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Efficient Suppression of Chain Transfer Reaction in Ethylene Coordination Polymerization with Dibenzosuberyl Substituents

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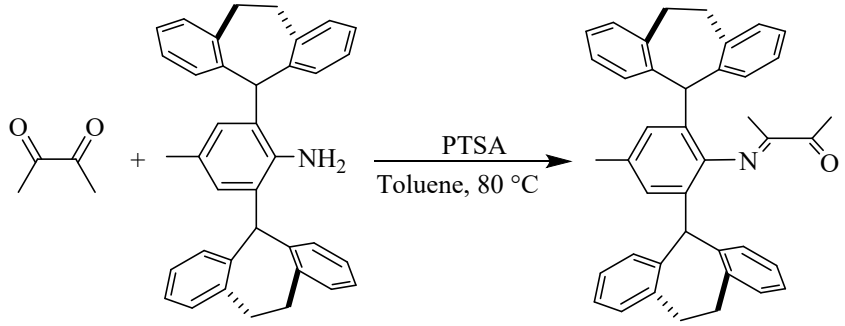
1.1 General Considerations

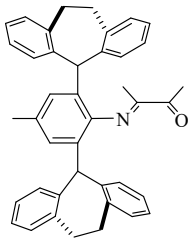
All chemicals were commercially sourced, except those whose synthesis is described. All experiments were carried out under a dry Nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H, ^{13}C NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer or a JEOL JNM-ECZ600R 600 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 using APCl-MS for **I1** and **L1**, **L2**. Mass spectra of **Ni1**, **Ni2** and **Pd1**, **Pd2** were determined on a Atouflex Speed MALDI-TOF MS. Elemental analysis was performed by the Analytical Center of the Anhui University. 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 with low solubility at room temperature 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 ^{o}C using trichlorobenzene as a solvent and calibrated with polystyrene standards. The molecular weight and the molecular weight distribution of the polymers with good solubility at room temperature were determined by gel permeation chromatography

(GPC) equipped with two linear Styragel columns (HR2 and HR4) at 40°C using THF as a solvent and calibrated with polystyrene standards, and THF was employed as the eluent at a flow rate of 1.0 mL/min. Differential scanning calorimetry(DSC). 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 -80°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 α-Keto-imine I1.



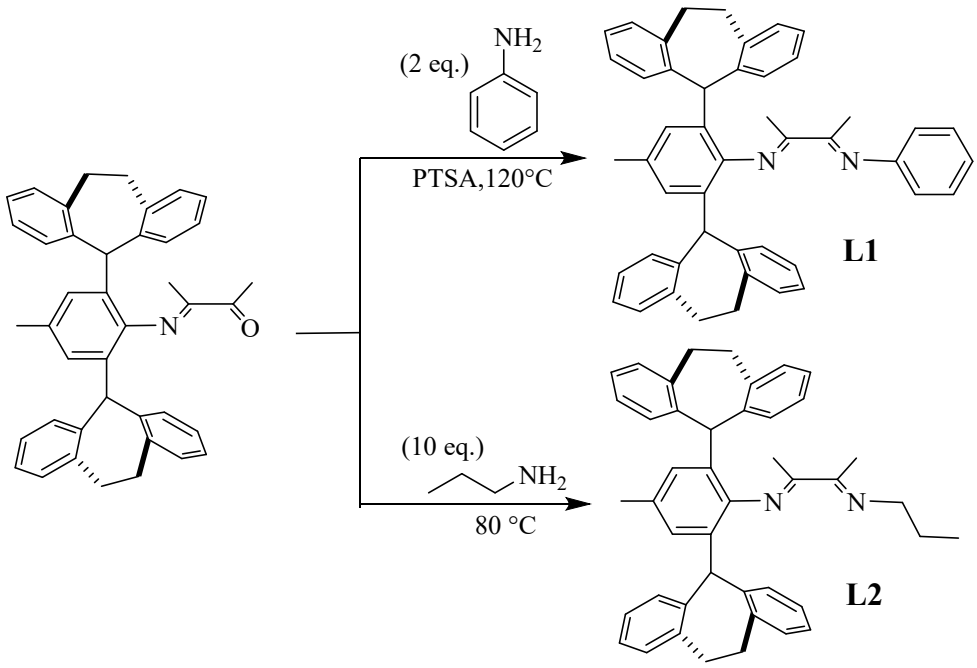
A solution of arylamine (10 mmol), 2, 3-butadione (30 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (100 mL) was stirred at 80 °C for 24 h, until there was one main point on the TLC plate. The solvent was partially evaporated under reduced pressure until the formation of a light yellow solid. The remaining solution was diluted in methanol (100 mL). The yellow solid was isolated by filtration, dried by vacuum.



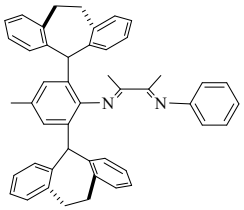
I1: (4.9 g, 88%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 – 6.94 (m, 16H, aryl-*H*), 6.68 (s, 2H, aryl-*H*), 4.77 (s, 2H, C*H*Ar$_2$), 3.43 (ddd, *J* = 15.1, 9.7, 5.1 Hz, 2H, C*H*$_2$CH$_2$), 3.30 (ddd, *J* = 16.5, 7.1, 5.1 Hz, 2H, C*H*$_2$CH$_2$), 2.77 (ddd, *J* = 15.8, 9.7, 5.3 Hz, 2H, C*H*$_2$CH$_2$), 2.61 (ddd, *J* = 15.4, 7.2, 5.4 Hz, 2H, C*H*$_2$CH$_2$), 2.38 (s, 3H, O=CC*H*$_3$), 2.10 (s, 3H, aryl-C*H*$_3$), 0.73 (s, 3H, N=CC*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.75

(*C*=O), 169.45 (*C*=N), 144.04, 141.04, 139.98, 139.60, 139.36, 130.97, 130.81, 130.31, 129.87, 129.39, 127.22, 127.06, 126.21, 56.34 (*C*HPh$_2$), 32.16 (CH$_2$*C*H$_2$), 31.23(CH$_2$*C*H$_2$), 24.81 (O=C-*C*H$_3$), 21.62 (aryl-*C*H$_3$), 14.38 (N=C-*C*H$_3$). APCI-MS (m/z): calcd for $C_{41}H_{38}NO^+$: 560.2875, Found, 560.2896, $[M+H]^+$.

1.3 Procedure for the Synthesis of Ligands L1, L2.

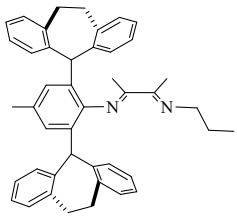


A mixture of α-imino-ketone (2 mmol) and aniline (4.0 mmol) or N-propylamine (20 mmol) in toluene (40 mL) was stirred at 120 °C or 80 °C for 24 h. The solvent was evaporated under reduced pressure. The remaining mixture was diluted with methanol (100 mL). The resulting yellow solid was collected by filtration to give the desired product.



L1: (0.93 g, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.6 Hz, 2H, aryl-*H*), 7.20 – 7.16 (m, 2H, aryl-*H*), 7.14 – 7.09 (m, 7H, aryl-*H*), 7.08 – 7.03 (m, 8H, aryl-*H*), 6.86 (d, *J* = 7.7 Hz, 2H, aryl-*H*), 6.73 (s, 2H, aryl-*H*), 4.90 (s, 2H, C*H*Ar$_2$), 3.52 (ddd,

J = 15.1, 9.7, 5.1 Hz, 2H, CH_2CH_2), 3.38 (dt, *J* = 16.3, 6.1 Hz, 2H, CH_2CH_2), 2.82 (ddd, *J* = 15.8, 9.7, 5.4 Hz, 2H, CH_2CH_2), 2.67 (dt, *J* = 15.4, 6.1 Hz, 2H, CH_2CH_2), 2.15 (s, 3H, aryl-CH_3), 2.04 (s, 3H, N=CCH_3), 0.99 (s, 3H, N=CCH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.97 (N=*C*), 167.83 (N=*C*), 151.38, 145.22, 141.35, 140.10, 139.43, 130.92, 130.26, 129.83, 129.19, 127.07, 126.93, 126.09, 123.83, 118.56, 56.43 (*C*HAr_2), 32.26 (*C*H_2CH_2), 31.33 (*C*H_2*C*H_2), 21.67 (aryl-*C*H_3), 15.73 (N=C-*C*H_3), 15.71 (N=C-*C*H_3). APCI-MS (m/z): calcd for $C_{47}H_{43}N_2^+$: 635.3348, Found, 635.3345, $[M+H]^+$.

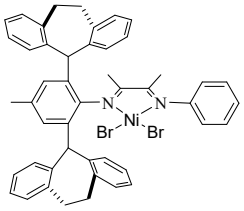


L2: (0.94 g, 78%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 7.8, 3.9 Hz, 2H, aryl-*H*), 7.09 (d, *J* = 7.2 Hz, 2H, aryl-*H*), 7.05 – 6.99 (m, 8H, aryl-*H*), 6.94 (dd, *J* = 23.9, 7.4 Hz, 4H, aryl-*H*), 6.69 (s, 2H, aryl-*H*), 4.84 (s, 2H, C*H*Ar_2), 3.54 – 3.50 (m, 2H, CH_2CH_2), 3.49 – 3.44 (m, 2H, CH_2CH_2CH_3), 3.42 – 3.32 (m, 2H, CH_2CH_2), 2.76 (ddd, *J* = 15.5, 9.4, 5.2 Hz, 2H, CH_2CH_2), 2.66 (dt, *J* = 13.7, 6.3 Hz, 2H, CH_2CH_2), 2.12 (s, 3H, aryl-CH_3), 2.07 (s, 3H, N=CCH_3), 1.78 (q, *J* = 7.4 Hz, 2H, CH_2CH_2CH_3), 1.08 (t, *J* = 7.4 Hz, 2H, CH_2CH_2CH_3), 0.98 (s, 3H, N=CCH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.02 (N=*C*), 166.87 (N=*C*), 145.52, 141.07, 140.05, 139.54, 131.18, 131.03, 130.66, 130.20, 129.72, 126.80, 125.98, 56.21 (*C*HAr_2), 54.69 (*C*H_2CH_2CH_3), 32.14 (*C*H_2*C*H_2), 31.52 (*C*H_2*C*H_2), 23.95 (CH_2*C*H_2CH_3), 21.62 (aryl-*C*H_3), 15.61 (N=C-*C*H_3), 12.85 (N=C-*C*H_3), 12.44 (CH_2CH_2*C*H_3). APCI-MS (m/z): calcd for $C_{44}H_{45}N_2^+$: 601.3504, Found, 601.3511, $[M+H]^+$.

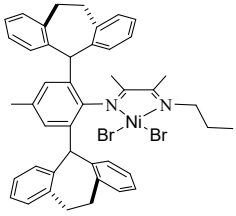
1.4 Procedure for the Synthesis of Nickel Complexes Ni1-2:

The nickel complexes were prepared in a similar manner by the reaction of 0.2 mmol ligands with 1 equivalent (DME)$NiBr_2$ in dichloromethane. After stirring overnight,

the solvent was removed, and the brown solid powder was washed with ether (10 mL × 2) and dried under vacuum to give the corresponding nickel complexes.



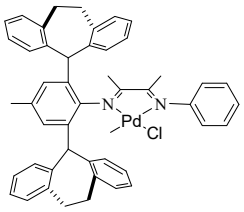
Ni1: (157 mg, 92%). ESI-MS (m/z): calcd for $C_{47}H_{42}BrN_2Ni$: 771.18, Found, 771.33, $[M\text{-}Br]^+$. Elemental analysis: calc. for $C_{47}H_{42}Br_2N_2Ni$: C, 66.15; H, 4.96; N, 3.28. Found: C, 66.27; H, 5.08; N, 3.19.



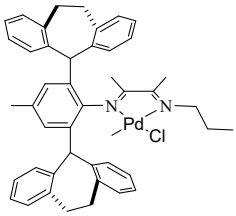
Ni2: (149 mg, 91%). ESI-MS (m/z): calcd for $C_{44}H_{44}BrN_2Ni^+$: 737.20, Found, 737.44, $[M\text{-}Br]^+$. Elemental analysis: calc. for $C_{44}H_{44}Br_2N_2Ni$: C, 64.50; H, 5.41; N, 3.42. Found: C, 64.67; H, 5.48; N, 3.59.

1.5 Procedure for the Synthesis of Palladium Complexes Pd1-2.

A mixture of the ligand (1 mmol), Pd(COD)MeCl (265 mg, 1 mmol) in CH_2Cl_2 (20 mL) was stirred for 1 day at room temperature. During stirring, the color of the solution was deepening. At the end of the reaction, the solution was concentrated to 5 mL. The product was crashed out with 20 ml ether and washed with ether (3 × 5 mL). Then dried under reduced pressure at room temperature for about 5 h. The pure compound was obtained as a red solid.



Pd1: (664 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H, aryl-*H*), 7.56 (dt, *J* = 15.5, 7.8 Hz, 2H, aryl-*H*), 7.48 – 7.30 (m, 1H, aryl-*H*), 7.19 – 6.90 (m, 16H, aryl-*H*), 6.79, 6.70 (s, 2H, aryl-*H*), 5.82, 5.59 (s, 2H, C*H*Ar_2), 3.71 (dtd, *J* = 35.5, 13.9, 4.3 Hz, 2H, CH_2CH_2), 3.47 – 3.30 (m, 2H, CH_2CH_2), 3.10 – 2.86 (m, 2H, CH_2CH_2), 2.48 (dt, *J* = 13.7, 3.8 Hz, 2H, CH_2CH_2), 2.13, 2.09 (s, 3H, aryl-CH_3), 1.44, 1.40 (s, 3H, N=CCH_3), 0.80, 0.79 (s, 3H, Pd-CH_3), -0.04, -0.16 (s, 3H, N=CCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.85 (N=*C*), 175.98 (N=*C*), 175.68 (N=*C*), 169.93 (N=*C*), 147.15, 145.98, 142.77, 142.22, 142.09, 141.72, 141.19, 140.51, 138.51, 138.38, 137.94, 137.36, 134.78, 133.73, 133.10, 132.68, 132.28, 132.17, 132.07, 131.76, 131.69, 131.22, 130.74, 130.41, 129.72, 129.25, 129.18, 129.03, 127.44, 127.27, 127.04, 126.96, 126.84, 126.02, 125.54, 121.33, 121.08, 55.99 (*C*HAr_2), 55.76 (*C*HAr_2), 33.35 (*C*H_2CH_2), 33.25 (*C*H_2CH_2), 30.28 (*C*H_2CH_2), 30.06 (*C*H_2CH_2), 21.95 (aryl-*C*H_3), 21.87 (aryl-*C*H_3), 20.17 (N=C-*C*H_3), 19.26 (N=C-*C*H_3), 18.76 (N=C-*C*H_3), 18.02 (N=C-*C*H_3), 4.06 (Pd-*C*H_3), 2.88 (Pd-*C*H_3). ESI-MS (m/z): calcd for $C_{48}H_{45}ClN_2Pd^+$: 792.23, Found, 792.17, $[M]^+$. Elemental analysis: calc. for $C_{48}H_{45}ClN_2Pd$: C, 72.81; H, 5.73; N, 3.54. Found: C, 72.68; H, 5.94; N, 3.67.



Pd2: (665 mg, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76, 7.65 (s, 1H, aryl-*H*), 7.41 (dd, *J* = 19.7, 6.7 Hz, 2H, aryl-*H*), 7.23 – 6.89 (m, 11H, aryl-*H*), 6.88 – 6.58 (m, 4H, aryl-*H*), 5.74, 5.51 (s, 2H, C*H*Ar_2), 4.17 – 3.96, 3.84 – 3.82, (m, 2H, CH_2CH_2CH_3), 3.64 (t, *J* = 15.4 Hz, 2H, CH_2CH_2), 3.36 (d, *J* = 14.7 Hz, 2H, CH_2CH_2), 3.00 (t, *J* = 15.1 Hz, 2H, CH_2CH_2), 2.45 (d, *J* = 11.1 Hz, 2H, CH_2CH_2), 2.11, 2.07 (s, 3H, aryl-CH_3), 2.02 – 1.85 (m, 2H, CH_2CH_2CH_3), 1.59, 1.51 (s, 3H, N=CCH_3), 1.26, 1.19 (s, 3H, CH_2CH_2CH_3), 1.18, 0.64 (s, 3H, Pd-CH_3), -0.16, -0.29 (s, 3H, N=CCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.34 (N=*C*), 168.04 (N=*C*), 141.90, 141.52, 140.44,

138.42, 137.41, 134.40, 133.18, 132.09, 131.72, 131.54, 130.61, 129.02, 127.27, 127.03, 126.70, 125.86, 55.82 (*C*HAr$_2$), 53.90 (*C*H$_2$CH$_2$CH$_3$), 33.19 (*C*H$_2$CH$_2$), 29.95 (*C*H$_2$*C*H$_2$), 22.98 (CH$_2$*C*H$_2$CH$_3$), 21.74 (aryl-*C*H$_3$), 18.92 (N=C-*C*H$_3$), 15.69 (N=C-*C*H$_3$), 11.98 (CH$_2$*C*H$_2$CH$_3$), 1.61 (Pd-*C*H$_3$). ESI-MS (m/z): calcd for $C_{45}H_{47}ClN_2Pd^+$: 762.25, Found, 762.23, $[M]^+$. Elemental analysis: calc. for $C_{45}H_{47}ClN_2Pd$: C, 71.33; H, 6.25; N, 3.70. Found: C, 71.29; H, 6.18; N, 3.57.

1.6 A General Procedure for the Homopolymerization of Ethylene Using Ni Complexes.

In a typical experiment, a 350 mL thick wall pressure glass 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 and the desired amount Et_2AlCl was added to the reactor under N_2 atmosphere, then the desired amount of catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 6 atm of ethylene. After 10 min, the pressure reactor was vented and the polymer was precipitated in ethanol, filtered and dried at 50 °C for at least 24 h under vacuum.

1.7 A General Procedure for the Homopolymerization of Ethylene Using Pd Complexes.

In a typical experiment, a 350 mL thick wall pressure glass 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. 38 mL of DCM and the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the 10 umol Pd catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 4 atm of ethylene. After the desired time, the pressure reactor was vented and the polymer was dried under vacuum overnight.

1.8 A General Procedure for the Copolymerization of Methyl Acrylate with

Ethylene Using Pd Complexes.

In a typical experiment, a 350 mL thick wall pressure glass 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. 18 mL of DCM with the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the desired amount of MA and 20 umol Pd 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 2 atm of ethylene. After 12 h, the pressure reactor was vented and the copolymer was dried under vacuum overnight.

2. Spectra Data

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

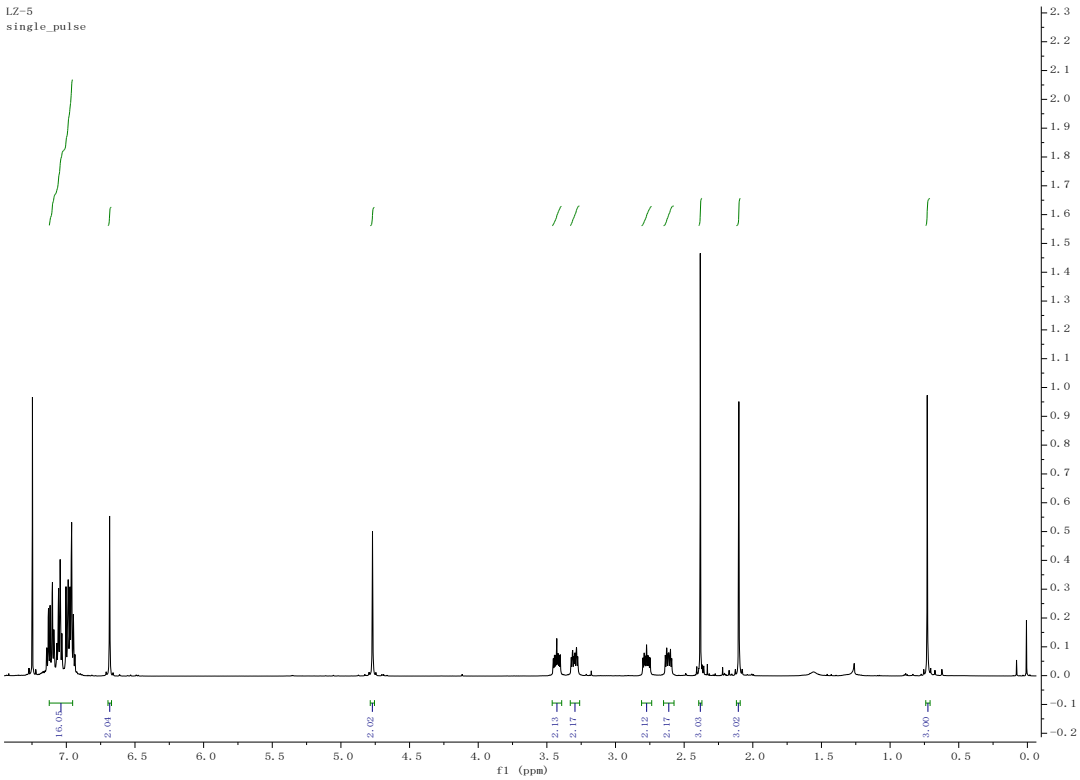


Figure S1. ^{1}H NMR spectrum of **I1** in $CDCl_3$.

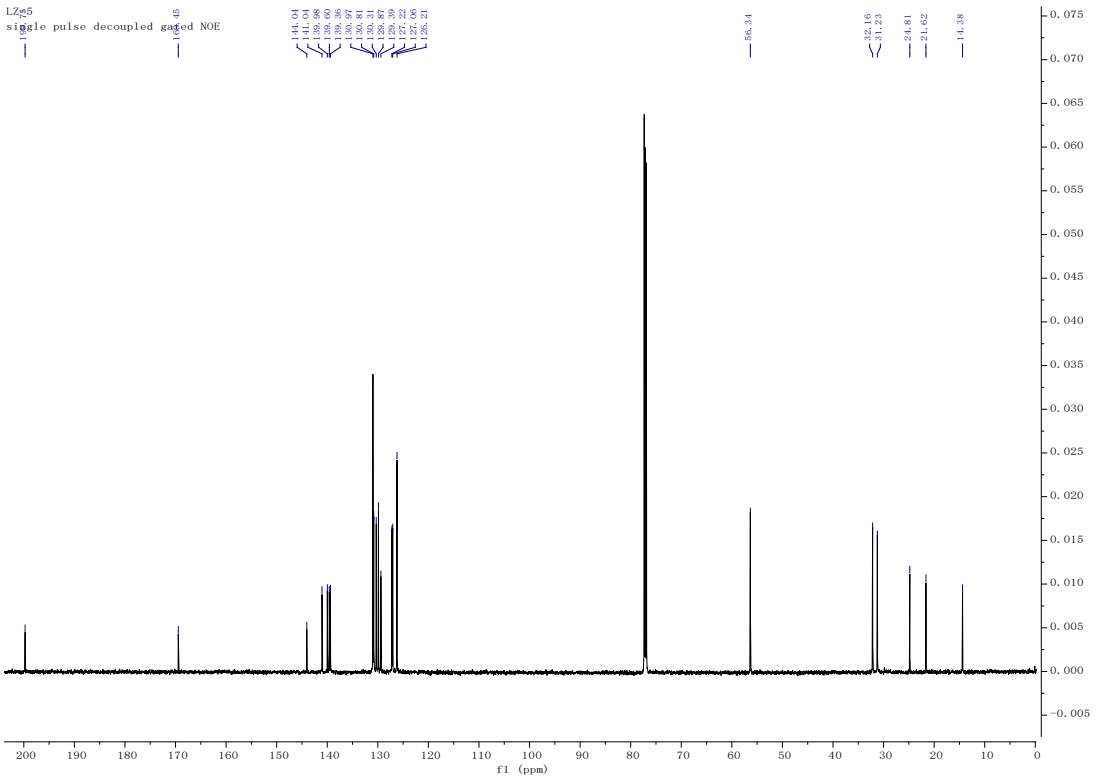


Figure S2. ^{13}C NMR spectrum of **I1** in $CDCl_3$.

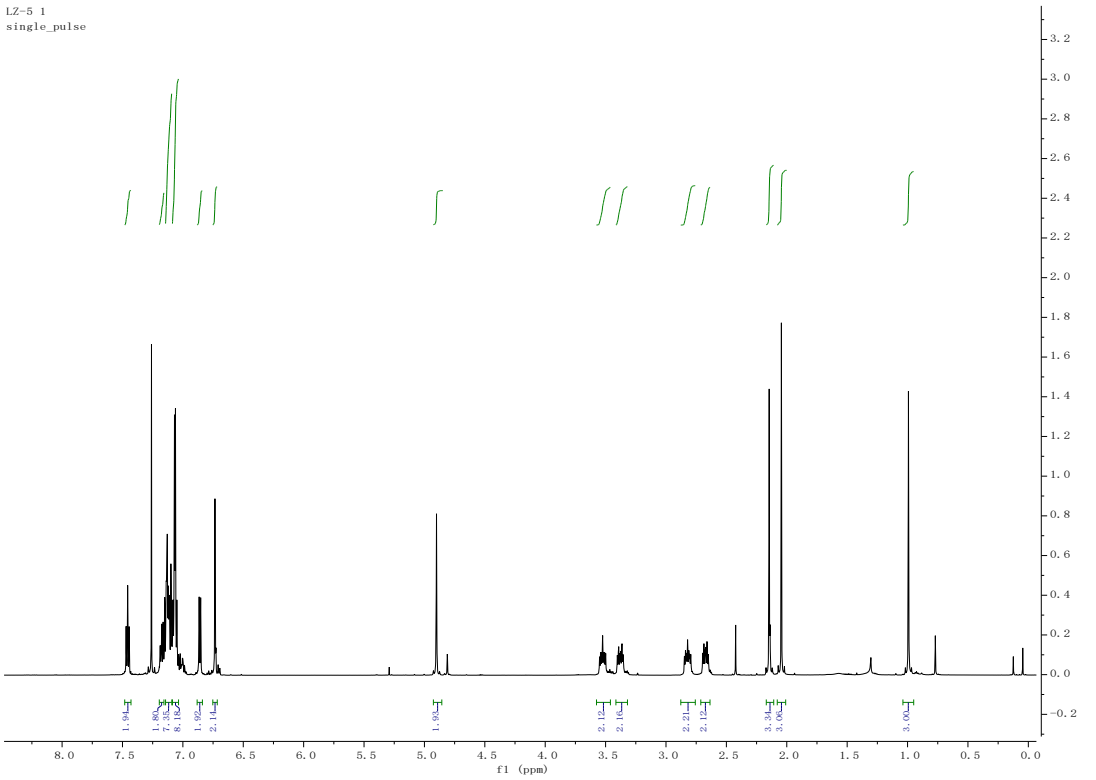


Figure S3. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

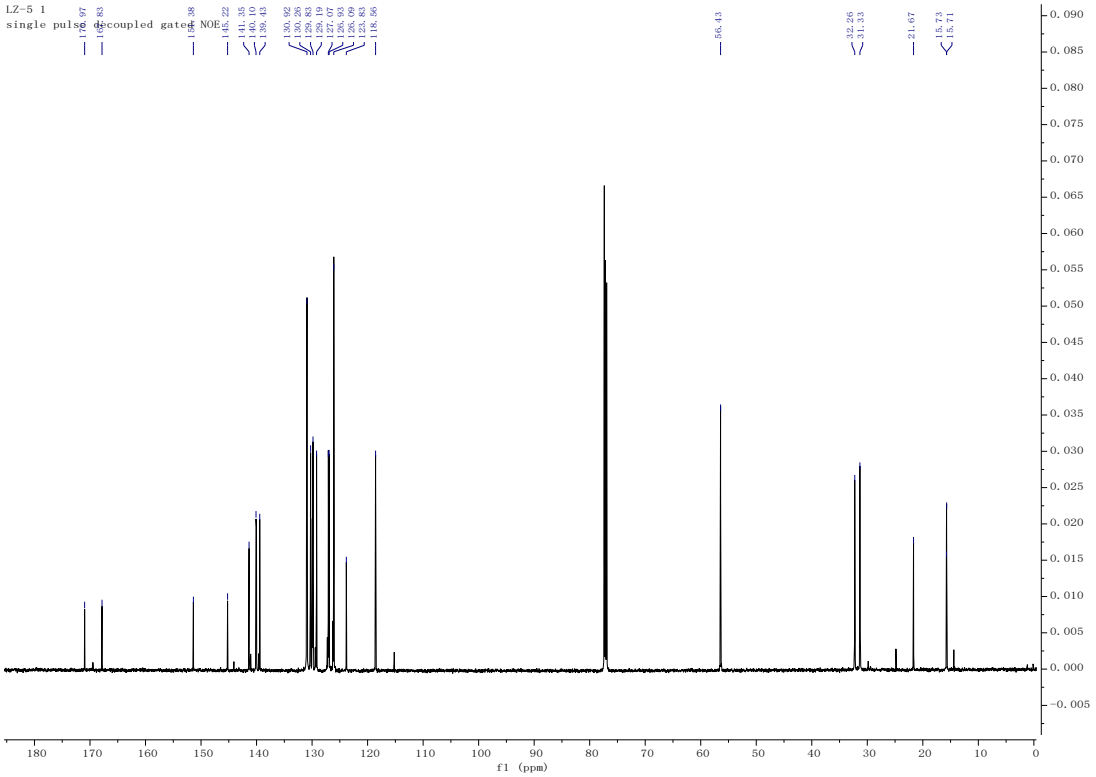


Figure S4. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

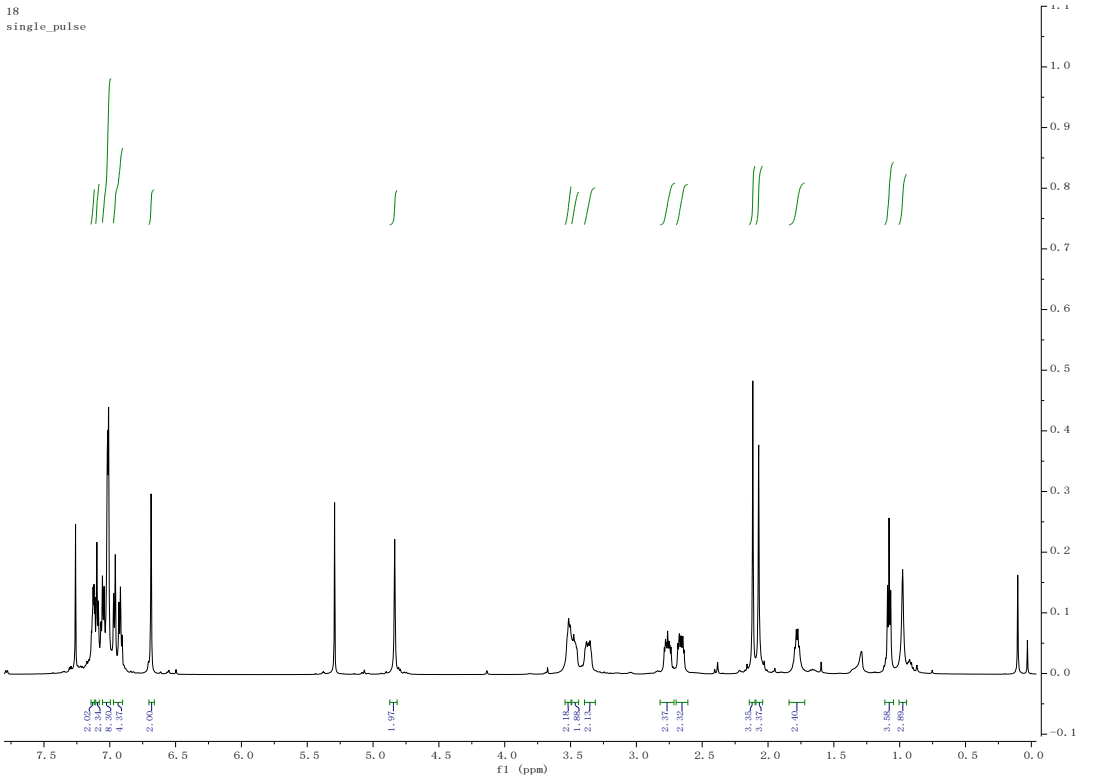


Figure S5. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

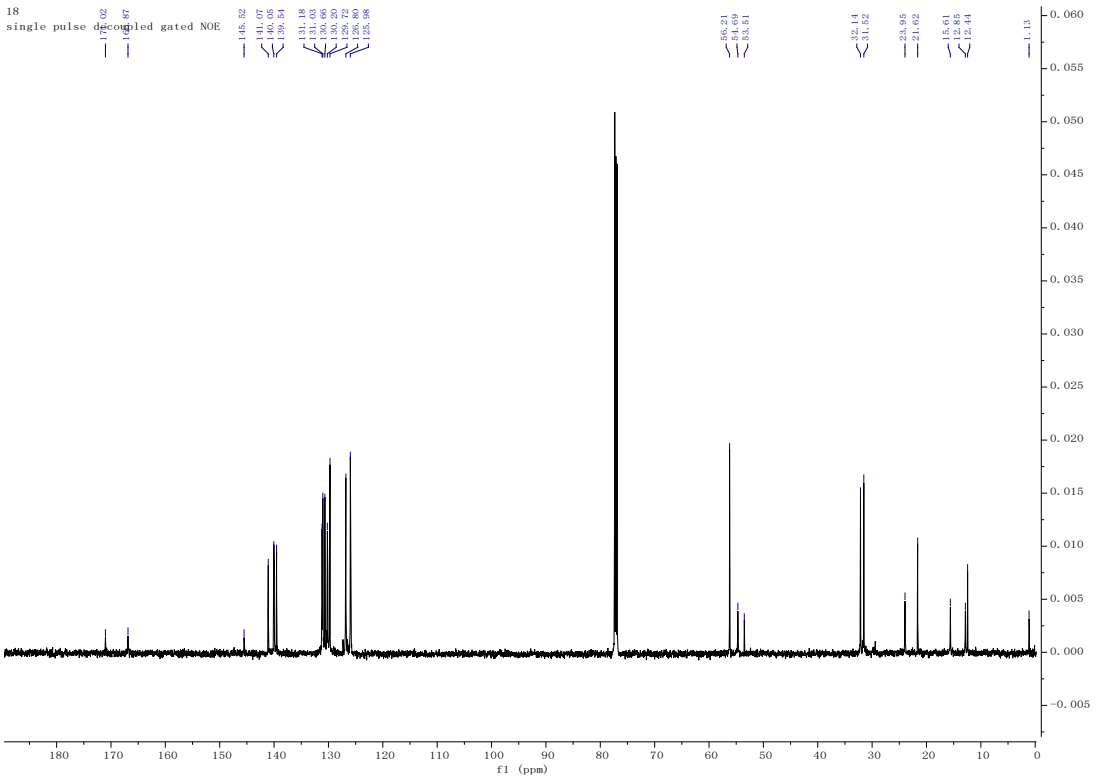


Figure S6. ^{13}C NMR spectrum of **L2** in $CDCl_3$.

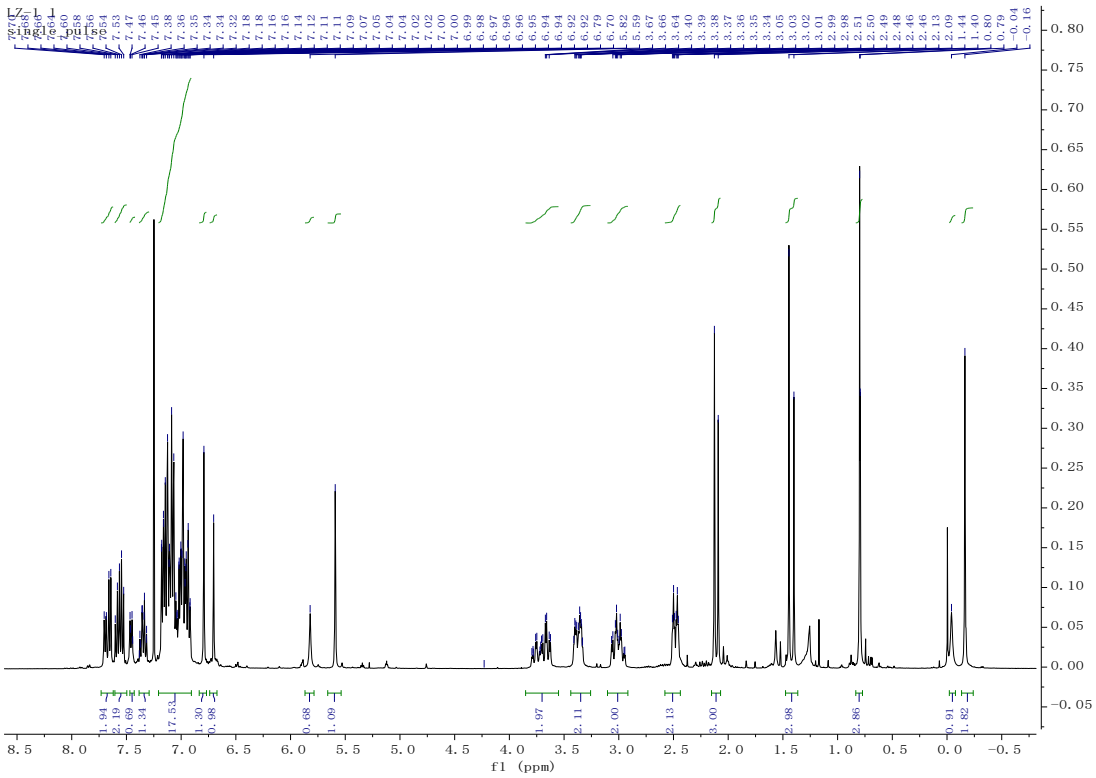


Figure S7. ^{1}H NMR spectrum of **Pd1** in $CDCl_3$.

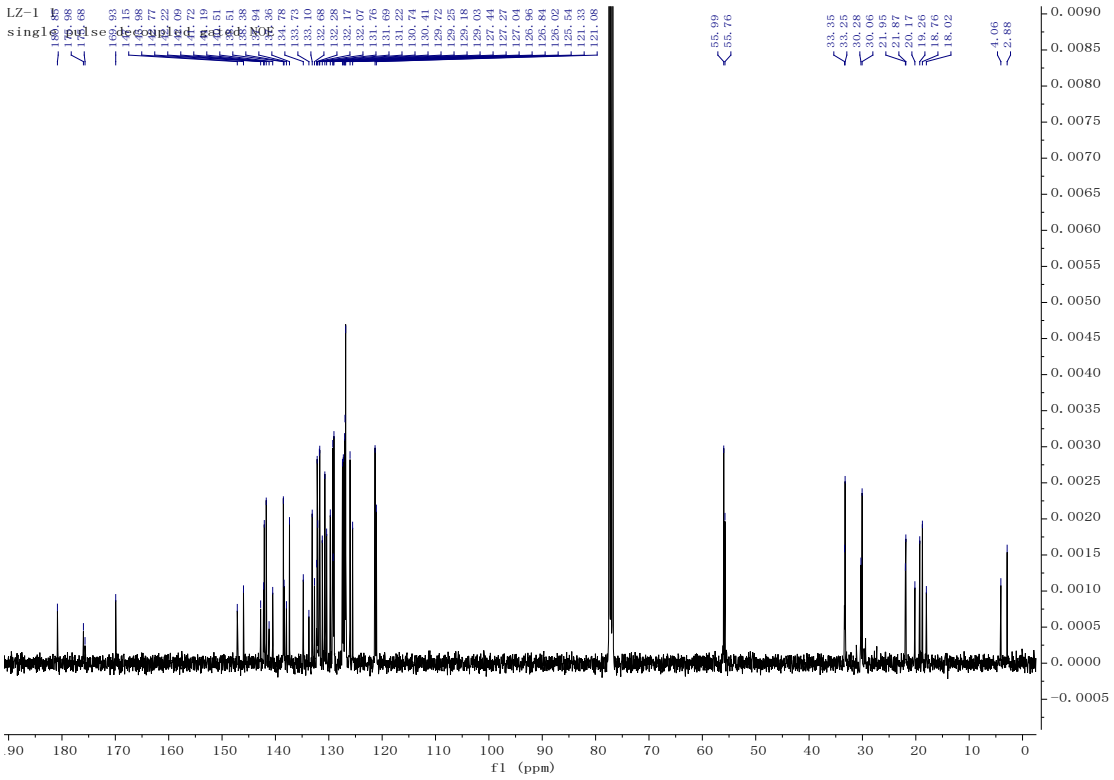


Figure S8. ^{13}C NMR spectrum of **Pd1** in $CDCl_3$.

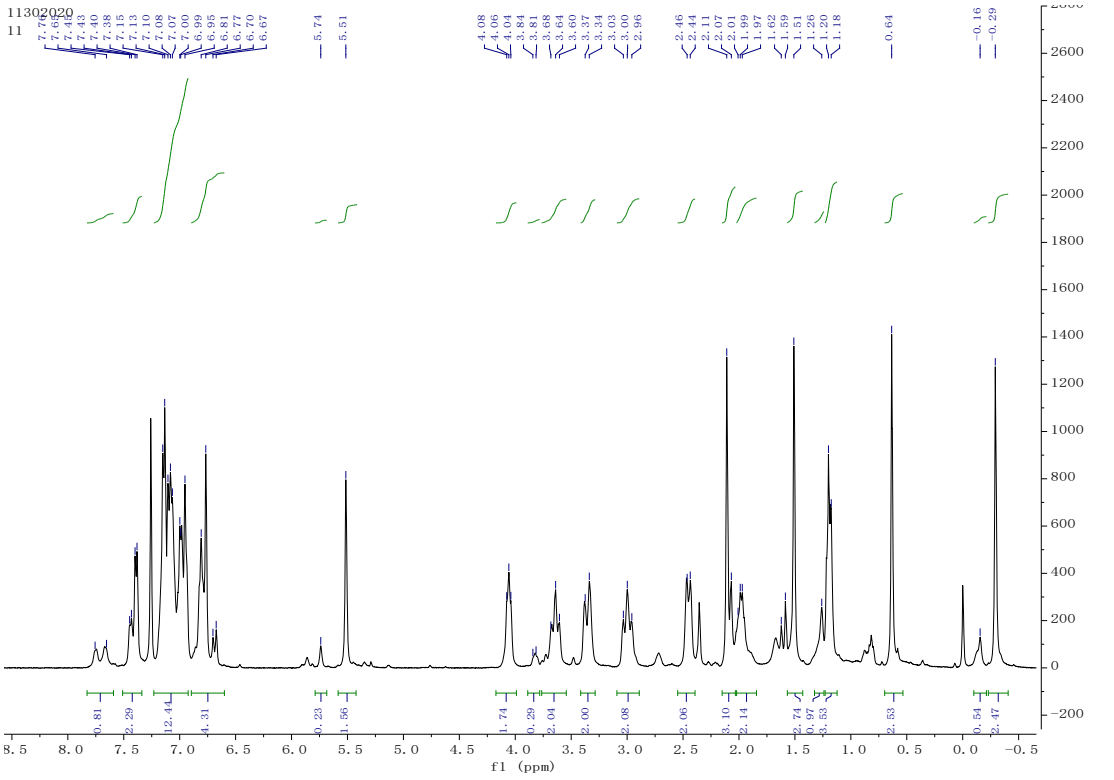


Figure S9. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

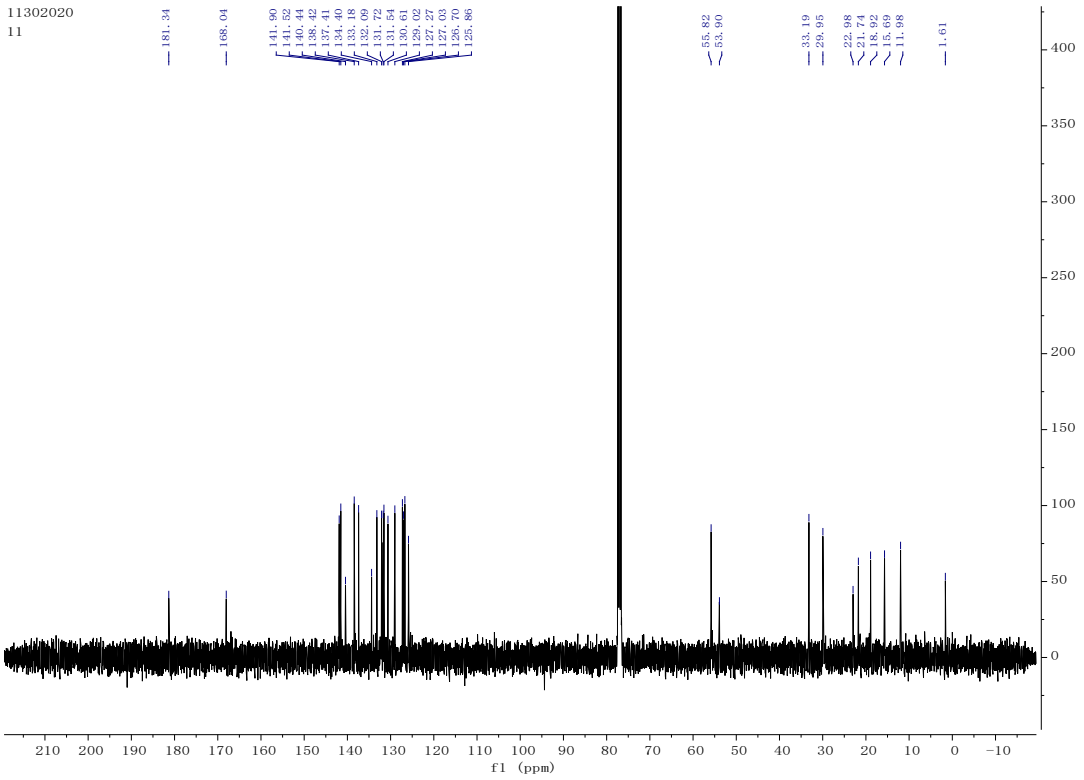


Figure S10. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

2.2 APCl-MS of α-Keto-imine I1.

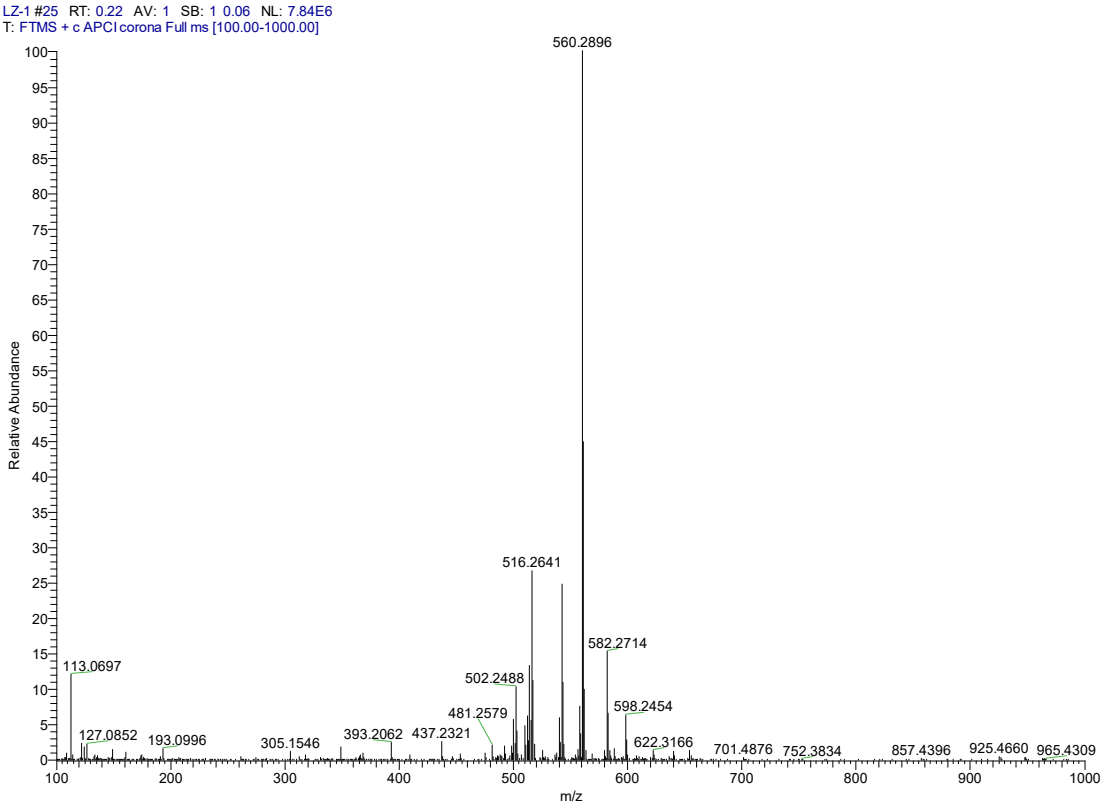


Figure S11. APCl-MS of **I1.**

2.3 APCl-MS of Ligand L1 and L2.

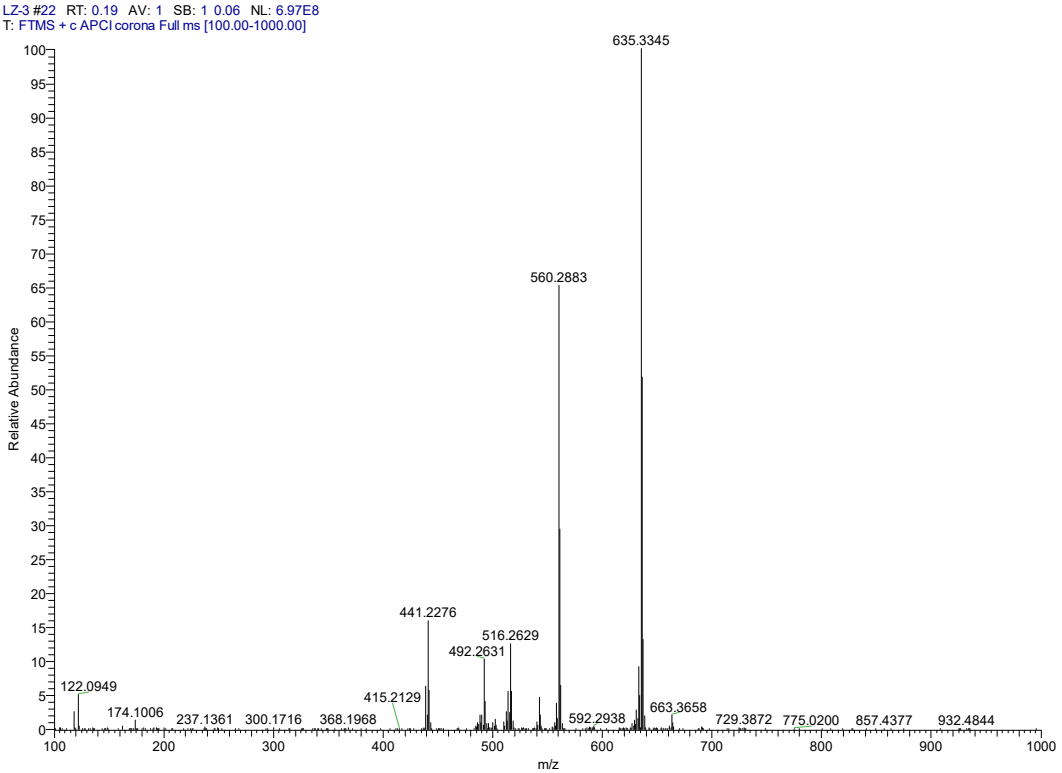


Figure S12. APCl-MS of **L1.**

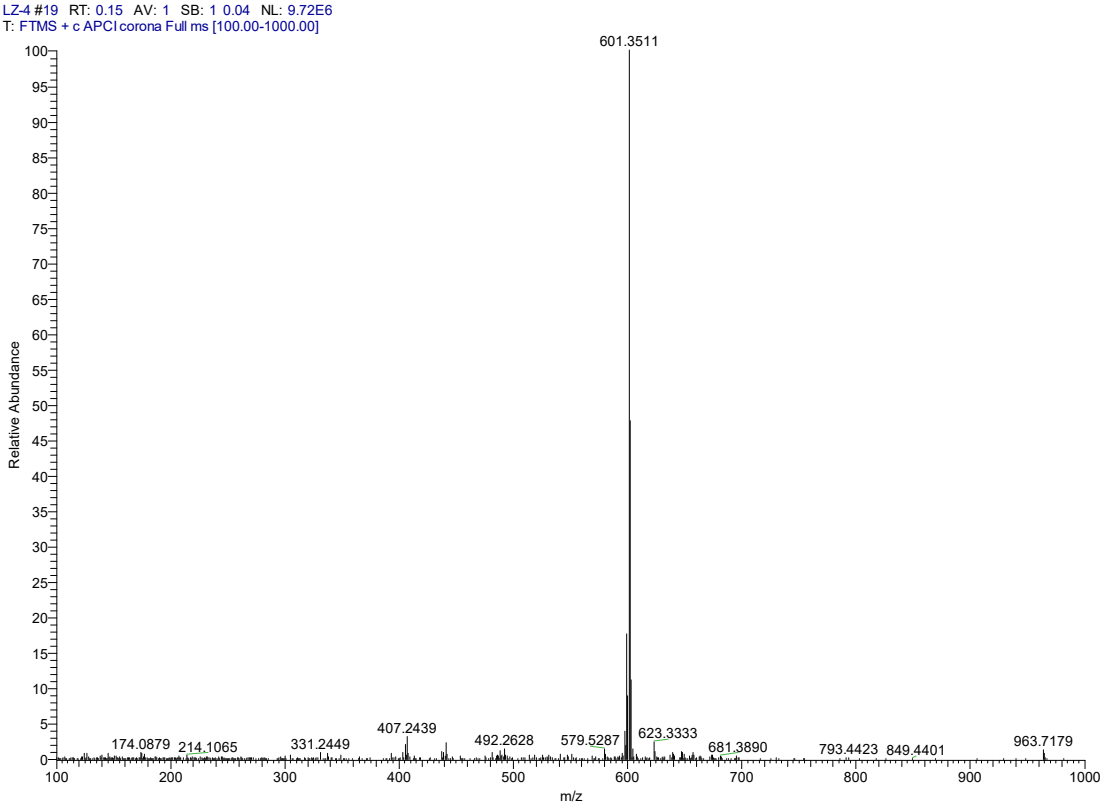


Figure S13. APCl-MS of **L2.**

2.4 ESI-MS of Complexes Ni1-Ni2 and Pd1-Pd2.

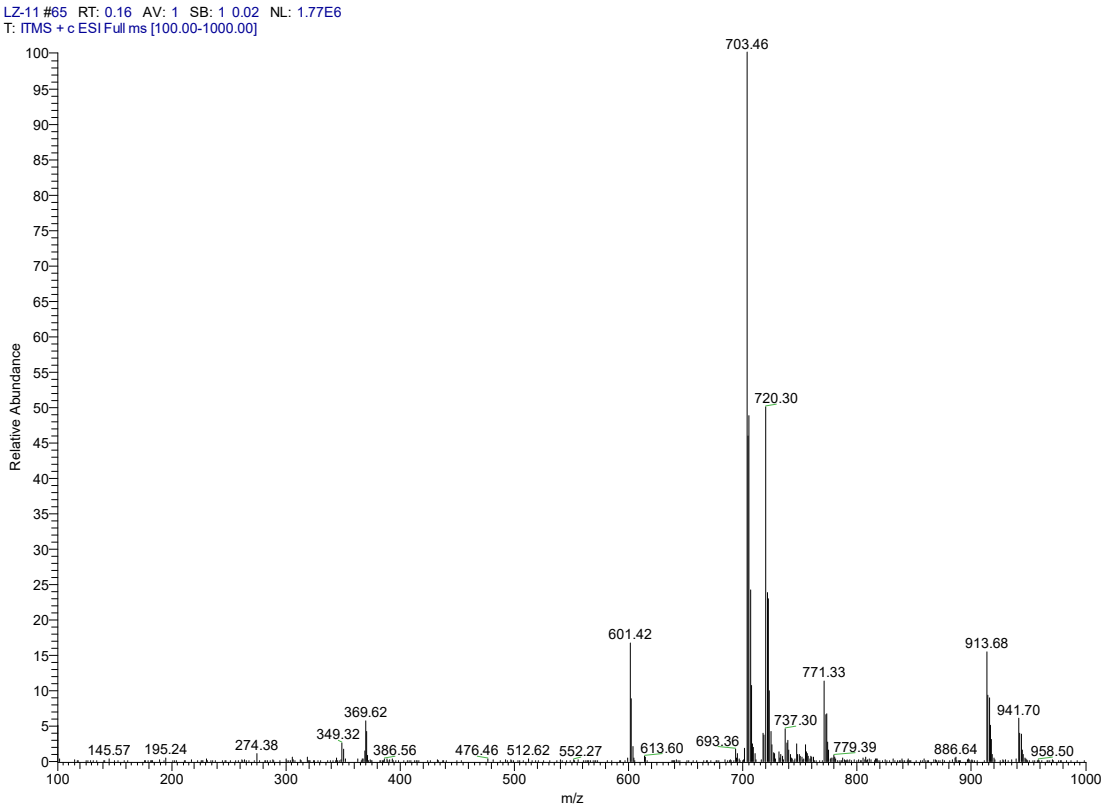


Figure S14. MALDI-TOF-MS of complex **Ni1**.

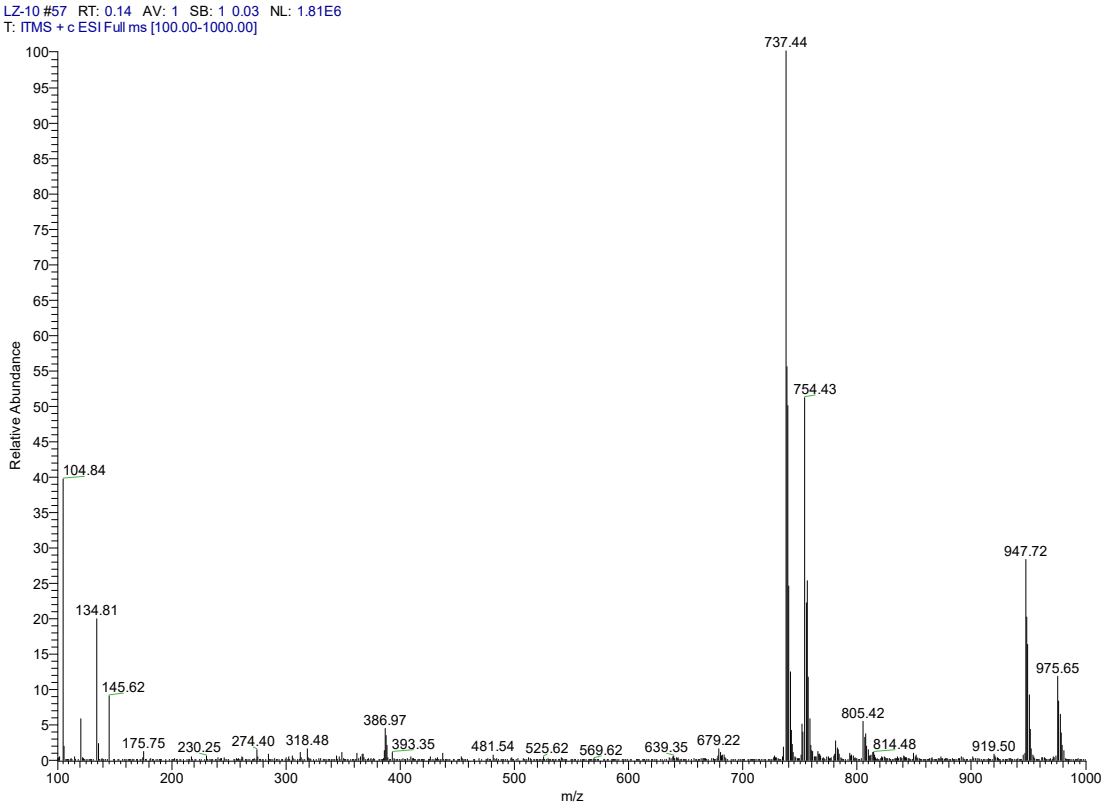


Figure S15. MALDI-TOF-MS of complex **Ni2**.

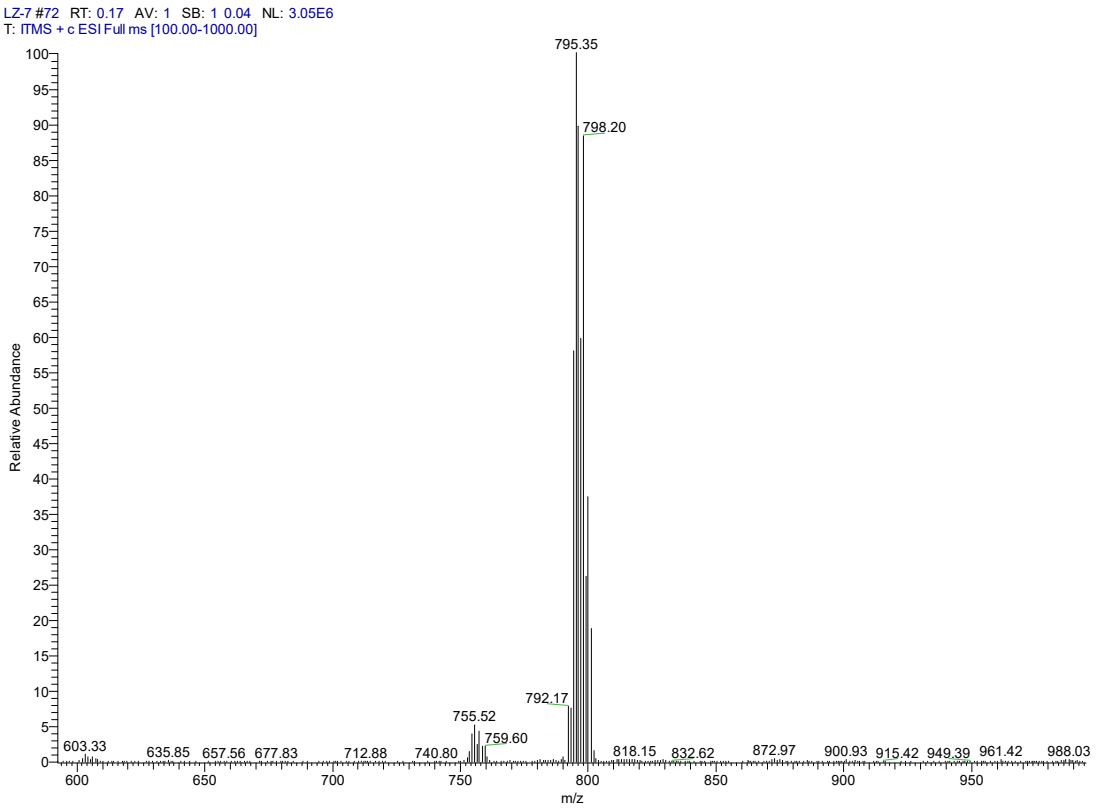


Figure S16. MALDI-TOF-MS of complex **Pd1**.

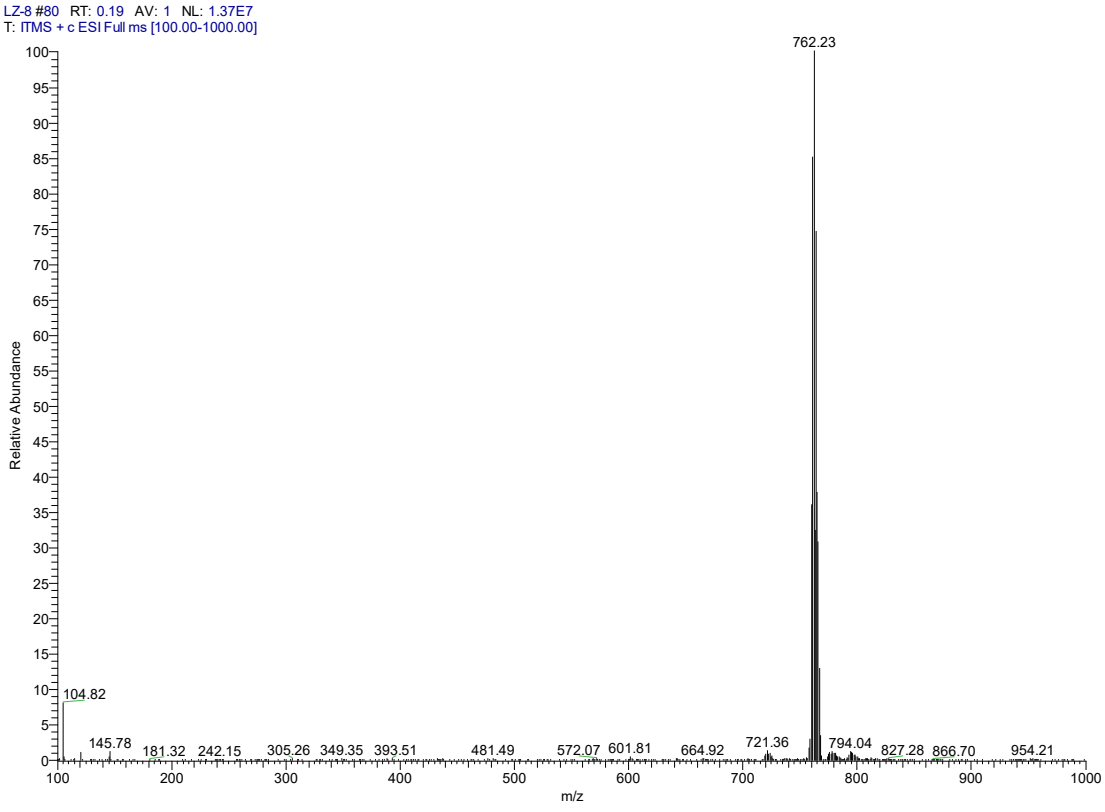


Figure S17. MALDI-TOF-MS of complex **Pd2**.

2.5 ^{1}H and ^{13}C NMR of Representative Polymers and Copolymers.

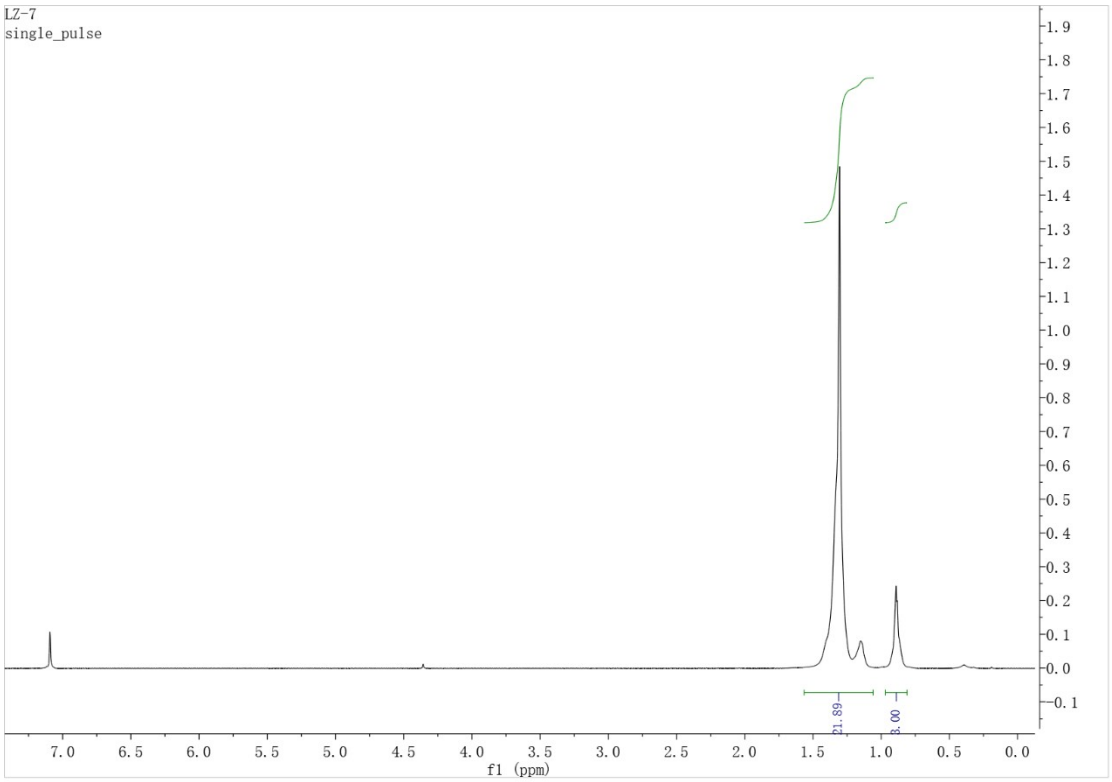


Figure S18. ^{1}H NMR spectrum of the polymer from table 1, entry 1 (d^{6}-benzene, 70 ^{o}C).

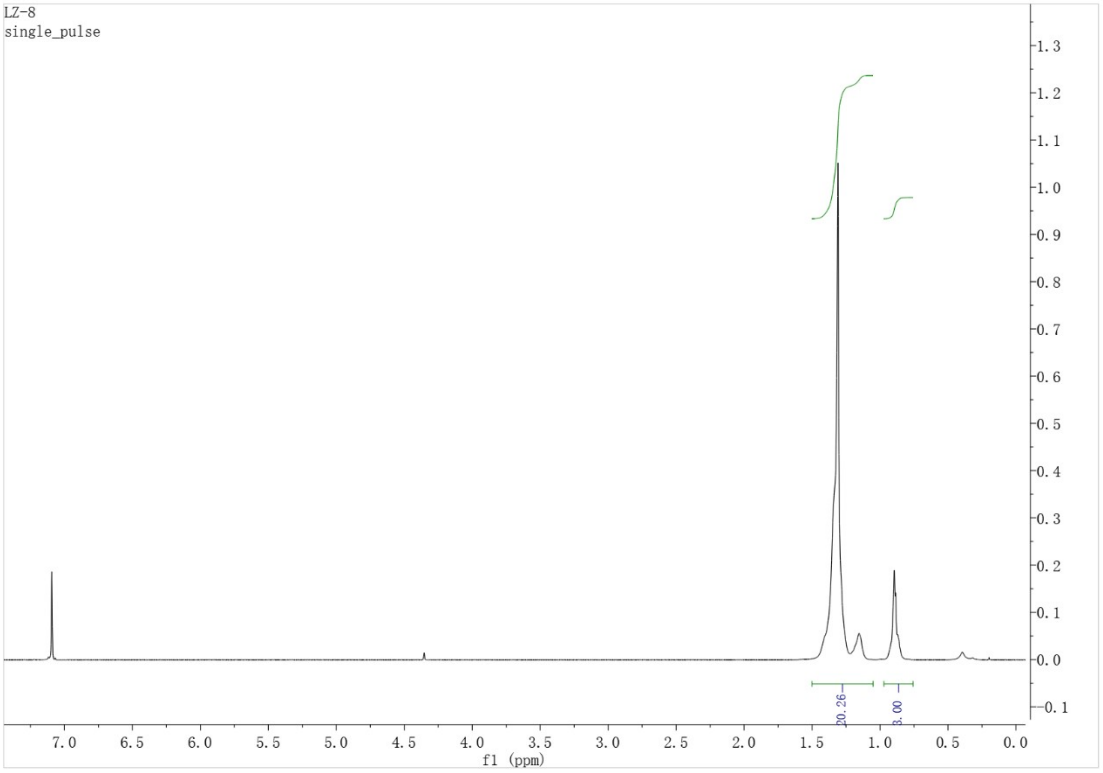


Figure S19. ^{1}H NMR spectrum of the polymer from table 1, entry 2 (d^{6}-benzene, 70 ^{o}C).

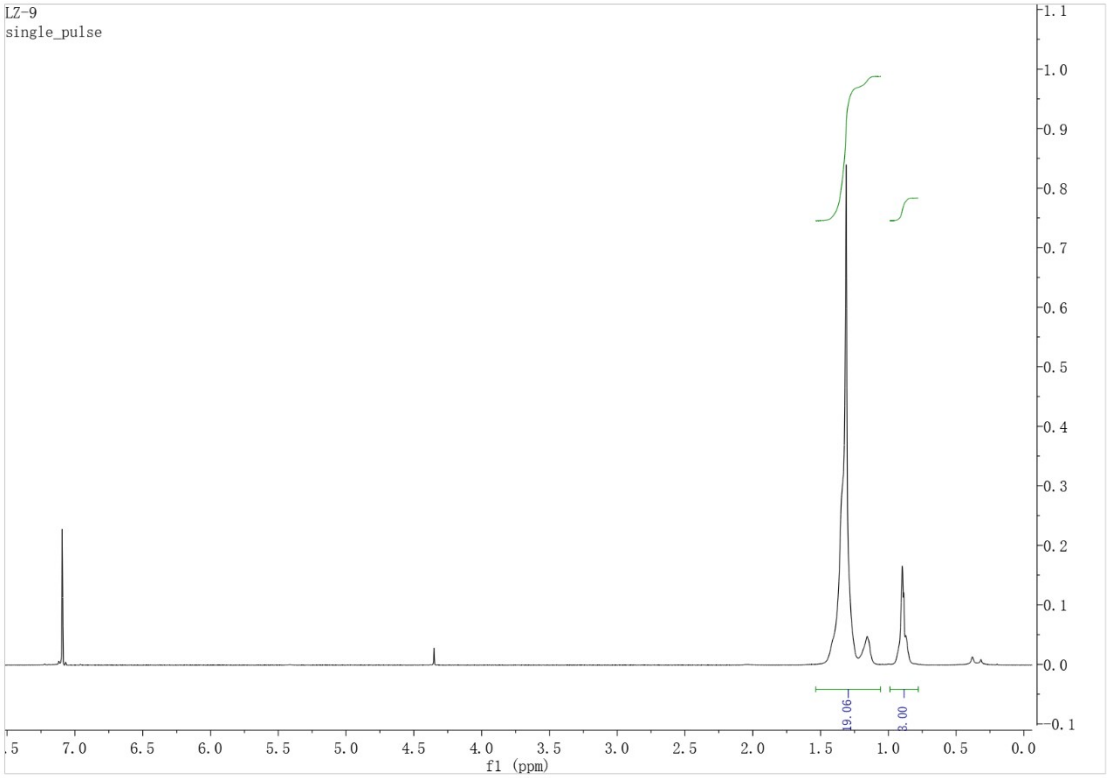


Figure S20. ^{1}H NMR spectrum of the polymer from table 1, entry 3 (d^{6}-benzene, 70 ^{o}C).

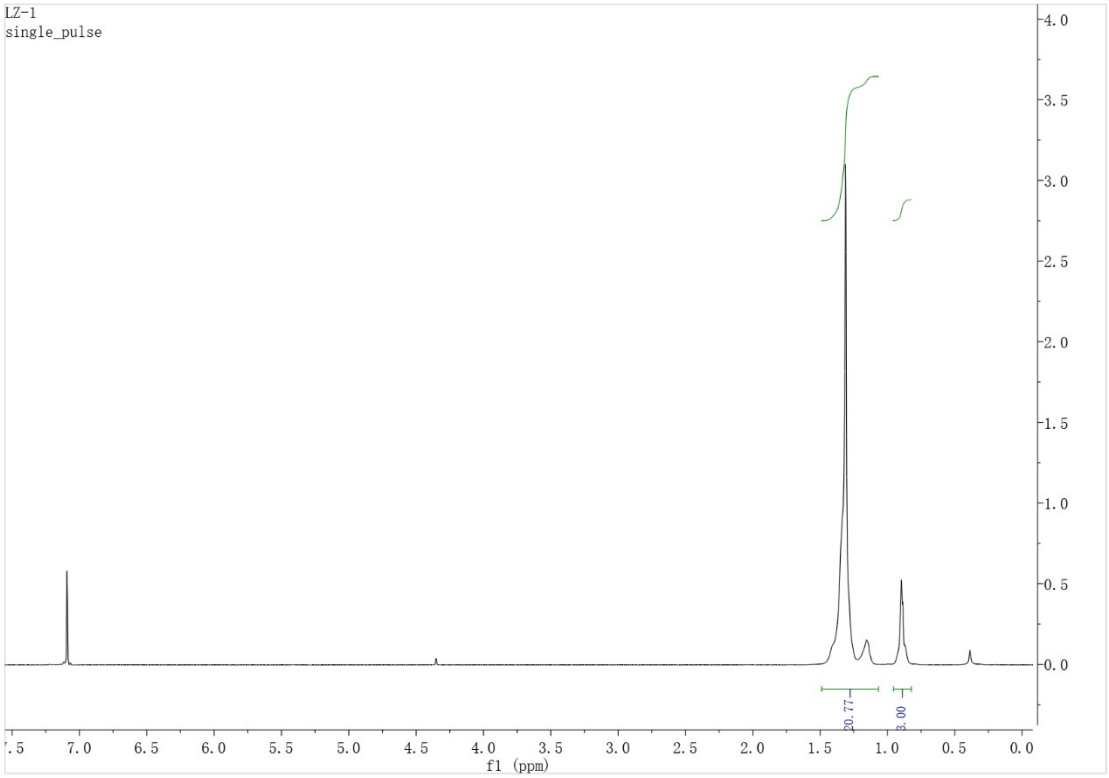


Figure S21. ^{1}H NMR spectrum of the polymer from table 1, entry 4 (d^{6}-benzene, 70 ^{o}C).

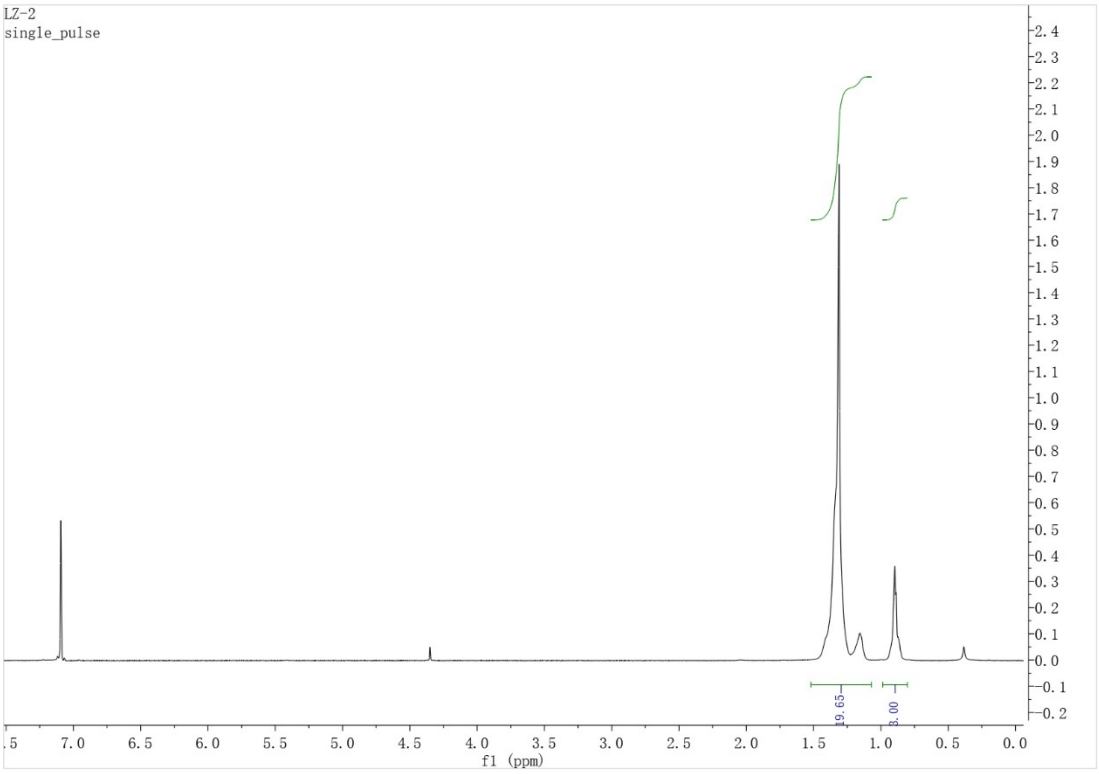


Figure S22. ^{1}H NMR spectrum of the polymer from table 1, entry 5 (d^{6}-benzene, 70 ^{o}C).

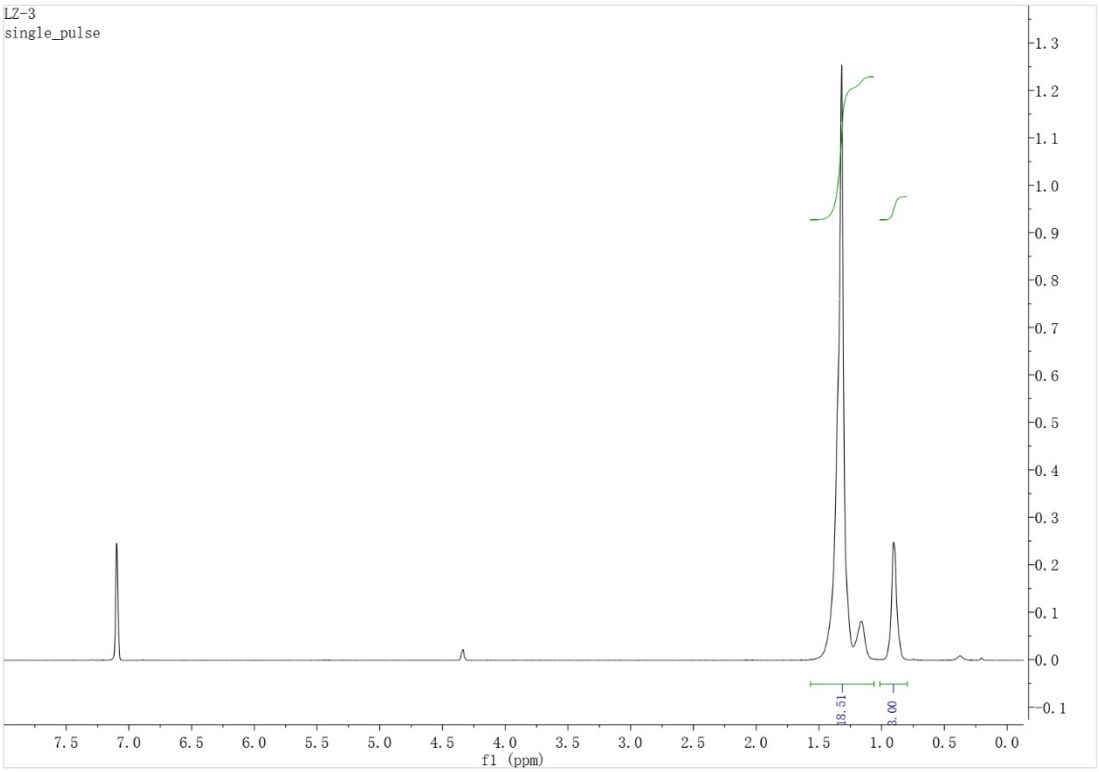


Figure S23. ^{1}H NMR spectrum of the polymer from table 1, entry 6 (d^{6}-benzene, 70 ^{o}C).

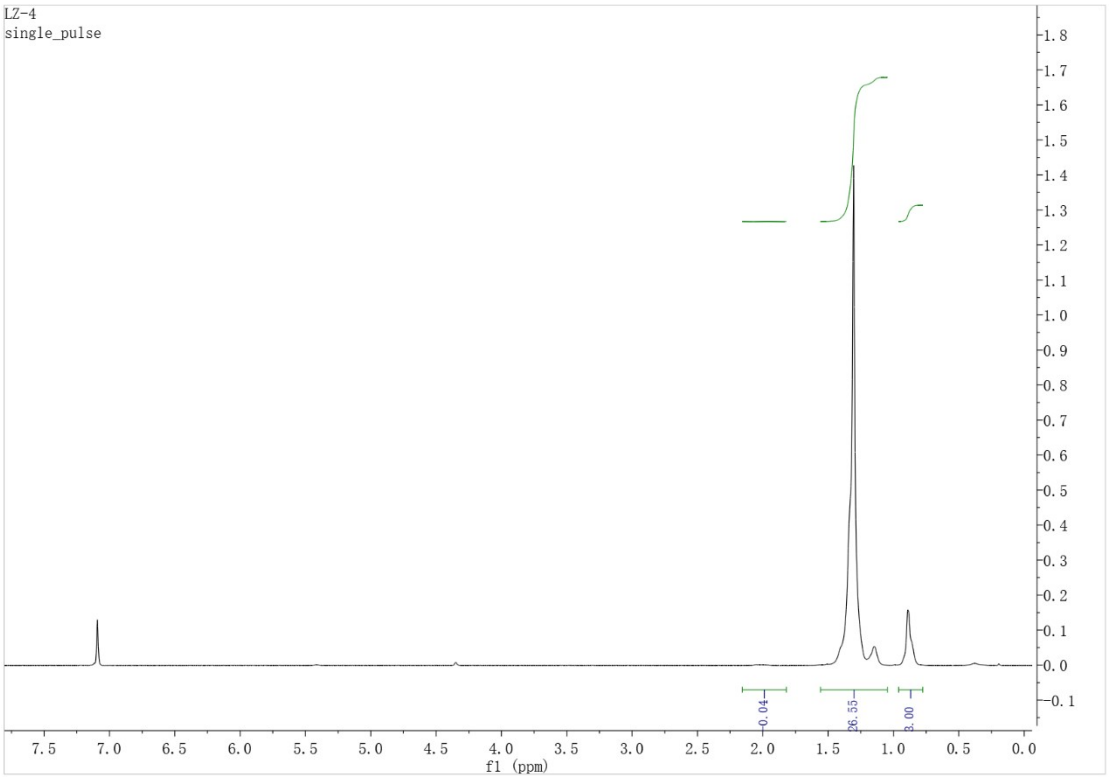


Figure S24. ^{1}H NMR spectrum of the polymer from table 1, entry 7 (d^{6}-benzene, 70 ^{o}C).

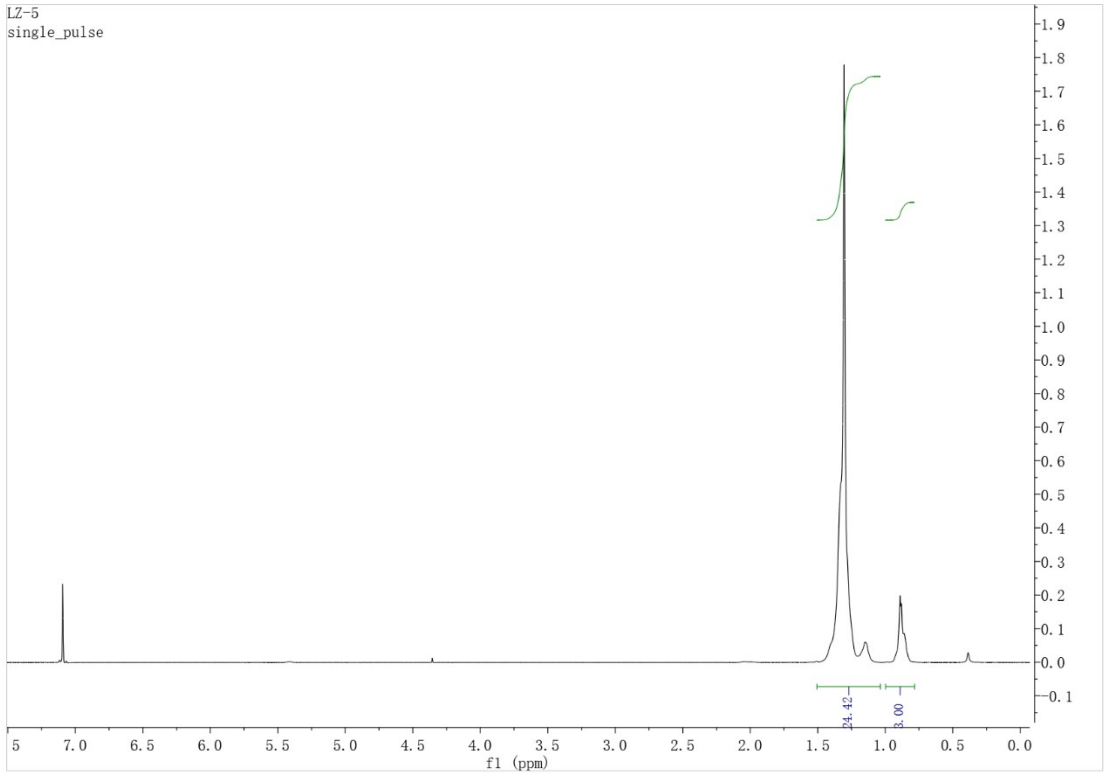


Figure S25. ^{1}H NMR spectrum of the polymer from table 1, entry 8 (d^{6}-benzene, 70 ^{o}C).

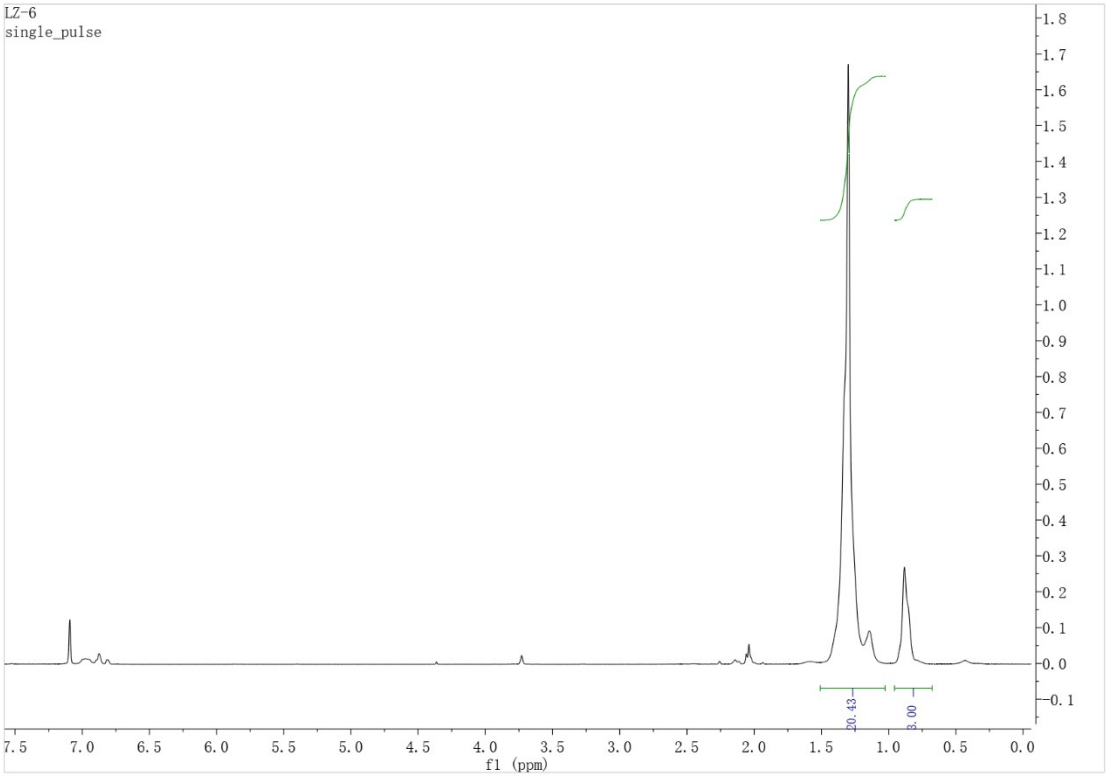


Figure S26. ^{1}H NMR spectrum of the polymer from table 1, entry 9 (d^{6}-benzene, 70 ^{o}C).

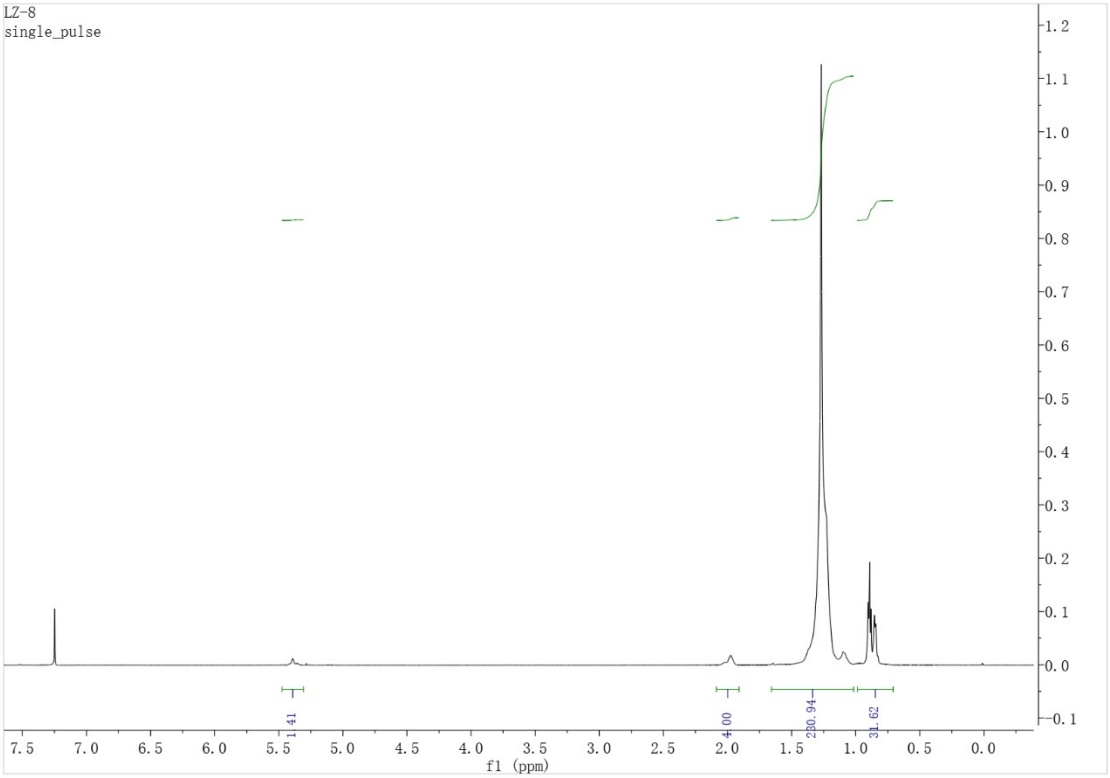


Figure S27. ^{1}H NMR spectrum of the polymer from table 2, entry 5 (d^{6}-benzene, 70 ^{o}C).

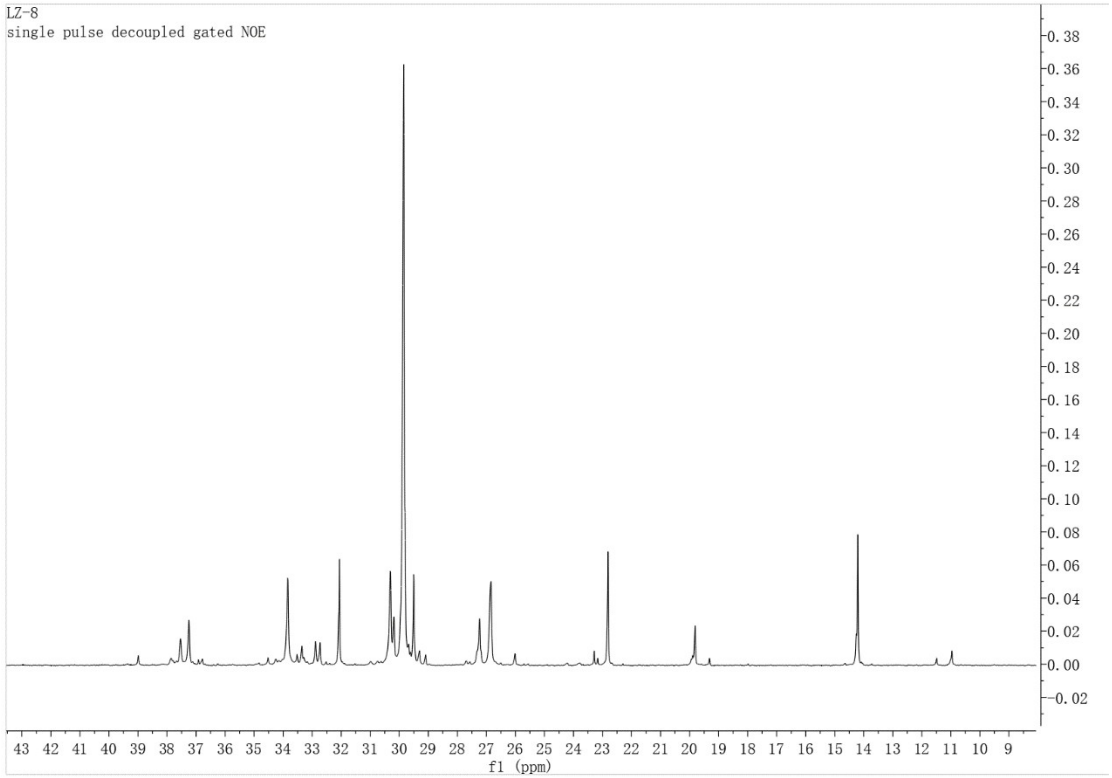


Figure S28. ^{13}C NMR spectrum of the polymer from table 2, entry 5 (d^6-benzene, 70 °C).

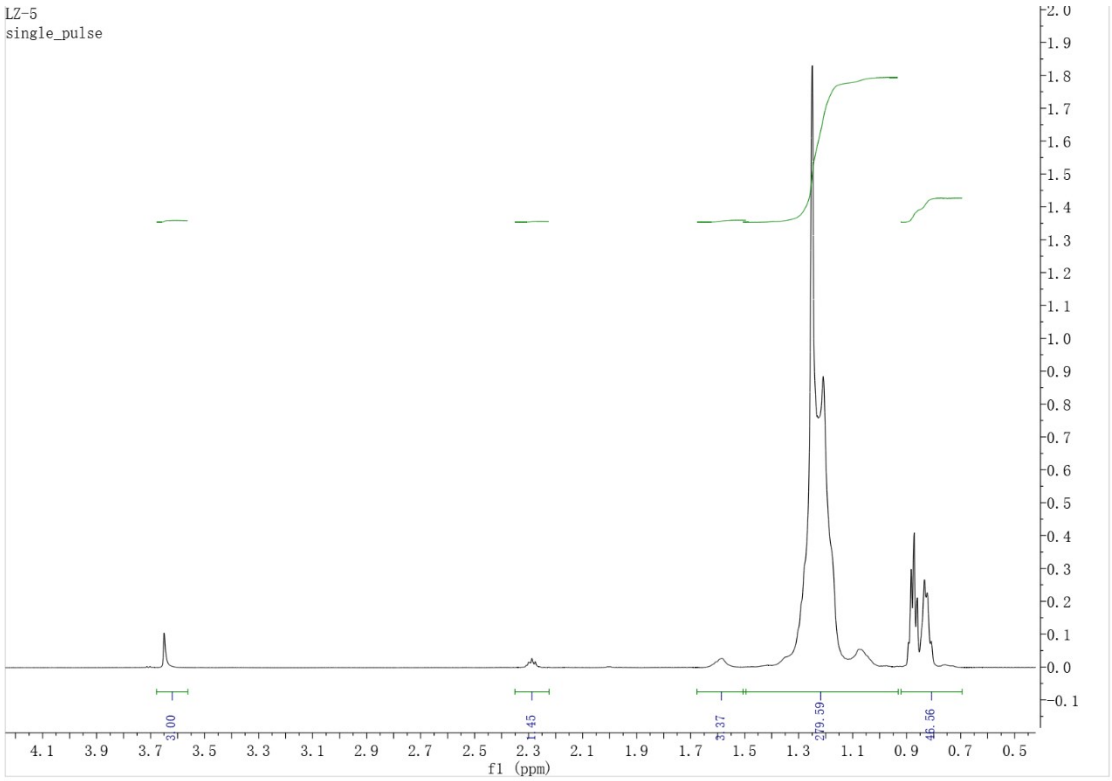


Figure S29. ^{1}H NMR spectrum of the polymer from table 3, entry 1 (d^6-benzene, 70 °C).

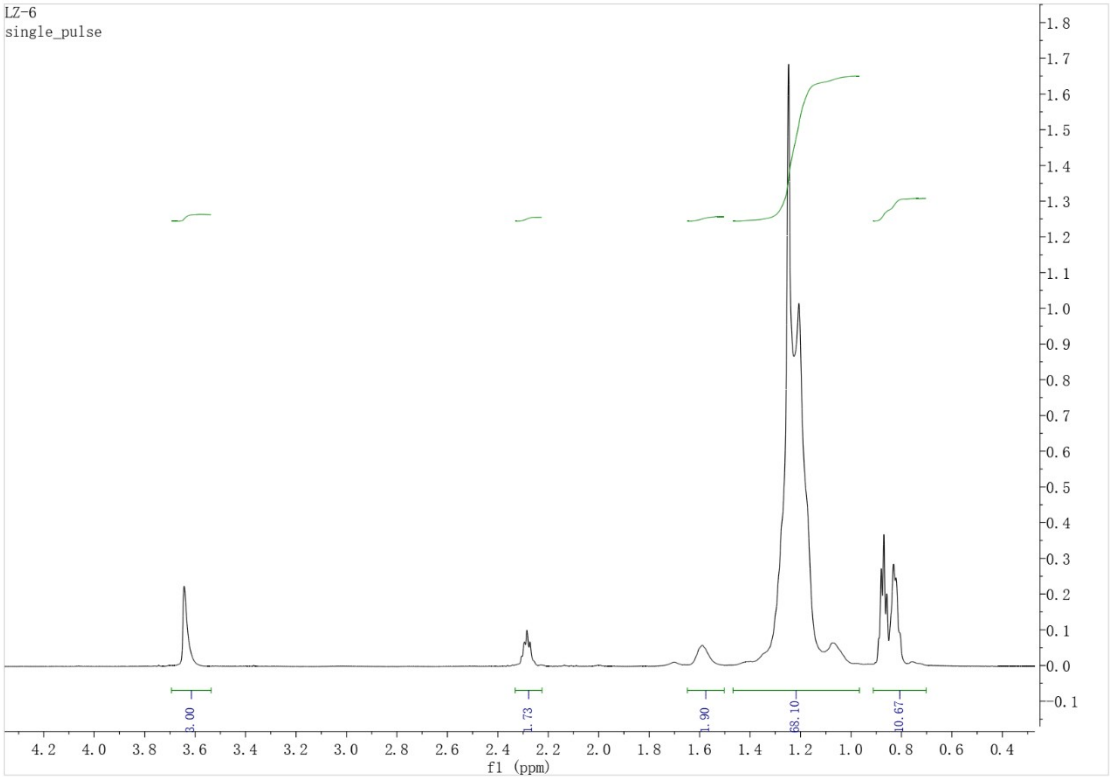


Figure S30. ^{1}H NMR spectrum of the polymer from table 3, entry 2 (d^{6}-benzene, 70 ^{o}C).

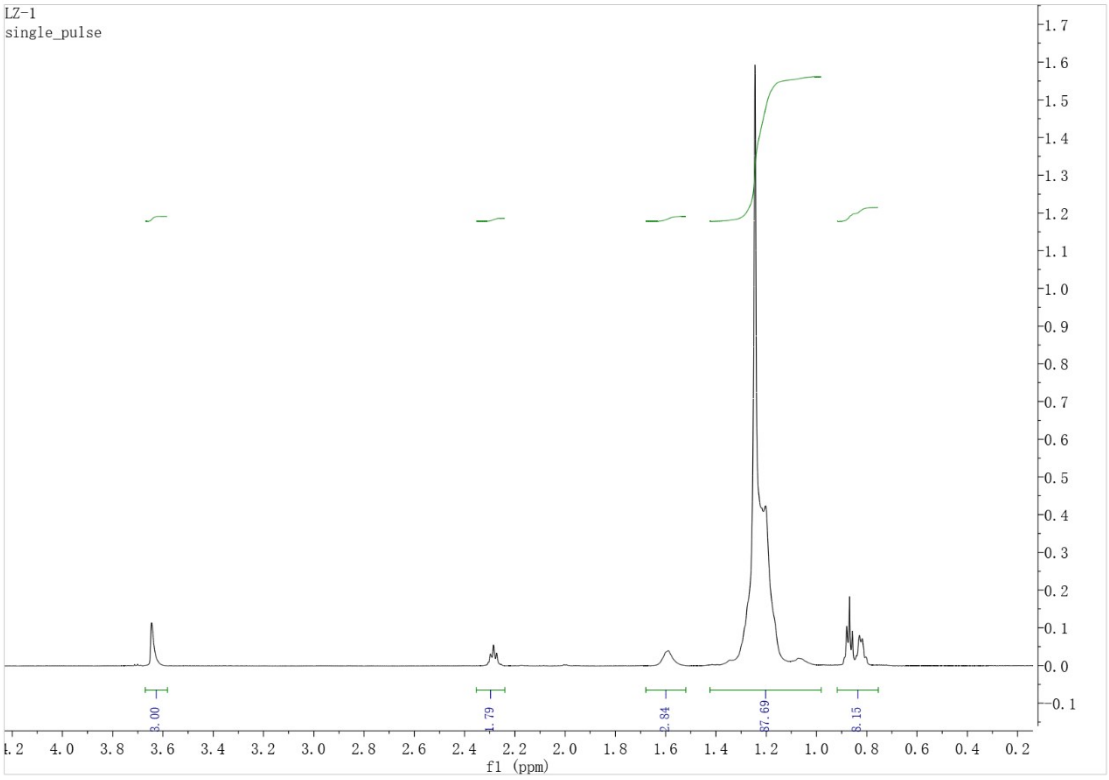


Figure S31. ^{1}H NMR spectrum of the polymer from table 3, entry 3 (d^{6}-benzene, 70 ^{o}C).

2.5 DSC and GPC of Representative Polymers and Copolymers.

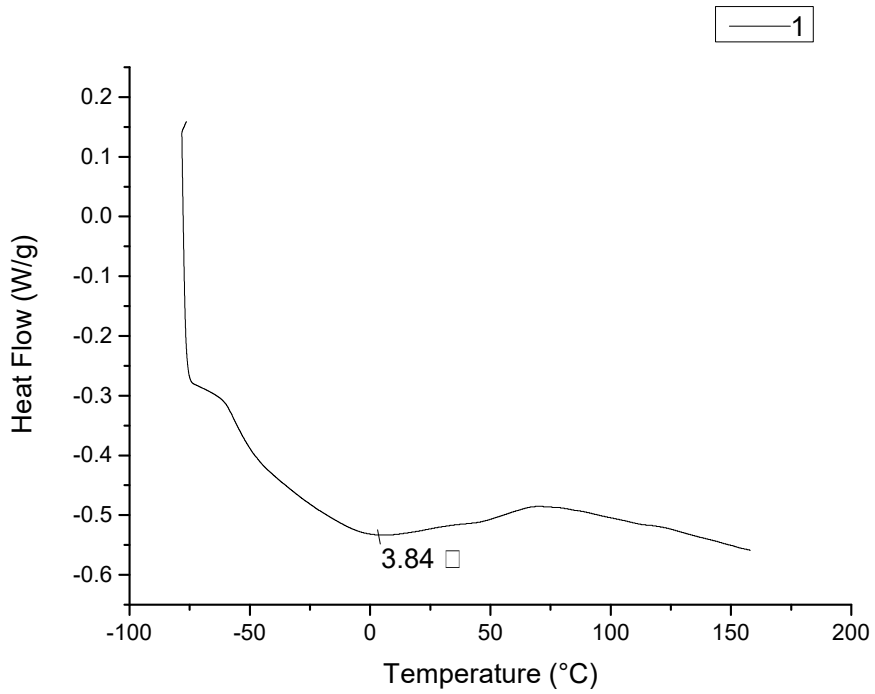


Figure S32. DSC of the polymer from table 1, entry 1.

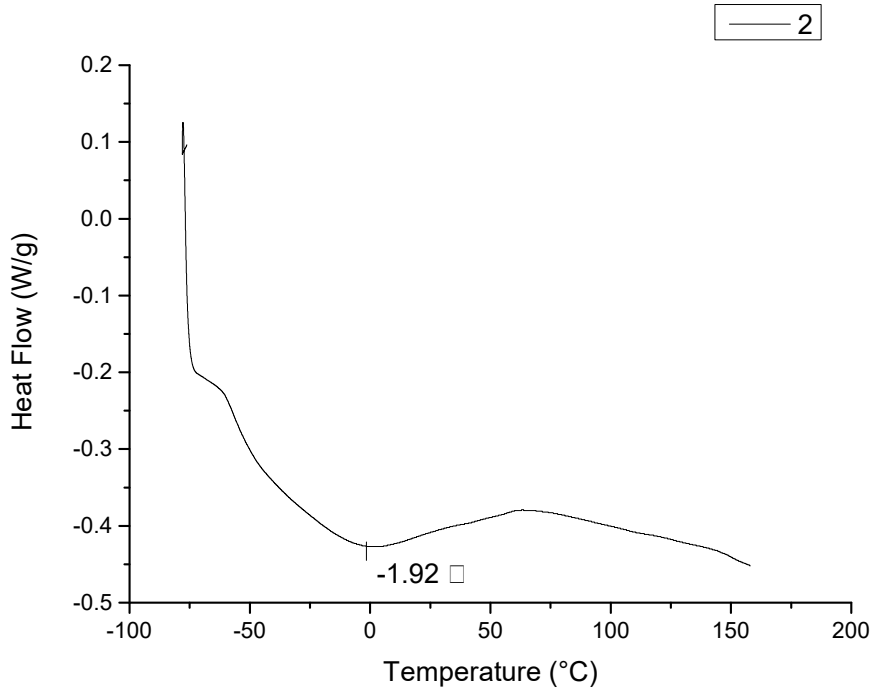


Figure S33. DSC of the polymer from table 1, entry 2.

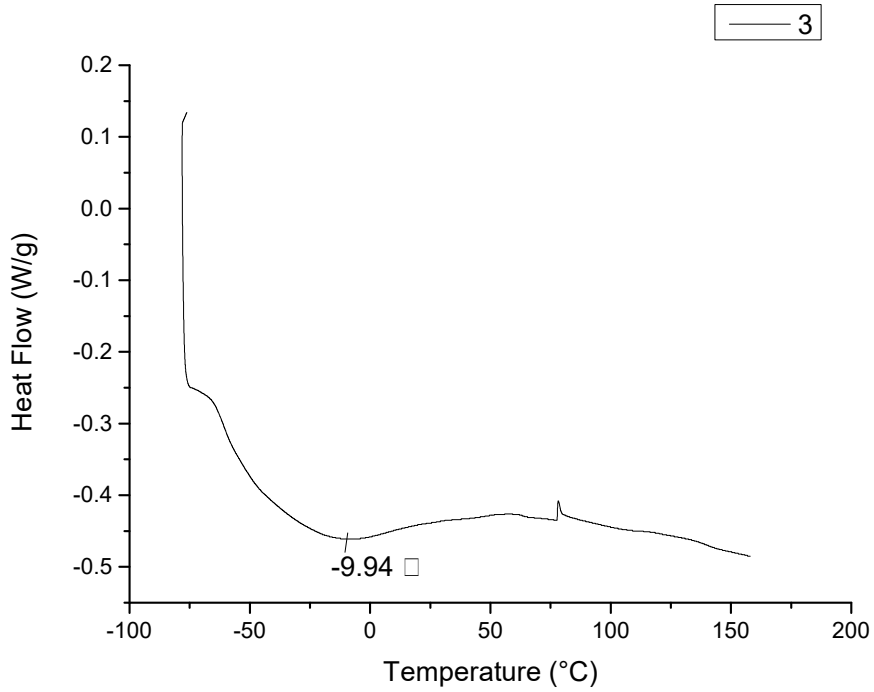


Figure S34. DSC of the polymer from table 1, entry 3.

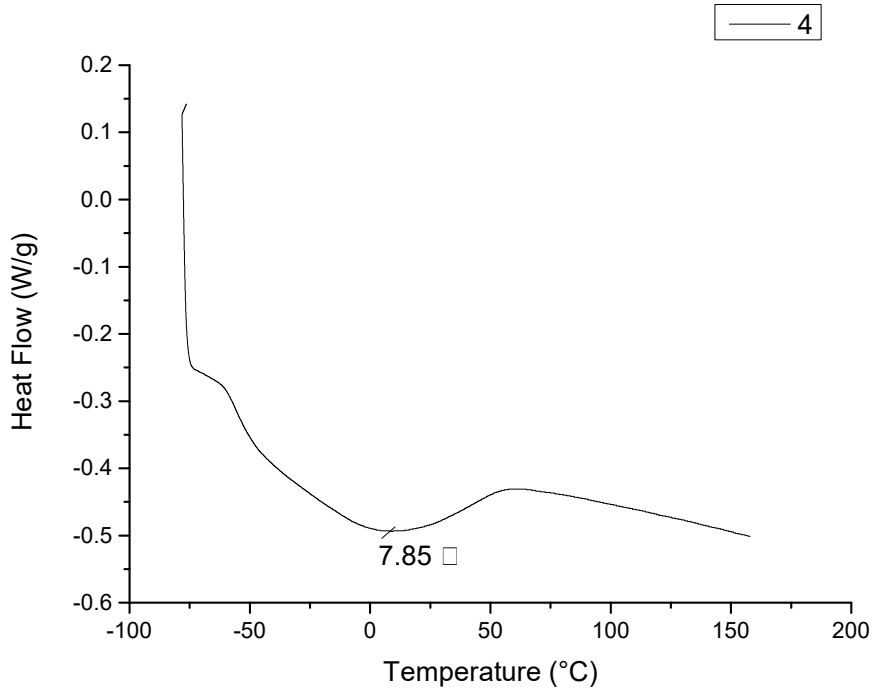


Figure S35. DSC of the polymer from table 1, entry 4.

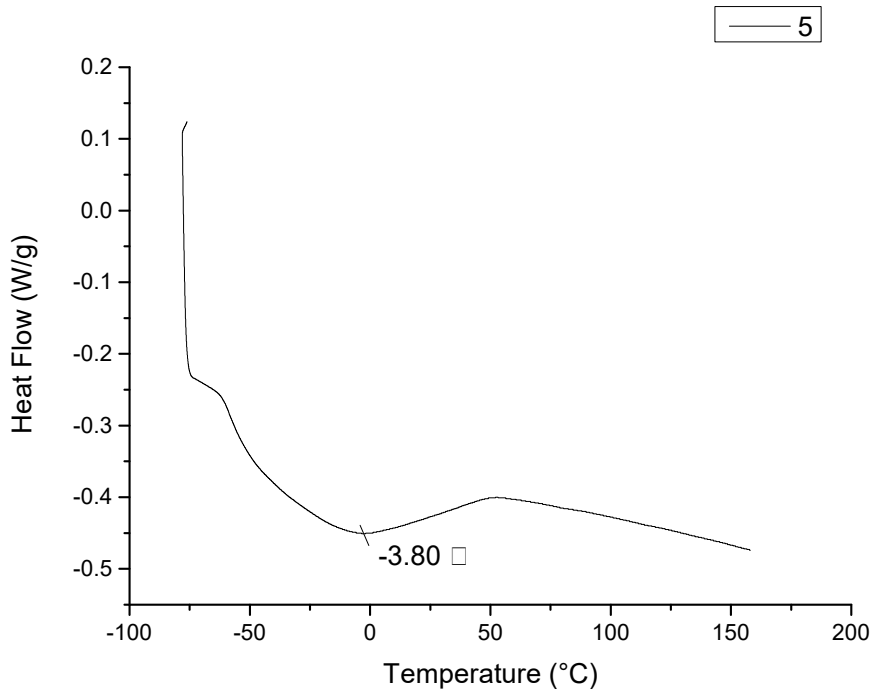


Figure S36. DSC of the polymer from table 1, entry 5.

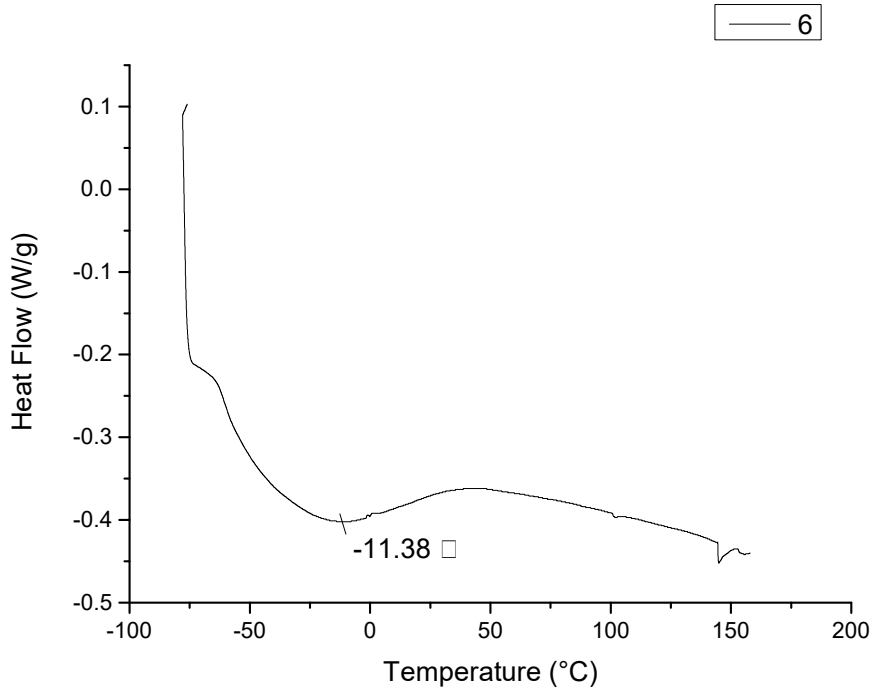


Figure S37. DSC of the polymer from table 1, entry 6.

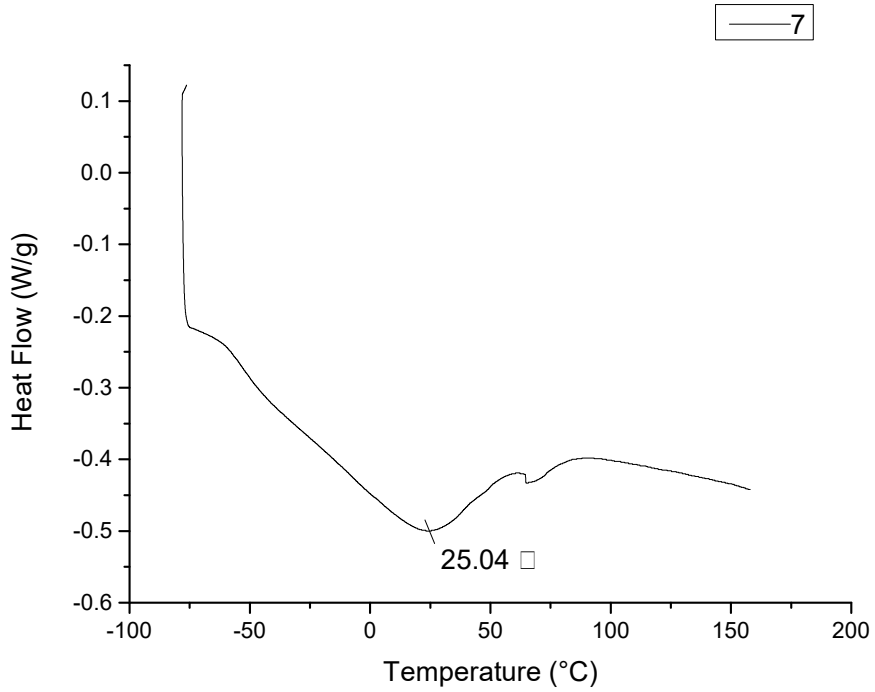


Figure S38. DSC of the polymer from table 1, entry 7.

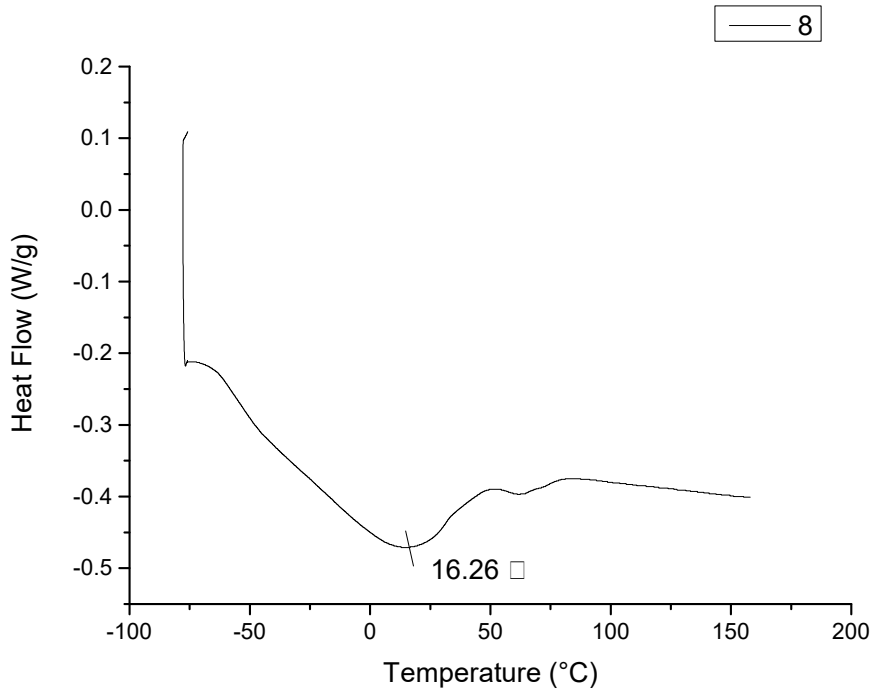


Figure S39. DSC of the polymer from table 1, entry 8.

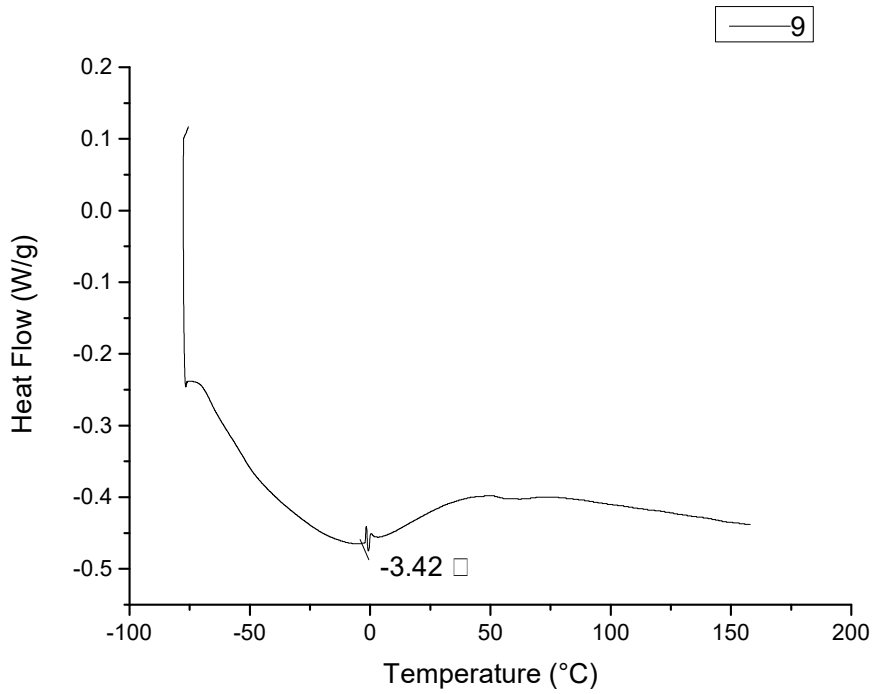
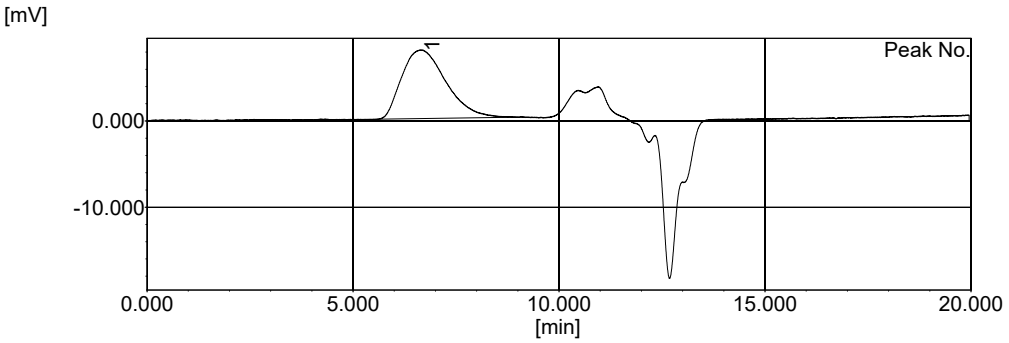


Figure S40. DSC of the polymer from table 1, entry 9.

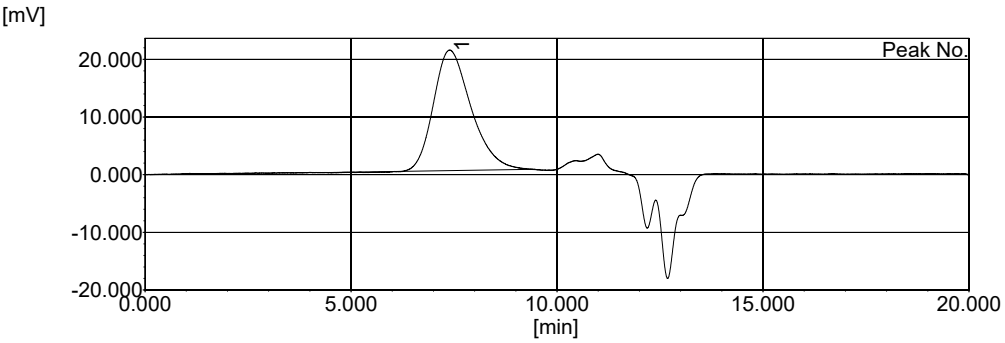


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.132	0.187	2,609,005	Mn	157,649
Peak top	6.622	8.254	282,900	Mw	283,003
Peak end	8.873	0.437	9,853	Mz	423,632
				Mz+1	599,737
				Mv	283,003
Height [mV]			7.967	Mp	282,900
Area [mV*sec]			594.838	Mz/Mw	1.497
Area% [%]			100.000	Mw/Mn	1.795
[eta]			283002.75660	Mz+1/Mw	2.119

Figure S41. GPC of the polymer from table 2, entry 3.

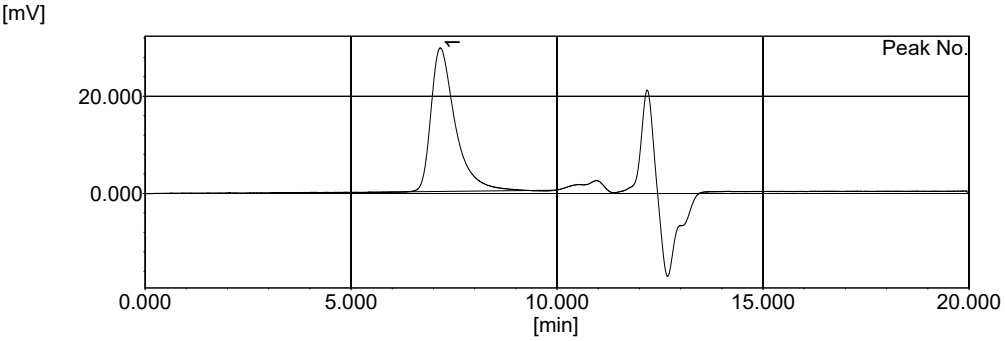


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	4.405	0.379	7,709,461	Mn	57,917
Peak top	7.390	21.642	89,971	Mw	102,060
Peak end	9.447	0.935	4,191	Mz	514,685
				Mz+1	3,859,879
				Mv	102,060
Height [mV]			20.934	Mp	89,971
Area [mV*sec]			1337.003	Mz/Mw	5.043
Area% [%]			100.000	Mw/Mn	1.762
[eta]			102060.44131	Mz+1/Mw	37.820

Figure S42. GPC of the polymer from table 2, entry 4.

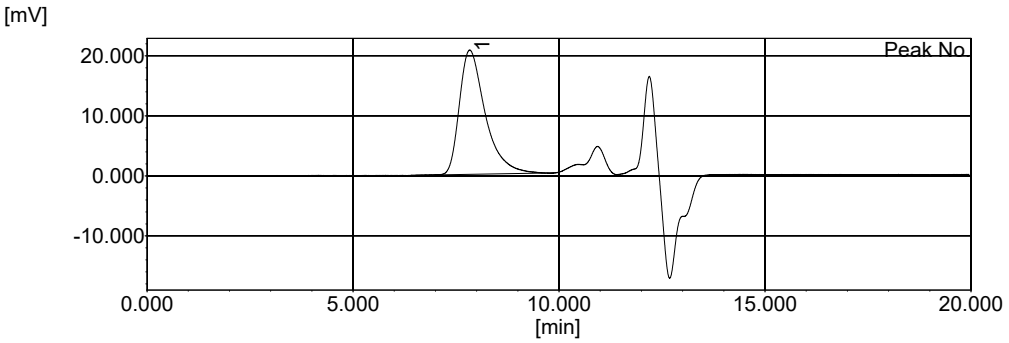


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.425	0.262	1,684,723	Mn	78,509
Peak top	7.163	29.981	126,147	Mw	113,771
Peak end	9.978	0.657	1,896	Mz	146,325
				Mz+1	251,111
				Mv	113,771
Height [mV]			29.568	Mp	126,148
Area [mV*sec]			1213.222	Mz/Mw	1.286
Area% [%]			100.000	Mw/Mn	1.449
[eta]			113770.62356	Mz+1/Mw	2.207

Figure S43. GPC of the polymer from table 3, entry 1.



Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	6.405	0.095	390,782	Mn	32,500
Peak top	7.835	20.986	46,338	Mw	42,898
Peak end	9.852	0.498	2,291	Mz	52,127
				Mz+1	64,963
				Mv	42,898
Height [mV]			20.724	Mp	46,339
Area [mV*sec]			902.568	Mz/Mw	1.215
Area% [%]			100.000	Mw/Mn	1.320
[eta]			42897.82080	Mz+1/Mw	1.514

Figure S44. GPC of the polymer from table 3, entry 3.

3. X-ray Crystallography

CCDC number of **Pd1** is 2155040. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

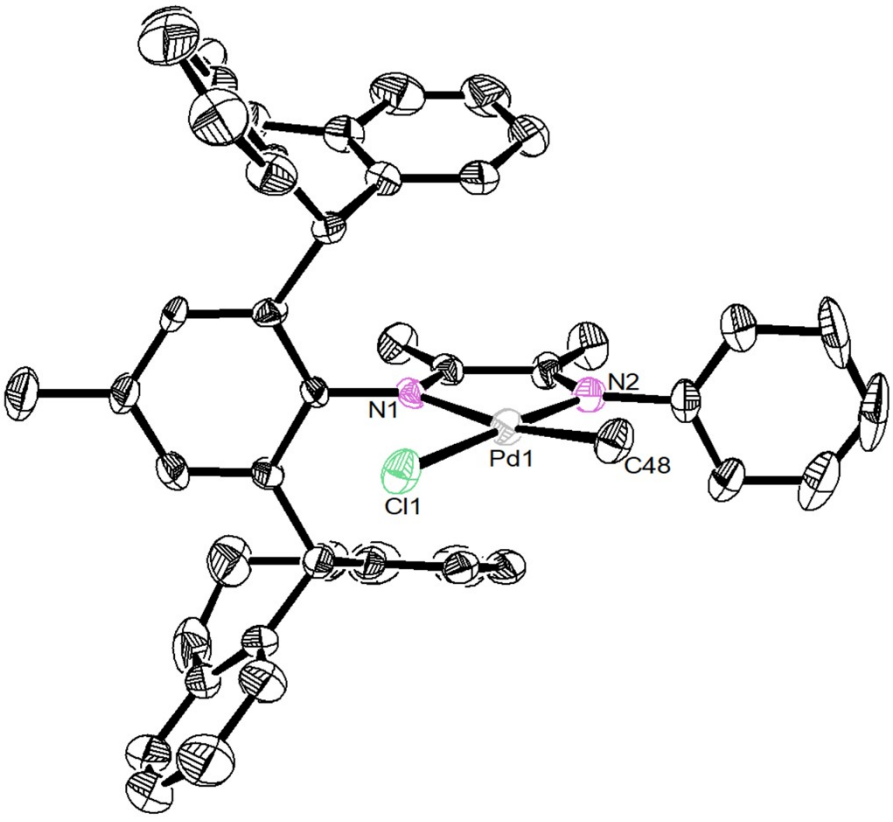


Table S1 Crystal data and structure refinement for Pd1.	
Identification code	**Pd1**
Empirical formula	C48 H45 Cl N2 Pd
Formula weight	791.71
Temperature/K	298(2)
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
a/Å	11.1910(13)
b/Å	18.5238(19)
c/Å	21.495(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4455.9(8)
Z	4
ρ_{calc}g/cm^3	1.180
μ/mm^{-1}	0.508
F(000)	1640
Crystal size/mm^3	0.40 x 0.23 x 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.05 to 25.01
Index ranges	-13<=h<=12, -22<=k<=20, -25<=l<=20
Reflections collected	18177
Independent reflections	7782 [R(int) = 0.0708]
Data/restraints/parameters	7782 / 0 / 476
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R1 = 0.0580, wR2 = 0.1261
Final R indexes [all data]	R1 = 0.0906, wR2 = 0.1404
Largest diff. peak/hole / e Å^{-3}	0.942 and -0.880