Supporting information for

Ligand Pre-inserted α-Diimine Palladium Catalysts and Mechanism Studies in Olefin Polymerization

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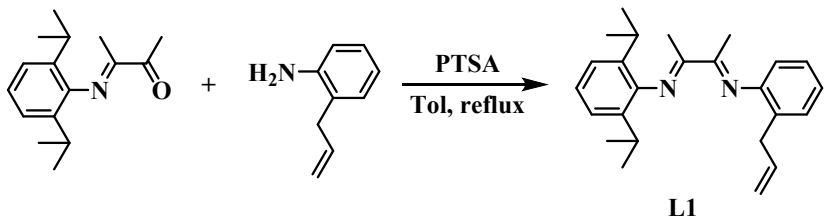
1. Experimental section

1.1. General Methods. All experiments were carried out under 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 spectra were recorded a Bruker AscendTm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters) at 40℃ with THF as the eluent, and the calibration was made using polystyrene standard. Dichloromethane, THF, toluene and hexane were purified by solvent purification systems.

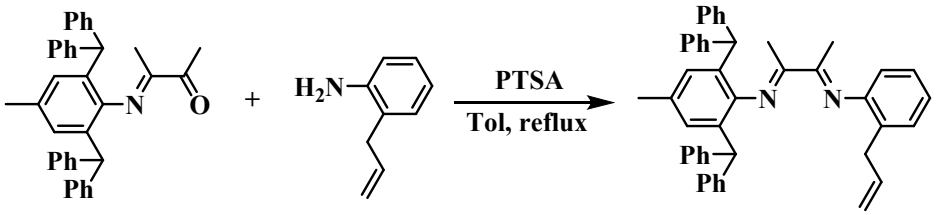
1.2. Computational Methods. All the DFT studies were performed by using the Gaussian 16 program. For geometry optimizations, the B3LYP hybrid exchange-correlation functional and the dispersion-corrected density functional theory (B3LYP-D3BJ) were used. The 6-31G(d) basis set was used for H, C, Cl and N atoms. Pd atoms were treated by the LANL2DZ basis set. In the single point energy calculations, the dispersion-corrected density functional theory B3LYP-D3(BJ) and a larger basis set BSII were used. In the BSII, 6-311+G(d,p) was used for H, C, Cl and N atoms, and Pd atoms were treated by the SDD basis set. In these single-point calculations, solvation effects were considered with the SMD model. The toluene was employed as a solvent in the SMD solvation calculations. Normal modes of all structures were examined. No imaginary frequency was observed except for the transition states.



L1

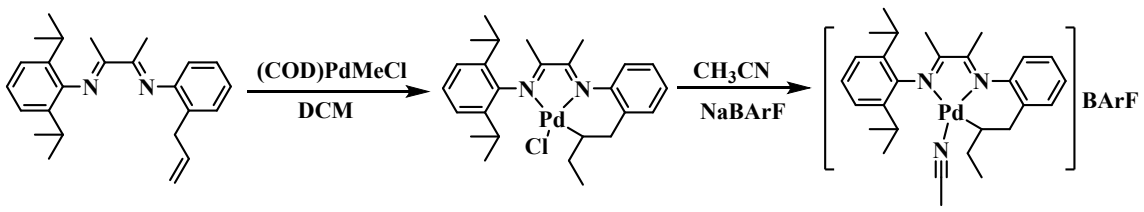
Preparation of L1. To a 250 mL round-bottomed flask equipped with a cold-water condenser was charged (E)-3-((2,6-diisopropylphenyl)imino)butan-2-one(2.45 g, 10 mmol), 2-allylaniline (1.33 g, 10 mmol), PTSA (5% mmol, 95 mg) and toluene (100 mL). The stirred solution was warmed to 140°C and held for 24 h while the toluene distilled. After removing toluene, the remaining volatiles were removed under vacuum. Afterwards, the crude product was purified by column chromatography using a gradual mixture of petroleum ether and ethyl

acetate to achieve the light yellow solid **L1** (3.2 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.13 (m, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.04-6.97 (m, 2H), 6.75-6.59 (m, 1H), 5.91-5.71 (m, 1H), 5.05-4.86 (m, 2H), 3.20 (m, 2H), 2.60&2.49-2.44 (m, 2H), 2.50&2.07 (s, 3H), 1.95 &1.74 (s, 3H), 1.13-1.02 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.11 (s), 167.08 (s), 166.65 (s), 148.13 (s), 145.11 (s), 135.86 (s), 133.92 (s), 128.75 (s), 128.10 (s), 125.86 (s), 123.12 (s), 122.71 (s), 121.92 (s), 117.10 (s), 114.23 (s), 76.31 (s), 75.99 (s), 75.67 (s), 35.57 (s), 27.27 (s), 22.08 (s), 21.77 (s), 15.36 (s), 14.80 (s).



L2

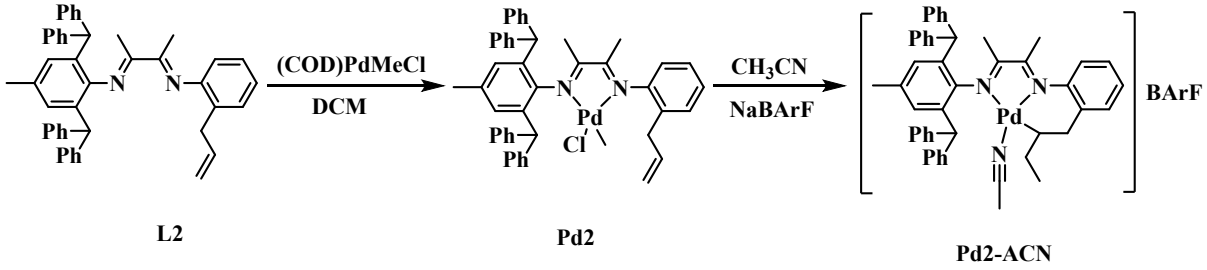
Preparation of L2. To a 250 mL round-bottomed flask equipped with a cold-water condenser was charged (E)-3-((2,6-dibenzhydryl-4-methylphenyl)imino)butan-2-one (5.0 g, 10 mmol), 2-allylaniline (1.33 g, 10 mmol), PTSA (5% mmol, 95 mg) and toluene (100 mL). The stirred solution was warmed to 140°C and held for 24 h while the toluene distilled. After removing toluene, the remaining volatiles were removed under vacuum. Afterwards, the crude product was purified by column chromatography using a gradual mixture of petroleum ether and ethyl acetate to achieve the light yellow solid **L2** (5.3 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.17-7.07 (m, 12H), 7.04-6.91 (m, 12H), 6.57 (s, 2H), 5.95-5.88 (m, 1H), 5.08 (d, *J* = 11.0 Hz, 2H), 5.02 (s, 2H), 3.40 (d, *J* = 5.7 Hz, 2H), 2.25 (s, 3H), 2.08 (s, 3H), 0.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.20 (s), 167.28 (s), 149.06 (s), 145.73 (s), 143.57 (s), 142.50 (s), 136.69 (s), 132.04 (s), 131.78 (s), 131.46 (s), 131.01 (s), 129.77 (s), 129.64 (s), 129.56 (s), 129.45 (s), 129.39 (s), 129.92 (s), 128.77 (s), 128.69 (s), 128.56 (s), 128.46 (s), 128.18 (s), 128.11 (s), 127.72 (s), 127.03 (s), 126.85 (s), 126.49 (s), 124.39 (s), 126.25 (s), 126.11 (s), 124.06 (s), 117.78 (s), 115.79 (s), 77.38 (s), 77.06 (s), 76.75 (s), 52.32 (s), 35.86 (s), 21.36 (s), 21.28 (s), 15.95 (s), 15.85 (s).



Preparation of Pd1. In nitrogen atmosphere, ligand **L1** (0.72 g, 2 mmol) was dissolved in DCM, and metal precursor (COD)PdMeCl (0.53 g, 2 mmol) was added, stirring for 12 h. Concentrated to remove the solvent and adding a little of acetone precipitate to obtain brick red solid **Pd1** (0.79 g,77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 1H), 7.30 (m, 2H), 7.22-7.16 (m, 3H), 7.07 (m, 1H), 3.54-3.48 (m, 1H), 3.16 (m, 1H), 2.94-2.84 (m, 2H), 2.50 (s, 3H), 2.03 (s, 3H), 1.93 (m, 1H), 1.42 (d, J = 6.7 Hz, 3H), 1.38 (d, J = 5.9 Hz, 1H), 1.34 (d, J = 6.8 Hz, 3H), 1.18 (d, J = 6.9 Hz, 3H), 1.08 (d, J = 6.9 Hz, 3H), 0.81 (t, J = 7.2 Hz, 3H), 0.71-0.62 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.63 (s), 168.29 (s), 141.80 (s), 141.44 (s), 140.67(s), 138.32 (s), 137.41 (s), 132.18 (s), 128.75 (s), 126.77 (s), 126.22 (s), 123.40 (s), 123.21(s), 77.34 (s), 77.02 (s), 76.70 (s), 47.62 (s), 36.98 (s), 28.61 (s), 27.10 (s), 24.49 (s), 23.67 (s), 23.45 (s), 22.52 (s), 19.79 (s), 12.53 (s). MALDI-TOF-MS (m/z) for $C_{26}H_{35}N_2Pd$: 481.1950 [M-Cl]. Anal. Calcd for $C_{26}H_{35}ClN_2Pd$: C, 60.35; H, 6.82; N, 5.41; Found: C, 60.31; H, 6.89; N, 5.48.

Preparation of Pd1-ACN. Pd1 (0.5 g, 1 mmol) and NaBArF (0.93 g, 1.05 mmol) were added into a 20 ml sample bottle, mixed with 10 ml DCM and 5 ml CH_3CN solvent, stirred for 12 h, filtered, drained, washed off the residual acetonitrile, and collected red solid to obtain **Pd1-ACN** (0.585 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 8H), 7.43 (s, 4H), 7.27-7.13 (m, 6H), 6.93 (d, J = 7.6 Hz, 1H), 3.23-3.12 (m, 1H), 2.91 (d, J = 15.5 Hz, 1H), 2.73-2.61 (m, 2H), 2.51 (s, 3H), 2.06 (s, 3H), 1.77 (d, J = 14.8 Hz, 1H), 1.59 (s, 3H), 1.19-1.13 (m, 6H), 1.09 (d, J = 6.9 Hz, 3H), 1.01 (d, J = 6.9 Hz, 3H), 0.87-0.80 (m, 1H), 0.72 (t, J = 7.1 Hz, 3H), 0.53-0.41 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.40 (s), 172.16 (s), 162.63 (s), 162.13 (s), 161.64 (s), 161.14 (s), 140.26 (s), 140.22(s), 139.14 (s), 138.53 (s), 137.29 (s), 135.01 (s), 132.57 (s), 130.75 (s), 129.26 (s), 128.95 (s), 128.13 (s), 127.46 (s), 126.11 (s), 124.35 (s), 123.40 (s), 120.88 (s), 120.69(s), 117.69 (s), 77.55 (s), 77.23 (s), 76.91 (s), 53.68 (s), 37.36

(s), 29.04 (s), 28.67 (s), 24.26 (s), 23.73 (s), 23.35 (s), 22.77 (s), 20.12 (s), 13.11 (s), 1.71 (s). MALDI-TOF-MS (m/z) for $C_{26}H_{35}N_2Pd$: 481.1424 [M-Anion-CH_3CN]. Anal. Calcd for $C_{26}H_{35}ClN_2Pd$: C, 51.99; H, 3.64; N, 3.03; Found: C, 60.01; H, 3.59; N, 3.09.



L2 Pd2 Pd2-ACN

Preparation of Pd2. In nitrogen atmosphere, ligand **L2** (1.24 g, 2 mmol) was dissolved in DCM, and metal precursor (COD)PdMeCl (0.53 g, 2 mmol) was added, stirring for 12 h. Concentrated to remove the solvent and adding a little of acetone precipitate to get brick red solid **Pd2** (1.1 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.32 (m, 6H), 7.28 (s, 7H), 7.24-7.05 (m, 10H), 6.90-6.74 (m, 2H), 6.66 (s, 1H), 6.15 (s, 1H), 6.05-5.84 (m, 2H), 5.23-4.96 (m, 2H), 3.85-3.55 (m, 2H), 2.23-2.14 (m, 3H), 1.45-1.38 (s, 3H), 1.03&0.65 (s, 3H), -0.35 (d, J = 19.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.34 (s), 175.11 (s), 174.02 (s), 169.69 (s), 144.96 (s), 143.1 (s), 142.97 (s), 142.2 (s), 141.97 (s), 141.51 (s), 136.60 (s), 135.46 (s), 134.78 (s), 134.67 (s), 130.43 (s), 129.97 (s), 129.62 (s), 129.56(s), 129.39 (s), 129.3 (s), 129.05 (s), 128.87 (s), 128.8 (s), 128.29 (s), 128.25 (s), 127.70 (s), 127.48 (s), 127.28 (s), 127.14 (s), 127.03 (s), 126.74 (s), 126.38 (s), 121.31 (s), 117.51 (s), 77.55 (s), 77.23 (s), 76.91 (s), 52.53 (s), 52.46 (s), 52.31 (s), 52.18 (s), 36.61 (s), 35.41 (s), 21.69 (s), 19.98 (s), 18.56 (s), 4.74 (s), 3.40 (s). MALDI-TOF-MS (m/z) for $C_{46}H_{42}ClN_2Pd$: 763.2634 [M-Me]; $C_{47}H_{45}N_2Pd$: 743.3975 [M-Cl]; $C_{46}H_{42}N_2Pd$: 728.2006 [M-Cl-Me]. Anal. Calcd for $C_{26}H_{35}ClN_2Pd$: C, 72.40; H, 5.82; N, 3.59; Found: C, 72.41; H, 5.89; N, 3.51.

Preparation of Pd2-ACN. Pd2 (0.78 g, 1 mmol) and NaBArF (0.93 g, 1.05 mmol) were added into a 20 ml sample bottle, mixed with 10 ml DCM and 5 ml CH_3CN solvent, stirred for 12 h, filtered, drained, washed off the residual acetonitrile, and collected red solid to obtain **Pd2-ACN** (0.83 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 8H), 7.51 (s, 4H), 7.40-7.35 (m, 4H), 7.34-7.21 (m, 11H), 7.18 (d, J = 7.0 Hz, 2H), 7.09 (d, J = 7.0 Hz, 2H),

7.03 (d, J = 7.1 Hz, 4H), 6.93 (d, J = 5.4 Hz, 2H), 6.79 (s, 1H), 5.47 (d, J = 7.7 Hz, 2H), 3.31-3.25 (m, 1H), 3.08 (d, J = 15.4 Hz, 1H), 2.22 (s, 3H), 2.18 (s, 3H), 1.91 (d, J = 12.9 Hz, 1H), 1.65 (s, 3H), 1.05-0.97 (m, 1H), 0.85 (t, J = 7.2 Hz, 3H), 0.76 (s, 3H), 0.69-0.60 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.26 (s), 170.31 (s), 160.39 (s), 159.90 (s), 159.40 (s), 158.90 (s), 139.23 (s), 139.19 (s), 139.07 (s), 138.88 (s), 137.78 (s), 137.10 (s), 134.68 (s), 132.75 (s), 131.58 (s), 130.36 (s), 128.46 (s), 127.44 (s), 127.28 (s), 127.14 (s), 126.99 (s), 126.97 (s), 126.85 (s), 126.77 (s), 126.68 (s), 126.57 (s), 125.42 (s), 125.38 (s), 125.28 (s), 125.23 (s), 123.86 (s), 121.15 (s), 120.52 (s), 118.52 (s), 118.44 (s), 115.43 (s), 75.26 (s), 75.15 (s), 74.95 (s), 74.63 (s), 52.73 (s), 51.28 (s), 50.71 (s), 34.92 (s), 25.63 (s), 19.81 (s), 19.21 (s), 17.03 (s), 10.61 (s). MALDI-TOF-MS (m/z) for $C_{47}H_{45}N_2Pd$: 743.2631 [M-Anion-CH_3CN]. Anal. Calcd for $C_{81}H_{60}BF_{24}N_3Pd$: C, 59.01; H, 3.67; N, 2.55; Found: C, 59.04; H, 3.69; N, 2.51.

Procedure for Ethylene Polymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with 18 mL toluene and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high-pressure line and the solution was degassed. The vessel was warmed to desired temperature using an oil bath and allowed to equilibrate for 15 minutes. 10 μmol of Pd catalyst in 2 mL CH_2Cl_2 was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized and maintained at 8.0 atm of ethylene. After a desired amount of time, the polymerization was quenched with methanol. The polyethylene was collected and dried at 45^{o}C in vacuum.

Procedure for Ethylene-Polar Monomer Copolymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with toluene and polar monomer in total 18 mL, a magnetic stir bar in the glovebox. The pressure vessel was connected to a high-pressure line and the solution was degassed. The vessel was warmed to desired temperature using an oil bath and allowed to equilibrate for 15 minutes 20 μmol of Pd complex in 2 mL CH_2Cl_2 was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized and maintained at 8.0 atm of ethylene. After 3 h, solvent toluene was evaporated and the copolymer products were dried at 45^{o}C in vacuum.

2. Mechanism investigation

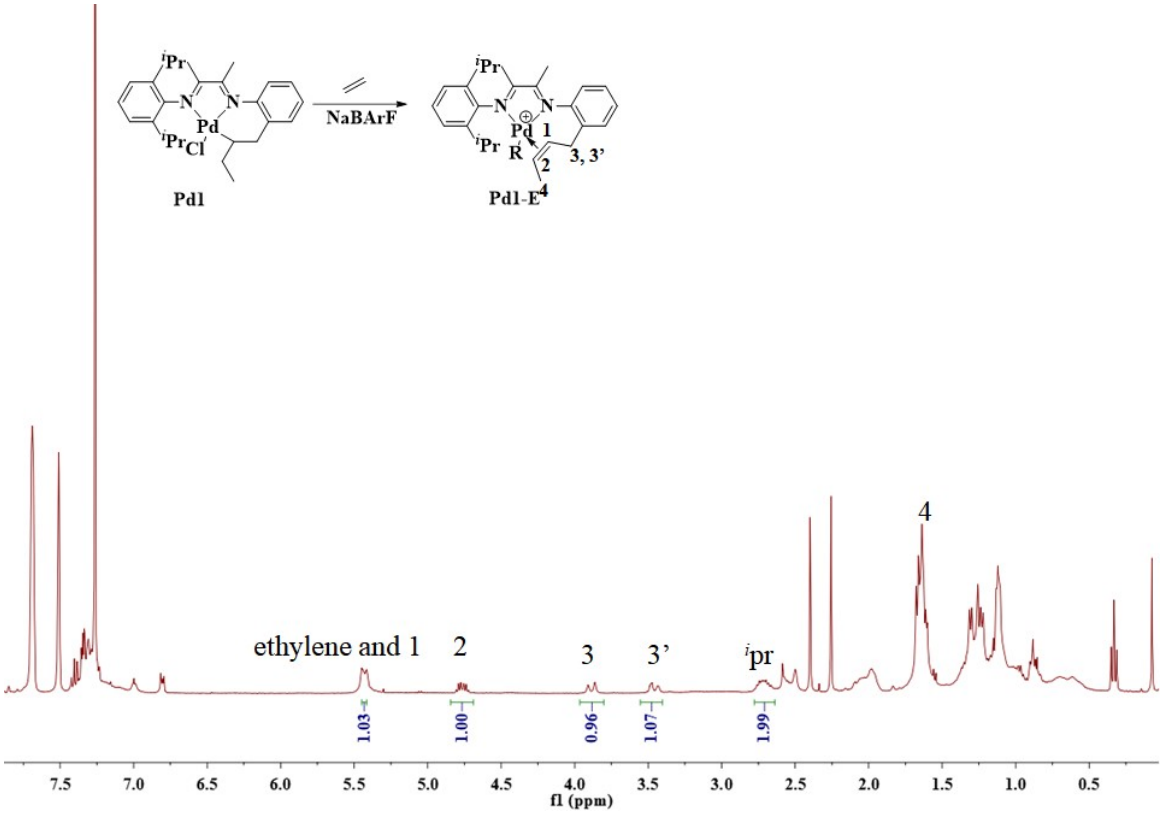


Figure S1. Insertion mechanism study using **Pd1** under stoichiometric ethylene at room temperature for 30 minutes. ^{1}H NMR spectrum of **Pd1-E** ($CDCl_3$).

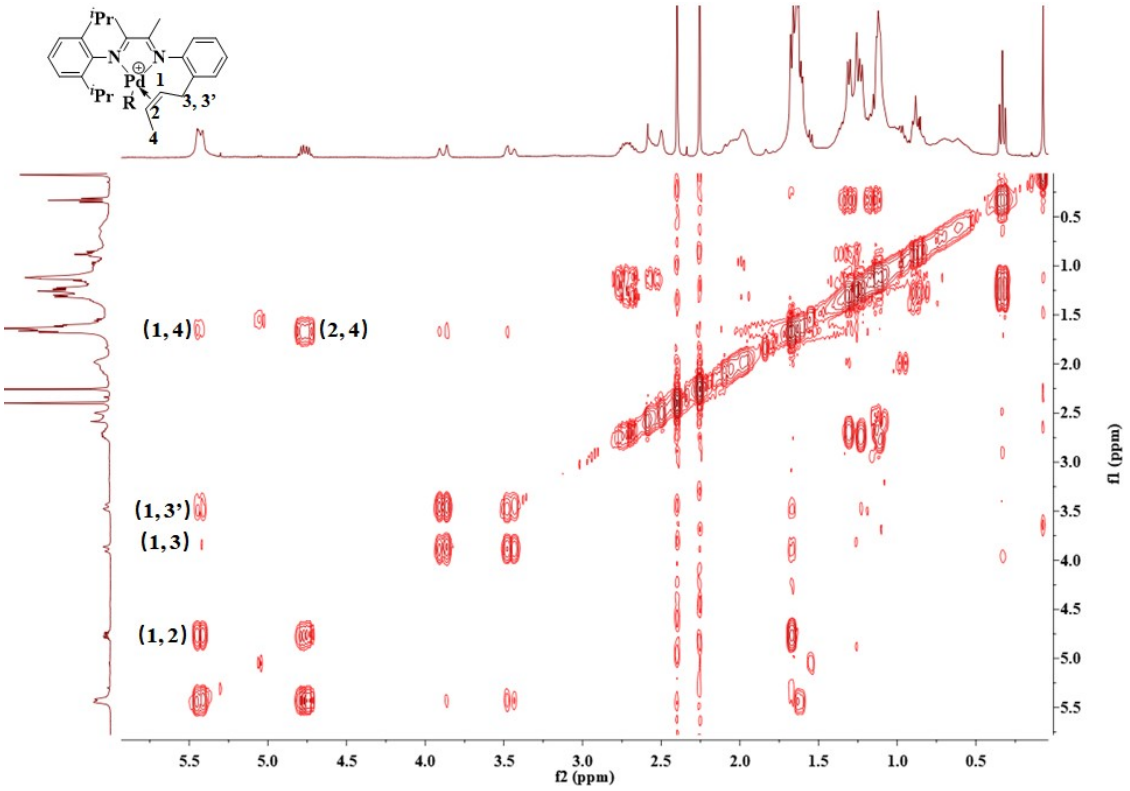


Figure S2. H-H COSY NMR spectrum of **Pd1-E** ($CDCl_3$).

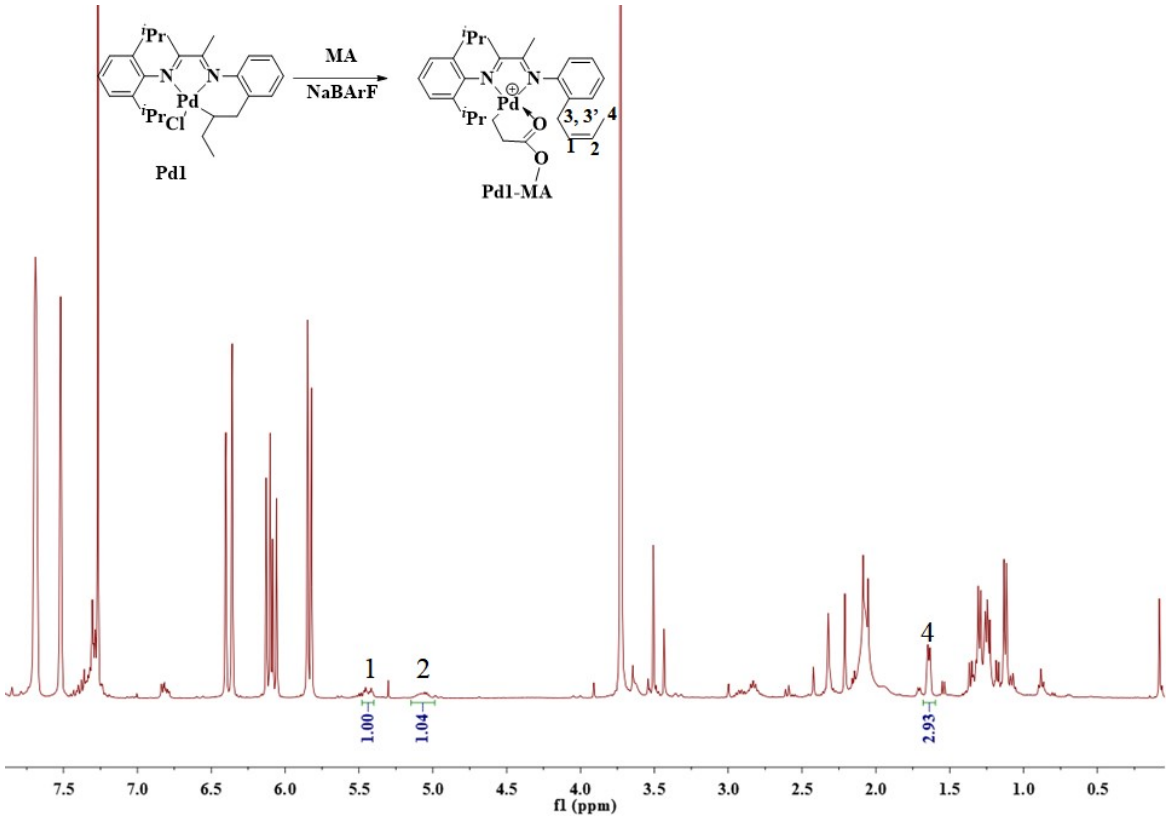


Figure S3. Insertion mechanism study using **Pd1** with 10 eq. of MA at room temperature for 30 minutes. ^1H NMR spectrum of **Pd1-MA** ($CDCl_3$).

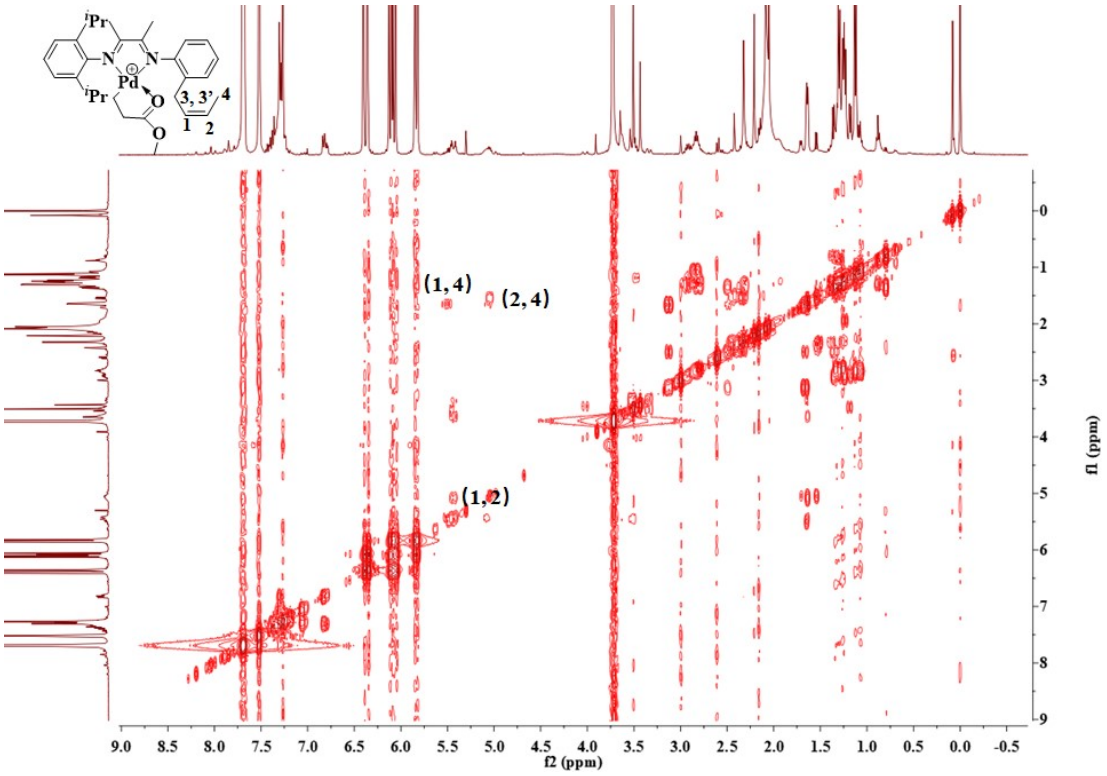


Figure S4. H-H COSY NMR spectrum of **Pd1-MA** ($CDCl_3$).

3. ^{1}H NMR, ^{13}C NMR and MALDI-TOF-MS of ligands and catalysts

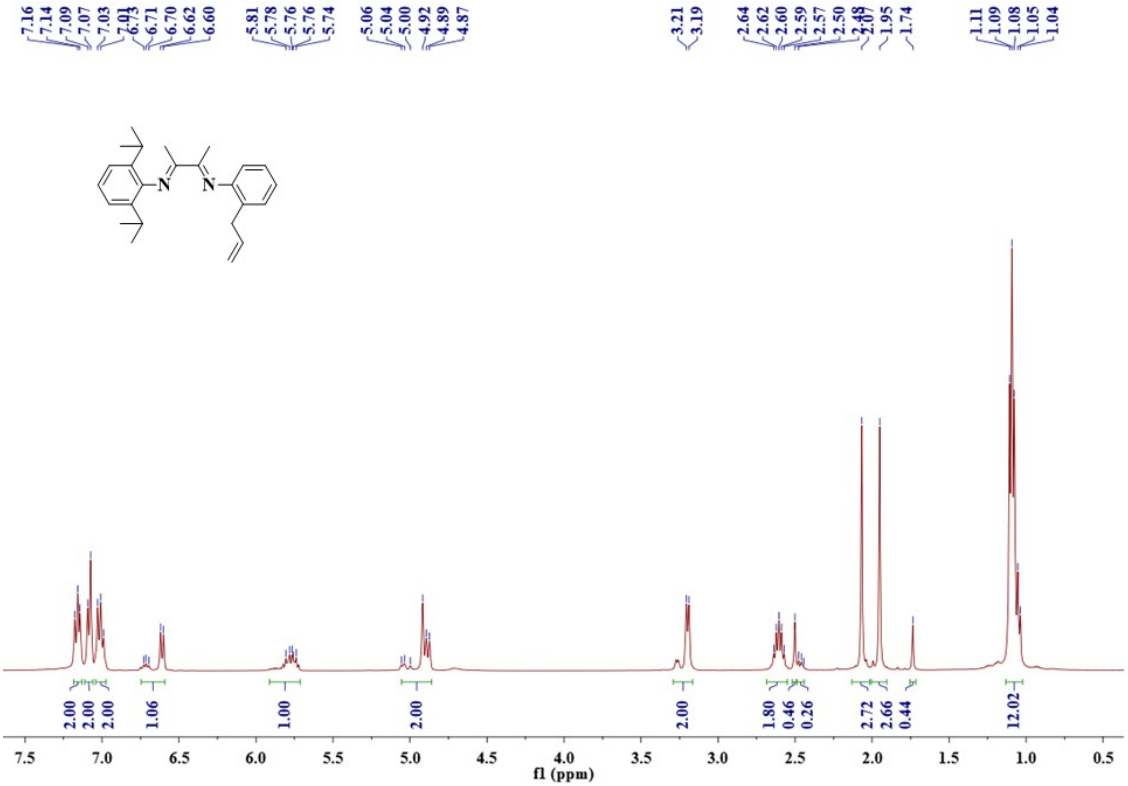


Figure S5. ^{1}H NMR spectrum of **L1** ($CDCl_3$).

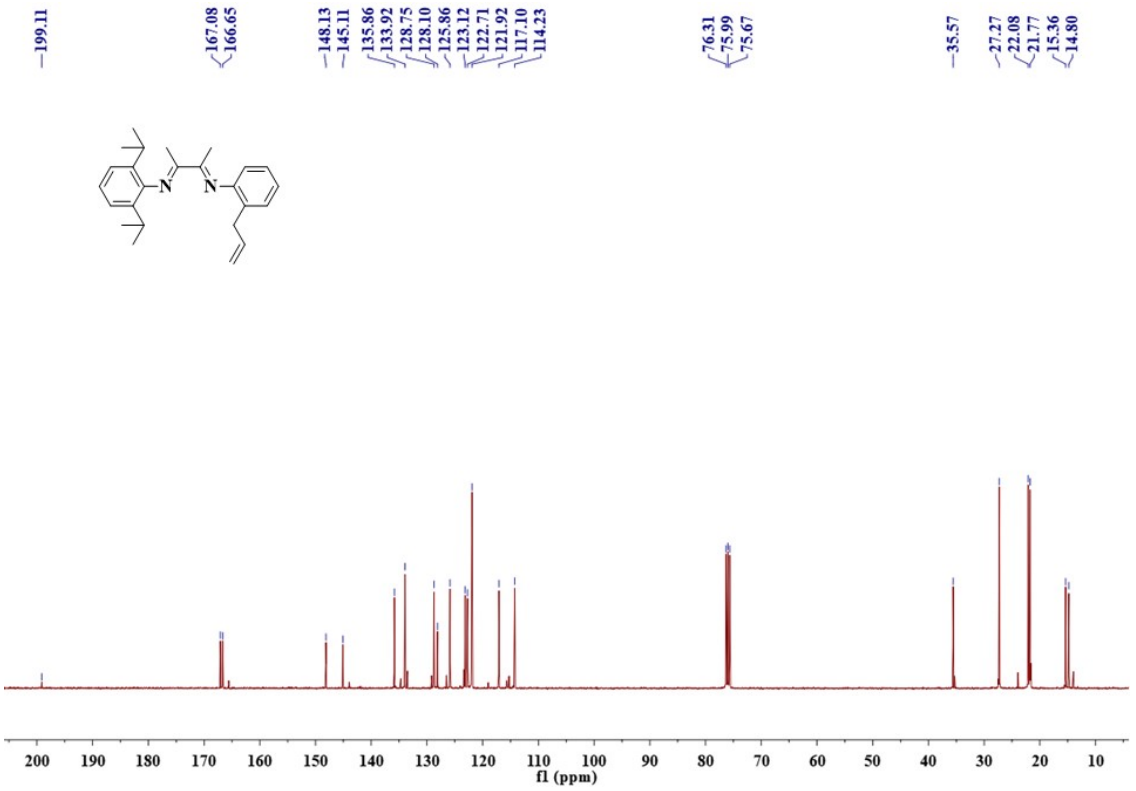


Figure S6. ^{13}C NMR spectrum of **L1** ($CDCl_3$).

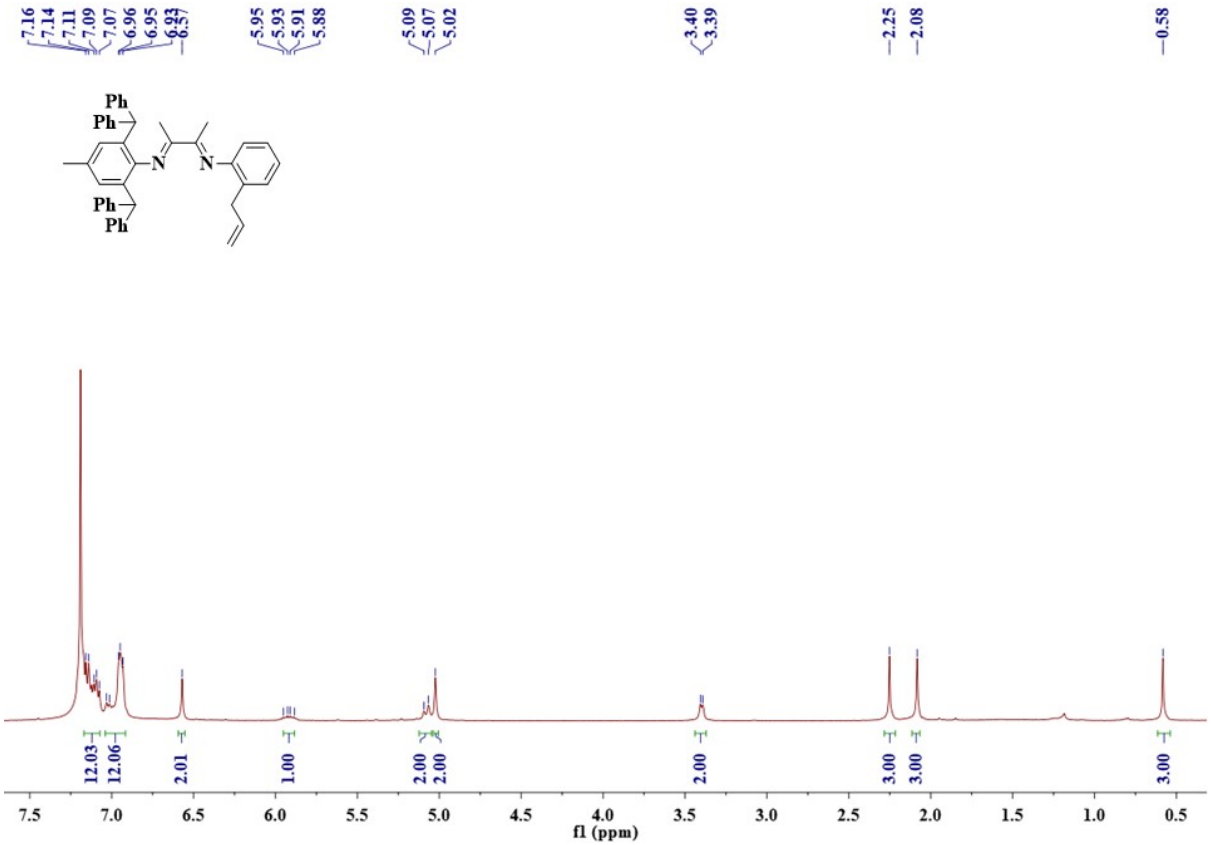


Figure S7. ^{1}H NMR spectrum of **L2** ($CDCl_3$).

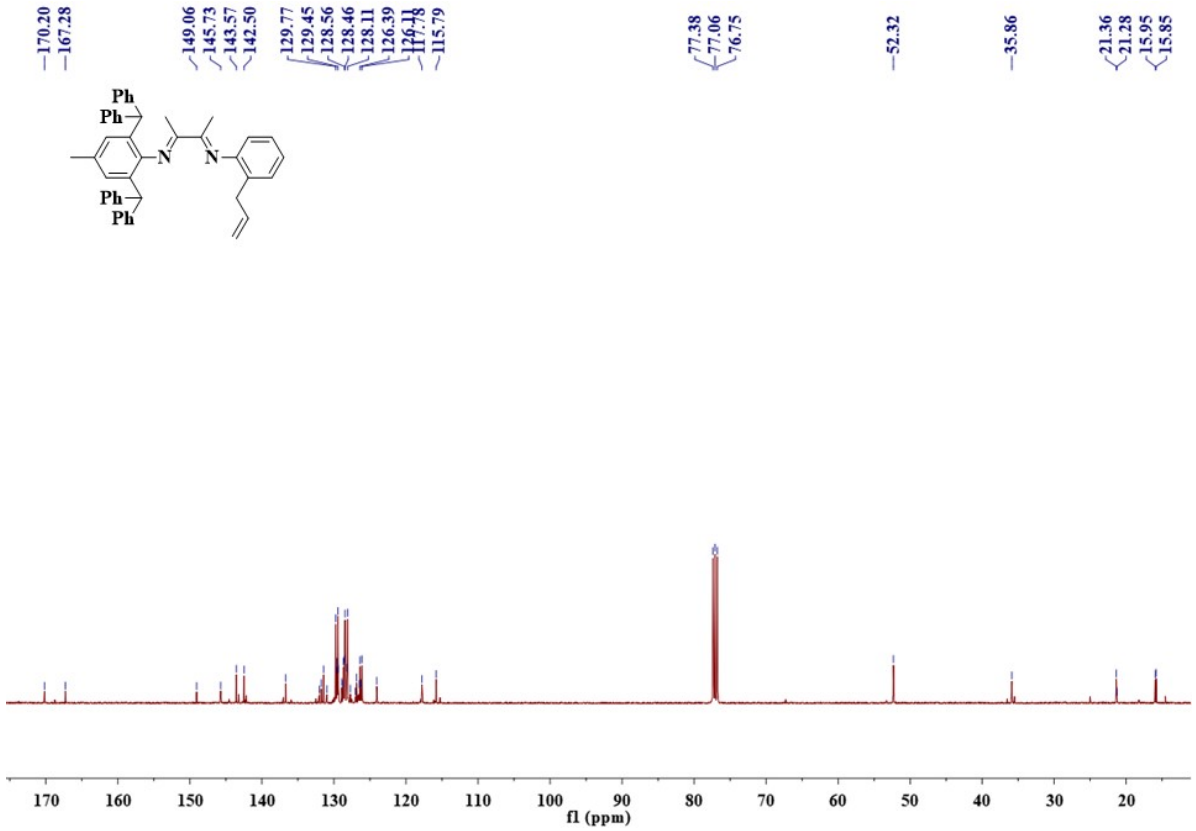


Figure S8. ^{13}C NMR spectrum of **L2** ($CDCl_3$).

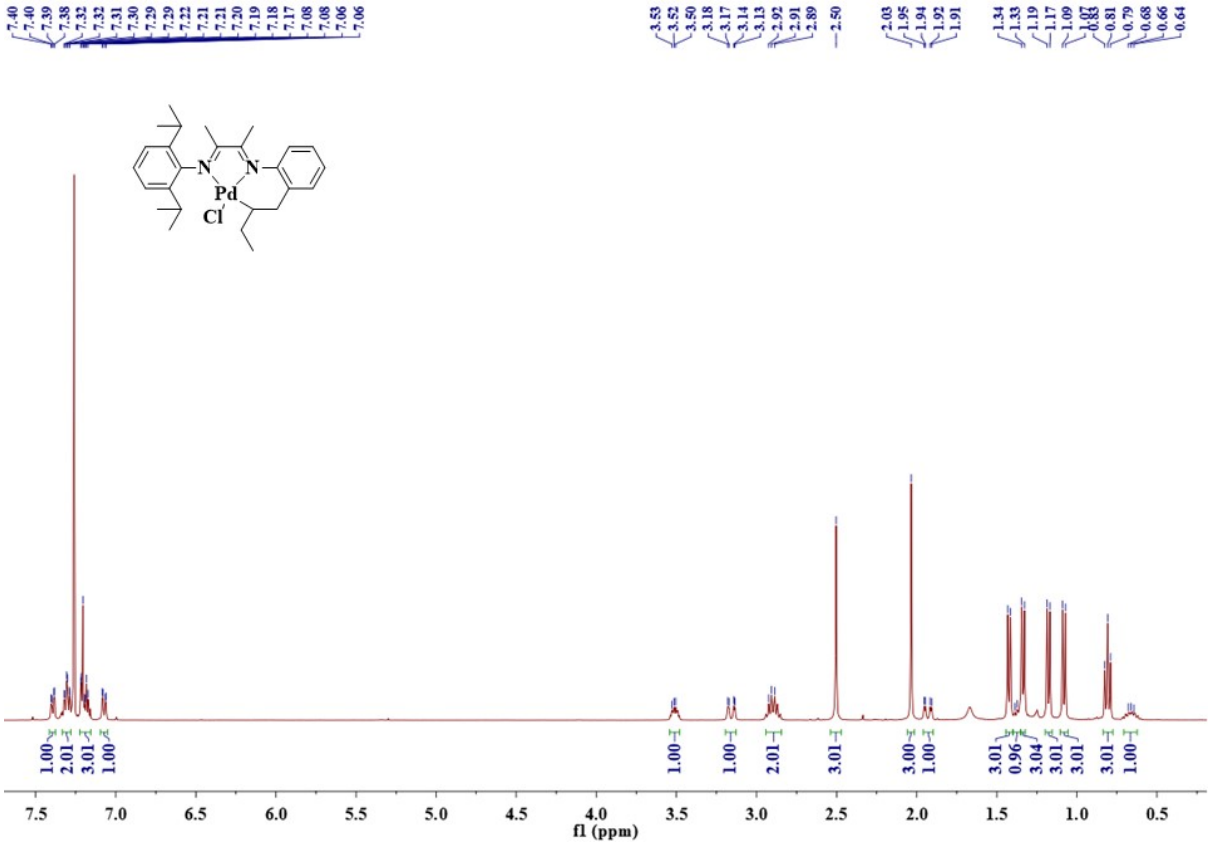


Figure S9. ^{1}H NMR spectrum of **Pd1** ($CDCl_3$).

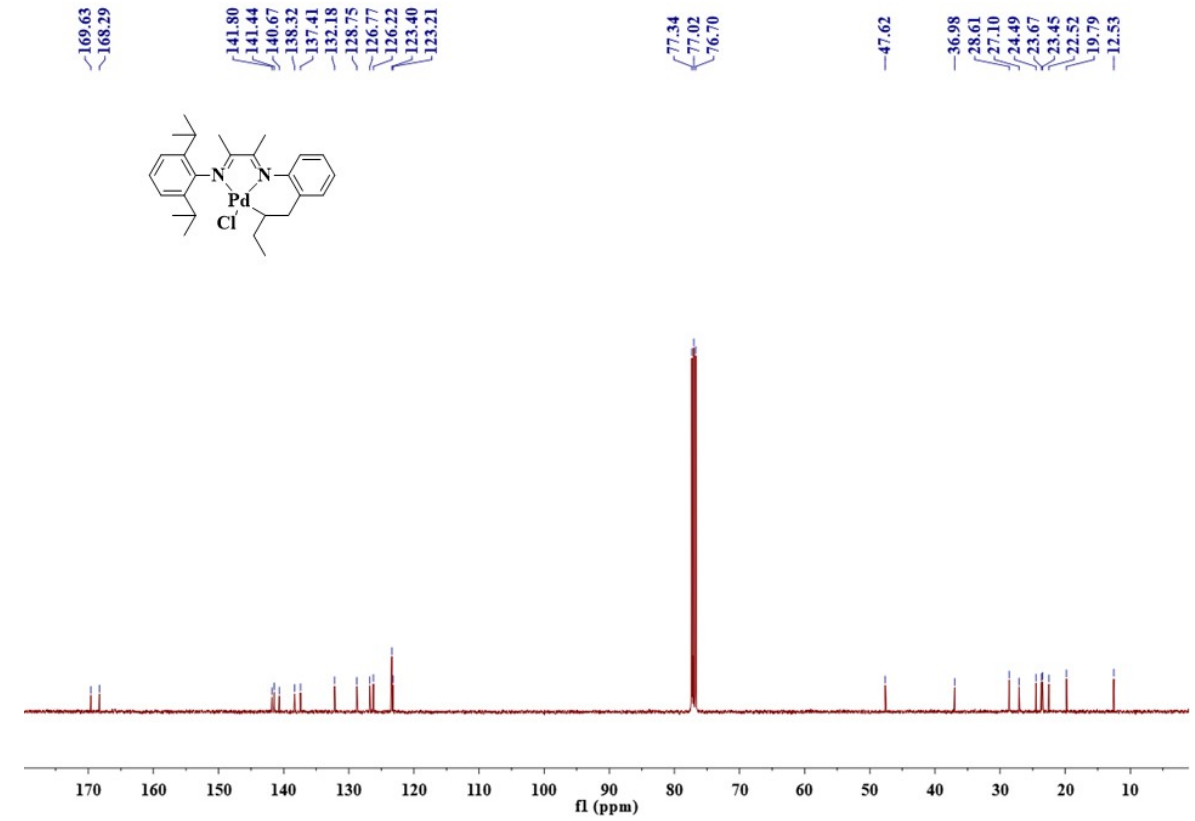


Figure S10. ^{13}C NMR spectrum of **Pd1** ($CDCl_3$).

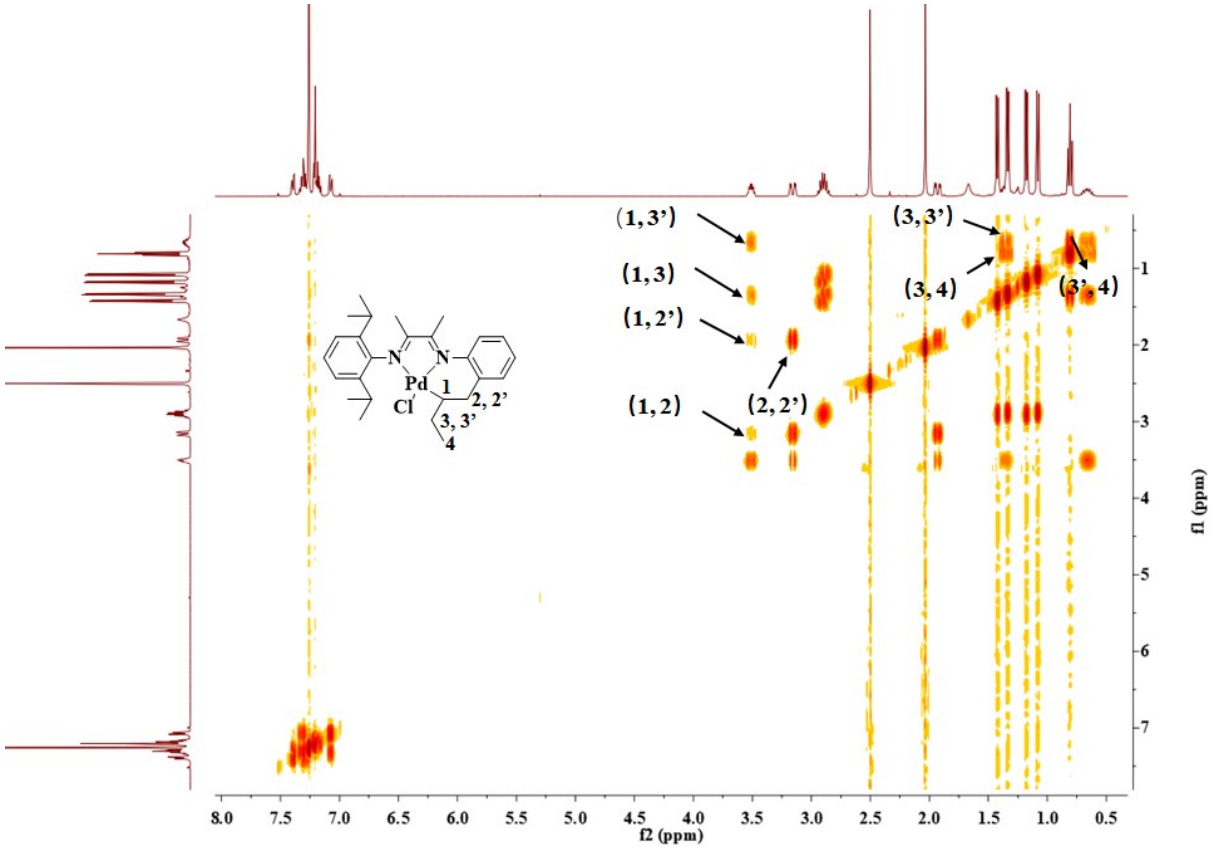


Figure S11. H-H COSY NMR spectrum of **Pd1** ($CDCl_3$).

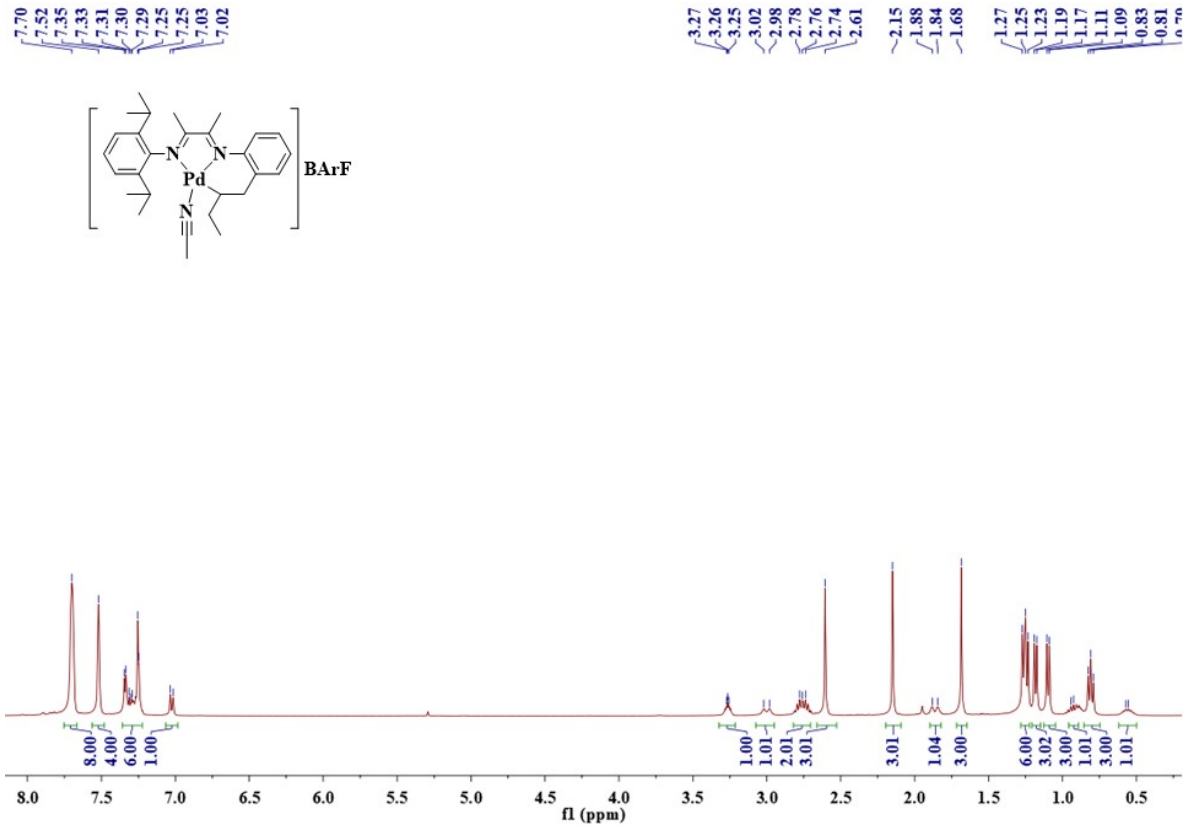


Figure S12. ^{1}H NMR spectrum of **Pd1-ACN** ($CDCl_3$).

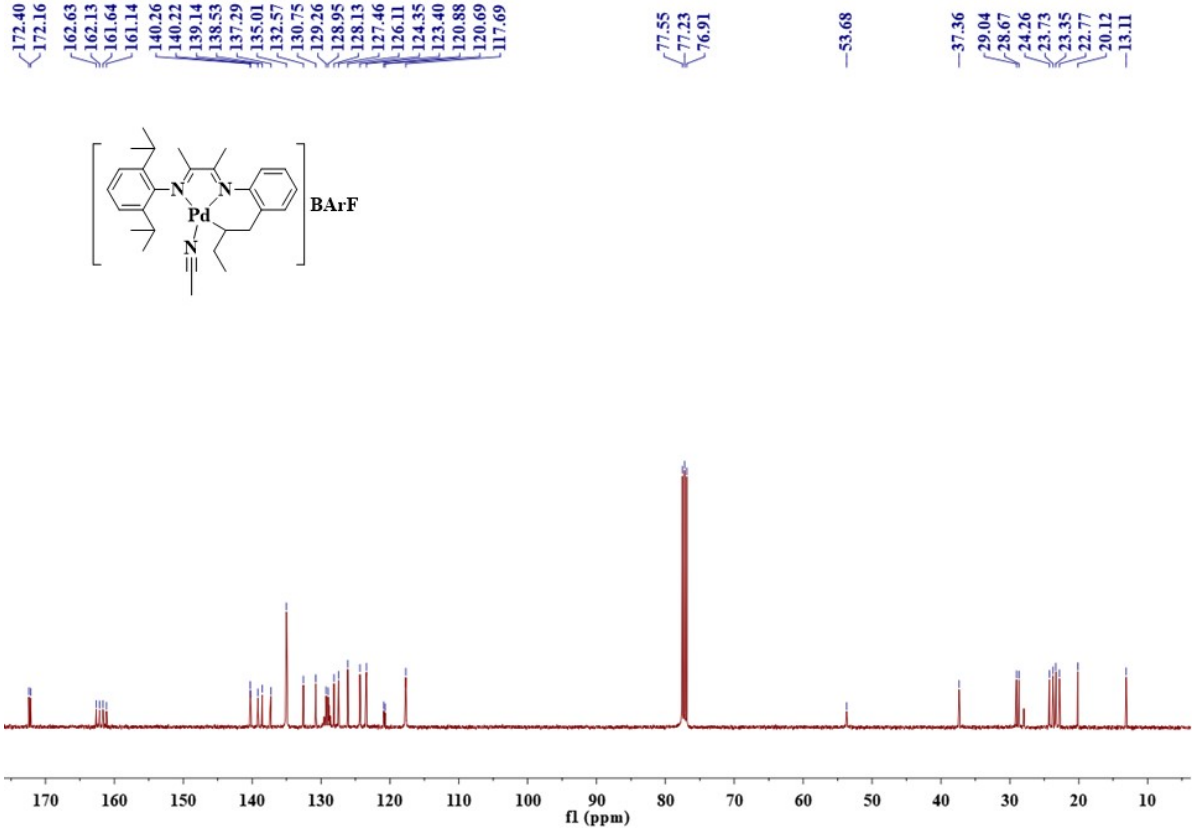


Figure S13. ^{13}C NMR spectrum of **Pd1-ACN** ($CDCl_3$).

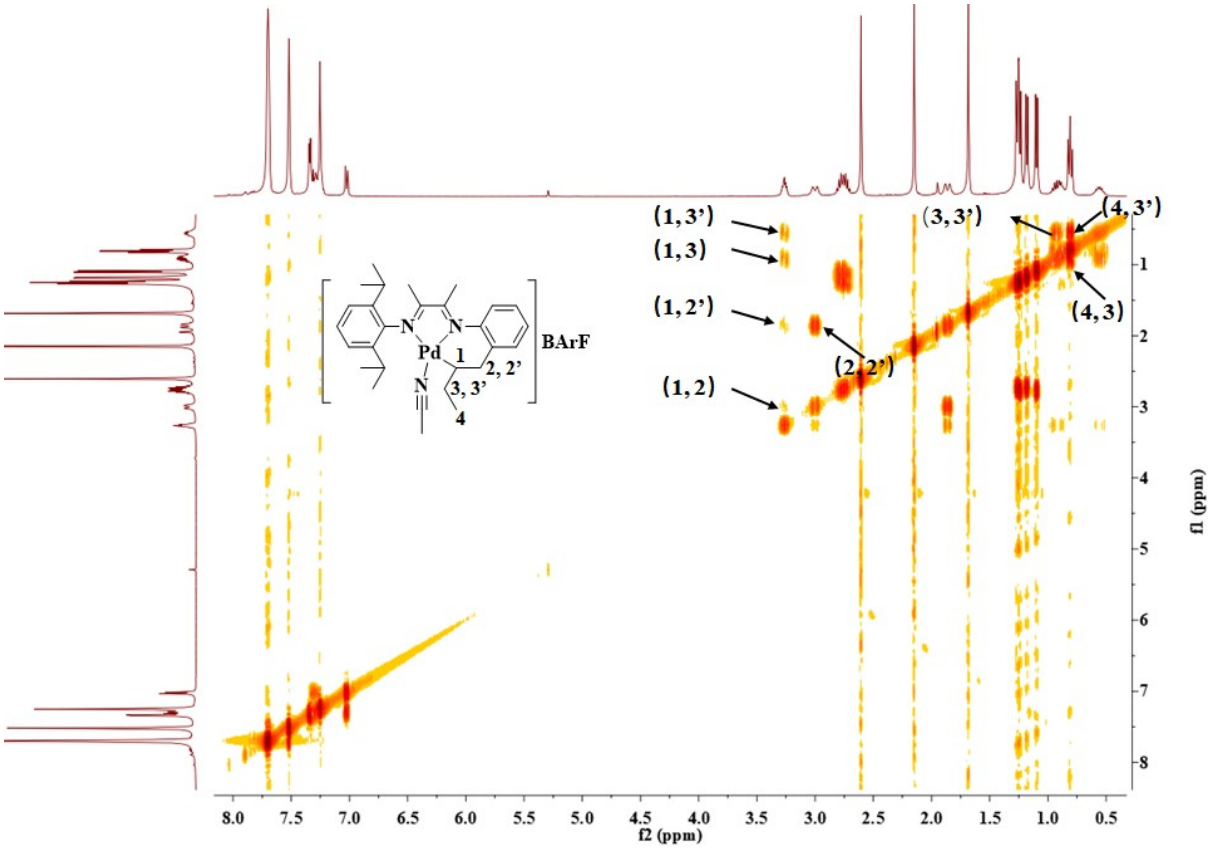


Figure S14. H-H COSY NMR spectrum of **Pd1-ACN** ($CDCl_3$).

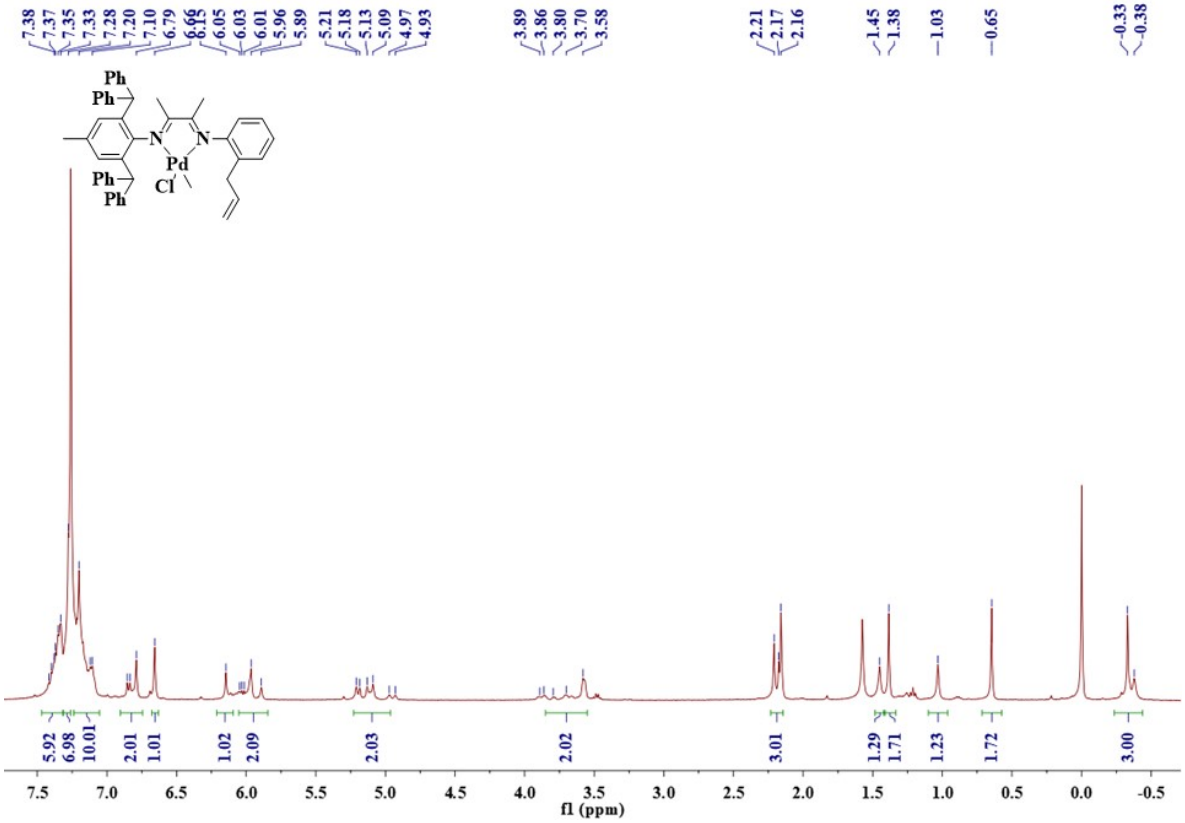


Figure S15. ^1H NMR spectrum of **Pd2** ($CDCl_3$).

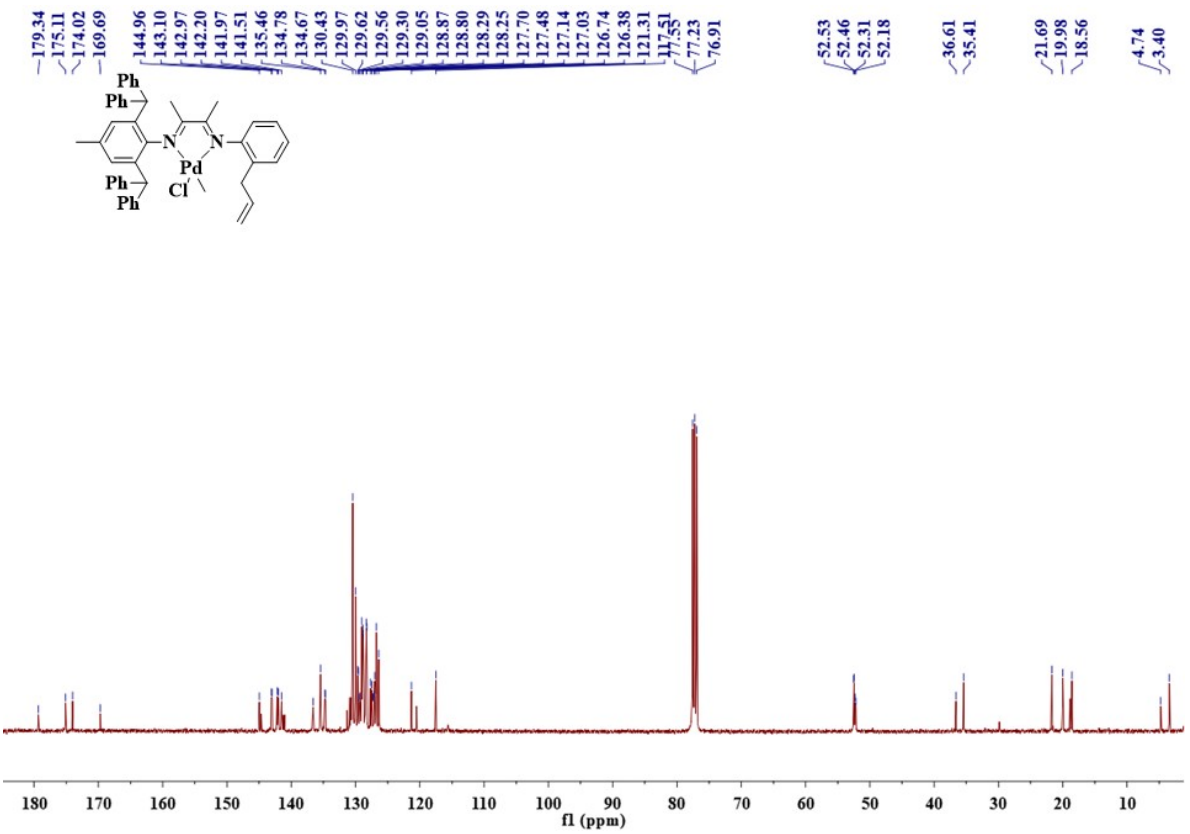


Figure S16. ^{13}C NMR spectrum of **Pd2** ($CDCl_3$).

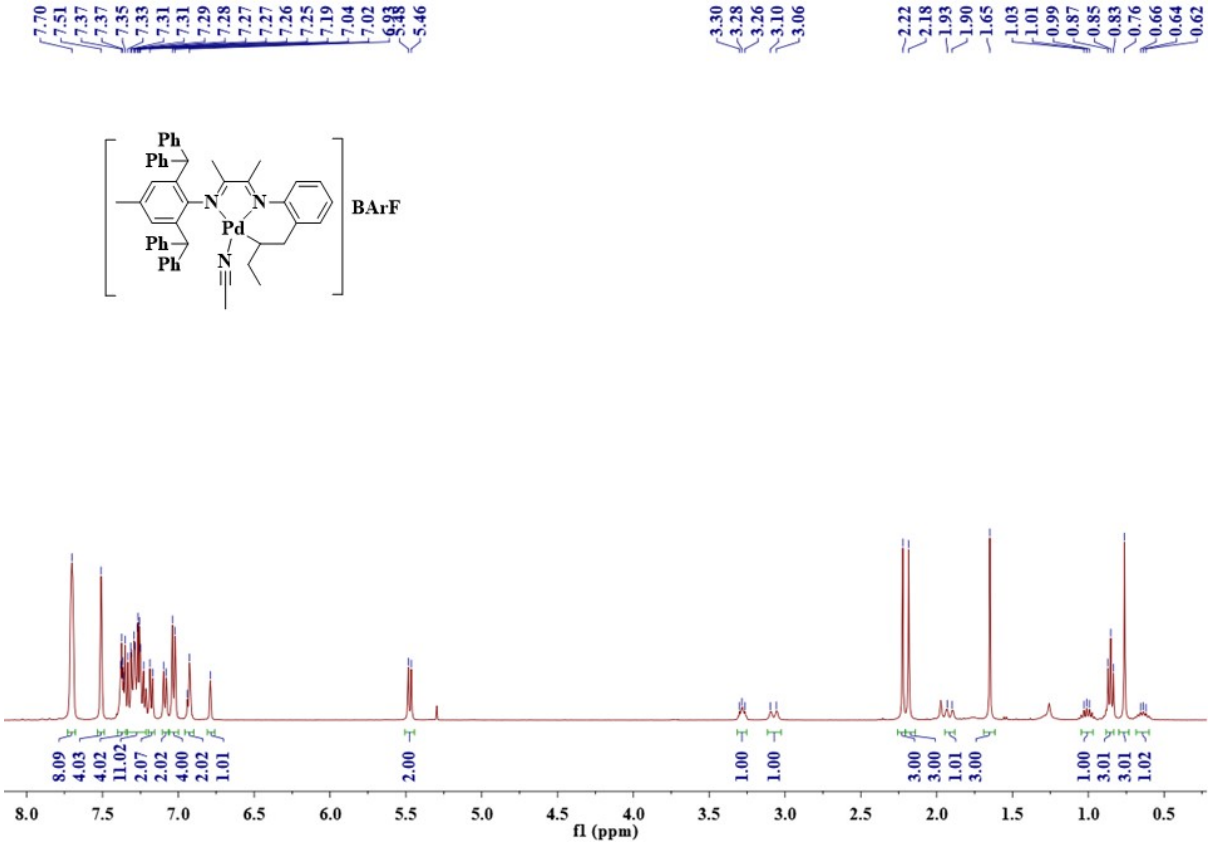


Figure S17. ^{1}H NMR spectrum of **Pd2-ACN** ($CDCl_3$).

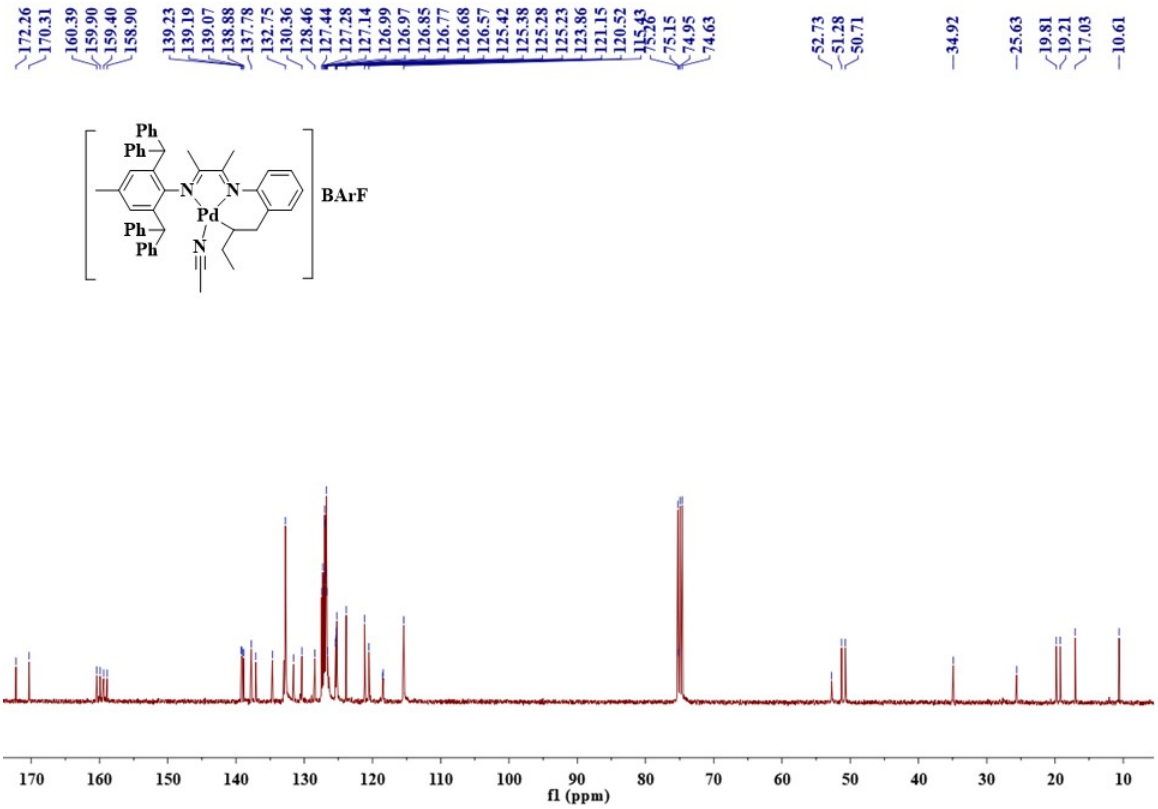


Figure S18. ^{13}C NMR spectrum of **Pd2-ACN** ($CDCl_3$).

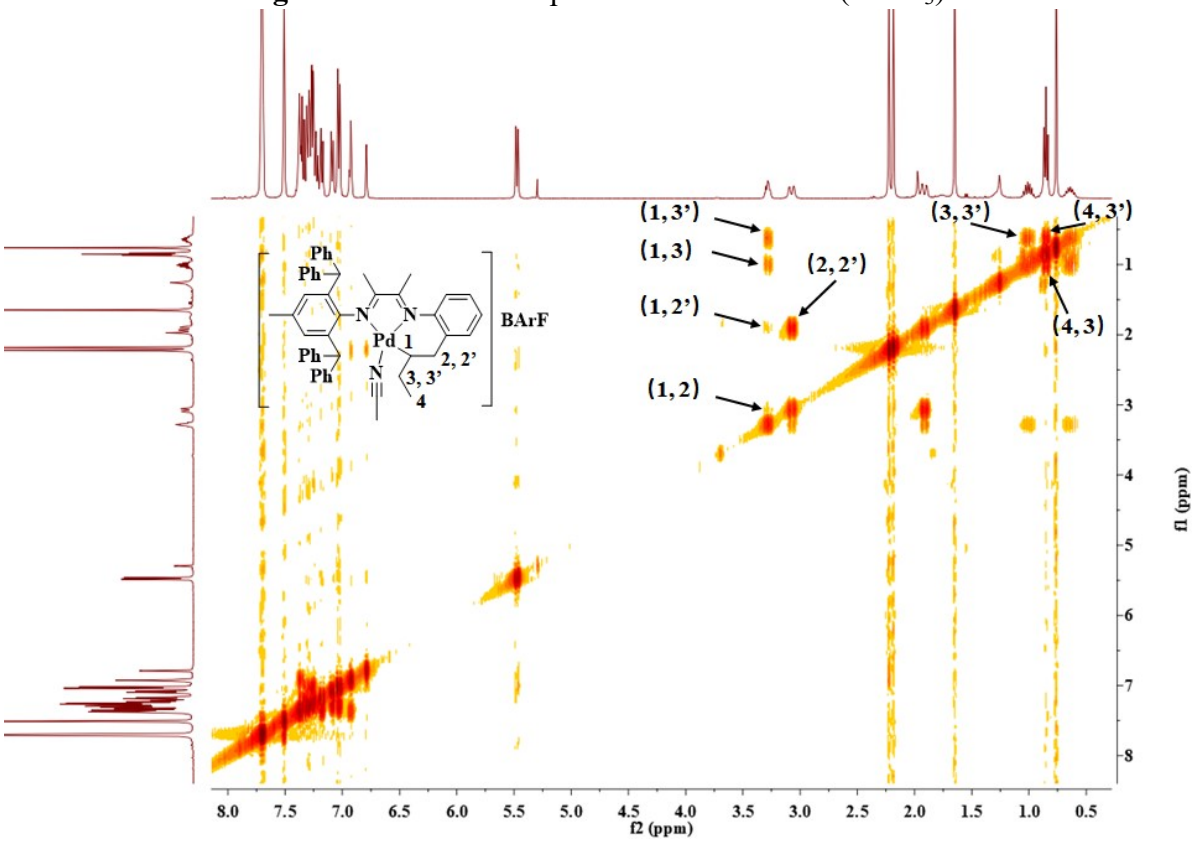


Figure S19. H-H COSY NMR spectrum of **Pd2-ACN** ($CDCl_3$).

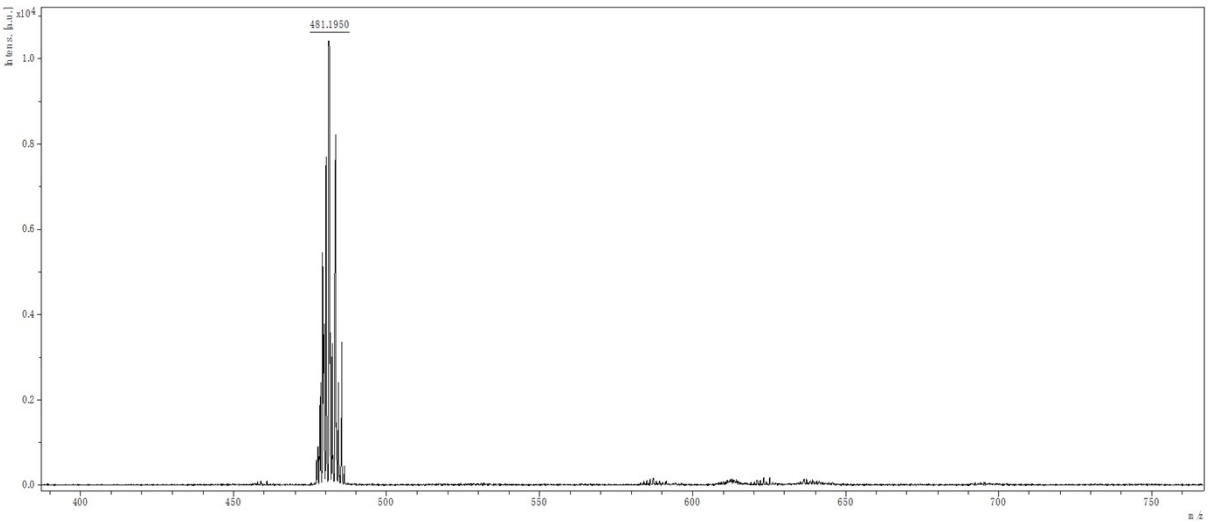


Figure S20. MALDI-TOF-MS (m/z) of complex **Pd1.**

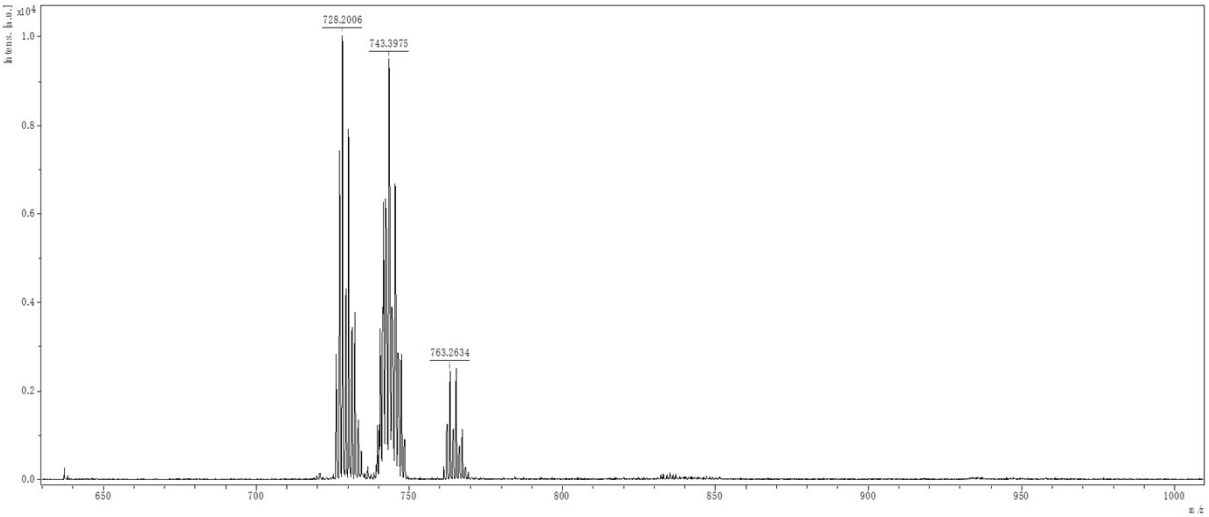


Figure S21. MALDI-TOF-MS of complex **Pd2.**

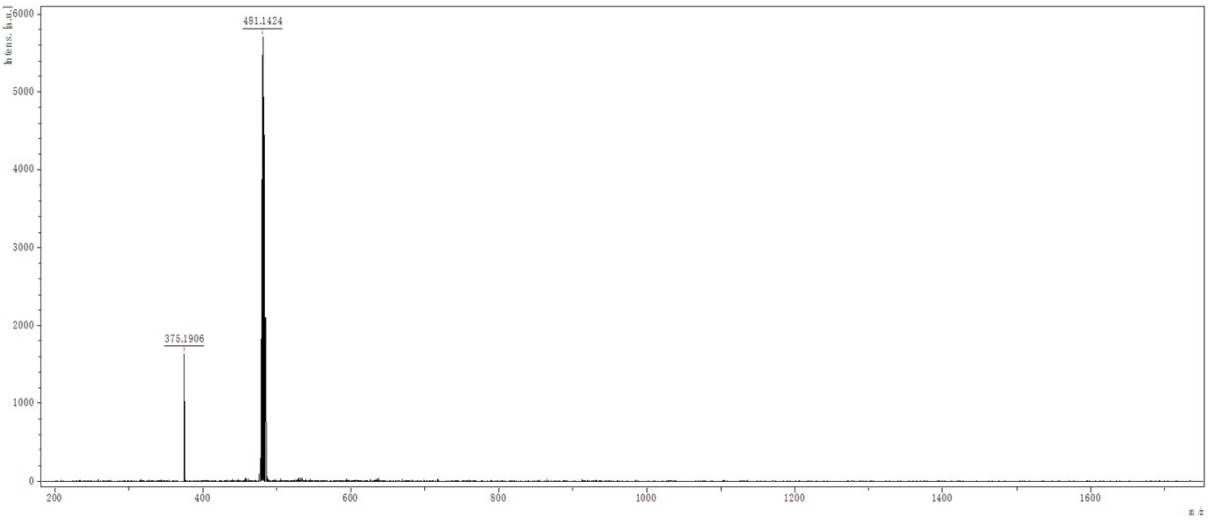


Figure S22. MALDI-TOF-MS of complex **Pd1-ACN.**

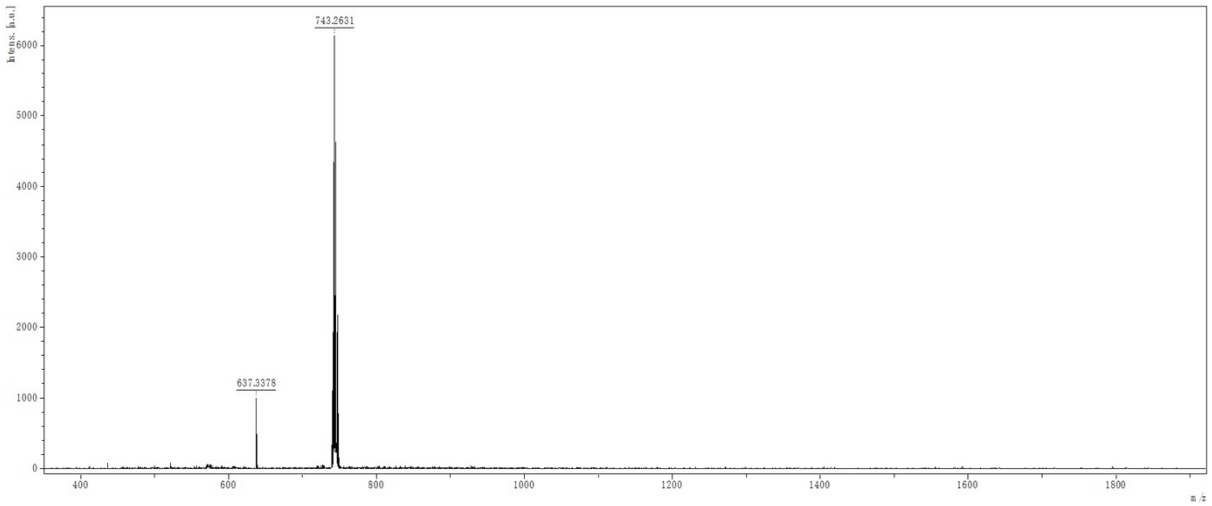


Figure S23. MALDI-TOF-MS of complex **Pd2-ACN.**

4. ^{1}H NMR of the Polymers

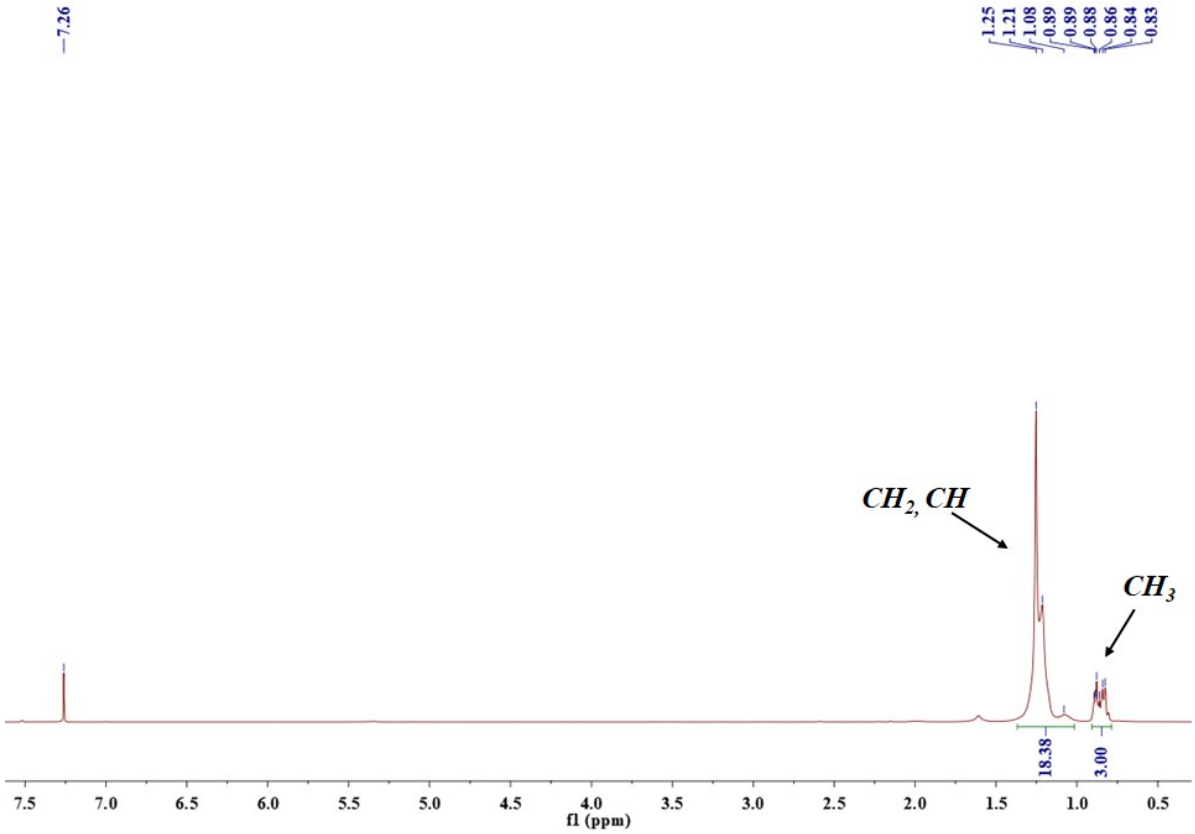


Figure S24. ^{1}H NMR spectrum of the polymer from Table 1, Entry 2 ($CDCl_3$).

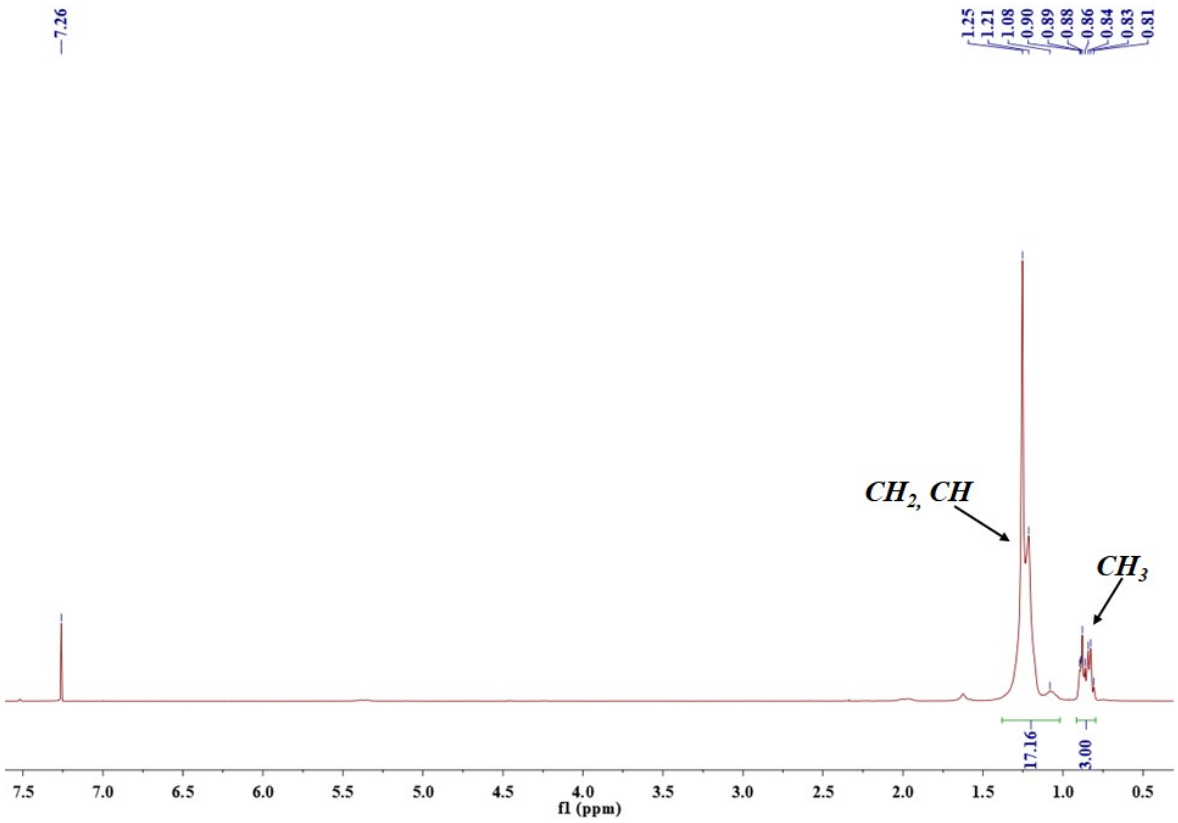


Figure S25. ^{1}H NMR spectrum of the polymer from Table 1, Entry 3 ($CDCl_3$).

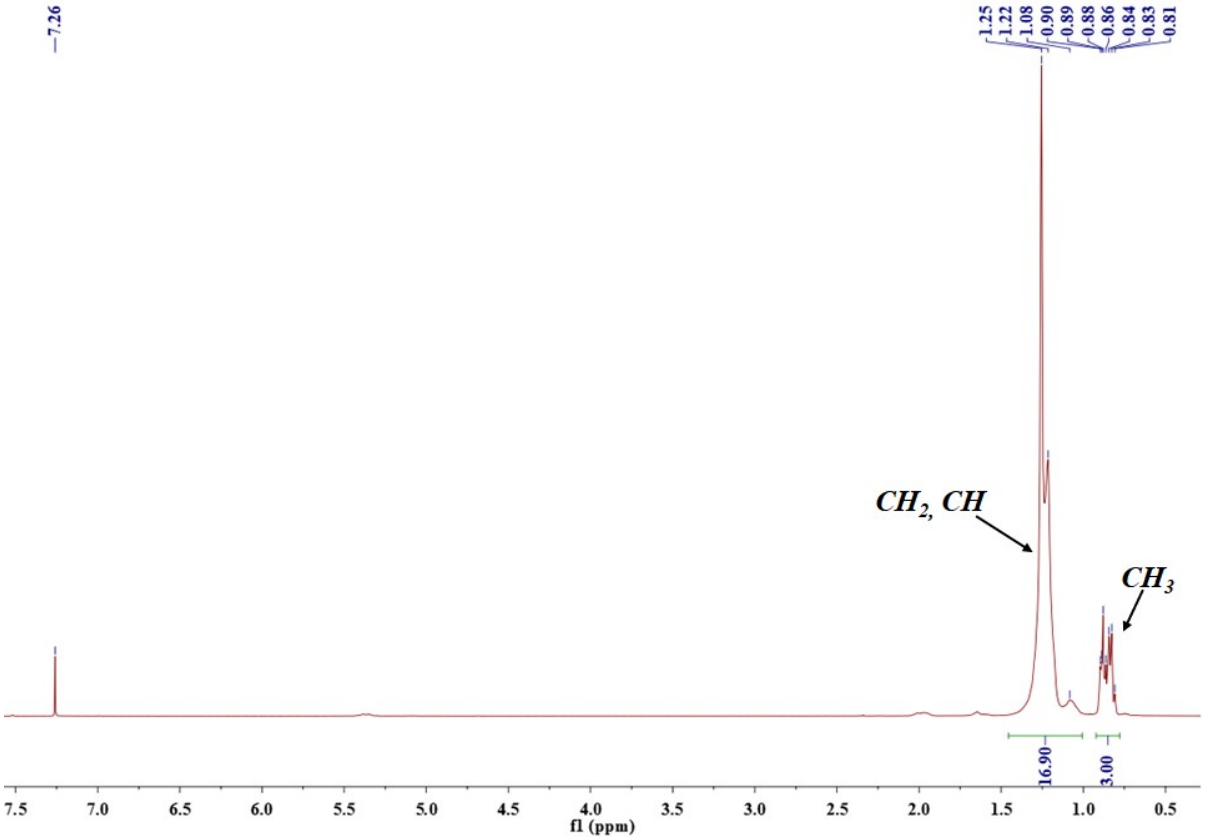


Figure S26. ^{1}H NMR spectrum of the polymer from Table 1, Entry 4 ($CDCl_3$).

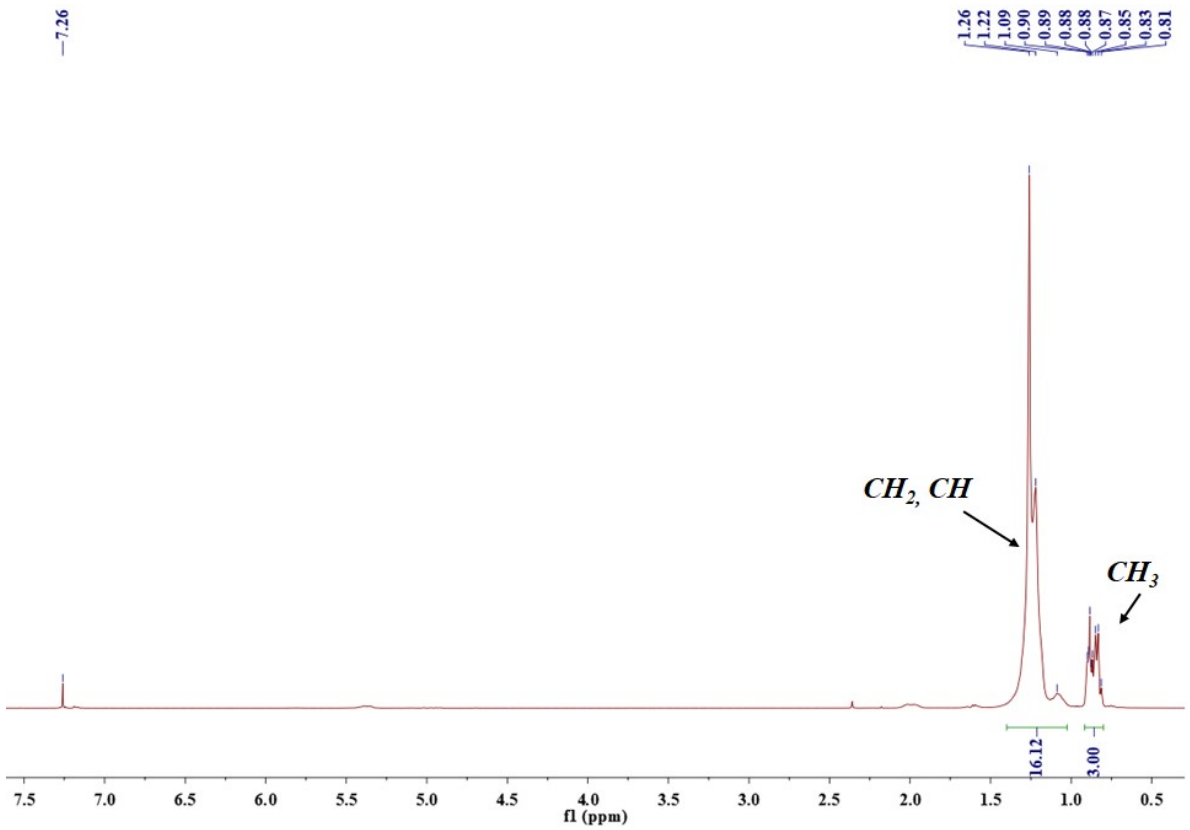


Figure S27. ^{1}H NMR spectrum of the polymer from Table 1, Entry 5 ($CDCl_3$).

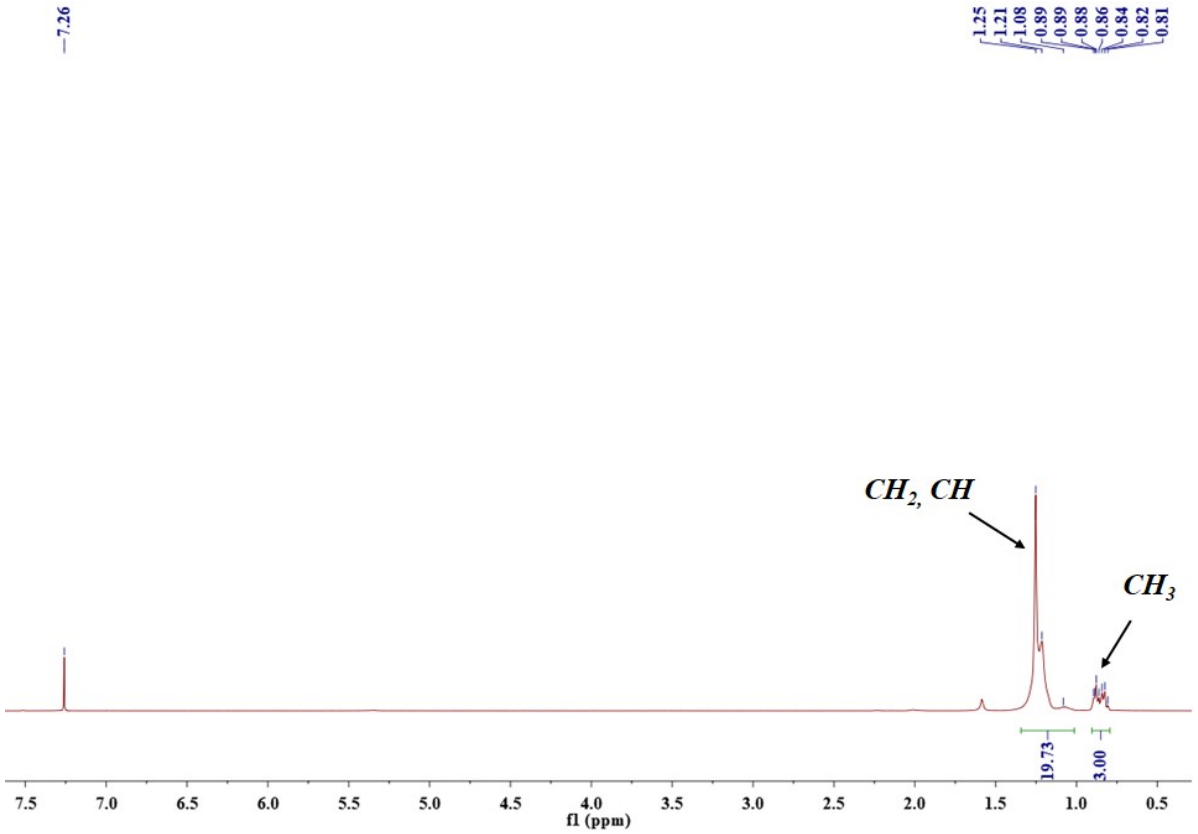


Figure S28. ^{1}H NMR spectrum of the polymer from Table 1, Entry 6 ($CDCl_3$).

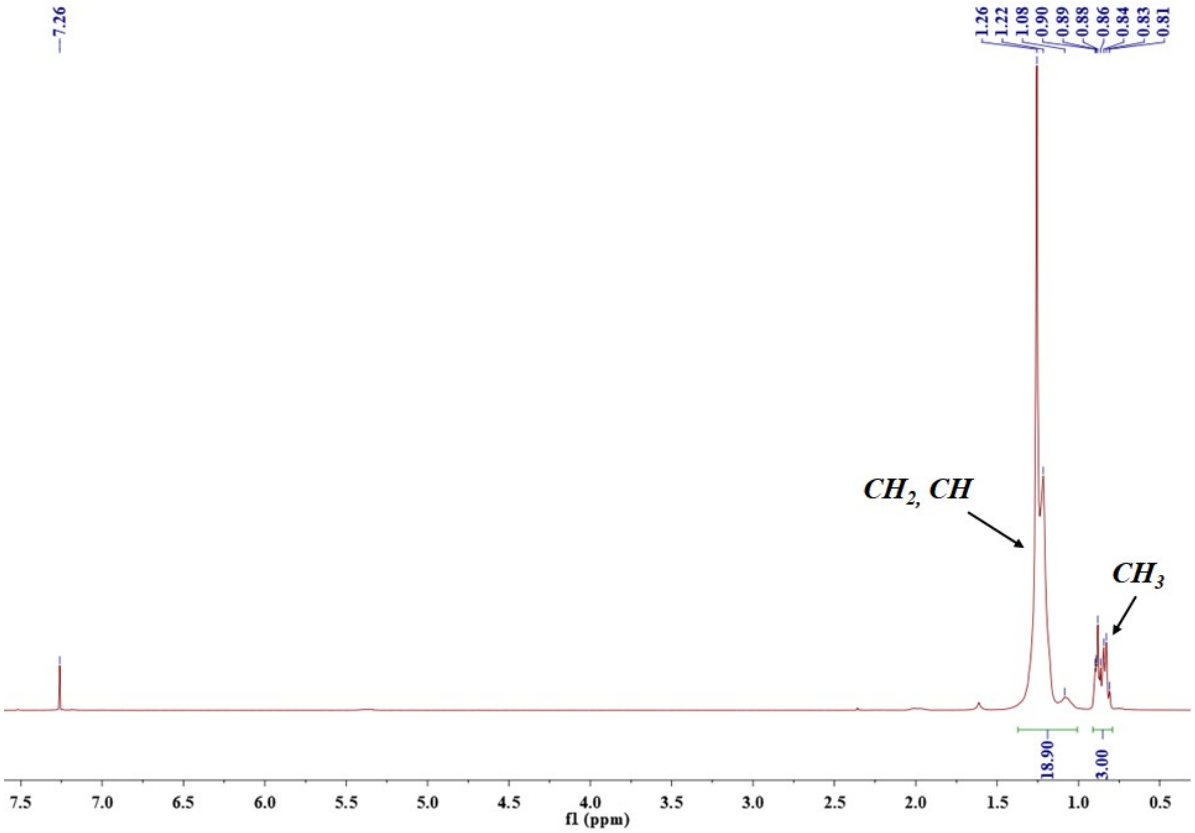


Figure S29. ^{1}H NMR spectrum of the polymer from Table 1, Entry 7 ($CDCl_3$).

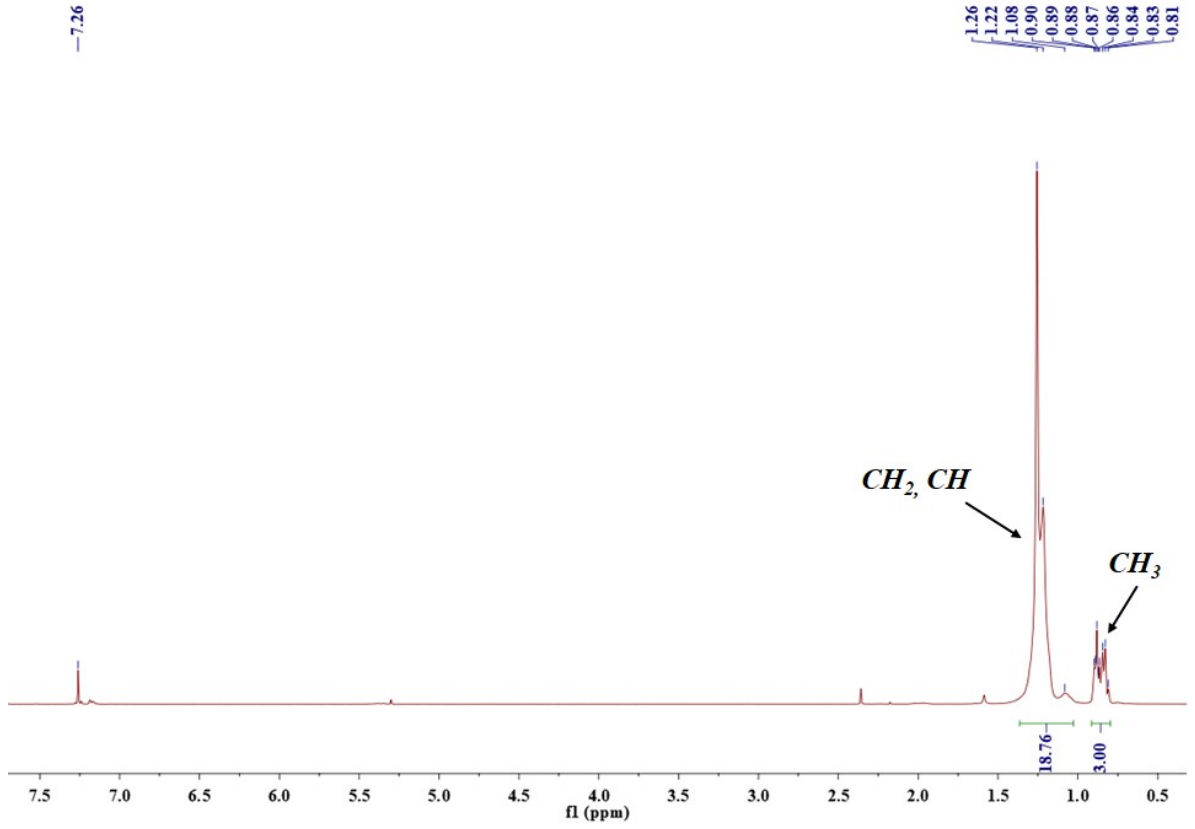


Figure S30. ^{1}H NMR spectrum of the polymer from Table 1, Entry 8 ($CDCl_3$).

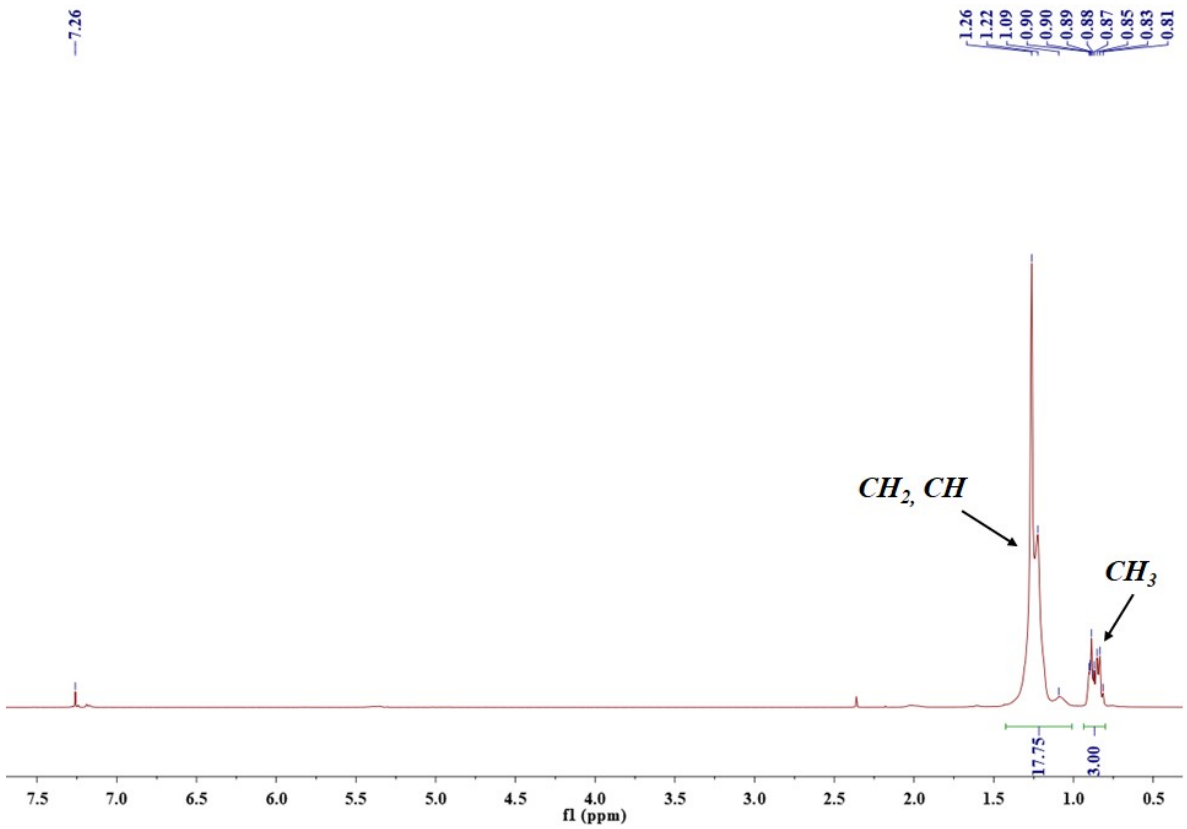


Figure S31. ^{1}H NMR spectrum of the polymer from Table 1, Entry 9 ($CDCl_3$).

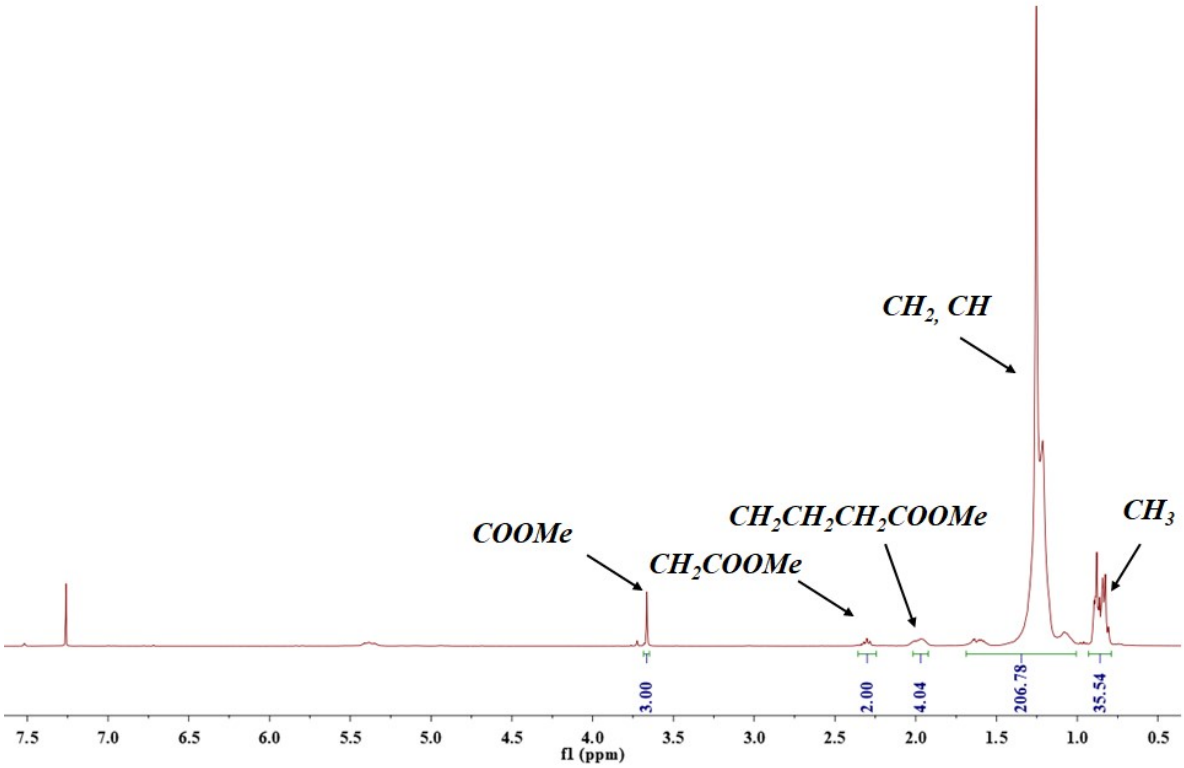


Figure S32. ^{1}H NMR spectrum of the polymer from Table 2, Entry 1($CDCl_3$).

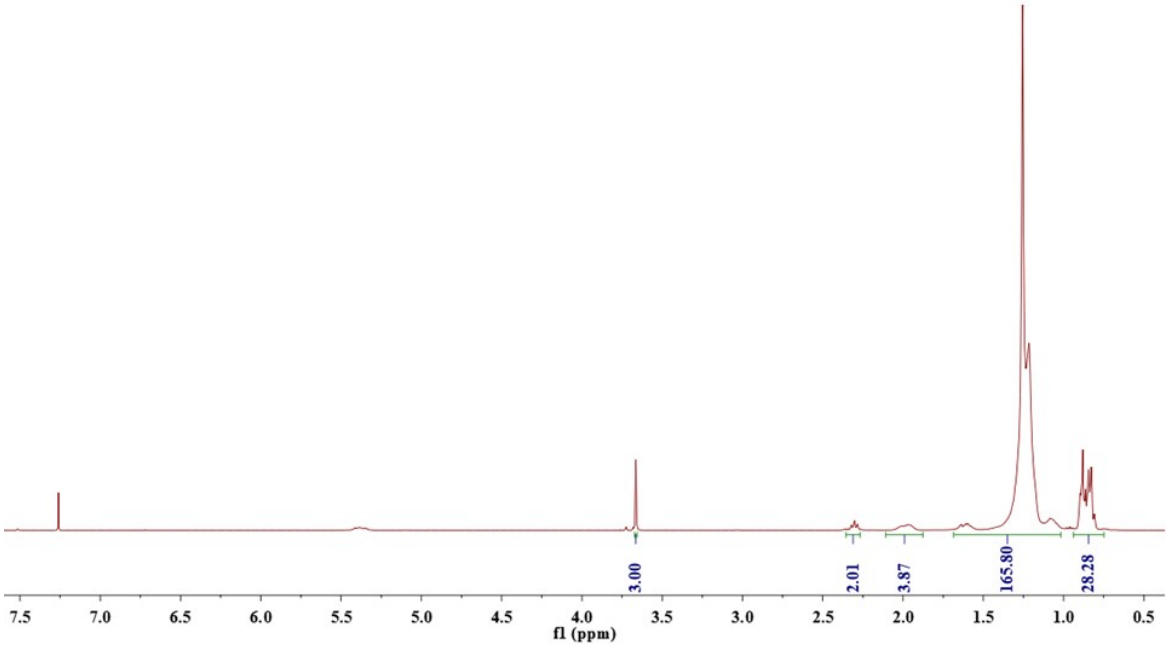


Figure S33. ^{1}H NMR spectrum of the polymer from Table 2, Entry 2 ($CDCl_3$).

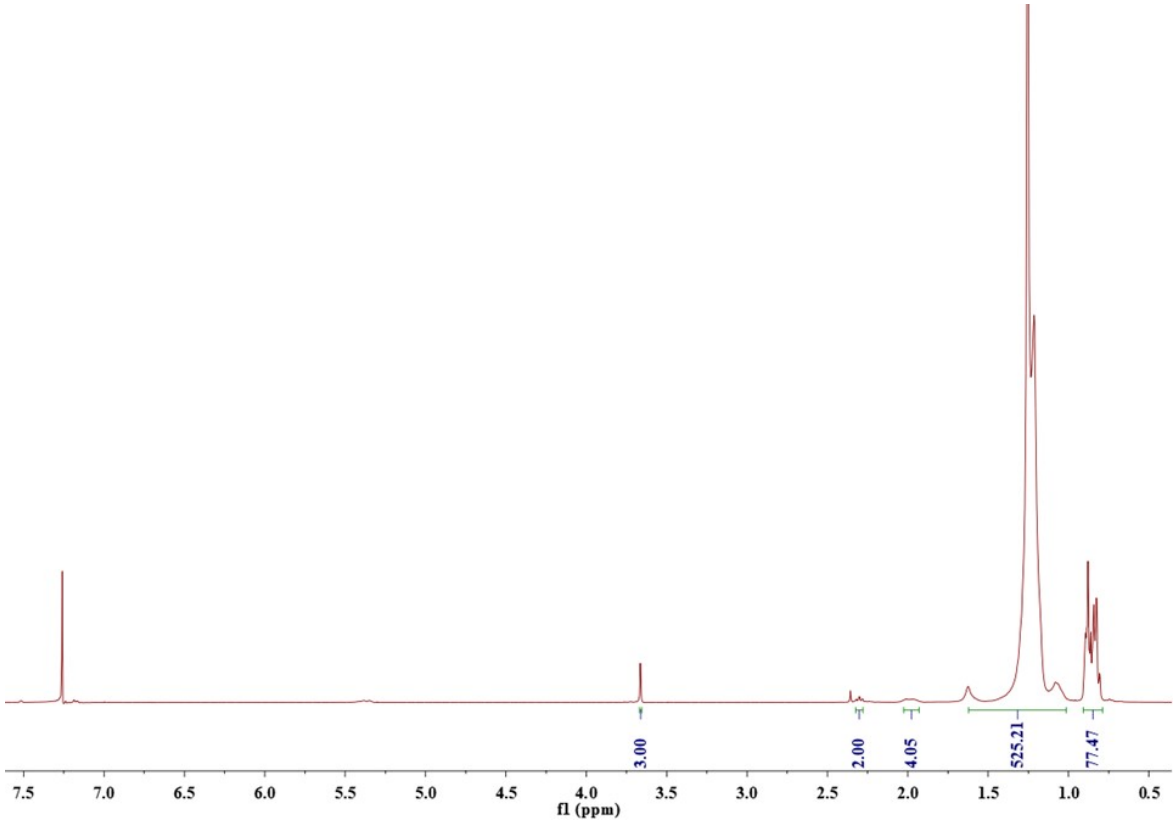


Figure S34. ^{1}H NMR spectrum of the polymer from Table 2, Entry 4 ($CDCl_3$).

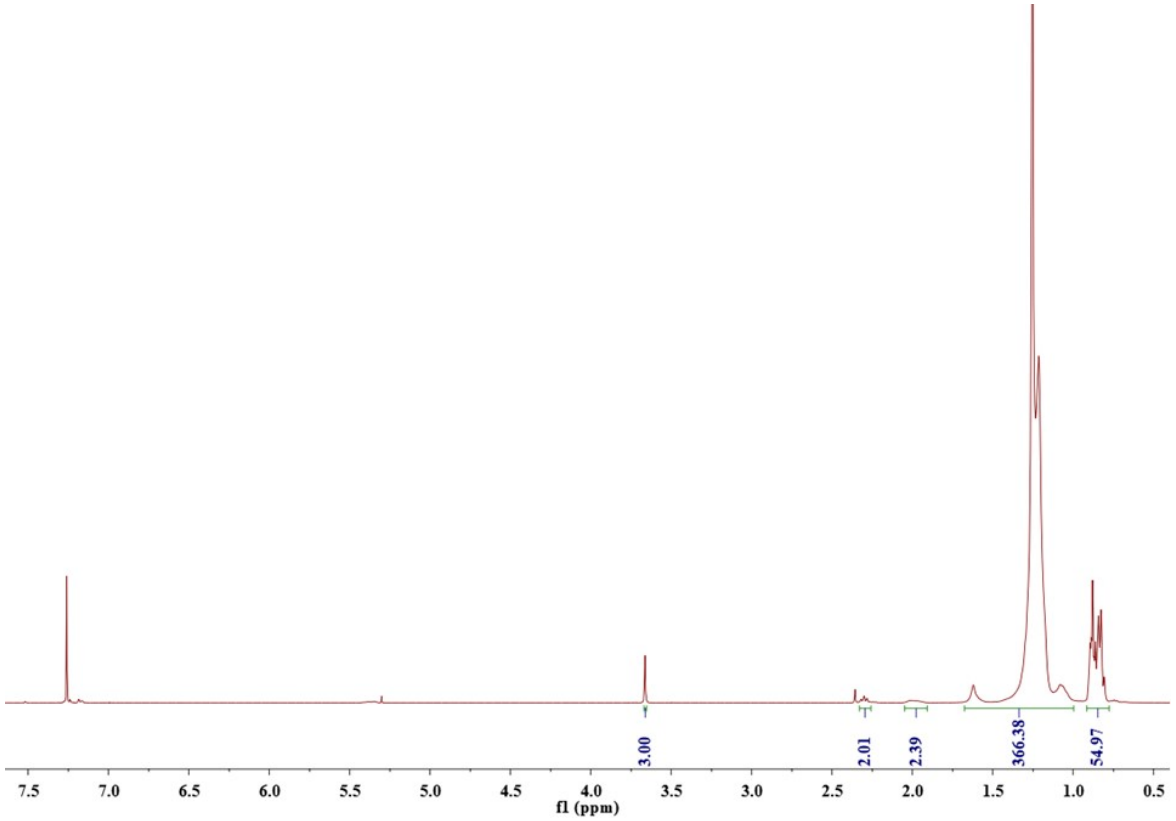


Figure S35. ^{1}H NMR spectrum of the polymer from Table 2, Entry 5 ($CDCl_3$).

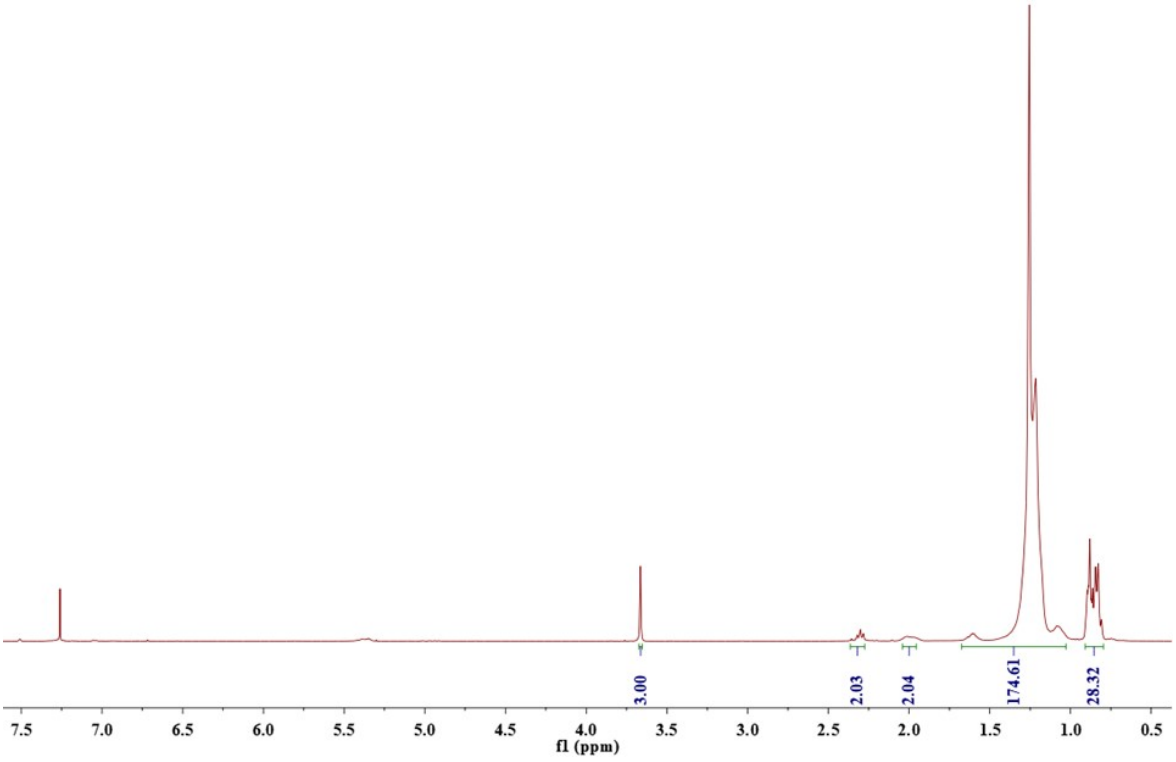


Figure S36. ^{1}H NMR spectrum of the polymer from Table 2, Entry 6 ($CDCl_3$).

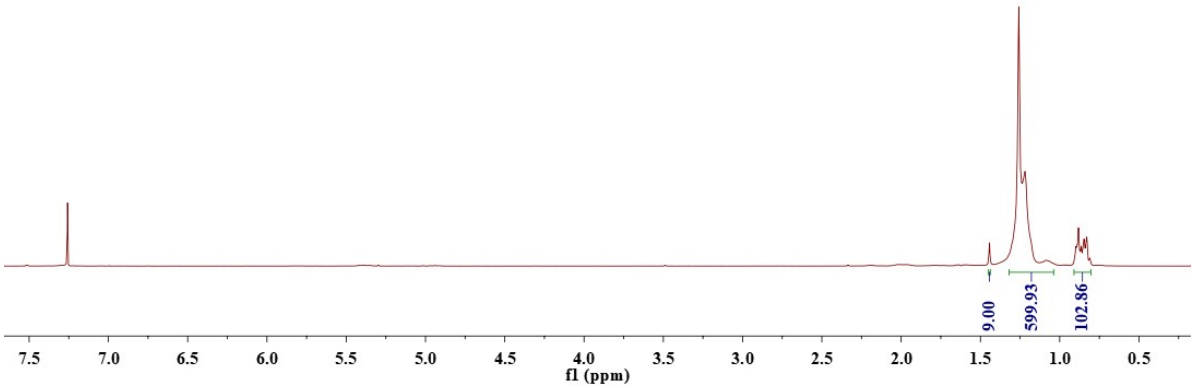


Figure S37. ^{1}H NMR spectrum of the polymer from Table 2, Entry 7 ($CDCl_3$).

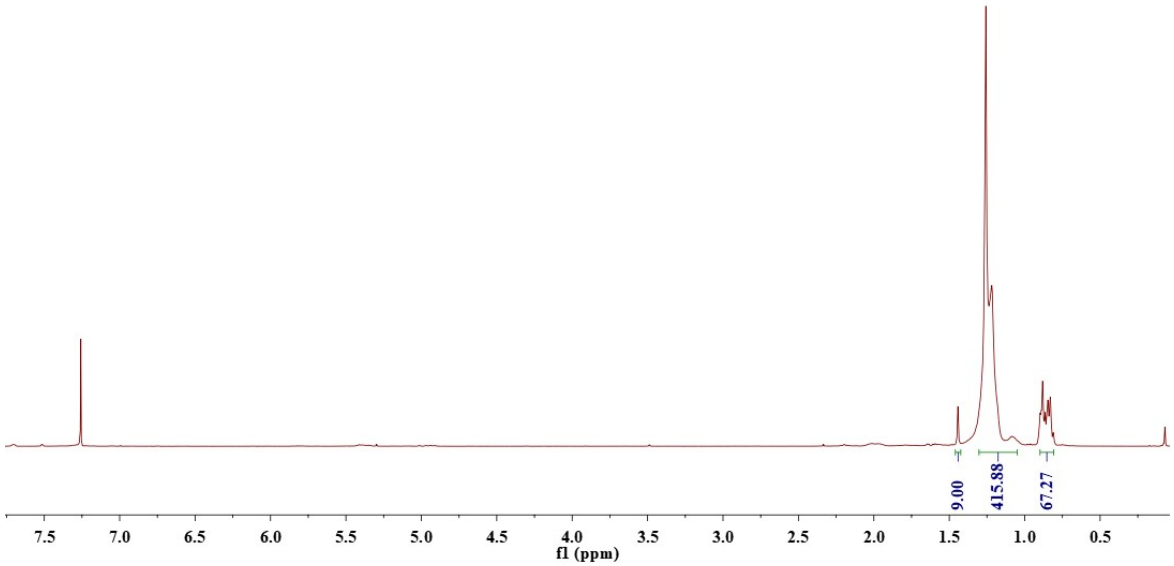


Figure S38. ^{1}H NMR spectrum of the polymer from Table 2, Entry 8 ($CDCl_3$).

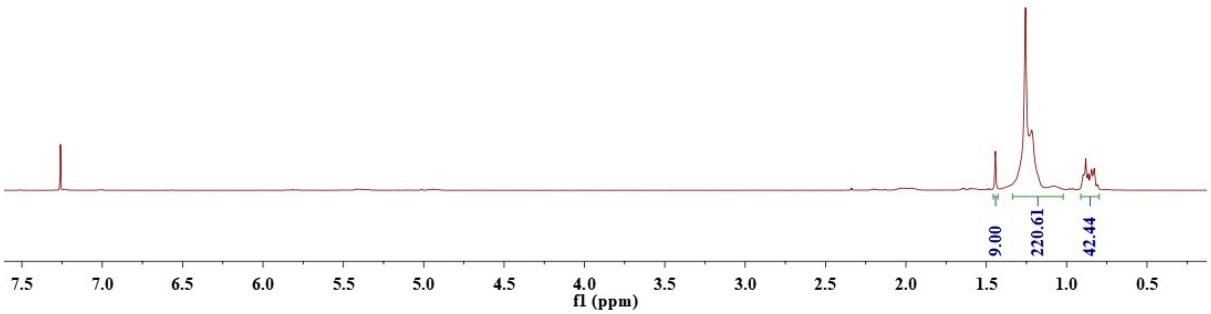
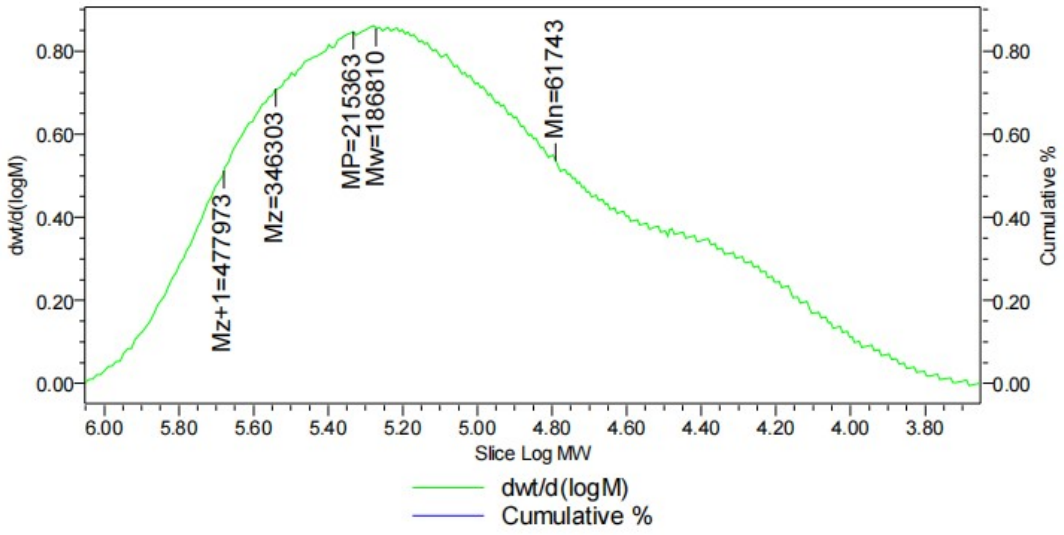


Figure S39. ^{1}H NMR spectrum of the polymer from Table 2, Entry 9 ($CDCl_3$).

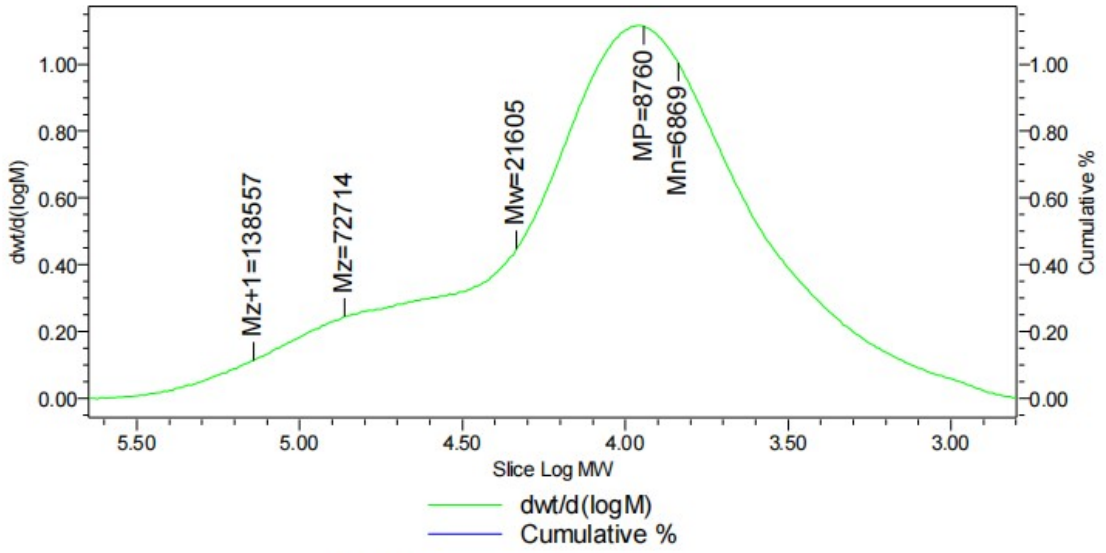
5. GPC traces of polymers



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		61743	186810	215363	346303	477973		3.025611		

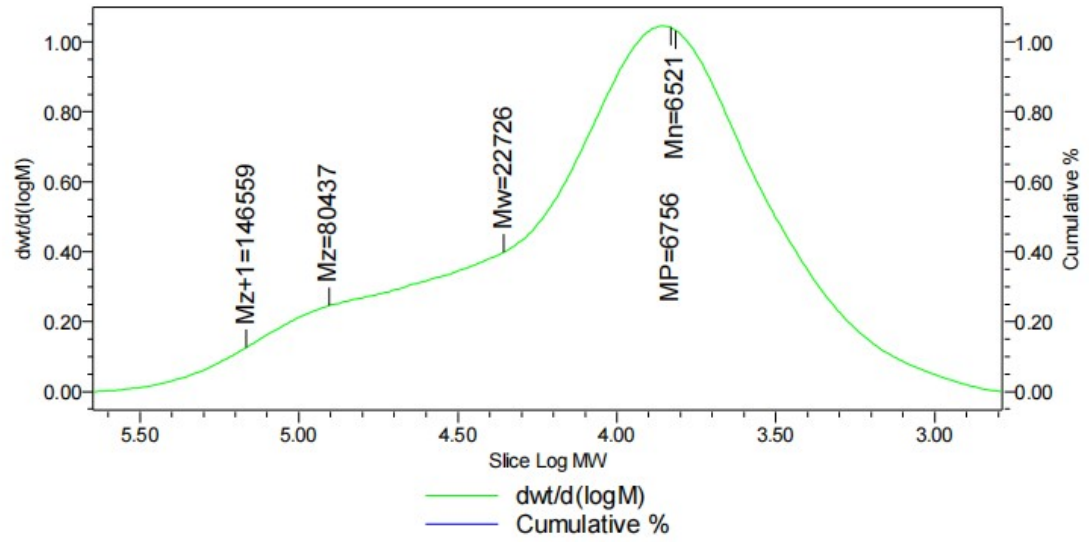
Figure S40. GPC trace of the polymer from Table 1, Entry 2.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		6869	21605	8760	72714	138557		3.145370		

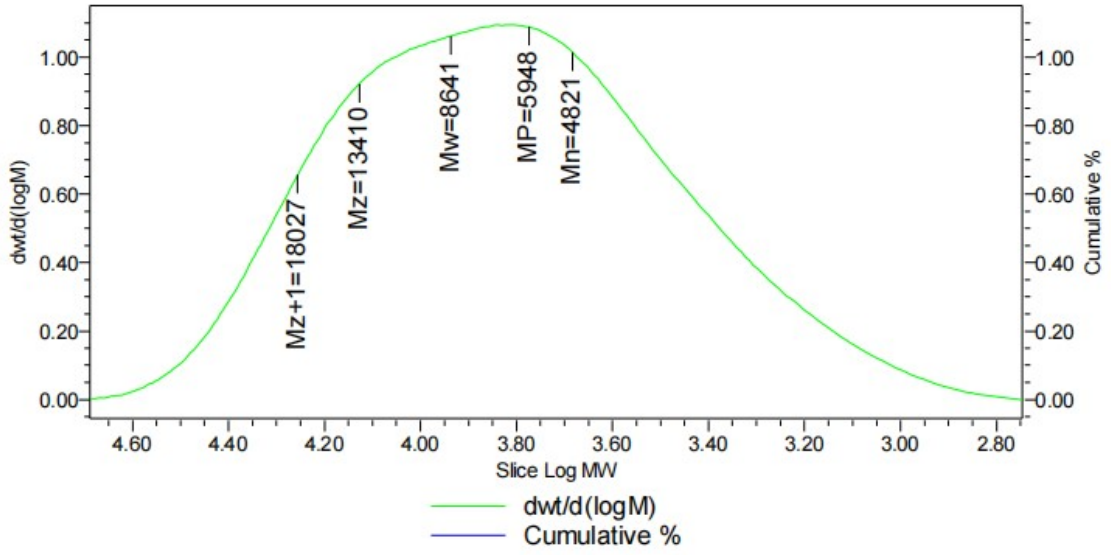
Figure S41. GPC trace of the polymer from Table 1, Entry 3.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		6521	22726	6756	80437	146559		3.485115		

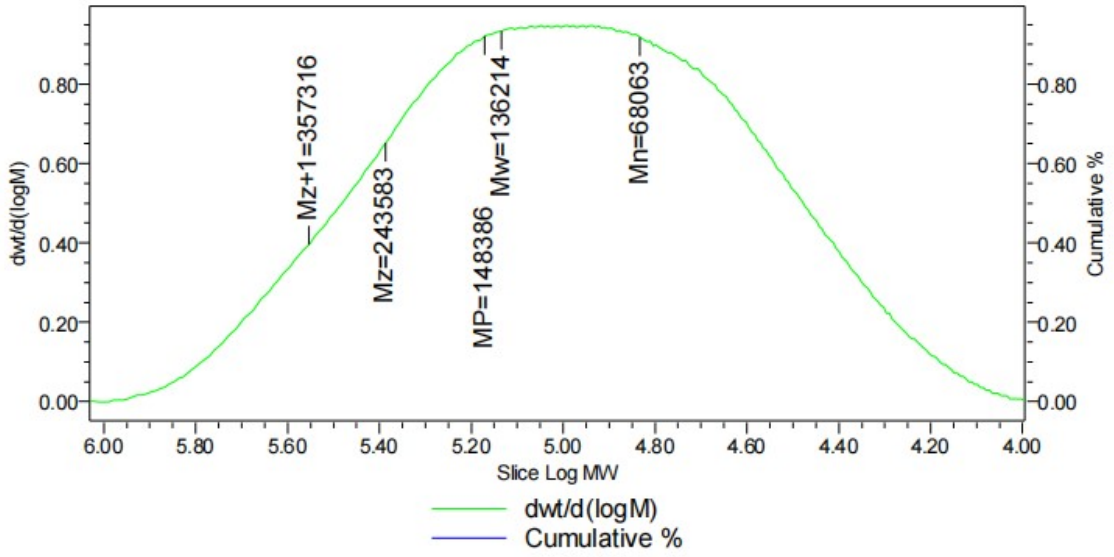
Figure S42. GPC trace of the polymer from Table 1, Entry 4.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		4821	8641	5948	13410	18027		1.792331		

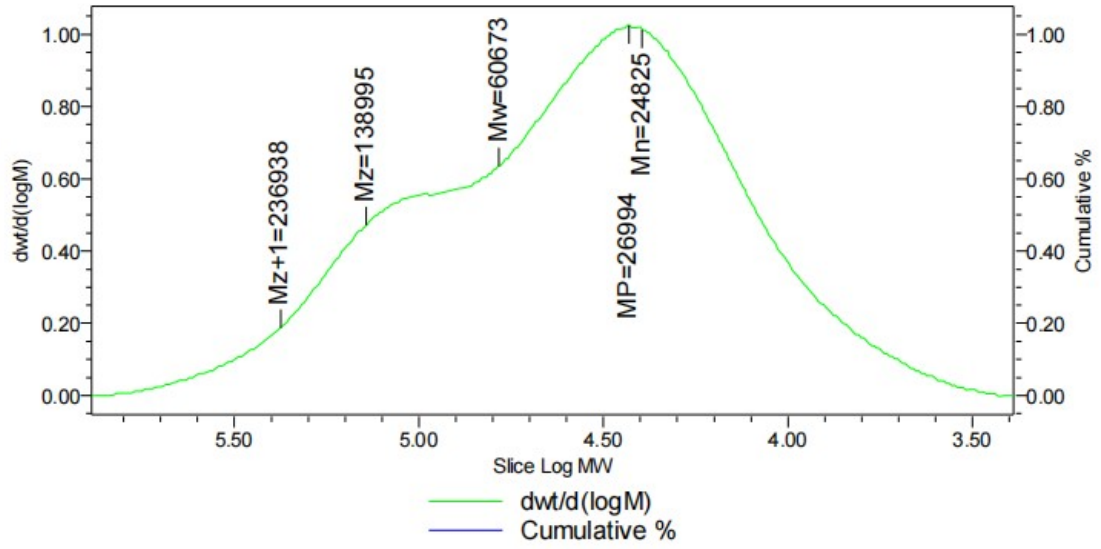
Figure S43. GPC trace of the polymer from Table 1, Entry 5.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		68063	136214	148386	243583	357316		2.001294		

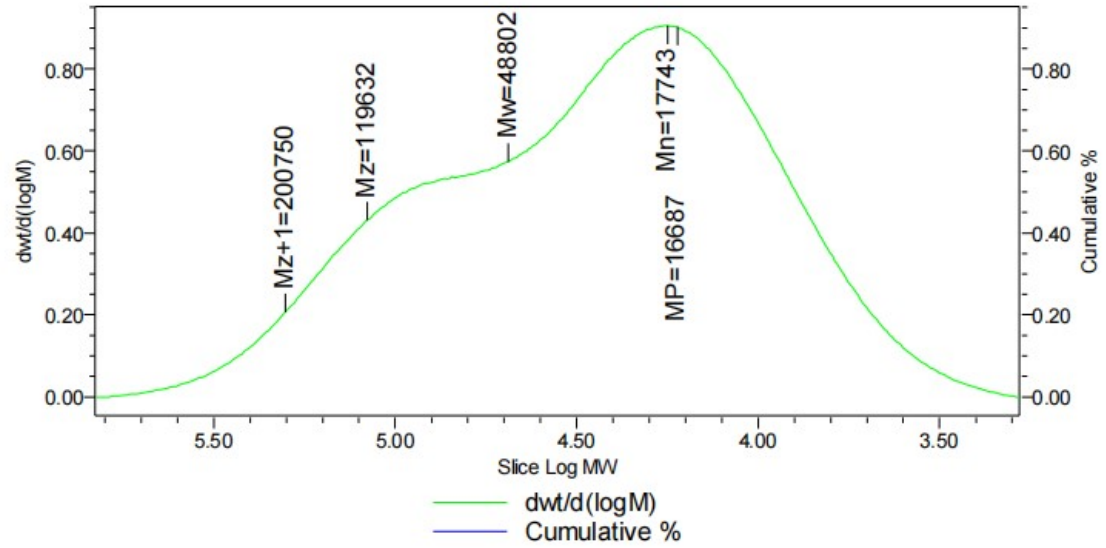
Figure S44. GPC trace of the polymer from Table 1, Entry 6.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		24825	60673	26994	138995	236938		2.443977		

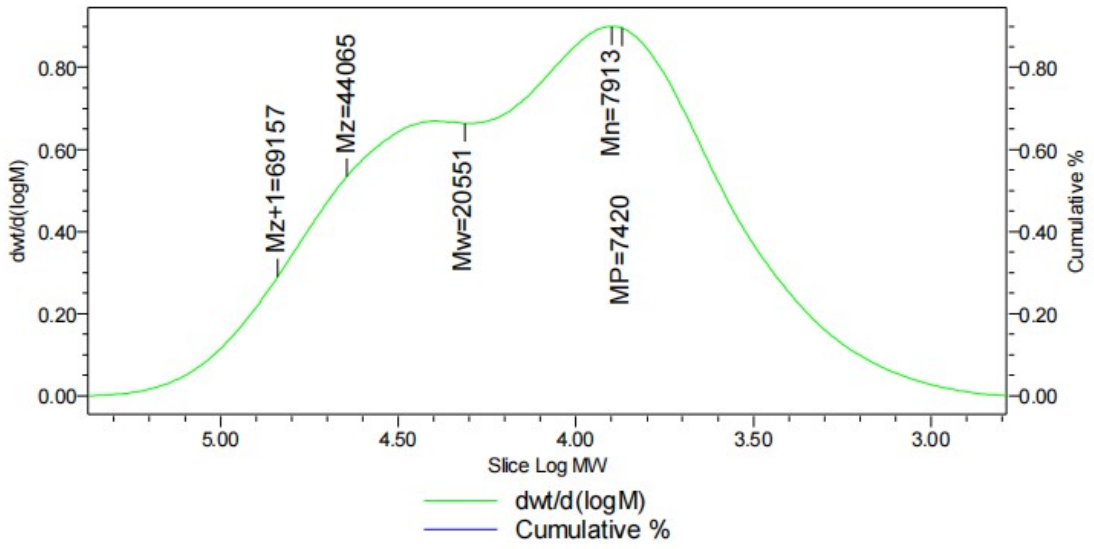
Figure S45. GPC trace of the polymer from Table 1, Entry 7.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		17743	48802	16687	119632	200750		2.750419		

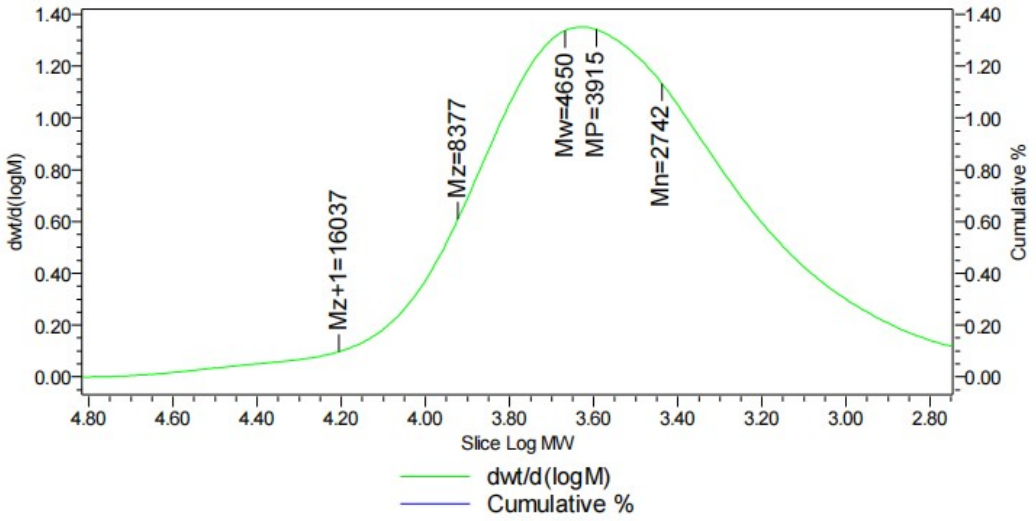
Figure S46. GPC trace of the polymer from Table 1, Entry 8.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		7913	20551	7420	44065	69157		2.597078		

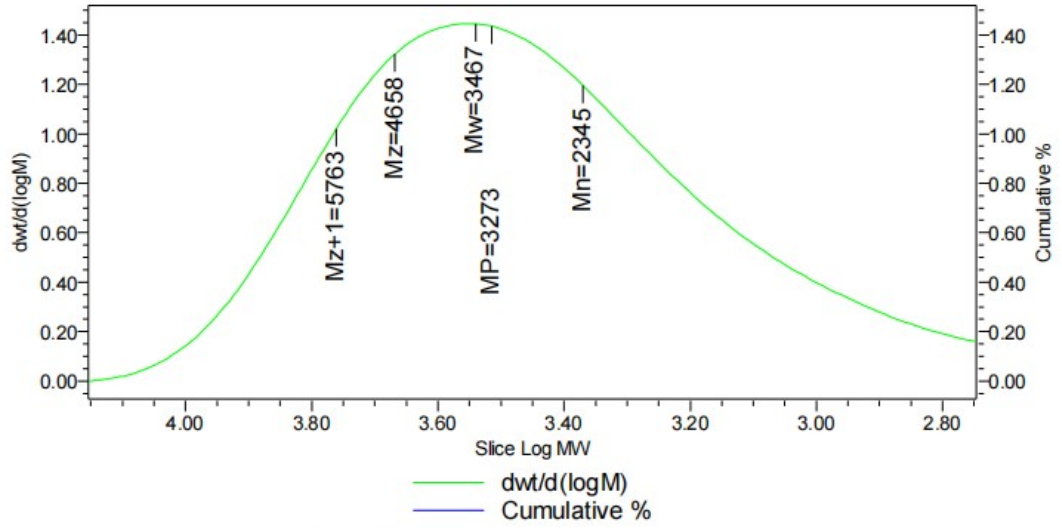
Figure S47. GPC trace of the polymer from Table 1, Entry 9.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		2742	4650	3915	8377	16037		1.695968		

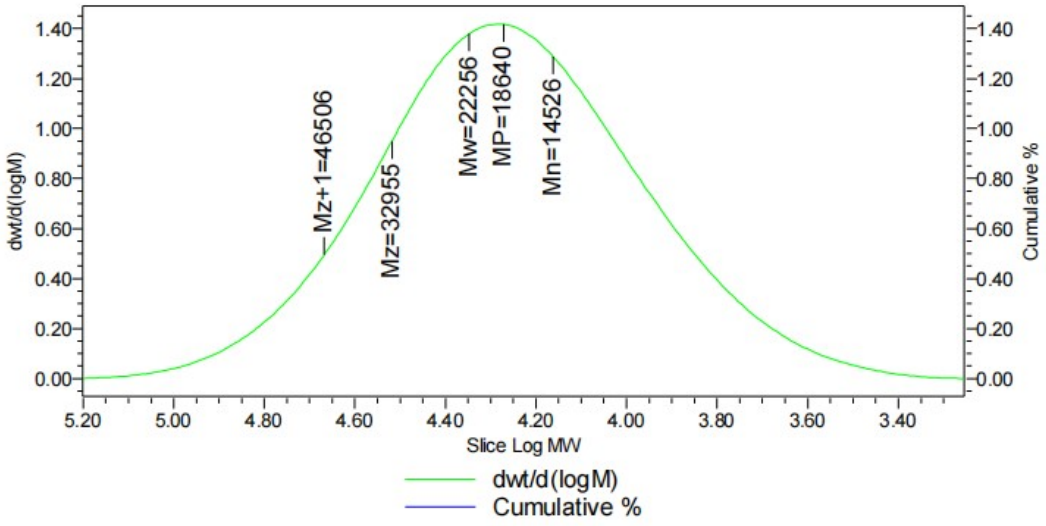
Figure S48. GPC trace of the polymer from Table 2, Entry 1.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		2345	3467	3273	4658	5763		1.478375		

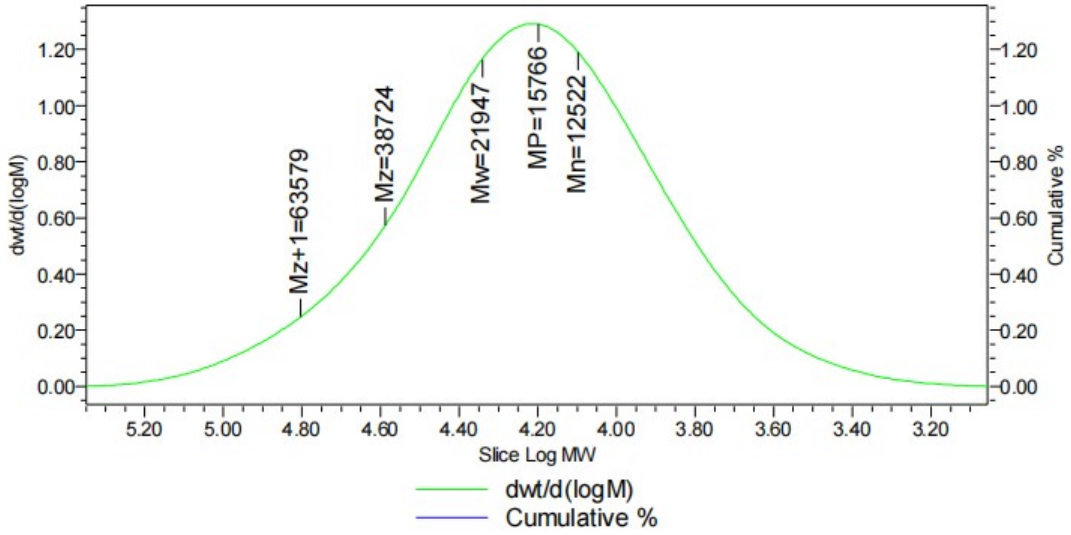
Figure S49. GPC trace of the polymer from Table 2, Entry 2.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		14526	22256	18640	32955	46506		1.532135		

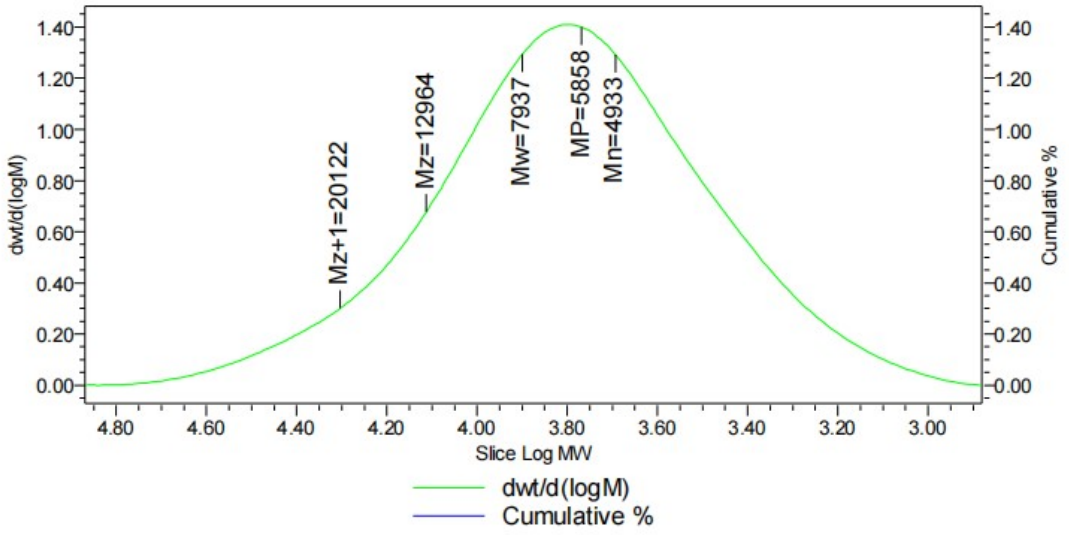
Figure S50. GPC trace of the polymer from Table 2, Entry 4.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		12522	21947	15766	38724	63579		1.752630		

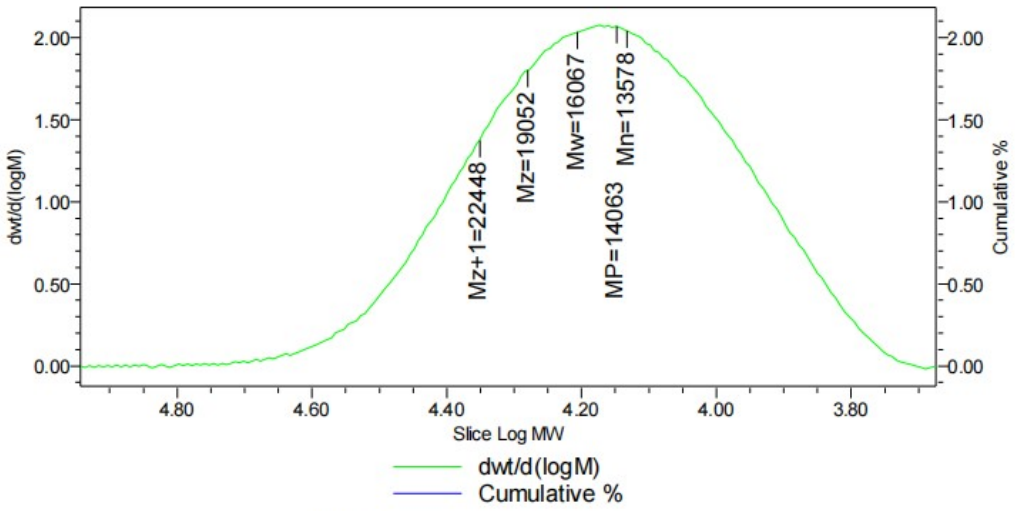
Figure S51. GPC trace of the polymer from Table 2, Entry 5.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		4933	7937	5858	12964	20122		1.608904		

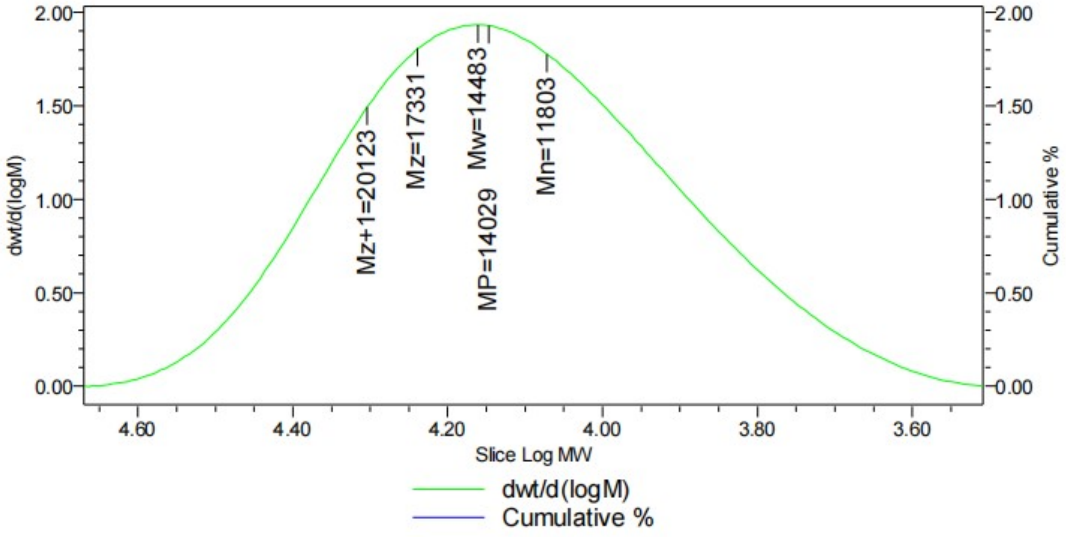
Figure S52. GPC trace of the polymer from Table 2, Entry 6.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		13578	16067	14063	19052	22448		1.183293		

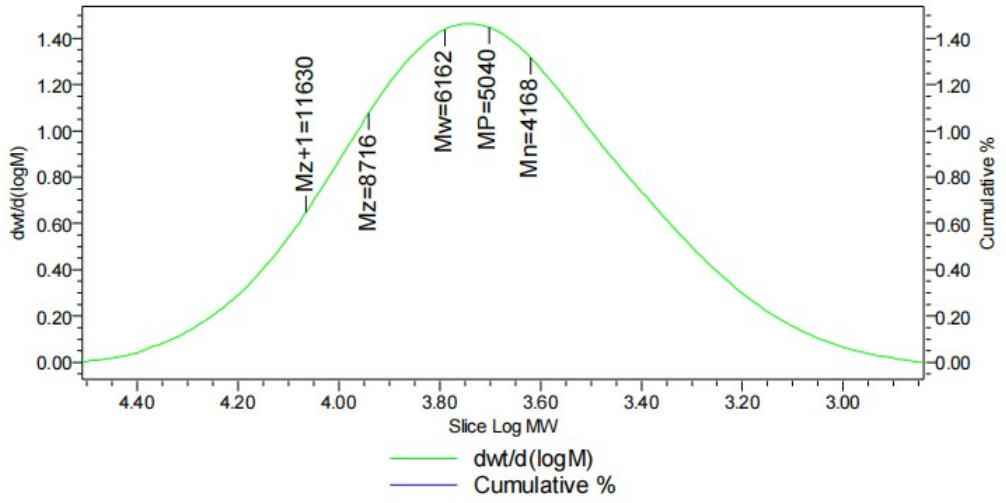
Figure S53. GPC trace of the polymer from Table 2, Entry 7.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		11803	14483	14029	17331	20123		1.227061		

Figure S54. GPC trace of the polymer from Table 2, Entry 8.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	PDI	MW 1	MW 2
1		4168	6162	5040	8716	11630		1.478413		

Figure S55. GPC trace of the polymer from Table 2, Entry 9.

6. X-ray crystallography

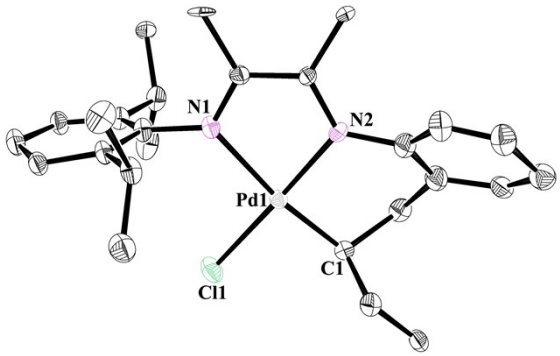


Table S1. Crystal data and structure refinement for Pd1.

Identification code	**Pd1**
Empirical formula	C26 H35 Cl N2 Pd
Formula weight	517.41
Temperature/K	170.0
Crystal system	monoclinic
Space group	P21
a/Å	15.119(3)
b/Å	15.120(3)
c/Å	24.857(5)
α/°	90
β/°	103.91(3)
γ/°	90
Volume/Å^3	5516(2)
Z	8
ρ_{calc}g/cm^3	1.246
μ/mm^{-1}	0.783
F(000)	2144
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	MoKa (λ = 0.71073)
2Θ range for data collection/°	4.23 to 52.76
Index ranges	-23≤h≤23, -13≤k≤12, -25≤l≤24
Reflections collected	29396
Independent reflections	9542 [R_{int} = 0.1292, R_{sigma} = 0.0983]
Data/restraints/parameters	9542/704/1109
Goodness-of-fit on F^2	1.300
Final R indexes [I>=2σ (I)]	R1 = 0.1223, wR2 = 0.3000
Final R indexes [all data]	R1 = 0.1360, wR2 = 0.3147

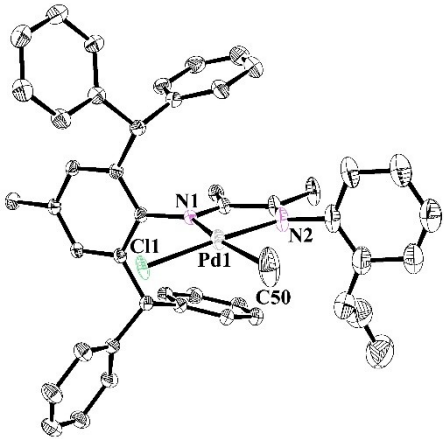


Table S2. Crystal data and structure refinement for Pd2.

Identification code	**Pd2**
Empirical formula	$C_{47}H_{44}ClN_2Pd$
Formula weight	778.69
Temperature/K	170
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.1884(5)
b/Å	10.6212(3)
c/Å	20.1144(5)
α/°	90
β/°	107.6140(10)
γ/°	90
Volume/Å^3	3907.20(18)
Z	4
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	0.578
F(000)	1612.0
Crystal size/mm^3	0.11 × 0.06 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.25 to 52.826
Index ranges	-23≤h≤23, -13≤k≤12, -25≤l≤24
Reflections collected	37208
Independent reflections	7963 [R_{int} = 0.0602, R_{sigma} = 0.0478]
Data/restraints/parameters	7963/485/488
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R1 = 0.0596, wR2 = 0.1702
Final R indexes [all data]	R1 = 0.662, wR2 = 0.1758

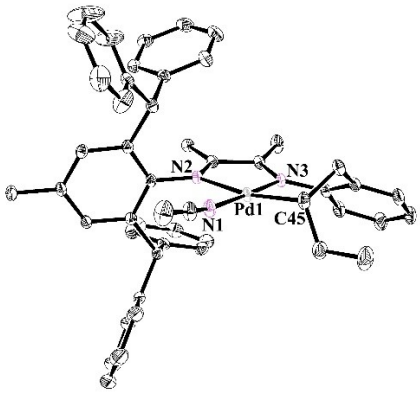


Table S3. Crystal data and structure refinement for Pd2-ACN.

Identification code	**Pd2-ACN**
Empirical formula	$C_{81}H_{60}BF_{24}N_3Pd$
Formula weight	1648.53
Temperature/K	150
Crystal system	triclinic
Space group	P-1
a/Å	10.0340(3)
b/Å	19.1514(7)
c/Å	20.3631(6)
α/°	100.5850(10)
β/°	95.0430(10)
γ/°	104.5800(10)
Volume/Å^3	3685.4(2)
Z	2
ρ_{calc}g/cm^3	1.486
μ/mm^{-1}	0.360
F(000)	1668.0
Crystal size/mm^3	0.15 × 0.06 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.236 to 52.762
Index ranges	-12≤h≤12, -23≤k≤23, -24≤l≤25
Reflections collected	43578
Independent reflections	14994 [R_{int} = 0.0508, R_{sigma} = 0.0592]
Data/restraints/parameters	14994/1116/1023
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R1 = 0.0553, wR2 = 0.1375
Final R indexes [all data]	R1 = 0.0679, wR2 = 0.1478