Synthesis of High MFI Polyolefin Elastomers Using Dibenzosuberyl Iminopyridyl Ni(II) Catalysts

Jun Gan[a,b], Shengyu Dai[a]*

[a]*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.*
[b]*School of Chemical and Environmental Engineering, Anhui Polytechnic University, Wuhu, Anhui 241000, China.*

*To whom correspondence should be addressed. daiyu@ustc.edu.cn (Shengyu Dai).

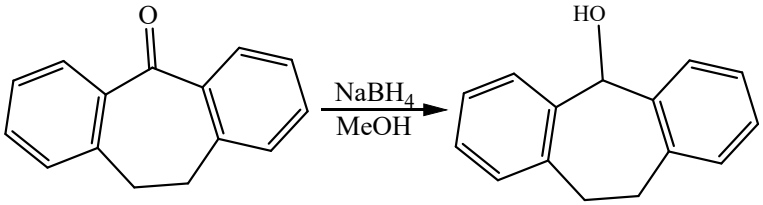
1. Experimental Sections

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 Bruker AV 400 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. 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 ℃ using trichlorobenzene as a solvent and calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was performed by a DSC Q25 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). Stress/strain experiments were performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature. Polymers were melt-pressed at 50 °C above their melting point to obtain the test specimens. The test specimens have 14-mm gauge length, 2-mm width, and thickness of 0.5 mm. The melt flow rate test was performed on the KY-RR fully automatic melt index analyzer. In the test, when

the melt outflow of the specimen is stable, the middle 10 sample sections are selected for weighing, and finally, the average value is taken. The transmittance test was performed on the Linshang LS183 108H 163 optical transmittance measuring instrument. The test mode was T% and the test wavelength was 380-760 nm. The volume resistivity test was performed on the Xinyang CXT5013/5015 volume resistivity tester.

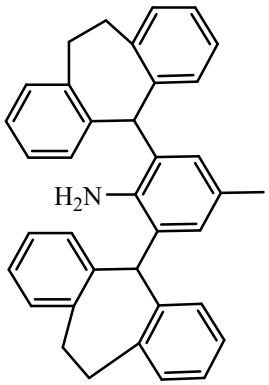
1.2 Procedure for the Synthesis of Dibenzosuberol.



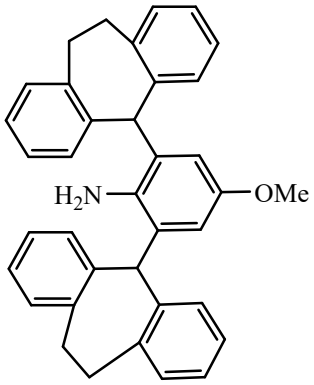
Dibenzosuberone (20 mmol, 1.0 equiv.) was dissolved in a mixture of MeOH and NaOH (5 wt%, aq.) (V:V = 250 mL:50 mL). Subsequently, $NaBH_4$ (0.76 g, 20 mmol, 1.0 equiv.) was carefully added in three portions, and the resulting mixture was stirred at room temperature overnight. The reaction was then quenched with 25 mL saturated aqueous NH_4Cl (10 wt%, aq.), followed by concentration in vacuo. The residue was dissolved in DCM (200 mL) and washed with water (50 mL × 3). The organic layers were dried over anhydrous $MgSO_4$ and concentrated to afford dibenzosuberol (3.82 g, 91% yield) as a white solid.

1.3 Procedure for the Synthesis of Anilines.

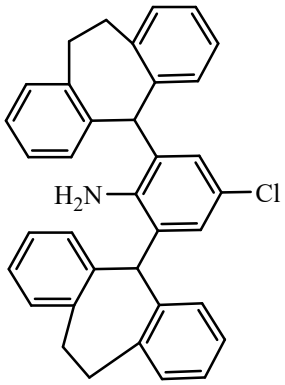
A mixture of dibenzosuberol (20.0 mmol, 2.0 equiv.) and the corresponding anilines (10 mmol, 1.0 equiv.) was heated to 120 °C. A solution of anhydrous zinc chloride (0.38 g, 2 mmol, 0.2 equiv.) in concentrated hydrochloric acid (0.6 mL, 37% in H_2O, 1.0 equiv.) was added to the mixture (exothermic + intense bubbling), and the temperature was raised to 160 °C. After 40 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 and then 100 mL of ethanol were added to precipitate and filter. The product was washed with EtOH (3 × 20 mL).



A1 was synthesized according to our previous work.[1]

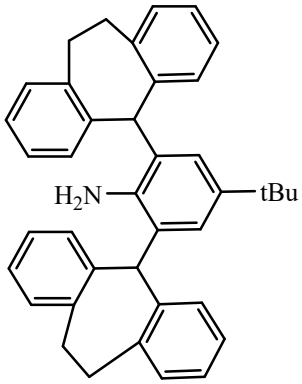


A2 (4.60 g, 90%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (d, *J* = 7.2 Hz, 4H, aryl-*H*), 7.18-7.08 (m, 12H, aryl-*H*), 6.36 (s, 2H, aryl-*H*), 5.08 (s, 2H, C*H*), 3.44 (s, 3H, OCH_3), 3.41-3.31 (m, 4H, CH_2), 2.76-2.67 (m, 4H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.88, 140.10, 139.91, 136.37, 130.92, 130.35, 127.44, 126.54, 115.15, 56.49 (O*C*H$_3$), 55.27 (*C*H), 31.62 (*C*H$_2$). APCI-MS (m/z): calcd for $C_{37}H_{34}ON^{+}$: 508.2635, Found, 508.2638, $[M+H]^{+}$.



A3 (4.45 g, 87%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.0 Hz, 2H, aryl-*H*), 7.23 – 7.06 (m, 14H, aryl-*H*), 6.64 (s, 2H, aryl-*H*), 5.02 (s, 2H, C*H*), 3.42 – 3.31 (m, 4H, CH_2), 2.80 – 2.67 (m, 4H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.82, 139.86, 139.48, 131.11, 130.49, 130.22,

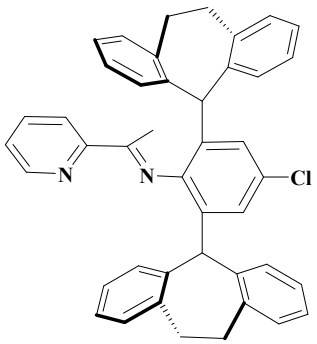
128.74, 127.68, 126.68, 122.21, 56.21 (*C*H), 31.50 (*C*H_2). APCI-MS (m/z): calcd for $C_{36}H_{30}ClN^+$: 512.2140, Found, 512.2144, $[M+H]^+$.



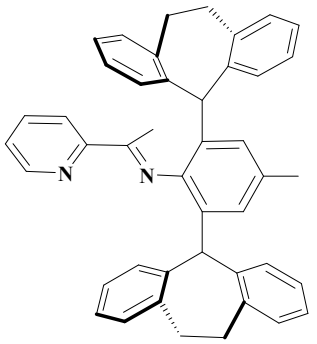
A4 (5.74 g, 90%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 4H, aryl-*H*), 7.19 – 7.09 (m, 12H, aryl-*H*), 6.73 (s, 2H, aryl-*H*), 5.11 (s, 2H, C*H*), 3.39 – 3.29 (m, 4H, CH_2), 2.77 – 2.68 (m, 4H, CH_2), 0.97 (s, 9H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.35, 139.89, 130.83, 130.28, 128.65, 127.33, 126.49, 126.15, 56.46 (*C*H), 33.68 (*C*$(CH_3)_3$), 31.59 (*C*H_2), 31.21 (C(*C*$H_3)_3$). APCI-MS (m/z): calcd for $C_{40}H_{40}N^+$: 534.3155, Found, 534.3161, $[M+H]^+$.

1.4 Procedure for the Synthesis of Ligands L1-L7.

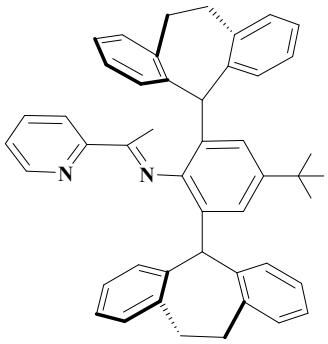
A round-bottom flask was charged with $ZnCl_2$ (0.16 g, 1.2 mmol), 2-acetylpyridine (3 mmol), and CH_3COOH (20 mL). Arylamines (1 mmol) was added, and the solution was heated to reflux for 5 h. The solid was separated by filtration and washed with diethyl ether (3 × 5 mL), to remove remaining acetic acid. Drying under vacuum gave yellow, poorly soluble solid. Then the zinc dichloride was removed from the zinc diimine complex. The product of the previous step was suspended in methylene chloride (15 mL), and a solution of potassium oxalate (0.22 g, 1.2 mmol) in water (20 mL) was added. The reaction mixture was stirred vigorously for 60 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 a pale yellow and dried under high vacuum. (For **L1-L4**)



L1 (0.18 g, 30%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.63 (d, *J* = 4.6Hz, 1H, Py-*H*), 8.15 (d, *J* = 8.0 Hz, 1H, Py-*H*), 7.85 (td, *J* = 7.7, 1.8 Hz, 1H, Py-*H*), 7.44 (m, 1H, Py-*H*), 7.14 – 6.75 (m, 16H, aryl-*H*), 6.62 – 6.55 (m, 2H, aryl-*H*), 4.89 (s, 2H, C*H*), 3.58 – 3.32 (m, 4H, CH_2), 2.86 – 2.61 (m, 4H, CH_2), 1.10 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.19 (N=*C*), 148.32, 146.44, 140.12, 139.82, 139.34, 138.63, 136.12, 132.99, 131.76, 131.62, 130.88, 130.01, 128.96, 127.09, 126.89, 125.93, 124.98, 122.23, 56.11 (*C*H), 32.20 (*C*H_2), 31.28 (*C*H_2), 16.49 (*C*H_3). APCI-MS (m/z): calcd for $C_{43}H_{36}ClN_2^+$: 615.2562, Found, 615.2563, $[M+H]^+$.

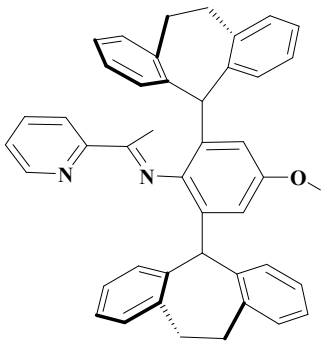


L2 was synthesized according to our previous work.[1]



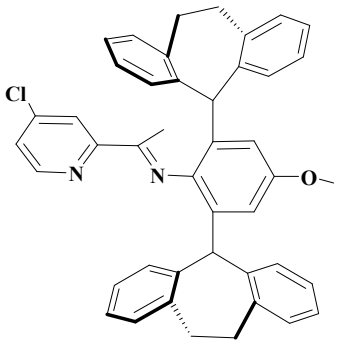
L3 (0.48 g, 76%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.65 (d, *J* = 4.4Hz, 1H, Py-*H*), 8.27 (d, *J* = 8.0 Hz, 1H, Py-*H*), 7.85 (td, *J* = 7.7, 1.8 Hz, 1H, Py-*H*), 7.52 – 7.37 (m, 1H, Py-*H*), 7.18 – 6.82 (m, 16H, aryl-*H*), 6.60 (m, 2H, aryl-*H*), 4.94 (s, 2H, C*H*), 3.57 – 3.32 (m, 4H, CH_2),

2.86 – 2.63 (m, 4H, CH_2), 1.12 (s, 3H, CH_3), 1.05 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.27 (N=*C*), 141.03, 139.83, 139.56, 139.44, 135.99, 131.66, 130.52, 129.85, 126.75, 126.73, 126.20, 125.82, 125.73, 124.73, 122.07, 56.39 (*C*H), 33.96 (*C*(CH$_3$)$_3$), 32.23 (*C*H$_2$), 31.32 (*C*H$_2$), 31.18 (C(*C*H$_3$)$_3$), 16.35 (*C*H$_3$-C=N). APCI-MS (m/z): calcd for $C_{47}H_{45}N_2^+$: 637.3577, Found, 637.3580, $[M+H]^+$.

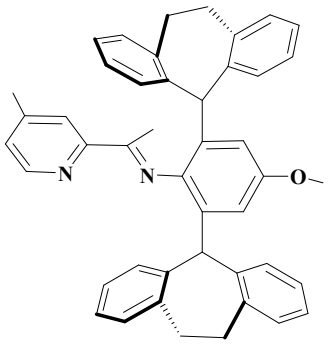


L4 (0.34 g, 56%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.65 (d, *J* = 4.3Hz, 1H, Py-*H*), 8.18 (d, *J* = 8.1 Hz, 1H, Py-*H*), 7.83 (t, *J* = 7.7 Hz, 1H, Py-*H*), 7.42 (m, 1H, Py-*H*), 7.09 – 6.80 (m, 16H, aryl-*H*), 6.54 (s, 2H, aryl-*H*), 4.92 (s, 2H, C*H*), 3.61-3.51 (m, 2H, CH_2), 3.51 (s, 3H, OCH_3), 3.43-3.32 (m, 2H, CH_2), 2.86-2.76 (m, 2H, CH_2), 2.71-2.60 (m, 2H, CH_2), 1.12 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.94 (N=*C*), 156.60, 153.61, 148.31, 140.65, 139.85, 139.38, 139.28, 135.88, 132.19, 131.83, 131.67, 130.70, 129.86, 126.86, 125.84, 125.82, 124.69, 122.05, 115.06, 56.32 (O*C*H$_3$), 55.11 (*C*H), 32.29 (*C*H$_2$), 31.37 (*C*H$_2$), 16.26 (*C*H$_3$). APCI-MS (m/z): calcd for $C_{44}H_{39}ON_2^+$: 611.3057, Found, 611.3063, $[M+H]^+$.

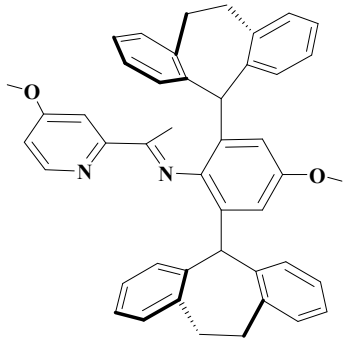
A mixture of **A2** (1 mmol), 4-substituted 2-acetylpyridines (1.1 mmol), and a catalytic amount of *p*-toluenesulfonic acid in 20 mL toluene was refluxed for 24 h. The solution was evaporated at reduced pressure, and the remaining solution was diluted in ethanol (20 mL). The pale yellow solid was isolated by filtration, and column chromatography separation. (For **L5-L7**)



L5 (0.13 g, 20%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.3 Hz, 1H, Py-*H*), 8.11 (s, 1H, Py-*H*), 7.42 (dd, *J* = 5.3, 2.1 Hz, 1H, Py-*H*), 7.25 – 6.79 (m, 16H, aryl-*H*), 6.66 – 6.59 (m, 2H, aryl-*H*), 4.88 (s, 2H, C*H*), 3.56-3.54 (m, 2H, CH_2), 3.50 (s, 3H, OCH_3), 3.41-3.30 (m, 2H, CH_2), 2.85-2.75 (m, 2H, CH_2), 2.70-2.66 (m, 2H, CH_2), 1.15 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.40 (N=*C*), 149.11, 144.26, 140.59, 139.79, 139.28, 131.65, 131.50, 130.68, 130.04, 129.06, 128.25, 126.92, 126.91, 125.85, 125.83, 115.02, 56.35 (O*C*H_3), 55.08 (*C*H), 32.15 (*C*H_2), 31.40 (*C*H_2), 16.30 (*C*H_3). APCI-MS (m/z): calcd for $C_{44}H_{38}OClN_2^+$: 645.2667, Found, 645.2672, $[M+H]^+$.



L6 (0.20 g, 32%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.0 Hz, 1H, Py-*H*), 7.96 (s, 1H, Py-*H*), 7.14 – 6.78 (m, 16H, aryl-*H*), 6.62 (dq, *J* = 8.2, 4.1 Hz, 2H, aryl-*H*), 6.53 (s, 1H, Py-*H*), 4.92 (s, 2H, C*H*), 3.61 – 3.53 (m, 2H, CH_2), 3.51 (s, 3H, OCH_3), 3.41 (m, 2H, CH_2), 2.80 (m, 2H, CH_2), 2.67 (m, 2H, CH_2), 2.50 (s, 3H, Py-CH_3), 1.16 (s, 3H, N=CCH_3) ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.74 (N=*C*), 147.93, 140.59, 139.81, 139.43, 139.40, 131.76, 131.70, 130.64, 129.95, 126.88, 126.77, 125.89, 125.74, 115.05, 56.29 (O*C*H3), 55.10 (*C*H), 32.22 (*C*H_2), 31.44 (*C*H_2), 21.21 (*C*H_3), 16.35 (*C*H_3). APCI-MS (m/z): calcd for $C_{45}H_{41}ON_2^+$: 625.3213, Found, 625.3218, $[M+H]^+$.

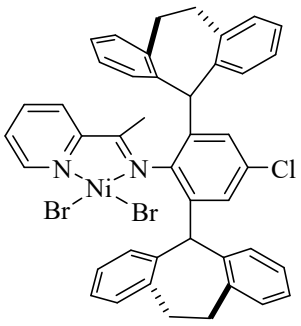


L7 (0.09 g, 15%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H, Py-*H*), 7.90 (d, *J* = 7.8 Hz, 2H, Py-*H*), 7.24 – 6.73 (m, 16H, aryl-*H*), 6.54 (d, *J* = 9.1 Hz, 2H, aryl-*H*), 4.95 (s, 2H, C*H*), 4.16

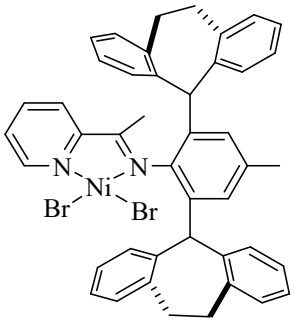
(s, 3H, Py-OCH_3), 3.70 – 3.54 (m, 2H, CH_2), 3.51 (s, 3H, OCH_3), 3.33 (m, 2H, CH_2), 2.96 – 2.79 (m, 2H, CH_2), 2.54 (d, J = 14.2 Hz, 2H, CH_2), 2.24 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.09 (N=*C*), 143.05, 140.39, 139.55, 138.65, 131.24, 131.16, 129.59, 128.66, 127.11, 126.99, 126.23, 126.14, 125.81, 115.13, 58.12 (Py-O*C*H$_3$), 56.01 (O*C*H$_3$), 55.07 (*C*H), 32.56 (*C*H$_2$), 30.55 (*C*H$_2$), 21.30 (*C*H$_3$). APCI-MS (m/z): calcd for $C_{45}H_{41}O_2N_2^+$: 641.3163, Found, 641.3169, $[M+H]^+$.

1.5 Procedure for the Synthesis of Nickel Complexes Ni1-Ni7.

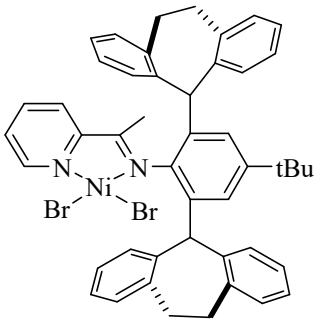
The **Ni1-Ni7** complexes were created through a reaction between (DME)$NiBr_2$ (where DME stands for 1,2-dimethoxyethane) and the respective ligands in dichloromethane. Specifically, in a nitrogen-filled environment, 0.2 mmol of the ligand was dissolved in 10 mL of dichloromethane. Subsequently, 0.2 mmol (62 mg) of (DME)$NiBr_2$ was introduced to the ligand solution. This mixture was stirred continuously at room temperature overnight. After evaporation of the solvent, the remaining residue was treated with a generous amount of anhydrous diethyl ether and sonicated to facilitate precipitation. The resulting yellow powder, upon filtration, produced the desired iminopyridyl Ni(II) complexes, namely **Ni1–Ni7**.



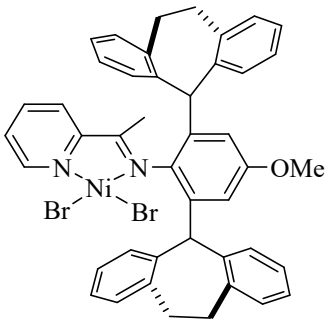
Ni1 (0.15 g, 90 %): Elemental analysis: calc. for $C_{43}H_{35}Br_2ClN_2Ni$: C, 61.95; H, 4.23; N, 3.36. Found: C, 61.78; H, 4.09; N, 3.45. MALDI-TOF-MS (m/z): calcd for $C_{43}H_{35}BrClN_2Ni^+$: 751.1020, Found, 751.1041, $[M-Br]^+$.



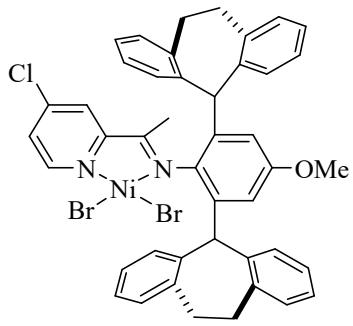
Ni2 (0.15 g, 92 %): Elemental analysis: calc. for $C_{44}H_{38}Br_2N_2Ni$: C, 64.98; H, 4.71; N, 3.44. Found: C, 64.87; H, 4.65; N, 3.49. MALDI-TOF-MS (m/z): calcd for $C_{44}H_{38}BrN_2Ni^+$: 731.1566, Found, 731.1598, $[M\text{-}Br]^+$.



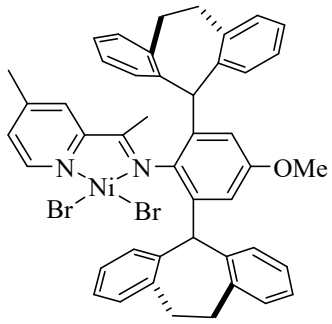
Ni3 (0.15 g, 89 %): Elemental analysis: calc. for $C_{47}H_{44}Br_2N_2Ni$: C, 66.00; H, 5.19; N, 3.28. Found: C, 66.12; H, 5.09; N, 3.17. MALDI-TOF-MS (m/z): calcd for $C_{47}H_{44}BrN_2Ni^+$: 773.2036, Found, 773.2066, $[M\text{-}Br]^+$.



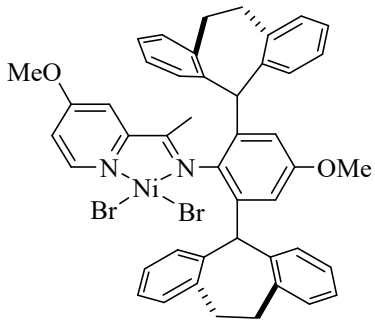
Ni4 (0.14 g, 87 %): Elemental analysis: calc. for $C_{44}H_{38}Br_2N_2NiO$: C, 63.73; H, 4.62; N, 3.38. Found: C, 63.68; H, 4.58; N, 3.27. MALDI-TOF-MS (m/z): calcd for $C_{44}H_{38}BrN_2NiO^+$: 747.1515, Found, 747.1532, $[M\text{-}Br]^+$.



Ni5 (0.15 g, 84 %): Elemental analysis: calc. for $C_{44}H_{37}Br_2ClN_2NiO$: C, 61.19; H, 4.32; N, 3.24. Found: C, 61.24; H, 4.18; N, 3.28. MALDI-TOF-MS (m/z): calcd for $C_{44}H_{37}BrClN_2NiO^+$: 781.1126, Found, 781.1120, $[M\text{-}Br]^+$.



Ni6 (0.15 g, 86 %): Elemental analysis: calc. for $C_{45}H_{40}Br_2N_2NiO$: C, 64.09; H, 4.78; N, 3.32. Found: C, 64.21; H, 4.84; N, 3.24. MALDI-TOF-MS (m/z): calcd for $C_{45}H_{40}BrN_2NiO^+$: 761.1672, Found, 761.1661, $[M\text{-}Br]^+$.



Ni7 (0.14 g, 84 %): Elemental analysis: calc. for $C_{45}H_{40}Br_2N_2NiO_2$: C, 62.90; H, 4.69; N, 3.26. Found: C, 62.84; H, 4.76; N, 3.18. MALDI-TOF-MS (m/z): calcd for $C_{45}H_{40}BrN_2NiO_2^+$: 777.1621, Found, 777.1654, $[M\text{-}Br]^+$.

1.6 A General Procedure for Ethylene Polymerization.

Firstly, the high-pressure polymerization reactor was subjected to air drying at 60 °C for 1 hour. Within a glovebox, 40 mL of toluene and the requisite amount of MAO were introduced into the reactor. Subsequently, the reactor was removed from the glovebox, connected to the ethylene pipeline, and positioned on a reactor that had been pre-set to the desired polymerization temperature. Under an atmosphere of ethylene, 2 μmol of Ni catalyst dissolved in 1 mL of CH_2Cl_2 was injected into the polymerization system using a syringe. The pressure was adjusted to the desired level, and the reaction was timed once the gas flow had stabilized. Upon completion of the polymerization reaction, the reactor was depressurized, and the contents were poured into 100 mL of acidic ethanol solution to terminate the reaction. The polymer was then precipitated, filtered, and thoroughly washed. Finally, it was dried under vacuum at 60 °C for a minimum of 24 hours before being weighed.

1.7 Supporting Figures

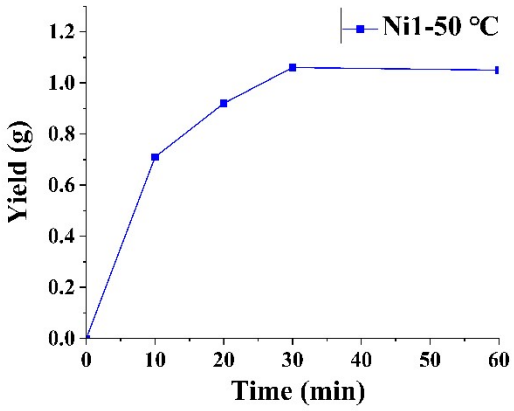


Figure SA. Time-dependent polymerization kinetics of **Ni1** at 50°C.

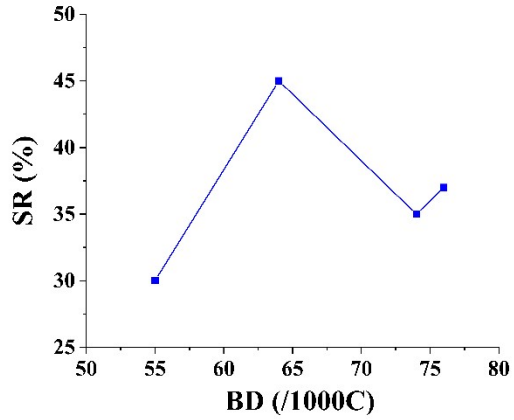


Figure SB. Plot of strain recovery (SR) ratio versus branching density.

2. Spectra Data

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

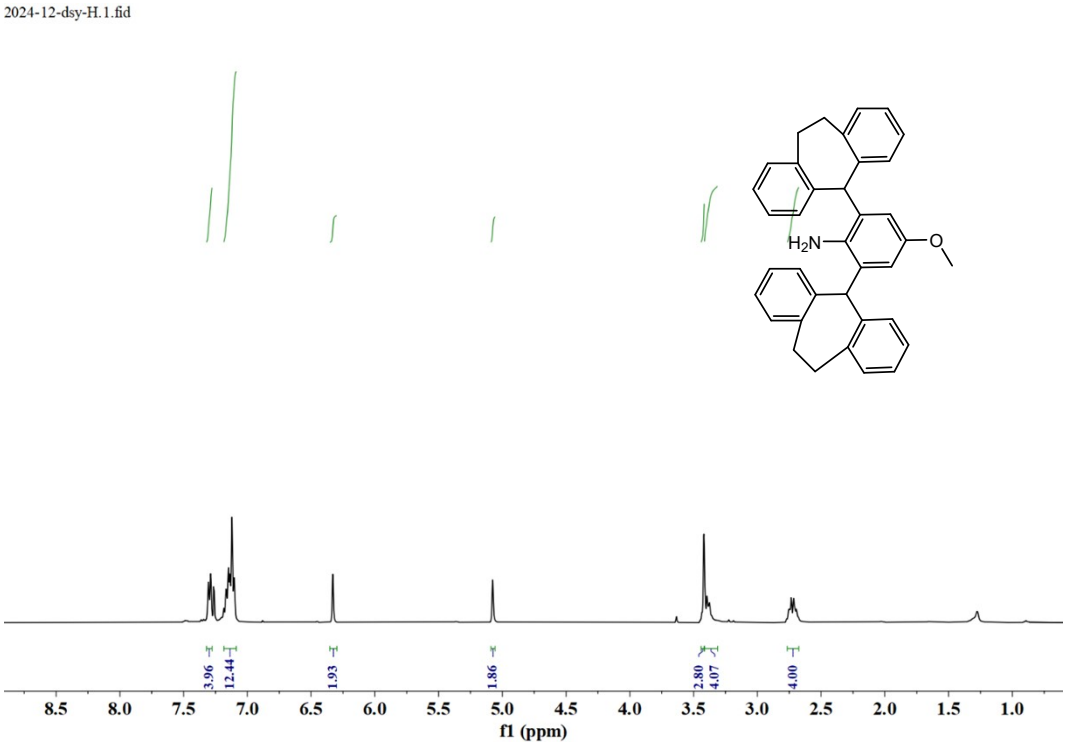


Figure S1. ^{1}H NMR spectrum of **A2** in $CDCl_3$.

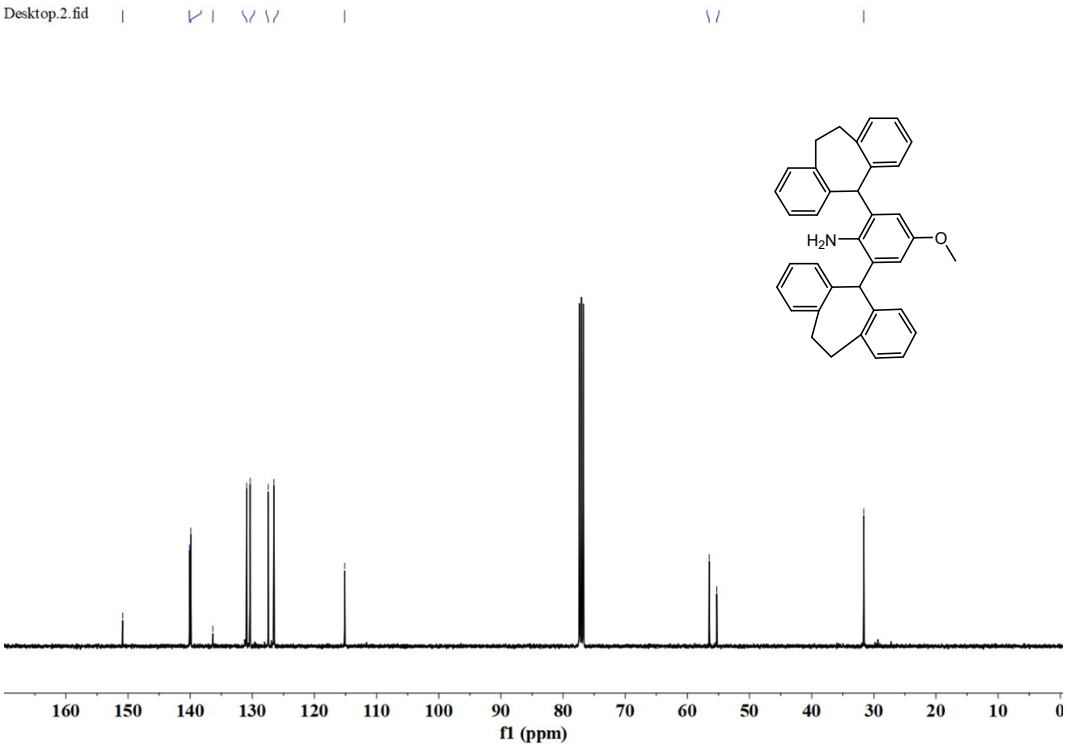


Figure S2. ^{13}C NMR spectrum of **A2** in $CDCl_3$.

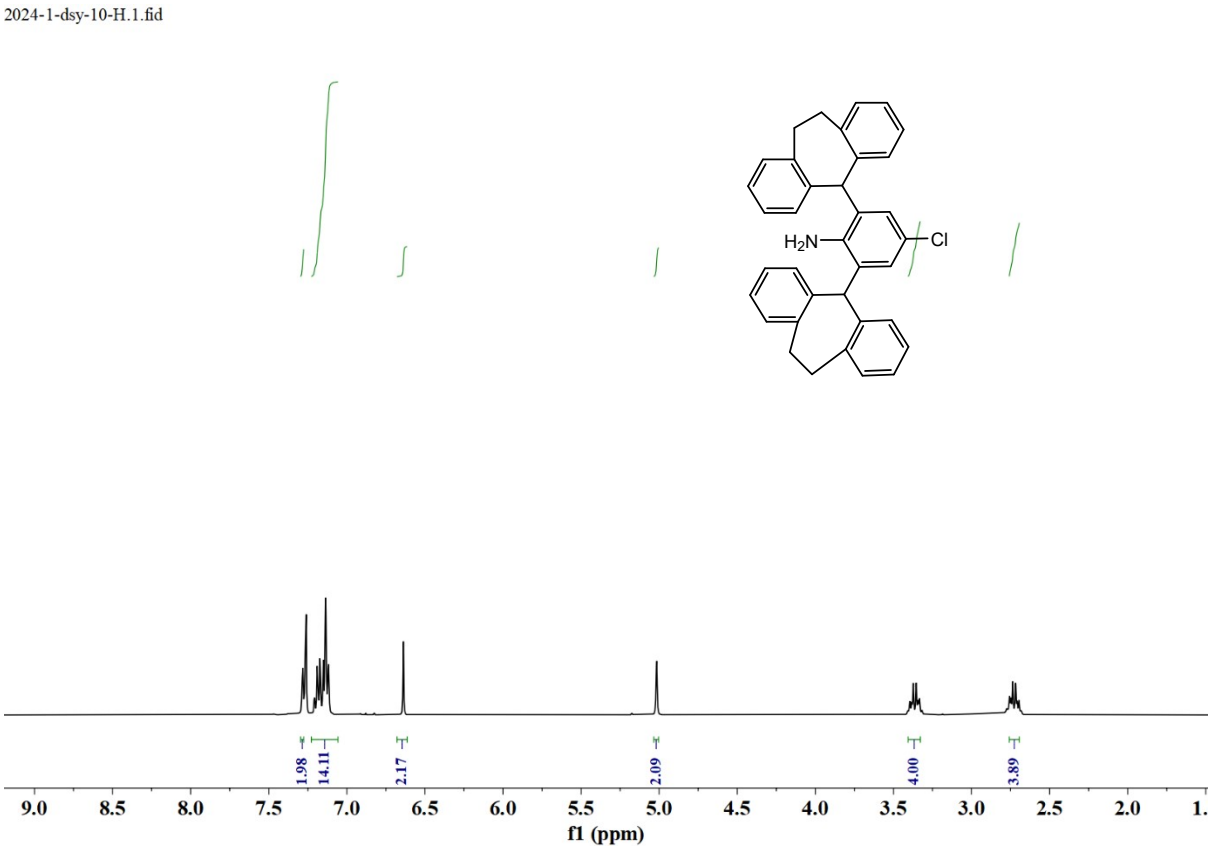


Figure S3. ^{1}H NMR spectrum of **A3** in $CDCl_3$.

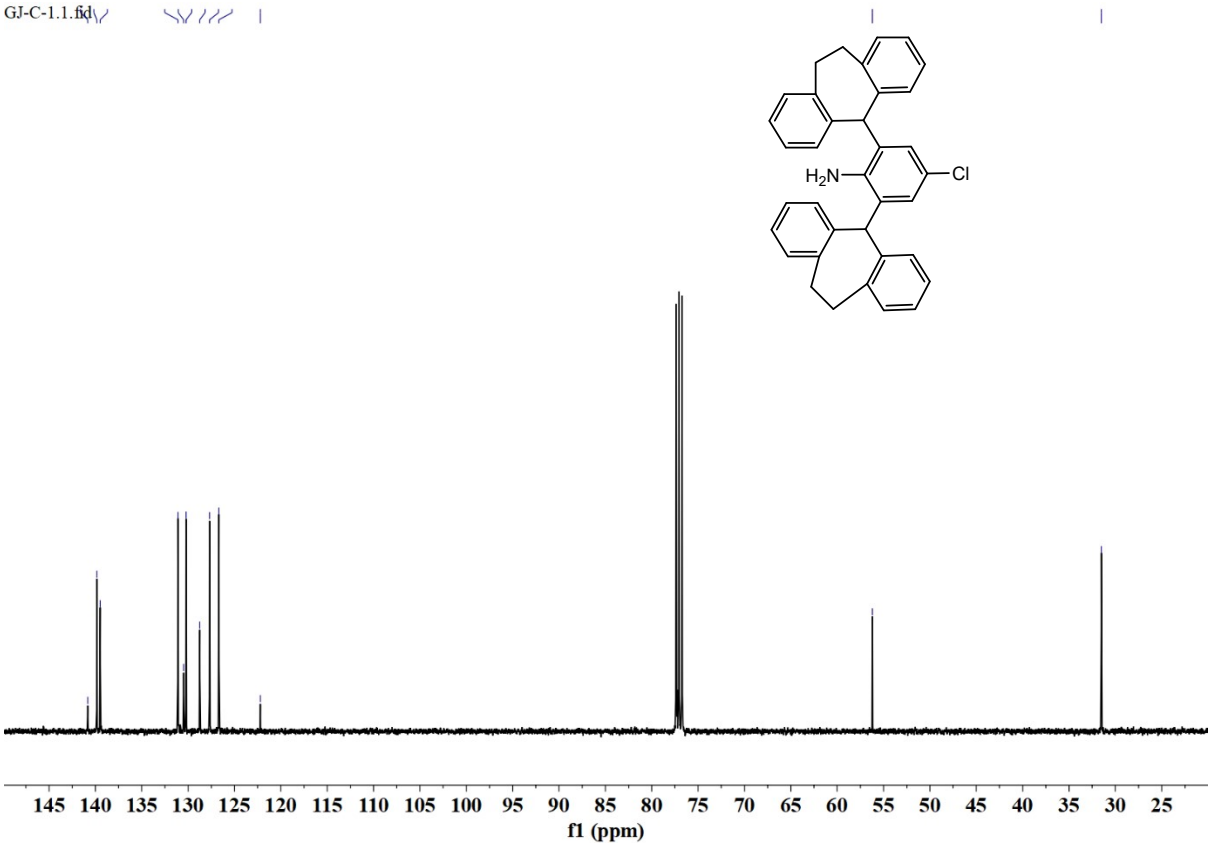


Figure S4. ^{13}C NMR spectrum of **A3** in $CDCl_3$.

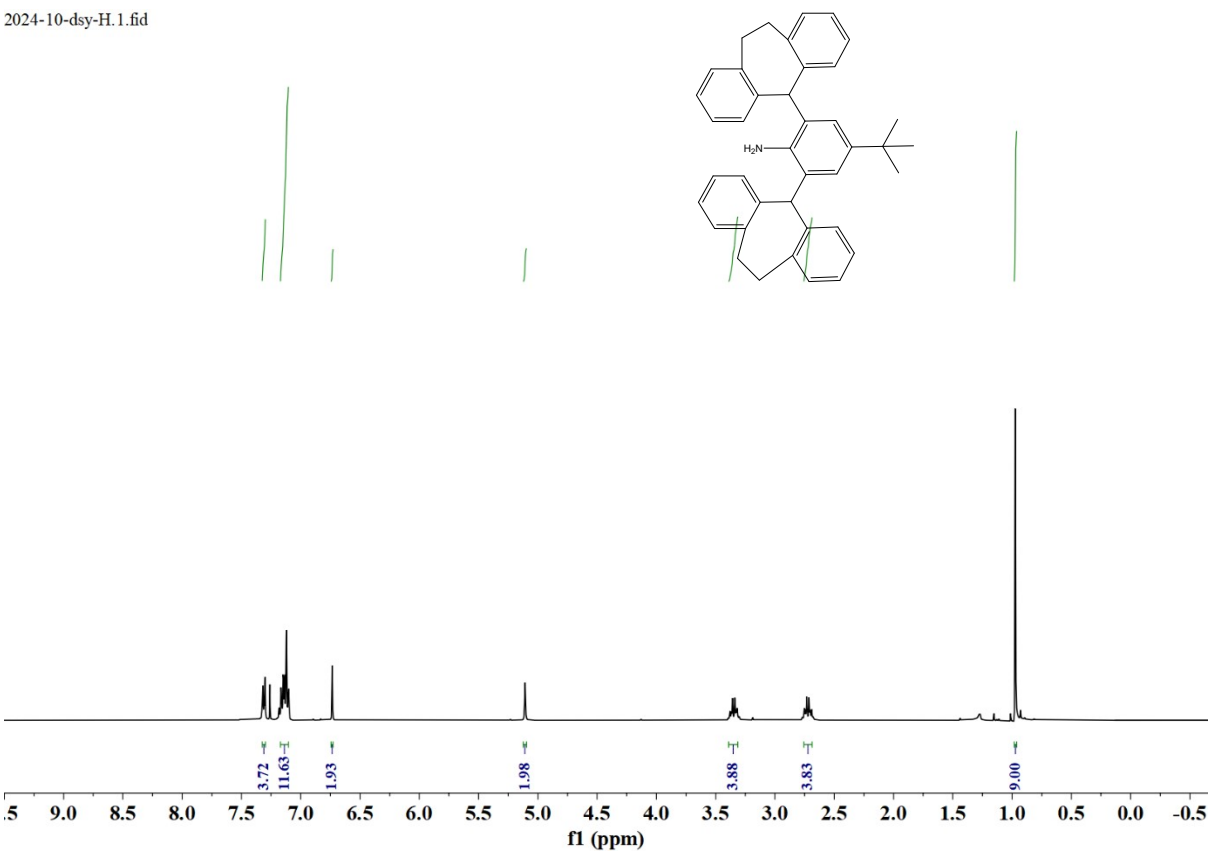


Figure S5. ^{1}H NMR spectrum of **A4** in $CDCl_3$.

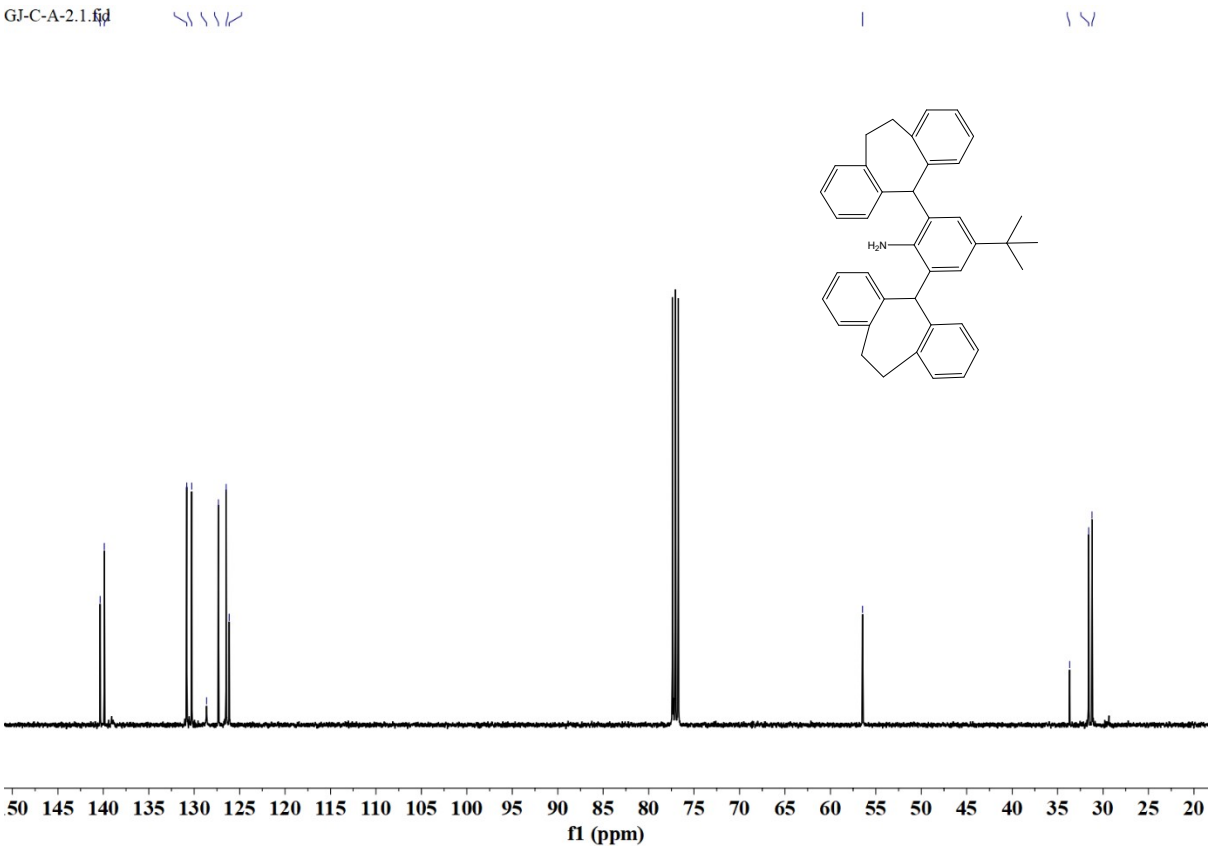


Figure S6. ^{13}C NMR spectrum of **A4** in $CDCl_3$.

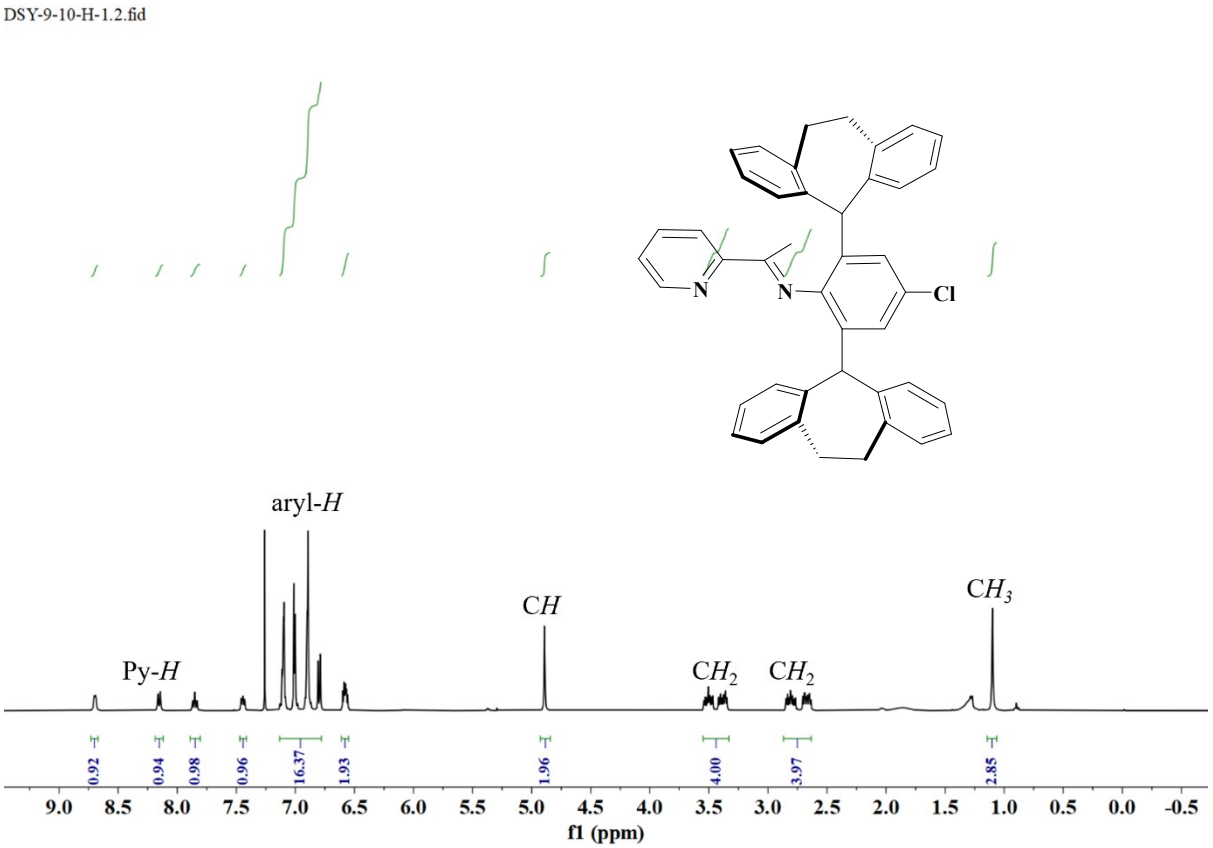


Figure S7. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

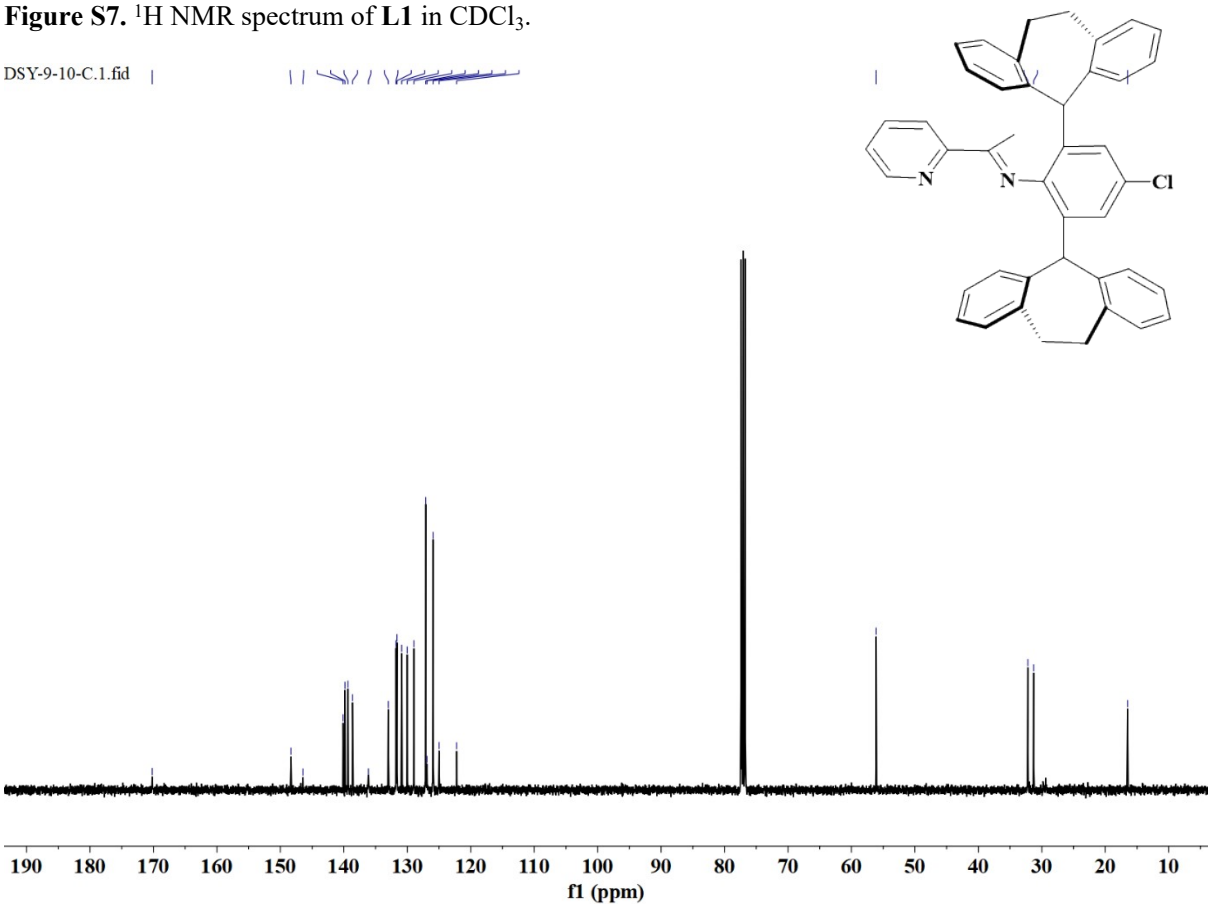


Figure S8. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

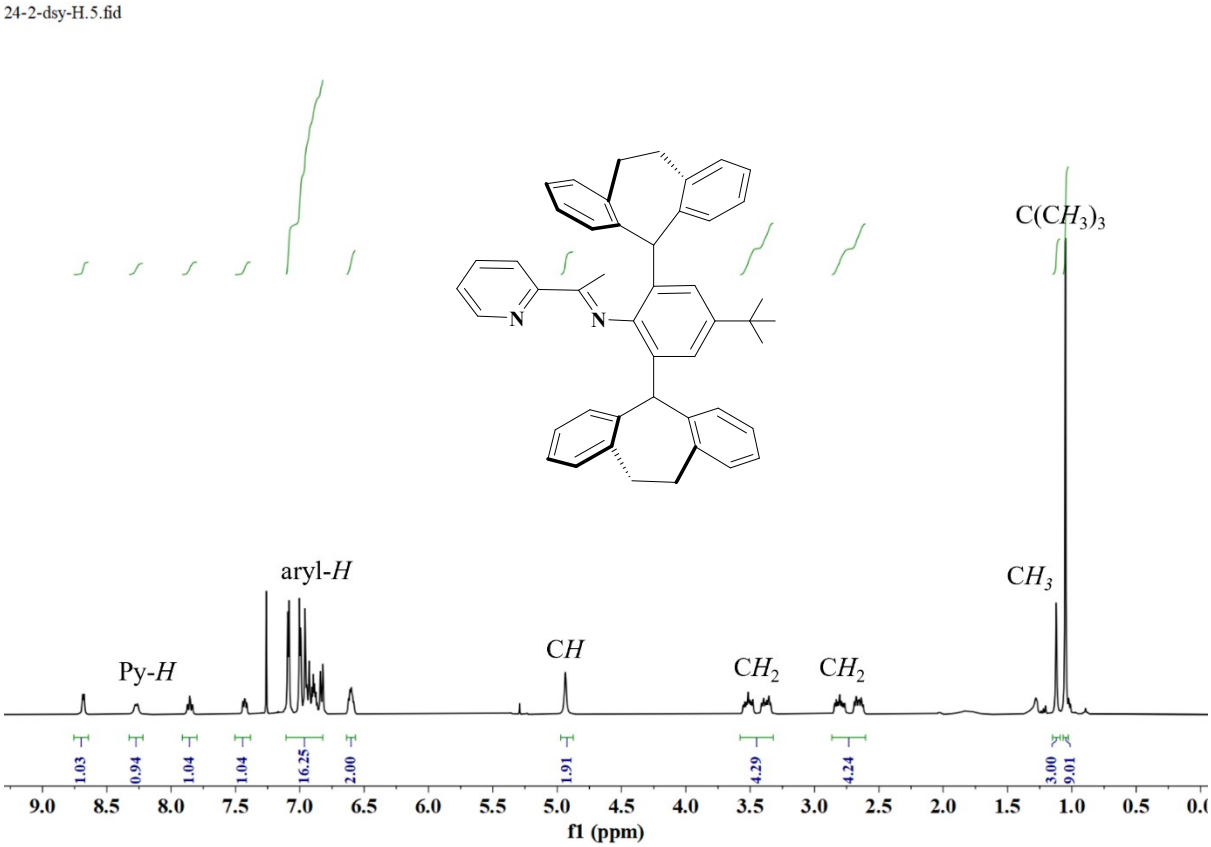


Figure S9. ^{1}H NMR spectrum of **L3** in $CDCl_3$.

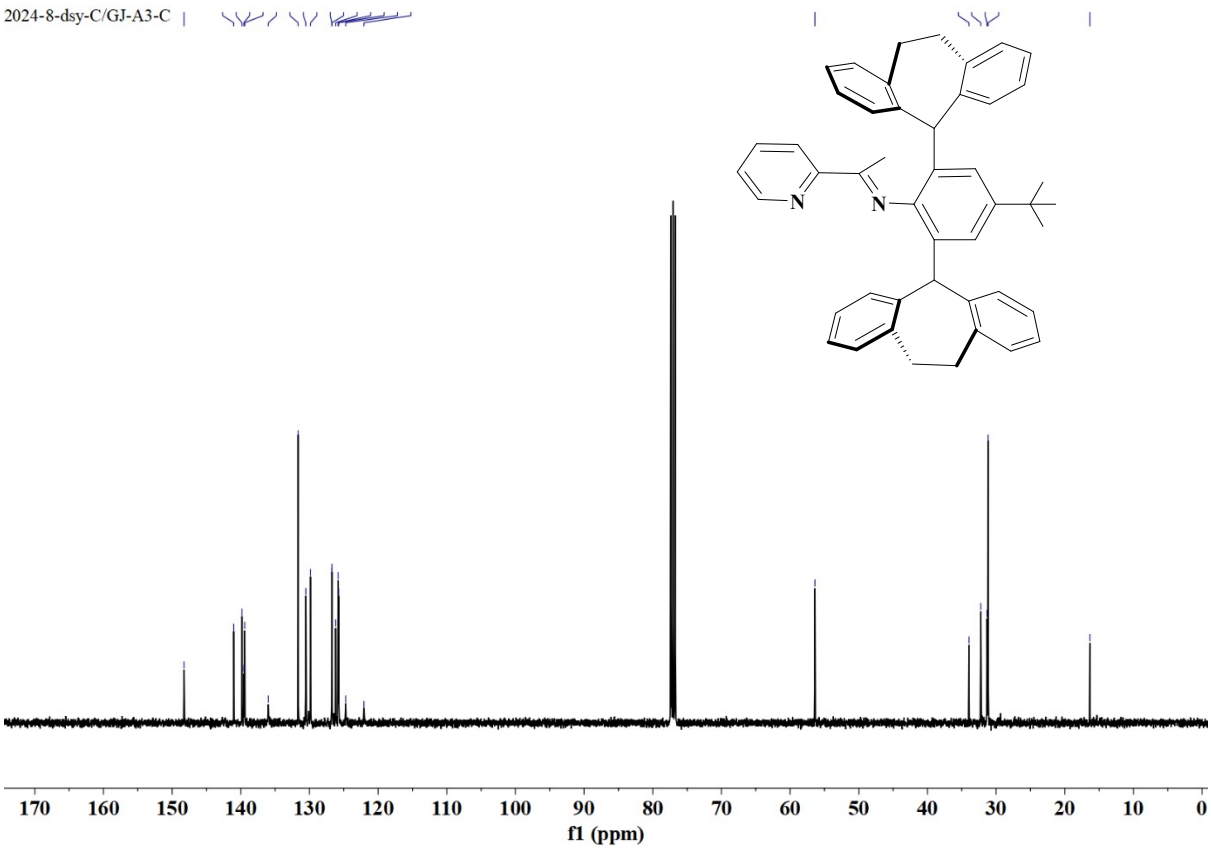


Figure S10. ^{13}C NMR spectrum of **L3** in $CDCl_3$.

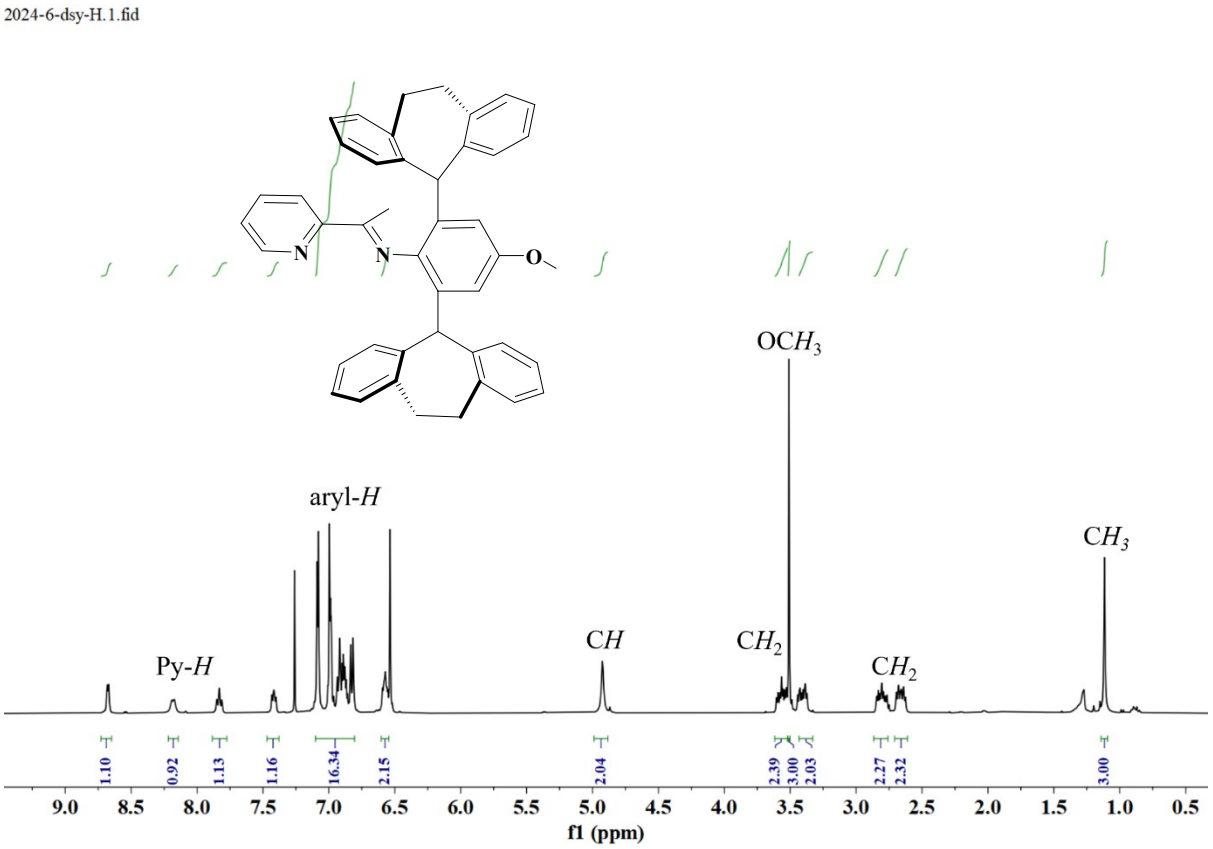


Figure S11. ^{1}H NMR spectrum of **L4** in $CDCl_3$.

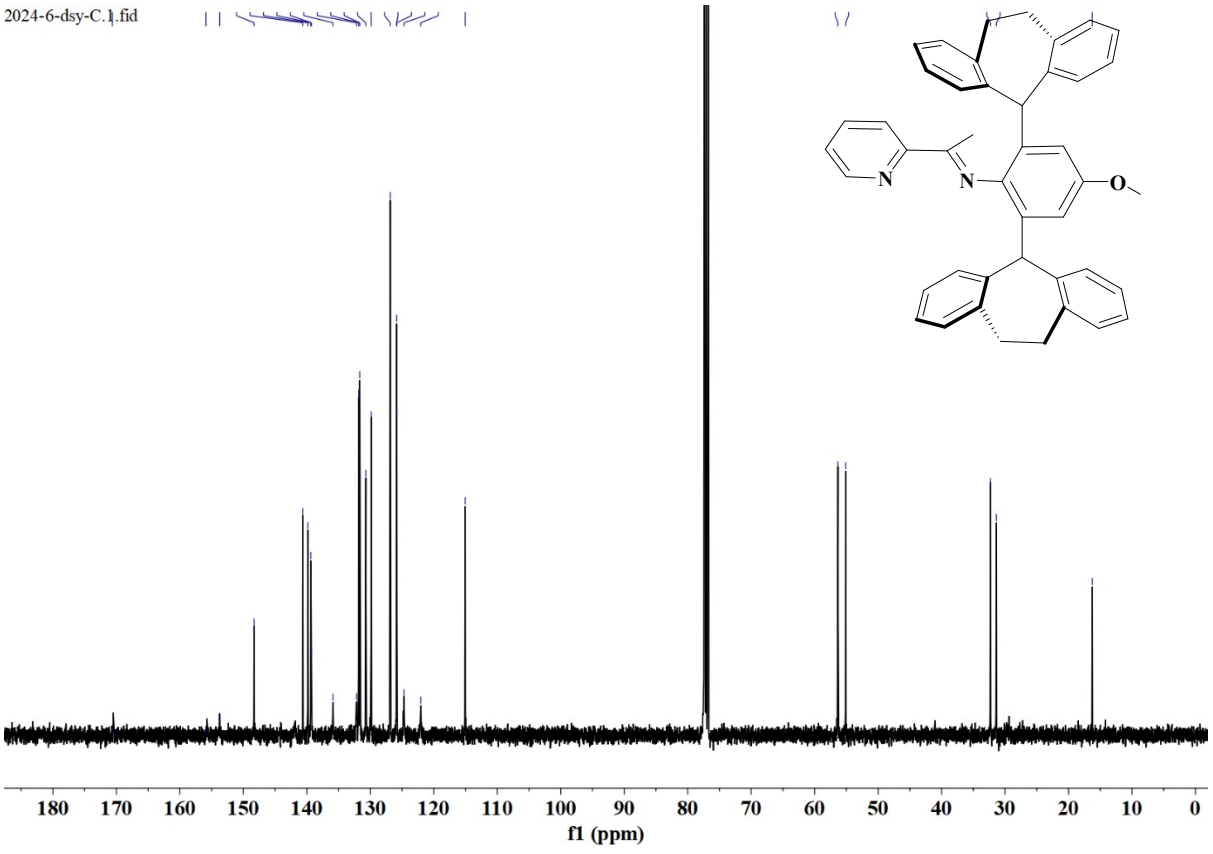


Figure S12. ^{13}C NMR spectrum of **L4** in $CDCl_3$.

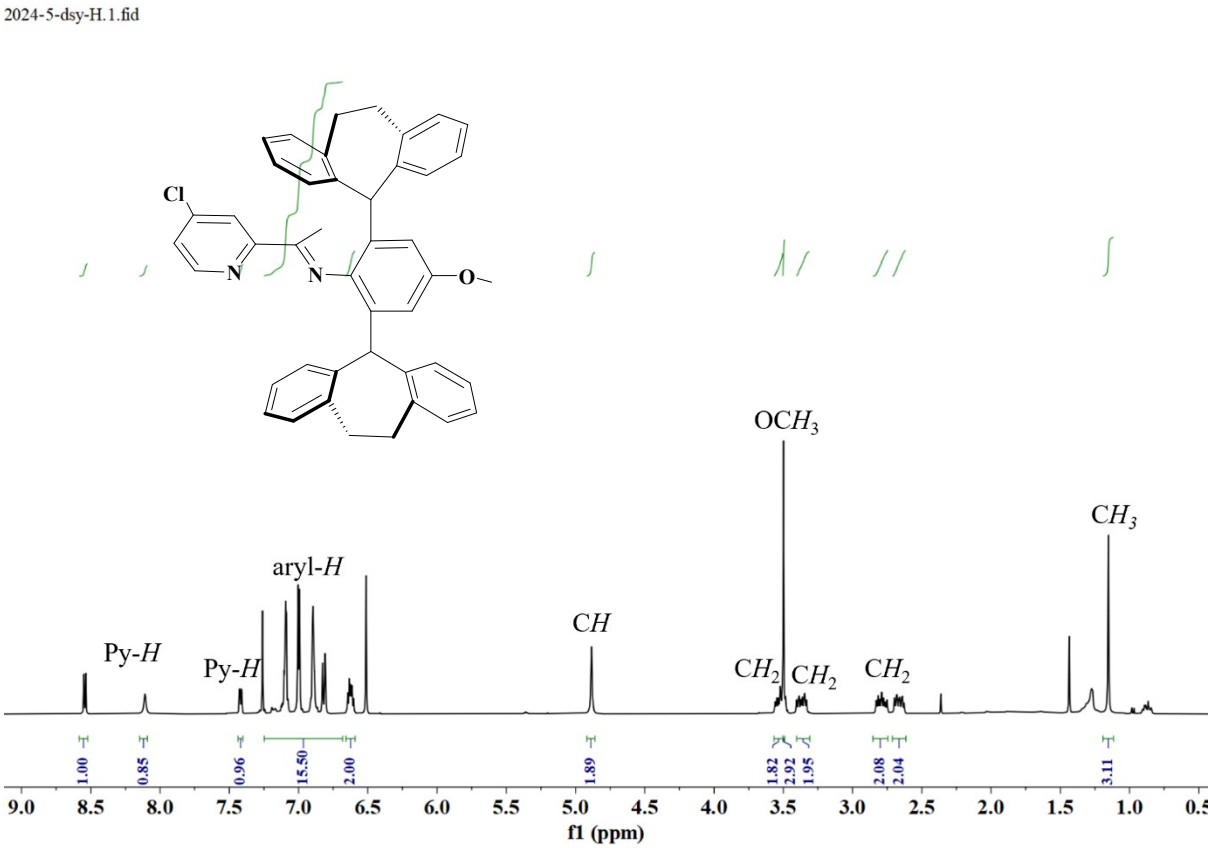


Figure S13. ^{1}H NMR spectrum of **L5** in $CDCl_3$.

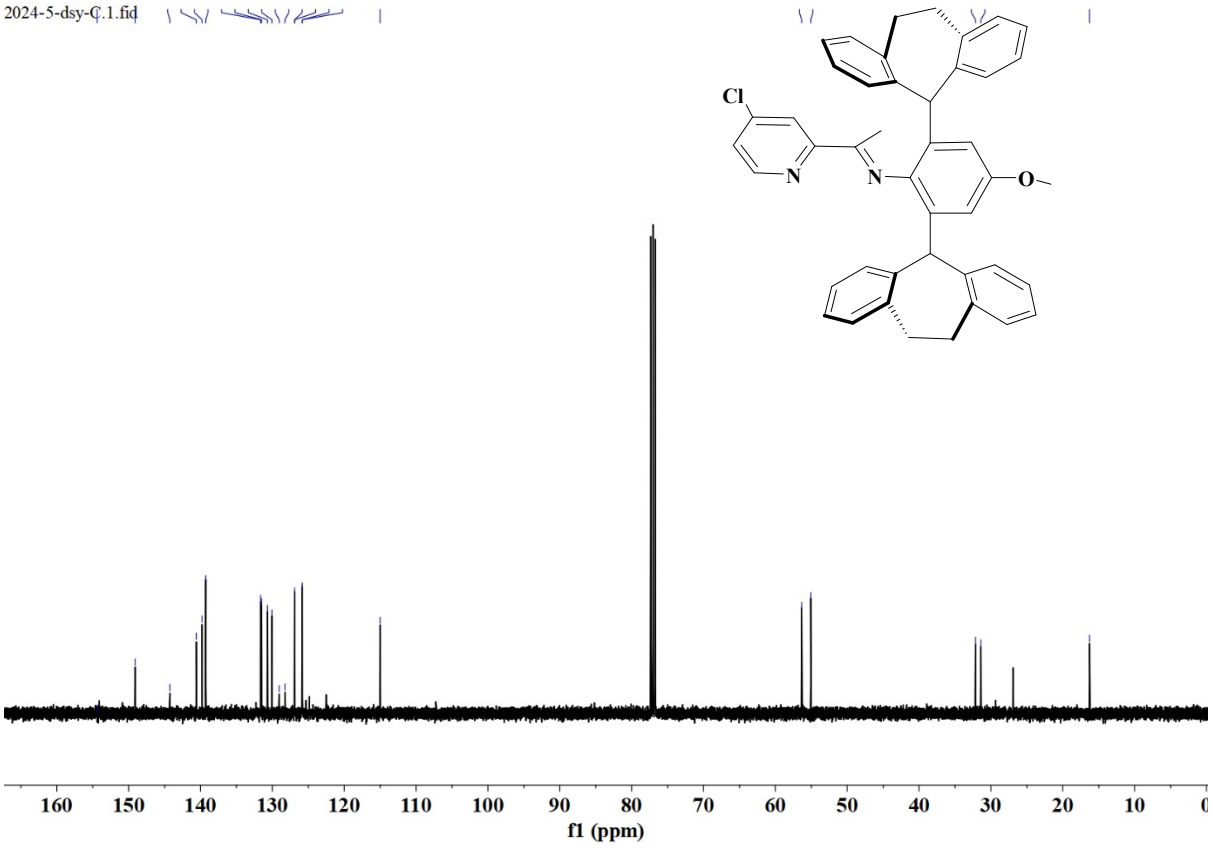


Figure S14. ^{13}C NMR spectrum of **L5** in $CDCl_3$.

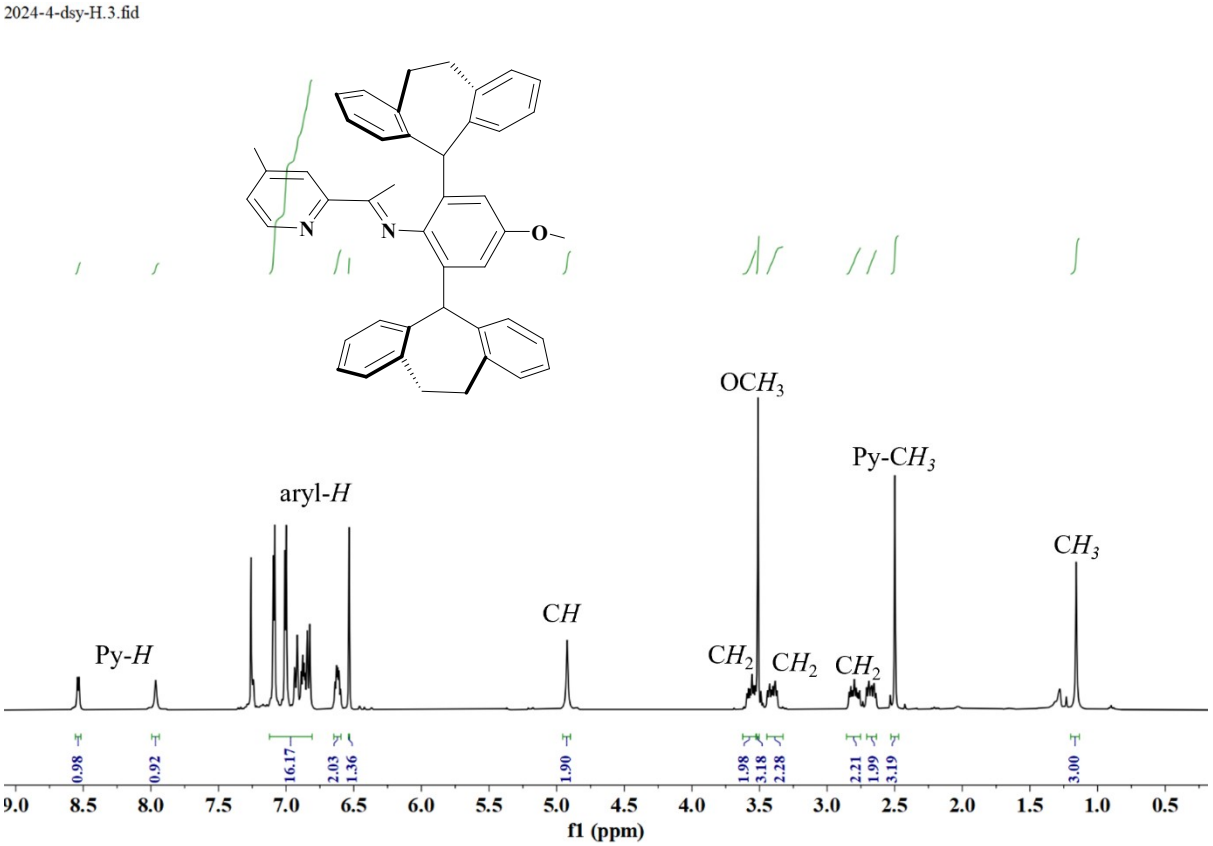


Figure S15. ^{1}H NMR spectrum of **L6** in $CDCl_3$.

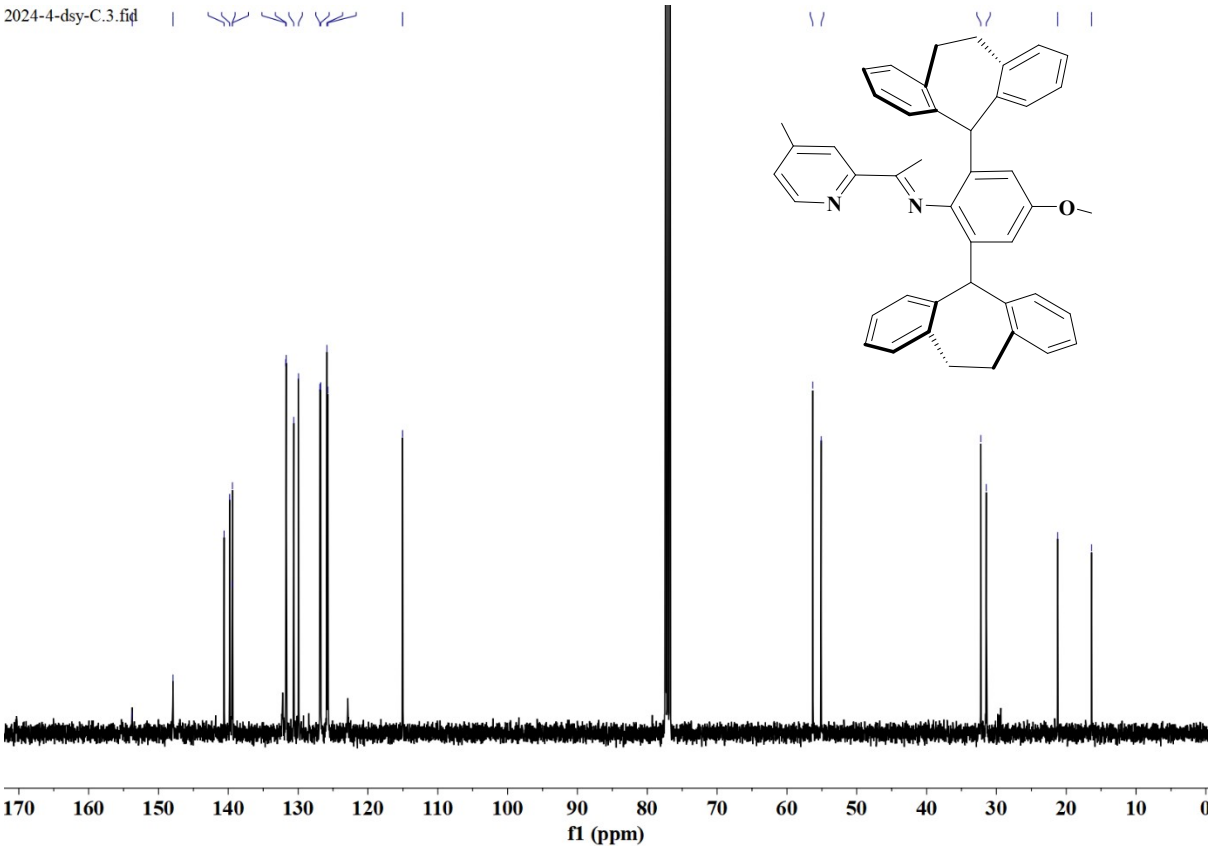


Figure S16. ^{13}C NMR spectrum of **L6** in $CDCl_3$.

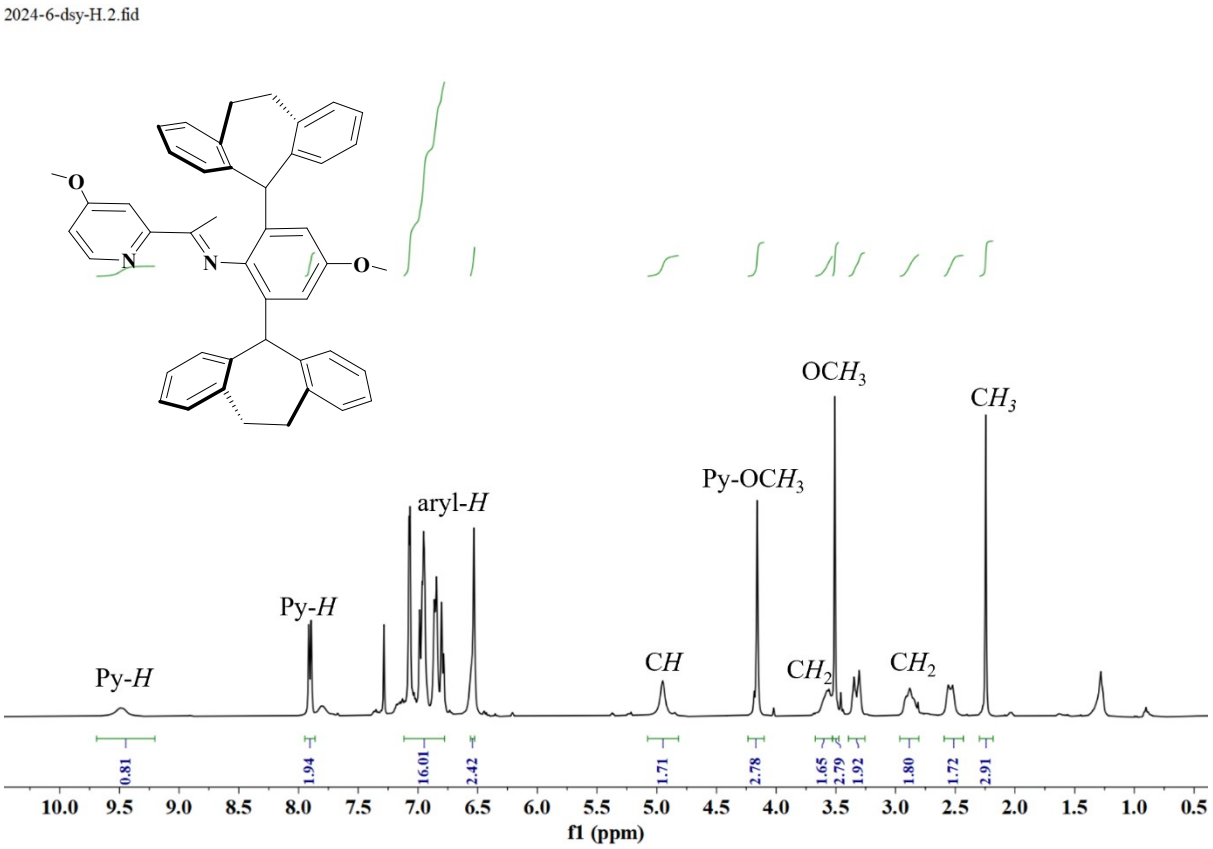


Figure S17. ^{1}H NMR spectrum of **L7** in $CDCl_3$.

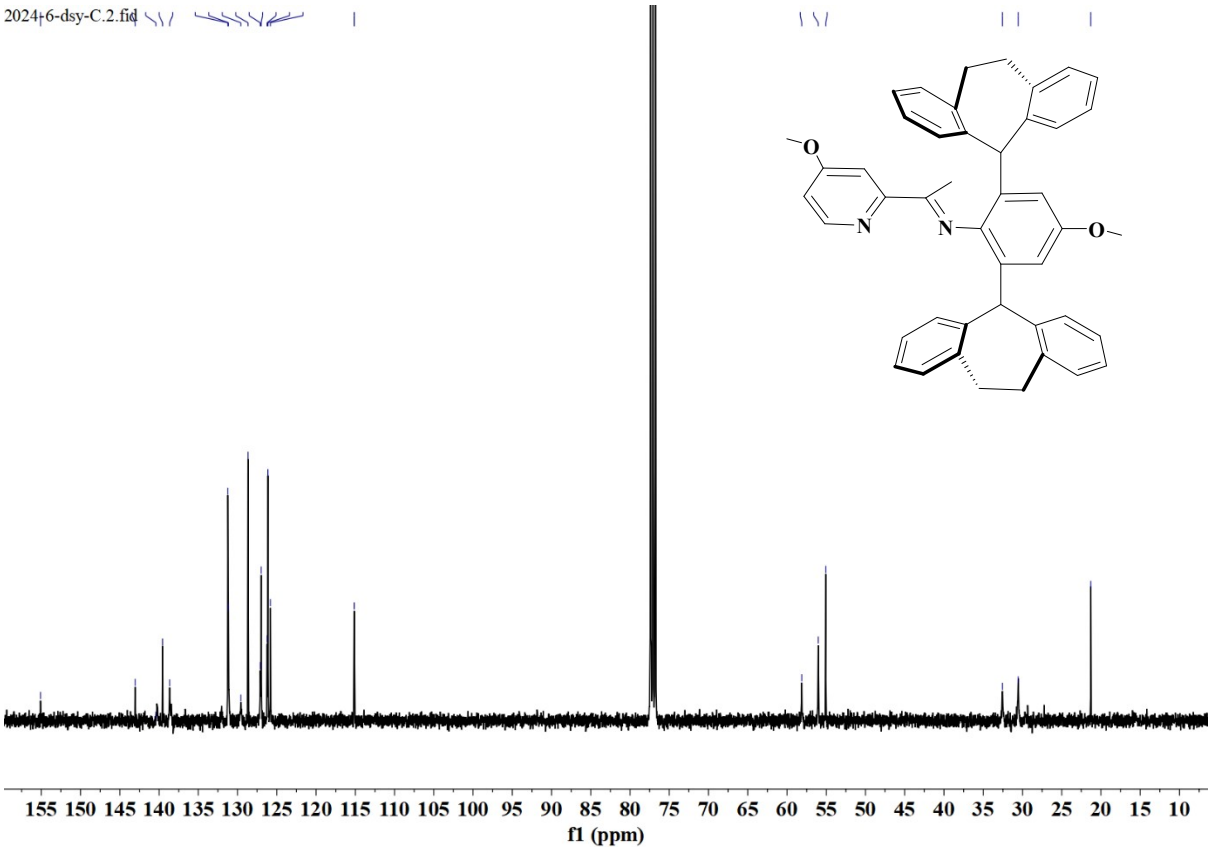


Figure S18. ^{13}C NMR spectrum of **L7** in $CDCl_3$.

2.2 APCl-MS of A2-A4, L1, L3-L7.

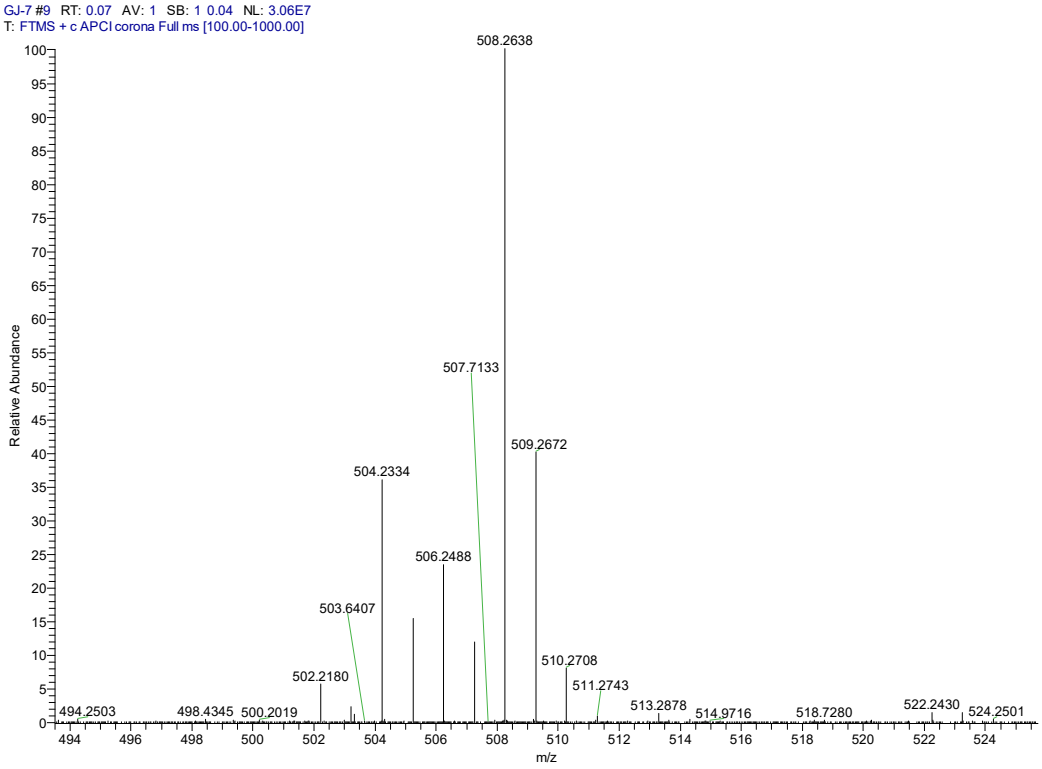


Figure S19. APCl-MS of **A2.**

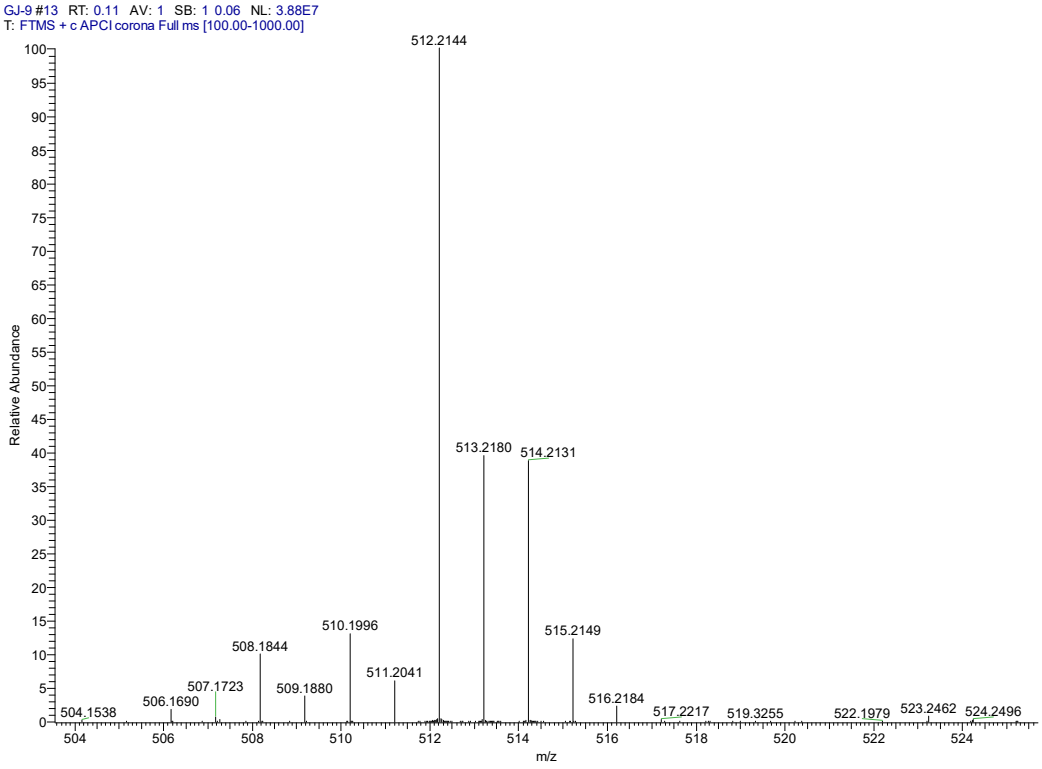


Figure S20. APCl-MS of **A3.**

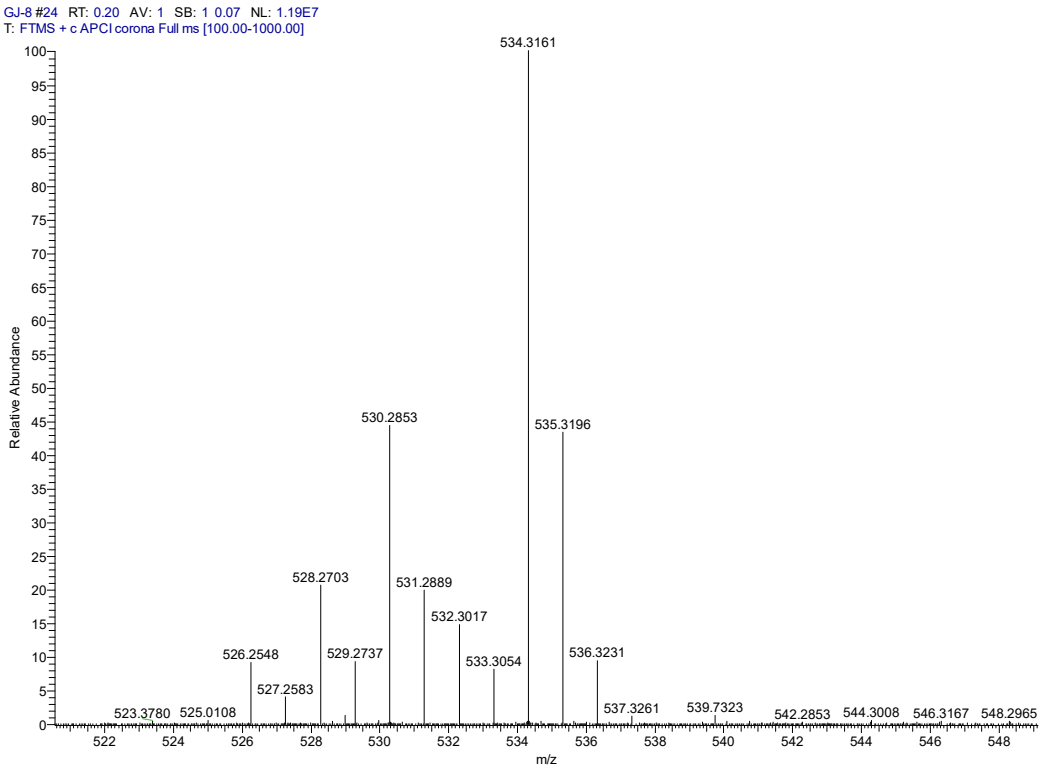


Figure S21. APCl-MS of **A4.**

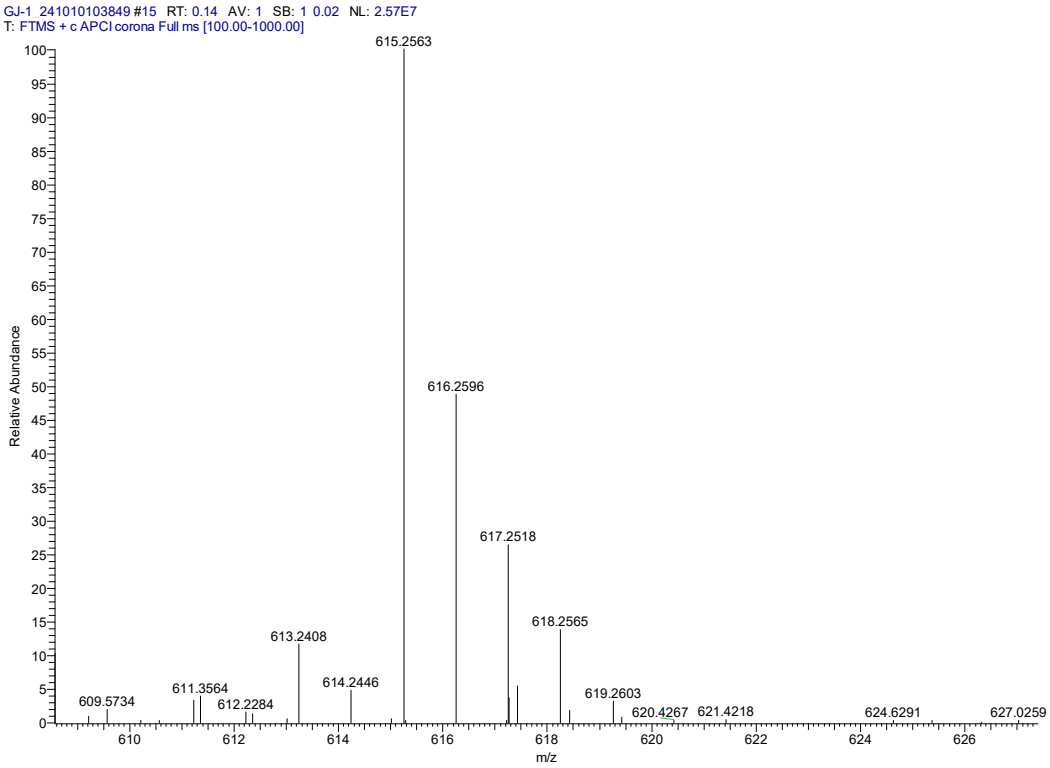


Figure S22. APCl-MS of **L1.**

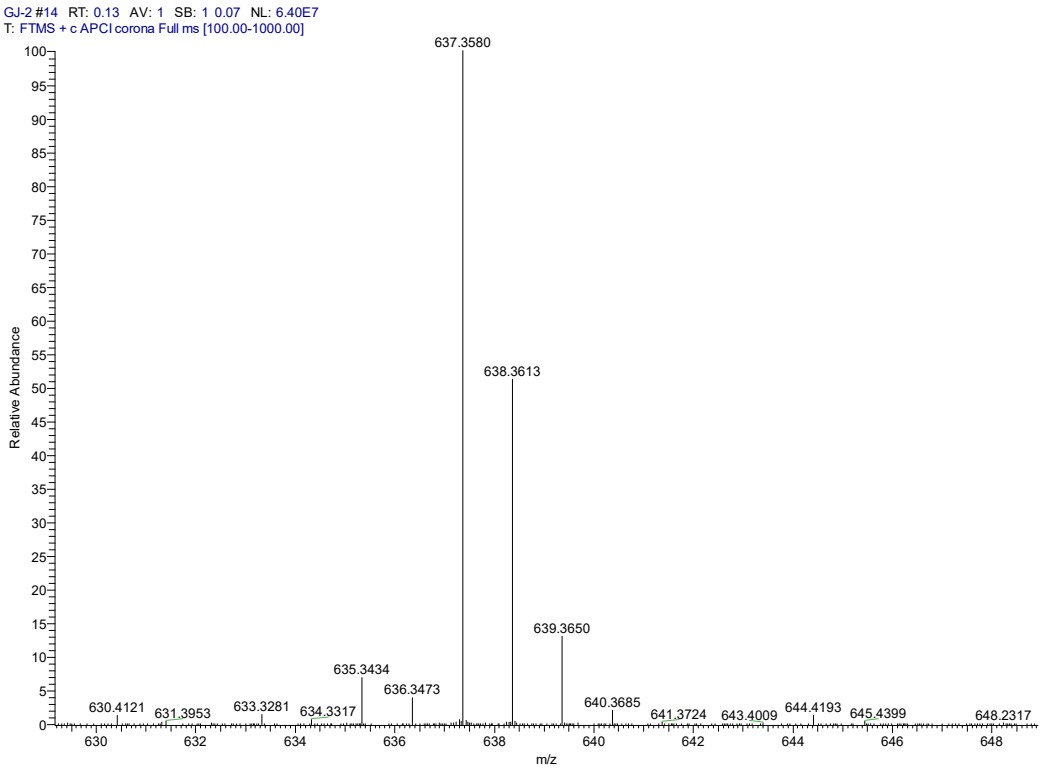


Figure S23. APCl-MS of **L3.**

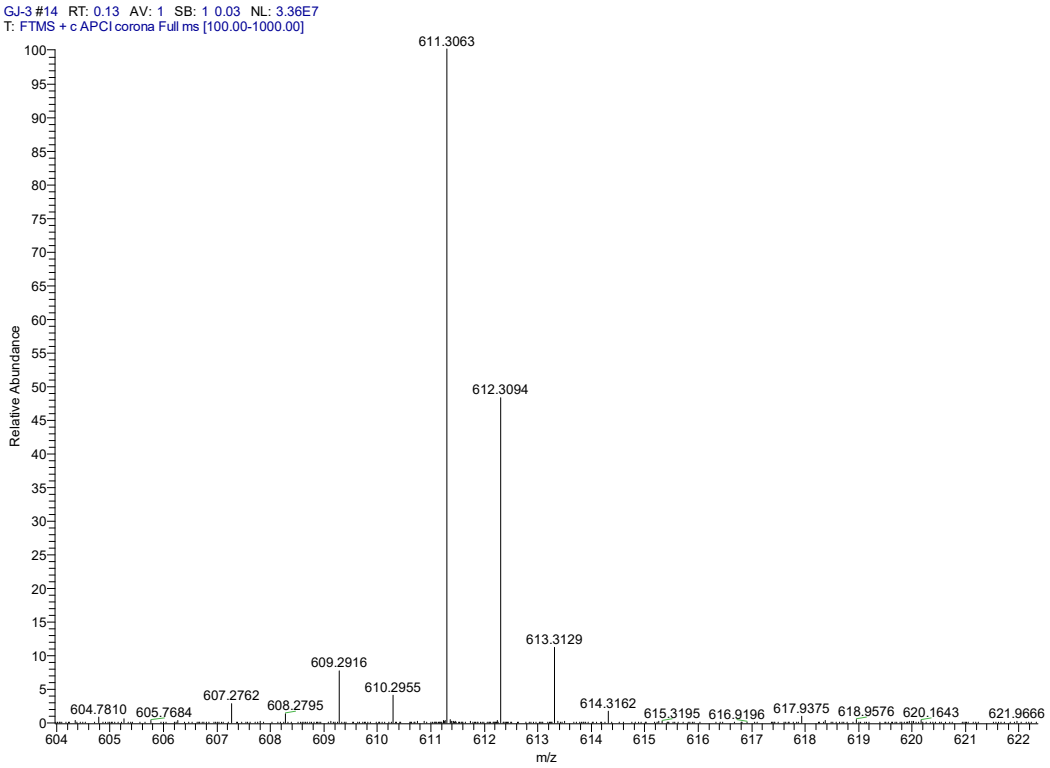


Figure S24. APCl-MS of **L4.**

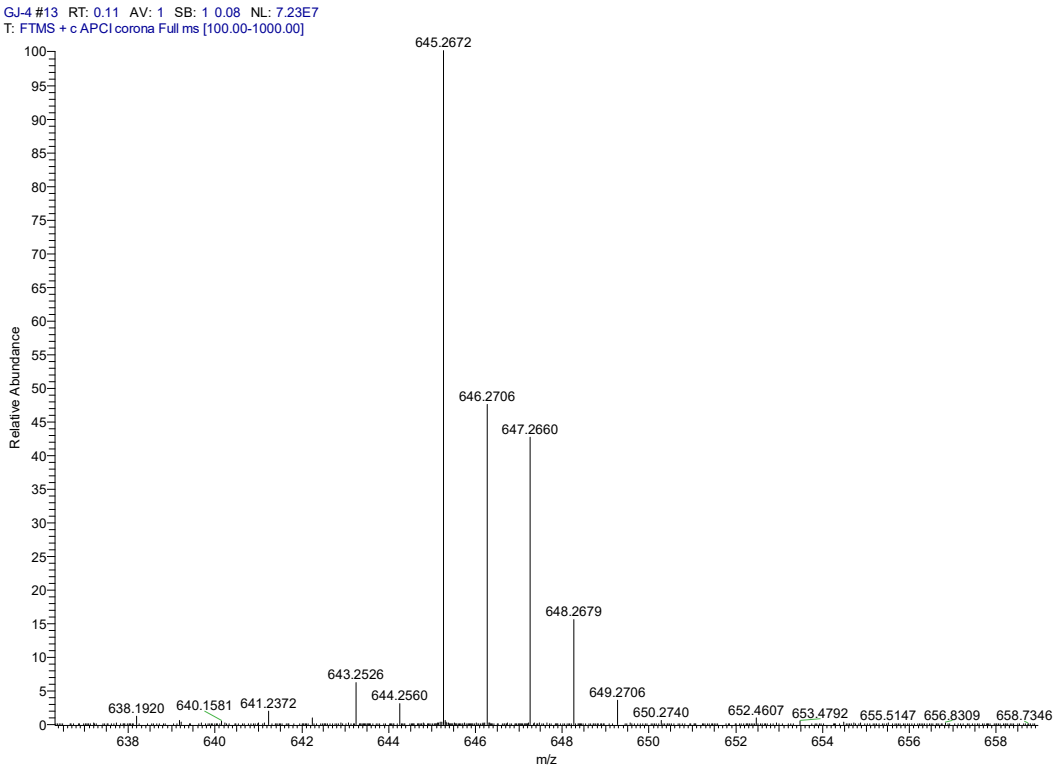


Figure S25. APCl-MS of **L5.**

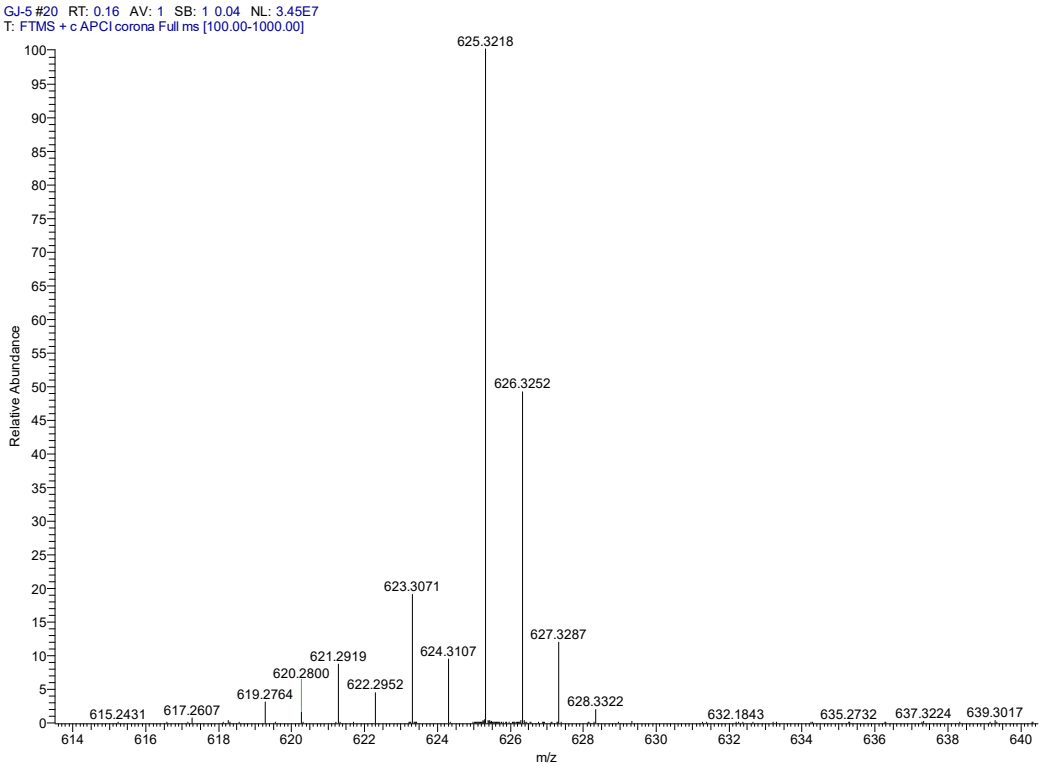


Figure S26. APCl-MS of **L6.**

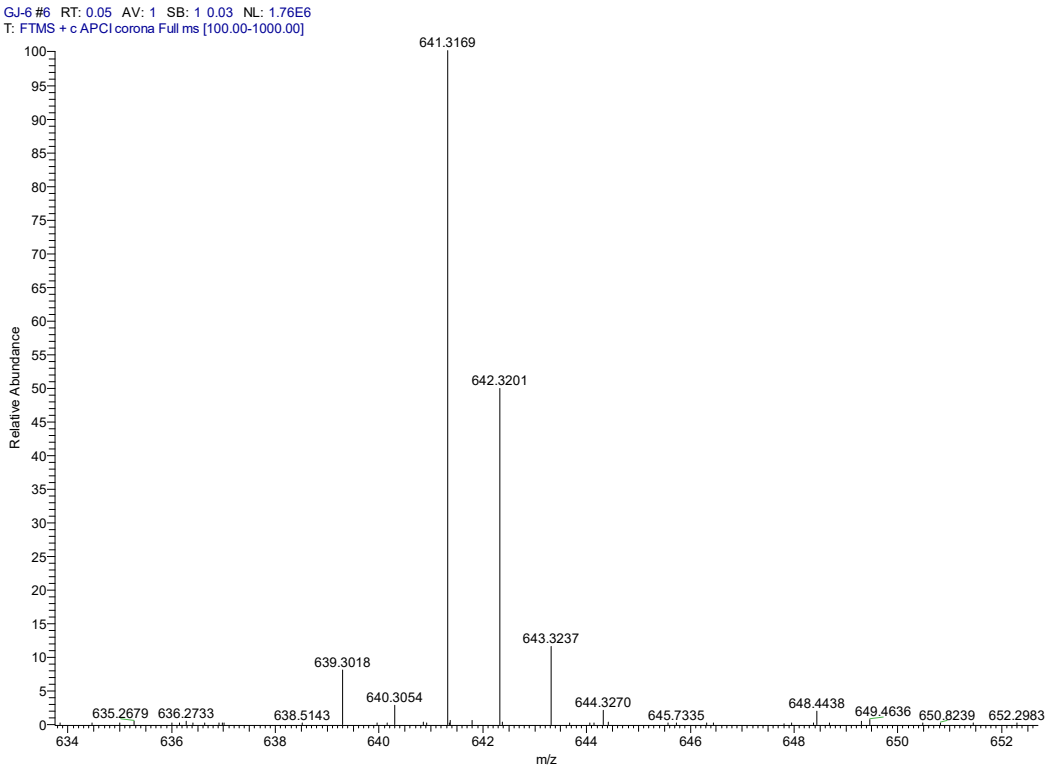


Figure S27. APCl-MS of **L7.**

2.3 MALDI-TOF MS of Complexes Ni1-Ni7

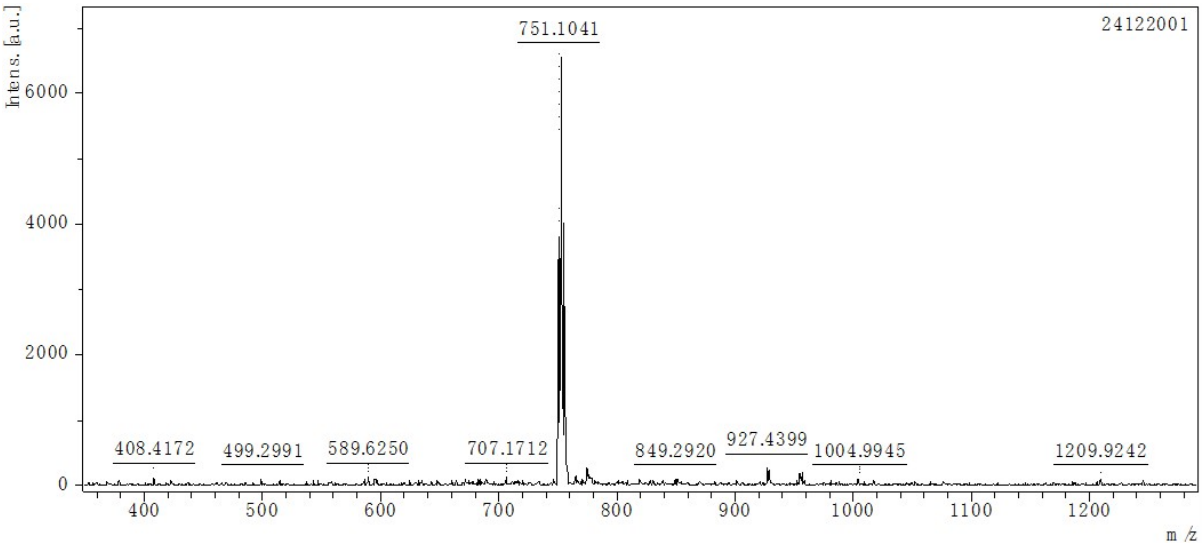


Figure S28. MALDI-TOF MS of **Ni1**.

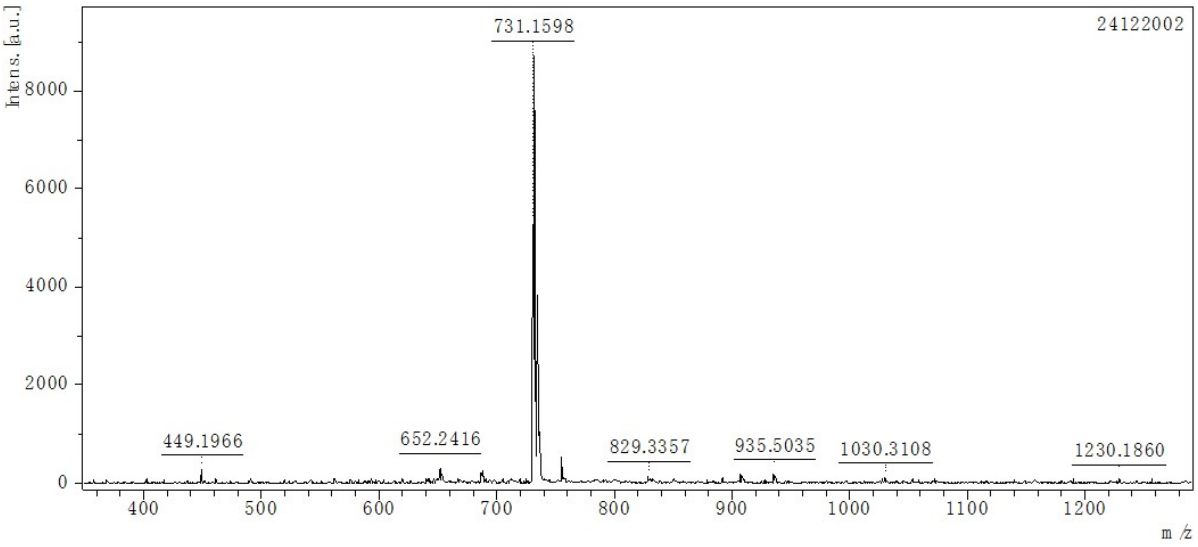


Figure S29. MALDI-TOF MS of **Ni2**.

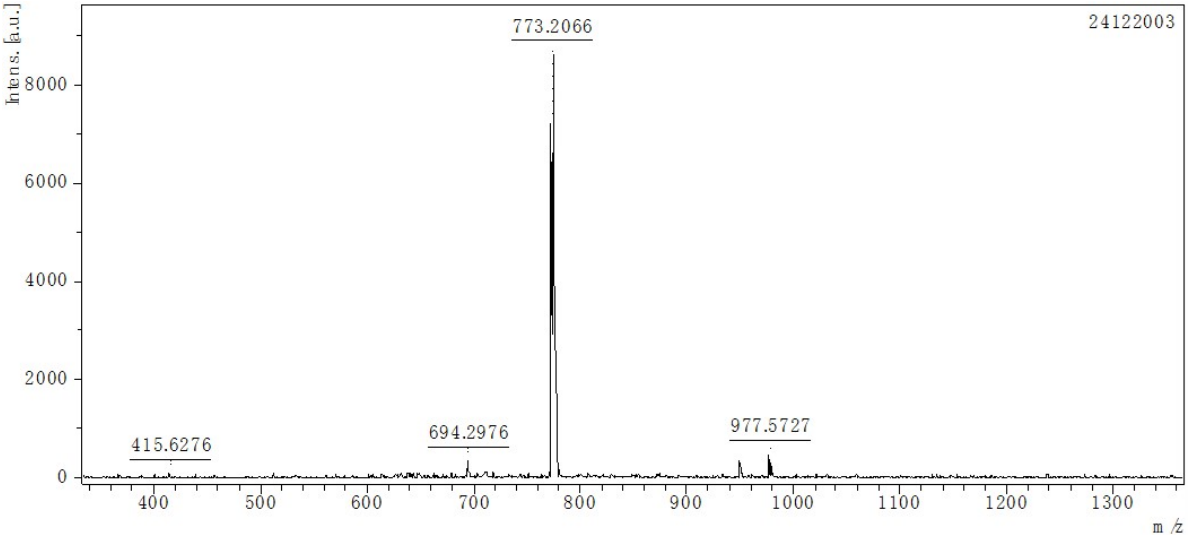


Figure S30. MALDI-TOF MS of **Ni3**.

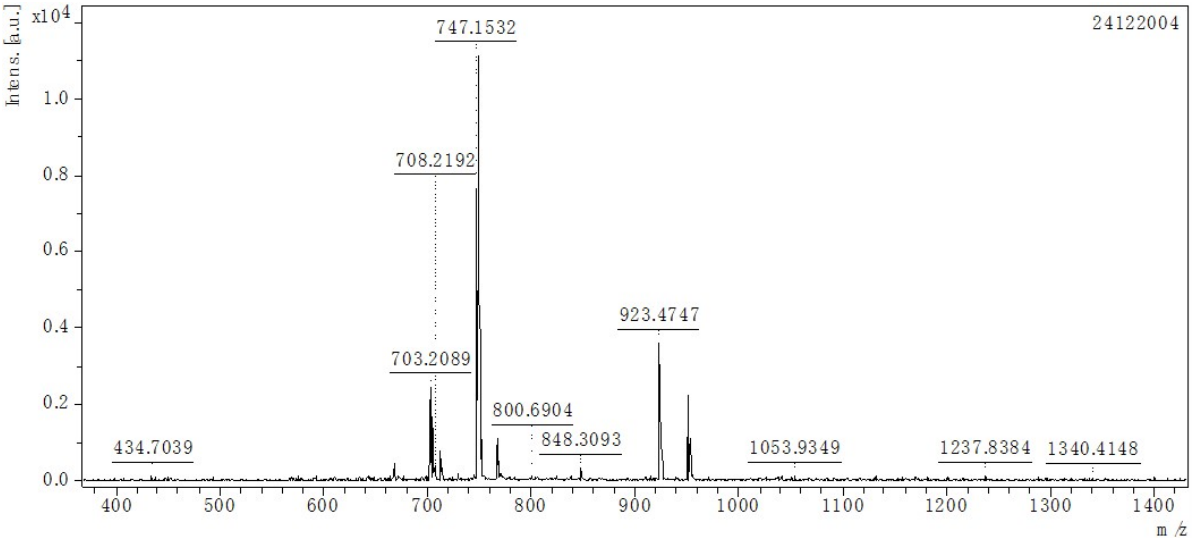


Figure S31. MALDI-TOF MS of **Ni4**.

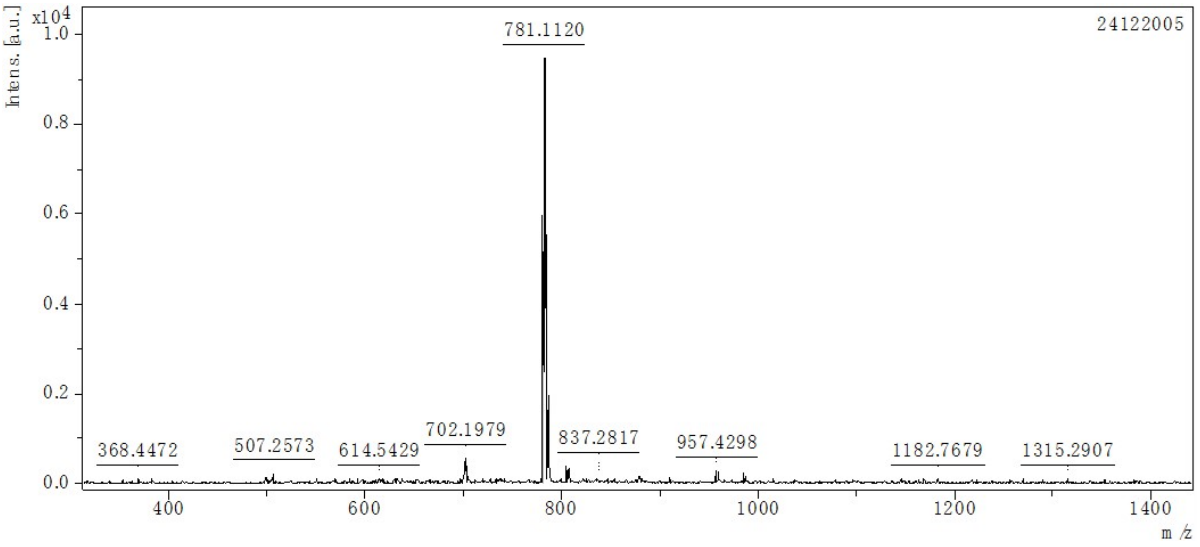


Figure S32. MALDI-TOF MS of **Ni5**.

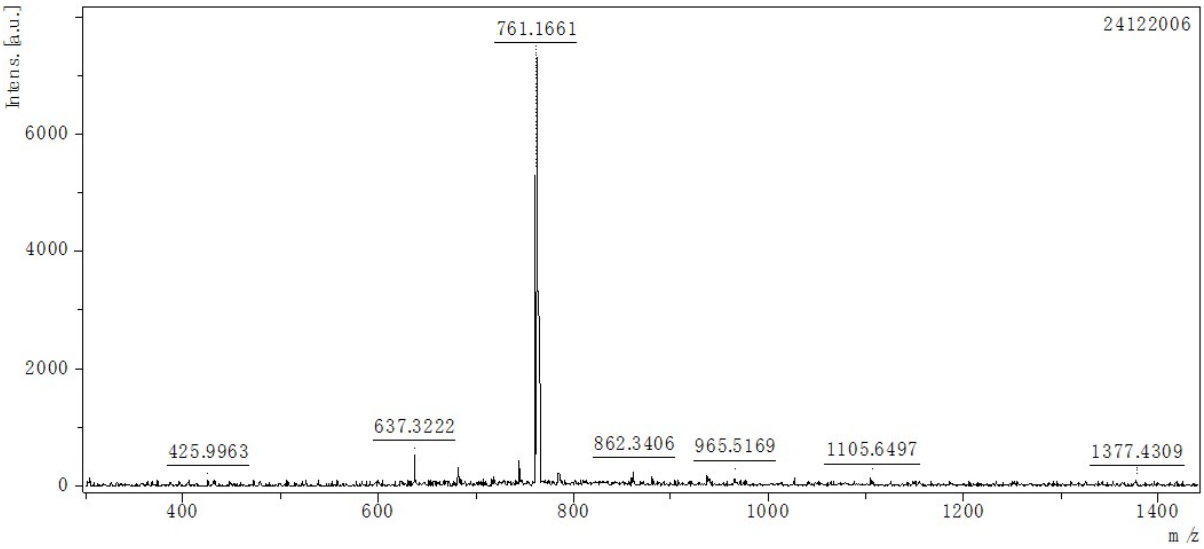


Figure S33. MALDI-TOF MS of **Ni6**.

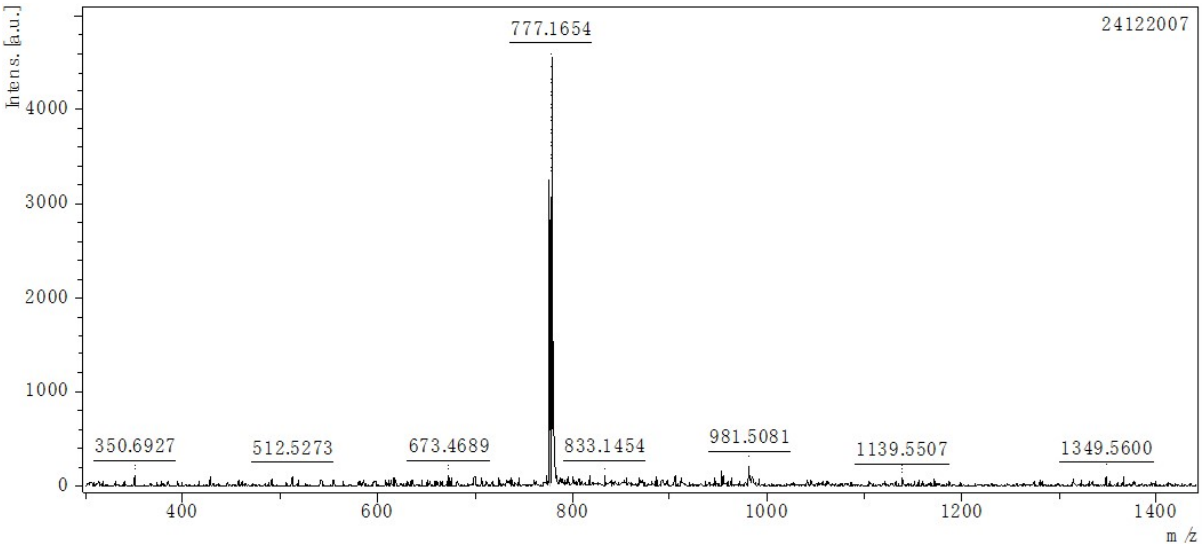


Figure S34. MALDI-TOF MS of **Ni7**.

2.3 ^{1}H NMR of Representative Polymers.

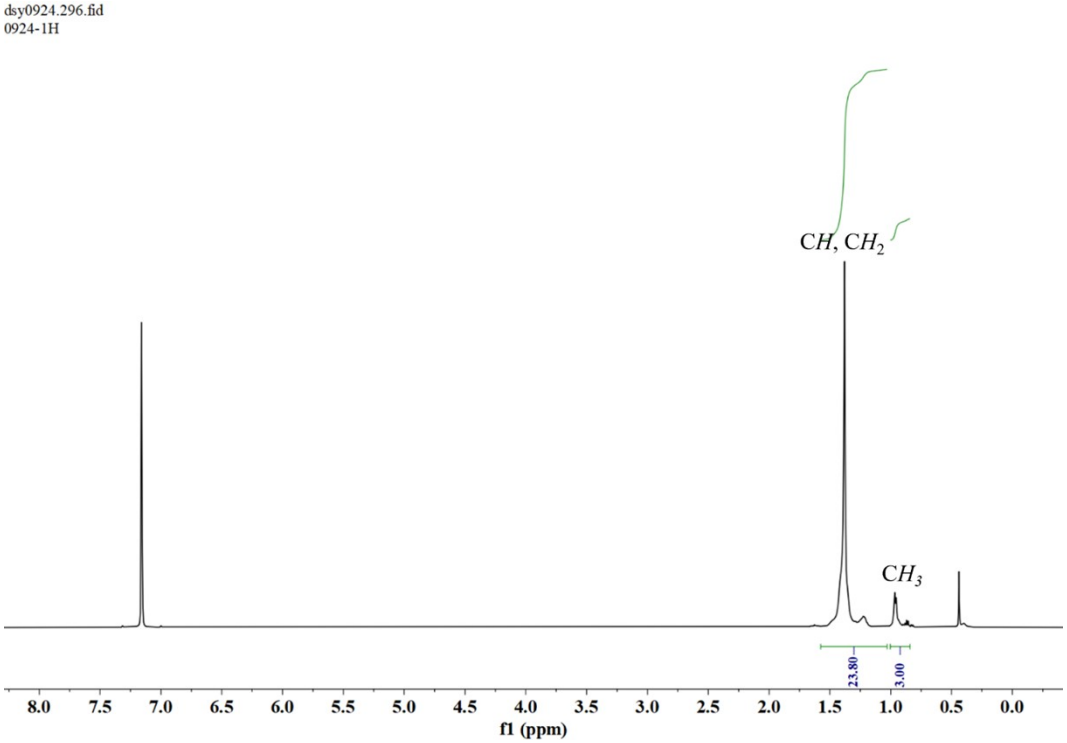


Figure S35. ^{1}H NMR spectrum of the polymer from table 1, entry 1 (d^{6}-benzene, 60 °C).

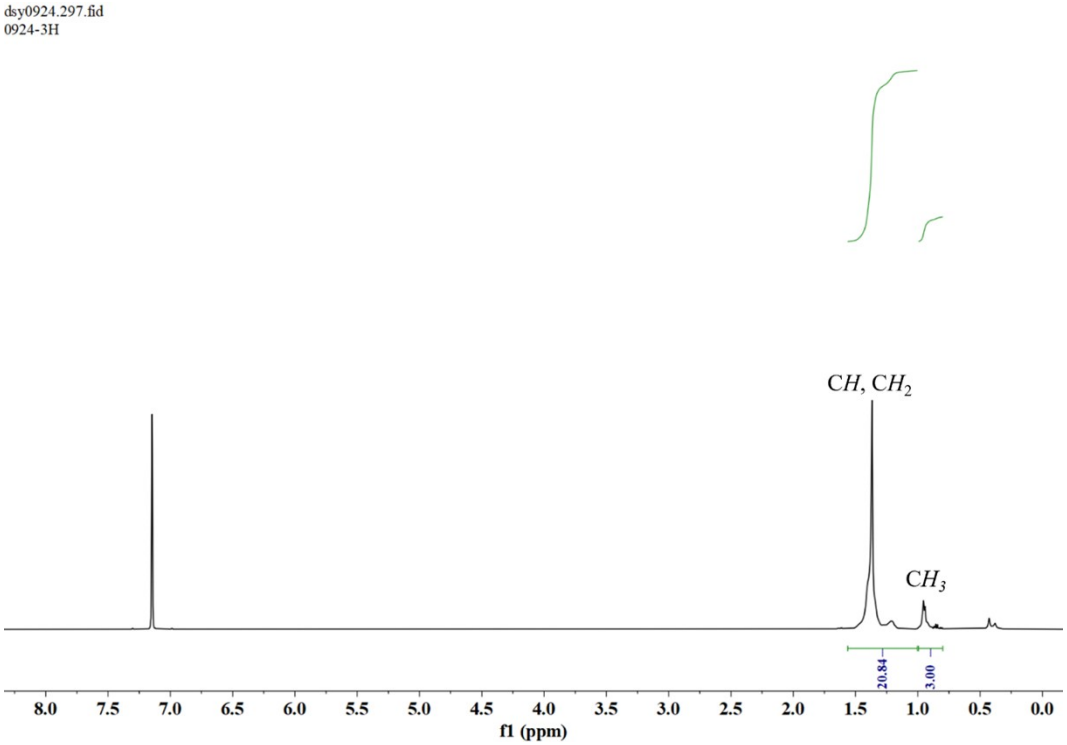


Figure S36. ^{1}H NMR spectrum of the polymer from table 1, entry 2 (d^{6}-benzene, 60 °C).

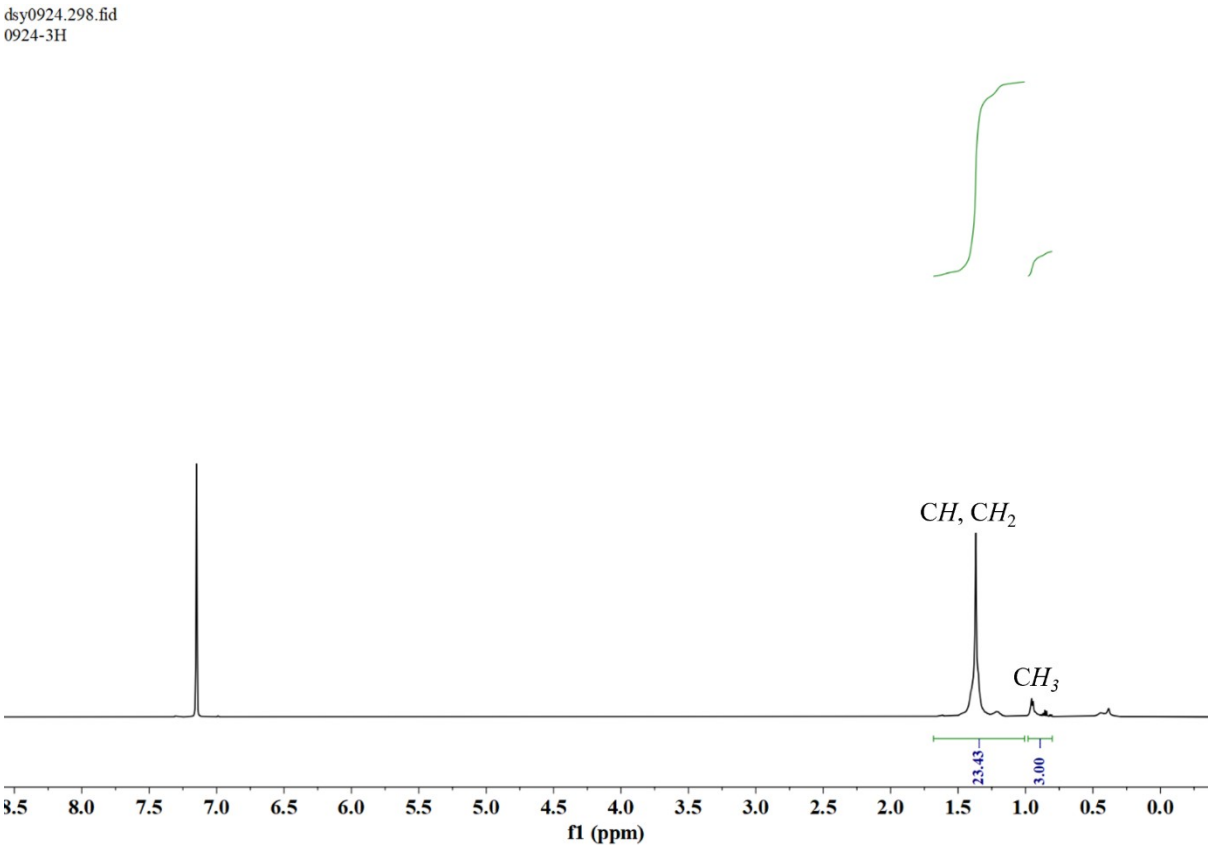


Figure S37. ^{1}H NMR spectrum of the polymer from table 1, entry 3 (d^{6}-benzene, 60 °C).

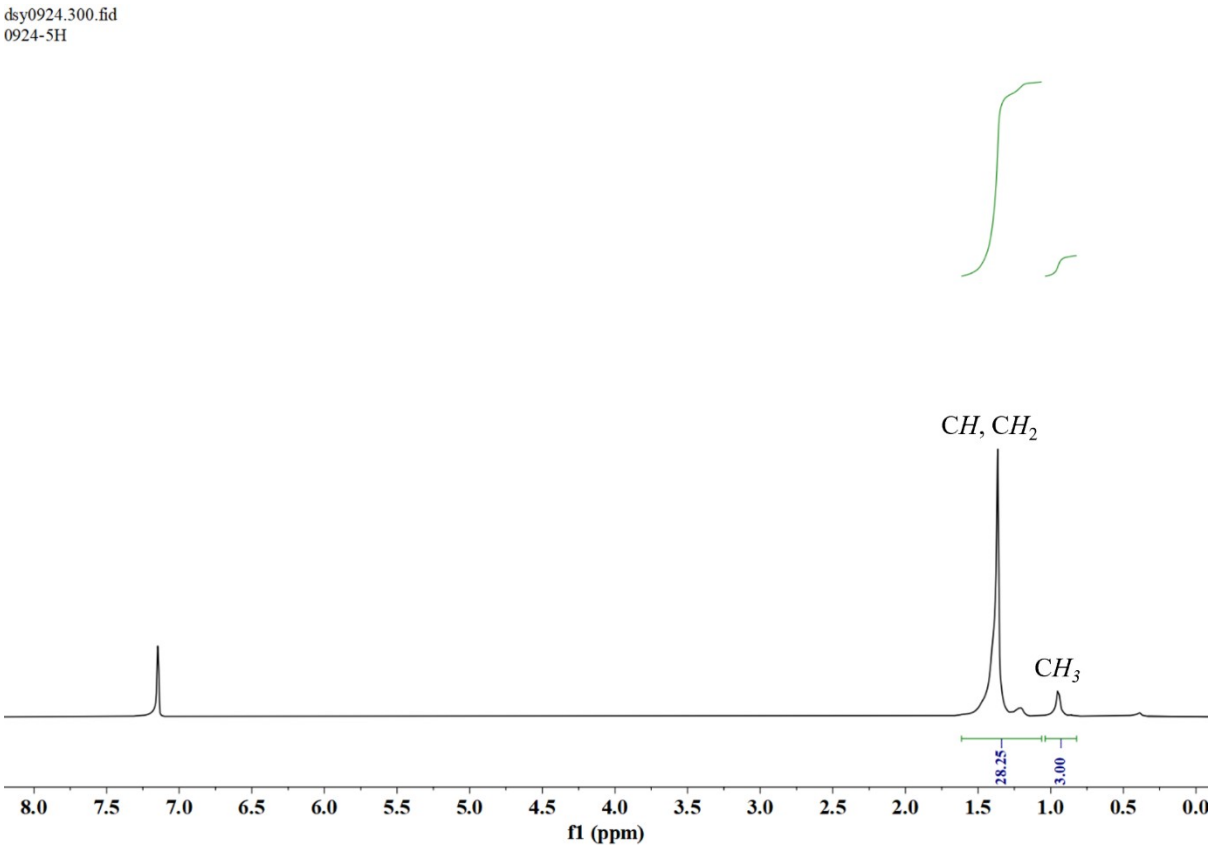


Figure S38. ^{1}H NMR spectrum of the polymer from table 1, entry 5 (d^{6}-benzene, 60 °C).

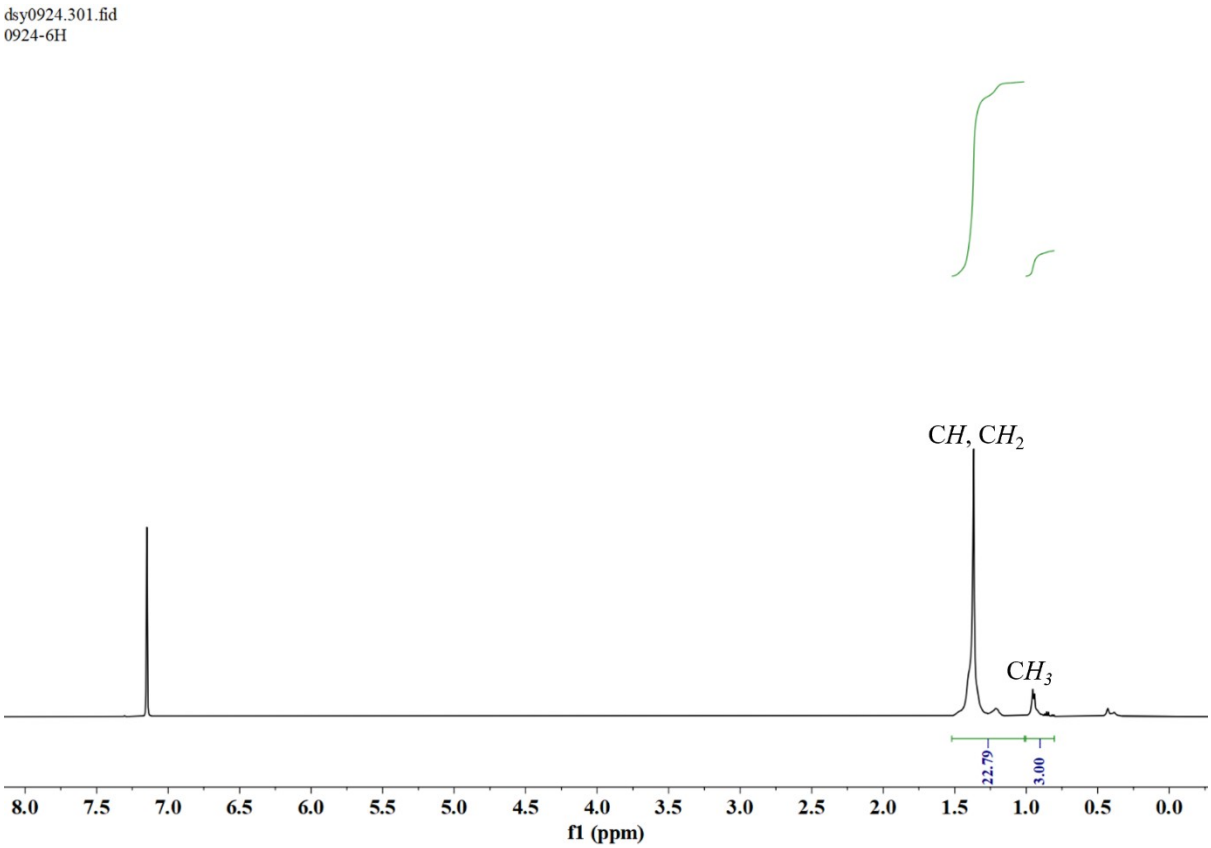


Figure S39. ^{1}H NMR spectrum of the polymer from table 1, entry 6 (d^{6}-benzene, 60 °C).

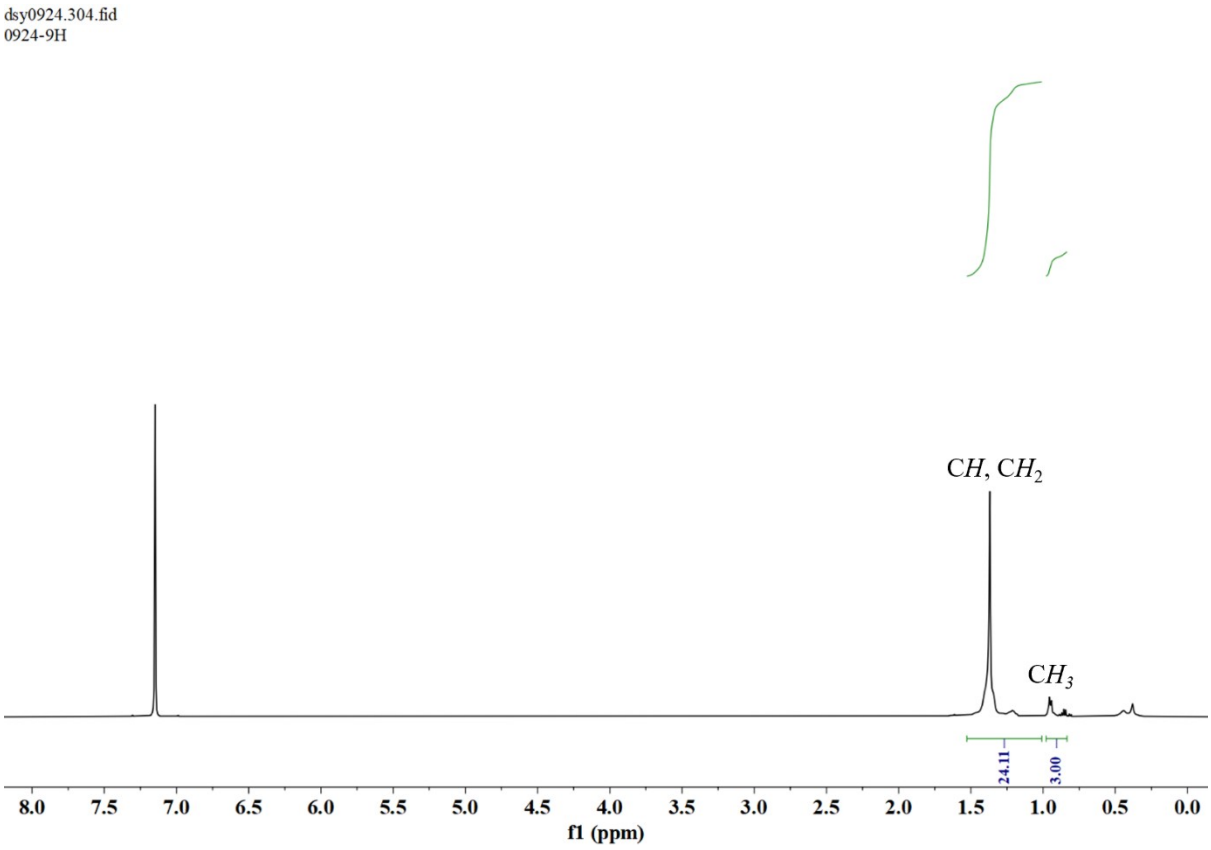


Figure S40. ^{1}H NMR spectrum of the polymer from table 1, entry 9 (d^{6}-benzene, 60 °C).

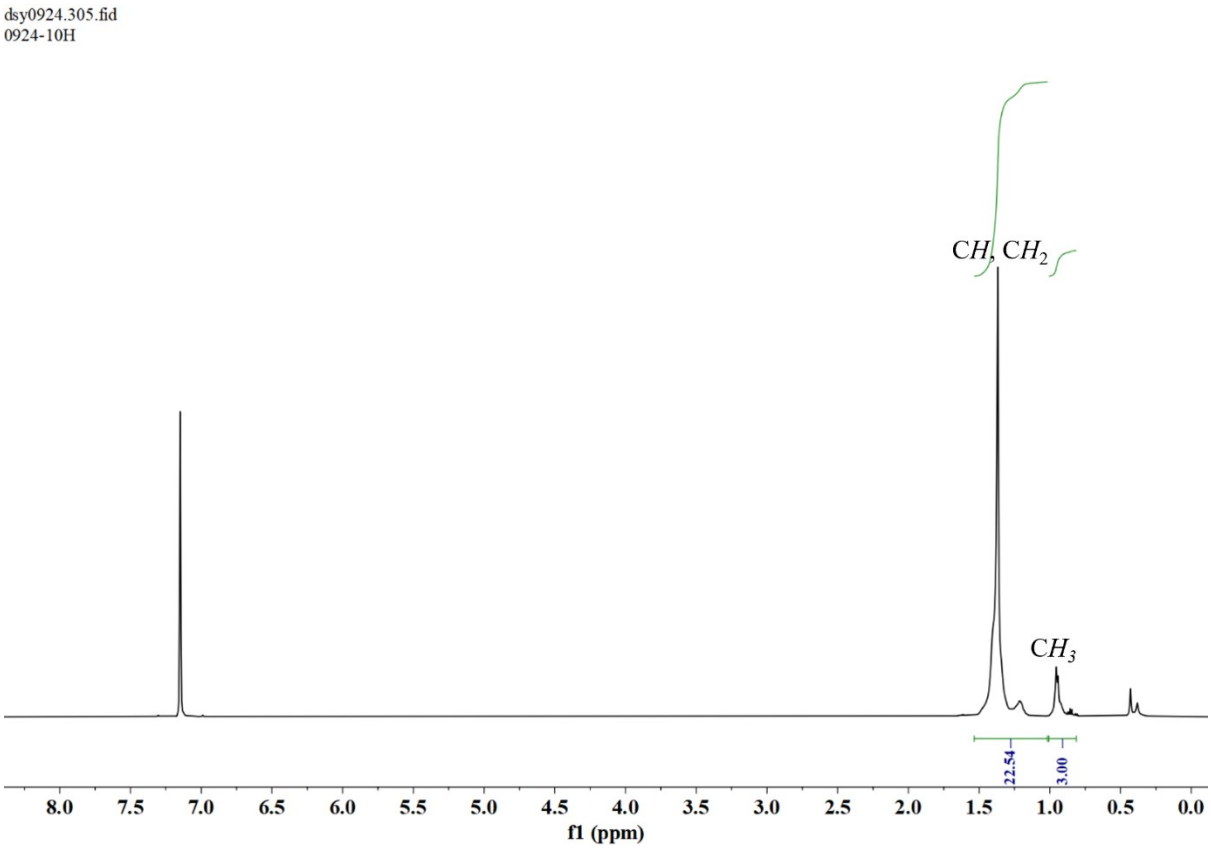


Figure S41. ^{1}H NMR spectrum of the polymer from table 1, entry 10 (d^{6}-benzene, 60 °C).

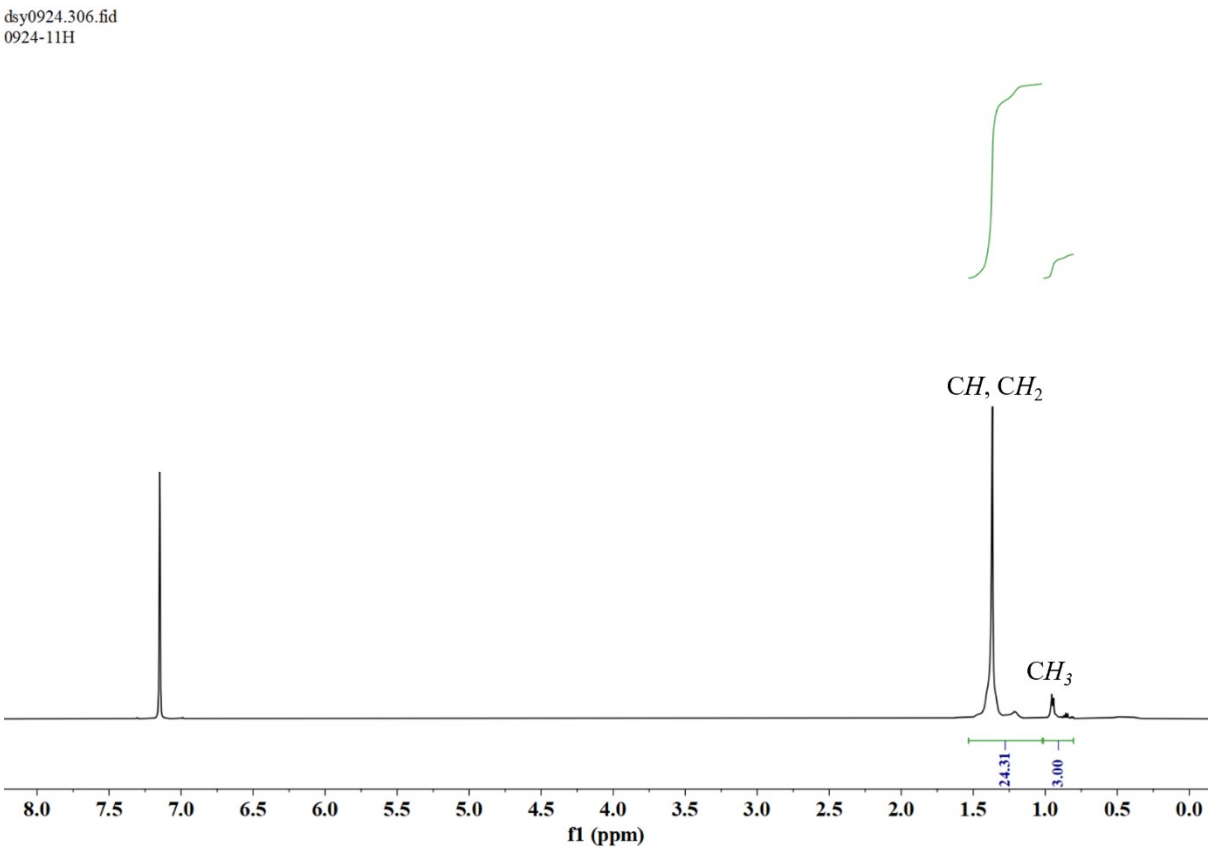


Figure S42. ^{1}H NMR spectrum of the polymer from table 1, entry 11 (d^{6}-benzene, 60 °C).

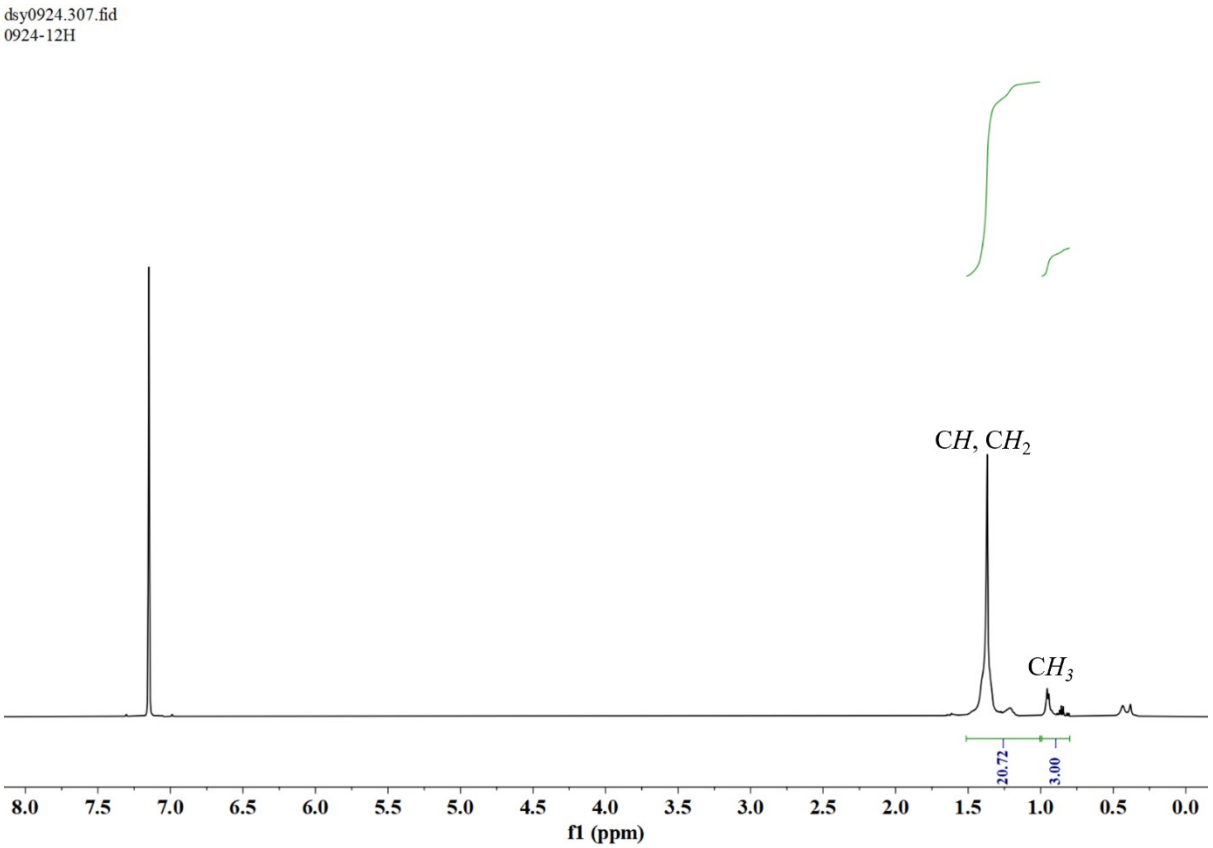


Figure S43. ^{1}H NMR spectrum of the polymer from table 1, entry 12 (d^{6}-benzene, 60 °C).

2.4 DSC and GPC of Representative Polymers.

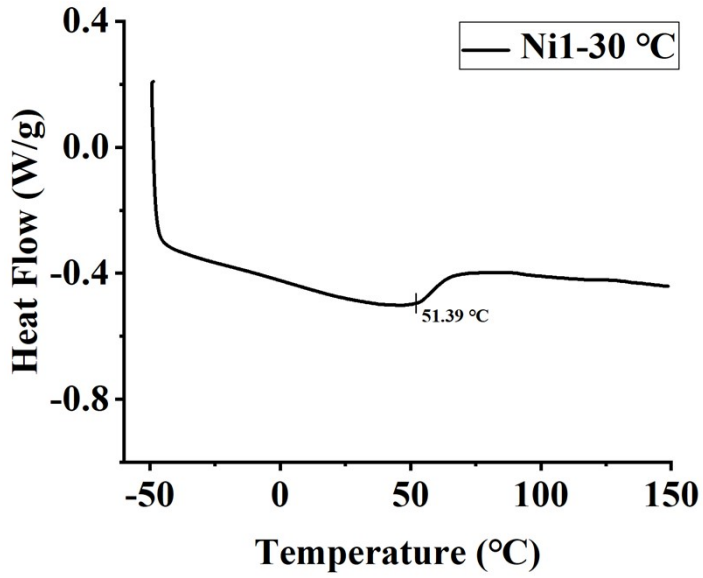


Figure S44. DSC of the polymer from table 1, entry 1.

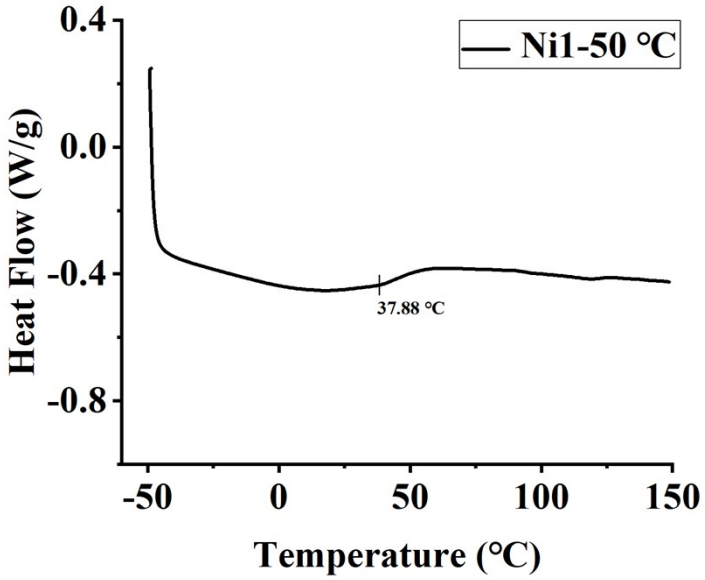


Figure S45. DSC of the polymer from table 1, entry 2.

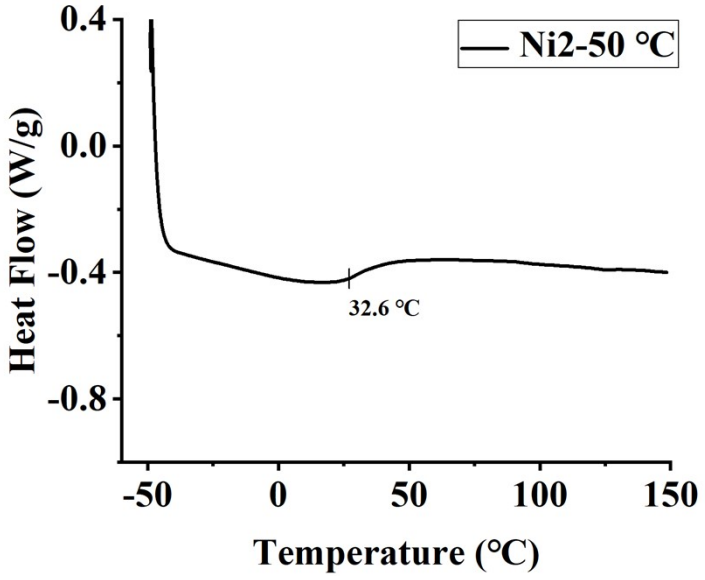


Figure S46. DSC of the polymer from table 1, entry 4.

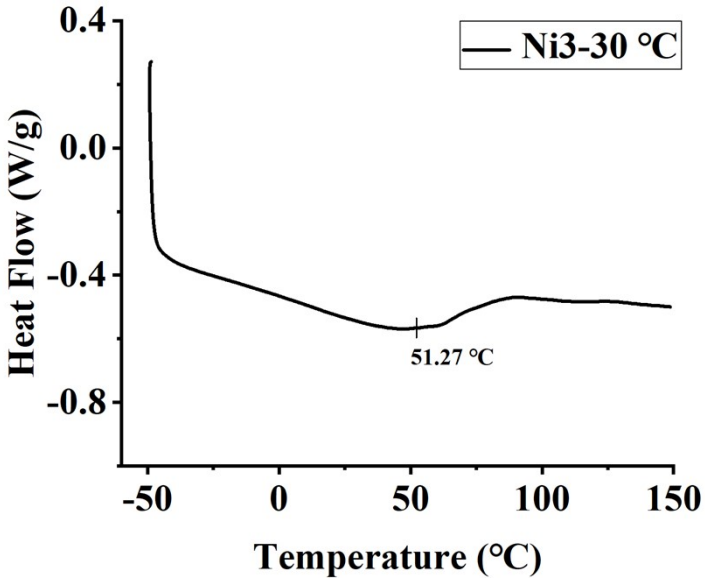


Figure S47. DSC of the polymer from table 1, entry 5.

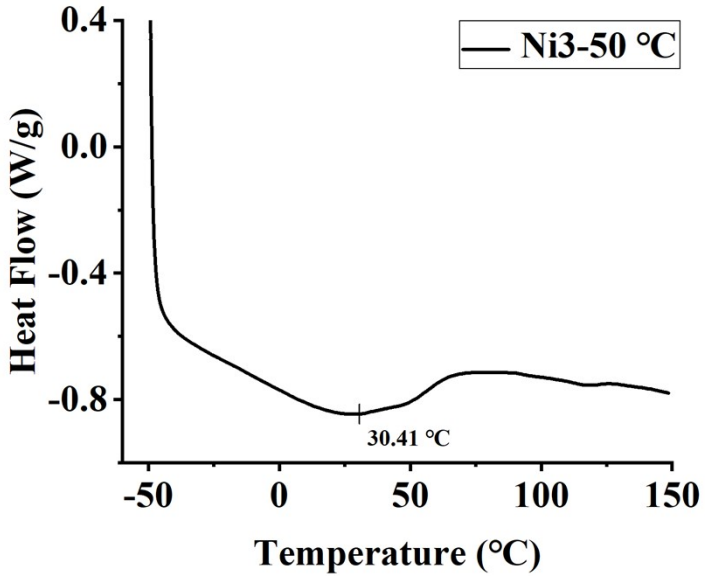


Figure S48. DSC of the polymer from table 1, entry 6.

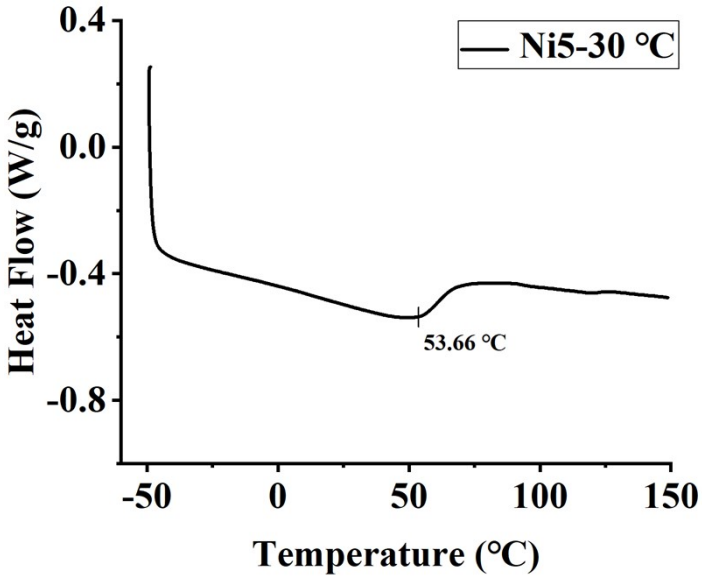


Figure S49. DSC of the polymer from table 1, entry 9.

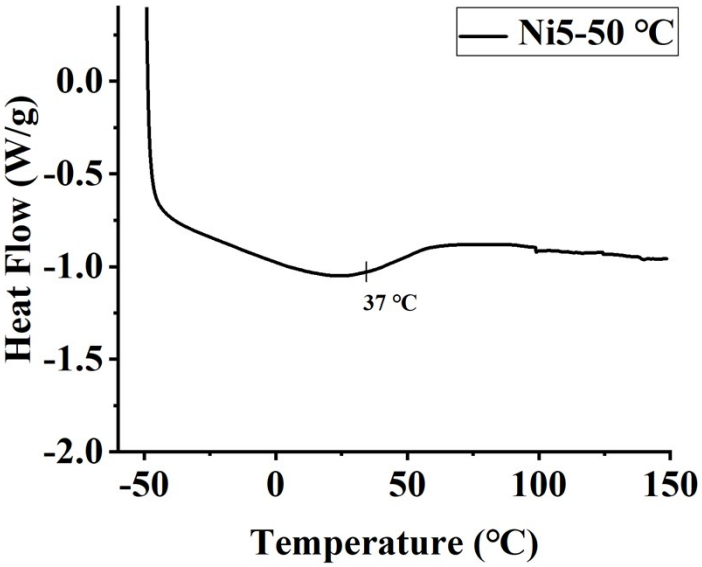


Figure S50. DSC of the polymer from table 1, entry 10.

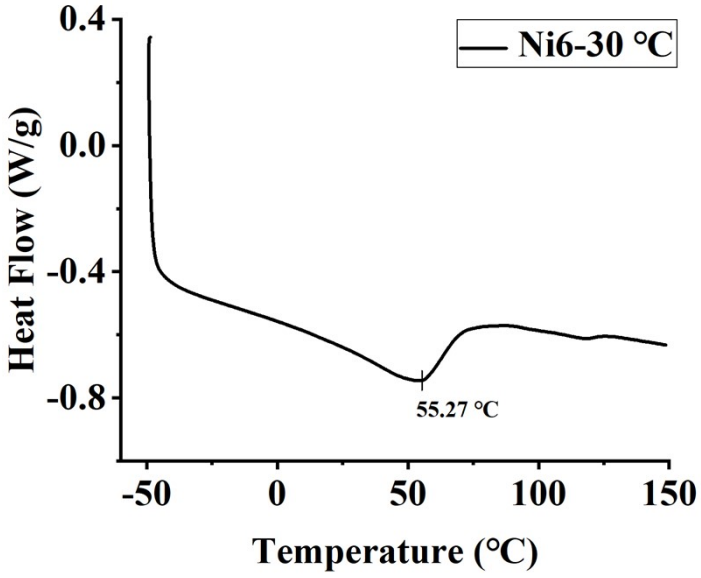


Figure S51. DSC of the polymer from table 1, entry 11.

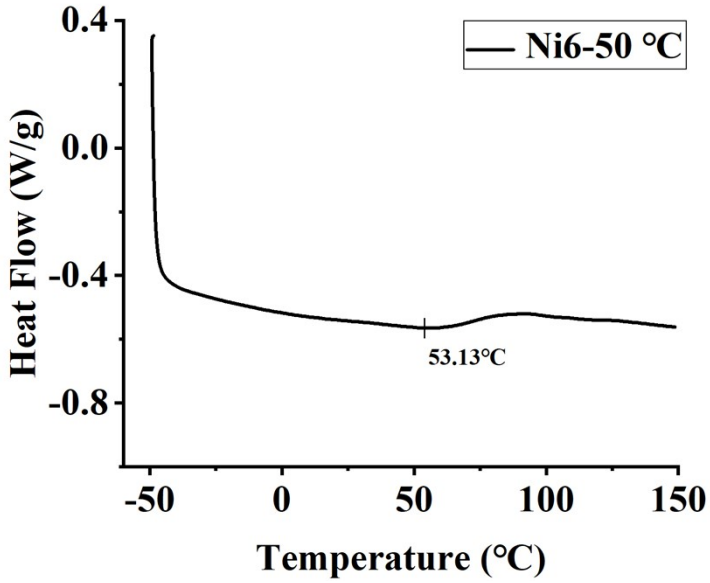


Figure S52. DSC of the polymer from table 1, entry 12.

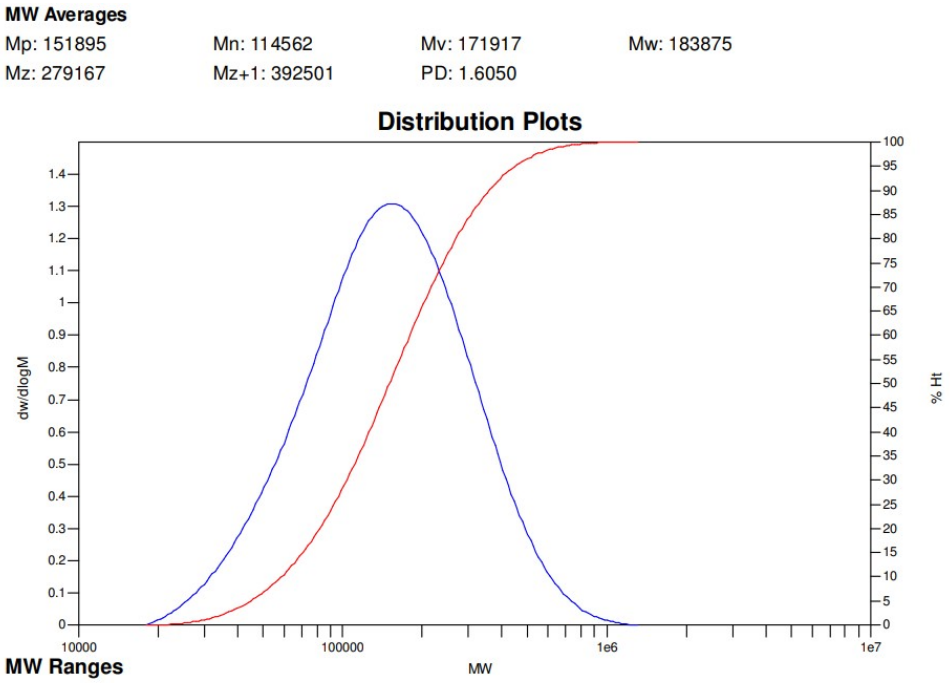


Figure S53. GPC of the polymer from table 1, entry 1.

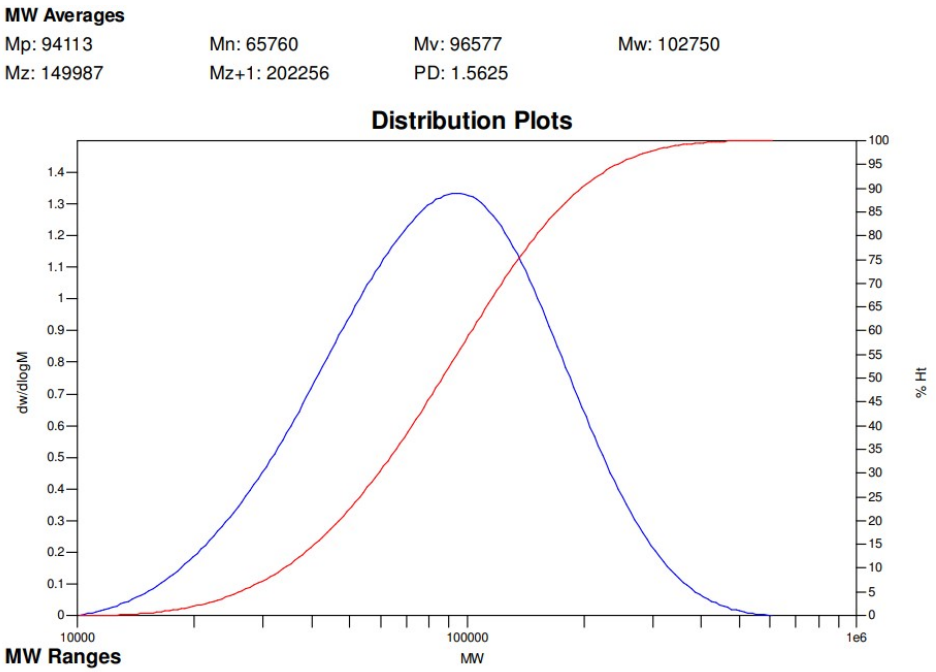


Figure S54. GPC of the polymer from table 1, entry 2.

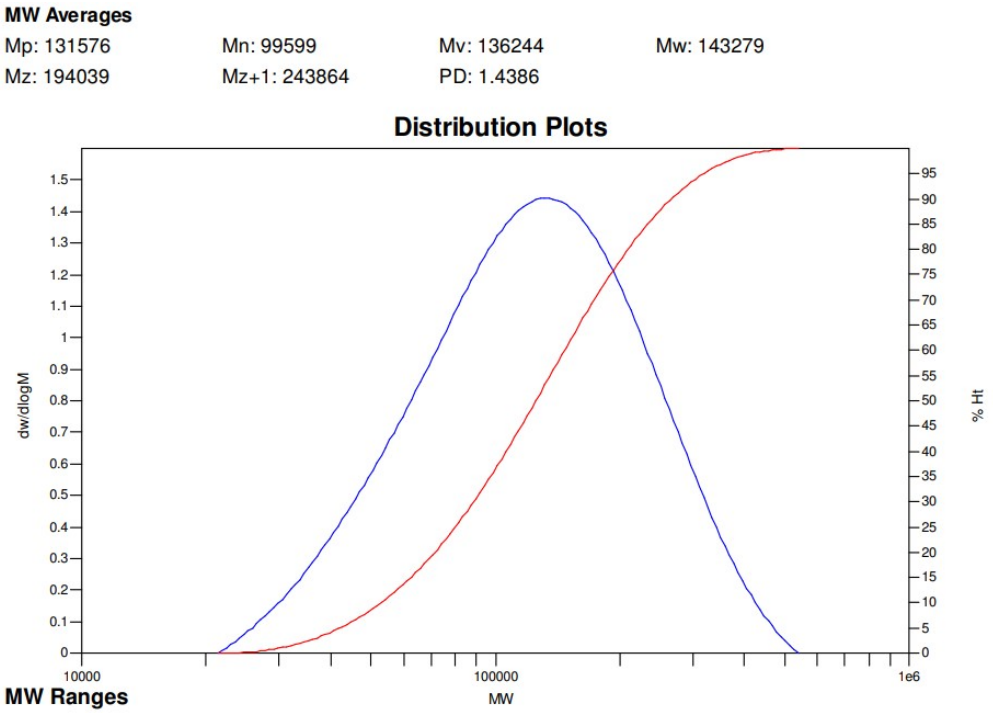


Figure S55. GPC of the polymer from table 1, entry 3.

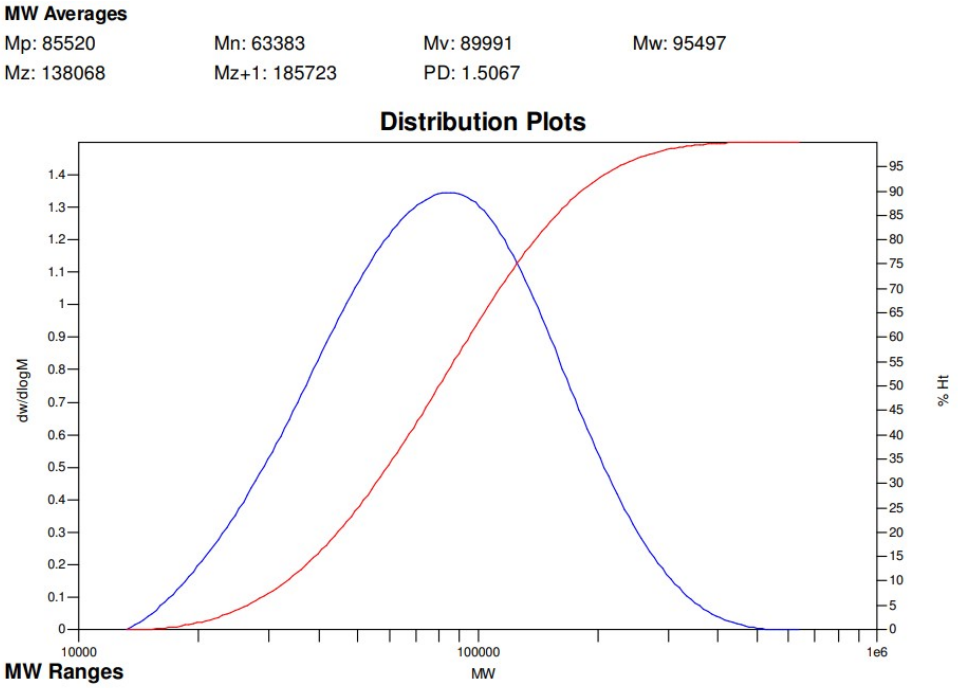


Figure S56. GPC of the polymer from table 1, entry 4.

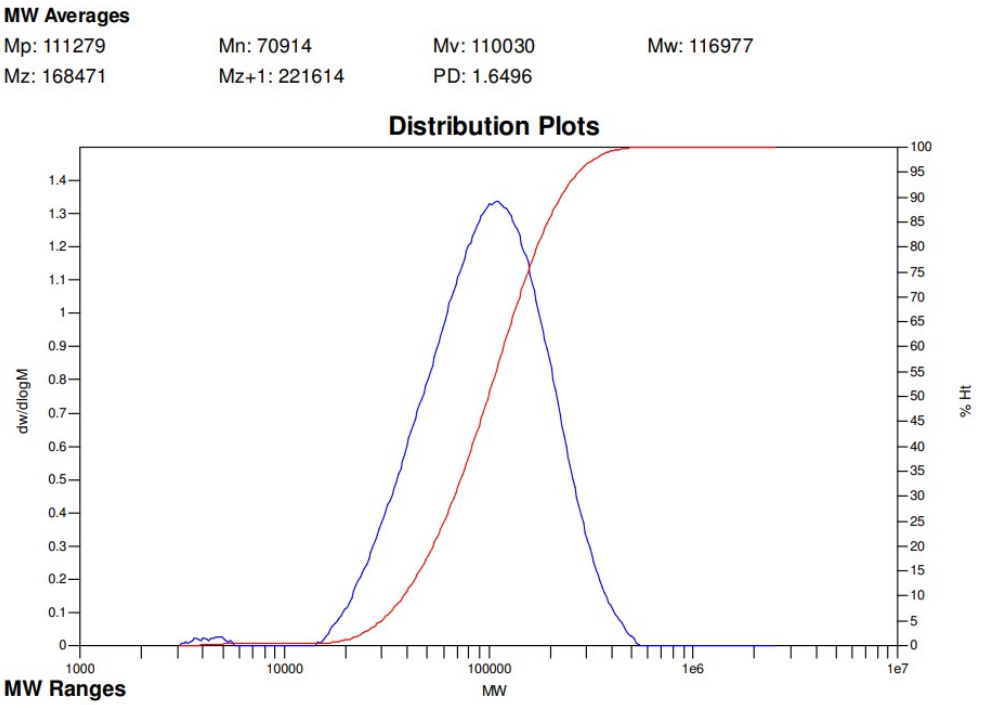


Figure S57. GPC of the polymer from table 1, entry 5.

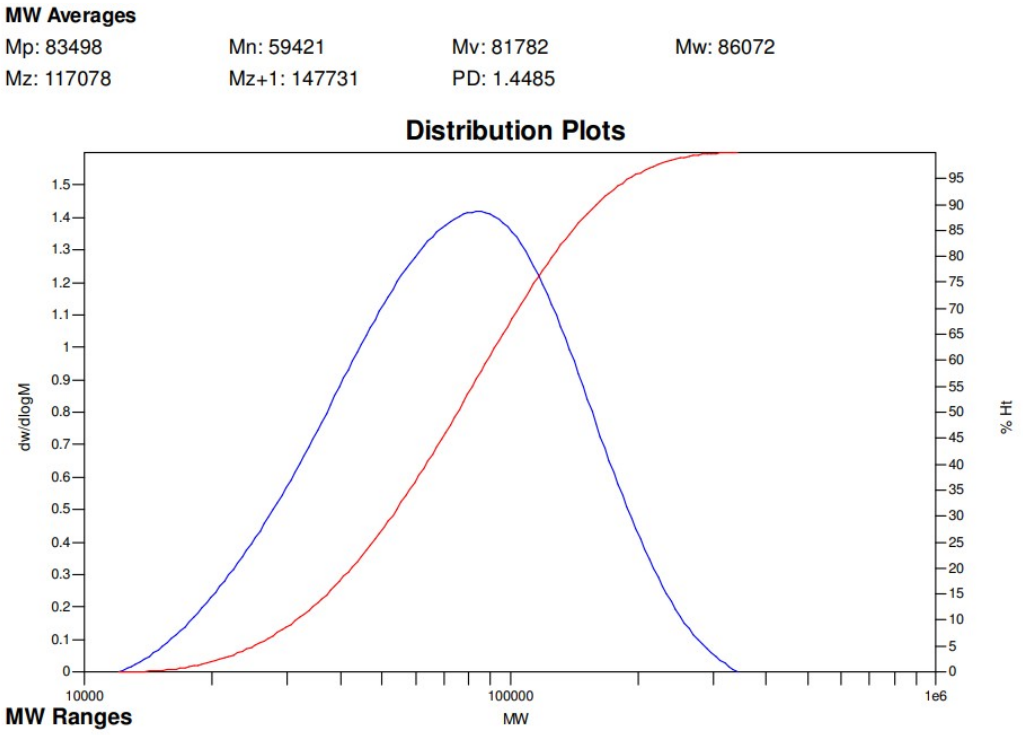


Figure S58. GPC of the polymer from table 1, entry 6.

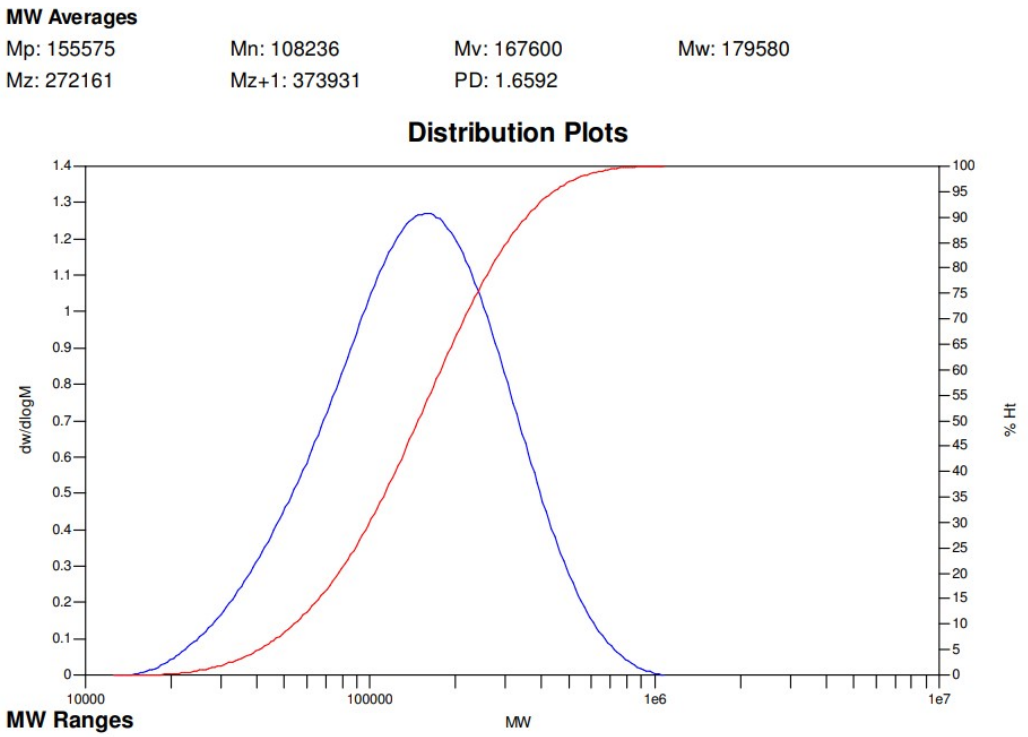


Figure S59. GPC of the polymer from table 1, entry 7.

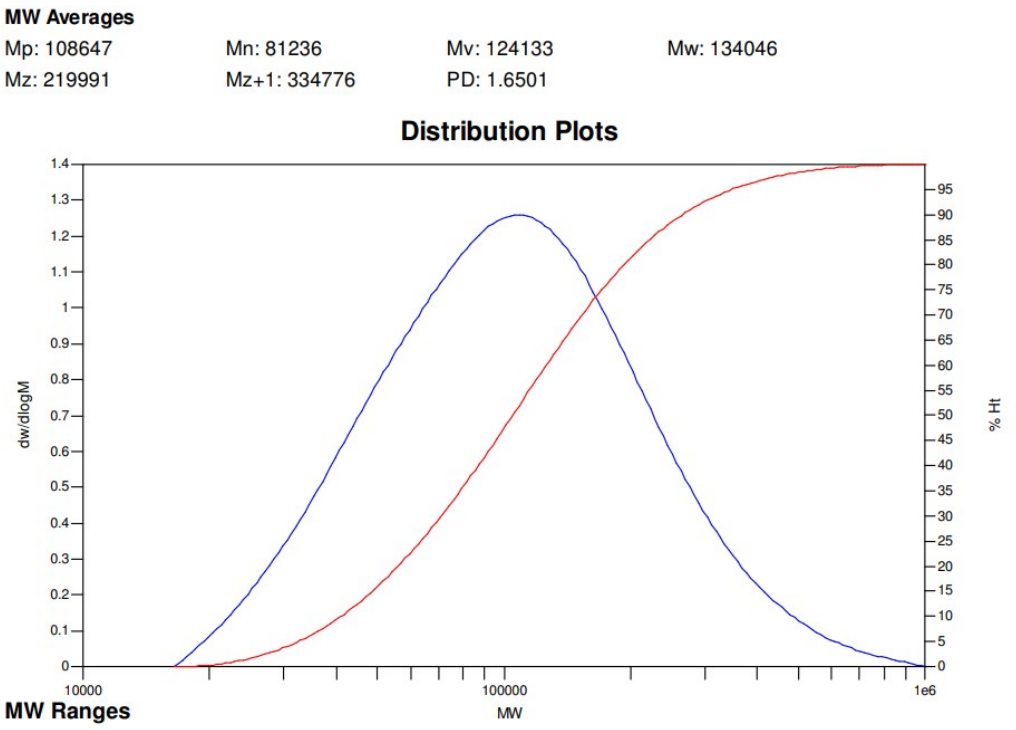


Figure S60. GPC of the polymer from table 1, entry 8.

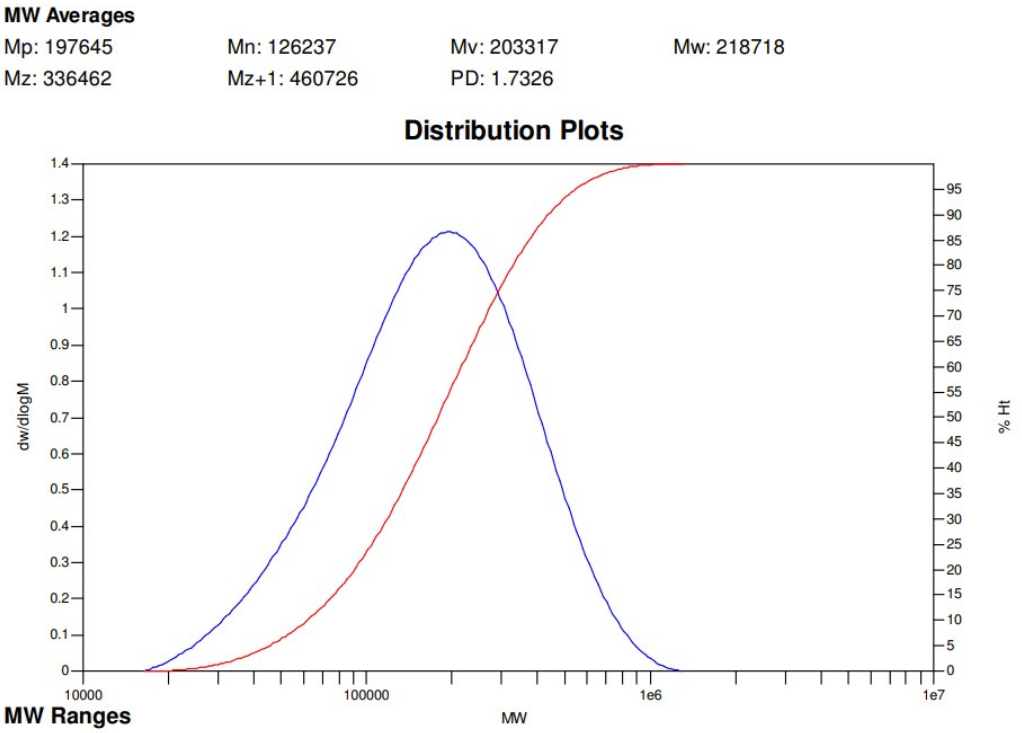


Figure S61. GPC of the polymer from table 1, entry 9.

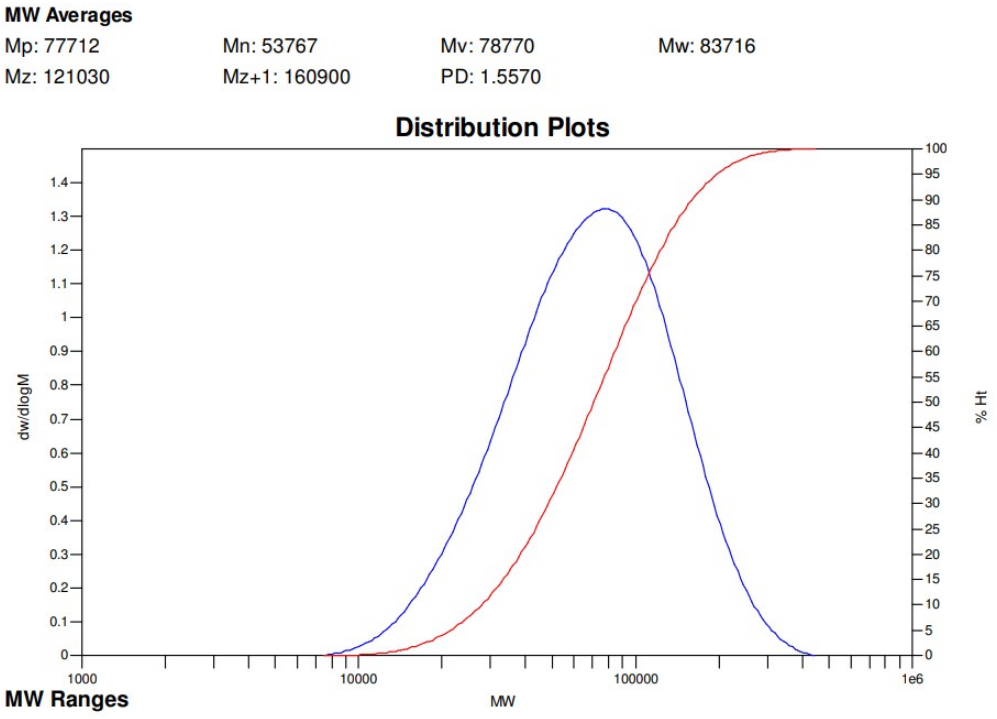


Figure S62. GPC of the polymer from table 1, entry 10.

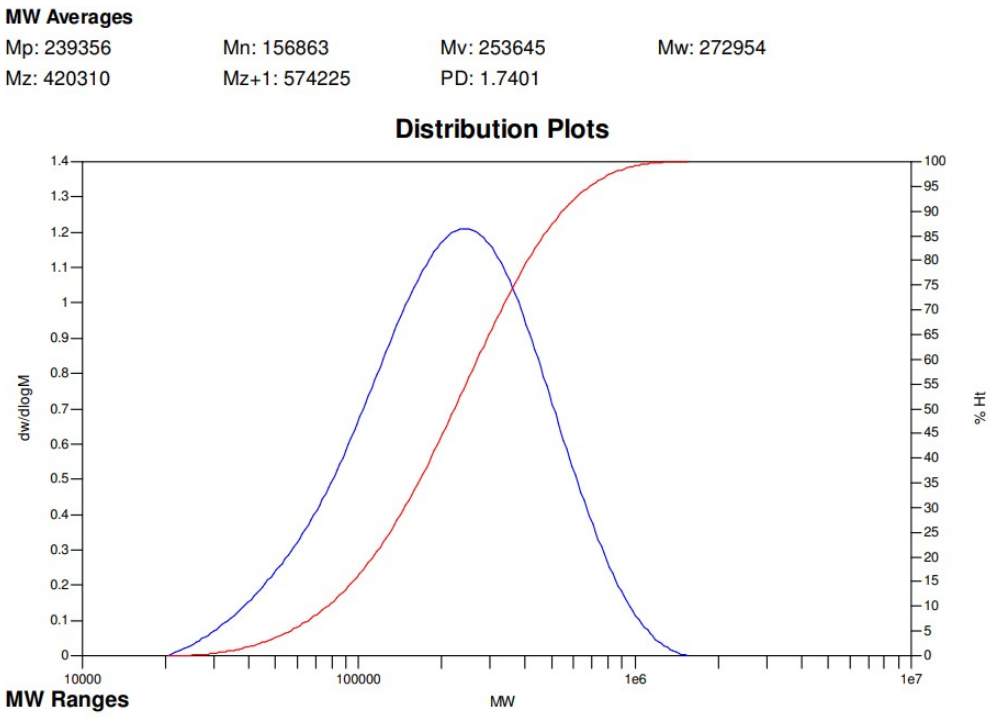


Figure S63. GPC of the polymer from table 1, entry 11.

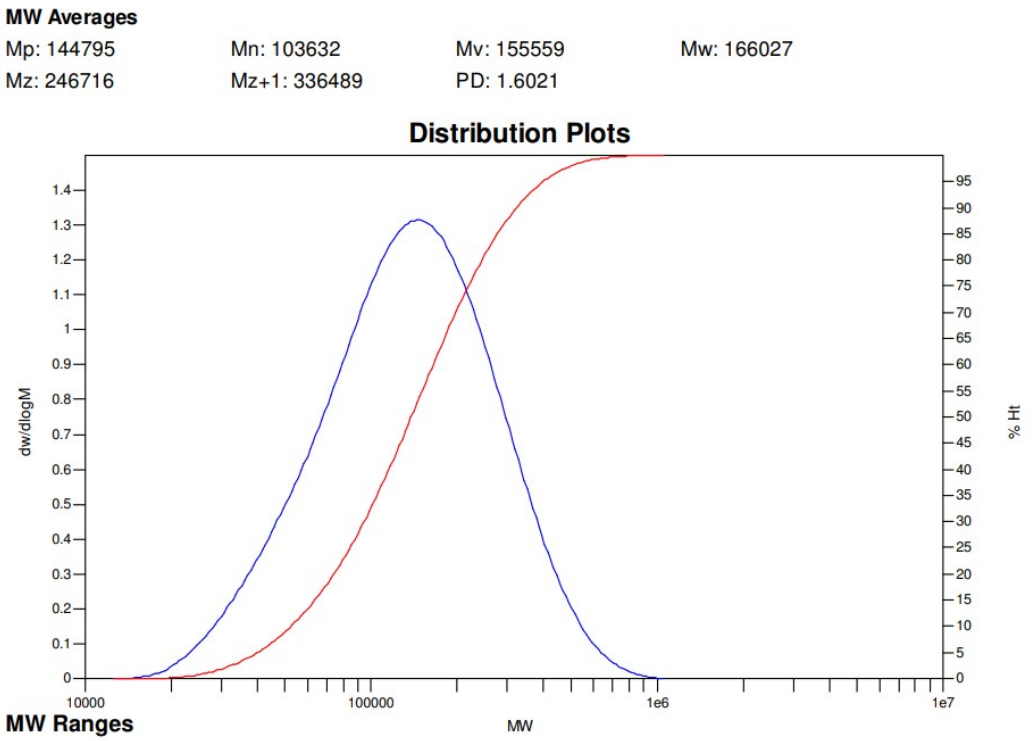


Figure S64. GPC of the polymer from table 1, entry 12.

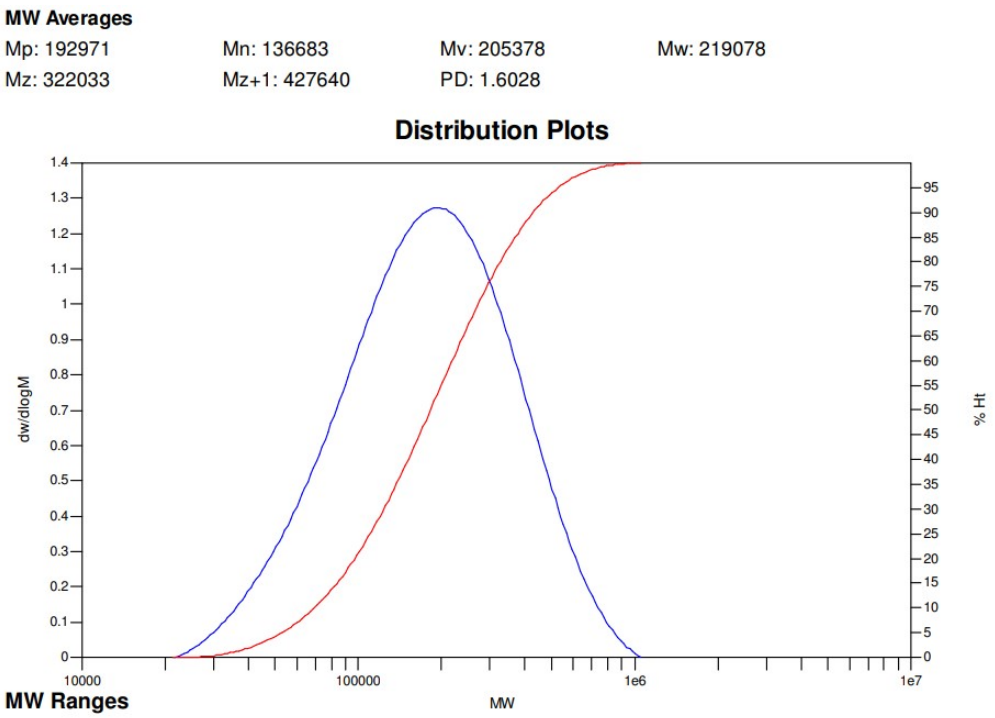


Figure S65. GPC of the polymer from table 1, entry 13.

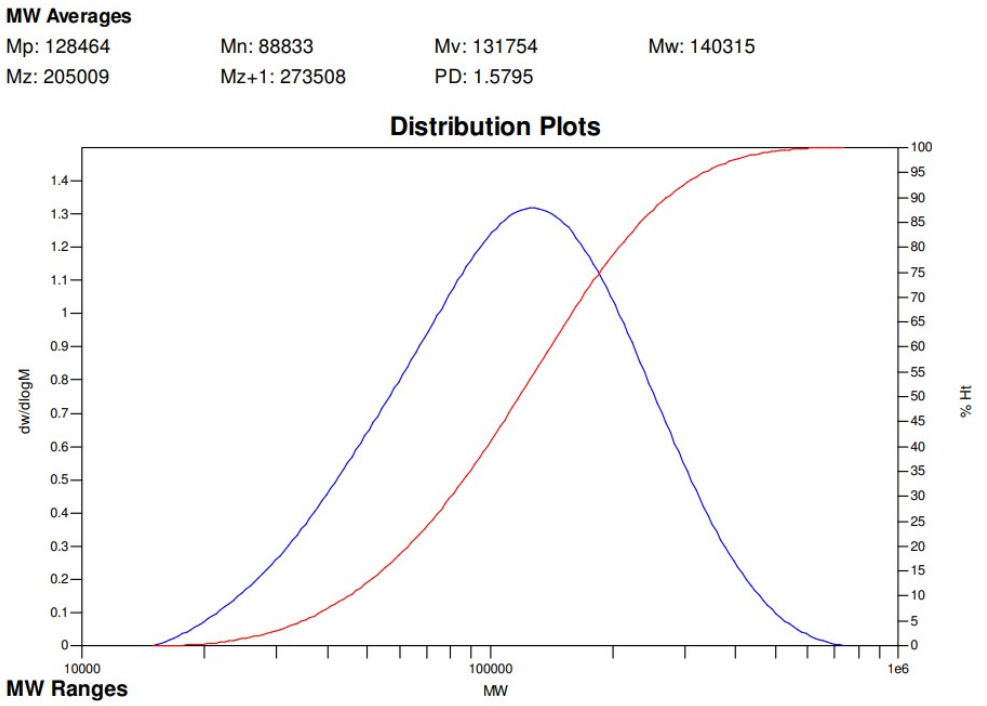


Figure S66. GPC of the polymer from table 1, entry 14.

3. References

[1] Li, S.; Dai, S. Highly Efficient Incorporation of Polar Comonomers in Copolymerizations with Ethylene Using Iminopyridyl Palladium System. *J. Catal.* **2021**, *393*, 51–59.