Supplementary Information

Comprehensive Studies of Ligand Electronic Effect on Unsymmetrical α-Diimine Nickel(II) Promoted Ethylene (Co)Polymerizations

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Contents

1 General information

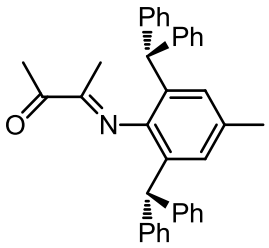
General Procedures: All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of nitrogen. All solvents were purified from the MBraun SPS system. NMR spectra for the ligands, complexes, and polymers were 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 ℃. 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. Stress/strain experiments were performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature. Polymers were melt-pressed at 150 ℃ to obtain the test specimens, which have 12-mm gauge length, 2-mm width, and thickness of 0.5 mm. At least three specimens of each polymer were tested.

X-Ray diffraction: Data collections were performed at −88.5 ℃ or −100 ℃ on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Cu Kα radiation (λ = 1.54178 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 Olex2.[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 complex **Cat1** and **Cat4**, 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.

Materials: 2,6-Bis(diphenylmethyl)-4-methoxyaniline[5], 2,6-bis(diphenylmethyl)-4-chloroaniline[5], 2,6-diphenylmethyl-4-methylaniline[5], 2,6-bis(bis(4-methylphenyl)methyl)-4-methylaniline[6], 2,6-bis(bis(4-fluorophenyl)methyl)-4-methylbenzenamine[6] and pentiptycene aminophenol[7] were prepared using literature procedure.

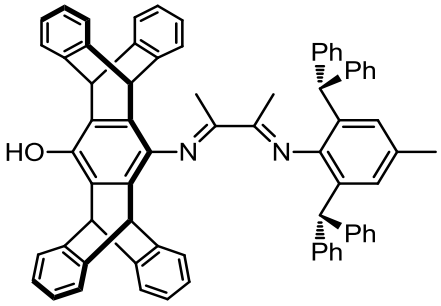
2 Preparation of Ligands and Catalysts



A solution of 2,6-diphenylmethyl-4-methylaniline (8.79 g, 20 mmol), 2,3-butadione (8.61 g, 100 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (200 mL) was stirred at 80 ℃ for 24 h, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration, washed three times by 20 mL methanol and dried under high vacuum. (8.14 g, 80.2% yield)

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 7.27-7.14(m, 12H, aryl-*H*), 7.03-7.00(m, 8H, aryl-*H*), 6.64 (s, 2H, aryl-*H*), 5.09 (s, 2H, C*H*Ph_2), 2.32 (s, 3H, O=C-*Me*), 2.15 (s, 3H, aryl- *Me*), 0.67 (s, 3H, N=C-*Me*)ppm.

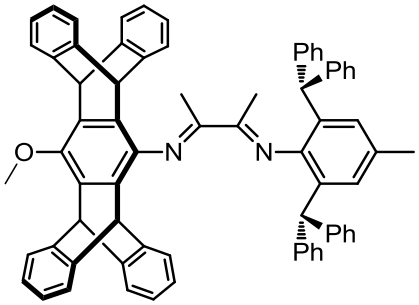
Elemental analysis: Anal. Calcd for $C_{37}H_{33}NO$: C, 87.54; H, 6.55; N, 2.76. Found: C, 87.61; H, 6.52; N, 2.74.



A solution of (2,6-dibenzhydryl -4-methylphenylimino) butanone (2.00 g, 3.94 mmol), pentiptycene aminophenol (2.18 g, 4.73 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (250 mL) was refluxed with Dean-stark trap for 3 days, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration and recrystallized from hot methanol, washed three times by 20 mL hot methanol and dried under high vacuum. (2.64 g, 70.5% yield)

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.47-7.43(m, 4H, aryl-*H*), 7.36-7.28(m, 14H, aryl-*H*), 7.25-7.22(m, 4H, aryl-*H*), 7.19-7.16(m, 6H, aryl-*H*), 6.95-6.90(m, 8H, aryl-*H*), 6.73(s, 2H, aryl-*H*), 5.65(s, 2H, C*H*Ar_3), 5.48(s, 2H, C*H*Ph_2), 4.97(s, 2H, C*H*Ar_3), 4.63(s, 1H, O*H*), 2.23(s, 3H, aryl-*Me*), 1.73 (s, 3H, N=C-*Me*), 1.19 (s, 3H, N=C-*Me*)ppm.

Elemental analysis: Anal. Calcd for $C_{71}H_{54}N_2O$: C, 89.65; H, 5.72; N, 2.95. Found: C, 89.61; H, 5.68; N, 2.91.

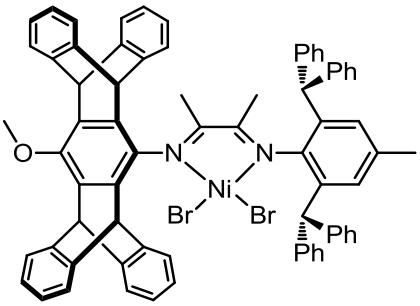


Preparation of Ligand L1: To the solution of 2-(2,6-dibenzhydryl-4-methylphenylimino)-3-pentiptycene aminophenol butane (2.64 g, 2.78 mmol) in DMF (200 mL) at 50 ℃ was added K_2CO_3 (4.61 g, 33.36 mmol). The mixture was stirred for 1 min and MeI (1.64 g, 11.12 mmol) was added. The reaction mixture was stirred overnight at 50 ℃. The yellow suspension was cooled to room temperature and poured into 300 mL of water. The yellow precipitate was collected by filtration, washed with water, methanol and diethyl ether. After drying in vacuo at 70 ℃, the product was obtained as a yellow powder (2.02 g, 75.4% yield).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.46-7.43(m, 4H, aryl-*H*), 7.35-7.28(m, 14H, aryl-*H*), 7.25-7.22(m, 4H, aryl-*H*), 7.19-7.15(m, 6H, aryl-*H*), 6.96-6.90(m, 8H, aryl-*H*), 6.73(s, 2H, aryl-*H*), 5.70(s, 2H, C*H*Ar_3), 5.48(s, 2H, C*H*Ph_2), 4.97(s, 2H, C*H*Ar_3), 3.90(s, 3H, OC*H*$_3$), 2.22(s, 3H, aryl-*Me*), 1.75 (s, 3H, N=C-*Me*), 1.16 (s, 3H, N=C-*Me*)ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): *δ* =170.43 (N=*C*-Me), 170.39 (N=*C*-Me), 146.90, 145.83, 145.74, 145.43, 145.33, 145.23, 143.96, 142.99, 138.16, 135.61, 132.22, 131.59, 131.55, 130.03, 129.70, 129.21, 128.87, 128.44, 126.73, 126.45, 125.36, 125.33, 125.25, 125.19, 123.76, 123.74, 123.65, 123.45, , 63.23(O*C*H_3), 52.52, 49.24, 48.33, 21.52(aryl-*Me*), 17.33(N=C-*Me*), 16.65(N=C-*Me*)ppm.

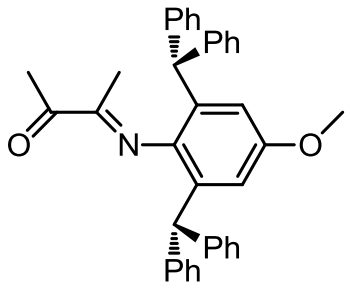
Elemental analysis: Anal. Calcd for $C_{72}H_{56}N_2O$: C, 89.59; H, 5.85; N, 2.90. Found: C, 89.82; H, 5.81; N, 2.98.



Preparation of Cat1: A mixture of **L1** (220 mg, 0.228 mmol) and (DME)$NiBr_2$ (70.3 mg, 0.228 mmol) (DME = 1,2-dimethoxyethane) were stirred in 25 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 an orange solid. (218 mg, 80.7% yield).

MALDI-TOF-MS (m/z): 1022.4 $[M-2Br]^+$, 1057.3 $[M-2Br+Cl]^+$, 1101.3 $[M-Br]^+$.

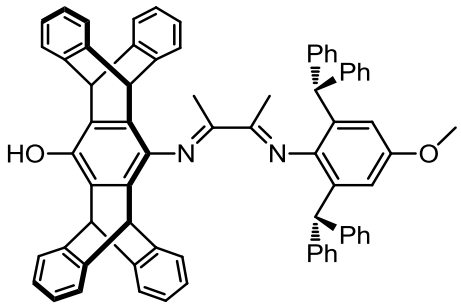
Elemental analysis: Anal. Calcd for $C_{72}H_{56}Br_2N_2NiO$: C, 73.05; H, 4.77; N, 2.37. Found: C, 73.23; H, 4.89; N, 2.45.



A solution of 2,6-bis(diphenylmethyl)-4-methoxyaniline (9.11 g, 20 mmol), 2,3-butadione (8.61 g, 100 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (200 mL) was stirred at 80 ℃ for 24 h, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration, washed three times by 20 mL methanol and dried under high vacuum. (7.40 g, 70.7% yield)

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.27-7.15(m, 12H, aryl-*H*), 7.03-7.02(m, 8H, aryl-*H*), 6.42 (s, 2H, aryl-*H*), 5.11 (s, 2H, C*H*Ph_2), 3.54 (s, 3H, OC*H*$_3$), 2.30 (s, 3H, O=C-*Me*), 0.71 (s, 3H, N=C-*Me*)ppm

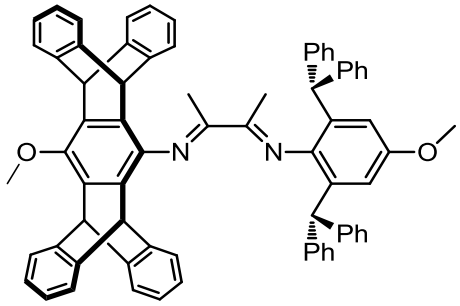
Elemental analysis: Anal. Calcd for $C_{37}H_{33}NO_2$: C, 84.86; H, 6.35; N, 2.67. Found: C, 84.73; H, 6.31; N, 2.63.



A solution of (2,6-dibenzhydryl -4-methoxyphenylimino) butanone (2.00 g, 3.82 mmol), pentiptycene aminophenol (2.12 g, 4.58 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (250 mL) was refluxed with Dean-stark trap for 3 days, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration and recrystallized from hot methanol, washed three times by 20 mL hot methanol and dried under high vacuum. (2.80g, 75.7% yield)

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.47-7.44(m, 4H, aryl-*H*), 7.36-7.29(m, 14H, aryl-*H*), 7.25-7.22(m, 4H, aryl-*H*), 7.18-7.17(m, 6H, aryl-*H*), 6.96-6.90(m, 8H, aryl-*H*), 6.51(s, 2H, aryl-*H*), 5.65(s, 2H, C*H*Ar_3), 5.50(s, 2H, C*H*Ph_2), 4.96(s, 2H, C*H*Ar_3), 4.63(s, 1H, O*H*), 3.60(s, 3H, OC*H*$_3$), 1.72 (s, 3H, N=C-*Me*), 1.23 (s, 3H, N=C-*Me*)ppm

Elemental analysis: Anal. Calcd for $C_{71}H_{54}N_2O_2$: C, 88.17; H, 5.63; N, 2.90. Found: C, 87.98; H, 5.55; N, 2.81.

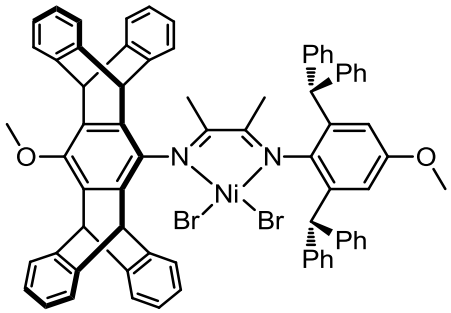


Preparation of Ligand L2: To the solution of 2-(2,6-dibenzhydryl-4-methoxyphenylimino)-3-pentiptycene aminophenol butane (2.80 g, 2.89 mmol) in DMF (200 mL) at 50 ℃ was added K_2CO_3 (4.80 g, 34.68 mmol). The mixture was stirred for 1 min and MeI (1.64 g, 11.56 mmol) was added. The reaction mixture was stirred overnight at 50 ℃. The yellow suspension was cooled to room temperature and poured into 300 mL of water. The yellow precipitate was collected by filtration, washed with water, methanol and diethyl ether. After drying in vacuo at 70 ℃, the product was obtained as a yellow powder (2.24 g, 78.9% yield).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.39-7.36(m, 4H, aryl-*H*), 7.28-7.22(m, 14H, aryl-*H*), 7.17-7.14(m, 4H, aryl-*H*), 7.11-7.09(m, 6H, aryl-*H*), 6.88-6.83(m, 8H, aryl-*H*), 6.44(s, 2H, aryl-*H*), 5.63(s, 2H, C*H*Ar_3), 5.42(s, 2H, C*H*Ph_2), 4.89(s, 2H, C*H*Ar_3), 3.83(s, 3H, OC*H*$_3$), 3.52(s, 3H, OC*H*$_3$), 1.67 (s, 3H, N=C-*Me*), 1.13 (s, 3H, N=C-*Me*)ppm

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): *δ* =171.00 (N=*C*-Me), 170.49 (N=*C*-Me), 155.53, 146.91, 145.74, 145.43, 145.33, 145.23, 143.58, 142.73, 141.89, 138.16, 135.62, 133.07, 131.55, 129.98, 129.66, 128.91, 128.50, 125.37, 125.33, 125.19, 123.75, 123.66, 123.45, 114.34, 63.23(O*C*H$_3$), 55.34(O*C*H$_3$), 52.68, 49.25, 48.34, 17.34(N=C-*Me*), 16.65(N=C-*Me*)ppm

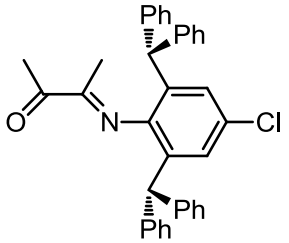
Elemental analysis: Anal. Calcd for $C_{72}H_{56}N_2O_2$: C, 88.13; H, 5.75; N, 2.85. Found: C, 88.02; H, 5.66; N, 2.92.



Preparation of Cat2: A mixture of **L2** (220 mg, 0.224 mmol) and (DME)$NiBr_2$ (69.2 mg, 0.224 mmol) (DME = 1,2-dimethoxyethane) were stirred in 25 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 an orange solid. (235 mg, 87.5% yield).

MALDI-TOF-MS (m/z) : 1038.4 $[M-2Br]^+$, 1073.3 $[M-2Br+Cl]^+$, 1117.3 $[M-Br]^+$.

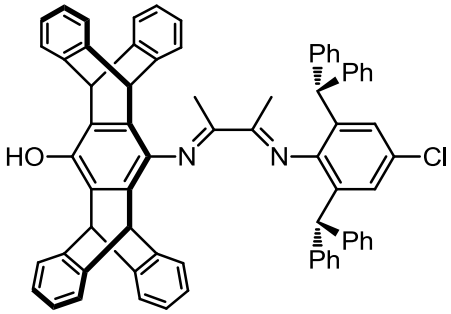
Elemental analysis: Anal. Calcd for $C_{72}H_{56}Br_2N_2NiO_2$: C, 72.08; H, 4.70; N, 2.33. Found: C, 72.34; H, 4.78; N, 2.41.



A solution of 2,6-diphenylmethyl-4-chloroaniline (9.20 g, 20 mmol), 2,3-butadione (8.61 g, 100 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (200 mL) was stirred at 80 ℃ for 24 h, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration, washed three times by 20 mL methanol and dried under high vacuum. (8.68 g, 82.2% yield)

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.29-7.17(m, 12H, aryl-*H*), 7.01-6.99(m, 8H, aryl-*H*), 6.82 (s, 2H, aryl-*H*), 5.08 (s, 2H, C*H*Ph_2), 2.30 (s, 3H, O=C-*Me*), 0.66 (s, 3H, N=C-*Me*)ppm.

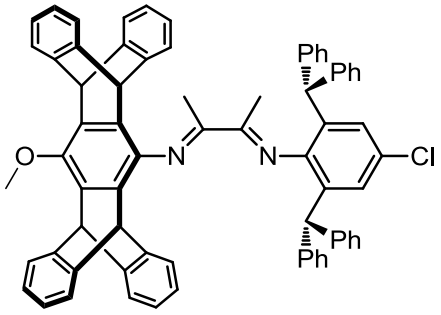
Elemental analysis: Anal. Calcd for $C_{36}H_{30}ClNO$: C, 81.88; H, 5.73; N, 2.65. Found: C, 81.72; H, 5.86; N, 2.78.



A solution of (2,6-dibenzhydryl -4-chlorophenylimino) butanone (2.00 g, 3.79 mmol), pentiptycene aminophenol (2.10 g, 4.54 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (250 mL) was refluxed with Dean-stark trap for 3 days, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration and recrystallized from hot methanol, washed three times by 20 mL hot methanol and dried under high vacuum. (2.93 g, 79.5% yield)

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.49-7.45(m, 4H, aryl-*H*), 7.38-7.32(m, 11H, aryl-*H*), 7.28-7.21(m, 7H, aryl-*H*), 7.18-7.14(m, 6H, aryl-*H*), 6.96-6.90(m, 10H, aryl-*H*), 5.65 (s, 2H, C*H*Ar_3), 5.47(s, 2H, C*H*Ph_2), 4.95(s, 2H, C*H*Ar_3), 4.65(s, 1H, O*H*), 1.72 (s, 3H, N=C-*Me*), 1.18 (s, 3H, N=C-*Me*)ppm.

Elemental analysis: Anal. Calcd for $C_{70}H_{51}ClN_2O$: C, 86.53; H, 5.29; N, 2.88. Found: C, 86.39; H, 5.43; N, 2.84.

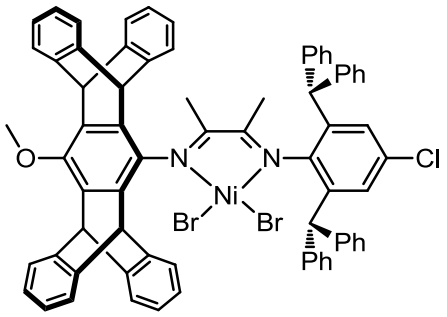


Preparation of Ligand L3: To the solution of 2-(2,6-dibenzhydryl-4-chlorophenylimino)-3-pentiptycene aminophenol butane (2.93 g, 2.97 mmol) in DMF (200 mL) at 50 ℃ was added K_2CO_3 (4.61 g, 35.67 mmol). The mixture was stirred for 1 min and MeI (1.69 g, 11.88 mmol) was added. The reaction mixture was stirred overnight at 50 ℃. The yellow suspension was cooled to room temperature and poured into 300 mL of water. The yellow precipitate was collected by filtration, washed with water, methanol and diethyl ether. After drying in vacuo at 70 ℃, the product was obtained as a yellow powder (2.09 g, 70.2% yield).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.48-7.45(m, 4H, aryl-*H*), 7.38-7.33(m, 10H, aryl-*H*), 7.28-7.21(m, 8H, aryl-*H*), 7.18-7.14(m, 6H, aryl-*H*), 6.96-6.91(m, 10H, aryl-*H*), 5.71(s, 2H, C*H*Ar_3), 5.46(s, 2H, C*H*Ph_2), 4.95(s, 2H, C*H*Ar_3), 3.90(s, 3H, OC*H*$_3$), 1.74 (s, 3H, N=C-*Me*), 1.16 (s, 3H, N=C-*Me*)ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): *δ* =170.90 (N=*C*-Me), 170.08 (N=*C*-Me), 147.01, 146.69, 145.71, 145.36, 145.24, 145.20, 142.96, 142.09, 137.95, 135.68, 133.81, 131.53, 129.92, 129.58, 129.09, 128.68, 128.61, 127.09, 126.86, 125.41, 125.38, 125.25, 125.21, 123.79, 123.71, 123.69, 123.39, 63.22(OC*H*$_3$), 52.52, 49.26, 48.32, 17.32(N=C-*Me*), 16.86(N=C-*Me*)ppm.

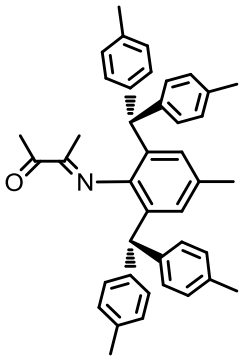
Elemental analysis: Anal. Calcd for $C_{71}H_{53}ClN_2O$: C, 86.52; H, 5.42; N, 2.84. Found: C, 86.68; H, 5.54; N, 2.79.



Preparation of Cat3: A mixture of **L3** (220 mg, 0.223 mmol) and (DME)$NiBr_2$ (68.9 mg, 0.223 mmol) (DME = 1,2-dimethoxyethane) were stirred in 25 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 an orange solid. (241 mg, 89.8% yield).

MALDI-TOF-MS (m/z): 1042.3 $[M-2Br]^+$, 1077.2 $[M-2Br+Cl]^+$, 1121.2 $[M-Br]^+$.

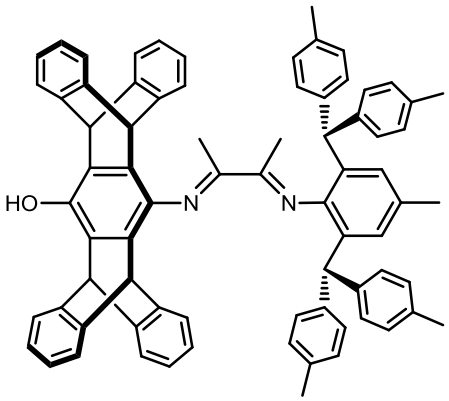
Elemental analysis: Anal. Calcd for $C_{71}H_{53}Br_2ClN_2NiO$: C, 70.82; H, 4.44; N, 2.33. Found: C, 70.67; H, 4.36; N, 2.38.



A solution of 2,6-bis(bis(4-methylphenyl)methyl)-4-methylaniline (9.91 g, 20 mmol), 2,3-butadione (8.61 g, 100 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (200 mL) was stirred at 80 ℃ for 24 h, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration, washed three times by 20 mL methanol and dried under high vacuum. (7.92 g, 70.2% yield)

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.05-7.00(m, 8H, aryl-*H*), 6.90-6.96(m, 8H, aryl-*H*), 6.65 (s, 2H, aryl-*H*), 5.00 (s, 2H, C*H*Ph_2), 2.35 (s, 3H, O=C-*Me*), 2.31{s, 6H, CH(Ph-*Me*)$_2$}, 2.27{s, 6H, CH(Ph-*Me*)$_2$}, 2.16 (s, 3H, aryl-*Me*), 0.65 (s, 3H, N=C-*Me*)ppm.

Elemental analysis: Anal. Calcd for $C_{41}H_{41}NO$: C, 87.35; H, 7.33; N, 2.48. Found: C, 87.31; H, 7.37; N, 2.44.

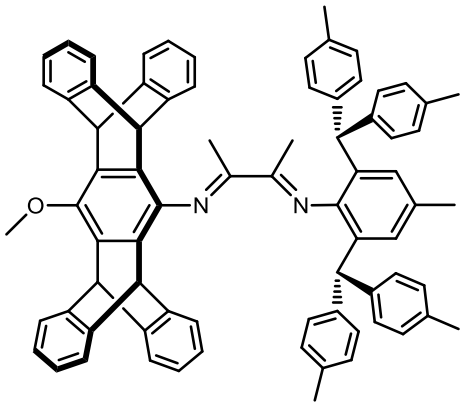


A solution of (2,6-bis(bis(4-methylphenyl)methyl)-4-methylphenylimino) butanone (2.00g, 3.55 mmol), pentiptycene aminophenol (2.18 g, 4.26 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (250 mL) was refluxed with Dean-stark trap for 3 days, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration and recrystallized from hot methanol, washed three times by 20 mL hot methanol and dried under high vacuum. (2.95 g, 82.5% yield)

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.34-7.33(m, 4H, aryl-*H*), 7.24-7.17(m, 6H, aryl-*H*), 7.17-7.11(m, 10H, aryl-*H*), 7.05-7.03(m, 4H, aryl-*H*), 6.95-6.89(m, 8H, aryl-*H*), 6.73(s, 2H, aryl-*H*), 5.65(s, 2H, C*H*Ar_3), 5.39(s, 2H, C*H*Ph_2),

4.98(s, 2H, C*H*Ar$_3$), 4.64(s, 1H, O*H*), 2.39{s, 6H, CH(Ph-*Me*)$_2$}, 2.33{s, 6H, CH(Ph-*Me*)$_2$}, 2.23(s, 3H, aryl-*Me*), 1.75 (s, 3H, N=C-*Me*), 1.19 (s, 3H, N=C-*Me*)ppm.

Elemental analysis: Anal. Calcd for $C_{75}H_{62}N_2O$: C, 89.43; H, 6.20; N, 2.78. Found: C, 89.28; H, 6.15; N, 2.81.

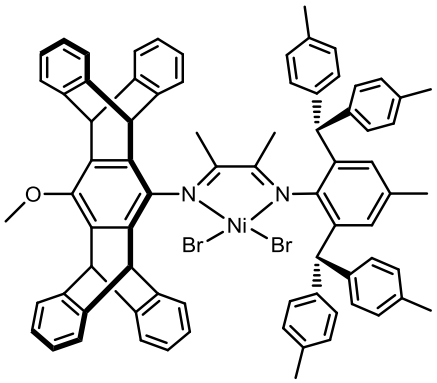


Preparation of Ligand L4: To the solution of 2-(2,6-bis(bis(4-methylphenyl)methyl)-4-methylphenylimino)-3-pentiptycene aminophenol butane (2.95 g, 2.93 mmol) in DMF (200 mL) at 50 ℃ was added K_2CO_3 (4.61 g, 35.14 mmol). The mixture was stirred for 1 min and MeI (1.64g, 11.72 mmol) was added. The reaction mixture was stirred overnight at 50 ℃. The yellow suspension was cooled to room temperature and poured into 300 mL of water. The yellow precipitate was collected by filtration, washed with water, methanol and diethyl ether. After drying in vacuo at 70 ℃, the product was obtained as a yellow powder (2.36 g, 78.8% yield).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.35-7.34(m, 4H, aryl-*H*), 7.24-7.21(m, 6H, aryl-*H*), 7.18-7.11(m, 10H, aryl-*H*), 7.05-7.03(m, 4H, aryl-*H*), 6.95-6.90(m, 8H, aryl-*H*), 6.73(s, 2H, aryl-*H*), 5.71(s, 2H, C*H*Ar$_3$), 5.38(s, 2H, C*H*Ph$_2$), 4.98(s, 2H, C*H*Ar$_3$), 3.90(s, 3H, OC*H*$_3$), 2.39{s, 6H, CH(Ph-*Me*)$_2$}, 2.33{s, 6H, CH(Ph-*Me*)$_2$}, 2.23(s, 3H, aryl-*Me*), 1.77 (s, 3H, N=C-*Me*), 1.16 (s, 3H, N=C-*Me*)ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ =170.56 (N=*C*-Me), 170.11 (N=*C*-Me), 146.89, 145.74, 145.71, 145.44, 145.36, 145.23, 141.23, 140.21, 138.20, 136.08, 135.82, 135.60, 132.04, 131.77, 131.58, 129.87, 129.51, 129.45, 129.11, 128.94, 125.35, 125.33, 125.27, 125.14, 123.80, 123.72, 123.66, 123.51 , 63.23(O*C*H$_3$), 51.70, 49.32, 48.34, 21.54(aryl-*Me*), 21.28{CH(Ph-*Me*)$_2$}, 21.20{CH(Ph-*Me*)$_2$}, 17.45(N=C-*Me*), 16.58(N=C-*Me*)ppm.

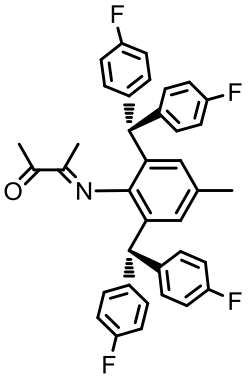
Elemental analysis: Anal. Calcd for $C_{76}H_{64}N_2O$: C, 89.37; H, 6.32; N, 2.74. Found: C, 89.21; H, 6.35; N, 2.77.



Preparation of Cat4: A mixture of **L4** (220 mg, 0.215 mmol) and (DME)$NiBr_2$ (66.5 mg, 0.215 mmol) (DME = 1,2-dimethoxyethane) were stirred in 25 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 an orange solid. (220 mg, 82.5% yield).

MALDI-TOF-MS (m/z): 1078.4 $[M-2Br]^+$, 1113.4 $[M-2Br+Cl]^+$, 1157.3 $[M-Br]^+$.

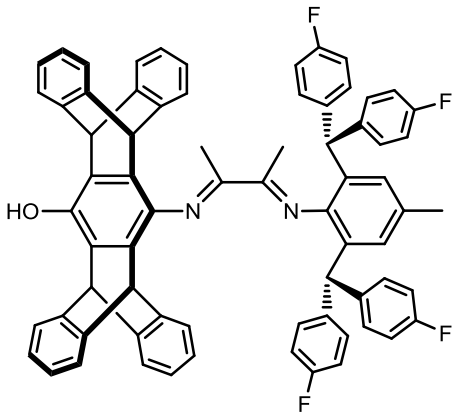
Elemental analysis: Anal. Calcd for $C_{76}H_{64}Br_2N_2NiO$: C, 73.62; H, 5.20; N, 2.26. Found: C, 73.78; H, 5.14; N, 2.37.



A solution of 2,6-bis(bis(4-fluorophenyl)methyl)-4-methylaniline (10.23 g, 20 mmol), 2,3-butadione (8.61 g, 100 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (200 mL) was stirred at 80 ℃ for 24 h, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration, washed three times by 20 mL methanol and dried under high vacuum. (7.98 g, 68.8% yield)

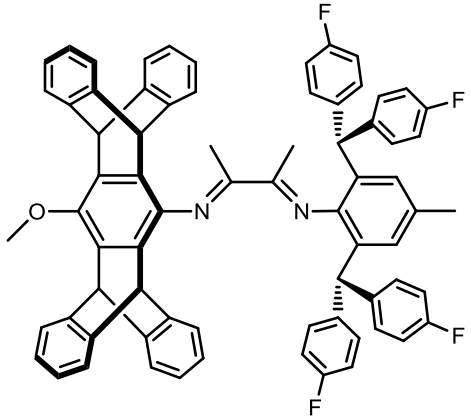
^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =6.97-6.91(m, 16H, aryl-*H*), 6.58 (s, 2H, aryl-*H*), 5.04 (s, 2H, C*H*Ph_2), 2.29 (s, 3H, O=C-*Me*), 2.17 (s, 3H, aryl-*Me*), 0.83 (s, 3H, N=C-*Me*)ppm.

Elemental analysis: Anal. Calcd for $C_{37}H_{29}F_4NO$: C, 76.67; H, 5.04; N, 2.42. Found: C, 76.64; H, 5.09; N, 2.39.



A solution of (2,6-bis(bis(4-fluorophenyl)methyl)-4-methylphenylimino) butanone (2.00 g, 3.45 mmol), pentiptycene aminophenol (1.91 g, 4.14 mmol) and p-toluenesulfonic acid (20 mg) in toluene (250 mL) was refluxed with Dean-stark trap for 3 days, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration and recrystallized from hot methanol, washed three times by 20 mL hot methanol and dried under high vacuum. (2.67 g, 75.5% yield) **^{1}H NMR** (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.35-7.33(m, 4H, aryl-*H*), 7.23-7.20(m, 6H, aryl-*H*), 7.17-7.13(m, 4H, aryl-*H*), 7.10-7.07(m, 6H, aryl-*H*), 7.03-7.00(m, 4H, aryl-*H*), 6.96-6.90(m, 8H, aryl-*H*), 6.67(s, 2H, aryl-*H*), 5.66(s, 2H, C*H*Ar_3), 5.42(s, 2H, C*H*Ph_2), 4.90(s, 2H, C*H*Ar_3), 4.66(s, 1H, O*H*), 2.23(s, 3H, aryl-*Me*), 1.70 (s, 3H, N=C-*Me*), 1.33 (s, 3H, N=C-*Me*)ppm.

Elemental analysis: Anal. Calcd for $C_{71}H_{50}F_4N_2O$: C, 83.35; H, 4.93; N, 2.74. Found: C, 83.21; H, 4.86; N, 2.66.

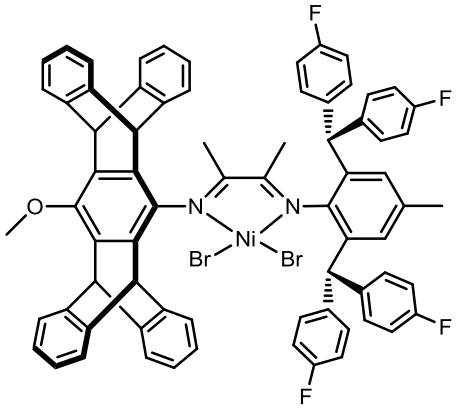


Preparation of Ligand L5: To the solution of 2-(2,6-bis(bis(4-fluorophenyl)methyl)-4-methylphenylimino)-3- pentiptycene aminophenol butane (2.67 g, 2.61 mmol) in DMF (200 mL) at 50 ℃ was added K_2CO_3 (4.61 g, 31.32 mmol). The mixture was stirred for 1 min and MeI (1.64 g, 10.44 mmol) was added. The reaction mixture was stirred overnight at 50 ℃. The yellow suspension was cooled to room temperature and poured into 300 mL of water. The yellow precipitate was collected by filtration, washed with water, methanol and diethyl ether. After drying in vacuo at 70 ℃, the product was obtained as a yellow powder (2.01 g, 74.1% yield).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ =7.36-7.34(m, 4H, aryl-*H*), 7.23-7.19(m, 6H, aryl-*H*), 7.17-7.13(m, 4H, aryl-*H*), 7.11-7.07(m, 6H, aryl-*H*), 7.04-7.00(m, 4H, aryl-*H*), 6.96-6.91(m, 8H, aryl-*H*), 6.67(s, 2H, aryl-*H*), 5.71(s, 2H, C*H*Ar_3), 5.42(s, 2H, C*H*Ph_2), 4.90(s, 2H, C*H*Ar_3), 3.91(s, 3H, OC*H*$_3$), 2.23(s, 3H, aryl-*Me*), 1.72 (s, 3H, N=C-*Me*), 1.31 (s, 3H, N=C-*Me*)ppm.

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 170.34(N=*C*-Me), 170.21 (N=*C*-Me), 162.79, 162.63, 160.83, 160.69, 147.07, 145.74, 145.53, 145.20, 145.11, 139.28, 139.26, 138.55, 138.53, 137.86, 135.71, 132.75, 131.54, 131.44, 131.32, 131.26, 130.97, 130.91, 129.19, 125.45, 125.33, 125.23, 123.88, 123.73, 123.69, 123.19, 115.95, 115.78, 115.47, 115.31, 63.23(O*C*H_3), 50.99, 49.42, 48.32, 21.49(aryl-*Me*), 17.25(N=C-*Me*), 16.95(N=C-*Me*) ppm.

Elemental analysis: Anal. Calcd for $C_{72}H_{52}F_4N_2O$: C, 83.38; H, 5.05; N, 2.70. Found: C, 83.53; H, 5.17; N, 2.79.



Preparation of Cat5: A mixture of **L5** (220 mg, 0.212 mmol) and (DME)$NiBr_2$ (65.5 mg, 0.212 mmol) (DME = 1,2-dimethoxyethane) were stirred in 25 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 an orange solid. (212 mg, 79.6% yield).

MALDI-TOF-MS (m/z): 1094.3 $[M-2Br]^+$, 1129.3 $[M-2Br+Cl]^+$, 1173.2 $[M-Br]^+$.

Elemental analysis: Anal. Calcd for $C_{72}H_{52}Br_2F_4N_2NiO$: C, 68.87; H, 4.17; N, 2.23. Found: C, 68.71; H, 4.10; N, 2.35.

3 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 5 min, the pressure reactor was vented and the polymerization was quenched via the addition of 100 mL acidic MeOH (5% HCl in MeOH) and the polymer was filtered, then dried at 60 ℃ under vacuum oven to constant weight.

The polyethylene precipitates during polymerization because it was insoluble in toluene at low temperature (30 ℃). After 5 min, the pressure reactor was vented and the polymerization was quenched via the addition of 100 mL acidic MeOH (5% HCl in MeOH) and the polymer was filtered, then dried at 60 ℃ under vacuum oven to constant weight.

A general procedure for the copolymerization of polar monomer with ethylene using Ni catalyst

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. 20 mL of CH_2Cl_2 with Et_2AlCl and polar monomer were 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 subsequently. With a rapid stirring, the reactor was pressurized and maintained at desired ethylene pressure. After 1 h, the pressure reactor was vented and the polymerization was quenched via the addition of 20 mL acidic MeOH (5% HCl in MeOH) and the polymer was filtered, washed three times with methanol to remove residual monomer, then dried at 60 ℃ under vacuum oven to constant weight.

4 Spectra Data

4.1 ^{1}H, ^{13}C NMR of Ligand

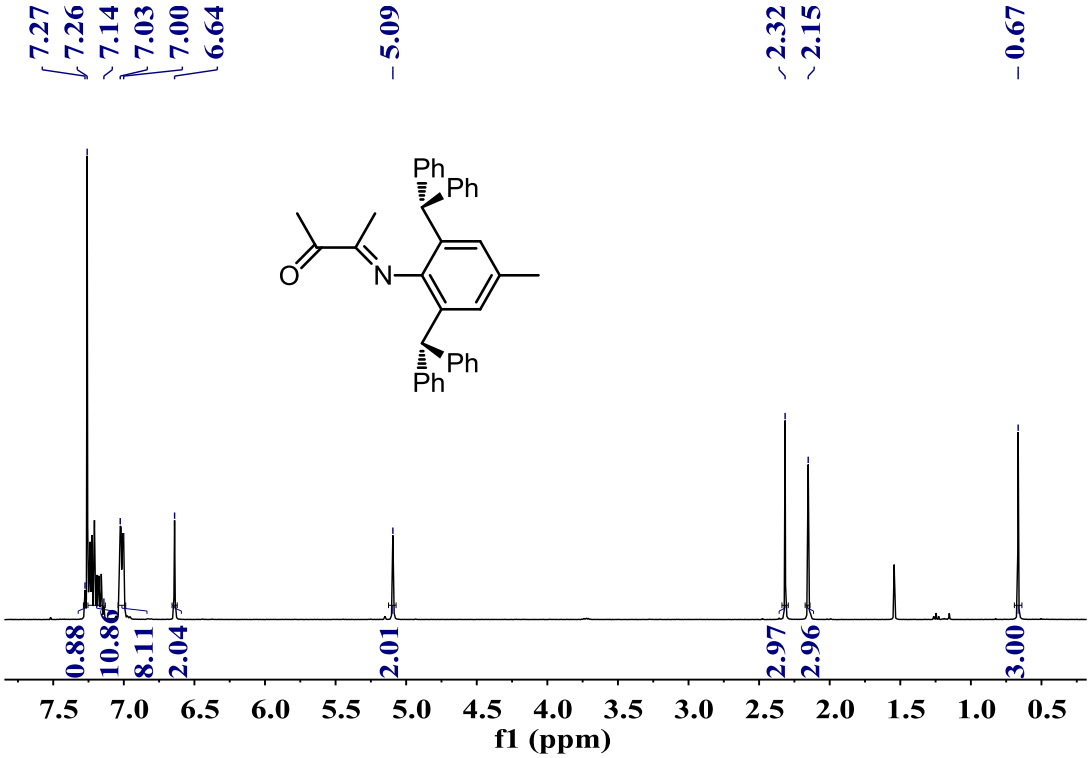


Figure S1. ^{1}H NMR spectrum of (2,6-dibenzhydryl-4-methylphenylimino) butanone in $CDCl_3$.

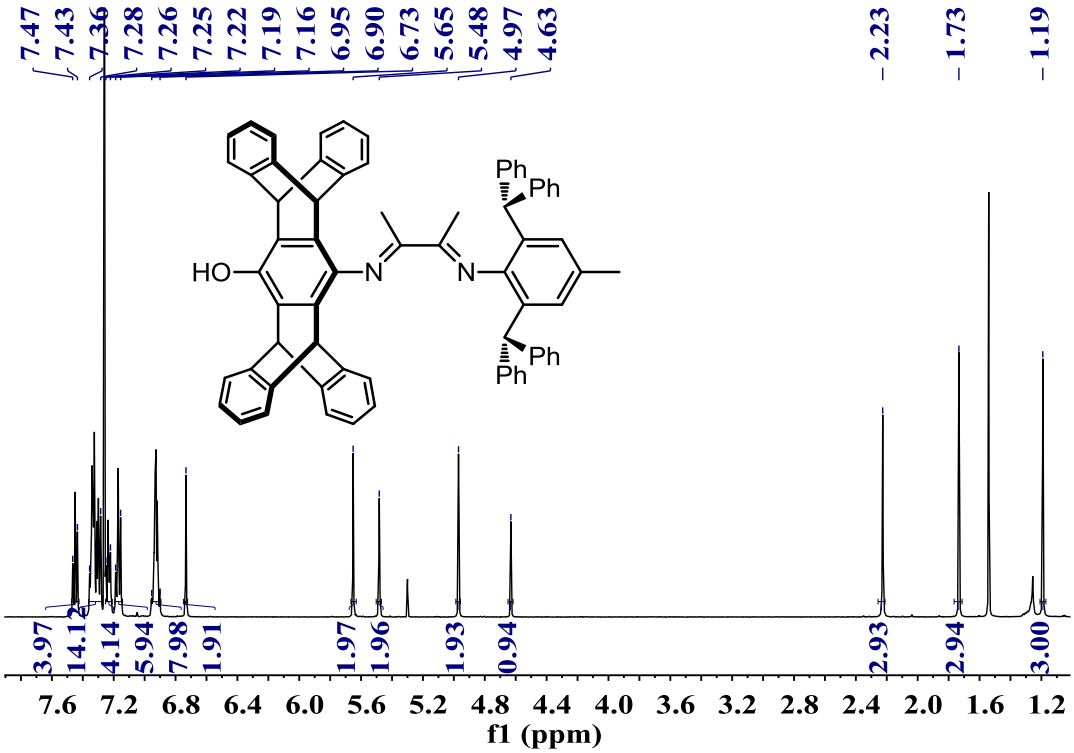


Figure S2. ^{1}H NMR spectrum of 2-(2,6-Dibenzhydryl-4-methylphenylimino)-3-pentiptycene aminophenol butane in $CDCl_3$

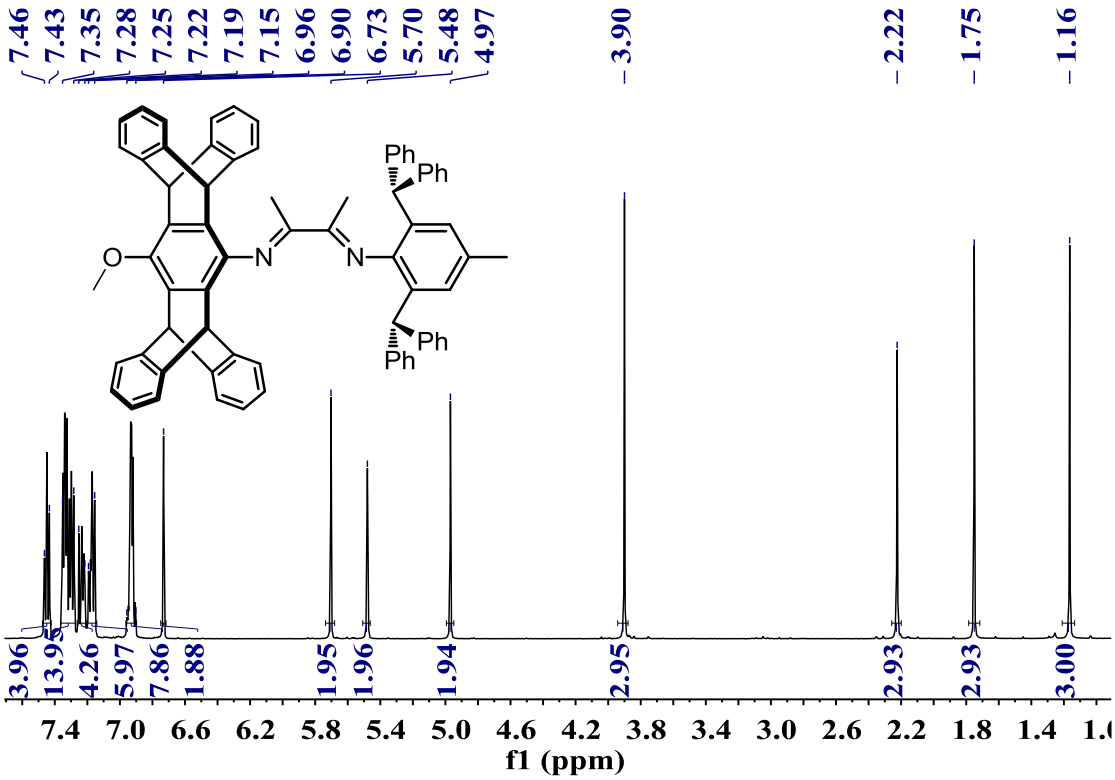


Figure S3. ^{1}H NMR spectrum of **L1** in $CDCl_3$

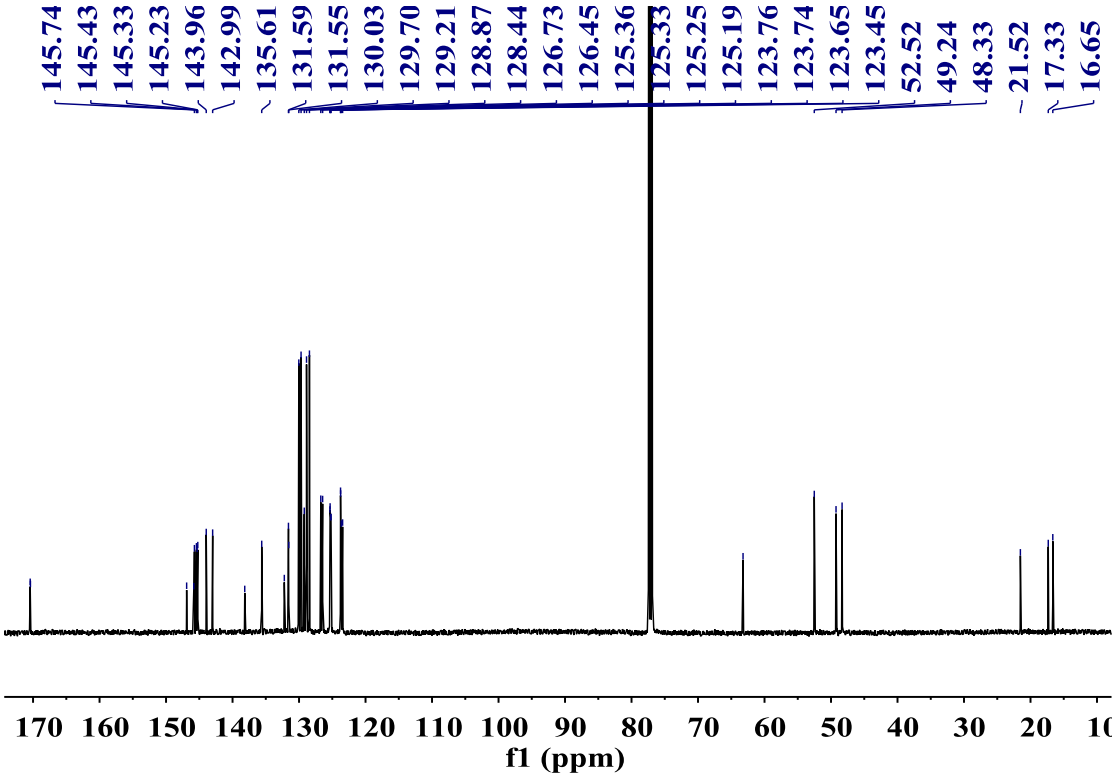


Figure S4. ^{13}C NMR spectrum of **L1** in $CDCl_3$

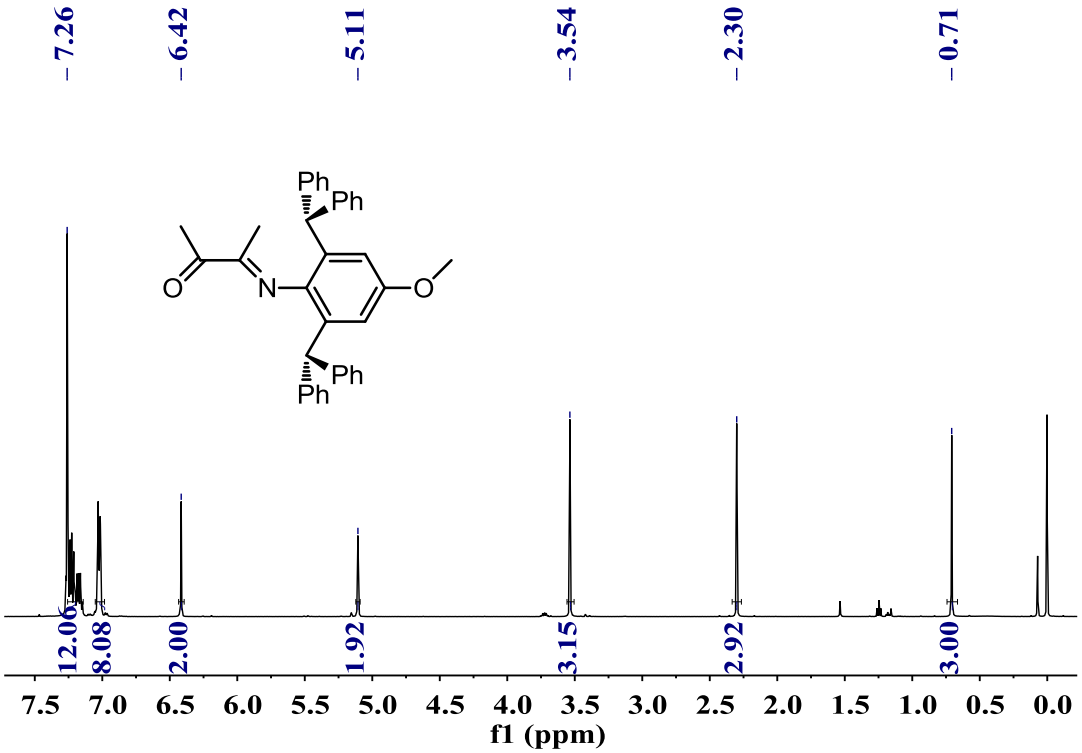


Figure S5. ^{1}H NMR spectrum of (2,6-dibenzhydryl -4-methoxyphenylimino) butanone in $CDCl_3$

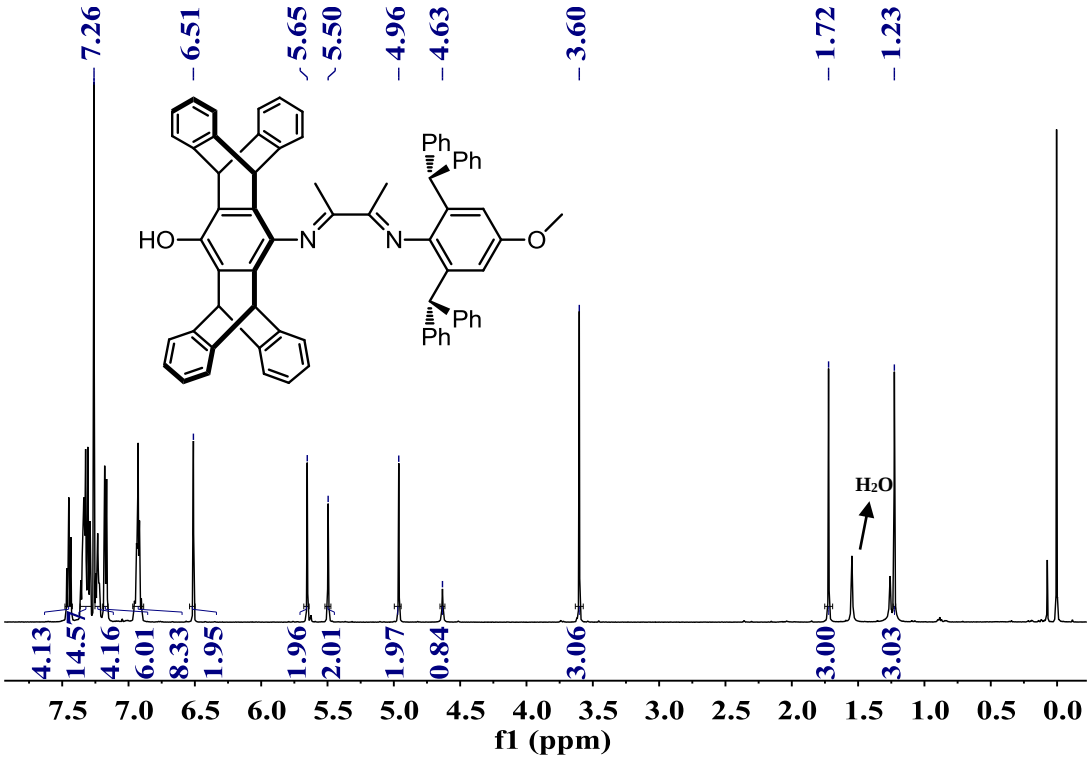


Figure S6. ^{1}H NMR spectrum of 2-(2,6-Dibenzhydryl-4-methylphenylimino)-3-pentiptycene aminophenol butane in $CDCl_3$

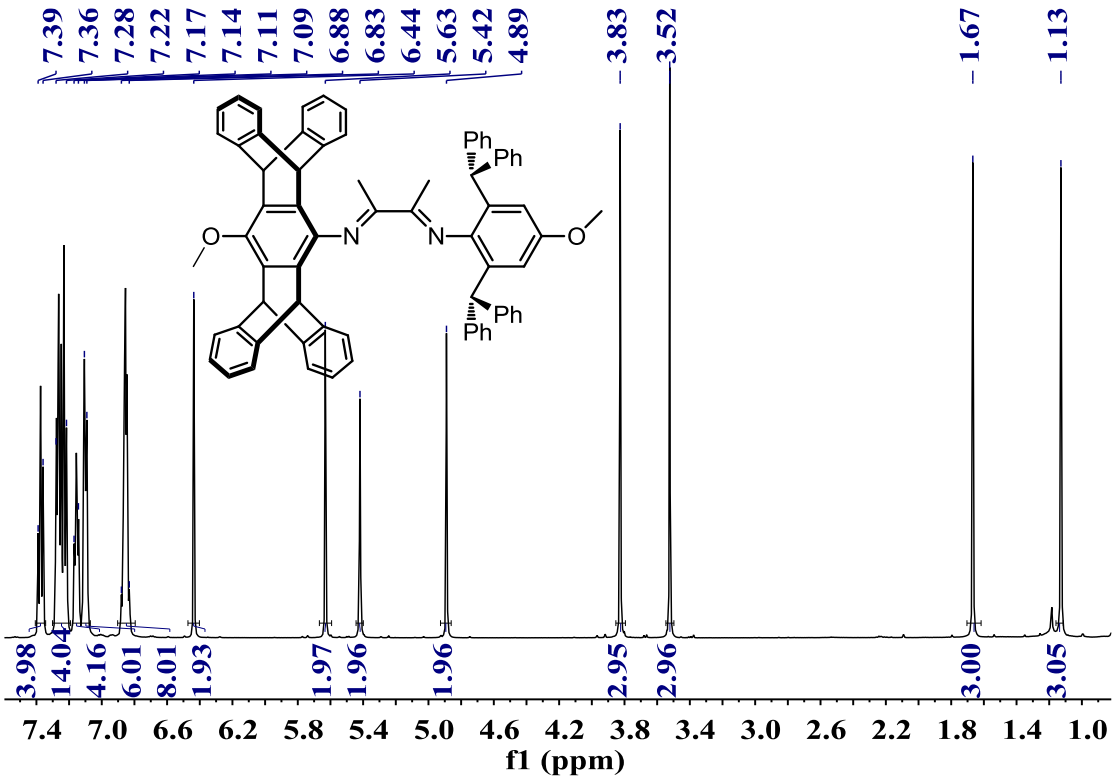


Figure S7. ^{1}H NMR spectrum of **L2** in $CDCl_3$

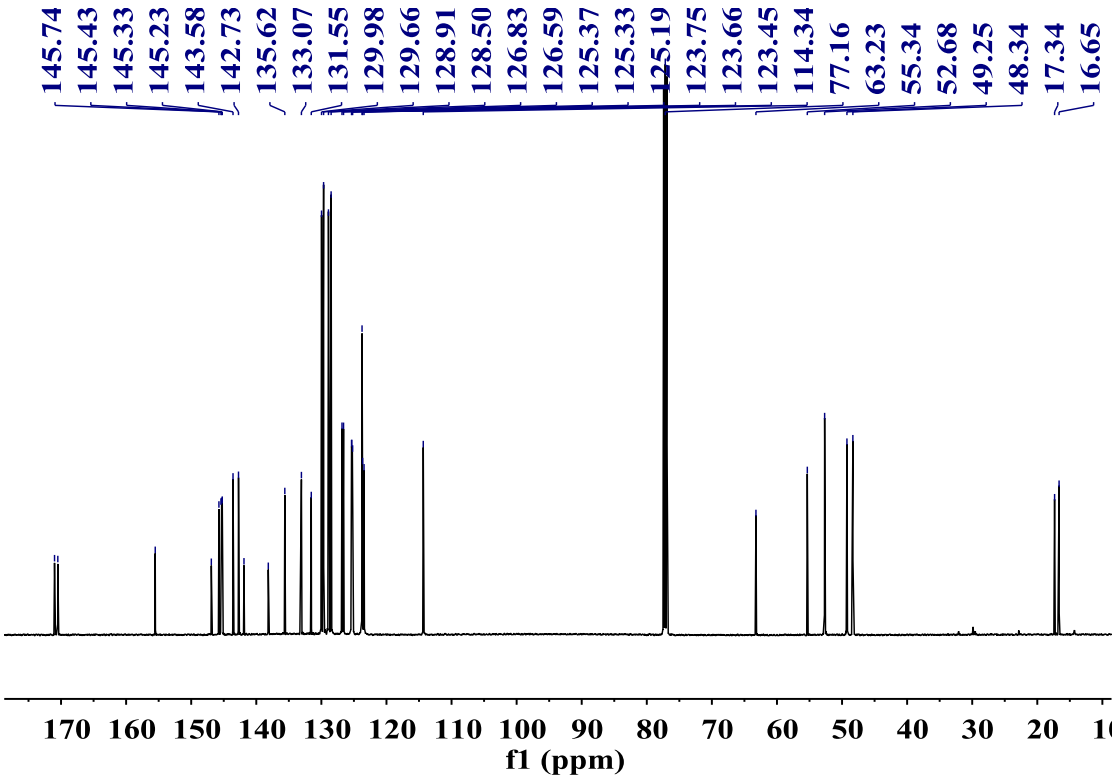


Figure S8. ^{13}C NMR spectrum of **L2** in $CDCl_3$

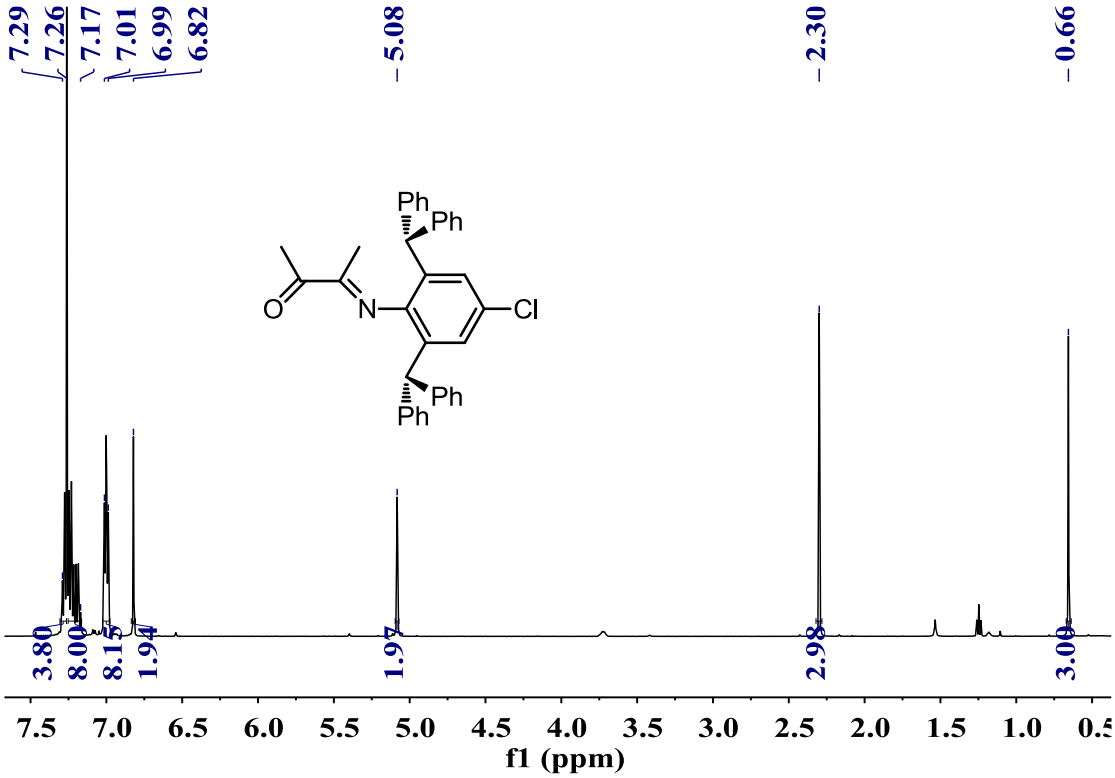


Figure S9. ^{1}H NMR spectrum of (2,6-dibenzhydryl-4-chlorophenylimino) butanone in $CDCl_3$

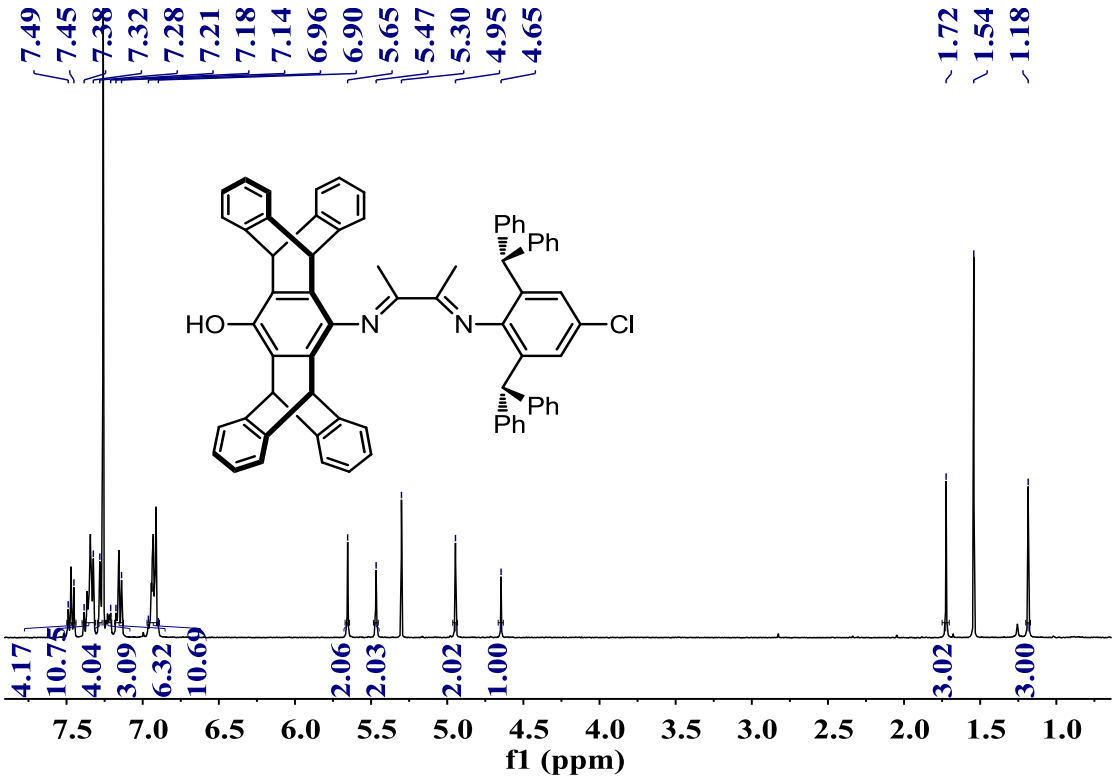


Figure S10. ^{1}H NMR spectrum of 2-(2,6-Dibenzhydryl-4-chlorophenylimino)-3-pentiptycene aminophenol butane in $CDCl_3$

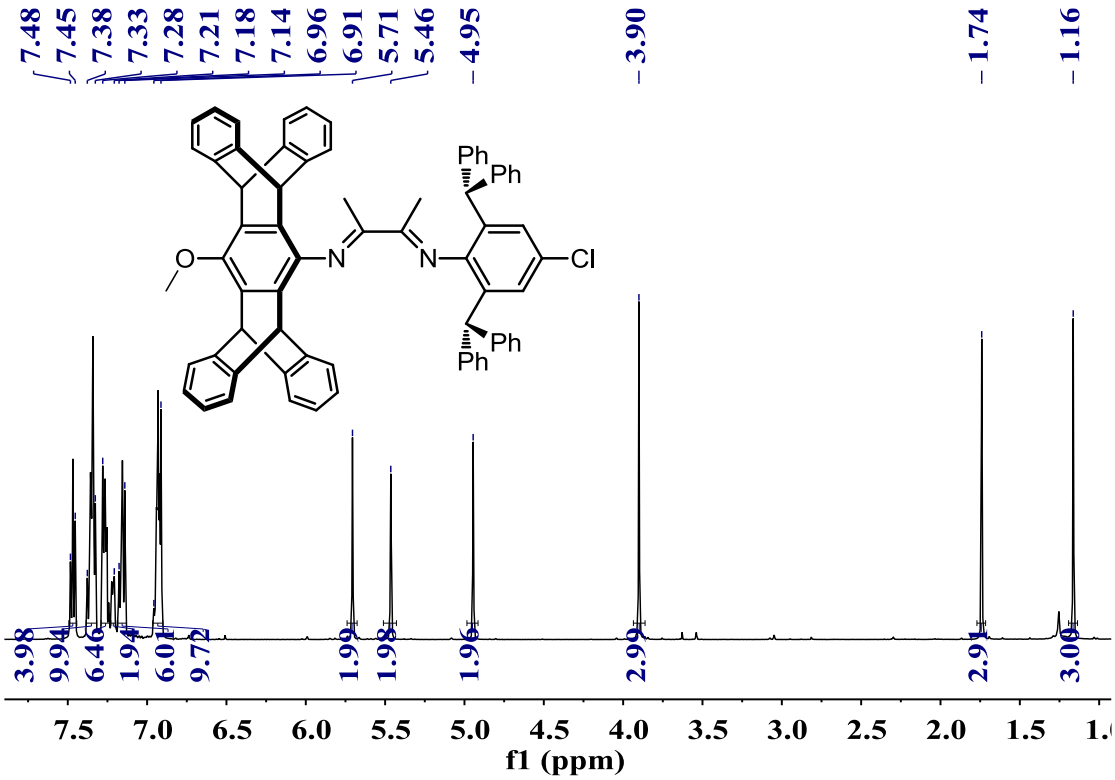


Figure S11. ^{1}H NMR spectrum of **L3** in $CDCl_3$

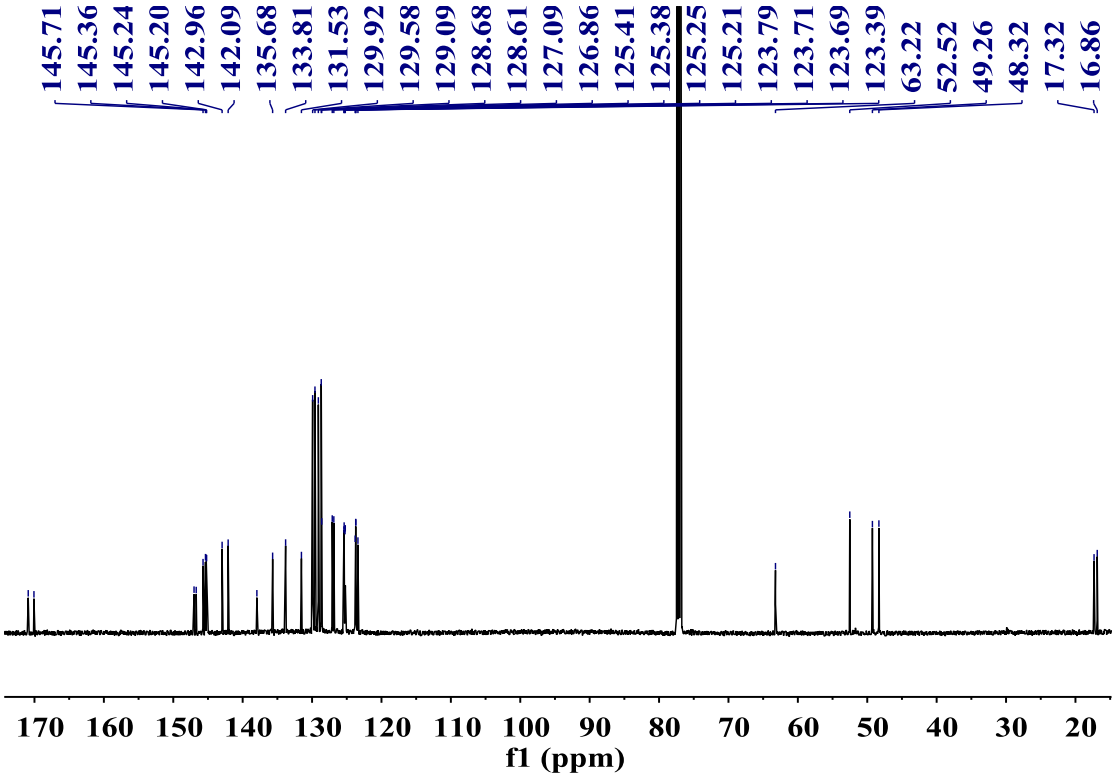


Figure S12. ^{13}C NMR spectrum of **L3** in $CDCl_3$

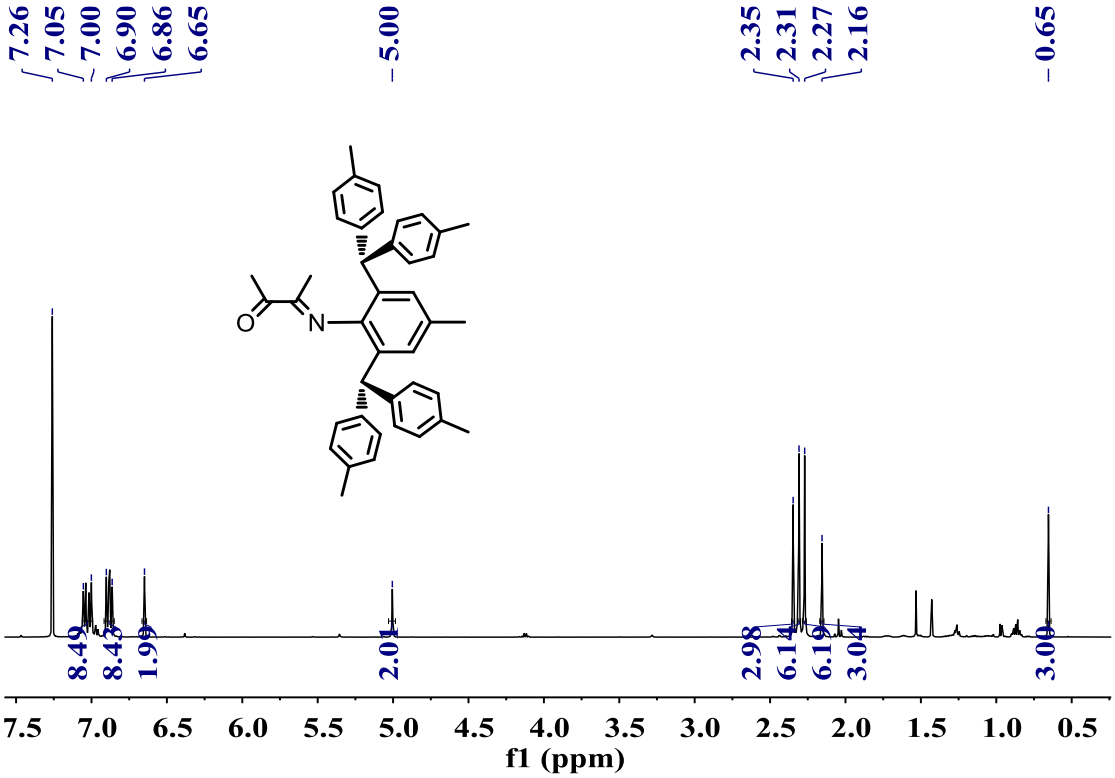


Figure S13. ^{1}H NMR spectrum of (2,6-bis(bis(4-methylphenyl)methyl)-4-methylphenylimino) butanone in $CDCl_3$

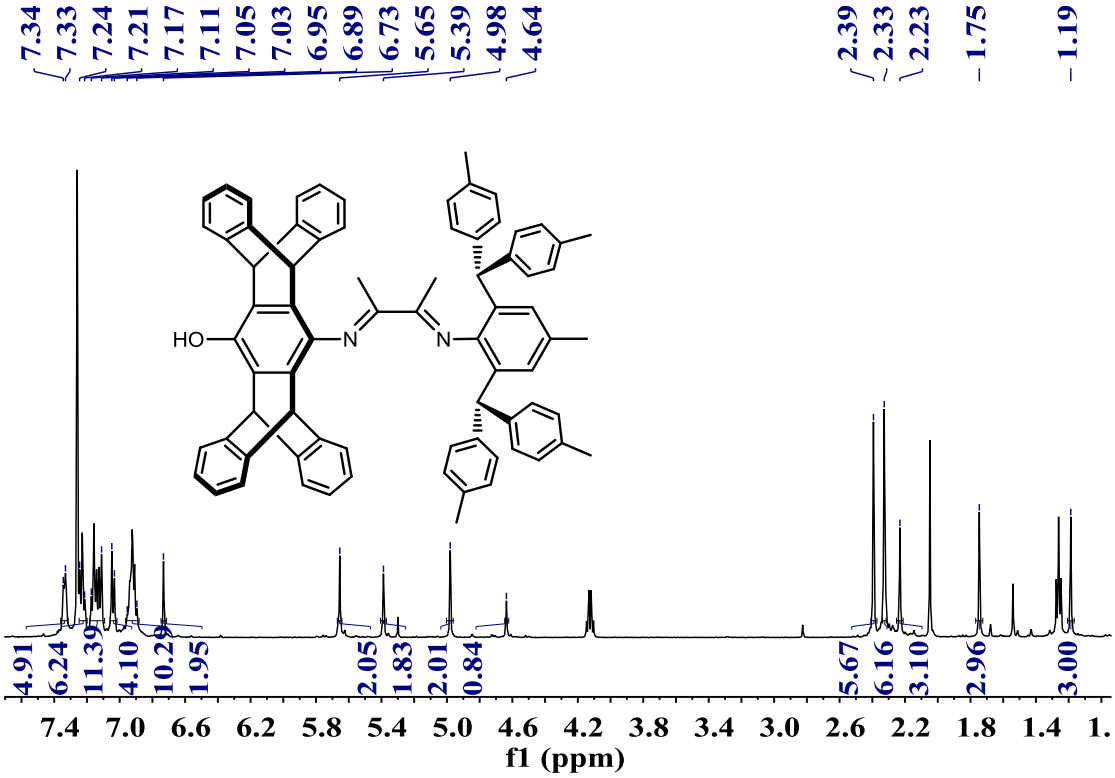


Figure S14. ^{1}H NMR spectrum of 2-(2,6-bis(bis(4-methylphenyl)methyl)-4-methylphenylimino)-3-pentiptycene aminophenol butane in $CDCl_3$

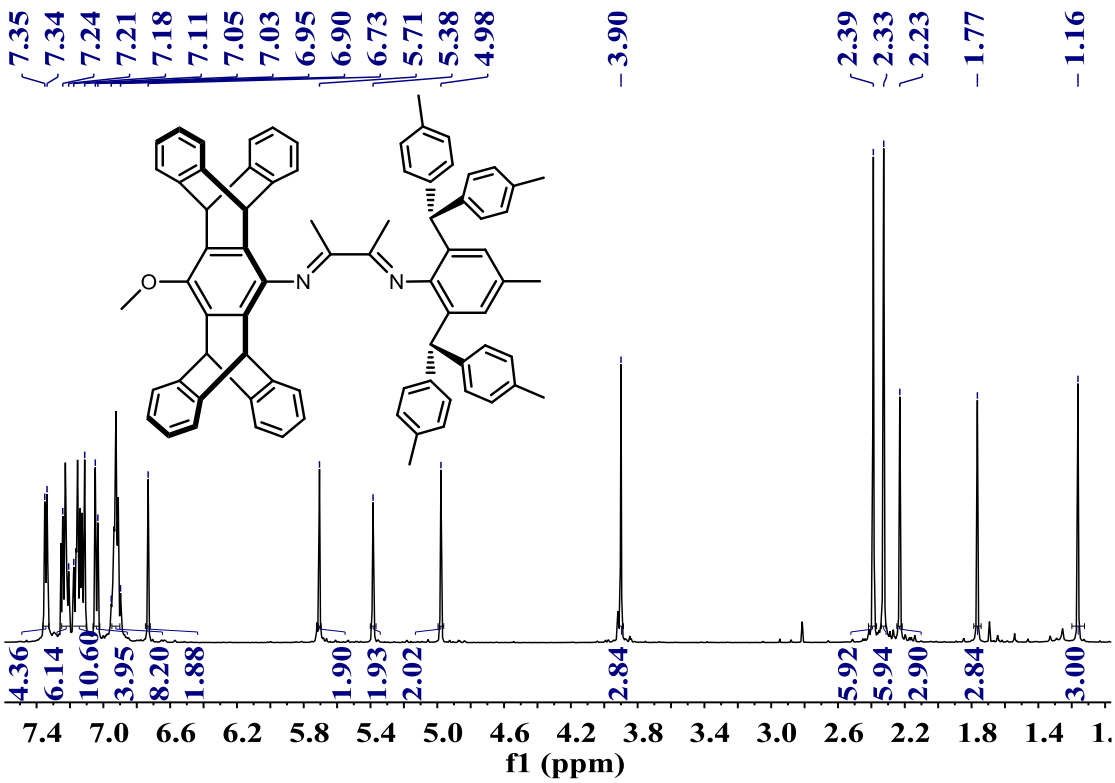


Figure S15. ^{1}H NMR spectrum of **L4** in $CDCl_3$

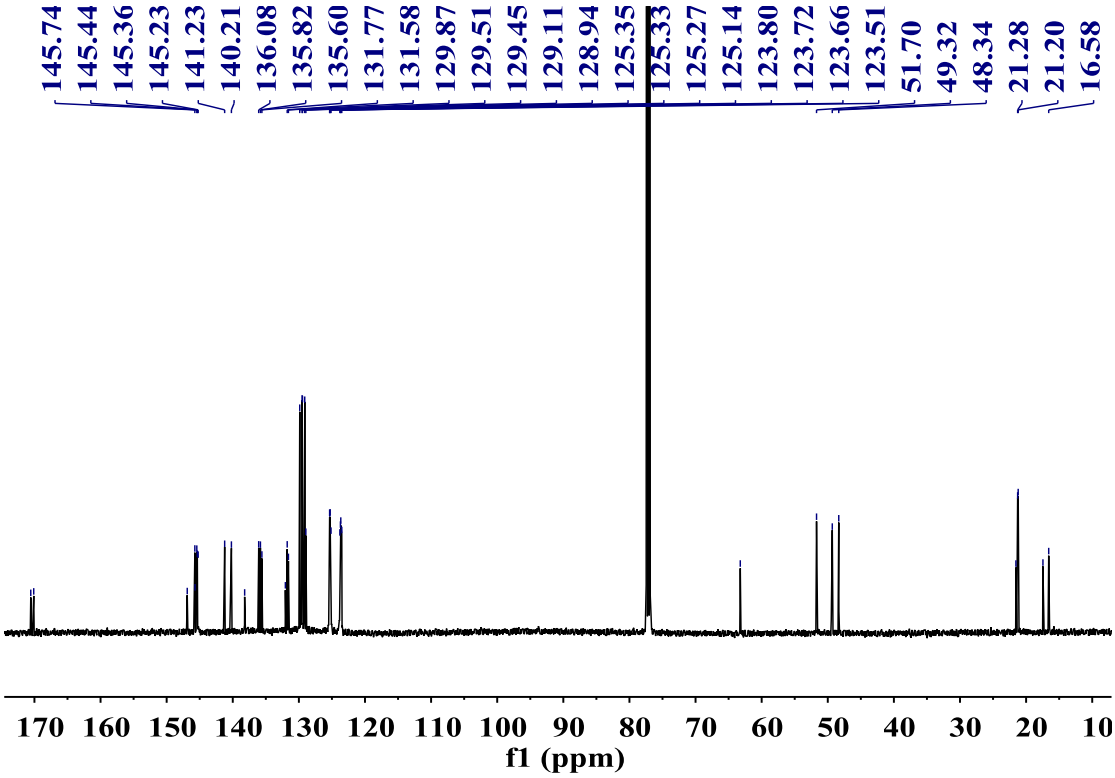


Figure S16. ^{13}C NMR spectrum of **L4** in $CDCl_3$

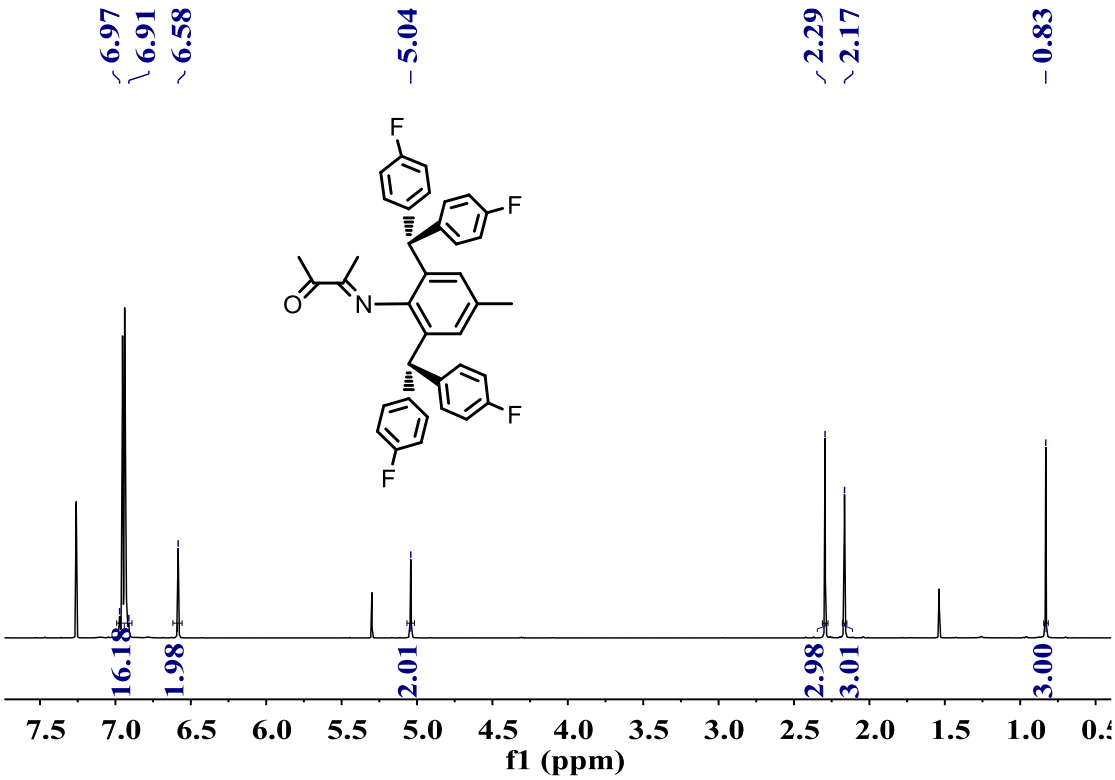


Figure S17. ^{1}H NMR spectrum of (2,6-bis(bis(4-fluorophenyl)methyl)-4-methylphenylimino) butanone in $CDCl_3$

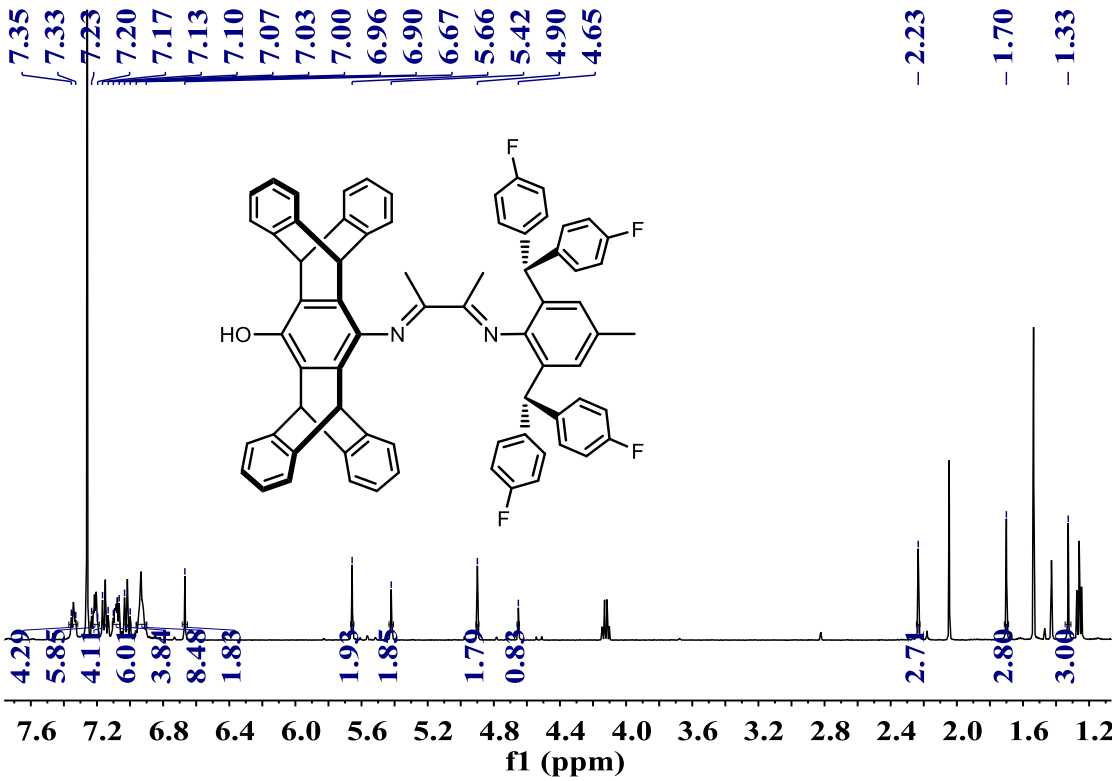


Figure S18. ^{1}H NMR spectrum of 2-(2,6-bis(bis(4-fluorophenyl)methyl)-4-methylphenylimino)-3- pentiptycene aminophenol butane in $CDCl_3$

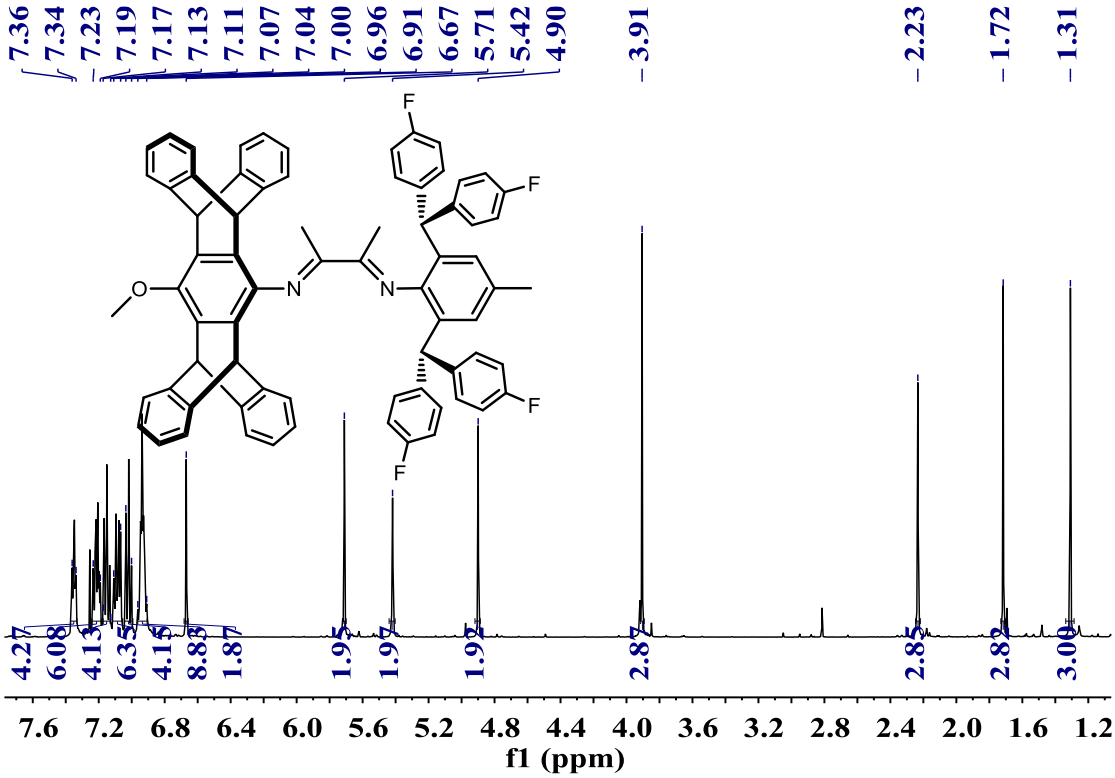


Figure S19. ^{1}H NMR spectrum of **L5** in $CDCl_3$

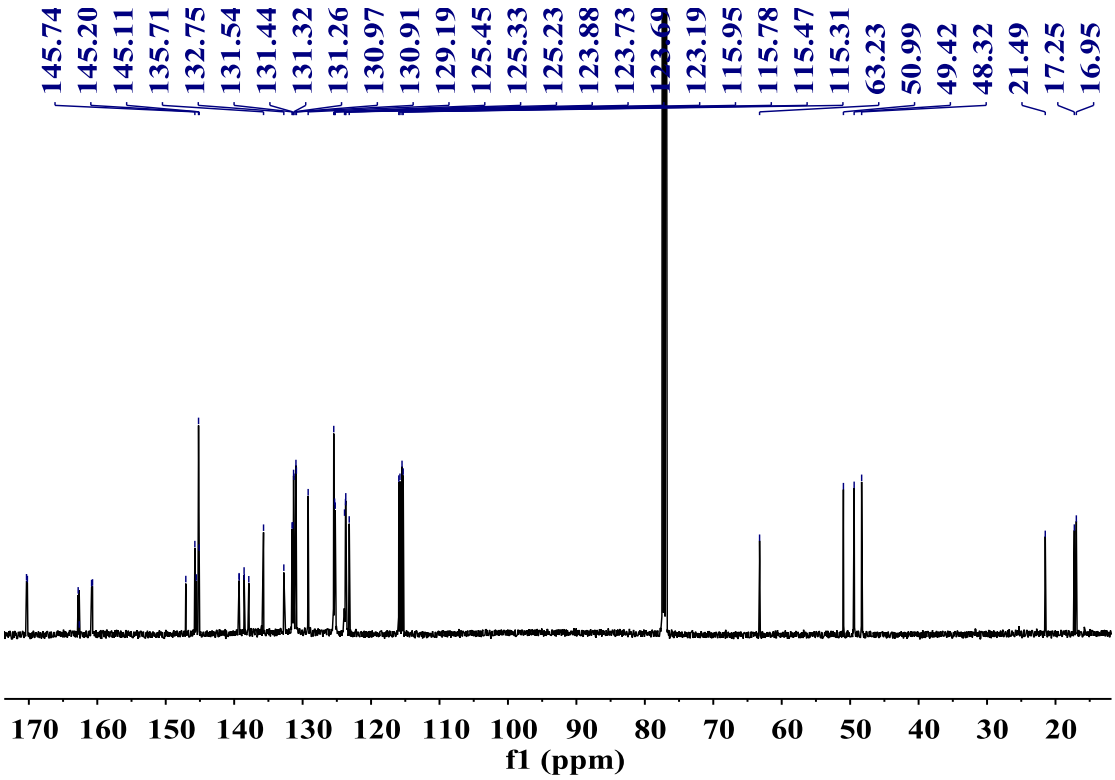


Figure S20. ^{13}C NMR spectrum of **L5** in $CDCl_3$

4.2 ^{1}H, ^{13}C, ^{1}H-^{1}H COSY NMR of Complexes

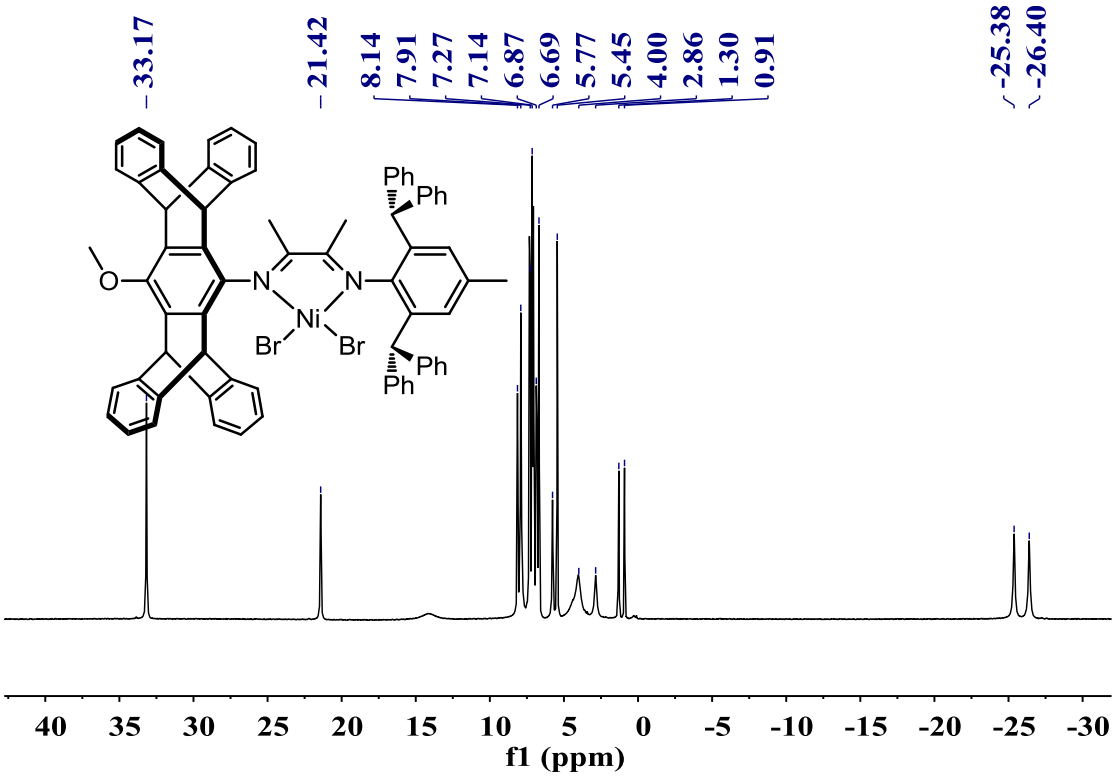


Figure S21. ^{1}H NMR spectrum of **Cat1** in $CDCl_3$

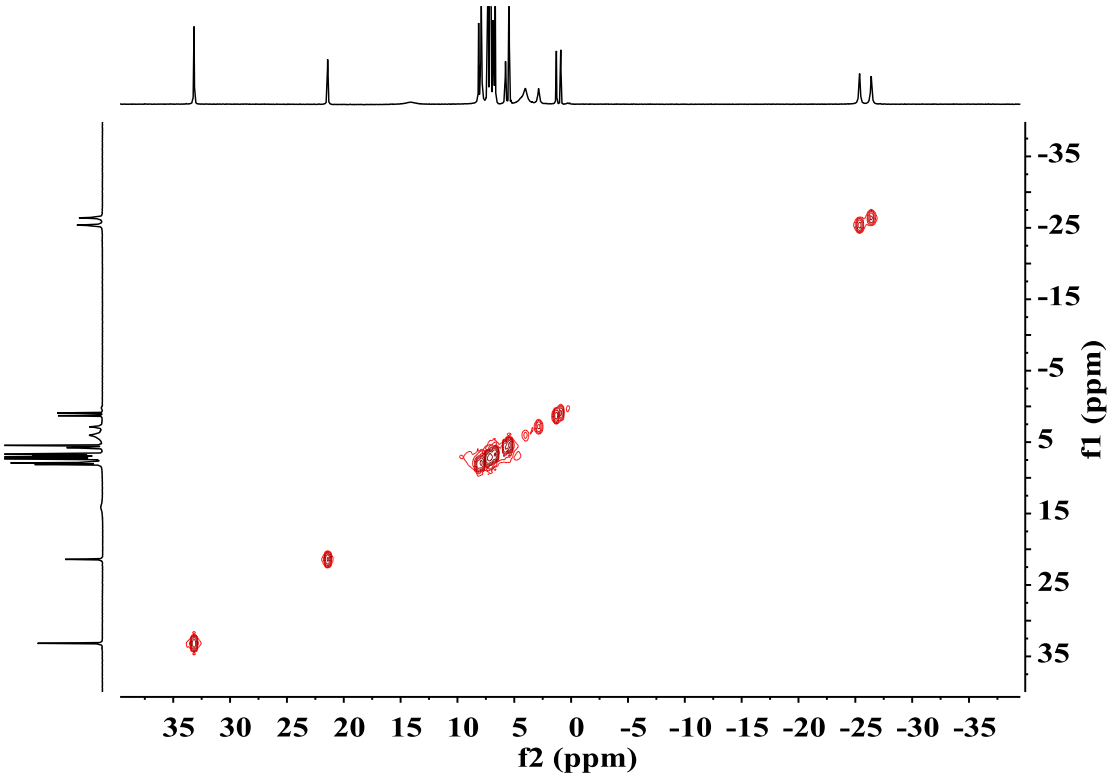


Figure S22. ^{1}H-^{1}H COSY NMR spectrum of **Cat1** in $CDCl_3$.

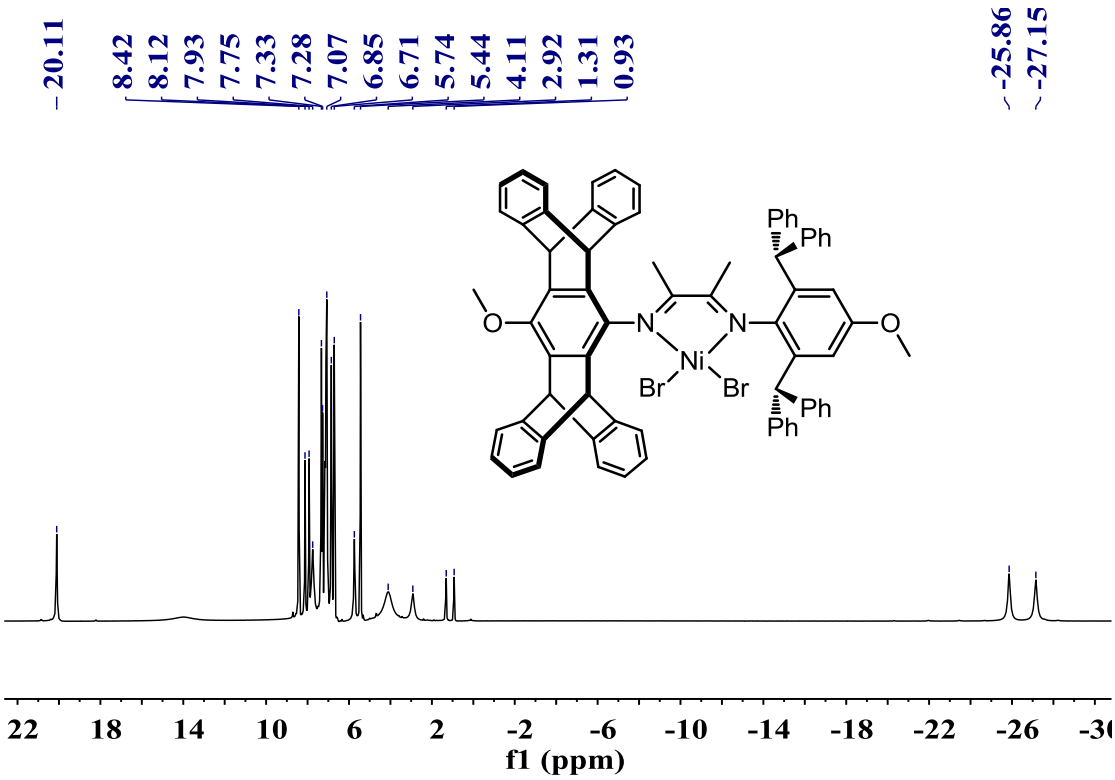


Figure S23. ^{1}H NMR spectrum of **Cat2** in $CDCl_3$

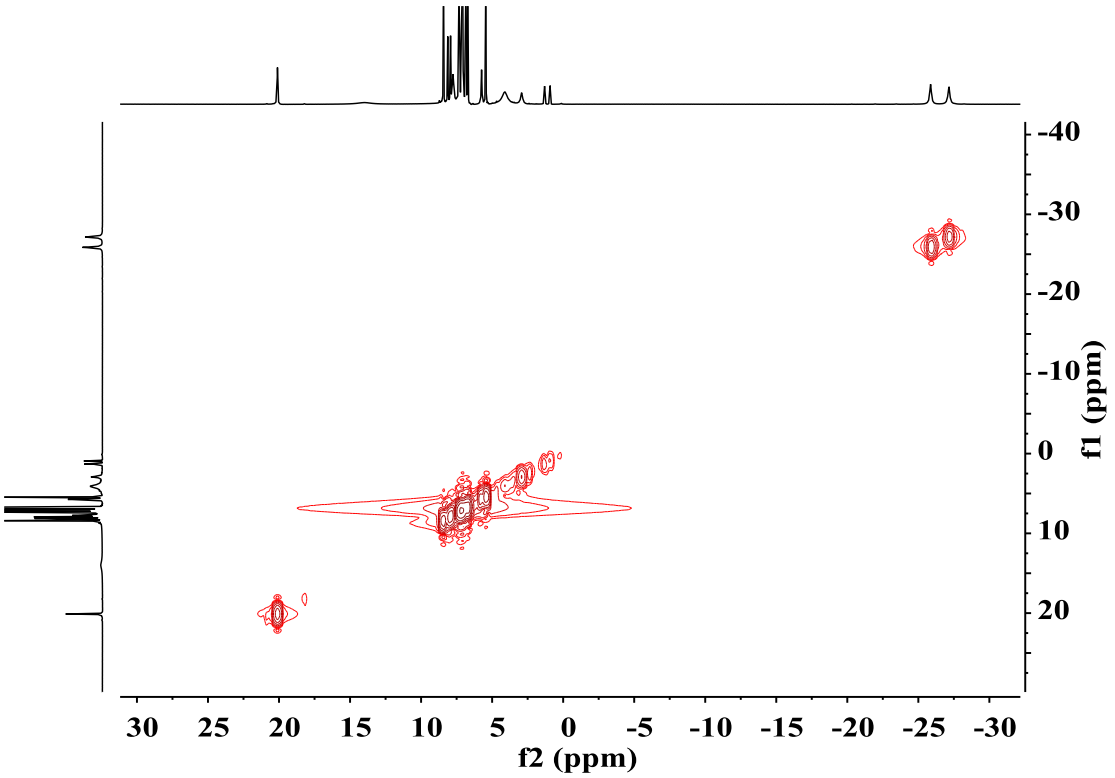


Figure S24. ^{1}H-^{1}H COSY NMR spectrum of **Cat2** in $CDCl_3$.

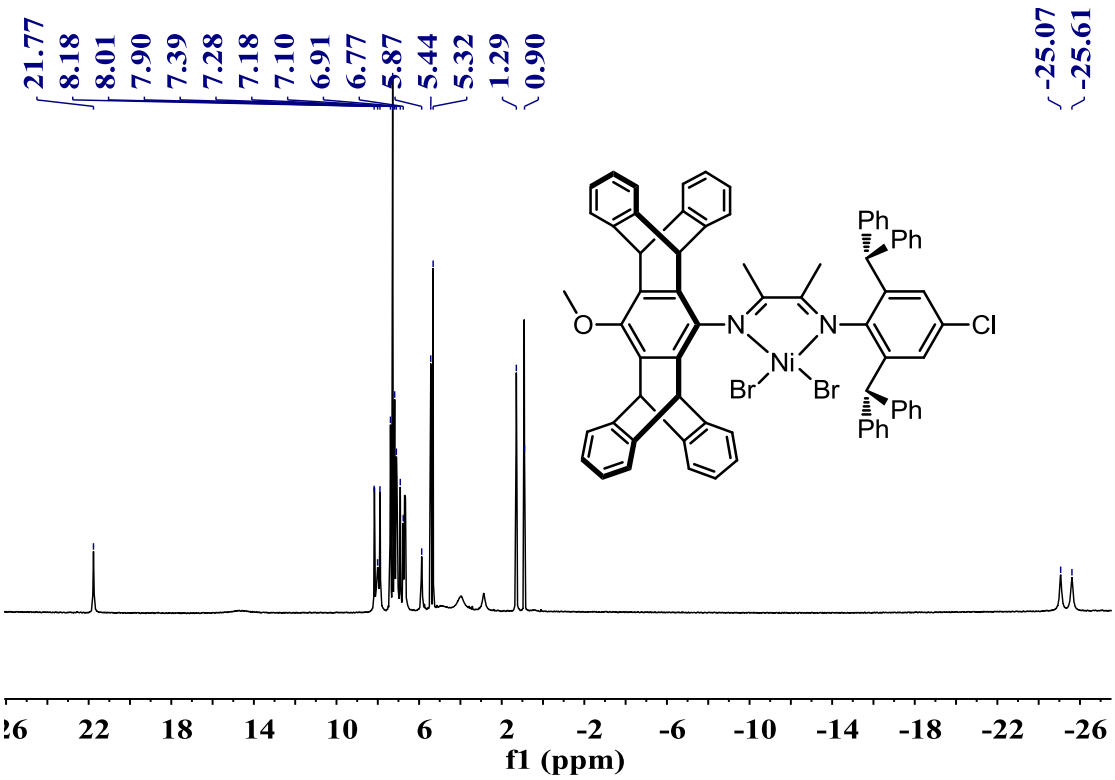


Figure S25. ^{1}H NMR spectrum of **Cat3** in $CDCl_3$

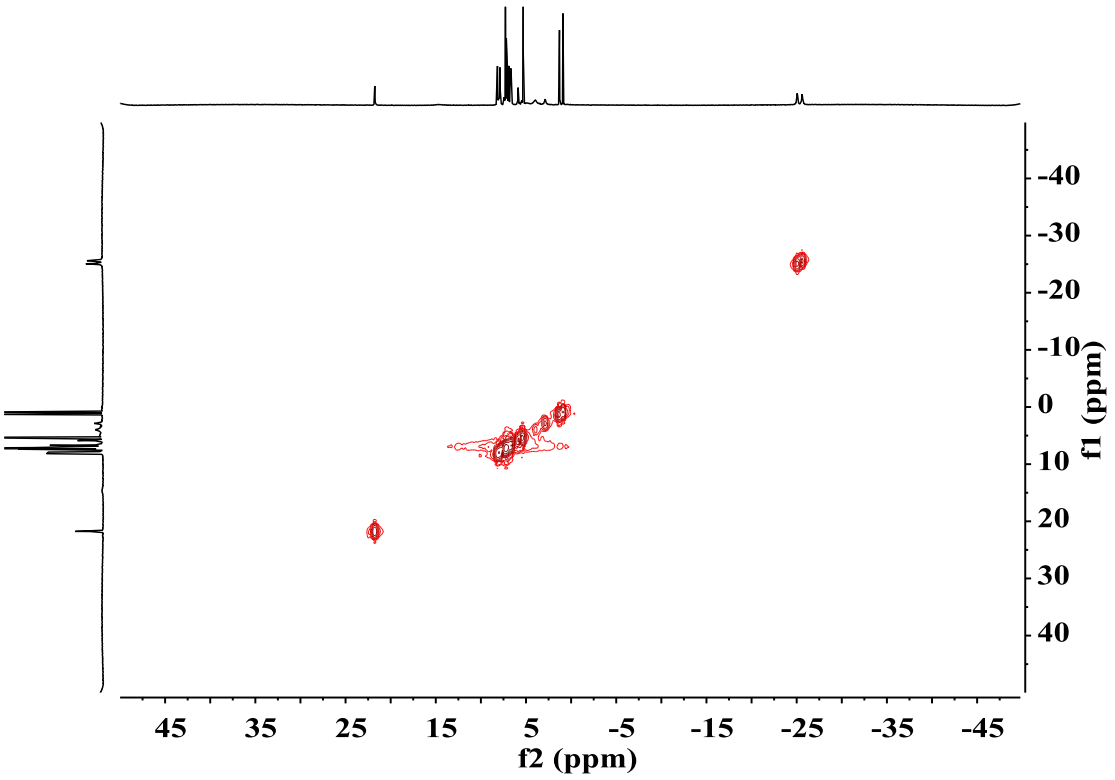


Figure S26. ^{1}H-^{1}H COSY NMR spectrum of **Cat3** in $CDCl_3$.

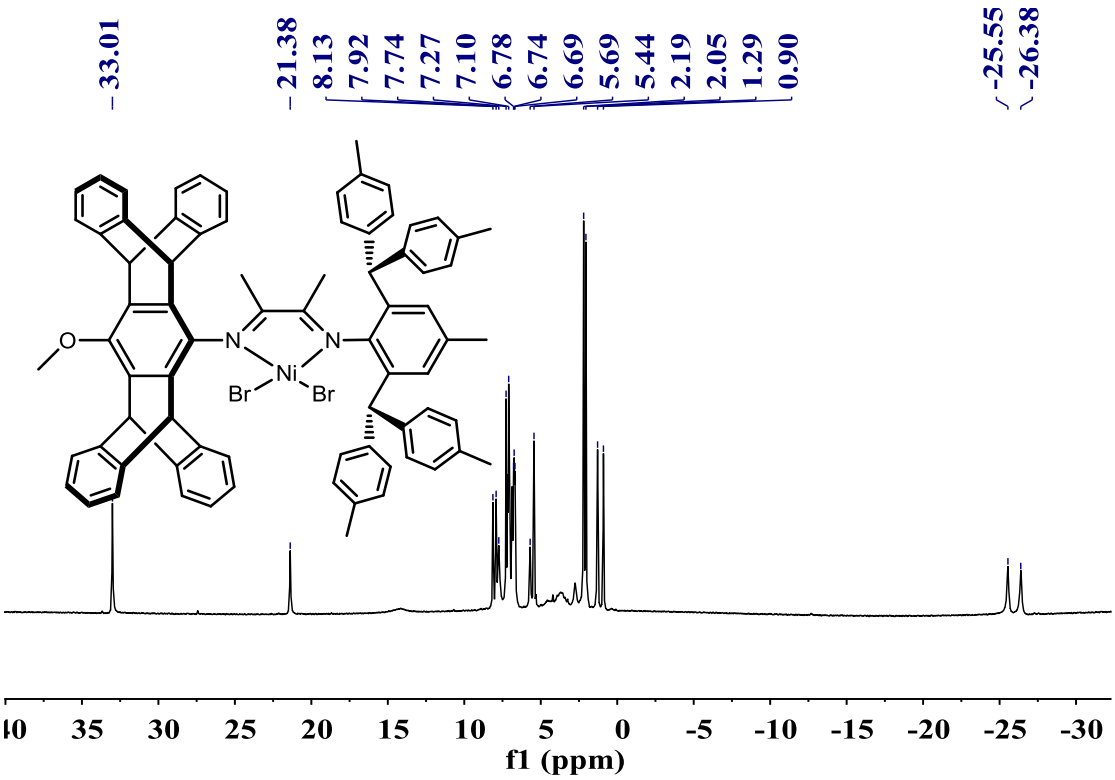


Figure S27. ^{1}H NMR spectrum of **Cat4** in $CDCl_3$

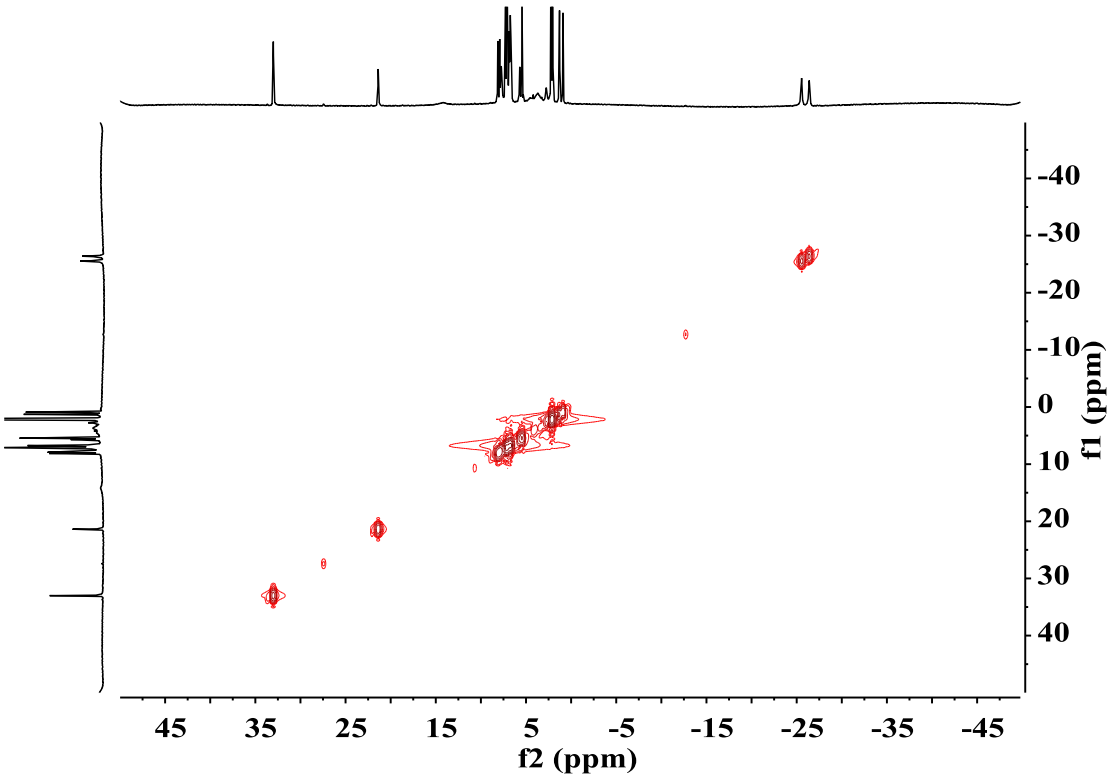


Figure S28. ^{1}H-^{1}H COSY NMR spectrum of **Cat4** in $CDCl_3$.

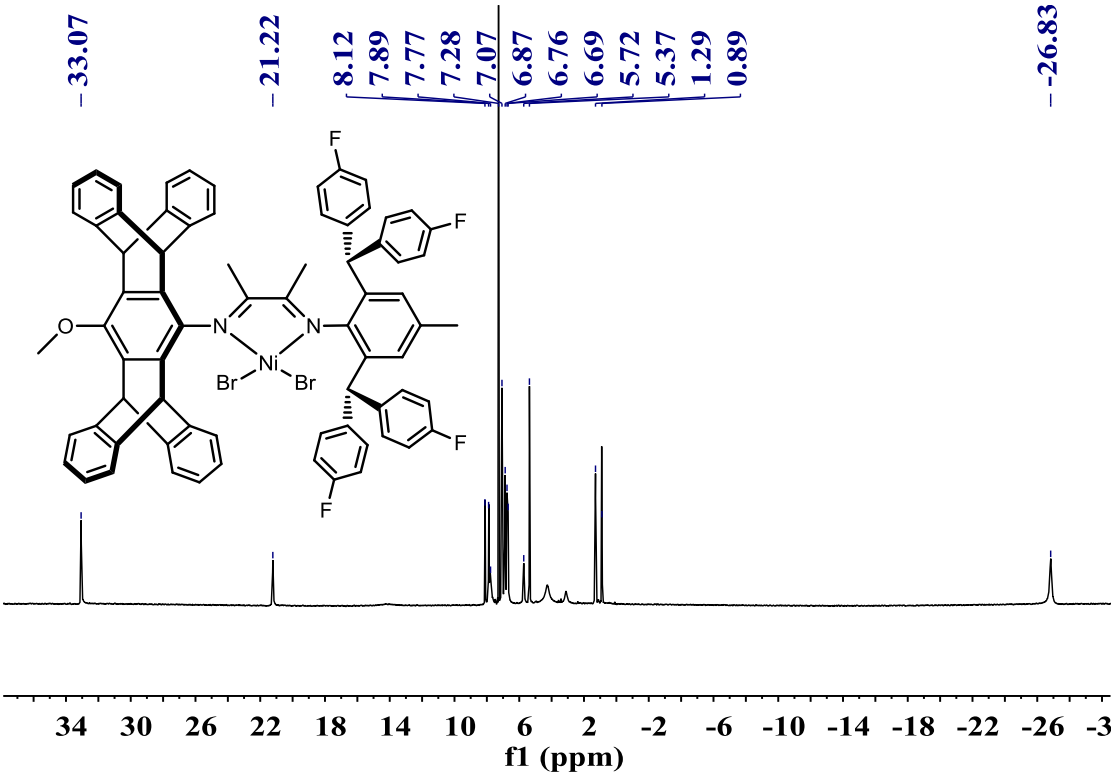


Figure S29. ^{1}H NMR spectrum of **Cat5** in $CDCl_3$

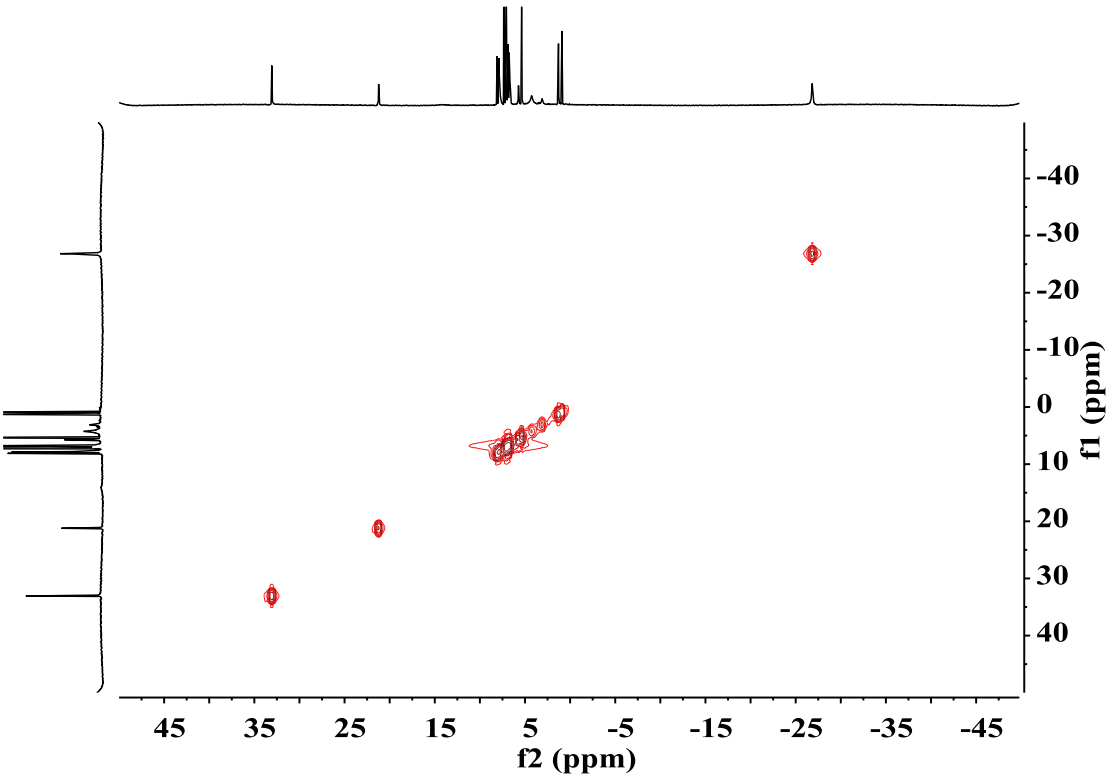


Figure S30. ^{1}H-^{1}H COSY NMR spectrum of **Cat5** in $CDCl_3$.

5 NMR figures of (co)polymers

Me groups / 1000C = $\frac{2*I_{Me}}{3*I_{tot}}$ * 1000 = $\frac{2*3}{3*(24.52+3)}$ * 1000 =73

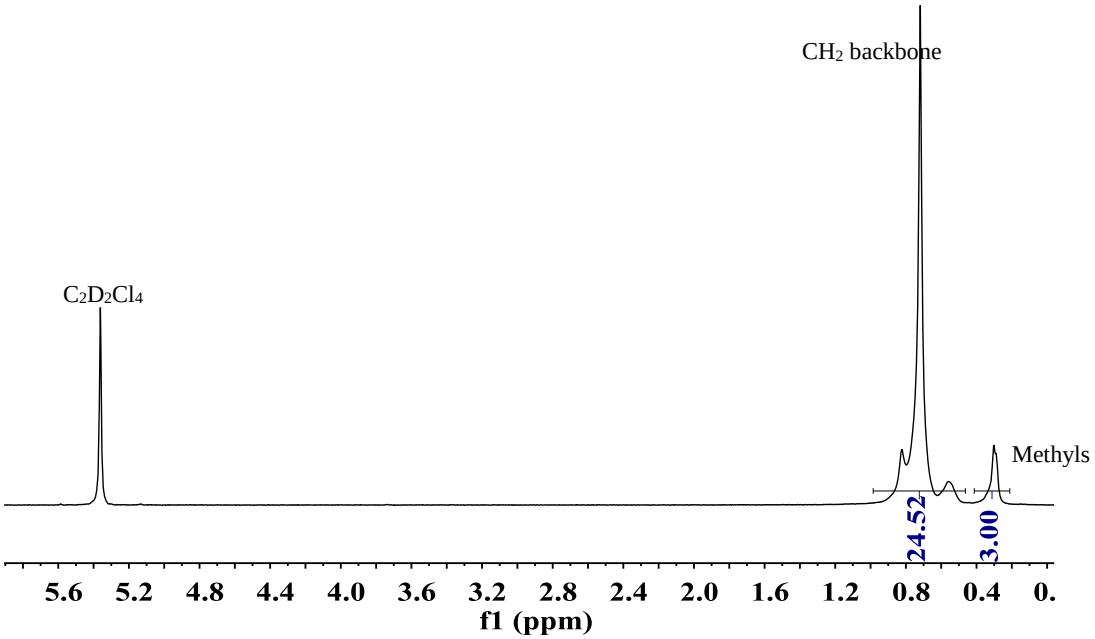


Figure S31. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat1** from table 1, entry 1.

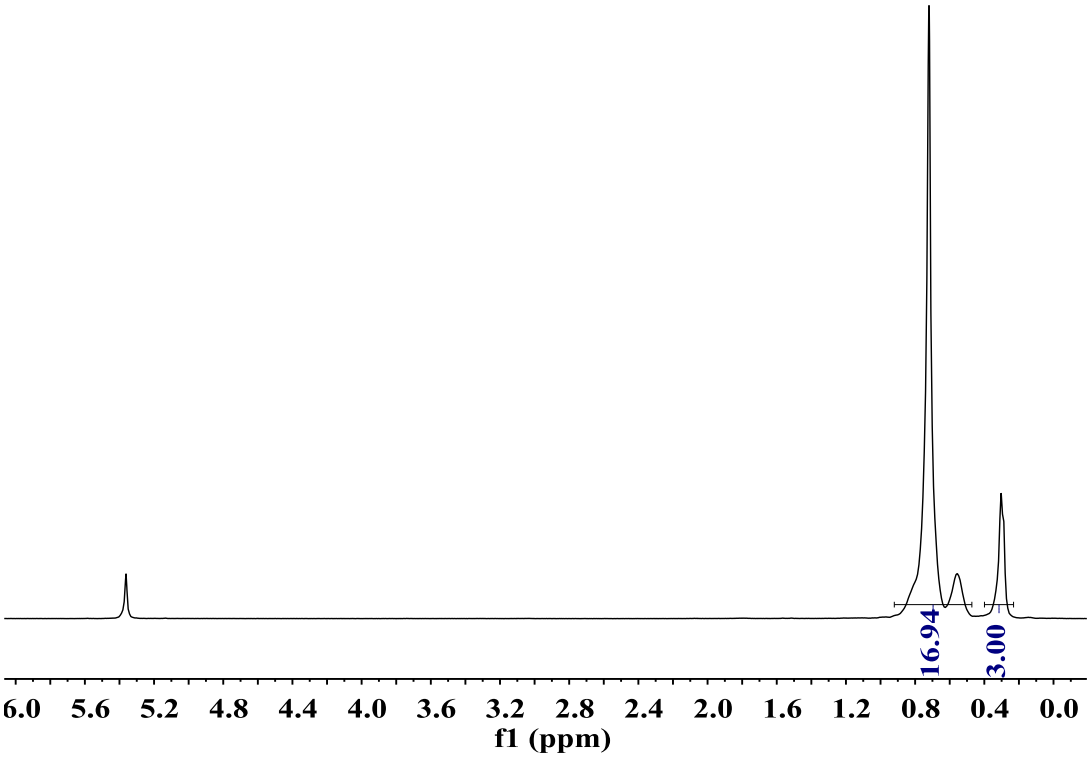


Figure S32. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat1** from table 1, entry 2.

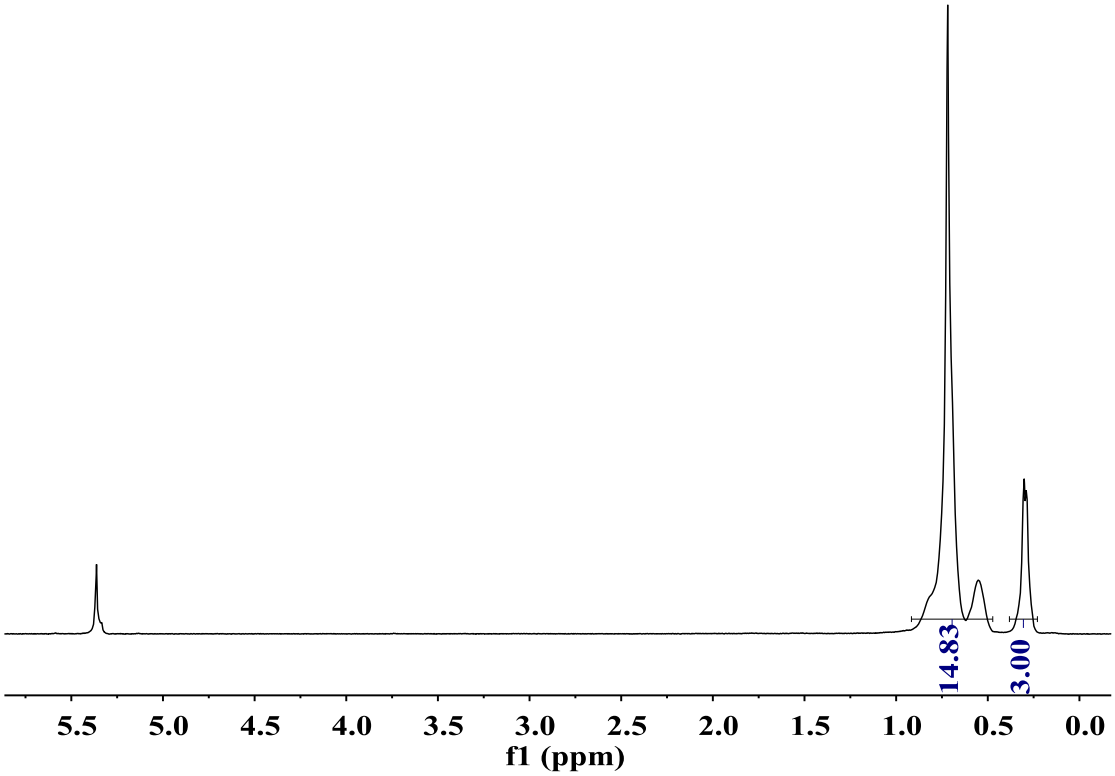


Figure S33. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat1** from table 1, entry 3.

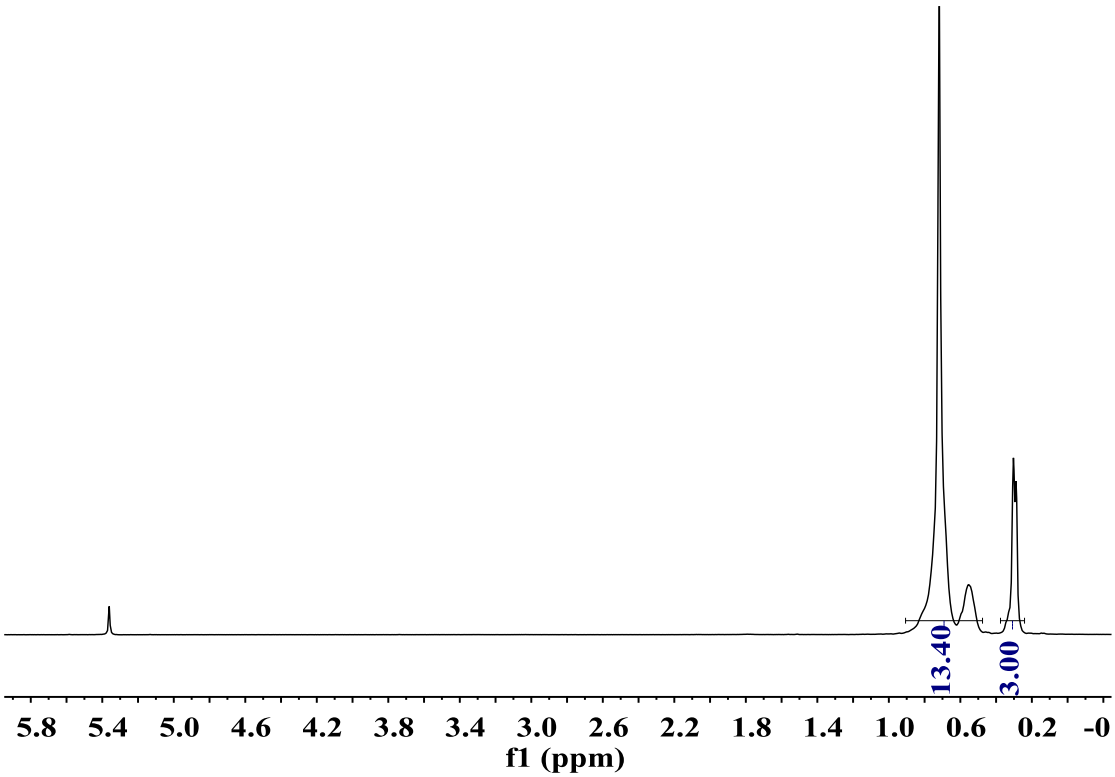


Figure S34. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat1** from table 1, entry 4.

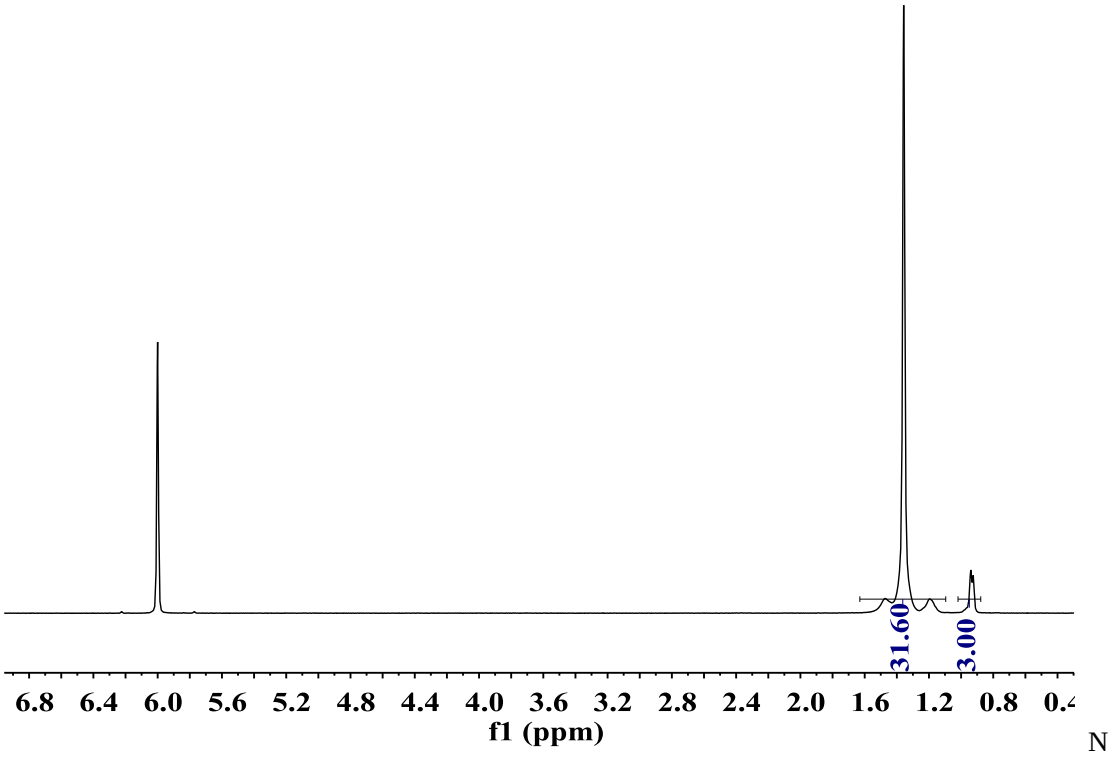


Figure S35. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat2** from table 1, entry 5.

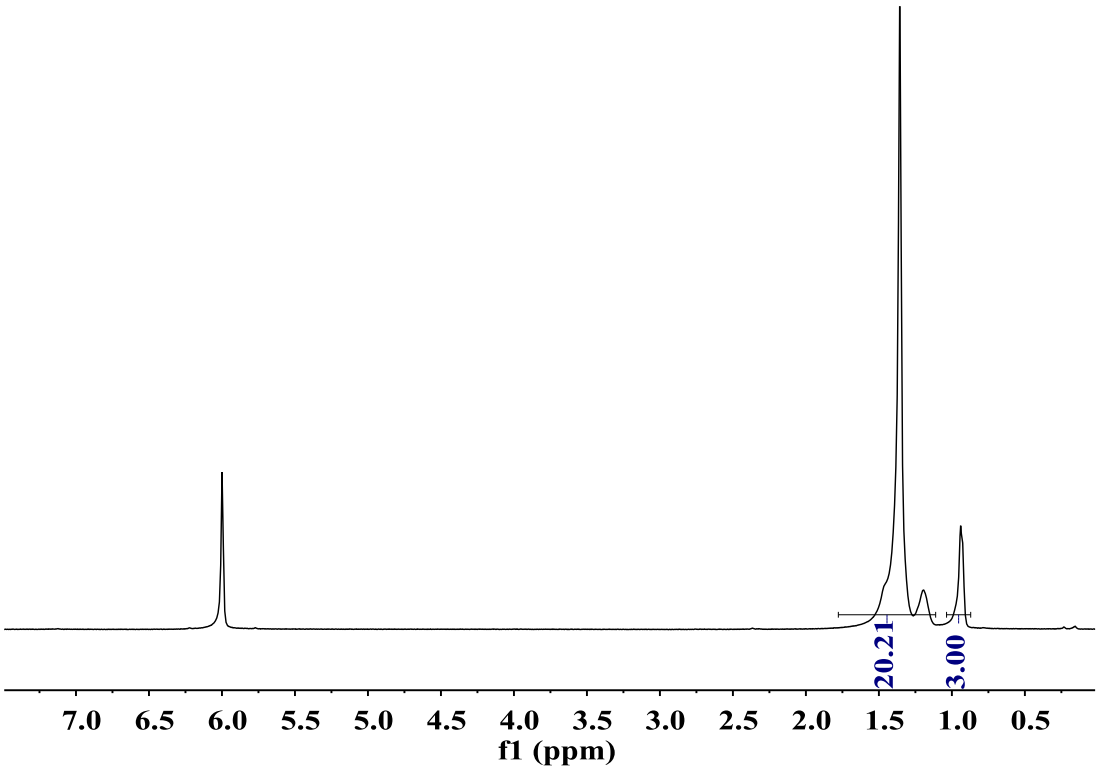


Figure S36. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat2** from table 1, entry 6.

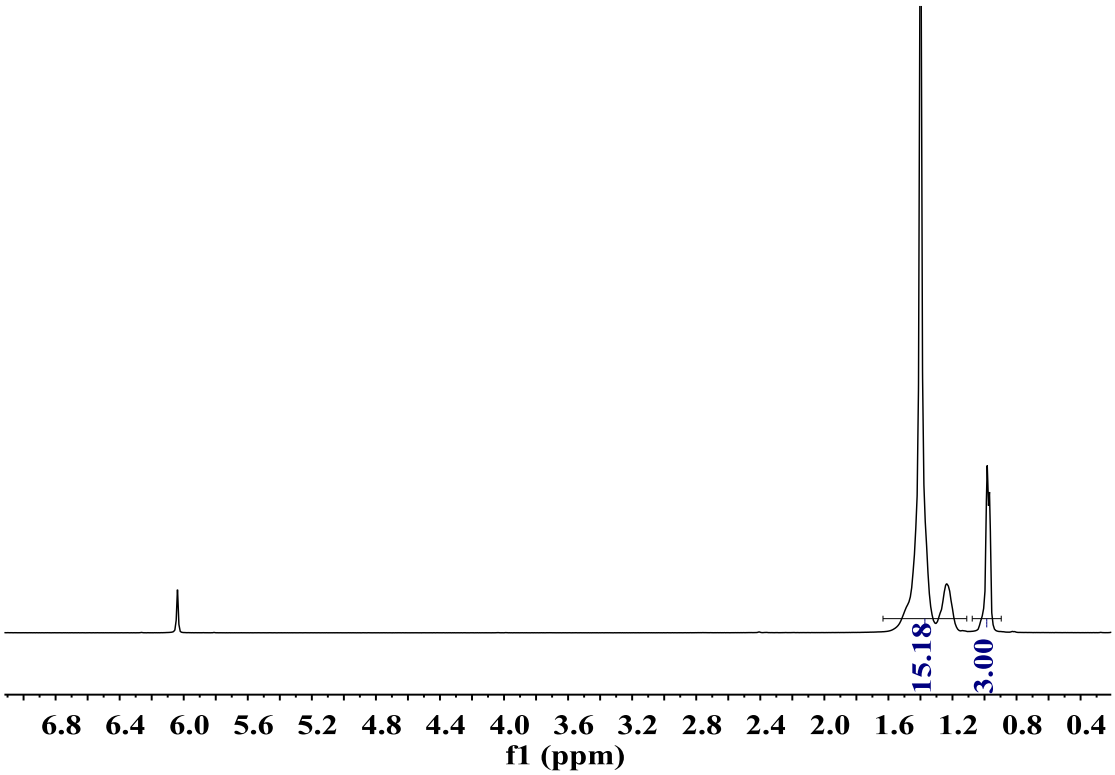


Figure S37. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat2** from table 1, entry 7.

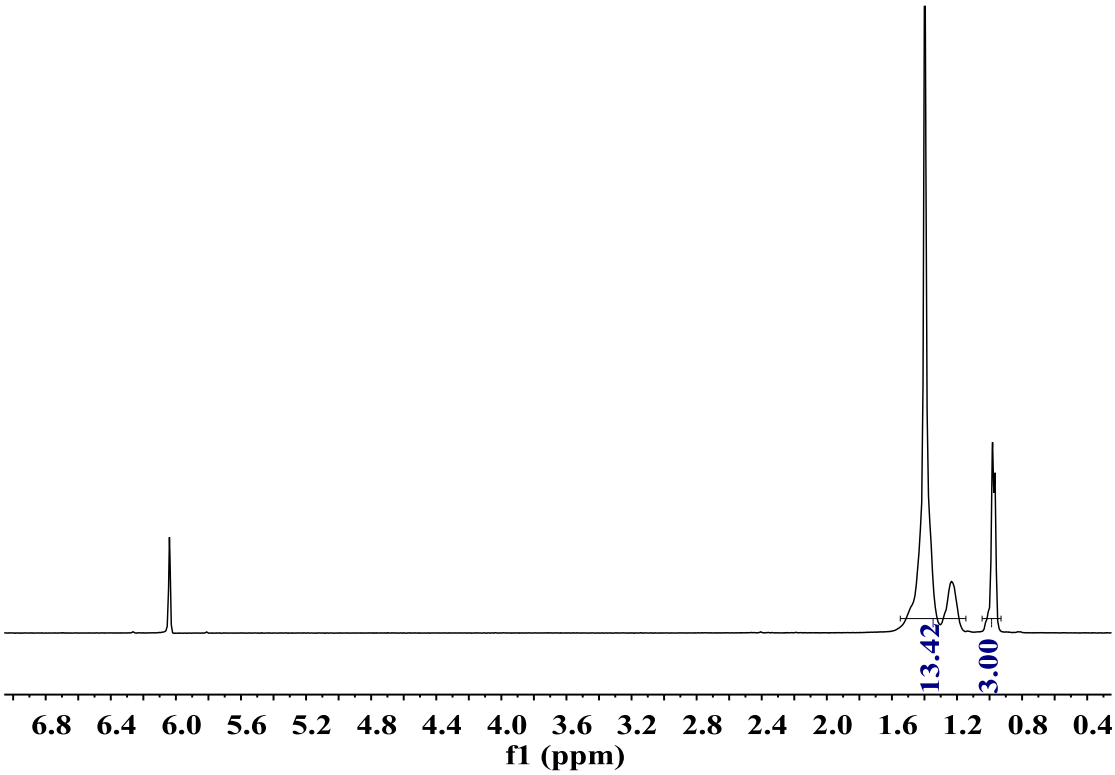


Figure S38. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat2** from table 1, entry 8.

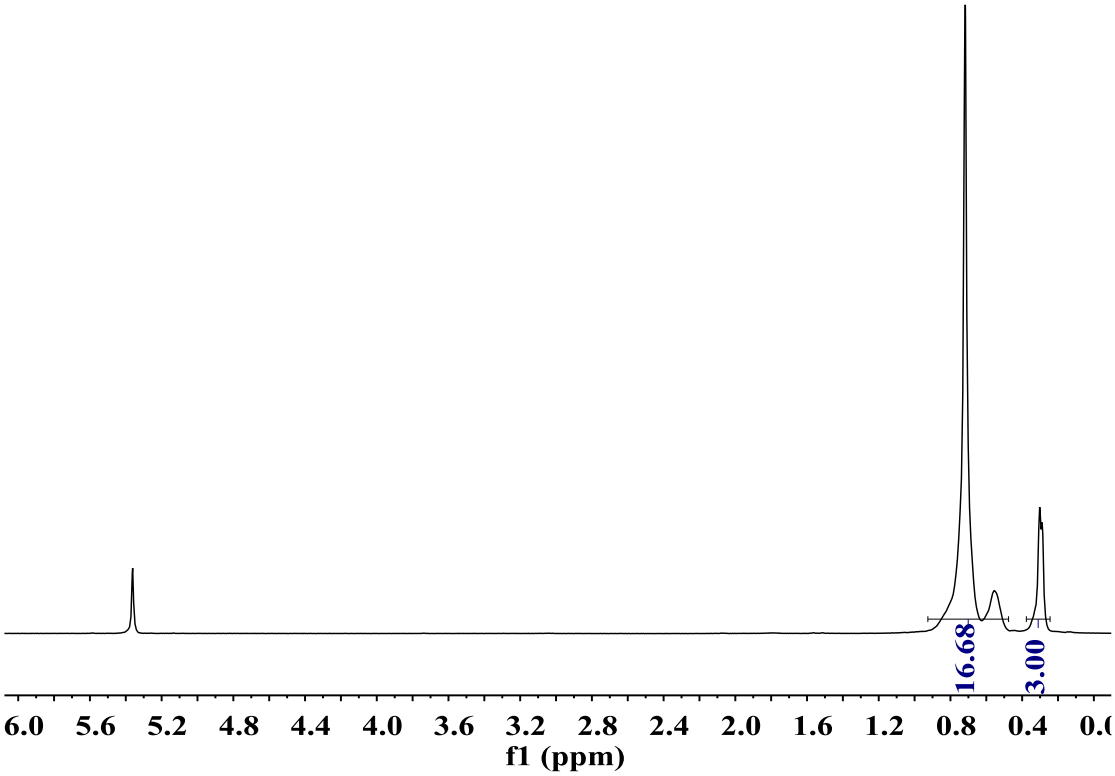


Figure S39. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat3** from table 1, entry 10.

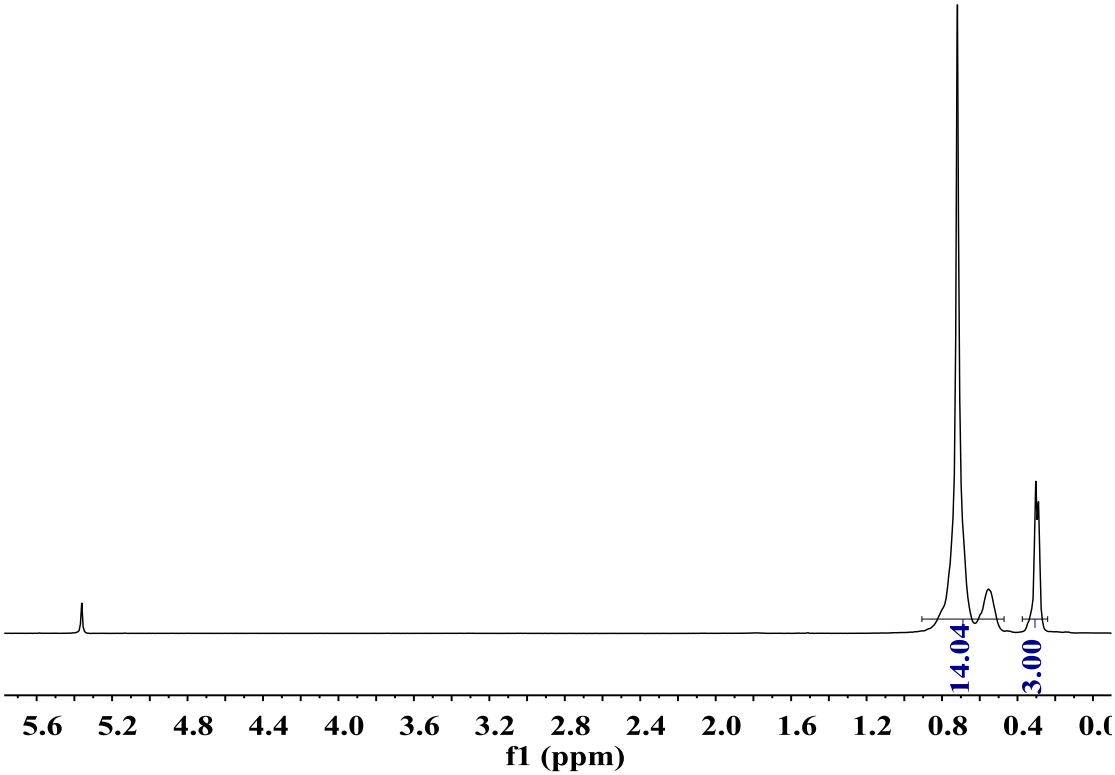


Figure S40. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat3** from table 1, entry 11.

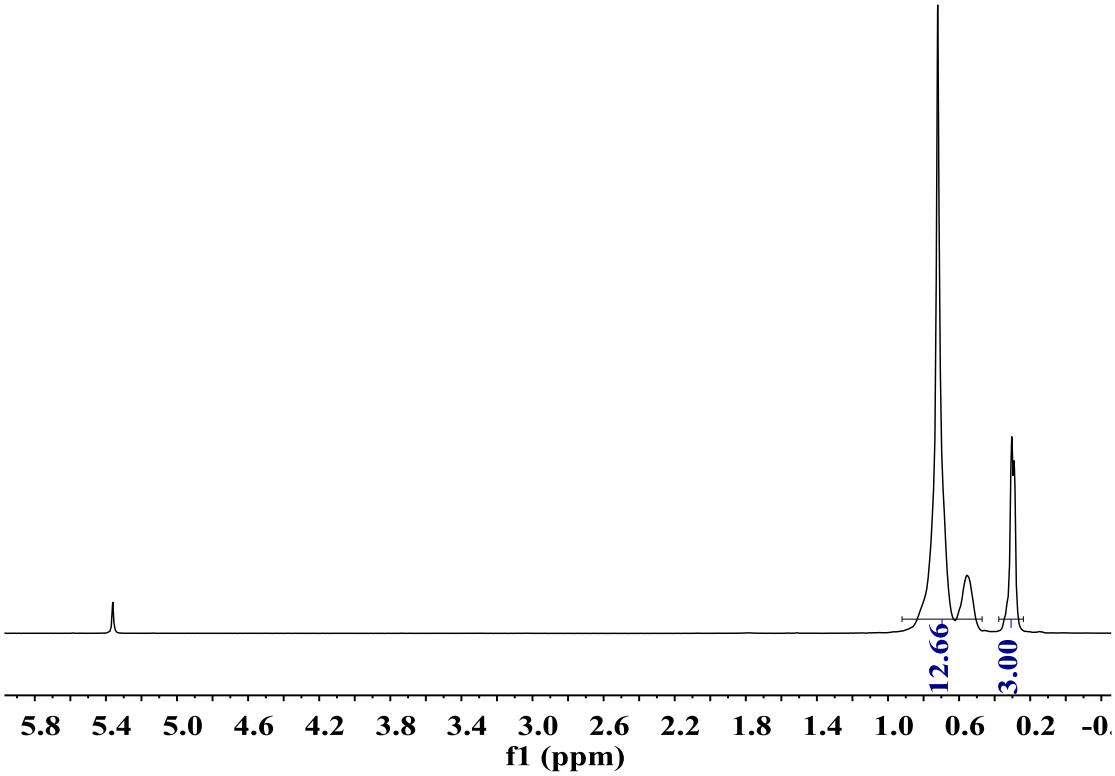


Figure S41. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat3** from table 1, entry 12.

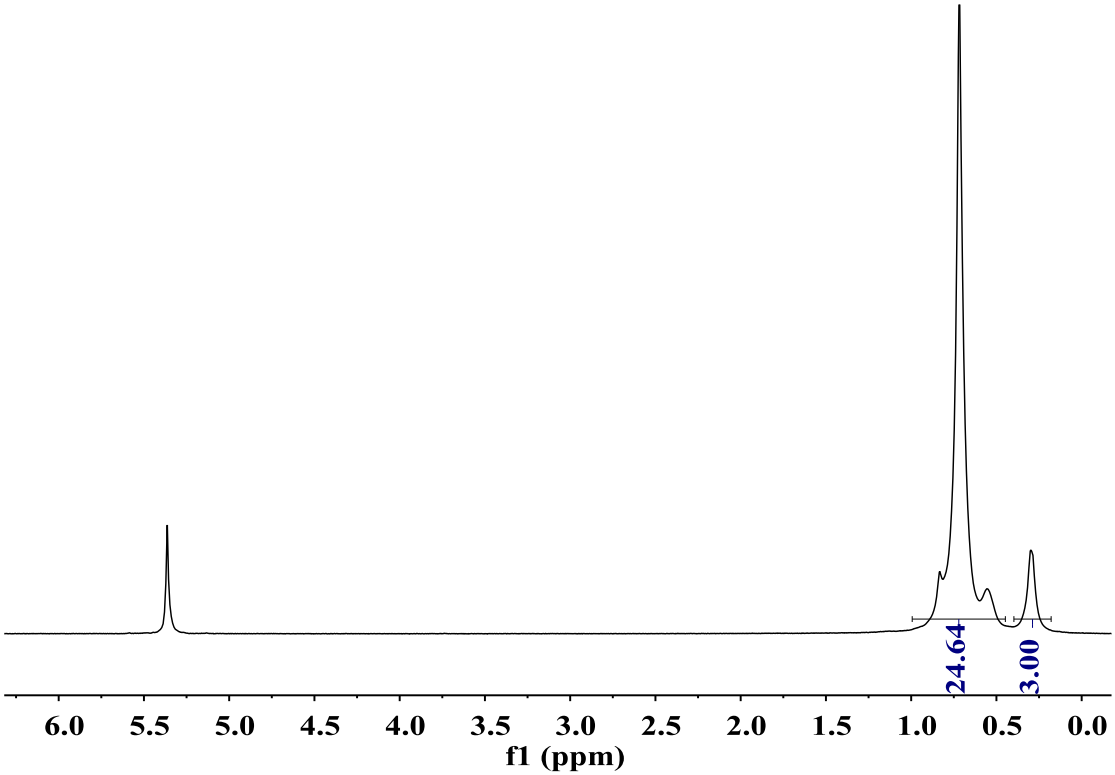


Figure S42. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat4** from table 1, entry 13.

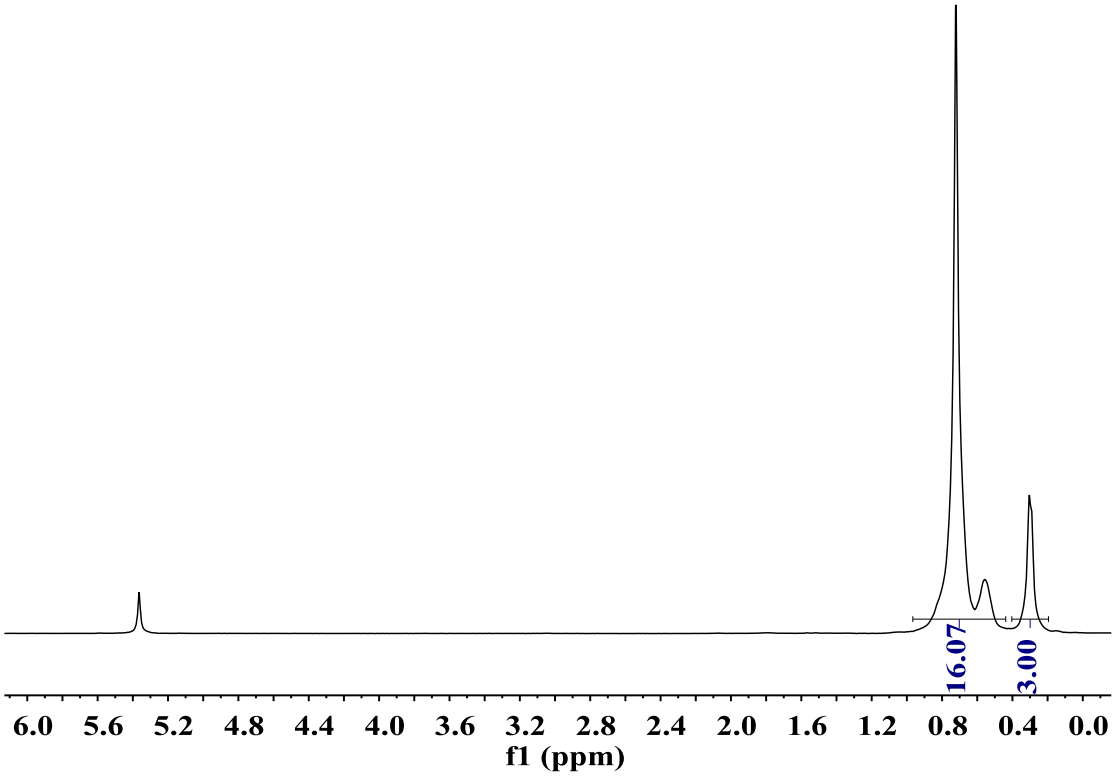


Figure S43. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat4** from table 1, entry 15.

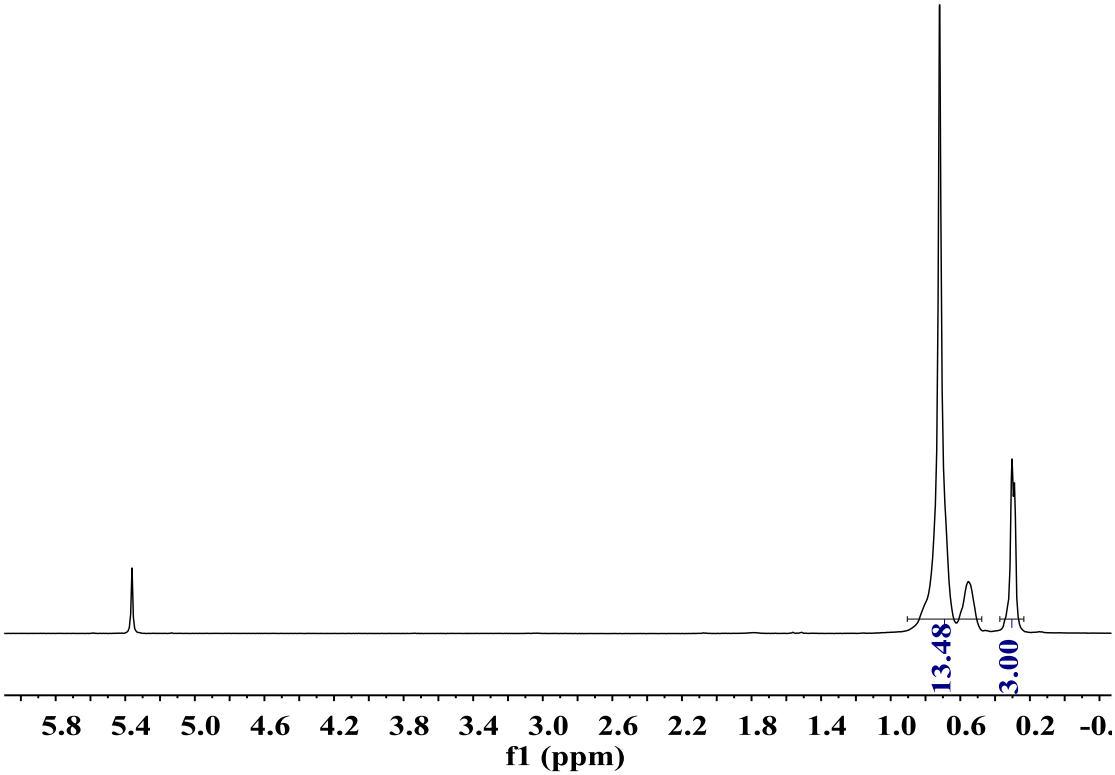


Figure S44. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat4** from table 1, entry 16.

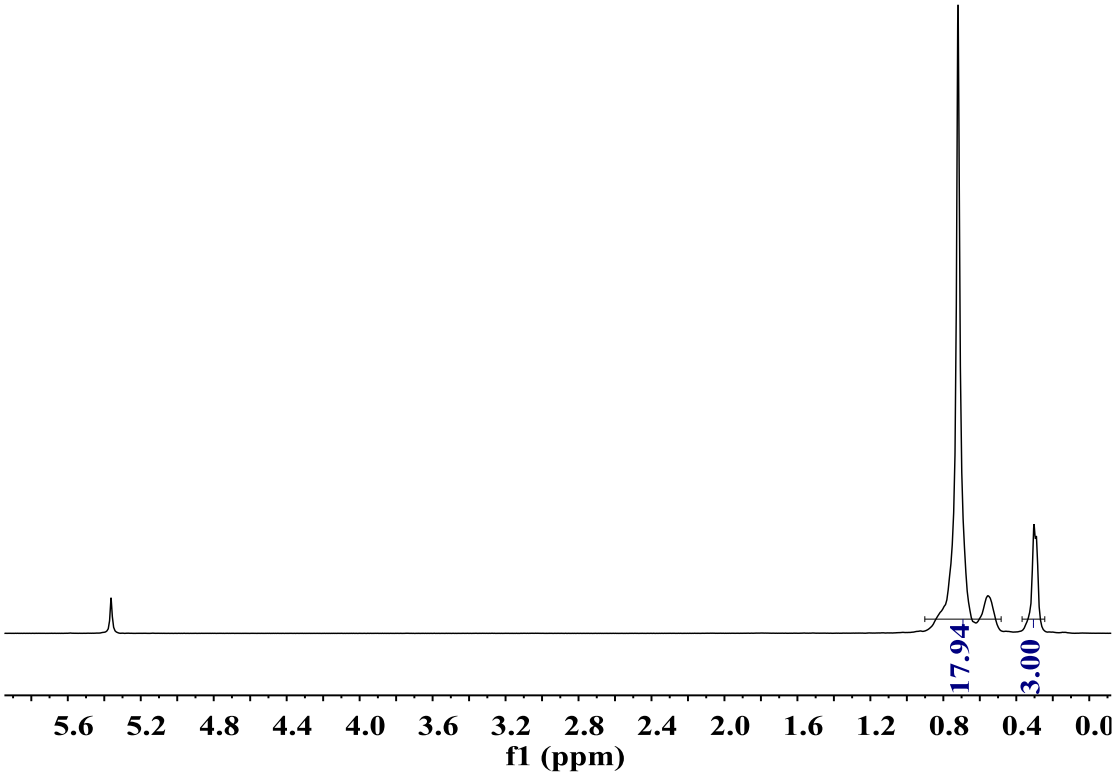


Figure S45. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat5** from table 1, entry 18.

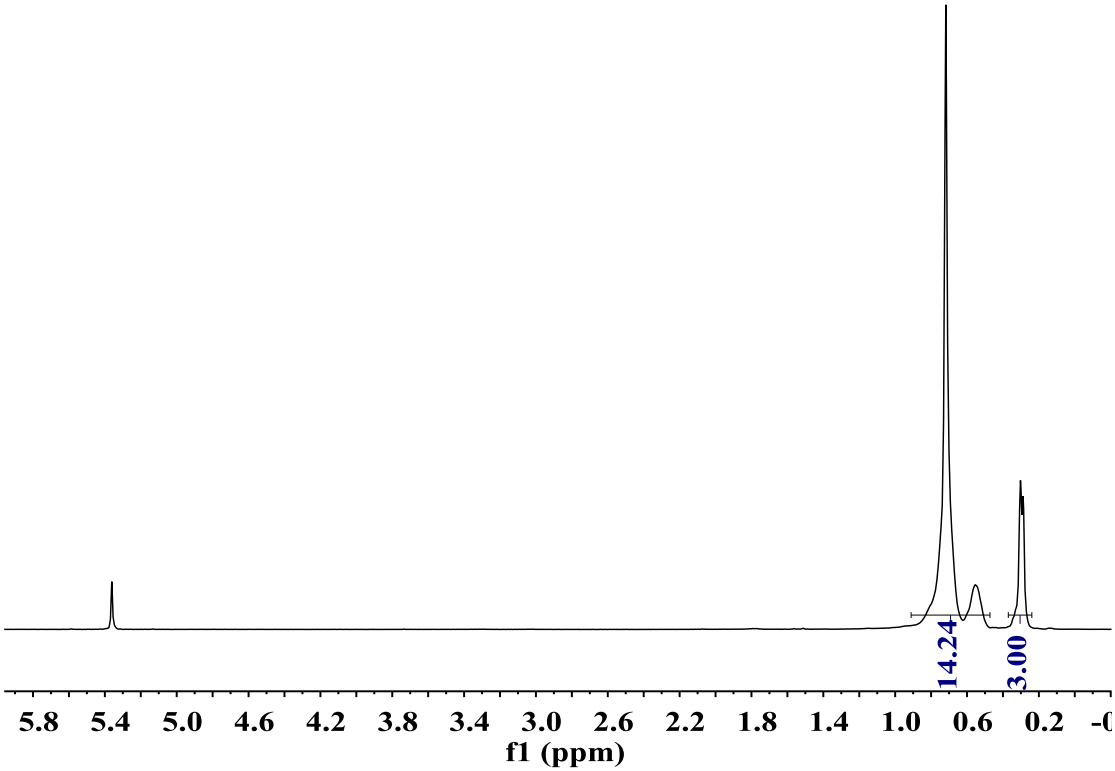


Figure S46. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat5** from table 1, entry 19.

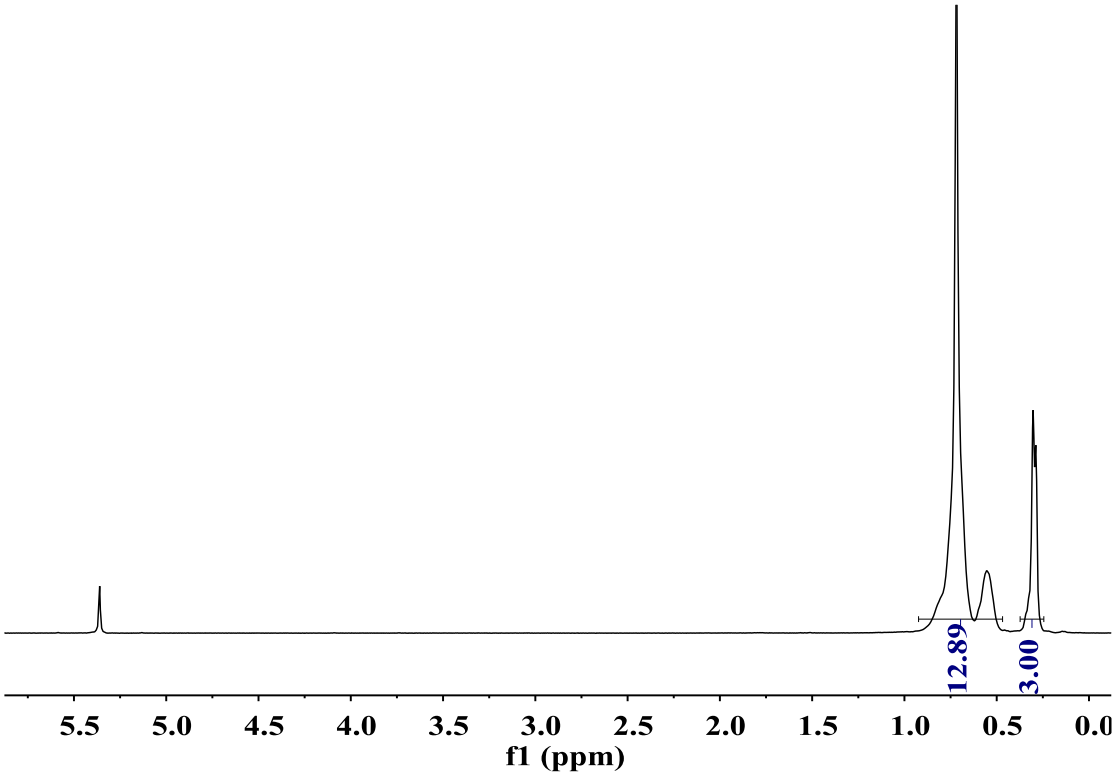


Figure S47. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat5** from table 1, entry 20.

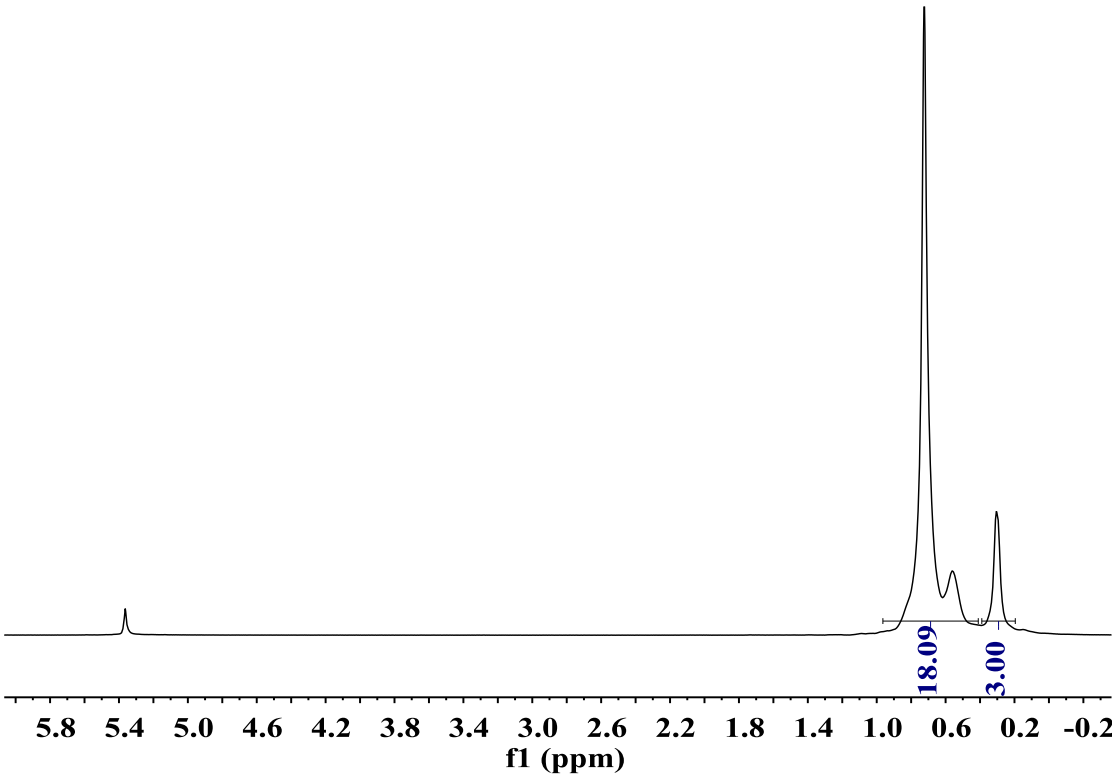


Figure S48. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat1** from table 1, entry 21.

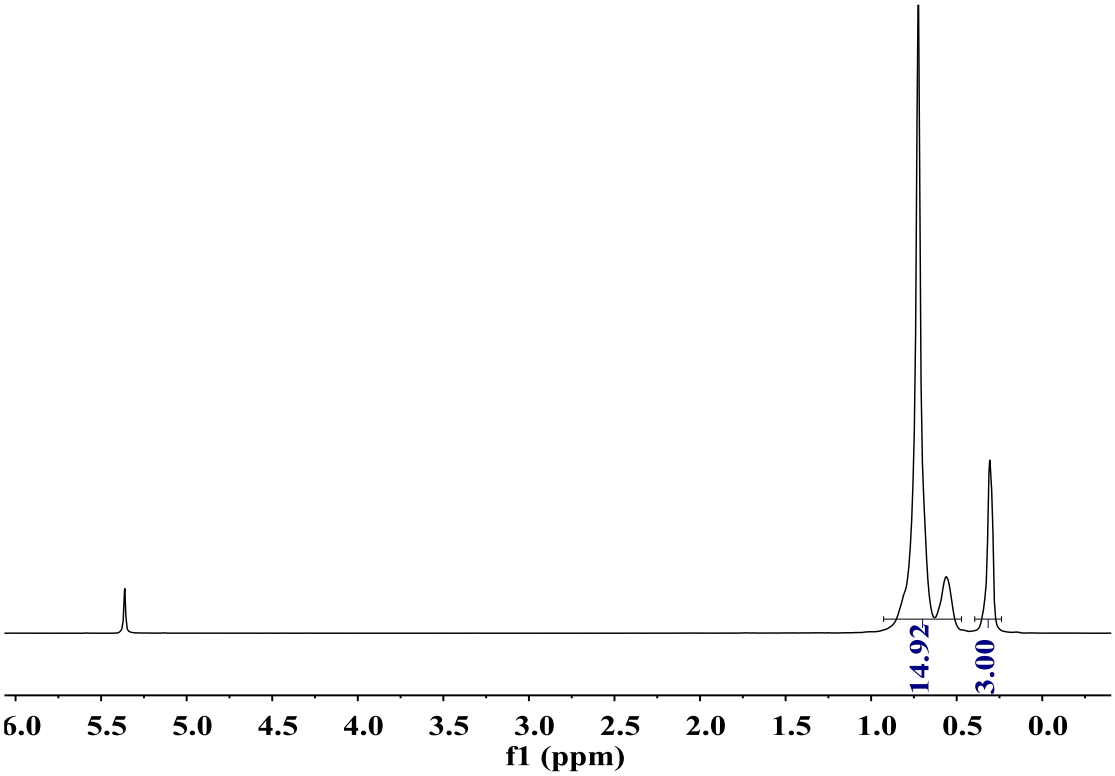


Figure S49. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat1** from table 1, entry 22.

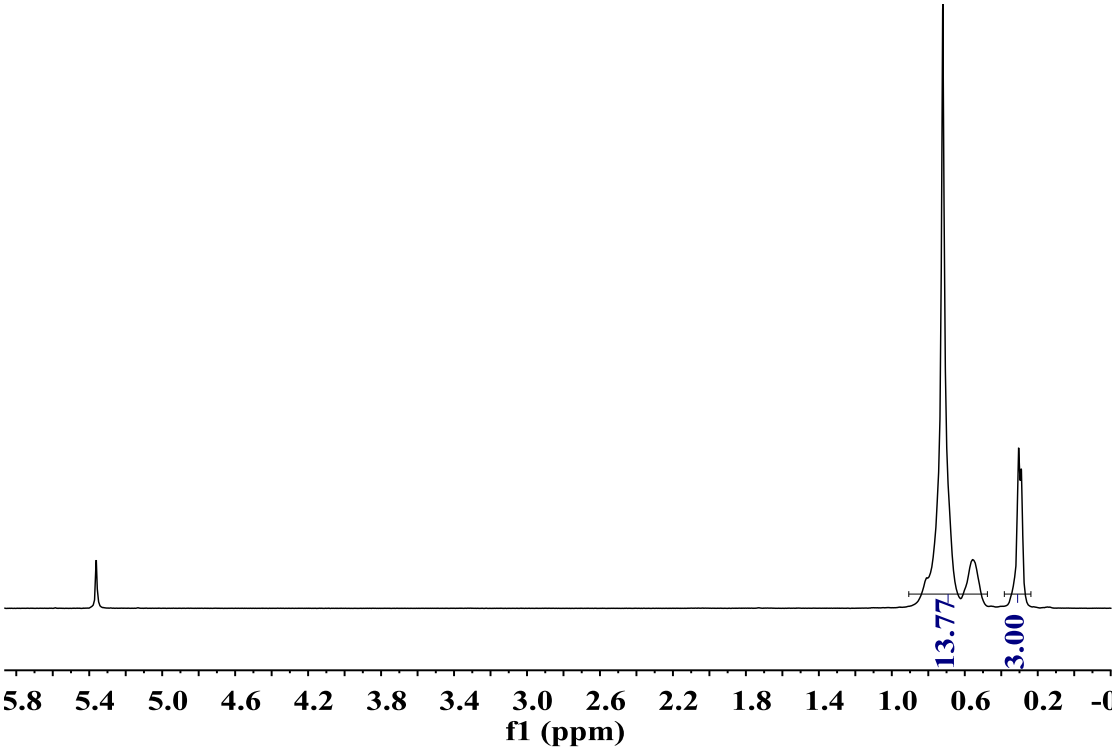


Figure S50. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat1** from table 1, entry 23.

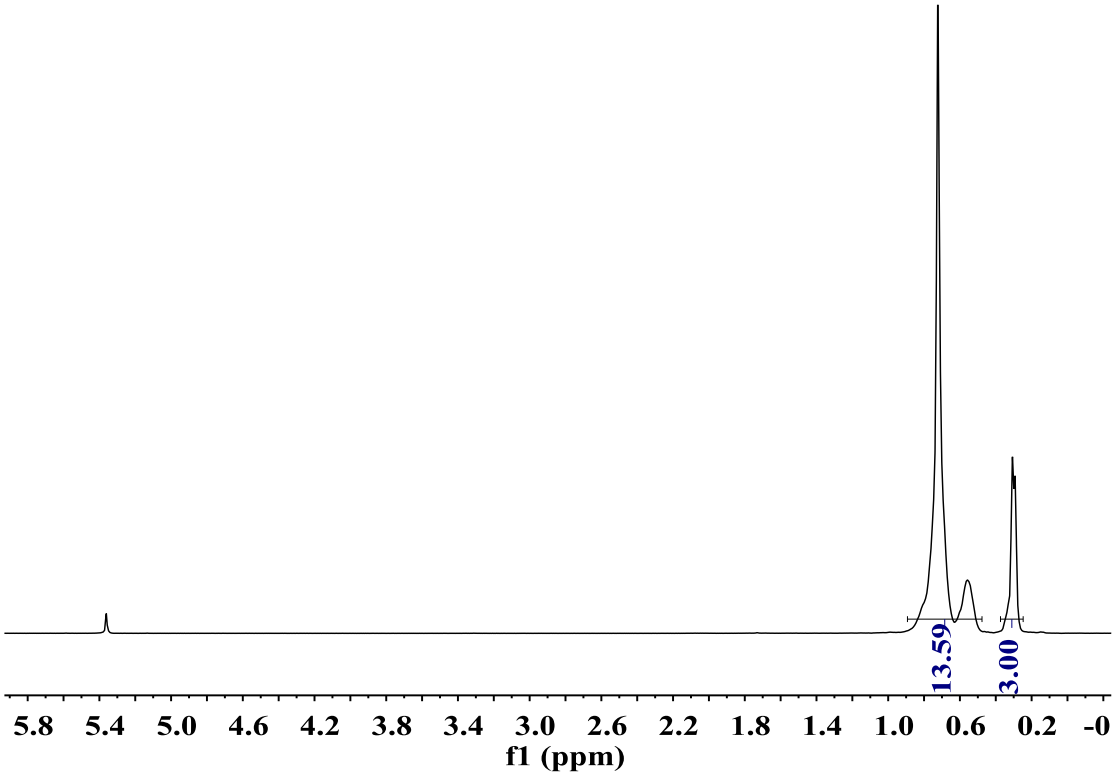


Figure S51. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat1** from table 1, entry 24.

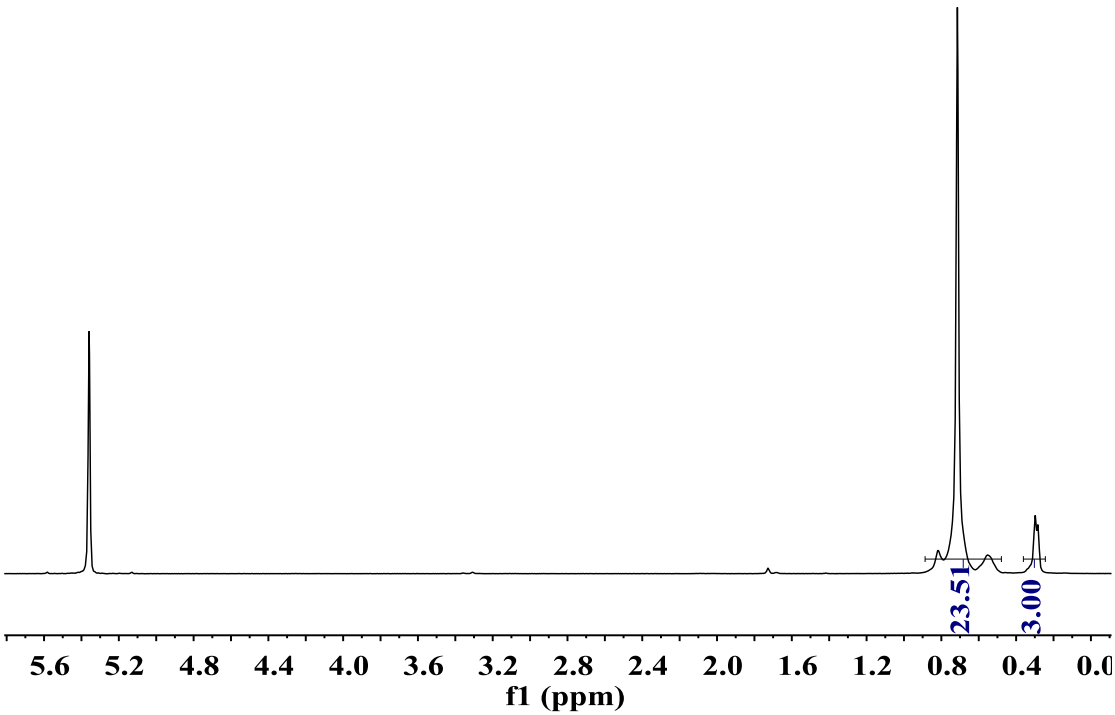


Figure S52. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat2** from table 1, entry 25.

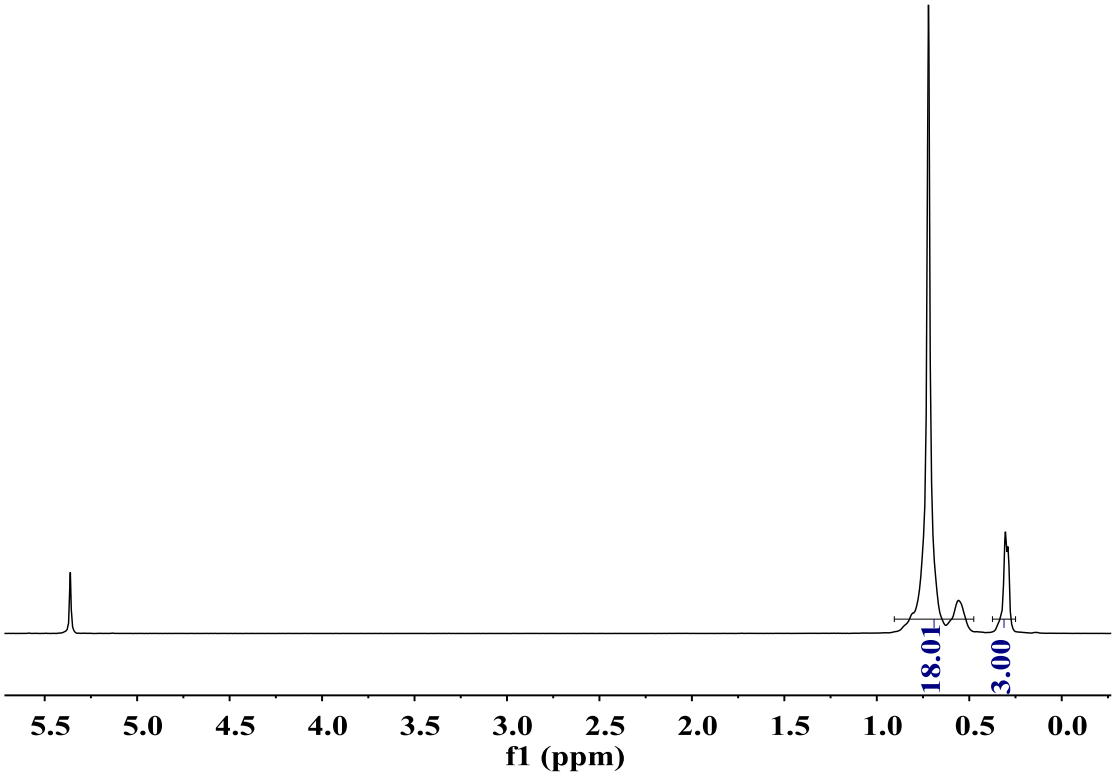


Figure S53. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat3** from table 1, entry 26.

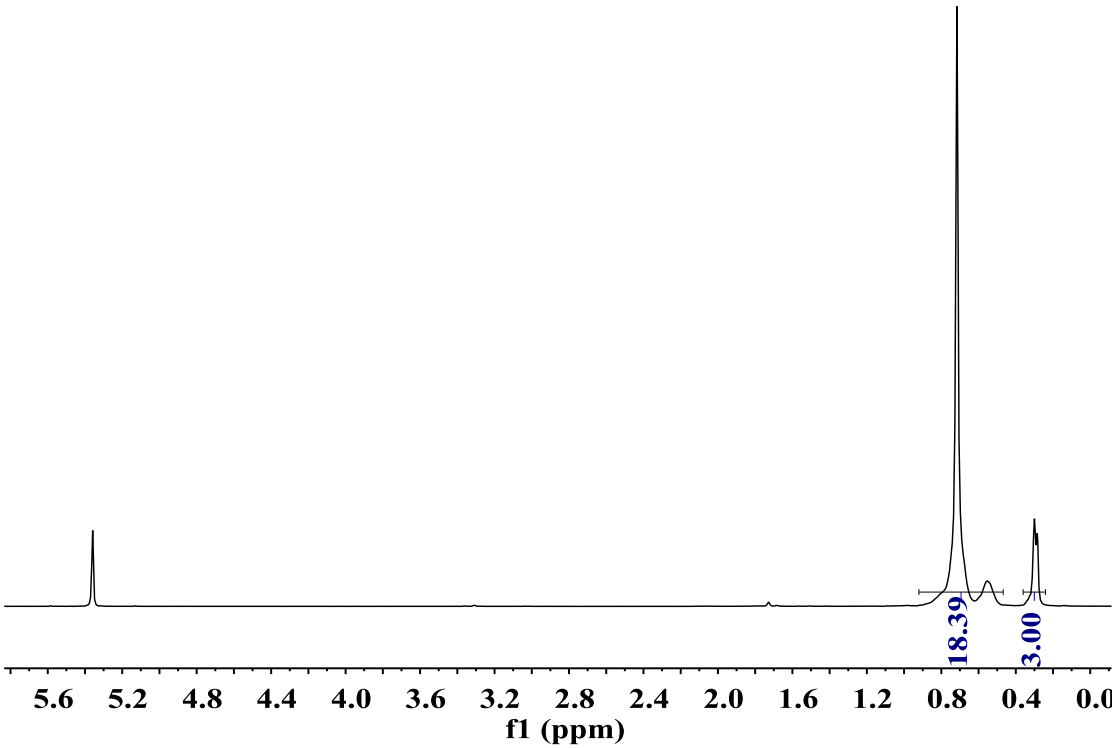


Figure S54. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat4** from table 1, entry 27.

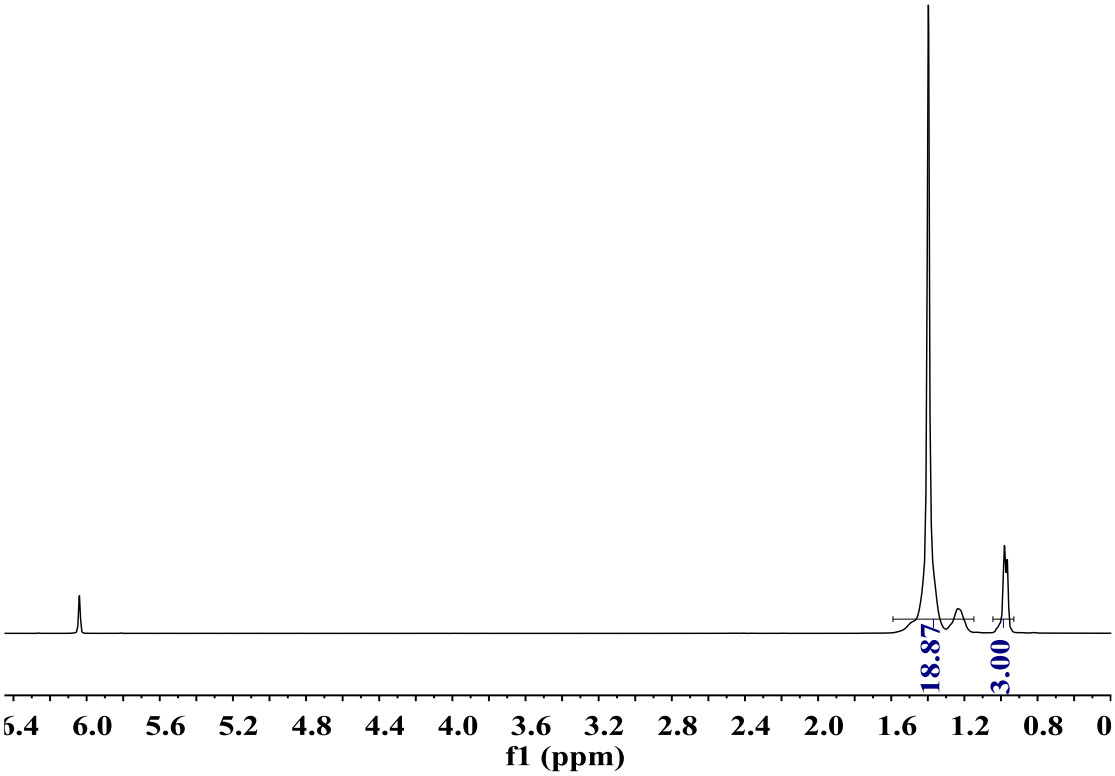


Figure S55. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat5** from table 1, entry 28.

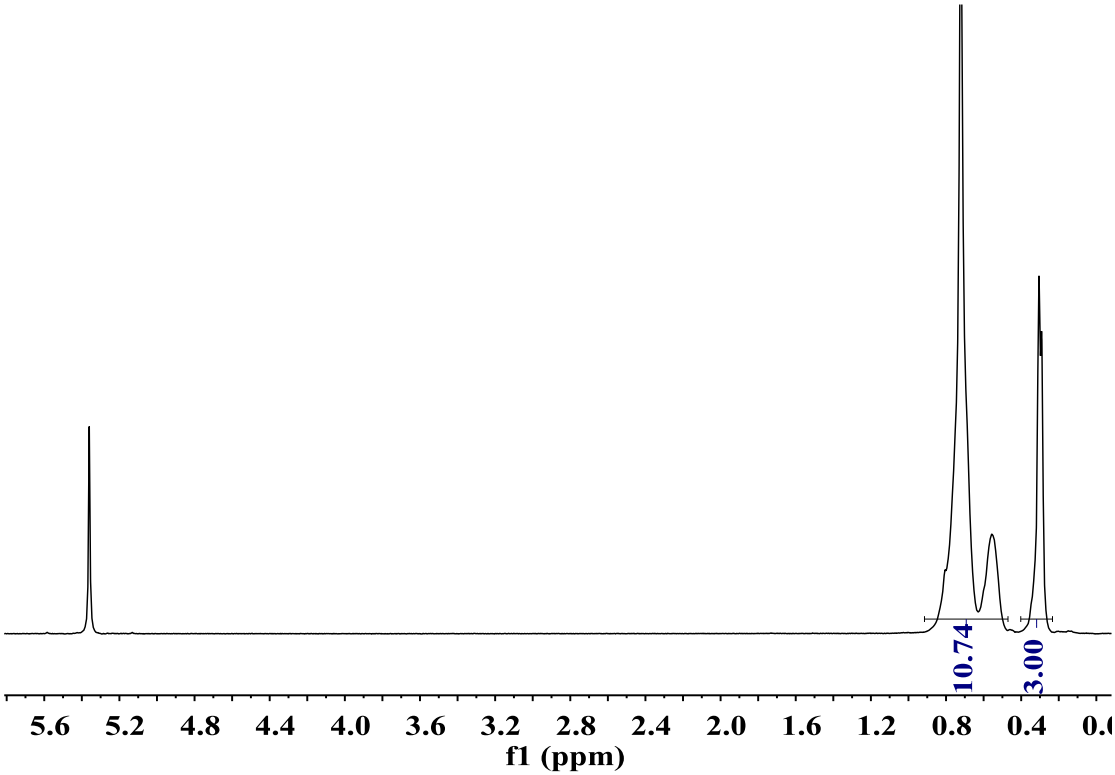


Figure S56. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat3** from table 1, entry 29.

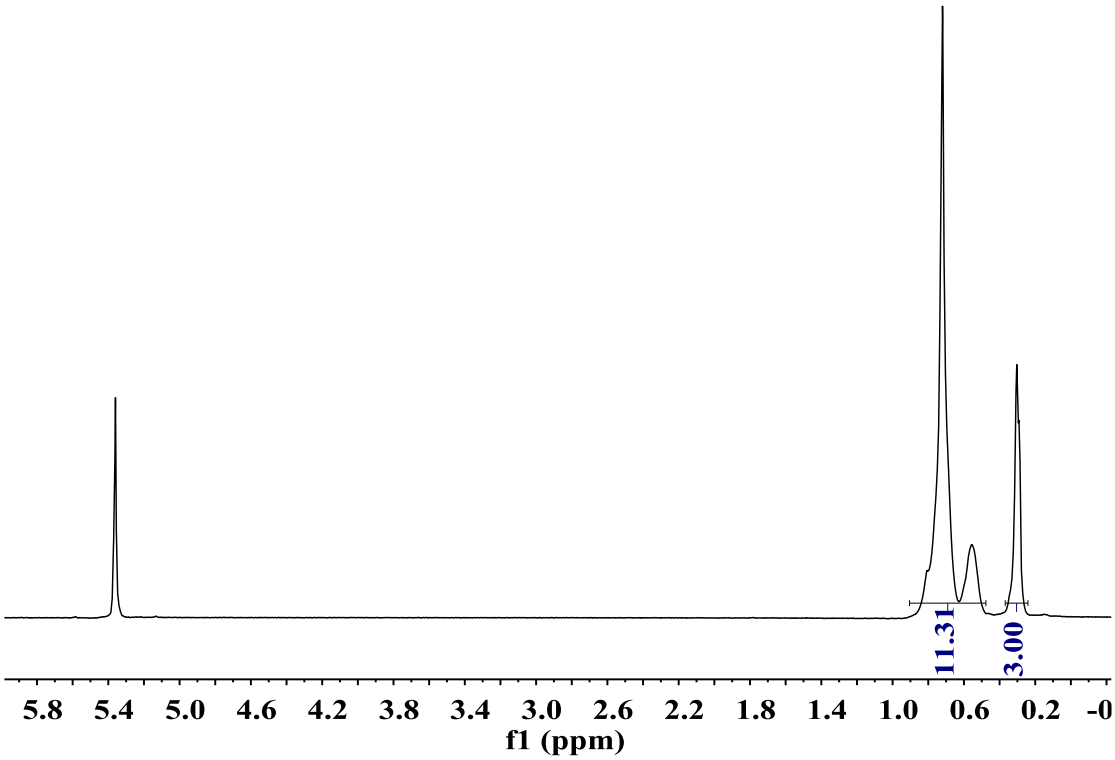


Figure S57. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat3** from table 1, entry 30.

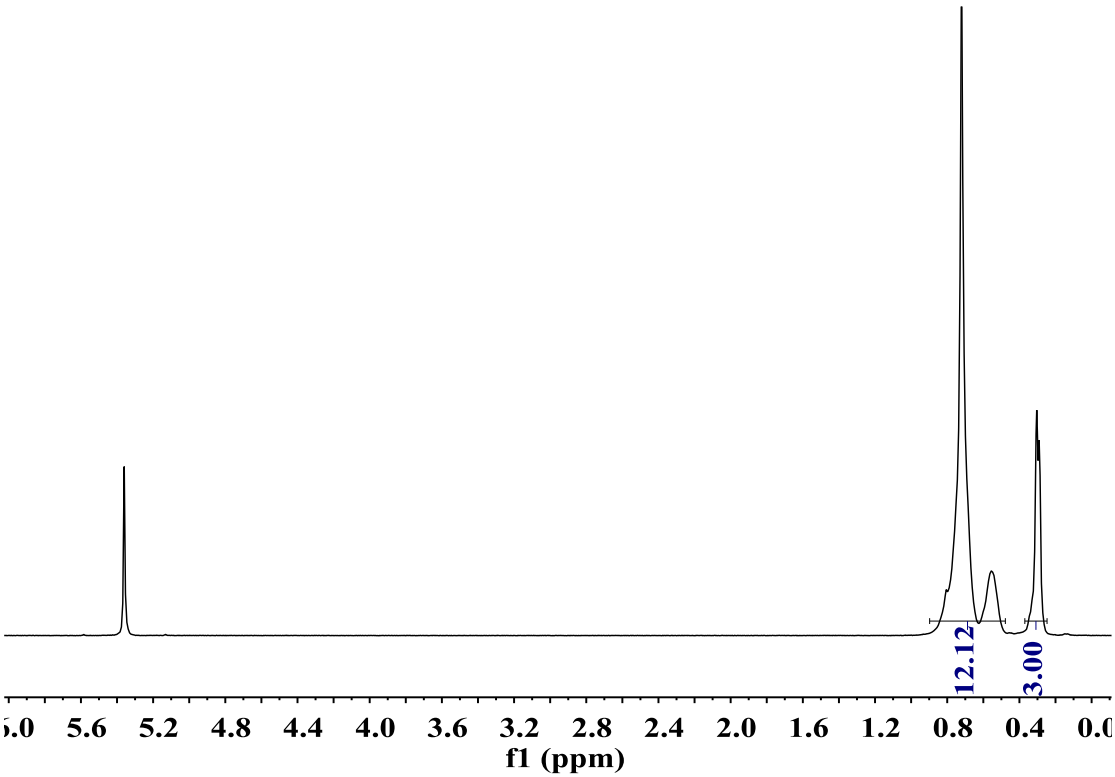


Figure S58. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by **Cat3** from table 1, entry 31.

$$X_M = \frac{\frac{I_{MeO}}{3}}{\frac{I_1+I_2}{4}+\frac{I_{MeO}}{3}} * 100\% = \frac{1}{1639.87} = 0.06\%$$

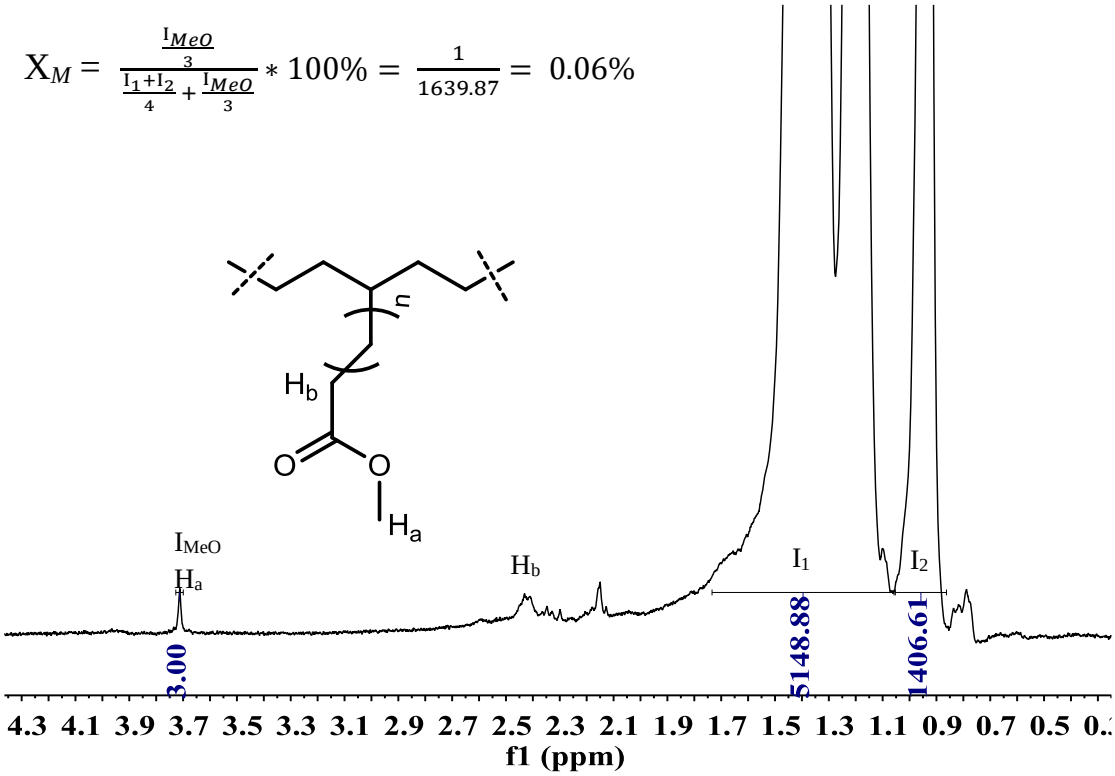


Figure S59. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the E-UA copolymer generated by **Cat1** from table 2, entry 1.

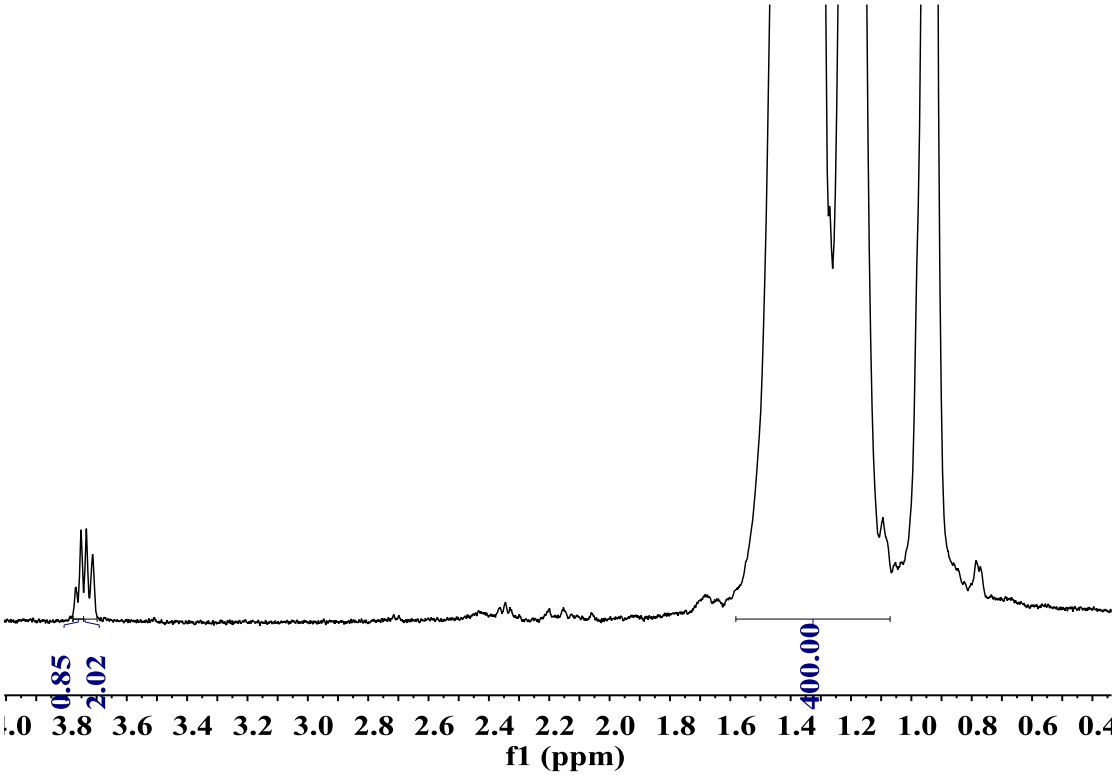


Figure S60. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the E-UA copolymer generated by **Cat2** from table 2, entry 2.

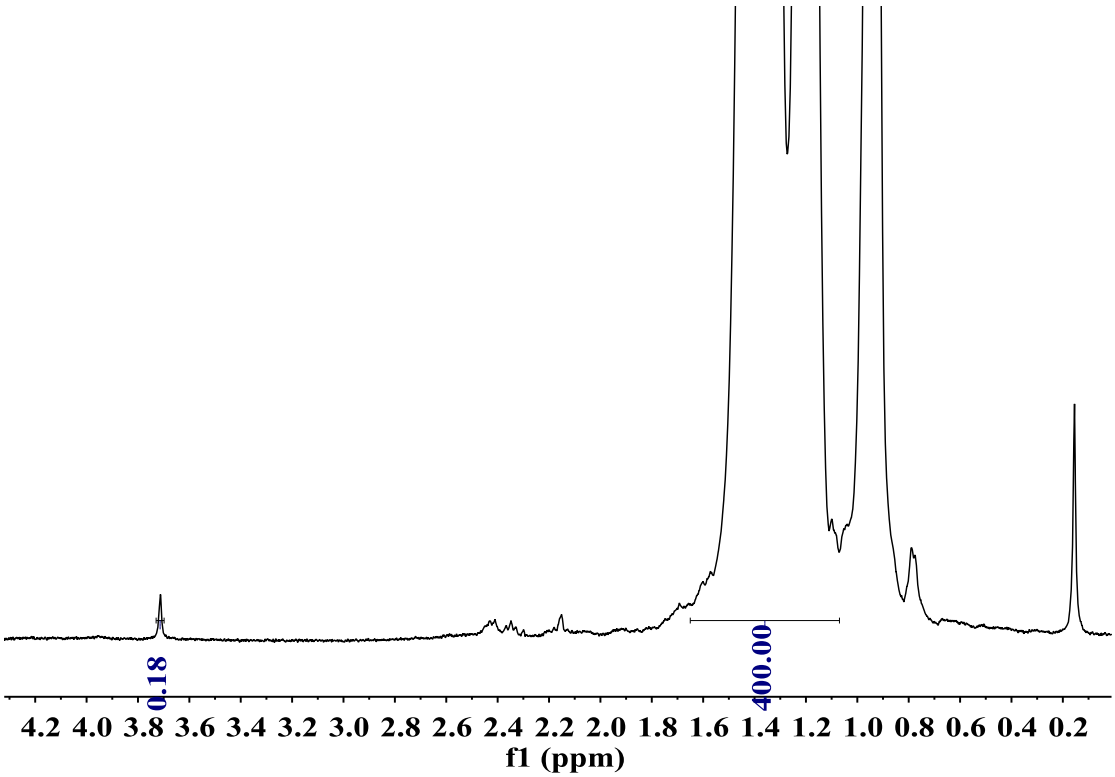


Figure S61. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the E-UA copolymer generated by **Cat3** from table 2, entry 3.

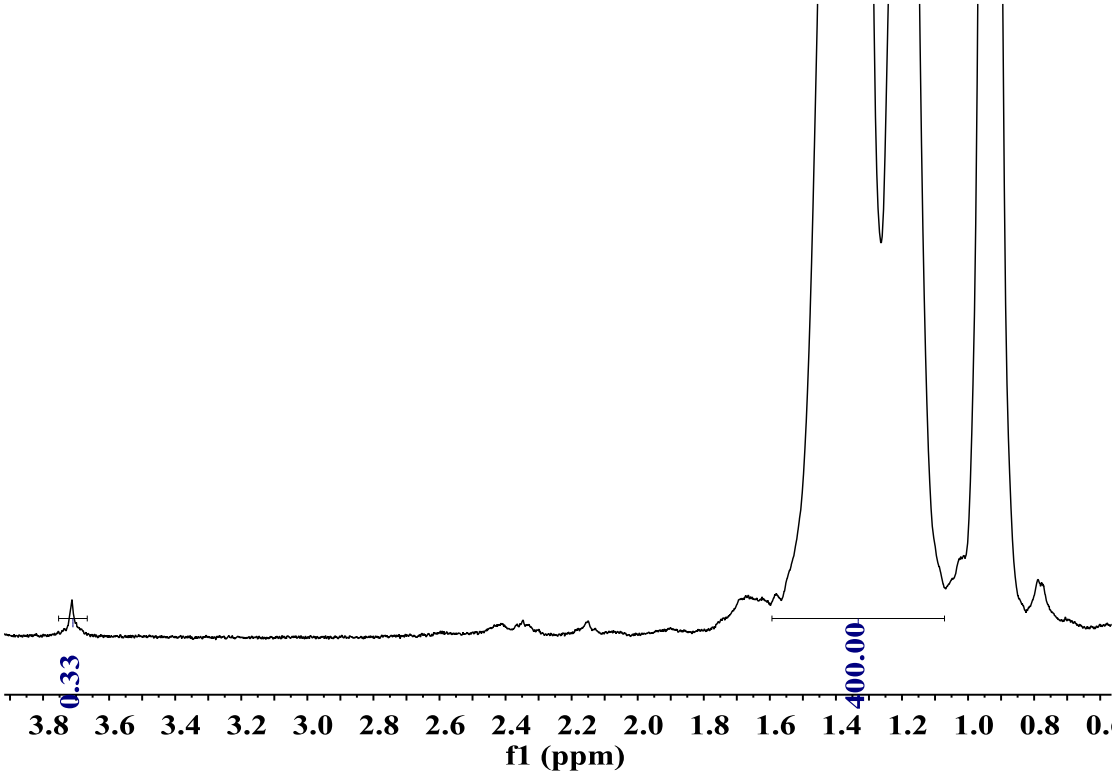


Figure S62. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the E-UA copolymer generated by **Cat4** from table 2, entry 4.

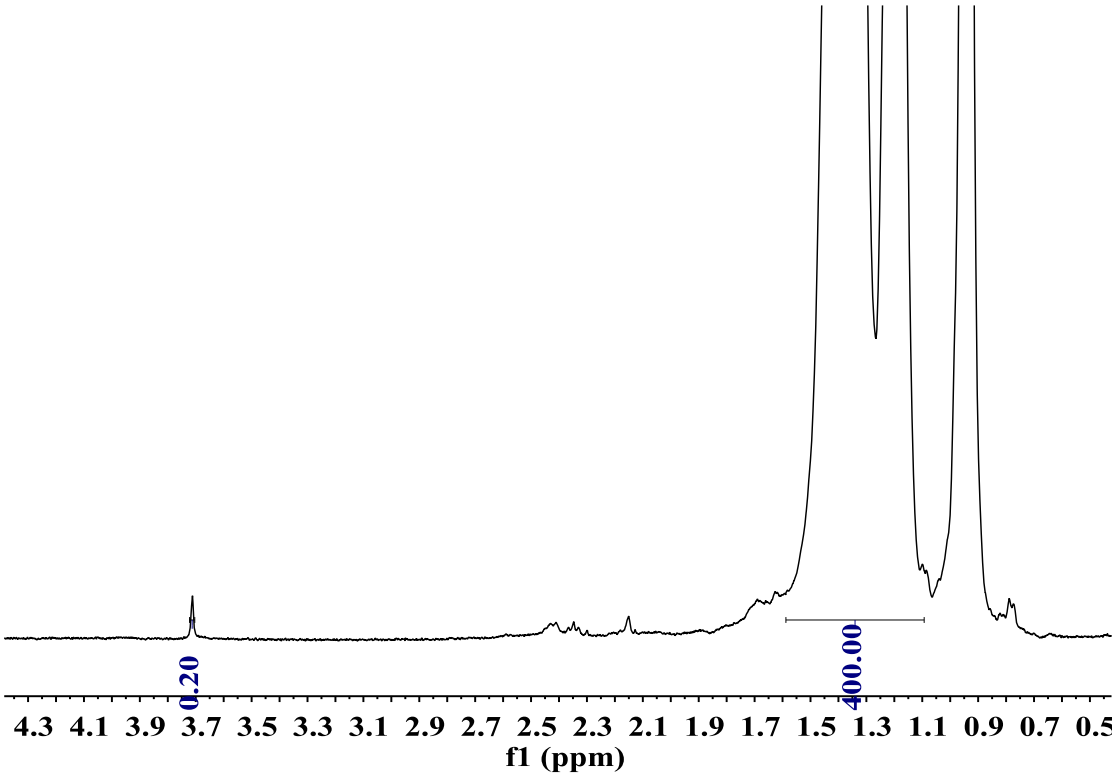


Figure S63. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the E-UA copolymer generated by **Cat1** from table 2, entry 6.

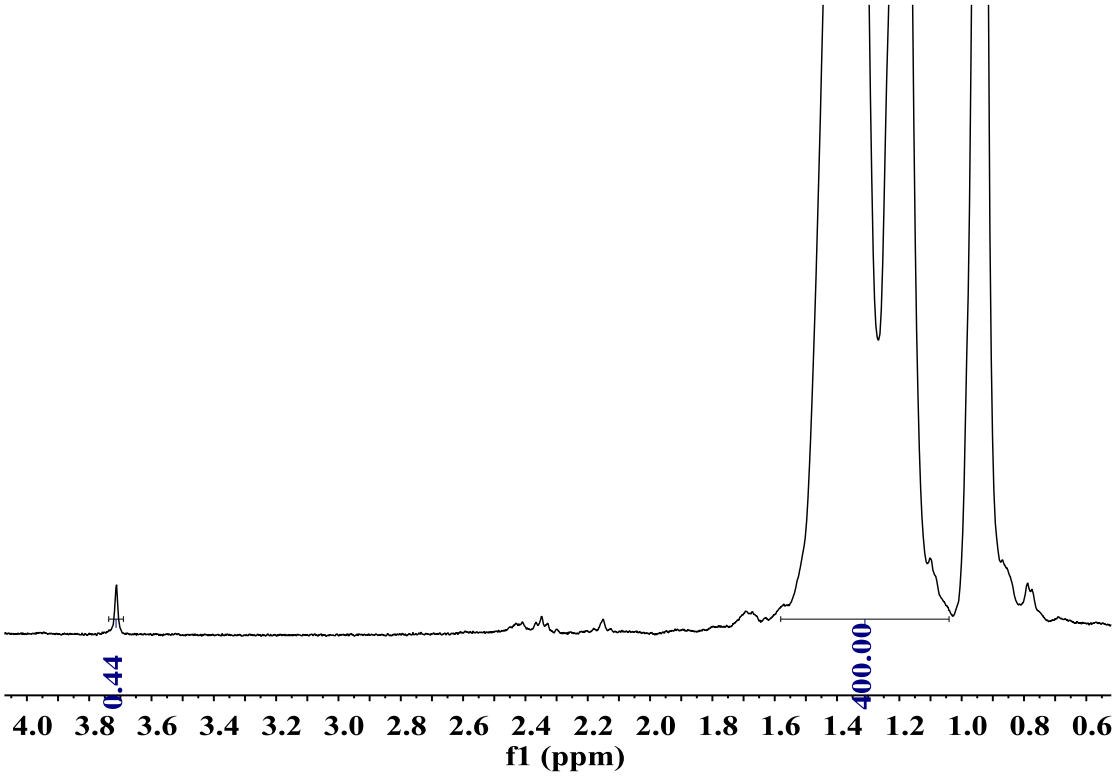


Figure S64. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the E-UA copolymer generated by **Cat4** from table 2, entry 7.

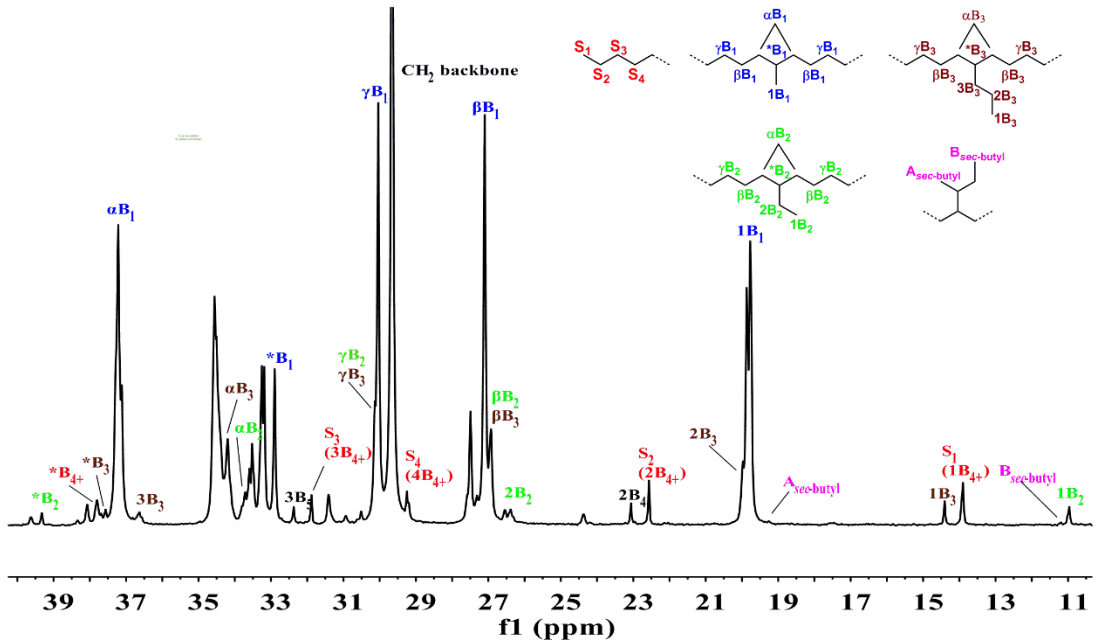


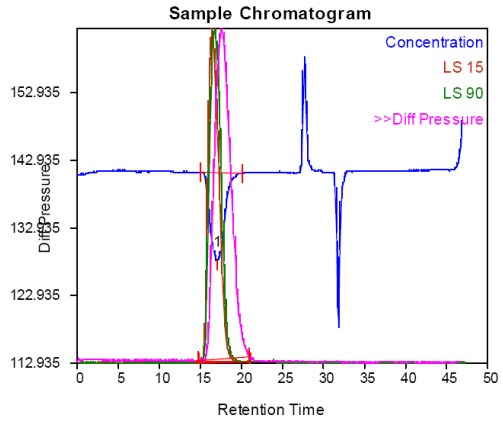
Figure S65. ^{13}C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by complex **Cat2** from table 1, entry 8.

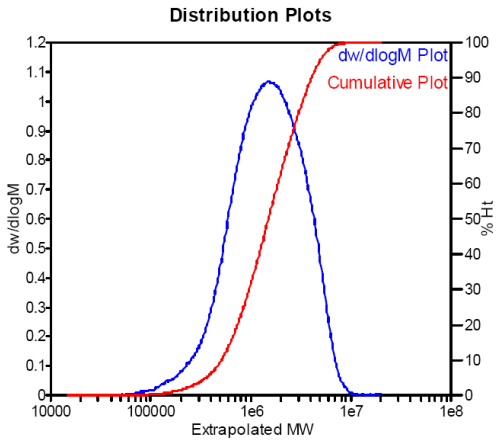
Table S1. Polyethylene Branching Distribution based on ^{13}C NMR analysis.[a]

polymer	methyl	ethyl	propyl	butyl+	Branching density (/1000C)[b]
PE	110.30	7.20	3.68	0.82	122
PE (%)	90.41	5.90	3.02	0.67	122

[a] Sample from Table 1, entry 12 (**PE**). [b] Measured by ^{13}C NMR in $C_2D_2Cl_4$ at 110 ℃.

6 GPC of polymer and copolymer





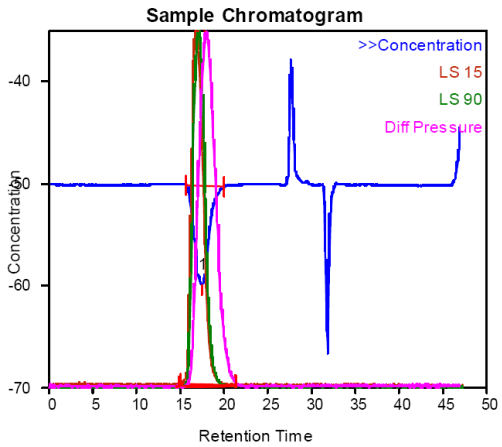
MW Averages

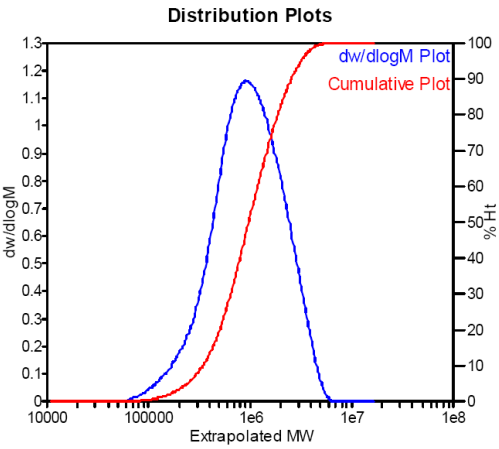
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1533176	992676	1933023	3103372	4371930	1015959	1.94729

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	14.98	16.98	20.20	-9.48569	0	1106.49	100
2	LS 15	14.80	16.32	21.17	118.593	0	11928.7	100
3	LS 90	14.68	16.70	20.97	229.64	0	24633.1	100
4	Diff Pressure	14.70	17.50	20.97	48.8867	0	6893.88	100

Figure S66. GPC trace of the polymer from table 1, entry 1.





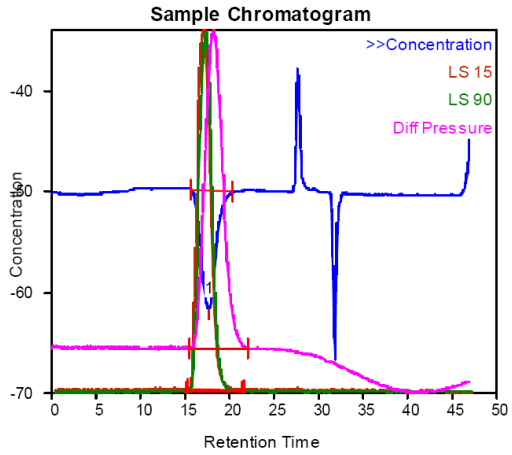
MW Averages

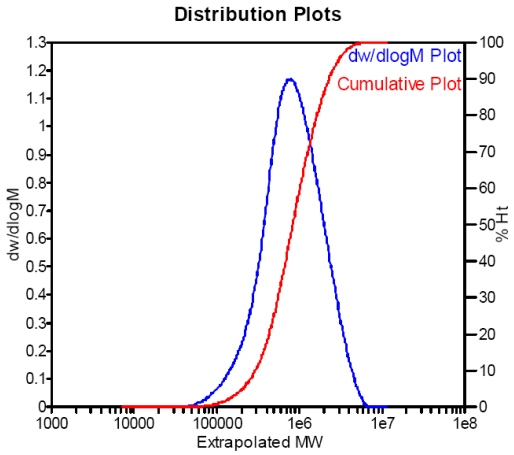
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	905961	675297	1230639	1922996	2605611	699756	1.82237

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.65	17.45	19.97	-9.67278	0	1049.09	100
2	LS 15	15.02	16.77	21.18	79.2771	0	8040.03	100
3	LS 90	14.80	17.05	21.18	208.649	0	21276.3	100
4	Diff Pressure	14.92	17.88	21.48	34.821	0	4808.87	100

Figure S67. GPC trace of the polymer from table 1, entry 2.





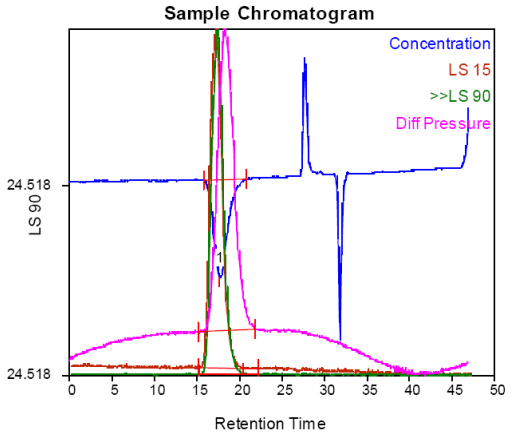
MW Averages

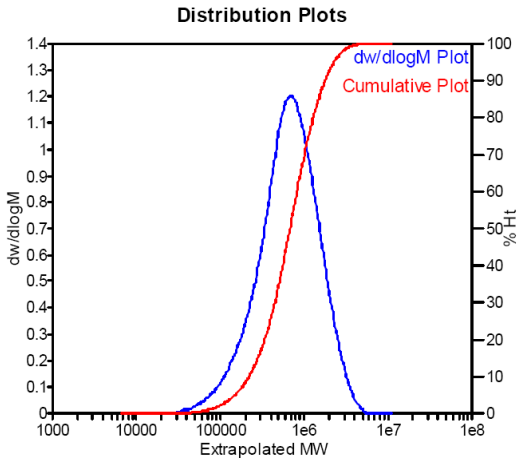
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	780068	579516	1095206	1812753	2596406	628286	1.88986

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.63	17.65	20.32	-11.7561	0	1292.86	100
2	LS 15	15.25	17.02	21.58	80.9045	0	8842.87	100
3	LS 90	15.17	17.28	21.35	235.651	0	24701.1	100
4	Diff Pressure	15.47	18.08	22.02	37.0882	0	5240.29	100

Figure S68. GPC trace of the polymer from table 1, entry 3.





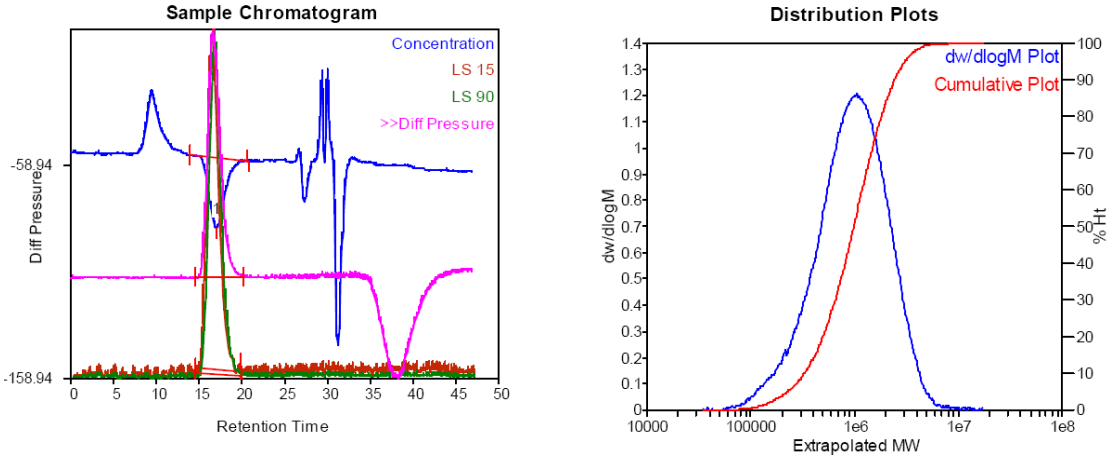
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	712894	443218	864047	1409937	2015264	490085	1.94949

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.77	17.72	20.77	-9.814	0	1068.91	100
2	LS 15	15.20	17.20	22.13	57.2247	0	5891.2	100
3	LS 90	15.35	17.38	20.43	181.684	0	18088.7	100
4	Diff Pressure	15.13	18.18	21.88	25.45	0	3512.42	100

Figure S69. GPC trace of the polymer from table 1, entry 4.



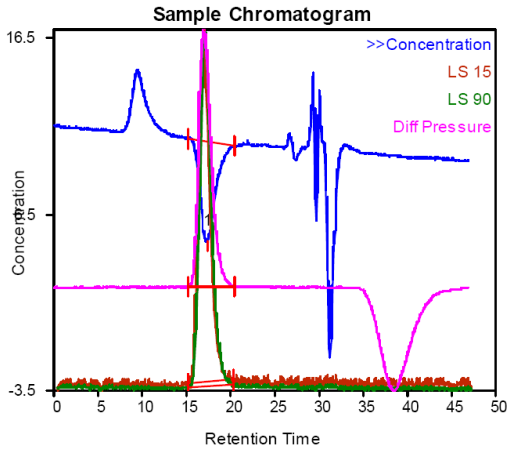
MW Averages

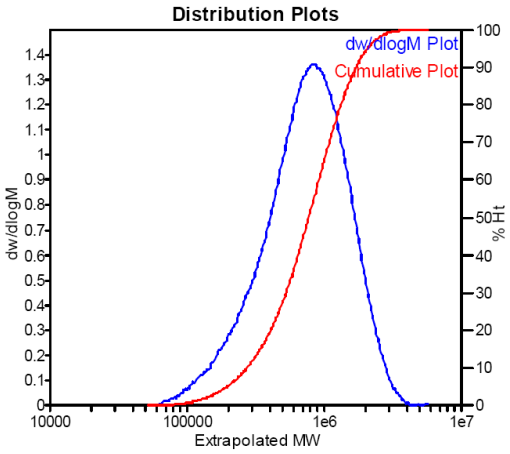
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1047796	657571	1229702	2061804	3509360	1096838	1.87007

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	13.97	16.98	20.68	-4.03286	0	500.473	100
2	LS 15	14.53	16.52	19.77	32.1946	0	3463.11	100
3	LS 90	14.47	16.80	19.93	82.6558	0	8815.64	100
4	Diff Pressure	14.48	16.62	20.22	116.586	0	12875.5	100

Figure S70. GPC trace of the polymer from table 1, entry 5.





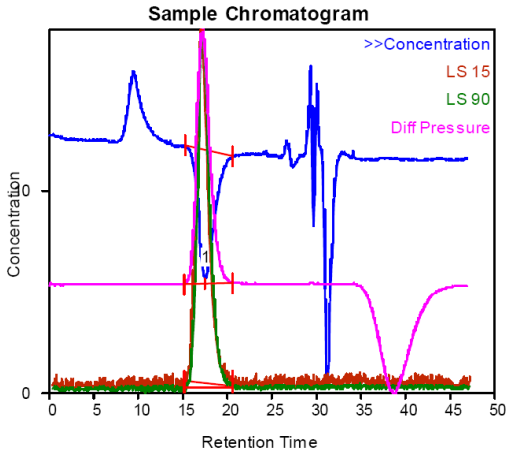
MW Averages

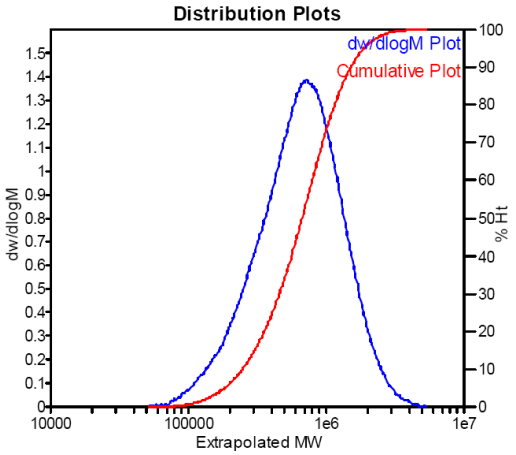
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	859907	544055	896740	1286110	1679968	828425	1.64825

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.22	17.32	20.42	-5.65098	0	655.369	100
2	LS 15	15.13	16.85	20.28	37.0034	0	3625.17	100
3	LS 90	15.18	17.07	20.32	111.44	0	10993.9	100
4	Diff Pressure	15.08	17.00	20.47	123.961	0	12741.4	100

Figure S71. GPC trace of the polymer from table 1, entry 6.





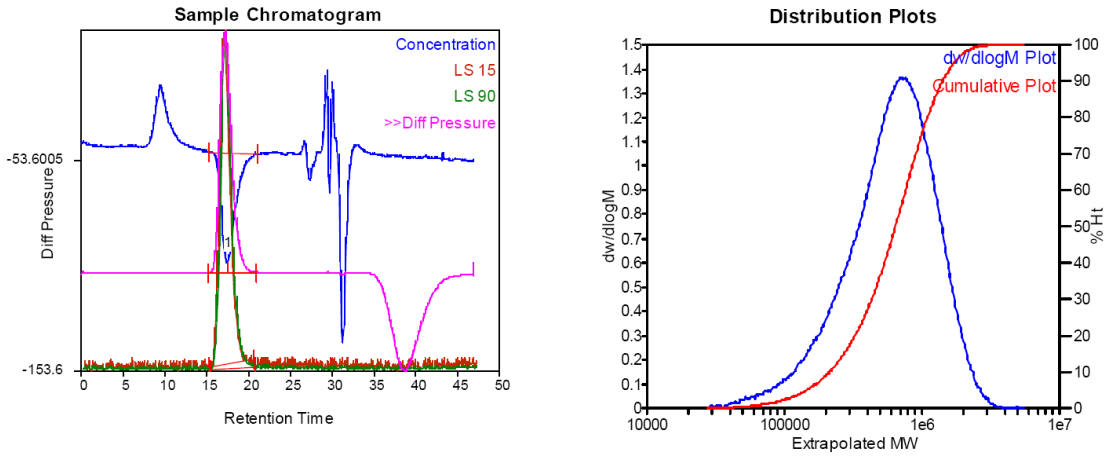
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	722381	487259	795527	1184519	1643906	731565	1.63266

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.25	17.52	20.67	-6.35247	0	756.338	100
2	LS 15	15.18	17.07	20.62	31.4845	0	3350.99	100
3	LS 90	15.17	17.23	20.65	102.777	0	10660.1	100
4	Diff Pressure	15.12	17.23	20.65	115.904	0	12530.2	100

Figure S72. GPC trace of the polymer from table 1, entry 7.



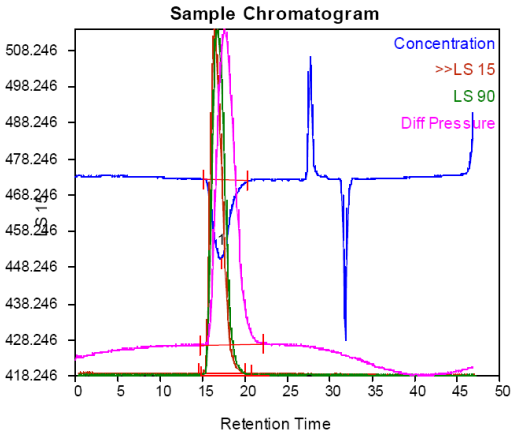
MW Averages

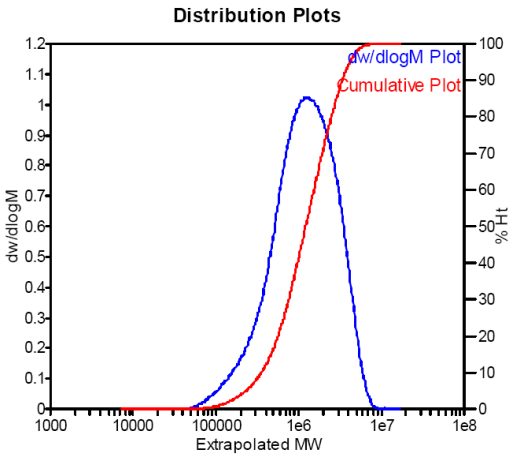
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	704928	417852	740636	1072711	1403874	686296	1.77248

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.28	17.48	21.08	-6.26736	0	704.603	100
2	LS 15	15.30	17.15	20.55	34.328	0	3289.92	100
3	LS 90	15.40	17.20	20.72	112.869	0	10980.2	100
4	Diff Pressure	15.22	17.20	20.87	115.583	0	11688.5	100

Figure S73. GPC trace of the polymer from table 1, entry 8.





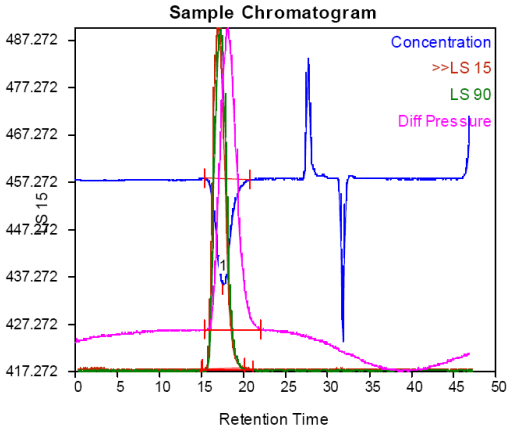
MW Averages

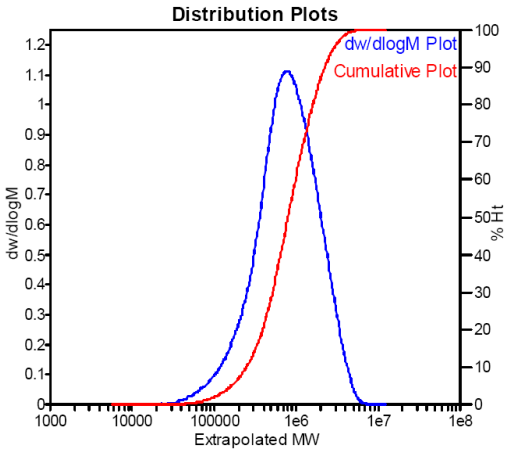
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1264265	735031	1580464	2584437	3528619	872496	2.1502

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.12	17.12	20.32	-7.97139	0	1053.58	100
2	LS 15	14.57	16.27	20.07	95.2609	0	9954.65	100
3	LS 90	14.85	16.73	20.72	190.81	0	21855.9	100
4	Diff Pressure	14.70	17.55	22.17	40.6225	0	6091.65	100

Figure S74. GPC trace of the polymer from table 1, entry 9.





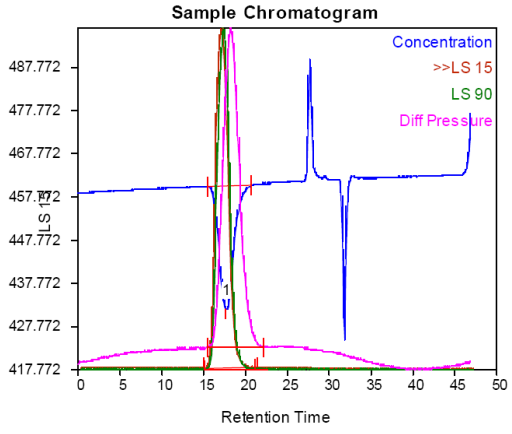
MW Averages

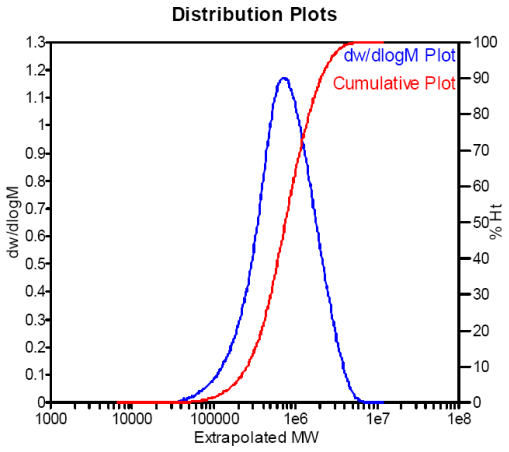
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	812933	497771	1050713	1776223	2549139	560008	2.11084

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.37	17.55	20.78	-10.267	0	1164.76	100
2	LS 15	15.10	16.97	20.18	71.8635	0	7572.22	100
3	LS 90	15.07	17.20	21.02	206.12	0	21322.8	100
4	Diff Pressure	15.37	18.02	22.07	32.9618	0	4606.48	100

Figure S75. GPC trace of the polymer from table 1, entry 10.





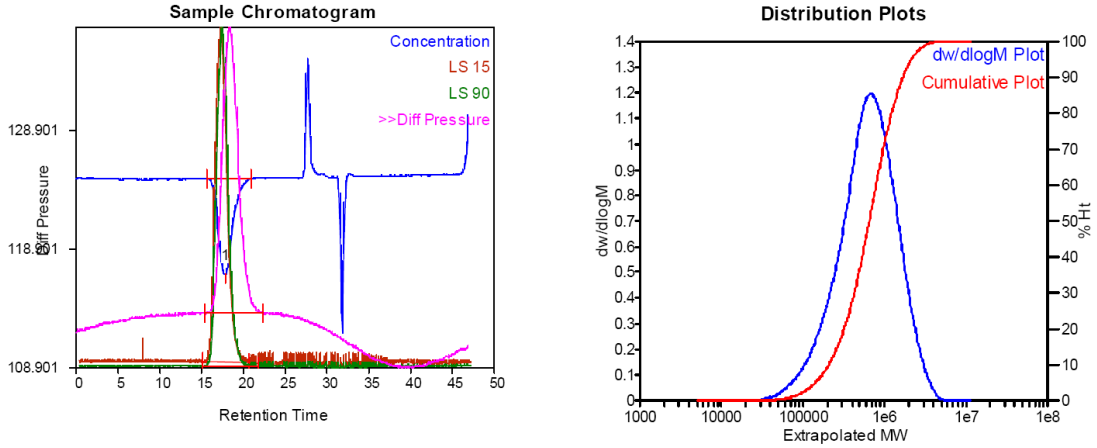
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	726355	506040	986805	1653362	2425350	556423	1.95005

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.48	17.70	20.65	-12.3528	0	1396.15	100
2	LS 15	15.03	17.08	21.48	78.6071	0	8599.28	100
3	LS 90	15.08	17.33	21.08	234.491	0	24595	100
4	Diff Pressure	15.43	18.15	22.20	39.1669	0	5516.39	100

Figure S76. GPC trace of the polymer from table 1, entry 11.



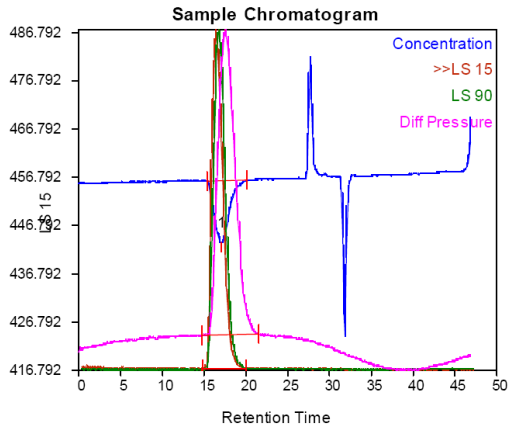
MW Averages

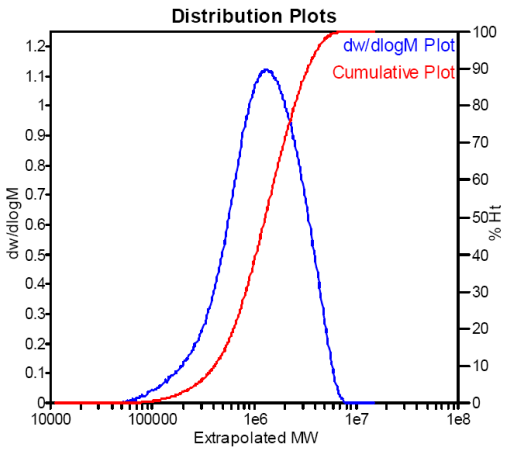
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	696448	424259	822492	1335748	1903889	473604	1.93866

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.70	17.75	20.87	-9.51279	0	1041.42	100
2	LS 15	15.23	17.27	20.58	53.7693	0	5476.59	100
3	LS 90	15.08	17.40	21.68	174.63	0	17270.3	100
4	Diff Pressure	15.37	18.27	22.40	24.1233	0	3306.67	100

Figure S77. GPC trace of the polymer from table 1, entry 12.





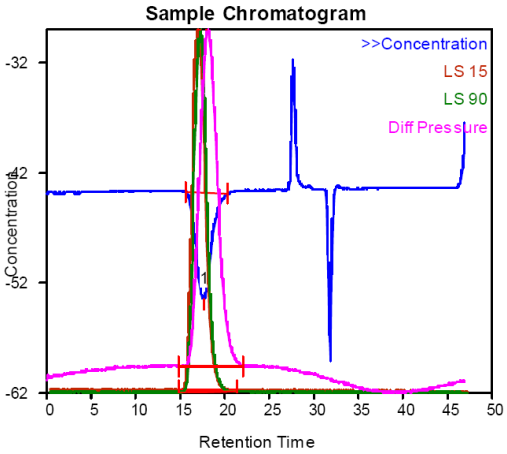
MW Averages

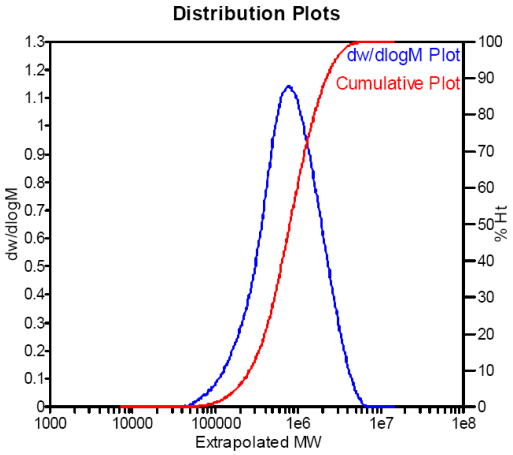
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1332937	810272	1604170	2500587	3320325	898697	1.97979

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.25	17.02	20.10	-6.22418	0	737.735	100
2	LS 15	14.83	16.38	19.95	70.3809	0	7177.61	100
3	LS 90	14.80	16.73	20.02	147.36	0	15567.4	100
4	Diff Pressure	14.68	17.48	21.62	31.2932	0	4490.51	100

Figure S78. GPC trace of the polymer from table 1, entry 13.





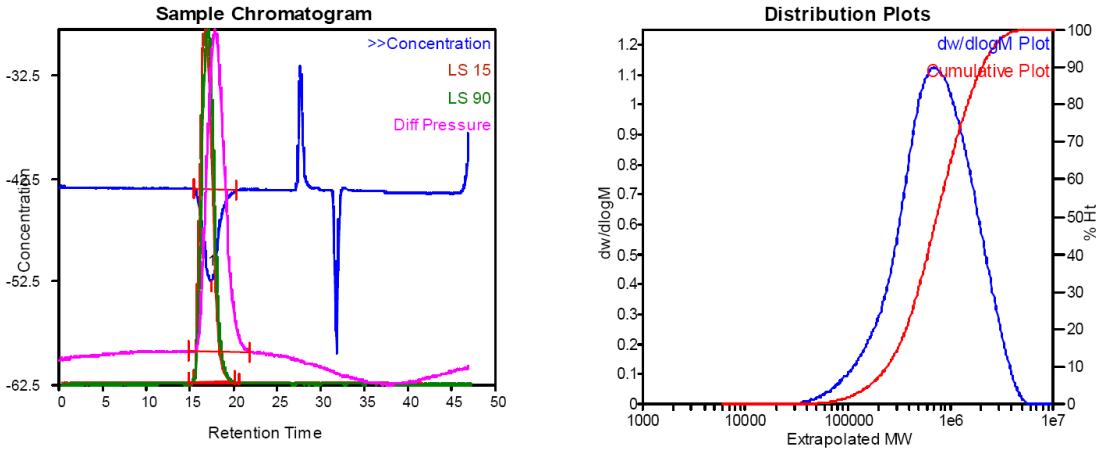
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	758012	534637	1047546	1753950	2518736	608514	1.95936

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.58	17.63	20.33	-9.63041	0	1086.12	100
2	LS 15	14.90	16.98	21.45	64.555	0	7094.56	100
3	LS 90	14.90	17.25	21.45	187.979	0	19809.6	100
4	Diff Pressure	14.90	18.03	21.98	33.4221	0	4766.13	100

Figure S79. GPC trace of the polymer from table 1, entry 14.



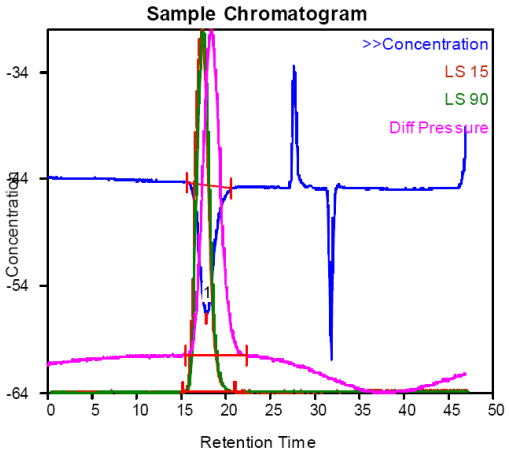
MW Averages

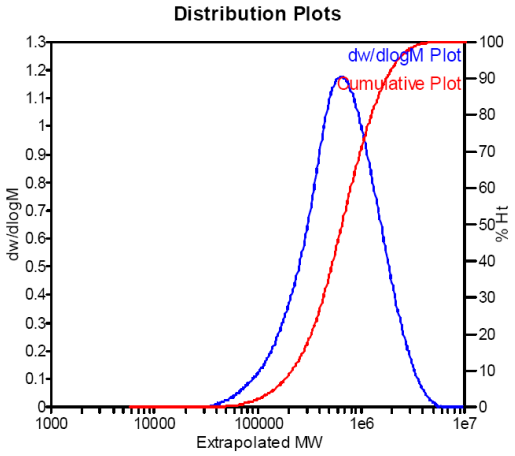
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	688601	484372	964158	1586855	2226207	539170	1.99053

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.47	17.43	20.25	-8.86025	0	1013.69	100
2	LS 15	14.90	16.72	20.18	75.2042	0	8037.24	100
3	LS 90	14.90	17.03	20.65	193.927	0	20493	100
4	Diff Pressure	14.90	17.80	21.83	34.4328	0	4894.19	100

Figure S80. GPC trace of the polymer from table 1, entry 15.





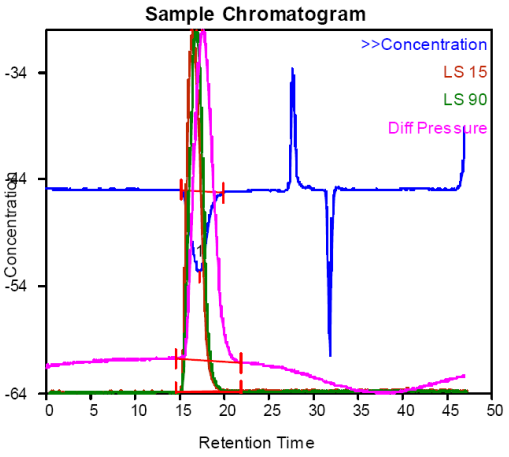
MW Averages

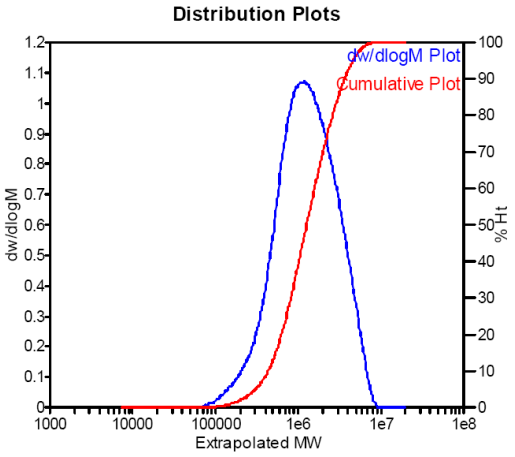
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	646795	434748	847977	1415490	2061625	491804	1.9505

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.65	17.83	20.63	-12.0737	0	1345.46	100
2	LS 15	15.22	17.23	20.98	67.7809	0	7266.09	100
3	LS 90	15.22	17.43	21.07	217.955	0	22417.5	100
4	Diff Pressure	15.40	18.25	22.28	33.1447	0	4598.53	100

Figure S81. GPC trace of the polymer from table 1, entry 16.





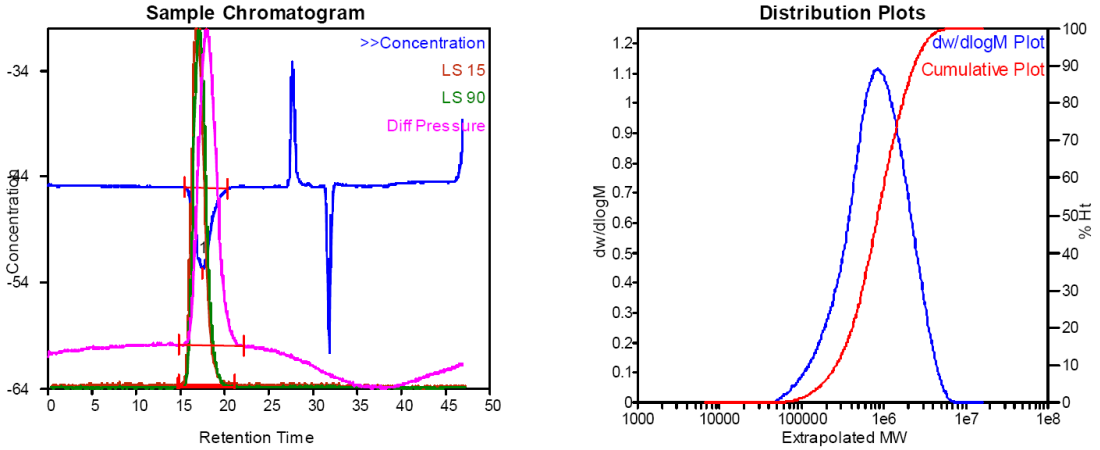
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1210550	867304	1693281	2796020	3870631	983708	1.95235

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.18	17.23	19.85	-7.5026	0	921.854	100
2	LS 15	14.50	16.30	21.95	80.3263	0	9200.93	100
3	LS 90	14.50	16.83	21.95	169.901	0	19501.4	100
4	Diff Pressure	14.50	17.50	21.95	40.9258	0	6059.75	100

Figure S82. GPC trace of the polymer from table 1, entry 17.



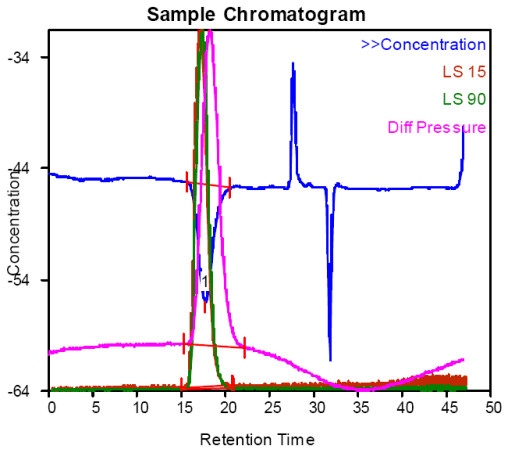
MW Averages

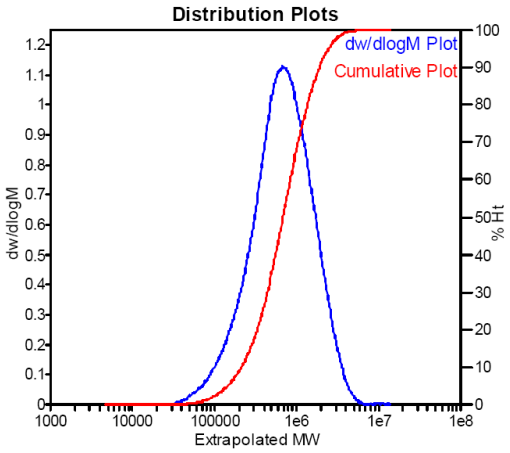
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	865318	549209	1110692	1856301	2635990	634654	2.02235

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.45	17.48	20.30	-7.61723	0	900.075	100
2	LS 15	14.87	16.80	21.12	56.5156	0	6138.84	100
3	LS 90	14.68	17.12	21.13	155.568	0	16594.9	100
4	Diff Pressure	14.88	17.90	22.13	27.9894	0	4004.66	100

Figure S83. GPC trace of the polymer from table 1, entry 18.





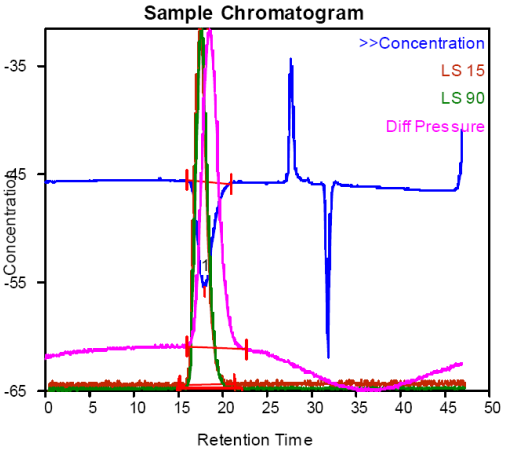
MW Averages

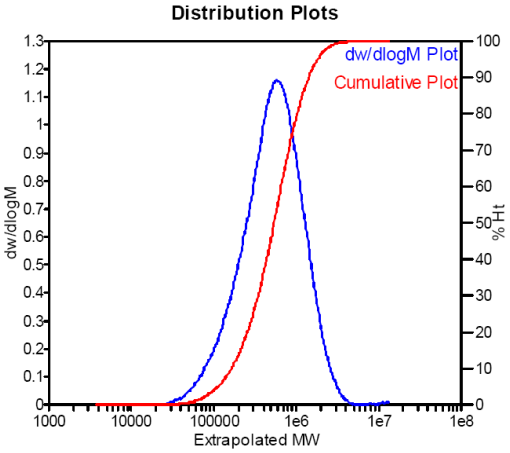
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	685938	439988	906523	1605457	2681506	502420	2.06034

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.62	17.72	20.48	-10.5474	0	1172.9	100
2	LS 15	14.98	17.10	20.85	63.8642	0	6624.04	100
3	LS 90	15.05	17.33	20.90	197.028	0	19927	100
4	Diff Pressure	15.27	18.13	22.23	31.3179	0	4299.74	100

Figure S84. GPC trace of the polymer from table 1, entry 19.





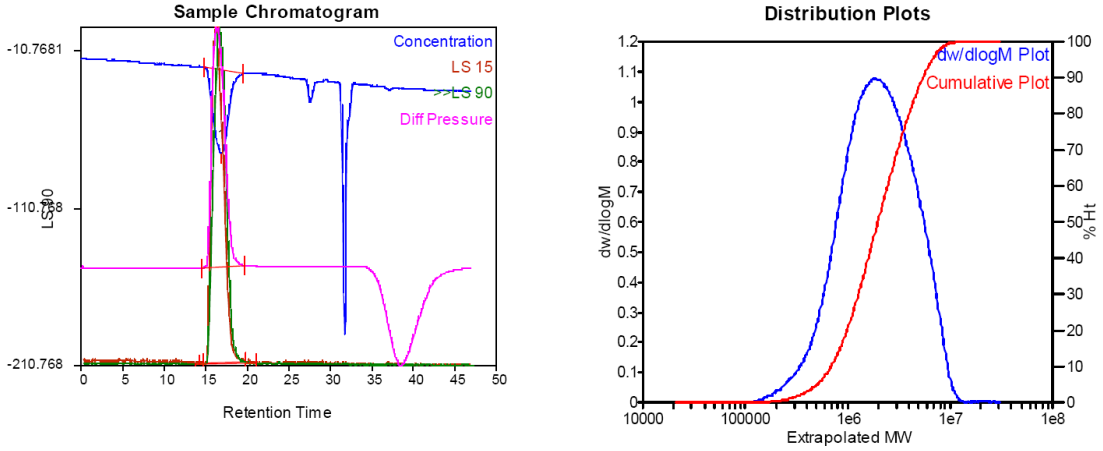
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	581939	343318	699090	1349272	3347177	389568	2.03628

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.87	17.92	20.87	-9.77539	0	1072.56	100
2	LS 15	15.23	17.42	21.23	47.552	0	4661.98	100
3	LS 90	15.03	17.55	21.48	164.154	0	15762.7	100
4	Diff Pressure	15.87	18.33	22.58	22.6773	0	3040.45	100

Figure S85. GPC trace of the polymer from table 1, entry 20.



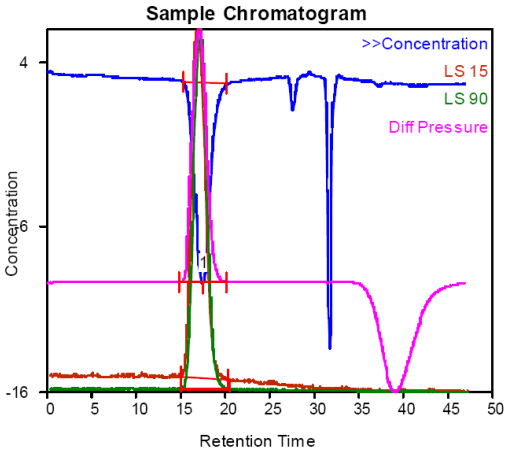
MW Averages

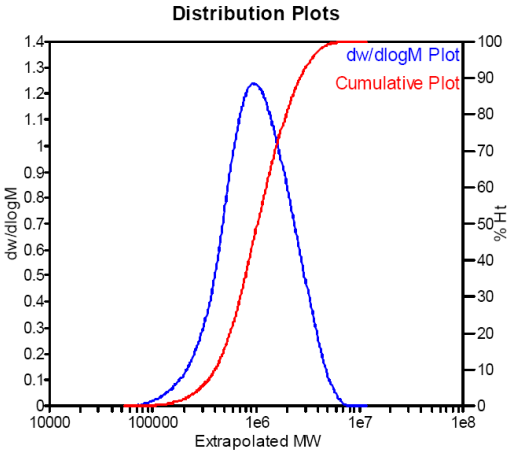
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1866650	1379094	2573156	4181044	6102837	2263752	1.86583

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	14.88	16.83	19.50	-8.55815	0	1040.99	100
2	LS 15	14.72	16.10	19.83	116.176	0	12747.1	100
3	LS 90	14.18	16.62	21.10	214.151	0	24344.7	100
4	Diff Pressure	14.58	16.35	19.70	347.933	0	38973.1	100

Figure S86. GPC trace of the polymer from table 1, entry 21.





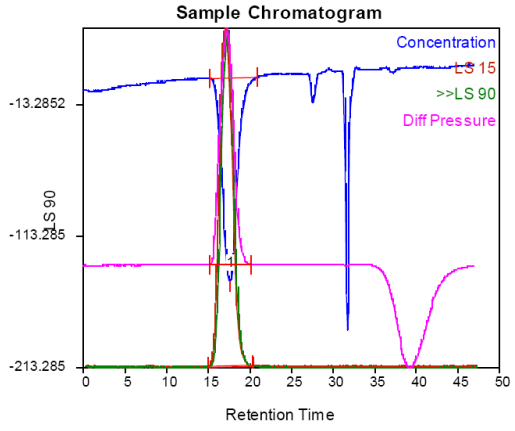
MW Averages

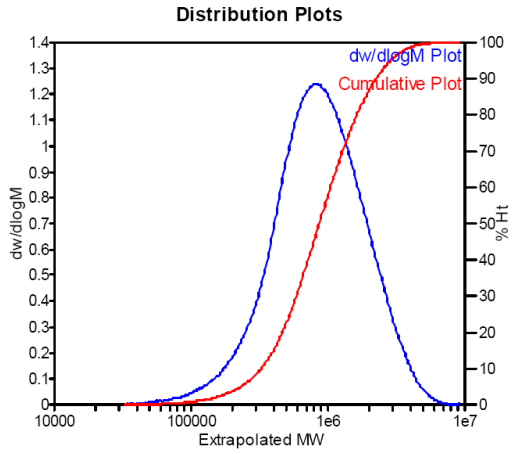
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	953050	765320	1314491	2055340	2862604	1203508	1.71757

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.30	17.47	20.20	-12.1883	0	1421.42	100
2	LS 15	14.98	16.83	20.25	92.9761	0	10775.8	100
3	LS 90	14.95	17.20	20.48	254.651	0	28144.7	100
4	Diff Pressure	14.83	17.07	20.12	306.731	0	34989.2	100

Figure S87. GPC trace of the polymer from table 1, entry 22.





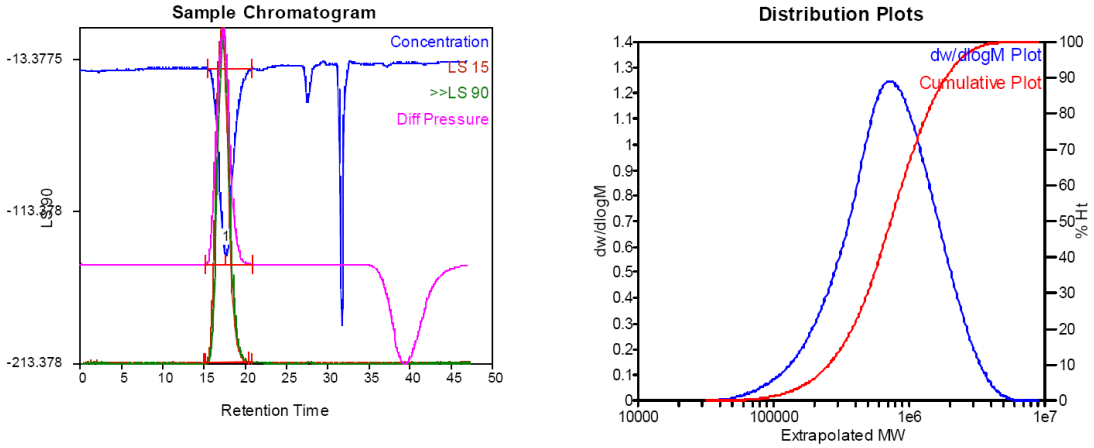
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	805052	612511	1107246	1780035	2574853	1009036	1.80772

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.23	17.60	20.98	-13.2125	0	1544.51	100
2	LS 15	15.07	17.05	20.25	87.1337	0	10089.6	100
3	LS 90	15.07	17.28	20.47	258.185	0	28354.8	100
4	Diff Pressure	15.13	17.20	20.17	289.068	0	32878.7	100

Figure S88. GPC trace of the polymer from table 1, entry 23.



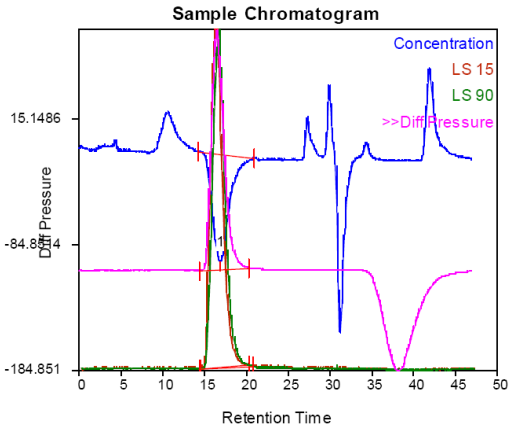
MW Averages

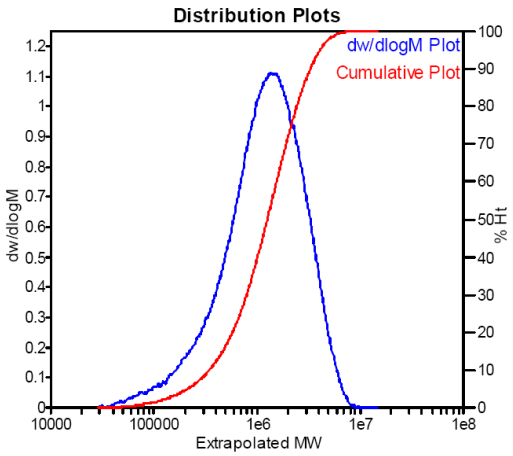
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	726171	505865	922307	1469354	2086880	849549	1.82323

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.48	17.67	20.73	-11.9364	0	1368.15	100
2	LS 15	15.07	17.17	20.52	69.901	0	7709.43	100
3	LS 90	15.12	17.35	20.72	220.284	0	23187.8	100
4	Diff Pressure	15.10	17.30	20.90	234.066	0	25820.1	100

Figure S89. GPC trace of the polymer from table 1, entry 24.





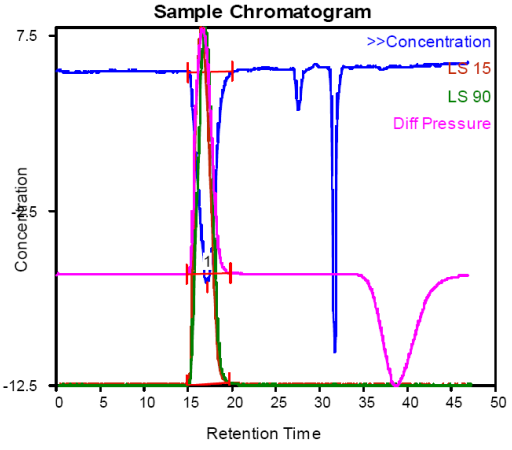
MW Averages

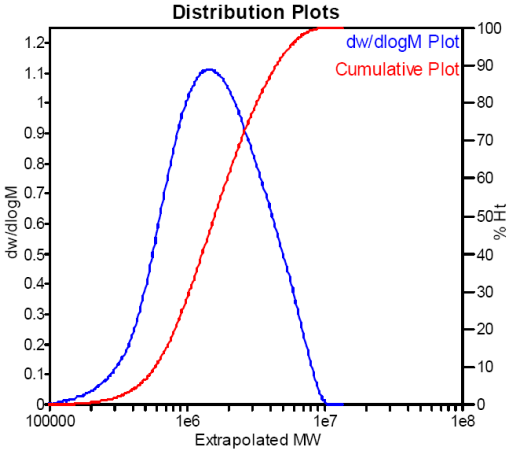
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1397583	689608	1577423	2548461	3473192	1384059	2.28742

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	14.28	16.80	20.95	-5.69956	0	757.936	100
2	LS 15	14.57	16.25	20.32	58.3614	0	6383.45	100
3	LS 90	14.43	16.60	20.72	130.136	0	14542.6	100
4	Diff Pressure	14.37	16.45	20.37	191.205	0	21487.6	100

Figure S90. GPC trace of the polymer from table 1, entry 25.





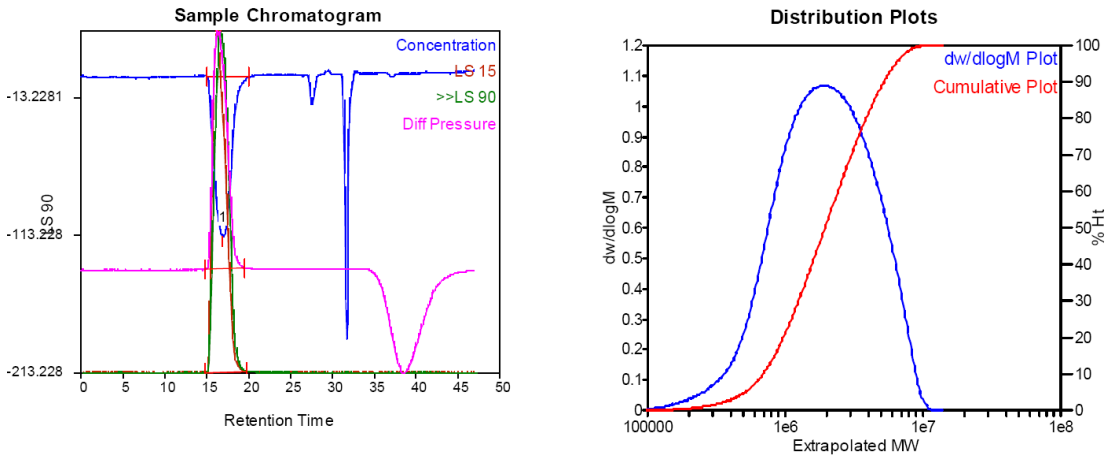
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1436268	1149317	2081404	3340612	4571949	1850493	1.81099

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.07	17.18	20.03	-12.0781	0	1573.84	100
2	LS 15	14.85	16.45	19.63	132.692	0	16666.3	100
3	LS 90	14.88	16.92	19.70	285.335	0	34802.9	100
4	Diff Pressure	14.83	16.68	19.78	427.535	0	53138.8	100

Figure S91. GPC trace of the polymer from table 1, entry 26.



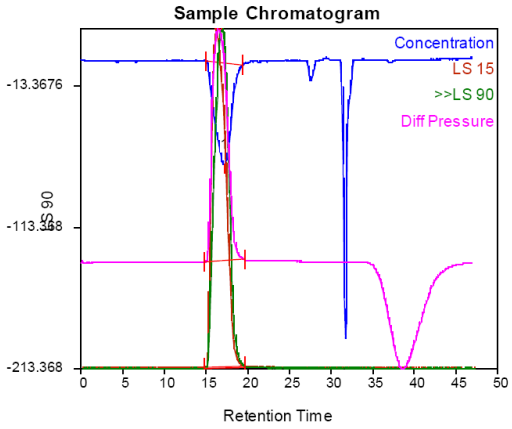
MW Averages

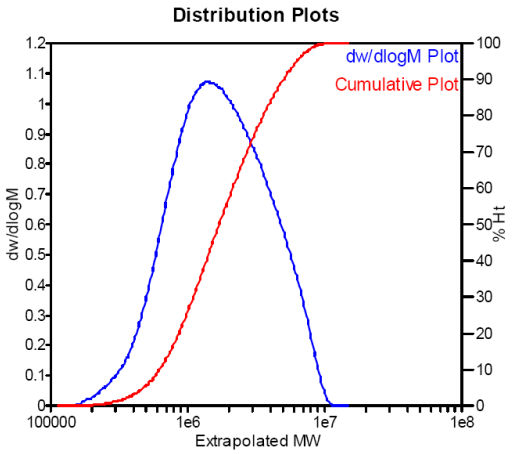
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1826421	1355615	2478732	3833770	5055964	2215060	1.82849

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.02	16.95	20.02	-9.87214	0	1329.38	100
2	LS 15	14.83	16.07	19.85	138.677	0	16080.2	100
3	LS 90	14.83	16.68	19.88	247.451	0	30679.7	100
4	Diff Pressure	14.83	16.35	19.57	425.559	0	50728.8	100

Figure S92. GPC trace of the polymer from table 1, entry 27.





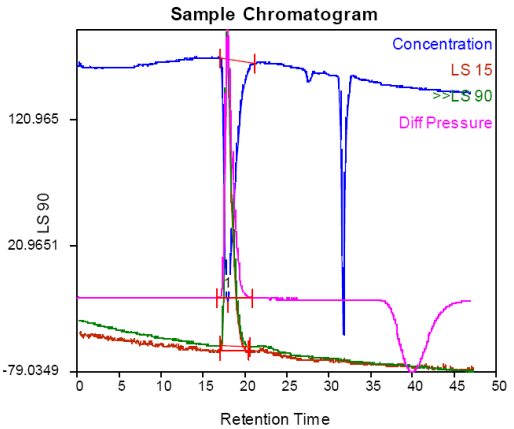
MW Averages

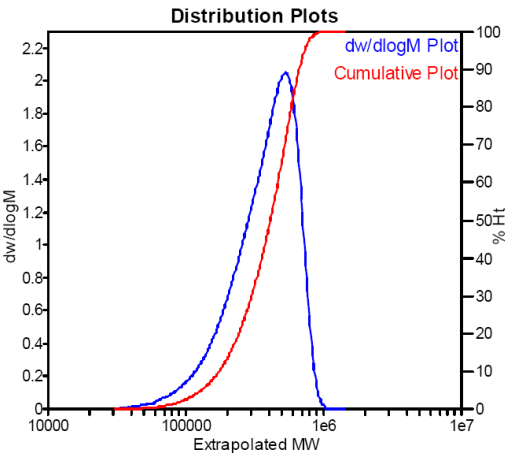
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1369354	1257330	2293526	3741206	5116978	2039536	1.82412

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.07	17.22	19.45	-10.419	0	1355.6	100
2	LS 15	14.83	16.13	19.68	122.876	0	15299.8	100
3	LS 90	14.85	16.92	19.75	240.112	0	30278.6	100
4	Diff Pressure	14.80	16.50	19.65	403.73	0	51554.1	100

Figure S93. GPC trace of the polymer from table 1, entry 28.





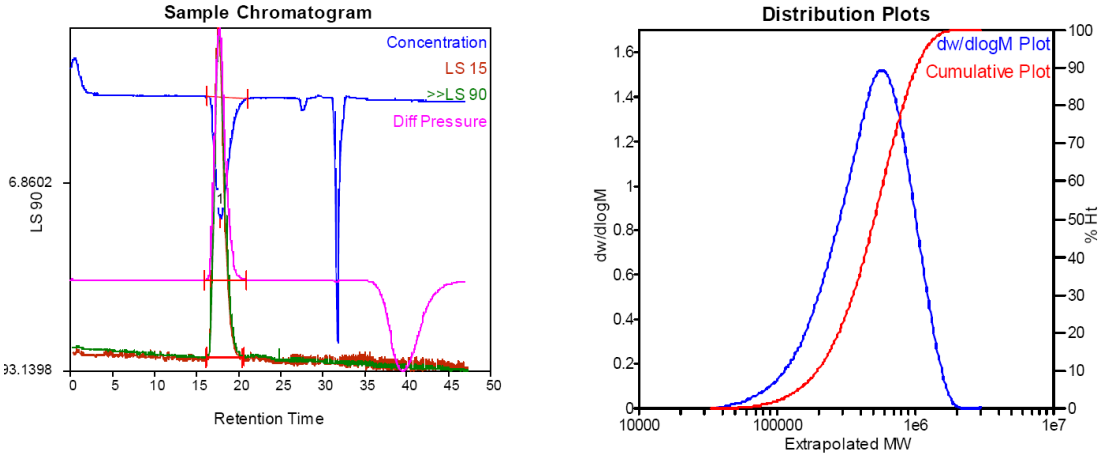
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	528975	308212	414338	495868	556862	400921	1.34433

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.00	17.93	21.30	-17.3467	0	1374.3	100
2	LS 15	17.05	17.87	20.43	63.906	0	3656.97	100
3	LS 90	17.00	17.87	20.55	251.237	0	14881.5	100
4	Diff Pressure	16.77	17.88	21.00	228.743	0	14676.7	100

Figure S94. GPC trace of the polymer from table 1, entry 29.



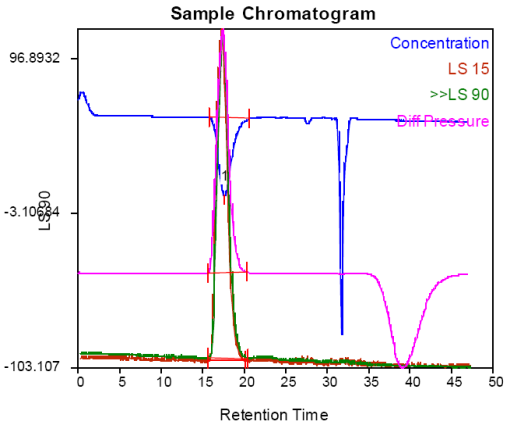
MW Averages

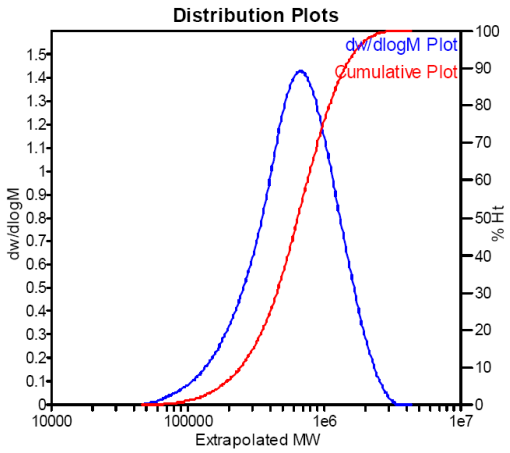
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	564174	367609	558688	745427	916280	531971	1.51979

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.25	17.88	21.07	-11.0756	0	1136.14	100
2	LS 15	16.12	17.57	20.53	48.3149	0	4107.33	100
3	LS 90	16.27	17.67	20.62	174.838	0	15043.6	100
4	Diff Pressure	16.00	17.65	20.92	170.159	0	15236.6	100

Figure S95. GPC trace of the polymer from table 1, entry 30.





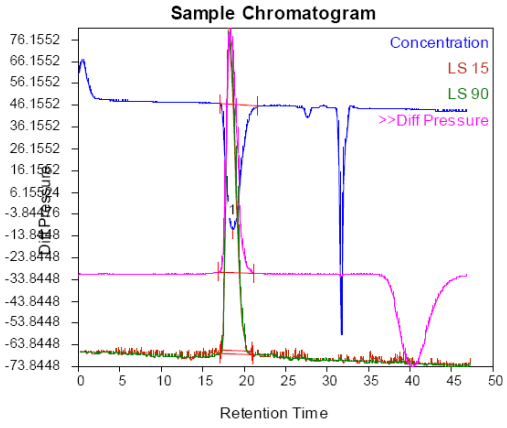
MW Averages

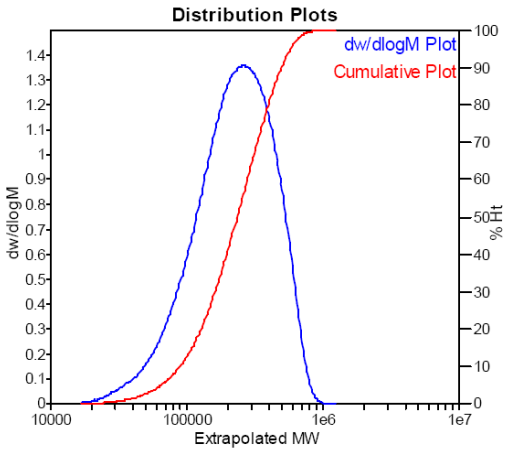
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	674920	465972	746336	1058557	1374231	700158	1.60167

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.83	17.63	20.58	-11.4477	0	1218.53	100
2	LS 15	15.62	17.30	20.22	65.9939	0	6434.65	100
3	LS 90	15.60	17.38	20.43	212.708	0	20278.7	100
4	Diff Pressure	15.60	17.37	20.30	222.805	0	21997.6	100

Figure S96. GPC trace of the polymer from table 1, entry 31.





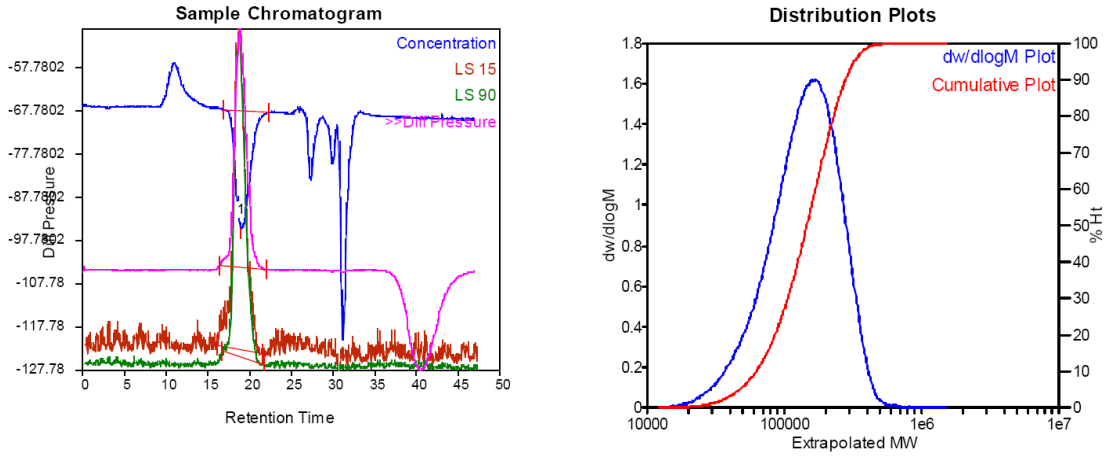
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	254840	169840	264517	357918	438756	249745	1.55745

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.10	18.63	21.53	-11.76	0	1272.05	100
2	LS 15	17.17	18.17	20.92	26.1584	0	2154.06	100
3	LS 90	17.05	18.20	21.03	108.723	0	9301.65	100
4	Diff Pressure	16.95	18.25	21.28	111.764	0	10208.1	100

Figure S97. GPC trace of the polymer from table 2, entry 1.



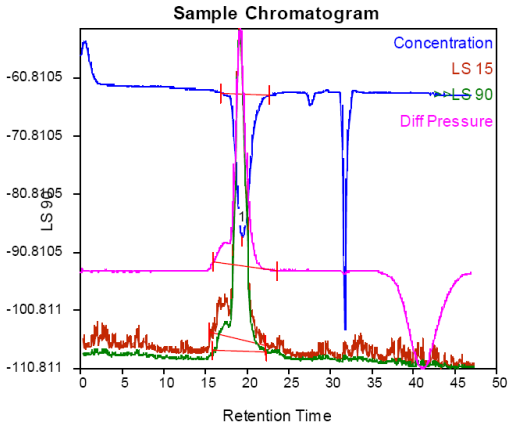
MW Averages

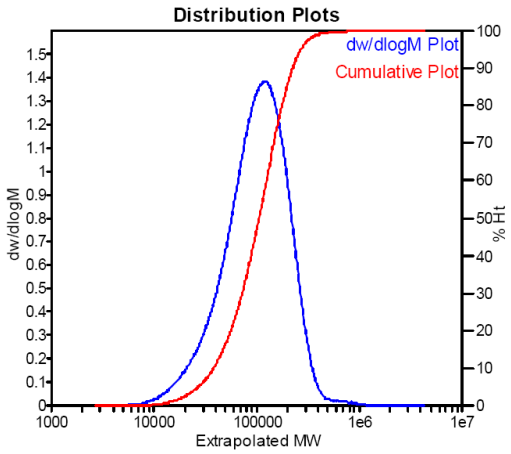
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	166564	113703	160026	206440	251206	153838	1.40741

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.87	18.98	22.38	-9.6272	0	1073.2	100
2	LS 15	16.10	18.65	21.60	11.7051	0	1184.18	100
3	LS 90	16.75	18.72	21.72	50.1494	0	4516.65	100
4	Diff Pressure	16.33	18.75	22.00	55.2498	0	5408.14	100

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





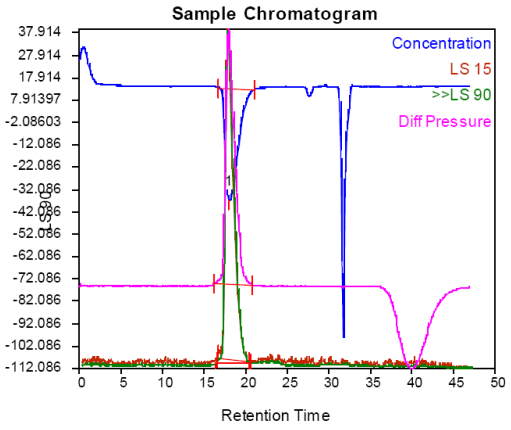
MW Averages

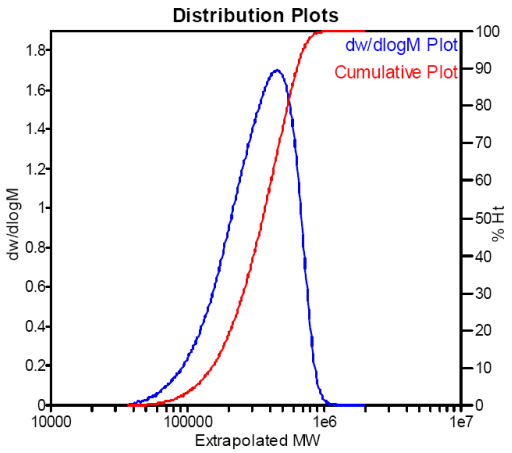
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	118850	73618	122343	184469	285966	116278	1.66185

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.83	19.38	22.70	-12.213	0	1328.55	100
2	LS 15	15.47	19.03	22.20	12.0472	0	1182.12	100
3	LS 90	15.83	19.03	22.20	55.6029	0	5180.4	100
4	Diff Pressure	15.95	19.08	23.52	64.264	0	6382.81	100

Figure S99. GPC trace of the polymer from table 2, entry 3.





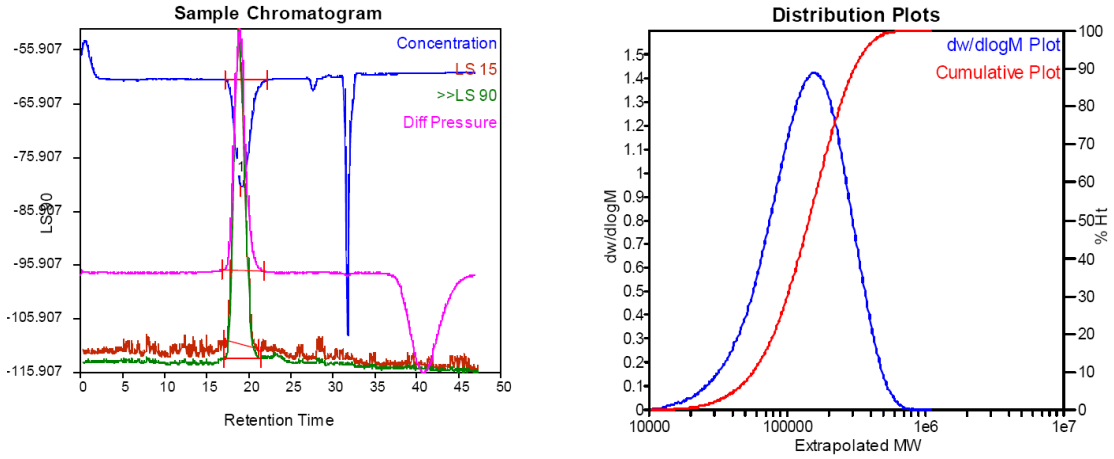
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	458561	272271	373748	462842	535228	362578	1.3727

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.75	18.03	21.03	-11.2236	0	1080.64	100
2	LS 15	16.72	17.82	20.47	38.0388	0	2656.53	100
3	LS 90	16.53	17.87	20.58	149.517	0	10819.2	100
4	Diff Pressure	16.30	17.88	20.80	146.117	0	11310.5	100

Figure S100. GPC trace of the polymer from table 2, entry 4.



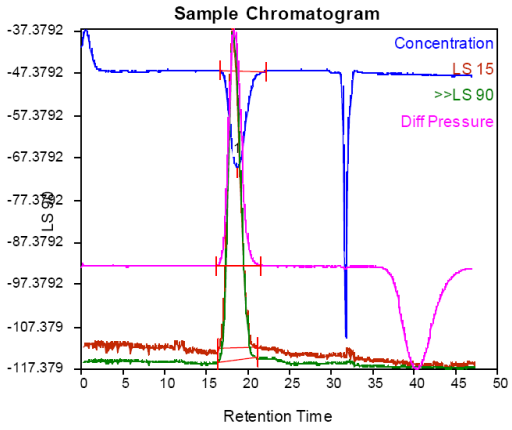
MW Averages

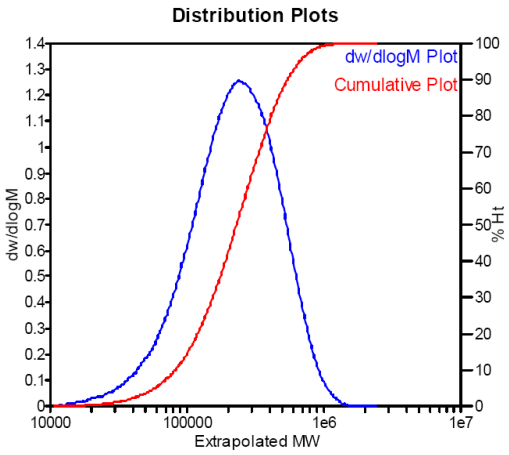
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	154430	106271	164551	227868	291242	157323	1.54841

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.13	19.13	22.22	-10.5244	0	1172.86	100
2	LS 15	17.10	18.72	21.25	14.0409	0	1257.55	100
3	LS 90	17.10	18.75	21.40	61.1789	0	5631.8	100
4	Diff Pressure	16.88	18.80	21.88	66.9535	0	6632.24	100

Figure S101. GPC trace of the polymer from table 2, entry 6.





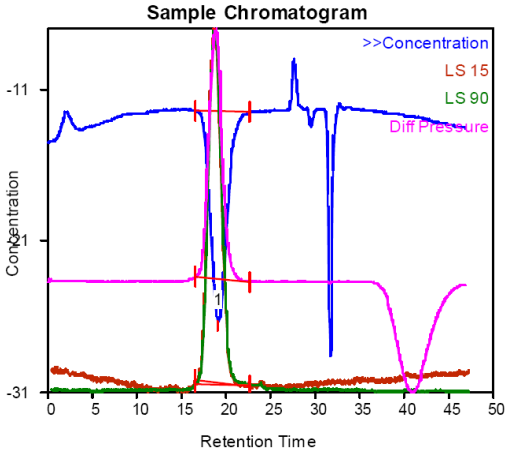
MW Averages

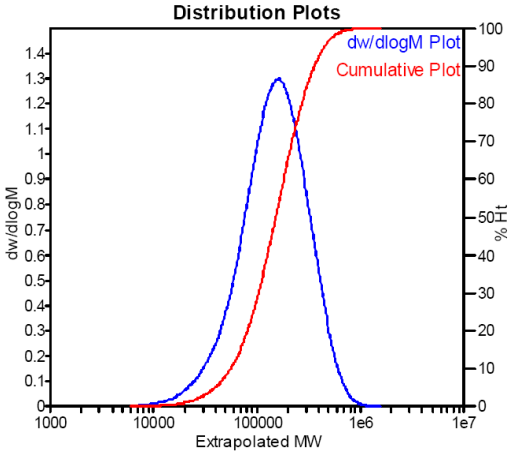
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	240789	159118	276868	412061	550391	259958	1.74002

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.68	18.73	22.12	-8.83509	0	1057.91	100
2	LS 15	16.45	18.17	21.27	18.8618	0	1896.45	100
3	LS 90	16.37	18.17	21.32	78.7007	0	7983.99	100
4	Diff Pressure	16.23	18.27	21.52	79.1671	0	8550.57	100

Figure S102. GPC trace of the polymer from table 2, entry 7.





MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	162329	106863	184532	278456	383754	174112	1.72681

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.57	19.07	22.72	-13.8327	0	1631.51	100
2	LS 15	16.57	18.57	22.72	18.9499	0	1998.86	100
3	LS 90	16.57	18.62	22.72	84.4463	0	8889.98	100
4	Diff Pressure	16.57	18.73	22.72	89.1549	0	9699.26	100

Figure S103. GPC trace of the polymer from table 2, entry 8.

7 DSC of polymer and copolymer

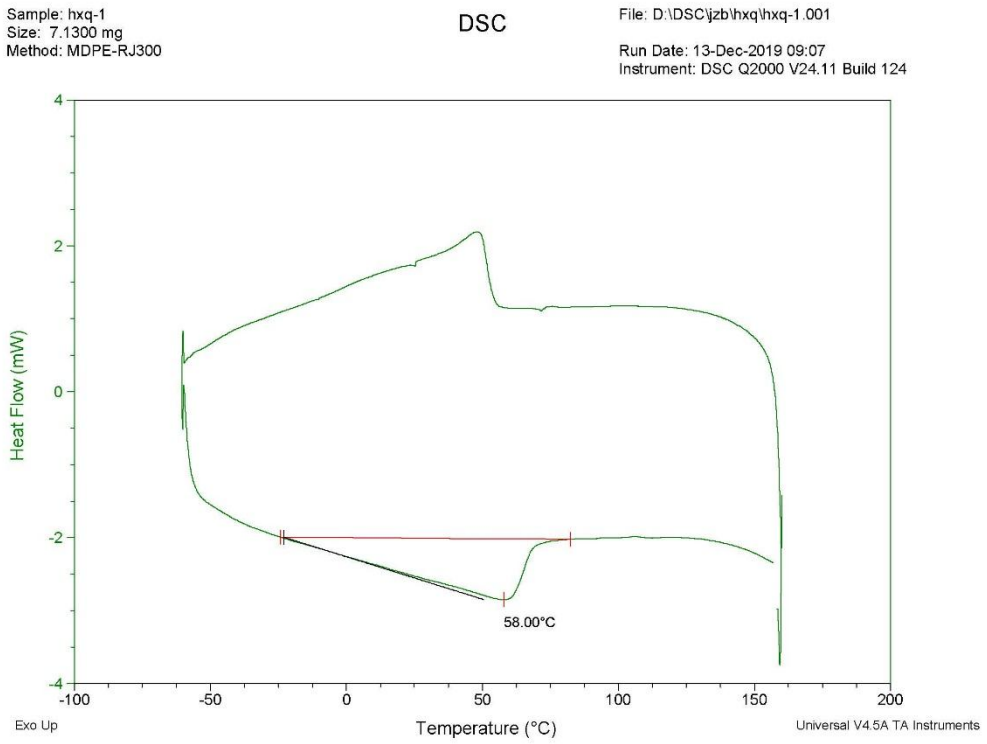


Figure S104. DSC data of the polymer from table 1, entry 1.

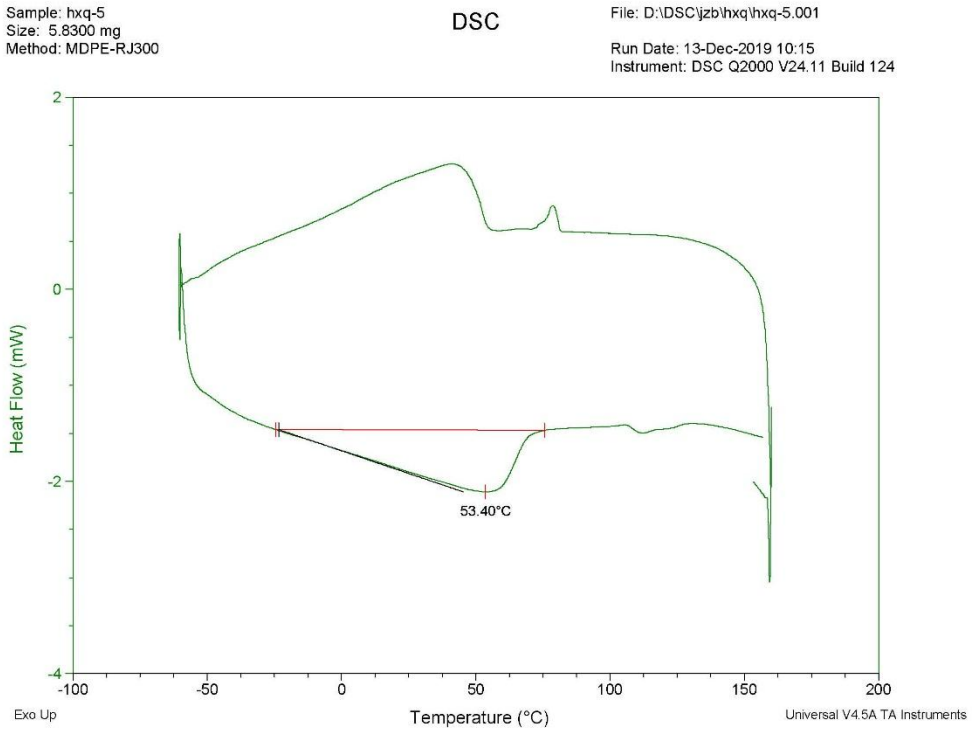


Figure S105. DSC data of the polymer from table 1, entry 9.

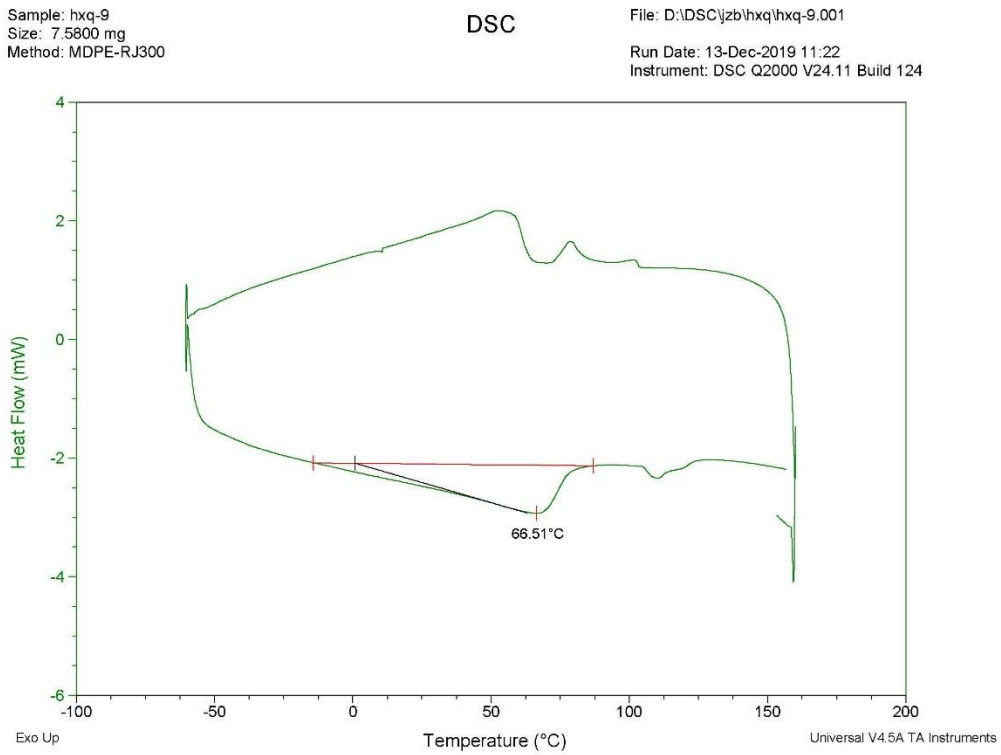


Figure S106. DSC data of the polymer from table 1, entry 13.

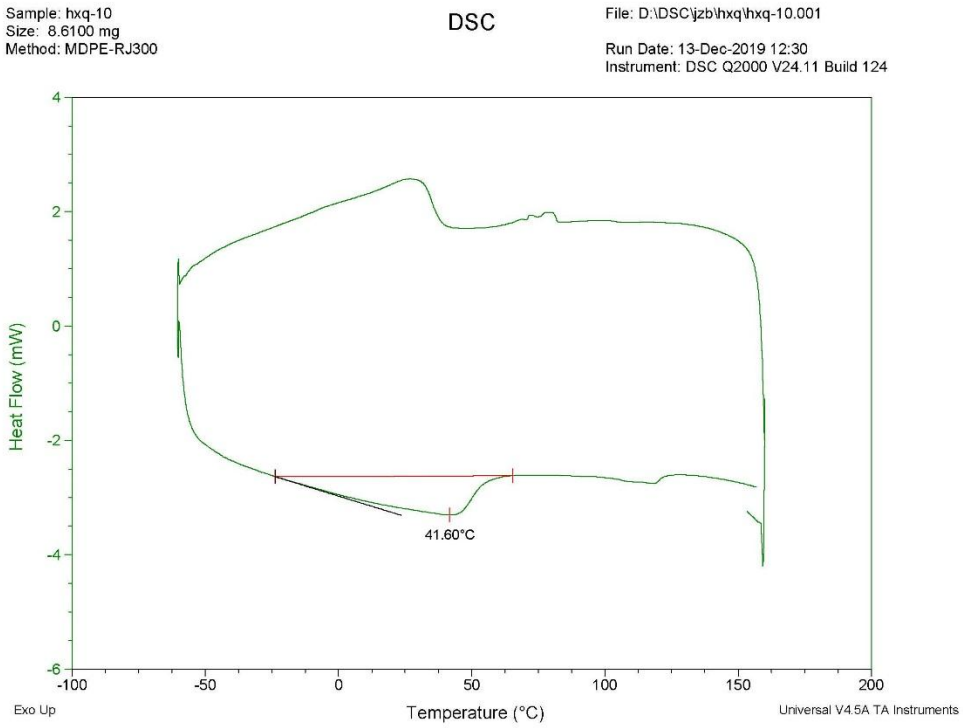


Figure S107. DSC data of the polymer from table 1, entry 14.

8 MALDI-TOF-MS of complex Ni

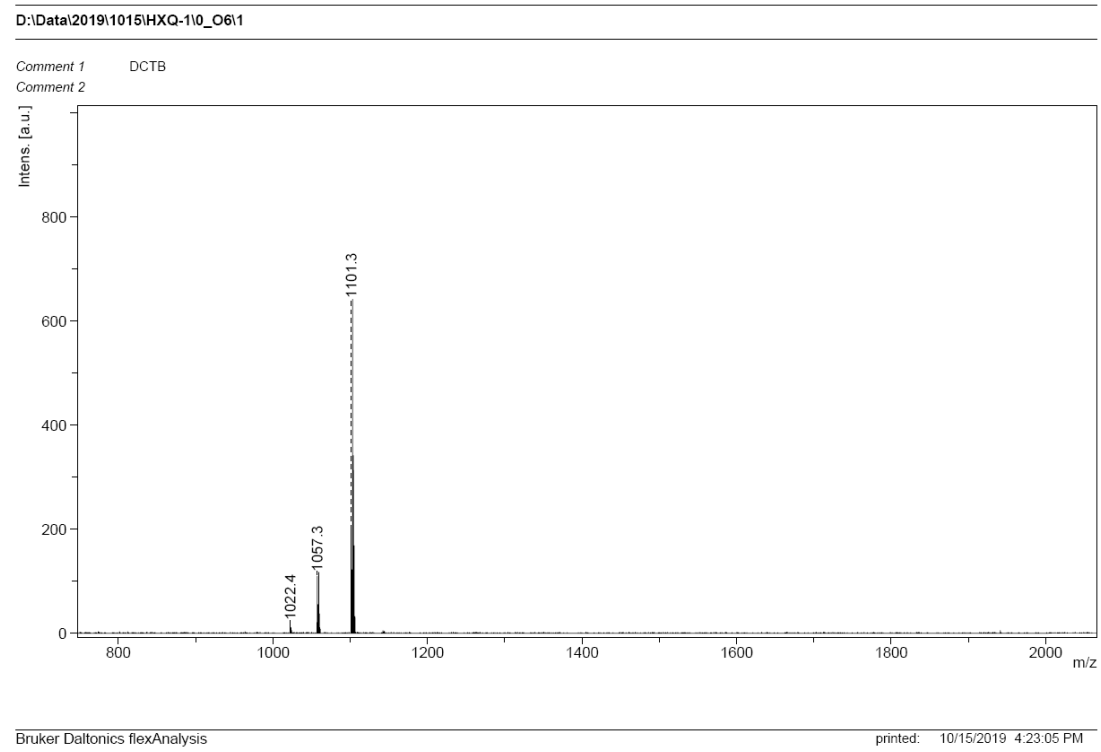


Figure S108. MALDI-TOF-MS of **Cat1**.

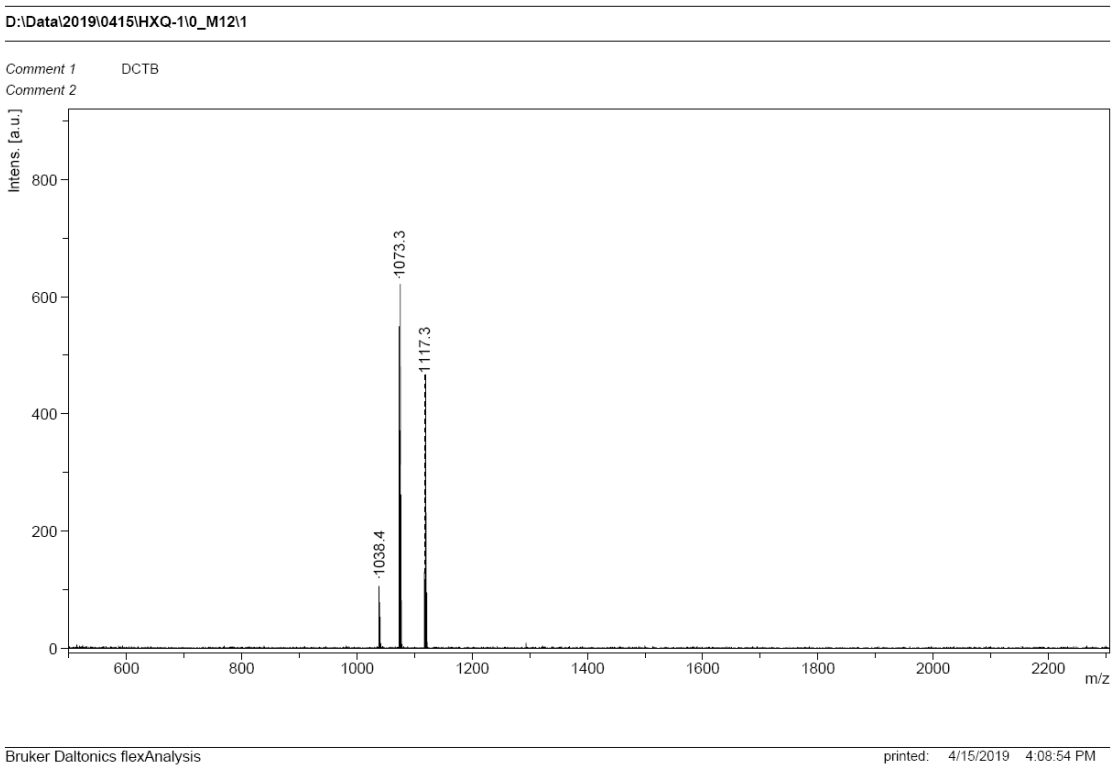


Figure S109. MALDI-TOF-MS of **Cat2**.

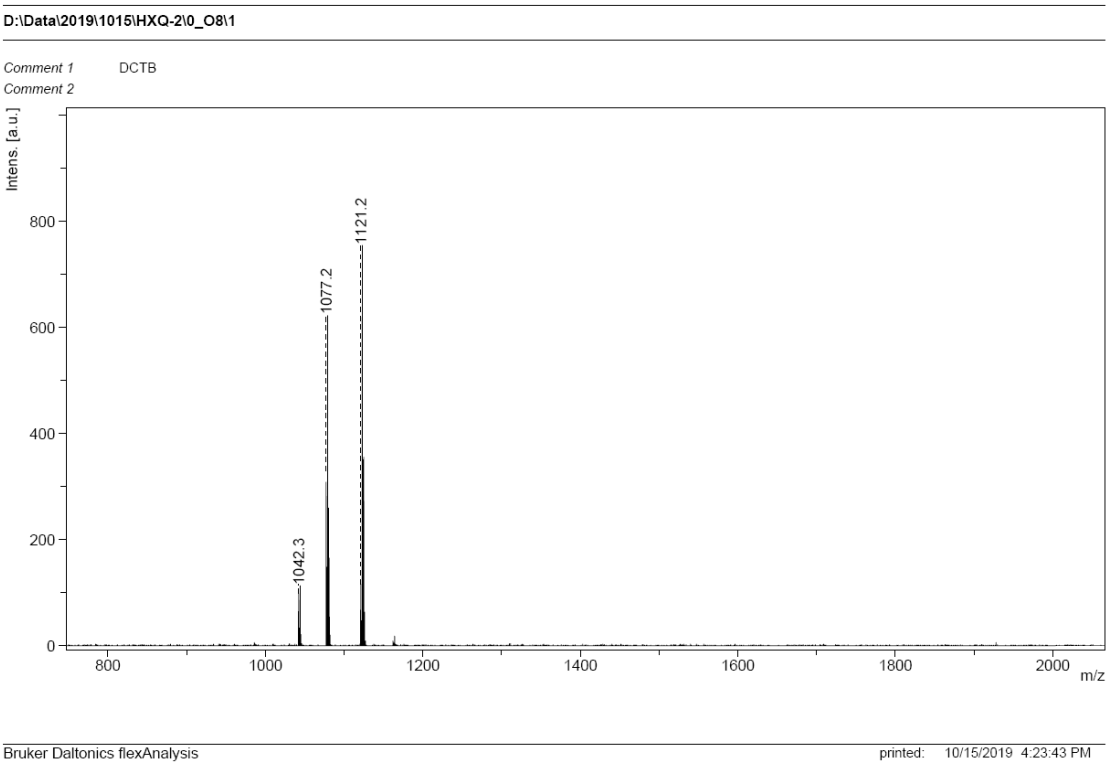


Figure S110. MALDI-TOF-MS of **Cat3**.

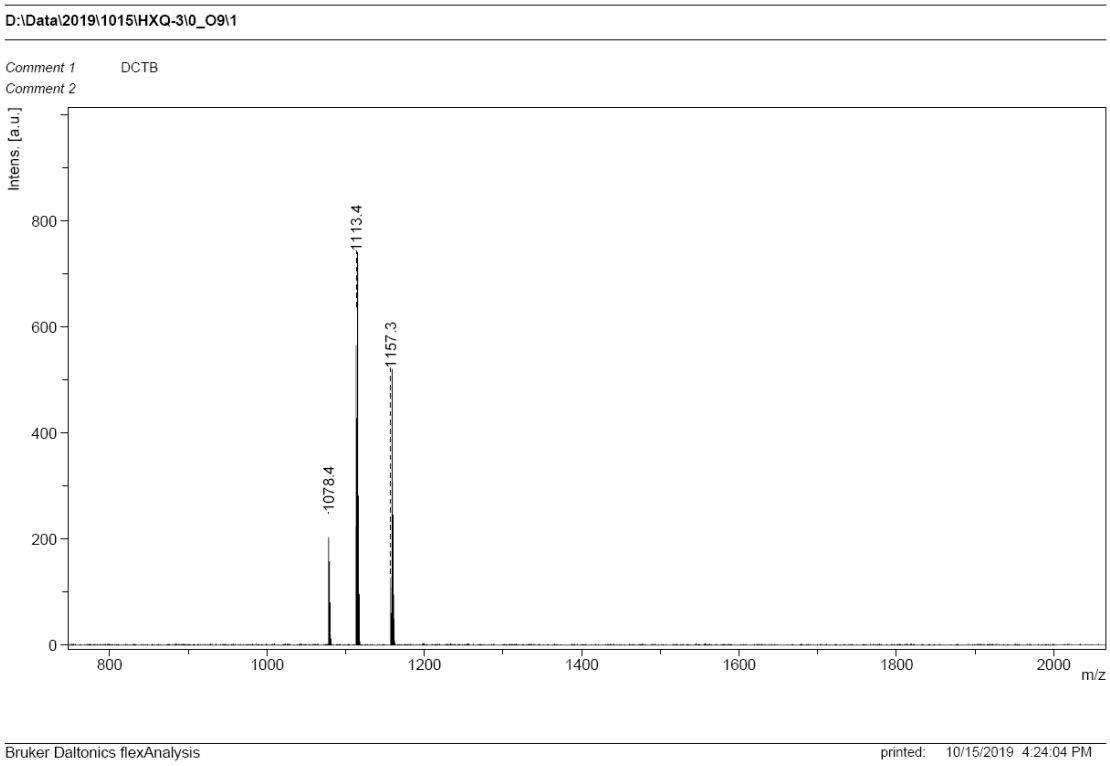


Figure S111. MALDI-TOF-MS of **Cat4**.

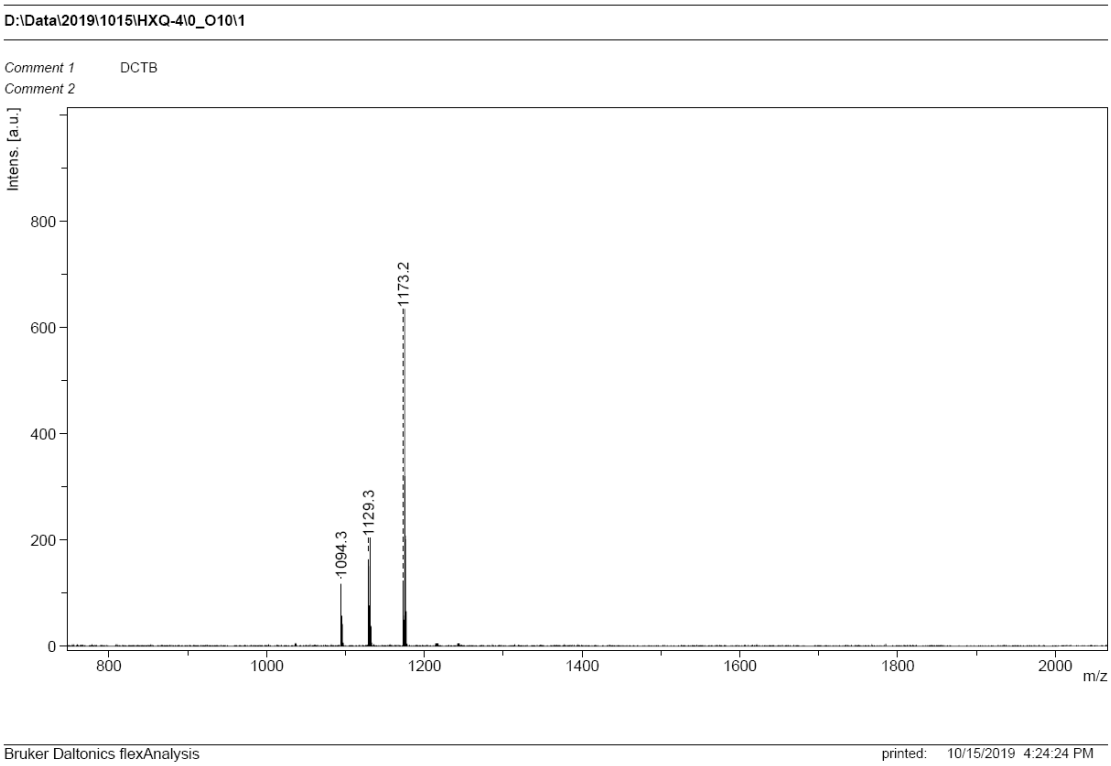


Figure S112. MALDI-TOF-MS of **Cat5**.

9 Crystallographic data and figures of crystal structure

Table S2. Crystallographic data for Cat1 and Cat5.

	Cat1 · $CHCl_3$	**Cat5**
Formula	$C_{73}H_{57}Br_2Cl_3N_2NiO$	$C_{72}H_{52}Br_2F_4N_2NiO$
Formula weight	1303.08	1255.68
Crystal dimensions (mm^3)	0.20 × 0.04 × 0.03	0.30 × 0.22 × 0.19
Crystal system	monoclinic	triclinic
Space group	P 1 21/c 1	P -1
a (Å)	26.3082(11)	11.6968(8)
b (Å)	13.2167(6)	14.6139(10)
c (Å)	19.6610(8)	20.2591(13)
α (°)	90	93.384(3)
β (°)	94.330(2)	95.778(3)
γ (°)	90	100.036(3)
Volume ($Å^3$)	6816.8(5)	3382.3(4)
Z	4	2
T (K)	173(2)	173(2)
D_{calcd} ($g\ cm^{-3}$)	1.270	1.233
μ (mm^{-1})	3.188	2.218
F (000)	2664	1280
No. of rflns. collected	30134	23727
No. of indep. rflns. /R_{int}	9623 / 0.0350	9503 / 0.0273
No. of obsd. rflns. [$I_0 > 2\sigma(I_0)$]	9109	8630
Data / restraints / parameters	9623/ 0 / 744	9503 / 0 / 743
R_1 / wR_2 [$I_0 > 2\sigma(I_0)$]	0.0552 / 0.1477	0.0408 / 0.0976
R_1 / wR_2 (all data)	0.0568 / 0.1492	0.0450 / 0.1016
GOF (on F^2)	1.091	1.059
Largest diff. peak and hole (e $Å^{-3}$)	2.416 / -0.377	0.412 / -0.323
CCDC No.	1975354	1975355

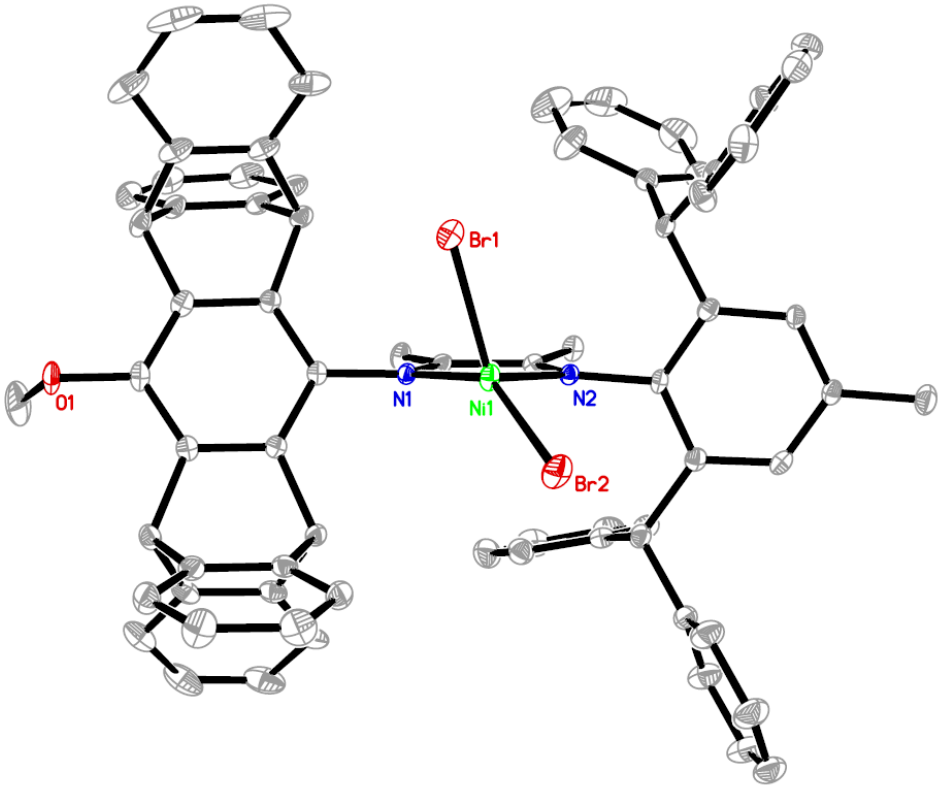


Figure S113. Crystal structure of **Cat1**.

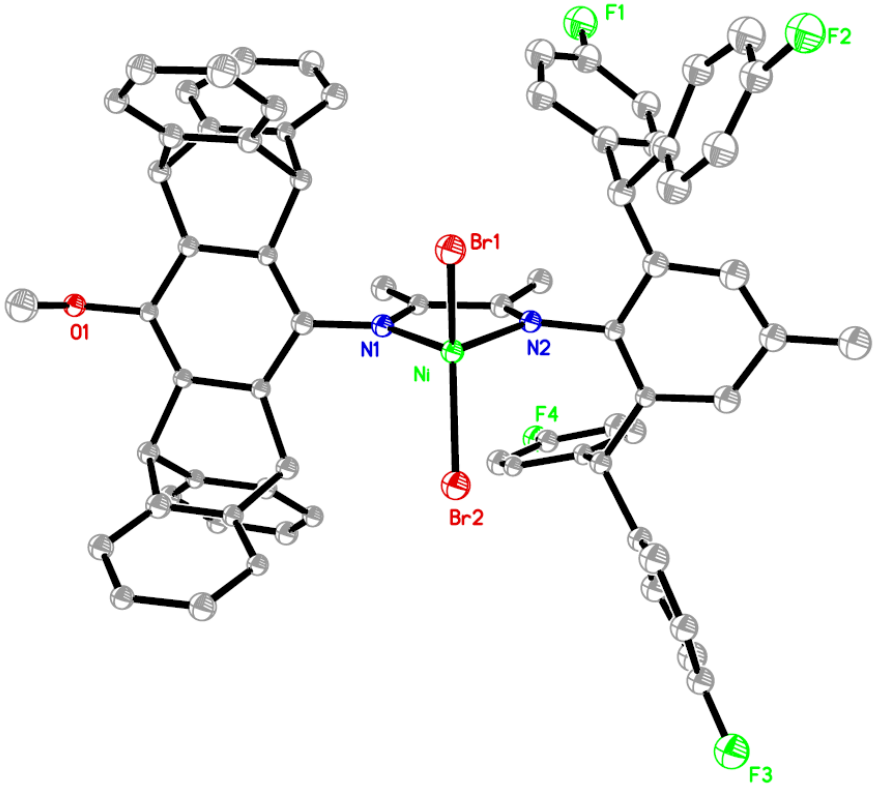


Figure S114. Crystal structure of **Cat5**.

10 References

(1) SMART, version 5.054; Bruker AXS Inc.: Madison, WI, 2000.

(2) SAINT and SADABS, version 6.22; Bruker AXS Inc.: Madison, WI, 2000.

(3) a) G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8. b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.

(4) Spek, A. L. *Acta Cryst.* **2015**, *C71*, 9-18.

(5) Dai, S. Y.; Sui, X. L.; Chen, C. L. *Angew.Chem. Int. Ed.* **2015**, *54*, 9948–9953.

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(7) Savka, R.; Foro, S.; Plenio, H. *Dalton Transactions*, **2016**, *45*, 11015-11024.