Supporting Information for:

8-Arylnaphthyl Substituent Retarding Chain Transfer in Insertion Polymerization with Unsymmetrical α-Diimine Systems

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1. Experimental sections

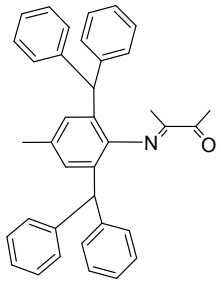
1.1 General Considerations

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, ^{13}C NMR spectra were recorded by a JEOL JNM-ECZ600R 600 spectrometer or JEOL JNM-ECZ400R 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 were obtained using electro spray ionization (HESI) LCMS-2010A for **I2~I3**, **L1~L4**. Mass spectra of the complexes **Ni1~Ni4** and **Pd1~Pd4** were recorded on a Atouflex Speed MALDI-TOF MS. Elemental analysis was performed by the Analytical Center of Anhui University. X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K^{α} radiation (λ = 0.71073 Å). Molecular weight and molecular weight distribution of the polymers 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. DSC was performed by a DSC Q20 from TA Instruments. Samples were quickly heated to 150°C and kept for 5 min to remove thermal history, then cooled to 0°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).

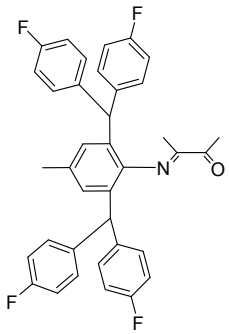
1.2 Procedure for the Synthesis of α-Imino-Ketones I1-I4.

A solution of arylamine (10 mmol), 2,3-butadione (30 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (100 mL) was stirred at 80 °C for 24 h, until there was one main point on the TLC plate. The solvent was partially evaporated under reduced pressure until the formation of

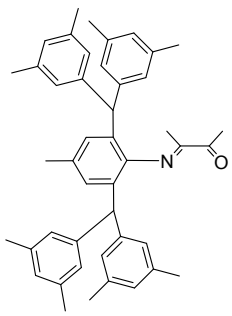
a light yellow solid. The remaining solution was diluted in methanol (100 mL). The yellow solid was isolated by filtration, dried by vacuum.



I1 (4.37 g, 86%), This compound is known[1].

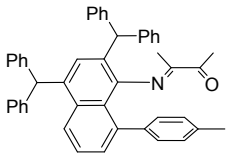


I2 (4.87 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 – 6.88 (m, 16H, aryl-*H*), 6.58 (s, 2H, aryl-*H*), 5.04 (s, 2H, C*H*Ar_2), 2.29 (s, 3H, COC*H*$_3$), 2.16 (s, 3H, aryl-C*H*$_3$), 0.83 (s, 3H, N=C*Me*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.29 (*C*OCH_3), 168.75 (N=*C*Me), 162.41, 162.35, 160.78, 160.72, 144.28, 138.69, 138.67, 137.83, 137.81, 133.09, 130.97, 130.92, 130.71, 130.66, 128.82, 115.68, 115.54, 115.22, 115.08, 50.74 (*C*HAr_2), 24.92 (CO*C*H$_3$), 21.34 (aryl-*C*H$_3$), 14.87 (N=C*Me*). ^{19}F NMR (565 MHz, $CDCl_3$) δ -115.53 – -115.66 (m), -116.38 (t, *J* = 6.3 Hz). HESI-MS (m/z): calcd for $C_{37}H_{30}ONF_4$: 580.2258, found: 580.2264 $[M+H]^+$.



I3 (5.52 g, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (s, 2H, aryl-*H*), 6.80 (s, 2H, aryl-*H*), 6.69 (s, 2H, aryl-*H*), 6.67 (s, 4H, aryl-*H*), 6.64 (s, 4H, aryl-*H*), 4.94 (s, 2H, C*H*Ar_2), 2.32 (s, 3H, COC*H*$_3$), 2.26 (s, 12H, aryl-C*H*$_3$), 2.22 (s, 15H, aryl-C*H*$_3$), 0.73 (s, 3H, N=C*Me*). ^{13}C NMR

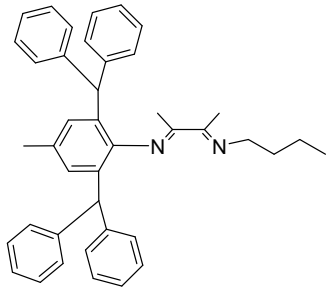
(151 MHz, $CDCl_3$) δ 199.76 (*C*OCH_3), 168.29 (N=*C*Me), 144.68, 143.19, 142.40, 137.86, 137.44, 132.24, 131.15, 128.48, 127.97, 127.89, 127.60, 127.36, 52.55 (*C*HAr_2), 24.77 (CO*C*H_3), 21.54 (aryl-*C*H_3), 21.49 (aryl-*C*H_3), 21.39 (aryl-*C*H_3), 14.46 (N=C*Me*). HESI-MS (m/z): calcd for $C_{45}H_{50}ON$: 620.3887, found: 620.3882 $[M+H]^+$.



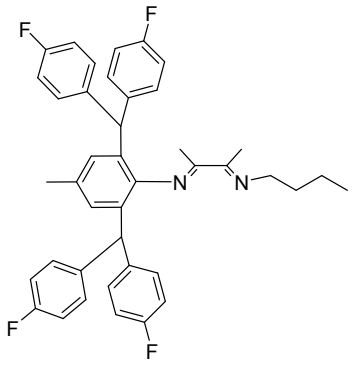
I4 (5.96 g, 94%). This compound is known [2].

1.3 Procedure for the Synthesis of Ligands L1-L4.

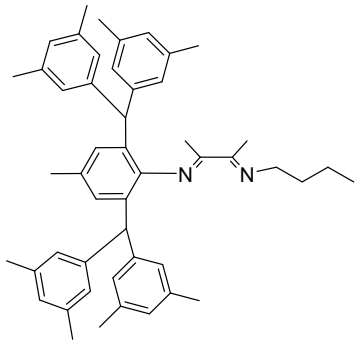
A mixture of α-imino-ketones (4 mmol) and n-butylamine (40.0 mmol) in toluene (40 mL) was stirred at 80 °C for 24 h. The solvent was evaporated under reduced pressure. The remaining mixture was diluted with methanol (100 mL). The resulting yellow solid was collected by filtration and recrystallized from CH_2Cl_2 and hexanes to afford the desired product.



L1 (1.46 g, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.12 (m, 12H, aryl-*H*), 7.03 (dt, *J* = 7.3, 3.3 Hz, 8H, aryl-*H*), 6.64 (s, 2H, aryl-*H*), 5.17 (s, 2H, C*H*Ph_2), 3.46 (t, *J* = 7.0 Hz, 2H, N-C*H*$_2$$CH_2CH_2CH_3$), 2.15 (s, 3H, aryl-C*H*$_3$), 1.97 (s, 3H, Bu-N=C*Me*), 1.62 (dt, *J* = 19.7, 7.1 Hz, 2H, N-CH_2C*H*$_2$$CH_2CH_3$), 1.39 (dt, *J* = 14.4, 7.2 Hz, 2H, N-CH_2CH_2C*H*$_2$$CH_3$), 0.98 (t, *J* = 7.4 Hz, 3H, N-$CH_2CH_2CH_2$C*H*$_3$), 0.90 (s, 3H, Ar-N=C*Me*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.70 (Bu-N=*C*Me), 166.38 (Ar-N=*C*Me), 146.12, 143.72, 142.77, 131.61, 129.85, 129.53, 128.65, 128.35, 128.08, 126.26, 126.05, 52.34 (N-*C*$H_2CH_2CH_2CH_3$), 52.18 (*C*HAr_2), 32.77 (N-CH_2*C*$H_2CH_2CH_3$), 21.38 (aryl-*C*H_3), 20.78 (N-CH_2CH_2*C*H_2CH_3), 15.95 (Bu-N=C*Me*), 14.11 (Ar-N=C*Me*), 12.64 (N-$CH_2CH_2CH_2$*C*H_3). HESI-MS (m/z): calcd for $C_{41}H_{43}N_2$: 563.3426, found: 563.3417 $[M+H]^+$.

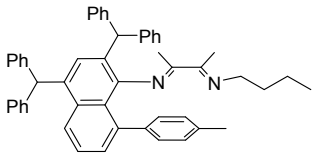


L2 (1.88 g, 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 – 6.88 (m, 16H, aryl-*H*), 6.58 (s, 2H, aryl-*H*)), 5.12 (s, 2H, C*H*Ar$_2$), 3.46 (t, *J* = 6.7 Hz, 2H, N-C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.16 (s, 3H, aryl-C*H*$_3$), 1.94 (s, 3H, Bu-N=C*Me*), 1.69 – 1.57 (m, 2H, N-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.41 (dt, *J* = 14.6, 7.2 Hz, 2H, N-CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.02 (s, 3H, Ar-N=C*Me*), 0.99 (t, *J* = 7.3 Hz, 3H, N-CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.71 (Bu-N=*C*Me), 166.06 (Ar-N=*C*Me), 162.31, 162.25, 160.69, 160.63, 145.81, 139.08, 138.28, 131.87, 131.45, 131.09, 131.04, 130.75, 130.70, 128.60, 115.38, 115.24, 115.04, 114.90, 52.41 (N-*C*H$_2$CH$_2$CH$_2$CH$_3$), 50.62 (*C*HAr$_2$), 32.76 (N-CH$_2$*C*H$_2$CH$_2$CH$_3$), 21.33 (aryl-*C*H$_3$), 20.78 (N-CH$_2$CH$_2$*C*H$_2$CH$_3$), 16.15 (Bu-N=C*Me*), 14.06 (Ar-N=C*Me*), 12.61 (N-CH$_2$CH$_2$CH$_2$*C*H$_3$). ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.24 (s), -116.87 (s). HESI-MS (m/z): calcd for $C_{41}H_{39}N_2F_4$: 635.3044, found: 635.3049 $[M+H]^+$.



L3 (2.27 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 (s, 2H, aryl-*H*), 6.78 (s, 2H, aryl-*H*), 6.67 (s, 6H, aryl-*H*), 6.65 (s, 4H, aryl-*H*), 5.00 (s, 2H, C*H*Ar$_2$), 3.47 (t, *J* = 7.1 Hz, 2H, N-C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.25 (s, 12H, aryl-C*H*$_3$), 2.20 (s, 15H, aryl-C*H*$_3$), 1.99 (s, 3H, Bu-N=C*Me*), 1.68 – 1.60 (m, 2H, N-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.43 (dp, *J* = 14.8, 7.2 Hz, 2H, N-CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.00 – 0.96 (m, 3H, N-CH$_2$CH$_2$CH$_2$C*H*$_3$), 0.87 (s, 3H, Ar-N=C*Me*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.24 (Bu-N=*C*Me), 166.73 (Ar-N=*C*Me), 146.06, 143.60, 142.76, 137.53, 137.21, 131.71, 131.10, 128.27, 127.73, 127.64, 127.44, 52.47 (N-*C*H$_2$CH$_2$CH$_2$CH$_3$), 52.34 (*C*HAr$_2$),

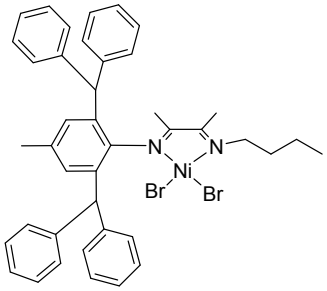
32.96 (N-CH_2*C*$H_2CH_2CH_3$), 21.53 (aryl-*C*H_3), 21.49 (aryl-*C*H_3), 21.42 (aryl-*C*H_3), 20.89 (N-CH_2CH_2*C*H_2CH_3), 15.83 (Bu-N=C*Me*), 14.13 (Ar-N=C*Me*), 12.48 (N-$CH_2CH_2CH_2$*C*H_3). HESI-MS (m/z): calcd for $C_{49}H_{59}N_2$: 675.4673, found: 675.4669 $[M+H]^+$.



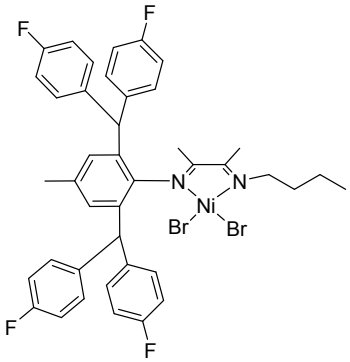
L4 (2.37 g, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.3 Hz, 1H, aryl-*H*), 7.34 – 7.30 (m, 1H, aryl-*H*), 7.28 – 7.24 (m, 2H, aryl-*H*), 7.21 – 7.00 (m, 18H, aryl-*H*), 6.94 (d, *J* = 7.5 Hz, 1H, aryl-*H*), 6.89 (d, *J* = 6.5 Hz, 2H, aryl-*H*), 6.78 (dd, *J* = 7.4, 1.3 Hz, 2H, aryl-*H*), 6.68 (s, 1H, aryl-*H*), 6.22 (s, 1H, C*H*Ar_2), 5.43 (s, 1H, C*H*Ar_2), 3.25 (dtd, *J* = 20.0, 13.3, 7.1 Hz, 2H, N-C*H*$_2CH_2CH_2CH_3$), 2.32 (s, 3H, aryl-C*H*$_3$), 1.68 (s, 3H, Bu-N=C*Me*), 1.56 – 1.47 (m, 2H, N-CH_2C*H*$_2CH_2CH_3$), 1.40 – 1.32 (m, 2H, N-CH_2CH_2C*H*$_2CH_3$), 0.97 (t, *J* = 7.3 Hz, 3H, N-$CH_2CH_2CH_2$C*H*$_3$), 0.79 (s, 3H, Ar-N=C*Me*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.74 (Bu-N=*C*Me), 166.38 (Ar-N=*C*Me), 145.24, 144.31, 143.91, 143.88, 142.61, 142.03, 139.78, 135.23, 134.24, 132.25, 130.83, 130.64, 129.65, 129.56, 129.45, 129.26, 128.48, 128.40, 128.37, 128.28, 128.14, 128.07, 127.95, 127.41, 126.47, 126.29, 126.21, 125.99, 125.87, 124.83, 123.97, 123.45, 53.44 (*C*HAr_2), 52.29 (*C*HAr_2), 52.06 (N-*C*$H_2CH_2CH_2CH_3$), 32.51 (N-CH_2*C*$H_2CH_2CH_3$), 21.18 (aryl-*C*H_3), 20.88 (N-CH_2CH_2*C*H_2CH_3), 16.12 (Bu-N=C*Me*), 14.17 (Ar-N=C*Me*), 11.90 (N-$CH_2CH_2CH_2$*C*H_3). HESI-MS (m/z): calcd for $C_{51}H_{49}N_2$: 689.3890, found: 689.3882 $[M+H]^+$.

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

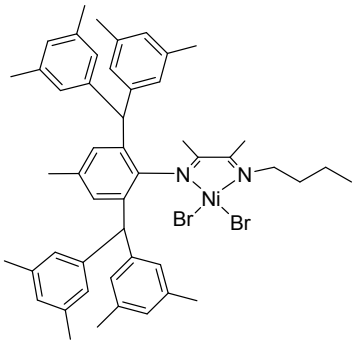
The nickel complexes were prepared in a similar manner by the reaction of 0.2 mmol ligand with 1 equivalent (DME)$NiBr_2$ in dichloromethane. After stirring overnight, the solvent was removed, and the brown solid powder was washed with ether (10 mL × 2) and dried under vacuum to give the corresponding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



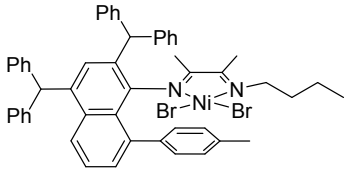
Ni1 (0.14 g, 89%). Anal. Calcd for ($C_{41}H_{42}Br_2N_2Ni$): C, 63.03; H, 5.42; N, 3.59. Found: C, 63.18; H, 5.65; N, 3.74. MALDI-TOF-MS (m/z): calcd for $C_{41}H_{42}BrN_2Ni$: 701.1864, found: 700.9077 $[M-Br]^+$.



Ni2 (0.15 g, 87%). Anal. Calcd for ($C_{41}H_{38}Br_2F_4N_2Ni$): C, 57.71; H, 4.49; N, 3.28. Found: C, 57.48; H, 4.71; N, 3.15. MALDI-TOF-MS (m/z): calcd for $C_{41}H_{38}BrF_4N_2Ni$: 773.1488, found: 772.8644 $[M-Br]^+$.



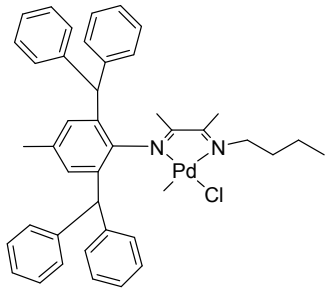
Ni3 (0.15 g, 82%). Anal. Calcd for ($C_{49}H_{58}Br_2N_2Ni$): C, 65.87; H, 6.54; N, 3.14. Found: C, 65.95; H, 6.72; N, 3.02. MALDI-TOF-MS (m/z): calcd for $C_{49}H_{58}BrN_2Ni$: 813.3116, found: 813.0918 $[M-Br]^+$.



Ni4 (0.16 g, 89%). Anal. Calcd for ($C_{51}H_{48}Br_2N_2Ni$): C, 67.50; H, 5.33; N, 3.09. Found: C, 67.28; H, 5.14; N, 3.13. MALDI-TOF-MS (m/z): calcd for $C_{51}H_{48}BrN_2Ni$: 827.2334, found: 826.9916 $[M-Br]^+$.

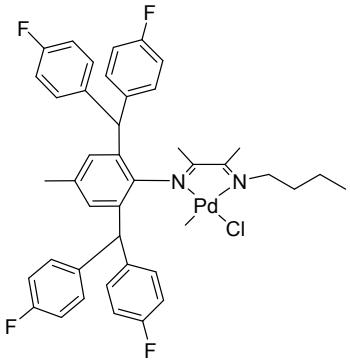
1.5 Procedure for the Synthesis of Palladium Complexes Pd1-Pd4.

A mixture of the ligand (1 mmol), Pd(COD)MeCl (265 mg, 1 mmol) in CH_2Cl_2 (20 mL) was stirred for 1 day at room temperature. During stirring, the color of the solution was deepening. At the end of the reaction, the solution was concentrated to 2 mL. The product was crashed out with 20 ml ether and washed with ether (3 × 5 mL). Then dried under reduced pressure at room temperature for about 5 h. The pure compound was obtained as an orange or yellow solid.

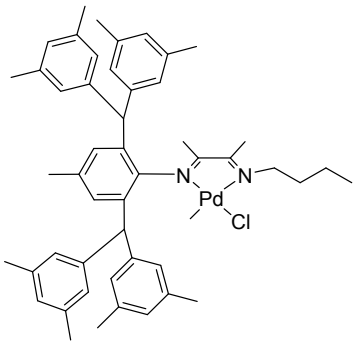


Pd1 (0.66 g, 91%). a-isomer: b-isomer = 20:1, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30, 7.20 (ddt, *J* = 21.4, 14.2, 7.1 Hz, 10H, aryl-*H*), 7.16 – 7.10 (m, 6H, aryl-*H*), 7.07 (d, *J* = 7.5 Hz, 4H, aryl-*H*), 6.75, 6.61 (s, 2H, aryl-*H*), 5.97, 5.87 (s, 2H, C*H*Ar_2), 4.03, 3.80 (t, *J* = 7.4 Hz, 2H, N-C$H_2$$CH_2CH_2CH_3$), 2.18, 2.13 (s, 3H, aryl-CH_3), 1.87 – 1.80, 1.74 (m, 2H, N-CH_2C$H_2$$CH_2CH_3$), 1.54 (s, 3H, Bu-N=C*Me*), 1.50 (dd, *J* = 14.7, 7.3 Hz, 2H, N-CH_2CH_2C$H_2$$CH_3$), 1.04, 0.87 (t, *J* = 7.3 Hz, 3H, N-$CH_2CH_2CH_2$CH_3), 1.09, 0.91 (s, 3H, Pd-CH_3), -0.43, -0.47 (s, 3H, Ar-N=C*Me*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.92 (Bu-N=*C*Me), 166.85 (Ar-N=*C*Me), 142.28, 141.33, 141.10, 136.22, 135.53, 130.36, 129.49, 129.19, 128.77, 128.25, 126.76, 126.58, 52.17 (N-*C*$H_2CH_2CH_2CH_3$), 51.99 (*C*HAr_2), 32.03 (N-CH_2*C*$H_2CH_2CH_3$), 21.53 (aryl-*C*H_3), 20.74 (N-CH_2CH_2*C*H_2CH_3), 19.73 (Bu-N=C*Me*), 15.52 (Ar-N=C*Me*), 14.13 (N-$CH_2CH_2CH_2$*C*H_3), 3.19 (Pd-*C*H_3). Anal. Calcd for ($C_{42}H_{45}ClN_2Pd$): C, 70.29; H, 6.30; N, 3.89. Found: C, 70.43; H, 6.17; N, 3.71. MALDI-TOF-MS (m/z): calcd for $C_{41}H_{42}N_2Pd$: 668.2383, found: 668.0474

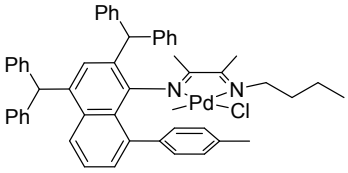
[M-Me-Cl]$^+$.



Pd2 (0.73 g, 92%). a-isomer: b-isomer = 5:1, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22, 7.17 – 7.11 (dd, m, *J* = 8.5, 5.5 Hz, 2H, aryl-*H*), 7.11 – 7.05 (m, 4H, aryl-*H*), 6.98 – 6.88 (m, 10H, aryl-*H*), 6.69, 6.56 (s, 2H, aryl-*H*), 5.90, 5.81 (s, 2H, C*H*Ar_2), 4.02, 3.79 (t, *J* = 7.6 Hz, 2H, N-C*H*$_2$$CH_2CH_2CH_3$), 2.19, 2.14 (s, 3H, aryl-C*H*$_3$), 1.84 – 1.76, 1.74 – 1.70 (m, 2H, N-CH_2C*H*$_2$$CH_2CH_3$), 1.68, 1.62 (s, 3H, Bu-N=C*Me*), 1.53 – 1.43 (m, 2H, N-CH_2CH_2C*H*$_2$$CH_3$), 1.09, 0.83 (s, 3H, Pd-C*H*$_3$), 1.02 (t, *J* = 7.4 Hz, 3H, N-$CH_2CH_2CH_2$C*H*$_3$), -0.19, -0.26 (s, 3H, Ar-N=C*Me*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.49 (Bu-N=*C*Me), 174.02 (Bu-N=*C*Me), 171.97 (Ar-N=*C*Me), 166.65 (Ar-N=*C*Me), 162.50, 160.87, 140.82, 139.17, 138.59, 137.96, 137.75, 137.36, 136.97, 136.79, 136.54, 135.35, 134.82, 134.68, 132.45, 131.56, 131.51, 131.24, 131.18, 130.84, 130.79, 129.25, 128.83, 115.90, 115.76, 115.67, 115.54, 115.28, 115.14, 115.03, 114.89, 114.34, 53.53 (N-*C*$H_2CH_2CH_2CH_3$), 52.34 (N-*C*$H_2CH_2CH_2CH_3$), 50.58 (*C*HAr_2), 50.35 (*C*HAr_2), 32.04 (N-CH_2*C*$H_2CH_2CH_3$), 31.84 (N-CH_2*C*$H_2CH_2CH_3$), 21.51 (aryl-*C*H_3), 20.73 (N-CH_2CH_2*C*H_2CH_3), 20.41 (aryl-*C*H_3), 20.29 (Bu-N=C*Me*), 19.28 (Bu-N=C*Me*), 16.99 (Ar-N=C*Me*), 15.72 (Ar-N=C*Me*), 14.08 (N-$CH_2CH_2CH_2$*C*H_3), 13.99 (N-$CH_2CH_2CH_2$*C*H_3), 3.23 (Pd-*C*H_3). ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.15 (d, *J* = 8.1 Hz), -114.86 (d, *J* = 6.8 Hz), -115.90 (t, *J* = 9.4 Hz), -116.74 (d, *J* = 7.4 Hz). Anal. Calcd for ($C_{42}H_{41}ClF_4N_2Pd$): C, 63.72; H, 5.22; N, 3.54. Found: C, 63.87; H, 5.37; N, 3.40. MALDI-TOF-MS (m/z): calcd for $C_{41}H_{38}F_4N_2Pd$: 740.2006, found: 739.3266 [M-Me-Cl]$^+$.



Pd3 (0.73 g, 88%). a-isomer: b-isomer = 30:1, ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 – 6.60 (m, 14H, aryl-*H*), 5.78, 5.65 (s, 2H, C*H*Ar$_2$), 4.02, 3.77 (t, *J* = 7.6 Hz, 2H, N-C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.28 – 2.09 (m, 27H, aryl-C*H*$_3$), 1.81 (dt, *J* = 15.3, 7.7 Hz, 2H, N-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.55 (dd, *J* = 13.3, 5.3 Hz, 2H, N-CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.51 (s, 3H, Bu-N=C*Me*), 1.02 (dd, *J* = 9.3, 5.4 Hz, 3H, N-CH$_2$CH$_2$CH$_2$C*H*$_3$), 1.07, 0.88 (s, 3H, Pd-C*H*$_3$), -0.37, -0.44 (s, 3H, Ar-N=C*Me*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.47 (Bu-N=*C*Me), 166.73 (Ar-N=*C*Me), 142.15, 141.47, 140.94, 138.03, 137.50, 135.92, 135.60, 128.81, 128.18, 128.02, 127.35, 52.11 (N-*C*H$_2$CH$_2$CH$_2$CH$_3$), 52.01 (*C*HAr$_2$), 32.32 (N-CH$_2$*C*H$_2$CH$_2$CH$_3$), 21.69 (aryl-*C*H$_3$), 21.53 (aryl-*C*H$_3$), 21.35 (aryl-*C*H$_3$), 20.83 (N-CH$_2$CH$_2$*C*H$_2$CH$_3$), 19.41 (Bu-N=C*Me*), 15.19 (Ar-N=C*Me*), 14.18 (N-CH$_2$CH$_2$CH$_2$*C*H$_3$), 3.46 (Pd-*C*H$_3$). Anal. Calcd for ($C_{50}H_{61}ClN_2Pd$): C, 72.19; H, 7.39; N, 3.37. Found: C, 72.44; H, 7.12; N, 3.43. MALDI-TOF-MS (m/z): calcd for $C_{49}H_{58}N_2Pd$: 780.3635, found: 780.1172 $[M\text{-}Me\text{-}Cl]^+$.



Pd4 (0.79 g, 93%). a-isomer: b-isomer = 4:1, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 1H, aryl-*H*), 8.00, 7.79 (d, *J* = 7.6 Hz, 1H, aryl-*H*), 7.59 – 7.51 (m, 1H, aryl-*H*), 7.40 – 7.34, 7.32 – 7.27 (m, 1H, aryl-*H*), 7.27 – 6.84 (m, 23H, aryl-*H*), 6.88, 6.78 (s, 1H, aryl-*H*), 6.64, 6.61 (s, 1H, C*H*Ar$_2$), 6.23, 6.19 (s, 1H, C*H*Ar$_2$), 3.96, 3.44 – 3.35 (m, 1H, N-C*H*$_2$CH$_2$CH$_2$CH$_3$), 3.49 (ddd, *J* = 20.9, 12.0, 6.5 Hz, 1H, N-C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.34 – 2.27 (m, 3H, aryl-C*H*$_3$), 1.77 – 1.67 (m, 1H, N-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.65 – 1.54 (m, 1H, N-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.51, 1.48 (s, 3H, Bu-N=C*Me*), 1.45 (dd, *J* = 14.7, 7.4 Hz, 2H, N-

$CH_2CH_2CH_2CH_3$), 1.21, 1.02 (t, *J* = 7.3 Hz, 3H, N-$CH_2CH_2CH_2CH_3$), 1.02, 0.76 (s, 3H, Pd-CH_3), 0.43, 0.42 (s, 3H, Ar-N=C*Me*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.81 (Bu-N=*C*Me), 170.80 (Bu-N=*C*Me), 170.57 (Ar-N=*C*Me), 165.69 (Ar-N=*C*Me), 144.06, 143.58, 143.28, 143.18, 142.51, 142.44, 141.73, 141.65, 141.11, 140.25, 139.69, 139.30, 138.80, 138.61, 137.68, 136.36, 135.60, 133.74, 133.46, 133.39, 132.09, 131.79, 131.59, 131.24, 130.66, 130.56, 130.36, 130.09, 129.69, 129.56, 129.51, 129.33, 129.23, 128.59, 128.53, 128.49, 128.43, 128.36, 128.14, 127.90, 127.43, 127.30, 126.69, 126.52, 126.47, 126.28, 126.08, 125.92, 125.75, 125.44, 125.16, 124.90, 124.85, 124.73, 124.43, 53.77 (N-*C*$H_2CH_2CH_2CH_3$), 53.69 (N-*C*$H_2CH_2CH_2CH_3$), 53.56 (*C*HAr_2), 53.11 (*C*HAr_2), 52.48 (*C*HAr_2), 52.06 (*C*HAr_2), 31.83 (N-CH_2*C*$H_2CH_2CH_3$), 31.57 (N-CH_2*C*$H_2CH_2CH_3$), 21.43 (aryl-*C*H_3), 21.35 (aryl-*C*H_3), 20.79 (N-CH_2CH_2*C*H_2CH_3), 20.56 (Bu-N=C*Me*), 20.42 (N-CH_2CH_2*C*H_2CH_3), 19.98 (Bu-N=C*Me*), 16.46 (Ar-N=C*Me*), 15.43 (Ar-N=C*Me*), 14.20 (N-$CH_2CH_2CH_2$*C*H_3), 14.10 (N-$CH_2CH_2CH_2$*C*H_3), 2.15 (Pd-*C*H_3). Anal. Calcd for ($C_{52}H_{51}ClN_2Pd$): C, 73.84; H, 6.08; N, 3.31. Found: C, 73.61; H, 6.24; N, 3.45. MALDI-TOF-MS (m/z): calcd for $C_{51}H_{48}ClN_2Pd$: 829.2541, found: 829.2955 $[M\text{-}Me]^+$.

1.6 A General Procedure for the Homopolymerization of Ethylene with Nickel Complexes

In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 20 mL of toluene and the desired amount MAO was added to the reactor under N_2 atmosphere, then the desired amount of catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 5 atm of ethylene. After 0.5 h, 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. For the reaction with oligomer as polymerization product, the oligomer was directly dried, dissolved and filtered with petroleum ether, and the filtrate was dried in vacuum for the polymerization product.

1.7 A General Procedure for the Homopolymerization of Ethylene with Palladium Complexes

In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure

gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 40 mL of toluene and the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the desired amount of catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 5 atm of ethylene. After 3 h, the pressure reactor was vented and the polymer was dried under vacuum.

1.8 A General Procedure for the Copolymerization of MA with Ethylene

In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 20 mL DCM and the desired polar monomer with the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the desired amount of Pd catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at the desired pressure of ethylene. After 3 h, the pressure reactor was vented and the copolymer was dried under vacuum.

2. Spectra Data

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

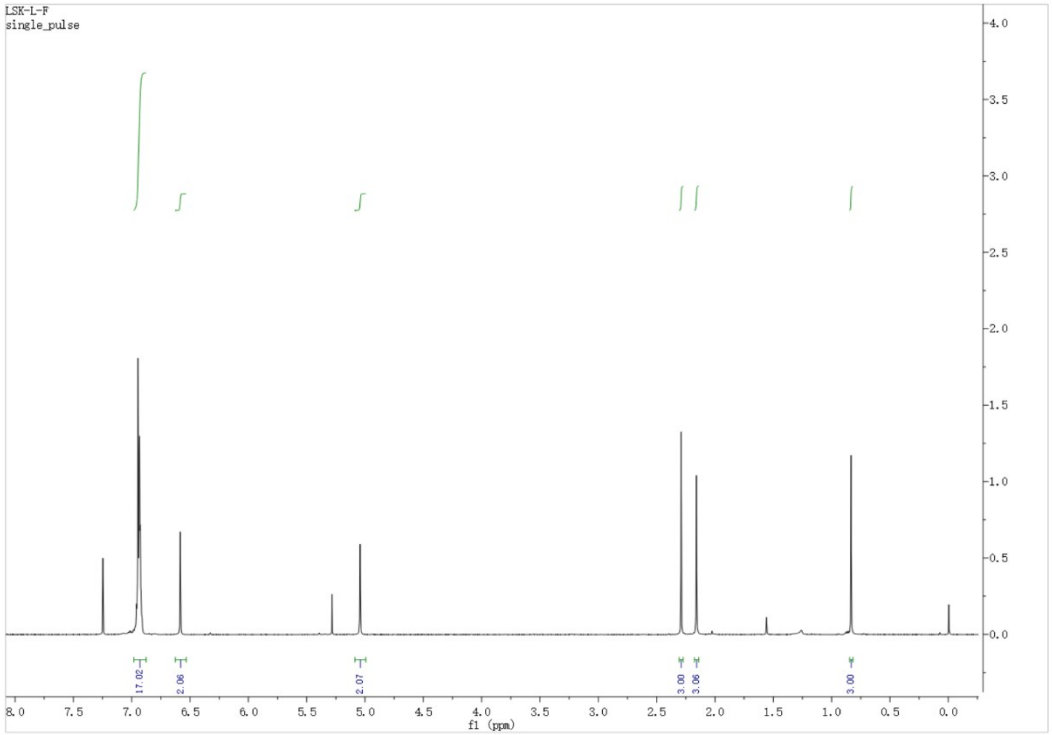


Figure S1. ^{1}H NMR spectrum of **I2** in $CDCl_3$.

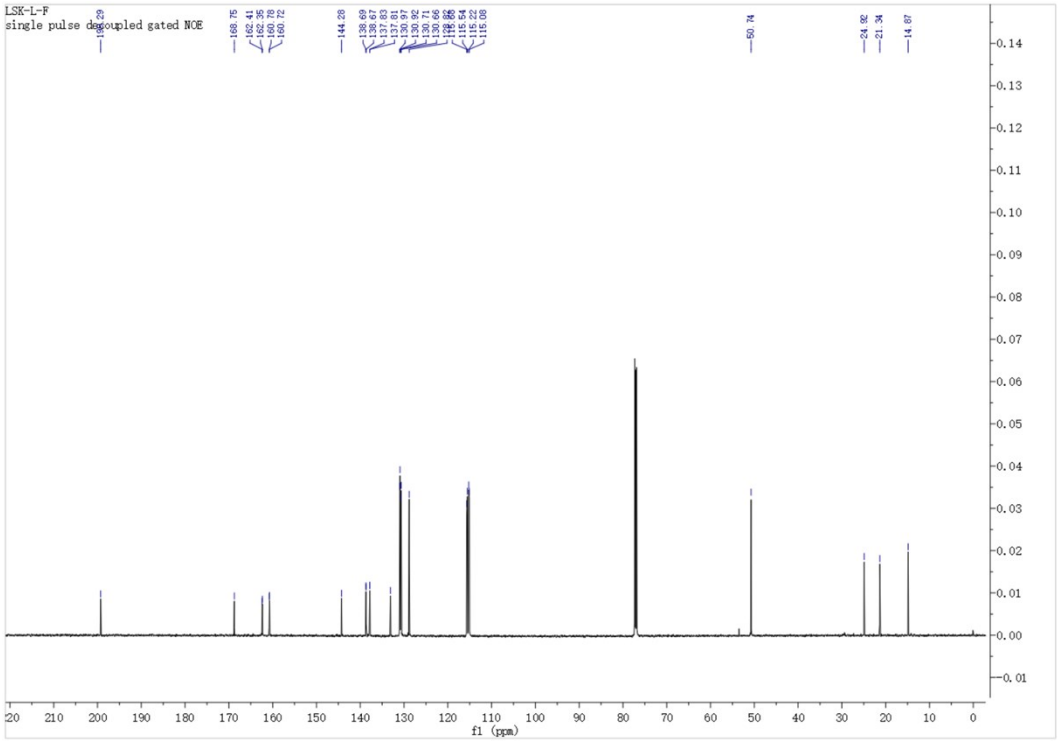


Figure S2. ^{13}C NMR spectrum of **I2** in $CDCl_3$.

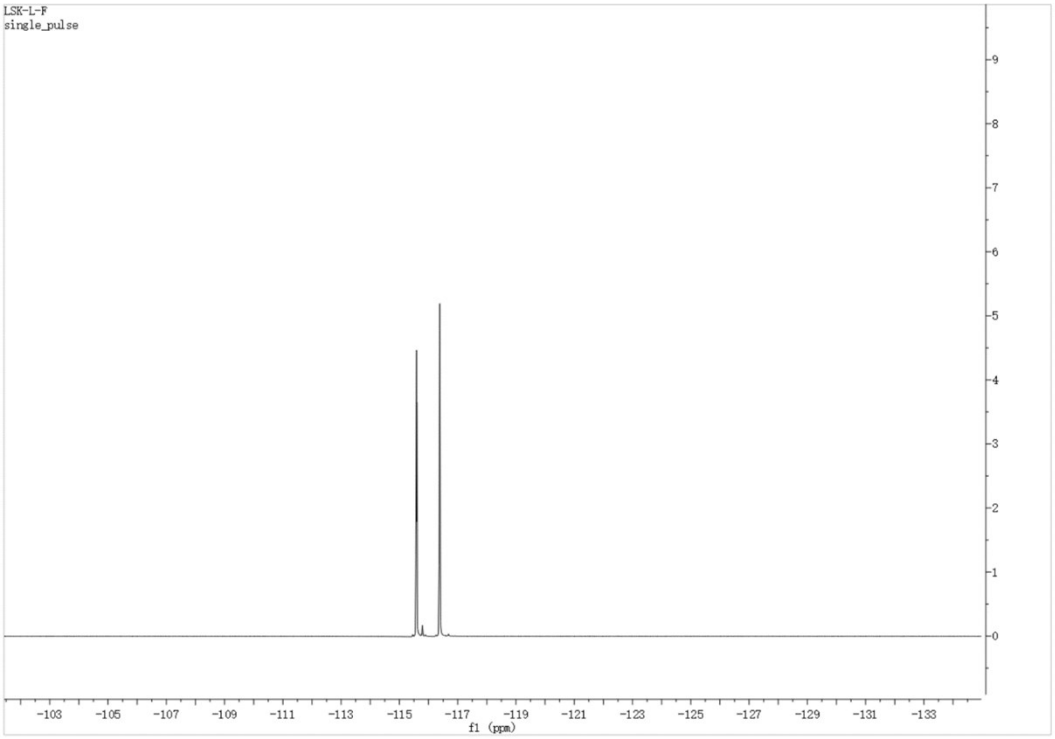


Figure S3. ^{19}F NMR spectrum of **I2** in $CDCl_3$.

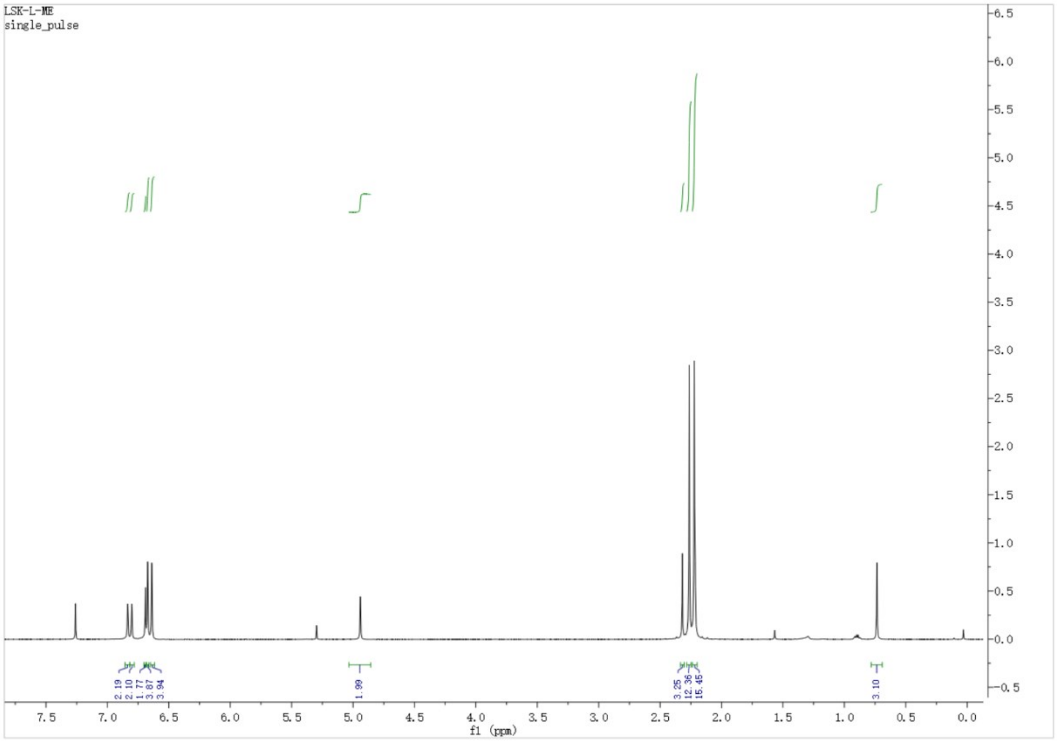


Figure S4. ^{1}H NMR spectrum of **I3** in $CDCl_3$.

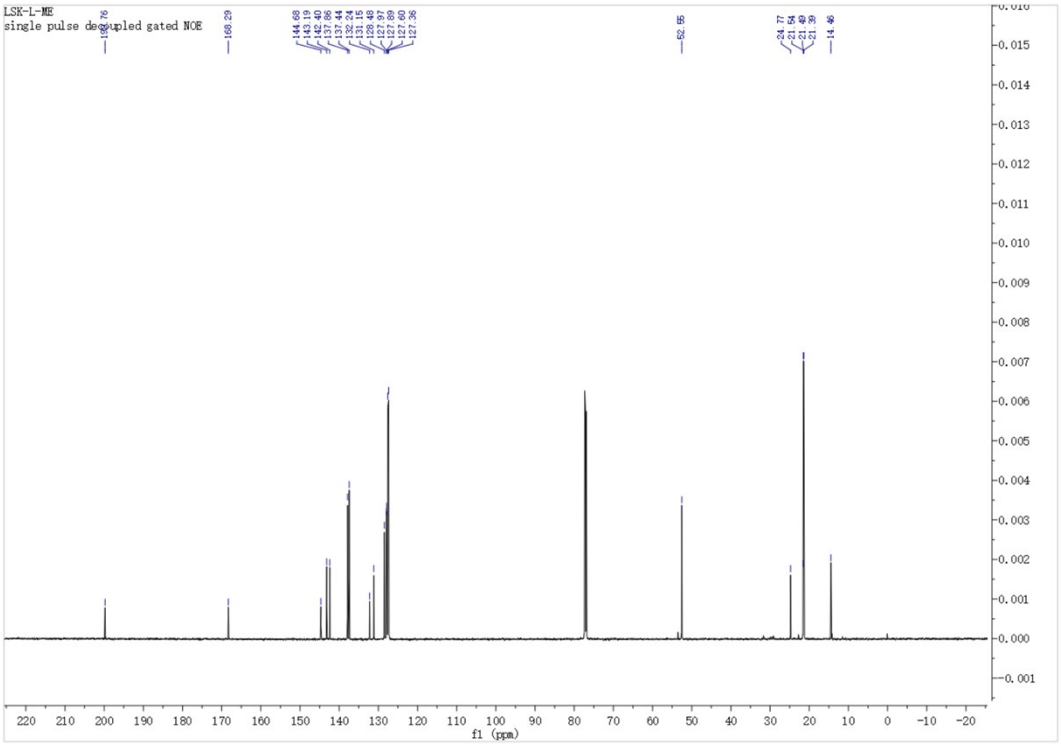


Figure S5. ^{13}C NMR spectrum of **I3** in $CDCl_3$.

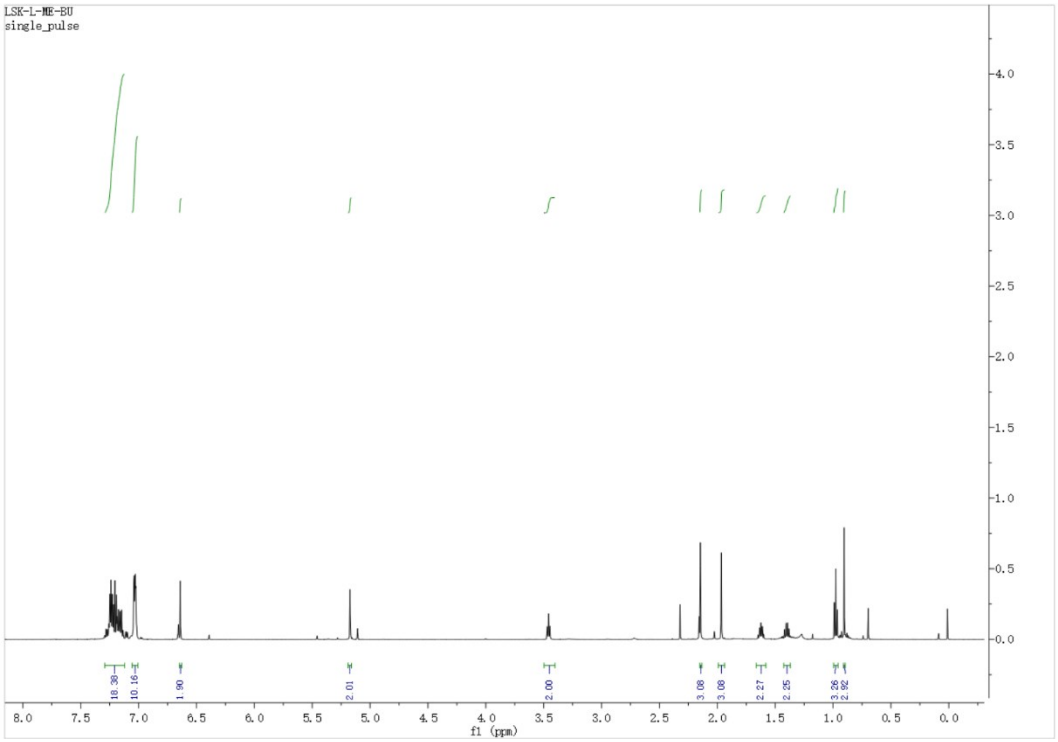


Figure S6. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

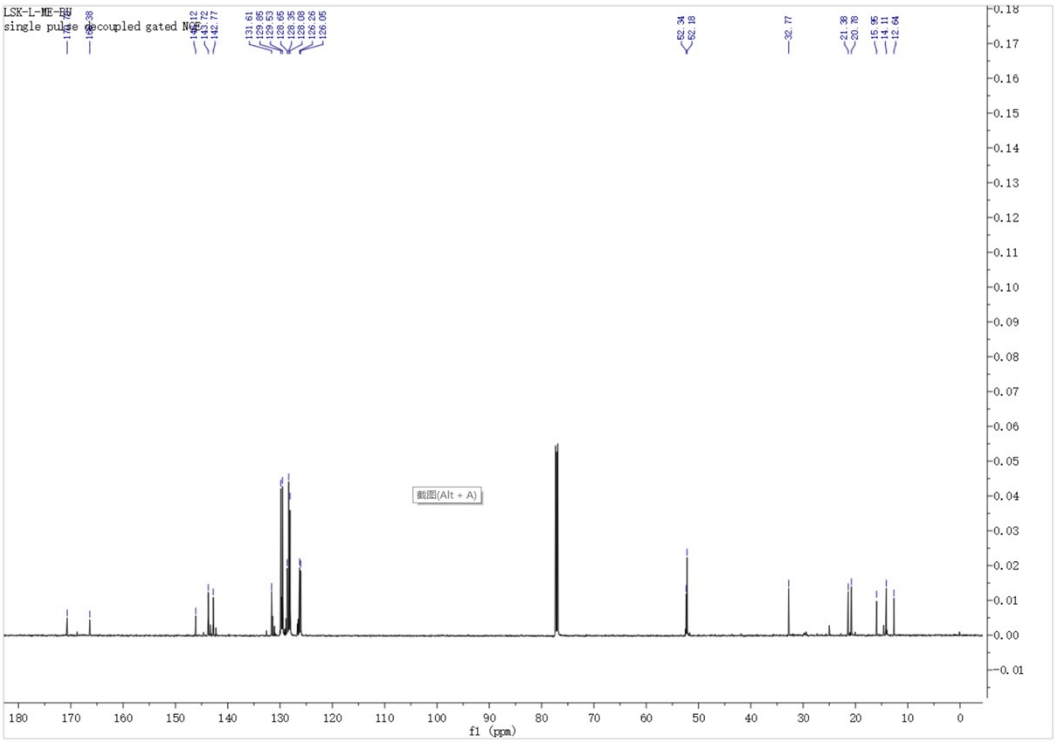


Figure S7. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

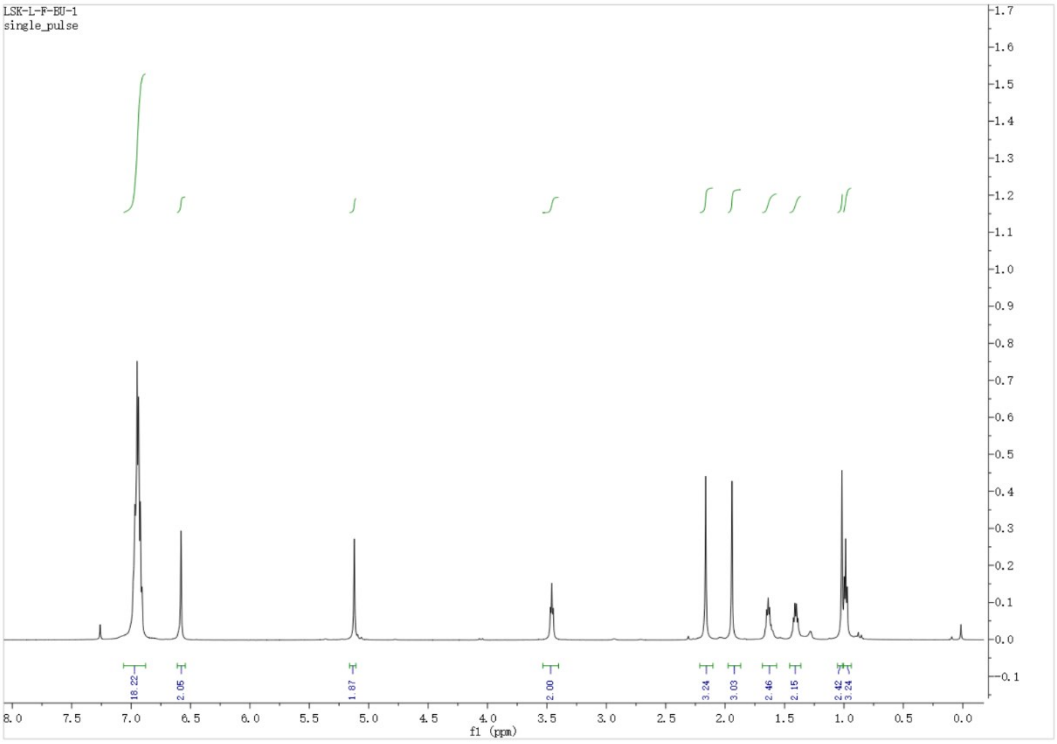


Figure S8. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

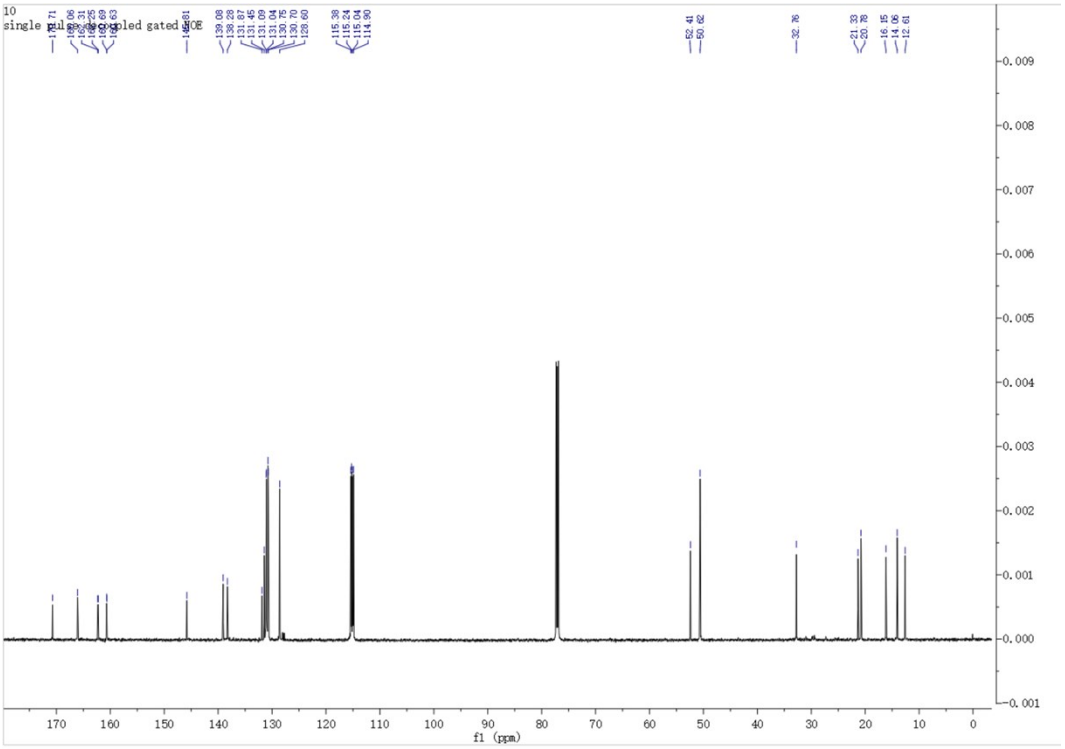


Figure S9. ^{13}C NMR spectrum of **L2** in $CDCl_3$.

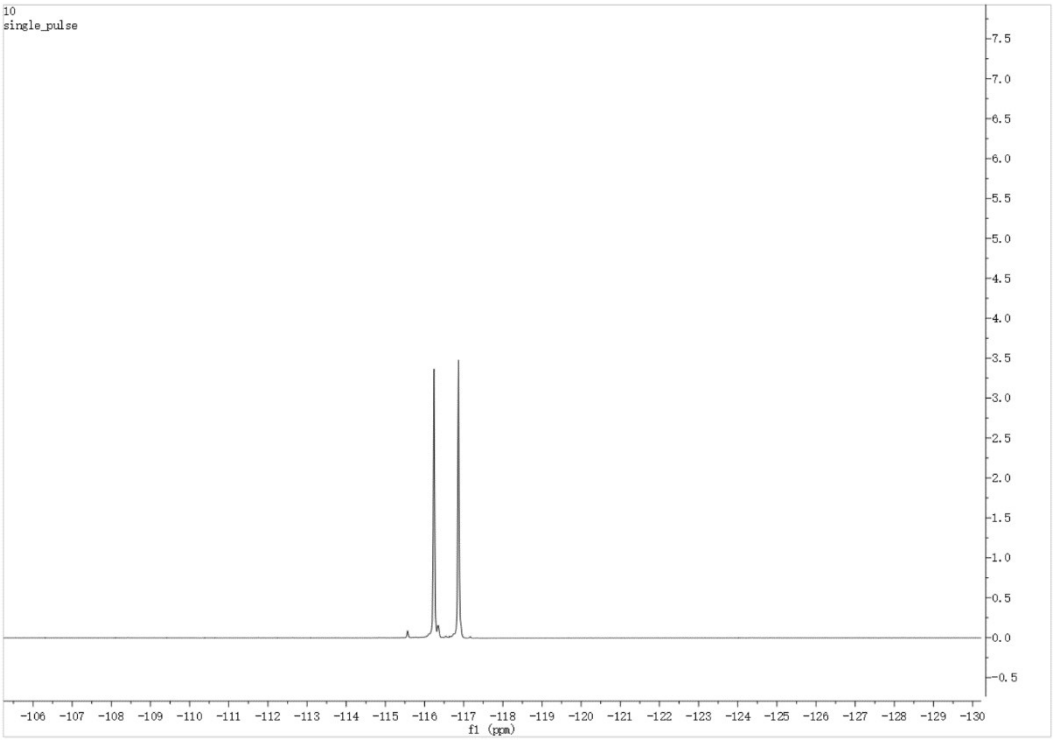


Figure S10. ^{19}F NMR spectrum of **L2** in $CDCl_3$.

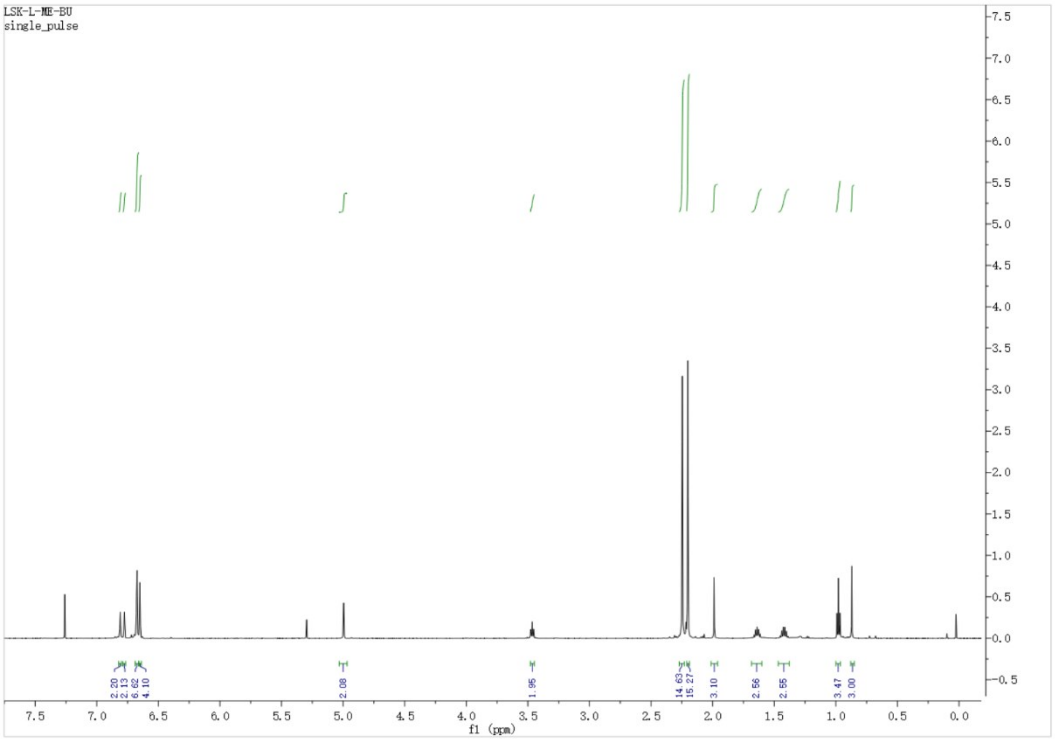


Figure S11. ^{1}H NMR spectrum of **L3** in $CDCl_3$.

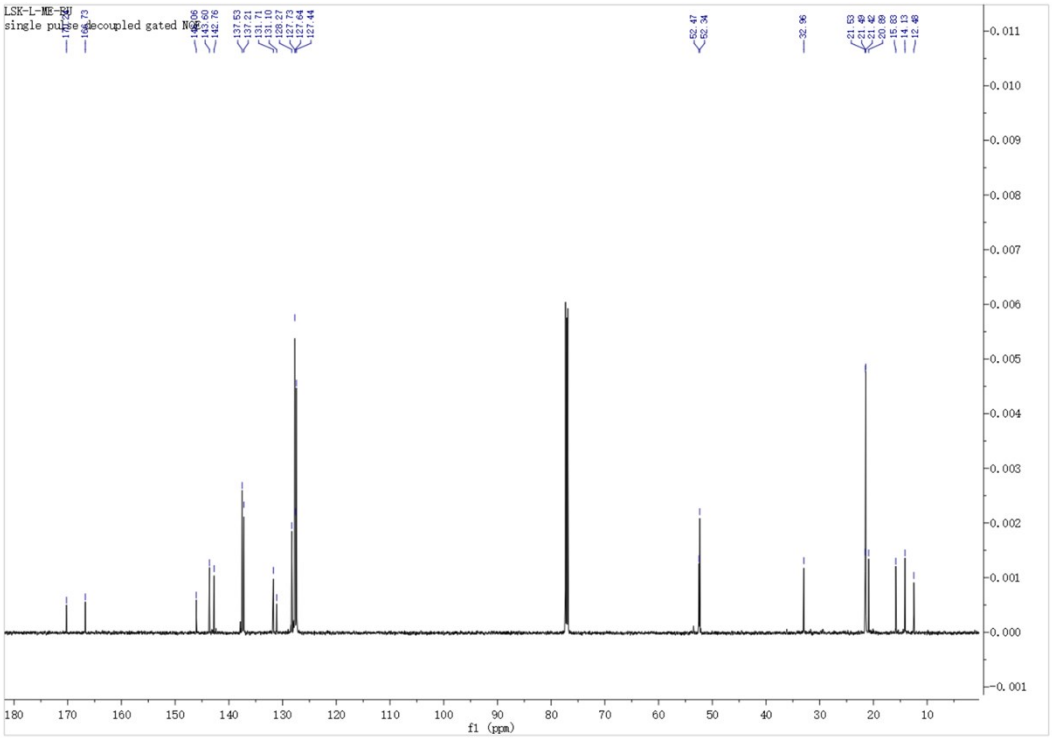


Figure S12. ^{13}C NMR spectrum of **L3** in $CDCl_3$.

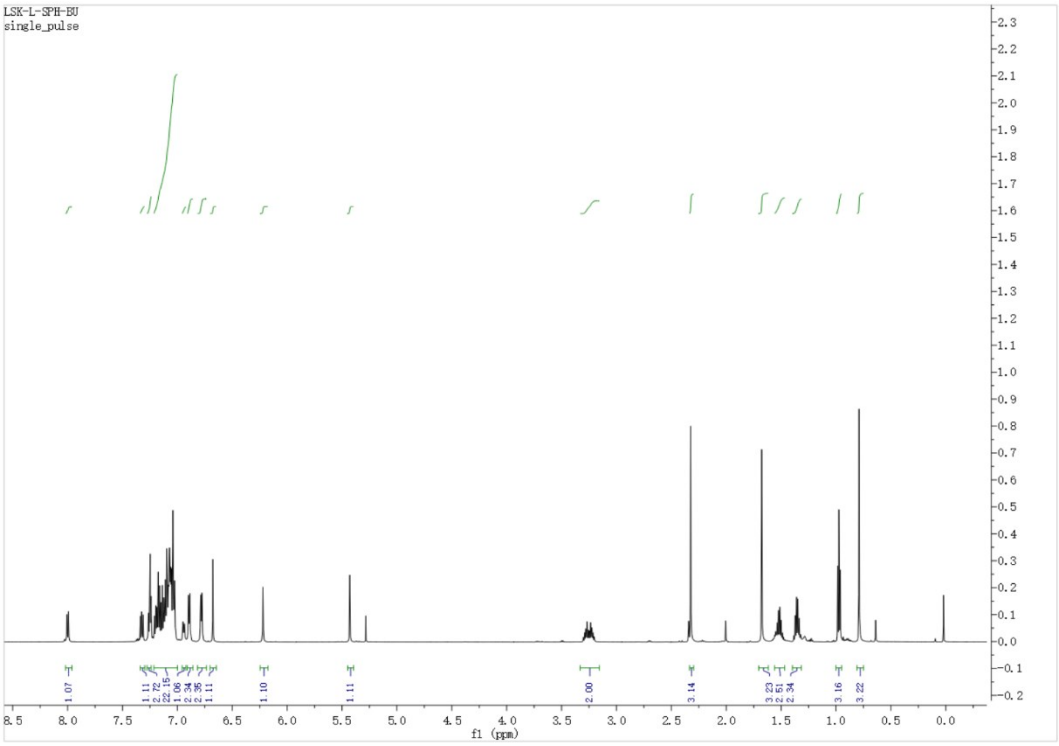


Figure S13. ^{1}H NMR spectrum of **L4** in $CDCl_3$.

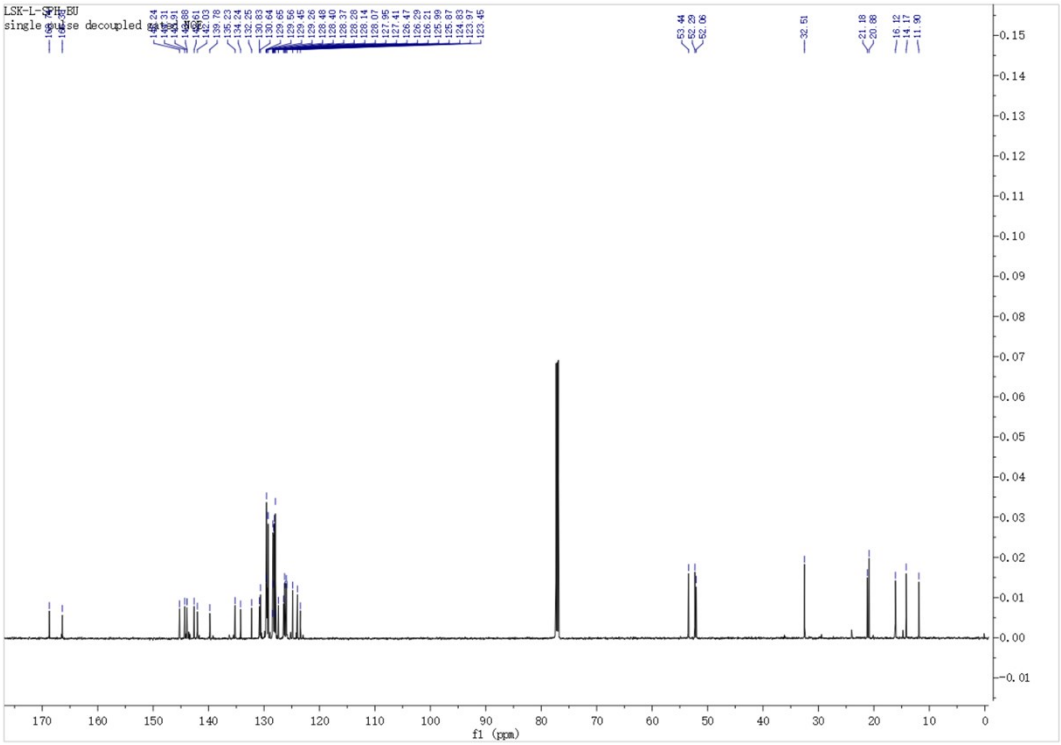


Figure S14. ^{13}C NMR spectrum of **L4** in $CDCl_3$.

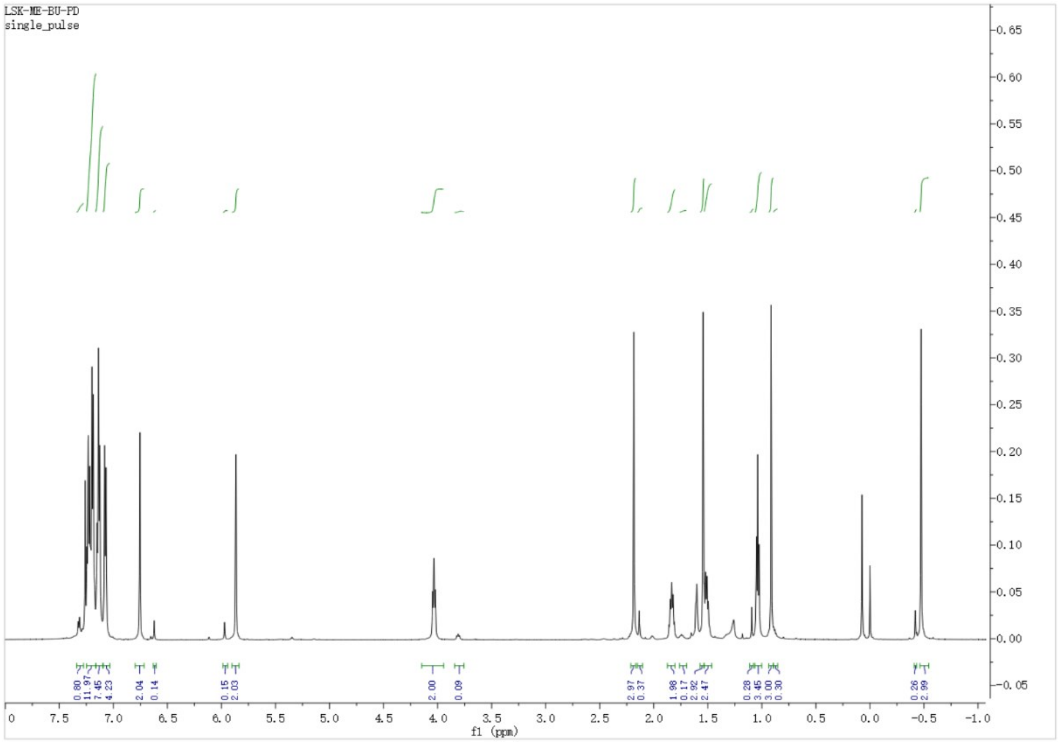


Figure S15. ^{1}H NMR spectrum of **Pd1** in $CDCl_3$.

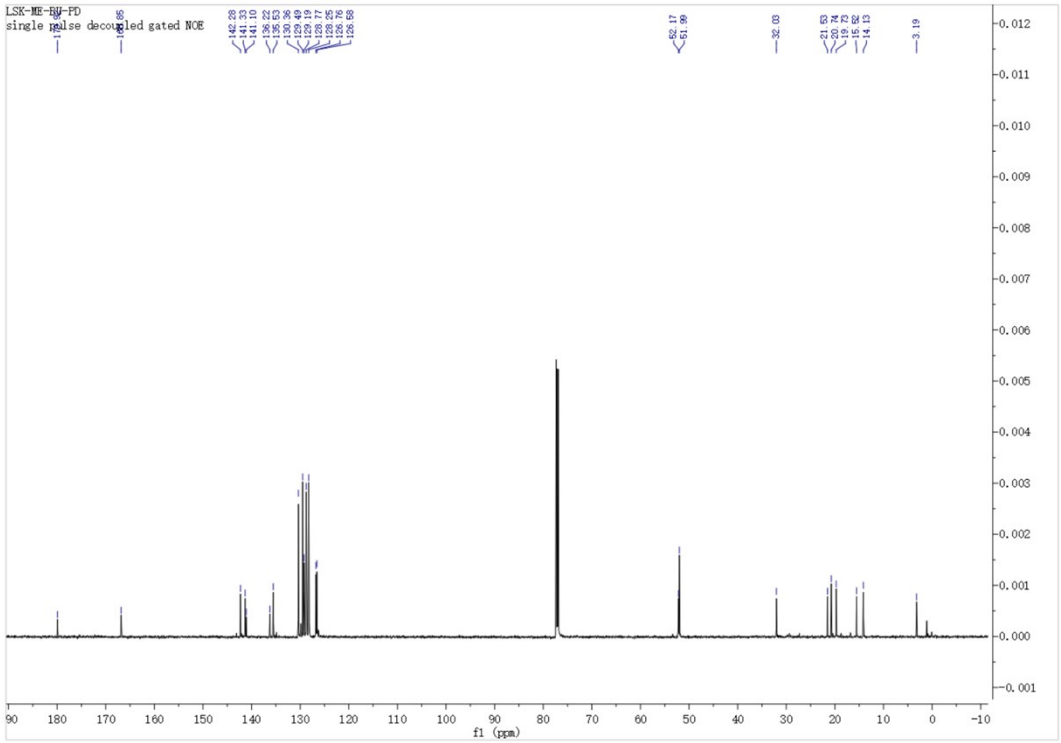


Figure S16. ^{13}C NMR spectrum of **Pd1** in $CDCl_3$.

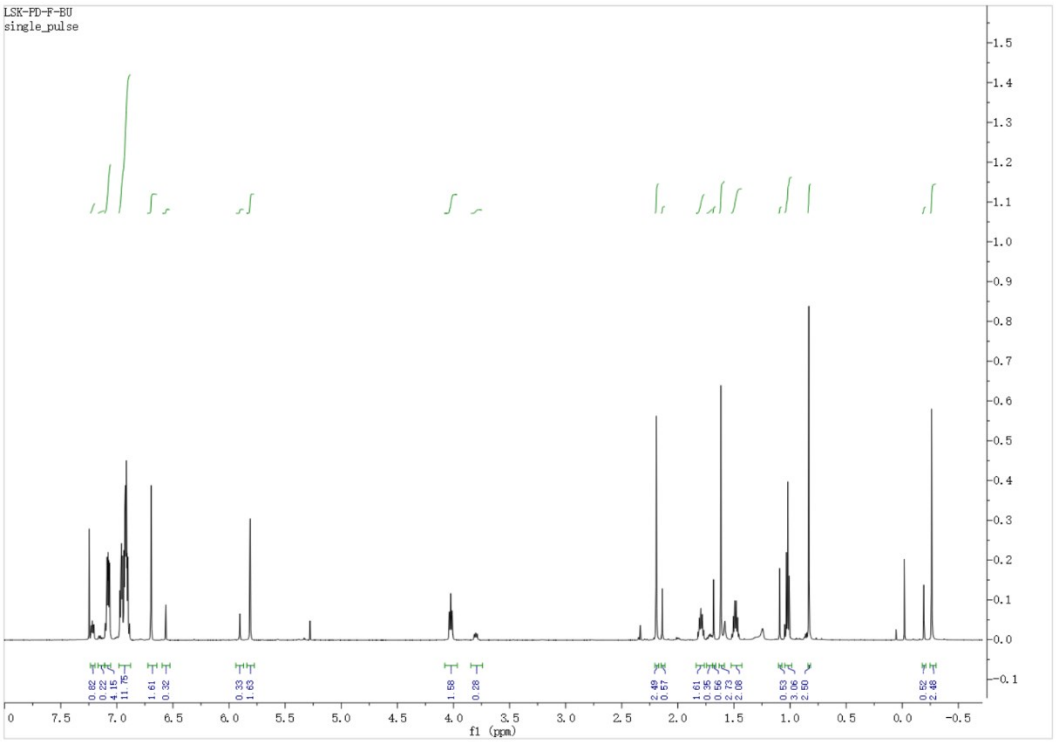


Figure S17. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

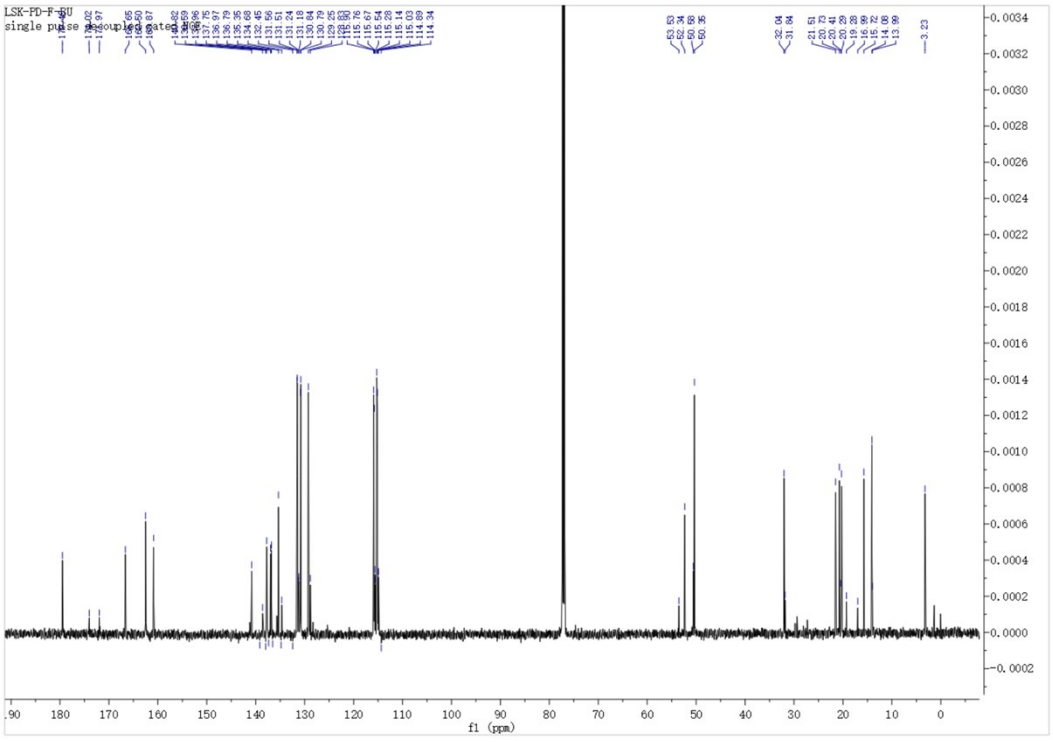


Figure S18. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

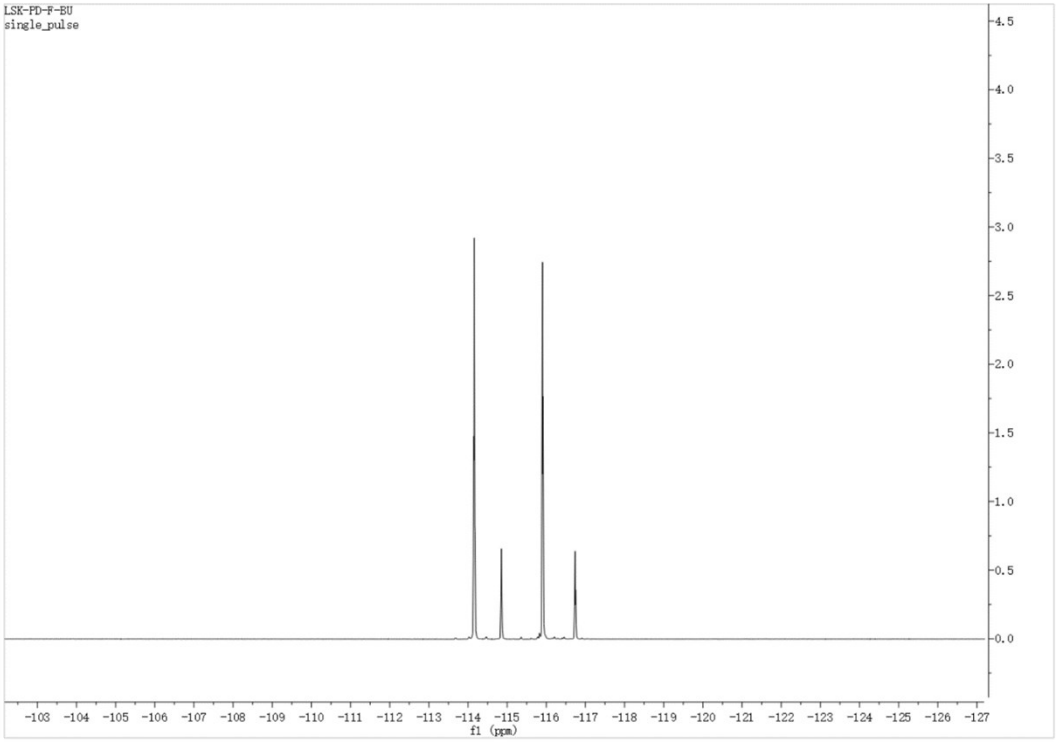


Figure S19. ^{19}F NMR spectrum of **Pd2** in $CDCl_3$.

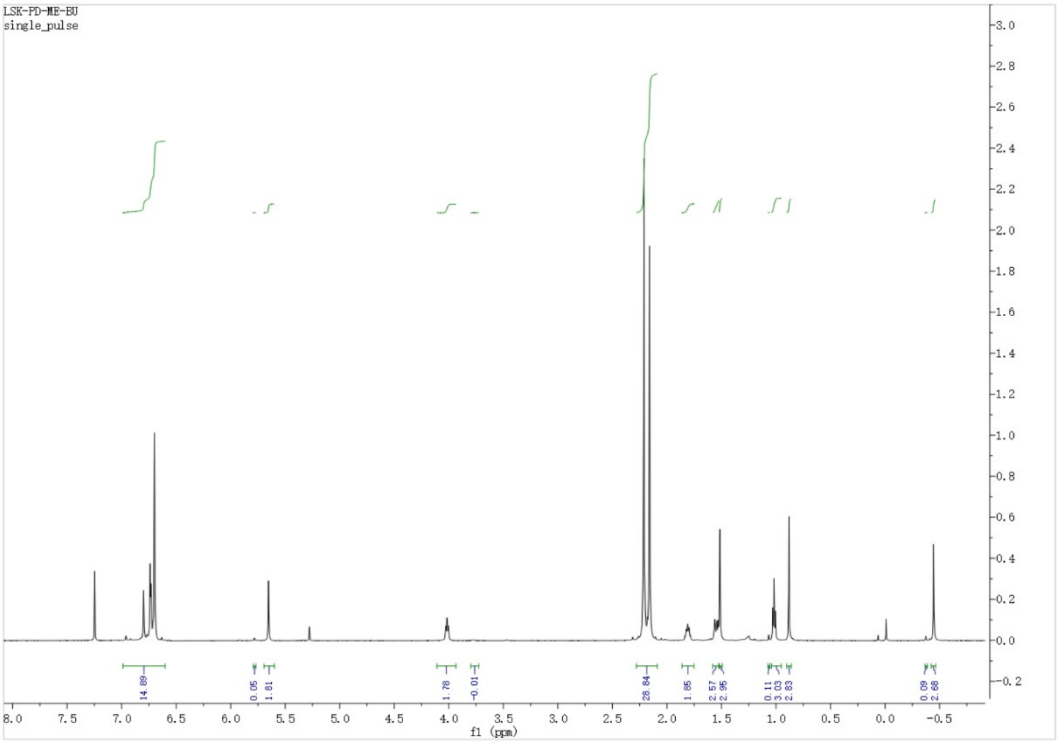


Figure S20. ^{1}H NMR spectrum of **Pd3** in $CDCl_3$.

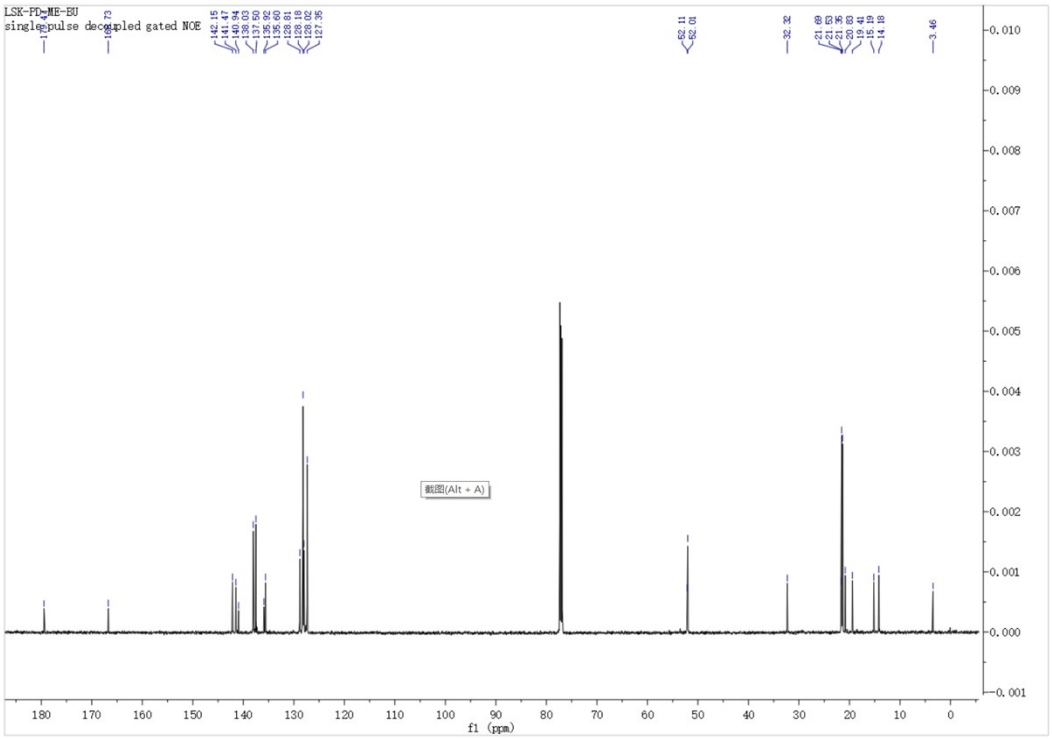


Figure S21. ^{13}C NMR spectrum of **Pd3** in $CDCl_3$.

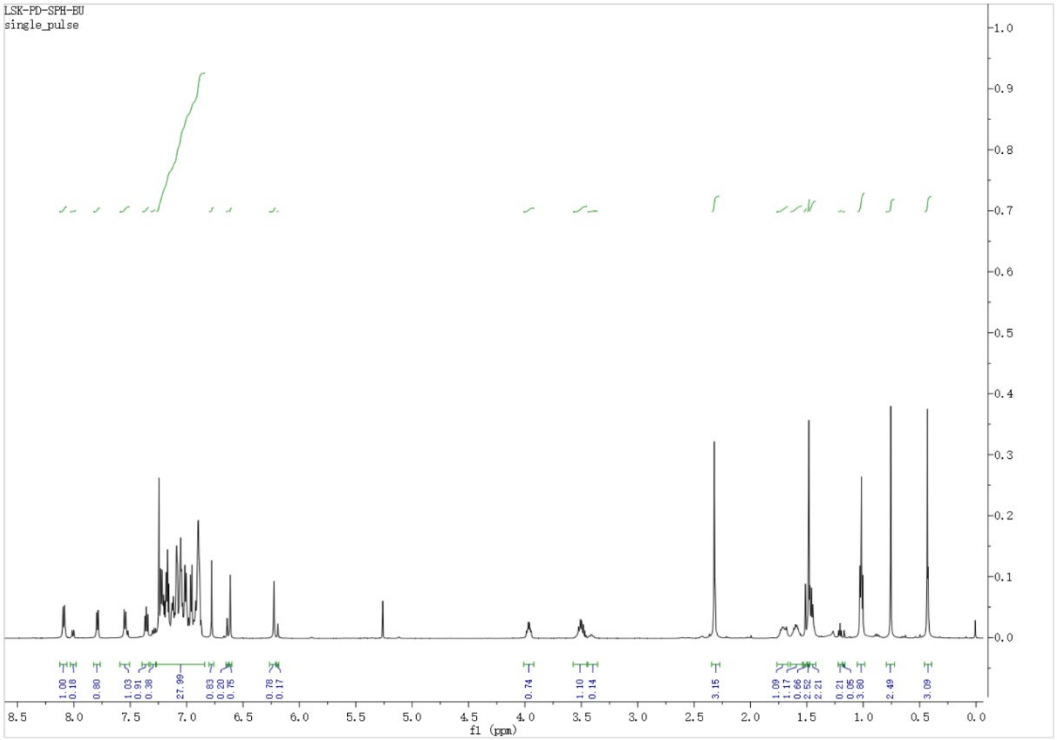


Figure S22. ^{1}H NMR spectrum of **Pd4** in $CDCl_3$.

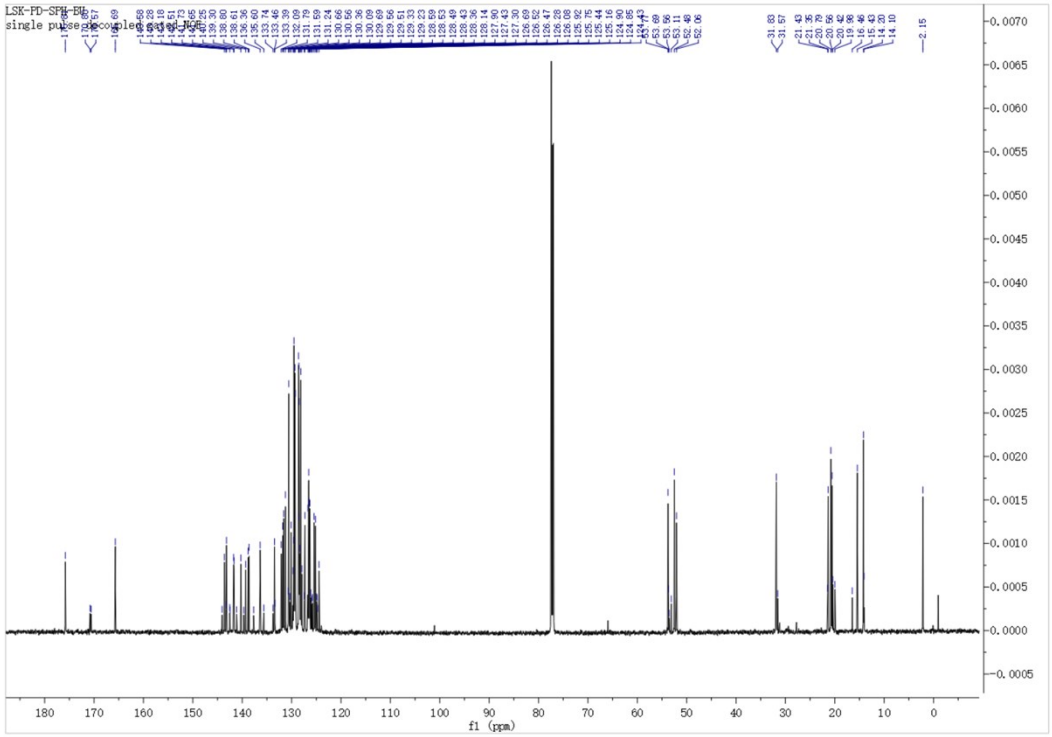


Figure S23. ^{13}C NMR spectrum of **Pd4** in $CDCl_3$.

2.2 HESI-MS of I2-I3, L1-L4.

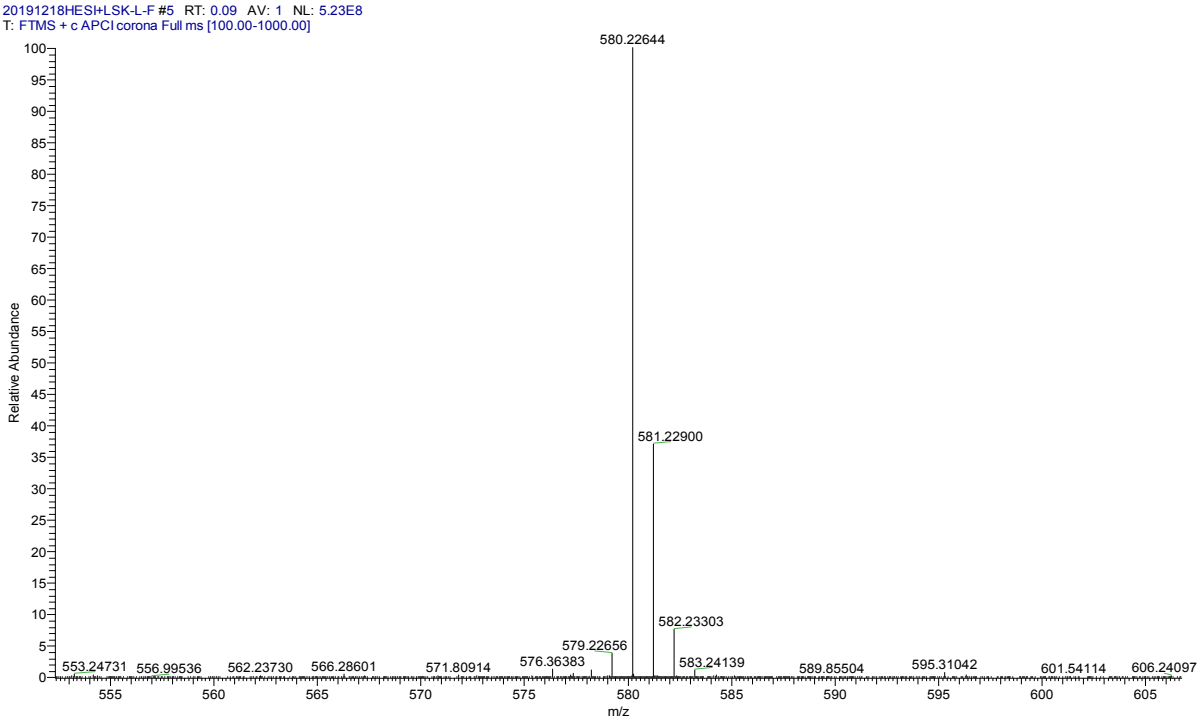


Figure S24. HESI-MS of **I2.**

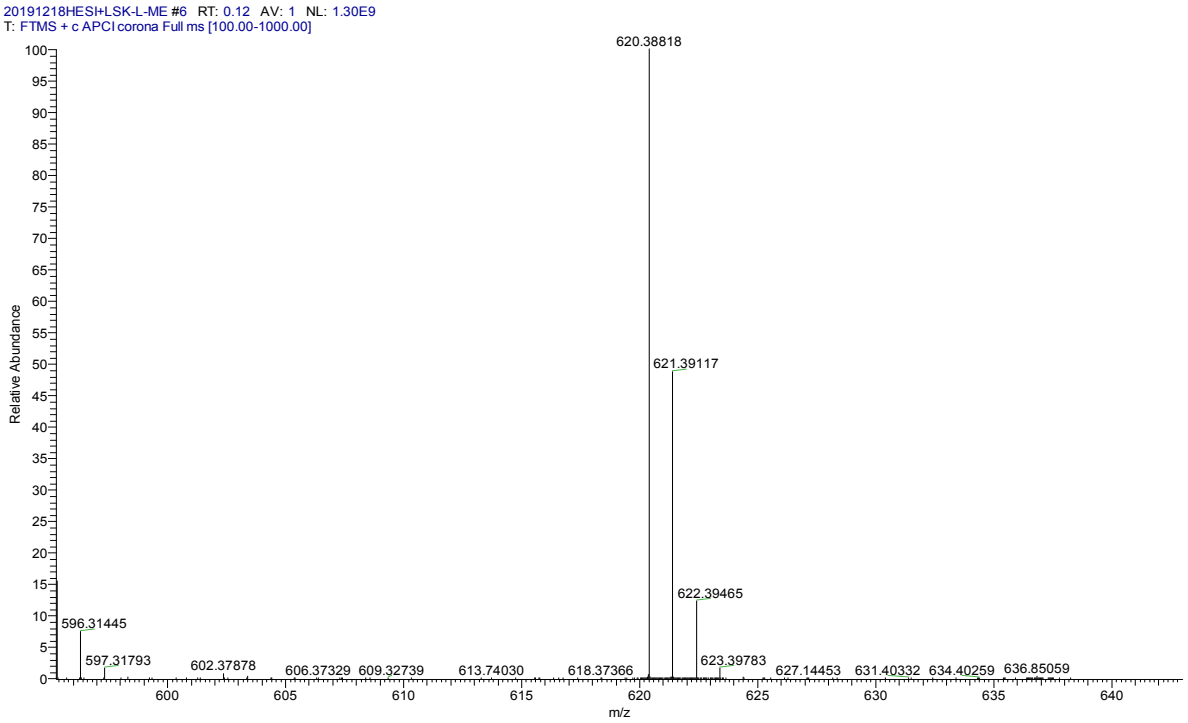


Figure S25. HESI-MS of **I3.**

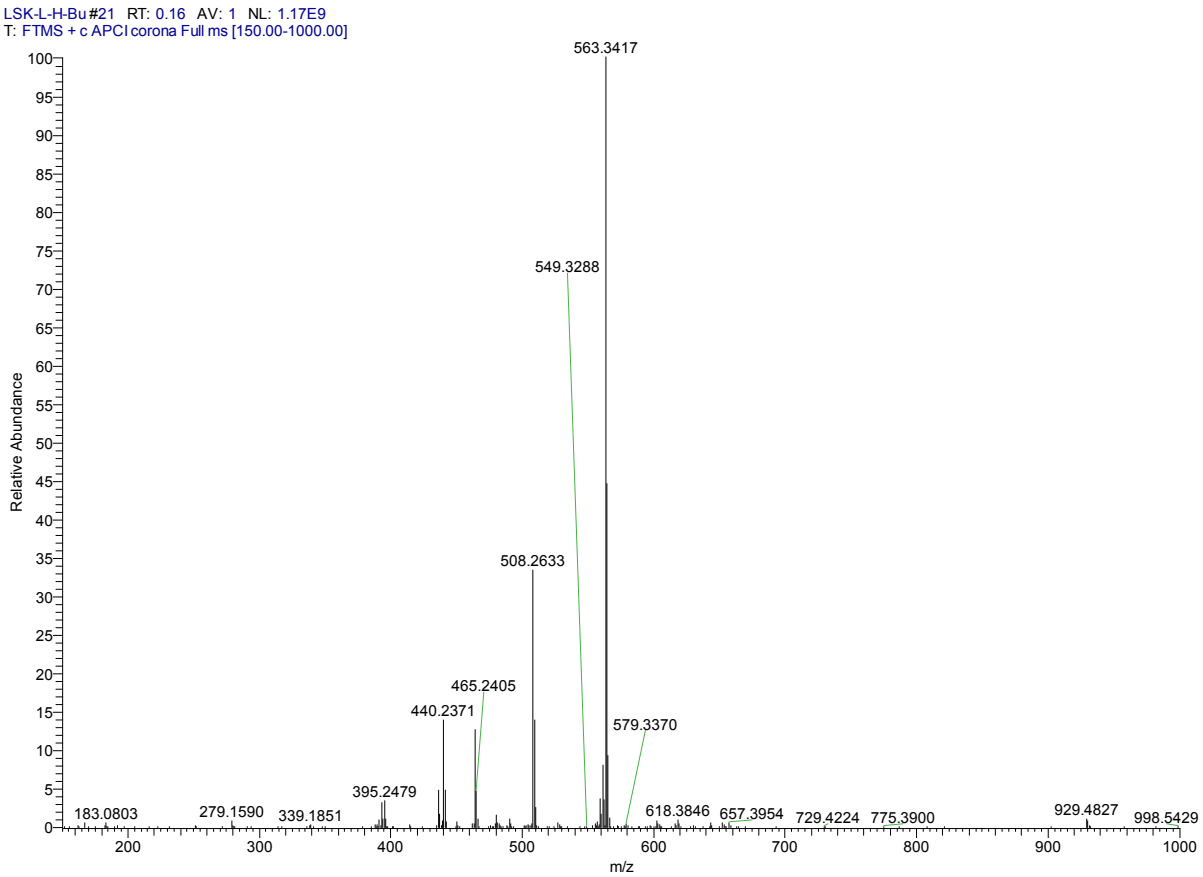


Figure S26. HESI-MS of **L1.**

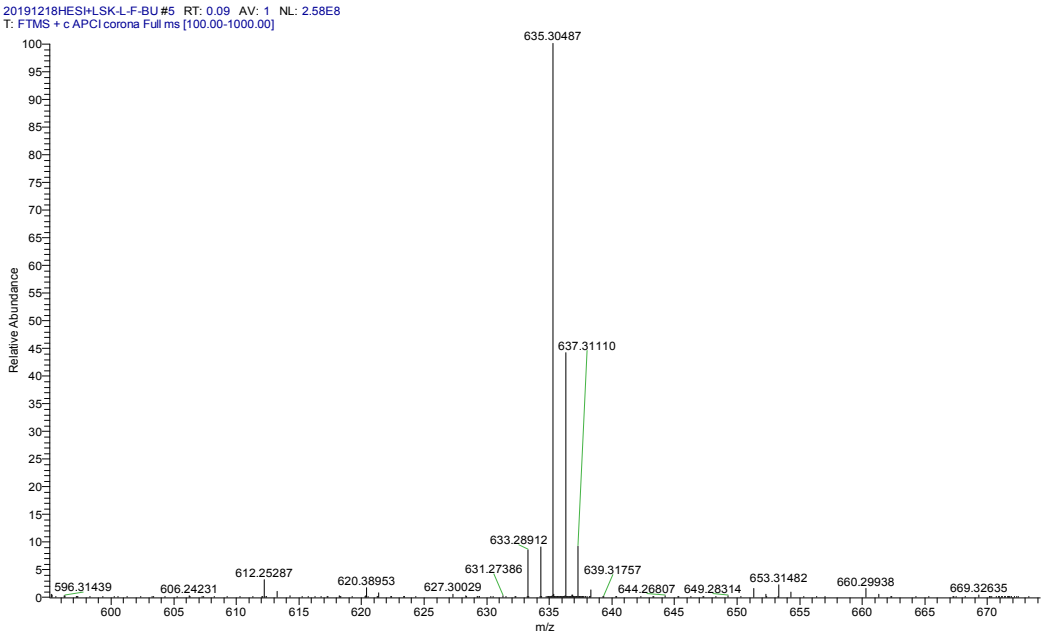


Figure S27. HESI-MS of **L2.**

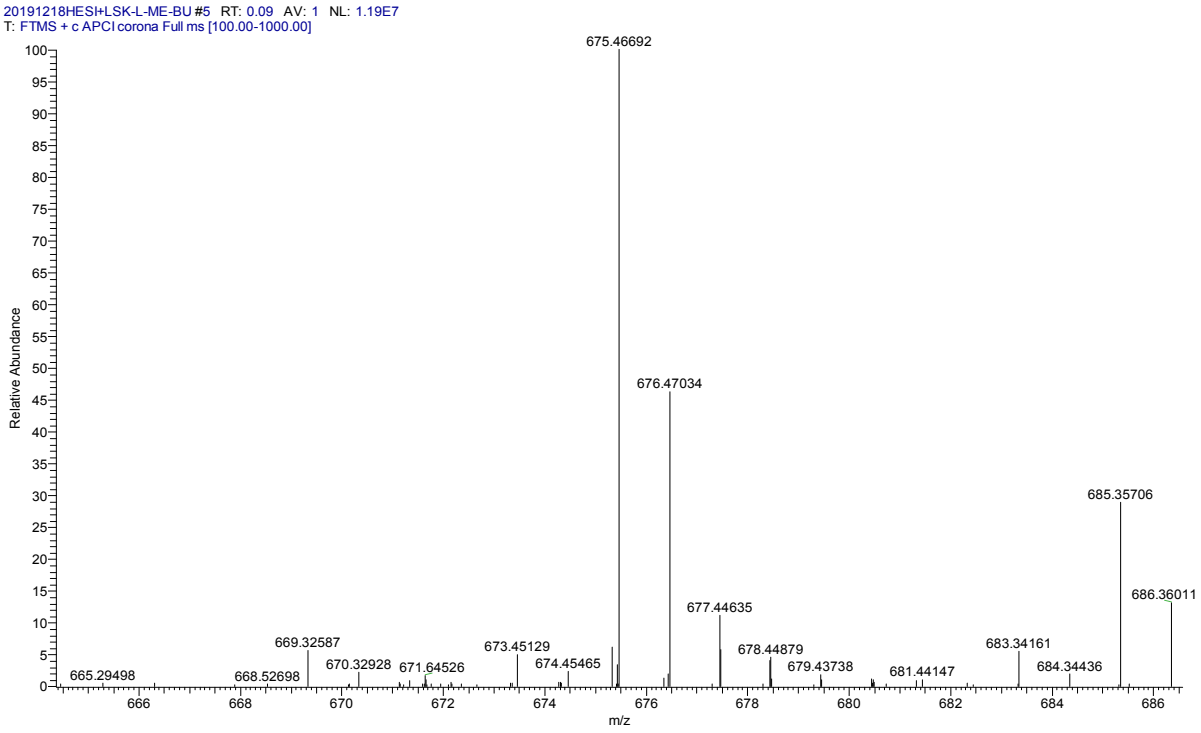


Figure S28. HESI-MS of **L3.**

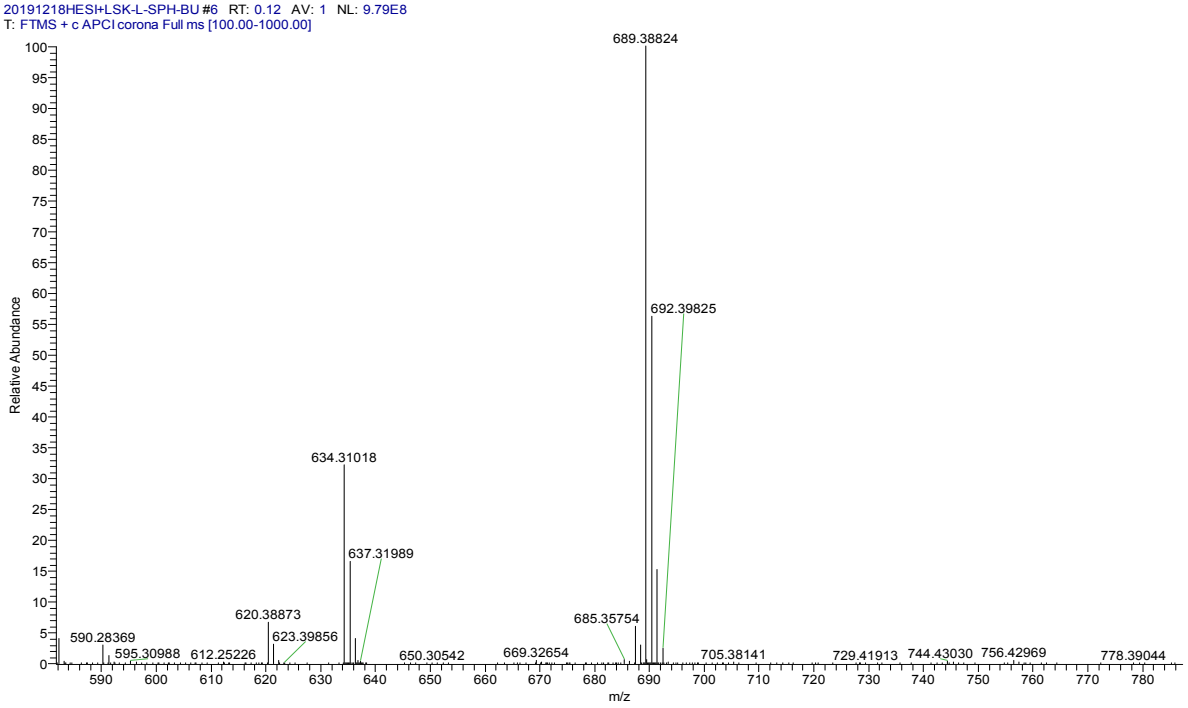


Figure S29. HESI-MS of **L4.**

2.3 MALDI-TOF of Complexes Ni1-Ni4 and Pd1-Pd4.

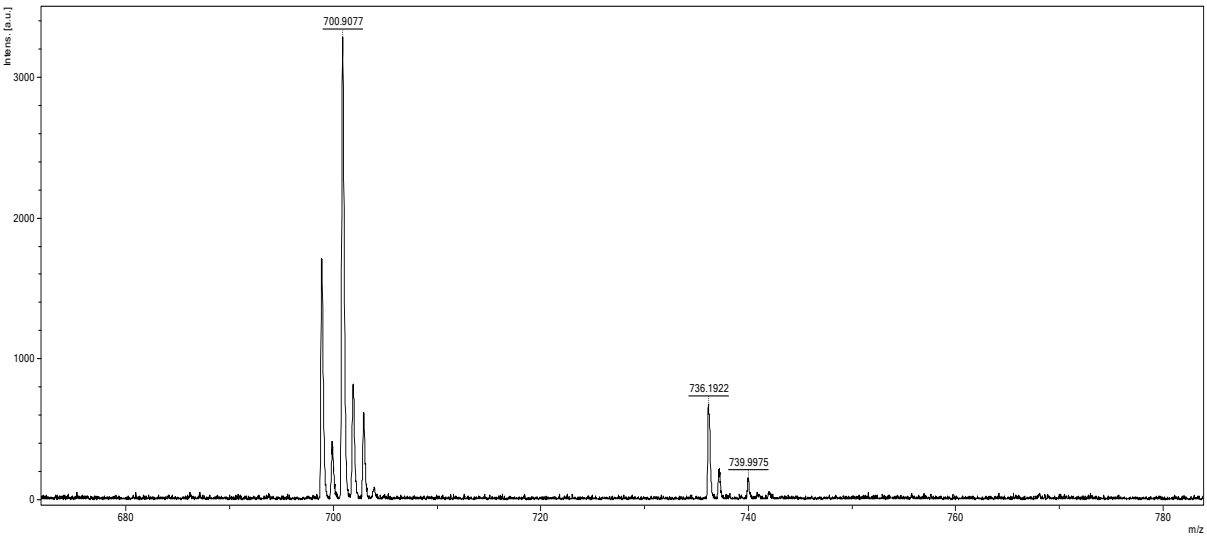


Figure S30. MALDI-TOF-MS of complex **Ni1**.

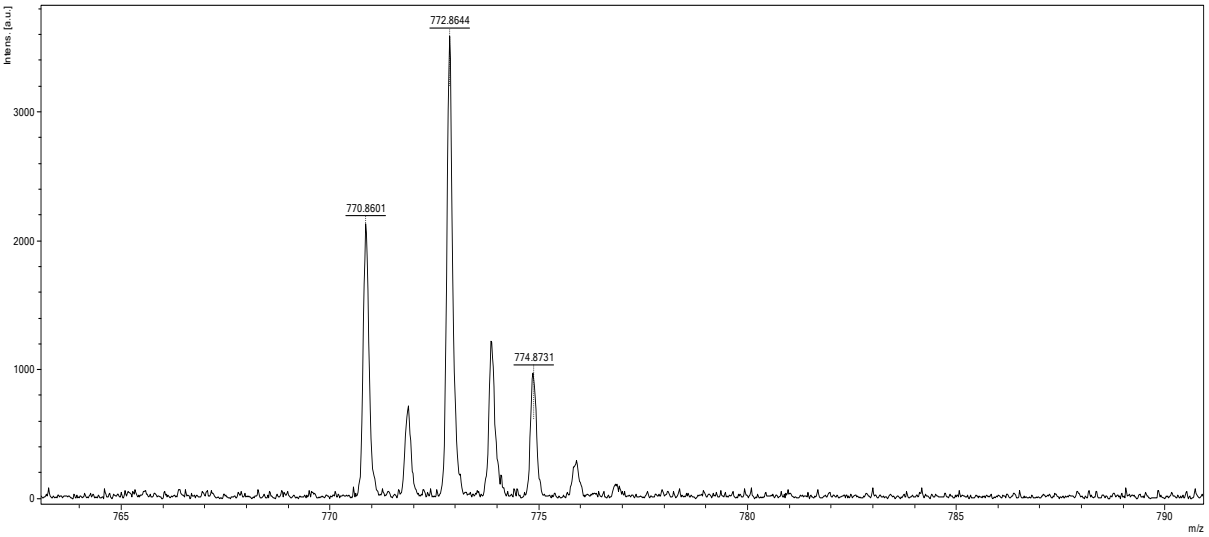


Figure S31. MALDI-TOF-MS of complex **Ni2**.

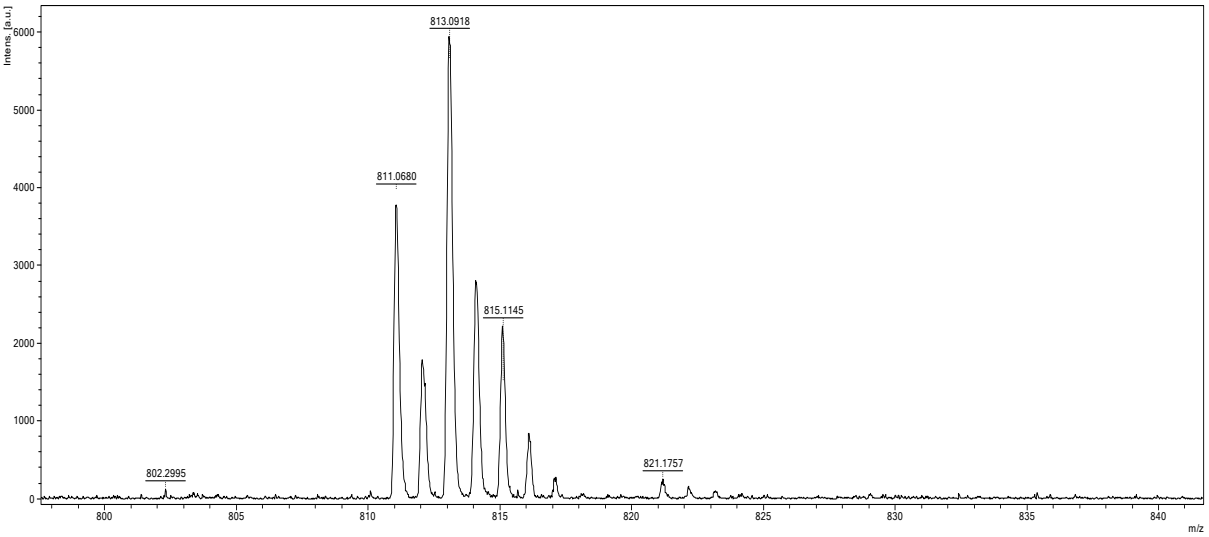


Figure S32. MALDI-TOF-MS of complex **Ni3**.

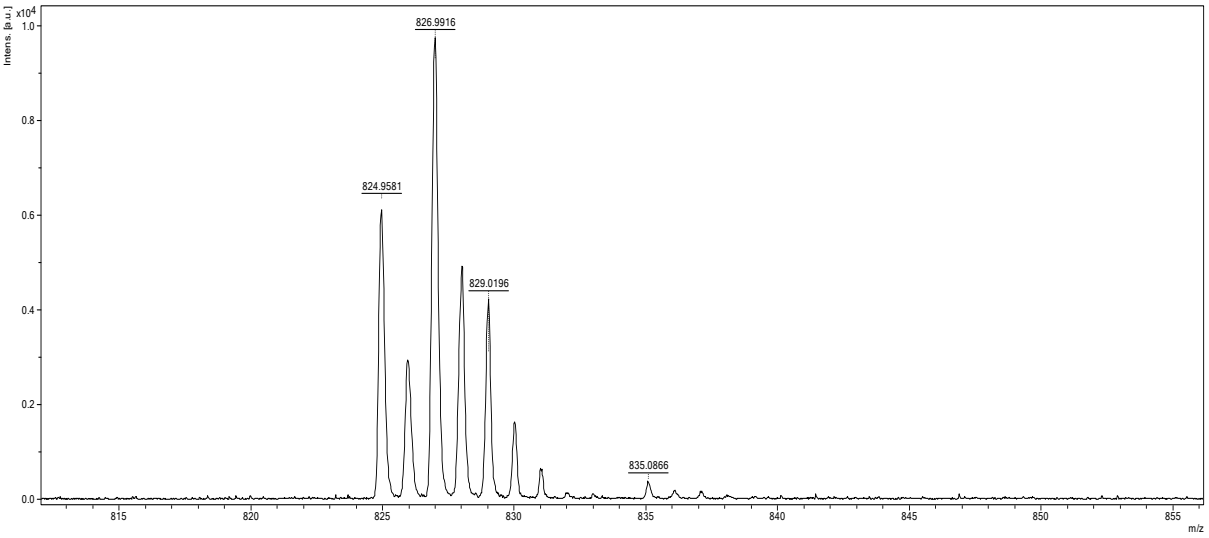


Figure S33. MALDI-TOF-MS of complex **Ni4**.

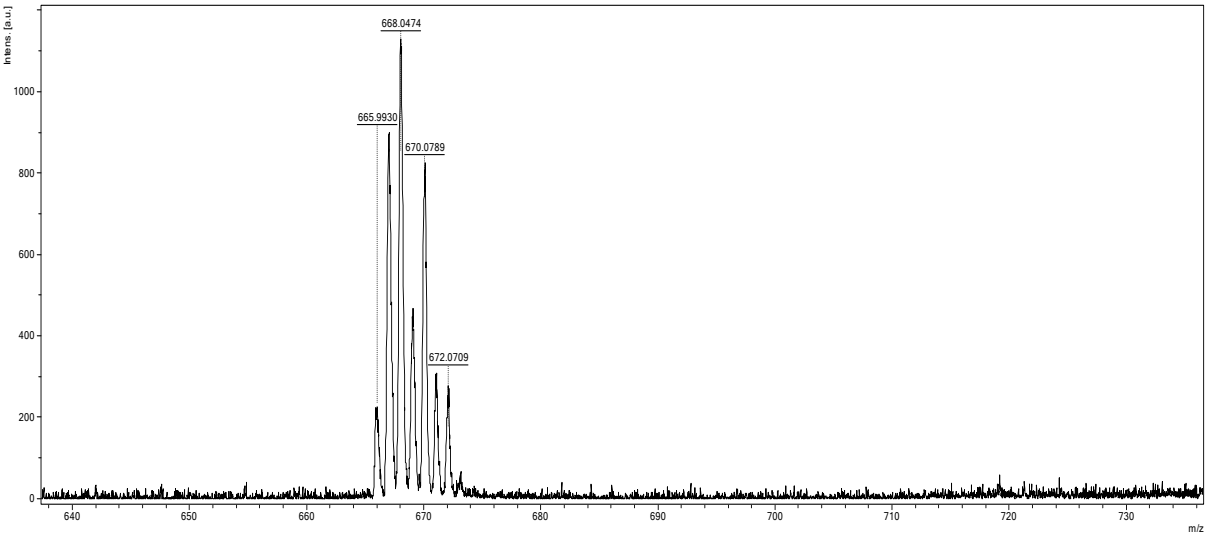


Figure S34. MALDI-TOF-MS of complex **Pd1**.

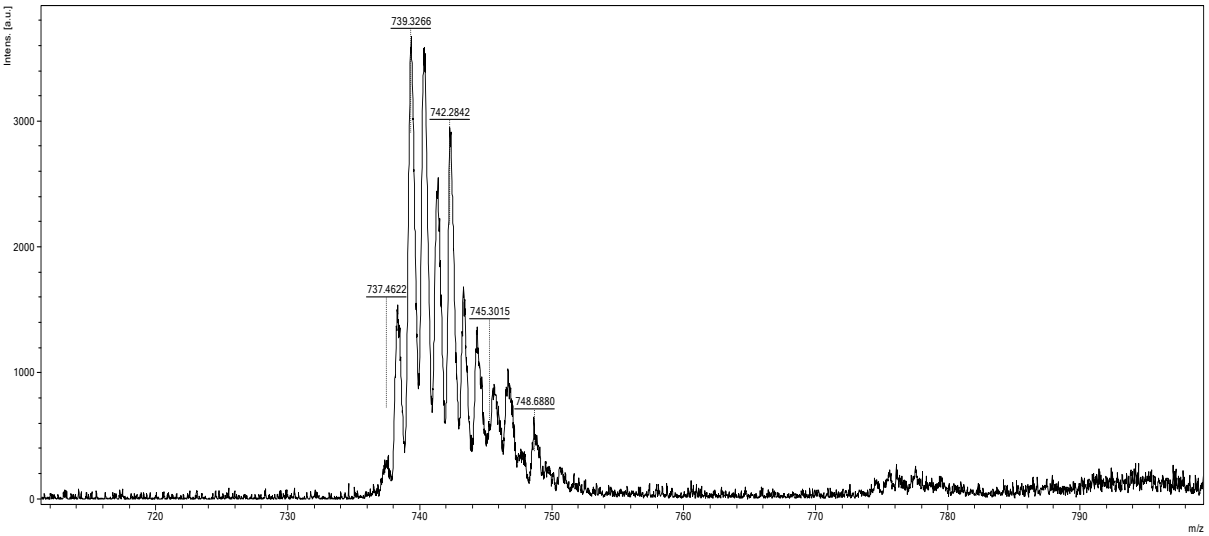


Figure S35. MALDI-TOF-MS of complex **Pd2**.

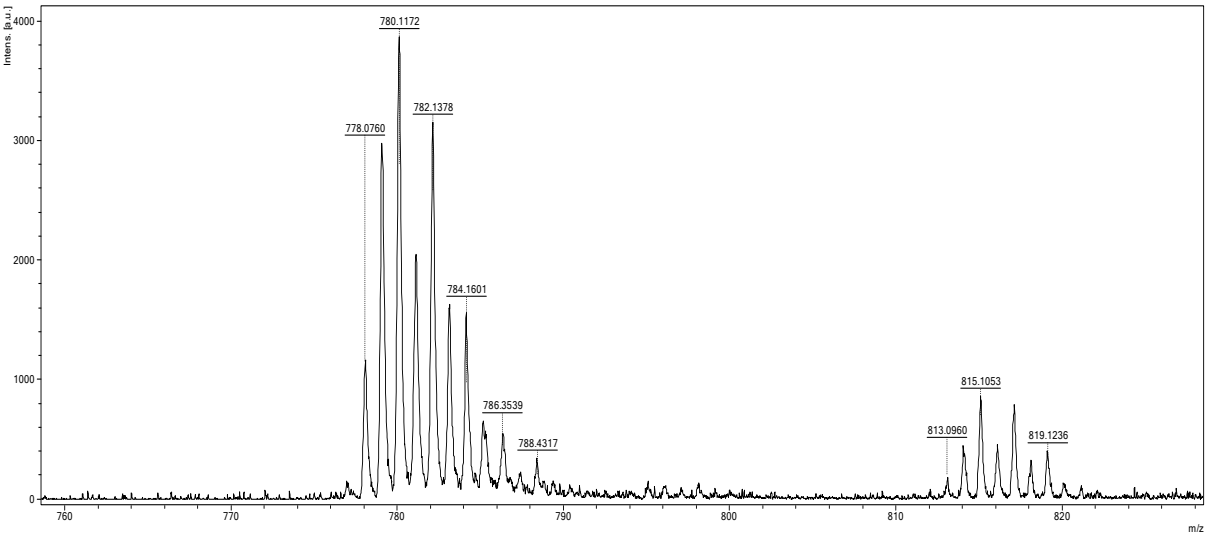


Figure S36. MALDI-TOF-MS of complex **Pd3**.

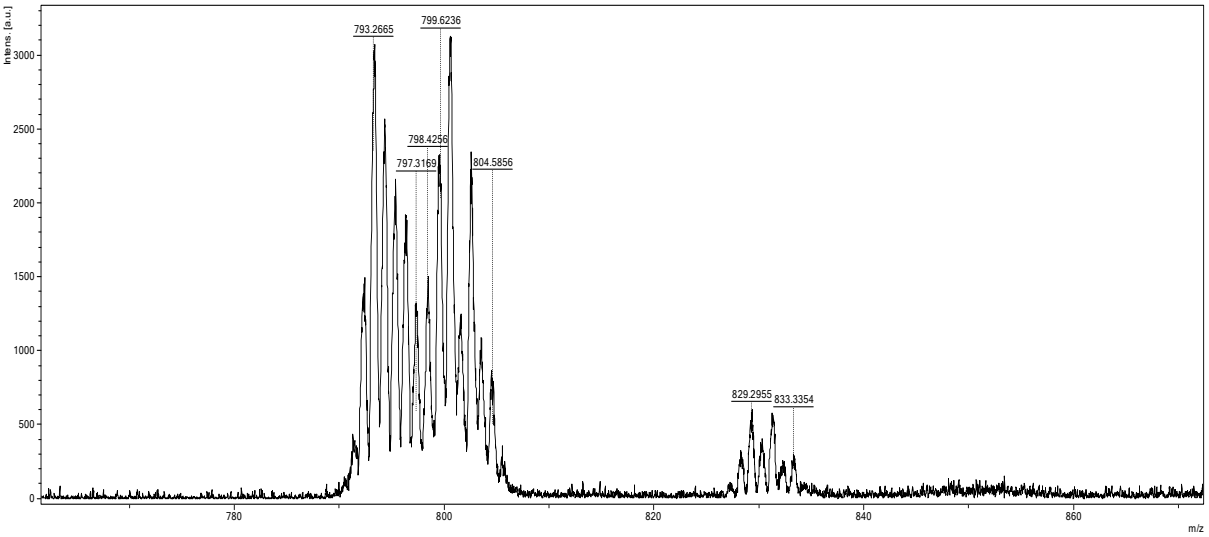


Figure S37. MALDI-TOF-MS of complex **Pd4**.

2.4 ^{1}H and ^{13}C NMR of Polymer and Copolymer.

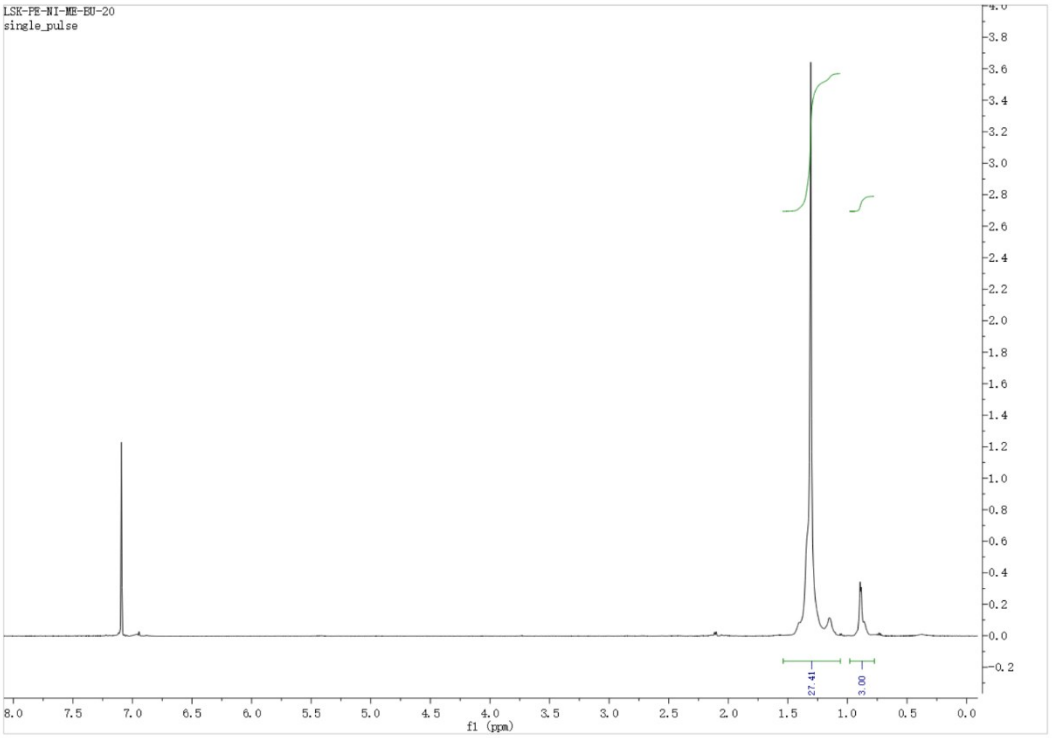


Figure S38. ^{1}H NMR spectrum of the polymer from table 1, entry 1 (d^{6}-benzene, 70 ^{o}C).

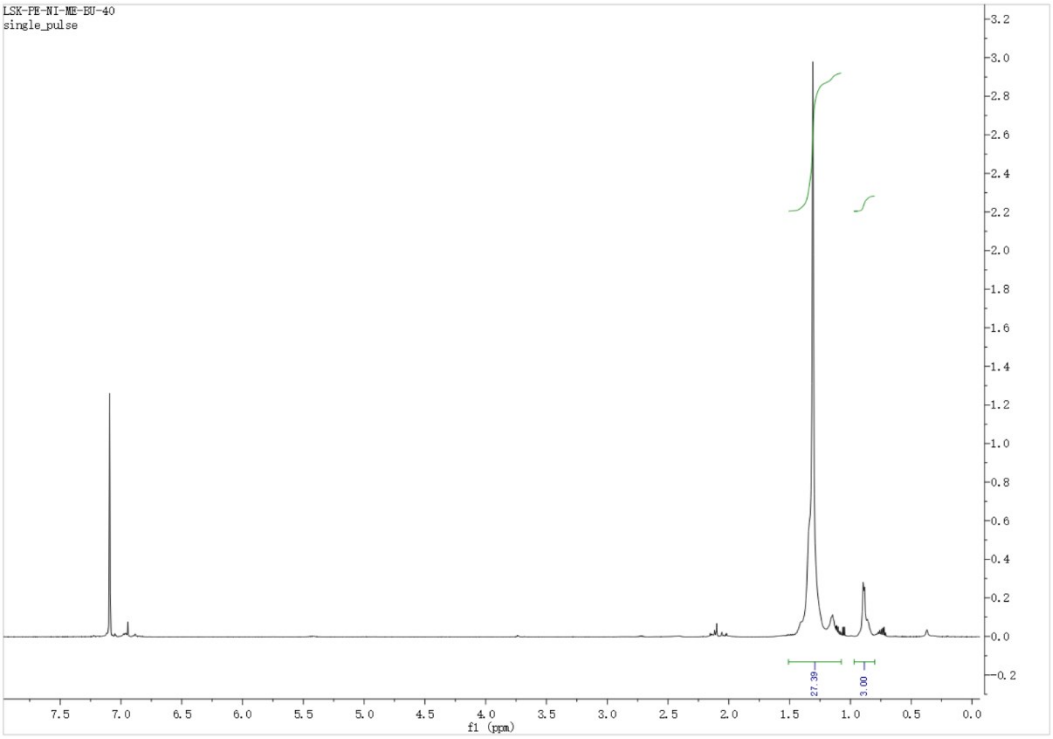


Figure S39. ^{1}H NMR spectrum of the polymer from table 1, entry 2 (d^{6}-benzene, 70 ^{o}C).

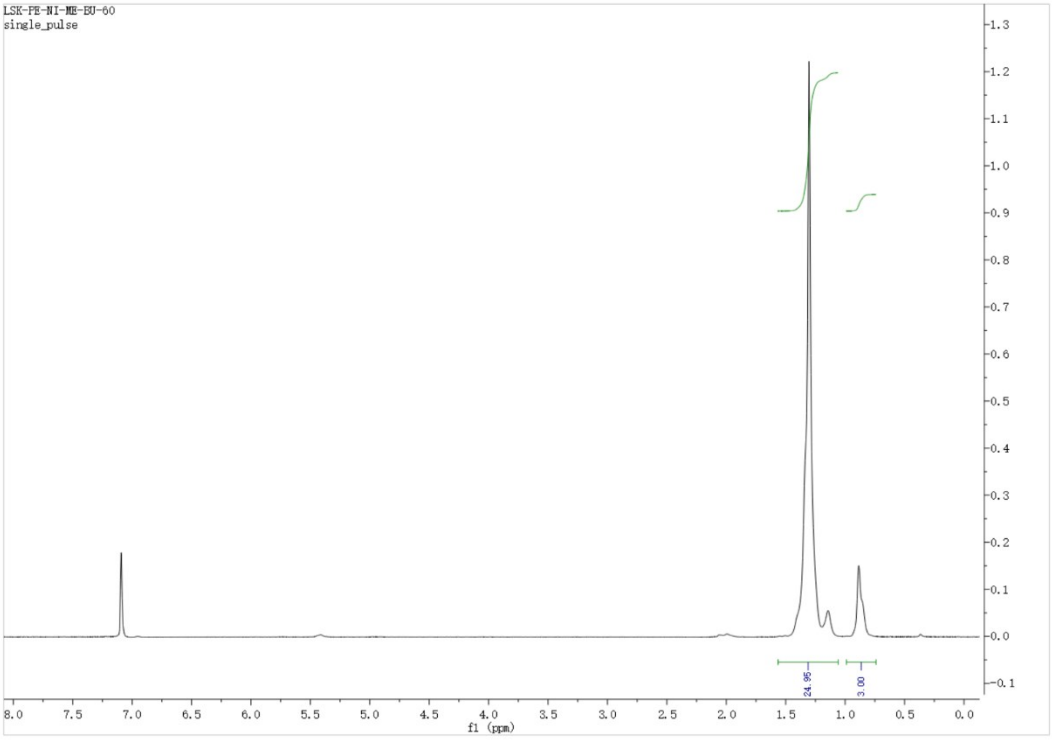


Figure S40. ^{1}H NMR spectrum of the polymer from table 1, entry 3 (d^{6}-benzene, 70 ^{o}C).

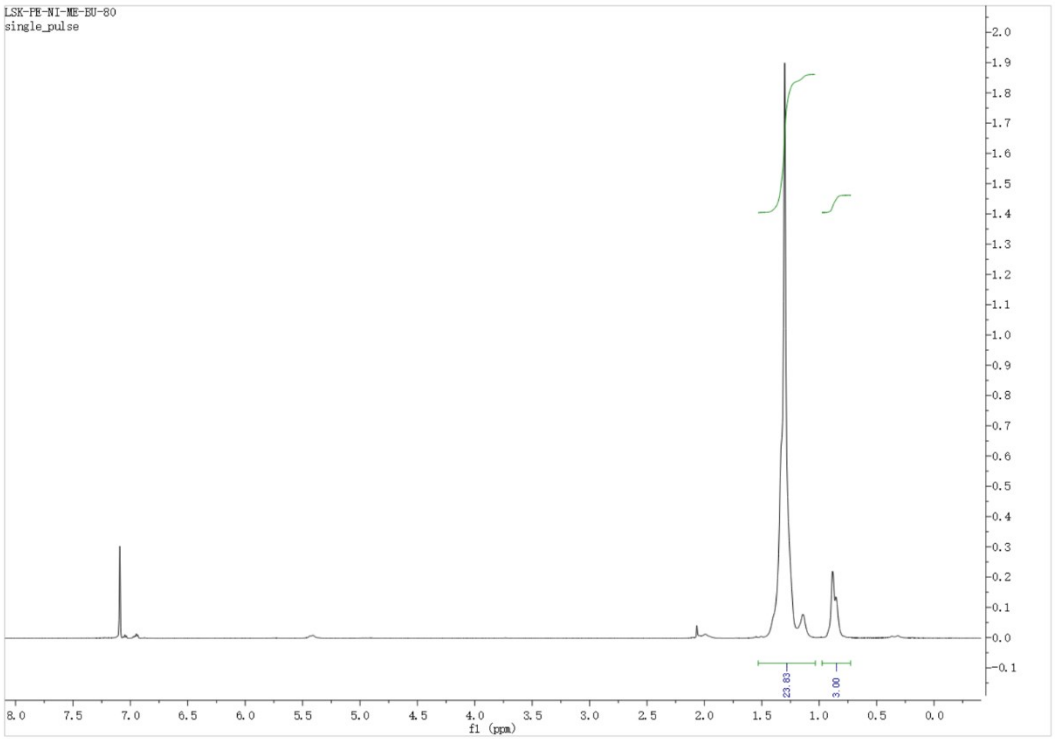


Figure S41. ^{1}H NMR spectrum of the polymer from table 1, entry 4 (d^{6}-benzene, 70 ^{o}C).

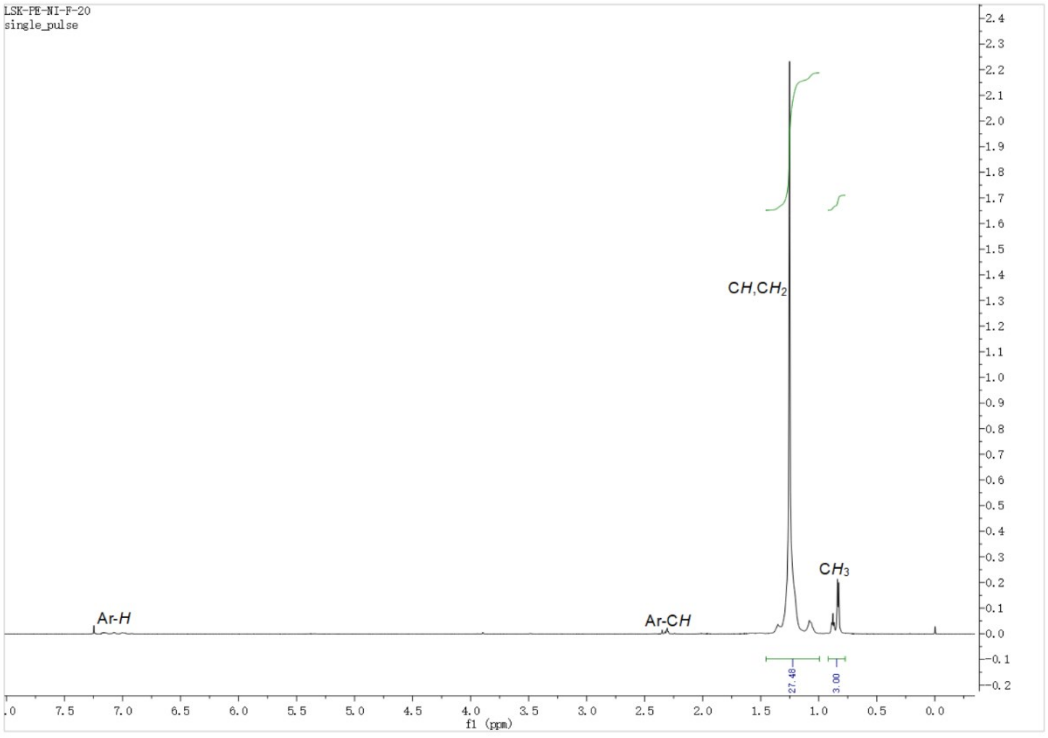


Figure S42. ^{1}H NMR spectrum of the polymer from table 1, entry 5 (d^{6}-benzene, 70 ^{o}C).

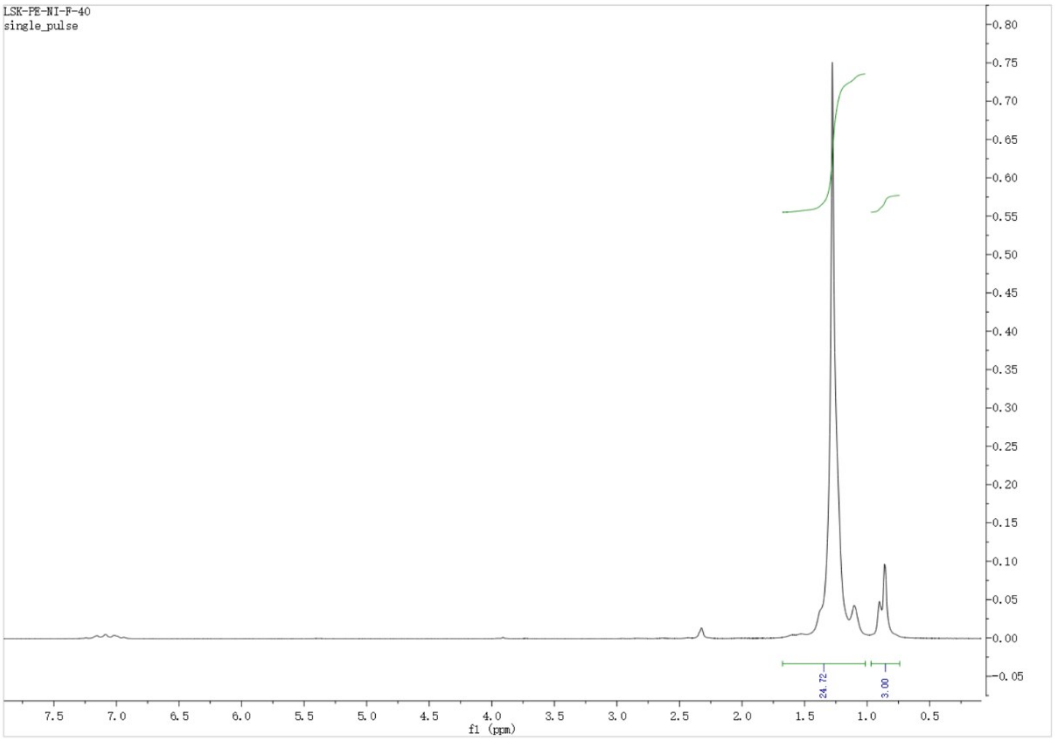


Figure S43. ^{1}H NMR spectrum of the polymer from table 1, entry 6 (d^{6}-benzene, 70 ^{o}C).

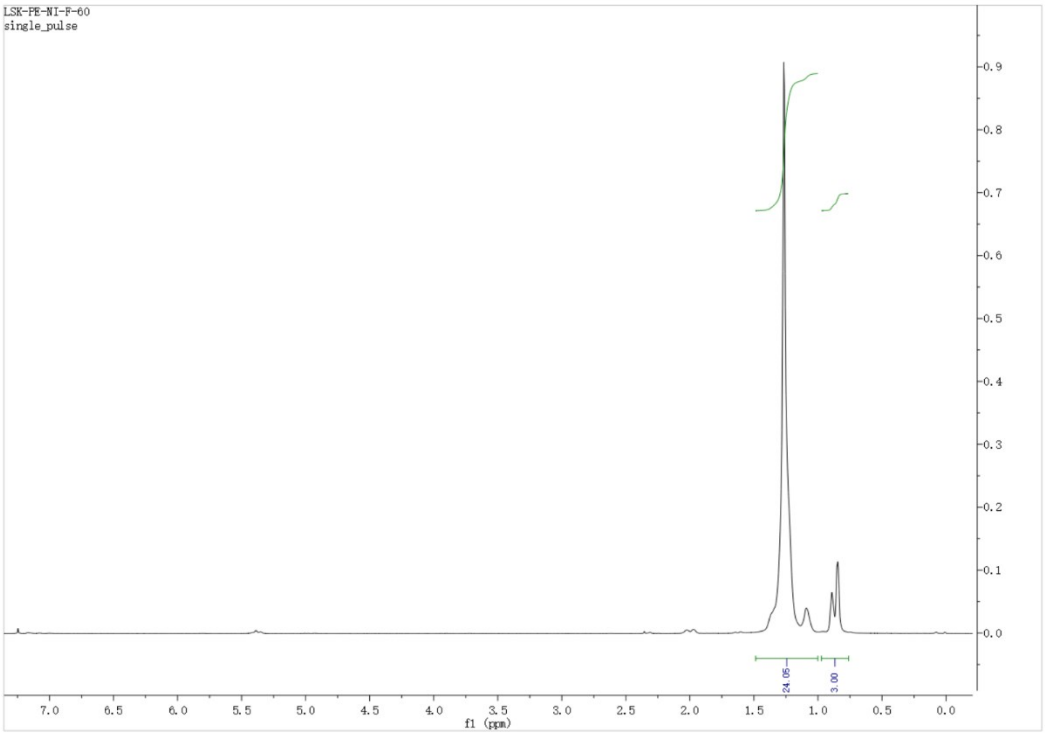


Figure S44. ^{1}H NMR spectrum of the polymer from table 1, entry 7 (d^{6}-benzene, 70 ^{o}C).

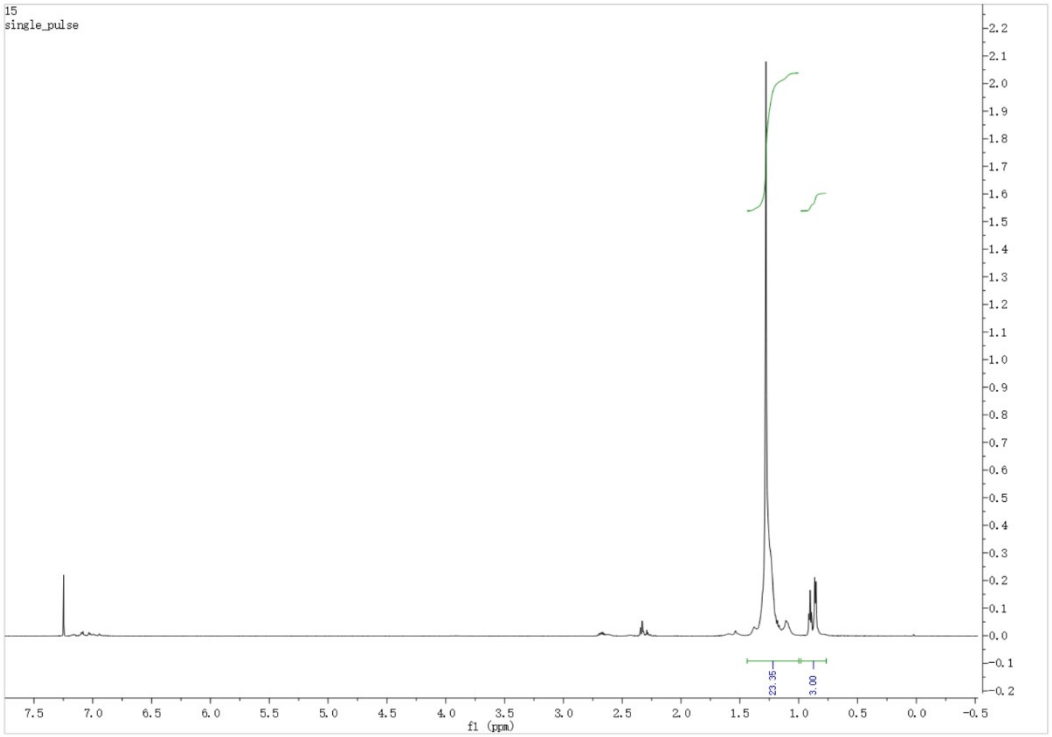


Figure S45. ^{1}H NMR spectrum of the polymer from table 1, entry 8 (d^{6}-benzene, 70 ^{o}C).

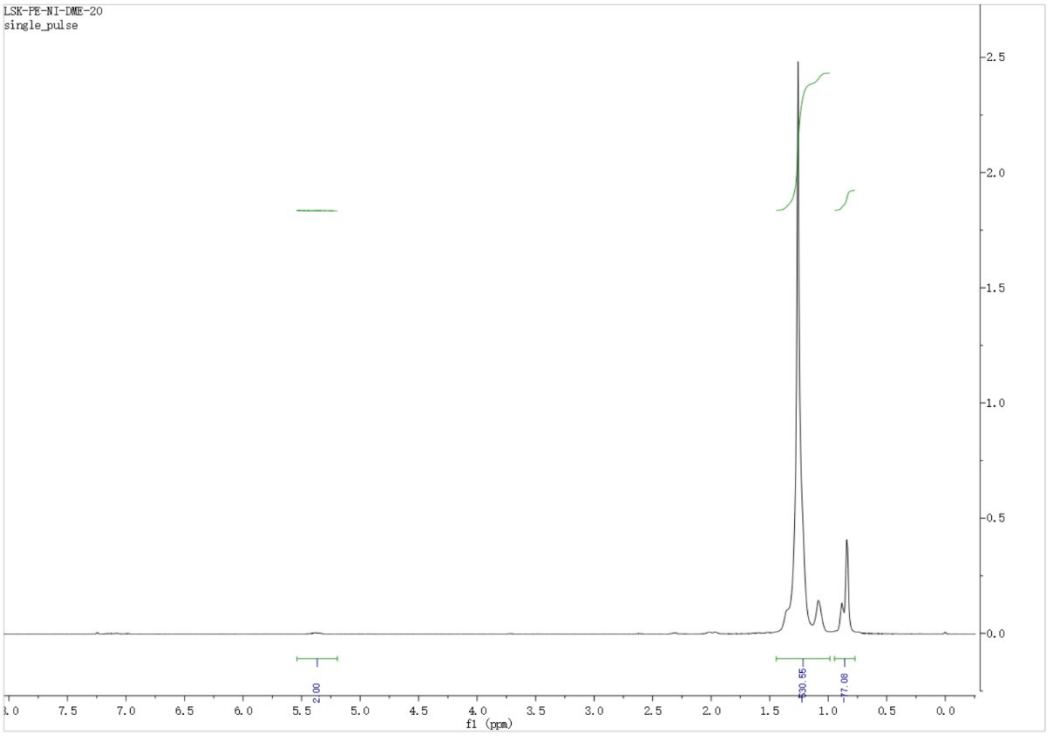


Figure S46. ^{1}H NMR spectrum of the polymer from table 1, entry 9 (d^{6}-benzene, 70 ^{o}C).

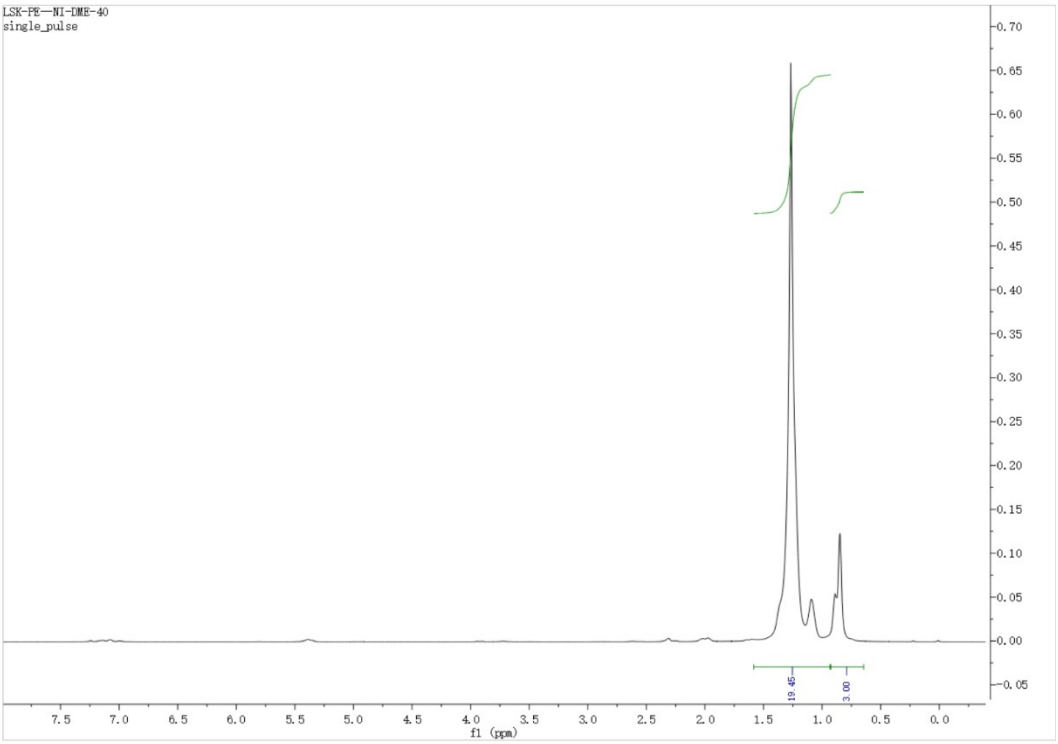


Figure S47. ^{1}H NMR spectrum of the polymer from table 1, entry 10 (d^{6}-benzene, 70 ^{o}C).

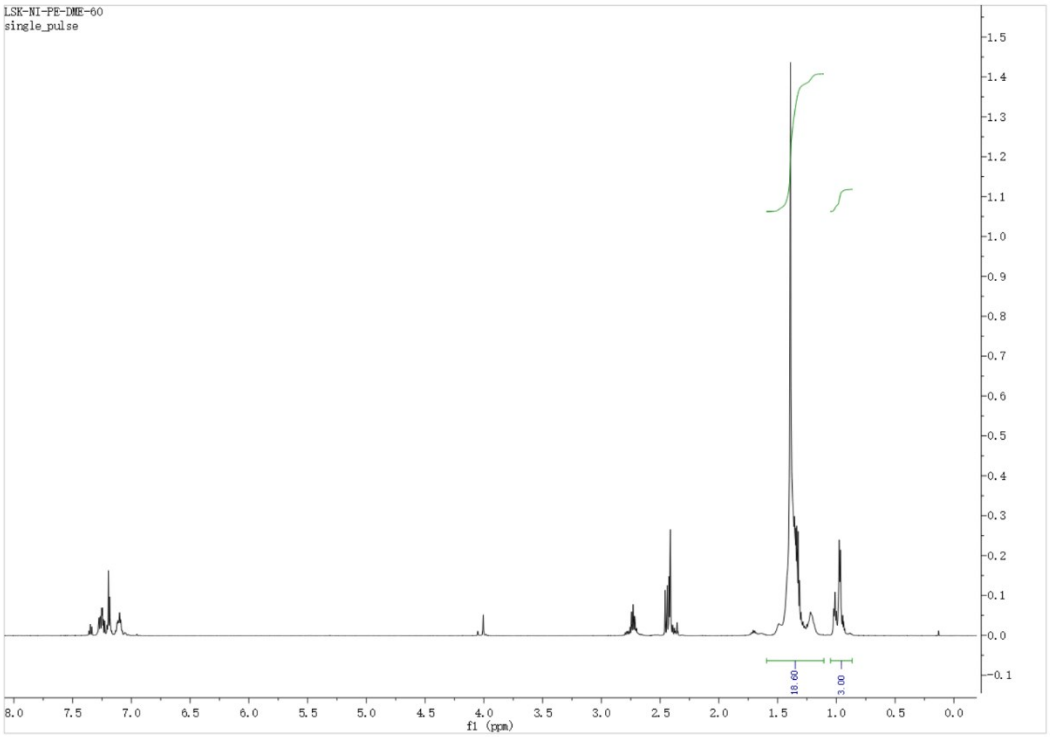


Figure S48. ^{1}H NMR spectrum of the polymer from table 1, entry 11 (d^{6}-benzene, 70 ^{o}C).

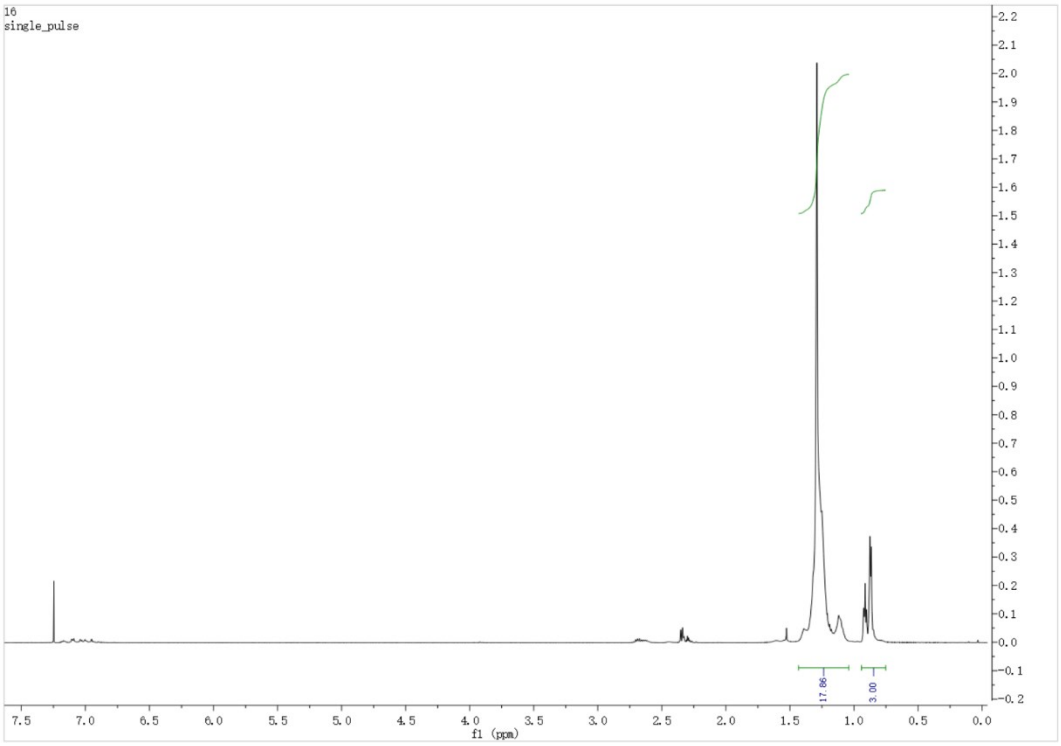


Figure S49. ^{1}H NMR spectrum of the polymer from table 1, entry 12 (d^{6}-benzene, 70 ^{o}C).

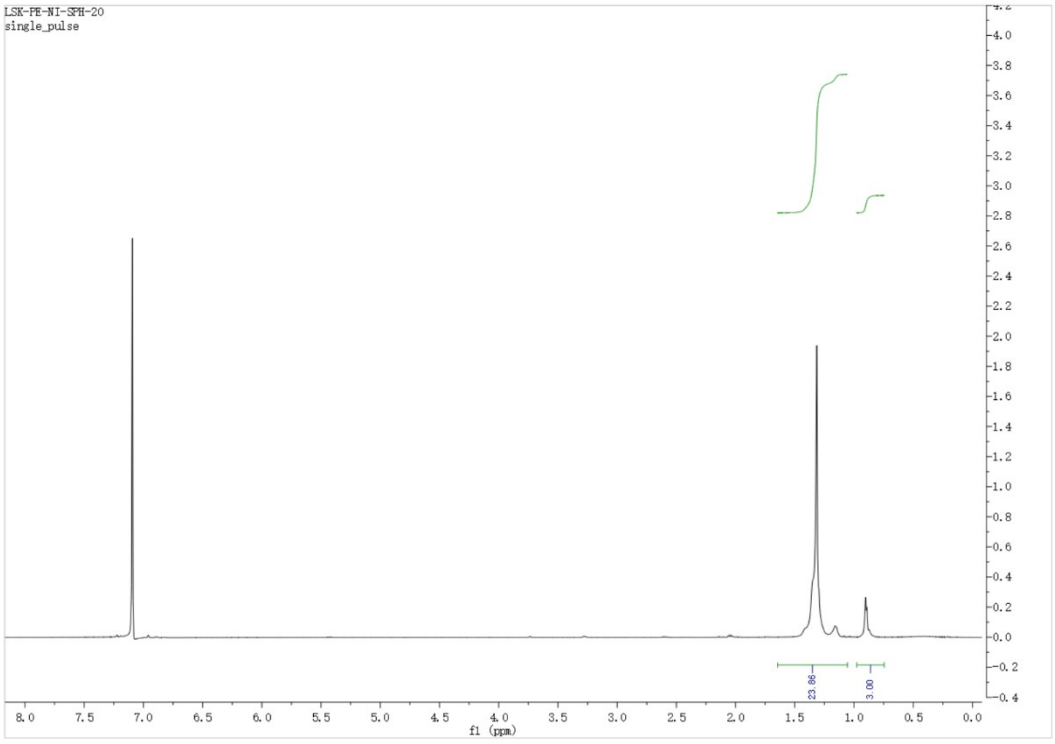


Figure S50. ^{1}H NMR spectrum of the polymer from table 1, entry 13 (d^{6}-benzene, 70 ^{o}C).

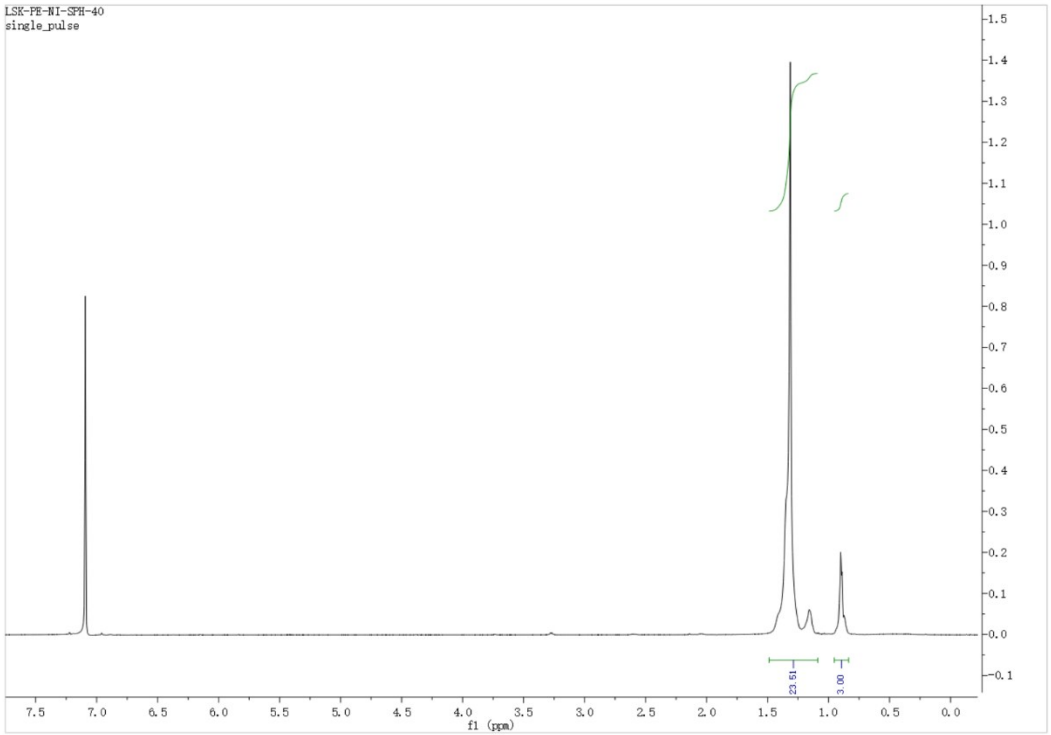


Figure S51. ^{1}H NMR spectrum of the polymer from table 1, entry 14 (d^{6}-benzene, 70 ^{o}C).

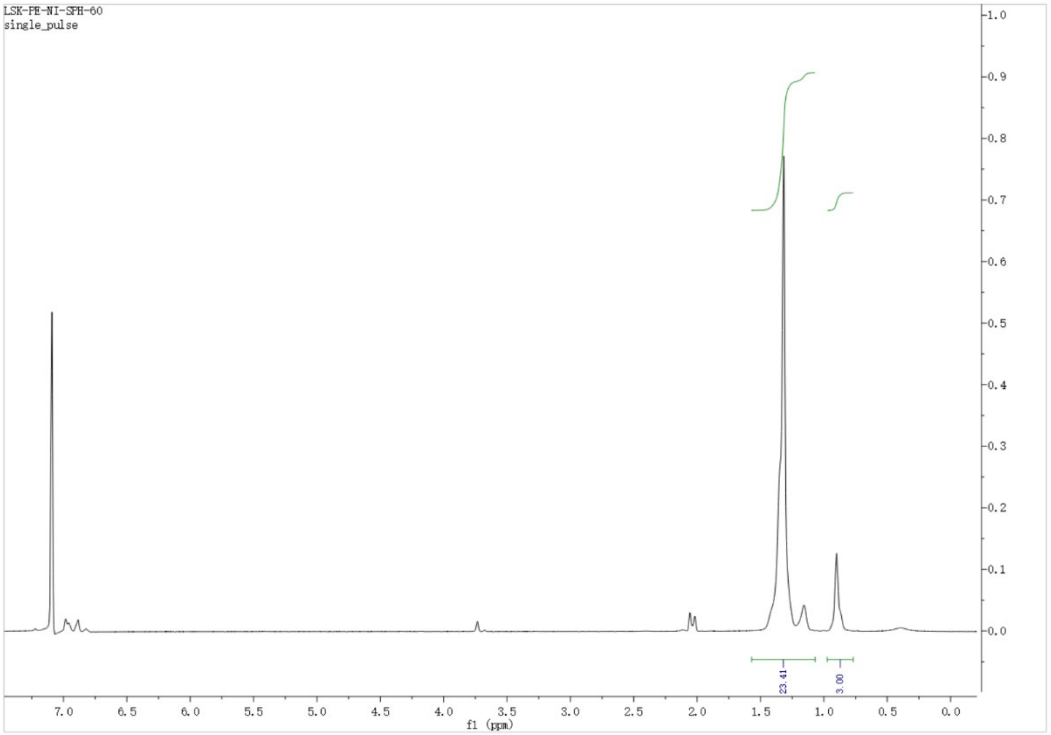


Figure S52. ^{1}H NMR spectrum of the polymer from table 1, entry 15 (d^{6}-benzene, 70 ^{o}C).

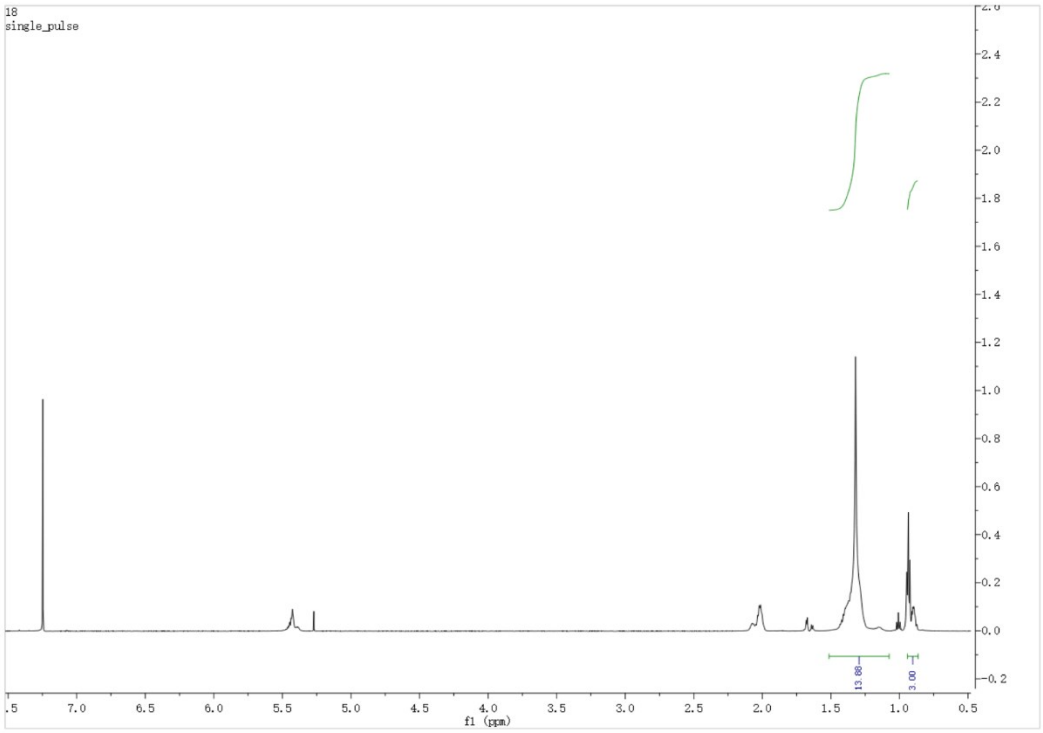


Figure S53. ^{1}H NMR spectrum of the polymer from table 1, entry 16 (d^{6}-benzene, 70 ^{o}C).

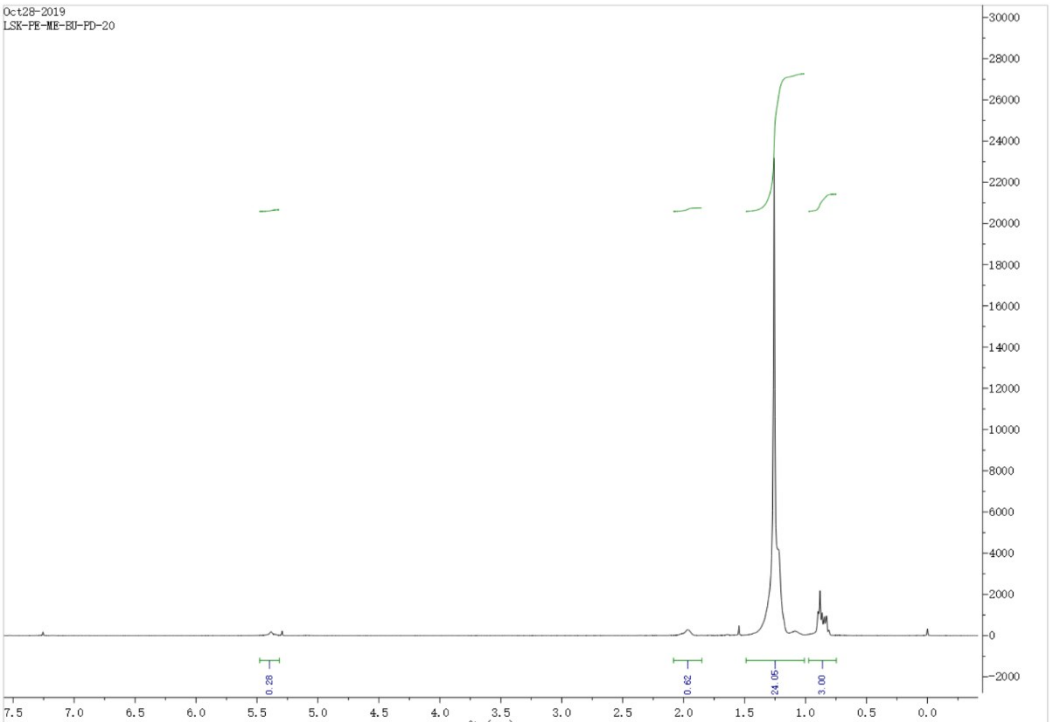


Figure S54. ^{1}H NMR spectrum of the polymer from table 2, entry 1 ($CDCl_3$, 20 ^{o}C).

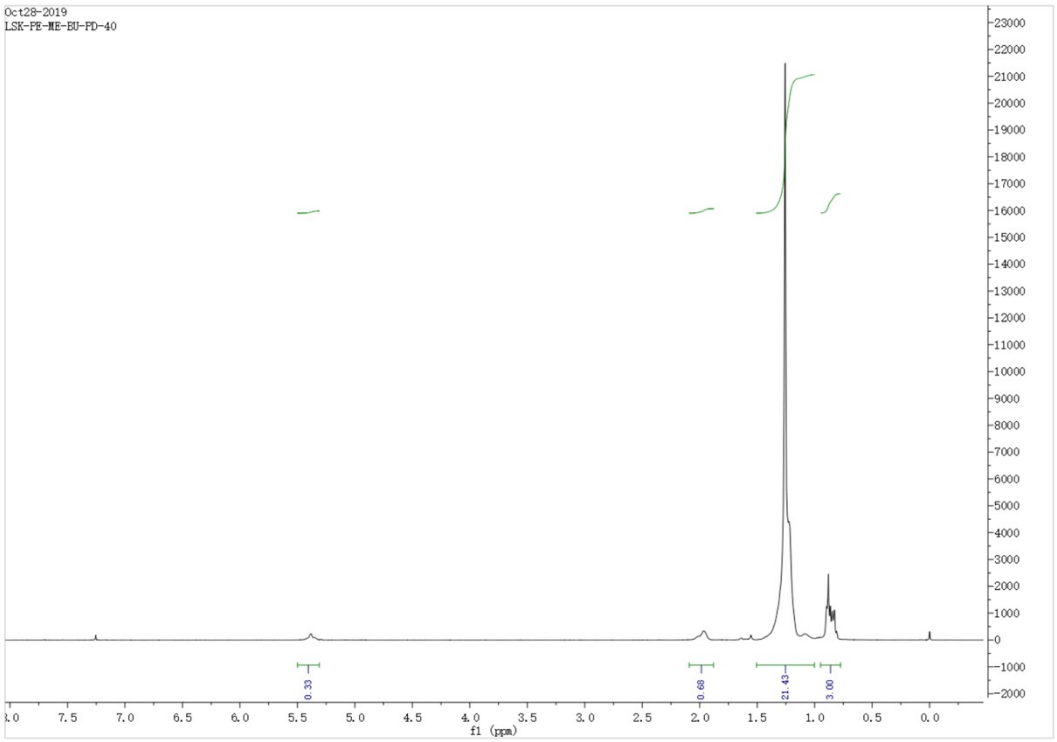


Figure S55. ^{1}H NMR spectrum of the polymer from table 2, entry 2 ($CDCl_3$, 20 ^{o}C).

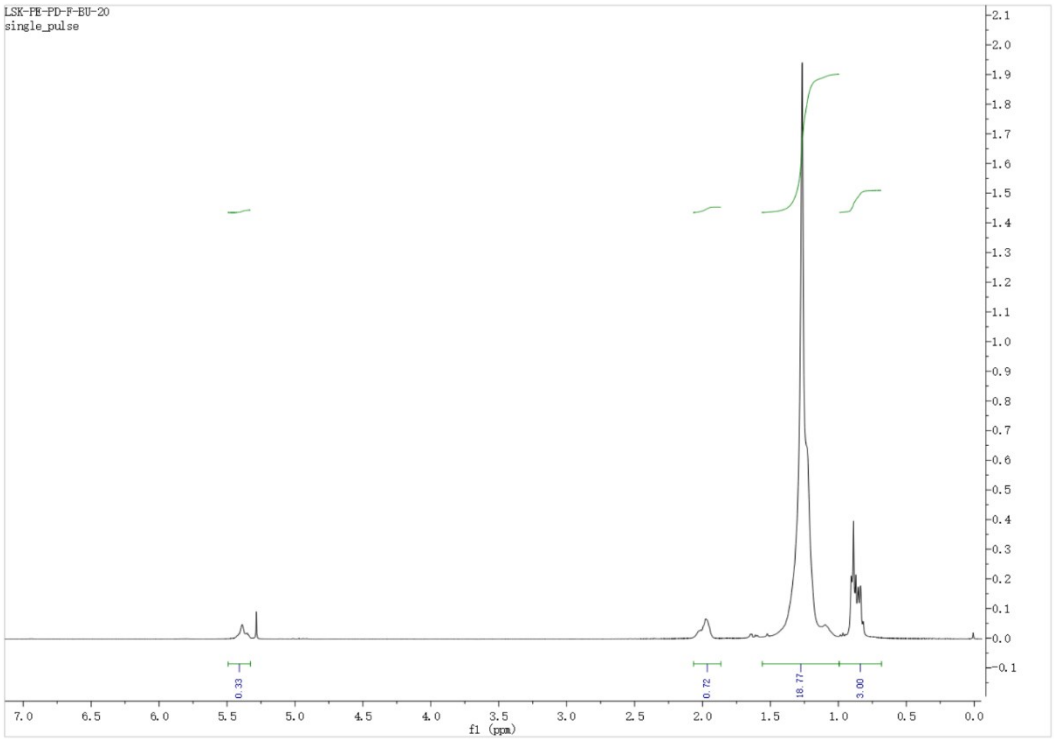


Figure S56. ^{1}H NMR spectrum of the polymer from table 2, entry 3 ($CDCl_3$, 20 ^{o}C).

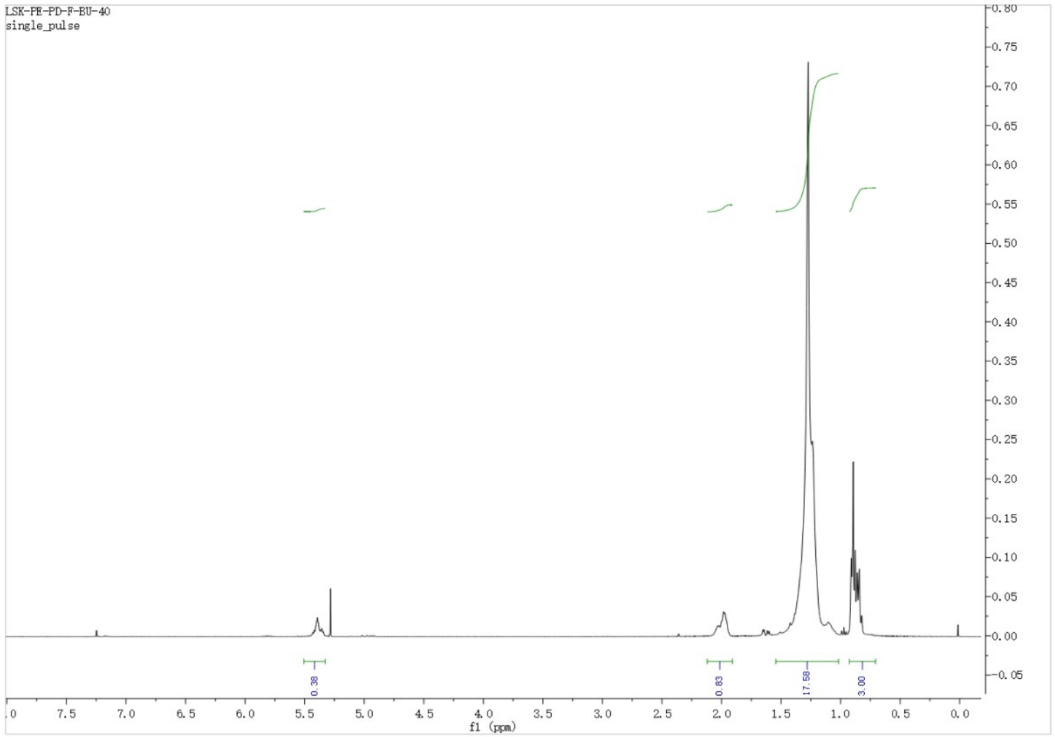


Figure S57. ^{1}H NMR spectrum of the polymer from table 2, entry 4 ($CDCl_3$, 20 ^{o}C).

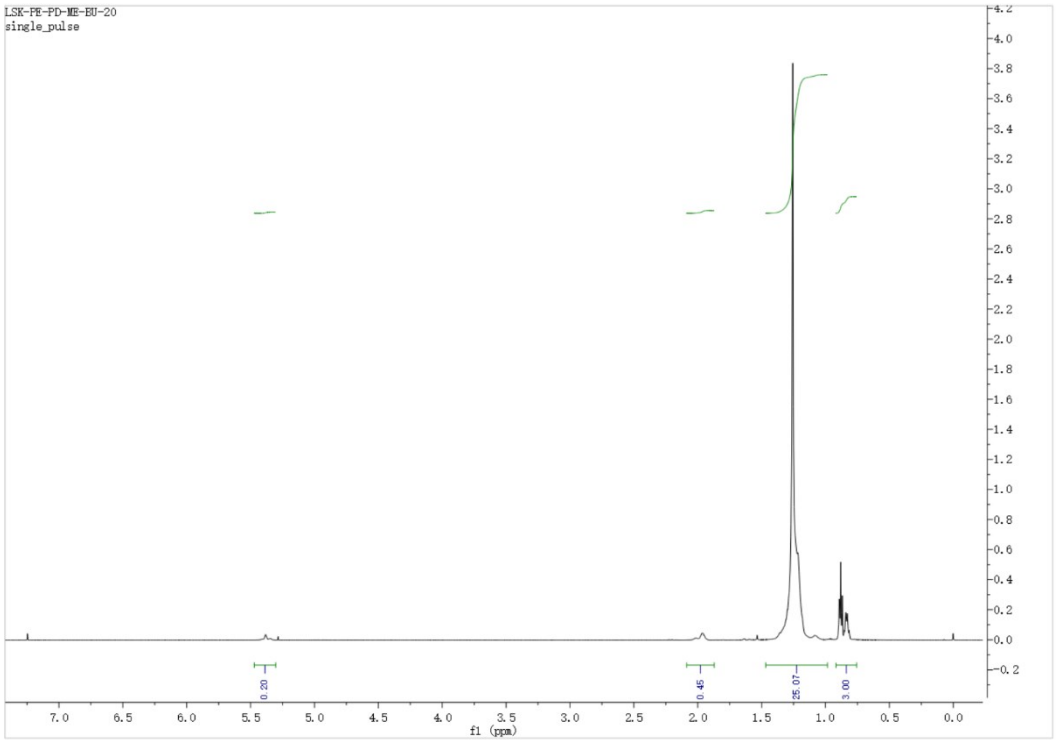


Figure S58. ^{1}H NMR spectrum of the polymer from table 2, entry 5 ($CDCl_3$, 20 ^{o}C).

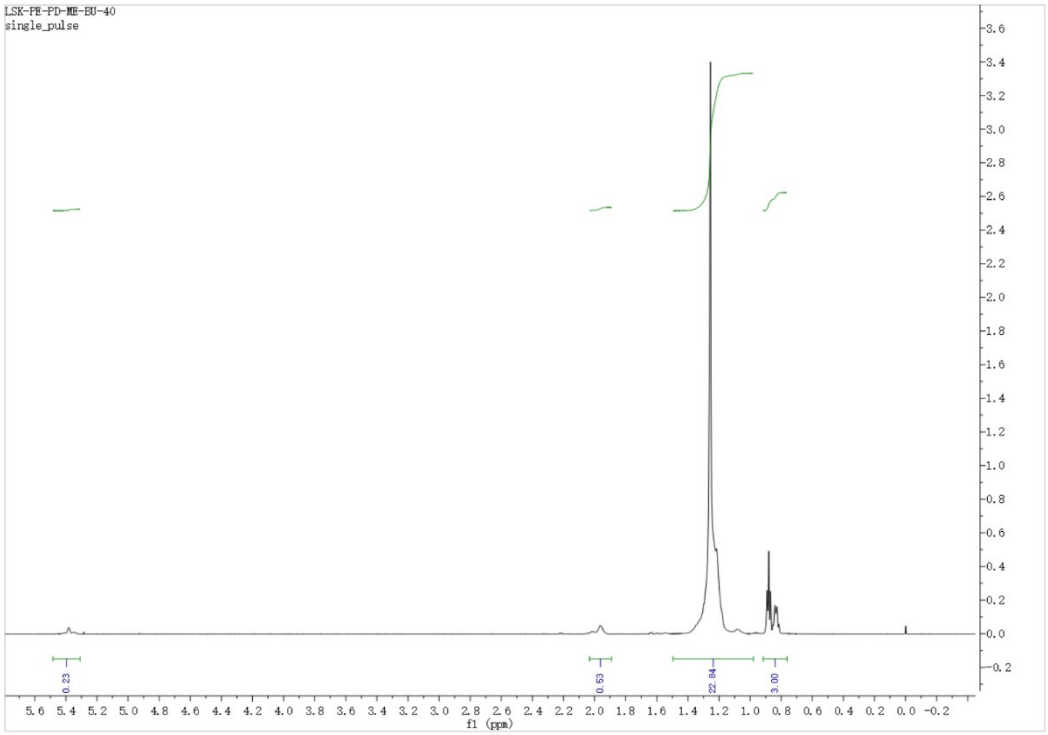


Figure S59. ^{1}H NMR spectrum of the polymer from table 2, entry 6 ($CDCl_3$, 20 ^{o}C).

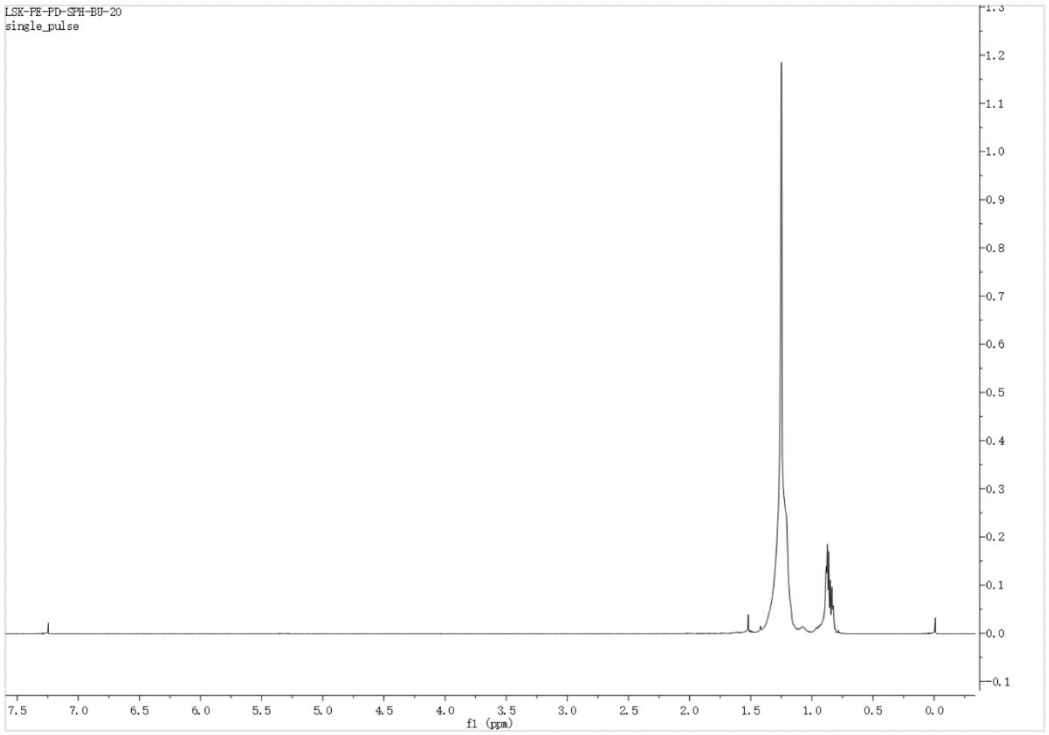


Figure S60. ^{1}H NMR spectrum of the polymer from table 2, entry 7 ($CDCl_3$, 20 ^{o}C).

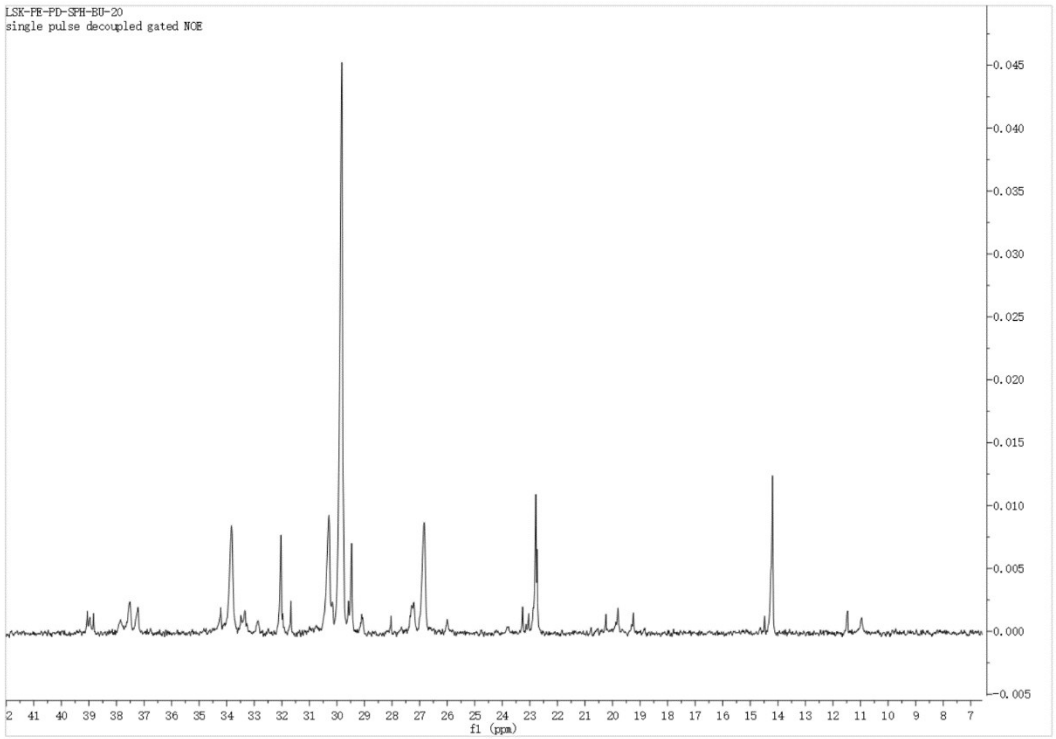


Figure S61. ^{13}C NMR spectrum of the polymer from table 2, entry 7 ($CDCl_3$, 20 °C).

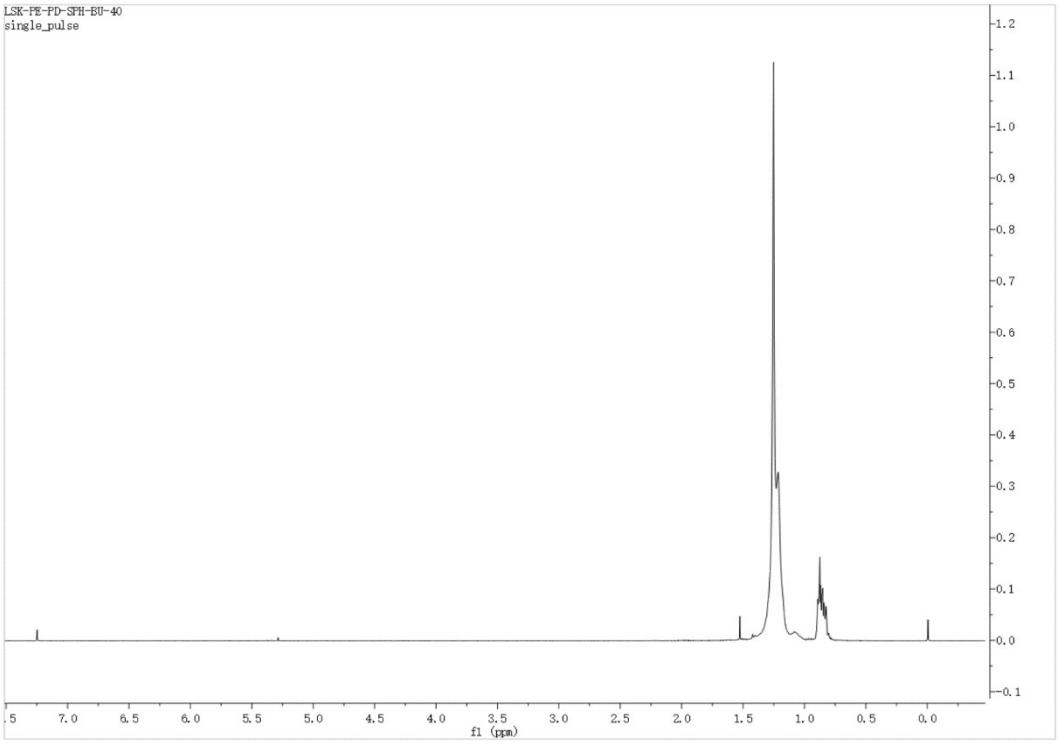


Figure S62. ^{1}H NMR spectrum of the polymer from table 2, entry 8 ($CDCl_3$, 20 °C).

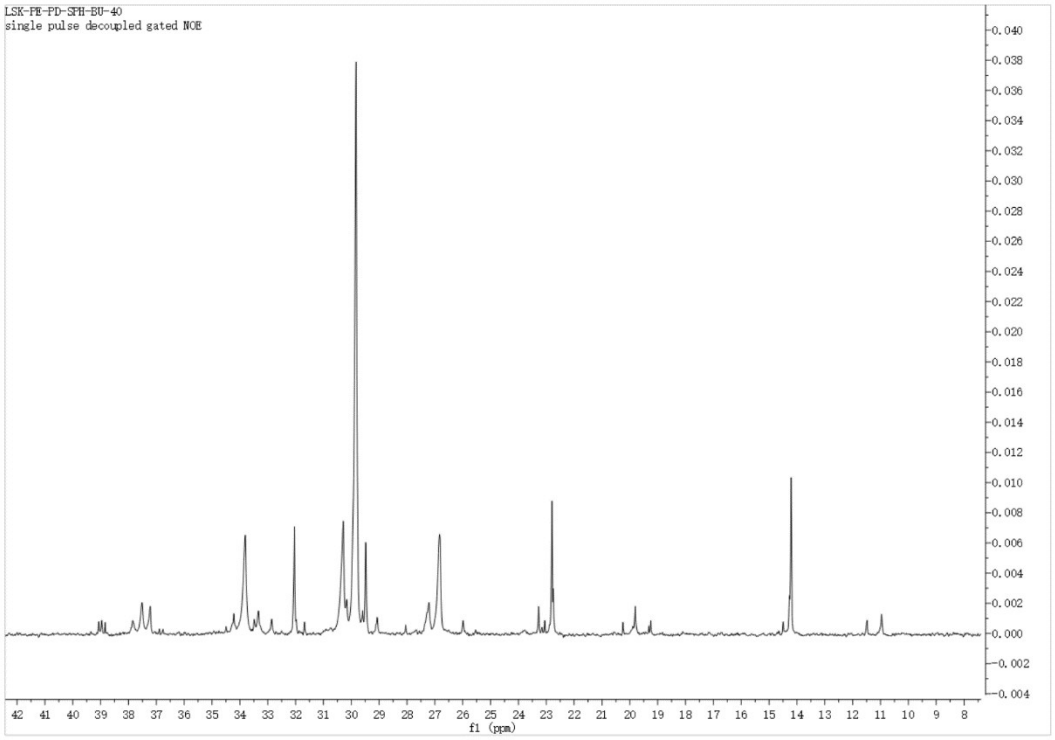


Figure S63. ^{13}C NMR spectrum of the polymer from table 2, entry 8 ($CDCl_3$, 20 °C).

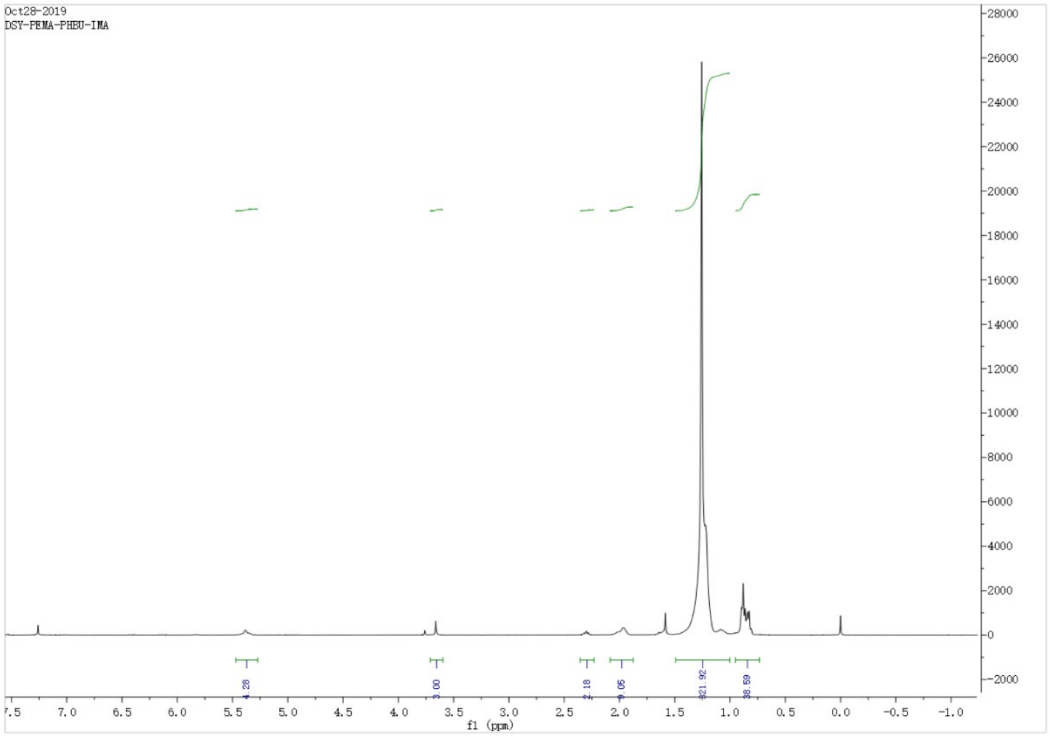


Figure S64. ^{1}H NMR spectrum of the polymer from table 3, entry 1 ($CDCl_3$, 20 °C).

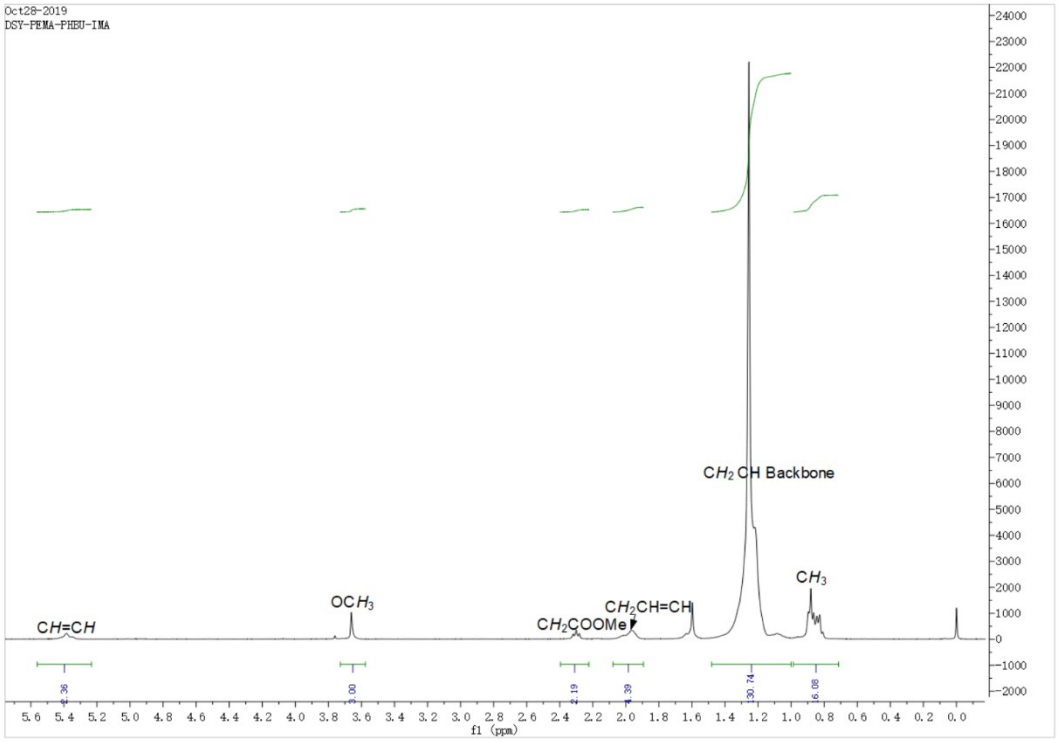


Figure S65. ^{1}H NMR spectrum of the polymer from table 3, entry 2 ($CDCl_3$, 20 ^{o}C).

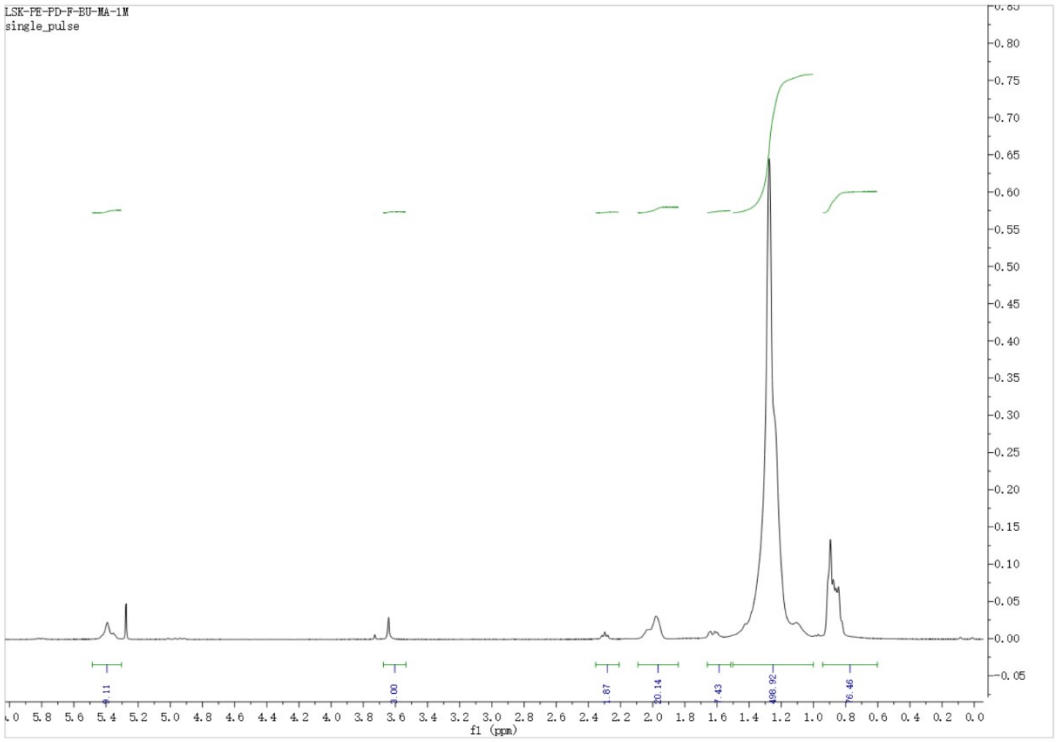


Figure S66. ^{1}H NMR spectrum of the polymer from table 3, entry 3 ($CDCl_3$, 20 ^{o}C).

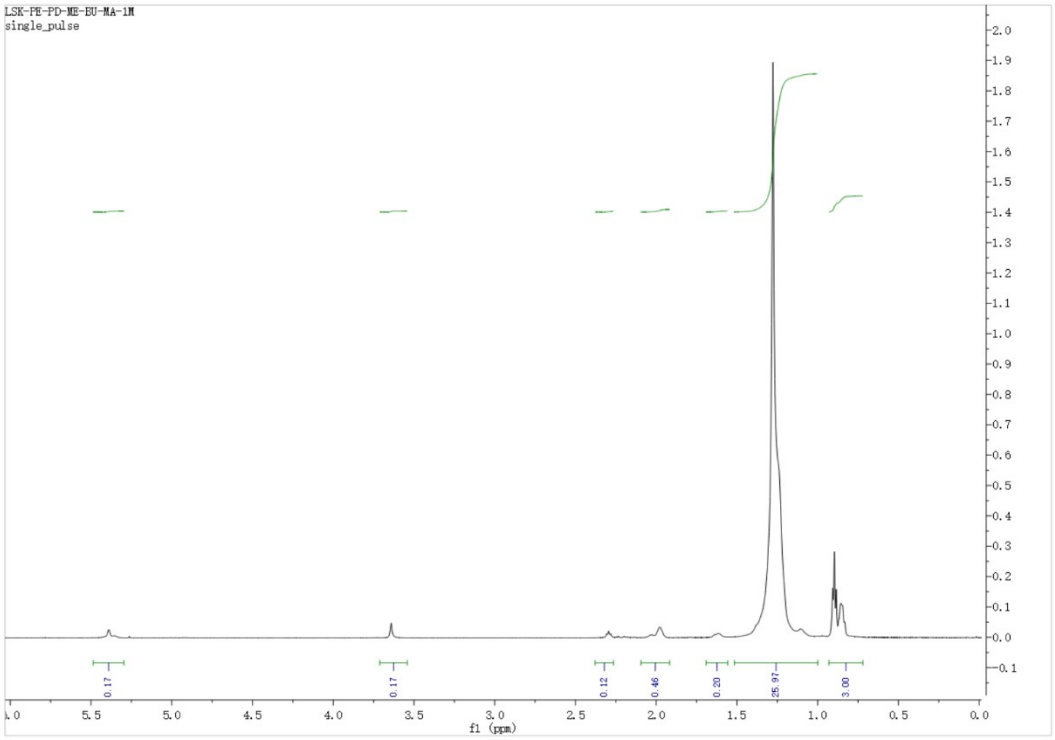


Figure S67. ^{1}H NMR spectrum of the polymer from table 3, entry 5 ($CDCl_3$, 20 ^{o}C).

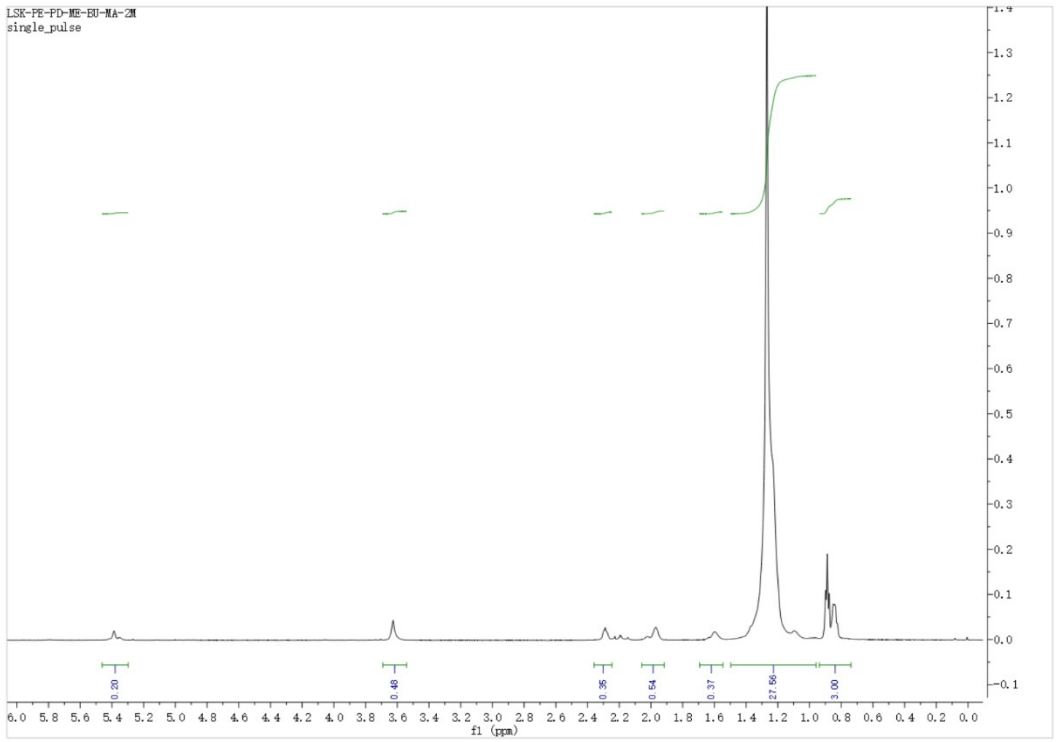


Figure S68. ^{1}H NMR spectrum of the polymer from table 3, entry 6 ($CDCl_3$, 20 ^{o}C).

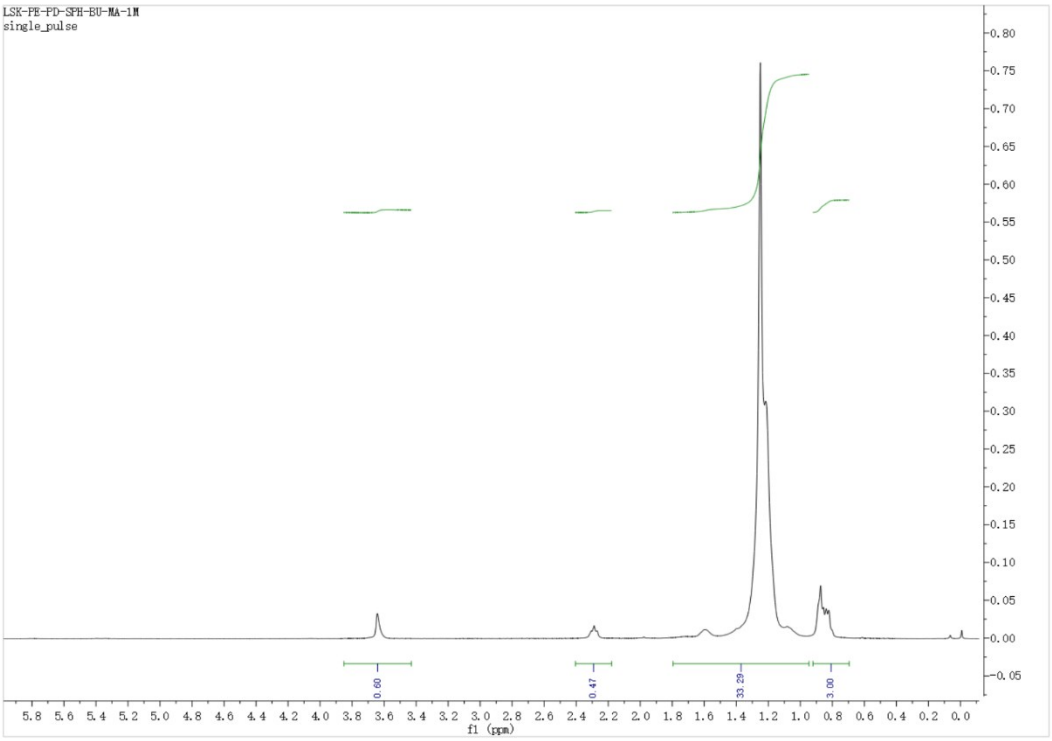


Figure S69. ^{1}H NMR spectrum of the polymer from table 3, entry 7 ($CDCl_3$, 20 ^{o}C).

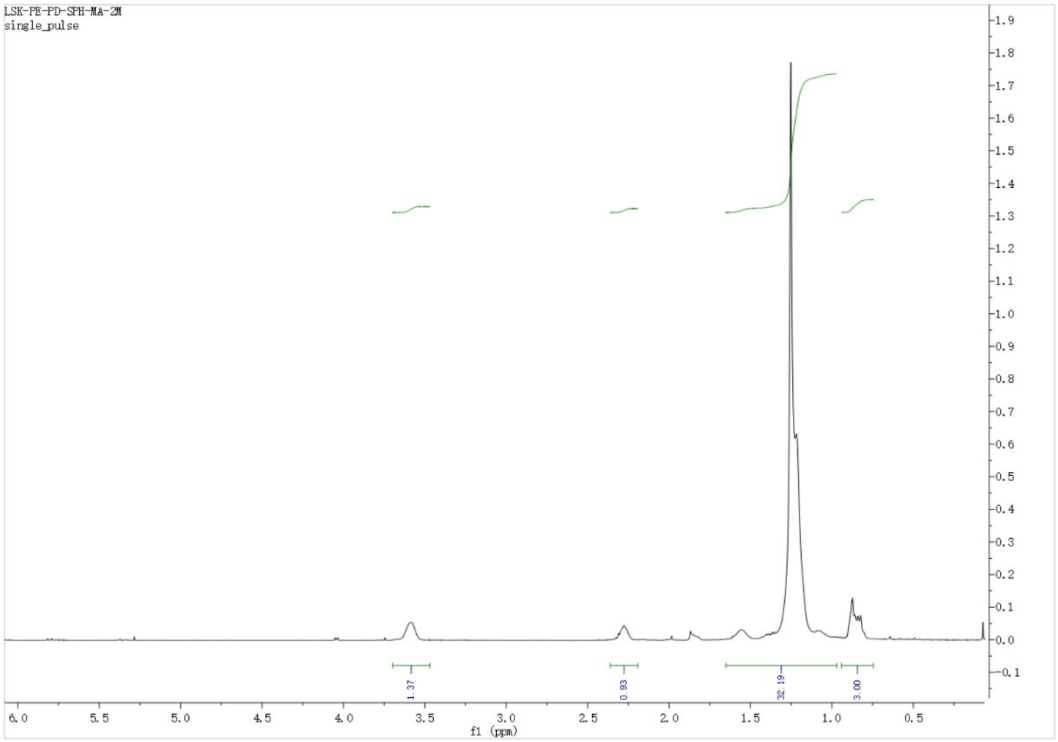


Figure S70. ^{1}H NMR spectrum of the polymer from table 3, entry 8 ($CDCl_3$, 20 ^{o}C).

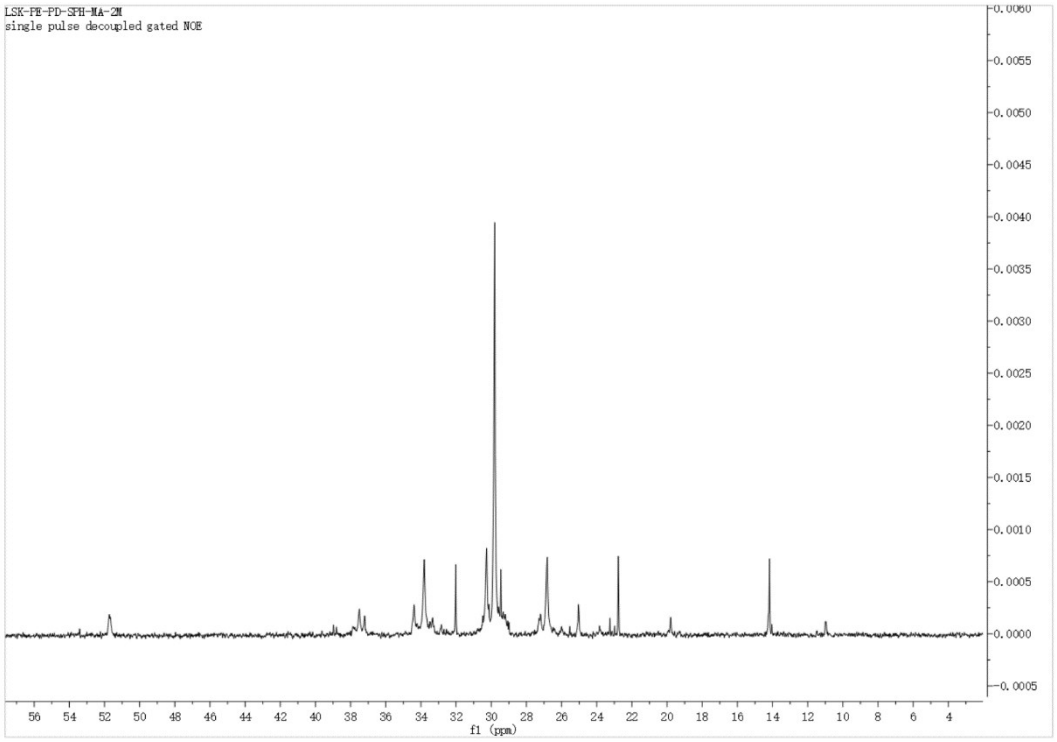


Figure S71. ^{13}C NMR spectrum of the polymer from table 3, entry 8 ($CDCl_3$, 20 °C).

2.5 DSC and GPC of Polymer and Copolymer and Time-Dependence Curves.

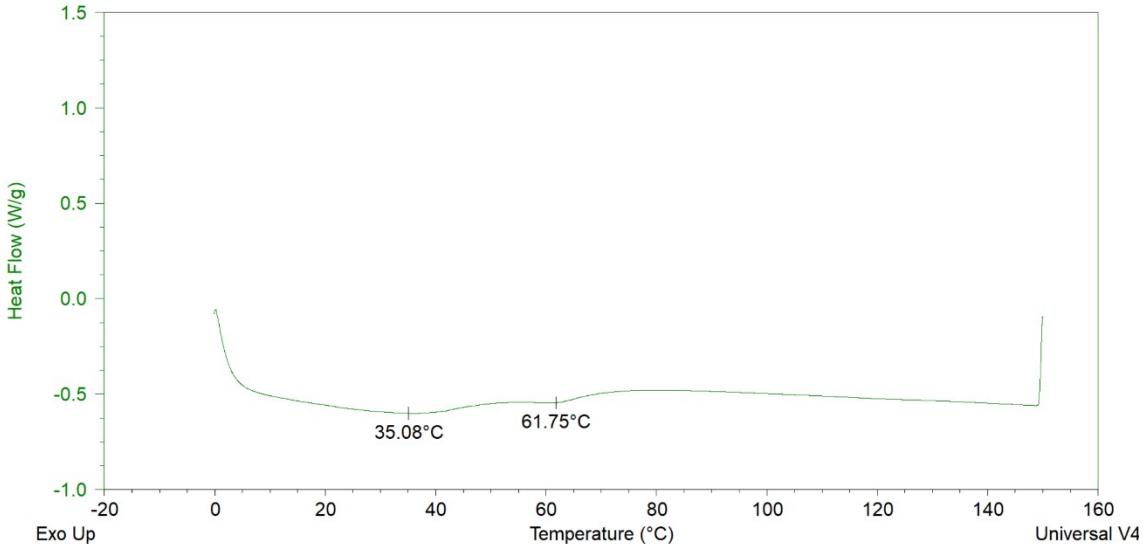


Figure S72. DSC of the polymer from table 1, entry 1.

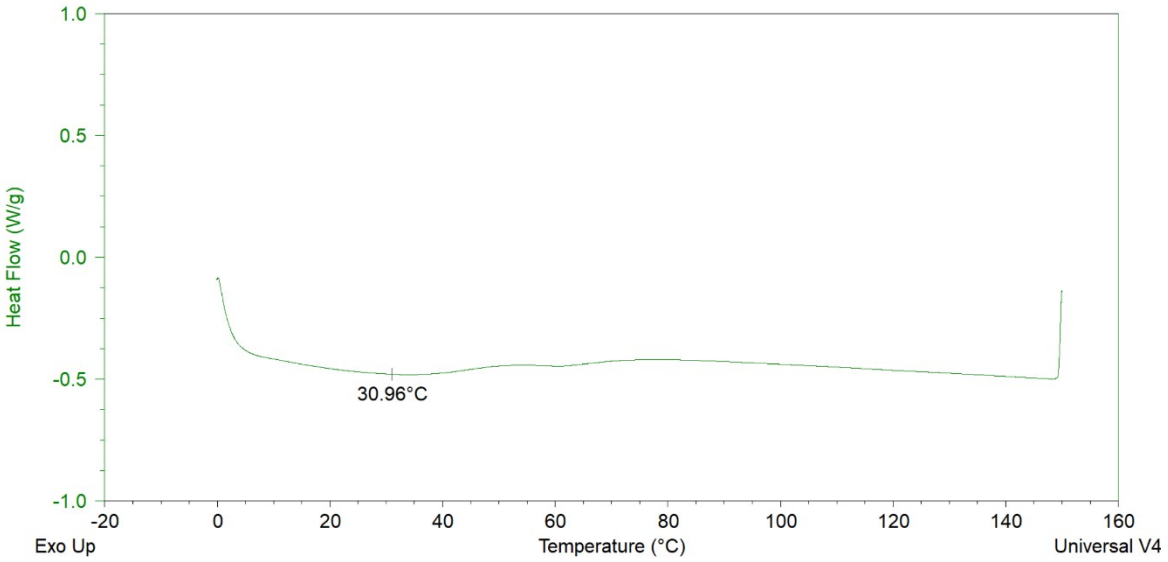


Figure S73. DSC of the polymer from table 1, entry 2.

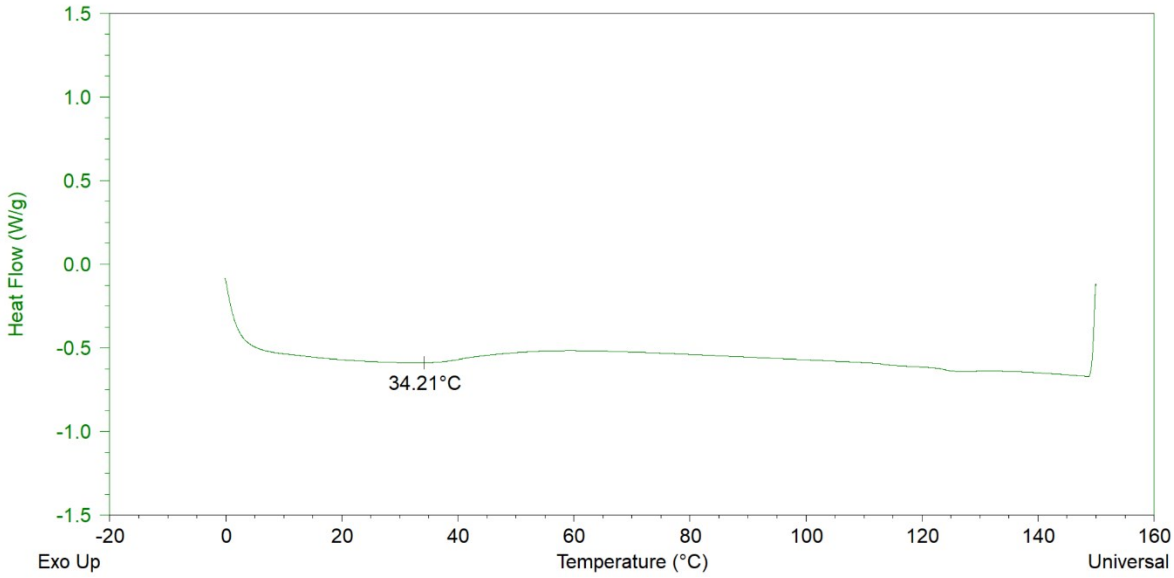


Figure S74. DSC of the polymer from table 1, entry 13.

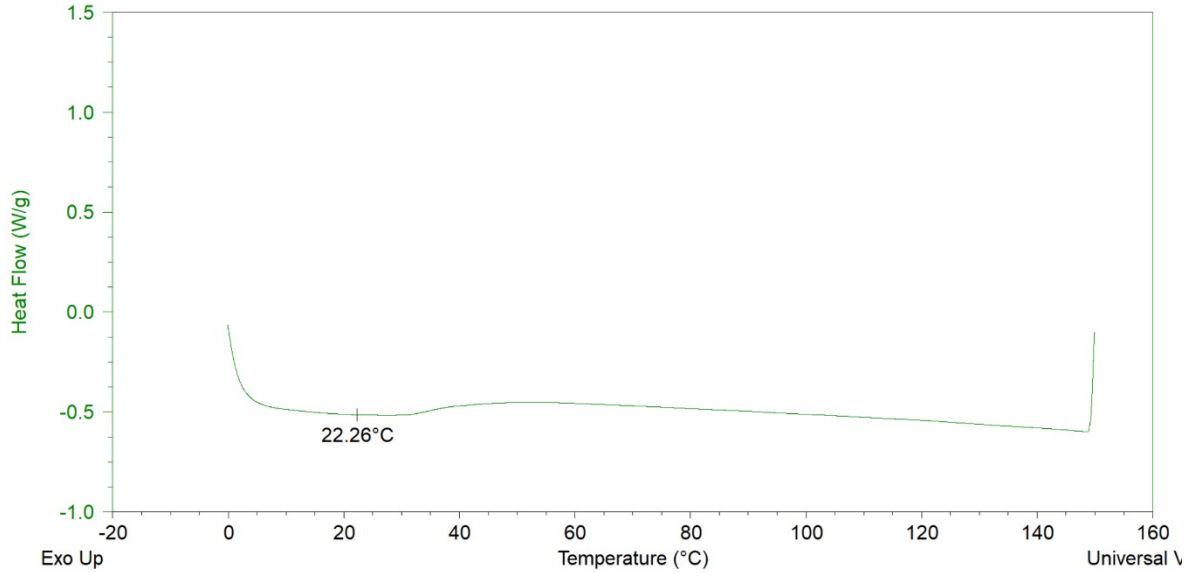


Figure S75. DSC of the polymer from table 1, entry 14.

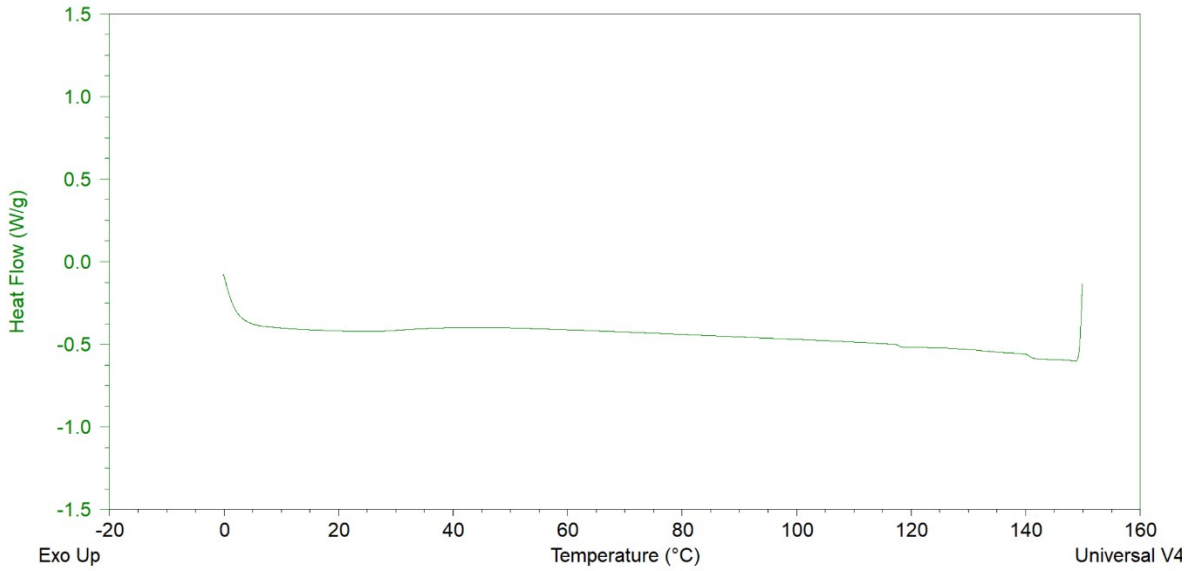
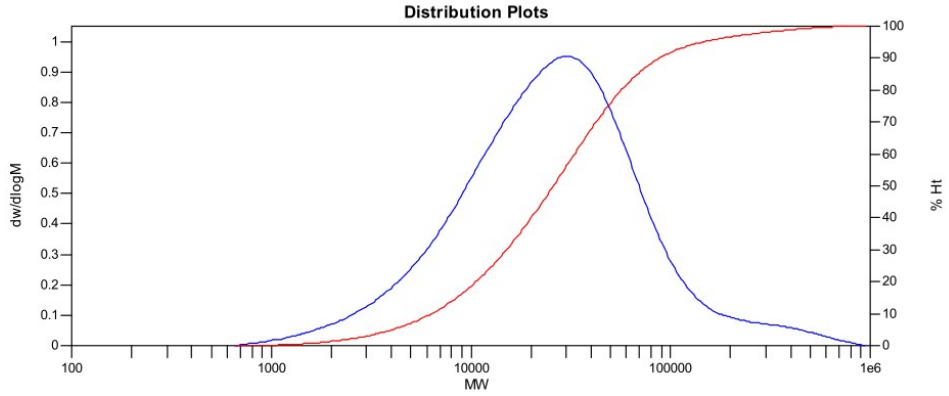


Figure S76. DSC of the polymer from table 1, entry 15.



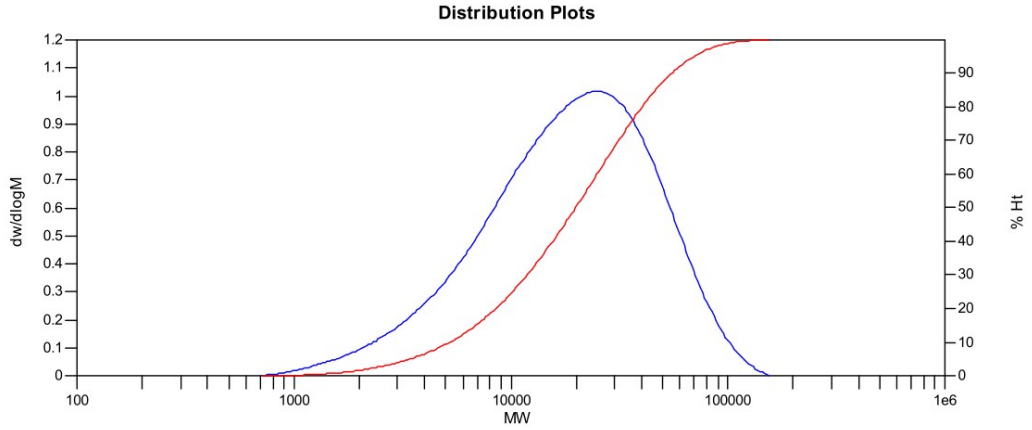
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	30178	13691	45025	159686	371135	37081	3.28866

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.20	14.55	17.17	-35.3232	100	3501.83	100

Figure S77. GPC of the polymer from table 1, entry 1.



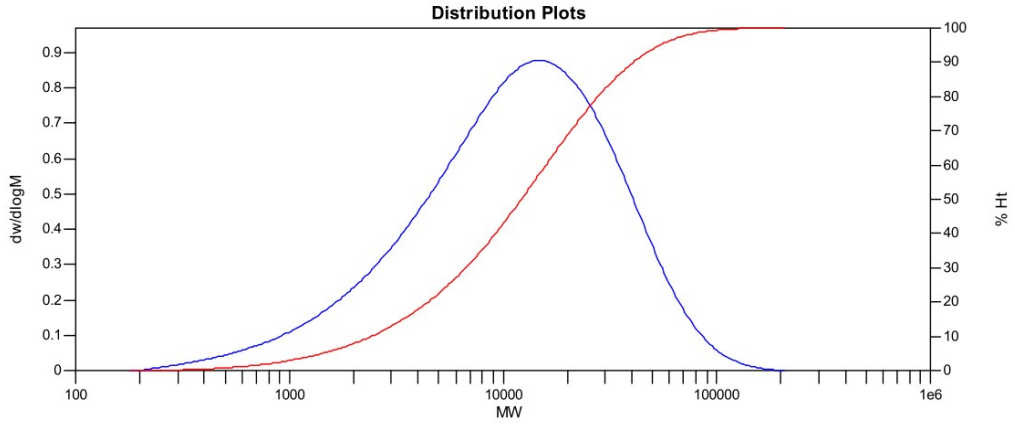
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	25437	11259	25546	43122	60082	23145	2.26894

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.43	14.67	17.10	-29.5531	100	2739.96	100

Figure S78. GPC of the polymer from table 1, entry 2.



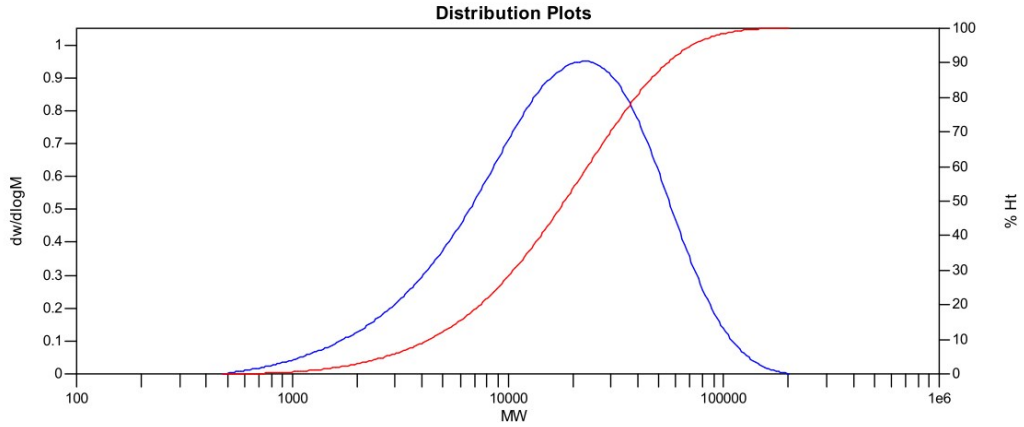
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14507	5287	17724	36413	58033	15460	3.35237

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.23	15.05	18.05	-58.1759	100	6247.9	100

Figure S79. GPC of the polymer from table 1, entry 3.



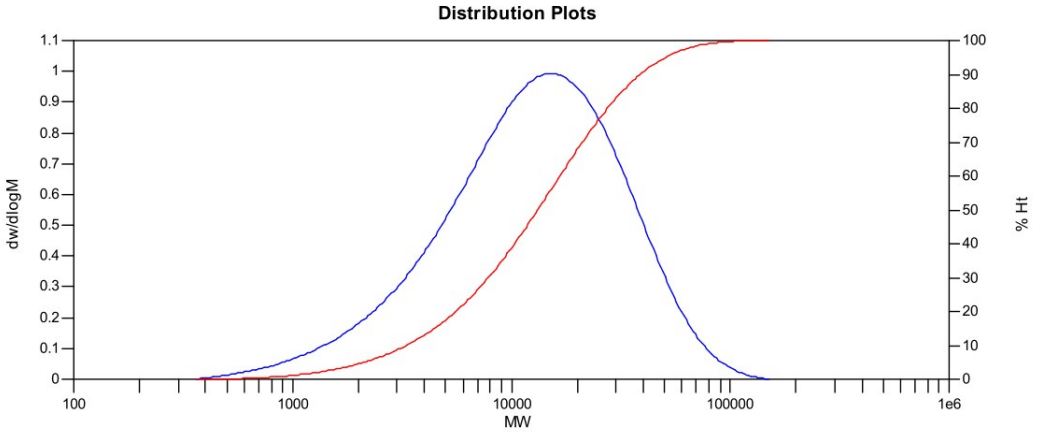
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	23070	9432	24836	45475	67164	22160	2.63316

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.25	14.73	17.38	-39.2765	100	3901.34	100

Figure S80. GPC of the polymer from table 1, entry 5.



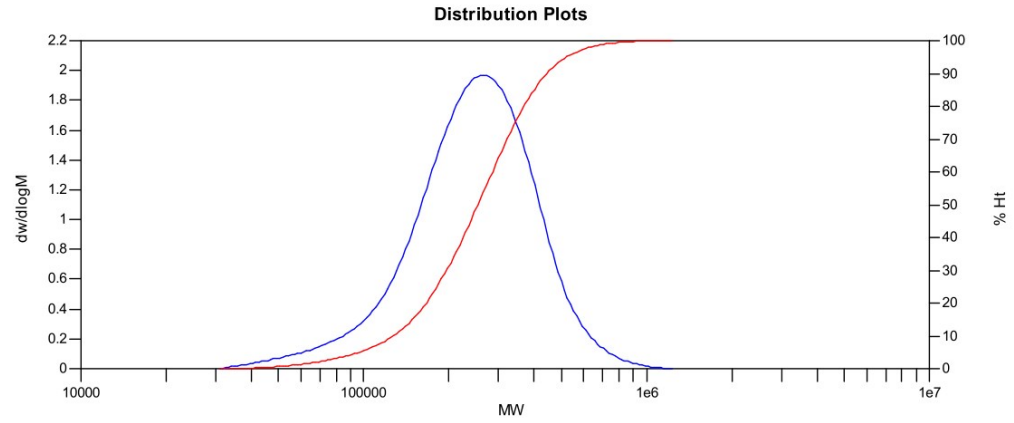
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	15233	7110	17726	32207	48150	15876	2.49311

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.45	15.02	17.57	-105.843	100	10058.2	100

Figure S81. GPC of the polymer from table 1, entry 6.



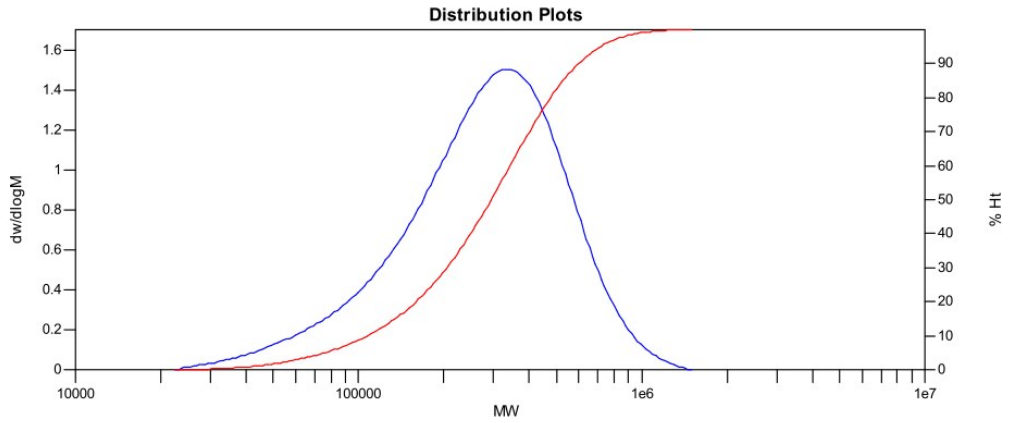
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	265102	207851	271079	335771	406468	261608	1.3042

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.02	13.07	14.53	-68.2667	100	3270.83	100

Figure S82. GPC of the polymer from table 1, entry 13.



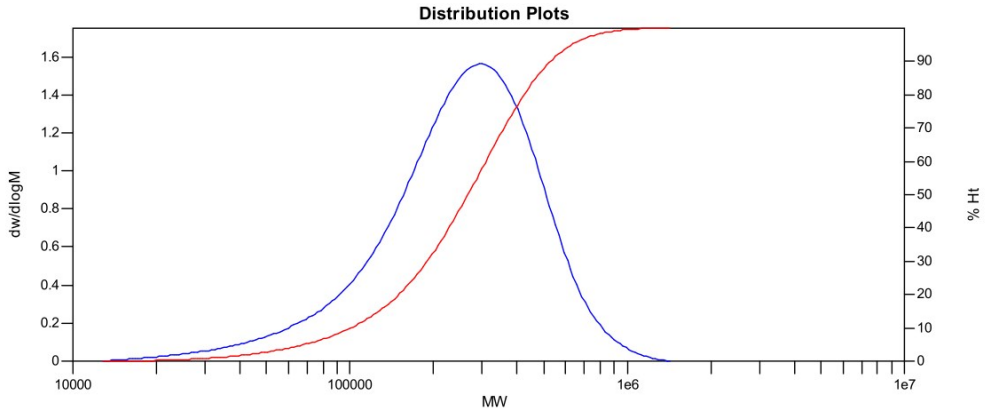
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	338413	206515	326312	447926	567510	308355	1.58009

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	12.92	14.75	-25.7067	100	1613.66	100

Figure S83. GPC of the polymer from table 1, entry 14.



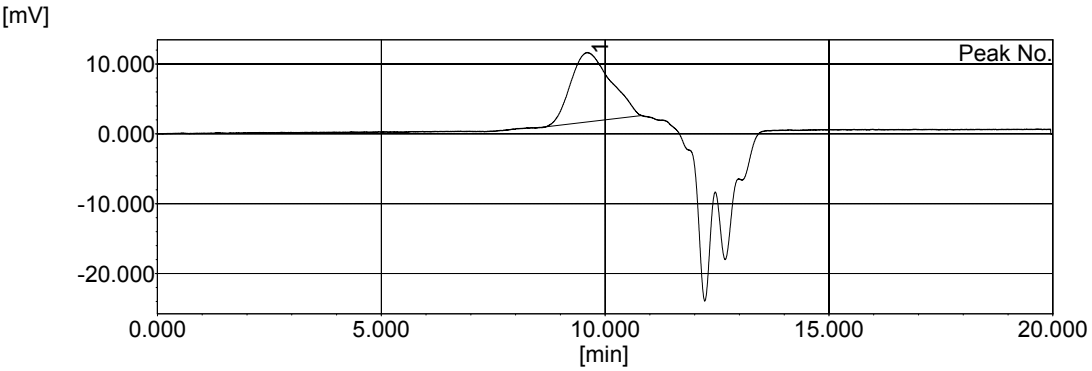
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	292298	183592	293559	398275	503538	277987	1.59897

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.92	13.00	15.13	-47.1068	100	2842.66	100

Figure S84. GPC of the polymer from table 1, entry 15.

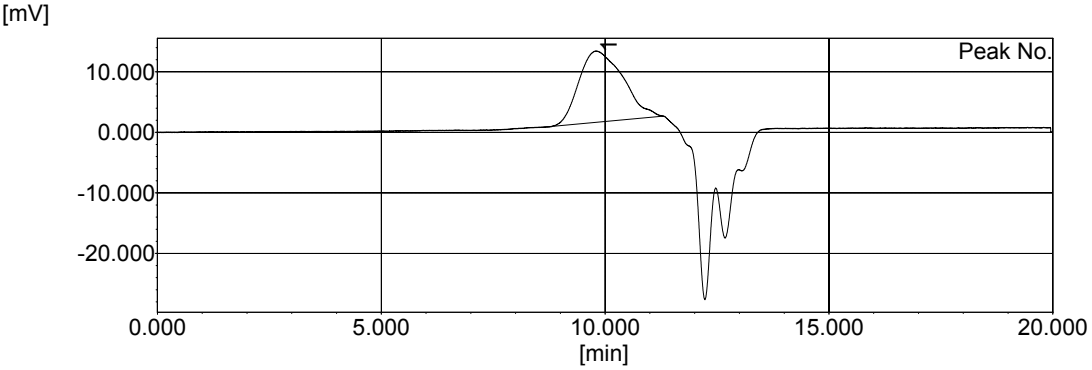


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	8.425	0.825	19,281	Mn	2,313
Peak top	9.593		3,370	Mw	3,303
		11.671		Mz	4,437
Peak end	10.808	2.618	549	Mz+1	5,608
				Mv	3,303
Height [mV]			9.967	Mp	3,371
Area [mV*sec]			616.388	Mz/Mw	1.344
Area% [%]			100.000	Mw/Mn	1.428
[eta]			3302.72495	Mz+1/Mw	1.698

Figure S85. GPC of the polymer from table 2, entry 1.

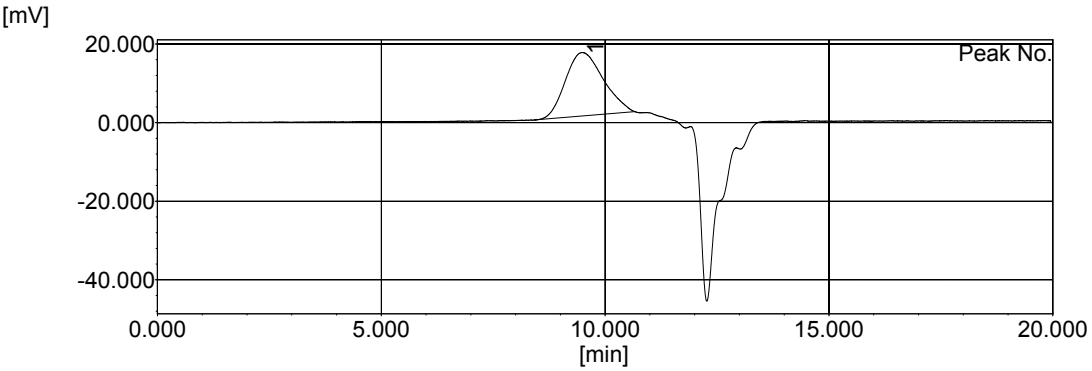


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	8.575	0.817	15,413	Mn	1,582
Peak top	9.790	13.458	2,513	Mw	2,398
Peak end		2.668	273	Mz	3,336
	11.277			Mz+1	4,292
				Mv	2,398
Height [mV]			11.809	Mp	2,513
Area [mV*sec]			803.658	Mz/Mw	1.391
Area% [%]			100.000	Mw/Mn	1.515
[eta]			2397.65622	Mz+1/Mw	1.790

Figure S86. GPC of the polymer from table 2, entry 2.

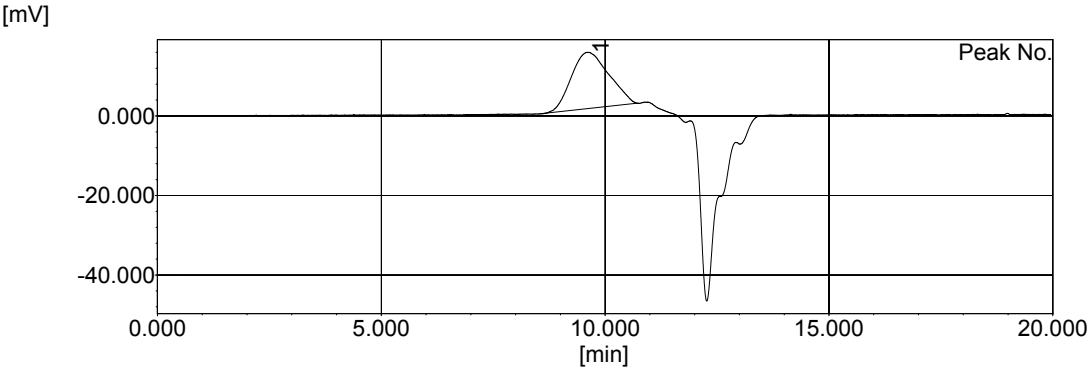


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	8.425	0.697	18,605	Mn	2,893
Peak top	9.485	17.878	3,862	Mw	3,958
Peak end	10.660	2.785	676	Mz	5,160
				Mz+1	6,381
				Mv	3,958
Height [mV]			16.191	Mp	3,863
Area [mV*sec]			949.568	Mz/Mw	1.304
Area% [%]			100.000	Mw/Mn	1.368
[eta]			3957.54591	Mz+1/Mw	1.612

Figure S87. GPC of the polymer from table 2, entry 3.

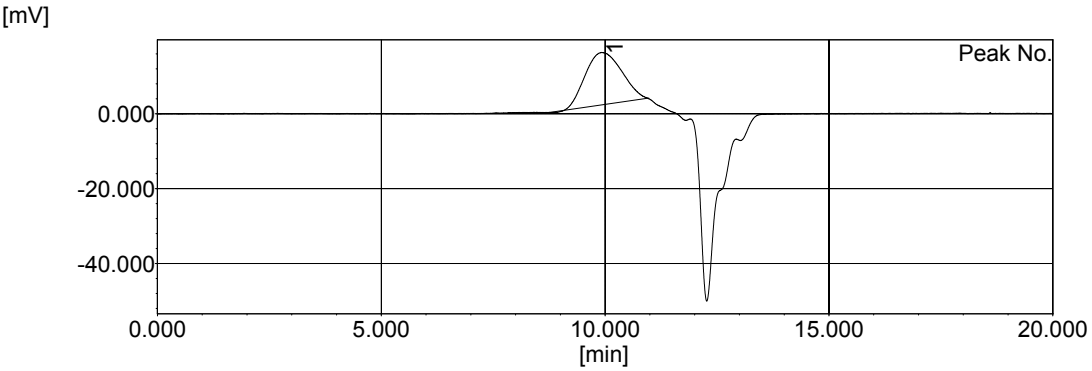


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	8.575	0.585	14,894	Mn	2,439
Peak top	9.610	16.038	3,208	Mw	3,280
Peak end	10.702	3.212	635	Mz	4,238
				Mz+1	5,208
				Mv	3,280
Height [mV]			14.174	Mp	3,209
Area [mV*sec]			825.185	Mz/Mw	1.292
Area% [%]			100.000	Mw/Mn	1.345
[eta]			3279.94940	Mz+1/Mw	1.588

Figure S88. GPC of the polymer from table 2, entry 4.

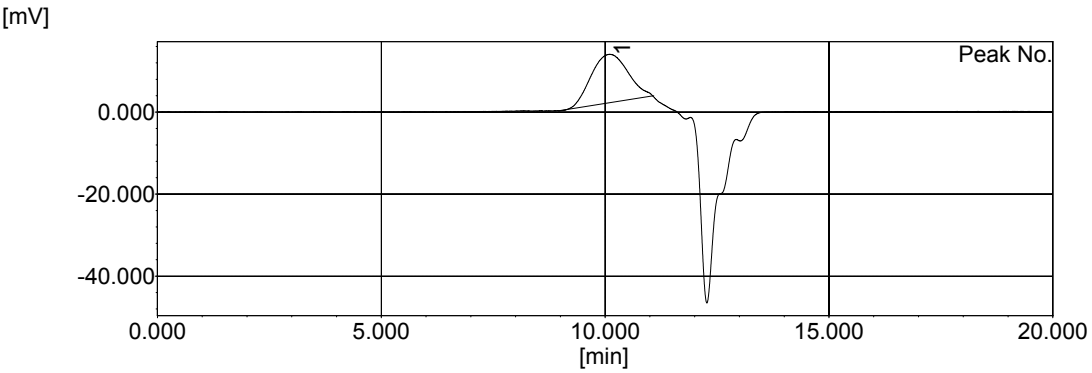


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	8.745	0.326		Mn	1,628
			11,574	Mw	2,137
Peak top	9.917	16.407	2,036	Mz	2,755
Peak end	10.957	4.158	435	Mz+1	3,479
				Mv	2,137
Height [mV]			14.051	Mp	2,036
Area [mV*sec]			799.384	Mz/Mw	1.289
Area% [%]			100.000	Mw/Mn	1.313
[eta]			2137.44377	Mz+1/Mw	1.628

Figure S89. GPC of the polymer from table 2, entry 5.

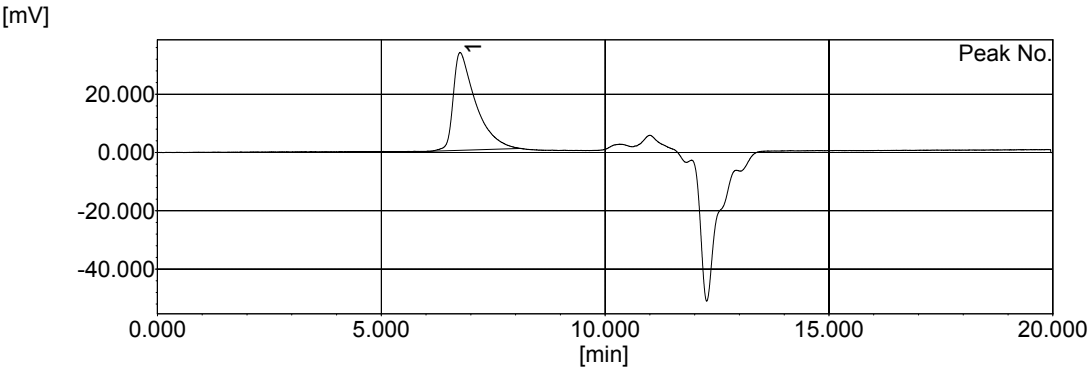


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	8.957	0.314	8,456	Mn	1,339
				Mw	1,761
Peak top	10.083	14.105	1,590	Mz	2,253
Peak end	11.063	3.969	371	Mz+1	2,771
				Mv	1,761
Height [mV]			11.836	Mp	1,586
Area [mV*sec]			678.683	Mz/Mw	1.279
Area% [%]			100.000	Mw/Mn	1.315
[eta]			1760.98304	Mz+1/Mw	1.574

Figure S90. GPC of the polymer from table 2, entry 6.

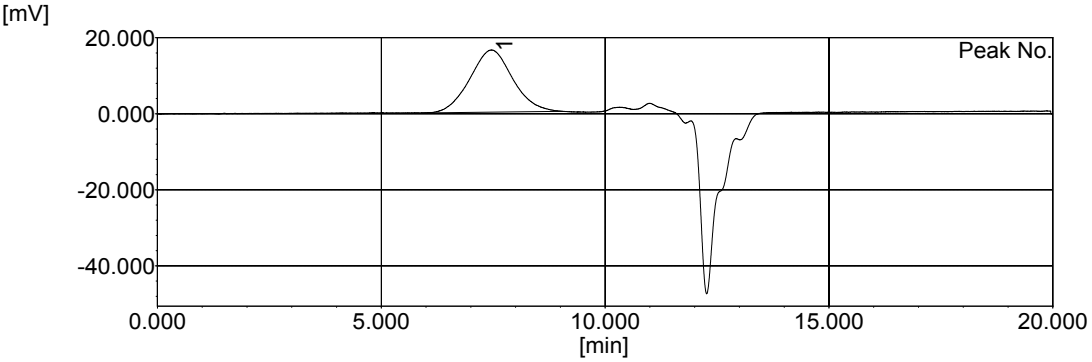


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	6.022	0.412	657,109	Mn	152,010
Peak top	6.755	34.350	221,458	Mw	183,129
Peak end	8.107	1.404	29,831	Mz	208,816
				Mz+1	230,878
				Mv	183,129
Height [mV]			33.589	Mp	221,458
Area [mV*sec]			1165.344	Mz/Mw	1.140
Area% [%]			100.000	Mw/Mn	1.205
[eta]			183128.64746	Mz+1/Mw	1.261

Figure S91. GPC of the polymer from table 2, entry 7.

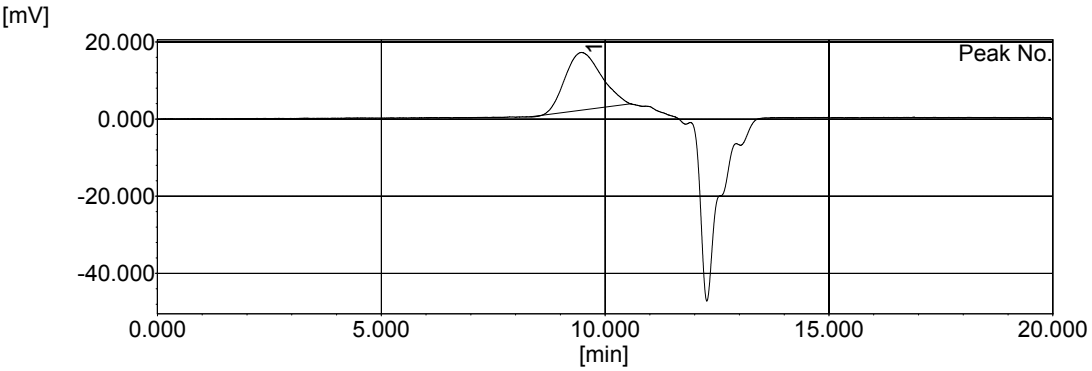


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.893	0.208	794,873	Mn	60,418
Peak top	7.457	16.802	78,224	Mw	95,730
Peak end	9.022	0.642	7,679	Mz	145,466
				Mz+1	209,518
				Mv	95,730
Height [mV]			16.377	Mp	78,224
Area [mV*sec]			1089.561	Mz/Mw	1.520
Area% [%]			100.000	Mw/Mn	1.584
[eta]			95729.99587	Mz+1/Mw	2.189

Figure S92. GPC of the polymer from table 2, entry 8.

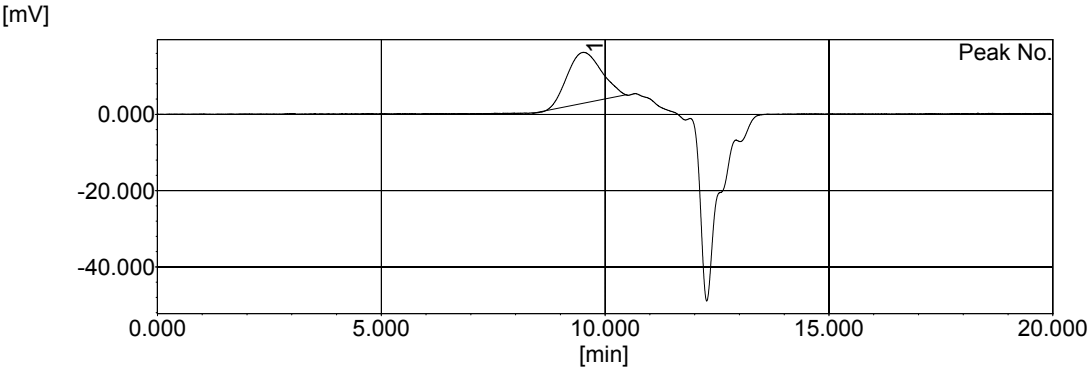


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	8.340	0.597	21,104	Mn	3,084
Peak top	9.458	17.278	4,018	Mw	4,117
Peak end	10.575	3.951	767	Mz	5,297
				Mz+1	6,561
				Mv	4,117
Height [mV]			15.003	Mp	4,018
Area [mV*sec]			847.338	Mz/Mw	1.287
Area% [%]			100.000	Mw/Mn	1.335
[eta]			4116.76976	Mz+1/Mw	1.594

Figure S93. GPC of the polymer from table 3, entry 3.

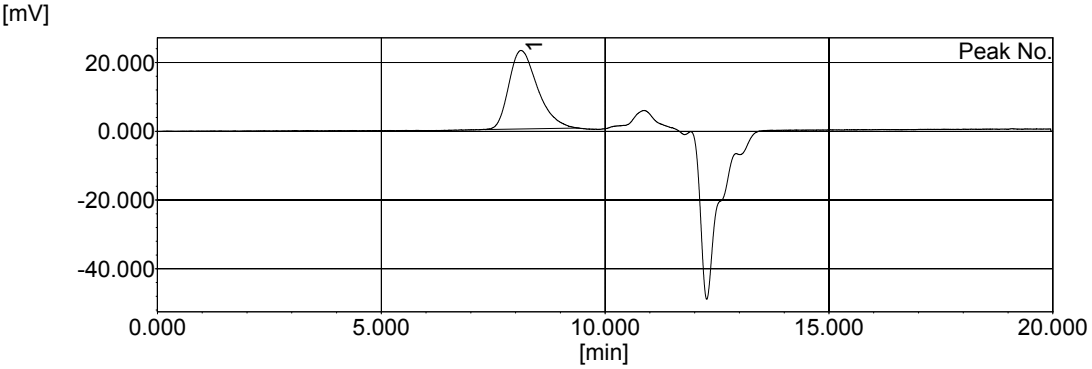


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	8.383	0.297	19,791	Mn	3,098
Peak top	9.473	16.207	3,929	Mw	3,972
Peak end	10.468	5.140	898	Mz	4,989
				Mz+1	6,114
				Mv	3,972
Height [mV]			13.378	Mp	3,930
Area [mV*sec]			713.507	Mz/Mw	1.256
Area% [%]			100.000	Mw/Mn	1.282
[eta]			3972.24592	Mz+1/Mw	1.539

Figure S94. GPC of the polymer from table 3, entry 4.

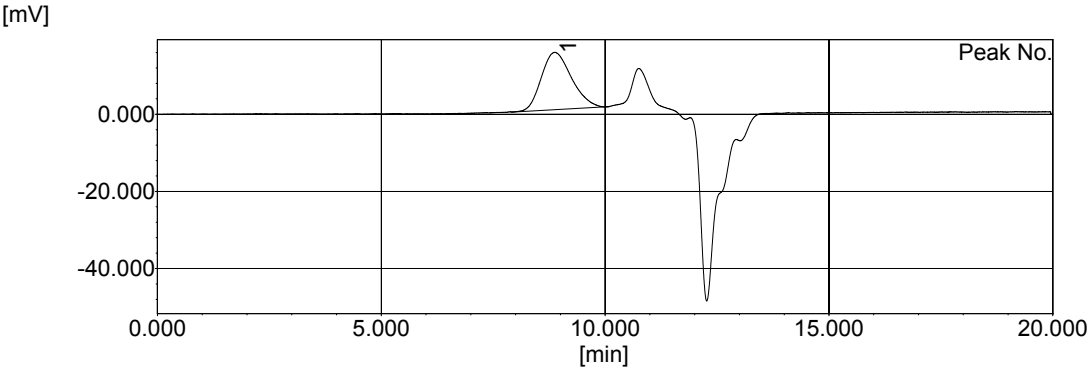


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	7.318	0.504	96,038	Mn	22,583
Peak top	8.118	23.533	29,319	Mw	28,006
Peak end	9.405	0.956	4,349	Mz	33,217
				Mz+1	38,163
				Mv	28,006
Height [mV]			22.856	Mp	29,320
Area [mV*sec]			1017.531	Mz/Mw	1.186
Area% [%]			100.000	Mw/Mn	1.240
[eta]			28006.42920	Mz+1/Mw	1.363

Figure S95. GPC of the polymer from table 3, entry 7.



Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	7.915	0.568	39,639	Mn	7,729
Peak top	8.878	16.090	9,498	Mw	9,572
Peak end	10.063	1.981	1,638	Mz	11,518
				Mz+1	13,514
				Mv	9,572
Height [mV]			14.888	Mp	9,498
Area [mV*sec]			695.650	Mz/Mw	1.203
Area% [%]			100.000	Mw/Mn	1.239
[eta]			9572.26994	Mz+1/Mw	1.412

Figure S96. GPC of the polymer from table 3, entry 8.

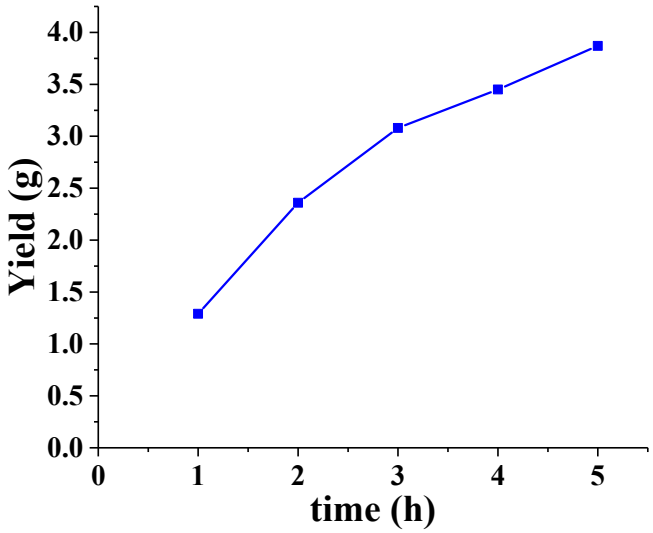


Figure S97. Plot of yield versus time for **Pd4** at 20 °C.

4. References

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

(2) Liang, T.; Goudari, S. B.; Chen, C. A simple and versatile nickel platform for the generation of branched high molecular weight polyolefins. *Nat. Commun.* **2020**, *11*, 1–8.

5. X-ray Crystallography

CCDC numbers of **Ni1** and **Pd1-3** are 2021535-2021538. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

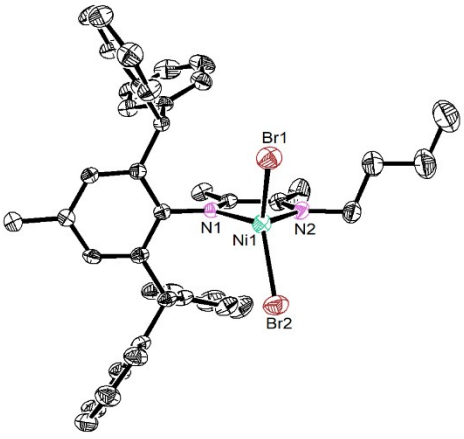


Table S1 Crystal data and structure refinement for **Ni1**.	
Identification code	**Ni1**
Empirical formula	C41 H42 Br2 N2 Ni
Formula weight	781.30

Temperature/K	298(2) K
Crystal system	Triclinic
Space group	P-1
a/Å	9.3405(8)
b/Å	10.8596(9)
c/Å	18.9774(17)
α/°	75.7240(10)
β/°	82.338(2)
γ/°	86.529(3)
Volume/Å^3	1848.1(3)
Z	2
ρ_{calc}g/cm^3	1.404
μ/mm^{-1}	2.717
F(000)	800
Crystal size/mm^3	0.30 x 0.23 x 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.34 to 25.02
Index ranges	-11<=h<=9, -12<=k<=12, -19<=l<=22
Reflections collected	9491
Independent reflections	6414 [R(int) = 0.0321]
Data/restraints/parameters	6414 / 30 / 419
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ(I)]	R1 = 0.0416, wR2 = 0.0859
Final R indexes [all data]	R1 = 0.0736, wR2 = 0.0910
Largest diff. peak/hole / e Å^{-3}	0.454 and -0.557

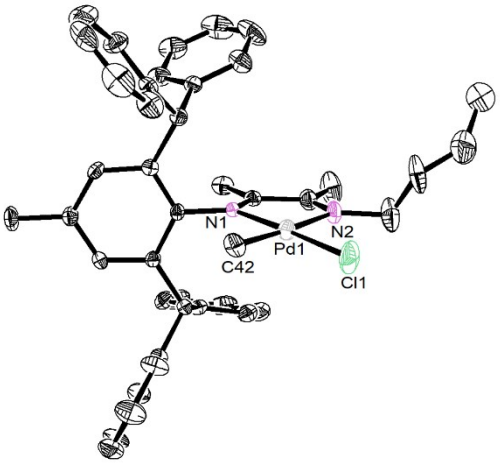


Table S2 Crystal data and structure refinement for Pd1.	
Identification code	Pd1
Empirical formula	C42 H45 Cl N2 Pd
Formula weight	719.65
Temperature/K	298(2) K
Crystal system	Monoclinic
Space group	P2(1)/c
a/Å	17.2731(15)
b/Å	12.4890(11)
c/Å	21.4769(19)
α/°	90.00
β/°	127.871(5)
γ/°	90.00
Volume/Å^3	3657.3(6)
Z	4
ρ_{calc}g/cm^3	1.307
μ/mm^{-1}	0.611
F(000)	1496
Crystal size/mm^3	0.40 x 0.37 x 0.34
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.50 to 25.02
Index ranges	-11<=h<=20, -14<=k<=14, -25<=l<=25
Reflections collected	16849
Independent reflections	6428 [R(int) = 0.0550]
Data/restraints/parameters	6428 / 47 / 439
Goodness-of-fit on F^2	1.028

Final R indexes [I>=2σ (I)]	R1 = 0.0573, wR2 = 0.1051
Final R indexes [all data]	R1 = 0.1080, wR2 = 0.1179
Largest diff. peak/hole / e Å^{-3}	0.663 and -0.493

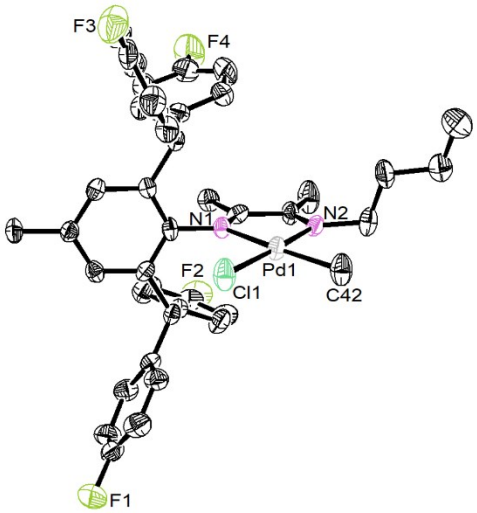


Table S3 Crystal data and structure refinement for Pd2.	
Identification code	Pd2
Empirical formula	C42 H41 Cl F4 N2 Pd
Formula weight	791.62
Temperature/K	298(2) K
Crystal system	Monoclinic
Space group	P2(1)/c
a/Å	9.2300(9)
b/Å	22.710(2)
c/Å	18.1601(17)
α/°	90
β/°	91.200(2)
γ/°	90
Volume/Å^3	3805.8(6)
Z	4
ρ_{calc}g/cm^3	1.382
μ/mm^{-1}	0.609
F(000)	1624
Crystal size/mm^3	0.17 x 0.10 x 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.12 to 25.02

Index ranges	-10<=h<=10, -26<=k<=23, -13<=l<=21
Reflections collected	18471
Independent reflections	6696 [R(int) = 0.1418]
Data/restraints/parameters	6696 / 0 / 452
Goodness-of-fit on F^2	0.988
Final R indexes [I>=2σ(I)]	R1 = 0.0671, wR2 = 0.0925
Final R indexes [all data]	R1 = 0.1684, wR2 = 0.1104
Largest diff. peak/hole / e $Å^{-3}$	0.518 and -0.653

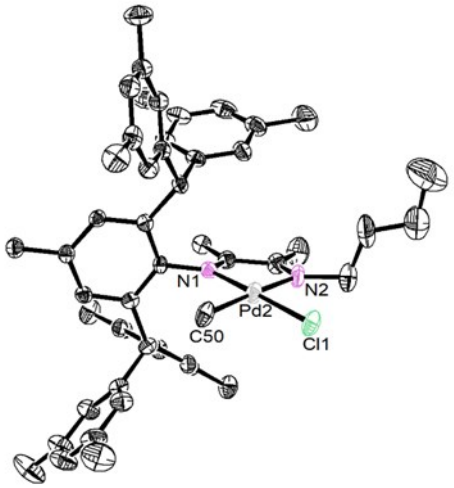


Table S4 Crystal data and structure refinement for Pd3.	
Identification code	Pd3
Empirical formula	C50 H61 Cl N2 Pd
Formula weight	831.86
Temperature/K	298(2) K
Crystal system	Triclinic
Space group	P-1
a/Å	12.9300(11)
b/Å	14.8499(13)
c/Å	15.1301(14)
α/°	105.570(3)
β/°	113.860(5)
γ/°	103.220(3)

Volume/Å^3	2364.4(4)
Z	2
ρ_{calc}g/cm^3	1.168
μ/mm^{-1}	0.481
F(000)	876
Crystal size/mm^3	0.40 x 0.35 x 0.34
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.76 to 25.02
Index ranges	-14<=h<=15, -17<=k<=17, -18<=l<=17
Reflections collected	11969
Independent reflections	8209 [R(int) = 0.0391]
Data/restraints/parameters	8209 / 33 / 488
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ(I)]	R1 = 0.0590, wR2 = 0.1715
Final R indexes [all data]	R1 = 0.0754, wR2 = 0.1827
Largest diff. peak/hole / e Å^{-3}	0.990 and -1.094