Supporting Information for:

Systematic Investigations of Ligand Steric Effects on α-Diimine Nickel Catalyzed Olefin Polymerization and Copolymerization

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1. Figures, Tables.

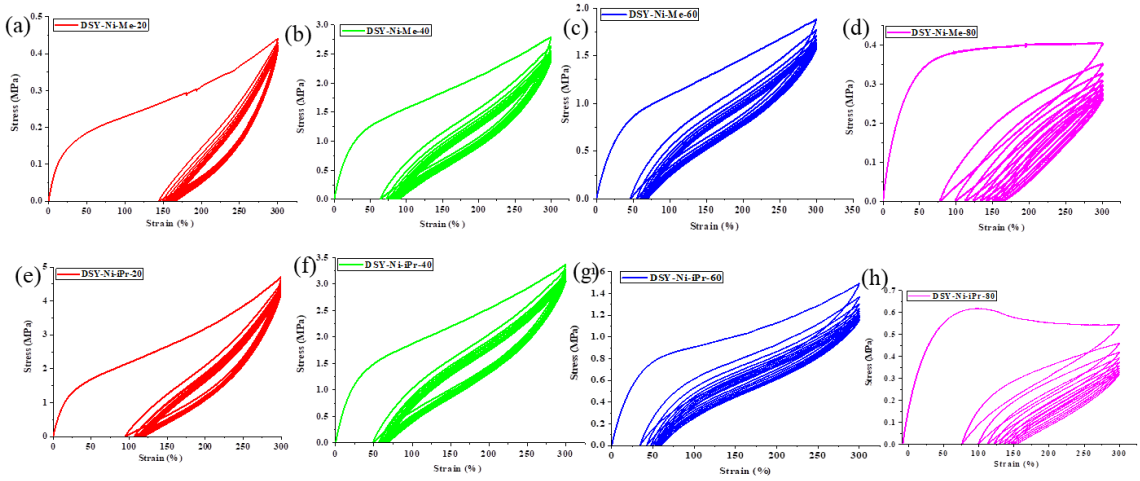


Figure S1. Plots of hysteresis experiments of ten cycles at a strain of 300% for samples generated by **2** at 20ºC (a), 40 ºC (b), 60 ºC (c), 80 ºC (d); **3** at 20ºC (e), 40 ºC (f), 60 ºC (g), 80 ºC (h).

Table S1. Mechanical properties.[a]

Ent.	Precat.	*T*/ºC	Strain at break (%)	Stress at break (MPa)	SR (%)[b]
1	**2**	20	325	4.9	45
2	**2**	40	529	6.0	63
3	**2**	60	826	5.5	77
4	**2**	80	1558	0.3	45
5	**3**	20	443	7.6	60
6	**3**	40	567	9.6	77
7	**3**	60	526	2.1	80
8	**3**	80	1078	0.5	49
9	**4**	20	329	20.3	-[c]
10	**4**	40	439	13.6	-
11	**4**	60	408	8.3	46
12	**4**	80	613	13.6	-
13	**5**	20	208	7.8	-
14	**5**	40	361	12.3	-
15	**5**	60	484	20.0	22
16	**5**	80	628	22.1	-

[a]Conditions: Performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature. [b]The strain recovery values (SR) can be calculated by $SR = 100(\varepsilon_a - \varepsilon_r)/\varepsilon_a$, where ε_a is the applied strain and ε_r is the strain in the cycle at zero load after 10th cycle. [c]Not determined.

Table S2. Effect of Catalyst on Ethylene Polymerization in Short Time.[a]

Ent.	Precat.	*T*/°C	Yield/g
1	**1**	20	3.03
2	**2**	20	2.01
3	**3**	20	1.51
4	**4**	20	1.32
5	**5**	20	0.38

[a]General conditions: Ni = 1.0 μmol, Al/Ni = 600, CH_2Cl_2 = 2 ml, toluene = 40 ml, ethylene = 8 atm, time = 10 min.

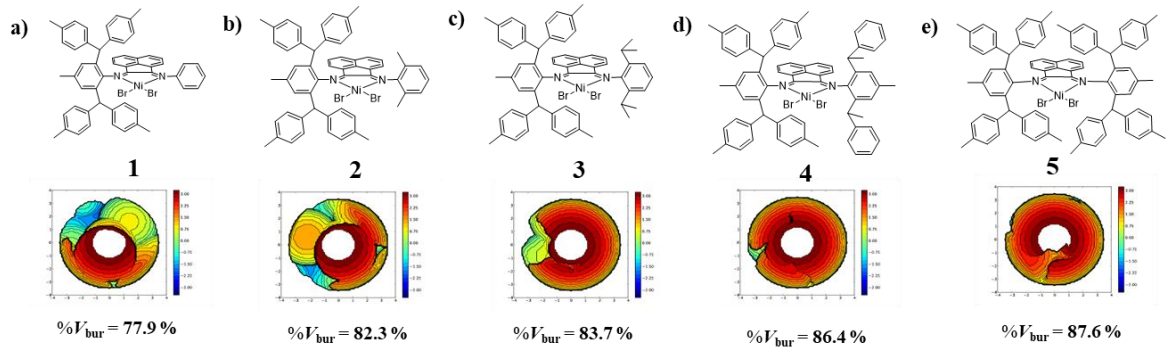


Figure S2. Steric maps for the complexes **1-5**: a) **1**; b) **2**; c) **3**; d) **4**; e) **5**.

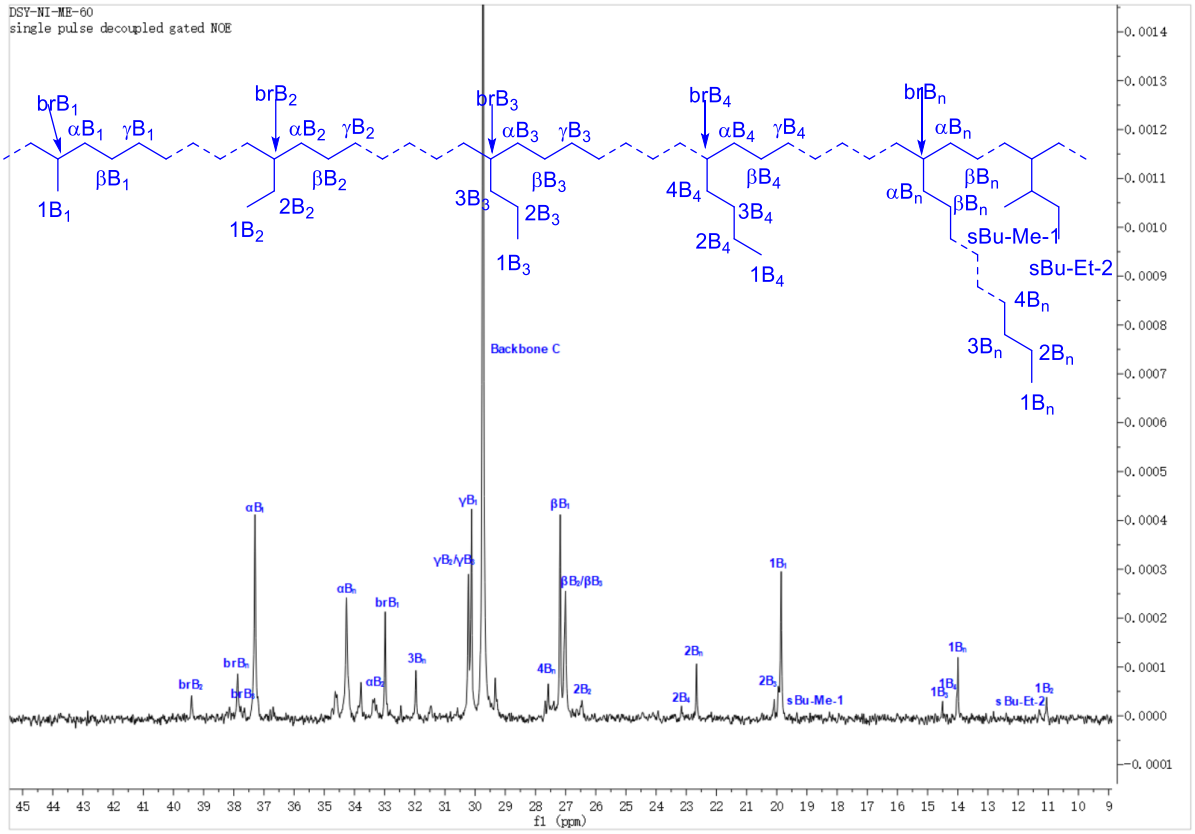


Figure S3. ^{13}C NMR spectrum of the polymer from table 1, entry 7 ($CDCl_2CDCl_2$, 110 °C).

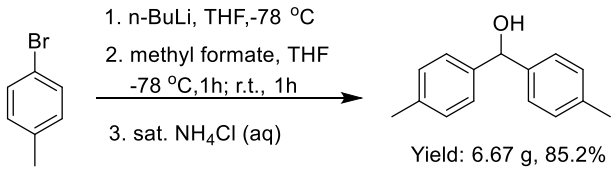
2. Experimental sections

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. ^{1}H, ^{13}C NMR spectra were recorded by a Bruker Ascend Tm 500 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H 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 K^{α} radiation (λ = 0.71073 Å). 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 150 ºC using trichlorobenzene as a solvent and calibrated with polystyrene standards.

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 30 to 35ºC above their melting point to obtain the test specimens. The test specimens had 14-mm gauge length, 2-mm width, and thickness of 0.5 mm.

2.2 Procedure for the Synthesis of Benzhyldrol.

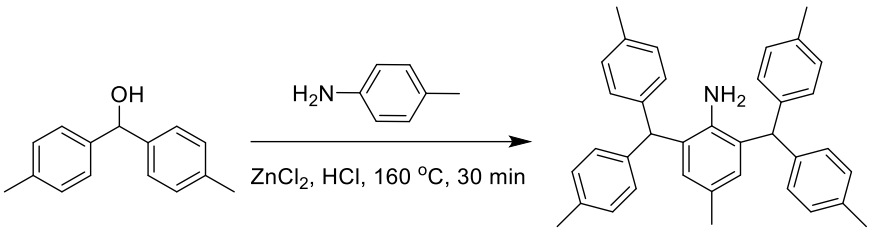


Yield: 6.67 g, 85.2%

Bis(3-methylphenyl)methanol. 4-methylbromobenzene (12.6 g, 73.8 mmol, 1.0 equiv.) was dissolved in dry THF (75 mL) and cooled to -78 ºC under N_2. *n*-Butyl lithium (46.2 mL, 1.6 M solution in hexane, 73.9 mmol, 1.0 equiv.) was added dropwise and the resulting suspension was stirred at-78 ºC for 1 h. Methyl formate (2.22 g, 36.9 mmol, 0.5 equiv.) in THF (15 mL) was then added dropwise over a period of 10 min, and the mixture was stirred at -78 ºC for 1 h, then at room temperature for 1 h. Saturated ammonium chloride (aqueous, 100 mL) was added and the mixture was extracted with Et_2O (3×30 mL). The combined organic layers were

washed with brine (2×30 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by recrystallization to give a colorless solid (6.67 g, 85.2% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 4H, aryl-*H*), 7.11 (d, *J* = 8.0 Hz, 4H, aryl-*H*), 5.72 (s, 1H, C*H*(PhMe)$_2$), 2.31 (s, 6H, Ar-C*H*$_3$) 2.28 (broad peak, 1H, O*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.21, 136.85, 129.02, 126.49, 75.69 (*C*H(PhMe)$_2$), 21.09 (Ar-C*H*$_3$).

2.3 Procedure for the Synthesis of Aniline.

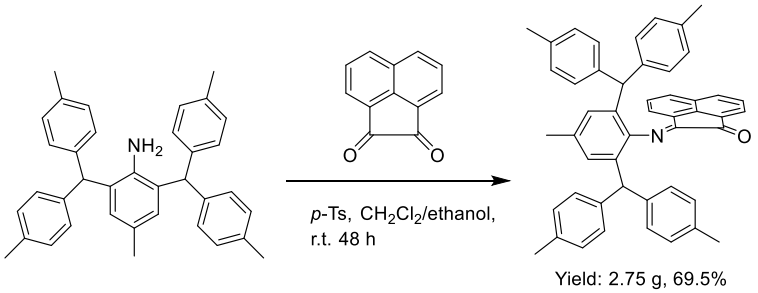


Yield: 4.94 g, 74%

2,6-Bis(di-p-tolylmethyl)-4-methylaniline. A mixture of *p*-toluidine (1.44 g, 13.5 mmol, 1.0 equiv.) and bis(p-methylphenyl)methanol (5.71 g, 27.0 mmol, 2.0 equiv.) was heated to 120 °C. A solution of anhydrous zinc chloride (0.92 g, 6.8 mmol, 0.5 equiv.) in concentrated hydrochloric acid (1.13 mL, 37% in H_2O, 1.0 equiv.) was added to the mixture (exothermic + intense bubbling), and the temperature was raised to 160 °C. After 30 min at 160 °C, the reaction mixture was cooled to room temperature and dissolved in CH_2Cl_2 (200 mL). The CH_2Cl_2 layer was washed with water (3 × 100 mL) and dried over anhydrous magnesium sulfate. The solution was concentrated to 20 mL. The product was crashed out with 200 ml methanol and washed with methanol (3 × 100 mL). The desired aniline was obtained as a white crystalline solid at 74.0 % (4.94 g) yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.9 Hz, 8H, aryl-*H*), 6.96 (d, *J* = 8.0 Hz, 8H, aryl-*H*), 6.38 (s, 2H, aryl-*H*), 5.36 (s, 2H, C*H*(PhMe)$_2$), 2.31 (s, 12H, CH(Ph*Me*)$_2$), 2.02 (s, 3H, Ar-C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.12, 139.73, 136.06, 129.59, 129.48, 129.38, 128.94, 126.62, 51.76 (*C*H(PhMe)$_2$), 21.20 (CH(Ph*Me*)$_2$), 21.16 (Ar-*C*H$_3$). This compound is knwon.[1]

2,6-*bis*-(*sec*-phenethyl)-4-methylaniline were synthesized according to the literature.[2]

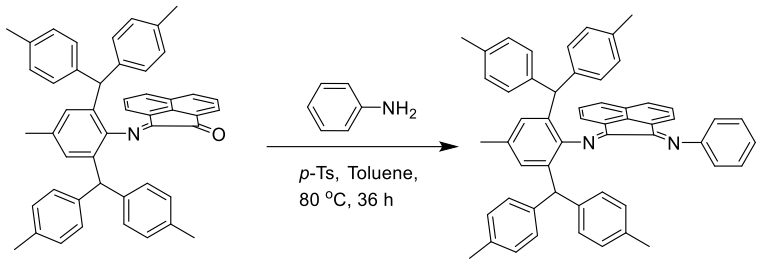
2.4 Procedure for the Synthesis Ligands L1-L5.



Yield: 2.75 g, 69.5%

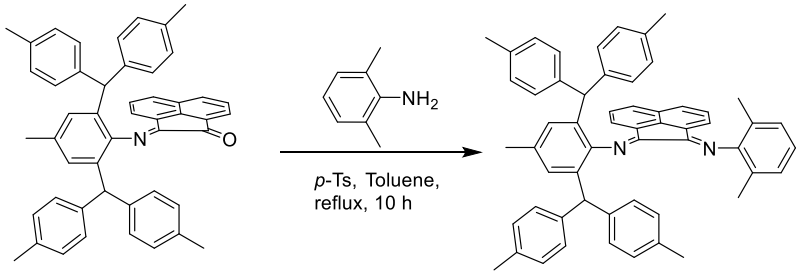
2-((2,6-bis(di-p-tolylmethyl)-4-methylphenyl)imino)acenaphthylen-1-one. A mixture of 2,6-bis(di-p-tolylmethyl)-4-methylaniline (2.97 g, 6 mmol, 1.0 equiv.) and acenaphthylen-1,2-dione (1.09 g, 6 mmol, 1.0 equiv.) were dissolved in 5 mL ethanol and 100 mL of CH_2Cl_2 containing a catalytic amount of *p*-toluenesulfonic acid and stirred for 48 h at room temperature.

The solvent was evaporated at reduced pressure to give the crude product, which was chromatographed on silica gel with petroleum ether-ethyl acetate (v/v = 30:1). A 2.75 g amount of the product was obtained as red powder in 69.5% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 10.8, 7.6 Hz, 2H, aryl-*H*), 7.76 -7.66 (m, 2H, aryl-*H*), 7.06-6.99 (m, 5H, aryl-*H*), 6.96 (t, *J* = 9.4 Hz, 4H, aryl-*H*), 6.77 (s, 2H, aryl-*H*), 6.71 (d, *J* = 7.9 Hz, 4H, aryl-*H*), 6.32 (d, *J* = 7.8 Hz, 4H, aryl-*H*), 6.03 (d, *J* = 7.1 Hz, 1H, aryl-*H*), 5.33 (s, 2H, C*H*(PhMe)$_2$), 2.29 (s, 6H, CH(Ph*Me*)$_2$), 2.25 (s, 3H, Ar-CH_3), 1.67 (s, 6H, *C*H(Ph*Me*)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.09 (*C*=O), 162.56 (*C*=N), 146.08, 142.38, 140.19, 139.12, 135.60, 134.86, 133.14, 132.77, 131.98, 131.67, 130.24, 129.97, 129.76, 129.47, 129.42, 129.31, 128.93, 128.64, 128.60, 128.43, 127.58, 127.56, 127.33, 126.86, 124.29, 122.22, 121.50, 51.53, 21.65 (Ar-*C*H_3), 21.19 (CH(Ph*Me*)$_2$), 20.48 (CH(Ph*Me*)$_2$). This compound is kwon.[1]



Yield: 0.23 g, 31.2%

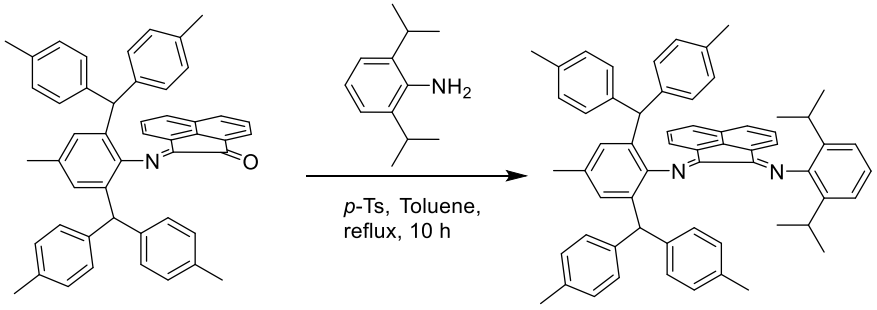
Acenaphthylene-1-[2,6-bis(di-*p*-tolylmethyl)-4-methylphenylimino]-2-phenylimine (L1). A solution of 2-((2,6-bis(di-p-tolylmethyl)-4-methylphenyl)imino)acenaphthylen-1-one (0.66 g, 1 mmol, 1.0 equiv.), aniline (0.19 g, 2 mmol, 2.0 equiv.) and *p*-toluenesulfonic acid (10 mg) in toluene (30 mL) was stirred at 80 °C for 36 h, until there was one main point on the TLC plate. The desired compound was isolated using column chromatography on silica gel with petroleum ether-ethyl acetate (v/v = 40:1). The pure compound was obtained as a yellow solid (31.2%, 0.23 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H, aryl-*H*), 7.61 (d, *J* = 8.2 Hz, 1H, aryl-*H*), 7.49 (t, *J* = 7.8 Hz, 2H, aryl-*H*), 7.24 (d, *J* = 4.6 Hz, 1H, aryl-*H*), 7.11-6.92 (m, 12H, aryl-*H*), 6.82-6.75 (m, 6H, aryl-*H*), 6.71 (d, *J* = 7.1 Hz, 1H, aryl-*H*), 6.36 (d, *J* = 7.8 Hz, 4H, aryl-*H*), 6.04 (d, *J* = 7.1 Hz, 1H, aryl-*H*), 5.47 (s, 2H, C*H*(PhMe)$_2$), 2.29 (s, 6H, CH(Ph*Me*)$_2$), 2.26 (s, 3H, Ar-CH_3), 1.68 (s, 6H, CH(Ph*Me*)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.50 (N=*C*), 160.99 (N=*C*), 152.16, 146.75, 140.56, 140.45, 139.29, 135.42, 134.70, 132.48, 132.44, 130.16, 129.88, 129.75, 129.51, 129.48, 129.41, 129.30, 129.25, 128.92, 128.86, 128.70, 128.63, 128.49, 128.35, 128.20, 127.30, 127.04, 126.86, 124.25, 124.22, 123.00, 118.25, 51.57 (*C*H(PhMe)$_2$), 21.67 (Ar-*C*H_3), 21.15 (CH(Ph*Me*)$_2$), 20.47 (CH(Ph*Me*)$_2$). ESI-MS (m/z): calcd for $C_{55}H_{47}N_2$: $[M+H]^+$ 735.3739, found: 735.3751.



Yield: 0.32 g, 41.3%

Acenaphthylene-1-[2,6-bis(di-*p*-tolylmethyl)-4-methylphenylimino]-2-(2,6-dimethylphenyl)imine (L2) .

A solution of 2-((2,6-bis(di-p-tolylmethyl)-4-methylphenyl)imino)acenaphthylen-1-one (0.66 g, 1 mmol, 1.0 equiv.), 2,6-dimethylaniline (0.24 g, 2 mmol, 2.0 equiv.) and *p*-toluenesulfonic acid (10 mg) in toluene (30 mL) was refluxed for 10 h, until there was one main point on the TLC plate. The desired compound was isolated using column chromatography on silica gel with petroleum ether-ethyl acetate (v/v = 40:1). The pure compound was obtained as a yellow solid (41.3%, 0.32 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 1H, aryl-*H*), 7.57 (d, *J* = 8.2 Hz, 1H, aryl-*H*), 7.24 (d, *J* = 7.5 Hz, 1H, aryl-*H*), 7.17 (d, *J* = 7.5 Hz, 2H, aryl-*H*), 7.09-6.99 (m, 9H, aryl-*H*), 6.93-6.88 (m, 1H, aryl-*H*), 6.79 (dd, *J* = 9.8, 7.6 Hz, 6H, aryl-*H*), 6.53 (d, *J* = 7.1 Hz, 1H, aryl-*H*), 6.30 (d, *J* = 7.8 Hz, 4H, aryl-*H*), 5.92 (d, *J* = 7.1 Hz, 1H, aryl-*H*), 5.51 (s, 2H, C*H*(PhMe)$_2$), 2.29 (s, 6H, CH(Ph*Me*)$_2$), 2.27 (s, 3H, Ar-CH_3), 2.23 (s, 6H, aryl-CH_3), 1.63 (s, 6H, CH(Ph*Me*)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.72 (N=*C*), 161.66 (N=*C*), 149.53, 146.89, 140.60, 139.87, 139.14, 135.50, 134.71, 132.54, 129.94, 129.87, 129.55, 129.03, 128.90, 128.57, 128.51, 128.47, 128.42, 128.40, 127.01, 126.99, 125.01, 124.59, 123.74, 121.68, 51.65 (*C*H(PhMe)$_2$), 29.84 (Ar-CH_3), 21.67 (Aryl-CH_3), 21.13 (CH(Ph*Me*)$_2$), 20.42 (CH(Ph*Me*)$_2$), 18.29 (aryl-CH_3). ESI-MS (m/z): calcd for $C_{57}H_{51}N_2$: $[M+H]^+$ 763.4052, found: 763.4066.

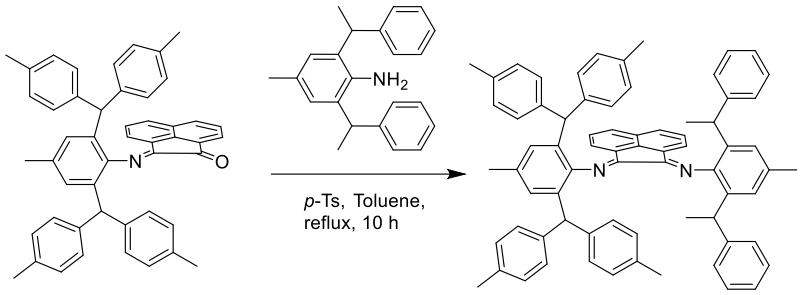


Yield: 0.44 g, 53.3%

Acenaphthylene-1-[2,6-bis(di-*p*-tolylmethyl)-4-methylphenylimino]-2-(2,6-diisopropylphenyl)imine (L3).

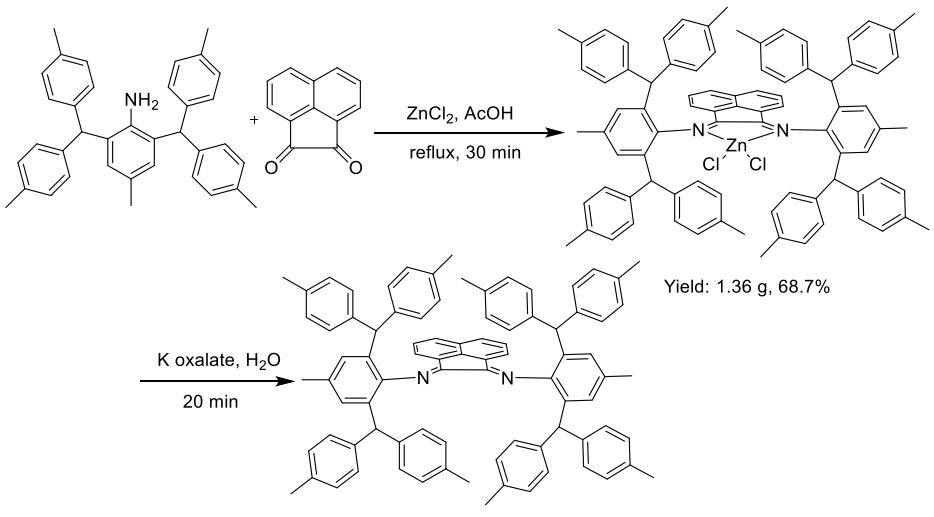
A solution of 2-((2,6-bis(di-p-tolylmethyl)-4-methylphenyl)imino)acenaphthylen-1-one (0.66 g, 1 mmol, 1.0 equiv.), 2,6-diisopropylaniline (0.35 g, 2 mmol, 2.0 equiv.) and *p*-toluenesulfonic acid (10 mg) in toluene (30 mL) was refluxed for 10 h, until there was one main point on the TLC plate. The solution was evaporated at reduced pressure, and the remaining solution was diluted in methanol (100 mL). The yellow solid was isolated by filtration, followed by recrystallization from dichloromethane and *n*-hexane (53.3%, 0.44 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.31-7.26 (m, 3H), 7.23-7.19 (m, 1H), 7.03 (dd, *J* = 19.8, 8.1 Hz, 8H), 6.79 (dd, *J* = 14.5, 8.4 Hz, 7H), 6.44 (d, *J* = 7.1 Hz, 1H), 6.25 (d, *J* = 7.8 Hz, 4H), 5.72 (d, *J* = 7.1 Hz, 1H), 5.54 (s, 2H, C*H*(PhMe)$_2$), 3.24-3.13 (m, 2H, C*H*(CH_3)$_2$), 2.30 (s, 6H, CH(Ph*Me*)$_2$), 2.28 (s, 3H, Ar-CH_3), 1.62 (s, 6H, CH(Ph*Me*)$_2$), 1.28 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.02 (d, *J* = 6.9 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.92 (N=*C*), 162.32 (N=*C*), 147.28, 146.96, 140.94, 140.11, 139.88, 138.94, 135.88, 135.54, 135.47, 134.69, 132.59, 132.53, 129.85, 129.68, 129.57, 129.46, 129.26, 129.00, 128.93, 128.81, 128.62, 128.56, 128.38, 128.11, 127.99, 126.96,

126.83, 126.58, 124.65, 124.51, 124.42, 123.64, 123.59, 123.47, 122.83, 51.51 (*C*H(PhMe)$_2$), 29.84 (*C*H(CH$_3$)$_2$), 28.62 (*C*H(CH$_3$)$_2$), 24.37 (CH(*C*H$_3$)$_2$), 23.84 (CH(*C*H$_3$)$_2$), 23.55 (CH(*C*H$_3$)$_2$), 23.27 (CH(*C*H$_3$)$_2$), 21.66 (Ar-*C*H$_3$), 21.12 (CH(Ph*Me*)$_2$), 20.43 (CH(Ph*Me*)$_2$). ESI-MS (m/z): calcd for $C_{61}H_{59}N_2$: $[M+H]^+$ 819.4678, found: 819.4694.



Yield: 0.47 g, 49.6%

Acenaphthylene-1-[2,6-bis(di-*p*-tolylmethyl)-4-methylphenylimino]-2-(2,6-*bis*-(*sec*-phenethyl)-4-methylphenyl)imine (L4). Using the same procedure as for the synthesis of **L3**, **L4** was obtained as a yellow powder at 49.6% yield (0.47 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.53 (m, 2H), 7.18 – 6.65 (m, 28H), 6.55 – 6.16 (m, 5H), 6.12 – 5.83 (m, 1H), 5.68 – 5.46 (m, 2H, C*H*(PhMe)$_2$), 4.34 – 4.24 (m, 2H, C*H*PhMe), 2.43 – 2.19 (m, 12H, CH(Ph*Me*)$_2$+ Ar-C*H*$_3$), 1.88 – 1.54 (m, 12H, CH(Ph*Me*)$_2$+ CHPh*Me*).^{13}C NMR (126 MHz, $CDCl_3$) δ 163.77 (*C*=N), 162.79 (*C*=N), 162.13 (*C*=N), 161.60 (*C*=N), 146.79, 145.71, 145.44, 145.07, 141.11, 140.64, 140.61, 140.08, 139.98, 139.82, 139.24, 135.97, 135.32, 135.26, 134.59, 133.73, 132.49, 132.13, 129.77, 129.47, 129.37, 129.17, 128.91, 128.70, 128.65, 128.50, 128.19, 128.10, 127.98, 127.84, 127.75, 127.67, 127.43, 126.51, 125.52, 125.01, 124.88, 123.60, 51.64 (*C*H(PhMe)$_2$), 51.43 (*C*H(PhMe)$_2$), 51.34 (*C*H(PhMe)$_2$), 51.28 (*C*H(PhMe)$_2$), 51.13 (*C*H(PhMe)$_2$), 40.59 (*C*HPhMe), 40.40 (*C*HPhMe), 40.32 (*C*HPhMe), 40.06 (*C*HPhMe), 39.73 (*C*HPhMe), 22.30 (Ar-*C*H$_3$), 22.27 (Ar-*C*H$_3$), 21.86 (CH(Ph*Me*)$_2$), 21.73 (CH(Ph*Me*)$_2$), 21.66 (CH(Ph*Me*)$_2$), 21.56(CH(Ph*Me*)$_2$), 21.19 (CHPh*Me*), 21.09 (CHPh*Me*), 21.02 (CHPh*Me*), 20.94 (CHPh*Me*), 20.37 (CHPh*Me*), 20.34 (CHPh*Me*). ESI-MS (m/z): calcd for $C_{72}H_{65}N_2$: $[M+H]^+$ 957.5148, found: 957.5170.

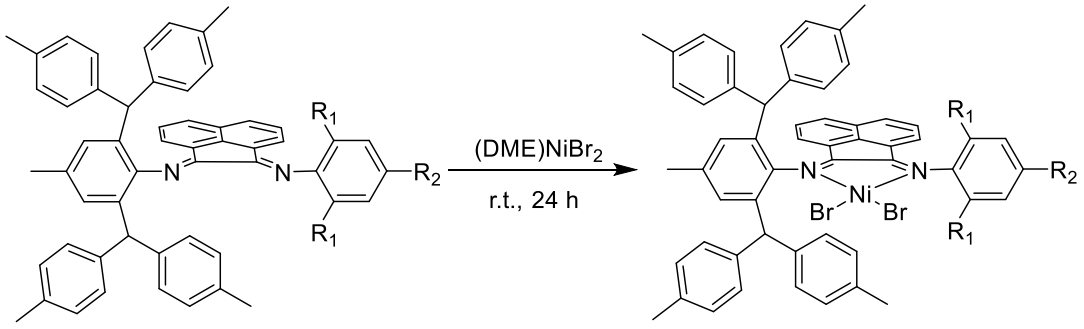


Yield: 1.36 g, 68.7%

Yield: 0.85 g, 70.1%

Acenaphthylene-bis[2,6-bis(di-*p*-tolylmethyl)-4-methylphenyl]-1,2-diimine (L4). $ZnCl_2$ (0.24 g, 1.79 mmol) and acenaphthenequinone (0.29 g, 1.57 mmol) were suspended in glacial acetic acid (6 mL). 2,6-Bis(diphenylmethyl)-4-methylaniline (1.77 g, 3.57 mmol) was added, and the reaction mixture was refluxed under stirring for 30 min. The solution was allowed to cool to room temperature, and a bright orange-red solid precipitated. The solid was separated by filtration and washed with acetic acid (3 × 5mL) and diethyl ether (5 × 5 mL), to remove remaining acetic acid. Drying under vacuum gave bright orange-red, poorly soluble solid (1.36 g, 68.7%). Then the zinc was removed from the zinc diimine complex. The product of the previous step was suspended in methylene chloride (24 mL), and a solution of potassium oxalate (0.22 g, 1.2 mmol) in water (2 mL) was added. The reaction mixture was stirred vigorously for 20 min. The two phases were separated, and the organic layer was washed with water (3 × 10 mL) and dried with $MgSO_4$. After filtration the solvent was removed under vacuum to afford the product as an orange powder (0.85 g, 70.1%), followed by recrystallization from dichloromethane and *n*-hexane. The total yield of two steps is 48.2%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2H), 6.99 – 6.83 (m, 22H), 6.72 (d, *J* = 5.6 Hz, 8H), 6.39 (d, *J* = 5.6 Hz, 8H), 6.12 (d, *J* = 5.1 Hz, 2H), 5.56 (s, 4H, C*H*(PhMe)$_2$), 2.27 (s, 6H, Ar-C*H*$_3$), 2.25 (s, 12H, CH(Ph*Me*)$_2$), 1.88 (s, 12H, CH(Ph*Me*)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.53 (*C*=N), 146.70, 141.17, 140.07, 139.82, 135.25, 134.80, 132.52, 131.84, 129.91, 129.49, 129.21, 128.78, 128.60, 128.55, 127.09, 126.57, 124.49, 50.73 (*C*H(PhMe)$_2$), 21.64 (Ar-*C*H$_3$), 21.09(CH(Ph*Me*)$_2$), 20.69 (CH(Ph*Me*)$_2$). This compound is known.[1]

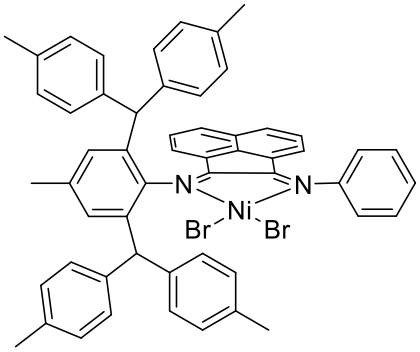
2.5 Procedure for the Synthesis of Nickel Complexes 1-5.



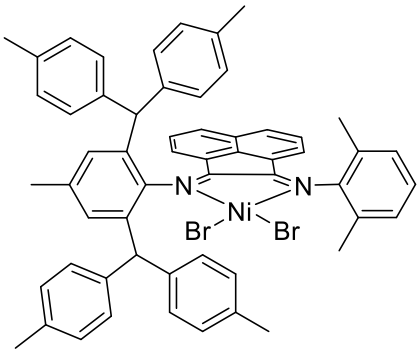
L1: R_1 = H, R_2 = H
L2: R_1= Me, R_2 = H
L3: R_1= CH(Me)$_2$.R_2 = H
L4: R_1 = CHMePh, R_2 = Me
L5: R_1= CH(PhMe)$_2$, R_2 = Me

1: R_1 = H, R_2 = H
2: R_1= Me, R_2 = H
3: R_1= CH(Me)$_2$, R_2 = H
4: R_1 = CHMePh, R_2 = Me
5: R_1= CH(PhMe)$_2$, R_2 = Me

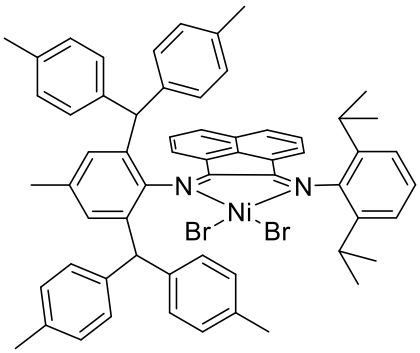
Complexes **1-5** were synthesized by the reaction of 1 equiv. of (DME)$NiBr_2$ with the corresponding ligands in methylene chloride. The corresponding ligand (0.3 mmol) was added in 10 mL of methylene chloride in a Schlenk tube under a nitrogen atmosphere. A suspension of (DME)$NiBr_2$ (0.3 mmol) in CH_2Cl_2 (10 mL) was added to the above solution. The resulting mixture was stirred at room temperature for 24 hours. The solvent was evaporated under reduced pressure to afford a solid. The product was washed with 4 × 5 mL diethyl ether and dried under vacuum. The single crystal can be obtained by diffusion from layering hexane on to the CH_2Cl_2 solution at room temperature.



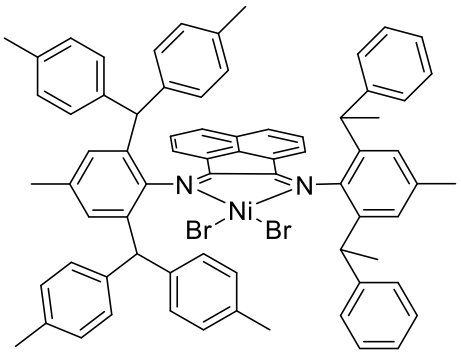
Complex 1. Brown solid. Yield: 0.25 g, 86%. Elem. Anal. Calcd for $C_{55}H_{46}Br_2N_2Ni$: C, 69.28; H, 4.86; N, 2.94. Found: C, 69.02; H, 4.83; N, 2.99. MALDI-TOF-MS(m/z): calcd for $C_{55}H_{47}BrN_2Ni$: $[M\text{-}Br+H]^+$ 872.2276, found:872.8820.



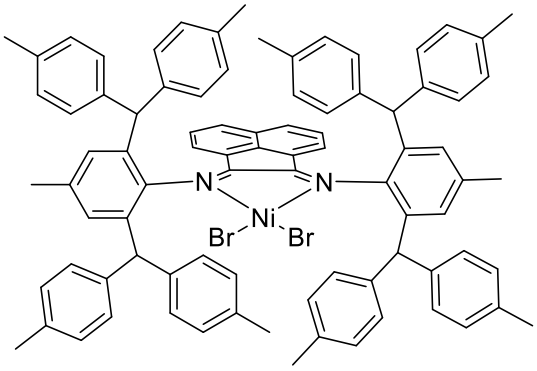
Complex 2. Brown solid. Yield: 0.26 g, 89.0%. Elem. Anal. Calcd for $C_{57}H_{50}Br_2N_2Ni$: C, 69.75; H, 5.13; N, 2.85. Found: C, 69.53; H, 4.99; N, 2.68. MALDI-TOF-MS(m/z): calcd for $C_{57}H_{50}BrN_2Ni$: $[M\text{-}Br]^+$ 901.2490, found: 901.2432.



Complex 3. Brown solid. Yield: 0.28 g, 91%. Elem. Anal. Calcd for $C_{61}H_{58}Br_2N_2Ni$: C, 70.61; H, 5.63; N, 2.70. Found: C, 70.75; H, 5.73; N, 2.47. MALDI-TOF-MS(m/z): calcd for $C_{61}H_{58}BrN_2Ni$: $[M\text{-}Br]^+$ 957.3116, found: 957.3694.



Complex 4. Brown solid. Yield 0.31 g, 87%. Elem. Anal. Calcd for $C_{72}H_{64}Br_2N_2Ni$: C, 73.55; H, 5.49; N, 2.38. Found: C, 73.40; H, 5.51; N, 2.46. MALDI-TOF-MS(m/z): calcd for $C_{72}H_{65}BrN_2Ni$: $[M-Br+H]^+$ 1094.3685, found: 1094.8672.



Complex 5. Brown solid. Yield: 0.38 g, 93%. This compound is known.[3]

2.6 General *in-Situ* Activated Polymerization Procedure.

Under an inert atmosphere, a 350 mL glass thick-walled pressure vessel was charged with MAO, 40 mL toluene, and a magnetic stir bar. The vessel was pressurized with 1 atm of ethylene and allowed to equilibrate under constant pressure for 10 minutes with stirring. The nickel complex in 1 mL CH_2Cl_2 was injected and the ethylene pressure was increased to 8 atm to initiate polymerization and stirred continuously for the desired time. The polymerization was quenched via the addition of MeOH (5 mL) and the polymer was precipitated using excess acidic MeOH (5% HCl in MeOH) and dried in a vacuum oven to constant weight. Polymer branching density was determined by ^1H NMR. $B = 1000\times2(I_{CH3})/3(I_{CH2+CH}+I_{CH3})$. CH_3 (m, 0.77-0.95 ppm); CH_2 and CH (m, ca. 1.0-1.45 ppm).

2.7 Copolymerization of Ethylene and UA

In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 20 mL of toluene with the desired amount Et_2AlCl was added to the reactor under N_2 atmosphere, then the desired polar monomer and the desired amount of Ni catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at the desired pressure of ethylene. After 1 h, the pressure reactor was vented and the copolymer was dried under vacuum overnight.

3. Spectra Data

3.1 ^{1}H and ^{13}C NMR of the Synthetic Compounds.

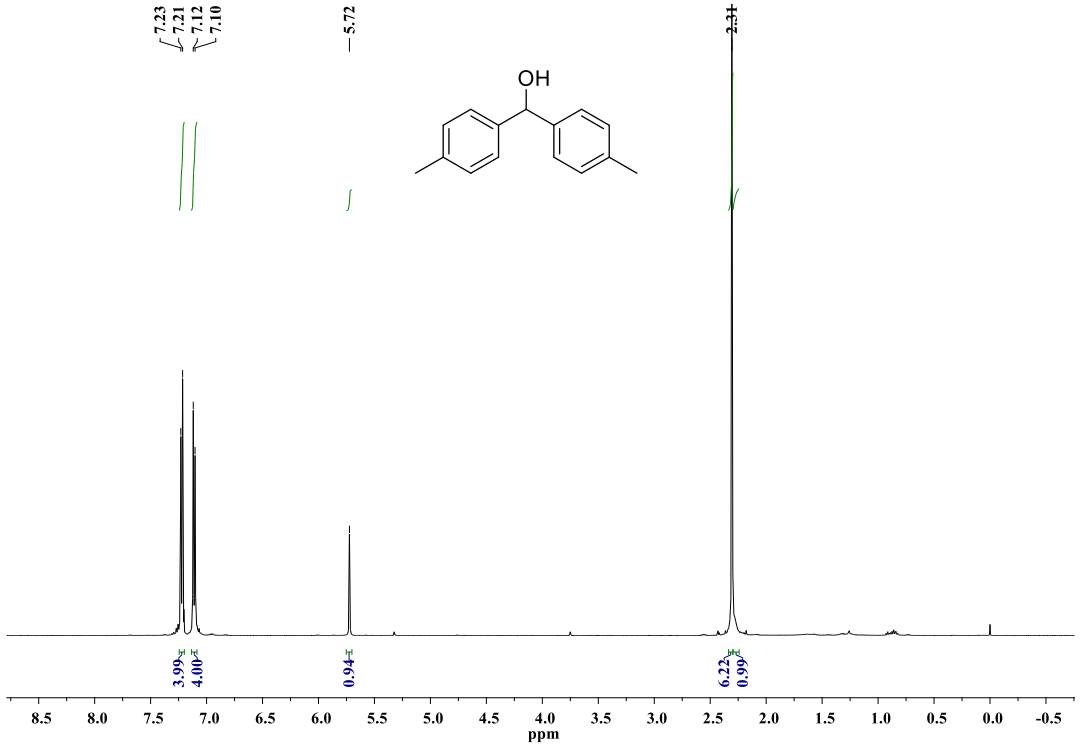


Figure S4. ^{1}H NMR spectrum of **bis(3-methylphenyl)methanol** in $CDCl_3$

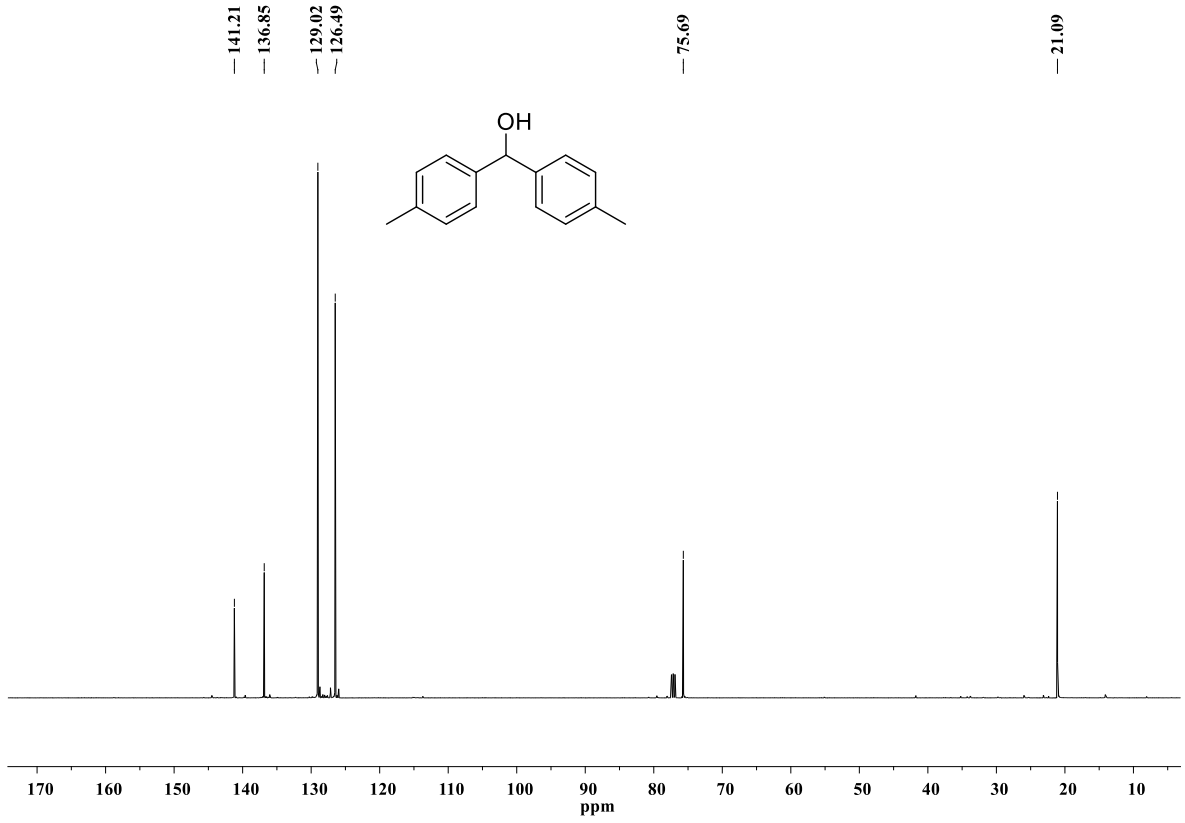


Figure S5. ^{13}C NMR spectrum of **bis(3-methylphenyl)methanol** in $CDCl_3$.

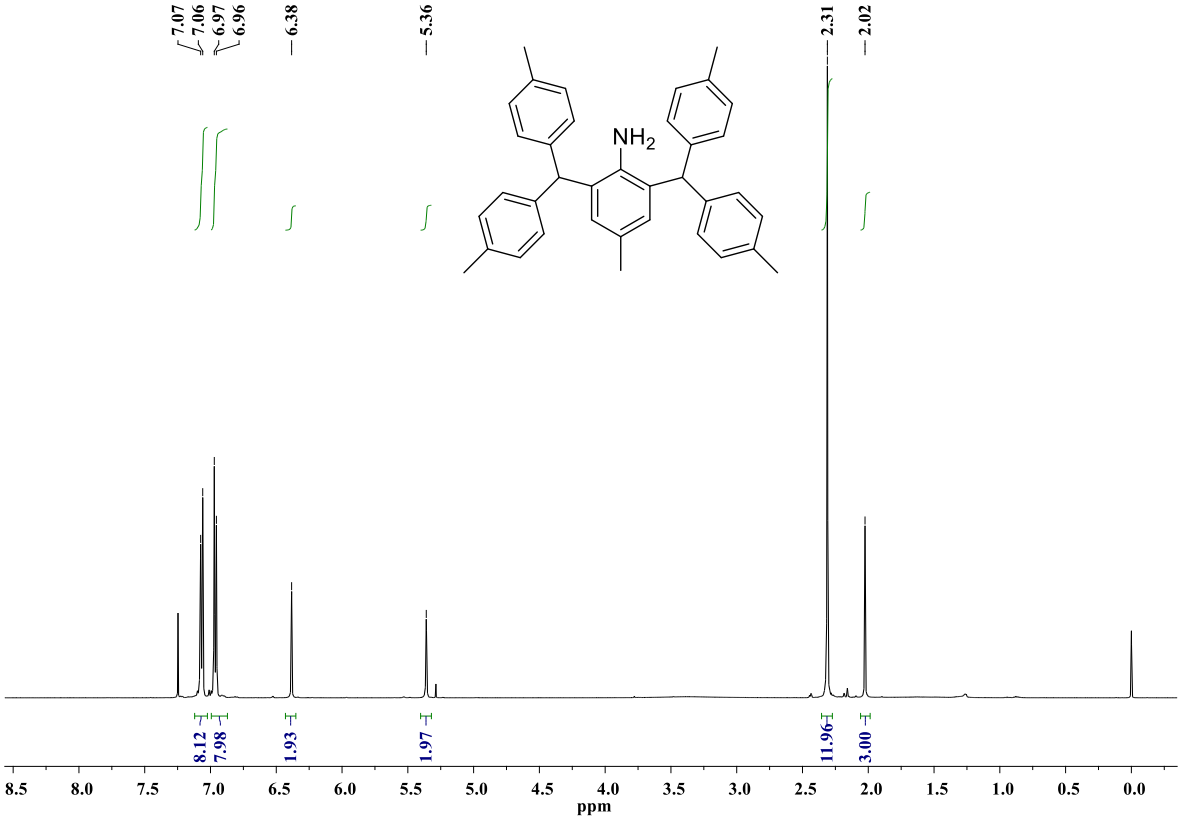


Figure S6. ^{1}H NMR spectrum of **2,6-Bis(di-p-tolylmethyl)-4-methylaniline** in $CDCl_3$.

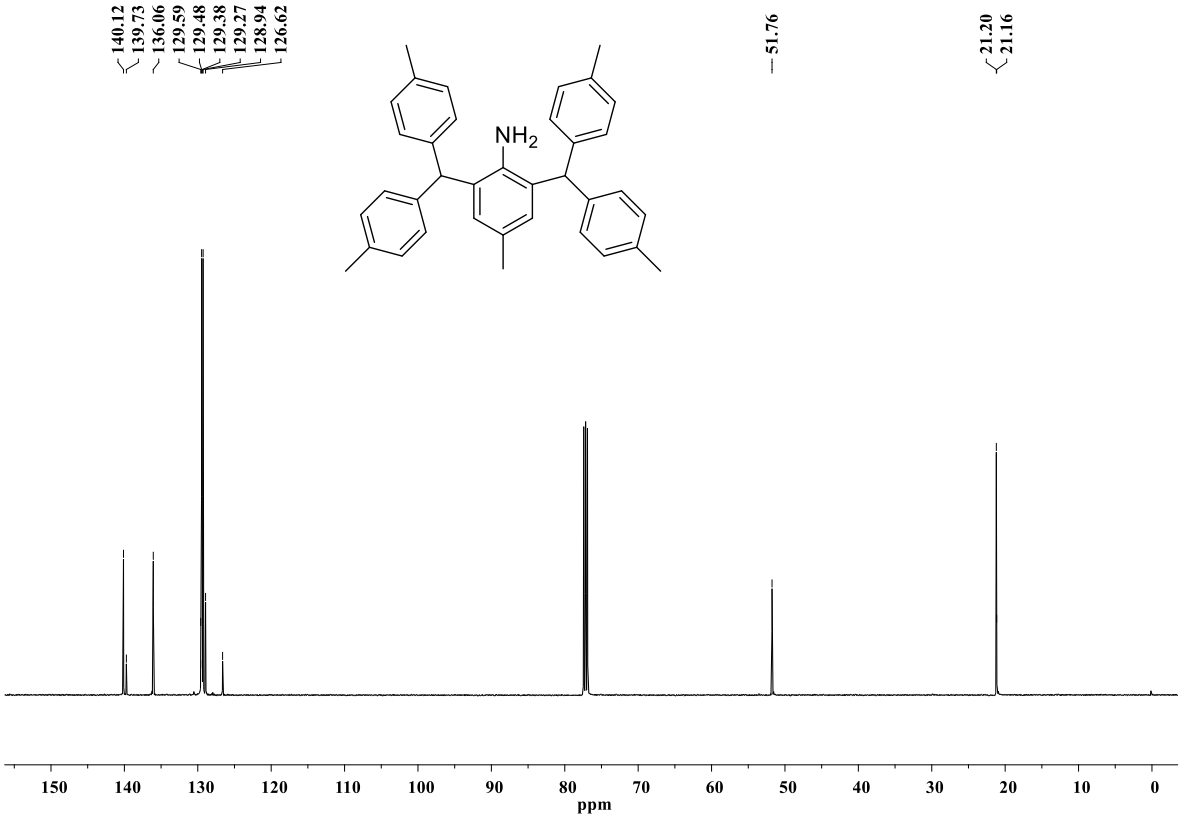


Figure S7. ^{13}C NMR spectrum of **2,6-Bis(di-p-tolylmethyl)-4-methylaniline** in $CDCl_3$.

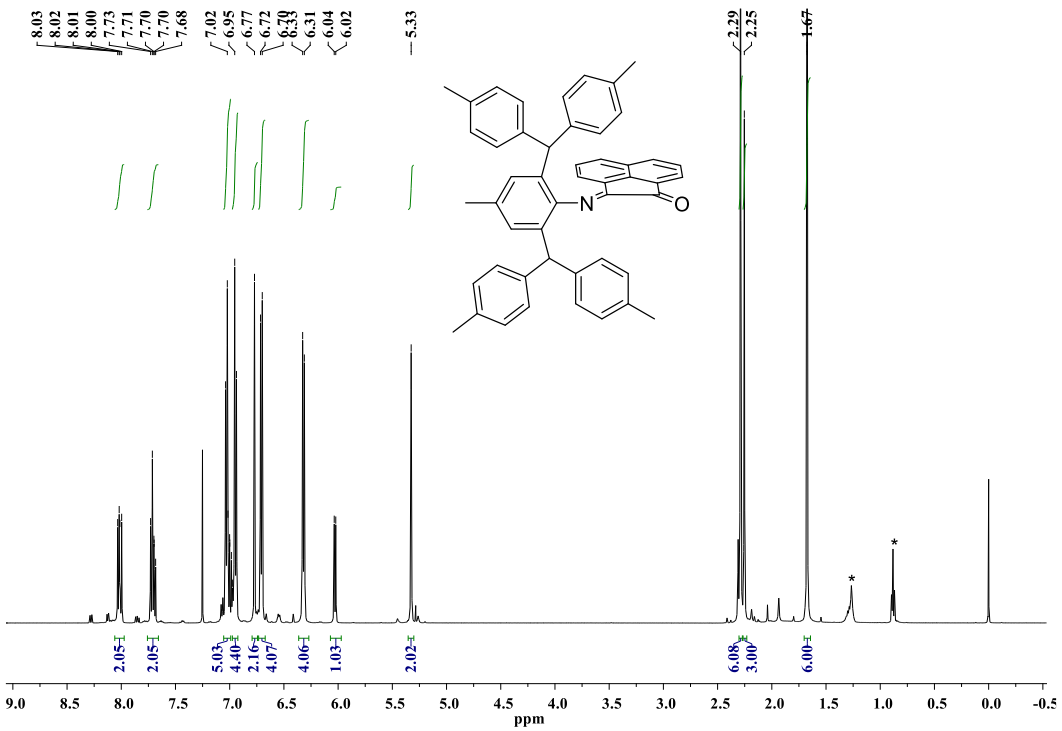


Figure S8. ^{1}H NMR spectrum of **2-((2,6-bis(di-p-tolylmethyl)-4-methylphenyl)imino)acenaphthylen-1-one** in $CDCl_3$. *hexanes

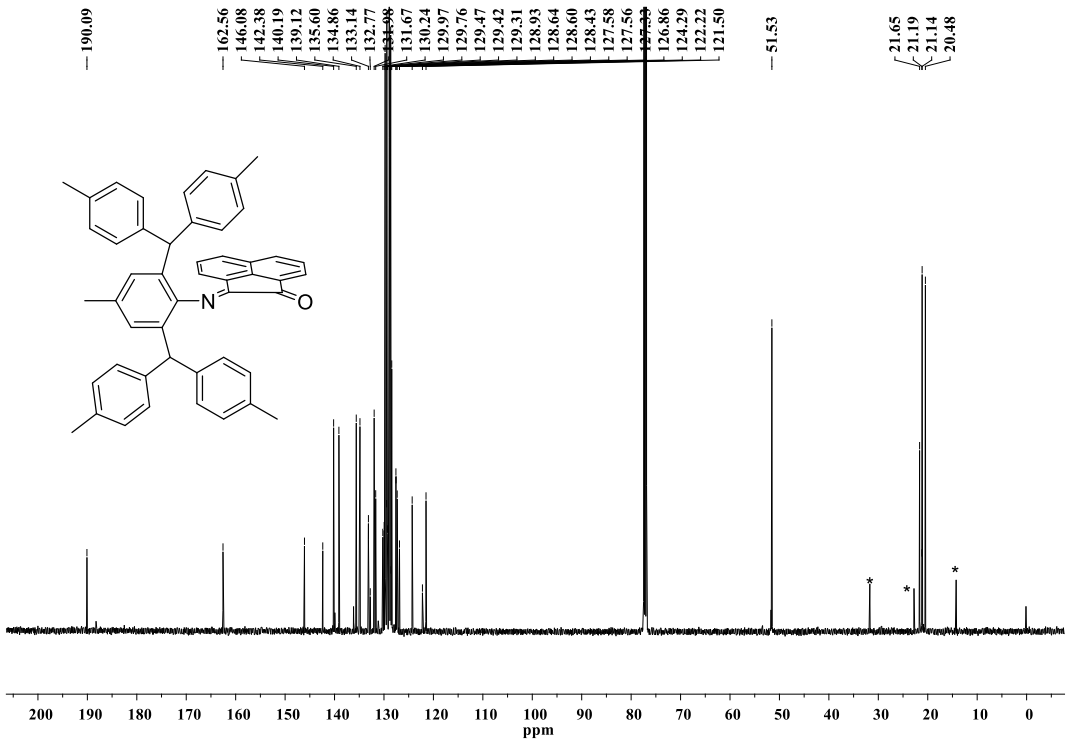


Figure S9. ^{13}C NMR spectrum of **2-((2,6-bis(di-p-tolylmethyl)-4-methylphenyl)imino)acenaphthylen-1-one** in $CDCl_3$. *hexanes

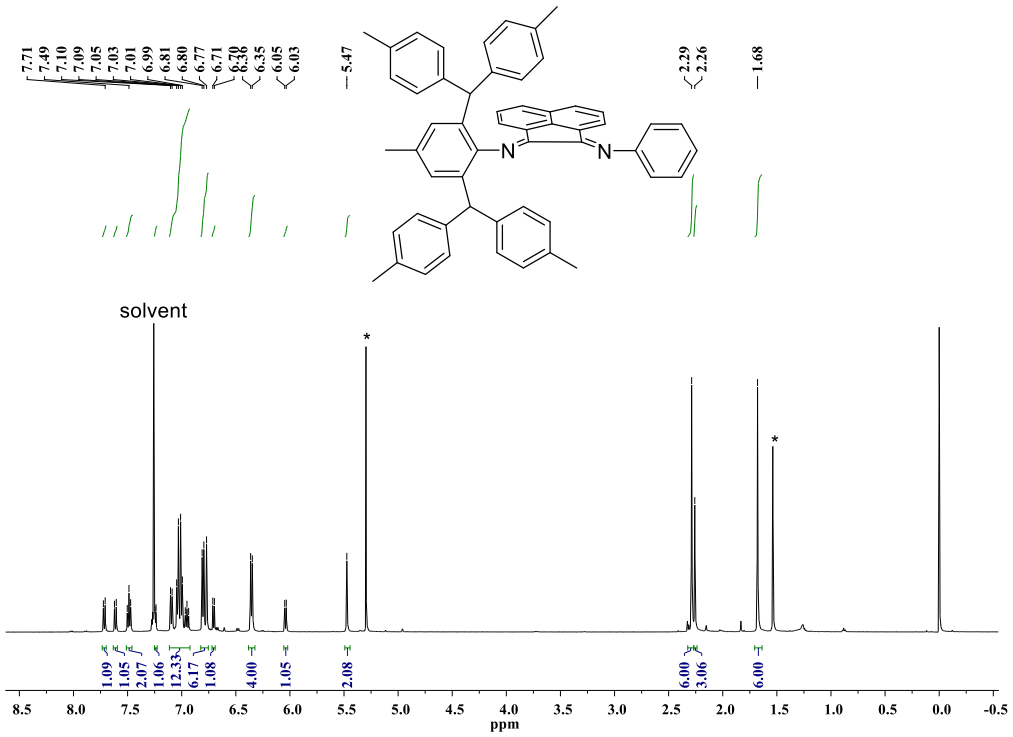


Figure S10. ^{1}H NMR spectrum of **L1** in $CDCl_3$.*DCM, water.

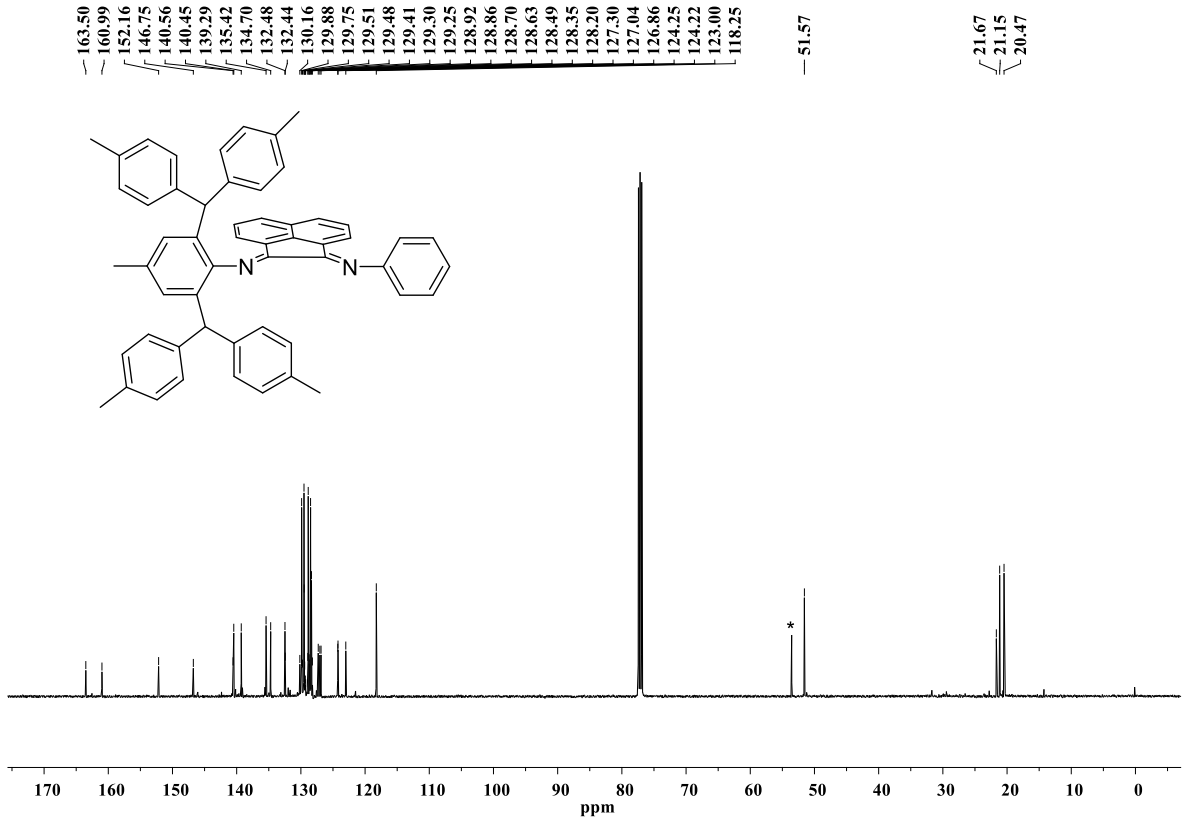


Figure S11. ^{13}C NMR spectrum of **L1** in $CDCl_3$. *DCM.

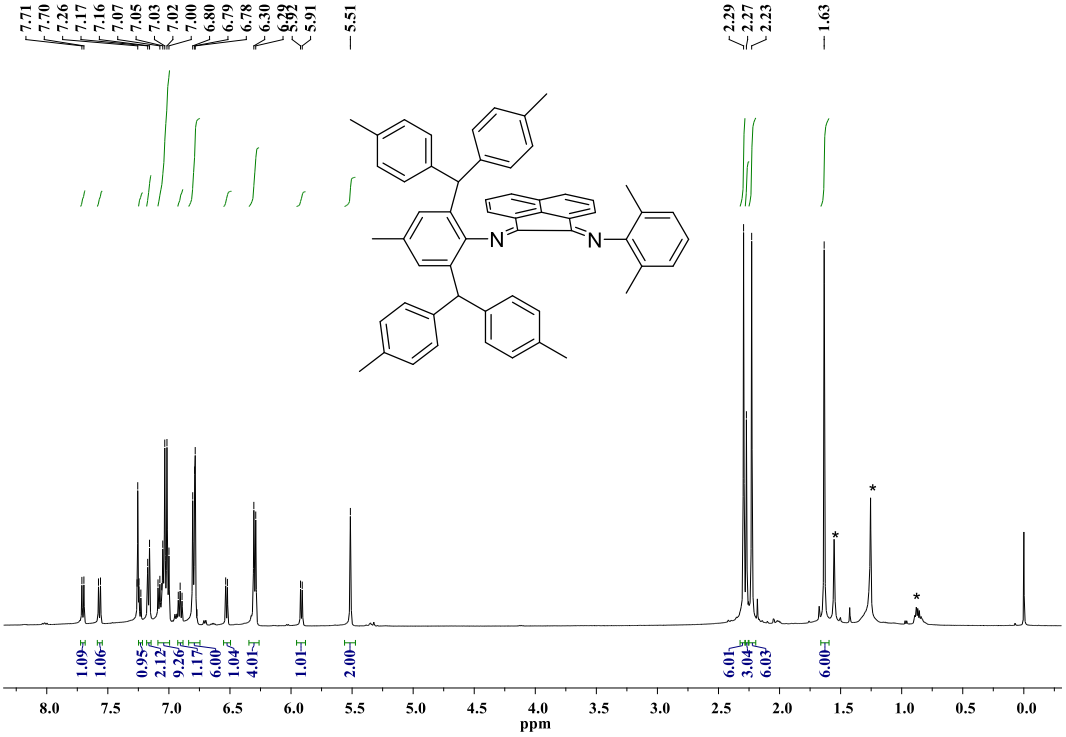


Figure S12. ^{1}H NMR spectrum of **L2** in $CDCl_3$. *hexanes, water.

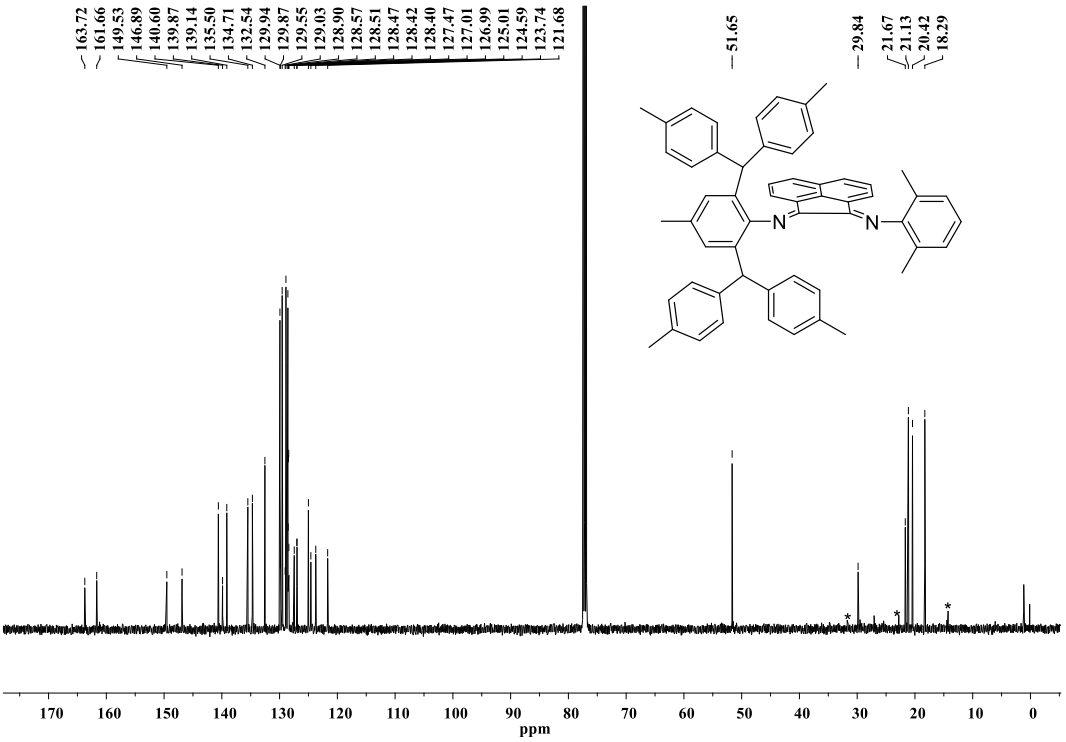


Figure S13. ^{13}C NMR spectrum of **L2** in $CDCl_3$. *hexanes

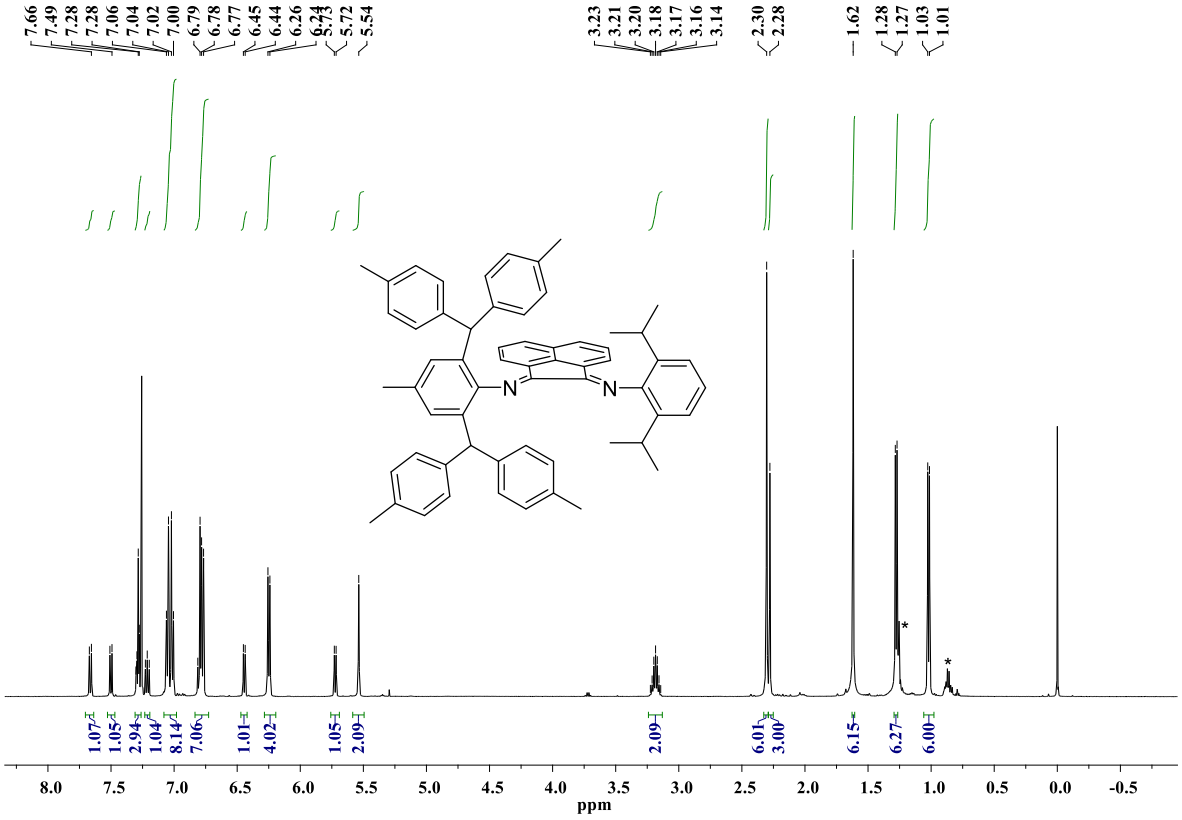


Figure S14. ^{1}H NMR spectrum of **L3** in $CDCl_3$. *hexanes

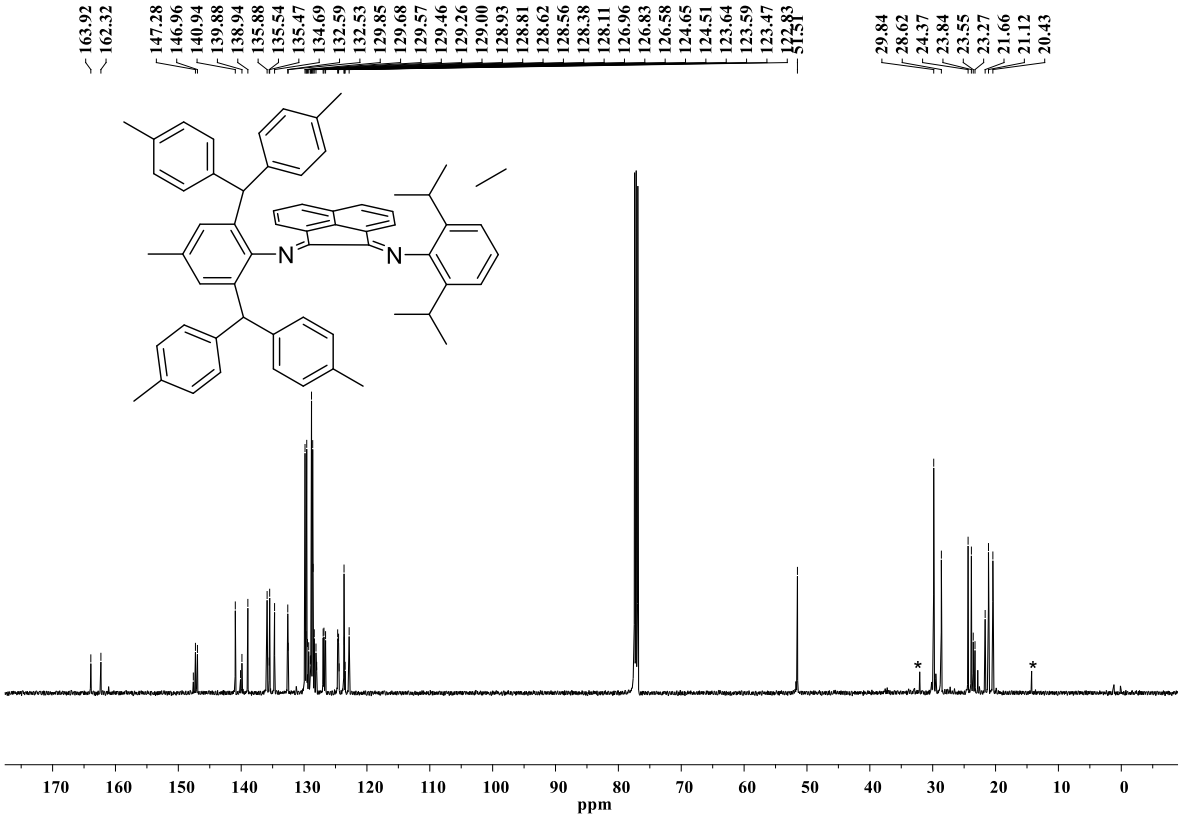


Figure S15. ^{13}C NMR spectrum of **L3** in $CDCl_3$. *hexanes

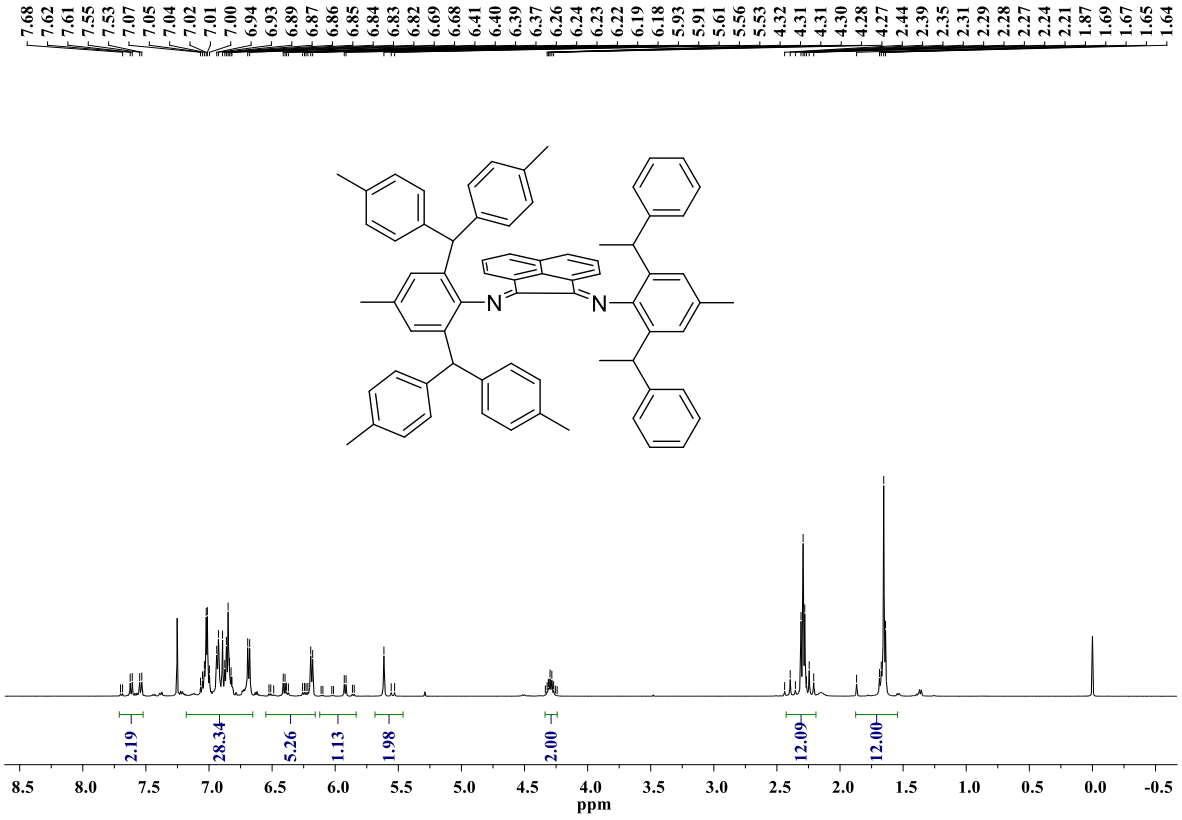


Figure S16. ^{1}H NMR spectrum of **L4** in $CDCl_3$.

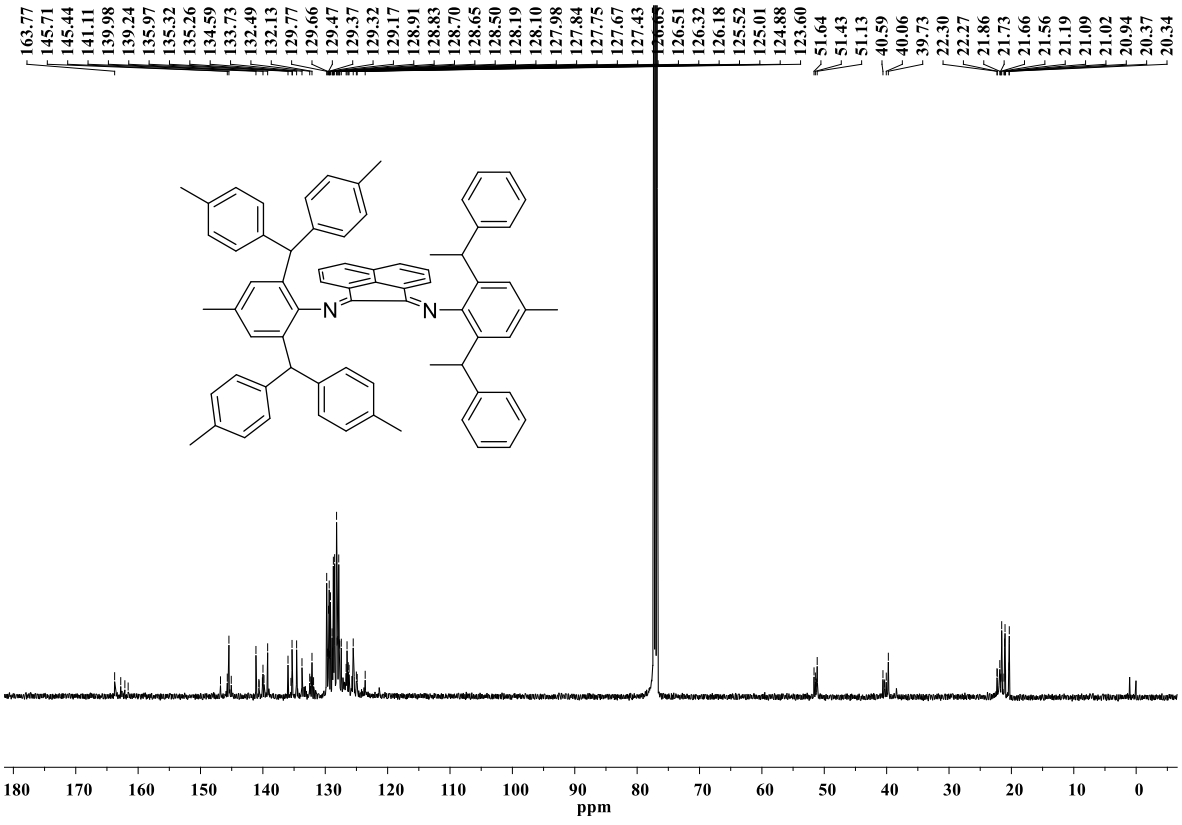


Figure S17. ^{13}C NMR spectrum of **L4** in $CDCl_3$.

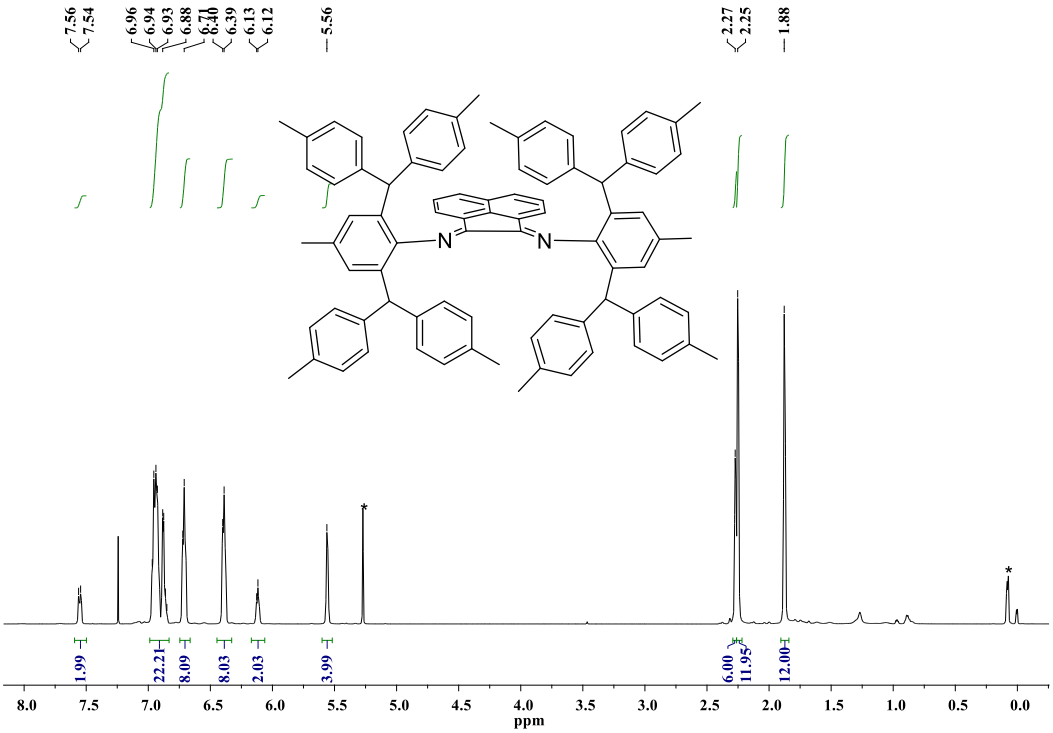


Figure S18. ^{1}H NMR spectrum of **L5** in $CDCl_3$. *DCM, greese.

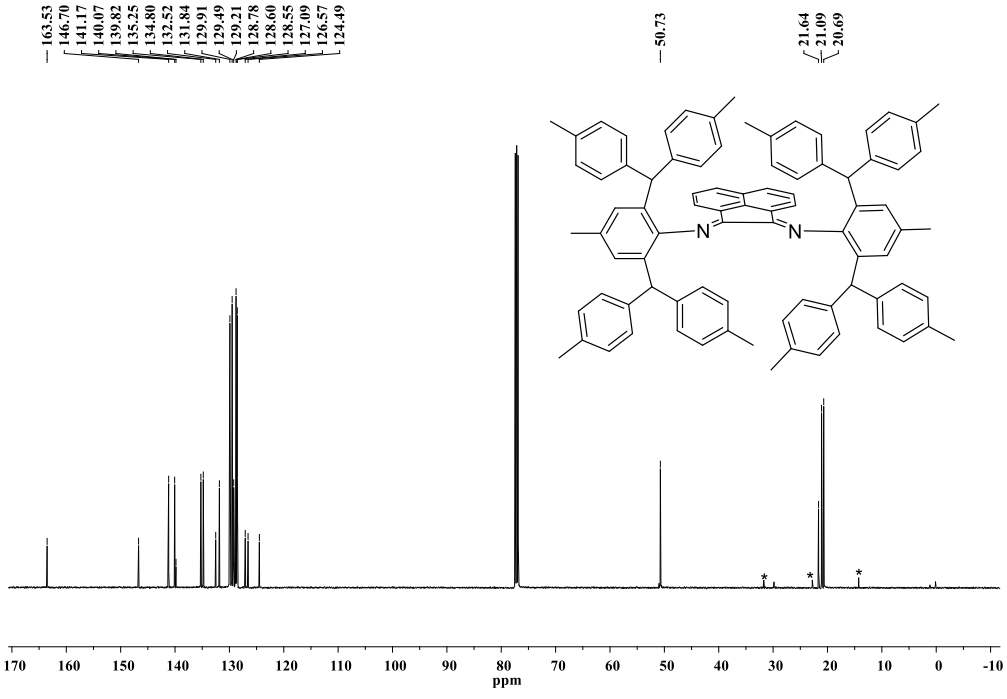


Figure S19. ^{13}C NMR spectrum of **L5** in $CDCl_3$. *hexanes.

3.2 ESI-MS of Ligand L1-L4.

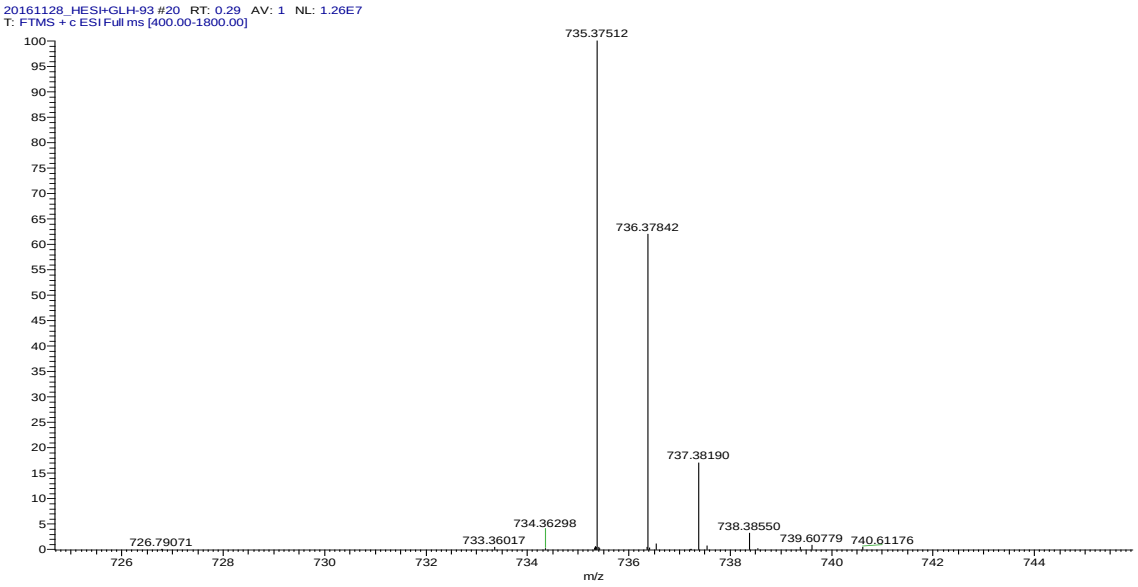


Figure S20. ESI-MS of **L1.**

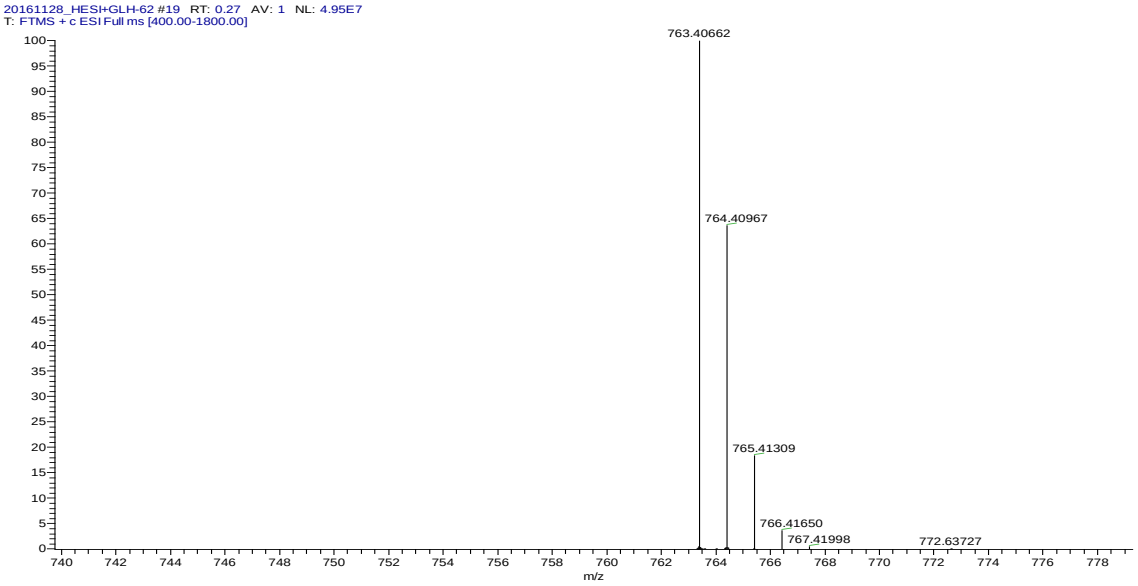


Figure S21. ESI-MS of **L2.**

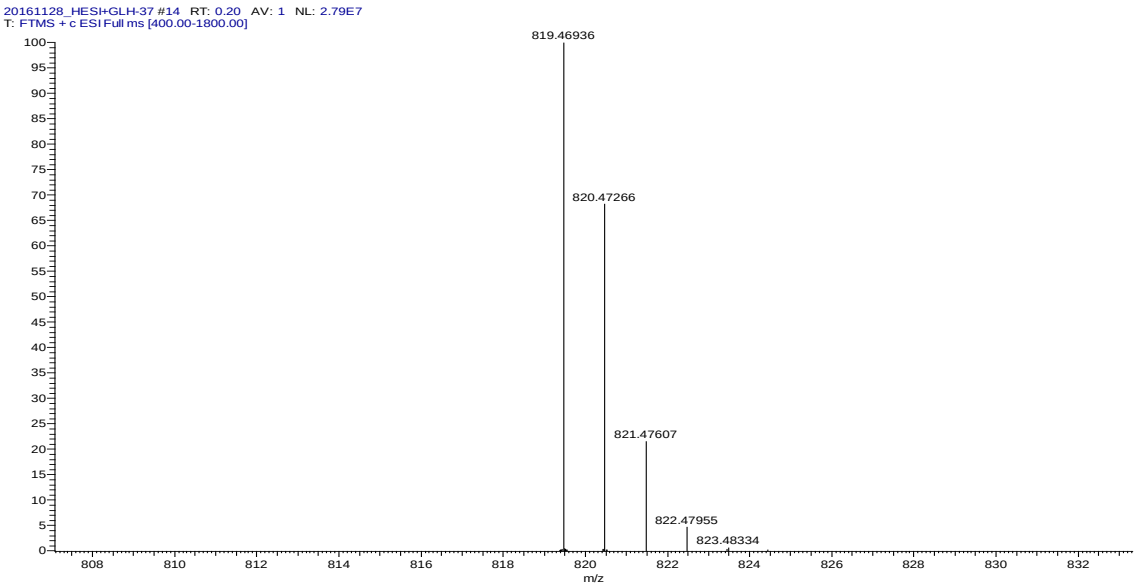


Figure S22. ESI-MS of **L3.**

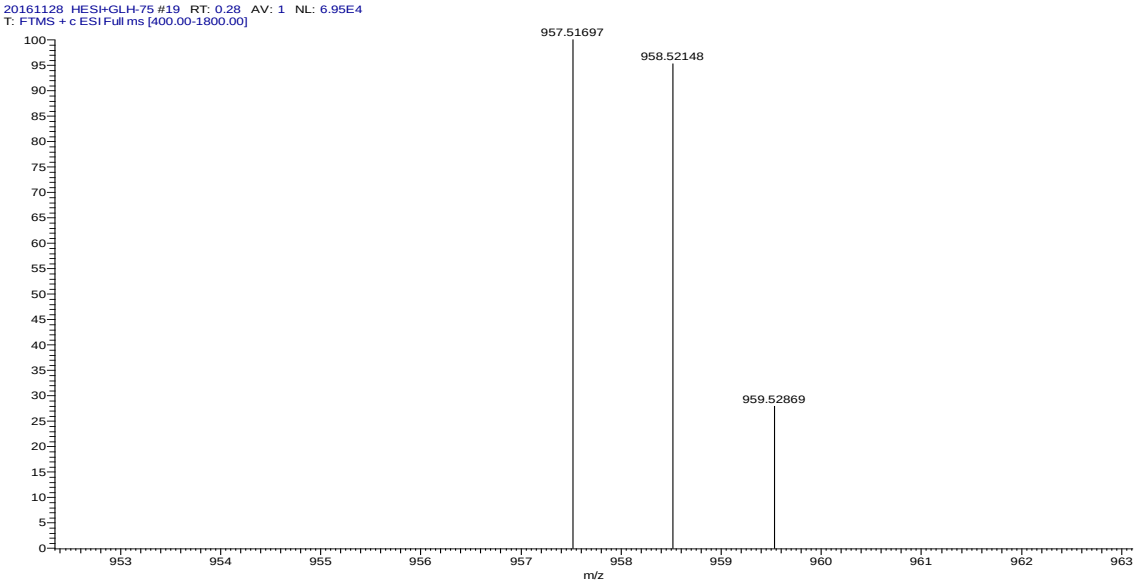


Figure S23. ESI-MS of **L4.**

3.3 MALDI-TOF of Complexes 1-4.

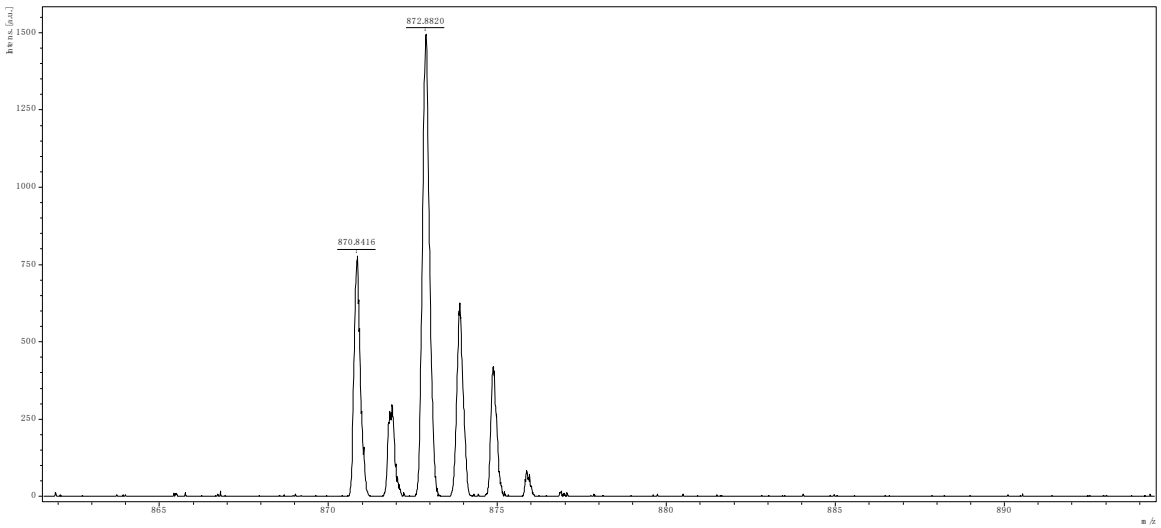


Figure S24. MALDI-TOF-MS of complex **1**.

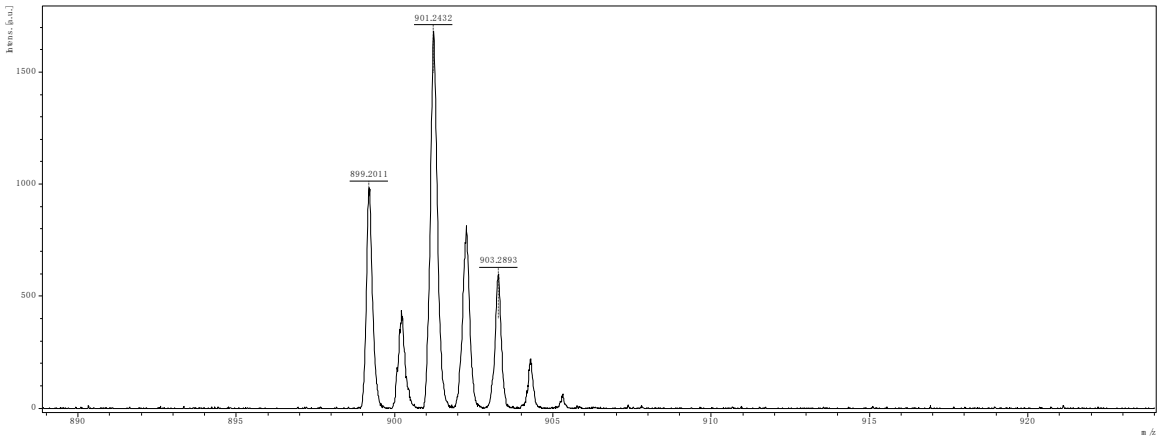


Figure S25. MALDI-TOF-MS of complex **2**.

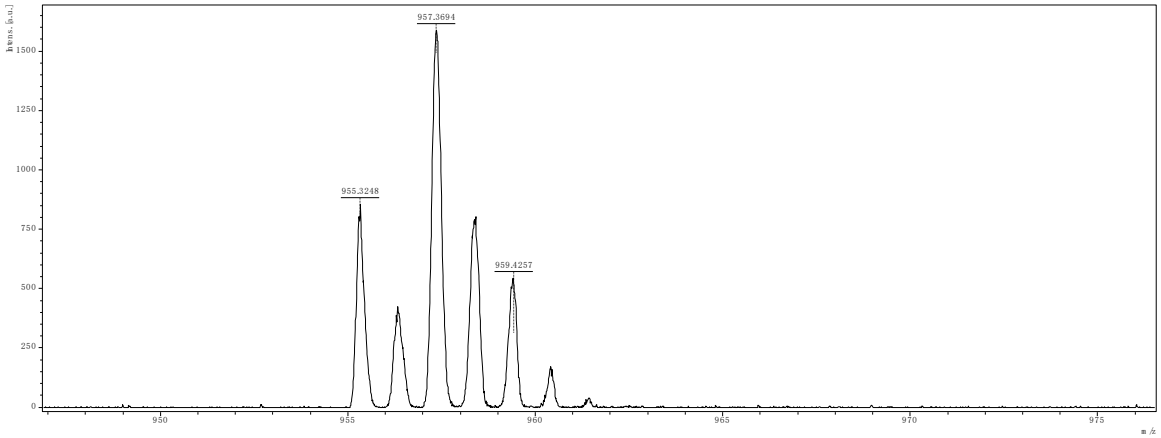


Figure S26. MALDI-TOF-MS of complex **3**.

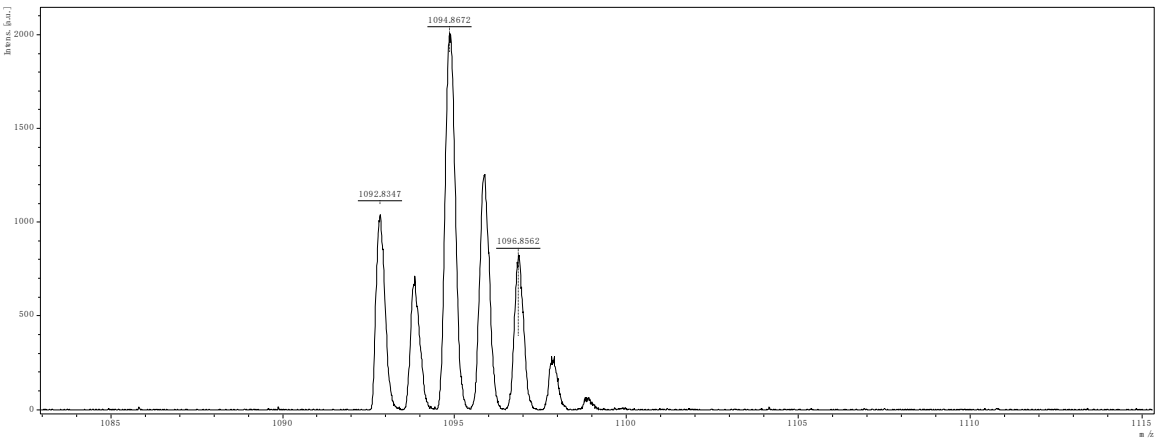


Figure S27. MALDI-TOF-MS of complex **4**.

3.4 ^{1}H and ^{13}C NMR of polymer and copolymer.

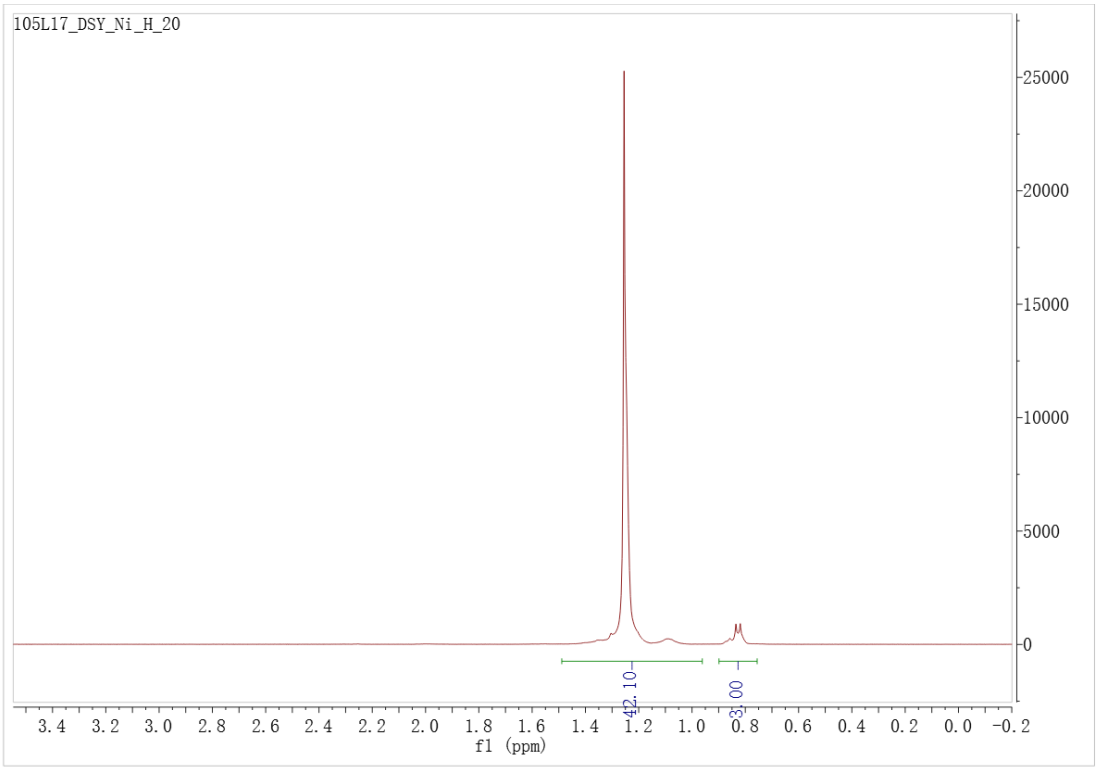


Figure S28. ^{1}H NMR spectrum of the polymer from table 1, entry 1 ($CDCl_2CDCl_2$, 120 ºC).

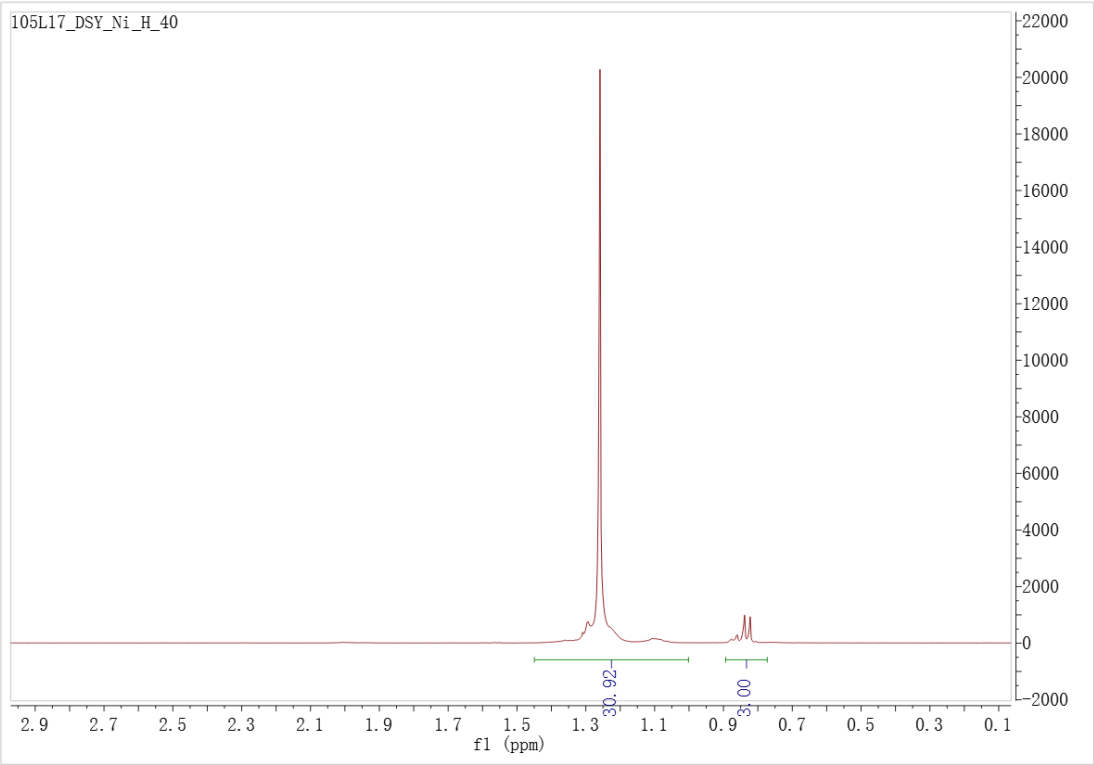


Figure S29. ^{1}H NMR spectrum of the polymer from table 1, entry 2 ($CDCl_2CDCl_2$, 120 ºC).

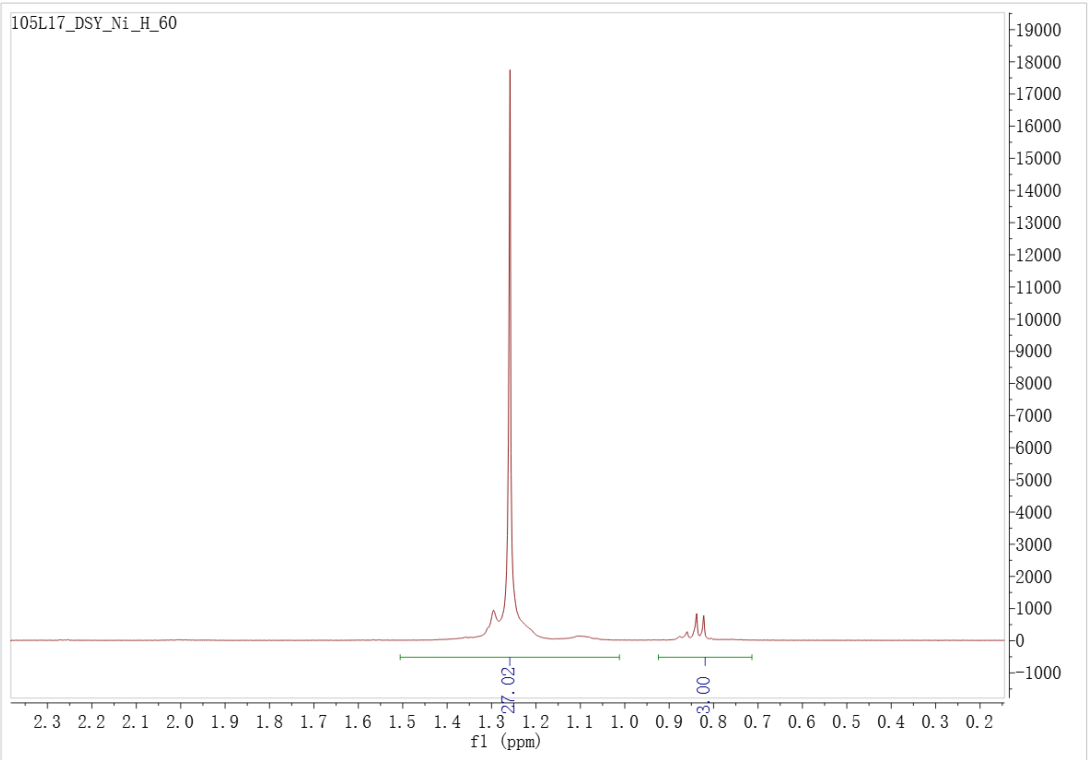


Figure S30. ^{1}H NMR spectrum of the polymer from table 1, entry 3 ($CDCl_2CDCl_2$, 120 ºC).

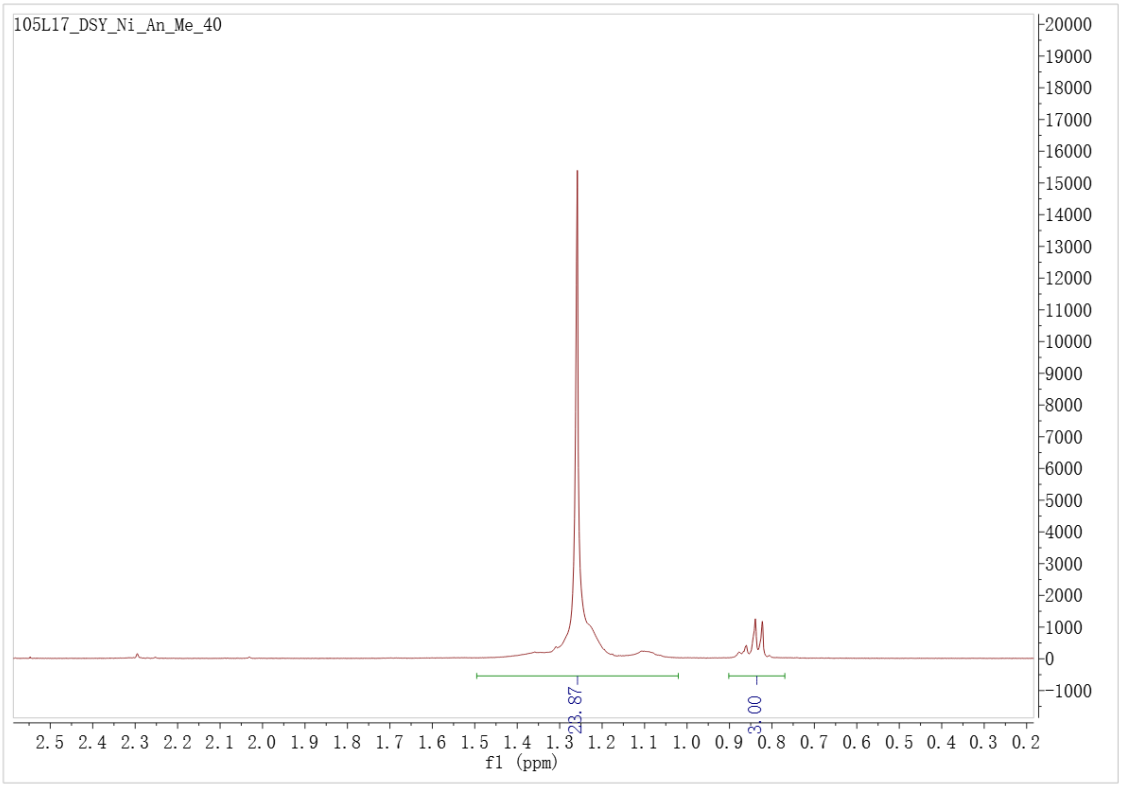


Figure S31. ^{1}H NMR spectrum of the polymer from table 1, entry 6 ($CDCl_2CDCl_2$, 120 ºC).

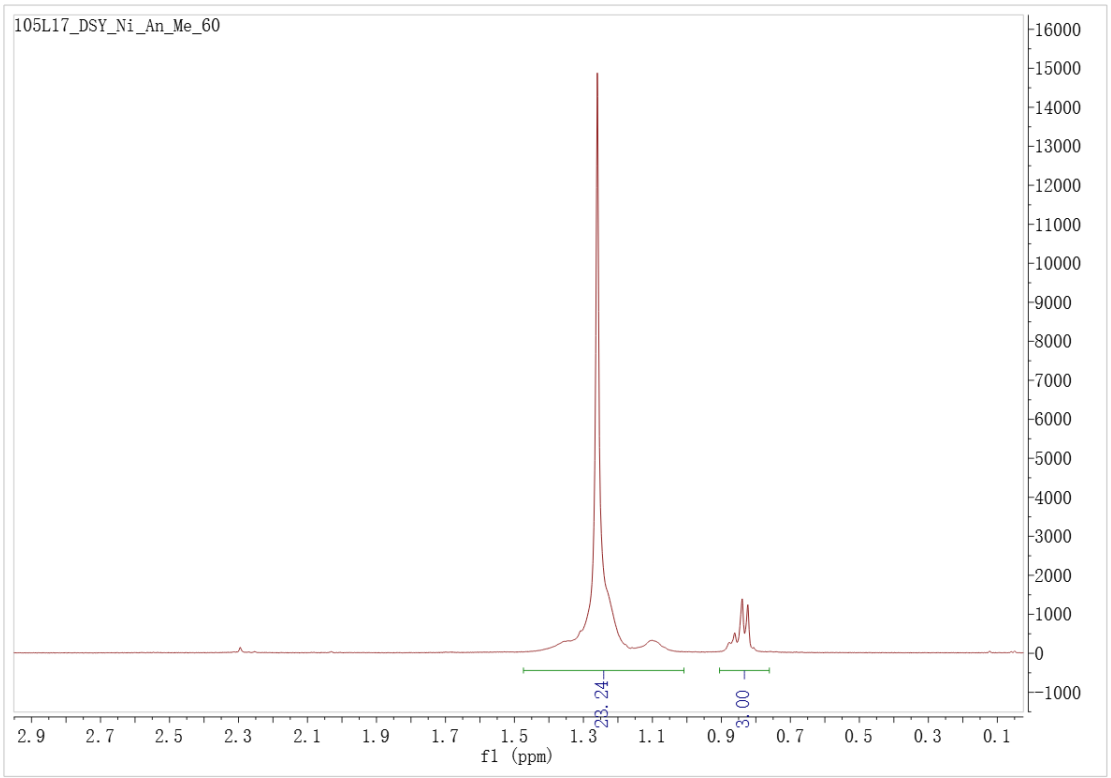


Figure S32. ^{1}H NMR spectrum of the polymer from table 1, entry 7 ($CDCl_2CDCl_2$, 120 ºC).

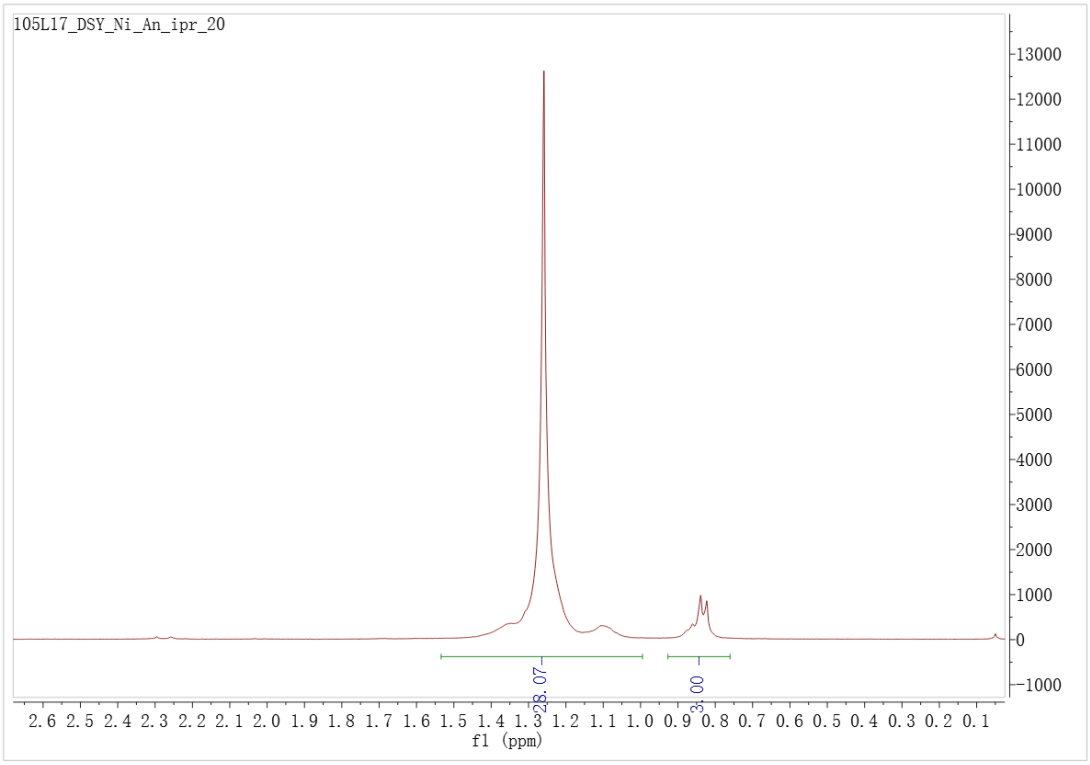


Figure S33. ^{1}H NMR spectrum of the polymer from table 1, entry 9 ($CDCl_2CDCl_2$, 120 ºC).

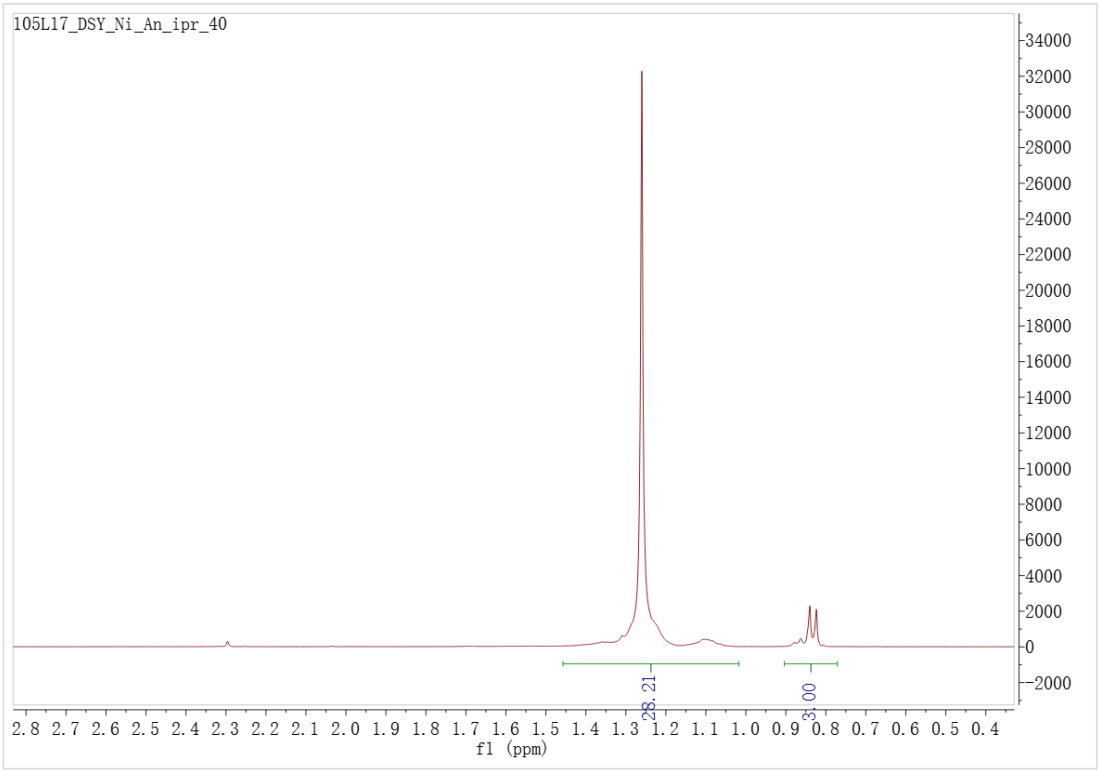


Figure S34. ^{1}H NMR spectrum of the polymer from table 1, entry 10 ($CDCl_2CDCl_2$, 120 ºC).

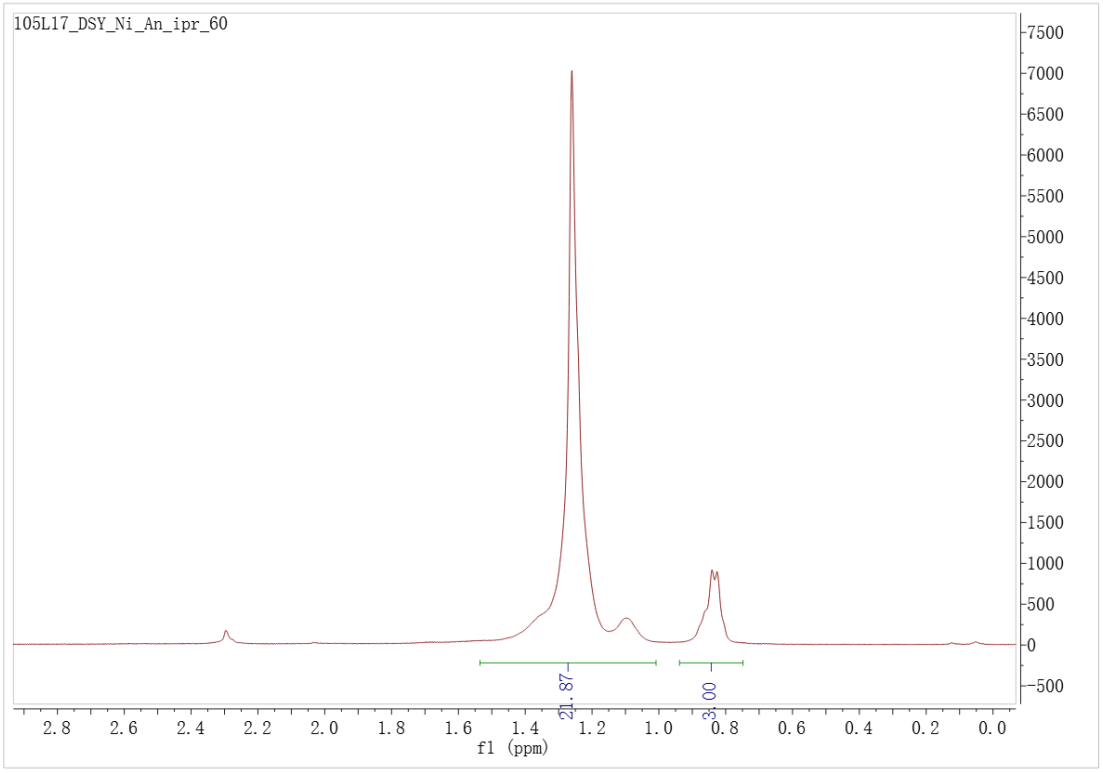


Figure S35. ^{1}H NMR spectrum of the polymer from table 1, entry 11 ($CDCl_2CDCl_2$, 120 ºC).

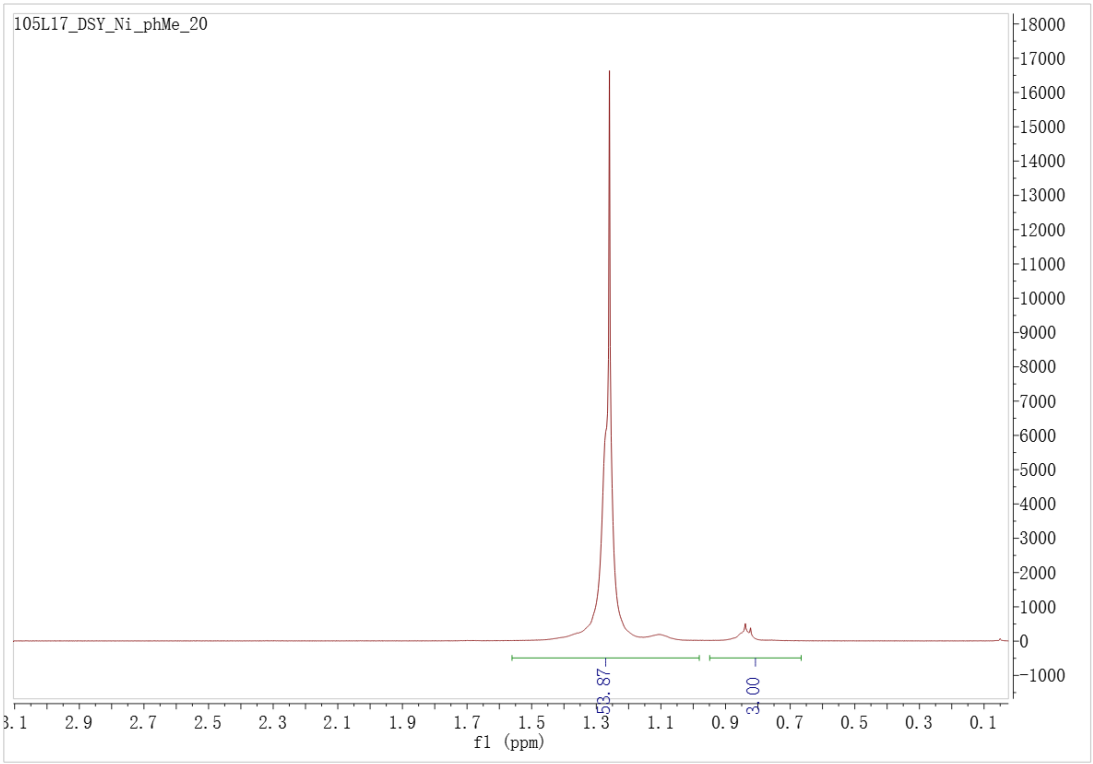


Figure S36. ^{1}H NMR spectrum of the polymer from table 1, entry 13 ($CDCl_2CDCl_2$, 120 ºC).

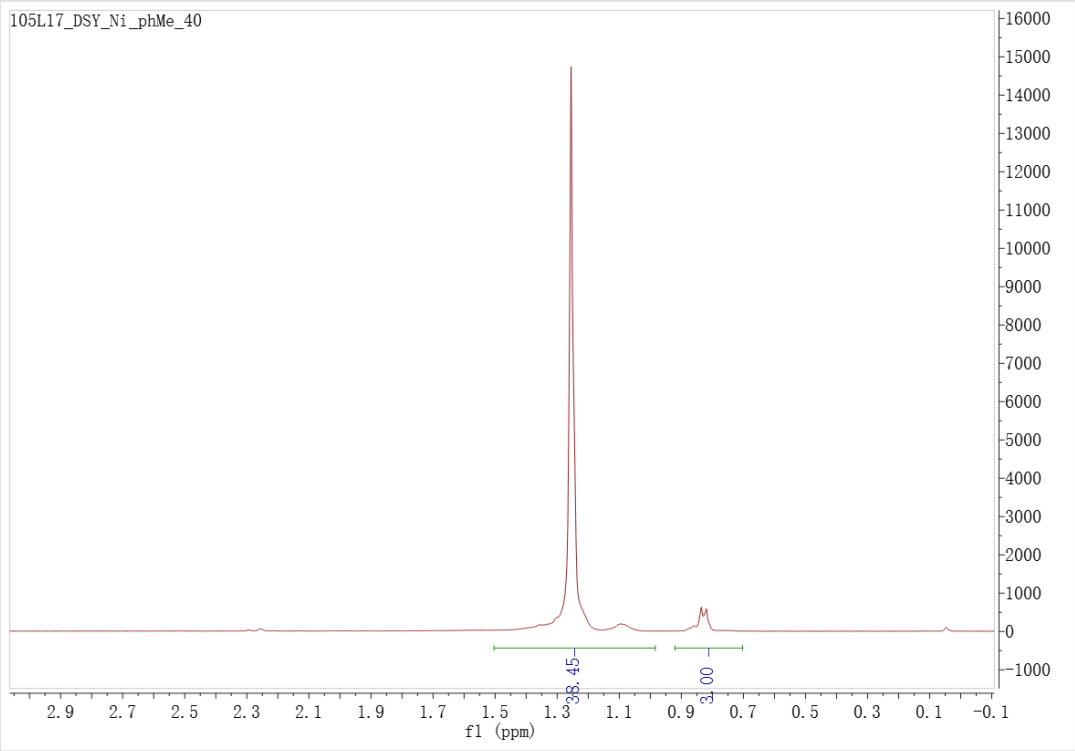


Figure S37. ^{1}H NMR spectrum of the polymer from table 1, entry 14 ($CDCl_2CDCl_2$, 120 ºC).

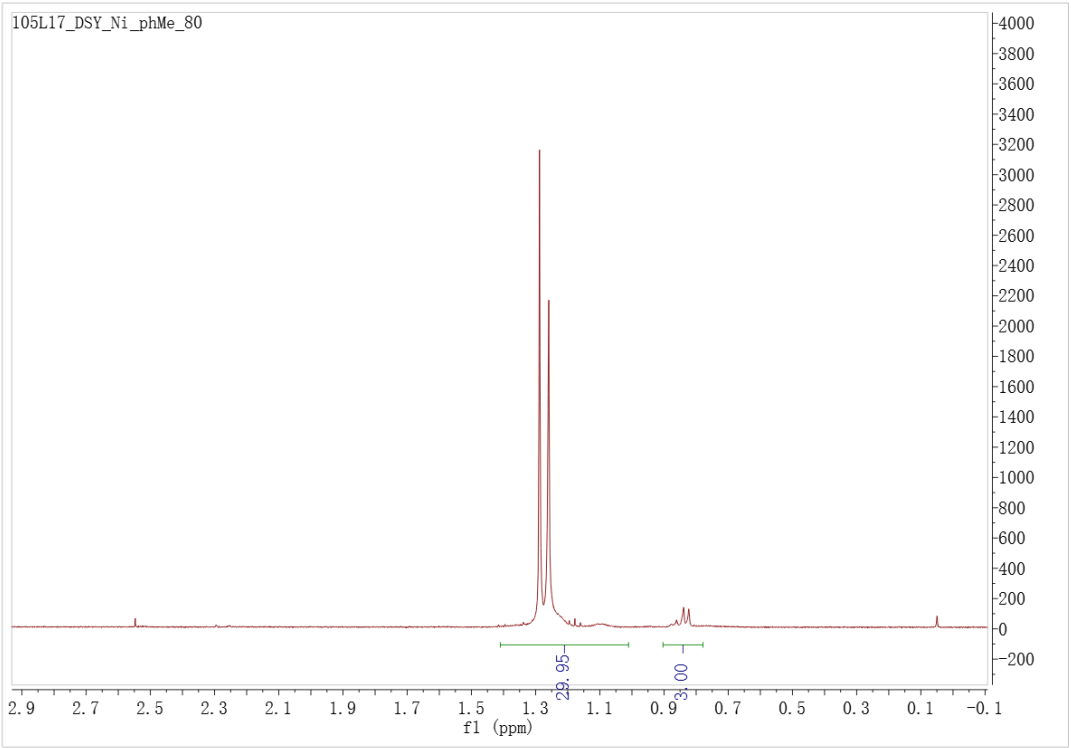


Figure S38. ^{1}H NMR spectrum of the polymer from table 1, entry 16 ($CDCl_2CDCl_2$, 120 ºC).

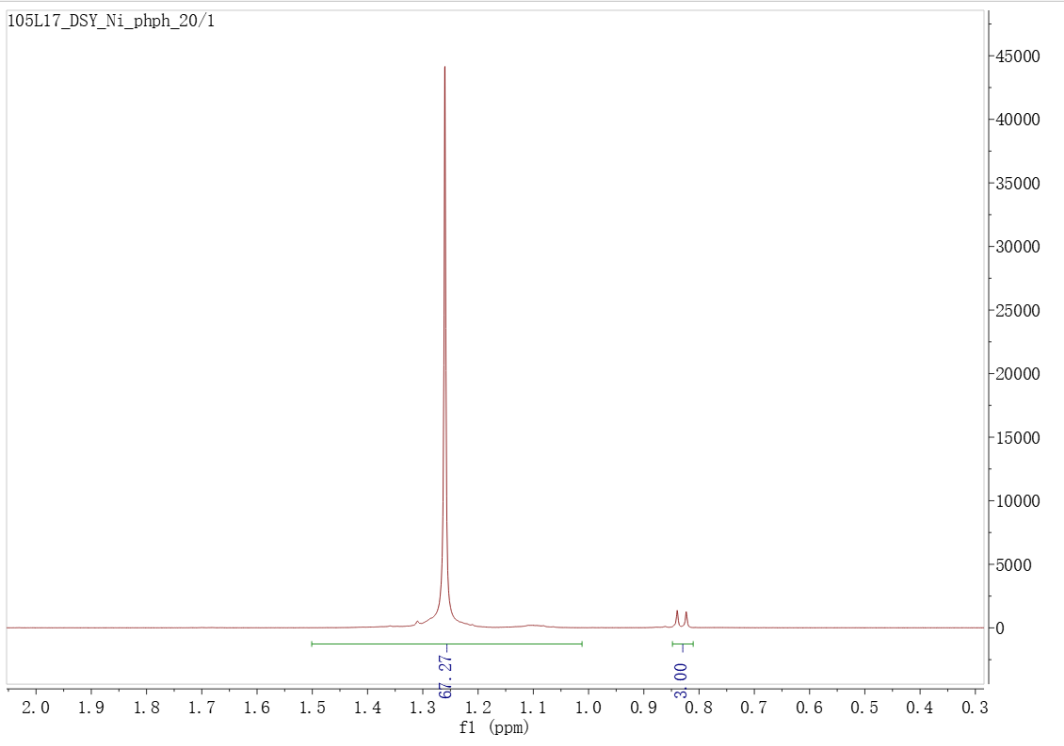


Figure S39. ^{1}H NMR spectrum of the polymer from table 1, entry 17 ($CDCl_2CDCl_2$, 120 ºC).

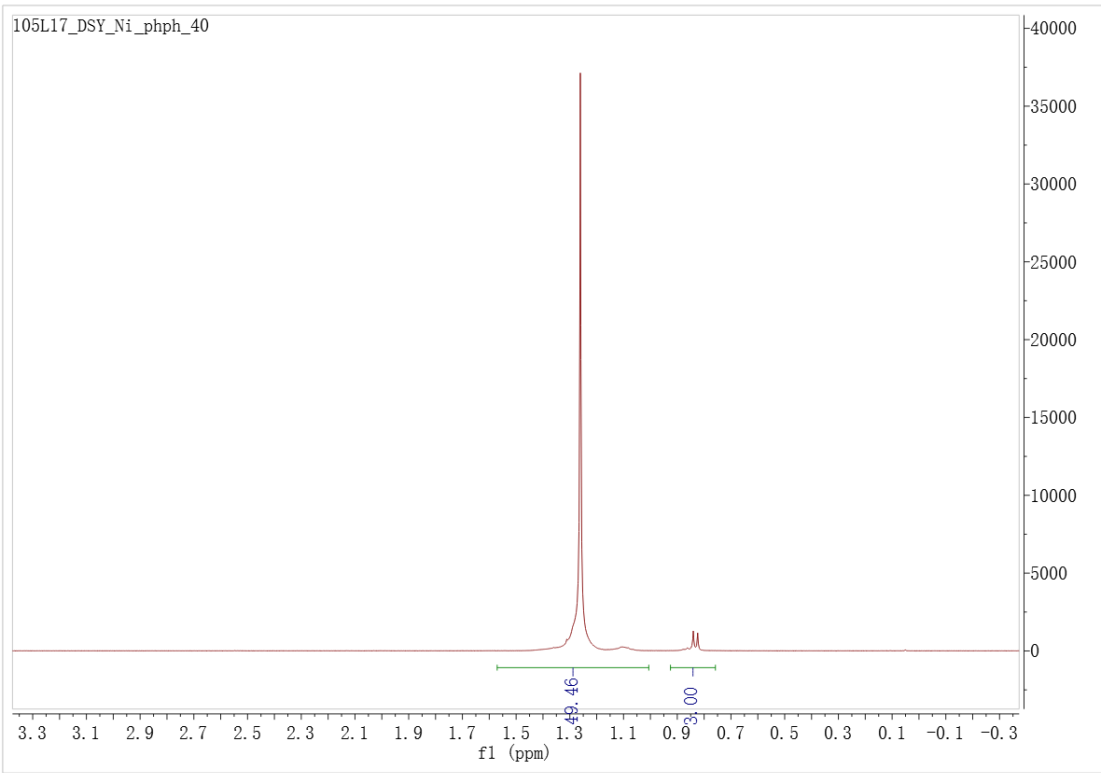


Figure S40. ^{1}H NMR spectrum of the polymer from table 1, entry 18 ($CDCl_2CDCl_2$, 120 ºC).

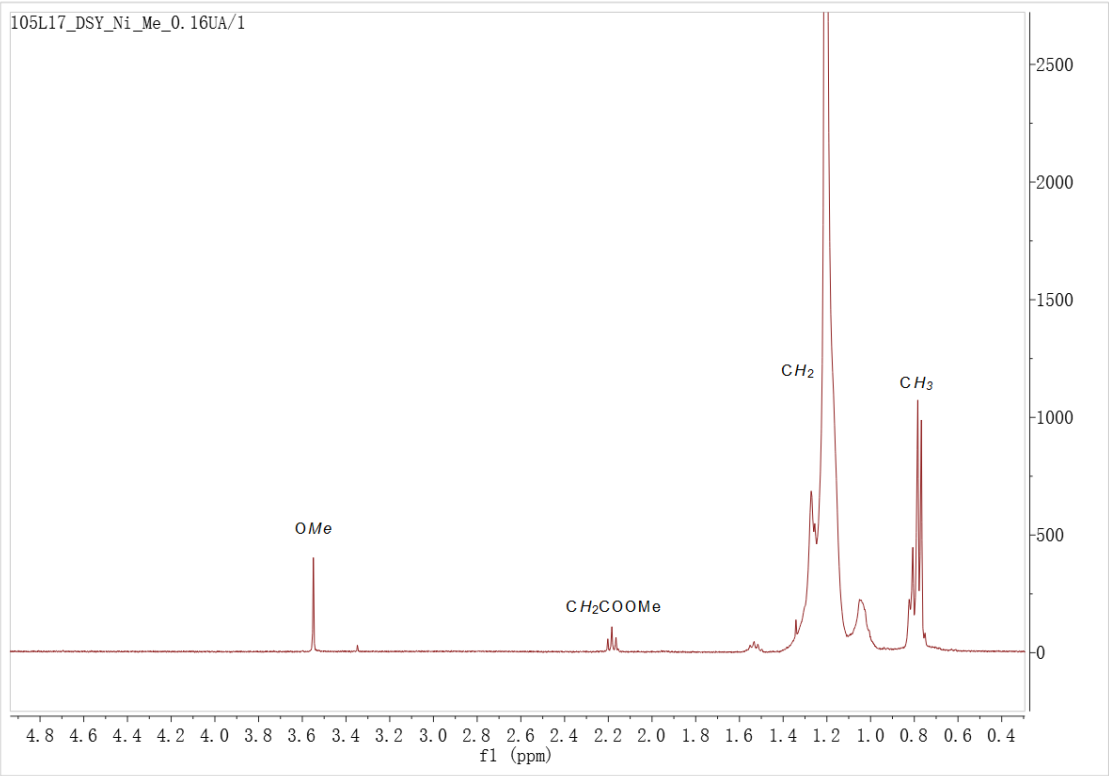


Figure S41. ^{1}H NMR spectrum of the polymer from table 3, entry 11 ($CDCl_2CDCl_2$, 120 ºC).

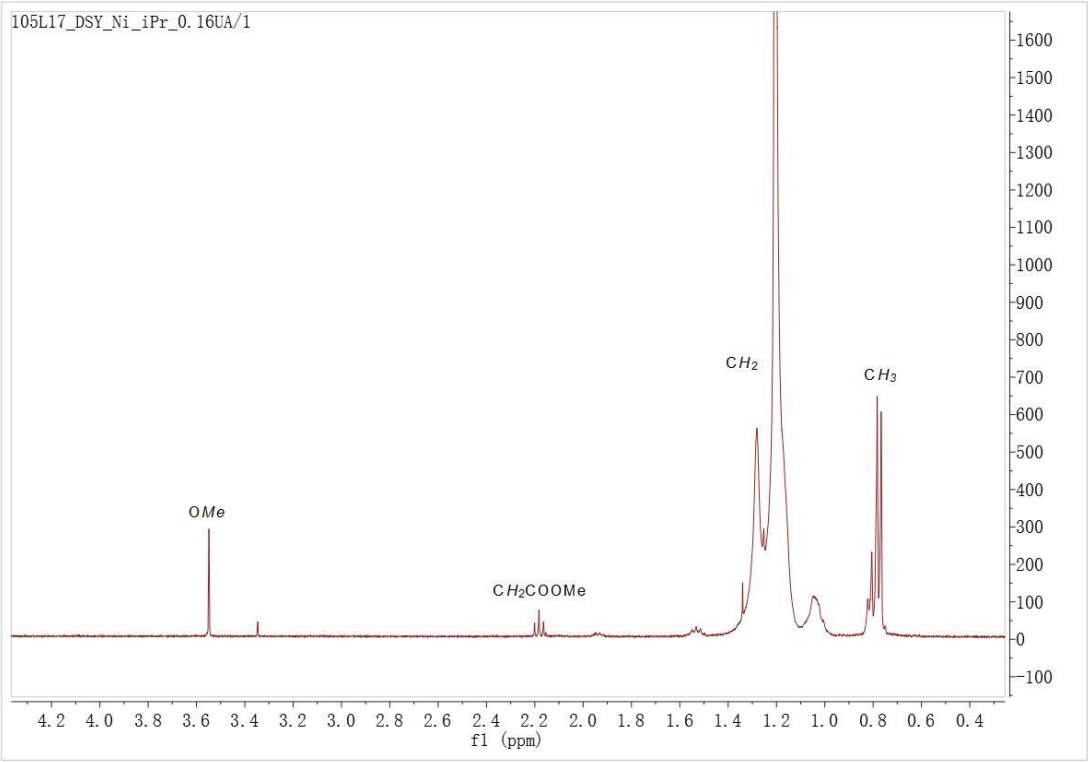


Figure S42. ^{1}H NMR spectrum of the polymer from table 3, entry 12 ($CDCl_2CDCl_2$, 120 ºC).

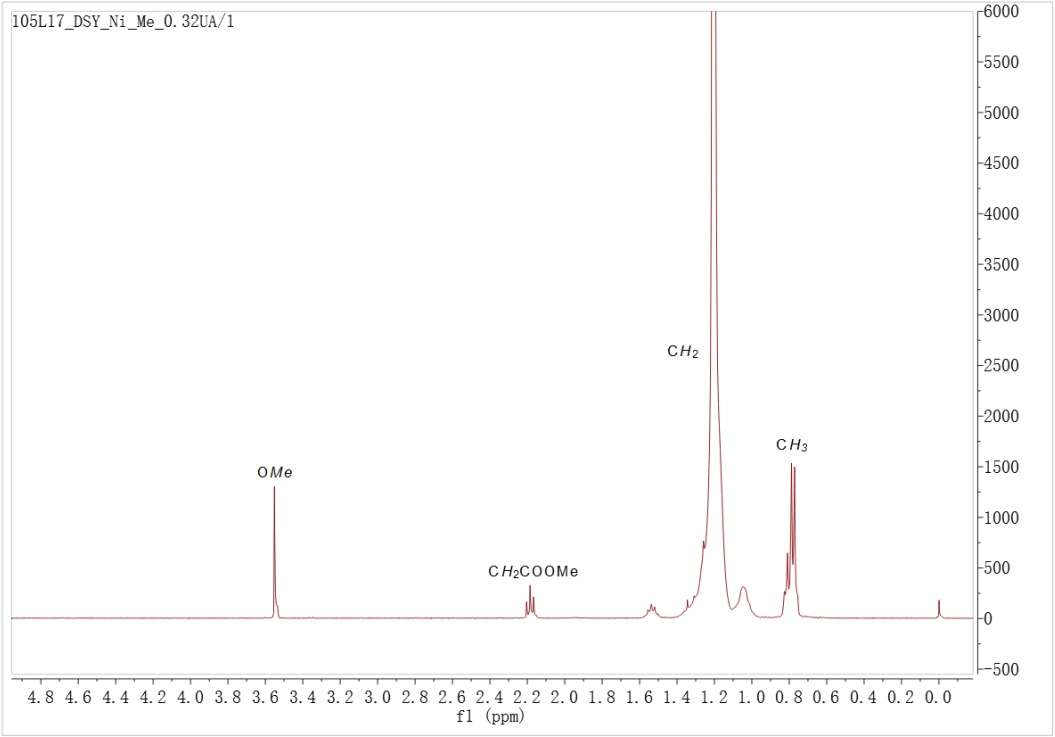


Figure S43. ^{1}H NMR spectrum of the polymer from table 3, entry 14 ($CDCl_2CDCl_2$, 120 ºC).

3.5 DSC, GPC of polymer and copolymer.

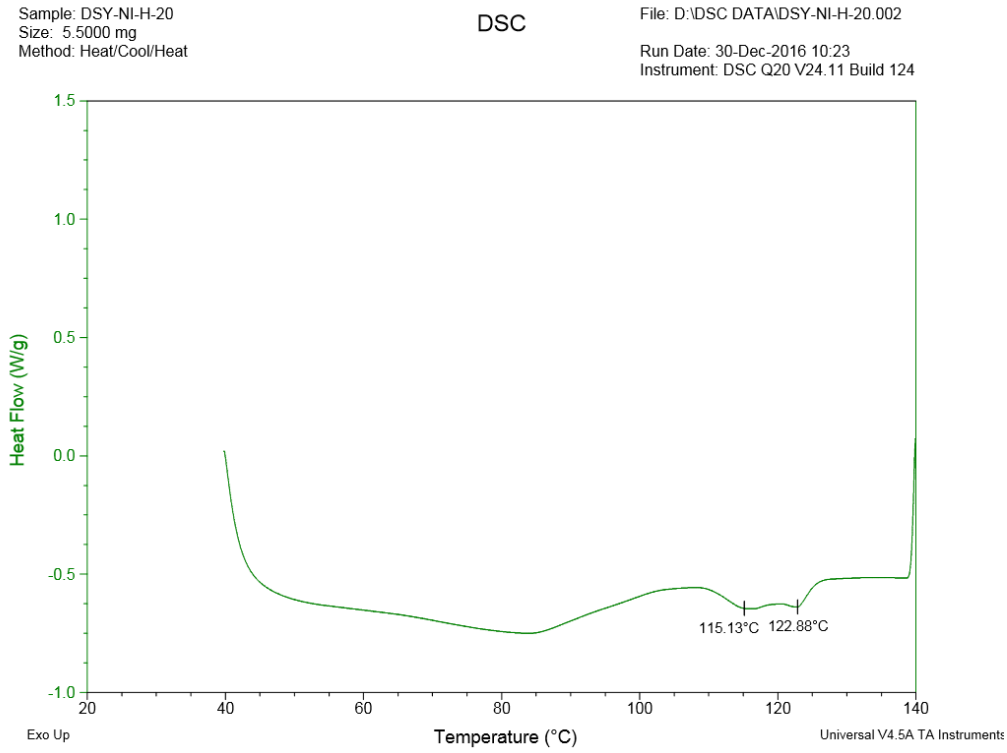


Figure S44. DSC of the polymer from table 1, entry 1.

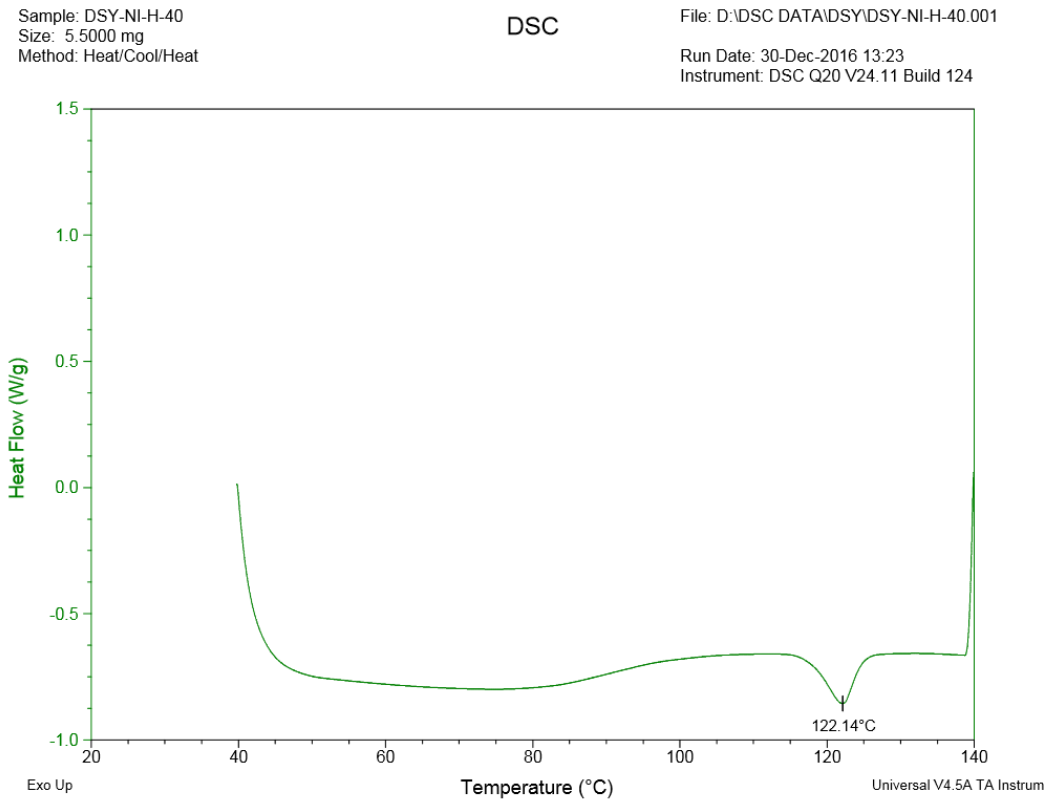


Figure S45. DSC of the polymer from table 1, entry 2.

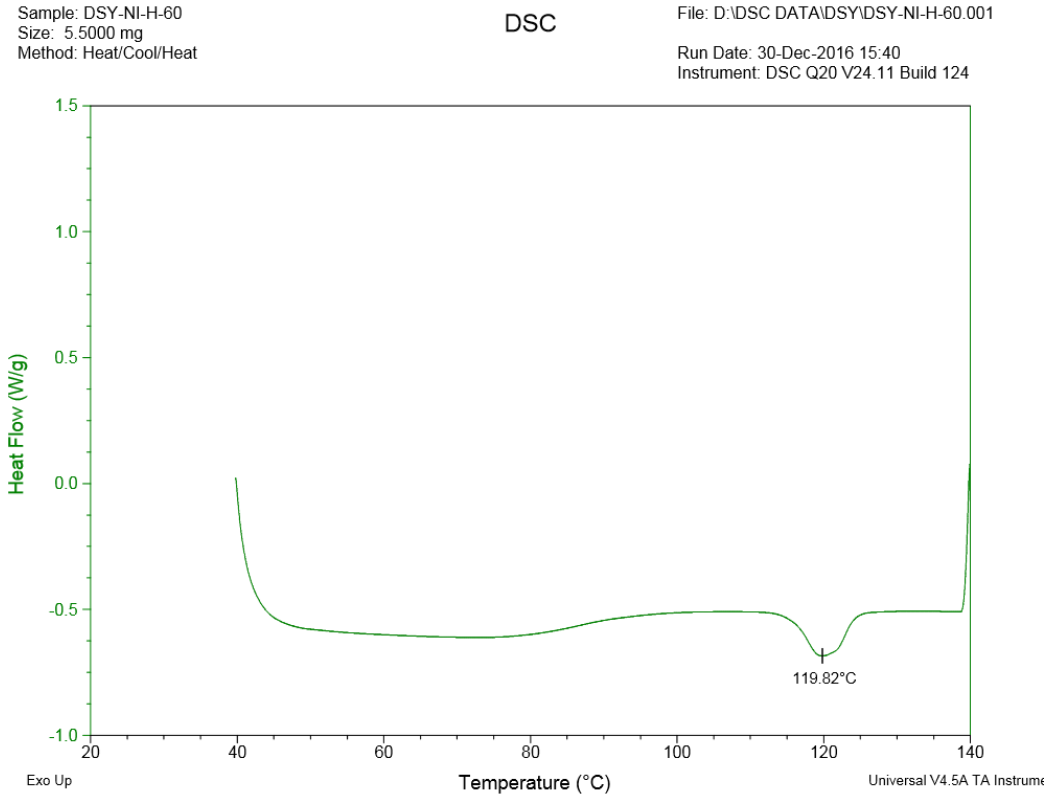


Figure S46. DSC of the polymer from table 1, entry 3.

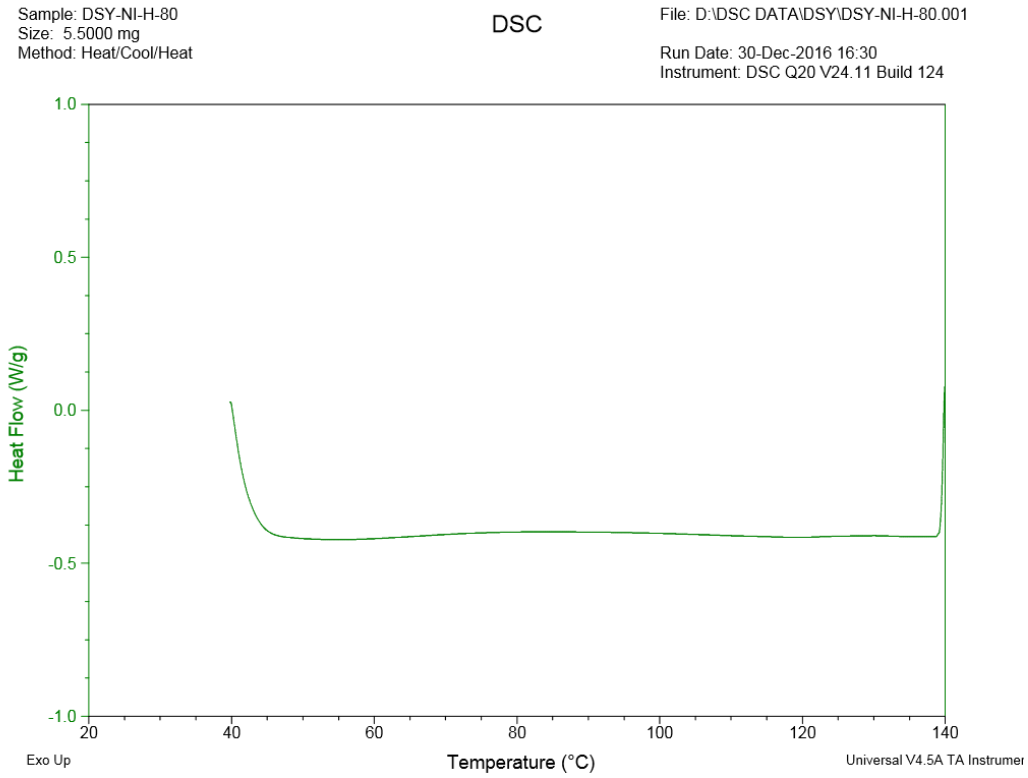


Figure S47. DSC of the polymer from table 1, entry 4.

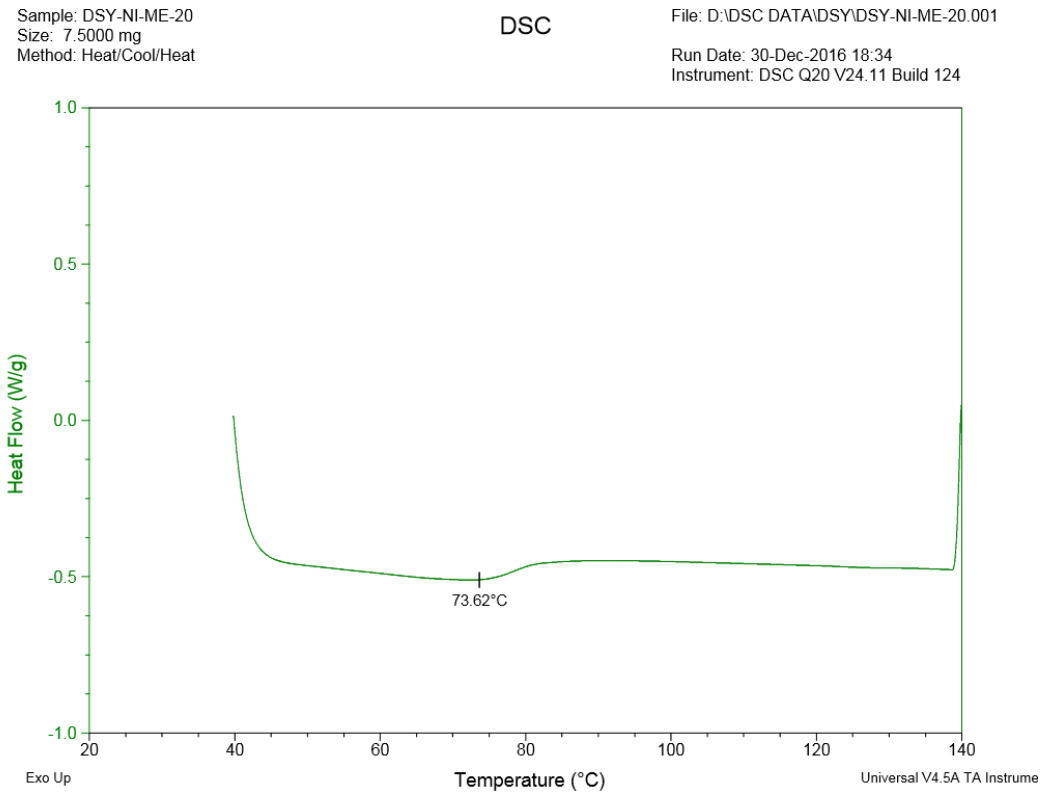


Figure S48. DSC of the polymer from table 1, entry 5.

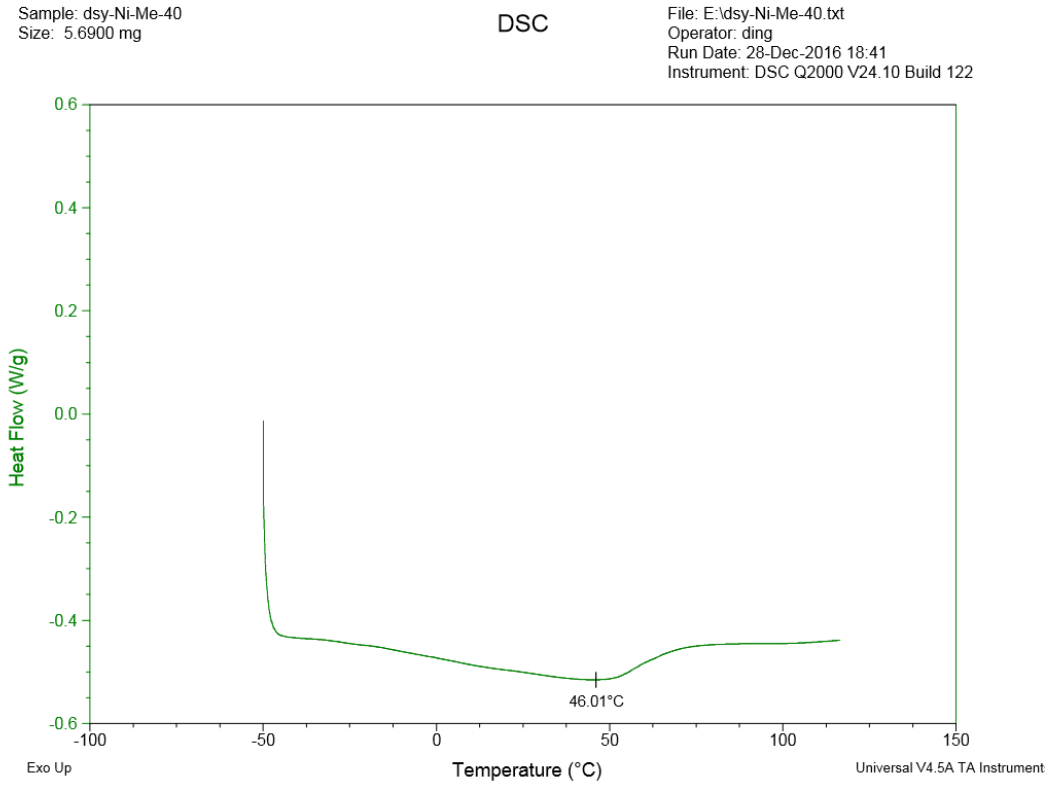


Figure S49. DSC of the polymer from table 1, entry 6.

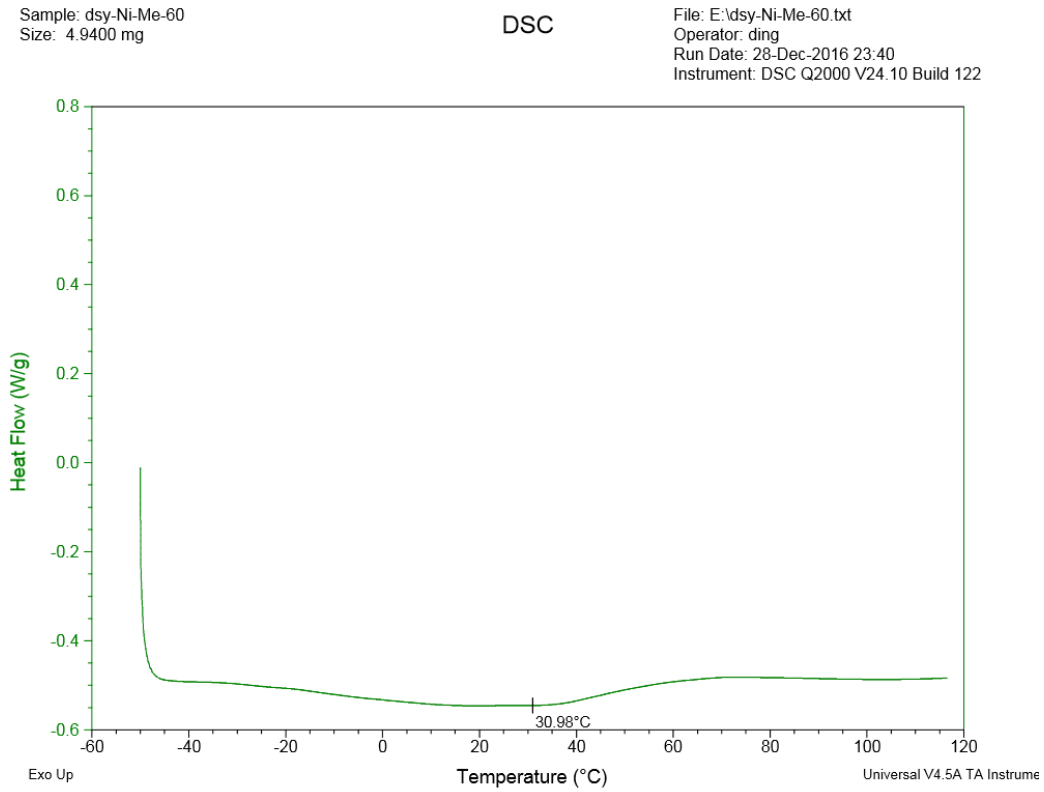


Figure S50. DSC of the polymer from table 1, entry 7.

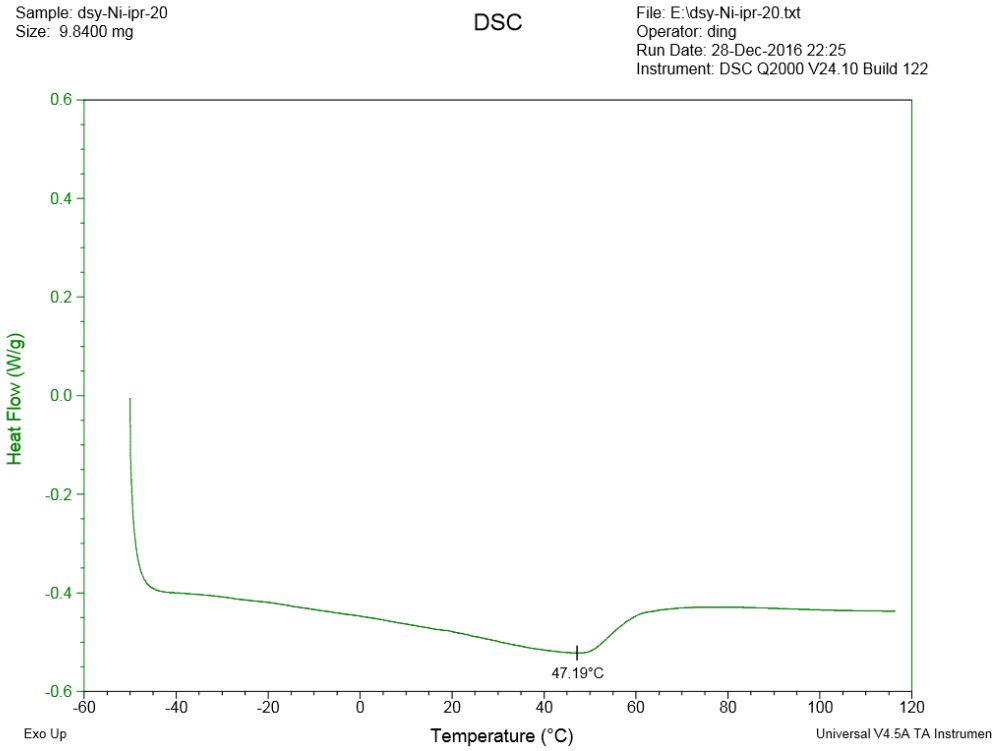


Figure S51. DSC of the polymer from table 1, entry 9.

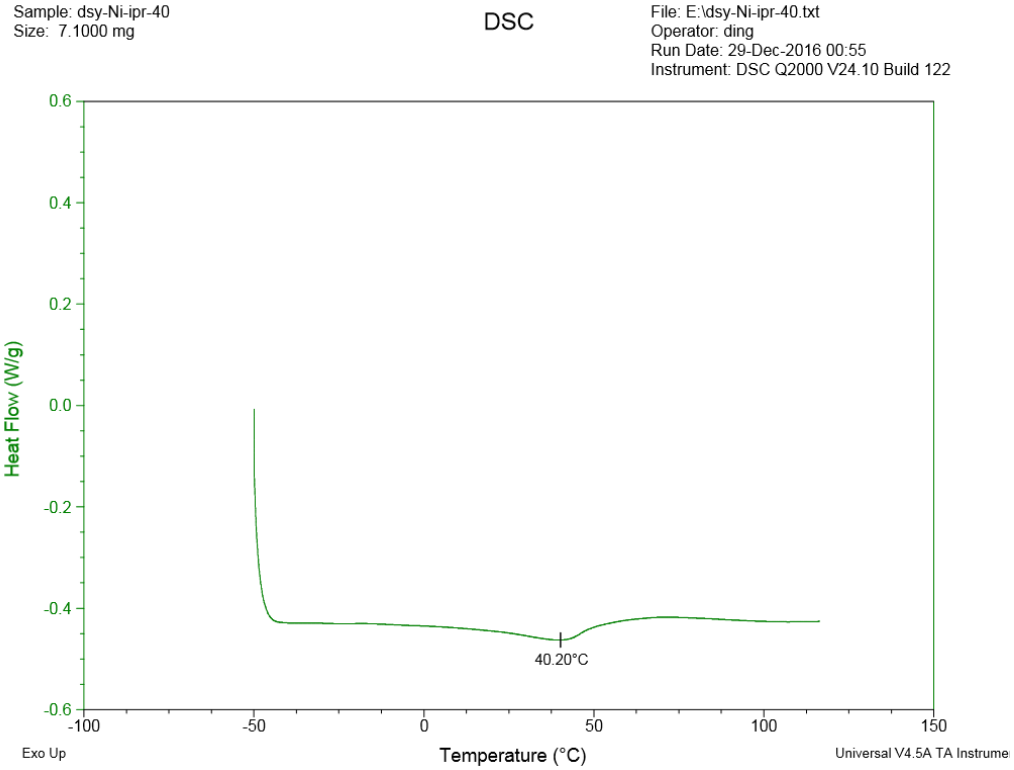


Figure S52. DSC of the polymer from table 1, entry 10.

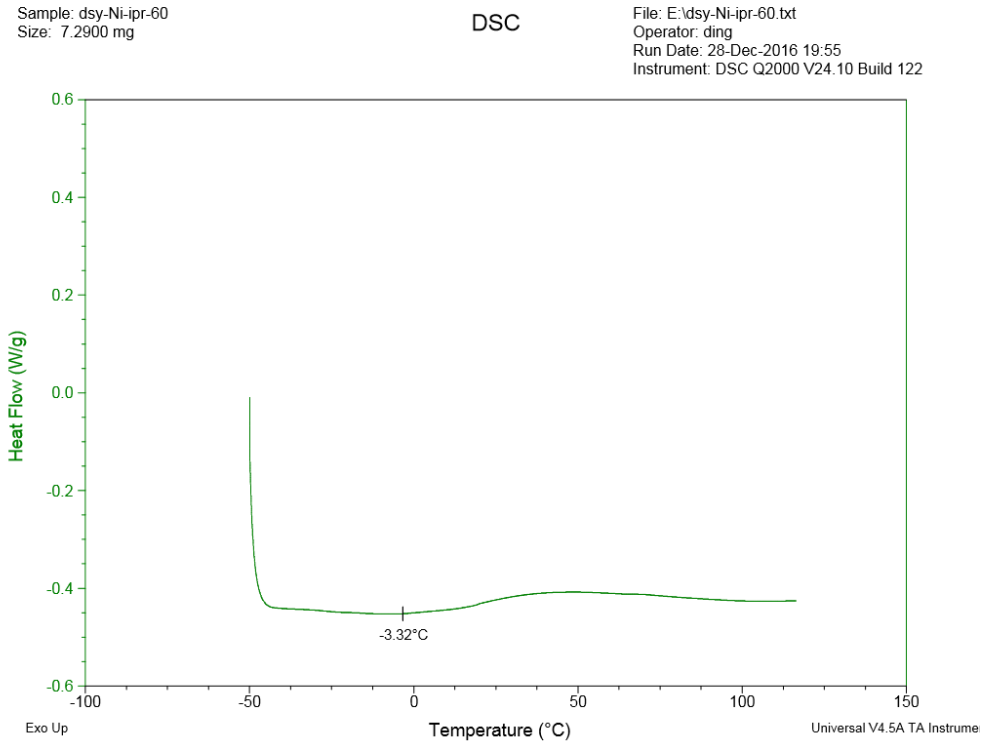


Figure S53. DSC of the polymer from table 1, entry 11.

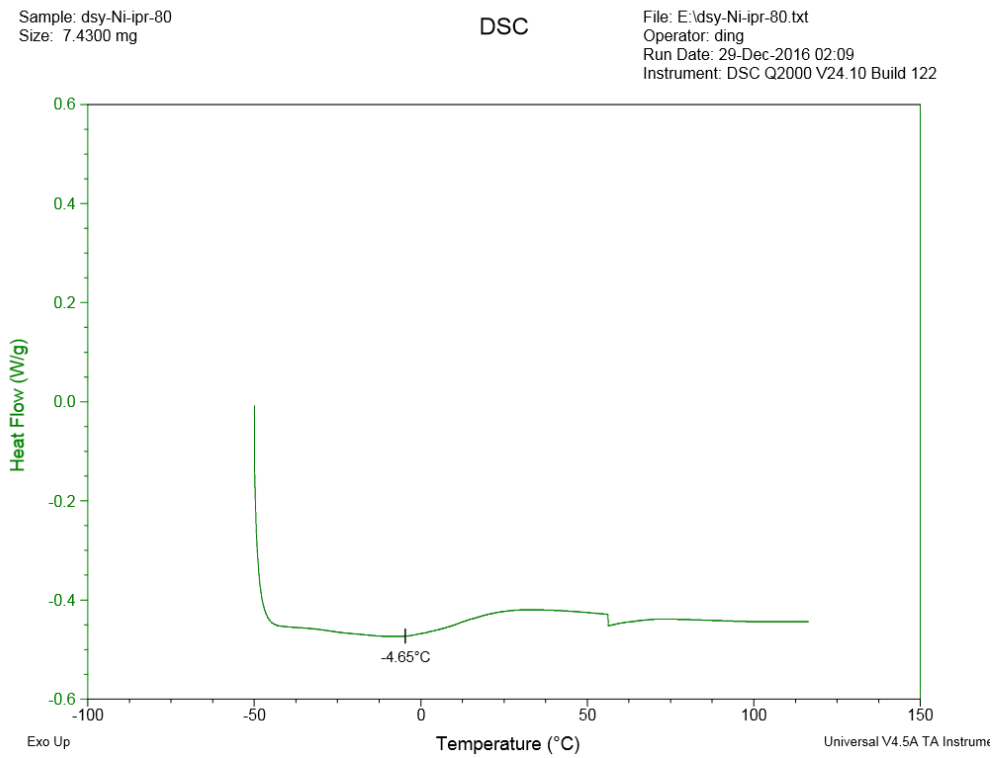


Figure S54. DSC of the polymer from table 1, entry 12.

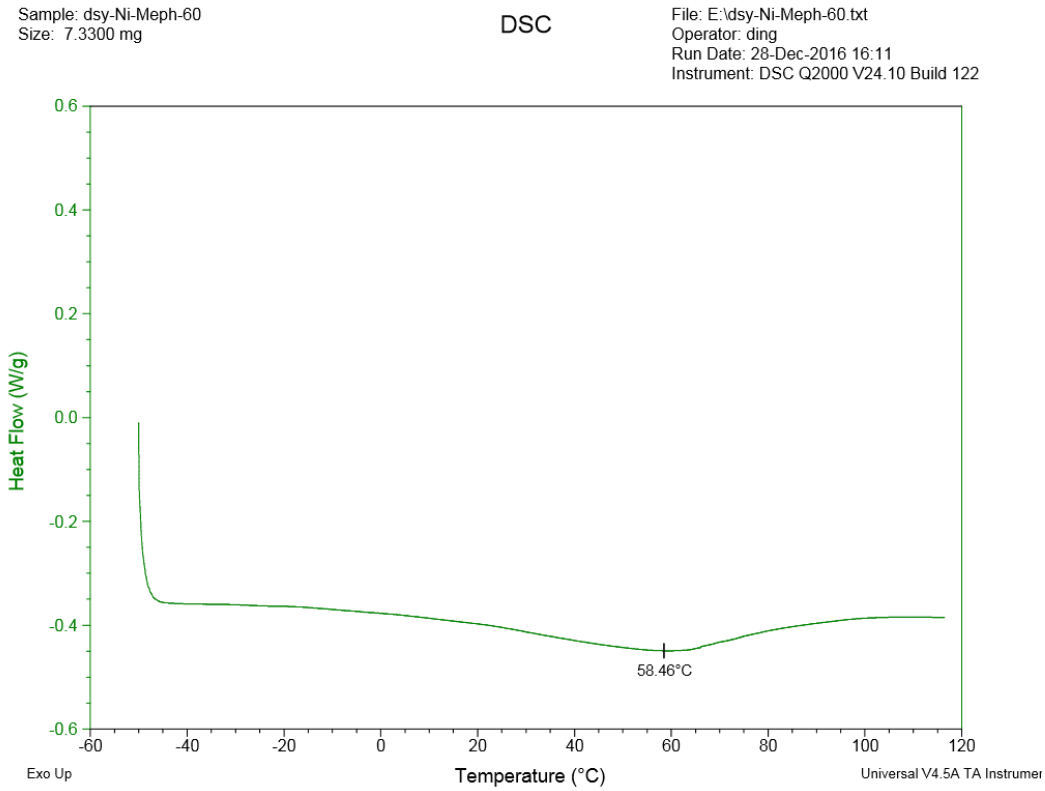


Figure S55. DSC of the polymer from table 1, entry 15.

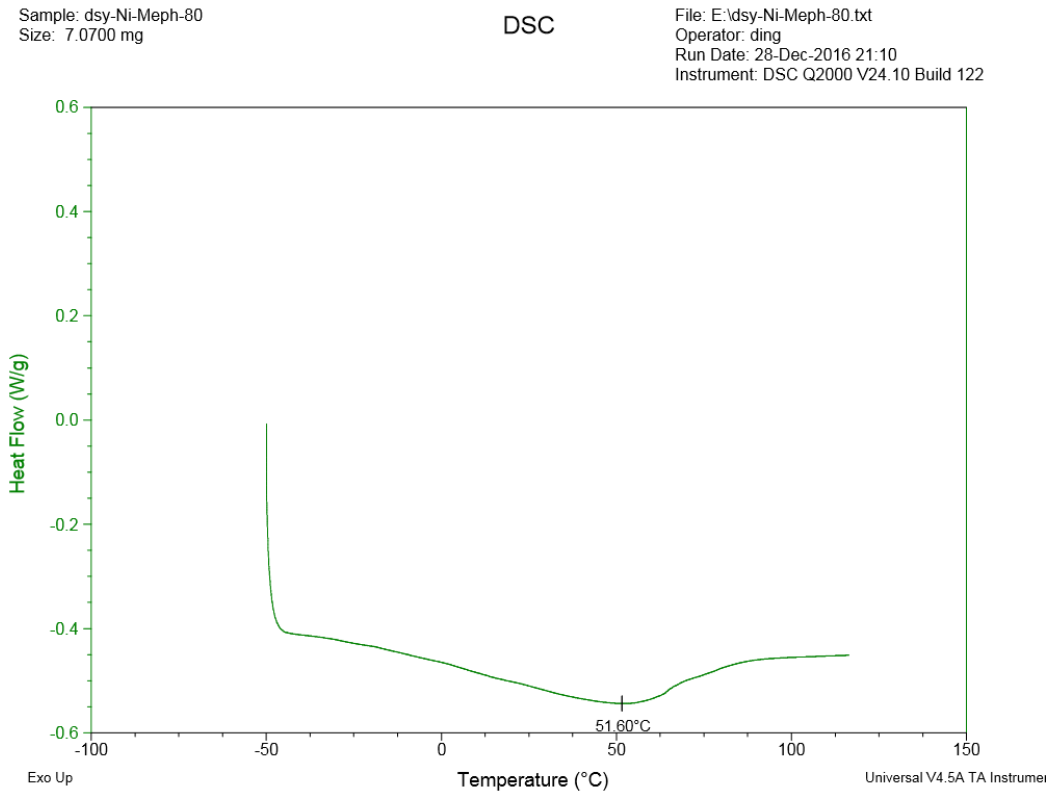


Figure S56. DSC of the polymer from table 1, entry 16.

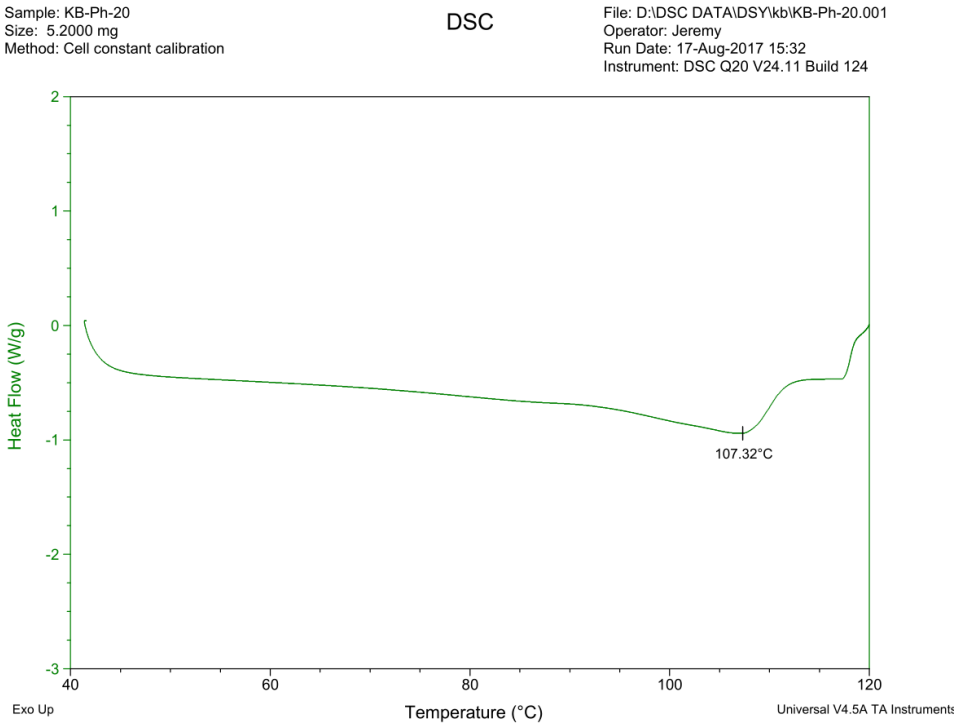


Figure S57. DSC of the polymer from table 1, entry 17.

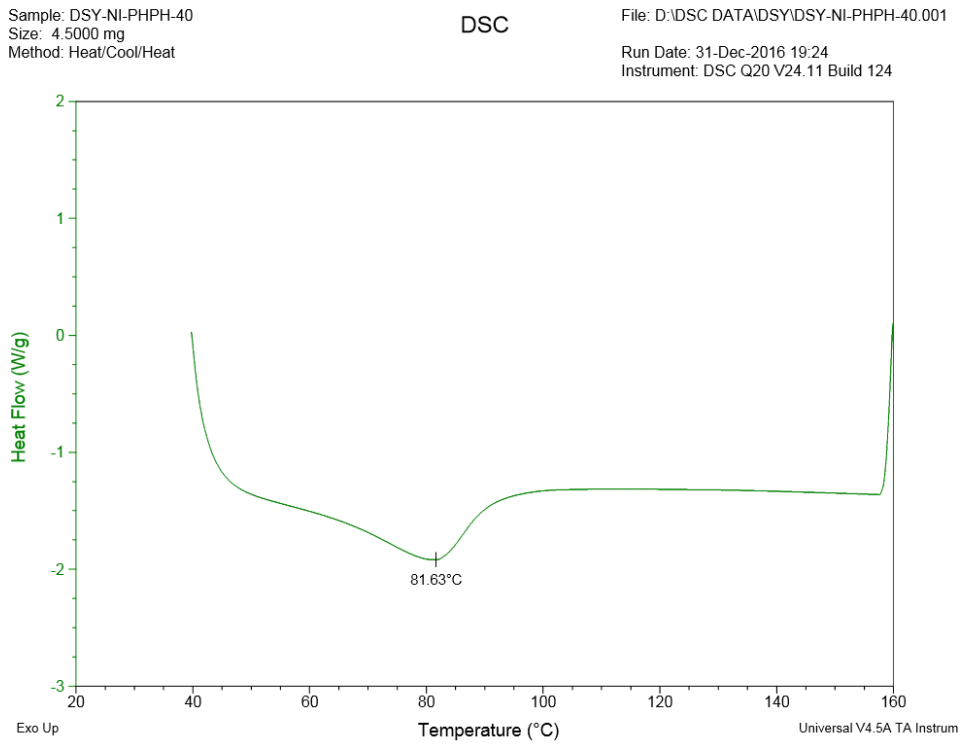


Figure S58. DSC of the polymer from table 1, entry 18.

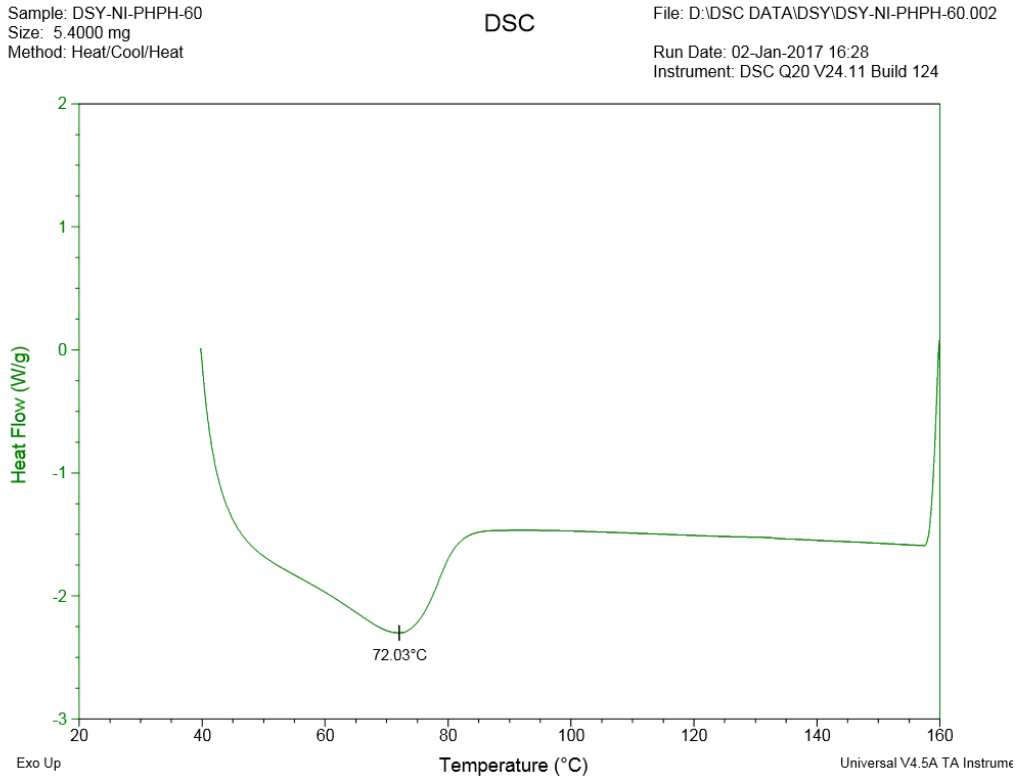


Figure S59. DSC of the polymer from table 1, entry 19.

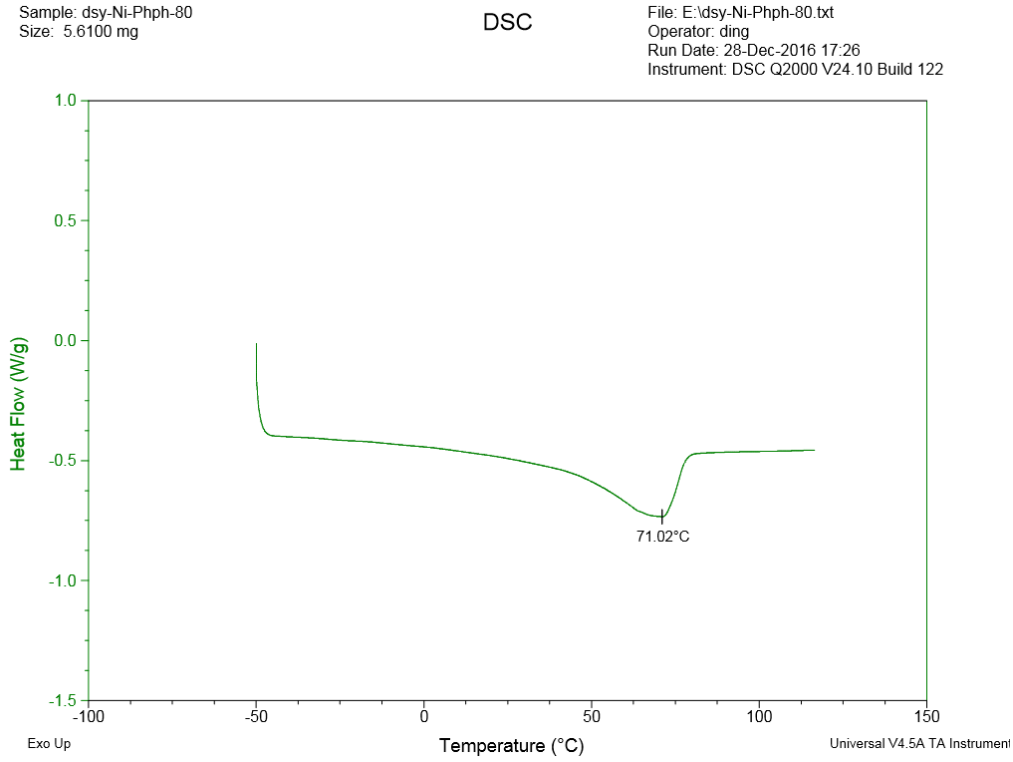


Figure S60. DSC of the polymer from table 1, entry 20.

Cirrus GPC Sample Injection Report

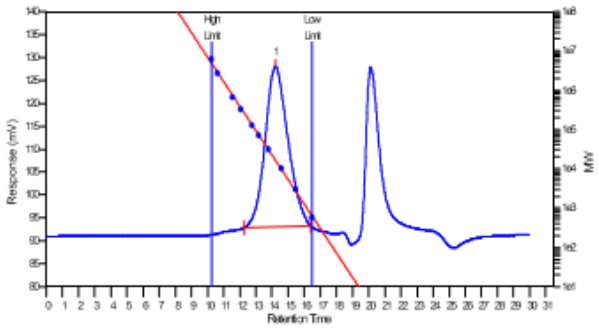
Generated by: HTGPC Saturday, April 15, 2017 10:07 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

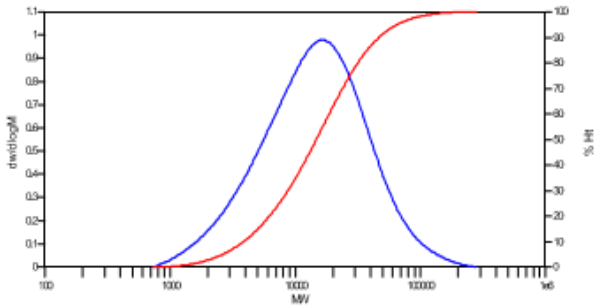
Sample Name: DSY-Ni-H-40
Acquired: 4/14/2017 5:11:23 AM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins
Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	16356	8642	21544	46731	84447	18988	2.49294

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.23	14.22	16.38	35.0676	0	3453.7	100

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Figure S61. GPC of the polymer from table 1, entry 2.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:08 AM

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

Sample Details

Sample Name: DSY-Ni-H-60

Acquired: 4/14/2017 5:44:15 AM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

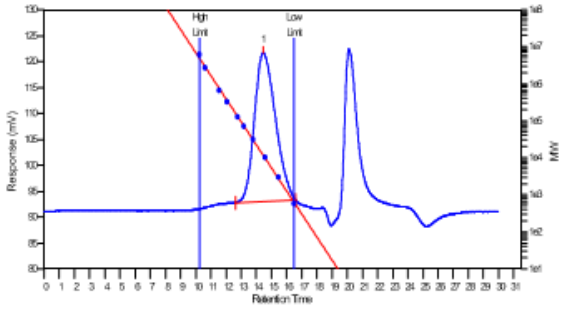
Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

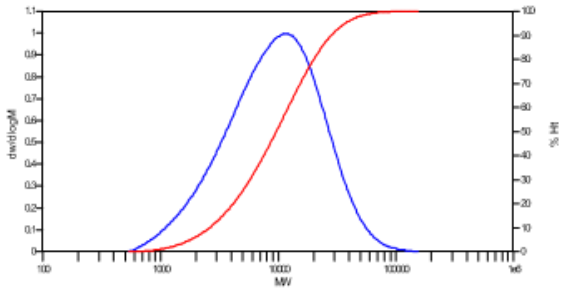
Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	11430	5793	13131	24782	40313	11794	2.2667

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.65	14.47	16.60	28.6611	0	2768.64	100

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Figure S62. GPC of the polymer from table 1, entry 3.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:08 AM

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

Sample Details

Sample Name: DSY-Ni-H-80

Acquired: 4/14/2017 6:17:05 AM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

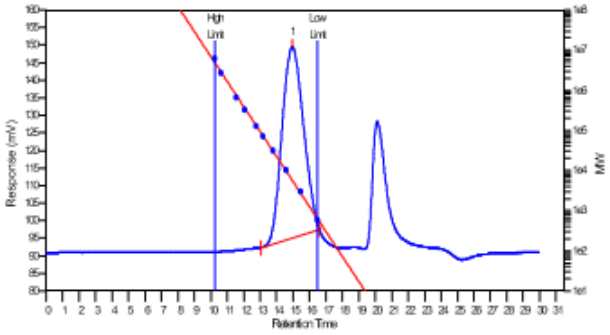
Calibration Used: 4/13/2017 8:58:56 AM

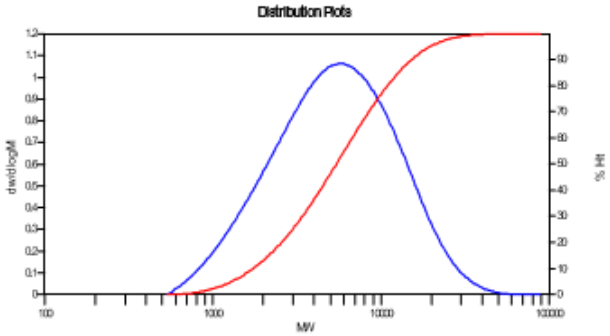
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	5716	3726	7174	12389	18527	6546	1.92539

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	14.97	16.60	54.3393	0	4929.46	100

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Figure S63. GPC of the polymer from table 1, entry 4.

Cirrus GPC Sample Injection Report

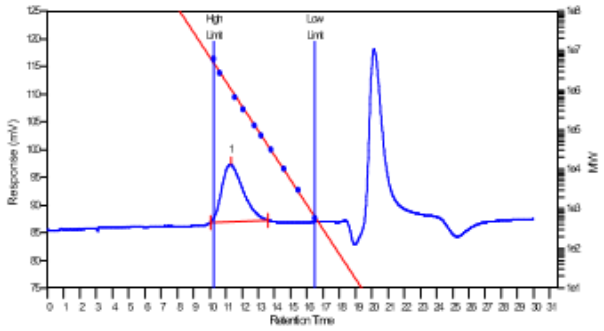
Generated by: HTGPC Saturday, April 15, 2017 10:00 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

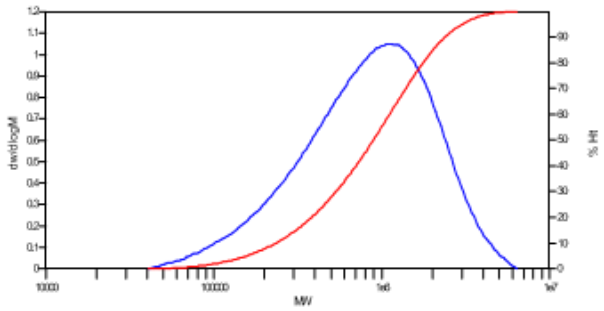
Sample Name: DSY-Ni-Me-20
Acquired: 4/13/2017 9:57:44 PM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins
Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1069956	512407	1121673	1856639	2563002	1023360	2.18903

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.05	11.30	13.58	10.3185	100	946.854	100

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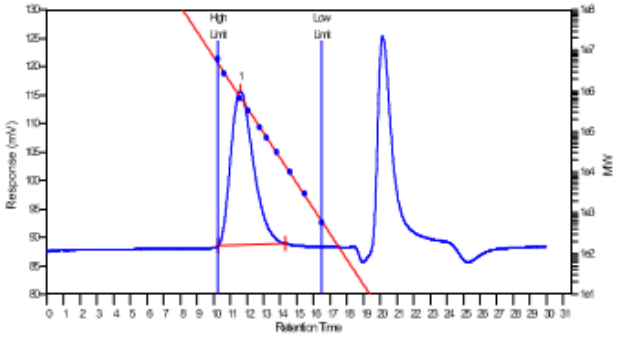
Figure S64. GPC of the polymer from table 1, entry 5.

Cirrus GPC Sample Injection Report

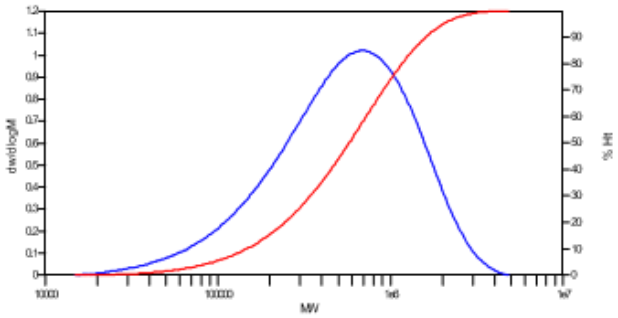
Generated by: HTGPC Saturday, April 15, 2017 10:00 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details
Sample Name: DSY-Ni-Me-40
Acquired: 4/13/2017 10:30:35 PM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins
Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	696000	312754	740033	1256830	1759568	671693	2.36618

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	14.28	27.0128	100	2553.31	100

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Figure S65. GPC of the polymer from table 1, entry 6.

Cirrus GPC Sample Injection Report

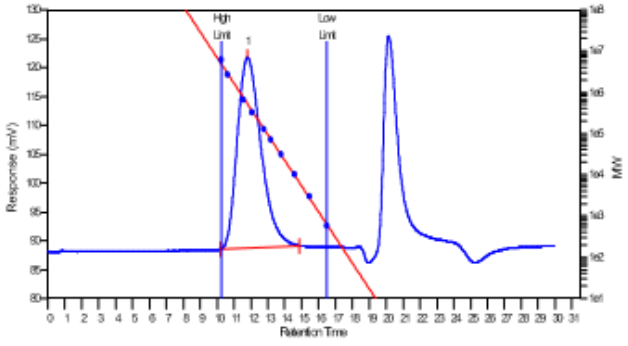
Generated by: HTGPC Saturday, April 15, 2017 10:01 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

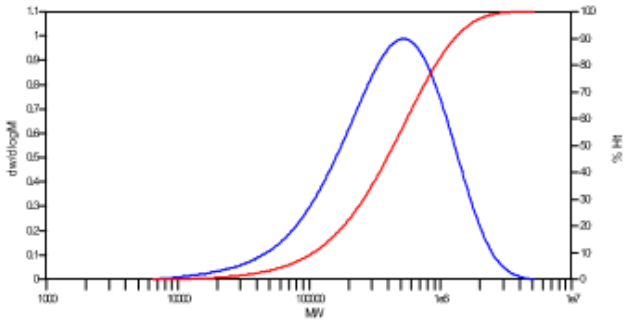
Sample Name: DSY-Ni-Me-60
Acquired: 4/13/2017 11:05:40 PM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins
Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	522522	217753	586910	1058362	1566417	527521	2.6953

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	11.80	14.87	33.0107	0	3221.46	100

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Figure S66. GPC of the polymer from table 1, entry 7.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:01 AM

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

Sample Details

Sample Name: DSY-Ni-Me-80

Acquired: 4/13/2017 11:38:30 PM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

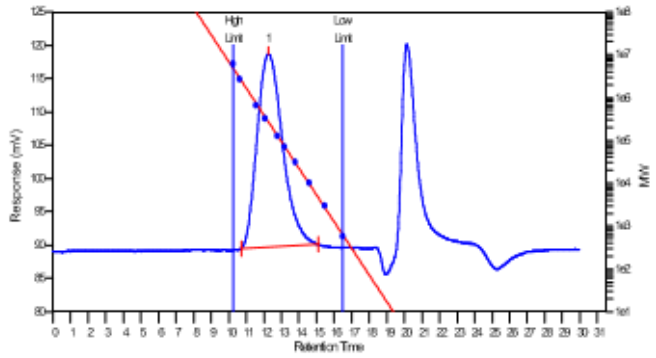
Calibration Used: 4/13/2017 8:58:56 AM

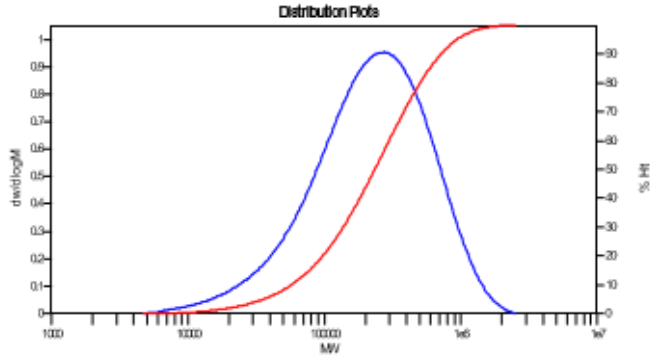
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	274138	120220	320759	591893	876210	287059	2.6681

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.70	12.25	15.08	28.9733	0	2930.76	100

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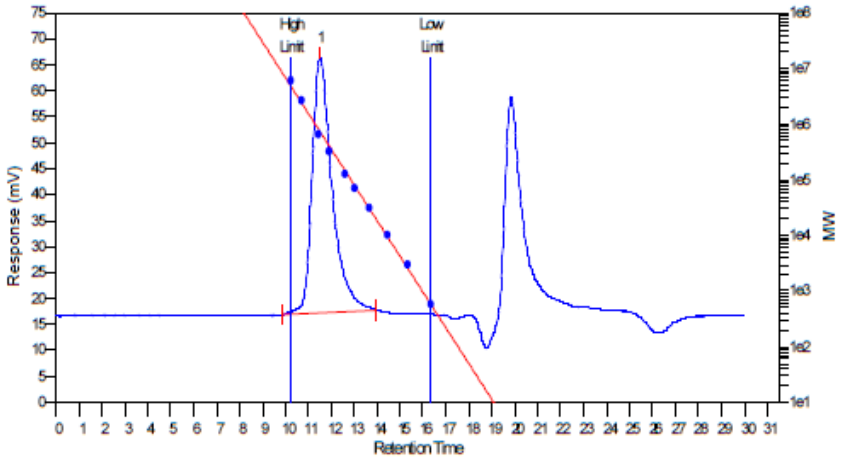
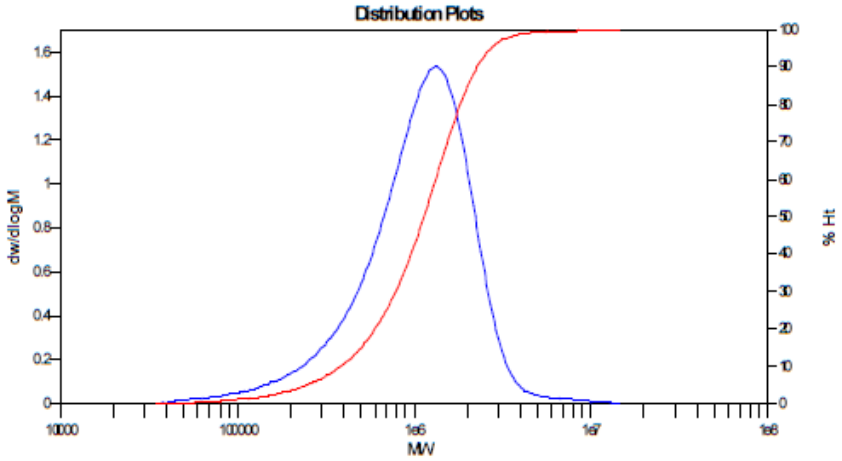
Figure S67. GPC of the polymer from table 1, entry 8.





MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1357361	715464	1280788	1930878	3100315	1198739	1.79015

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.90	11.50	13.97	48.9572	0	2966.53	100

Figure S68. GPC of the polymer from table 1, entry 9.

Sample Name: DSY-Ni-iPr-40

Acquired: 4/14/2017 12:44:10 AM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

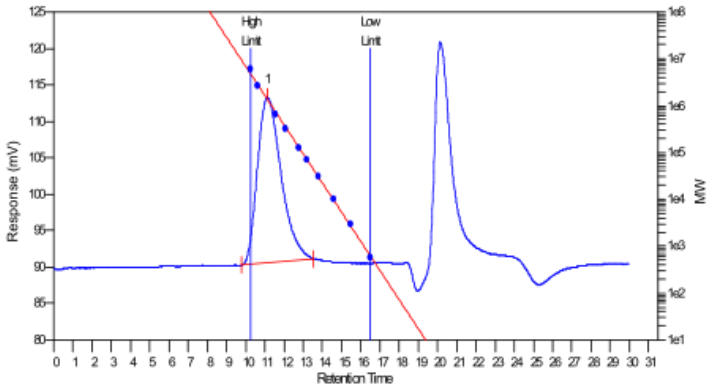
Calibration Used: 4/13/2017 8:58:56 AM

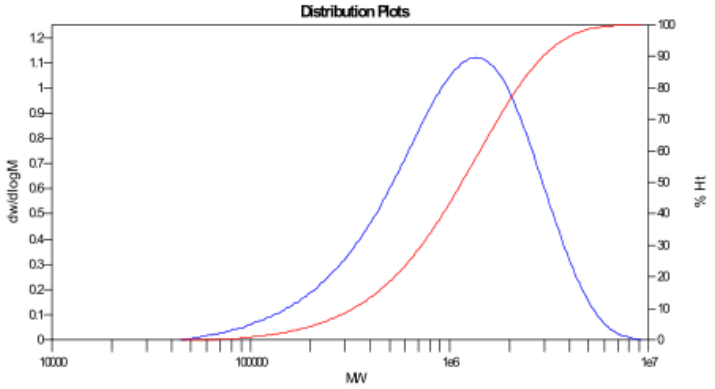
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	1358687	685301	1425028	2287835	3148161	1309307	2.07942

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.80	11.13	13.52	22.7238	0	1953.43	100

Figure S69. GPC of the polymer from table 1, entry 10.

Sample Details

Sample Name: DSY-Ni-iPr-60

Acquired: 4/14/2017 1:17:02 AM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

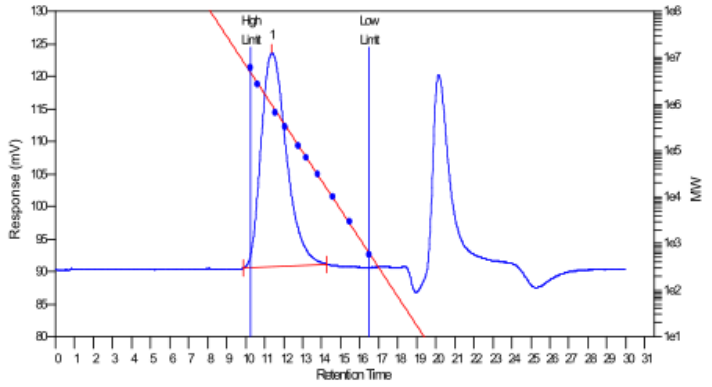
Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

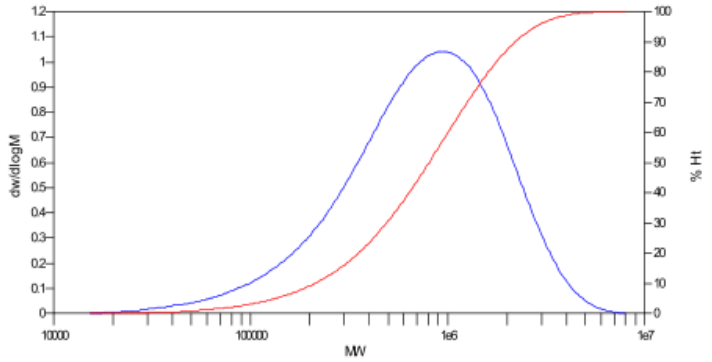
Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	949487	434587	1036930	1768717	2531450	942013	2.38601

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.90	11.38	14.27	32.8438	0	3042.38	100

Figure S70. GPC of the polymer from table 1, entry 11.

Sample Details

Sample Name: DSY-Ni-iPr-80

Acquired: 4/14/2017 1:52:05 AM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

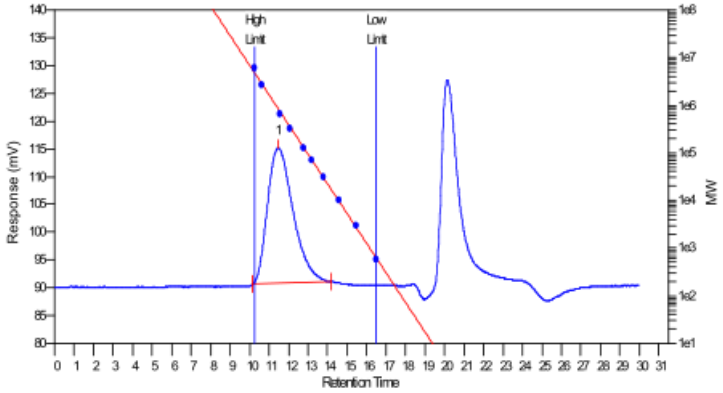
Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

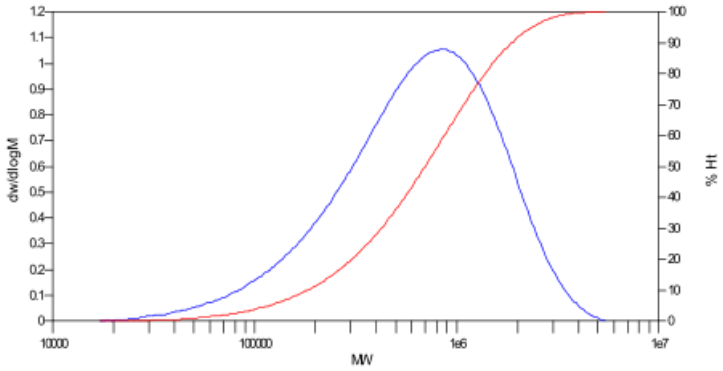
Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	842582	384406	883077	1467951	2035900	804905	2.29725

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.17	11.48	14.18	24.3397	0	2228.15	100

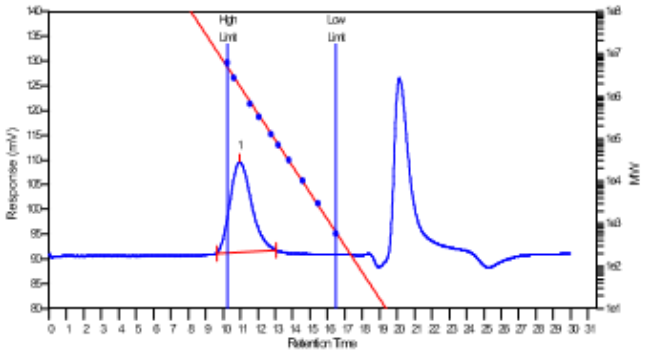
Figure S71. GPC of the polymer from table 1, entry 12.

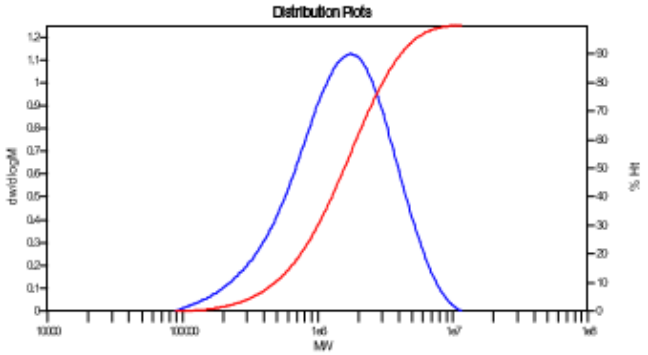
Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:06 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details
Sample Name: DSY-Ni-MePh-60-1
Acquired: 4/14/2017 4:03:28 AM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	1767048	1002455	1975661	3199327	4452538	1816062	1.97082

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.63	10.95	13.03	18.1171	0	1550.69	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 10:06 AM

Figure S72. GPC of the polymer from table 1, entry 13.

Cirrus GPC Sample Injection Report

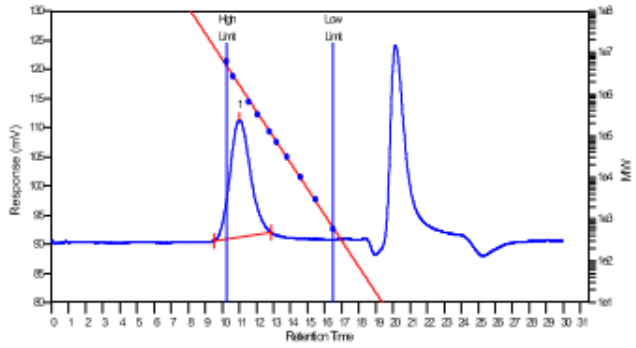
Generated by: HTGPC Saturday, April 15, 2017 10:05 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details

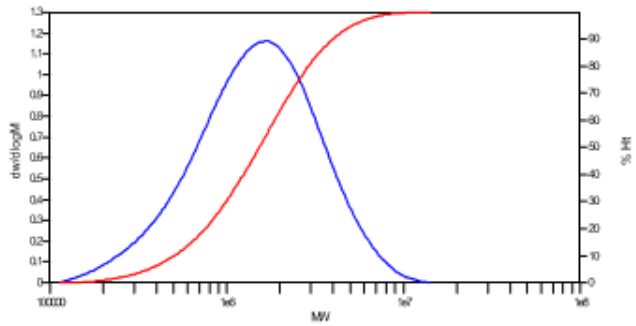
Sample Name: DSY-Ni-MePh-40-1
Acquired: 4/14/2017 2:57:48 AM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins
Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1644835	1037576	1934645	3177555	4612495	1780440	1.86458

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.50	11.00	12.87	20.1195	0	1670.05	100

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Figure S73. GPC of the polymer from table 1, entry 14.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:06 AM

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

Sample Details

Sample Name: DSY-Ni-MePh-60

Acquired: 4/14/2017 3:30:38 AM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

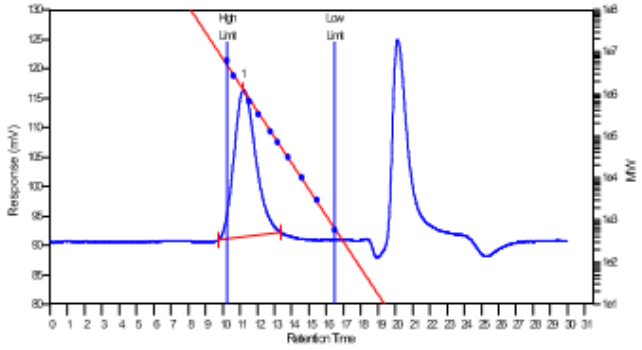
Calibration Used: 4/13/2017 8:58:56 AM

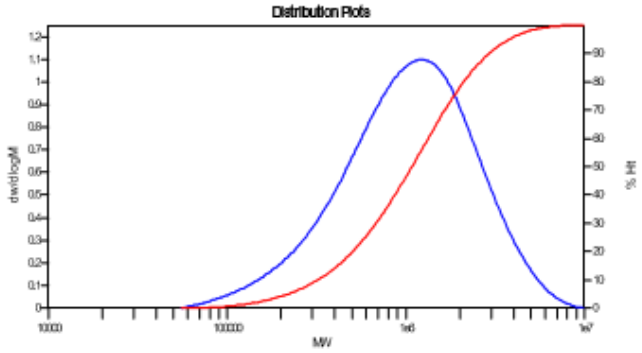
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	1234861	675475	1387605	2344878	3399596	1267490	2.05427

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.75	11.20	13.37	24.9227	0	2187.08	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 10:06 AM

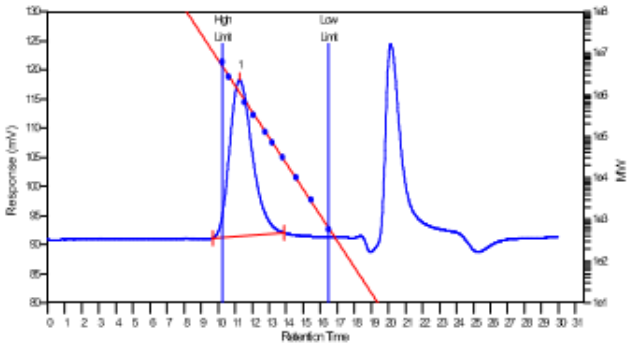
Figure S74. GPC of the polymer from table 1, entry 15.

Cirrus GPC Sample Injection Report

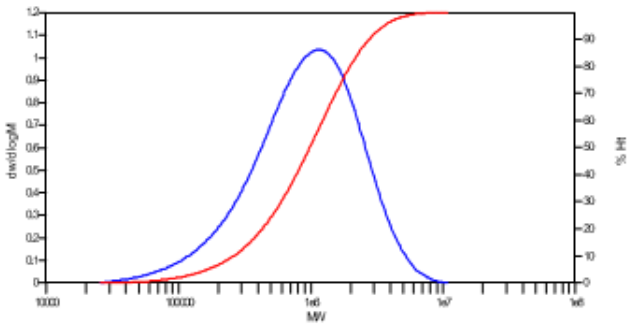
Generated by: HTGPC Saturday, April 15, 2017 10:07 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details
Sample Name: DSY-Ni-MePh-80
Acquired: 4/14/2017 4:38:33 AM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins
Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1177246	545617	1284471	2258629	3347101	1162810	2.35416

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.68	11.27	13.90	26.8033	0	2494.6	100

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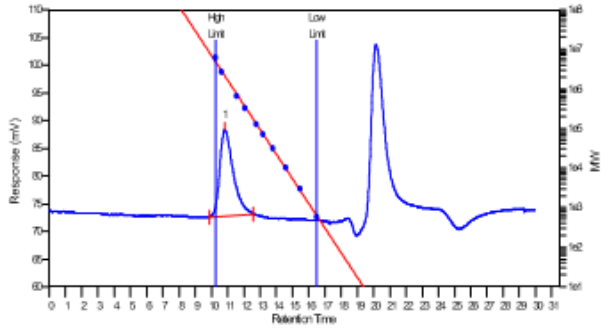
Figure S75. GPC of the polymer from table 1, entry 16.

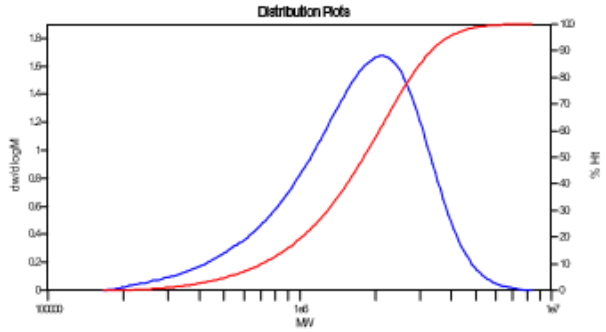
Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 9:35 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details
Sample Name: DSY-Ni-PhPh-20
Acquired: 4/13/2017 8:19:13 PM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	2139199	1315100	1914864	2475241	2994691	1831322	1.45606

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.87	10.82	12.60	15.4972	0	890.571	100

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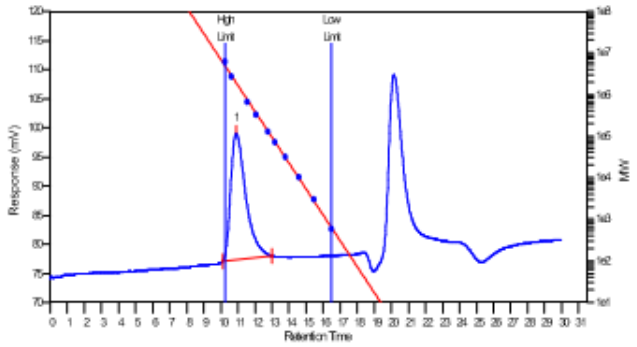
Figure S76. GPC of the polymer from table 1, entry 17.

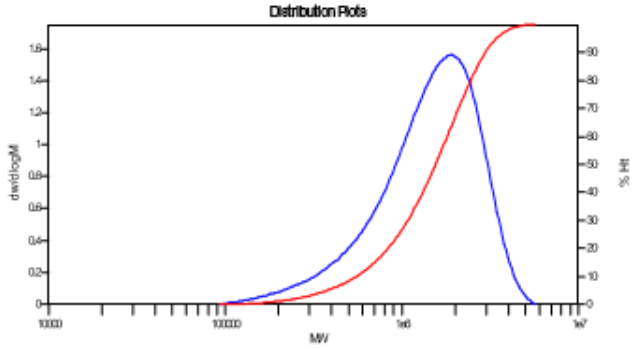
Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 9:57 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details
Sample Name: DSY-Ni-PhPh-40
Acquired: 4/13/2017 8:52:04 PM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	1898342	1048375	1652196	2165677	2588254	1572598	1.57596

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.13	10.90	13.02	21.6415	100	1334.64	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 9:57 AM

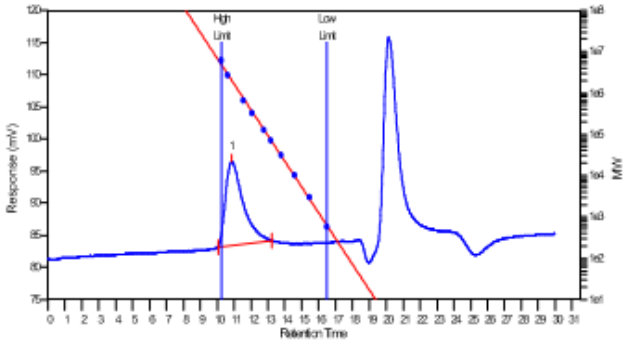
Figure S77. GPC of the polymer from table 1, entry 18.

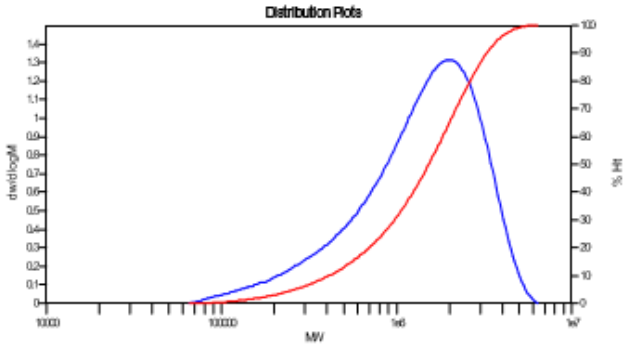
Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 9:59 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details
Sample Name: DSY-Ni-PhPh-80
Acquired: 4/13/2017 9:24:54 PM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	2039391	863420	1685450	2392648	2939645	1575735	1.95206

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.05	10.85	13.25	12.9397	0	948.181	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 9:59 AM

Figure S78. GPC of the polymer from table 1, entry 20.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:09 AM

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

Sample Details

Sample Name: DSY-Ni-PhPh-80-5min

Acquired: 4/14/2017 3:38:36 PM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

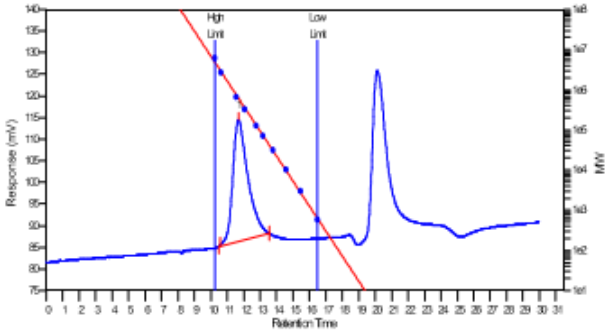
Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

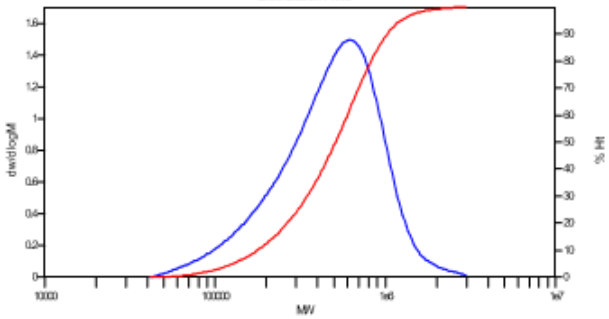
Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	617636	351527	565684	797939	1057795	533752	1.60922

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.58	11.70	13.57	28.1191	0	1812.39	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 10:09 AM

Figure S79. GPC of the polymer from table 2, entry 1.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:10 AM

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

Sample Details

Sample Name: DSY-Ni-PhPh-80-10min

Acquired: 4/14/2017 4:11:26 PM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

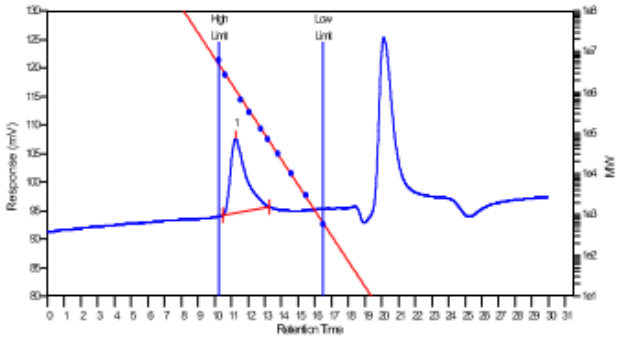
Calibration Used: 4/13/2017 8:58:56 AM

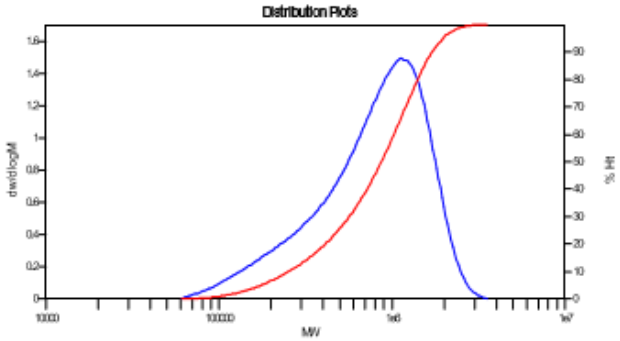
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	1122320	539756	923709	1253551	1509242	871924	1.71135

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.47	11.27	13.30	13.0202	0	841.354	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 10:10 AM

Figure S80. GPC of the polymer from table 2, entry 2.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:10 AM

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

Sample Details

Sample Name: DSY-Ni-PhPh-80-15min

Acquired: 4/14/2017 4:44:16 PM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

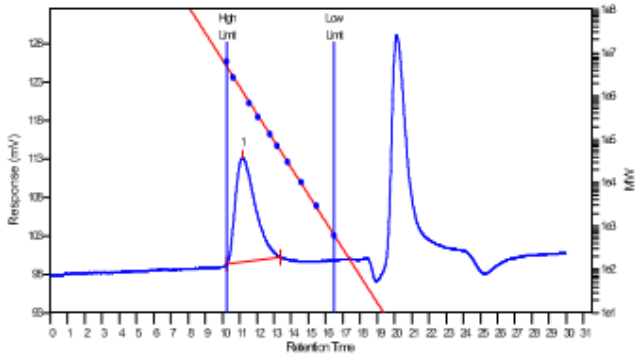
Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

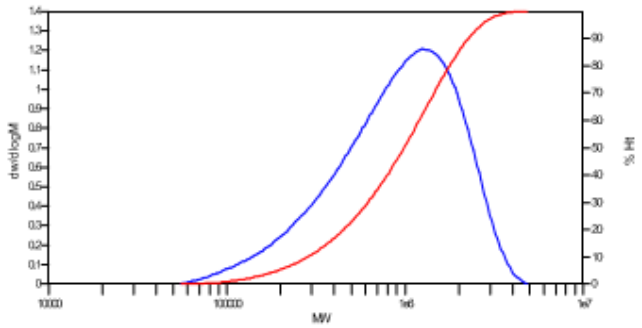
Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1264717	603268	1134484	1659749	2094108	1056916	1.88056

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	11.18	13.37	13.549	0	1082.06	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 10:10 AM

Figure S81. GPC of the polymer from table 2, entry 3.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:11 AM

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

Sample Details

Sample Name: DSY-Ni-PhPh-80-60min

Acquired: 4/14/2017 5:18:09 PM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

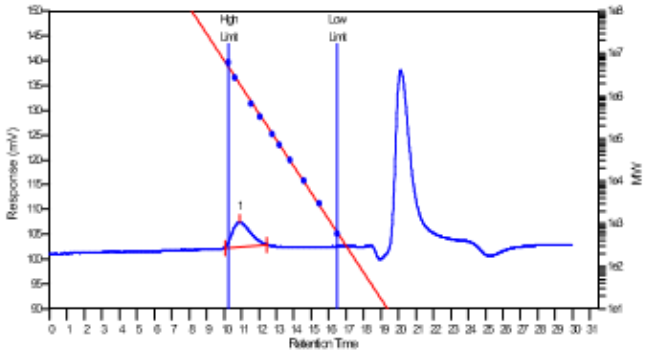
Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

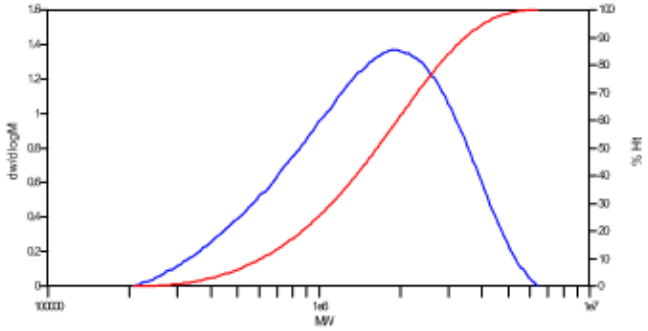
Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1898342	1209401	1843157	2506177	3085816	1746591	1.52402

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.05	10.90	12.45	4.9251	0	346.379	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 10:11 AM

Figure S82. GPC of the polymer from table 2, entry 5.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:11 AM

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

Sample Details

Sample Name: DSY-Ni-PhPh-100-5min

Acquired: 4/14/2017 5:53:14 PM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

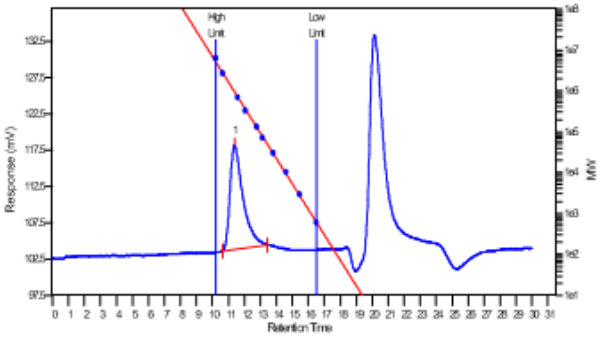
Calibration Used: 4/13/2017 8:58:56 AM

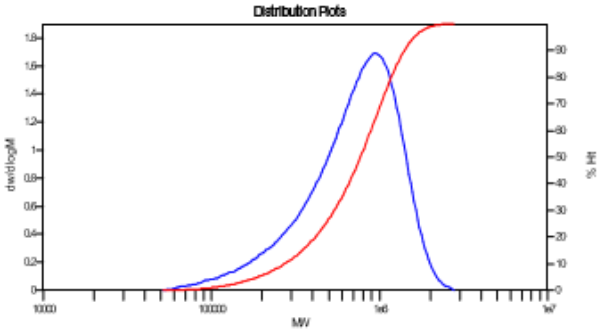
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	927072	521547	802183	1033500	1221075	765783	1.53808

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.63	11.40	13.42	14.3886	0	820.017	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 10:11 AM

Figure S83. GPC of the polymer from table 2, entry 6.

Cirrus GPC Sample Injection Report

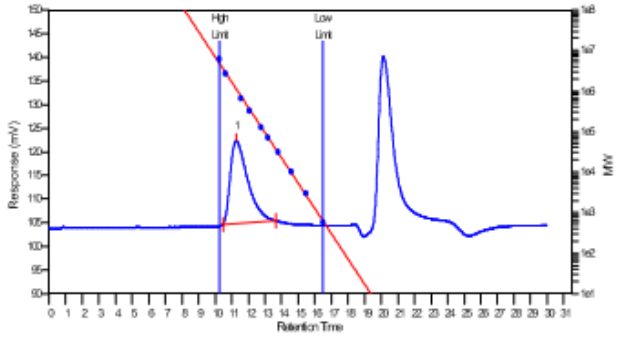
Generated by: HTGPC Saturday, April 15, 2017 10:12 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

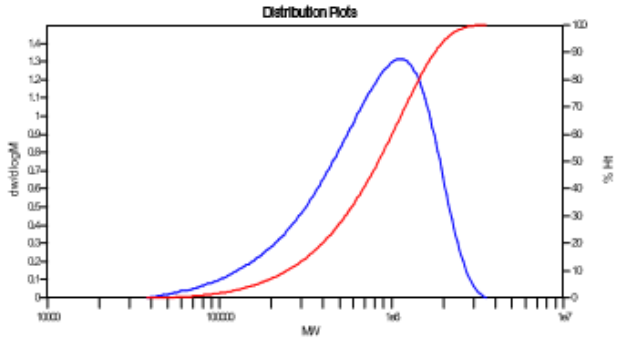
Sample Details

Sample Name: DSY-Ni-PhPh-100-10min
Acquired: 4/14/2017 6:26:04 PM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	1122320	507762	928942	1303471	1598810	871453	1.82948

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.47	11.27	13.63	17.3733	0	1274.14	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 10:12 AM

Figure S84. GPC of the polymer from table 2, entry 7.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:12 AM

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

Sample Details

Sample Name: DSY-Ni-PhPh-100-15min

Acquired: 4/14/2017 6:58:54 PM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

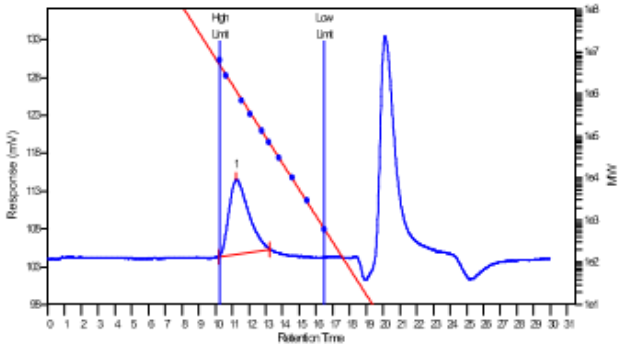
Calibration Used: 4/13/2017 8:58:56 AM

Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

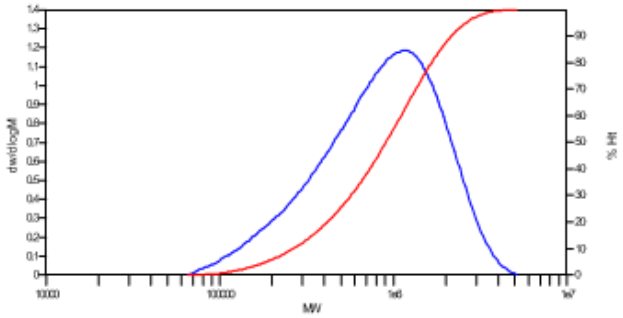
Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:



Distribution Plots



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1177246	573046	1069047	1609004	2093908	992610	1.86555

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	11.25	13.25	9.79539	0	796.426	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 10:12 AM

Figure S85. GPC of the polymer from table 2, entry 8.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, April 15, 2017 10:13 AM

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

Sample Details

Sample Name: DSY-Ni-PhPh-100-60min

Acquired: 4/14/2017 7:31:46 PM By Analyst: HTGPC Batch Name: DSY

Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS2016113001

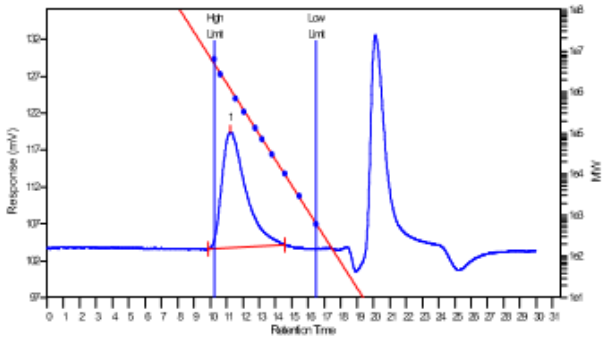
Calibration Used: 4/13/2017 8:58:56 AM

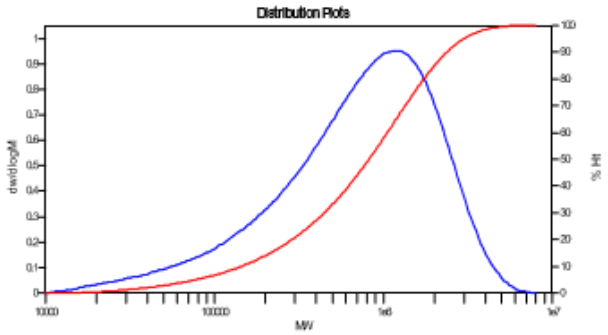
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

Calibration Curve: y = 13.063857 - 0.622521x^1

High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	1149455	302847	1063686	1892053	2633659	949438	3.51229

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.90	11.25	14.57	15.6703	0	1586.46	100

Cirrus GPC Version 3.4 Page 1 4/15/2017 10:13 AM

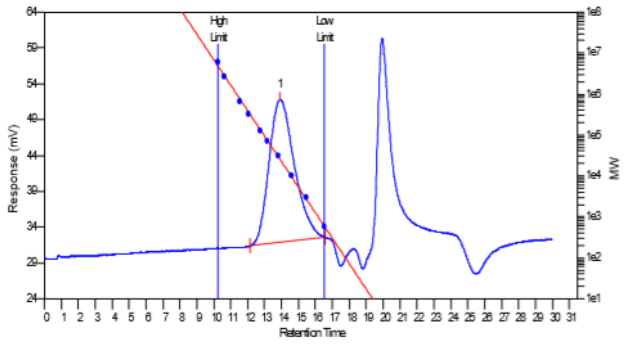
Figure S86. GPC of the polymer from table 2, entry 10.

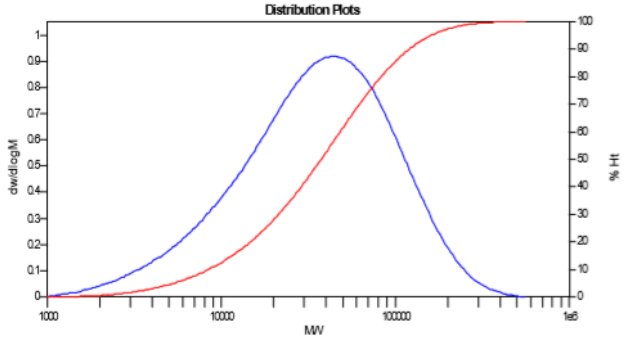
Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, June 03, 2017 10:47 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details
Sample Name: DSY-Me-Ni-0.16UA
Acquired: 6/1/2017 4:09:58 PM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	45792	18903	53404	106154	167724	47026	2.82516

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.17	13.90	16.57	19.9483	0	2080.94	100

Cirrus GPC Version 3.4 Page 1 6/3/2017 10:47 AM

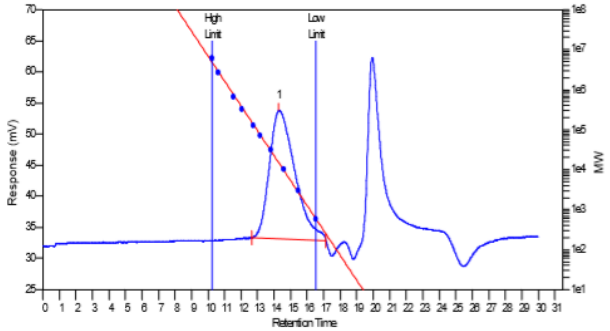
Figure S87. GPC of the polymer from table 3, entry 11.

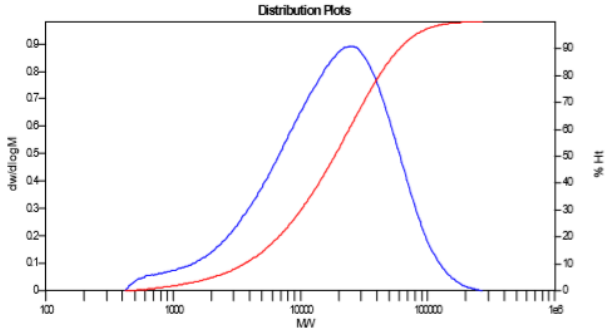
Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, June 03, 2017 10:47 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details
Sample Name: DSY-Me-Ni-0.32UA
Acquired: 6/1/2017 4:42:49 PM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	24515	7769	26442	53152	83341	23134	3.40353

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.67	14.28	17.15	20.6287	0	2217.98	100

Cirrus GPC Version 3.4 Page 1 6/3/2017 10:47 AM

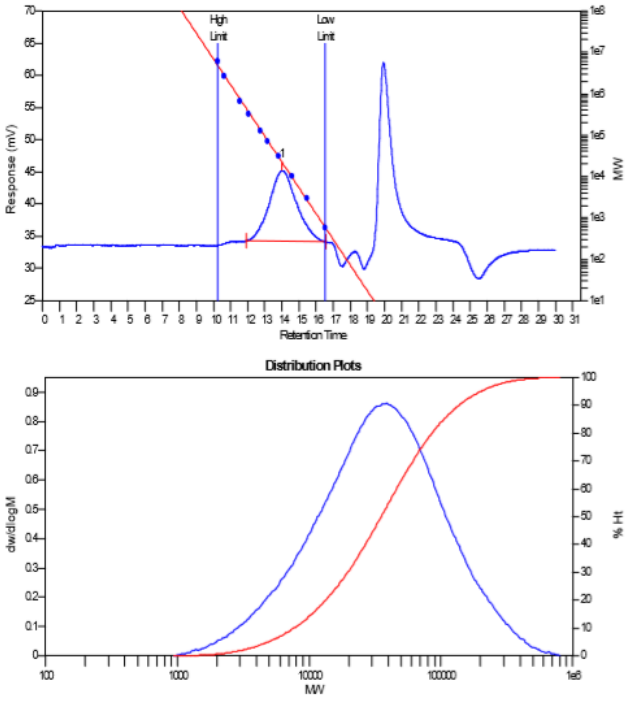
Figure S88. GPC of the polymer from table 3, entry 14.

Cirrus GPC Sample Injection Report

Generated by: HTGPC Saturday, June 03, 2017 10:48 AM
Workbook: E:\Cirrus Workbooks\20161130\20161130.plw

Sample Details
Sample Name: DSY-PhMe-Ni-0.32UA
Acquired: 6/1/2017 5:50:44 PM By Analyst: HTGPC Batch Name: DSY
Concentration: 0.10 Injection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000
Analysis Using Method: PS2016113001

Calibration Used: 4/13/2017 8:58:56 AM
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000
Calibration Curve: y = 13.063857 - 0.622521x^1
High Limit MW RT: 10.23 mins Low Limit MW RT: 16.52 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	38702	17684	58582	146951	265872	49694	3.31271

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.92	14.02	16.60	11.0171	0	1224.68	100

Cirrus GPC Version 3.4 Page 1 6/3/2017 10:48 AM

Figure S89. GPC of the polymer from table 3, entry 16.

4. References

1, Guo, L. H.; Kong, W. Y.; Xu, Y. J.; Yang, Y. L.; Ma, R.; Cong, L.; Dai, S. Y.; Liu, Z. Large-scale synthesis of novel sterically hindered acenaphthene-based α-diimine ligands and their application in coordination chemistry. *J. Organomet. Chem.* **2018**, *859*, 58-67.

2, Cherian, A. E.; Domski, G. J.; Rose, J. M.; Lobkovsky, E. B.; Coates, G. W. Acid-catalyzed ortho-alkylation of anilines with styrenes: An improved route to chiral anilines with bulky substituents. *Org. Lett.* **2005,** *7*, 5135-5137.

3, Guo, L. H.; Lian, K.; Kong, W.; Xu, S.; Jiang, G.; Dai, S. Y. Synthesis of Various Branched Ultra-High-Molecular-Weight Polyethylenes Using Sterically Hindered Acenaphthene-Based α-Diimine Ni (II) Catalysts. *Organometallics* **2018**, *37*, 2442−2449.

5. X-ray Crystallography

CCDC numbers of **1, 2** and **3** are **1886685, 1886683 and 1886684** respectively. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

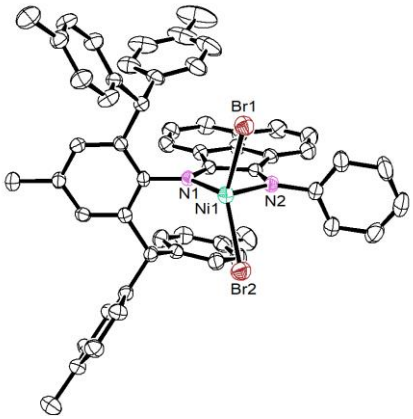


Table S3 Crystal data and structure refinement for 1.	
Identification code	**1**
Empirical formula	C57 H52 Br2 Cl4 N2 Ni O
Formula weight	1141.34
Temperature/K	298(2) K
Crystal system	Triclinic
Space group	P-1
a/Å	12.5431(11)
b/Å	14.4530(12)
c/Å	15.8001(13)
α/°	83.121(2)
β/°	76.6860(10)
γ/°	79.3150(10)
Volume/Å^3	2730.1(4)
Z	2

ρ_{calc}g/cm^3	1.388
μ/mm^{-1}	2.054
F(000)	1164
Crystal size/mm^3	0.40 x 0.20 x 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.36 to 25.02
Index ranges	-14<=h<=14, -17<=k<=13, -18<=l<=18
Reflections collected	13979
Independent reflections	9472 [R(int) = 0.0344]
Data/restraints/parameters	9472 / 0 / 628
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R1 = 0.0467, wR2 = 0.0801
Final R indexes [all data]	R1 = 0.1112, wR2 = 0.0866
Largest diff. peak/hole / e Å^{-3}	0.573 and -0.619

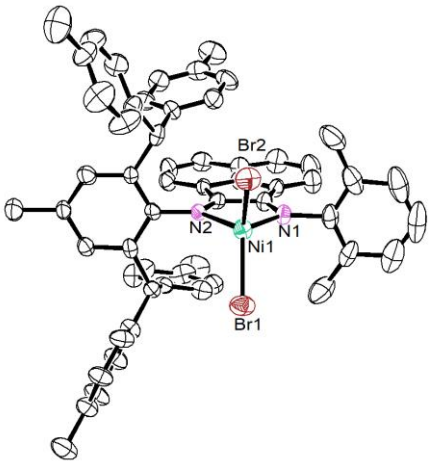


Table S4 Crystal data and structure refinement for 2.	
Identification code	**2**
Empirical formula	C57 H50 Br2 N2 Ni
Formula weight	981.52
Temperature/K	298(2) K
Crystal system	Monoclinic
Space group	P2
a/Å	10.813(5)
b/Å	20.216(5)
c/Å	26.480(5)
α/°	90.000(5)
β/°	100.049(5)
γ/°	90.000(5)
Volume/Å^3	5700(3)

Z	4
ρ_{calc}g/cm^3	1.144
μ/mm^{-1}	1.775
F(000)	2016
Crystal size/mm^3	0.30 x 0.20 x 0.20
Radiation	MoKα (λ = 0.71069)
2Θ range for data collection/°	2.393 to 25.707
Index ranges	-12<=h<=11, -23<=k<=24, -31<=l<=31
Reflections collected	28707
Independent reflections	9978[R(int) = 0.1810]
Data/restraints/parameters	9978 / 0 / 566
Goodness-of-fit on F^2	0.660
Final R indexes [I>=2σ (I)]	R1 = 0.0760, wR2 = 0.1632
Final R indexes [all data]	R1 = 0.1932, wR2 = 0.1944
Largest diff. peak/hole / e Å^{-3}	0.459 and -0.358

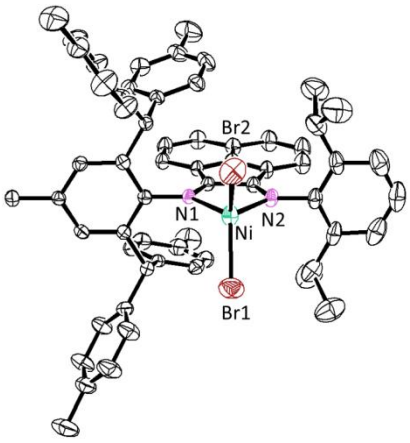


Table S5 Crystal data and structure refinement for 3.	
Identification code	**3**
Empirical formula	C61 H58 Br2 N2 Ni
Formula weight	1037.62
Temperature/K	298(2) K
Crystal system	Monoclinic
Space group	P2(1)/m
a/Å	11.7600(11)
b/Å	20.6272(18)
c/Å	12.0491(12)
α/°	90.000(5)
β/°	106.947(2)
γ/°	90.000(5)
Volume/Å^3	2795.9(5)

Z	2
ρ_{calc}g/cm^3	1.233
μ/mm^{-1}	1.813
F(000)	1072
Crystal size/mm^3	0.21 x 0.20 x 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.35 to 25.02
Index ranges	-13<=h<=13, -21<=k<=24, -14<=l<=14
Reflections collected	14293
Independent reflections	5065[R(int) = 0.0629]
Data/restraints/parameters	9978 / 0 / 333
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R1 = 0.0507, wR2 = 0.0895
Final R indexes [all data]	R1 = 0.1203, wR2 = 0.0976
Largest diff. peak/hole / e Å^{-3}	0.452 and -0.397