Impact of *o*-Aryl Halogen Effects on Ethylene Polymerization: Steric vs Electronic Effects

JianJian Dai[a], Shengyu Dai[b]*

[a]*Institutes of Physical Science and Information Technology, Anhui University, Hefei, Anhui, 230601, China.*
[b]*Anhui Laboratory of Molecule-Based Materials, Key Laboratory of Functional Molecular Solids, Ministry of Education, School of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China.*

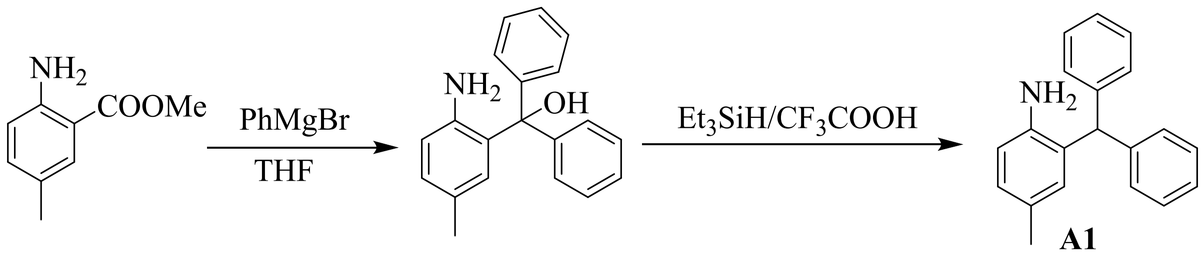
*To whom correspondence should be addressed. daiyu@ustc.edu.cn (Shengyu Dai, +86/13955189794).

1. Experimental section

1.1 General Considerations

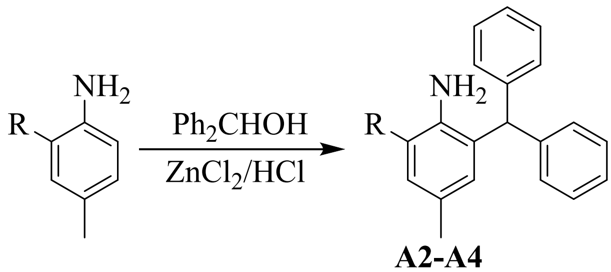
All chemicals were commercially sourced, except those whose synthesis is described. All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded by a JNM-ECZ600R or JNM-ECZ400R 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. Mass spectra were obtained by the Analytical Center of Anhui University. Elemental analysis was performed by the Analytical Center of Anhui University. 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 °C using trichlorobenzene as a solvent and calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was performed by a DSC Q2000 from TA Instruments. Samples were quickly heated to 150 °C and kept for 5 min to remove thermal history, then cooled to -50 °C at a rate of 10 K/min, and finally reheated to 150 °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).

1.2 Procedure for the Synthesis of Arylamines A1-A4.



A1

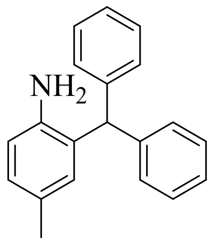
2-Amino-5-methylbenzoate (1.66 g, 10.0 mmol, 1.0 equivalent) was added to tetrahydrofuran in an N_2 atmosphere, followed by the addition of phenylmagnesium bromide (15 mL, 30.0 mmol, 1.0 eq) at 0 °C. The reaction was allowed to proceed at room temperature for two hours. Next, it was quenched with NH_4Cl solution and ethyl acetate was added. The ethyl acetate layer was washed three times with water (3 x 200 mL) and dried with anhydrous magnesium sulfate for 30 minutes. Subsequently, a white powder was obtained by ethanol precipitation. The obtained white powder (2.89 g, 2 mmol, 1.0 equivalent) was added successively to trifluoroacetic acid (0.60 mL, 8 mmol, 4.0 equivalent) and triethylsilane (0.64 mL, 4 mmol, 2.0 equivalent) at 0 °C for a reaction time of 4 hours. After the reaction, the mixture was dissolved in ethyl acetate and the pH was adjusted to 7 using $NaHCO_3$. The ethyl acetate layer was washed three times with 200 mL of water, dried with anhydrous magnesium sulfate for 30 minutes, and recrystallized with ethanol to obtain white powder (**A1**).



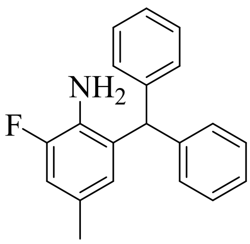
A2-A4

2: R = F, **3**: R = Cl, **4**: R = Br

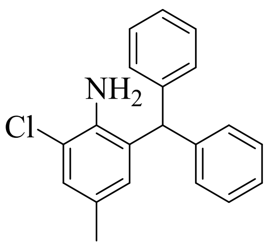
A mixture of 2-halogenated-4-methylaniline (10.0 mmol, 1.0 eq) and diphenylmethanol (1.84 g, 10 mmol, 1.0 eq) was heated to 120 ˚C. After the mixture was melted, a concentrated hydrochloric acid (1.0 mL) solution of dissolved anhydrous zinc chloride (0.68 g, 5 mmol, 0.5 equivalent) was added to the mixture and the temperature was raised to 160 ℃. After 30 minutes of reaction at 160 ° C, the mixture was cooled to room temperature and dissolved in dichloromethane (200 mL). The dichloromethane layer was washed with water (3 × 200 mL) and dried with anhydrous magnesium sulfate for 30 minutes. White powder (**A2-A4**) was obtained by recrystallization with ethanol.



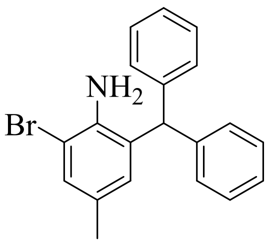
A1(1.53 g, 66%): **A1** is known [1].



A2 (2.58 g, 89%): **A2** is known [2].

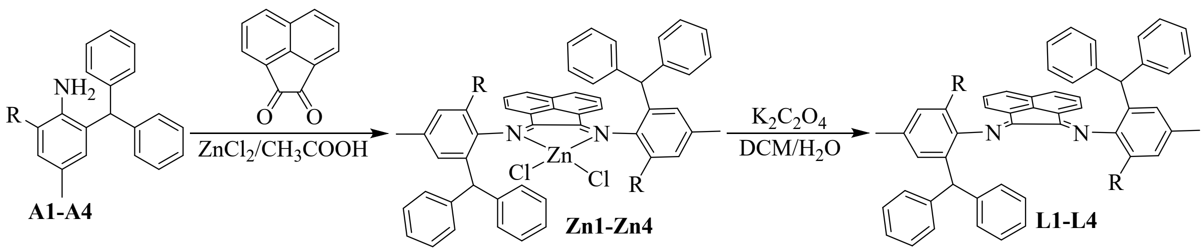


A3 (2.25 g, 75%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H, Ar-*H*), 7.28 (d, *J* = 1.6 Hz, 1H, Ar-*H*), 7.24 (d, *J* = 1.3 Hz, 1H, Ar-*H*), 7.16 – 7.01 (m, 5H, Ar-*H*), 6.39 (s, 1H, Ar-*H*), 5.47 (s, 1H, -C*H*-), 3.95 – 3.12 (*br*, 2H, -NH_2), 2.13 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.00, 138.38, 130.45, 129.48, 129.16, 128.66, 127.83, 126.85, 120.25, 52.71 (-*C*H-), 20.51 (-*C*H_3). APCI-MS (m/z): calcd for $C_{20}H_{19}ClN^+$: 308.1201, Found, 308.1195, $[M+H]^+$



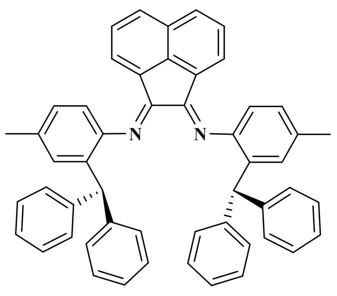
A4 (2.78 g, 93%): **A4** is known [3].

1.3 Procedure for the Synthesis of Ligands L1-L4.

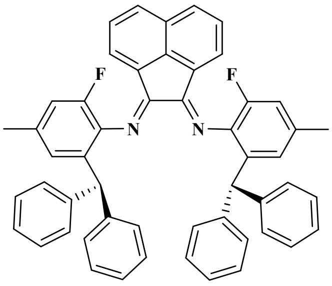


1: R = H, **2**: R = F,
3: R = Cl, **4**: R = Br

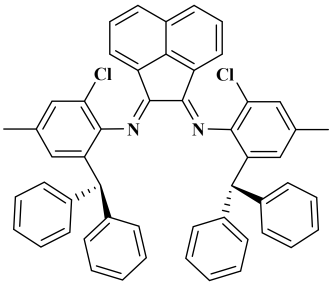
The condensation of arylamines **A1-A4** (2 mmol, 1.0 equivalent) and acenaphthenone (1 mmol, 0.5 equivalent) was performed using the template method. To the reaction system, 2 mL of acetic acid dissolved in $ZnCl_2$ (1.0 equivalent) was added to the arylamines and acenaphthenone acetate solution (10 mL), and the mixture was reacted at 90 °C for four hours. At the end of the reaction, the yellow solid powder was obtained by filtration and ether washing. The yellow powder was dissolved in 40 mL of dichloromethane. Then, 10% potassium oxalate solution was added and stirred at room temperature for one hour. Afterward, the dichloromethane layer was washed with water (3 × 20 mL) and dried with anhydrous magnesium sulfate for 30 minutes. Finally, the yellow powder (**L1-L4**) was obtained by ethanol precipitation.



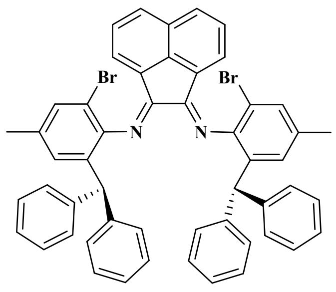
L1 (0.48 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.62 (m, 2H, Ar-*H*), 7.17 – 7.00 (m, 14H, Ar-*H*), 6.96 – 6.76 (m, 13H, Ar-*H*), 6.72 – 6.46 (m, 3H, Ar-*H*), 5.83 (s, 2H, -C*H*-), 2.36 (s, 6H, -C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.90 (*C*=N), 147.91, 146.90, 147.91, 146.90, 143.10, 142.62, 140.90, 134.45, 134.05, 133.81, 131.97, 130.57, 130.49, 130.35, 130.27, 129.86, 129.64, 129.54, 128.80, 128.18, 128.08, 128.05, 127.89, 127.70, 127.50, 126.98, 126.86, 126.69, 125.79, 125.73, 123.71, 123.44, 121.79, 117.93, 117.20, 116.66, 76.83, 52.48 (-*C*H-), 52.09 (-*C*H-), 21.45 (-*C*H$_3$), 20.85 (-CH_3). APCI-MS (m/z): calcd for $C_{52}H_{41}N_2^+$: 693.3265, Found, 693.3242, $[M+H]^+$



L2 (0.50 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.59 (m, 3H, Ar-*H*), 7.35 – 7.27 (m, 2H, Ar-*H*), 7.17 (td, *J* = 13.1, 7.3 Hz, 8H, Ar-*H*), 7.03 – 6.31 (m, 16H, Ar-*H*), 6.13 – 5.94 (m, 1H, Ar-*H*), 5.86, 5.80 (s, s, 2H, -C*H*-), 2.33 (s, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.29 (*C*=N), 149.68, 142.53, 141.64, 141.46, 141.27, 141.01, 140.47, 137.46, 137.06, 136.90, 135.35, 135.21, 134.87, 134.47, 134.41, 133.97, 131.77, 130.04, 129.87, 129.74, 129.65, 128.99, 128.80, 128.41, 128.21, 127.95, 127.83, 127.55, 127.36, 126.99, 126.30, 125.93, 125.31, 125.00, 122.47, 114.39, 114.20, 52.59 (-*C*H-), 21.45 (-*C*H_3). APCI-MS (m/z) : calcd for $C_{52}H_{39}F_2N_2^+$: 729.3076, Found, 729.3068, $[M+H]^+$

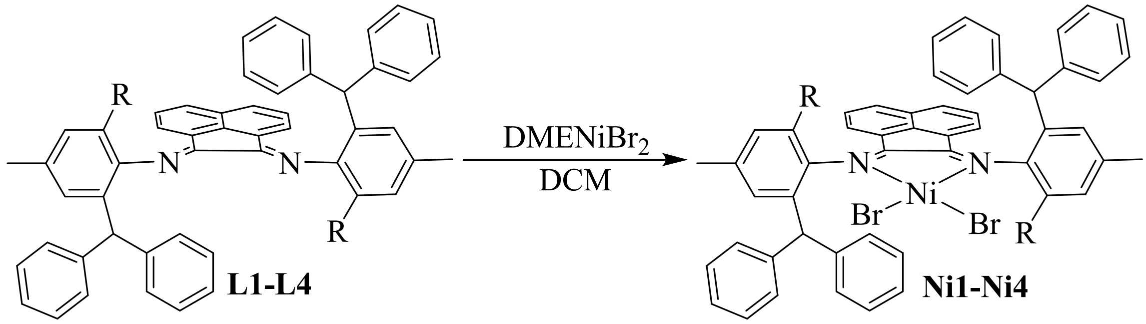


L3 (0.45 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73, 7.59 (s, s, 2H, Ar-*H*), 7.23 – 7.06 (m, 13H, Ar-*H*), 6.92 (d, J = 7.5 Hz, 4H, Ar-*H*), 6.83, 6.77 (s, s, 2H, Ar-*H*), 6.64 (dt, *J* = 14.7, 6.9 Hz, 1H, Ar-*H*), 6.41 – 6.27 (m, 6H, Ar-*H*), 6.03 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 5.79, 5.74 (s, s, 2H, -C*H*-), 2.32 (s, 6H, -CH_3). ^{13}C NMR (101 MHz, CDCl3) δ 164.37 (*C*=N), 144.54, 142.75, 142.30, 140.87, 140.31, 136.25, 134.21, 130.13, 129.79, 129.72, 129.64, 129.55, 129.19, 128.78, 128.75, 128.61, 128.39, 128.28, 128.21, 128.16, 128.00, 127.59, 127.50, 127.00, 126.94, 126.36, 126.30, 125.91, 125.08, 122.83, 122.22, 121.85, 52.80 (-*C*H-), 52.17 (-*C*H-), 21.18 (-*C*H_3). APCI-MS (m/z) : calcd for $C_{52}H_{39}Cl_2N_2^+$: 761.2485, Found, 761.2470, $[M+H]^+$

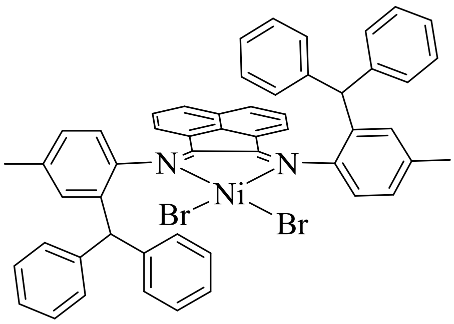


L4 (0.55 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74, 7.60 (s, s, 2H, Ar-*H*), 7.43, 7.39 (s, s, 2H, Ar-*H*),7.25 – 7.17 (m, 5H, Ar-*H*), 7.18 – 7.04 (m, 6H, Ar-*H*), 6.95 (d, *J* = 7.6 Hz, 5H, Ar-*H*), 6.84 (s, 1H, Ar-*H*), 6.68, 6.57 (s, s, 2H, Ar-*H*), 6.35 (q, *J* = 7.3 Hz, 5H, Ar-*H*), 6.10 (t, J = 7.5 Hz, 2H, Ar-*H*), 5.81, 5.74 (s, s, 2H, -C*H*-), 2.34 (s, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.52 (*C*=N), 164.05 (*C*=N), 145.91, 143.31, 142.97, 142.26, 136.05, 135.08, 134.63, 131.86, 131.41, 130.36, 130.21, 129.92, 129.86, 129.74, 129.63, 129.08, 128.93, 128.77, 128.44, 128.24, 128.06, 127.64, 127.49, 127.08, 126.39, 126.33, 125.97, 125.24, 123.09, 112.08, 111.72, 52.86 (-*C*H-), 52.38 (-*C*H-), 21.08 (-*C*H_3). APCI-MS (m/z): calcd for $C_{52}H_{39}Br_2N_2^+$: 851.1455, Found, 851.1457, $[M+H]^+$

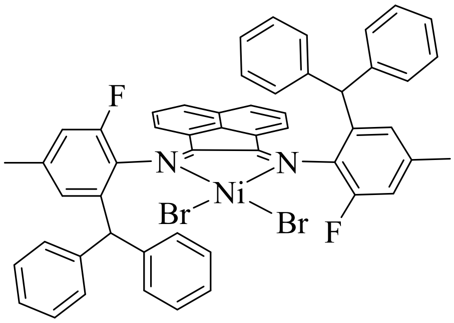
1.4 Procedure for the Synthesis of Complexes Ni1-Ni4.



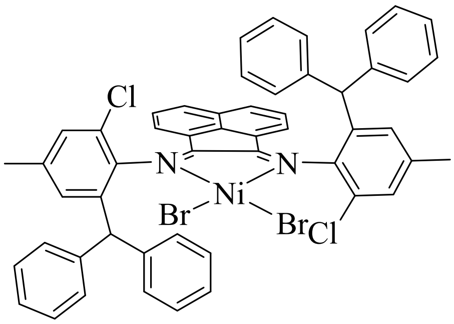
In a nitrogen atmosphere, a mixture consisting of 0.2 mmol of ligand and an equivalent amount of (DME)NiBr_2 was introduced into 10 mL of methylene chloride. This mixture was then stirred at room temperature for an extended period of time, overnight, resulting in a noticeable deepening of the solution's color. Following the completion of the reaction, the solvent was partially evaporated under reduced pressure. Subsequently, the remaining mixture was diluted with 20 mL of anhydrous ether, leading to the formation of an orange-red solid precipitate. The solids were then separated through filtration, washed thoroughly with ether, and finally dried under vacuum conditions to yield the desired **Ni1-Ni4** compounds.



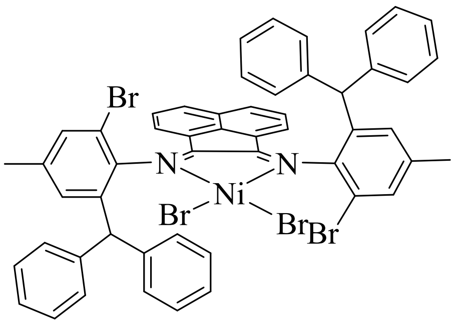
Ni1 (0.14 g, 65%), IR: C=N (1621 cm^{-1}). MALDI-TOF-MS (m/z): calcd for $C_{52}H_{40}BrN_2Ni$: 829.1728, Found, 829.1714, $[M-Br]^+$. Elemental analysis: calc. for $C_{52}H_{40}Br_2N_2Ni$: C, 68.53; H, 4.42; N, 3.07. Found: C, 68.47; H, 4.23; N, 3.11.



Ni2 (0.15 g, 78%), IR: C=N (1628 cm^{-1}). MALDI-TOF-MS (m/z): calcd for $C_{52}H_{38}BrF_2N_2Ni$: 865.1540, Found, 865.1519, $[M-Br]^+$. Elemental analysis: calc. for $C_{52}H_{38}Br_2F_2N_2Ni$: C, 65.93; H, 4.04; N, 2.96. Found: C, 65.89; H, 4.07; N, 2.91.



Ni3 (0.17 g, 87%), IR: C=N (1625 cm^{-1}). MALDI-TOF-MS (m/z): calcd for $C_{52}H_{38}BrCl_2N_2Ni$: 897.0949, Found, 897.0944, $[M-Br]^+$. Elemental analysis: calc. for $C_{52}H_{38}Br_2Cl_2N_2Ni$: C, 63.71; H, 3.91; N, 2.86. Found: C, 63.64; H, 3.96; N, 2.81.



Ni4 (0.20 g, 90%), IR: C=N (1623 cm^{-1}). MALDI-TOF-MS (m/z): calcd for $C_{52}H_{38}Br_3N_2Ni$: 984.9939, Found, 984.9927, $[M-Br]^+$. Elemental analysis: calcd for $C_{52}H_{38}Br_4N_2Ni$: C, 58.41; H, 3.58; N, 2.62. Found: C, 58.23; H, 3.64; N, 2.65.

1.5 A General Procedure for Ethylene Polymerization.

In a standard experimental procedure, a 350 mL thick-walled glass pressure vessel underwent drying for 2 hours in a hot air circulation oven maintained at 60 °C. Once it cooled to room temperature, 40 mL of toluene and 200 equivalents of Et_2AlCl were introduced into the vessel in a nitrogen-rich environment. Following this, 2 μmol of a Ni(II) catalyst dissolved in 1 mL of CH_2Cl_2 was injected into the polymerization system using a syringe. With vigorous stirring at 350 RPM, the reactor was pressurized to maintain a constant 6 atm of ethylene. After a duration of 10 minutes, the pressurized reactor was depressurized, and the resulting polymer was precipitated in ethanol. Subsequently, the polymer was filtered, and then dried at 50 °C for a minimum of 24 hours under vacuum conditions.

2.1 ^{1}H and ^{13}C NMR of the Synthetic Compounds.

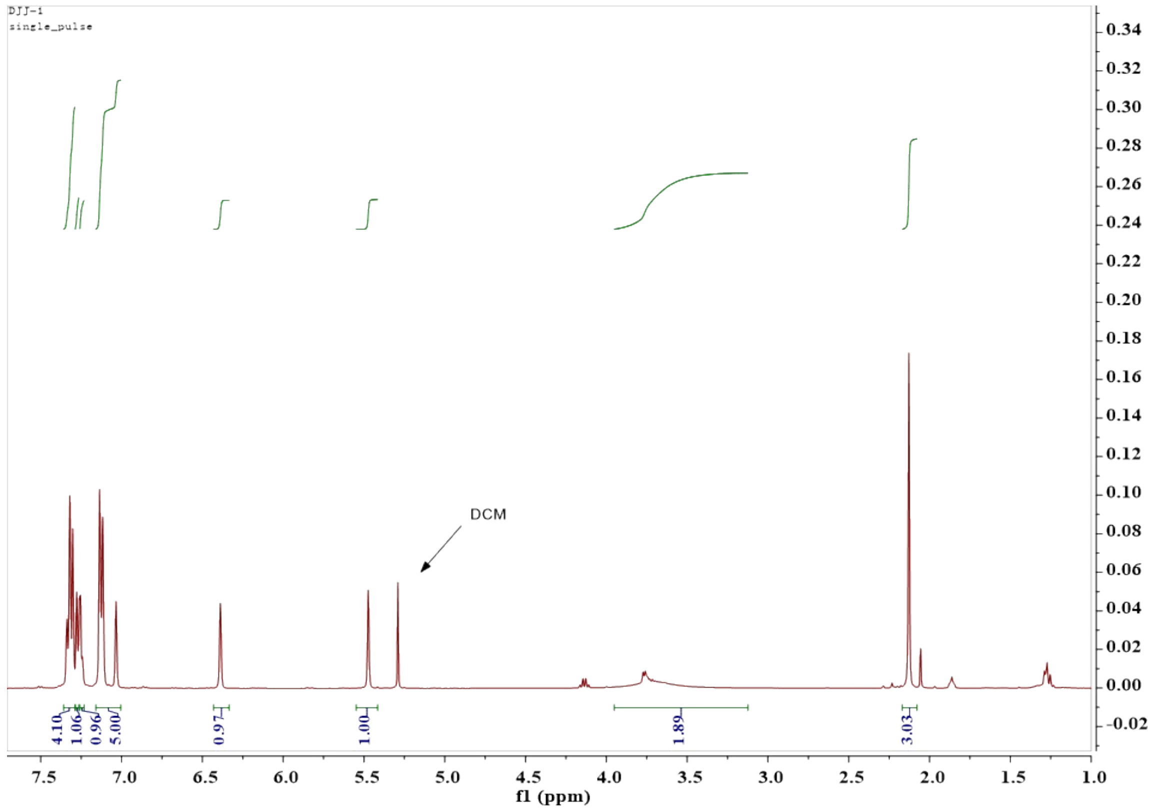


Figure S1. ^{1}H NMR spectrum of **A3** in $CDCl_3$ (400 MHz, 20 °C).

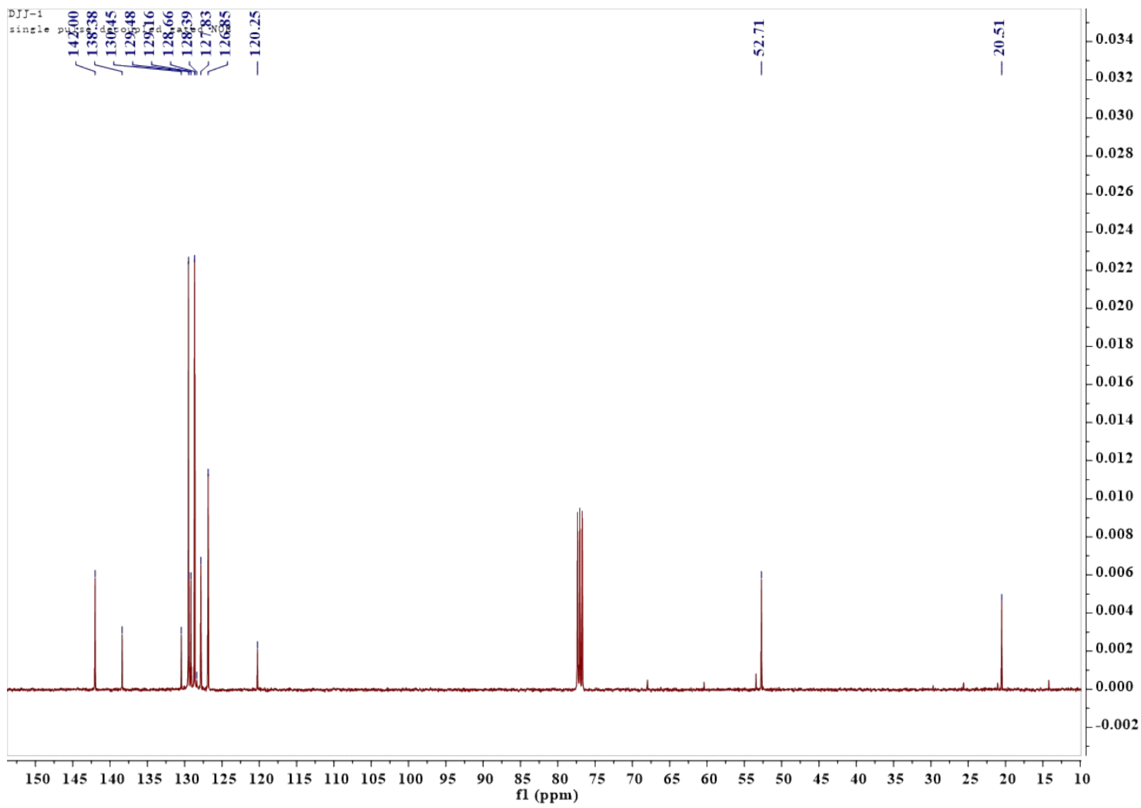


Figure S2. ^{13}C NMR spectrum of **A3** in $CDCl_3$ (400 MHz, 20 °C).

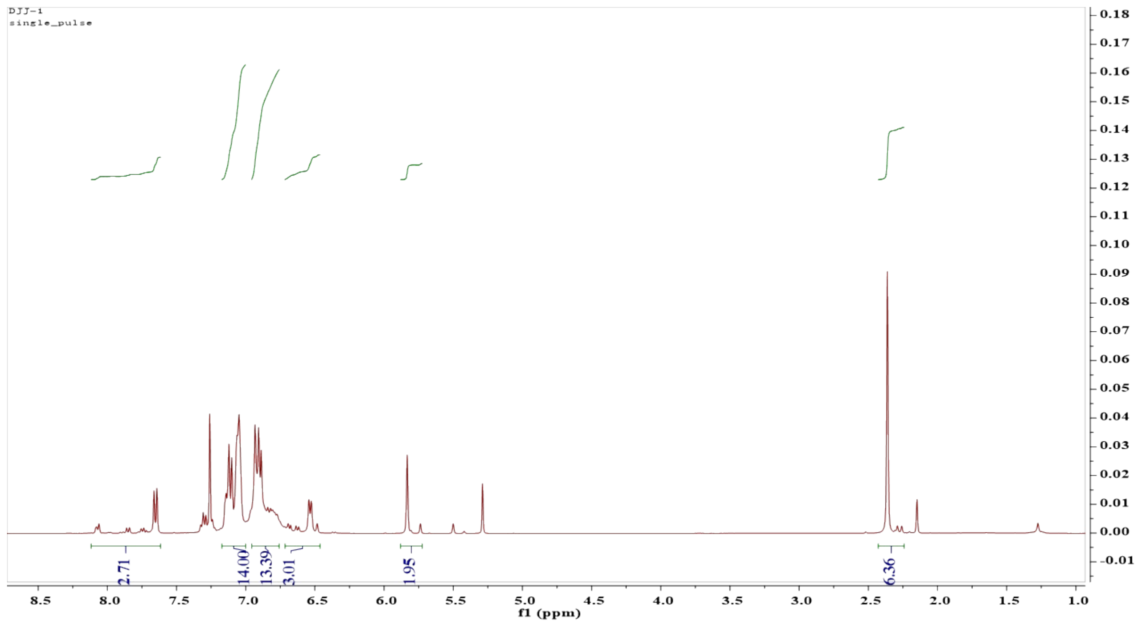


Figure S3. ^{1}H NMR spectrum of **L1** in $CDCl_3$ (400 MHz, 20 °C).

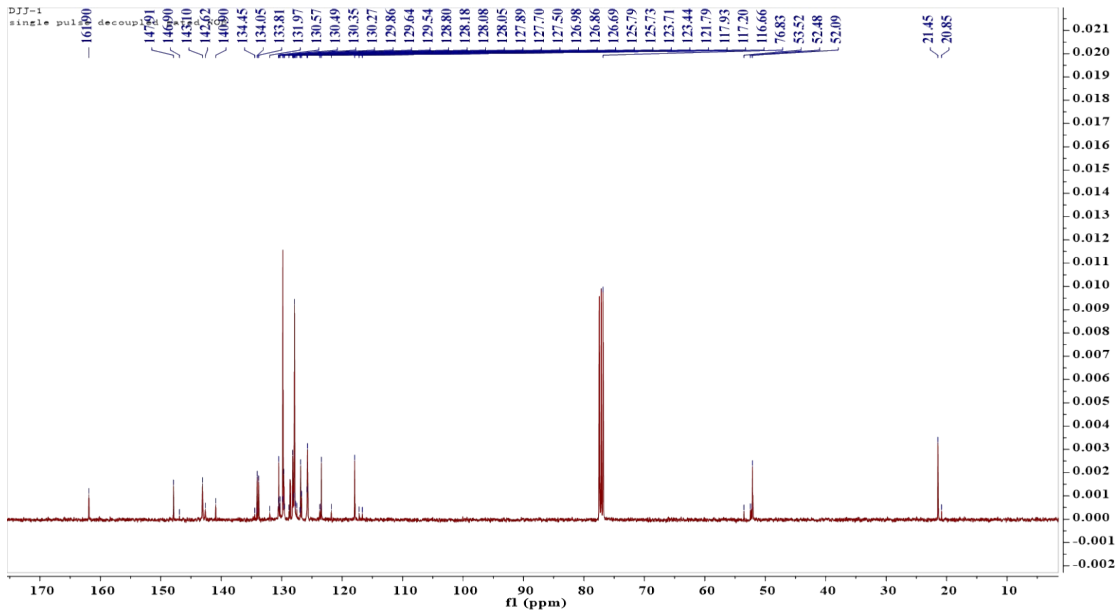


Figure S4. ^{13}C NMR spectrum of **L1** in $CDCl_3$ (400 MHz, 20 °C).

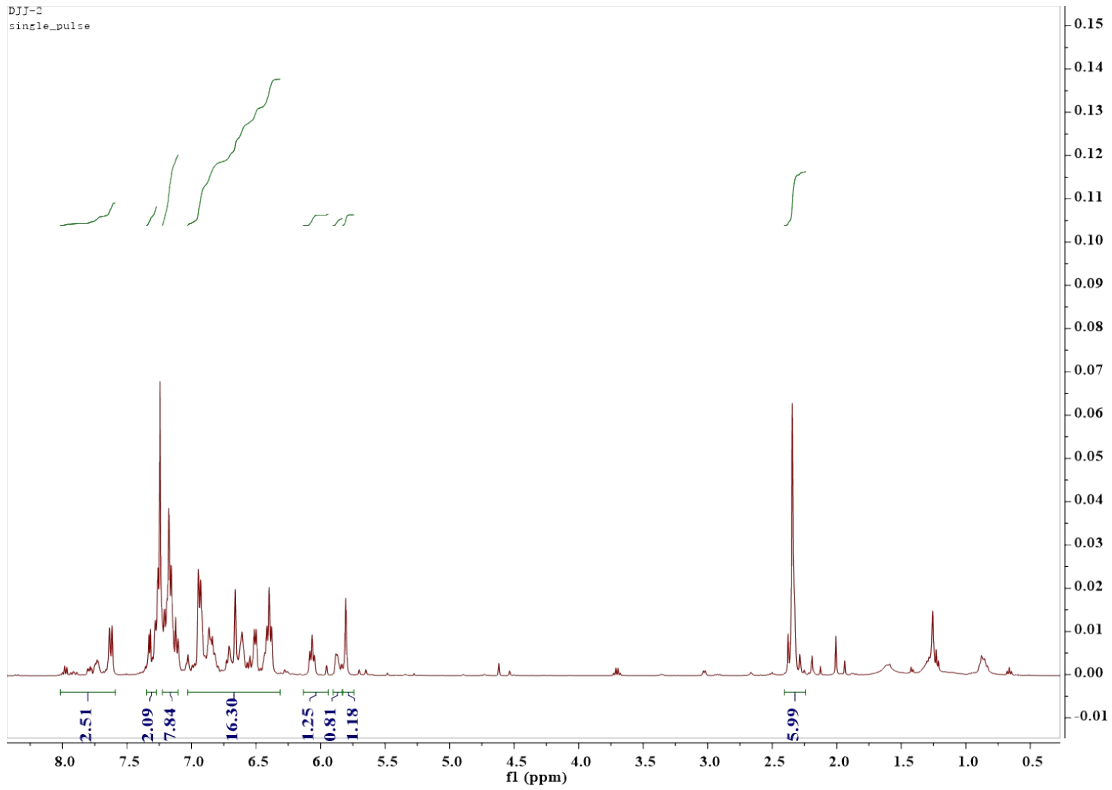


Figure S5. ^{1}H NMR spectrum of **L2** in $CDCl_3$ (400 MHz, 20 °C).

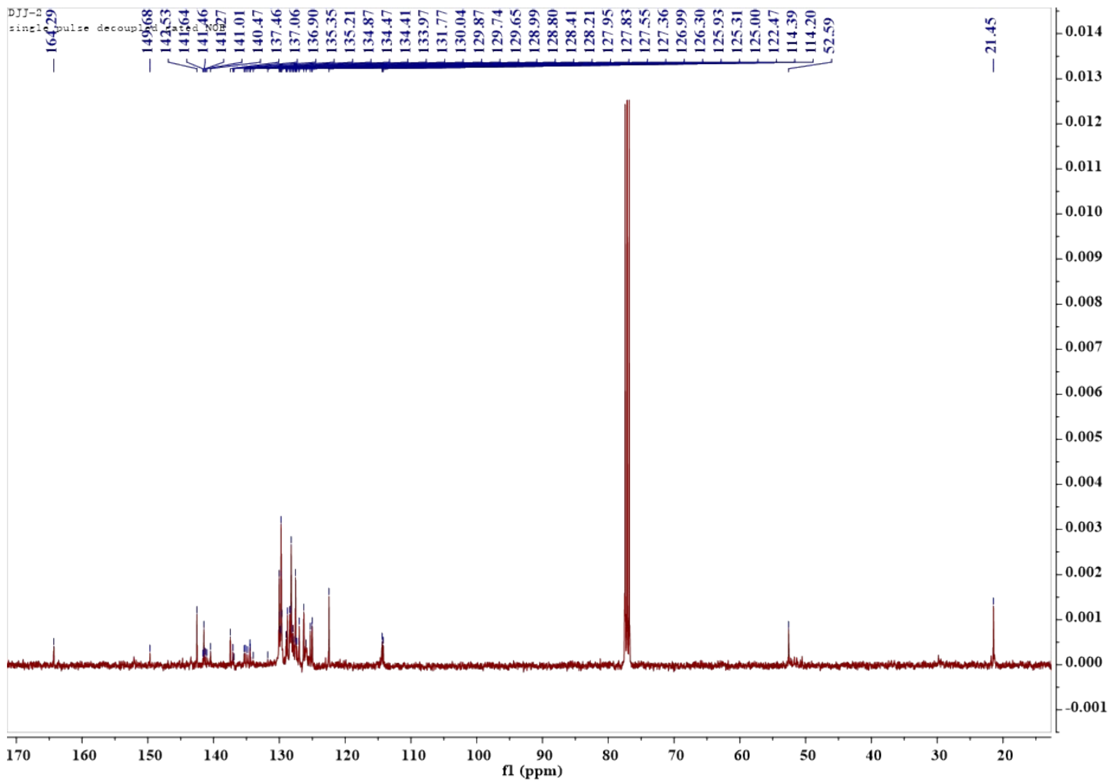


Figure S6. ^{13}C NMR spectrum of **L2** in $CDCl_3$ (400 MHz, 20 °C).

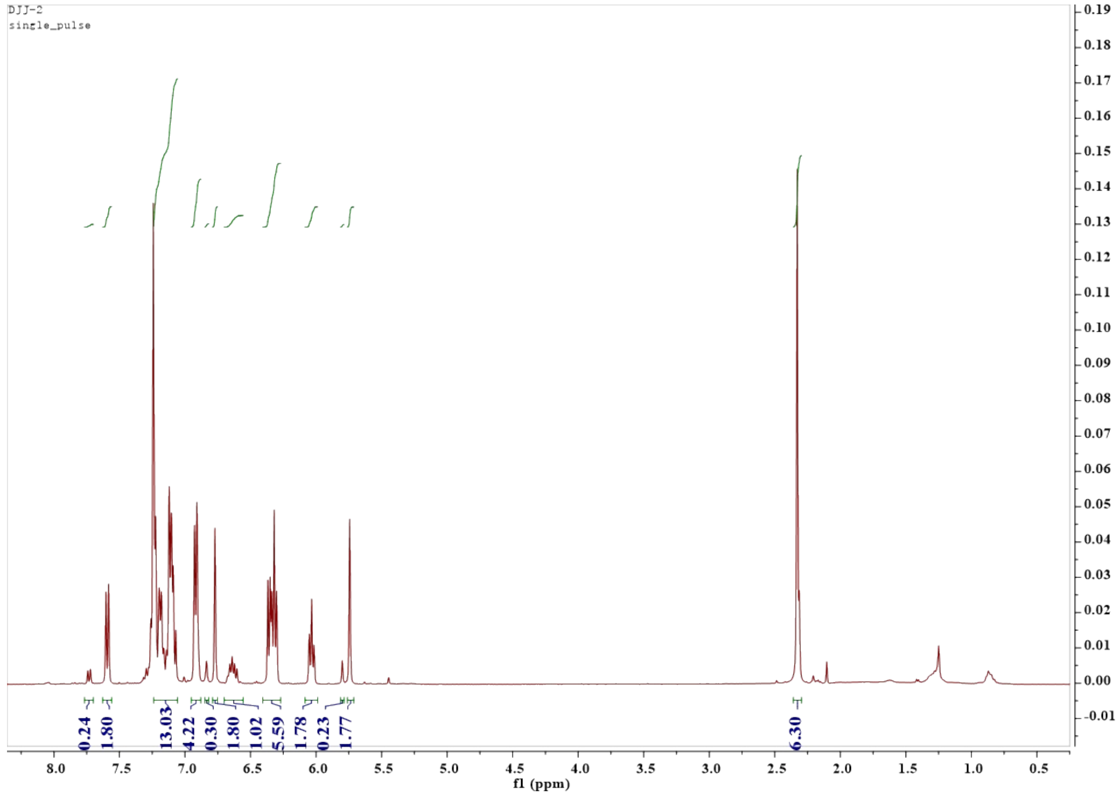


Figure S7. ^{1}H NMR spectrum of **L3** in $CDCl_3$ (400 MHz, 20 °C).

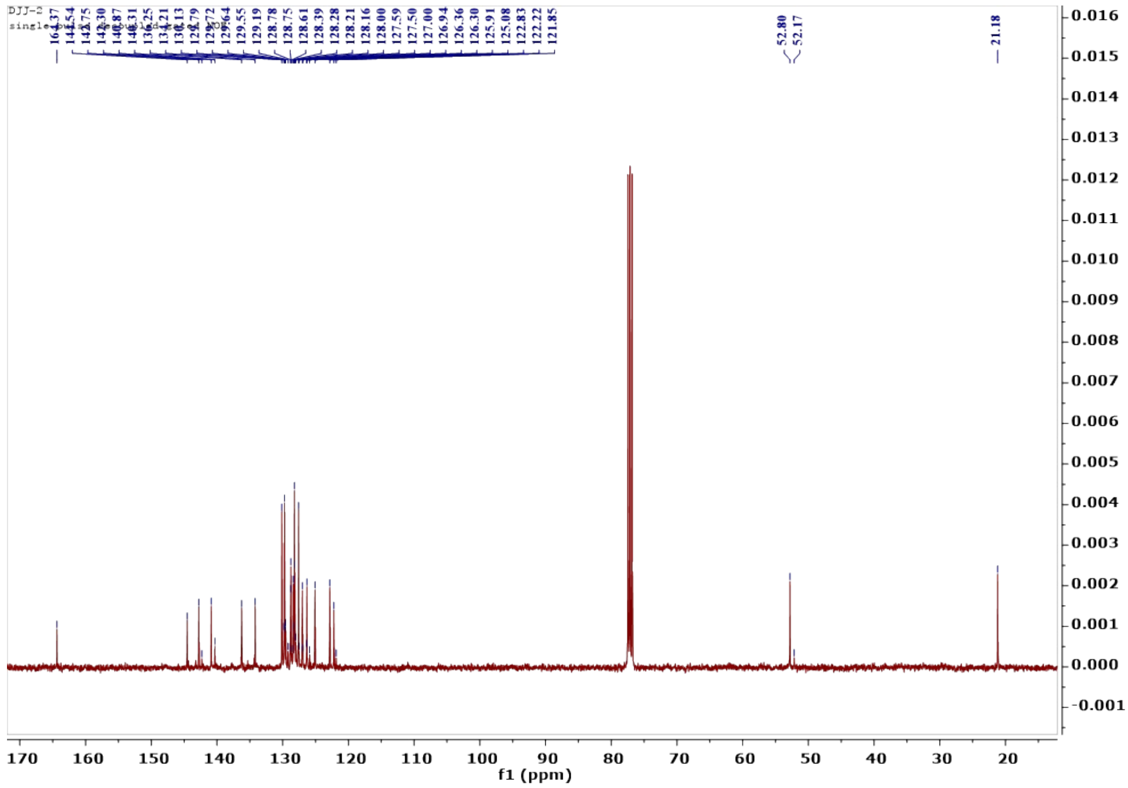


Figure S8. ^{13}C NMR spectrum of **L3** in $CDCl_3$ (400 MHz, 20 °C).

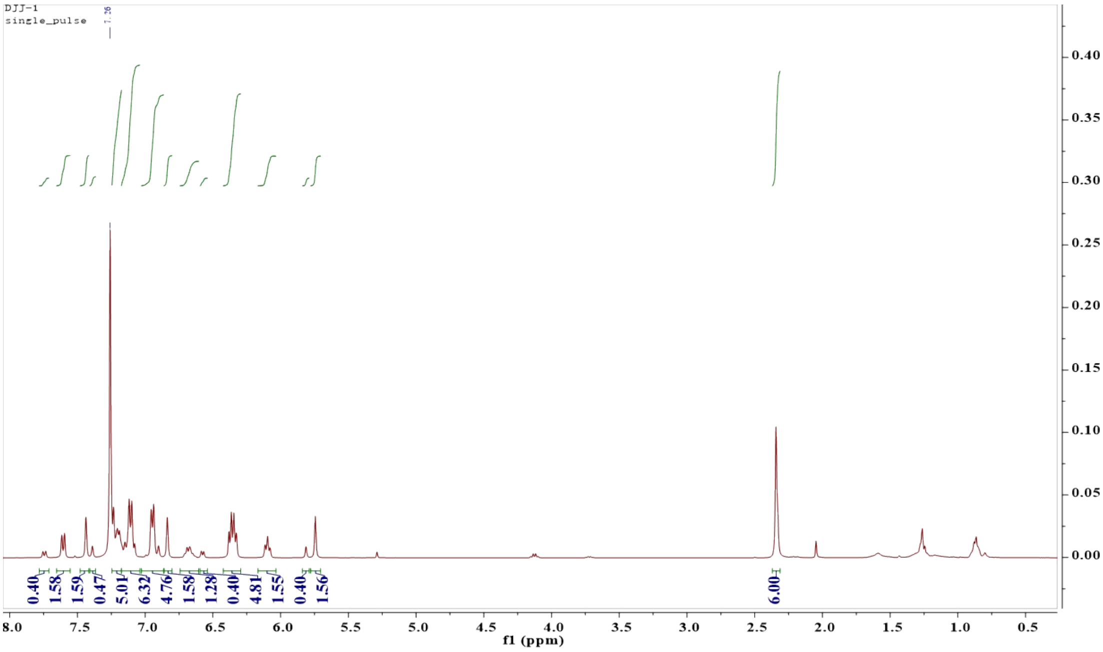


Figure S9. ^{1}H NMR spectrum of **L4** in $CDCl_3$ (400 MHz, 20 °C).

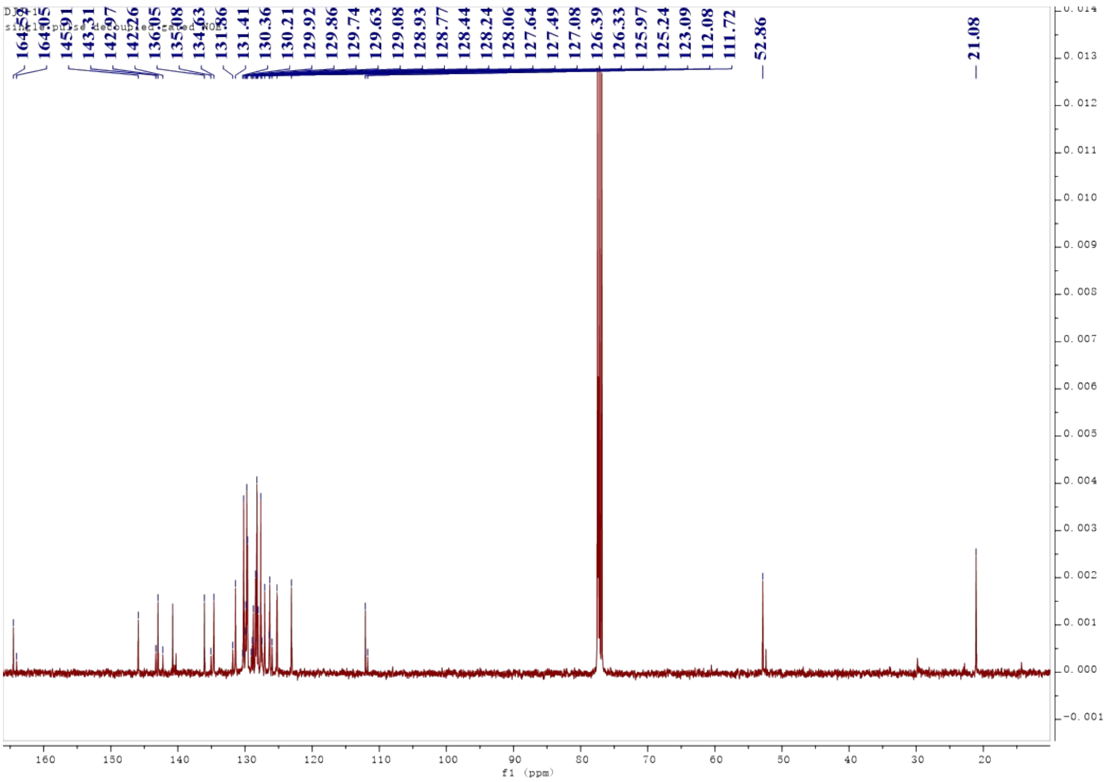


Figure S10. ^{13}C NMR spectrum of **L4** in $CDCl_3$ (400 MHz, 20 °C).

2.2 MS of A3 and L1-L4.

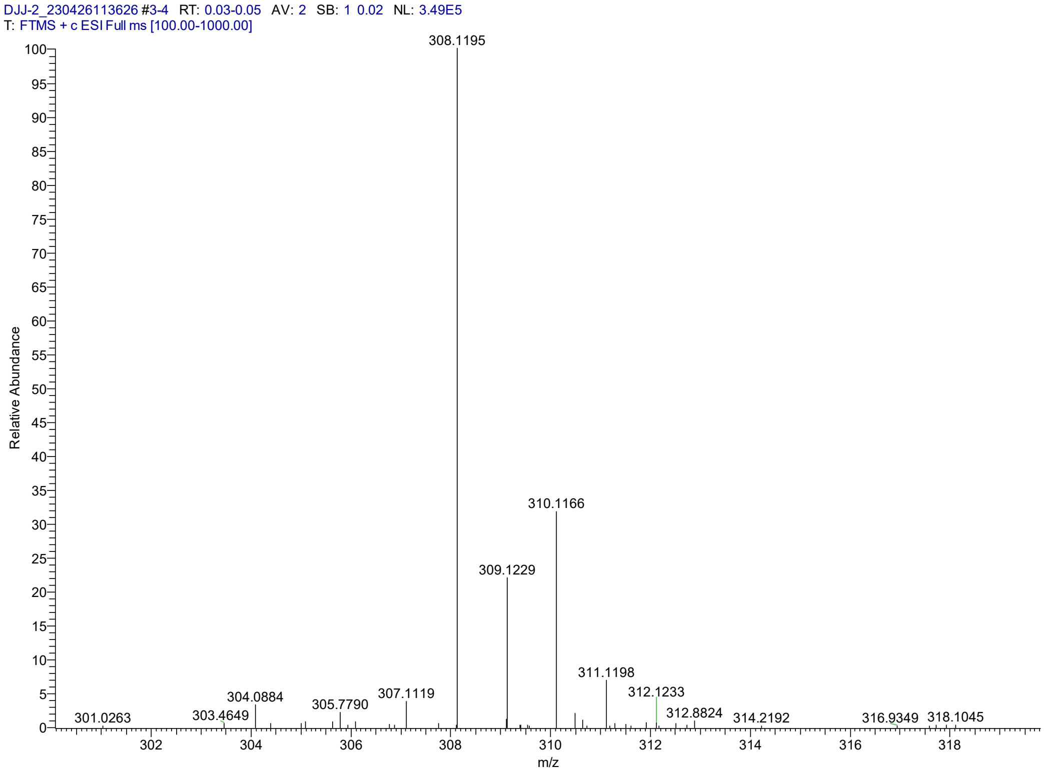


Figure S11. APCI-MS of **A3**.

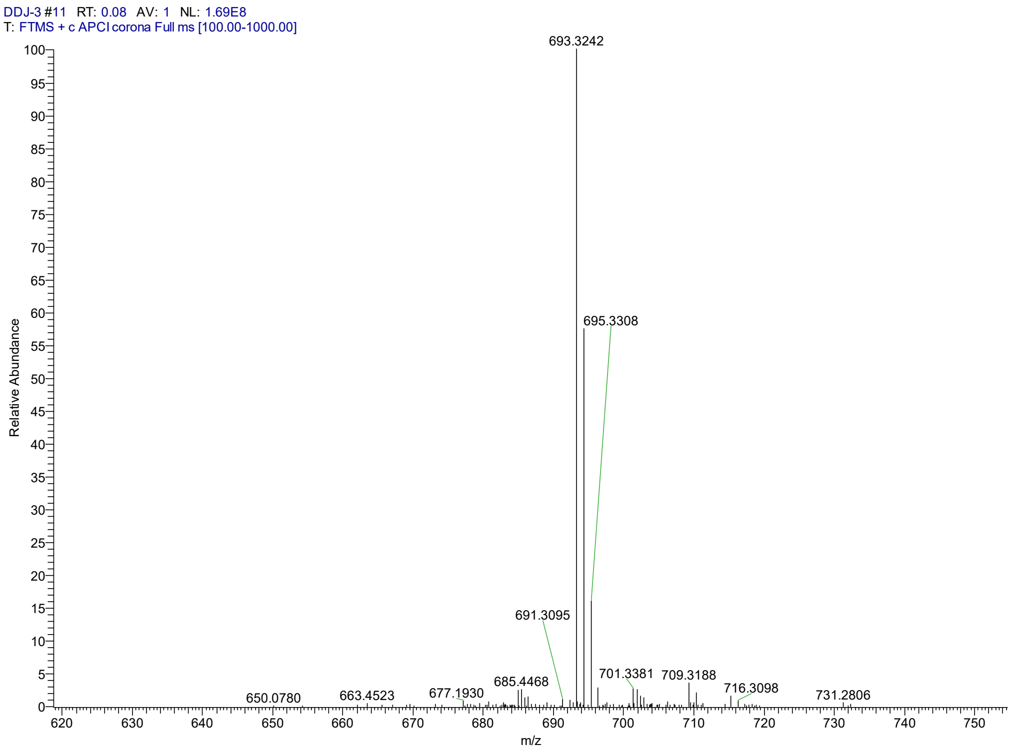


Figure S12. APCI-MS of **L1**.

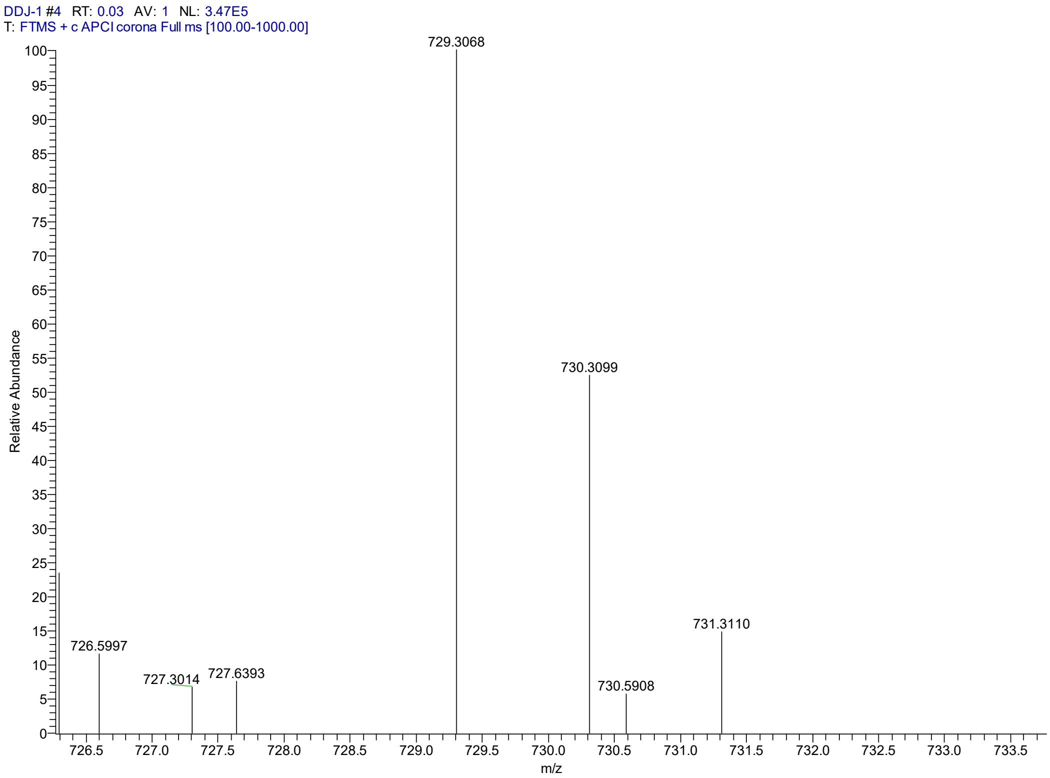


Figure S13. APCI-MS of **L2**.

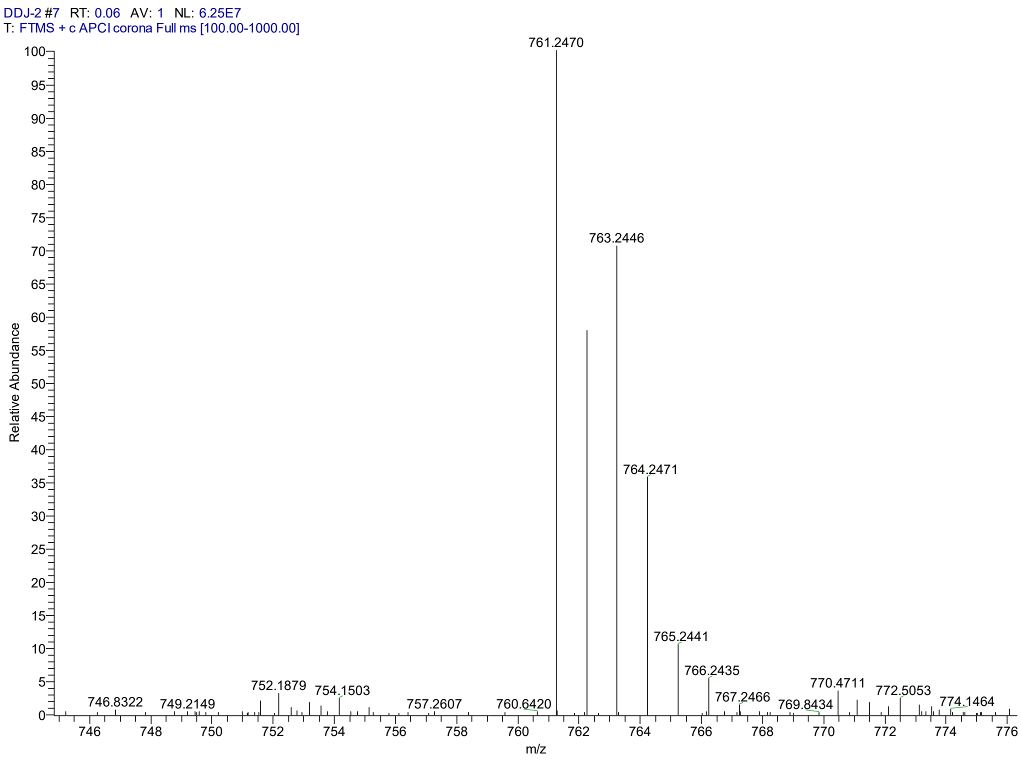


Figure S14. APCI-MS of **L3**.

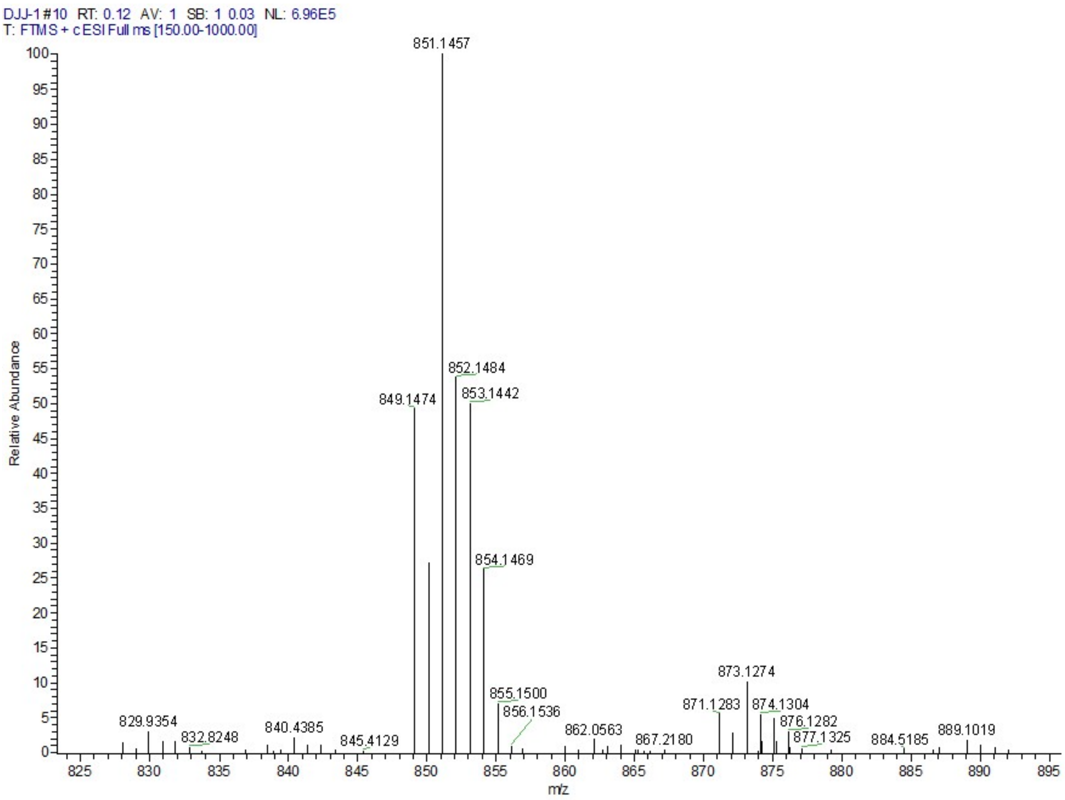


Figure S15. APCI-MS of **L4**.

2.3 MS of Complexes Ni1-Ni4.

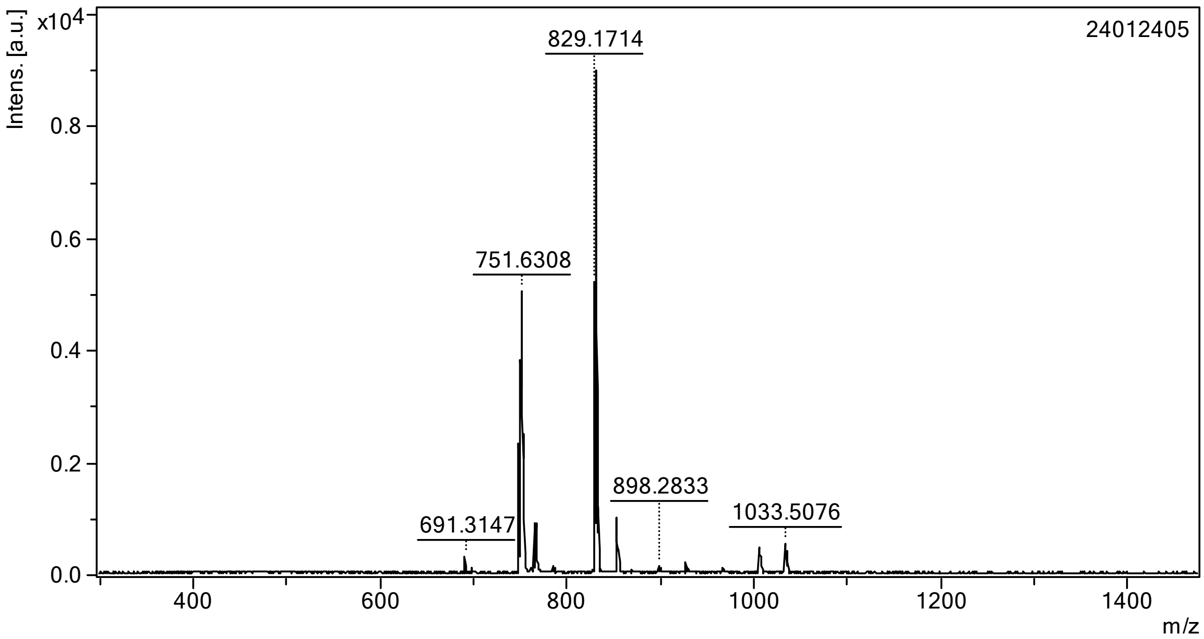


Figure S16. MALDI-TOF-MS of **Ni1**.

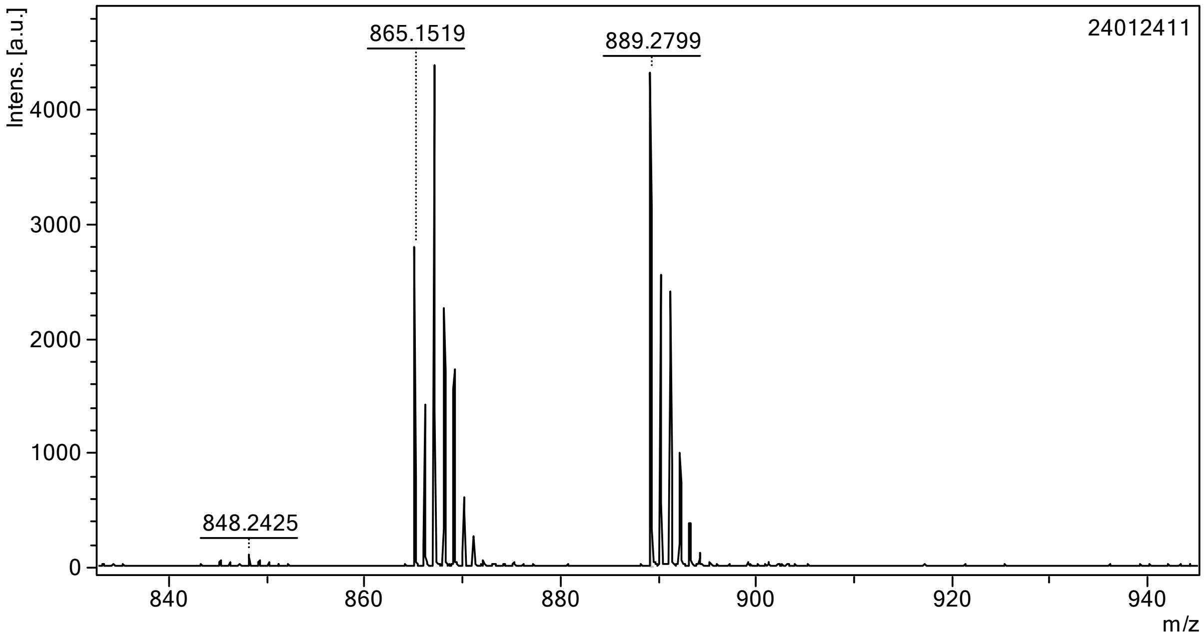


Figure S17. MALDI-TOF-MS of **Ni2**.

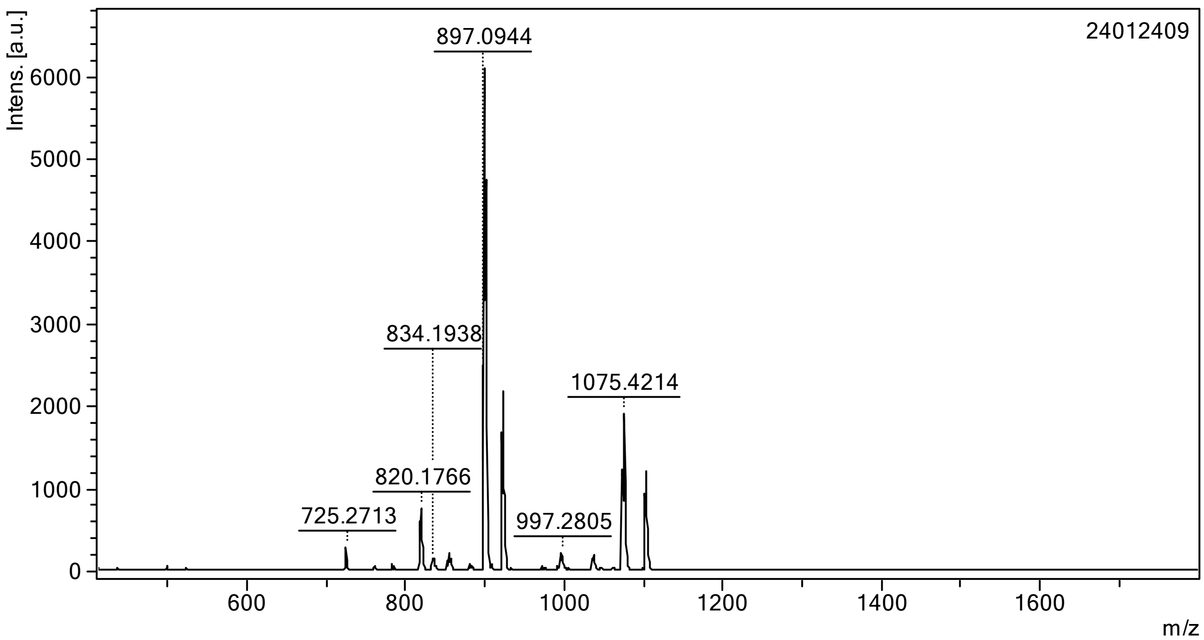


Figure S18. MALDI-TOF-MS of **Ni3**.

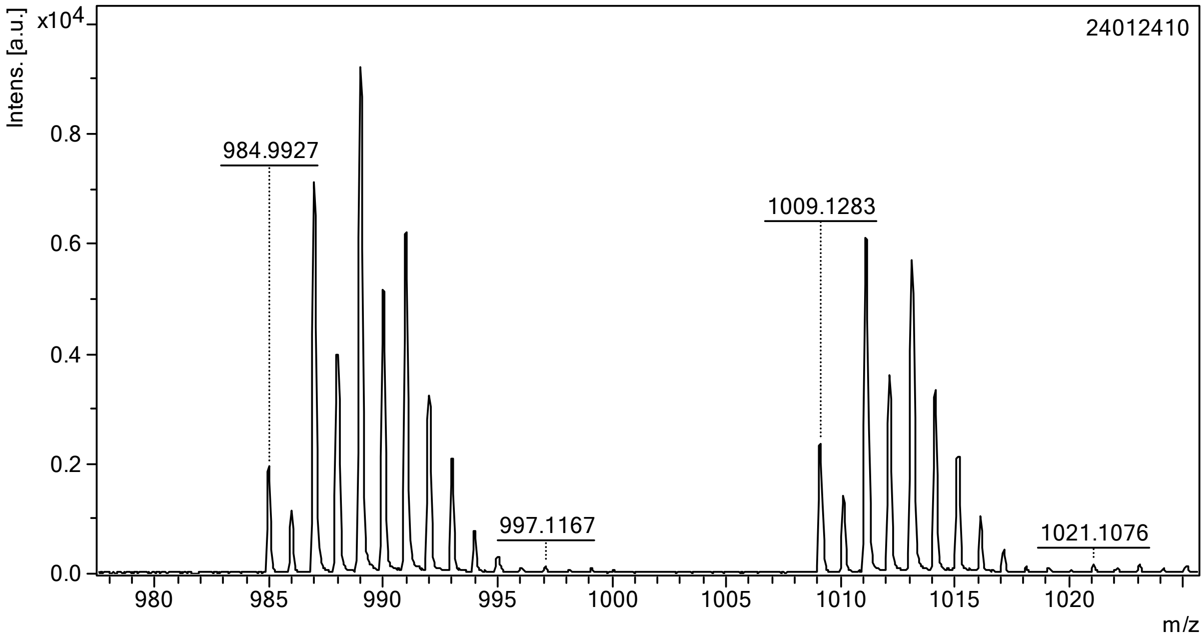


Figure S19. MALDI-TOF-MS of **Ni4**.

2.4 ^{1}H NMR of Representative Polymers.

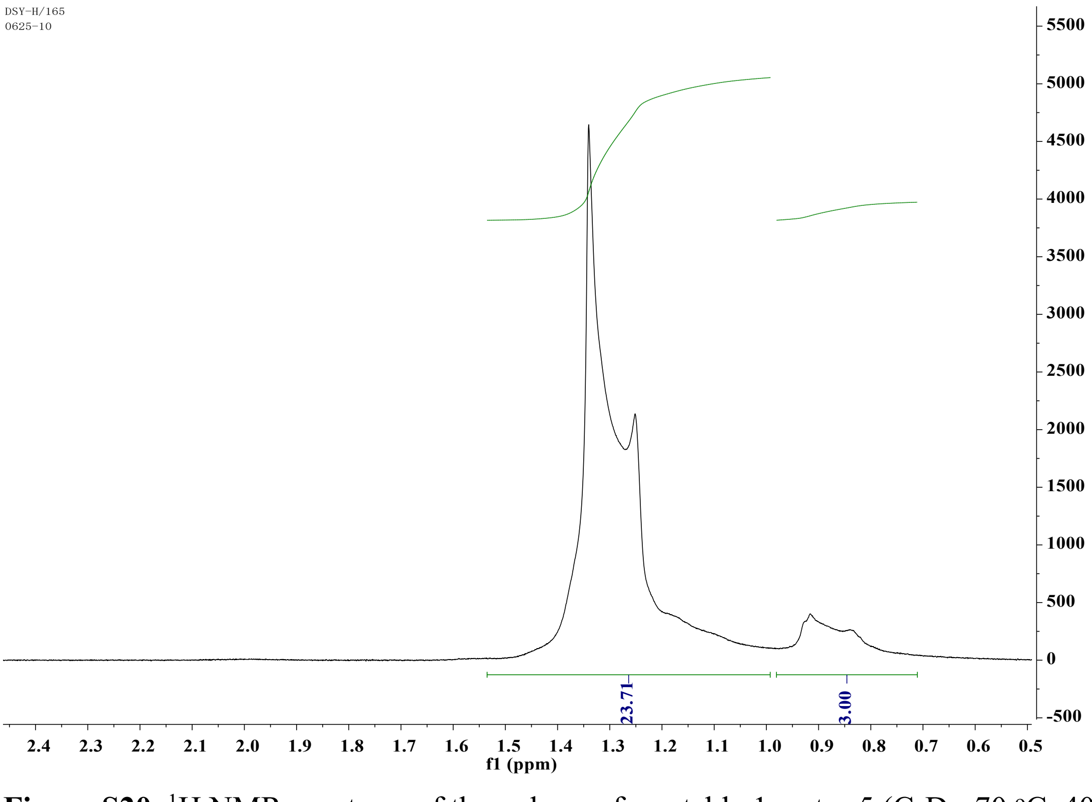


Figure S20. ^{1}H NMR spectrum of the polymer from table 1, entry 5 (C_6D_6, 70 ^{o}C, 400 MHz).

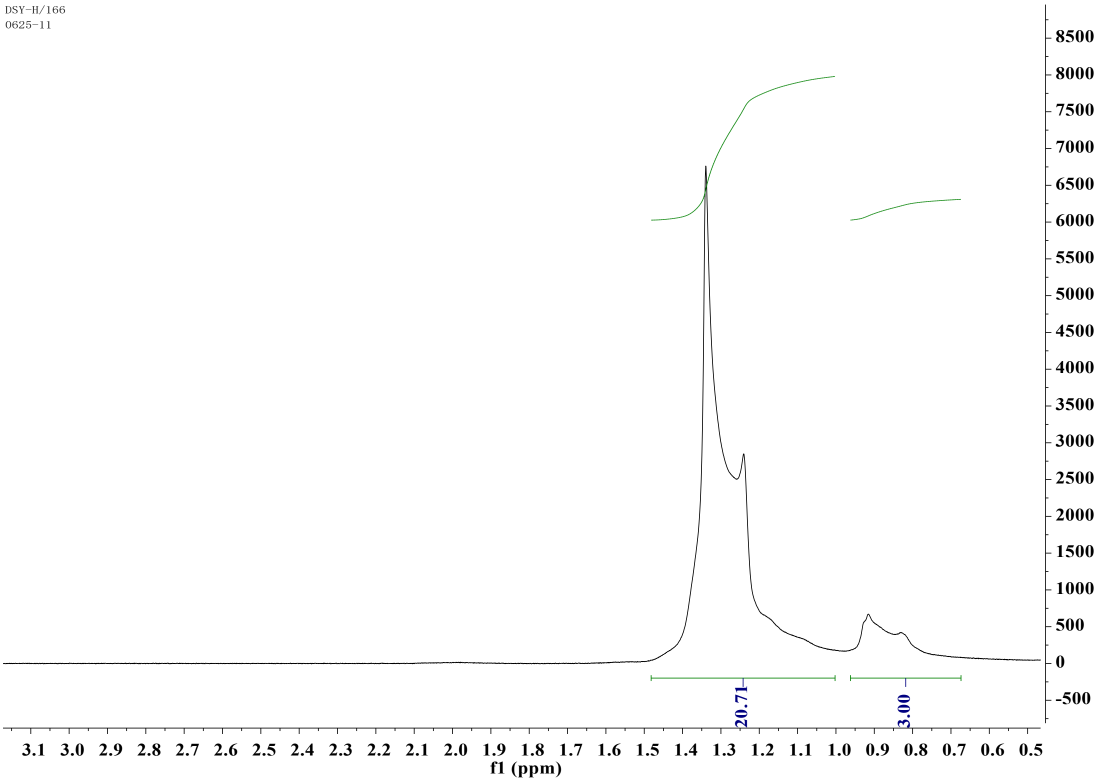


Figure S21. ^{1}H NMR spectrum of the polymer from table 1, entry 6 (C_6D_6, 70 °C, 400 MHz).

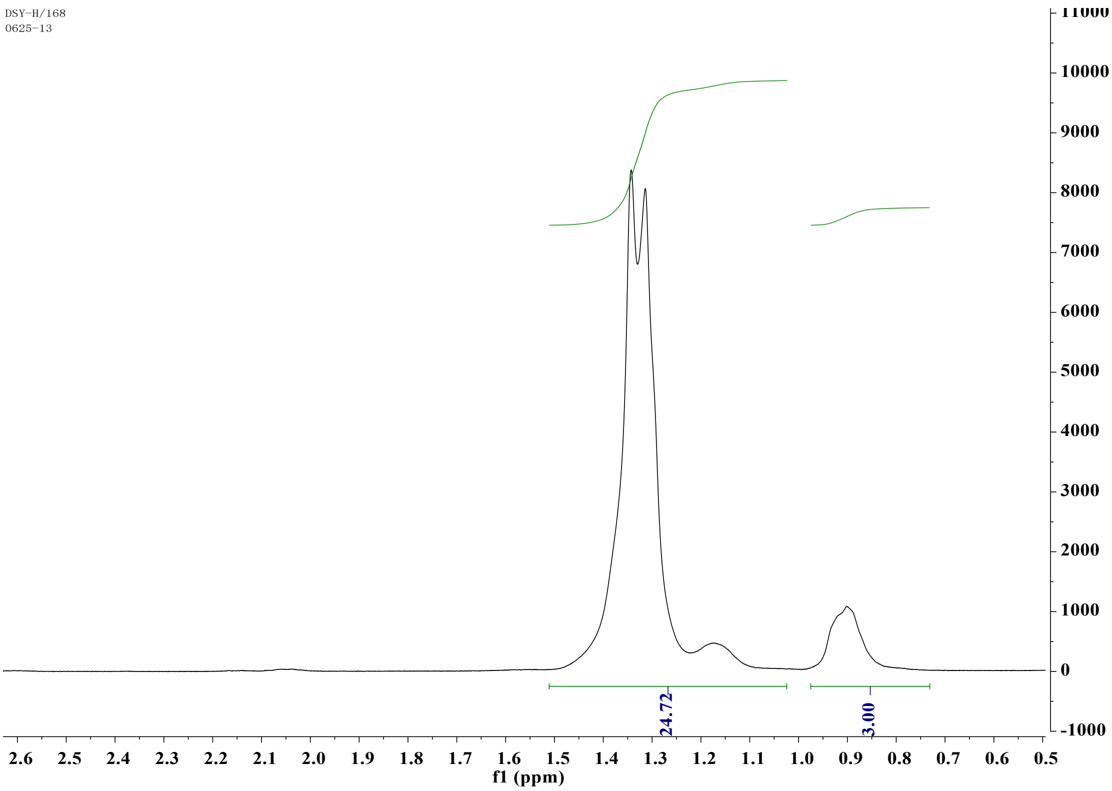


Figure S22. ^{1}H NMR spectrum of the polymer from table 1, entry 8 (C_6D_6, 70 °C, 400 MHz).

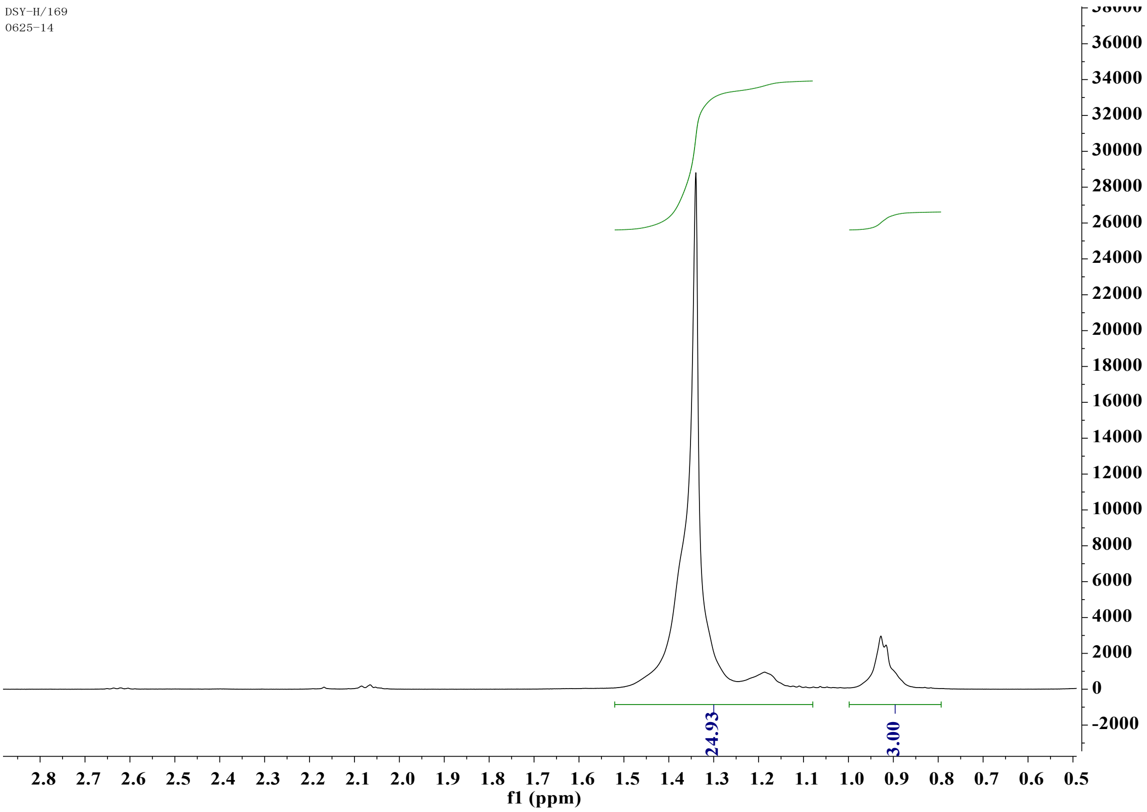


Figure S23. [1]H NMR spectrum of the polymer from table 1, entry 9 (C_6D_6, 70 ^{o}C, 400 MHz).

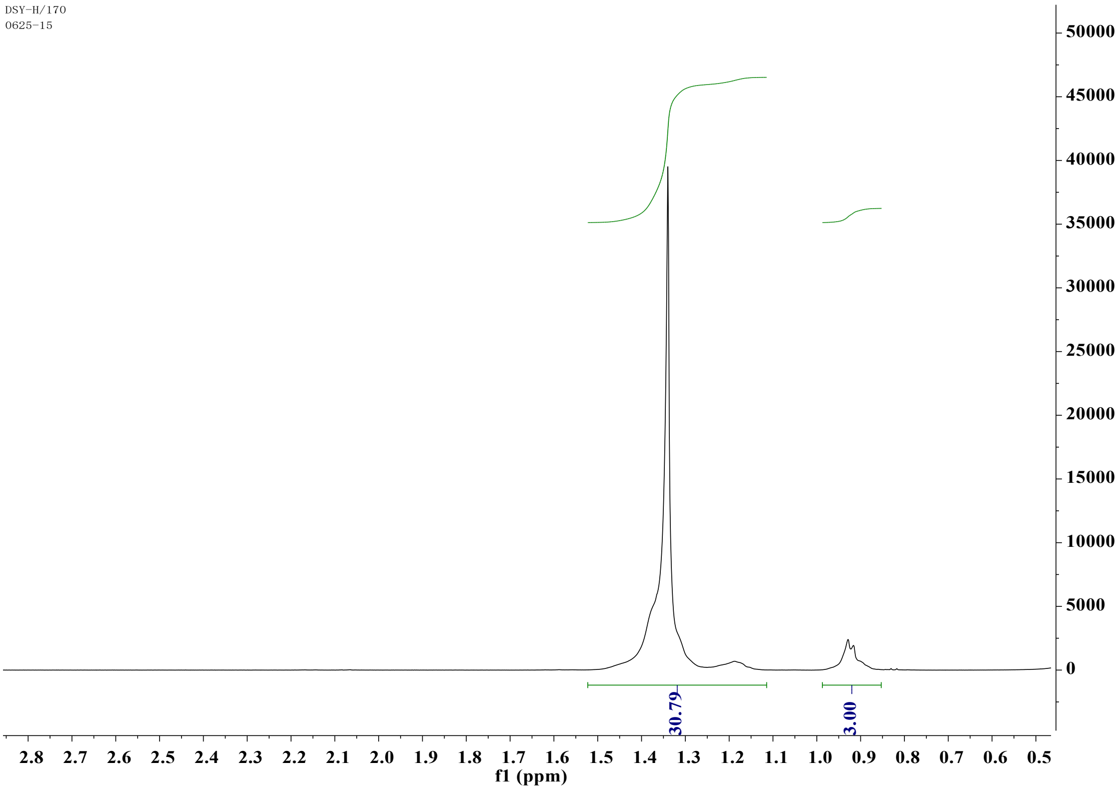


Figure S24. [1]H NMR spectrum of the polymer from table 1, entry 10 (C_6D_6, 70 ^{o}C, 400 MHz).

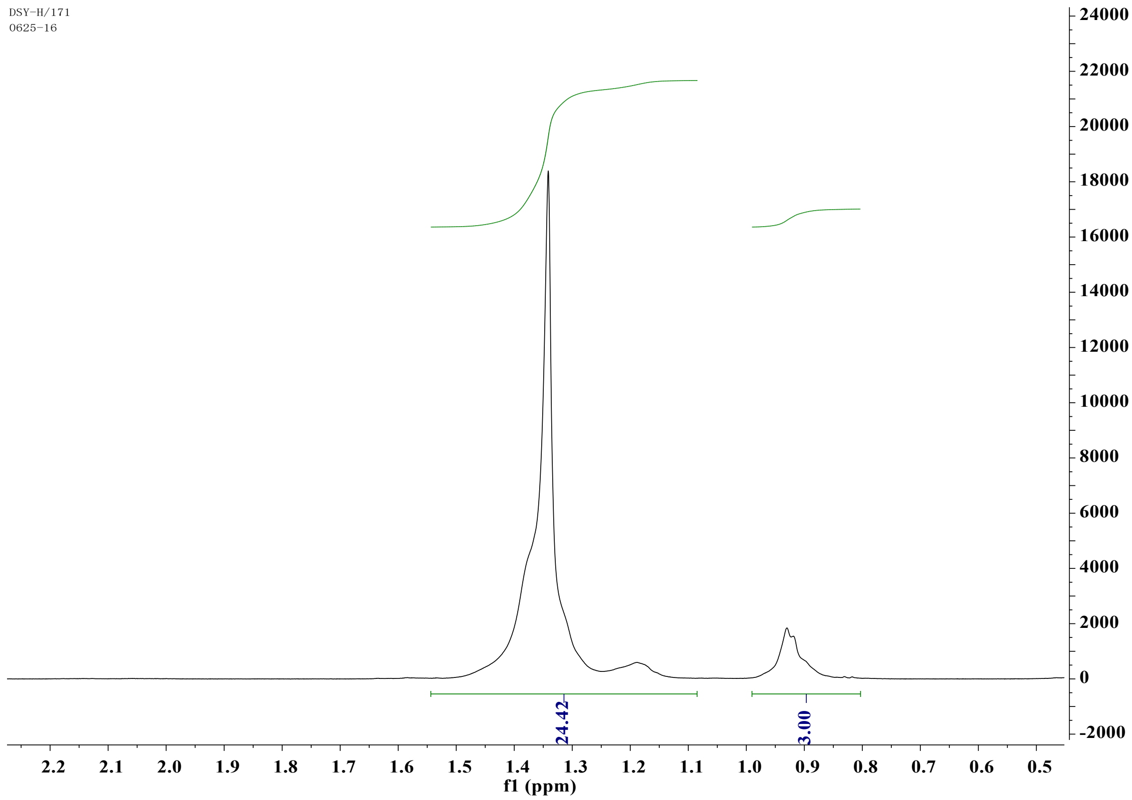


Figure S25. ^{1}H NMR spectrum of the polymer from table 1, entry 11 (C_6D_6, 70 ^{o}C, 400 MHz).

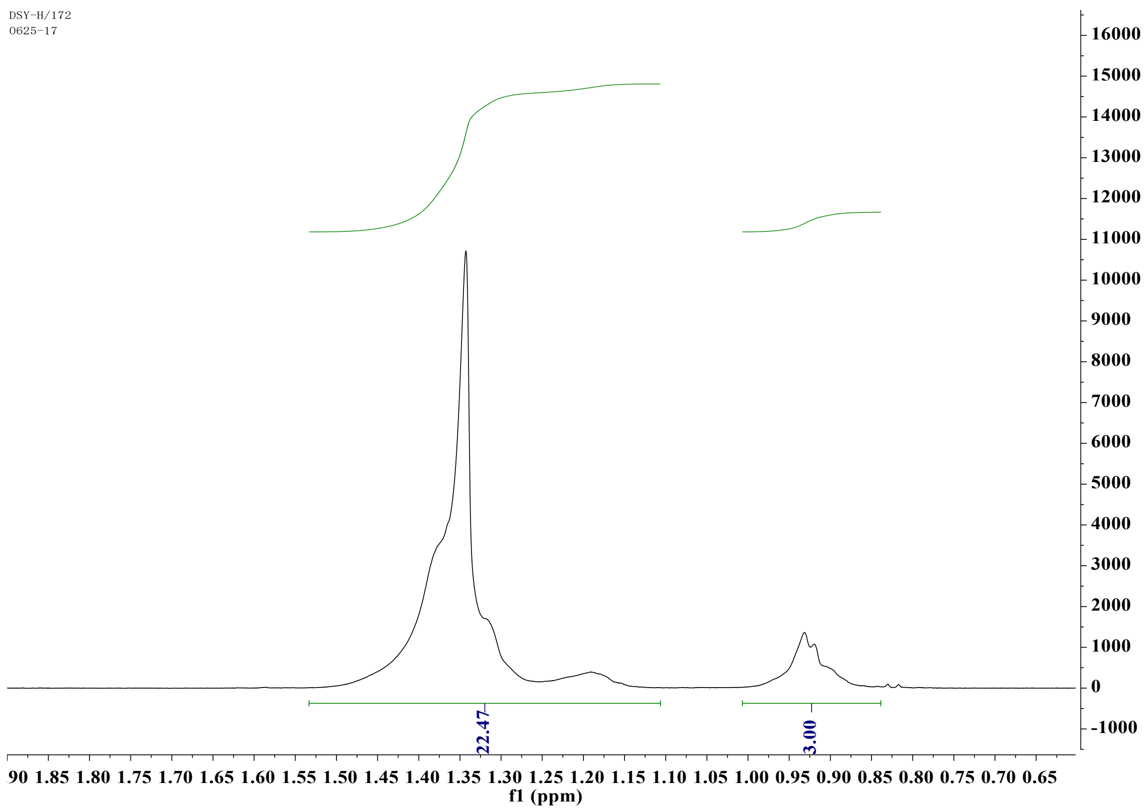


Figure S26. ^{1}H NMR spectrum of the polymer from table 1, entry 12 (C_6D_6, 70 ^{o}C, 400 MHz).

2.5 DSC and GPC of Representative Polymers.

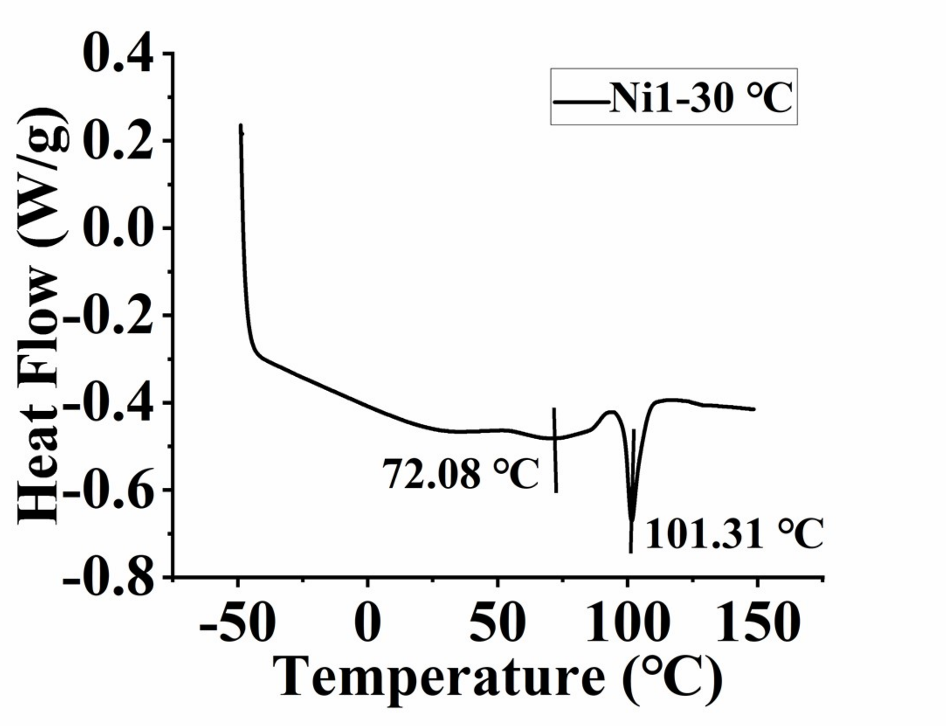


Figure S27. DSC of the polymer from table 1, entry 1.

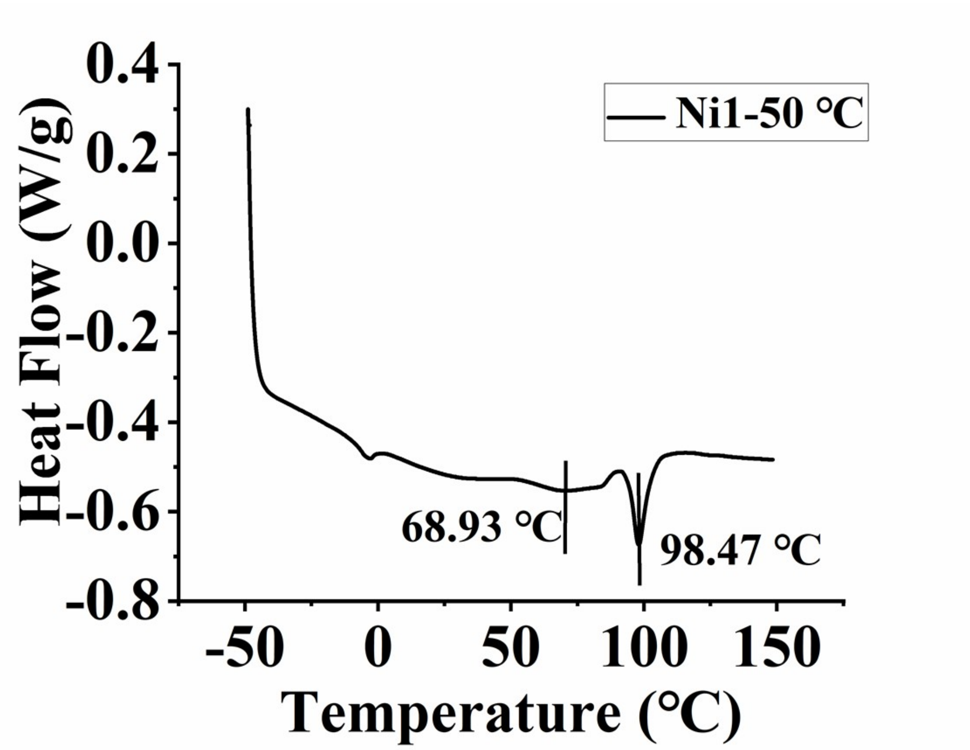


Figure S28. DSC of the polymer from table 1, entry 2.

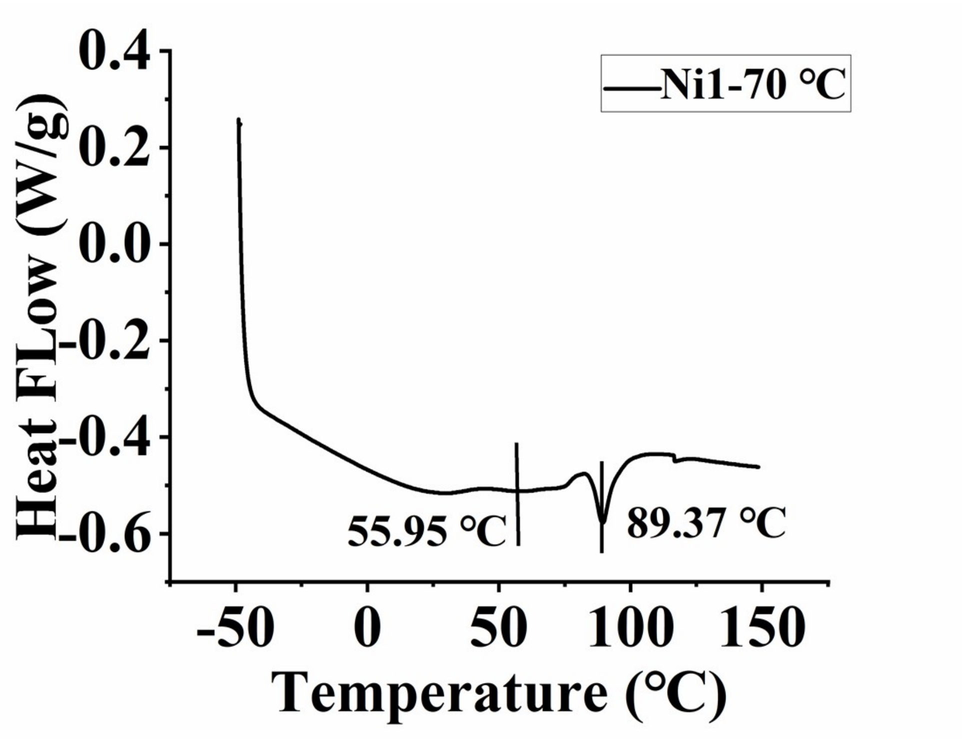


Figure S29. DSC of the polymer from table 1, entry 3.

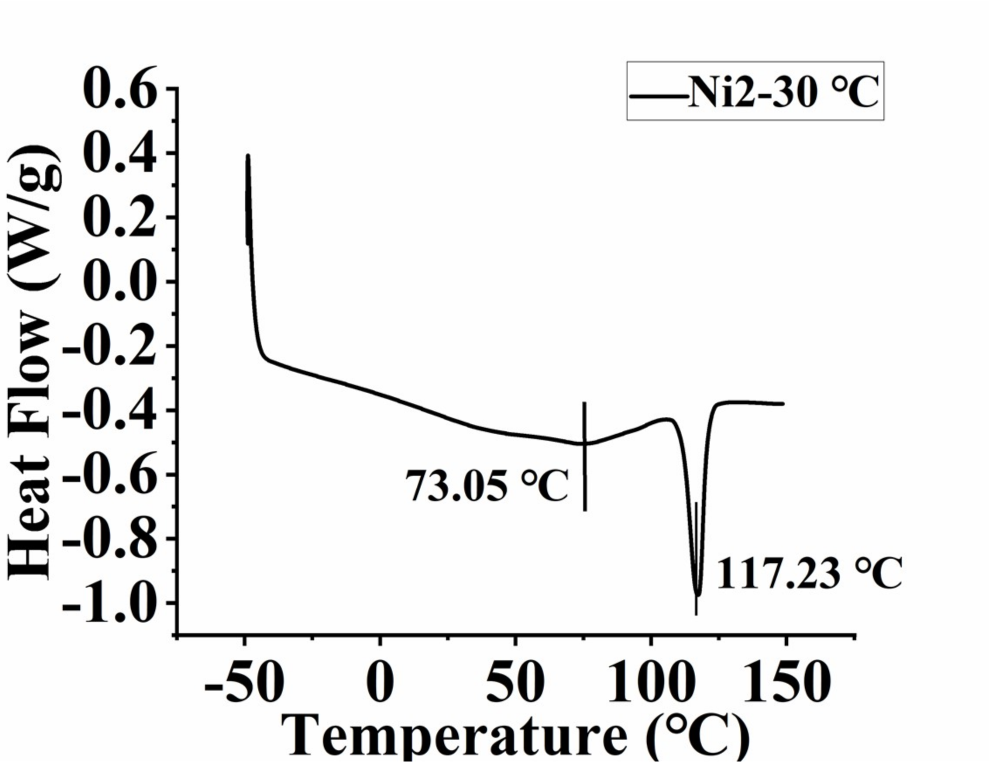


Figure S30. DSC of the polymer from table 1, entry 4.

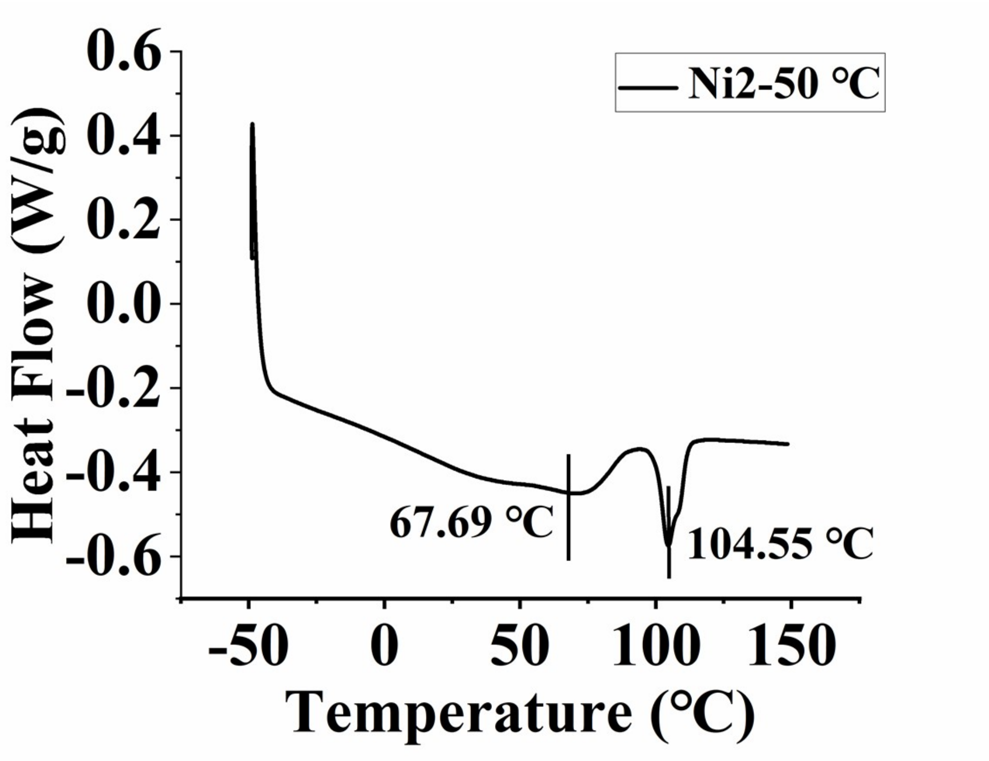


Figure S31. DSC of the polymer from table 1, entry 5.

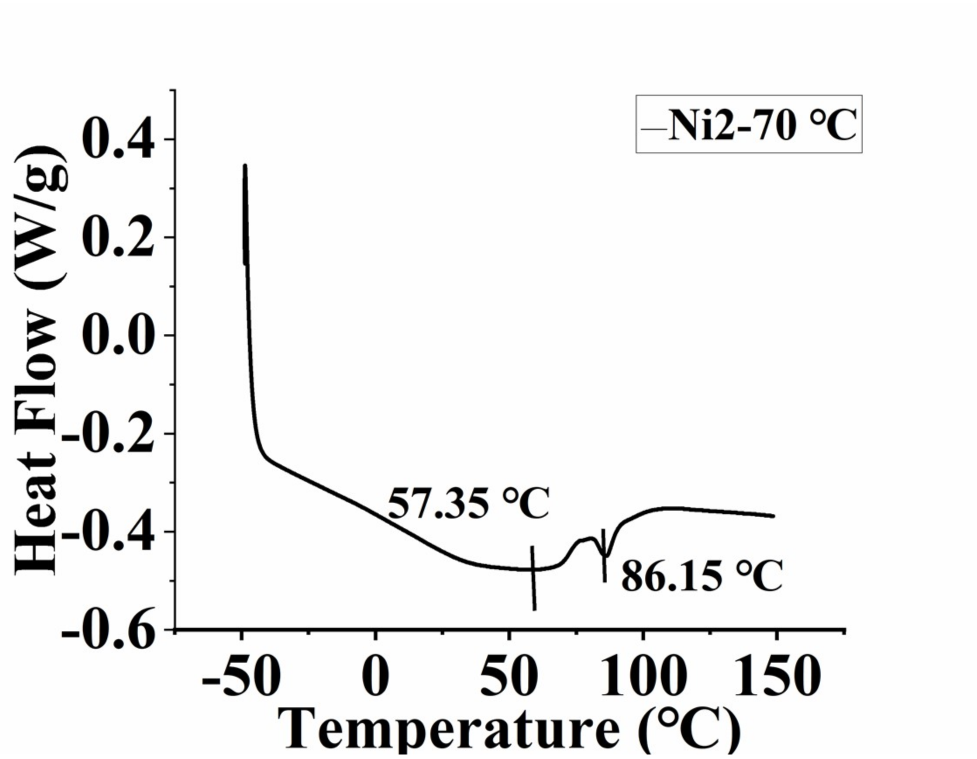


Figure S32. DSC of the polymer from table 1, entry 6.

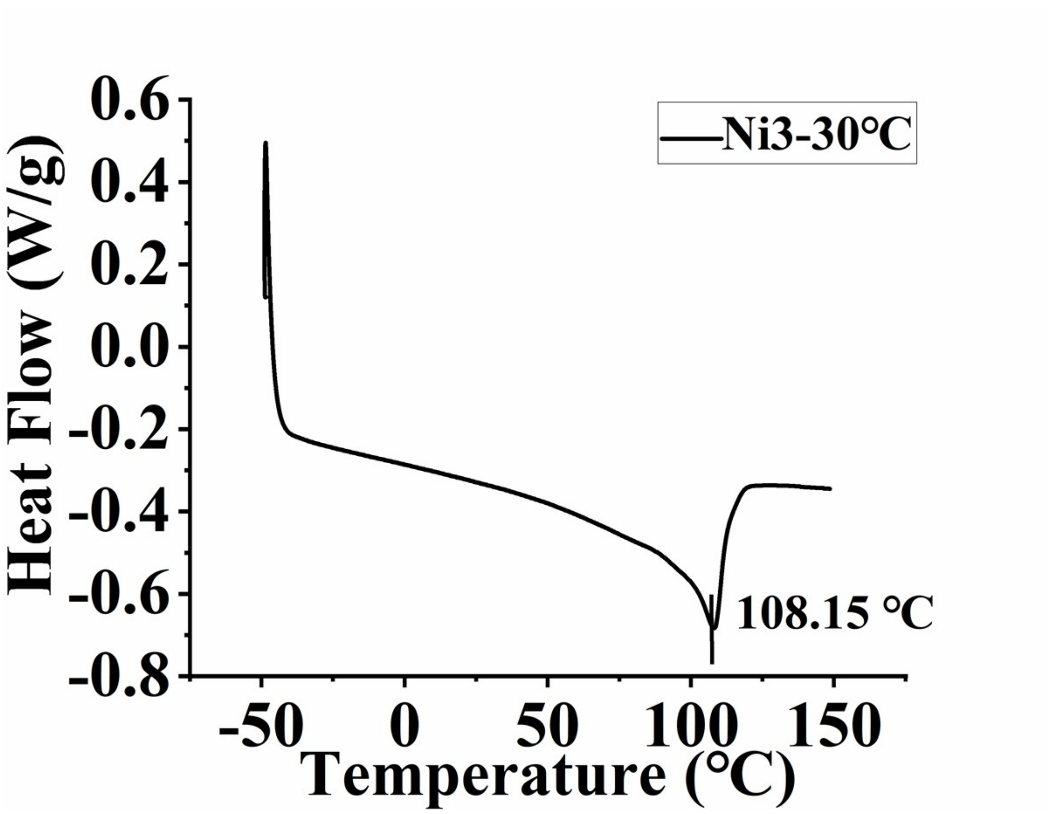


Figure S33. DSC of the polymer from table 1, entry 7.

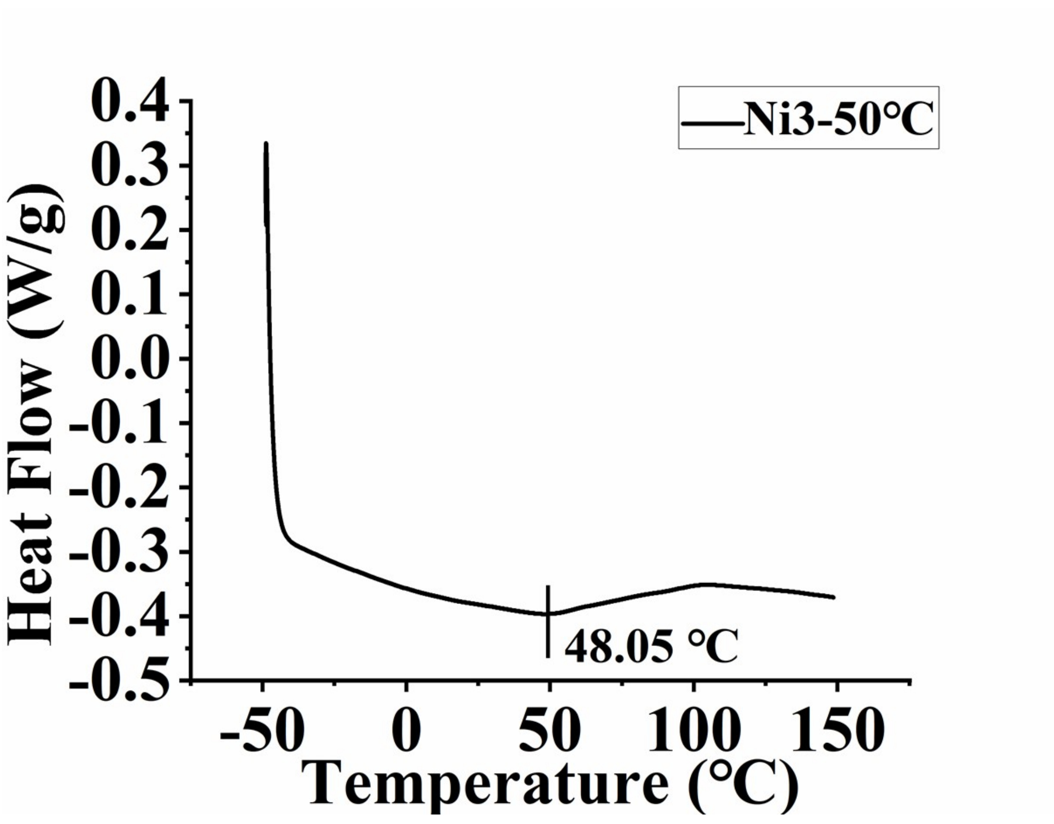


Figure S34. DSC of the polymer from table 1, entry 8.

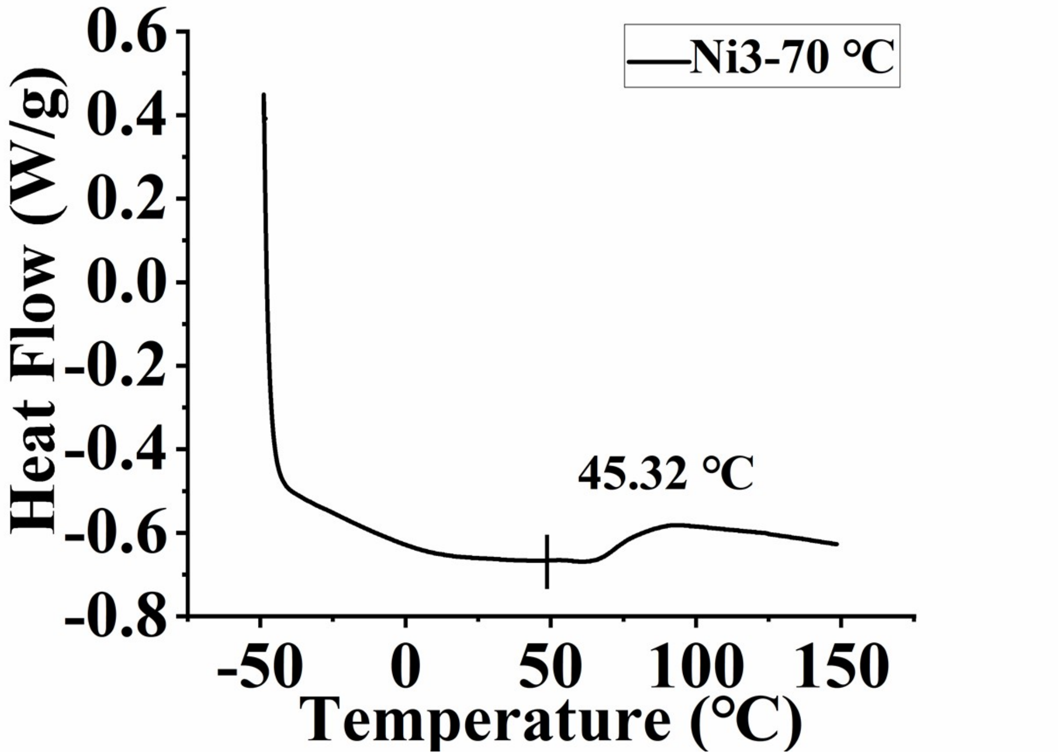


Figure S35. DSC of the polymer from table 1, entry 9.

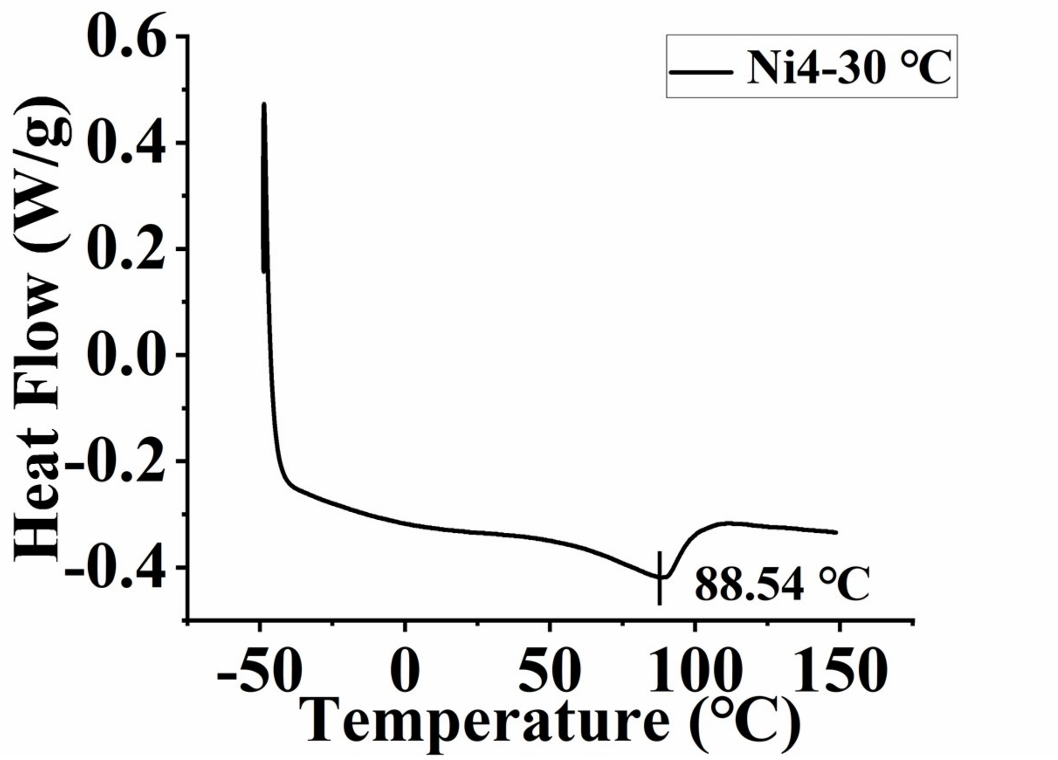


Figure S36. DSC of the polymer from table 1, entry 10.

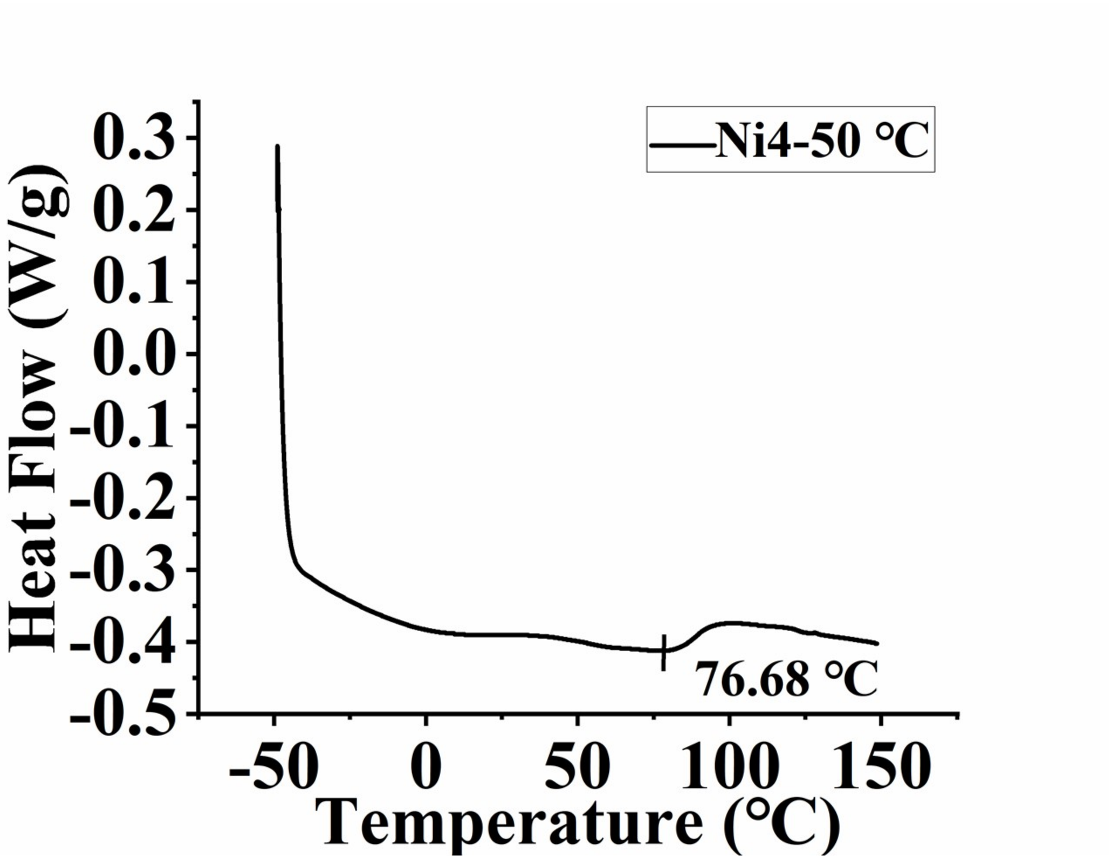


Figure S37. DSC of the polymer from table 1, entry 11.

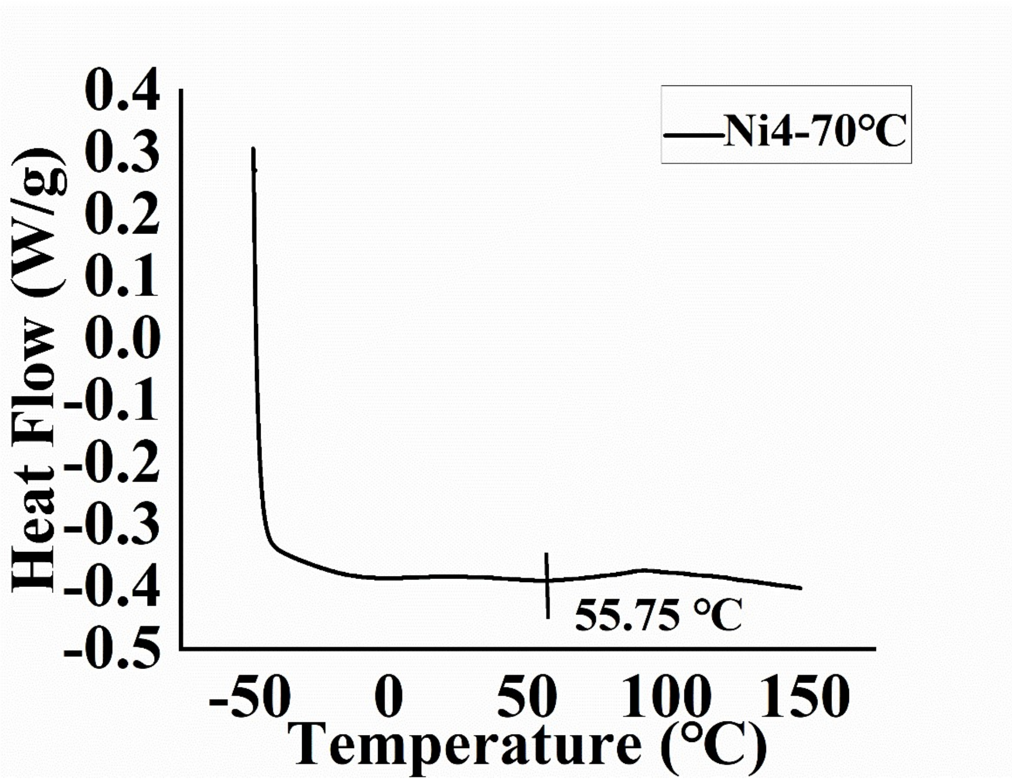
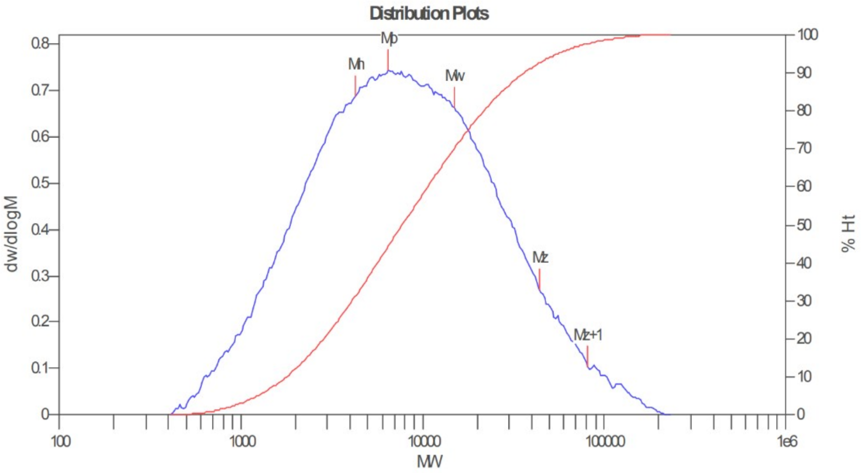


Figure S38. DSC of the polymer from table 1, entry 12.



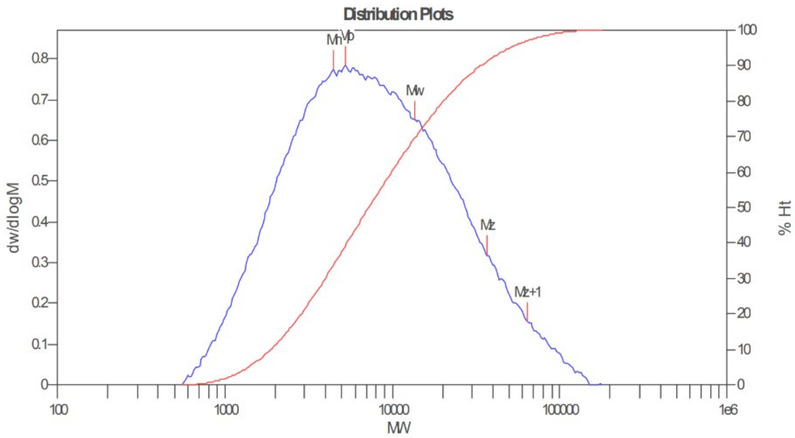
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6495	4289	15004	43821	81396	12430	3.49825

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.90	15.40	17.33	1.84216	0	239.225	100

Figure S39. GPC of the polymer from table 1, entry 1.



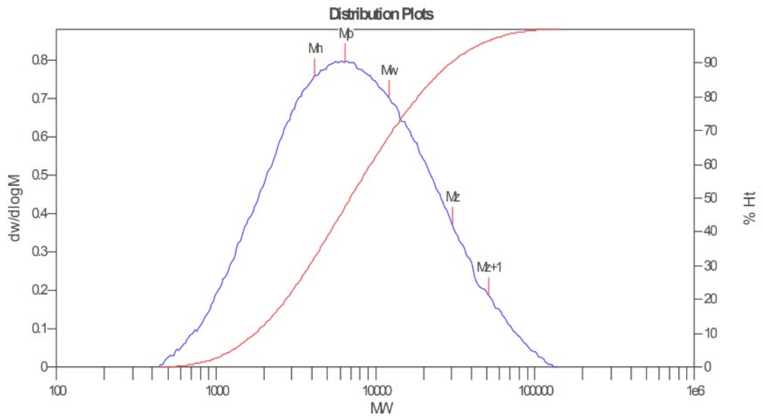
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	5240	4451	13727	36796	63816	11528	3.08403

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.08	15.55	17.12	1.80667	0	222.14	100

Figure S40. GPC of the polymer from table 1, entry 2.



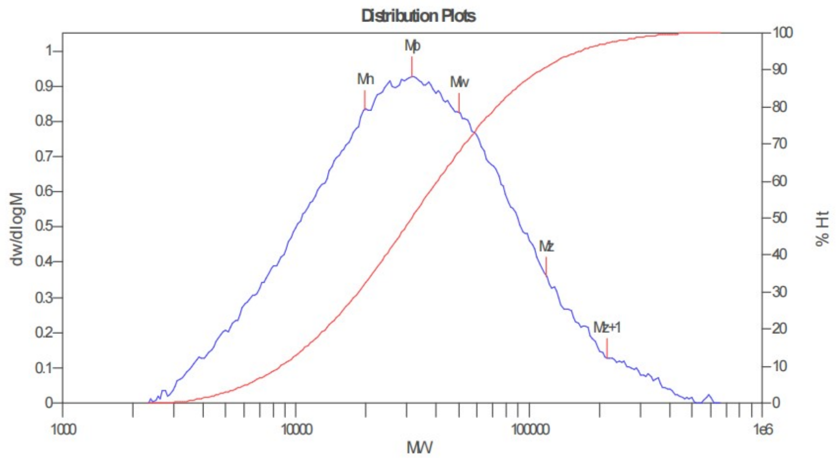
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6495	4139	12248	30269	51271	10437	2.95917

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.25	15.50	17.28	3.30091	0	400.308	100

Figure S41. GPC of the polymer from table 1, entry 3.



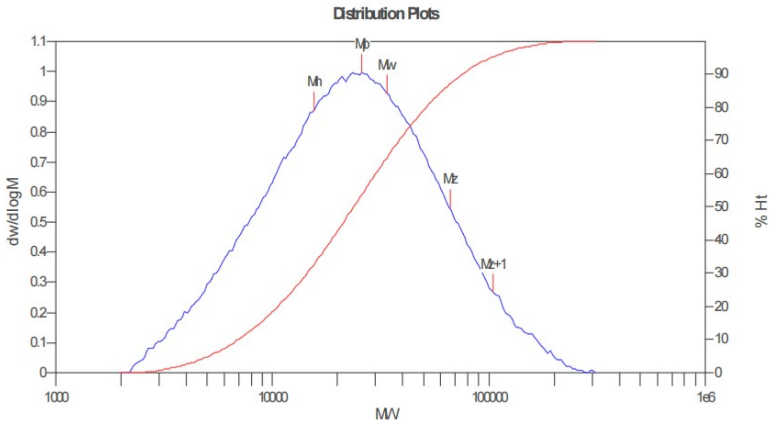
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	31348	19644	50076	118727	216909	43475	2.54918

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	14.30	16.12	1.64372	0	171.05	100

Figure S42. GPC of the polymer from table 1, entry 4.



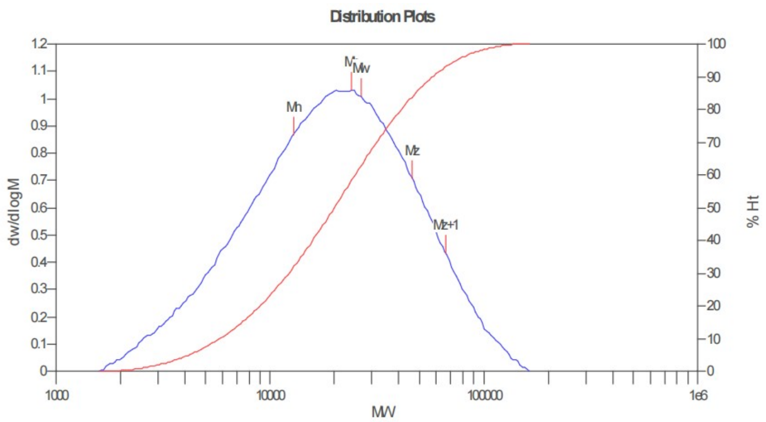
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	25903	15485	33975	66098	104732	30369	2.19406

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.70	14.50	16.23	1.99231	0	193.376	100

Figure S43. GPC of the polymer from table 1, entry 5.



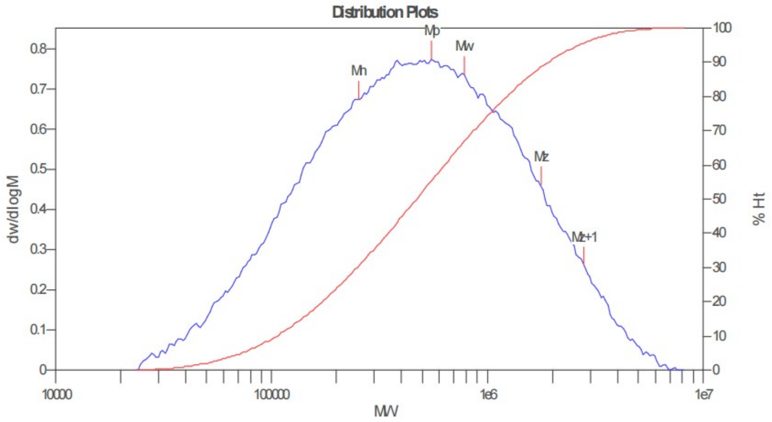
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	24114	12878	26630	46145	66282	24188	2.06787

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.15	14.60	16.38	3.13681	0	294.397	100

Figure S44. GPC of the polymer from table 1, entry 6.



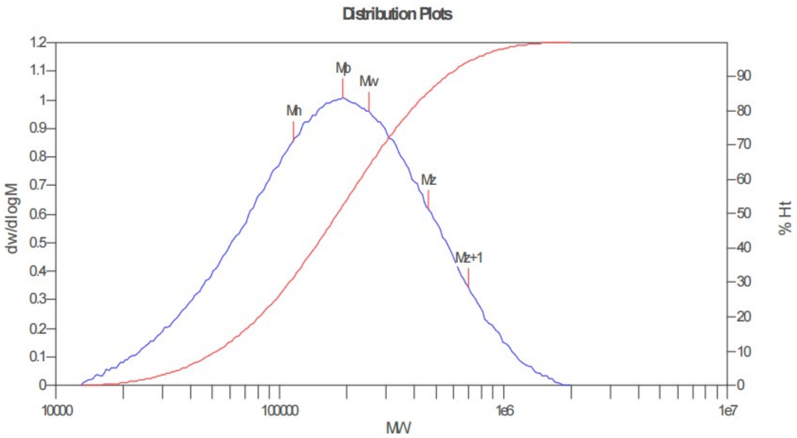
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	548394	252157	779869	1766560	2800125	670615	3.09279

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.42	12.55	14.50	1.36981	0	171.619	100

Figure S45. GPC of the polymer from table 1, entry 7.



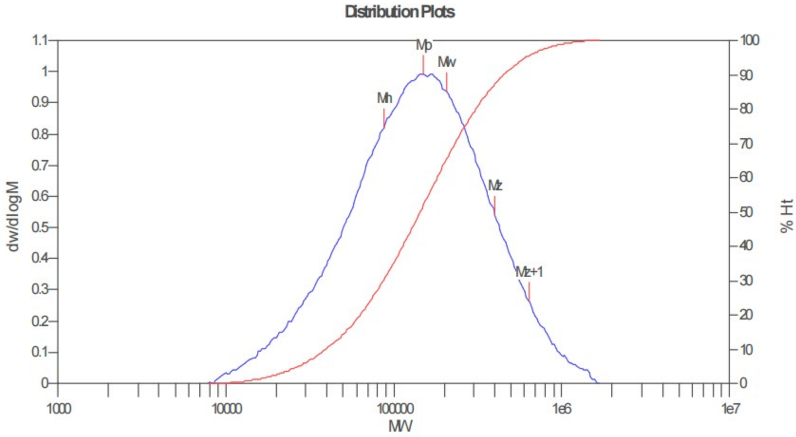
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	192030	114979	250820	461706	697499	225774	2.18144

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.40	13.03	14.92	2.83165	0	271.746	100

Figure S46. GPC of the polymer from table 1, entry 8.



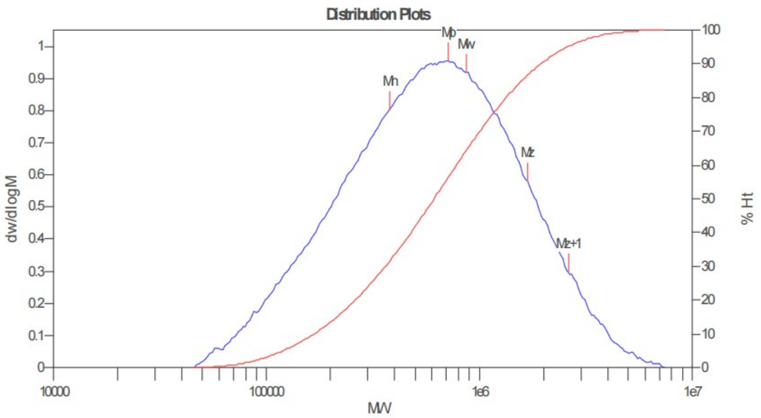
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	151285	87358	205121	402671	641971	182885	2.34805

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.52	13.22	15.27	3.24867	0	315.658	100

Figure S47. GPC of the polymer from table 1, entry 9.



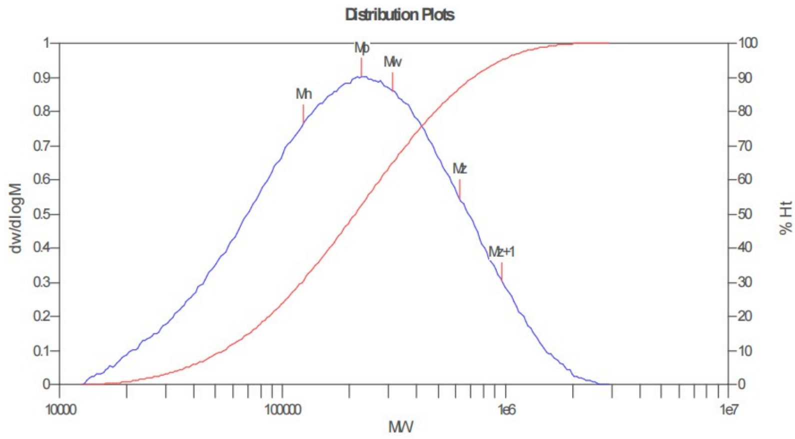
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	712892	380400	871681	1680043	2618644	778246	2.29149

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.48	12.12	14.03	2.35644	0	238.418	100

Figure S48. GPC of the polymer from table 1, entry 10.



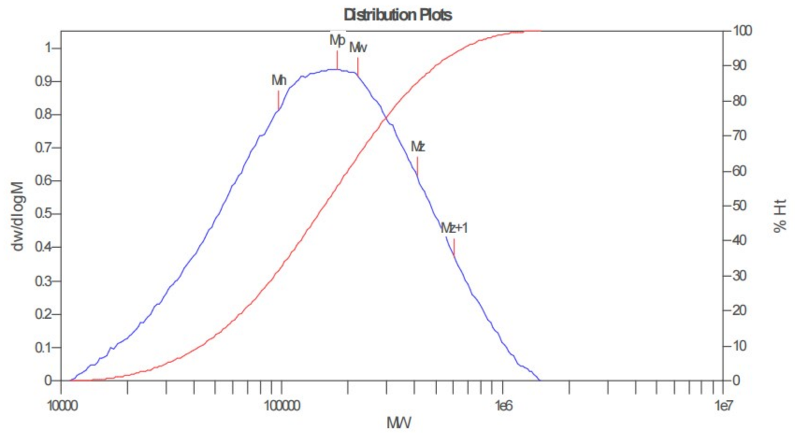
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	226919	123994	312260	622529	961821	276266	2.51835

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.13	12.92	14.93	3.18354	0	340.7	100

Figure S49. GPC of the polymer from table 1, entry 11.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	178771	96376	220382	410787	607034	197356	2.28669

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.60	13.10	15.03	3.45794	0	356.581	100

Figure S50. GPC of the polymer from table 1, entry 12.

3. Reference

[1] S.-S. Meng, X. Tang, X. Luo, R. Wu, J.-L. Zhao and A. S. Chan, *ACS Catal.*, 2019, **9**, 8397–8403.

[2] F. Kamal, S. Colombel-Rouen, A. Dumas, J.-P. Guégan, T. Roisnel, V. Dorcet, O. Baslé, M. Rouen and M. Mauduit, *Chem. Commun.*, 2019, **55**, 11583–11586.

[3] J. Xia, S. Kou, H. Mu and Z. Jian, *Eur. Polym. J.*, 2022, **166**, 111022.