Enhanced Suppression of Chain Transfer in Ethylene (Co)Polymerization via Synergistic Axial Substituent Effects in Pyridine-Imine Ni(II) and Pd(II) Catalysts

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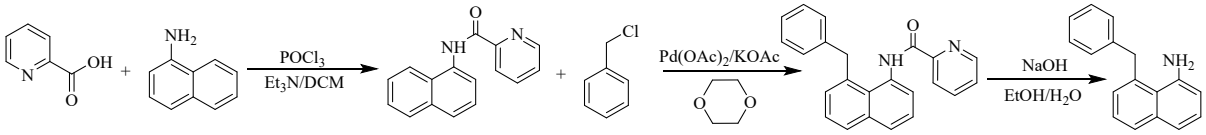
1. Experimental Sections

1.1 General Considerations

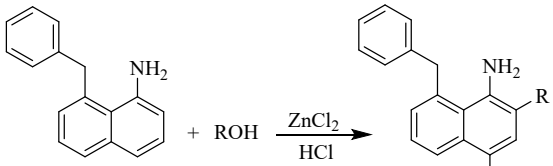
All chemicals were commercially sourced, except those whose synthesis is described. All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded by a JEOL JNM-ECZ600R 600 or 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Mass spectra and elemental analysis were performed by the Analytical Center of the Anhui University. X-ray Diffraction data were collected at 293(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K^{α} radiation (λ = 0.71073 Å). Molecular weight and molecular weight distribution of the polymers with low solubility at room temperature were determined by gel permeation chromatography (GPC) with a PL 210 equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 150 ^{o}C using trichlorobenzene as a solvent and calibrated with polystyrene standards. The molecular weight and the molecular weight distribution of the polymers with good solubility at room temperature were determined by gel permeation chromatography (GPC) equipped with two linear Styragel columns (HR2 and HR4) at 40°C using THF as a solvent and calibrated with polystyrene standards, and THF was employed as the eluent at a flow rate of 1.0 mL/min. 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).

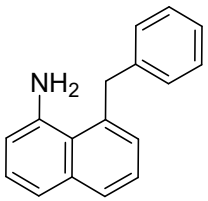
1.2 Procedure for the Synthesis of Arylamines A1-A3.



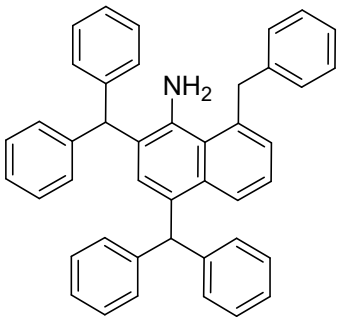
The key intermediate, 8-benzylnaphthylamine, was synthesized via directed C–H functionalization at the 8-position of naphthylamine using a pyridylcarbonyl directing group, followed by its removal according to literature procedures.[1]



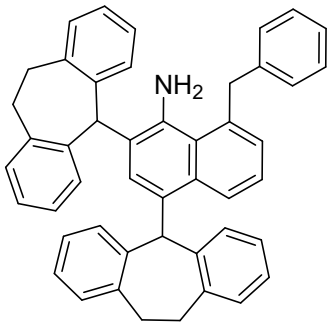
In a typical reaction, a mixture of 8-benzylnaphthylamine (10 mmol, 1.0 equiv.) and either diphenylmethanol or dibenzosuberol (20.0 mmol, 2.0 equiv.) was heated to 120 °C under an inert atmosphere, followed by dropwise addition of a solution of anhydrous zinc chloride (1.36 g, 10 mmol, 0.5 equiv.) in concentrated hydrochloric acid (1.2 mL, 37% w/w, 1.0 equiv.), during which exothermic and intense bubbling were observed. The temperature was then raised to 160 °C and maintained for 30 min. After cooling to room temperature, the mixture was dissolved in CH_2Cl_2 (200 mL), washed with water (3 × 100 mL), and dried over anhydrous $MgSO_4$. The solution was concentrated to ~20 mL under reduced pressure, and the product was precipitated by addition to methanol (200 mL). The resulting solid was collected by filtration and washed with cold methanol (3 × 100 mL) to afford the pure product.



A1 (0.96 g, 41%, two steps). **A1** is known.[1]

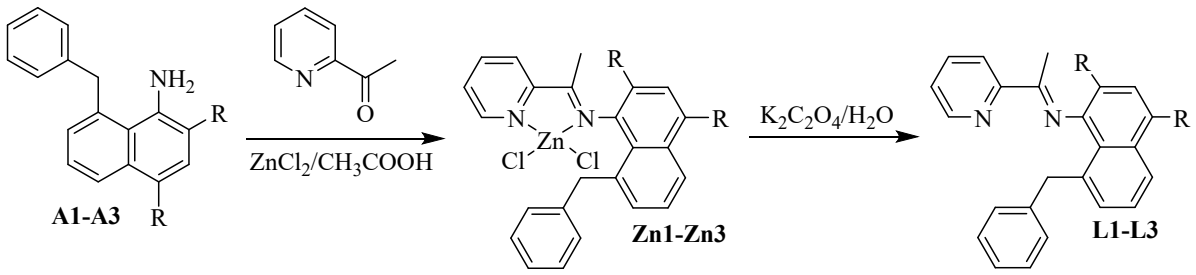


A2 (1.81 g, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 7.37 – 7.04 (m, 19H, Ar-*H*), 7.02 – 6.71 (m, 8H, Ar-*H*), 6.31 (s, 1H, Ar-*H*), 6.03 (s, 1H, C*H*Ar_2), 5.46 (s, 1H, C*H*Ar_2), 4.68 (s, 2H, -CH_2-), 3.93 (s, *br*, 2H, NH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.21, 142.54, 141.01, 140.19, 134.68, 133.31, 130.81, 130.38, 129.41, 129.30, 128.91, 128.60, 128.40, 128.16, 126.48, 126.44, 125.97, 125.64, 125.12, 123.75, 122.76, 53.32 (*C*HAr_2), 52.18 (*C*HAr_2), 42.27 (-*C*H_2-). APCI-MS (m/z): calcd for $C_{43}H_{36}N$: 566.2842, Found, 566.2859, $[M+H]^+$.



A3 (1.79 g, 29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.6 Hz, 1H, Ar-*H*), 7.40 (d, *J* = 6.9 Hz, 2H, Ar-*H*), 7.30 – 7.22 (m, 5H, Ar-*H*), δ 7.21 – 7.02 (m, 12H, Ar-*H*), 6.96 (s, 1H, Ar-*H*), 6.90 (dd, *J* = 14.5, 7.1 Hz, 4H, Ar-*H*), 5.69 (s, 1H, C*H*Ar_2), 5.07 (s, 1H, C*H*Ar_2), 4.61 (s, 2H, -CH_2-), 4.19 (s, 2H, *br*, 2H, NH_2), 2.82 – 2.62 (m, 4H, -CH_2-CH_2-), 2.44 – 2.26 (m, 4H, -CH_2-CH_2-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.10, 140.41, 140.24, 140.17, 140.05, 134.76, 133.15, 132.92, 131.15, 130.94, 130.87, 130.09, 128.85, 128.61, 127.45, 127.10, 126.62, 126.40, 126.21, 126.07, 125.92, 124.69, 124.05, 121.78, 57.22 (*C*HAr_2), 56.60 (*C*HAr_2), 42.32 (-*C*H_2-), 31.36 (-*C*H_2-CH_2-), 31.31 (-CH_2-*C*H_2-). APCI-MS (m/z): calcd for $C_{47}H_{36}N$: 614.2842, Found, 614.2844, $[M-4H+H]^+$.

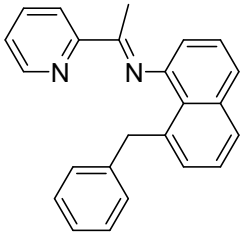
1.3 Procedure for the Synthesis of Ligands L1-L3.



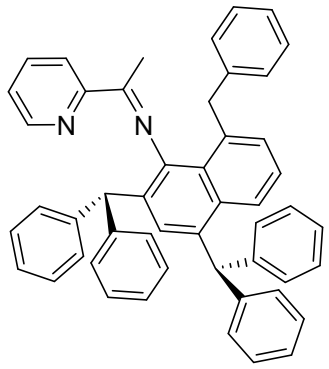
R = H (**L1**), $CHPh_2$ (**L2**), DBH (**L3**)

The ligands **L1–L3** were synthesized via a two-step procedure. First, a suspension of $ZnCl_2$ (0.34 g, 2.5 mmol) and 2-acetylpyridine (2.0 mmol) in glacial acetic acid (5 mL) was treated with the corresponding aniline **A1-A3** (2 mmol). The reaction mixture was refluxed with stirring for 4 h, yielding a yellow precipitate upon cooling to room temperature. The solid was isolated by filtration and thoroughly washed with acetic acid (3 × 5 mL) followed by diethyl ether (5 × 5 mL) to remove residual acetic acid. Drying under vacuum afforded the zinc-iminopyridine complex as a yellow, poorly soluble solid.

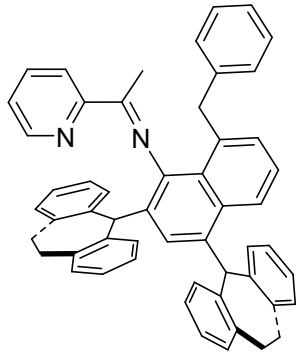
Subsequent demetallation was achieved by suspending the zinc complex in methylene chloride (30 mL) and adding an aqueous solution of potassium oxalate (0.41 g, 2.2 mmol in 5 mL H_2O). The biphasic mixture was vigorously stirred for 1 h, after which the organic layer was separated, washed with water (3 × 20 mL), and dried over $MgSO_4$. Filtration and solvent removal under reduced pressure yielded a crude product, which was further purified by precipitation from ethanol (20 mL). Ligands **L2** and **L3** were obtained as stable yellow powders after drying under high vacuum. However, **L1** proved unstable and prone to decomposition in solution, precluding the acquisition of pure NMR spectroscopic data.



L1 (0.29 g, 63%). **L1** exhibits instability in solution, precluding the acquisition of pure NMR spectroscopic data. APCI-MS (m/z): calcd for $C_{24}H_{21}N_2$: 337.1699, Found, 337.1701, $[M+H]^+$.



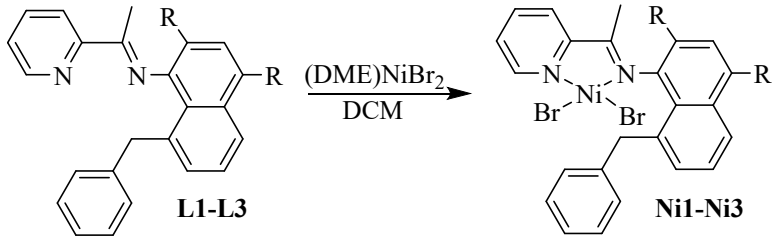
L2 (1.02 g, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.3 Hz, 1H, Ar-*H*), 8.28 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.93 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 7.82 – 7.72 (m, 1H, Ar-*H*), 7.34 (dd, *J* = 6.9, 5.4 Hz, 1H, Ar-*H*), 7.28 – 7.24 (m, 4H, Ar-*H*), 7.22 – 7.16 (m, 3H, Ar-*H*), 7.15 – 7.09 (m, 4H, Ar-*H*), 7.08 – 7.02 (m, 6H, Ar-*H*), 7.02 – 6.98 (m, 4H, Ar-*H*), 6.87 – 6.83 (m, 2H, Ar-*H*), 6.82 – 6.77 (m, 2H, Ar-*H*), 6.72 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 6.69 (s, 1H, Ar-*H*), 6.19 (s, 1H, C*H*Ar_2), 5.40 (s, 1H, C*H*Ar_2), 4.50 (d, *J* = 16.5 Hz, 1H, -CH_2-), 4.28 (d, *J* = 16.5 Hz, 1H, -CH_2-), 1.17 (s, 3H, Ar-C(CH_3)=N). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.70 (*C*=N), 155.73, 148.43, 145.46, 144.34, 143.95, 143.80, 142.37, 141.45, 136.84, 136.12, 134.63, 132.79, 130.66, 129.92, 129.62, 129.49, 129.18, 128.91, 128.35, 128.30, 128.24, 127.95, 127.89, 126.52, 126.28, 126.19, 126.13, 125.89, 125.59, 125.39, 124.71, 123.20, 121.24, 53.49 (*C*HAr_2), 52.07 (*C*HAr_2), 42.43 (-*C*H_2-), 16.92 (Ar-C(*C*H_3)=N). APCI-MS (m/z): calcd for $C_{50}H_{41}N_2$: 669.3264, Found, 669.3259, $[M+H]^+$.



L3 (1.02 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.0 Hz, 1H, Ar-*H*), 8.31 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.80 (td, *J* = 7.8, 1.7 Hz, 1H, Ar-*H*), 7.55 – 7.43 (m, 2H, Ar-*H*), 7.40 – 7.34 (m, 1H, Ar-*H*), 7.29 – 7.10 (m, 8H, Ar-*H*), 7.02 – 6.89 (m, 9H, Ar-*H*), 6.84 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 6.67 – 6.59 (m, 3H, Ar-*H*), 5.82 (s, 1H, C*H*Ar_2), 5.03 (s, 1H, C*H*Ar_2), 4.44 (d, *J* = 16.6 Hz, 1H, -CH_2-), 4.21 (d, *J* = 16.6 Hz, 1H, -CH_2-), 2.87 – 2.58 (m, 4H, -CH_2-CH_2-), 2.52 – 2.29 (m, 4H, -CH_2-CH_2-), 1.31 (s, 3H, Ar-C(CH_3)=N). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29

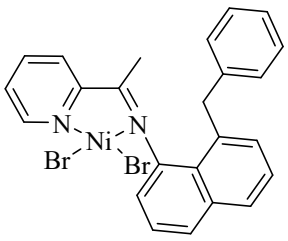
(*C*=N), 155.41, 148.25, 145.23, 141.39, 141.06, 140.95, 140.44, 140.29, 140.25, 140.07, 139.93, 139.63, 136.75, 135.88, 132.50, 132.07, 131.62, 131.51, 131.12, 130.98, 130.92, 130.80, 130.70, 130.46, 129.67, 128.81, 127.59, 126.88, 126.84, 126.76, 126.62, 126.07, 125.99, 125.66, 125.37, 125.32, 124.88, 124.67, 124.39, 123.40, 121.66, 57.41 (*C*HAr_2), 56.34 (*C*HAr_2), 42.54 (-*C*H_2-), 31.63 (-*C*H_2-*C*H_2-), 31.54 (-*C*H_2-*C*H_2-), 31.32 (-*C*H_2-*C*H_2-), 31.16 (-*C*H_2-*C*H_2-), 16.31 (Ar-C(*C*H_3)=N). APCI-MS (m/z): calcd for $C_{54}H_{45}N_2$: 721.3577, Found, 721.3564, $[M+H]^+$.

1.4 Procedure for the Synthesis of Nickel Complexes Ni1-Ni3.

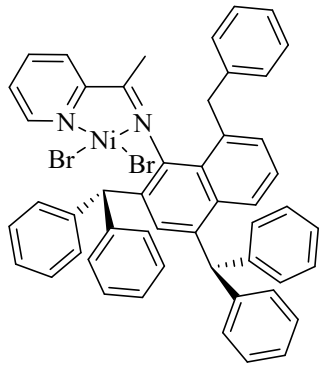


R = H (**Ni1**), $CHPh_2$ (**Ni2**), DBH (**Ni3**)

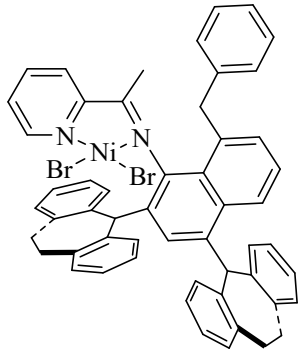
Complexes **Ni1-Ni3** were synthesized by reacting (DME)$NiBr_2$ with the corresponding ligands in methylene chloride under nitrogen atmosphere. In a typical procedure, the ligand (0.2 mmol) was dissolved in methylene chloride (5 mL) in a Schlenk tube. (DME)$NiBr_2$ (0.2 mmol, 62 mg) was then added to the solution, and the resulting mixture was stirred at room temperature for 12 hours. After removal of the solvent under reduced pressure, the solid product was washed with diethyl ether (4 × 5 mL) and dried in vacuo.



Ni1: (92 mg, 83%). Elemental analysis: calc. for $C_{24}H_{20}Br_2N_2Ni$: C, 51.95; H, 3.63; N, 5.05. Found: C, 51.87; H, 3.65; N, 5.12.

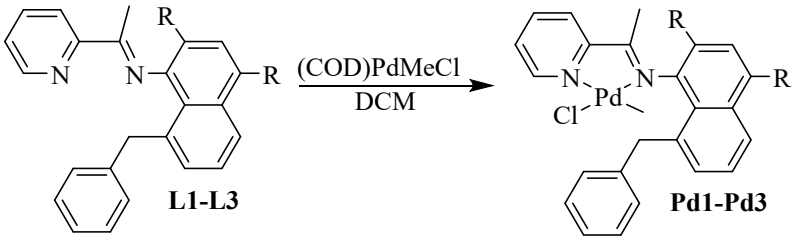


Ni2: (162 mg, 91%). Elemental analysis: calc. for $C_{50}H_{40}Br_2N_2Ni$: C, 67.68; H, 4.54; N, 3.16. Found: C, 67.54; H, 4.36; N, 3.28.



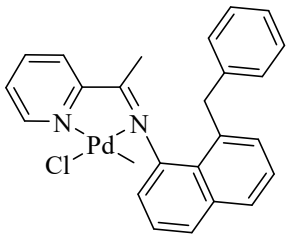
Ni3: (169 mg, 90%). Elemental analysis: calc. for $C_{54}H_{44}Br_2N_2Ni$: C, 69.04; H, 4.72; N, 2.98. Found: C, 69.21; H, 4.77; N, 2.89.

1.5 Procedure for the Synthesis of Palladium Complexes Pd1-Pd3.

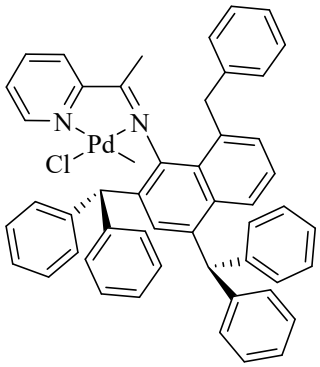


R = H (**Pd1**), $CHPh_2$ (**Pd2**), DBH (**Pd3**)

A solution of the ligand (0.5 mmol) and (COD)PdMeCl (133 mg, 0.5 mmol) in dichloromethane (20 mL) was stirred at room temperature for 12 h. During the reaction, the solution gradually darkened in color. After completion, the mixture was concentrated to ~2 mL under reduced pressure, and the product was precipitated by addition of diethyl ether (20 mL). The resulting solid was collected, washed with additional diethyl ether (3 × 5 mL), and dried *in vacuo* for 1 h to afford the pure compound as a yellow solid.

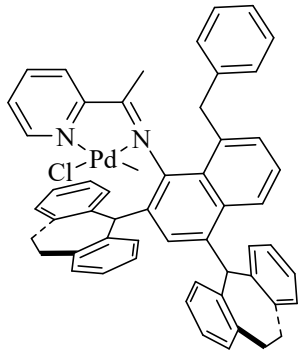


Pd1: (200 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, *J* = 5.0 Hz, 1H, Ar-*H*), 7.92 (td, *J* = 7.8, 1.3 Hz, 1H, Ar-*H*), 7.87 (d, *J* = 8.1 Hz, 1H, Ar-*H*), 7.81 (d, *J* = 8.1 Hz, 1H, Ar-*H*), 7.68 (dd, *J* = 7.6, 5.2 Hz, 1H, Ar-*H*), 7.51 (q, *J* = 6.9 Hz, 1H, Ar-*H*), 7.48 – 7.40 (m, 1H, Ar-*H*), 7.36 (d, *J* = 6.9 Hz, 1H, Ar-*H*), 7.29 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 6.96 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 6.84 – 6.74 (m, 3H, Ar-*H*), 6.55 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.26 (d, *J* = 17.2 Hz, 1H, -CH_2-), 4.30 (d, *J* = 17.2 Hz, 1H, -CH_2-), 1.31 (s, 3H, Ar-C(CH_3)=N), 0.45 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.80 (*C*=N), 153.41, 149.11, 144.76, 141.75, 138.28, 136.36, 133.92, 132.96, 128.71, 128.59, 128.13, 126.85, 126.49, 125.83, 125.12, 124.95, 120.28, 42.72 (-*C*H_2-), 18.65 (C(*C*H_3)=N-Ar), -0.36 (Pd-*C*H_3). Key ^{13}C and ^{1}H HSQC correlations ($CDCl_3$): 18.65 (C(*C*H_3)=N-Ar)/1.31 (s, 3H, Ar-C(CH_3)=N); -0.36 (Pd-*C*H_3)/0.45 (s, 3H, Pd-CH_3). Elemental analysis: calc. for $C_{25}H_{23}ClN_2Pd$: C, 60.87; H, 4.70; N, 5.68. Found: C, 60.78; H, 4.69; N, 5.74.



Pd2: (363 mg, 88%). a-isomer: b-isomer = 10:1 ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56, 9.33 (d, *J* = 5.4 Hz, 1H, Ar-*H*), 8.02, 7.94 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.74 (td, *J* = 7.8, 1.5 Hz, 1H, Ar-*H*), 7.63 (dd, *J* = 14.9, 8.0 Hz, 1H, Ar-*H*), 7.44 – 7.38 (m, 1H, Ar-*H*), 7.31 (d, *J* = 7.0 Hz, 1H, Ar-*H*), 7.25 (d, *J* = 6.0 Hz, 4H, Ar-*H*), 7.14 (dd, *J* = 13.1, 7.0 Hz, 3H, Ar-*H*), 6.89 – 6.83 (m, 5H, Ar-*H*), 6.94 (d, *J* = 6.9 Hz, 3H, Ar-*H*), 6.88 – 6.82 (m, 6H, Ar-*H*), 6.72 (dd, *J* = 14.5, 7.0 Hz, 5H, Ar-*H*), 6.62 (dd, *J* = 9.8, 5.8 Hz, 1H, Ar-*H*), 6.49 (s, 1H, C*H*Ar_2), 6.20 (s, 1H, C*H*Ar_2), 6.10 (d, *J* = 17.1 Hz, 1H, -CH_2-), 4.52, 4.35 (d, *J* = 17.6 Hz, 1H, -CH_2-), 0.78, 0.71 (s, 3H, C(CH_3)=N-Ar), 0.22, 0.17 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.17 (*C*=N),

153.12, 148.86, 143.88, 142.91, 142.22, 141.06, 140.26, 140.08, 139.00, 137.89, 134.00, 133.52, 133.05, 132.29, 130.53, 130.29, 129.56, 129.33, 129.08, 128.57, 128.53, 128.43, 128.11, 127.77, 127.70, 126.59, 126.55, 126.42, 126.32, 125.97, 125.85, 124.32, 123.94, 53.68 (*C*HAr$_2$), 52.42 (*C*HAr$_2$), 42.59 (-*C*H$_2$-), 18.17 (Ar-C(*C*H$_3$)=N), 1.44 (Pd-*C*H$_3$). Elemental analysis: calc. for $C_{51}H_{43}ClN_2Pd$: C, 74.18; H, 5.25; N, 3.39. Found: C, 74.24; H, 5.36; N, 3.43.



Pd3: (395 mg, 90%). a-isomer: b-isomer = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57, 9.35 (d, *J* = 4.8 Hz, 1H, Ar-*H*), 8.76, 8.42 (d, *J* = 8.6 Hz, 1H, Ar-*H*), 7.68 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.65 – 7.59 (m, 1H, Ar-*H*), 7.39 (dd, *J* = 14.3, 6.0 Hz, 2H, Ar-*H*), 7.31 – 7.27 (m, 2H, Ar-*H*), 7.25 – 7.15 (m, 6H, Ar-*H*), 7.14 – 7.05 (m, 2H, Ar-*H*), 6.92 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 6.83 (t, *J* = 6.4 Hz, 2H, Ar-*H*), 6.78 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 6.74 – 6.66 (m, 4H, Ar-*H*), 6.53 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 6.13 (d, *J* = 17.4 Hz, 1H, -C*H*$_2$-), 6.07 (s, 1H, C*H*Ar$_2$), 5.95 (t, *J* = 6.9 Hz, 1H, Ar-*H*), 5.82 (s, 1H, C*H*Ar$_2$), 4.47, 4.32 (d, *J* = 17.3 Hz, 1H, -C*H*$_2$-), 3.09 (td, *J* = 14.0, 4.5 Hz, 1H, -C*H*$_2$-C*H*$_2$-), 2.89 – 2.75 (m, 1H, -C*H*$_2$-C*H*$_2$-), 2.68 – 2.53 (m, 2H, -C*H*$_2$-C*H*$_2$-), 2.25 – 2.00 (m, 4H, -C*H*$_2$-C*H*$_2$-), 0.89, 0.78 (s, 3H, C(C*H*$_3$)=N-Ar), 0.40, 0.37 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.80 (*C*=N), 153.39, 148.69, 142.44, 141.48, 140.99, 140.69, 140.16, 140.00, 139.39, 138.95, 137.76, 137.72, 136.44, 133.76, 133.51, 133.06, 132.89, 132.56, 132.20, 131.32, 130.69, 130.61, 130.06, 128.71, 128.65, 128.51, 128.40, 127.63, 127.58, 127.39, 127.07, 126.99, 126.87, 126.49, 126.25, 126.13, 125.77, 125.55, 125.38, 124.60, 124.41, 57.80 (*C*HAr$_2$), 56.15 (*C*HAr$_2$), 42.73 (-*C*H$_2$-), 32.54 (-*C*H$_2$-*C*H$_2$-), 32.42 (-*C*H$_2$-*C*H$_2$-), 29.94 (-*C*H$_2$-*C*H$_2$-), 29.41 (-*C*H$_2$-*C*H$_2$-), 18.01 (C(*C*H$_3$)=N-Ar), 1.27 (Pd-*C*H$_3$). Elemental analysis: calc. for $C_{55}H_{47}ClN_2Pd$: C, 75.25; H, 5.40; N, 3.19. Found: C, 75.33; H, 5.44; N, 3.12.

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

In a typical experiment, a 350 mL thick-walled glass pressure reactor was dried at 90 °C under vacuum for ≥1 h. After cooling to the desired polymerization temperature, the reactor was charged with toluene (20 mL) and the appropriate amount of Et_2AlCl under a nitrogen atmosphere in a glovebox. The glass polymerization reactor was subsequently integrated into a medium-pressure polymerization line, where the catalyst (dissolved in 1 mL of CH_2Cl_2) was injected into the system via syringe under ethylene atmosphere. Under vigorous stirring (350 rpm), the reactor was pressurized with ethylene (6 atm) and maintained at this pressure for 10 min. The reaction was then quenched by venting the reactor, and the polyethylene was precipitated by addition of ethanol. The product was isolated by filtration and dried *in vacuo* at 50 °C for ≥24 h.

1.7 A General Procedure for the Homopolymerization of Ethylene Using Pd Complexes.

In a typical experiment, a 350 mL thick-walled glass pressure reactor was dried at 90 °C under vacuum for ≥1 h. After cooling to the desired polymerization temperature, the reactor was charged with toluene (38 mL) and the appropriate amount of NaBArF under a nitrogen atmosphere in a glovebox. The glass polymerization reactor was subsequently integrated into a medium-pressure polymerization line, where the Pd catalyst (dissolved in 2 mL of CH_2Cl_2) was injected into the system via syringe under ethylene atmosphere. Under vigorous stirring (350 rpm), the reactor was pressurized with ethylene (4 atm) and maintained at this pressure for 1 h. The reaction was then quenched by venting the reactor, and the polyethylene product was isolated by rotary evaporation to remove volatile solvents and subsequently dried under vacuum.

1.8 A General Procedure for the Copolymerization of Methyl Acrylate with Ethylene using Pd Complexes.

In a typical experiment, a 350 mL thick-walled glass pressure reactor was dried at 90 °C under vacuum for ≥1 h. After cooling to the desired polymerization temperature, the reactor was charged with CH_2Cl_2 (18 mL) and the appropriate amount of NaBArF and MA under a nitrogen atmosphere in a glovebox. The glass polymerization reactor was subsequently integrated into a medium-pressure polymerization line, where the Pd catalyst (dissolved in 2 mL of CH_2Cl_2)

was injected into the system via syringe under ethylene atmosphere. Under vigorous stirring, the reactor was pressurized with ethylene (4 atm) and maintained at this pressure for 3 h. The reaction was then quenched by venting the reactor, and the E-MA copolymer was isolated by rotary evaporation to remove volatile solvents and subsequently dried under vacuum.

2. Spectra Data

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

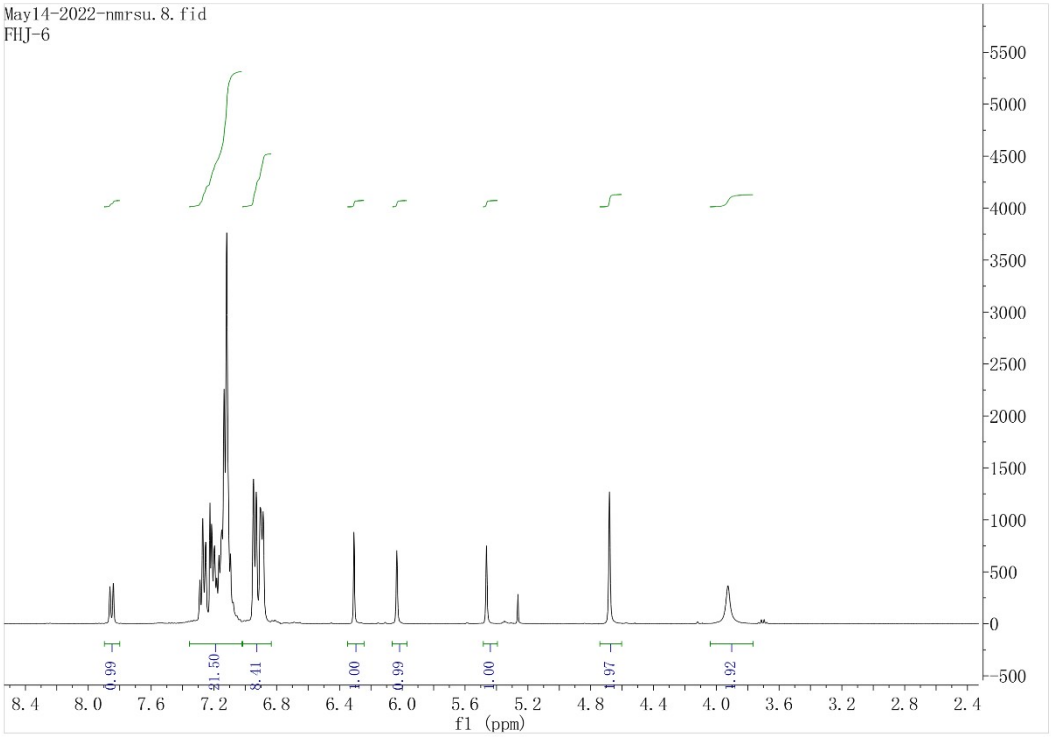


Figure S1. ^{1}H NMR spectrum of **A2** in $CDCl_3$.

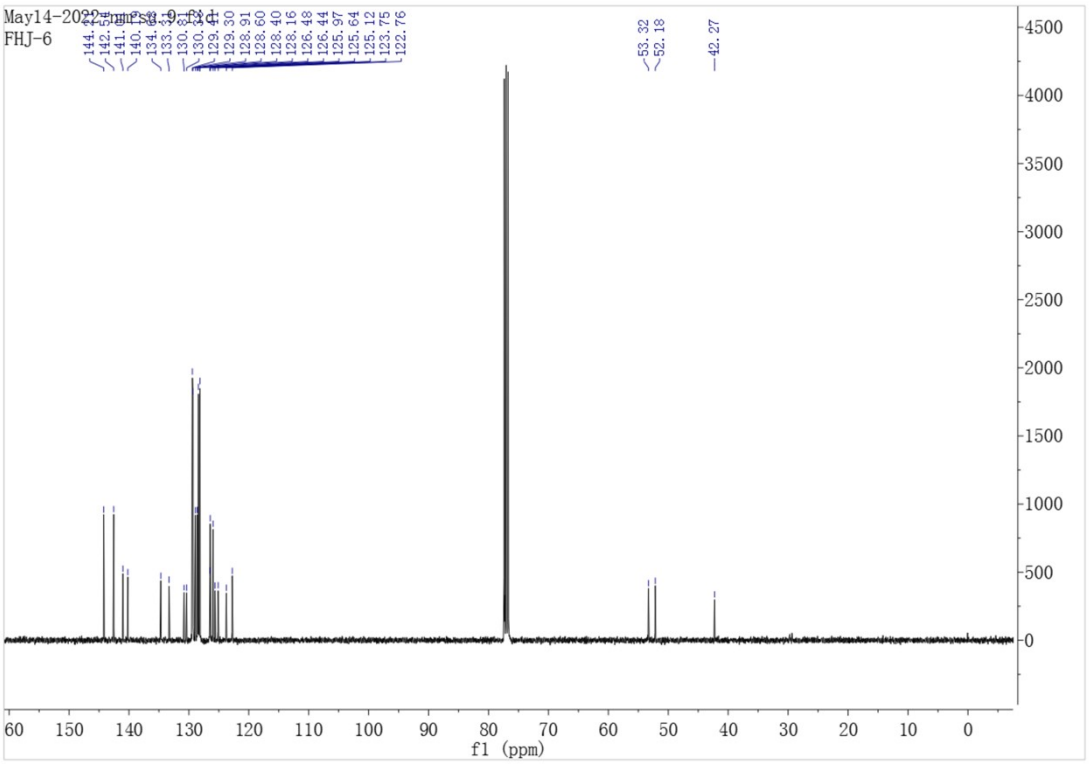


Figure S2. ^{13}C NMR spectrum of **A2** in $CDCl_3$.

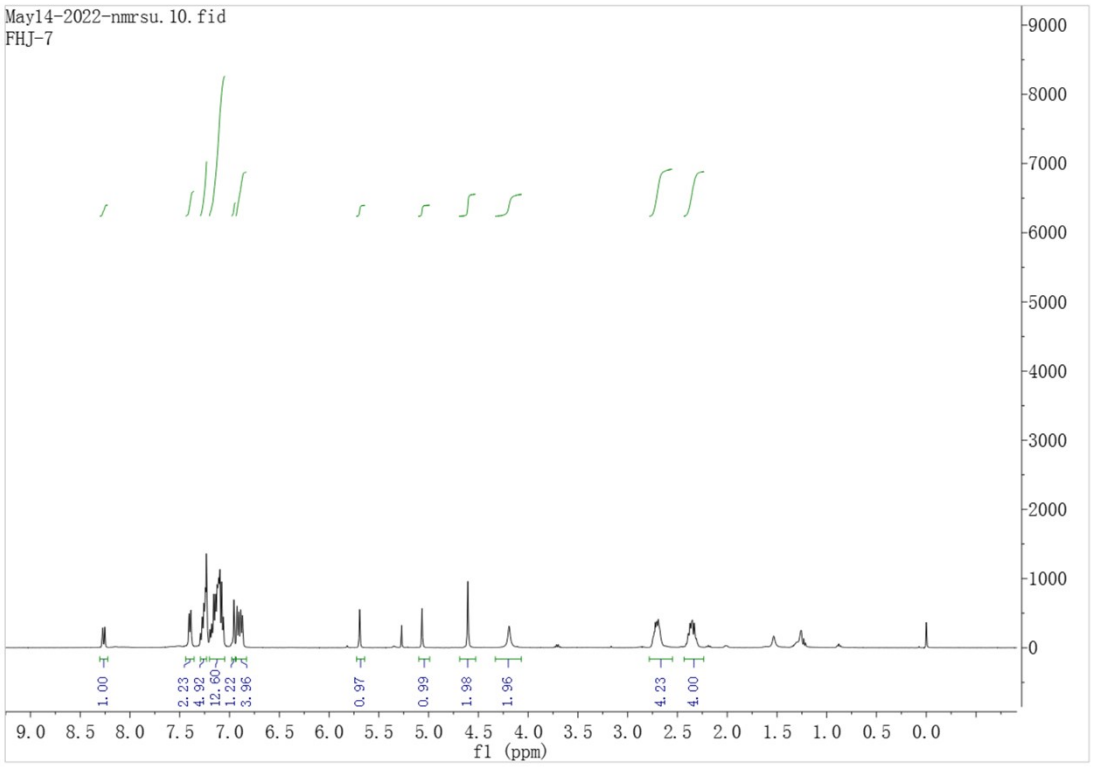


Figure S3. ^{1}H NMR spectrum of **A3** in $CDCl_3$.

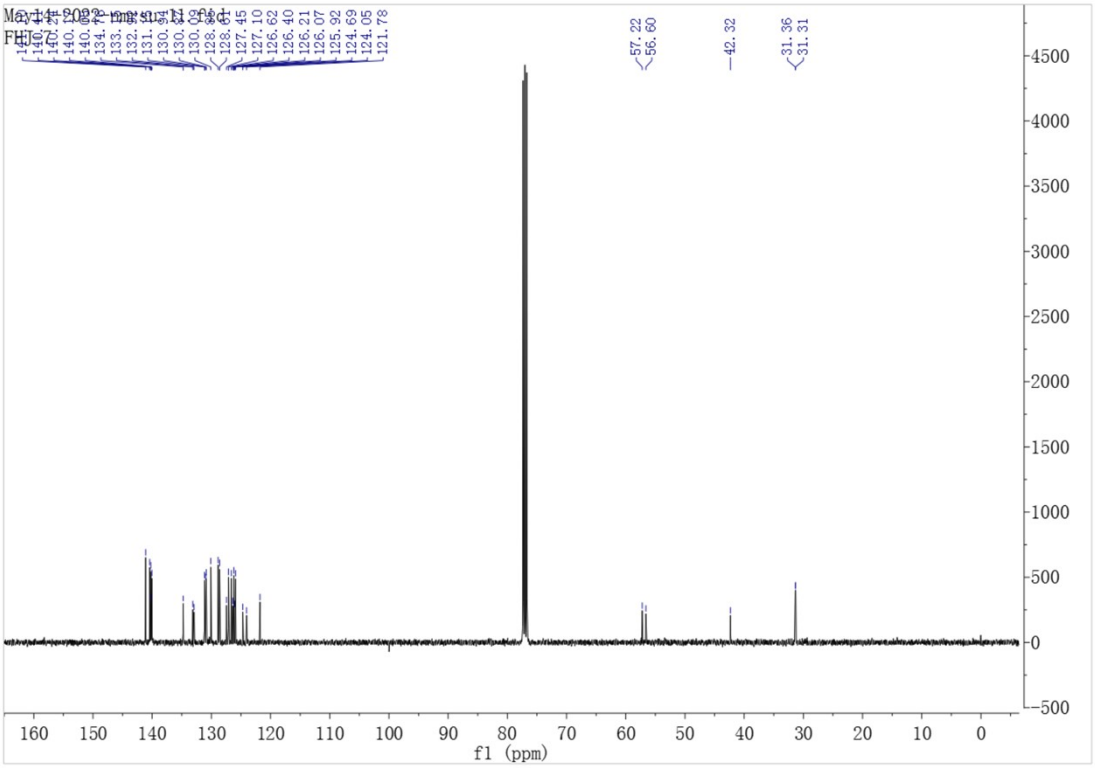


Figure S4. ^{13}C NMR spectrum of **A3** in $CDCl_3$.

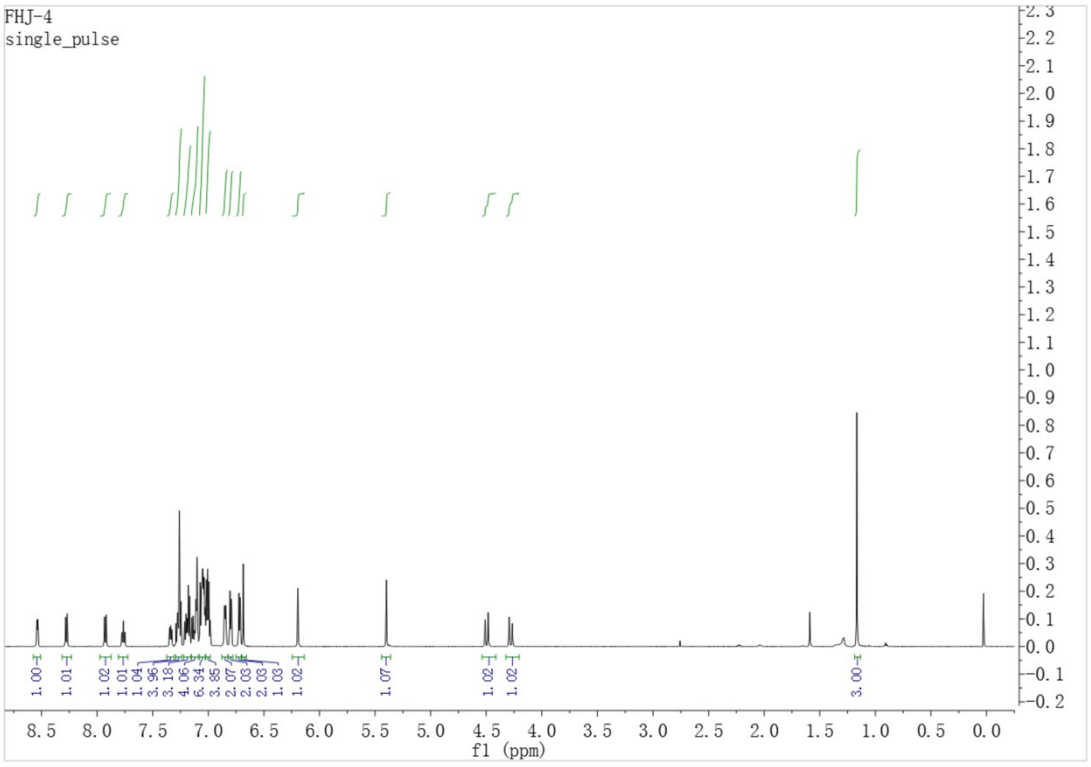


Figure S5. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

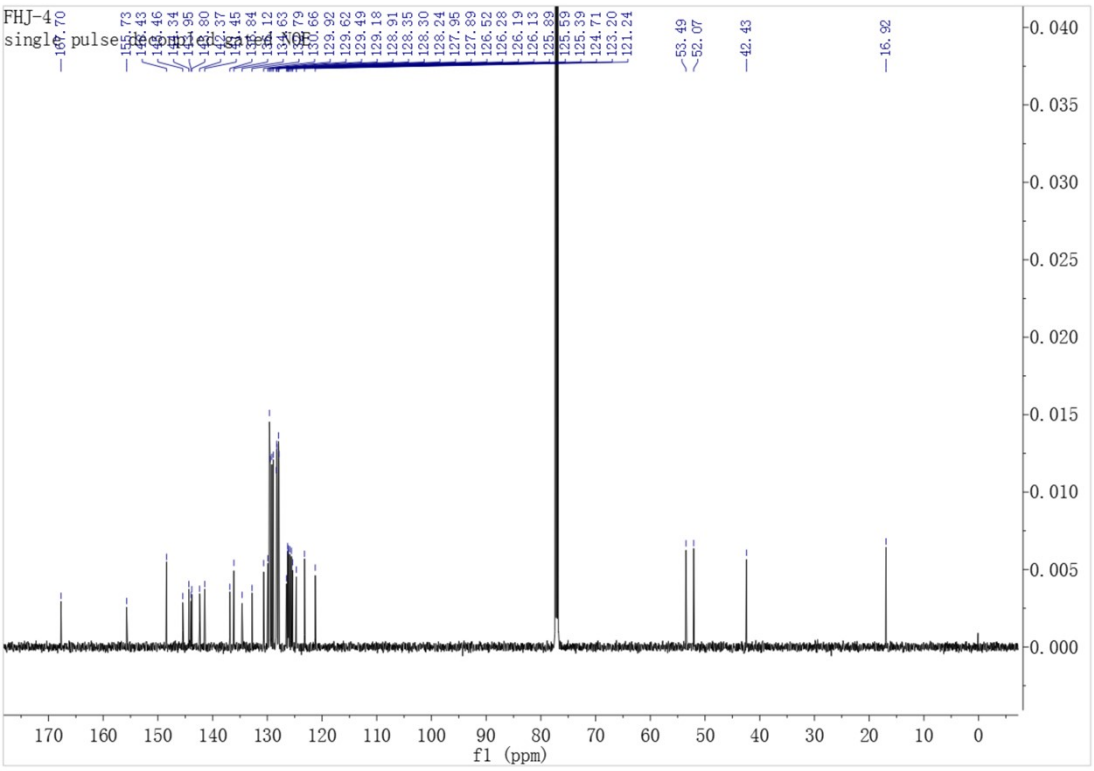


Figure S6. ^{13}C NMR spectrum of **L2** in $CDCl_3$.

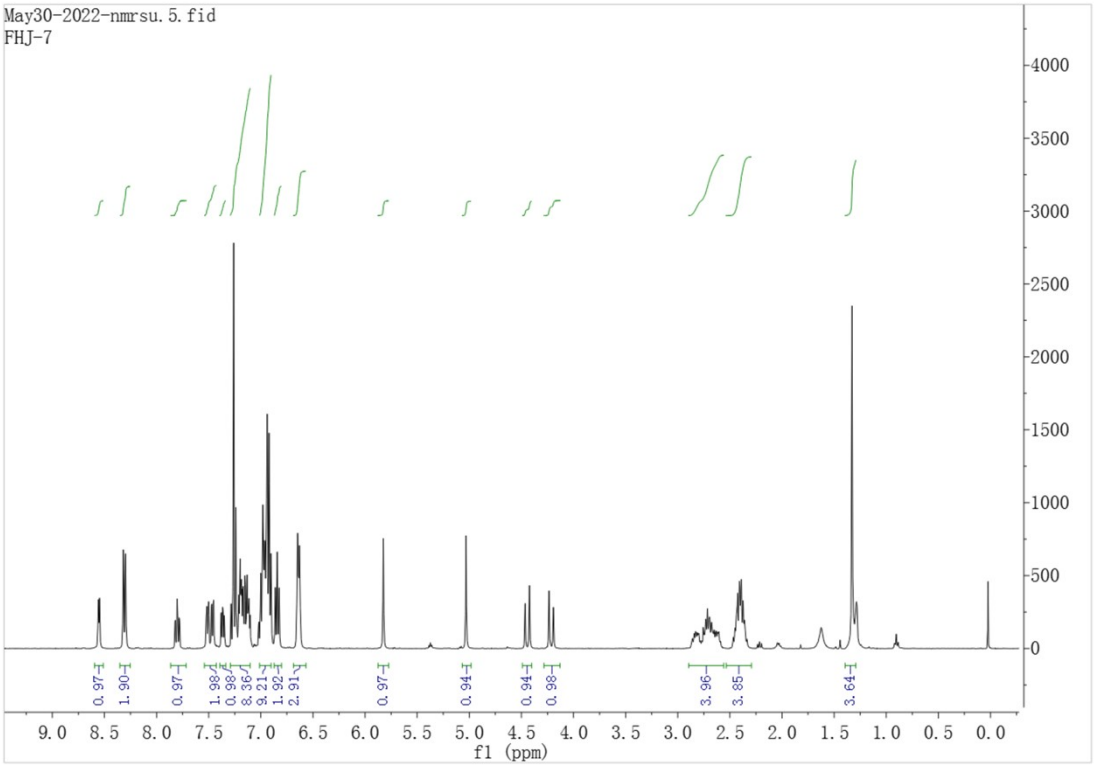


Figure S7. ^{1}H NMR spectrum of **L3** in $CDCl_3$.

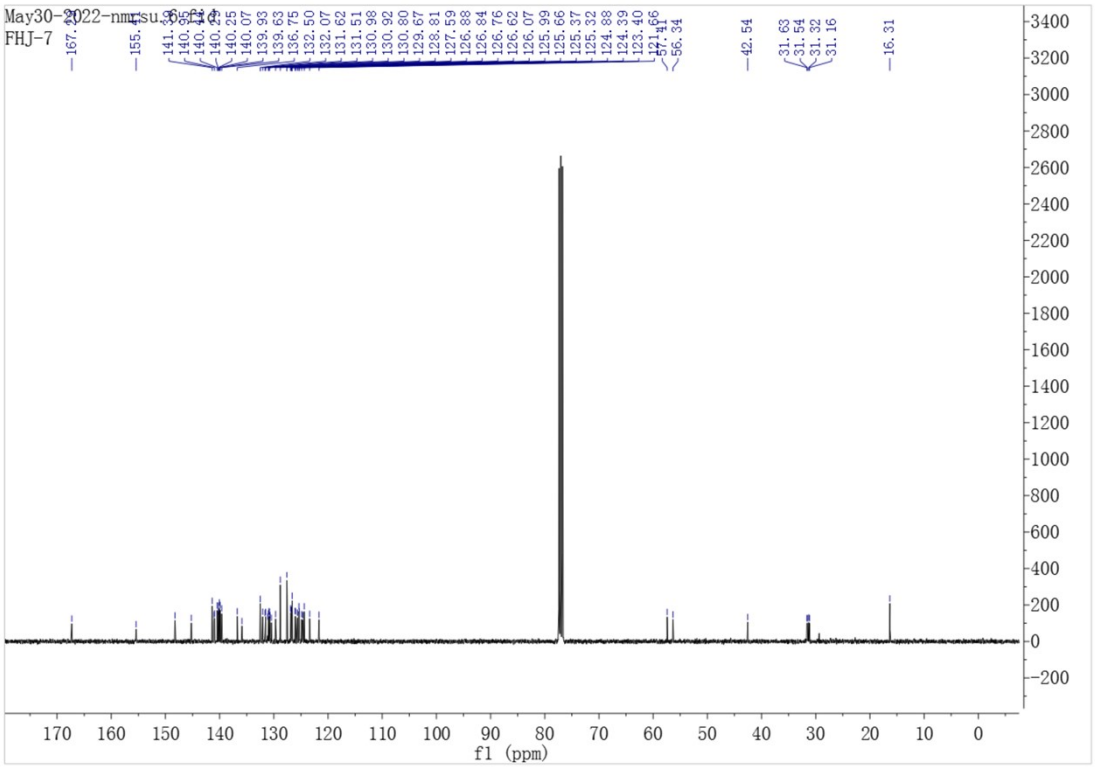


Figure S8. ^{13}C NMR spectrum of **L3** in $CDCl_3$.

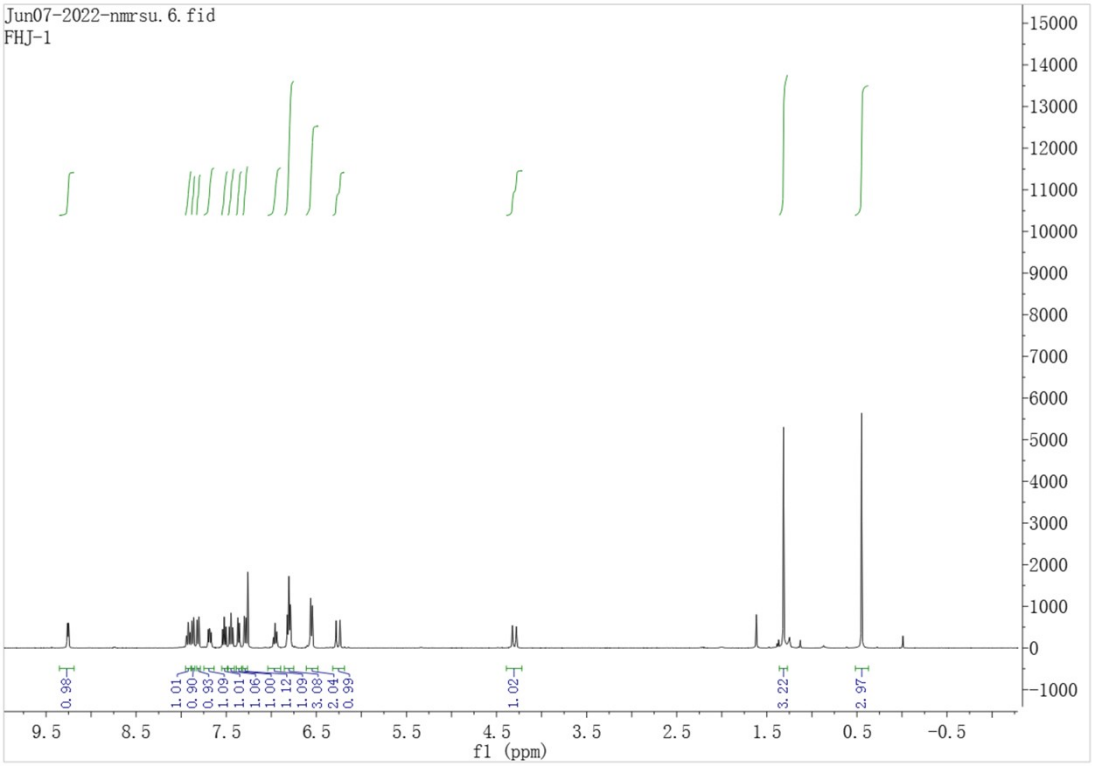


Figure S9. ^{1}H NMR spectrum of **Pd1** in $CDCl_3$.

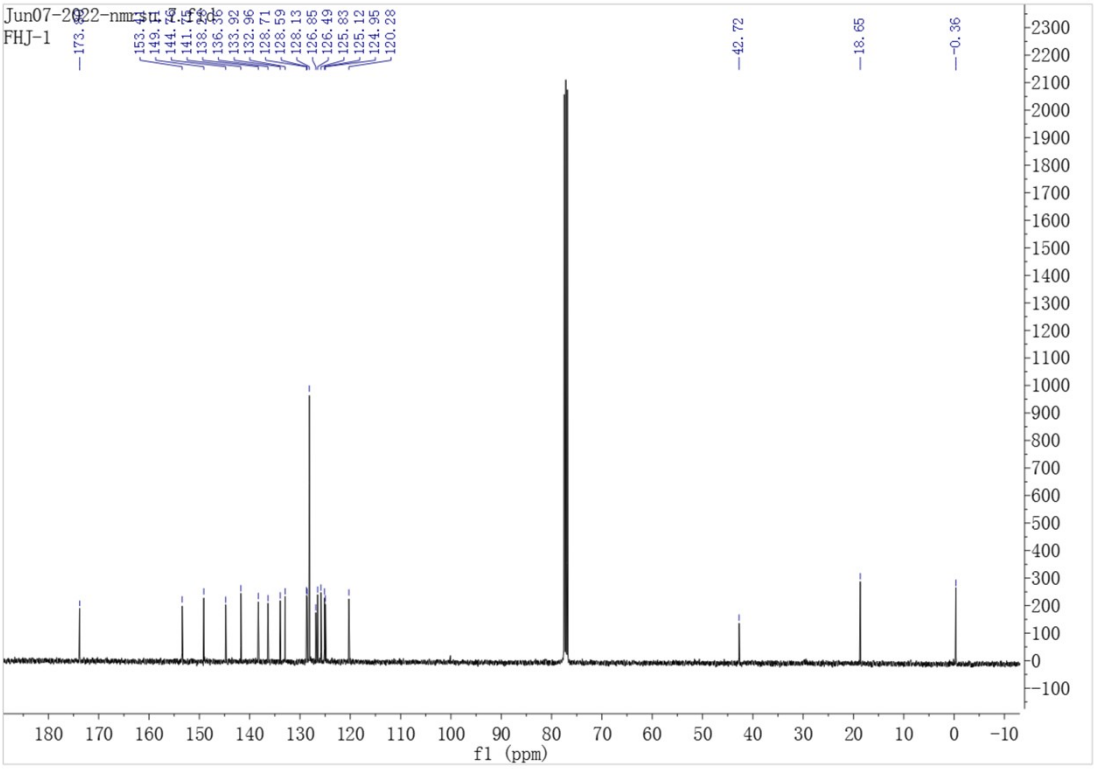


Figure S10. ^{13}C NMR spectrum of **Pd1** in $CDCl_3$.

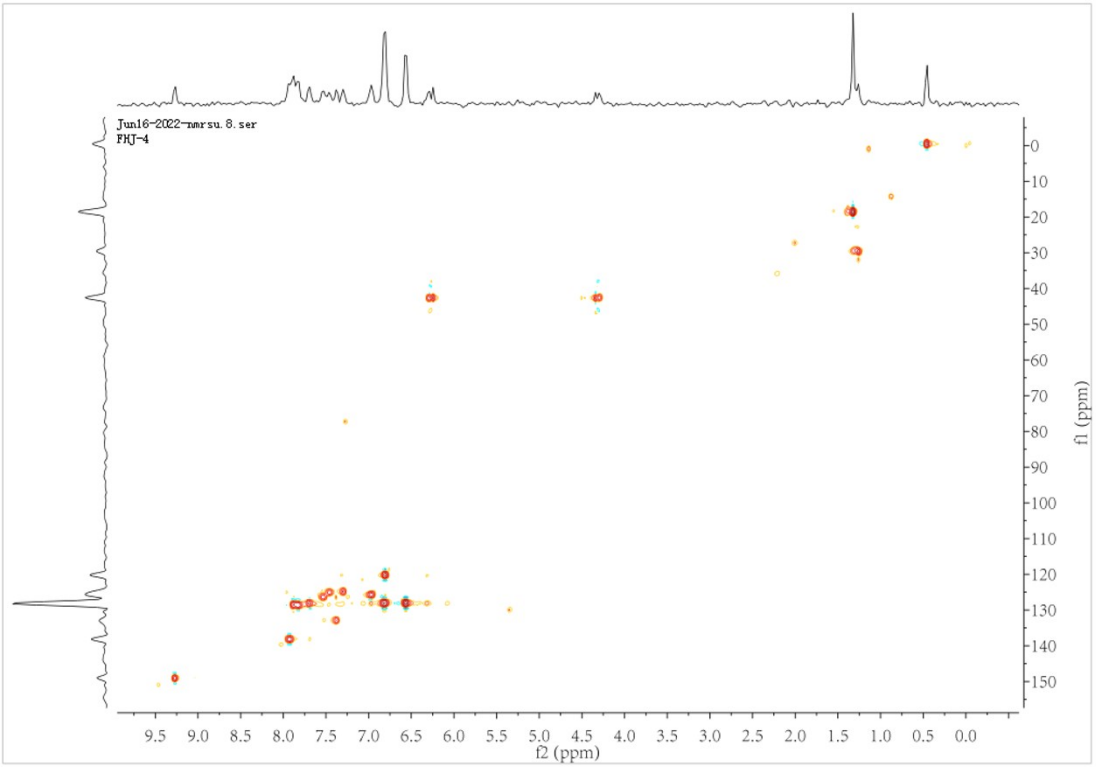


Figure S11. ^{1}H-^{13}C HSQC NMR spectrum of **Pd1** in $CDCl_3$.

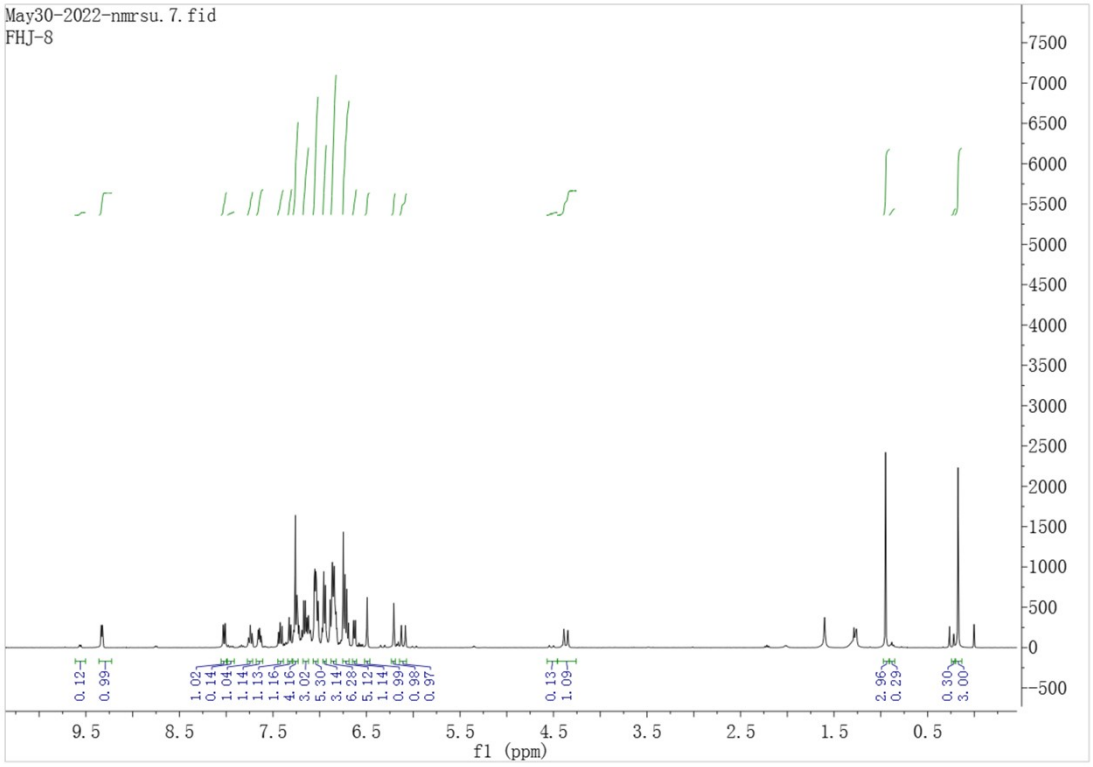


Figure S12. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

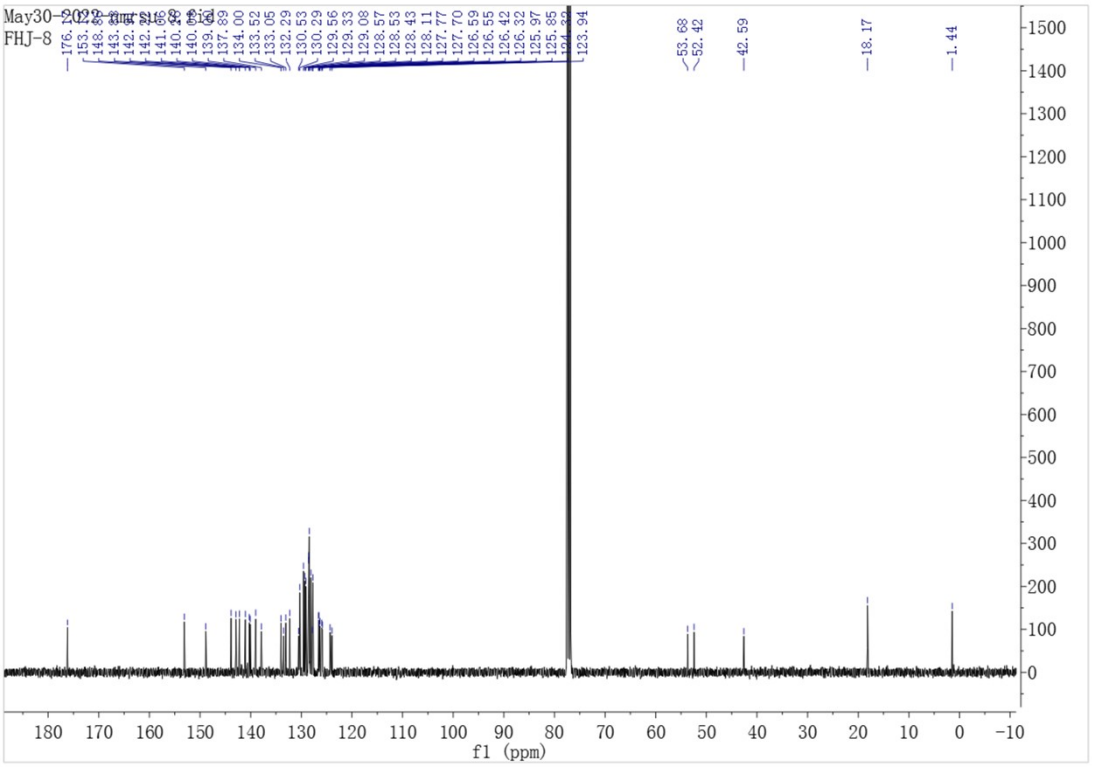


Figure S13. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

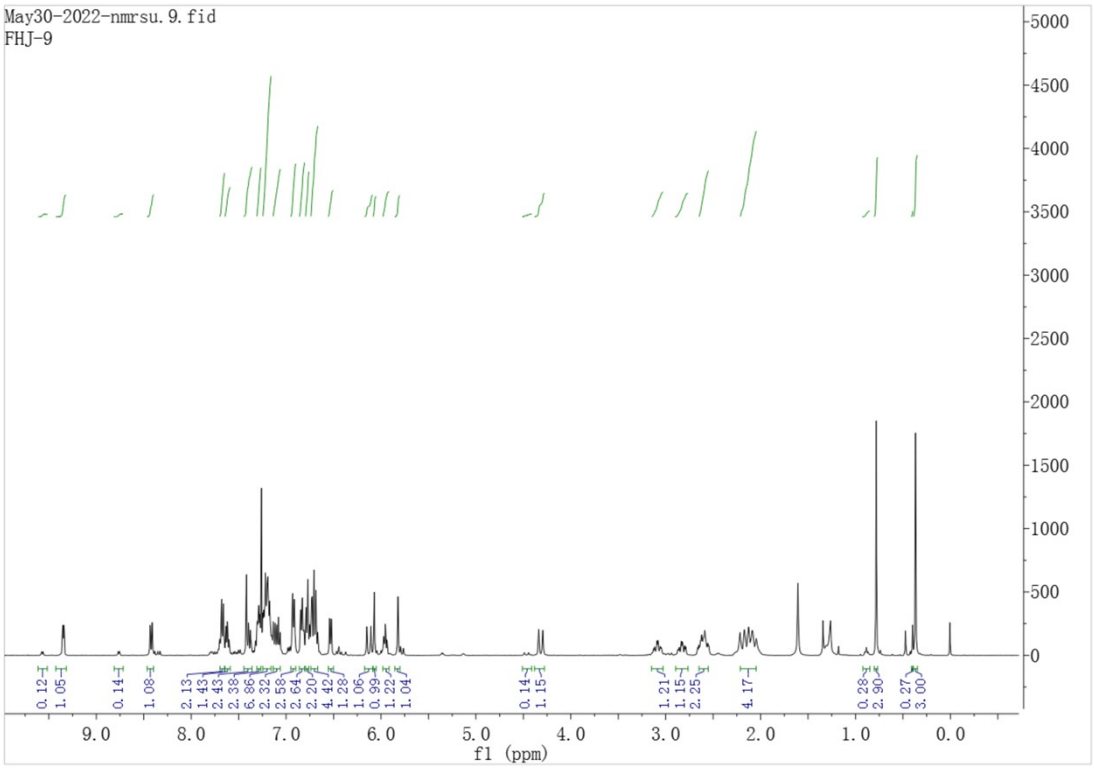


Figure S14. ^{1}H NMR spectrum of **Pd3** in $CDCl_3$.

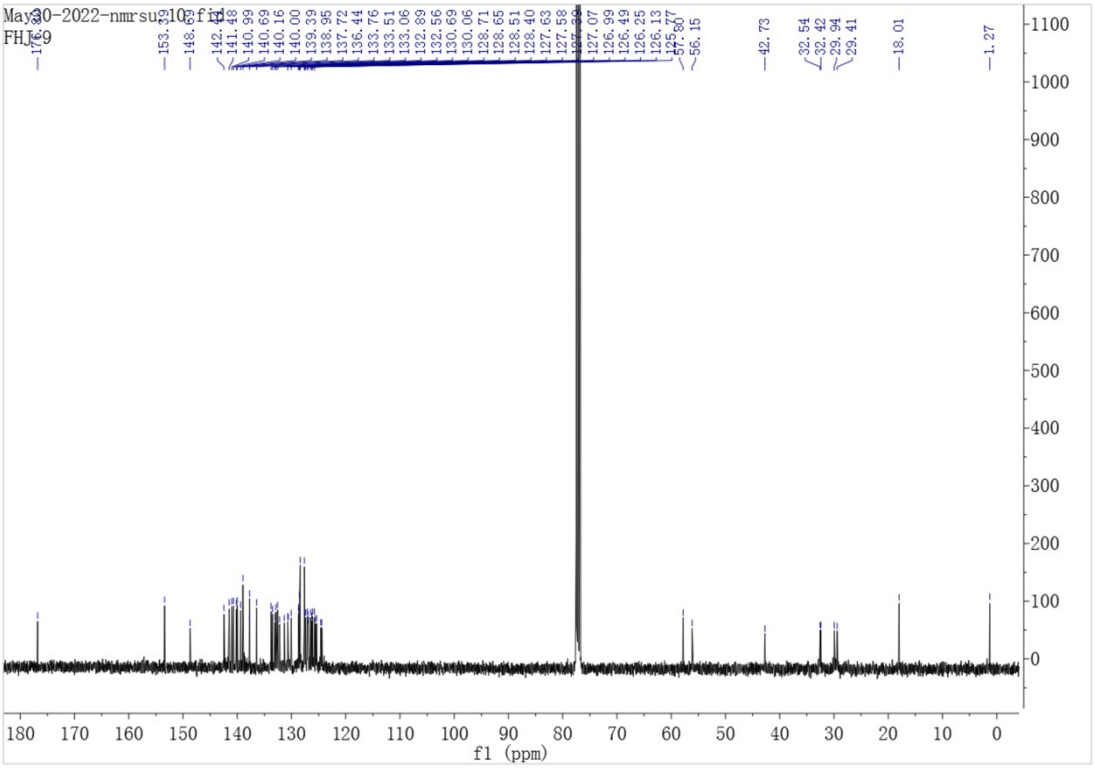


Figure S15. ^{13}C NMR spectrum of **Pd3** in $CDCl_3$.

2.2 APCI-MS of Arylamines A2-A3.

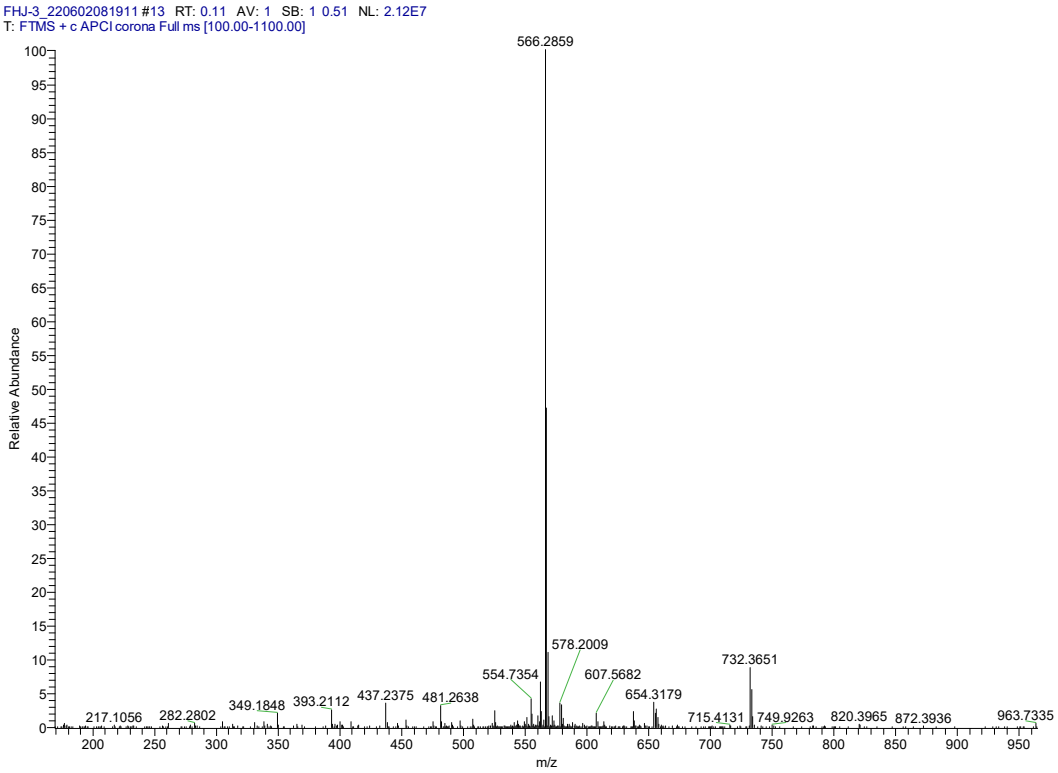


Figure S16. APCI-MS of **A2**.

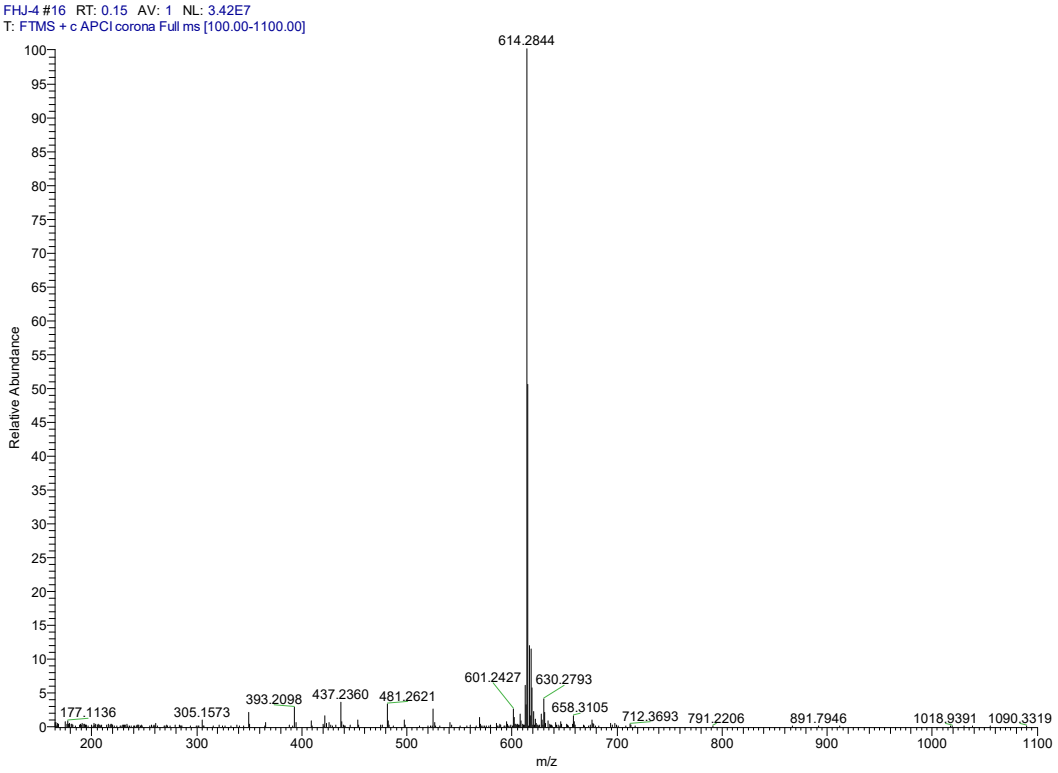


Figure S17. APCI-MS of **A3**.

2.3 APCI-MS of Ligands L1-L3.

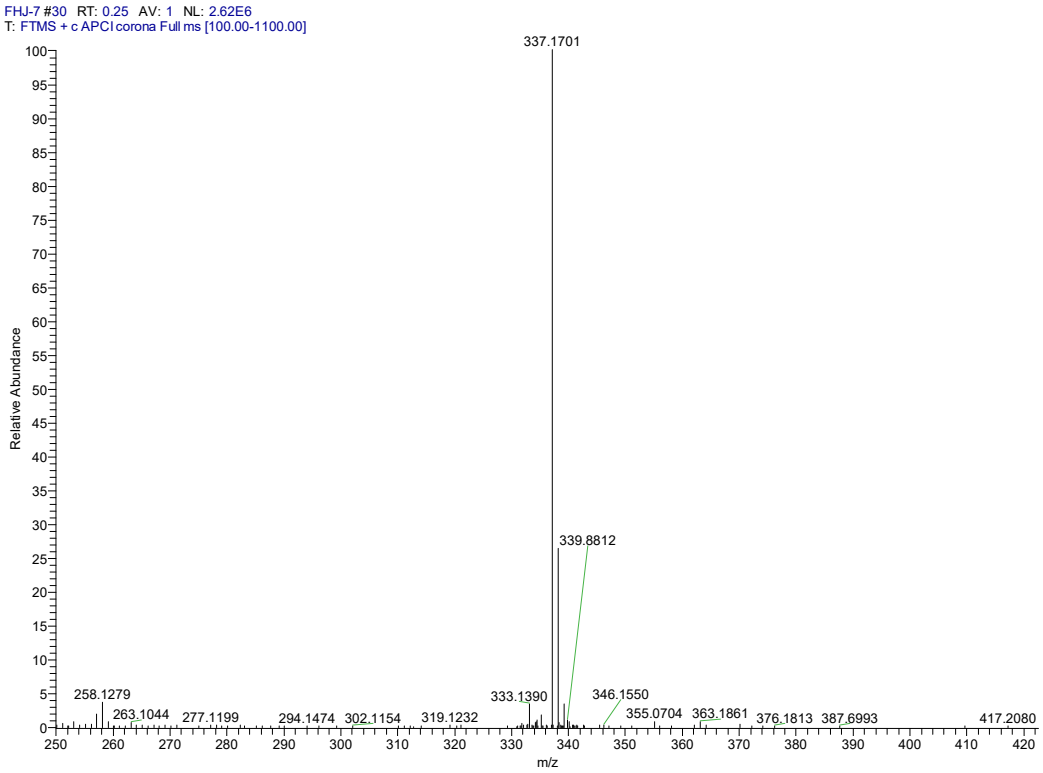


Figure S18. APCI-MS of **L1**.

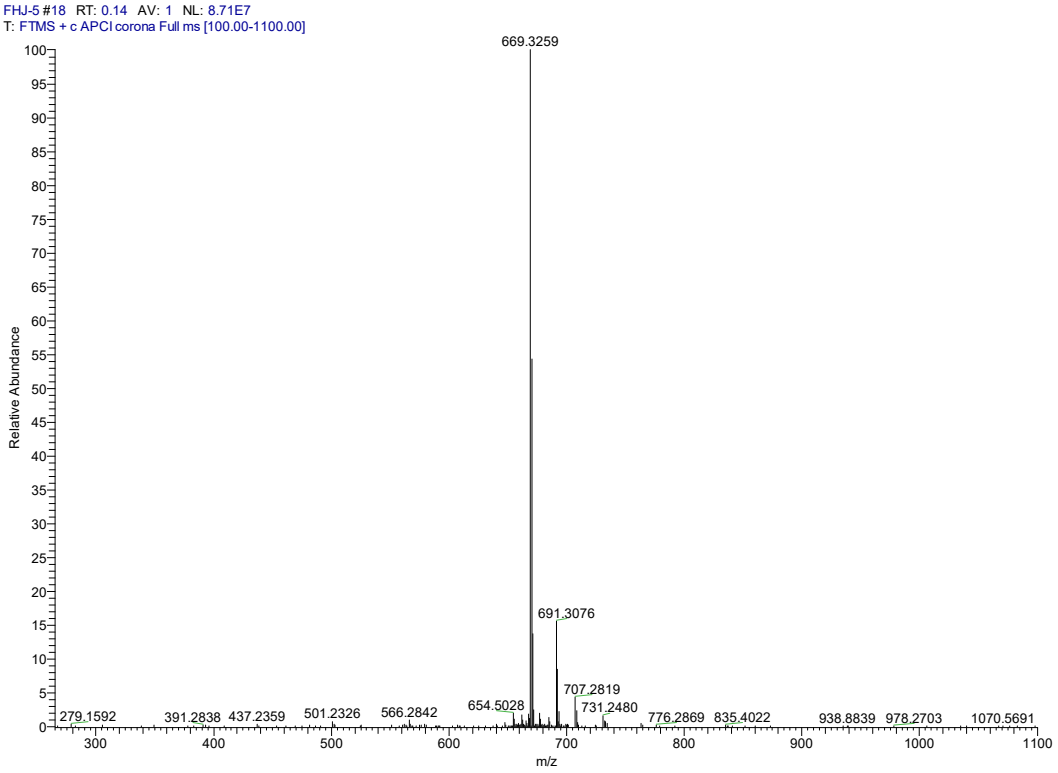


Figure S19. APCI-MS of **L2**.

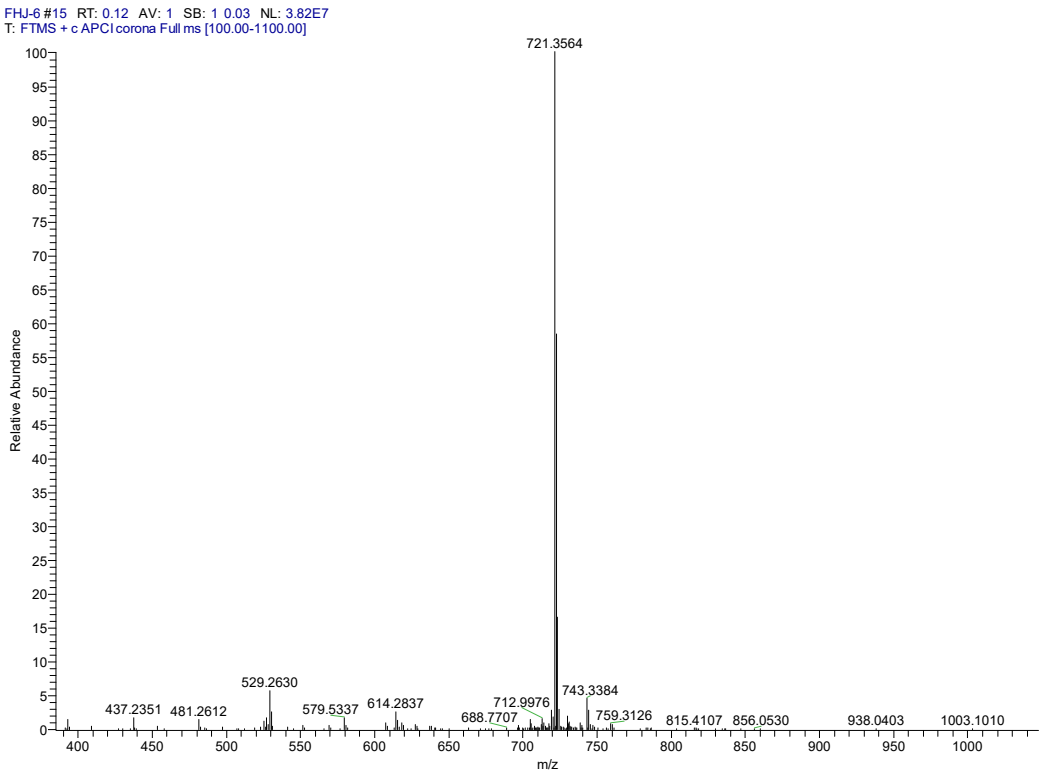


Figure S20. APCI-MS of **L3**.

2.4 ^{1}H and ^{13}C NMR of Representative Polymers and Copolymers.

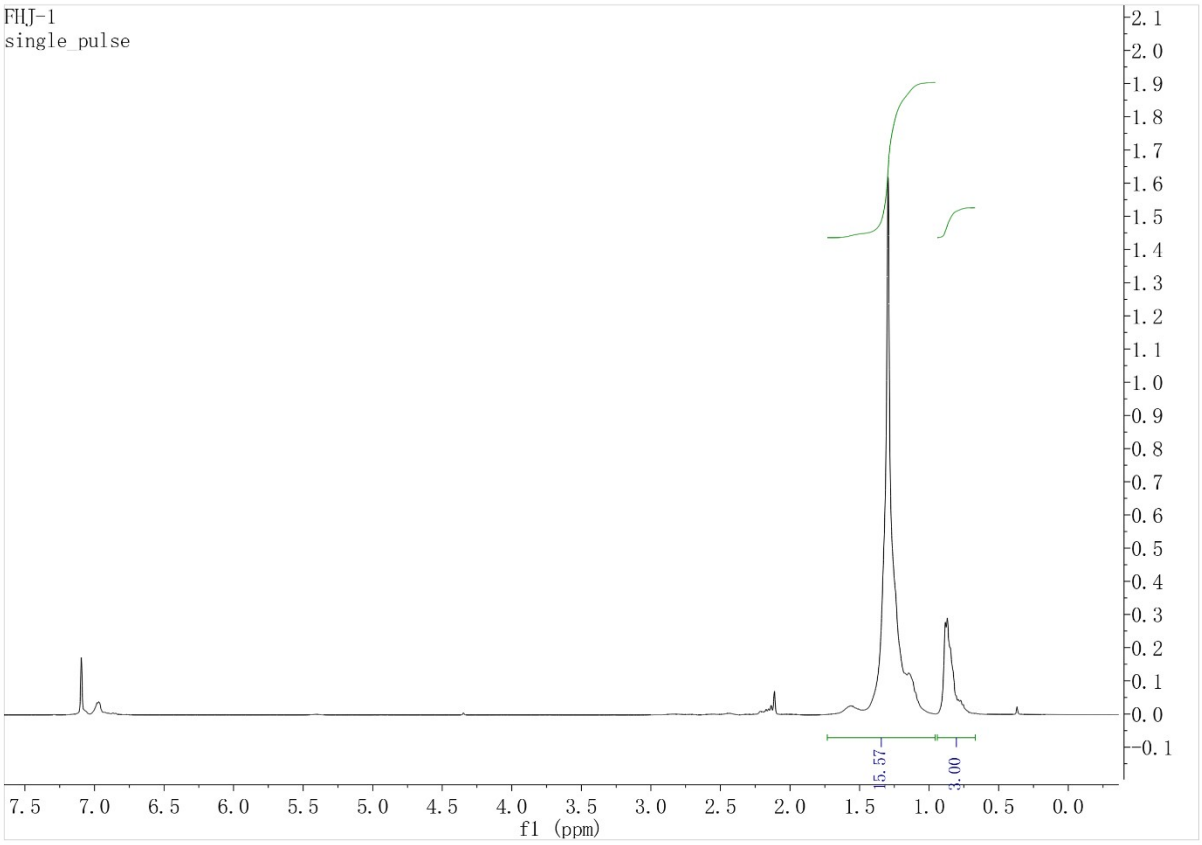


Figure S21. ^{1}H NMR spectrum of the polymer from table 1, entry 2 (C_6D_6, 70 °C).

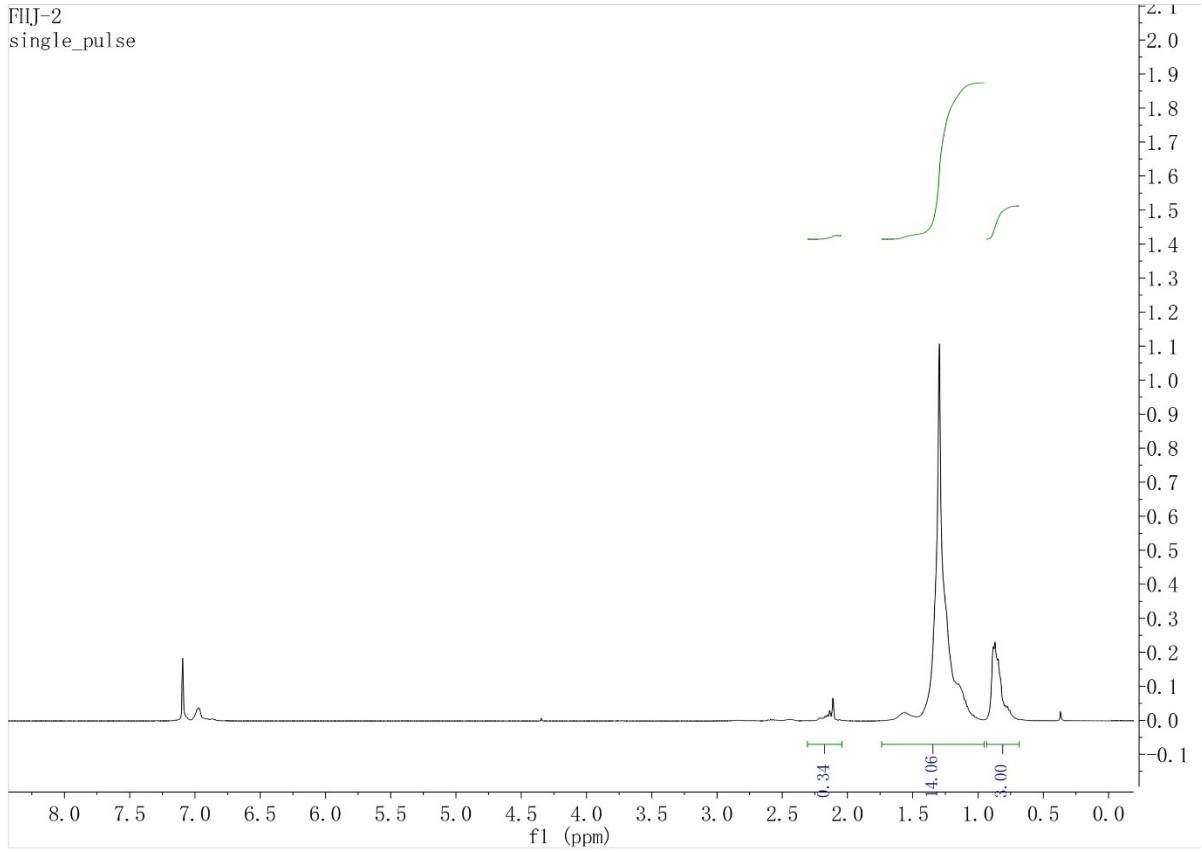


Figure S22. ^{1}H NMR spectrum of the polymer from table 1, entry 3 (C_6D_6, 70 °C).

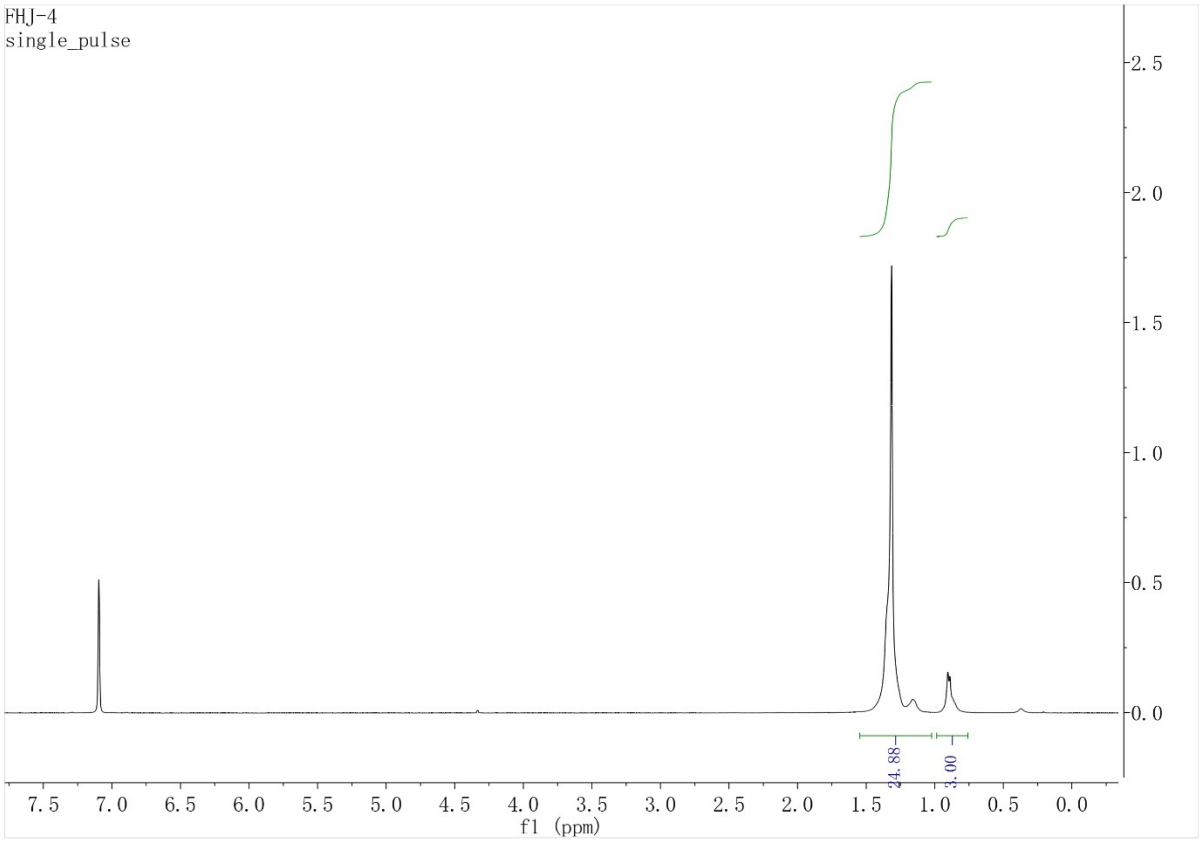


Figure S23. ^{1}H NMR spectrum of the polymer from table 1, entry 4 (C_6D_6, 70 °C).

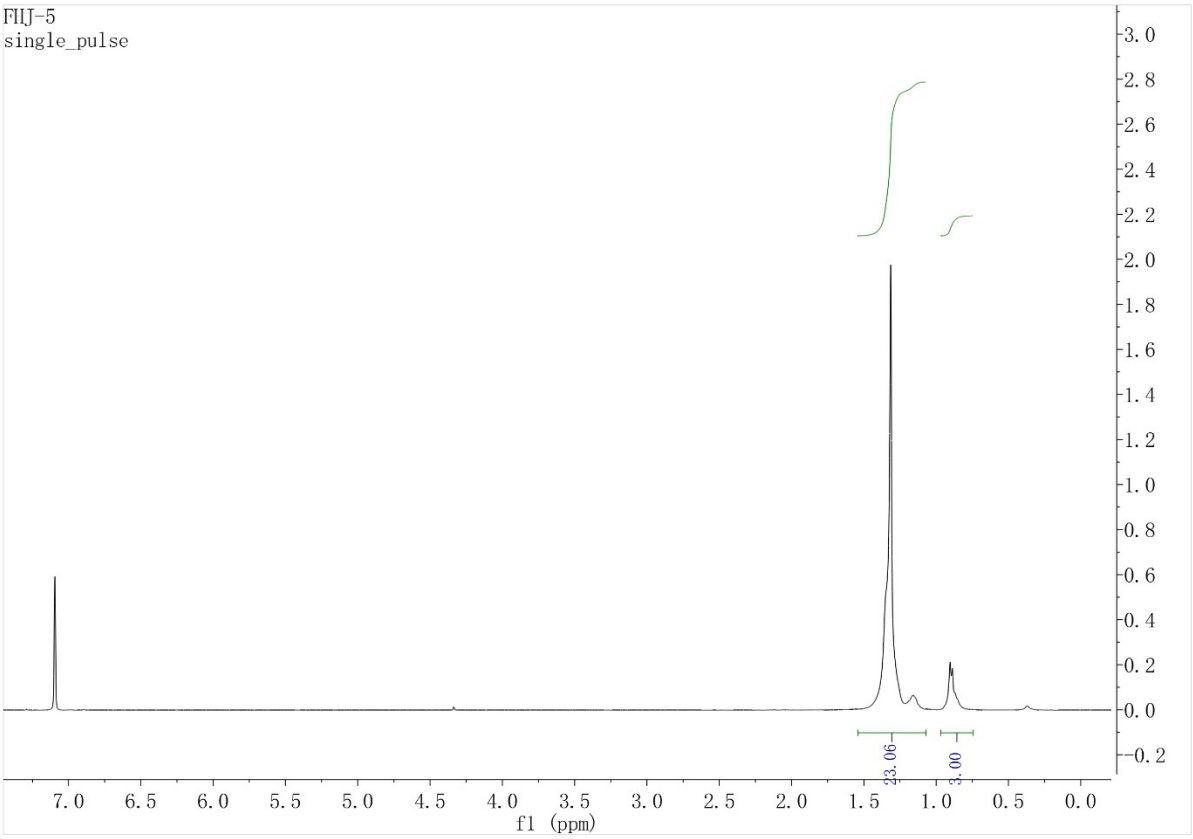


Figure S24. ^{1}H NMR spectrum of the polymer from table 1, entry 5 (C_6D_6, 70 °C).

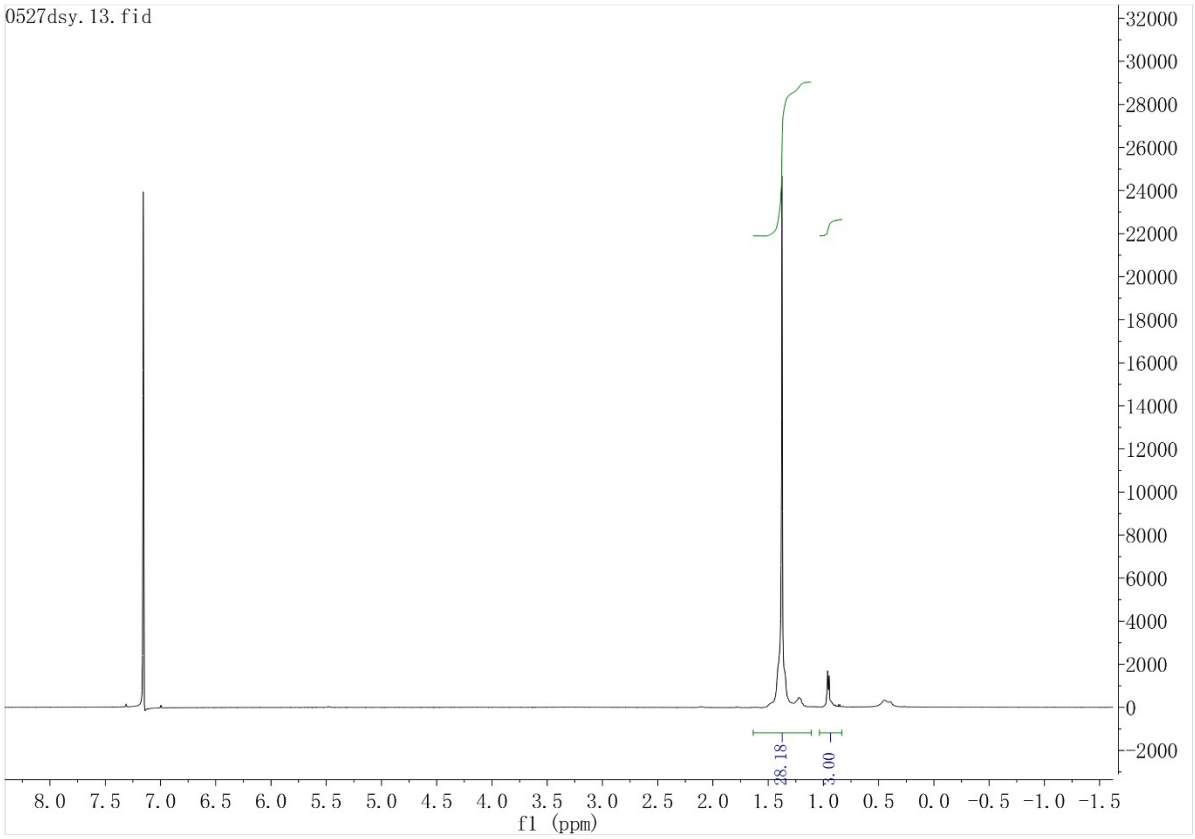


Figure S25. ^{1}H NMR spectrum of the polymer from table 1, entry 7 (C_6D_6, 70 °C).

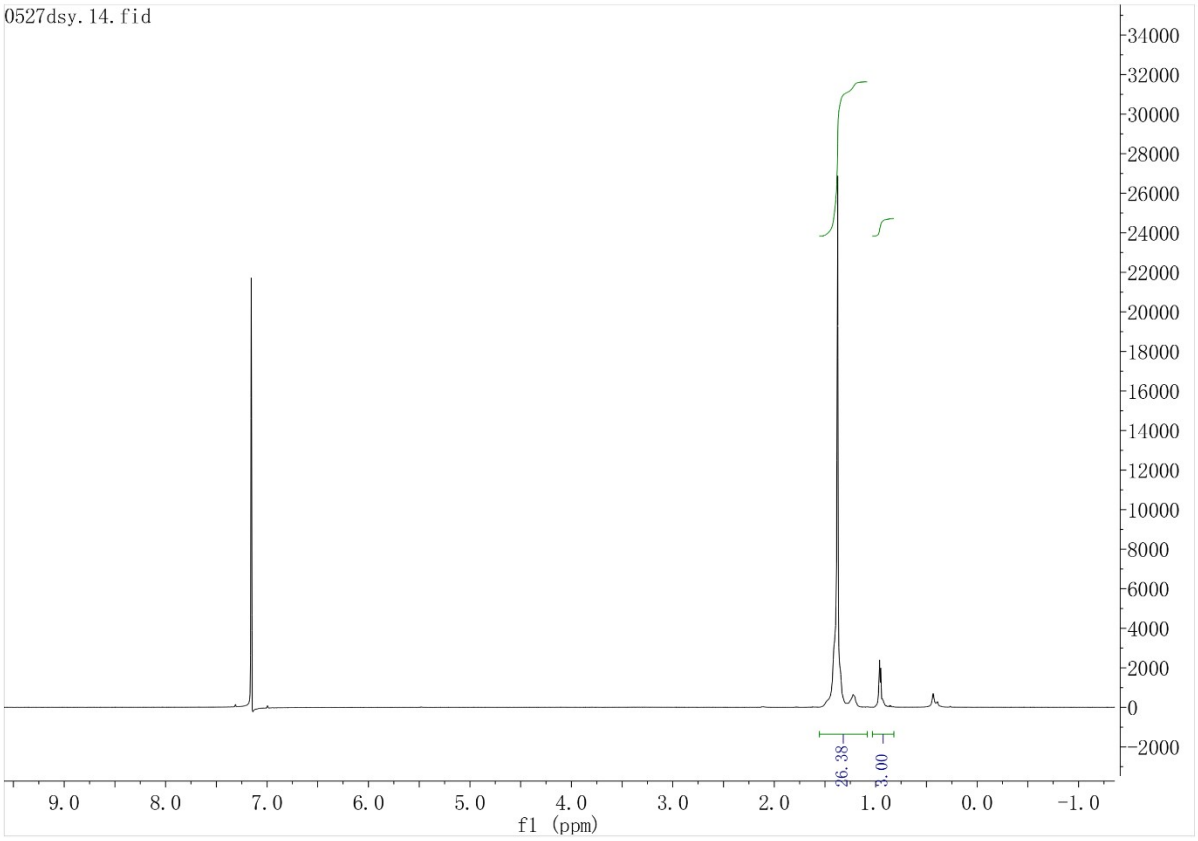


Figure S26. ^{1}H NMR spectrum of the polymer from table 1, entry 8 (C_6D_6, 70 °C).

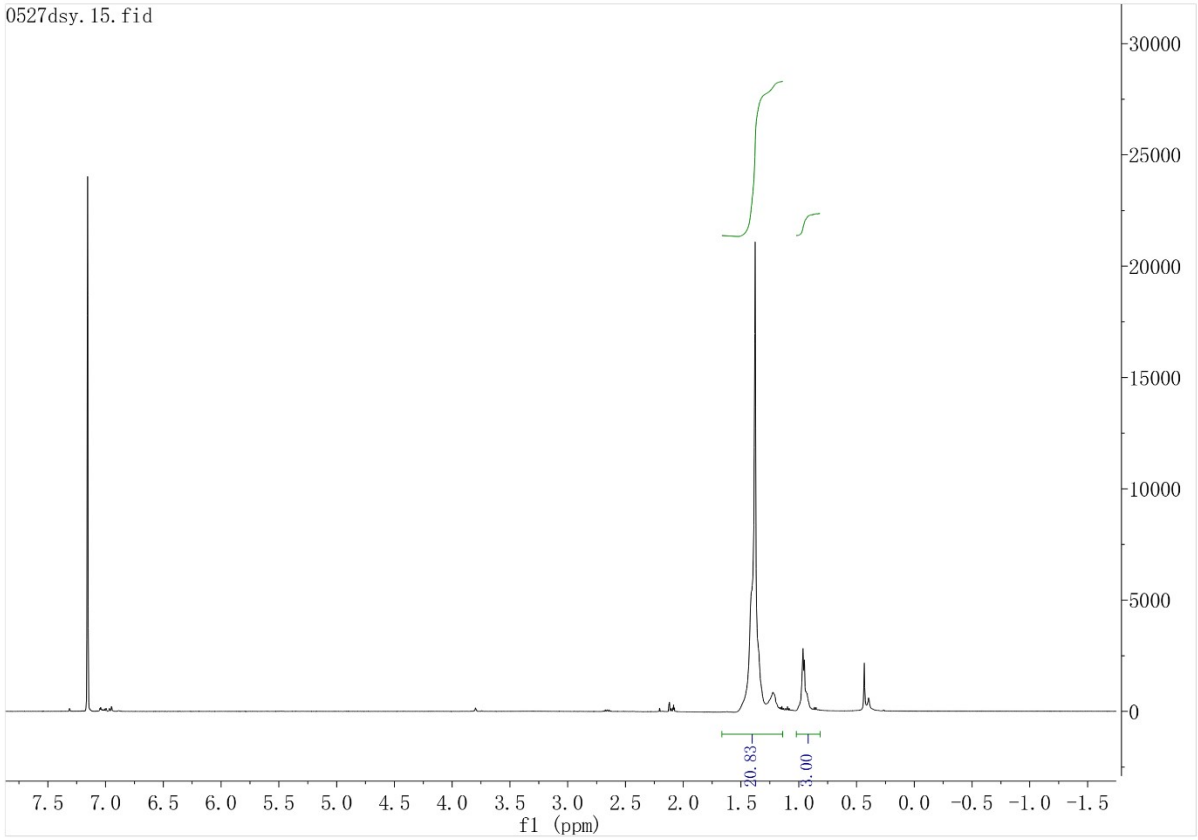


Figure S27. ^{1}H NMR spectrum of the polymer from table 1, entry 9 (C_6D_6, 70 °C).

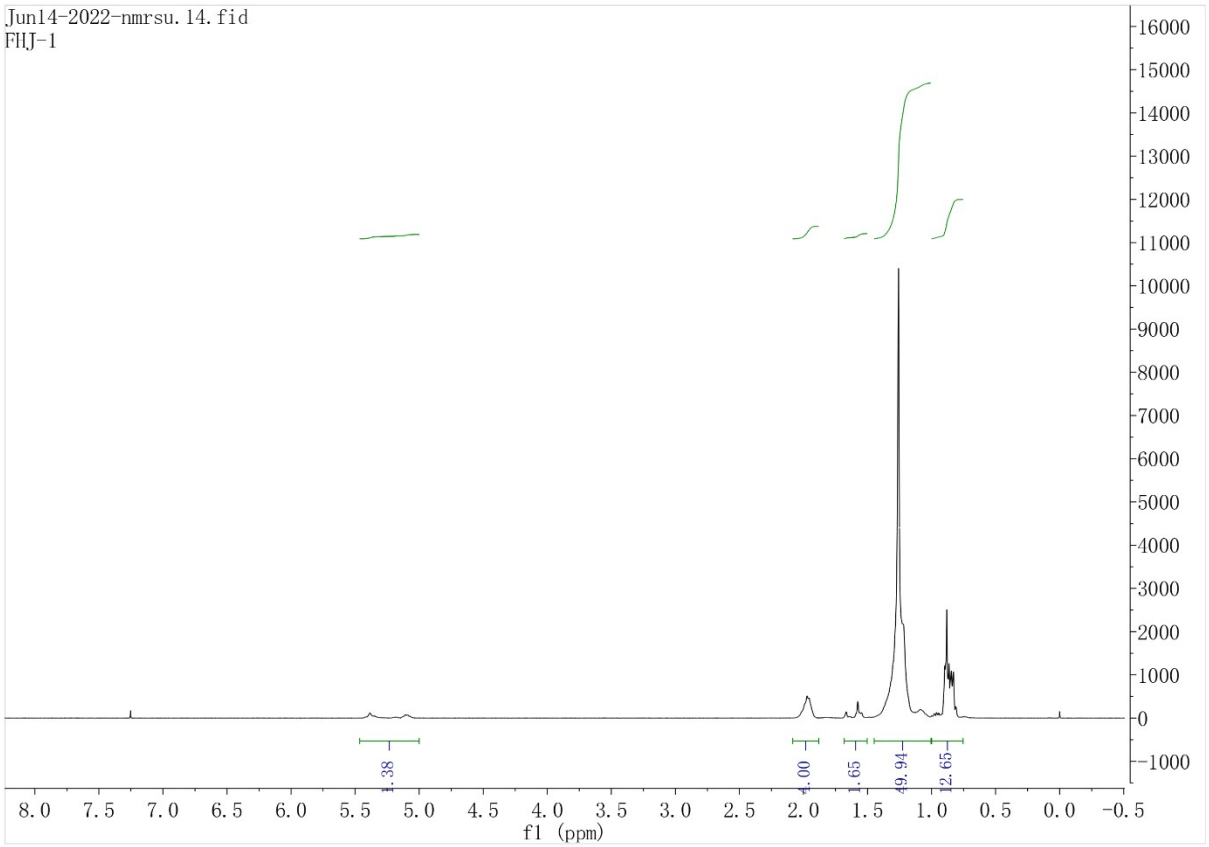


Figure S28. ^{1}H NMR spectrum of the polymer from table 2, entry 1 ($CDCl_3$, 20 °C).

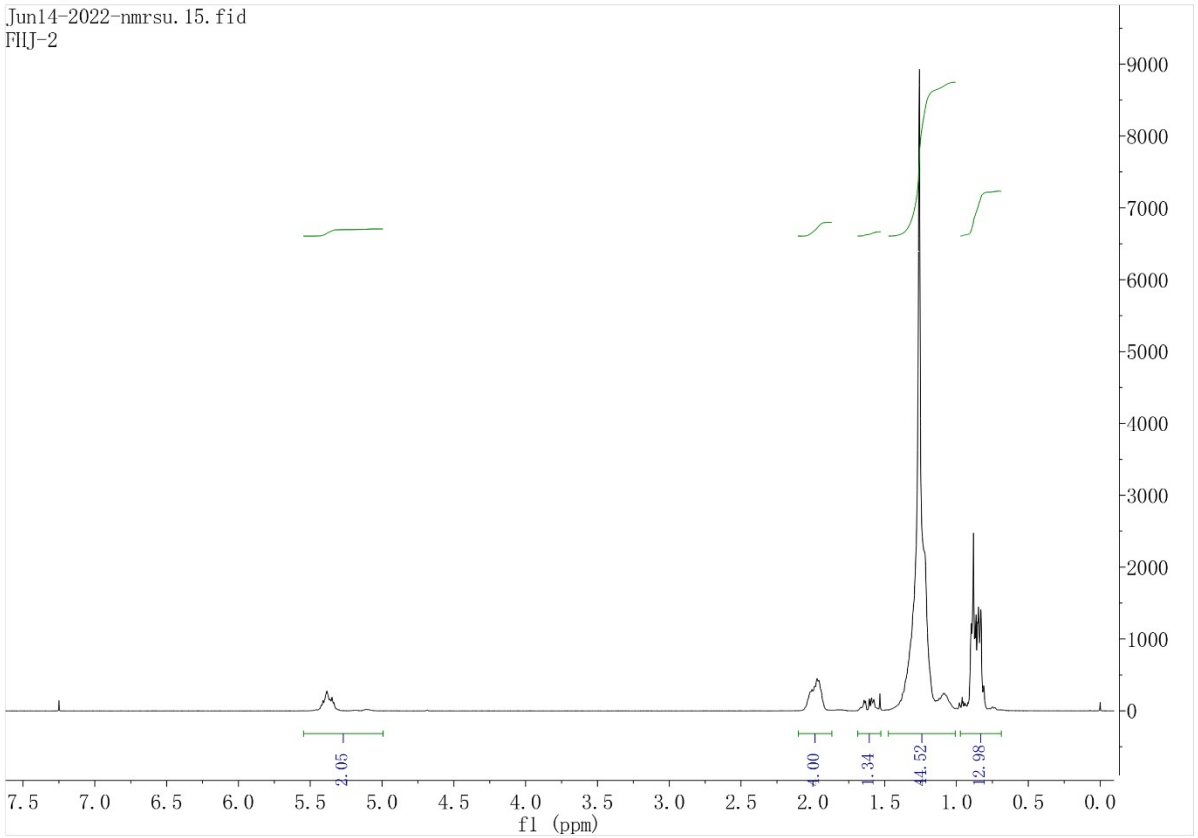


Figure S29. ^{1}H NMR spectrum of the polymer from table 2, entry 2 ($CDCl_3$, 20 °C).

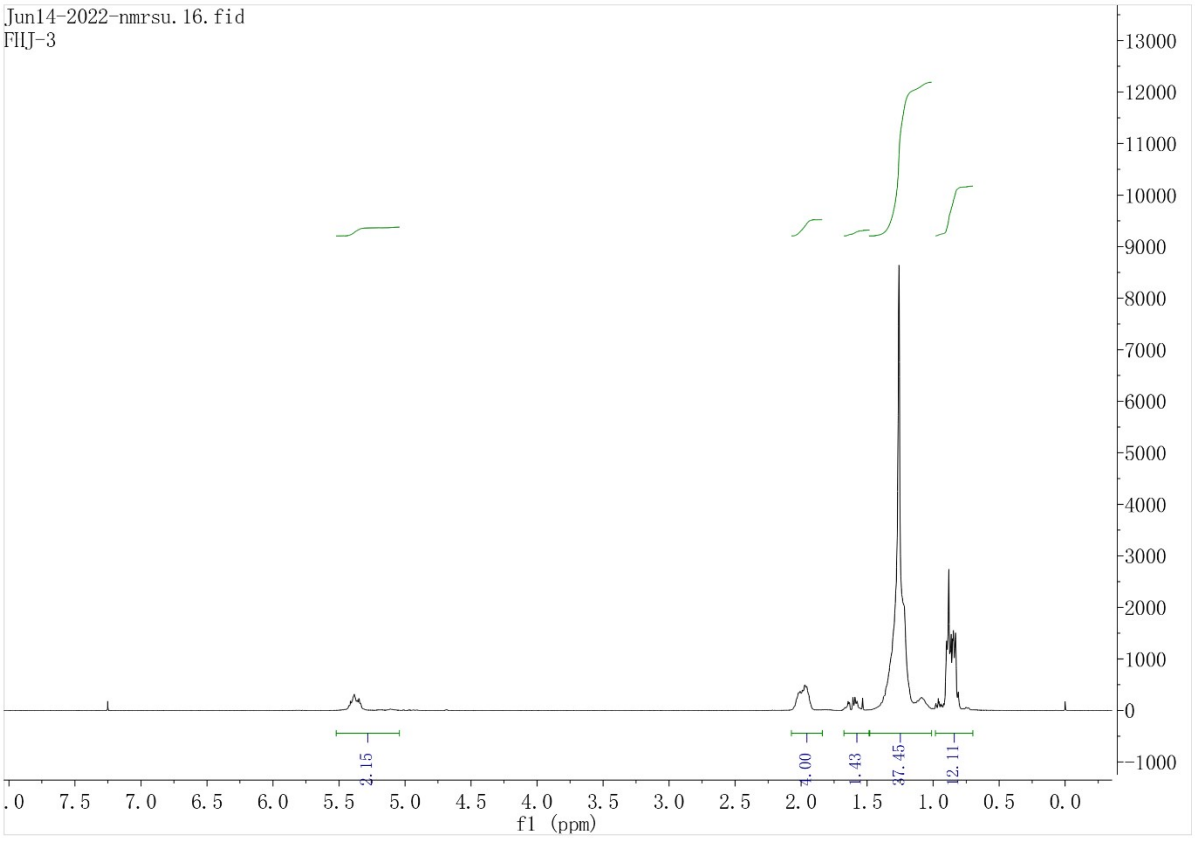


Figure S30. ^{1}H NMR spectrum of the polymer from table 2, entry 3 ($CDCl_3$, 20 °C).

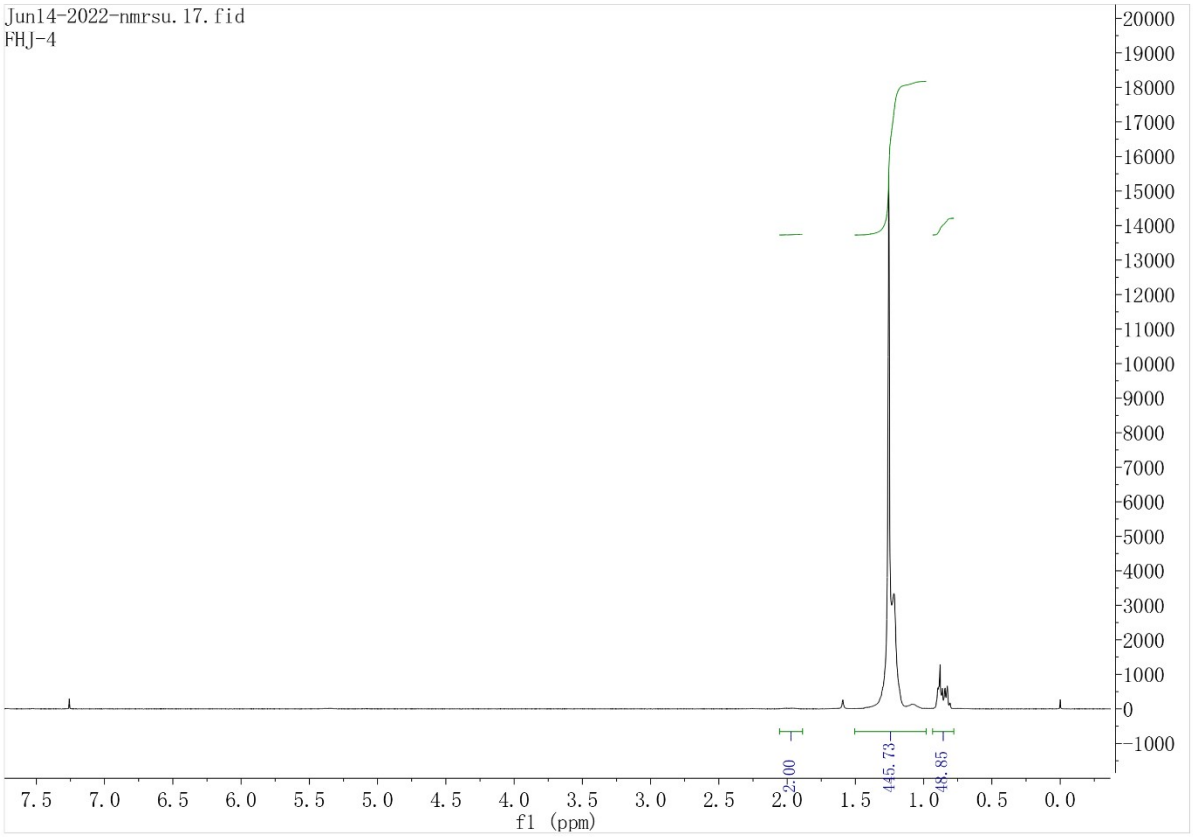


Figure S31. ^{1}H NMR spectrum of the polymer from table 2, entry 4 ($CDCl_3$, 20 °C).

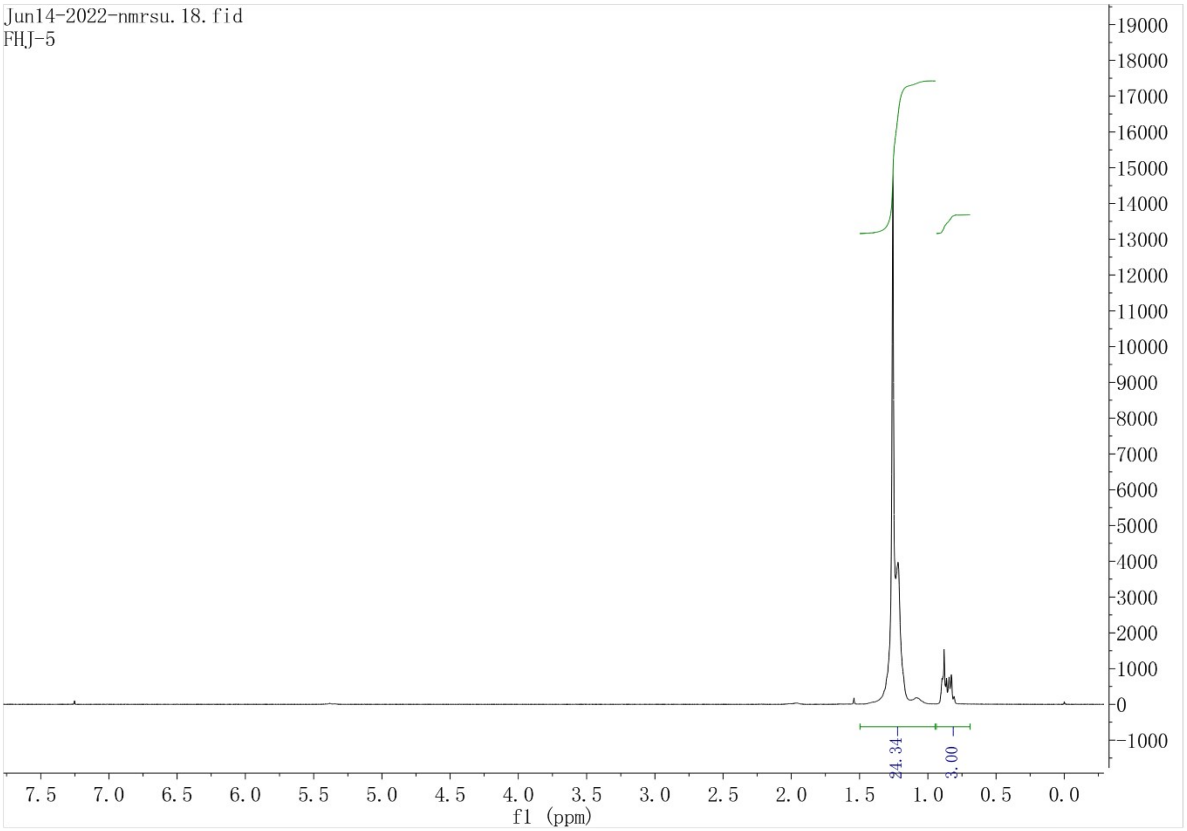


Figure S32. ^{1}H NMR spectrum of the polymer from table 2, entry 5 ($CDCl_3$, 20 °C).

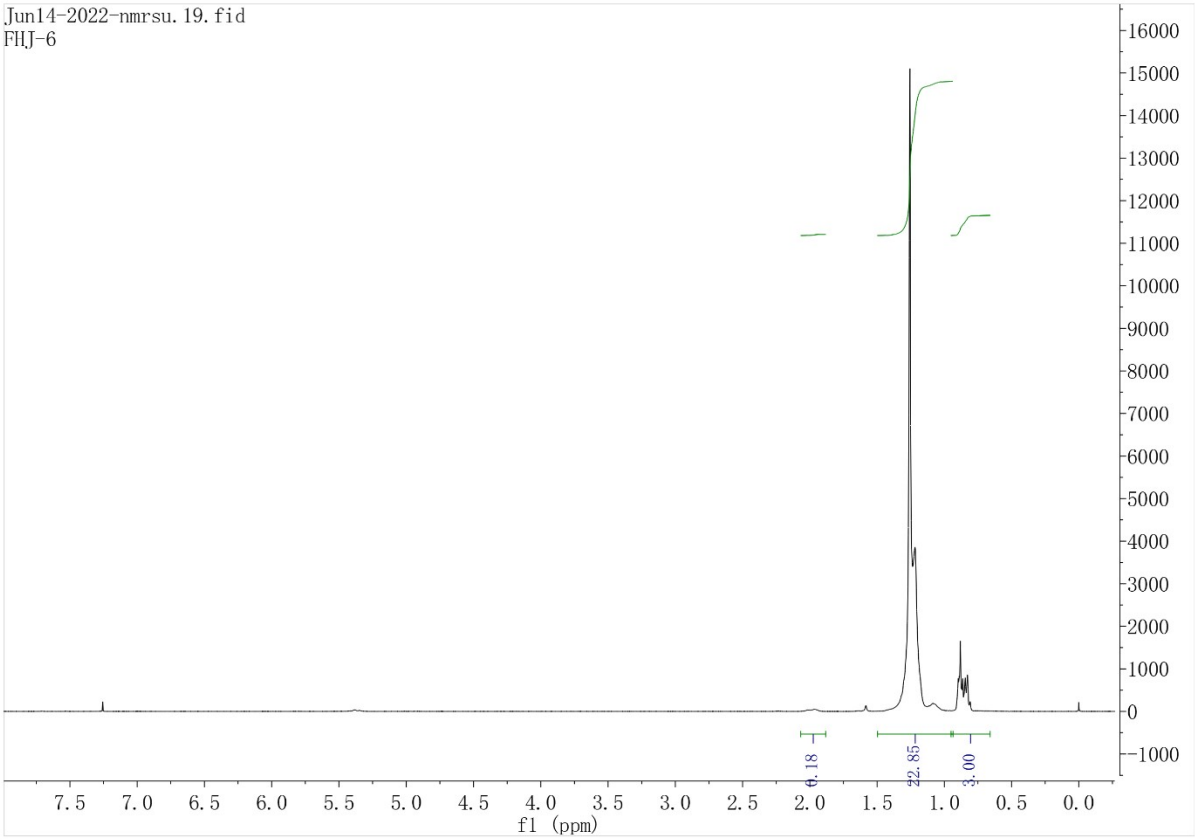


Figure S33. ^{1}H NMR spectrum of the polymer from table 2, entry 6 ($CDCl_3$, 20 °C).

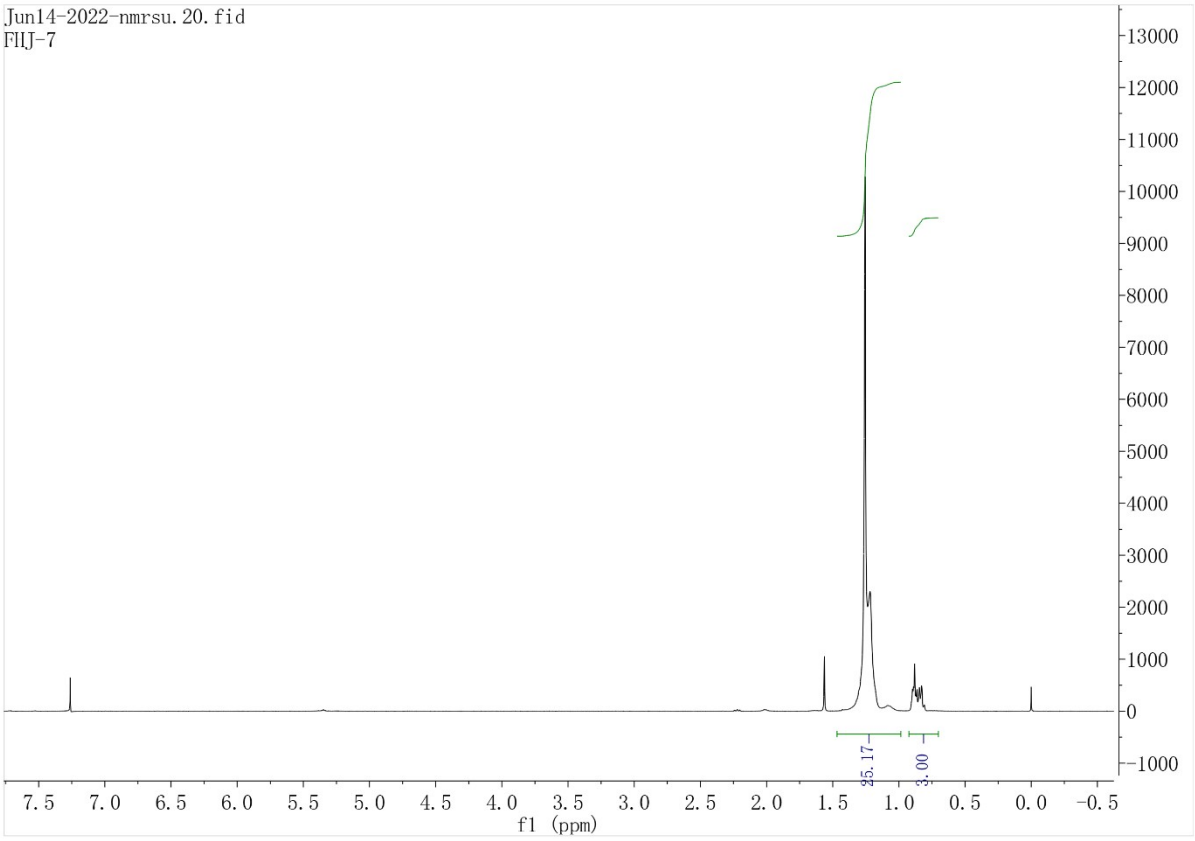


Figure S34. ^{1}H NMR spectrum of the polymer from table 2, entry 7 ($CDCl_3$, 20 °C).

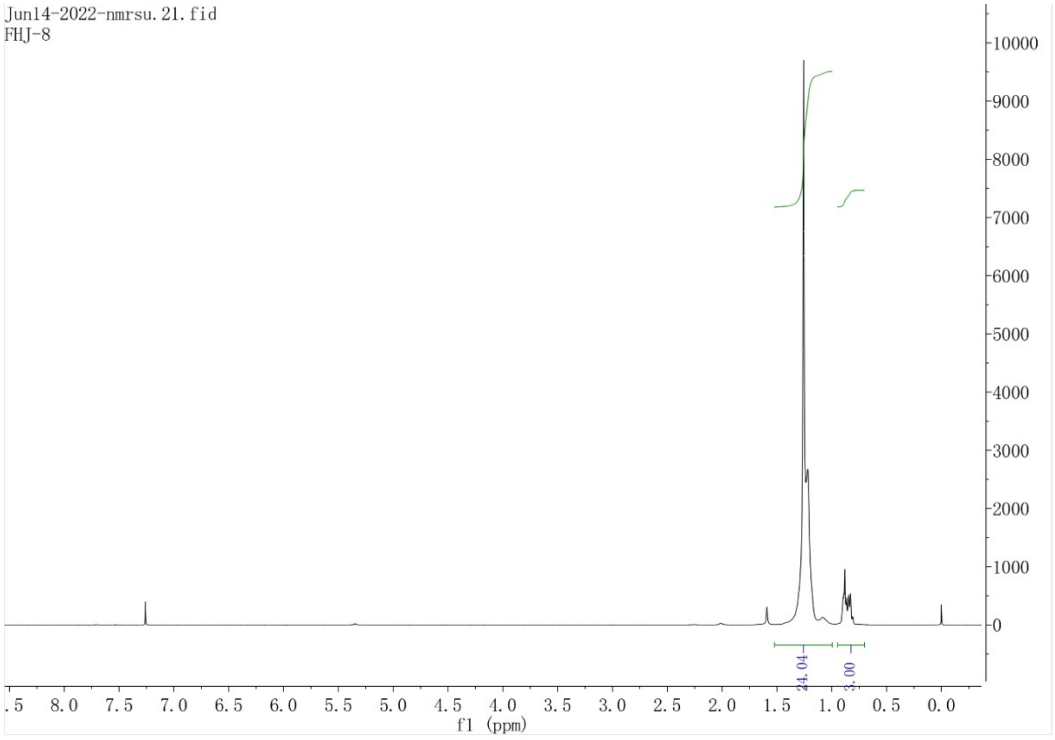


Figure S35. ^{1}H NMR spectrum of the polymer from table 2, entry 8 ($CDCl_3$, 20 °C).

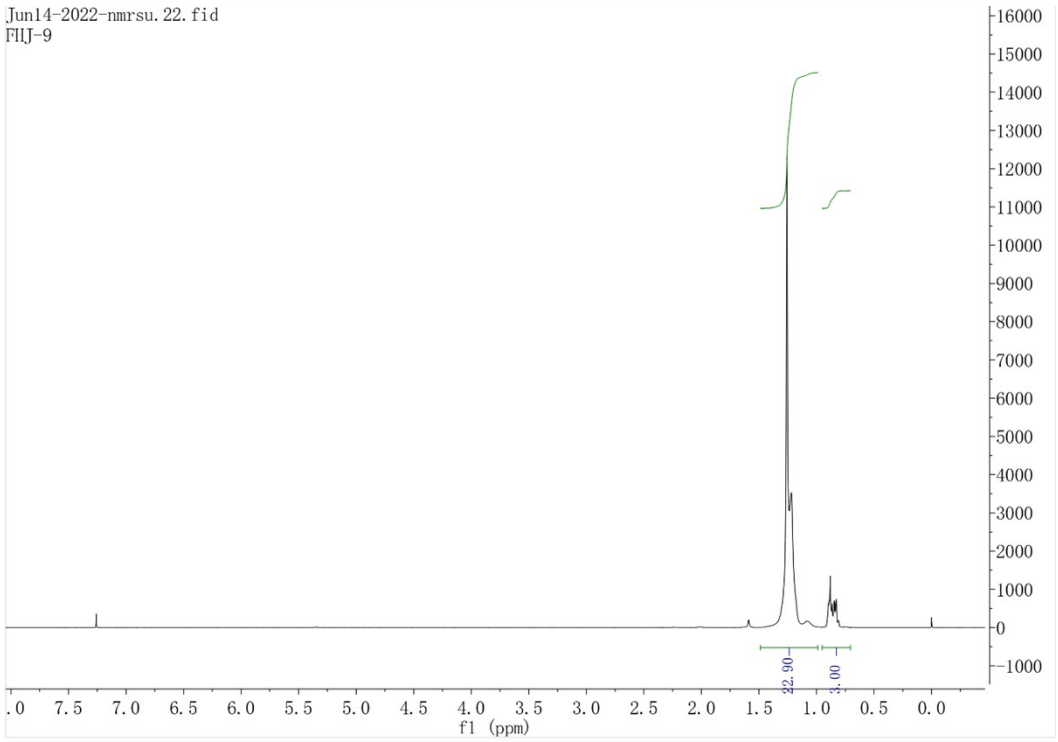


Figure S36. ^{1}H NMR spectrum of the polymer from table 2, entry 9 ($CDCl_3$, 20 °C).

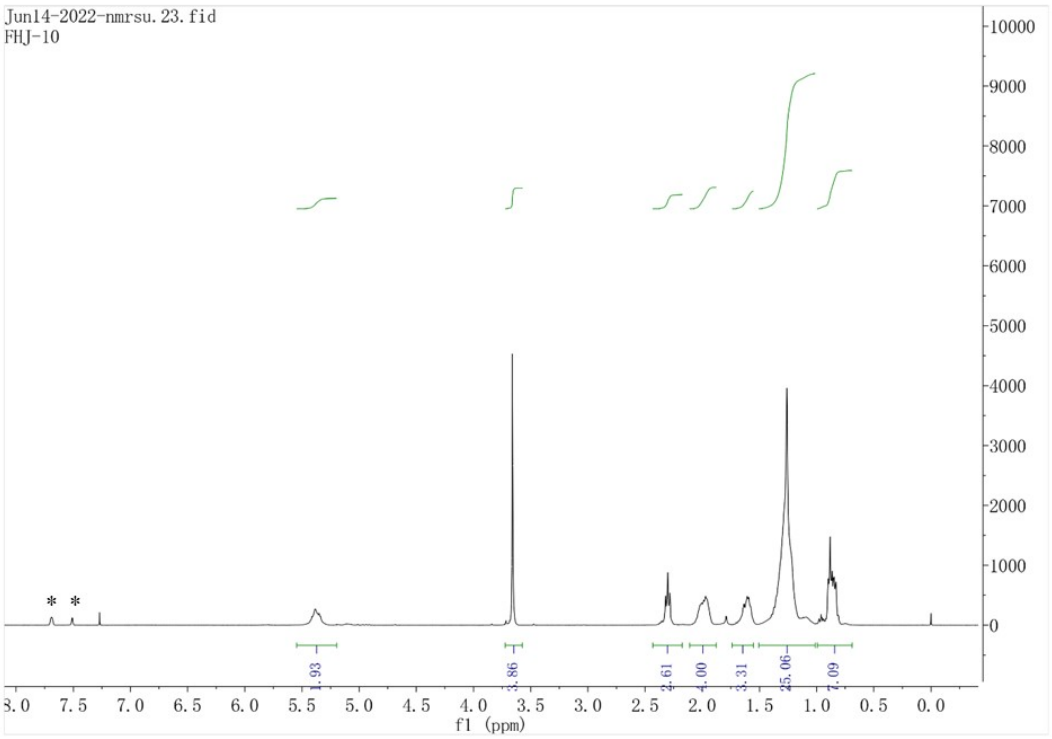


Figure S37. ^{1}H NMR spectrum of the copolymer from table 3, entry 1 ($CDCl_3$, 20 °C). * H of $BArF^-$ anion (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

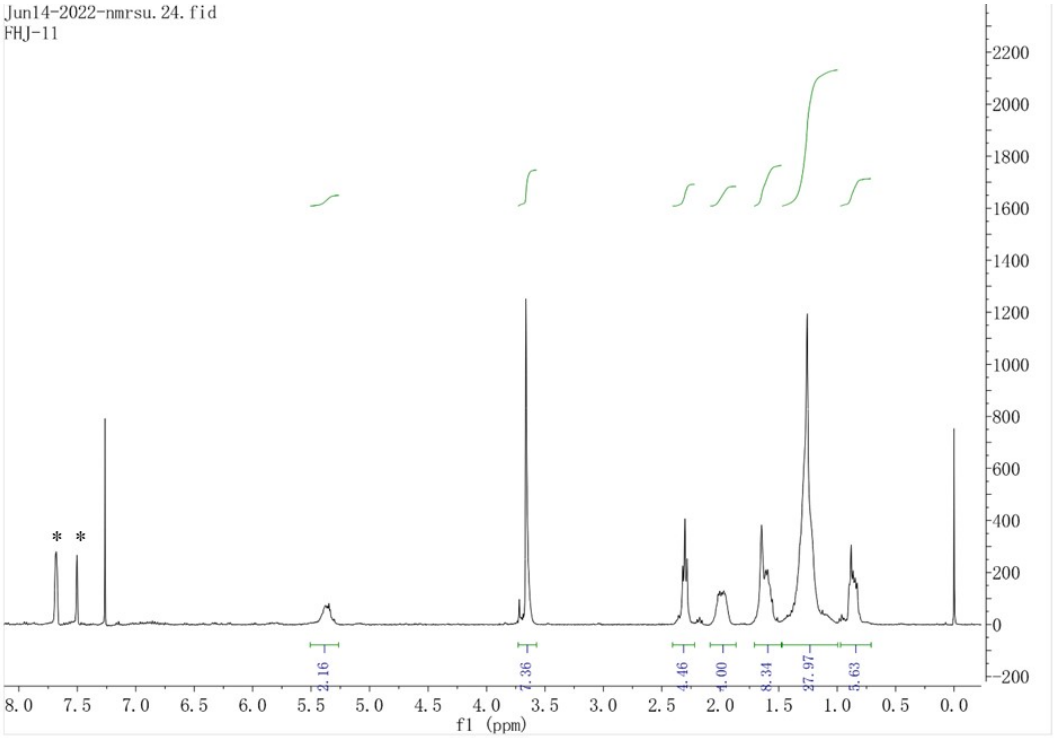


Figure S38. ^{1}H NMR spectrum of the copolymer from table 3, entry 2 ($CDCl_3$, 20 °C). *H of $BArF^-$ anion (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

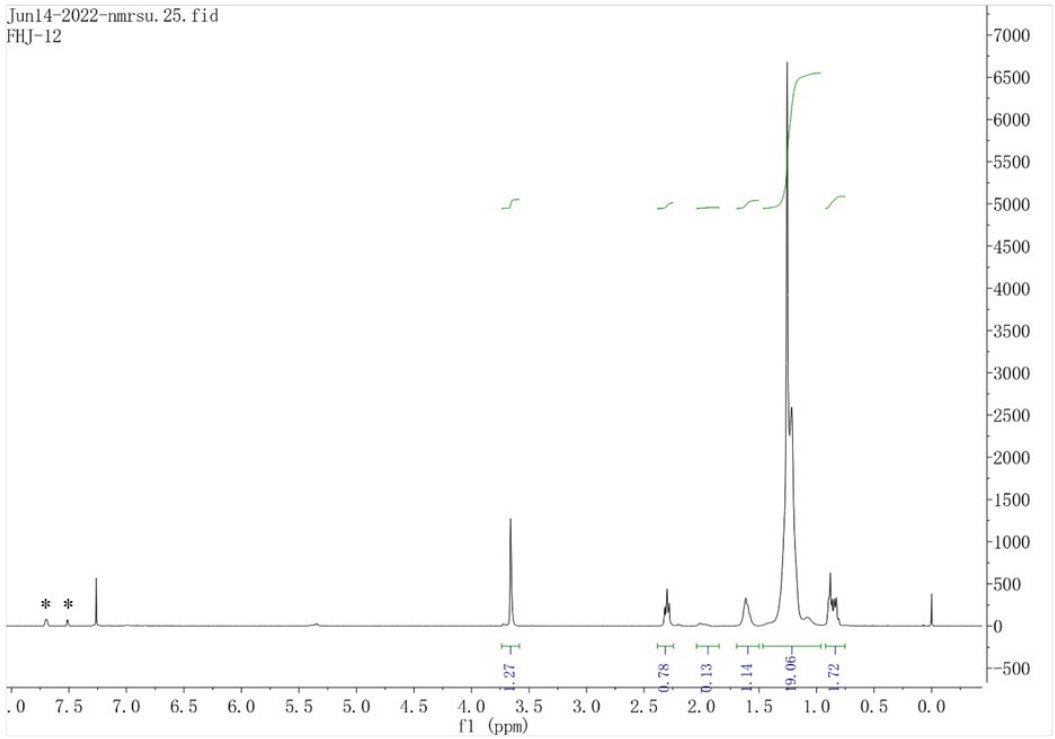


Figure S39. ^{1}H NMR spectrum of the copolymer from table 3, entry 3 ($CDCl_3$, 20 °C). * H of $BArF^-$ anion (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

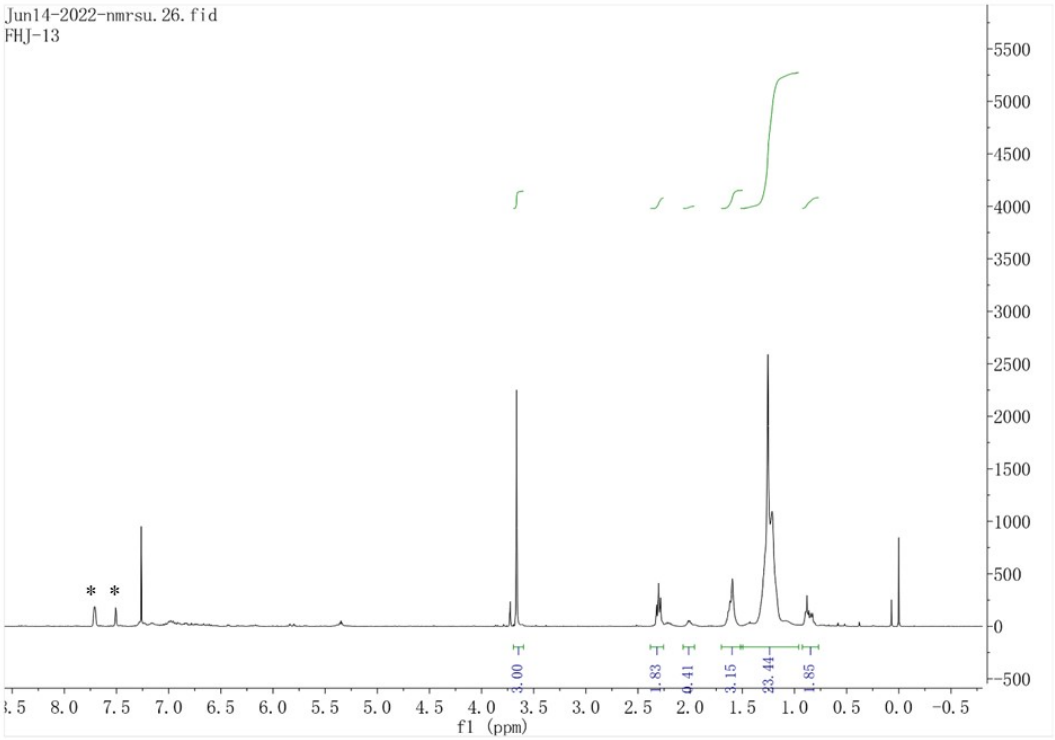


Figure S40. ^{1}H NMR spectrum of the copolymer from table 3, entry 4 ($CDCl_3$, 20 °C). * H of $BArF^-$ anion (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

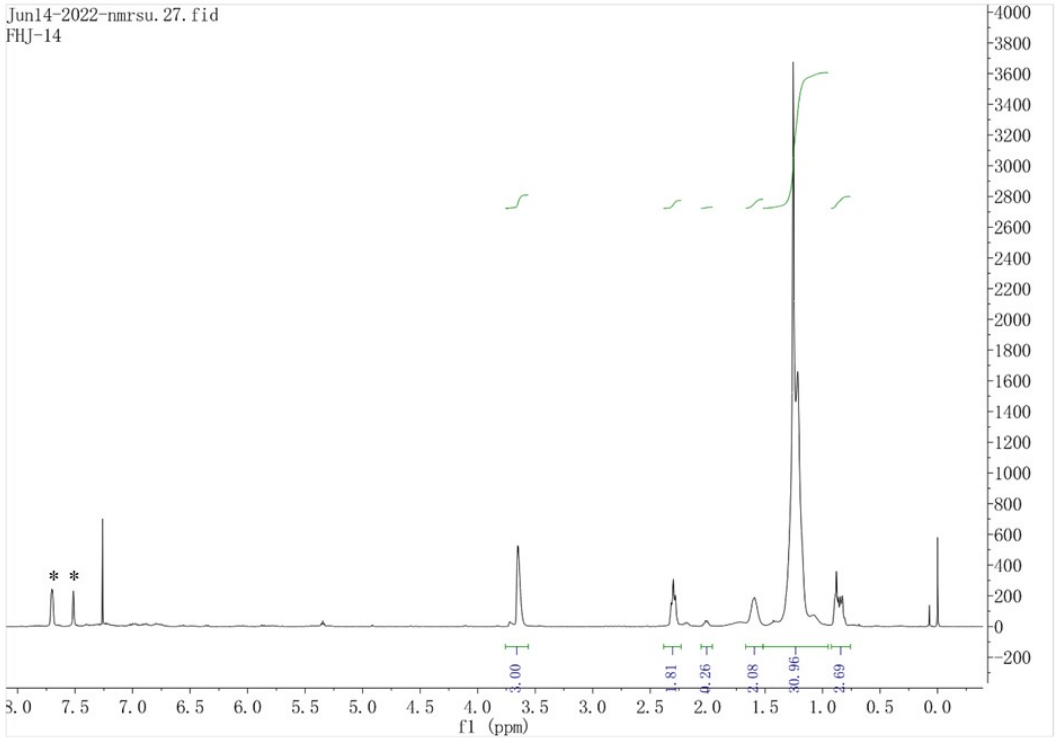


Figure S41. ^{1}H NMR spectrum of the copolymer from table 3, entry 5 ($CDCl_3$, 20 °C). * H of $BArF^-$ anion (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

2.5 DSC and GPC of Representative Polymers and Copolymers.

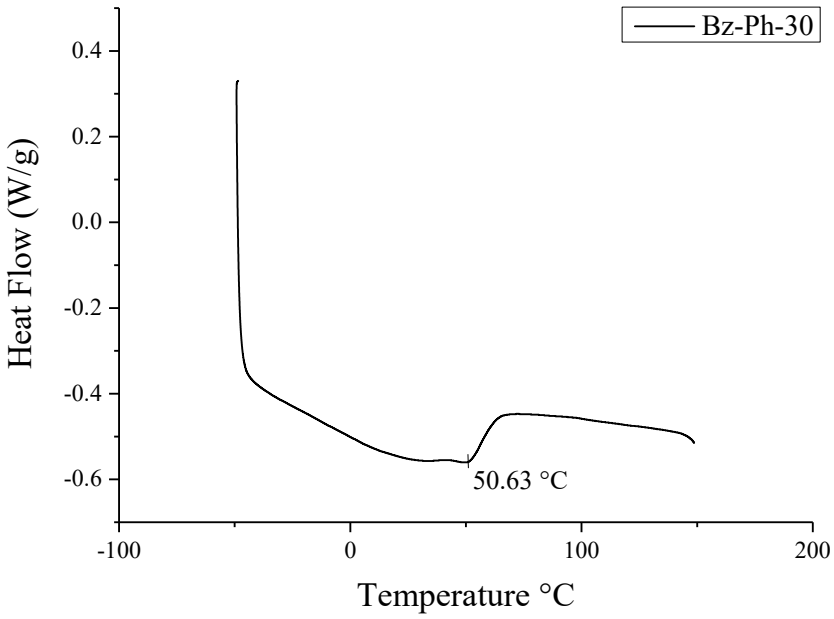


Figure S42. DSC of the polymer from table 1, entry 4.

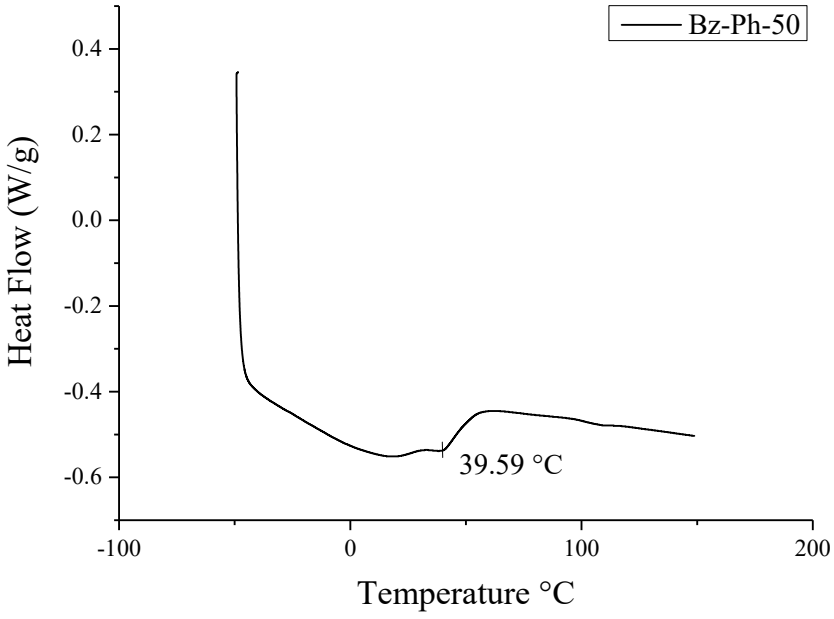


Figure S43. DSC of the polymer from table 1, entry 5.

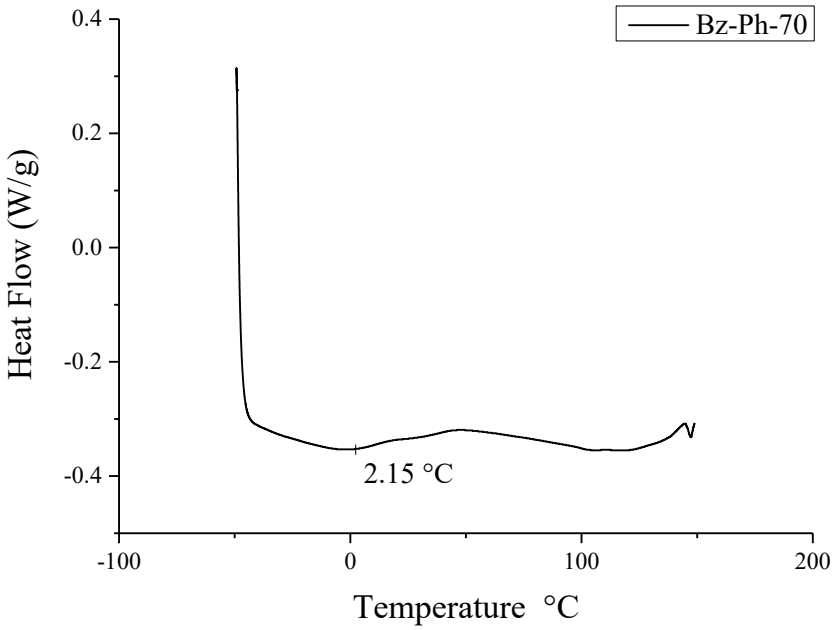


Figure S44. DSC of the polymer from table 1, entry 6.

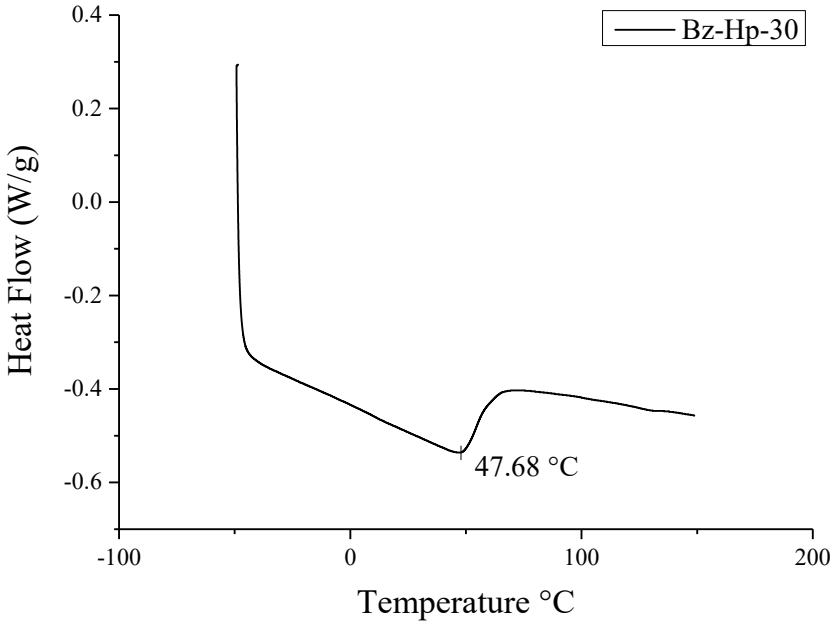


Figure S45. DSC of the polymer from table 1, entry 7.

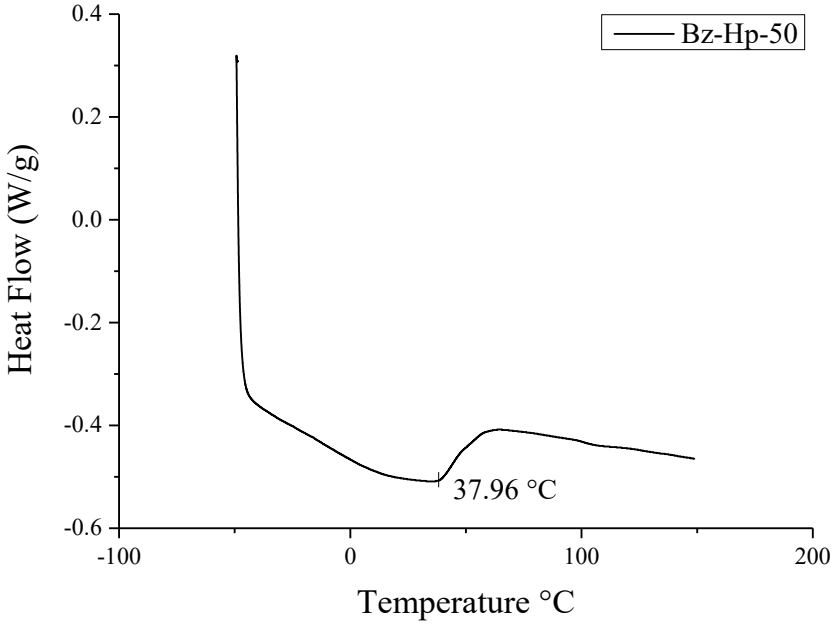


Figure S46. DSC of the polymer from table 1, entry 8.

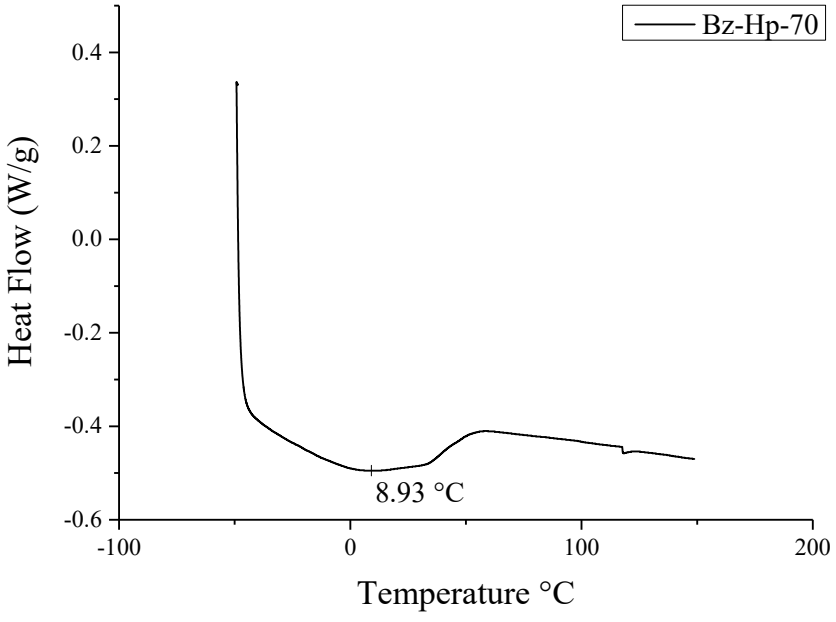
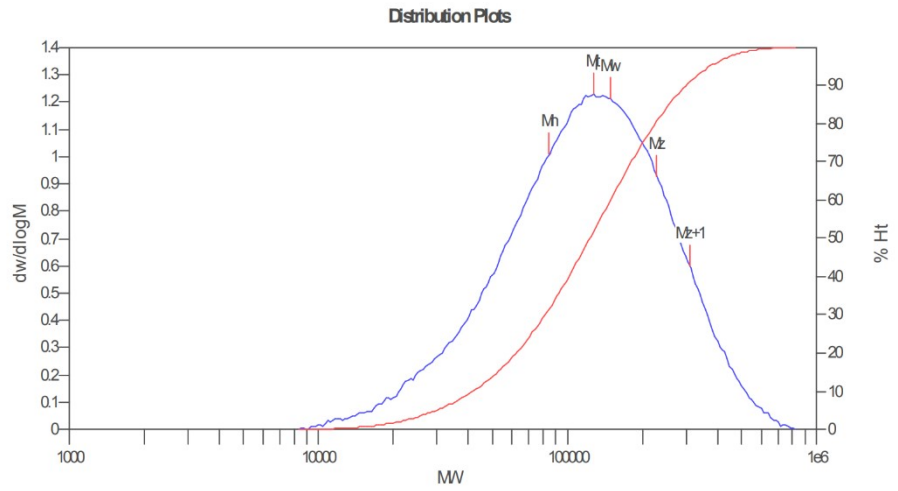


Figure S47. DSC of the polymer from table 1, entry 9.



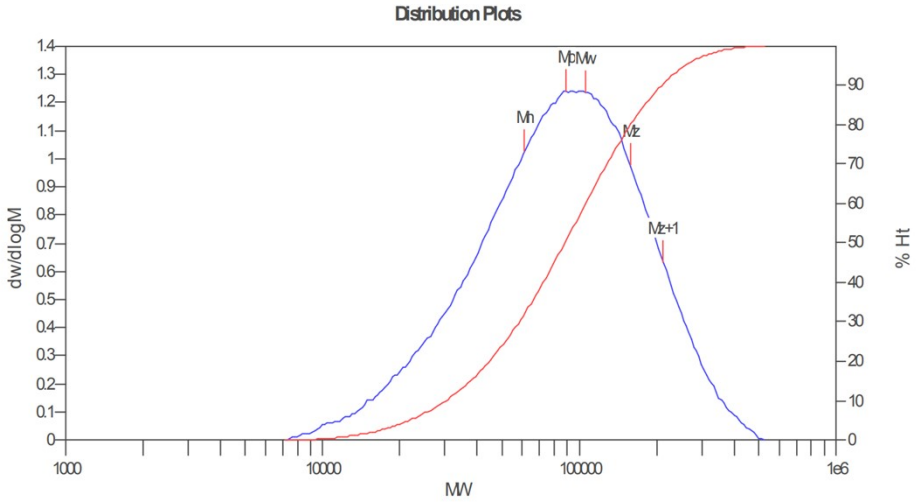
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	126943	84420	149456	228583	310452	138960	1.77039

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.18	13.57	15.58	3.08981	0	257.253	100

Figure S48. GPC of the polymer from table 1, entry 4.



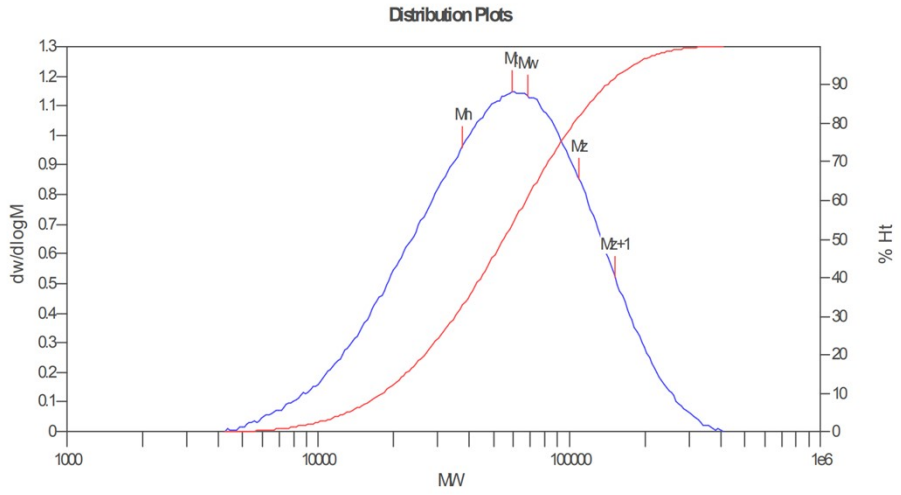
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	88556	61135	105367	158098	211301	98270	1.72351

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.52	13.83	15.70	3.72485	0	306.485	100

Figure S49. GPC of the polymer from table 1, entry 5.



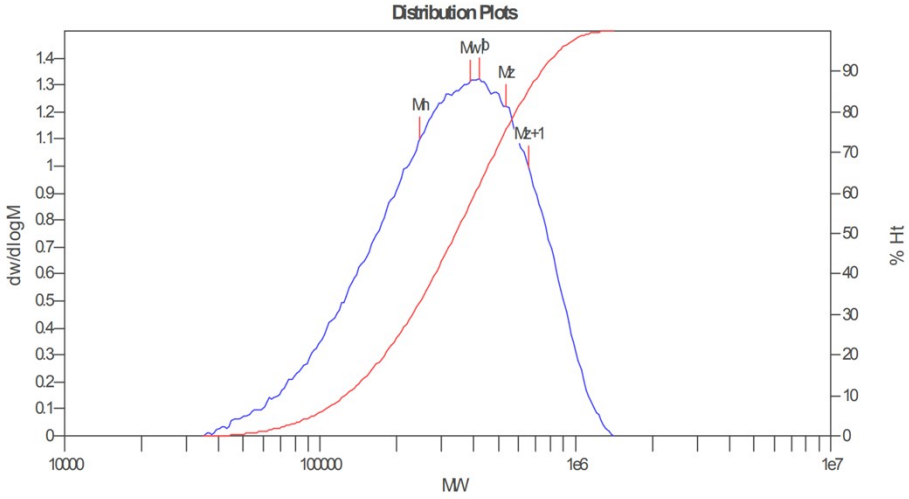
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	59057	37334	68610	109446	152442	63333	1.83774

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.70	14.13	16.08	3.80998	0	339.957	100

Figure S50. GPC of the polymer from table 1, entry 6.



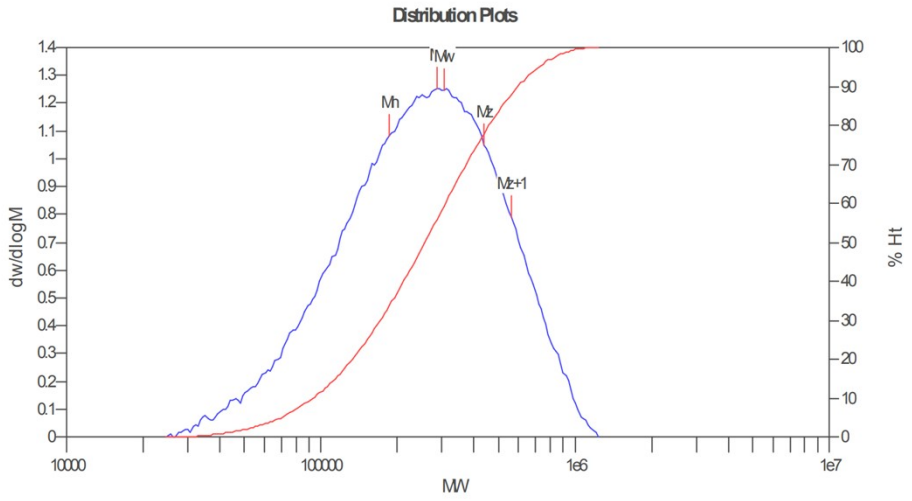
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	418466	246438	386210	531314	657352	365079	1.56717

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.78	12.68	14.52	2.36463	0	182.76	100

Figure S51. GPC of the polymer from table 1, entry 7.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	285426	185372	303465	437466	561382	284769	1.63706

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	12.97	14.78	1.95501	0	159.711	100

Figure S52. GPC of the polymer from table 1, entry 8.

3. References

1. Y. Ge, S. Li, W. Fan and S. Dai, Flexible "Sandwich" (8-Alkylnaphthyl α-Diimine) Catalysts in Insertion Polymerization, *Inorganic Chemistry*, 2021, **60**, 5673-5681.

4. X-ray Crystallography

Table S1 Crystal data and structure refinement for Pd1.	
Identification code	**Pd1**
Empirical formula	C25 H23 Cl N2 Pd
Formula weight	493.30
Temperature/K	298(2)
Crystal system	Triclinic
Space group	P-1
a/Å	8.2420(8)
b/Å	9.4049(9)
c/Å	15.0201(14)
α/°	103.390(3)
β/°	98.220(2)
γ/°	103.075(3)

Volume/Å^3	1079.57(18)
Z	2
ρ_{calc}g/cm^3	1.518
μ/mm^{-1}	0.997
F(000)	500
Crystal size/mm^3	0.30 x 0.27 x 0.13
2Θ range for data collection/°	2.31 to 25.02
Index ranges	-9<=h<=9, -11<=k<=9, -17<=l<=13
Reflections collected	5234
Independent reflections	3731 [R(int) = 0.0373
Data/restraints/parameters	3731 / 6 / 266
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R1 = 0.0626, wR2 = 0.1731
Final R indexes [all data]	R1 = 0.0698, wR2 = 0.1800
Largest diff. peak/hole / e Å^{-3}	1.850 and -1.938

Table S2 Crystal data and structure refinement for Pd2.	
Identification code	**Pd2**
Empirical formula	C51 H43 Cl N2 Pd
Formula weight	825.72
Temperature/K	298(2)
Crystal system	Triclinic
Space group	P-1
a/Å	7.9650(8)
b/Å	11.2240(12)
c/Å	27.180(3)
α/°	92.890(2)
β/°	95.260(3)
γ/°	106.440(4)
Volume/Å^3	2313.3(4)
Z	2
ρ_{calc}g/cm^3	1.185
μ/mm^{-1}	0.492
F(000)	852
Crystal size/mm^3	0.11 x 0.08 x 0.03
2Θ range for data collection/°	1.90 to 25.02
Index ranges	-9<=h<=9, -13<=k<=13, 0<=l<=32
Reflections collected	7920
Independent reflections	7920 [R(int) = 0.0000]

Data/restraints/parameters	7920 / 234 / 499
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R1 = 0.1660, wR2 = 0.3410
Final R indexes [all data]	R1 = 0.3004, wR2 = 0.3908
Largest diff. peak/hole / e $Å^{-3}$	1.178 and -0.986