 1.26 (m, 40H, a$_1$, C*H*$_2$), 1.16 (s, 6H, a$_6$, C(C*H*$_3$)=N). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7 (*C*=N, d*), 145.7, 145.6, 145.4, 141.2, 140.6, 131.4, 131.3, 129.6, 129.2, 128.6, 126.6, 126.4, 50.8 (*C*HAr$_2$, b*), 44.1 (Ar-*C*H, a$_2$*), 44.0 (Ar-*C*H, a$_2$*), 34.5 (*C*H$_2$, a$_1$*), 34.5 (*C*H$_2$, a$_1$*), 34.4 (*C*H$_2$, a$_1$*), 27.0 (*C*H$_2$, a$_1$*), 26.9 (*C*H$_2$, a$_1$*), 26.3 (*C*H$_2$, a$_1$*), 26.2 (*C*H$_2$, a$_1$*), 21.3 (Ar-*C*H$_3$, a$_5$*), 16.5 (C(*C*H$_3$)=N, a$_6$*). ESI-MS (m/z): calcd for $C_{118}H_{141}N_2^+$: 1587.1123, Found, 1587.1163, $[M+H]^+$.

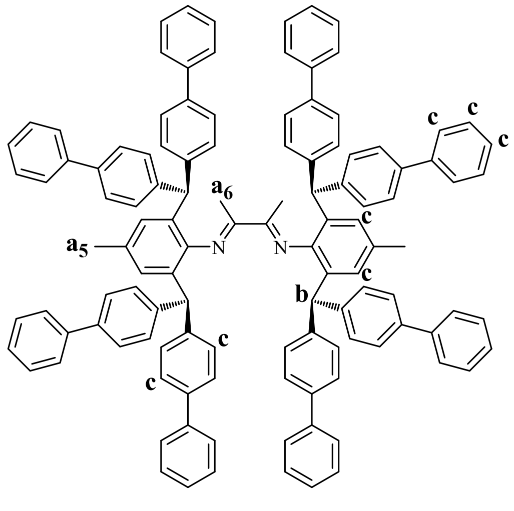


^{1}H NMR

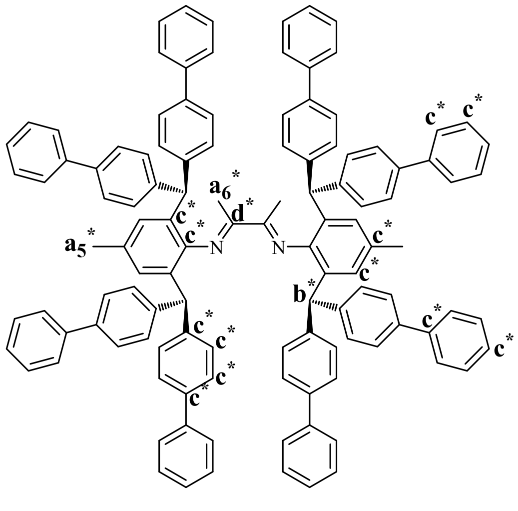


^{13}C NMR

L2 (0.98 g, 54%). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 7.04 (d, J = 8.1 Hz, 8H, c, Ar-H), 6.97 (t, J = 8.2 Hz, 16H, c, Ar-H), 6.92 (d, J = 8.2 Hz, 8H, c, Ar-H), 6.73 (s, 4H, c, Ar-H), 5.11 (s, 4H, b, CHAr$_2$), 2.40 (td, J = 12.0, 2.7 Hz, 8H, a$_2$, Ar-CH), 2.17 (s, 6H, a$_5$, Ar-CH_3), 1.94 – 1.78 (m, 32H, a$_1$, CH_2), 1.44 – 1.34 (m, 16H, a$_1$, CH_2), 1.27 (dd, J = 12.5, 6.9 Hz, 16H, a$_1$, CH_2), 1.12 (s, 6H, a$_6$, C(CH_3)=N), 1.22 – 1.15 (m, 8H, a$_3$, CH), 1.08 – 0.98 (m, 16H, a$_1$, CH_2), 0.92 (td, J = 7.3, 3.2 Hz, 24H, a$_4$, CH_3). ^{13}C NMR (101 MHz, CDCl$_3$) δ 169.7 (C=N, d*), 145.6, 145.5, 145.2, 141.3, 140.6, 131.5, 131.2, 129.5, 129.2, 128.6, 126.6, 126.4, 50.8 (CHAr$_2$, b*), 44.1 (Ar-CH, a$_2^*$), 44.1 (Ar-CH, a$_2^*$), 39.2 (CH, a$_3^*$), 39.1 (CH, a$_3^*$), 34.4 (CH$_2$, a$_1^*$), 34.3 (CH$_2$, a$_1^*$), 33.3 (CH$_2$, a$_1^*$), 33.2 (CH$_2$, a$_1^*$), 30.1 (CH$_2$, a$_1^*$), 21.4 (Ar-CH$_3$, a$_5^*$), 16.5 (C(CH$_3$)=N, a$_6^*$), 11.6 (CH$_3$, a$_4^*$), 11.5 (CH$_3$, a$_4^*$). This compound cannot be effectively determined in high-resolution mass spectrometry tests due to its low solubility.



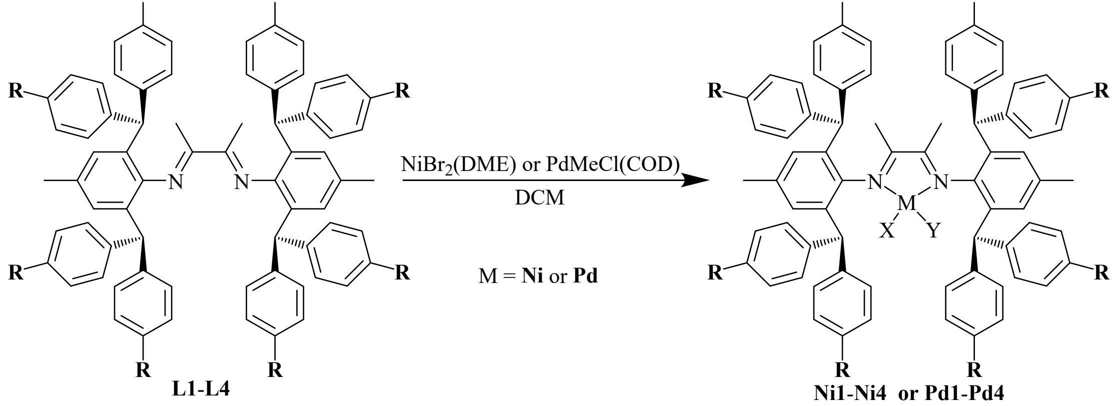
^{1}H NMR



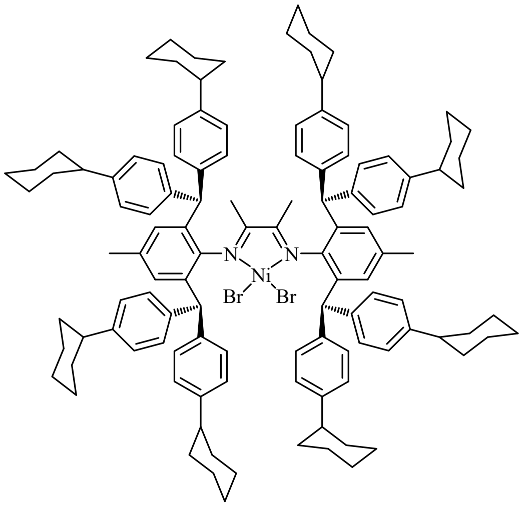
^{13}C NMR

L3 (0.64 g, 42%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.53 (d, J = 1.5 Hz, 8H, c, Ar-H), 7.51 (s, 8H, c, Ar-H), 7.42 – 7.27 (m, 40H, c, Ar-H), 7.21 (s, 4H, c, Ar-H), 7.19 (s, 4H, c, Ar-H), 7.11 (s, 4H, c, Ar-H), 7.09 (s, 4H, c, Ar-H), 6.82 (s, 4H, c, Ar-H), 5.32 (s, 4H, b, CHAr$_2$), 2.23 (s, 6H, a_5, Ar-CH_3), 1.41 (s, 6H, a_6, C(CH_3)=N). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (C=N, d*), 145.6, 142.7, 142.1, 140.8, 140.5, 139.1, 138.8, 132.2, 130.9, 130.1, 129.8, 129.0, 128.8, 128.7, 127.2, 127.0, 126.9, 126.8, 51.0 (CHAr$_2$, b*), 21.4 (Ar-CH$_3$, a_5^*), 17.1 (C(CH$_3$)=N, a_6^*). ESI-MS (m/z): calcd for $C_{118}H_{93}N_2^+$: 1538.7367, Found, 1538.7410, $[M+H]^+$.

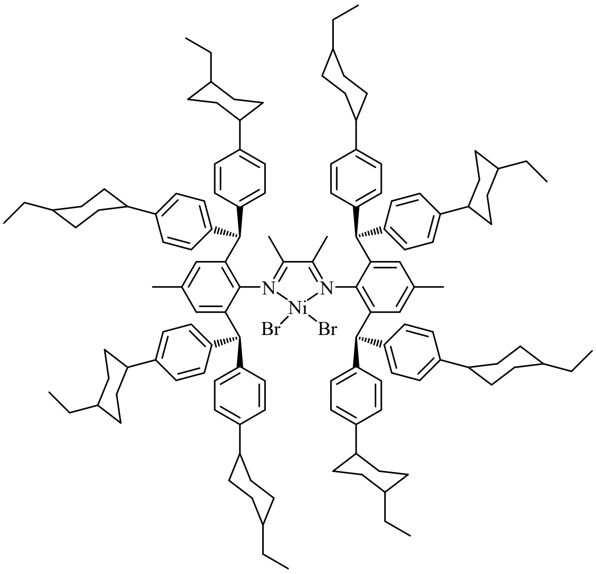
1.4 Procedure for the Synthesis of Ni1-Ni4 and Pd1-Pd4



A mixture of the ligand (0.5 mmol), Pd(COD)MeCl (133 mg, 0.5 mmol) in CH_2Cl_2 (10 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 with CH_2Cl_2/hexane (1:1). The pure compound was obtained as an orange or red solid. The nickel complexes were prepared in a similar manner by the reaction of 0.2 mmol ligands with 1 equivalent $NiBr_2$(DME) in dichloromethane. After stirring 2 days, the solvent was removed, and the brown solid powder was washed with ether (2 mL × 2) and dried under vacuum to give the corresponding nickel complexes.

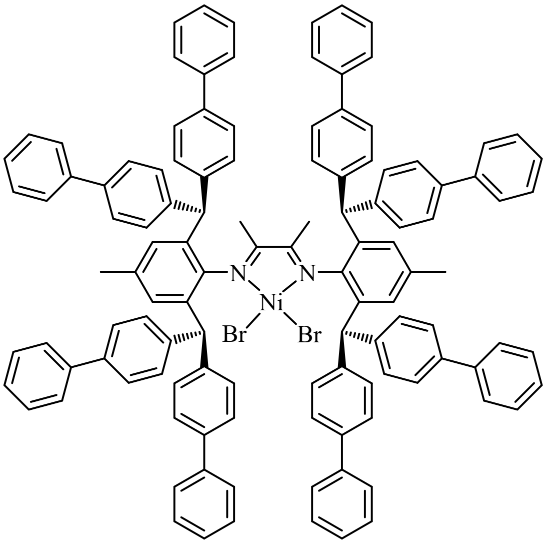


Ni1 (0.26 g, 72%). MALDI-MS (m/z): calcd for $C_{118}H_{140}BrN_2Ni^+$: 1723.95, Found, 1723.97, $[M-Br]^+$. Elemental analysis: calc. for $C_{118}H_{140}Br_2N_2Ni$: C, 78.52; H, 7.82; N, 1.55. Found:C, 78.64; H, 7.94; N, 1.61.

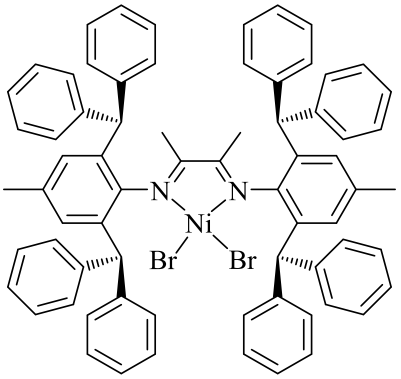


Ni2 (0.28 g, 68%). MALDI-MS (m/z): calcd for $C_{134}H_{172}BrN_2Ni^+$: 1948.20, Found, 1948.22, $[M-Br]^+$. Elemental analysis: calc. for $C_{134}H_{172}Br_2N_2Ni$: C, 79.21; H, 8.54; N,

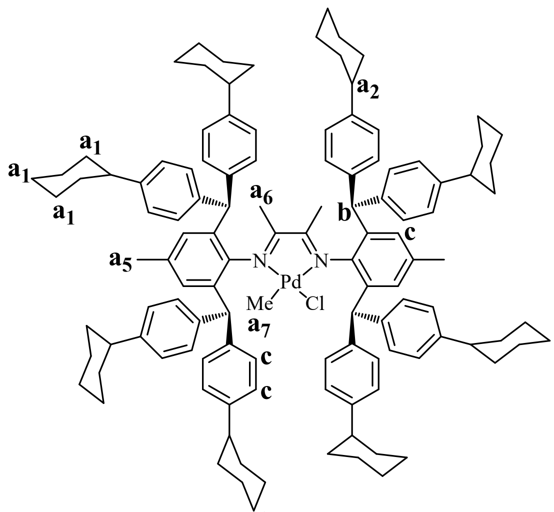
1.38. Found:C, 79.11; H, 8.61; N, 1.42.



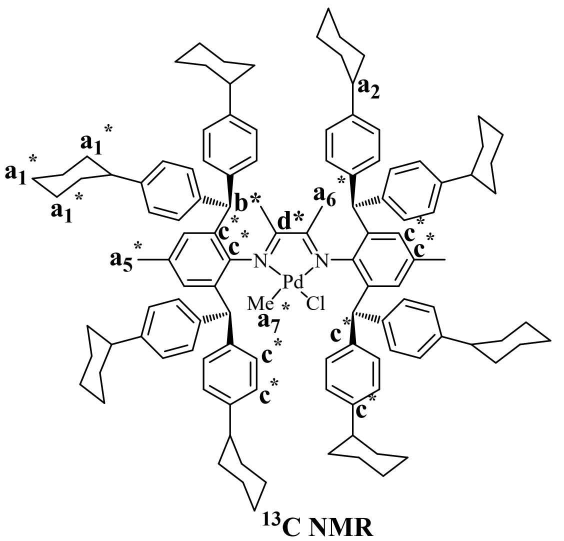
Ni3 (0.18 g, 46%). MALDI-MS (m/z): calcd for $C_{118}H_{92}BrN_2Ni^+$: 1675.58, Found, 1675.50, $[M-Br]^+$. Elemental analysis: calc. for $C_{118}H_{92}Br_2N_2Ni$: C, 80.69; H, 5.28; N, 1.59. Found:C, 80.48; H, 5.16; N, 1.54.



Ni4 (4.38 g, 65%). **Ni4** was prepared in the manner reported in the literature.[2]

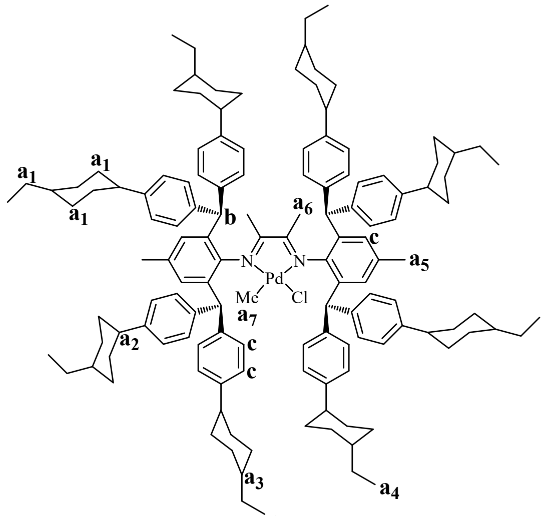


^{1}H NMR

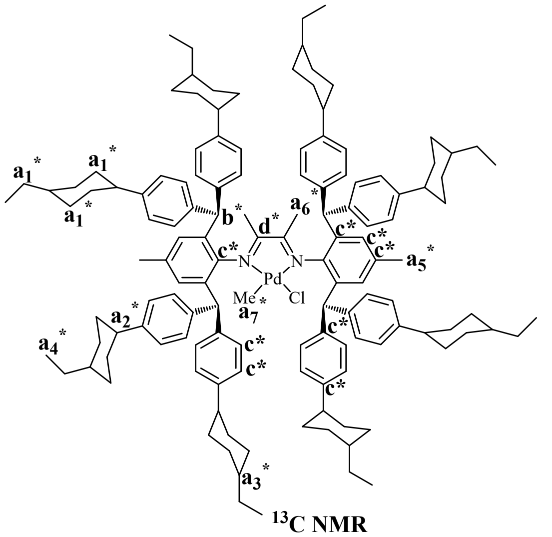


^{13}C NMR

Pd1 (0.58 g, 67%). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 7.43 (d, J = 7.5 Hz, 4H, c, Ar-*H*), 7.33 (d, J = 7.5 Hz, 4H, c, Ar-*H*), 7.13 – 7.02 (m, 14H, c, Ar-*H*), 6.95 (dd, J = 15.4, 7.4 Hz, 8H, c, Ar-*H*), 6.86 – 6.75 (m, 6H, c, Ar-*H*), 5.93 (s, 2H, b, C*H*Ar$_2$), 5.66 (s, 2H, b, C*H*Ar$_2$), 2.50 – 2.32 (m, 8H, a$_2$, Ar-C*H*), 2.27 (s, 3H, a$_5$, Ar-CH_3), 2.19 (s, 3H, a$_5$, Ar-CH_3), 1.92 – 1.65 (m, 40H, a$_1$, CH_2), 1.43 – 1.19 (m, 40H, a$_1$, CH_2), 0.68 (s, 3H, a$_7$, Pd-CH_3), 0.27 (s, 3H, a$_6$, C(CH_3)=N), 0.05 (s, 3H, a$_6$, C(CH_3)=N). ^{13}C NMR (101 MHz, CDCl$_3$) δ 177.34 (*C*=N, d*), 172.71 (*C*=N, d*), 146.26, 146.04, 145.83, 145.62, 141.64, 141.30, 140.82, 140.11, 139.83, 135.89, 134.95, 134.20, 129.95, 129.81, 129.75, 129.61, 129.46, 126.84, 126.75, 126.42, 50.89 (*C*HAr$_2$, b*), 50.53 (*C*HAr$_2$, b*), 44.15 (Ar-*C*H, a$_2^*$), 44.05 (Ar-*C*H, a$_2^*$), 44.00 (Ar-*C*H, a$_2^*$), 43.96 (Ar-*C*H, a$_2^*$), 34.72 (*C*H$_2$, a$_1^*$), 34.58 (*C*H$_2$, a$_1^*$), 34.53 (*C*H$_2$, a$_1^*$), 34.48 (*C*H$_2$, a$_1^*$), 34.38 (*C*H$_2$, a$_1^*$), 34.30 (*C*H$_2$, a$_1^*$), 27.01 (*C*H$_2$, a$_1^*$), 26.96 (*C*H$_2$, a$_1^*$), 26.85 (*C*H$_2$, a$_1^*$), 26.24 (*C*H$_2$, a$_1^*$), 26.07 (*C*H$_2$, a$_1^*$), 21.63 (Ar-*C*H$_3$, a$_5^*$), 21.55 (Ar-*C*H$_3$, a$_5^*$), 19.74 (C(*C*H$_3$)=N, a$_6^*$), 18.74 (C(*C*H$_3$)=N, a$_6^*$), 6.02 (Pd-*C*H$_3$, a$_7^*$). MALDI-MS (m/z): calcd for $C_{118}H_{140}ClN_2Pd^+$: 1728.98, Found, 1728.93, [M-Me]$^+$. Elemental analysis: calc. for $C_{119}H_{143}ClN_2Pd$: C, 81.99; H, 8.27; N, 1.61. Found: C, 81.86; H, 8.44; N, 1.60.

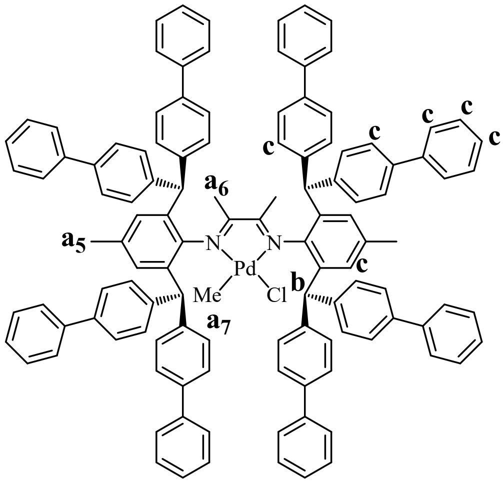


^{1}H NMR

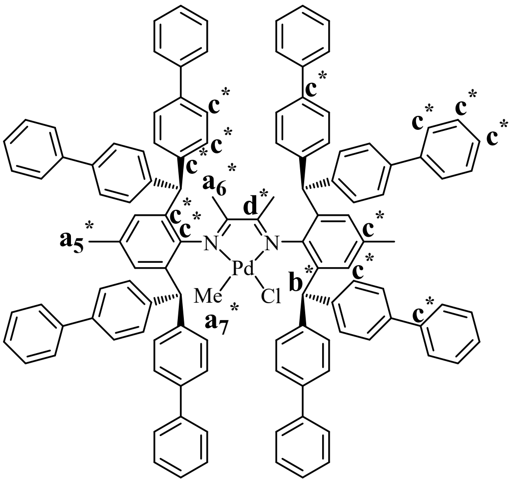


^{13}C NMR

Pd2 (0.59 g, 60%). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 7.43 (d, *J* = 8.1 Hz, 4H, c, Ar-*H*), 7.33 (d, *J* = 8.0 Hz, 4H, c, Ar-*H*), 7.12 – 7.02 (m, 16H, c, Ar-*H*), 6.95 (d, *J* = 5.6 Hz, 6H, c, Ar-*H*), 6.83 (d, *J* = 8.0 Hz, 4H, c, Ar-*H*), 6.78 (s, 2H, c, Ar-*H*), 5.92 (s, 2H, b, C*H*Ar$_2$), 5.66 (s, 2H, b, C*H*Ar$_2$), 2.46 – 2.28 (m, 8H, a$_2$, Ar-C*H*), 2.27 (s, 3H, a$_5$, Ar-C*H*$_3$), 2.19 (s, 3H, a$_5$, Ar-C*H*$_3$), 1.92 – 1.73 (m, 32H, a$_1$, C*H*$_2$), 1.37 – 1.22 (m, 32H, a$_1$, C*H*$_2$), 1.17 (d, *J* = 7.6 Hz, 8H, a$_3$, C*H*), 1.01 (dd, *J* = 22.9, 11.8 Hz, a$_1$, 16H, C*H*$_2$), 0.92 (*br*, 6H, a$_4$, C*H*$_3$), 0.90 (*br*, 12H, a$_4$, C*H*$_3$), 0.89 (d, *J* = 2.4 Hz, 6H, a$_4$, C*H*$_3$), 0.67 (s, 3H, a$_7$, Pd-C*H*$_3$), 0.27 (s, 3H, a$_6$, C(C*H*$_3$)=N), 0.05 (s, 3H, a$_6$, C(C*H*$_3$)=N). ^{13}C NMR (101 MHz, CDCl$_3$) δ 177.33 (C=N, d*), 172.69 (C=N, d*), 146.07, 145.82, 145.61, 145.43, 141.63, 141.29, 140.80, 140.13, 139.84, 135.90, 134.93, 134.83, 134.19, 129.93, 129.80, 129.73, 129.59, 129.44, 126.85, 126.77, 126.44, 50.88 (C*H*Ar$_2$, b*), 50.51 (C*H*Ar$_2$, b*), 44.21 (Ar-*C*H, a$_2^*$), 44.12 (Ar-*C*H, a$_2^*$), 44.05 (Ar-*C*H, a$_2^*$), 44.02 (Ar-*C*H, a$_2^*$), 39.15 (*C*H, a$_3^*$), 39.12 (*C*H, a$_3^*$), 39.02 (*C*H, a$_3^*$), 34.53 (*C*H$_2$, a$_1^*$), 34.36 (*C*H$_2$, a$_1^*$), 34.29 (*C*H$_2$, a$_1^*$), 34.18 (*C*H$_2$, a$_1^*$), 33.30 (*C*H$_2$, a$_1^*$), 33.25 (*C*H$_2$, a$_1^*$), 33.14 (*C*H$_2$, a$_1^*$), 30.07 (*C*H$_2$, a$_1^*$), 29.98 (*C*H$_2$, a$_1^*$), 21.63 (Ar-C*H*$_3$, a$_5^*$), 21.55 (Ar-C*H*$_3$, a$_5^*$), 19.75 (C(*C*H$_3$)=N, a$_6^*$), 18.75 (C(*C*H$_3$)=N, a$_6^*$), 11.55 (*C*H$_3$, a$_4^*$), 11.48 (*C*H$_3$, a$_4^*$), 6.06 (Pd-*C*H$_3$, a$_7^*$). MALDI-MS (m/z): calcd for $C_{134}H_{172}N_2Pd^+$: 1915.26, Found, 1915.20, [M-Me-Cl]$^+$. Elemental analysis: calc. for $C_{135}H_{175}ClN_2Pd$: C, 82.40; H, 8.96; N, 1.42. Found: C, 82.34; H, 8.85; N, 1.55.

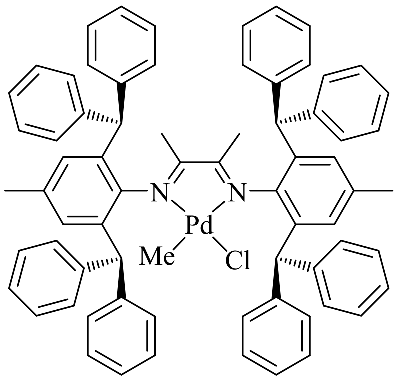


^{1}H NMR



^{13}C NMR

Pd3 (0.53g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.68 (d, *J* = 8.2 Hz, 4H, c, Ar-*H*), 7.59 – 7.50 (m, 20H, c, Ar-*H*), 7.42 – 7.35 (m, 20H, c, Ar-*H*), 7.30 (d, *J* = 8.6 Hz, 8H, c, Ar-*H*), 7.27 – 7.19 (m, 20H, c, Ar-*H*), 7.17 (s, 2H, c, Ar-*H*), 6.93 (s, 2H, c, Ar-*H*), 6.17 (s, 2H, b, C*H*Ar_2), 5.93 (s, 2H, b, C*H*Ar_2), 2.34 (s, 3H, a_5, Ar-CH_3), 2.26 (s, 3H, a_5, Ar-CH_3), 0.95 (s, 3H, a_7, Pd-CH_3), 0.46 (s, 3H, a_6, C(CH_3)=N), 0.32 (s, 3H, a_6, C(CH_3)=N). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.89 (*C*=N, d^*), 173.21 (*C*=N, d^*), 143.10, 141.81, 141.38, 141.30, 141.17, 141.03, 140.70, 139.79, 139.64, 139.62, 139.40, 139.23, 139.06, 136.80, 135.77, 134.69, 134.01, 130.56, 130.49, 130.29, 130.25, 130.02, 129.92, 128.89, 128.87, 128.74, 128.69, 127.52, 127.43, 127.30, 127.16, 127.13, 127.10, 127.06, 127.01, 126.70, 126.58, 51.22 (*C*HAr_2, b^*), 50.82 (*C*HAr_2, b^*), 21.69 (Ar-*C*H_3, a_5^*), 21.66 (Ar-*C*H_3, a_5^*), 20.76 (C(*C*H_3)=N, a_6^*), 19.84 (C(*C*H_3)=N, a_6^*), 6.68 (Pd-*C*H_3, a_7^*). MALDI-MS (m/z): calcd for $C_{118}H_{92}N_2Pd^+$: 1642.63, Found, 1642.64, [M-Me-Cl]$^+$. Elemental analysis: calc. for $C_{119}H_{95}ClN_2Pd$: C, 84.33; H, 5.65; N, 1.65. Found: C, 84.26; H, 5.54; N, 1.59.



Pd4 (4.38 g, 65%). **Pd4** was prepared in the manner reported in the literature.[3]

1.5 A General Procedure for the Ethylene Homopolymerization Using Ni(II) and Pd(II) Complexes

(a) In a typical experiment, a 350 mL thick wall pressure glass reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 40 mL of hexanes and the desired amount Et_2AlCl were added to the reactor under N_2 atmosphere, then the desired amount of catalyst in 2 mL of hexanes 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.

(b) In a typical experiment, a 350 mL thick wall pressure glass reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 38 mL of hexanes and the desired amount NaBArF wereadded to the reactor under N_2 atmosphere, then the desired amount of catalyst in 2 mL of hexanes was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 6 atm of ethylene. After 0.5 h, the pressure reactor was vented and the polymer was washed by ethanol and dried under vacuum overnight.

1.6 A General Procedure for the Copolymerization of Methyl Acrylate with Ethylene Using Pd(II) Complexes

In a typical experiment, a 350 mL thick wall pressure glass reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 18 mL of hexanes with the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the desired amount of MA and the desired amount of Pd catalyst in 2 mL of hexanes was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at the 2 atm pressure of ethylene. After 12 h, the pressure reactor was vented and the copolymer was dried under vacuum overnight.

1.7 A General Procedure for the Copolymerization of Long-Chain Polar Monomers with Ethylene Using Pd(II) Complexes

In a typical experiment, a 350 mL thick wall pressure glass reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 15 mL of hexanes with the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the desired amount of polar monomer and the desired amount of Pd catalyst in 5 mL of hexanes were injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at the 4 atm pressure of ethylene. After 12 h, the pressure reactor was vented and the copolymer was dried under vacuum overnight.

1.8 Effect of Reaction Time on Ethylene Polymerizations Using Ni1 and Ni2 at 80 °C

Table S1. Effect of Reaction Time on Ethylene Polymerizations Using Ni1-2 at 80 °C[a]

Entry	Complex	t (min)	Yield (g)	M_n (10^4)[b]	M_w/M_n[b]
1	**Ni1**	10	0.36	27.2	1.11

2	**Ni1**	20	0.80	60.8	1.20
3	**Ni1**	30	1.20	88.2	1.20
4	**Ni1**	40	1.51	115.6	1.30
5	**Ni2**	10	0.31	33.1	1.16
6	**Ni2**	20	0.85	60.9	1.15
7	**Ni2**	30	1.28	92.0	1.19
8	**Ni2**	40	1.54	117.7	1.23

[a]Conditions: Ni(II) catalyst (2 μmol), 500 eq. Et_2AlCl, 40mL hexanes, 6 atm. [b]M_n are in unit of 10^4 g mol^{-1}, determined by SEC in trichlorobenzene at 150 °C.

2. Spectra Data

2.1 ^{1}H and ^{13}C NMR of the Synthetic Compounds

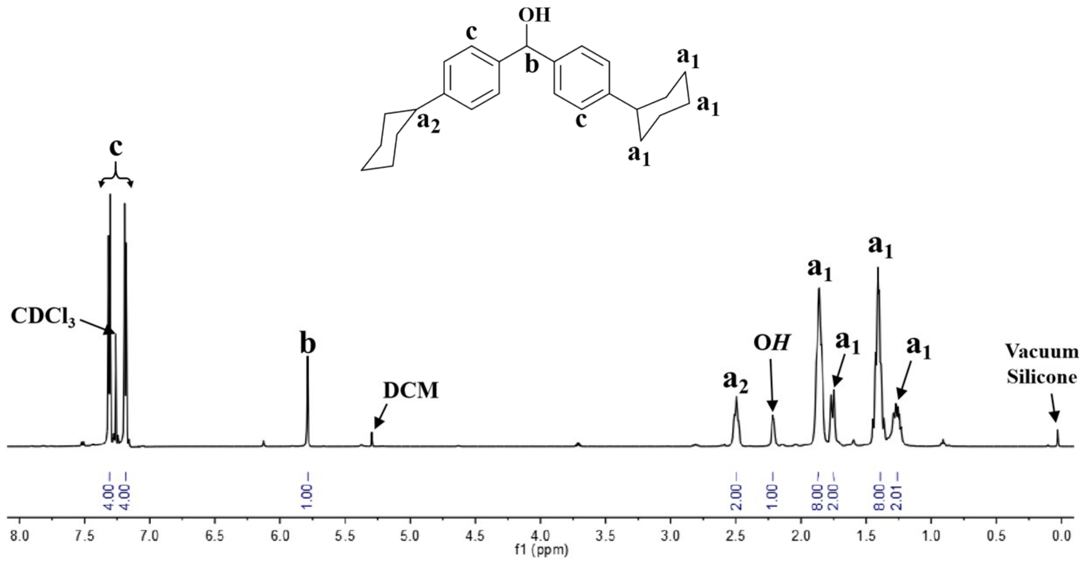


Figure S1. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) assignment of **O1**.

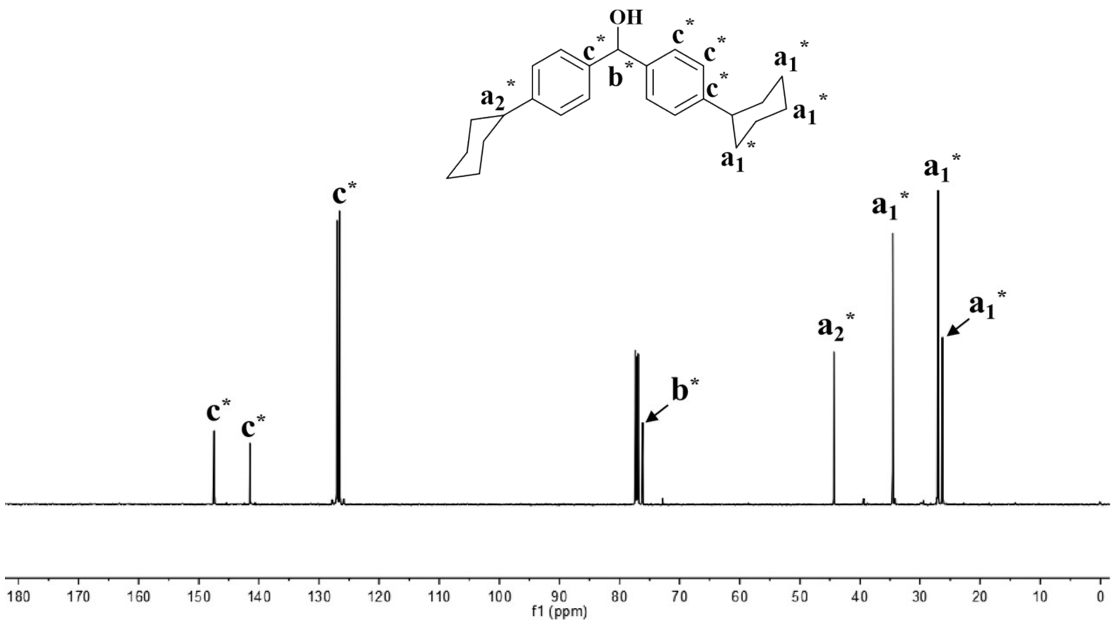


Figure S2. ^{13}C NMR (151 MHz, CDCl$_3$, 25 °C) assignment of **O1**.

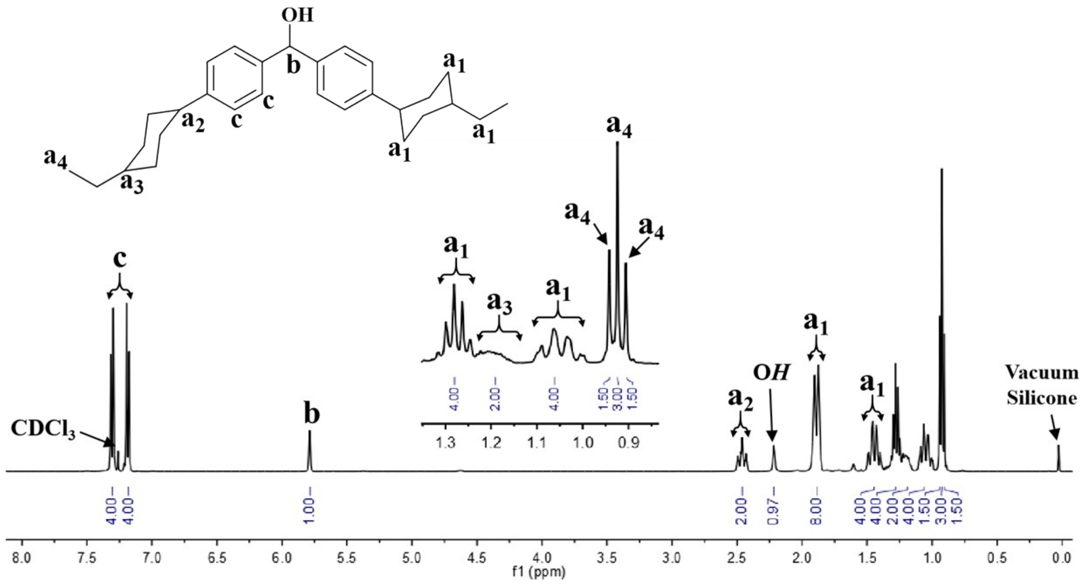


Figure S3. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) assignment of **O2**.

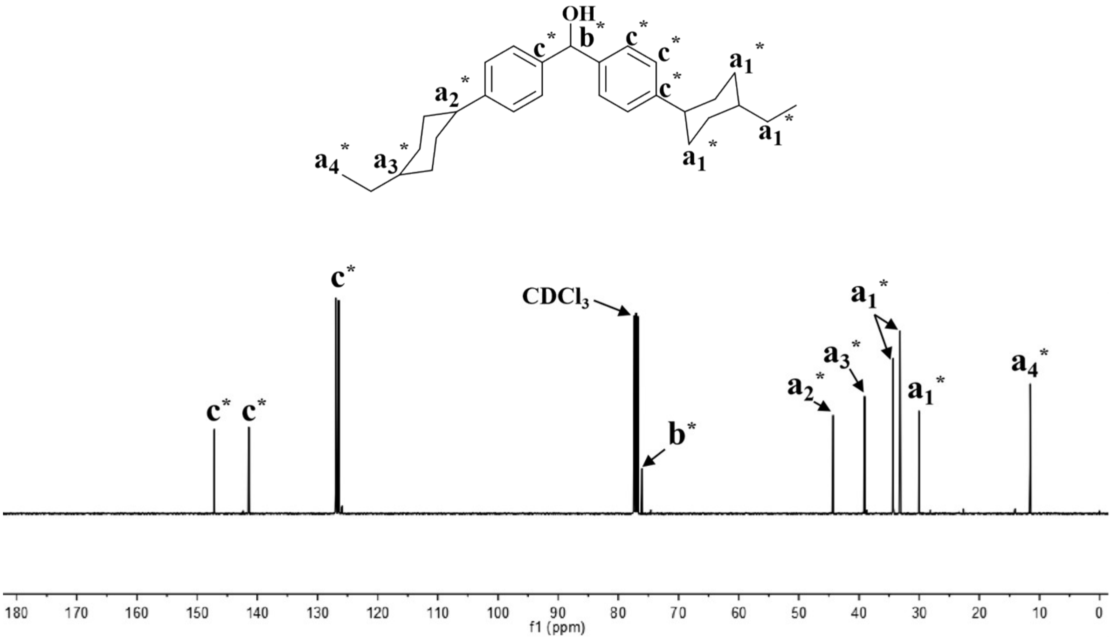


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) assignment of **O2**.

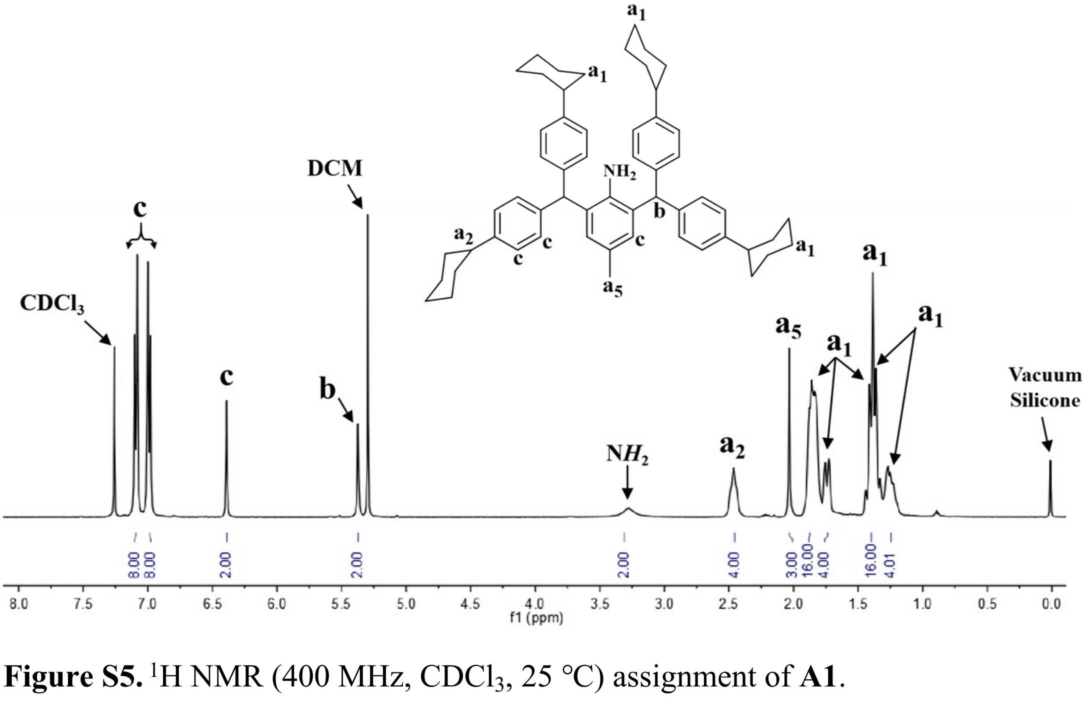


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) assignment of **A1**.

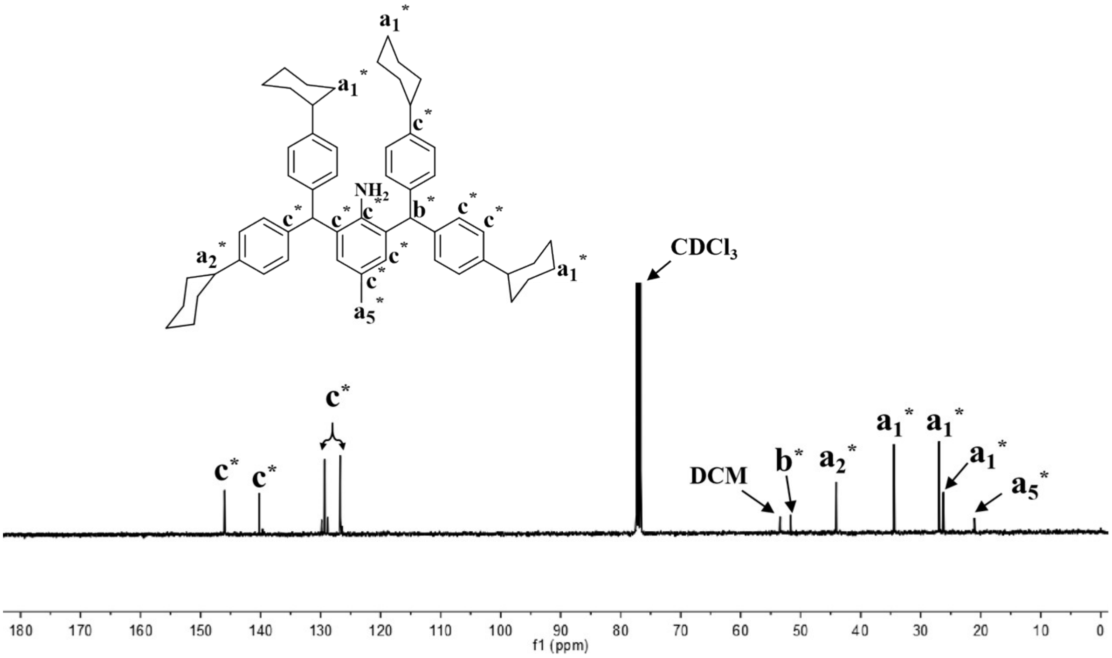


Figure S6. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) assignment of **A1**.

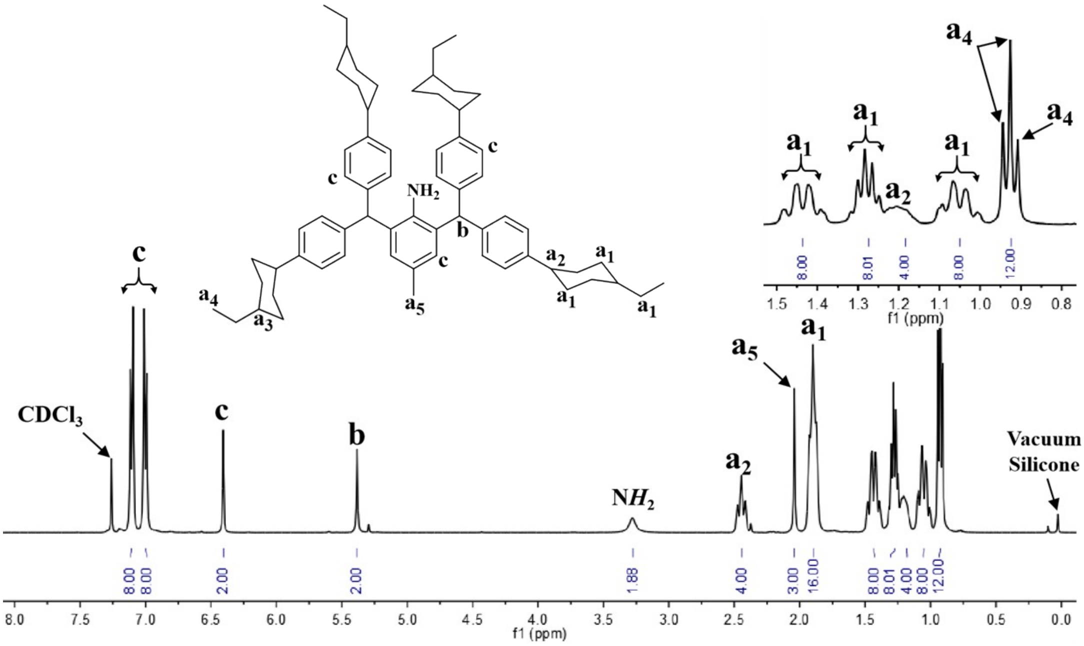


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) assignment of **A2**.

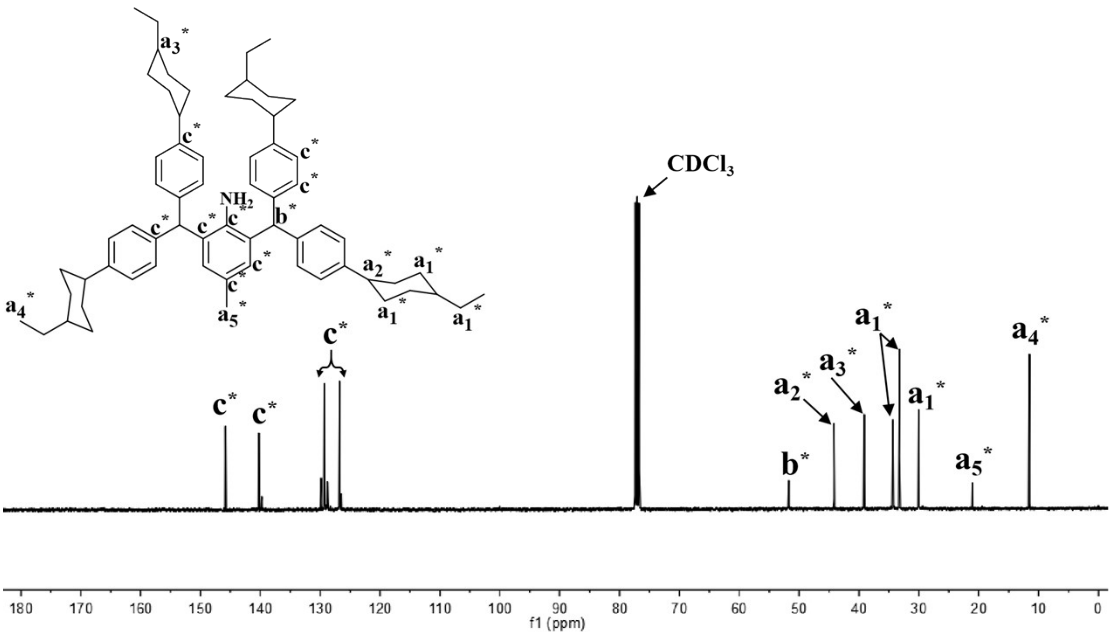


Figure S8. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) assignment of **A2**.

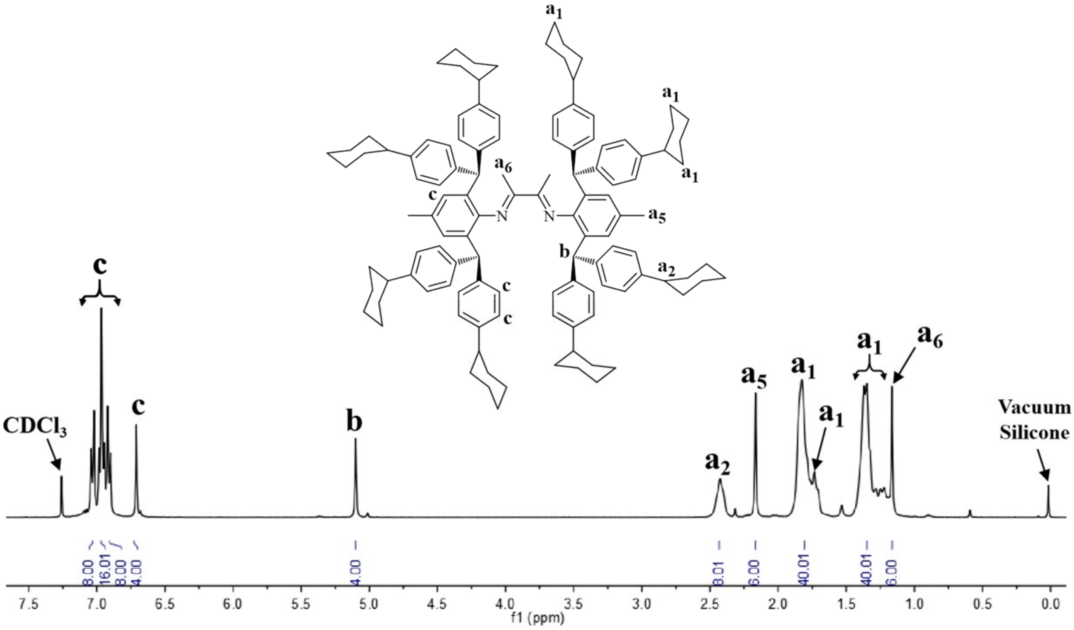


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) assignment of **L1**.

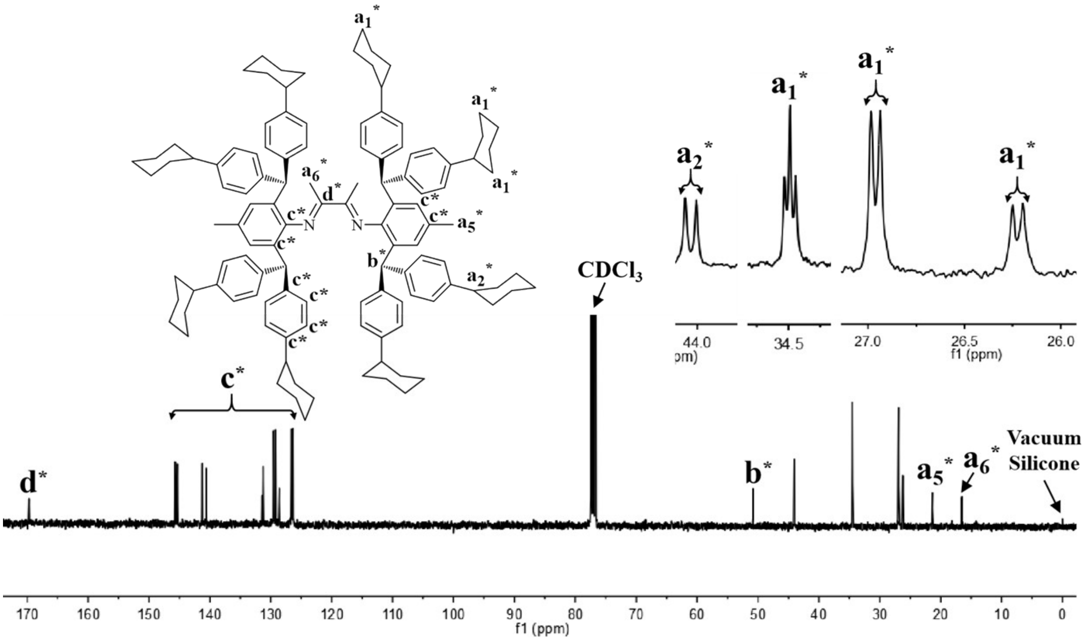


Figure S10. ^{13}C NMR (101 MHz, CDCl$_3$, 25 °C) assignment of **L1**.

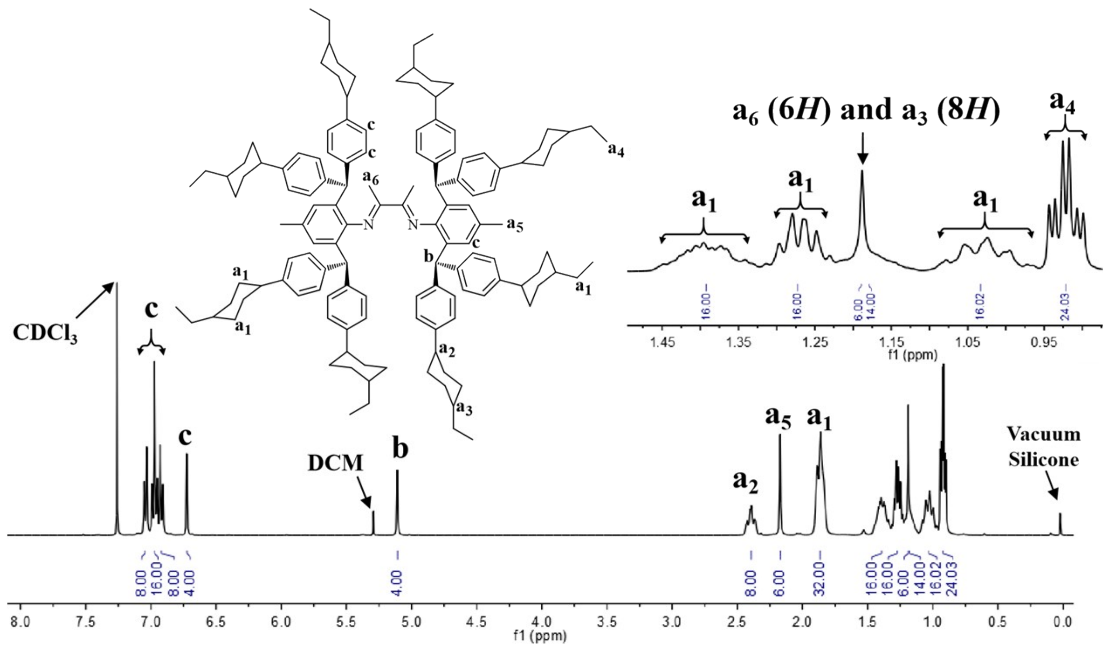


Figure S11. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) assignment of **L2**.

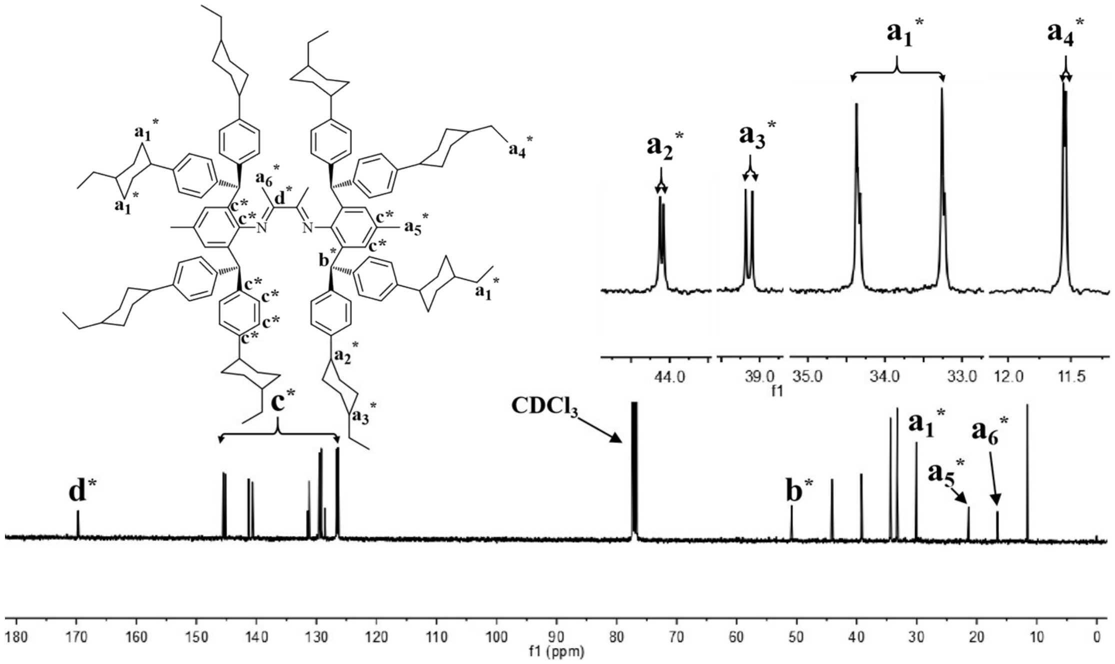


Figure S12. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C) assignment of **L2**.

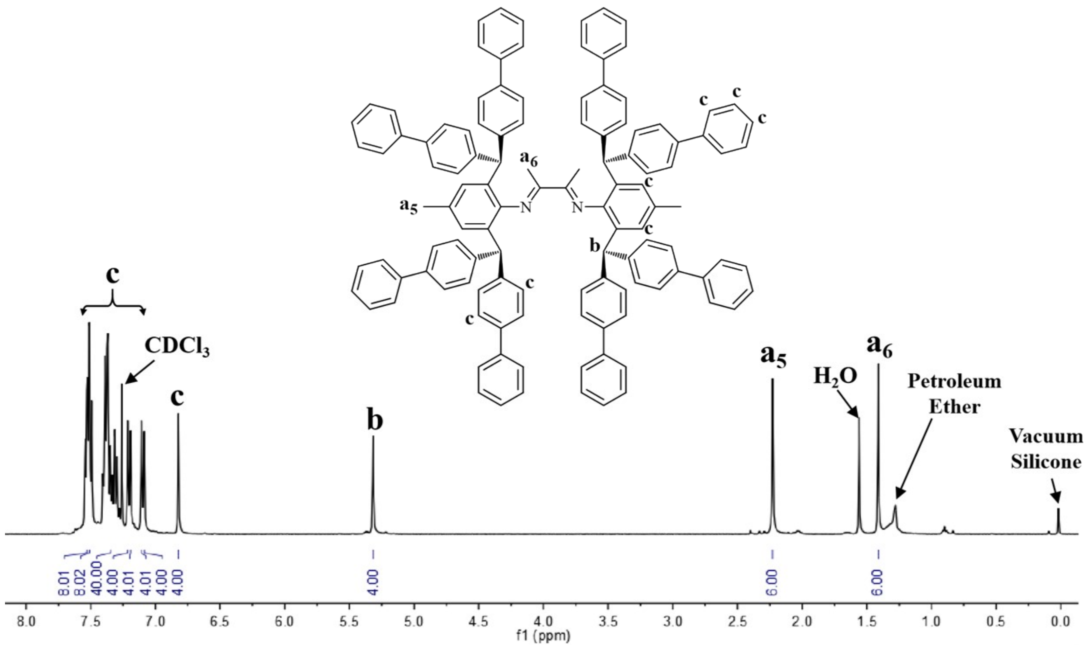


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) assignment of **L3**.

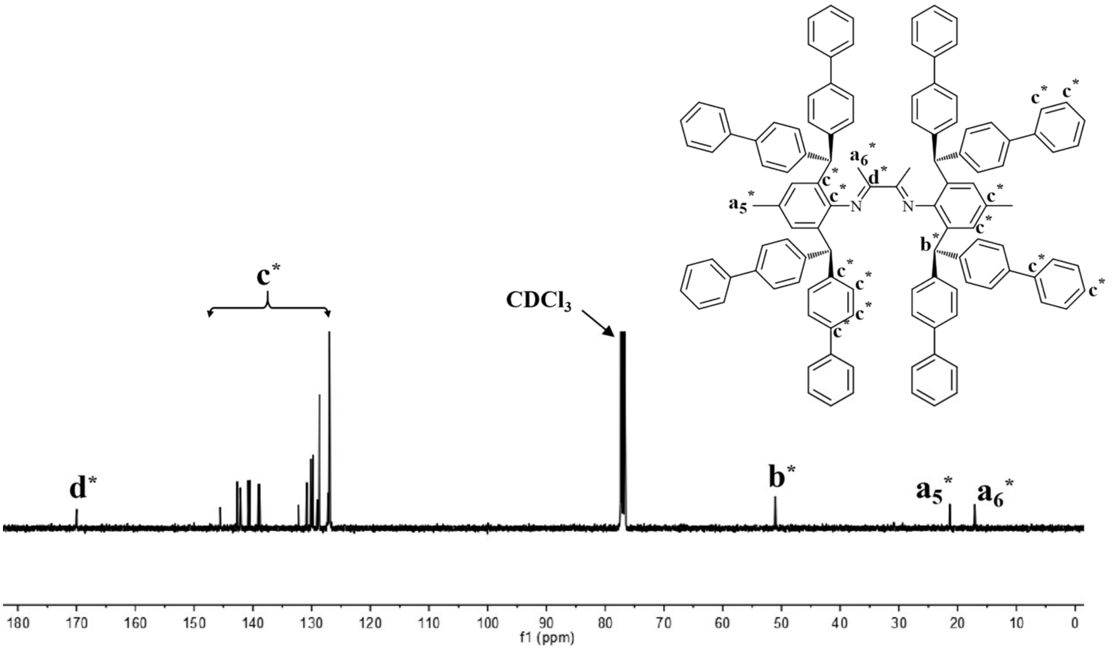


Figure S14. ^{13}C NMR (101 MHz, CDCl$_3$, 25 °C) assignment of **L3**.

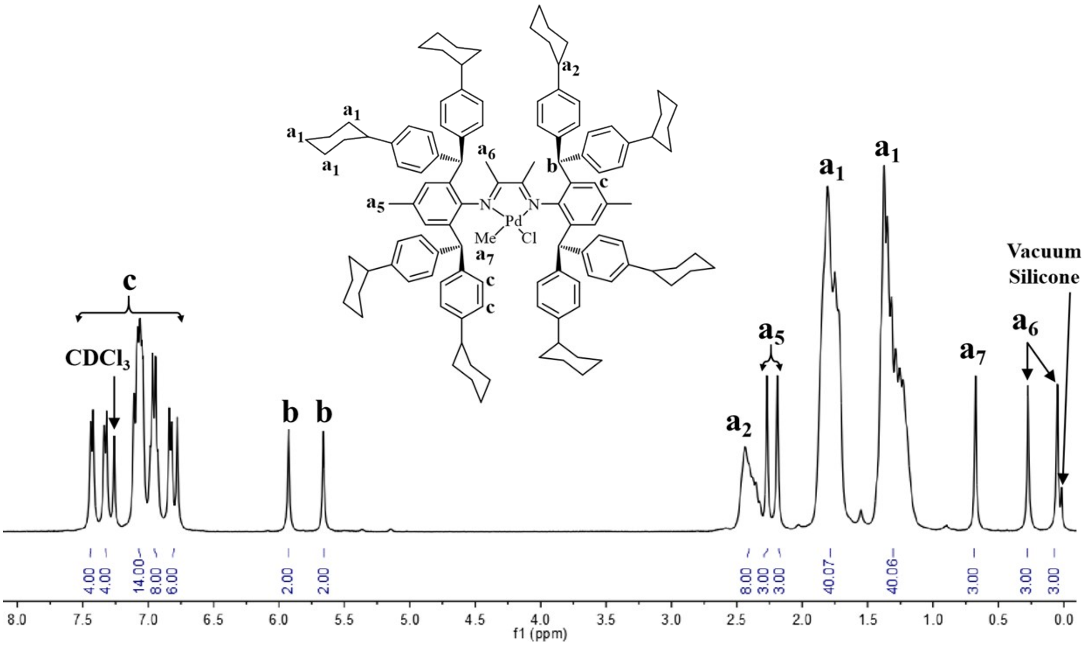


Figure S15. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) assignment of **Pd1**.

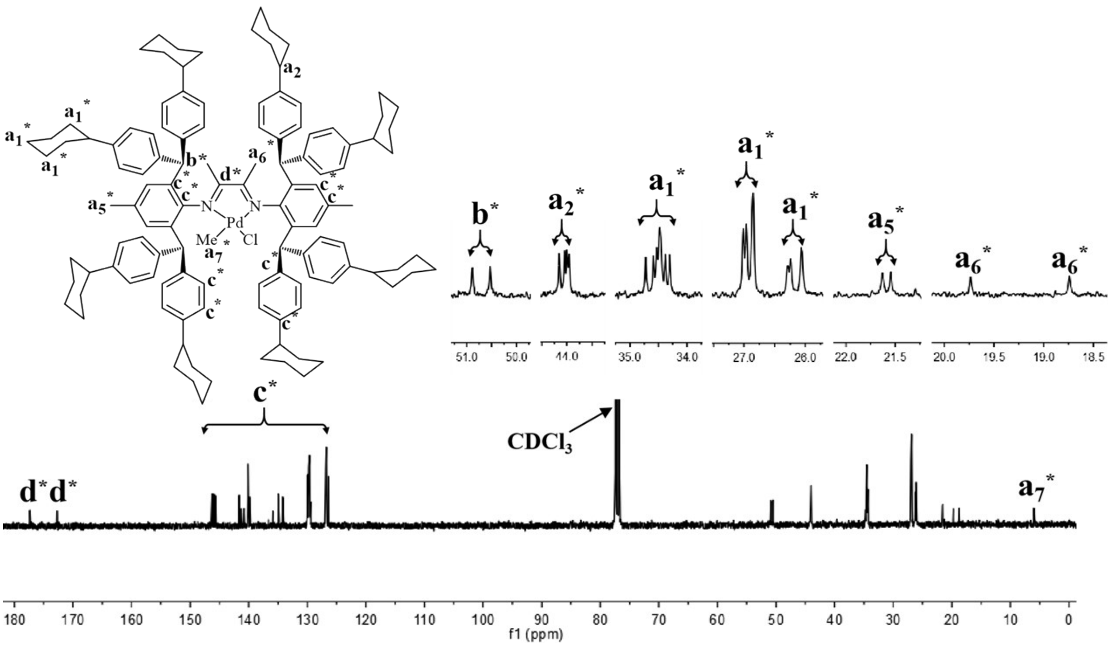


Figure S16. ^{13}C NMR (101 MHz, CDCl$_3$, 25 °C) assignment of **Pd1**.

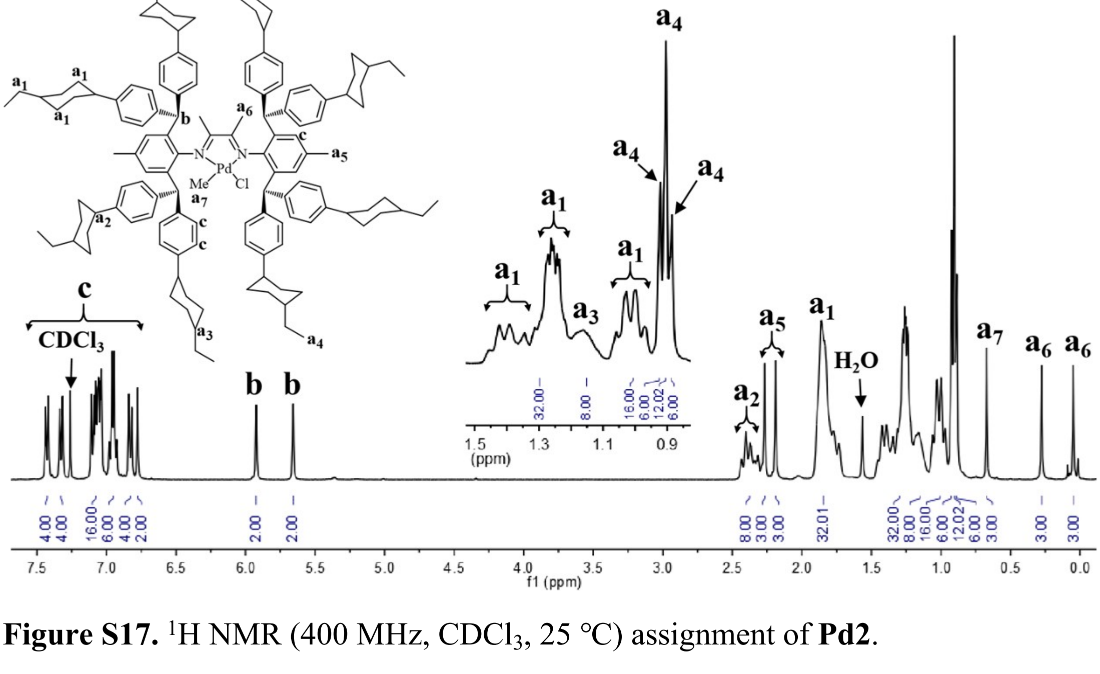


Figure S17. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) assignment of **Pd2**.

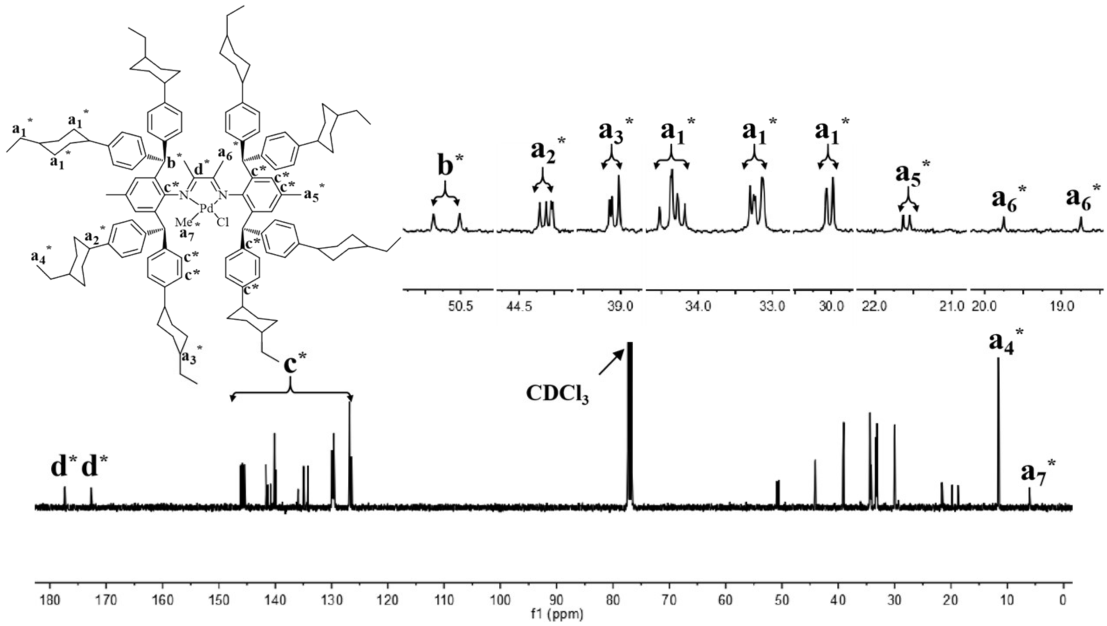


Figure S18. ^{13}C NMR (101 MHz, CDCl$_3$, 25 °C) assignment of **Pd2**.

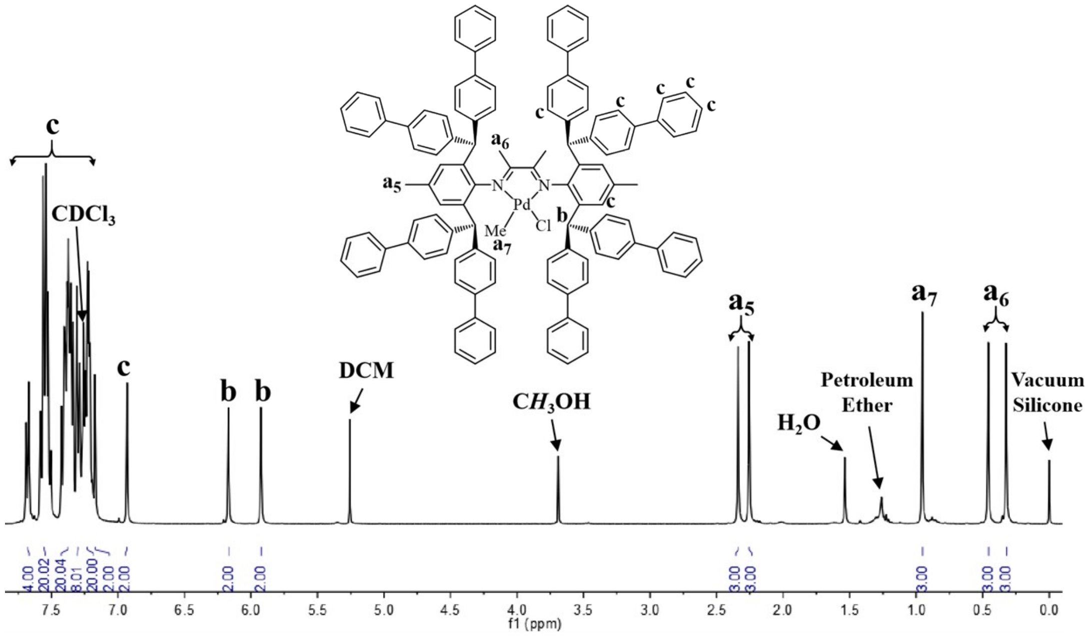


Figure S19. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) assignment of **Pd3**.

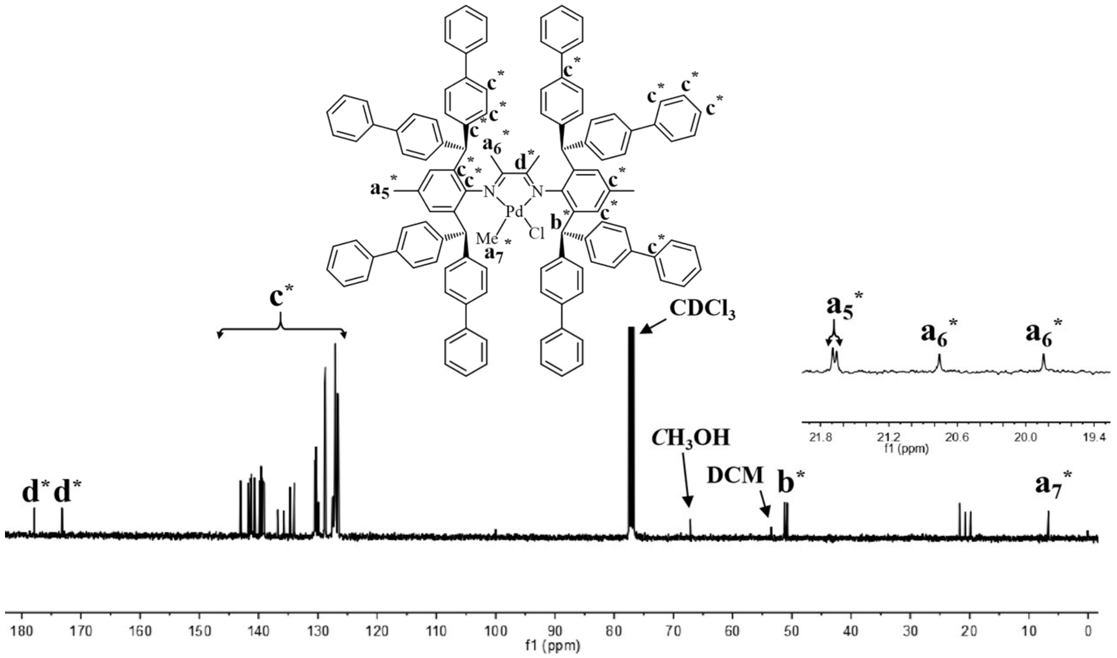


Figure S20. ^{13}C NMR (101 MHz, CDCl$_3$, 25 °C) assignment of **Pd3**.

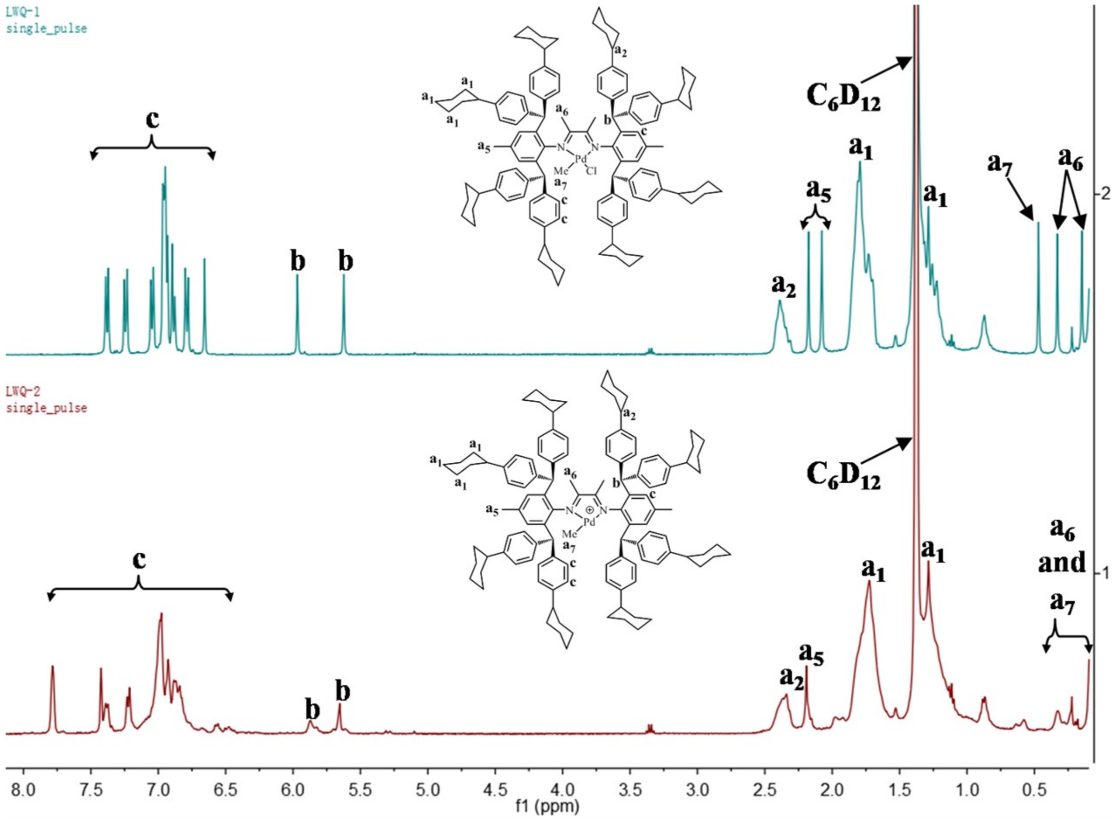


Figure S21. ^{1}H NMR (600 MHz, C$_6$D$_{12}$, 25 °C) assignment of **Pd1** and its active species.

2.2 ESI-MS and MALDI-TOF-MS Data

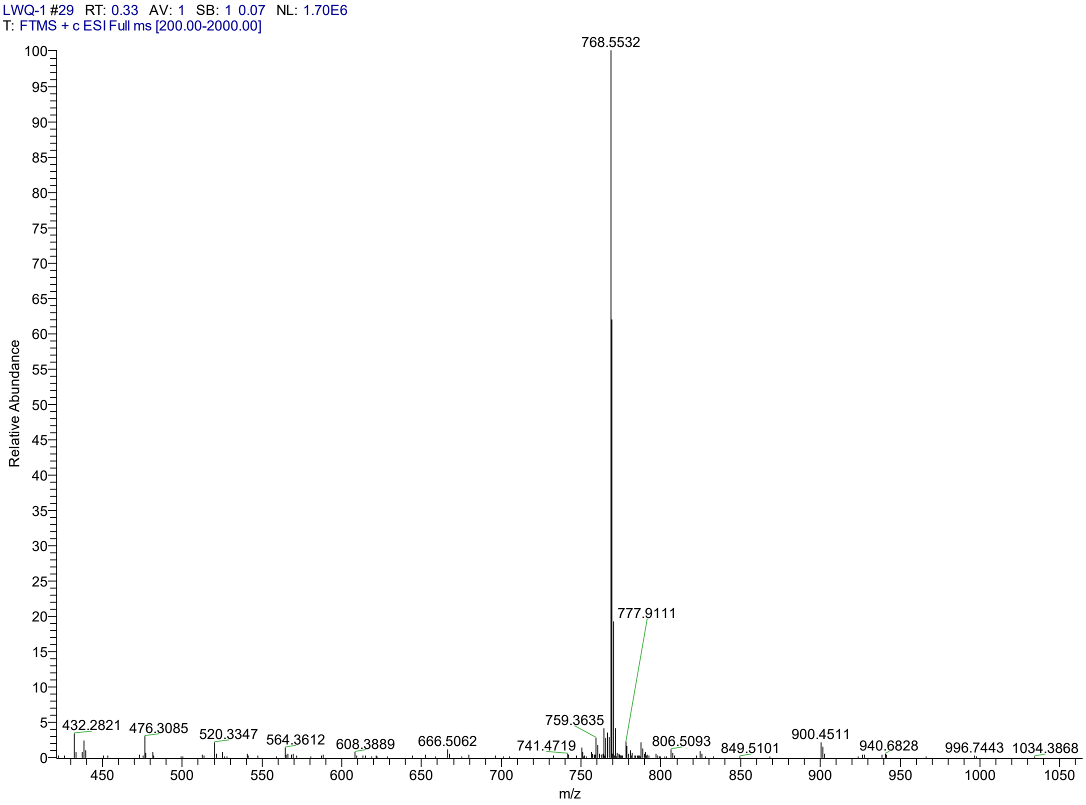


Figure S22. ESI-MS of **A1.**

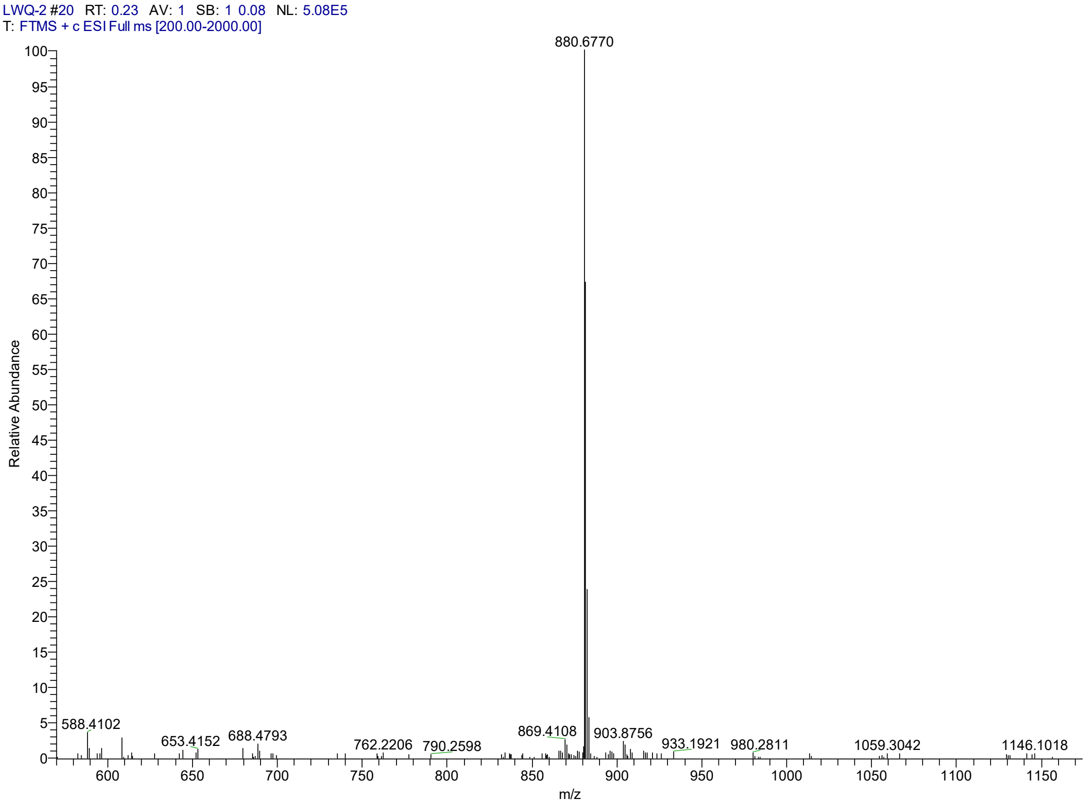


Figure S23. ESI-MS of **A2.**

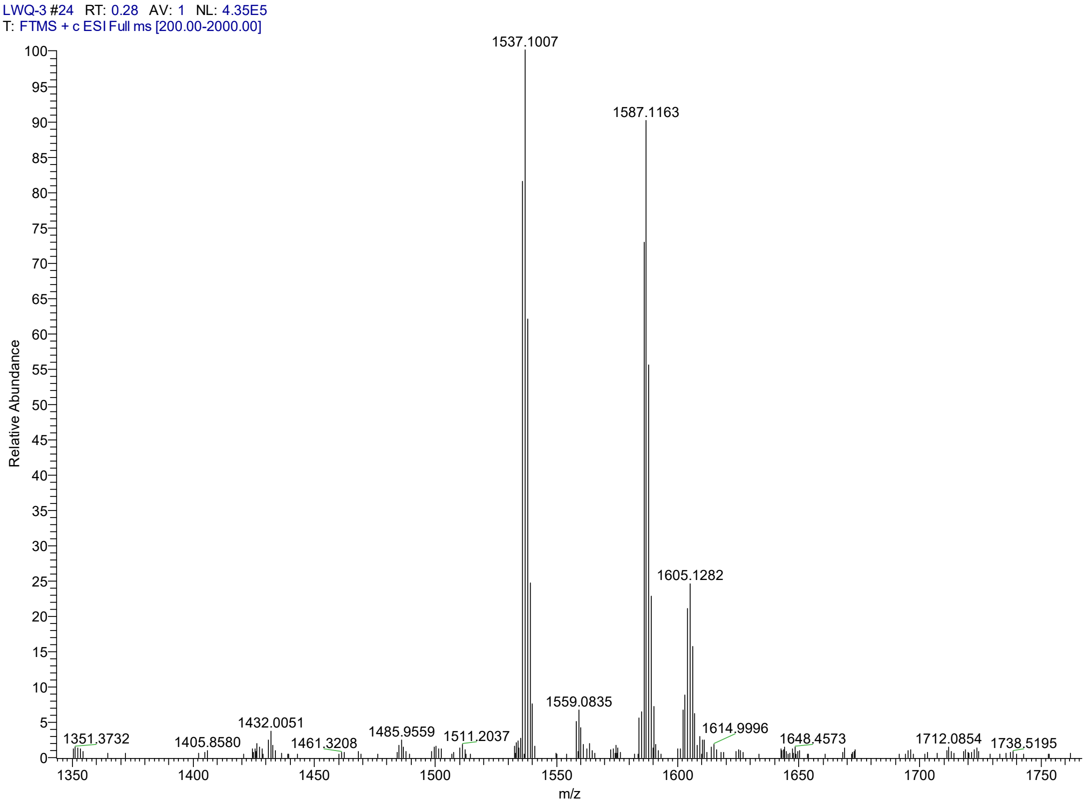


Figure S24. ESI-MS of **L1.**

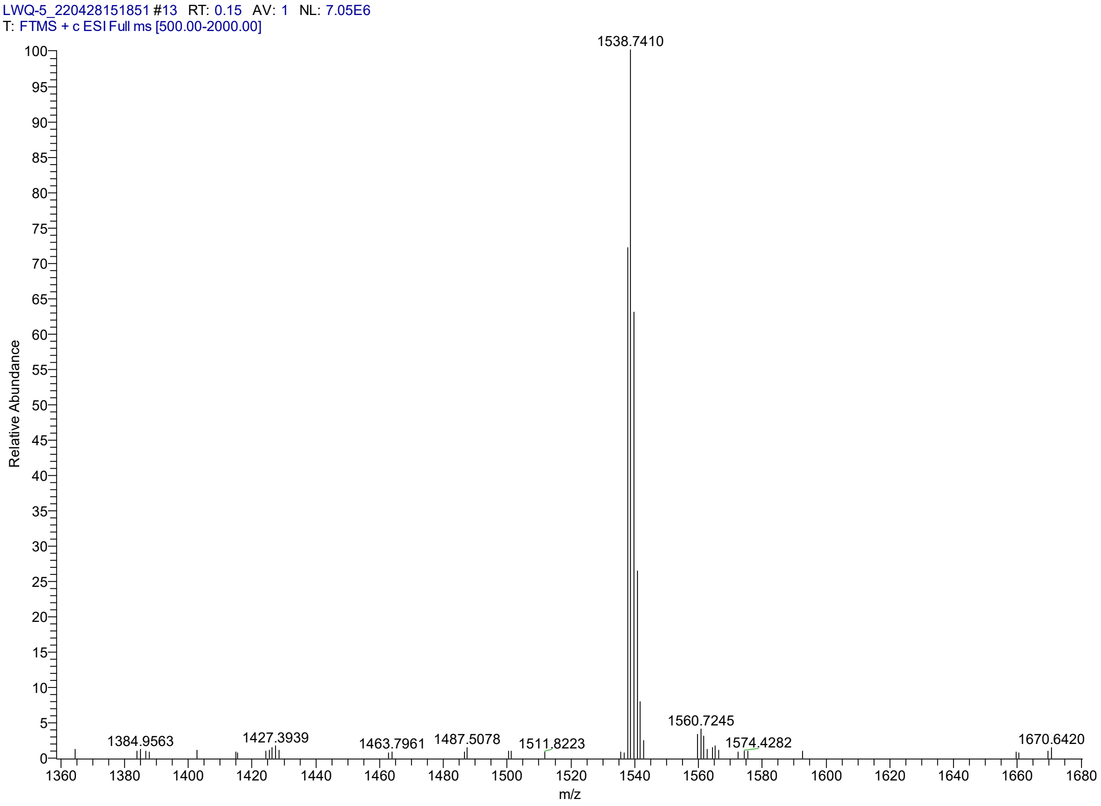


Figure S25. ESI-MS of **L3.**

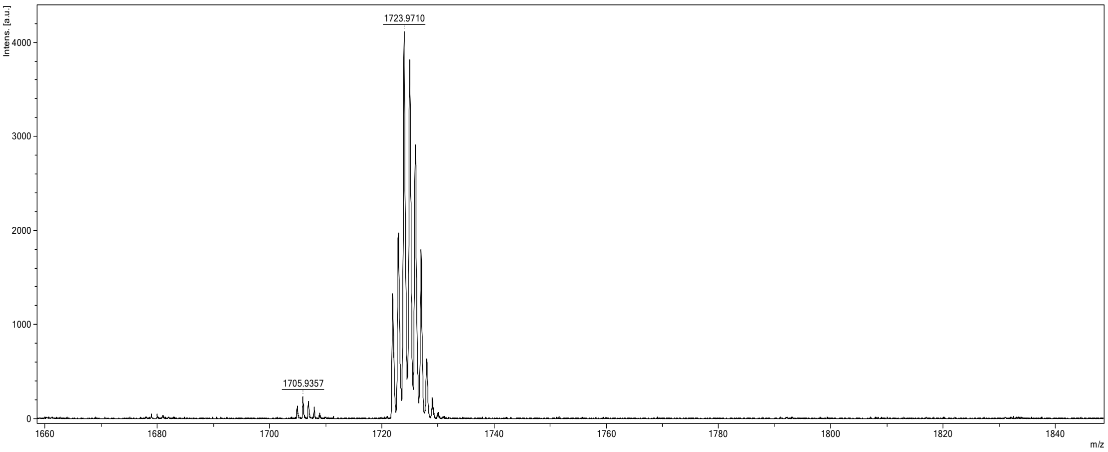


Figure S26. MALDI-TOF-MS of **Ni1.**

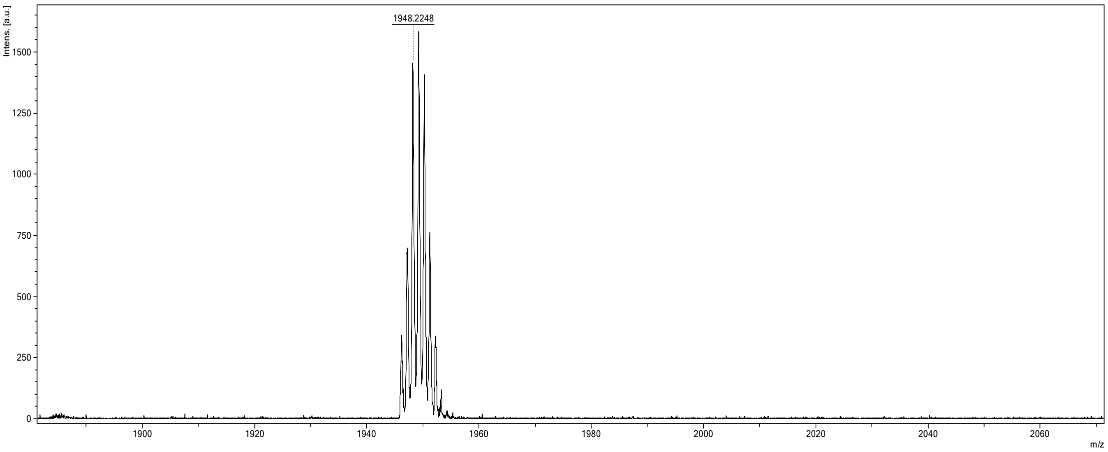


Figure S27. MALDI-TOF-MS of **Ni2.**

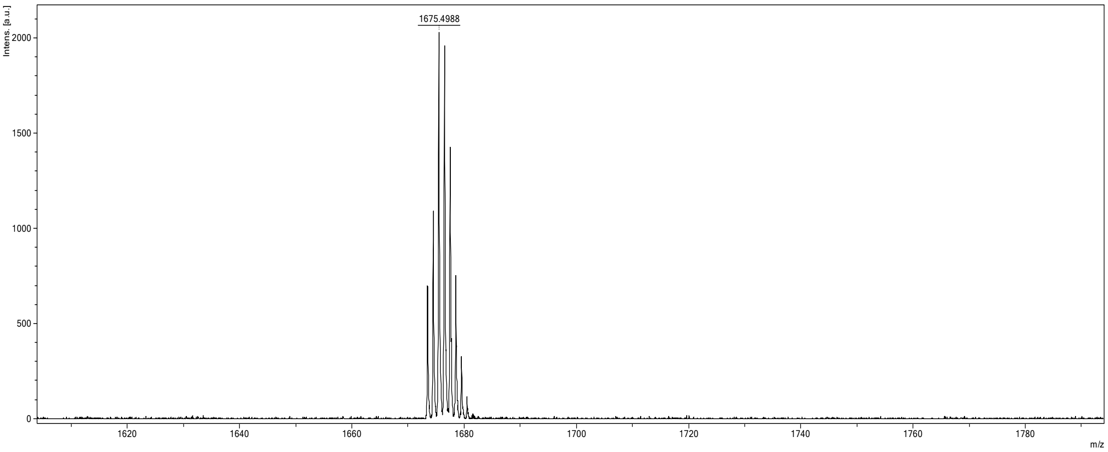


Figure S28. MALDI-TOF-MS of **Ni3.**

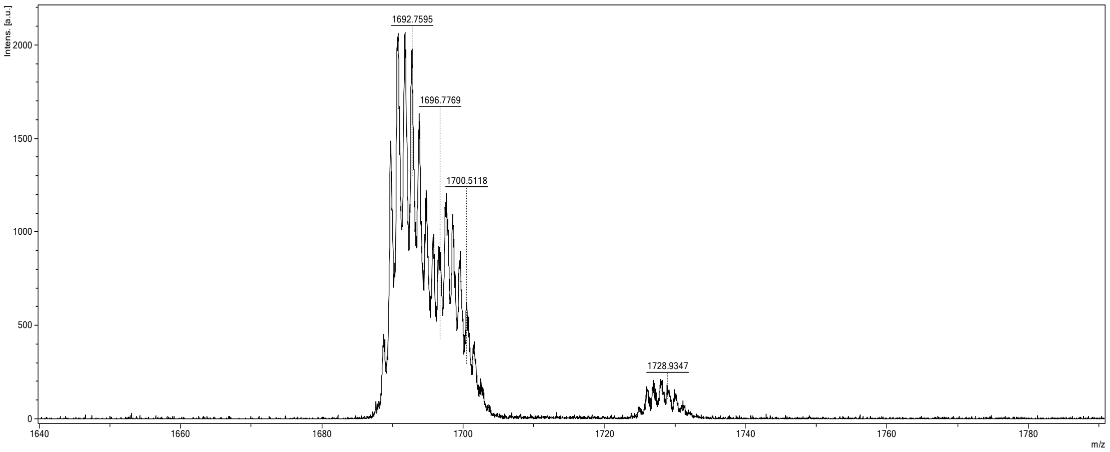


Figure S29. MALDI-TOF-MS of **Pd1.**

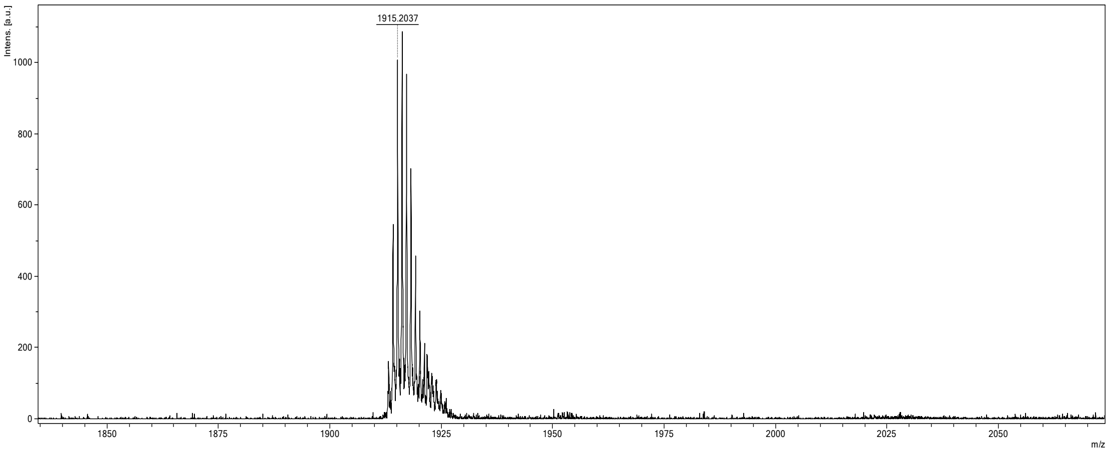


Figure S30. MALDI-TOF-MS of **Pd2.**

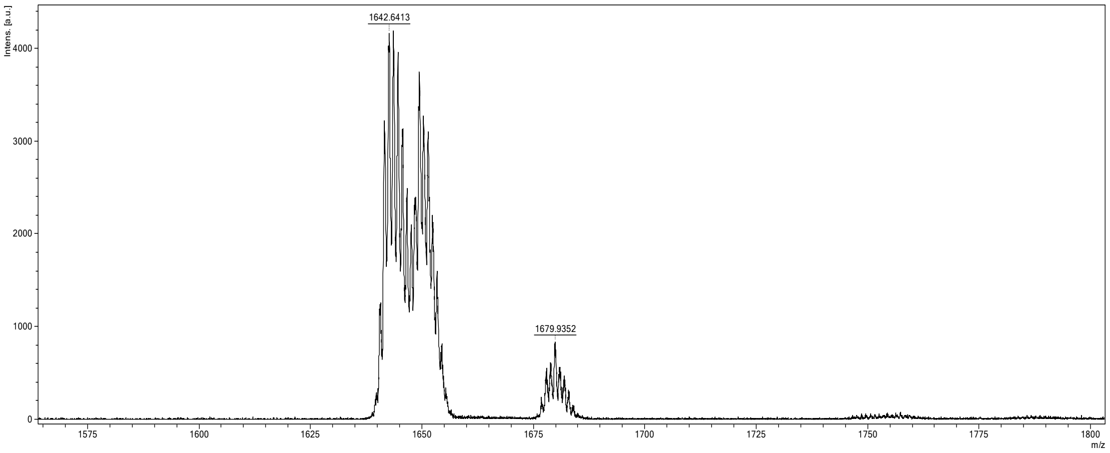


Figure S31. MALDI-TOF-MS of **Pd3.**

2.3 ^{1}H NMR of Representative Polymers and Copolymers

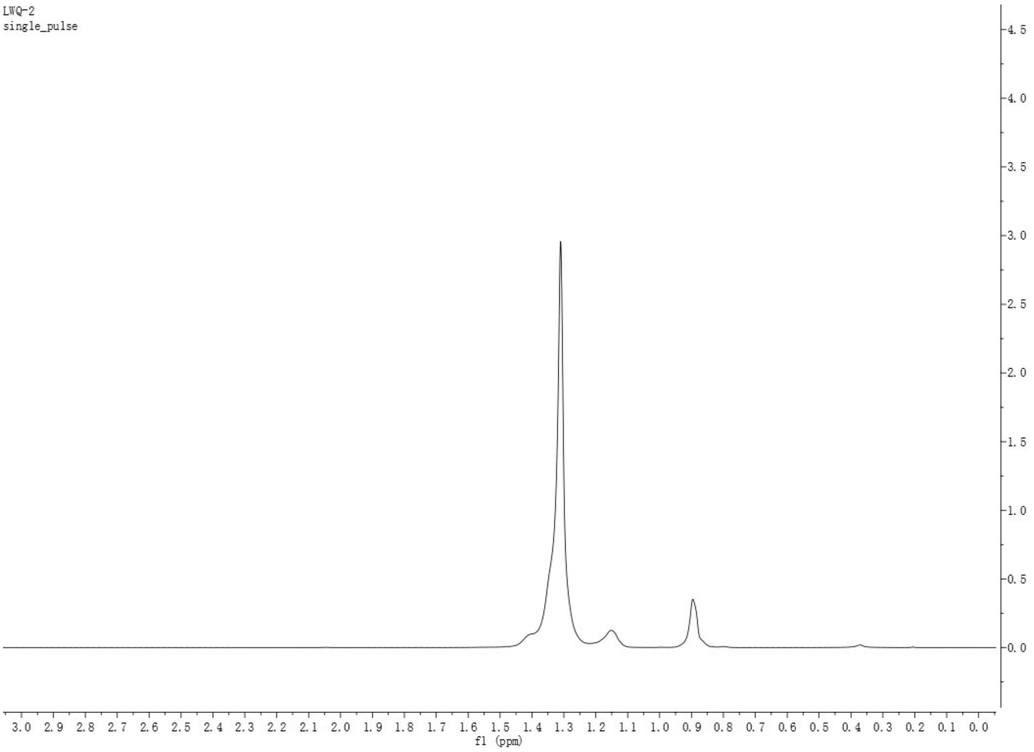


Figure S32. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 2, Table 1.

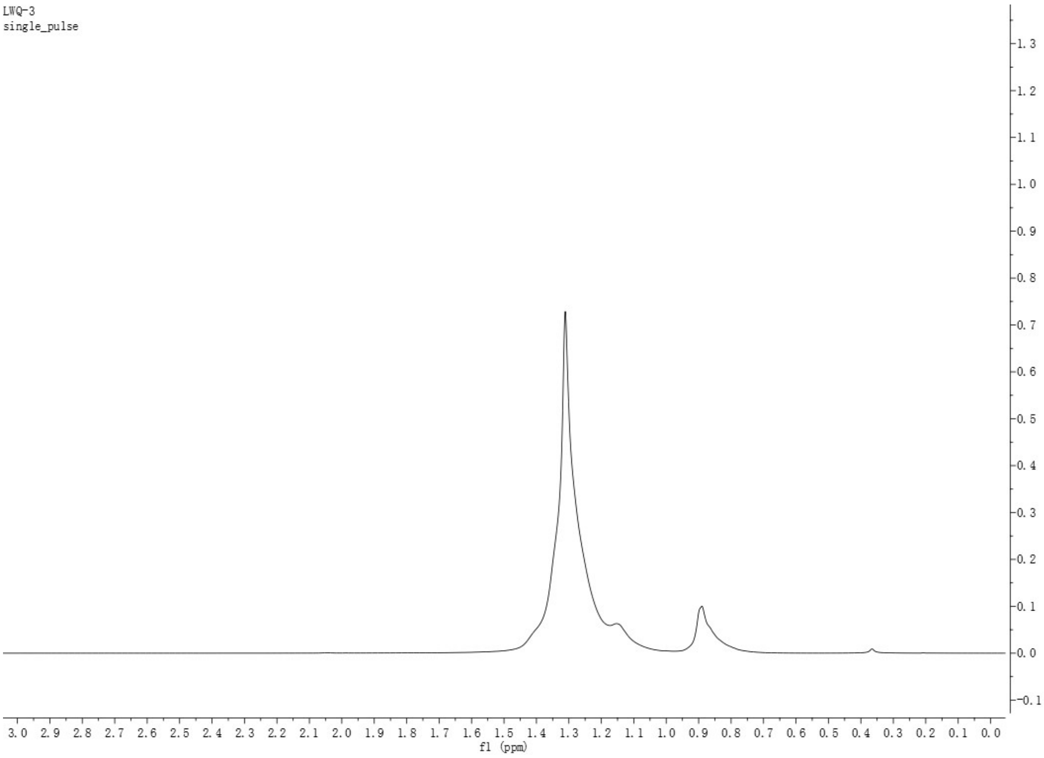


Figure S33. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 3, Table 1.

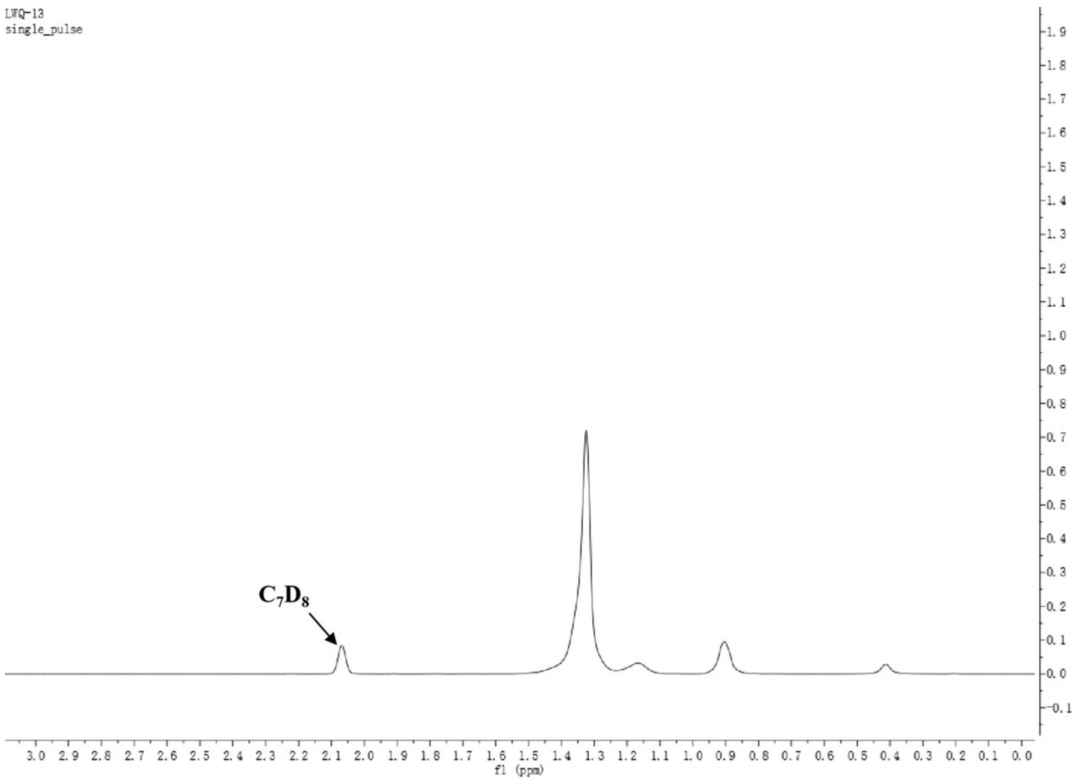


Figure S34. ^{1}H NMR (400 MHz, C_7D_8, 100 °C) spectrum of the polymer from entry 4, Table 1.

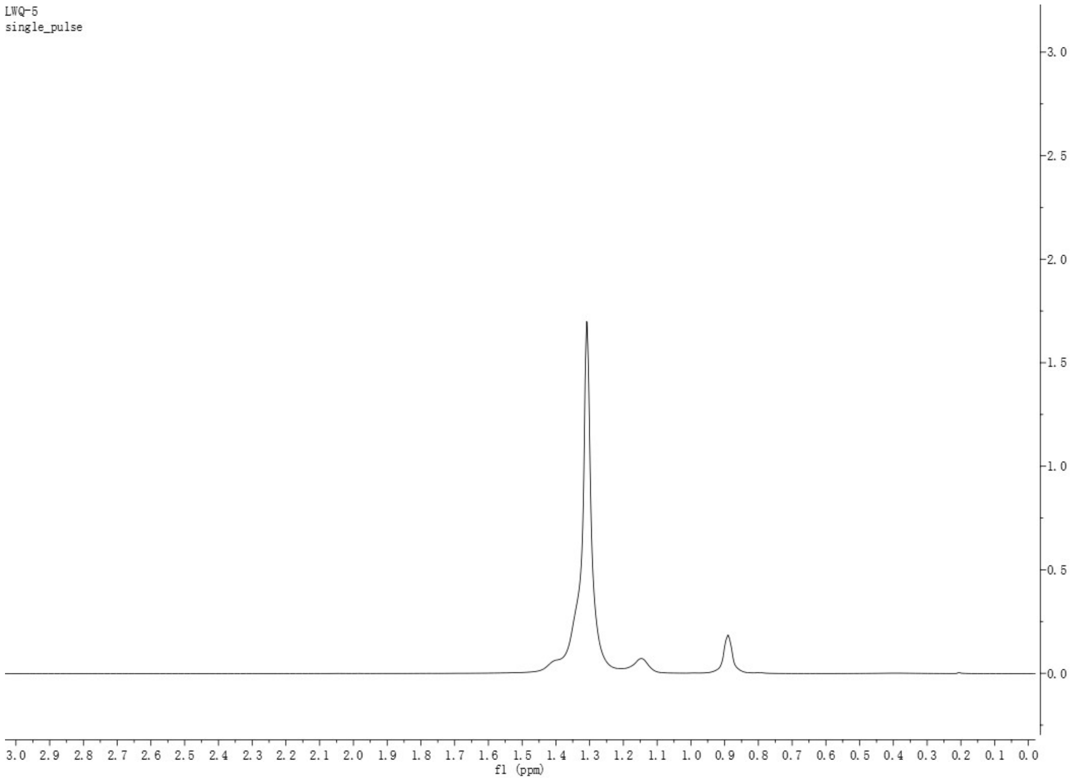


Figure S35. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 5, Table 1.

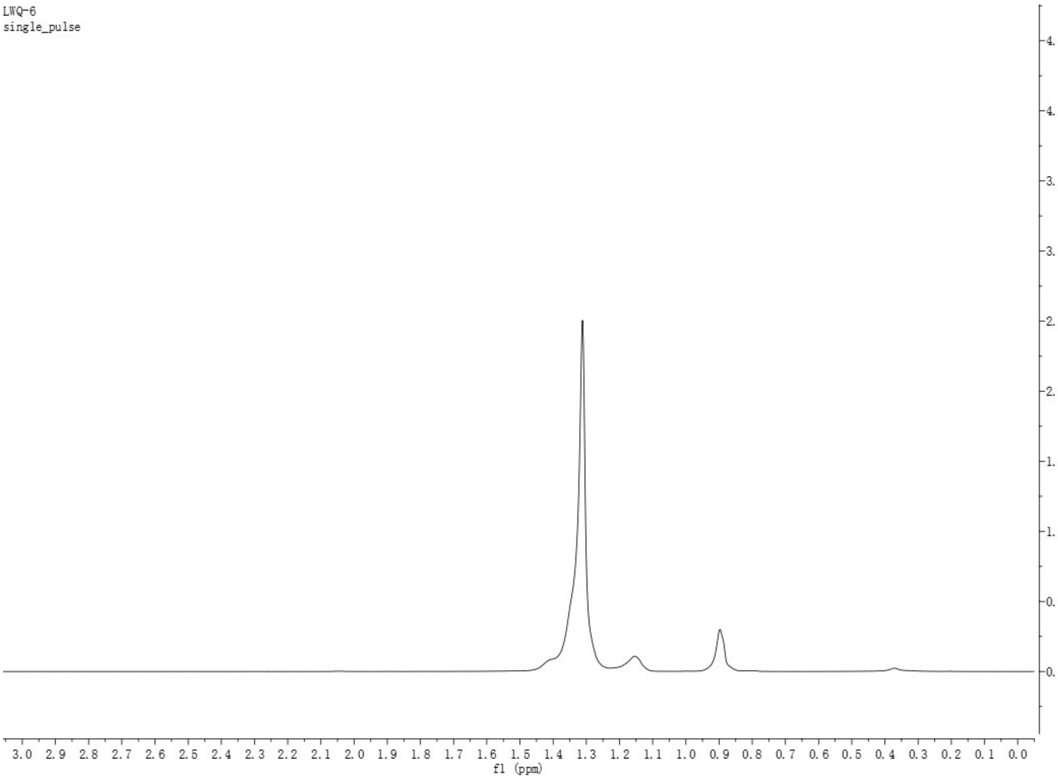


Figure S36. ^{1}H NMR (600 MHz, C_6D_6, 75 ℃) spectrum of the polymer from entry 6, Table 1.

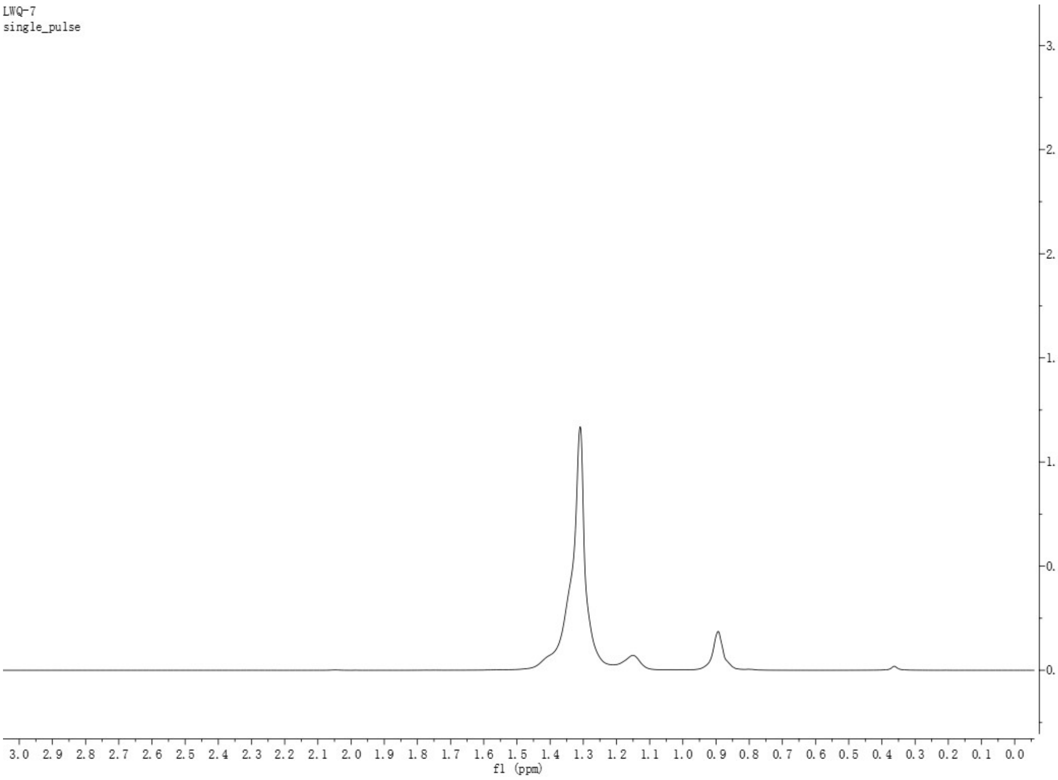


Figure S37. ^{1}H NMR (600 MHz, C_6D_6, 75 ℃) spectrum of the polymer from entry 7, Table 1.

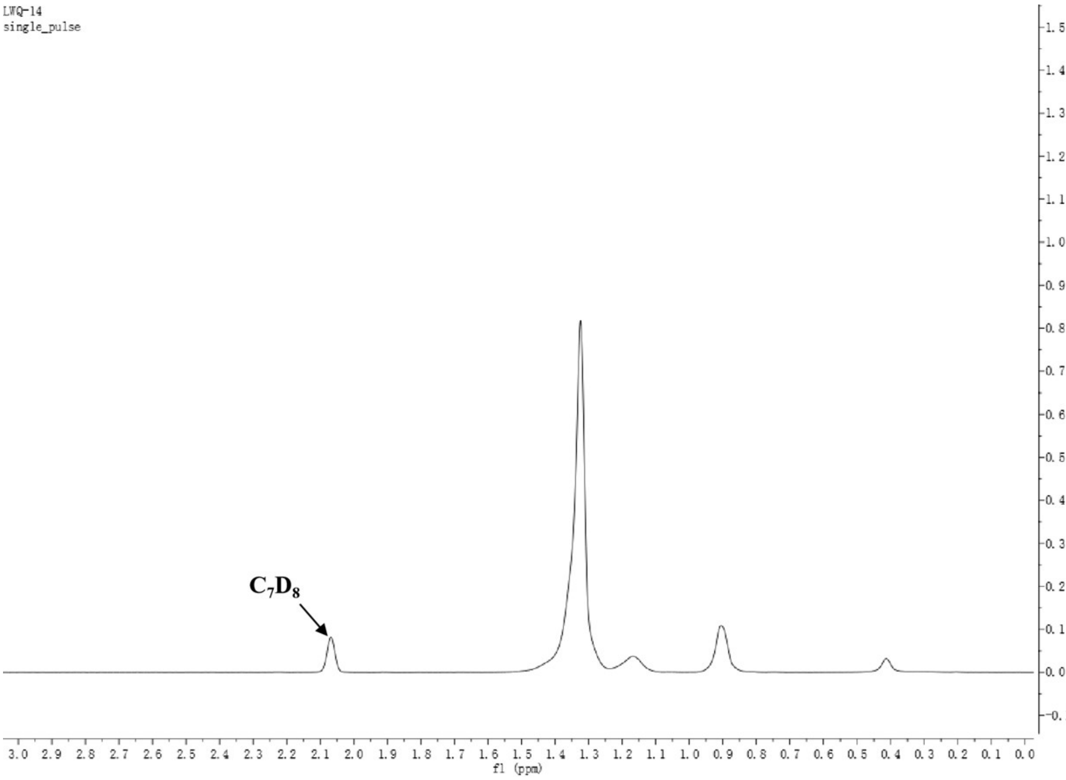


Figure S38. ^{1}H NMR (400 MHz, C_7D_8, 100 °C) spectrum of the polymer from entry 8, Table 1(C_7D_8, 100 °C).

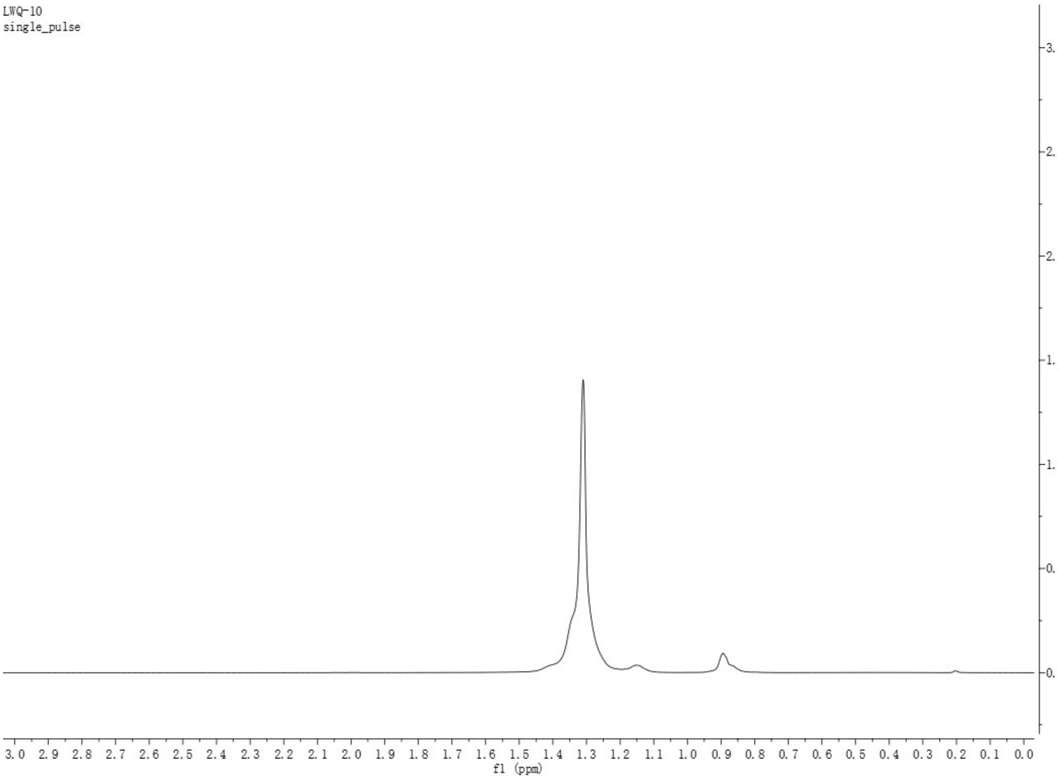


Figure S39. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 10, Table 1.

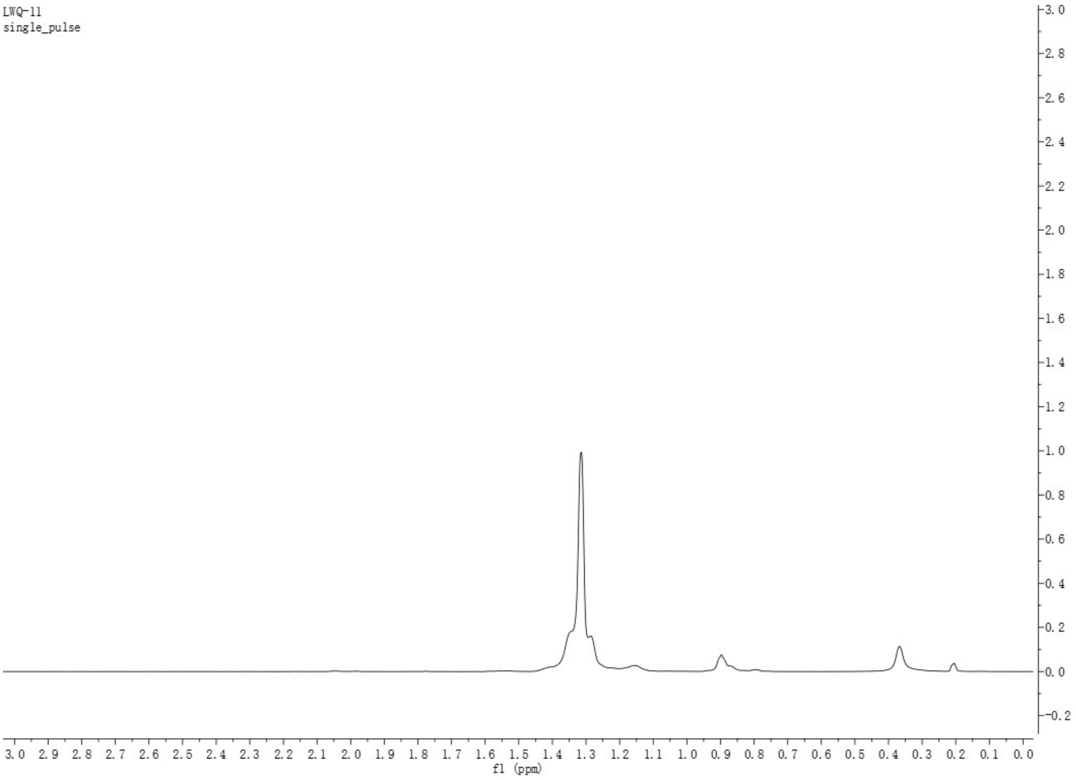


Figure S40. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 11, Table 1.

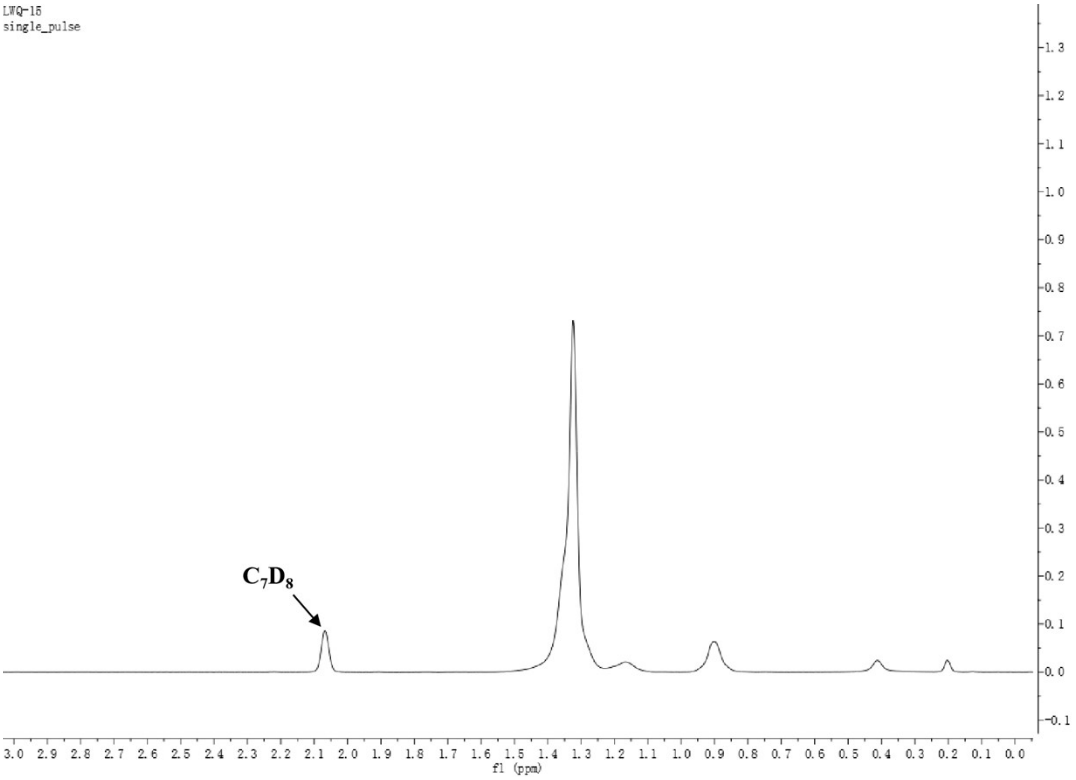


Figure S41. ^{1}H NMR (400 MHz, C_7D_8, 100 °C) spectrum of the polymer from entry 12, Table 1.

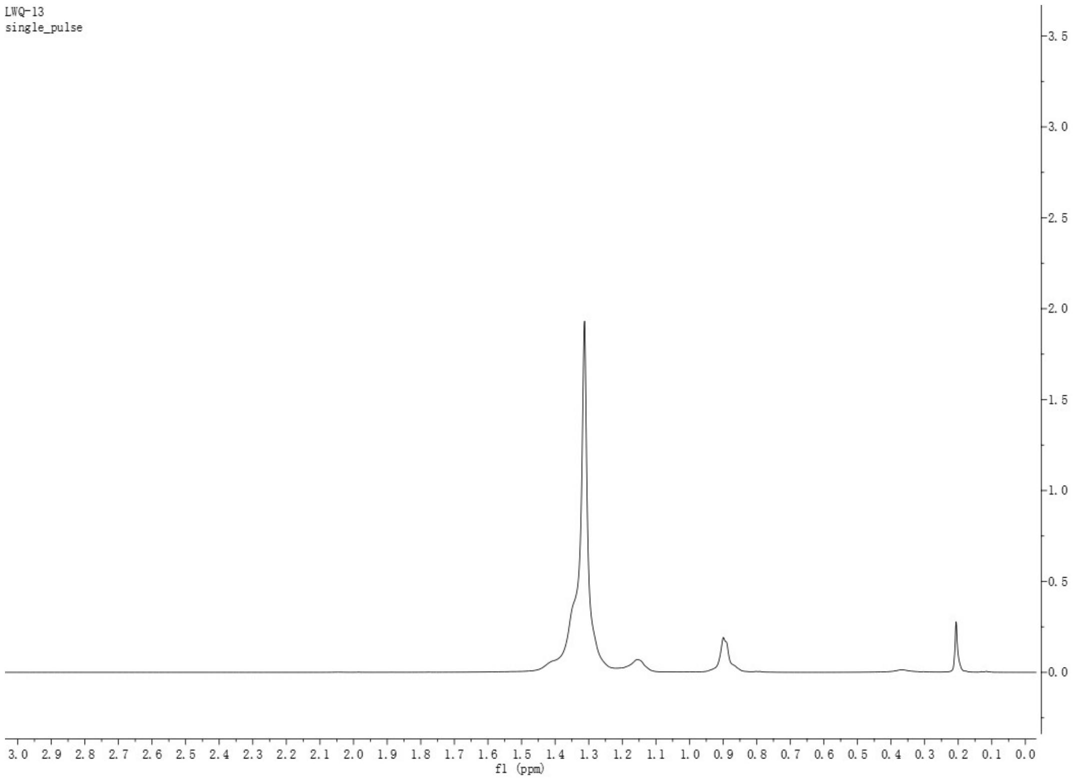


Figure S42. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 13, Table 1.

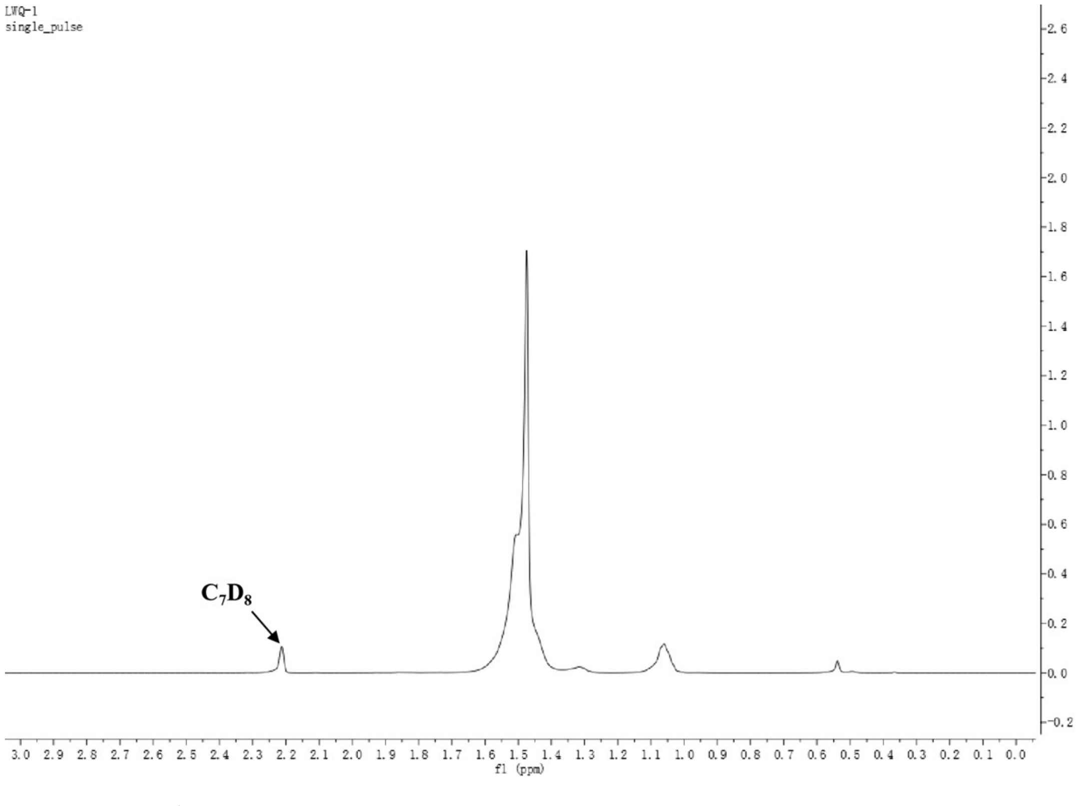


Figure S43. ^{1}H NMR (600 MHz, C_7D_8, 100 °C) spectrum of the polymer from entry 1,Table 2.

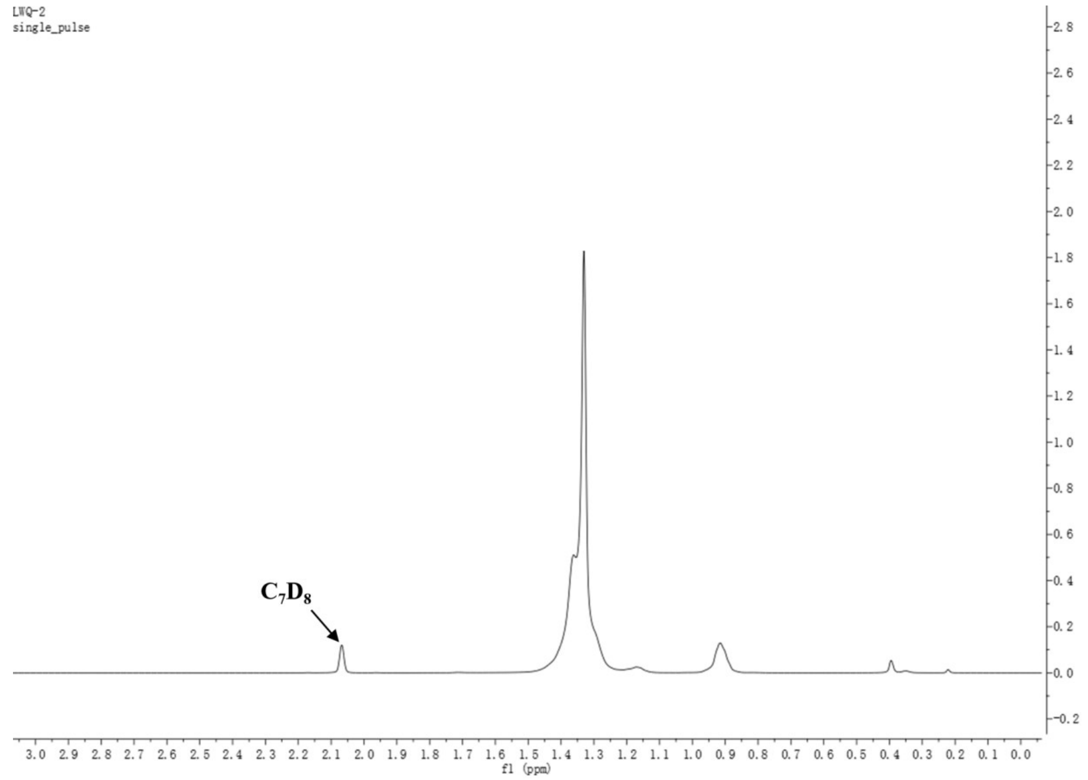


Figure S44. ^{1}H NMR (600 MHz, C_7D_8, 100 °C) spectrum of the polymer from entry 2, Table 2.

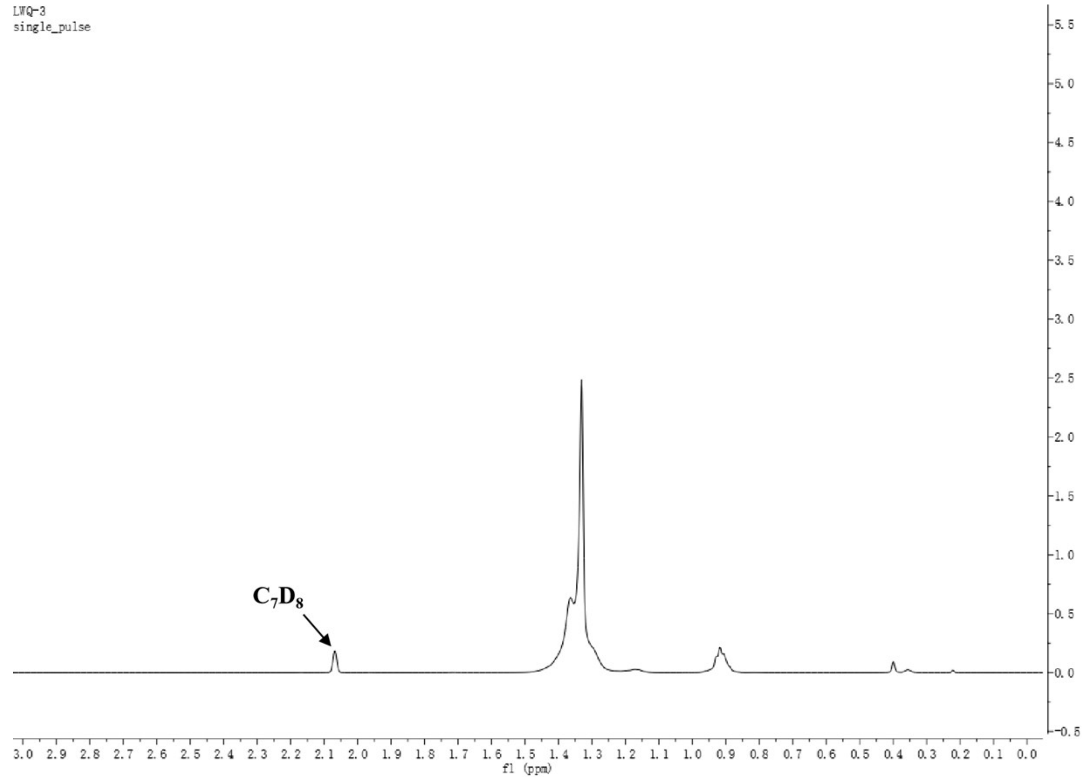


Figure S45. ^{1}H NMR (600 MHz, C_7D_8, 100 °C) spectrum of the polymer from entry 3, Table 2.

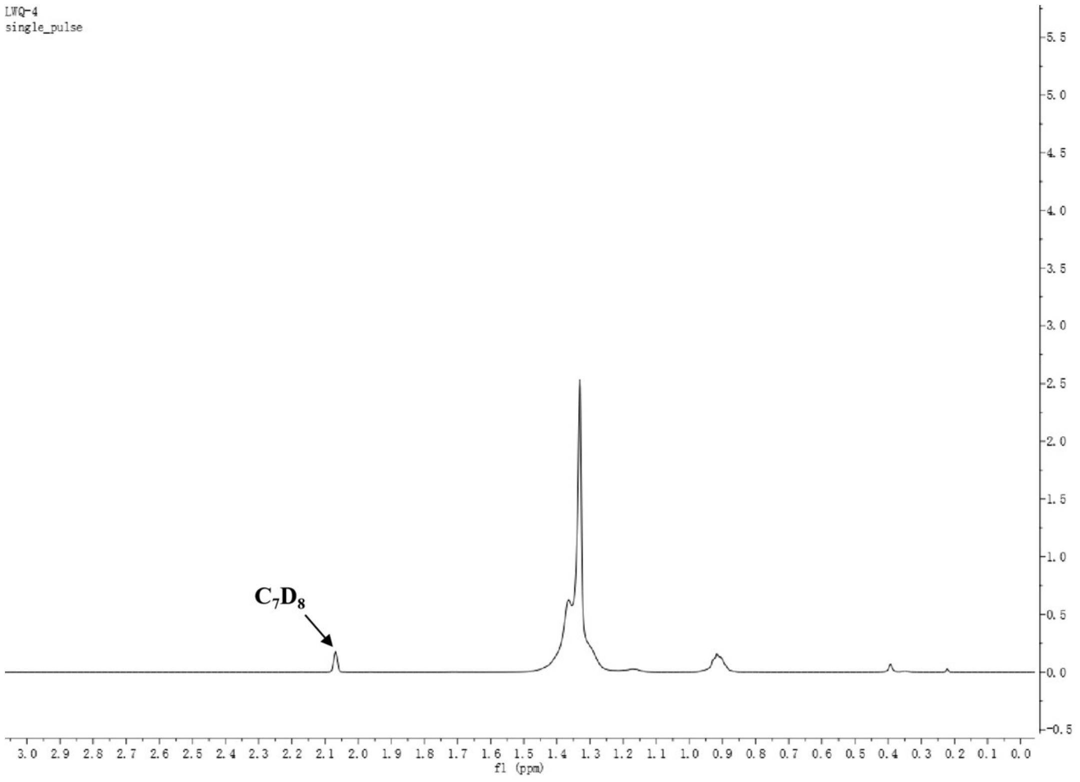


Figure S46. ^{1}H NMR (600 MHz, C_7D_8, 100 °C) spectrum of the polymer from entry 4, Table 2.

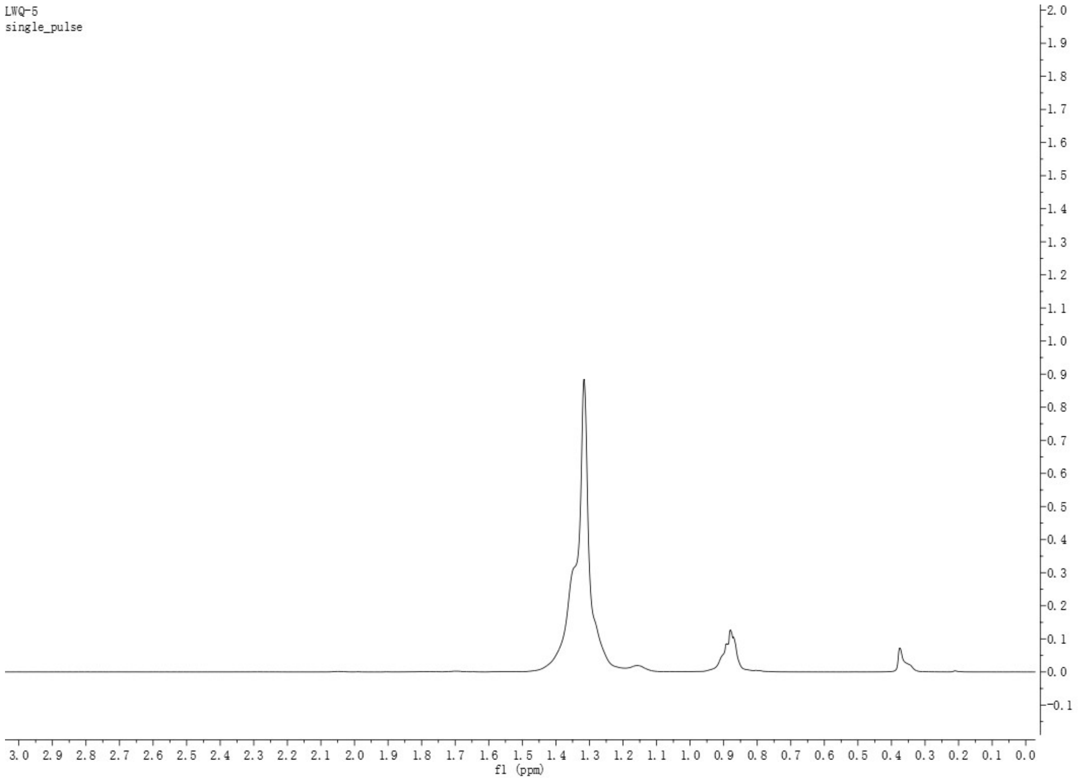


Figure S47. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 5, Table 2.

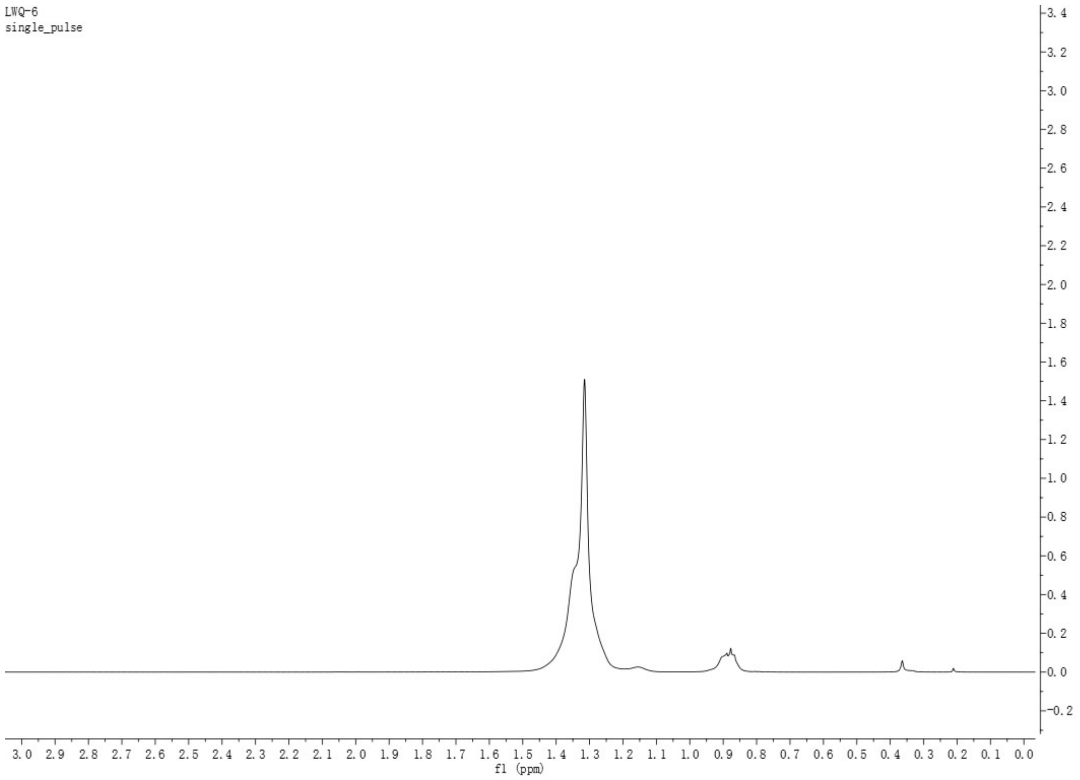


Figure S48. ^{1}H NMR (600 MHz, C_6D_6, 75 ℃) spectrum of the polymer from entry 6, Table 2.

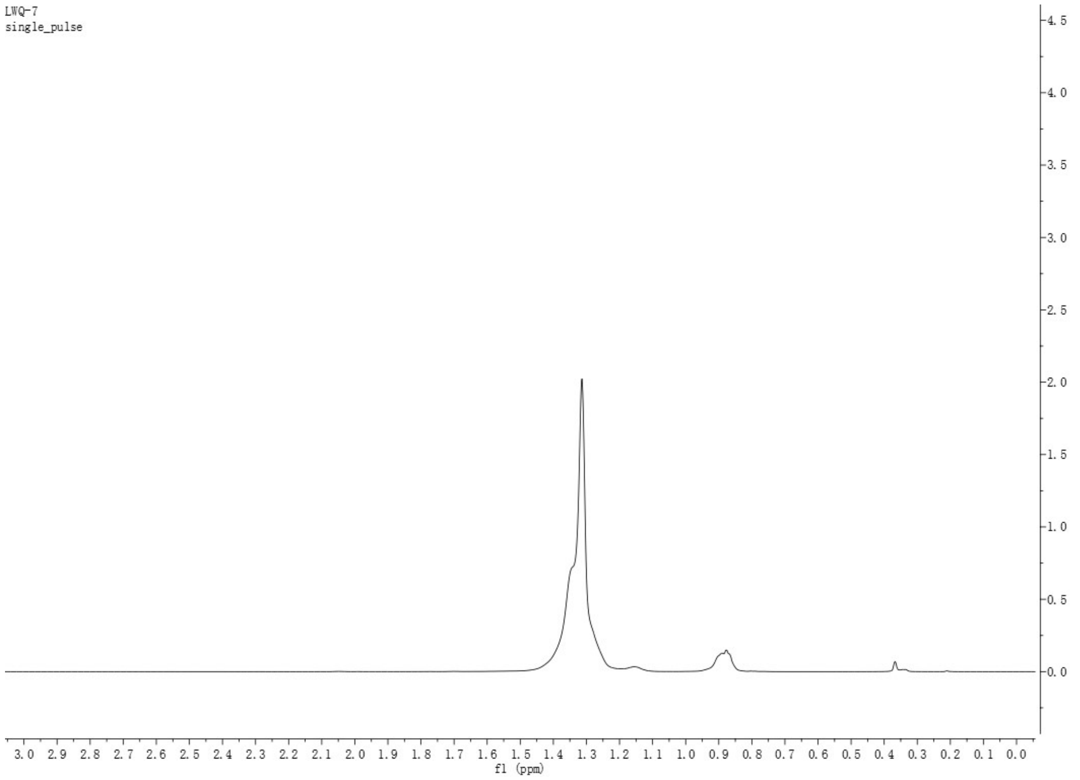


Figure S49. ^{1}H NMR (600 MHz, C_6D_6, 75 ℃) spectrum of the polymer from entry 7, Table 2.

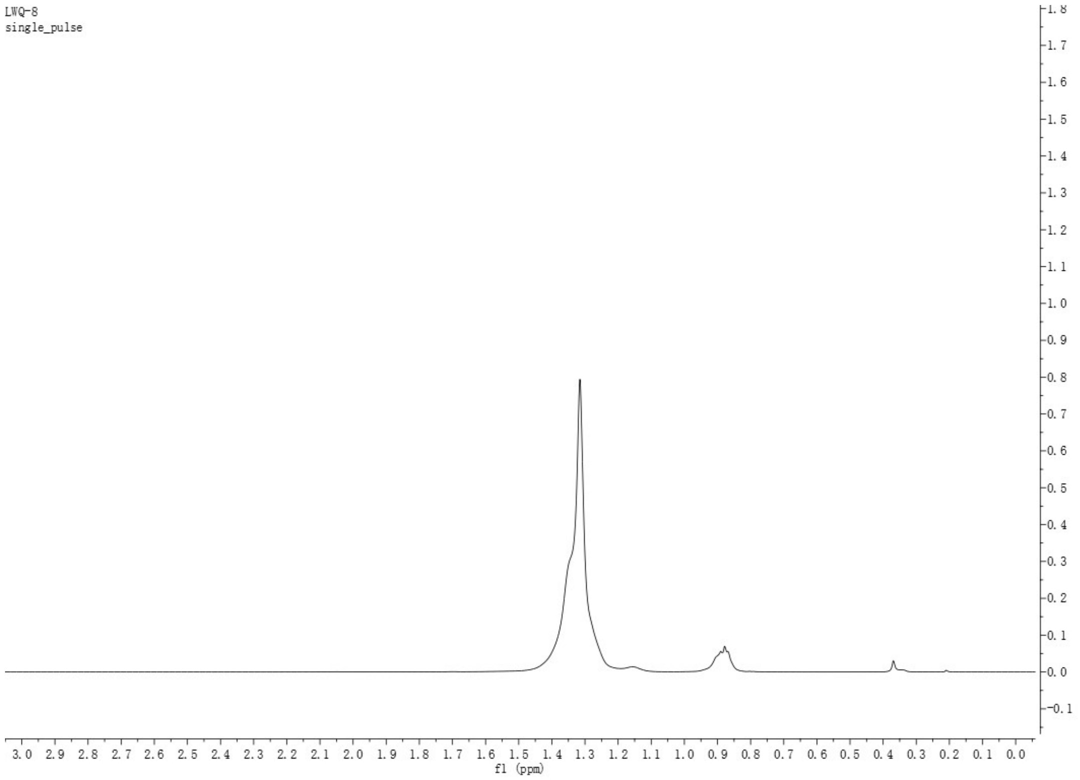


Figure S50. ^{1}H NMR (600 MHz, C_6D_6, 75 ℃) spectrum of the polymer from entry 8, Table 2.

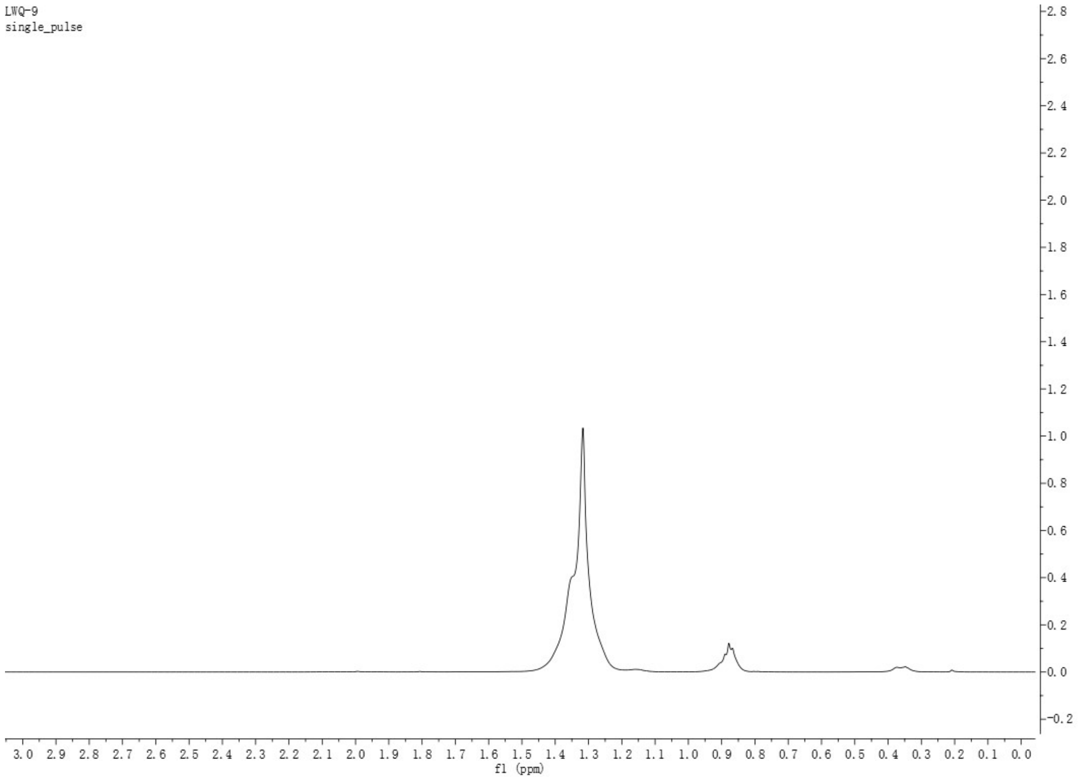


Figure S51. ^{1}H NMR (600 MHz, C_6D_6, 75 ℃) spectrum of the polymer from entry 9, Table 2.

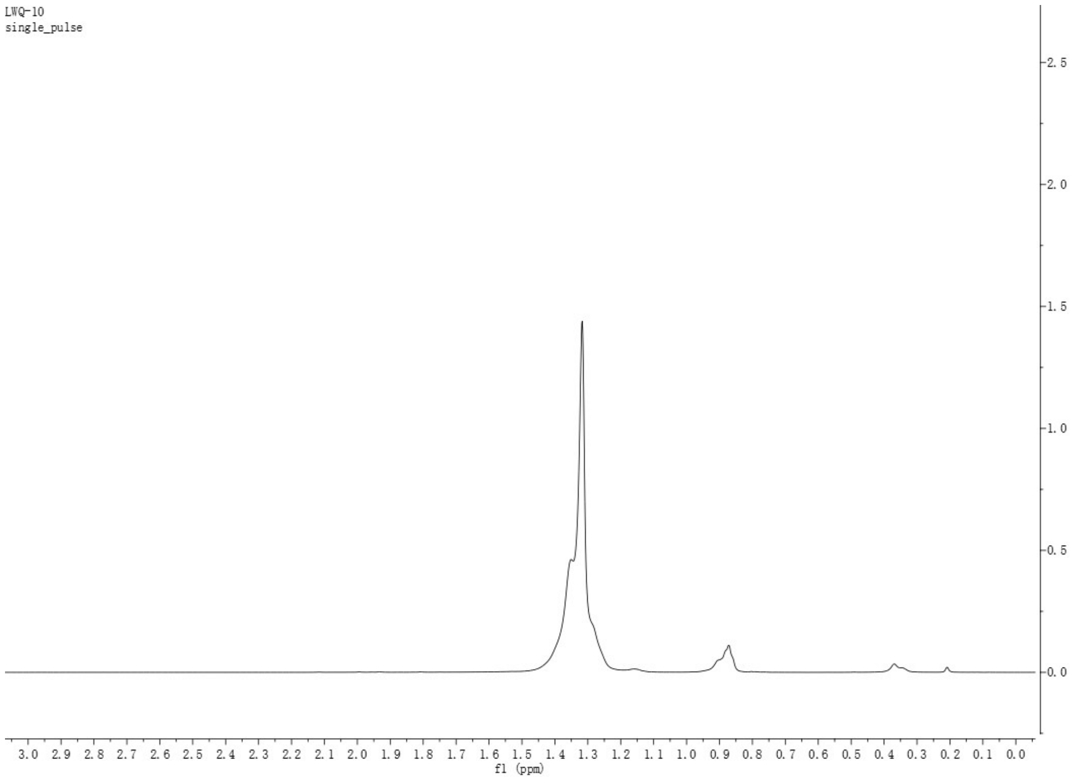


Figure S52. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 10, Table 2.

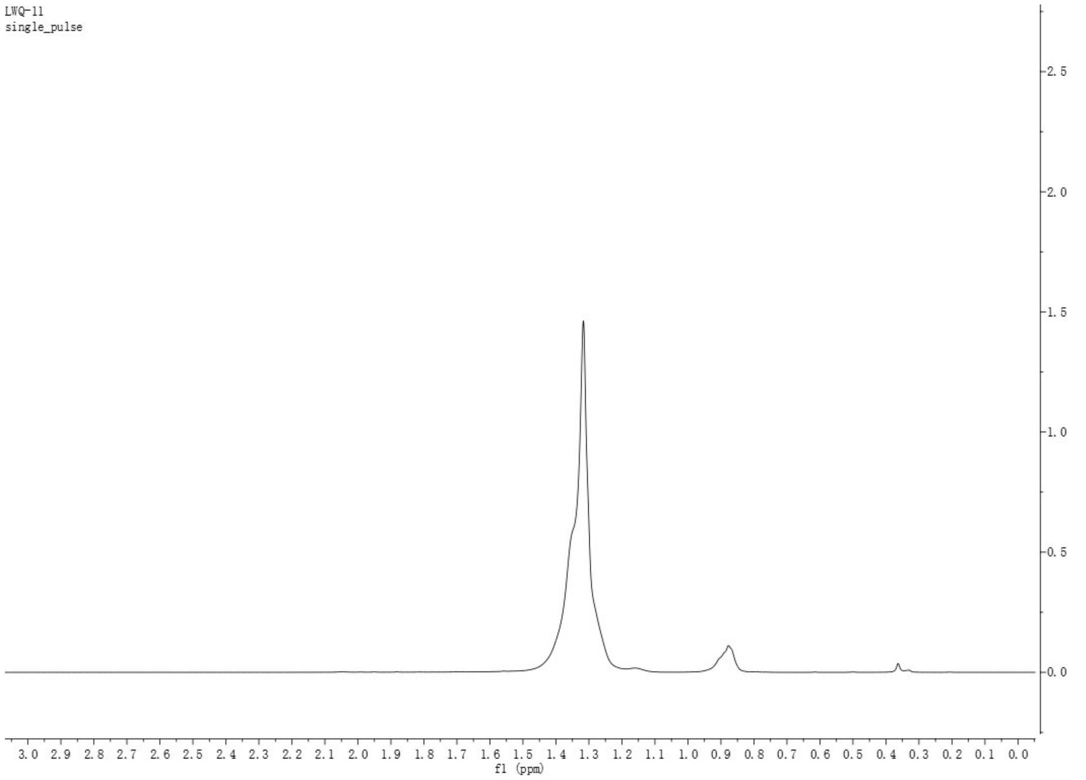


Figure S53. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 11, Table 2.

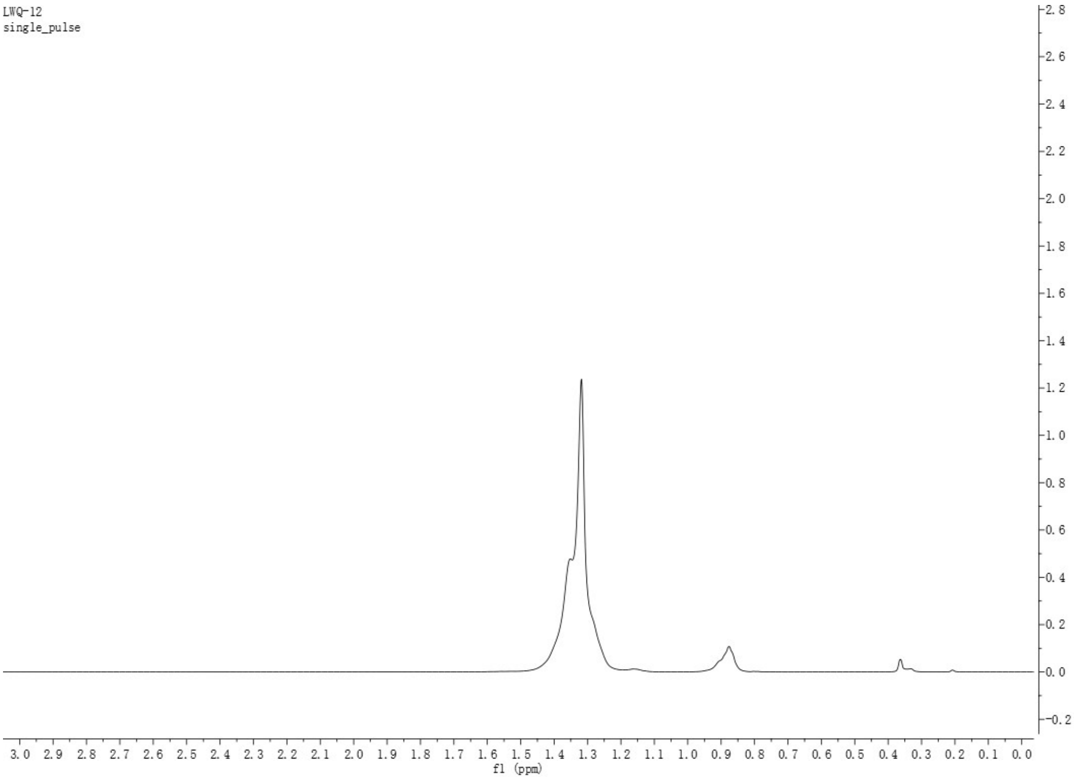


Figure S54. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 12, Table 2.

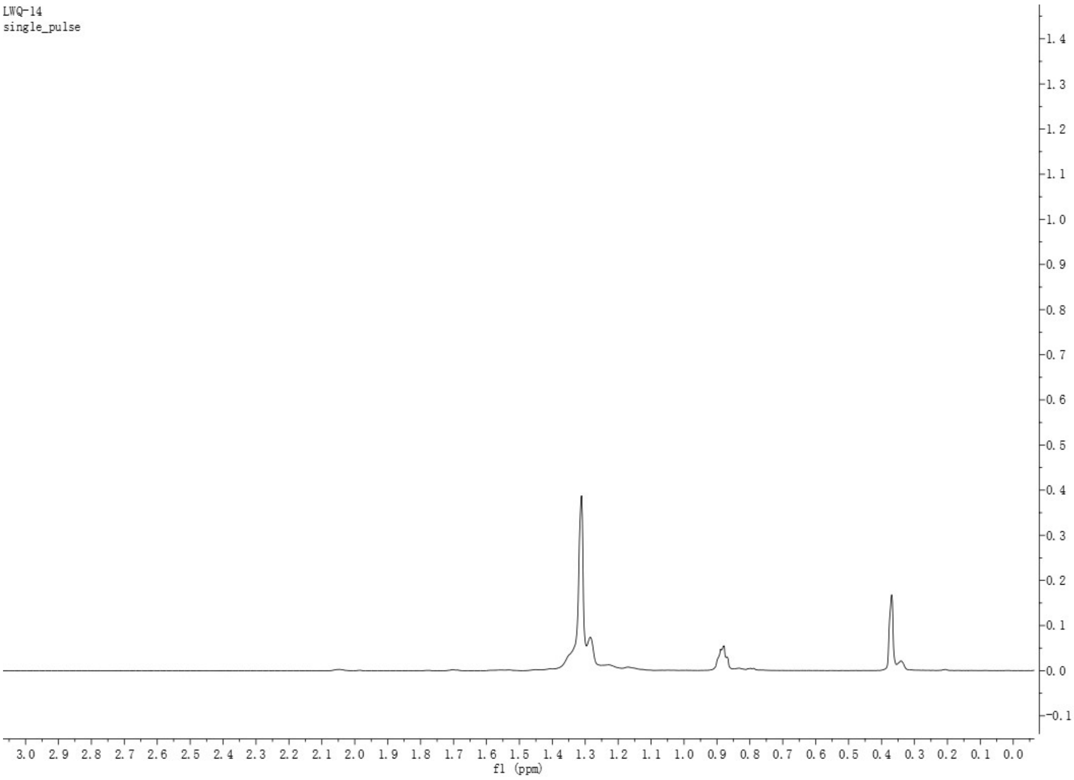


Figure S55. ^{1}H NMR (600 MHz, C_6D_6, 75 °C) spectrum of the polymer from entry 13, Table 2.

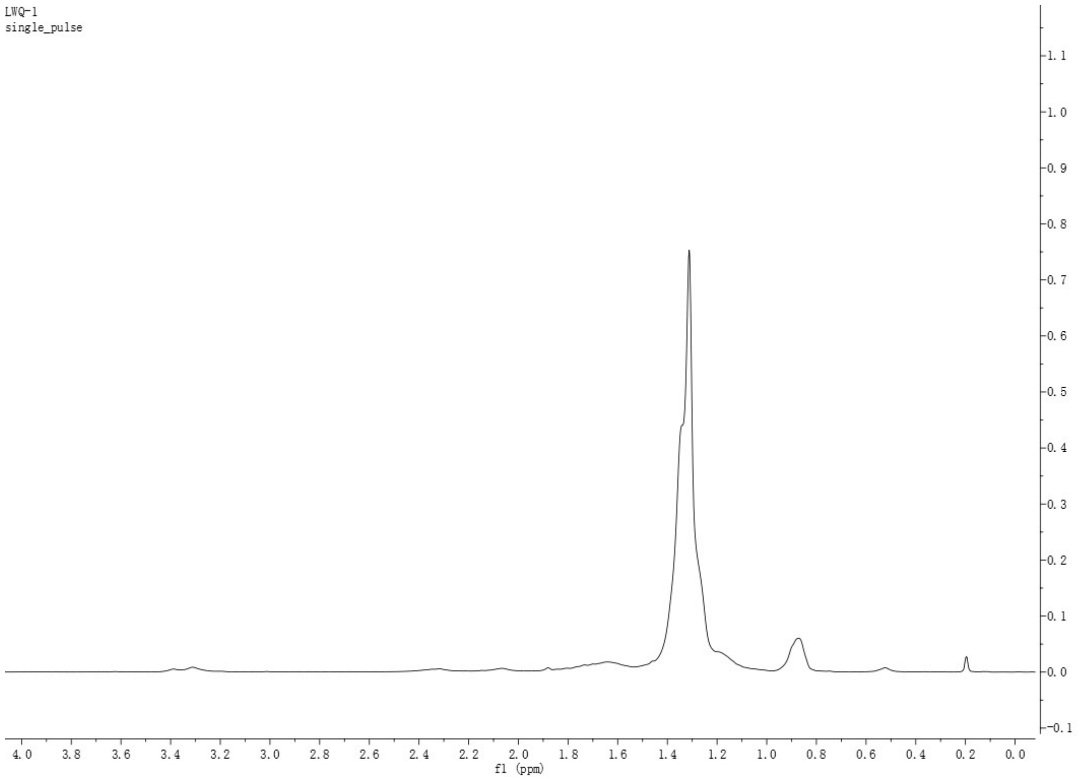


Figure S56. ^{1}H NMR (400 MHz, C_6D_6, 75 °C) spectrum of the copolymer from entry 1,Table 3.

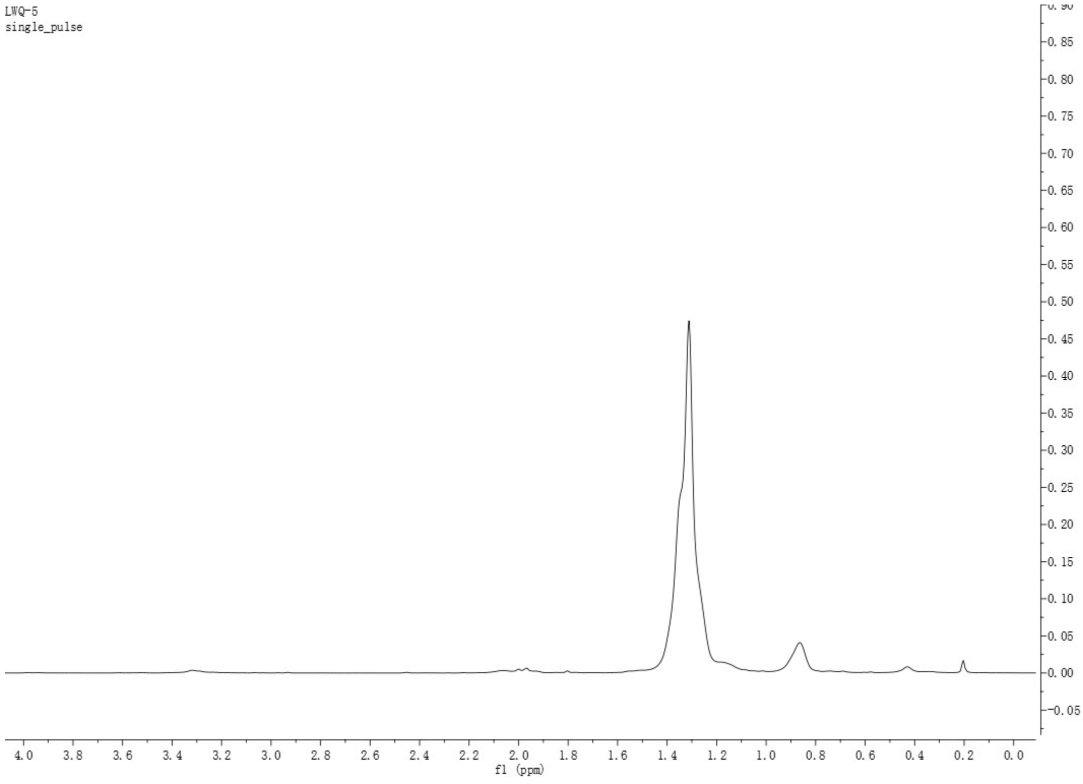


Figure S57. ^{1}H NMR (400 MHz, C_6D_6, 75 °C) spectrum of the copolymer from entry 5, Table 3.

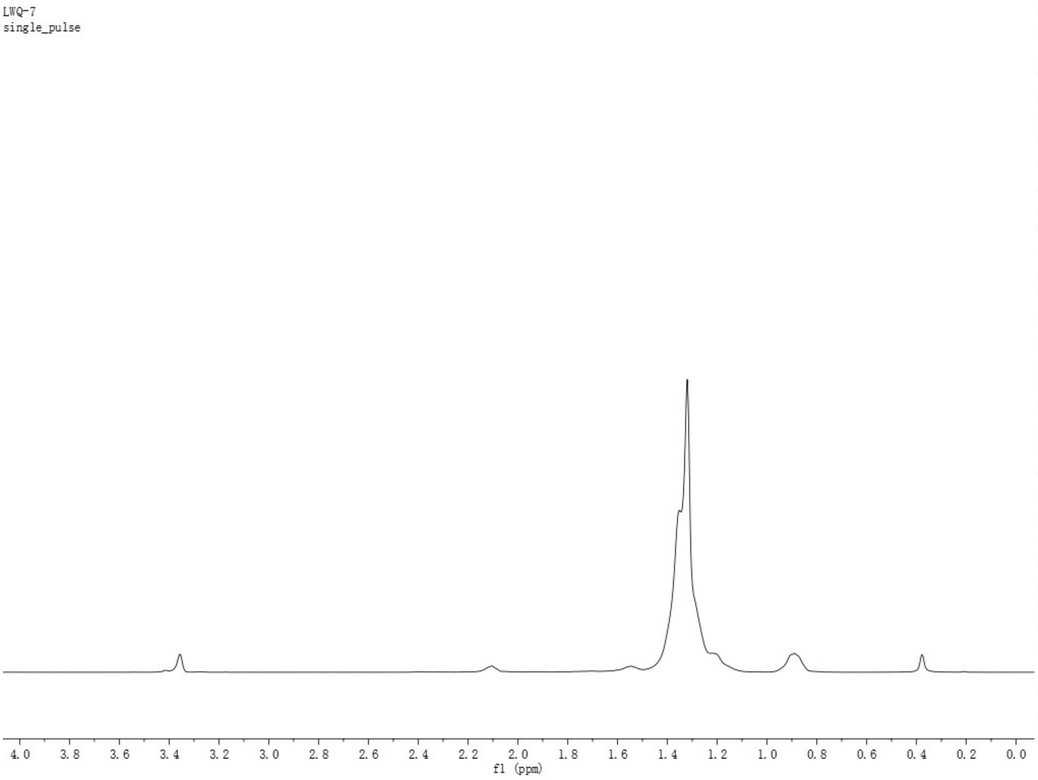


Figure S58. ^{1}H NMR (400 MHz, C_6D_6, 75 ℃) spectrum of the copolymer from entry 7, Table 3.

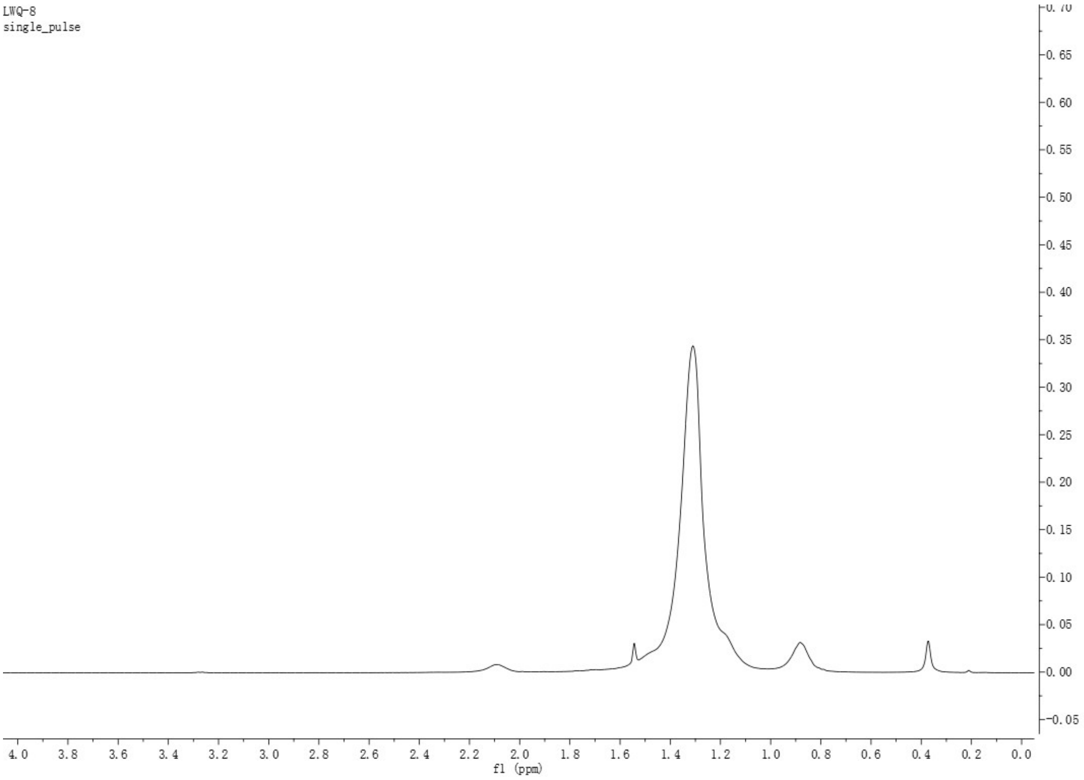


Figure S59. ^{1}H NMR (400 MHz, C_6D_6, 75 ℃) spectrum of the copolymer from entry 10, Table 3.

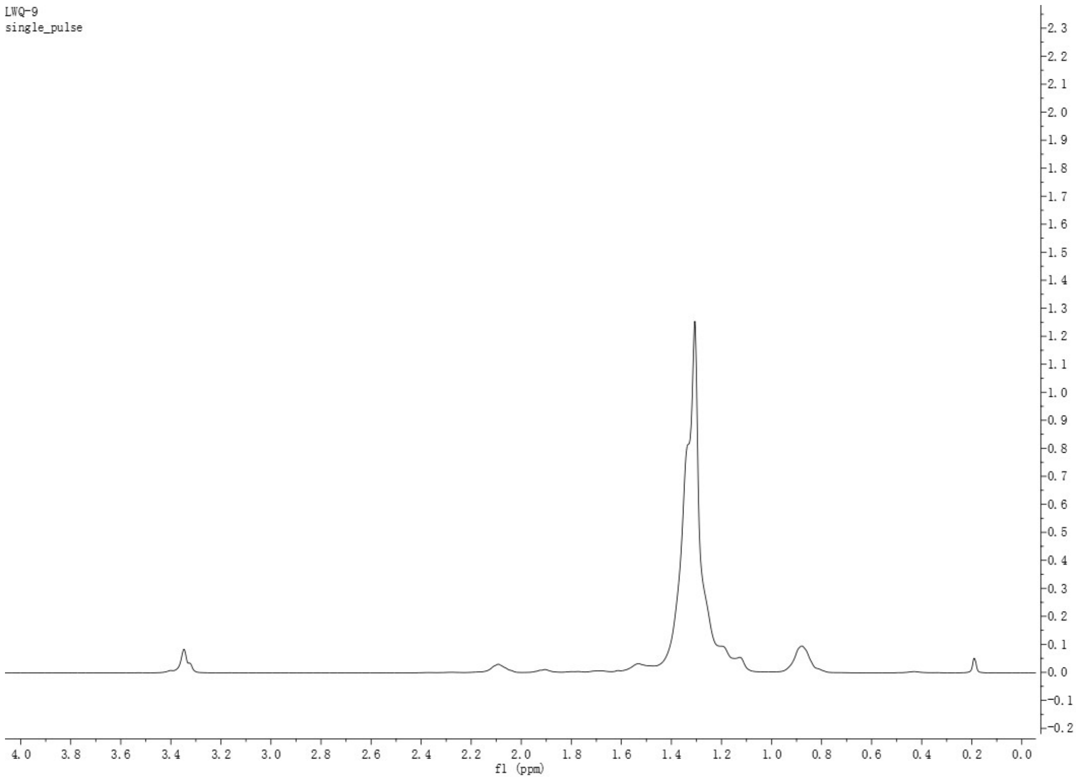


Figure S60. ^{1}H NMR (400 MHz, C_6D_6, 75 ℃) spectrum of the copolymer from entry 8, Table 3.

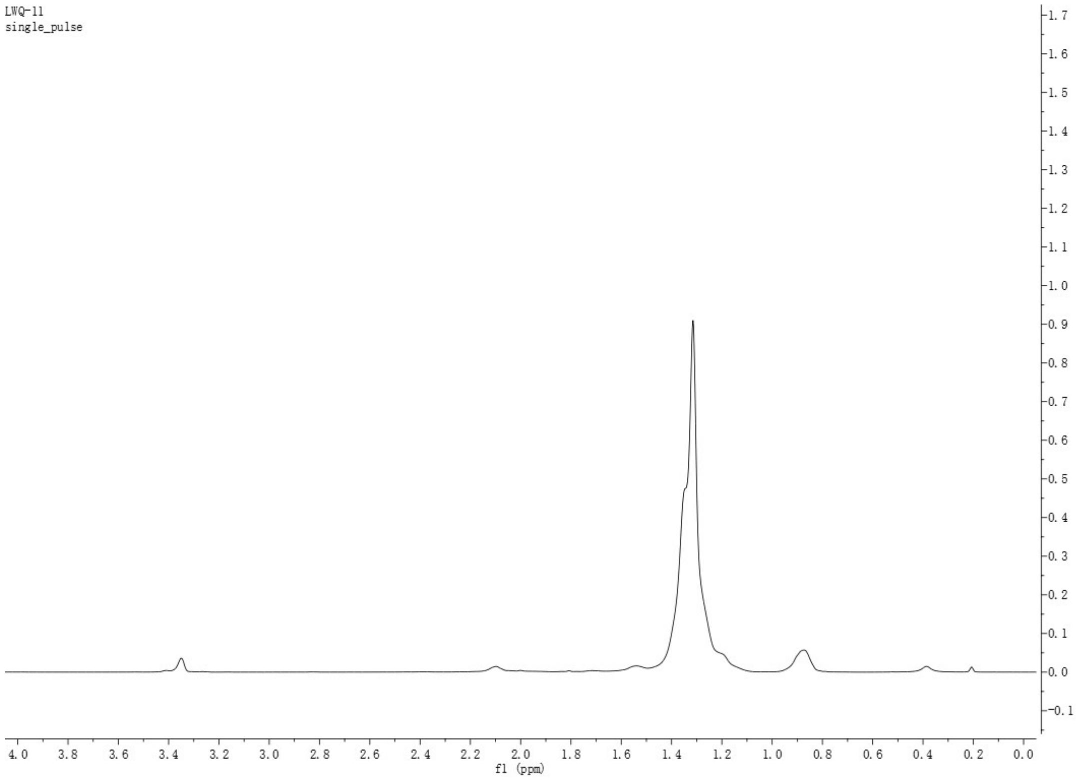


Figure S61. ^{1}H NMR (400 MHz, C_6D_6, 75 ℃) spectrum of the copolymer from entry 9, Table 3.

2.4 DSC of Representative Polymers

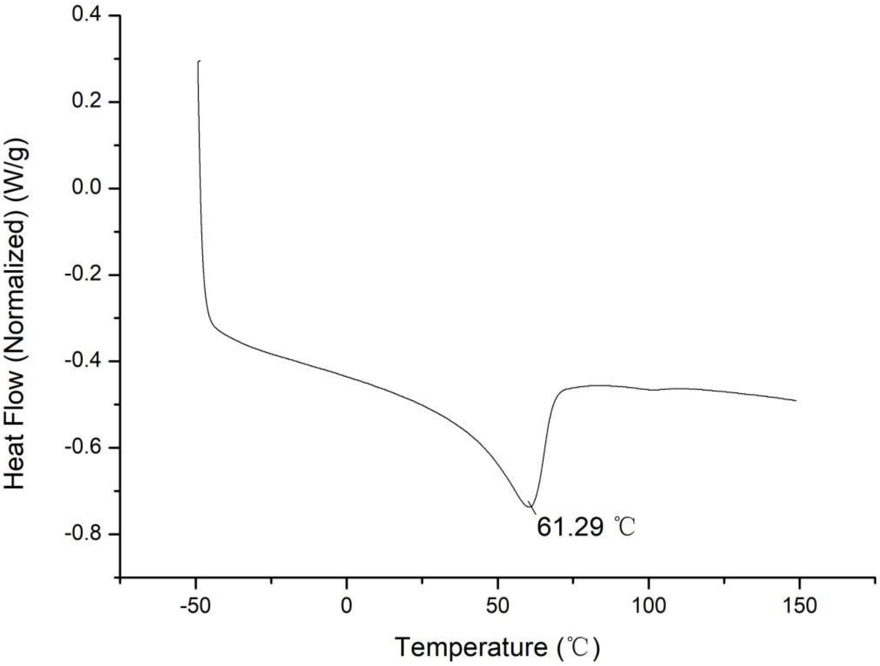


Figure S62. DSC of the polymer from entry 1, Table 1.

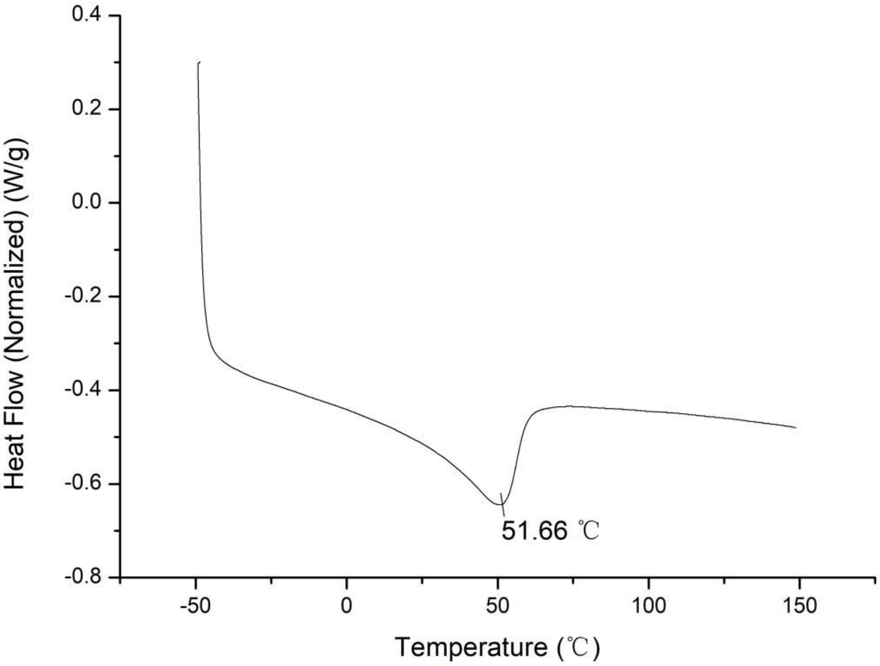


Figure S63. DSC of the polymer from entry 2, Table 1.

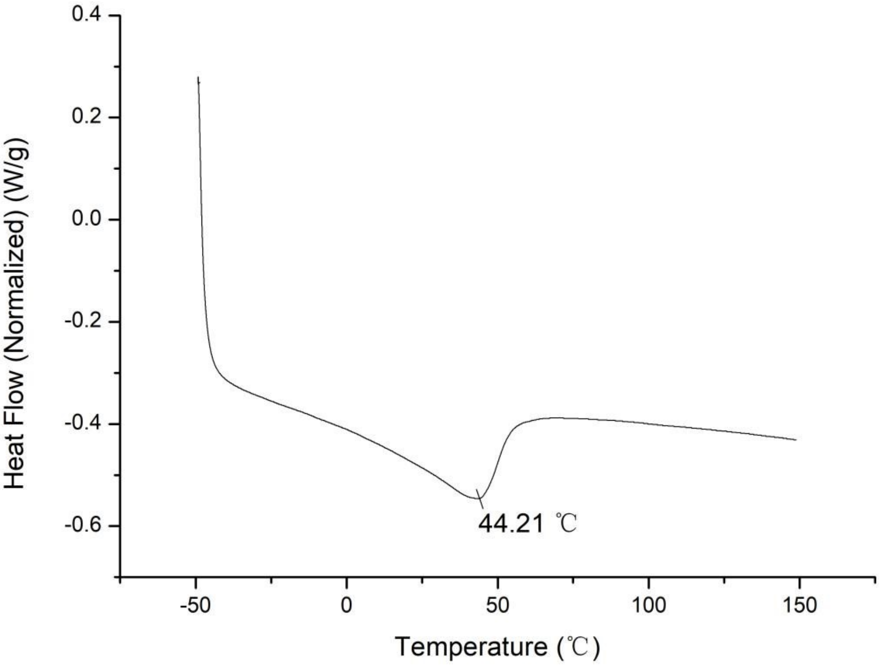


Figure S64. DSC of the polymer from entry 3, Table 1.

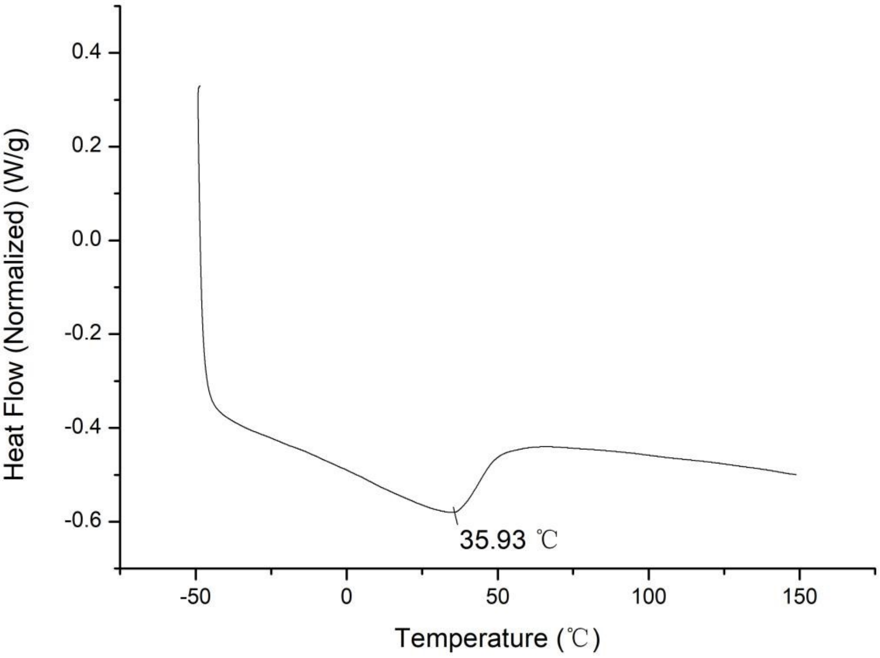


Figure S65. DSC of the polymer from entry 4, Table 1.

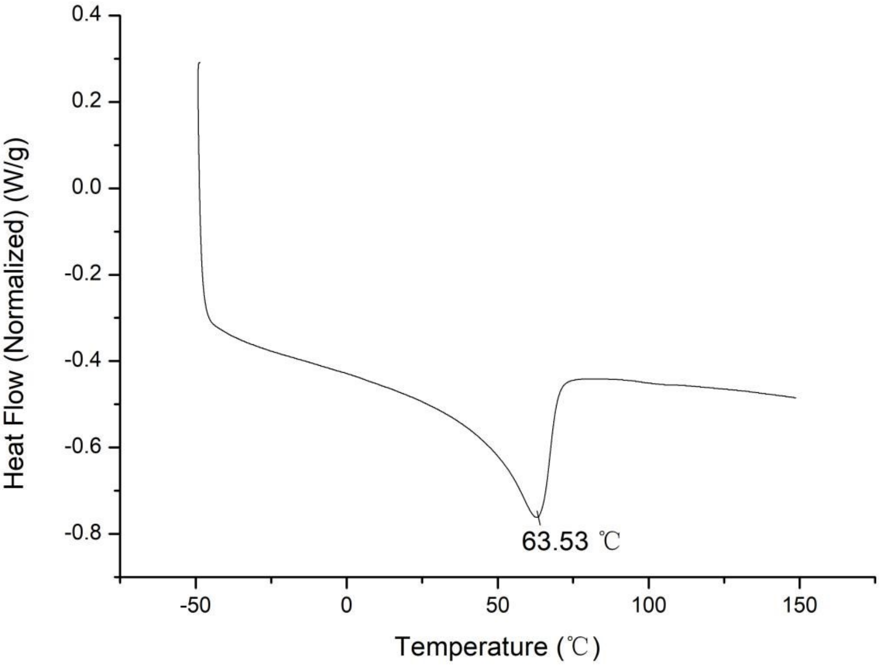


Figure S66. DSC of the polymer from entry 5, Table 1.

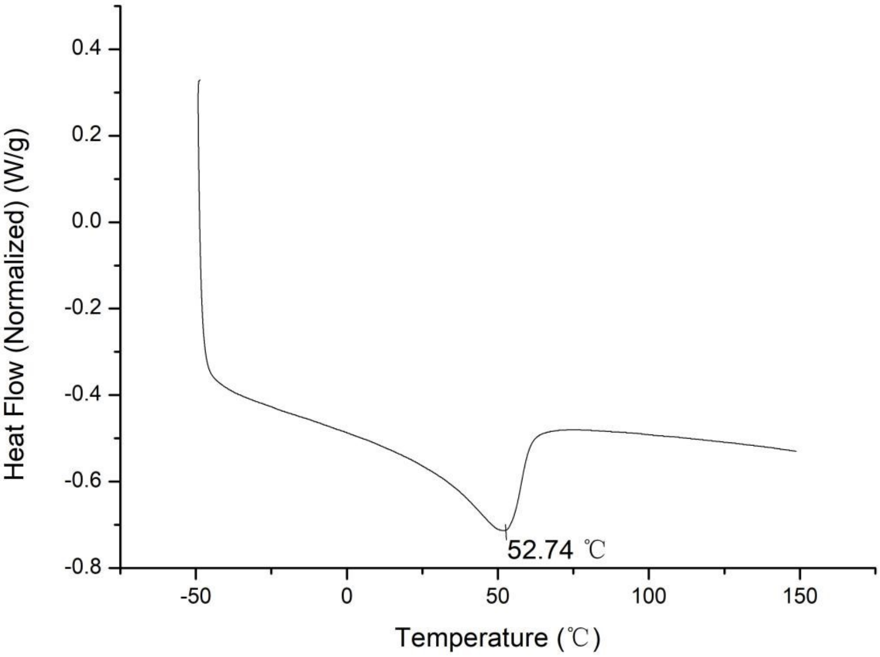


Figure S67. DSC of the polymer from entry 6, Table 1.

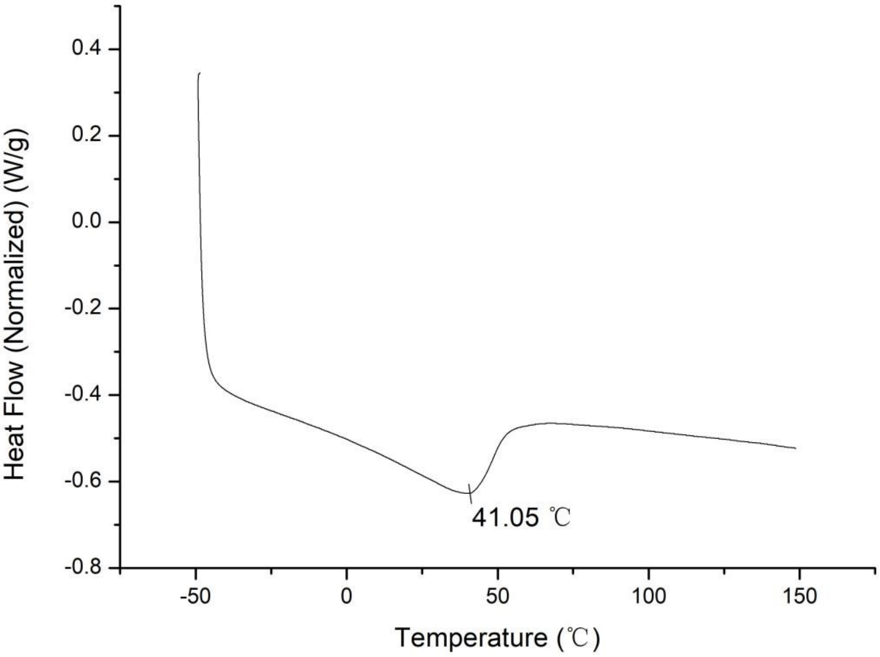


Figure S68. DSC of the polymer from entry 7, **Table 1.**

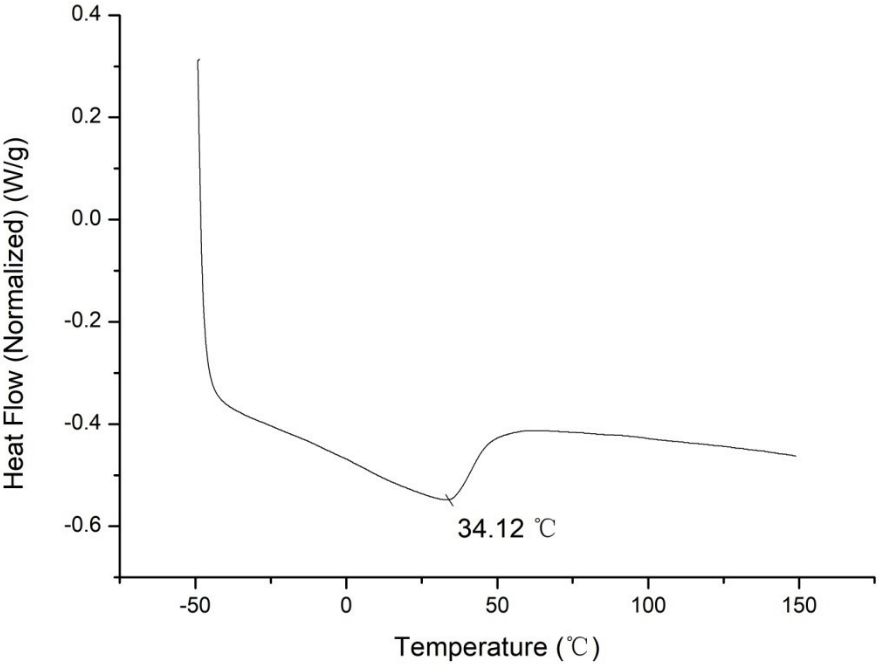


Figure S69. DSC of the polymer from entry 8, Table 1.

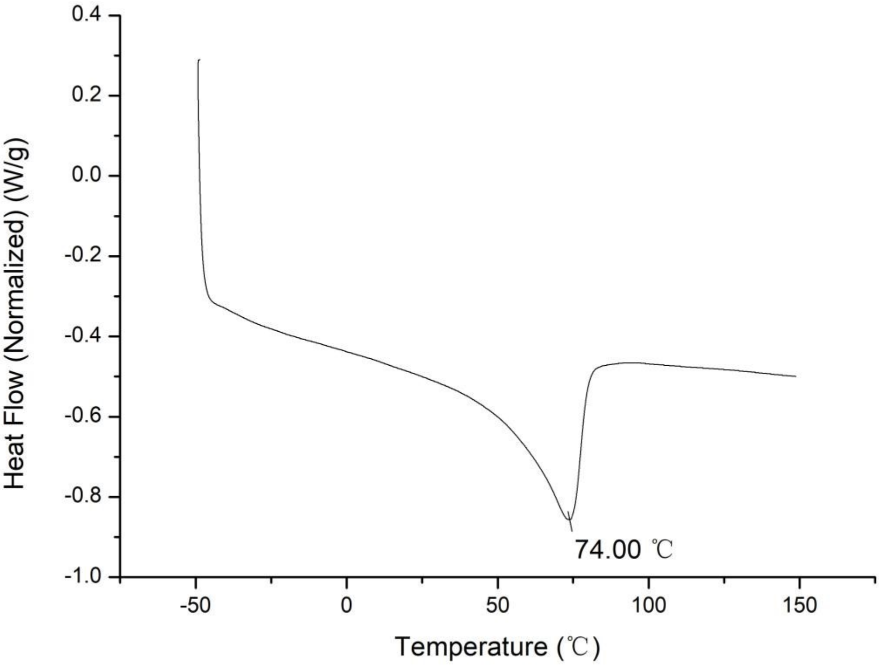


Figure S70. DSC of the polymer from entry 9, Table 1.

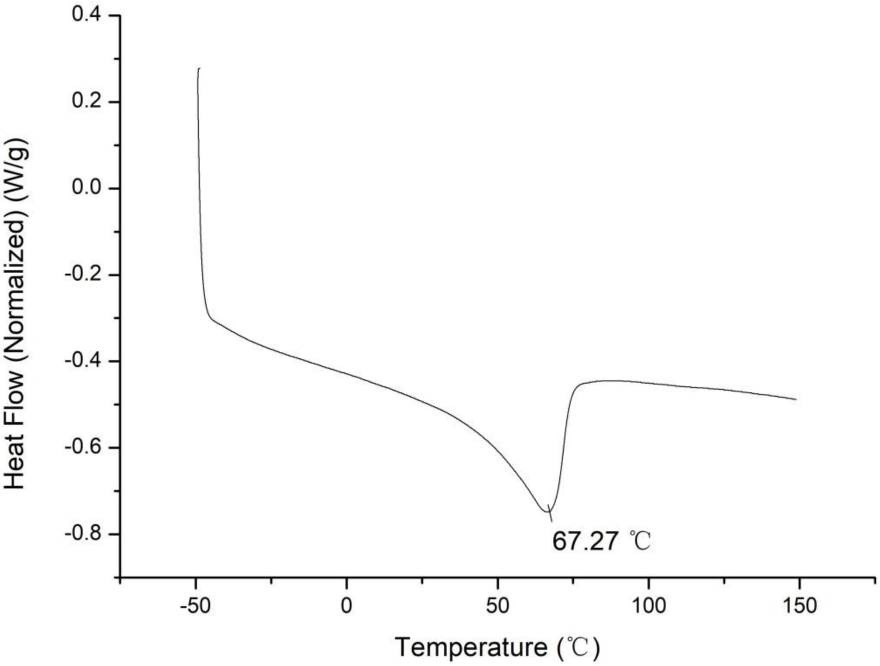


Figure S71. DSC of the polymer from entry 10, Table 1.

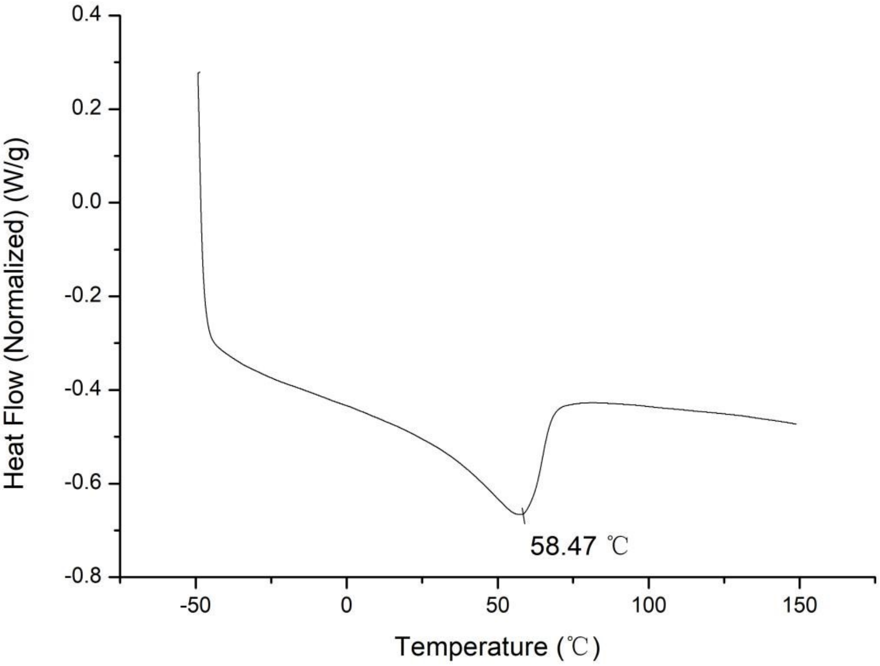


Figure S72. DSC of the polymer from entry 11, Table 1.

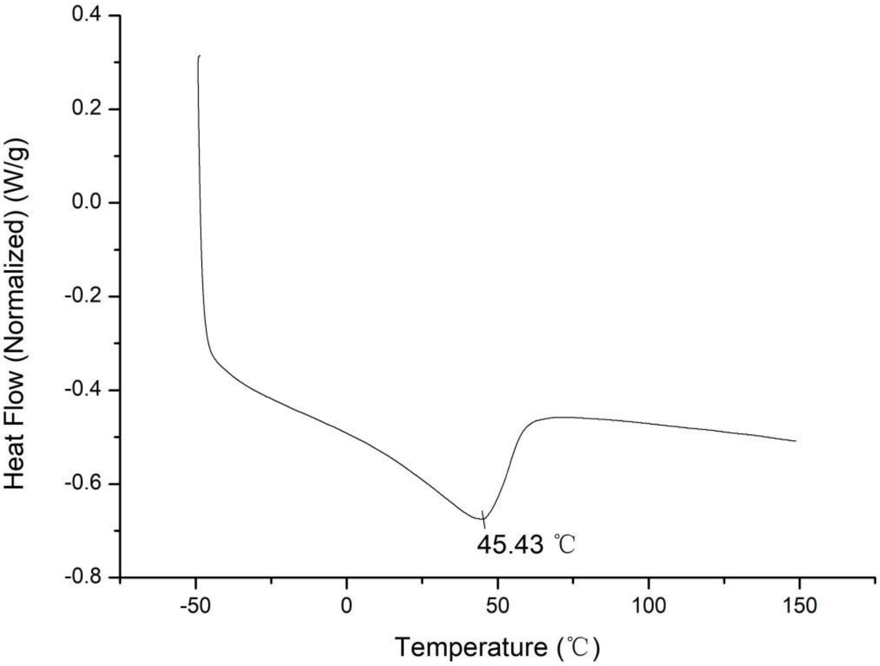


Figure S73. DSC of the polymer from entry 12, Table 1.

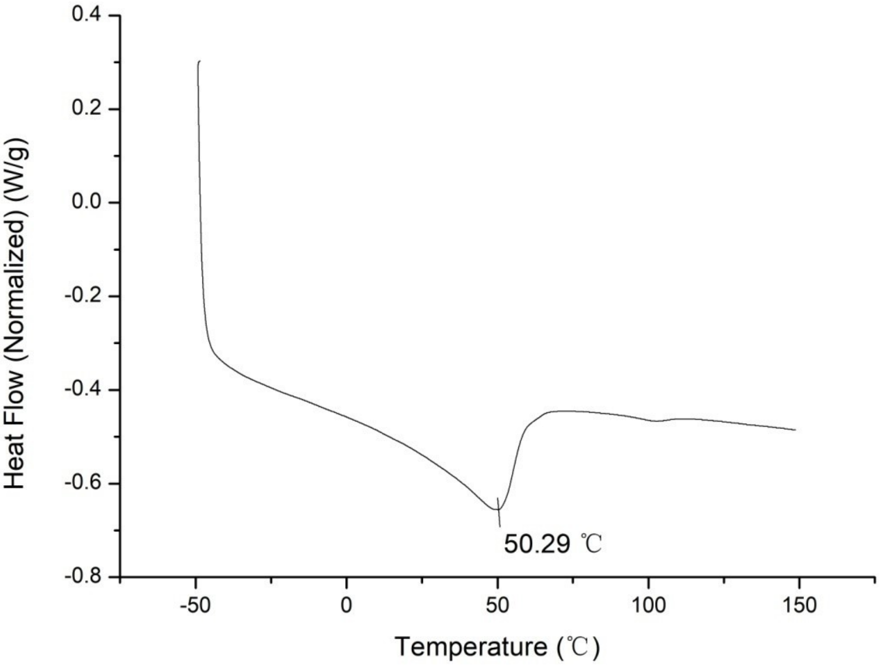


Figure S74. DSC of the polymer from entry 13,Table 1.

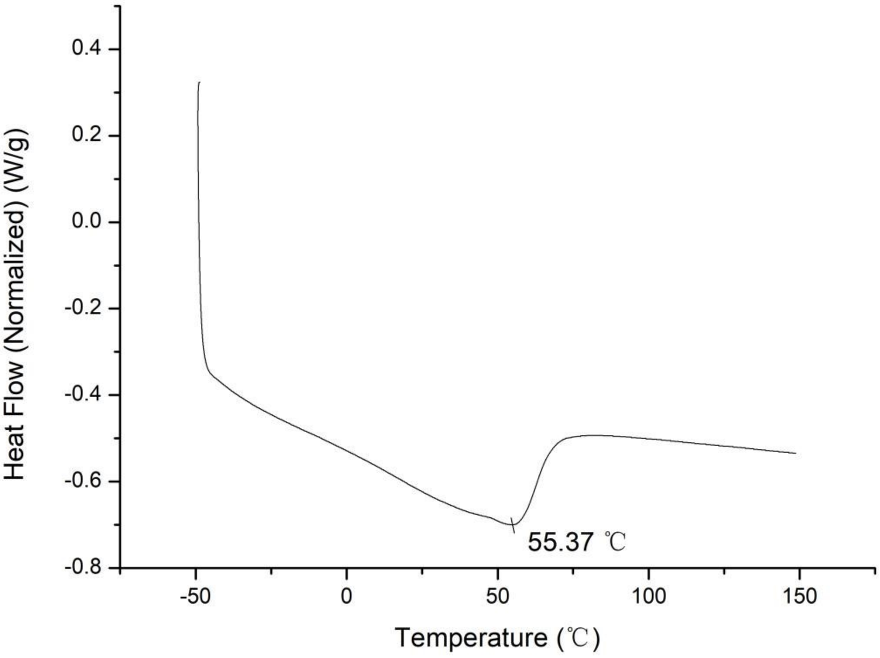


Figure S75. DSC of the polymer from entry 1, Table 2.

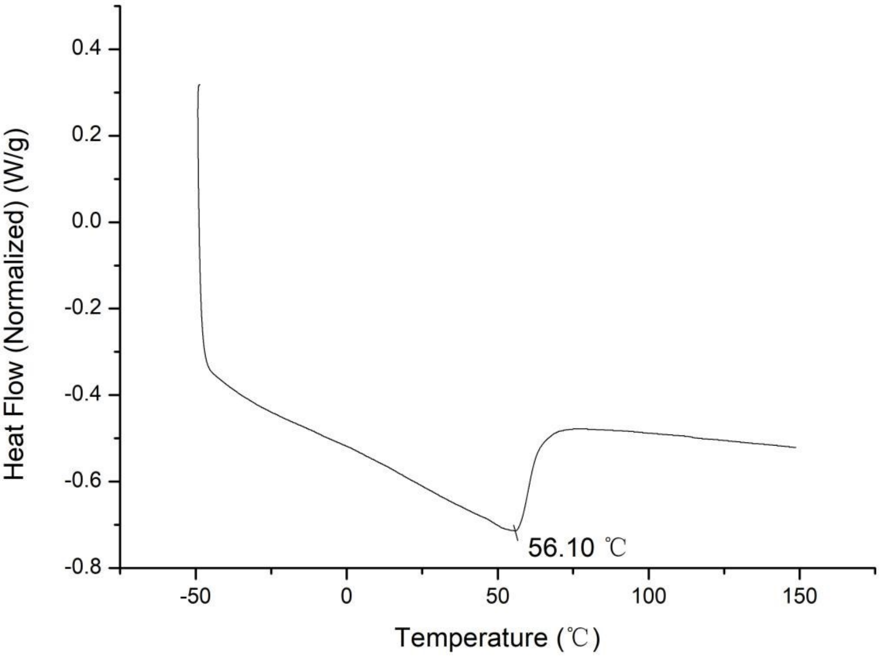


Figure S76. DSC of the polymer from entry 2, Table 2.

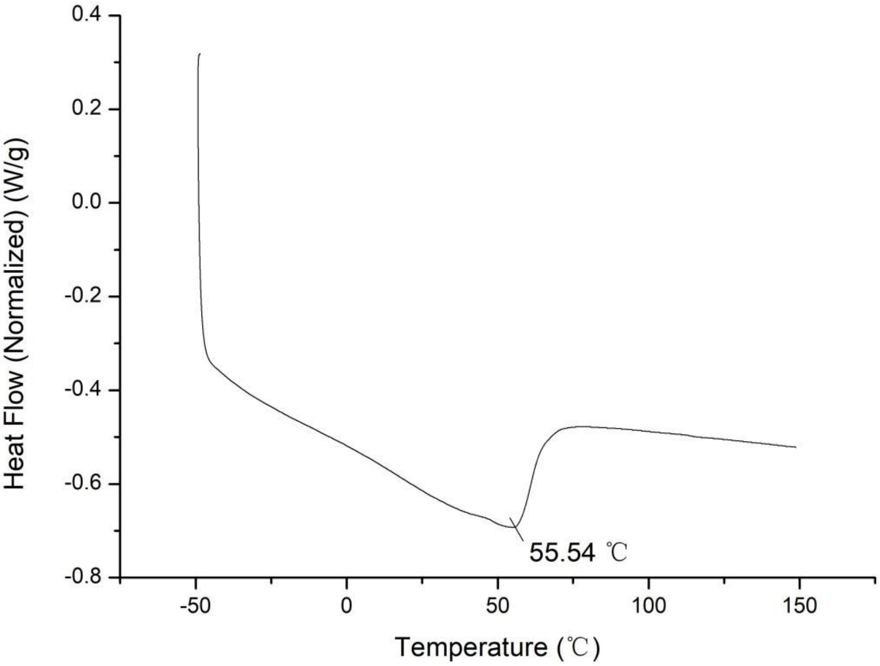


Figure S77. DSC of the polymer from entry 3, Table 2.

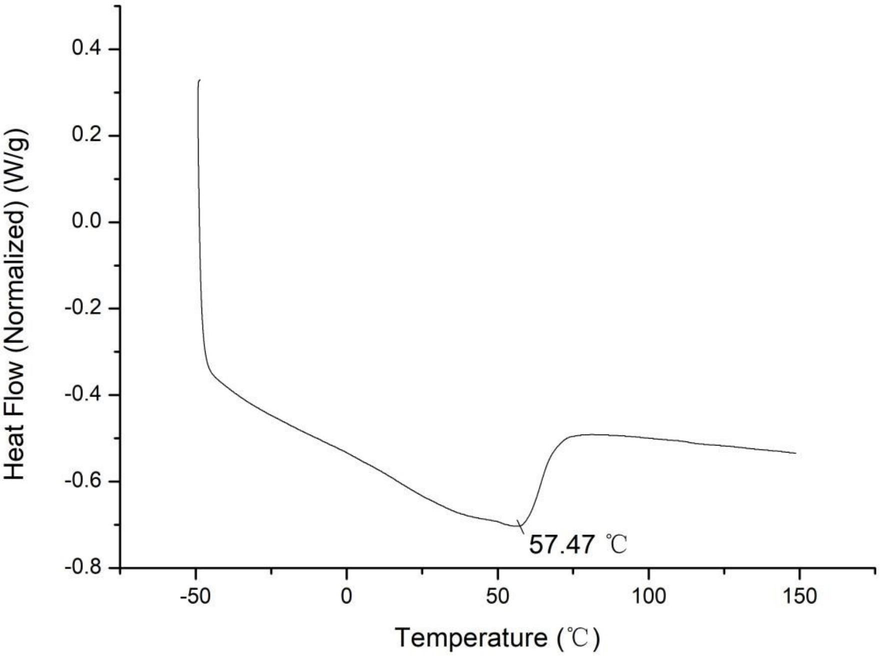


Figure S78. DSC of the polymer from entry 4, Table 2.

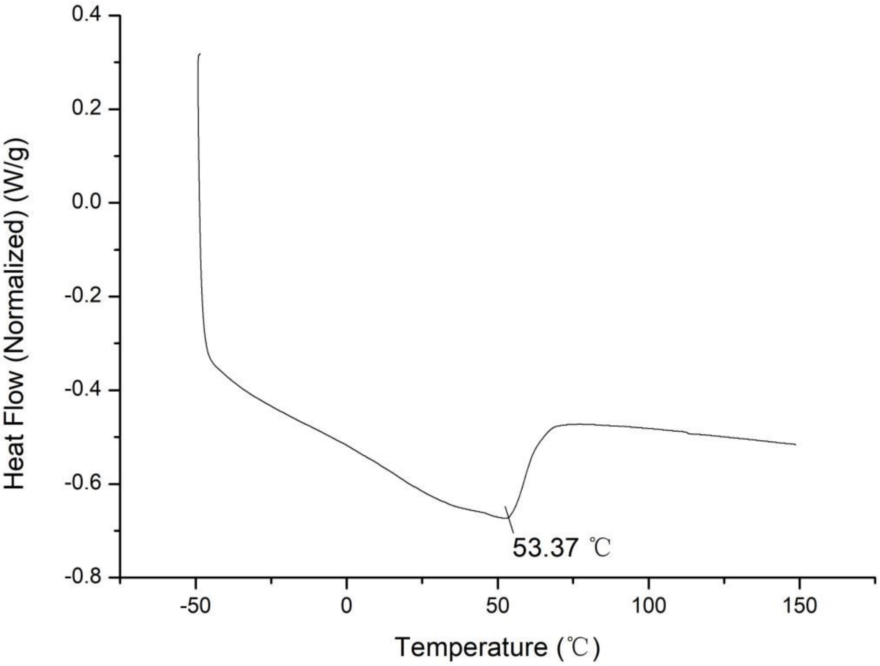


Figure S79. DSC of the polymer from entry 5, Table 2.

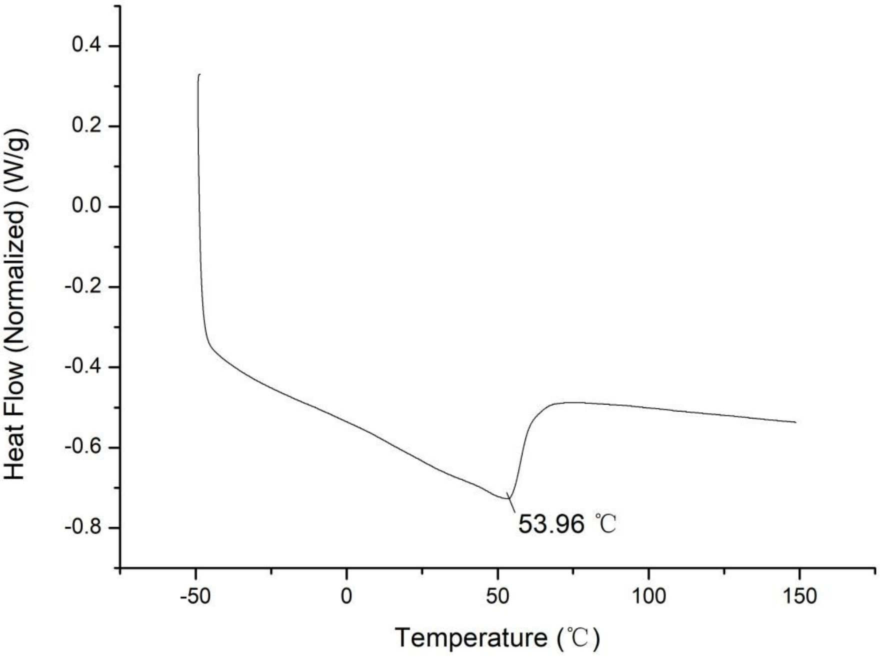


Figure S80. DSC of the polymer from entry 6, Table 2.

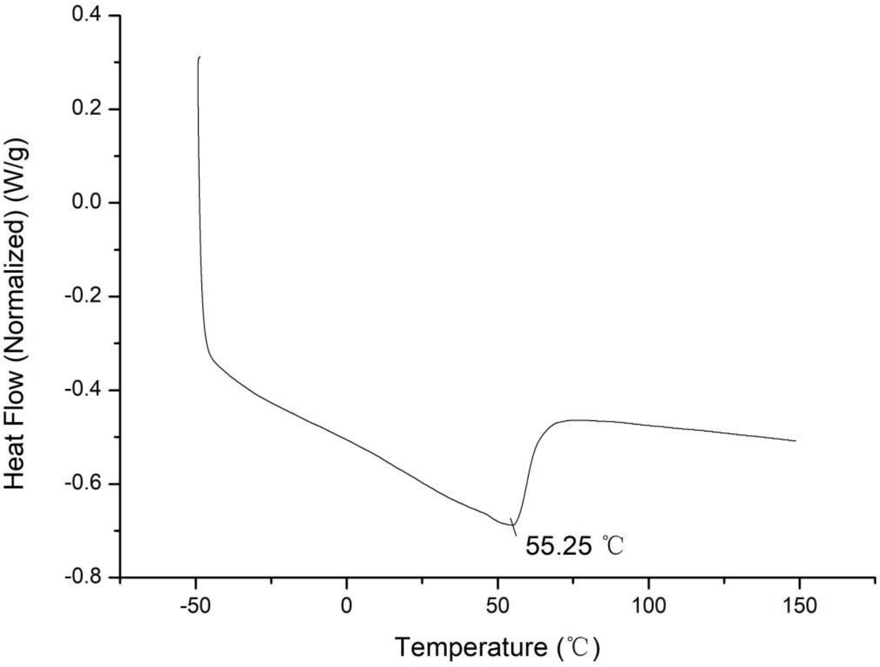


Figure S81. DSC of the polymer from entry 7, Table 2.

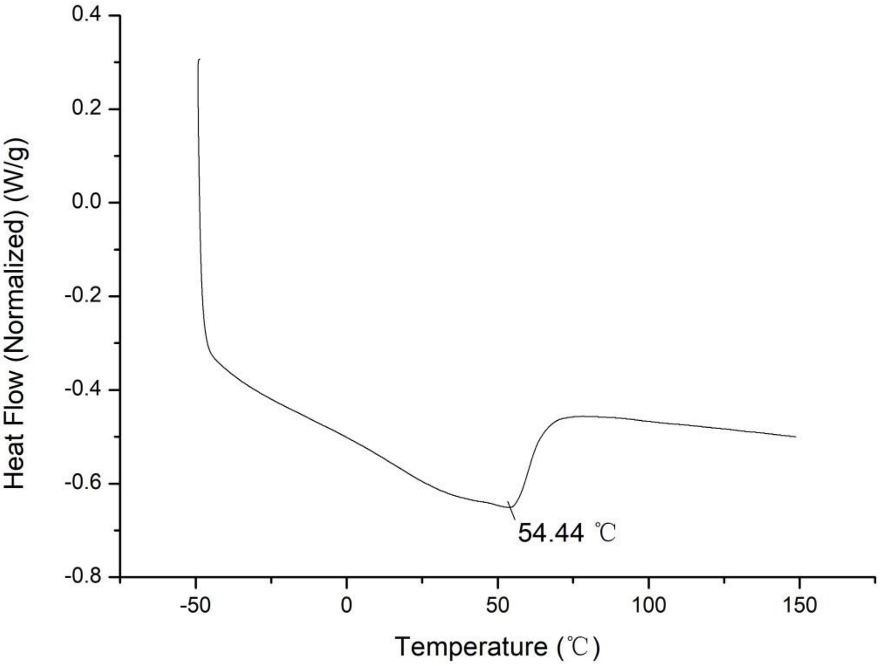


Figure S82. DSC of the polymer from entry 8, Table 2.

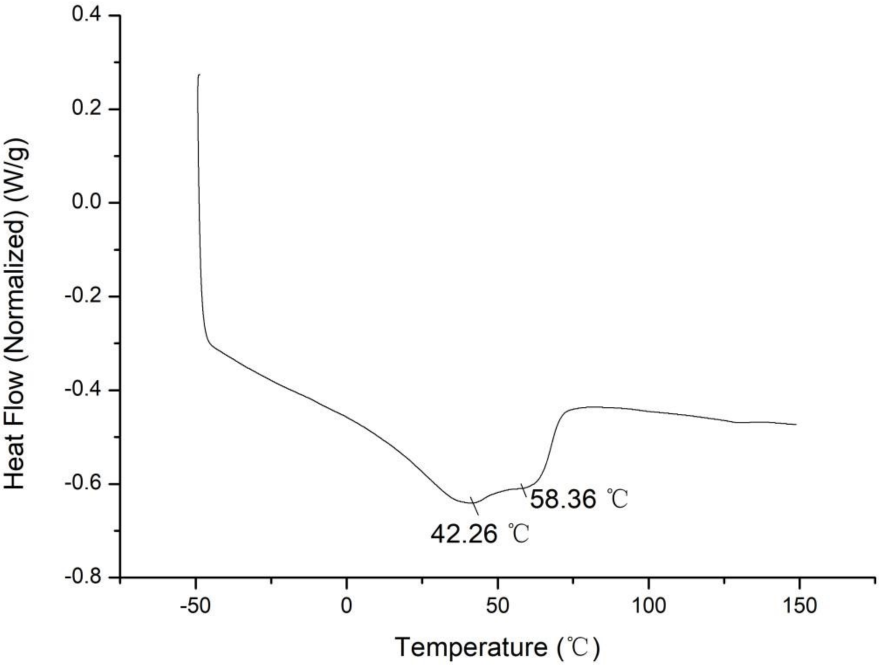


Figure S83. DSC of the polymer from entry 9, Table 2.

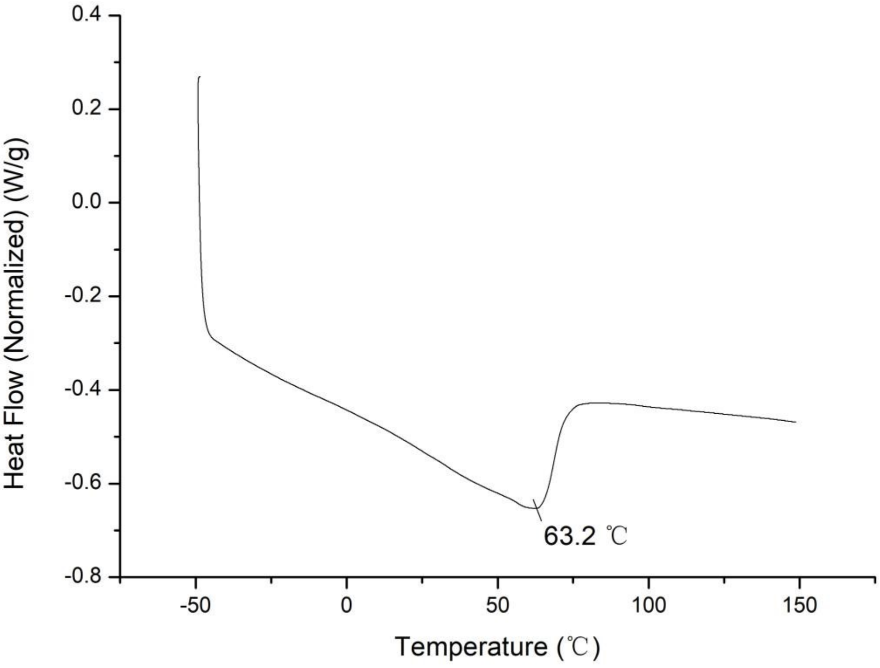


Figure S84. DSC of the polymer from entry 10, Table 2.

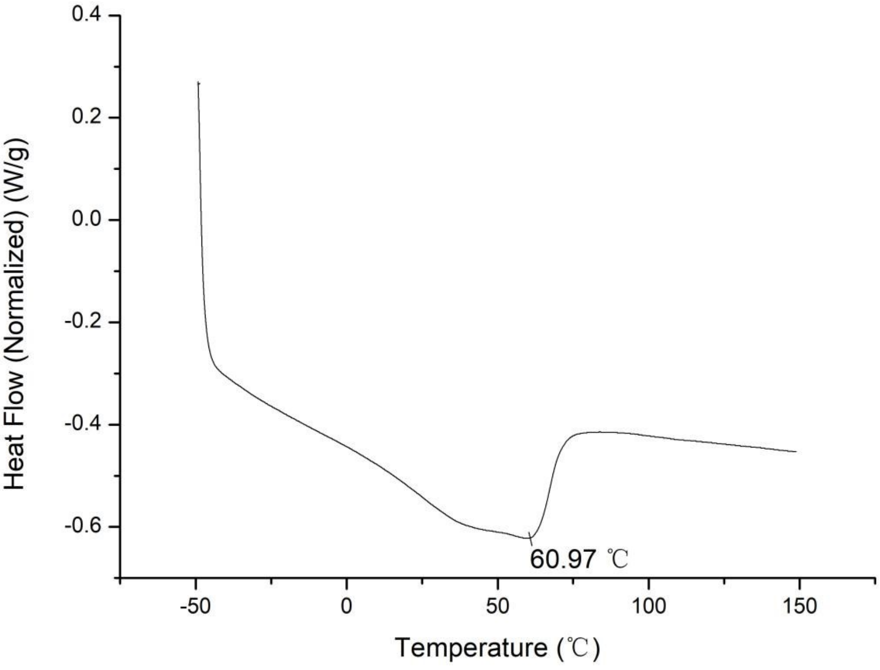


Figure S85. DSC of the polymer from entry 11, Table 2.

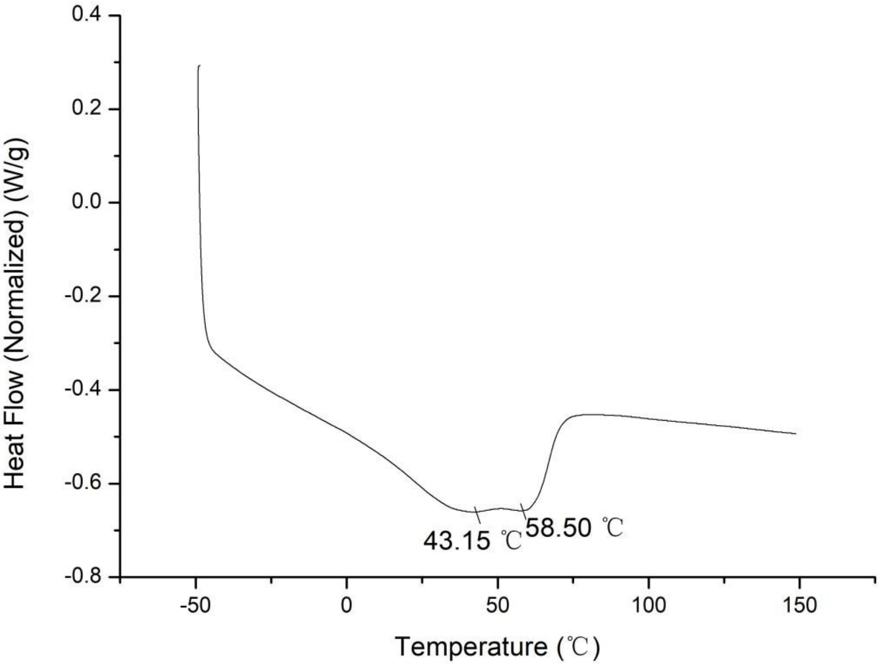


Figure S86. DSC of the polymer from entry 12, Table 2.

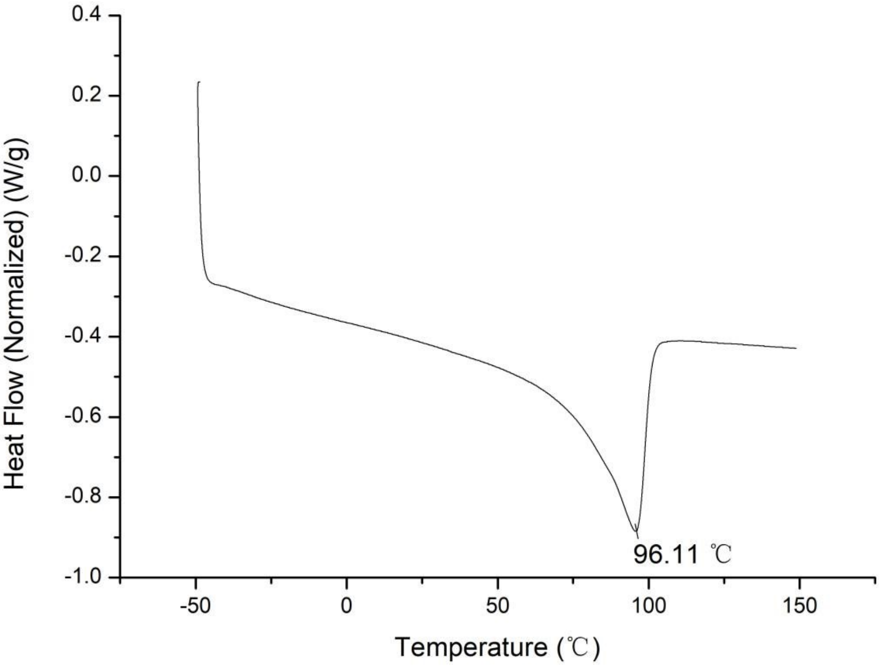
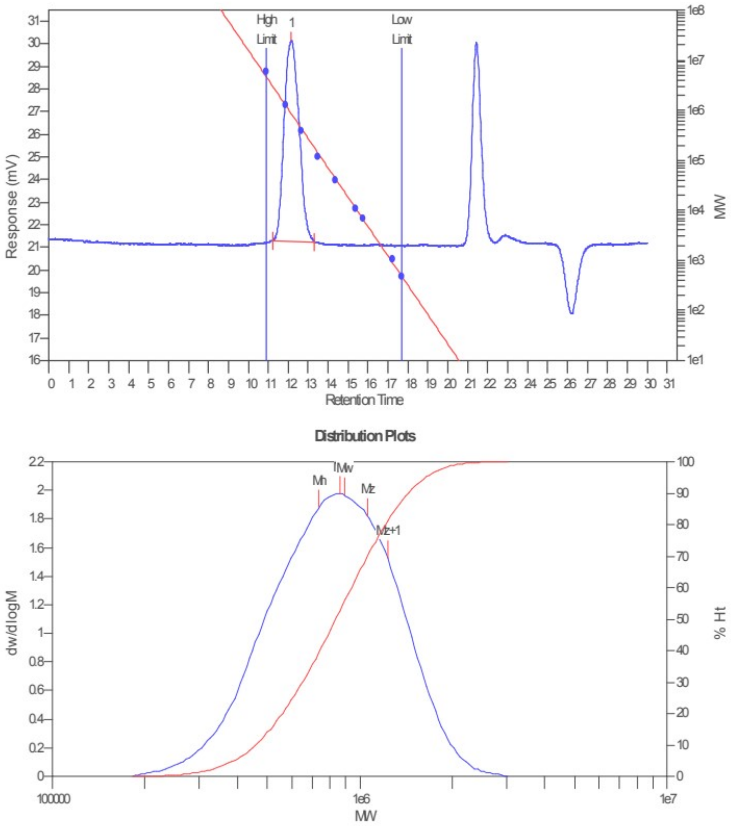


Figure S87. DSC of the polymer from entry 13, Table 2.

2.5 SEC of Representative Polymers and Copolymers.



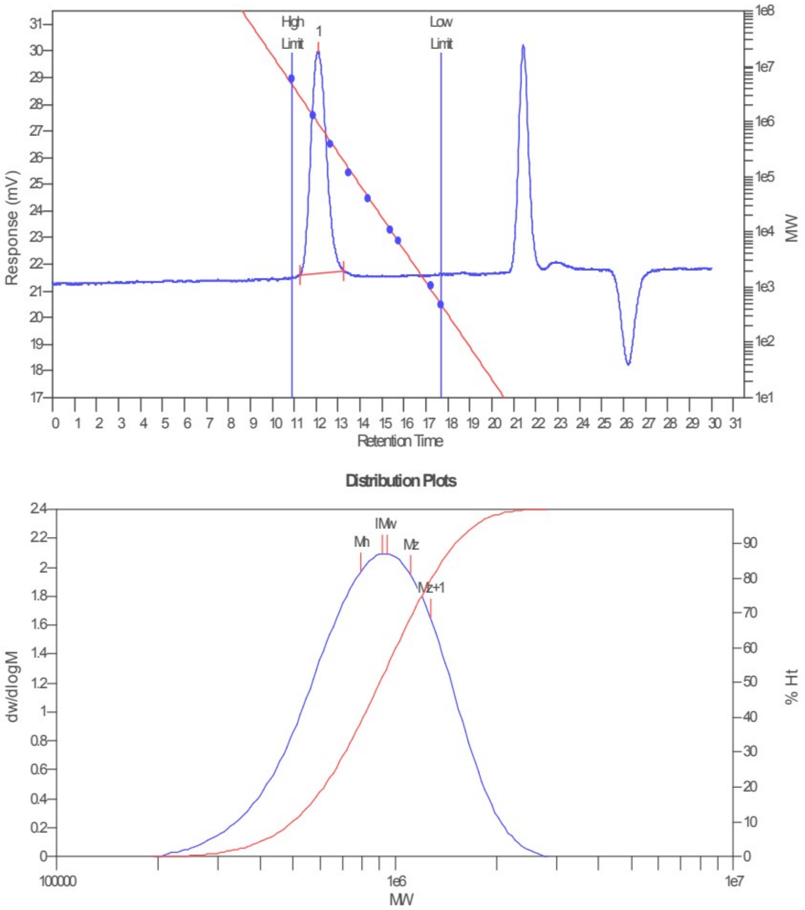
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	859894	735692	892110	1060493	1231303	867988	1.21261

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.22	12.15	13.30	8.87605	0	459.771	100

Figure S88. SEC of the polymer from entry 1, Table 1.



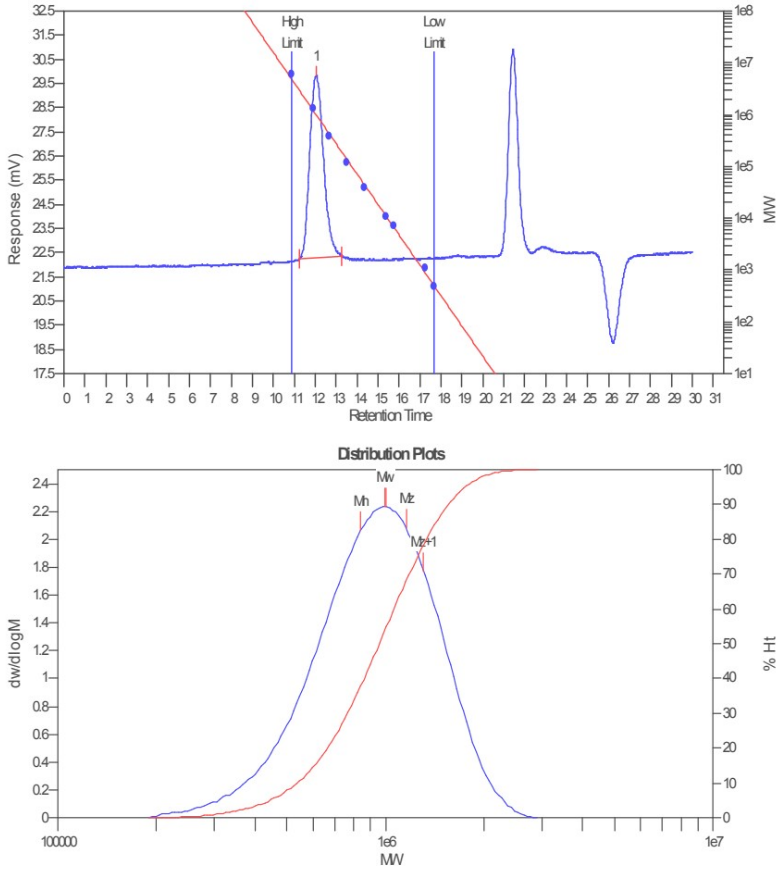
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	919959	792995	951237	1114380	1274629	927437	1.19955

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.27	12.10	13.25	8.30824	0	406.085	100

Figure S89. SEC of the polymer from entry 2, Table 1.



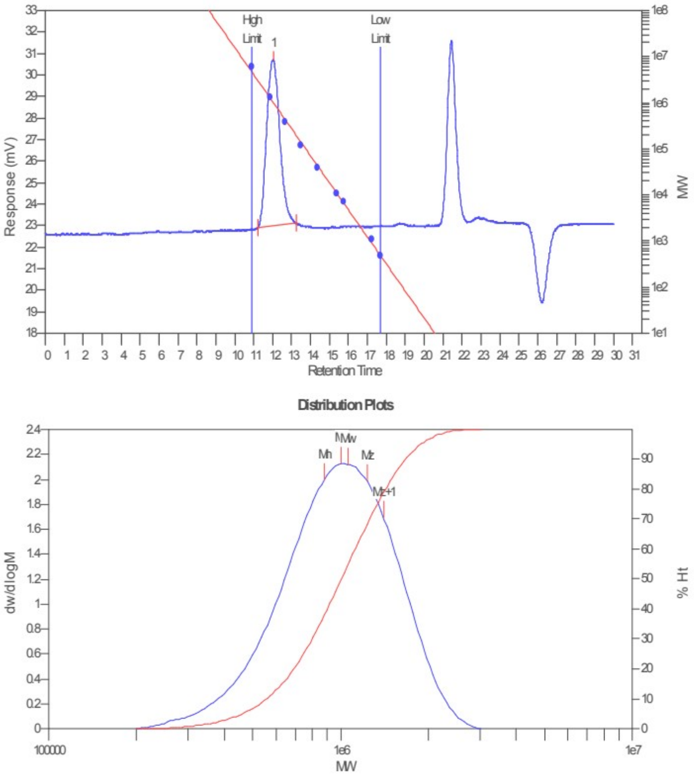
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1006623	839395	999189	1156816	1308914	975844	1.19037

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.25	12.03	13.27	7.54053	0	345.702	100

Figure S90. SEC of the polymer from entry 3, Table 1.



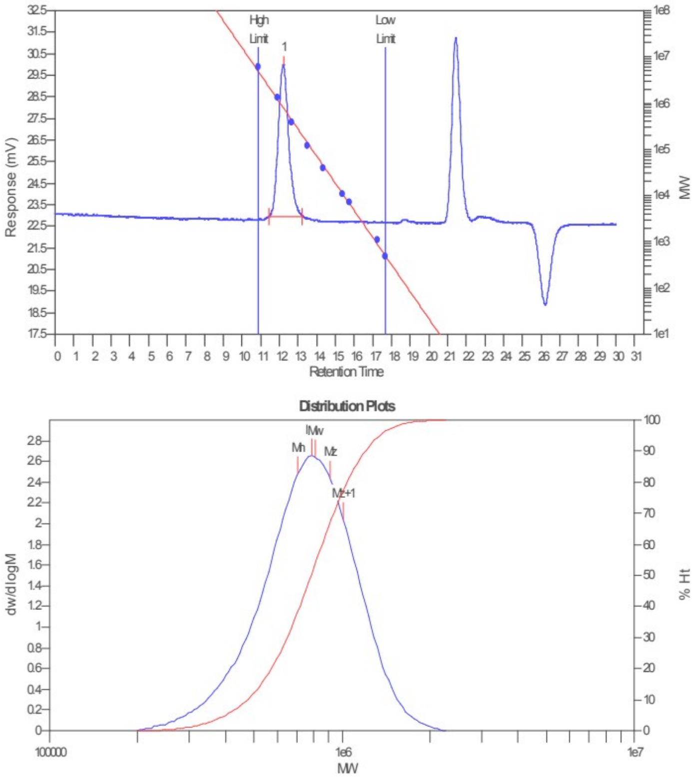
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1006623	881557	1057783	1234176	1403981	1031765	1.1999

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.22	12.03	13.23	7.72079	0	370.807	100

Figure S91. SEC of the polymer from entry 4, Table 1.



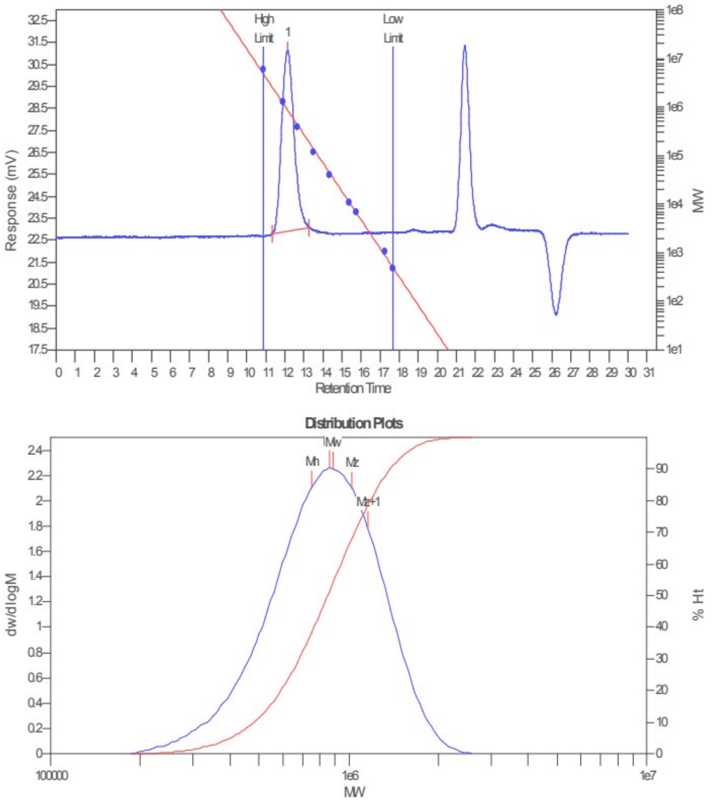
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	785863	707416	807997	909147	1010975	793127	1.14218

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.43	12.22	13.23	7.0373	0	271.109	100

Figure S92. SEC of the polymer from entry 5, Table 1.



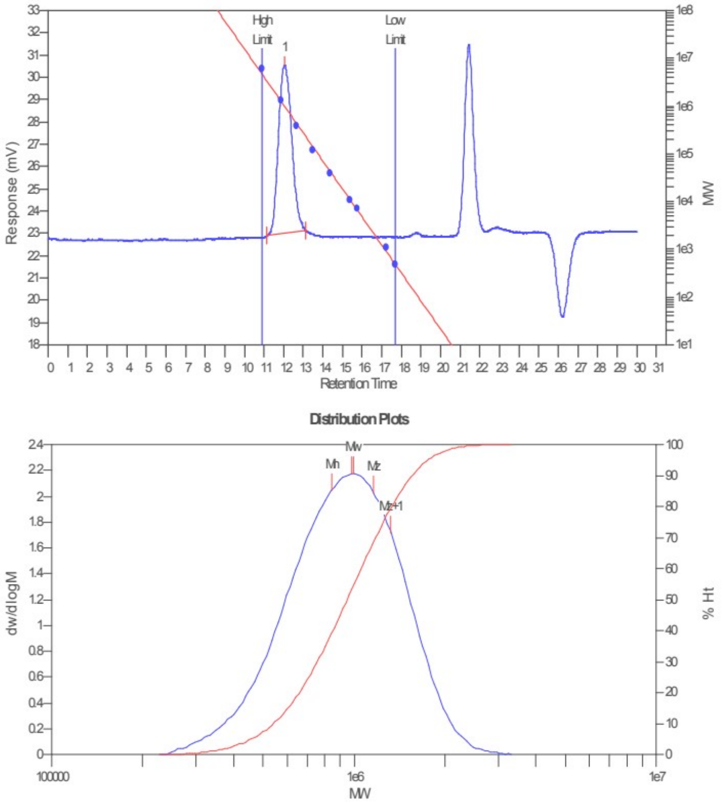
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	859894	750349	887412	1024770	1158703	867167	1.18267

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.33	12.15	13.28	8.23033	0	372.218	100

Figure S93. SEC of the polymer from entry 6, Table 1.



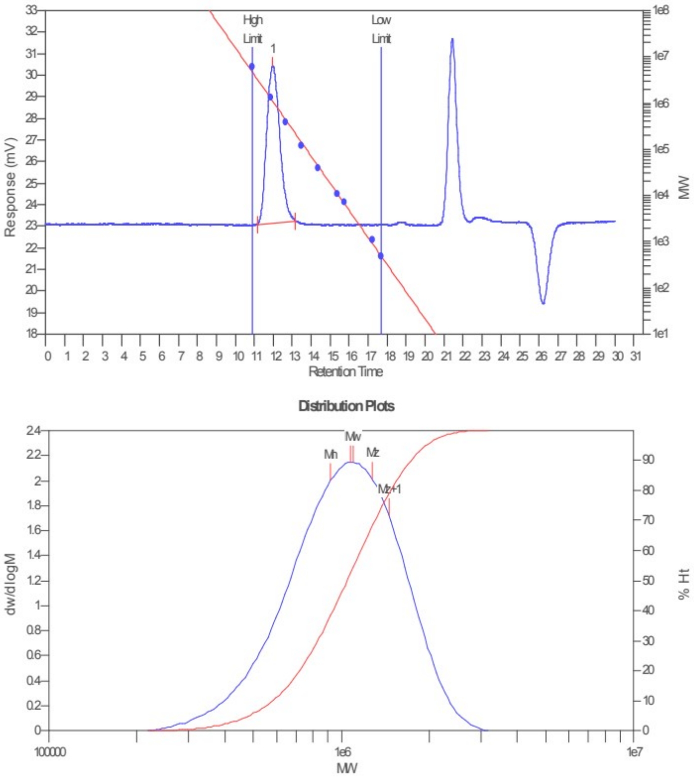
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	984220	844786	999023	1160484	1323915	975641	1.18258

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.15	12.05	13.13	7.53807	0	355.211	100

Figure S94. SEC of the polymer from entry 7, Table 1.



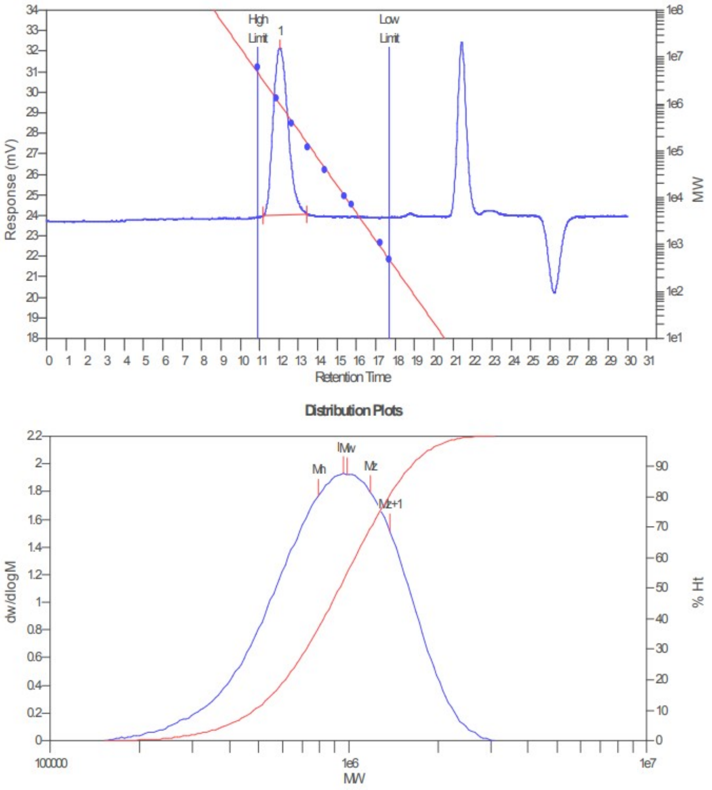
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1076937	920067	1098811	1278752	1452480	1072299	1.19427

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.18	11.98	13.17	7.25174	0	345.613	100

Figure S95. SEC of the polymer from entry 8, Table 1.



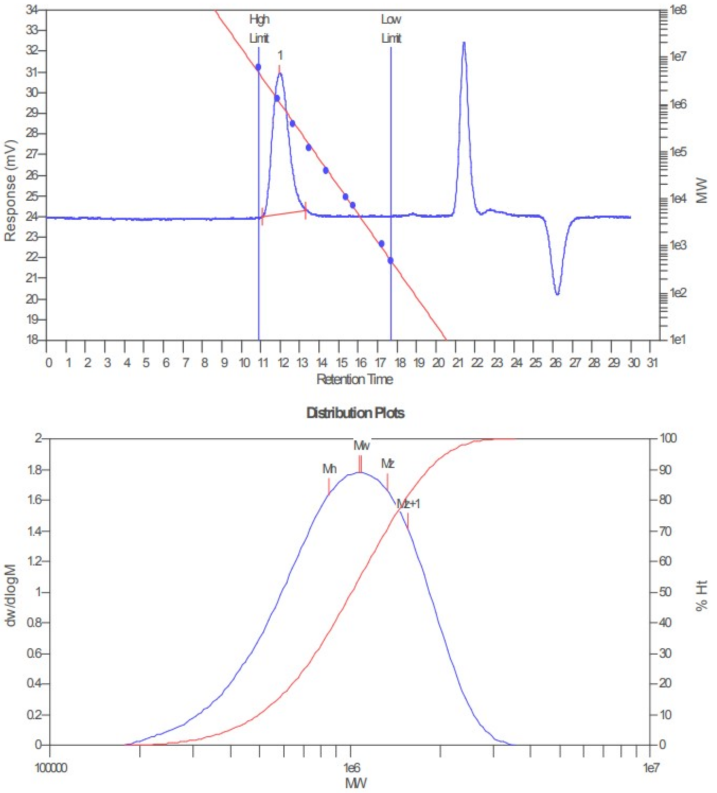
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	962316	792415	989697	1186601	1374235	960706	1.24896

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.20	12.07	13.43	8.14284	0	431.061	100

Figure S96. SEC of the polymer from entry 9, Table 1.



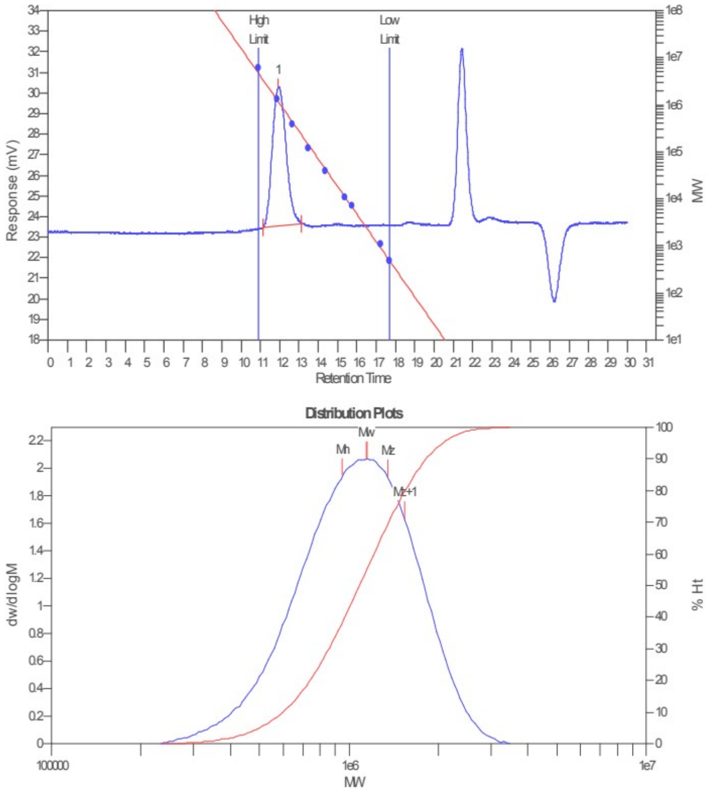
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1076937	848346	1089032	1333637	1563982	1053173	1.28371

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.10	11.98	13.32	6.79997	0	390.824	100

Figure S97. SEC of the polymer from entry 10, Table 1.



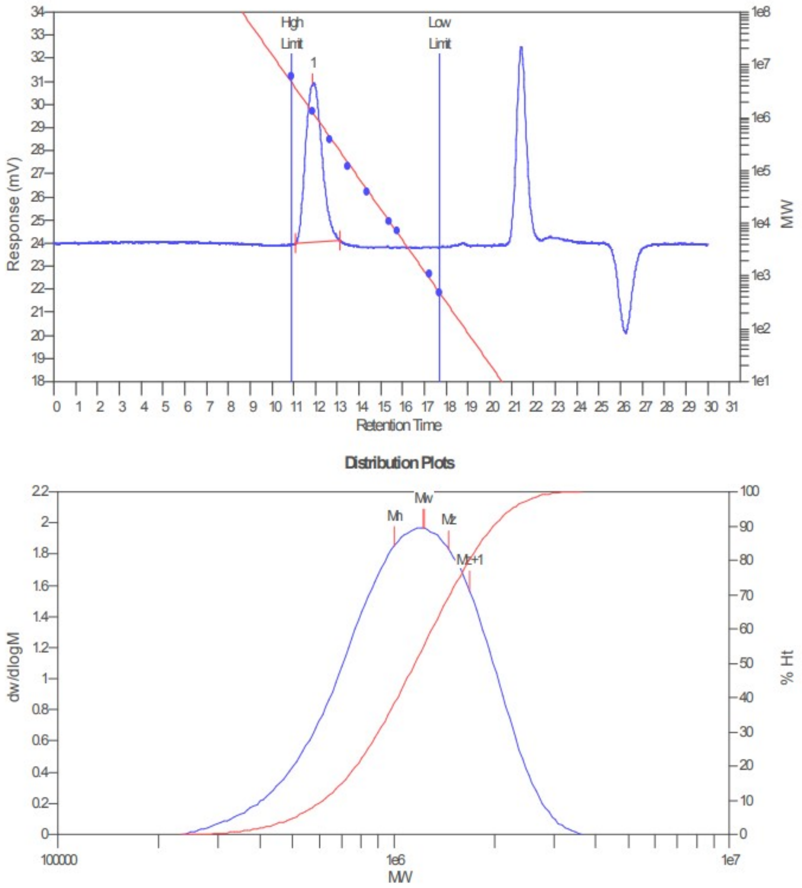
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1152163	952322	1146116	1345890	1542678	1116999	1.2035

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.12	11.93	13.12	6.73364	0	332.48	100

Figure S98. SEC of the polymer from entry 11, Table 1.



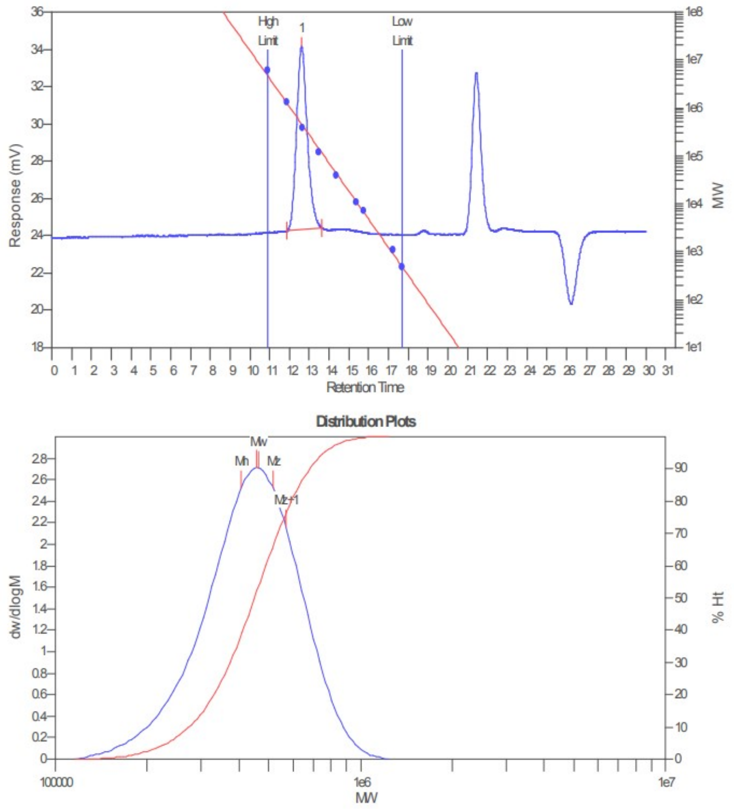
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1232643	1001525	1228425	1458876	1679413	1194592	1.22655

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.08	11.88	13.12	6.91059	0	359.777	100

Figure S99. SEC of the polymer from entry 12, Table 1.



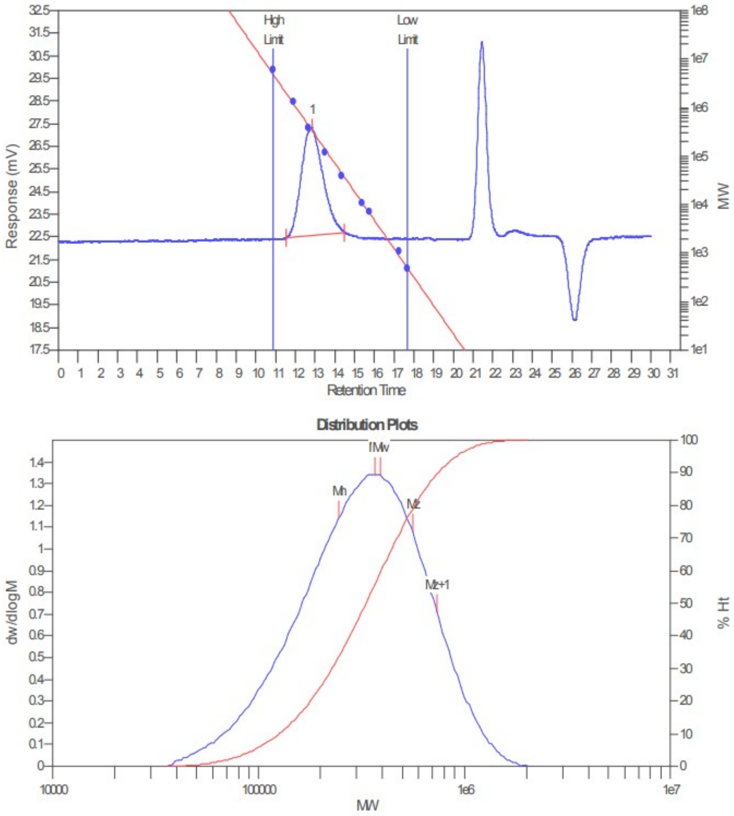
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	457887	406917	461728	515970	569389	453682	1.1347

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.88	12.62	13.63	9.81837	0	370.509	100

Figure S100. SEC of the polymer from entry 13, Table 1.



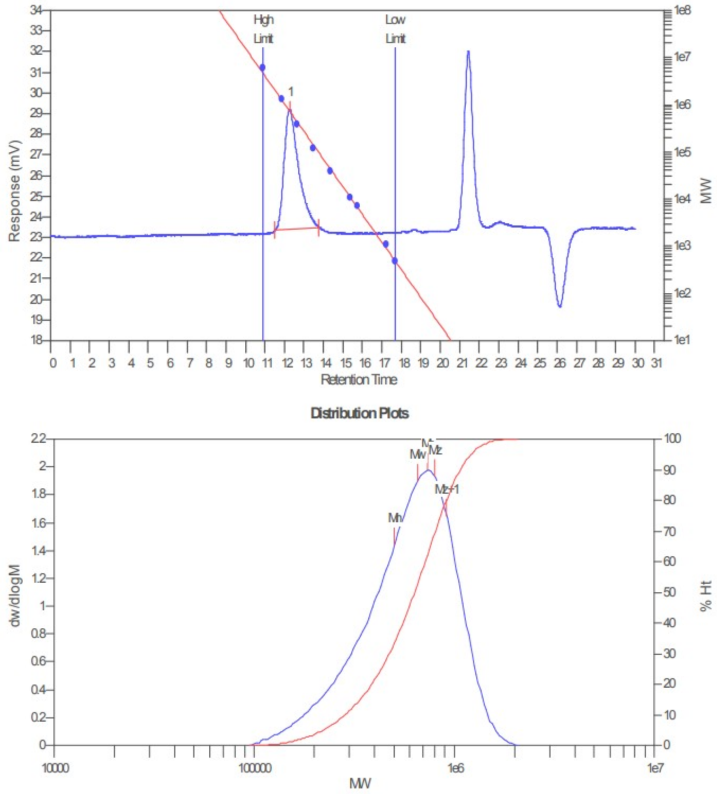
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	365606	245980	389237	559403	735655	366248	1.58239

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.52	12.83	14.50	4.76065	0	362.92	100

Figure S101. SEC of the polymer from entry 4, Table 2.



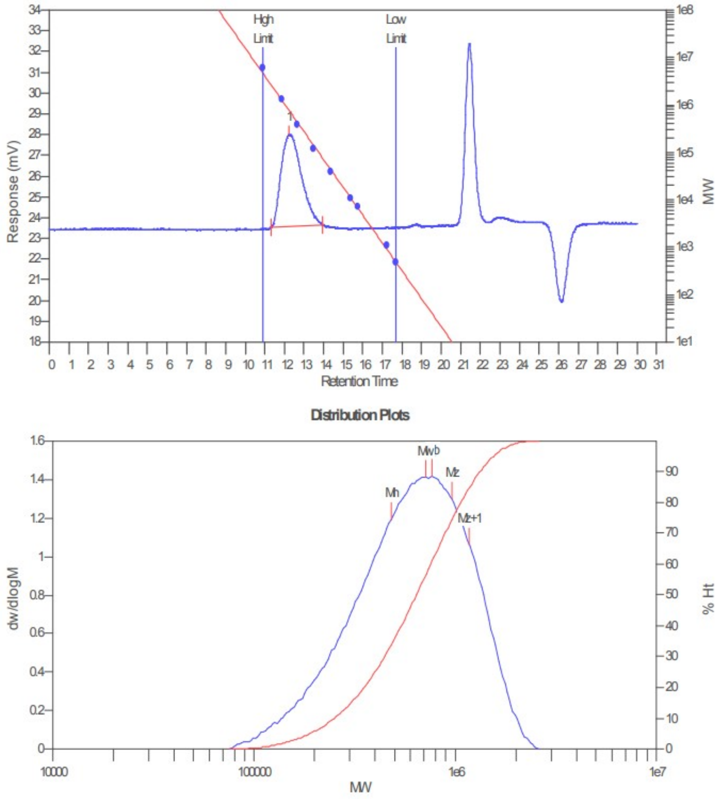
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	734553	503460	656061	794905	916373	634788	1.3031

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.50	12.27	13.78	5.80468	0	301.032	100

Figure S102. SEC of the polymer from entry 6, Table 2.



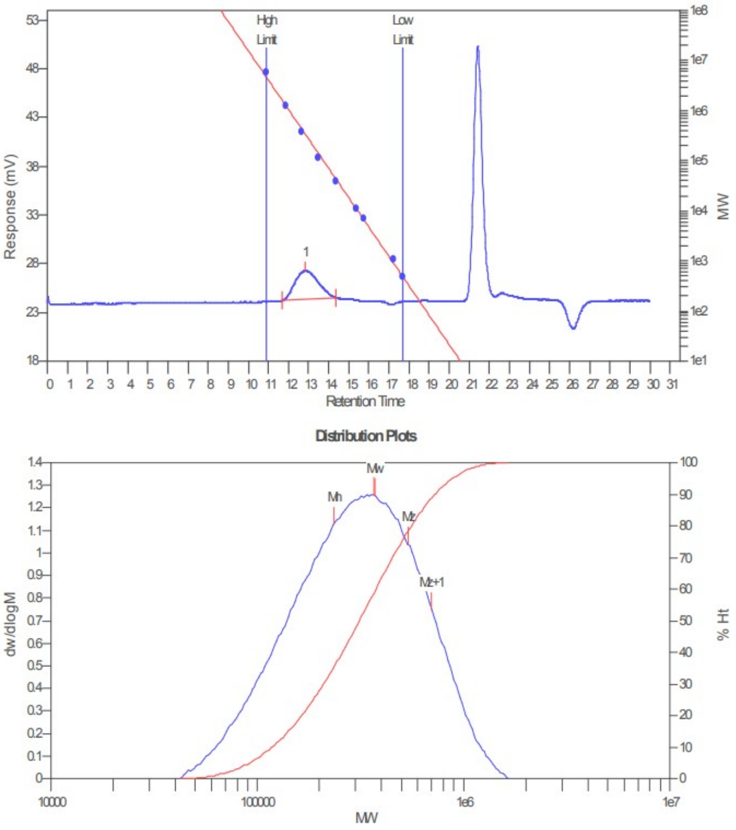
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	768373	480411	716408	958569	1173699	681046	1.49124

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.33	12.23	13.95	4.43645	0	320.392	100

Figure S103. SEC of the polymer from entry 7, Table 2.



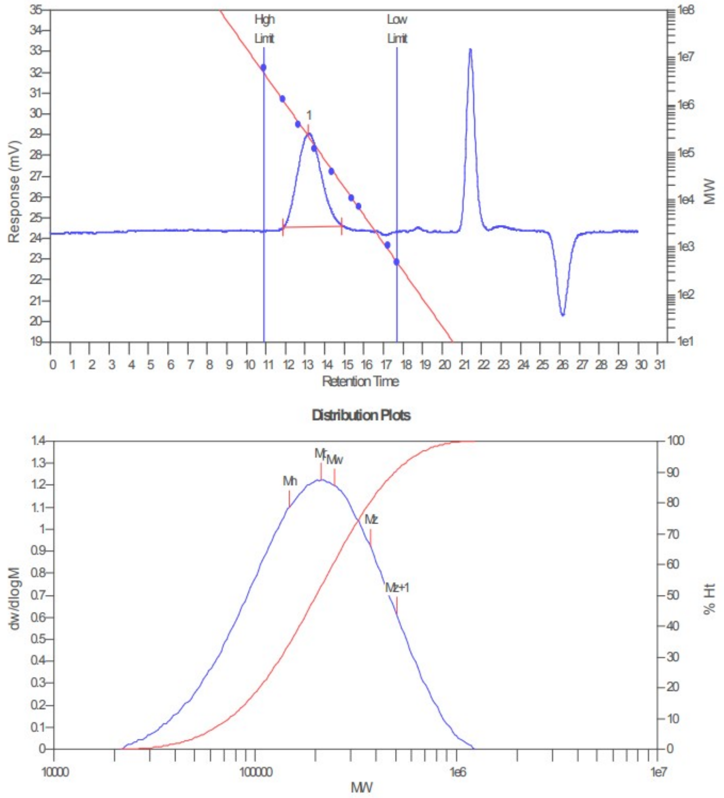
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	365606	234568	371728	537611	699364	349150	1.58473

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.67	12.83	14.38	2.95686	0	240.708	100

Figure S104. SEC of the polymer from entry 11, Table 2.



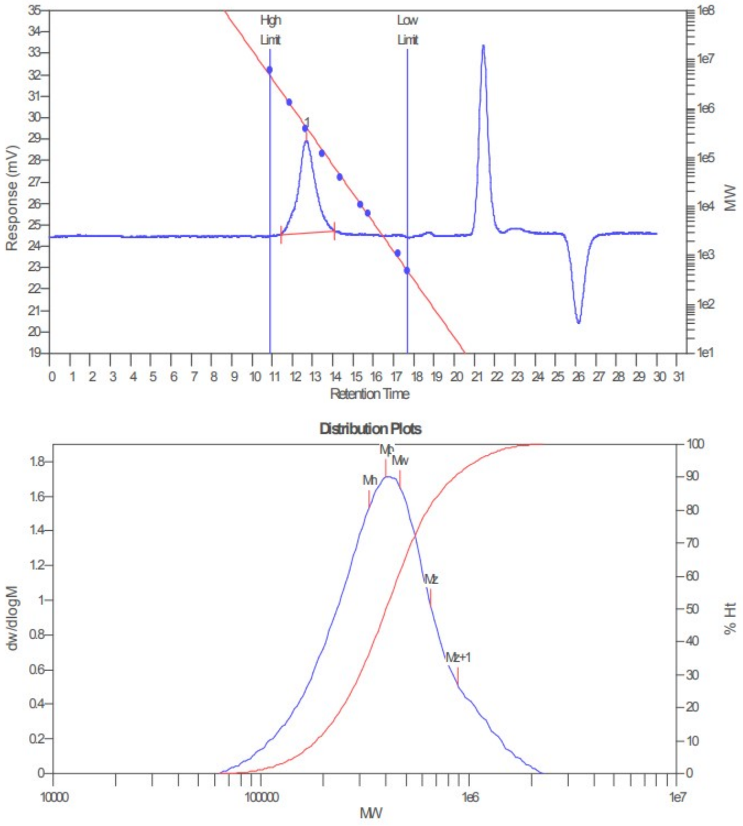
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	213022	147818	247384	374623	505333	230655	1.67357

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.88	13.18	14.88	4.50238	0	376.209	100

Figure S105. SEC of the polymer from entry 12, Table 2.



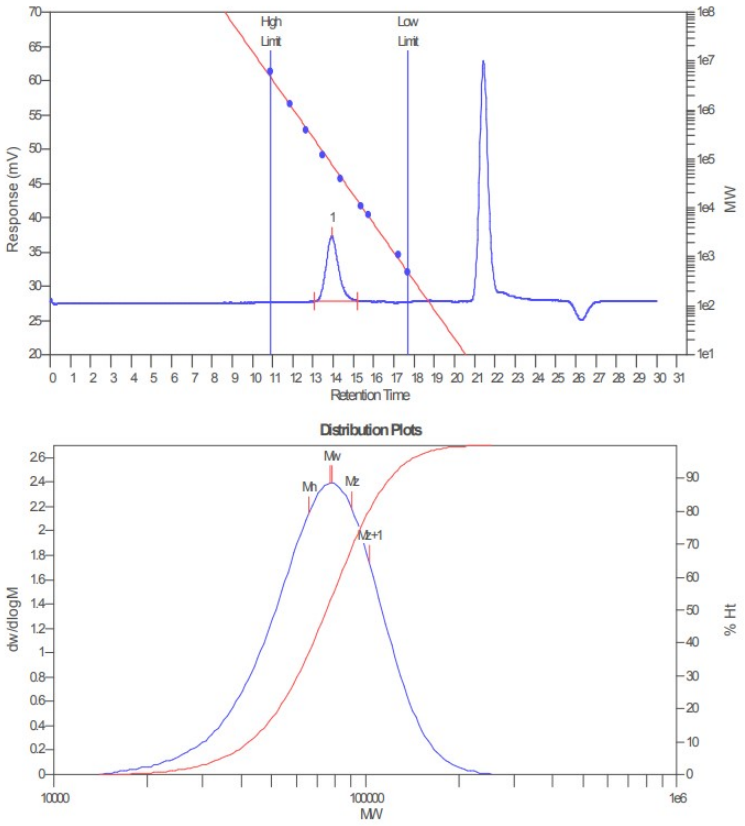
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	400047	329829	467089	654719	886698	443575	1.41616

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.43	12.72	14.08	4.28576	0	255.693	100

Figure S106. SEC of the polymer from entry 13, Table 2.



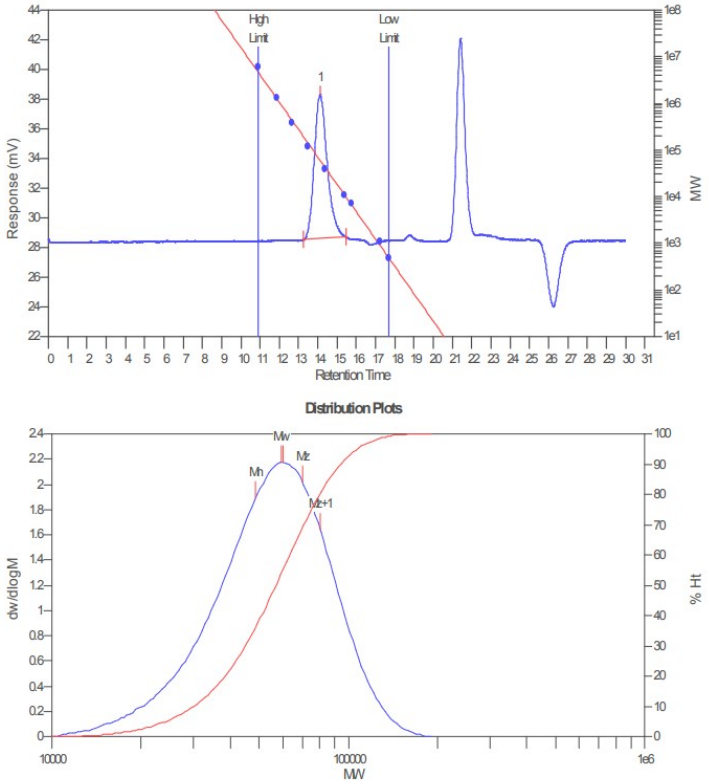
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	77369	65776	78146	90494	103101	76341	1.18806

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.05	13.93	15.20	9.46686	100	404.864	100

Figure S107. SEC of the polymer from entry 7, Table 3.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	60402	48664	59538	70175	80478	57964	1.22345

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.27	14.12	15.45	9.69081	100	455.609	100

Figure S108. SEC of the polymer from entry 9, Table 3.

2.6 Solubility of Ni1 and Ni4

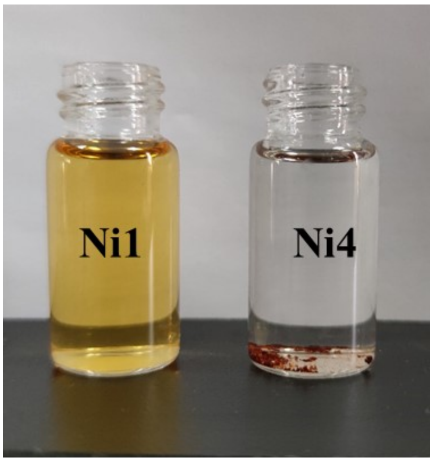


Figure S109. Solubility of **Ni1** and **Ni4** in hexanes (10 mL).

3. X-ray Crystallography

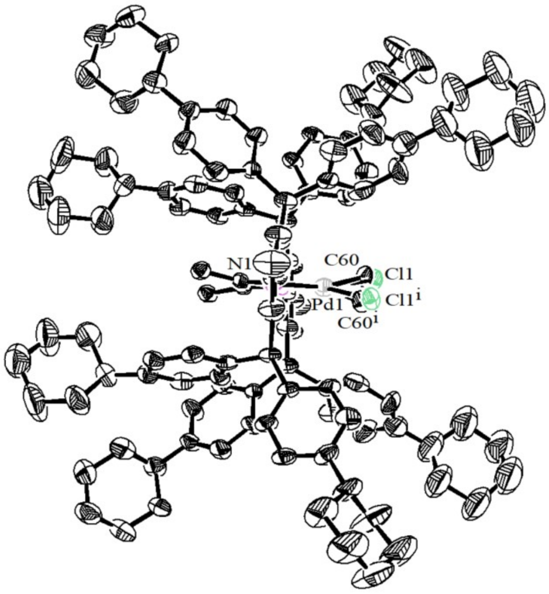


Table S2. Crystal data and structure refinement for **Pd1**.

Identification code	**Pd1**
Empirical formula	$C_{119}H_{143}ClN_2Pd$
Formula weight	1743.20
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2/n
a/Å	14.2248 (13)
b/Å	17.9165 (16)
c/Å	22.501 (2)
α/°	90.00
β/°	100.050 (4)
γ/°	90.00
Volume/Å^3	5646.5 (9)
Z	2
ρ_{calc}g/cm^3	1.025
μ/mm^{-1}	0.231
F(000)	1868.0
Crystal size/mm^3	17 × 0.33 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.32 to 50.04
Index ranges	$-16 \le h \le 16$, $0 \le k \le 21$, $0 \le l \le 26$
Reflections collected	9918
Independent reflections	9918 [R_{int} = 0.0000, R_{sigma} = 0.2152]

Data/restraints/parameters	9918/98/563
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	$R_1 = 0.0898$, $wR_2 = 0.1298$
Final R indexes [all data]	$R_1 = 0.1962$, $wR_2 = 0.1474$
Largest diff. peak/hole / e Å^{-3}	0.81/-0.96

4. References

[1] Guo, L.; Kong, W.; Xu, Y.; YangY.; Ma, R.; Cong, L.; Dai, S.; 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] Guo, L.; Dai, S.; Chen, C. Investigations of the Ligand Electronic Effects on α-diimine Nickel(II) Catalyzed Ethylene Polymerization. *Polymers* **2016**, *8*, 37.

[3] Dai, S.; Sui, X.; Chen, C. Highly Robust Palladium(II) α-Diimine Catalysts for Slow-Chain-Walking Polymerization of Ethylene and Copolymerization with Methyl Acrylate. *Angew. Chem. Int. Ed.* **2015**, *54*, 9948-9953.