

Supporting Information:

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1. Figures and Tables

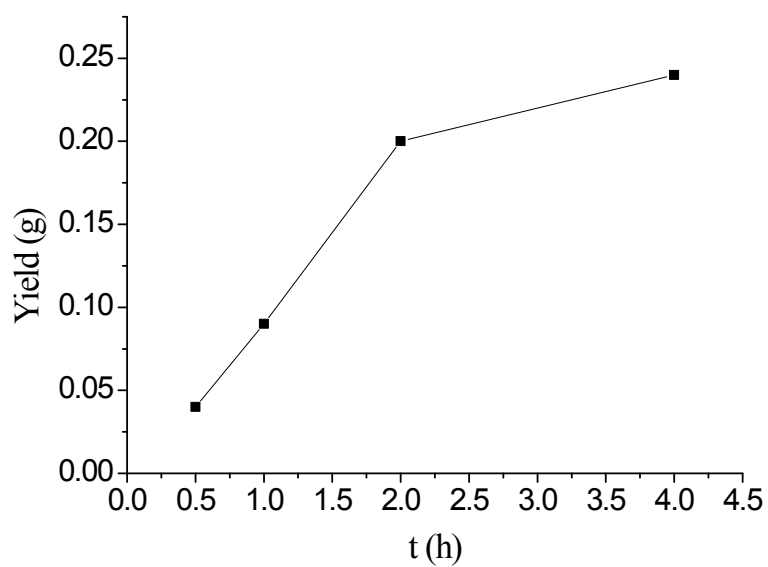


Figure S1. Productivity versus time for complex **Ni3** at 30 °C.

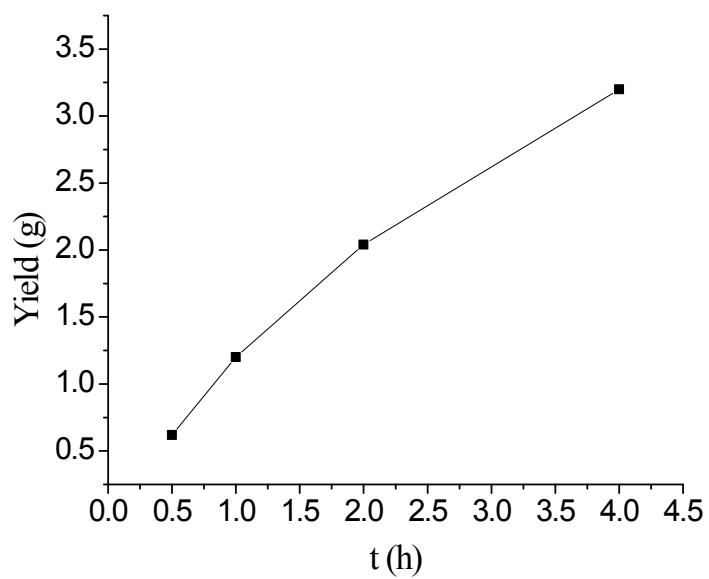


Figure S2. Productivity versus time for complex **Ni3** at 80 °C.

Table S1. Ethylene homopolymerization with **Ni1-Ni3**^a

Ent.	Cat.	cocatalyst (eq)	T (°C)	Yield (g)	Act. ^b	<i>T</i> _m ^c (°C)
1	Ni1-Br	MAO (100)	30	-	-	-
2	Ni1-Br	MAO (100)	80	-	-	-
3	Ni1-allyl	B(C ₆ F ₅) ₃ (10)	80	0.19	1.9	115
4	Ni1-allyl	MAO (100)	80	0.28	2.8	118
5	Ni1-allyl	AlEt ₂ Cl (100)	80	-	-	-
6	Ni1-allyl	AlEtCl ₂ (100)	80	-	-	-

^aPolymerization conditions: 10 μmol catalyst, 18 mL toluene, 2 mL dichloromethane, 9 atm ethylene pressure, 1.2 eq. NaBAF, 1 h. ^bActivity is in unit of 10⁴ g·mol⁻¹·h⁻¹.

^cDetermined by differential scanning calorimetry, third heating.


2. Experimental sections

2.1 General Considerations

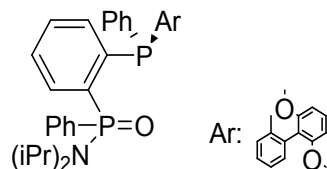
All experiments were carried out under a dry Nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^1H , ^{13}C NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^1H and ^{13}C NMR spectra were referenced to the residual solvent; 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 $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Molecular weight and molecular weight distribution of the polymers 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 o-dichlorobenzene as a solvent and calibrated with polystyrene standards. Dichloromethane, toluene and hexanes were purified by solvent purification systems. Ligands were prepared by literature procedure. All other reagents were purchased from commercial sources and used without purification.

Differential scanning calorimetry (DSC). DSC was performed by a DSC Q20 from TA Instruments. Samples were quickly heated to 150°C and kept for 5 min to remove thermal history, then cooled to 40°C at a rate of 10 K/min, and finally reheated to 120°C at the same rate under a nitrogen flow (50 mL/min). The maximum points endotherm (heating scan) were taken as the melting temperature (T_m).

2.2 Standard Procedure for the Synthesis of L3

To a solution of phosphinic amide (2.31 mmol) in 20 mL of toluene and TMEDA (0.49 mL, 2.54 mmol) a solution of n-BuLi (1.0 mL of a 2.4 M solution in hexane, 2.4 mmol) was added at - 80 °C. After one hour, ClPR_1R_2 (R_1 :  R_2 : Ph) was added. The reaction was stirred at room temperature for 2 hours and then was poured into ice-water, extracted with dichloromethane (3×15 mL), washed with sodium

thiosulphate (2×15 mL), dried over anhydrous sodium sulphate and evaporated to dryness under vacuum to give a white solid. Purification by column chromatography afforded white solids.

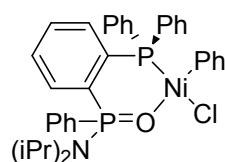


Yield 62% (0.372 g). White solid. ¹H NMR (400 MHz, CDCl₃): δ 7.93 (s, aryl-*H*), 7.72 (s, aryl-*H*), 7.59 (dd, *J* = 11.2, 8.0 Hz, 1H, aryl-*H*), 7.44 – 7.27 (m, 6H, aryl-*H*), 7.22 – 7.09 (m, 7H, aryl-*H*), 7.00 (dt, *J* = 25.2, 6.8 Hz, 2H, aryl-*H*), 6.90 – 6.75 (m, 2H, aryl-*H*), 6.54 (d, *J* = 8.3 Hz, aryl-*H*), 6.33 (d, *J* = 8.3 Hz, aryl-*H*), 6.23 (d, *J* = 8.2 Hz, aryl-*H*), 5.86 (d, *J* = 8.2 Hz, aryl-*H*), 3.79 (s, 2H, -OCH₃), 3.65 (s, 1H, -OCH₃), 3.36 (dd, *J* = 13.7, 6.8 Hz, 2H, -CH(CH₃)₂), 3.30 (s, 2H, -OCH₃), 2.84 (s, 1H, -OCH₃), 1.11 – 0.98 (m, 12H, -CH(CH₃)₂). ³¹P NMR (162 MHz, CDCl₃): δ 31.08 (s), 30.00 (s), -11.74 (s), -12.54 (s). ¹³C NMR (101 MHz, CDCl₃): δ 156.86 (d, *J* = 1.5 Hz), 156.45 (s), 156.40 (d, *J* = 2.0 Hz), 156.02 (s), 143.49 (d, *J* = 12.8 Hz), 143.21 (s), 143.08 (d, *J* = 2.8 Hz), 142.82 (d, *J* = 13.9 Hz), 140.64 (s), 140.46 (d, *J* = 5.7 Hz), 140.24 (s), 140.10 (s), 139.86 (d, *J* = 11.2 Hz), 139.66 (s), 138.89 (d, *J* = 5.6 Hz), 138.68 (d, *J* = 6.1 Hz), 138.19 (s), 137.94 (s), 137.51 (s), 137.28 (s), 136.91 (s), 136.66 (s), 136.26 (s), 136.03 (s), 135.12 (s), 134.96 (s), 134.83 (s), 134.47 (s), 134.10 (s), 133.89 (s), 133.28 (s), 132.75 (d, *J* = 5.8 Hz), 132.54 (d, *J* = 5.3 Hz), 131.91 (d, *J* = 9.7 Hz), 131.55 (dd, *J* = 9.3, 4.9 Hz), 131.22 (d, *J* = 9.2 Hz), 130.00 (d, *J* = 4.5 Hz), 129.91 (d, *J* = 4.4 Hz), 129.41 (m), 129.25 (d, *J* = 2.0 Hz), 129.18 (d, *J* = 2.1 Hz), 127.63 (s), 127.03 (s), 126.95 (s), 126.63 (s), 126.59 (s), 126.51 (t, *J* = 3.6 Hz), 126.14 (d, *J* = 3.8 Hz), 125.95 (d, *J* = 7.4 Hz), 125.59 (d, *J* = 11.4 Hz), 125.26 (d, *J* = 12.0 Hz), 118.17 (d, *J* = 6.1 Hz), 117.67 (s), 103.12 (s), 102.77 (s), 102.15 (s), 101.68 (s), 54.95 (s, -OCH₃), 54.86 (d, *J* = 1.7 Hz, -OCH₃), 54.10 (s, -OCH₃), 46.47 (d, *J* = 3.6 Hz, -CH(CH₃)₂), 46.28 (d, *J* = 3.7 Hz, -CH(CH₃)₂), 22.63 (d, *J* = 3.2 Hz, -CH(CH₃)₂), 22.44 (dd, *J* = 5.1, 3.0 Hz, -CH(CH₃)₂), 21.90 (d, *J* = 2.9 Hz, -CH(CH₃)₂). ³¹P NMR

(162 MHz, CDCl₃): δ 31.08 (s, 1H), 30.00 (s, 1H), -11.74 (s, 1H), -12.54 (s, 1H).
 HRMS (m/z): calcd for C₃₈H₄₂NO₃P₂: 622.2640, found: 622.2627 [M + H]⁺.

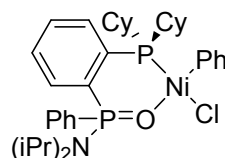
2.3 Standard Procedure for the Synthesis of Complexes Ni1-Ni3

Ligand (1 mmol) and Ni(COD)₂ (0.96 mmol) were weighed into a small vial on the bench top. Chlorobenzene (5 mL) was added to the solids, and the mixture was stirred at room temperature for 12 hours. Hexane was then layered onto the filtrate and let it stir. After several hours, the yellow solid that had formed was collected by filtration, washed with hexane (3 \times 2mL), and dried under vacuum to afford a yellow solid.



Ni1

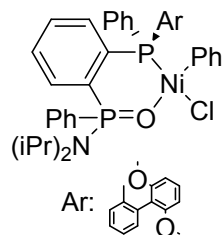
Yield 72 % (0.453 g). Red solid. ¹H NMR (400 MHz, C₆D₆) δ 8.34 – 7.40 (m, 11H, aryl-*H*), 7.06 – 6.44 (m, 13H, aryl-*H*), 3.36 (s, 2H, -CH(CH₃)₂), 1.22 (s, 6H, -CH(CH₃)₂), 1.13 (s, 6H, -CH(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃) δ 140.75 (s), 140.37 (s), 137.50 (s), 136.63 (s), 135.45 (d, *J* = 10.5 Hz), 134.25 (d, *J* = 11.4 Hz), 133.81 (d, *J* = 10.3 Hz), 133.50 (d, *J* = 10.1 Hz), 132.30 (s), 131.81 (s), 131.44 (s), 130.07 (s), 129.94 (s), 129.76 (s), 128.48 (s), 128.35 (s), 128.23 (s), 128.10 (s), 127.99 (s), 125.34 (s), 120.78 (s), 48.73 (s, -CH(CH₃)₂), 23.81 (s, -CH(CH₃)₂), 23.55 (s, -CH(CH₃)₂). ³¹P NMR (162 MHz, C₆D₆) δ 32.16 (d, *J* = 7.9 Hz), 20.86 (d, *J* = 9.1 Hz). MALDI-TOF-MS (m/z): calcd for C₃₀H₃₆NNiO₂P₂: 562.1575, found: 562.0959 [M-Cl-Ph+H₃O]⁺. Anal. Calcd for C₃₆H₃₈ClNNiOP₂: C, 65.83; H, 5.83; N, 2.13; Found: C, 65.46; H, 5.75; N, 2.15.



Ni2

Yield 75 % (0.496 g). Orange solid. ³¹P NMR (162 MHz, CDCl₃) δ 36.11 (d, *J* = 12.8 Hz), 14.08 (d, *J* = 13.2 Hz). MALDI-TOF-MS (m/z): calcd for C₃₀H₄₈NNiO₂P₂:

574.2514, found: 574.1851 $[M-Cl-Ph+H_3O]^+$. Anal. Calcd for $C_{36}H_{50}ClNNiOP_2$: C, 64.64; H, 7.53; N, 2.09; Found: C, 64.41; H, 7.45; N, 2.25.

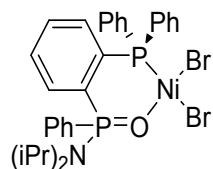


Ni3

Yield 53 % (0.403 g). Yellow solid. ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.31 (s), 35.20 (s), 16.74 (s), 12.09 (s). MALDI-TOF-MS (m/z): calcd for $C_{38}H_{44}NNiO_4P_2$: 698.2099, found: 698.1234 $[M-Cl-Ph+H_3O]^+$. Anal. Calcd for $C_{44}H_{46}ClNNiO_3P_2$: C, 66.65; H, 5.85; N, 1.77; Found: C, 66.96; H, 5.65; N, 1.65.

2.4 Standard Procedure for the Synthesis of Complex Ni1-Br

The mixture of ligand (1 mmol), $DMENiBr_2$ (308 mg, 1 mmol) and CH_2Cl_2 (20 mL) was stirred overnight at room temperature. During stirring, the color of the solution was changed from yellow to purple and some solid precipitated. The desired compound can be isolated from recrystallization from diethylether and dichloromethane. The pure compound was obtained as a purple solid.



Ni1-Br

Yield 85 % (0.600 g). Purple solid. MALDI-TOF-MS (m/z): calcd for $C_{30}H_{33}BrNNiOP_2$: 622.0574, found: 621.9866 $[M-Br]^+$. Anal. Calcd for $C_{30}H_{33}Br_2NNiOP_2$: C, 51.18; H, 4.72; N, 1.99; Found: C, 51.24; H, 4.63; N, 2.05.

2.5 General in-Situ-Activated Polymerization Procedure.

Under an inert atmosphere, a 350 mL glass thick-walled pressure vessel was charged with NaBAF (1.2 equiv), 18 mL of toluene, and a magnetic stir bar. The bottle was sealed and placed in an oil bath at the desired temperature. The vessel was pressurized with ethylene and allowed to equilibrate under constant pressure for 10

minutes with stirring. 1 μmol of nickel complex in 2 mL CH_2Cl_2 was injected into the polymerization system via syringe and stirred continuously for the desired time. With rapid stirring, the reactor was pressurized and maintained at 9.0 atm of ethylene. The polymerization was quenched via the addition of MeOH (5 mL) and the polymer was precipitated using excess acidic MeOH (methanol/HCl =50/1) and dried at 60 $^\circ\text{C}$ for 24 h under vacuum.

2.6 Procedure for Copolymerization of Ethylene and Polar Monomer

In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with NaBAF (1.2 equiv), desired amount of toluene, polar monomer 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 desired temperature using an oil bath and allowed to equilibrate for 5min. 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 desired pressure of ethylene. After a desired amount of polymerization time, the pressure vessel was vented and the polymer was precipitated in methanol and dried at 60 $^\circ\text{C}$ for 24 h under vacuum, The polar monomer incorporation (mol %) was calculated from ^1H NMR analysis.

2.7 Procedure for α -olefin polymerization by nickel complexes.

In a typical experiment, a 20 mL glass tube was charged with the required amount of NaBAF (1.2 eq) and a magnetic stirrer bar in the glovebox. Then toluene and α -olefin (8 mL) was added into the tube. The tube was warmed to 30 $^\circ\text{C}$ by using an oil bath with rapid stirring and allowed to equilibrate for 5 min. The nickel complex (3 μmol) in CH_2Cl_2 (2 mL) was injected into the tube with a syringe. After 12 h, the methanol was decanted off, and the sticky polymer was redissolved in toluene. The polymer solution was filtered through alumina or silica to remove catalyst residues. After evaporation, the resulting polymer was collected and dried under vacuum at 40 $^\circ\text{C}$ to a constant weight..

3. NMR-Spectra Data

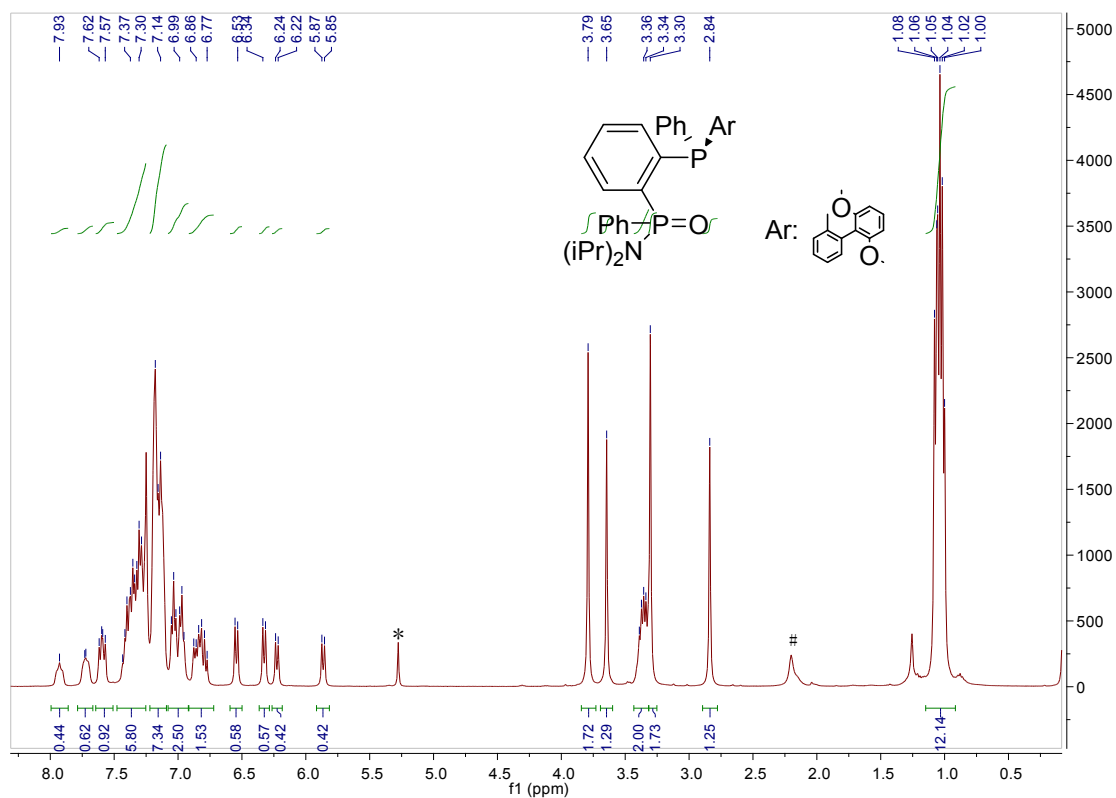


Figure S3. ¹H NMR spectrum of L3 in CDCl₃ (* is DCM, # is impurity).

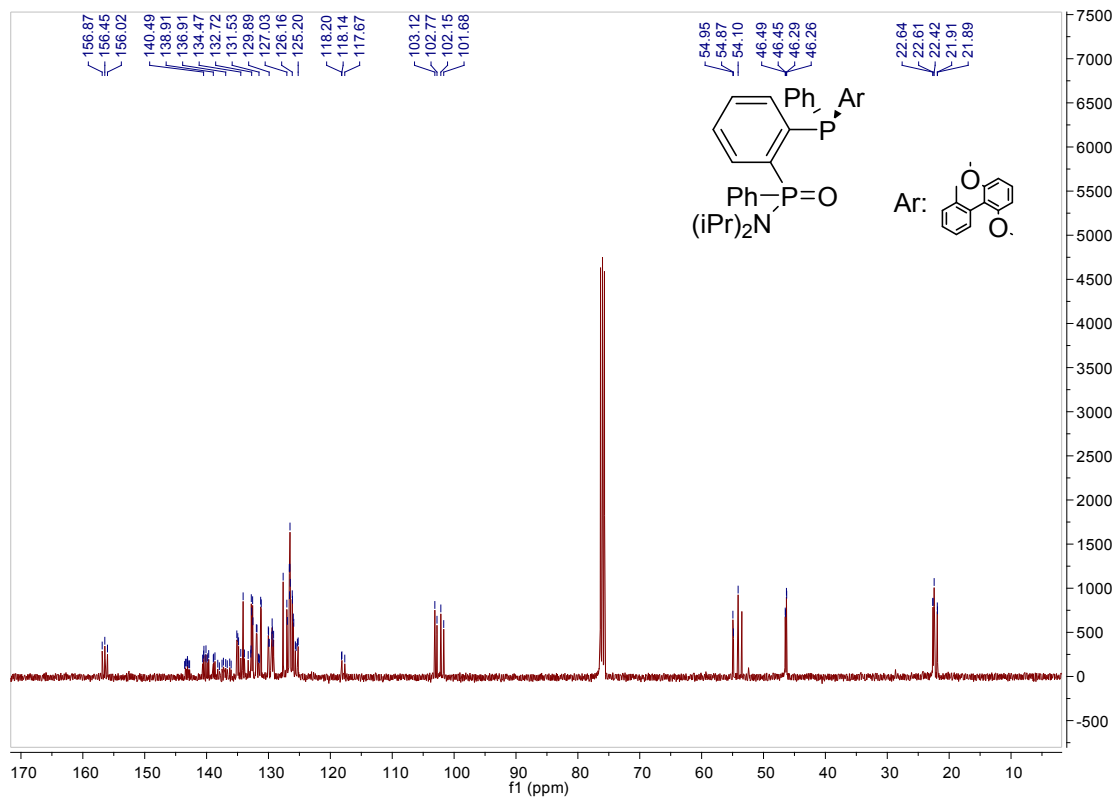


Figure S4. ¹³C NMR spectrum of L3 in CDCl₃.

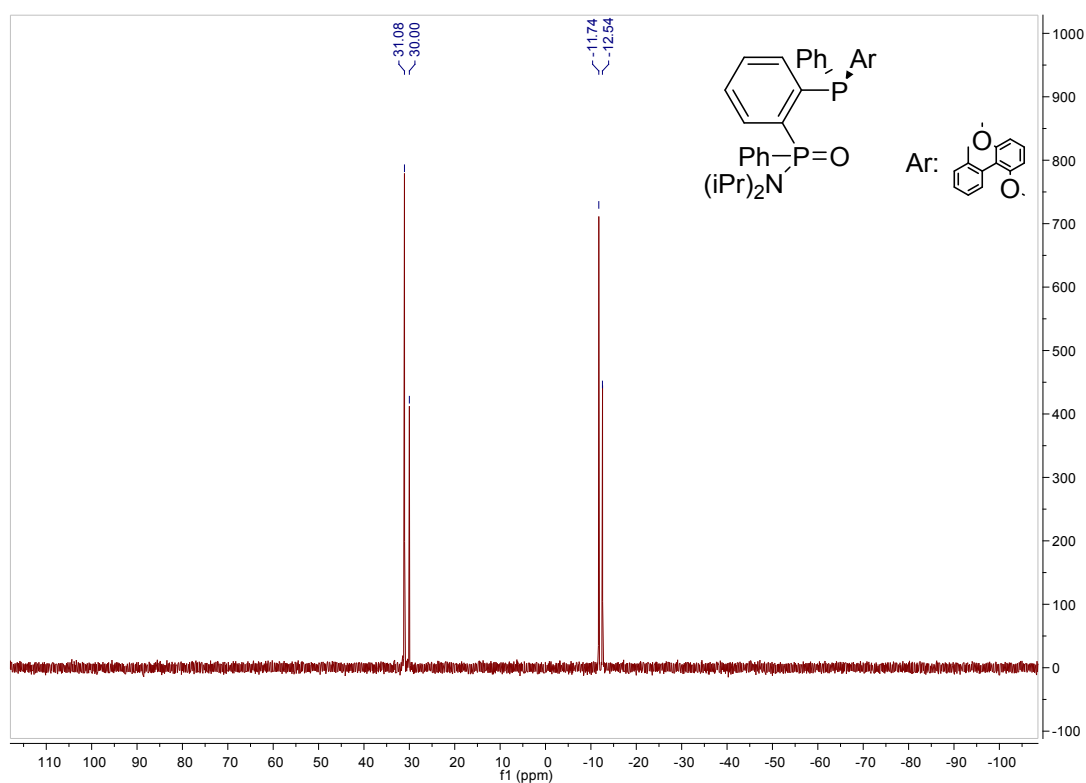


Figure S5. ³¹P NMR spectrum of **L3** in CDCl₃.

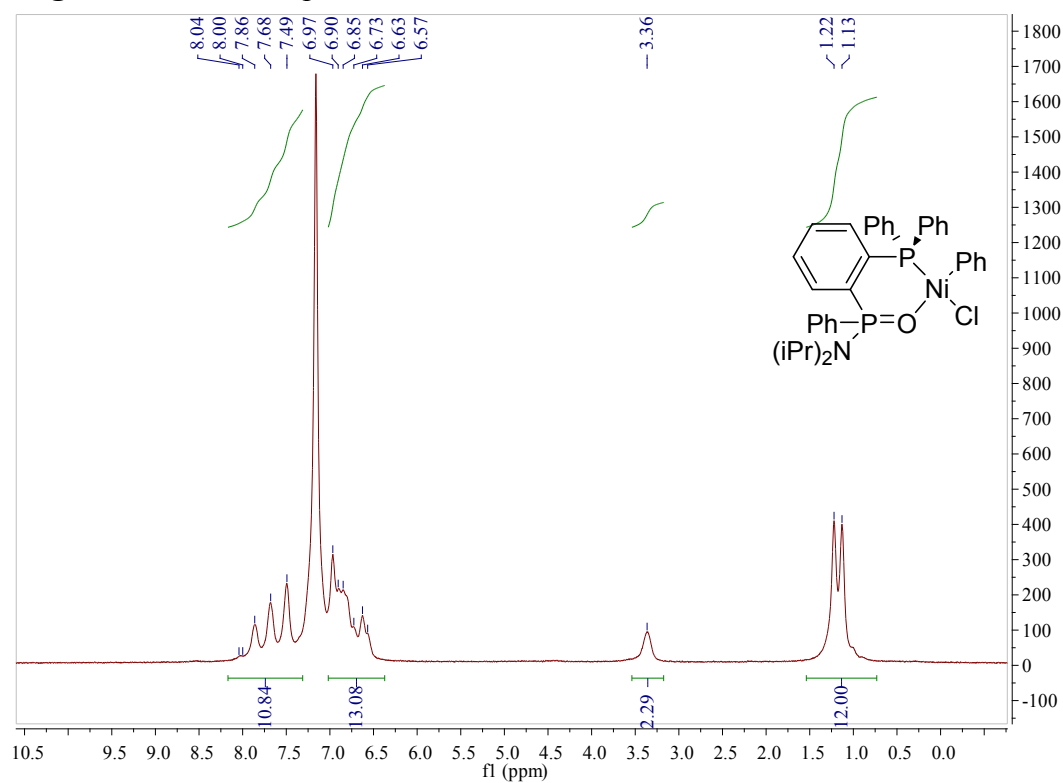


Figure S6. ¹H NMR spectrum of **Ni1** in C₆D₆.

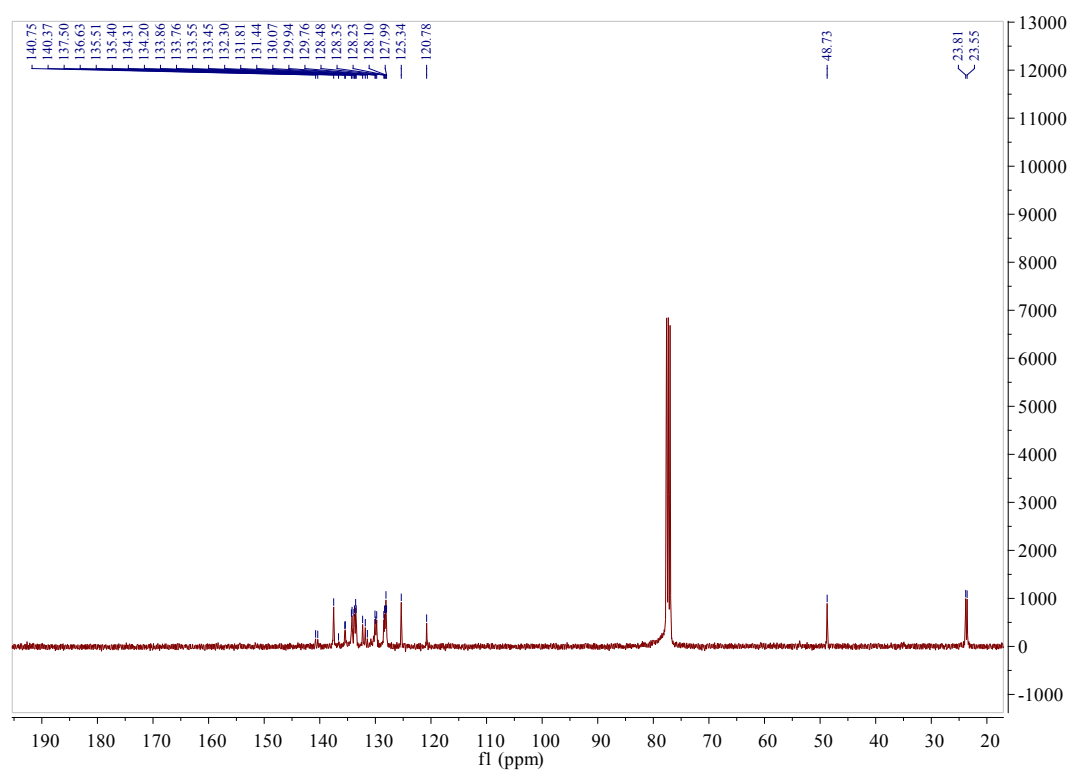


Figure S7. ^{13}C NMR spectrum of **Ni1** in CDCl_3 .

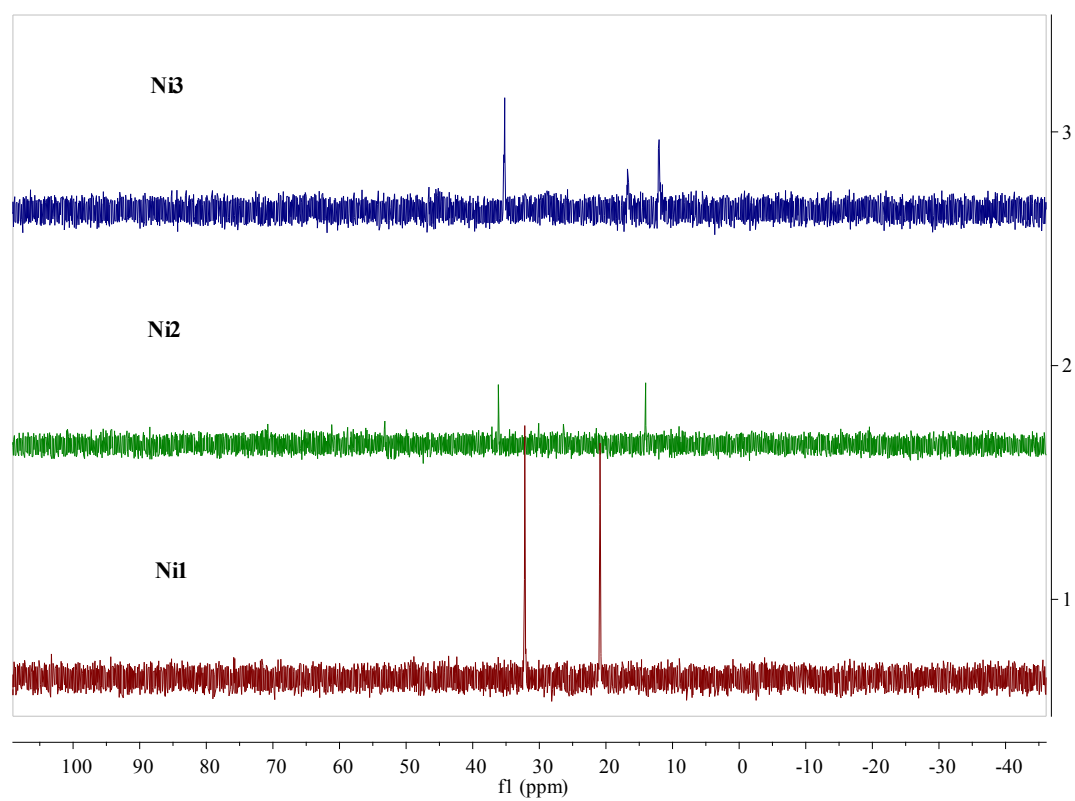


Figure S8. ^{31}P NMR spectrum of **Ni1** in C_6D_6 , **Ni2** and **Ni3** in CDCl_3 .

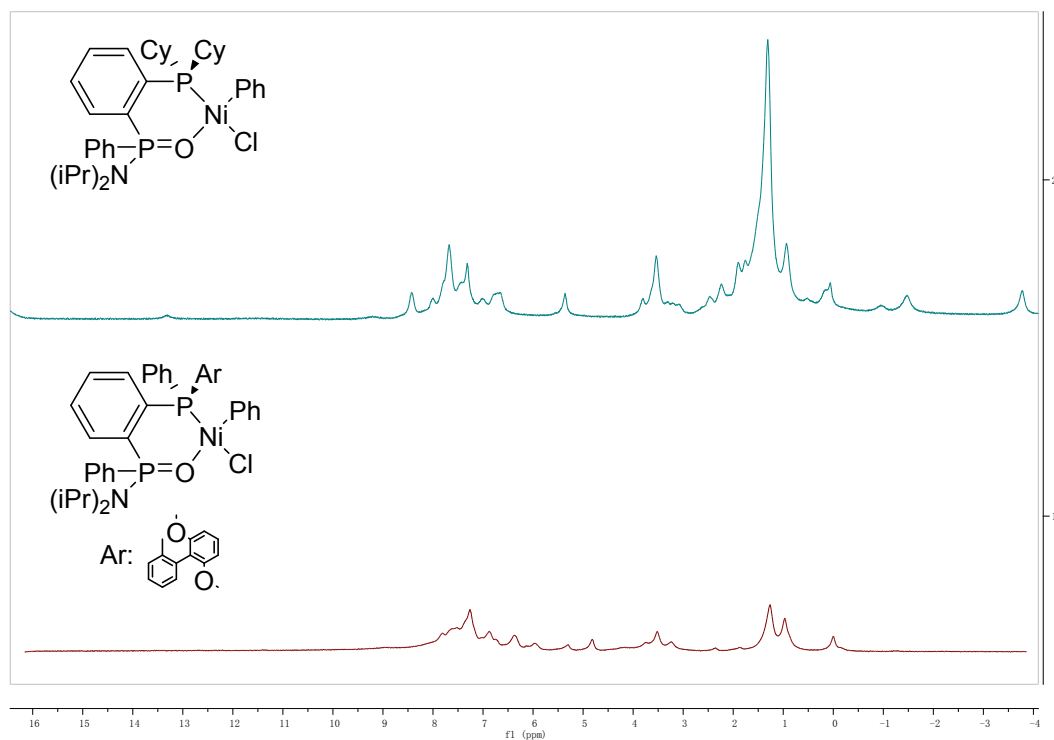


Figure S9. ^1H NMR spectrum of **Ni2** and **Ni3** in CDCl_3 .

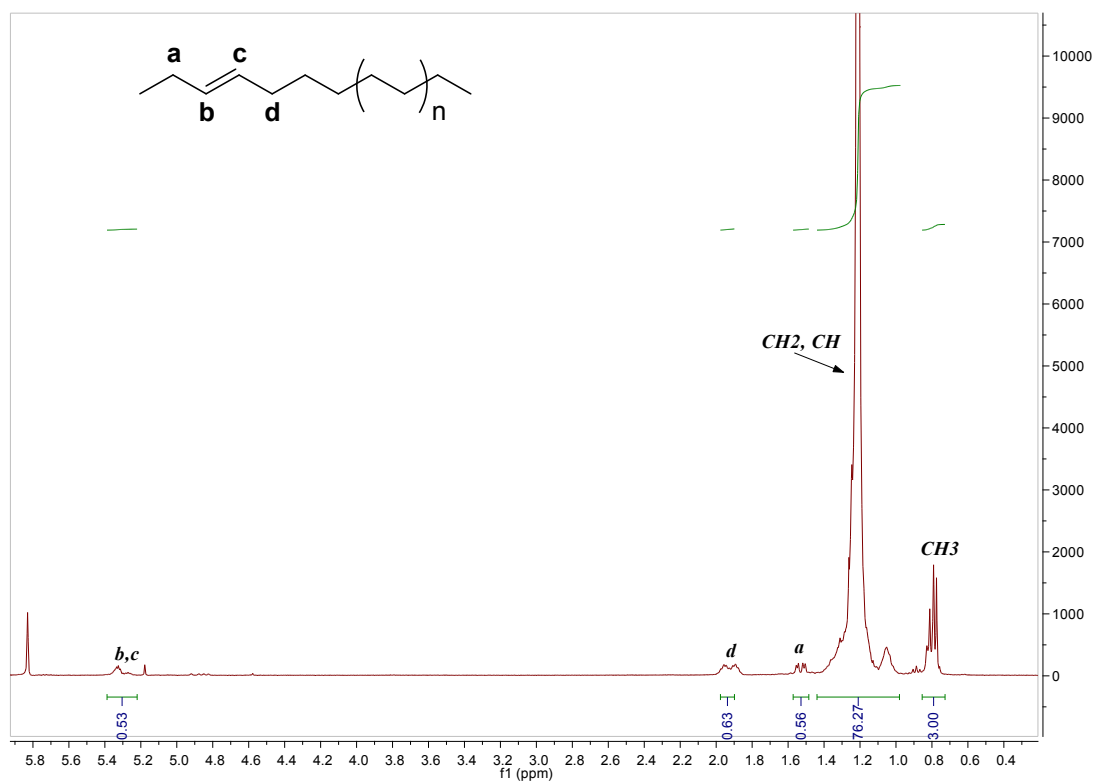


Figure S10. ^1H NMR spectrum of the polyethylene generated by complex **Ni3** from table 1, entry 5. (in $\text{CDCl}_2\text{CDCl}_2$ at 120°C).

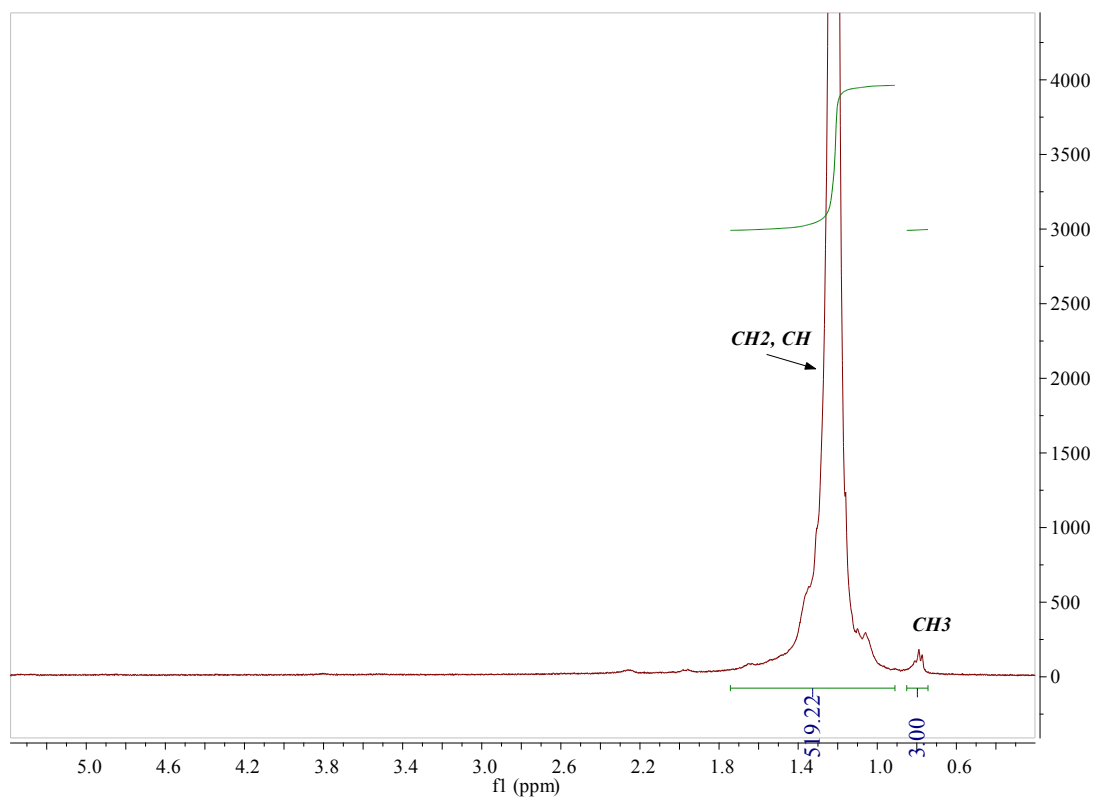


Figure S11. ¹H NMR spectrum of the polyethylene generated by complex **Ni3** from table 1, entry 6. (in CDCl₂CDCl₂ at 120 °C).

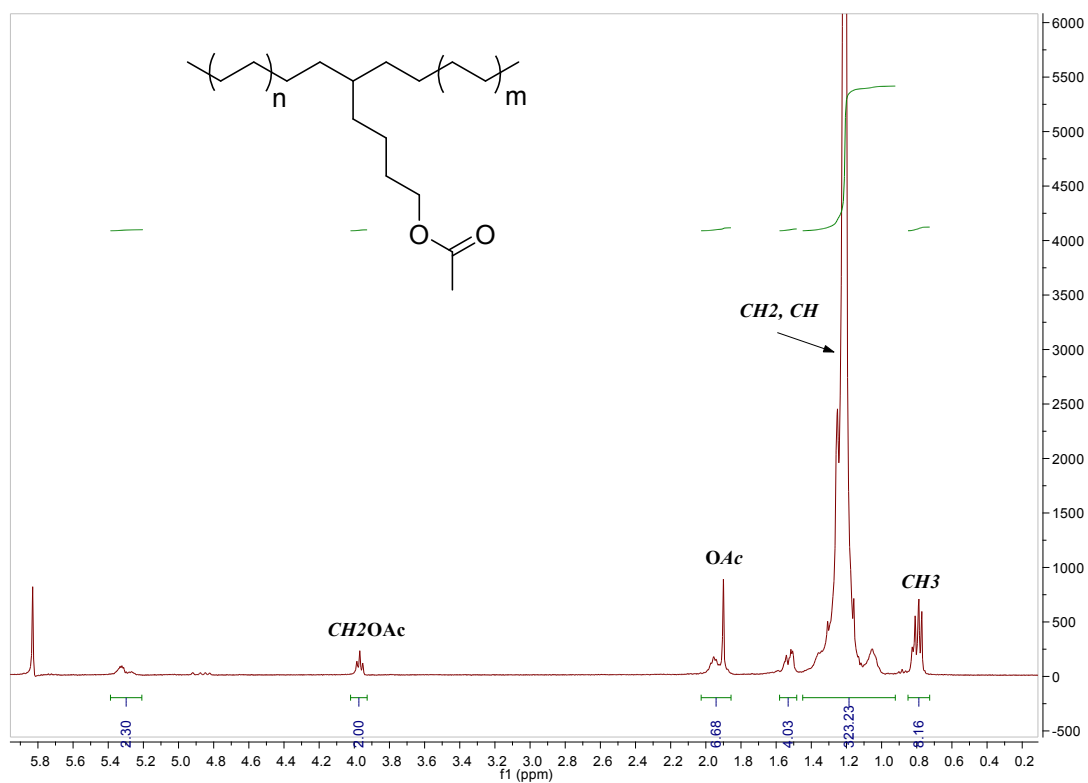


Figure S12. ¹H NMR spectrum of the copolymer generated by complex **Ni3** from table 2, entry 9. (in CDCl₂CDCl₂ at 120 °C).

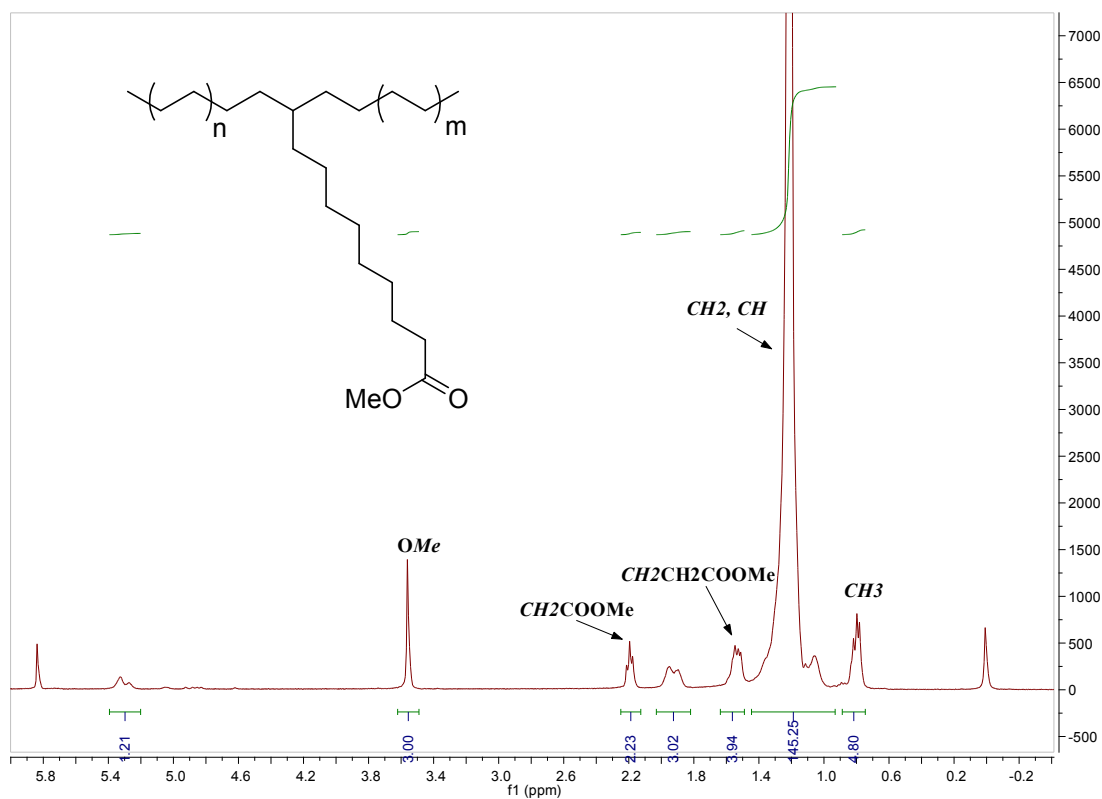


Figure S13. ^1H NMR spectrum of the copolymer generated by complex **Ni3** from table 2, entry 4. (in $\text{CDCl}_2\text{CDCl}_2$ at 120°C).

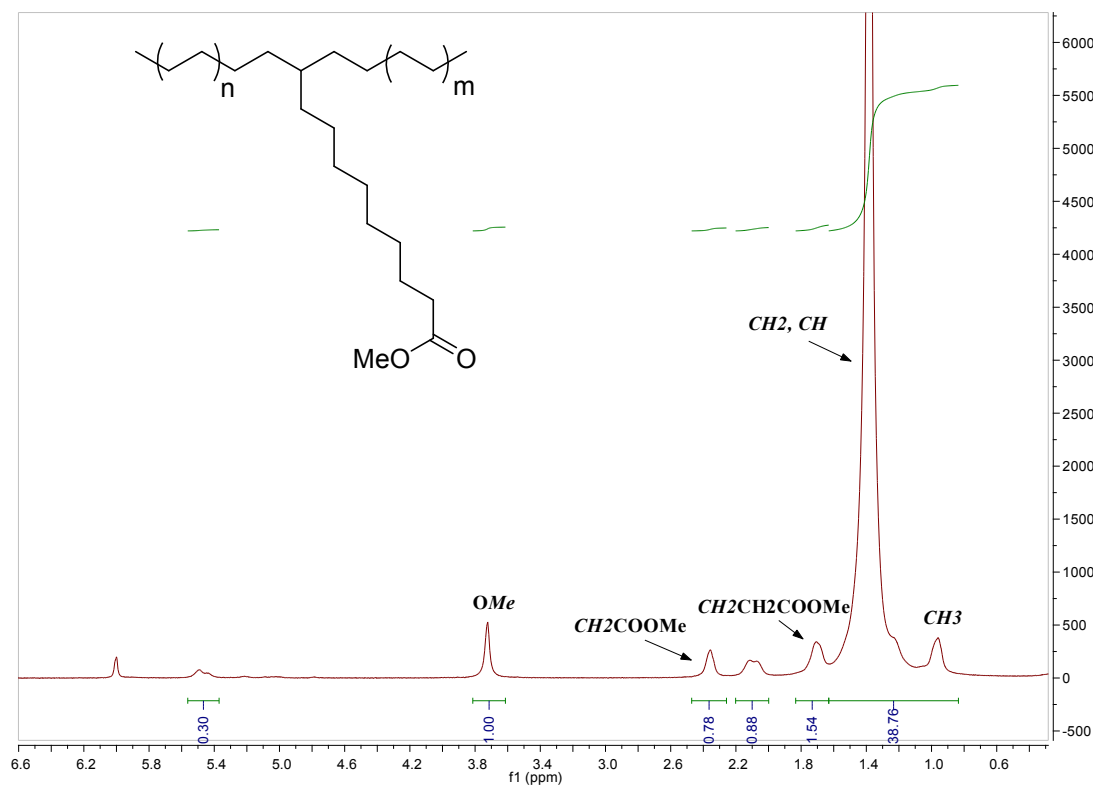


Figure S14. ^1H NMR spectrum of the copolymer generated by complex **Ni3** from table 2, entry 5. (in $\text{CDCl}_2\text{CDCl}_2$ at 120°C).

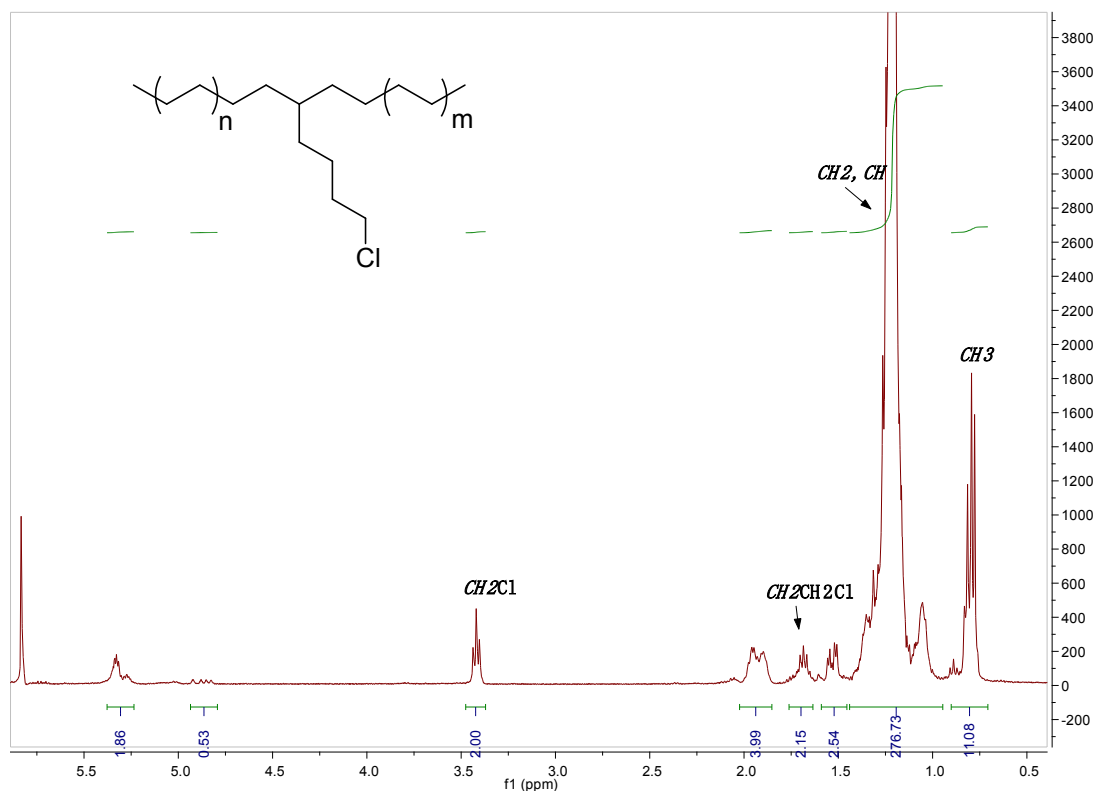


Figure S15. ^1H NMR spectrum of the copolymer generated by complex **Ni3** from table 2, entry 6. (in $\text{CDCl}_2\text{CDCl}_2$ at $120\text{ }^\circ\text{C}$).

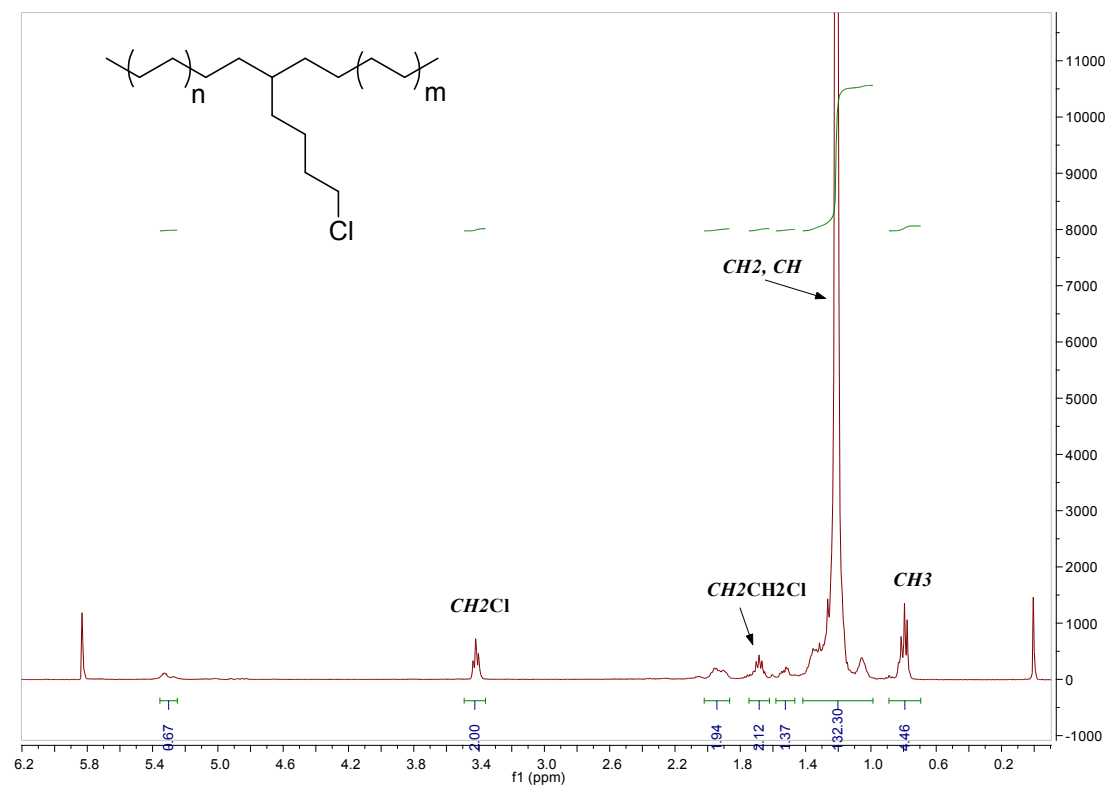
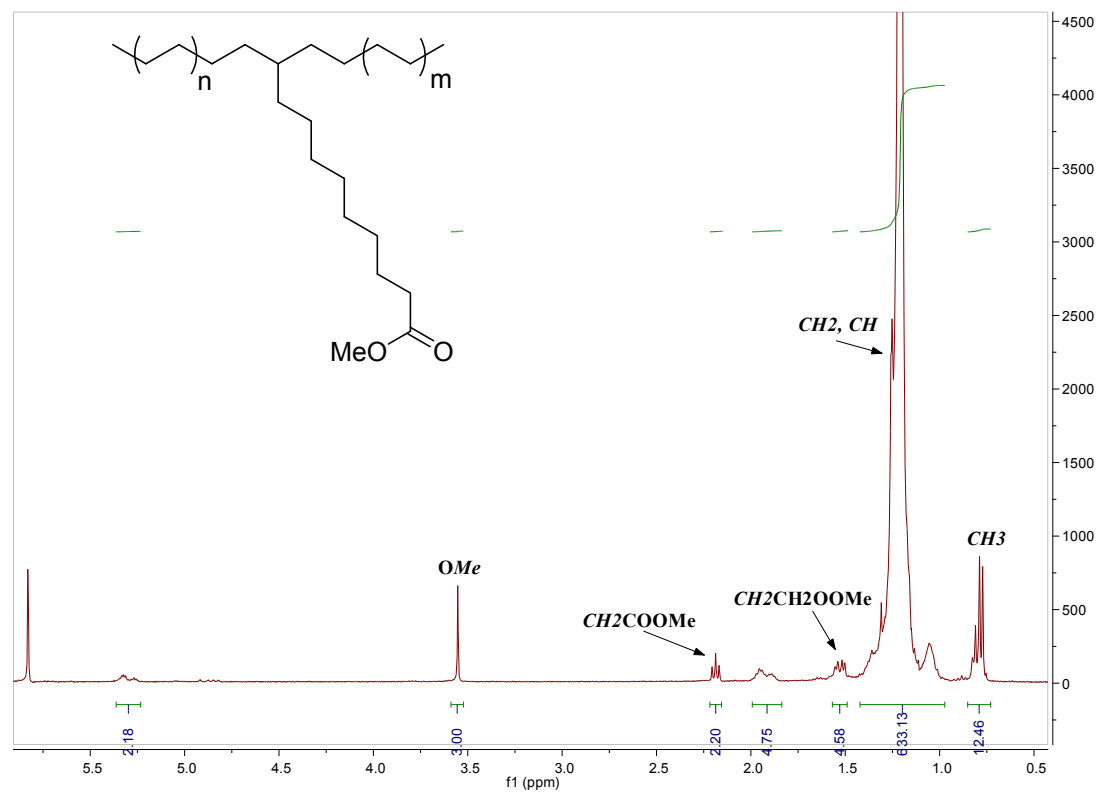
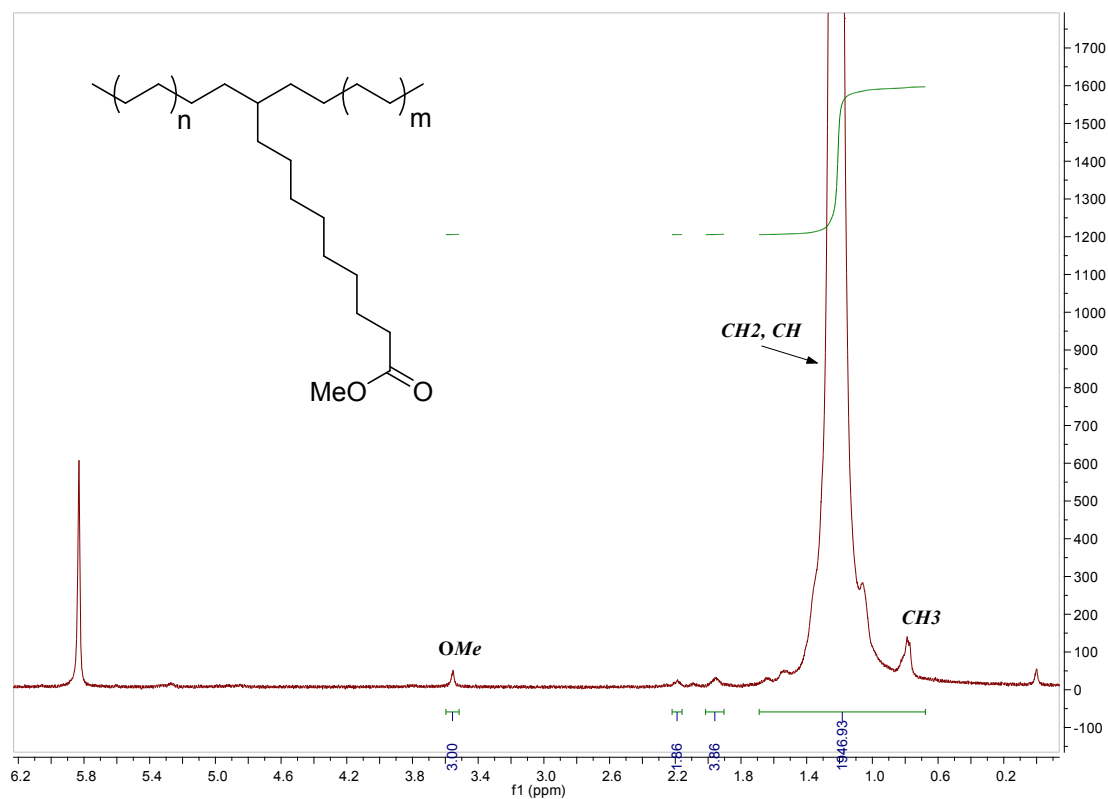


Figure S16. ^1H NMR spectrum of the copolymer generated by complex **Ni3** from table 2, entry 7. (in $\text{CDCl}_2\text{CDCl}_2$ at $120\text{ }^\circ\text{C}$).



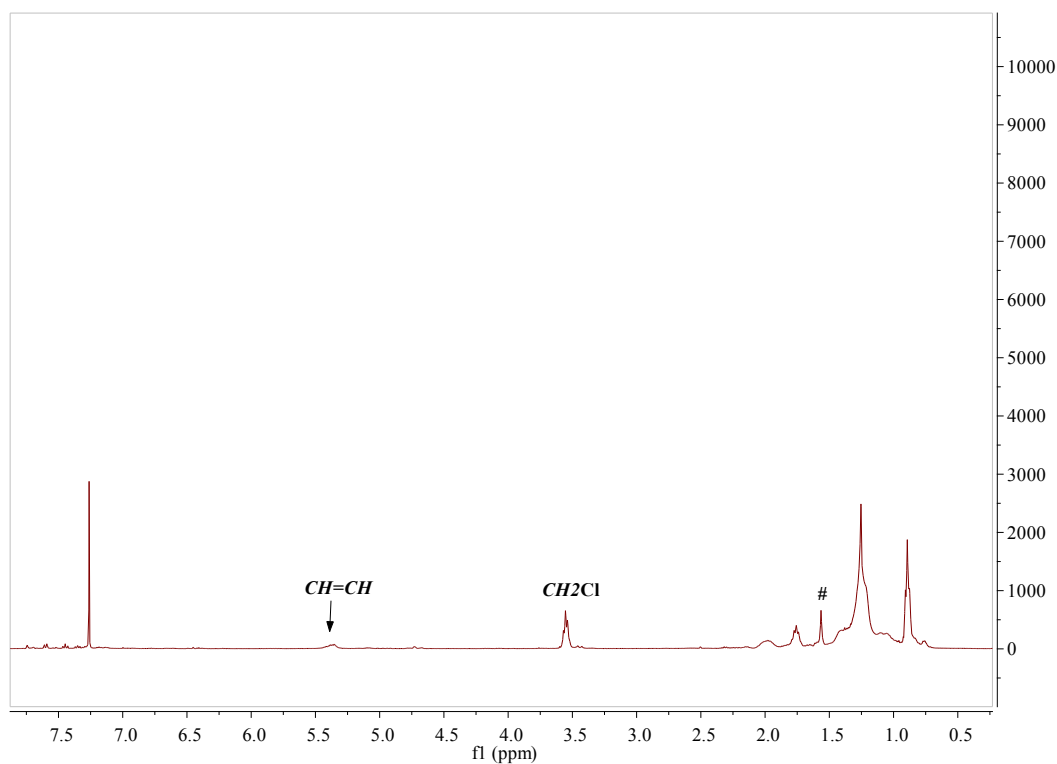


Figure S19. ^1H NMR spectrum of the oligomer generated by **Ni2** from table 3, entry 4. (in CDCl_3 , #: H_2O).

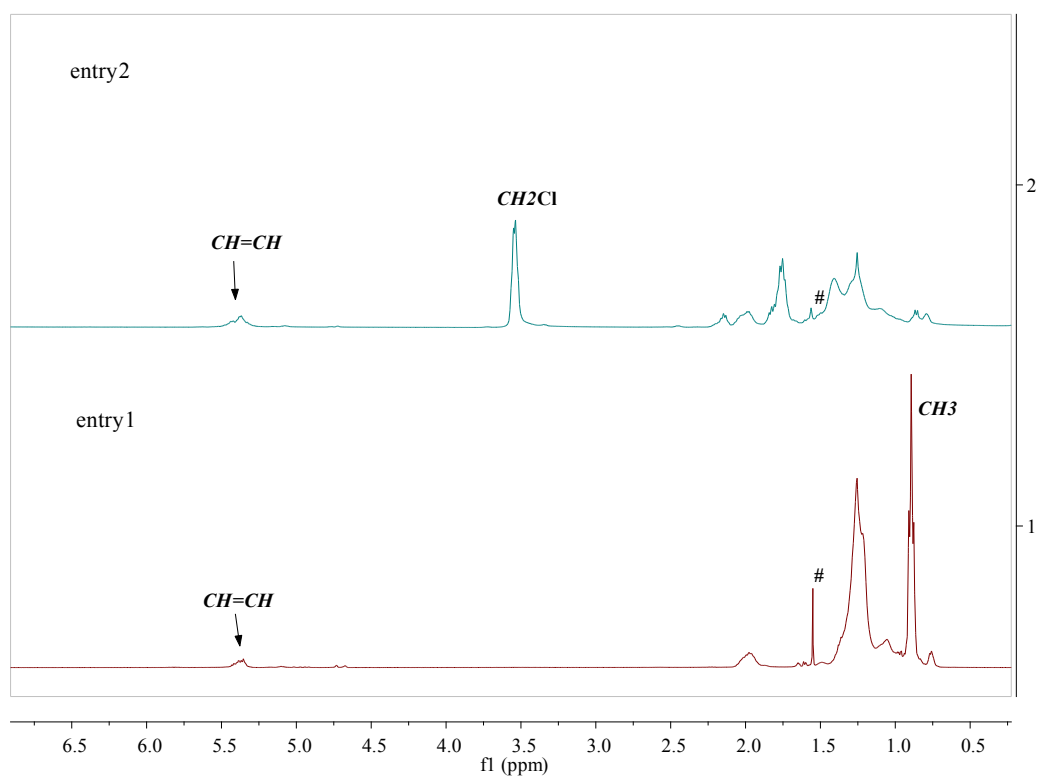


Figure S20. ^1H NMR spectrum of the oligomer generated by **Ni1** from table 3, entry 1 and entry 2. (in CDCl_3 , #: H_2O).

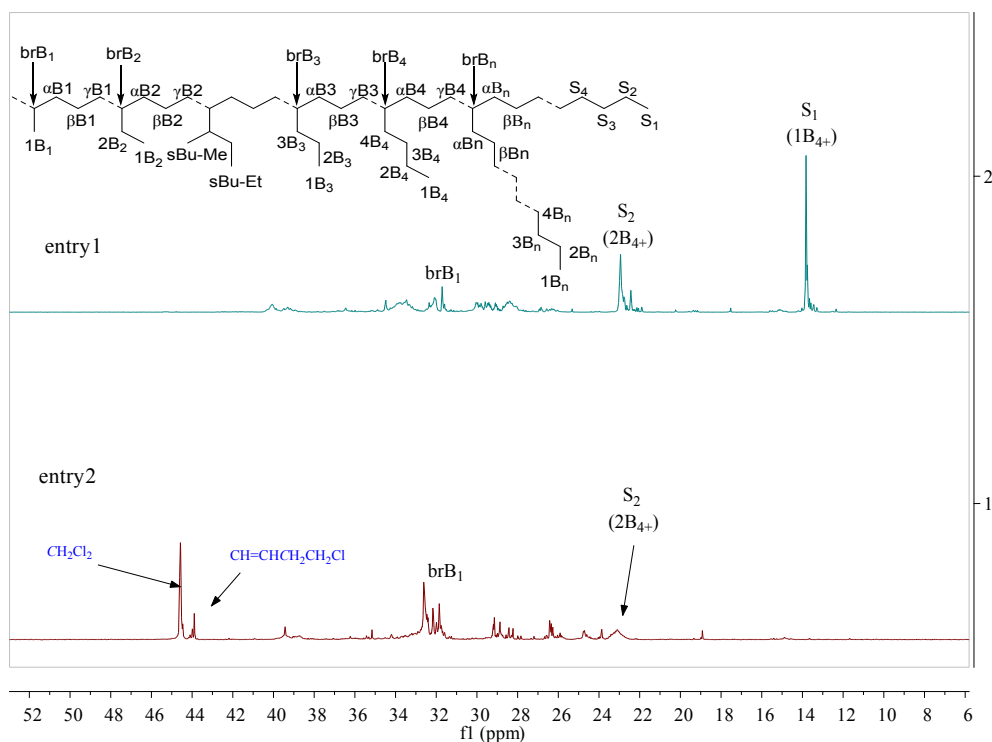


Figure S21. ^{13}C NMR spectrum of the oligomer generated by **Ni1** from table 3, entry 1 and entry 2. (in CDCl_3).

4. DSC and GPC of polymers

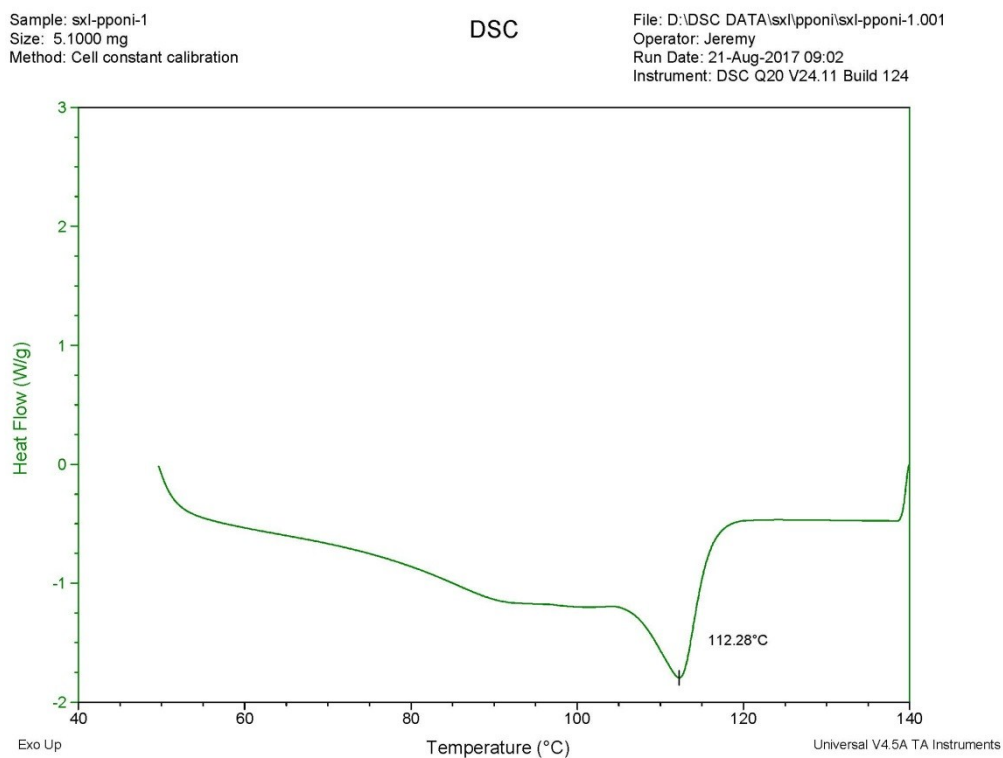


Figure S22. DSC of the polymer from table 1, entry 1.

Sample: sxl-pponi-2
Size: 5.3000 mg
Method: Cell constant calibration

DSC

File: D:\DSC DATA\sxl\pponi\sxl-pponi-2.001
Operator: Jeremy
Run Date: 21-Aug-2017 10:00
Instrument: DSC Q20 V24.11 Build 124

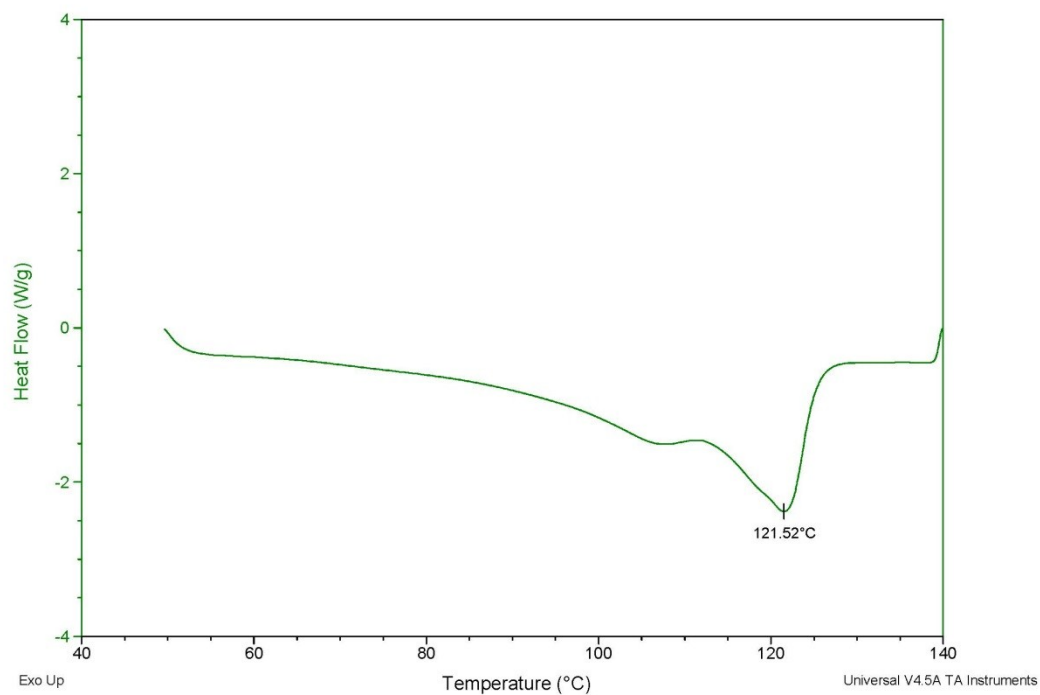


Figure S23. DSC of the polymer from table 1, entry 5.

Sample: sxl-pponi-6
Size: 5.1000 mg
Method: Cell constant calibration

DSC

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Operator: Jeremy
Run Date: 21-Aug-2017 18:36
Instrument: DSC Q20 V24.11 Build 124

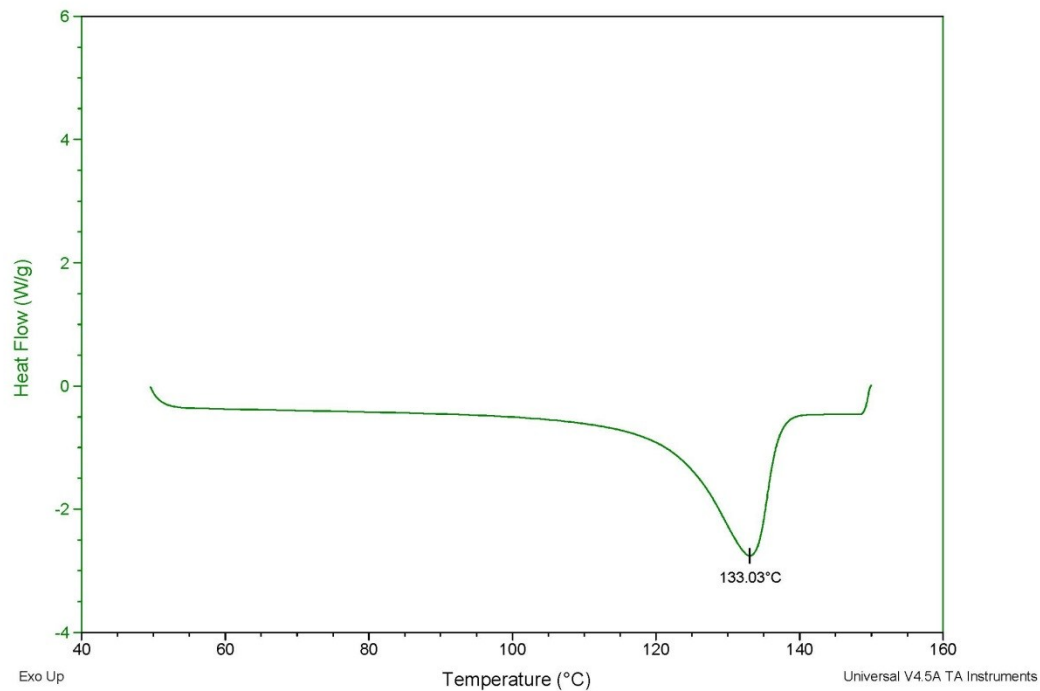


Figure S24. DSC of the polymer from table 1, entry 6.

Sample: sxl-pponi-8
Size: 4.9000 mg
Method: Cell constant calibration

DSC

File: E:\ \pponi\sxl-pponi-8.001
Operator: Jeremy
Run Date: 22-Aug-2017 10:39
Instrument: DSC Q20 V24.11 Build 124

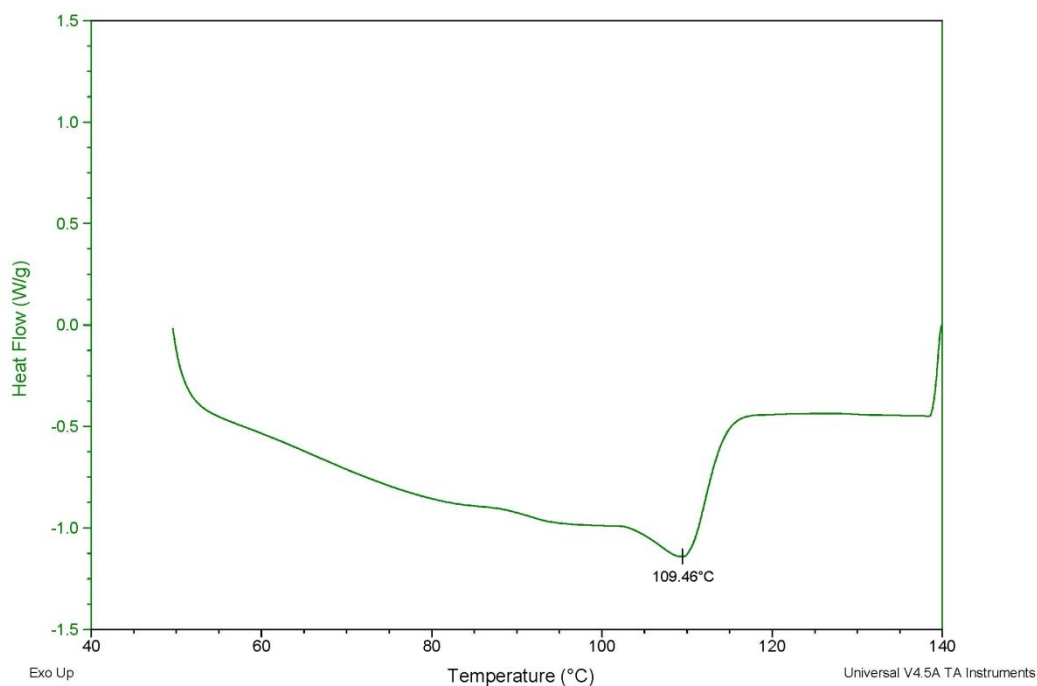


Figure S25. DSC of the copolymer from table 2, entry 2.

Sample: sxl-pponi-10
Size: 5.0000 mg
Method: Cell constant calibration

DSC

File: E:\ \pponi\sxl-pponi-10.001
Operator: Jeremy
Run Date: 22-Aug-2017 16:34
Instrument: DSC Q20 V24.11 Build 124

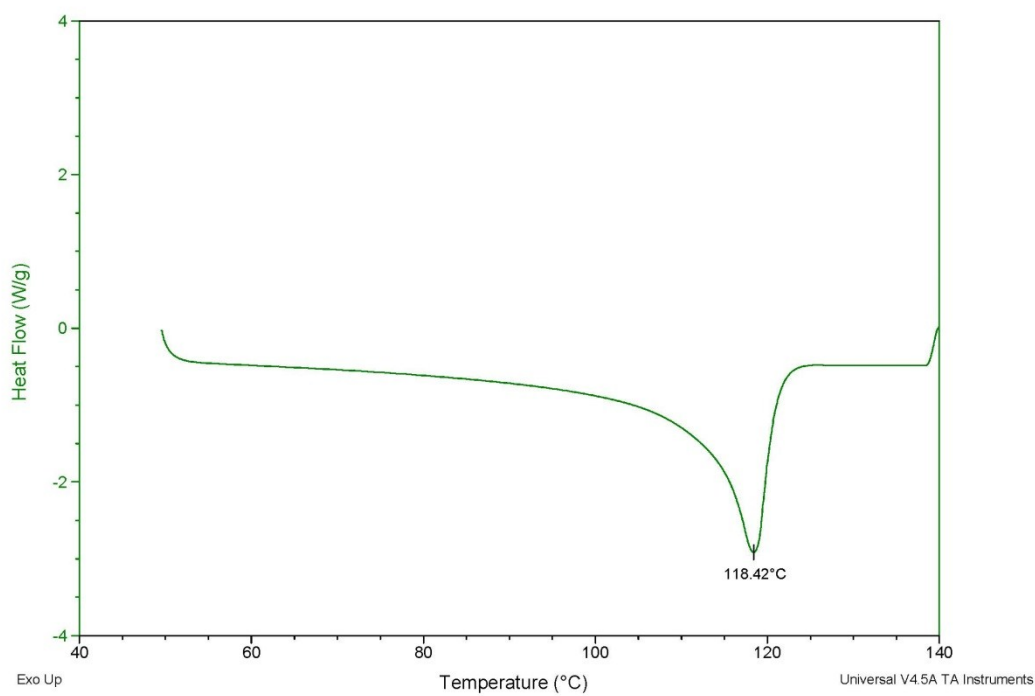


Figure S26. DSC of the copolymer from table 2, entry 3.

Sample: sxl-pponi-16
Size: 5.0000 mg
Method: Cell constant calibration

DSC

File: E:\pponi\sxl-pponi-16.001
Operator: Jeremy
Run Date: 23-Aug-2017 17:23
Instrument: DSC Q20 V24.11 Build 124

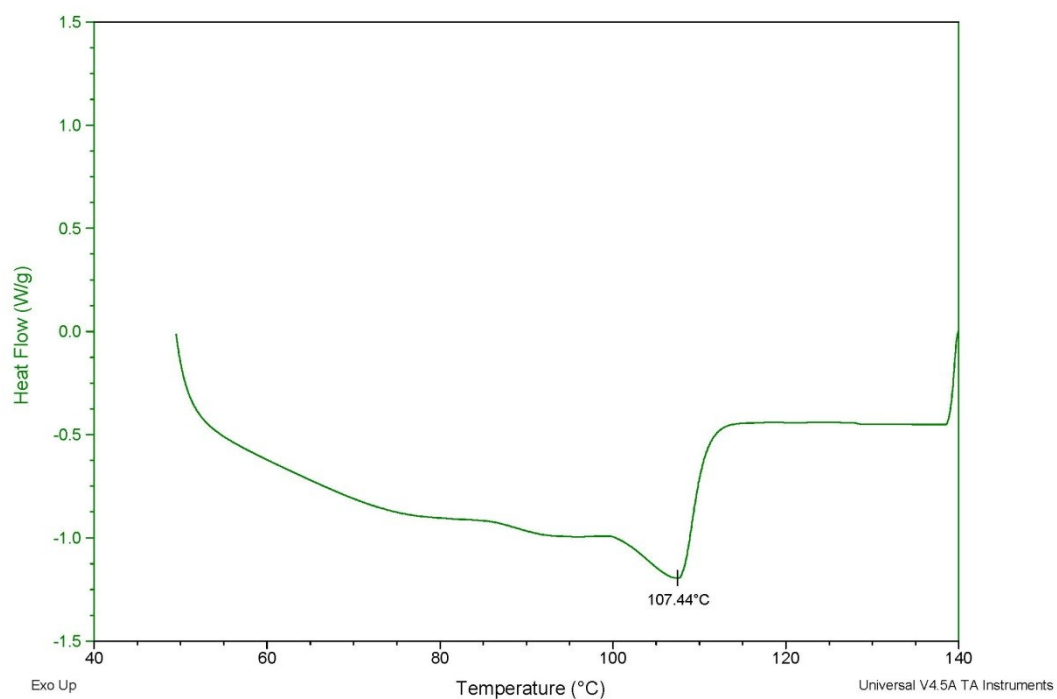


Figure S27. DSC of the copolymer from table 2, entry 8.

Cirrus GPC Sample Injection Report

Generated by: HTGPC

Thursday, October 26, 2017 9:04 AM

Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

Sample Name: S-8

Acquired: 10/20/2017 1:21:33 PM

By Analyst: HTGPC

Batch Name: SXL

Concentration: 0.10

Injection Volume: 200.0 ul K of Sample: 14.1000

Alpha of Sample:

Analysis Using Method: PS2016113001

0.7000

Calibration Used: 8/12/2017 3:25:40 PM

Calibration Type: Narrow Standard Curve Fit Used: 1

K: 14.1000

Alpha: 0.7000

Calibration Curve: $y = 13.269036 - 0.643042x^{*1}$

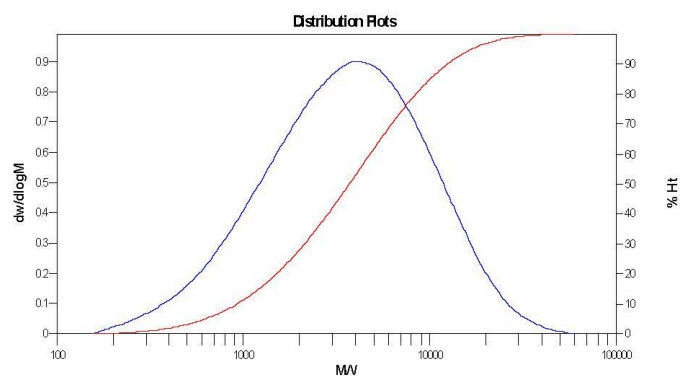
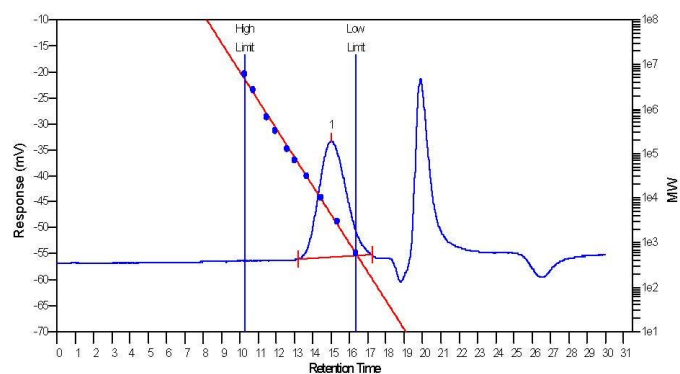
High Limit MW RT: 10.27 mins

Low Limit MW RT: 16.37 mins

Flow Marker RT: 0.00 mins

FRCF: 1.0000

FRM Name:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4099	2086	5473	11235	18243	4827	2.62368

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	15.02	17.22	22.3146	0	2312.79	100

Figure S28. GPC of the polyethylene generated by complex **Ni1** from table 1, entry 2.

Cirrus GPC Sample Injection Report

Generated by: HTGPC

Thursday, October 26, 2017 9:04 AM

Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

Sample Name: S-9

Acquired: 10/20/2017 1:56:36 PM

By Analyst: HTGPC

Batch Name: SXL

Concentration: 0.10

Injection Volume: 200.0 ul K of Sample: 14.1000

Alpha of Sample:

Analysis Using Method: PS2016113001

0.7000

Calibration Used: 8/12/2017 3:25:40 PM

Calibration Type: Narrow Standard Curve Fit Used: 1

K: 14.1000

Alpha: 0.7000

Calibration Curve: $y = 13.269036 - 0.643042x^{*1}$

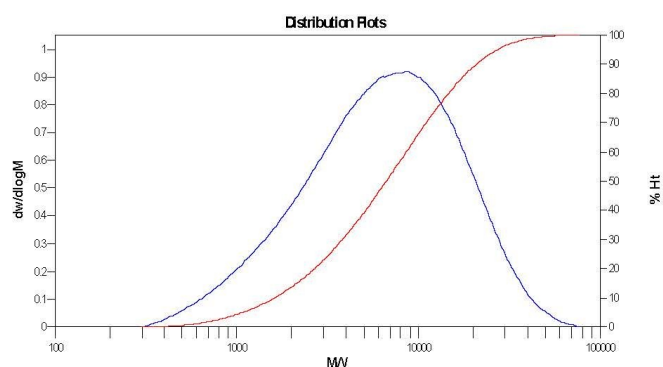
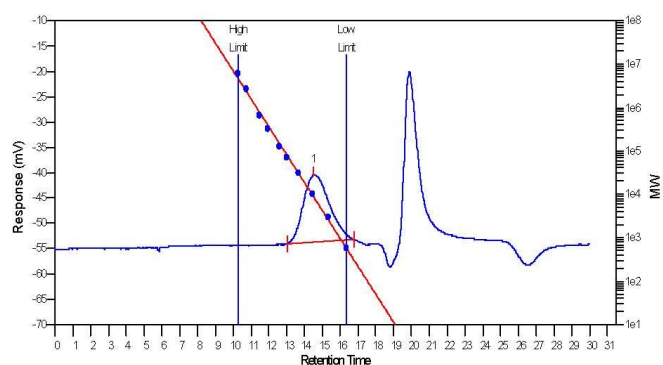
High Limit MW RT: 10.27 mins

Low Limit MW RT: 16.37 mins

Flow Marker RT: 0.00 mins

FRCF: 1.0000

FRM Name:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8594	3705	9300	17521	26350	8298	2.51012

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.03	14.52	16.78	13.1702	0	1338.63	100

Figure S29. GPC of the polyethylene generated by complex **Ni2** from table 1, entry 4.

Cirrus GPC Sample Injection Report

Generated by: HTGPC

Thursday, October 26, 2017 9:08 AM

Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

Sample Name: S-18

Acquired: 10/20/2017 6:54:27 PM

By Analyst: HTGPC

Batch Name: SXL

Concentration: 0.10

Injection Volume: 200.0 ul K of Sample: 14.1000

Alpha of Sample:

Analysis Using Method: PS2016113001

0.7000

Calibration Used: 8/12/2017 3:25:40 PM

Calibration Type: Narrow Standard Curve Fit Used: 1

K: 14.1000

Alpha: 0.7000

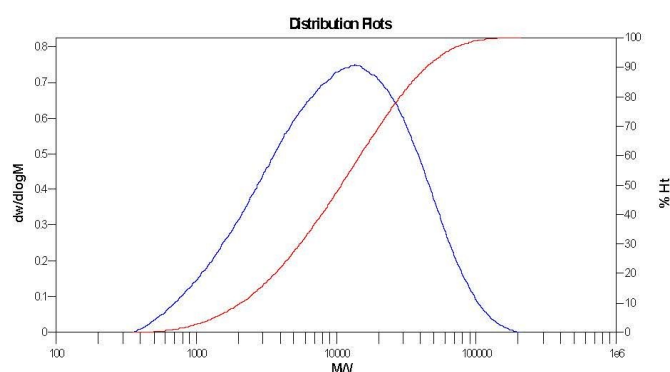
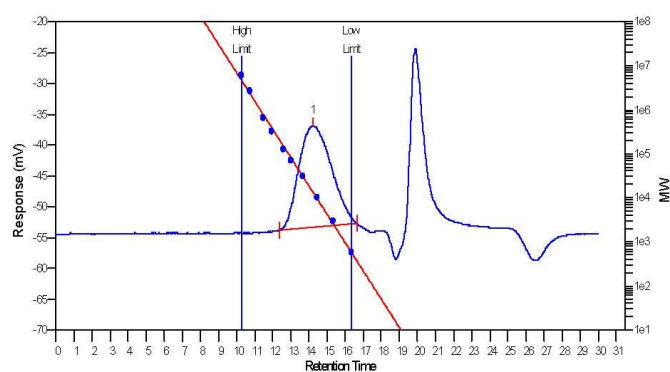
Calibration Curve: $y = 13.269036 - 0.643042x^{\wedge}1$

High Limit MW RT: 10.27 mins

Low Limit MW RT: 16.37 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000

FRM Name:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	13735	5105	18052	41840	67782	15420	3.53614

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.37	14.20	16.67	16.5894	0	2068.61	100

Figure S30. GPC of the copolymer generated by complex **Ni3** from table 2, entry 3.

Cirrus GPC Sample Injection Report

Generated by: HTGPC

Thursday, October 26, 2017 9:14 AM

Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

Sample Name: S-24

Acquired: 10/24/2017 3:18:13 AM

By Analyst: HTGPC

Batch Name: SXL

Concentration: 0.10

Injection Volume: 200.0 μ l K of Sample: 14.1000

Alpha of Sample:

Analysis Using Method: PS2016113001

0.7000

Calibration Used: 8/12/2017 3:25:40 PM

Calibration Type: Narrow Standard Curve Fit Used: 1

K: 14.1000

Alpha: 0.7000

Calibration Curve: $y = 13.269036 - 0.643042x^{\wedge}1$

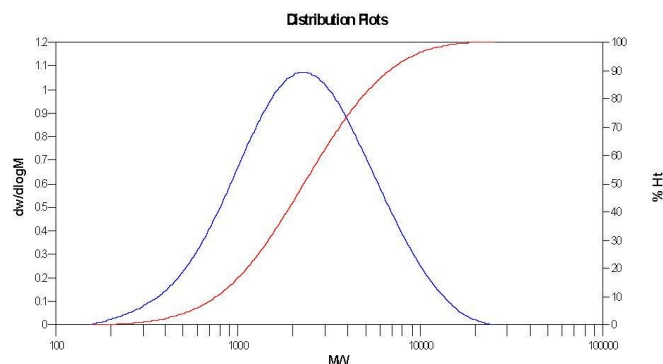
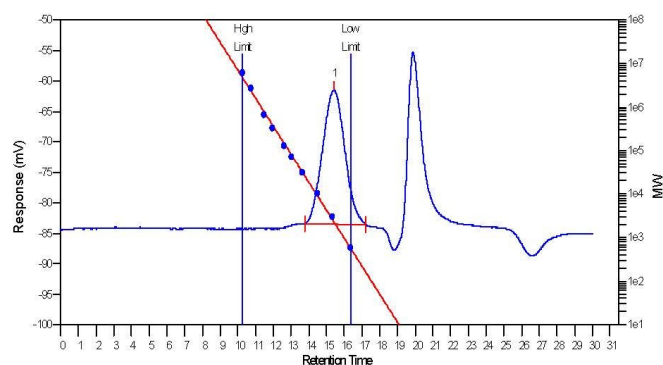
High Limit MW RT: 10.27 mins

Low Limit MW RT: 16.37 mins

Flow Marker RT: 0.00 mins

FRCF: 1.0000

FRM Name:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2267	1572	3149	5644	8585	2857	2.00318

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.78	15.42	17.22	21.9909	0	1909.54	100

Figure S31. GPC of the copolymer generated by complex **Ni3** from table 2, entry 8.

Cirrus GPC Sample Injection Report

Generated by: HTGPC

Thursday, October 26, 2017 9:13 AM

Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

Sample Name: S-21

Acquired: 10/24/2017 1:37:27 AM

By Analyst: HTGPC

Batch Name: SXL

Concentration: 0.10

Injection Volume: 200.0 uL of Sample: 14.1000

Alpha of Sample:

Analysis Using Method: PS2016113001

0.7000

Calibration Used: 8/12/2017 3:25:40 PM

Calibration Type: Narrow Standard Curve Fit Used: 1

K: 14.1000

Alpha: 0.7000

Calibration Curve: $y = 13.269036 - 0.643042x^{*1}$

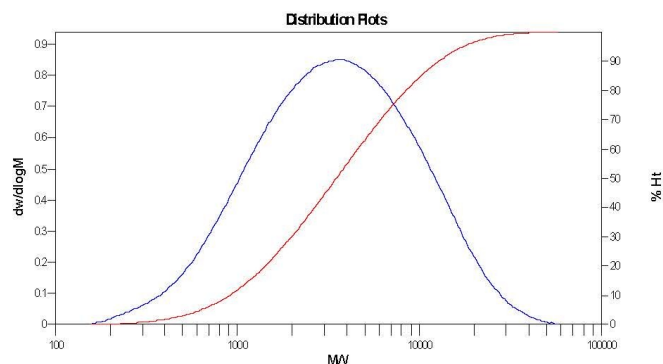
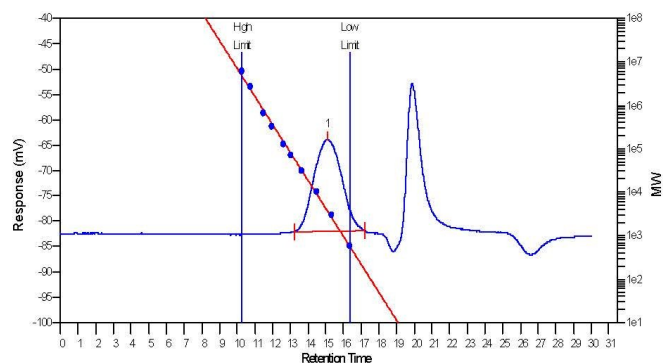
High Limit MW RT: 10.27 mins

Low Limit MW RT: 16.37 mins

Flow Marker RT: 0.00 mins

FRCF: 1.0000

FRM Name:



MW Averages

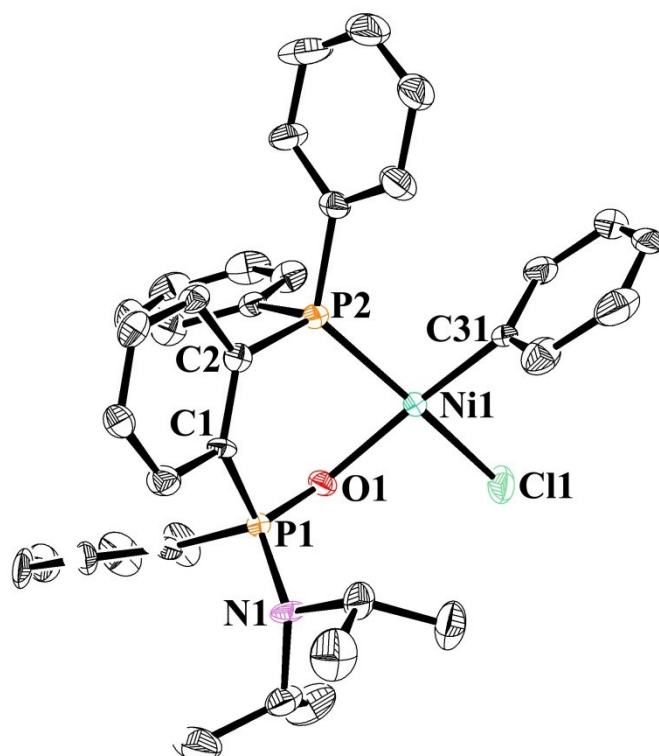
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3713	2042	5451	11655	18951	4769	2.66944

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.23	15.08	17.22	18.017	0	1974.58	100

Figure S32. GPC of the copolymer generated by complex **Ni3** from table 2, entry 9.

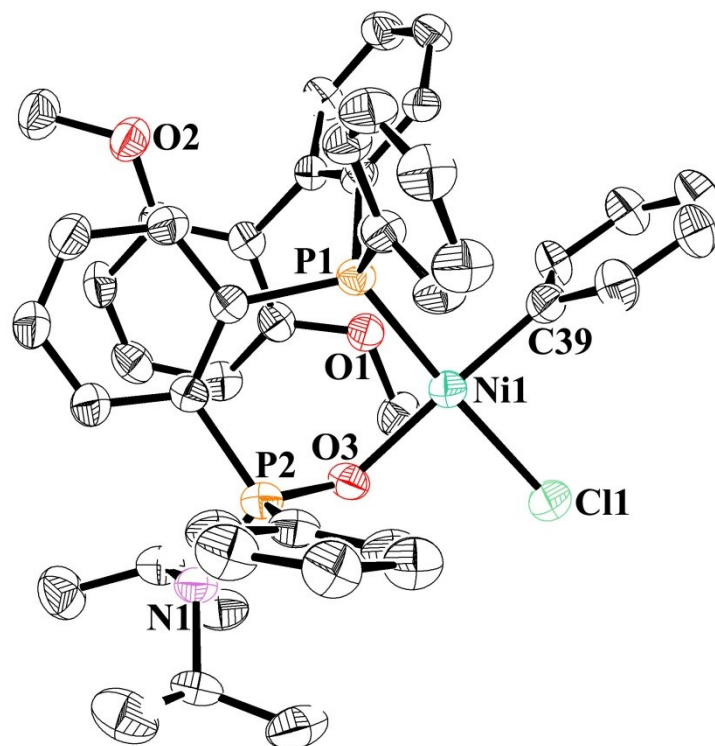
5. X-Ray Crystallography of complex Ni-1.



Entry	Ni1
Formula	C ₃₆ H ₃₈ Cl N Ni O P ₂
Formula weight	656.77
Temperature[K]	298(2)
$\lambda(\text{Mo-K}\alpha)[\text{\AA}]$	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
a[\AA]	17.7789(14)
b[\AA]	11.3500(9)
c[\AA]	16.4332(13)
$\alpha[^\circ]$	90.00
$\beta[^\circ]$	95.6100(10)
$\gamma[^\circ]$	90.00
Volume[\AA^3]	3300.2(5)
Z	4
D(calc)[$\text{g}\cdot\text{cm}^{-3}$]	1.322
$\mu[\text{mm}^{-1}]$	0.795
F(000)	1376
θ min-max ($^\circ$)	2.412-27.039
<i>h</i>	-21 \rightarrow 20
<i>k</i>	-10 \rightarrow 13

<i>l</i>	-19→15
Reflections collected	16009
Reflections unique	5824
R(int)	0.0415
Data / restraints / parameters	5824 / 0 / 383
Final R indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0496
	<i>wR</i> ₂ = 0.1264
R indices (all data)	<i>R</i> ₁ = 0.0923
	<i>wR</i> ₂ = 0.1521
GOF on <i>F</i> ²	1.034

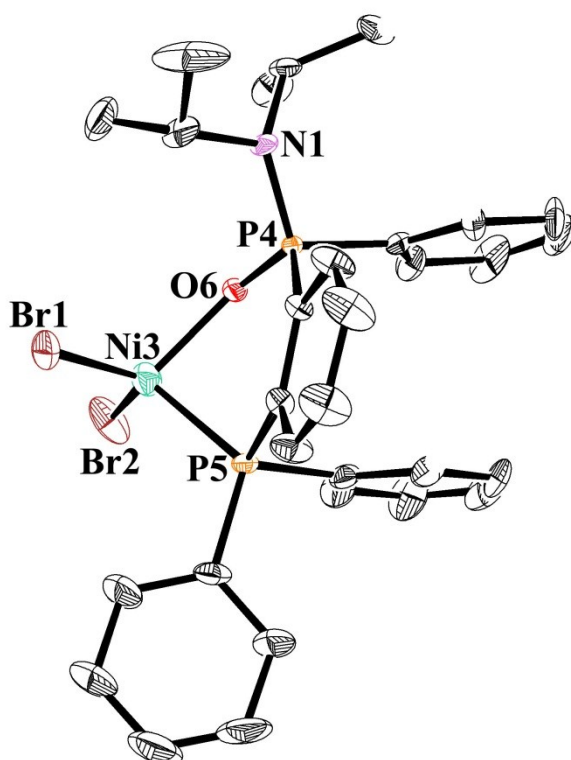
6. X-Ray Crystallography of complex Ni-3.



Entry	Ni3
Formula	C44 H46 Cl N Ni O3 P2
Formula weight	792.92
Temperature[K]	293(2)
λ (Mo-K α)[Å]	1.54178
Crystal system	Monoclinic
Space group	P2(1)/n
<i>a</i> [Å]	17.4215(12)
<i>b</i> [Å]	14.7742(9)
<i>c</i> [Å]	19.0672(15)

α [°]	90.00
β [°]	90.882(2)
γ [°]	90.00
Volume [Å ³]	4907.1(6)
Z	4
D(calc) [g·cm ⁻³]	1.073
μ [mm ⁻¹]	1.943
F(000)	1664
θ min-max (°)	3.4090 -67.3150
<i>h</i>	-16→20
<i>k</i>	-17→11
<i>l</i>	-22→19
Reflections collected	16694
Reflections unique	4777
R(int)	0.0882
Data / restraints / parameters	8555 / 0 / 521
Final R indices [I>2 σ (I)]	R ₁ = 0.0680
	wR ₂ = 0.1399
R indices (all data)	R ₁ = 0.1038
	wR ₂ = 0.1175
GOF on F ²	1.054

7. X-Ray Crystallography of complex Ni1-Br.



Entry	Ni1-Br
Formula	C30 H33 Br2 N Ni O P2
Formula weight	704.04
Temperature[K]	298(2)
$\lambda(\text{Mo-K}\alpha)[\text{\AA}]$	0.71073
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
a[\AA]	11.2291(9)
b[\AA]	15.8955(12)
c[\AA]	17.3816(13)
$\alpha[^\circ]$	90.00
$\beta[^\circ]$	90.00
$\gamma[^\circ]$	90.00
Volume[\AA^3]	3102.5(4)
Z	4
D(calc)[$\text{g}\cdot\text{cm}^{-3}$]	1.507
$\mu[\text{mm}^{-1}]$	3.327
F(000)	1424
θ min-max ($^\circ$)	2.22 -25.02
<i>h</i>	-11 \rightarrow 13
<i>k</i>	-18 \rightarrow 8
<i>l</i>	-20 \rightarrow 19
Reflections collected	15721

Reflections unique	5444
R(int)	0.0581
Data / restraints / parameters	5444 / 0 / 368
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0526$ $wR_2 = 0.1357$
R indices (all data)	$R_1 = 0.0830$ $wR_2 = 0.1553$
GOF on F^2	1.094