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Unexpected *o*-Aryl tBu Group Effect on Suppression of Chain Transfer in Pyridine-Imine Ni(II) and Pd(II) Catalyzed Ethylene (Co)Polymerization

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1. Experimental Sections

1.1 General Considerations

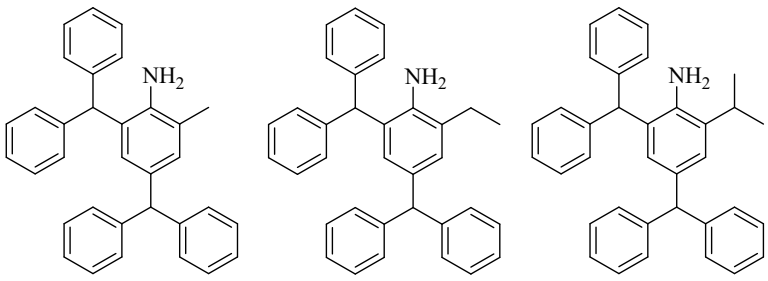
All chemicals were commercially sourced, except those whose synthesis is described. All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer or a JEOL JNM-ECZ600R 600 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C 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. The molecular weight and the molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) of Waters 2695 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.

X-Ray diffraction: For **Ni4**, data collections were performed at 298 K on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package[1]. The raw

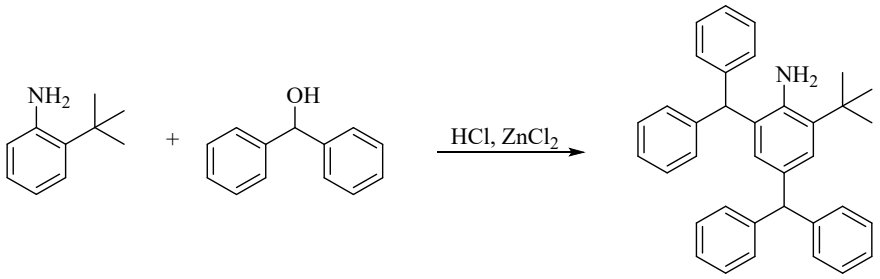
frame data were processed using SAINT and SADABS to yield the reflection data file[2]. The crystal data of **Pd3** was collected on a STOE STADIVARI diffractometer with Pilatus300K detector, using Cu Kα radiation (λ = 1.54186 Å) at 293 K. The determination of crystal class and unit cell parameters was carried out by the X-Area program package. The raw frame data were processed using Area Integrate and X-Area LANA to yield the reflection data file. Absorption corrections were applied by using the multi-scan program STOE LANA. All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using and Olex2[3] program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

Exceptions and special features: For **Ni4**, the thermal parameters of two phenyl ring were restrained to be similar with the adjacent atoms, and the "SIMU" restraint was used with the deviation being 0.02 0.04 to help the refinement. The "ISOR" restraint was used restraint was used for one phenyl ring with the deviation being 0.01 to help the refinement. The "DELU" restraint was used restraint was used for C27 and C28 with the deviation being 0.01 0.02 to help the refinement. For **Pd3**, the "SHEL" restraint was used with the deviation being 999 084 to help the refinement.

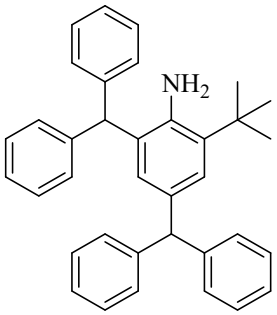
1.2 Procedure for the Synthesis of Arylamine A4.



These compounds were synthesized by the reported literature.[4]

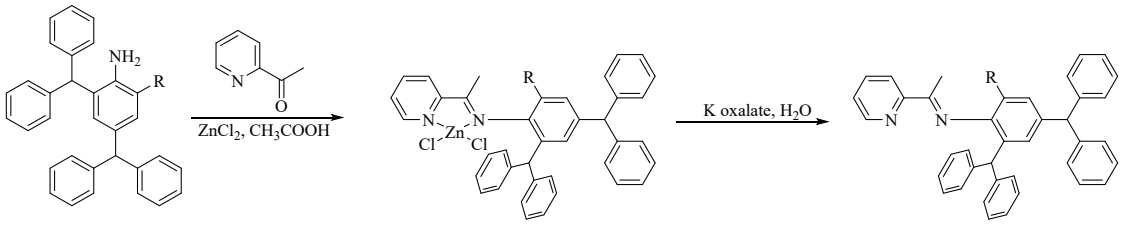


A mixture of 2-(tert-butyl)aniline (10.0 mmol, 1.0 equiv.) and diphenylmethanol (20 mmol, 2.0 equiv.) was heated to 120 °C. A solution of anhydrous zinc chloride (5 mmol, 0.5 equiv.) in concentrated hydrochloric acid (1.0 equiv.) was added to the mixture (exothermic + intense bubbling), and the temperature was raised to 160 °C. After 30 min at 160 °C, the reaction mixture was cooled to room temperature and dissolved in CH_2Cl_2 (200 mL). The CH_2Cl_2 layer was washed with water (3 × 200 mL) and dried over anhydrous magnesium sulfate. The solution was concentrated to 20 mL. The product was crashed out with 200 ml methanol and washed with methanol (3 × 100 mL). The desired aniline was obtained as a white crystalline solid.



A4 (3.90 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 11H, Ar-*H*), 7.06 – 6.93 (m, 10H, Ar-*H*), 6.28 (d, *J* = 1.7 Hz, 1H, Ar-*H*), 5.47 (s, 1H, -C*H*-), 5.28 (s, 1H, -C*H*-), 3.68 (s, *br*, 2H, -NH_2), 1.32 (s, 9H, -C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.94, 142.90, 140.74, 133.84, 132.30, 129.95, 129.47, 129.25, 128.41, 127.99, 126.46, 126.12, 125.78, 56.55 (-*C*H-), 52.50 (-*C*H-), 34.26 (-*C*(CH$_3$)$_3$), 30.14 (-C(*C*H$_3$)$_3$). ESI-MS (m/z): calcd for $C_{36}H_{36}N$: 482.28, Found, 482.28, $[M+H]^+$.

1.3 Procedure for the Synthesis of Ligands L1-L4.

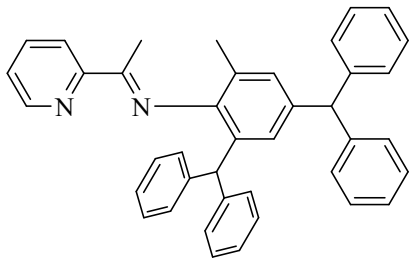


R= Me, **A1**
R= Et, **A2**
R= iPr, **A3**
R= tBu, **A4**

R= Me, **Zn1**
R= Et, **Zn2**
R= iPr, **Zn3**
R= tBu, **Zn4**

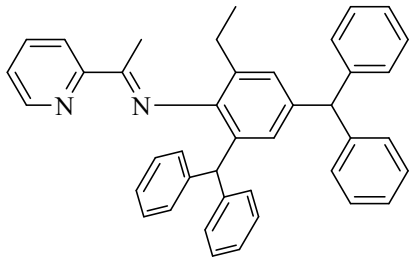
R= Me, **L1**
R= Et, **L2**
R= iPr, **L3**
R= tBu, **L4**

The ligands **L1-L4** were prepared as follows: $ZnCl_2$ (0.34 g, 2.5 mmol) and 2-acetylpyridine (2.0 mmol), were suspended in glacial acetic acid (5 mL). Anilines (2 mmol) were added, and the reaction mixture was refluxed under stirring for 4 h. The solution was allowed to cool to room temperature, and a bright yellow solid precipitated. The solid was separated by filtration and washed with acetic acid (3 × 5 mL) and diethyl ether (5 × 5 mL), to remove residual raw materials, by-products and the remaining acetic acid. Drying under vacuum gave bright yellow, poorly soluble solid. Then the zinc was then removed from the zinc pyridine-imine complex. The product of the previous step was suspended in methylene chloride (30 mL), and a solution of potassium oxalate (0.36 g, 2.2 mmol) in water (5 mL) was added. The reaction mixture was stirred vigorously for 1 h. The two phases were separated, and the organic layer was washed with water (3 × 20 mL) and dried with $MgSO_4$. After filtration, the solvent was removed under vacuum to afford the product as a yellow powder and dried under high vacuum.

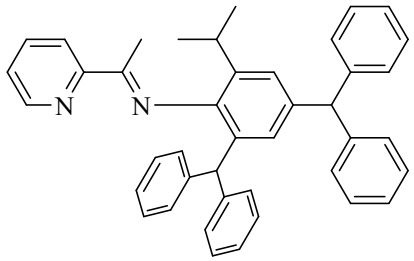


L1 (0.83 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.3 Hz, 1H, Ar-*H*), 8.29 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.77 (td, *J* = 7.9, 1.5 Hz, 1H, Ar-*H*), 7.33 (dd, *J* = 6.8, 5.4 Hz, 1H, Ar-*H*), 7.26 – 7.06 (m, 16H, Ar-*H*), 6.98 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 6.93 – 6.88 (m, 2H, Ar-*H*), 6.84 (s, 1H, Ar-*H*), 6.61 (s, 1H, Ar-*H*), 5.40 (s, 2H, -C*H*-), 1.91 (s, 3H, Ar-CH_3), 1.53 (s, 3H, -C(CH_3)=N). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.60 (-*C*(CH_3)=N), 156.20, 148.51, 146.54, 144.51, 144.41, 143.53, 142.56, 138.03, 136.29,

133.11, 129.76, 129.41, 129.36, 128.75, 128.19, 128.13, 128.11, 127.93, 126.12, 126.04, 125.91, 125.07, 124.72, 121.20, 56.33 (-*C*H-), 52.27 (-*C*H-), 17.94 (Ar-*C*H_3), 16.59 (-C(*C*H_3)=N). ESI-MS (m/z): calcd for $C_{40}H_{35}N_2$: 543.2800, Found, 543.2806, $[M+H]^+$.

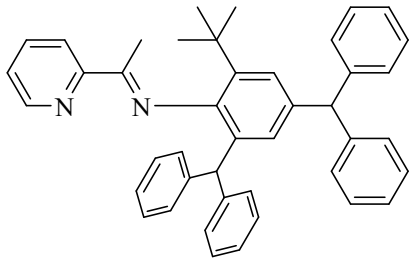


L2 (0.91 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.8, 0.8 Hz, 1H, Ar-*H*), 8.29 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.76 (td, *J* = 7.9, 1.7 Hz, 1H, Ar-*H*), 7.35 – 7.31 (m, 1H, Ar-*H*), 7.25 – 7.04 (m, 16H, Ar-*H*), 6.96 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 6.89 (t, *J* = 4.6 Hz, 3H, Ar-*H*), 6.60 (d, *J* = 1.6 Hz, 1H, Ar-*H*), 5.42 (s, 1H, -C*H*-), 5.37 (s, 1H, -C*H*-), 2.34 – 2.11 (m, 2H, -CH_2CH$_3$), 1.52 (s, 3H, -C(CH_3)=N), 1.03 (t, *J* = 7.5 Hz, 3H, -CH$_2$CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.39 (-*C*(CH$_3$)=N), 156.21, 148.50, 146.10, 144.58, 144.51, 143.64, 142.57, 138.01, 136.28, 132.69, 130.84, 129.77, 129.34, 128.73, 128.19, 128.10, 127.89, 127.37, 126.11, 126.01, 125.87, 124.69, 121.18, 56.47 (-*C*H-), 52.30 (-*C*H-), 24.20 (-*C*H$_2$CH$_3$), 16.80 (-C(*C*H_3)=N), 13.52 (-CH$_2$*C*H$_3$). ESI-MS (m/z): calcd for $C_{41}H_{37}N_2$: 557.2957, Found, 557.2961, $[M+H]^+$.



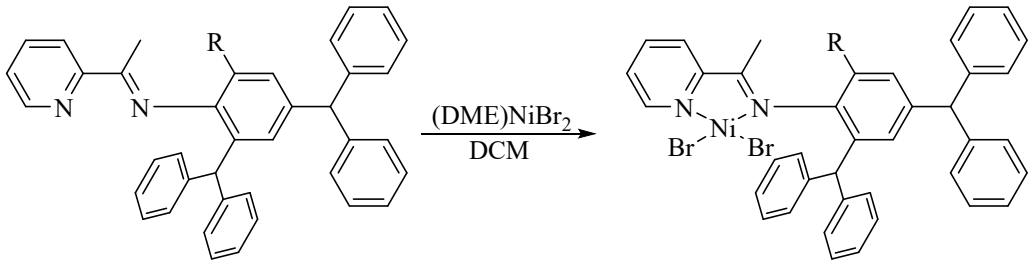
L3 (0.96 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.56 (m, 1H, Ar-*H*), 8.29 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.77 (td, *J* = 7.8, 1.7 Hz, 1H, Ar-*H*), 7.39 – 7.30 (m, 1H, Ar-*H*), 7.26 – 6.85 (m, 16H, Ar-*H*), 6.96 (d, *J* = 6.7 Hz, 3H, Ar-*H*), 6.90 – 6.84 (m, 2H, Ar-*H*), 6.58 (d, *J* = 1.7 Hz, 1H, Ar-*H*), 5.42 (s, 1H, -C*H*-), 5.35 (s, 1H, -C*H*-), 2.65 – 2.51

(m, 1H, -C*H*(CH_3)$_2$), 1.52 (s, 3H, -C(CH_3)=N), 1.05 (d, *J* = 6.9 Hz, 3H, -CH(CH_3)$_2$), 1.01 (d, *J* = 6.8 Hz, 3H, -CH(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.43 (-*C*(CH_3)=N), 156.21, 148.50, 145.35, 144.66, 144.59, 143.71, 142.56, 138.02, 136.29, 135.59, 132.46, 129.78, 129.35, 129.34, 129.32, 128.61, 128.18, 128.07, 127.86, 126.10, 125.98, 125.84, 124.89, 124.69, 56.58 (-*C*H-), 52.43 (-*C*H-), 27.90 (-*C*H(CH_3)$_2$), 23.63 (-CH(*C*H_3)$_2$), 22.54 (-CH(*C*H_3)$_2$), 17.00 (-C(*C*H_3)=N). ESI-MS (m/z): calcd for $C_{42}H_{39}N_2$: 571.3113, Found, 571.3122, $[M+H]^+$.



L4 (0.82 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.1 Hz, 1H, Ar-*H*), 8.18 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.74 (td, *J* = 7.9, 1.6 Hz, 1H, Ar-*H*), 7.39 – 7.30 (m, 1H, Ar-*H*), 7.26 – 7.03 (m, 17H, Ar-*H*), 6.92 – 6.87 (m, 2H, Ar-*H*), 6.86 – 6.81 (m, 2H, Ar-*H*), 6.60 (d, *J* = 1.5 Hz, 1H, Ar-*H*), 5.41 (s, 1H, -C*H*-), 5.22 (s, 1H, -C*H*-), 1.67 (s, 3H, -C(CH_3)=N), 1.17 (s, 9H, -C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.39 (-*C*(CH_3)=N), 156.13, 148.52, 146.76, 144.66, 144.63, 144.25, 142.66, 137.51, 137.07, 136.28, 131.38, 129.69, 129.54, 129.33, 129.20, 128.22, 128.07, 127.79, 126.14, 126.10, 125.97, 125.96, 125.72, 124.68, 121.41, 56.61 (-*C*H-), 52.03 (-*C*H-), 35.35 (-*C*(CH_3)$_3$), 30.18 (-C(*C*H_3)$_3$), 18.33 (-C(*C*H_3)=N). ESI-MS (m/z): calcd for $C_{43}H_{41}N_2$: 585.3270, Found, 585.3282, $[M+H]^+$.

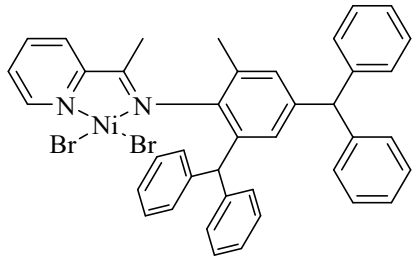
1.4 Procedure for the Synthesis of Nickel Complexes Ni1-Ni4.



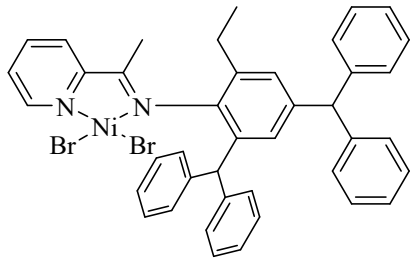
R= Me, **L1**
R= Et, **L2**
R= iPr, **L3**
R= tBu, **L4**

R= Me, **Ni1**
R= Et, **Ni2**
R= iPr, **Ni3**
R= tBu, **Ni4**

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

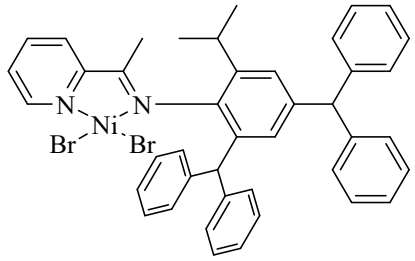


Ni1 (0.12 g, 80%), Elemental analysis: calc. for $C_{40}H_{34}Br_2N_2Ni$: C, 63.11; H, 4.50; N, 3.68. Found: C, 63.23; H, 4.46; N, 3.57.

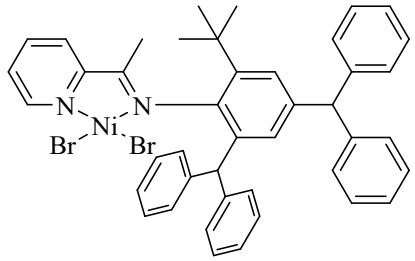


Ni2 (0.13 g, 86%), Elemental analysis: calc. for $C_{41}H_{36}Br_2N_2Ni$: C, 63.52; H, 4.68; N,

3.61. Found: C, 63.43; H, 4.57; N, 3.48.

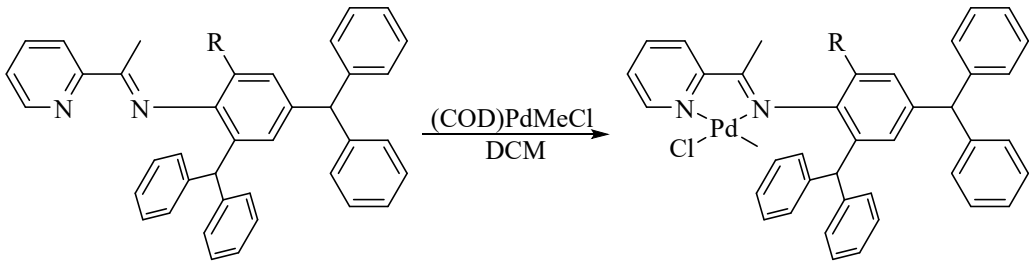


Ni3 (0.13 g, 82%), Elemental analysis: calc. for $C_{42}H_{38}Br_2N_2Ni$: C, 63.91; H, 4.85; N, 3.55. Found: C, 63.78; H, 4.75; N, 3.51.



Ni4 (0.14 g, 85%), Elemental analysis: calc. for $C_{43}H_{40}Br_2N_2Ni$: C, 64.27; H, 5.02; N, 3.49. Found: C, 64.18; H, 4.95; N, 3.44.

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

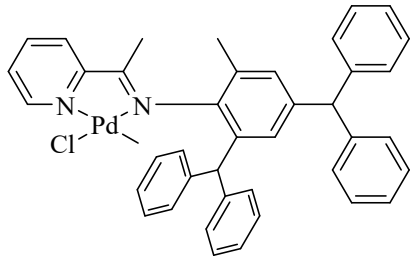


R= Me, **L1**
R= Et, **L2**
R= iPr, **L3**
R= tBu, **L4**

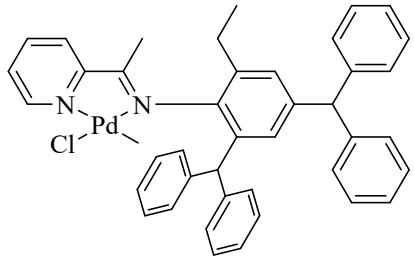
R= Me, **Pd1**
R= Et, **Pd2**
R= iPr, **Pd3**
R= tBu, **Pd4**

A mixture of the ligand (0.4 mmol), (COD)PdMeCl (106 mg, 0.4 mmol) in CH_2Cl_2 (10 mL) was stirred for 24 h at room temperature. During stirring, the color of the solution was deepening. At the end of the reaction, the solvent was partially evaporated under reduced pressure. The remaining mixture was diluted with Et_2O (20

mL). The resulting yellow solid was collected by filtration, dried in vacuum. The single crystal can be obtained by diffusion from layering diethyl ether on to the CH_2Cl_2 solution at room temperature.

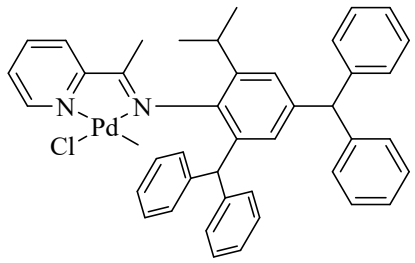


Pd1 (0.24 g, 85%). a isomer : b isomer = 8:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53, 9.28 (d, *J* = 5.3 Hz, 1H, Ar-*H*), 8.12, 7.97 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 7.78 – 7.73, 7.72 – 7.66 (m, 1H, Ar-*H*), 7.42 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.29 – 6.97 (m, 18H, Ar-*H*), 6.90 (d, *J* = 6.6 Hz, 3H, Ar-*H*), 6.69, 6.58 (s, 1H, Ar-*H*), 6.28, 6.06 (s, 1H, -C*H*-), 5.44, 5.40 (s, 1H, -C*H*-), 2.09, 2.02 (s, 3H, Ar-CH_3), 1.15, 1.09 (s, 3H, -C(CH_3)=N), 0.64, 0.08 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.12 (-*C*(CH_3)=N), 176.11 (-*C*(CH_3)=N), 152.56, 149.38, 143.86, 143.73, 142.08, 141.92, 141.86, 141.59, 138.66, 136.00, 130.32, 129.59, 129.39, 129.35, 129.25, 128.79, 128.65, 128.39, 128.14, 126.65, 126.43, 124.48, 56.34 (-*C*H-), 52.12 (-*C*H-), 18.40 (Ar-*C*H_3), 17.99 (Ar-*C*H_3), 17.24 (-C(*C*H_3)=N), 17.10 (-C(*C*H_3)=N), 1.13 (Pd-*C*H_3), 0.57 (Pd-*C*H_3). Elemental analysis: calc. for $C_{41}H_{37}ClN_2Pd$: C, 70.39; H, 5.33; N, 4.00. Found: C, 70.31; H, 5.24; N, 3.94.

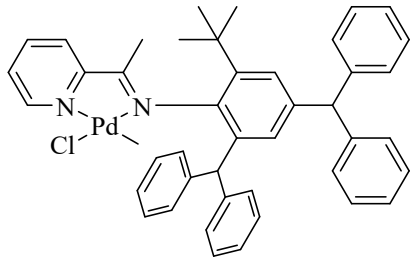


Pd2 (0.24 g, 83%). a isomer : b isomer = 5:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55, 9.29 (dd, *J* = 5.4, 0.9 Hz, 1H, Ar-*H*), 8.12, 7.97 (td, *J* = 7.8, 1.6 Hz, 1H, Ar-*H*), 7.78 – 7.74, 7.73 – 7.68 (m, 1H, Ar-*H*), 7.41 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.28 – 6.99 (m, 19H, Ar-*H*), 6.90 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 6.69, 6.57 (s, 1H, Ar-*H*), 6.32, 6.09 (s, 1H, -

C*H*-), 5.46, 5.42 (s, 1H, -C*H*-), 2.61 – 2.35 (m, 1H, -CH_2CH$_3$), 2.29 – 2.13 (m, 1H, -CH_2CH$_3$), 1.19, 1.13 (t, *J* = 7.5 Hz, 3H, -CH$_2$CH_3), 1.07 (s, 3H, -C(CH_3)=N), 0.67 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.22 (-*C*(CH$_3$)=N), 176.20 (-*C*(CH$_3$)=N), 155.97, 152.57, 151.54, 149.38, 143.90, 143.82, 142.16, 141.96, 141.56, 141.41, 138.65, 135.80, 134.13, 130.34, 129.37, 129.33, 129.24, 128.64, 128.37, 128.11, 127.32, 126.63, 126.40, 124.50, 56.48 (-*C*H-), 52.19 (-*C*H-), 23.61 (-*C*H$_2$CH$_3$), 17.66 (-C(*C*H$_3$)=N), 13.14 (-CH$_2$*C*H$_3$), 1.20 (Pd-*C*H$_3$). Elemental analysis: calc. for $C_{42}H_{39}ClN_2Pd$: C, 70.69; H, 5.51; N, 3.93. Found: C, 70.56; H, 5.43; N, 3.97.



Pd3 (0.25 g, 87%). a isomer : b isomer = 5:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58, 9.31 (d, *J* = 4.5 Hz, 1H, Ar-*H*), 8.11, 7.97 (td, *J* = 7.1 Hz, 1H, Ar-*H*), 7.80 – 7.74, 7.73 – 7.68 (m, 1H, Ar-*H*), 7.41 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.24 – 6.91 (m, 17H, Ar-*H*), 6.95 (d, *J* = 5.5Hz, 2H, Ar-*H*), 6.90 (d, *J* = 5.5Hz, 2H, Ar-*H*), 6.66, 6.54 (s, 1H, Ar-*H*), 6.37, 6.13 (s, 1H, -C*H*-), 5.46 (s, 1H, -C*H*-), 2.81 – 2.71 (m, 1H, -C*H*(CH$_3$)$_2$), 1.16 (d, *J* = 6.8 Hz, 3H, -CH(CH_3)$_2$), 1.09 (s, 3H, -C(CH_3)=N), 1.01 (d, *J* = 6.9 Hz, 3H, -CH(CH_3)$_2$), 0.73 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.24 (-*C*(CH$_3$)=N), 176.31 (-*C*(CH$_3$)=N), 152.69, 149.54, 144.05, 143.94, 142.49, 142.11, 141.67, 140.77, 139.28, 138.67, 135.83, 130.48, 129.44, 129.40, 129.34, 128.72, 128.51, 128.46, 128.41, 128.20, 126.68, 126.49, 125.74, 124.61, 56.64 (-*C*H-), 52.41 (-*C*H-), 27.91 (-*C*H(CH$_3$)$_2$), 23.91 (-CH(*C*H$_3$)$_2$), 23.44 (-CH(*C*H$_3$)$_2$), 18.31 (-C(*C*H$_3$)=N), 1.80 (Pd-*C*H$_3$). Elemental analysis: calc. for $C_{43}H_{41}ClN_2Pd$: C, 70.97; H, 5.68; N, 3.85. Found: C, 70.87; H, 5.54; N, 3.91.



Pd4 (0.27 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56, 9.31 (d, *J* = 5.5 Hz, 1H, Ar-*H*), 7.96 (td, *J* = 7.8, 1.7 Hz, 1H, Ar-*H*), 7.73 – 7.63 (m, 1H, Ar-*H*), 7.36 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.28 – 6.95 (m, 17H, Ar-*H*), 6.92 (m, 2H, Ar-*H*), 6.86 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 6.71 (d, *J* = 1.7 Hz, 1H, Ar-*H*), 6.37 (s, 1H, -C*H*-), 5.45 (s, 1H, -C*H*-), 1.30 (s, 9H, -C(CH_3)$_3$), 1.04 (s, 3H, -C(CH_3)=N), 0.86 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.94 (-*C*(CH_3)=N), 152.83, 149.59, 143.98, 143.86, 142.78, 141.61, 141.50, 141.11, 139.99, 138.61, 136.53, 130.51, 130.32, 129.42, 129.39, 129.37, 128.71, 128.46, 128.33, 128.11, 126.72, 126.50, 126.34, 124.74, 56.51 (-*C*H-), 52.62 (-*C*H-), 37.25 (-*C*(CH_3)$_3$), 33.36 (-C(*C*H_3)$_3$), 19.21 (-C(*C*H_3)=N), 2.38 (Pd-*C*H_3). Elemental analysis: calc. for $C_{44}H_{43}ClN_2Pd$: C, 71.25; H, 5.84; N, 3.78. Found: C, 71.34; H, 5.73; N, 3.81.

1.6 A General Procedure for the Ethylene Polymerization Using Ni Complexes.

In a typical experiment, a 350 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 temperature. 20 mL of toluene and the desired amount Et_2AlCl was added to the reactor under N_2 atmosphere, then, 1 μmol Ni catalyst in 1 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 6 atm of ethylene. After 10 min, the pressure reactor was vented and the ethylene oligomers or polyethylene evaporated by a rotary evaporator and dried at 50 °C for at least 24 h under vacuum.

1.7 A General Procedure for the Ethylene Polymerization Using Pd Complexes.

In a typical experiment, a 350 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 temperature. 38 mL of DCM and desired amount NaBArF were added to the reactor, then, 10 μmol Pd catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at 4 atm of ethylene. After 3 h, the pressure reactor was vented and the ethylene oligomers or polyethylene were dried under vacuum by a rotary evaporator.

1.8 A General Procedure for the Copolymerization of MA with Ethylene Using Pd Complexes.

In a typical experiment, a 350 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 temperature. 18 mL of DCM with the desired amount of NaBArF was added to the reactor, then the desired amount of MA and 20 μmol Pd catalyst in 2 mL of CH_2Cl_2 were injected into the copolymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at 2 atm of ethylene. After 12 h, the pressure reactor was vented and the ethylene-MA co-oligomers or copolymers were dried under vacuum by a rotary evaporator.

2. Spectra Data

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

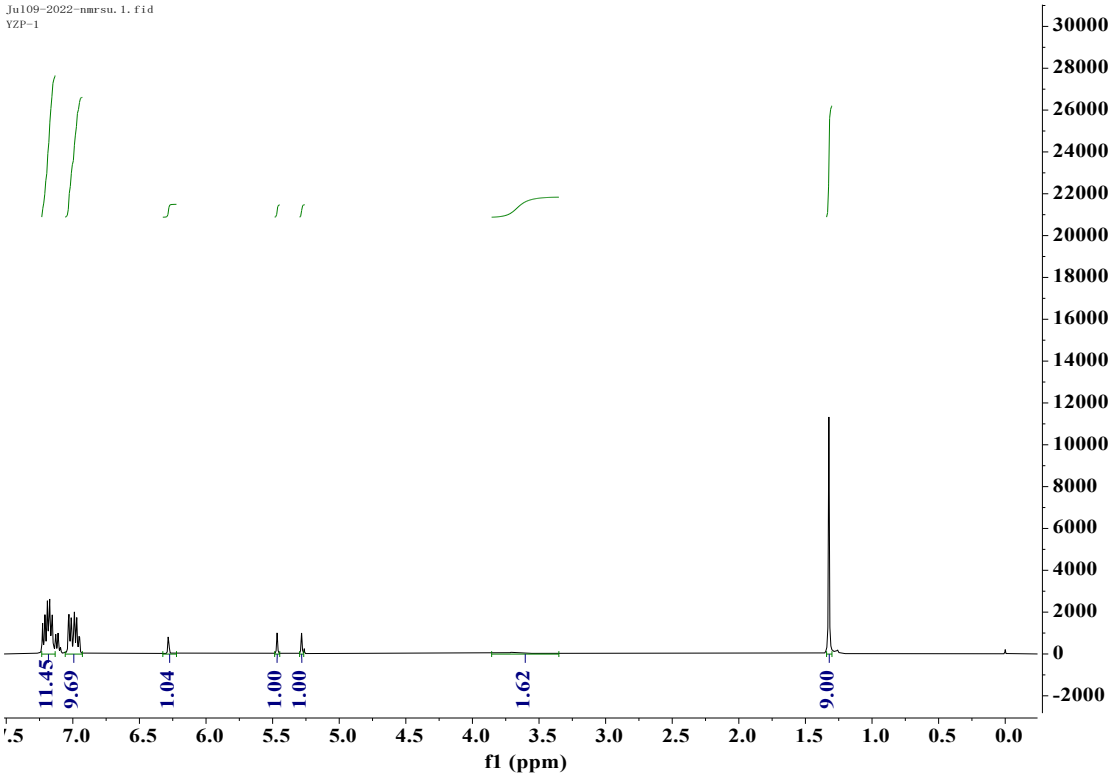


Figure S1. ^{1}H NMR spectrum of **A4** in $CDCl_3$.

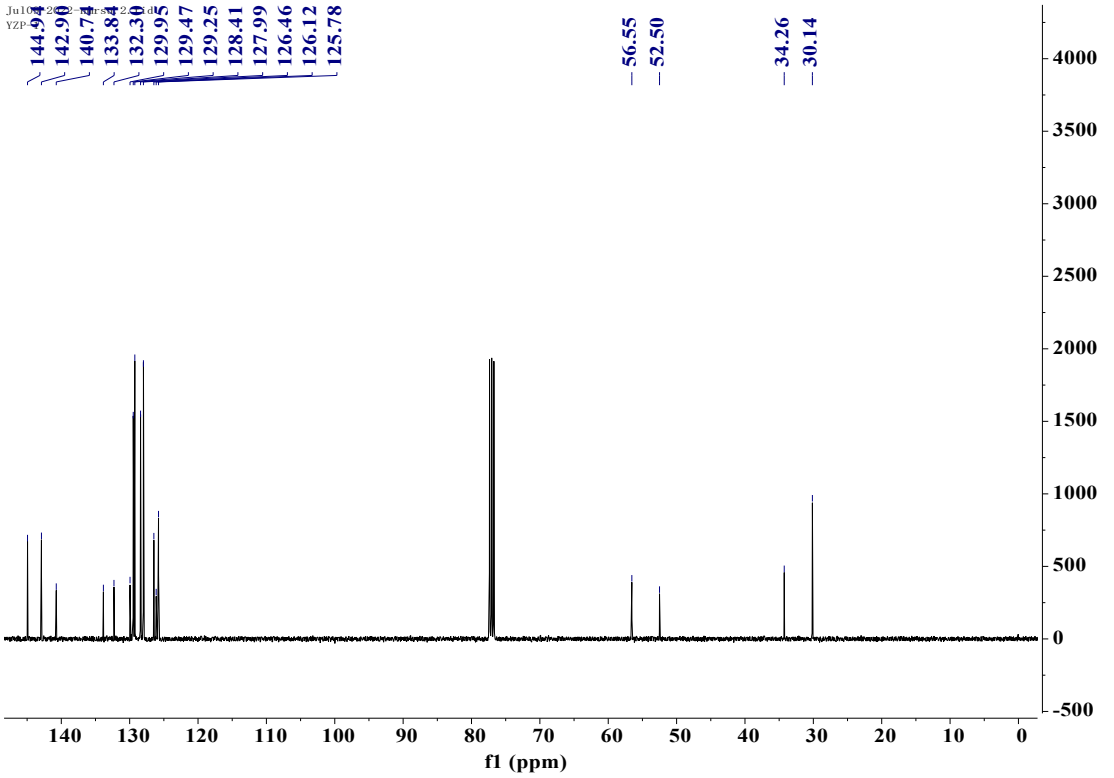


Figure S2. ^{13}C NMR spectrum of **A4** in $CDCl_3$.

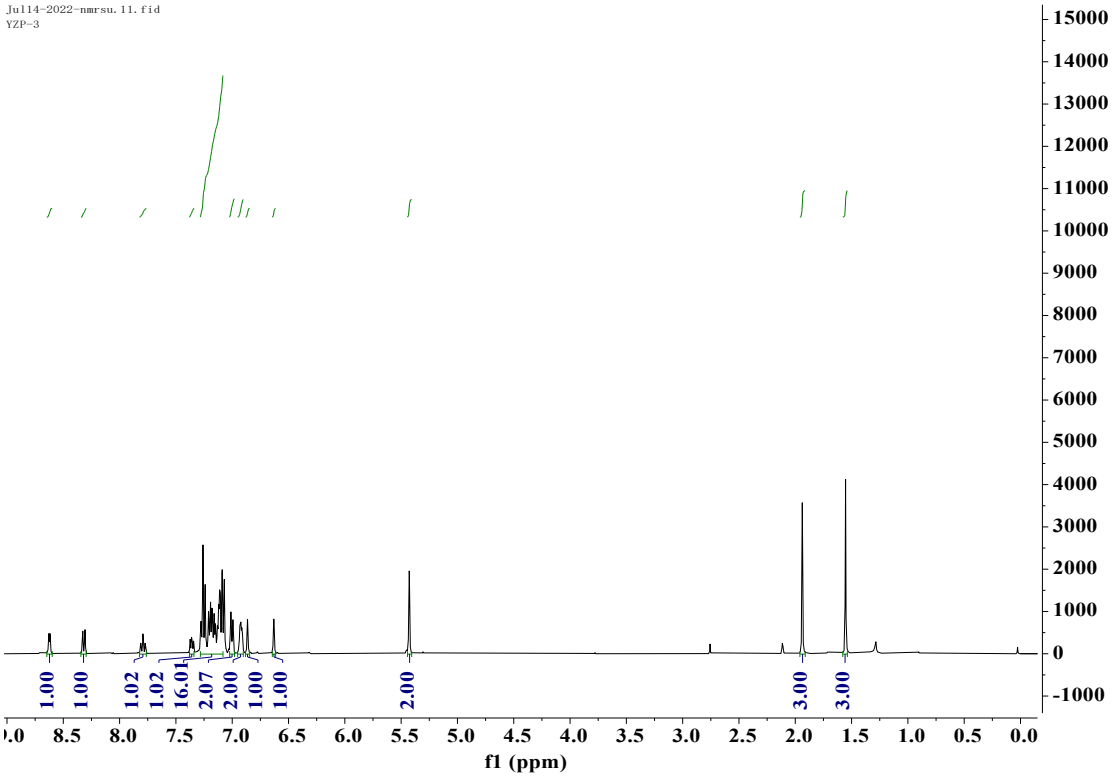


Figure S3. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

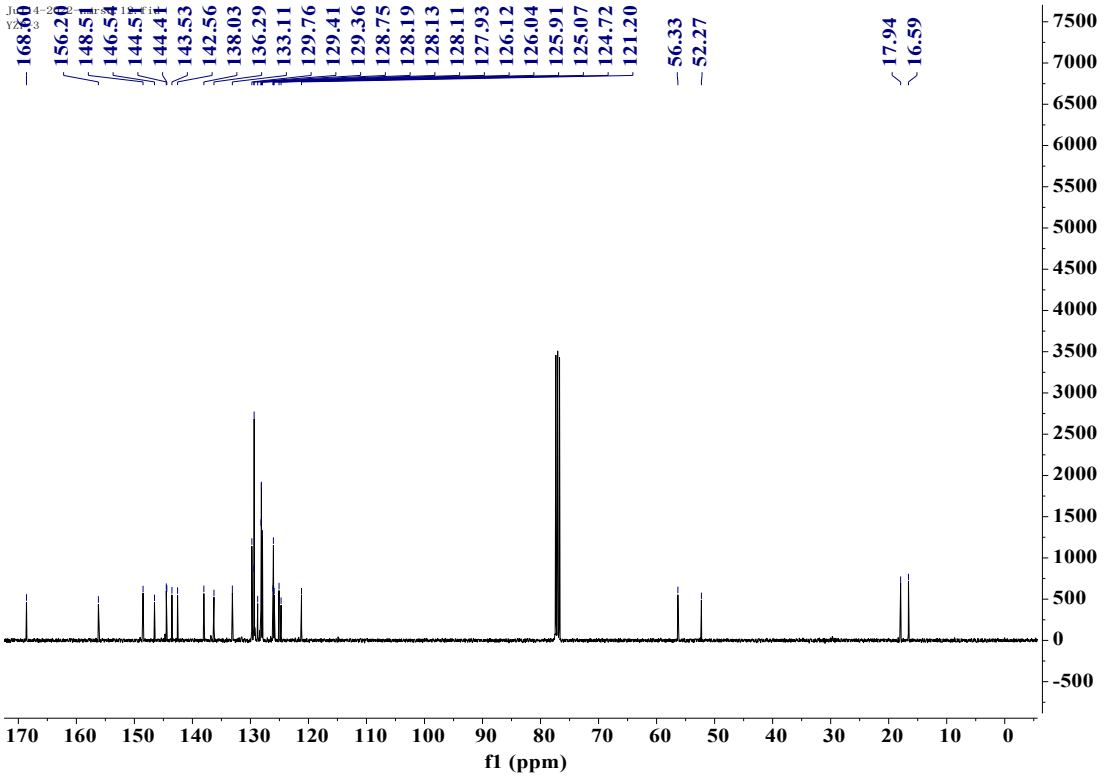


Figure S4. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

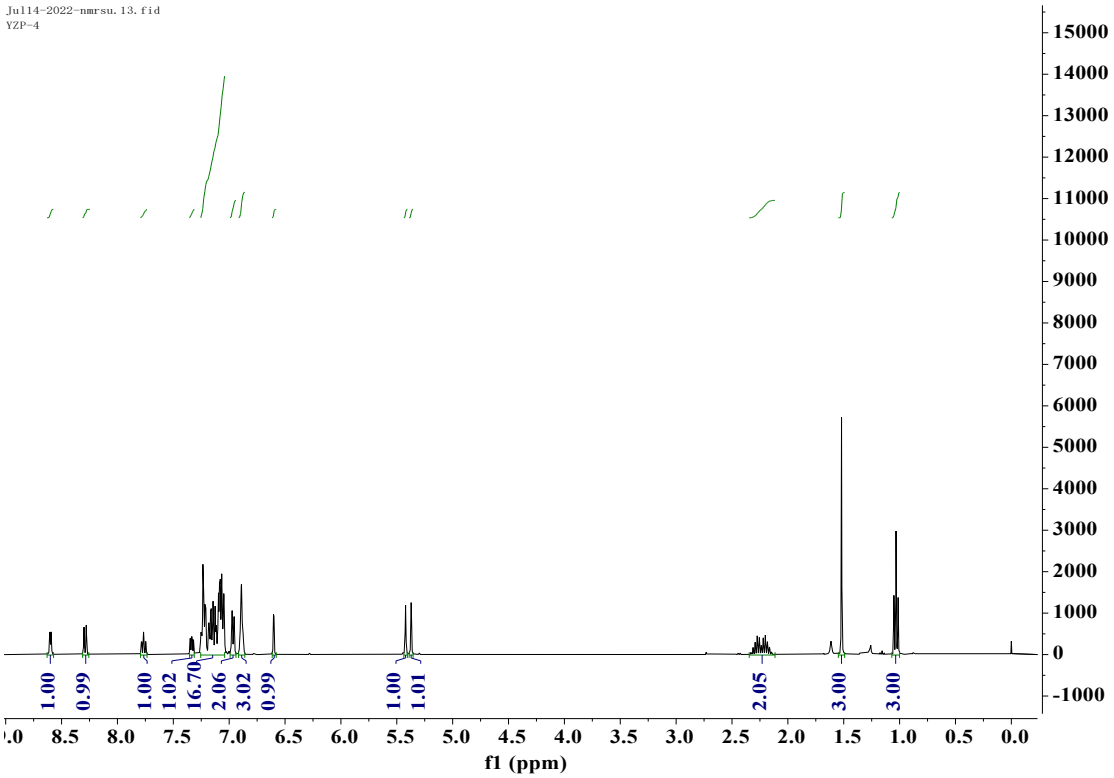


Figure S5. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

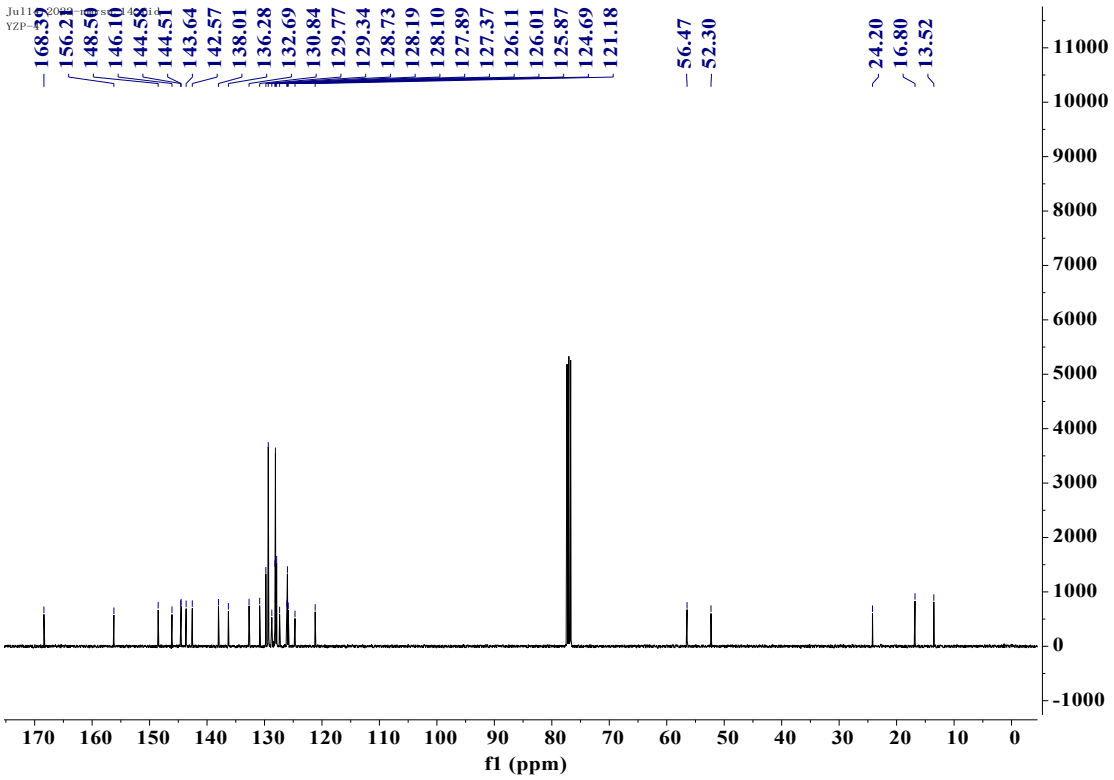


Figure S6. ^{13}C NMR spectrum of **L2** in $CDCl_3$.

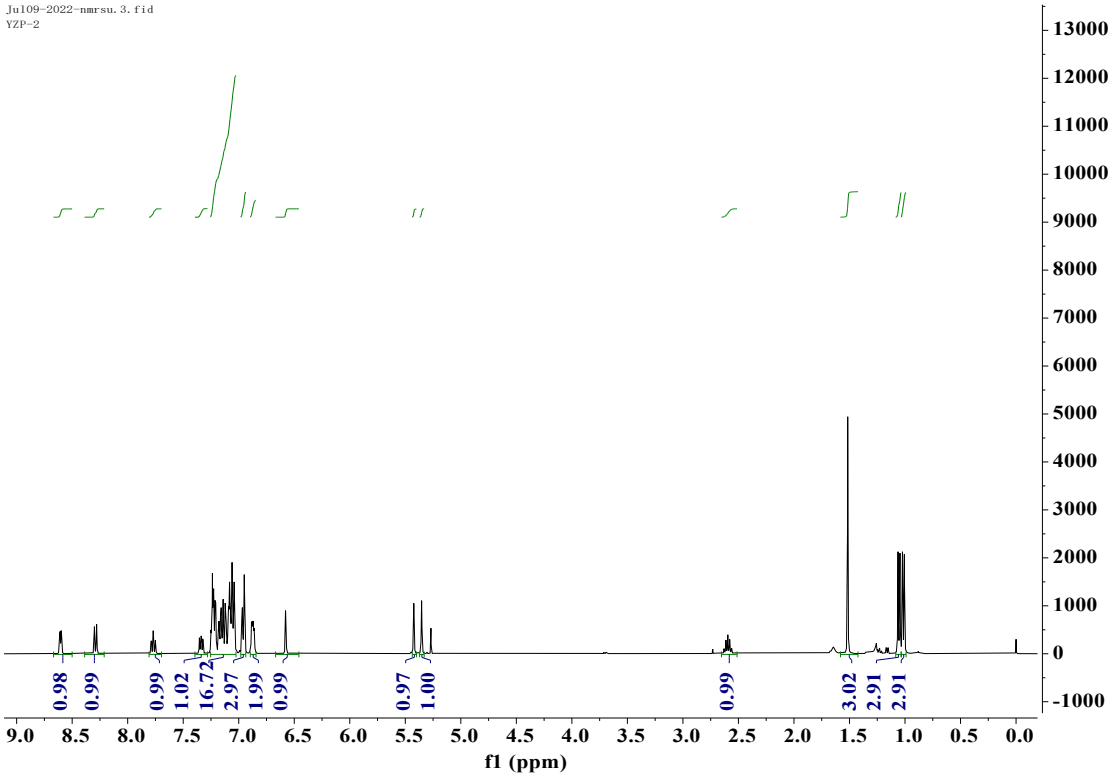


Figure S7. ^{1}H NMR spectrum of **L3** in $CDCl_3$.

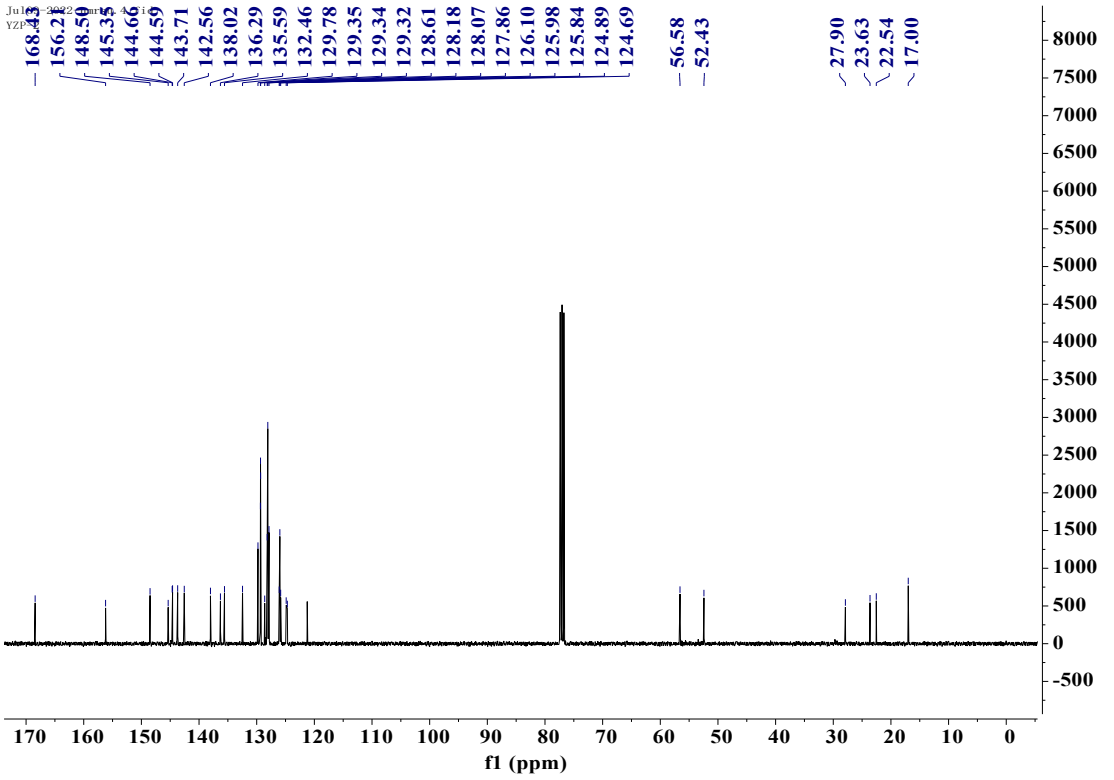


Figure S8. ^{13}C NMR spectrum of **L3** in $CDCl_3$.

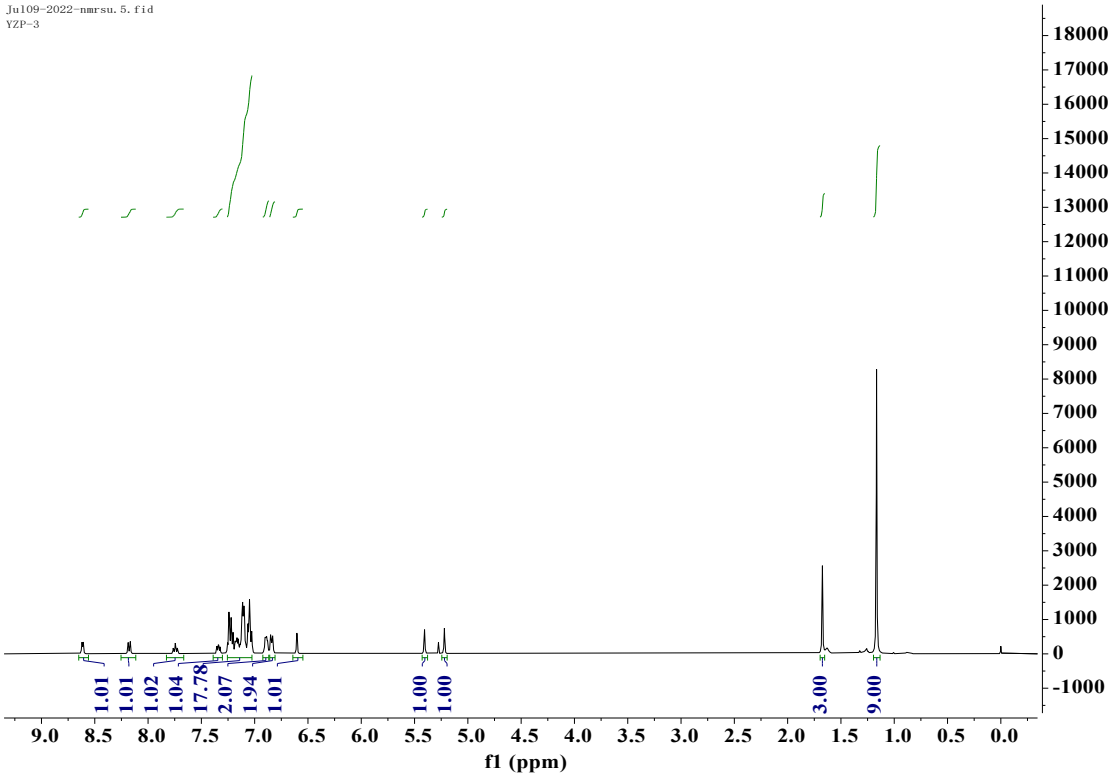


Figure S9. ^{1}H NMR spectrum of **L4** in $CDCl_3$.

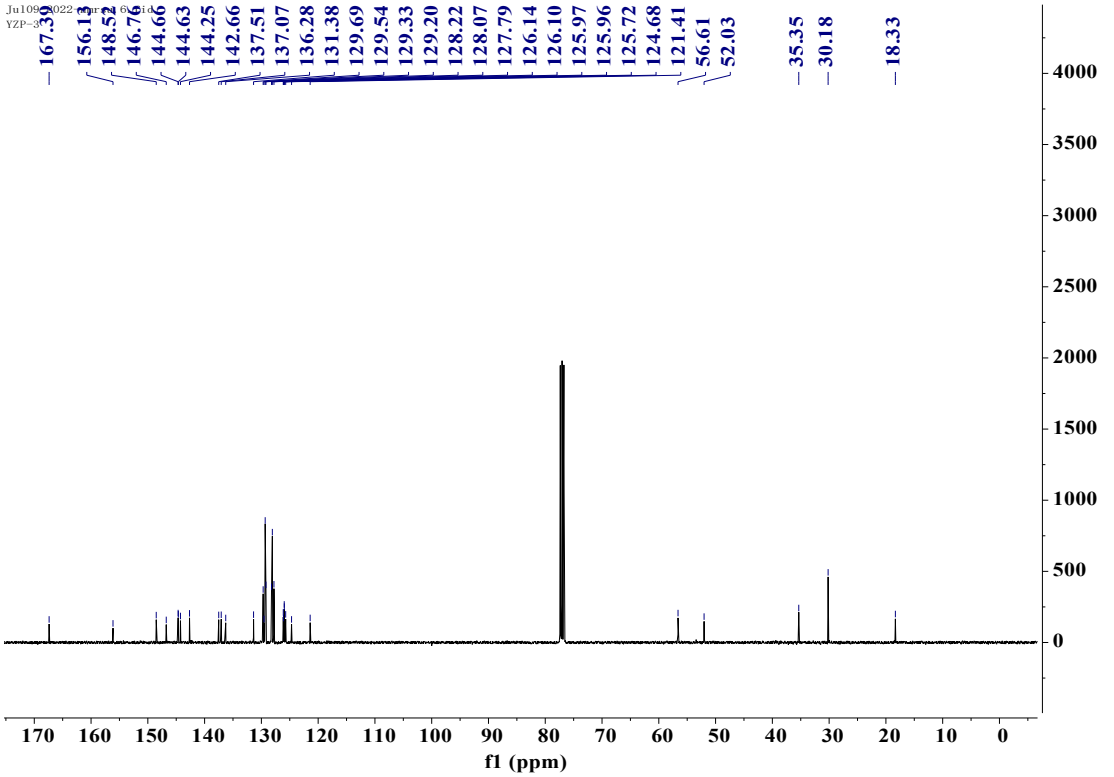


Figure S10. ^{13}C NMR spectrum of **L4** in $CDCl_3$.

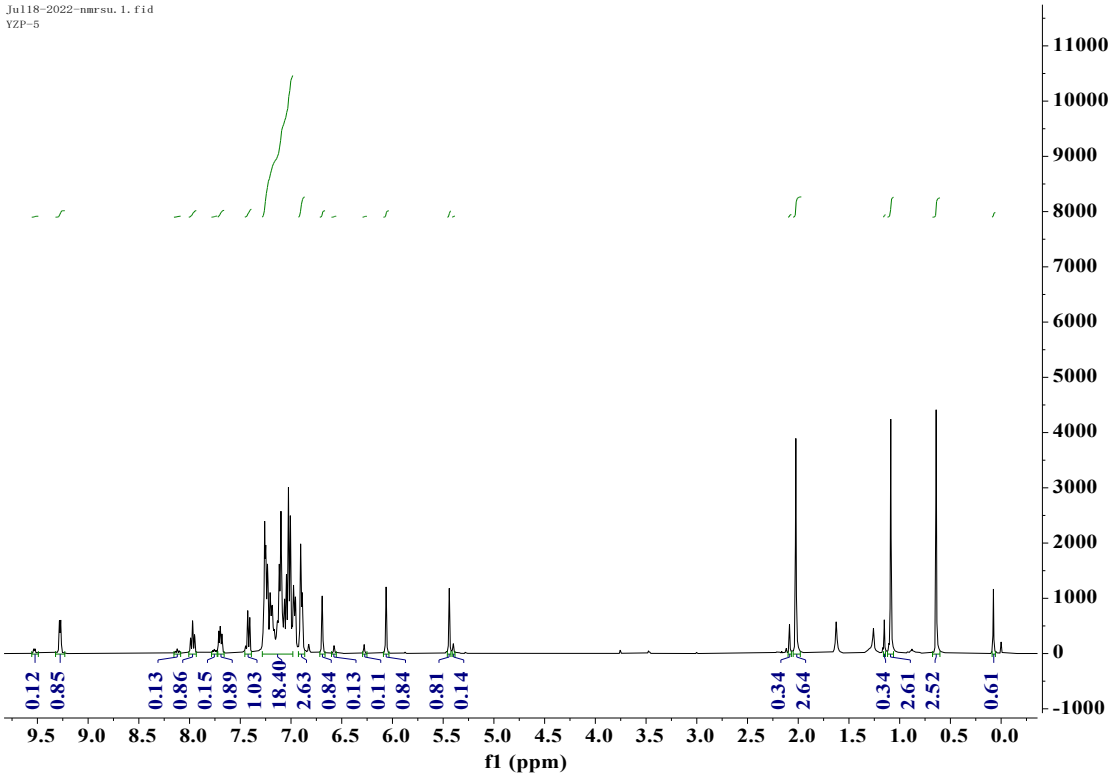


Figure S11. ^{1}H NMR spectrum of **Pd1** in $CDCl_3$.

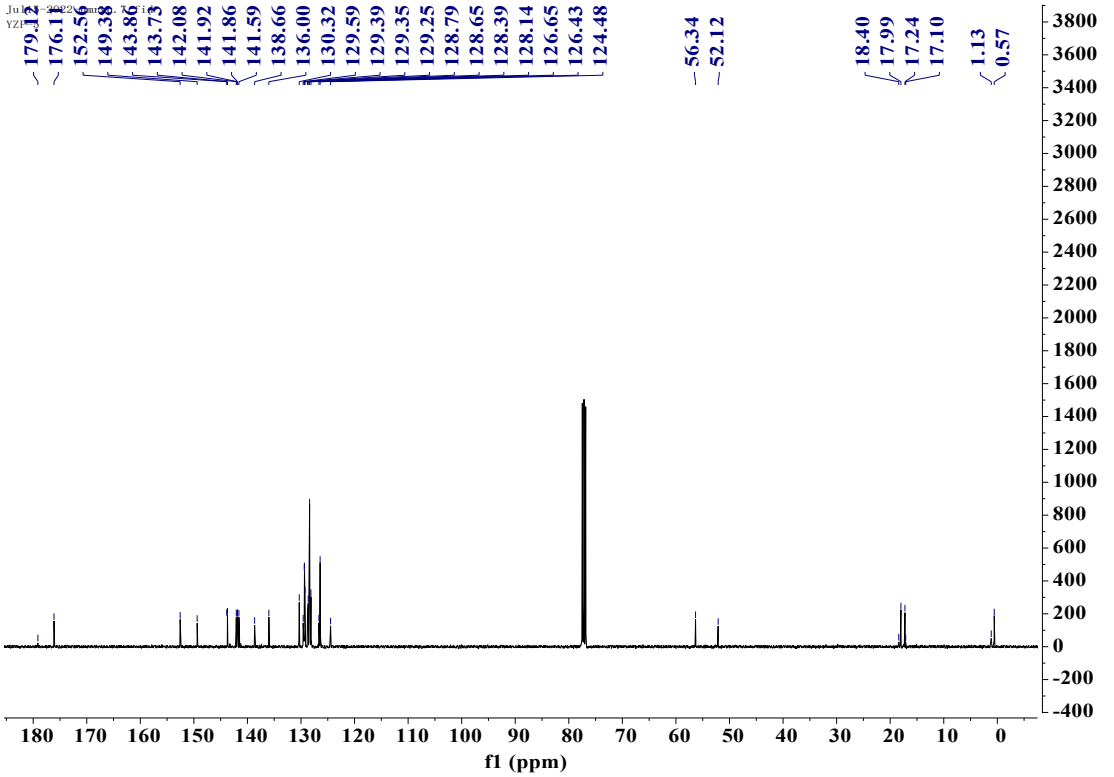


Figure S12. ^{13}C NMR spectrum of **Pd1** in $CDCl_3$.

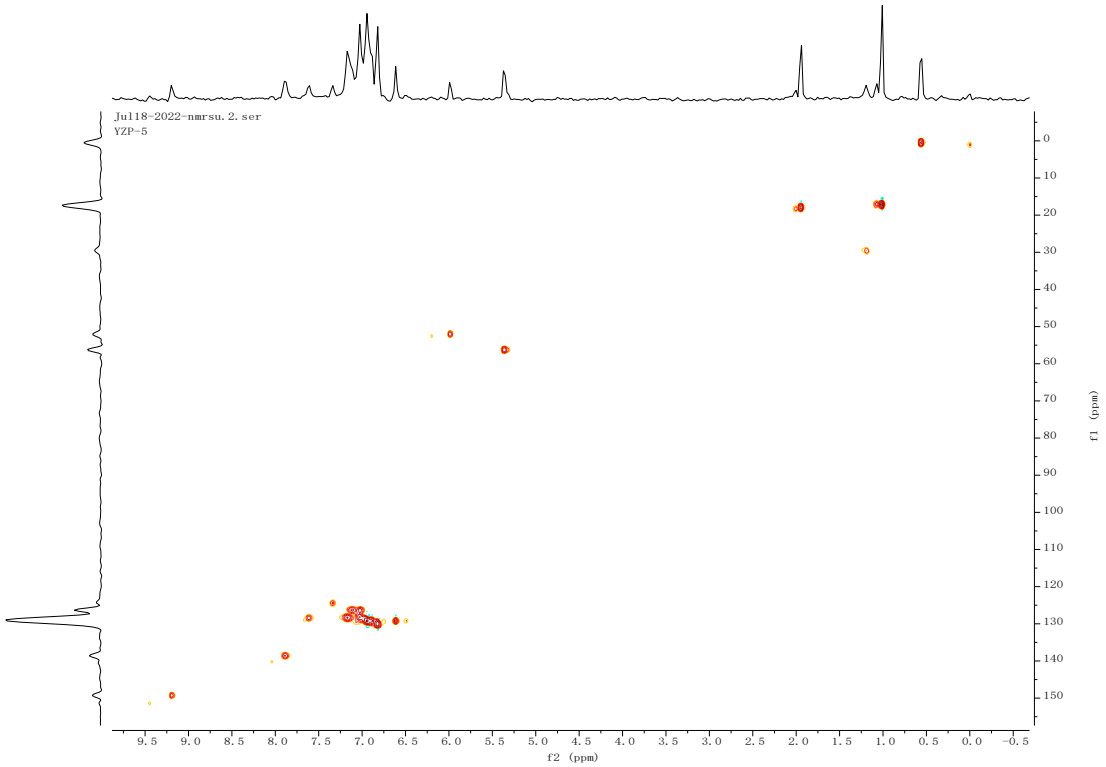


Figure S13. ^{1}H -^{13}C HSQC NMR spectrum of **Pd1** in $CDCl_3$.

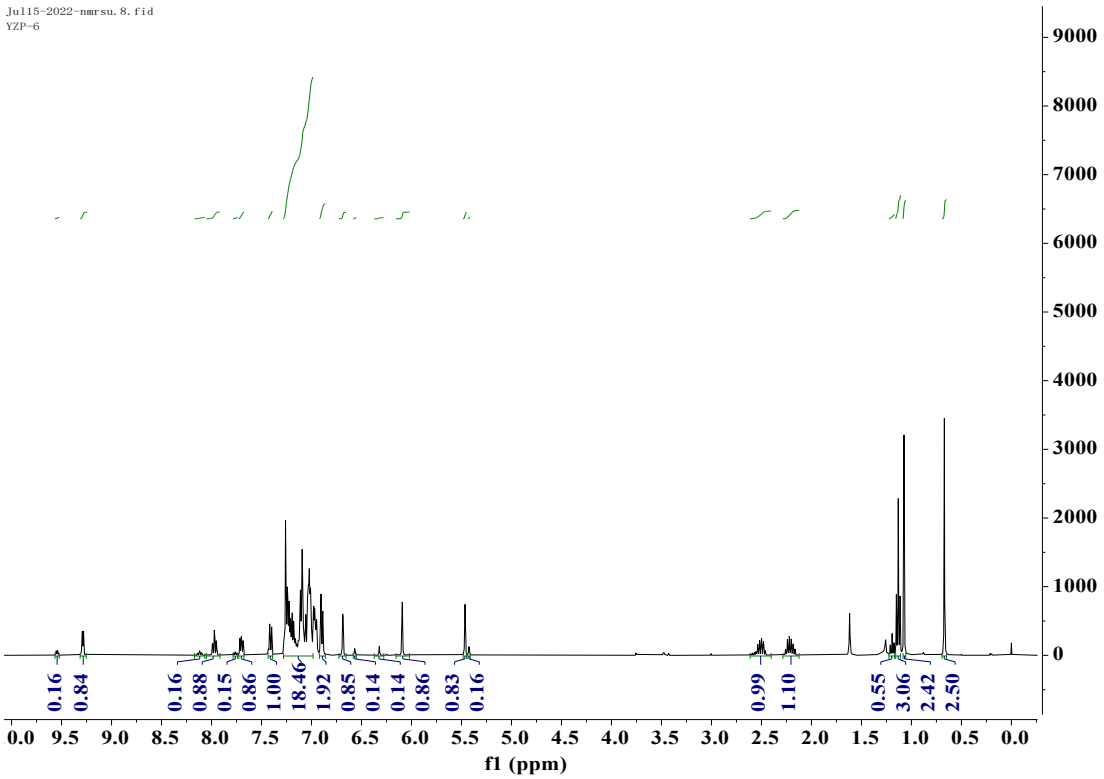


Figure S14. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

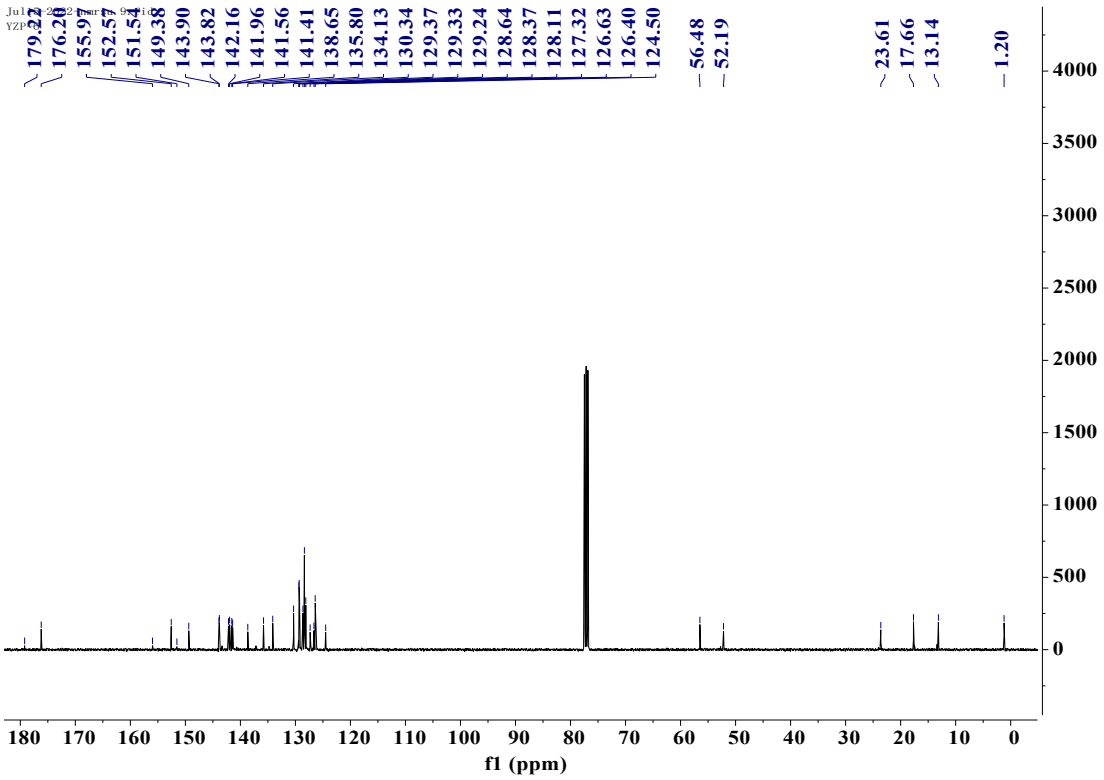


Figure S15. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

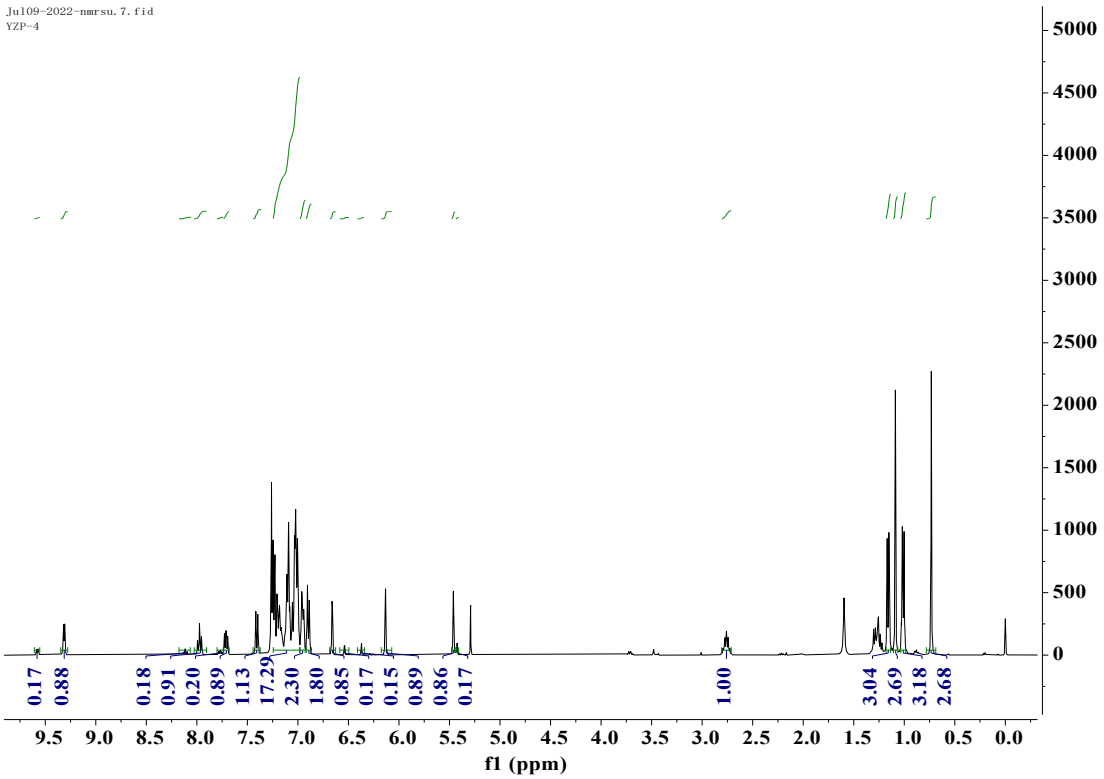


Figure S16. ^{1}H NMR spectrum of **Pd3** in $CDCl_3$.

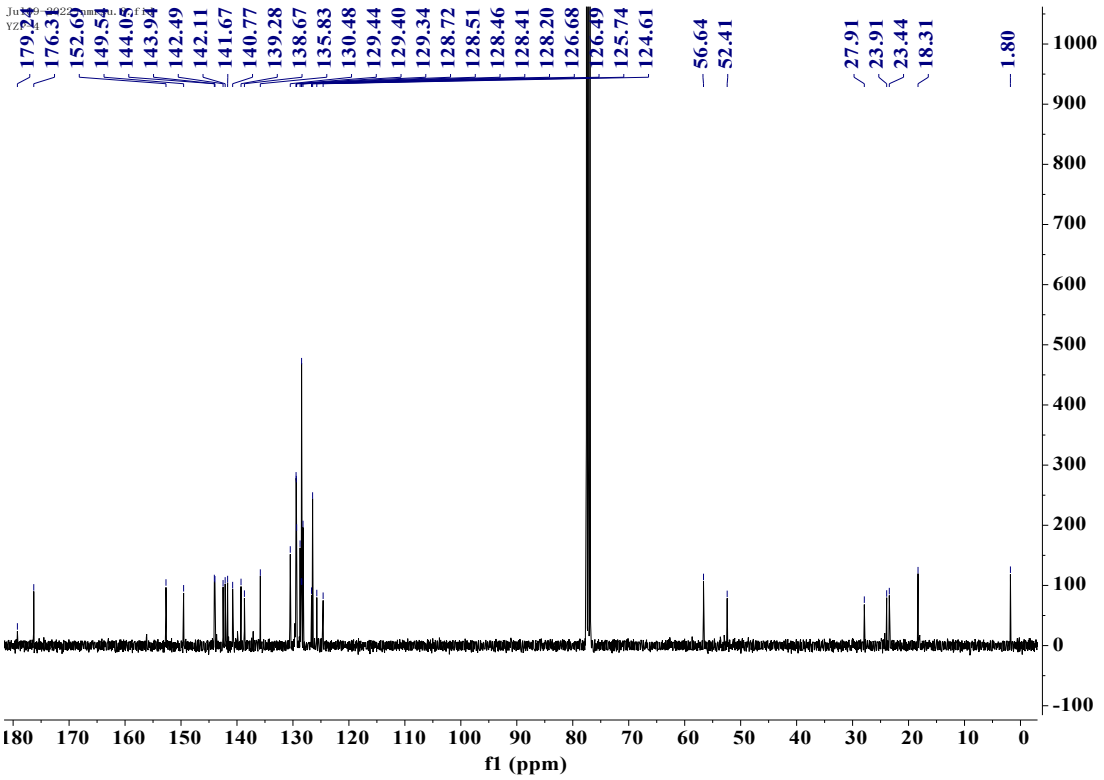


Figure S17. ^{13}C NMR spectrum of **Pd3** in $CDCl_3$.

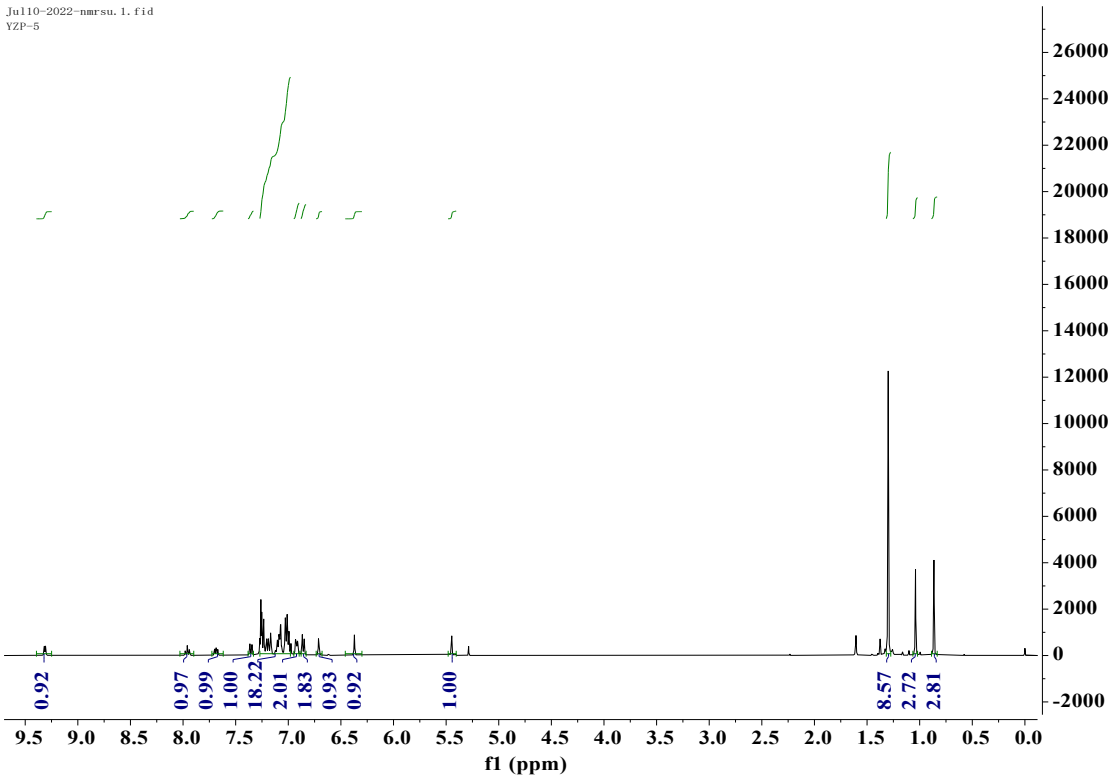


Figure S18. ^{1}H NMR spectrum of **Pd4** in $CDCl_3$.

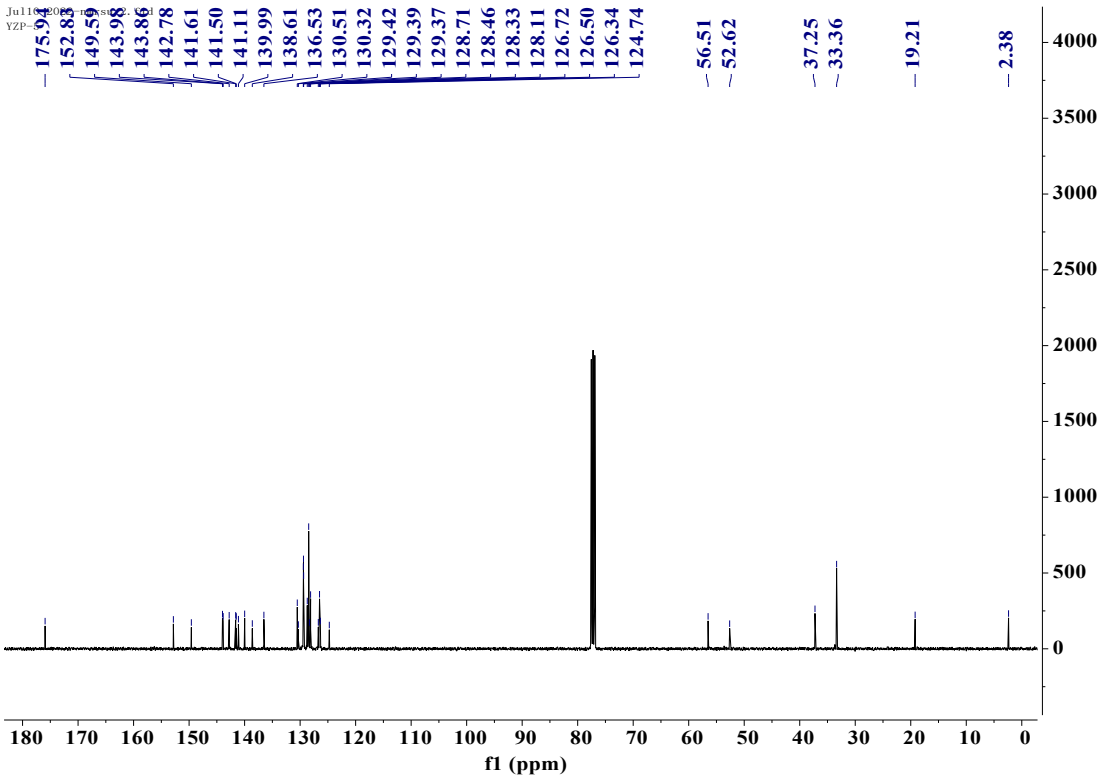


Figure S19. ^{13}C NMR spectrum of **Pd4** in $CDCl_3$.

2.2 MS of A4 and L1-L4.

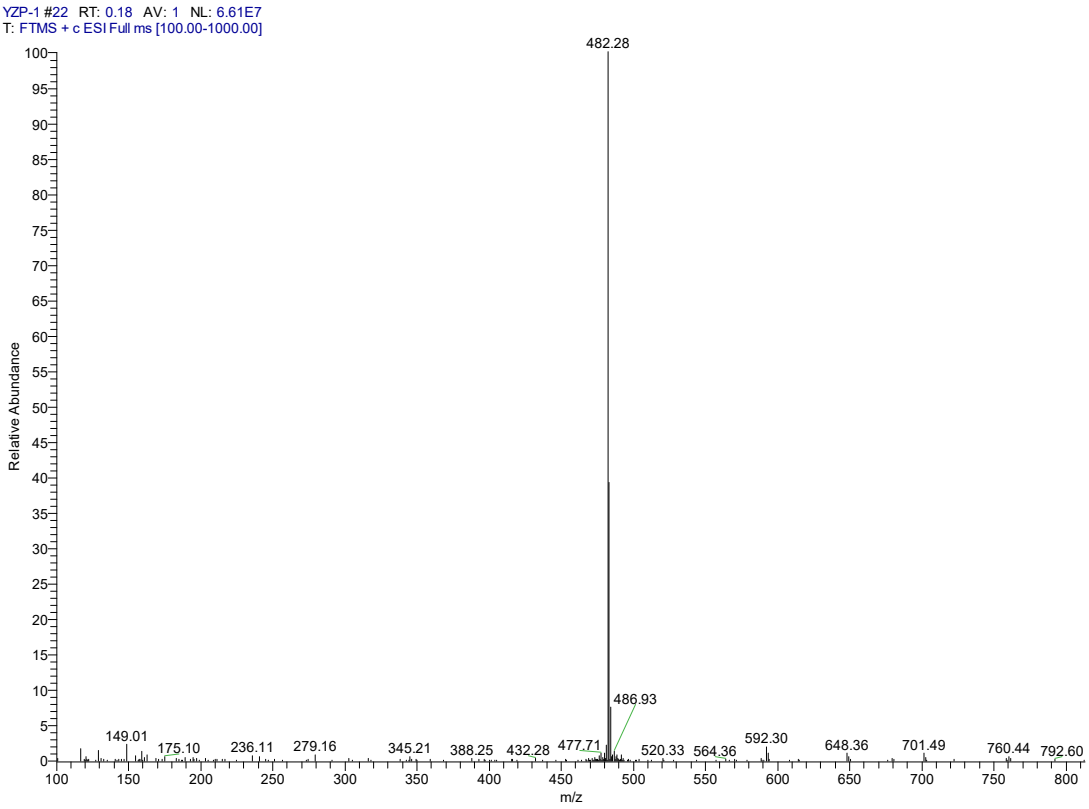


Figure S20. ESI-MS of **A4**.

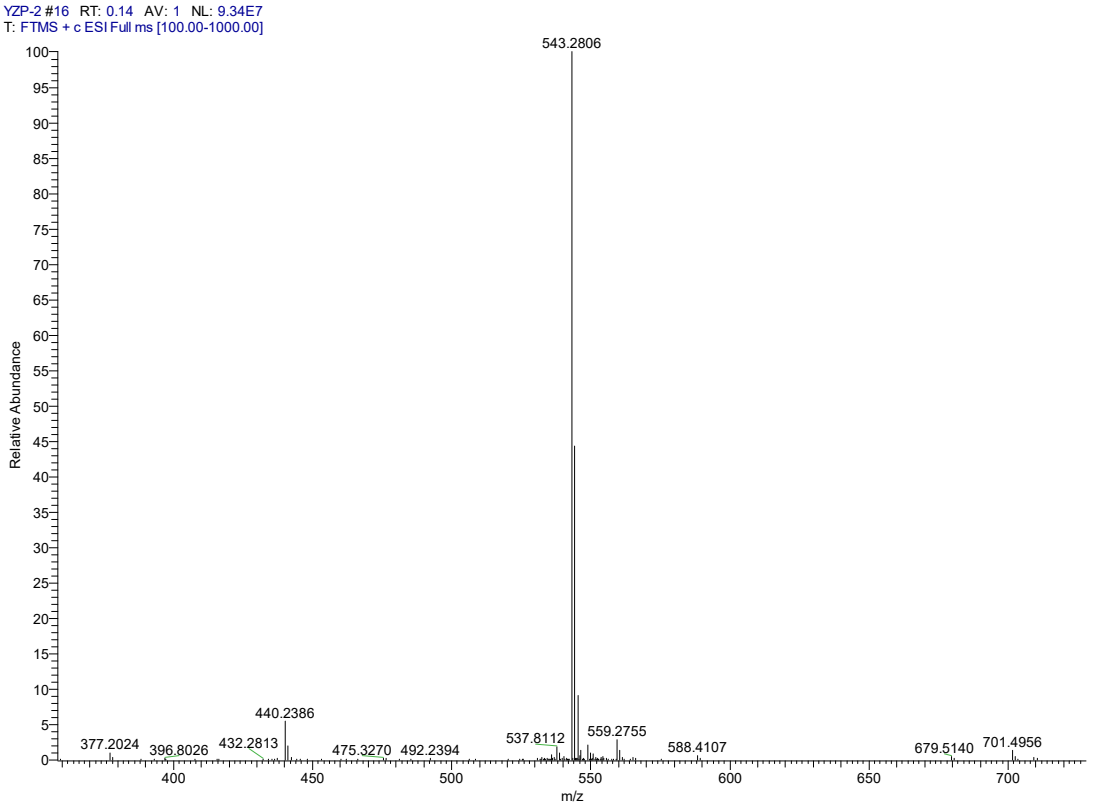


Figure S21. ESI-MS of **L1**.

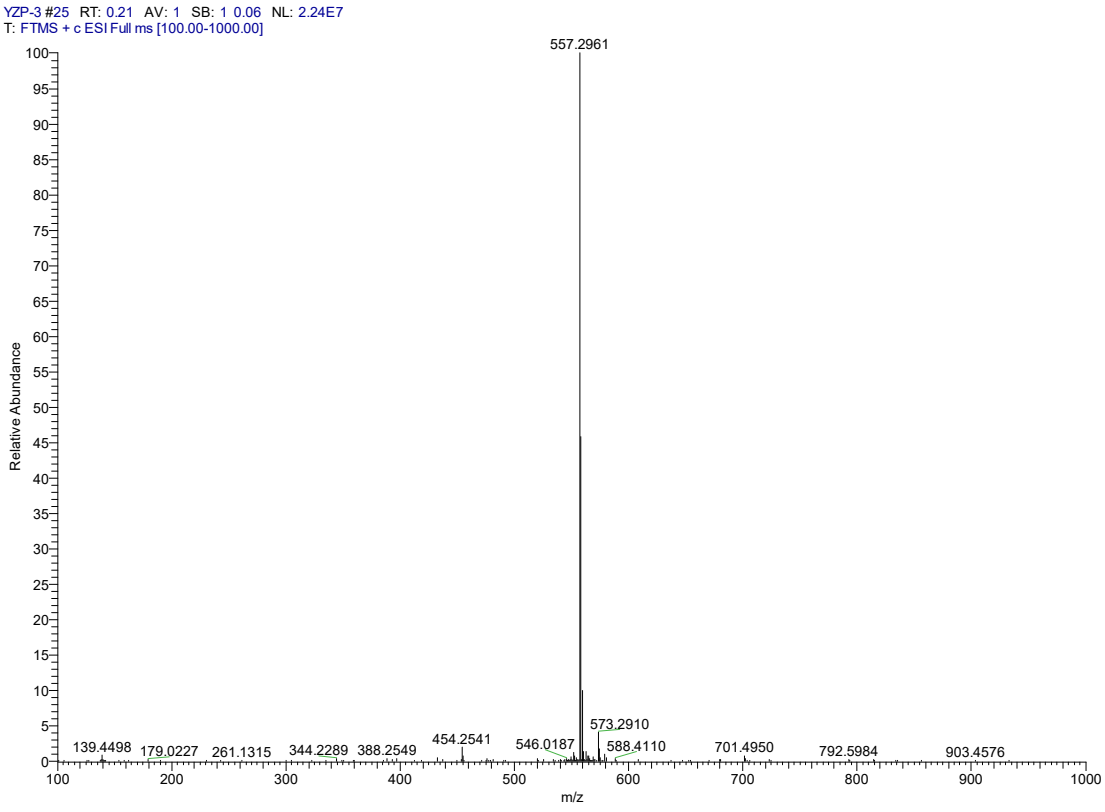


Figure S22. ESI-MS of **L2**.

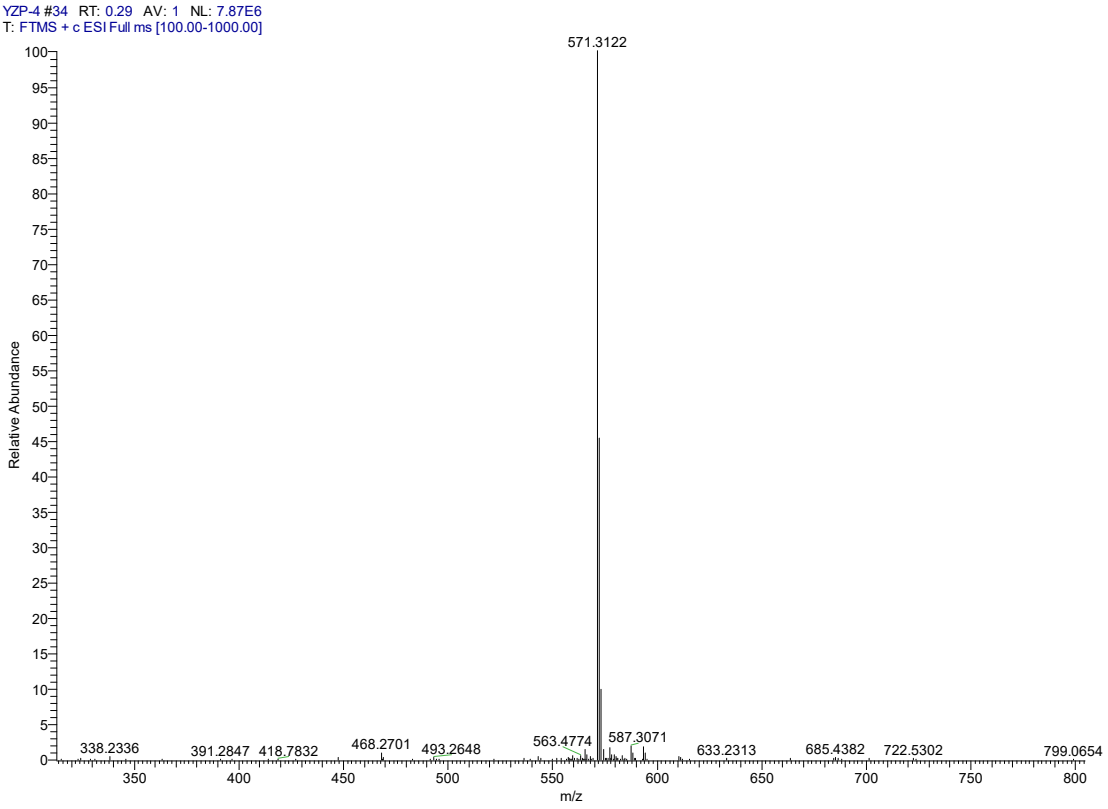


Figure S23. ESI-MS of **L3**.

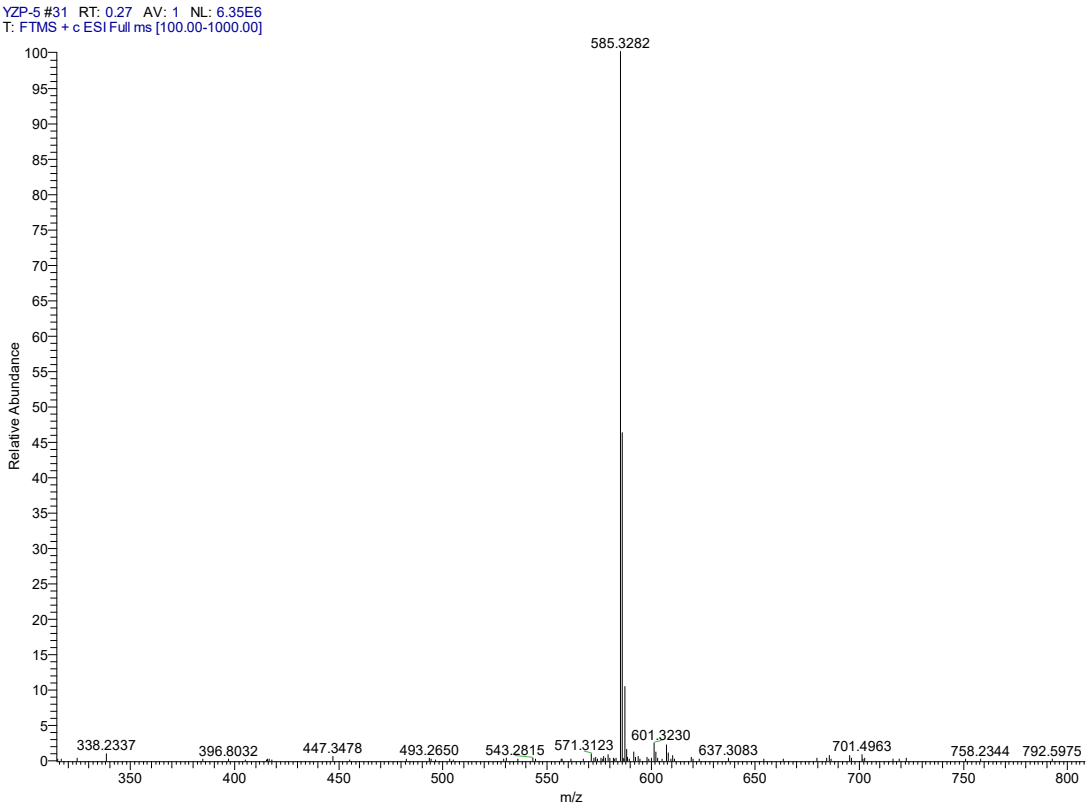


Figure S24. ESI-MS of **L4**.

2.3 ^{1}H and ^{13}C NMR of Representative Polyethylene and E-MA Copolymers.

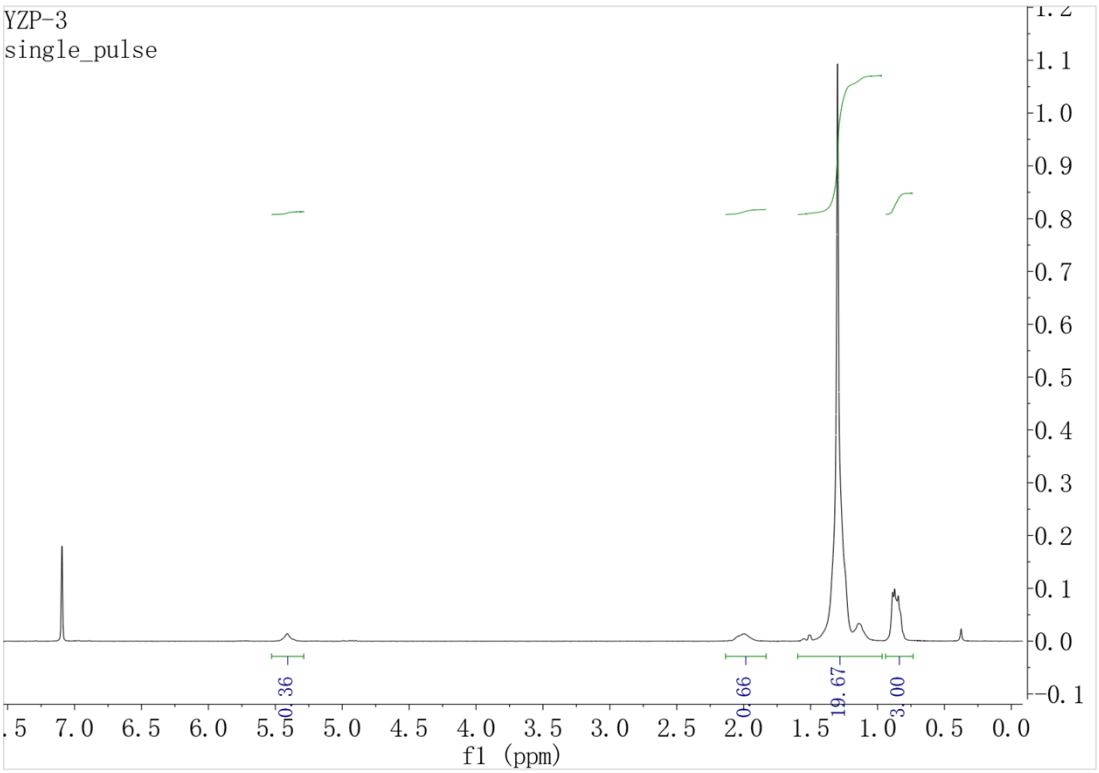


Figure S25. ^{1}H NMR spectrum of the polyethylene from table 1, entry 1.

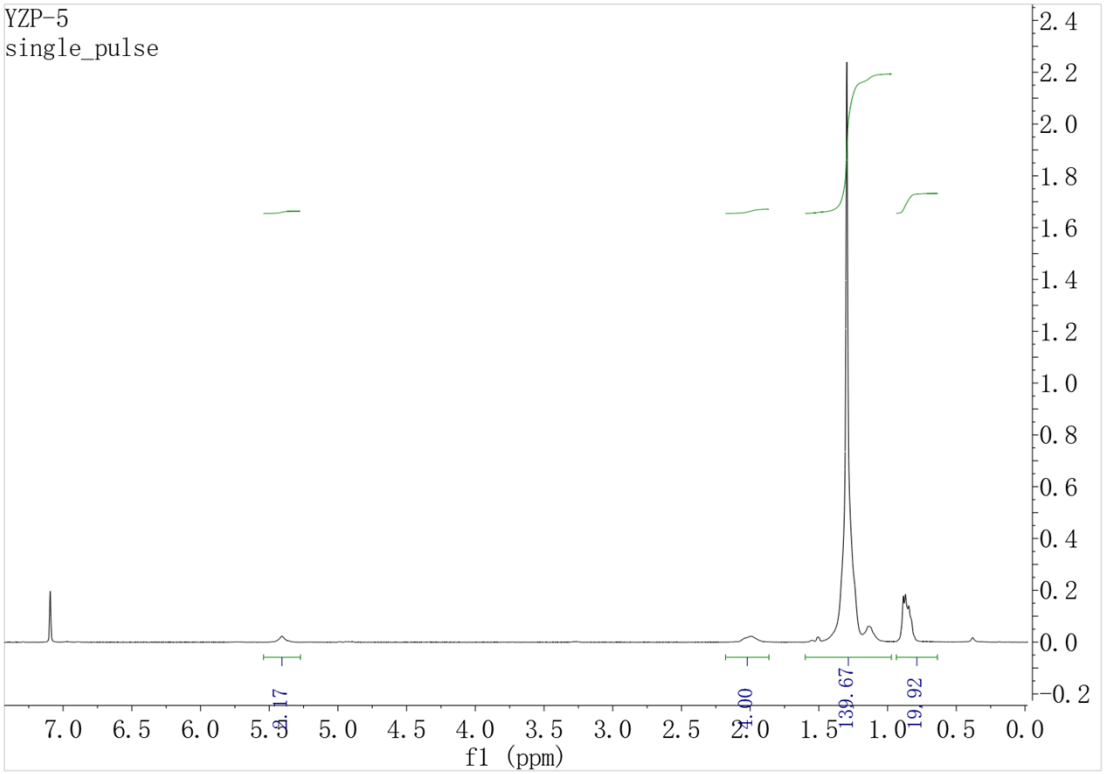


Figure S26. ^{1}H NMR spectrum of the polyethylene from table 1, entry 3.

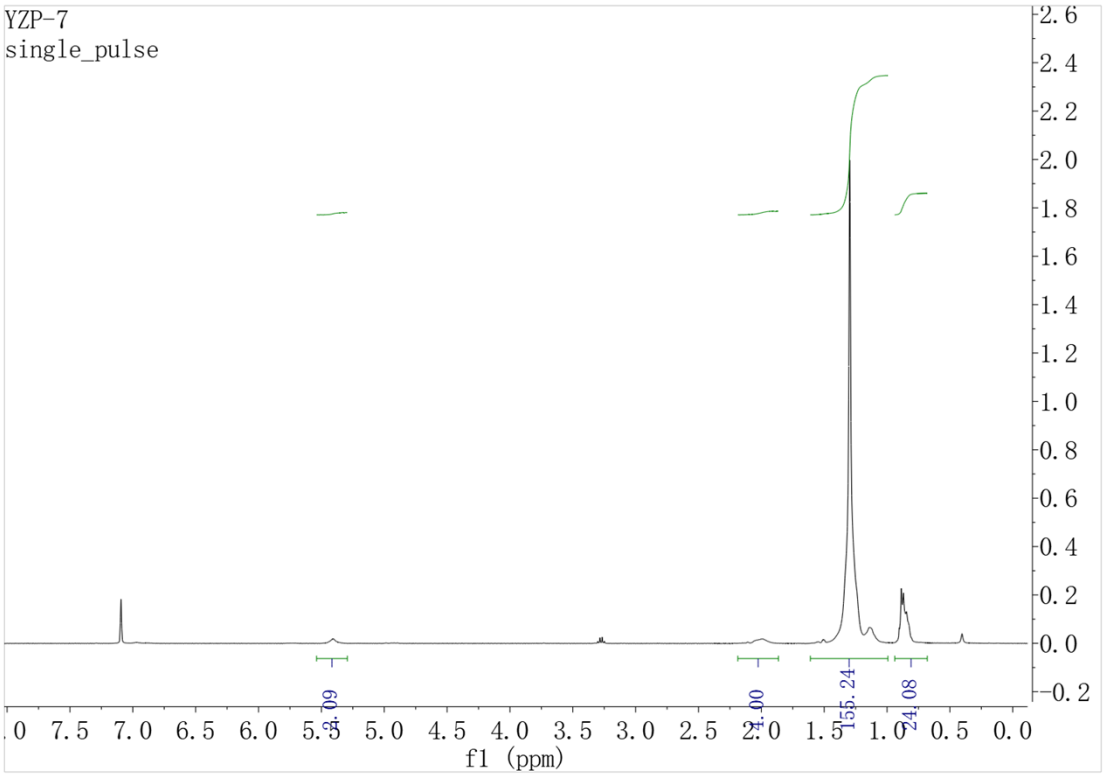


Figure S27. ^{1}H NMR spectrum of the polyethylene from table 1, entry 5.

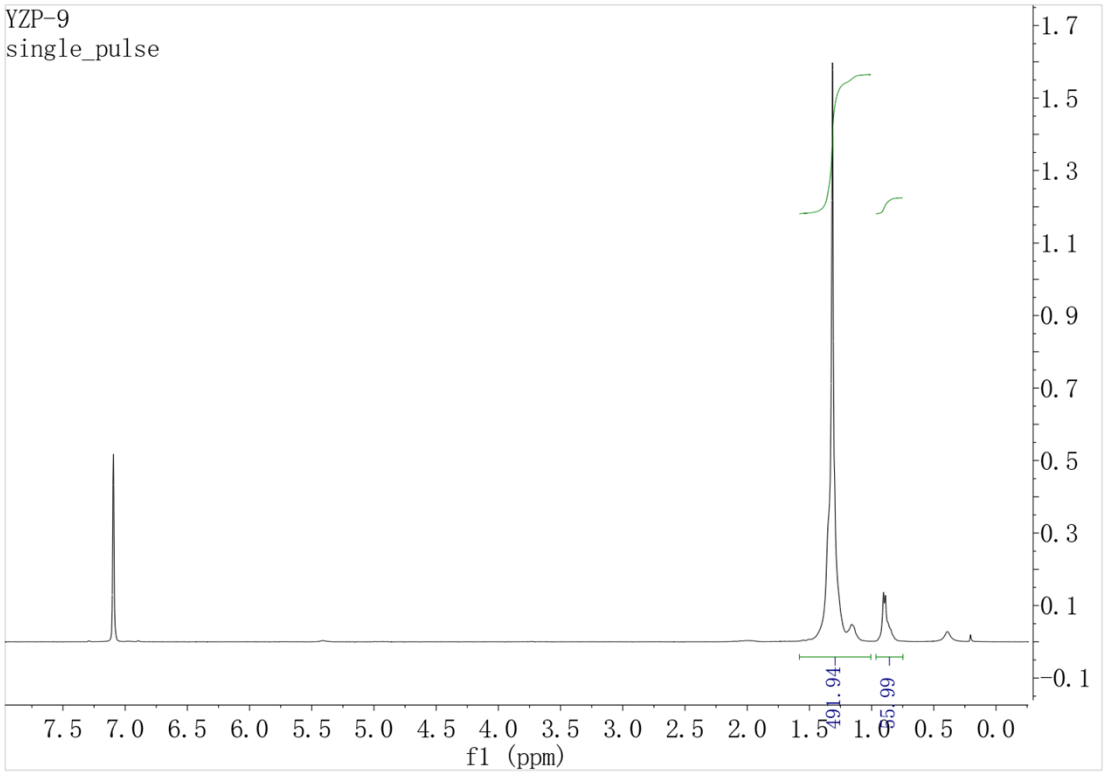


Figure S28. ^{1}H NMR spectrum of the polyethylene from table 1, entry 7.

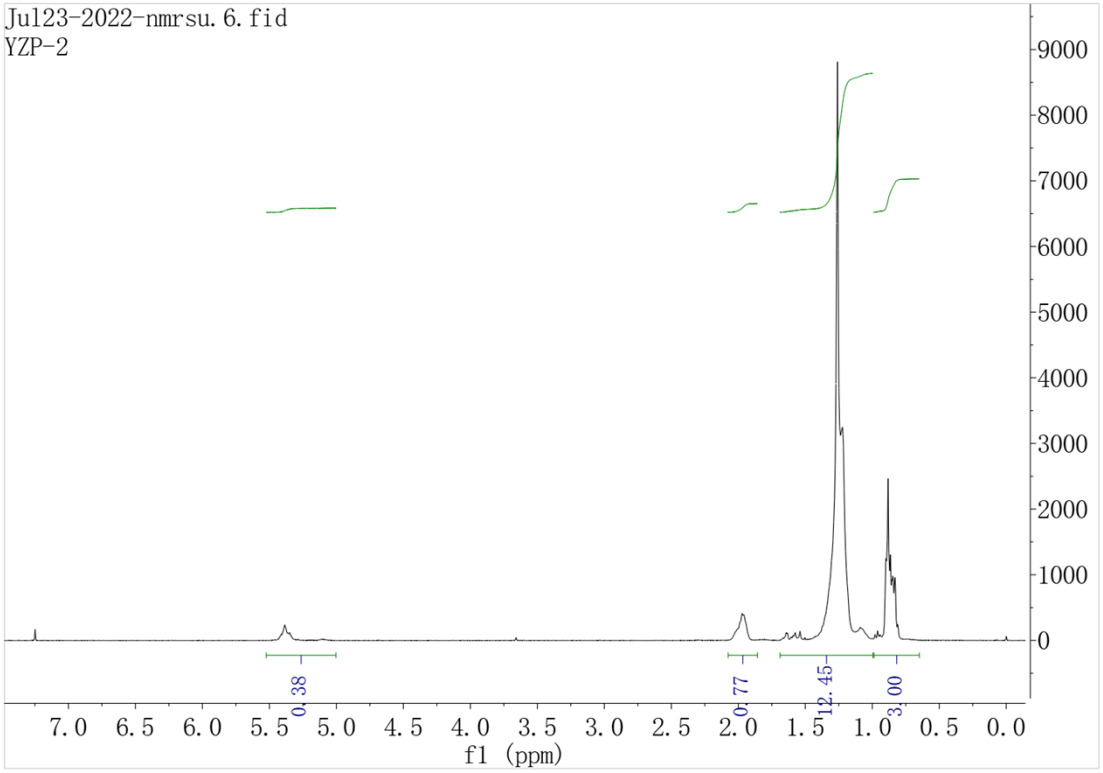


Figure S29. ^{1}H NMR spectrum of the polyethylene from table 2, entry 1.

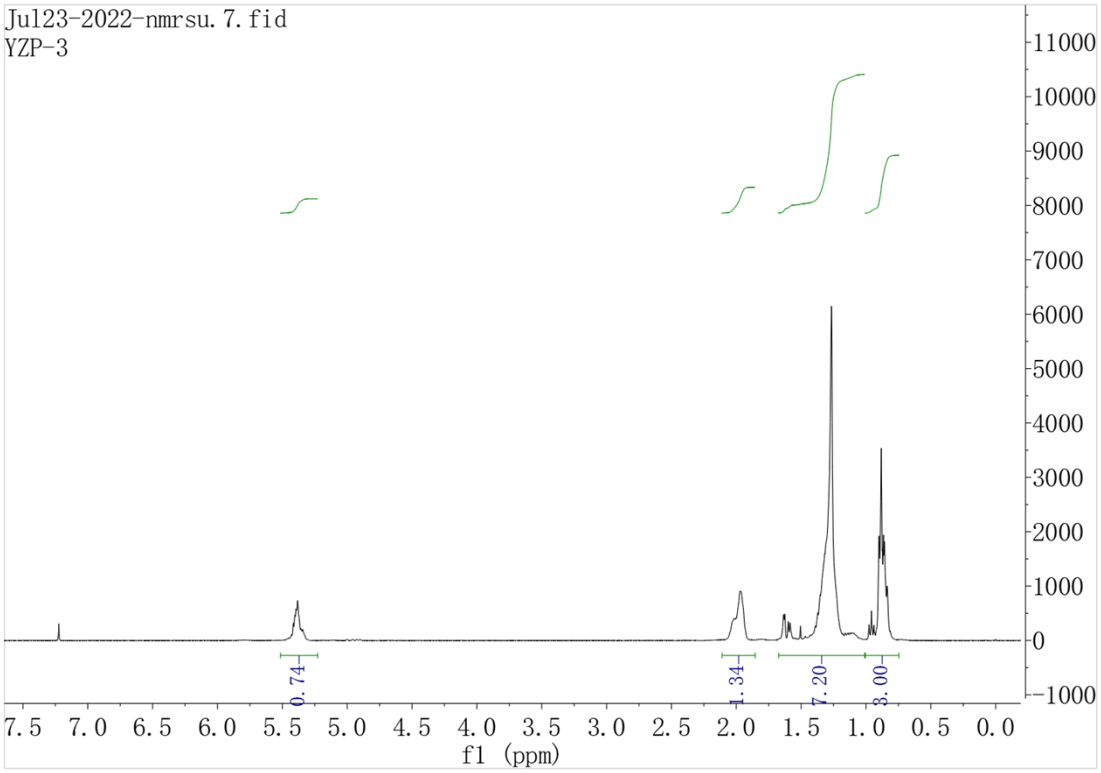


Figure S30. ^{1}H NMR spectrum of the polyethylene from table 2, entry 2.

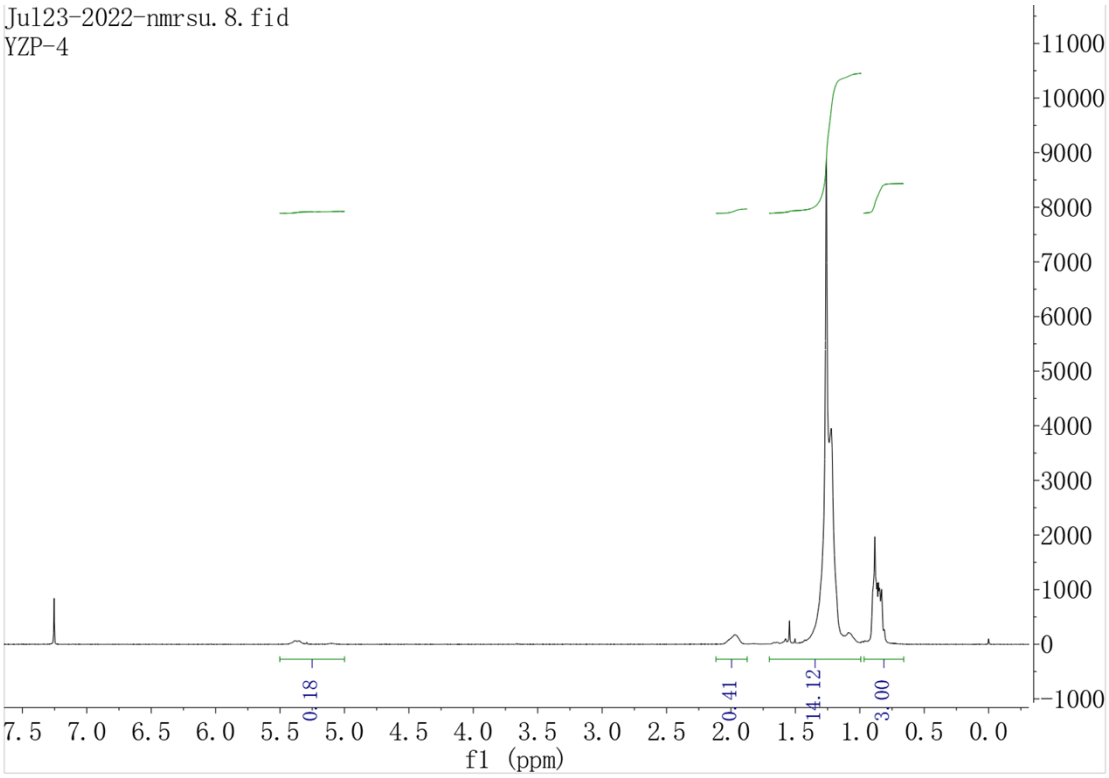


Figure S31. ^{1}H NMR spectrum of the polyethylene from table 2, entry 3.

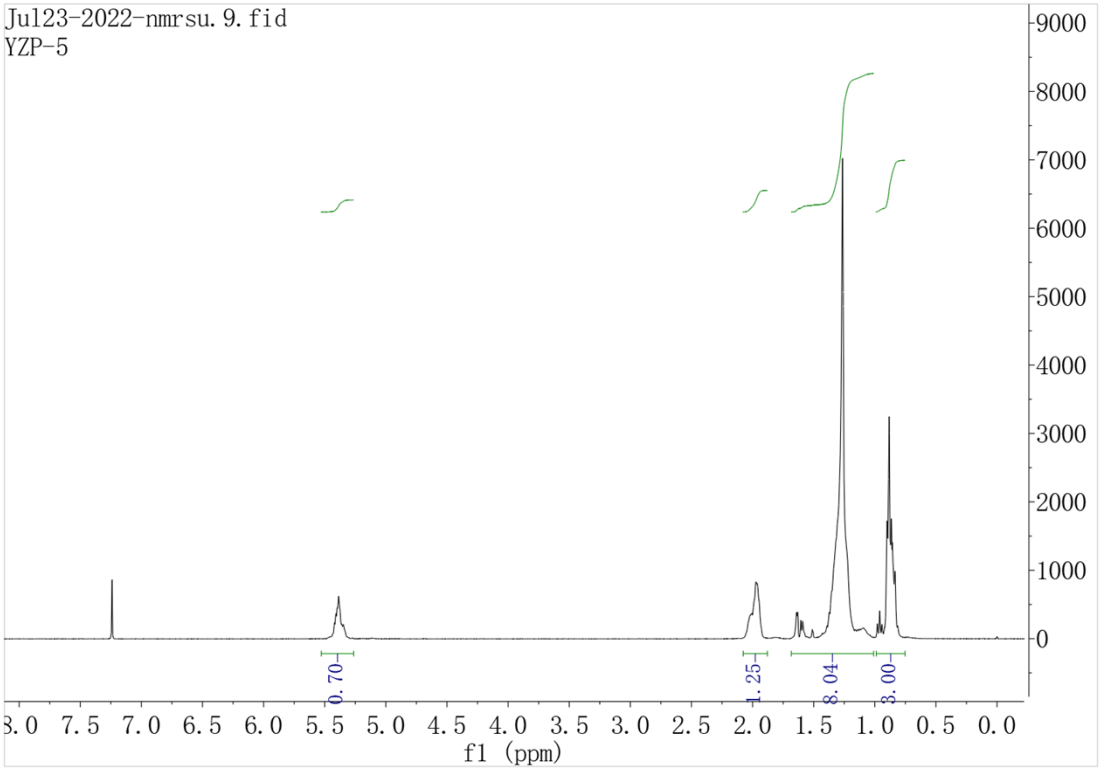


Figure S32. ^{1}H NMR spectrum of the polyethylene from table 2, entry 4.

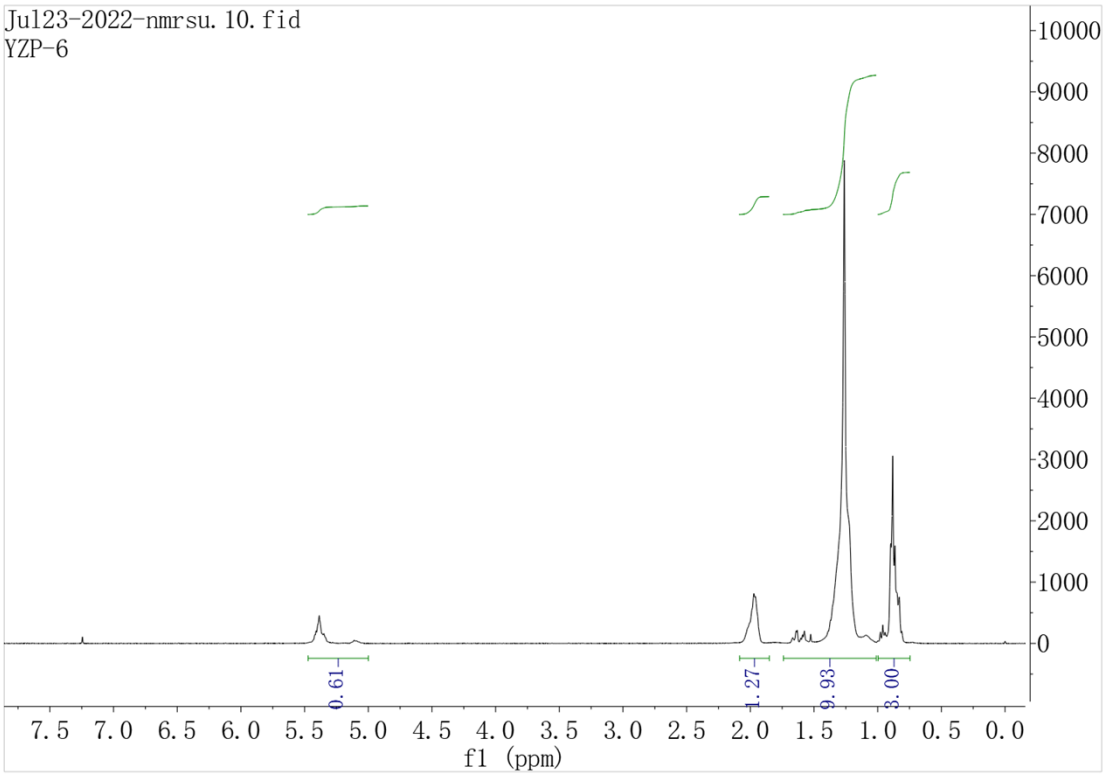


Figure S33. ^{1}H NMR spectrum of the polyethylene from table 2, entry 5.

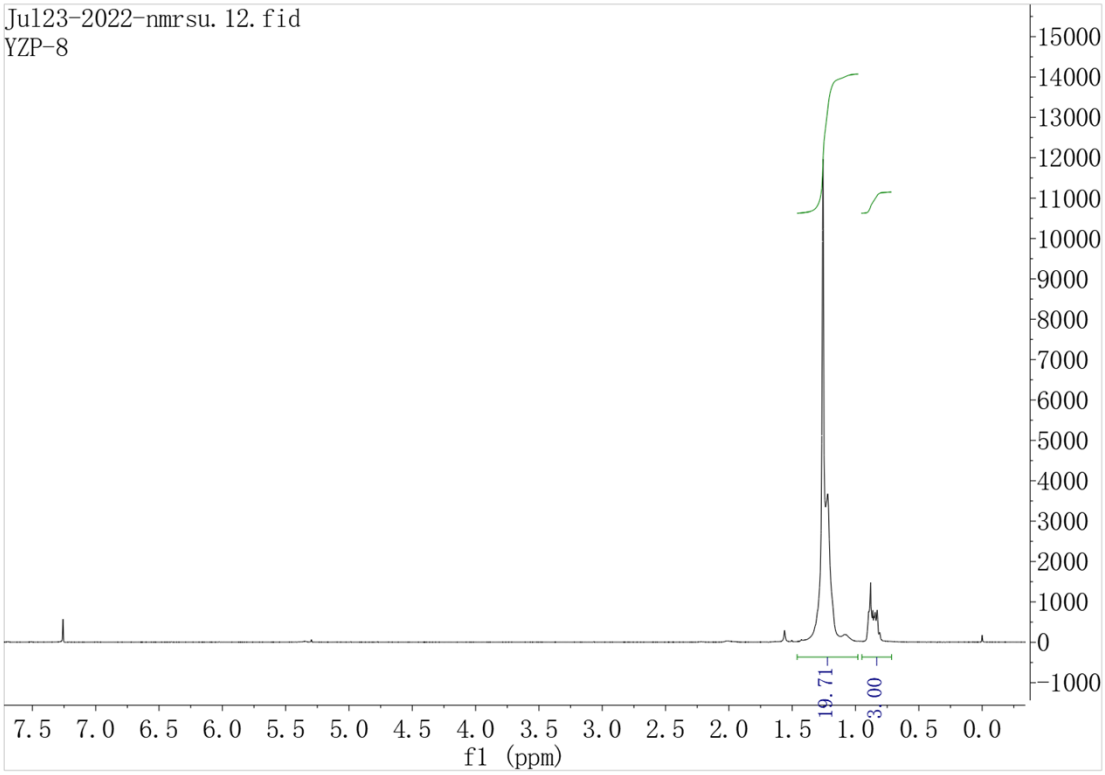


Figure S34. ^{1}H NMR spectrum of the polyethylene from table 2, entry 7.

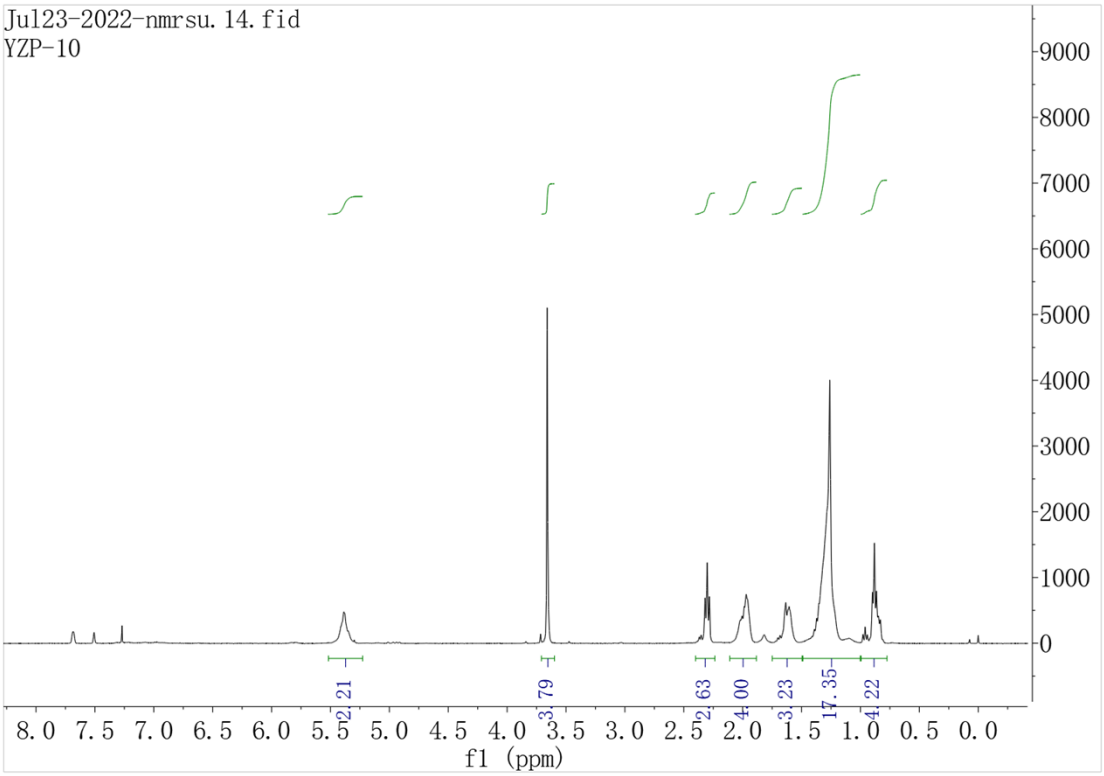


Figure S35. ^{1}H NMR spectrum of the polyethylene from table 3, entry 1.

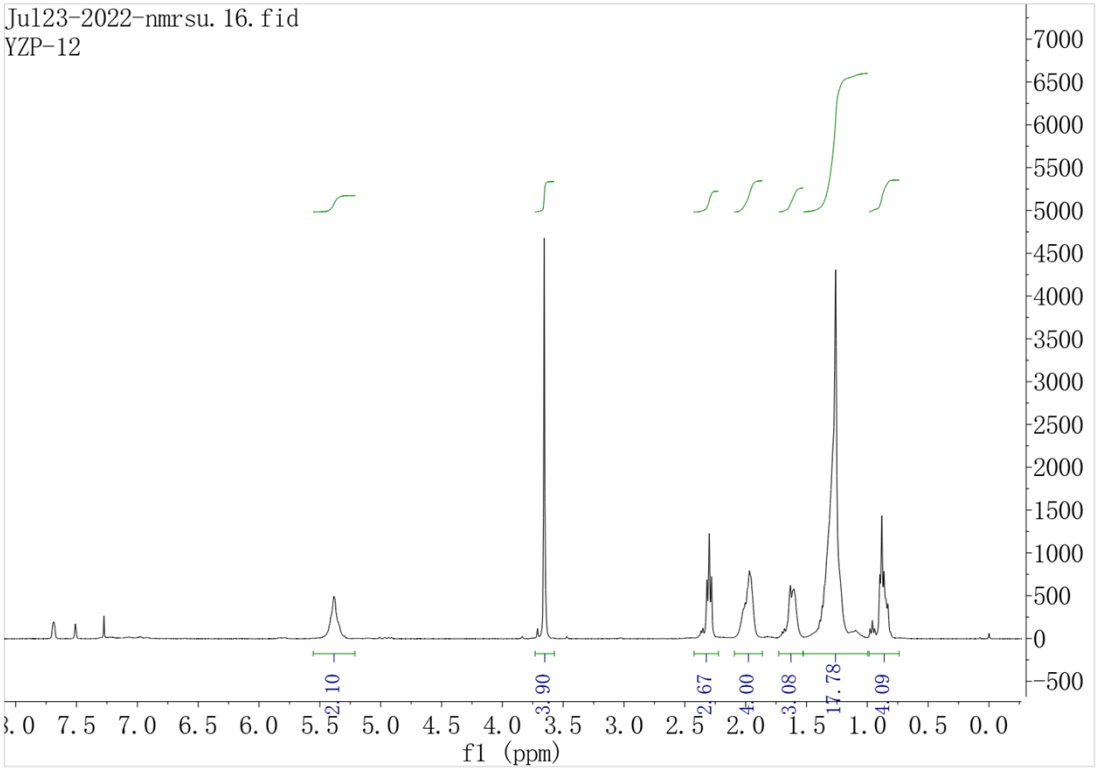


Figure S36. ^{1}H NMR spectrum of the polyethylene from table 3, entry 3.

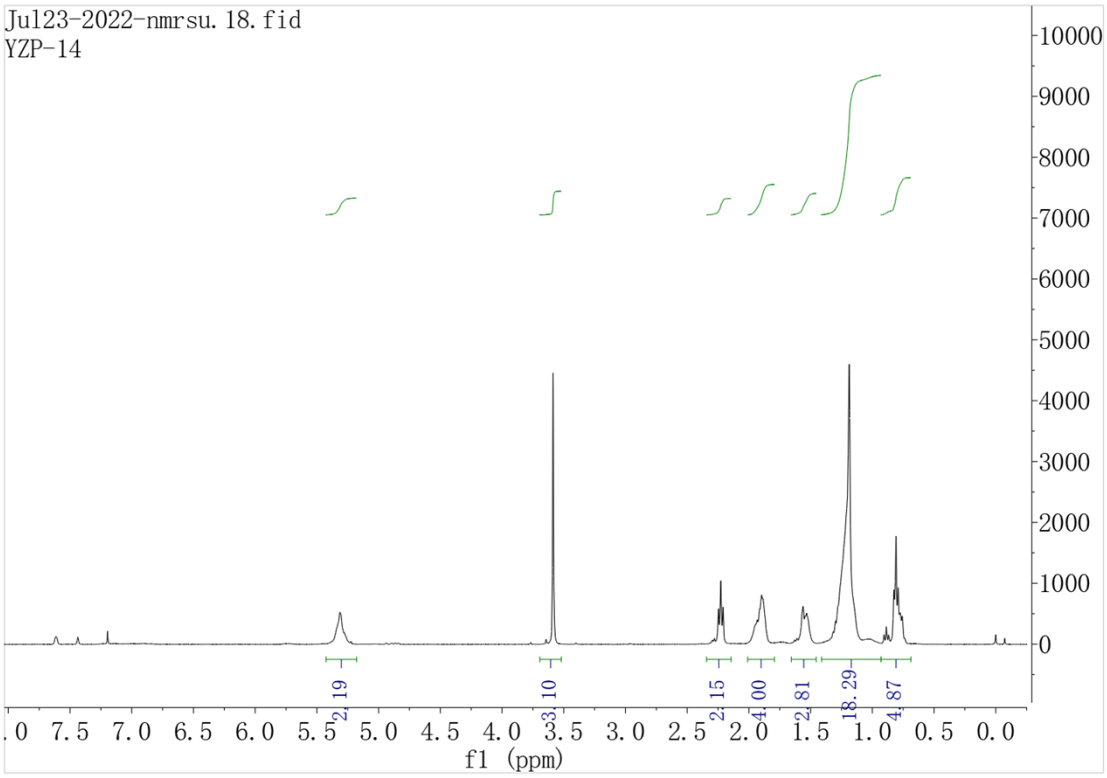


Figure S37. ^{1}H NMR spectrum of the polyethylene from table 3, entry 5.

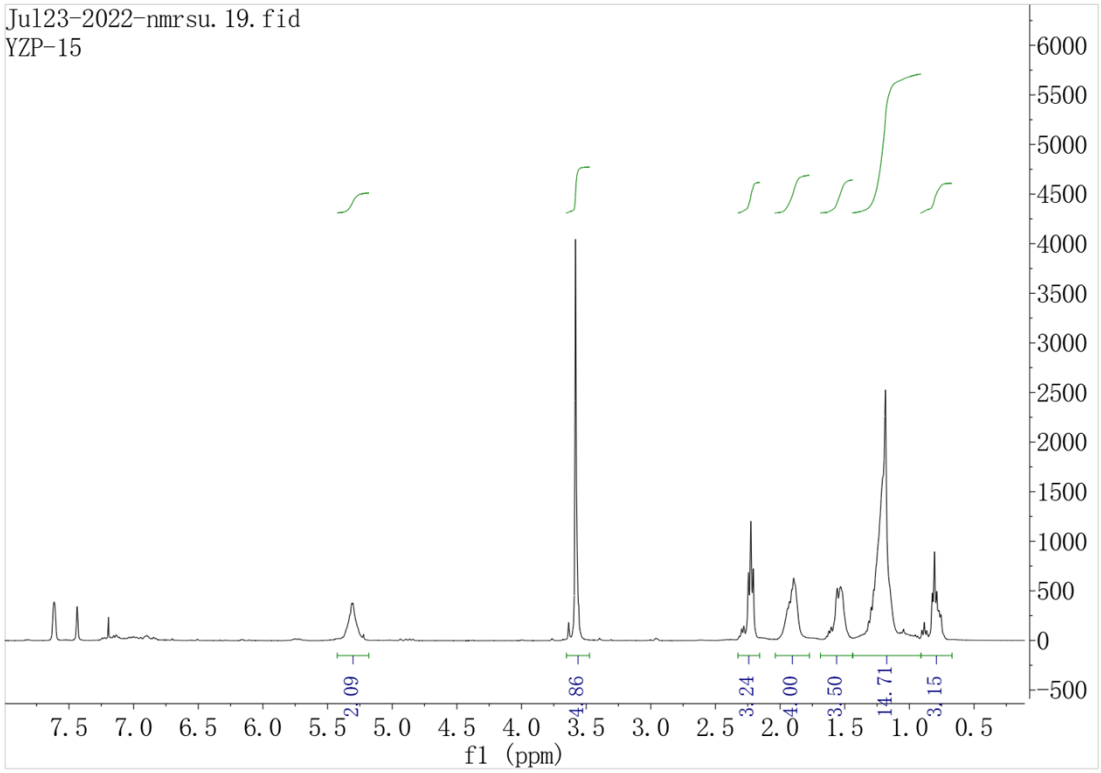


Figure S38. ^{1}H NMR spectrum of the polyethylene from table 3, entry 6.

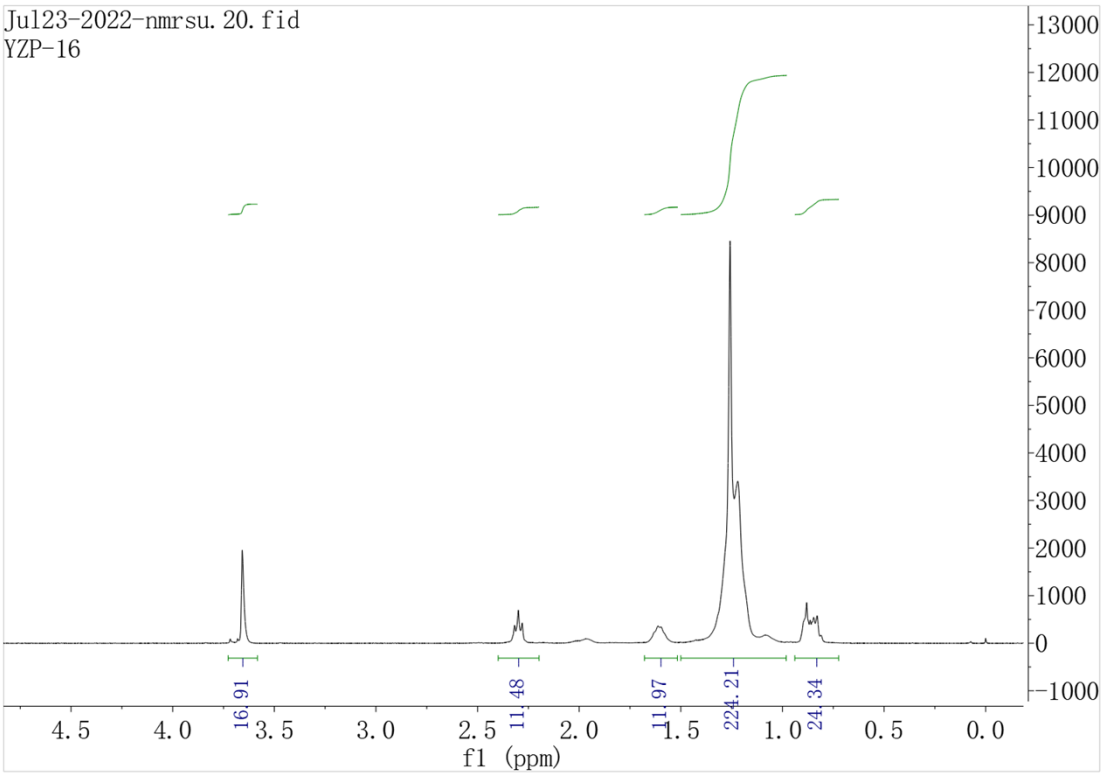
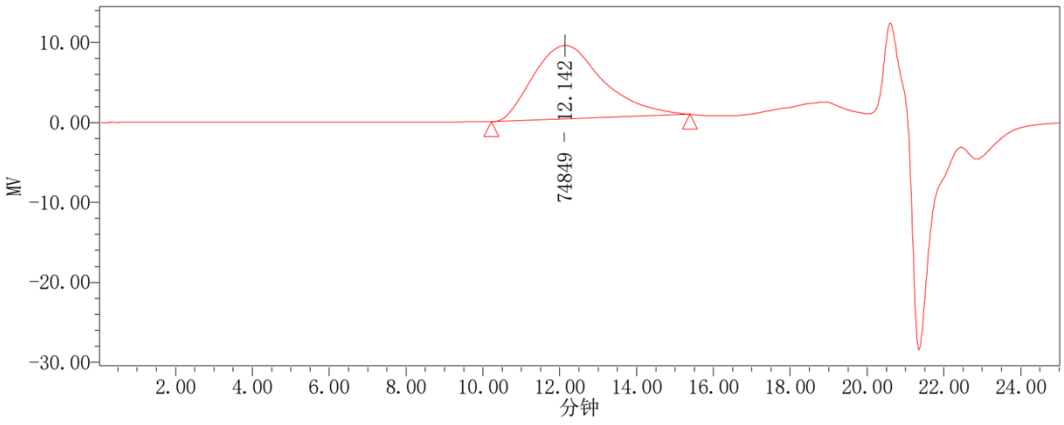


Figure S39. ^{1}H NMR spectrum of the polyethylene from table 3, entry 7.

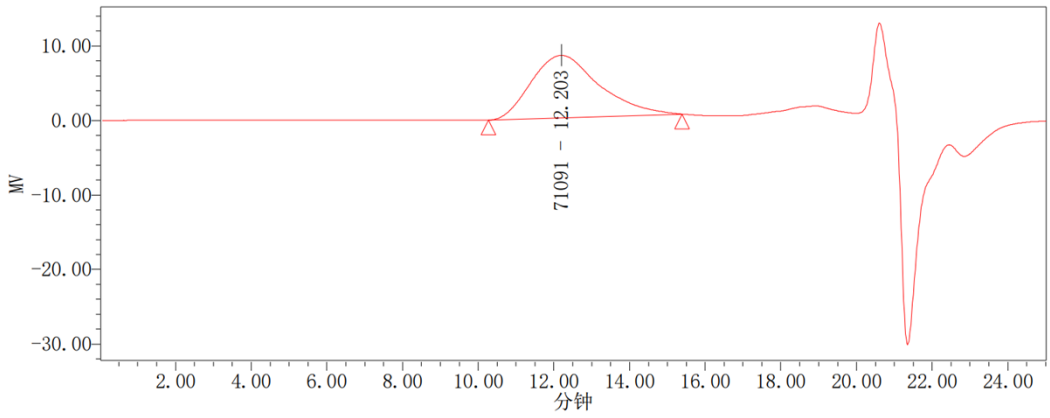
2.5 GPC and GC-MS of Representative Polymers and Copolymers.



GPC 结果

	分布名	Mn (道尔顿)	Mw (道尔顿)	MP	Mz (道尔顿)	Mz+1 (道尔顿)	多分散性	MW 标记 1 (道尔顿)	MW 标记 2 (道尔顿)
1		51276	84089	74849	126292	171460	1.639940		

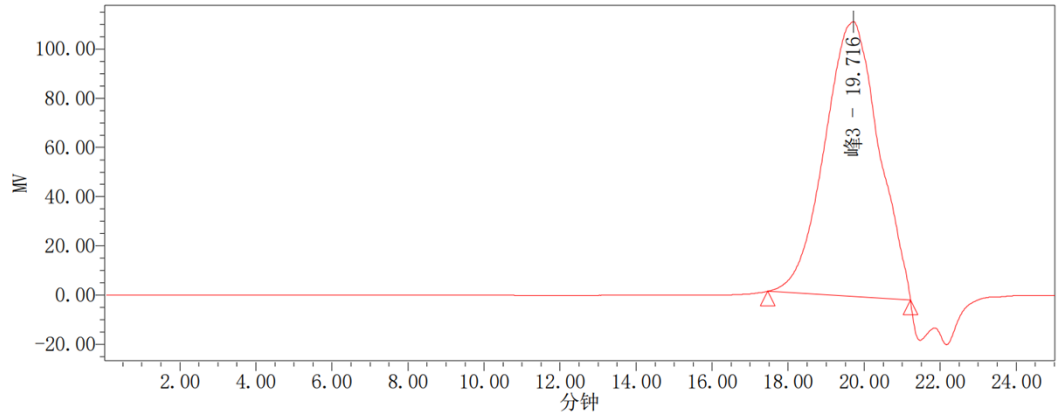
Figure S40. GPC of the polymer from table 1, entry 7.



GPC 结果

	分布名	Mn (道尔顿)	Mw (道尔顿)	MP	Mz (道尔顿)	Mz+1 (道尔顿)	多分散性	MW 标记 1 (道尔顿)	MW 标记 2 (道尔顿)
1		48508	77967	71091	116326	158982	1.607309		

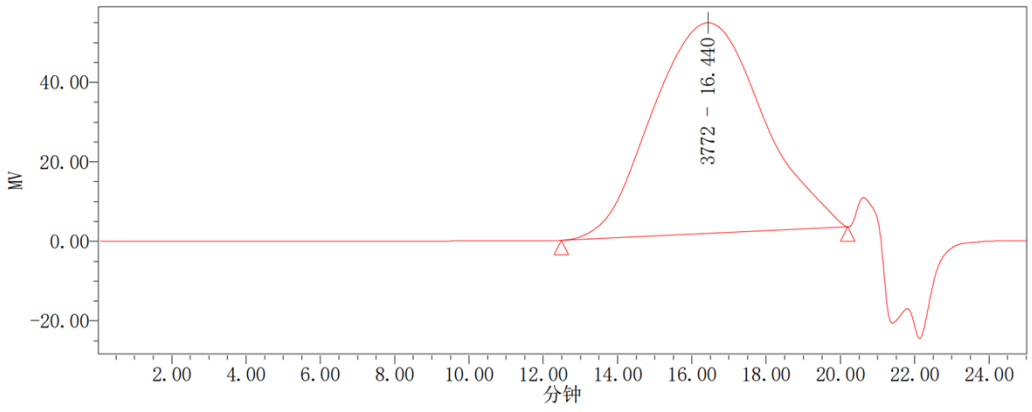
Figure S41. GPC of the polymer from table 1, entry 8.



GPC 结果

	分布名	Mn (道尔顿)	Mw (道尔顿)	MP	Mz (道尔顿)	Mz+1 (道尔顿)	多分散性	MW 标记 1 (道尔顿)	MW 标记 2 (道尔顿)
1		1401	1408		1416	1424	1.005169		

Figure S42. GPC of the polymer from table 2, entry 2.



GPC 结果

	分布名	Mn (道尔顿)	Mw (道尔顿)	MP	Mz (道尔顿)	Mz+1 (道尔顿)	多分散性	MW 标记 1 (道尔顿)	MW 标记 2 (道尔顿)
1		3699	6018	3772	9881	14864	1.626819		

Figure S43. GPC of the polymer from table 2, entry 3.

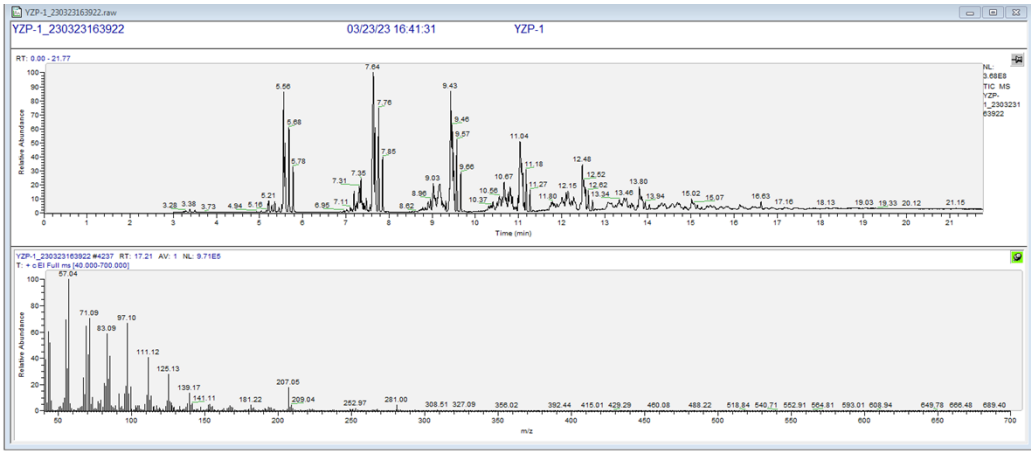


Figure S44. GC-MS of the ethylene oligomers from table 2, entry 6 catalyzed by **Pd3** at 50 °C.

3. References

(1) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. *J. Chem. Phys.* **2003**, *119*, 12129-12137.

(2) CYLview20; Legault, C. Y., Université de Sherbrooke, **2020** (http://www.cylview.org).

(3) Kitaura, K.; Morokuma, K. A New Energy Decomposition Scheme for Molecular Interactions within the Hartree-Fock Approximation. *J. Quantum Chem.* **1976**, *10*,

325-340.

(4) Guo, L.; Liu, Y.; Sun, W.; Du, Q.; Yang, Y.; Kong, W.; Liu, Z.; Chen, D. Synthesis, characterization, and olefin (co)polymerization behavior of unsymmetrical α-diimine palladium complexes containing bulky substituents at 4-position of aniline moieties, *Journal of Organometallic Chemistry*, **2018**, *877*, 12-15.

4. X-ray Crystallography

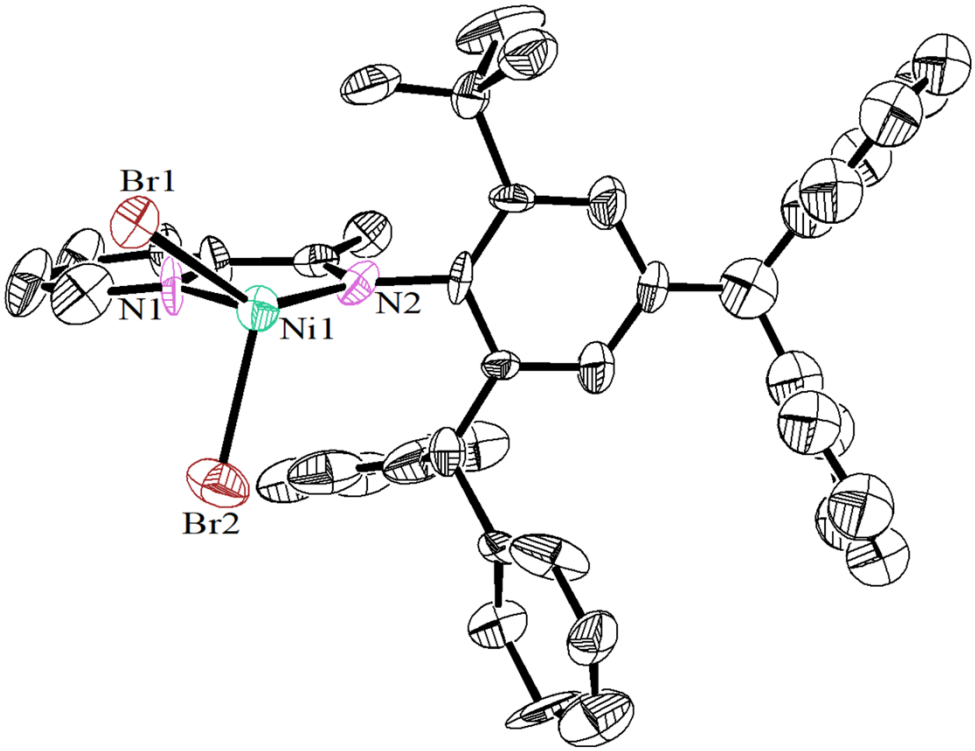


Table S1 Crystal data and structure refinement for Ni4.	
Identification code	**Ni4**
Empirical formula	C86 H80 Br4 N4 Ni2
Formula weight	1606.60
Temperature/K	298(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	20.718(2)
b/Å	9.0100(11)

c/Å	21.438(2)
α/°	90
β/°	92.285(3)
γ/°	90
Volume/Å^3	3998.6(8)
Z	2
ρ_{calc}g/cm^3	1.334
μ/mm^{-1}	2.514
F(000)	1640
Crystal size/mm^3	0.25 x 0.05 x 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.802 to 50.04
Index ranges	-24<=h<=24, 0<=k<=10, 0<=l<=25
Reflections collected	7025
Independent reflections	7025 [R(sigma) = 0.3171]
Data/restraints/parameters	7025 / 497 / 420
Goodness-of-fit on F^2	0.851
Final R indexes [I>=2σ (I)]	R1 = 0.1063, wR2 = 0.2299
Final R indexes [all data]	R1 = 0.2689, wR2 = 0.2830
Largest diff. peak/hole / e Å^{-3}	0.84 and -0.54

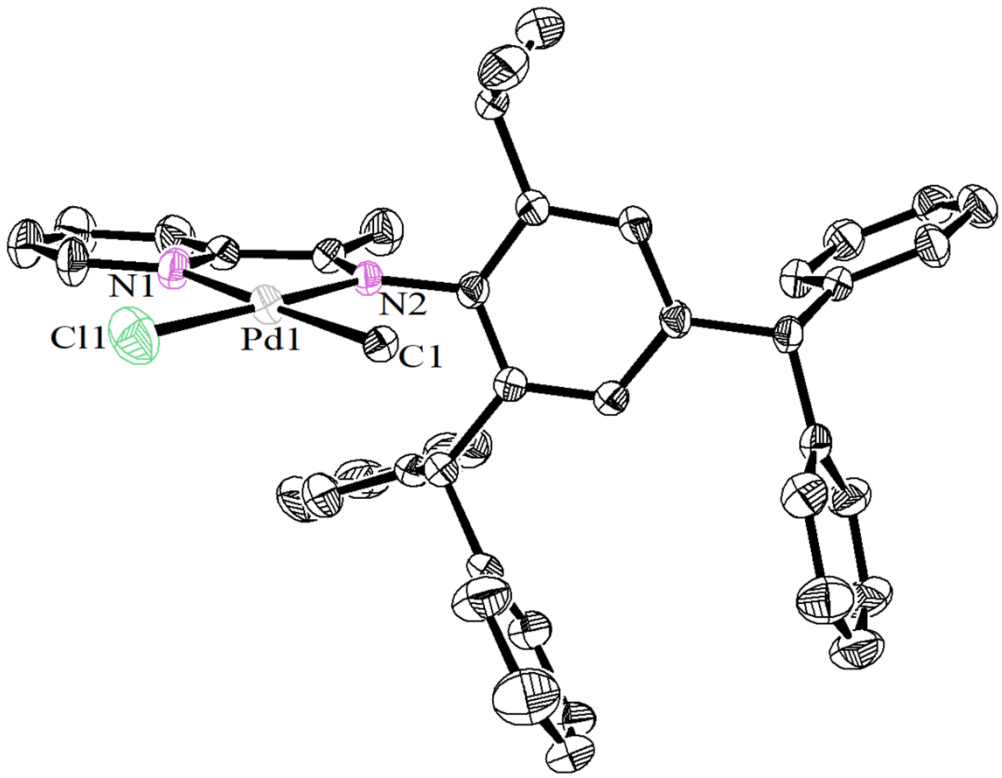


Table S2 Crystal data and structure refinement for Pd3.	
Identification code	**Pd3**
Empirical formula	C43 H41 Cl N2 Pd
Formula weight	727.63
Temperature/K	295(2)
Crystal system	Triclinic
Space group	P-1
a/Å	11.2154(16)
b/Å	11.8439(18)
c/Å	14.4771(19)
α/°	73.502(11)
β/°	80.941(11)
γ/°	78.858(12)
Volume/Å^3	1798.3(5)
Z	2
ρ_{calc}g/cm^3	1.344
μ/mm^{-1}	5.080
F(000)	752
Crystal size/mm^3	0.12 x 0.05 x 0.03
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	6.406 to 133.198
Index ranges	-13<=h<=8, -13<=k<=14, -16<=l<=17
Reflections collected	12917
Independent reflections	6098 [R(int) = 0.0478]
Data/restraints/parameters	6098 / 0 / 431
Goodness-of-fit on F^2	1.116
Final R indexes [I>=2σ (I)]	R1 = 0.0765, wR2 = 0.2127
Final R indexes [all data]	R1 = 0.0937, wR2 = 0.2369
Largest diff. peak/hole / e Å^{-3}	2.08 and -1.40