

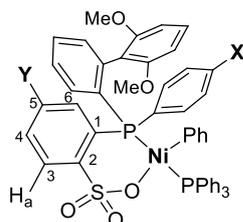
Supporting Information for  
**Position Makes a Difference: Electronic Effects in Nickel-catalyzed  
Ethylene Polymerizations and Copolymerizations**

Tao Liang, Changle Chen \*

**Table of Contents**

1. Tables and Figures. ....	S2
2. General methods. ....	S4
3. NMR and ESI-MS of ligand L, Ni. ....	S11
4. NMR figures of (co)polymers. ....	S28
5. DSC data of (co)polymers. ....	S33
6. GPC data of (co)polymers. ....	S38
7. Tensile tests of the polymer products. ....	S49
8. X-ray Crystallography .....	S50

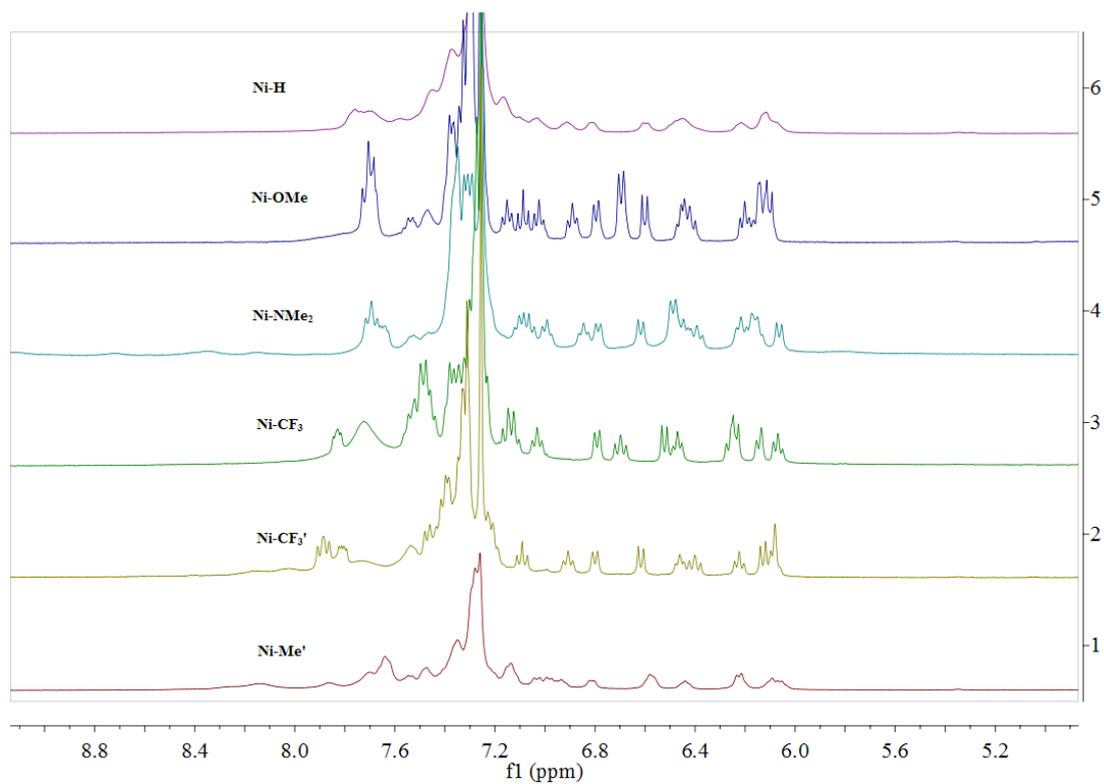
## 1. Tables and Figures.



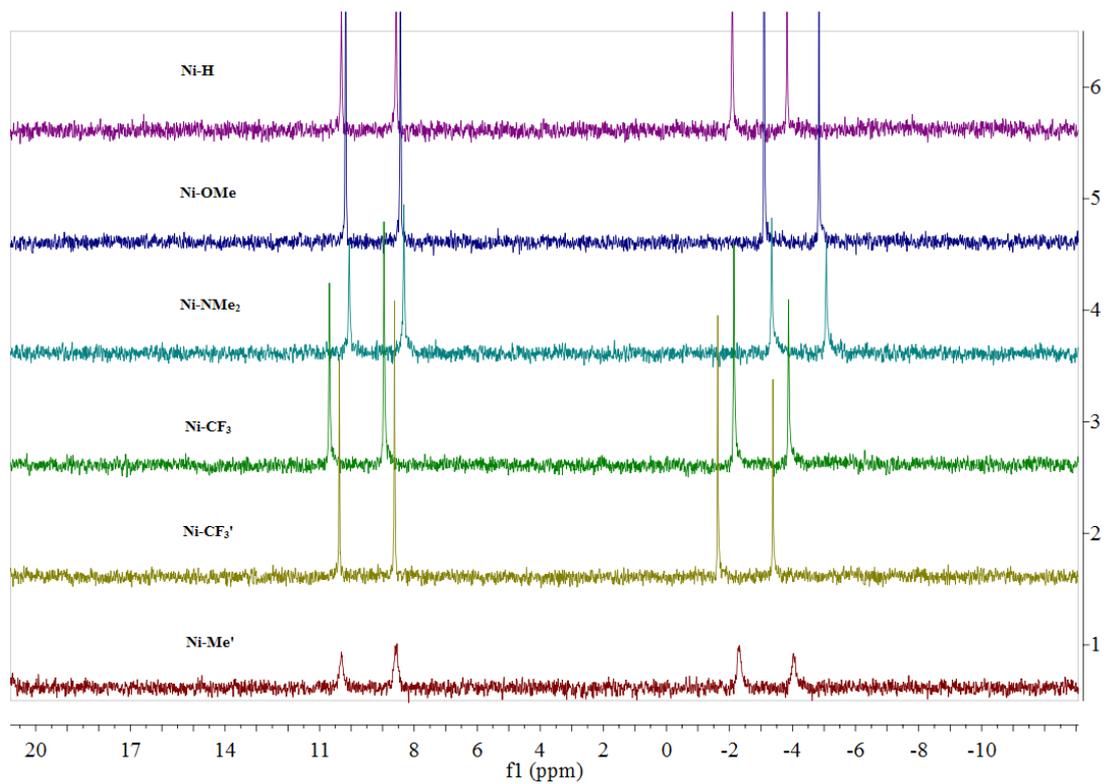
**Table S1.** NMR data of Nickel Complexes.<sup>a</sup>

Entry	Cat.	<sup>1</sup> H	<sup>13</sup> C	<sup>31</sup> P
1	<b>Ni-H</b>	7.81-7.73	146.9 <sup>b</sup>	9.44, -2.96
2	<b>Ni-OMe</b>	7.77-7.64	146.15	9.30, -3.97
3	<b>Ni-NMe<sub>2</sub></b>	7.76-7.63	-	9.19, -4.21
4	<b>Ni-CF<sub>3</sub></b>	7.86-7.81	146.59	9.82, -3.01
5	<b>Ni-CF<sub>3</sub>'</b>	7.94-7.85	149.39	9.50, -2.50
6	<b>Ni-Me'</b>	7.76-7.68	-	9.42, -3.16

<sup>a</sup><sup>1</sup>H NMR data of H<sub>a</sub> spectrum range, <sup>13</sup>C NMR data of C<sup>2</sup>-ArSO<sub>3</sub>. <sup>b</sup>Data from Ref 1.



**Figure S1.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of Nickel Complexes.

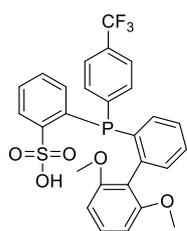


**Figure S2.**  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ ) of Nickel Complexes.

## 2. General methods.

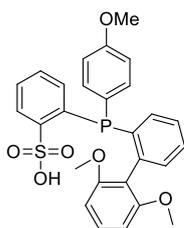
All experiments were carried out under dry Nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra were recorded a Bruker AscendTm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to tetramethylsilane; the  $^{31}\text{P}$  NMR spectra were referenced to an external 85%  $\text{H}_3\text{PO}_4$  solution. Coupling constants are in Hz. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. X-ray Diffraction data were collected at 298 (2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) with a PL 210 equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 140 °C using trichlorobenzene as a solvent, and the calibration was made using polystyrene standard and are corrected for linear polyethylene by universal calibration using the Mark–Houwink parameters of Rudin:  $K = 1.75 \times 10^{-2} \text{ cm}^3/\text{g}$  and  $R = 0.67$  for polystyrene and  $K = 5.90 \times 10^{-2} \text{ cm}^3/\text{g}$  and  $R = 0.69$  for polyethylene. Dichloromethane, THF, hexanes, and toluene were purified by solvent purification systems. 4-(Trifluoromethyl)phenylphosphonous dichloride,<sup>1</sup> (4-Methoxyphenyl)phosphonous dichloride<sup>2</sup> and dichloro-4-(*N,N*-dimethylamino)phenylphosphane were prepared according to literature procedures.<sup>3</sup>

Stress/strain experiments were performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature. At least three specimens of each polymer were tested. Polymers were melt-pressed at 150 °C to obtain the test specimens. The test specimens have 25-mm gauge length, 2-mm width, and thickness of 0.5 mm.

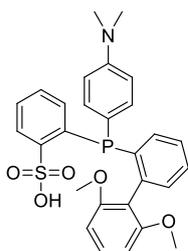


**Preparation of Ligand L-CF<sub>3</sub>.** At 0 °C,  $^n\text{BuLi}$  (2.5 M, 8 mL, 20 mmol) was added slowly to a solution of benzenesulfonic acid (1.58 g, 10 mmol) in THF (25 mL). The suspension was stirred for 1 h before added to the solution of 4-(Trifluoromethyl)phenylphosphonous dichloride (2.47 g, 10.0 mmol) in THF (30 mL) at -78 °C. The resulting mixture one was stirred for another 2 h at room temperature. 2'-bromo-2,6-dimethoxybiphenyl (3.14 g, 10.7 mmol) was dissolved in dry THF (40 mL) under nitrogen and cooled to -78 °C in a separate Schlenk.  $^n\text{BuLi}$  (2.5 M in hexane, 4.28 mL, 10.7 mmol) was added dropwise. The resulting solution was stirred for 1 h at -78 °C before added to the mixture one. The new resulting mixture was stirred for another 24 h at room temperature. The volatiles were removed, and the residue was

taken up in distilled water. The mixture was acidified with concentrated HCl/H<sub>2</sub>O solution, and extracted three times with CH<sub>2</sub>Cl<sub>2</sub> (150 ml). The extracts were combined, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The crude product was purified by chromatography (DCM/CH<sub>3</sub>OH = 50/1) to afford ligand **L-CF<sub>3</sub>** (2.8 g, 52%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.35 (br, 1H), 7.78 (br, 2H), 7.66 (br, 2H), 7.50 (br, 5H), 7.39 - 7.28 (m, 3H), 6.47 (dd, *J* = 17.2, 7.8 Hz, 2H), 3.66 (s, 3H, *OMe*), 3.38 (s, 3H, *OMe*). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 0.57. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.32. The solubility of **L-CF<sub>3</sub>** is poor in common organic solvents; therefore, only <sup>1</sup>H NMR, <sup>31</sup>P and <sup>19</sup>F data were collected. [M-H]<sup>-</sup> Calcd for: C<sub>27</sub>H<sub>21</sub>O<sub>5</sub>F<sub>3</sub>PS, 545.0794; Found: 545.0805.

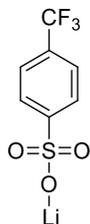


**Preparation of Ligand L-OMe.** Similar procedure as above was employed except (4-Methoxyphenyl)phosphonous dichloride (2.09 g, 10 mmol) was used. **L-OMe** was obtained as a white solid (3.04 g, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (br, 1H), 7.73 (d, *J* = 6.4 Hz, 2H), 7.47 (d, *J* = 17.8 Hz, 3H), 7.40-7.22 (m, 5H), 6.93 (d, *J* = 7.5 Hz, 2H), 6.47 (d, *J* = 8.3 Hz, 2H), 3.82 (s, 3H, *OMe*), 3.65 (s, 3H, *OMe*), 3.38 (s, 3H, *OMe*). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -0.03. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.62 (s), 156.97 (s), 156.56 (s), 151.90 (s), 140.97 (s), 140.87 (s), 134.92 (s), 134.79 (s), 134.14 (s), 134.04 (s), 133.50 (d, *J* = 9.7 Hz), 131.44 (s), 129.49 (s), 129.36 (s), 128.77 (d, *J* = 8.8 Hz), 127.90 (d, *J* = 12.2 Hz), 115.12 (s), 114.98 (s), 103.84 (s), 103.81 (s), 55.60 (s, *OMe*), 55.50 (s, *OMe*), 55.23 (s, *OMe*). [M-H]<sup>-</sup> Calcd for: C<sub>27</sub>H<sub>24</sub>O<sub>6</sub>PS, 507.1026; Found: 507.1042.

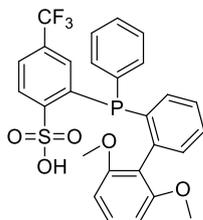


**Preparation of Ligand L-NMe<sub>2</sub>.** Similar procedure as above was employed except dichloro-4-(*N,N*-dimethylamino)phenylphosphane (2.22 g, 10 mmol) was used. **L-NMe<sub>2</sub>** was obtained as a white solid (3.12 g, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (dd, *J* = 6.9, 5.2 Hz, 1H), 7.69 (dt, *J* = 21.6, 7.4 Hz, 2H), 7.48 (t, *J* = 6.5 Hz, 1H), 7.45 - 7.36 (m, 3H), 7.34 - 7.29 (m, 1H), 7.24 (t, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 13.7, 8.8 Hz, 2H), 6.62 (d, *J* = 6.9 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 3.63 (s, 3H, *OMe*), 3.40 (s, 3H, *OMe*), 3.00 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -0.34. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.05 (s), 156.63 (s), 153.27 (s), 152.14 (d, *J* = 8.6 Hz), 140.91 (d, *J* = 9.8 Hz), 134.91 (d, *J* = 10.5 Hz), 134.40 (d, *J* = 12.8 Hz), 133.96 (s), 133.82 (d, *J* =

6.9 Hz), 133.66 (s), 133.46 (d,  $J = 9.9$  Hz), 131.29 (s), 129.13 (d,  $J = 12.5$  Hz), 128.87 (d,  $J = 8.9$  Hz), 127.75 (d,  $J = 12.6$  Hz), 120.33 (d,  $J = 92.1$  Hz), 114.72 (d,  $J = 94.7$  Hz), 111.78 (d,  $J = 14.4$  Hz), 103.79 (d,  $J = 4.1$  Hz), 100.60 (d,  $J = 101.7$  Hz), 55.50 (s, *OMe*), 55.28 (s, *OMe*), 39.87 (s,  $N(CH_3)_2$ ).  $[M-H]^-$  Calcd for:  $C_{28}H_{27}O_5NPS$ , 520.1342; Found: 520.1357.

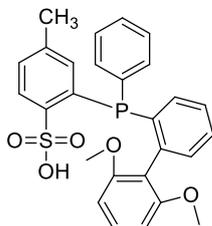


**Preparation of Lithium 4-(Trifluoromethyl)benzene Sulfonate.** 4-(Trifluoromethyl)benzenesulphonyl chloride (7.32 g, 30 mmol) was dissolved 50 ml 2 mol/L NaOH solution. The mixture was stirred for 12 h at 100 °C. Then the mixture was cooled and acid with concentrated HCl to pH1. A solution of p-toluidine (3.21 g, 30.0 mmol) in hydrochloric acid solution (45 mL of  $H_2O$  with 5 mL of concentrated HCl) was added at 0 °C. The resulting mixture was stirred for 6 h at 0 °C. A lot of solid was generated. The solid was filtered, pressed, and washed with cooled water, ether, and dried under vacuum at 40 °C for 48 h to yield toluidinium 4-(Trifluoromethyl)benzene sulfonate salt (8.49 g, 85%). A suspension of this compound (6.67 g, 20 mmol) in THF (200 mL) was cooled to 0°C. A solution of  $n$ BuLi (8.0 mL, 2.5 M solution in hexane, 20.0 mmol) was added dropwise over 3 min. The mixture was warmed to room temperature and stirred for 12 h. The white solid was isolated by filtration, washed with THF, and dried under vacuum to afford a white powder (3.71 g, 80%).

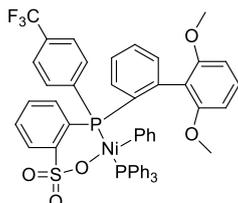


**Preparation of Ligand L-CF3'.** At -78 °C,  $n$ BuLi (2.5 M, 2 mL, 5 mmol) was added slowly to a solution of 2'-bromo-2,6-dimethoxybiphenyl (1.47 g, 5 mmol) in THF (30 mL). The suspension was stirred for 1 h at -78 °C and then added to the solution of dichlorophenyl-phosphine (0.67 mL, 5 mmol) in THF (20 mL) at -78°C. The mixture one was stirred for 12 h at -78 °C. Lithium 4-(Trifluoromethyl)benzene sulfonate was suspended in dry THF (20 mL) under nitrogen and cooled to -5 °C.  $n$ BuLi (2.5 M in hexane, 2 mL, 5 mmol) was added dropwise. The resulting red solution was stirred for 1 h at -5 °C before added to the mixture one. Then the reaction was stirred for another 24 h at room temperature. The volatiles were removed, and the residue was taken up in distilled water (150 mL). The mixture was acidified to pH2 with concentrated HCl/ $H_2O$  solution, and extracted three times with  $CH_2Cl_2$  (total volume 150 mL). The extracts were combined, dried over  $MgSO_4$ , and concentrated under vacuum. The crude product was purified by chromatography (DCM/ $CH_3OH = 50/1$ ) to afford ligand L-CF3' (1.09

g, 40%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (br, 1H), 7.85 (br, 1H), 7.71 (br, 1H), 7.56 (br, 1H), 7.45 - 7.35 (m, 7H), 7.24 - 7.20 (m, 2H), 6.43 (t,  $J = 7.7$  Hz, 2H), 3.61 (s, 3H, *OMe*), 3.34 (s, 3H, *OMe*).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  1.70.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.75. The stability of **L-CF<sub>3</sub>'** is poor; therefore, only  $^1\text{H}$  NMR,  $^{31}\text{P}$  and  $^{19}\text{F}$  data were collected. [M-H]<sup>-</sup> Calcd for:  $\text{C}_{27}\text{H}_{21}\text{O}_5\text{F}_3\text{PS}$ , 545.0794; Found: 545.0806.

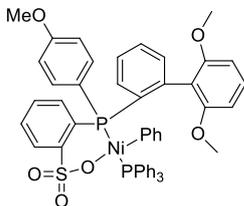


**Preparation of Ligand L-Me'.** At 0 °C, <sup>n</sup>BuLi (2.5 M, 8 mL, 20 mmol) was added slowly to a solution of p-Toluenesulfonic acid (1.72 g, 10 mmol) in THF (25 mL). The suspension was stirred for 1 h before added to the solution of  $\text{PhPCl}_2$  (1.35 mL, 10.0 mmol) in THF (30 mL) at -78 °C. The mixture one was stirred for another 2 h at room temperature. 2'-bromo-2,6-dimethoxybiphenyl (2.92 g, 10 mmol) was dissolved in dry THF (40 mL) under nitrogen and cooled to -78 °C in a separate Schlenk. <sup>n</sup>BuLi (2.5 M in hexane, 4 mL, 10 mmol) was added dropwise. The resulting solution was stirred for 1.0 h at -78 °C before added to the mixture one. The resulting new mixture was stirred for another 24 h at room temperature. The volatiles were removed, and the residue was taken up in distilled water. The mixture was acidified with concentrated HCl/ $\text{H}_2\text{O}$  solution, and extracted three times with  $\text{CH}_2\text{Cl}_2$  (150 ml). The extracts were combined, dried over  $\text{MgSO}_4$ , and concentrated under vacuum. The crude product was recrystallized from dichloromethane/ether at room temperature. The resulting white powder was filtered and dried to give the desired ligand **L-Me'** (2.84 g, 58%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (dd,  $J = 11.9, 6.7$  Hz, 1H), 7.75 (t,  $J = 8.2$  Hz, 1H), 7.59 (t,  $J = 8.2$  Hz, 1H), 7.55 - 7.47 (m, 2H), 7.48 - 7.30 (m, 6H), 7.24 (s, 1H), 7.04 (d,  $J = 14.5$  Hz, 1H), 6.45 (dd,  $J = 26.8, 8.9$  Hz, 2H), 3.62 (s, 3H, *OMe*), 3.43 (s, 3H, *OMe*), 2.32 (s, 3H, *Me*).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  0.90.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.89 (s), 156.50 (s), 149.60 (d,  $J = 8.5$  Hz), 140.79 (d,  $J = 9.9$  Hz), 139.78 (d,  $J = 12.6$  Hz), 135.00 (d,  $J = 2.7$  Hz), 134.89 (d,  $J = 10.6$  Hz), 134.21 (d,  $J = 11.0$  Hz), 134.04 (s), 133.43 (d,  $J = 10.0$  Hz), 132.61 (d,  $J = 11.2$  Hz), 131.46 (s), 129.19 (d,  $J = 13.5$  Hz), 128.77 (d,  $J = 9.7$  Hz), 127.92 (d,  $J = 12.7$  Hz), 119.79 (d,  $J = 80.1$  Hz), 118.88 (d,  $J = 81.1$  Hz), 113.82 (d,  $J = 5.9$  Hz), 112.75 (d,  $J = 94.7$  Hz), 103.71 (d,  $J = 2.9$  Hz), 55.39 (s, *OMe*), 55.29 (s, *OMe*), 21.21 (s, *Me*). [M-H]<sup>-</sup> Calcd for:  $\text{C}_{27}\text{H}_{24}\text{O}_5\text{PS}$ , 491.1077; Found: 491.1091.

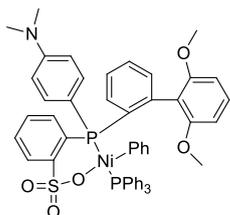


**Preparation of catalyst Ni-CF<sub>3</sub>.** A suspension of **L-CF<sub>3</sub>** (100 mg, 0.183 mmol) and  $\text{Na}_2\text{CO}_3$  (58.3 mg, 0.55 mmol) in 10 mL dichloromethane was stirred for 6 h at room

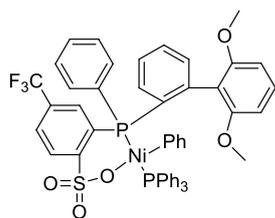
temperature. Solid trans-[(PPh<sub>3</sub>)<sub>2</sub>Ni(Cl)Ph] (127 mg, 0.183 mmol) was then added in small portions. Dichloromethane was added until the volume of the solution reached 15 mL, and the reaction mixture was stirred for 24 h at room temperature. The resulting yellow-orange mixture was filtered over celite and the volatiles were removed under vacuum. Toluene (3 mL) was first added to the orange residue to afford a slurry, then hexanes (15 mL) were added and the mixture was stirred for 12 h. The precipitate was recovered by filtration, washed with hexanes (3 x 10 mL) and dried for 20 h under dynamic vacuum to yield a yellow powder (146 mg, 84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86-7.81 (m, 1H), 7.73 (br, 2H), 7.57 - 7.44 (m, 7H), 7.40 - 7.33 (m, 5H), 7.32 (m, 7H), 7.23 (s, 1H), 7.14 (dd, *J* = 17.4, 8.5 Hz, 3H), 7.06-7.01 (m, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.74-6.67 (m, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.47 (t, *J* = 6.9 Hz, 1H), 6.25 (t, *J* = 9.6 Hz, 2H), 6.15 (d, *J* = 7.7 Hz, 1H), 6.07 (t, *J* = 7.2 Hz, 1H), 3.71 (s, 3H, *OMe*), 3.14 (s, 3H, *OMe*). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 9.82 (d, *J* = 280.5 Hz), -3.01 (d, *J* = 280.5 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.98. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.69 (d, *J* = 30.4 Hz), 146.59 (d, *J* = 13.8 Hz), 139.72 (d, *J* = 12.8 Hz), 138.70 (d, *J* = 38.6 Hz), 137.26 (d, *J* = 33.7 Hz), 136.33 (d, *J* = 47.4 Hz), 134.77 (d, *J* = 5.6 Hz), 134.10 (d, *J* = 10.0 Hz), 133.68 (d, *J* = 8.6 Hz), 133.36 (s), 131.73 (s), 130.33 (q, *J* = 33 Hz), 129.68 (d, *J* = 8.4 Hz), 129.53 (s), 129.38 (d, *J* = 5.9 Hz), 129.05 (d, *J* = 3.1 Hz), 128.95 (s), 128.13 (s), 127.77 (s), 127.51 (d, *J* = 9.5 Hz), 126.02 (s), 125.48 (d, *J* = 7.8 Hz), 124.85 (s), 124.54 (s), 123.70 (s), 121.35 (s), 117.56 (d, *J* = 3.4 Hz), 104.39 (s), 102.84 (s), 55.87 (s, *OMe*), 54.16 (s, *OMe*). Anal. Calcd for C<sub>51</sub>H<sub>41</sub>F<sub>3</sub>NiO<sub>5</sub>P<sub>2</sub>S: C, 64.92; H, 4.38; Found: C, 64.87; H, 4.41.



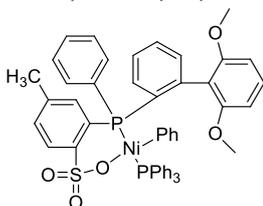
**Preparation of catalyst Ni-OMe.** Similar procedure as catalyst Ni-CF<sub>3</sub> was employed except L-OMe (100 mg, 0.20 mmol) was used. Ni-OMe was obtained as a yellow powder (126 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 - 7.64 (m, 4H), 7.60-7.51 (m, 1H), 7.47 (br, 2H), 7.38 (m, 3H), 7.35 - 7.28 (m, 11H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 8.4 Hz, 1H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 1H), 6.51 - 6.37 (m, 2H), 6.20 (t, *J* = 7.2 Hz, 1H), 6.13 (dd, *J* = 21.5, 8.5 Hz, 3H), 3.89 (s, 3H, *OMe*), 3.76 (s, 3H, *OMe*), 3.27 (s, 3H, *OMe*). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 9.30 (d, *J* = 281.5 Hz), -3.97 (d, *J* = 281.5 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.45 (s), 157.25 (s), 156.47 (s), 146.15 (d, *J* = 13.6 Hz), 139.71 (s), 139.38 (d, *J* = 11.6 Hz), 138.63 (s), 136.09 (d, *J* = 12.9 Hz), 135.01 (s), 134.42 (d, *J* = 10.0 Hz), 133.58 (s), 133.40 (d, *J* = 8.2 Hz), 130.07 (s), 129.71 (s), 129.15 (d, *J* = 19.9 Hz), 128.70 (s), 127.83 (d, *J* = 9.0 Hz), 126.16 (s), 126.04 (d, *J* = 4.7 Hz), 125.44 (d, *J* = 6.8 Hz), 124.30 (s), 122.63 (s), 122.11 (s), 121.37 (s), 118.21 (s), 113.34 (d, *J* = 11.0 Hz), 104.94 (s), 102.92 (s), 56.74 (s, *OMe*), 55.09 (s, *OMe*), 54.48 (s, *OMe*). Anal. Calcd for C<sub>51</sub>H<sub>44</sub>NiO<sub>6</sub>P<sub>2</sub>S: C, 67.64; H, 4.90; Found: C, 67.71; H, 4.87.



**Preparation of catalyst Ni-NMe<sub>2</sub>.** Similar procedure as catalyst Ni-CF<sub>3</sub> was employed except L-NMe<sub>2</sub> (100 mg, 0.19 mmol) was used. Ni-NMe<sub>2</sub> was obtained as a yellow powder (131 mg, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 - 7.63 (m, 3H), 7.53 (br, 1H), 7.48 (br, 1H), 7.36 (br, 8H), 7.34 - 7.28 (m, 7H), 7.17 - 7.03 (m, 3H), 7.03 - 6.97 (m, 1H), 6.89 - 6.83 (m, 1H), 6.80 (d, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 2H), 6.47 - 6.41 (m, 1H), 6.39 (d, *J* = 9.0 Hz, 1H), 6.24-6.14(m, 3H), 6.07 (d, *J* = 8.1 Hz, 1H), 3.93 (s, 3H, *OMe*), 3.31 (s, 3H, *OMe*), 2.93 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 9.19 (d, *J* = 281.0 Hz), -4.21 (d, *J* = 281.0 Hz). The solubility of Ni-NMe<sub>2</sub> is poor in common organic solvents; therefore, only <sup>1</sup>H NMR and <sup>31</sup>P data were collected. Anal. Calcd for C<sub>52</sub>H<sub>47</sub>NNiO<sub>5</sub>P<sub>2</sub>S: C, 67.99; H, 5.16; Found: C, 68.03; H, 5.12.



**Preparation of catalyst Ni-CF<sub>3</sub>'.** Similar procedure as catalyst Ni-CF<sub>3</sub> was employed except L-CF<sub>3</sub>' (100 mg, 0.18 mmol) was used. Ni-CF<sub>3</sub>' was obtained as a yellow powder (132 mg, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94-7.85 (m, 2H), 7.82 (d, *J* = 4.3 Hz, 2H), 7.54 (br, 1H), 7.47 (d, *J* = 7.7 Hz, 3H), 7.43-7.37 (m, 5H), 7.33 (d, *J* = 7.5 Hz, 10H), 7.24-7.18 (m, 3H), 7.09 (t, *J* = 8.3 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 6.50-6.44 (m, 1H), 6.44-6.37 (m, 1H), 6.23 (t, *J* = 7.5 Hz, 1H), 6.13 (d, *J* = 8.2 Hz, 1H), 6.09 (d, *J* = 6.6 Hz, 1H), 3.94 (s, 3H, *OMe*), 3.28 (s, 3H, *OMe*). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 9.50 (d, *J* = 283.3 Hz), -2.50 (d, *J* = 283.3 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.72. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.36 (s), 156.78 (s), 149.39 (d, *J* = 12.9 Hz), 139.63 (s), 139.42 (d, *J* = 11.0 Hz), 138.54 (s), 134.97 (d, *J* = 6.3 Hz), 134.44 (s), 134.34 (s), 133.52 (d, *J* = 8.4 Hz), 130.73 (q, *J* = 16 Hz), 130.64 (s), 130.44 (s), 129.79 (d, *J* = 6.3 Hz), 129.36 (s), 128.02 (s), 127.92 (s), 127.69 (s), 127.24 (s), 126.94 (d, *J* = 4.5 Hz), 126.51 (s), 126.35 (s), 125.63 (d, *J* = 8.5 Hz), 124.50 (s), 124.50 (s), 121.68 (s), 118.51 (s), 105.31 (s), 103.65 (s), 57.01 (s, *OMe*), 55.15 (s, *OMe*). Anal. Calcd for C<sub>51</sub>H<sub>41</sub>F<sub>3</sub>NiO<sub>5</sub>P<sub>2</sub>S: C, 64.92; H, 4.38; Found: C, 64.88; H, 4.41.



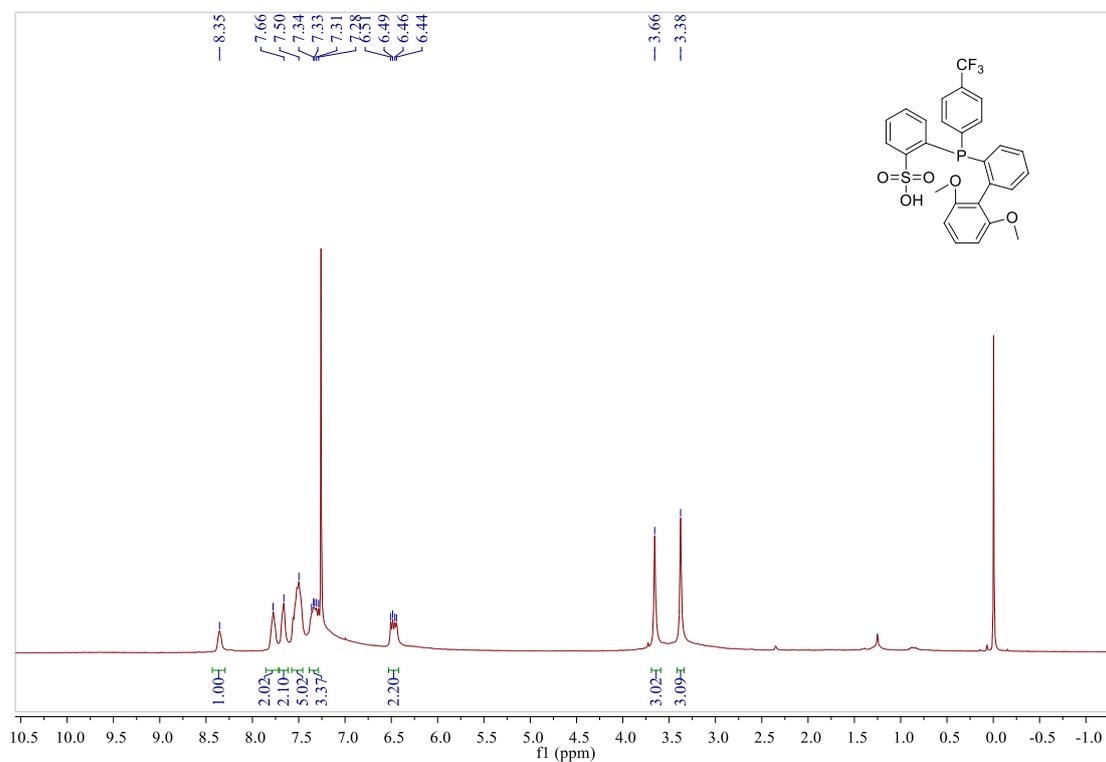
**Preparation of catalyst Ni-Me'.** Similar procedure as catalyst Ni-CF<sub>3</sub> was employed except L-Me' (100 mg, 0.20 mmol) was used. Ni-Me' was obtained as a yellow powder (124 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (br, 2H), 7.64 (br, 4H), 7.57 - 7.42 (m, 4H), 7.35 (br, 11H), 7.14 (s, 3H), 7.05 - 6.91 (m, 3H), 6.81 (d, *J* = 6.4 Hz, 1H), 6.58 (s, 2H), 6.44 (s, 1H), 6.22 (d, *J* = 7.3 Hz, 2H), 6.14- 6.00 (m, 2H), 3.82 (s, 3H), 3.23 (s, 3H), 2.11 (s, 3H). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 9.42 (d, *J* = 280.2 Hz), -3.16 (d, *J* = 280.2 Hz). The solubility of Ni-Me' is poor in common organic solvents; therefore, only <sup>1</sup>H NMR and <sup>31</sup>P data were collected. Anal. Calcd for C<sub>51</sub>H<sub>44</sub>NiO<sub>5</sub>P<sub>2</sub>S: C, 68.86; H, 4.99; Found: C, 68.85; H, 4.97.

**Procedure for ethylene homopolymerization.** In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with 18 mL toluene and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high pressure line and the solution was degassed. The vessel was warmed to 80 °C using an oil bath (water bath for the case of polymerization at room temperature) and allowed to equilibrate for 15 min. Desired amount of Ni complex in 2 mL CH<sub>2</sub>Cl<sub>2</sub> was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized and maintained at 8.0 atm of ethylene. After desired amount of time, the pressure vessel was vented and the polymer was precipitated in acidified methanol (methanol/HCl = 50/1) and dried at 80 °C for 24 h under vacuum.

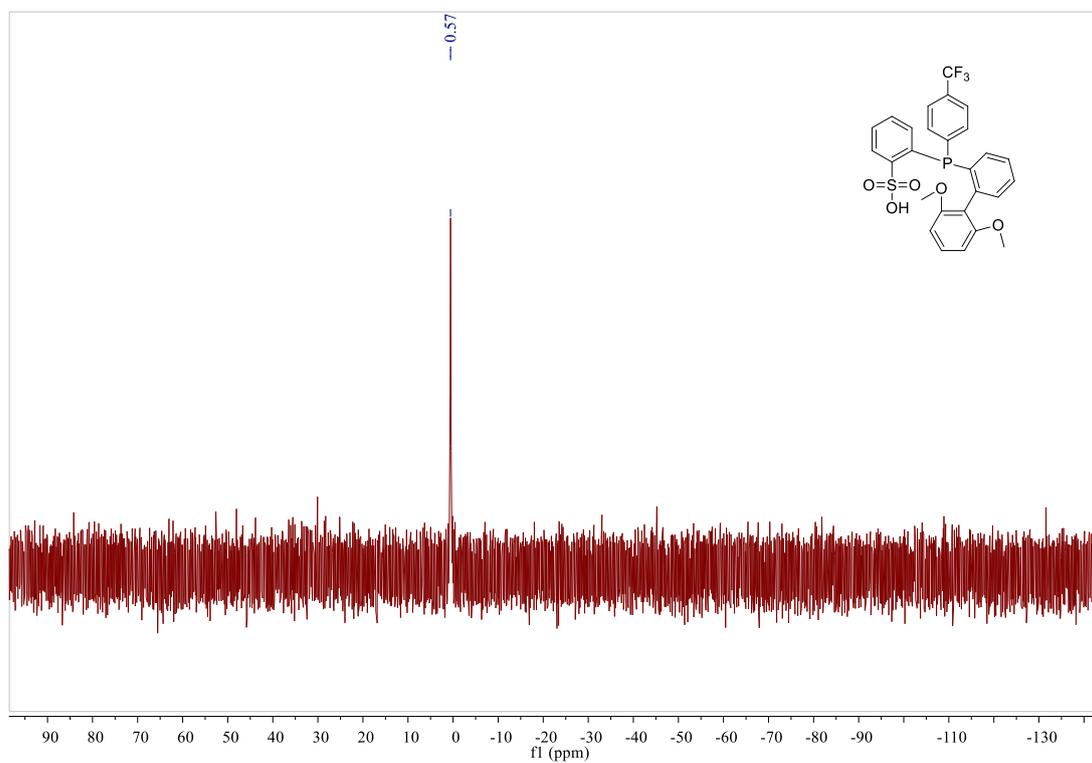
**Procedure for ethylene-polar monomer copolymerization.** In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with toluene and polar monomer in total 18 mL and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high pressure line and the solution was degassed. The vessel was warmed to 80 °C using an oil bath (water bath for the case of polymerization at room temperature) and allowed to equilibrate for 15 min. 20 μmol of Ni complex in 2 mL CH<sub>2</sub>Cl<sub>2</sub> was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized and maintained at 8.0 atm of ethylene. After 1 h, the pressure vessel was vented and the polymer was precipitated in acidified methanol (methanol/HCl = 50/1) and dried at 80 °C for 24 h under vacuum.

**X-ray crystallography.** Single crystals of complexes **1** and **2** suitable for X-ray structure determination were grown from slow diffusion of n-hexane into a concentrated toluene solution at -30 °C in a glove box. The crystallographic data are summarized in Table S1-S16. Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The crystal structures were solved using SHELXS-97<sup>4</sup> and refined against F<sup>2</sup> by full-matrix least squares using SHELXL-97.<sup>5</sup> The positions of hydrogen atoms were placed in the calculated positions.

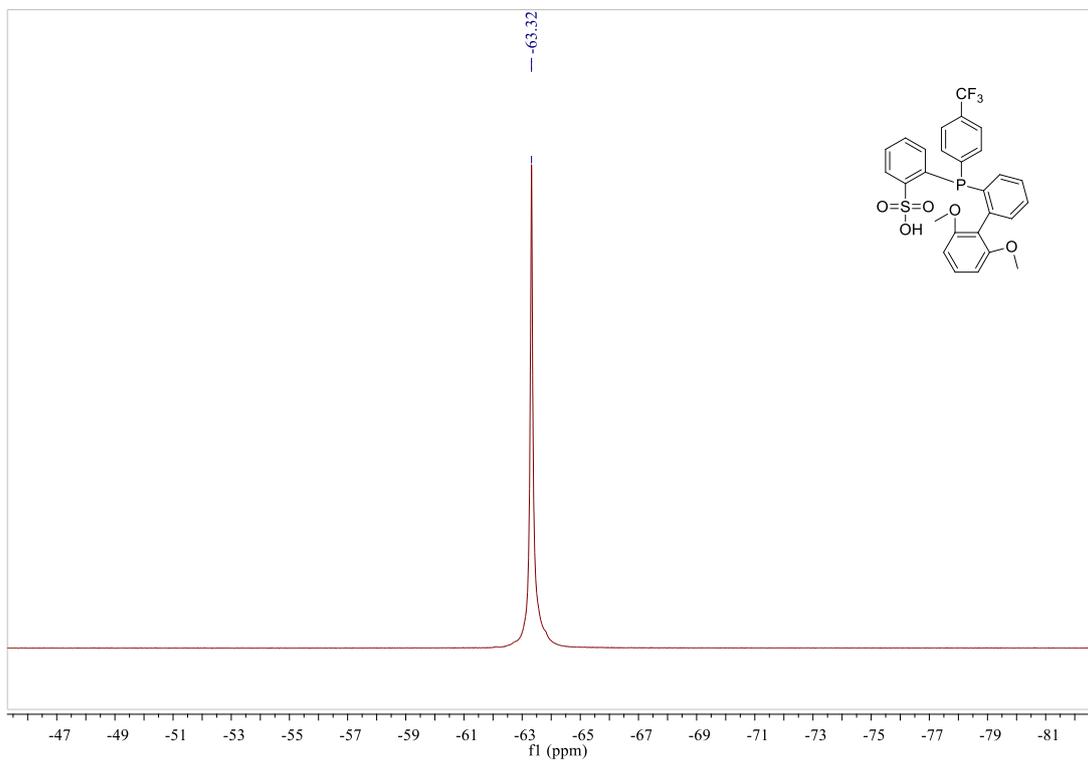
### 3. NMR and ESI-MS of ligand L, Ni.



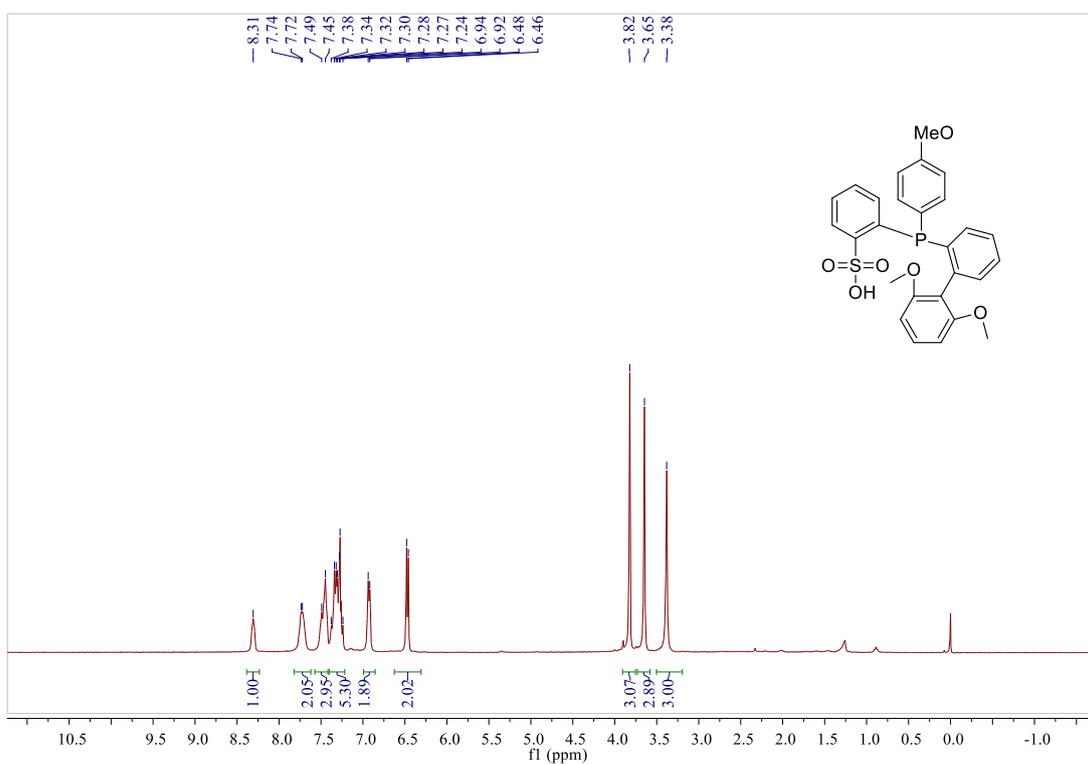
**Figure S3.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of  $\text{L-CF}_3$ .



**Figure S4.**  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ ) of  $\text{L-CF}_3$ .



**Figure S5.** <sup>19</sup>F NMR spectrum (CDCl<sub>3</sub>) of L-CF<sub>3</sub>.



**Figure S6.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of L-OMe.

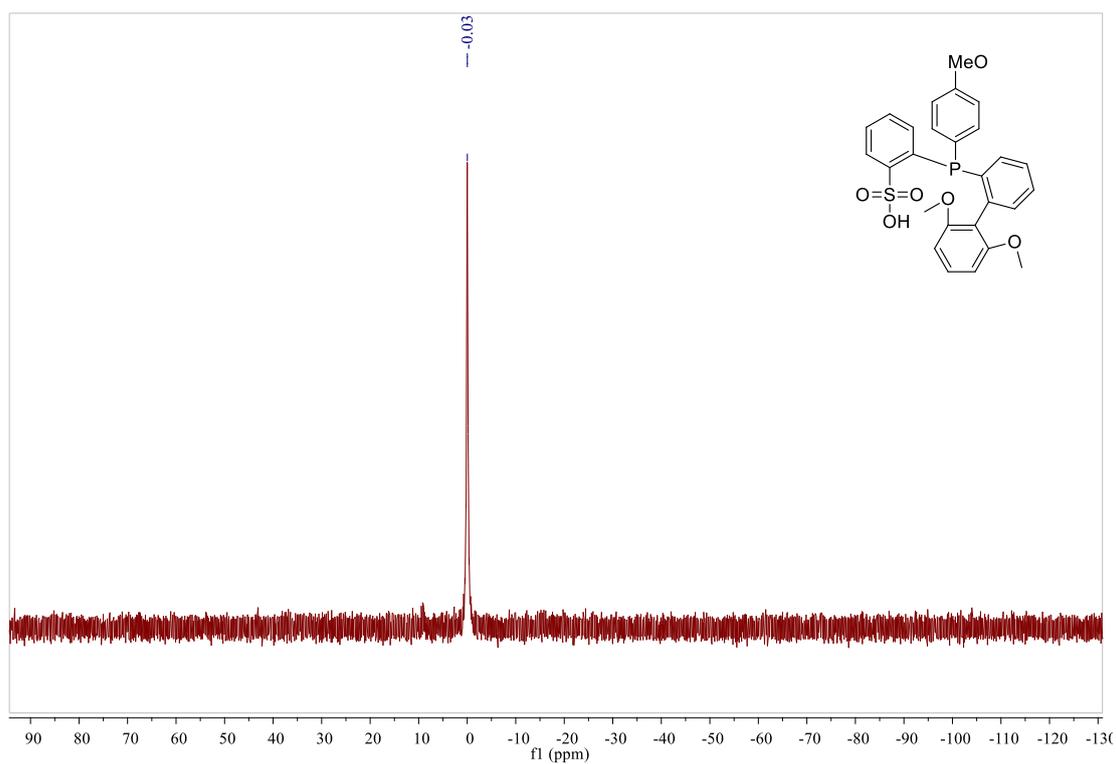


Figure S7.  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ ) of L-OMe.

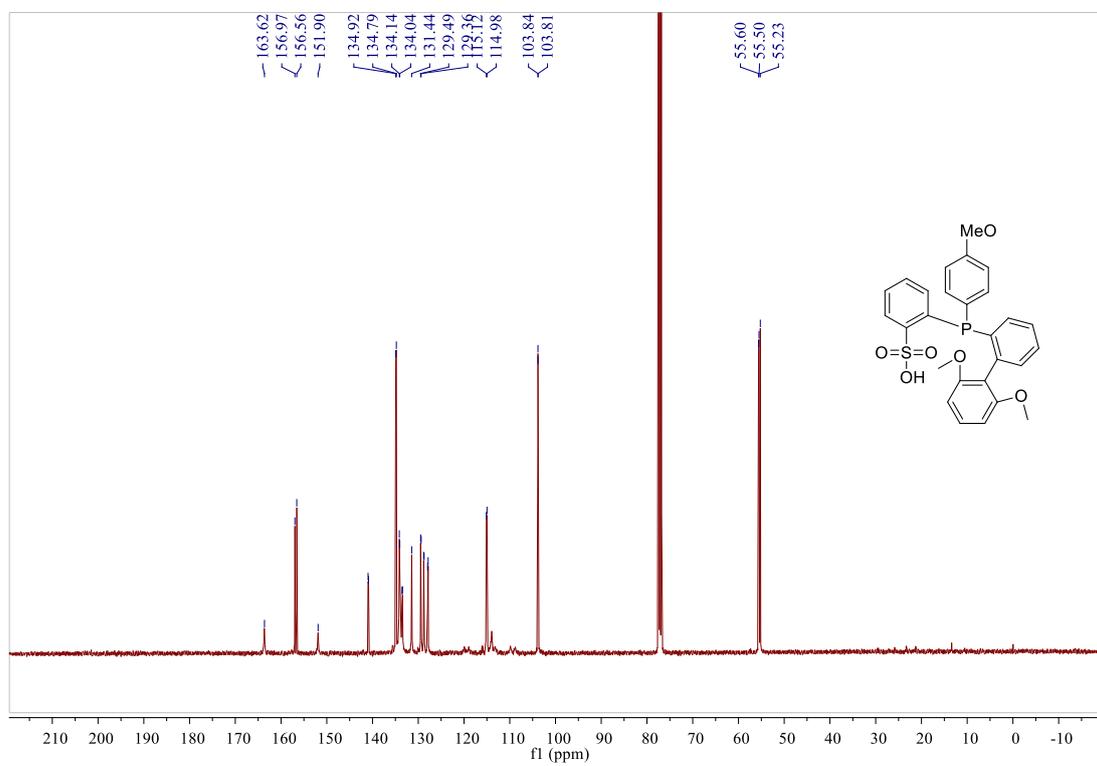
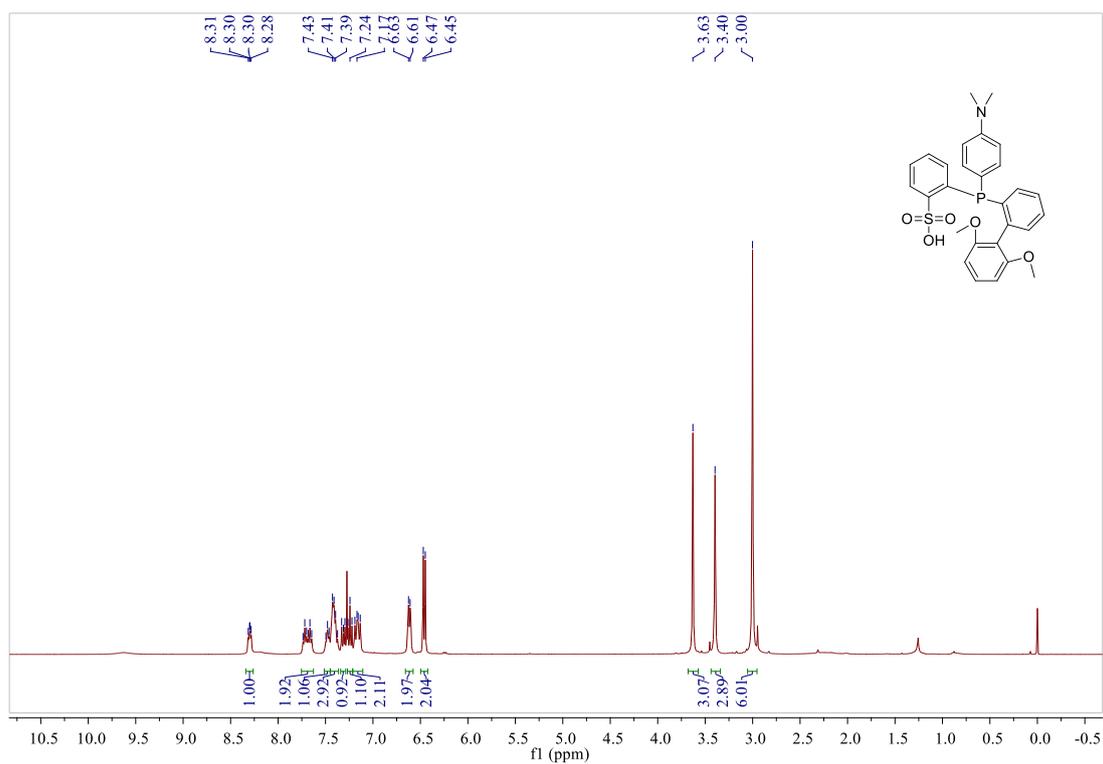
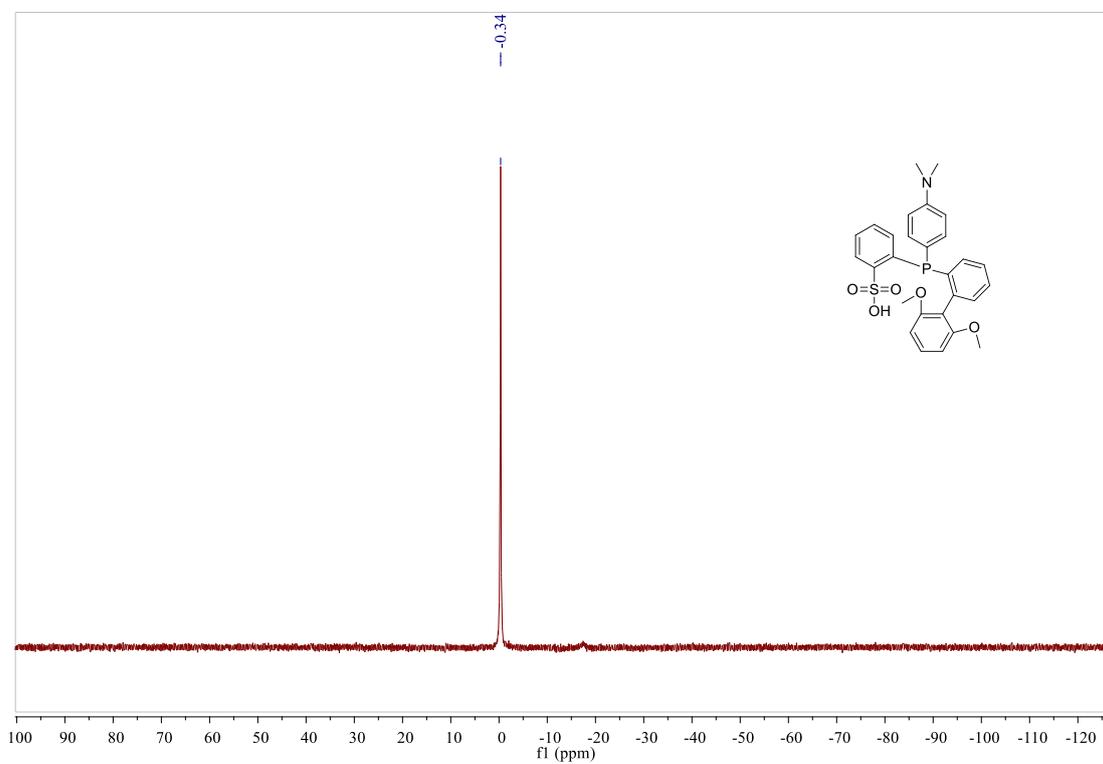


Figure S8.  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  of L-OMe.



**Figure S9.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of L-NMe<sub>2</sub>.



**Figure S10.** <sup>31</sup>P NMR spectrum (CDCl<sub>3</sub>) of L-NMe<sub>2</sub>.

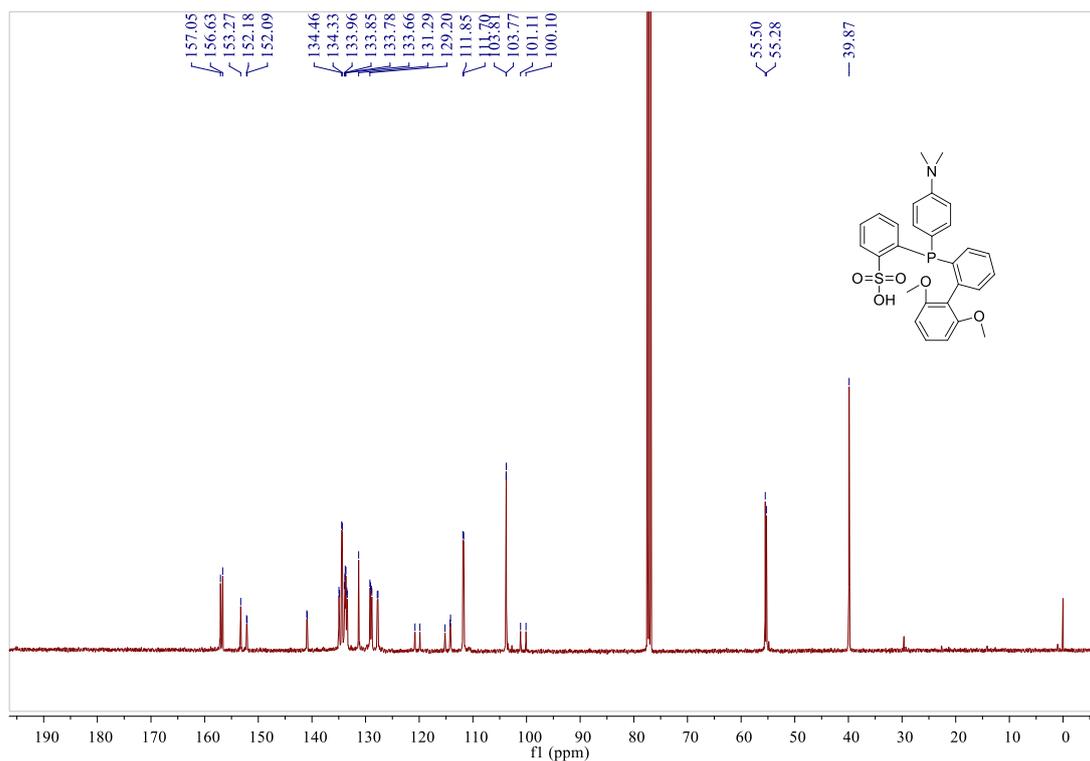


Figure S11. <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub> of L-NMe<sub>2</sub>.

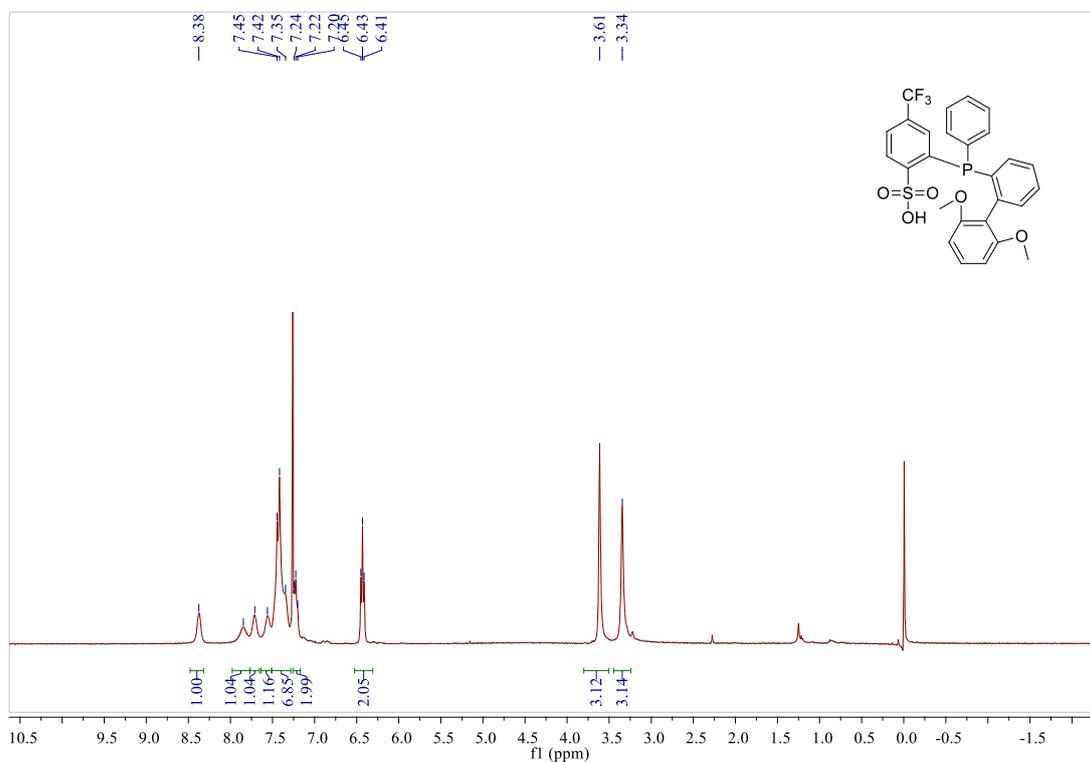
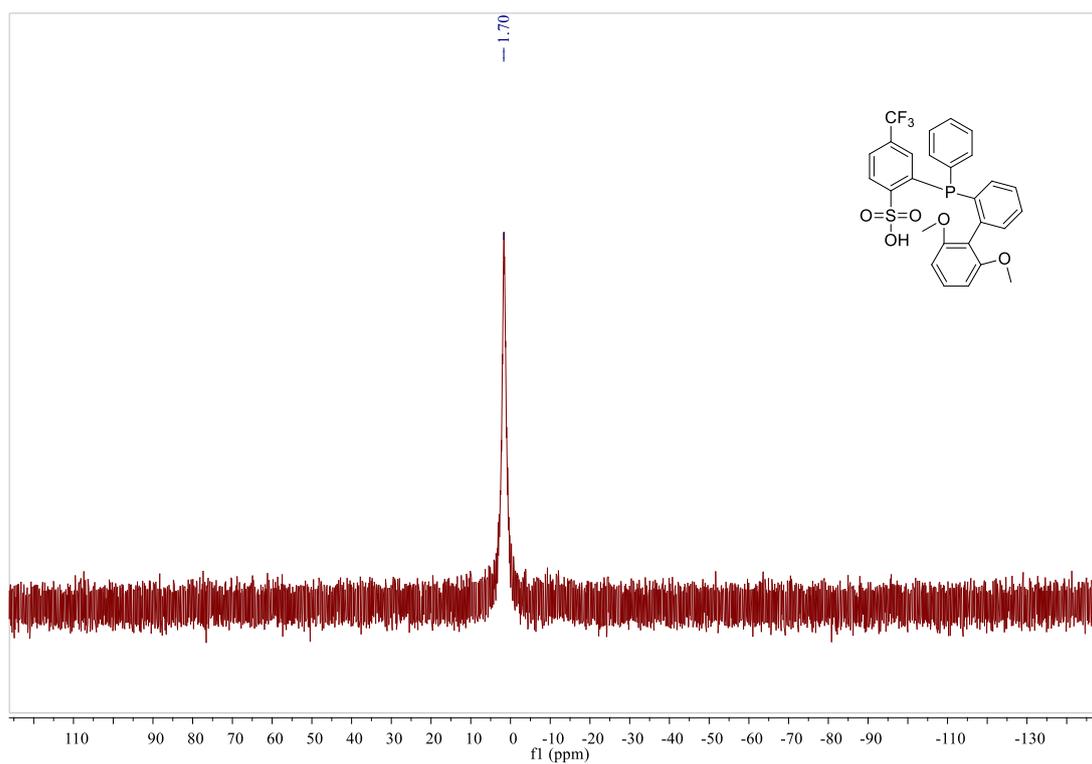
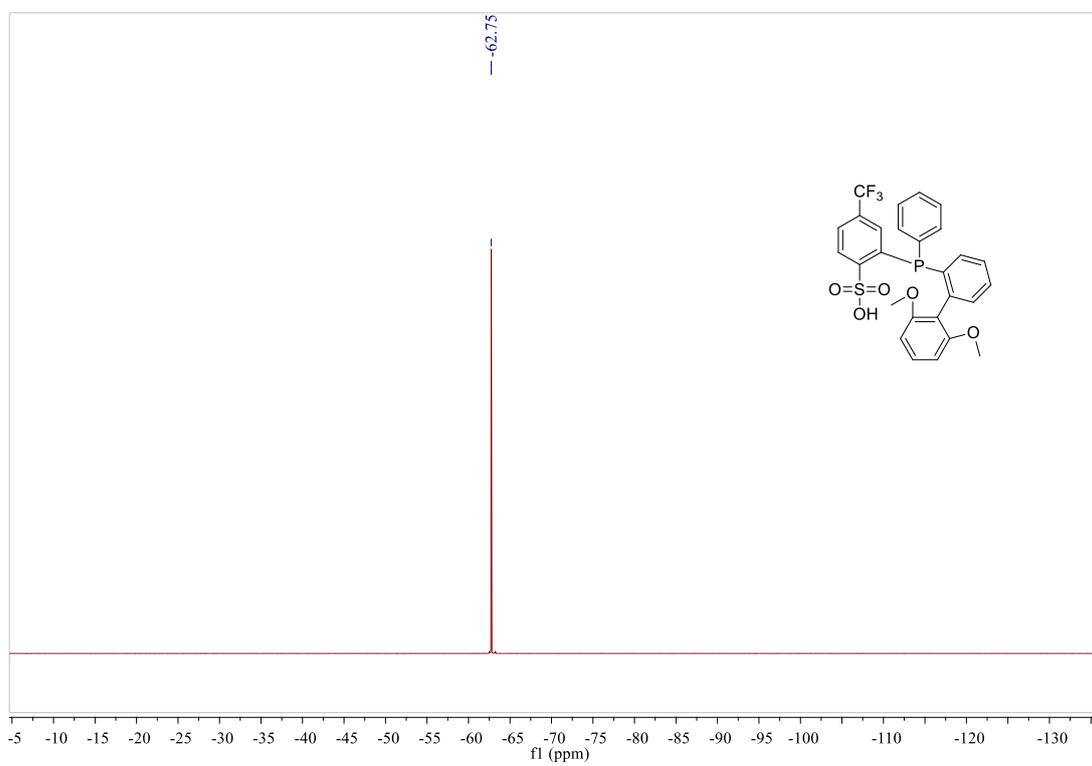


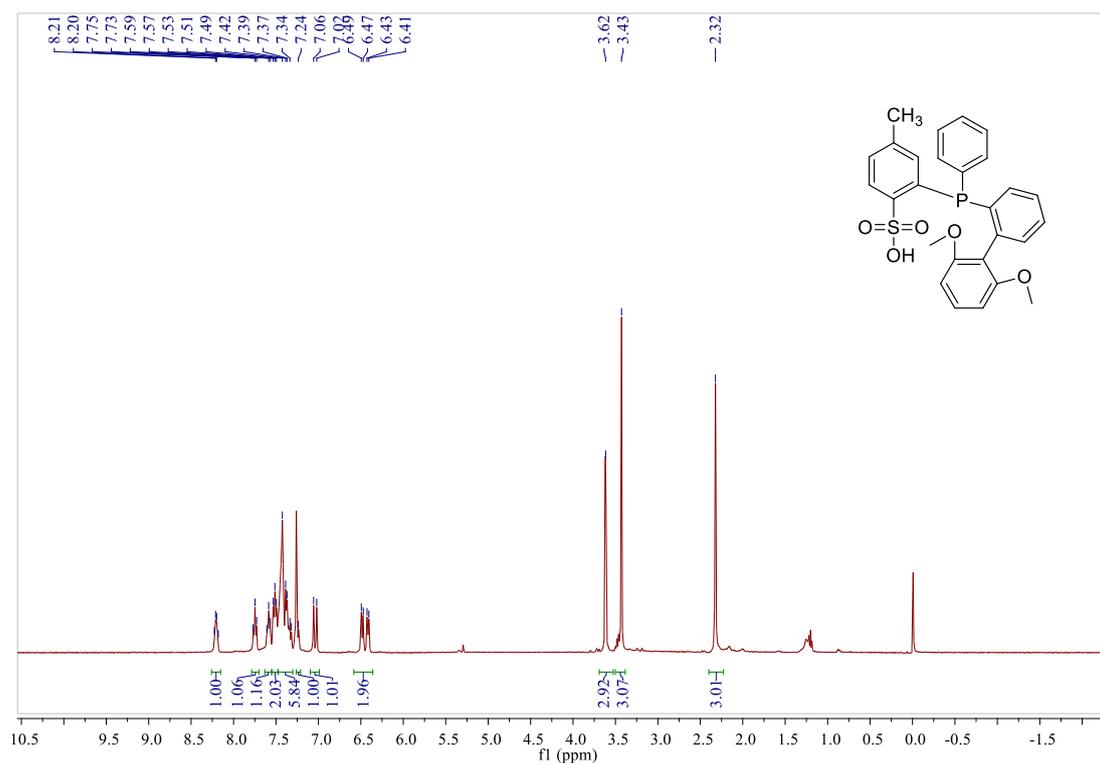
Figure S12. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of L-CF<sub>3</sub>'.



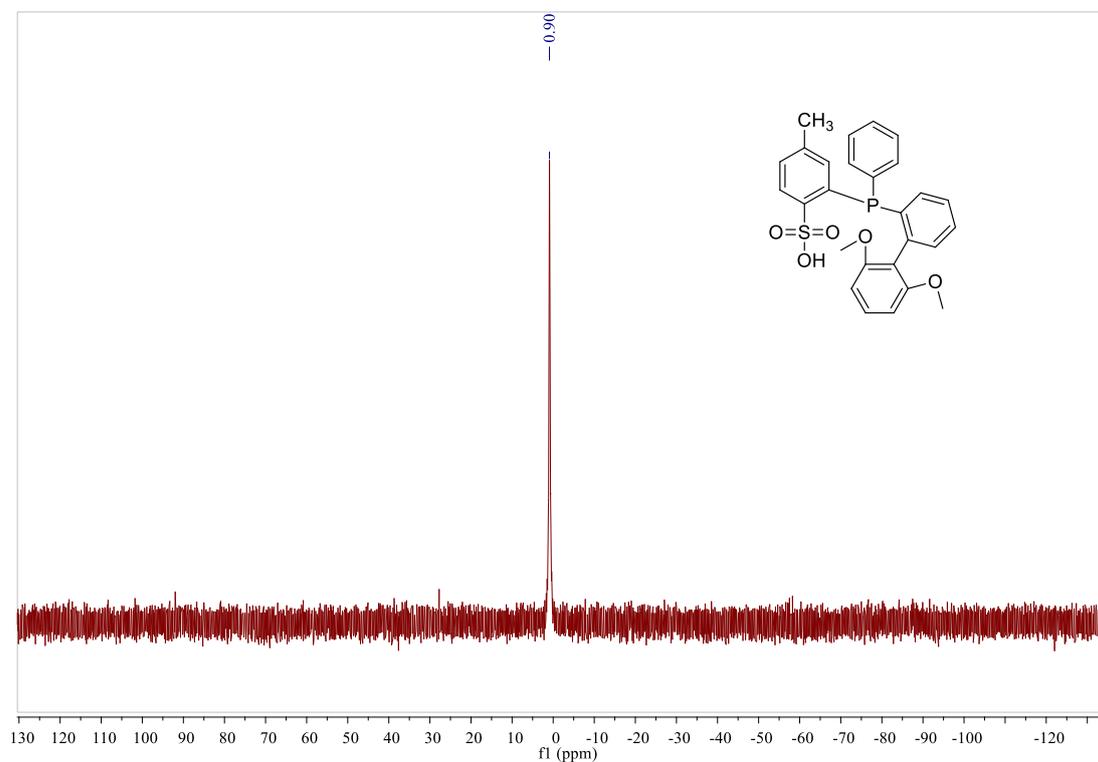
**Figure S13.**  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ ) of **L-CF<sub>3</sub>'**.



**Figure S14.**  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ) of **L-CF<sub>3</sub>'**.



**Figure S15.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of L-Me'.



**Figure S16.**  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ ) of L-Me'.

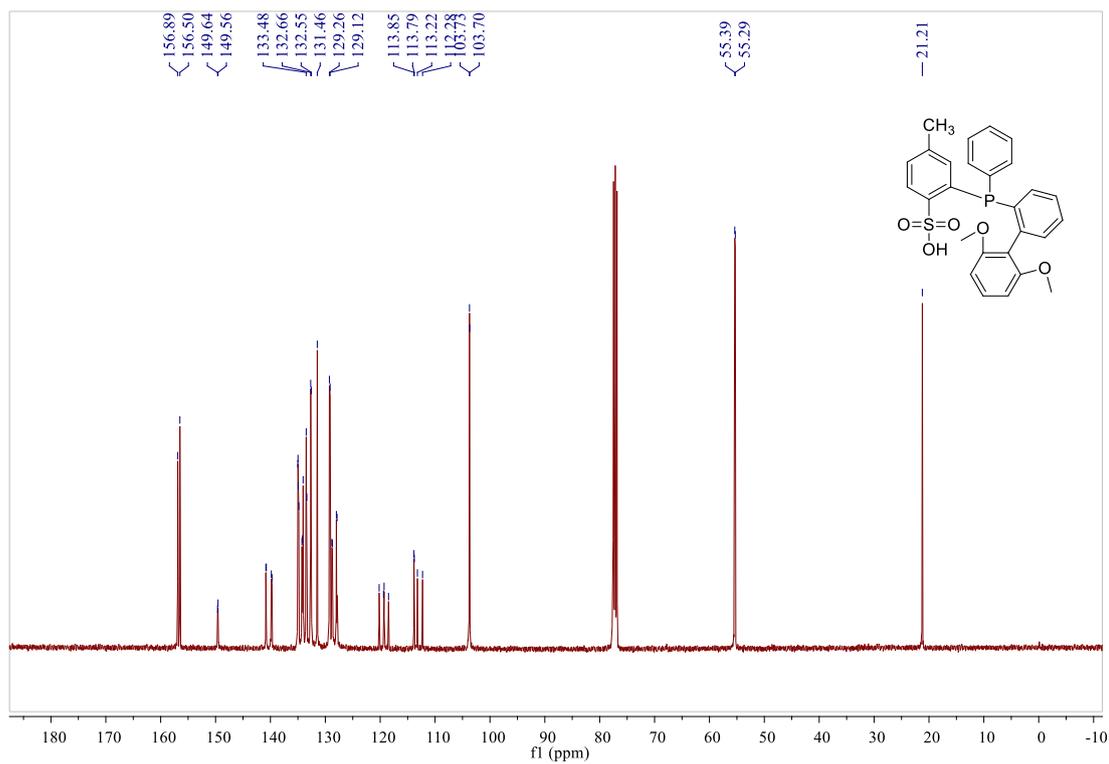


Figure S17.  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  of L-Me'.

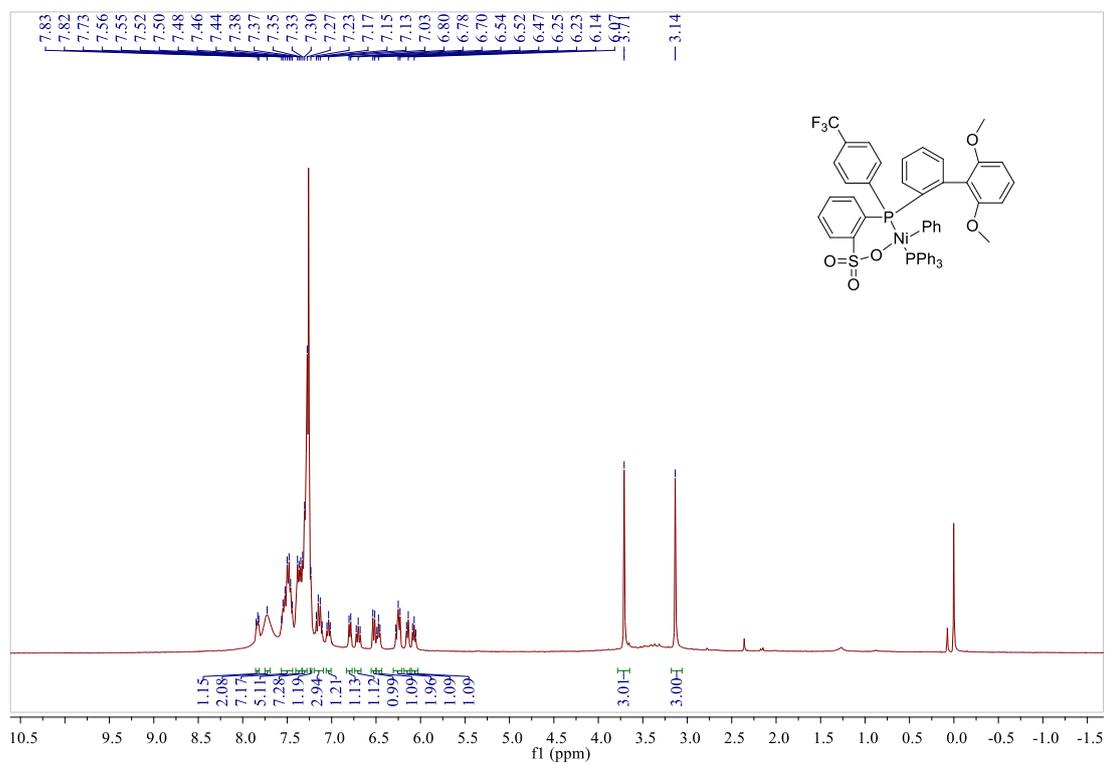
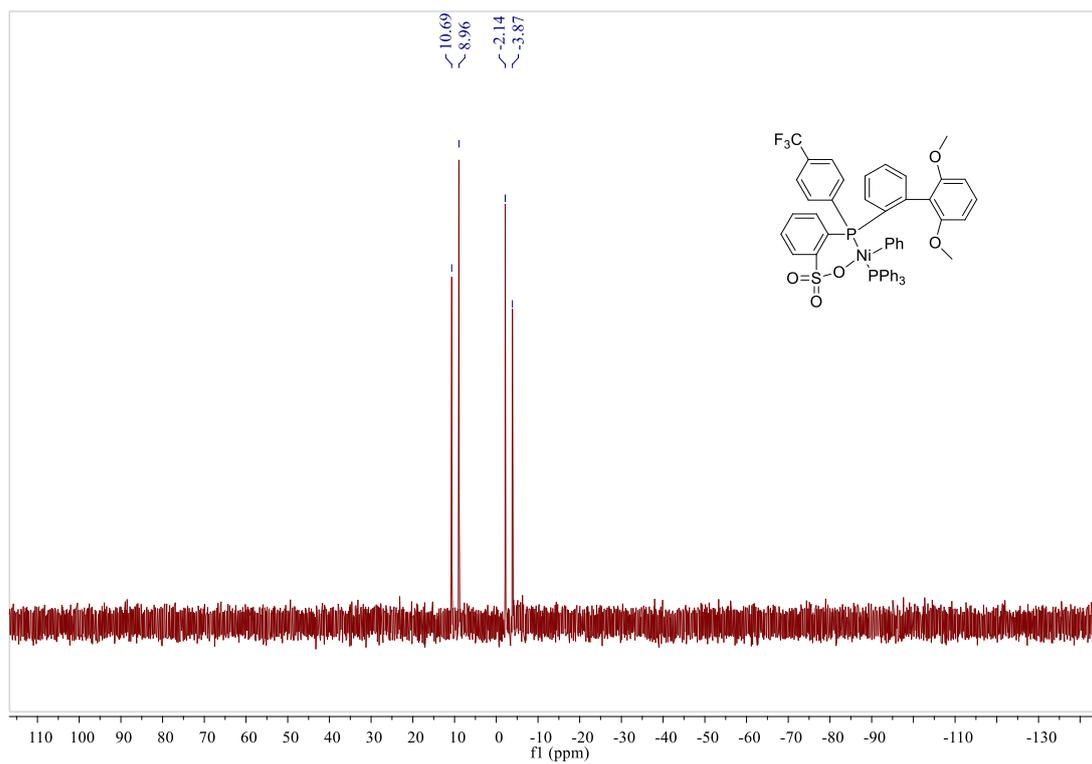
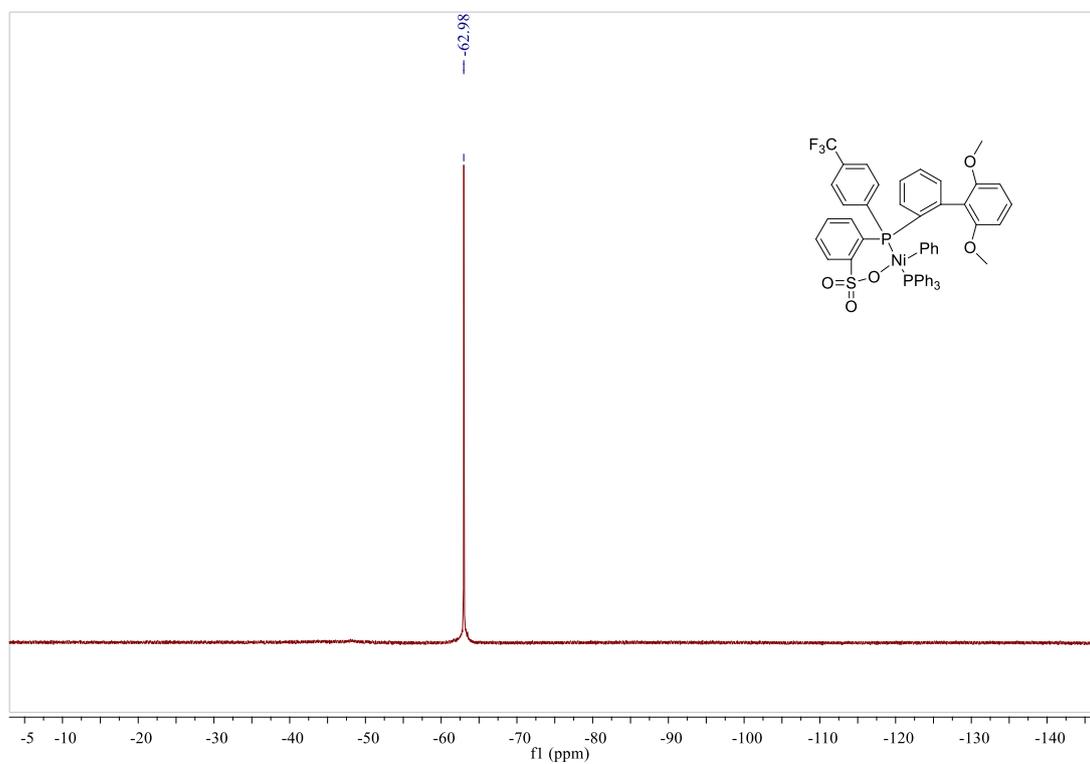


Figure S18.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of Ni-CF<sub>3</sub>.



**Figure S19.**  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ ) of Ni-CF<sub>3</sub>.



**Figure S20.**  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ) of Ni-CF<sub>3</sub>.

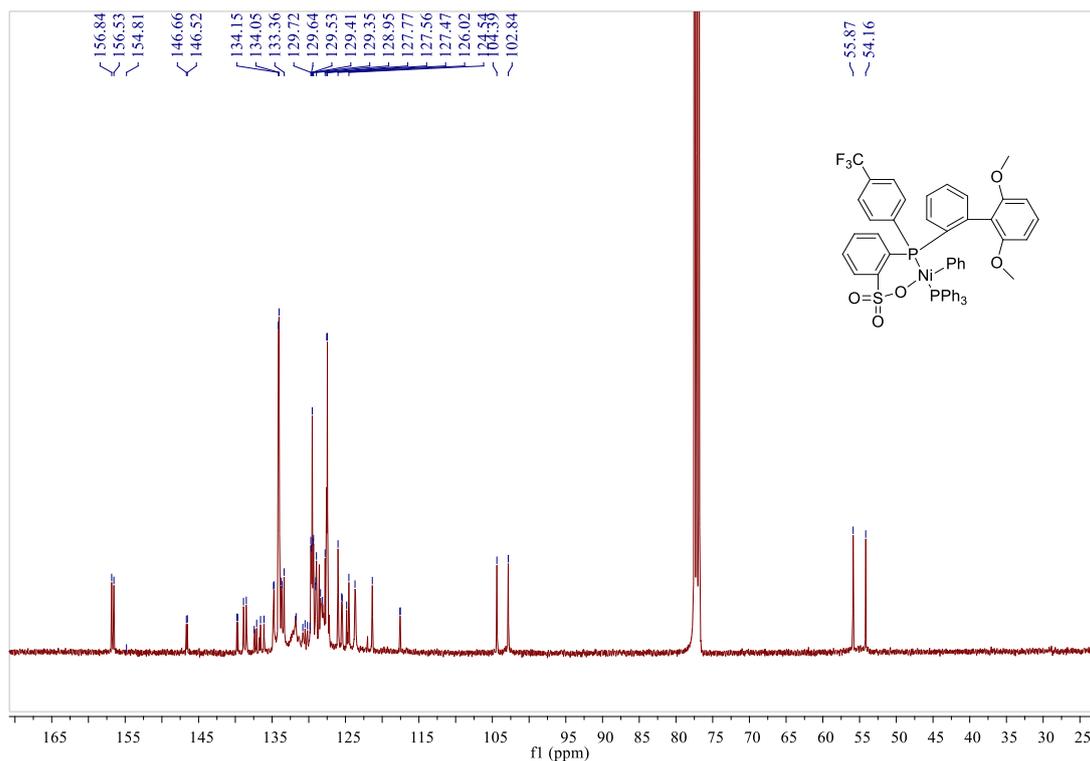


Figure S21. <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub> of Ni-CF<sub>3</sub>.

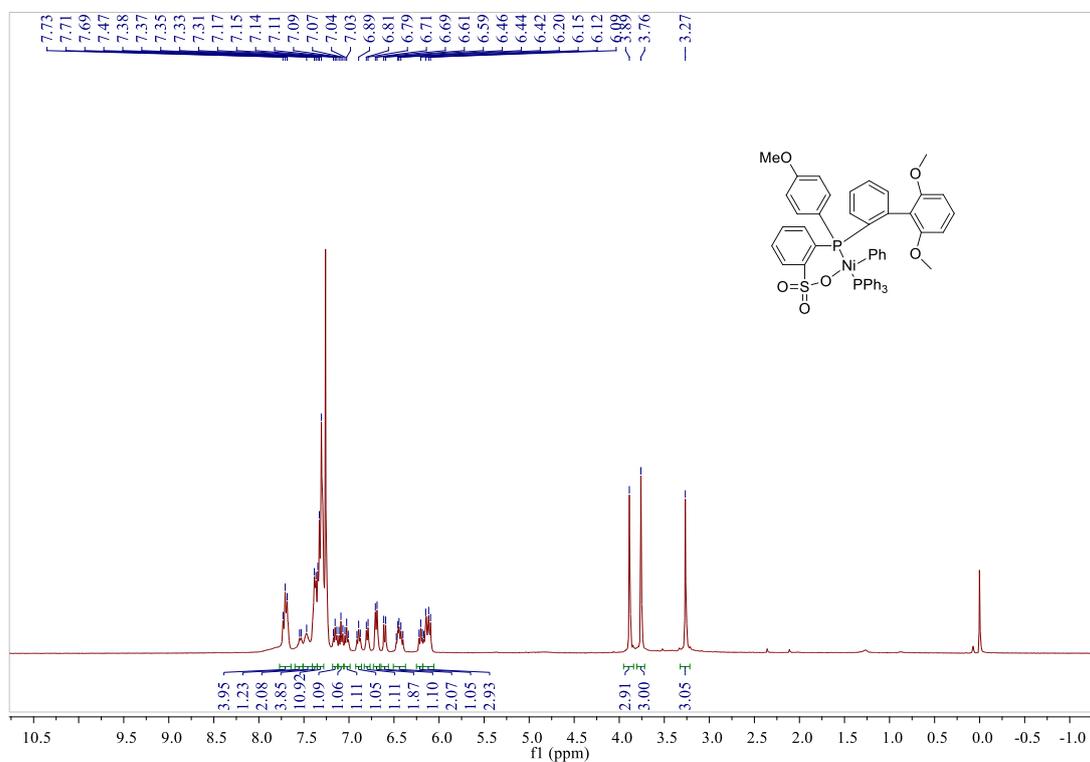


Figure S22. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of Ni-OMe.

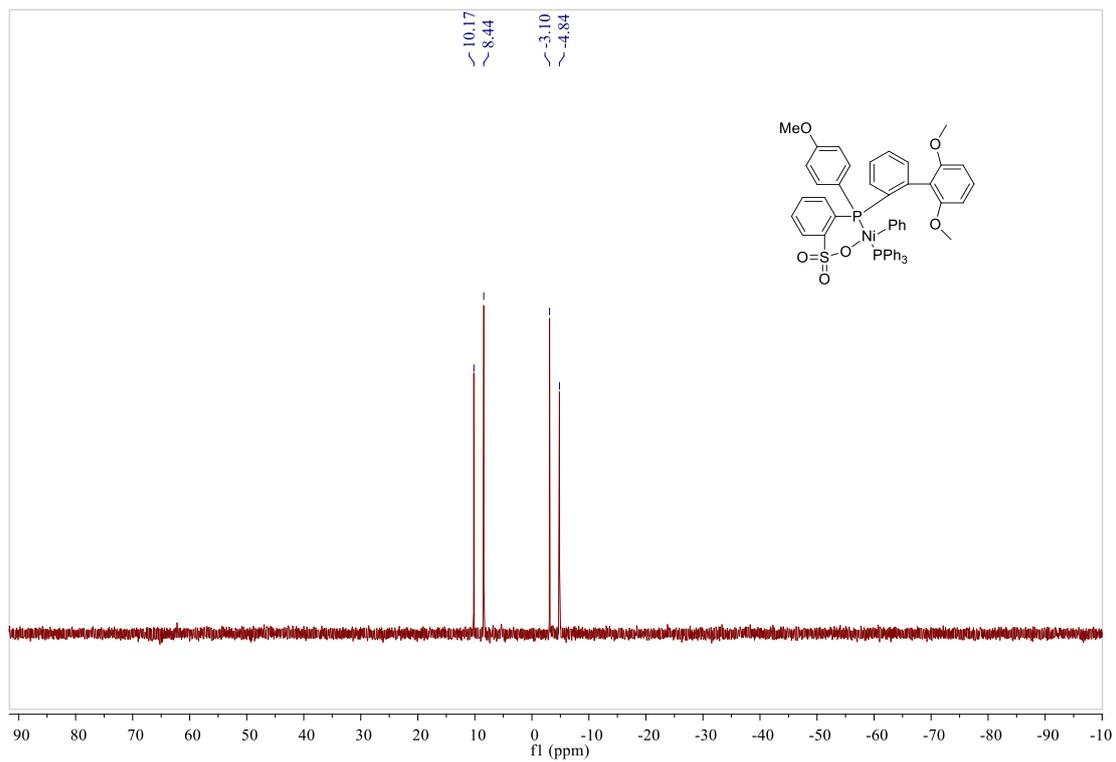


Figure S23.  $^{31}\text{P}$  NMR spectrum (CDCl<sub>3</sub>) of Ni-OMe.

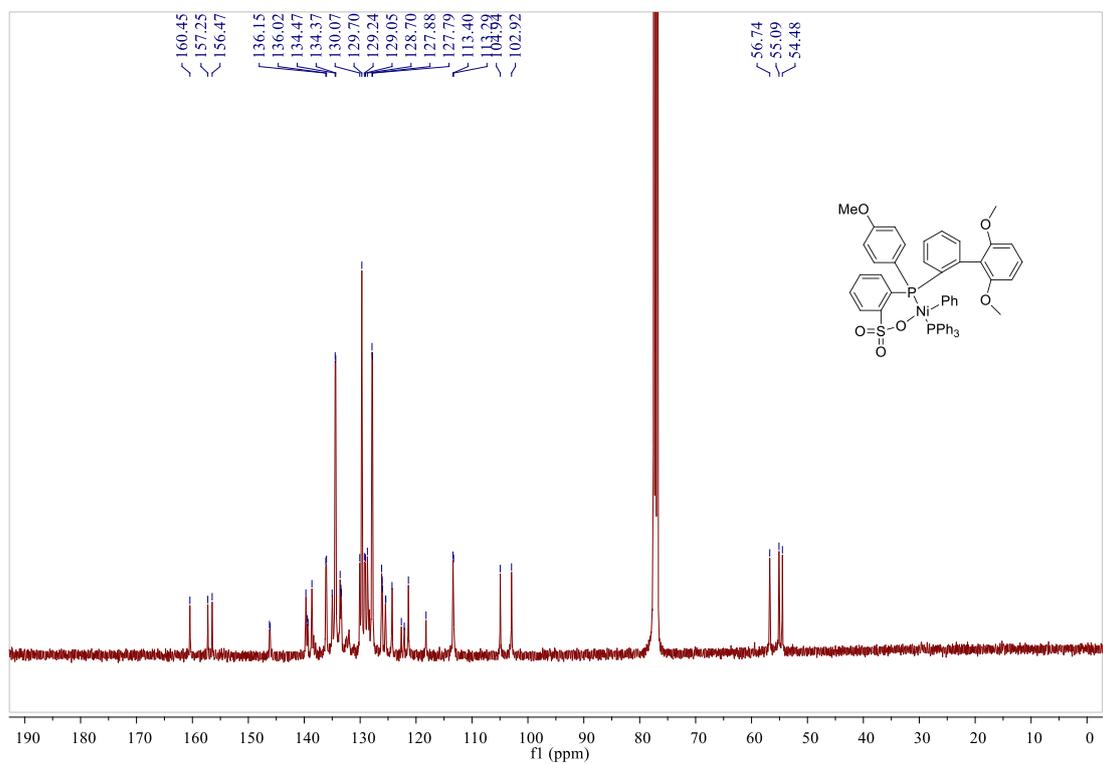


Figure S24.  $^{13}\text{C}$  NMR spectrum in CDCl<sub>3</sub> of Ni-OMe.

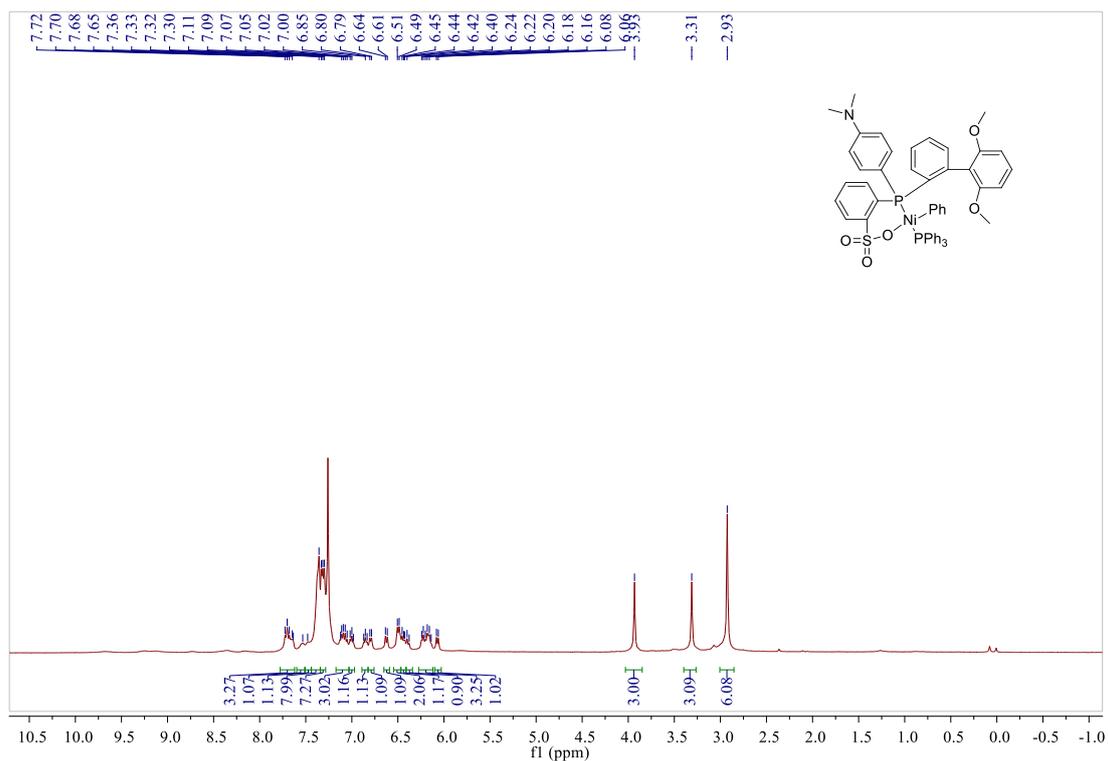


Figure S25. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of Ni-NMe<sub>2</sub>.

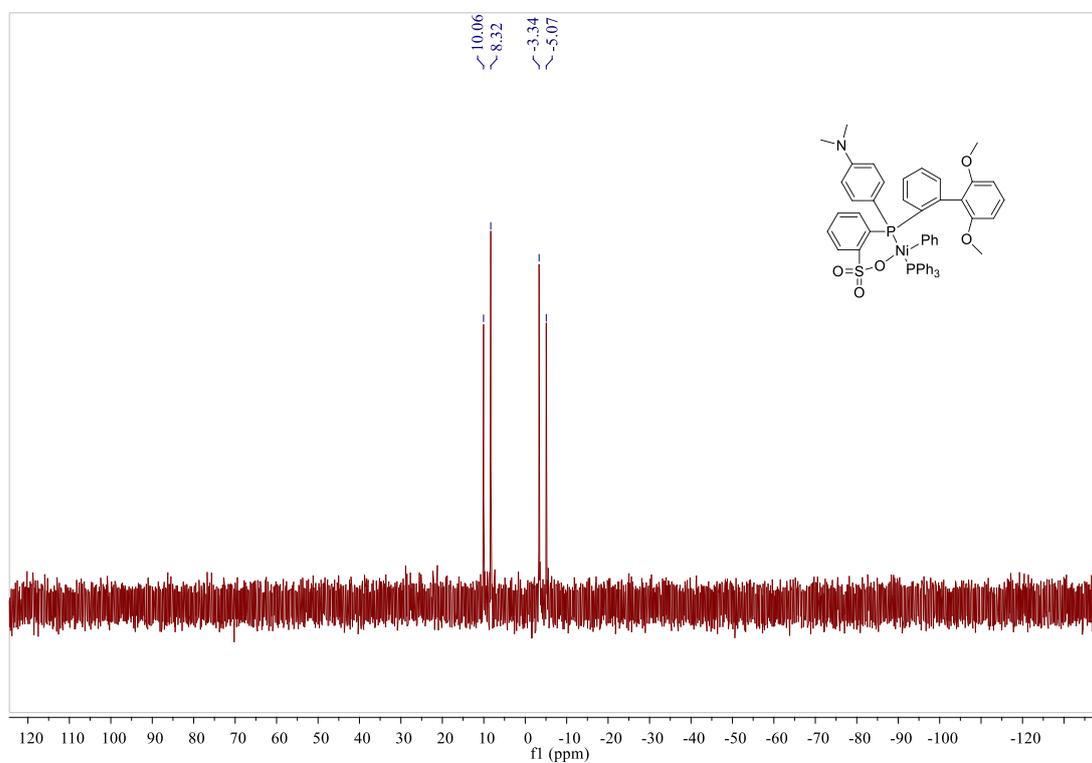


Figure S26. <sup>31</sup>P NMR spectrum (CDCl<sub>3</sub>) of Ni-NMe<sub>2</sub>.

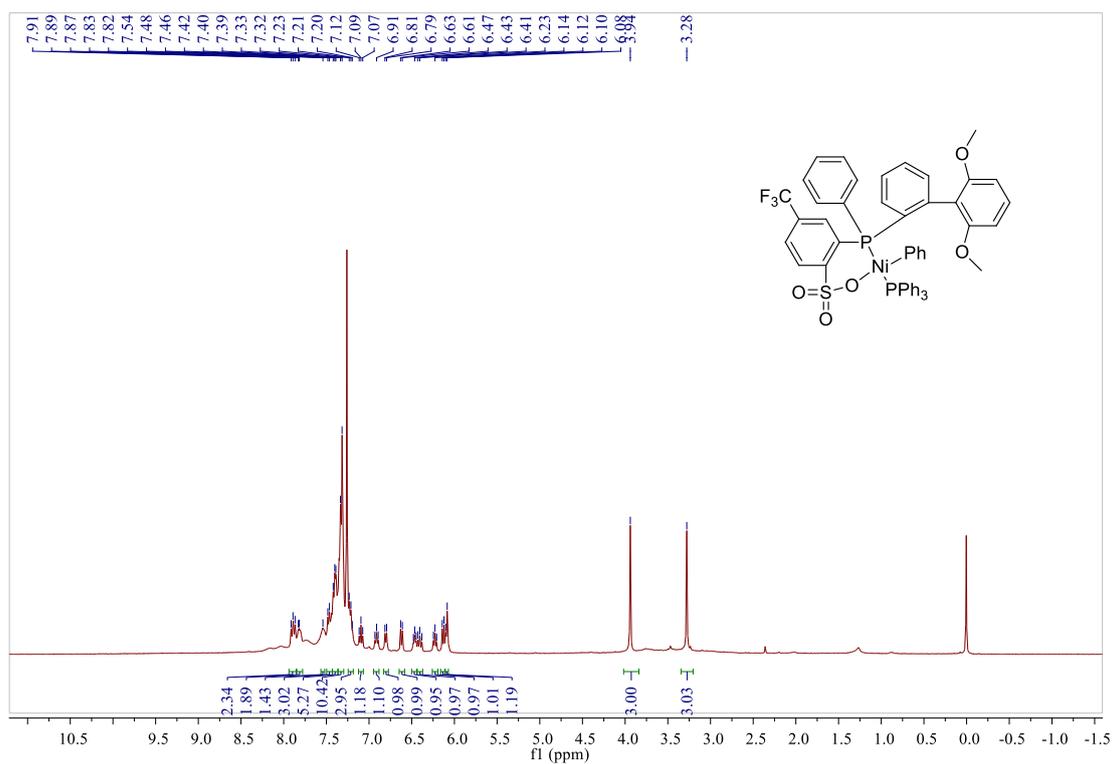


Figure S27. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of Ni-CF<sub>3</sub>'.

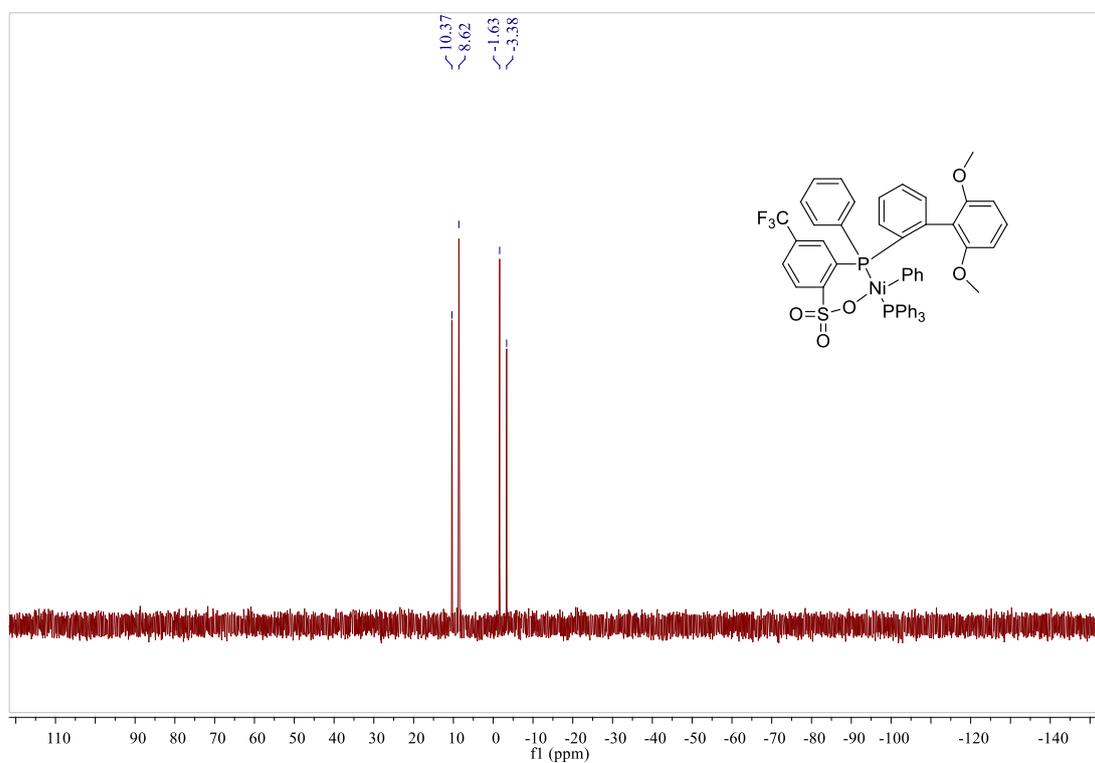
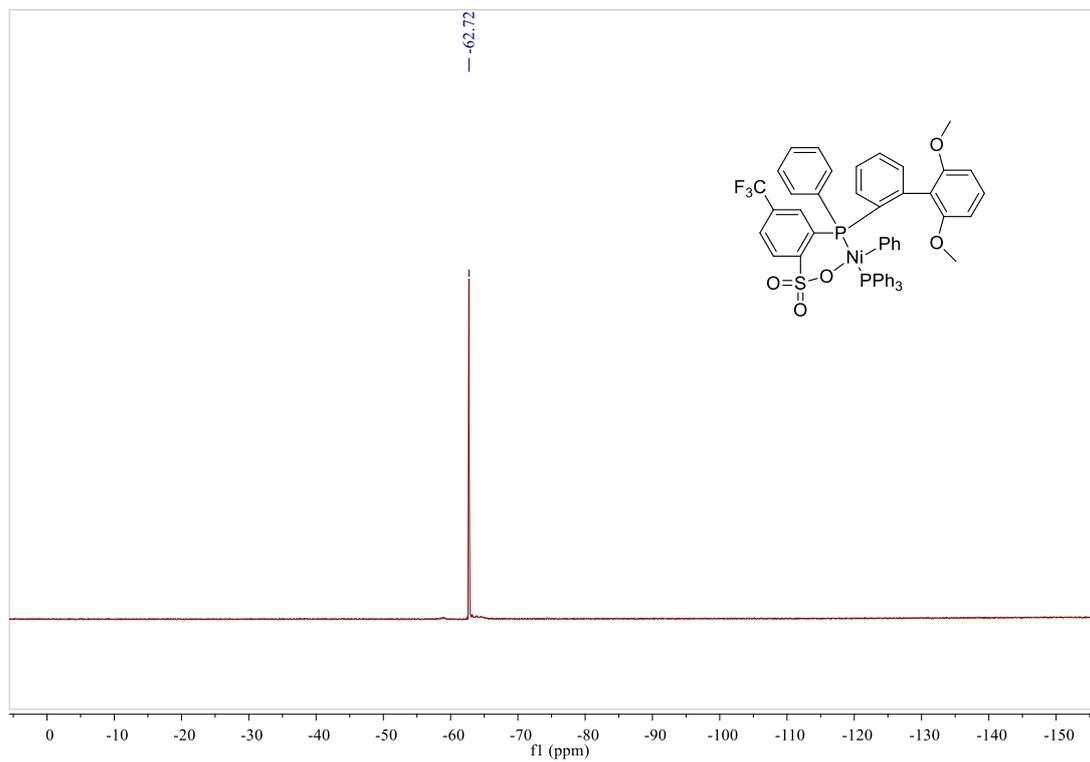
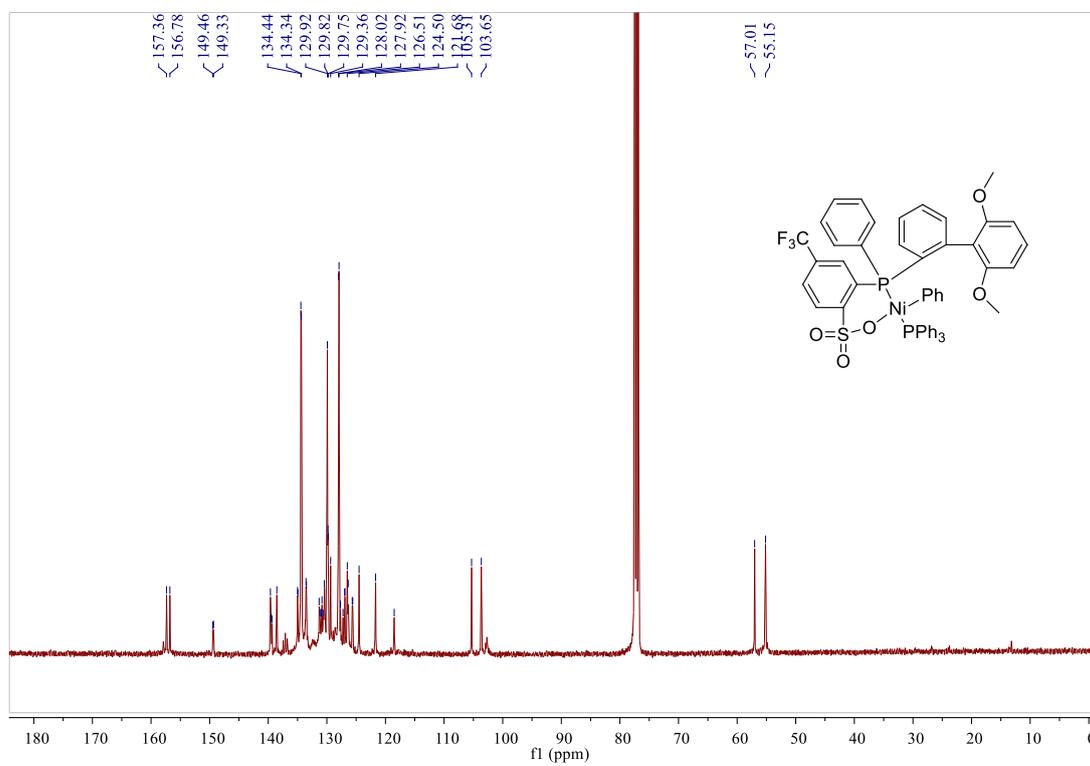


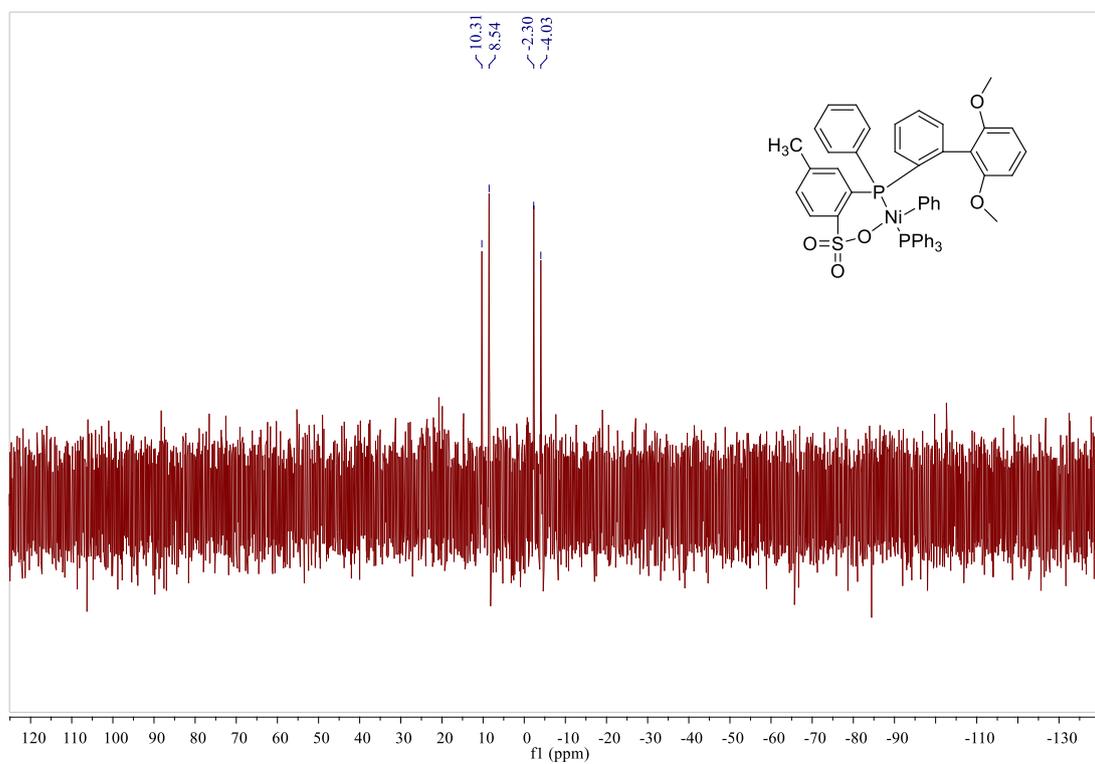
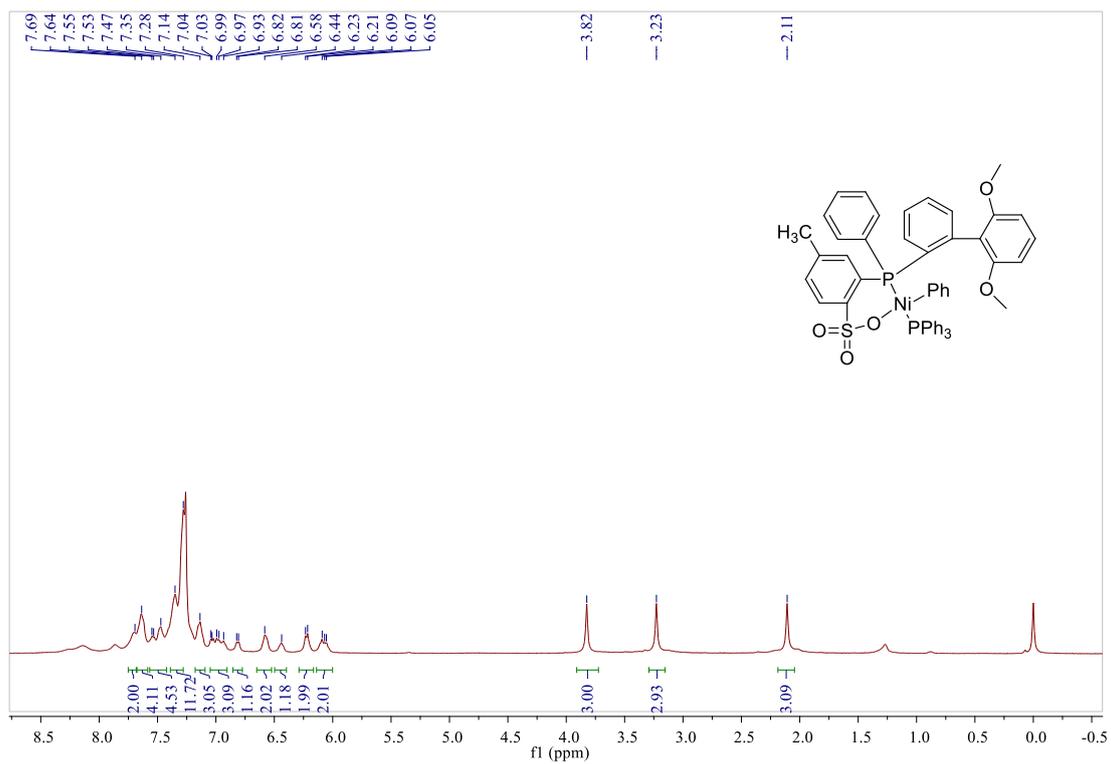
Figure S28. <sup>31</sup>P NMR spectrum (CDCl<sub>3</sub>) of Ni-CF<sub>3</sub>'.

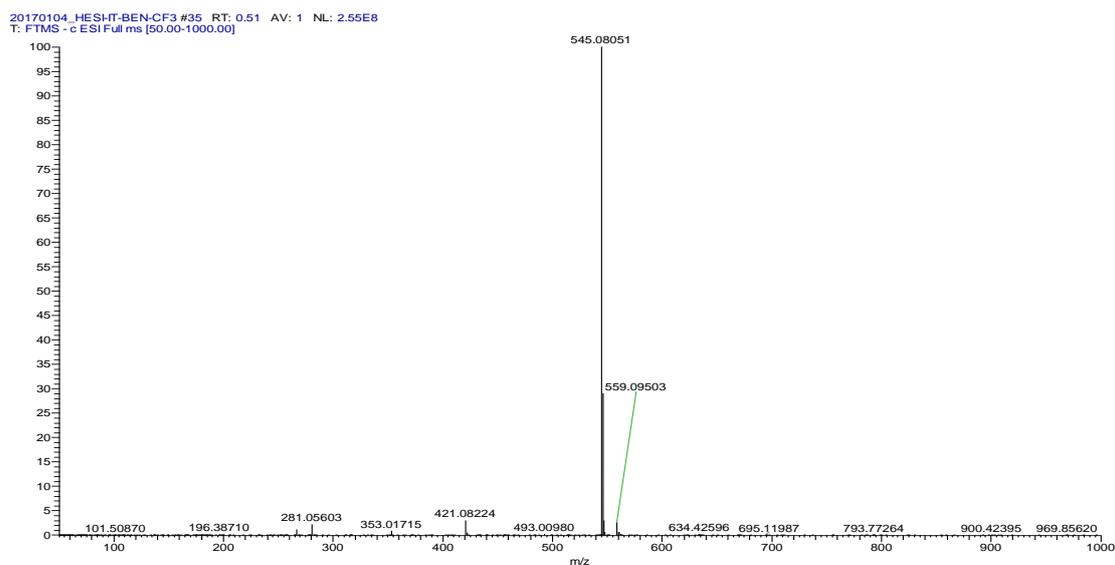


**Figure S29.**  $^{19}\text{F}$  NMR spectrum (CDCl<sub>3</sub>) of Ni-CF<sub>3</sub>'.

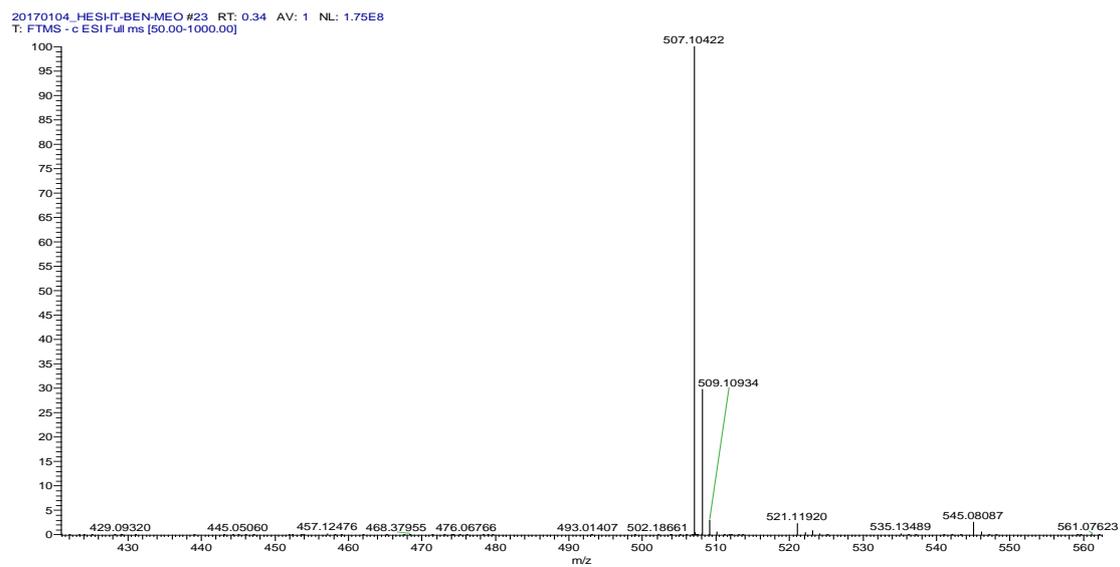


**Figure S30.**  $^{13}\text{C}$  NMR spectrum in CDCl<sub>3</sub> of Ni-CF<sub>3</sub>'.

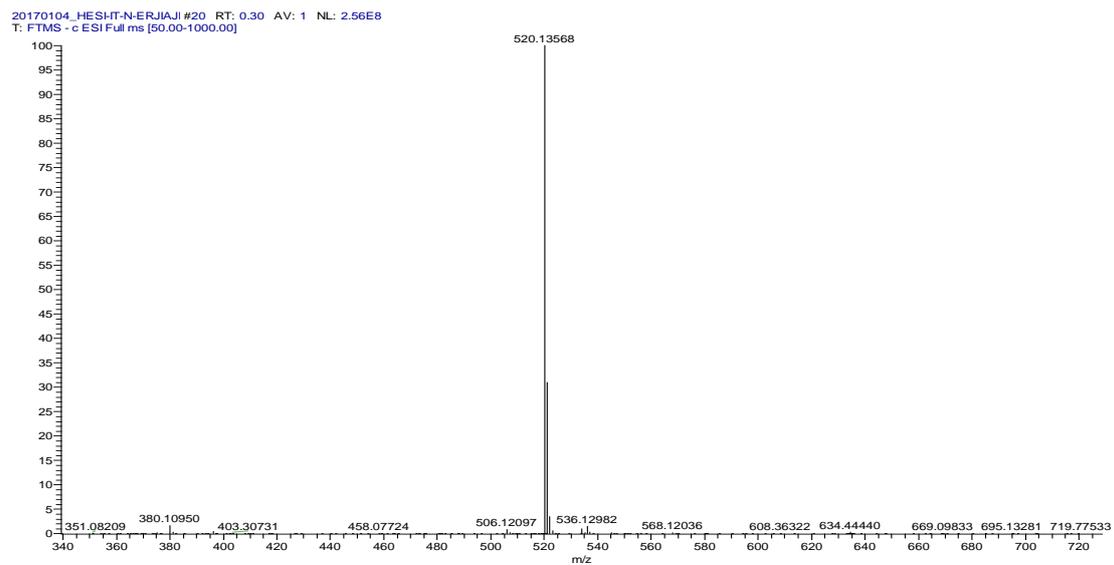




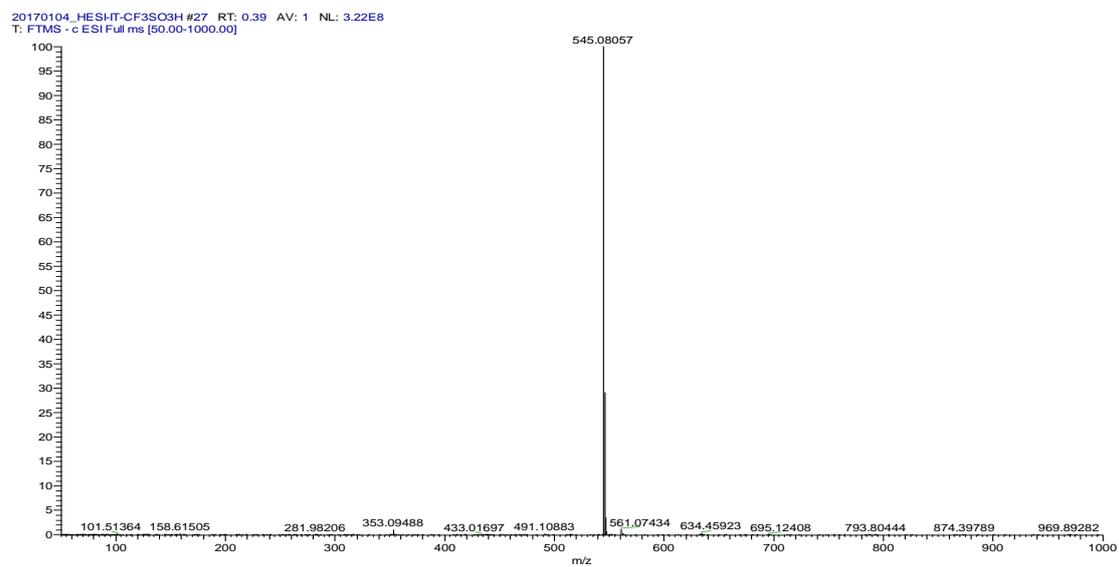
**Figure S33.** ESI-MS of L-CF<sub>3</sub>.



**Figure S34.** ESI-MS of L-OMe.



**Figure S35.** ESI-MS of L-NMe<sub>2</sub>.



**Figure S36.** ESI-MS of L-CF<sub>3</sub>'.

20170104\_HESI-CH3SO3H #30 RT: 0.44 AV: 1 NL: 4.37E7  
T: FTMS - c ESI Full ms [50.00-1000.00]

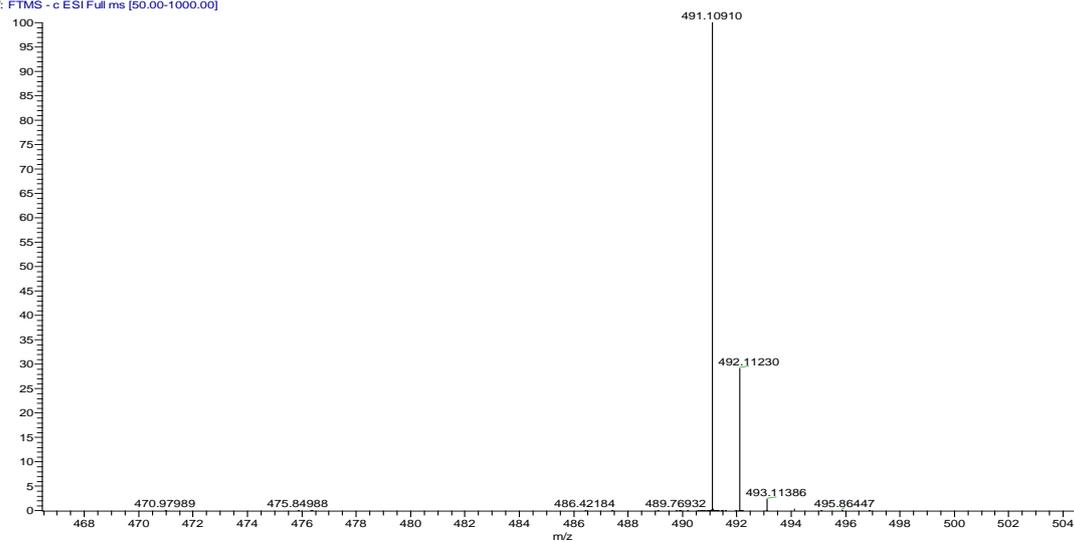


Figure S37. ESI-MS of L-Me'.

#### 4. NMR figures of (co)polymers.

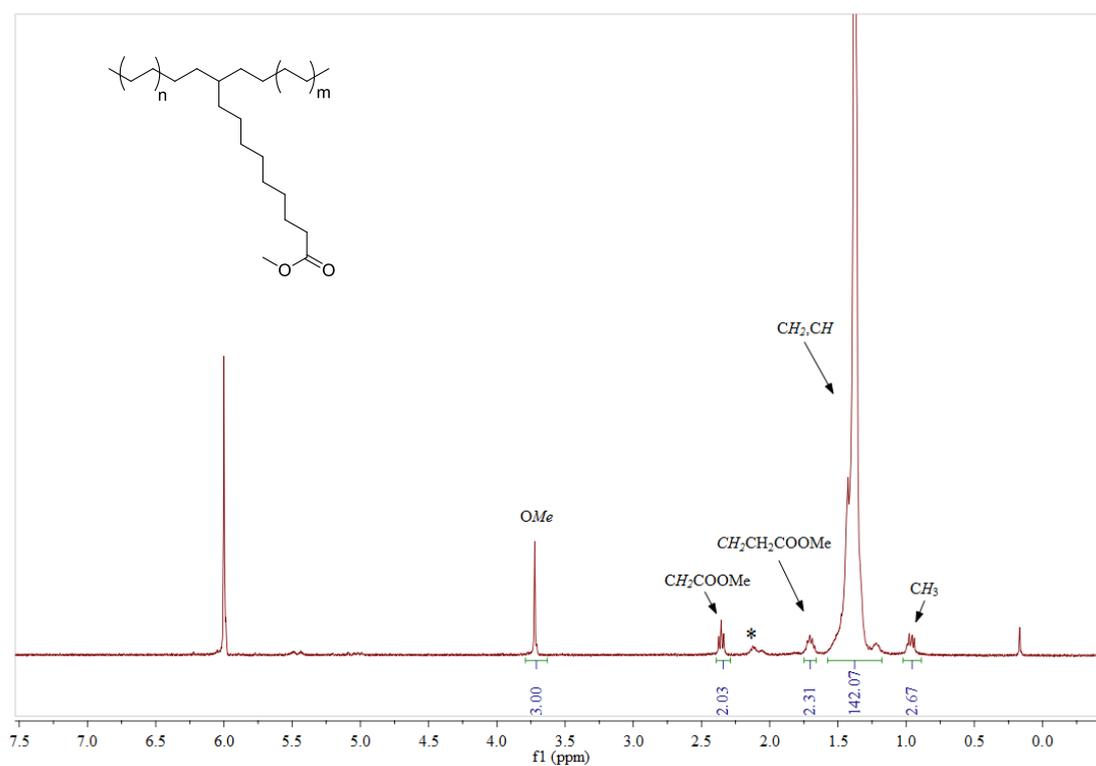
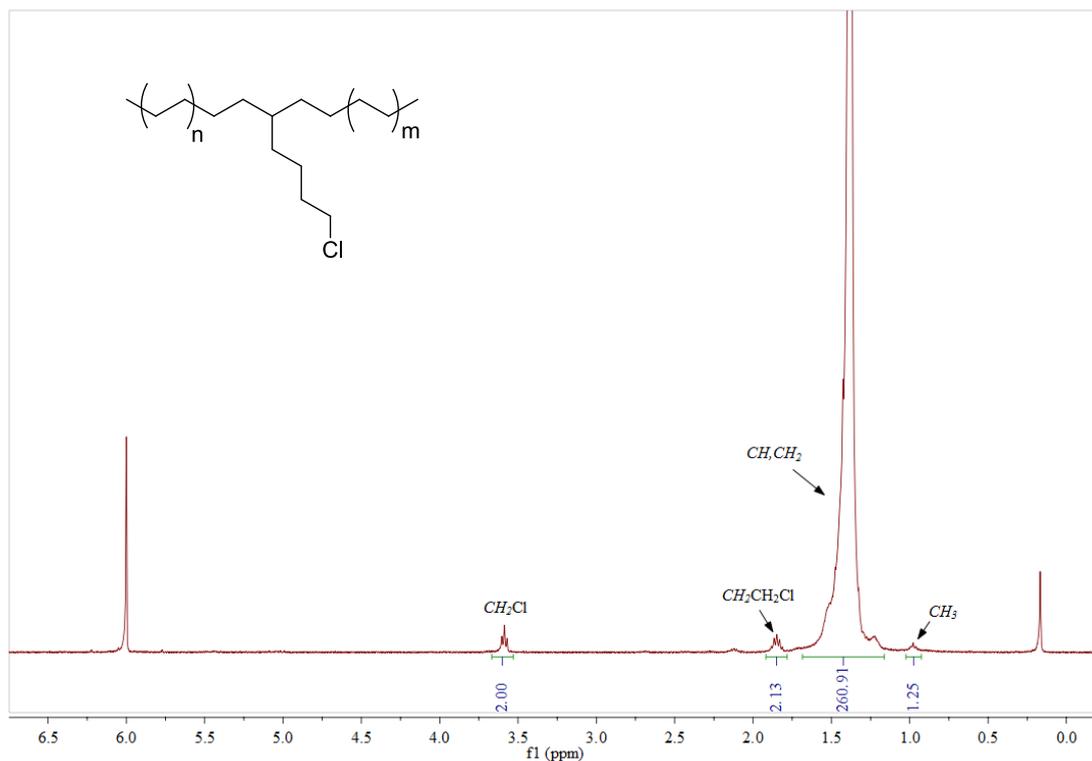


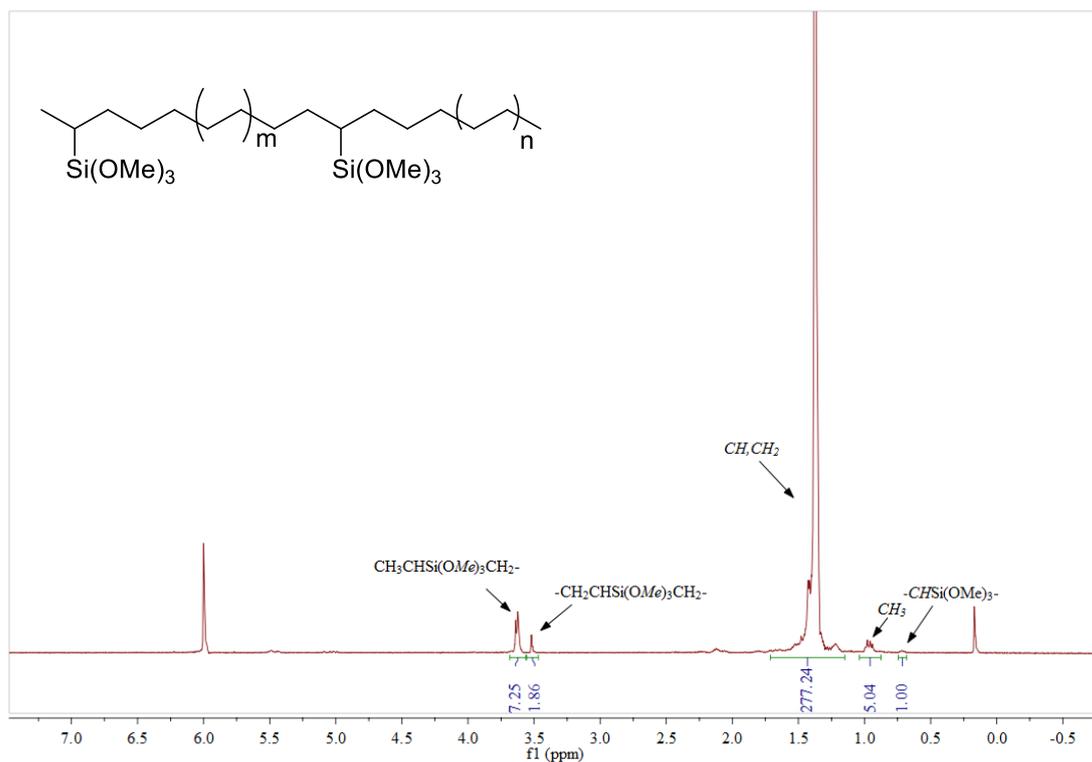
Figure S38. <sup>1</sup>H NMR spectrum of the polymer from table 2, entry 1 (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 120°C).  
\*Solvent impurity in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>.



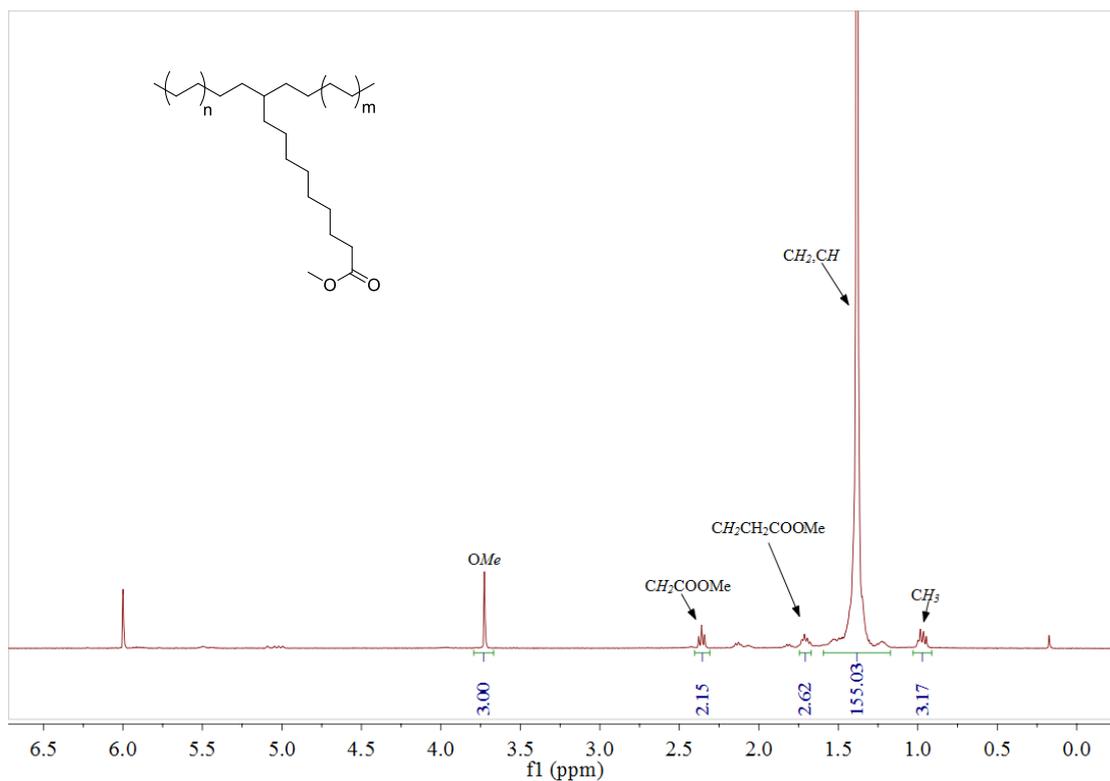




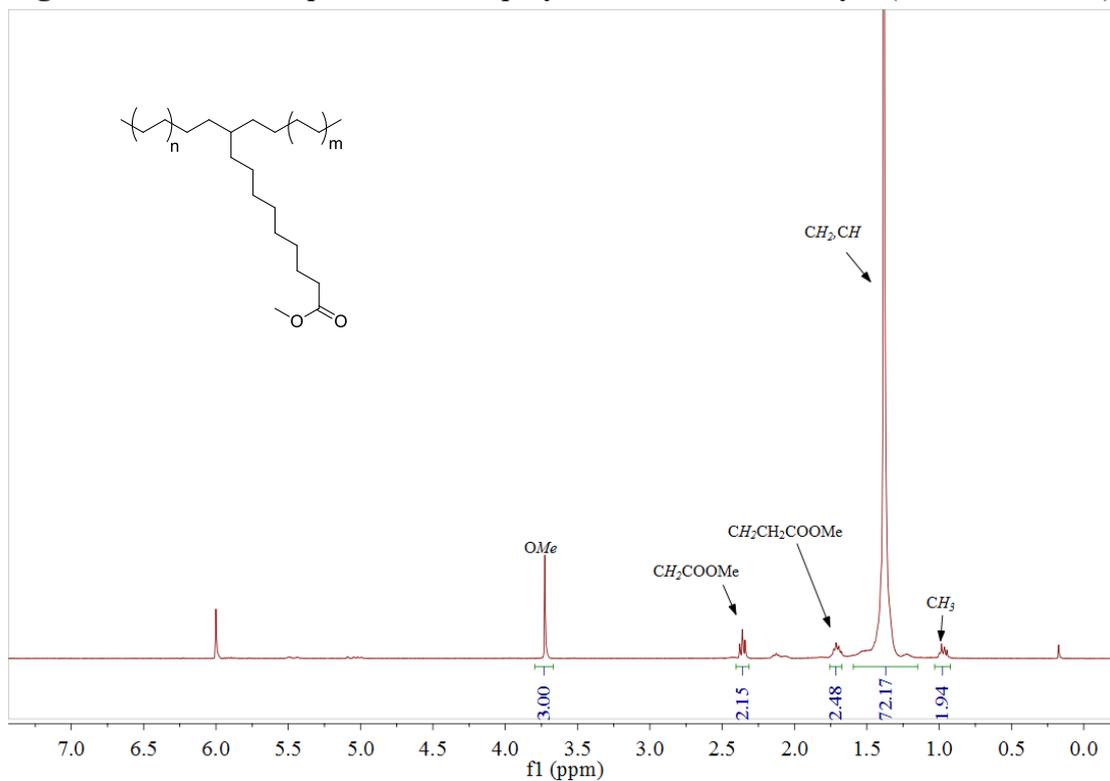
**Figure S43.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 6 ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $120^\circ\text{C}$ ).



**Figure S44.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 7 ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $120^\circ\text{C}$ ).



**Figure S45.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 9 ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $120^\circ\text{C}$ ).



**Figure S46.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 10 ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $120^\circ\text{C}$ ).

## 5. DSC data of (co)polymers.

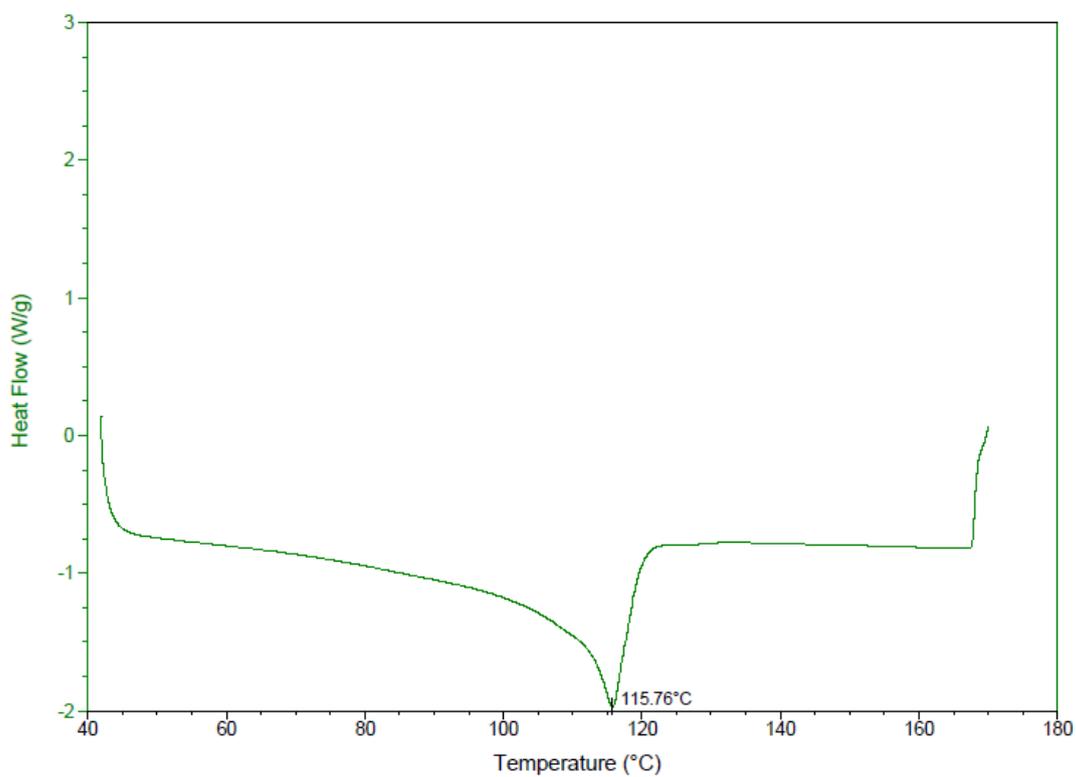


Figure S47. DSC data of the polymer from table 2, entry 1.

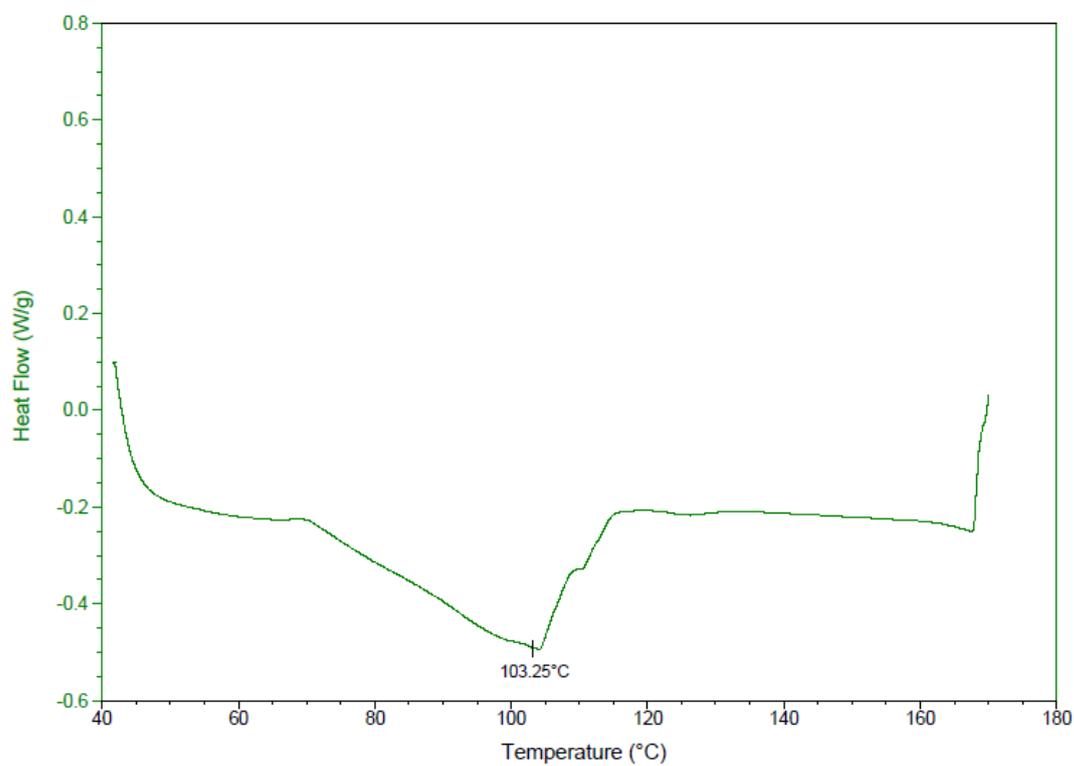
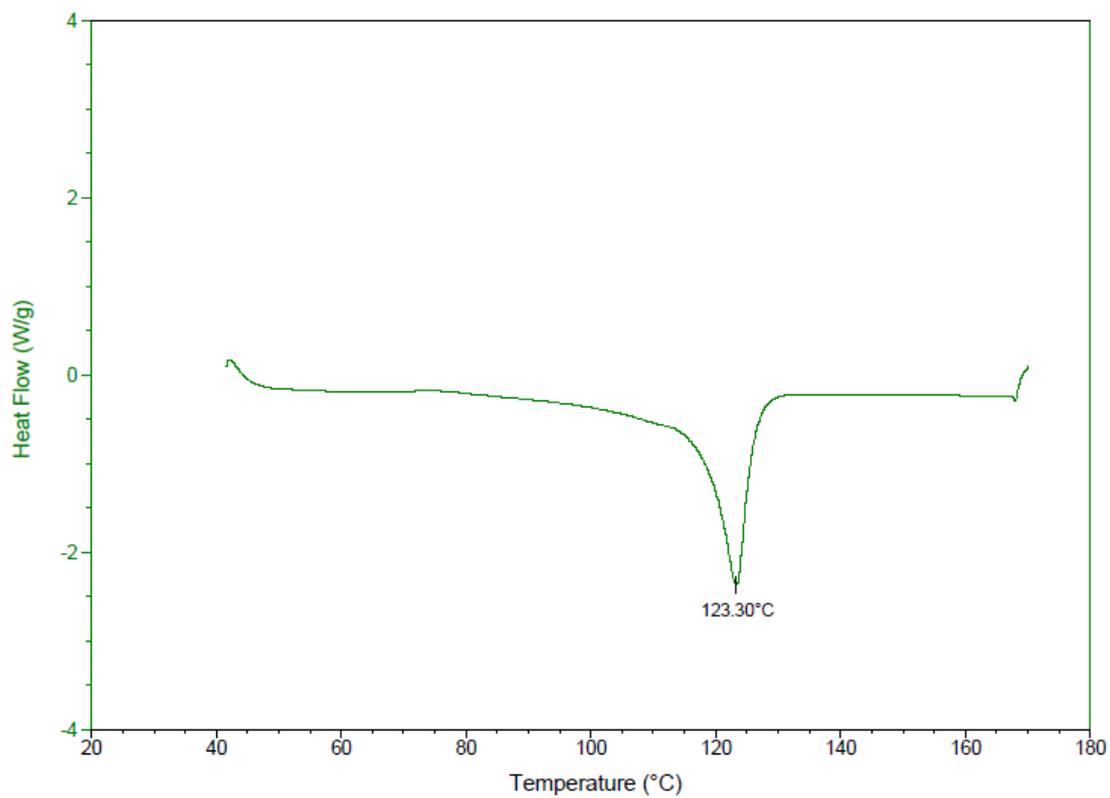
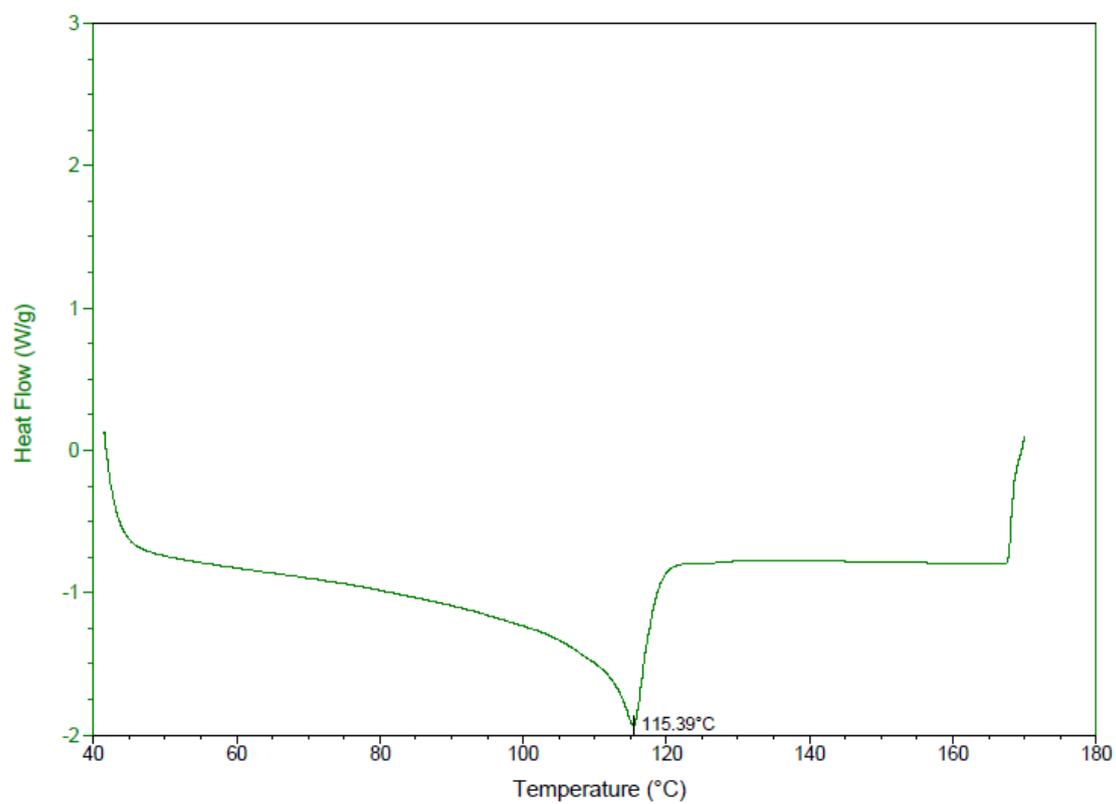


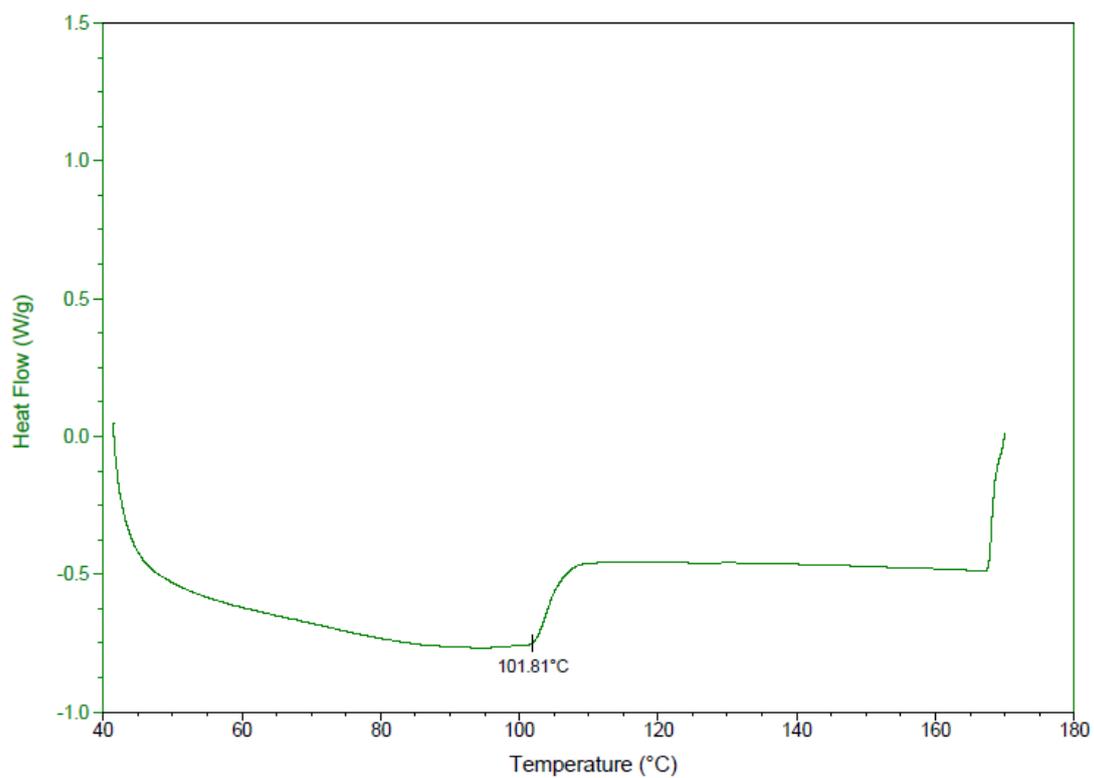
Figure S48. DSC data of the polymer from table 2, entry 2.



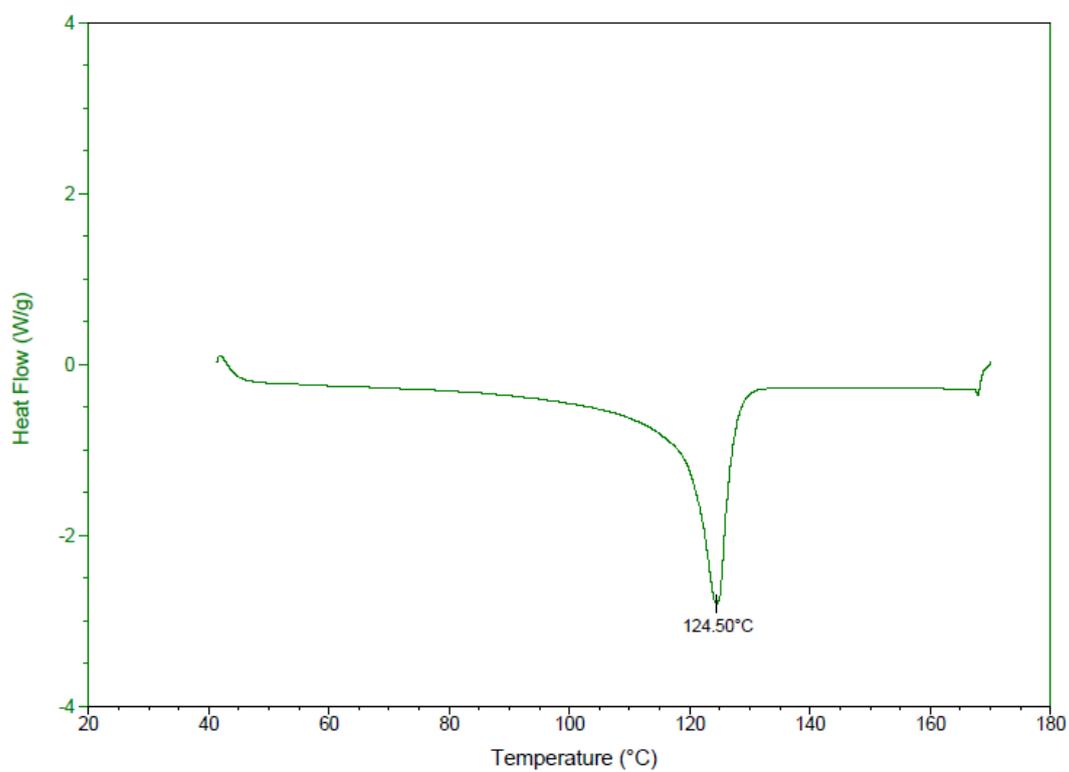
**Figure S49.** DSC data of the polymer from table 2, entry 3.



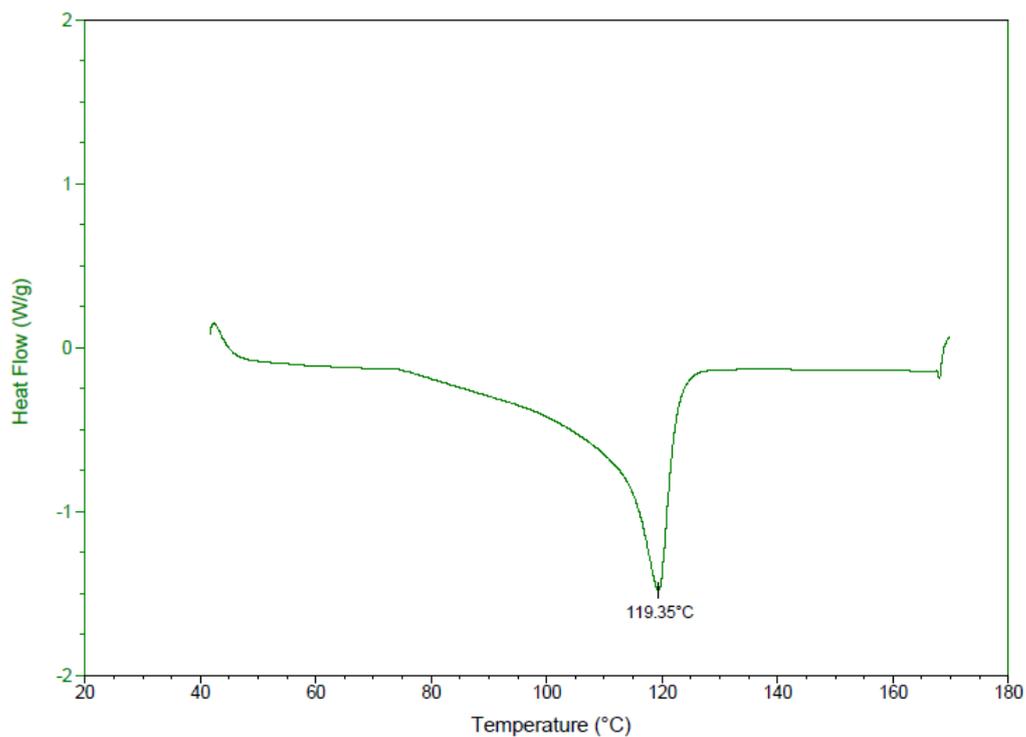
**Figure S50.** DSC data of the polymer from table 2, entry 4.



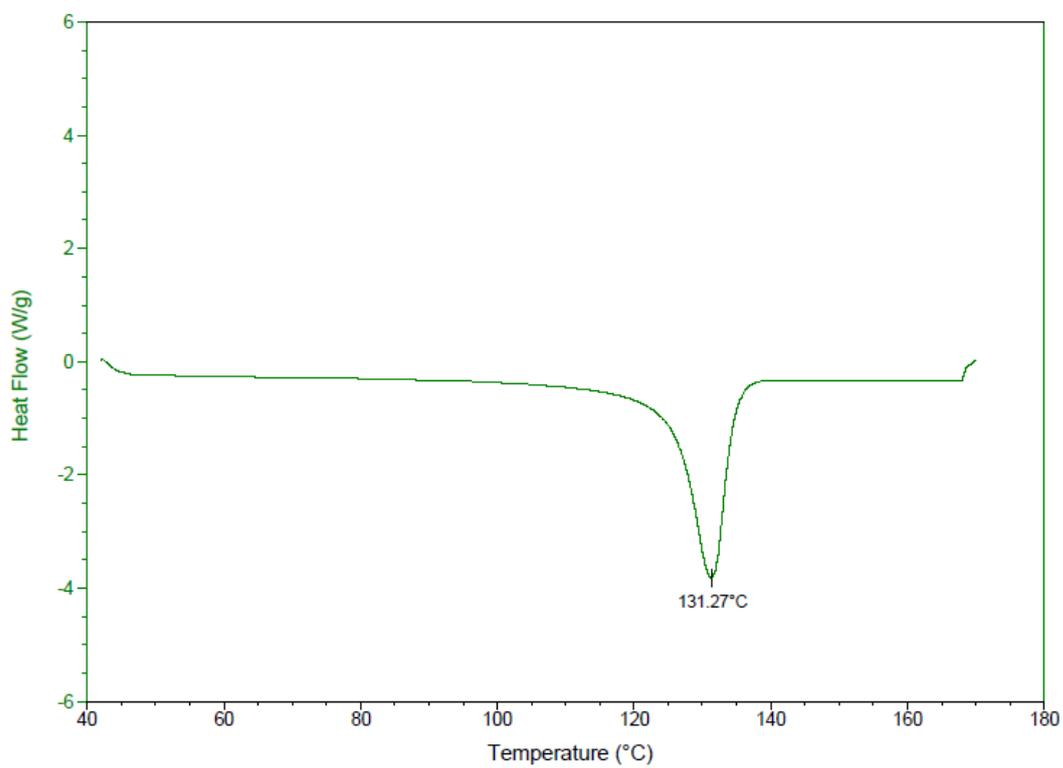
**Figure S51.** DSC data of the polymer from table 2, entry 5.



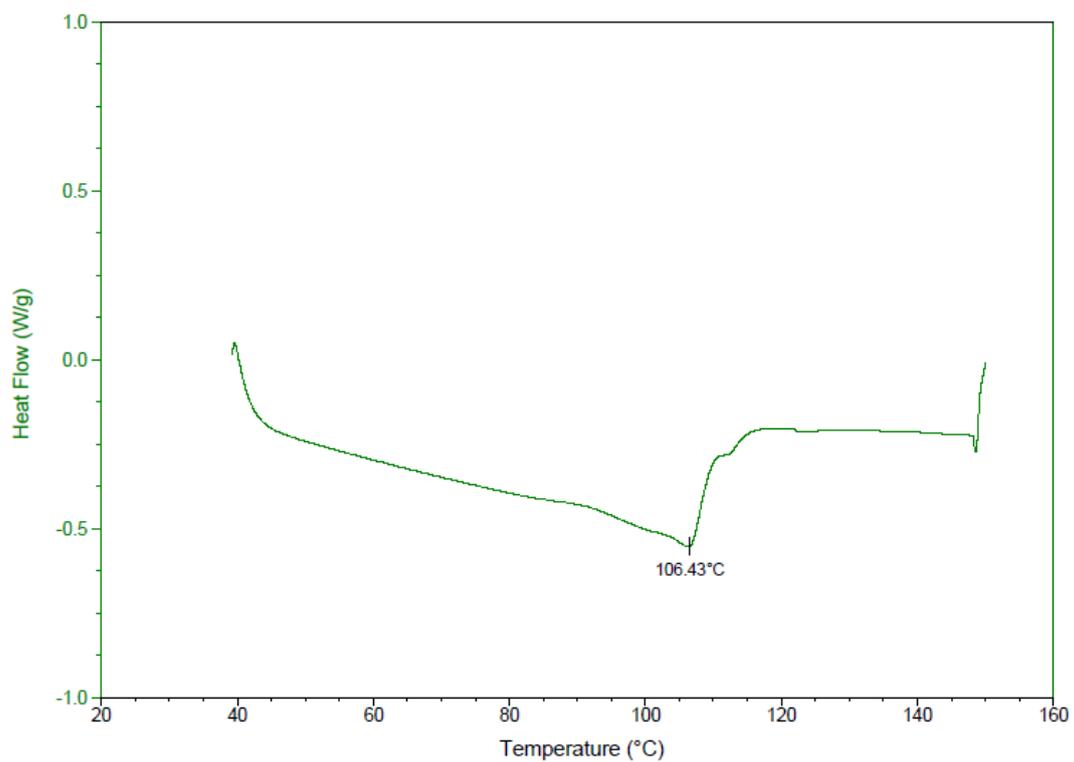
**Figure S52.** DSC data of the polymer from table 2, entry 6.



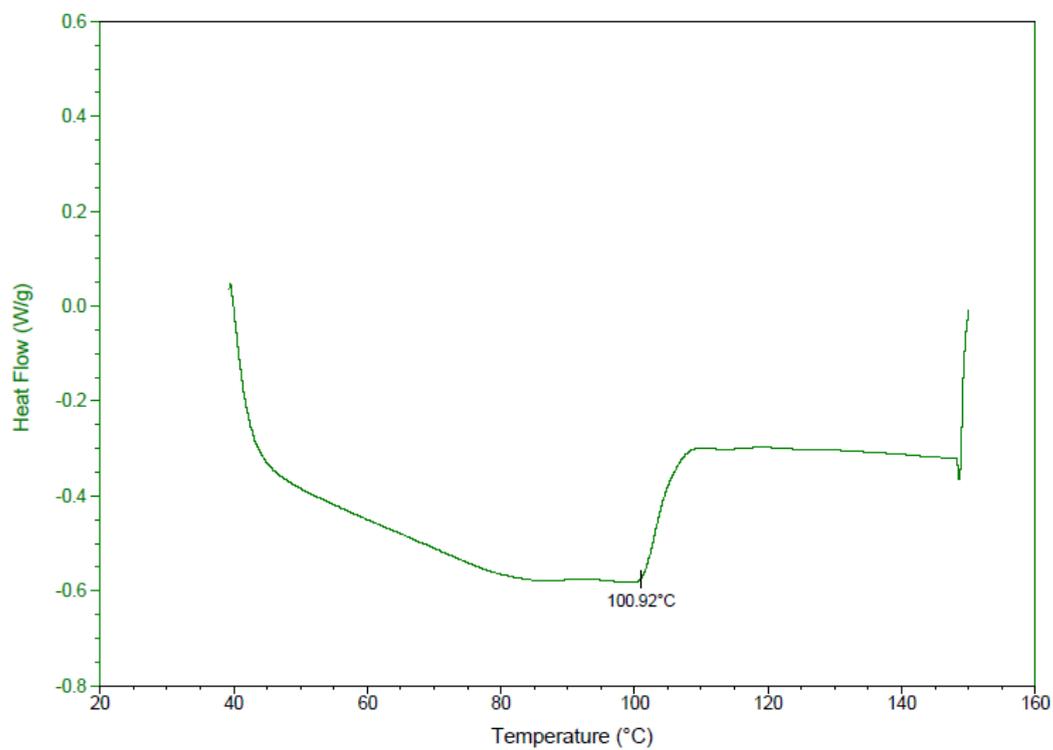
**Figure S53.** DSC data of the polymer from table 2, entry 7.



**Figure S54.** DSC data of the polymer from table 2, entry 8.

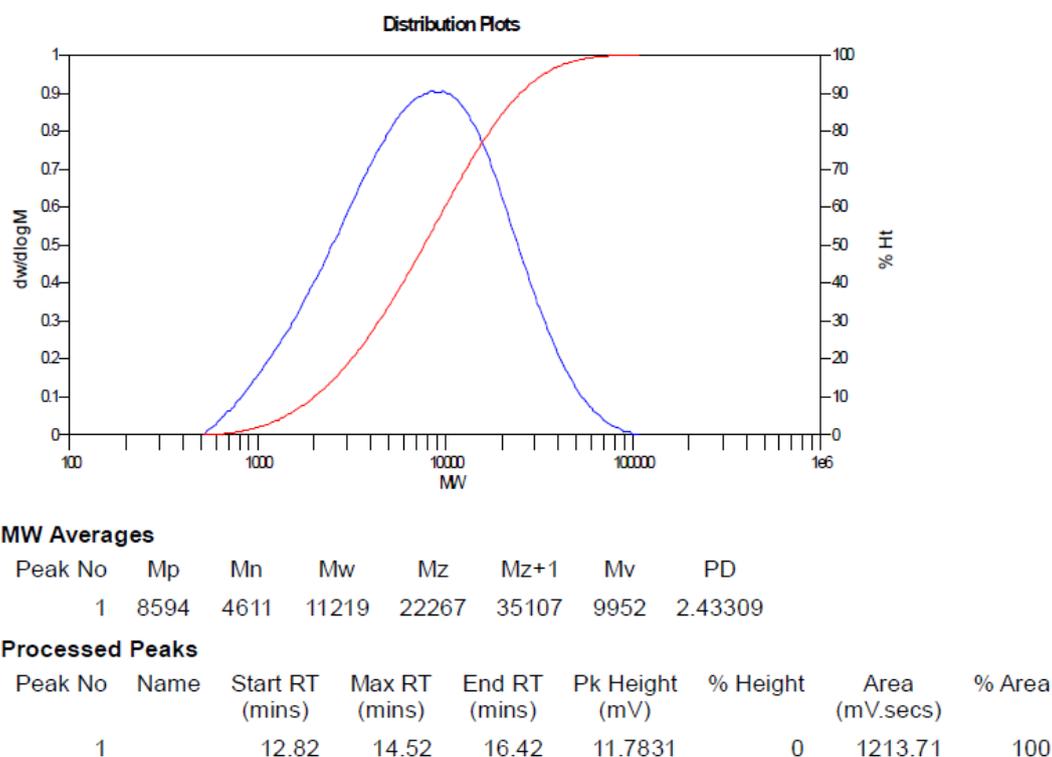


**Figure S55.** DSC data of the polymer from table 2, entry 9.

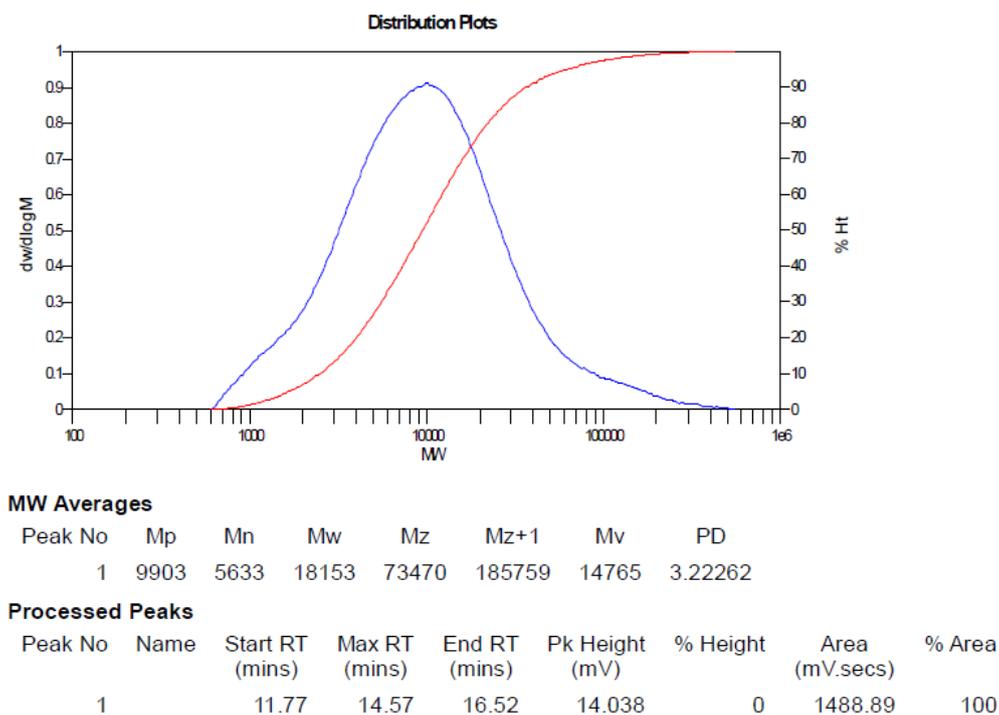


**Figure S56.** DSC data of the polymer from table 2, entry 10.

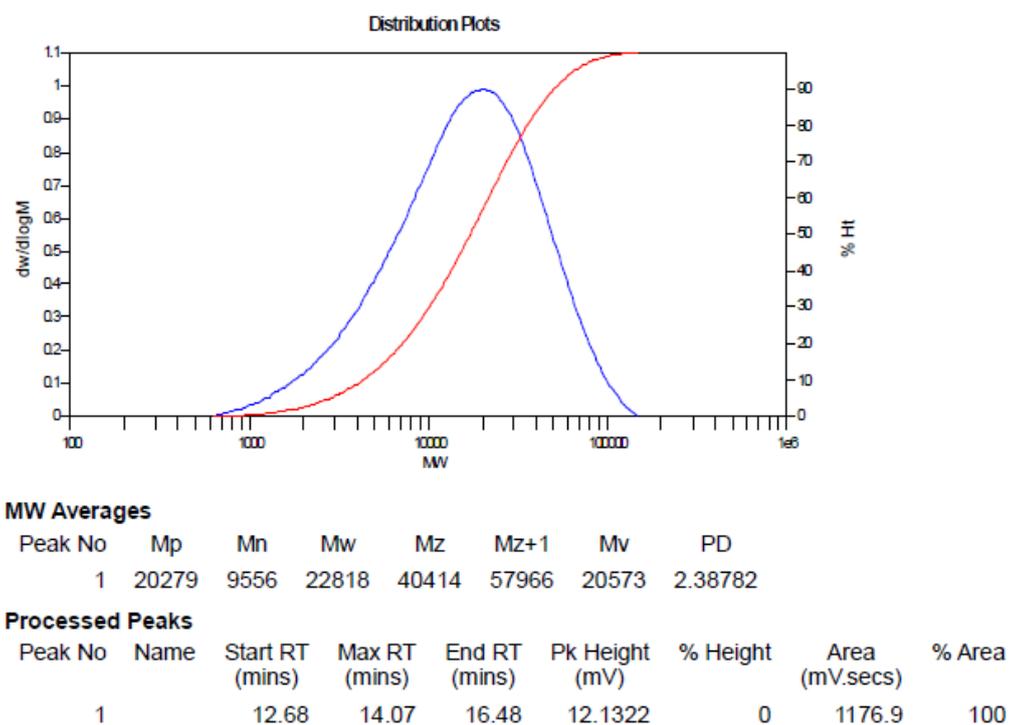
## 6. GPC data of (co)polymers.



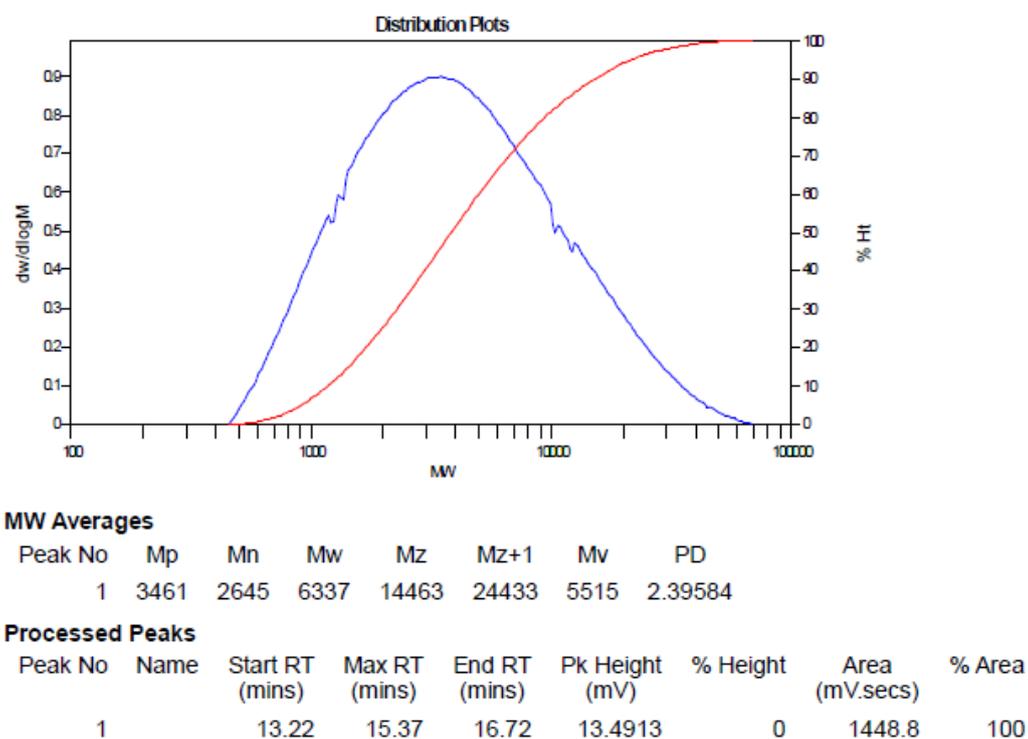
**Figure S57.** GPC data of the polymer from table 1, entry 1.



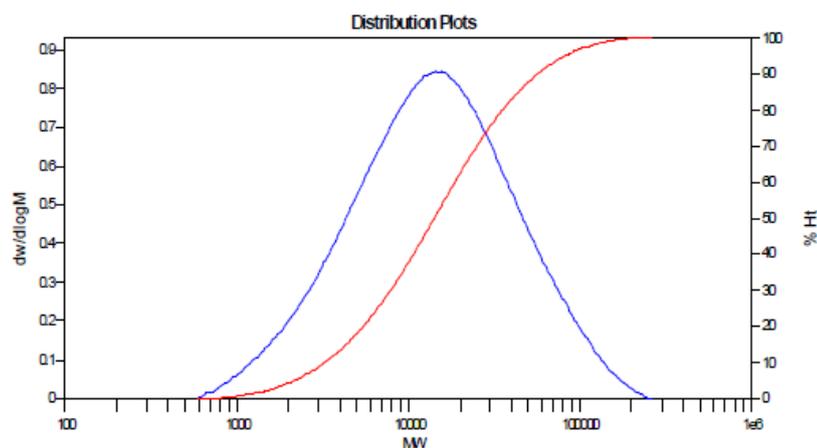
**Figure S58.** GPC data of the polymer from table 1, entry 2.



**Figure S59.** GPC data of the polymer from table 1, entry 3.



**Figure S60.** GPC data of the polymer from table 1, entry 4.



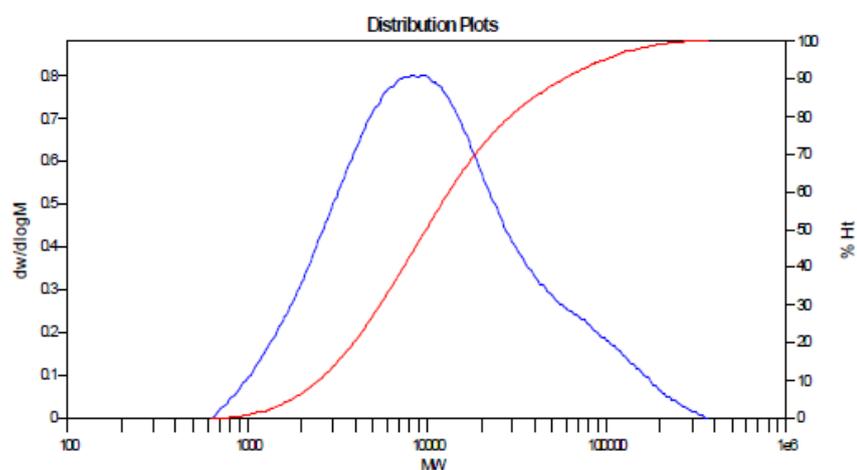
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14514	7626	23547	55908	93666	20194	3.08773

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.28	14.30	16.53	11.5761	0	1321.49	100

**Figure S61.** GPC data of the polymer from table 1, entry 5.



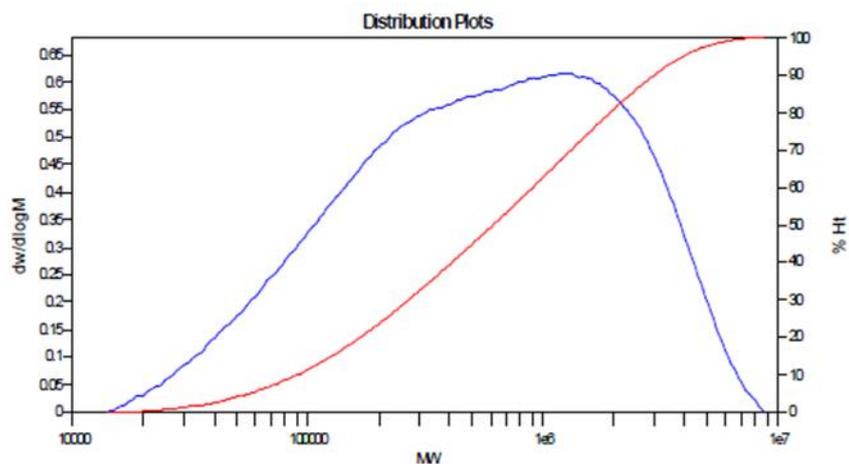
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9441	5895	22460	78772	145293	17946	3.81001

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.05	14.77	16.48	7.71434	0	933.47	100

**Figure S62.** GPC data of the polymer from table 1, entry 6.



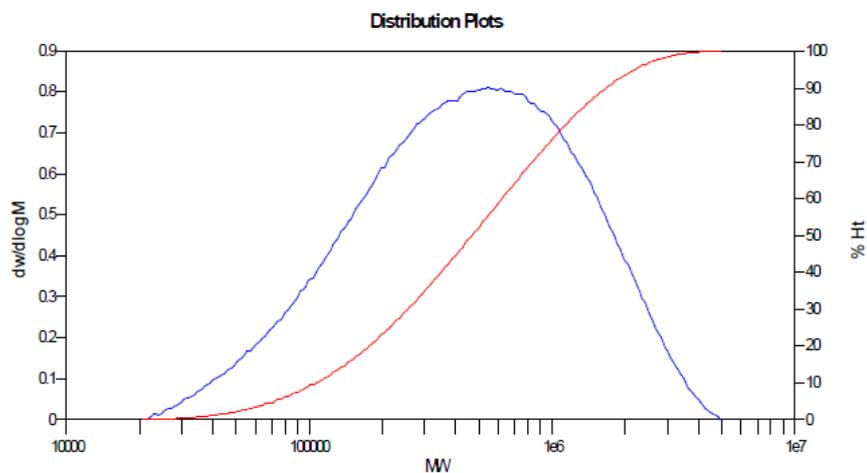
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1259949	232719	1116081	2594398	3758143	928824	4.79583

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.25	11.60	14.57	7.75534	0	1169.42	100

Figure S63. GPC data of the polymer from table 1, entry 7.



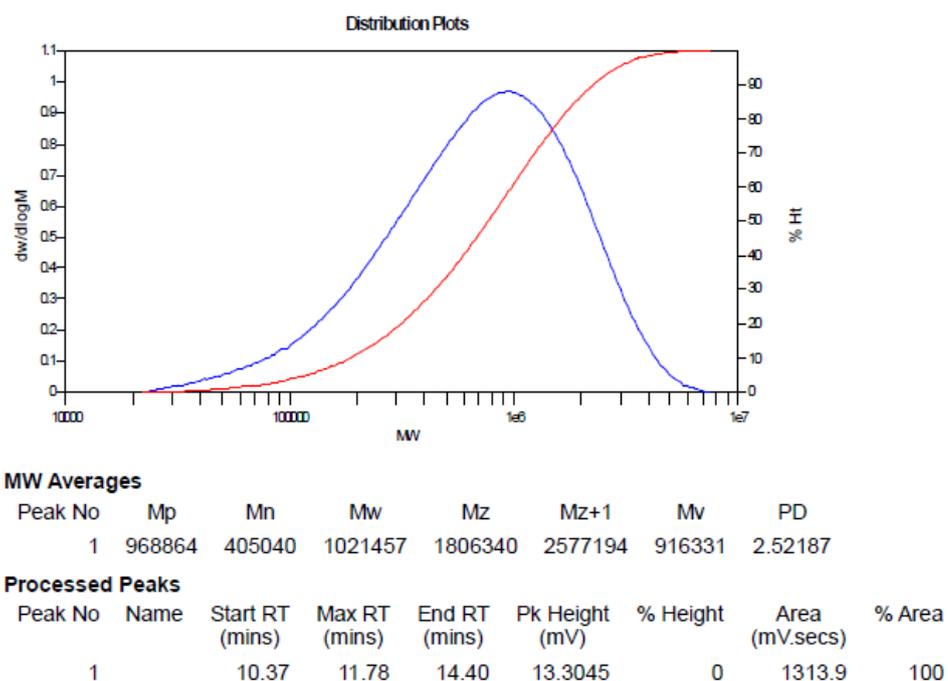
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	544228	250446	704554	1396877	2042496	616630	2.8132

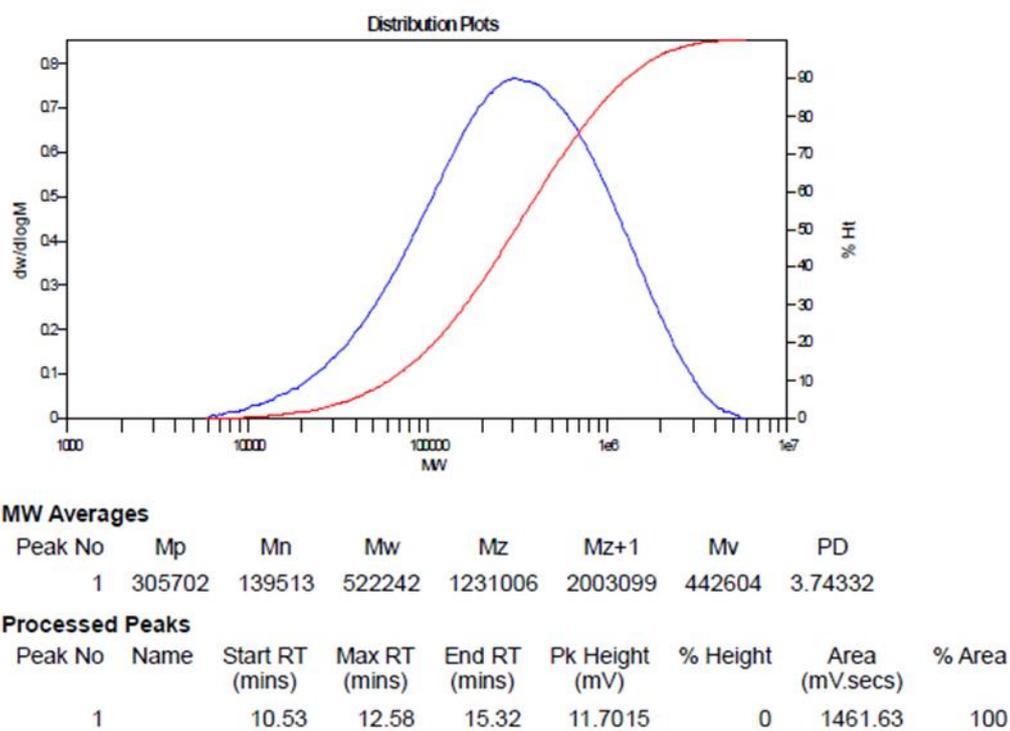
**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.65	12.18	14.45	5.36136	0	633.453	100

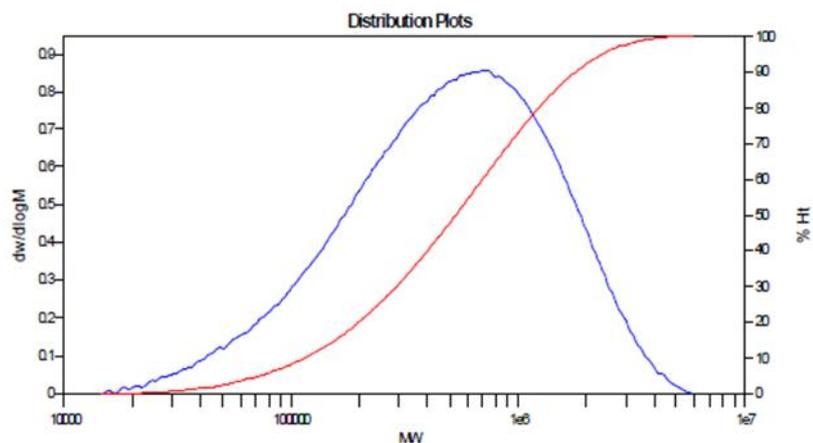
Figure S64. GPC data of the polymer from table 1, entry 8.



**Figure S65.** GPC data of the polymer from table 1, entry 9.



**Figure S66.** GPC data of the polymer from table 1, entry 10.



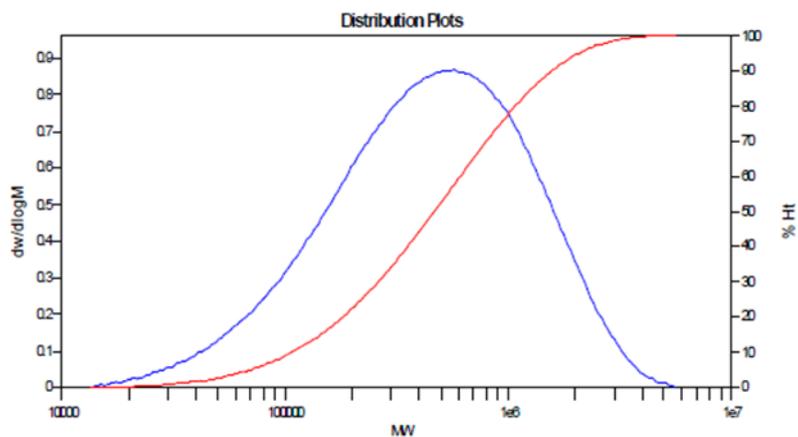
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	708900	262111	768450	1495872	2205896	675228	2.93177

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.53	12.00	14.70	7.39751	0	828.088	100

Figure S67. GPC data of the polymer from table 1, entry 11.



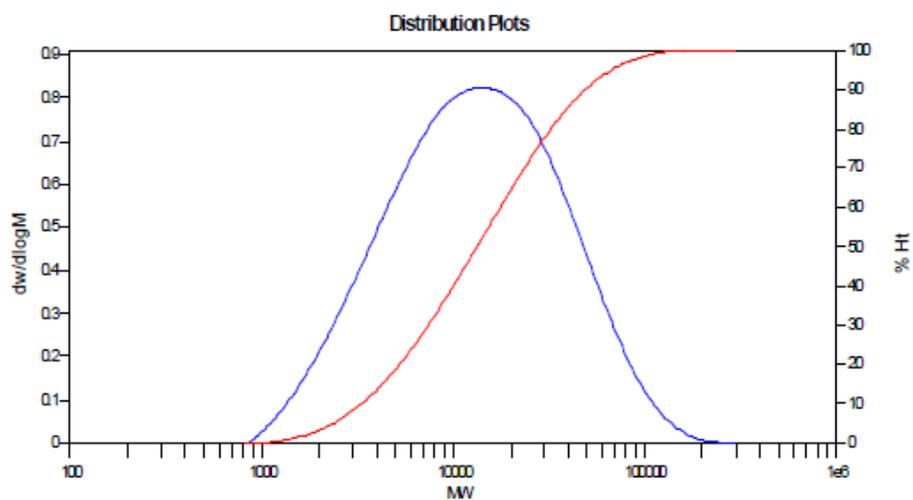
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	571024	243195	677258	1323071	1985785	596258	2.78484

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.57	12.15	14.75	10.865	0	1200.04	100

Figure S68. GPC data of the polymer from table 1, entry 12.



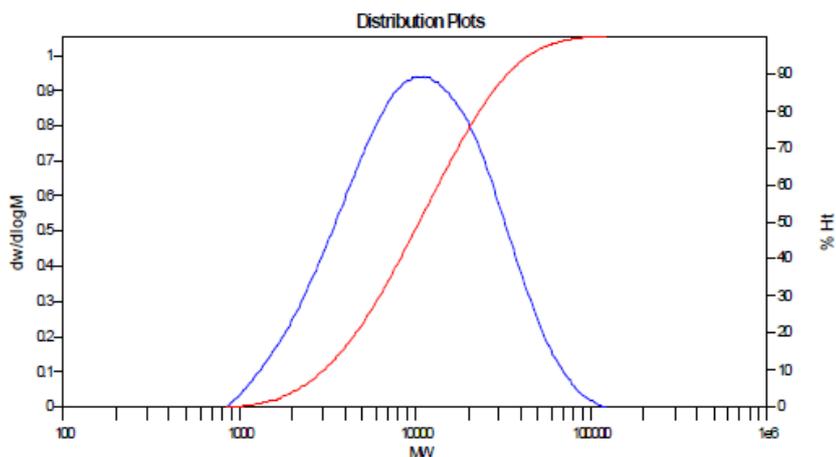
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14093	7837	20982	45682	75311	18210	2.6773

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.52	14.58	16.48	20.9544	0	2360.89	100

Figure S69. GPC data of the polymer from table 2, entry 1.



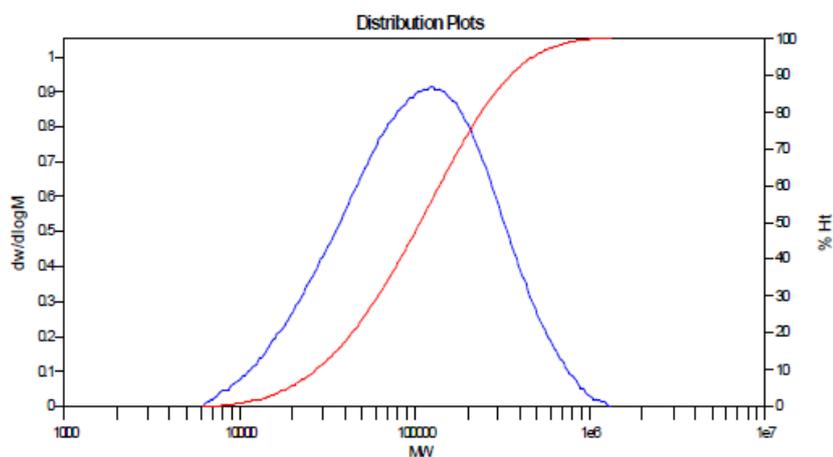
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	10726	6785	14986	28075	42420	13385	2.2087

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.12	14.78	16.45	10.9968	0	1087.91	100

Figure S70. GPC data of the polymer from table 2, entry 2.



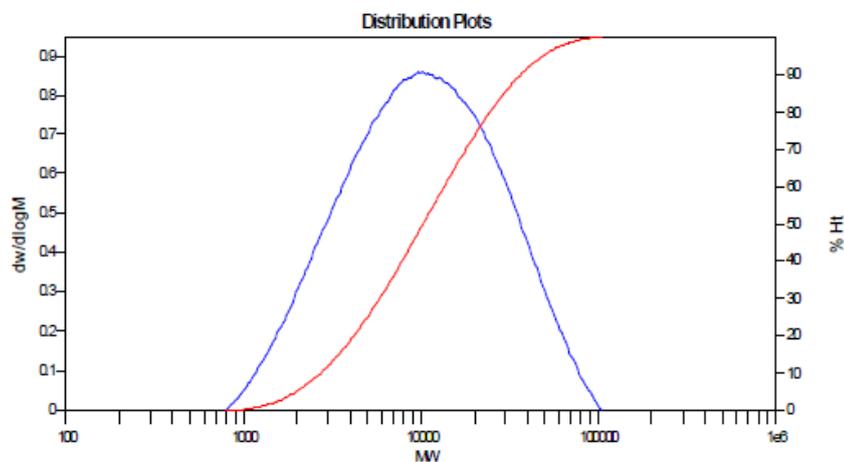
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	125239	62798	155265	305322	472241	137219	2.47245

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.52	13.10	15.12	6.60059	0	669.34	100

Figure S71. GPC data of the polymer from table 2, entry 3.



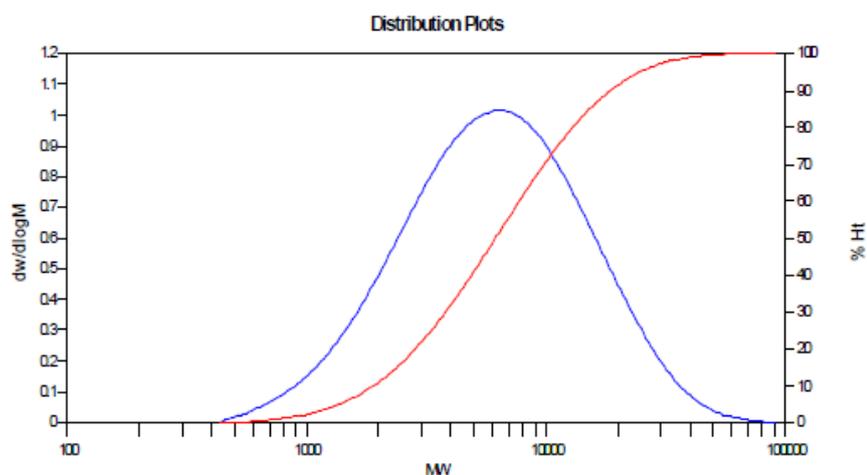
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	10206	6343	15449	30271	44721	13618	2.4356

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.22	14.82	16.50	6.25848	0	676.887	100

Figure S72. GPC data of the polymer from table 2, entry 4.



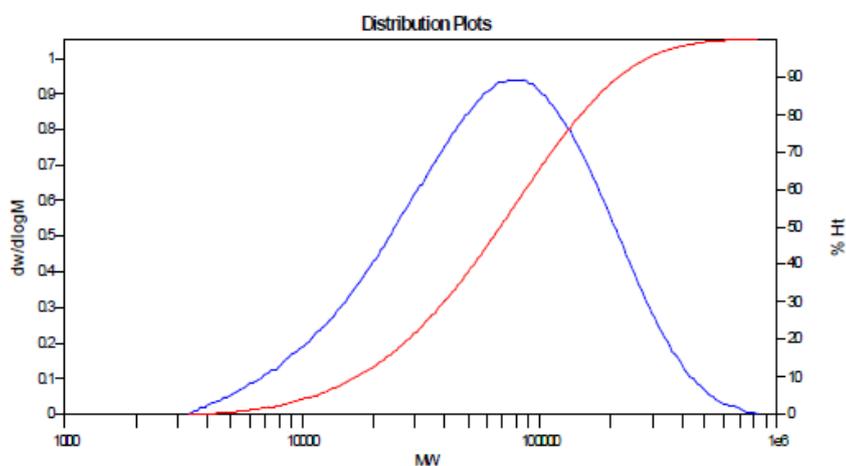
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6368	4073	8565	15989	25361	7692	2.10287

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.32	15.10	16.90	28.5035	0	2603.51	100

**Figure S73.** GPC data of the polymer from table 2, entry 5.



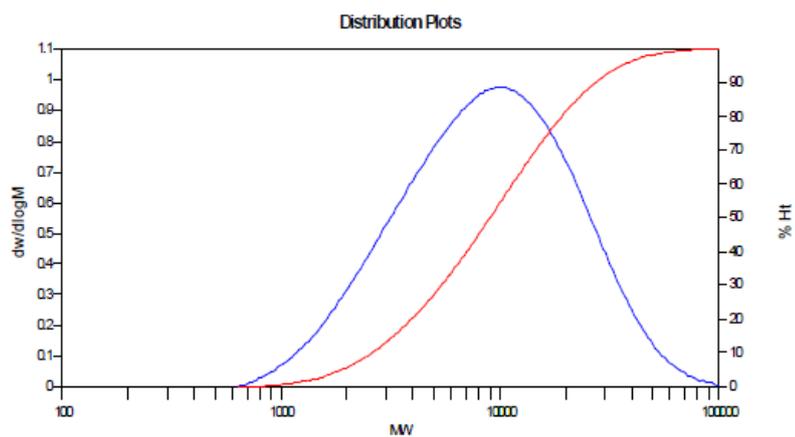
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	76229	38636	95928	182892	279620	85203	2.48287

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.83	13.43	15.53	8.38985	0	828.358	100

**Figure S74.** GPC data of the polymer from table 2, entry 6.



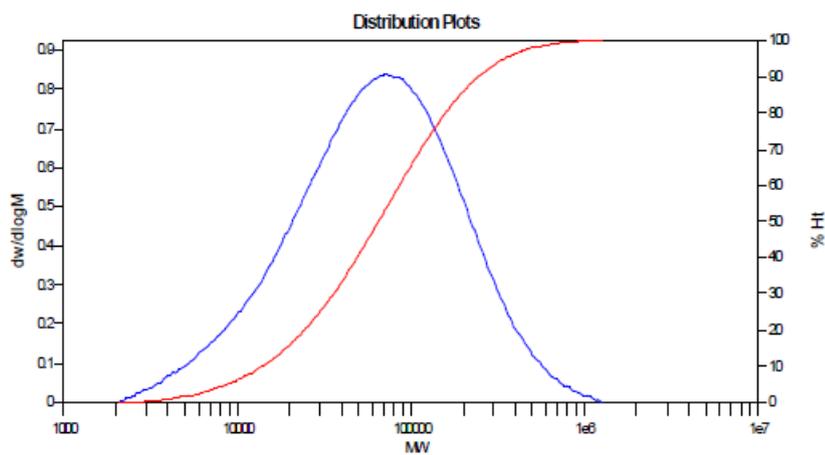
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	10206	5748	12421	22878	34872	11142	2.16093

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.25	14.78	16.65	10.229	0	971.249	100

Figure S75. GPC data of the polymer from table 2, entry 7.



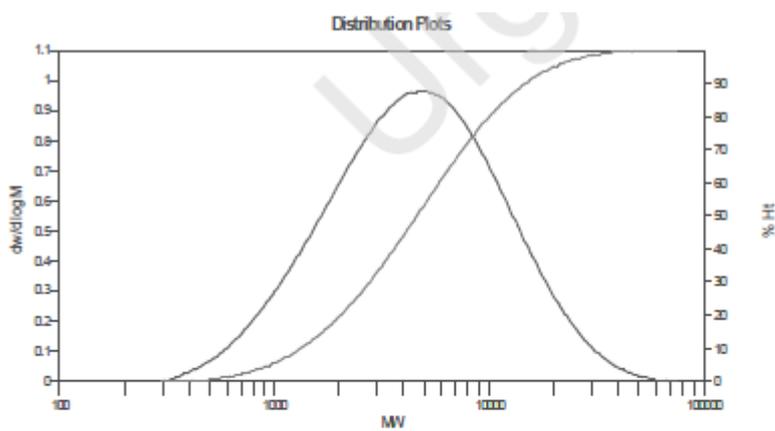
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	70759	32386	104813	247810	434086	89657	3.23637

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.55	13.48	15.85	7.80742	0	861.667	100

Figure S76. GPC data of the polymer from table 2, entry 8.



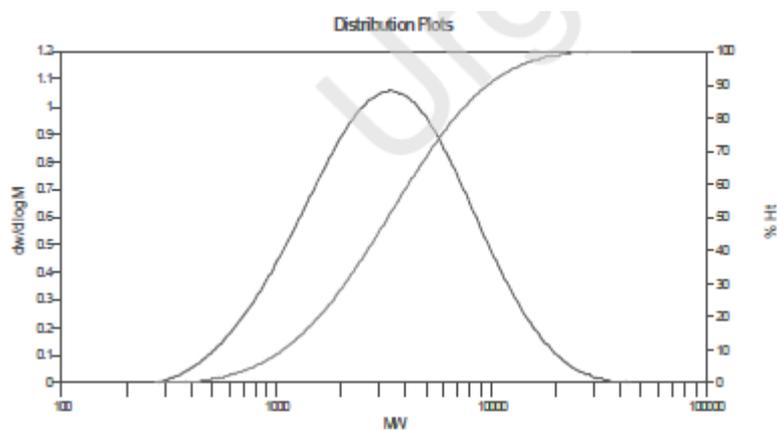
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	5008	2944	6656	13239	21745	5932	2.26087
2	114	83	101	115	125	99	1.21687

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		14.03	16.02	18.02	26.0876	34.2512	2681.08	61.4404
2		18.15	18.70	20.22	50.078	65.7488	1682.62	38.5596

Figure S77. GPC data of the polymer from table 2, entry 9.



**MW Averages**

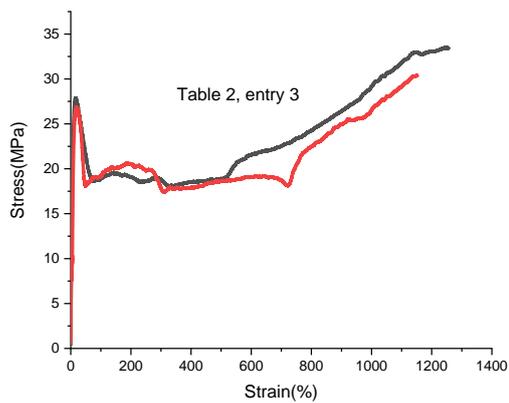
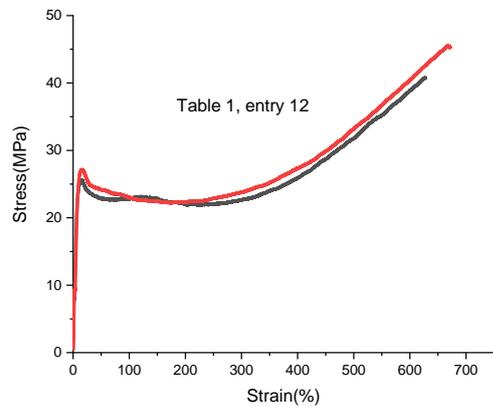
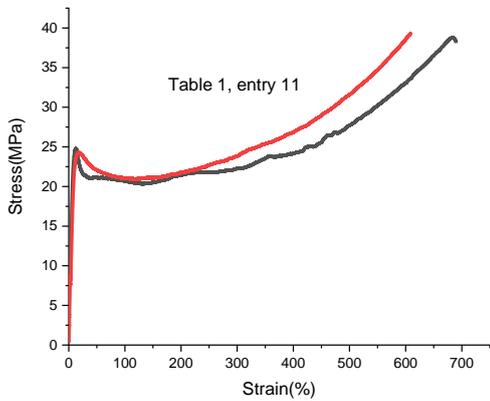
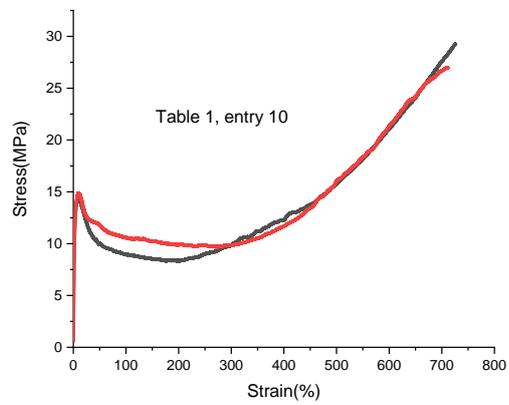
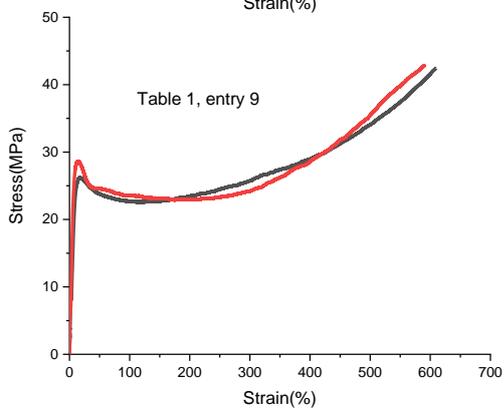
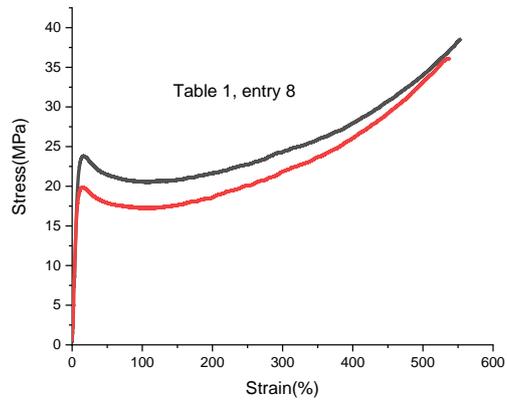
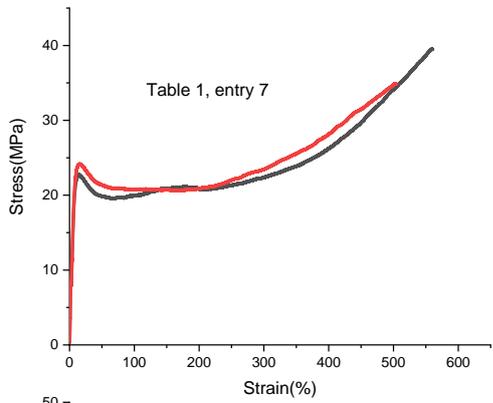
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3376	2288	4550	8299	13037	4122	1.98864
2	114	83	101	115	125	99	1.21687

**Processed Peaks**

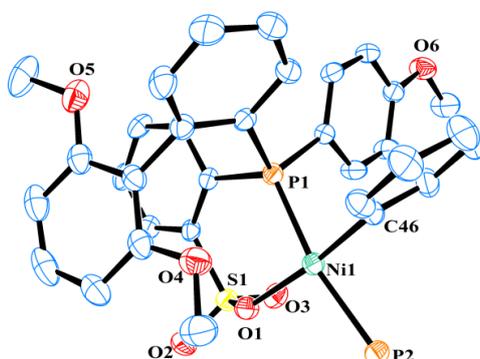
Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		14.42	16.27	18.07	29.6918	40.3242	2789.13	65.5196
2		18.12	18.70	20.22	43.941	59.6758	1467.81	34.4804

Figure S78. GPC data of the polymer from table 2, entry 10.

## 7. Tensile tests of the polymer products



## 8. X-ray Crystallography

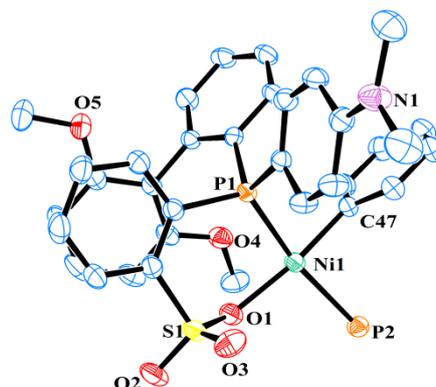


**Table S2 Crystal data and structure refinement for Ni-OMe**

Molecular structures of **Ni-OMe**. Selected bond lengths (Å) and angles (°): Ni1-C46 = 1.895(3), Ni1-O1 = 1.9420(19), Ni1-P1 = 2.1913(10), Ni1-P2 = 2.2771(10), O1-Ni1-P1 = 91.50(6), C46-Ni1-P2 = 88.00(10).

Formula	C <sub>51</sub> H <sub>44</sub> Ni O <sub>6</sub> P <sub>2</sub> S
Formula weight	905.57
Temperature[K]	298(2)
$\lambda$ (Mo-K $\alpha$ )[Å]	0.71073
Crystal system	Triclinic
Space group	P-1
a[Å]	12.7586(9)
b[Å]	12.9056(9)
c[Å]	14.4120(11)
$\alpha$ [°]	93.6340(10)
$\beta$ [°]	108.977(2)
$\gamma$ [°]	101.293(2)
Volume[Å <sup>3</sup> ]	2179.9(3)
Z	2
D(calc)[g·cm <sup>-3</sup> ]	1.380
$\mu$ [mm <sup>-1</sup> ]	0.618
F(000)	944
$\theta$ min-max (°)	2.635-25.774
<i>h</i>	-13→15
<i>k</i>	-15→13
<i>l</i>	-17→17
Reflections collected	11215
Reflections unique	7587
R(int)	0.0343
Data / restraints / parameters	7587 / 0 / 553

Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0457$ $wR_2 = 0.0705$
R indices (all data)	$R_1 = 0.0858$ $wR_2 = 0.0776$
GOF on $F^2$	1.063



**Table S3 Crystal data and structure refinement for Ni-NMe<sub>2</sub>**

Molecular structures of Ni-NMe<sub>2</sub>. Selected bond lengths (Å) and angles (°): Ni1-C47 = 1.901(3), Ni1-O1 = 1.954(2), Ni1-P1 = 2.1871(10), Ni1-P2 = 2.2772(10), C47-Ni1-P2 = 88.36(10), O1-Ni1-P1 = 91.65(7).

Formula	C <sub>52</sub> H <sub>47</sub> N Ni O <sub>5</sub> P <sub>2</sub> S
Formula weight	918.62
Temperature[K]	298(2)
$\lambda(\text{Mo-K}\alpha)[\text{Å}]$	0.71073
Crystal system	Triclinic
Space group	P-1
a[Å]	13.0106(12)
b[Å]	16.8571(14)
c[Å]	21.1770(19)
$\alpha$ [°]	93.5750(10)
$\beta$ [°]	95.9950(10)
$\gamma$ [°]	105.224(2)
Volume[Å <sup>3</sup> ]	4437.5(7)
Z	4
D(calc)[g·cm <sup>-3</sup> ]	1.375
$\mu$ [mm <sup>-1</sup> ]	0.607
F(000)	1920
$\theta$ min-max (°)	2.602-25.083
<i>h</i>	-11→15
<i>k</i>	-18→20
<i>l</i>	-25→24
Reflections collected	22668

---

Reflections unique	15365
R(int)	0.0410
Data / restraints / parameters	15365 / 0 / 1125
Final R indices [ $I > 2\sigma(I)$ ]	R <sub>1</sub> = 0.0521 wR <sub>2</sub> = 0.1040
R indices (all data)	R <sub>1</sub> = 0.0982 wR <sub>2</sub> = 0.1148
GOF on F <sup>2</sup>	1.071

---

## References.

- (1) Perrotin, P.; McCahill, J. S. J.; Wu, G.; Scott, S. L. *Chem. Commun.* **2011**, *47*, 6948-6950.
- (2) Coyle EE, Doonan BJ, Holohan AJ, et al. *Angew Chem Int Ed.* **2014**, *53*: 12907-12911.
- (3) Jansen H, Samuels M, Couzijn E, et al. *Chem.-Eur. J.* **2010**, *16*: 1454-1458.
- (4) Sheldrick, G. M. *Acta Cryst.*, 1990, **46**, 467.
- (5) Sheldrick, G. M. SHELXL 97, Programs for structure refinement, Universität Göttingen, 1997.