

## Supplementary information

### Design of Hybrid Steric $\alpha$ -Diimine Nickel Precatalysts with Intramolecular $\pi$ - $\pi$ Interactions for the Synthesis of Polyethylene Elastomers

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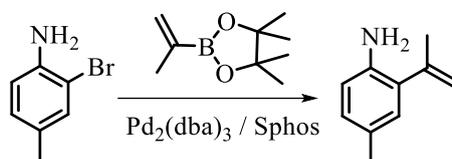
## 1. General Information

**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 ( $^1\text{H}$ : 400 MHz,  $^{13}\text{C}$ : 100 MHz) or a Bruker AV500 ( $^1\text{H}$ : 500 MHz,  $^{13}\text{C}$ : 125 MHz). MALDI-TOF-MS spectra were recorded on an Acquity UPLC & Quattro Premier at the National Analytical Research Centre of Changchun Institute of Applied Chemistry. Elemental analysis was performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry. The molecular weights and molecular weight distributions ( $M_w/M_n$ ) of polyethylenes were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10  $\mu\text{m}$  Mixed-B LS type columns at 150  $^\circ\text{C}$ . Stress/strain experiments were performed at 10 mm/min by means of an Electromechanical Universal Test Machine (E43.104) at room temperature. Polymers were melt-pressed at 150  $^\circ\text{C}$  to obtain the test specimens, which have 15 mm gauge length, 2 mm width, and thickness of 0.92 mm.

## 2. Experimental section

### 2.1 Procedure for the Synthesis of Compounds

#### (1) Synthesis of 2-isopropenyl-4-methylaniline <sup>1</sup>

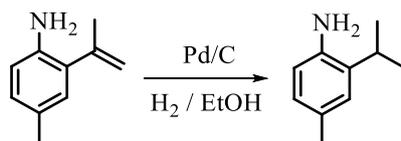


To a mixture of 2-bromo-4-methylaniline (18.61 g, 100 mmol), isopropenylboronic acid pinacol ester (25.21 g, 150 mmol), K<sub>2</sub>CO<sub>3</sub> (61.16 g, 500 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (1.62 g, 4 mmol) were added toluene (160 mL), EtOH (40 mL) and H<sub>2</sub>O (40 mL) at room temperature under N<sub>2</sub> atmosphere. The suspension was degassed under reduced pressure, followed by the refilling of N<sub>2</sub> gas. After that, Pd<sub>2</sub>(dba)<sub>3</sub> (0.90 g, 1 mmol) was added to the suspension. After stirring for 24 h at 90 °C, the organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The residue was filtered through Celite pad, and evaporated. The residue was purified by column chromatography (hexane: CH<sub>2</sub>Cl<sub>2</sub> = 4:1) to afford the title compound as yellow liquid (12.57 g, yield: 85 %).

<sup>1</sup>H NMR (500 MHz, 298 K, CDCl<sub>3</sub>, 7.26 ppm): δ = 6.86 (m, 2H, Ar-*H*), 6.64 (d, 1H, Ar-*H*), 5.28 (s, 1H, -C=CH<sub>2</sub>), 5.04 (s, 1H, -C=CH<sub>2</sub>), 3.71 (br, 2H, -NH<sub>2</sub>), 2.24 (s, 3H, -CH<sub>3</sub>), 2.07 (m, 3H, -CH<sub>3</sub>) ppm.

**Elemental analysis:** calc. for C<sub>10</sub>H<sub>13</sub>N: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.61; H, 8.92; N, 9.47.

#### (2) Synthesis of 2-isopropyl-4-methylaniline <sup>1</sup>

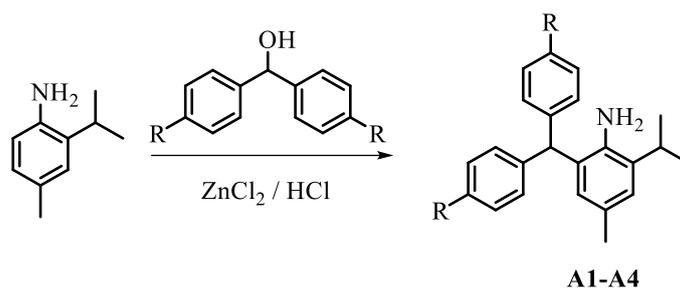


2-isopropenyl-4-methylaniline (12.57 g, 425 mmol) was dissolved in ethanol (100 mL), and 5% Pd/C (0.2 g, 2.0 mmol) was added. After stirring and refluxing for 48 hours under N<sub>2</sub> atmosphere, the brownish-yellow liquid was obtained by vacuum evaporation (11.98 g, yield: 94%).

<sup>1</sup>H NMR (500 MHz, 298 K, CDCl<sub>3</sub>, 7.26 ppm): δ = 6.97 (s, 1H, Ar-*H*), 6.85 (d, 1H, Ar-*H*), 6.63 (d, 1H, Ar-*H*), 3.53 (br, 2H, -NH<sub>2</sub>), 2.92 (m, 1H, -CH-), 2.28 (s, 3H, -CH<sub>3</sub>), 1.28 (d, 6H, -CH<sub>3</sub>) ppm.

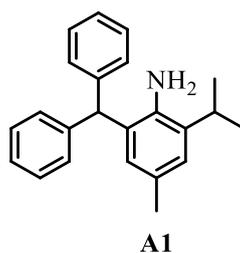
**Elemental analysis:** calc. for C<sub>10</sub>H<sub>15</sub>N: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.52; H, 10.18; N, 9.30.

(3) Synthesis of arylamines **A1-A4** <sup>2</sup>



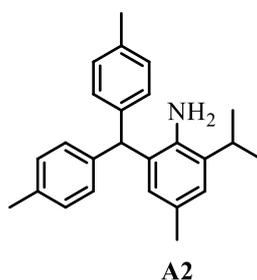
**A1:** R = H, **A2:** R = CH<sub>3</sub>, **A3:** R = OCH<sub>3</sub>, **A4:** R = F

The mixture of 2-isopropyl-4-methylaniline (10 mmol, 1.0 equivalent) and diarylmethanol (10 mmol, 1.0 equivalent) was heated to 120 °C. After the mixture was melted, a concentrated hydrochloric acid (1.0 mL) solution of dissolved anhydrous zinc chloride (0.68 g, 5 mmol, 0.5 equivalent) was added to the mixture and the temperature was raised to 160 °C. After 30 minutes, the mixture was cooled to room temperature and dissolved in dichloromethane (200 mL). The dichloromethane layer was washed with water (3 × 200 mL) and dried with anhydrous magnesium sulfate for 30 minutes. Crystallize the mixture through ethanol to obtain pale yellow crystals (**A1-A4**).



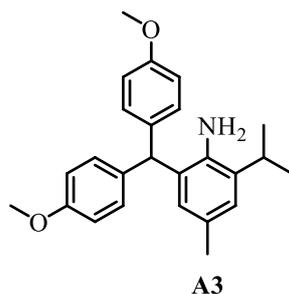
**A1** (2.68 g, 85%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.31 (m, 4H, Ar-H), 7.24 (m, 2H, Ar-H), 7.15 (m, 4H, Ar-H), 6.91 (s, 1H, Ar-H), 6.34 (s, 1H, Ar-H), 5.52 (s, 1H, -CH-), 3.43 (br, 2H, -NH<sub>2</sub>), 2.86 (m, 1H, -CH-), 2.16 (s, 3H, -CH<sub>3</sub>), 1.26 (d, 6H, -CH<sub>3</sub>).

**Elemental analysis:** calc. for C<sub>23</sub>H<sub>25</sub>N: C, 87.57; H, 7.99; N, 4.44. Found: C, 87.61; H, 8.02; N, 4.37.



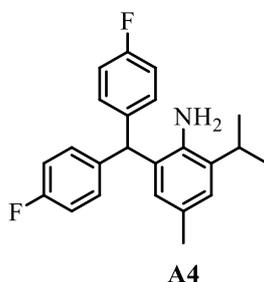
**A2** (2.64 g, 77%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.09 (m, 4H, Ar-H), 7.03 (m, 4H, Ar-H), 6.90 (s, 1H, Ar-H), 6.37 (s, 1H, Ar-H), 5.43 (s, 1H, -CH-), 3.44 (br, 2H, -NH<sub>2</sub>), 2.86 (m, 1H, -CH-), 2.34 (s, 6H, -CH<sub>3</sub>), 2.17 (s, 3H, -CH<sub>3</sub>), 1.26 (d, 6H, -CH<sub>3</sub>).

**Elemental analysis:** calc. for C<sub>25</sub>H<sub>29</sub>N: C, 87.41; H, 8.51; N, 4.08. Found: C, 87.44; H, 8.55; N, 4.01.



**A3** (1.76 g, 72%):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.03 (m, 4H, Ar-H), 6.90 (s, 1H, Ar-H), 6.83 (m, 4H, Ar-H), 6.35 (s, 1H, Ar-H), 5.41 (s, 1H, -CH-), 3.80 (s, 6H, -OCH<sub>3</sub>), 3.45 (br, 2H, -NH<sub>2</sub>), 2.86 (m, 1H, -CH-), 2.17 (s, 3H, -CH<sub>3</sub>), 1.26 (d, 6H, -CH<sub>3</sub>).

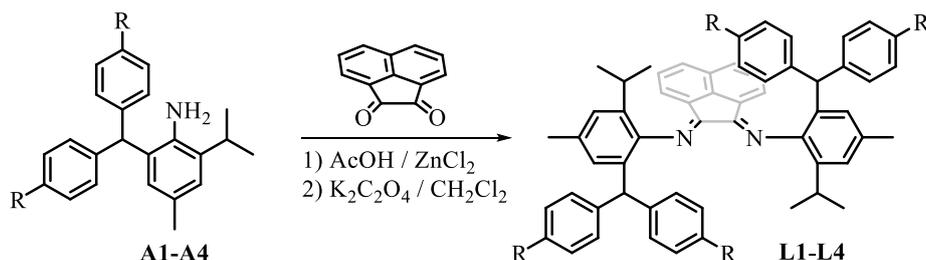
**Elemental analysis:** calc. for C<sub>25</sub>H<sub>29</sub>NO<sub>2</sub>: C, 79.96; H, 7.78; N, 3.73. Found: C, 80.00; H, 7.81; N, 3.64.



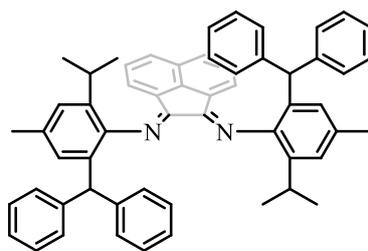
**A4** (2.88 g, 82%):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.07 (m, 4H, Ar-H), 7.00 (m, 4H, Ar-H), 6.92 (s, 1H, Ar-H), 6.28 (s, 1H, Ar-H), 5.47 (s, 1H, -CH-), 3.40 (br, 2H, -NH<sub>2</sub>), 2.86 (m, 1H, -CH-), 2.16 (s, 3H, -CH<sub>3</sub>), 1.26 (d, 6H, -CH<sub>3</sub>).

**Elemental analysis:** calc. for C<sub>23</sub>H<sub>23</sub>F<sub>2</sub>N: C, 78.61; H, 6.60; N, 3.99. Found: C, 78.63; H, 6.62; N, 3.93.

#### (4) Synthesis of Ligands **L1** - **L4**<sup>2,3</sup>



The condensation of arylamines **A1-A4** (2 mmol, 1.0 equivalent) and acenaphthenone (1 mmol, 0.5 equivalent) was performed using the template method. To the reaction system, 2 mL of acetic acid dissolved in ZnCl<sub>2</sub> (1.0 equivalent) was added to the arylamines and acenaphthenone acetate solution (10 mL), and the mixture was reacted at 90 °C for four hours. At the end of the reaction, the yellow solid powder was obtained by filtration and ether washing. The yellow powder was dissolved in 40 mL of dichloromethane. Then, 10% potassium oxalate solution was added and stirred at room temperature for one hour. Afterward, the dichloromethane layer was washed with water (3 × 20 mL) and dried with anhydrous magnesium sulfate for 30 minutes. Finally, the yellow powder (**L1-L4**) was obtained by ethanol precipitation.

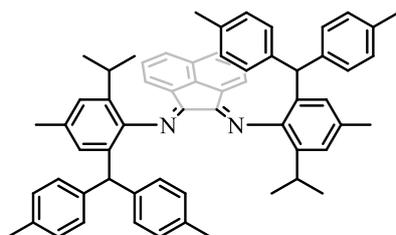


L1

**L1** (1.07 g, 69%):  $^1\text{H NMR}$  (500 MHz, 298 K,  $\text{CDCl}_3$ , 7.26 ppm):  $\delta$  = 7.67 - 7.52 (m, 2H, Ar-H), 7.22 - 6.68 (m, 22H, Ar-H), 6.35 - 6.12 (m, 6H, Ar-H), 5.75, 5.69 (s, 2H, -CH-), 3.13 - 3.84 (m, 2H, -CH-), 2.34 (s, 6H, -CH<sub>3</sub>), 1.30, 0.85 (m, 6H, -CH<sub>3</sub>), 1.18 - 1.12 (m, 6H, -CH<sub>3</sub>) ppm. Isomer ratio = 2.1:1

$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, 298 K,  $\text{CDCl}_3$ , 77.16 ppm):  $\delta$  = 163.21, 144.01, 142.92, 141.69, 143.41, 135.71, 133.08, 132.76, 129.98, 129.85, 129.76, 129.67, 128.34, 128.11, 128.05, 127.90, 127.42, 127.18, 126.64, 126.01, 125.97, 125.68, 125.14, 125.04, 124.76, 123.67, 123.46, 52.65, 51.80, 28.36, 27.99, 24.51, 23.59, 23.45, 23.21, 21.65 ppm.

**Elemental analysis:** calc. for  $\text{C}_{58}\text{H}_{52}\text{N}_2$ : C, 89.65; H, 6.75; N, 3.61. Found: C, 89.69; H, 6.78; N, 3.56.

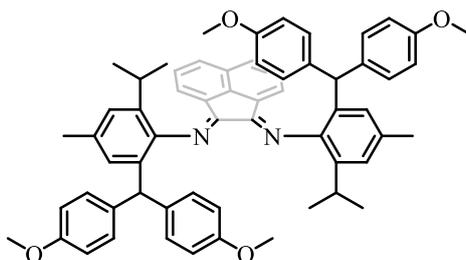


L2

**L2** (1.13 g, 68%):  $^1\text{H NMR}$  (500 MHz, 298 K,  $\text{CDCl}_3$ , 7.26 ppm):  $\delta$  = 7.70 - 7.56 (m, 2H, Ar-H), 7.11 - 6.66 (m, 18H, Ar-H), 6.43 - 6.04 (m, 6H, Ar-H), 5.64, 5.57 (s, 2H, -CH-), 3.17 - 3.87 (m, 2H, -CH-), 2.36 (s, 6H, -CH<sub>3</sub>), 2.30, 2.27 (s, 6H, -CH<sub>3</sub>), 1.87, 1.43 (s, 6H, -CH<sub>3</sub>), 1.31 - 1.16 (m, 12H, -CH<sub>3</sub>) ppm. Isomer ratio = 3.2:1

$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, 298 K,  $\text{CDCl}_3$ , 77.16 ppm):  $\delta$  = 163.33, 145.69, 144.10, 138.85, 135.70, 135.39, 135.23, 134.73, 134.18, 132.96, 130.02, 129.82, 129.64, 129.55, 128.77, 128.75, 128.60, 128.21, 128.15, 127.47, 126.66, 124.95, 124.53, 123.57, 51.94, 51.07, 28.35, 28.02, 24.51, 23.56, 23.22, 21.67, 21.10, 20.67, 20.23 ppm.

**Elemental analysis:** calc. for  $\text{C}_{62}\text{H}_{60}\text{N}_2$ : C, 89.38; H, 7.26; N, 3.36. Found: C, 89.42; H, 7.29; N, 3.32.

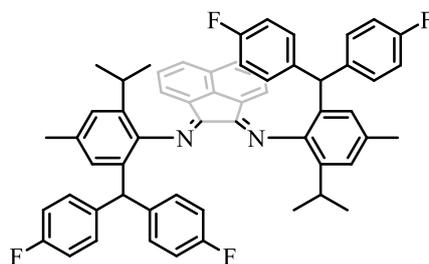


L3

**L3** (1.11 g, 62%):  $^1\text{H NMR}$  (500 MHz, 298 K,  $\text{CDCl}_3$ , 7.26 ppm):  $\delta = 7.69 - 7.58$  (m, 2H, Ar-H), 7.15 - 6.68 (m, 18H, Ar-H), 6.37 - 5.81 (m, 6H, Ar-H), 5.66, 5.56 (s, 2H, -CH-), 3.77, 3.74 (s, 6H, -CH<sub>3</sub>), 3.33, 3.04 (s, 6H, -CH<sub>3</sub>), 3.17, 2.87 (m, 2H, -CH-), 2.36 (s, 6H, -CH<sub>3</sub>), 1.31, 0.88 (m, 6H, -CH<sub>3</sub>), 1.17 (m, 6H, -CH<sub>3</sub>) ppm. Isomer ratio = 1.3:1

$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, 298 K,  $\text{CDCl}_3$ , 77.16 ppm):  $\delta = 157.85, 157.81, 157.19, 156.56, 136.83, 135.27, 130.93, 130.82, 130.62, 130.59, 128.34, 128.11, 127.94, 127.21, 126.70, 124.99, 124.56, 123.63, 113.46, 113.25, 112.84, 55.34, 55.31, 54.80, 51.08, 50.25, 28.35, 28.04, 24.53, 23.63, 23.51, 23.14, 21.69$  ppm.

**Elemental analysis:** calc. for  $\text{C}_{62}\text{H}_{60}\text{N}_2\text{O}_4$ : C, 83.00; H, 6.74; N, 3.12. Found: C, 83.03; H, 6.77; N, 3.08.



**L4**

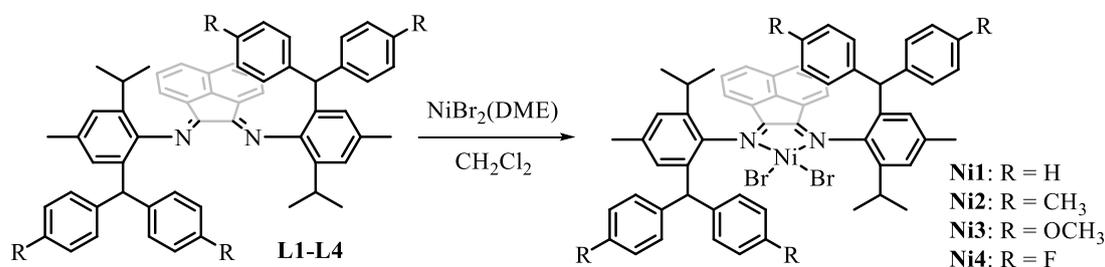
**L4** (1.12 g, 66%):  $^1\text{H NMR}$  (500 MHz, 298 K,  $\text{CDCl}_3$ , 7.26 ppm):  $\delta = 7.77 - 7.67$  (m, 2H, Ar-H), 7.17 - 6.62 (m, 18H, Ar-H), 6.36 - 6.04 (m, 6H, Ar-H), 5.65, 5.61 (s, 2H, -CH-), 3.09, 2.86 (m, 2H, -CH-), 2.37 (s, 6H, -CH<sub>3</sub>), 1.31, 0.89 (m, 6H, -CH<sub>3</sub>), 1.19 - 1.15 (m, 6H, -CH<sub>3</sub>) ppm. Isomer ratio = 1.4:1

$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, 298 K,  $\text{CDCl}_3$ , 77.16 ppm):  $\delta = 163.33, 162.43, 161.29, 160.48, 159.34, 145.45, 139.99, 139.35, 137.52, 135.88, 132.22, 131.21, 131.15, 131.03, 130.97, 129.94, 128.80, 128.42, 128.13, 126.84, 125.10, 123.54, 115.05, 114.88, 114.45, 114.28, 51.09, 28.17, 24.41, 23.50, 21.65$  ppm.

$^{19}\text{F NMR}$  (470 MHz, 298 K,  $\text{CDCl}_3$ , 7.26 ppm):  $\delta = -117.00, -117.23, -117.25, -117.72$

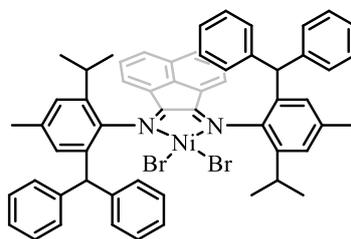
**Elemental analysis:** calc. for  $\text{C}_{58}\text{H}_{48}\text{F}_4\text{N}_2$ : C, 82.05; H, 5.70; N, 3.30. Found: C, 82.09; H, 5.73; N, 3.25.

#### (5) Synthesis of Complexes Ni1-Ni4



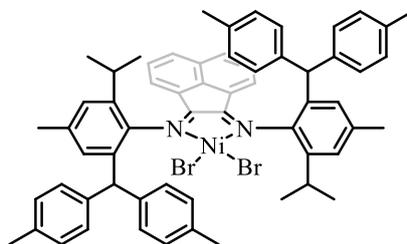
In a nitrogen atmosphere, a mixture of 0.2 mmol of ligand **L1-L4** and 0.2 mmol of  $\text{NiBr}_2(\text{DME})$  was introduced into 10 mL of methylene chloride. This mixture was then stirred at room temperature overnight. Following the completion of the reaction, the solvent was partially evaporated under reduced pressure. Subsequently, the remaining

mixture was diluted with 20 mL of anhydrous ether, leading to the formation of an orange-red solid precipitate. The solids were then separated through filtration, washed thoroughly with ether, and finally dried under vacuum conditions to obtain the desired **Ni1-Ni4** compounds.



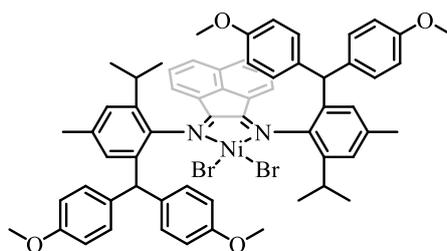
**Ni1**

**Ni1** (177.2 mg, 89%): **MALDI-TOF MS** (m/z): calcd for  $C_{58}H_{52}Br_2N_2Ni$ : 992.2, Found, 992.3,  $[M-2Br]^+$ . **Elemental analysis**: calc. for  $C_{58}H_{52}Br_2N_2Ni$ : C, 69.97; H, 5.26; N, 2.81. Found: C, 70.01; H, 5.28; N, 2.77.



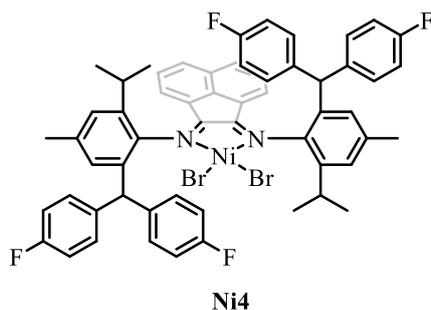
**Ni2**

**Ni2** (185.1 mg, 88%): **MALDI-TOF MS** (m/z): calcd for  $C_{62}H_{60}Br_2N_2Ni^+$ : 969.3, Found, 969.3,  $[M-Br]^+$ . **Elemental analysis**: calc. for  $C_{62}H_{60}Br_2N_2Ni$ : C, 70.81; H, 5.75; N, 2.66. Found: C, 70.83; H, 5.77; N, 2.63.



**Ni3**

**Ni3** (189.7 mg, 85%): **MALDI-TOF MS** (m/z): calcd for  $C_{62}H_{60}Br_2N_2NiO_4$ : 1112.2, Found, 1112.2,  $[M-2Br]^+$ . **Elemental analysis**: calc. for  $C_{62}H_{60}Br_2N_2NiO_4$ : C, 66.75; H, 5.42; N, 2.51. Found: C, 66.78; H, 5.44; N, 2.48.



**Ni4** (187.9 mg, 88%): **MALDI-TOF MS** ( $m/z$ ): calcd for  $C_{58}H_{48}BrF_4N_2Ni^+$ : 985.2, Found, 985.2,  $[M-Br]^+$ . **Elemental analysis**: calc. for  $C_{58}H_{48}Br_2F_4N_2Ni$ : C, 65.26; H, 4.53; N, 2.62. Found: C, 65.30; H, 4.56; N, 2.57.

**Ni1'** was prepared using literature procedure <sup>4</sup>.

## 2.2 Ethylene Polymerization

In a typical experiment, a 350 mL glass pressure reactor connected with a high-pressure gas line was firstly dried at 100 °C 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(II) precatalyst 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 bar of ethylene. After specific time, the pressure reactor was vented and the polymerization was quenched via the addition of 100 mL acidic EtOH (5% HCl in EtOH) and dried in a vacuum oven to constant weight.

### 3. NMR Spectra of Compounds and MALDI-TOF of Precatalysts

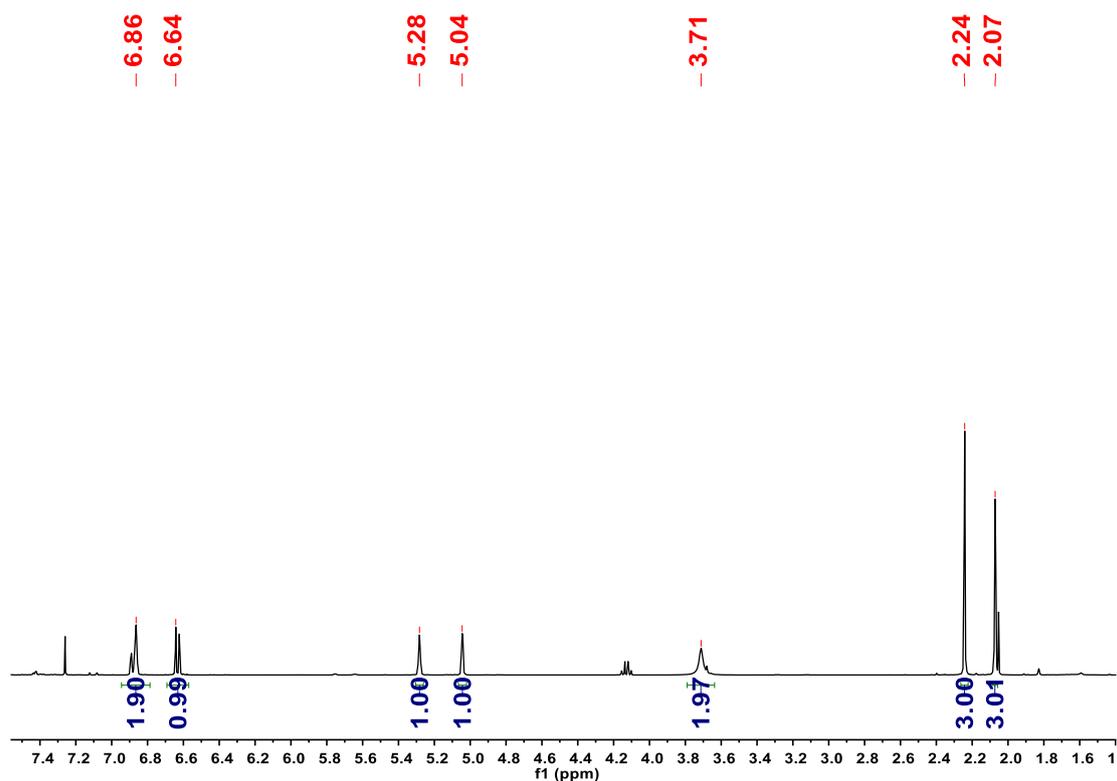


Figure S1.  $^1\text{H}$  NMR spectrum of 2-isopropenyl-4-methylaniline in  $\text{CDCl}_3$ .

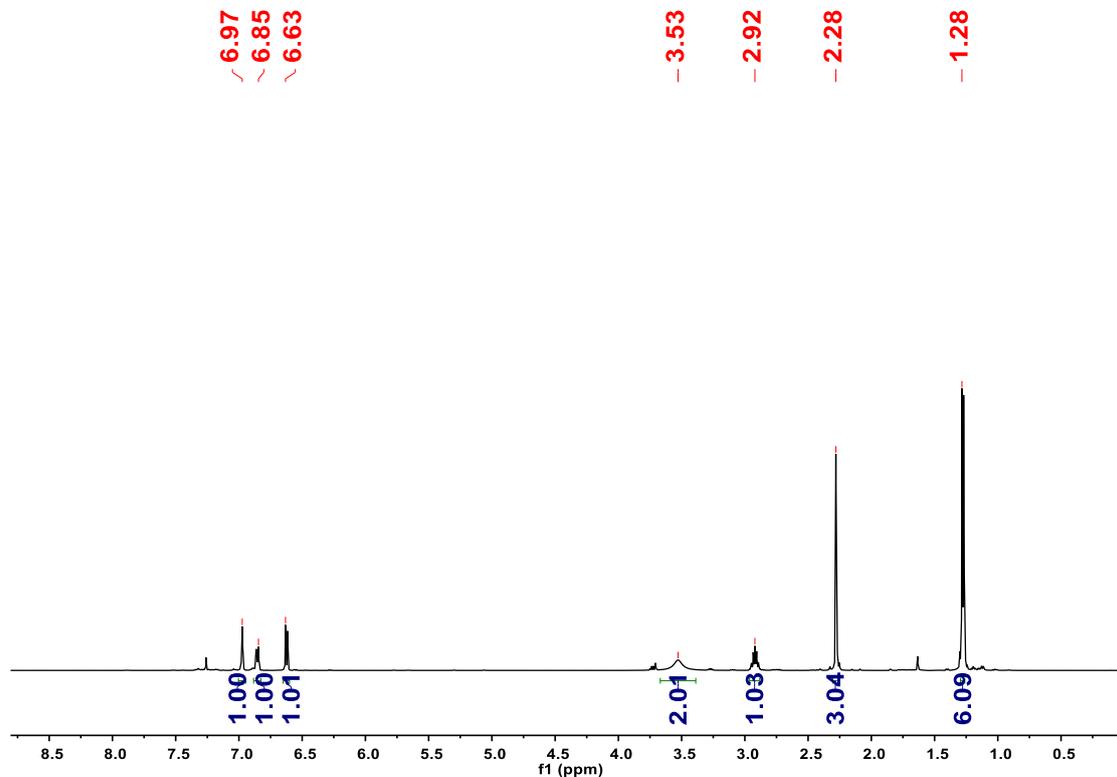


Figure S2.  $^1\text{H}$  NMR spectrum of 2-isopropyl-4-methylaniline in  $\text{CDCl}_3$ .

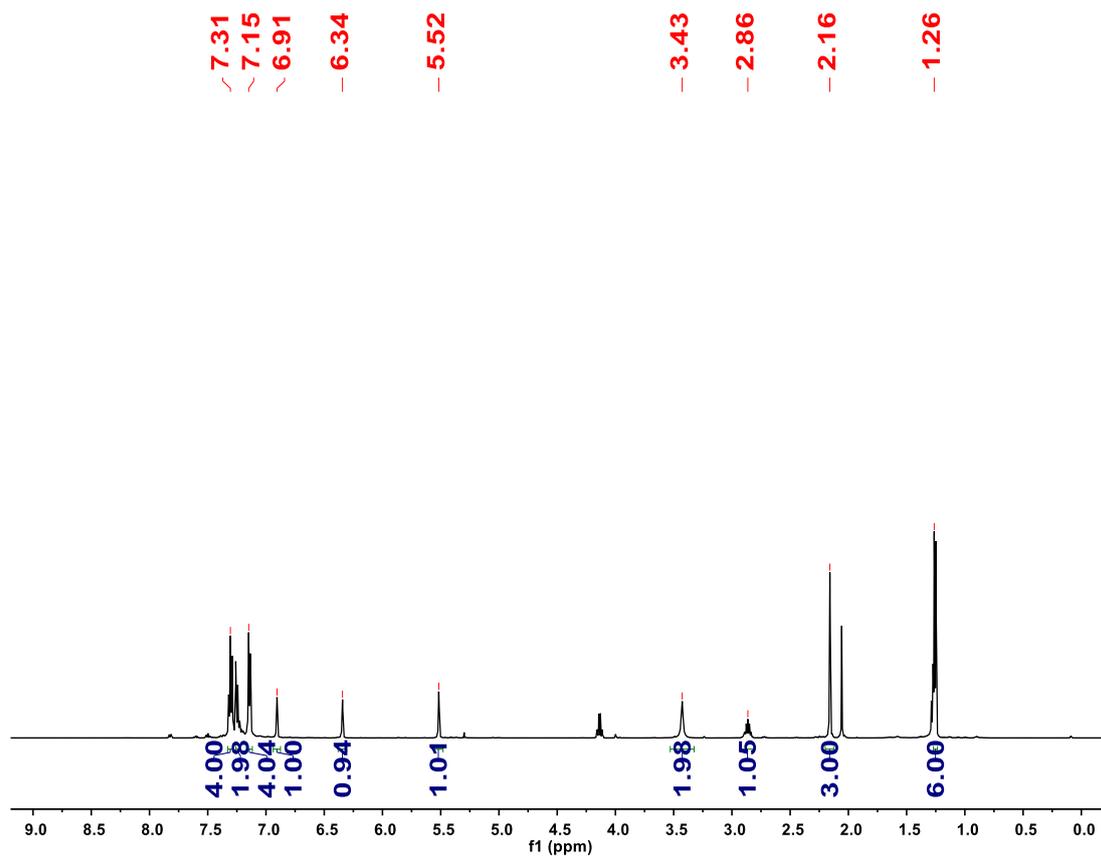


Figure S3.  $^1\text{H}$  NMR spectrum of **A1** in  $\text{CDCl}_3$ .

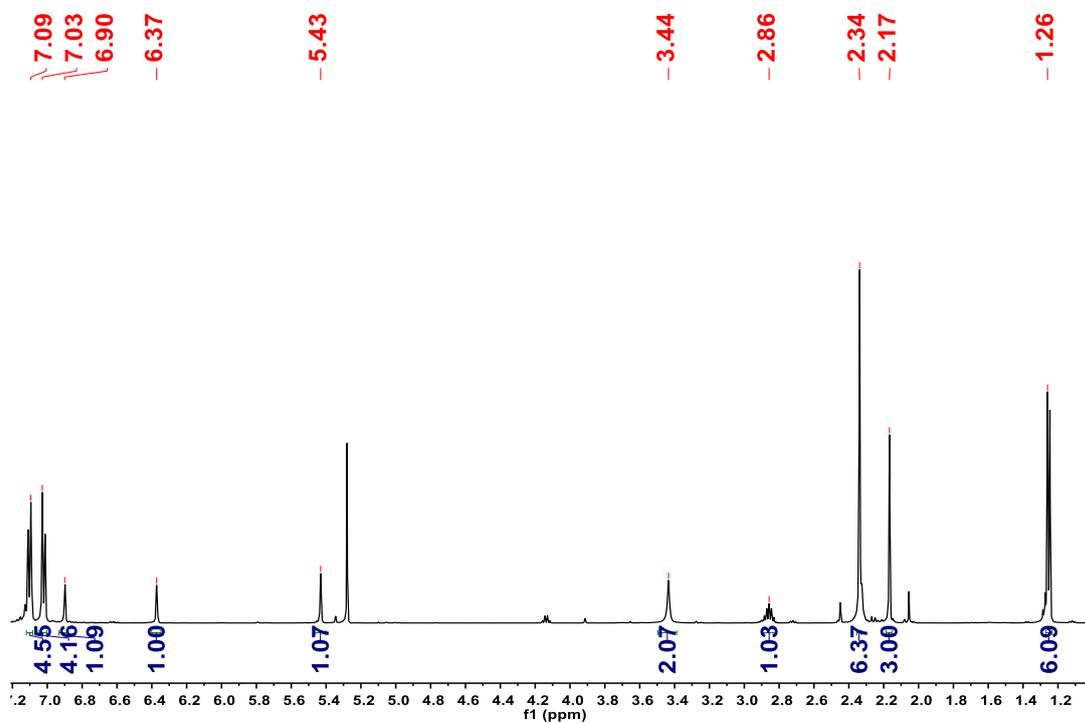


Figure S4.  $^1\text{H}$  NMR spectrum of **A2** in  $\text{CDCl}_3$ .

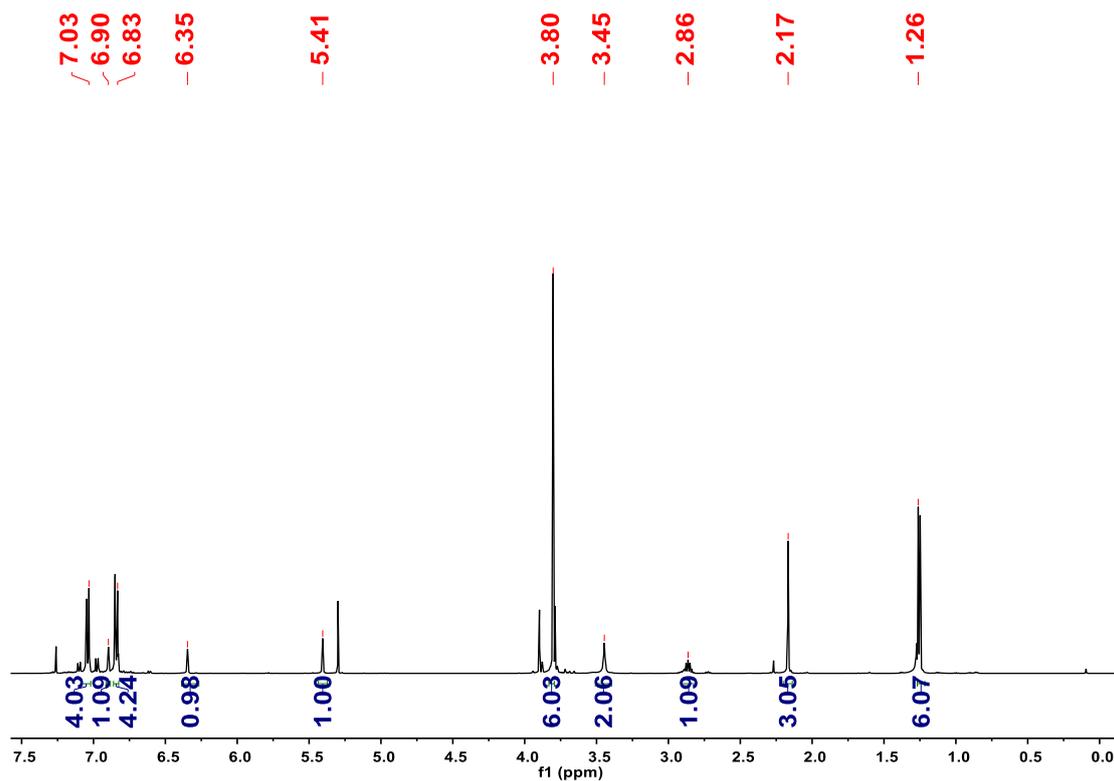


Figure S5.  $^1\text{H}$  NMR spectrum of **A3** in  $\text{CDCl}_3$ .

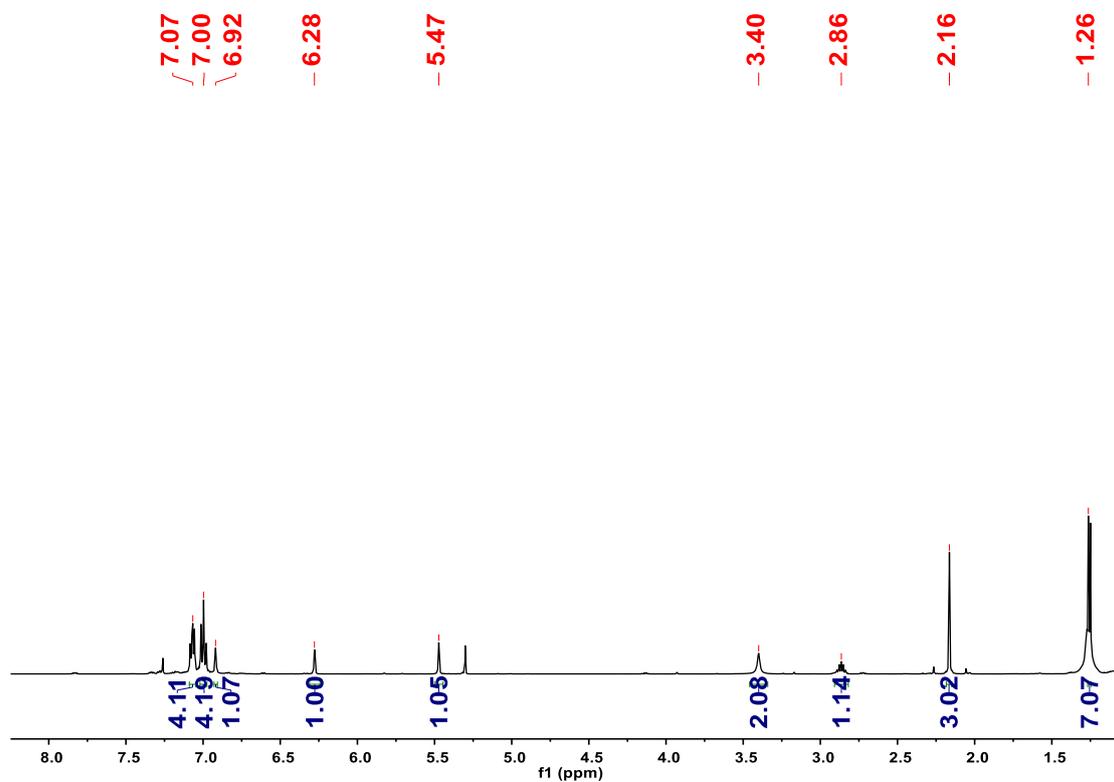


Figure S6.  $^1\text{H}$  NMR spectrum of **A4** in  $\text{CDCl}_3$ .

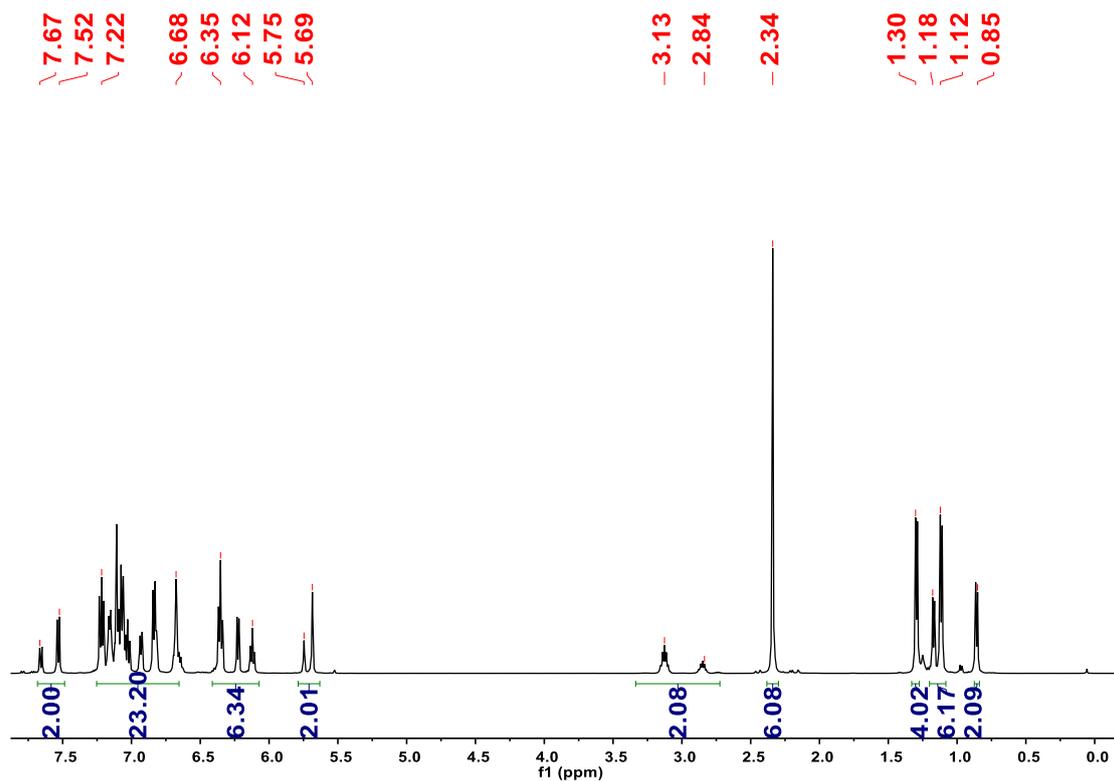


Figure S7.  $^1\text{H}$  NMR spectrum of L1 in  $\text{CDCl}_3$ .

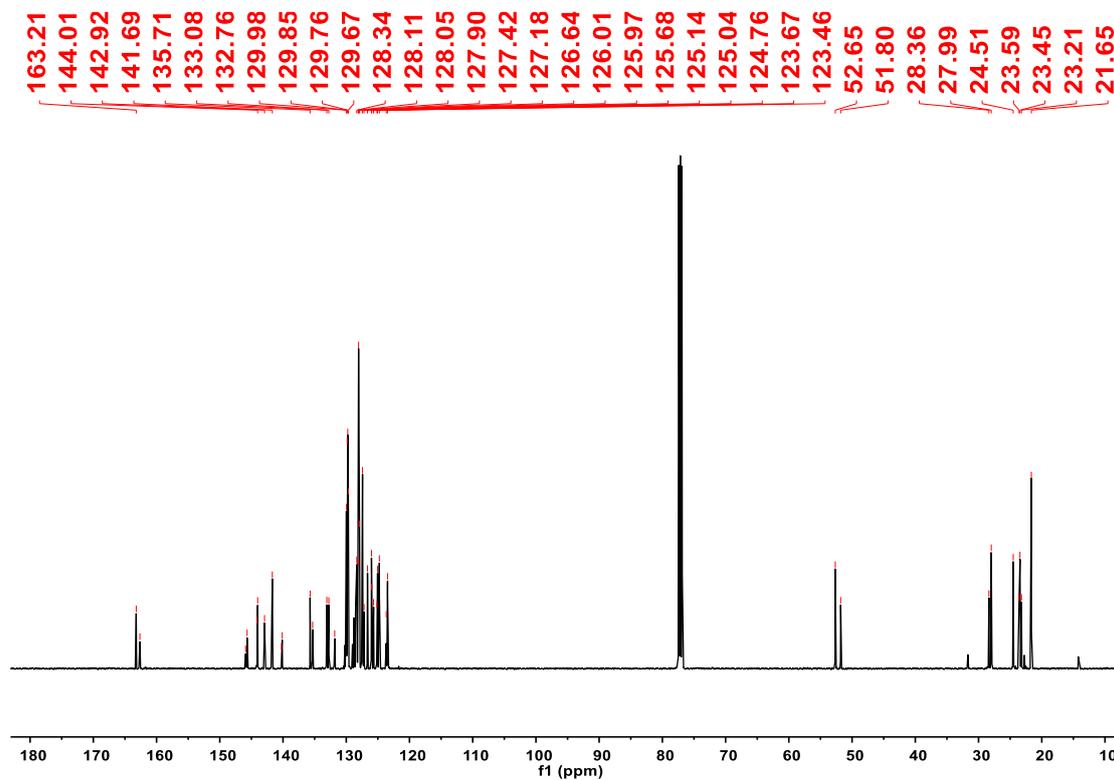


Figure S8.  $^{13}\text{C}$  NMR spectrum of L1 in  $\text{CDCl}_3$ .

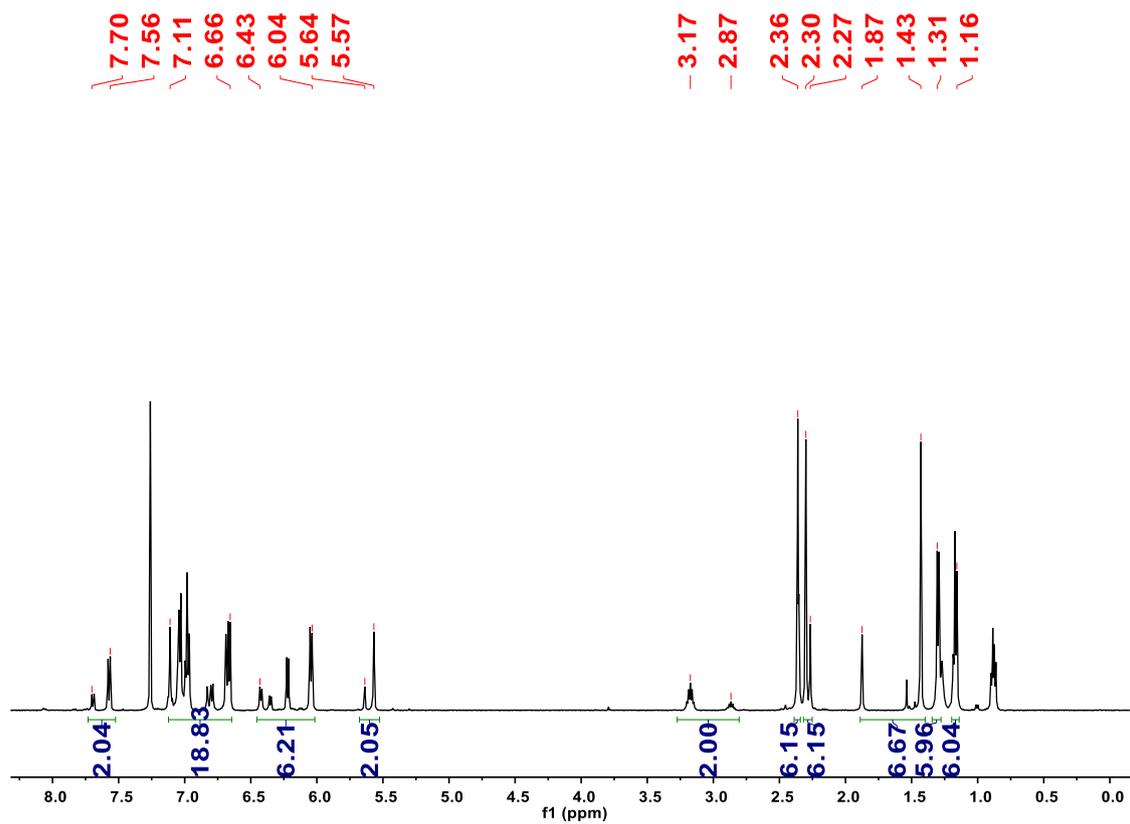


Figure S9.  $^1\text{H}$  NMR spectrum of L2 in  $\text{CDCl}_3$ .

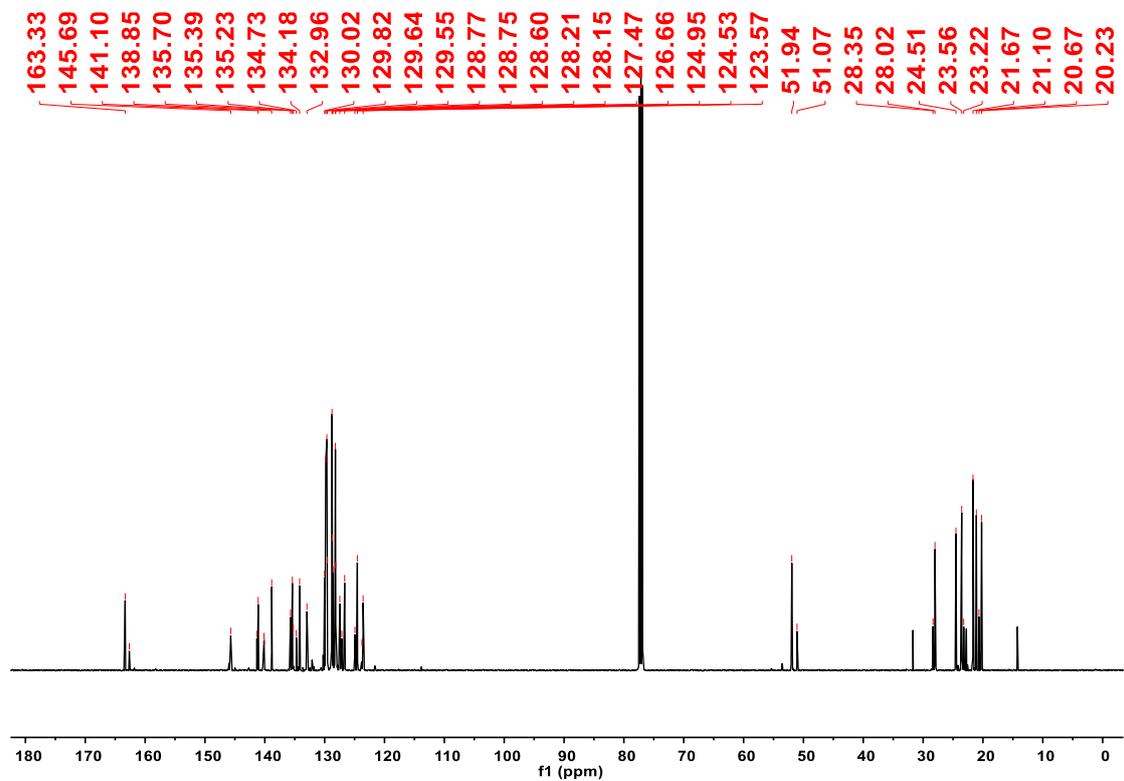


Figure S10.  $^{13}\text{C}$  NMR spectrum of L2 in  $\text{CDCl}_3$ .

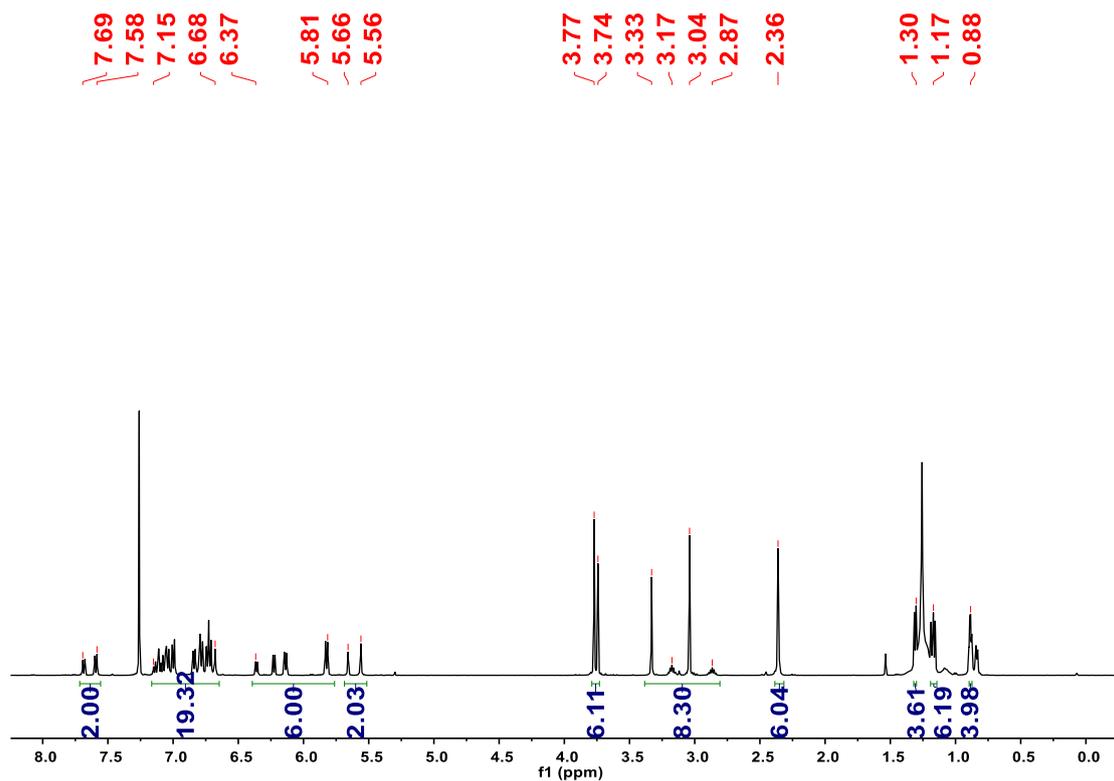


Figure S11.  $^1\text{H}$  NMR spectrum of L3 in  $\text{CDCl}_3$ .

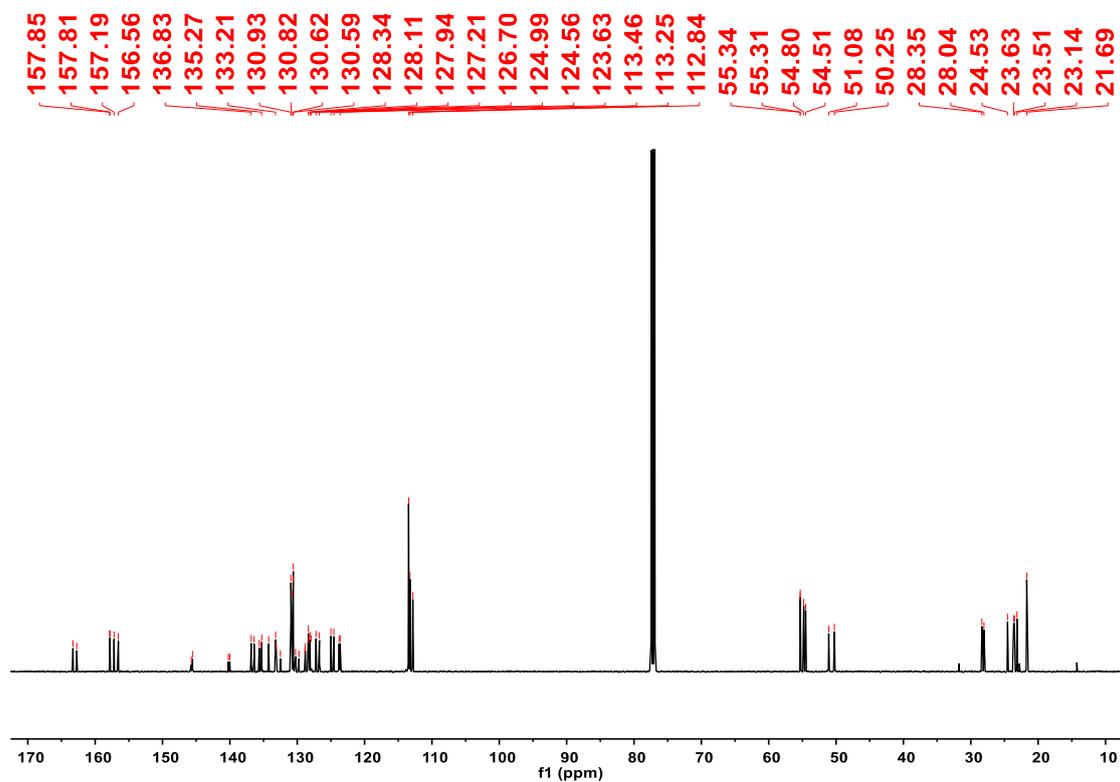


Figure S12.  $^{13}\text{C}$  NMR spectrum of L3 in  $\text{CDCl}_3$ .

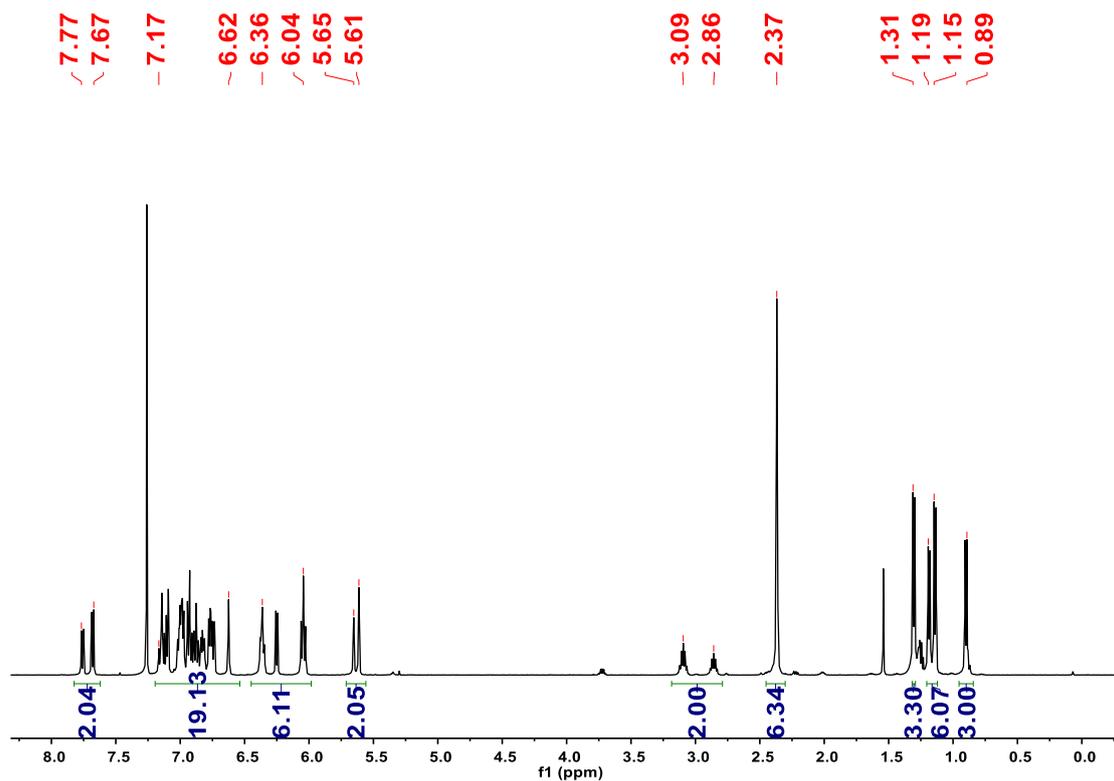


Figure S13.  $^1\text{H}$  NMR spectrum of L4 in  $\text{CDCl}_3$ .

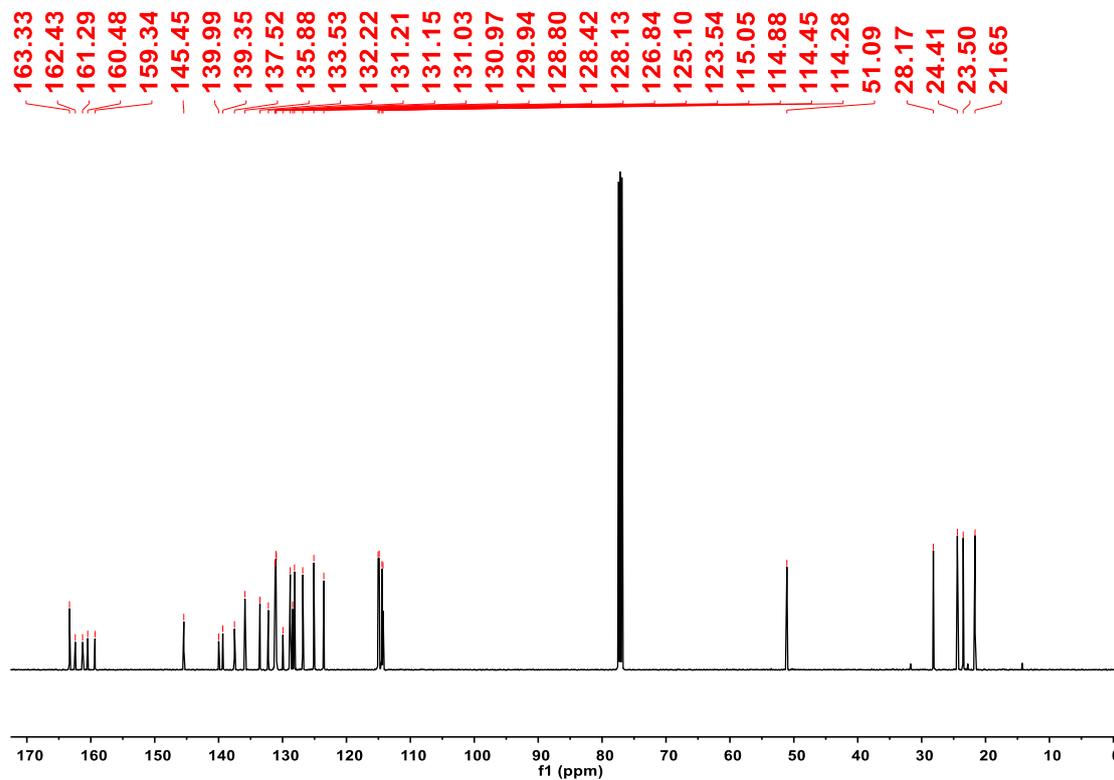
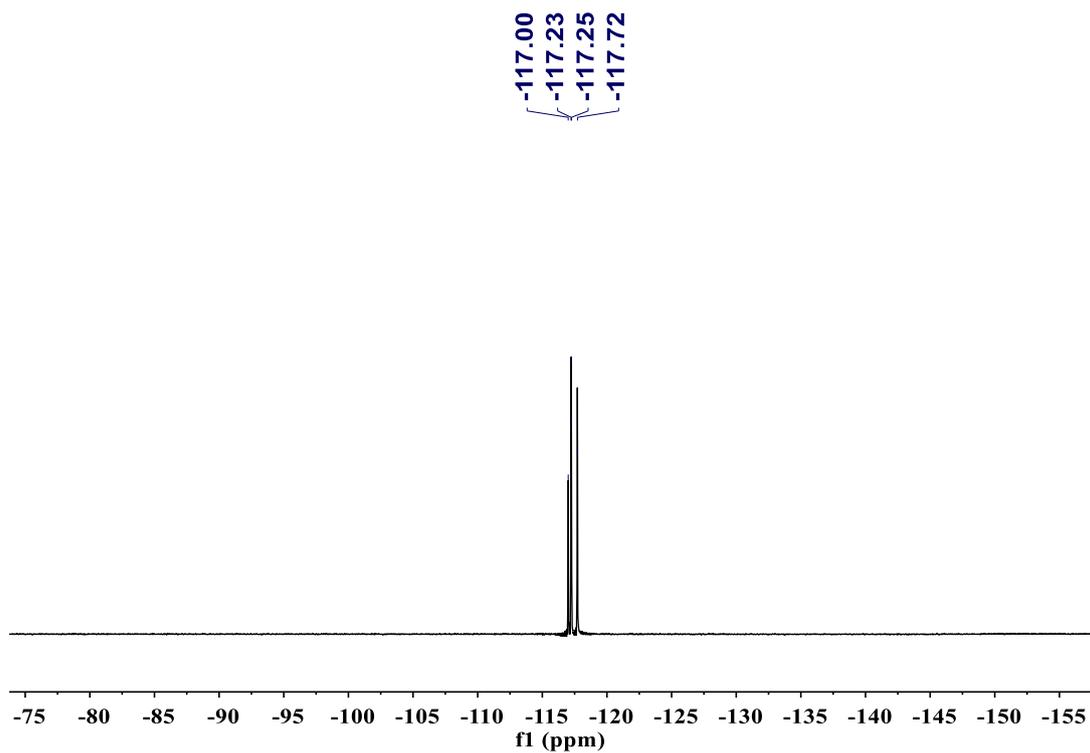
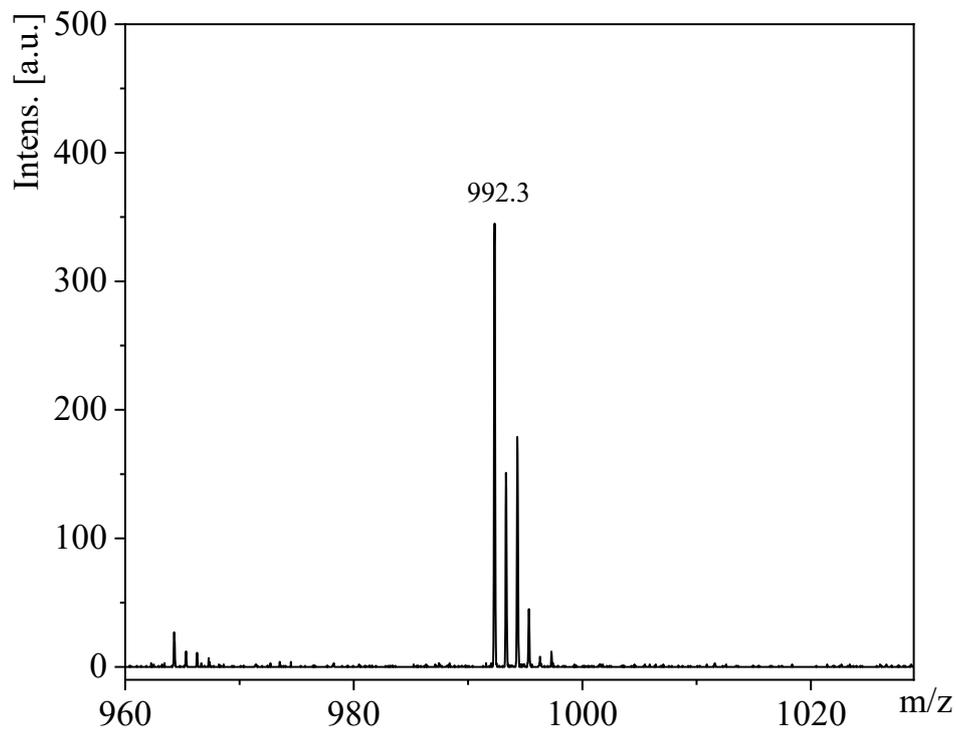


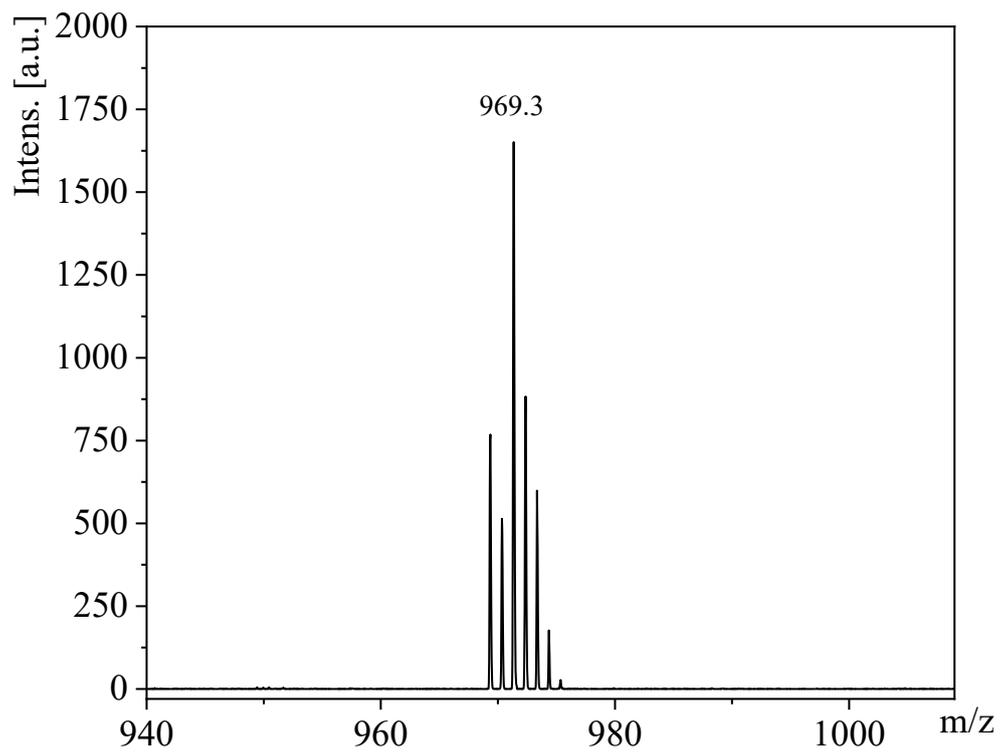
Figure S14.  $^{13}\text{C}$  NMR spectrum of L4 in  $\text{CDCl}_3$ .



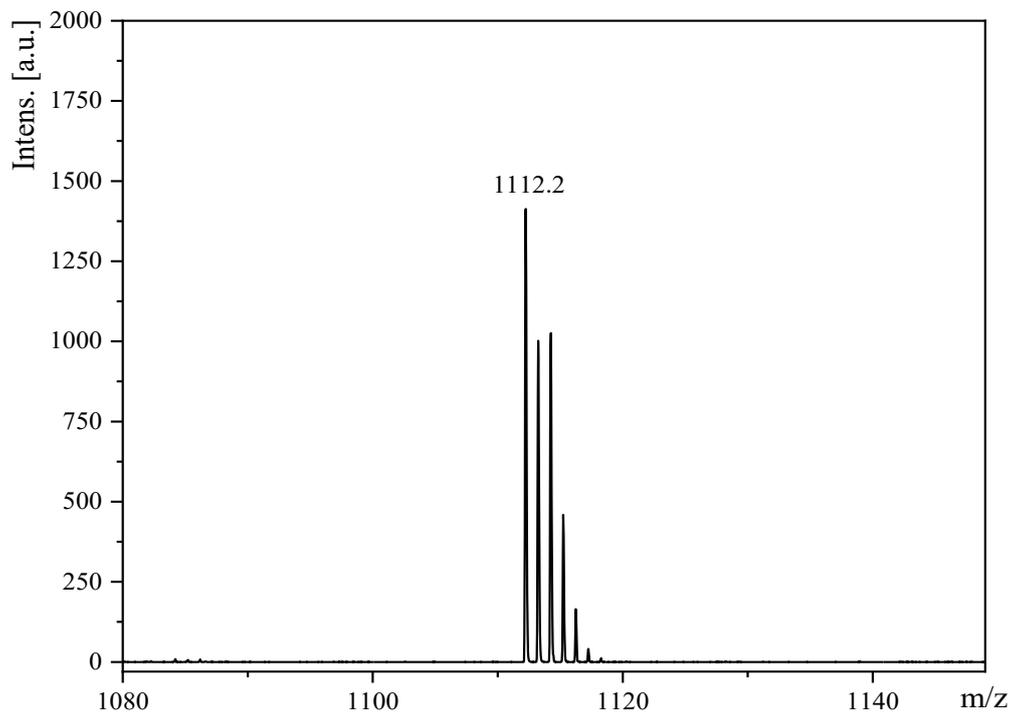
**Figure S15.**  $^{19}\text{F}$  NMR spectrum of **L4** in  $\text{CDCl}_3$ .



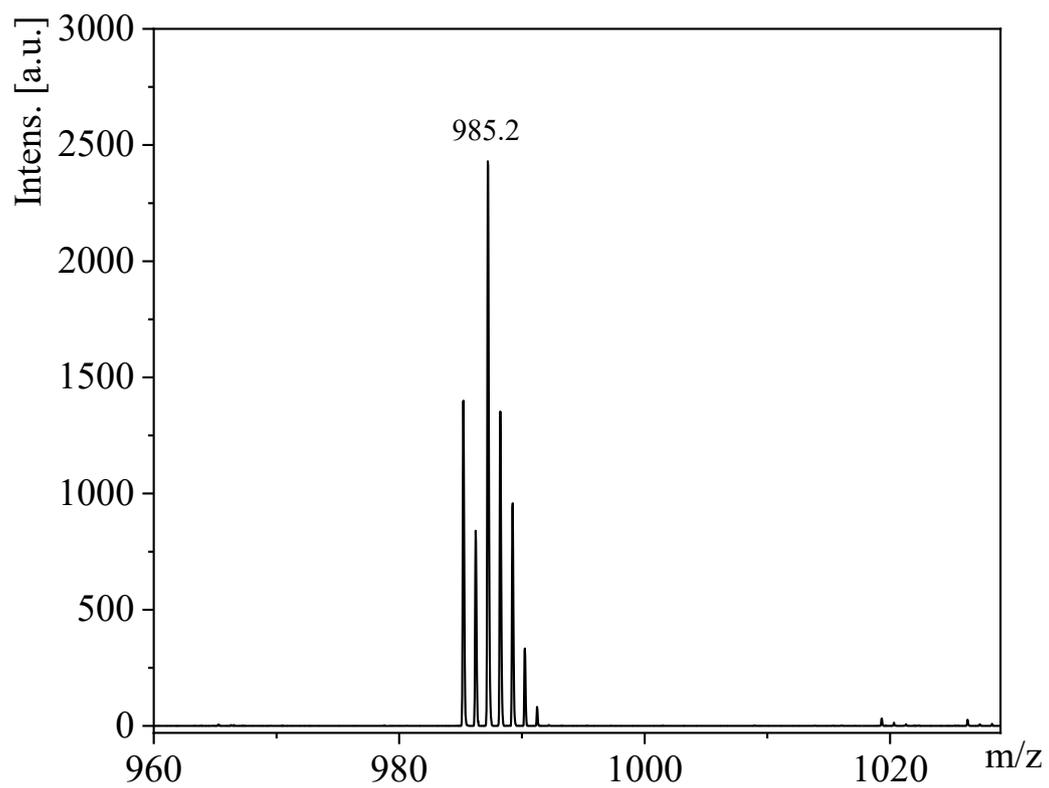
**Figure S16.** MALDI-TOF MS of **Ni1** in  $\text{CH}_2\text{Cl}_2$ .



**Figure S17.** MALDI-TOF MS of Ni<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>.



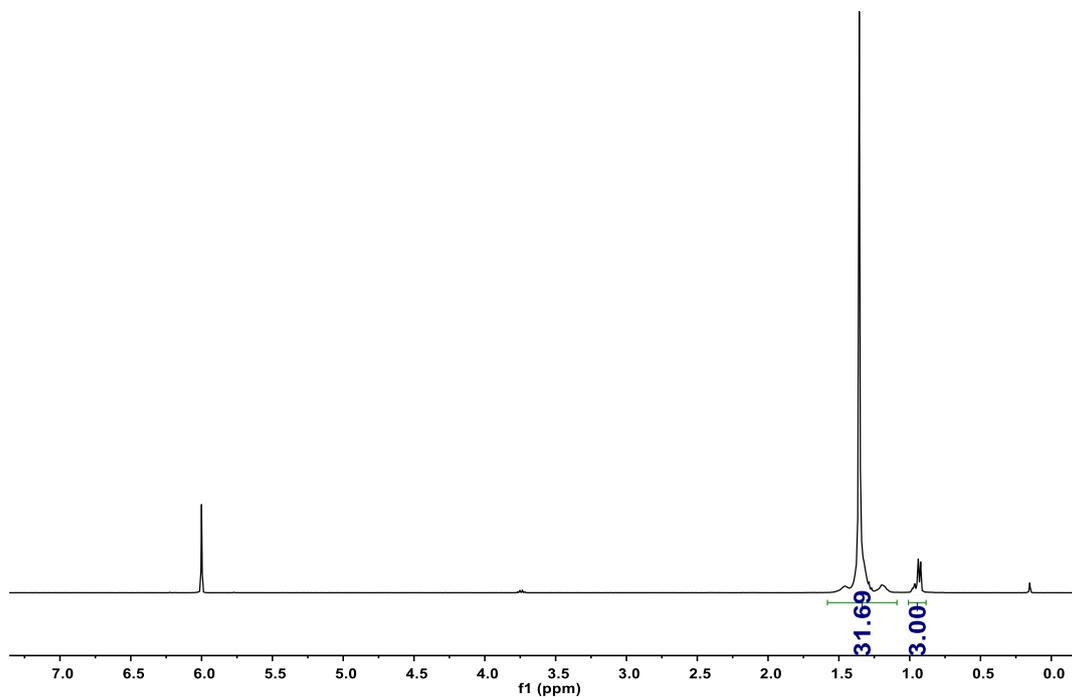
**Figure S18.** MALDI-TOF MS of Ni<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>.



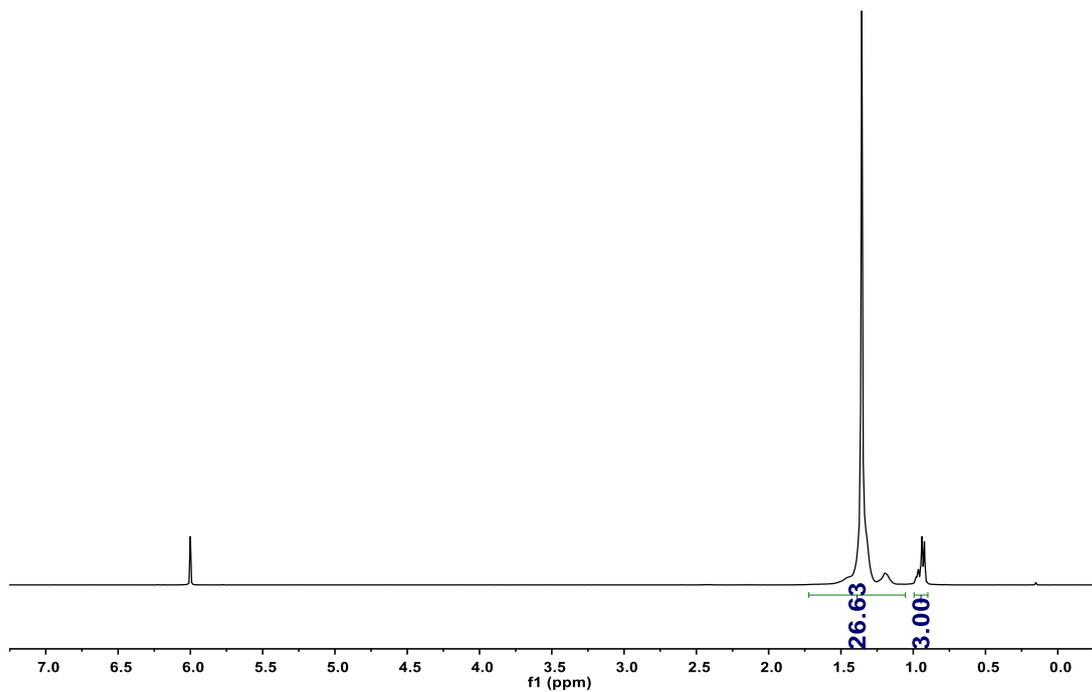
**Figure S19.** MALDI-TOF MS of **Ni4** in  $\text{CH}_2\text{Cl}_2$ .

#### 4. $^1\text{H}$ NMR Spectra of Polymers

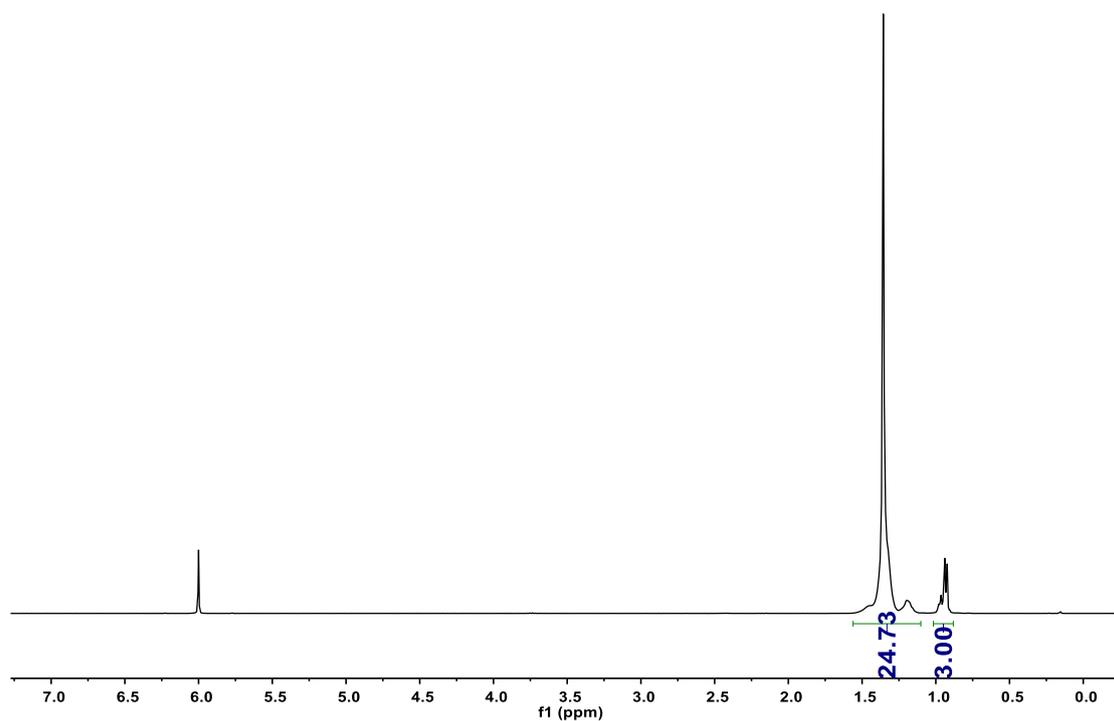
$$\text{Me groups} / 1000\text{C} = \frac{2 \cdot I_{\text{Me}}}{3 \cdot I_{\text{tot}}} * 1000 = \frac{2 \times 3}{3 \times (31.69 + 3)} \times 1000 = 58$$



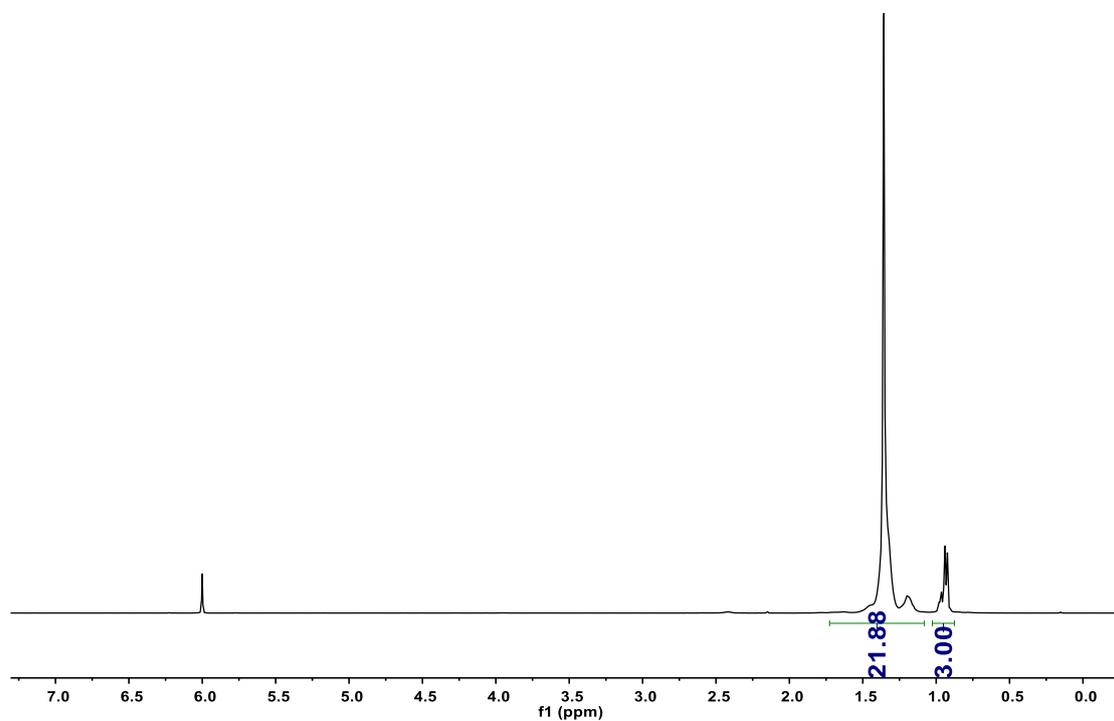
**Figure S20.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110  $^\circ\text{C}$ ) of the polyethylene generated by Ni1 from table 1, entry 1.



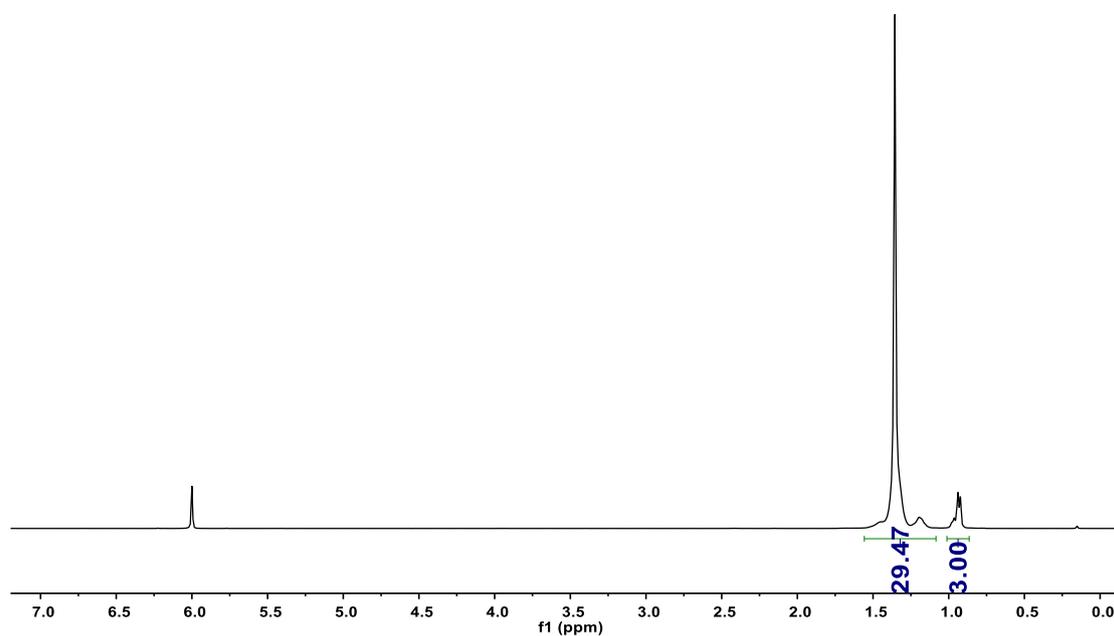
**Figure S21.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110  $^\circ\text{C}$ ) of the polyethylene generated by Ni1 from table 1, entry 2.



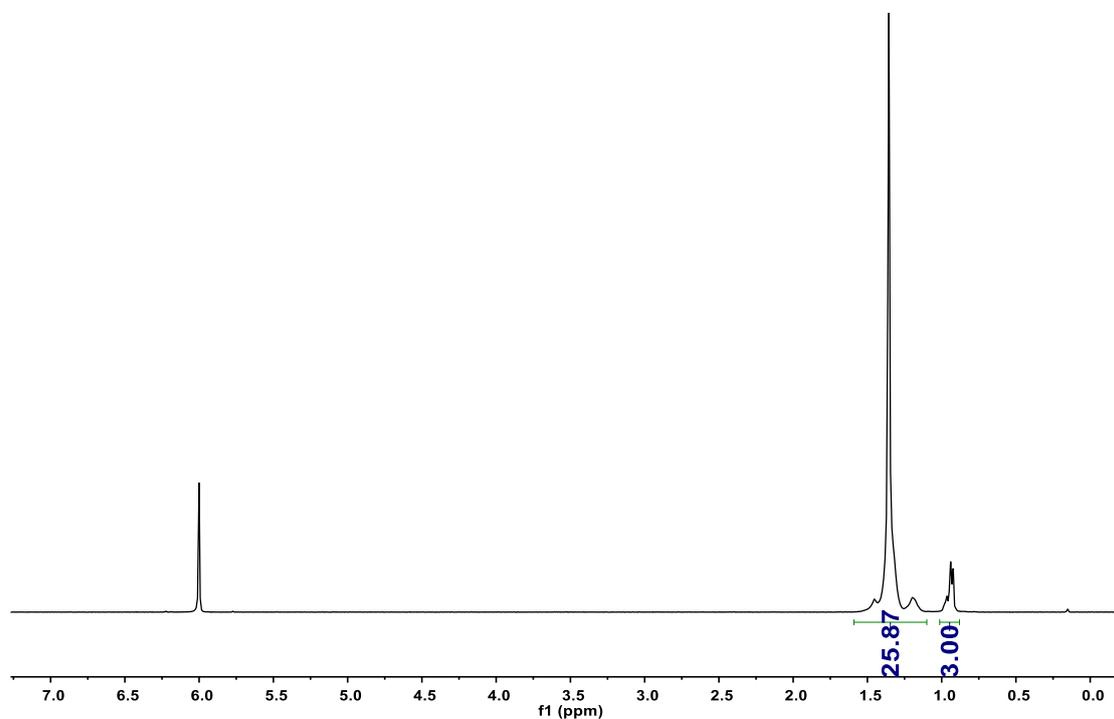
**Figure S22.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C) of the polyethylene generated by **Ni1** from table 1, entry 3.



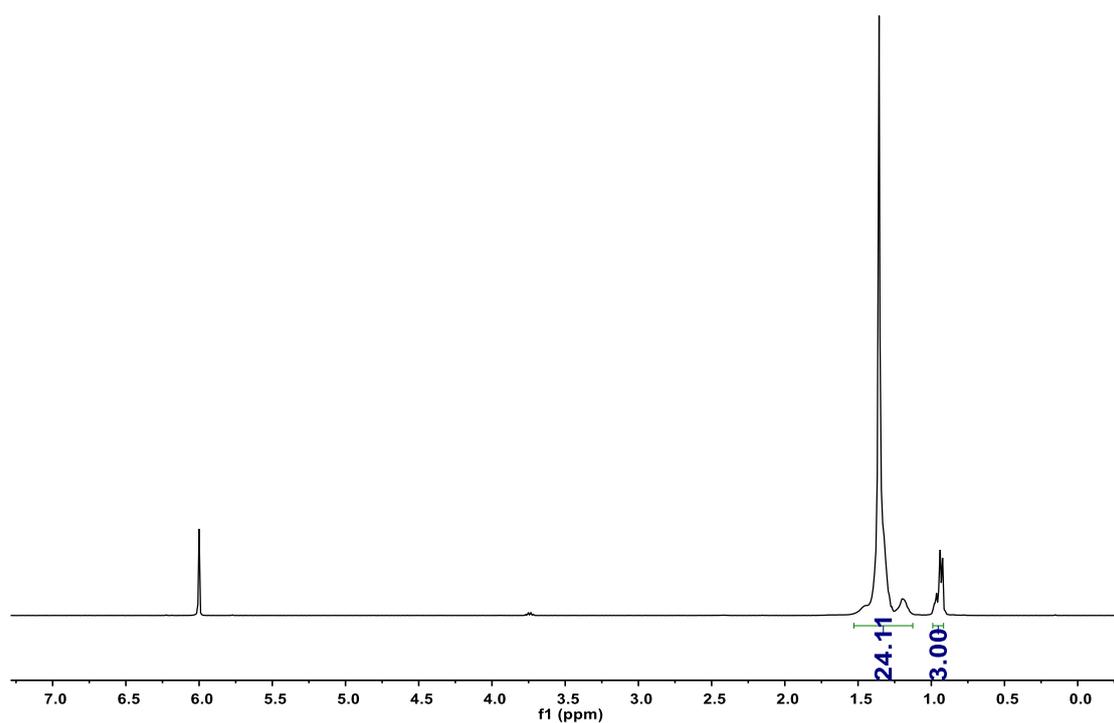
**Figure S23.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C) of the polyethylene generated by **Ni1** from table 1, entry 4.



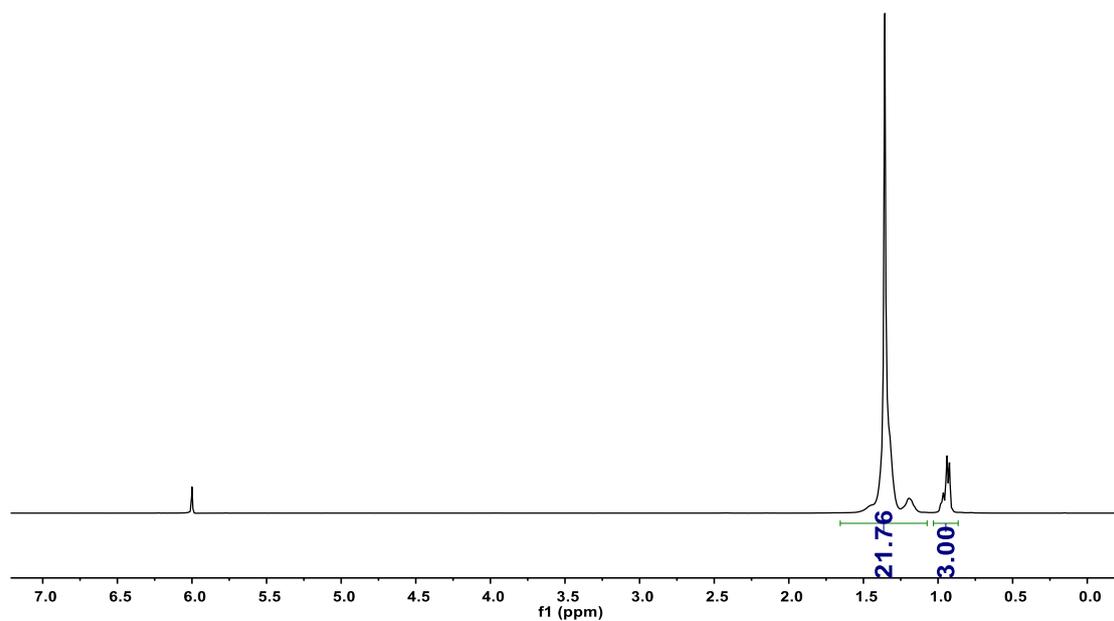
**Figure S24.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C) of the polyethylene generated by **Ni2** from table 1, entry 5.



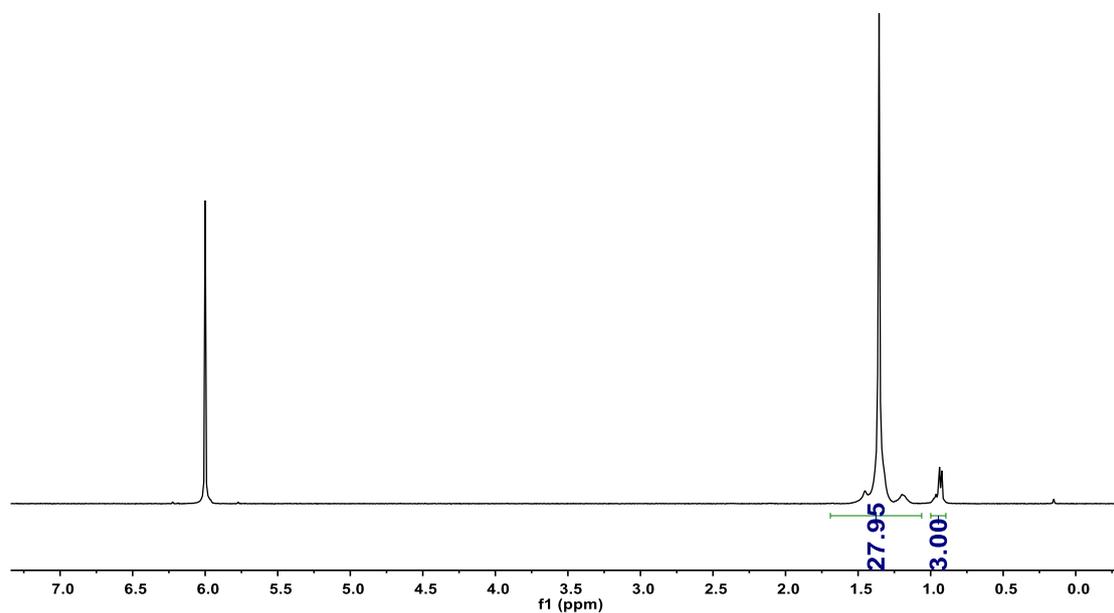
**Figure S25.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C) of the polyethylene generated by **Ni2** from table 1, entry 6.



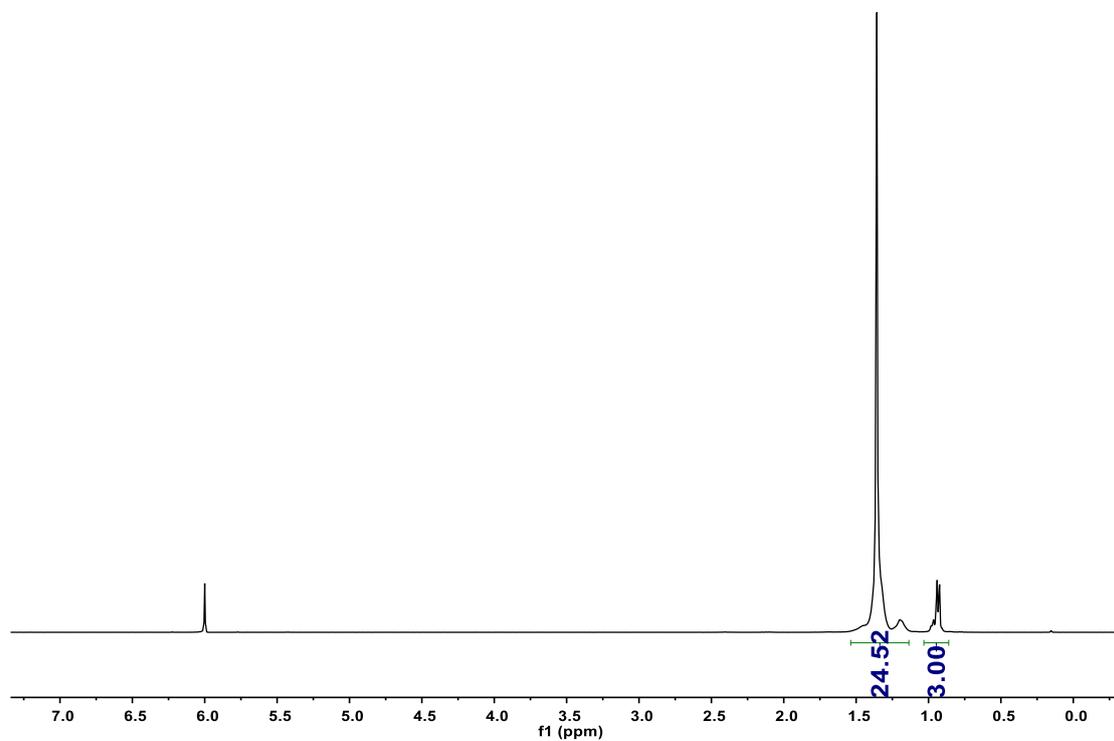
**Figure S26.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110  $^\circ\text{C}$ ) of the polyethylene generated by **Ni2** from table 1, entry 7.



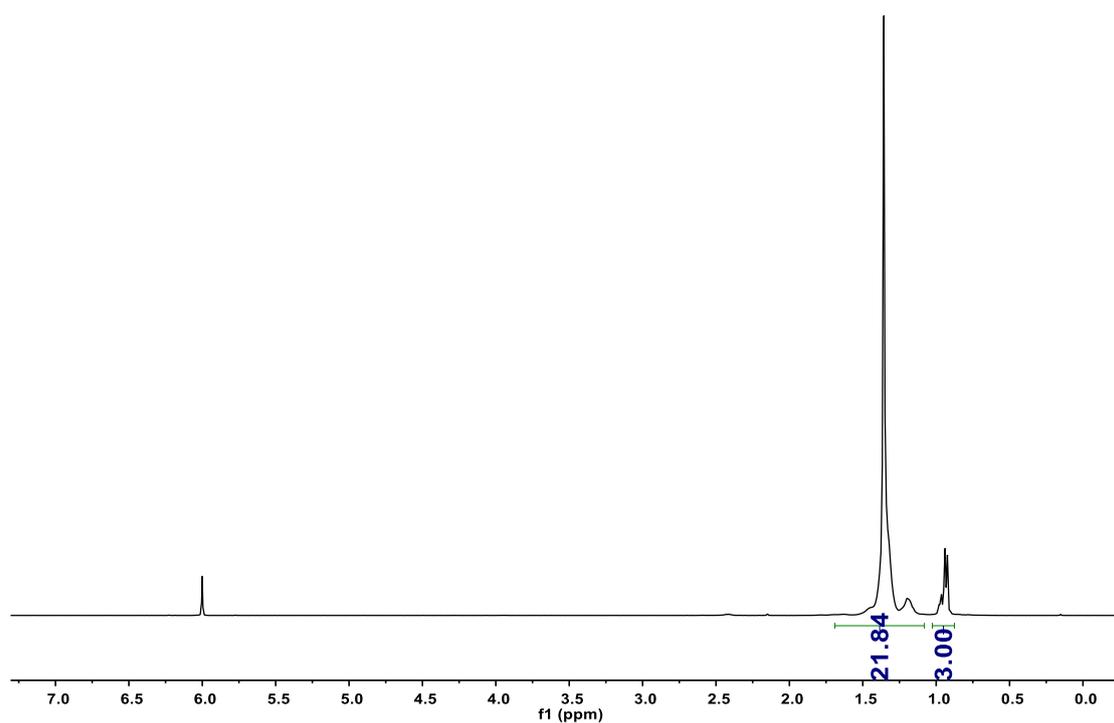
**Figure S27.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110  $^\circ\text{C}$ ) of the polyethylene generated by **Ni2** from table 1, entry 8.



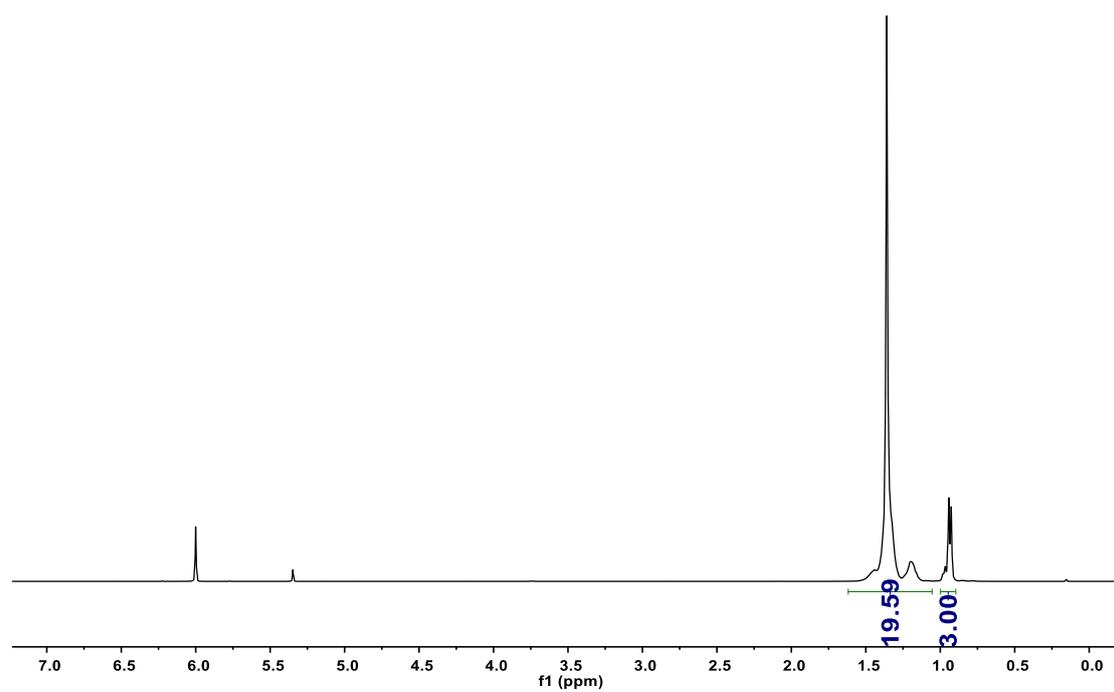
**Figure S28.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C) of the polyethylene generated by **Ni3** from table 1, entry 9.



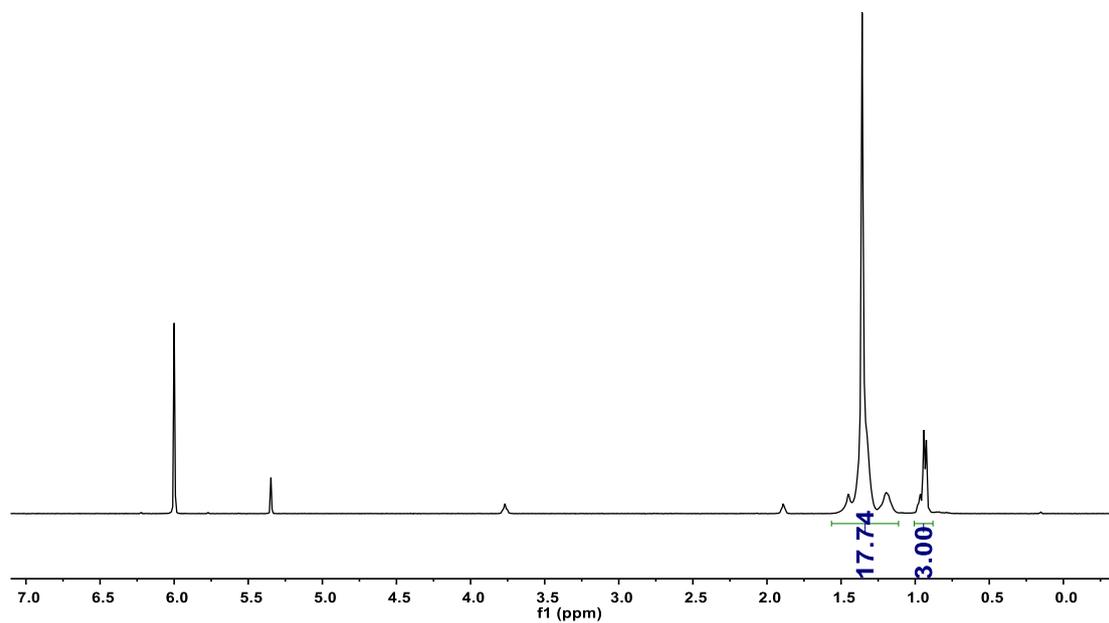
**Figure S29.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C) of the polyethylene generated by **Ni3** from table 1, entry 10.



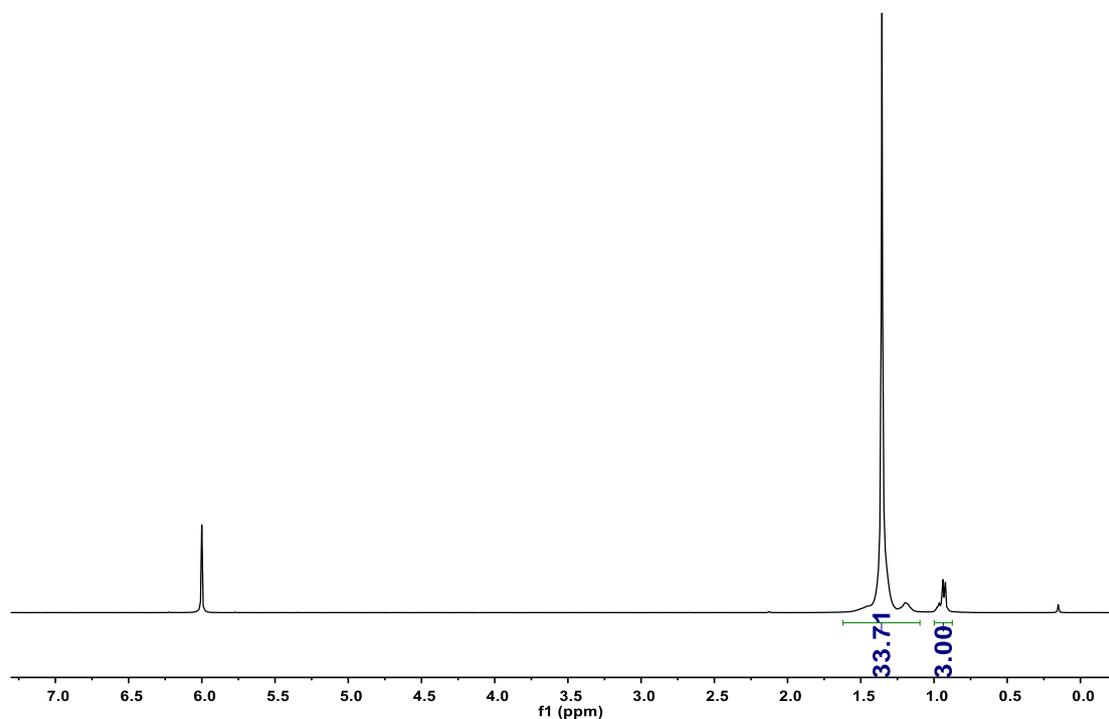
**Figure S30.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C) of the polyethylene generated by **Ni3** from table 1, entry 11.



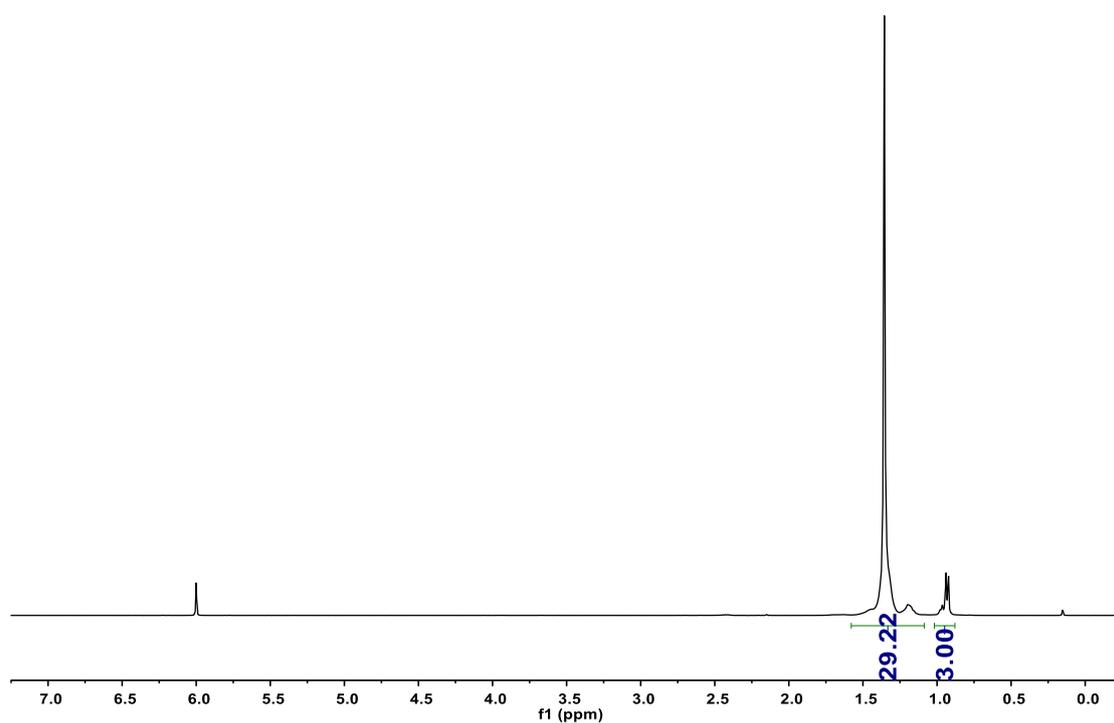
**Figure S31.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C) of the polyethylene generated by **Ni3** from table 1, entry 12.



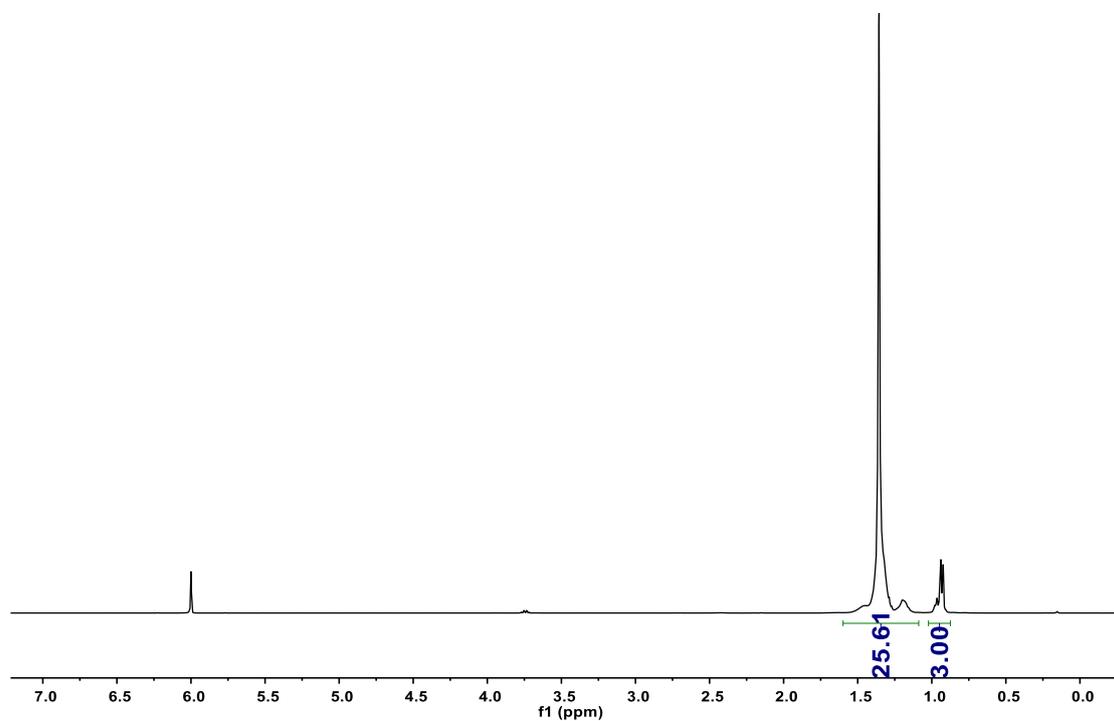
**Figure S32.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni3** from table 1, entry 13.



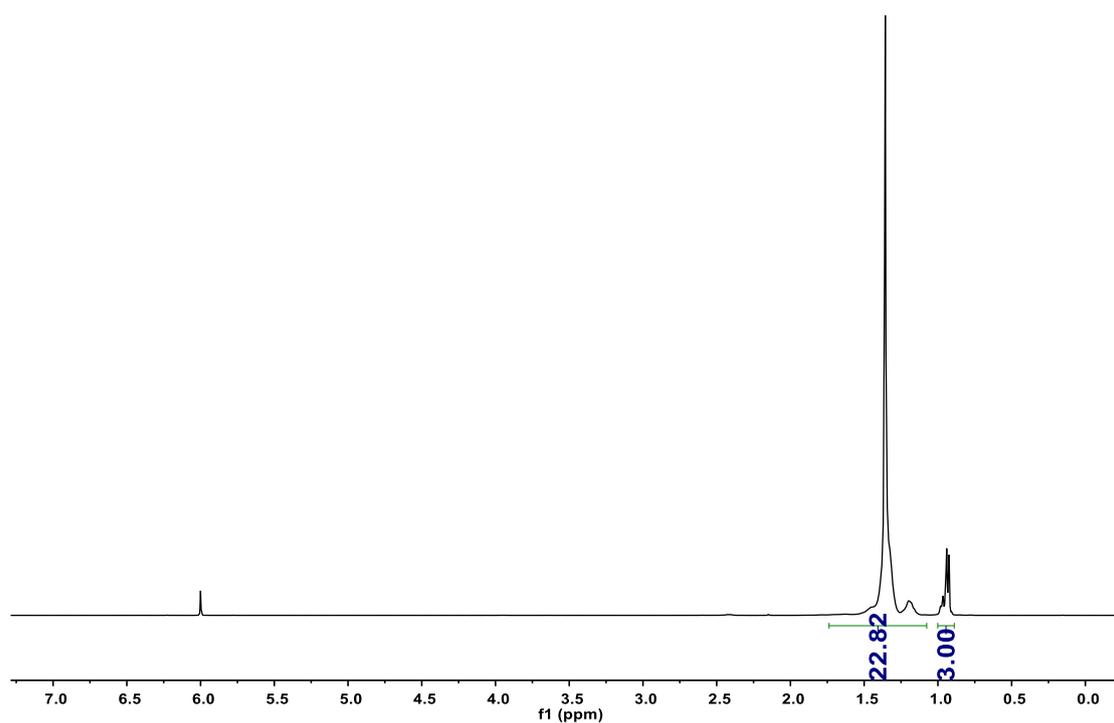
**Figure S33.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni4** from table 1, entry 14.



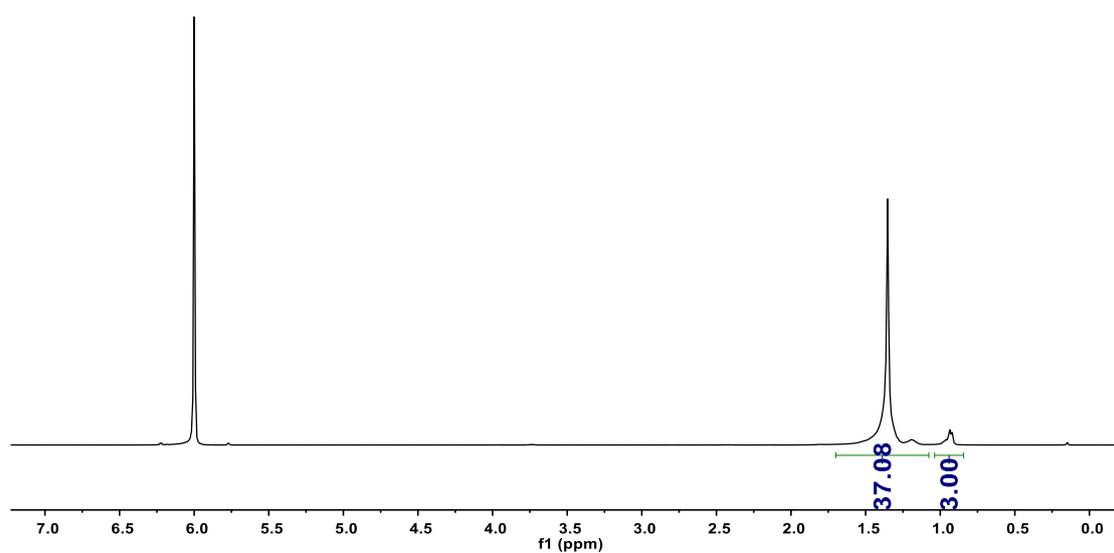
**Figure S34.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C) of the polyethylene generated by **Ni4** from table 1, entry 15.



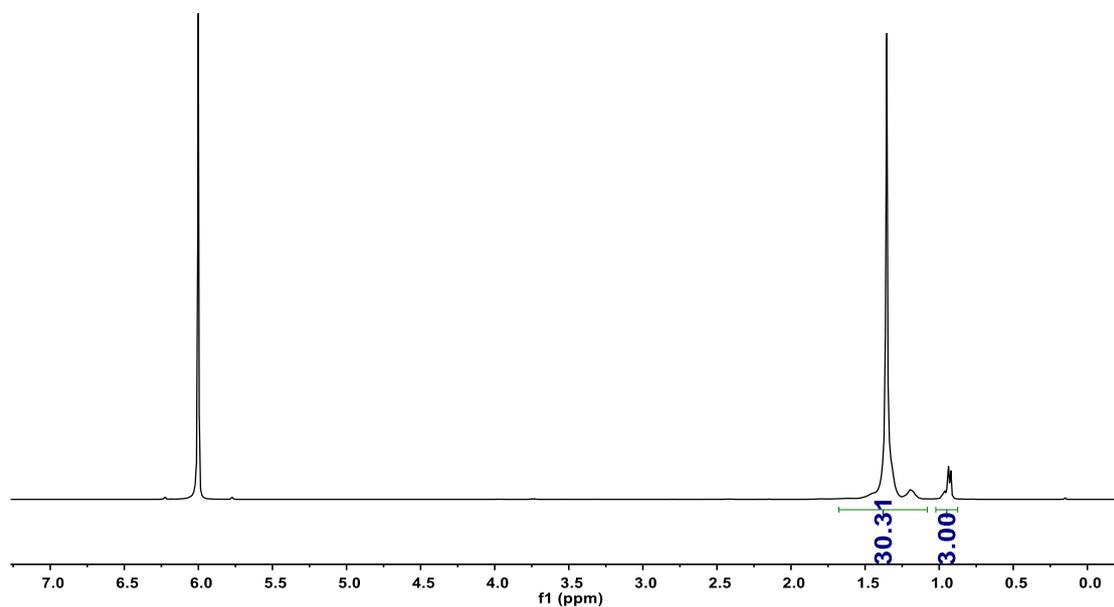
**Figure S35.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 110 °C) of the polyethylene generated by **Ni4** from table 1, entry 16.



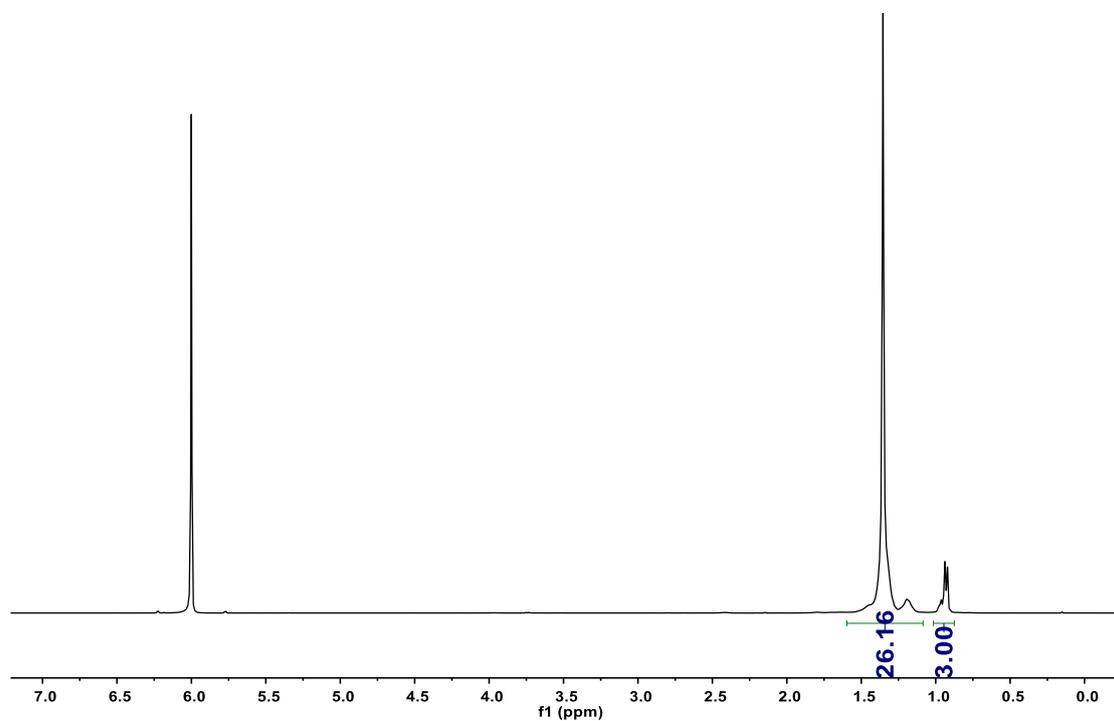
**Figure S36.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni4** from table 1, entry 17.



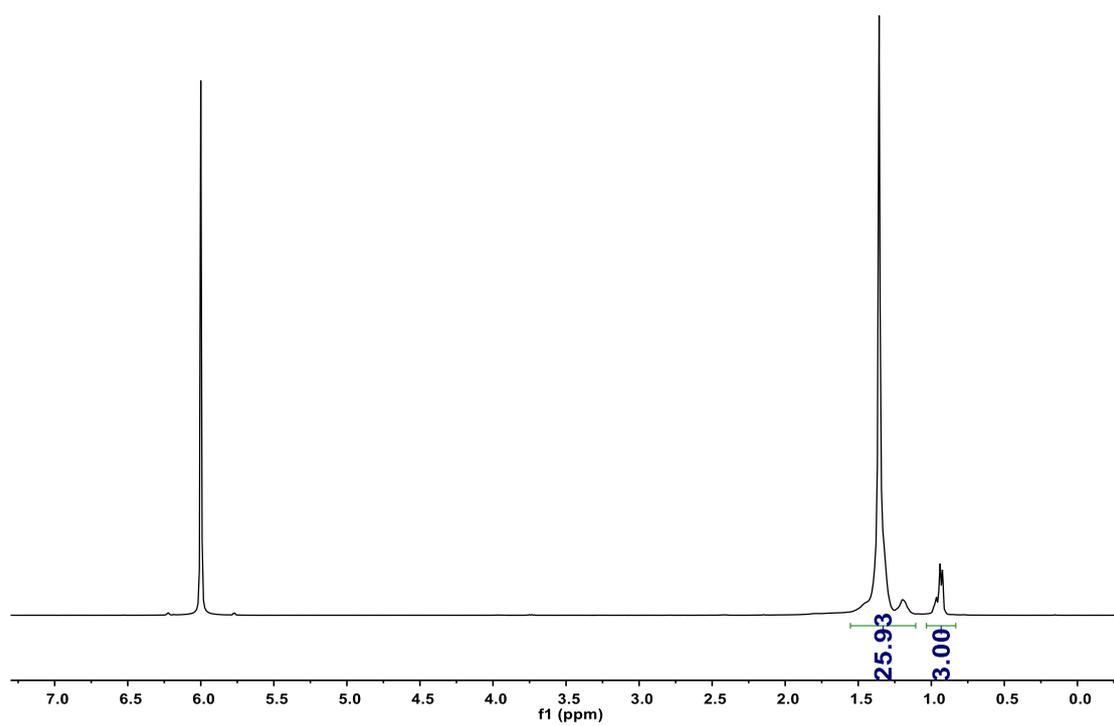
**Figure S37.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni1'** from table 1, entry 18.



**Figure S38.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by Ni1' from table 1, entry 19.



**Figure S39.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by Ni1' from table 1, entry 20.



**Figure S40.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 110 °C) of the polyethylene generated by **Ni1'** from table 1, entry 21.

## 5. GPC of Polymers

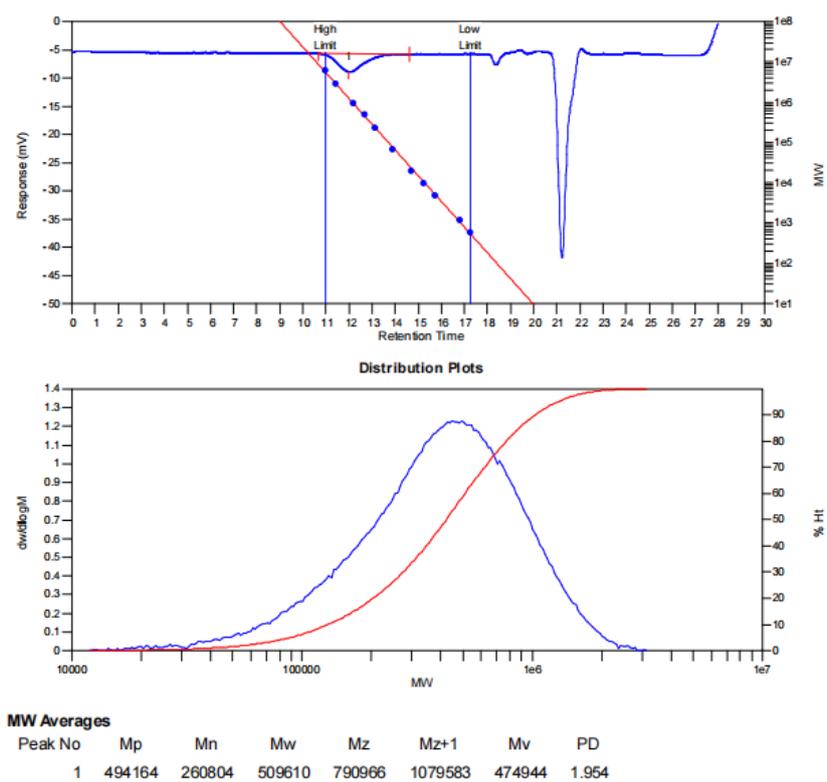


Figure S41. GPC trace of the polymer from table 1, entry 1.

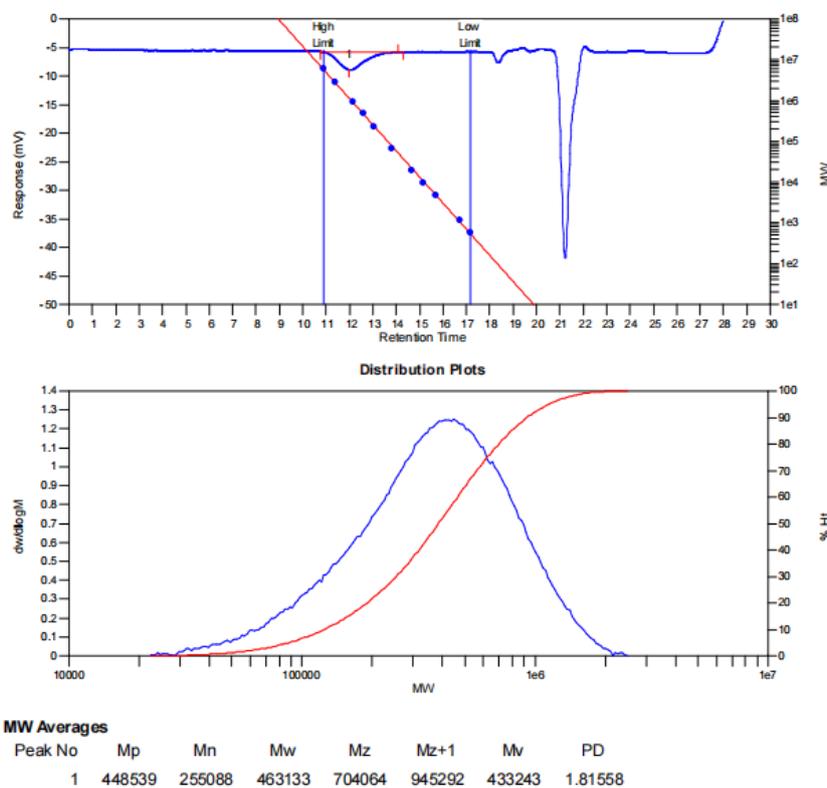


Figure S42. GPC trace of the polymer from table 1, entry 2.

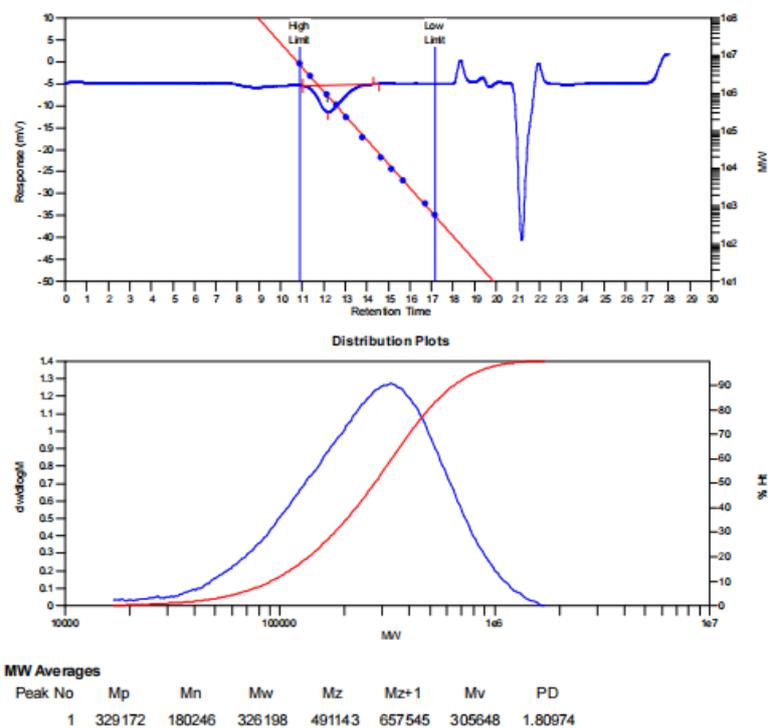


Figure S43. GPC trace of the polymer from table 1, entry 3.

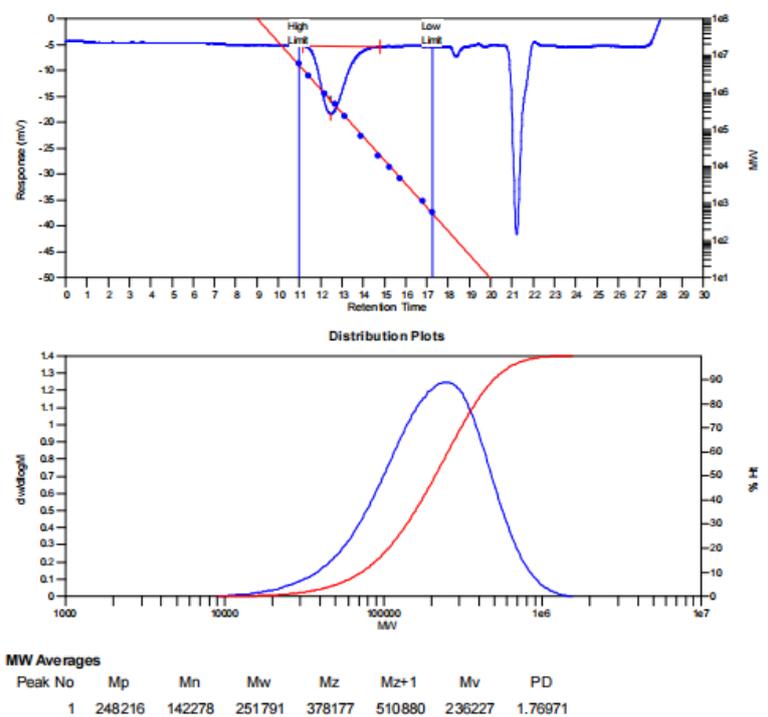
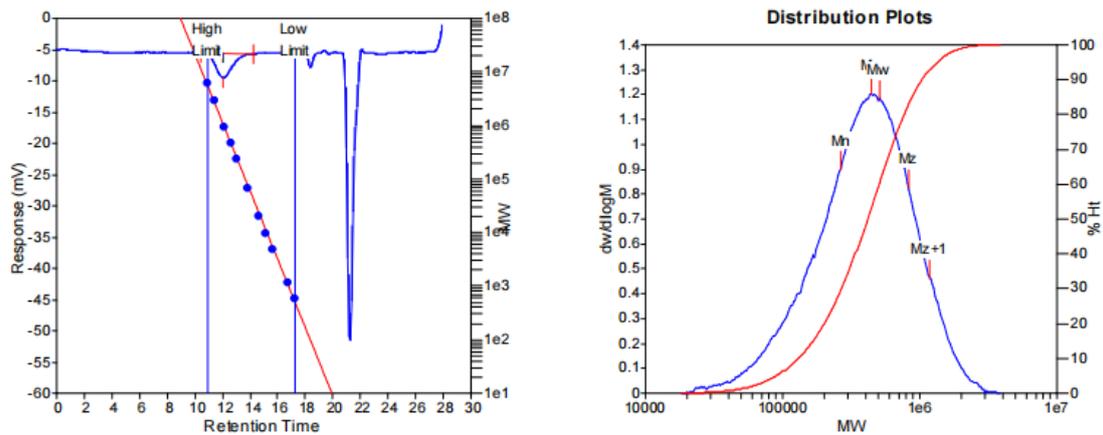


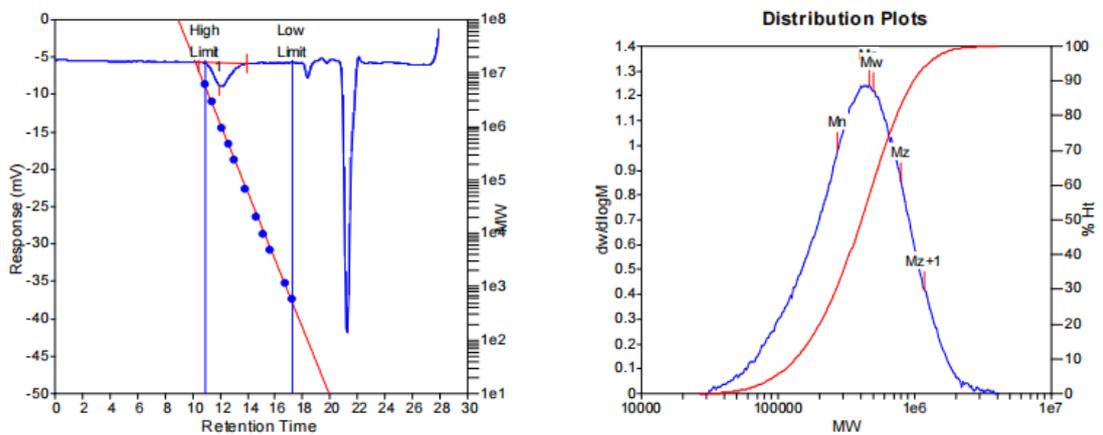
Figure S44. GPC trace of the polymer from table 1, entry 4.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	439924	265679	514668	830170	1185310	477673	1.93718

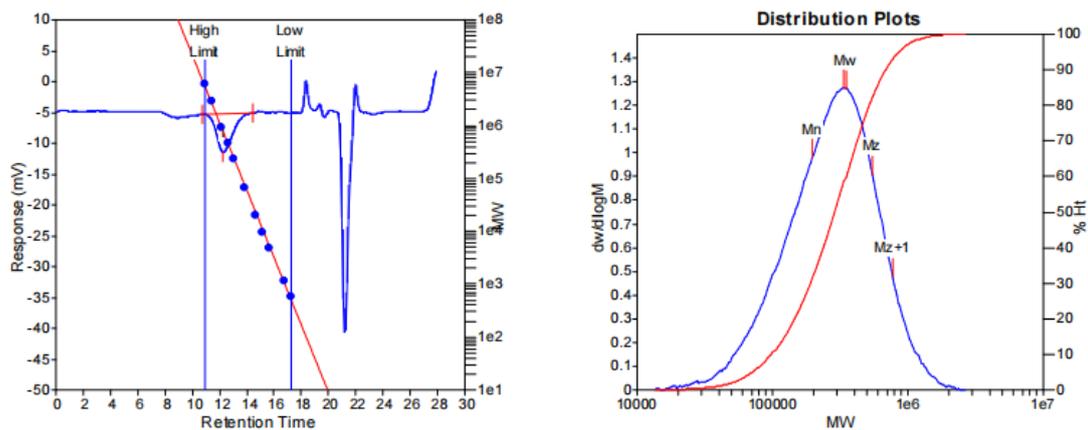
**Figure S45.** GPC trace of the polymer from table 1, entry 5.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	461287	274074	497557	797688	1178527	463360	1.81541

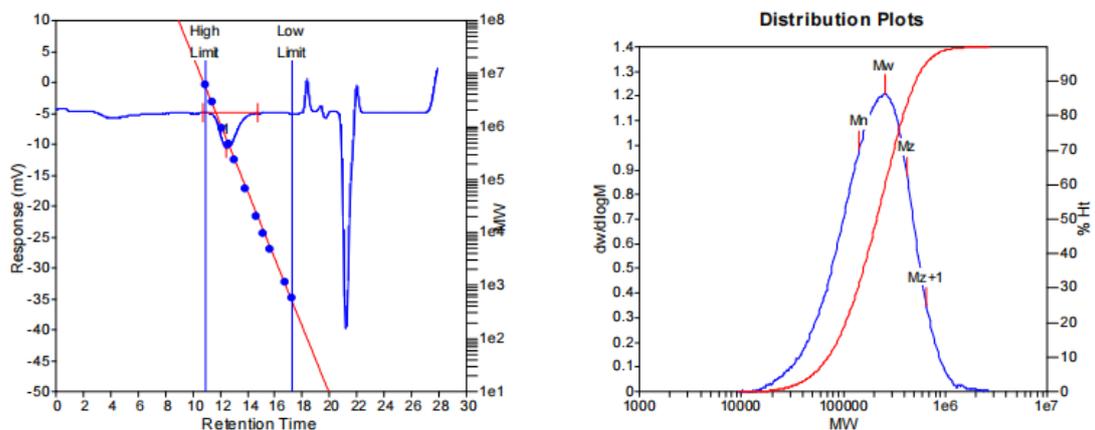
**Figure S46.** GPC trace of the polymer from table 1, entry 6.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	338932	196640	349675	544576	775424	326865	1.77825

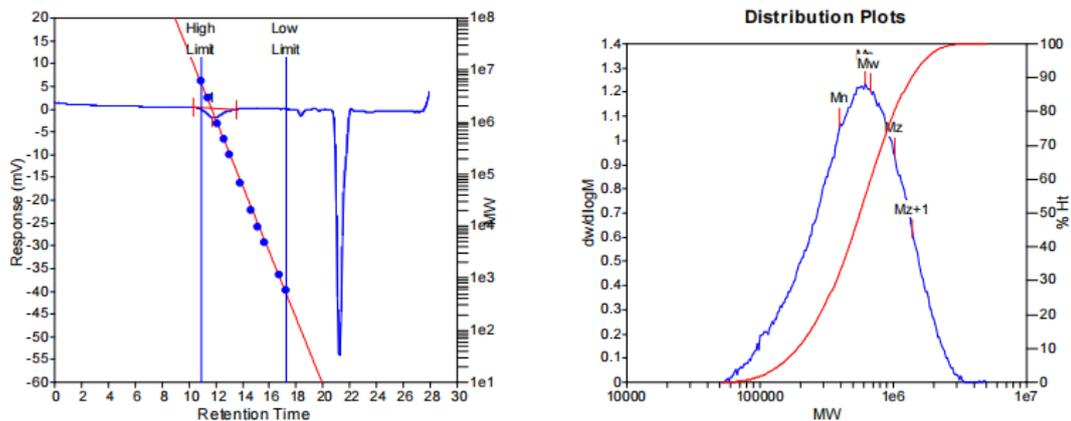
**Figure S47.** GPC trace of the polymer from table 1, entry 7.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	255006	143068	260736	421543	650465	242806	1.82246

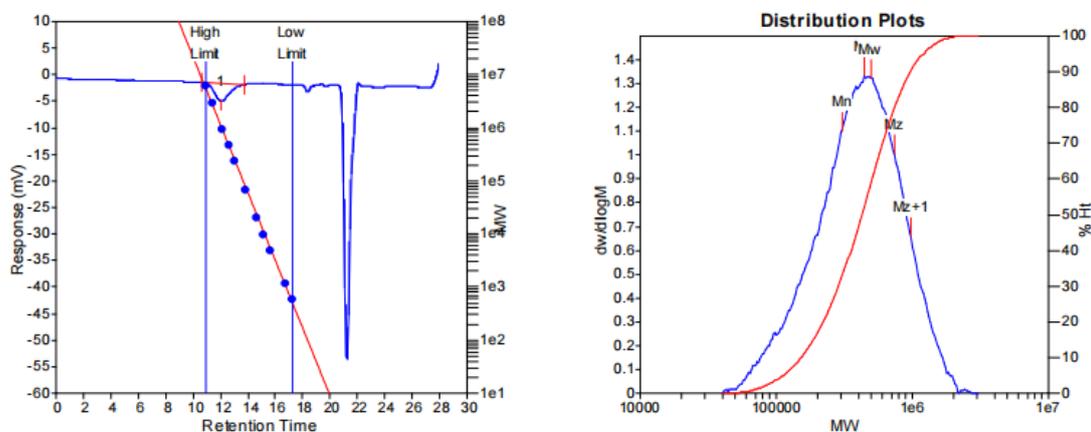
**Figure S48.** GPC trace of the polymer from table 1, entry 8.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	613103	392422	679229	1032759	1396253	636090	1.73086

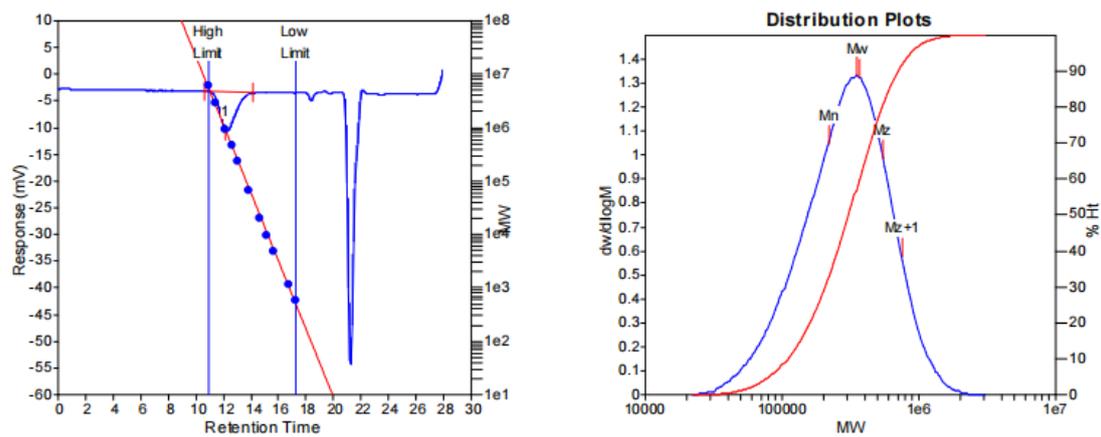
**Figure S49.** GPC trace of the polymer from table 1, entry 9.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	439924	304563	500352	734279	977425	471523	1.64285

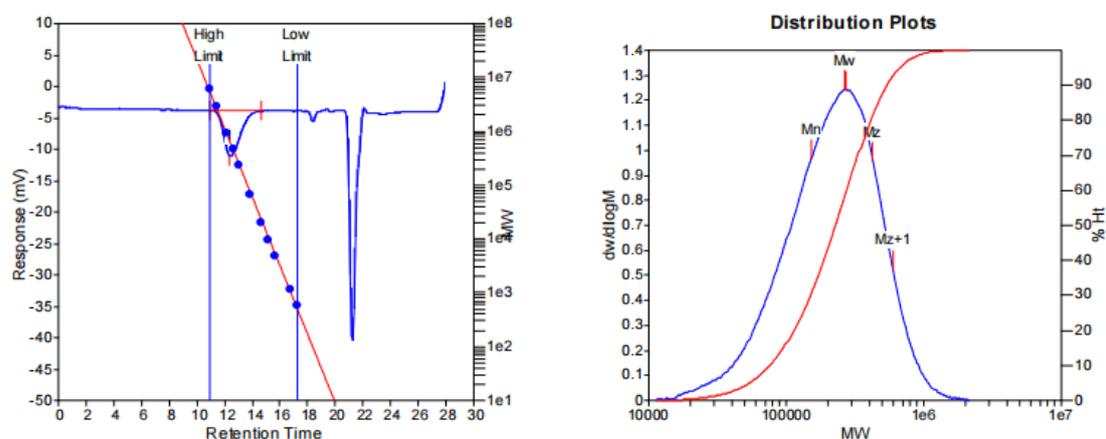
**Figure S50.** GPC trace of the polymer from table 1, entry 10.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	347064	218728	364424	545245	748867	342726	1.66611

**Figure S51.** GPC trace of the polymer from table 1, entry 11.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	267389	151844	274229	423252	596189	256446	1.80599

**Figure S52.** GPC trace of the polymer from table 1, entry 12.

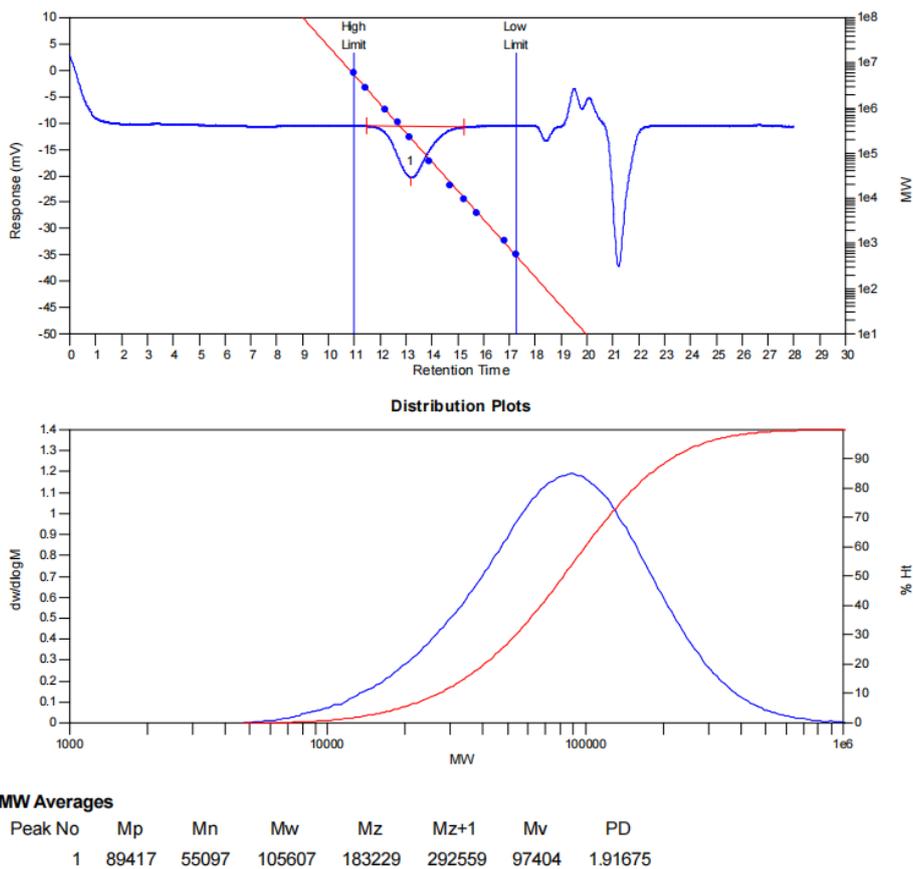


Figure S53. GPC trace of the polymer from table 1, entry 13.

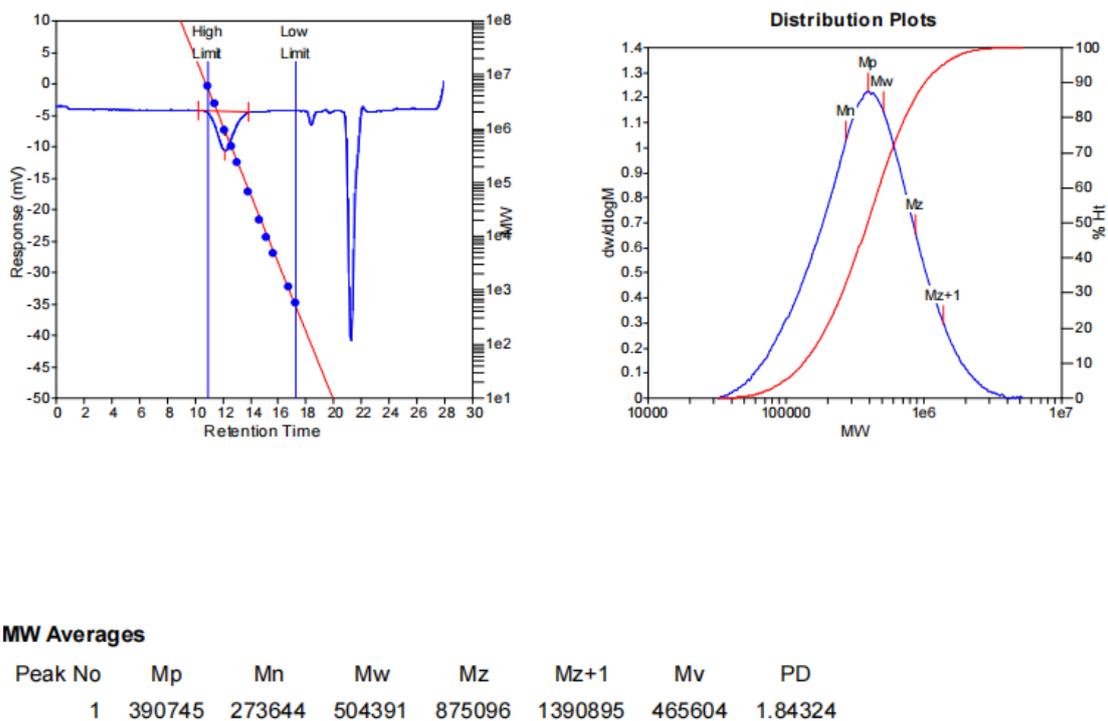
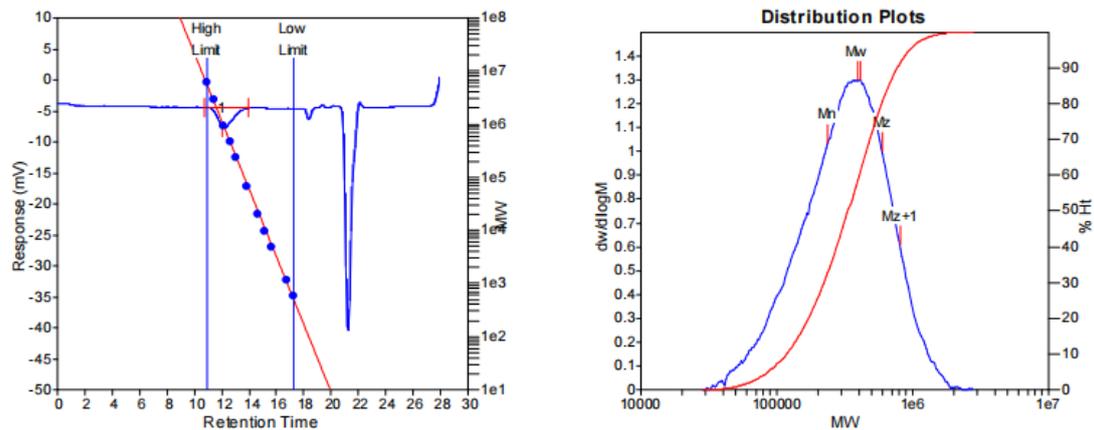


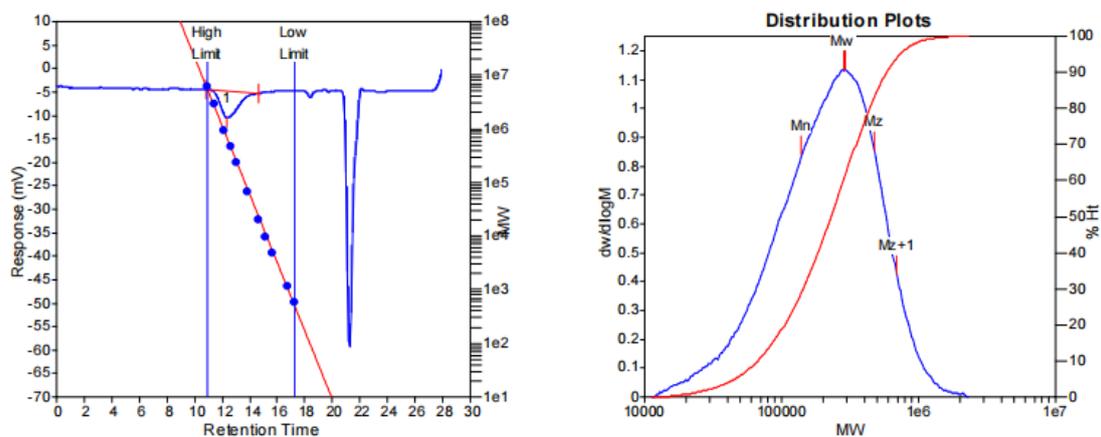
Figure S54. GPC trace of the polymer from table 1, entry 14.



#### MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	409720	236800	396950	592595	804891	373175	1.67631

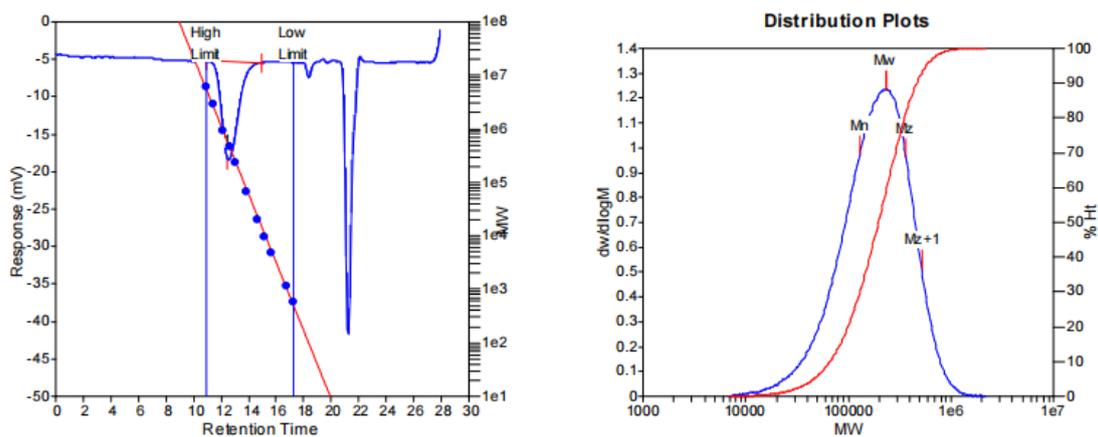
Figure S55. GPC trace of the polymer from table 1, entry 15.



#### MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	293989	139853	286652	474028	695391	264810	2.04967

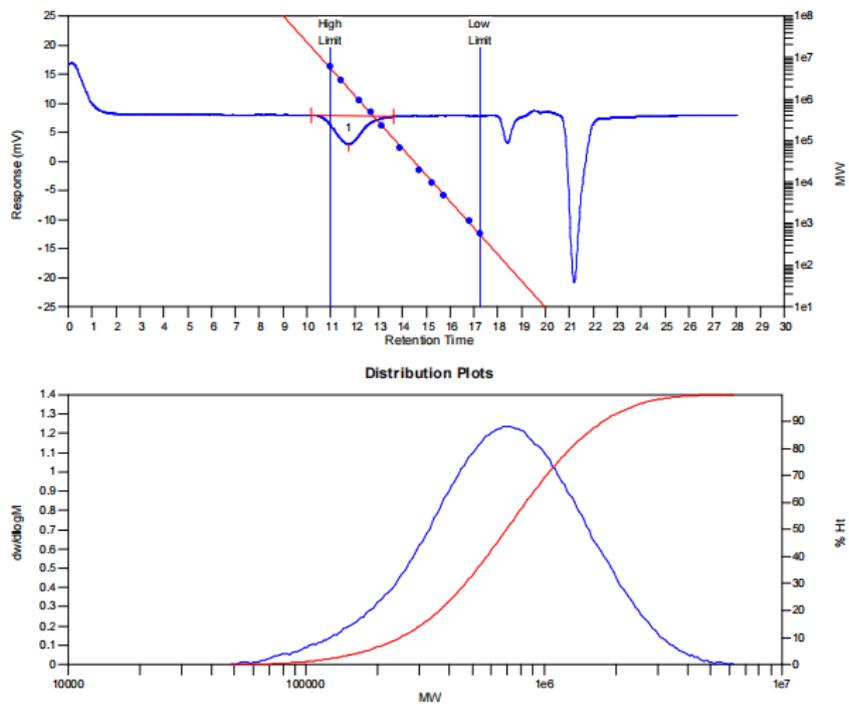
Figure S56. GPC trace of the polymer from table 1, entry 16.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	231933	128911	236798	365344	517786	221465	1.83691

**Figure S57.** GPC trace of the polymer from table 1, entry 17.



**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	722537	491075	872309	1396889	2016461	812615	1.77633

**Figure S58.** GPC trace of the polymer from table 1, entry 18.

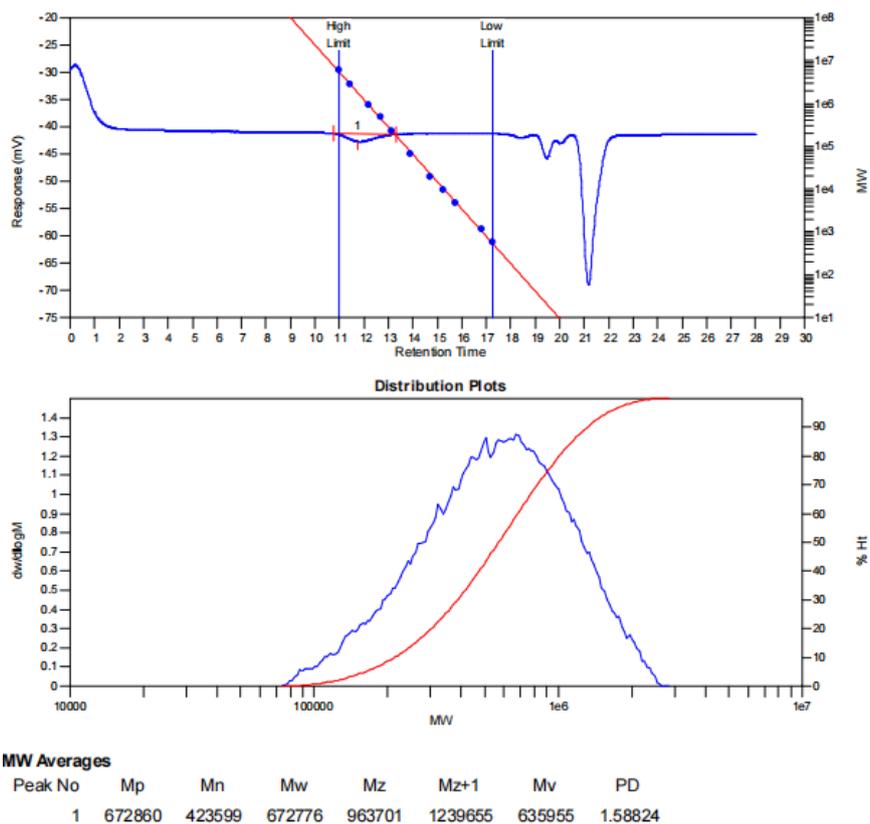


Figure S59. GPC trace of the polymer from table 1, entry 19.

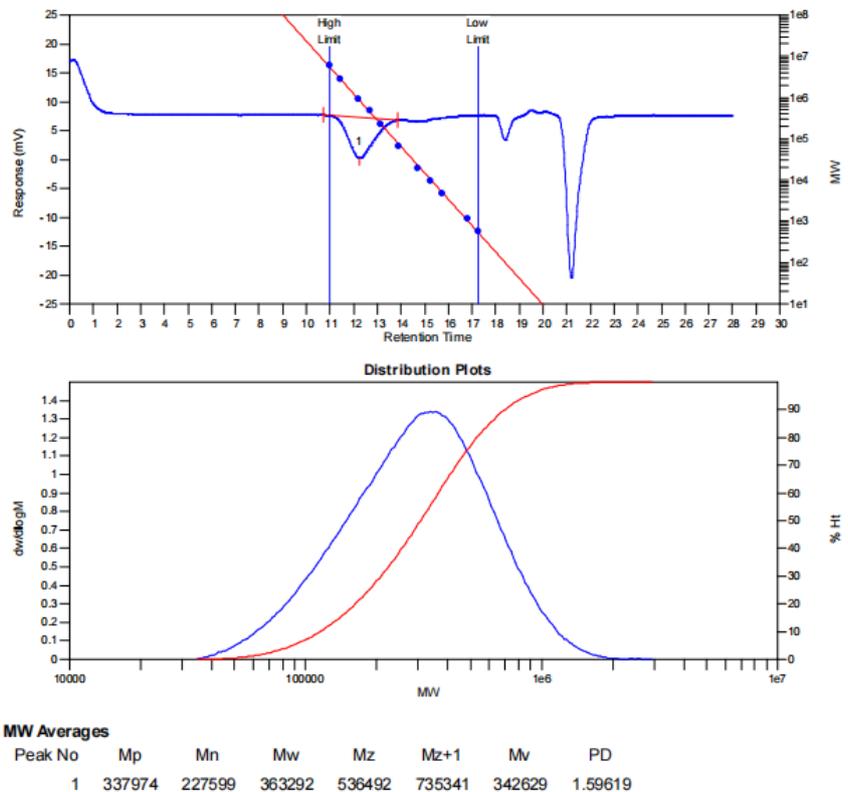
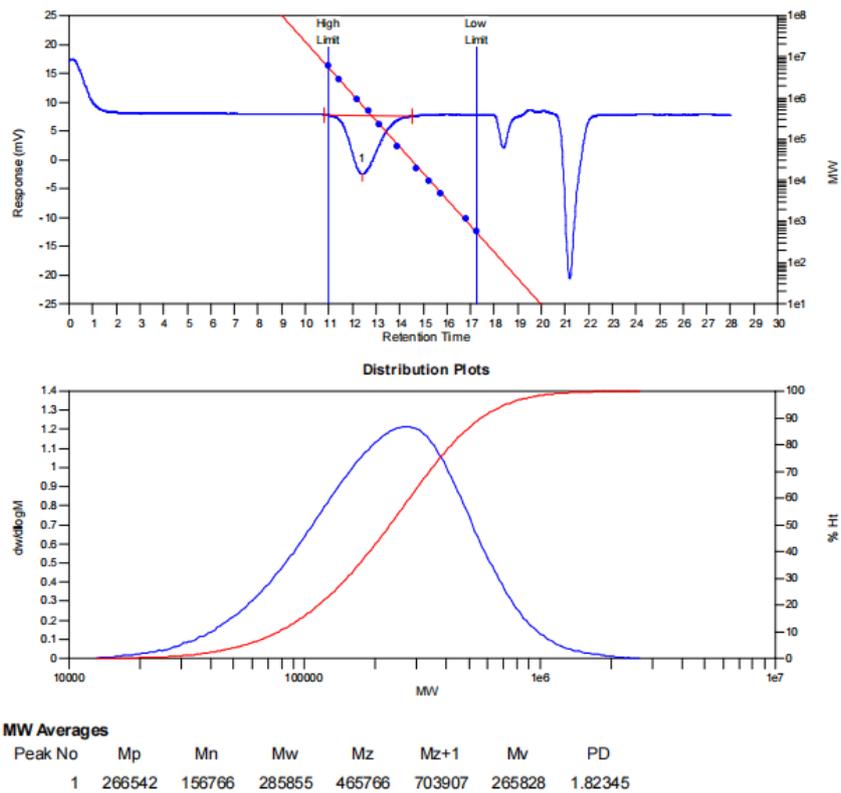
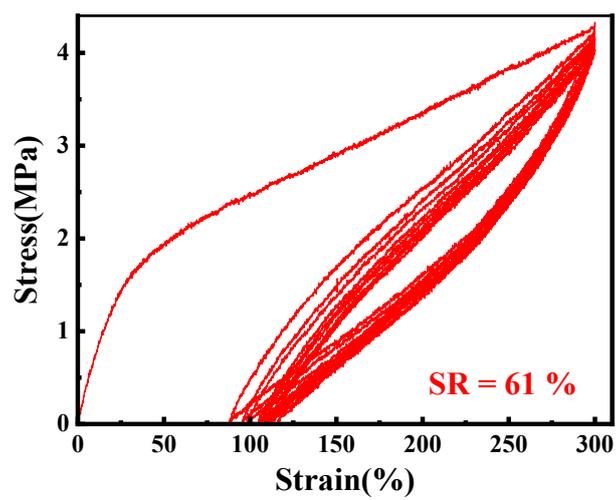


Figure S60. GPC trace of the polymer from table 1, entry 20.



**Figure S61.** GPC trace of the polymer from table 1, entry 21.

## 6. Tensile Test for Polymers



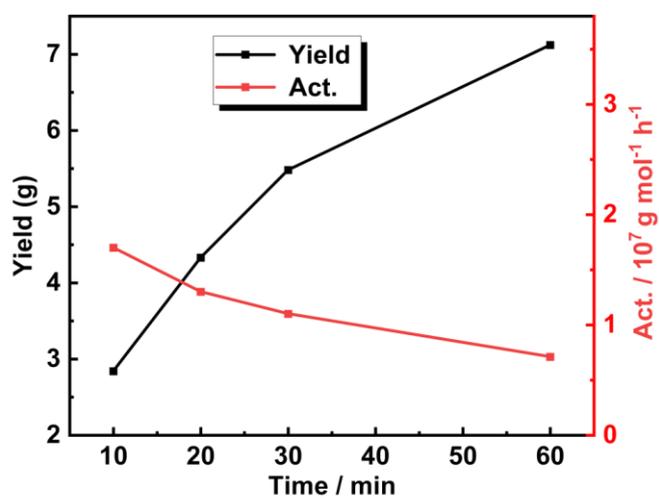
**Figure S62.** SR of the polymer from table 1, entry 19.

## 7. Time-dependence study

**Table S1.** Effect of reaction time on ethylene polymerizations using **Ni3** at 70 °C. <sup>a</sup>

Entry	Cat.	<i>t</i> (min)	Yield (g)	Act. (10 <sup>7</sup> ) <sup>b</sup>
1	<b>Ni3</b>	10	2.84	1.70
2	<b>Ni3</b>	20	4.33	1.30
3	<b>Ni3</b>	30	5.48	1.10
4	<b>Ni3</b>	60	7.12	0.71

<sup>a</sup> Reaction conditions: Ni(II) precatalyst (1 μmol), MAO (500 equiv.), toluene/CH<sub>2</sub>Cl<sub>2</sub> (98 mL/2 mL), ethylene pressure (8 bar), polymerization temperature (70 °C). <sup>b</sup> Activity is in unit of g mol<sup>-1</sup> h<sup>-1</sup>.



**Figure S63.** Time-dependence curves of **Ni3** catalyzed ethylene polymerization at 70 °C.

## 8. Crystallographic data for Ni1 and Ni2.

	Ni1	Ni2
Formula	C <sub>58</sub> H <sub>52</sub> Br <sub>2</sub> N <sub>2</sub> Ni	C <sub>62</sub> H <sub>60</sub> Br <sub>2</sub> N <sub>2</sub> Ni
Formula weight	995.54	1051.65
Crystal dimensions (mm <sup>3</sup> )	0.10 × 0.12 × 0.30	0.10 × 0.12 × 0.30
Crystal system	orthorhombic	orthorhombic
Space group	Pccn	Pccn
a (Å)	14.7079(6)	14.7157(9)
b (Å)	19.3048(9)	19.3384(14)
c (Å)	22.4475(8)	22.4651(12)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å <sup>3</sup> )	6373.6(5)	6393.1(7)
Z	4	4
T (K)	301(2)	302(2)
D <sub>calcd</sub> (g cm <sup>-3</sup> )	1.037	1.093
μ (mm <sup>-1</sup> )	1.588	1.587
F (000)	2048	2176
No. of rflns. collected	46688	46313
No. of indep. rflns. /R <sub>int</sub>	9333 / 0.1044	9355 / 0.1155
No. of obsd. rflns. [I <sub>0</sub> > 2σ(I <sub>0</sub> )]	3759	3660
Data / restraints / parameters	9333 / 0 / 293	9355 / 0 / 309
R <sub>1</sub> / wR <sub>2</sub> [I <sub>0</sub> > 2σ(I <sub>0</sub> )]	0.1095 / 0.3377	0.0623 / 0.1346
R <sub>1</sub> / wR <sub>2</sub> (all data)	0.2145 / 0.3981	0.1782 / 0.1748
GOF (on F <sup>2</sup> )	1.154	0.975
Largest diff. peak and hole (e Å <sup>-3</sup> )	3.053 / -0.532	0.271 / -0.465
CCDC No.	2503322	2502780

## 9. References

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