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Preparation and in situ chain-end-functionalization of branched ethylene oligomers by monosubstituted α-diimine nickel catalysts

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Contents

1 Time-dependence study

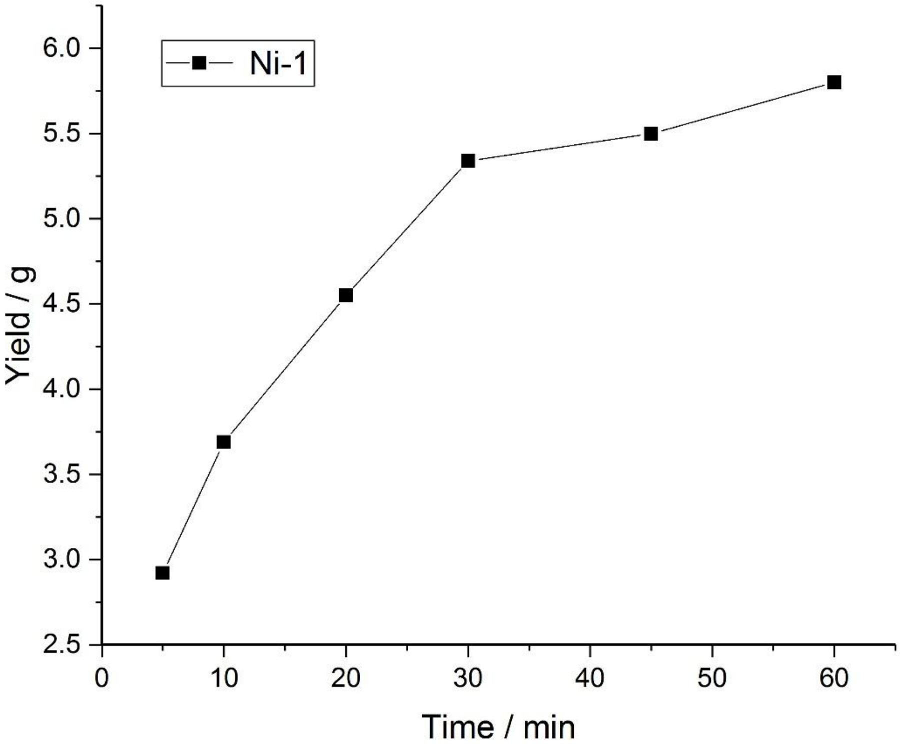


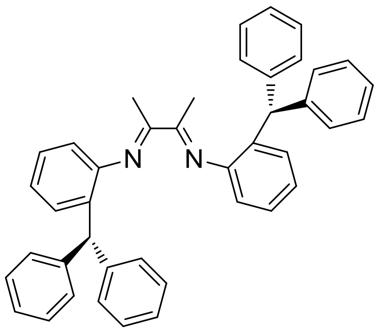
Figure S1. Polymer yield versus time for catalyst **Ni-1** at 70 ℃.

2 General Procedures and Materials: All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of nitrogen. All solvents were purified from the MBraun SPS system. NMR spectra for the ligands, complexes, and polymers were recorded on a Bruker AV400 (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{31}P: 162 MHz, ^{19}F: 376 MHz) or a Bruker AV500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{31}P: 202 MHz, ^{19}F: 470 MHz). NMR assignments were confirmed by ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC and ^{1}H−^{13}C HMBC experiments when necessary. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polyethylenes and copolymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 ℃ or on a TOSOH HLC-8220 GPC at 40 ℃ using THF as eluent (the flow rate is 0.35 mL/min) against polystyrene standards. Melting points (T_m) of polyethylenes and copolymers were measured through DSC analyses, which were carried out on a Mettler TOPEM TM DSC Instruments under nitrogen atmosphere at heating and cooling rates of 10 ℃/min (temperature range: 0−160 °C). Mass spectra of the complexes were recorded on an Acquity UPLC & Quattro Premier. Elemental analysis were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry.

X-Ray diffraction: Data collections were performed at −88.5 ℃ 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] All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXTL 2014.[3] 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 complexes **Ni-2**, **Pd-2**, and **Pd-5**, the program SQUEEZE[4] was used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules. For complex **Pd-5**, the thermal parameters of carbon and oxygen atoms on one OMe group were restrained to be similar with the adjacent atoms, and the “simu” restraint was used with the deviation being 0.02 to avoid the Hirshfeld Test Diff on several C–O bonds. Two C–O bond distances in the OMe group were fixed at 1.45 Å. The “isor” restraint was used with the deviation being 0.001 to help the refinement.

Materials: (2-aminophenyl)diphenylmethanol[5], 2-benzhydrylaniline[5], 2-[Bis(3,4-dimethoxyphenyl)methyl]aniline[6], 1-[bis(3,4-dimethoxyphenyl)methyl]-2-nitrobenzene[6], 4,5-Dimethoxy-{2-[Bis(3,4-dimethoxyphenyl)methyl]}aniline[6], 1-[Bis(3,4-dimethoxyphenyl)methyl]-3,4-dimethoxy-2-nitrobenzene[6] were prepared according to the literature procedures. All other reagents were commercially available and used as received.

3 Preparation of Ligands and Catalysts

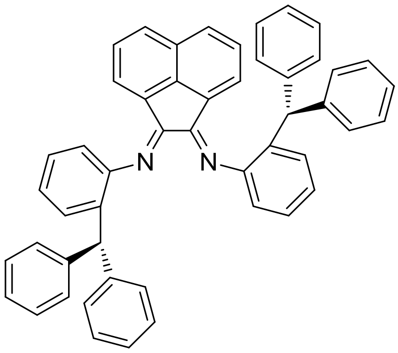


Preparation of Ligand L1: To the solution of 2-benzhydrylaniline (1.00 g, 3.86 mmol) in ^{i}PrOH (100 mL) at 80 ℃ were added diacetyl (153 μL, 1.75 mmol) and three drops of formic acid. The reaction mixture was stirred for 4 days at 80 ℃. The formed yellow suspension was cooled to room temperature and concentrated to a half of its original volume. The yellow precipitate was collected by filtration, washed with ^{i}PrOH and dried in vacuo (0.52g, 52.1% yield).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 7.26-7.19 (m, 10H, aryl-*H*), 7.19-7.14 (m, 4H, aryl-*H*), 7.08-7.01 (m, 10H, aryl-*H*), 6.94 (d, *J* = 7.7 Hz, 2H, aryl-*H*), 6.54 (d, *J* = 7.6 Hz, 2H, aryl-*H*), 5.44 (s, 2H, C*H*Ph_2), 1.58 (s, 6H, N=C*Me*) ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 168.17 (N=*C*Me), 149.25, 143.21, 134.21, 129.67, 128.36, 127.08, 126.39, 123.91, 118.06, 52.29 (*C*HPh_2), 15.29 (N=*C*-Me) ppm.

Elemental analysis: Anal. Calcd for $C_{42}H_{36}N_2$: C, 88.69; H, 6.38; N, 4.93. Found: C, 88.46; H, 6.24; N, 5.03.

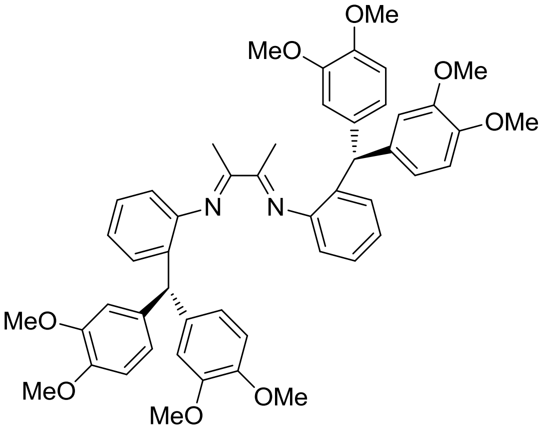


Preparation of Ligand L2: Step 1: $ZnCl_2$ (0.13 g, 0.96 mmol) and acenaphthenequinone (0.16 g, 0.88 mmol) were suspended in glacial acetic acid (10 mL).2-benzhydrylaniline (0.50 g, 1.93 mmol) was added, and the reaction mixture was refluxed under stirring for 4 h. The solution was allowed to cool to room temperature, and a bright yellow solid precipitated. The solid was separated by filtration and washed with 10 mL acetic acid (3 times) and 20 mL diethyl ether (5 times), to remove remaining acetic acid. Drying under vacuum gave bright orange solid (0.58 g, 82.3% yield). Step 2: The zinc was removed from the zinc diamine complex. The product of the previous step was suspended in methylene chloride (20 mL), and a solution of potassium oxalate (0.36 g, 1.93 mmol) in water (3 mL) was added. The reaction mixture was stirred vigorously for 1 h. The two phases were separated, and the organic layer was washed with 20 mL water (3 times) and dried with $MgSO_4$. After filtration the solvent was removed under vacuum to afford the product as an orange powder (0.32 g, 66.5%), followed by recrystallization from dichloromethane and n-hexane.The total yield of two steps is 54.7%.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 7.64 (d, J = 8.2 Hz, 2H, aryl-*H*), 7.30 (t, 2H, aryl-*H*), 7.19 (t, 3H, aryl-*H*), 7.14-6.58 (m, 25H, aryl-*H*), 6.44 (s, 2H, aryl-*H*), 5.83 (s, 2H, C*H*Ph_2) ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 161.91 (N=*C*Me), 150.44, 142.96, 141.01, 134.29, 130.28, 130.06, 129.82, 128.44, 128.36, 127.96, 127.26, 126.95, 125.84, 124.43, 123.55, 118.08, 52.22 (*C*HPh_2) ppm.

Elemental analysis: Anal. Calcd for $C_{50}H_{36}N_2$: C, 90.33; H, 5.46; N, 4.21. Found: C, 90.45; H, 5.37; N, 4.12.

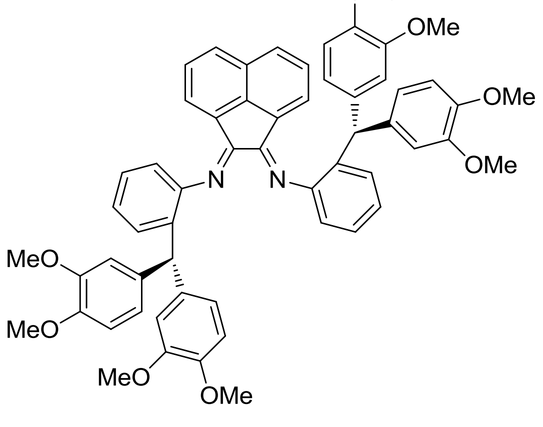


Preparation of Ligand L3: Using the same procedure as for the synthesis of L1, L3 was obtained as a yellow powder (0.63g, 64.5% yield).

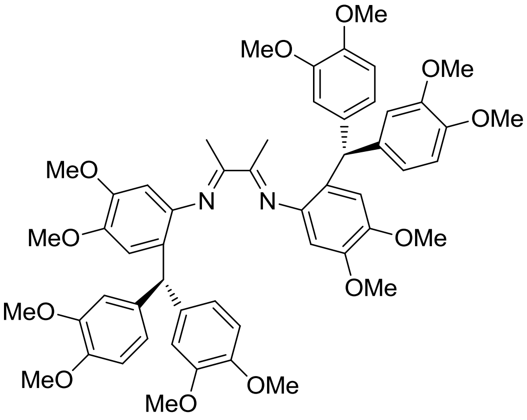
^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 7.22 (t, 2H, aryl-*H*), 7.04 (t, 2H, aryl-*H*), 6.96 (d, *J*=7.7Hz, 2H, aryl-*H*), 6.74 (d, *J*=8.3Hz, 4H, aryl-*H*), 6.61 (d, J=2.1Hz, 4H, aryl-*H*), 6.57-6.50 (m, 6H, aryl-*H*), 5.34 (s, 2H, C*H*Ph_2), 3.81 (s, 12H, -OMe), 3.73 (s, 12H, -OMe), 1.66 (s, 6H, N=C*Me*) ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 168.02 (N=*C*Me), 149.12, 148.87, 147.53, 135.97, 134.53, 129.51, 127.04, 123.94, 121.59, 117.90, 112.88, 110.87, 55.93(OMe), 51.35(*C*HPh_2), 15.46(N=*C*-Me) ppm.

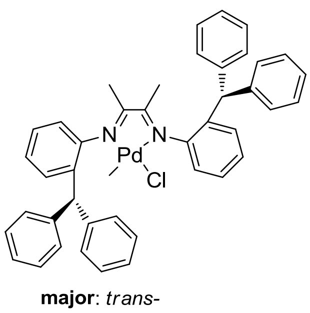
Elemental analysis: Anal. Calcd for $C_{50}H_{52}N_2O_8$: C, 74.24; H, 6.48; N, 3.46. Found: C, 74.40; H, 6.54; N, 3.38.



Preparation of Ligand L4: Using the same procedure as for the synthesis of L2, L4 was obtained as a orange powder (0.32 g, 59.2% yield).
^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 7.67 (d, *J*=8.2Hz, 2H, aryl-*H*), 7.36-7.27 (t, 2H, aryl-*H*), 7.23-7.16 (t, 2H, aryl-*H*), 7.15-7.04 (m, 4H, aryl-*H*), 7.01 (d, *J*=7.6Hz, 2H, aryl-*H*), 6.87-6.14 (m, 14H, aryl-*H*), 5.71 (s, 2H, C*H*Ph_2), 3.89-3.08 (m, 24H, -OMe) ppm.
^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 162.17 (N=*C*Me), 150.43, 148.45, 146.97, 140.72, 135.81, 134.45, 130.16, 129.74, 128.40, 128.13, 127.24, 126.66, 124.44, 123.30, 121.80, 117.93, 112.98, 110.33, 55.69. 51.42(*C*HPh_2) ppm.
Elemental analysis: Anal. Calcd for $C_{58}H_{52}N_2O_8$: C, 76.97; H, 5.79; N, 3.10. Found: C, 77.07; H, 5.65; N, 3.14.



Preparation of Ligand L5: Using the same procedure as for the synthesis of L1, L5 was obtained as a yellow powder (0.55g, 57.5% yield).
^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 6.73 (d, *J*=8.3Hz, 4H, aryl-*H*), 6.62 (d, *J*=2.1Hz, 4H, aryl-*H*), 6.56-6.49 (m, 6H, aryl-*H*), 6.13 (s, 2H, aryl-*H*), 5.30 (s, 2H, C*H*Ph_2), 3.87-3.79 (m, 18H, -OMe), 3.75-3.66 (m, 18H, -OMe), 1.74 (s, 6H, N=C*Me*) ppm.
^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 168.67 (N=*C*Me), 148.84, 147.90, 147.50, 145.60, 142.24, 136.29, 126.39, 121.47, 113.37, 112.78, 110.87, 102.64, 56.41, 56.17, 55.94, 55.92, 50.77(*C*HPh_2), 15.76(N=*C*-Me) ppm.
Elemental analysis: Anal. Calcd for $C_{54}H_{60}N_2O_{12}$: C, 69.81; H, 6.51; N, 3.02. Found: C, 69.98; H, 6.63; N, 2.93.



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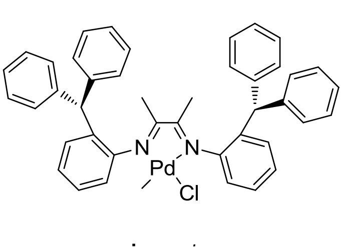


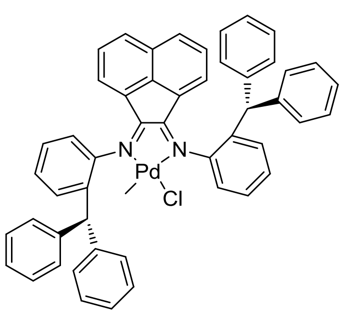
minor: *cis-*

Preparation of complex Pd-1: To a solution of ligand L1 (130 mg, 0.23 mmol) in dry dichloromethane (10 mL) was added 60.6 mg (0.23 mmol) of Pd(COD)MeCl. After stirring the mixture for 3 days at room temperature, the solvent was evaporated under reduced pressure, the desired compound can be isolated from repeated recrystallized from n-hexane and dichloromethane. The pure compound was obtained as an orange solid. (120 mg, 72.2% yield)

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): **major:** δ = 7.47-7.43 (m, 2H, aryl-*H*), 7.43-7.38 (m, 1H, aryl-*H*), 7.36-7.08 (m, 22H, aryl-*H*), 7.00-6.96 (m, 1H, aryl-*H*), 6.85-6.81 (m, 1H, aryl-*H*), 6.79-6.76 (m, 1H, aryl-*H*), 6.51 (s, 1H, C*H*Ph_2), 6.11 (s, 1H, C*H*Ph_2), 0.75 (s, 3H, N=C*Me*), 0.64 (s, 3H, N=C*Me*), 0.88 (s, 3H, Pd-*Me*). **minor:** the signals of **aryl-H** are overlapped by the major product, δ = 6.67 (s, 1H, C*H*Ph_2), 6.01 (s, 1H, C*H*Ph_2), 0.80 (s, 3H, N=C*Me*), 0.72 (s, 3H, N=C*Me*), 0.76 (s, 3H, Pd-*Me*) ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): **major:** δ = 176.53 (N=*C*Me), 170.86 (N=*C*Me), 145.29, 145.16, 142.89, 142.01, 141.80, 141.23, 136.82, 136.33, 130.70, 130.56, 130.12, 129.71, 129.57, 128.87, 128.54, 128.50, 128.28, 127.67, 127.11, 127.09, 126.89, 126.77, 126.64, 126.48, 126.31, 121.34, 120.12, 52.60 (*C*HPh_2), 52.20 (*C*HPh_2), 19.66 (N=*C*-Me), 18.30 (N=*C*-Me), 3.75 (Pd-*Me*). **minor:** the signals of **aryl-C** are overlapped by the major product, δ = 177.85 (N=*C*Me), 174.30 (N=*C*Me), 53.06 (*C*HPh_2), 52.73 (*C*HPh_2), 20.20 (N=*C*-Me), 19.05 (N=*C*-Me), 4.21 (Pd-*Me*) ppm.

Elemental analysis: Anal. Calcd for $C_{43}H_{39}ClN_2Pd$: C, 71.17; H, 5.42; N, 3.86. Found: C, 71.35; H, 5.49; N, 3.80.



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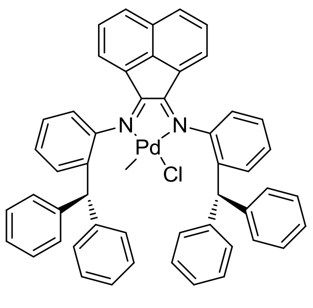


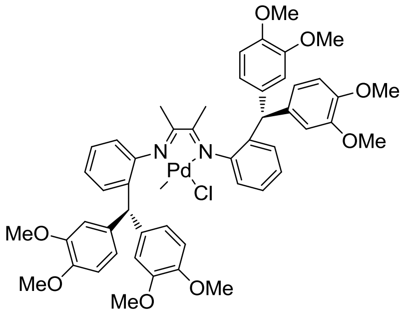
minor: *cis-*

Preparation of complex Pd-2: Using the same procedure as for the synthesis of **Pd-1**, **Pd-2** was obtained as an orange powder (133 mg, 83.1% yield).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): **major:** δ = 7.77-7.72 (dd, $^3J_{HH}$= 12.2 Hz, $^4J_{HH}$=8.3 Hz, 2H, aryl-*H*), 7.53-7.50 (m, 1H, aryl-*H*), 7.46-7.40 (m, 4H, aryl-*H*), 7.33-7.07 (m, 19H, aryl-*H*), 6.79 (s, 1H, C*H*Ph_2), 6.42-6.37 (m, 4H, aryl-*H*), 6.34-6.33 (br, 2H, C*H*Ph_2 & aryl-*H*), 6.04-6.00 (m, 3H, aryl-*H*), 1.14 (s, 3H, Pd-*Me*). **minor:** the signals of **aryl-H** are overlapped by the major product, δ = 6.70 (s, 1H, C*H*Ph_2), 5.91 (s, 1H, C*H*Ph_2), 0.99 (s, 3H, Pd-*Me*) ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): **major:** δ =173.33 (N=*C*), 168.10 (N=*C*), 145.23, 144.88, 143.87, 142.21, 141.50, 140.80, 137.46, 137.33, 130.65, 130.37, 130.24, 130.17, 130.10, 129.93, 129.86, 129.58, 128.45, 128.26, 127.99, 127.79, 127.76, 127.56, 127.53, 127.46, 127.28, 127.12, 126.78, 126.38, 125.99, 125.41, 125.34, 125.07, 125.00, 124.88, 121.57, 120.15, 52.81 (*C*HPh_2), 52.46 (*C*HPh_2), 4.03 (Pd-*Me*). **minor:** the signals of **aryl-C** are overlapped by the major product, δ = 172.89 (N=*C*Me), 167.53 (N=*C*Me), 52.02 (*C*HPh_2), 51.61 (*C*HPh_2), 4.64 (Pd-*Me*) ppm.

Elemental analysis: Anal. Calcd for $C_{51}H_{39}ClN_2Pd$: C, 74.54; H, 4.78; N, 3.41. Found: C, 74.67; H, 4.90; N, 3.34.



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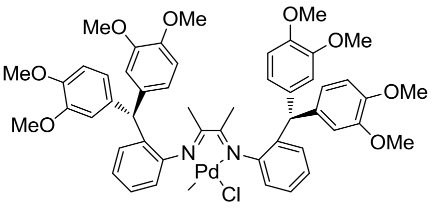


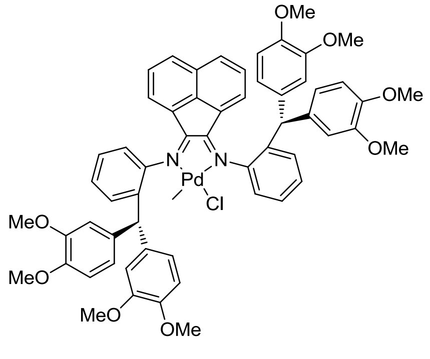
minor: *cis-*

Preparation of complex Pd-3: Using the same procedure as for the synthesis of **Pd-1**, **Pd-3** was obtained as an orange powder (126 mg, 81.2% yield).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): **major:** *δ* = 7.47 (s, 1H, aryl-*H*), 7.42-7.16 (m, 5H, aryl-*H*), 7.10 (d, *J* = 7.8 Hz, 1H, aryl-*H*), 7.04-6.99 (m, 1H, aryl-*H*), 6.84-6.62 (m, 10H, aryl-*H*), 6.57-6.51 (m, 2H, aryl-*H*), 6.26 (s, 1H, C*H*Ar$_2$), 5.89 (s, 1H, C*H*Ar$_2$), 3.85, 3.84, 3.83, 3.80, 3.79, 3.78, 3.73 (s, 24H, O*Me*), 0.89 (s, 3H, N=C*Me*), 0.80 (s, 3H, N=C*Me*), 0.86 (s, 3H, Pd-*Me*). **minor:** the signals of **aryl-H** are overlapped by the major product, *δ* = 6.44 (s, 1H, C*H*Ar$_2$), 6.23 (s, 1H, C*H*Ar$_2$), 3.74, 3.63, 3.55 (s, 24H, O*Me*), 0.92 (s, 3H, N=C*Me*), 0.78 (s, 3H, Pd-*Me*) ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): **major:** *δ* = 176.36 (N=*C*Me), 170.70 (N=*C*Me), 149.38, 149.19, 149.13, 149.08, 148.03, 147.94, 147.72, 147.68, 145.18, 145.03, 137.00, 136.70, 135.47, 135.35, 134.39, 134.30, 130.11, 129.76, 127.63, 127.20, 127.10, 126.73, 122.55, 122.45, 121.13, 121.09, 120.65, 119.77, 114.15, 114.00, 113.63, 112.81, 111.34, 111.19, 110.63, 110.08, 56.44, 56.42, 56.41, 56.15, 56.14, 55.98, 55.97, 55.90 (OMe), 51.61 (*C*HAr$_2$), 51.21 (*C*HAr$_2$), 19.89 (N=*C*-Me), 18.42 (N=*C*-Me), 3.59 (Pd-*Me*). **minor:** the signals of **aryl-C** are overlapped by the major product, *δ* = 177.67 (N=*C*Me), 174.11 (N=*C*Me), 56.61, 56.59, 56.54, 56.31, 56.07, 56.02, 55.81, 55.80 (OMe), 52.13 (*C*HAr$_2$), 50.96 (*C*HAr$_2$), 20.54 (N=*C*-Me), 19.13 (N=*C*-Me), 4.20 (Pd-*Me*) ppm.

Elemental analysis: Anal. Calcd for $C_{51}H_{55}ClN_2O_8Pd$: C, 63.42; H, 5.74; N, 2.90. Found: C, 63.28; H, 5.81; N, 2.85.



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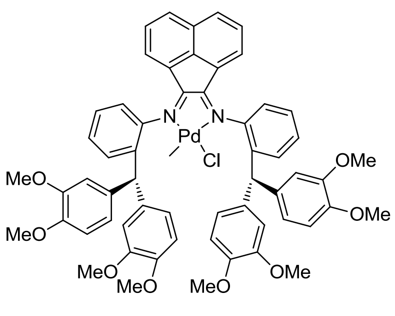


minor: *cis-*

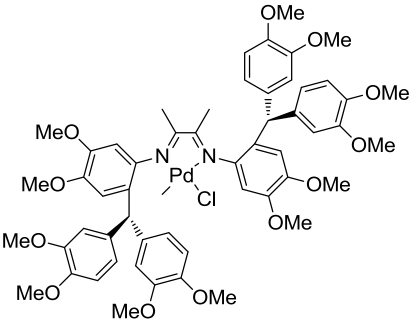
Preparation of complex Pd-4: Using the same procedure as for the synthesis of **Pd-1**, **Pd-4** was obtained as an orange powder (117 mg, 76.5% yield).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): **major:** *δ* = 7.84-7.79 (m, 2H, aryl-*H*)，7.55-7.51 (m, 1H, aryl-*H*), 7.45-7.33 (m, 5H, aryl-*H*), 7.19-7.11 (m, 5H, aryl-*H*), 6.76-6.73 (m, 3H, aryl-*H*), 6.66-6.59 (m, 5H, aryl-*H*), 6.56 (s, 1H, C*H*Ar$_2$), 6.48 (d, *J* = 2.0 Hz, 1H，aryl-*H*), 6.36 (d, *J* = 7.3 Hz, 1H，aryl-*H*), 6.15 (s, 1H, C*H*Ar$_2$), 6.05 (d, *J* = 7.2 Hz, 1H，aryl-*H*), 5.70-5.67 (m, ,2H, aryl-*H*), 3.86, 3.73, 3.57, 3.55, 2.99, 2.96 (s, 24H, O*Me*), 1.12 (s, 3H, Pd-

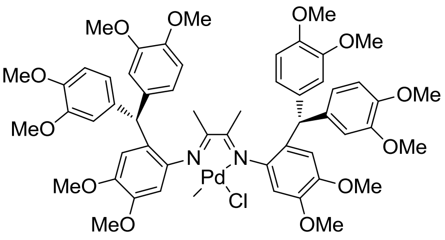
Me). **minor:** the signals of **aryl-H** are overlapped by the major product, *δ* = 6.65 (s, 1H, C*H*Ar$_2$)，5.90 (s, 1H, C*H*Ar$_2$), 3.89, 3.85, 3.84, 3.73, 3.55, 3.43, 2.98 (s, 24H, O*Me*), 1.08 (s, 3H, Pd-*Me*) ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): **major:** *δ* = 173.20 (N=*C*), 168.00 (N=*C*), 149.14, 149.01, 148.24, 148.15, 147.89, 147.64, 146.47, 146.30, 145.18, 144.89, 143.52, 137.63, 137.62, 135.35, 134.94, 134.38, 133.60, 130.41, 130.38, 129.97, 129.96, 129.92, 128.02, 127.84, 127.42, 127.34, 127.28, 127.24, 125.75, 125.23, 124.65, 124.51, 122.29, 122.25, 121.46, 121.24, 120.84, 119.91, 114.01, 113.68, 113.30, 112.80, 110.72, 110.24, 110.15, 110.06, 56.34, 56.00, 55.98, 55.87, 55.73, 55.72, 55.11, 55.09 (O*Me*), 51.94 (*C*HAr$_2$), 51.52 (*C*HPh$_2$), 3.78 (Pd-*Me*). **minor:** *δ* = 173.32 (N=*C*), 167.87 (N=*C*), 149.10, 148.95, 148.69, 148.56, 147.92, 147.54, 147.06, 146.54, 145.39, 145.22, 143.77, 137.68, 137.66, 137.10, 135.95, 134.86, 132.82, 131.63, 130.27, 130.23, 128.15, 127.72, 127.65, 127.55, 125.67, 125.49, 124.98, 124.71, 122.45, 122.16, 121.69, 121.37, 121.24, 114.73, 113.23, 112.93, 112.64, 110.79, 109.98, 109.39, 56.63, 56.04, 55.94, 55.70, 55.53, 55.41, 54.63 (O*Me*), 51.05 (*C*HAr$_2$), 51.00 (*C*HAr$_2$), 4.46 (Pd-*Me*) ppm.

Elemental analysis: Anal. Calcd for $C_{59}H_{55}ClN_2O_8Pd$: C, 66.73; H, 5.22; N, 2.64. Found: C, 66.98; H, 5.13; N, 2.58.



major: *trans-*



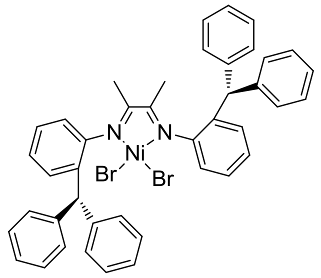
minor: *cis-*

Preparation of complex Pd-5: Using the same procedure as for the synthesis of **Pd-1**, **Pd-5** was obtained as an orange powder (120 mg, 81.2% yield).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): **major:** *δ* = 7.48 (s, 1H, aryl-*H*), 6.79-6.69 (m, 8H, aryl-*H*), 6.55 (s, 1H, aryl-*H*), 6.53-6.46 (m, 4H, aryl-*H*), 6.34-6.28 (m, 2H, aryl-*H*), 6.15 (s, 1H, C*H*Ar$_2$), 5.73 (s, 1H, C*H*Ar$_2$), 3.90, 3.87, 3.86, 3.85, 3.84, 3.81, 3.79, 3.78, 3.77, 3.73, 3.70, 3.68 (s, 36H, O*Me*), 0.92 (s, 3H, N=C*Me*), 0.82 (s, 3H, N=C*Me*), 0.90 (s, 3H, Pd-*Me*). **minor:** the signals of **aryl-H** are overlapped by the major product, *δ* = 6.19 (s, 1H, C*H*Ar$_2$), 5.56 (s, 1H, C*H*Ar$_2$), 3.91, 3.87, 3.83, 3.80, 3.78, 3.77, 3.75, 3.73, 3.65, 3.64, 3.55 (s, 36H, O*Me*), 1.41 (s, 3H, N=C*Me*), 1.15 (s, 3H, N=C*Me*), 0.85 (s, 3H, Pd-*Me*) ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): **major:** *δ* = 177.17 (N=*C*Me), 171.46 (N=*C*Me), 149.29, 149.17, 149.03, 148.40, 148.07, 147.90, 147.82, 147.80, 147.75, 147.66, 147.40, 137.99, 137.83, 135.68, 135.60, 134.62, 129.03, 128.54, 124.01, 122.57, 122.47, 121.07, 120.57, 114.34, 114.11, 113.88, 112.74, 112.72, 112.68, 111.37, 111.21, 110.58, 110.05, 104.97, 104.17, 100.96, 56.57, 56.52, 56.48, 56.42, 56.33, 56.28, 56.24, 56.13, 56.12, 55.95, 55.94, 55.80 (OMe), 51.06 (*C*HAr$_2$), 50.66 (*C*HAr$_2$), 20.02 (N=*C*-Me), 18.50 (N=*C*-Me), 3.91 (Pd-*Me*). **minor:** the signals of **aryl-C** are overlapped by the major product, *δ* = 177.00 (N=*C*Me), 171.03 (N=*C*Me), 56.66, 56.45, 56.38, 56.19, 56.09, 56.07, 56.06, 56.00, 55.86 (OMe), 50.53 (*C*HAr$_2$), 50.15 (*C*HAr$_2$), 20.51 (N=*C*-Me), 19.63 (N=*C*-Me), 4.56 (Pd-*Me*) ppm.

Elemental analysis: Anal. Calcd for $C_{55}H_{63}ClN_2O_{12}Pd$: C, 60.83; H, 5.85; N, 2.58. Found: C, 60.99; H, 5.83; N, 2.45.



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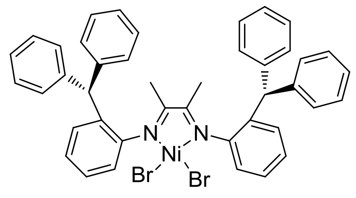
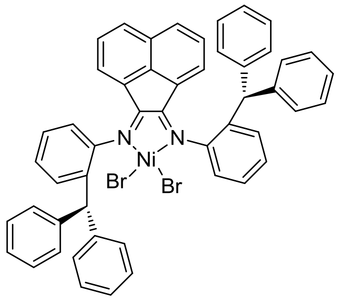


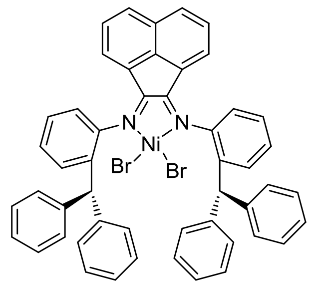
minor: *cis-*

Preparation of complex Ni-1: A mixture of L1 (120 mg, 0.21 mmol) and (DME)NiBr$_2$ (65.1 mg, 0.21 mmol) (DME = 1,2-dimethoxyethane) were stirred in 20 mL of dichloromethane overnight at room temperature. the solvent was evaporated under reduced pressure, the desired compound can be isolated from repeated recrystallized from n-hexane and dichloromethane. The pure compound was obtained as a yellow solid (133 mg, 80.2% yield). As a result of their paramagnetic nature, this complex could not be characterized by ^{1}H and ^{13}C NMR. MALDI-TOF-MS (m/z) : 705.1 [M-Br]$^+$.

Elemental analysis: Anal. Calcd for $C_{42}H_{36}Br_2N_2Ni$: C, 64.08; H, 4.61; N, 3.56. Found: C, 64.34; H, 4.53; N, 3.44.



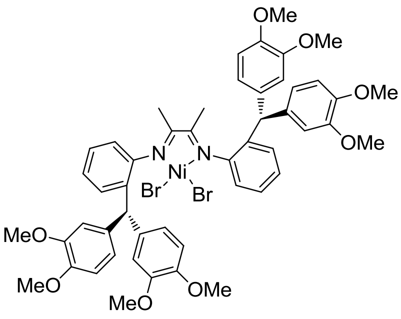
major: *trans-*



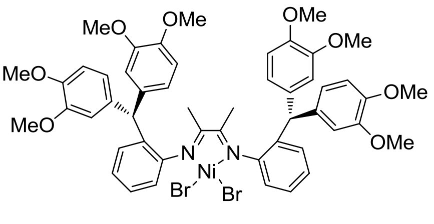
minor: *cis-*

Preparation of complex Ni-2: Using the same procedure as for the synthesis of **Ni-1**, **Ni-2** was obtained as a yellow powder (137 mg, 86.2% yield). As a result of their paramagnetic nature, this complex could not be characterized by ^{1}H and ^{13}C NMR. MALDI-TOF-MS (m/z) : 801.1 [M-Br]$^+$.

Elemental analysis: Anal. Calcd for $C_{50}H_{36}Br_2N_2Ni$: C, 67.98; H, 4.11; N, 3.17. Found: C, 68.11; H, 4.18; N, 3.11.



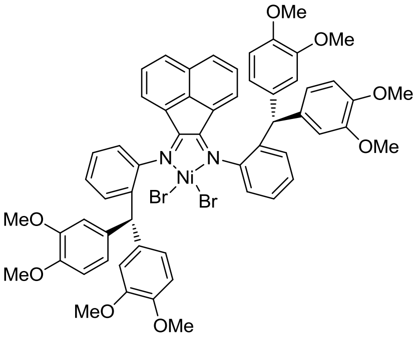
major: *trans-*



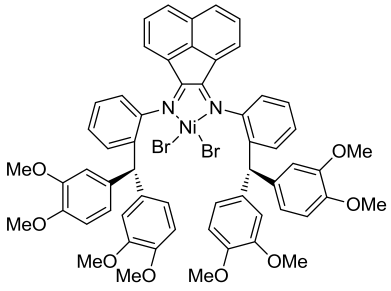
minor: *cis-*

Preparation of complex Ni-3: Using the same procedure as for the synthesis of **Ni-1**, **Ni-3** was obtained as a yellow powder (130 mg, 86.1% yield). As a result of their paramagnetic nature, this complex could not be characterized by ^{1}H and ^{13}C NMR. MALDI-TOF-MS (m/z) : 945.2 [M-Br]$^+$.

Elemental analysis: Anal. Calcd for $C_{50}H_{52}Br_2N_2NiO_8$: C, 58.45; H, 5.10; N, 2.73. Found: C, 58.67; H, 5.03; N, 2.67.



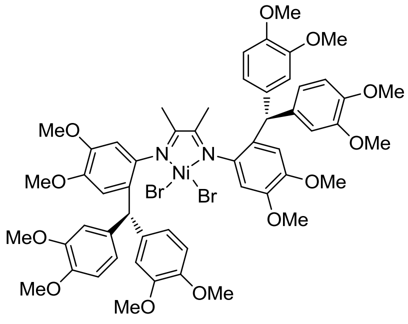
major: *trans-*



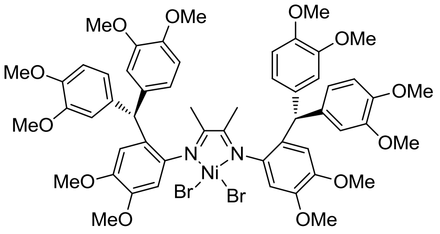
minor: *cis-*

Preparation of complex Ni-4: Using the same procedure as for the synthesis of **Ni-1**, **Ni-4** was obtained as a yellow powder (123 mg, 82.7% yield). As a result of their paramagnetic nature, this complex could not be characterized by ^{1}H and ^{13}C NMR. MALDI-TOF-MS (m/z) : 1041.2 [M-Br]$^+$.

Elemental analysis: Anal. Calcd for $C_{58}H_{52}Br_2N_2NiO_8$: C, 62.00; H, 4.66; N, 2.49. Found: C, 62.32; H, 4.54; N, 2.41.



major: *trans-*



minor: *cis-*

Preparation of complex Ni-5: Using the same procedure as for the synthesis of **Ni-1**, **Ni-5** was obtained as a yellow powder (128 mg, 84.2% yield). As a result of their paramagnetic nature, this complex could not be characterized by ^{1}H and ^{13}C NMR. MALDI-TOF-MS (m/z) : 1065.3 [M-Br]$^+$.

Elemental analysis: Anal. Calcd for $C_{54}H_{60}Br_2N_2NiO_{12}$: C, 56.52; H, 5.27; N, 2.44. Found: C, 56.65; H, 5.32; N, 2.32.

4 General procedures for the polymerizations

A general procedure for the homopolymerization of ethylene using Ni catalyst

In a typical experiment, a 350 mL glass pressure reactor connected with a high pressure gas line was firstly dried at 90 ℃ under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 98 mL of toluene and MAO was added to the reactor under N_2 atmosphere, then the desired amount of Ni 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 8 atm of ethylene. After 0.5 h, the pressure reactor was vented and the polymerization was quenched via the addition of 10 mL acidic MeOH (5% HCl in MeOH) and dried in a vacuum oven to constant weight.

A general procedure for the homopolymerization of ethylene using Pd catalyst

In a typical experiment, a 350 mL glass pressure reactor connected with a high pressure gas line was firstly dried at 90 ℃ under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 98 mL of CH_2Cl_2 and 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. With a rapid stirring, the reactor was pressurized and maintained at 6 atm of ethylene. After 5 h, the pressure reactor was vented and the solvent was removed under vacuum, than the residue was dissolved in Et_2O, after filtration the solvent was removed under vacuum and dried in a vacuum oven to constant weight.

A general procedure for the copolymerization of polar monomer with ethylene

In a typical experiment, a 150 mL glass pressure reactor connected with a high pressure gas line was firstly dried at 90 ℃ under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 23 mL of CH_2Cl_2 with NaBArF and galvinoxyl were added to the reactor under N_2 atmosphere, then the desired polar monomer and 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 6 atm of ethylene. After 10 h, the pressure reactor was vented and the solvent was removed under vacuum, than the residue was dissolved in Et_2O, after filtration the solvent was removed under vacuum and dried in a vacuum oven to constant weight.

5 Spectra Data

5.1 ^{1}H NMR of Amine

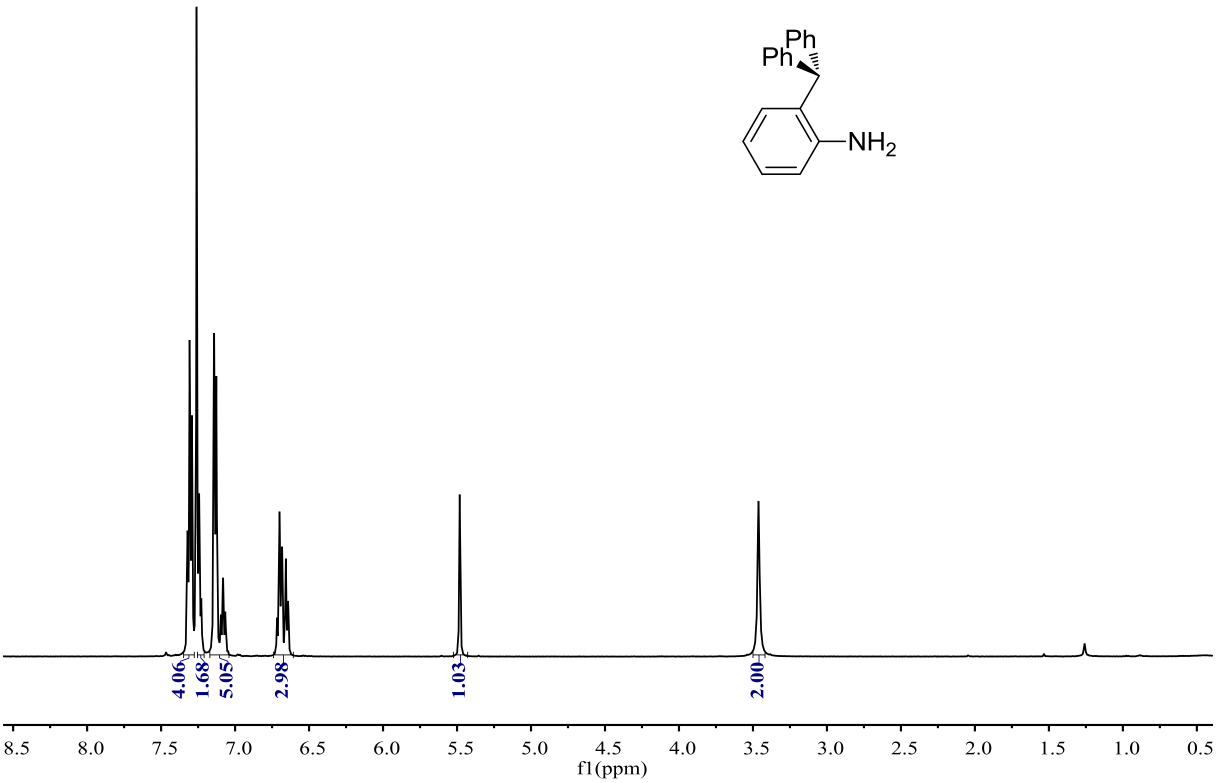


Figure S2. ^{1}H NMR spectrum of **Aniline-H** in $CDCl_3$.

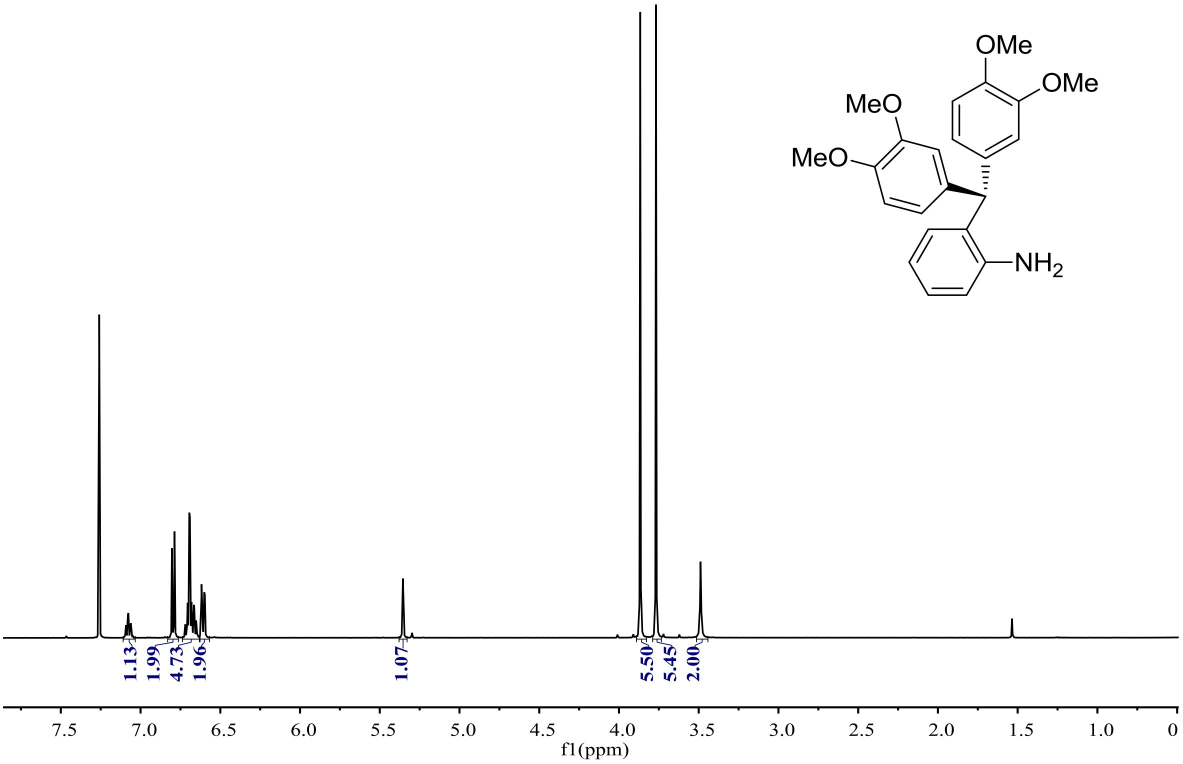


Figure S3. ^{1}H NMR spectrum of **Aniline-MeO$_4$** in $CDCl_3$.

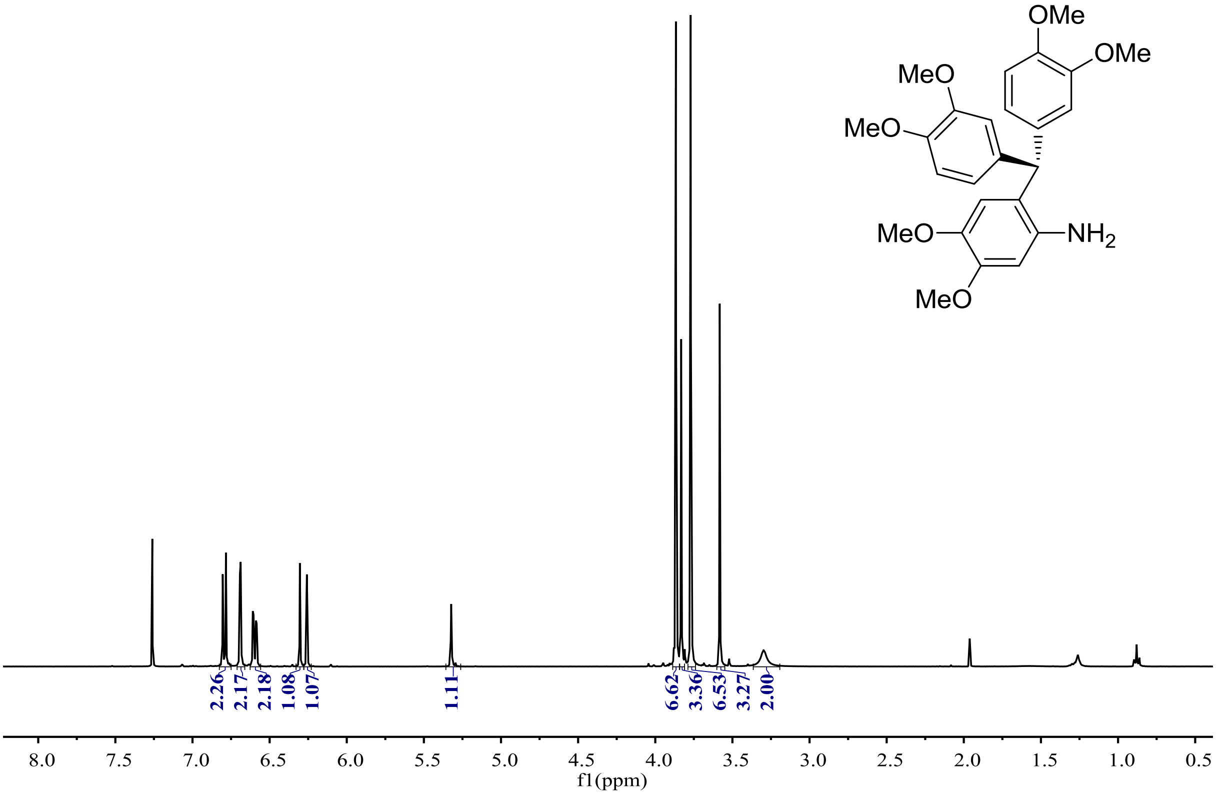


Figure S4. ^{1}H NMR spectrum of **Aniline-MeO$_6$** in CDCl$_3$.

5.2 ^{1}H, ^{13}C NMR of Ligand

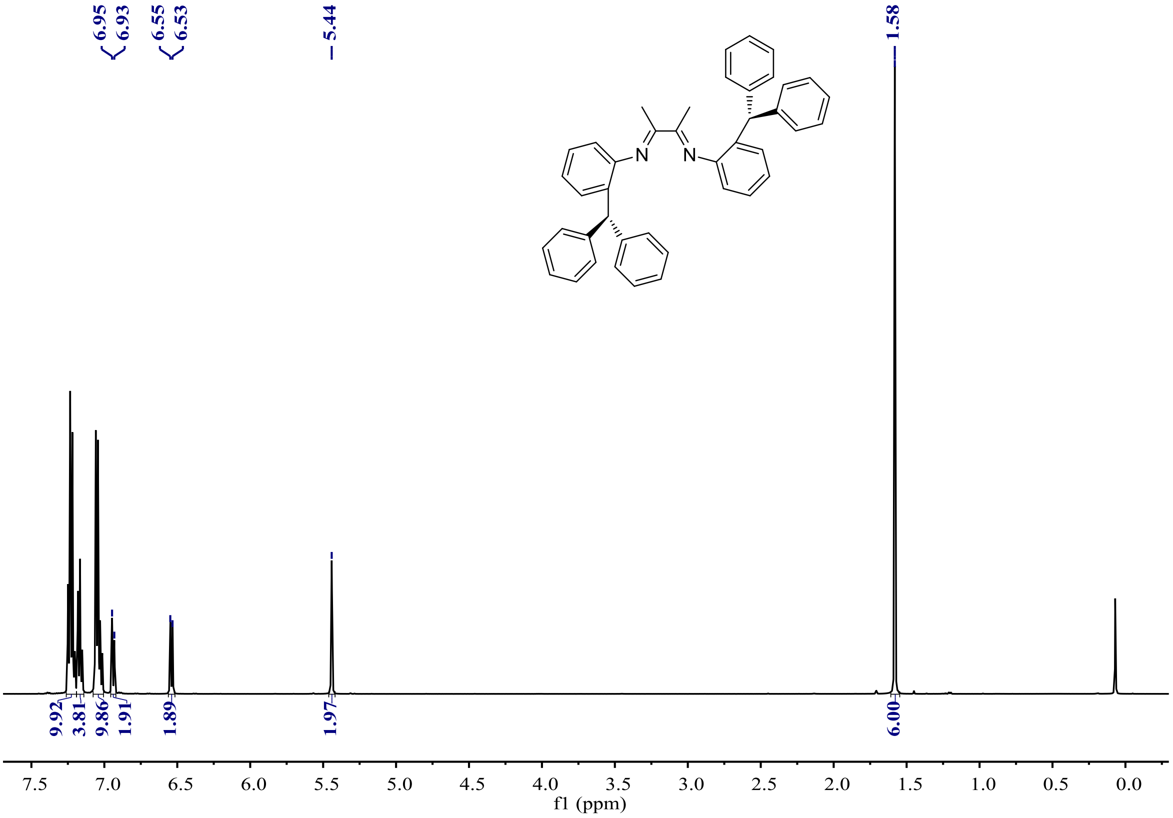


Figure S5. ^{1}H NMR spectrum of **Ligand 1** in CDCl$_3$.

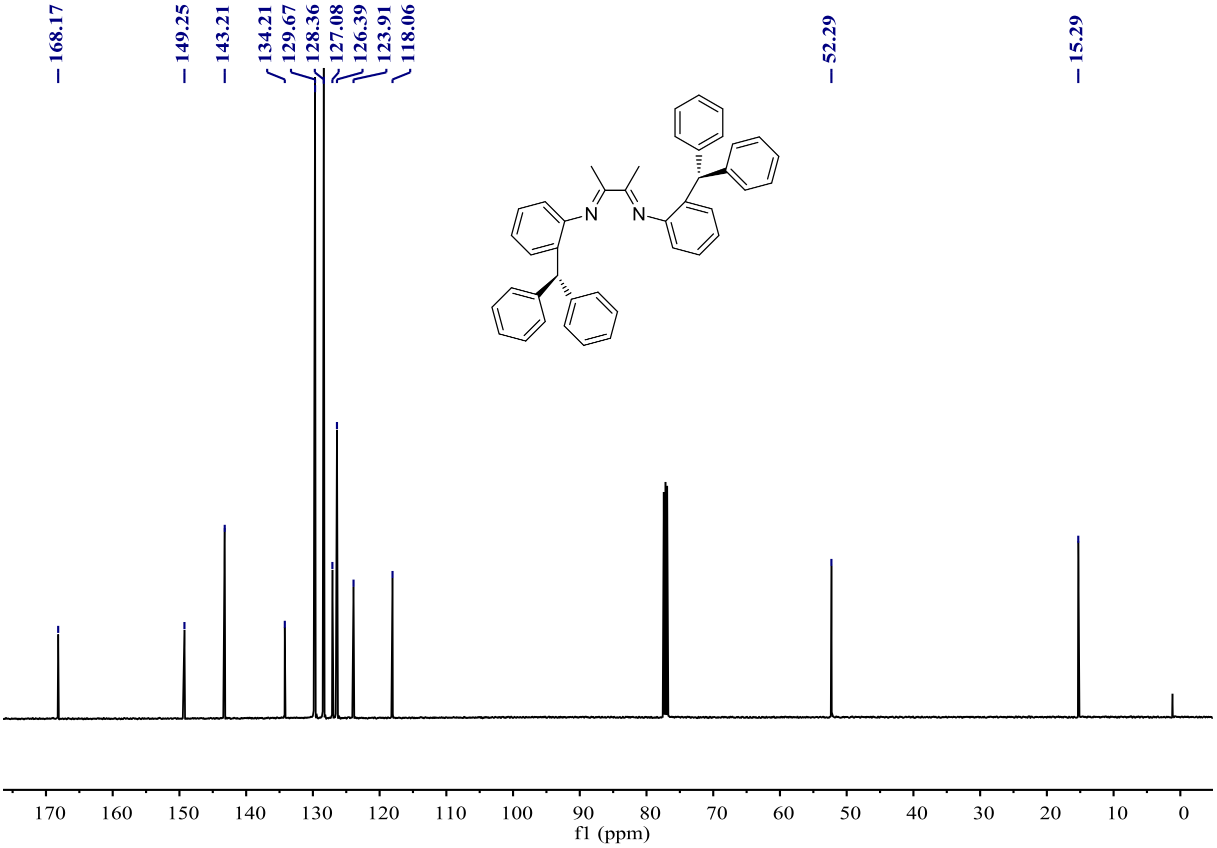


Figure S6. ^{13}C NMR spectrum of **Ligand 1** in CDCl$_3$.

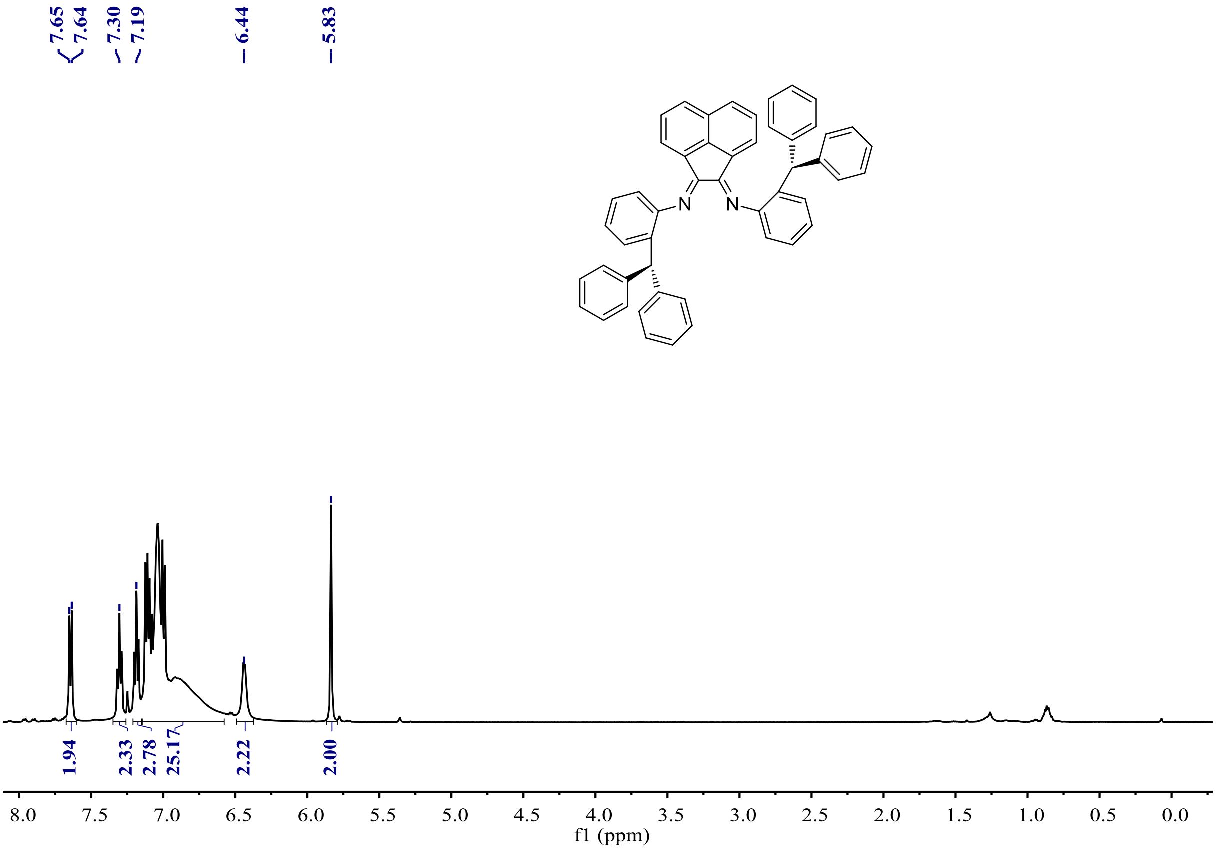


Figure S7. ^{1}H NMR spectrum of **Ligand 2** in CDCl$_3$.

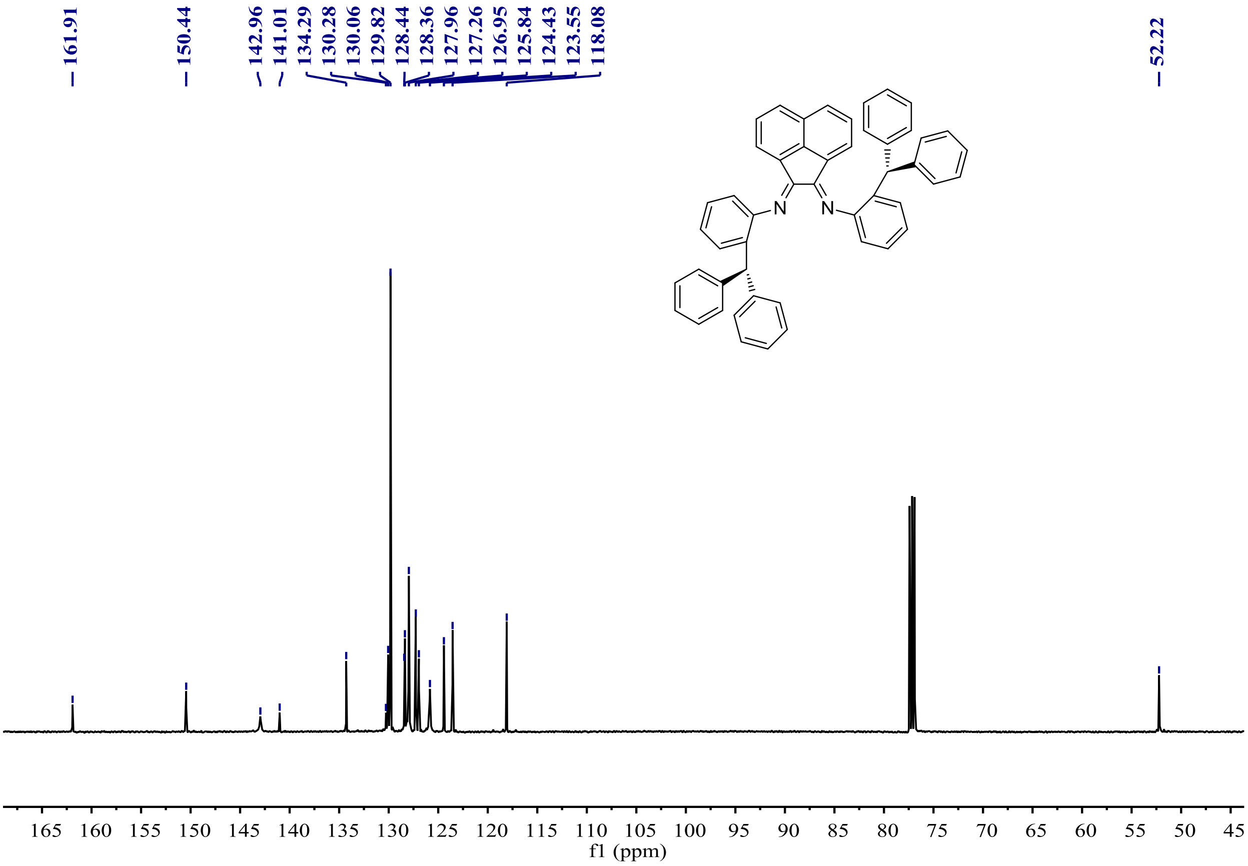


Figure S8. ^{13}C NMR spectrum of **Ligand 2** in $CDCl_3$.

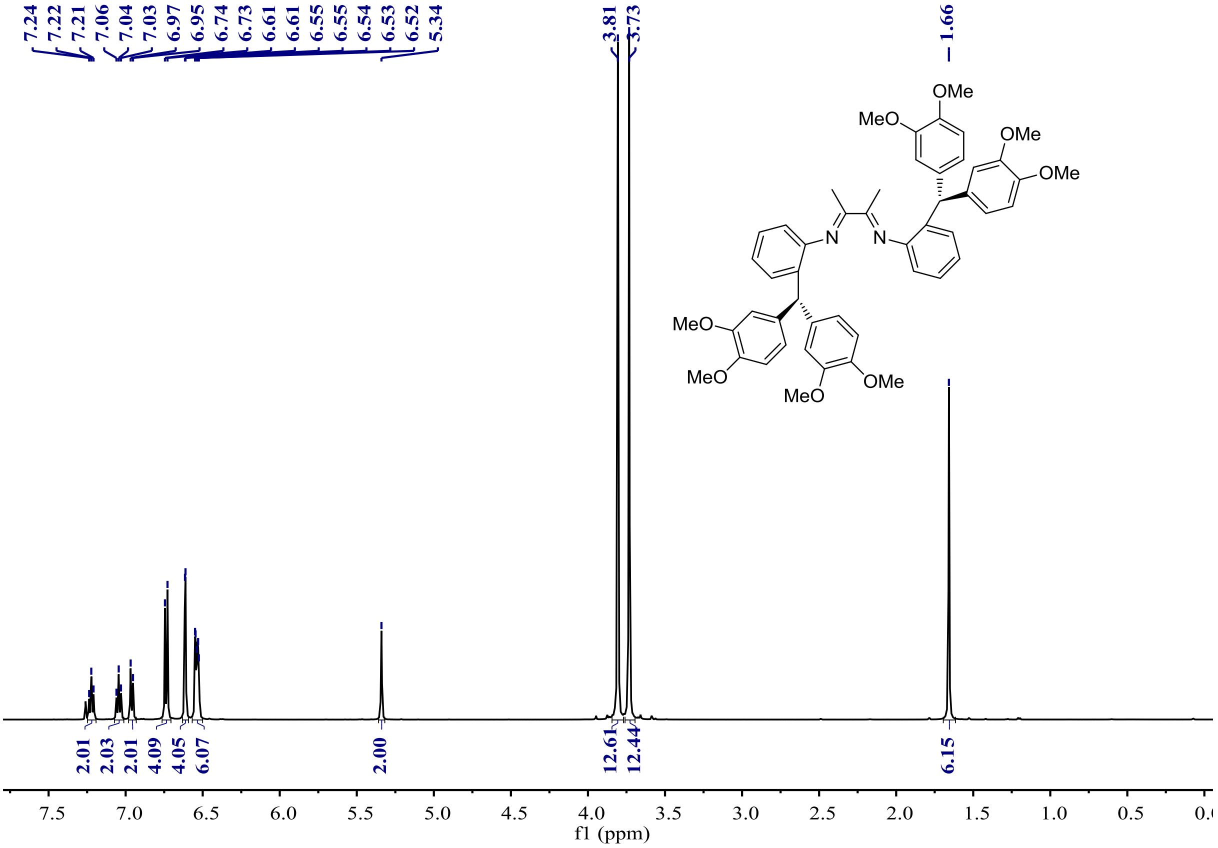


Figure S9. ^{1}H NMR spectrum of **Ligand 3** in $CDCl_3$.

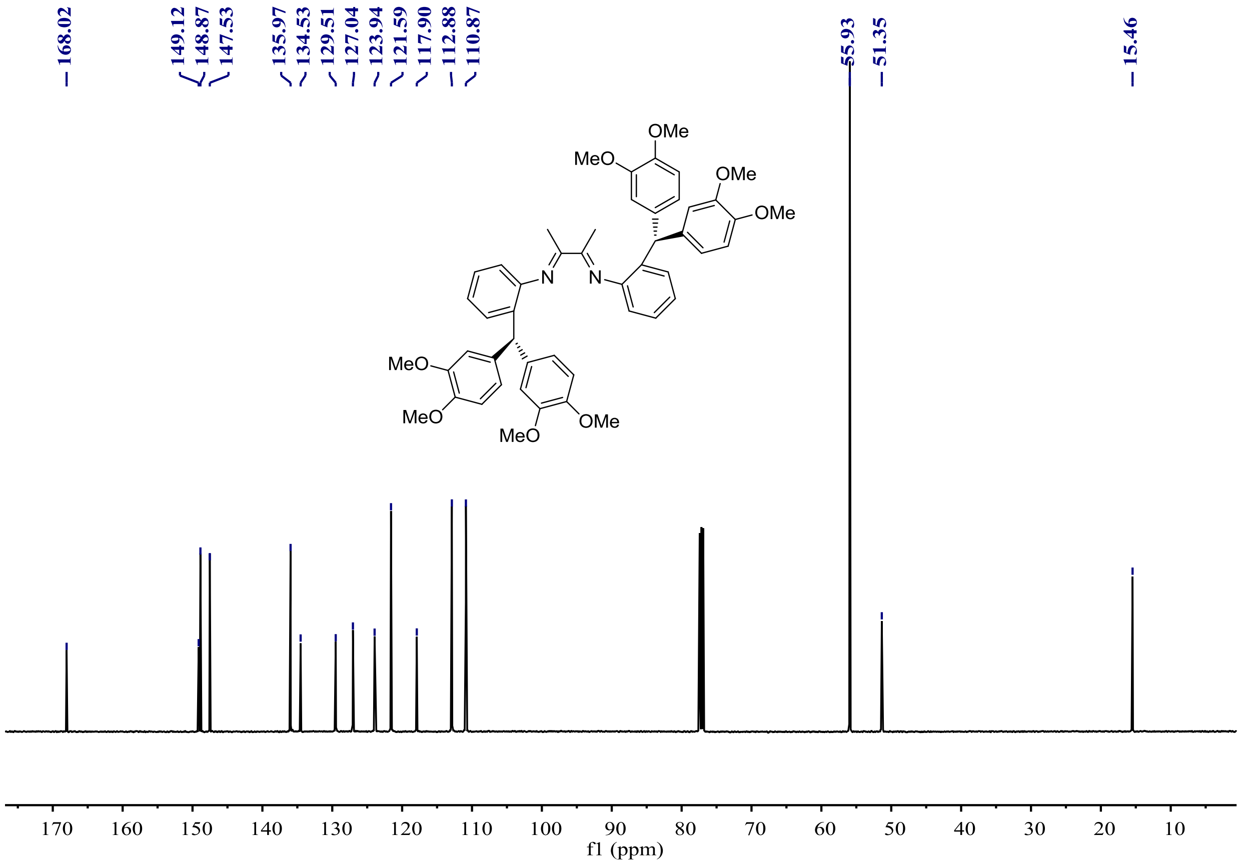


Figure S10. ^{13}C NMR spectrum of **Ligand 3** in $CDCl_3$.

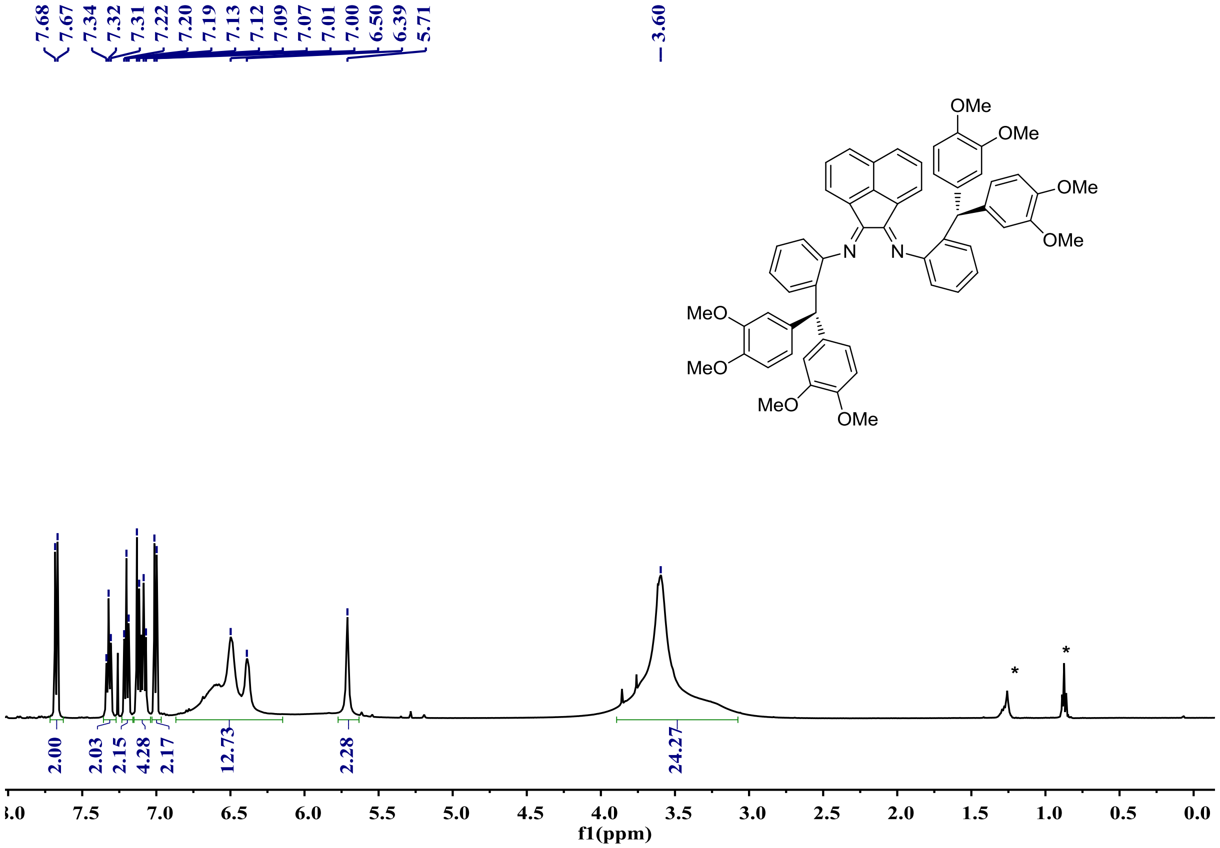


Figure S11. ^{1}H NMR spectrum of **Ligand 4** in $CDCl_3$. (*: Hexane)

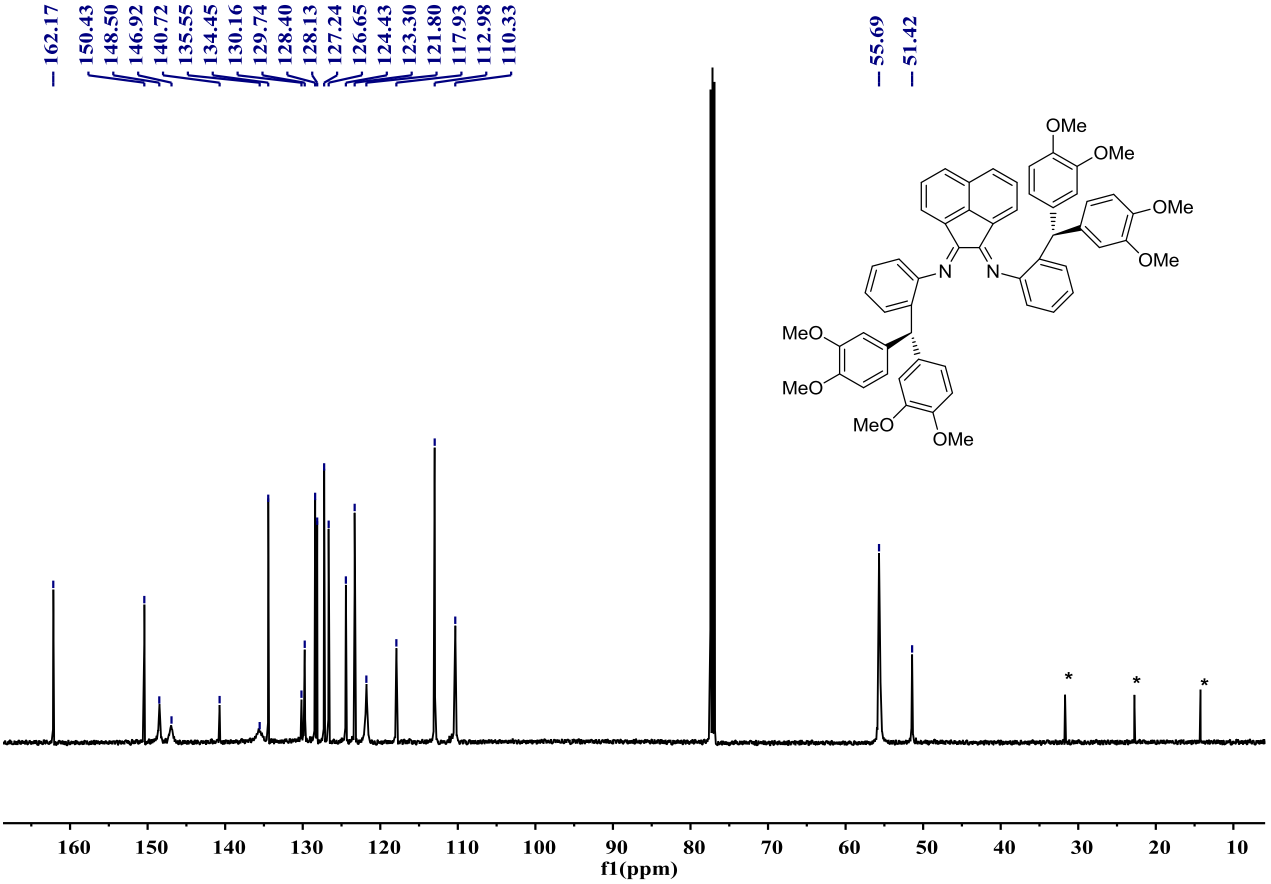


Figure S12. ^{13}C NMR spectrum of **Ligand 4** in CDCl$_3$. (*: Hexane)

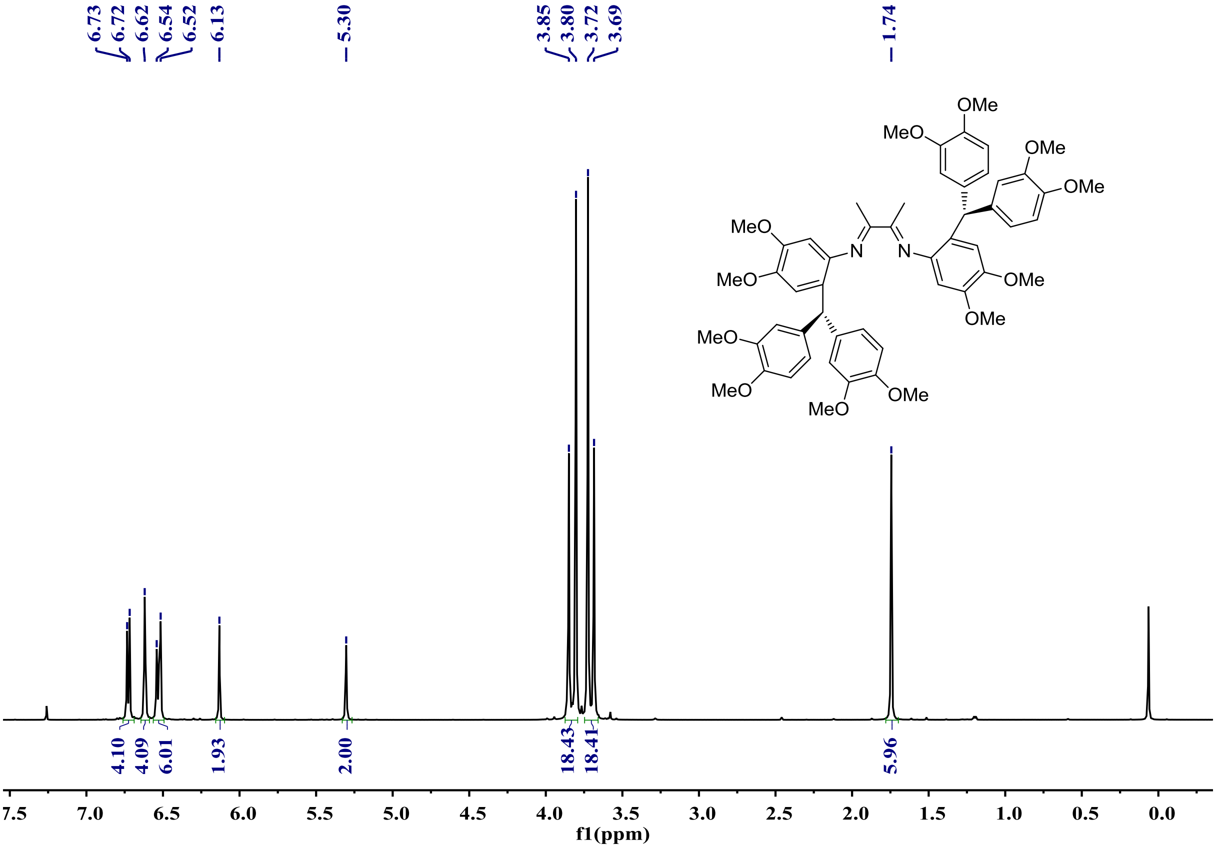


Figure S13. ^{1}H NMR spectrum of **Ligand 5** in CDCl$_3$.

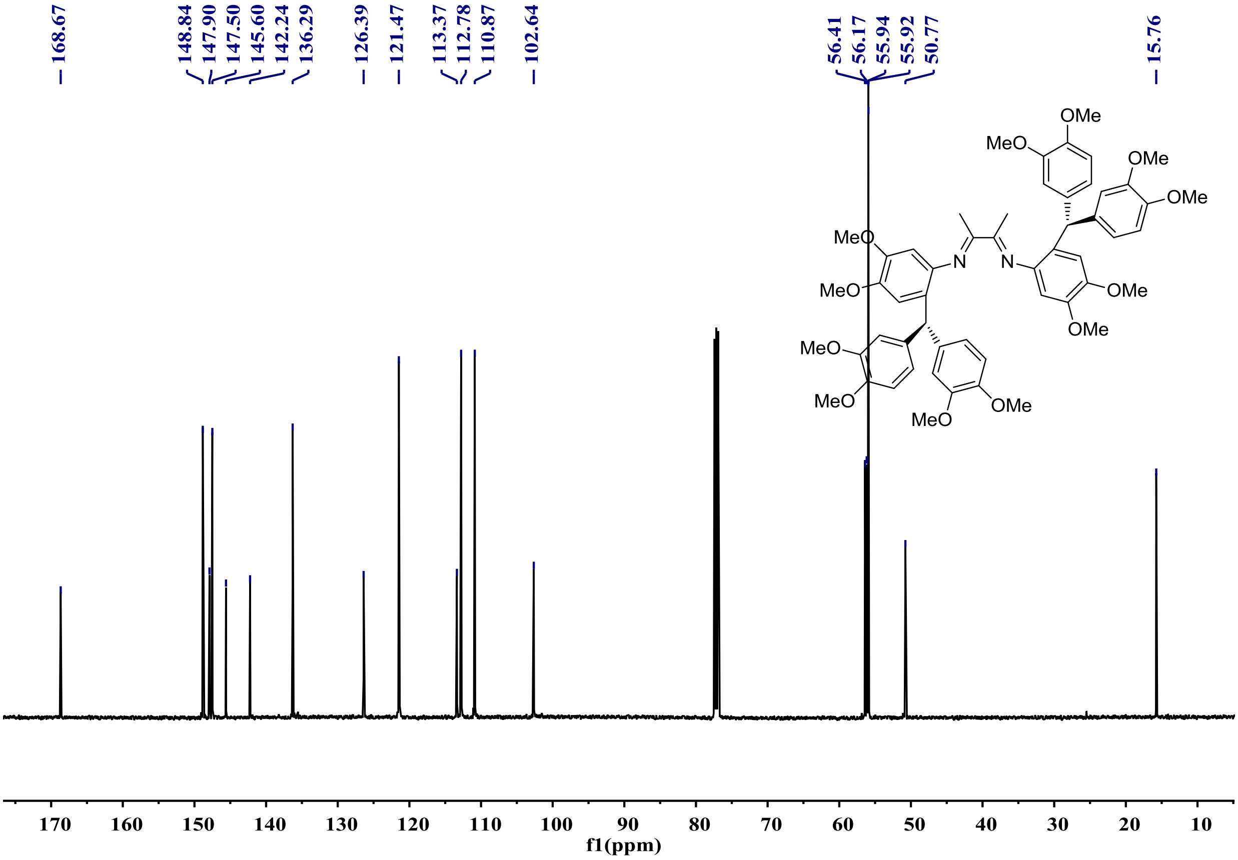


Figure S14. ^{13}C NMR spectrum of **Ligand 5** in $CDCl_3$.

5.3 ^{1}H, ^{13}C, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC NMR of Complexes

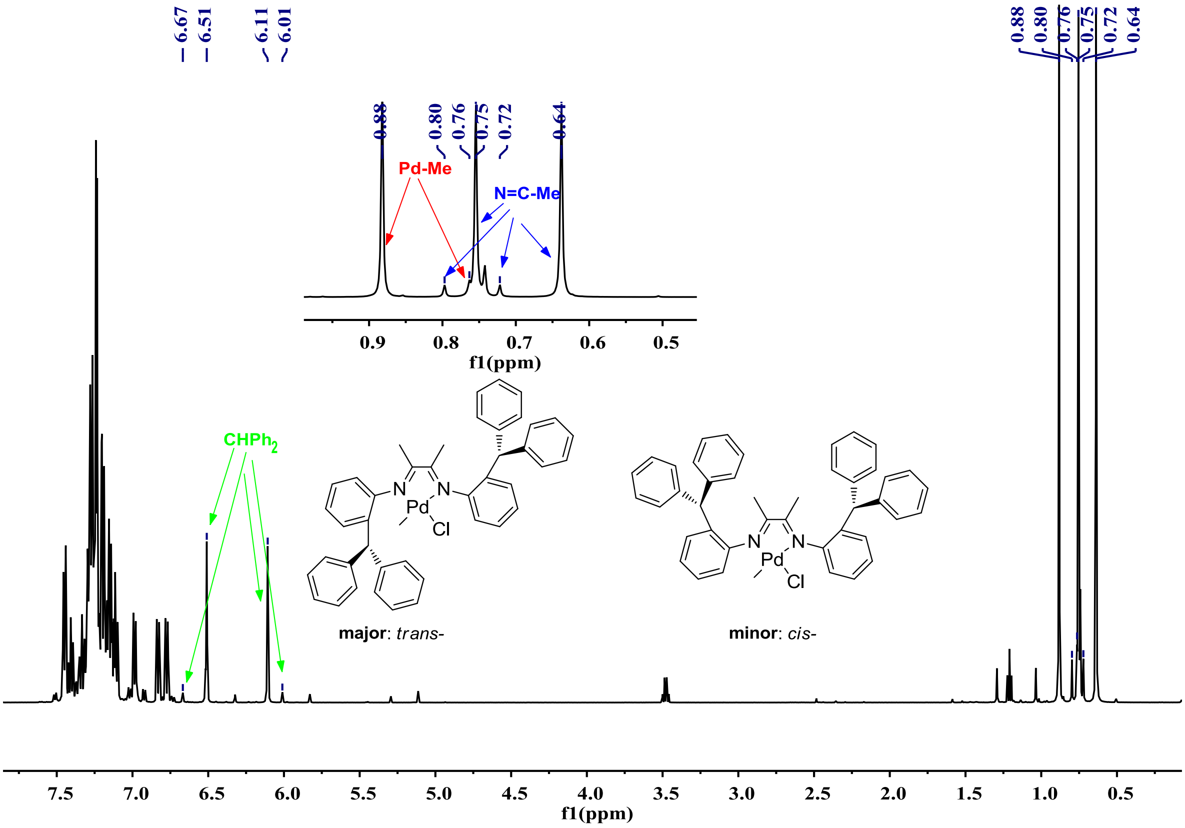


Figure S15. ^{1}H NMR spectrum of **Pd-1** in $CDCl_3$.

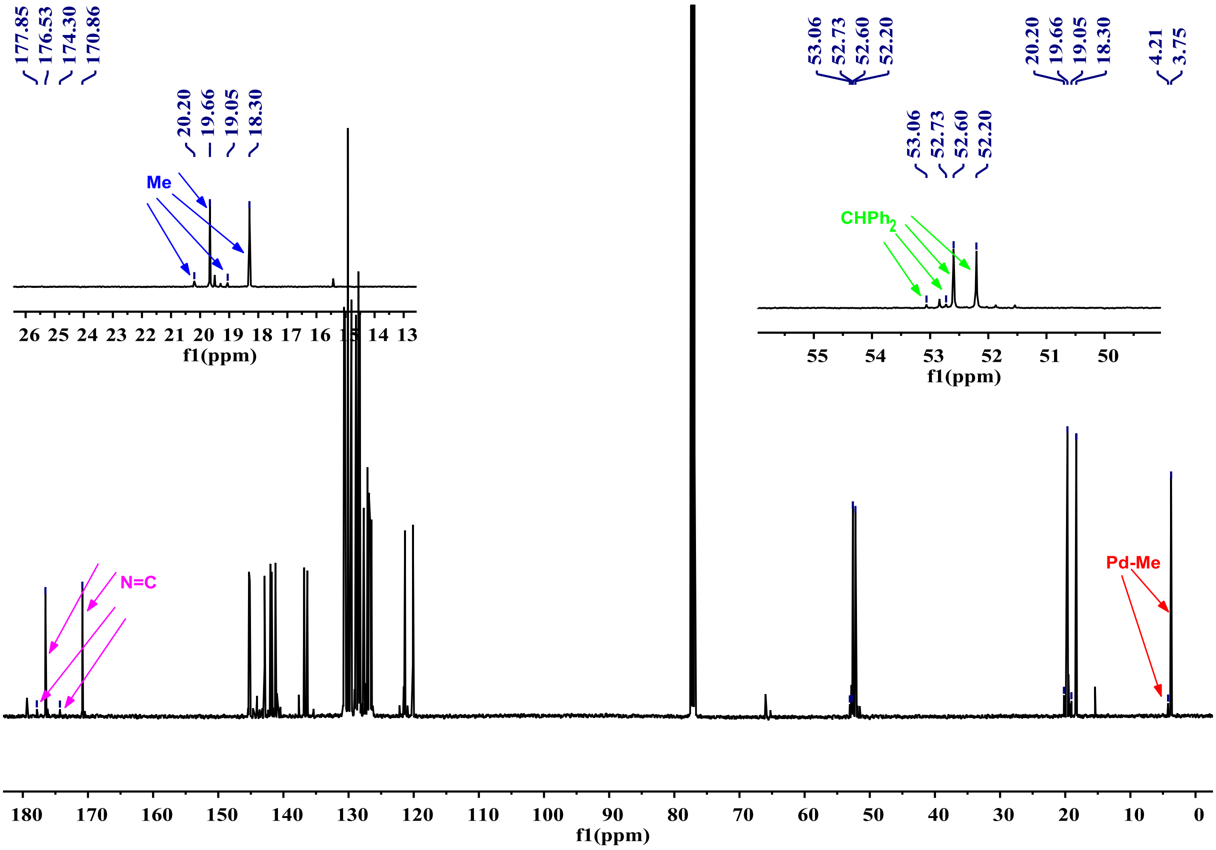


Figure S16. ^{13}C NMR spectrum of **Pd-1** in $CDCl_3$.

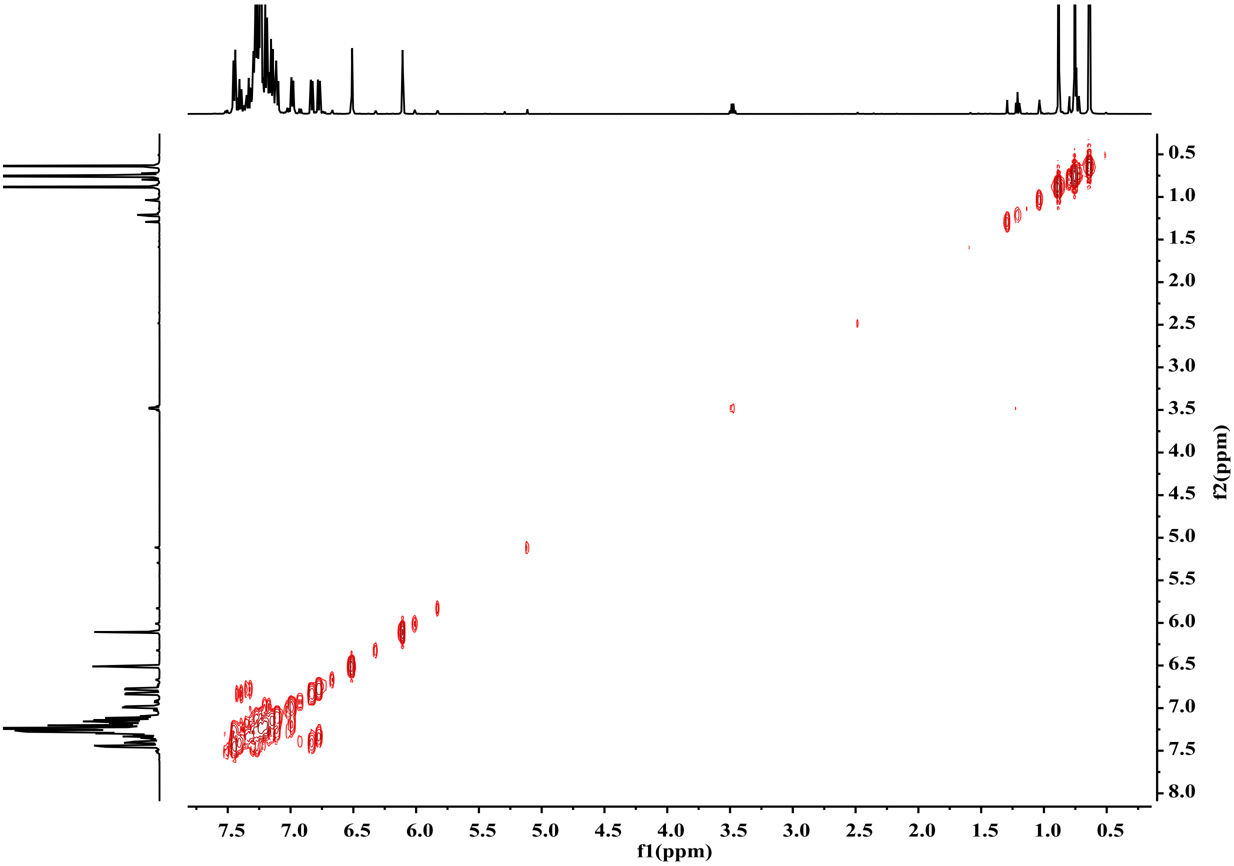


Figure S17. ^{1}H-^{1}H COSY NMR spectrum of **Pd-1** in $CDCl_3$.

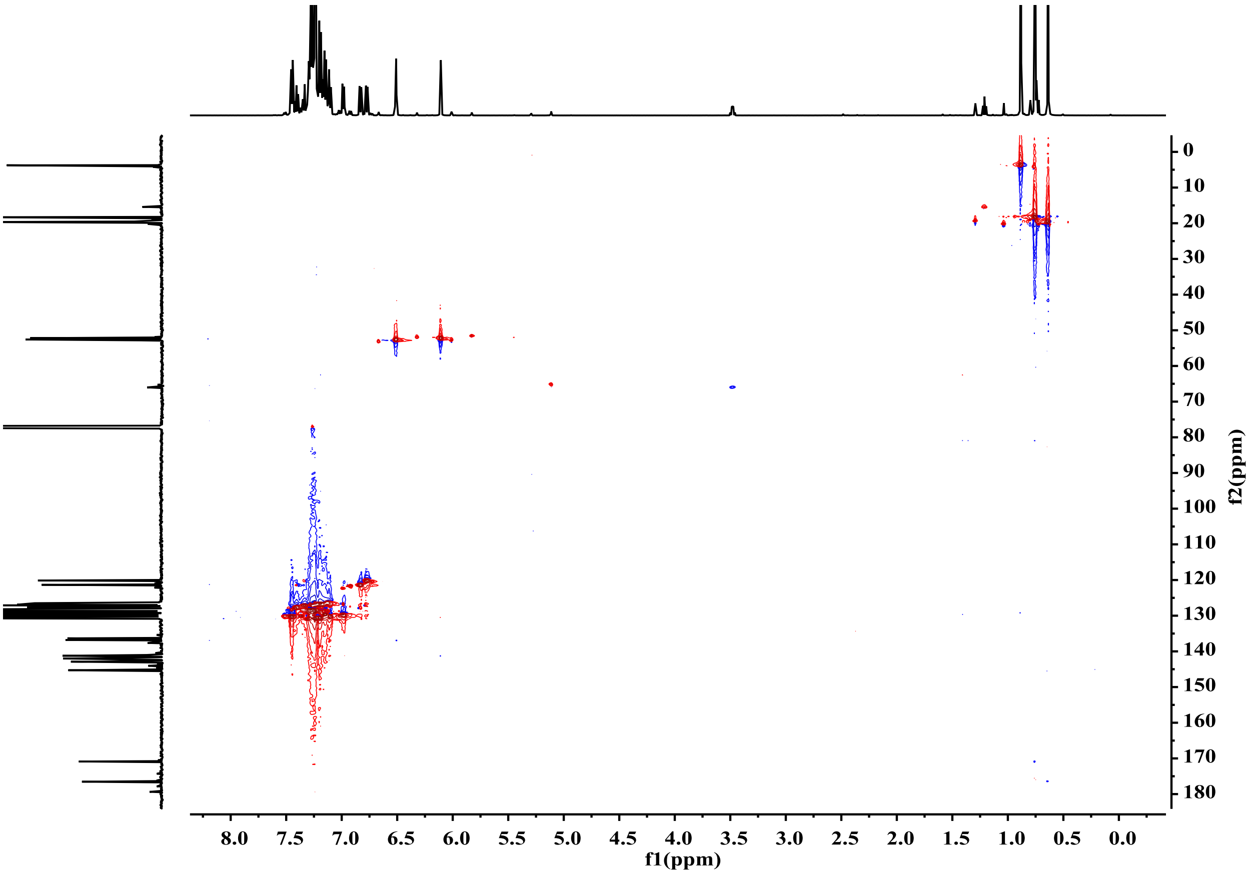


Figure S18. ^{1}H-^{13}C HSQC NMR spectrum of **Pd-1** in CDCl$_3$.

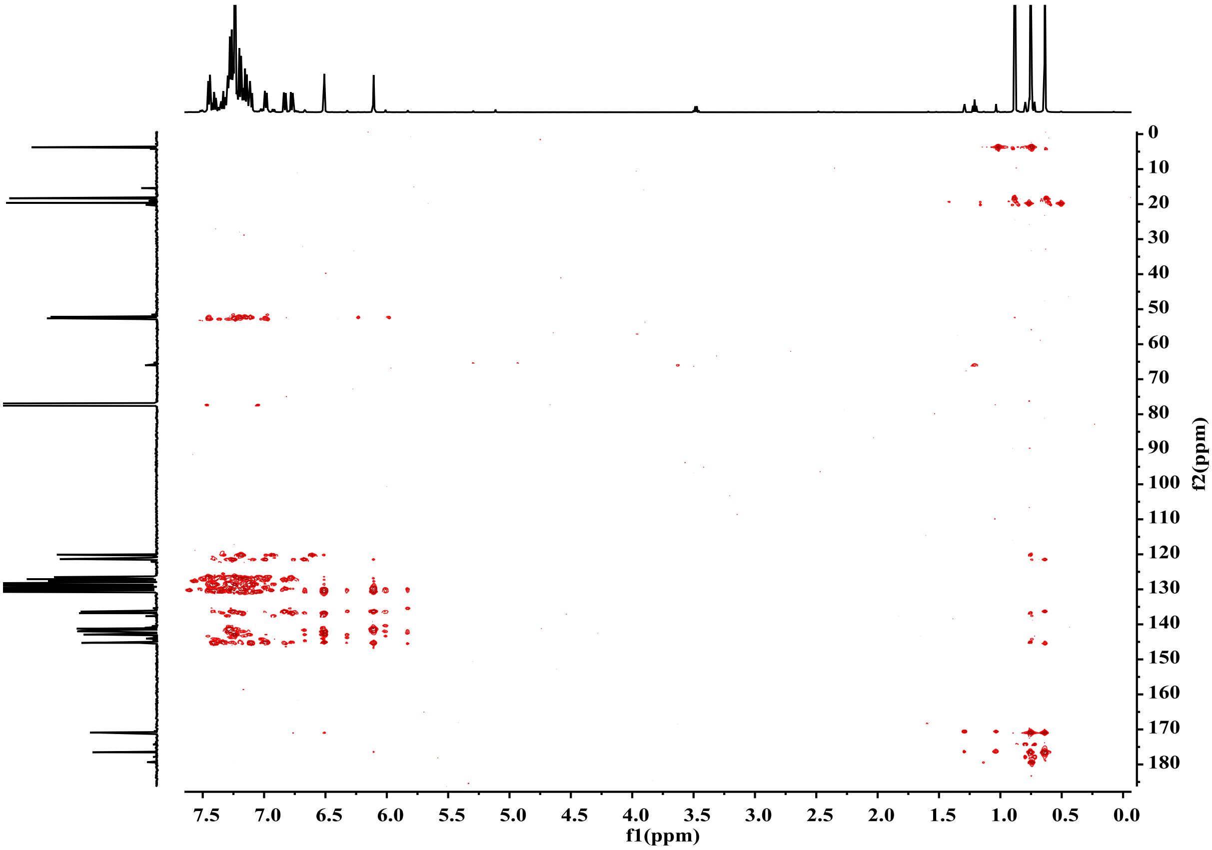


Figure S19. ^{1}H-^{13}C HMBC NMR spectrum of **Pd-1** in CDCl$_3$.

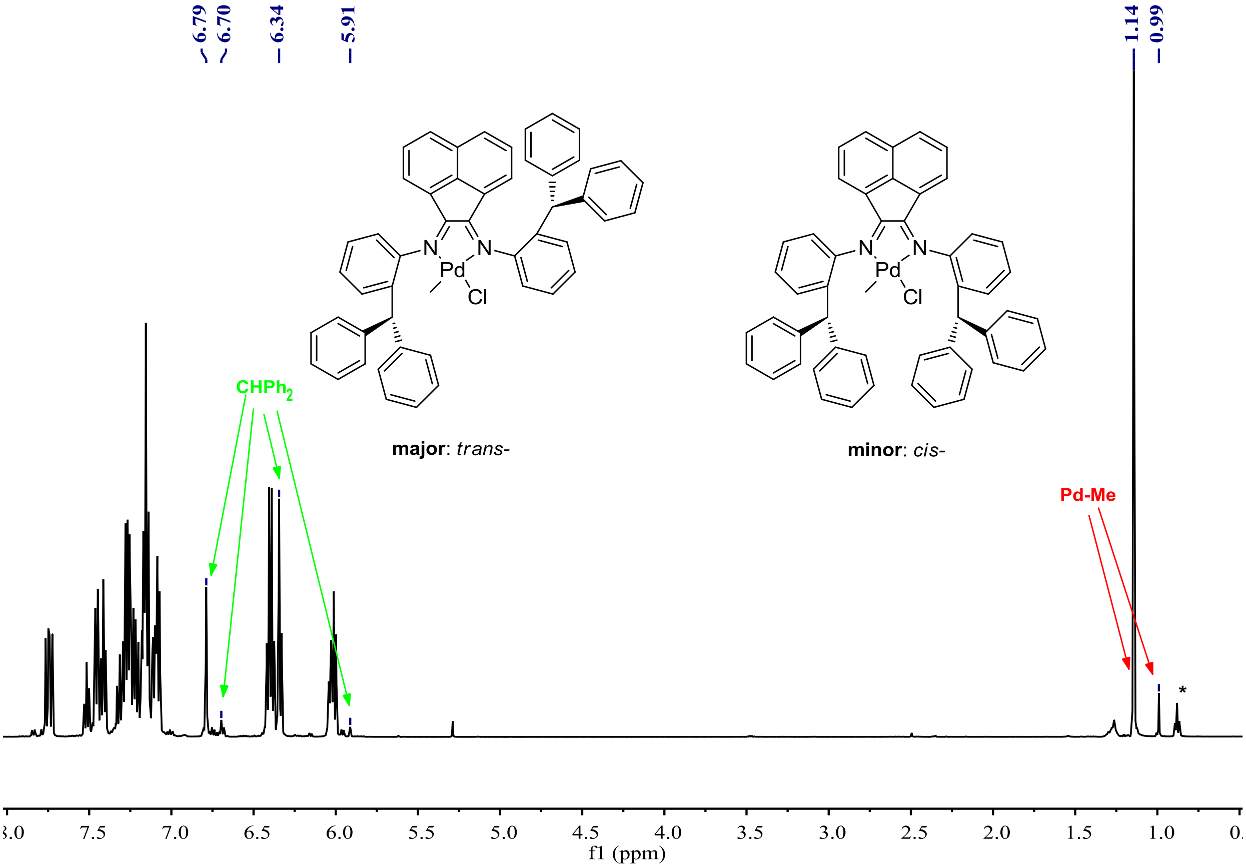


Figure S20. ^{1}H NMR spectrum of **Pd-2** in CDCl$_3$. (*: Hexane)

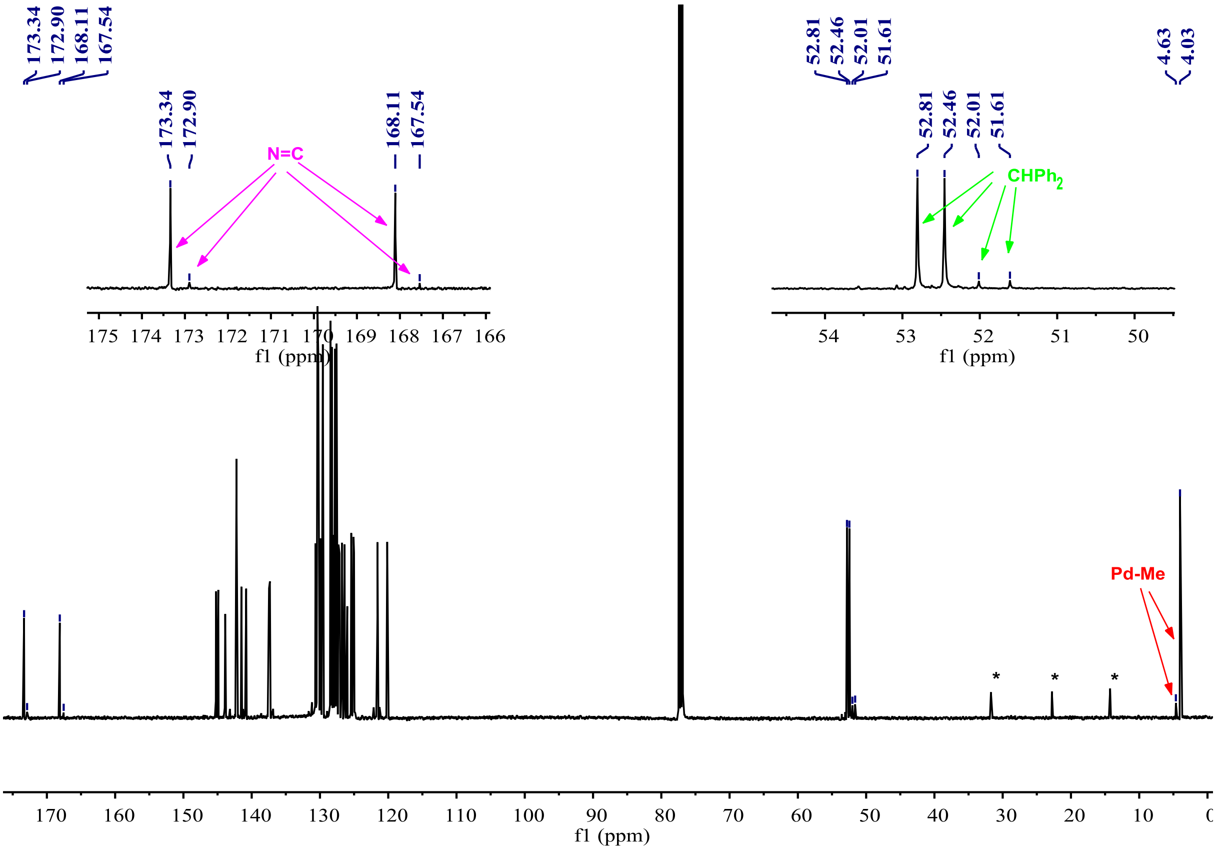


Figure S21. ^{13}C NMR spectrum of **Pd-2** in CDCl$_3$. (*: Hexane)

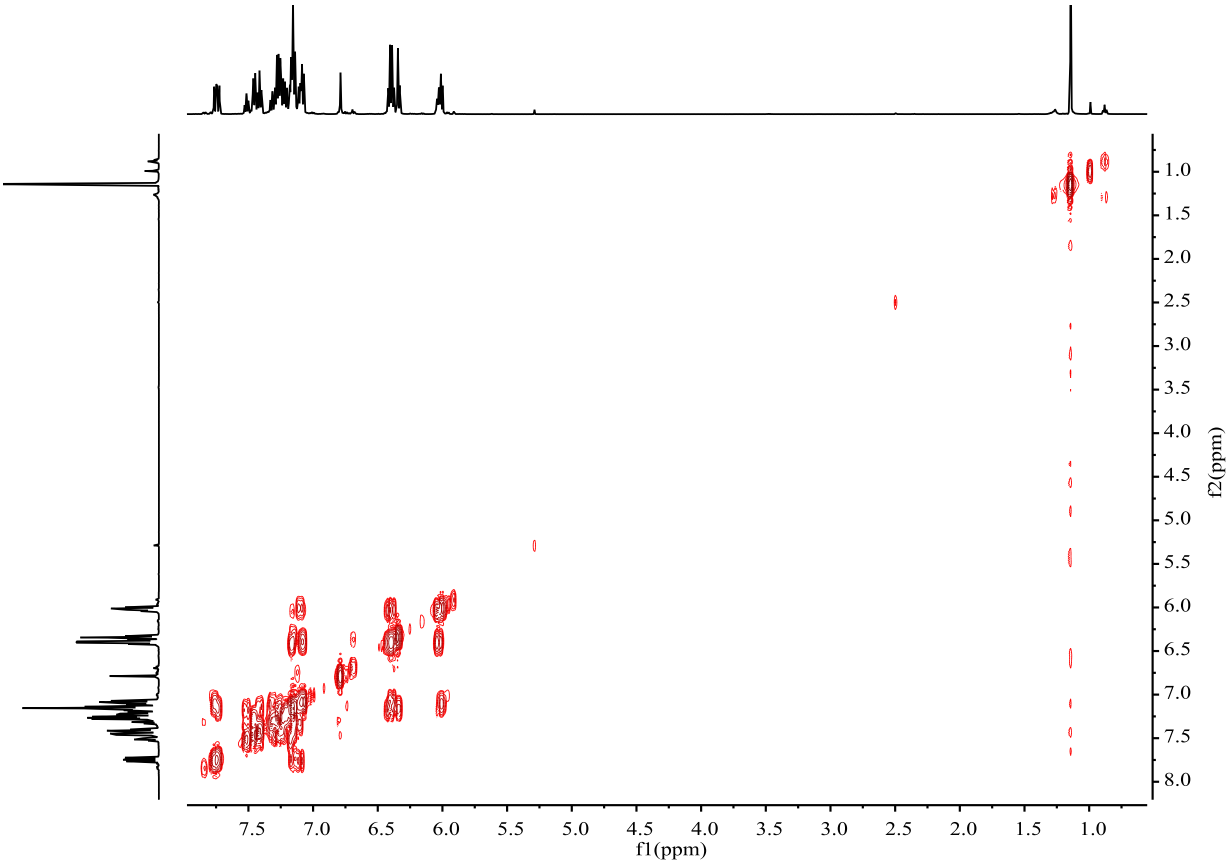


Figure S22. ^{1}H-^{1}H COSY NMR spectrum of **Pd-2** in CDCl$_3$.

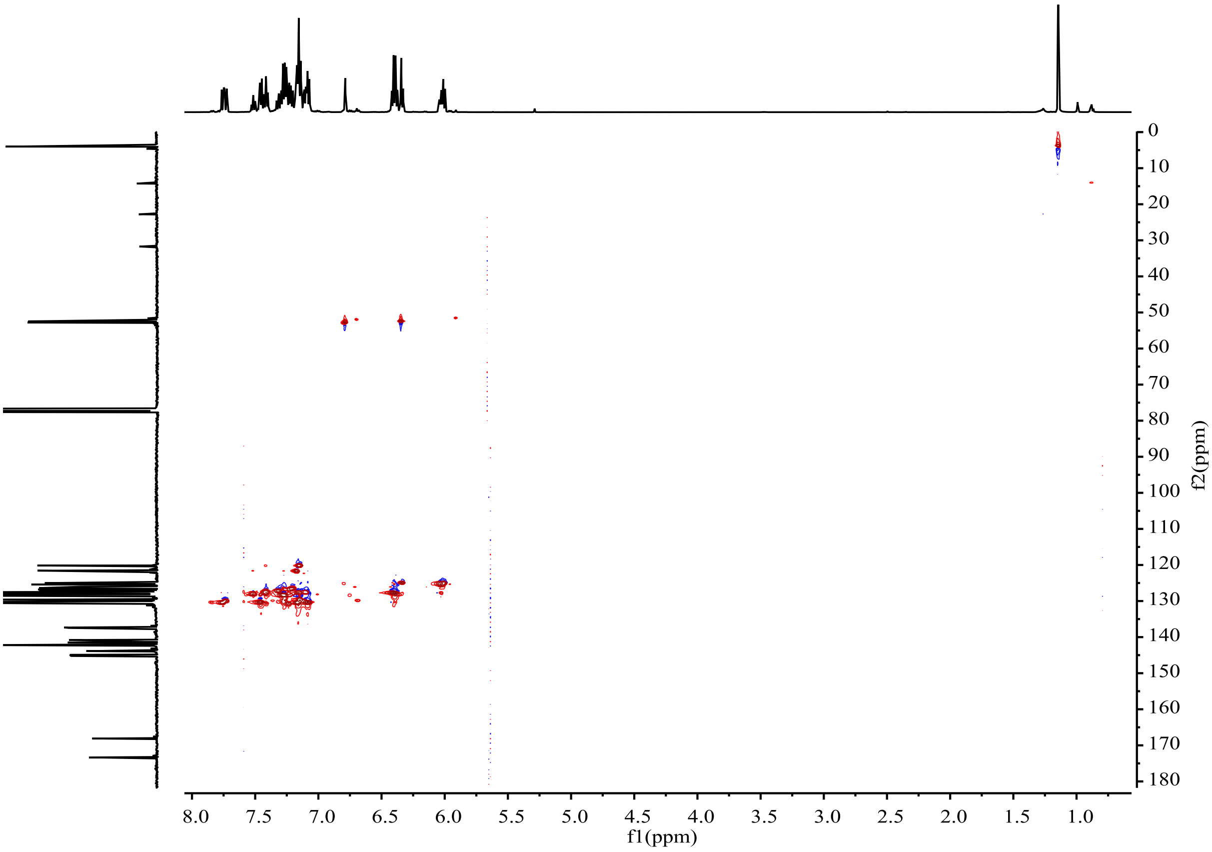


Figure S23. ^{1}H-^{13}C HSQC NMR spectrum of **Pd-2** in CDCl$_3$**.**

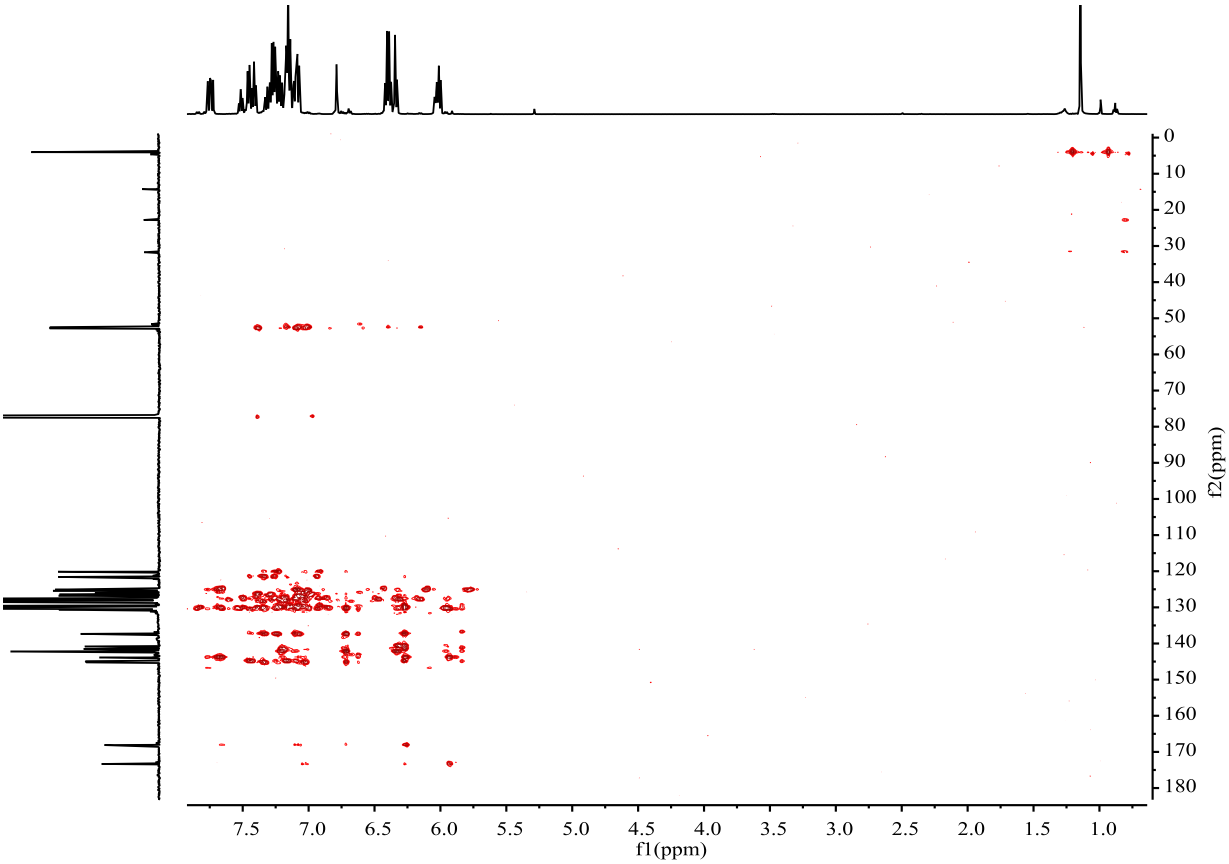


Figure S24. ^{1}H-^{13}C HMBC NMR spectrum of **Pd-2** in $CDCl_3$**.**

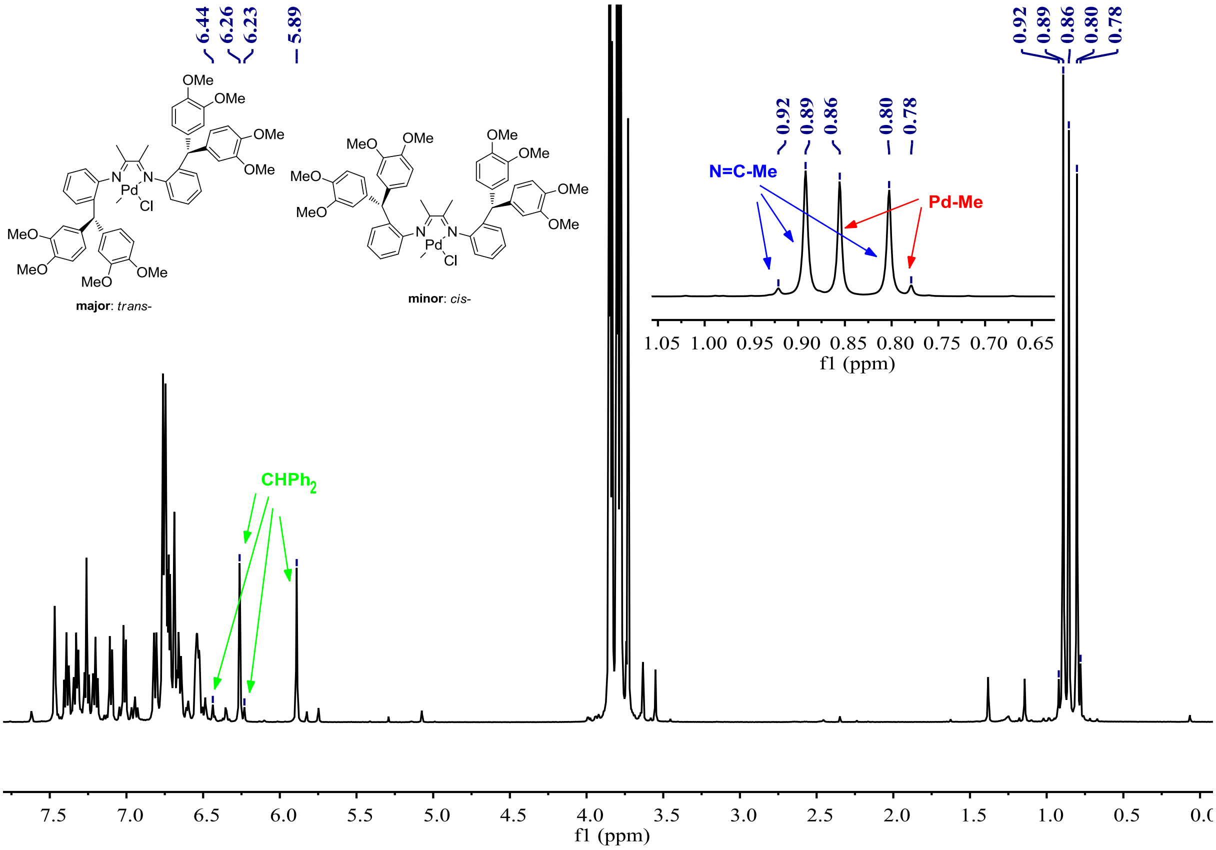


Figure S25. ^{1}H NMR spectrum of **Pd-3** in $CDCl_3$.

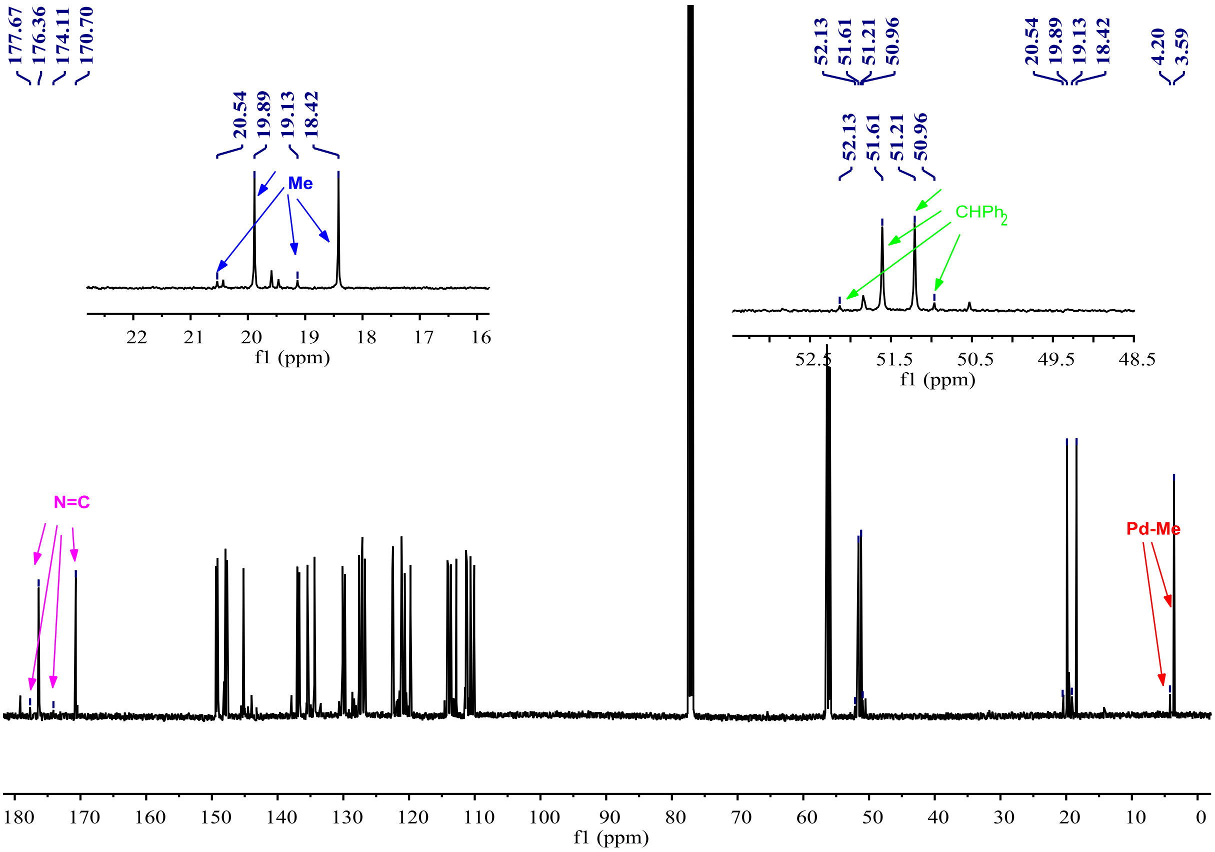


Figure S26. ^{13}C NMR spectrum of **Pd-3** in CDCl$_3$.

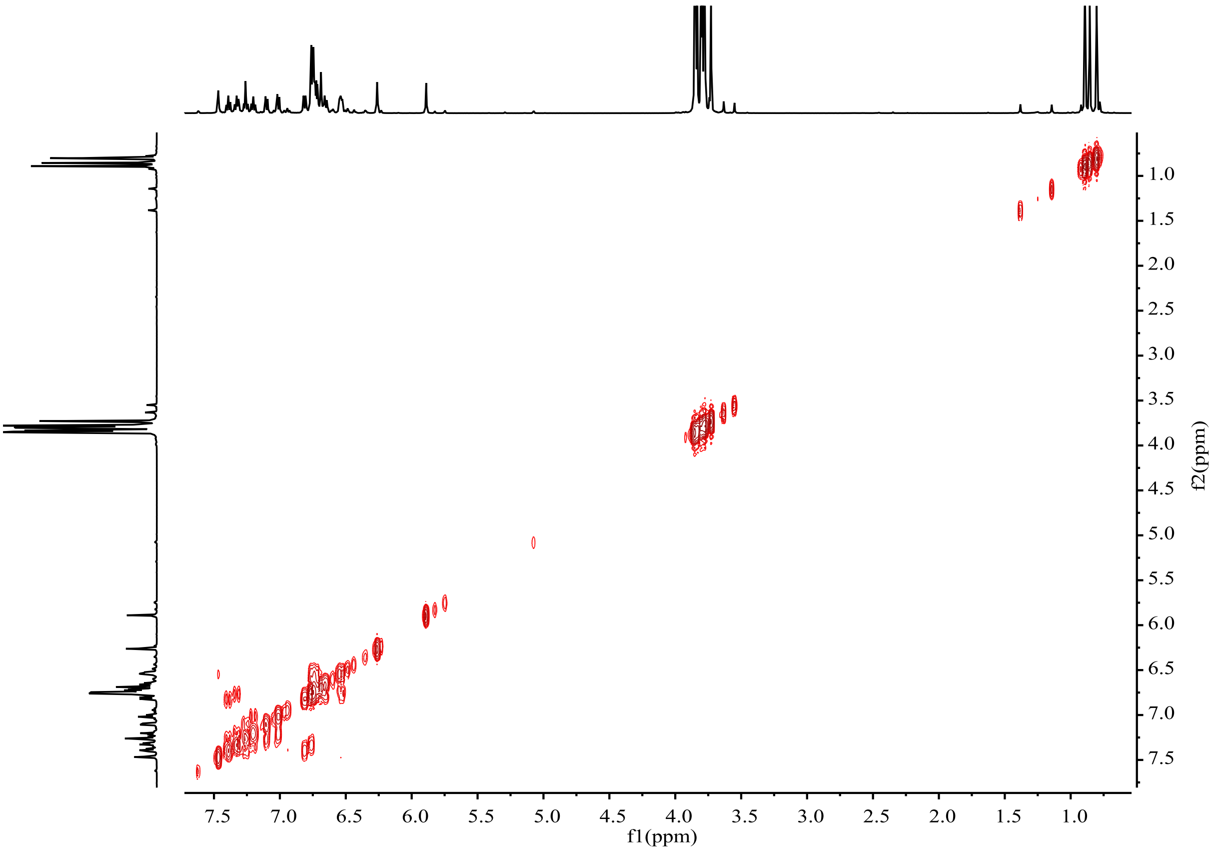


Figure S27. ^{1}H-^{1}H COSY NMR spectrum of **Pd-3** in CDCl$_3$.

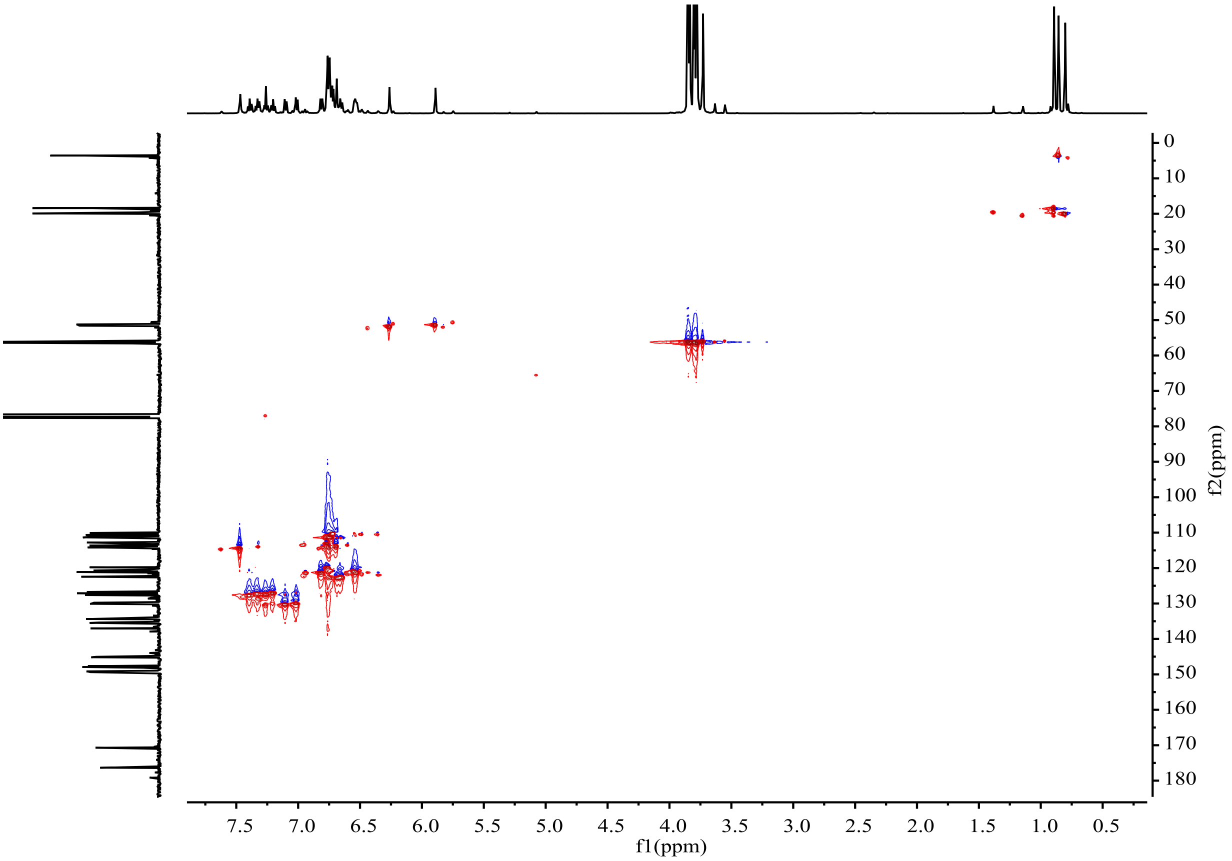


Figure S28. ^{1}H-^{13}C HSQC NMR spectrum of **Pd-3** in $CDCl_3$**.**

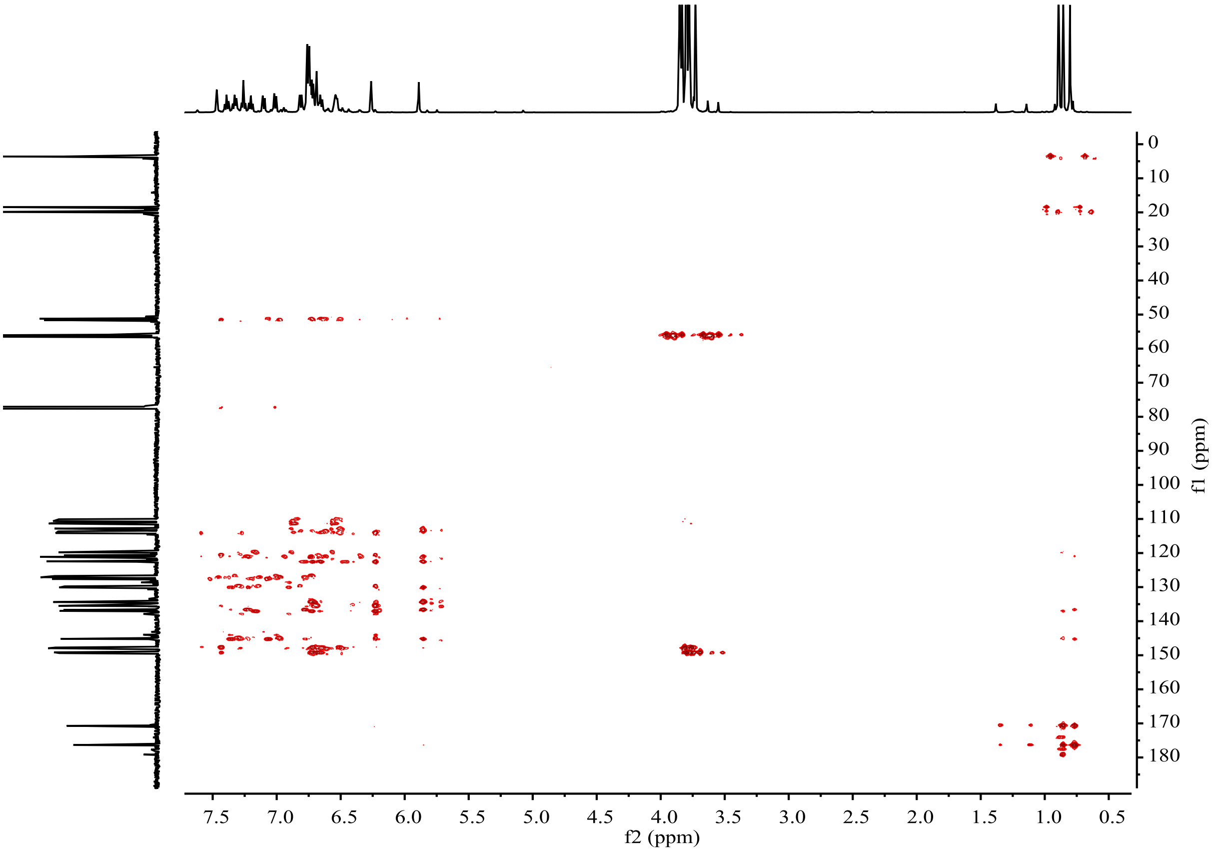


Figure S29. ^{1}H-^{13}C HMBC NMR spectrum of **Pd-3** in $CDCl_3$**.**

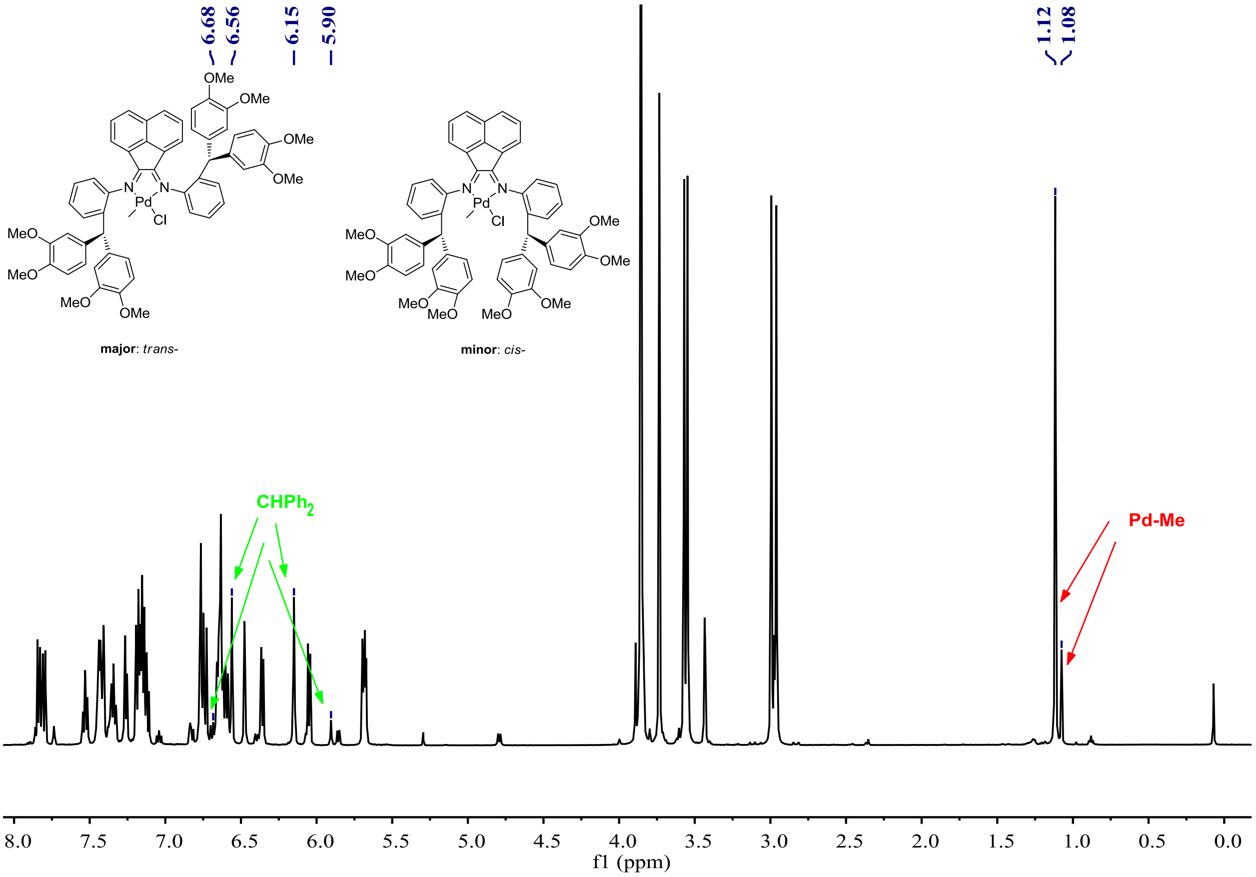


Figure S30. ^{1}H NMR spectrum of **Pd-4** in CDCl$_3$.

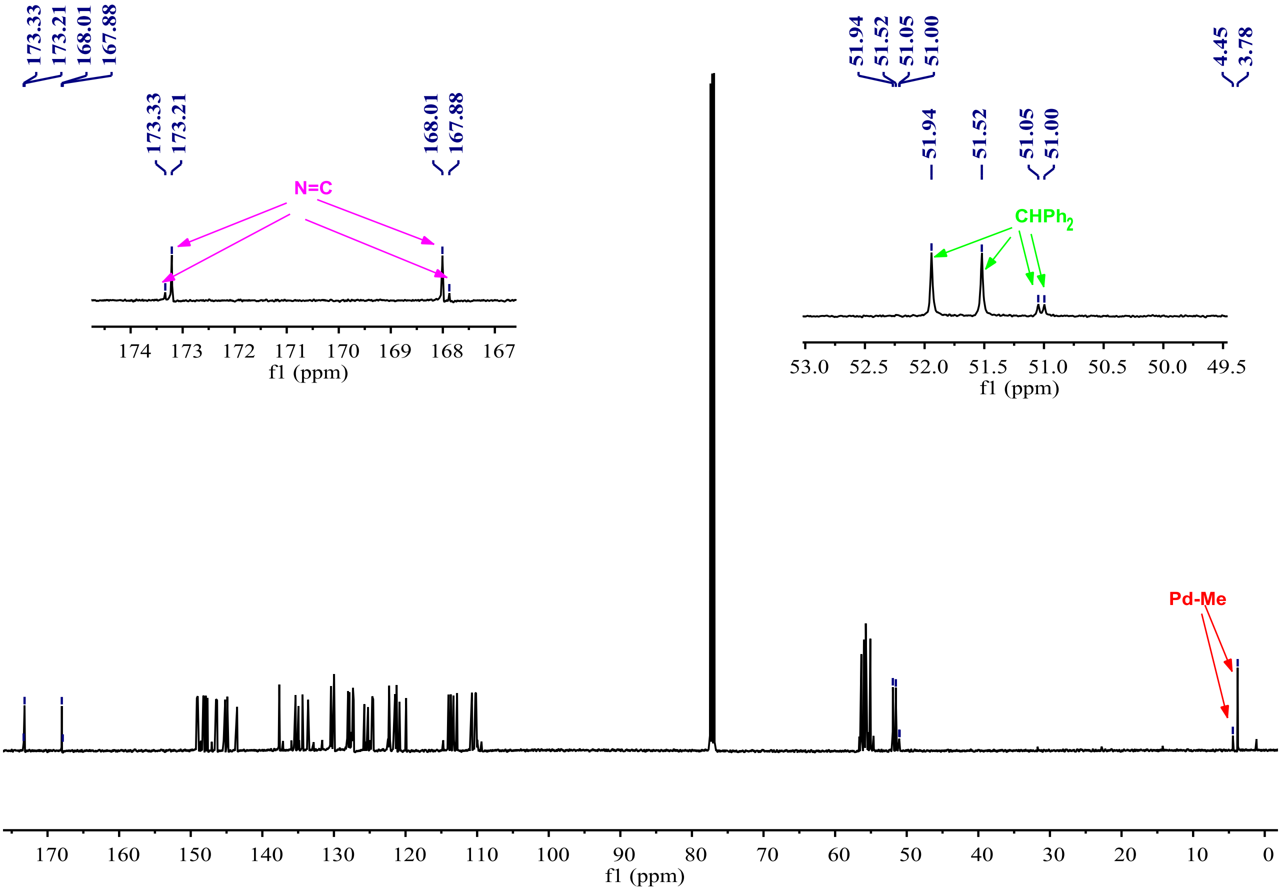


Figure S31. ^{13}C NMR spectrum of **Pd-4** in CDCl$_3$.

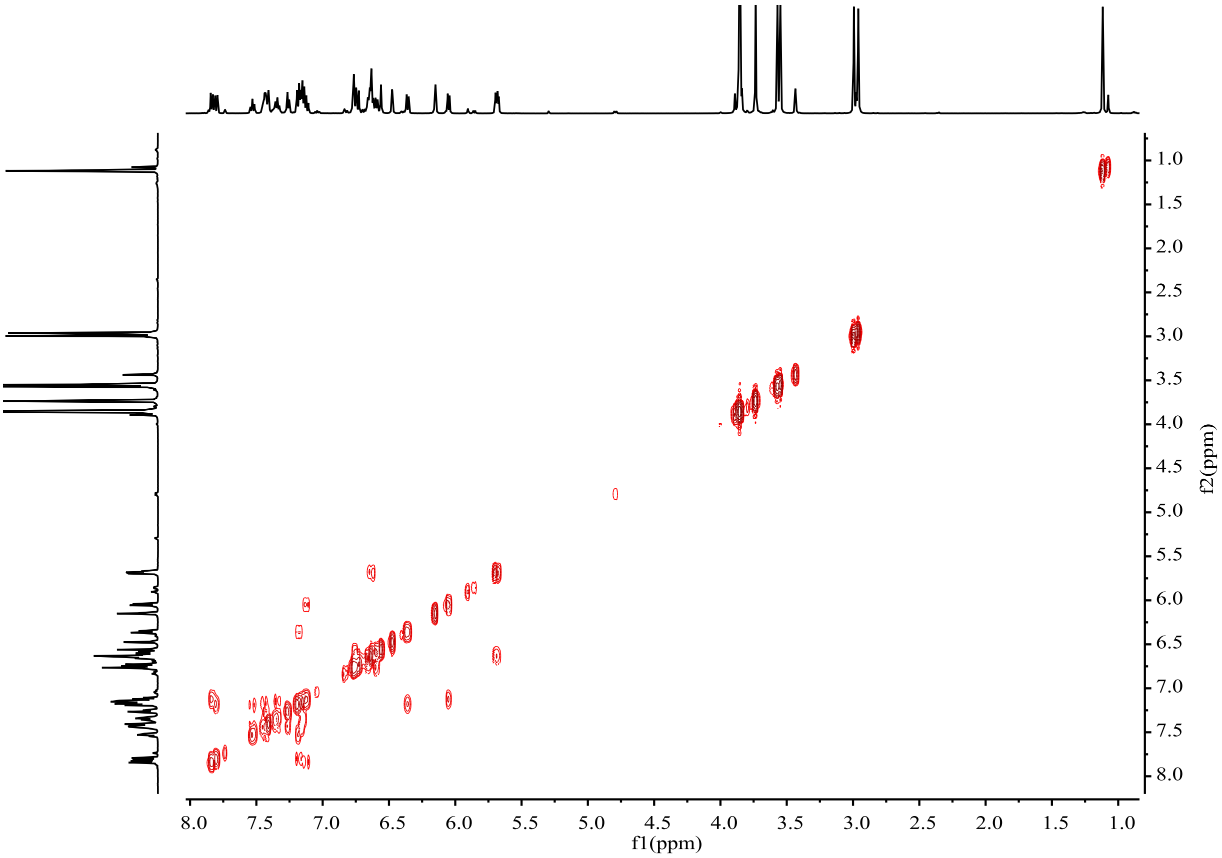


Figure S32. ^{1}H-^{1}H COSY NMR spectrum of **Pd-4** in $CDCl_3$.

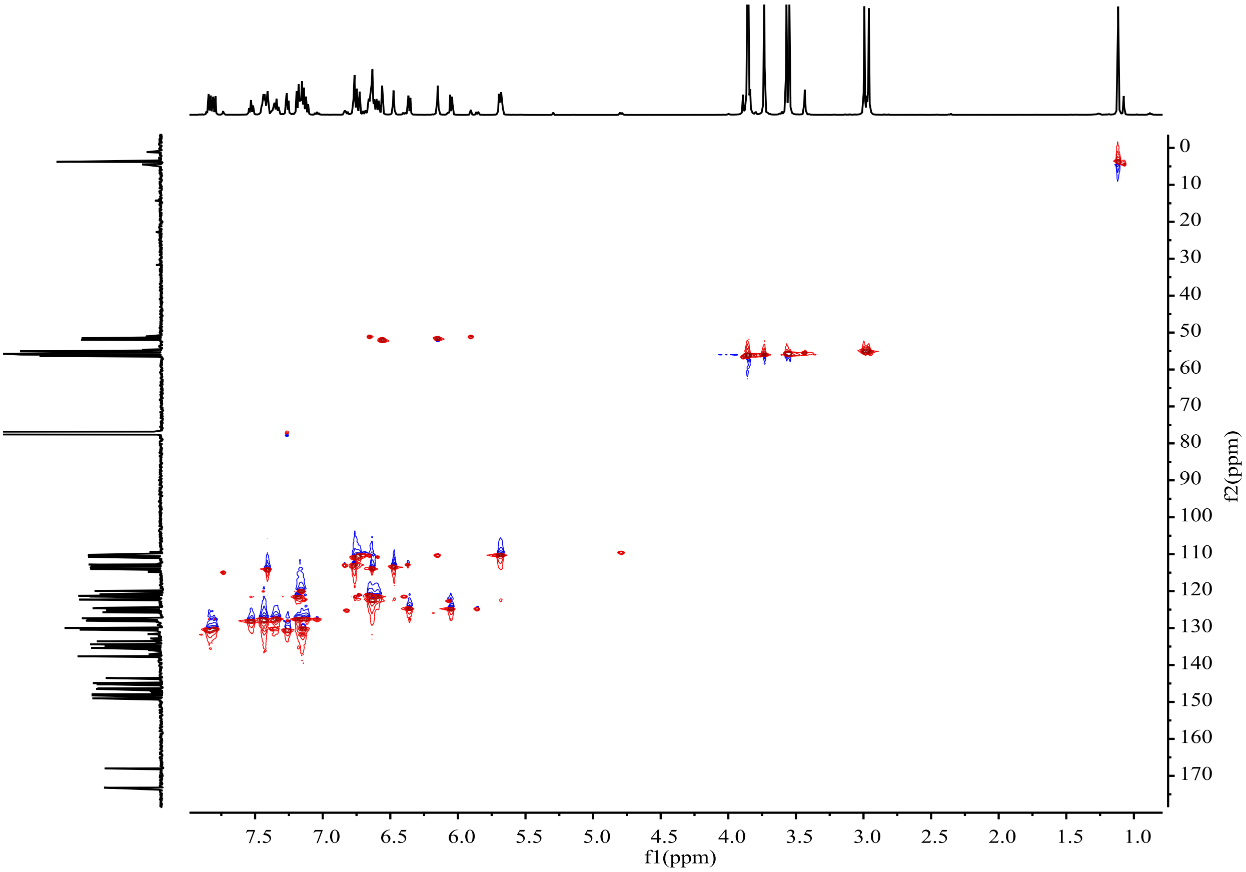


Figure S33. ^{1}H-^{13}C HSQC NMR spectrum of **Pd-4** in $CDCl_3$**.**

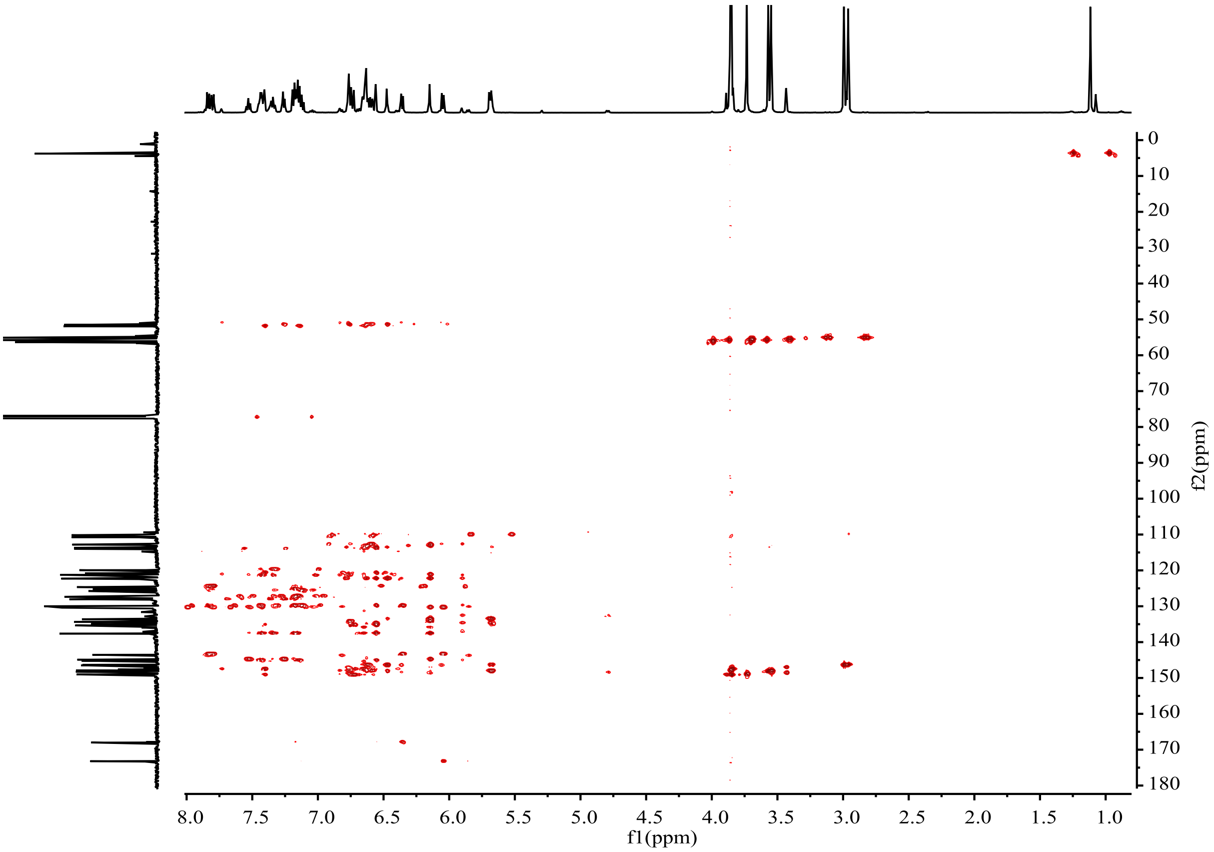


Figure S34. ^{1}H-^{13}C HMBC NMR spectrum of **Pd-4** in CDCl$_3$**.**

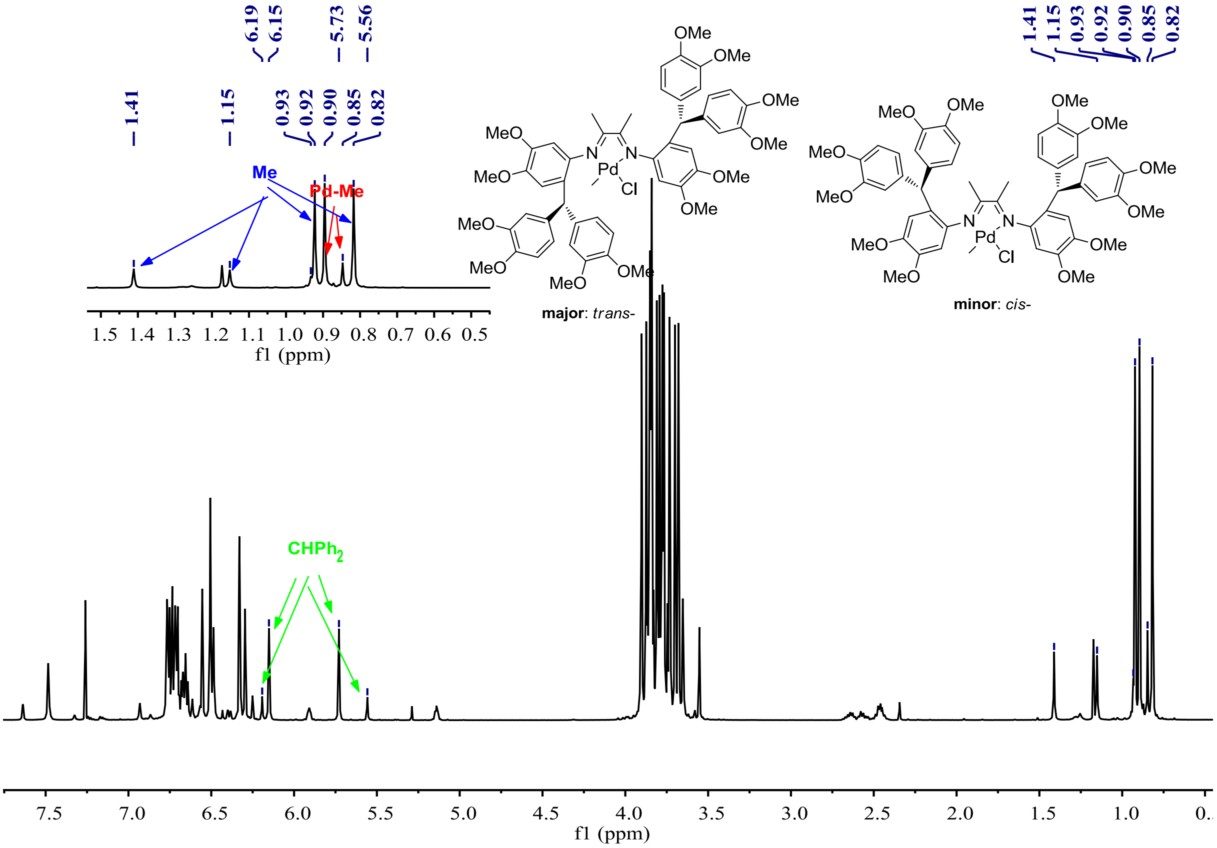


Figure S35. ^{1}H NMR spectrum of **Pd-5** in CDCl$_3$.

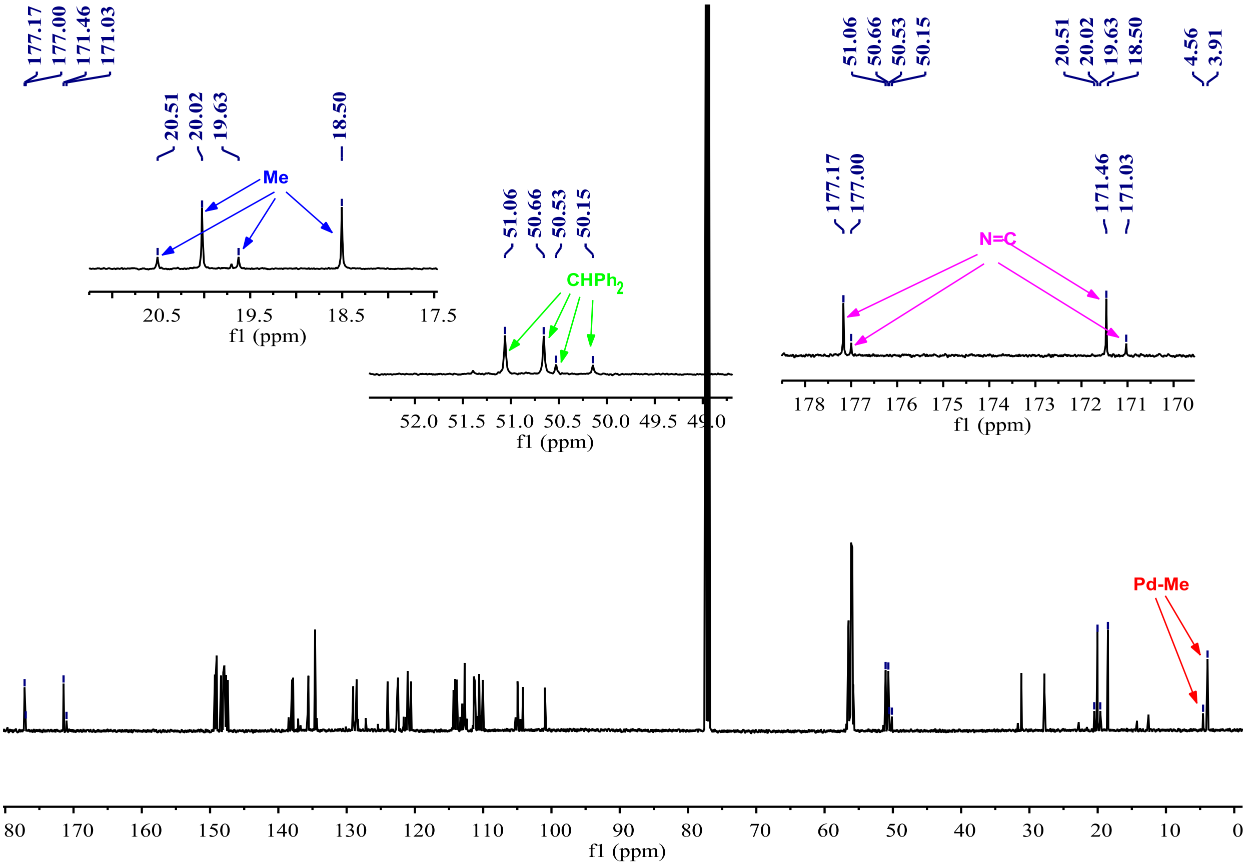


Figure S36. ^{13}C NMR spectrum of **Pd-5** in CDCl$_3$.

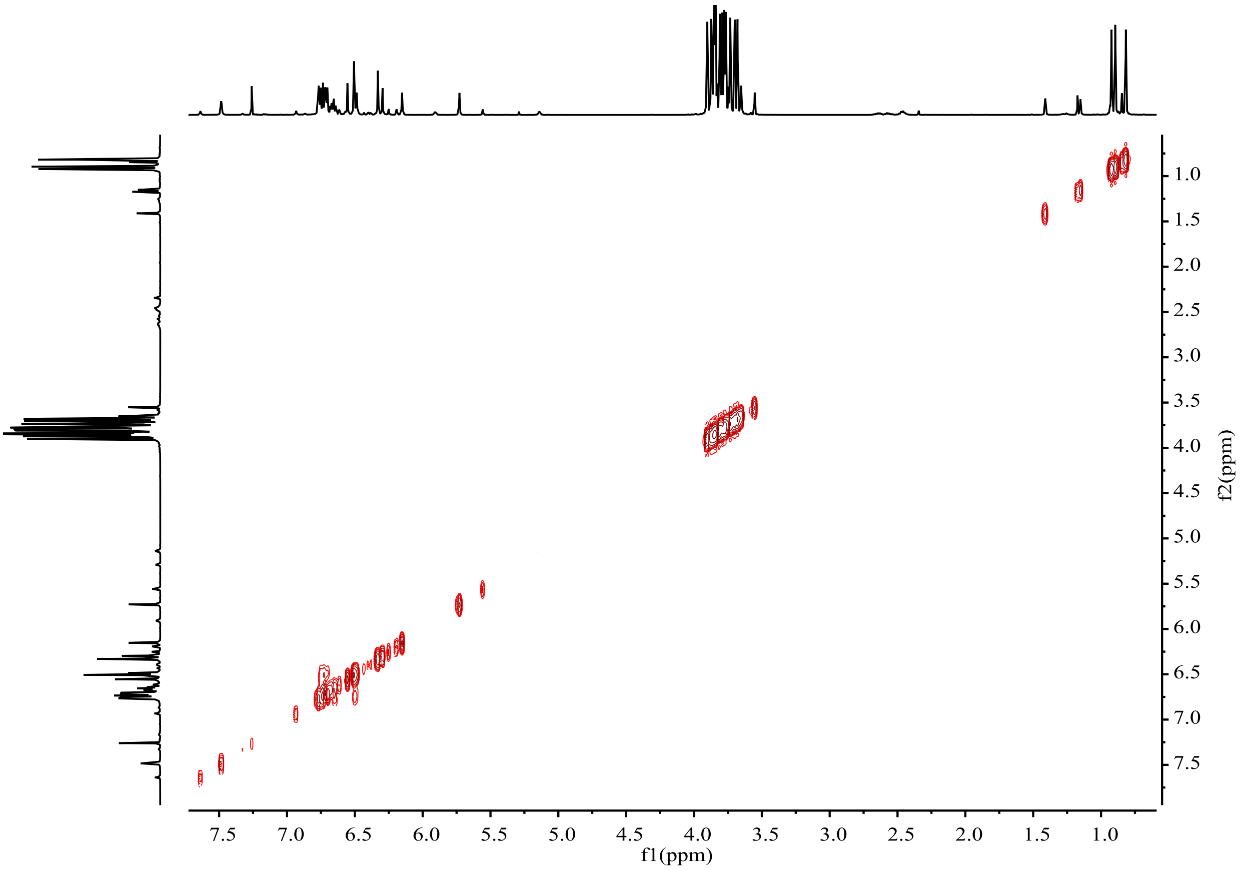


Figure S37. ^{1}H-^{1}H COSY NMR spectrum of **Pd-5** in CDCl$_3$.

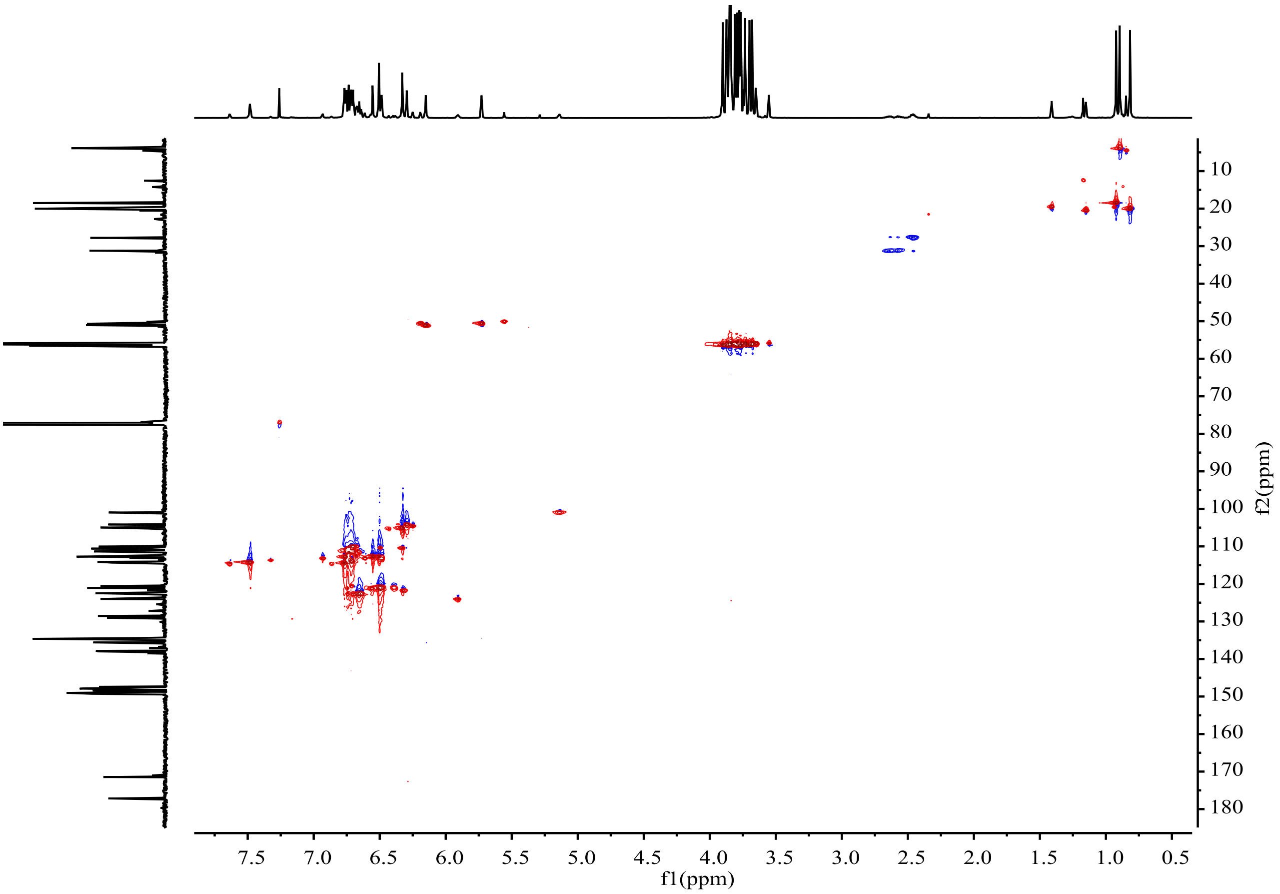


Figure S38. ^{1}H-^{13}C HSQC NMR spectrum of **Pd-5** in CDCl$_3$**.**

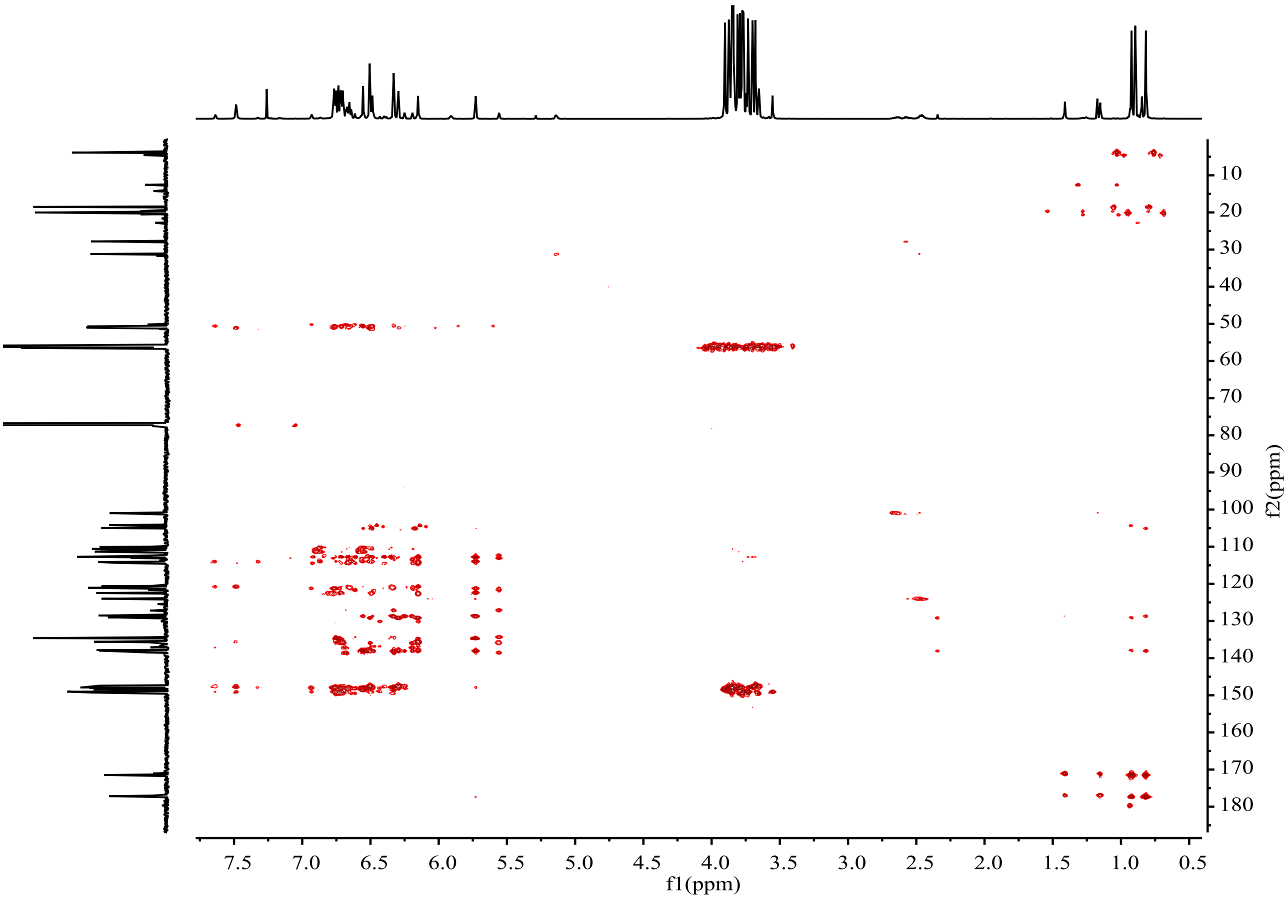


Figure S39. ^{1}H-^{13}C HMBC NMR spectrum of **Pd-5** in CDCl$_3$**.**

6 NMR figures of (co)polymers

6.1 ^{1}H NMR of polymer by Ni Catalyst

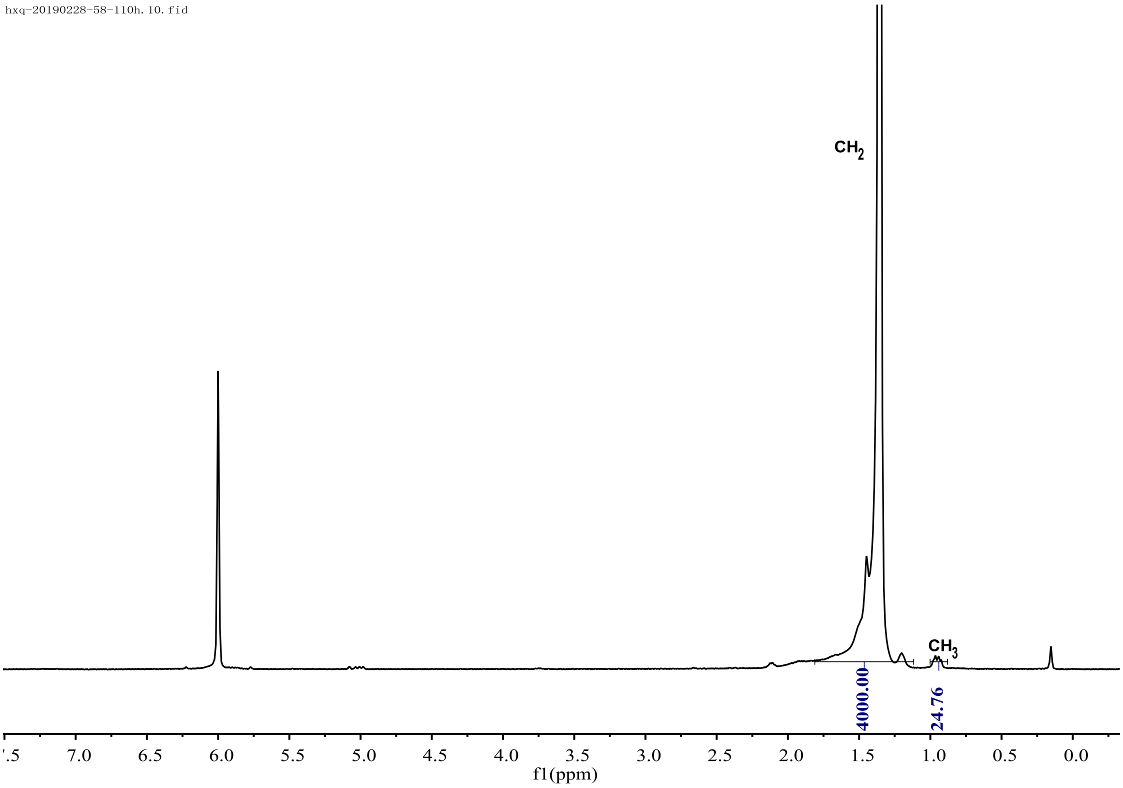


Figure S40. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-1** from table 1, entry 1.

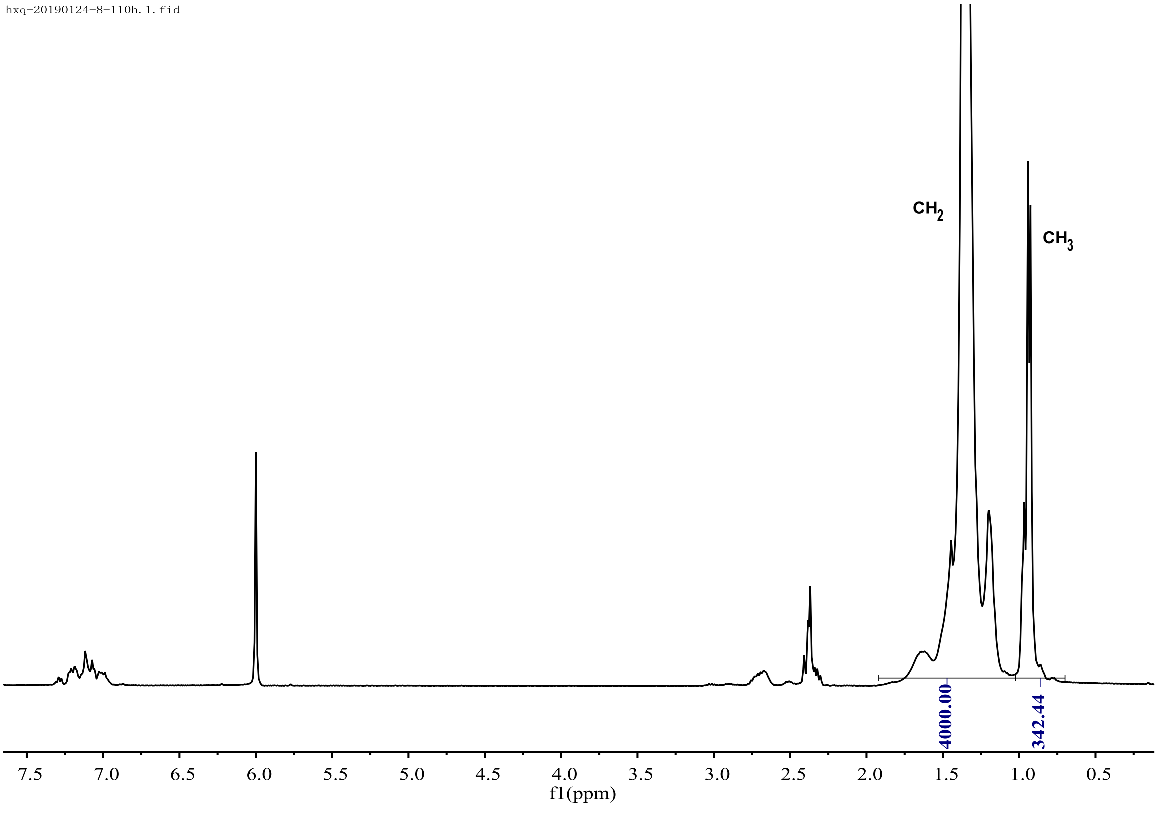


Figure S41. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-1** from table 1, entry 2.

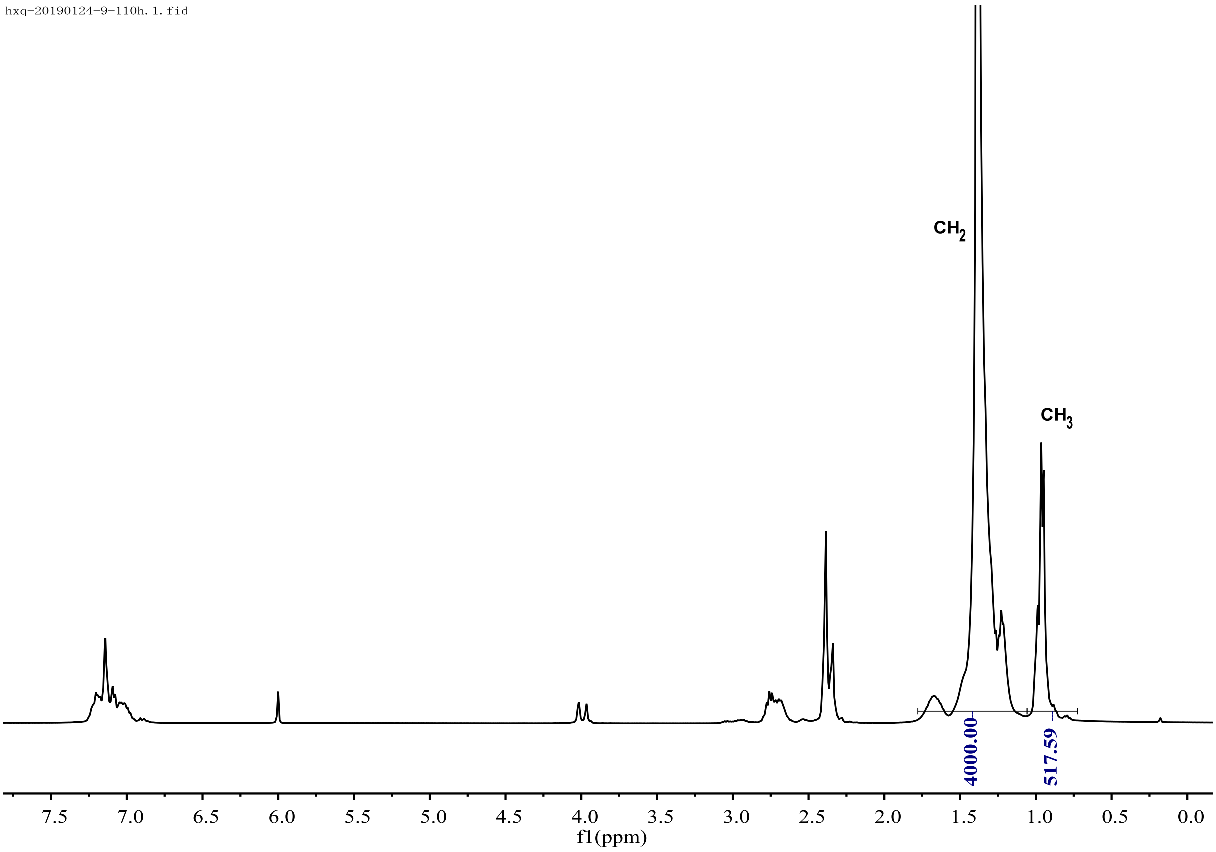


Figure S42. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-1** from table 1, entry 3.

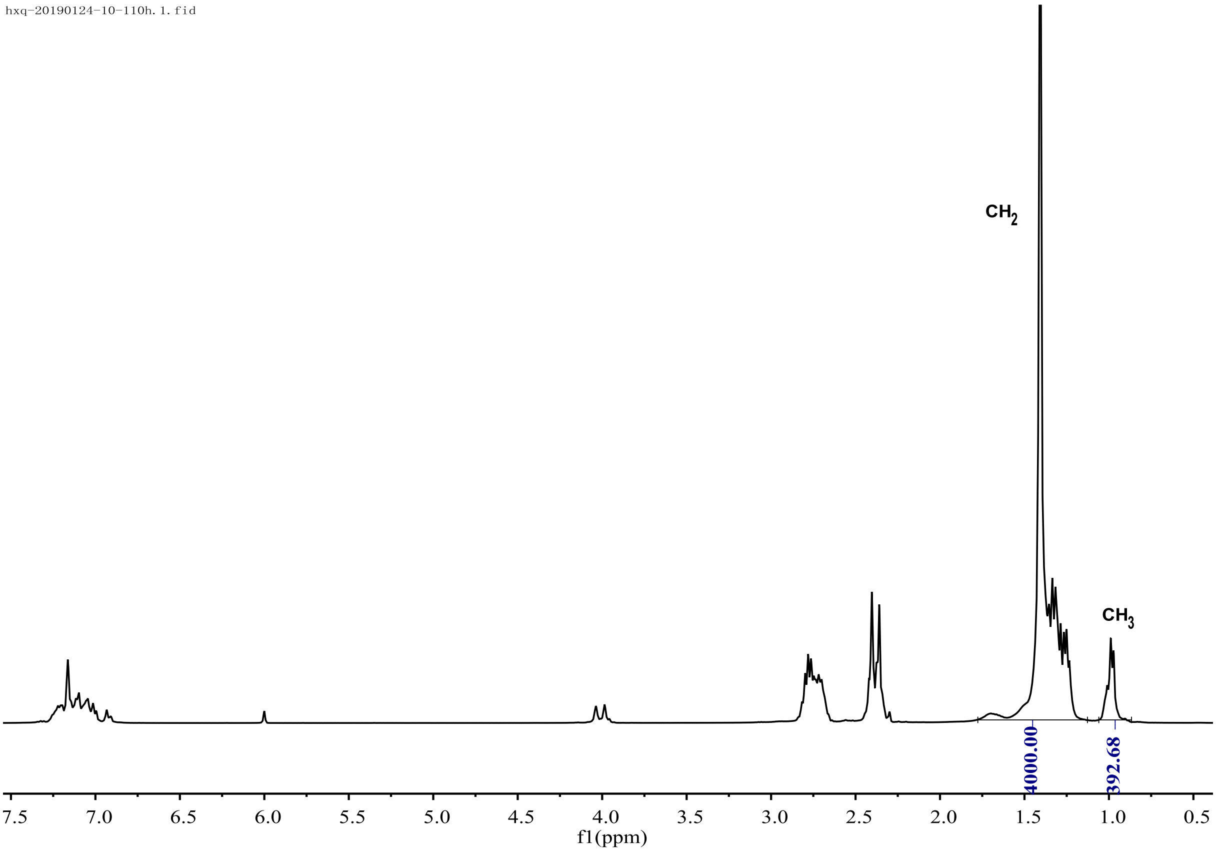


Figure S43. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-1** from table 1, entry 4.

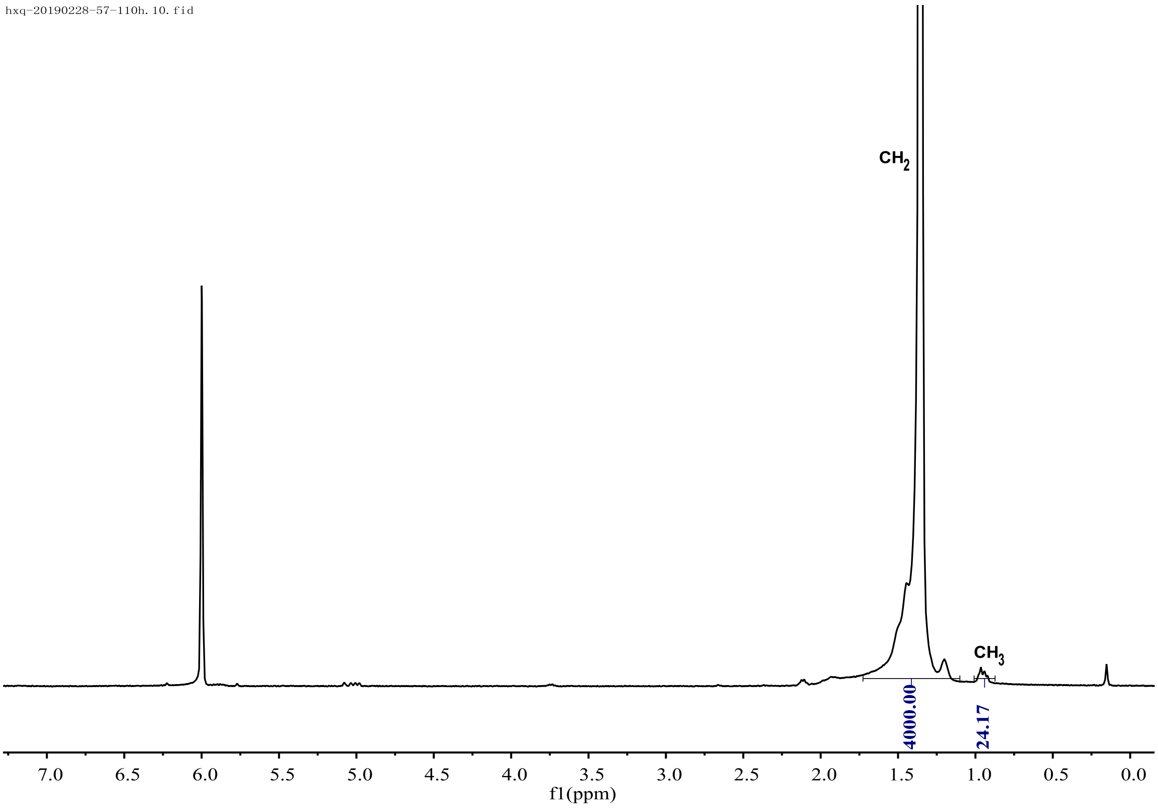


Figure S44. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-2** from table 1, entry 5.

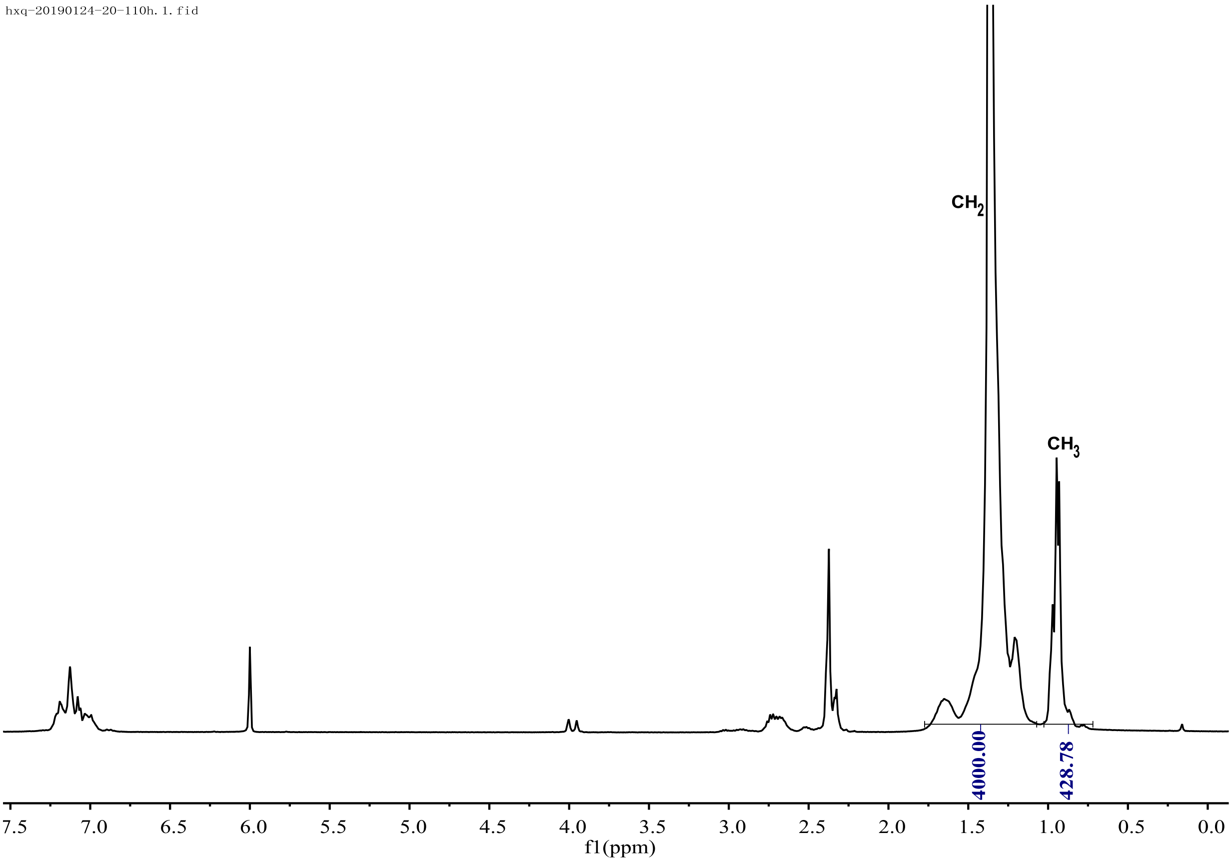


Figure S45. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-2** from table 1, entry 6.

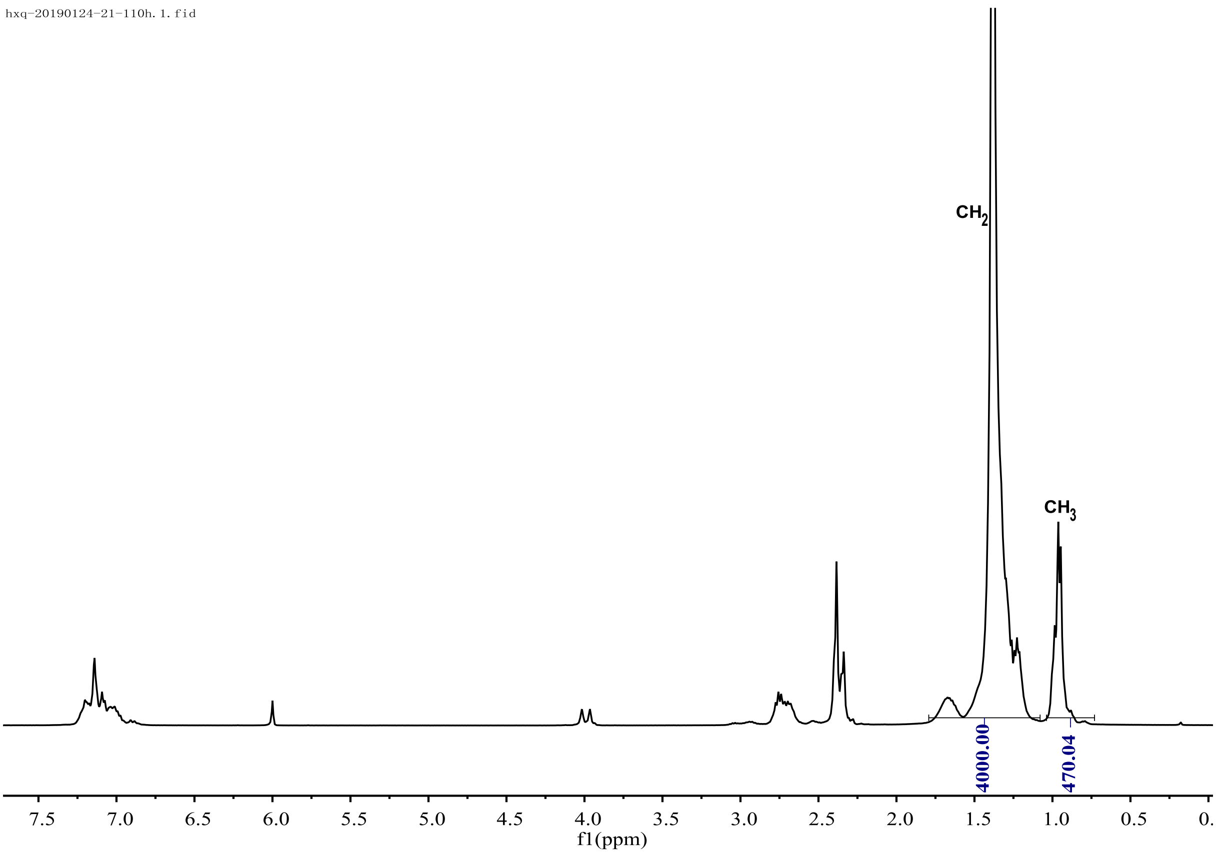


Figure S46. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-2** from table 1, entry 7.

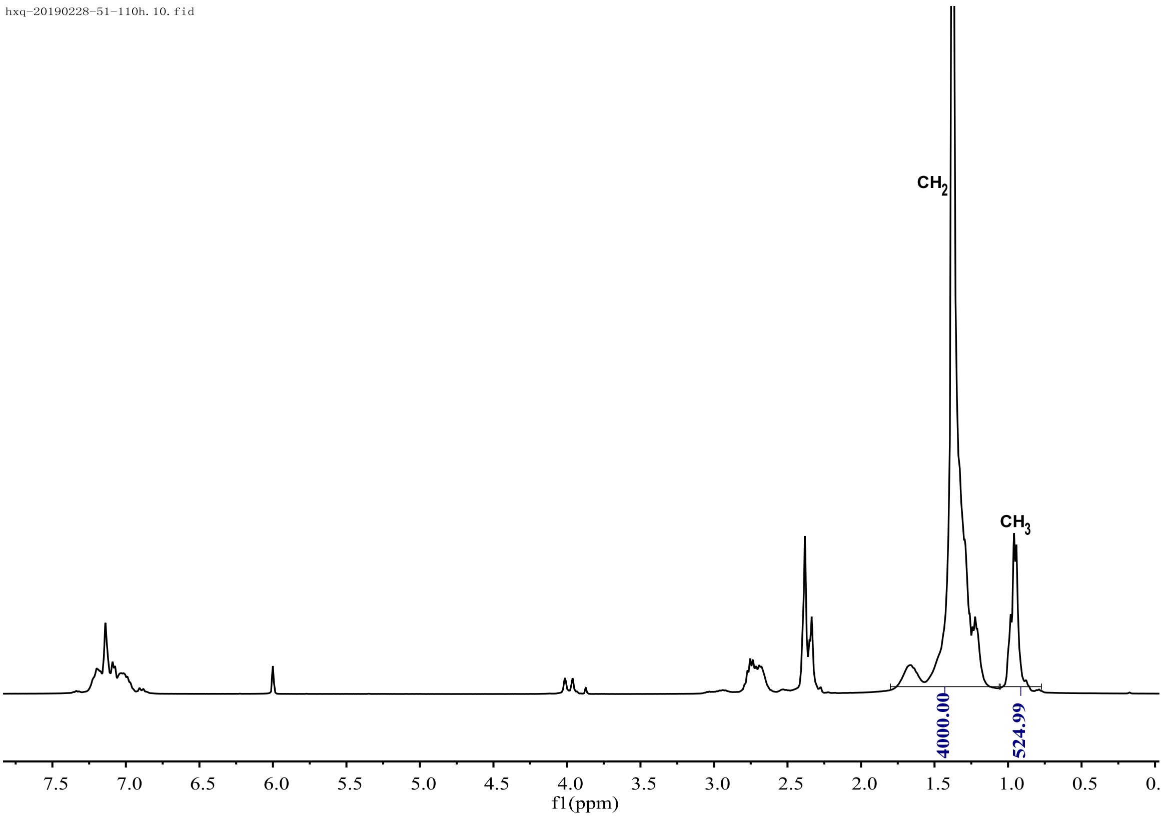


Figure S47. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-2** from table 1, entry 8.

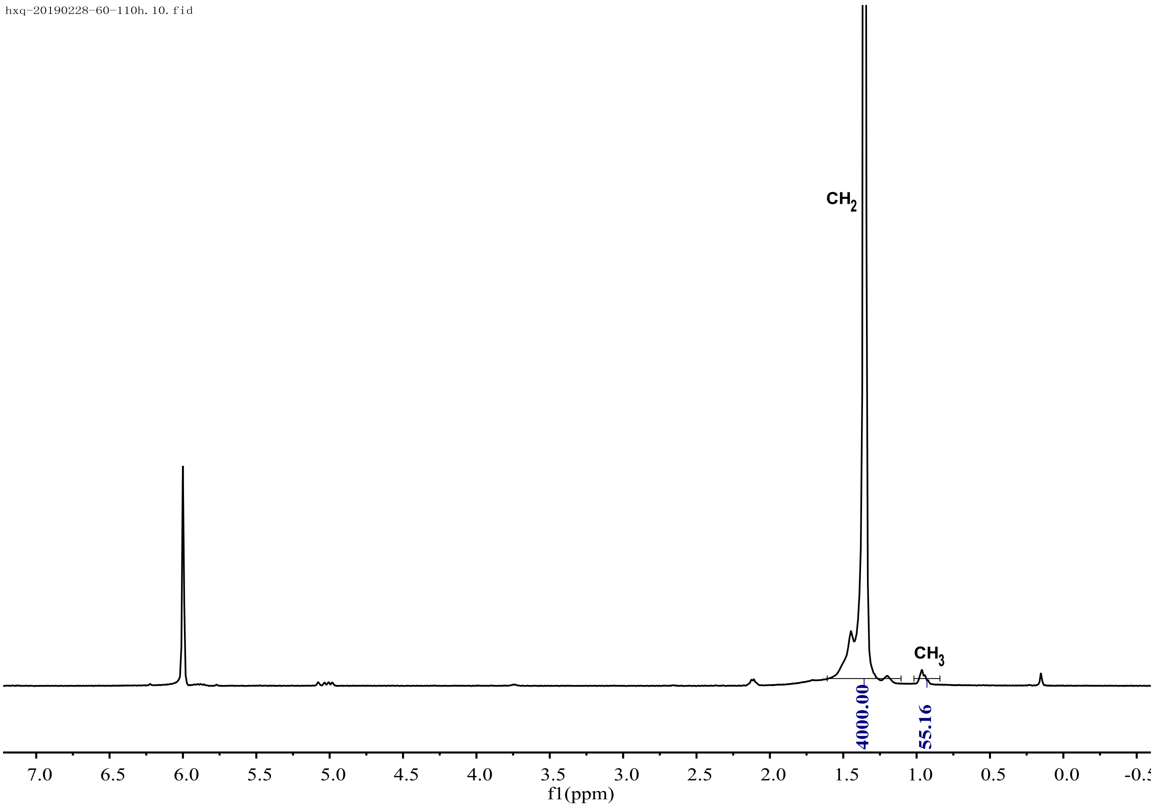


Figure S48. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-3** from table 1, entry 9.

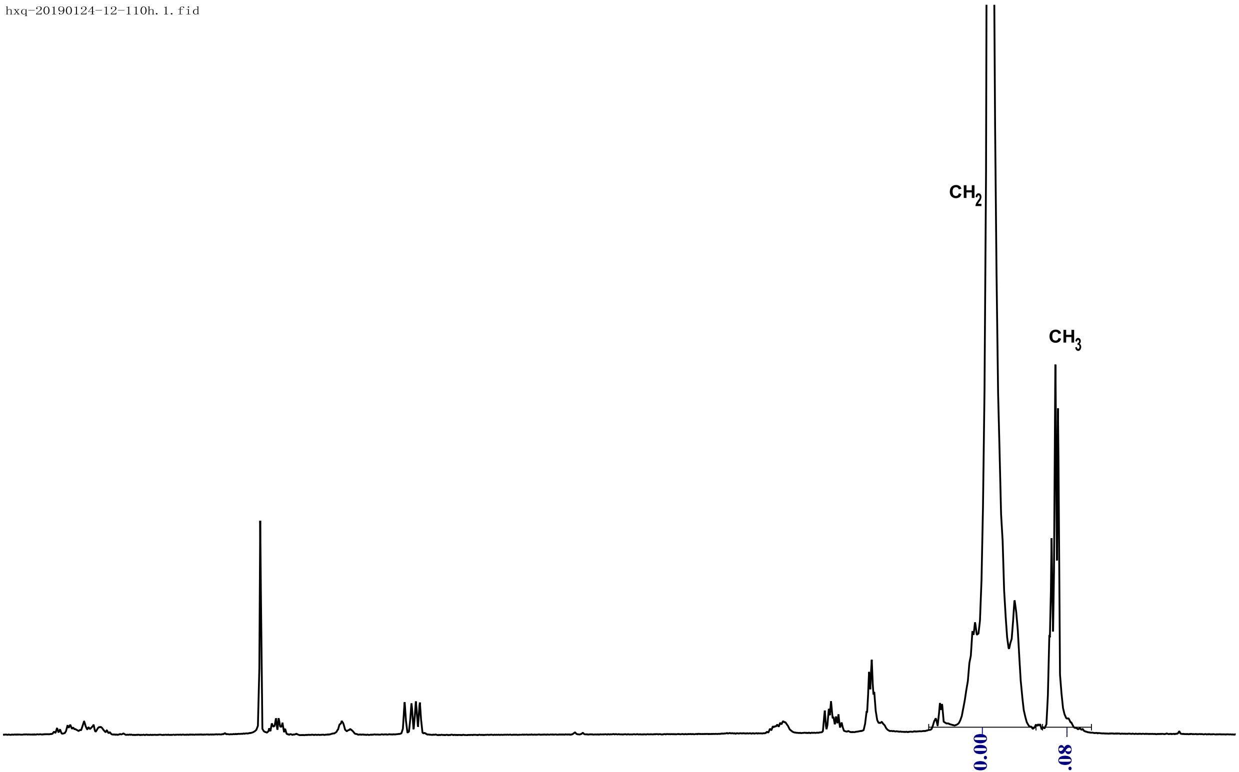


Figure S49. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-3** from table 1, entry 10.

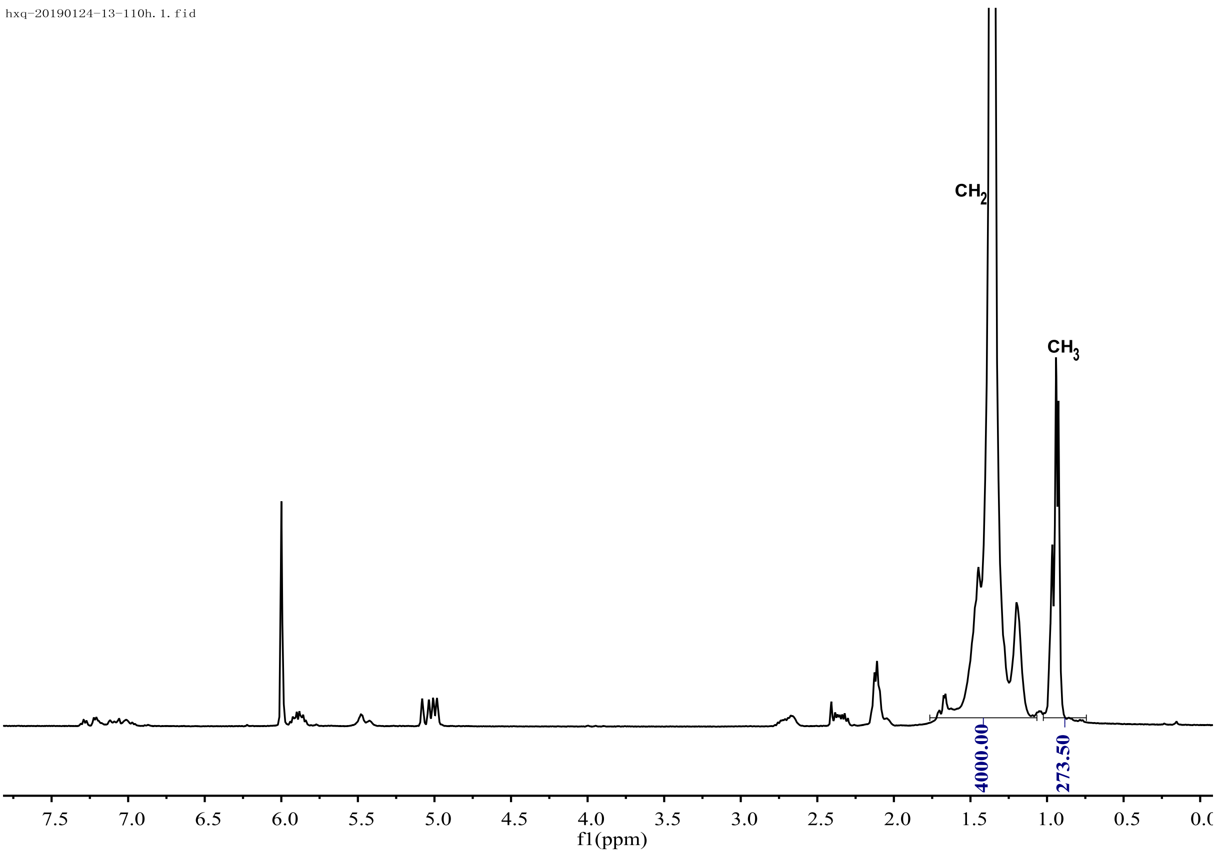


Figure S50. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-3** from table 1, entry 11.

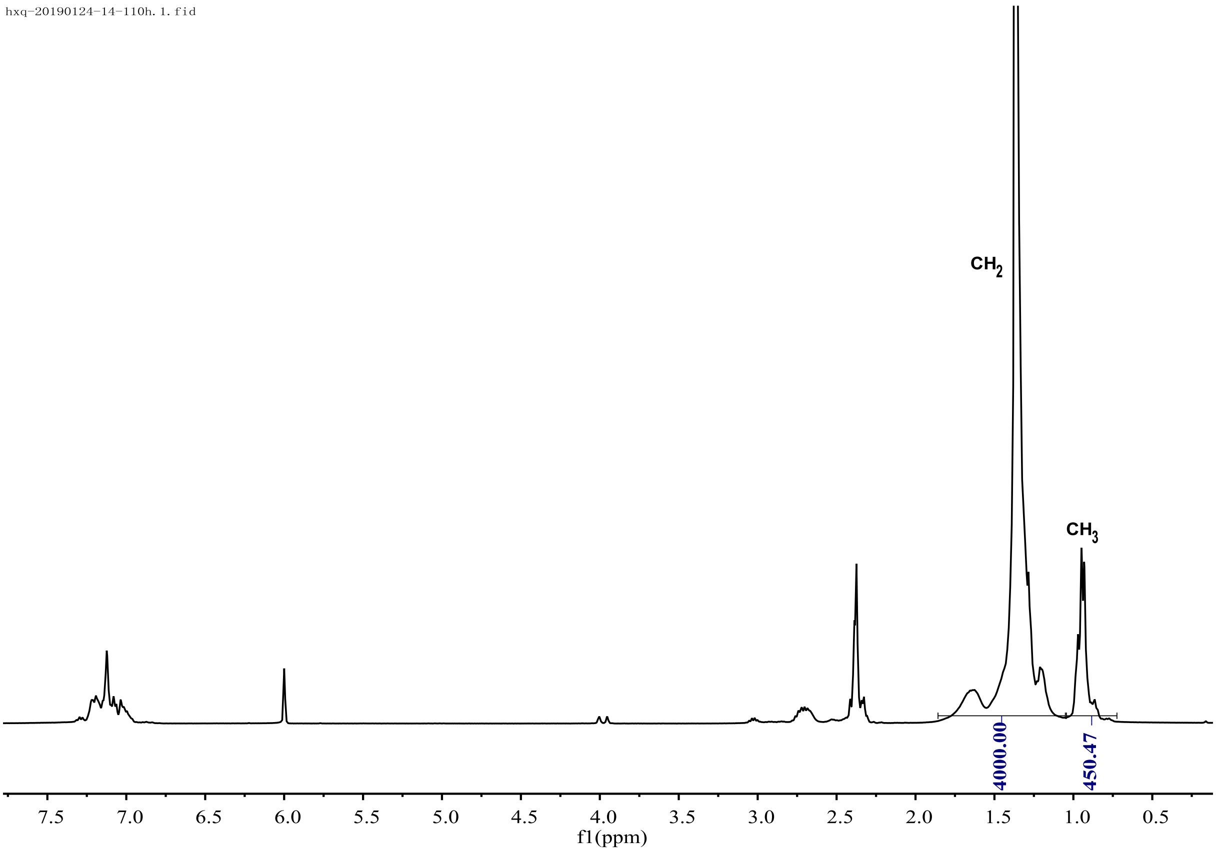


Figure S51. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-3** from table 1, entry 12.

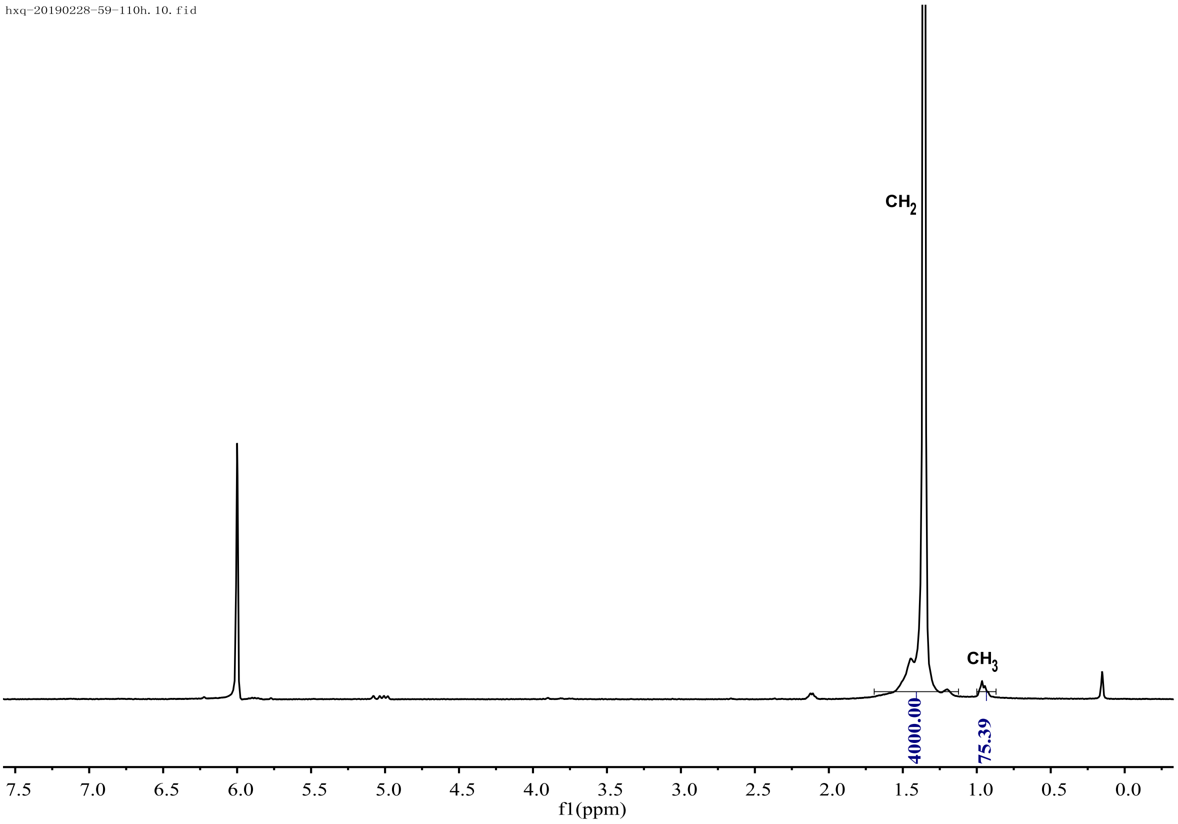


Figure S52. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-4** from table 1, entry 13.

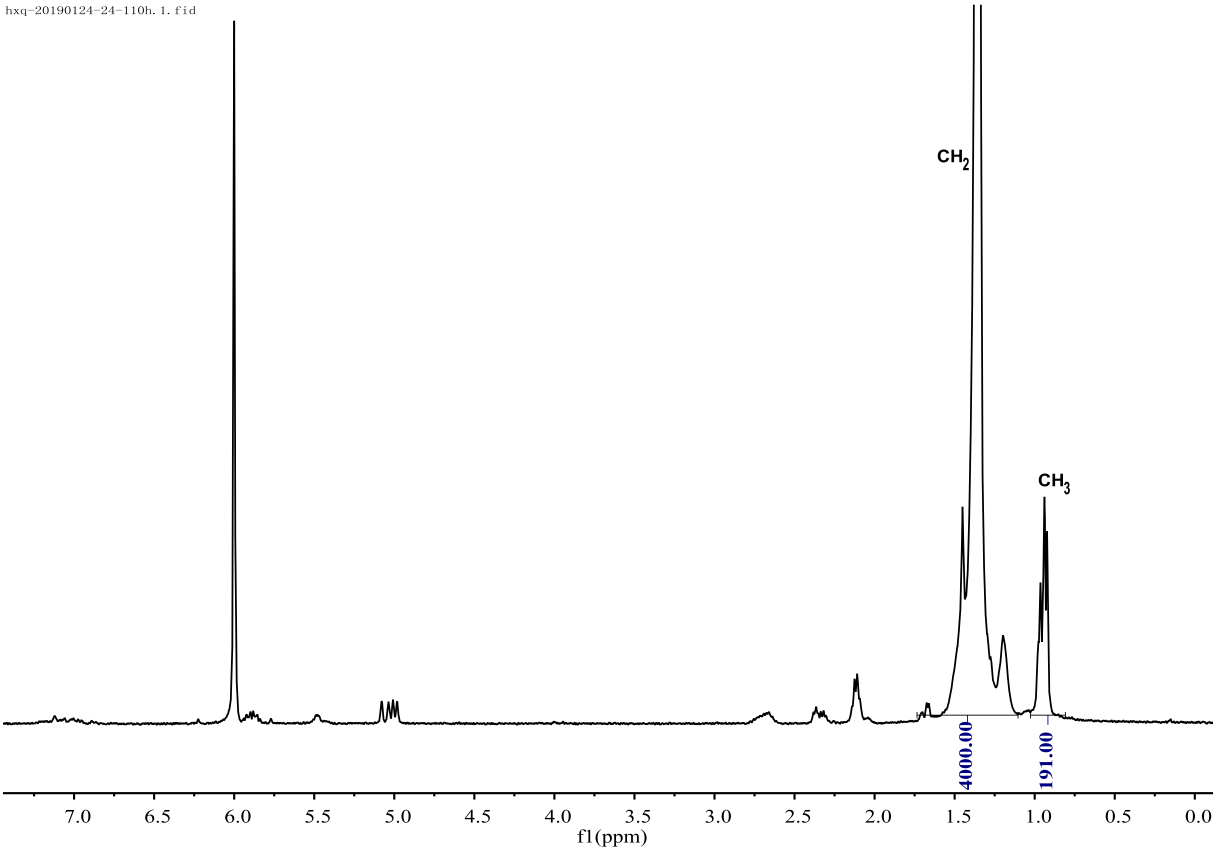


Figure S53. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-4** from table 1, entry 14.

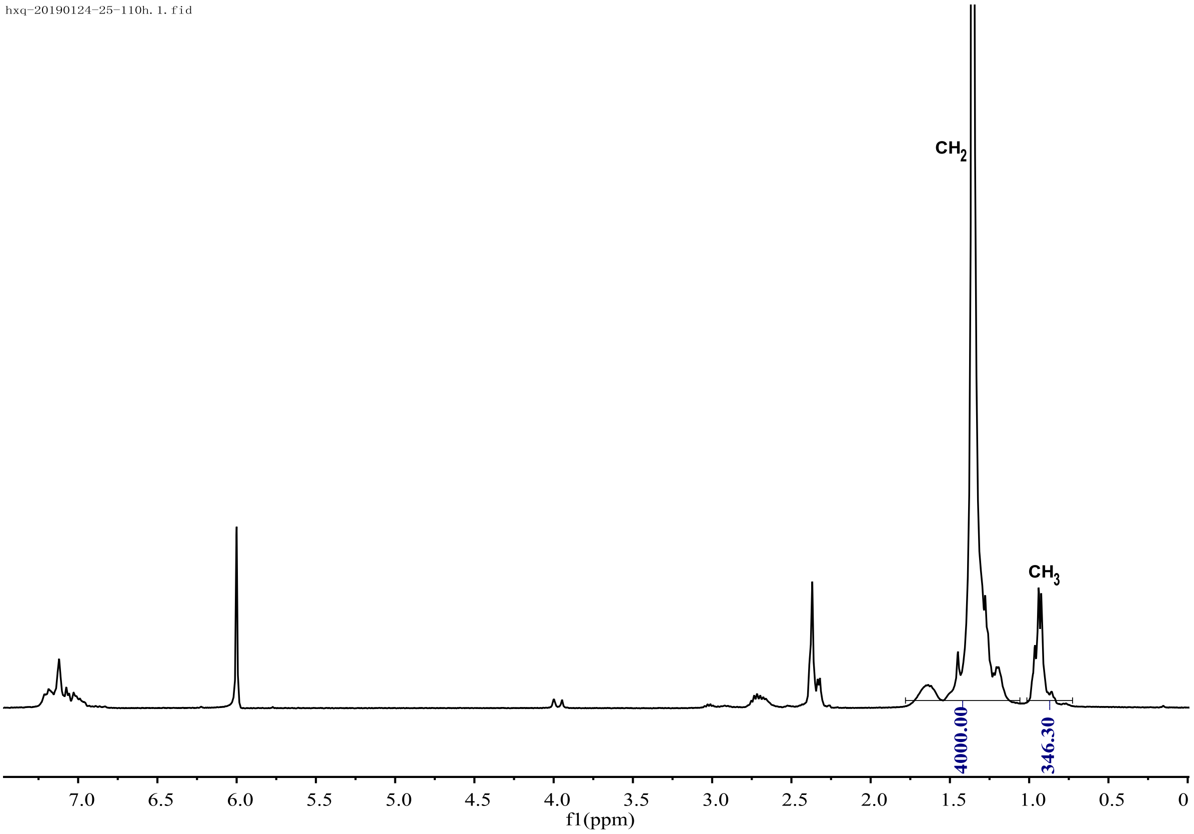


Figure S54. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-4** from table 1, entry 15.

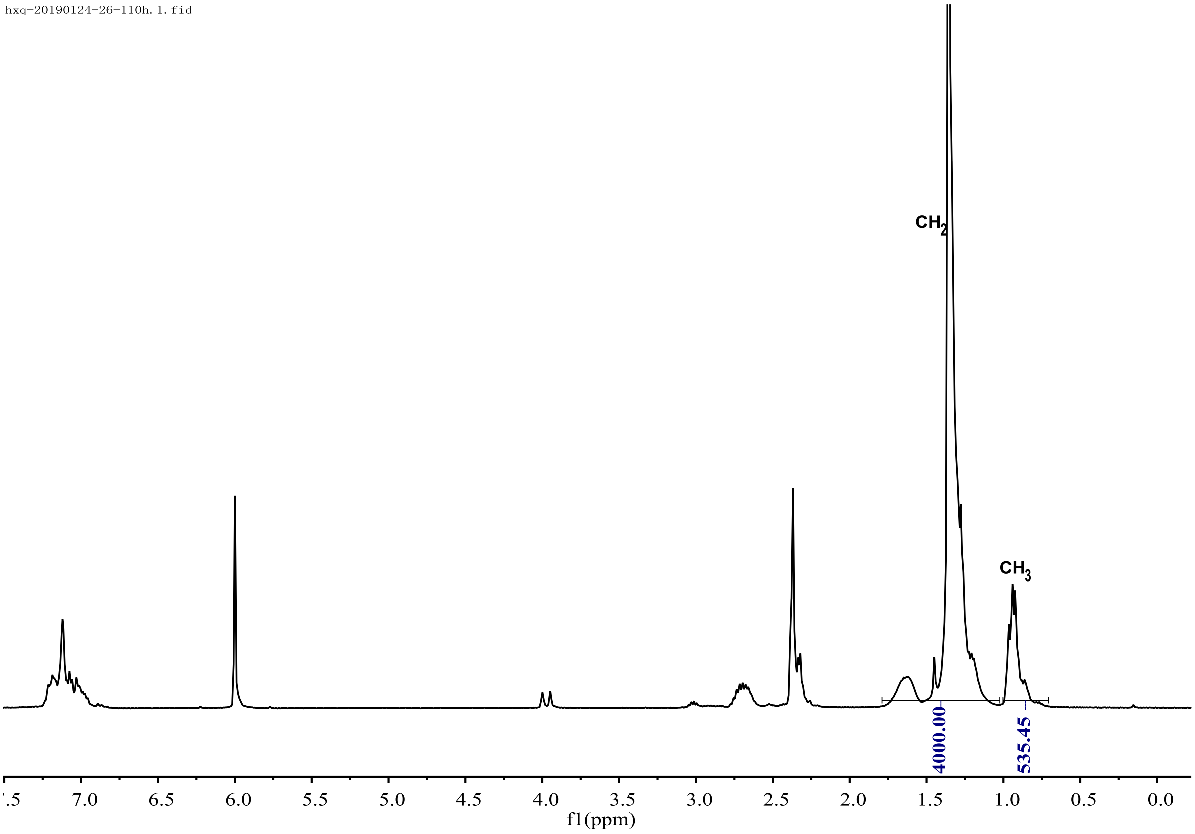


Figure S55. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-4** from table 1, entry 16.

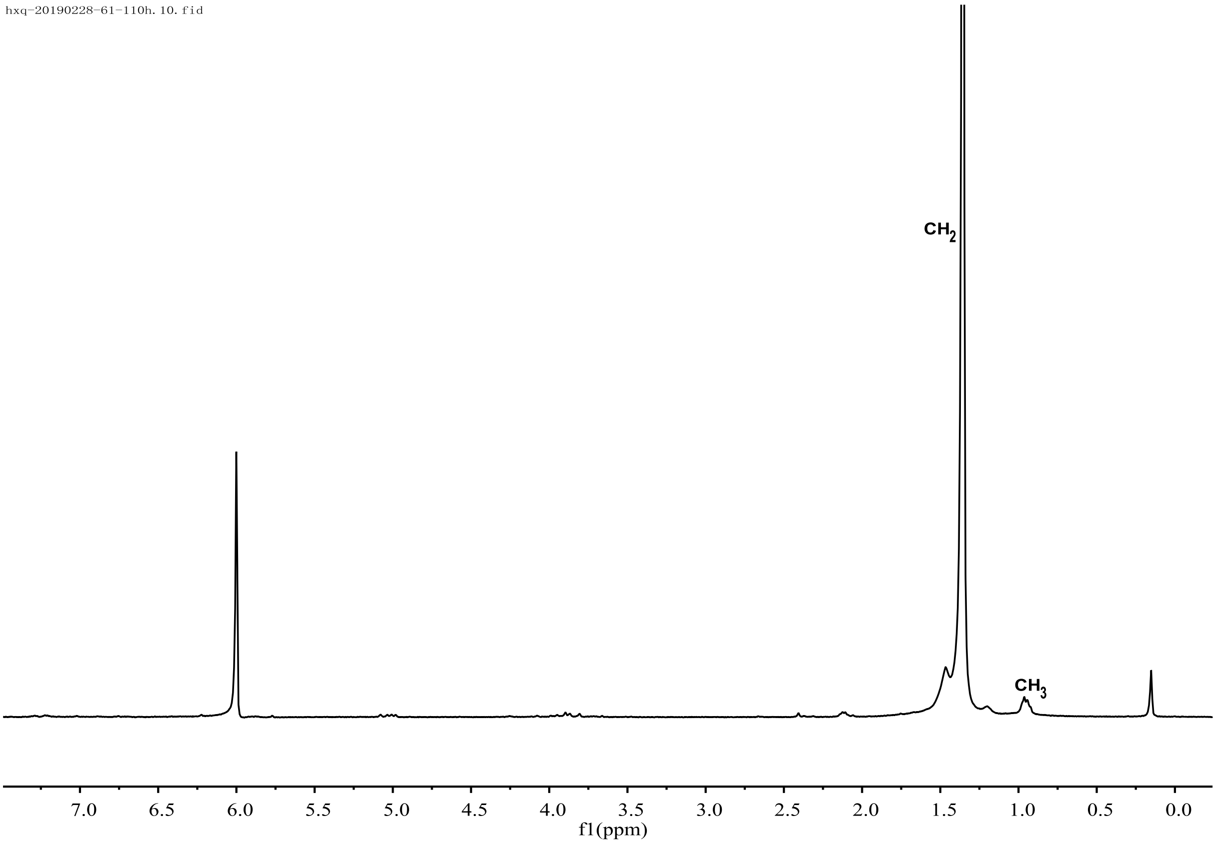


Figure S56. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-5** from table 1, entry 17.

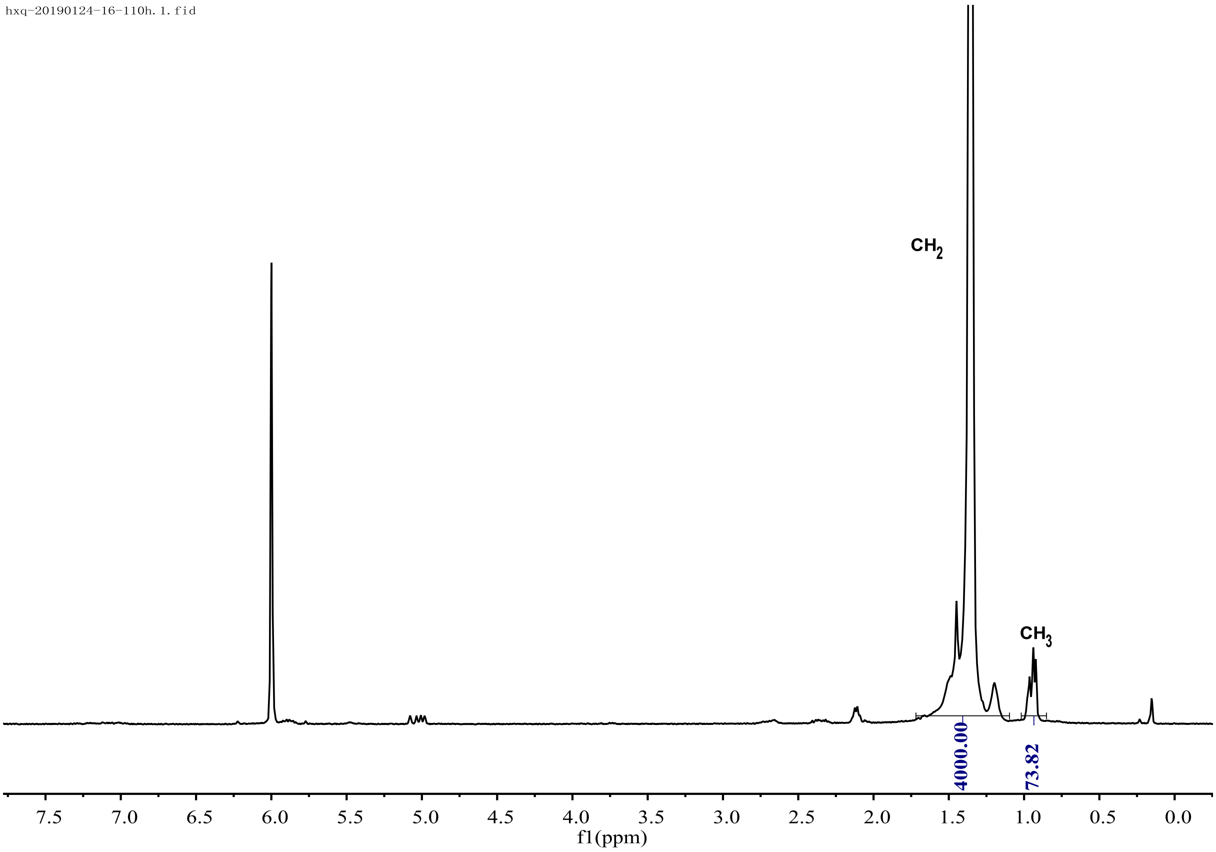


Figure S57. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-5** from table 1, entry 18.

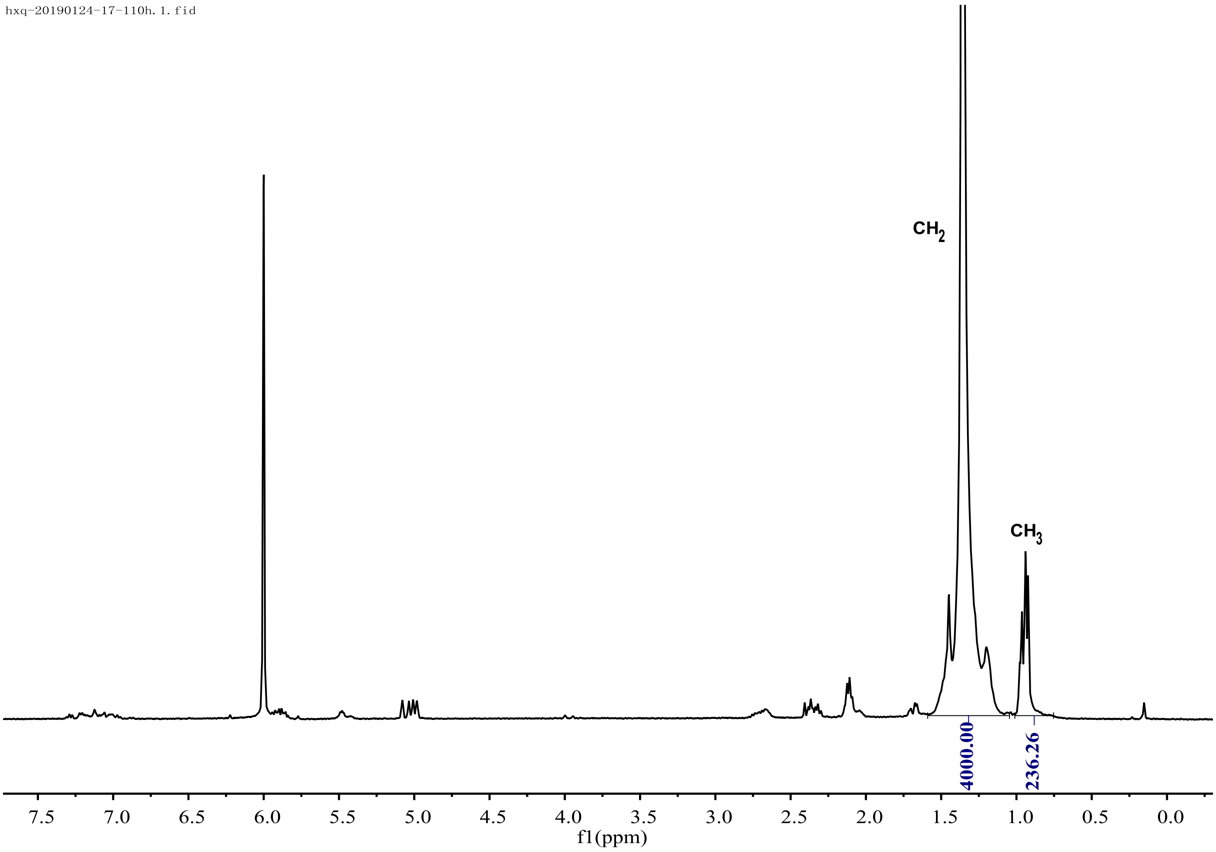


Figure S58. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-5** from table 1, entry 19.

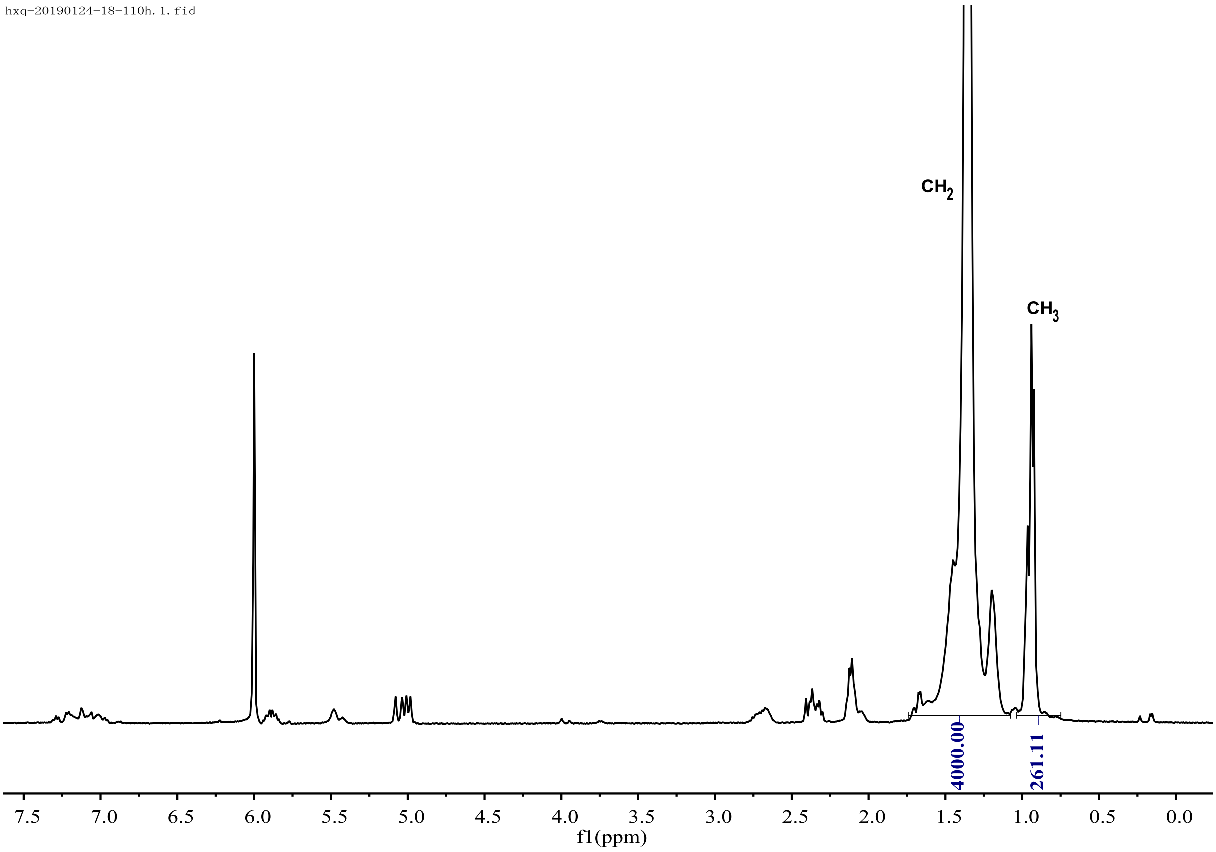


Figure S59. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-5** from table 1, entry 20.

6.2 ^{1}H NMR of polymer by Ni catalyst with different solvent

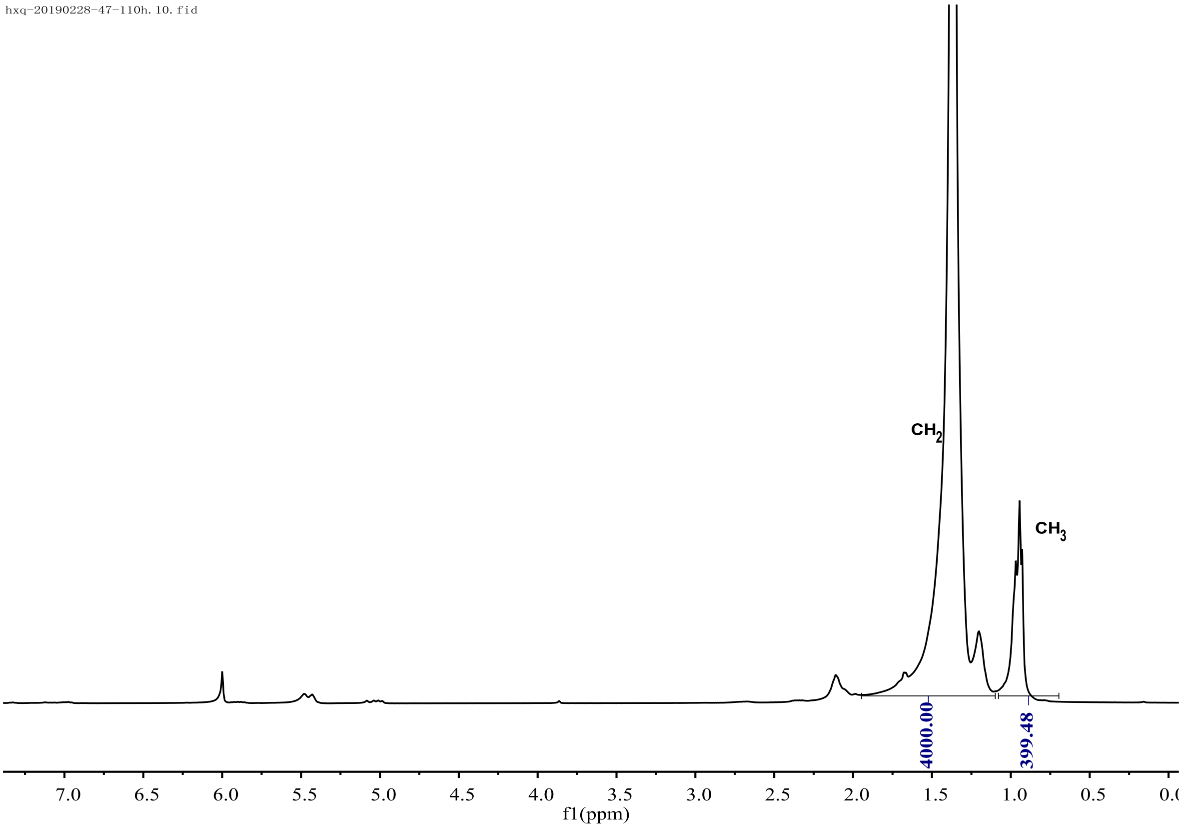


Figure S60. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-1** with **hexane** from table 2, entry 1.

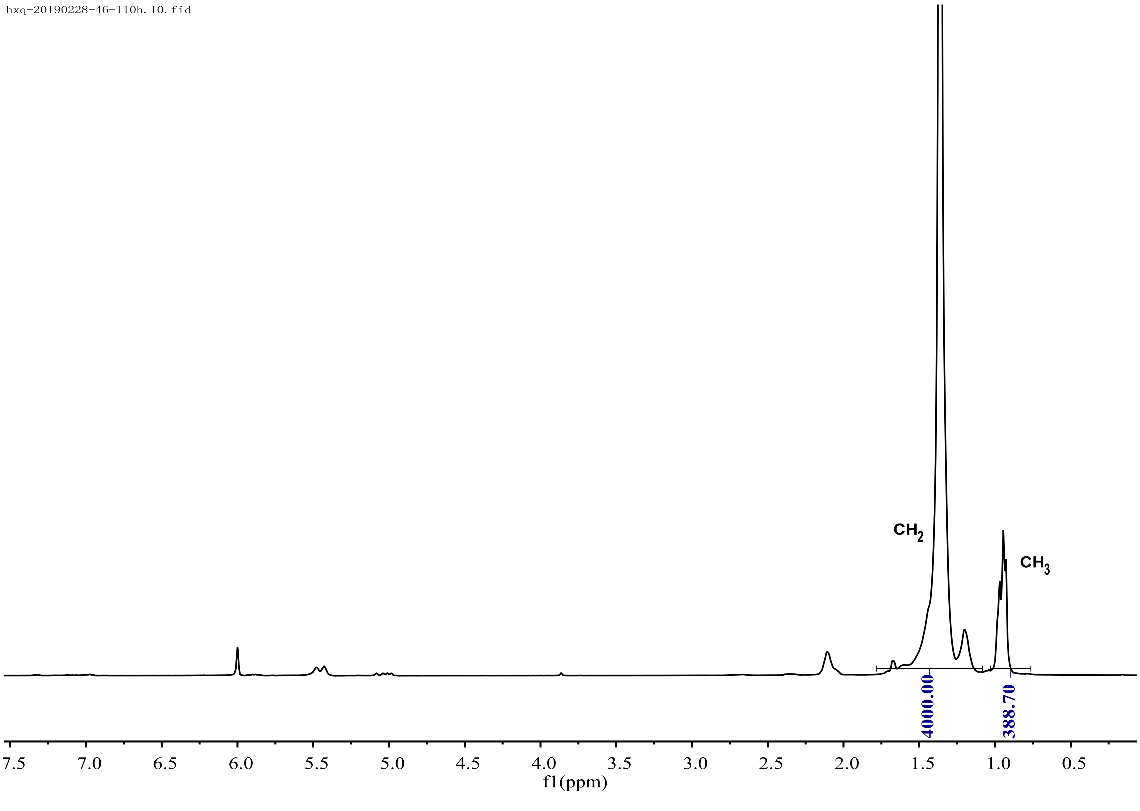


Figure S61. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-2** with **hexane** from table 2, entry 2.

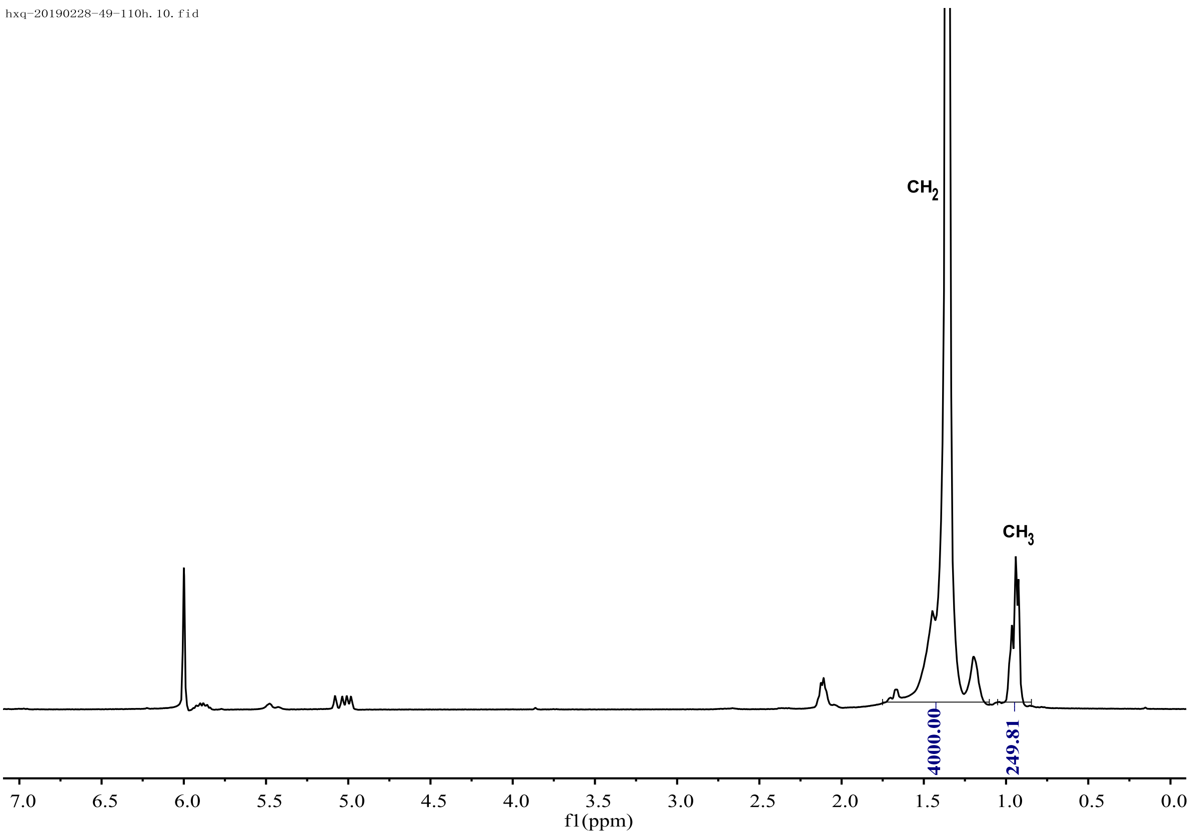


Figure S62. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-3** with **hexane** from table 2, entry 3.

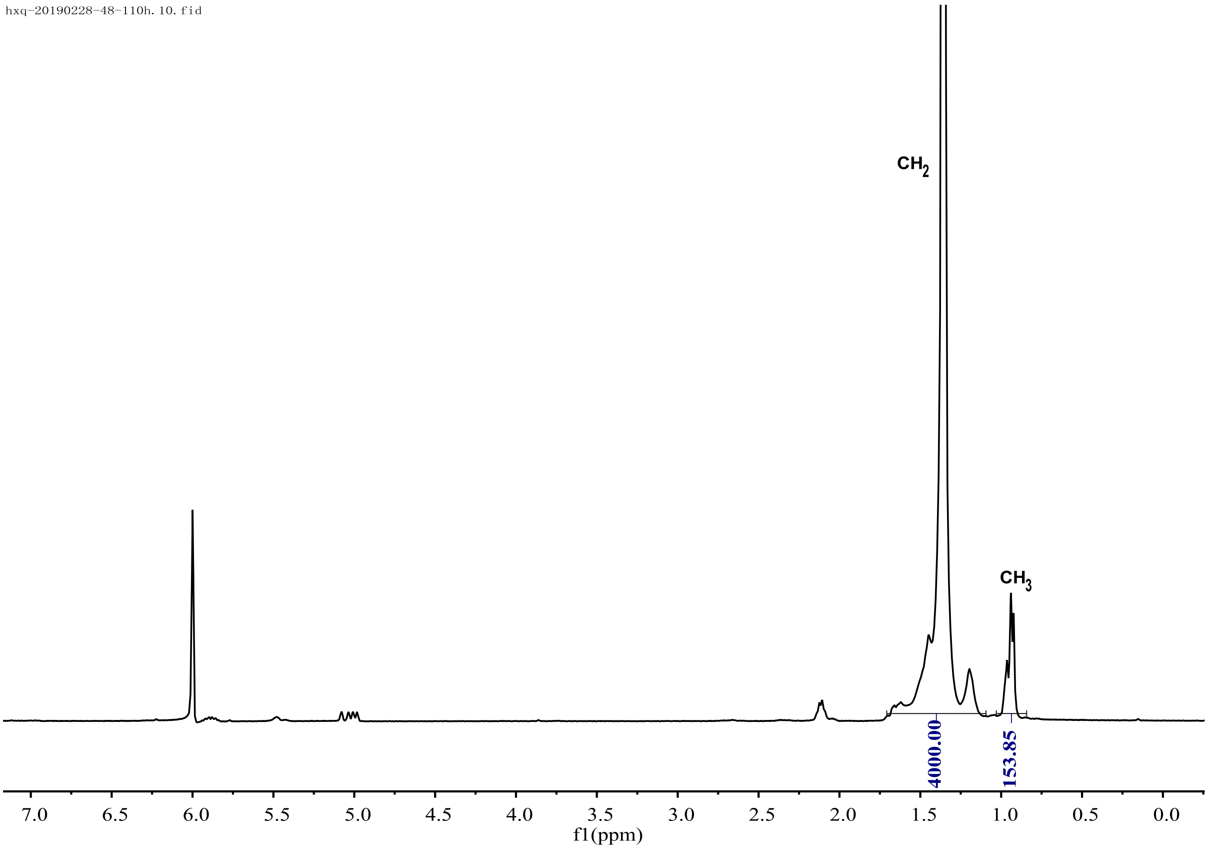


Figure S63. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-4** with **hexane** from table 2, entry 4.

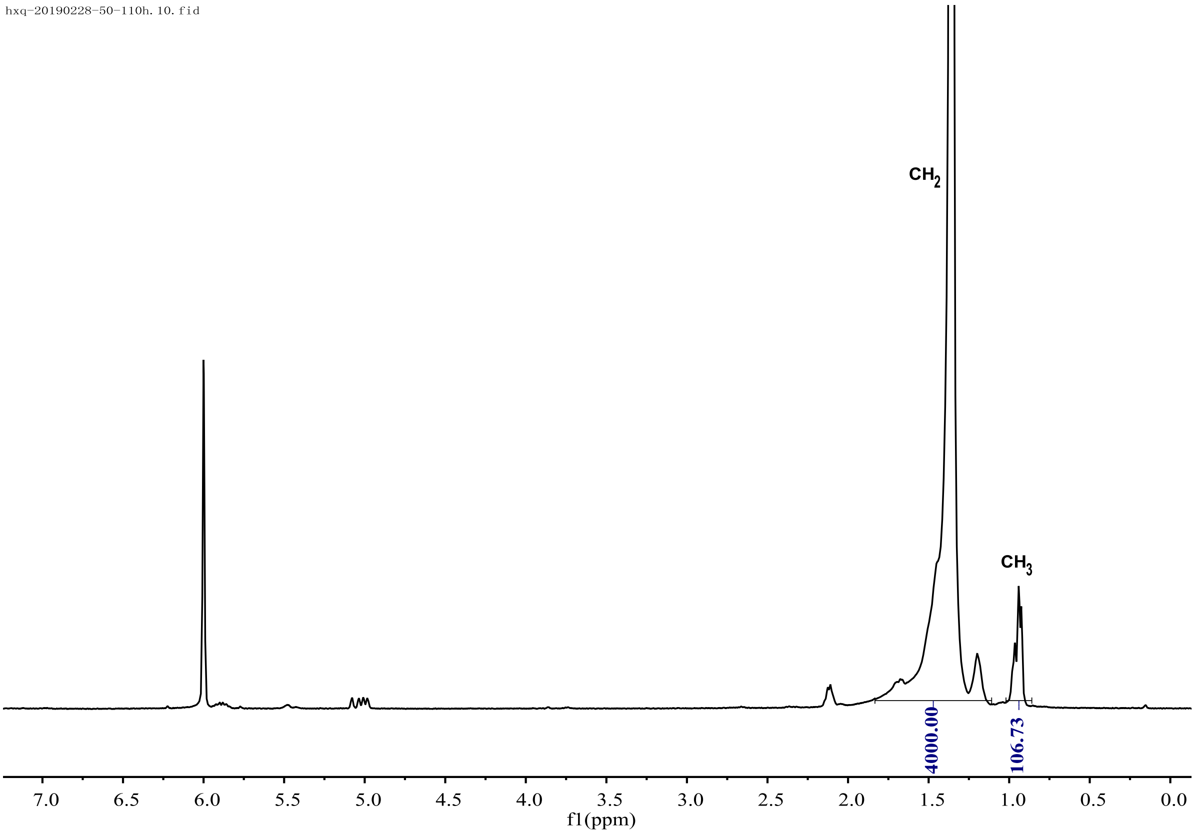


Figure S64. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-5** with **hexane** from table 2, entry 5.

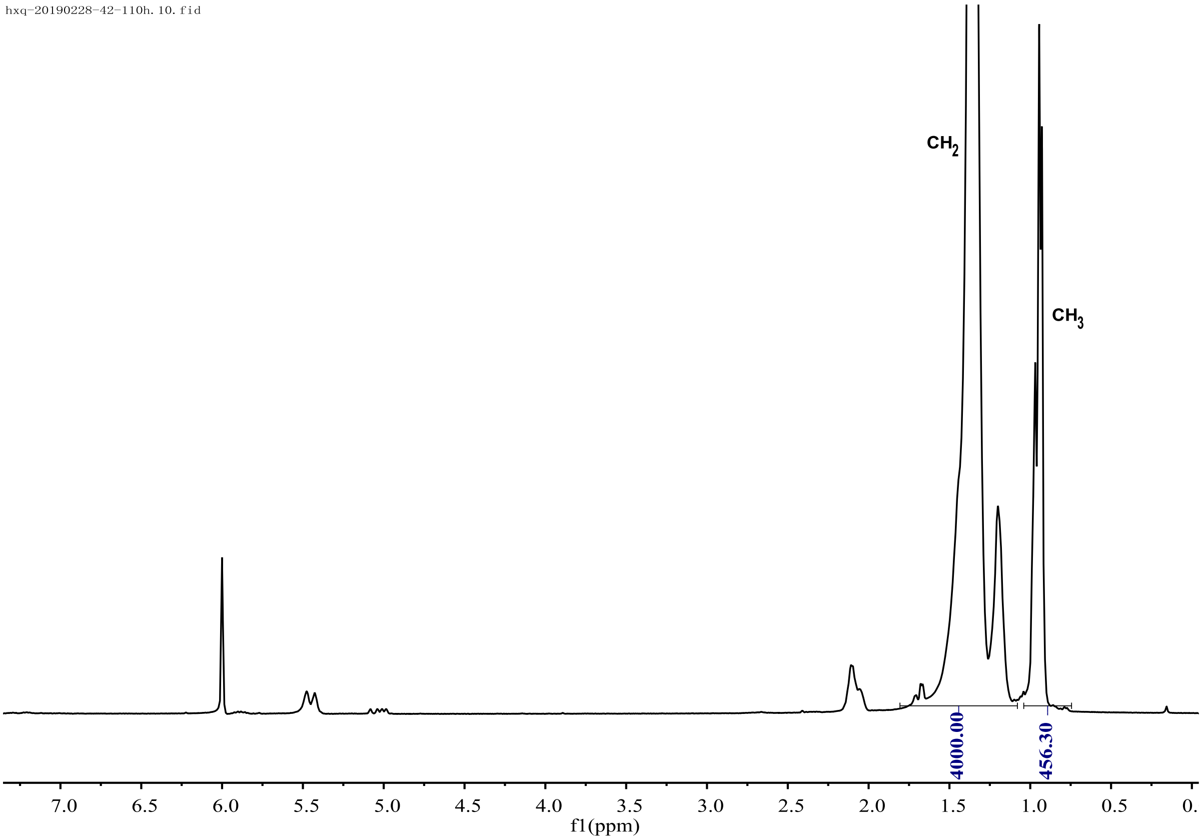


Figure S65. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-1** with **chlorobenzene** from table 2, entry 6.

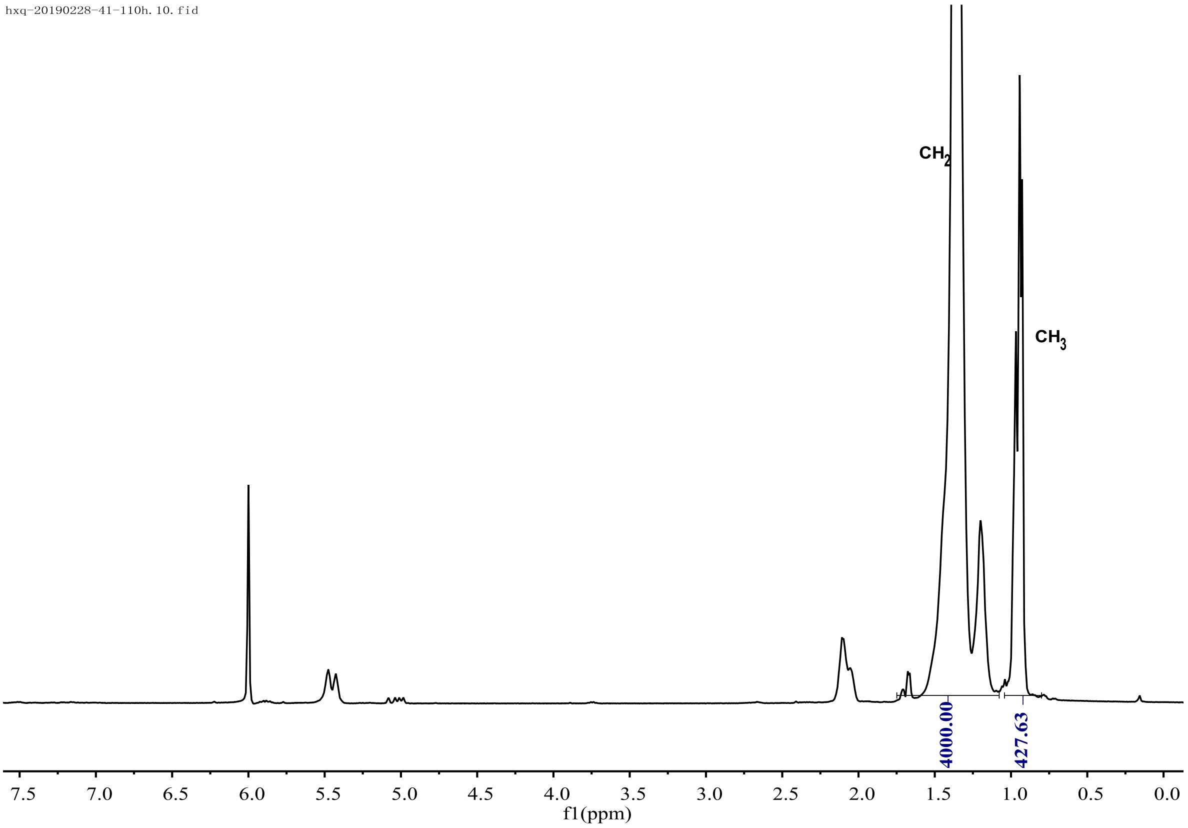


Figure S66. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-2** with **chlorobenzene** from table 2, entry 7.

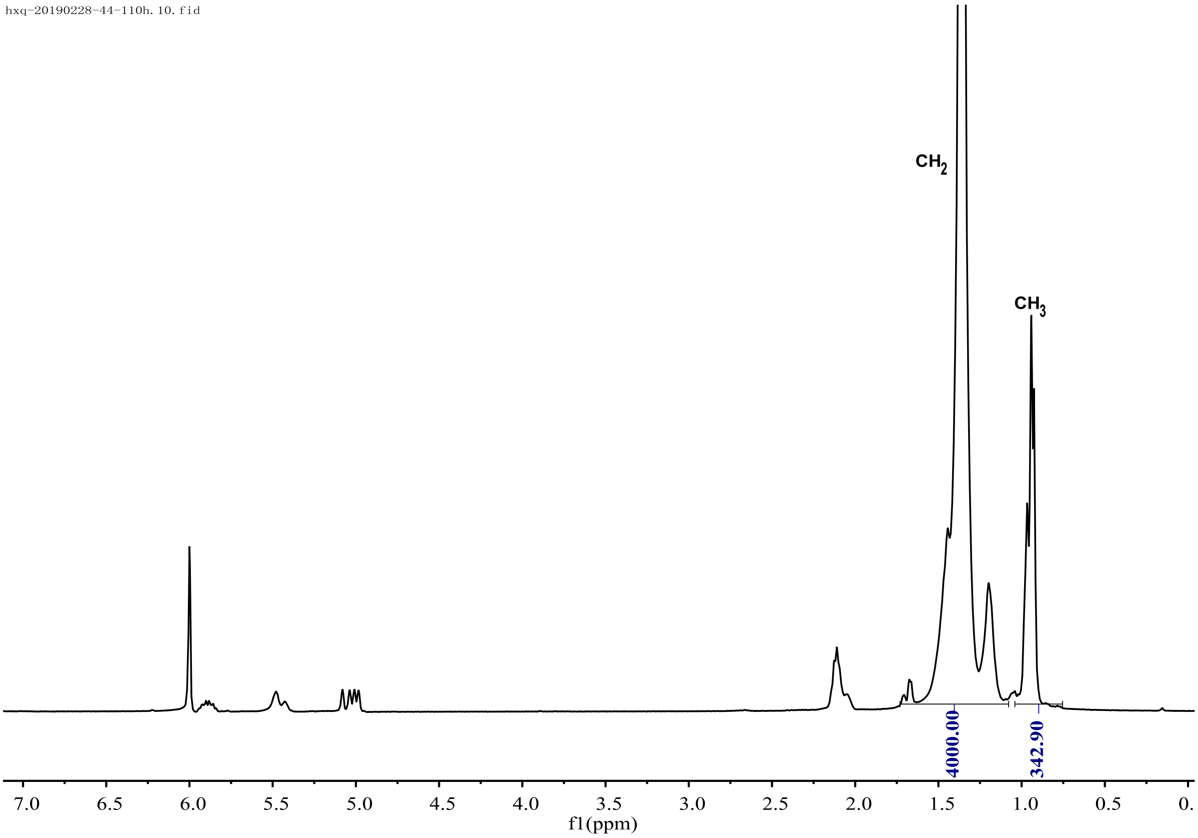


Figure S67. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-3** with **chlorobenzene** from table 2, entry 8.

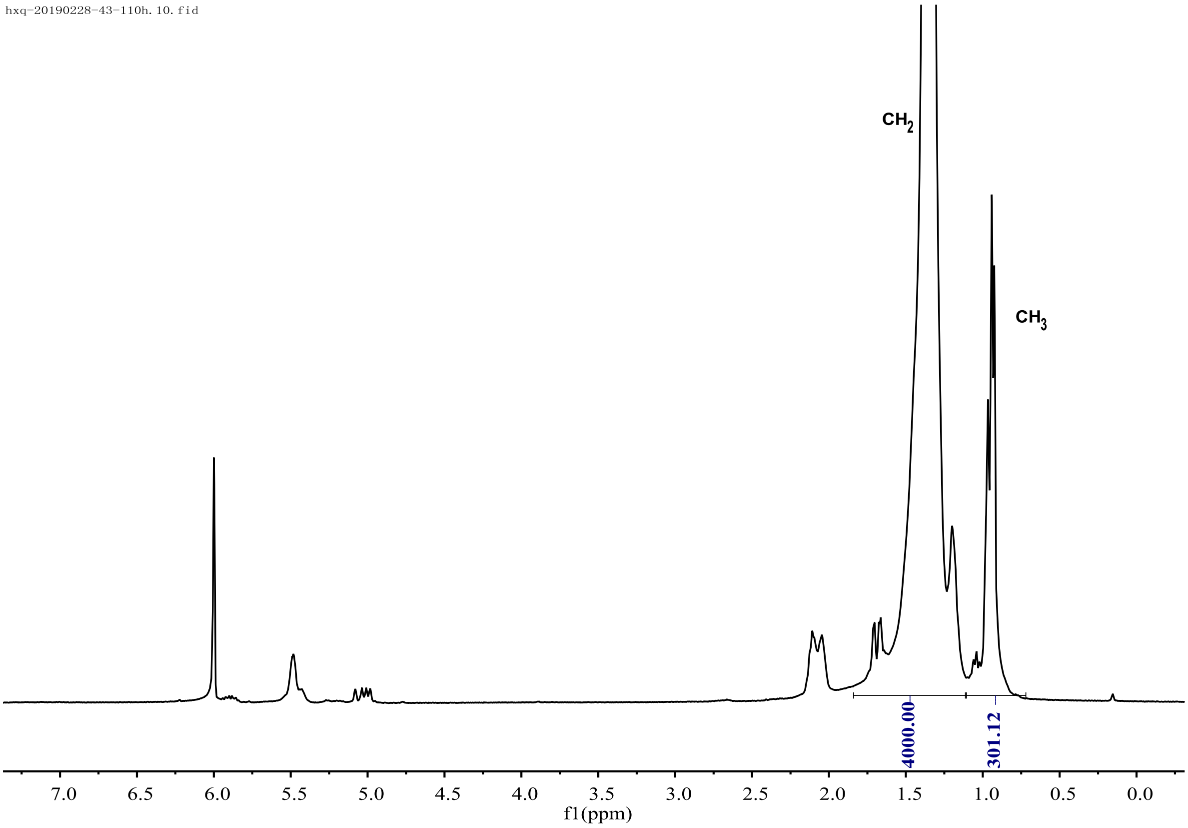


Figure S68. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-4** with **chlorobenzene** from table 2, entry 9.

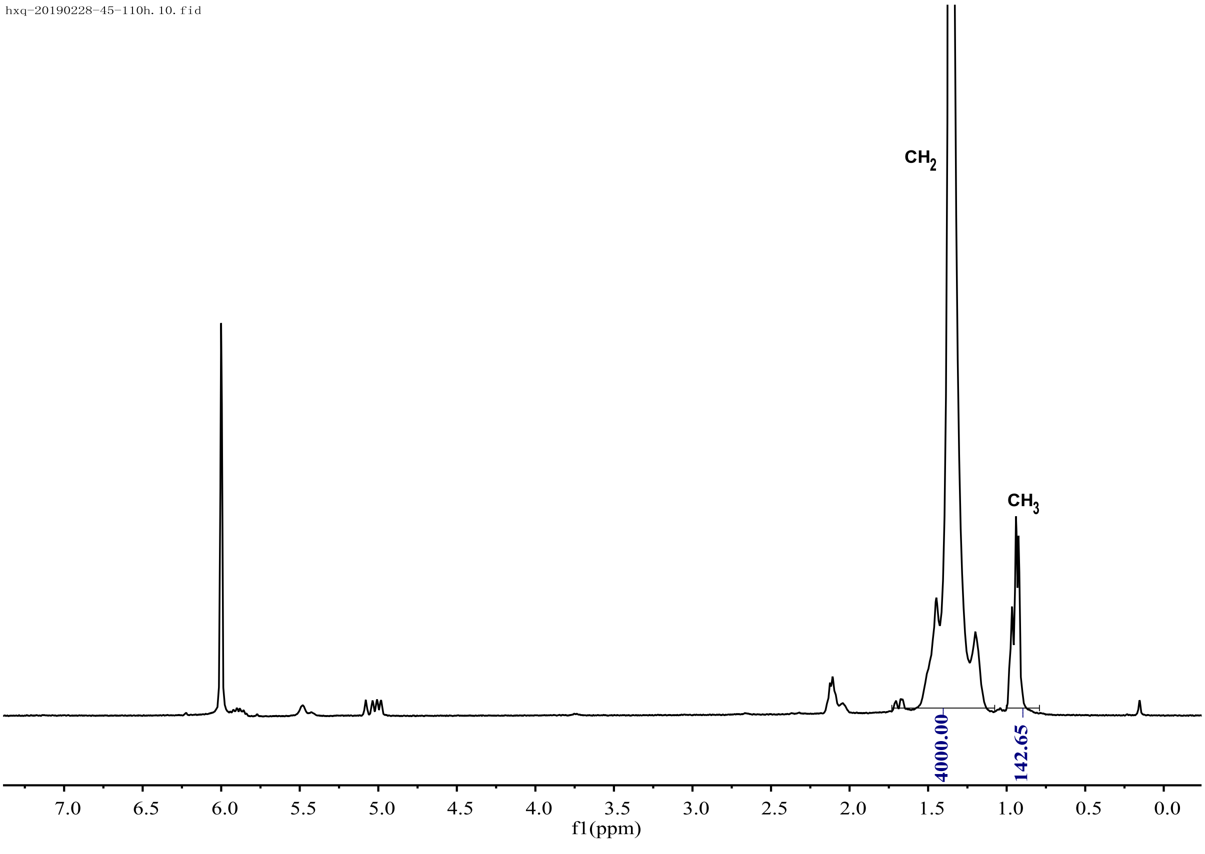


Figure S69. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-5** with **chlorobenzene** from table 2, entry 10.

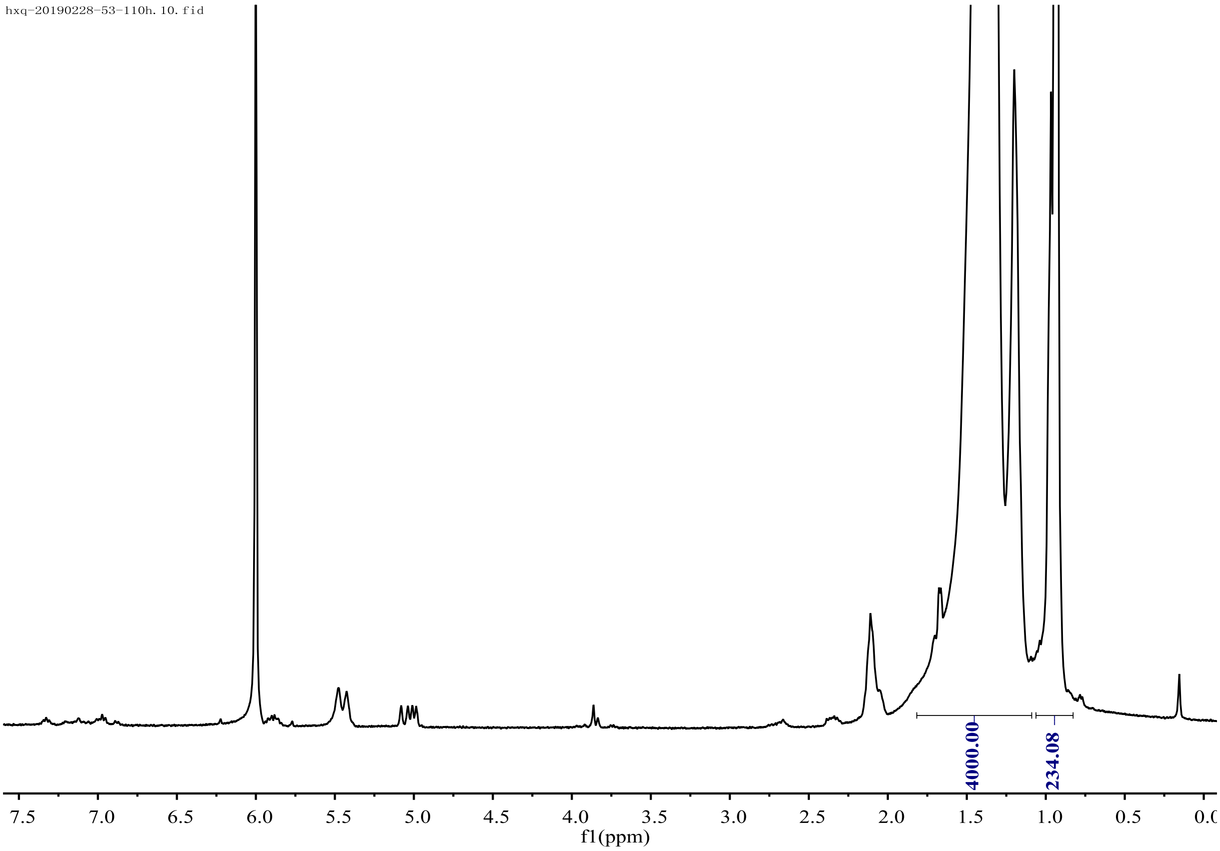


Figure S70. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-1** with **anisole** from table 2, entry 11.

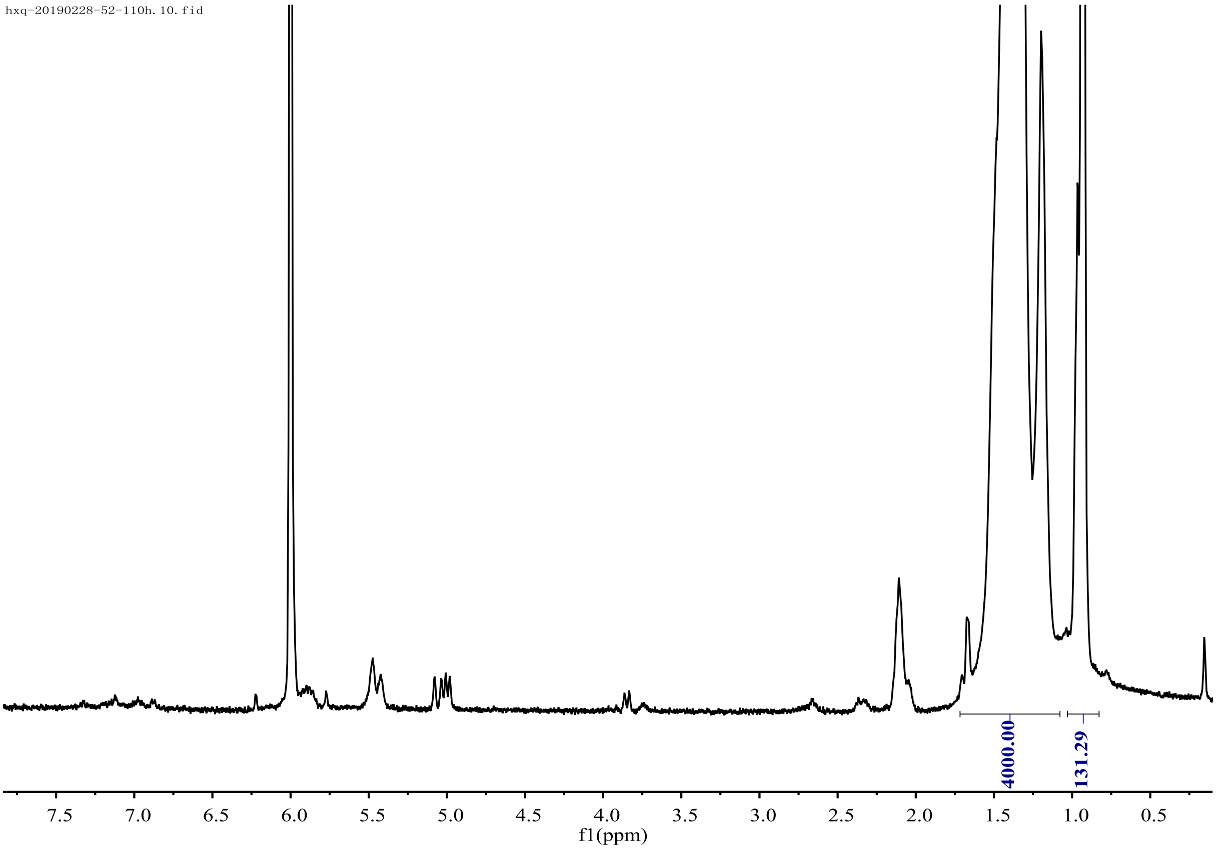


Figure S71. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-2** with **anisole** from table 2, entry 12.

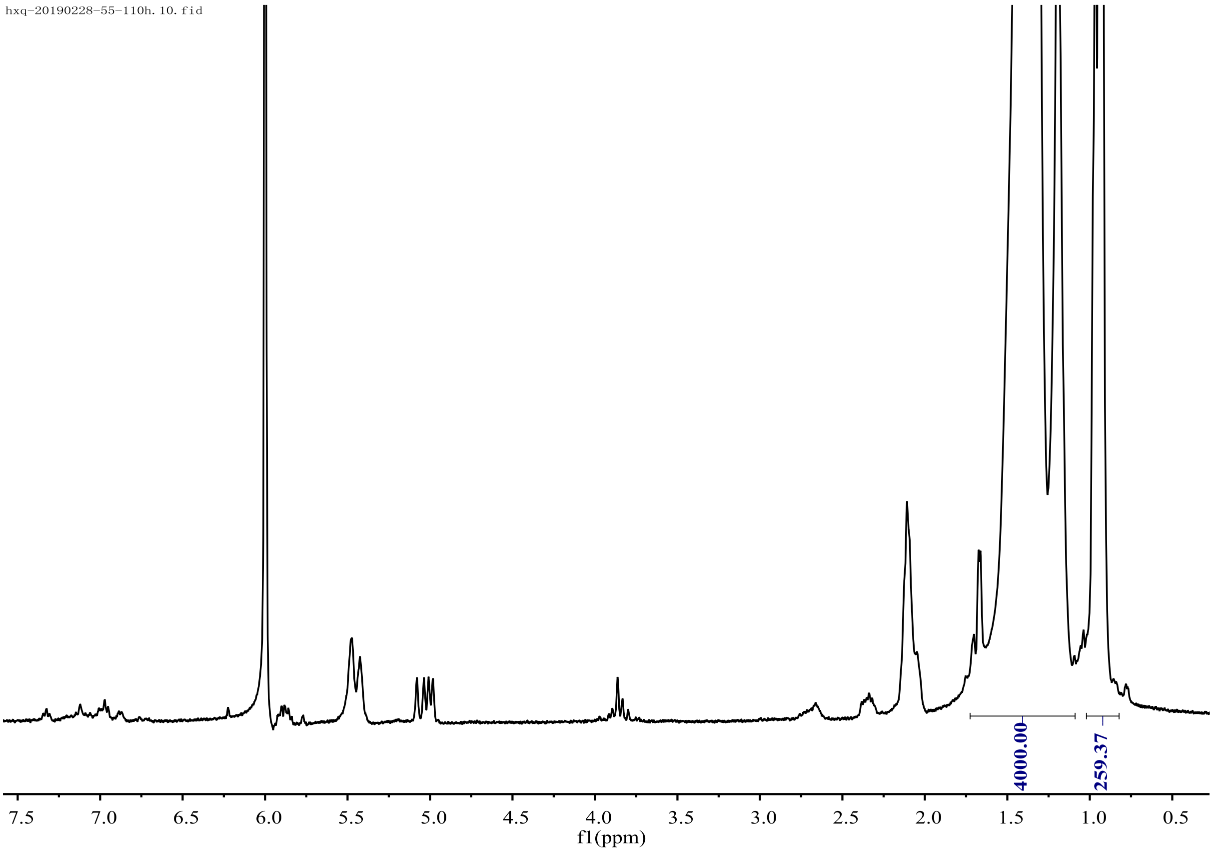


Figure S72. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-3** with **anisole** from table 2, entry 13.

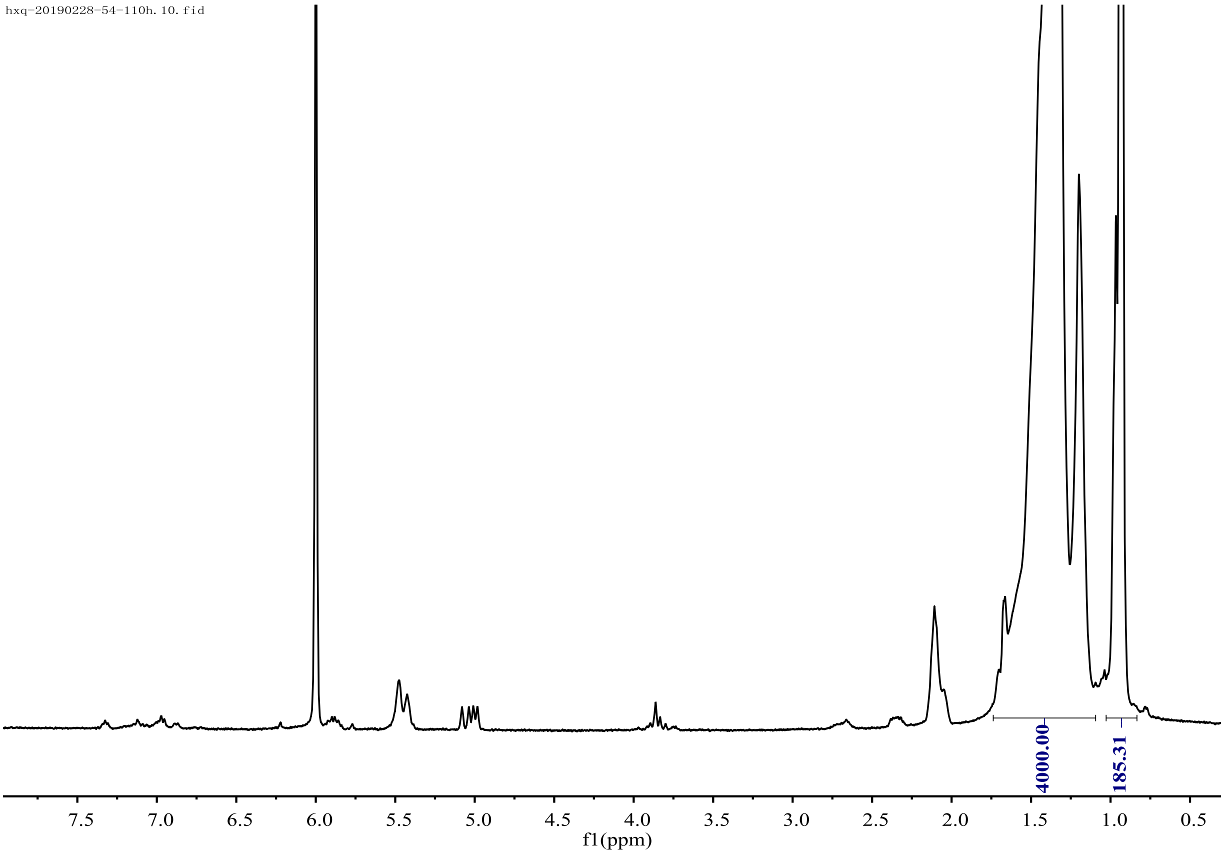


Figure S73. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-4** with **anisole** from table 2, entry 14.

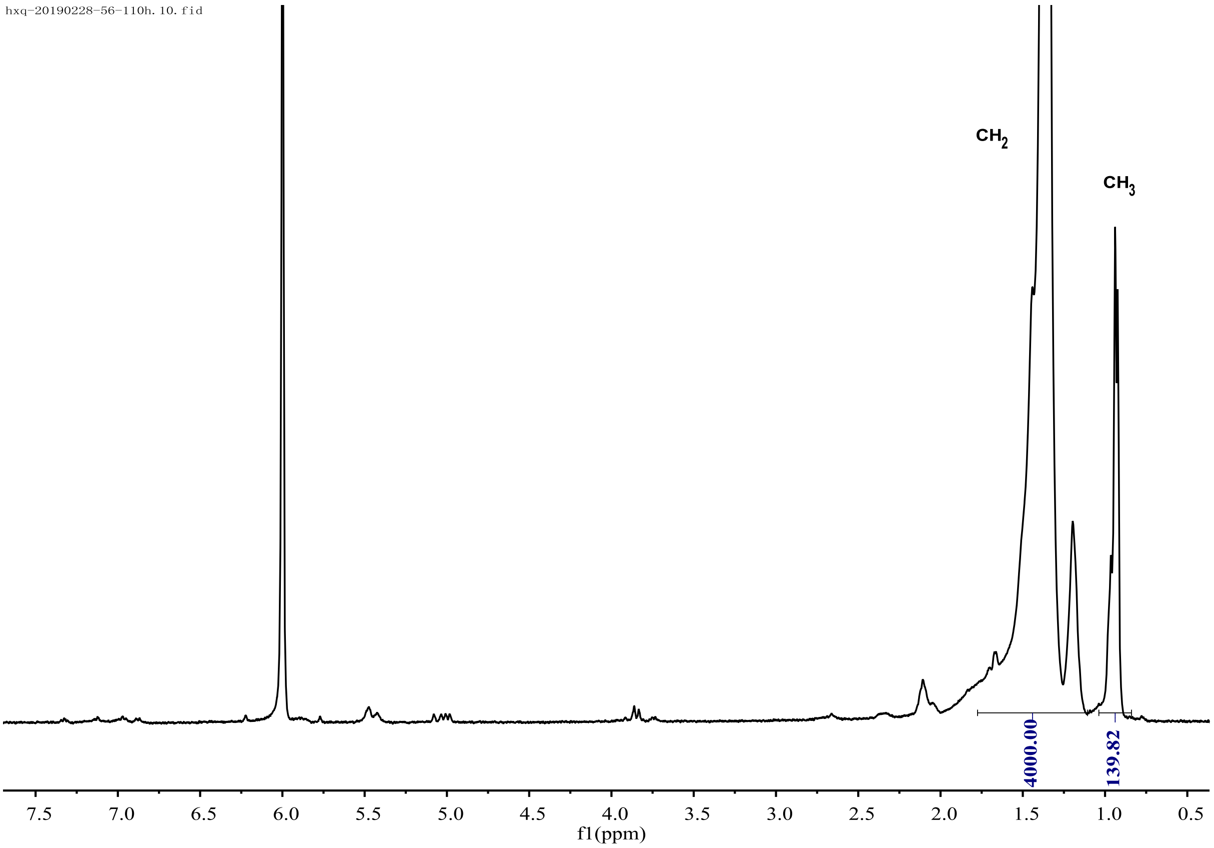


Figure S74. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-5** with **anisole** from table 2, entry 15.

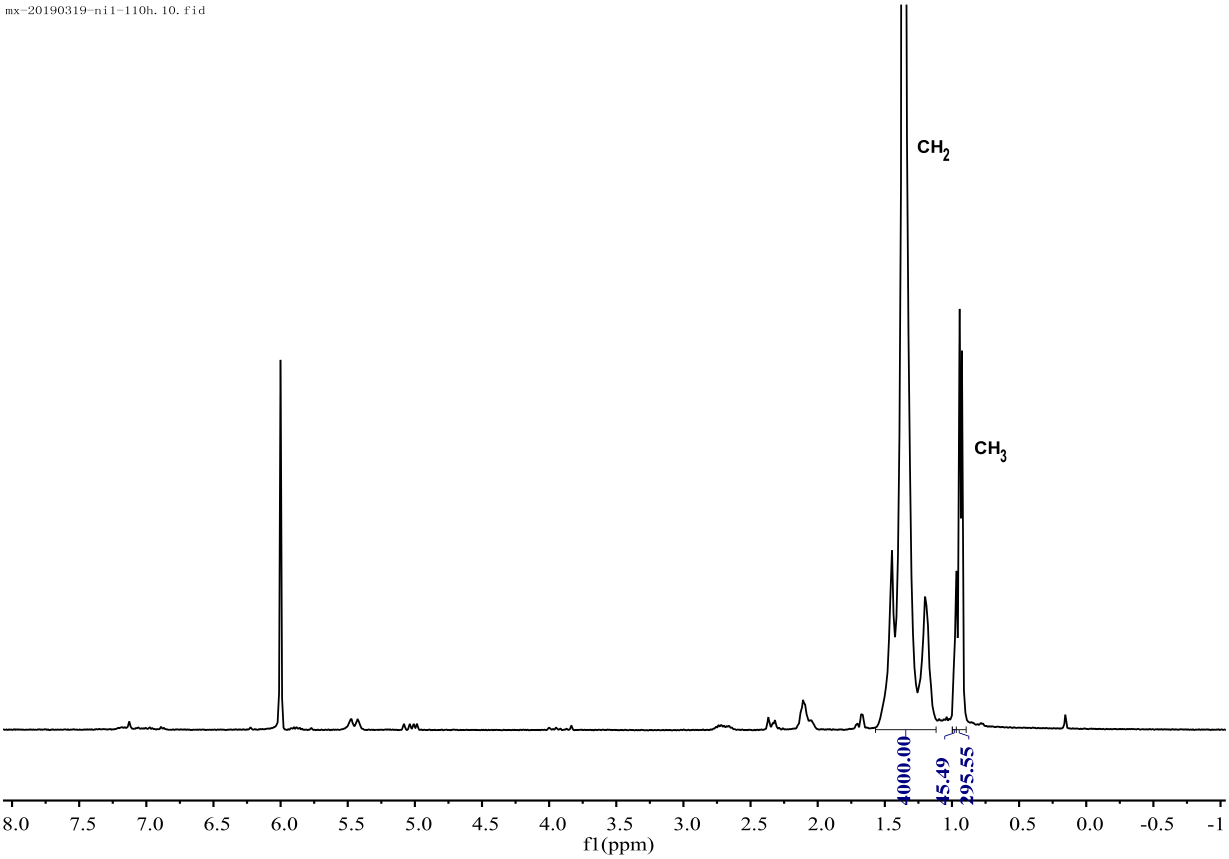


Figure S75. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-1** with **anisole** from table 2, entry 16.

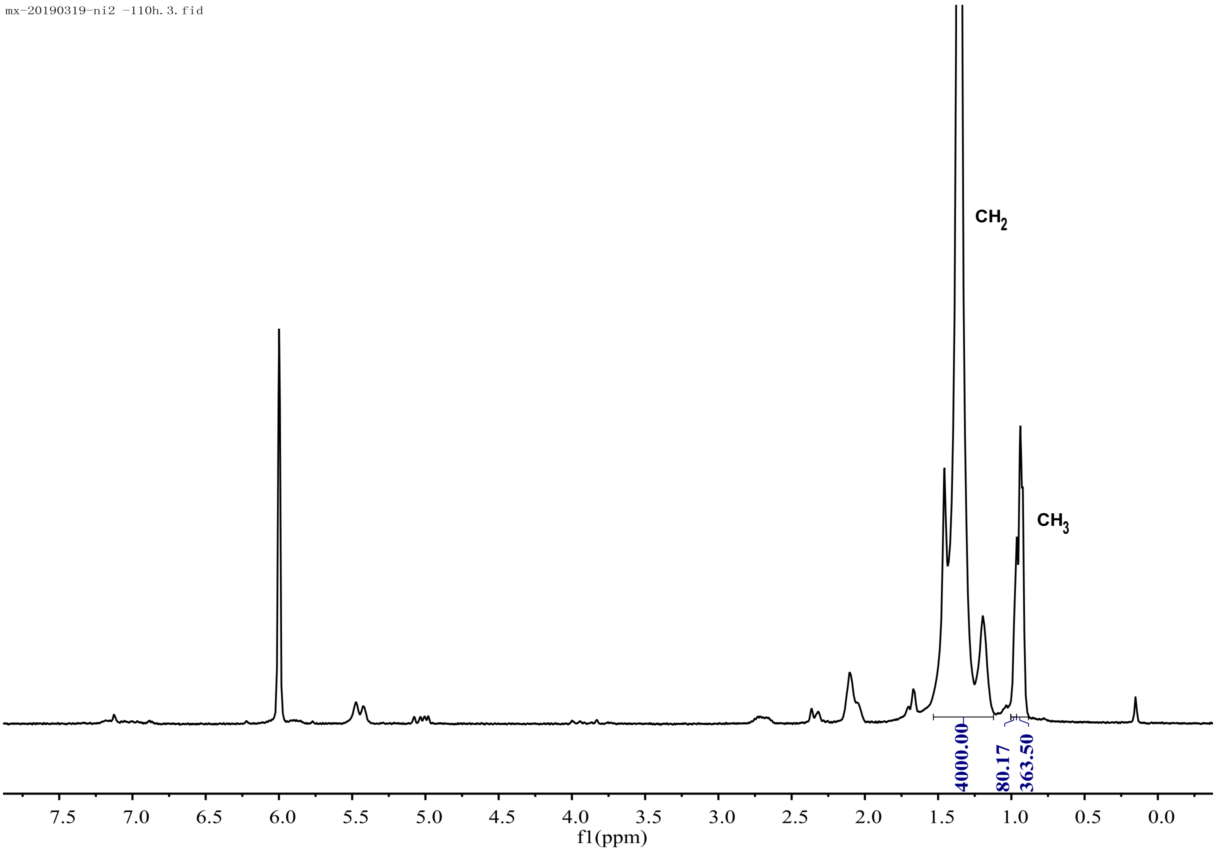


Figure S76. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-2** with **anisole** from table 2, entry 17.

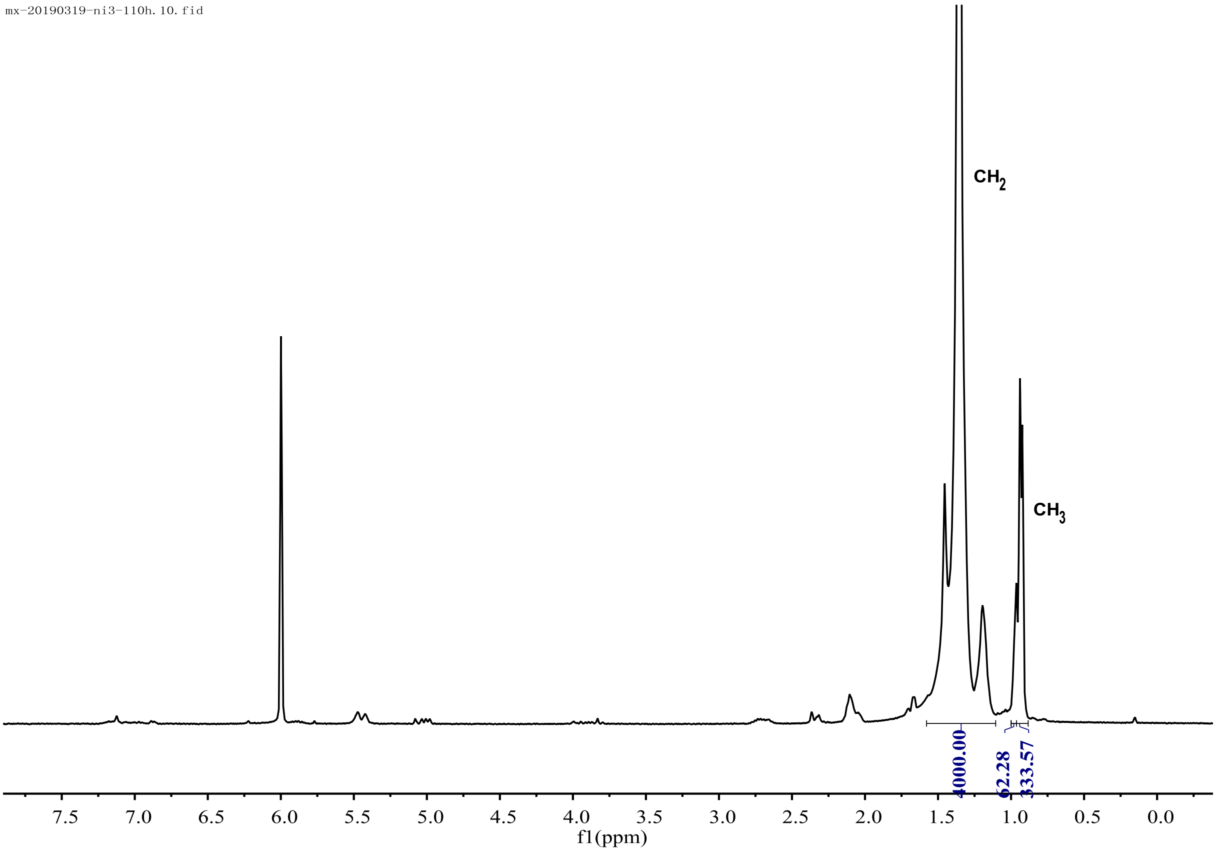


Figure S77. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-3** with **anisole** from table 2, entry 18.

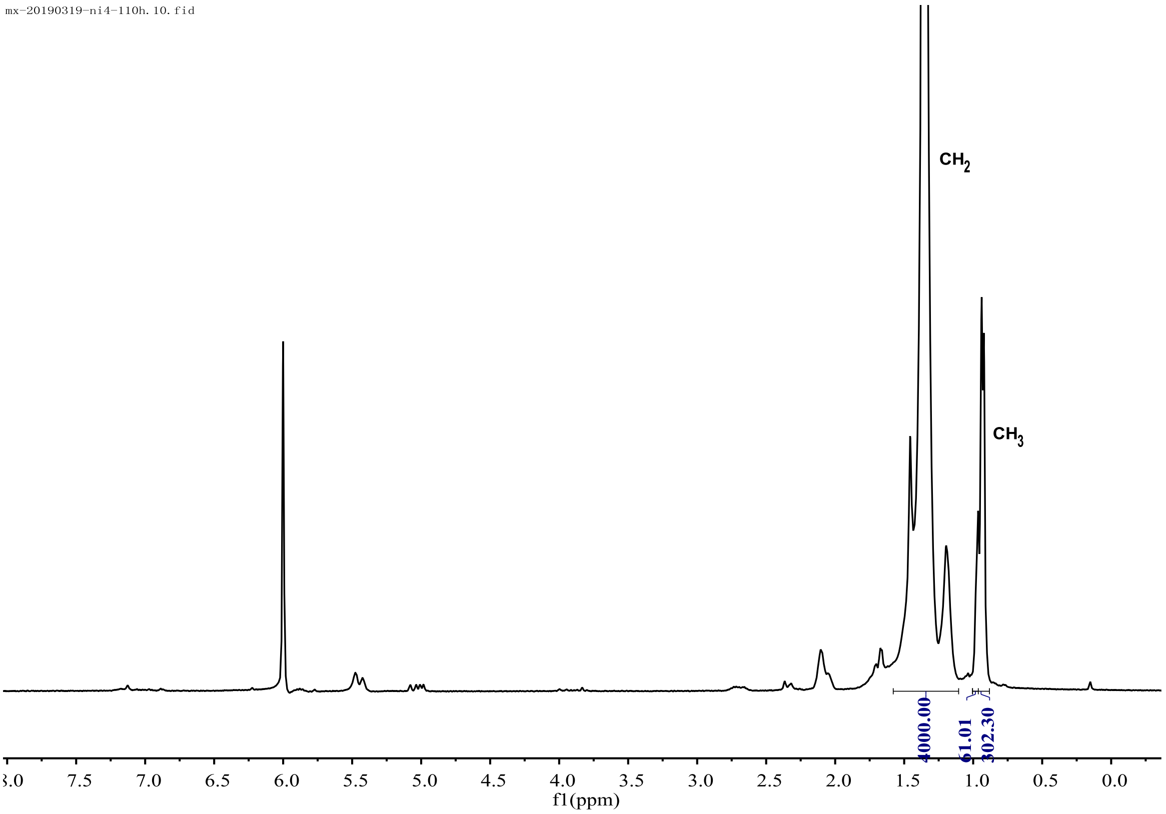


Figure S78. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-4** with **anisole** from table 2, entry 19.

6.3 ^{1}H NMR of polymer by Pd Catalyst

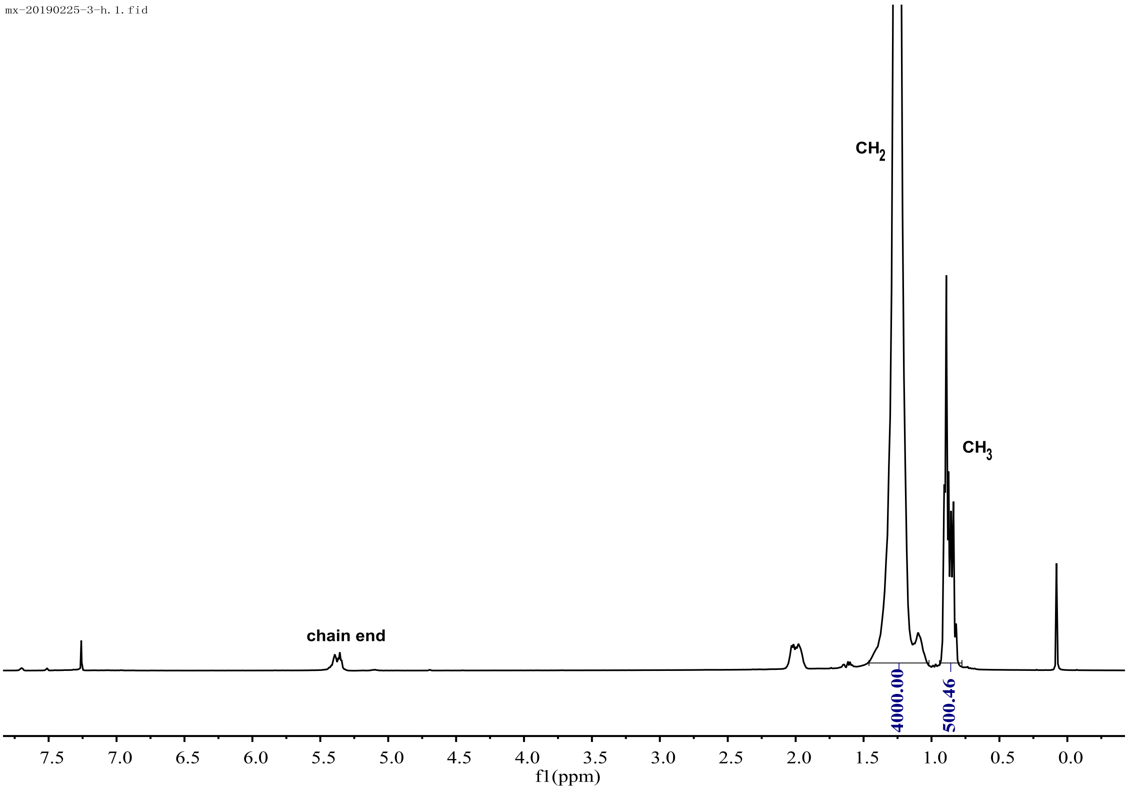


Figure S79. ^{1}H NMR spectrum of the polyethylene generated by complex **Pd-1** from table 3, entry 1.

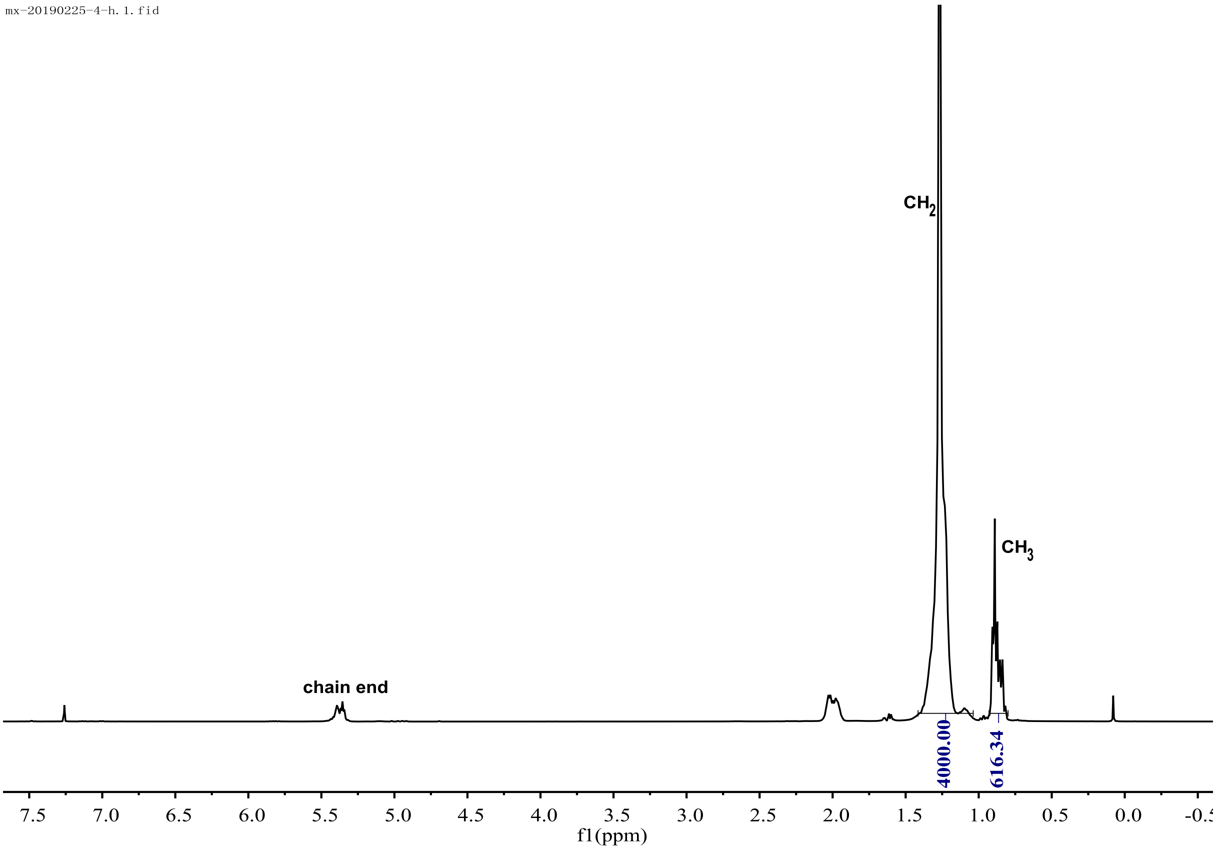


Figure S80. ^{1}H NMR spectrum of the polyethylene generated by complex **Pd-2** from table 3, entry 2.

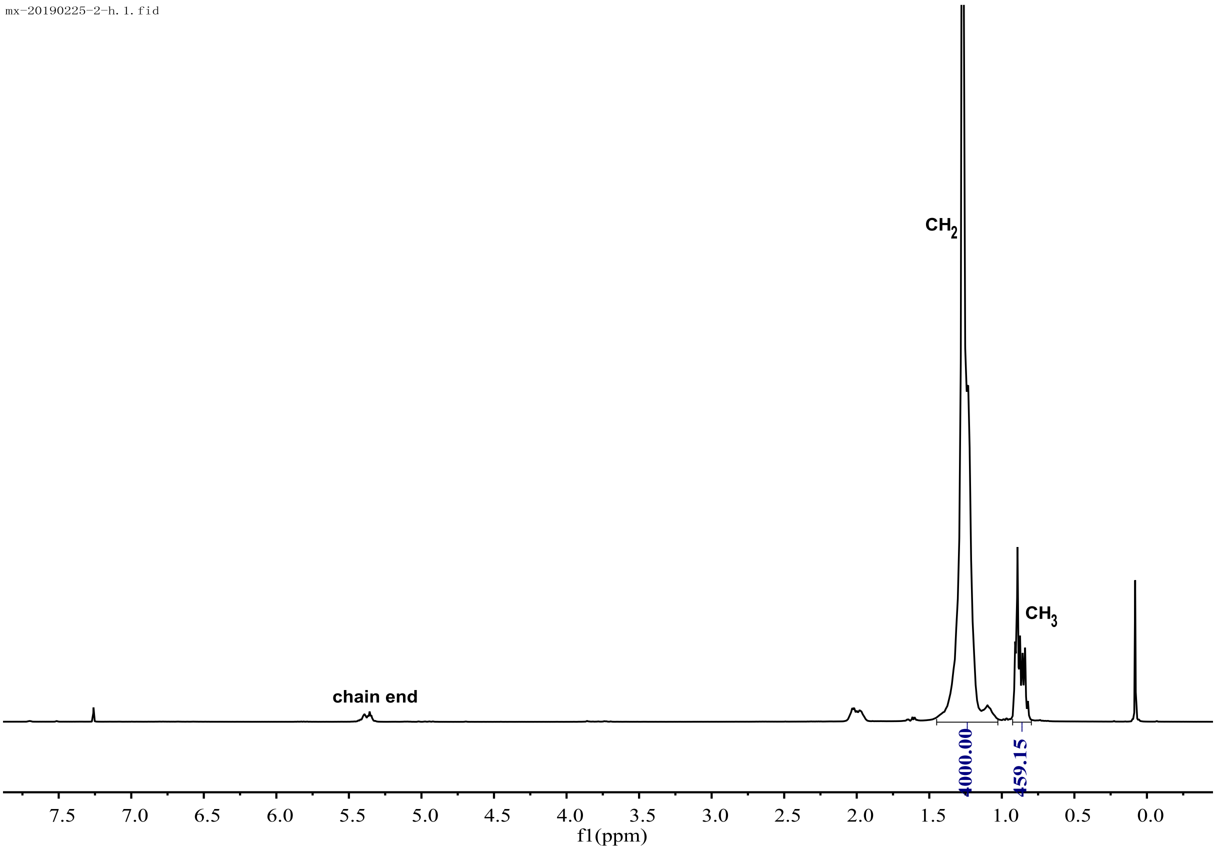


Figure S81. ^{1}H NMR spectrum of the polyethylene generated by complex **Pd-3** from table 3, entry 3.

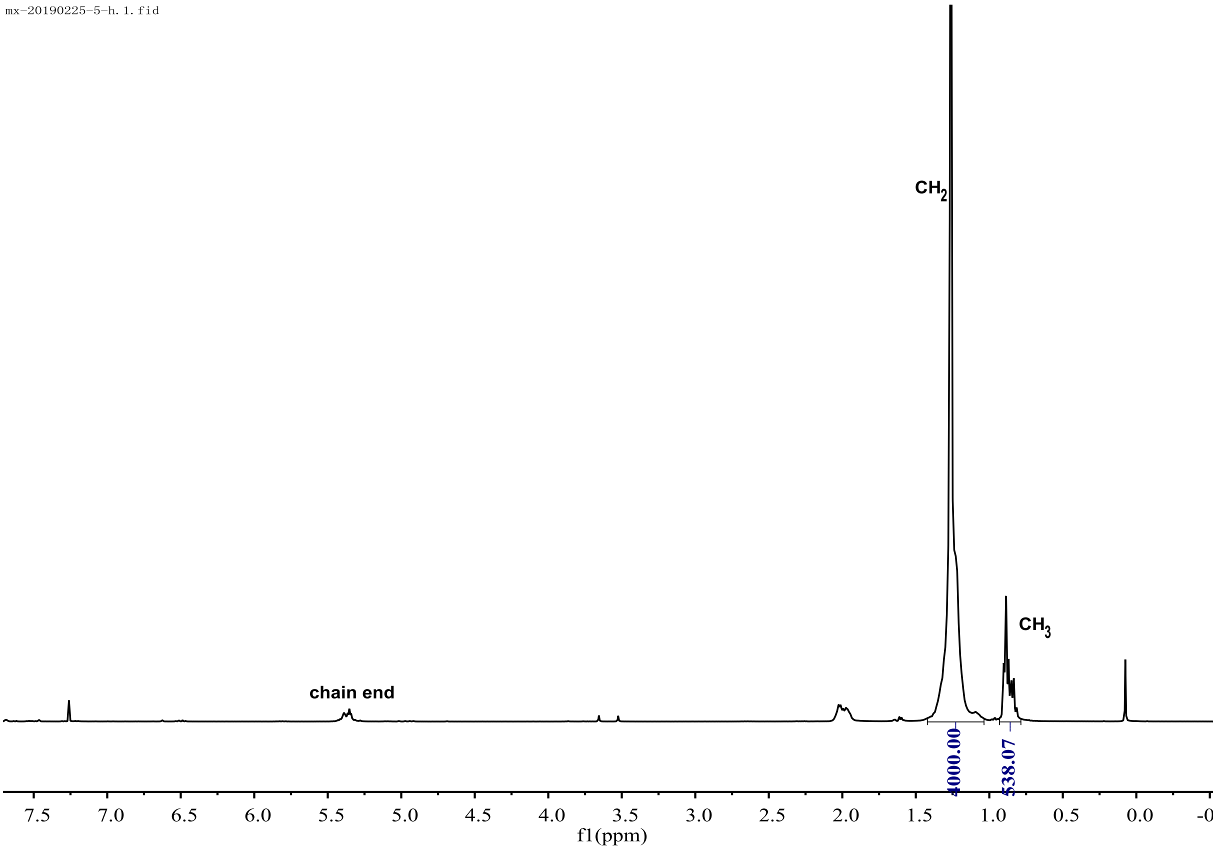


Figure S82. ^{1}H NMR spectrum of the polyethylene generated by complex **Pd-4** from table 3, entry 4.

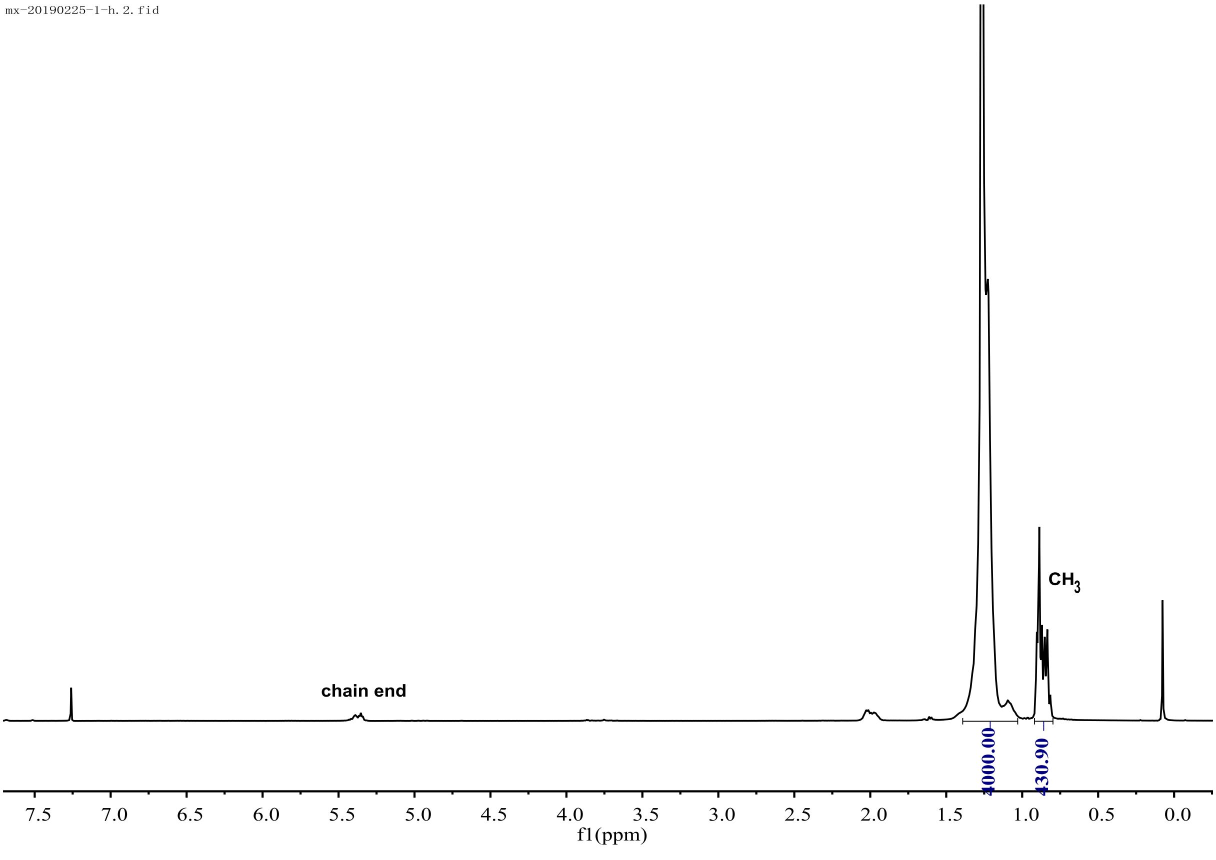


Figure S83. ^{1}H NMR spectrum of the polyethylene generated by complex **Pd-5** from table 3, entry 5.

6.4 ^{1}H NMR of copolymers by Pd Catalysts

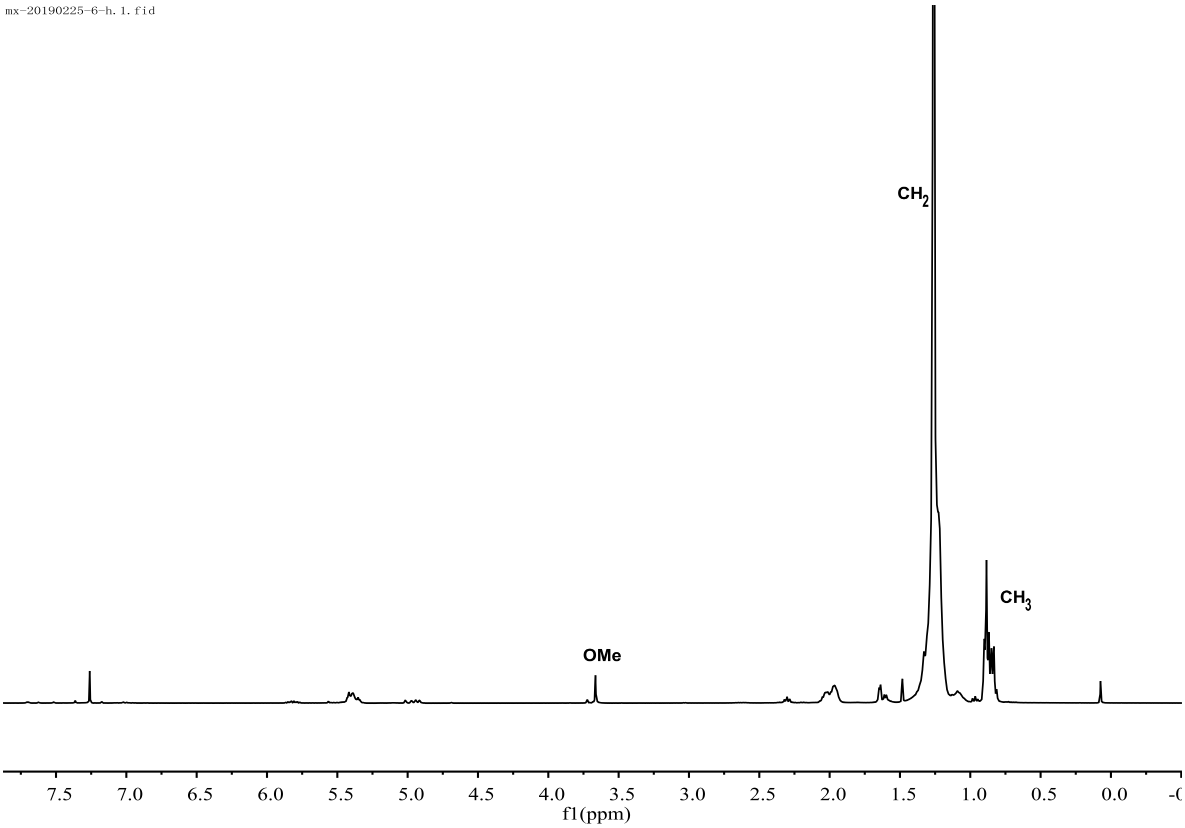


Figure S84. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **Pd-1** from table 4, entry 1.

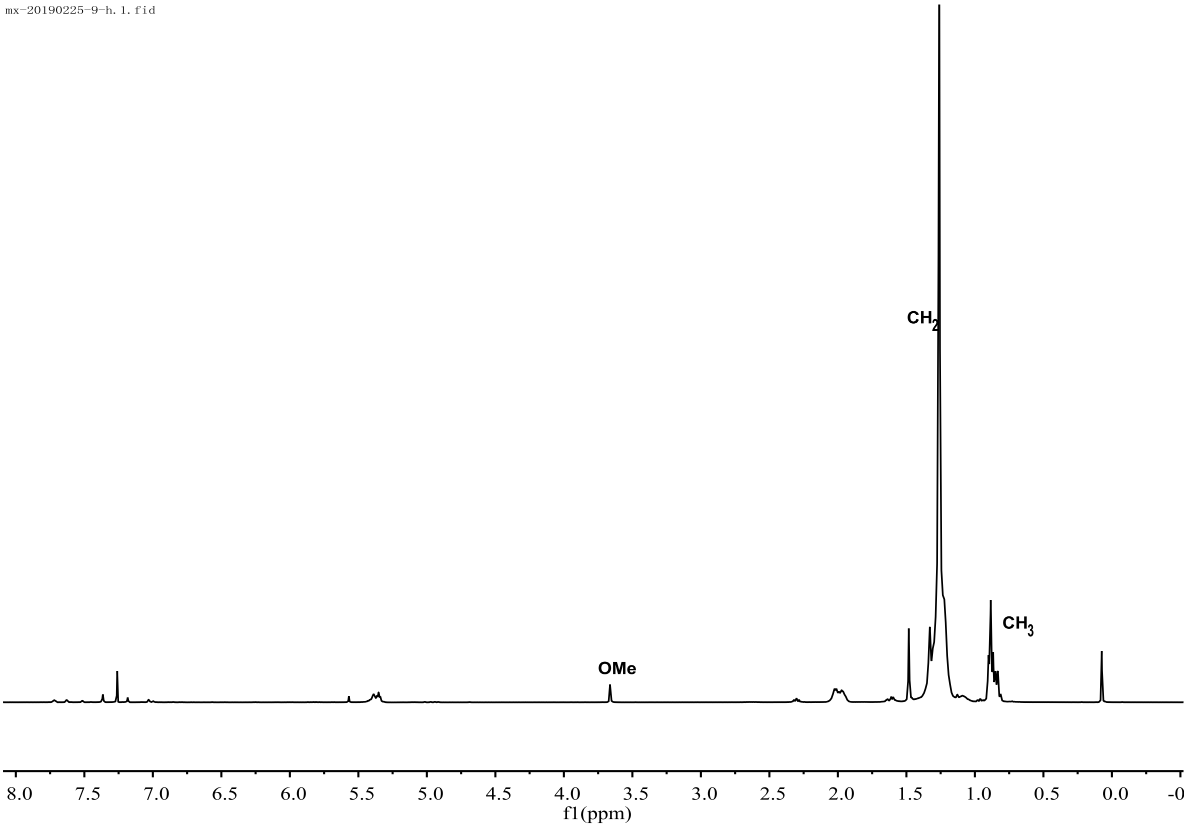


Figure S85. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **Pd-2** from table 4, entry 2.

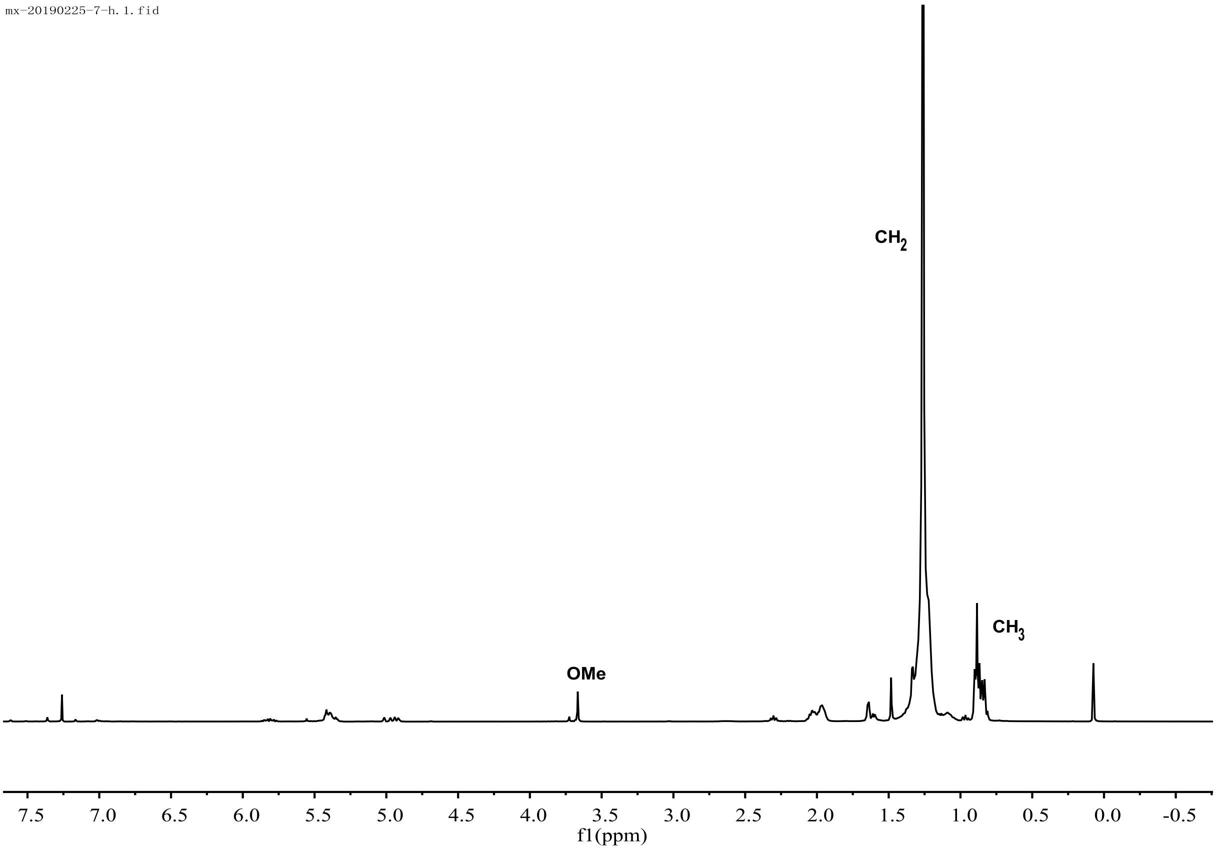


Figure S86. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **Pd-3** from table 4, entry 3.

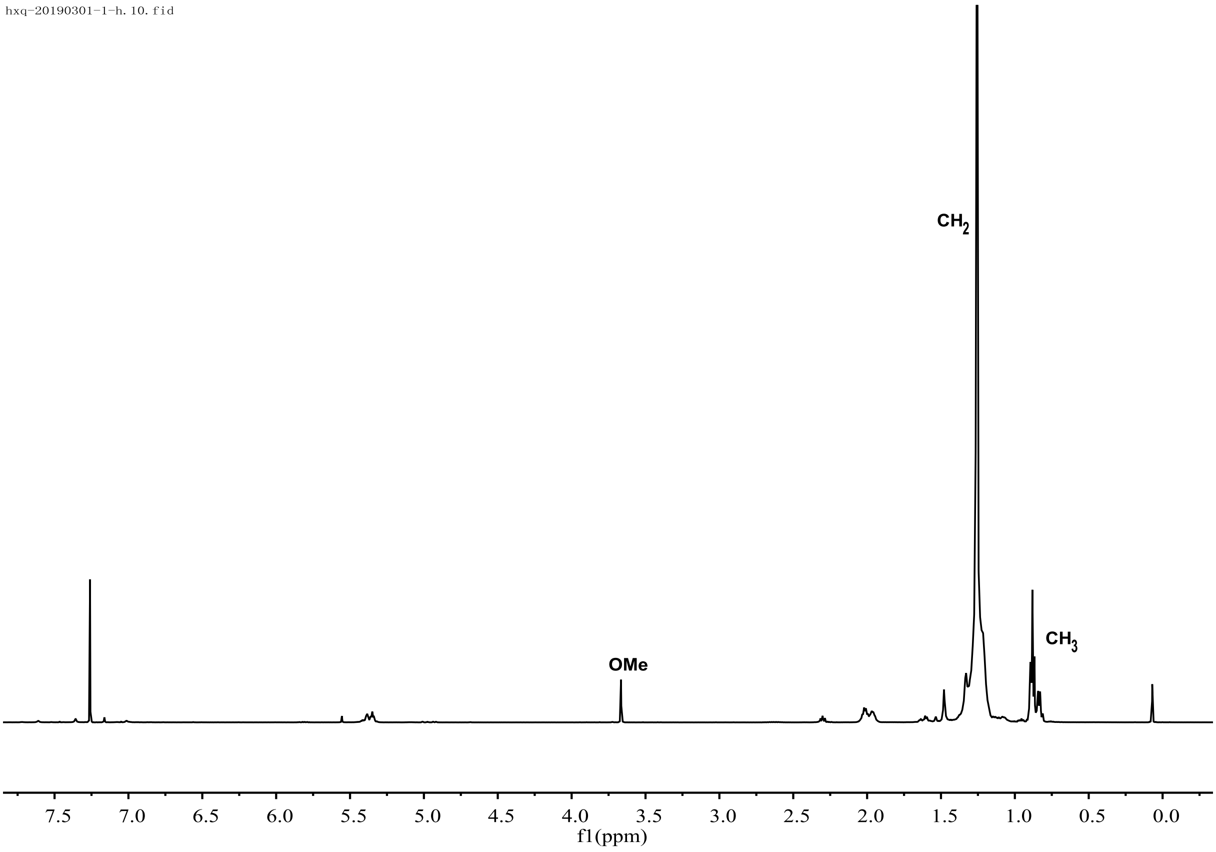


Figure S87. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **Pd-4** from table 4, entry 4.

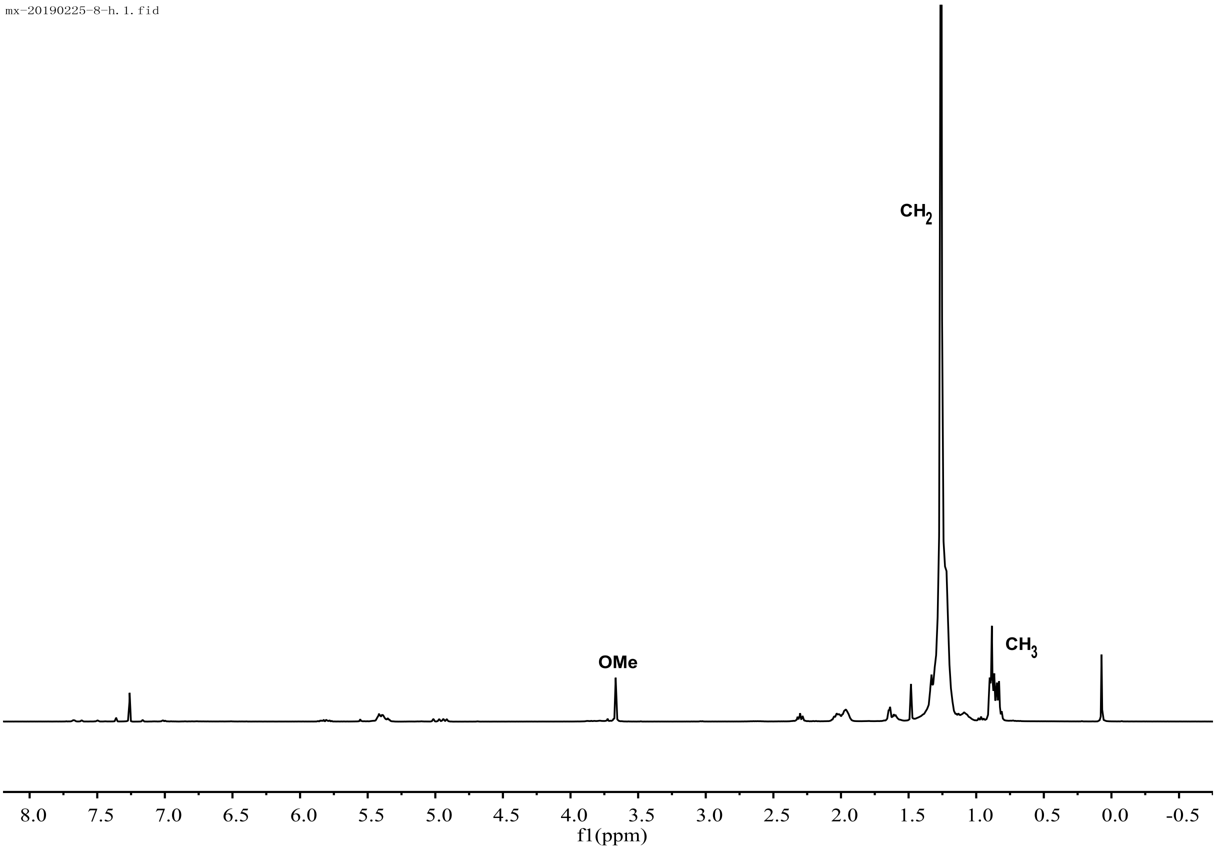


Figure S88. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **Pd-5** from table 4, entry 5.

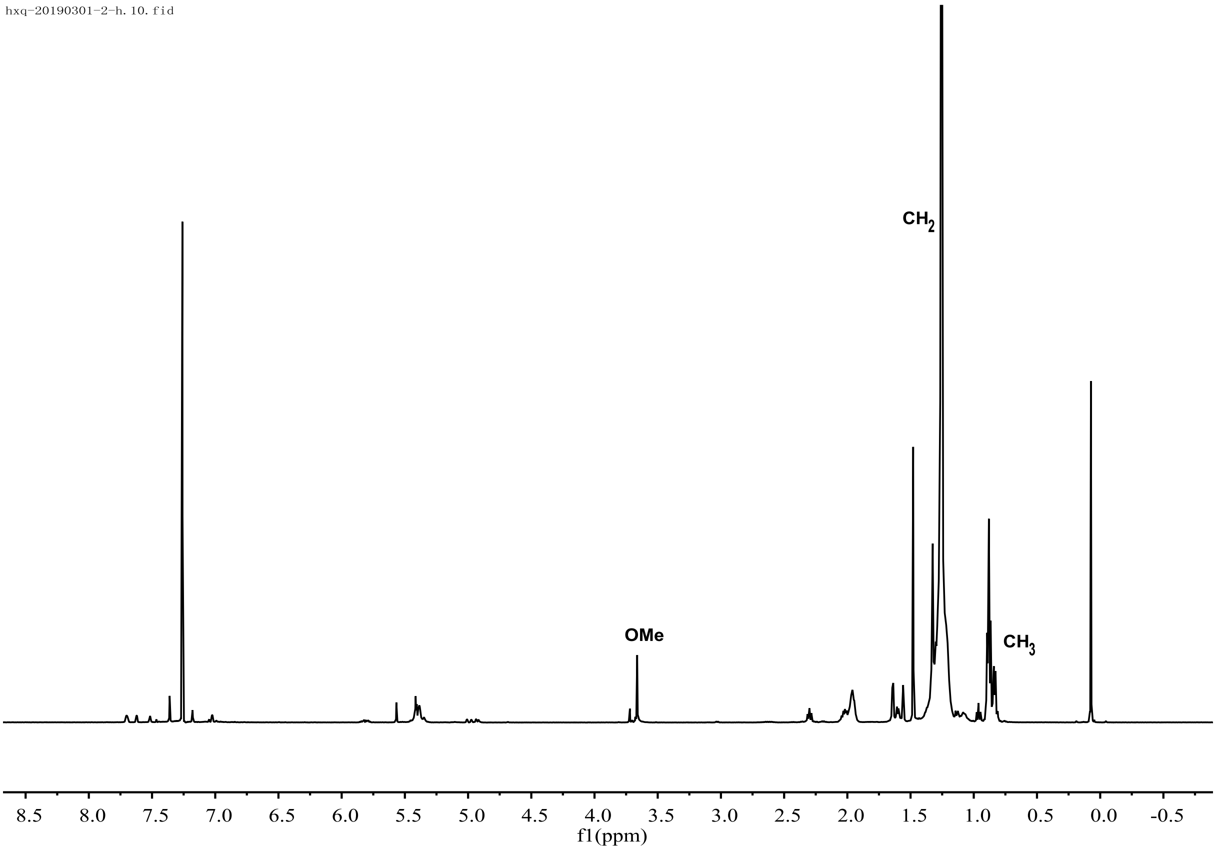


Figure S89. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **Pd-1** from table 4, entry 6.

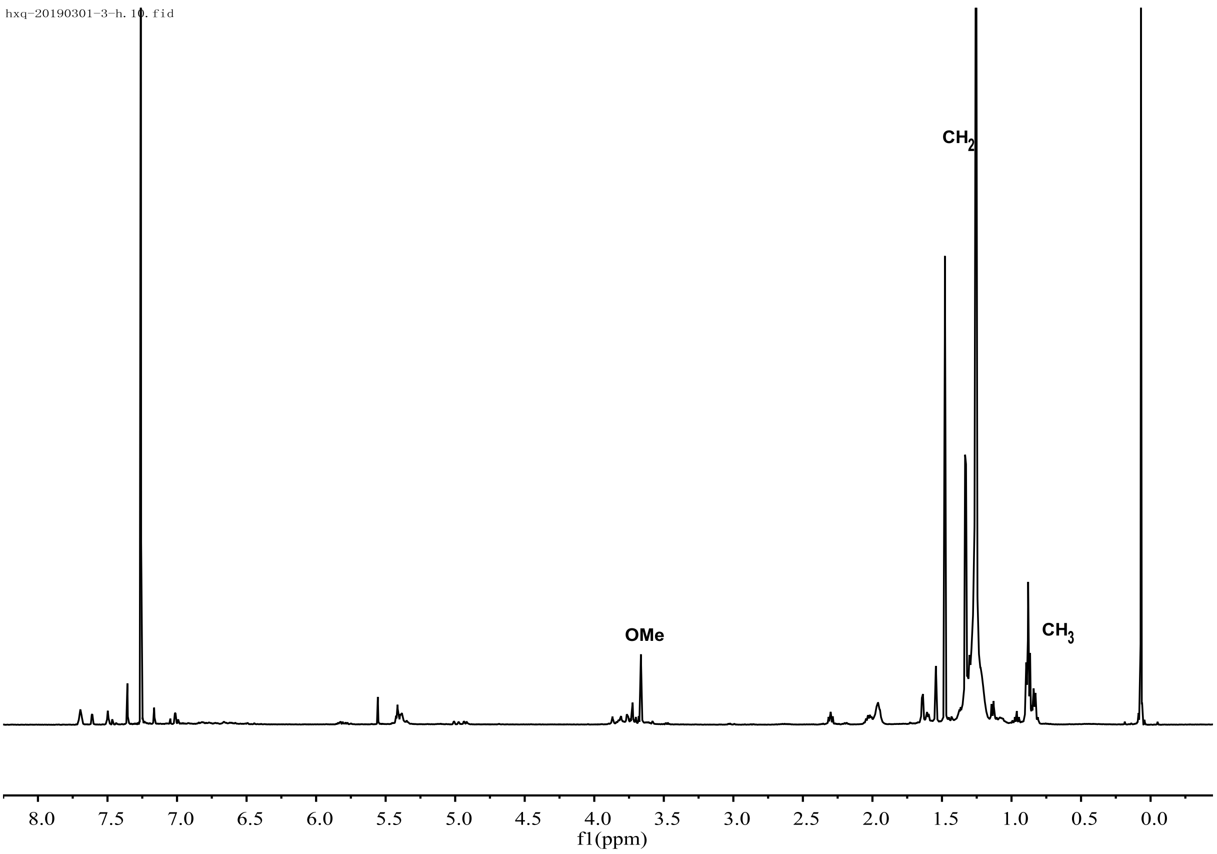


Figure S90. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **Pd-3** from table 4, entry 7.

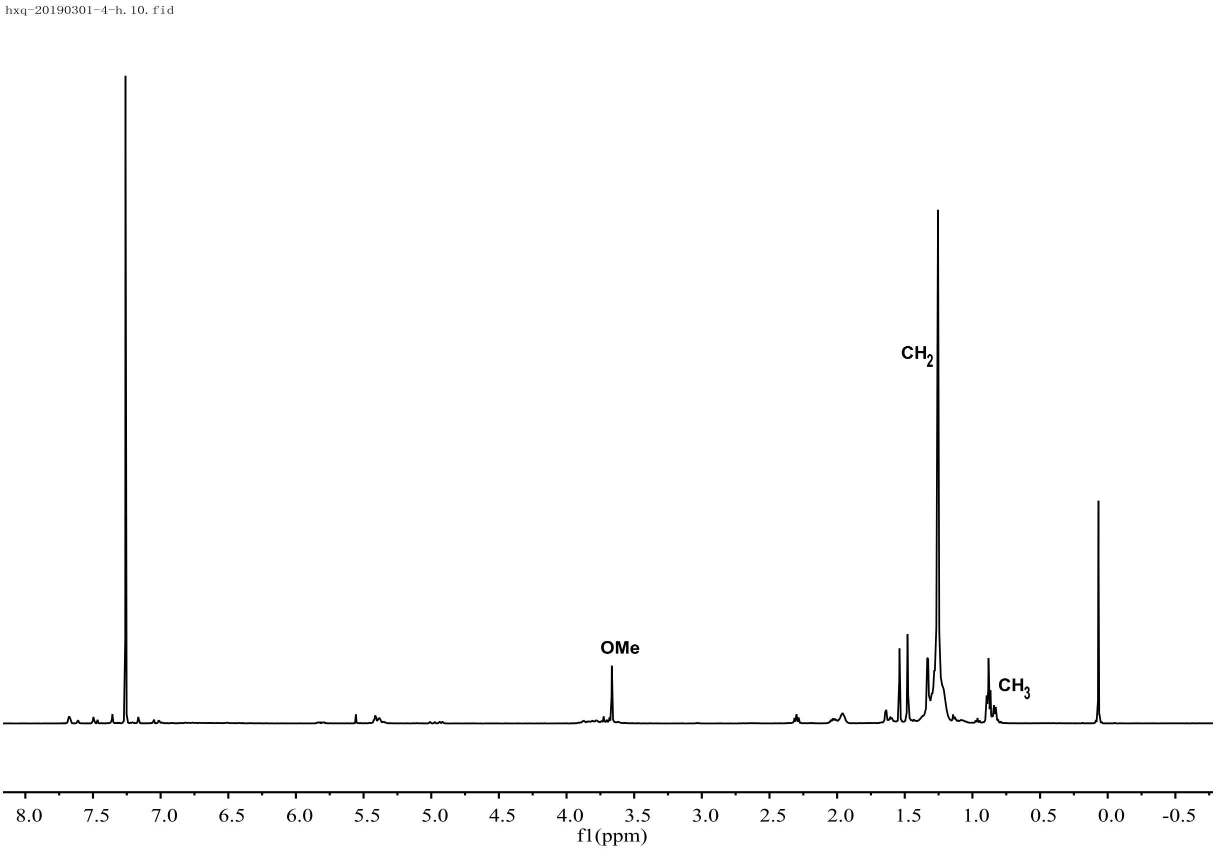


Figure S91. ^{1}H NMR spectrum of the E-MA copolymer generated by complex **Pd-5** from table 4, entry 8.

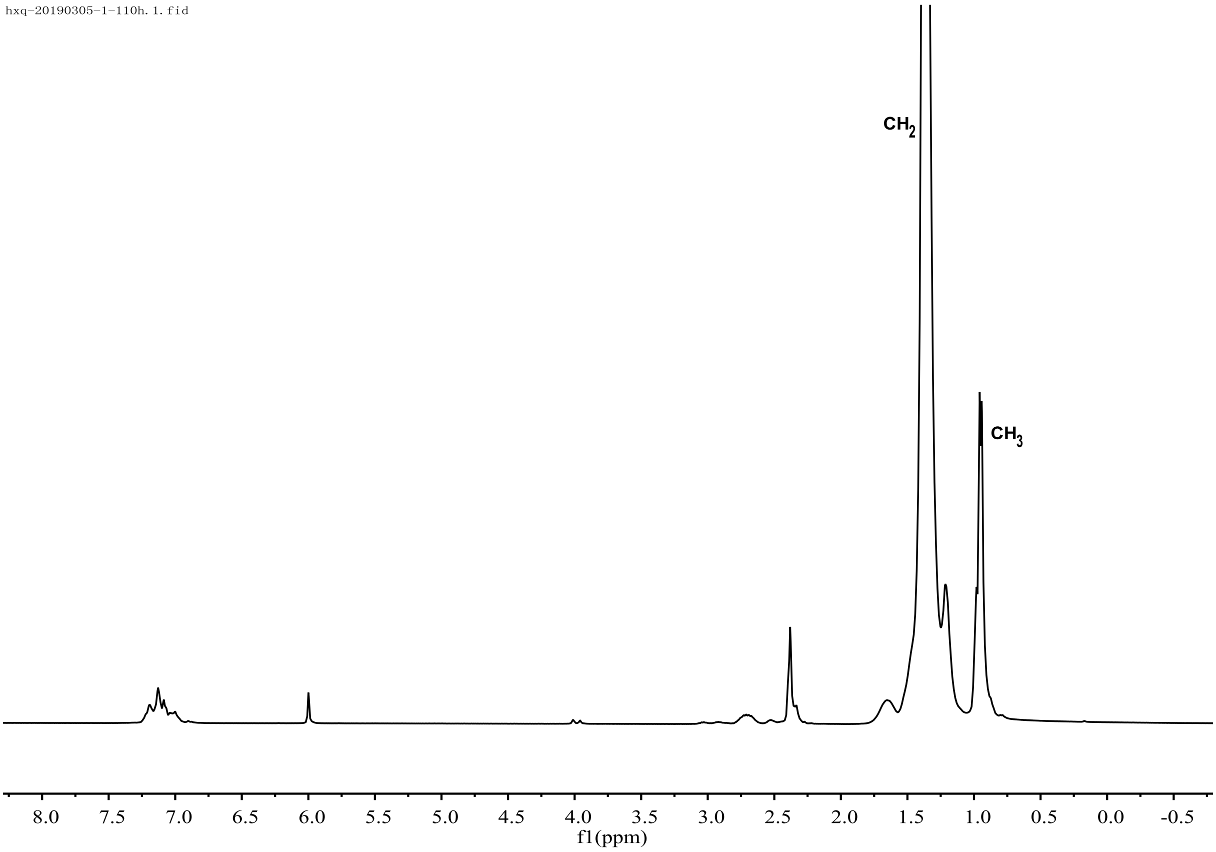


Figure S92. ^{1}H NMR spectrum of the polyethylene generated by complex **Ni-1** from table 1, entry 2.

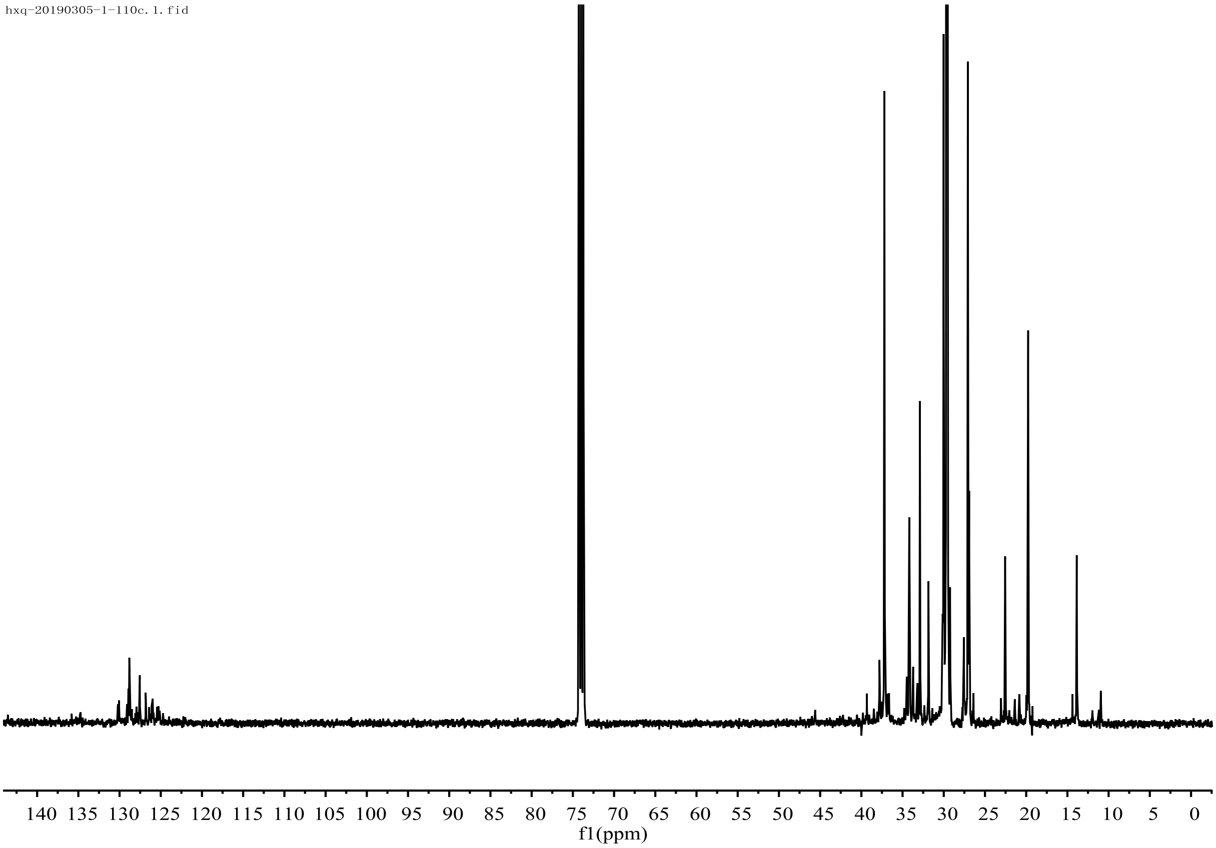


Figure S93. ^{13}C NMR spectrum of the polyethylene generated by complex **Ni-1** from table 1, entry 2.

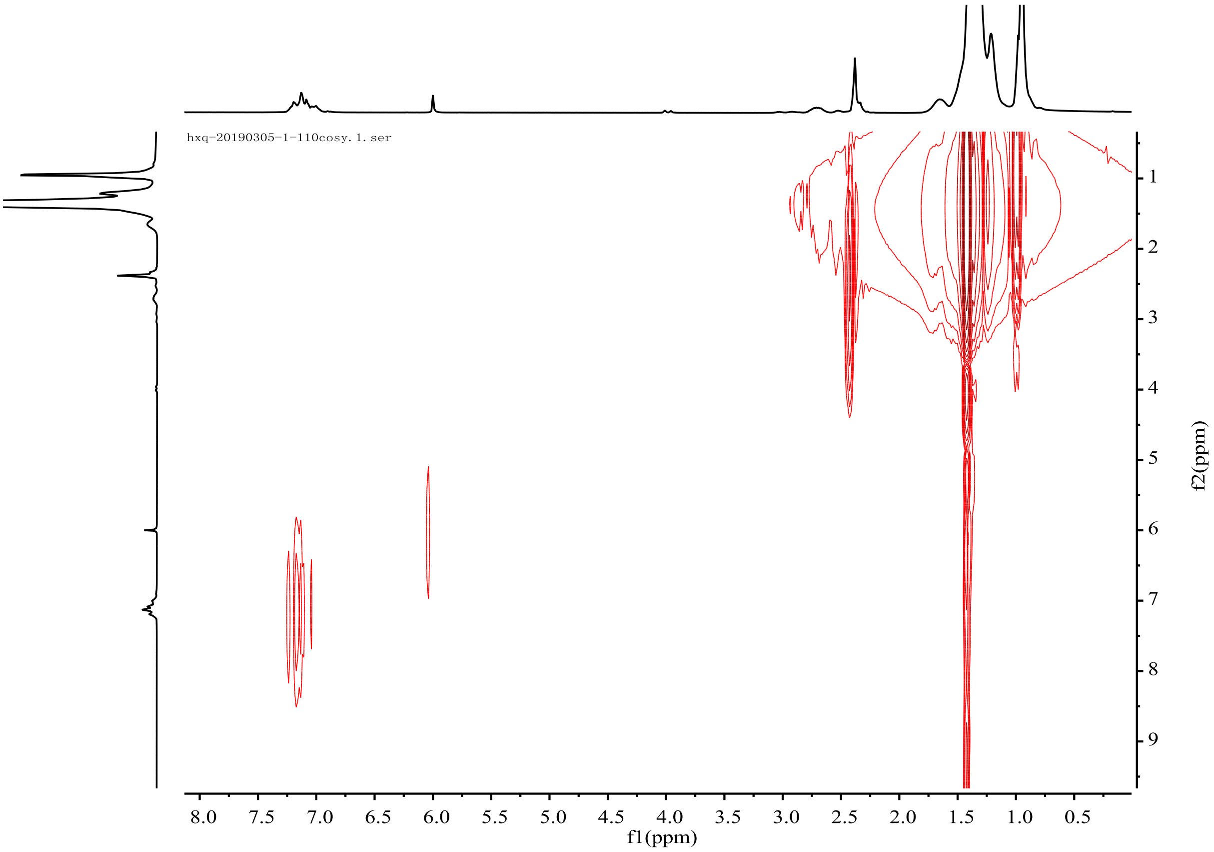


Figure S94. ^{1}H-^{1}H COSY NMR spectrum of the polyethylene generated by complex **Ni-1** from table 1, entry 2.

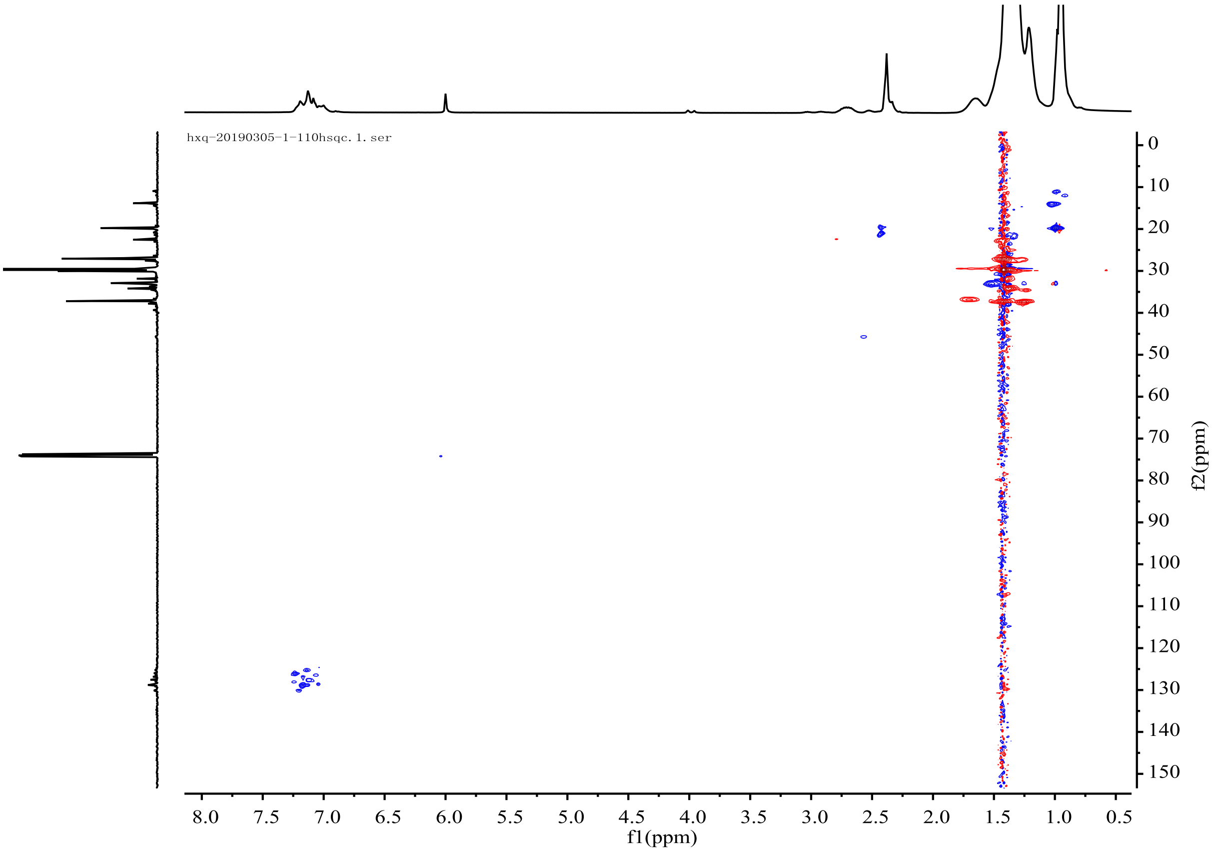


Figure S95. ^{1}H-^{13}C HSQC NMR spectrum of the polyethylene generated by complex **Ni-1** from table 1, entry 2.

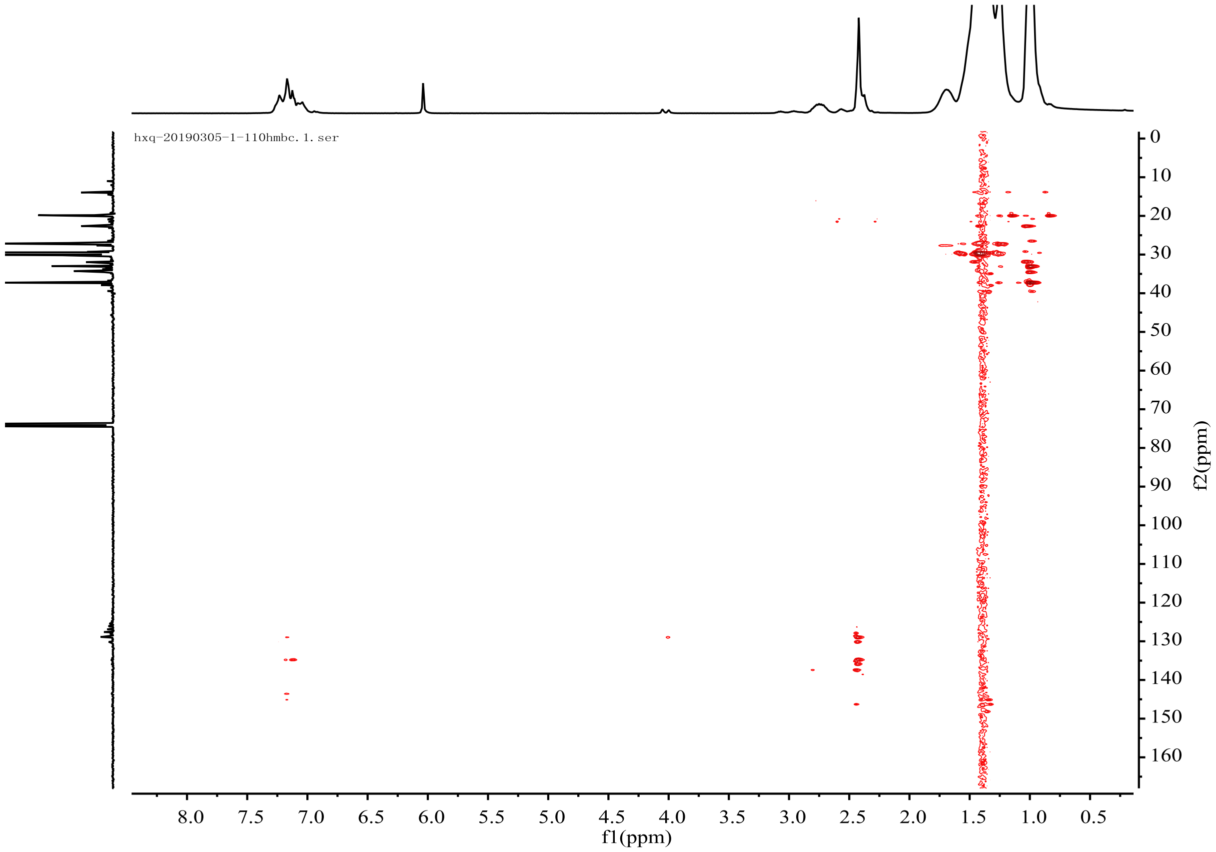
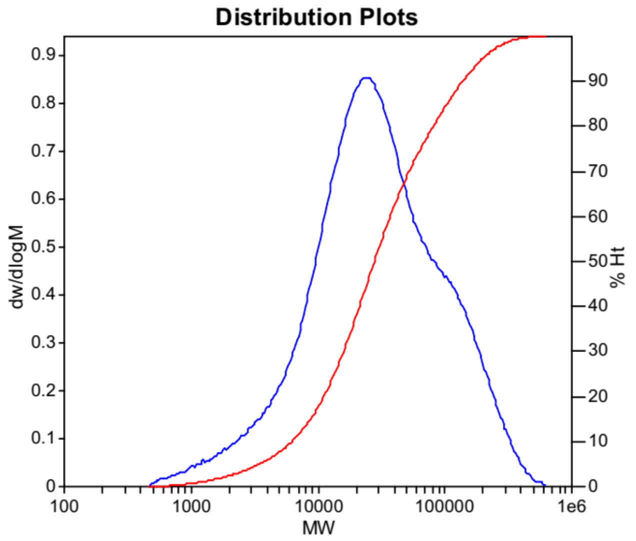


Figure S96. ^{1}H-^{13}C HMBC NMR spectrum of the polyethylene generated by complex **Ni-1** from table 1, entry 2.

7 GPC traces and DSC data of (co)polymers

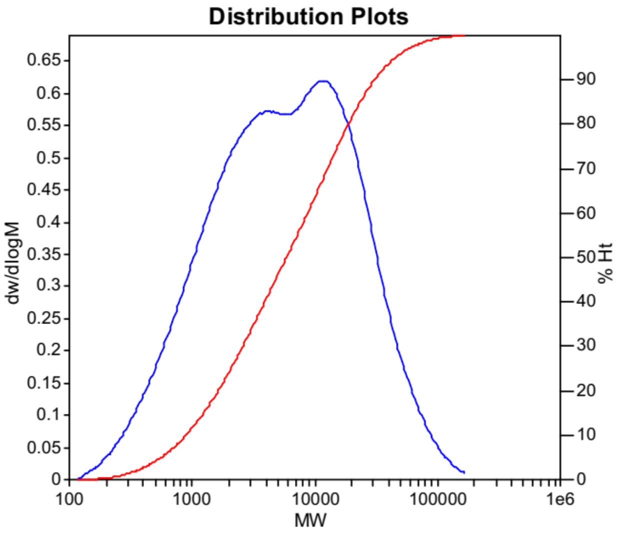


MW Averages

Mp: 24631 Mn: 12512 Mv: 44941 Mw: 52871

Mz: 137778 Mz+1: 228630 PD: 4.2256

Figure S97. GPC trace of the polymer from table 1, entry 1.

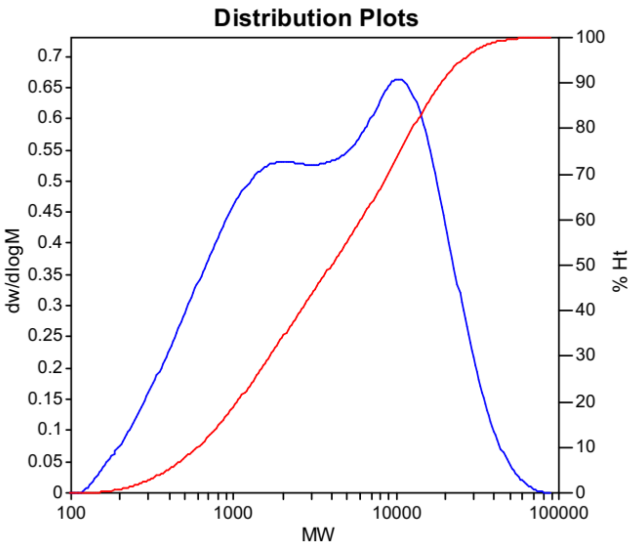


MW Averages

Mp: 11702 Mn: 2257 Mv: 9981 Mw: 12107

Mz: 36340 Mz+1: 65407 PD: 5.3642

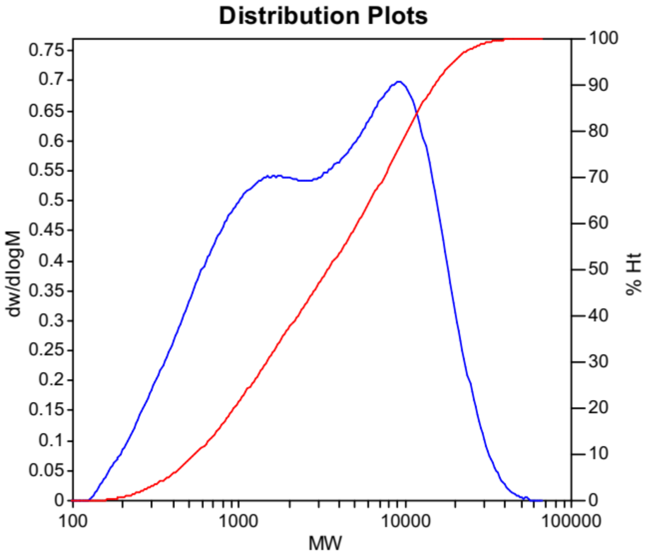
Figure S98. GPC trace of the polymer from table 1, entry 2.



MW Averages

Mp: 10347	Mn: 1563	Mv: 6222	Mw: 7338
Mz: 17647	Mz+1: 27109	PD: 4.6948	

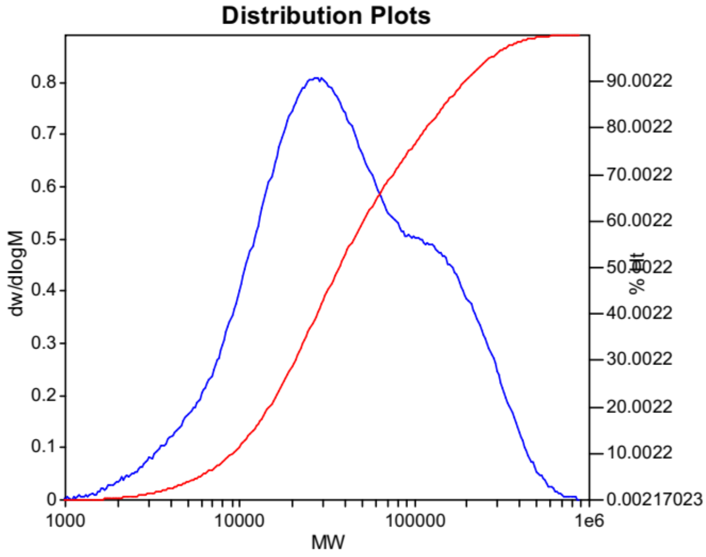
Figure S99. GPC trace of the polymer from table 1, entry 3.



MW Averages

Mp: 9378	Mn: 1434	Mv: 5077	Mw: 5904
Mz: 13119	Mz+1: 19280	PD: 4.1172	

Figure S100. GPC trace of the polymer from table 1, entry 4.

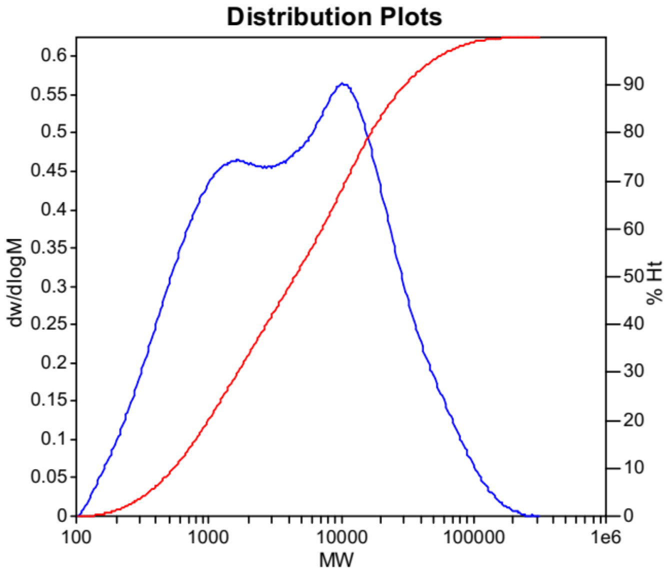


MW Averages

Mp: 27178 Mn: 20022 Mv: 62107 Mw: 72995

Mz: 185920 Mz+1: 299113 PD: 3.6457

Figure S101. GPC trace of the polymer from table 1, entry 5.

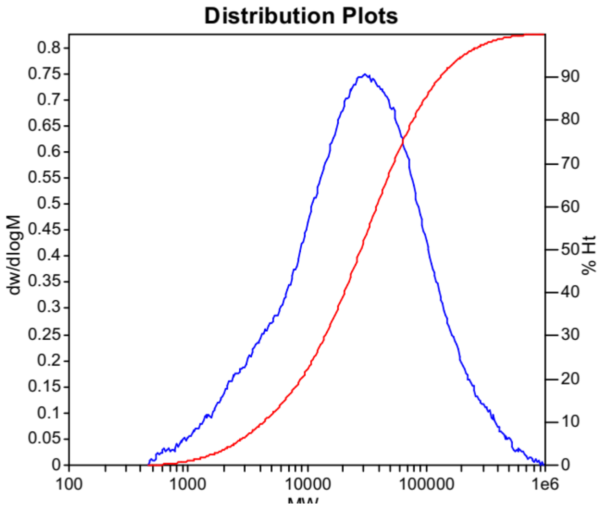


MW Averages

Mp: 10096 Mn: 1492 Mv: 9095 Mw: 11620

Mz: 44693 Mz+1: 86410 PD: 7.7882

Figure S102. GPC trace of the polymer from table 1, entry 6.

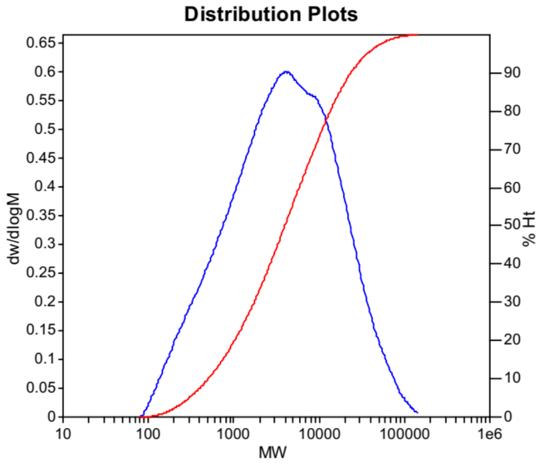


MW Averages

Mp: 30736 Mn: 10281 Mv: 45085 Mw: 54498

Mz: 173937 Mz+1: 341834 PD: 5.3008

Figure S103. GPC trace of the polymer from table 1, entry 9.

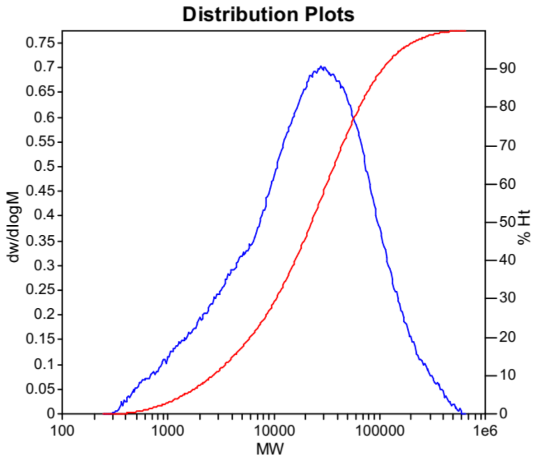


MW Averages

Mp: 4164 Mn: 1339 Mv: 7302 Mw: 9084

Mz: 30806 Mz+1: 56357 PD: 6.7842

Figure S104. GPC trace of the polymer from table 1, entry 12.

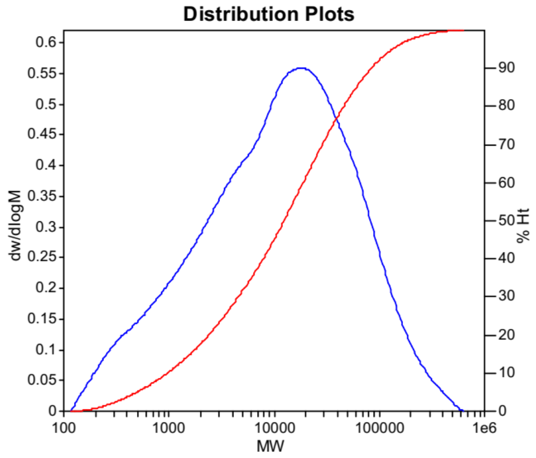


MW Averages

Mp: 27855 Mn: 6605 Mv: 35693 Mw: 43099

Mz: 127577 Mz+1: 230866 PD: 6.5252

Figure S105. GPC trace of the polymer from table 1, entry 13.

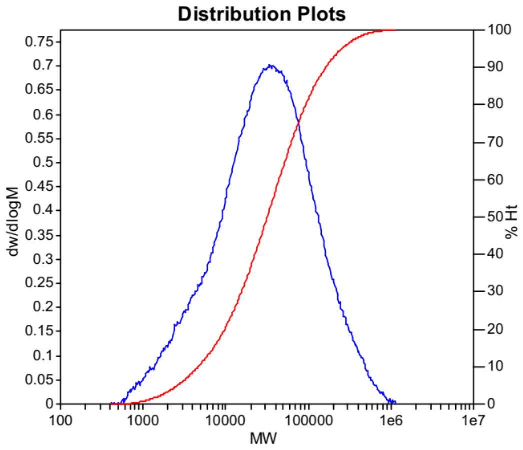


MW Averages

Mp: 18221 Mn: 2544 Mv: 24642 Mw: 31726

Mz: 123958 Mz+1: 234655 PD: 12.4709

Figure S106. GPC trace of the polymer from table 1, entry 14.

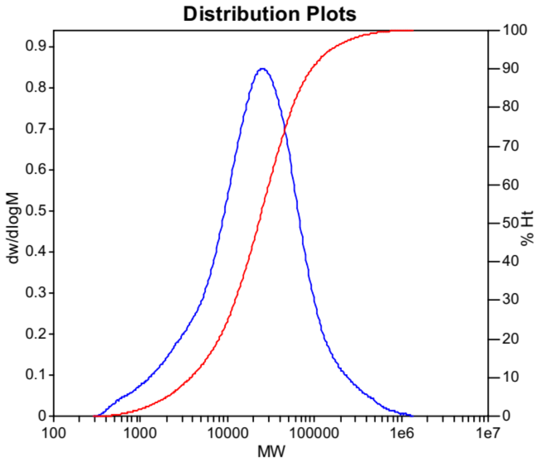


MW Averages

Mp: 33915 Mn: 11255 Mv: 53432 Mw: 65215

Mz: 212199 Mz+1: 402738 PD: 5.7943

Figure S107. GPC trace of the polymer from table 1, entry 17.

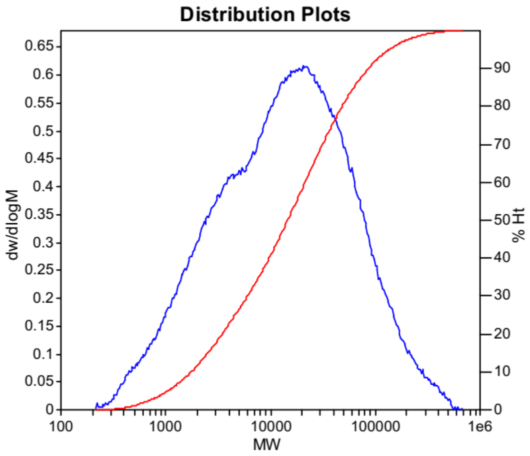


MW Averages

Mp: 24631 Mn: 8309 Mv: 35861 Mw: 43962

Mz: 179244 Mz+1: 446495 PD: 5.2909

Figure S108. GPC trace of the polymer from table 1, entry 18.



MW Averages

Mp: 20231

Mn: 4572

Mv: 26874

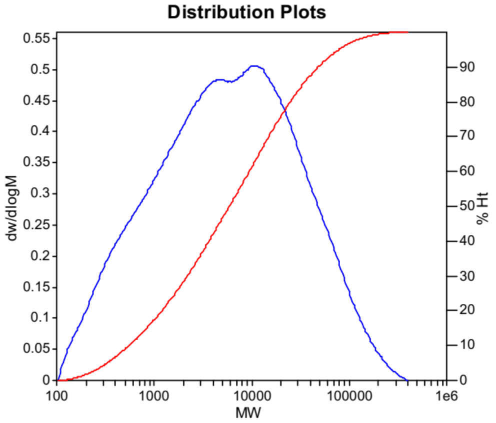
Mw: 33813

Mz: 124773

Mz+1: 239196

PD: 7.3957

Figure S109. GPC trace of the polymer from table 1, entry 19.



MW Averages

Mp: 10869

Mn: 1573

Mv: 13492

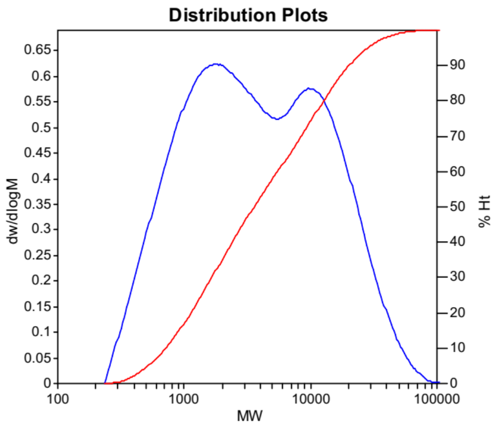
Mw: 17746

Mz: 75326

Mz+1: 141217

PD: 11.2816

Figure S110. GPC trace of the polymer from table 1, entry 20.

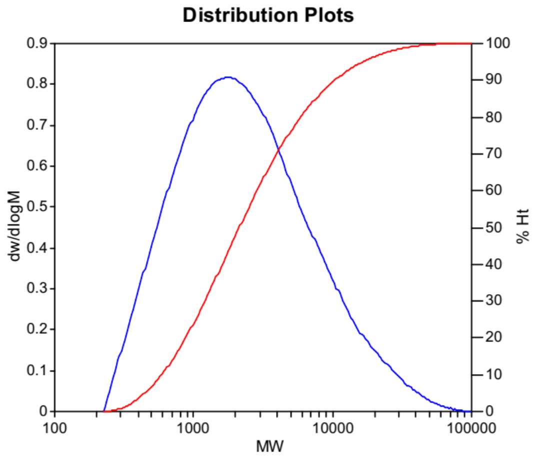


MW Averages

Mp: 1771 Mn: 1848 Mv: 6400 Mw: 7664

Mz: 20782 Mz+1: 34082 PD: 4.1472

Figure S111. GPC trace of the polymer from table 2, entry 1.

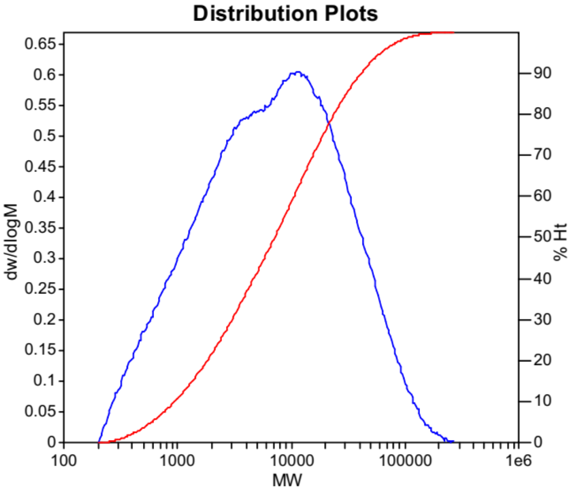


MW Averages

Mp: 1728 Mn: 1387 Mv: 3638 Mw: 4365

Mz: 14442 Mz+1: 29591 PD: 3.1471

Figure S112. GPC trace of the polymer from table 2, entry 2.

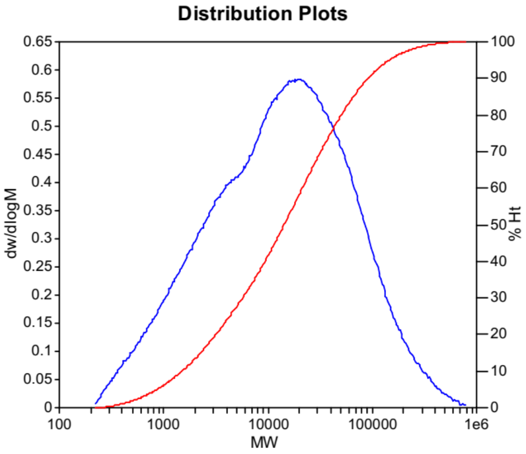


MW Averages

Mp: 11775 Mn: 2561 Mv: 12633 Mw: 15532

Mz: 48880 Mz+1: 87302 PD: 6.0648

Figure S113. GPC trace of the polymer from table 2, entry 3.

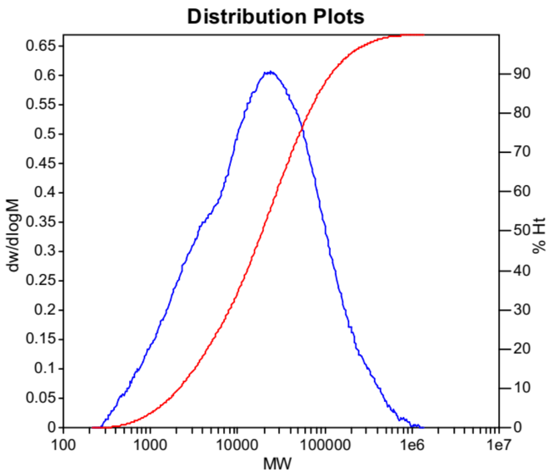


MW Averages

Mp: 19739 Mn: 3981 Mv: 28011 Mw: 35896

Mz: 146181 Mz+1: 297045 PD: 9.0168

Figure S114. GPC trace of the polymer from table 2, entry 4.

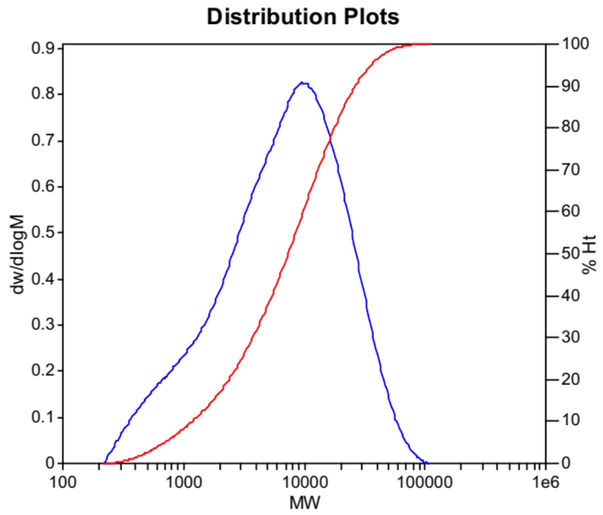


MW Averages

Mp: 24033 Mn: 5554 Mv: 37017 Mw: 47391

Mz: 197475 Mz+1: 413408 PD: 8.5328

Figure S115. GPC trace of the polymer from table 2, entry 5.

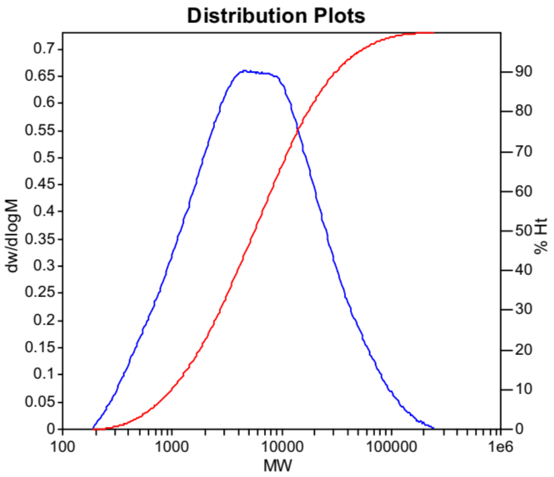


MW Averages

Mp: 9436 Mn: 2977 Mv: 9713 Mw: 11088

Mz: 23615 Mz+1: 36412 PD: 3.7246

Figure S116. GPC trace of the polymer from table 2, entry 6.

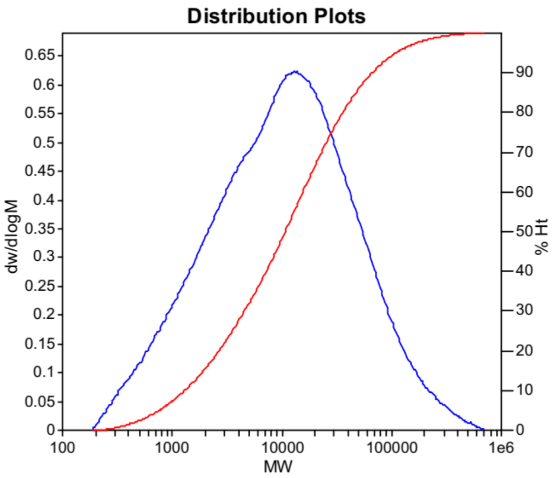


MW Averages

Mp: 4623 Mn: 2502 Mv: 10107 Mw: 12484

Mz: 44536 Mz+1: 88538 PD: 4.9896

Figure S117. GPC trace of the polymer from table 2, entry 9.

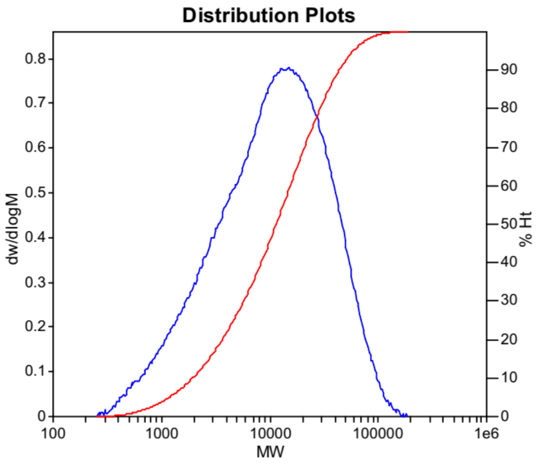


MW Averages

Mp: 12992 Mn: 3385 Mv: 20955 Mw: 26983

Mz: 119379 Mz+1: 255494 PD: 7.9713

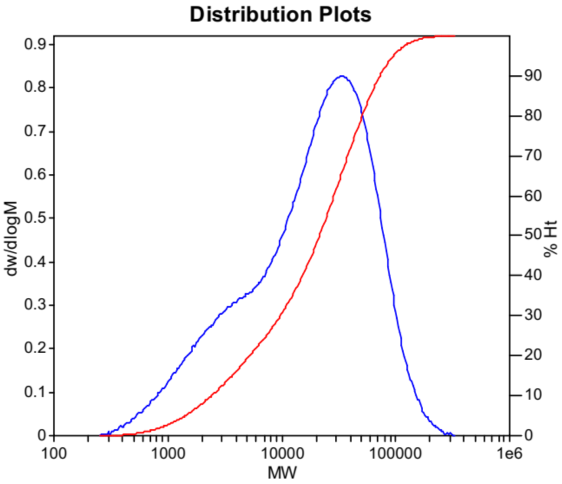
Figure S118. GPC trace of the polymer from table 2, entry 10.



MW Averages

Mp: 15059
Mn: 4709
Mv: 15658
Mw: 17972
Mz: 39440
Mz+1: 61369
PD: 3.8165

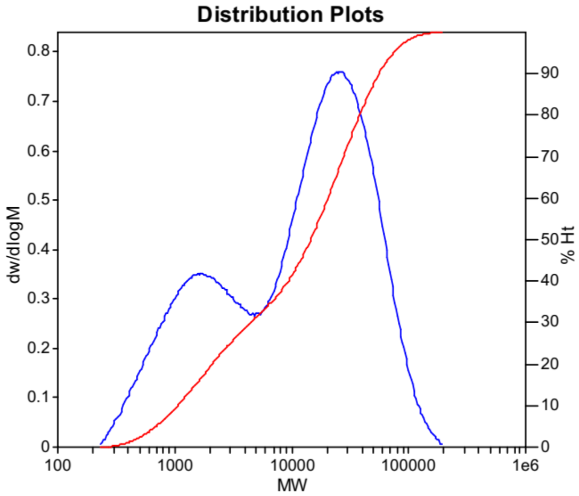
Figure S119. GPC trace of the polymer from table 2, entry 11.



MW Averages

Mp: 33915
Mn: 6328
Mv: 26868
Mw: 30815
Mz: 64932
Mz+1: 99607
PD: 4.8696

Figure S120. GPC trace of the polymer from table 2, entry 12.

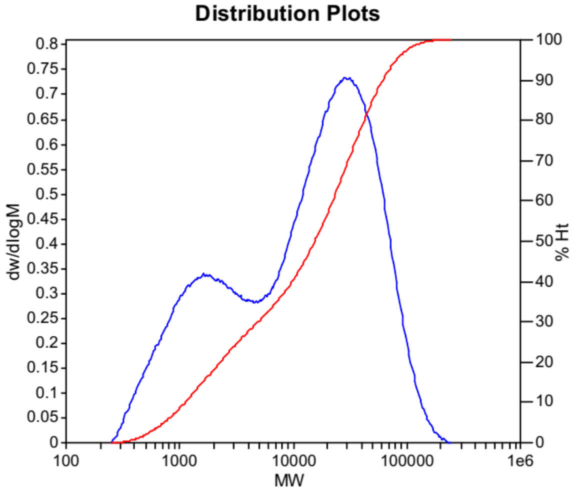


MW Averages

Mp: 25874 Mn: 3221 Mv: 18835 Mw: 22212

Mz: 50502 Mz+1: 74455 PD: 6.8960

Figure S121. GPC trace of the polymer from table 2, entry 13.

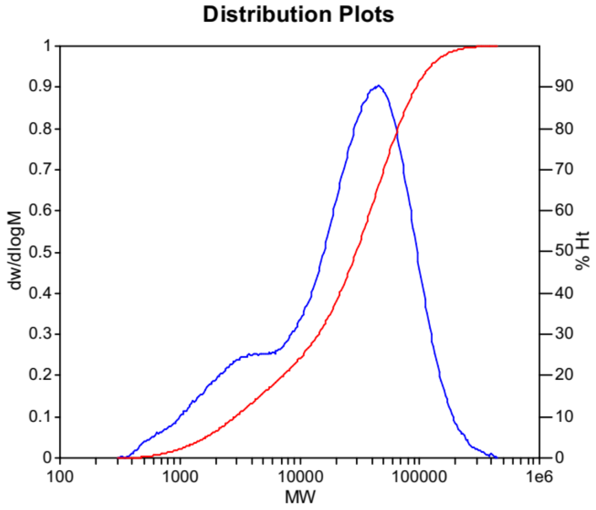


MW Averages

Mp: 31502 Mn: 3433 Mv: 20546 Mw: 24276

Mz: 55396 Mz+1: 81164 PD: 7.0714

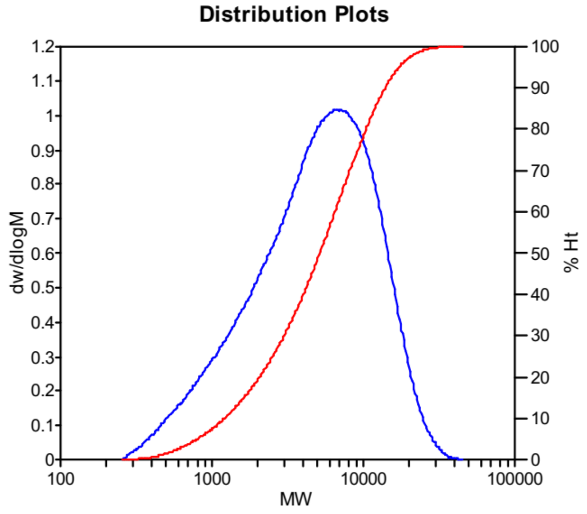
Figure S122. GPC trace of the polymer from table 2, entry 14.



MW Averages

Mp: 45562
Mn: 7756
Mv: 35781
Mw: 40871
Mz: 84982
Mz+1: 133938
PD: 5.2696

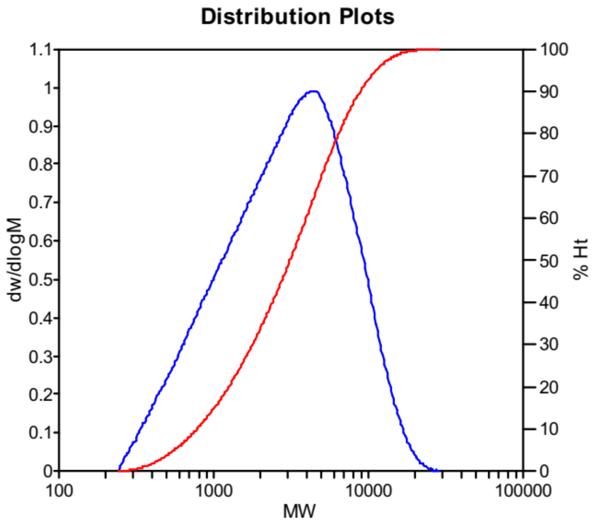
Figure S123. GPC trace of the polymer from table 2, entry 15.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6513	2820	6549	10913	14917	6002	2.32234

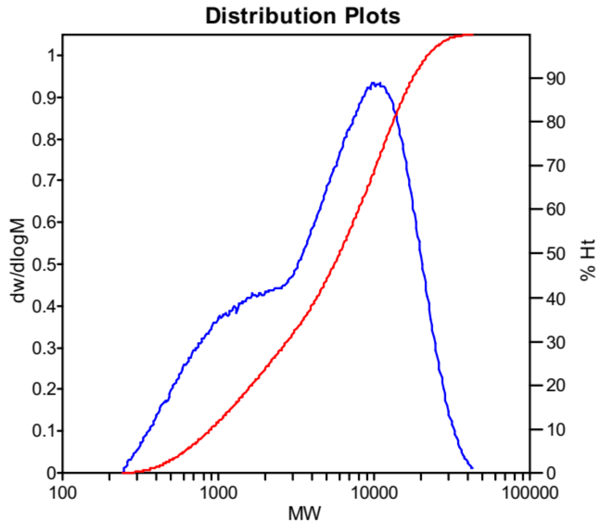
Figure S124. GPC trace of the polymer from table 2, entry 16.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4576	1843	4087	7027	9821	3732	2.21758

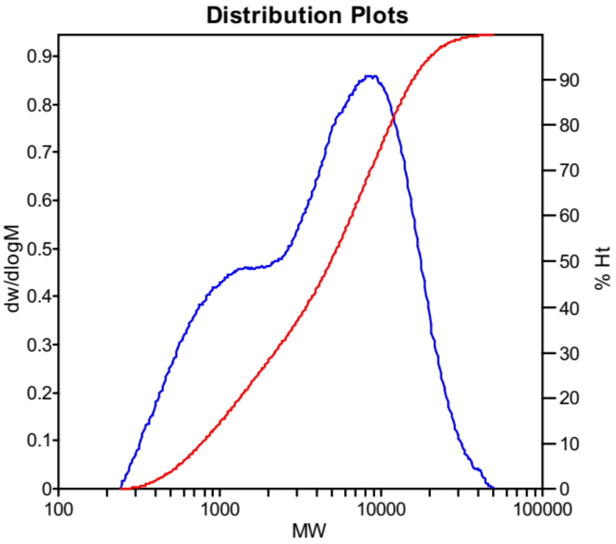
Figure S125. GPC trace of the polymer from table 2, entry 17.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9885	2456	7841	14049	18741	7023	3.19259

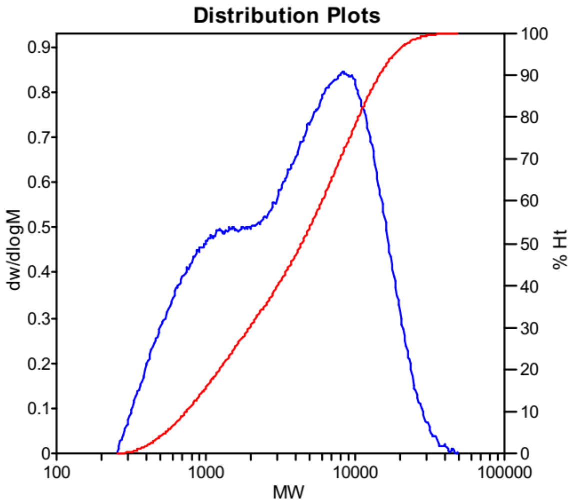
Figure S126. GPC trace of the polymer from table 2, entry 18.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8154	2109	6813	13234	18908	6035	3.23044

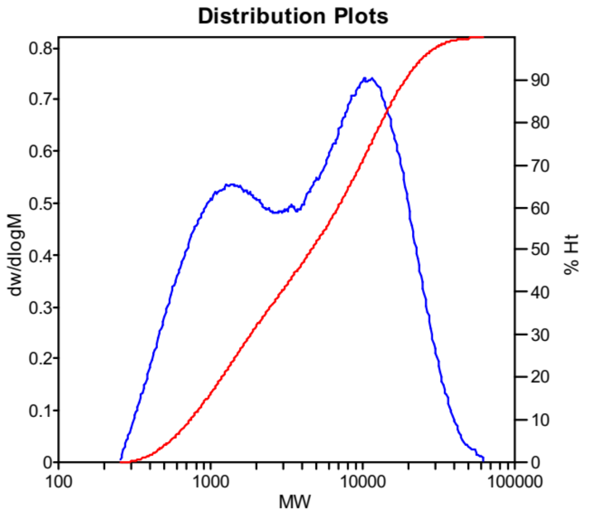
Figure S127. GPC trace of the polymer from table 2, entry 19.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8285	1998	6237	12032	16959	5528	3.12162

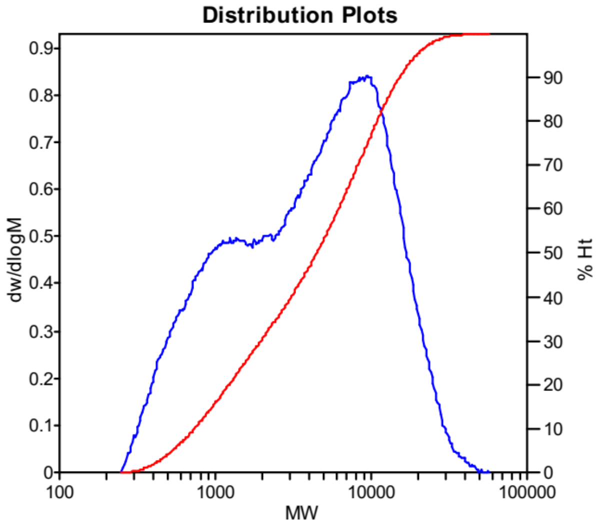
Figure S128. GPC trace of the polymer from table 2, entry 20.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	11605	2007	7664	16654	24147	6617	3.81863

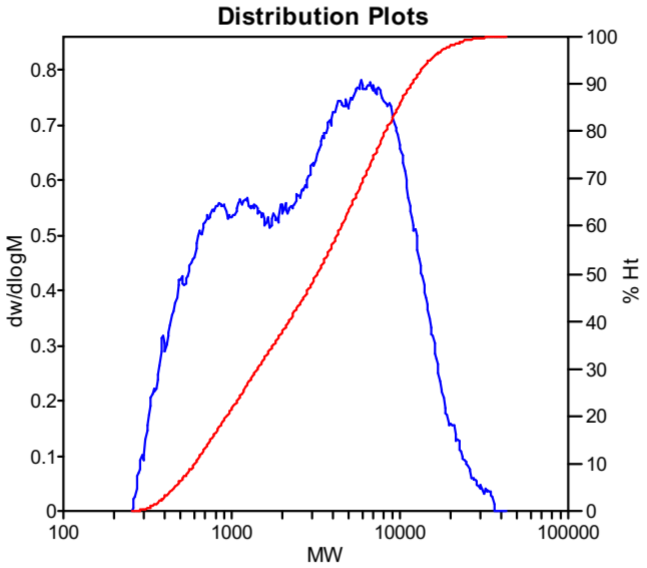
Figure S129. GPC trace of the polymer from table 2, entry 21.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9420	1997	6470	12803	18378	5710	3.23986

Figure S130. GPC trace of the polymer from table 2, entry 22.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	5915	1603	4927	10163	15003	4328	3.07361

Figure S131. GPC trace of the polymer from table 2, entry 23.

DSC of polymer and copolymer

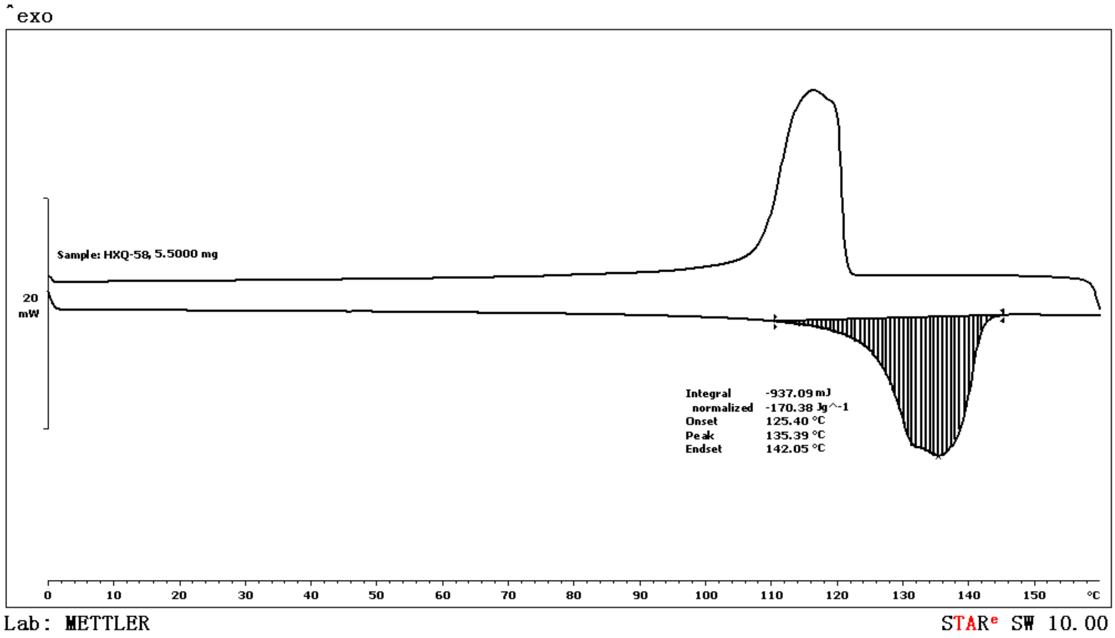


Figure S132. DSC data of the polymer from table 1, entry 1.

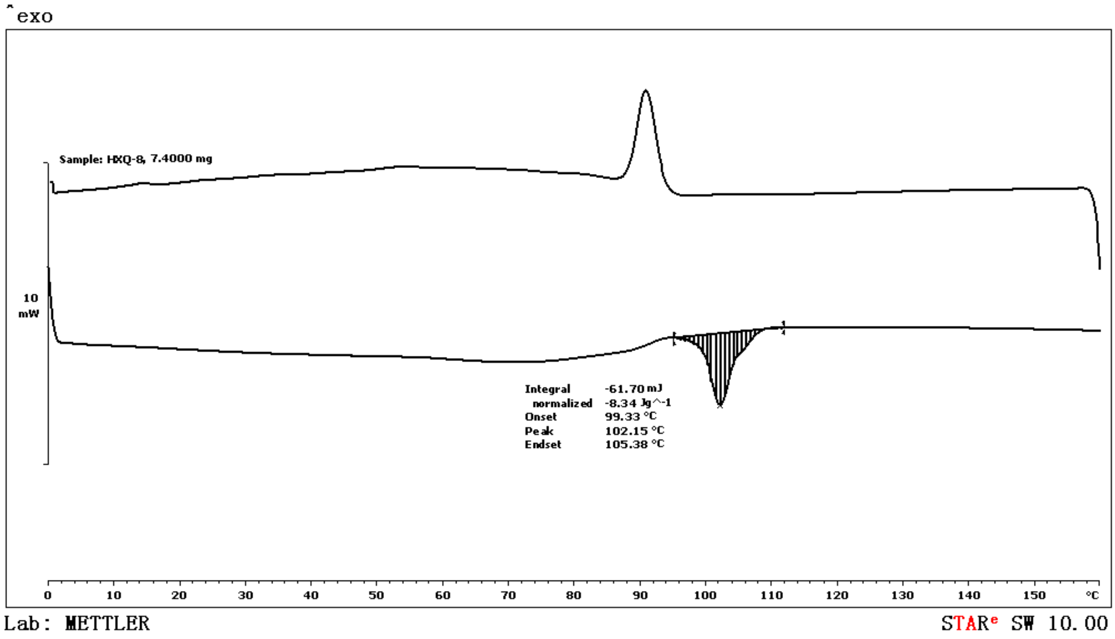


Figure S133. DSC data of the polymer from table 1, entry 2.

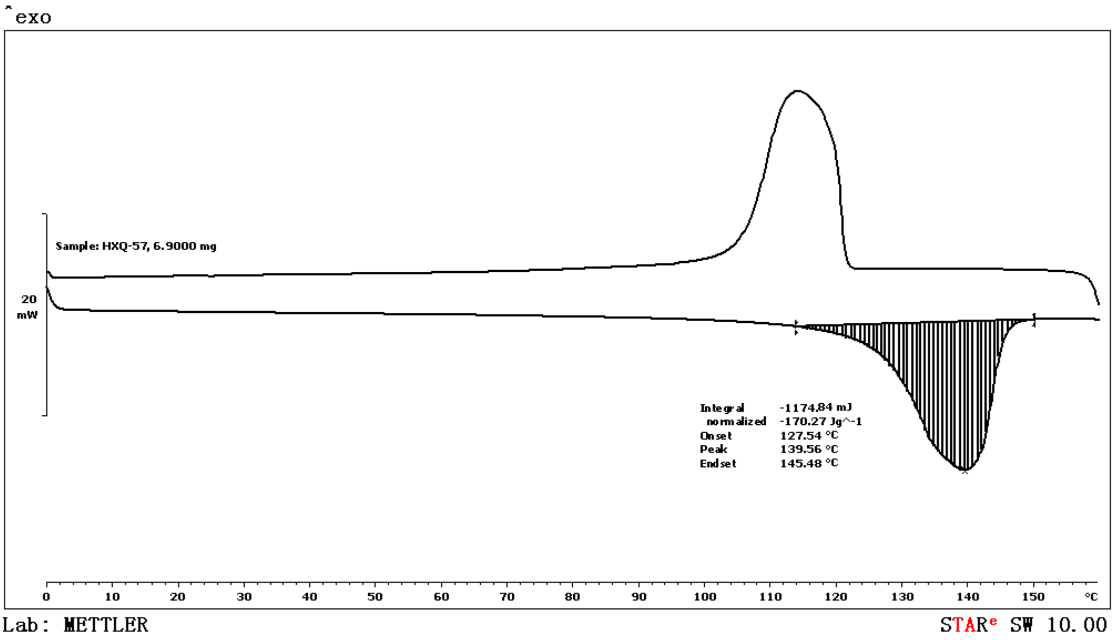


Figure S134. DSC data of the polymer from table 1, entry 5.

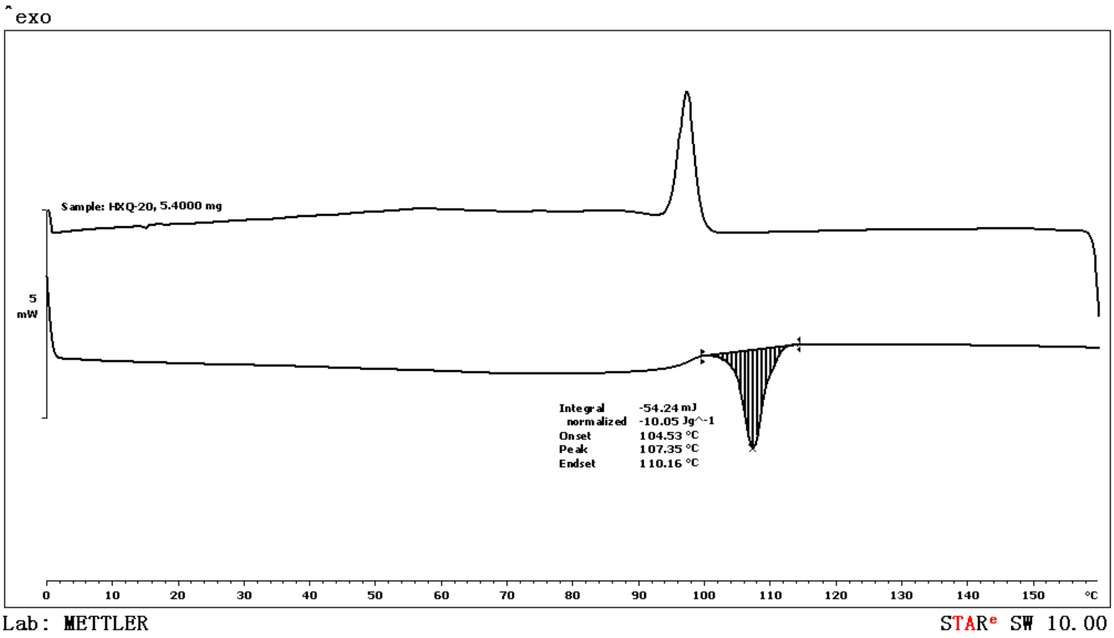


Figure S135. DSC data of the polymer from table 1, entry 6.

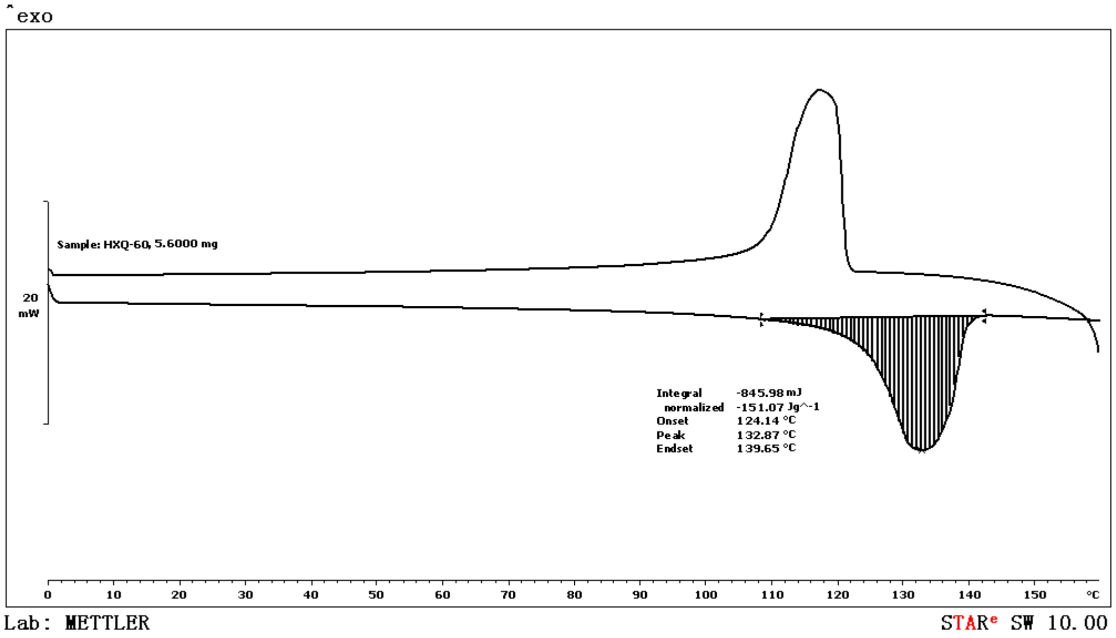


Figure S136. DSC data of the polymer from table 1, entry 9.

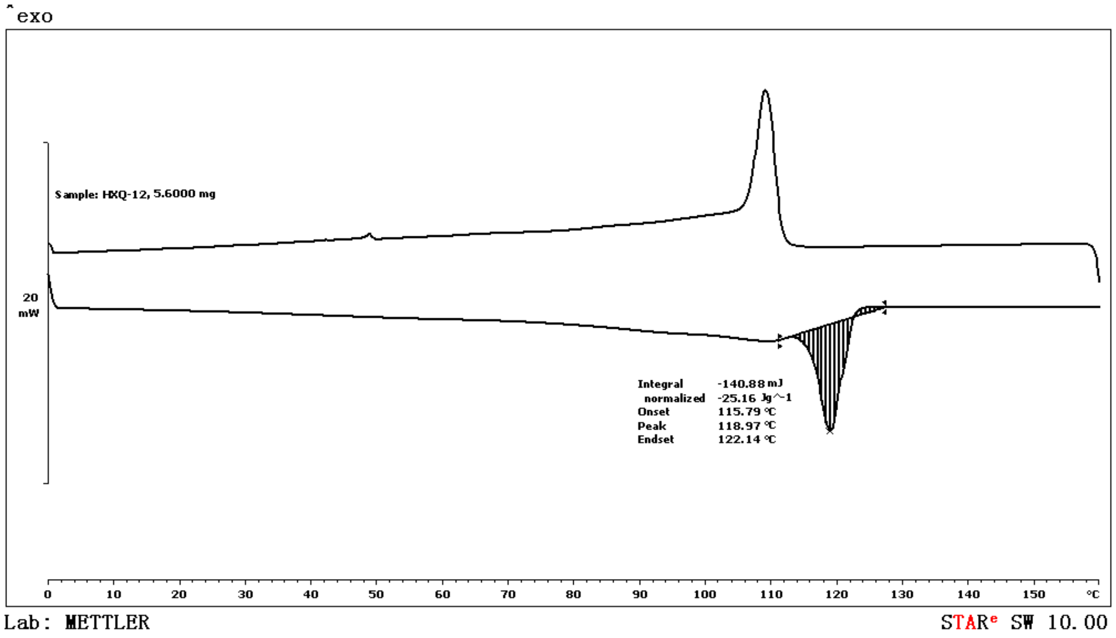


Figure S137. DSC data of the polymer from table 1, entry 10.

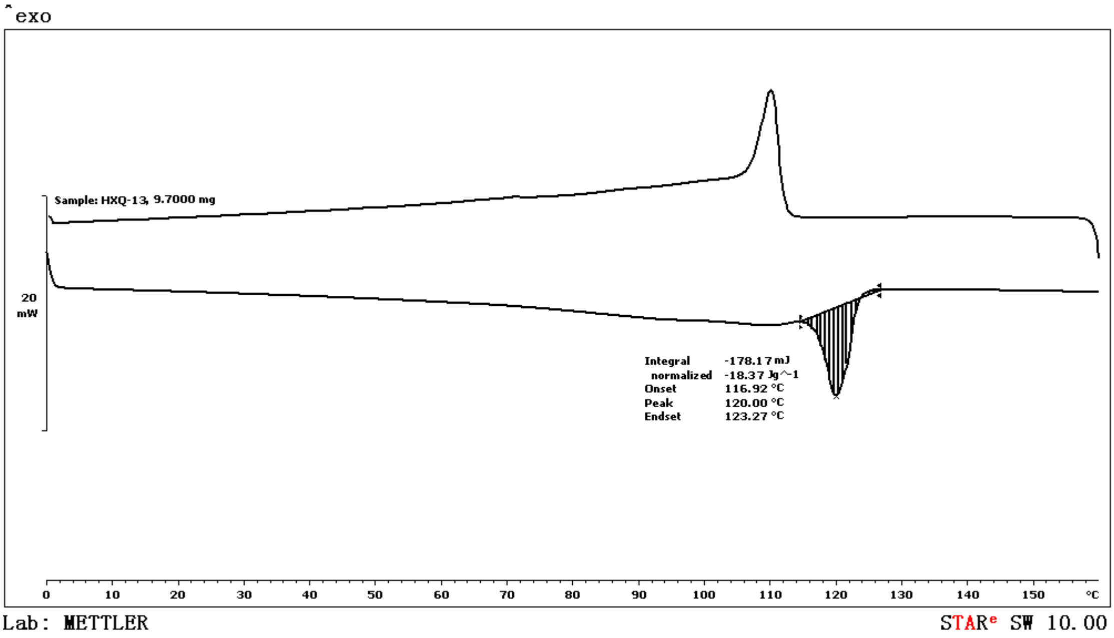


Figure S138. DSC data of the polymer from table 1, entry 11.

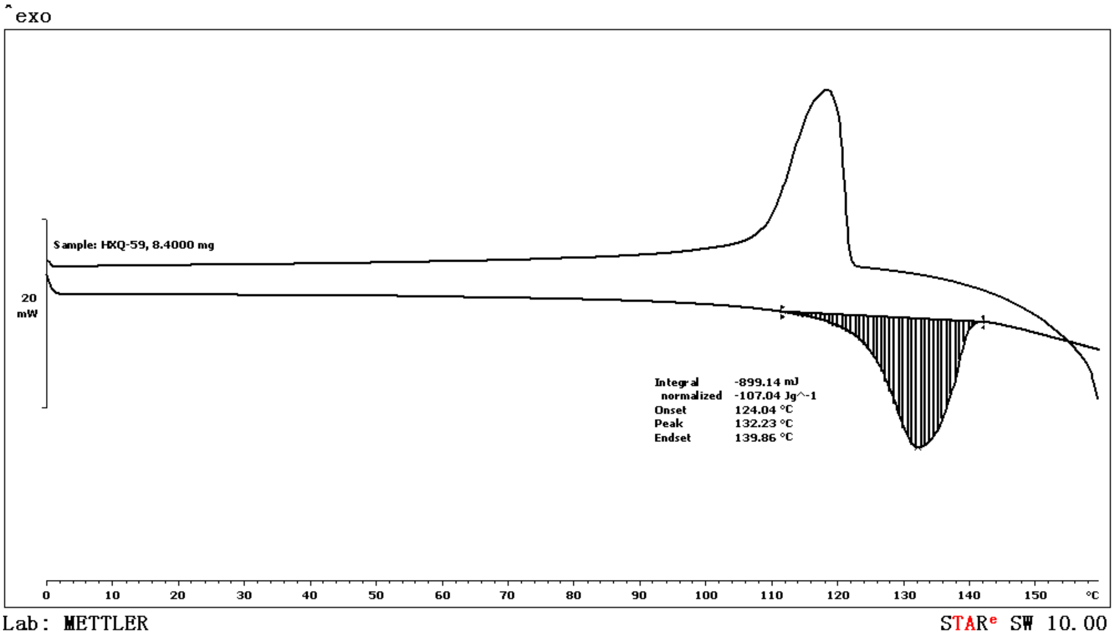


Figure S139. DSC data of the polymer from table 1, entry 13.

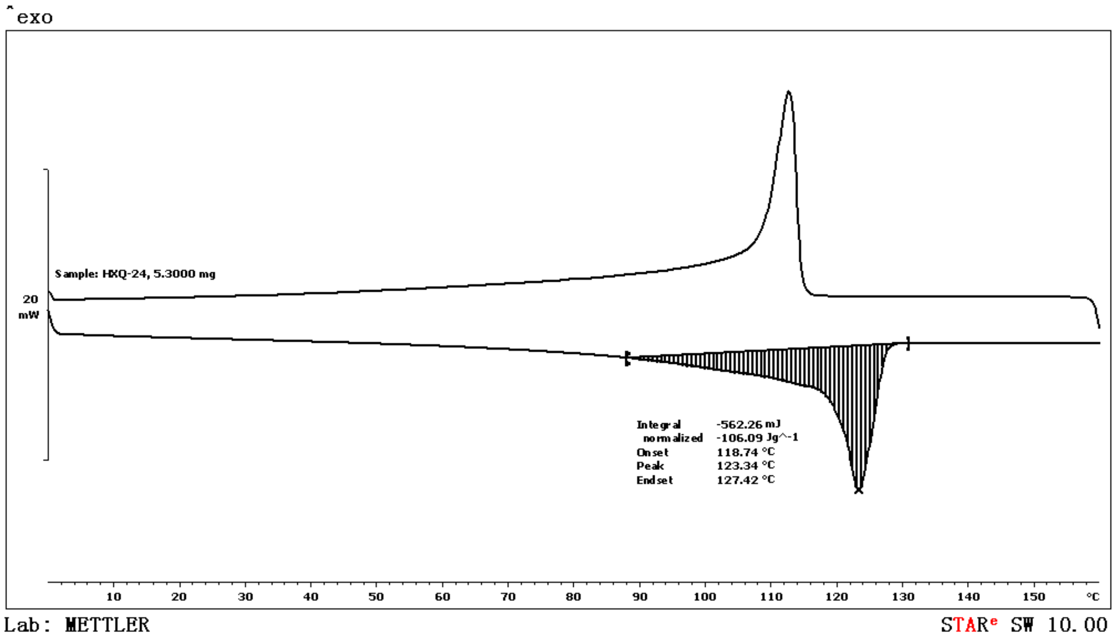


Figure S140. DSC data of the polymer from table 1, entry 14.

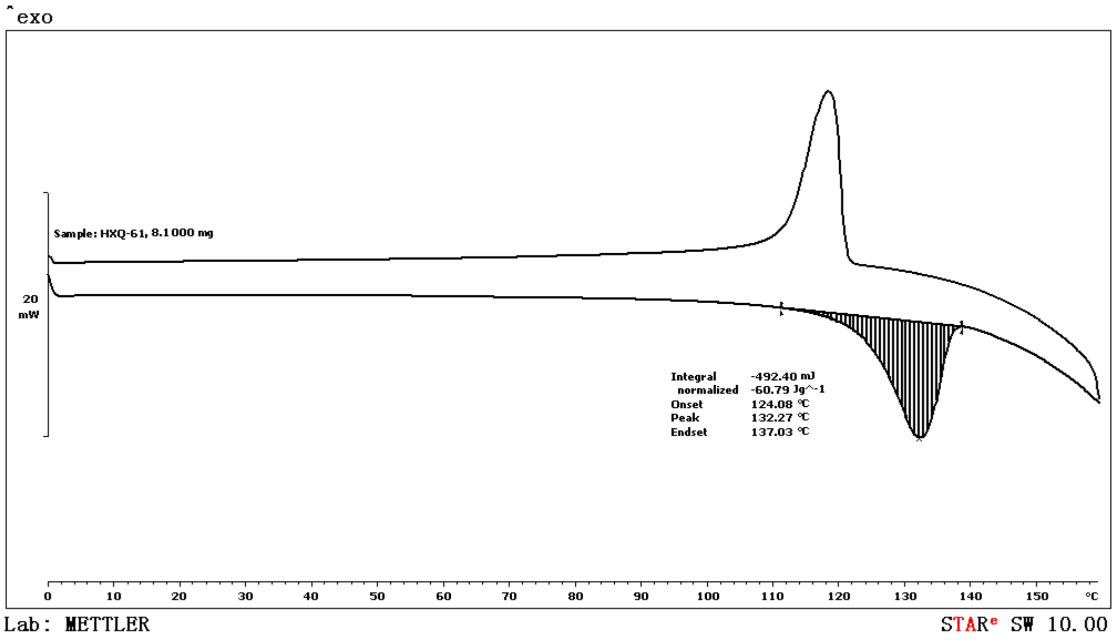


Figure S141. DSC data of the polymer from table 1, entry 17.

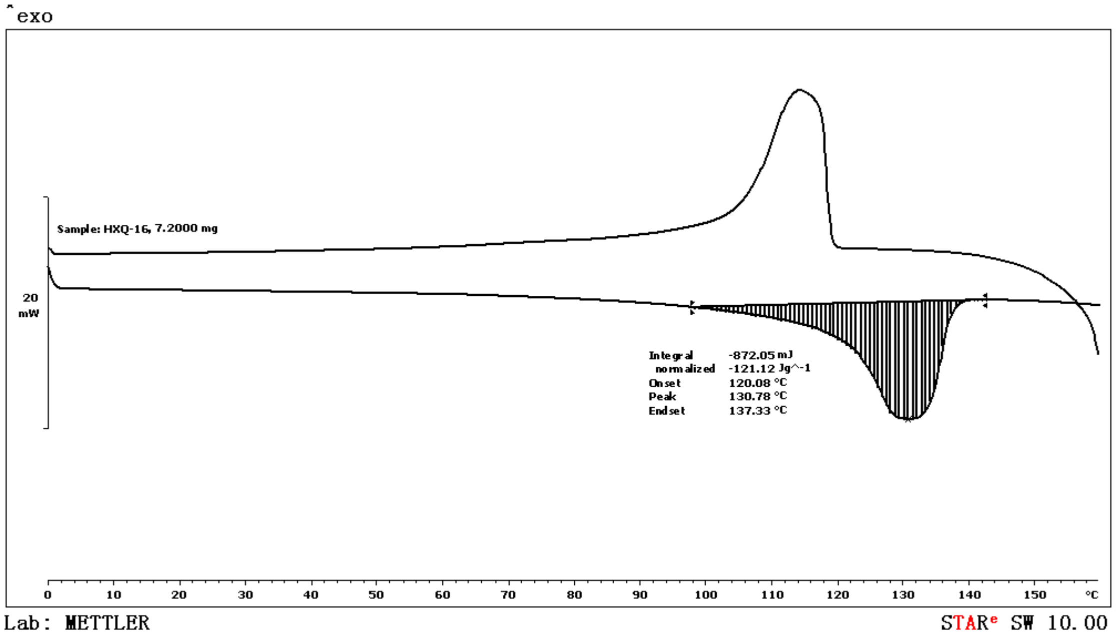


Figure S142. DSC data of the polymer from table 1, entry 18.

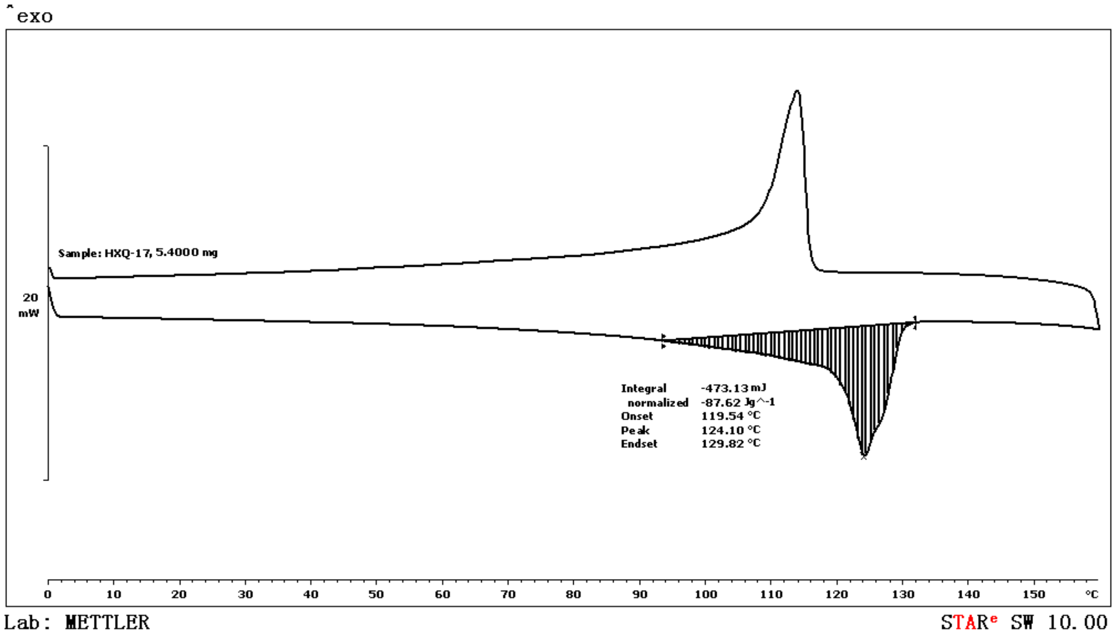


Figure S143. DSC data of the polymer from table 1, entry 19.

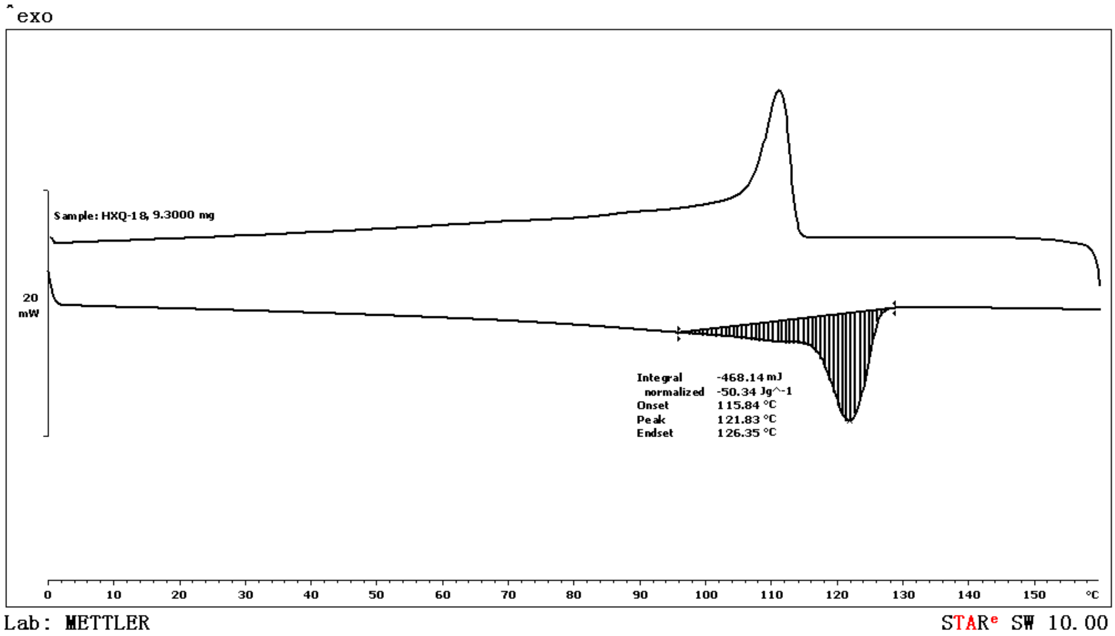


Figure S144. DSC data of the polymer from table 1, entry 20.

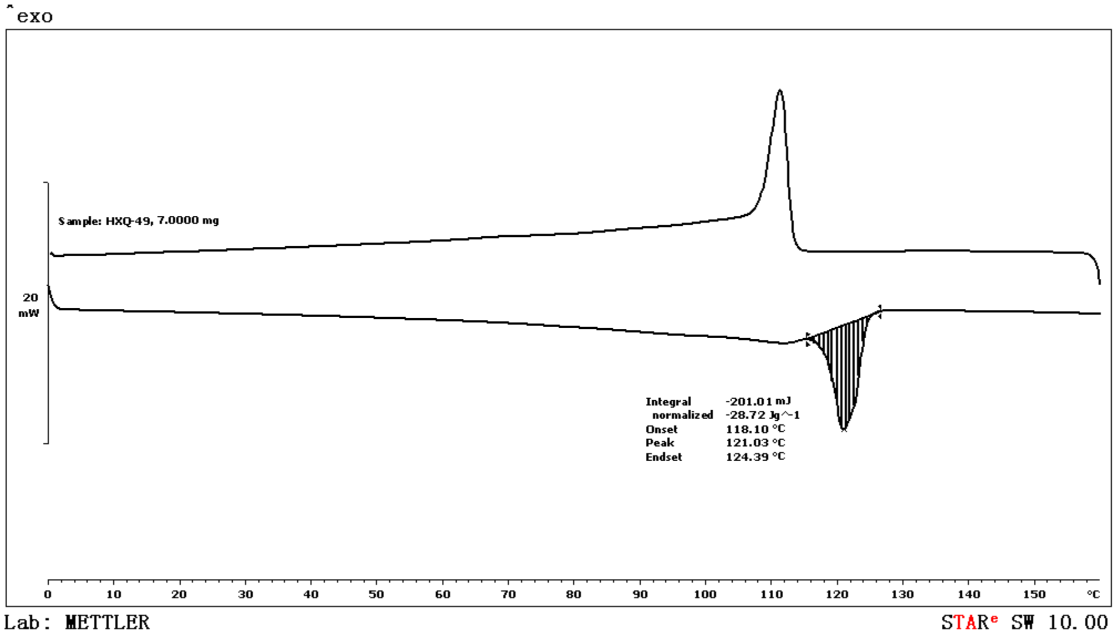


Figure S145. DSC data of the polymer from table 2, entry 3.

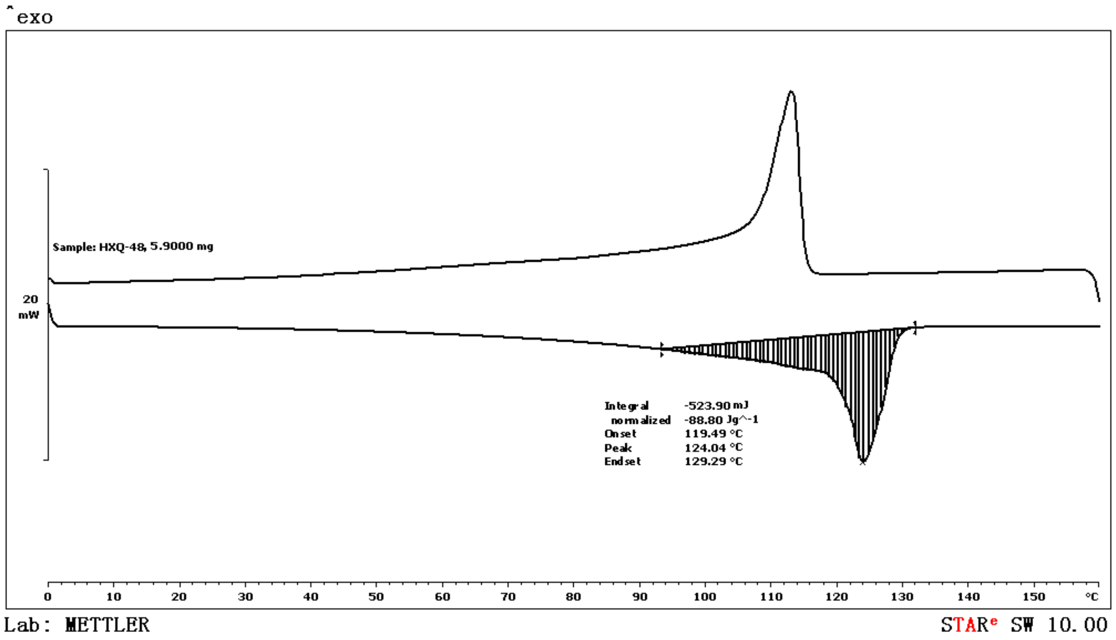


Figure S146. DSC data of the polymer from table 2, entry 4.

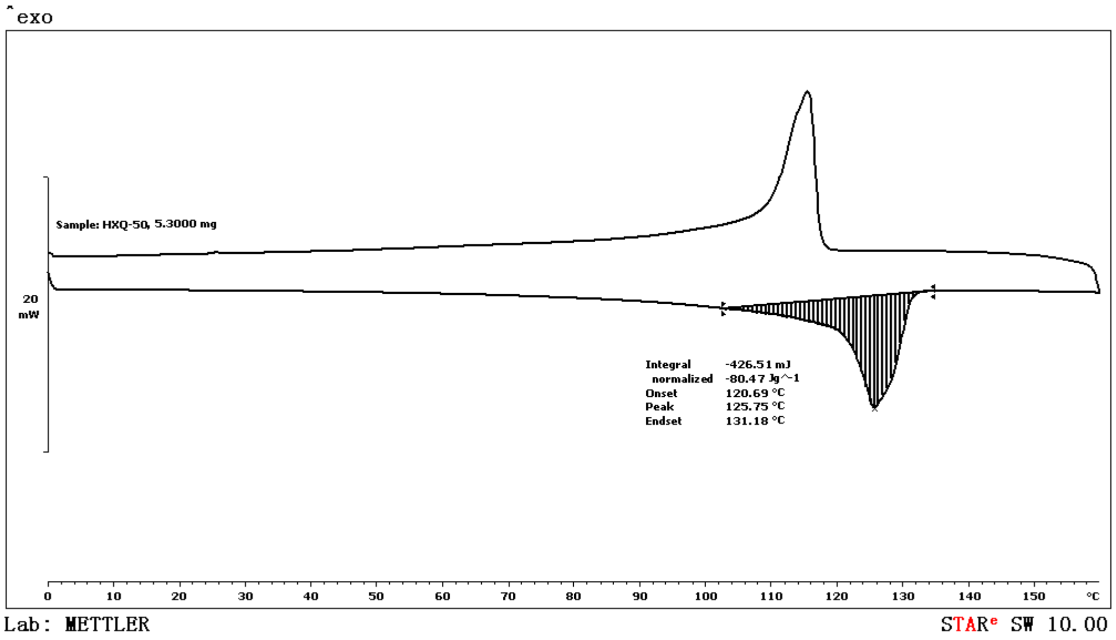


Figure S147. DSC data of the polymer from table 2, entry 5.

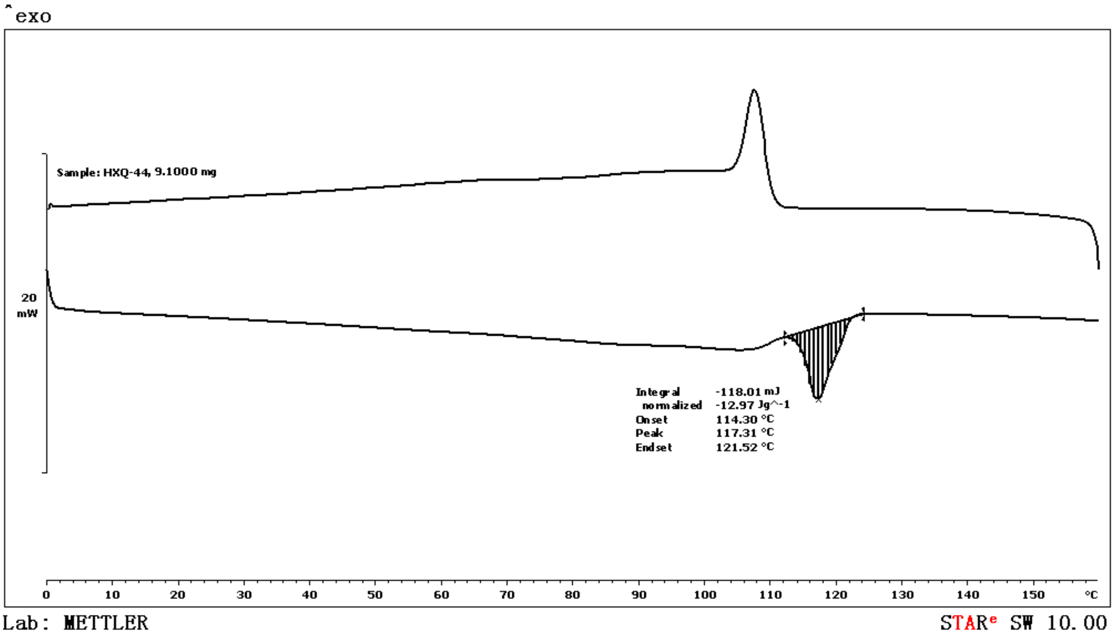


Figure S148. DSC data of the polymer from table 2, entry 8.

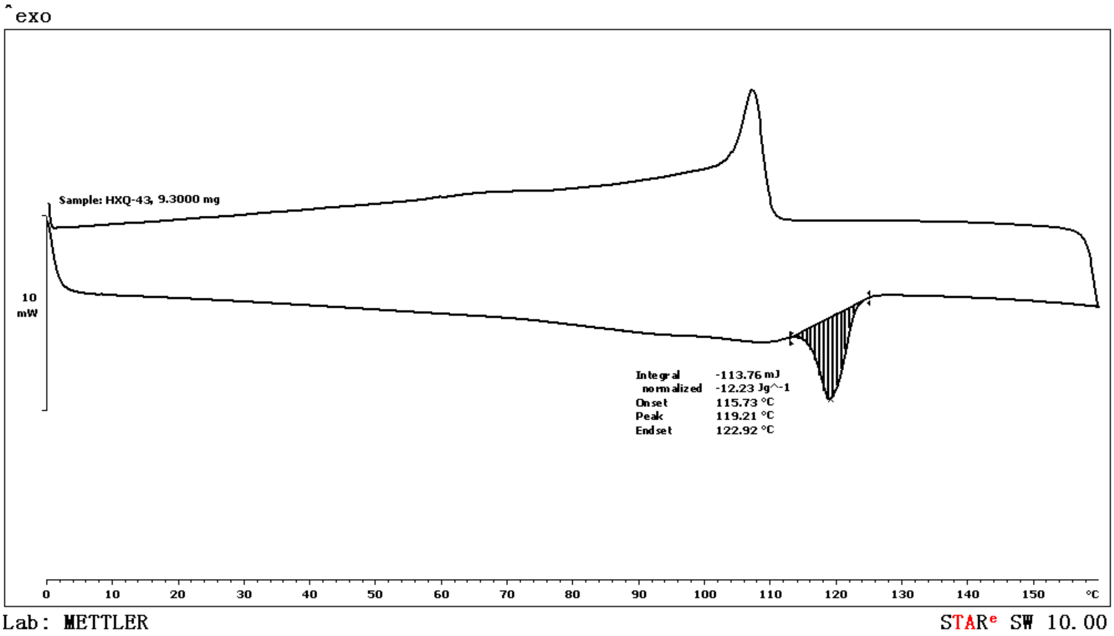


Figure S149. DSC data of the polymer from table 2, entry 9.

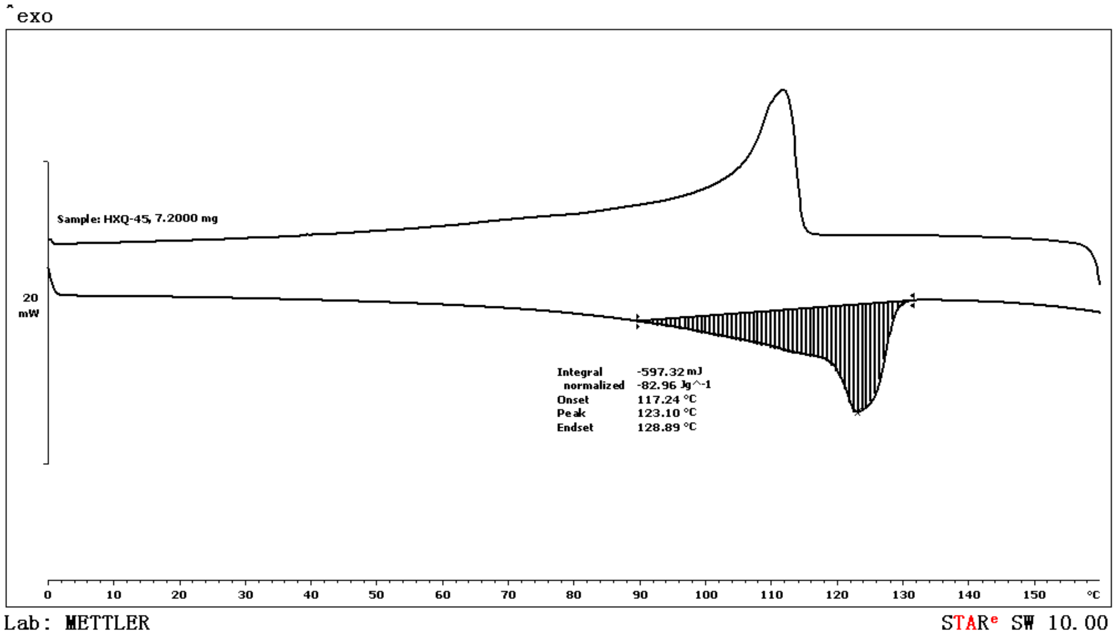


Figure S150. DSC data of the polymer from table 2, entry 10.

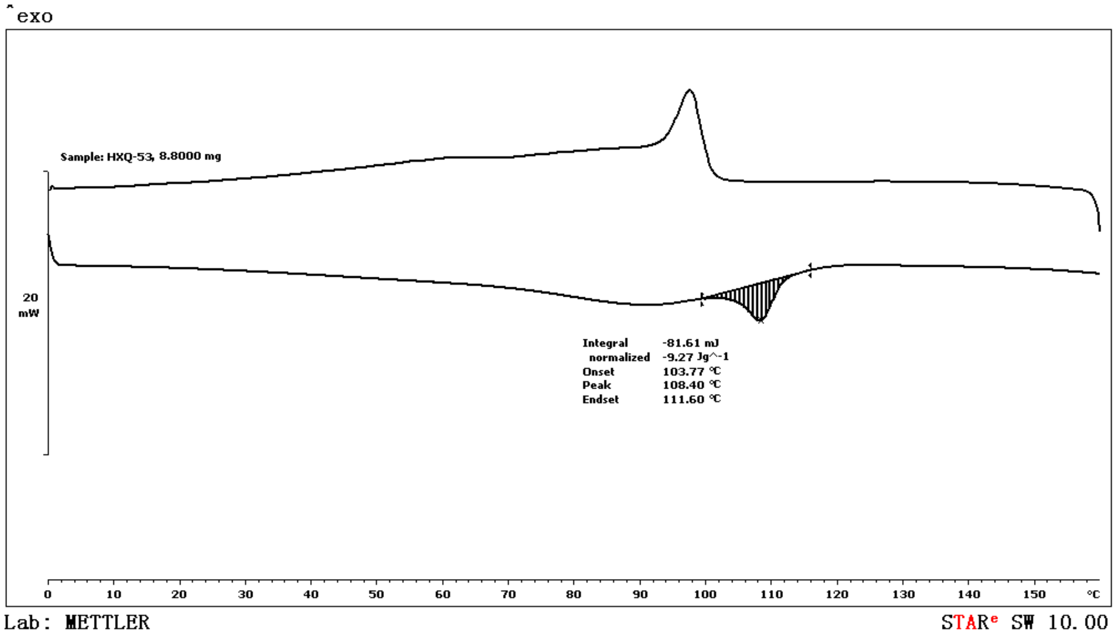


Figure S151. DSC data of the polymer from table 2, entry 11.

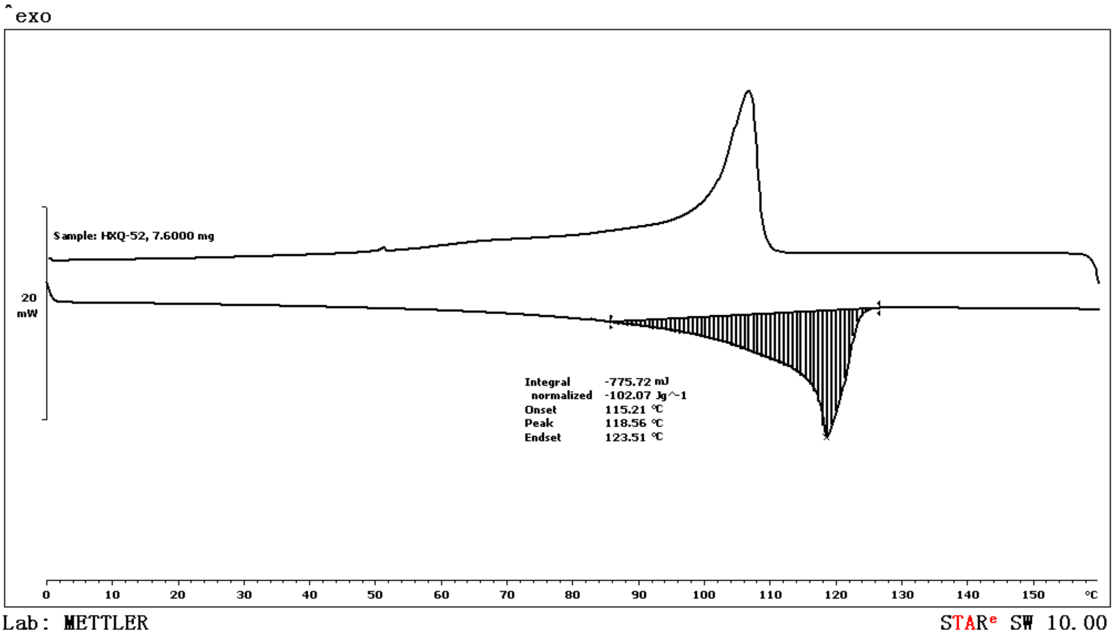


Figure S152. DSC data of the polymer from table 2, entry 12.

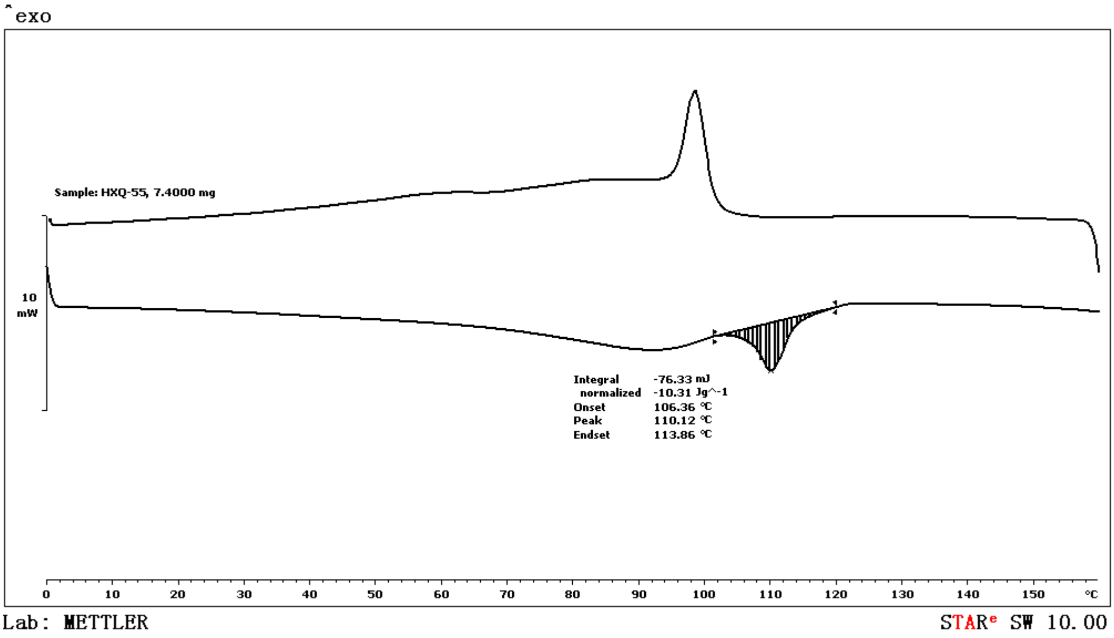


Figure S153. DSC data of the polymer from table 2, entry 13.

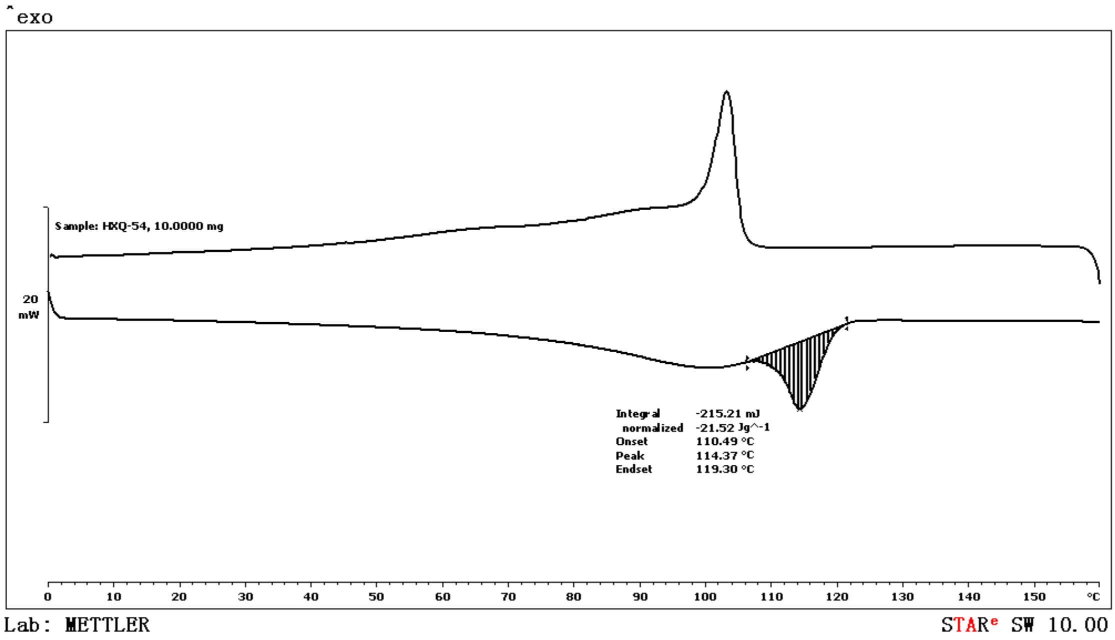


Figure S154. DSC data of the polymer from table 2, entry 14.

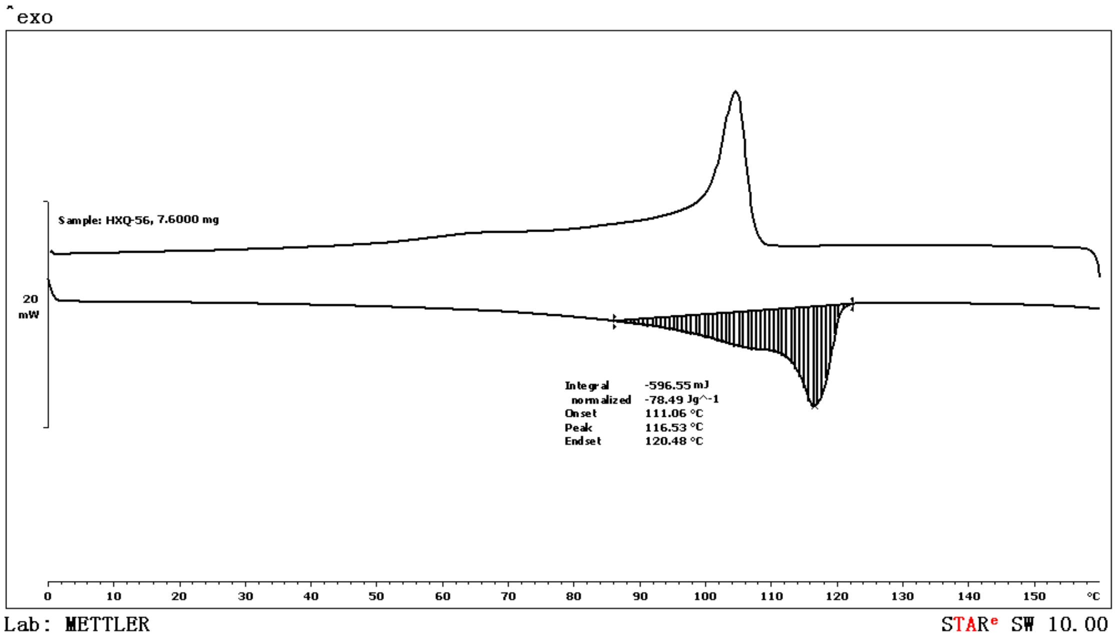


Figure S155. DSC data of the polymer from table 2, entry 15.

8 MALDI-TOF-MS of Ni complexes

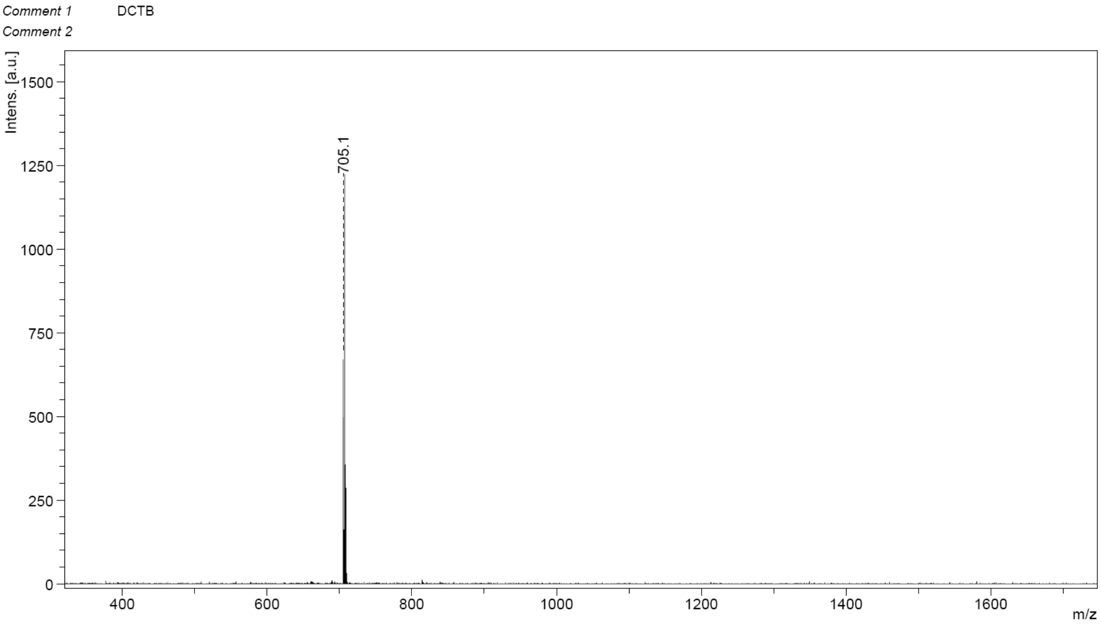


Figure S156. MALDI-TOF-MS of complex **Ni-1**

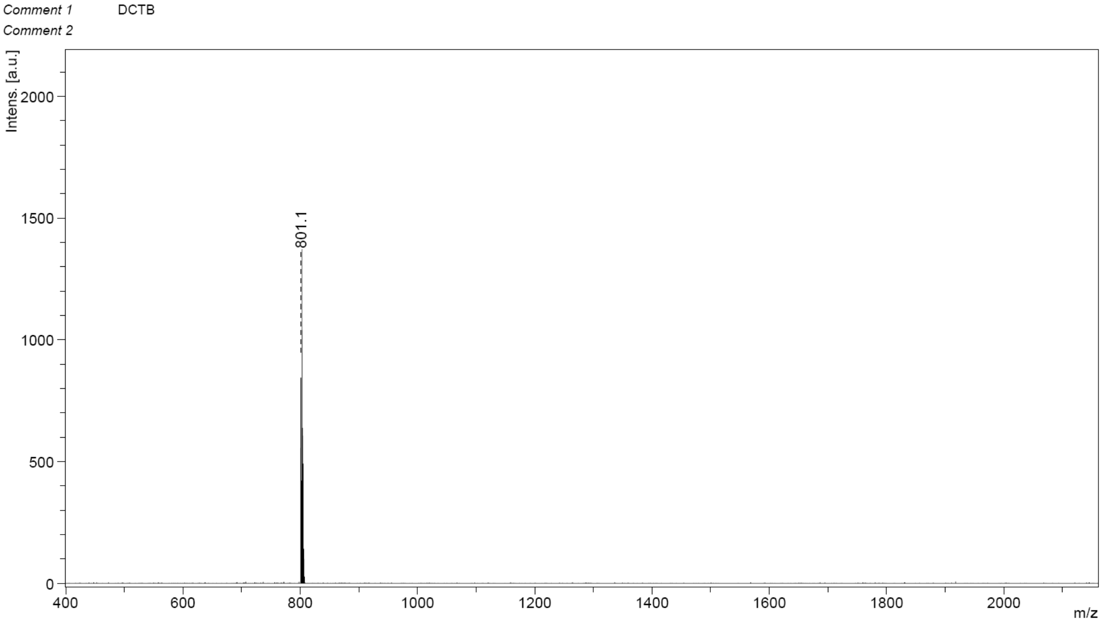


Figure S157. MALDI-TOF-MS of complex **Ni-2**

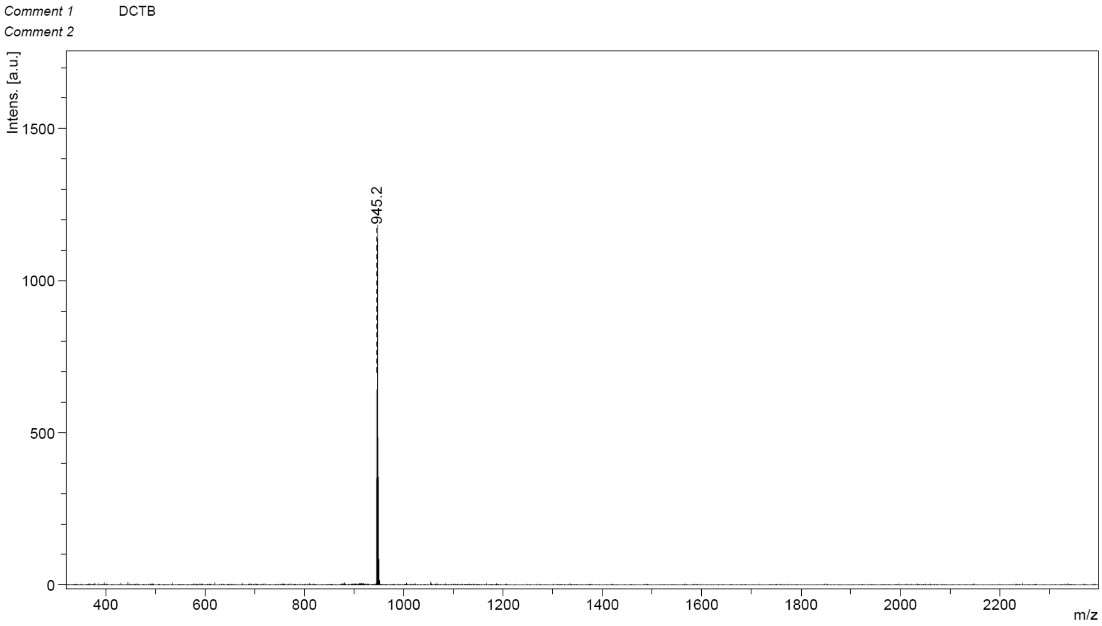


Figure S158. MALDI-TOF-MS of complex **Ni-3**

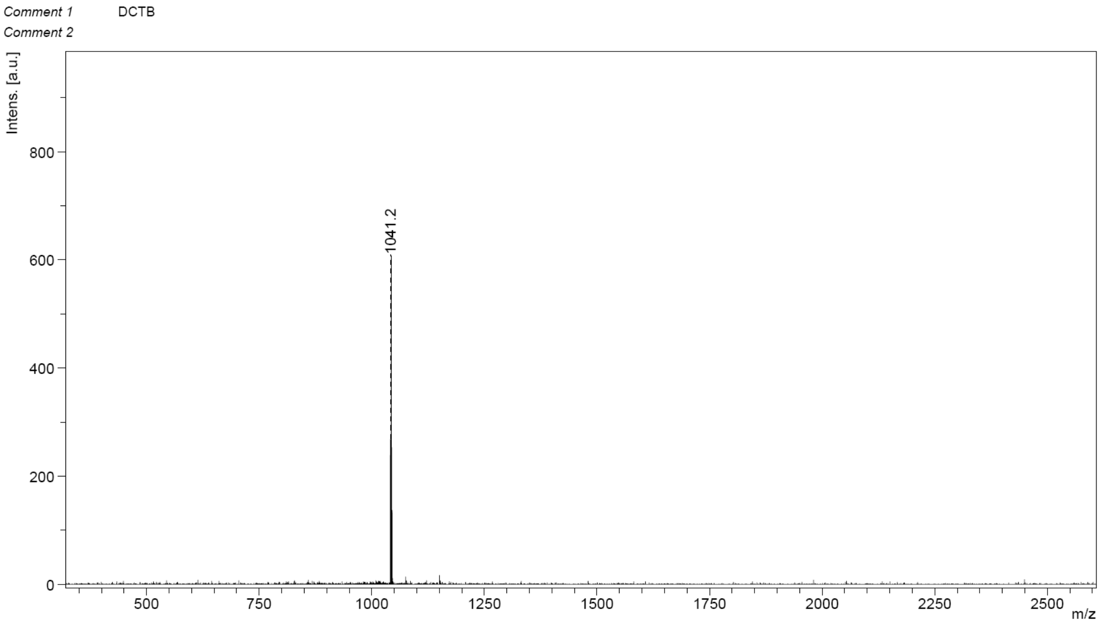


Figure S159. MALDI-TOF-MS of complex **Ni-4**

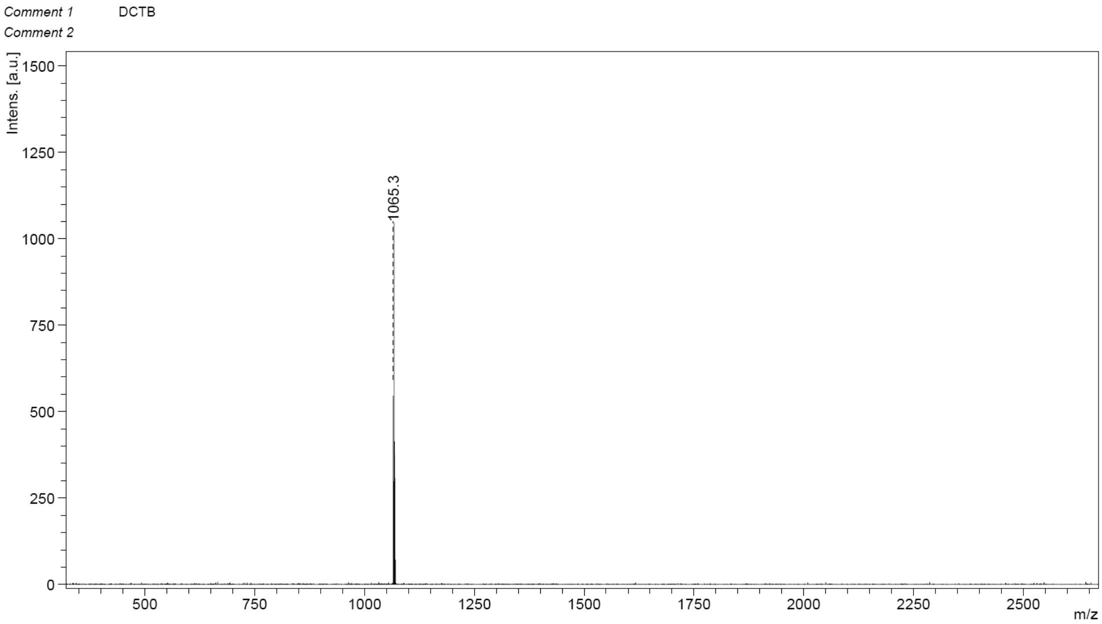
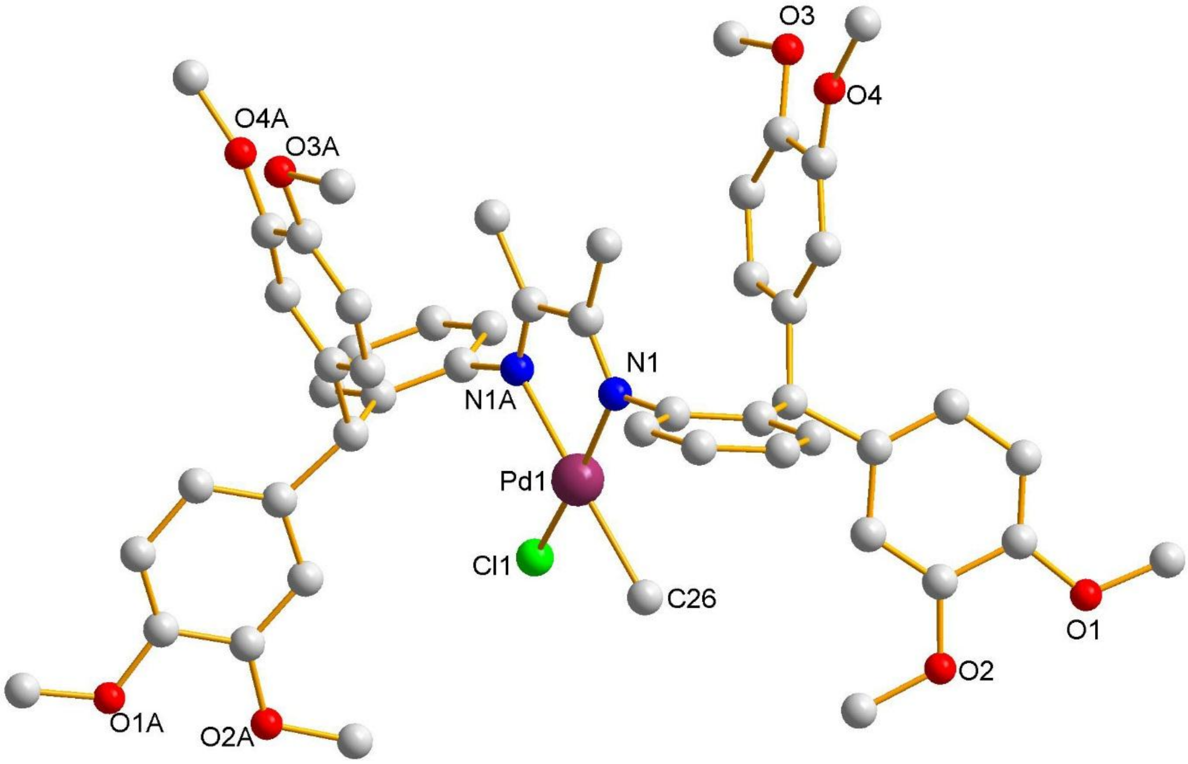


Figure S160. MALDI-TOF-MS of complex **Ni-5**

9 Figure of crystal structure of Pd-3



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