Supporting Information for:

Unsymmetrical α-diimine Palladium Catalysts and Their Properties in Olefin (co)Polymerization

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Content

Experimental Section

General Considerations. 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 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. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) with a PL 210 equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 140 °C using o-dichlorobenzene as a solvent and calibrated with polystyrene standards. Water contact angles on polymer films were measured with Contact Angle Meter SL200B (Solon Tech. Co., Ltd.) by the dynamic sessile drop method.

Standard Procedure for the Synthesis of 2-bisphenylmethylanilines. A 150 mL thick wall pressure bottle was charged with aniline (20.0 mmol, 1.0 equiv.) and diphenylmethanol (20 mmol, 1.0 equiv.), and heated to 120 °C. A solution of anhydrous zinc chloride (5 mmol, 0.4 equiv.) in concentrated hydrochloric acid (37% in H_2O, 0.8 equiv.) was added to the mixture (exothermic + intense bubbling), and the temperature was raised to 160 °C. After 30 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. For Me and NO_2, the product was crashed out with 200 ml methanol and washed with methanol (3 × 100 mL). The pure desired aniline was obtained at 80-90 % yield. For OMe and Cl, the product was purified by column chromatography (EtOAc: PE = 1:20) at 60-70%.

2-benzhydryl-4-methoxy-6-methylaniline. Yield 55% (5.63 g). R_f = 0.3 (hexanes/EtOAc, 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.23 (m, 4H, aryl-*H*), 7.18 (dd, J = 13.3, 6.1 Hz, 2H, aryl-*H*), 7.12 (s, 2H, aryl-*H*), 7.10 (s, 2H, aryl-*H*), 6.58 (d, J = 2.6 Hz, 1H, aryl-*H*), 6.17 (d, J = 2.6 Hz, 1H, aryl-*H*), 5.48 (s, 1H, C*H*Ph_2), 3.57 (s, 3H, OMe), 3.12 (s, 2H, NH_2), 2.12 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.99 (s), 142.61 (s), 136.19 (s), 130.38 (s), 129.63 (s), 128.66 (s), 128.54 (s), 126.78 (s), 126.64 (s), 123.92 (s), 114.57 (s), 113.95 (s), 55.52 (s, O*C*H_3), 52.58 (s, *C*HPh_2),

18.26 (s, *C*CH_3). HRMS (m/z): calcd for $C_{21}H_{22}NO$: 304.1701, found: 304.1697 $[M+H]^+$.

2-benzhydryl-4-chloro-6-methylaniline. Yield 63 % (6.55 g). R_f = 0.34 (hexanes/EtOAc, 1:10). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, J = 8.1 Hz, 1H, aryl-*H*), 7.32 (s, 1H, aryl-*H*), 7.29 (d, J = 7.6 Hz, 2H, aryl-*H*), 7.24 (dd, J = 9.2, 5.0 Hz, 2H, aryl-*H*), 7.11 (s, 2H, aryl-*H*), 7.09 (s, 2H, aryl-*H*), 6.97 (s, 1H, aryl-*H*), 6.49 (s, 1H, aryl-*H*), 5.41 (s, 1H, C*H*Ph_2), 3.45 (s, 2H, NH_2), 2.12 (s, 3H, CH_3). ^{13}C NMR (101 MHz, CDCl3): δ 141.88 (s), 141.03 (s), 130.05 (s), 129.46 (s), 128.75 (s), 128.54 (s), 128.49 (s), 127.57 (s), 126.96 (s), 126.57 (s), 124.18 (s), 122.60 (s), 52.37 (s, *C*HPh_2), 17.66 (s, *C*H_3). HRMS (m/z): calcd for $C_{20}H_{19}ClN$: 308.1206, found: 308.1199 $[M+H]^+$.

2-benzhydryl-6-methyl-4-nitroaniline. Yield 70 % (7.52 g). R_f = 0.25 (hexanes/EtOAc, 1:10). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 1.9 Hz, 1H, aryl-*H*), 7.50 (d, J = 2.1 Hz, 1H, aryl-*H*), 7.32 (t, J = 7.2 Hz, 4H, aryl-*H*), 7.26 (dd, J = 13.4, 6.0 Hz, 2H, aryl-*H*), 7.12 (s, 2H, aryl-*H*), 7.10 (s, 2H, aryl-*H*), 5.38 (s, 1H, C*H*Ph_2), 4.23 (s, 2H, NH_2), 2.19 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.89 (s), 140.92 (s), 138.48 (s), 129.29 (s), 129.00 (s), 127.38 (s), 127.24 (s), 125.00 (s), 124.55 (s), 121.71 (s), 52.43 (s, *C*HPh_2), 17.62 (s, *C*H_3). HRMS (m/z): calcd for $C_{20}H_{19}N_2O_2$: 319.1447, found: 319.1438 $[M+H]^+$.

Standard Procedure for the Synthesis of Ligands L1-L4. A solution of 2-bisphenylmethylanilines (20 mmol), 2,3-butadione (10 mmol) and p-toluenesulfonic acid (20 mg) in toluene (200 mL) was stirred at 80 °C for 24 h, then the mixture was refluxed with Dean-stark trap for 3-14 days until there was one main point on the TLC plate. (3 days for **L1**, 1 days for **L2**, 7 days for **L3**, 14 days for **L4**). The solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in methanol (300 mL). The yellow solid was filtered, washed three times by 20 mL methanol and dried under high vacuum.

N,N'-(butane-2,3-diylidene)bis(2-benzhydryl-4-methoxy-6-methylaniline) (L1). Yield 80 % (5.25 g). R_f = 0.42 (hexanes/EtOAc, 1:10). ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, J = 10.9, 3.3 Hz, 6H, aryl-*H*), 7.19 – 7.11 (m, 6H, aryl-*H*), 7.09 – 6.99 (m, 8H, aryl-*H*), 6.67 (d, J = 1.9 Hz, 2H, aryl-*H*), 6.41, 6.36 (d, d, J = 2.0 Hz, 2H, aryl-*H*), 5.32, 5.27 (s, s, 2H, C*H*Ph_2), 3.68 (s, 6H, OCH_3), 1.96 (s, 5H, CH_3), 1.93 (s, 1H, CH_3), 1.56 (s, 1H, N=C-CH_3), 1.27 (s, 5H, N=C-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.00 (s, N=*C*-CH_3), 169.65 (s, N=*C*-CH_3), 155.49 (s), 155.45 (s), 143.33 (s), 142.93 (s), 142.34 (s), 141.64 (s), 141.49 (s), 134.31 (s), 133.79 (s), 129.60 (s), 129.53 (s), 129.50 (s), 128.47 (s), 128.39 (s), 128.15 (s), 126.42 (s), 126.33 (s), 126.21 (s), 125.61 (s), 125.41 (s), 113.93 (s), 113.78 (s), 113.33 (s), 113.15 (s), 55.31 (s, O*C*H_3), 55.28 (s,

O*C*H$_3$), 52.54 (s, *C*HPh$_2$), 52.03 (s, *C*HPh$_2$), 18.23 (s, *C*H$_3$), 18.09 (s, *C*H$_3$), 16.20 (s, N=C-*C*H$_3$), 15.63 (s, N=C-*C*H$_3$). HRMS (m/z): calcd for $C_{46}H_{45}N_2O_2$: 657.3481, found: 657.3469 $[M+H]^+$.

N,N'-(butane-2,3-diylidene)bis(2-benzhydryl-4,6-dimethylaniline) (L2). Yield 76 % (4.74 g). R_f = 0.71 (hexanes/EtOAc, 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.23 (m, 4H, aryl-*H*), 7.21 (d, J = 5.5 Hz, 4H, aryl-*H*), 7.19 – 7.11 (m, 4H, aryl-*H*), 7.09 – 7.00 (m, 8H, aryl-*H*), 6.92, 6.90 (s, s, 2H, aryl-*H*), 6.62, 6.57 (s, s, 2H, aryl-*H*), 5.30, 5.29 (s, s, 2H, C*H*Ph$_2$), 2.22 (s, 6H, C*H*$_3$), 1.94 (s, 5H, C*H*$_3$), 1.91 (s, 1H, C*H*$_3$), 1.55 (s, 1H, N=C-C*H*$_3$), 1.26 (s, 5H, N=C-C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.36 (s, N=*C*-CH$_3$), 169.02 (s, N=*C*-CH$_3$), 145.58 (s), 145.45 (s), 143.74 (s), 143.21 (s), 142.62 (s), 132.60 (s), 132.27 (s), 132.14 (s), 132.09 (s), 129.68 (s), 129.62 (s), 129.57 (s), 129.54 (s), 129.39 (s), 129.28 (s), 128.47 (s), 128.36 (s), 128.07 (s), 127.78 (s), 126.32 (s), 126.25 (s), 126.09 (s), 126.05 (s), 124.31 (s), 124.16 (s), 52.39 (s, *C*HPh$_2$), 51.84 (s, *C*HPh$_2$), 21.05 (s, *C*H$_3$), 17.84 (s, *C*H$_3$), 17.69 (s, *C*H$_3$), 16.17 (s, N=C-*C*H$_3$), 15.61 (s, N=C-*C*H$_3$). HRMS (m/z): calcd for $C_{46}H_{45}N_2$: 625.3583, found: 625.3569 $[M+H]^+$.

N,N'-(butane-2,3-diylidene)bis(2-benzhydryl-4-chloro-6-methylaniline) (L3). Yield 71 % (4.72 g). R_f = 0.54 (hexanes/EtOAc, 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 1.9 Hz, 2H, aryl-*H*), 7.23 (s, 3H, aryl-*H*), 7.23 – 7.21 (m, 3H, aryl-*H*), 7.20 – 7.14 (m, 4H, aryl-*H*), 7.11 (d, J = 1.9 Hz, 1H, aryl-*H*), 7.09 (d, J = 1.9 Hz, 1H, aryl-*H*), 7.05 (d, J = 6.9 Hz, 2H, aryl-*H*), 6.99 (dd, J = 7.0, 2.5 Hz, 6H, aryl-*H*), 6.79, 6.74 (d, d, J = 2.0 Hz, 1H, aryl-*H*), 5.29, 5.26 (s, s, 2H, C*H*Ph$_2$), 1.94 (s, 5H, C*H*$_3$), 1.91 (s, 1H, C*H*$_3$), 1.53 (s, 1H, N=C-C*H*$_3$), 1.24 (s, 5H, N=C-C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.57 (s, N=*C*-CH$_3$), 169.23 (s, N=*C*-CH$_3$), 146.36 (s), 146.23 (s), 142.65 (s), 142.24 (s), 141.75 (s), 134.57 (s), 134.10 (s), 129.53 (s), 129.46 (s), 129.40 (s), 129.37 (s), 128.62 (s), 128.55 (s), 128.42 (s), 128.32 (s), 128.29 (s), 127.41 (s), 127.14 (s), 126.70 (s), 126.58 (s), 126.50 (s), 126.37 (s), 126.22 (s), 52.38 (s, *C*HPh$_2$), 51.87 (s, *C*HPh$_2$), 17.78 (s, *C*H$_3$), 17.62 (s, *C*H$_3$), 16.31 (s, N=C-*C*H$_3$), 15.80 (s, N=C-*C*H$_3$). HRMS (m/z): calcd for $C_{44}H_{39}Cl_2N_2$: 665.2490, found: 665.2483 $[M+ H]^+$.

N,N'-(butane-2,3-diylidene)bis(2-benzhydryl-6-methyl-4-nitroaniline) (L4). Yield 45 % (3.09 g). R_f = 0.51 (hexanes/EtOAc, 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06, 8.04 (d, J = 2.1 Hz, 2H, aryl-*H*), 7.75, 7.69 (d, d, J = 2.2 Hz, 2H, aryl-*H*), 7.34 – 7.20 (m, 12H, aryl-*H*), 7.07, 7.00 (d, d, J = 7.0 Hz, 8H, aryl-*H*), 5.29 (s, 2H, C*H*Ph$_2$), 2.07 (s, 5H, C*H*$_3$), 2.04 (s, 1H, C*H*$_3$), 1.55 (s, 1H, N=C-C*H*$_3$), 1.27 (s, 5H, N=C-C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.72 (s, N=*C*-CH$_3$), 168.34 (s, N=*C*-CH$_3$), 153.30 (s), 143.93 (s), 143.83 (s), 141.82 (s), 141.77 (s), 141.41 (s), 141.03 (s), 133.99 (s), 133.56 (s), 129.45 (s), 129.37 (s), 129.26 (s), 129.22 (s), 128.92 (s), 128.87 (s), 128.64 (s), 128.60 (s), 127.19 (s), 127.03 (s), 125.78 (s), 125.65 (s), 124.19 (s), 123.25 (s), 122.93

(s), 52.52 (s, *C*HPh$_2$), 51.99 (s, *C*HPh$_2$), 18.03 (s, *C*H$_3$), 17.89 (s, *C*H$_3$), 16.83 (s, N=C-*C*H$_3$), 16.40 (s, N=C-*C*H$_3$). HRMS (m/z): calcd for $C_{44}H_{39}N_4O_4$: 687.2971, found: 687.2964 $[M+H]^+$.

Synthesis of Ligand N,N'-(acenaphthylene-1,2-diylidene)bis(2-benzhydryl-4,6-dimethylaniline) (L5).

A 100 mL round-bottom flask was charged with $ZnCl_2$ (0.86 g, 6.25 mmol), acenaphthenequinone (1 g, 5.5 mmol) and glacial acetic acid (10 mL). 2-bisphenylmethyl-4,6-dimethylaniline (12.5 mmol) was added, and the mixture was refluxed under stirring for 30 min. The solution was cooled to room temperature, and a bright orange-red solid precipitated. The solid was separated by filtration and washed with acetic acid (3 × 10 mL) and diethyl ether (8 × 15 mL) to remove remaining acetic acid. The solid was suspended in methylene chloride (200 mL), and a solution of potassium oxalate (1.84 g, 10 mmol) in water (10 mL) was added. The reaction mixture was stirred vigorously for 15 min. A white precipitate of zinc oxalate was generated in the aqueous phase. 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 orange powder. Yield 67 % (2.65 g). R_f = 0.54 (hexanes/EtOAc, 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 2H, aryl-*H*), 7.23 (t, J = 7.3 Hz, 4H, aryl-*H*), 7.16 (t, J = 7.1 Hz, 2H, aryl-*H*), 7.10 (d, J = 7.5 Hz, 4H, aryl-*H*), 7.08 – 7.03 (m, 3H, aryl-*H*), 7.02 (s, 2H, aryl-*H*), 6.86 (d, J = 7.4 Hz, 4H, aryl-*H*), 6.70 (s, 2H, aryl-*H*), 6.32 (dd, J = 15.0, 7.4 Hz, 6H, aryl-*H*), 6.09 (t, J = 7.3 Hz, 2H, aryl-*H*), 5.72 (s, 2H, C*H*Ph$_2$), 2.31 (s, 6H, C*H*$_3$), 2.26 (s, 6H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.93 (s, N=*C*), 145.44 (s), 142.59 (s), 140.68 (s), 138.77 (s), 132.02 (s), 131.68 (s), 128.78 (s), 128.60 (s), 128.20 (s), 127.91 (s), 127.01 (s), 126.99 (s), 126.95 (s), 126.16 (s), 125.89 (s), 124.90 (s), 123.97 (s), 123.80 (s), 121.35 (s), 51.47 (s, *C*HPh$_2$), 20.21 (s, *C*H$_3$), 16.83 (s, *C*H$_3$). HRMS (m/z): calcd for $C_{54}H_{45}N_2$: 721.3583, found: 721.3574 $[M+H]^+$.

Standard Procedure for the Synthesis of Complexes 1-5.

The mixture of ligand (1 mmol), Pd(COD)MeCl (265 mg, 1 mmol) and CH_2Cl_2 (20 mL) was stirred for 3-9 days (2 days for **1**, 1 days for **2**, 7 days for **3**, 10 days for **4**, 2 days for **5**) at room temperature. During the stirring, the solid was completely dissolved and the color of the solution was changed from yellow to red. The desired compound can be isolated from recrystallization from n-hexane and dichloromethane. For complex **4**, the desired compound can be isolated by using column chromatography. The mixture was eluted on silica gel with first 1:1 hexanes/CH_2Cl_2

then pure CH_2Cl_2 as the mobile phase. The pure compound was obtained as an orange solid.

(OMeN^N)PdMeCl (1). Yield 76 % (0.618 g). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 2H, aryl-*H*), 7.28 (dd, J = 6.4, 4.6 Hz, 4H, aryl-*H*), 7.24 (dd, J = 11.1, 5.0 Hz, 4H, aryl-*H*), 7.20 (s, 3H, aryl-*H*), 7.17 (d, J = 8.3 Hz, 4H, aryl-*H*), 7.13 (t, J = 6.3 Hz, 3H, aryl-*H*), 6.77 (d, J = 2.2 Hz, 1H, aryl-*H*), 6.72 (d, J = 2.3 Hz, 1H, aryl-*H*), 6.48 (d, J = 2.3 Hz, 1H, aryl-*H*), 6.38 (d, J = 2.2 Hz, 1H, aryl-*H*), 6.23 (s, 1H, C*H*Ph_2), 5.95 (s, 1H, C*H*Ph_2), 3.73 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 2.34 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 0.80 (s, 3H, Pd-CH_3), 0.64 (s, 3H, N=C-CH_3), 0.58 (s, 3H, N=C-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.24 (s, N=*C*-CH_3), 172.15 (s, N=*C*-CH_3), 157.76 (s), 157.30 (s), 142.39 (s), 142.29 (s), 141.49 (s), 137.25 (s), 137.19 (s), 137.12 (s), 136.74 (s), 130.42 (s), 130.26 (s), 129.95 (s), 129.77 (s), 129.47 (s), 128.69 (s), 128.39 (s), 128.31 (s), 128.25 (s), 128.06 (s), 126.78 (s), 126.76 (s), 126.37 (s), 126.33 (s), 114.15 (s), 113.81 (s), 113.32 (s), 113.03 (s), 55.27 (s, O*C*H_3), 55.07 (s, O*C*H_3), 52.52 (s, *C*HPh_2), 52.30 (s, *C*HPh_2), 18.87 (s, *C*H_3), 18.61 (s, *C*H_3), 18.50 (s, N=C-*C*H_3), 17.83 (s, N=C-*C*H_3), 3.04 (s, Pd-*C*H_3). MALDI-TOF-MS (m/z): calcd for $C_{46}H_{44}N_2O_2Pd$: 762.2438, found: 762.2181 $[M\text{-}Cl\text{-}CH_3]^+$. Anal. Calcd for $C_{47}H_{47}ClN_2O_2Pd$: C, 69.37; H, 5.82; N, 3.44; Found: C, 69.19; H, 6.05; N, 3.43.

(MeN^N)PdMeCl (2). Yield 75 % (0.586 g). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 2H, aryl-*H*), 7.28 (dd, J = 7.7, 3.8 Hz, 4H, aryl-*H*), 7.26 – 7.22 (m, 4H, aryl-*H*), 7.19 (dd, J = 9.6, 4.8 Hz, 6H, aryl-*H*), 7.16 – 7.10 (m, 4H, aryl-*H*), 7.05 (s, 1H, aryl-*H*), 7.00 (s, 1H, aryl-*H*), 6.73 (s, 1H, aryl-*H*), 6.62 (s, 1H, aryl-*H*), 6.21 (s, 1H, C*H*Ph_2), 5.95 (s, 1H, C*H*Ph_2), 2.32 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 0.79 (s, 3H, Pd-CH_3), 0.62 (s, 3H, N=C-CH_3), 0.57 (s, 3H, N=C-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.59 (s, N=*C*-CH_3), 168.87 (s, N=*C*-CH_3), 143.27 (s), 143.15 (s), 142.27 (s), 141.76 (s), 141.33 (s), 140.77 (s), 140.56 (s), 136.99 (s), 136.54 (s), 136.20 (s), 135.85 (s), 130.24 (s), 130.08 (s), 130.03 (s), 129.89 (s), 129.74 (s), 129.64 (s), 129.57 (s), 129.51 (s), 129.16 (s), 128.93 (s), 128.47 (s), 128.19 (s), 127.96 (s), 127.72 (s), 127.64 (s), 127.47 (s), 127.41 (s), 126.47 (s), 126.05 (s), 125.63 (s), 125.31 (s), 124.97 (s), 123.94 (s), 123.92 (s), 52.63 (s, *C*HPh_2), 52.34 (s, *C*HPh_2), 21.43 (s, *C*H_3), 21.40 (s, *C*H_3), 18.23 (s, N=C-*C*H_3), 17.99 (s, N=C-*C*H_3), 3.50 (s, Pd-*C*H_3). MALDI-TOF-MS (m/z): calcd for $C_{46}H_{44}N_2Pd$: 730.2539, found: 730.2225 $[M\text{-}Cl\text{-}CH_3]^+$. Anal. Calcd for $C_{47}H_{47}ClN_2Pd$: C, 72.21; H, 6.06; N, 3.58; Found: C, 71.94; H, 6.16; N, 3.57.

(ClN^N)PdMeCl (3). Yield 60 % (0.493 g). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.3 Hz, 2H, aryl-*H*), 7.29 (s, 2*H*), 7.26 (d, J = 5.8 Hz, 4H, aryl-*H*), 7.24 – 7.19 (m, 6H, aryl-*H*), 7.17 (d, J = 7.1 Hz, 2H, aryl-*H*), 7.13 (d, J = 7.9 Hz, 3H, aryl-*H*), 7.08 (d, J = 8.2 Hz, 3H, aryl-*H*), 6.91 (s, 1H, aryl-*H*), 6.79 (s, 1H, aryl-*H*),

6.17 (s, 1H, C*H*Ph_2), 5.90 (s, 1H, C*H*Ph_2), 2.32 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 0.79 (s, 3H, Pd-CH_3), 0.62 (s, 3H, N=C-CH_3), 0.56 (s, 3H, N=C-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.10 (s, N=*C*-CH_3), 172.06 (s, N=*C*-CH_3), 141.97 (s), 141.69 (s), 141.60 (s), 140.90 (s), 140.74 (s), 137.71 (s), 137.67 (s), 132.51 (s), 131.67 (s), 130.47 (s), 130.34 (s), 130.17 (s), 129.87 (s), 129.40 (s), 129.06 (s), 128.96 (s), 128.67 (s), 128.61 (s), 128.32 (s), 127.99 (s), 127.59 (s), 127.23 (s), 127.16 (s), 126.82 (s), 126.71 (s), 52.43 (s, *C*HPh_2), 52.22 (s, *C*HPh_2), 19.09 (s, *C*H_3), 18.27 (s, *C*H_3), 18.12 (s, N=C-*C*H_3), 18.07 (s, N=C-*C*H_3), 3.47 (s, Pd-*C*H_3). MALDI-TOF-MS (m/z): calcd for $C_{44}H_{38}Cl_2N_2Pd$: 770.1447, found: 770.1151 $[M\text{-}Cl\text{-}CH_3]^+$. Anal. Calcd for $C_{45}H_{41}Cl_3N_2Pd$: C, 65.70; H, 5.02; N, 3.41; Found: C, 65.95; H, 5.30; N, 3.29.

(NO_2N^N)PdMeCl (4). Yield 35 % (0.295 g). Orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.11 (d, J = 2.0 Hz, 1H, aryl-*H*), 8.06 (d, J = 2.0 Hz, 1H, aryl-*H*), 7.72 (d, J = 2.2 Hz, 1H, aryl-*H*), 7.58 (d, J = 2.2 Hz, 1H, aryl-*H*), 7.29 (d, J = 6.6 Hz, 2H, aryl-*H*), 7.25 (d, J = 4.3 Hz, 4H, aryl-*H*), 7.23 (s, 2H, aryl-*H*), 7.22 – 7.18 (m, 4H, aryl-*H*), 7.18 – 7.12 (m, 2H, aryl-*H*), 7.09 – 7.00 (m, 6H, aryl-*H*), 6.13 (s, 1H, C*H*Ph_2), 5.91 (s, 1H, C*H*Ph_2), 2.38 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 0.64 (s, 3H, Pd-CH_3), 0.57 (s, 3H, N=C-CH_3), 0.52 (s, 3H, N=C-CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 174.99 (s, N=*C*-CH_3), 169.98 (s, N=*C*-CH_3), 146.55 (s), 145.90 (s), 144.20 (s), 143.77 (s), 139.15 (s), 138.78 (s), 138.23 (s), 138.09 (s), 138.09 (s), 135.79 (s), 135.69 (s), 128.86 (s), 128.07 (s), 127.94 (s), 127.55 (s), 127.48 (s), 127.20 (s), 127.17 (s), 126.93 (s), 126.74 (s), 126.39 (s), 125.59 (s), 125.44 (s), 125.24 (s), 125.07 (s), 122.32 (s), 121.73 (s), 121.01 (s), 120.51 (s), 50.46 (s, *C*HPh_2), 50.31 (s, *C*HPh_2), 17.23 (s, *C*H_3), 16.39 (s, *C*H_3), 16.32 (s, N=C-*C*H_3), 16.28 (s, N=C-*C*H_3), 0.90 (s, Pd-*C*H_3). MALDI-TOF-MS (m/z): calcd for $C_{44}H_{38}N_4O_4Pd$: 792.1928, found: 791.2520 $[M\text{-}Cl\text{-}CH_3]^+$. Anal. Calcd for $C_{45}H_{41}ClN_4O_4Pd$: C, 64.06; H, 4.90; N, 6.64; Found: C, 63.77; H, 4.73; N, 6.49.

(MeN^N)NapPdMeCl (5). Yield 67 % (0.588 g). Orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 14.0, 8.3 Hz, 2H, aryl-*H*), 7.39 (d, J = 6.9 Hz, 2H, aryl-*H*), 7.24 (d, J = 8.2 Hz, 5H, aryl-*H*), 7.17 (dd, J = 14.4, 7.0 Hz, 4H, aryl-*H*), 7.12 – 7.04 (m, 3H, aryl-*H*), 6.98 (dd, J = 19.2, 7.0 Hz, 4H, aryl-*H*), 6.83 (s, 1H, aryl-*H*), 6.70 (s, 1H, aryl-*H*), 6.53 (s, 1H, aryl-*H*), 6.31 (d, J = 5.8 Hz, 4H, aryl-*H*), 6.23 (s, 1H, aryl-*H*), 6.11 (d, J = 6.9 Hz, 1H, aryl-*H*), 6.03 (s, 2H, C*H*Ph_2), 2.42 (s, 6H, CH_3), 2.36 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 1.05 (s, 3H, Pd-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.64 (s, N=*C*), 168.91 (s, N=*C*), 143.26 (s), 143.10 (s), 142.22 (s), 141.68 (s), 141.26 (s), 140.71 (s), 140.48 (s), 137.01 (s), 136.52 (s), 136.18 (s), 135.87 (s), 130.27 (s), 130.07 (s), 130.03 (s), 129.93 (s), 129.89 (s), 129.77 (s), 129.57 (s), 129.54 (s), 129.14 (s), 128.90 (s), 128.43 (s), 128.20 (s), 127.98 (s), 127.72 (s), 127.66 (s), 127.45 (s), 127.42 (s), 126.49 (s), 126.07 (s), 125.93 (s), 125.53 (s), 125.31 (s), 124.97 (s), 123.95 (s), 123.92 (s), 52.60 (s, *C*HPh_2), 52.31 (s, *C*HPh_2), 21.48 (s, *C*H_3), 21.45 (s, *C*H_3), 18.26

(s, *C*H_3), 18.03 (s, *C*H_3), 3.60 (s, Pd-*C*H_3). MALDI-TOF-MS (m/z): calcd for $C_{54}H_{44}N_2Pd$: 826.2639, found: 826.2083 $[M\text{-}Cl\text{-}CH_3]^+$. Anal. Calcd for $C_{55}H_{47}ClN_2Pd$: C, 75.25; H, 5.40; N, 3.19; Found: C, 74.99; H, 5.46; N, 3.18.

Standard Procedure for the Synthesis of Complexes 6-7.

The mixture of ligand (1 mmol), DMENiBr_2 (308 mg, 1 mmol) and CH_2Cl_2 (20 mL) was stirred overnight at room temperature. During stirring, the color of the solution was changed from yellow to red and some solid precipitated. The desired compound can be isolated from recrystallization from diethylether and dichloromethane. The pure compound was obtained as an red solid.

(MeN^N)NiBr_2 (6) Yield 72 % (0.605 g). Red solid. MALDI-TOF-MS (m/z): calcd for $C_{46}H_{44}BrN_2Ni$: 761.2041; 763.2021, found: 760.9582; 762.9939 $[M\text{-}Br]^+$. Anal. Calcd for $C_{46}H_{44}Br_2N_2Ni$: C, 65.51; H, 5.26; N, 3.32; Found: C, 65.46; H, 5.45; N, 3.15.

(MeN^N)NapNiBr_2 (7) Yield 80 % (0.751 g). Red solid. MALDI-TOF-MS (m/z): calcd for $C_{54}H_{44}BrN_2Ni$: 857.2041; 859.2021, found: 856.8847; 858.9317 $[M\text{-}Br]^+$. Anal. Calcd for $C_{54}H_{44}Br_2N_2Ni$: C, 69.04; H, 4.72; N, 2.98; Found: C, 69.29; H, 4.56; N, 3.08.

General in-Situ-Activated Polymerization Procedure by palladium complexes. Under an inert atmosphere, a Fisher Porter bottle was charged with NaBAF, 43 mL of toluene, and a magnetic stir bar. The bottle was sealed and placed in an oil bath at the desired temperature. The vessel was pressurized with ethylene and allowed to equilibrate under constant pressure for 10 minutes with stirring. The palladium catalyst was injected to initiate the polymerization. The polymerization was quenched via the addition of MeOH (5 mL) and the polymer was precipitated using excess acidic MeOH (5% HCl in MeOH) and dried in a vacuum oven to constant weight.

Procedure for ethylene polymerization by nickel complexes. In a typical experiment, a 350 mL thick-walled glass pressure vessel was charged with the required amount of MAO (600 eq), toluene (100 mL) and a magnetic stirrer bar in the glovebox. The pressure vessel was connected to a high pressure polymerization line and the solution was degassed. The vessel was warmed to 30 ^oC by using an oil bath and allowed to equilibrate for 5 min. The nickel complex (3 mmol) in CH_2Cl_2 (2 mL) was injected into the vessel with a syringe. With rapid stirring, the reactor was pressurized and maintained at 9.0 atm of ethylene. After 0.5 h, the vessel was vented and the polymer was precipitated in acidified methanol (methanol/HCl = 50:1) and dried at 50 ^oC for 24 h under vacuum.

Copolymerization of Ethylene and MA. In a typical procedure, a 100 mL round-bottom Schlenk flask with a stirring bar was heated for 3 h to 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 15 psi of ethylene and vented three times. The appropriate toluene solvent, MA and NaBAF were introduced into the glass reactor under an ethylene atmosphere, then a 2 mL solution of the palladium catalyst (10 μmol) in CH_2Cl_2 was syringed into the well-stirred solution and the total reaction volume was kept at 45 mL. The ethylene pressure was kept at a constant value of 15 psi by continuous feeding of gaseous ethylene throughout the reaction. The polymerization was terminated by the addition of a large amount of methanol after continuous stirring for 12 h. Then the methanol was decanted off, and the sticky polymer was redissolved in hot toluene. The polymer solution was filtered through alumina or silica to remove catalyst residues. After evaporation, the resulting polymer was collected and dried under vacuum at 40 °C to a constant weight. The MA incorporation (mol %) was calculated from ^{1}H NMR analysis, as was done before in previous studies of MA copolymers.

X-ray crystallography. Single crystals of complexes **2**, **5** and **6** suitable for X-ray structure determination were grown from slow diffusion of n-hexane into a concentrated dichloromethane solution at room temperature in a glove box. The crystallographic data are summarized in Table S1-S16. Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal structures were solved using SHELXS-97[1] and refined against F2 by full-matrix least squares using SHELXL-97.[2] The positions of hydrogen atoms were placed in the calculated positions.

Mechanical properties of the polyethylene sample.

Standard test method ASTM 638 was followed to measure the mechanical properties of the polyethylene sample. Polymers were melt-pressed at 30 to 35°C above their melting point to obtain the test specimens. The test specimens had 28-mm gauge length, 3-mm width, and thickness of 1 mm. Stress/strain experiments were performed at 10 m/min by means of a Universal Test Machine (UTM2502) at room temperature. At least five specimens of each copolymer were tested.

Sample preparation for water contact angle. A round-bottom glass (20 ml) was charged with the polyethylene or E-MA copolymer (100 mg) and toluene (10 ml). After the mixture was heated at 60 °C for 30 min, the solution was added dropwise onto a glass slide. The sample was dried in air for one day.

Hydrolyzation of E-MA copolymer. A round-bottom glass (100 ml) was charged with E-MA copolymer (100 mg, sample from Table 2, entry 2), THF (50 ml) and NaOH solution (20 ml, 2M). The mixture was refluxed for 10 hours. The mixture was

filtered, yielding a cream like residue. Ethanol (10 ml) was added to the residue and stirred for 30 min. The solution was added dropwise to a glass slide, and dried in air for one day.

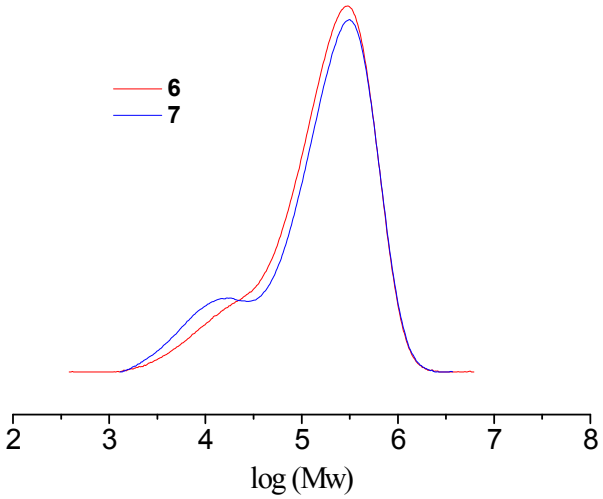

Figure S1. GPC traces for the polymers generated from catalyst 6 and 7 at 30 °C.

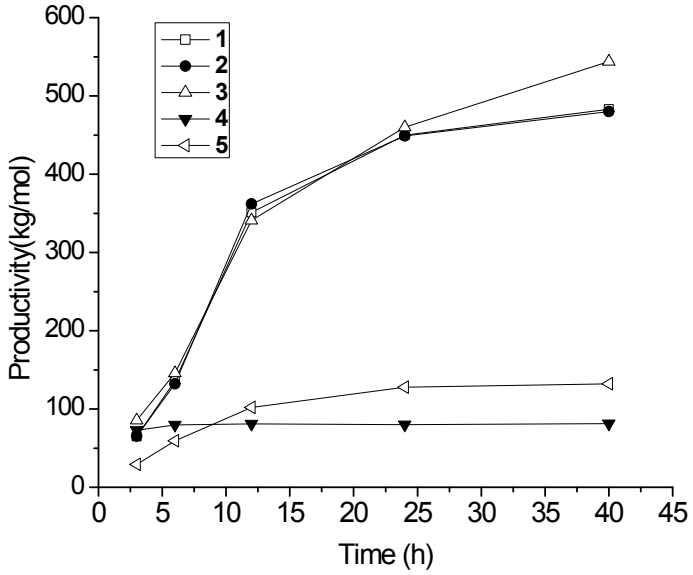

Figure S2. Productivity versus time for complexes 1-5 at room temperature.

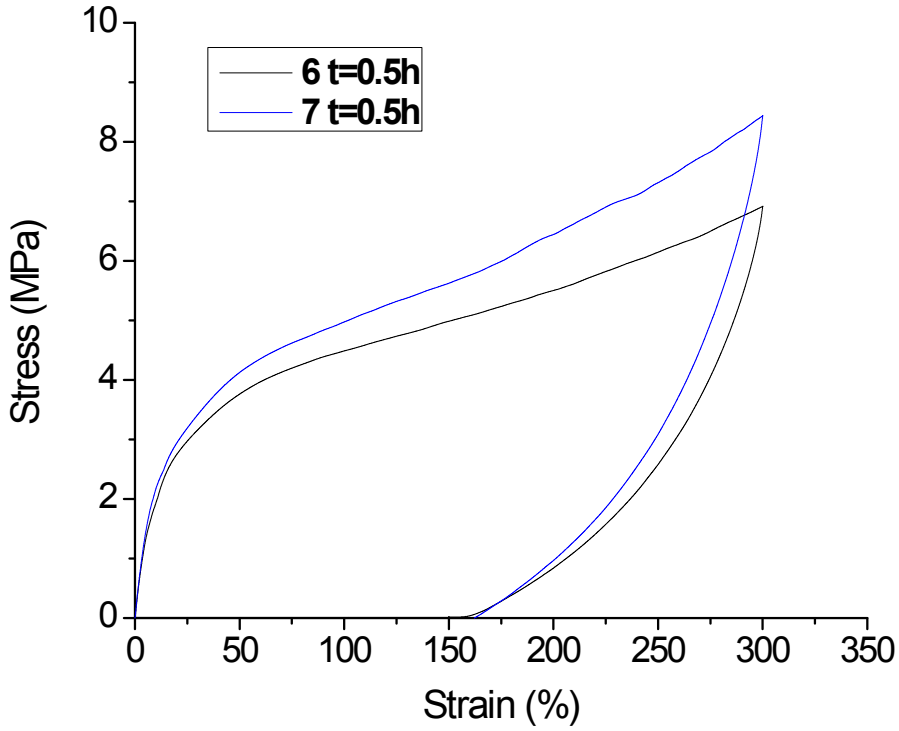

Figure S3. Stress−strain recovery tests of polyethylene generated using complexes 6 and 7 (samples from Table 1, entries 12 and 13).

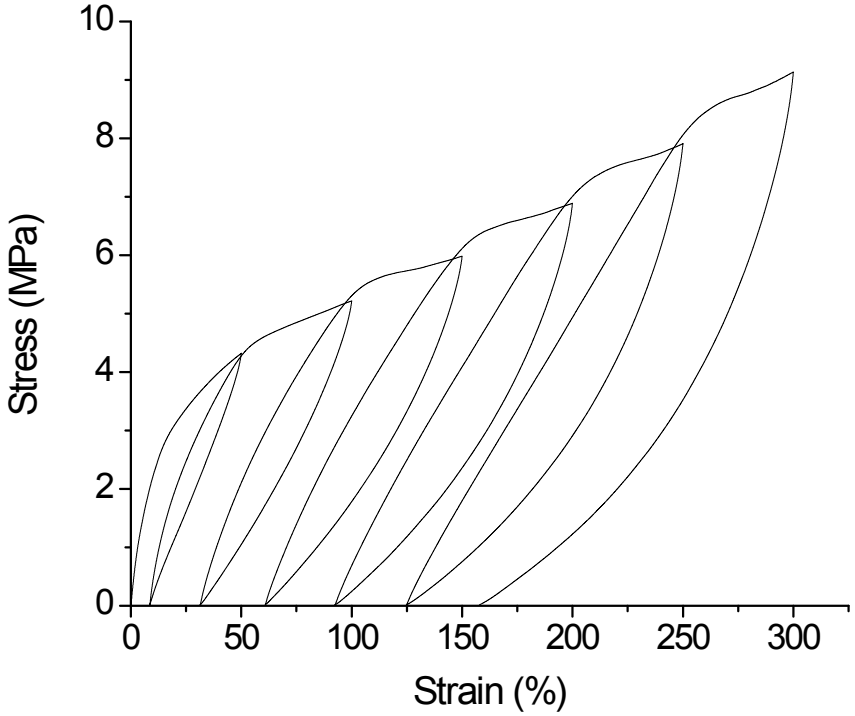

Figure S4. Step-cycle stress−strain curve for polyethylene generated using complexes 6 (samples from Table 1, entrys 12).

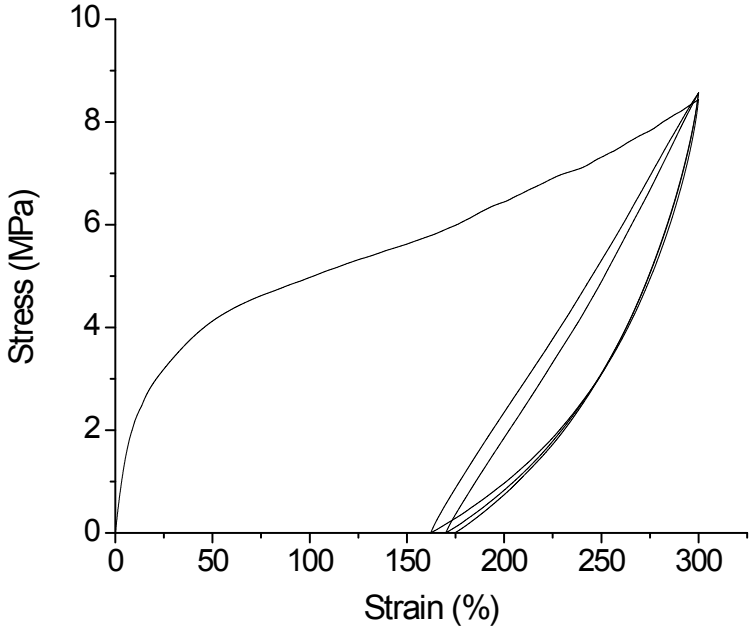

Figure S5. Cyclic tensile tests for polyethylene generated using complexes 6 (samples from Table 1, entry 12). The sample was cyclically tested for 3 cycles with a maximum strain of 300 %

^{1}H NMR, ^{13}C NMR of Amine.

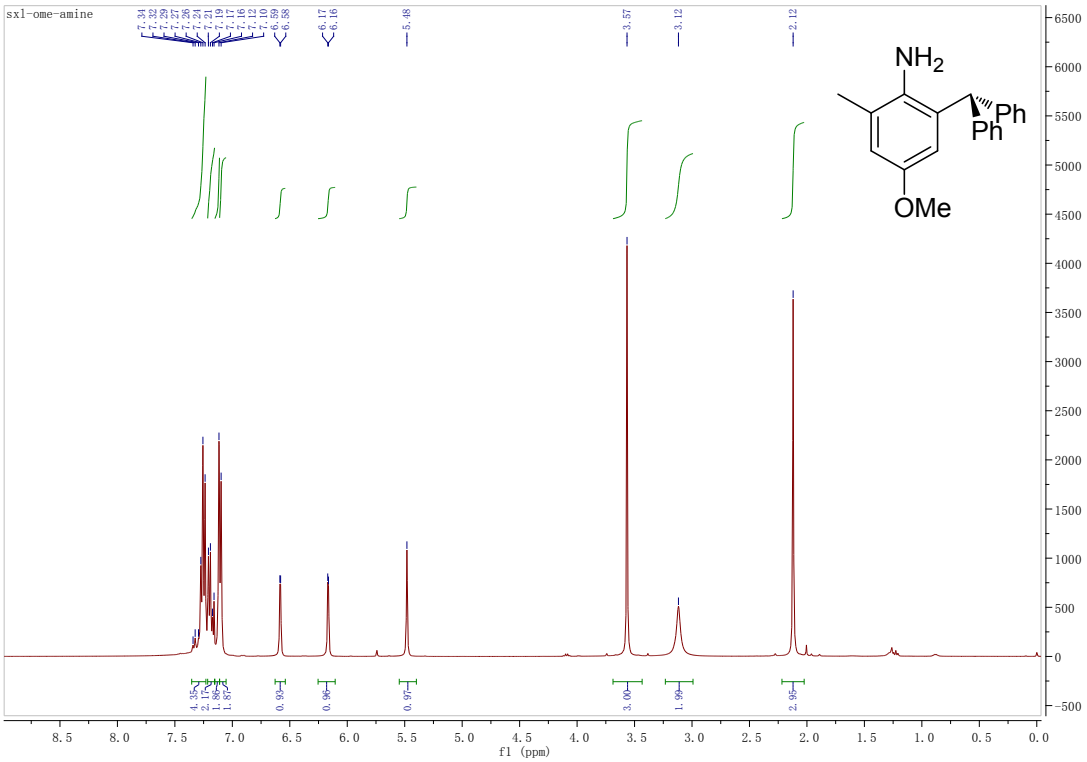

Figure S6. ^{1}H NMR spectrum of **Amine-OMe** in $CDCl_3$.

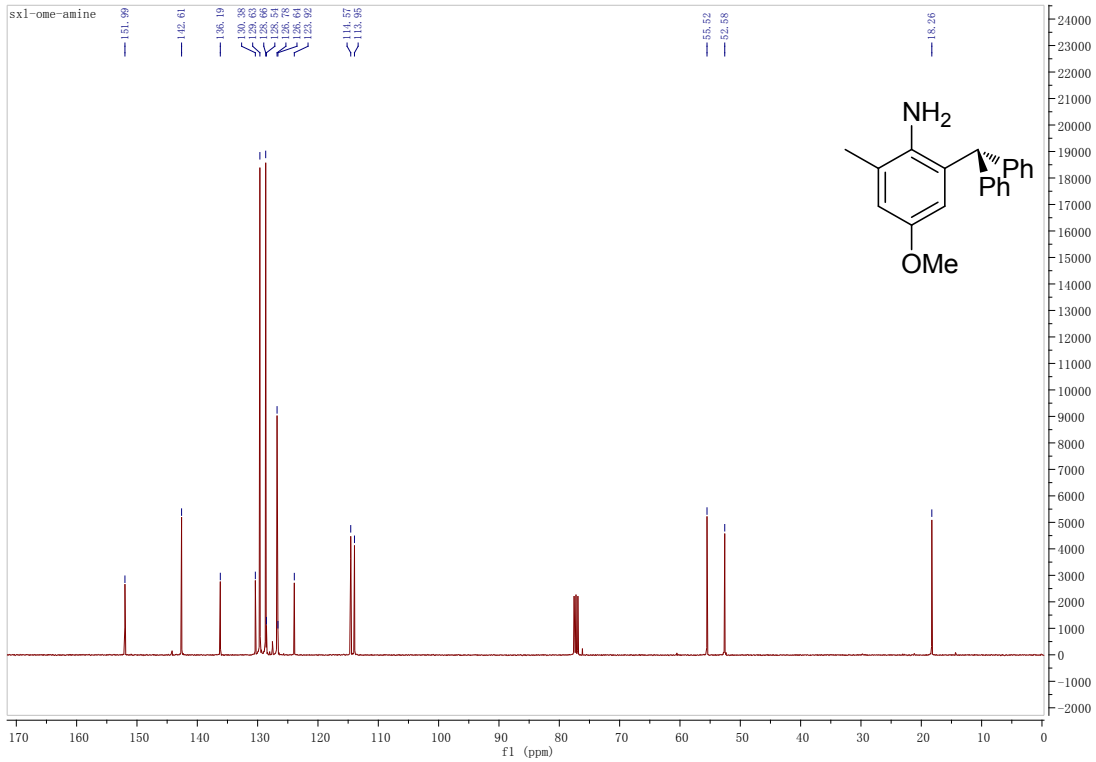

Figure S7. ^{13}C NMR spectrum of **Amine-OMe** in $CDCl_3$.

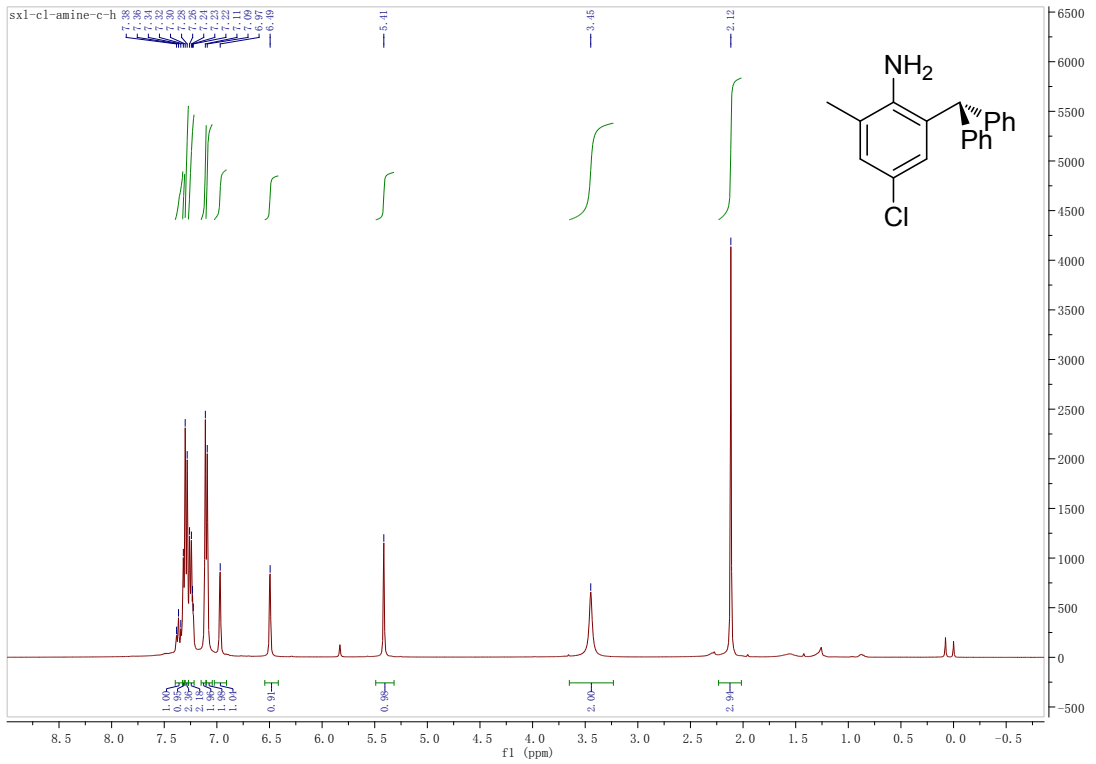

Figure S8. ^{1}H NMR spectrum of **Amine-Cl** in $CDCl_3$.

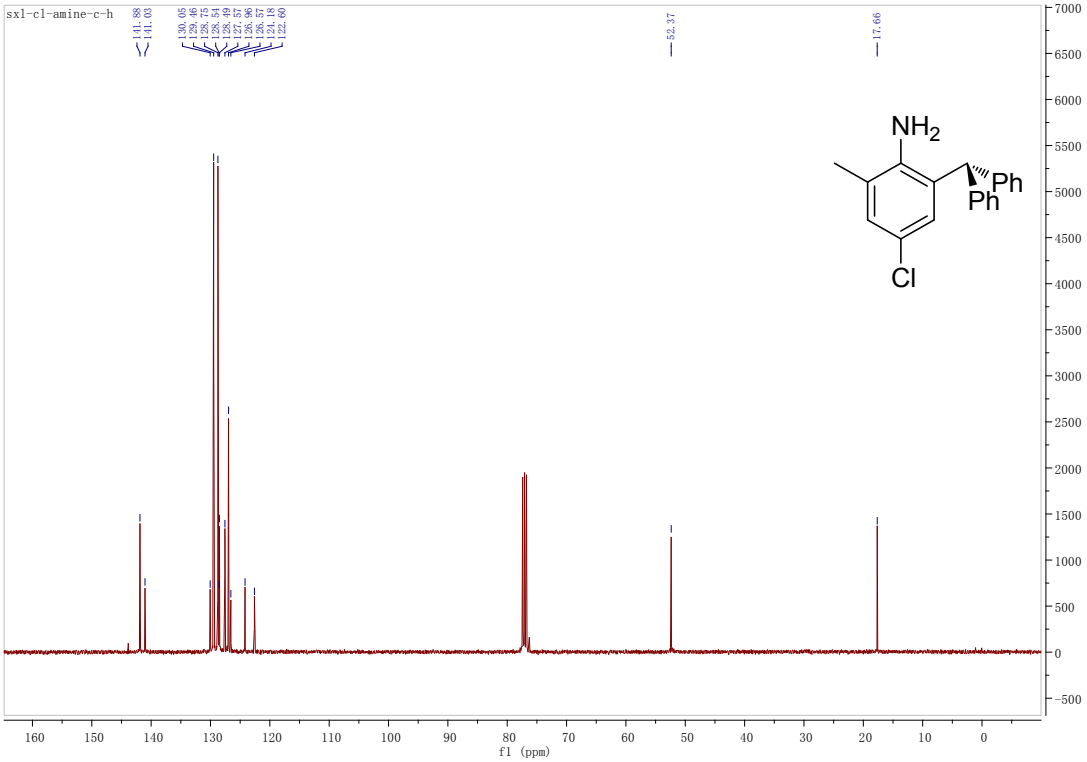

Figure S9. ^{13}C NMR spectrum of **Amine-Cl** in $CDCl_3$.

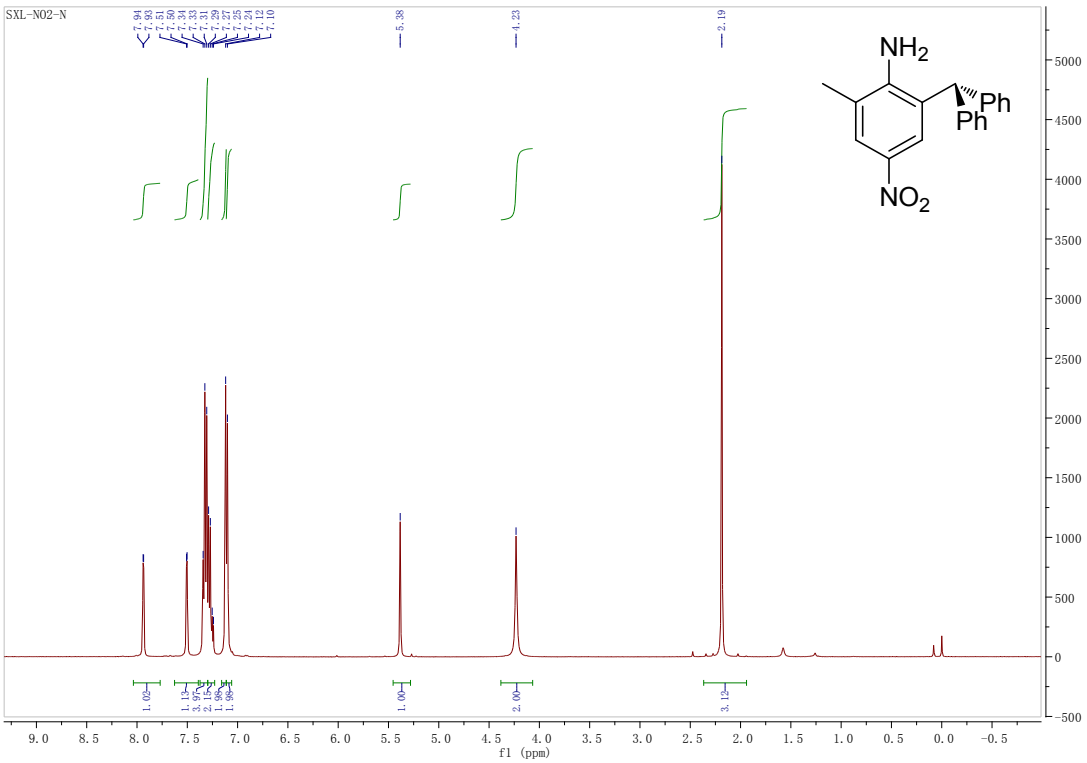

Figure S10. ^{1}H NMR spectrum of **Amine-NO_2** in $CDCl_3$.

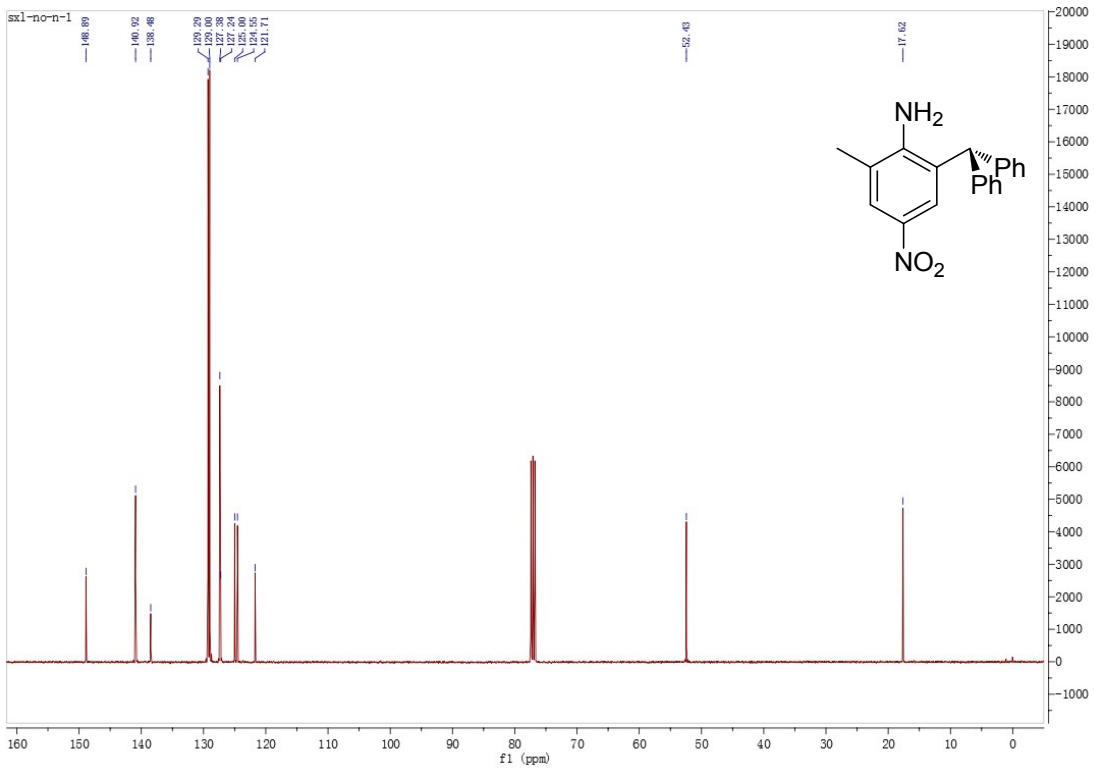

Figure S11. ^{13}C NMR spectrum of **Amine-NO$_2$** in $CDCl_3$.

^{1}H NMR, ^{13}C NMR of Ligand.

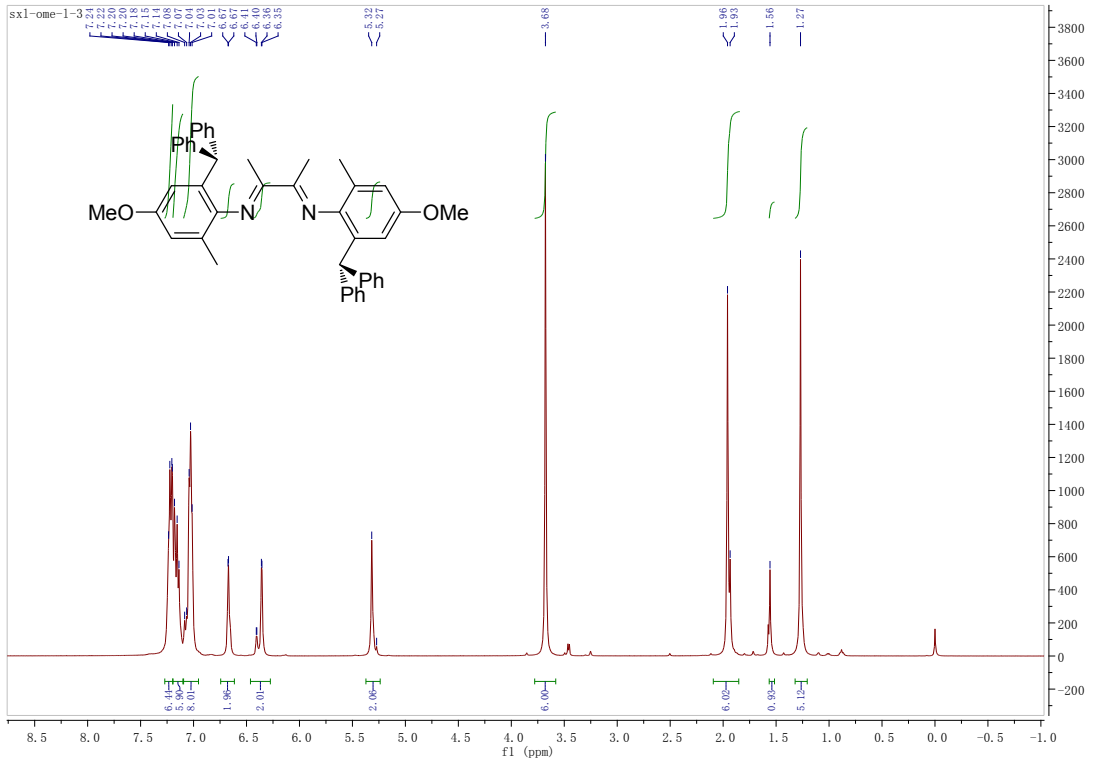

Figure S12. ^{1}H NMR spectrum of **Ligand-1** in $CDCl_3$.

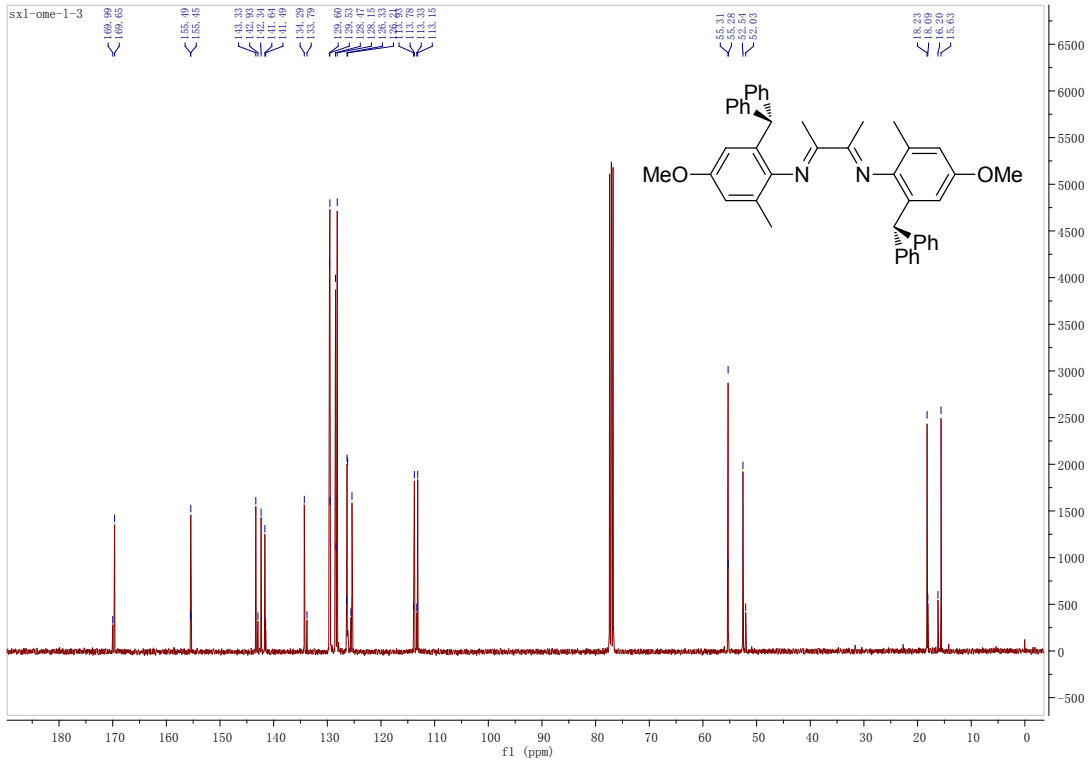

Figure S13. ^{13}C NMR spectrum of **Ligand-1** in $CDCl_3$.

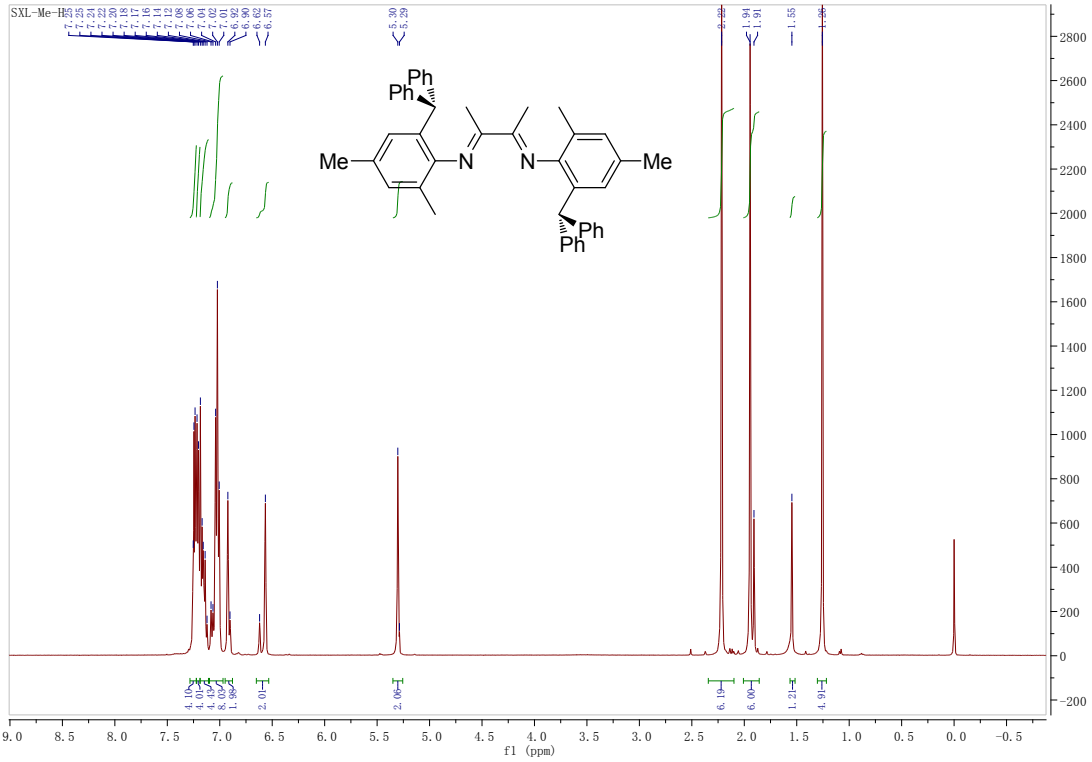

Figure S14. ^{1}H NMR spectrum of **Ligand-2** in $CDCl_3$.

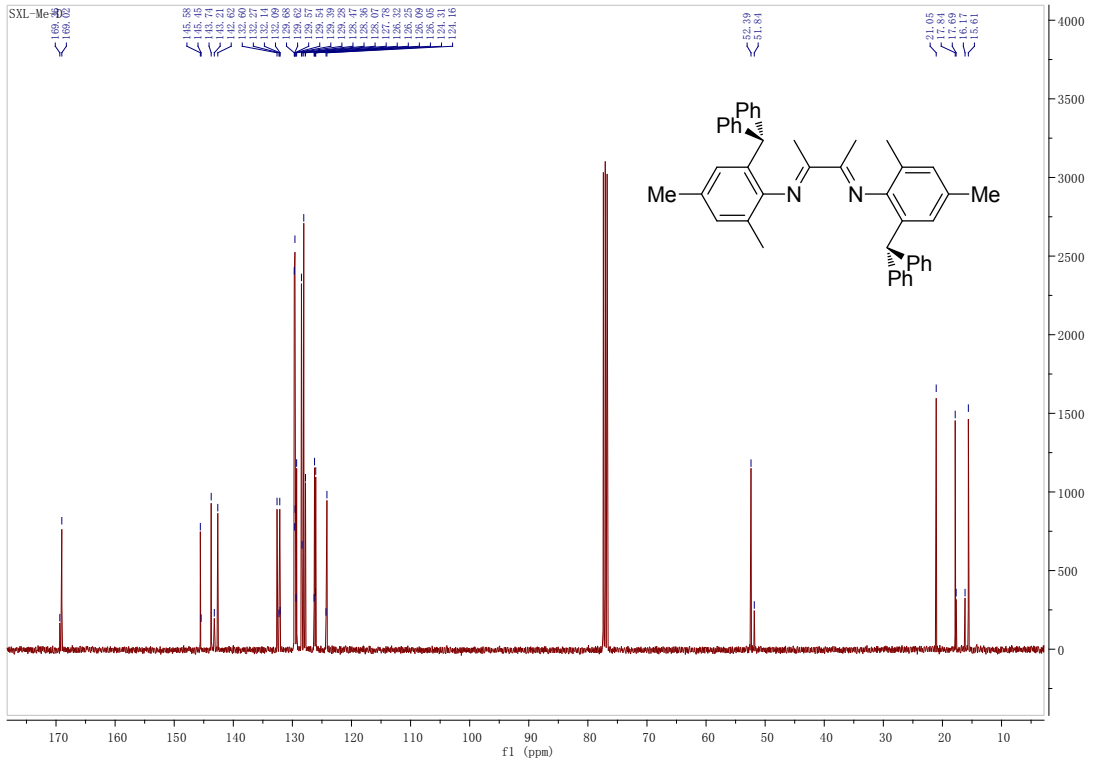

Figure S15. ^{13}C NMR spectrum of **Ligand-2** in $CDCl_3$.

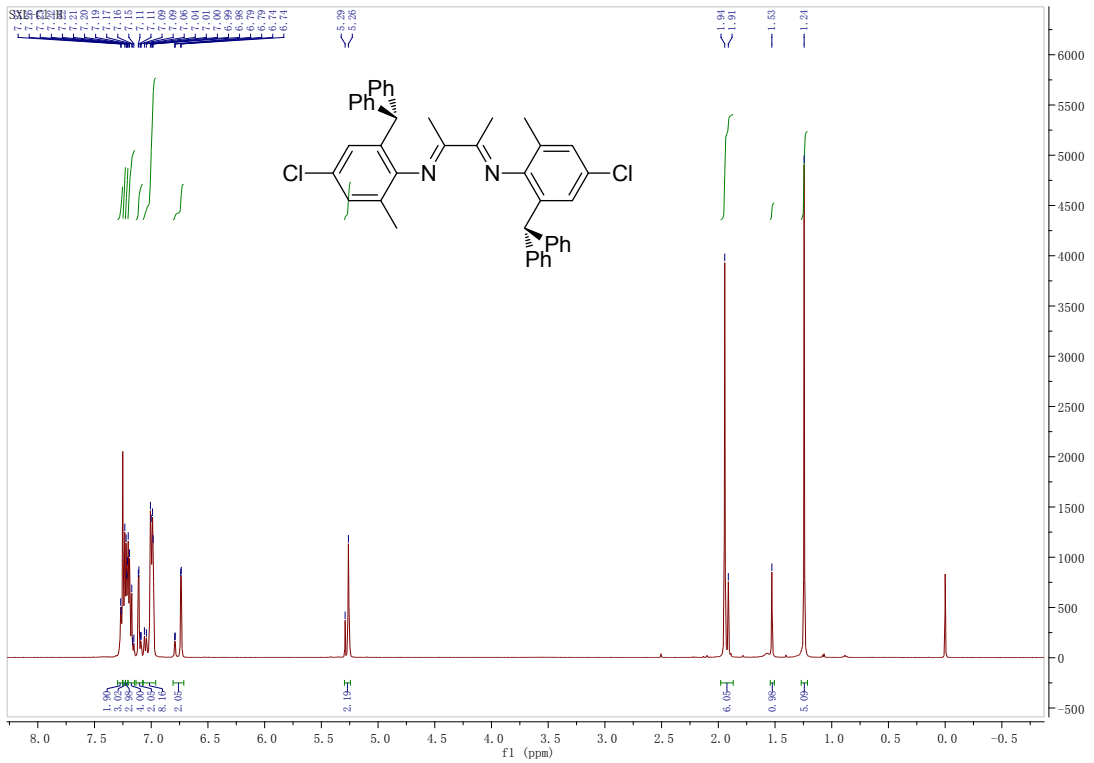

Figure S16. ^{1}H NMR spectrum of **Ligand-3** in $CDCl_3$.

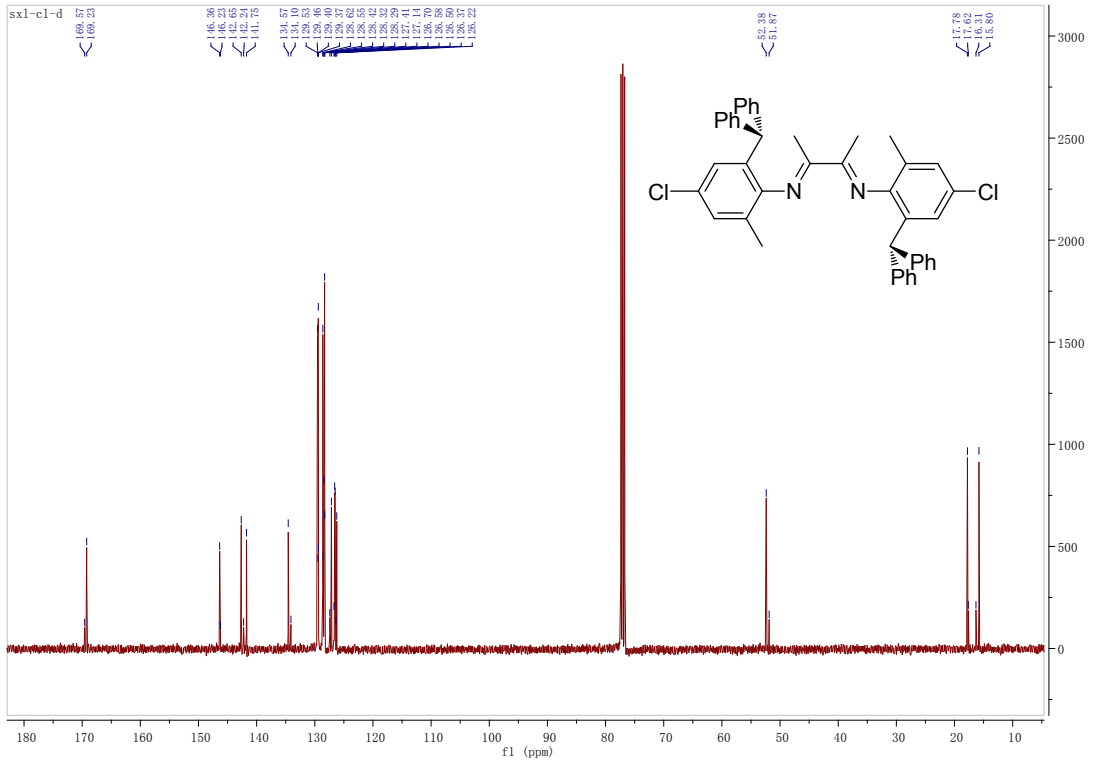

Figure S17. ^{13}C NMR spectrum of **Ligand-3** in $CDCl_3$.

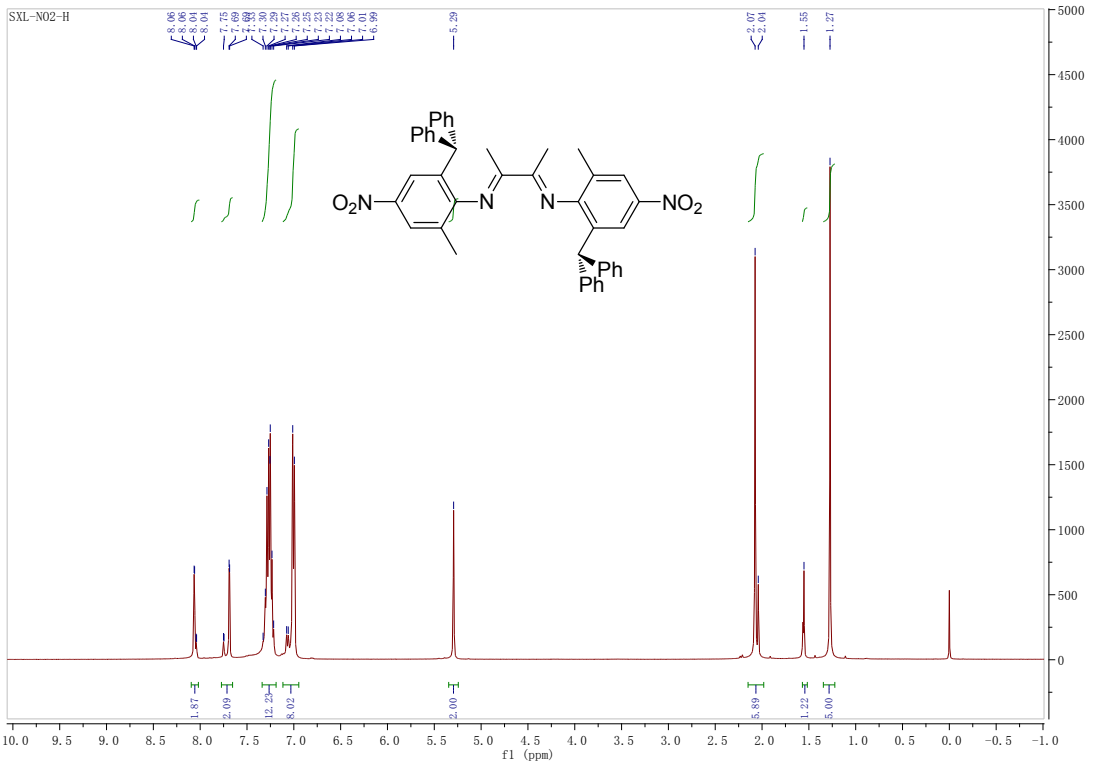

Figure S18. ^{1}H NMR spectrum of **Ligand-4** in $CDCl_3$.

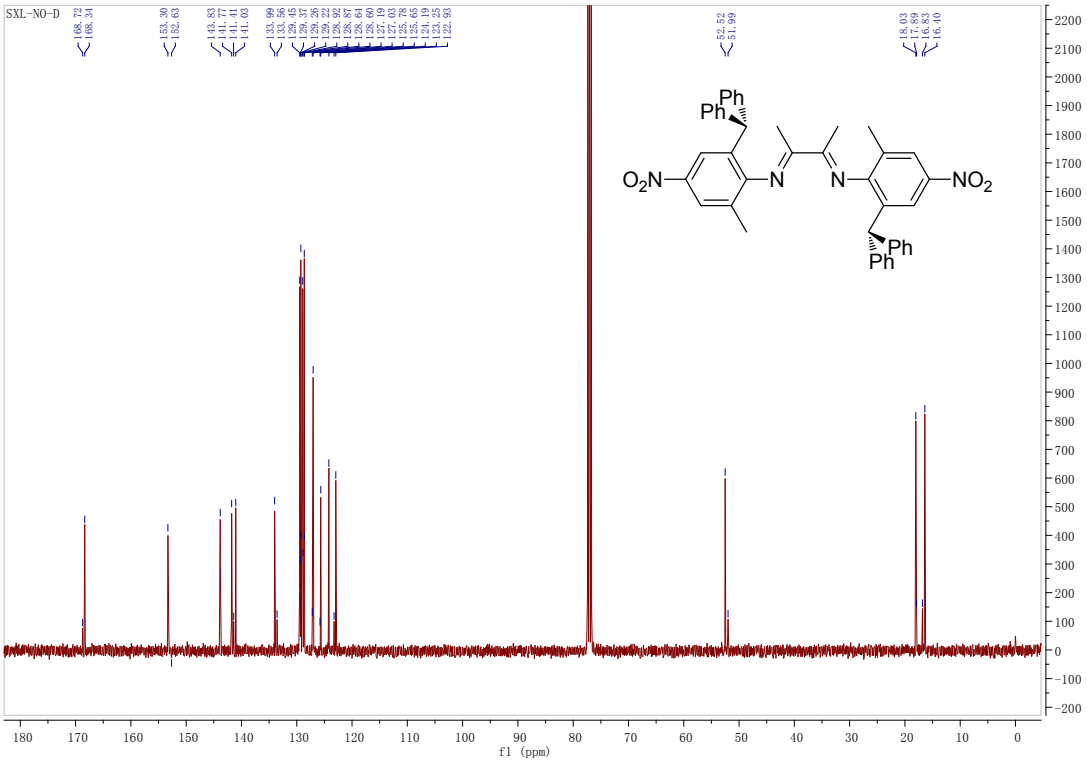

Figure S19. ^{13}C NMR spectrum of **Ligand-4** in $CDCl_3$.

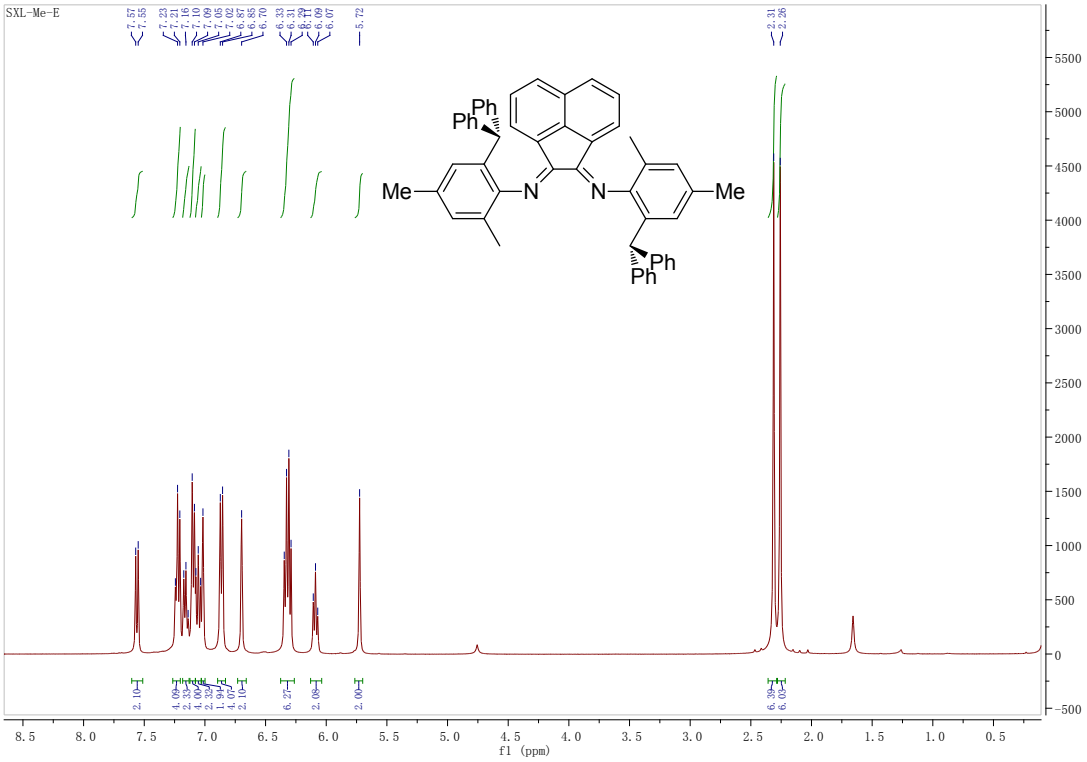

Figure S20. ^{1}H NMR spectrum of **Ligand-5** in $CDCl_3$.

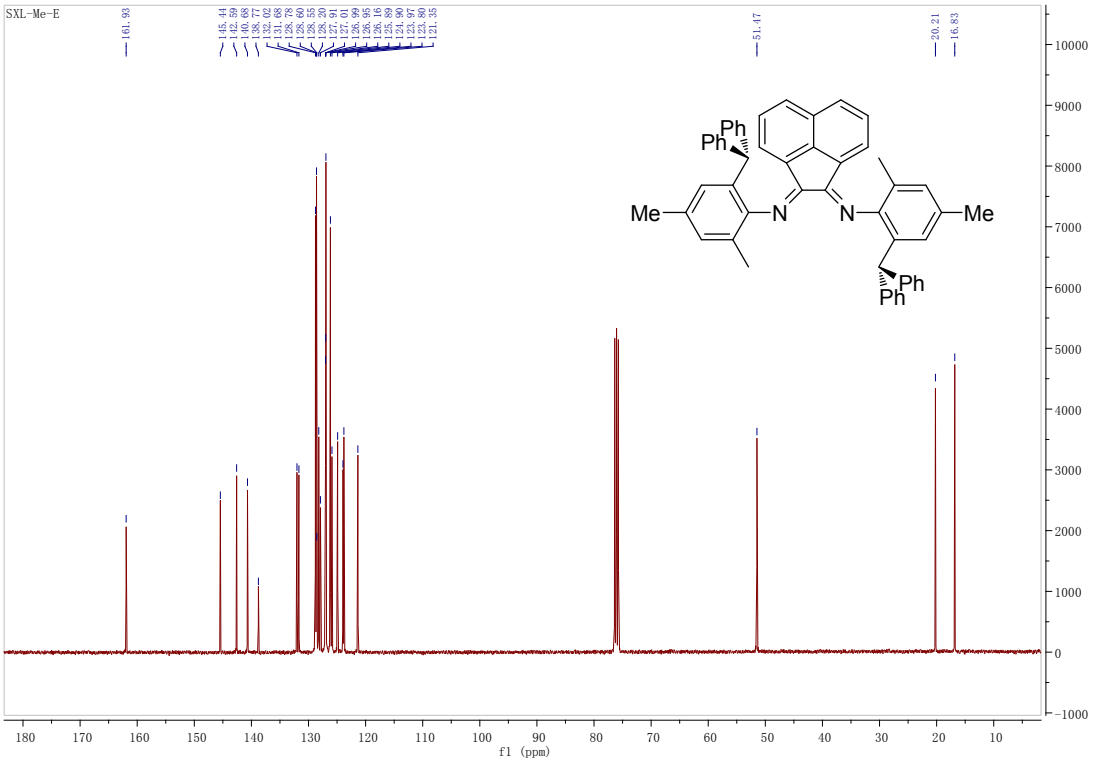

Figure S21. ^{13}C NMR spectrum of **Ligand-5** in $CDCl_3$.

^{1}H NMR, ^{13}C NMR of Complex.

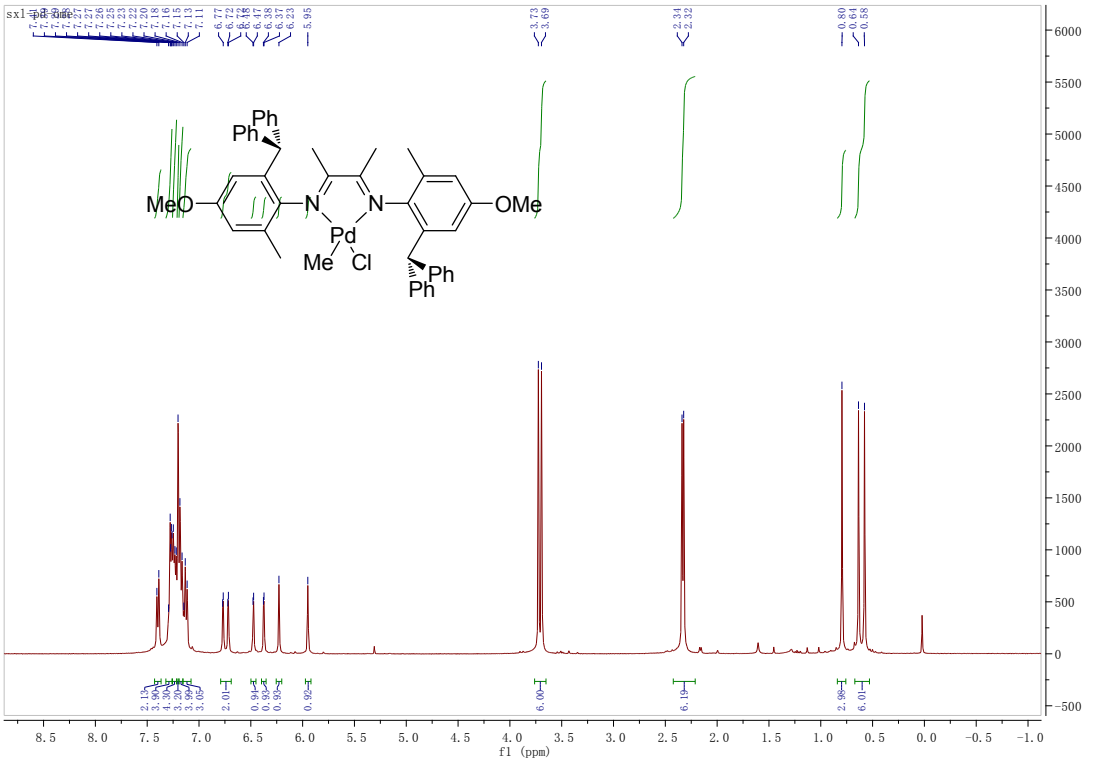

Figure S22. ^{1}H NMR spectrum of **Complex-1** in $CDCl_3$.

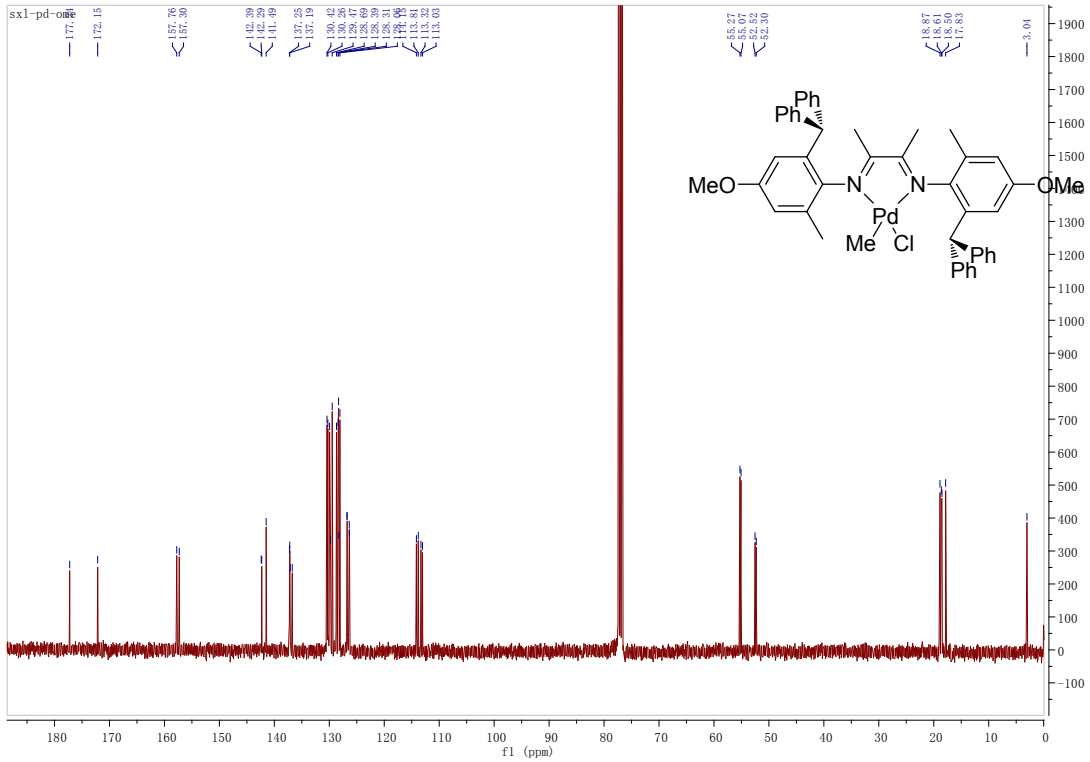

Figure S23. ^{13}C NMR spectrum of **Complex-1** in $CDCl_3$.

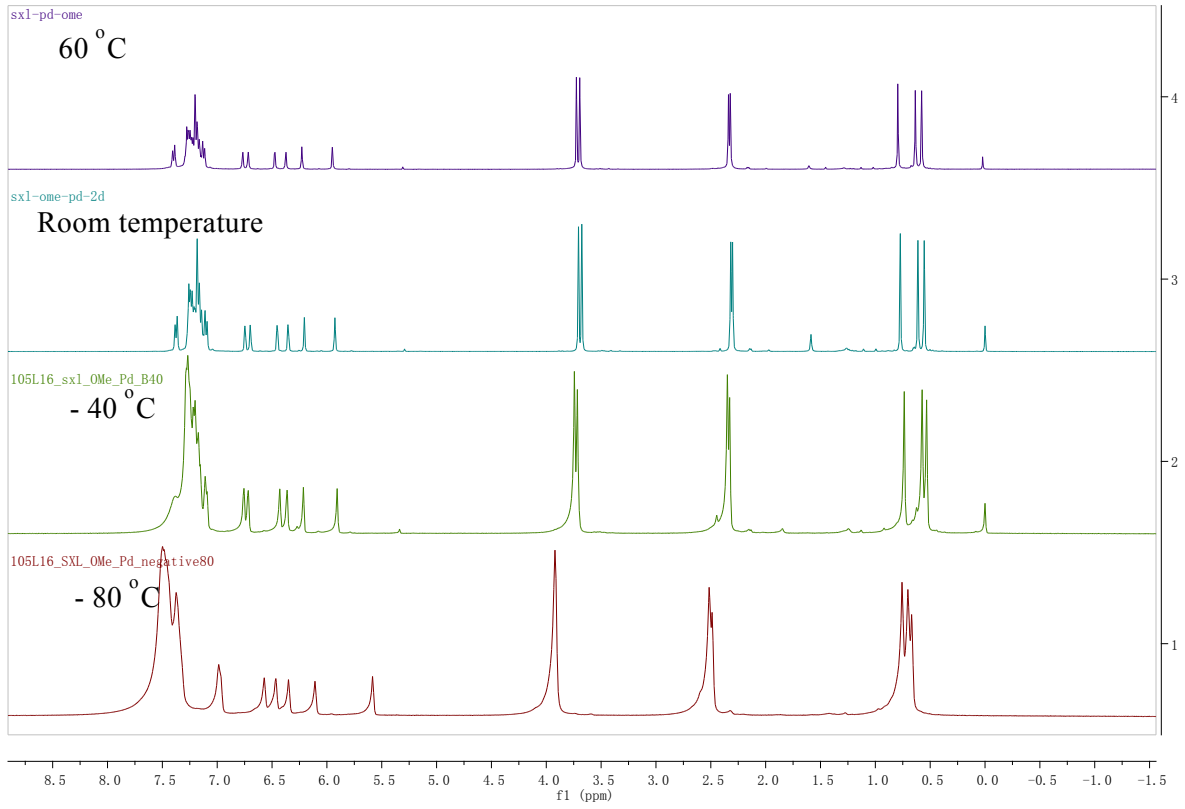

Figure S24. ^{1}H NMR spectrum of **Complex-1** in $CDCl_3$ at 60 °C, room temperature, -40 °C and -80 °C.

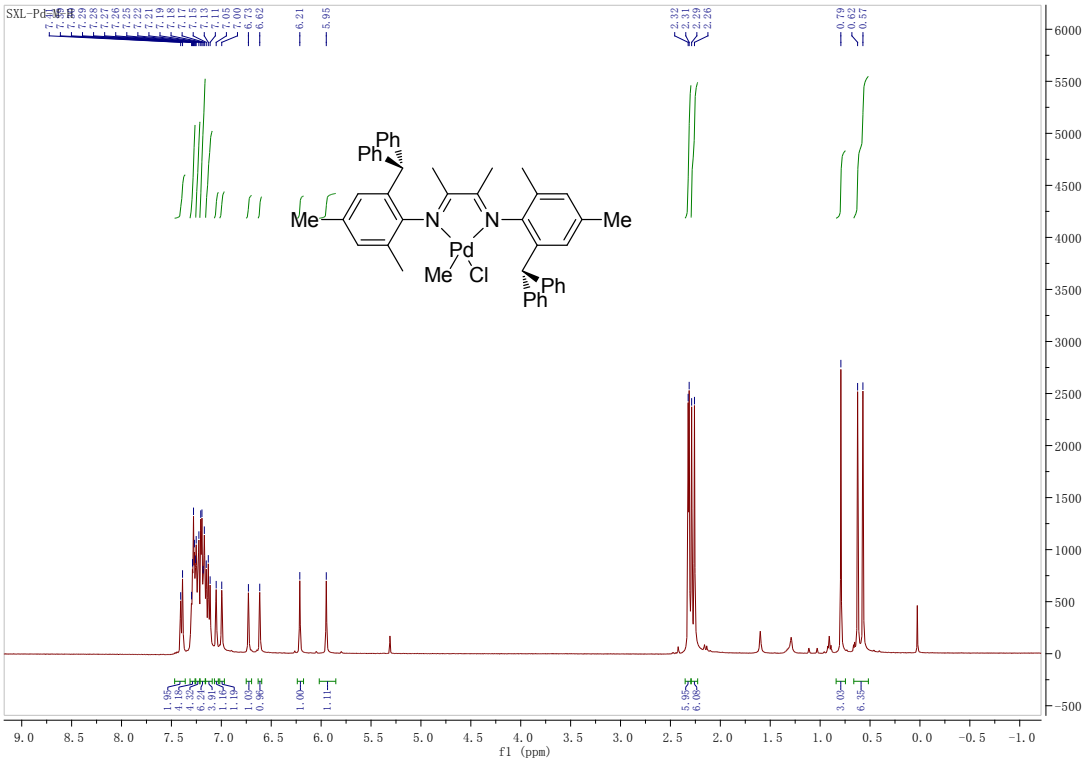

Figure S25. ^{1}H NMR spectrum of **Complex-2** in $CDCl_3$.

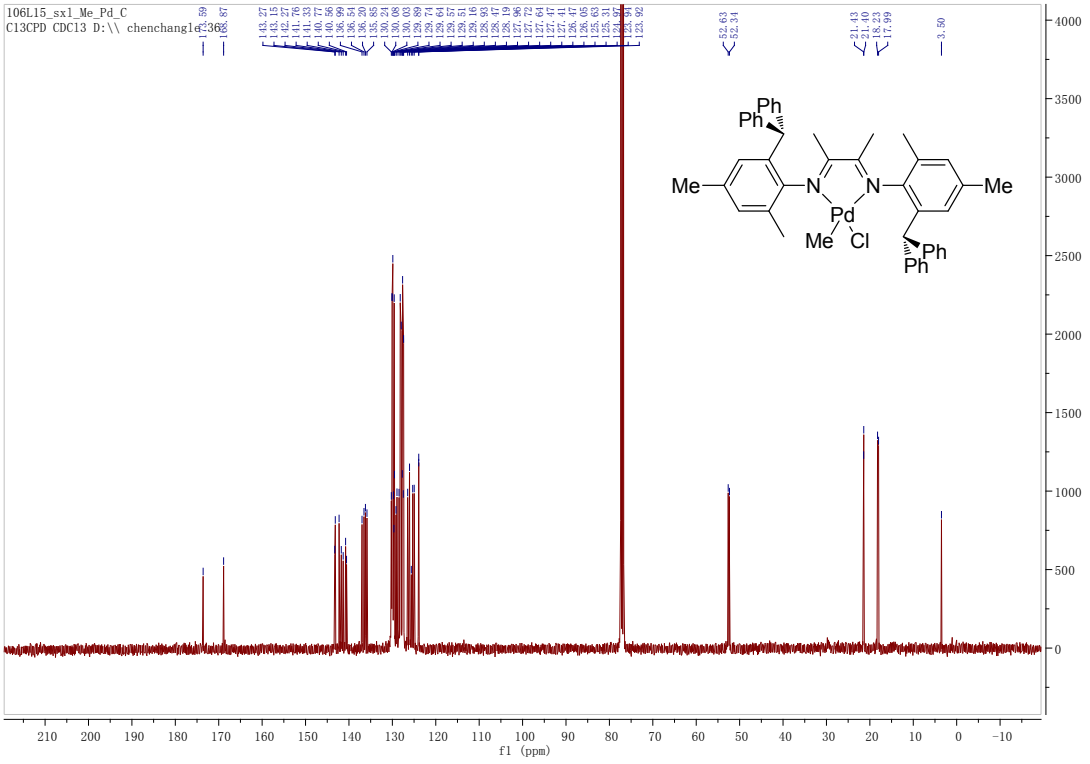

Figure S26. ^{13}C NMR spectrum of **Complex-2** in $CDCl_3$.

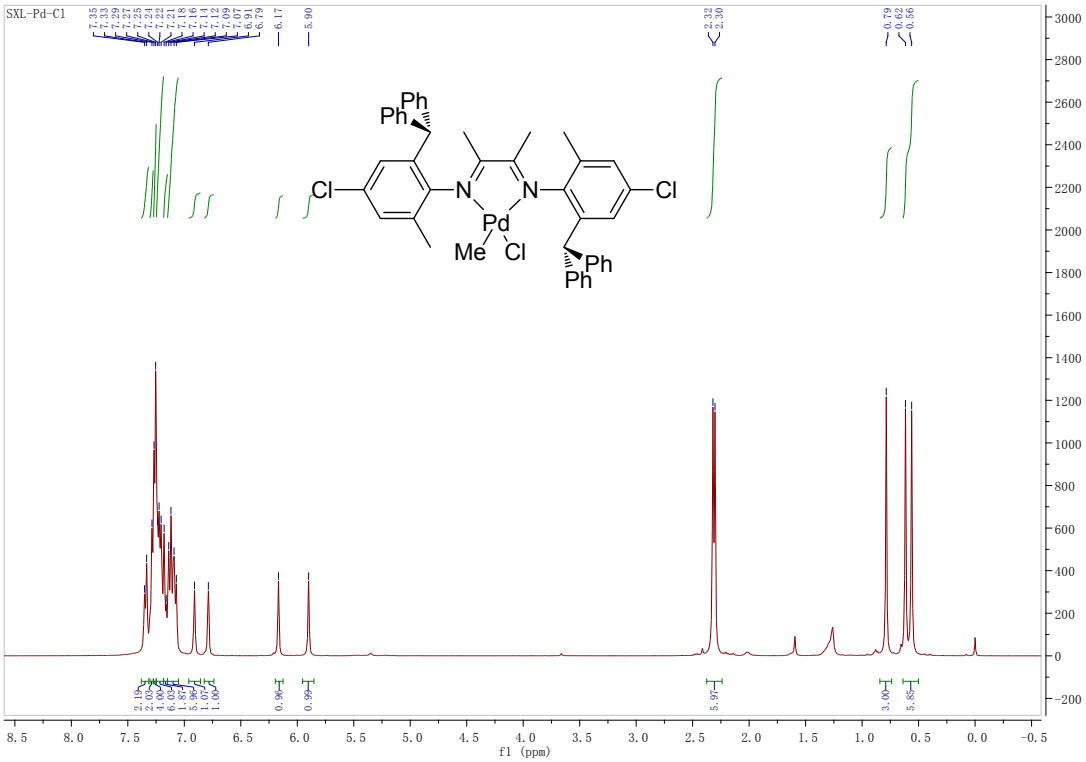

Figure S27. ^{1}H NMR spectrum of **Complex-3** in $CDCl_3$.

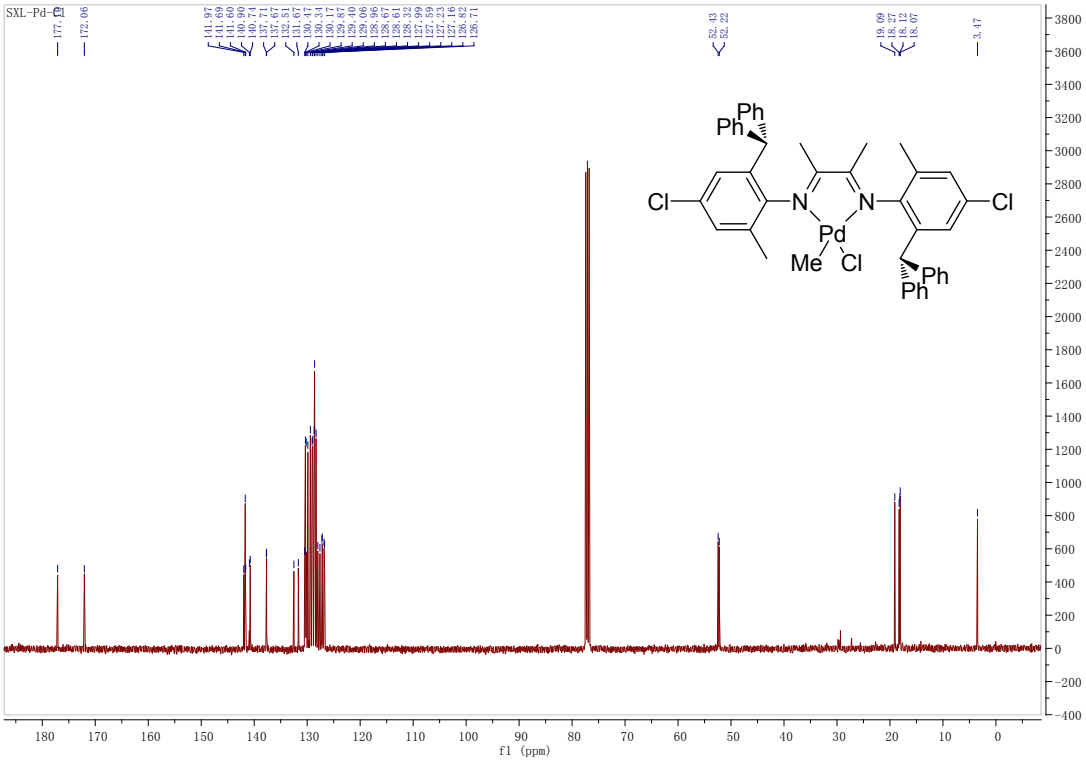

Figure S28. ^{13}C NMR spectrum of **Complex-3** in $CDCl_3$.

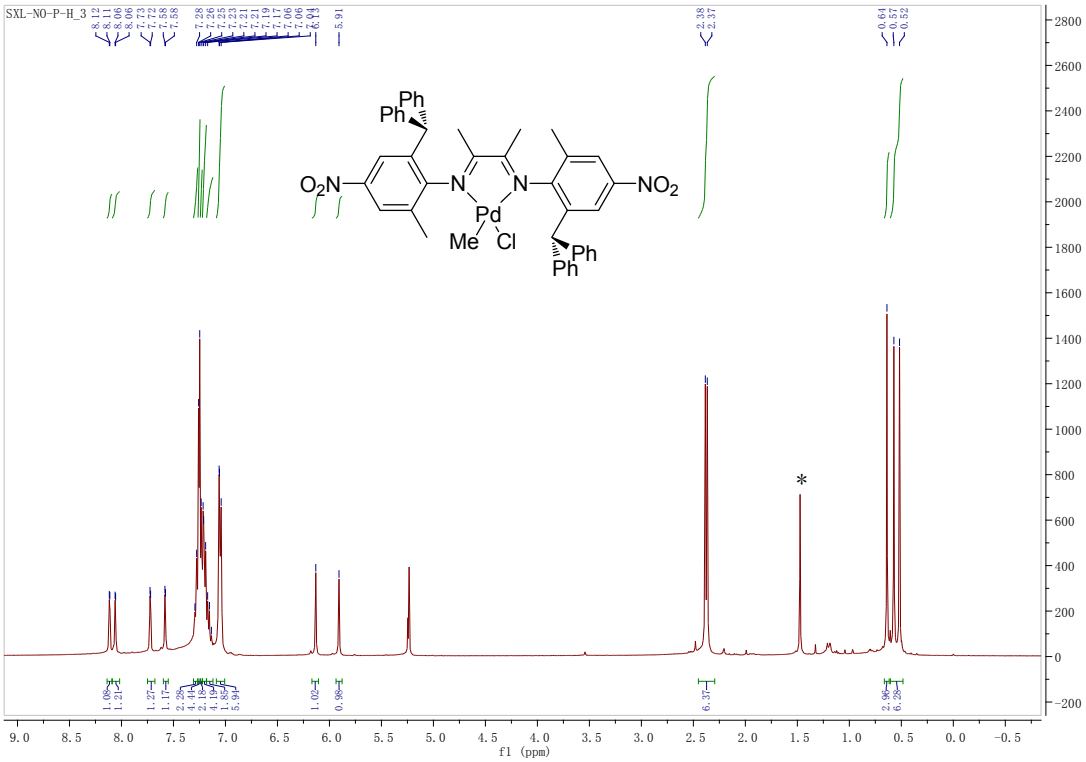

Figure S29. ^{1}H NMR spectrum of **Complex-4** in CD_2Cl_2. *H_2O.

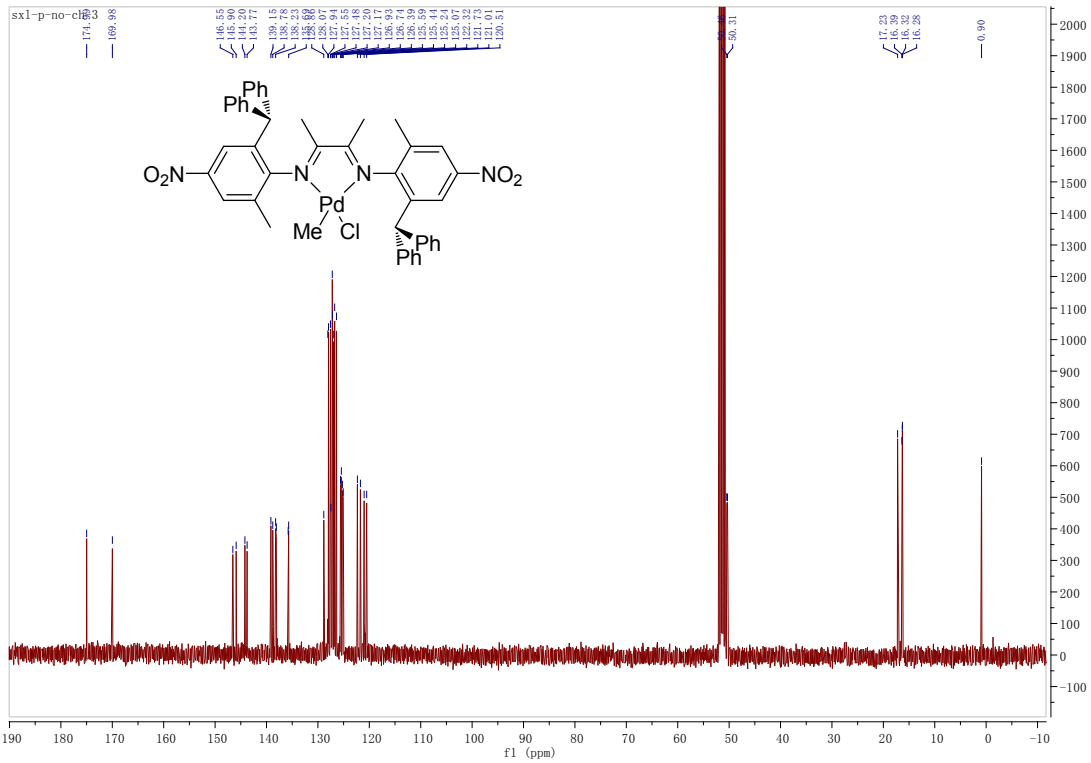

Figure S30. ^{13}C NMR spectrum of **Complex-4** in CD_2Cl_2.

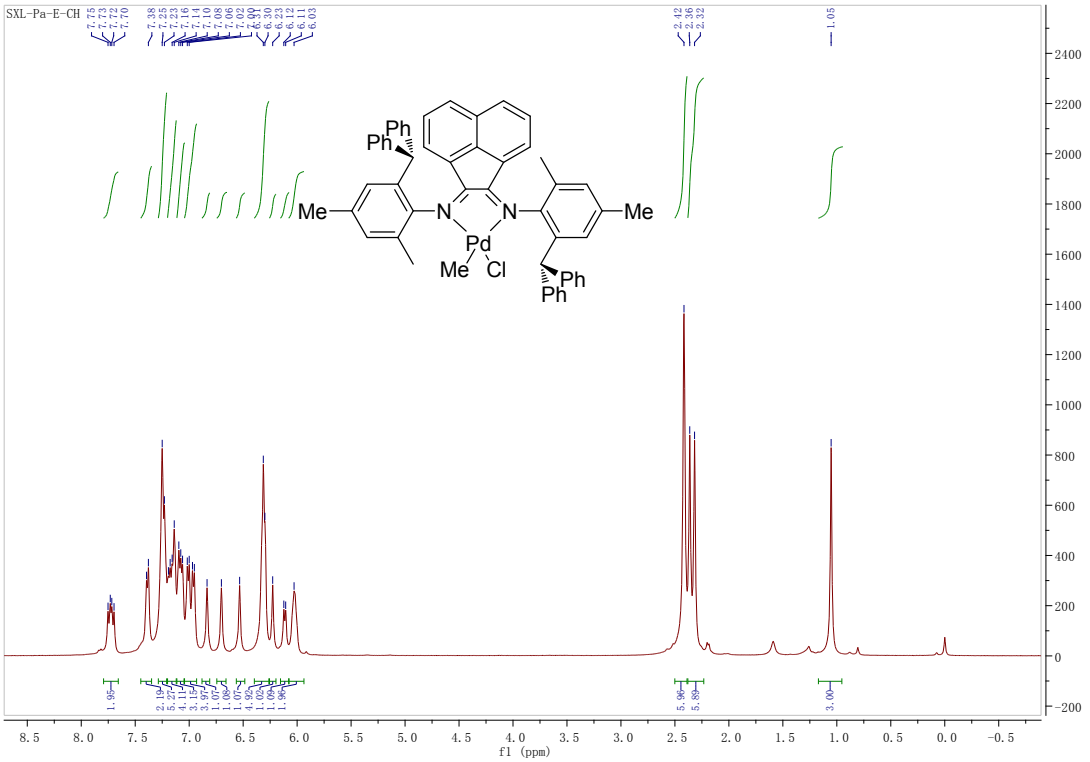

Figure S31. ^{1}H NMR spectrum of **Complex-5**in $CDCl_3$.

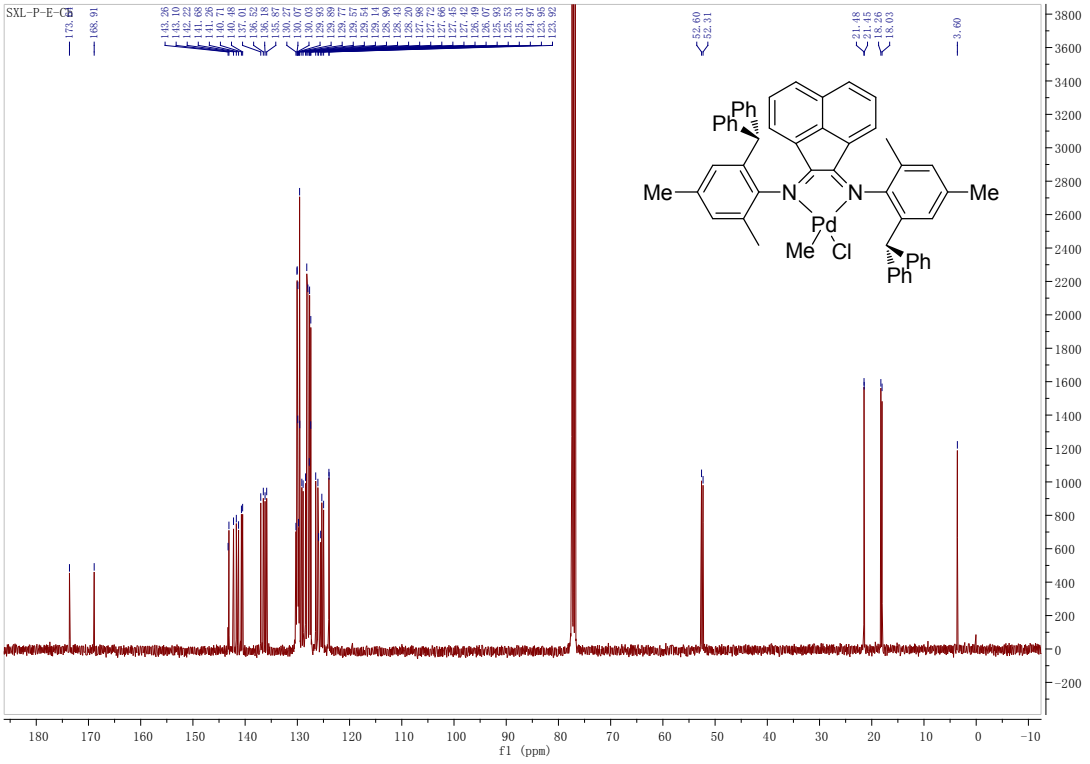

Figure S32. ^{13}C NMR spectrum of **Complex-5** in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of polymer and copolymer.

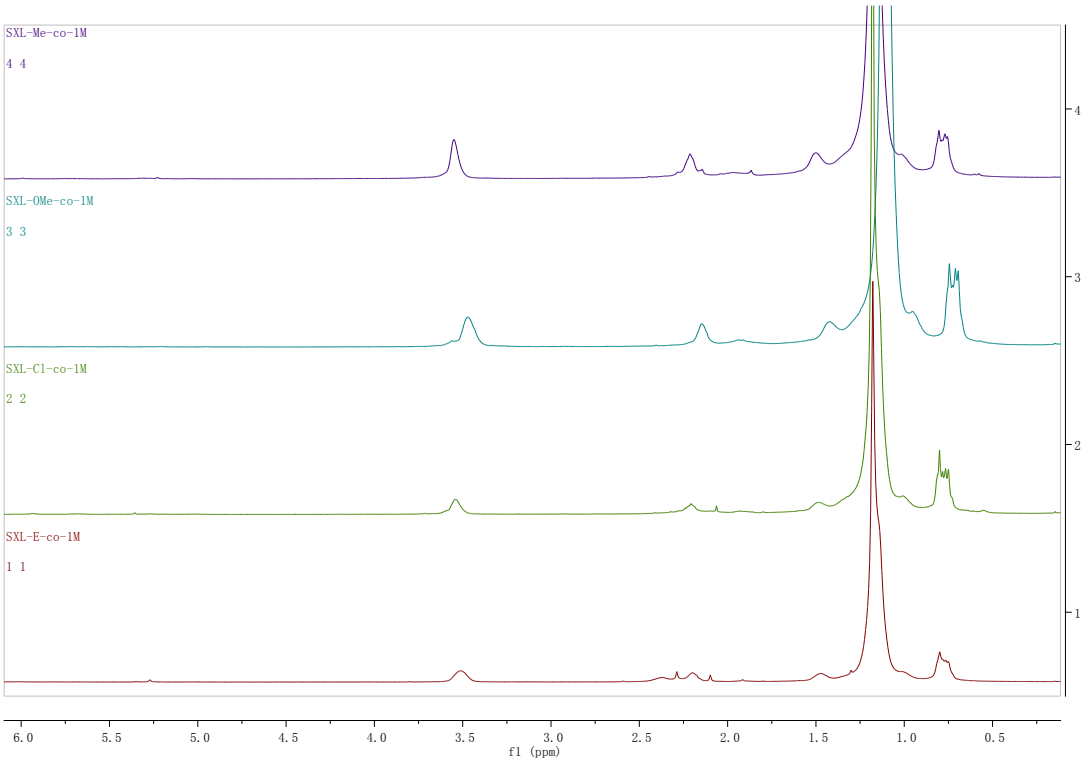

Figure S33. ^{1}H NMR spectrum of the E-MA copolymer from table 2.

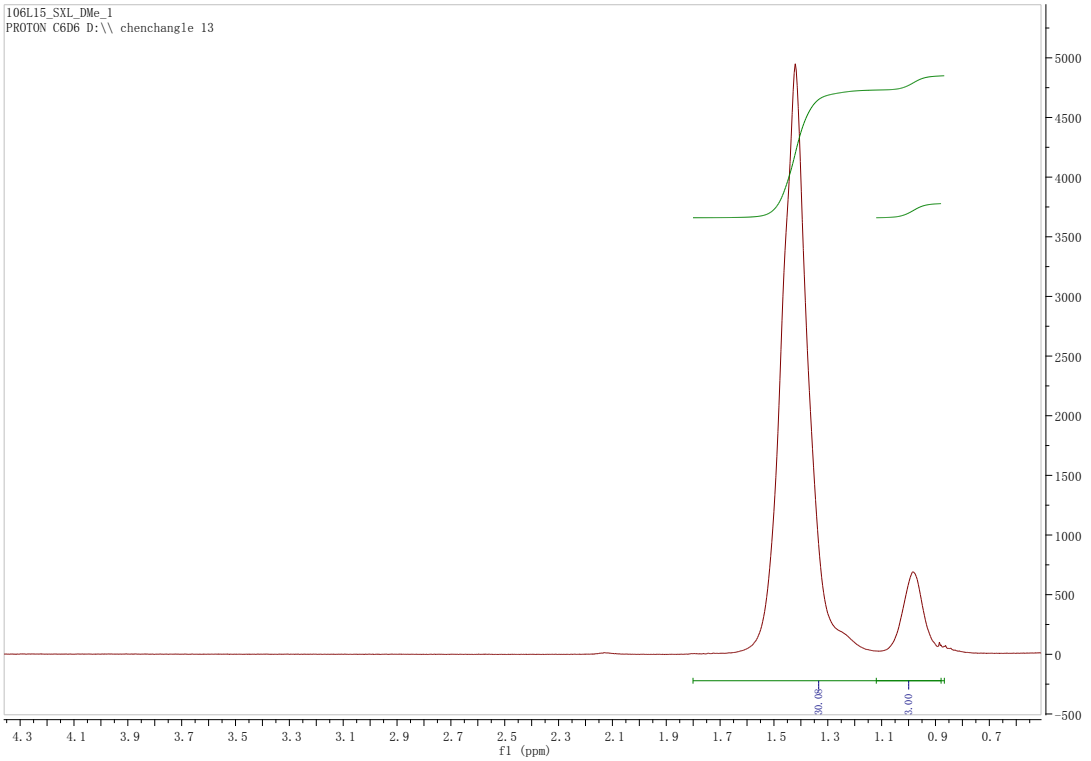

Figure S34. ^{1}H NMR spectrum of the polyethylene generated by complex **2** from table 2, entry 3. (in C_6D_6)

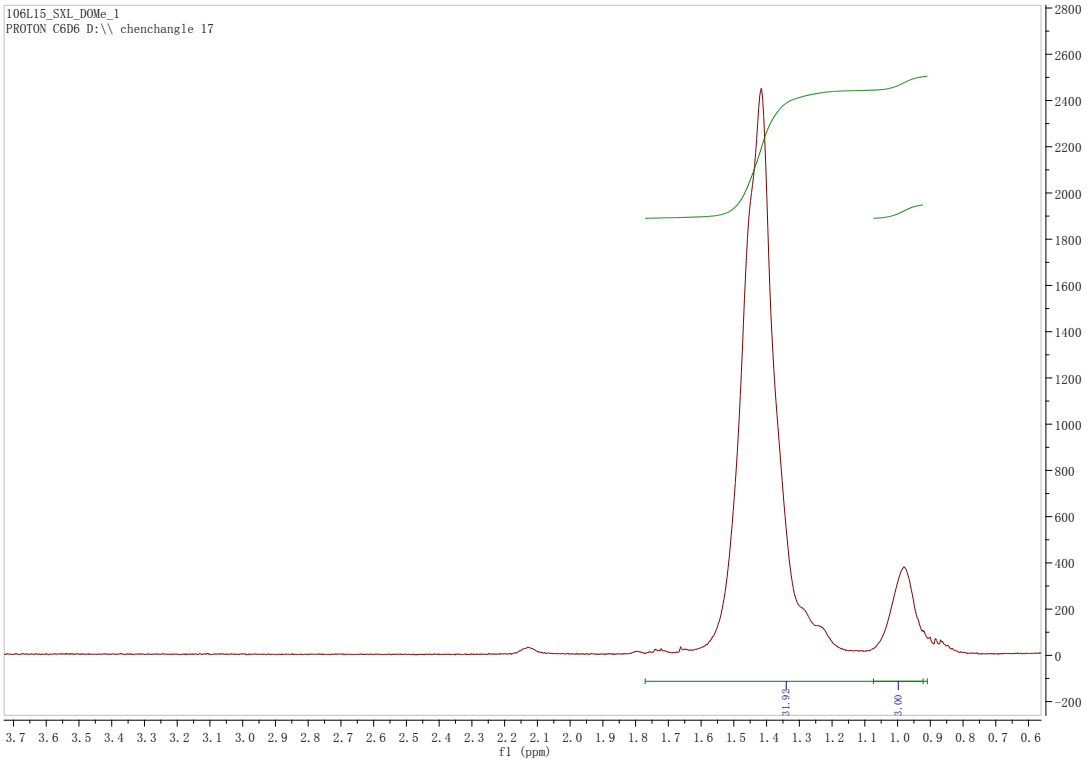

Figure S35. ^{1}H NMR spectrum of the polyethylene generated by complex **1** from table 2, entry 1. (in C_6D_6)

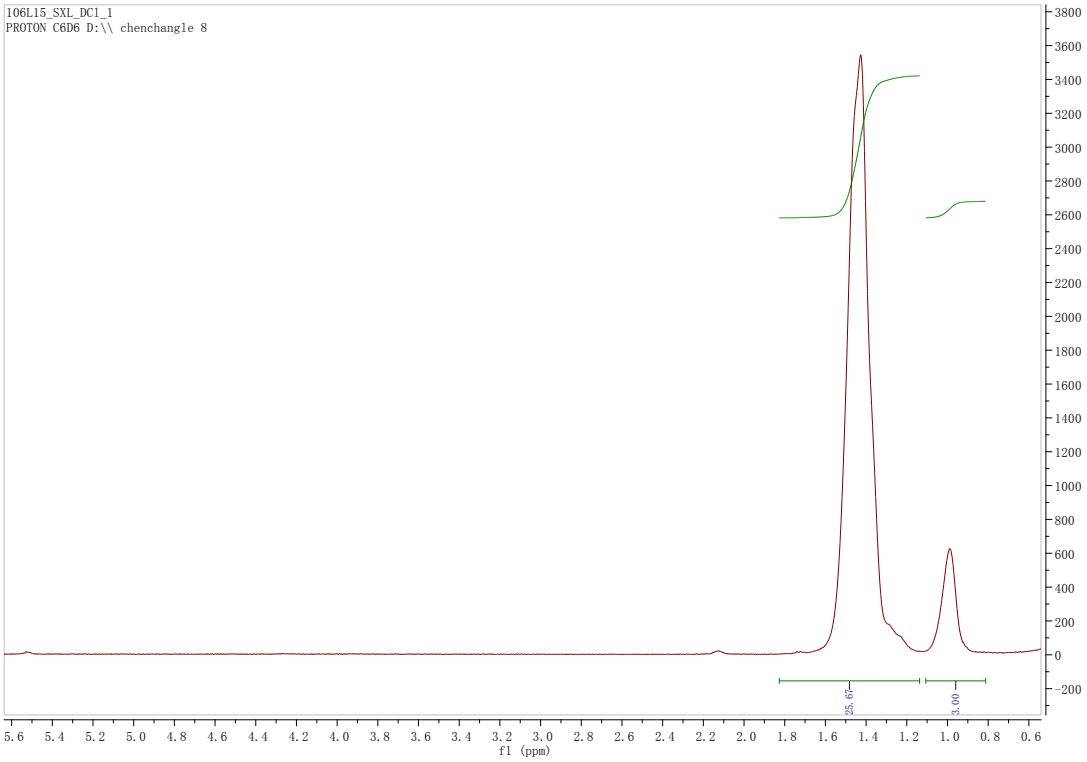

Figure S36. ^{1}H NMR spectrum of the polyethylene generated by complex **3** from table 2, entry 5. (in C_6D_6)

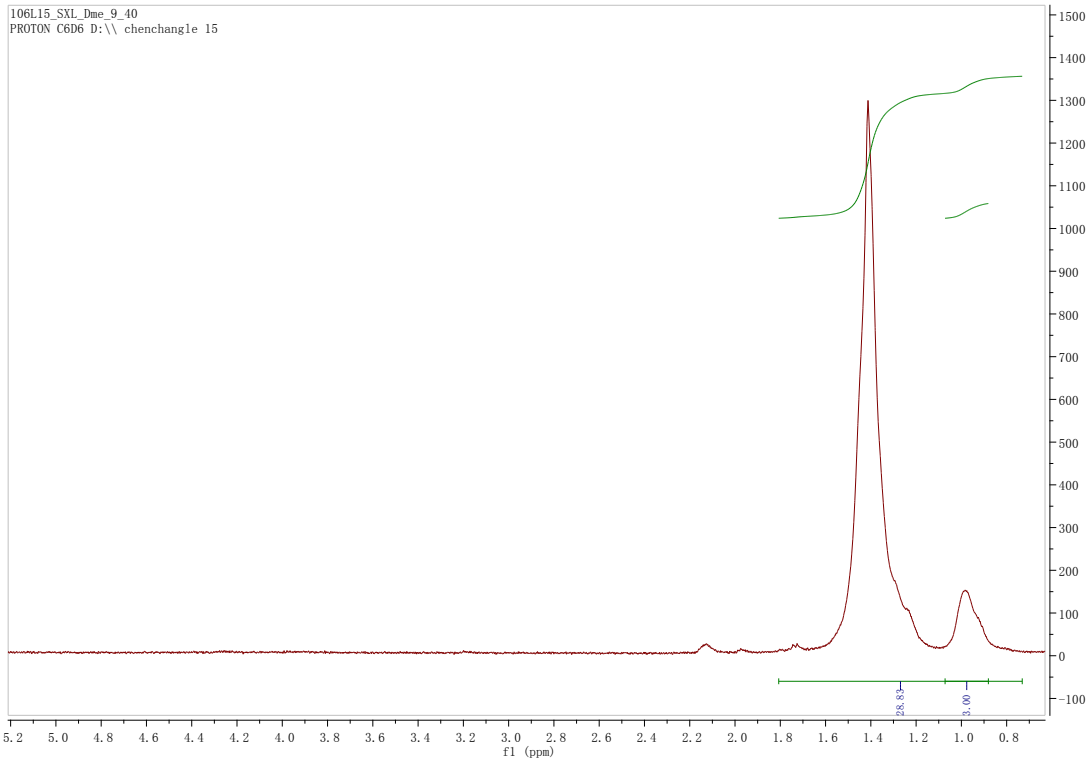

Figure S37. ^{1}H NMR spectrum of the polyethylene generated by complex **2** from table 1, entry 2. (in C_6D_6)

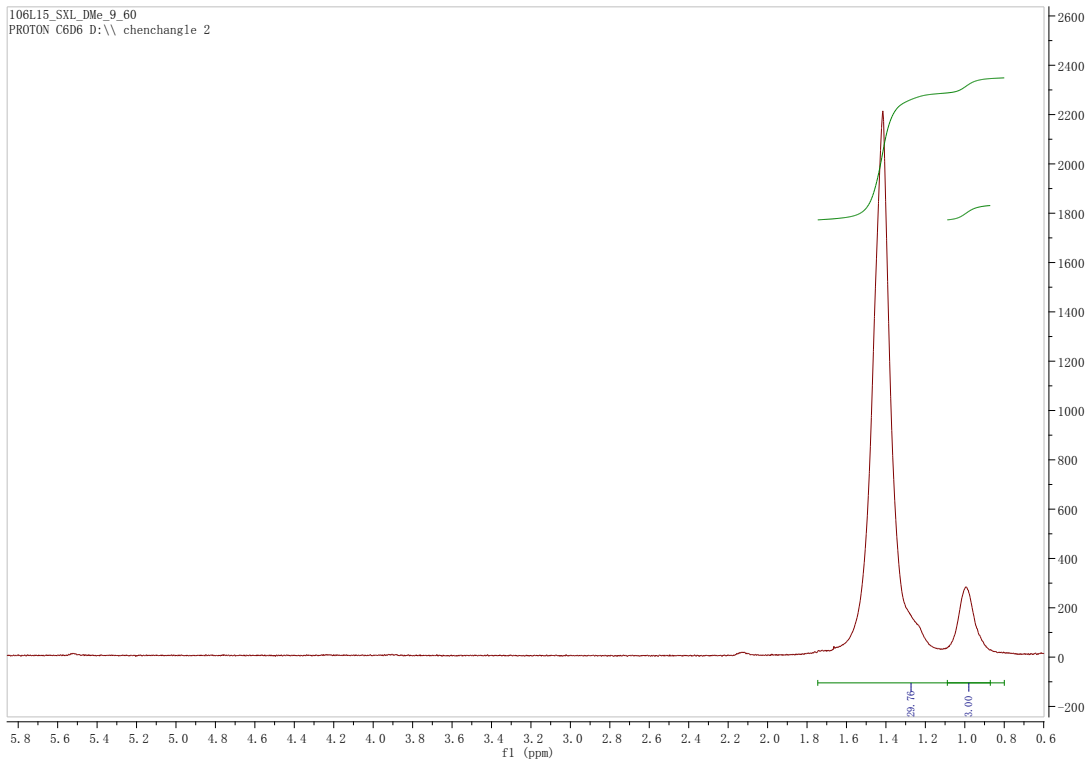

Figure S38. ^{1}H NMR spectrum of the polyethylene generated by complex **2** from table 1, entry 5. (in C_6D_6)

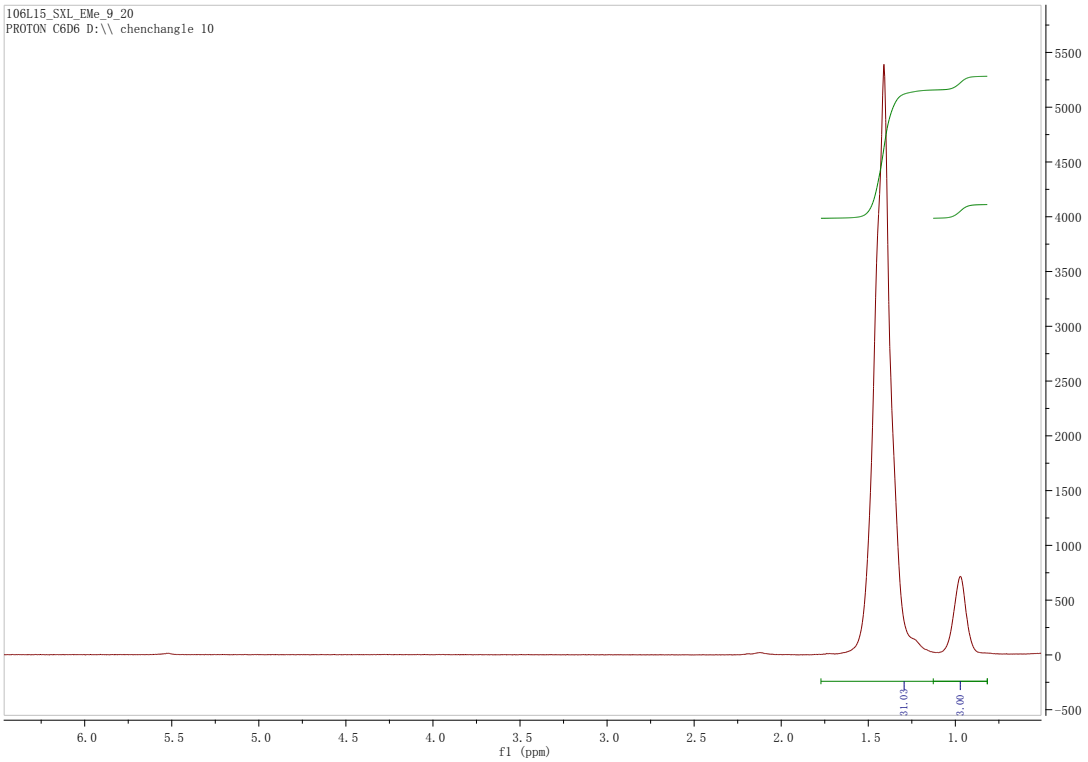

Figure S39. ^{1}H NMR spectrum of the polyethylene generated by complex **5** from table 1, entry 10. (in C_6D_6)

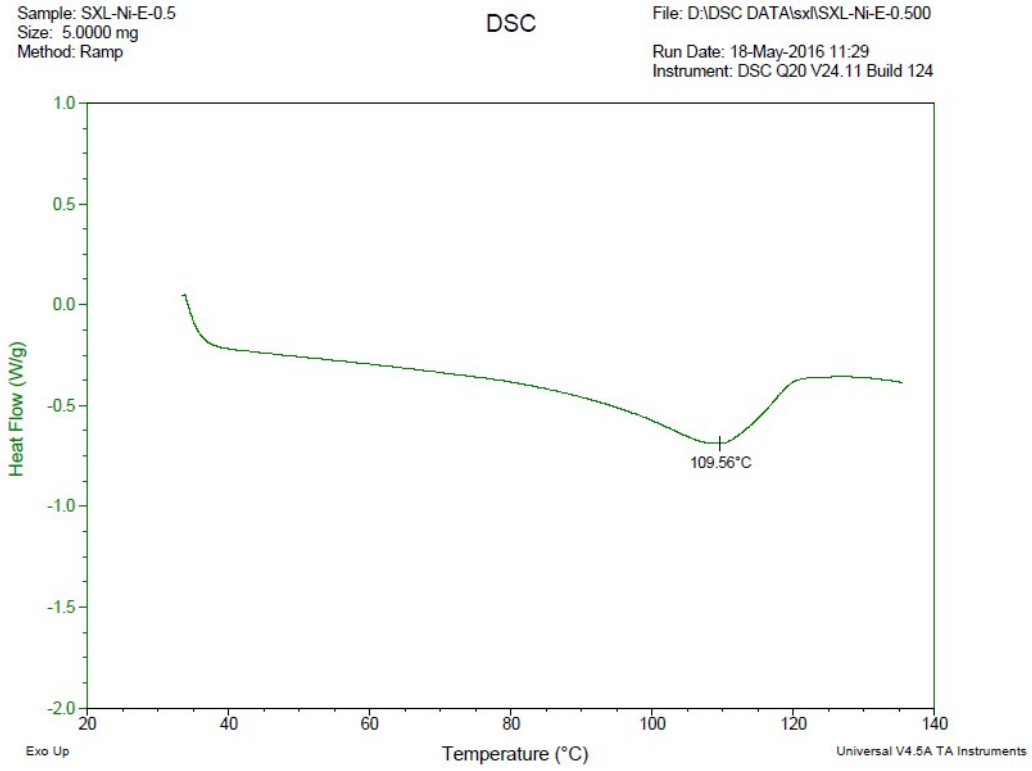

Figure S40. DSC of the polyethylene generated by complex **6** from table 1, entry 12.

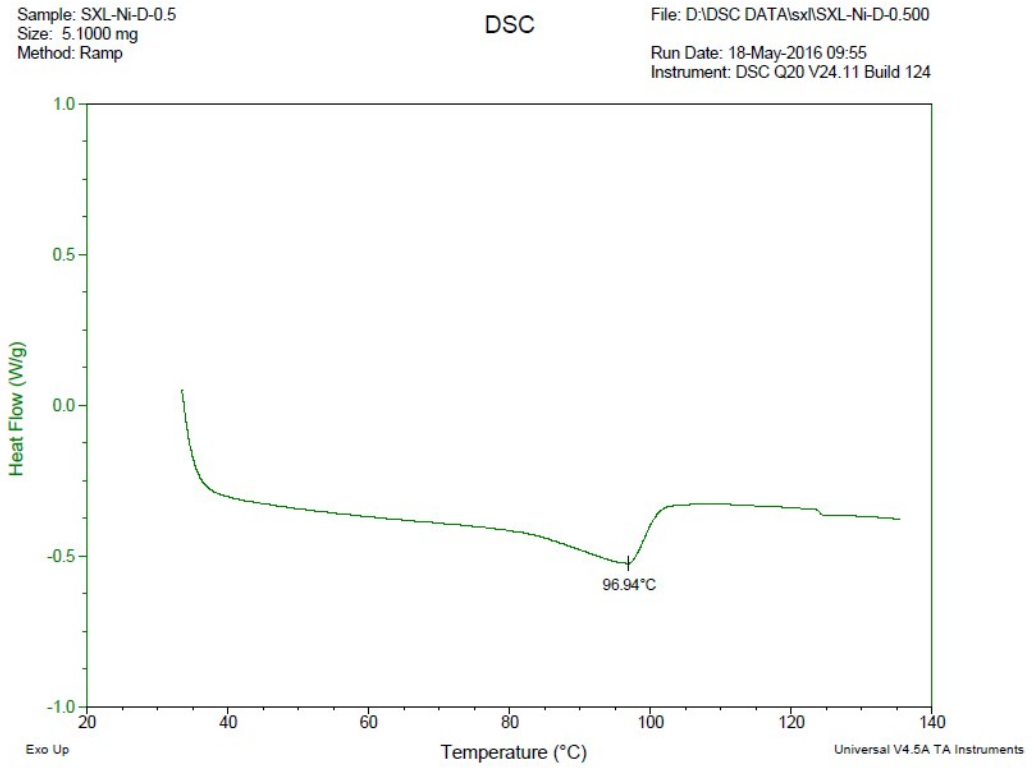

Figure S41. DSC of the polyethylene generated by complex **7** from table 1, entry 13.

X-Ray Crystallography of complex 2, 5 and 6.

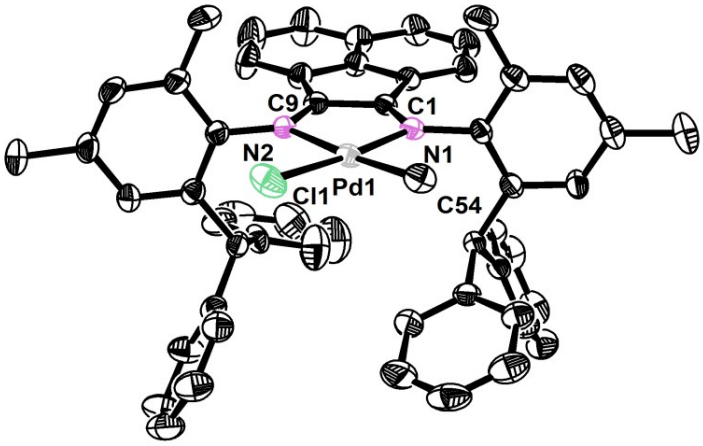

Table S1 Crystal data and structure refinement for 2 (sxl-c-2).

Data	**2**
Identification code	sxl-c-2
Empirical formula	$C_{56}H_{49}Cl_3N_2Pd$
Formula weight	962.72
Temperature/K	290(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.7748(4)
b/Å	24.3601(8)
c/Å	18.0013(8)
α/°	90
β/°	95.951(4)
γ/°	90
Volume/Å^3	4699.4(3)
Z	4
ρ_{calc}g/cm^3	1.361
μ/mm^{-1}	0.605
F(000)	1984.0

Crystal size/mm^3	0.360 × 0.320 × 0.300
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.828 to 58.494
Index ranges	-13 ≤ h ≤ 13, -32 ≤ k ≤ 32, -18 ≤ l ≤ 23
Reflections collected	30323
Independent reflections	10960 [R_{int} = 0.0341, R_{sigma} = 0.0515]
Data/restraints/parameters	10960/34/574
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0612, wR_2 = 0.1733
Final R indexes [all data]	R_1 = 0.1005, wR_2 = 0.2173
Largest diff. peak/hole / e Å^{-3}	1.01/-1.19

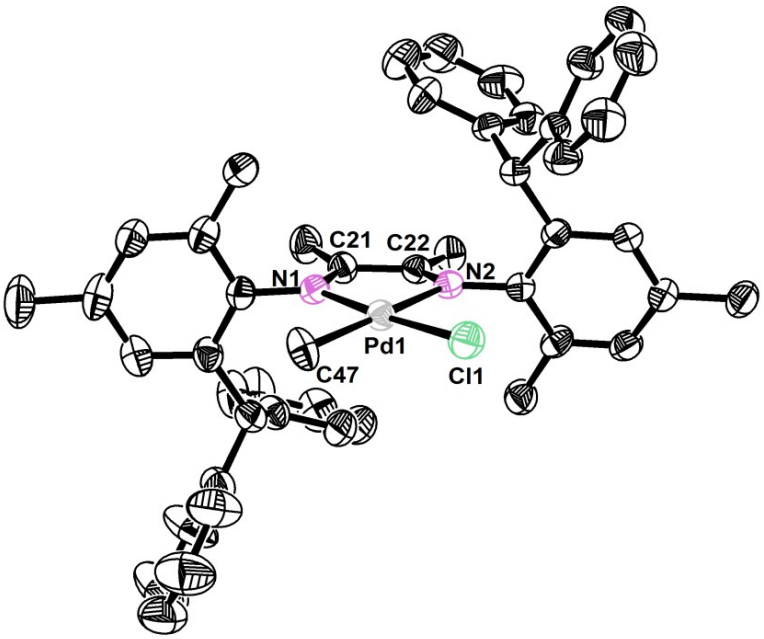

Table S2 Crystal data and structure refinement for 5 (sxl-c-1).

Data	**5**
Identification code	sxl-c-1
Empirical formula	$C_{47}H_{47}ClN_2Pd$
Formula weight	781.71
Temperature/K	290(2)
Crystal system	triclinic
Space group	P-1
a/Å	13.1491(6)
b/Å	19.2193(10)
c/Å	19.3227(8)
α/°	105.127(4)
β/°	109.315(4)
γ/°	96.896(4)
Volume/Å^3	4333.0(4)
Z	4
ρ_{calc}g/cm^3	1.198
μ/mm^{-1}	4.250
F(000)	1624.0
Crystal size/mm^3	0.320 × 0.300 × 0.250
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.17 to 139.888

Index ranges	$-14 \leq h \leq 16$, $-23 \leq k \leq 22$, $-23 \leq l \leq 17$
Reflections collected	28063
Independent reflections	15681 [$R_{int} = 0.0393$, $R_{sigma} = 0.0664$]
Data/restraints/parameters	15681/3/933
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	$R_1 = 0.0893$, $wR_2 = 0.2273$
Final R indexes [all data]	$R_1 = 0.1046$, $wR_2 = 0.2380$
Largest diff. peak/hole / e $Å^{-3}$	1.27/-1.46

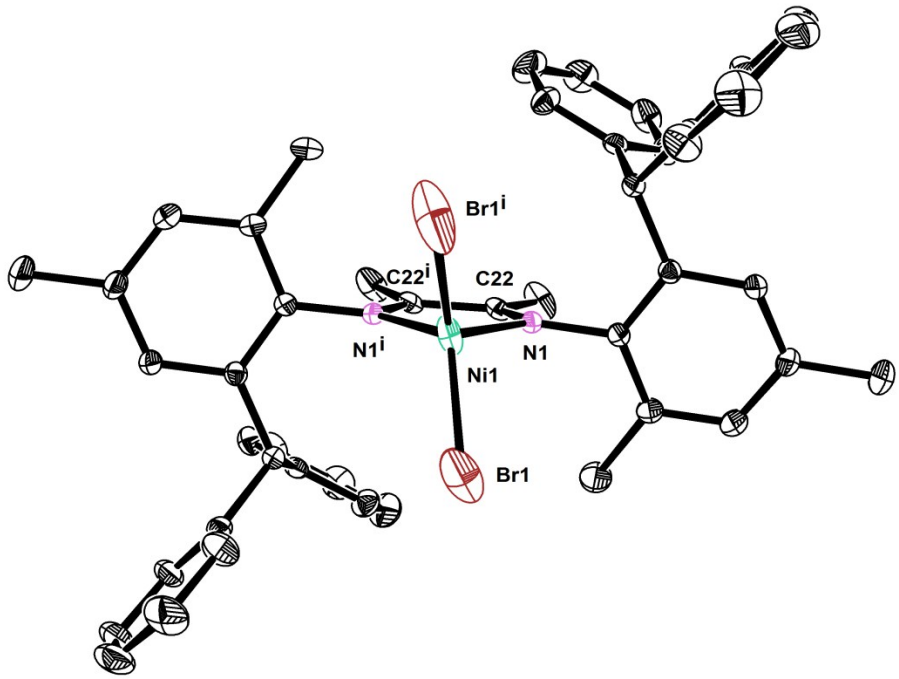

Table S3 Crystal data and structure refinement for 6 (sxl-c-2).

Data	**6**
Formula	C46 H44 Br2 N2 Ni
Formula weight	843.36
Temperature[K]	293(2)
λ(Mo-Kα)[Å]	1.54178
Crystal system	Monoclinic
Space group	C2/c
a[Å]	9.6692(2)
b[Å]	15.1682(3)
c[Å]	28.4042(5)
α[°]	90
β[°]	95.927(2)
γ[°]	90
Volume[Å^3]	4143.61(14)
Z	4
D(calc)[g·cm^{-3}]	1.352
μ[mm^{-1}]	3.173
F(000)	1728
θ min-max (°)	2.56-26.60
h	-10→11
k	-18→16
l	-23→34
Reflections collected	7632
Reflections unique	3880
R(int)	0.0180
Data / restraints / parameters	

	3880 / 0 / 234
Final R indices [I>2σ(I)]	R_1 = 0.1202 wR_2 = 0.3249
R indices (all data)	R_1 = 0.1277 wR_2 = 0.3336
GOF on F^2	1.062