Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

1. 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}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded a Bruker AscendTm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane; the ^{31}P NMR spectra were referenced to an external 85% H_3PO_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 Cu Kα radiation (λ = 1.54178 Å). 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 ^{o}C using o-dichlorobenzene 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: $K = 1.75 \times 10^{-2}$ cm^3/g and R = 0.67 for polystyrene and $K = 5.90 \times 10^{-2}$ cm^3/g and R = 0.69 for polyethylene. Dichloromethane, THF, and hexanes were purified by solvent purification systems. **L-OMe**, **Ni-OMe** and **L-H** were prepared using literature procedure. [1, 2]

Preparation of Ligand L-OiPr. Anhydrous benzenesulfonic acid (1.58 g, 10.0 mmol) was dissolved in dry THF (100 mL) under nitrogen and cooled to 0 ^{o}C. ^{n}BuLi (2.5 M in hexane, 8 mL, 20.0 mmol) was added dropwise. The resulting red solution was stirred for 1.0 h at room temperature. The above solution was added slowly to the solution of $PhPCl_2$(1.36 mL, 10.0 mmol) in 50 mL THF at -78 ^{0}C. The mixture was stirred for another 2 h at room temperature. The solution of (2', 6'-diisopropoxy-[1,1'-biphenyl]-2-yl)lithium (10.0 mmol) was added to the above solution. The mixture was stirred for another 24 h at room temperature. The resulting mixture was evaporated to dryness under vacuum and acidified using 3 mL of concentrated HCl in 60 mL of water. The aqueous phase was extracted with dichloromethane (100 × 2 mL). The organic phases were combined, dried over $MgSO_4$, and filtered. The filtrate was evaporated to dryness under vacuum. The residue was washed with diethyl ether to yield a white solid (2.9 g, 56%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.17 (1H), 7.79-7.76 (m, 2H), 7.48 (br, 0.5H, P*H*),7.66 (m, 1H), 7.52-7.44 (m, 7H), 7.36-7.23 (m, 3H), 4.58 (1H), 4.32 (1H), 1.36-0.93 (m,12H). ^{13}C NMR (CD_2Cl_2,100 MHz): δ 156.1 (s), 155.0 (s), 152.7 (d, J_{PC} = 9.0 Hz), 142.4 (d, J_{PC} = 10.0 Hz), 135.0 (d, J_{PC} = 10.0 Hz), 134.7 (d, J_{PC} = 15.0 Hz), 134.6 (s), 133.8 (d, J_{PC} = 3.0 Hz), 133.6 (d, J_{PC} = 7.0 Hz), 133.5 (s), 132.6 (d, J_{PC} = 12.0 Hz), 131.0 (s), 129.1(d, J_{PC} = 11.0 Hz), 129.3 (d, J_{PC} = 14.0 Hz), 128.4 (d, J_{PC} = 9.0 Hz), 127.7 (d, J_{PC} = 12.0 Hz), 120.4 (s), 119.8 (s), 119.5 (s), 118.9 (s), 116.6 (d, J_{PC} = 6.0 Hz), 113.3 (s), 112.3 (s), 106.2 (d, J_{PC} = 5.0 Hz), 70.7 (d, J_{PC} = 1.0 Hz), 22.4 (s). 21.5(d, J_{PC} = 8.0 Hz), 21.3 (s). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ 0.6.

Preparation of Ligand L-F. Similar procedure as above was employed except (2', 6'-difluoro-[1, 1'-biphenyl]-2-yl)lithium (10.0 mmol) was used. **L-F**. was obtained as a light white solid (2.8 g, 62%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.17-8.14 (m, 1H), 7.88-7.84 (m, 1H), 7.80-7.76 (m, 1H), 7.73-7.69 (m, 1H), 7.68-7.62 (m, 1H), 7.58-7.30 (m, 8H), 7.24-7.19 (m, 1H), 5.45 (br, 1H). ^{13}C NMR (100 MHz, d^6-DMSO): δ 160.8 (d, J_{PC} = 8.0 Hz), 160.4 (d, J_{PC} = 6.0 Hz), 158.3 (d, J_{PC} = 7.0 Hz), 157.9 (d, J_{PC} = 7.0 Hz), 150.9 (d, J_{PC} = 6.0 Hz), 140.2 (d, J_{PC} = 19.0 Hz), 138.8 (d, J_{PC} = 15.0 Hz) (s), 134.6 (s), 134.5 (s), 134.3 (s), 134.2 (s), 133.3 (s), 133.2 (s), 133.0 (s), 132.9 (s), 130.8 (d, J_{PC} = 3.0 Hz), 129.9 (t), 128.9 (s), 128.3 (s), 128.2 (s), 127.8 (t), 127.3 (d, J_{PC} = 4.0 Hz), 117.7 (td), 112.2 (dd). ^{19}F NMR (CD_2Cl_2, 376 MHz): δ -110.2 (J = 3.8 Hz), -110.7 (J = 3.8 Hz). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ 1.5.

Preparation of catalyst Ni-O^{i}Pr. A 100 mL Schlenk flask was charged with **L-OiPr** (534 mg, 1.0 mmol), NaH (29 mg, 1.2 mmol) and 20 mL THF. After stirring for 12 h at room temperature, the yellow solution was filtrated and evaporated. Then the residual was dissolved in 20 mL CH_2Cl_2, a solution of $(PPh_3)_2NiPhCl$ (694 mg, 1.0 mmol) in 20 mL of CH_2Cl_2 was added to the mixture and stirred for another 12 h. The resulting mixture was filtered through Celite. The filtrate was dried under vacuum to get a yellow powder. The powder was washed with a 2:1 mixture of hexane and toluene. **Ni-O^{i}Pr** was obtained as a yellow solid (670 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.78 (m, 2H), 7.69-7.66 (m, 2H), 7.53-7.45 (m, 2H), 7.35-7.27(m, 13H), 7.16-7.11 (m, 6H), 7.03-6.87 (m, 4H), 4.47-4.41 (m, 1H), 4.10-4.04 (m, 1H), 1.25 (d, J_{PH} = 8 Hz, 3H), 1.05 (d, J_{HH} = 4 Hz, 3H), 1.02 (d, J_{HH} = 4 Hz, 3H), 0.95 (d, J_{PH} = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2 (s), 147.1 (d, J_{PC} = 14.0 Hz), 141.4 (d, J_{PC} = 14.0 Hz), 140.3 (t), 139.7 (s), 139.5 (t), 139.3 (d, J_{PC} = 2.0 Hz), 139.0 (s), 136.0 (d, J_{PC} = 9.0 Hz), 135.2 (d, J_{PC} = 10.0 Hz), 134.0 (d, J_{PC} = 8.0 Hz), 133.2 (s), 132.7 (s), 132.5 (s), 130.4 (d, J_{PC} = 2.0 Hz), 130.3 (d, J_{PC} = 2.0 Hz), 130.1 (t), 129.3 (d, J_{PC} = 5.0 Hz), 128.9 (s), 128.7 (t), 128.4 (d, J_{PC} = 10.0 Hz), 128.2 (d, J_{PC} = 11.0 Hz), 126.8 (d, J_{PC} = 6.0 Hz), 126.2 (s), 125.5 (d, J_{PC} = 9.0 Hz), 124.9 (s), 122.8 (d, J_{PC} = 3.0 Hz), 121.9 (s), 110.2 (s), 104.4 (s), 106.7 (s), 73.8 (s), 70.6 (s), 24.1 (s), 23.2 (s), 22.3 (s), 21.9 (s). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 10.7 (d, J_{PP} = 283 Hz), -0.7 (d, J_{PP} = 283 Hz, PPh_3). Anal. Calcd for$C_{54}H_{50}NiO_5P_2S$: C, 69. 61; H, 5.41; Found: C, 69.90; H, 5.53.

Preparation of catalyst Ni-F. Similar procedure was employed to the above method except **L-F** (454 mg, 1.0 mmol) was used. **Ni-F** was obtained as a bright yellow solid (645 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (br, 2H), 7.53 (m, 7H), 7.45 - 7.27 (m, 15H), 7.11 (m, 2H), 7.03 - 6.96 (m, 1H), 6.94 - 6.84 (m, 2H), 6.59 (d, J = 8.0 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 6.36 (d, J = 8.0 Hz, 1H), 6.32 - 6.15 (m, 3H), 6.04 (t, J = 8.0 Hz, 1H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.8 (d, J_{PP} = 279 Hz), -2.0 (dd, J_{PP} = 279 Hz, J_{PF} = 16 Hz, PPh_3). Anal. Calcd for $C_{48}H_{36}F_2NiO_3P_2S$: C, 67. 71 ; H, 4.26; Found: C, 67.88; H, 4.35.

Preparation of catalyst Ni-H. Similar procedure was employed to the above method except **L-H** (418 mg, 1.0 mmol) was used. **Ni-H** was obtained as a bright yellow solid (651 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (br, 2H), 7.73 - 7.63 (m, 3H), 7.42 - 7.35 (m, 6H), 7.35 - 7.21 (m, 14H), 7.17 - 7.05 (m, 4H), 6.99 (d, J = 8.0 Hz, 2H), 6.80 (t, J = 8.0 Hz, 1H), 6.73

(d, J = 8.0 Hz, 1H), 6.37 (t, J = 8.0 Hz, 1H), 6.32 - 6.26 (m, 2H), 6.20 (d, J = 8.0 Hz, 1H), 5.92 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0 (d, J_{PC} = 11.0 Hz), 135.1 (d, J_{PC} = 5.0 Hz), 134.9 (d, J_{PC} = 10.0 Hz), 134.4 (s), 134.2 (s), 132.3 (d, J_{PC} = 7.0 Hz), 130.9 (s), 130.7 (s), 130.5 (d, J_{PC} = 2.0 Hz), 130.4 (d, J_{PC} = 2.0 Hz), 130.2 (d, J_{PC} = 2.0 Hz), 130.0 (s), 129.8 (s), 129.7 (s), 129.3 (s), 129.0 (s), 128.9 (s), 128.7 (d, J_{PC} = 10.0 Hz), 128.5 (s), 128.4 (s), 127.3 (d, J_{PC} = 7.0 Hz), 126.8 (d, J_{PC} = 8.0 Hz), 126.6 (d, J_{PC} = 6.0 Hz), 122.1 (s). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 14.7 (d, J_{PP} = 279 Hz), -0.6 (d, J_{PP} = 279 Hz, PPh_3). Anal. Calcd for $C_{48}H_{38}NiO_3P_2S$: C, 70. 69; H, 4.70; Found: C, 70.91; H, 4.83.

Procedure for ethylene homopolymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with 48 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 ^{o}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_2Cl_2 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 50 °C for 24 h under vacuum.

Procedure for ethylene and NB-polar monomer copolymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with toluene and NB-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 ^{o}C using an oil bath and allowed to equilibrate for 15 min. 20 μmol of Ni complex in 2 mL CH_2Cl_2 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 50 °C for 24 h under vacuum.

2. NMR figures of ligand L and catalyst Ni.

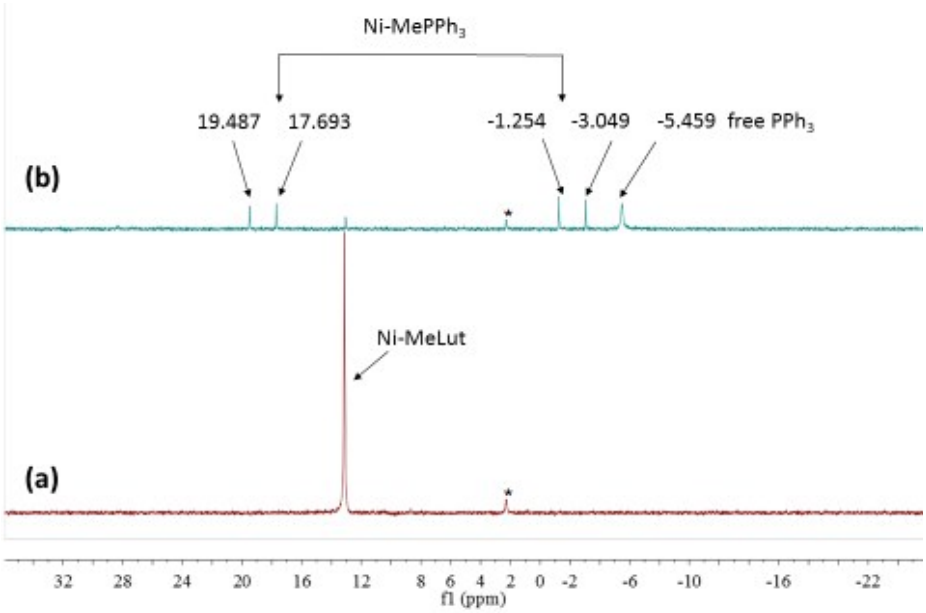


Figure S1. Comparison of ^{31}P NMR spectrums (162 MHz, $CDCl_3$): (a) Ni-Lut (contains a little bit of impurity$_*$); (b) When Ni-Lut was added 1eq. PPh_3 for 1h at room temperature, new complex Ni-$MePPh_3$ pruduced.

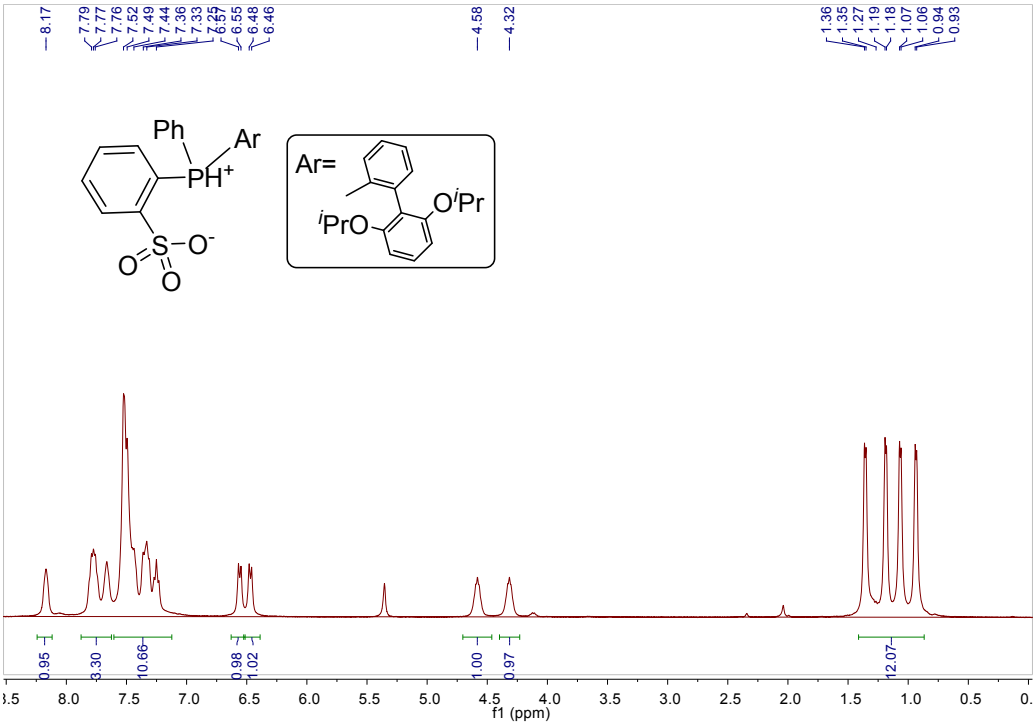


Figure S2. ^1H NMR spectrum (400 MHz, CD_2Cl_2) of **L-O^{i}Pr**.

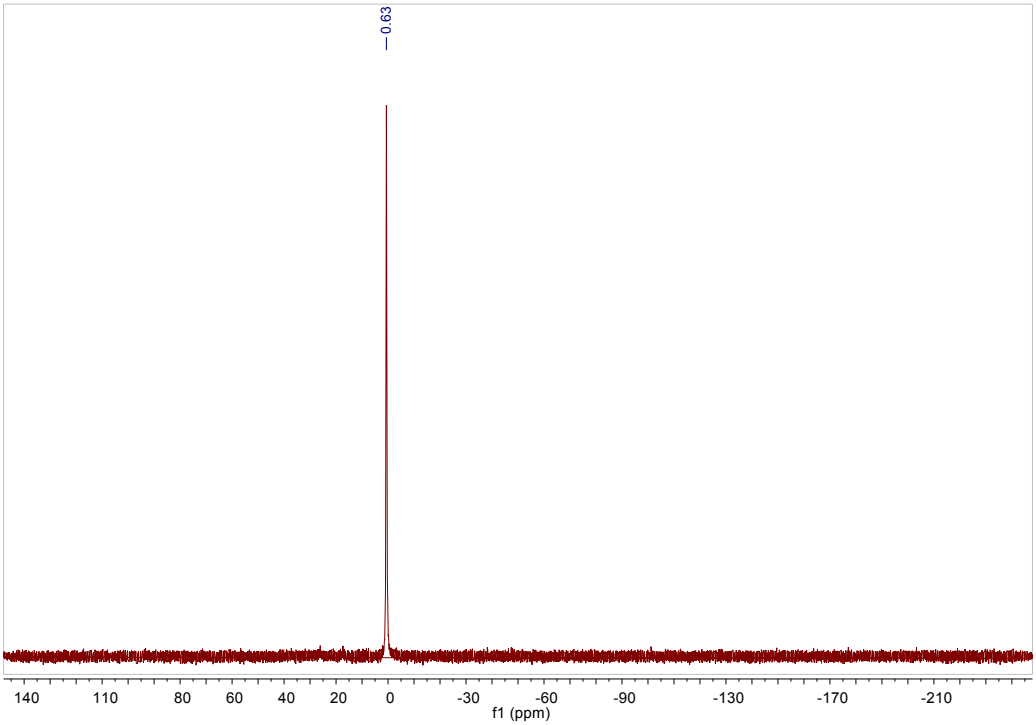


Figure S3. ^{31}P NMR spectrum (162 MHz, CD_2Cl_2) of **L-O^{i}Pr**.

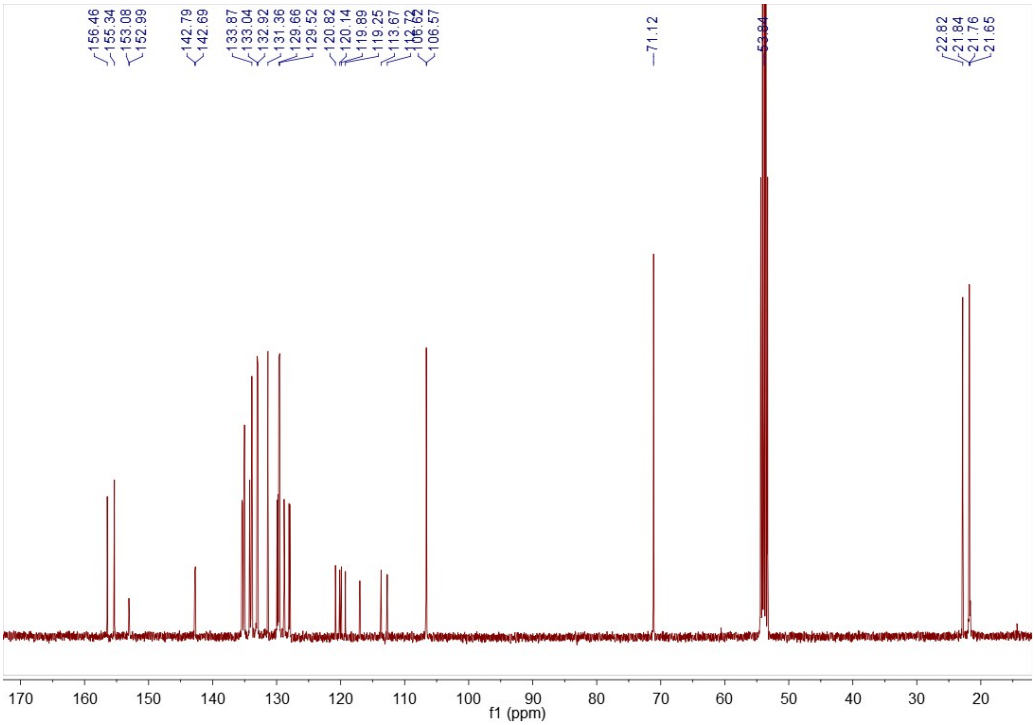


Figure S4. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2) of **L-O^{i}Pr**.

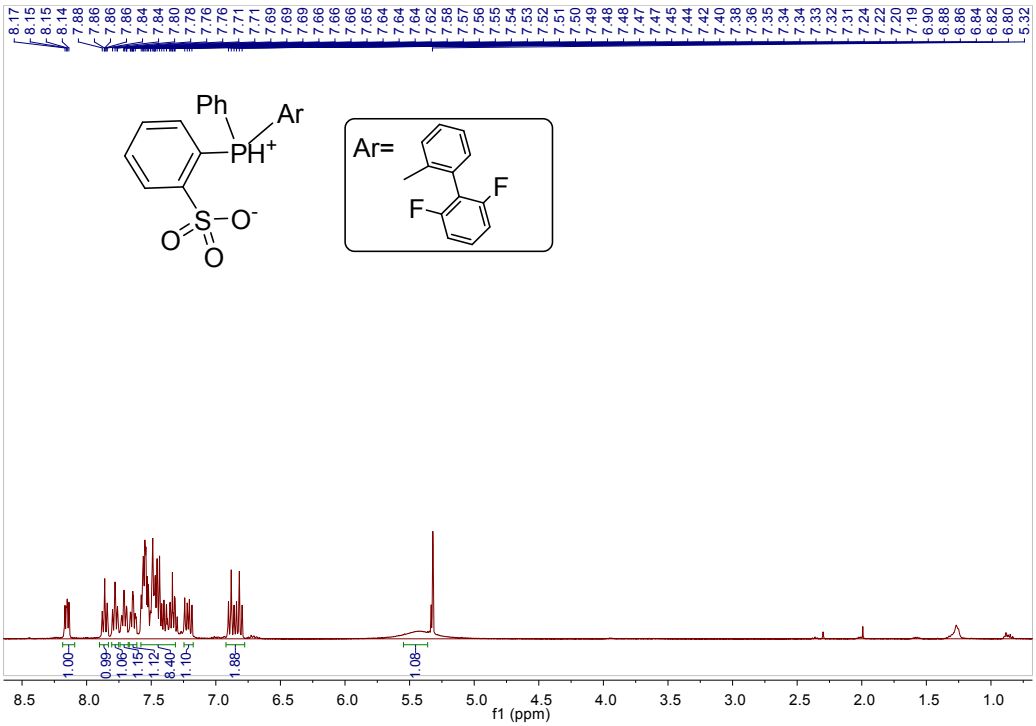


Figure S5. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **L-F**.

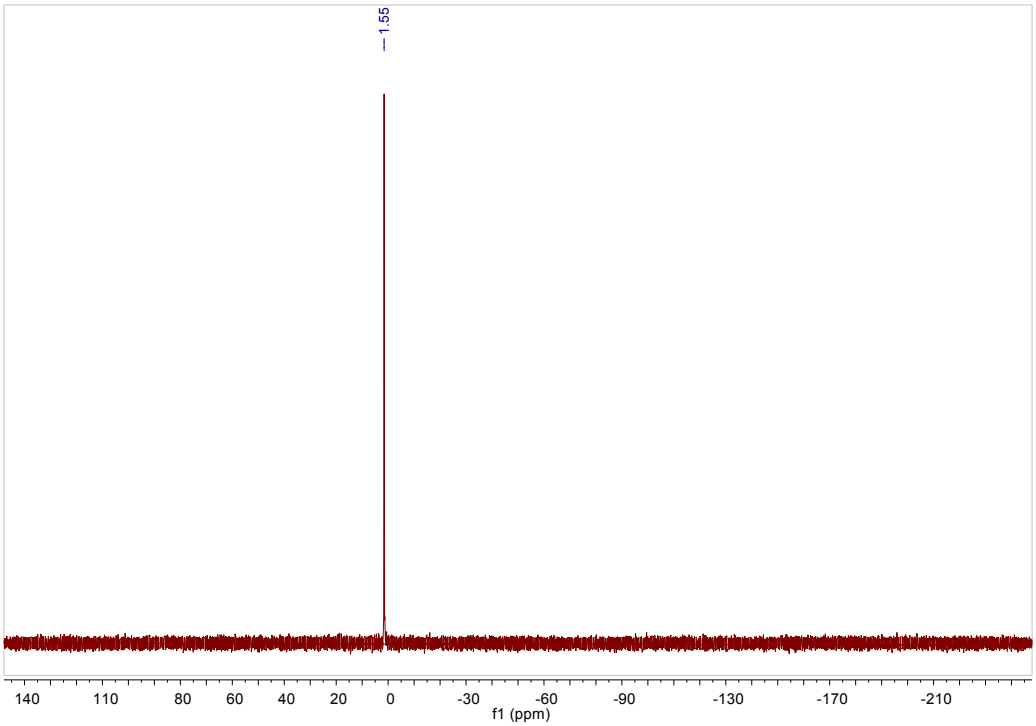


Figure S6. ^{31}P NMR spectrum (162 MHz, CD_2Cl_2) of **L-F**.

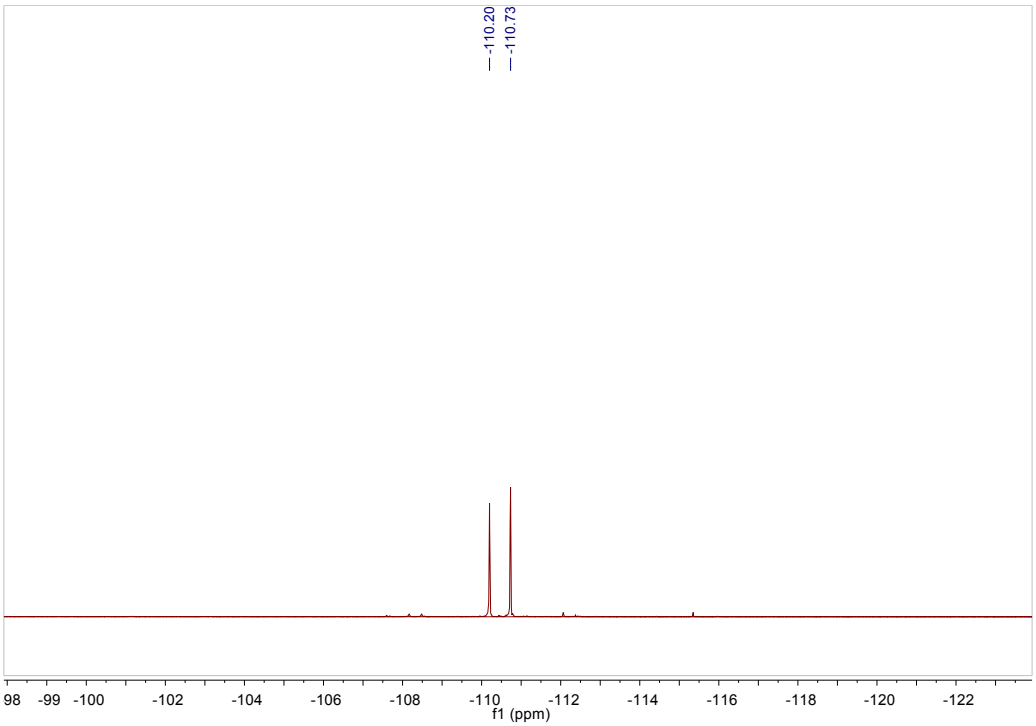


Figure S7. ^{19}F NMR spectrum (376 MHz, CD_2Cl_2) of **L-F**.

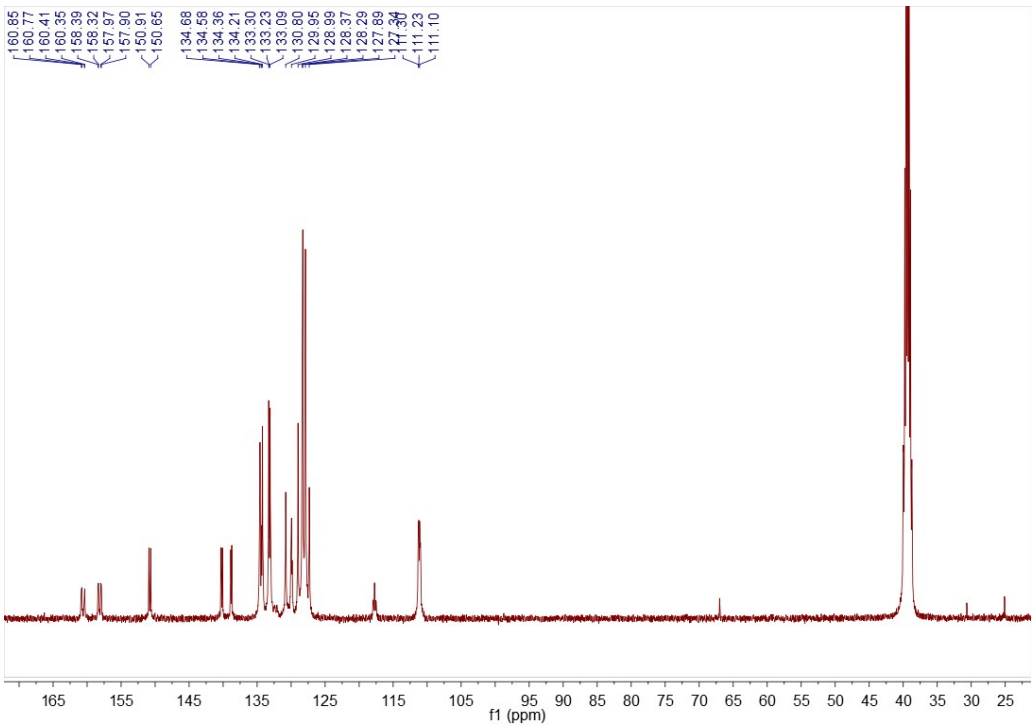


Figure S8. ^{13}C NMR spectrum (100 MHz, d^6-DMSO) of **L-F**.

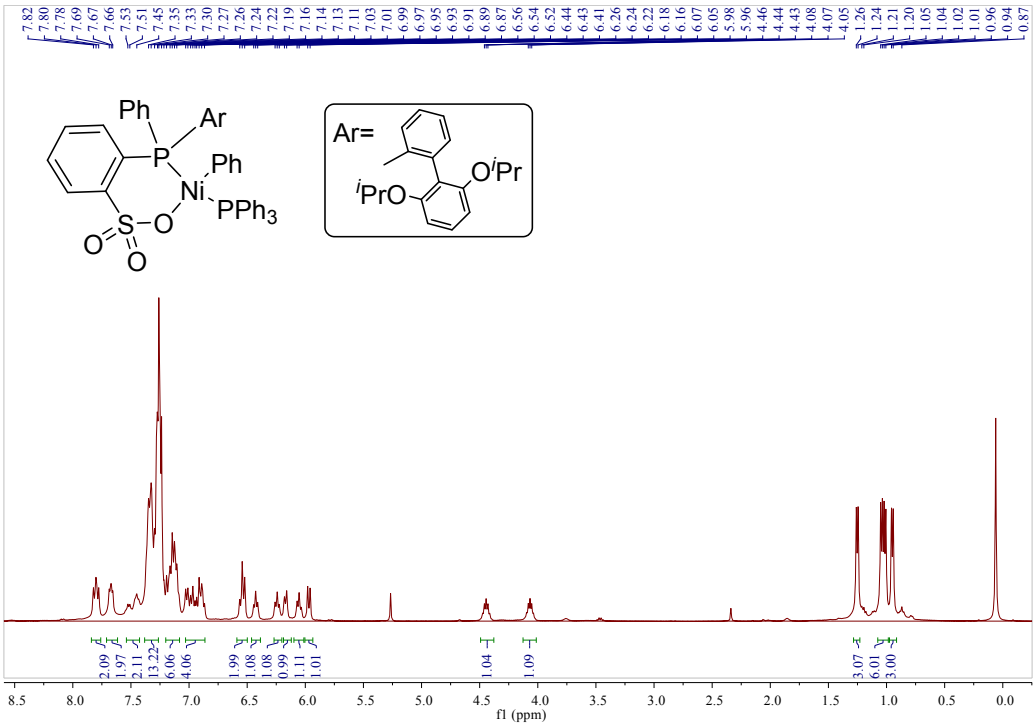


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **Ni-O^{i}Pr**.

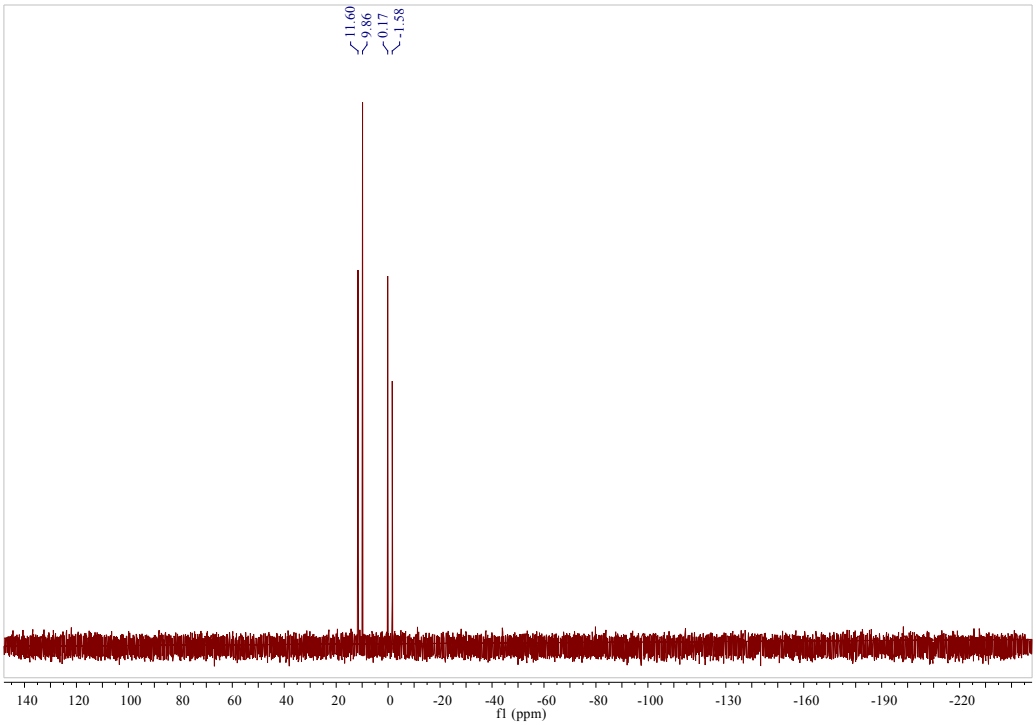


Figure S10. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **Ni-O^{i}Pr**.

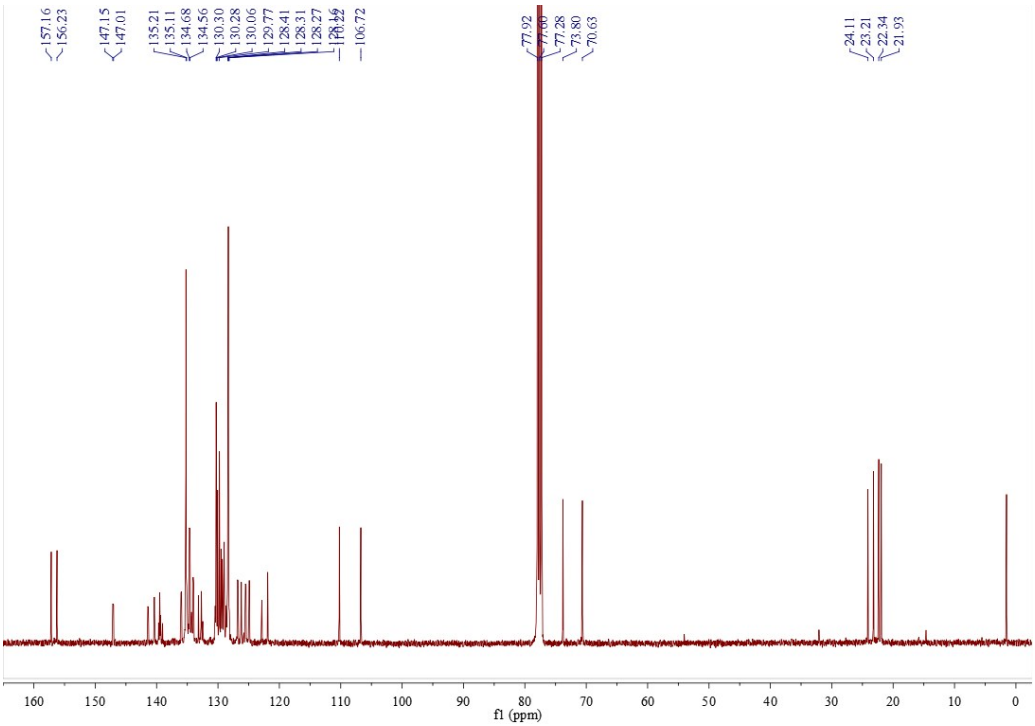


Figure S11. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **Ni-O^{i}Pr**.

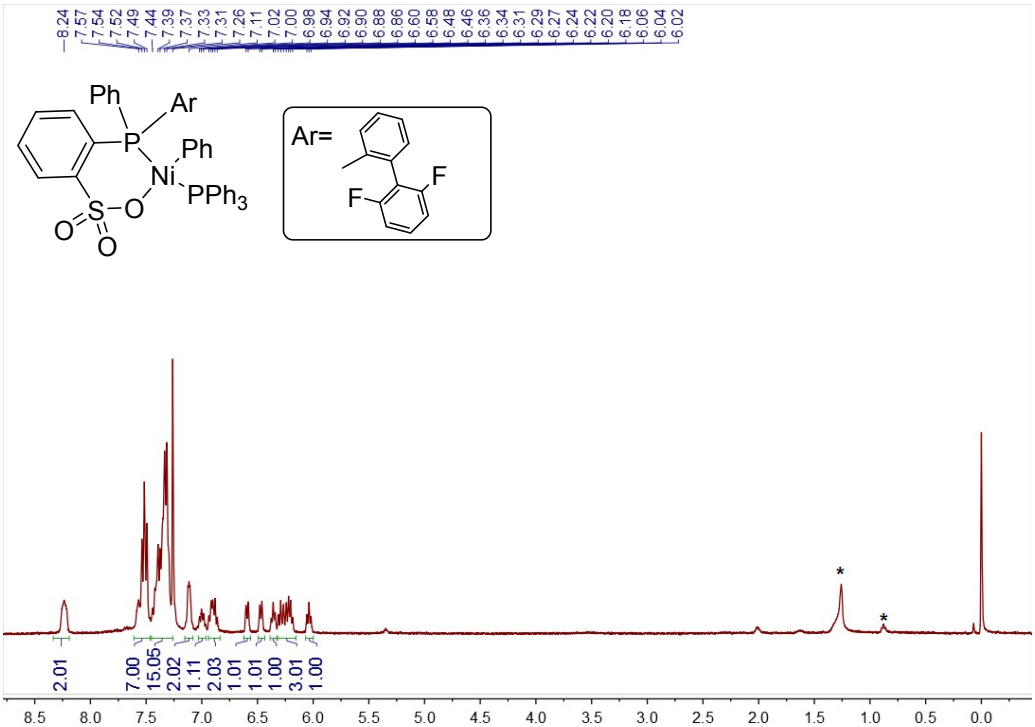


Figure S12. ^1H NMR spectrum (400 MHz, $CDCl_3$) of **Ni-F** (* is hexane).

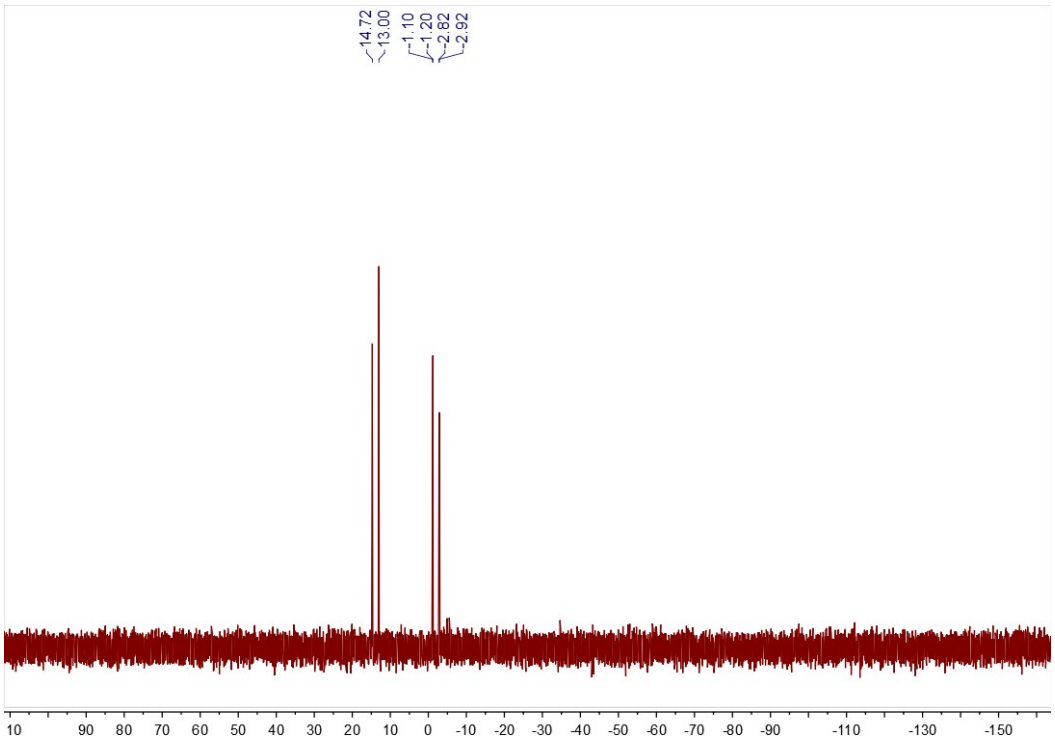


Figure S13. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **Ni-F**.

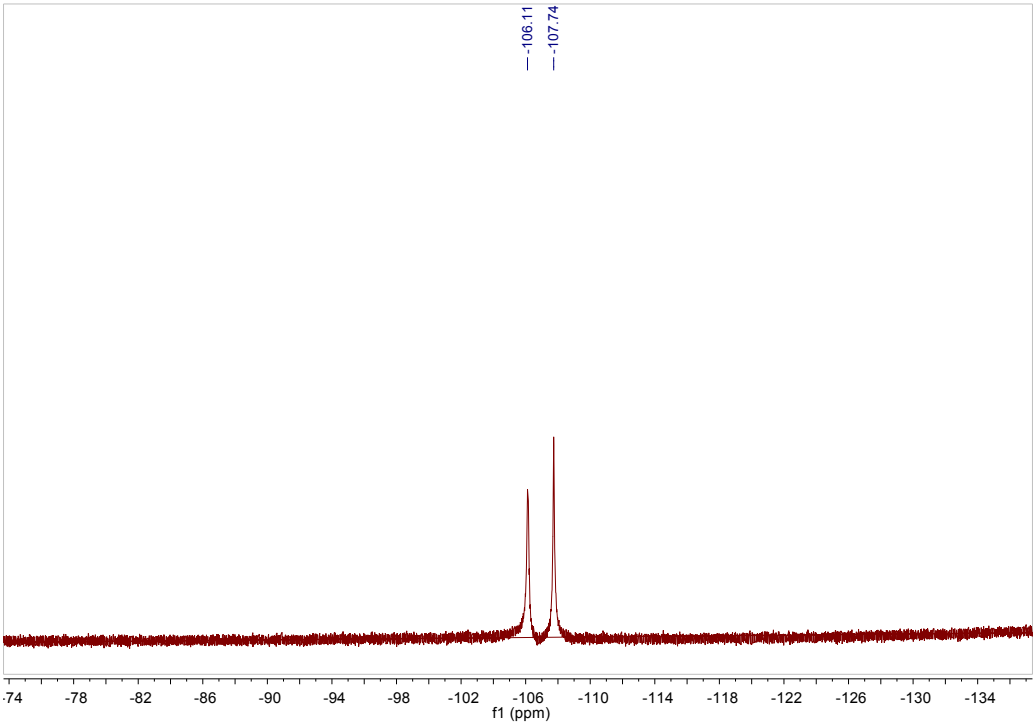


Figure S14.^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **Ni-F**.

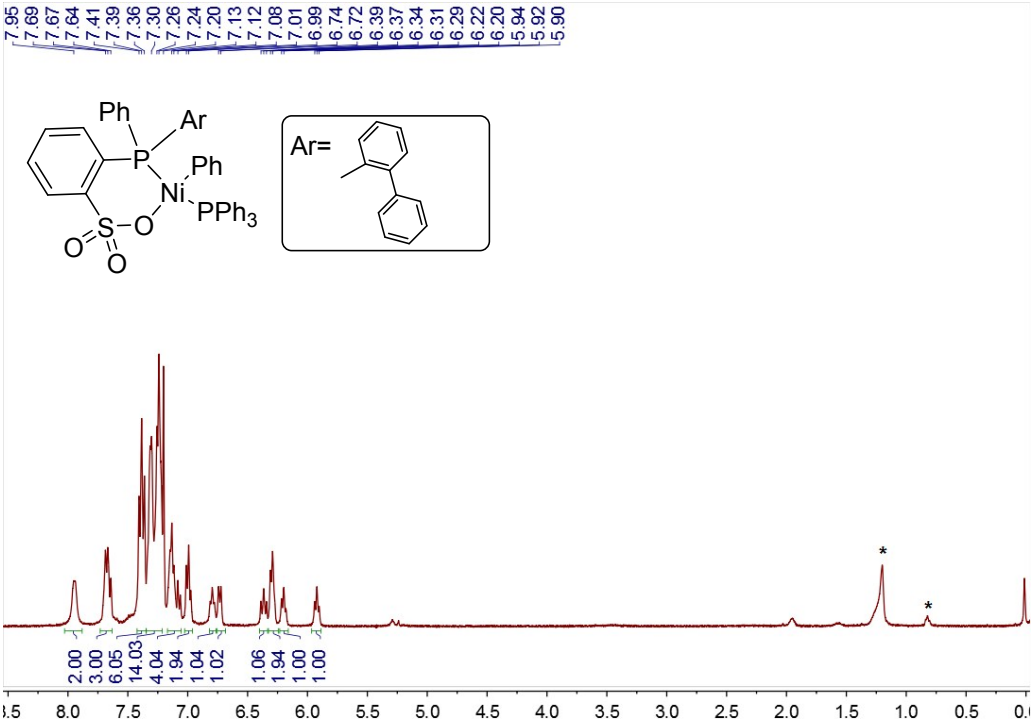


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **Ni-H** (∗ is hexane).

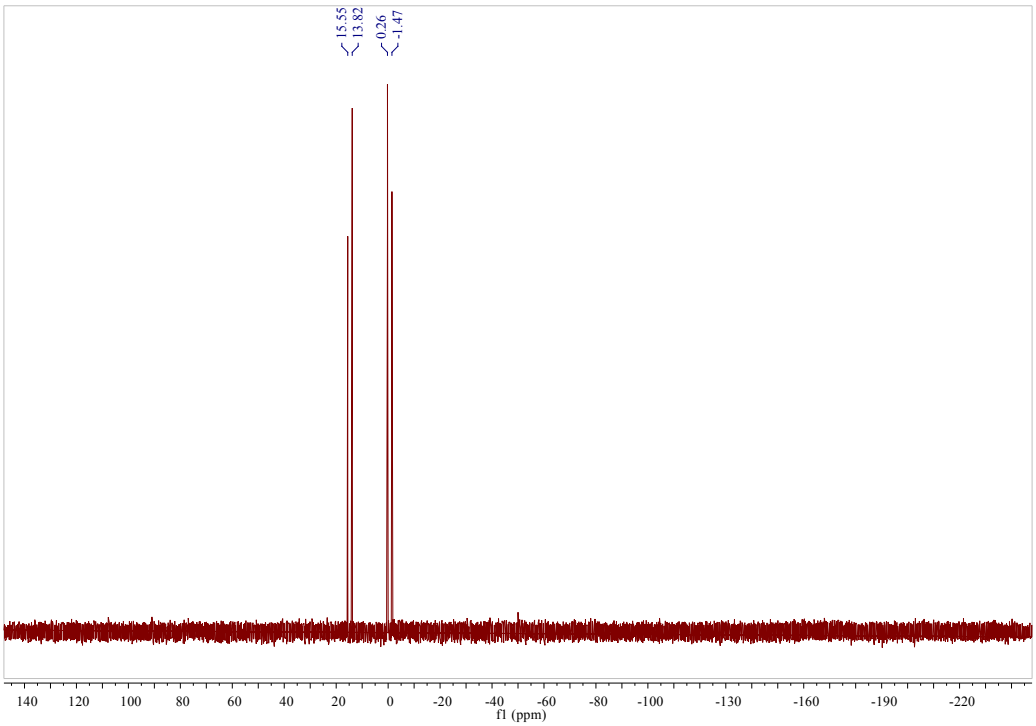


Figure S16. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **Ni-H**.

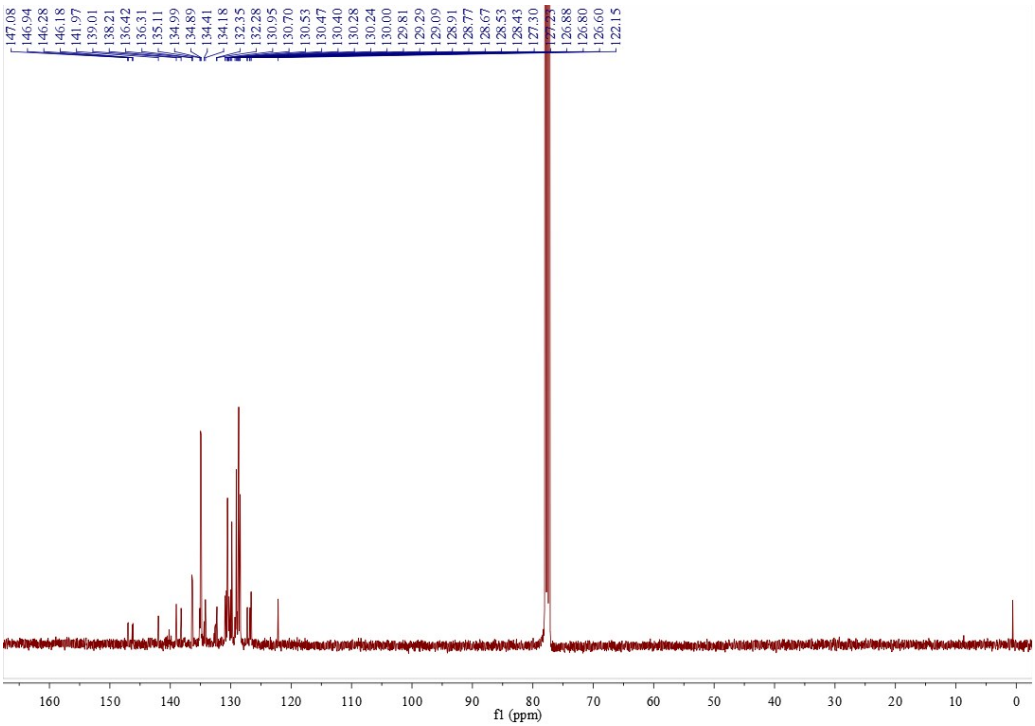


Figure S17. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **Ni-H**.

3. NMR figures of (co)polymers[3].

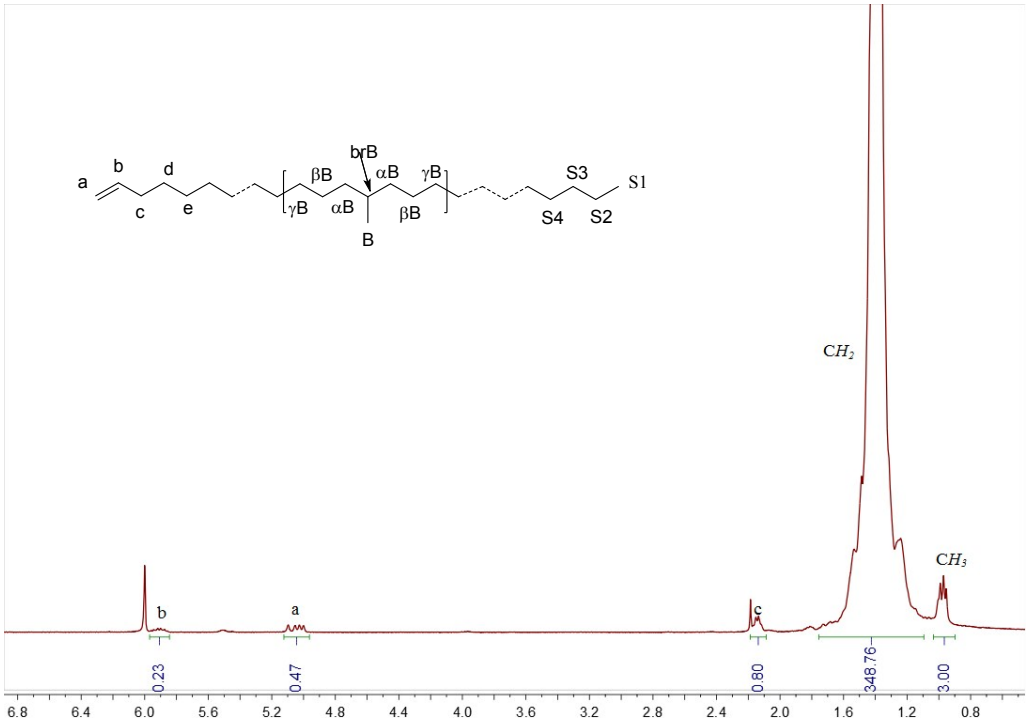


Figure S18. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120°C) of polymer (table 1, entry 3).

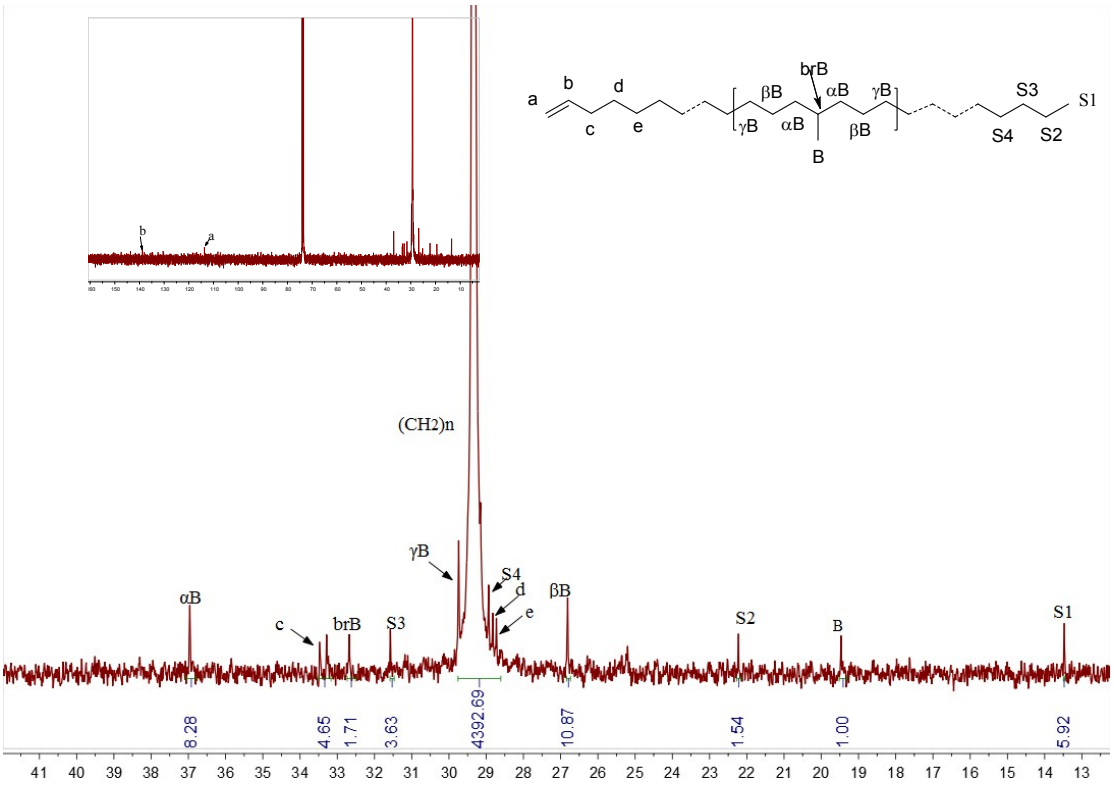


Figure S19. ^{13}C NMR spectrum (100 MHz, $C_2D_2Cl_4$, 120°C) of polymer (table 1, entry 3). The degree of branching B=[1/total (integrated area)] =(1/4430.3) * 1000 =0.23.

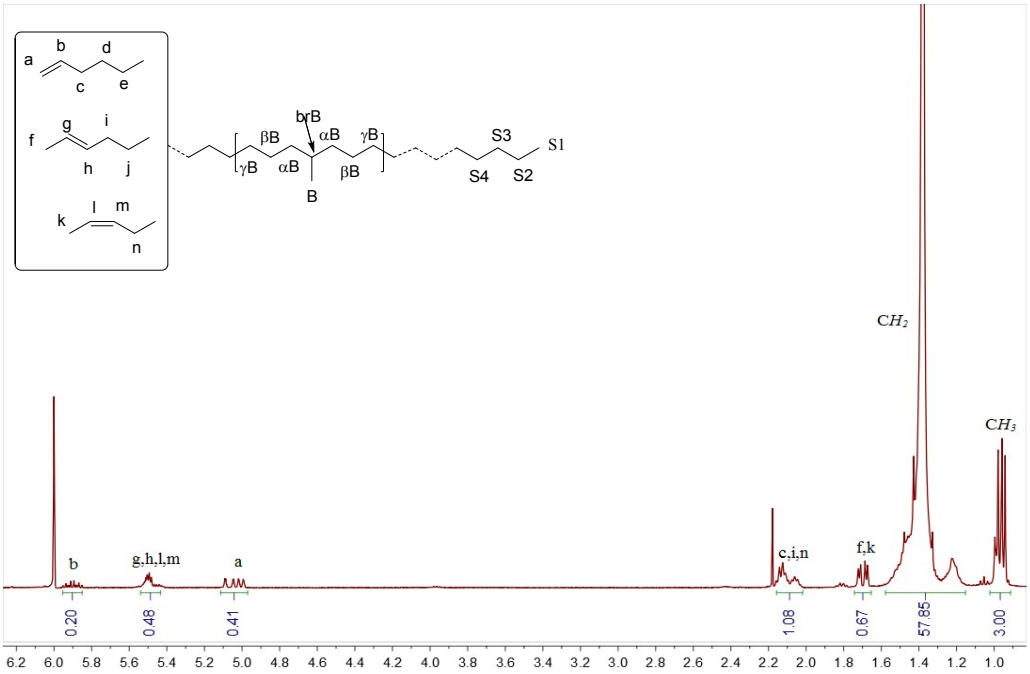


Figure S20. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120°C) of polymer (table 1, entry 7).

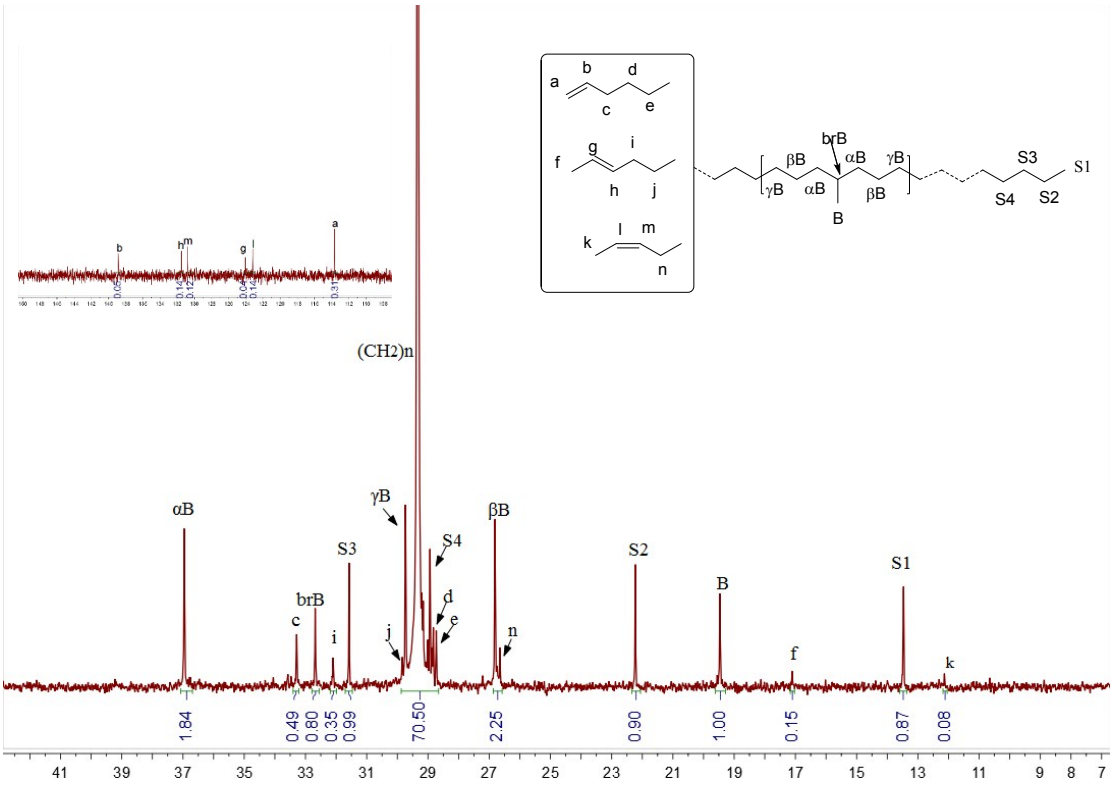


Figure S21. ^{13}C NMR spectrum (100 MHz, $C_2D_2Cl_4$, 120°C) of polymer (table 1, entry 7). The degree of branching B=[1/total (integrated area)] =(1/81.02) * 1000 =12.3.

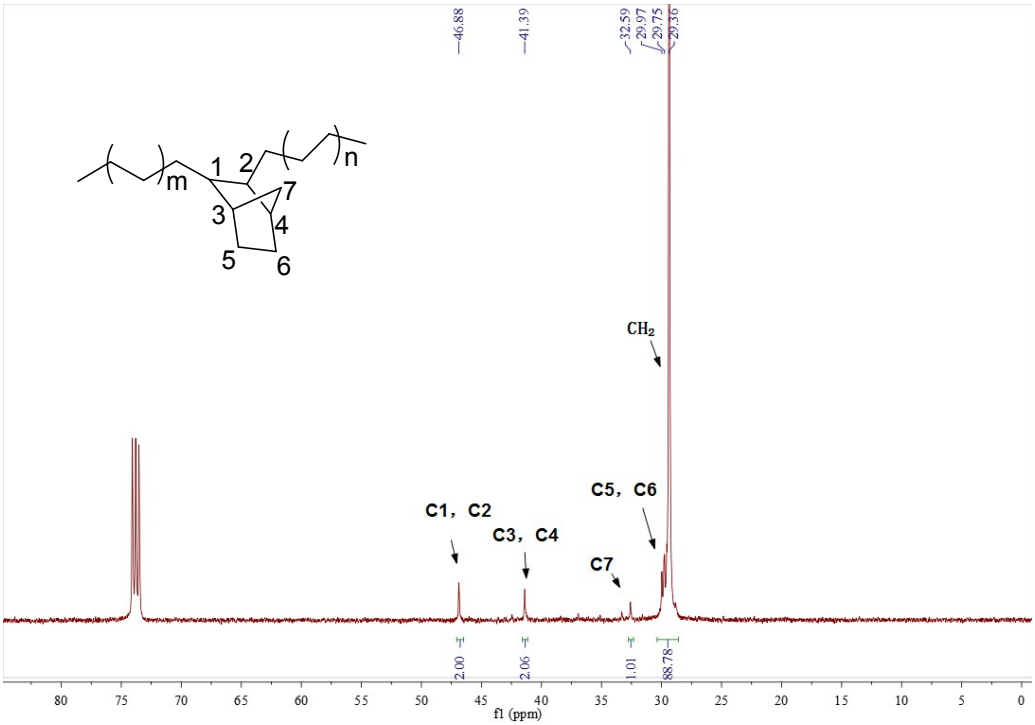


Figure S22. ^{13}C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120°C) of copolymer (table 2, entry1).

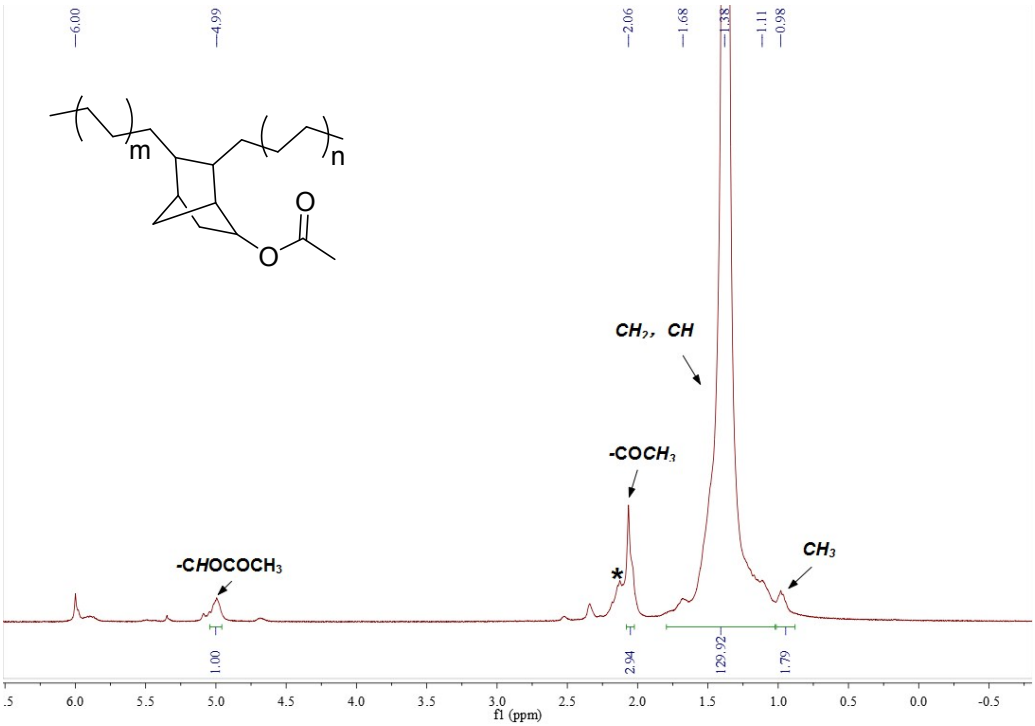


Figure S23. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120°C) of copolymer (table 2, entry 3).

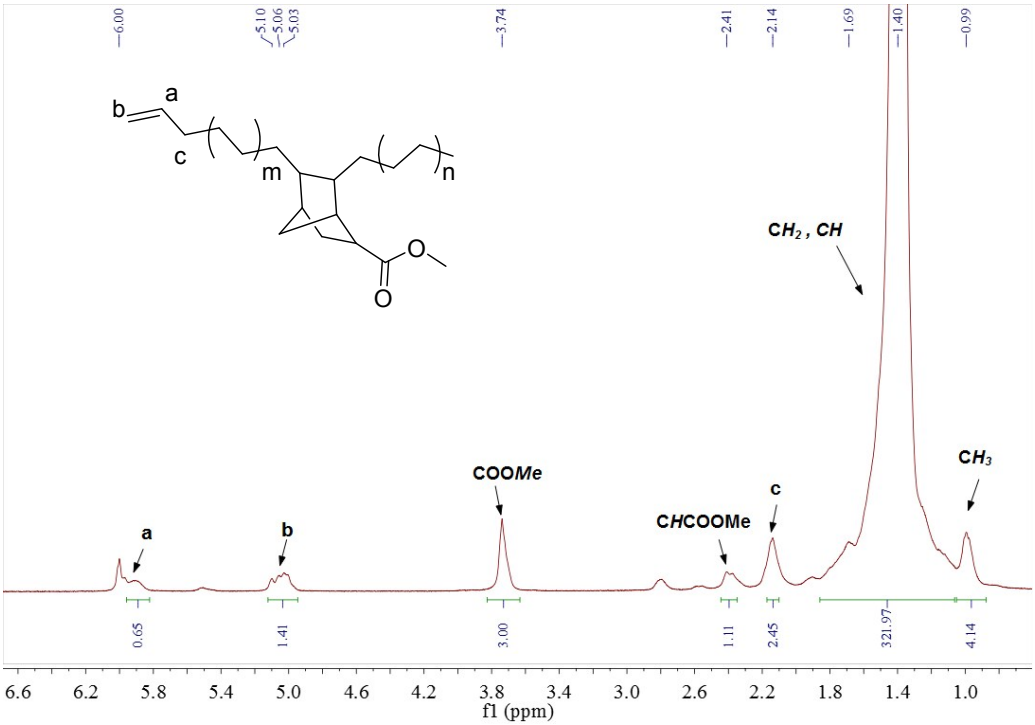


Figure S24. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120°C) of copolymer (table 2, entry 4).

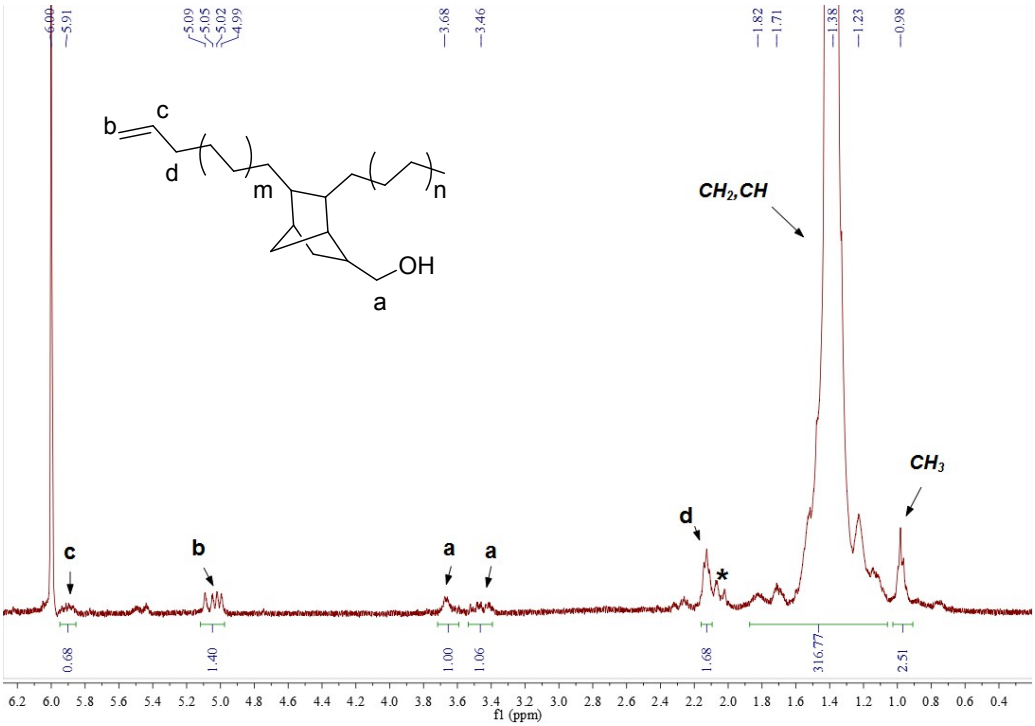


Figure S25. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120°C) of copolymer (table 2, entry 5).

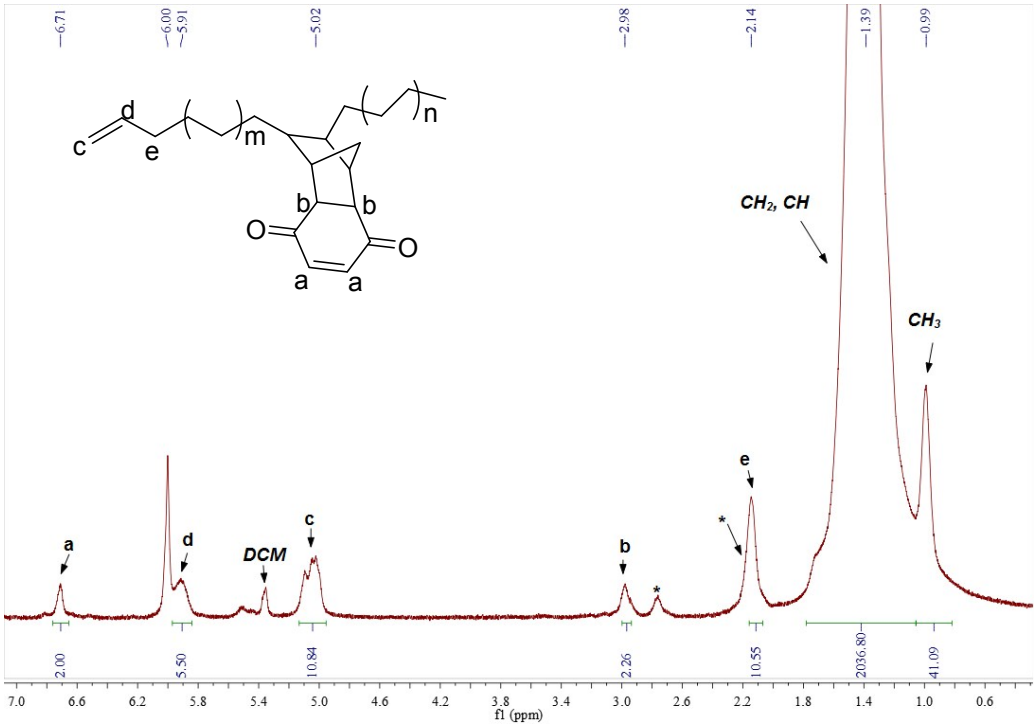


Figure S26. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120°C) of copolymer (table 2, entry 6).

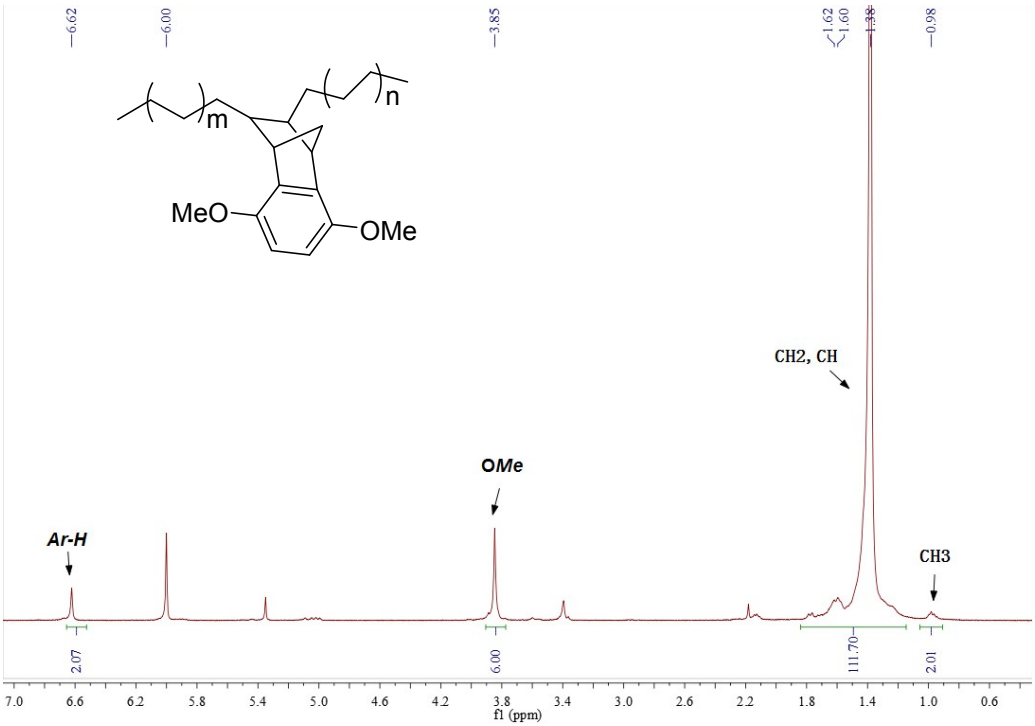


Figure S27. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120°C) of copolymer (table 2, entry 7).

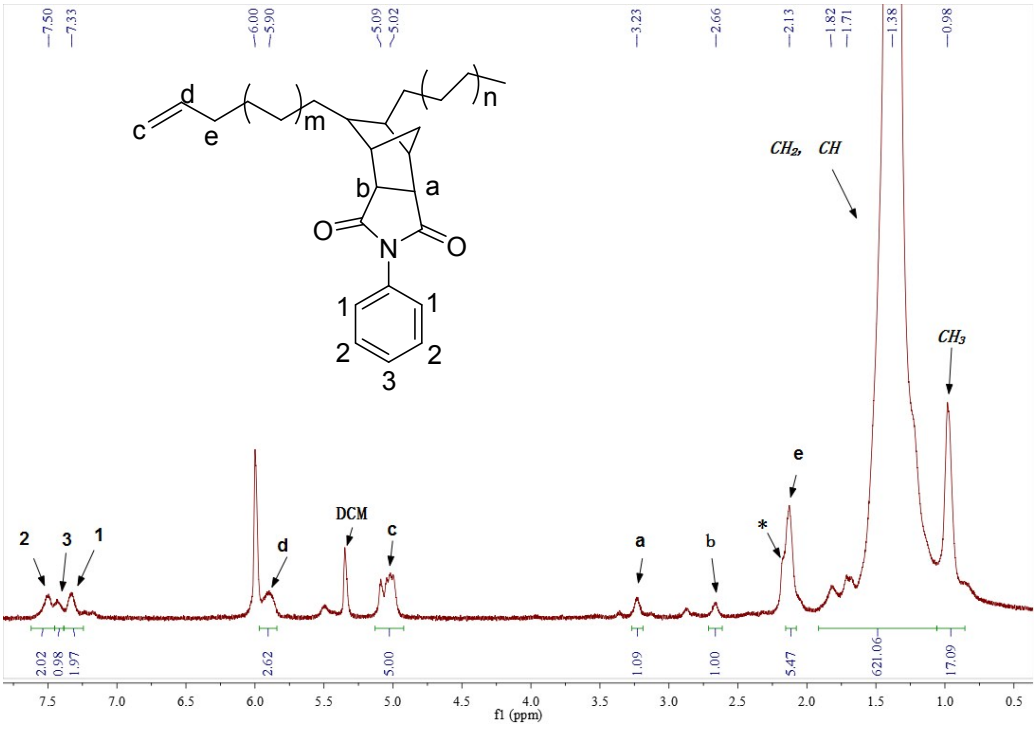
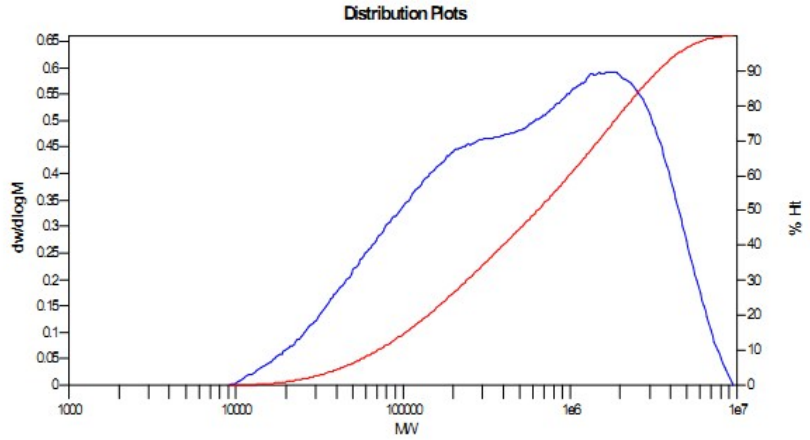


Figure S28. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120°C) of copolymer (table 2, entry 8).

4. GPC traces and DSC data of (co)polymers.



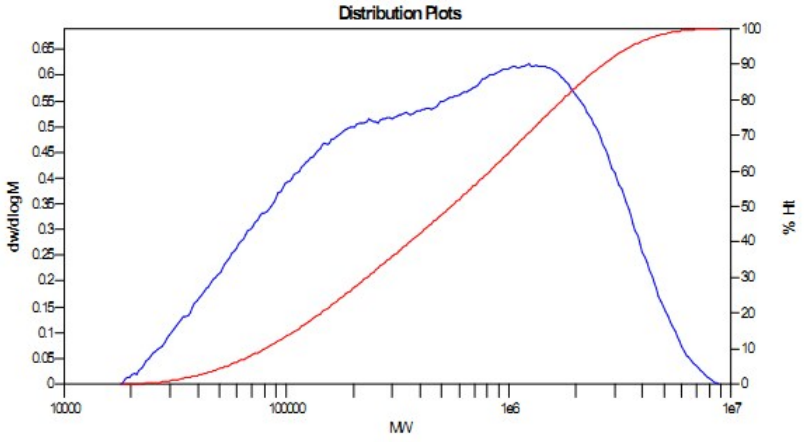
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1766776	188242	1233739	2984341	4247675	1006771	6.554

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.20	11.37	15.02	8.12218	0	1313.82	100

Figure S29. GPC trace of the polymer (table 1, entry 1).



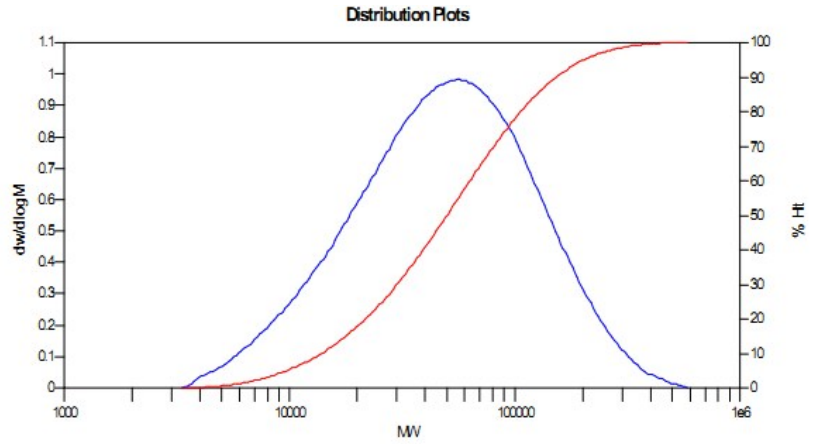
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1232055	216220	1011225	2386144	3497013	838675	4.67683

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	11.62	14.55	5.23427	0	807.216	100

Figure S30. GPC trace of the polymer (table 1, entry 2).



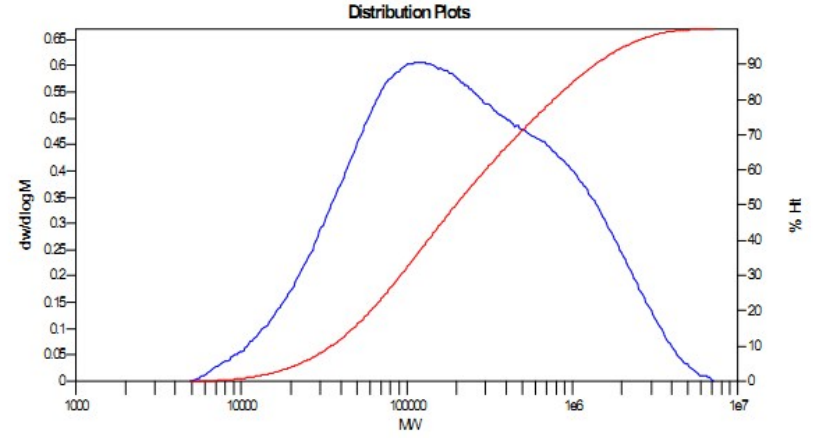
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	56849	30900	69575	130700	201886	62181	2.25162

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.13	13.75	15.72	8.74489	0	852.362	100

Figure S31. GPC trace of the polymer (table 1, entry 3).



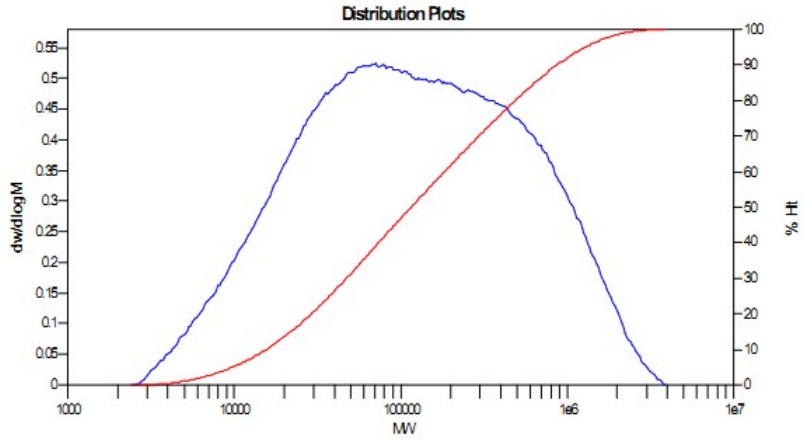
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	114128	86385	498290	1602912	2689518	389818	5.76825

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.40	13.27	15.45	9.03055	0	1428.19	100

Figure S32. GPC trace of the polymer (table 1, entry 4).



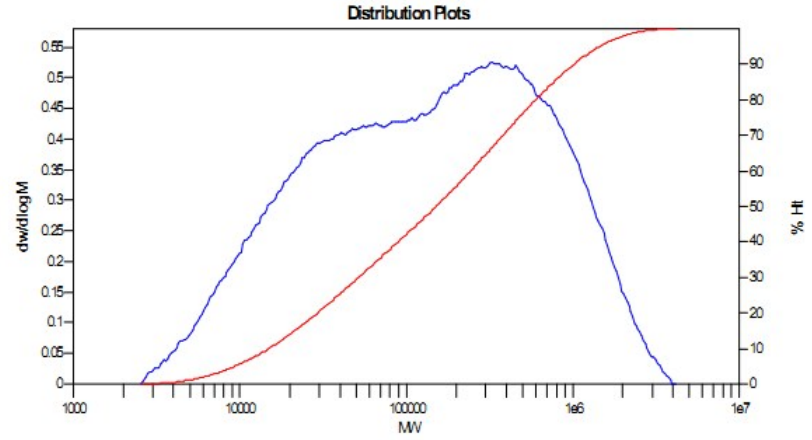
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	70759	41220	303440	970233	1550970	234398	7.36148

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.80	13.48	15.75	5.48912	0	970.688	100

Figure S33. GPC trace of the polymer (table 1, entry 12).



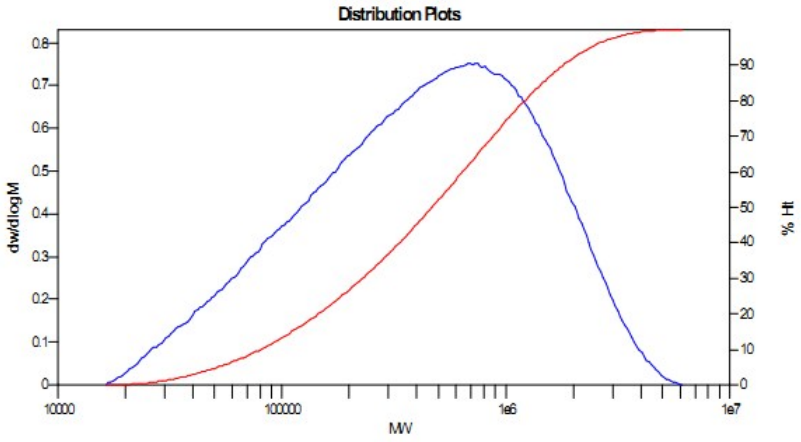
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	329754	41793	358110	1063517	1650404	278999	8.56866

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.75	12.45	15.72	4.03144	0	711.117	100

Figure S34. GPC trace of the polymer (table 1, entry 13).



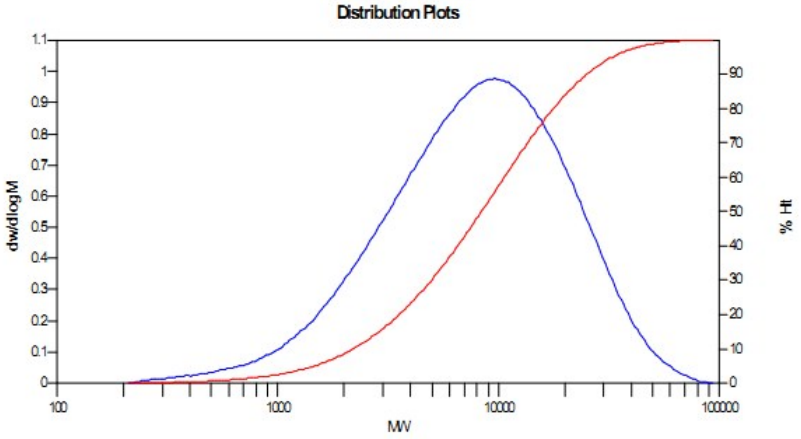
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	748094	204780	733634	1555671	2302571	629271	3.58255

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.48	11.95	14.47	7.18177	0	886.528	100

Figure S35. GPC trace of the polymer (table 1, entry 14).



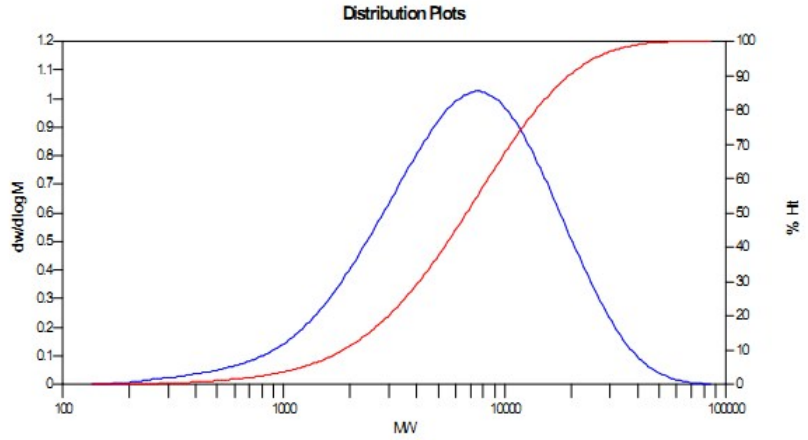
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9603	4611	11398	20784	30913	10203	2.47191

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.40	14.98	17.63	17.0614	0	1672.84	100

Figure S36. GPC trace of the copolymer (table 2, entry 2).



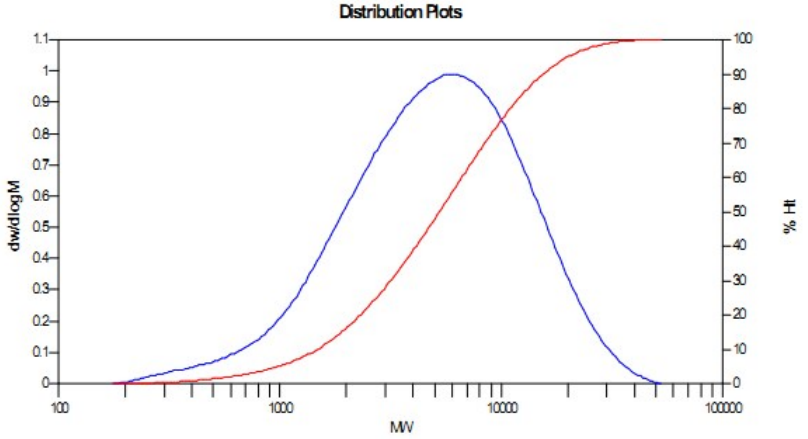
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	7735	3770	9056	16372	24856	8139	2.40212

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.47	15.13	17.93	40.7005	0	3808.37	100

Figure S37. GPC trace of the copolymer (table 2, entry 4).



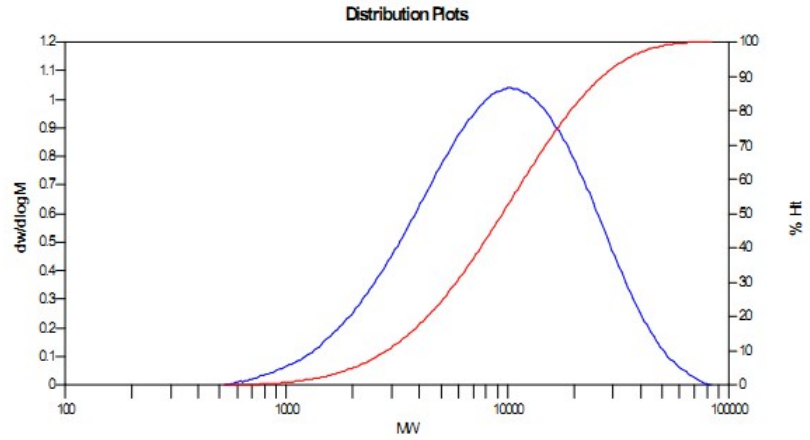
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6082	3055	7102	12688	18661	6387	2.32471

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.80	15.30	17.75	19.9426	0	1931.17	100

Figure S38. GPC trace of the copolymer (table 2, entry 6).



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	10320	6068	12532	21452	30819	11373	2.06526

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.48	14.93	17.00	11.4124	0	1051.57	100

Figure S39. GPC trace of the copolymer (table 2, entry 8).

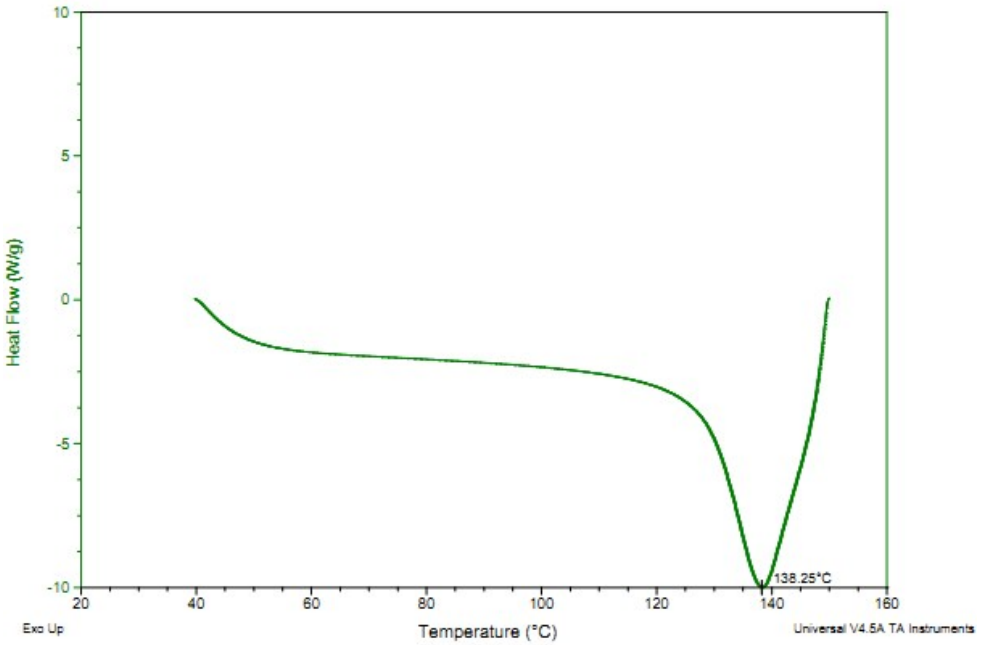


Figure S40. DSC data of the polymer (table 1, entry 1).

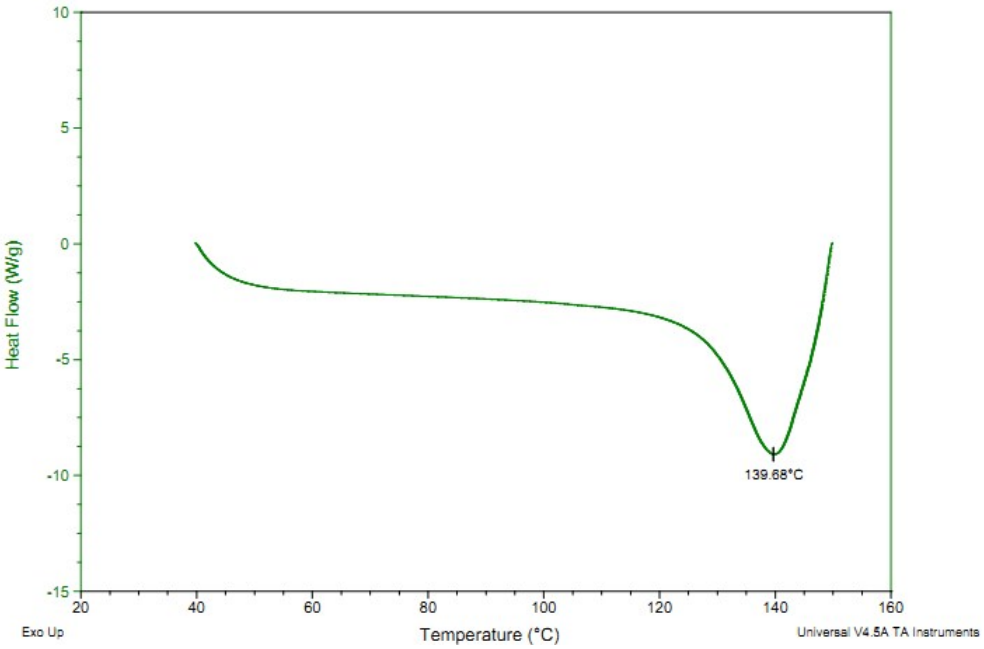


Figure S41. DSC data of the polymer (table 1, entry 2).

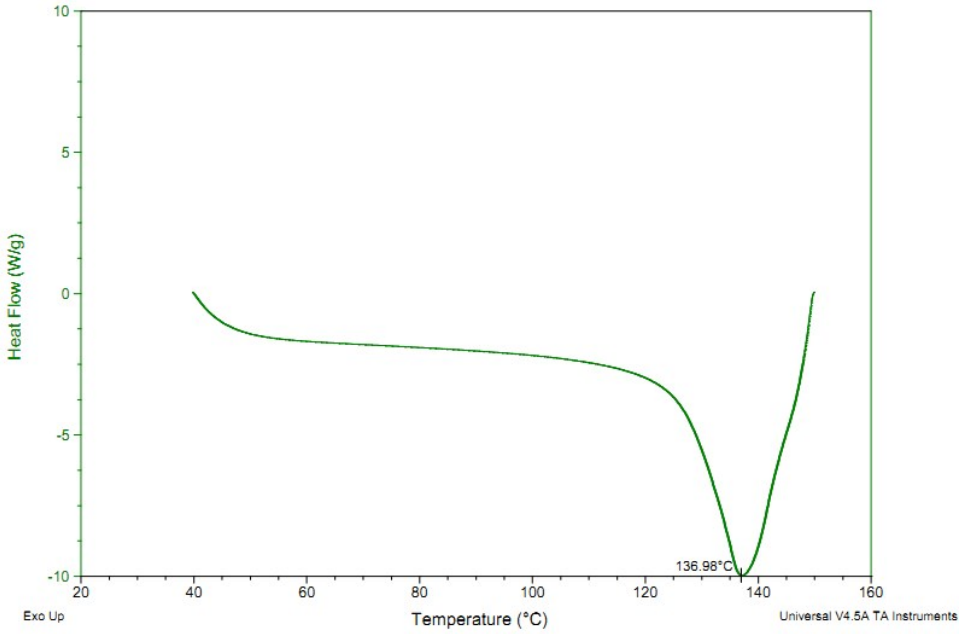


Figure S42. DSC data of the polymer (table 1, entry 3).

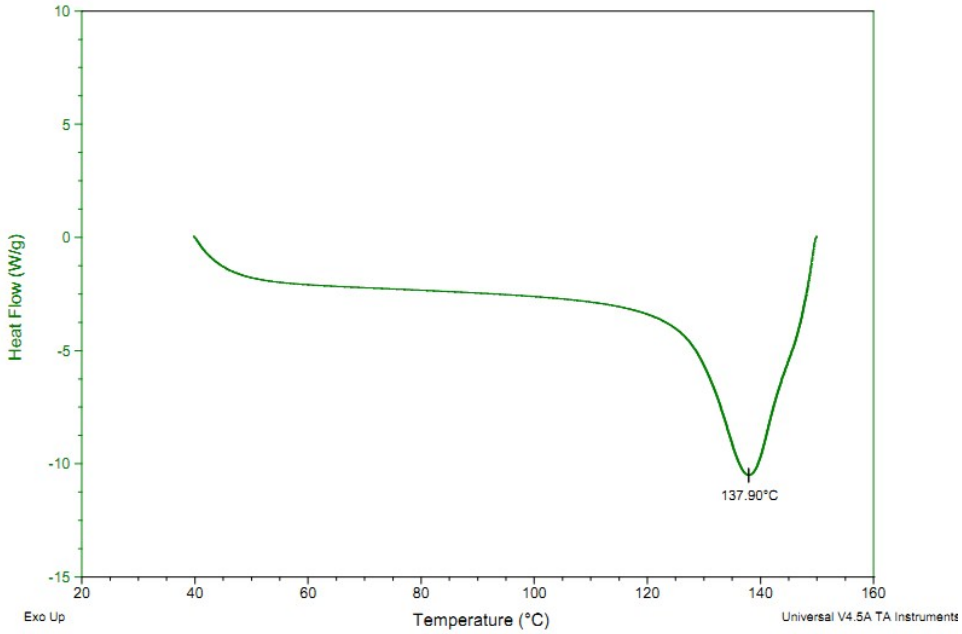


Figure S43. DSC data of the polymer (table 1, entry 4).

5. References.

1 P. Perrotin, J. S. J. McCahill, G. Wu and S. L. Scott, *Chem. Commun.,* 2011, **47,** 6948-6950.

2 A. Nakamura, T. Kageyama, H. Goto, B. P. Carrow, S. Ito and K. Nozaki, *J. Am. Chem. Soc.,* 2012, **134,** 12366-12369.

3 Polymer characteristics can be referred to (a) S. Liu, S. Borkar, D. Newsham, H. Yennawar and A. Sen, *Organometallics,* 2007, **26,** 210-216; (b) A. Ravasio, L. Boggioni and I. Tritto, *Macromolecules,* 2011, **44,** 4180-4186; (c) Y. Na, D. Zhang and C. Chen, *Polym. Chem.,* 2017, **8,** 2405-2409.

6. X-ray Crystallography.

Table S1. Crystal data and structure refinement for Ni-O^{i}Pr.

Identification code	**Ni-O^{i}Pr**
Empirical formula	$C_{54}H_{50}NiO_5P_2S$
Formula weight	931.65
Temperature/K	293
Crystal system	Monoclinic
Space group	P2(1)/c
a/Å	20.5636(16)
b/Å	12.4414(7)
c/Å	20.1995(14)
α/°	90
β/°	113.317(3)
γ/°	90
Volume/Å^3	4745.8(6)
Z	4
ρ_{calc}g/cm^3	1.304
μ/mm^{-1}	2.014
F(000)	1952
Crystal size/mm^3	0.18 × 0.10 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.52 to 132.10
Index ranges	-22 ≤ h ≤ 24, -8 ≤ k ≤ 14, -23 ≤ l ≤ 22
Reflections collected	16945
Independent reflections	8272 [Rint = 0.0718, Rsigma = 0.1114]
Data/restraints/parameters	8272/0/594
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R1 = 0.0655, wR2 = 0.1367
Final R indexes [all data]	R1 = 0.1367, wR2 = 0.1570

Table S2. Crystal data and structure refinement for Ni-F.

Identification code	**Ni-F**
Empirical formula	C_{48} H_{36} F_2 Ni O_3 P_2 S
Formula weight	851.48
Temperature/K	293 K
Crystal system	Triclinic
Space group	P-1
a/Å	11.0856(7)
b/Å	12.1478(9)
c/Å	17.3866(10)
α/°	87.173(5)
β/°	74.800(5)
γ/°	62.917(7)
Volume/Å^3	2005.0(2)
Z	2
ρ_{calc}g/cm^3	1.410
μ/mm^{-1}	2.368
F(000)	880
Crystal size/mm^3	0.11 × 0.10× 0.06
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.20 to 132.06
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 14, -18≤ l ≤ 20
Reflections collected	12166
Independent reflections	6978 [R_{int} = 0.0464, R_{sigma} = 0.0878]
Data/restraints/parameters	6978/0/514
Goodness-of-fit on F^2	11.016
Final R indexes [I>=2σ (I)]	R1 = 0.0531, wR2 = 0.0830
Final R indexes [all data]	R1 = 0.0844, wR2 = 0.0934

Table S3. Crystal data and structure refinement for Ni-H.

Identification code	**Ni-H**
Empirical formula	$C_{98}H_{80}Cl_4Ni_2O_6P_4S_2$
Formula weight	1800.84
Temperature/K	298 K
Crystal system	Monoclinic
Space group	P2(1)/c
a/Å	11.0906(10)
b/Å	18.6539(12)
c/Å	21.9850(18)
α/°	90.00
β/°	114.088(3)
γ/°	90.00
Volume/Å^3	4152.3(6)
Z	2
ρ_{calc}g/cm^3	1.440
μ/mm^{-1}	3.402
F(000)	1864
Crystal size/mm^3	0.12× 0.08× 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.46 to 132.08
Index ranges	-13≤ h ≤ 13, -22 ≤ k ≤ 16, -26 ≤ l ≤ 21
Reflections collected	14900
Independent reflections	7239 [R_{int} = 0.0572, R_{sigma} = 0.0881]
Data/restraints/parameters	7239/0/533
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R1 = 0.0579, wR2 = 0.1260
Final R indexes [all data]	R1 = 0.1013, wR2 = 0.1468