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A Rigid-Flexible Double-Layer Steric Strategy for Ethylene (Co)oligomerization with Pyridine-imine Ni(II) and Pd(II) Complexes

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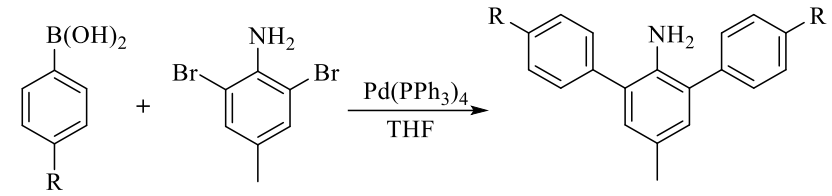
1. Experimental sections

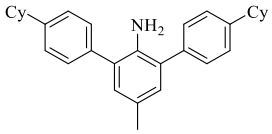
1.1 General Considerations

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 JNM-ECZ600R or JNM-ECZ400R spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Mass spectra were obtained by the Analytical Center of Anhui University. Elemental analysis was performed by the Analytical Center of Anhui University. X-ray Diffraction data were collected at 293(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K^{α} radiation (λ = 0.71073 Å).

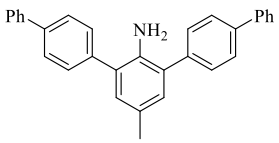
1.2 Procedure for the Synthesis of Arylamines A1-A2.



To a mixture of arylboronic acid (25 mmol, 2.5 eq.), 2,6-dibromo-4-methylaniline (10 mmol, 1 eq.), $Pd(PPh_3)_4$ (1 mmol, 0.1 eq.) and K_2CO_3 (50 mmol, 5 eq.) under a nitrogen atmosphere in a Schlenk flash, THF (200 ml) and water (50 ml) were added. The suspension was heated to 75 °C with vigorous stirring for 24 h. After removal of the solvent in vacuo, the residue was exacted by dichloromethane, washed by water, and dried over $MgSO_4$. After filtration, the organic phases were concentrated to dryness. The resulting residue was then purified by column chromatography (silica gel; PE/DCM = 4:1) to afford product as a white solid.



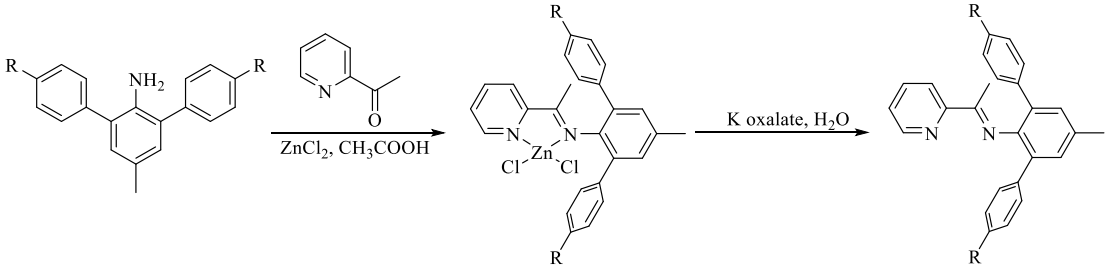
A1 (2.97 g, 70%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 7.28 (d, *J* = 8.1 Hz, 4H, Ar-*H*), 6.95 (s, 2H, Ar-*H*), 3.86 (s, *br*, 2H, -N*H*$_2$), 2.58 – 2.49 (m, 2H, -C*H*-), 2.29 (s, 3H, -C*H*$_3$), 1.92 (d, *J* = 11.8 Hz, 4H, -C*H*$_2$-), 1.87 (d, *J* = 12.2 Hz, 4H, -C*H*$_2$-), 1.77 (d, *J* = 13.1 Hz, 2H, -C*H*$_2$-), 1.51 – 1.37 (m, 8H, -C*H*$_2$-), 1.30 – 1.25 (m, 2H, -C*H*$_2$-). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.07, 137.29, 130.28, 129.25, 127.27, 44.41 (-*C*H-), 34.57 (-*C*H$_2$-), 27.02 (-*C*H$_2$-), 26.28 (-*C*H$_2$-), 20.47 (Ar-*C*H$_3$). APCI-MS (m/z): calcd for $C_{31}H_{37}N$: 424.2960, Found, 424.2978, $[M+H]^+$.



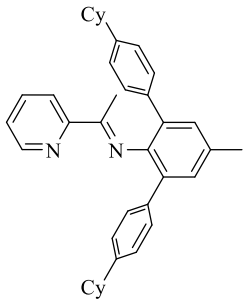
A2 (3.00 g, 73%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dt, *J* = 18.2, 8.2 Hz, 12H, Ar-*H*), 7.45 (t, *J* = 7.6 Hz, 4H, Ar-*H*), 7.36 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 7.02 (s, 2H, Ar-*H*), 3.80 (s, *br*, 2H, -N*H*$_2$), 2.33 (s, 3H, -C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.77, 140.05, 138.86, 138.45, 130.42, 129.75, 128.86, 127.78, 127.51, 127.47,

127.39, 127.08, 20.44 (-*C*H_3). APCI-MS (m/z): calcd for $C_{31}H_{25}N$: 412.2021, Found, 412.2042, $[M+H]^+$.

1.3 Procedure for the Synthesis of Ligands L1-L2.

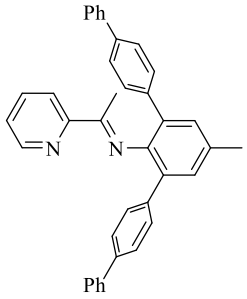


The ligands **L1-L2** were prepared as follows: $ZnCl_2$ (0.34 g, 2.5 mmol) and 2-acetylpyridine (2.0 mmol), were suspended in glacial acetic acid (5 mL). Anilines (2 mmol) was added, and the reaction mixture was refluxed under stirring for 4 h. The solution was allowed to cool to room temperature, and a bright yellow solid precipitated. The solid was separated by filtration and washed with acetic acid (3 × 5mL) and diethyl ether (5 × 5 mL), to remove remaining acetic acid. Drying under vacuum gave bright yellow, poorly soluble solid. Then the zinc was removed from the zinc pyridine-imine complex. The product of the previous step was suspended in methylene chloride (30 mL), and a solution of potassium oxalate (0.36 g, 2.2 mmol) in water (5 mL) was added. The reaction mixture was stirred vigorously for 1 h. The two phases were separated, and the organic layer was washed with water (3 × 20 mL) and dried with $MgSO_4$. After filtration, the solvent was removed under vacuum to afford the product as an yellow powder and dried under high vacuum.



L1 (0.93 g, 88%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 4.3 Hz, 1H, Ar-*H*), 7.88 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.58 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.27 (d, *J* = 7.9 Hz, 4H,

Ar-*H*), 7.18 – 7.11 (m, 3H, Ar-*H*), 7.03 (d, *J* = 7.9 Hz, 4H, Ar-*H*), 2.36 (s, 2H, -C*H*-), 2.35 (s, 3H, -CH_3), 1.79 (s, 3H, Ar-C(CH_3)=N), 1.78 – 1.62 (m, 8H, -CH_2-), 1.34 – 1.15 (m, 12H, -CH_2-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.03 (*C*=N), 156.47, 148.11, 146.22, 144.13, 137.83, 136.10, 133.18, 131.81, 130.17, 129.15, 126.23, 124.28, 121.48, 44.16 (-*C*H-), 34.41 (-*C*H_2-), 34.38 (-*C*H_2-), 26.93 (-*C*H_2-), 26.22 (-*C*H_2-), 20.87 (-*C*H_3), 17.83 (Ar-C(*C*H_3)=N). APCI-MS (m/z): calcd for $C_{38}H_{42}N_2$: 527.3382, Found, 527.3406, $[M+H]^+$.



L2 (0.95 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.2 Hz, 1H, Ar-*H*), 8.03 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.65 (td, *J* = 7.9, 1.6 Hz, 1H, Ar-*H*), 7.58 – 7.48 (m, 12H, Ar-*H*), 7.39 (t, *J* = 7.5 Hz, 4H, Ar-*H*), 7.33 – 7.18 (m, 5H, Ar-*H*), 2.46 (s, 3H, -CH_3), 1.91 (s, 3H, Ar-C(CH_3)=N). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.31 (*C*=N), 156.10, 148.26, 144.27, 140.81, 139.42, 139.21, 136.23, 133.50, 131.44, 130.44, 129.68, 128.70, 127.16, 126.98, 126.54, 124.49, 121.32, 20.90 (-*C*H_3), 17.83 (Ar-C(*C*H_3)=N). APCI-MS (m/z): calcd for $C_{38}H_{30}N_2$: 515.2443, Found, 515.2461, $[M+H]^+$.

2. Spectra Data

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

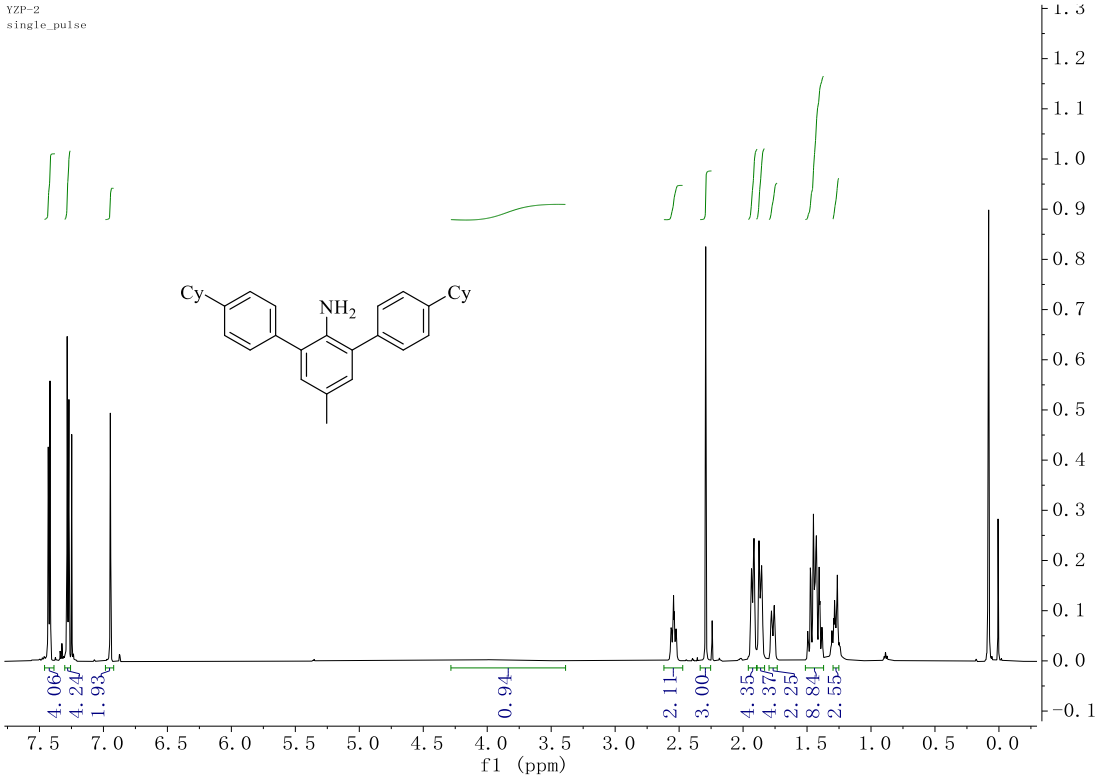


Figure S1. ^{1}H NMR spectrum of **A1** in $CDCl_3$.

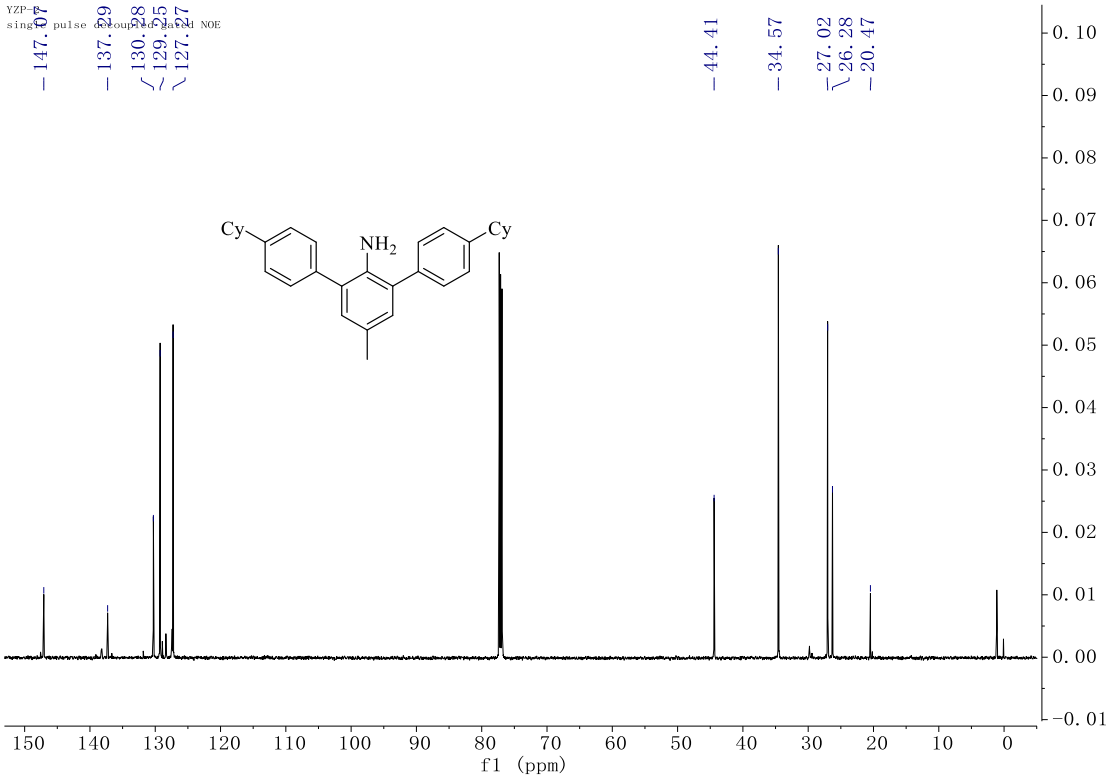


Figure S2. ^{13}C NMR spectrum of **A1** in $CDCl_3$.

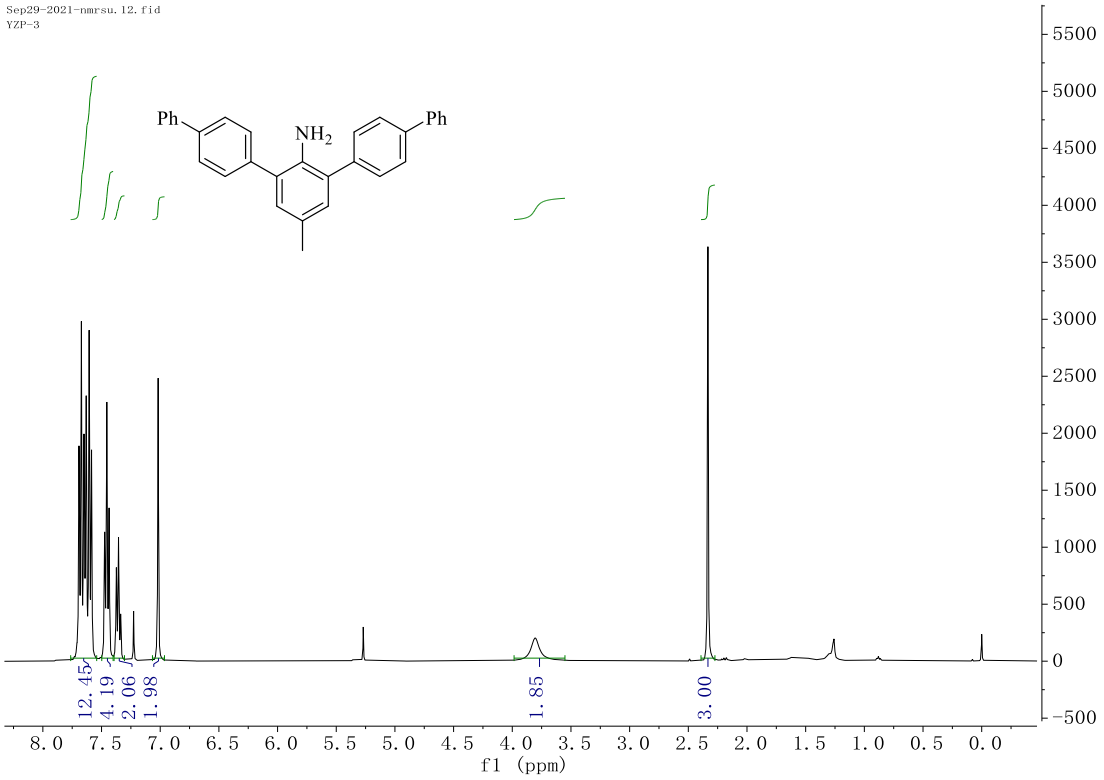


Figure S3. ^{1}H NMR spectrum of **A2** in $CDCl_3$.

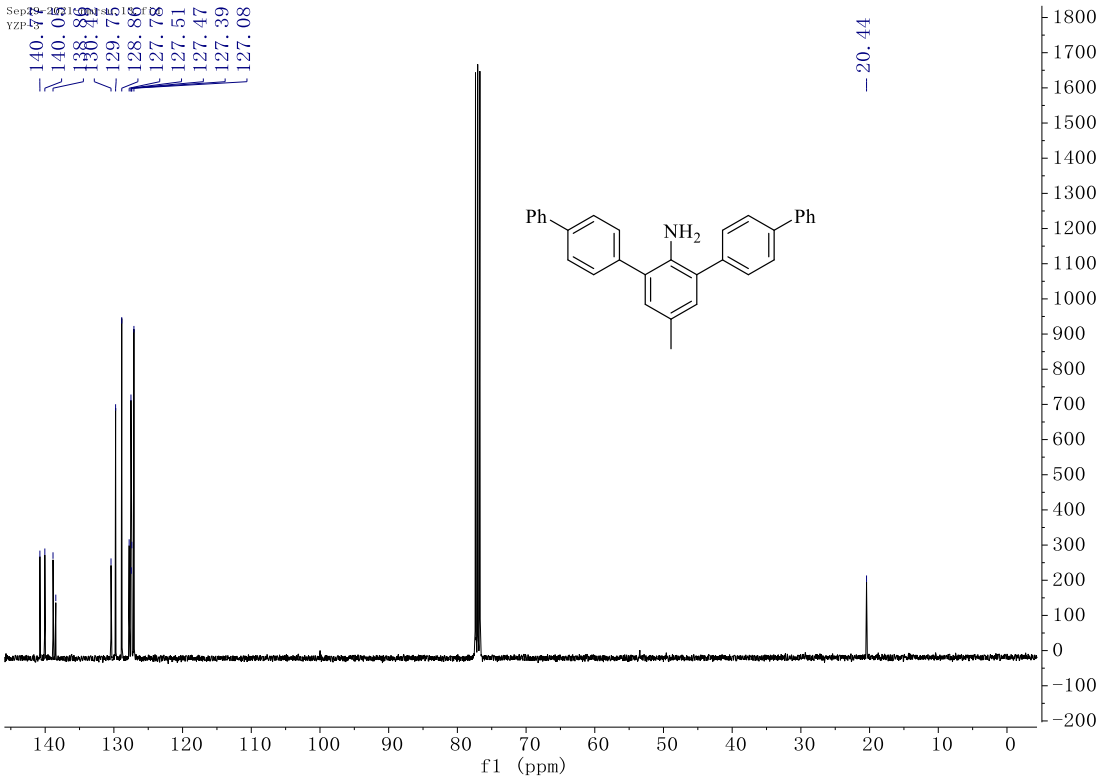


Figure S4. ^{13}C NMR spectrum of **A2** in $CDCl_3$.

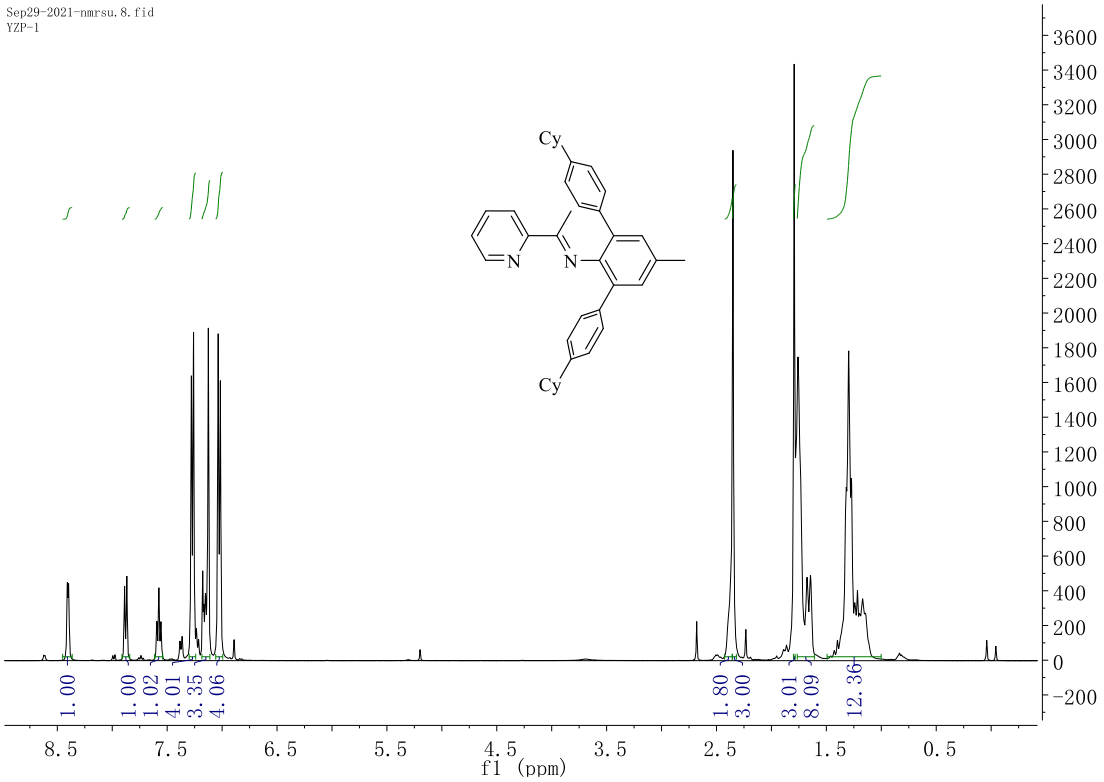


Figure S5. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

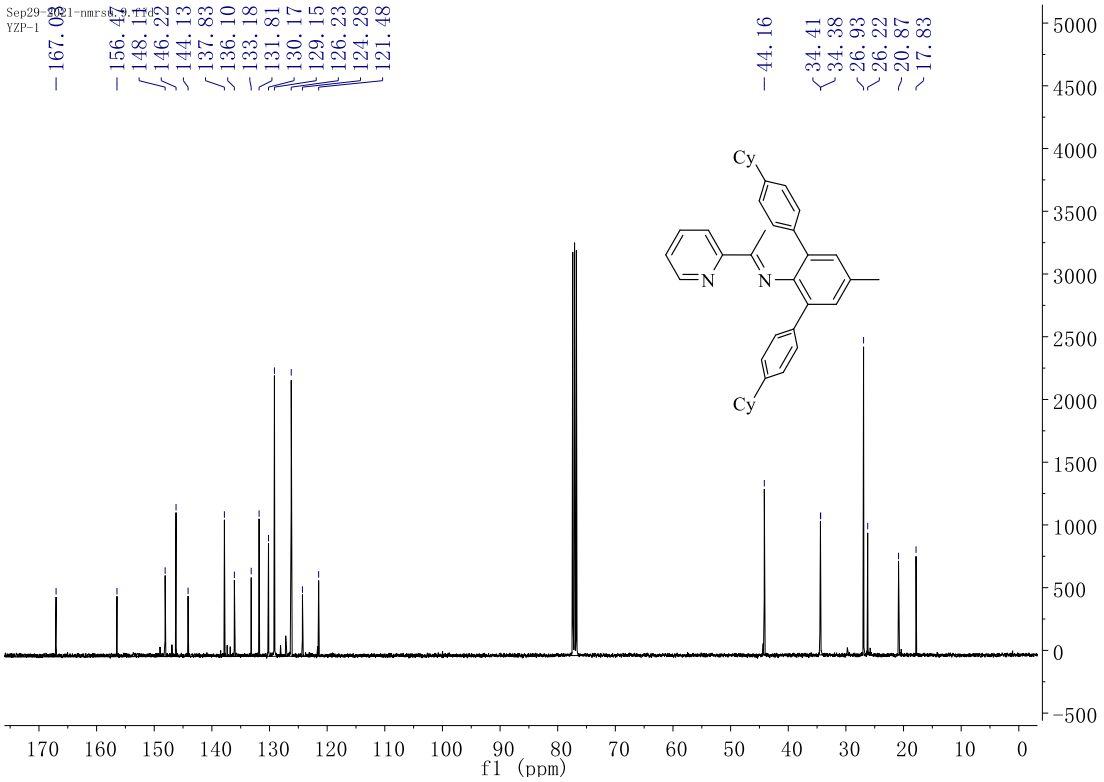


Figure S6. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

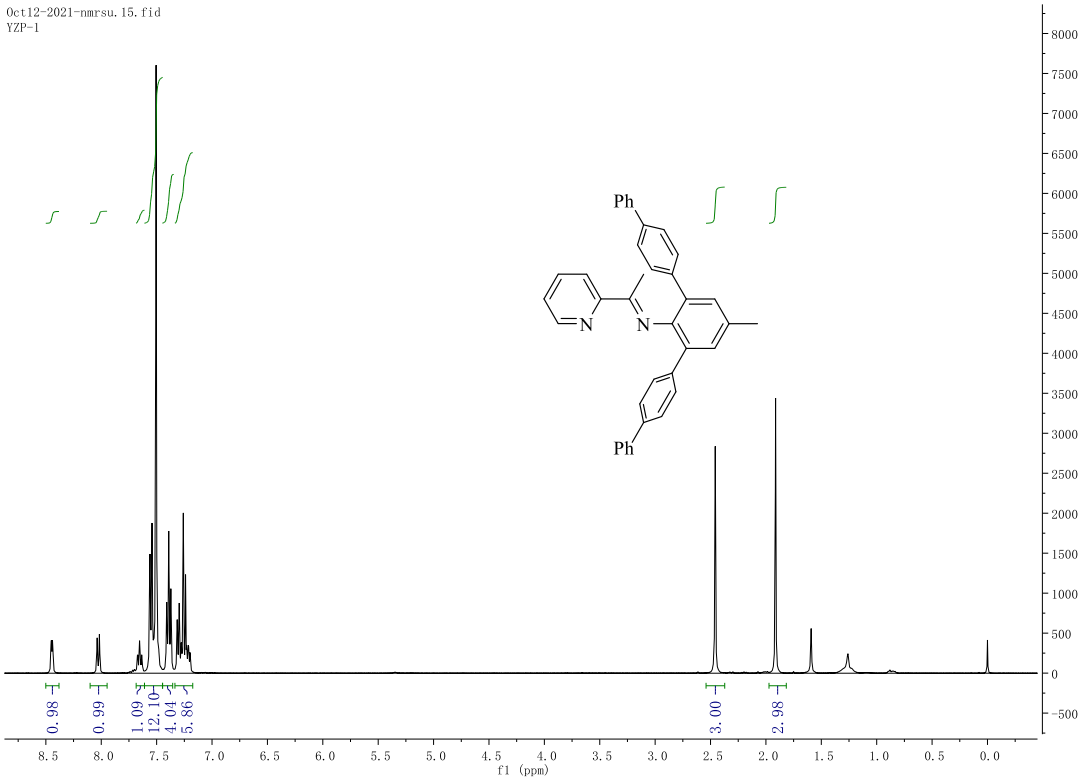


Figure S7. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

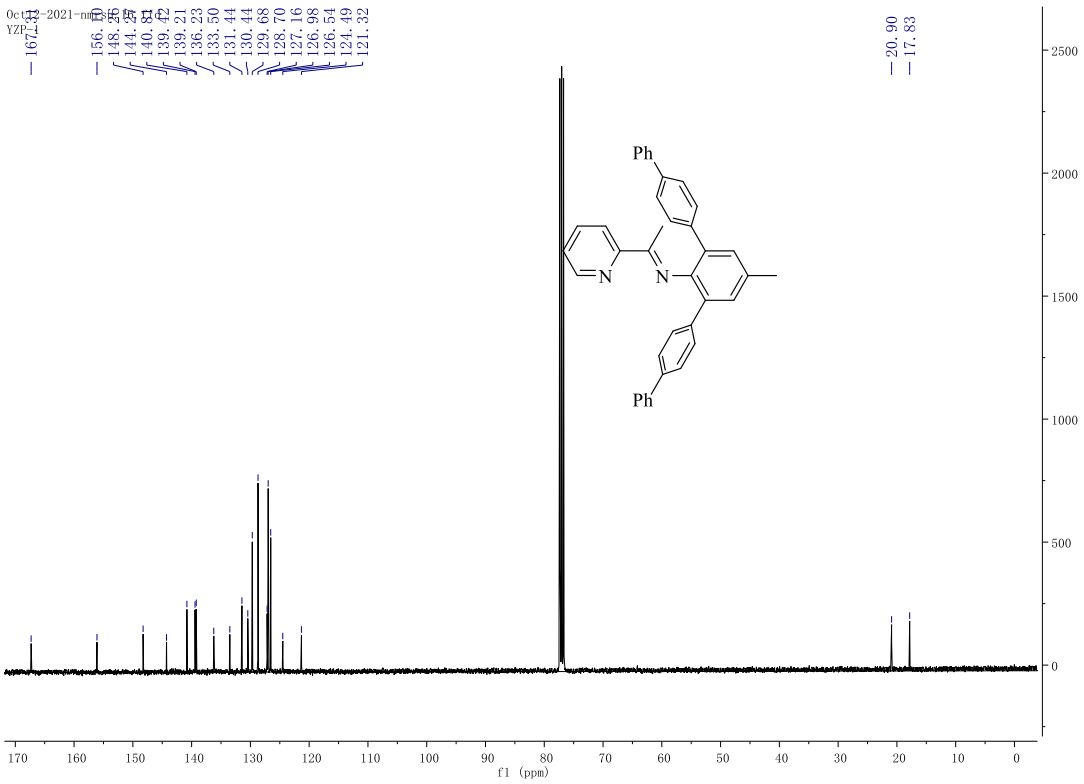


Figure S8. ^{13}C NMR spectrum of **L2** in $CDCl_3$.

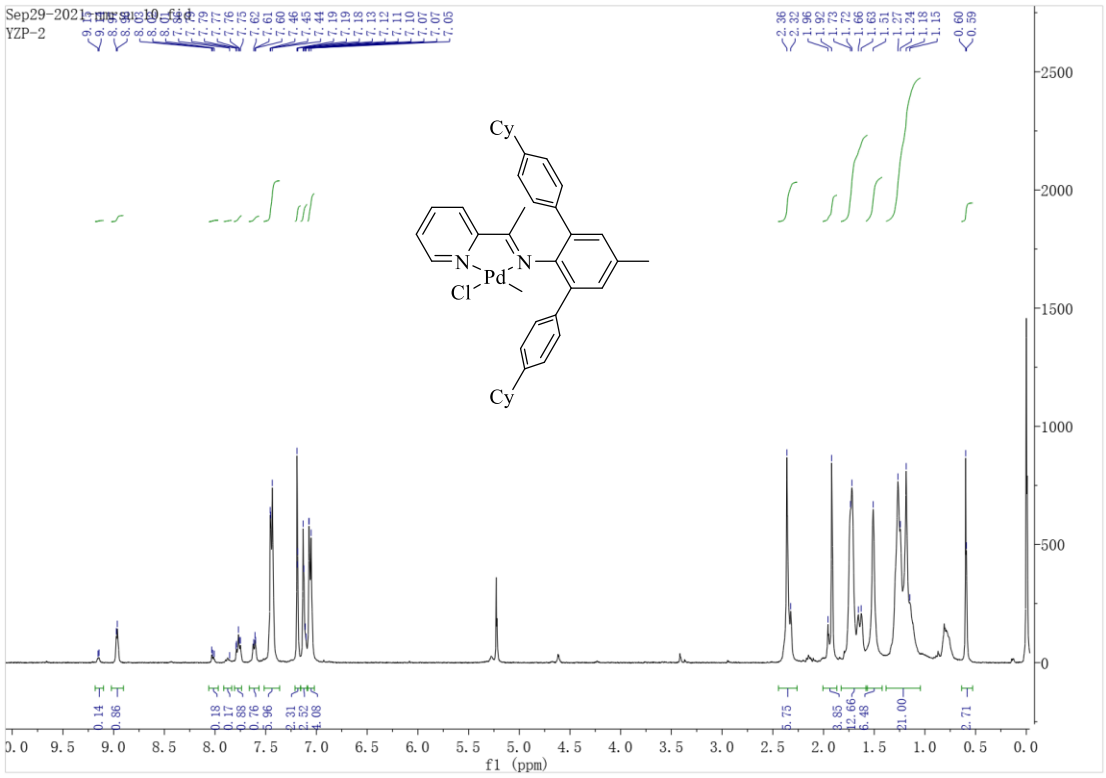


Figure S9. ^{1}H NMR spectrum of **Pd1** in $CDCl_3$.

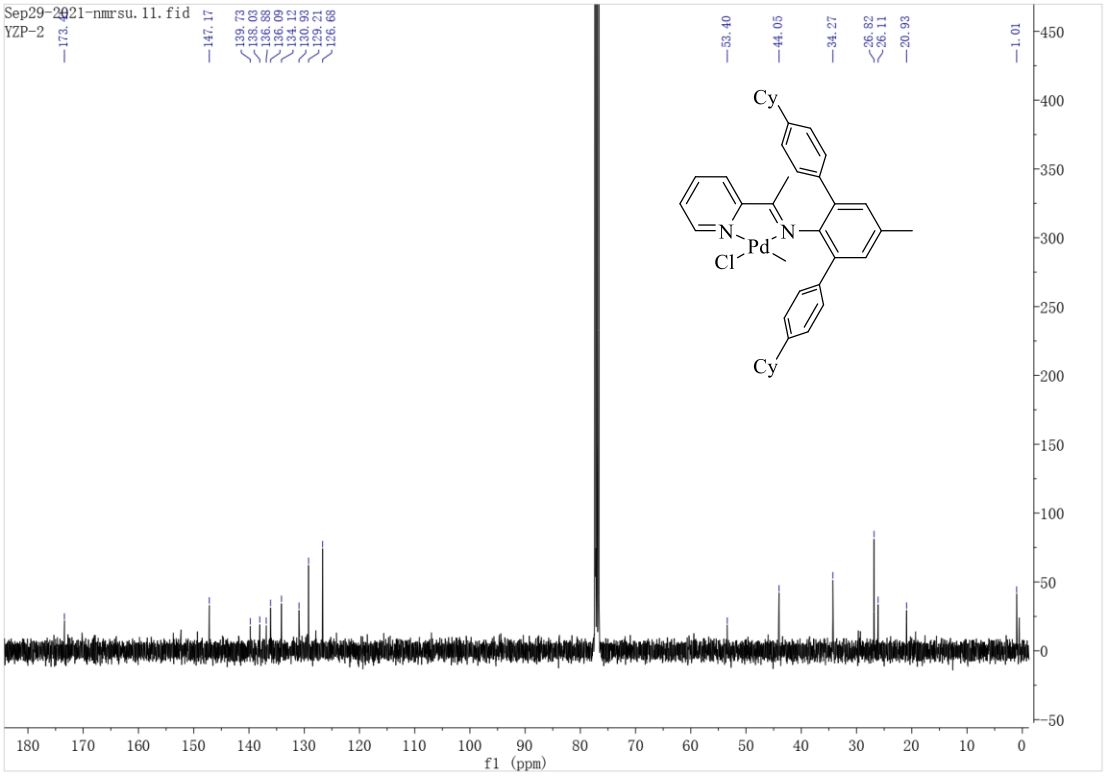


Figure S10. ^{13}C NMR spectrum of **Pd1** in $CDCl_3$.

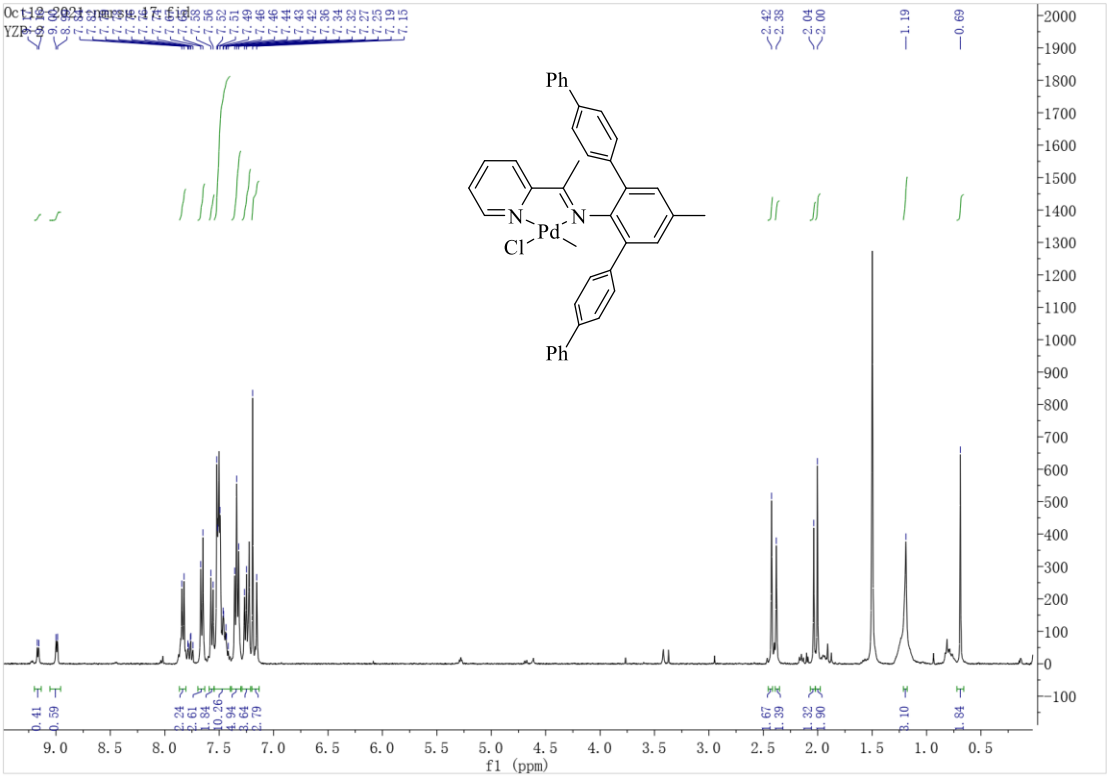


Figure S11. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

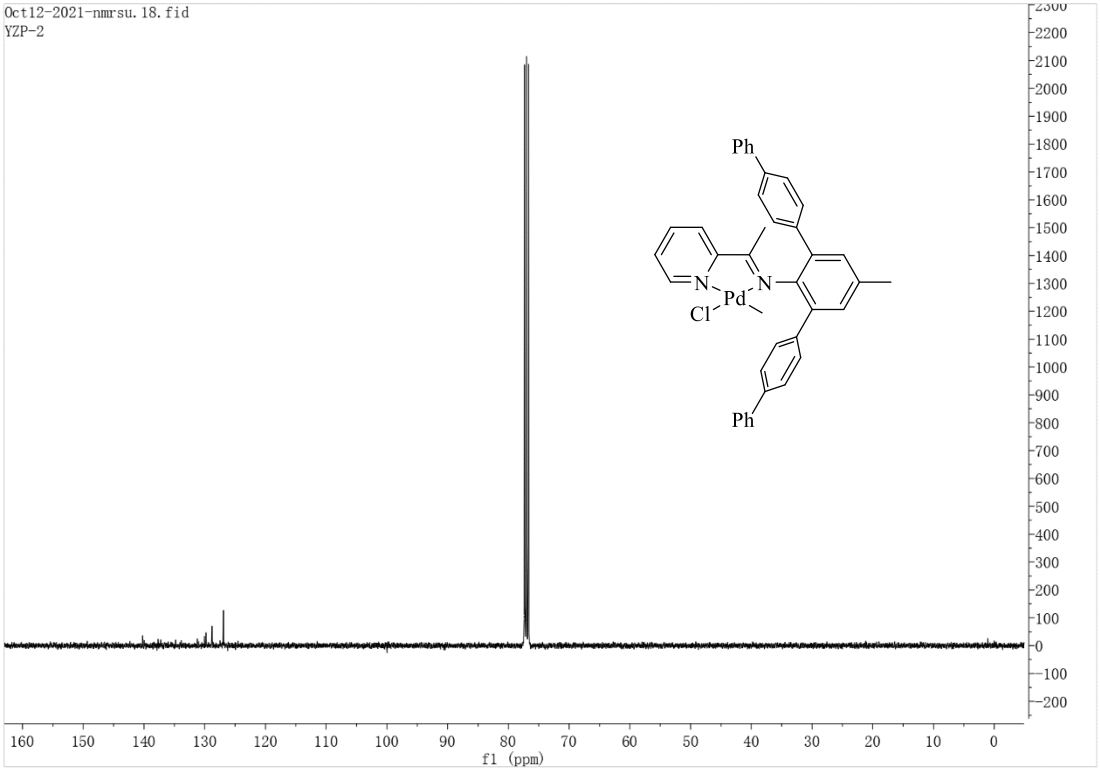


Figure S12. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

2.2 MS of A1-A2 and L1-L2.

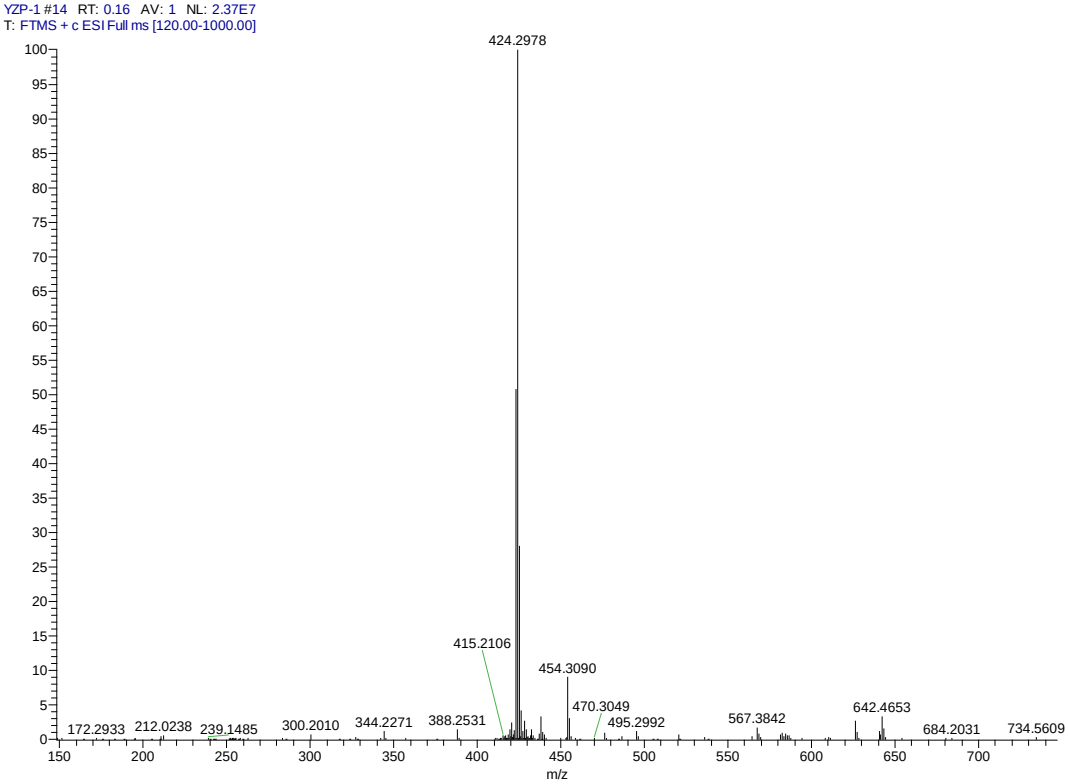


Figure S13. ESI MS of **A1**.

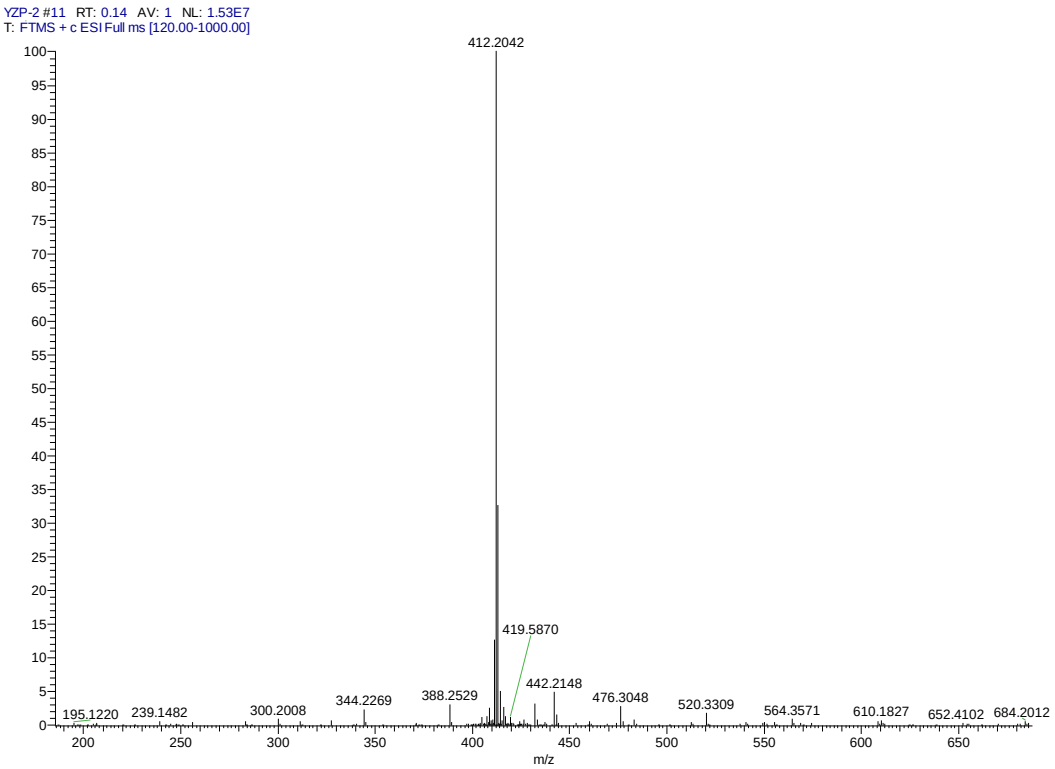


Figure S14. ESI MS of **A2**.

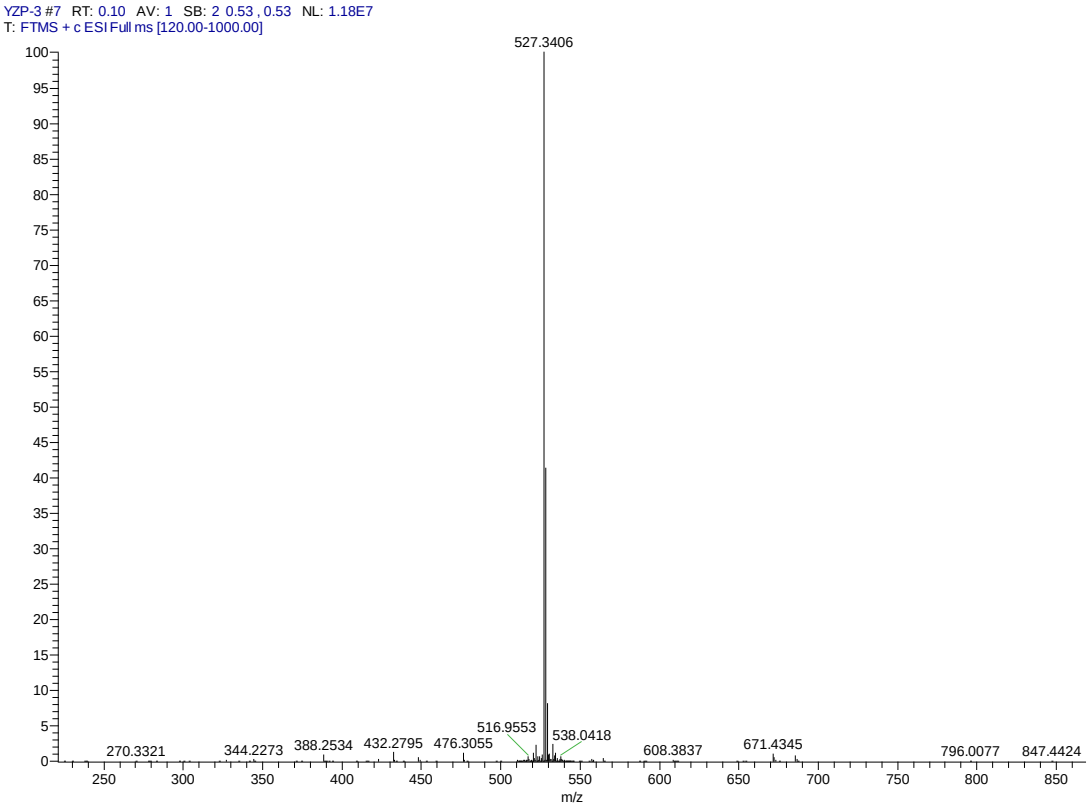


Figure S15. ESI MS of **L1**.

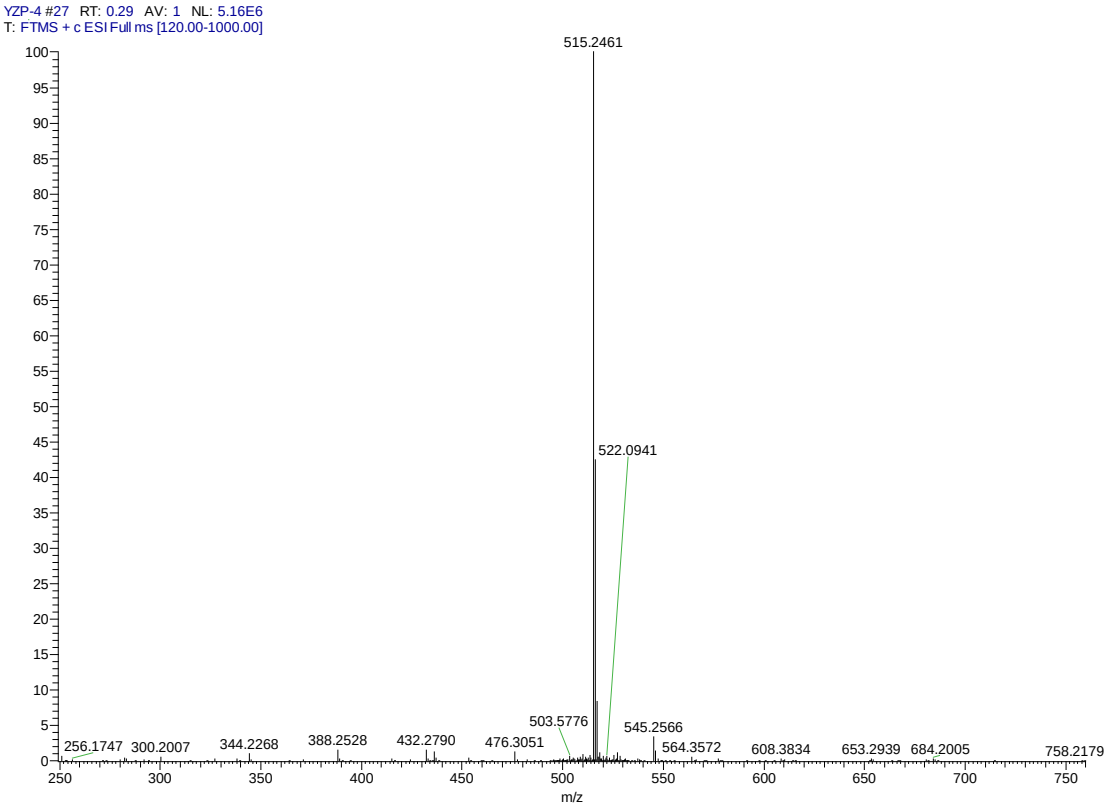


Figure S16. ESI MS of **L2**.

2.3 MS of Complexes Ni1-Ni2 and Pd1-Pd2.

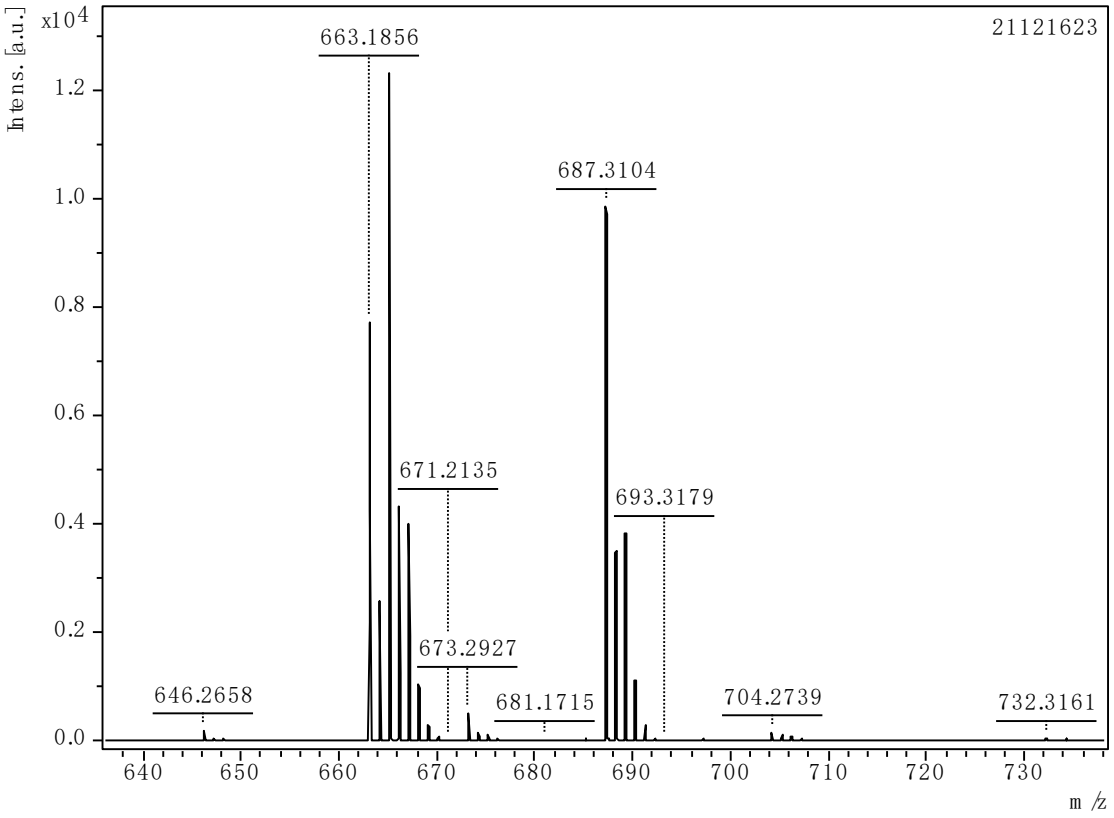


Figure S17. MALDI-TOF-MS of **Ni1**.

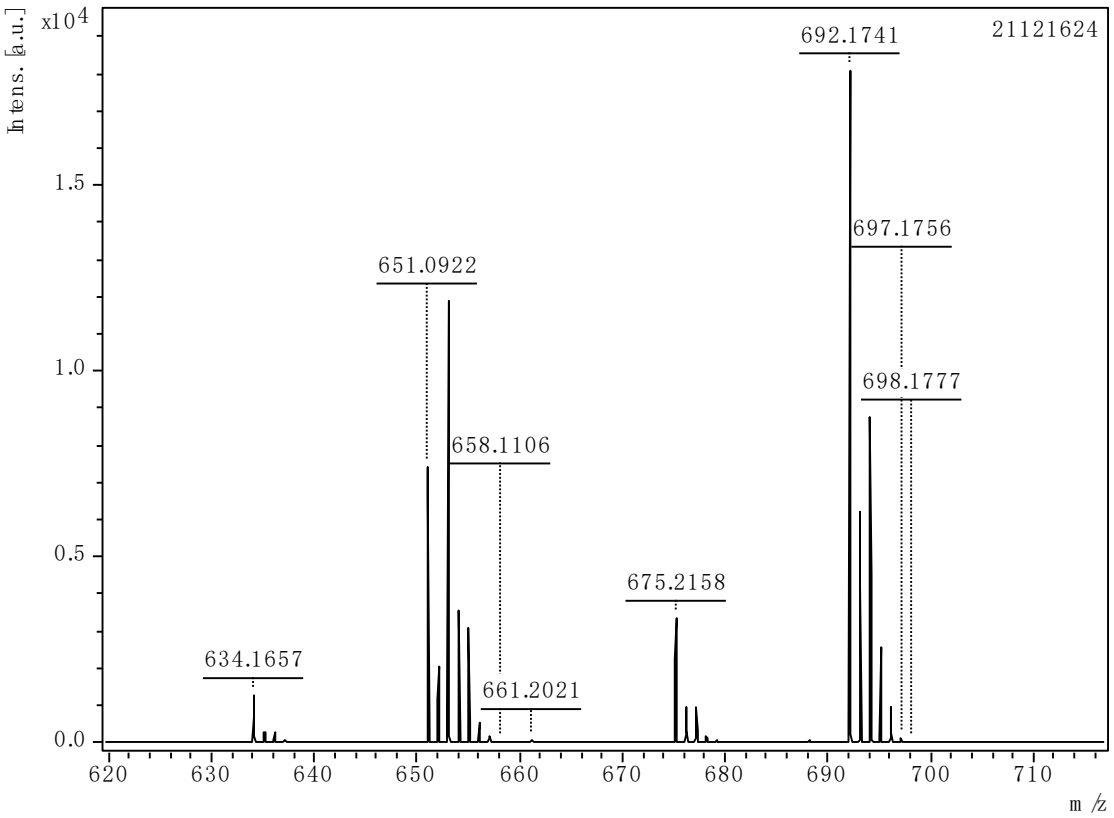


Figure S18. MALDI-TOF-MS of **Ni2**.

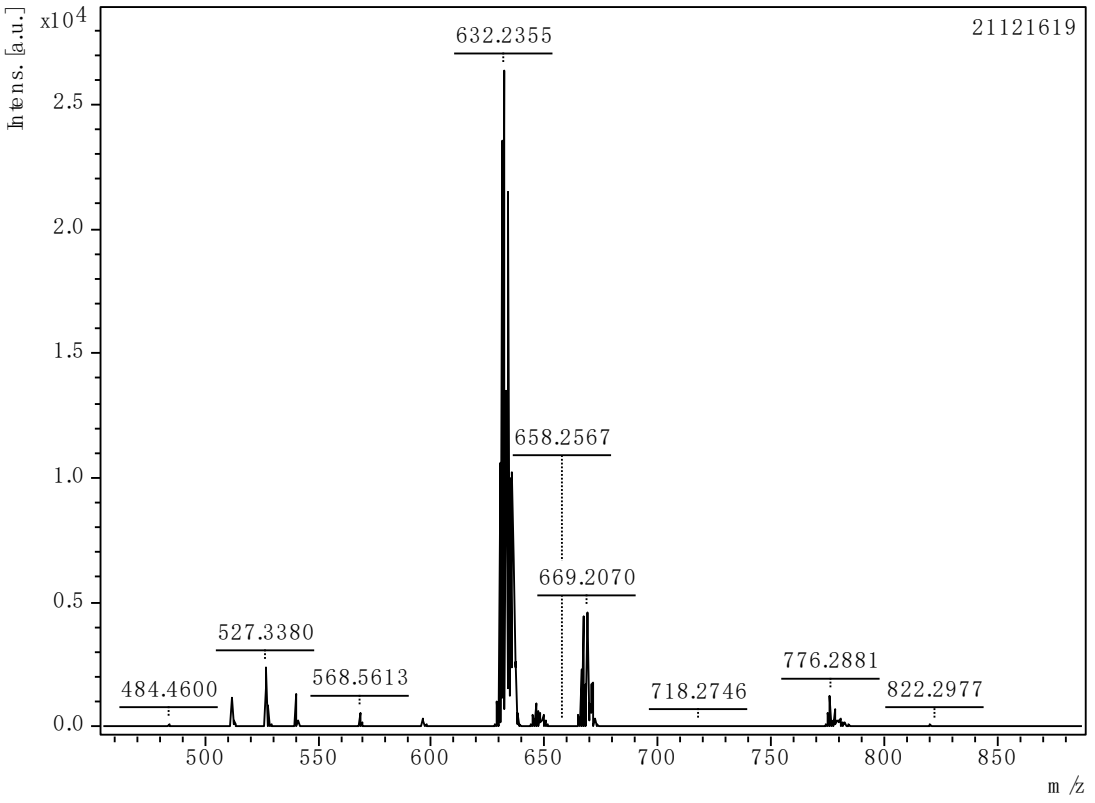


Figure S19. MALDI-TOF-MS of **Pd1**.

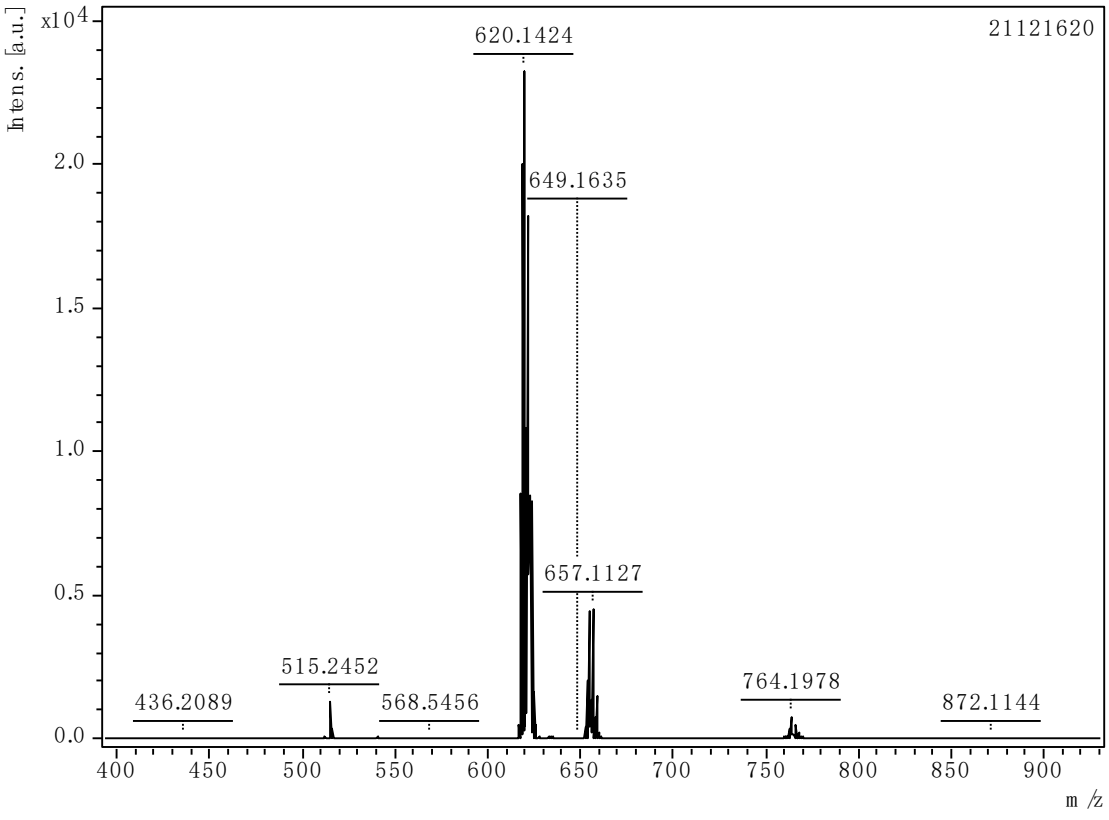


Figure S20. MALDI-TOF-MS of **Pd2**.

2.4 ^{1}H and ^{13}C NMR of Representative Ethylene Oligomers and E-MA Co-oligomers.

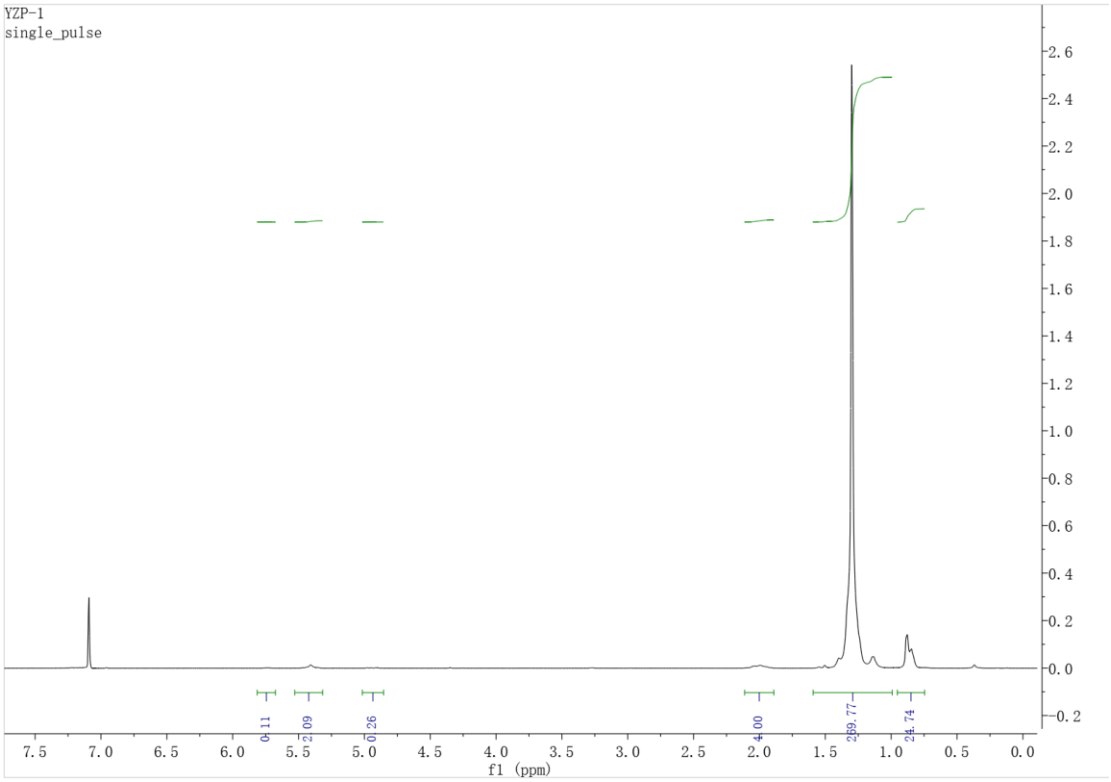


Figure S21. ^{1}H NMR spectrum of the ethylene oligomer from table 1, entry 1.

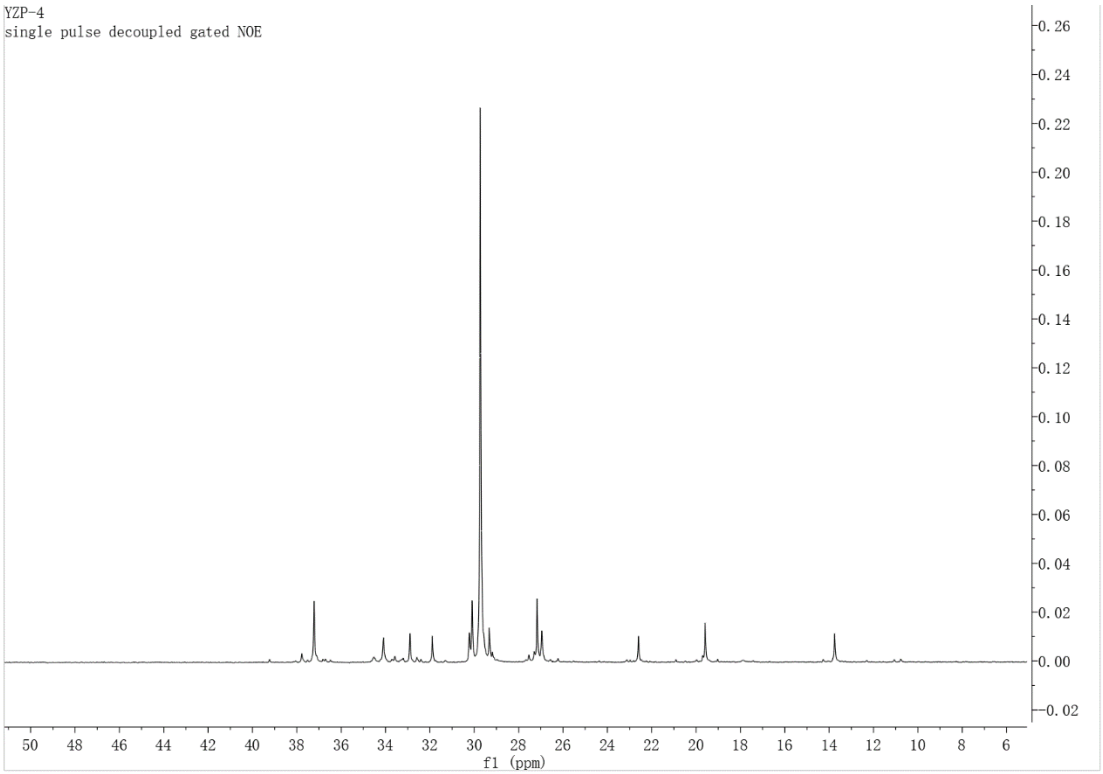


Figure S22. ^{13}C NMR spectrum of the ethylene oligomer from table 1, entry 4.

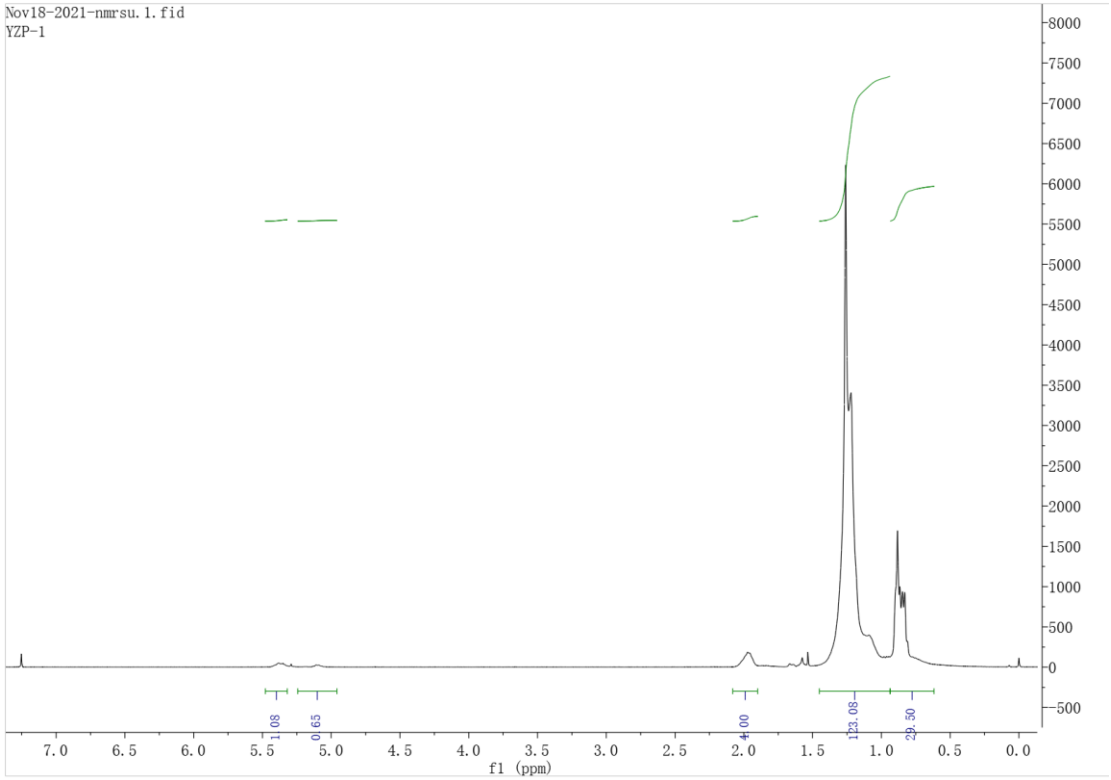


Figure S23. ^{1}H NMR spectrum of the ethylene oligomer from table 2, entry 1.

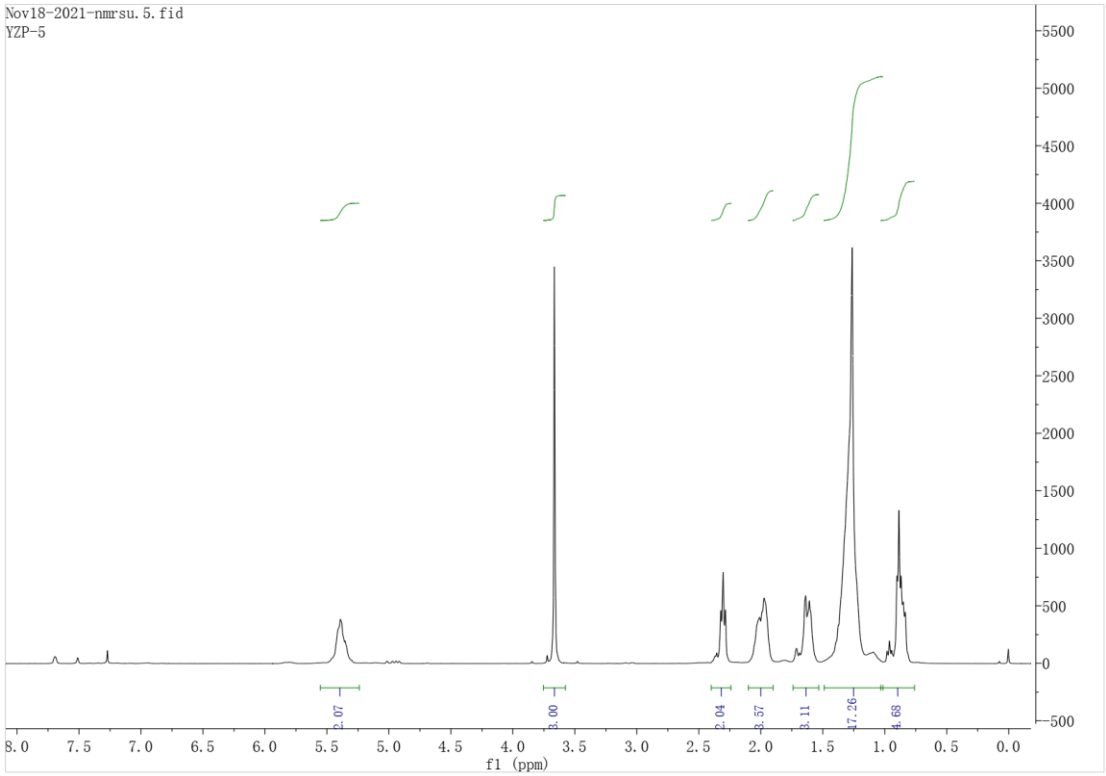


Figure S24. ^{1}H NMR spectrum of the ethylene oligomer from table 3, entry 1.

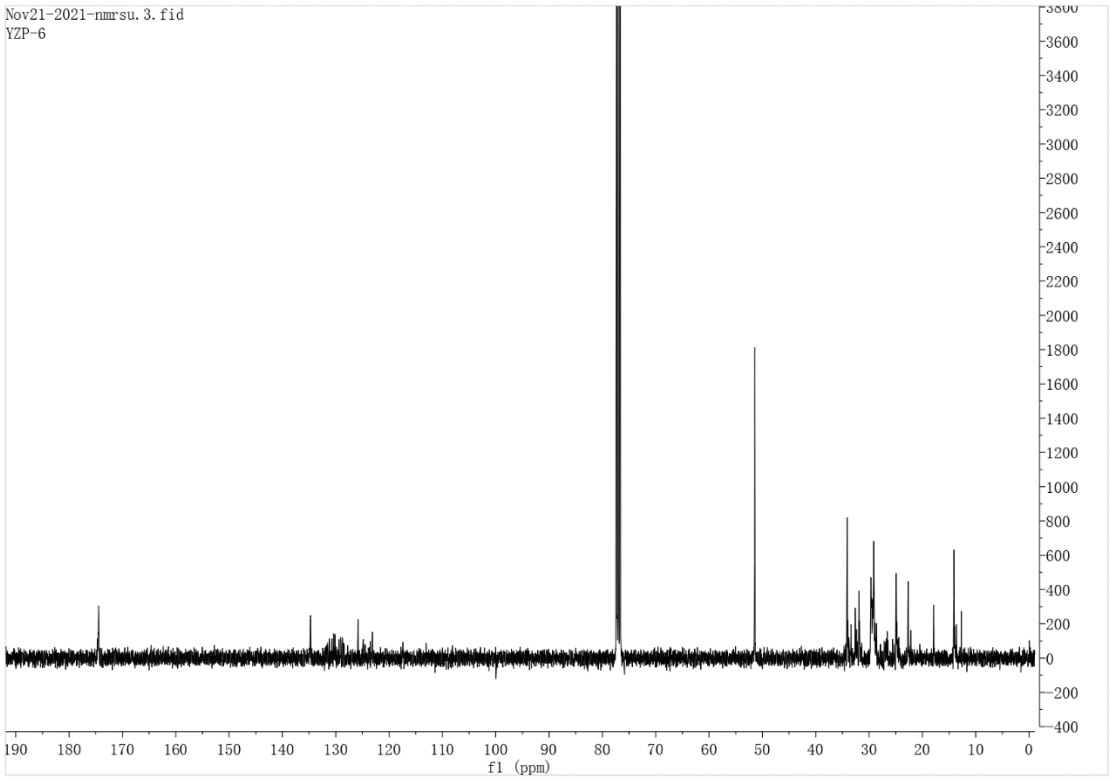


Figure S25. ^{13}C NMR spectrum of the ethylene oligomer from table 3, entry 4.

3. X-ray Crystallography

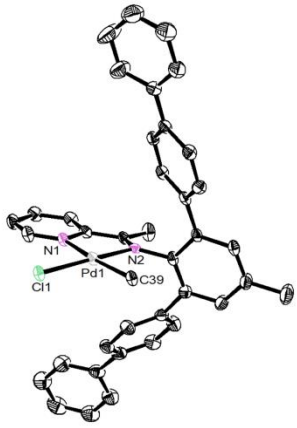


Table S1 Crystal data and structure refinement for Pd2.	
Identification code	**Pd2**
Empirical formula	C39 H33 Cl N2 Pd
Formula weight	671.52
Temperature/K	293(2)
Crystal system	Triclinic
Space group	P-1
a/Å	9.2957(9)
b/Å	11.7588(11)

c/Å	15.4097(14)
α/°	87.540(3)
β/°	87.042(3)
γ/°	70.733(2)
Volume/$Å^3$	1587.3(3)
Z	2
$\rho_{calc}g/cm^3$	1.405
μ/mm^{-1}	0.699
F(000)	688
Crystal size/mm^3	0.40 x 0.20 x 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.23 to 25.02
Index ranges	-10<=h<=11, -8<=k<=13, -18<=l<=18
Reflections collected	7660
Independent reflections	5404 [R(int) = 0.0437]
Data/restraints/parameters	5404 / 12 / 393
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R1 = 0.0646, wR2 = 0.1569
Final R indexes [all data]	R1 = 0.0878, wR2 = 0.1671
Largest diff. peak/hole / e $Å^{-3}$	1.187 and -1.149