Supporting Information for:

Influence of Ligand Second Coordination Sphere Effects on the Olefin (Co)Polymerization Properties of α–diimine Pd(II) Catalysts

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1. 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 for NMR were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded 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 TMS. Coupling constants are in Hz. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. Mass spectra were recorded on a P-SIMS-Gly of Bruker Daltonics Inc (EI+). X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K$^{\alpha}$ radiation (λ = 0.71073 Å). Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) employing a series of two linear Styragel columns (HR2 and HR4) at an oven temperature of 45 °C. A Waters 1515 pump and Waters 2414 differential refractive index detector (30 °C) were used. The eluent was THF at a flow rate of 1.0 mL min^{-1}. A series of low polydispersity polystyrene standards was used for calibration. Dichloromethane, toluene, THF and hexanes were purified by solvent purification systems.[S1] 6-bromo-3,5-diisopropylaniline,[S2] 9,9-dimethylxanthene-4,5-diboronic acid,[S3] were prepared according to reported procedure. All other reagents were purchased from commercial sources and used without purification.

Synthetic procedures of the anilines were the same with that of 4-(2,6-diisopropylaniline)-5-(4-biphenyl)-(9,9-dimethylxanthene-4,5-diyl).

4-(2,6-diisopropylaniline)-5-(4-biphenyl)-(9,9-dimethylxanthene-4,5-diyl) A 200 mL Schlenk flask was charged with 6-bromo-3,5-diisopropylaniline (0.86 g, 3.36 mmol), 9,9-dimethylxanthene-4,5-diboronic acid (1.02 g, 3.36 mmol), Na_2CO_3 (1.03 g, 9.43 mmol), Pd(dba)$_2$ (0.21 g, 0.35 mmol), PPh_3 (0.10 g, 0.382 mmol), H_2O (6 mL), EtOH (12 mL) and toluene (40 mL). After refluxing overnight, the reaction mixture was cooled to room temperature and extracted with ethyl acetate, washed with brine, and dried over $MgSO_4$. The volatile fraction was evaporated and the residue was subjected to column chromatography (silica gel, CH_2Cl_2/EtOAc (40:1)) to afford 4-(2,6-diisopropylaniline)-5-diboronic acid-(9,9-dimethylxanthene-4,5-diyl) as a grey solid (0.52 g, 35 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 1H, aryl-*H*), 7.55 (dd, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 1H, aryl-*H*), 7.42 (dd, ^3J = 7.2 Hz, ^4J = 2.1 Hz, 1H, aryl-*H*), 7.20-7.08 (m, 5H, aryl-*H*), 5.24 (s, 2H, B(O*H*)$_2$), 3.87 (s, 2H, N*H*$_2$), 3.01 (sept, ^3J = 6.8 Hz, 2H, $(CH_3)_2CH$), 1.70 (s, 6H, xanthene-C*H*$_3$), 1.30 (d, ^3J = 6.8 Hz, 12H, $(CH_3)_2CH$). A 200 mL

Schlenk flask was charged with 4-(2,6-diisopropylaniline)-5-diboronic acid-(9,9-dimethylxanthene-4,5-diyl) (1.03 g, 2.40 mmol), 4-bromobiphenyl (0.83 g, 3.55 mmol), Na_2CO_3 (1.00 g, 9.43 mmol), $Pd(dba)_2$ (0.20 g, 0.35 mmol), PPh_3 (0.10 g, 0.38 mmol), H_2O (6 mL), EtOH (12 mL) and toluene (40 mL). After refluxing overnight, the reaction mixture was cooled to room temperature and extracted with ethyl acetate, washed with brine, and dried over $MgSO_4$. The volatile fraction was evaporated and the residue was subjected to column chromatography (silica gel, petroleum ether/EtOAc (160:1)) to afford 4-(2,6-diisopropylaniline) -5-(4-biphenyl)-(9,9-dimethylxanthene-4,5-diyl) as a white solid (0.71g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, ^3J = 7.3 Hz, 2H, aryl-*H*), 7.24-7.39 (m, 5H, aryl-*H*), 7.02-7.16 (m, 8H, aryl-*H*), 6.95 (s, 2H, aryl-*H*), 3.43 (s, 2H, NH_2-*H*), 2.64 (sept, ^3J = 6.8 Hz, 2H, $(CH_3)_2CH$), 1.64 (s, 6H, xanthene-CH_3), 0.99 (d, ^3J = 6.5 Hz, 12H, $(CH_3)_2CH$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.7, 148.4, 141.2, 139.7, 138.7, 136.5, 132.2, 131.9, 131.0, 129.8, 129.3, 129.0, 128.9, 128.8, 128.3, 127.2, 127.1, 126.2, 124.8, 124.6, 123.8, 123.2, 123.0, 35.0 ($C(CH_3)_2$), 31.5 ($C(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$). HRMS (*m/z*): calcd for $C_{39}H_{40}NO$: 538.3110, found: 538.3101 $[M + H]^+$.

(2,6-diisopropylaniline)-5-(4-trifluoridephenyl)-(9,9-dimethylxanthene-4,5-diyl) was afforded as a white solid (0.75 g, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, ^3J = 18.7 Hz, ^4J = 6.8 Hz, 2H, aryl-*H*), 7.17 (d, ^3J = 7.1 Hz, 3H, aryl-*H*), 7.06 (s, 5H, aryl-*H*), 6.91 (s, 2H, aryl-*H*), 3.69 (s, 2H, NH_2), 2.74 (sept, ^3J = 6.8 Hz, 2H, $(CH_3)_2CH$), 1.62 (s, 6H, xanthene-CH_3), 1.00 (d, ^3J = 6.2 Hz, 12H, $(CH_3)_2CH$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.8, 148.2, 141.1, 139.9, 132.3, 132.2, 131.8, 131.0, 129.7, 129.0, 128.9, 128.2, 127.98, 127.97 (q, $^2J_{CF}$ = 32 Hz, $PhCH\text{-}CF_3$), 125.6, 124.7 (q, $^1J_{CF}$ = 270 Hz, CF_3) 124.5, 124.4 (q, $^3J_{CF}$ = 3.5 Hz, $PhC^{m\text{-}Ar}H$), 123.8, 123.3, 123.2, 35.1 ($C(CH_3)_2$), 31.3 ($C(CH_3)_2$), 28.0 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$). ^{19}F $\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ -61.81. HRMS (*m/z*): calcd for $C_{34}H_{35}F_3NO$: 530.2671, found: 530.2658 $[M + H]^+$.

4-(2,6-diisopropylaniline)-5-(4-nitrobenzene)-(9,9-dimethylxanthene-4,5-diyl) was afforded as a white solid (0.75 g, 64 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.76 (m, 2H, aryl-*H*), 7.50 (dd, ^3J = 7.0 Hz, ^4J = 2.4 Hz, 1H, aryl-*H*), 7.42 (dd, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, aryl-*H*), 7.27-7.31 (m, 2H, aryl-*H*), 7.23-7.25 (m, 1H, aryl-*H*), 7.13-7.19 (m, 3H, aryl-*H*), 7.00 (s, 2H, aryl-*H*), 3.82 (s, 2H, NH_2-*H*), 2.78-2.89 (sept, ^3J = 6.8 Hz, 2H, $(CH_3)_2CH$), 1.72 (s, 6H, xanthene-CH_3), 1.12 (d, ^3J = 6.8 Hz, 12H, $(CH_3)_2CH$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.8, 148.1, 146.1, 144.4, 140.4, 132.5, 132.2, 131.8, 130.9, 130.2, 129.1, 128.6, 127.9, 127.4, 126.3, 124.5, 123.9, 123.4, 123.3, 122.7, 35.1 ($C(CH_3)_2$), 31.3 ($C(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 22.4 (CH(*C*H$_3$)$_2$). HRMS (*m*/*z*): calcd for $C_{33}H_{35}N_2O_3$: 507.2648, found: 507.2634 [M + H]$^+$.

4-(2,6-diisopropylaniline)-5-(4-methoxybenzene)-(9,9-dimethylxanthene-4,5-diyl) was afforded as a white solid (0.65 g, 57 %). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31-7.46 (m, 2H, aryl-*H*), 7.21-7.23 (m, 1H, aryl-*H*), 7.13-7.17 (m, 2H, aryl-*H*), 7.06-7.11 (m, 3H, aryl-*H*), 7.02 (s, 2H, aryl-*H*), 6.42-6.45 (m, 2H, aryl-*H*), 3.80 (s, 3H, OCH$_3$-*H*), 3.79 (s, 2H, NH$_2$-*H*), 2.79-2.89 (sept, ^3J = 6.7 Hz, 2H, (CH$_3$)$_2$C*H*), 1.71 (s, 6H, xanthene-C*H*$_3$), 1.12 (d, ^3J = 6.8 Hz, 12H, (C*H*$_3$)$_2$CH). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 158.2, 148.5, 139.6, 132.2, 131.9, 131.7, 131.1, 130.5, 129.8, 129.4, 128.9, 128.8, 128.5, 124.6, 124.2, 123.9, 123.1, 122.9, 113.0, 55.3 (O*C*H$_3$), 35.0 (*C*(CH$_3$)$_2$), 31.5 (C(*C*H$_3$)$_2$), 28.1 (*C*H(CH$_3$)$_2$), 22.4 (CH(*C*H$_3$)$_2$). HRMS (*m*/*z*): calcd for $C_{34}H_{38}NO_2$: 492.2903, found: 492.2894 [M + H]$^+$.

The synthesis of corresponding imine ligands was based on a "template method".[18] A typical procedure is as follows: After stirring a mixture of ZnCl$_2$ (0.11 g, 0.79 mmol), acenaphthenequinone (0.13 g, 0.70 mmol) and glacial acetic acid (10 mL) at 80 °C for 30 min, 4-(2,6-diisopropylaniline)-5-(4-biphenyl)-(9,9-dimethylxanthene-4,5-diyl) (0.81 g, 1.49 mmol) was added. The reaction mixture was refluxed at 130 °C for 2h. The solid precipitated was separated and suspended in CH$_2$Cl$_2$ (30 mL), and a solution of potassium oxalate in water (10 mL) was added. The two phases were separated, and the organic layer was washed with water and dried with MgSO$_4$. After filtration the solvent was removed under vacuum to afford the product **L-Ph** as an orange powder (0.6 g, 69 %). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.86 (dd, ^3J = 8.1 Hz, ^4J = 3.9 Hz, 2H, aryl-*H*), 7.59 (d, ^3J = 8.1 Hz, 2H, aryl-*H*), 7.38-7.55 (m, 16H, aryl-*H*), 7.17-7.34 (m, 13H, aryl-*H*), 7.10 (d, ^3J = 7.5 Hz, 4H, aryl-*H*), 6.99 (d, ^3J = 3.6 Hz, 1H, An-*H*), 6.84 (d, ^3J = 4.8 Hz, 1H, An-*H*), 6.65 (d, ^3J = 7.4 Hz, 1H, An-*H*), 3.26 and 2.95 (sept, ^3J = 6.8 Hz, 4H, (CH$_3$)$_2$C*H*), 1.81 (d, ^3J = 5.5 Hz, 12H, xanthene-C*H*$_3$), 1.17 (d, ^3J = 6.5 Hz, 4H, (C*H*$_3$)$_2$CH), 0.97 (d, ^3J = 6.4 Hz, 8H, (C*H*$_3$)$_2$CH), 0.86 (d, ^3J = 6.4 Hz, 8H, (C*H*$_3$)$_2$CH), 0.69 (d, ^3J = 6.8 Hz, 4H, (C*H*$_3$)$_2$CH). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 165.1, 160.3, 148.7, 148.6, 148.1, 147.5, 140.7, 140.4, 140.1, 139.6, 139.1, 137.0, 136.5, 134.9, 134.5, 132.3, 131.8, 131.7, 131.6, 131.4, 131.3, 131.1, 130.5, 130.1, 129.9, 129.8, 129.4, 128.8, 128.7, 128.0, 127.3, 127.2, 126.9, 126.8, 126.4, 125.4, 124.8, 124.5, 123.4, 123.2, 35.0 and 34.8 (*C*(CH$_3$)$_2$), 32.4 and 31.8 (C(*C*H$_3$)$_2$), 29.0 and 28.9 (*C*H(CH$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$). HRMS (*m*/*z*): calcd for $C_{90}H_{81}N_2O_2$: 1221.6298, found: 1221.6362 [M + H]$^+$.

L-CF$_3$ was obtained as an orange solid (0.51 g, 56 %).^{1}H NMR (400 MHz, CDCl$_3$): δ 7.86 (m, 2H, aryl-*H*), 7.34-7.57 (m, 15H, aryl-*H*), 6.84-7.32 (m, 13H, aryl-*H*), 3.74, 3.00 and 2.82 (m, 4H, (CH$_3$)$_2$C*H*), 1.77 and

1.72 (s, 12H, xanthene-CH_3), 0.90-1.19 (m, 24H, (CH_3)$_2$CH). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 148.9, 148.7, 140.9, 134.8, 132.4 (m), 129.7, 129.5, 128.5, 125.4, 125.0, 124.5, 124.2, 123.5, 123.2, 35.1 (*C*(CH$_3$)$_2$), 31.3 (C(*C*H$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 28.5 (*C*H(CH$_3$)$_2$), 28.0 (*C*H(CH$_3$)$_2$), 22.8 (CH(*C*H$_3$)$_2$), 22.5 (CH(*C*H$_3$)$_2$). ^{19}F {^{1}H} NMR (282 MHz, CDCl$_3$): δ -62.62. HRMS (*m*/*z*): calcd for $C_{80}H_{71}F_6N_2O_2$: 1205.5420, found: 1205.5436 [M + H]$^+$.

L-NO$_2$ was obtained as an orange solid (0.67 g, 72 %).^{1}H NMR (400 MHz, CDCl$_3$): δ 7.76-8.53 (m, 7H, aryl-*H*), 7.11-7.61 (m, 22H, aryl-*H*), 6.94 and 6.20 (s, 1H, aryl-*H*), 2.97 and 2.60 (m, 4H, (CH$_3$)$_2$C*H*), 1.76 (s, 12H, xanthene-CH_3), 1.12, 0.98 and 0.74 (m, 24H, (CH_3)$_2$CH). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 148.8, 148.3, 146.9, 144.1, 132.5, 130.1, 129.4, 128.7, 127.6, 126.2, 124.8, 124.3, 123.4, 123.3, 35.1 (*C*(CH$_3$)$_2$), 31.5 (C(*C*H$_3$)$_2$), 29.0 (m, *C*H(CH$_3$)$_2$), 22.5 (m, CH(*C*H$_3$)$_2$). HRMS (*m*/*z*): calcd for $C_{78}H_{71}N_4O_6$: 1159.5374, found: 1159.5388 [M + H]$^+$.

L-OMe was obtained as an orange solid (0.54 g, 62 %).^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88 (d, ^3J = 8.2 Hz, 2H, aryl-*H*), 7.50 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 2H, aryl-*H*), 7.37-7.43 (m, 6H, aryl-*H*), 7.33 (s, 4H, aryl-*H*), 7.23-7.25 (m, 8H, aryl-*H*), 7.14 (t, ^3J = 7.6 Hz, 2H, aryl-*H*), 6.80 (s, 2H, aryl-*H*), 6.67 (d, ^3J = 8.3 Hz, 4H, An-*H*), 4.01 (s, 6H, OCH$_3$-*H*), 2.94 (sept, ^3J = 6.8 Hz, 4H, (CH$_3$)$_2$C*H*), 1.77 (s, 12H, xanthene-CH_3), 1.03 (d, ^3J = 6.5 Hz, 12H, (CH_3)$_2$CH), 0.97 (d, ^3J = 6.8 Hz, 12H, (CH_3)$_2$CH). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 160.5, 159.0. 149.0, 148.7, 147.3, 140.7, 134.6, 134.5, 132.0, 131.9, 131.8, 131.3, 130.5, 129.7, 129.5, 129.2, 129.1, 128.7, 128.0, 125.4, 124.2, 123.9, 123.3, 122.9, 113.4, 55.7 (O*C*H$_3$), 35.1 (*C*(CH$_3$)$_2$), 31.3 (C(*C*H$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$), 22.5 (CH(*C*H$_3$)$_2$). HRMS (*m*/*z*): calcd for $C_{80}H_{77}N_2O_4$: 1129.5883, found: 1129.5897 [M + H]$^+$.

The palladium complexes were prepared by the reaction of 0.50 g ligand with 1 equivalent (COD)PdMeCl in 25 mL CH$_2$Cl$_2$. After stirring overnight at room temperature, the desired compound was isolated in high yield using column chromatography. The mixture was eluted on silica gel with first 10:1 hexanes/EA, then pure EA as the mobile phase. The pure compound was obtained as a red solid.

Pd-Ph. Yield 45 % (270 mg) **.**^{1}H NMR (400 MHz, CDCl$_3$): δ 7.89 (dd, ^3J = 15.3 Hz, ^4J = 8.3 Hz, 2H, aryl-*H*), 7.17-7.62 (m, 29H, aryl-*H*), 7.09 (m, 4H, aryl-*H*, An-*H*), 6.78-6.92 (m, 5H, aryl-*H*, An-*H*), 6.43 (d, ^3J = 7.3 Hz, 1H, An-*H*), 3.24-3.34 (m, 4H, (CH$_3$)$_2$C*H*), 1.82 (s, 6H, xanthene-CH_3), 1.80 (s, 6H, xanthene-CH_3), 1.24 (d, ^3J = 6.7 Hz, 6H, (CH_3)$_2$CH), 1.11 (d, ^3J = 6.7 Hz, 6H, (CH_3)$_2$CH), 0.80 (s, 3H, Pd-CH_3), 0.71 (d, ^3J = 6.9 Hz, 6H, (CH_3)$_2$CH)), 0.69 (d, ^3J = 6.9 Hz, 6H, (CH_3)$_2$CH)). ^{13}C{^{1}H} NMR (100 MHz,

$CDCl_3$): δ 171.8, 167.2, 148.0, 147.8, 147.7, 147.6, 143.4, 141.7, 140.7, 140.4, 140.3, 140.2, 139.7, 139.2, 138.6, 138.2, 137.4, 137.3, 131.5, 131.4, 131.3, 131.2, 131.1, 131.0, 130.9, 130.3, 129.7, 129.6, 129.5, 129.4, 128.8, 128.7, 128.6, 128.1, 127.5, 127.2, 127.1, 127.0, 126.9, 126.7, 126.6, 125.8, 125.7, 125.3 (m), 124.8, 124.7, 123.5, 123.4, 123.3, 34.6 ($\mathit{C}(CH_3)_2$), 34.5 ($\mathit{C}(CH_3)_2$), 32.9 ($C(\mathit{C}H_3)_2$), 32.8 ($C(\mathit{C}H_3)_2$), 29.3 ($\mathit{C}H(CH_3)_2$), 28.7 ($\mathit{C}H(CH_3)_2$), 23.9 ($CH(\mathit{C}H_3)_2$), 23.7 ($CH(\mathit{C}H_3)_2$), 23.2 ($CH(\mathit{C}H_3)_2$), 23.1 ($CH(\mathit{C}H_3)_2$), 4.1 (Pd-$\mathit{C}H_3$). Anal. Calcd for ($C_{91}H_{83}ClN_2O_2Pd$): C, 79.29; H, 6.07; N, 2.03. Found: C, 79.59; H, 5.98; N, 2.09. MALDI-TOF-MS (m/z): calcd for $C_{90}H_{81}N_2O_2Pd$: 1327.5333, found: 1327.4407 $[M-CH_3-Cl+H]^+$.

Pd-CF$_3$. Yield 61 % (362 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, ^3J = 12.0 Hz, ^4J = 8.3 Hz, 2H, aryl-*H*), 7.65 (dd, ^3J = 14.1 Hz, ^4J = 8.1 Hz, 4H, aryl-*H*), 7.49-7.56 (m, 6H, aryl-*H*), 7.43 (s, 2H, aryl-*H*), 7.39 (dd, ^3J = 8.1 Hz, ^4J = 4.4 Hz, 4H, aryl-*H*), 7.17-7.27 (m, 10H, aryl-*H*, An-*H*), 7.00 (d, ^3J = 7.2 Hz, 1H, An-*H*), 6.50 (d, ^3J = 7.3 Hz, 1H, An-*H*). 3.34-3.44 (m, 4H, $(CH_3)_2C\mathit{H}$), 1.81 (s, 6H, xanthene-$C\mathit{H}_3$), 1.79 (s, 6H, xanthene-$C\mathit{H}_3$), 1.29 (d, ^3J = 6.7 Hz, 6H, $(C\mathit{H}_3)_2CH$), 1.16 (d, ^3J = 6.6 Hz, 6H, $(C\mathit{H}_3)_2CH$), 0.97 (s, 3H, Pd-$C\mathit{H}_3$), 0.75 (d, ^3J = 6.6 Hz, 12H, $(C\mathit{H}_3)_2CH$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.0, 167.3, 148.0, 147.7, 147.5, 147.4, 143.8, 142.1, 142.0, 141.7, 140.8, 139.5, 138.5, 137.2, 131.5, 131.4, 131.3, 131.2, 131.1, 130.9, 130.2, 129.7, 129.6, 129.5, 128.7, 128.2, 128.1, 127.5, 126.8, 126.3, 126.2, 125.7, 125.2, 125.1, 124.9, 124.7, 123.6, 123.5, 123.4, 34.6 ($\mathit{C}(CH_3)_2$), 34.5 ($\mathit{C}(CH_3)_2$), 32.8 ($C(\mathit{C}H_3)_2$), 29.2 ($\mathit{C}H(CH_3)_2$), 28.7 ($\mathit{C}H(CH_3)_2$), 23.8 ($CH(\mathit{C}H_3)_2$), 23.2 ($CH(\mathit{C}H_3)_2$), 23.1 ($CH(\mathit{C}H_3)_2$). 3.8 (Pd-$\mathit{C}H_3$). ^{19}F $\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ -62.31, -62.62. Anal. Calcd for ($C_{81}H_{73}ClF_6N_2O_2Pd$): C, 71.41; H, 5.40; N, 2.06. Found: C, 71.58; H, 5.58; N, 2.09. MALDI-TOF-MS (m/z): calcd for $C_{80}H_{71}F_6N_2O_2Pd$: 1311.4455, found: 1311.1568 $[M-CH_3-Cl+H]^+$.

Pd-NO$_2$. Yield 58% (350 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (t, ^3J = 8.3 Hz, 2H, aryl-*H*), 7.98 (dd, ^3J = 8.8 Hz, ^4J = 3.3 Hz, 4H, aryl-*H*), 7.70 (t, ^3J = 9.1 Hz, 4H, aryl-*H*), 7.41-7.59 (m, 10H, aryl-*H*), 7.18-7.32 (m, 8H, aryl-*H*, An-*H*), 6.94 (d, ^3J = 7.2 Hz, 1H, An-*H*), 6.37 (d, ^3J = 7.3 Hz, 1H, An-*H*), 3.32-3.42 (m, 4H, $(CH_3)_2C\mathit{H}$), 1.80 (s, 6H, xanthene-$C\mathit{H}_3$), 1.79 (s, 6H, xanthene-$C\mathit{H}_3$), 1.31 (d, ^3J = 6.7 Hz, 6H, $(C\mathit{H}_3)_2CH$), 1.14 (d, ^3J = 6.8 Hz, 6H, $(C\mathit{H}_3)_2CH$), 0.82 (s, 3H, Pd-$C\mathit{H}_3$), 0.77 (d, ^3J = 6.9 Hz, 12H, $(C\mathit{H}_3)_2CH$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.2, 167.3, 148.0, 147.7, 147.4, 147.3, 147.0, 145.2, 144.9, 143.8, 141.7, 140.8, 139.5, 138.4, 138.3, 137.2, 131.7, 131.7, 131.7, 131.6, 131.5, 131.3, 131.2, 131.1, 130.7, 130.5, 130.4, 130.2, 130.1, 129.9, 129.7, 128.7, 127.5, 127.3, 126.9, 126.8, 126.7, 125.7, 125.2, 125.1, 124.6, 124.3, 123.7, 123.6, 123.5, 123.3, 34.7 ($C(\mathit{C}H_3)_2$), 34.6($C(\mathit{C}H_3)_2$), 32.7 ($C(\mathit{C}H_3)_2$), 32.6 ($\mathrm{C}(\mathit{C}\mathrm{H}_3)_2$), 29.2 ($\mathit{C}\mathrm{H}(\mathrm{CH}_3)_2$), 28.6 ($\mathit{C}\mathrm{H}(\mathrm{CH}_3)_2$), 23.9 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 23.8 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 23.2 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 23.1 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 3.4 ($\mathrm{Pd}\text{-}\mathit{C}\mathrm{H}_3$). Anal. Calcd for ($\mathrm{C_{79}H_{73}ClN_4O_6Pd}$): C, 72.08; H, 5.59; N, 4.26. Found: C, 72.39; H, 5.78; N, 4.59. MALDI-TOF-MS (m/z): calcd for $\mathrm{C_{78}H_{71}N_4O_6Pd}$: 1265.4408, found: 1265.4520 $[\mathrm{M\text{-}CH_3\text{-}Cl{+}H}]^+$.

Pd-OMe. Yield 41 % (242 mg). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 8.01 (dd, ^{3}J = 14.2 Hz, ^{4}J = 8.3 Hz, 2H, aryl-*H*), 7.46-7.55 (m, 7H, aryl-*H*), 7.36-7.46 (m, 8H, aryl-*H*), 7.13-7.25 (m, 7H, aryl-*H*), 6.86 (d, ^{3}J = 8.6 Hz, 2H, An-*H*), 6.71 (dd, ^{3}J = 13.4 Hz, ^{4}J = 8.0 Hz, 4H, An-*H*), 6.22 (d, ^{3}J = 7.3 Hz, 1H, An-*H*), 3.74 (s, 3H, $\mathrm{OC}\mathit{H}_3$), 3.68 (s, 3H, $\mathrm{OC}\mathit{H}_3$), 3.30-3.41 (m, 4H, $(\mathrm{CH_3})_2\mathrm{C}\mathit{H}$), 1.79 (s, 6H, xanthene-$\mathrm{C}\mathit{H}_3$), 1.78 (s, 6H, xanthene-$\mathrm{C}\mathit{H}_3$), 1.31 (d, ^{3}J = 6.7 Hz, 6H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{CH}$), 1.14 (d, ^{3}J = 6.7 Hz, 6H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{CH}$), 1.07 (s, 3H, Pd-$\mathrm{C}\mathit{H}_3$), 0.82 (d, ^{3}J = 6.7 Hz, 6H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{CH}$), 0.81 (d, ^{3}J = 6.7 Hz, 6H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{CH}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz, $\mathrm{CDCl_3}$): δ 172.2, 167.5, 159.2, 148.0, 148.0, 147.8, 147.5, 143.5, 141.9, 140.9, 139.3, 138.7, 138.1, 137.5, 131.5, 131.3, 131.3, 131.2, 131.1, 131.0, 130.9, 130.9, 130.6, 130.4, 130.3, 130.3, 130.2, 130.1, 129.1, 128.9, 127.6, 126.9, 125.9, 125.6, 125.5, 125.2, 124.9, 124.7, 124.6, 124.5, 123.5, 123.3, 123.2, 123.1, 114.5, 113.9, 56.1 ($\mathrm{O}\mathit{C}\mathrm{H}_3$), 55.3 ($\mathrm{O}\mathit{C}\mathrm{H}_3$), 34.7 ($\mathit{C}(\mathrm{CH}_3)_2$), 34.6 ($\mathit{C}(\mathrm{CH}_3)_2$), 32.7 ($\mathrm{C}(\mathit{C}\mathrm{H}_3)_2$), 32.6 ($\mathrm{C}(\mathit{C}\mathrm{H}_3)_2$), 29.5 ($\mathit{C}\mathrm{H}(\mathrm{CH}_3)_2$), 28.8 ($\mathit{C}\mathrm{H}(\mathrm{CH}_3)_2$), 24.1 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 23.6 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 23.4 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 23.1 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 4.3 ($\mathrm{Pd}\text{-}\mathit{C}\mathrm{H}_3$). Anal. Calcd for ($\mathrm{C_{81}H_{79}ClN_2O_4Pd}$): C, 75.63; H, 6.19; N, 2.18. Found: C, 75.42; H, 6.45; N, 2.54. MALDI-TOF-MS (m/z): calcd for $\mathrm{C_{80}H_{77}N_2O_4Pd}$: 1235.4918, found: 1235.4573 $[\mathrm{M\text{-}CH_3\text{-}Cl{+}H}]^+$.

General Procedure for the Synthesis of Pd carbonyl complexes **Pd-A-CO**, **Pd-Ph-CO, Pd-CF$_3$-CO Pd-NO$_2$-CO** and **Pd-OMe-CO**.

A 10 mL Schlenk flask was charged with 30.0 μmol of the Pd complex, NaBAF (30.0 μmol) and 5.0 mL of dry $\mathrm{CH_2Cl_2}$. The solution was stirred for 60 min under a balloon of CO, leading to darkening of the solution. The mixture was filtered through Celite and concentrated in vacuo to afford the desired complexes.

Pd-A-CO ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 8.06 (dd, ^{3}J = 11.6 Hz, ^{4}J = 8.3 Hz, 2H, aryl-*H*), 7.67 (m, 8H, BAF-*H*), 7.48 (m, 12H, aryl-*H*, BAF-*H*), 6.78 (d, ^{3}J = 7.3 Hz, 1H, An-*H*), 6.58 (d, ^{3}J = 7.4 Hz, 1H, An-*H*), 3.15 (sept, ^{3}J = 6.8 Hz, 2H, $(\mathrm{CH_3})_2\mathrm{C}\mathit{H}$), 2.97(sept, ^{3}J = 6.8 Hz, 2H, $(\mathrm{CH_3})_2\mathrm{C}\mathit{H}$), 1.42 (d, ^{3}J = 6.8 Hz, 6H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{CH}$), 1.34 (d, ^{3}J = 6.8 Hz, 6H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{CH}$),1.14 (s, 3H, Pd-$\mathrm{C}\mathit{H}_3$), 1.06 (d, ^{3}J = 6.8 Hz, 6H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{CH}$), 0.96 (d, ^{3}J = 6.8 Hz, 6H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{CH}$). IR (KBr) 2133cm^{-1} [*ν* (CO)].

Pd-Ph-CO ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.91 (dd, ^3J = 19.3 Hz, ^4J = 8.3 Hz, 2H, aryl-*H*), 7.67 (m, 8H, BAF-*H*), 7.52-7.60 (m, 12H, aryl-*H*, BAF-*H*), 7.47 (s, 4H, aryl-*H*), 7.33-7.40 (m, 6H, aryl-*H*), 7.17-7.28 (m, 18H, aryl-*H*), 6.67 (d, ^3J = 7.3 Hz, 1H, An-*H*), 6.36 (d, ^3J = 7.4 Hz, 1H, An-*H*), 2.88 (sept, ^3J = 6.8 Hz, 2H, (CH$_3$)$_2$C*H*), 2.67 (sept, ^3J = 6.8 Hz, 2H, (CH$_3$)$_2$C*H*), 1.83 (s, 6H, xanthene-C*H*$_3$), 1.82 (s, 6H, xanthene-C*H*$_3$), 1.12 (d, ^3J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 1.00 (d, ^3J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 0.83 (d, ^3J = 6.7 Hz, 6H, (C*H*$_3$)$_2$CH), 0.76 (d, ^3J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 0.38 (s, 3H, Pd-C*H*$_3$). IR (KBr) 2133cm^{-1} [ν (CO)].

Pd-CF$_3$-CO ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.02 (dd, ^3J = 13.7 Hz, ^4J = 8.4 Hz, 2H, aryl-*H*), 7.68 (m, 12H, BAF-*H*), 7.56-7.64 (m, 8H, aryl-*H*), 7.47 (m, 6H, aryl-*H*), 7.41 (d, ^3J = 8.0 Hz, 2H, aryl-*H*), 7.36 (d, ^3J = 8.0 Hz, 2H, aryl-*H*), 7.17-7.29 (m, 8H, aryl-*H*), 6.74 (d, ^3J = 7.3 Hz, 1H, An-*H*), 6.49 (d, ^3J = 7.4 Hz, 1H, An-*H*), 3.06 (sept, ^3J = 6.7 Hz, 2H, (CH$_3$)$_2$C*H*), 2.90(sept, ^3J = 6.78 Hz, 2H, (CH$_3$)$_2$C*H*), 1.82 (s, 6H, xanthene-C*H*$_3$), 1.81 (s, 6H, xanthene-C*H*$_3$), 1.32 (s, 3H, Pd-C*H*$_3$), 1.13 (d, ^3J = 6.7 Hz, 6H, (C*H*$_3$)$_2$CH), 1.05 (d, ^3J = 6.6 Hz, 6H, (C*H*$_3$)$_2$CH), 0.88 (d, ^3J = 6.6 Hz, 6H, (C*H*$_3$)$_2$CH), 0.81 (d, ^3J = 6.7 Hz, 6H, (C*H*$_3$)$_2$CH). IR (KBr) 2131cm^{-1} [ν (CO)].

Pd-NO$_2$-CO ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.90-7.96 (m, 4H, aryl-*H*), 7.81 (d, ^3J = 8.7 Hz, 2H, aryl-*H*), 7.59 (m, 14H, BAF-*H*, aryl-*H*), 7.47-7.53 (m, 8H, aryl-*H*), 7.38 (s, 6H, aryl-*H*), 7.14-7.22 (m, 8H, aryl-*H*), 6.63 (d, ^3J = 7.4 Hz, 1H, An-*H*), 6.29 (d, ^3J = 7.4 Hz, 1H, An-*H*), 2.97 (sept, ^3J = 6.78 Hz, 2H, (CH$_3$)$_2$C*H*), 2.80 (sept, ^3J = 6.78 Hz, 2H, (CH$_3$)$_2$C*H*), 1.73 (s, 6H, xanthene-C*H*$_3$), 1.71 (s, 6H, xanthene-C*H*$_3$), 1.23 (s, 3H, Pd-C*H*$_3$), 1.05 (d, ^3J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 0.96 (d, ^3J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 0.80 (d, ^3J = 6.7 Hz, 6H, (C*H*$_3$)$_2$CH), 0.74 (d, ^3J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, the resonances from the BAF anion were also included): δ 179.0, 174.6, 172.4 (CO), 162.2 (q, J_{CB} = 49.5 Hz, C$_{\mathrm{ipso}}$), 148.0, 147.8, 147.7, 147.5, 147.4, 147.3, 146.9, 146.8, 146.8, 146.7, 146.1, 145.8, 145.3, 141.6, 141.0, 140.3, 139.5, 137.8, 137.0, 135.0 (C$_\mathrm{o}$), 133.9, 131.9, 131.8, 131.6, 131.4, 131.0, 130.6, 130.5, 130.4, 130.1, 129.9 (q, J_{CF} = 31.7 Hz, C$_\mathrm{m}$), 129.8, 129.5, 128.9, 128.8, 128.8, 128.7, 128.6, 127.5, 126.5, 126.4 (q, J_{CF} = 272.1 Hz, CF$_3$), 126.0, 124.1, 124.0, 123.4, 123.3, 123.1, 120.6, 117.6 (m, C$_\mathrm{p}$), 34.8 (C(*C*H$_3$)$_2$), 32.9 (C(*C*H$_3$)$_2$), 32.6 (C(*C*H$_3$)$_2$), 29.9 (*C*H(CH$_3$)$_2$), 29.7 (*C*H(CH$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$), 11.4 (Pd-*C*H$_3$). IR (KBr) 2131cm^{-1} [ν (CO)].

Pd-OMe-CO ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.01 (dd, ^3J = 10.8 Hz, ^4J = 8.2 Hz, 2H, aryl-*H*), 7.67 (m, 10H, BAF-*H*), 7.64 (s, 2H, BAF-*H*), 7.58 (m, 4H, aryl-*H*), 7.57 (m, 6H, aryl-*H*), 7.42 (d, ^3J = 8.7 Hz, 2H, aryl-*H*), 7.37 (d, ^3J = 8.8 Hz, 2H, aryl-*H*), 7.28 (m, 4H, aryl-*H*), 7.20 (m, 4H, aryl-*H*), 6.66 (dd, ^3J = 8.0 Hz, ^4J = 2.8 Hz, 3H, An-*H*), 6.56 (d, ^3J = 8.8 Hz, 1H, An-*H*), 6.36 (d, ^3J = 7.6 Hz, 1H, An-*H*), 3.74 (s, 3H, OC*H*$_3$), 3.73 (s, 3H, OC*H*$_3$), 3.05 (sept, ^3J = 6.78 Hz, 2H, (CH$_3$)$_2$C*H*), 2.93 (sept, ^3J = 6.78 Hz, 2H, (CH$_3$)$_2$C*H*), 1.81 (s, 6H, xanthene-C*H*$_3$), 1.78 (s, 6H, xanthene-C*H*$_3$), 1.44 (s, 3H, Pd-C*H*$_3$), 1.22 (d, ^3J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 8.01 (dd, ^3J = 10.8 Hz, ^4J = 8.2 Hz, 6H, (C*H*$_3$)$_2$CH), 0.92 (d, ^3J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH), 0.86 (d, ^3J = 6.8 Hz, 6H, (C*H*$_3$)$_2$CH). IR (KBr) 2131cm^{-1} [ν (CO)].

General in-Situ Activated Polymerization Procedure. A 350 mL glass thick-walled pressure vessel was charged with required amount of NaBAF, required amount of comonomers for the case of copolymerization, toluene and a magnetic stir 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 the desired temperature using an oil bath and allowed to equilibrate for 10 min. The metal complex was injected to initiate polymerization and stirred continuously for the desired time. 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.

2. Plot of the molecular weight versus time

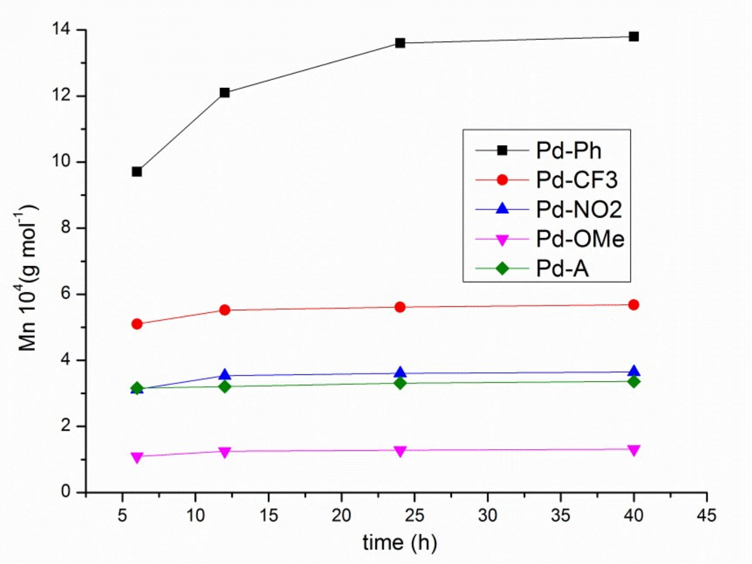


Figure S1. Plot of the molecular weight versus time for these Pd complexes.

3. Spectra data

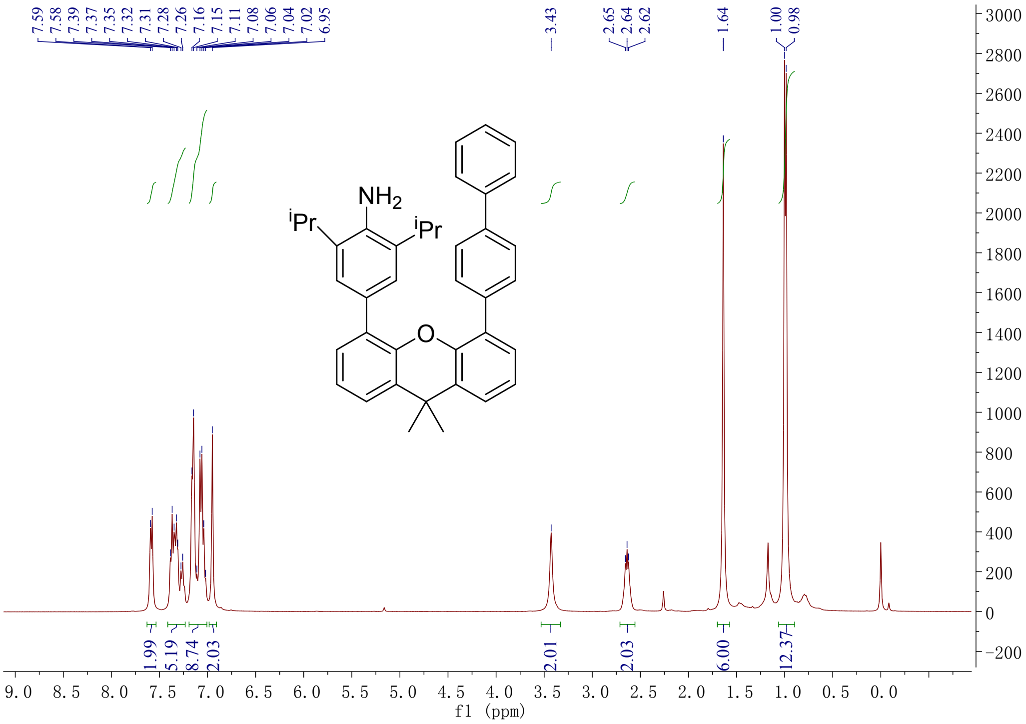


Figure S2. ^{1}H NMR spectrum of **4-(2,6-diisopropylaniline)-5-(4-biphenyl)-(9,9-dimethylxanthene -4,5-diyl)** in $CDCl_3$.

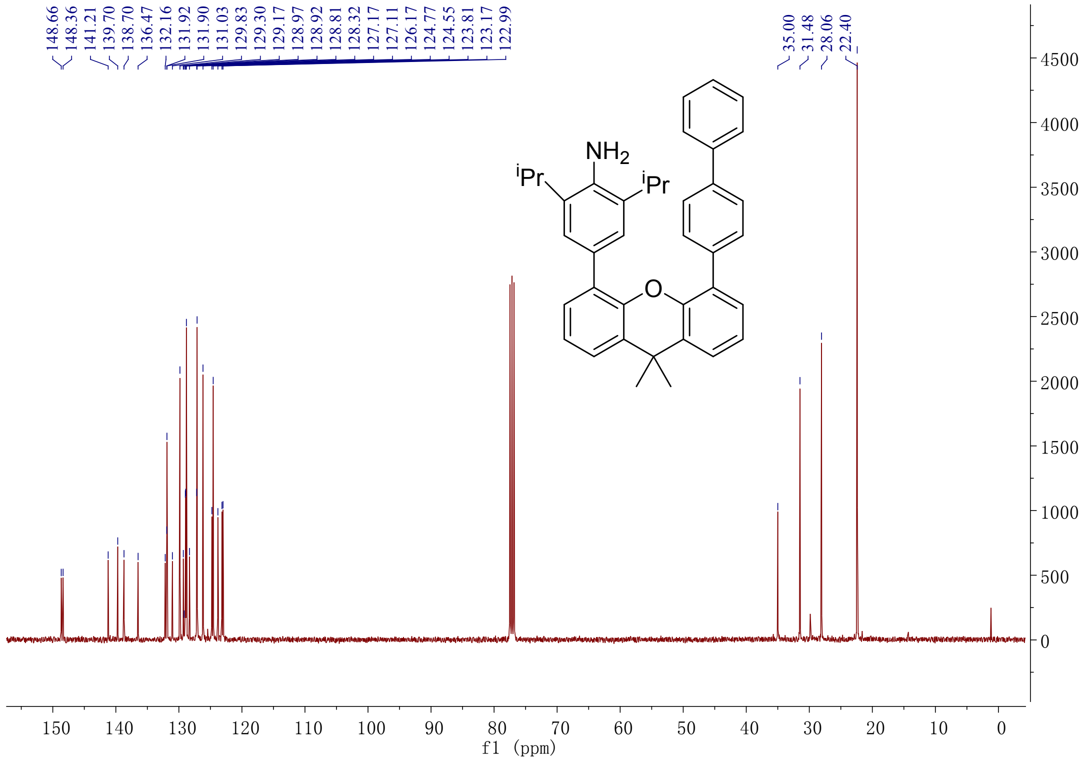


Figure S3. ^{13}C NMR spectrum of **4-(2,6-diisopropylaniline)-5-(4-biphenyl)-(9,9-dimethylxanthene -4,5-diyl)** in CDCl$_3$.

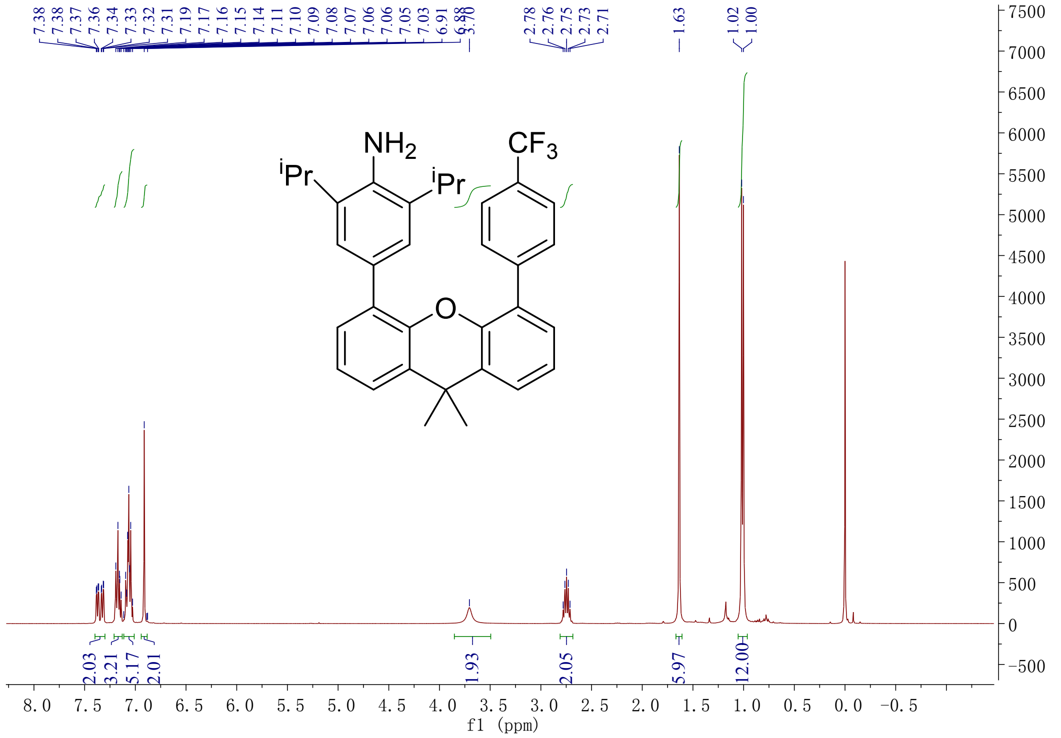


Figure S4. ^{1}H NMR spectrum of **4-(2,6-diisopropylaniline)-5-(4-trifluoridephenyl)-(9,9-dimethyl xanthene-4,5-diyl)** in CDCl$_3$.

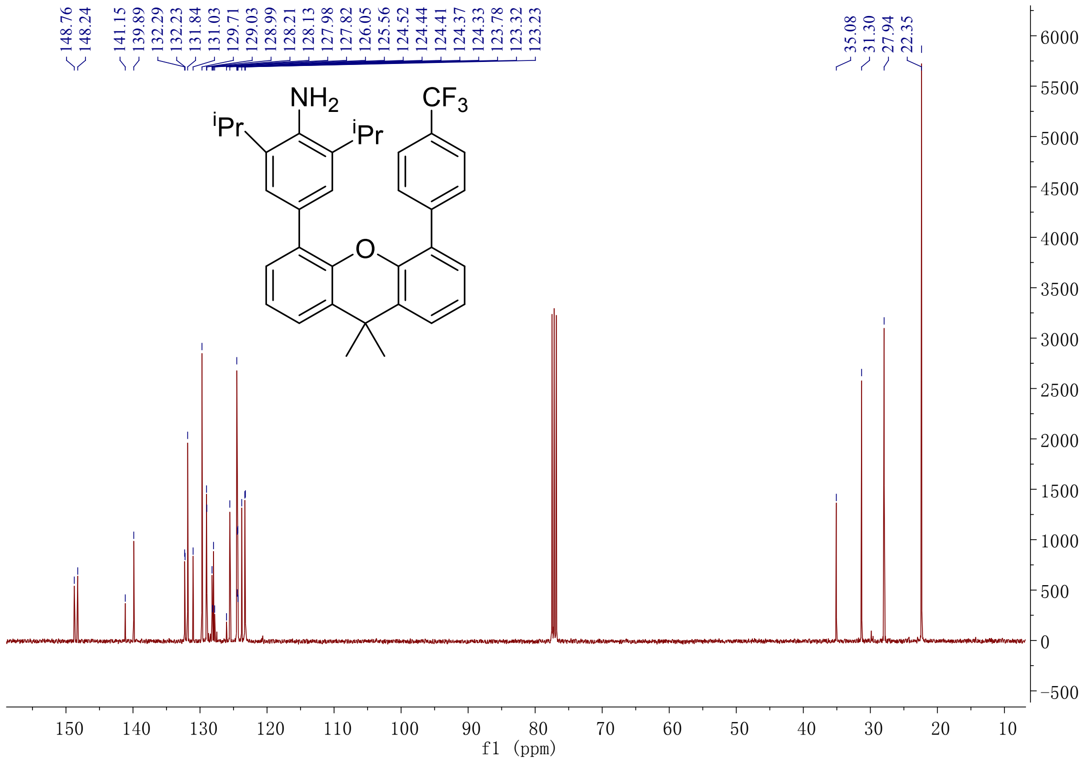


Figure S5. ^{13}C NMR spectrum of **4-(2,6-diisopropylaniline)-5-(4-trifluoridephenyl) -(9,9-dimethylxanthene-4,5-diyl)** in $CDCl_3$.

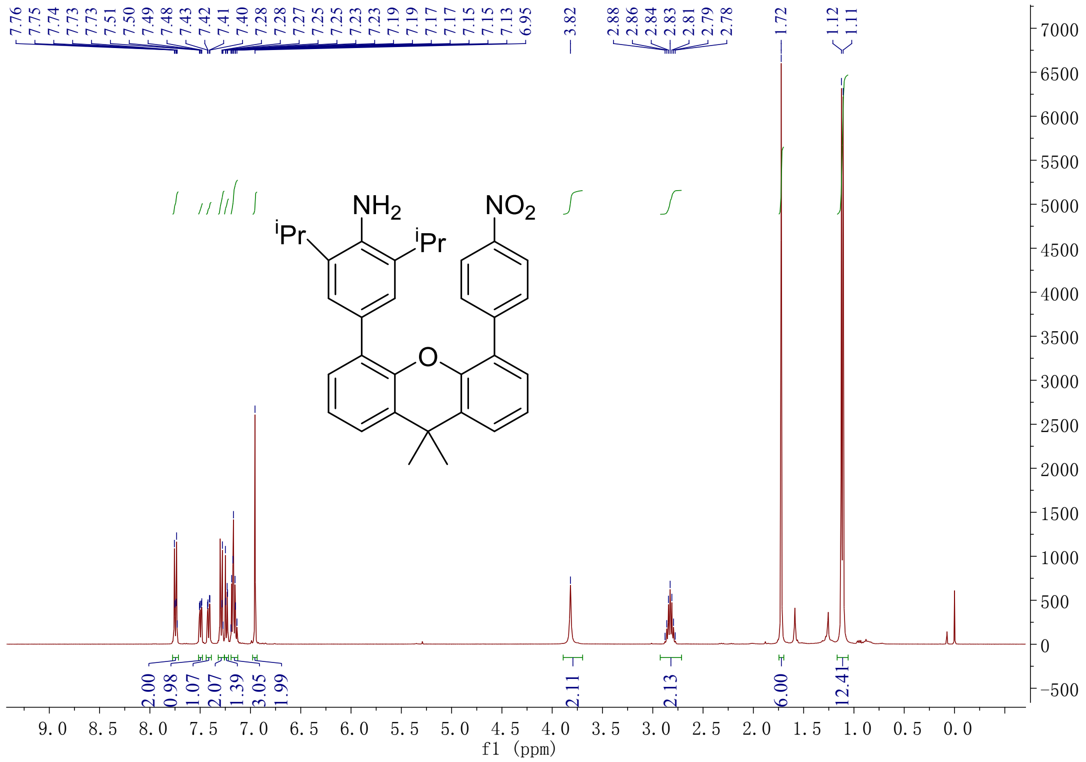


Figure S6. ^{1}H NMR spectrum of **4-(2,6-diisopropylaniline)-5-(4-nitrobenzene)-(9,9-dimethyl xanthene-4,5-diyl)** in $CDCl_3$.

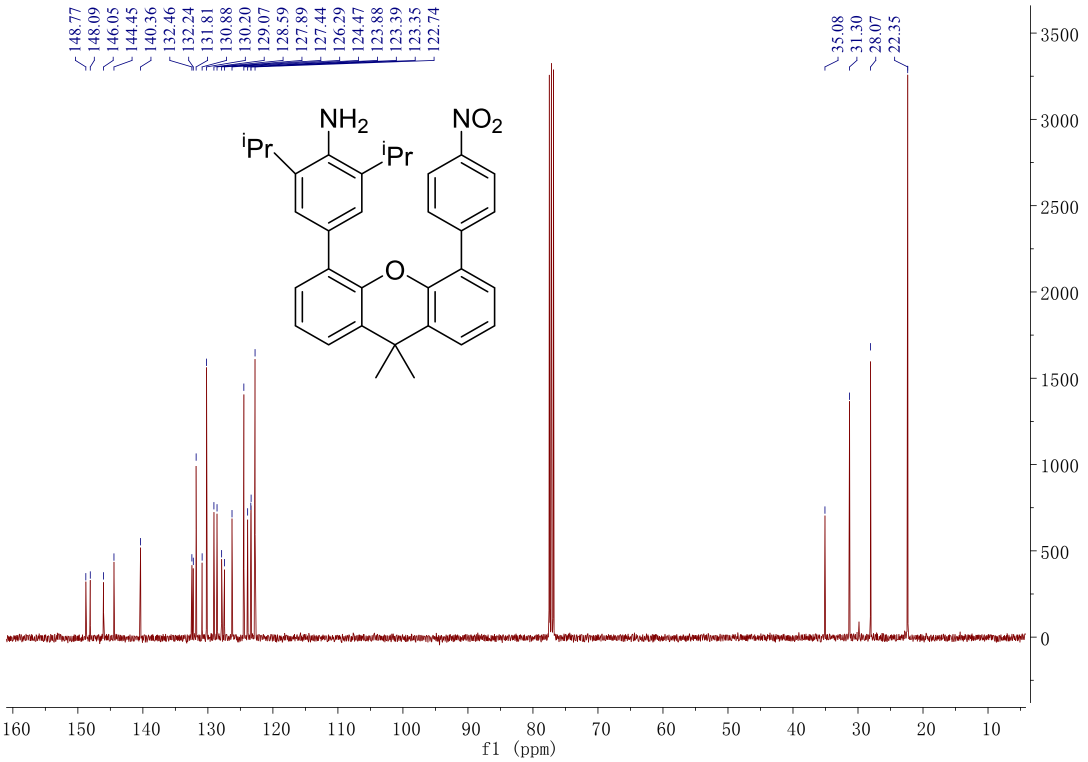


Figure S7. ^{13}C NMR spectrum of **4-(2,6-diisopropylaniline)-5-(4-nitrobenzene)-(9,9-dimethylxanthene-4,5-diyl)** in $CDCl_3$.

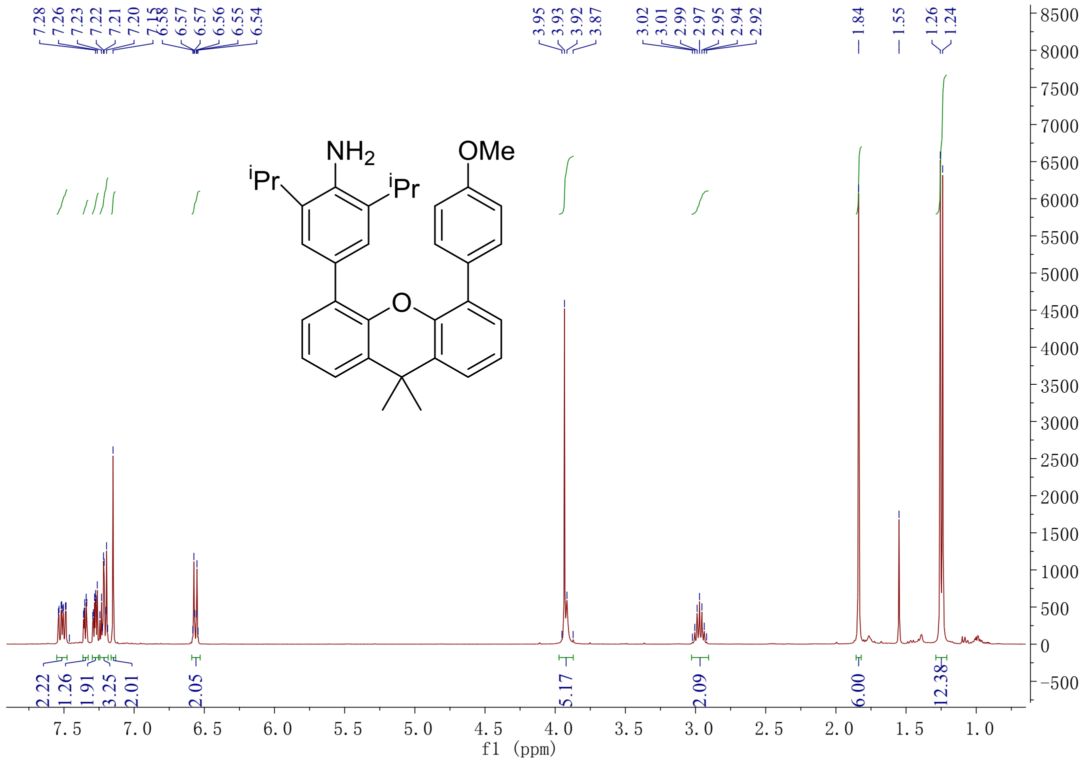


Figure S8. ^{1}H NMR spectrum of **4-(2,6-diisopropylaniline)-5-(4-methoxybenzene)-(9,9-dimethylxanthene-4,5-diyl)** in $CDCl_3$.

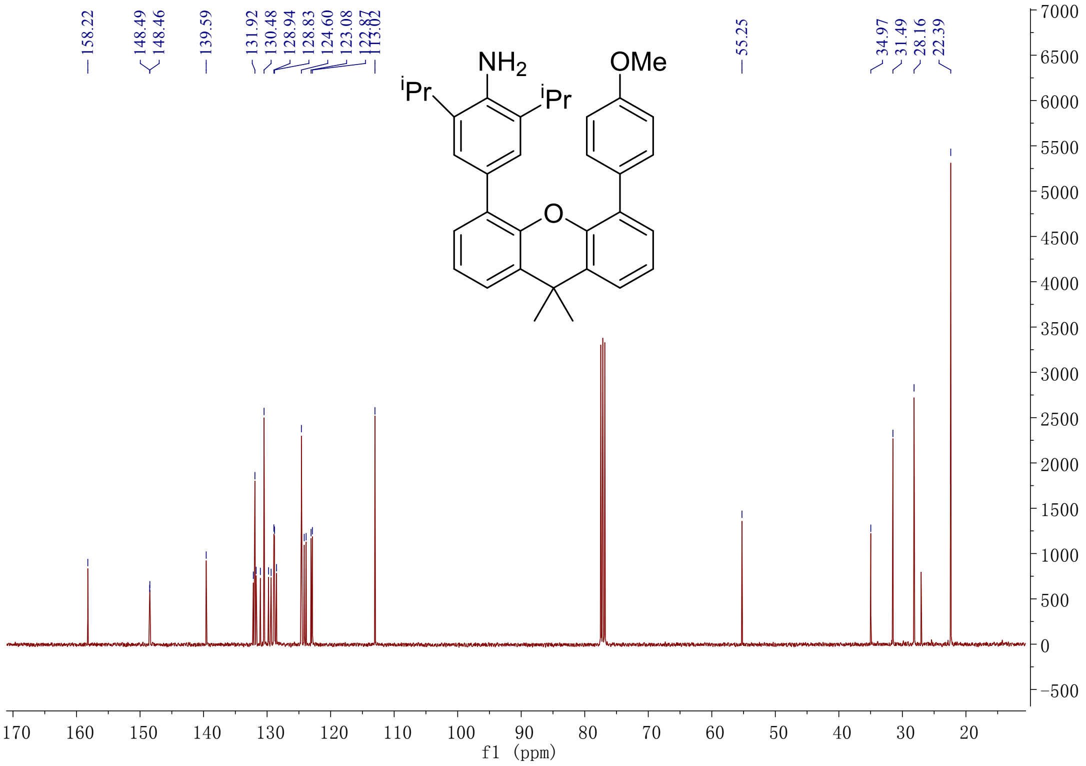


Figure S9. ^{13}C NMR spectrum of **4-(2,6-diisopropylaniline)-5-(4-methoxybenzene)-(9,9-dimethyl xanthene-4,5-diyl)** in $CDCl_3$.

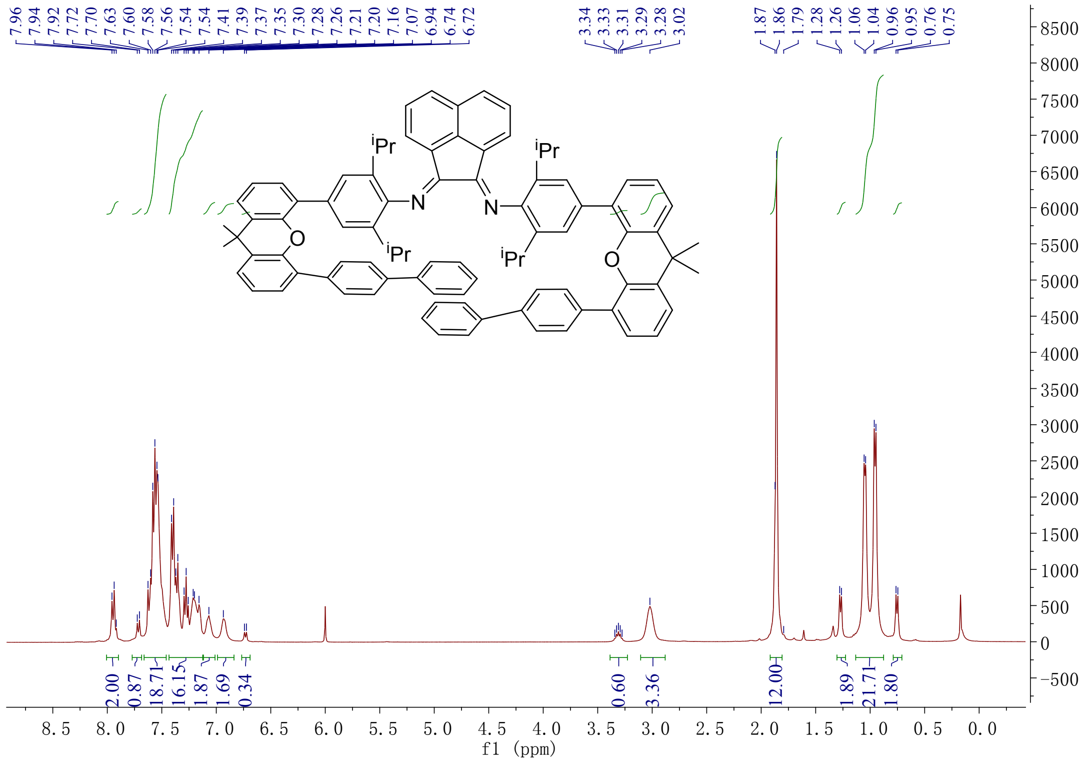


Figure S10. ^{1}H NMR spectrum of **L-Ph** in $C_2D_2Cl_4$.

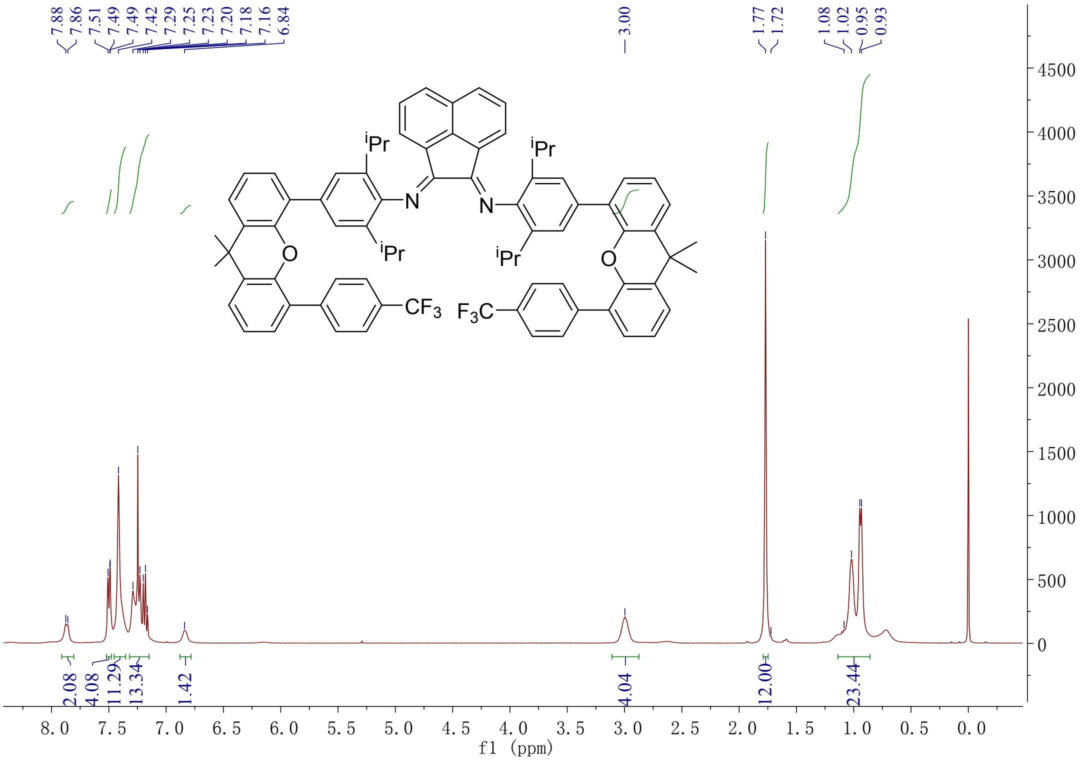


Figure S11. ^{1}H NMR spectrum of **L-CF$_3$** in CDCl$_3$.

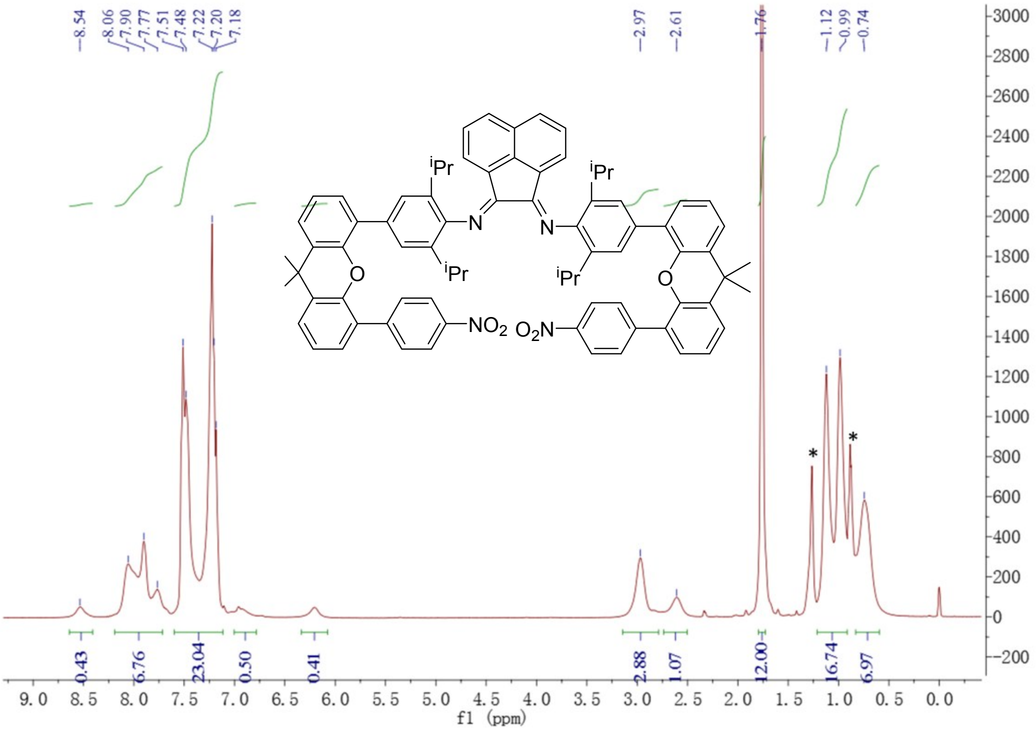


Figure S12. ^{1}H NMR spectrum of **L-NO2** in CDCl$_3$. *Hexane.

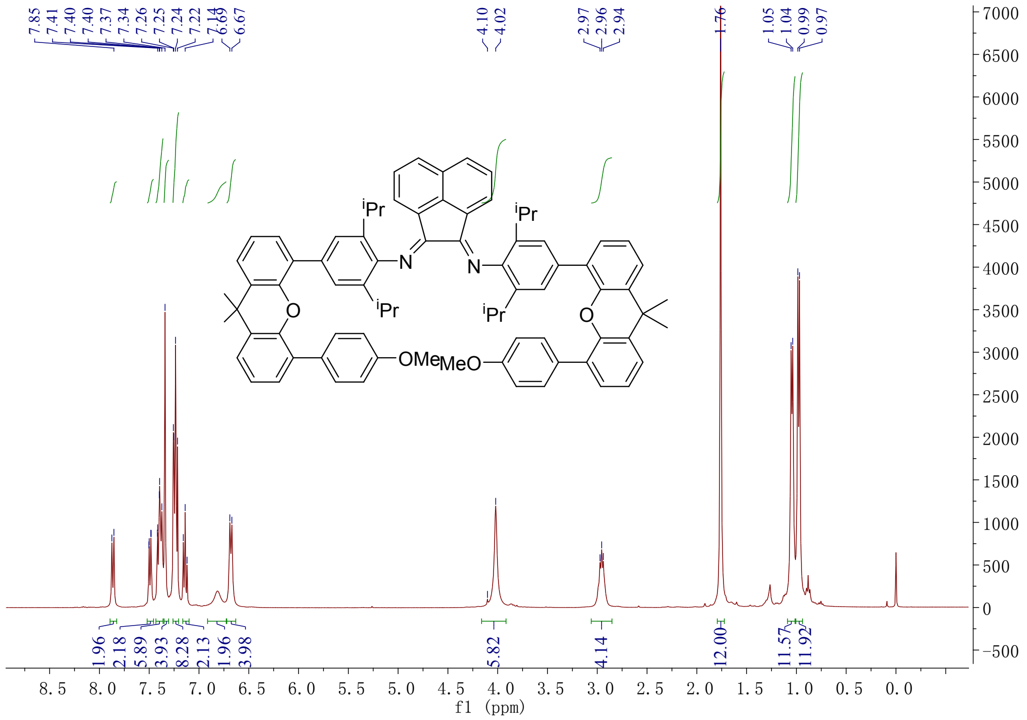


Figure S13. ^{1}H NMR spectrum of **L-OMe** in $CDCl_3$.

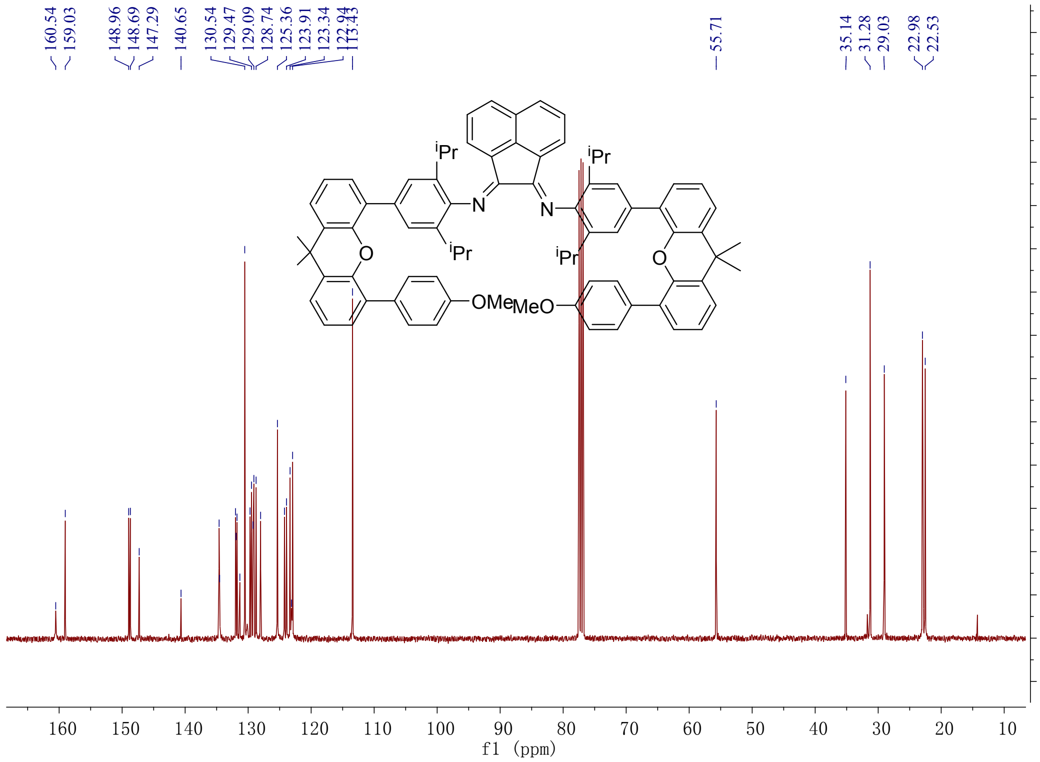


Figure S14. ^{13}C NMR spectrum of **L-OMe** in $CDCl_3$.

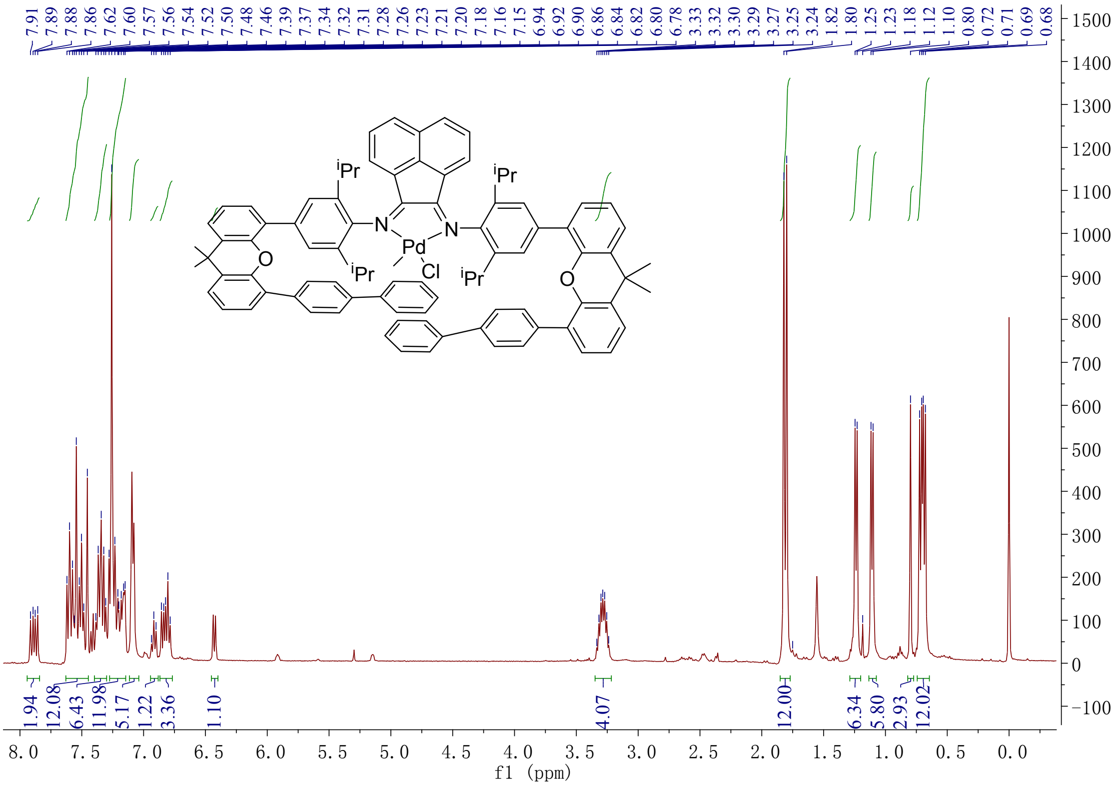


Figure S15. ^{1}H NMR spectrum of **Pd-Ph** in $CDCl_3$.

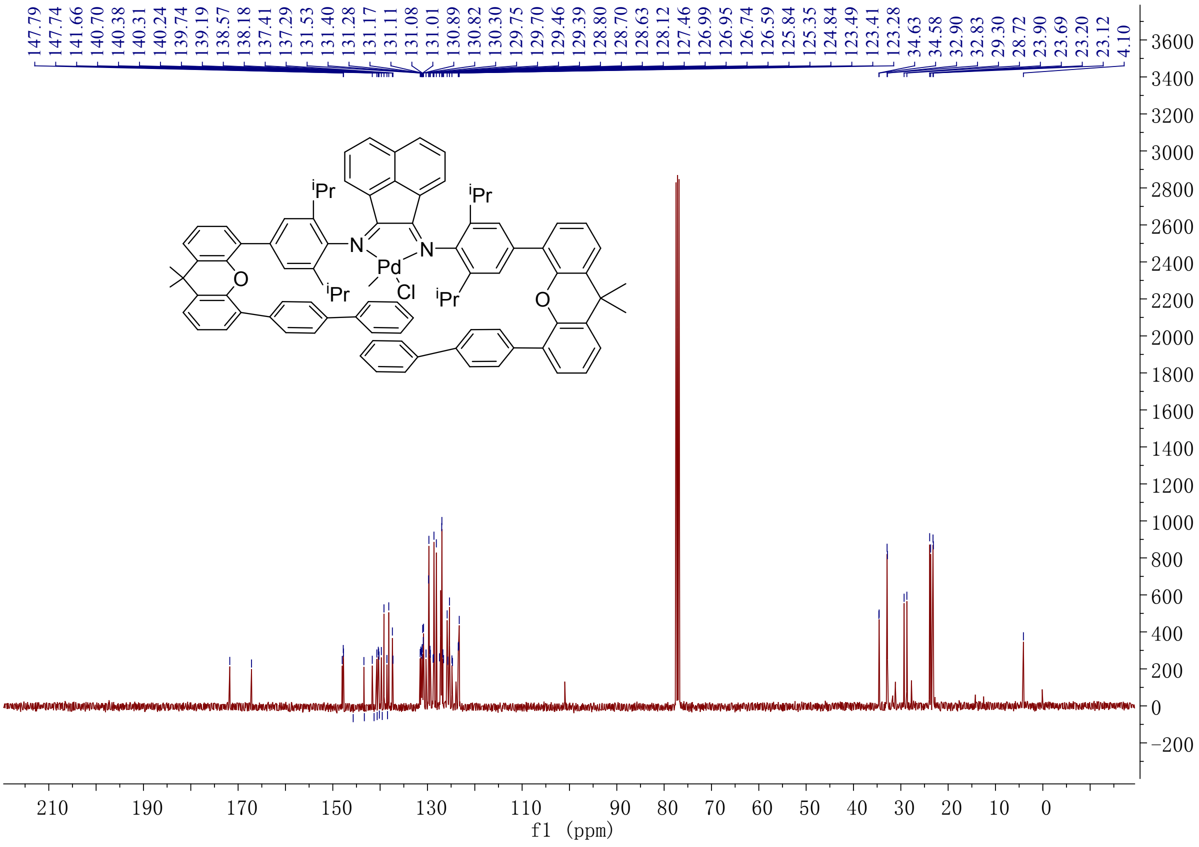


Figure S16. ^{13}C NMR spectrum of **Pd-Ph** in $CDCl_3$.

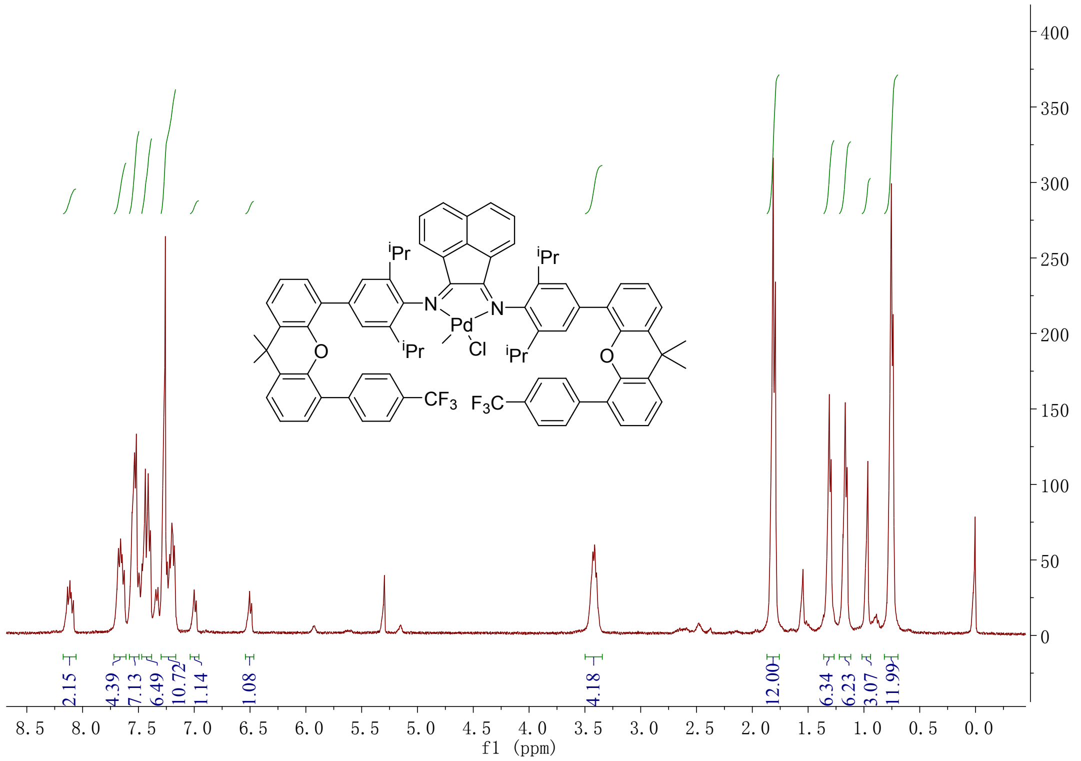


Figure S17. ^{1}H NMR spectrum of **Pd-CF$_3$** in CDCl$_3$.

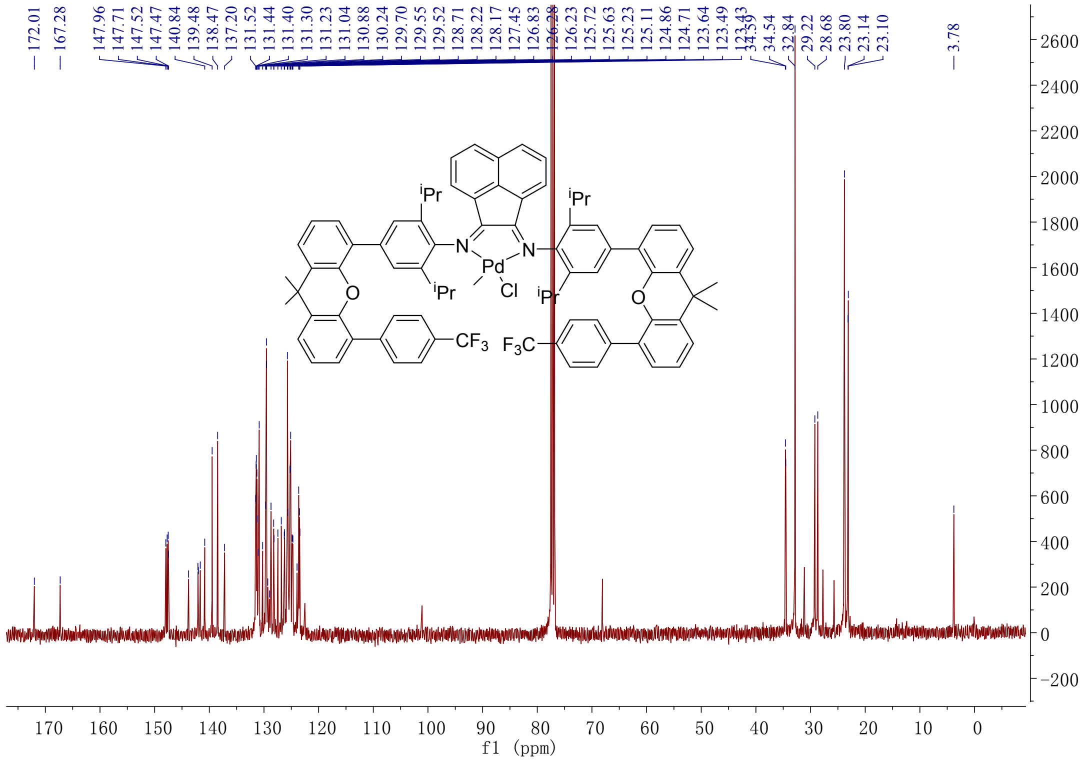


Figure S18. ^{13}C NMR spectrum of **Pd-CF$_3$** in CDCl$_3$.

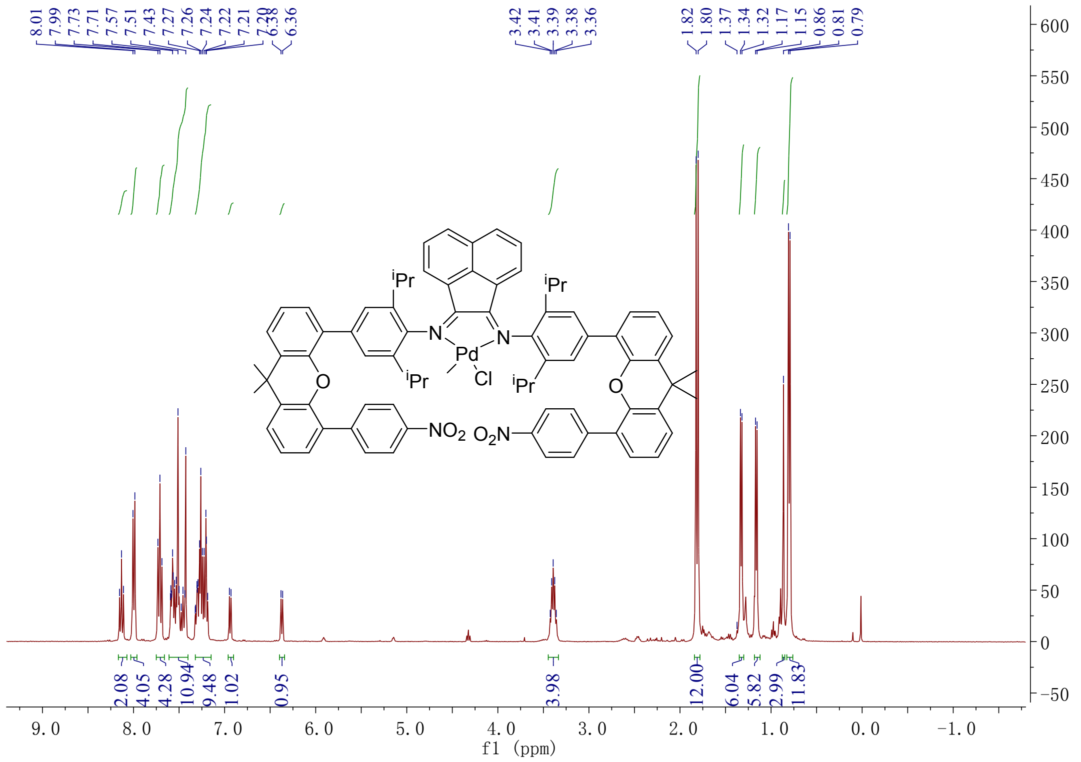


Figure S19. ^{1}H NMR spectrum of **Pd-NO$_2$** in CDCl$_3$.

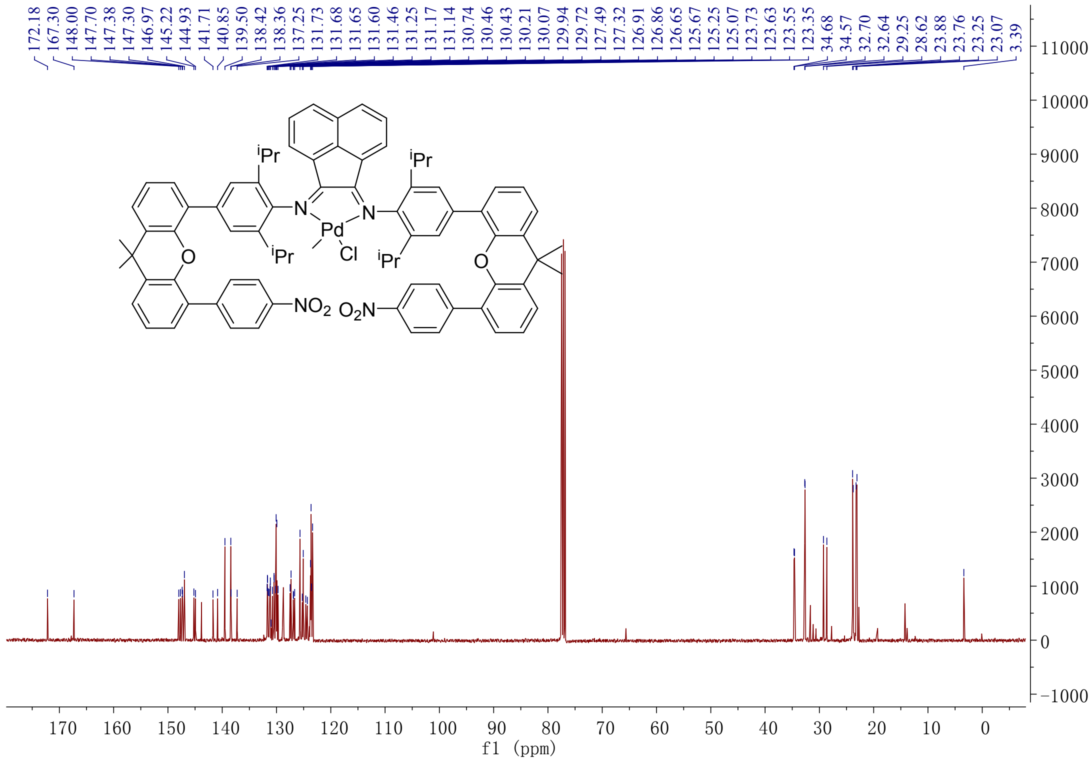


Figure S20. ^{13}C NMR spectrum of **Pd-NO$_2$** in CDCl$_3$.

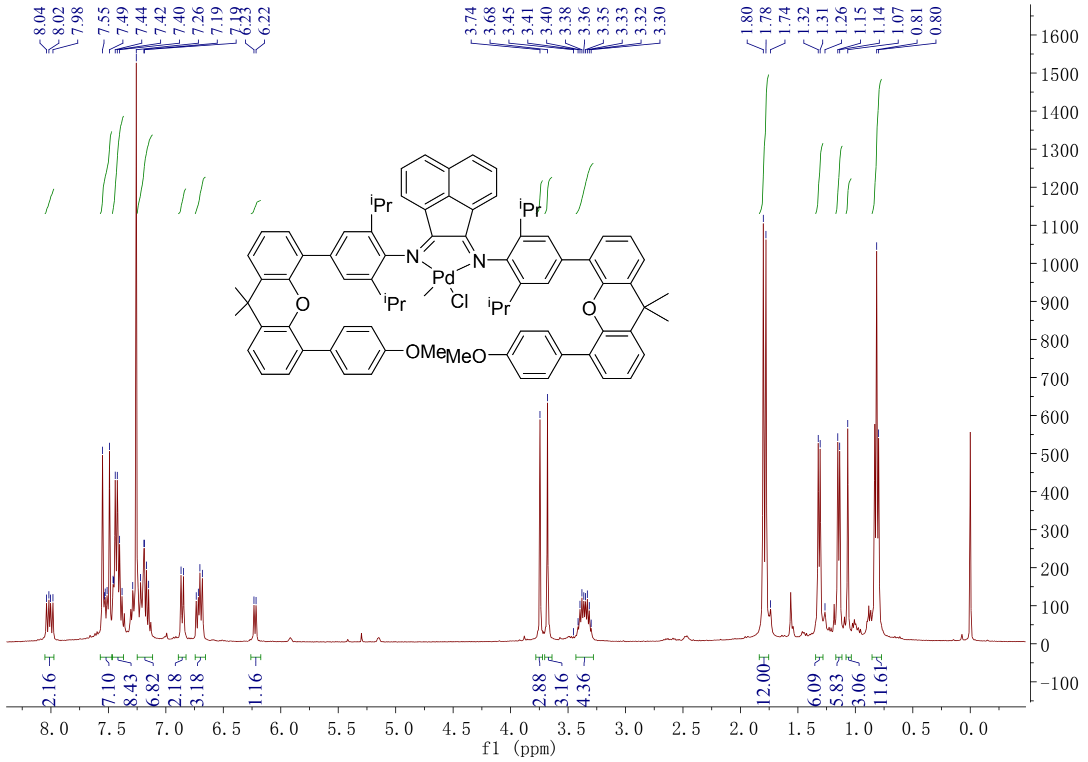


Figure S21. ^{1}H NMR spectrum of **Pd-OMe** in $CDCl_3$.

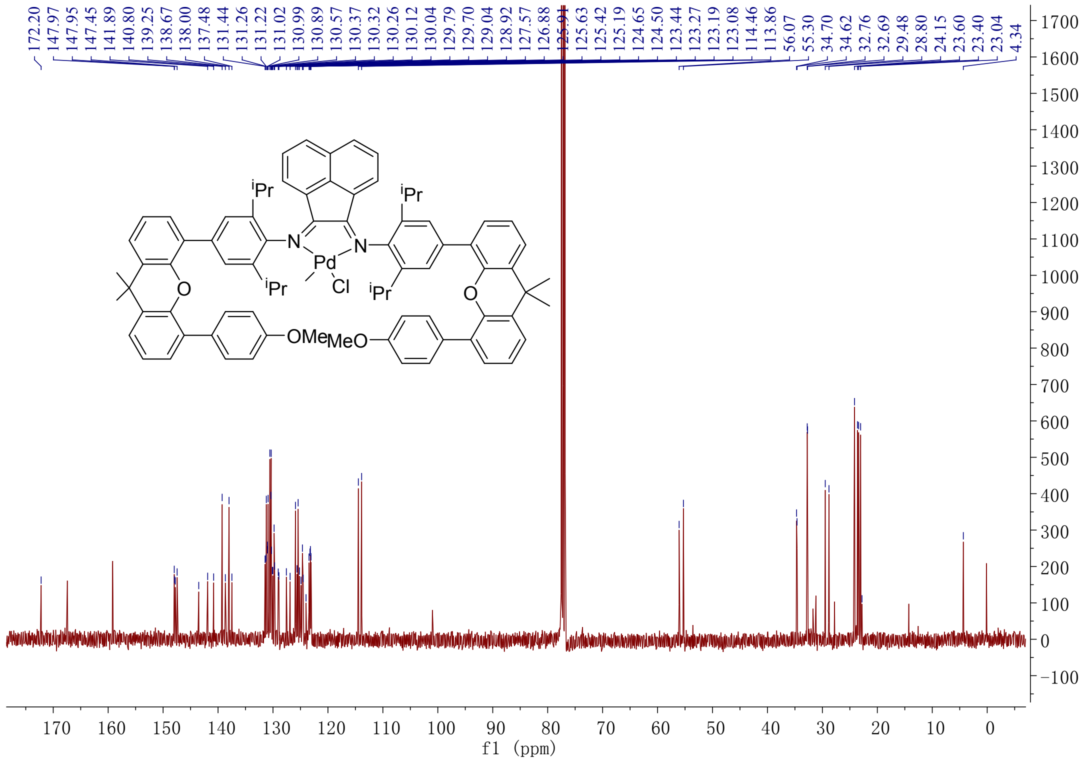


Figure S22. ^{13}C NMR spectrum of **Pd-OMe** in $CDCl_3$.

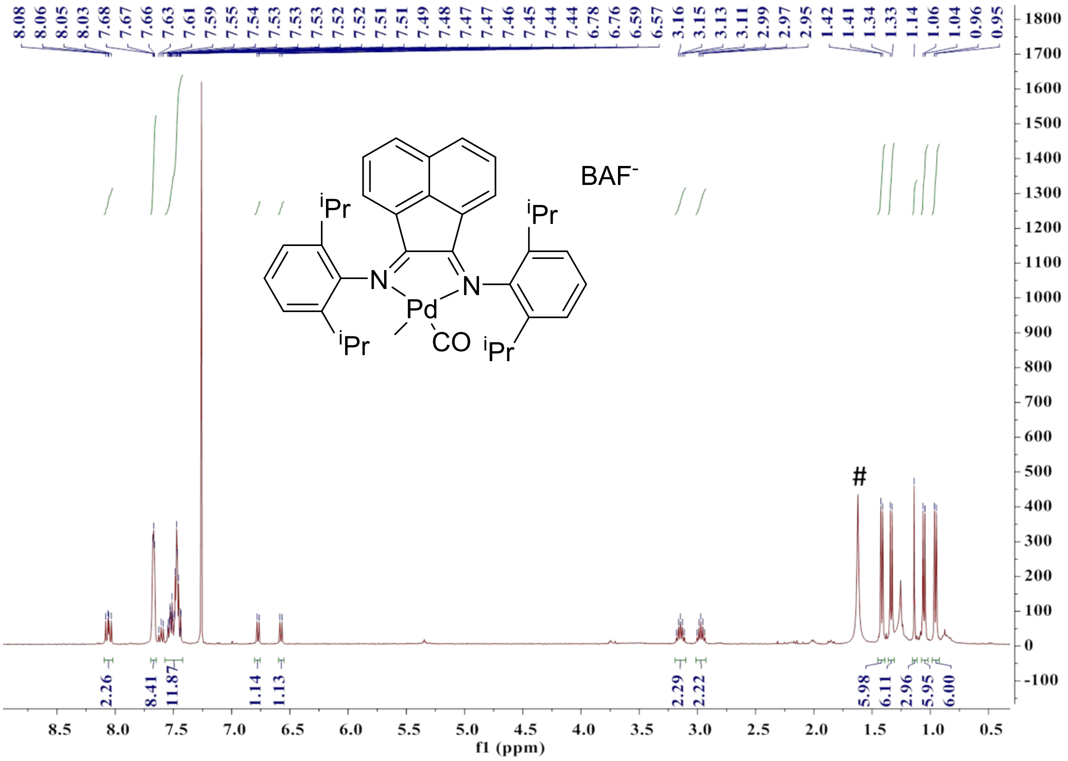


Figure S23. ^{1}H NMR spectrum of **Pd-A-CO** in $CDCl_3$. #H_2O.

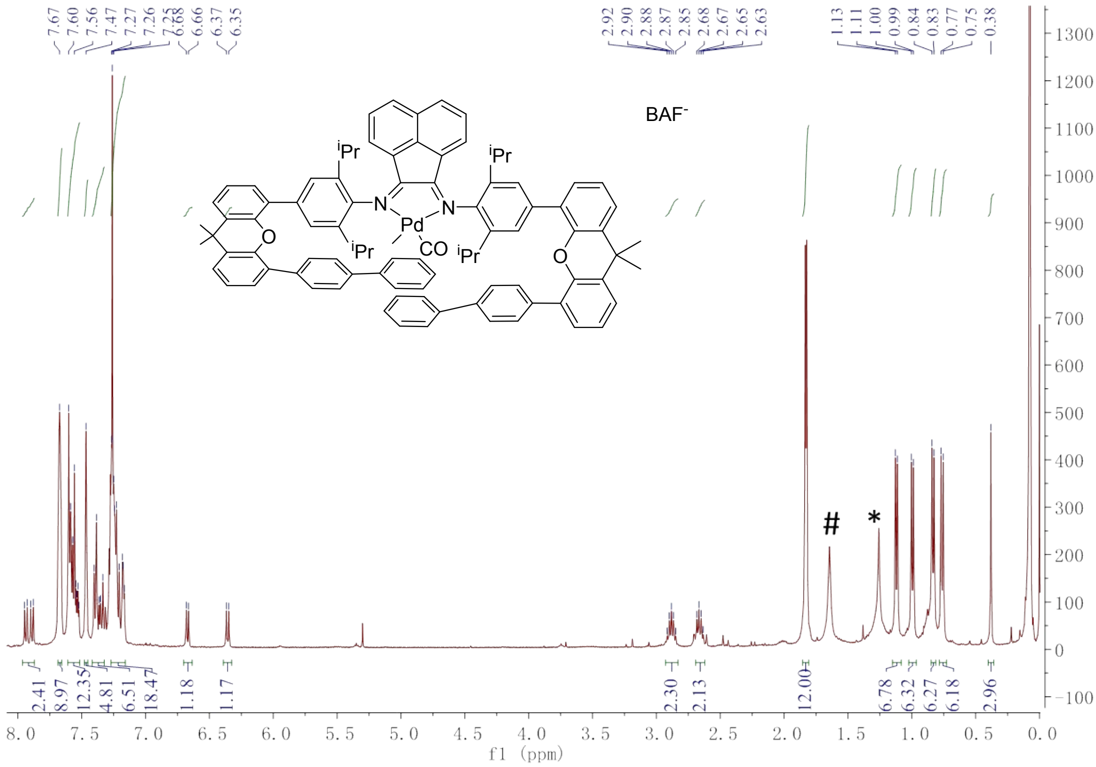


Figure S24. ^{1}H NMR spectrum of **Pd-Ph-CO** in $CDCl_3$. #H_2O.*Hexane.

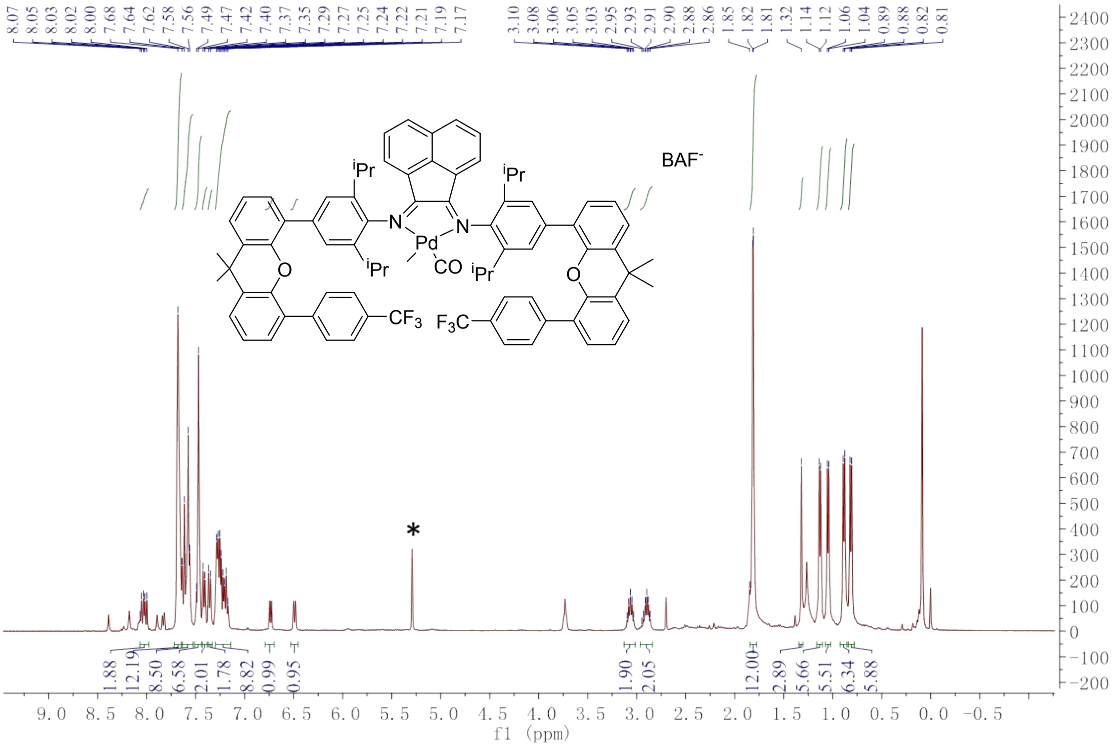


Figure S25. ^{1}H NMR spectrum of **Pd-CF$_3$-CO** in CDCl$_3$.*CH$_2$Cl$_2$.

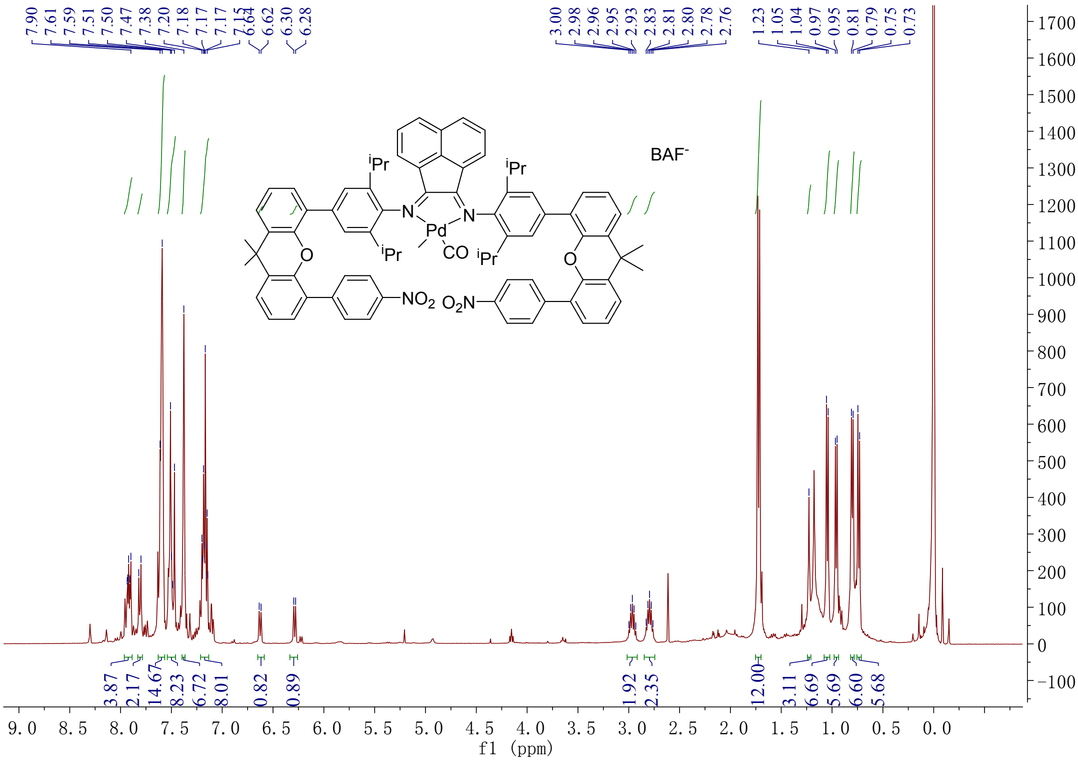


Figure S26. ^{1}H NMR spectrum of **Pd-NO$_2$-CO** in CDCl$_3$.

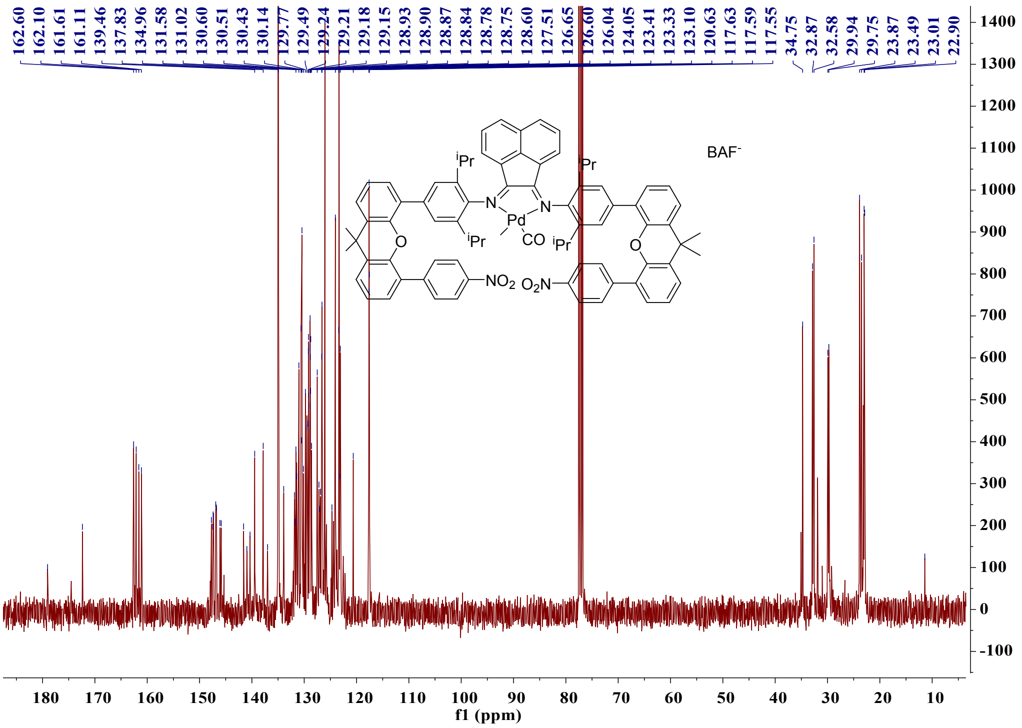


Figure S27. ^{13}C NMR spectrum of **Pd-NO$_2$-CO** in CDCl$_3$.

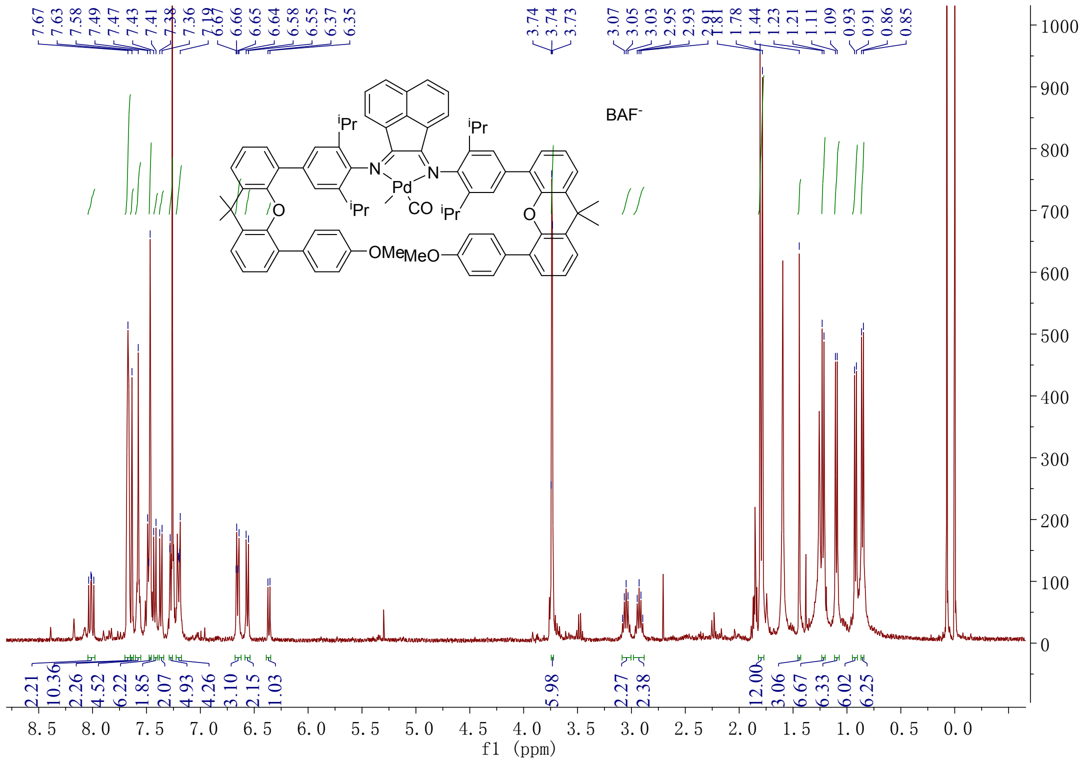


Figure S28. ^{1}H NMR spectrum of **Pd-OMe-CO** in CDCl$_3$.

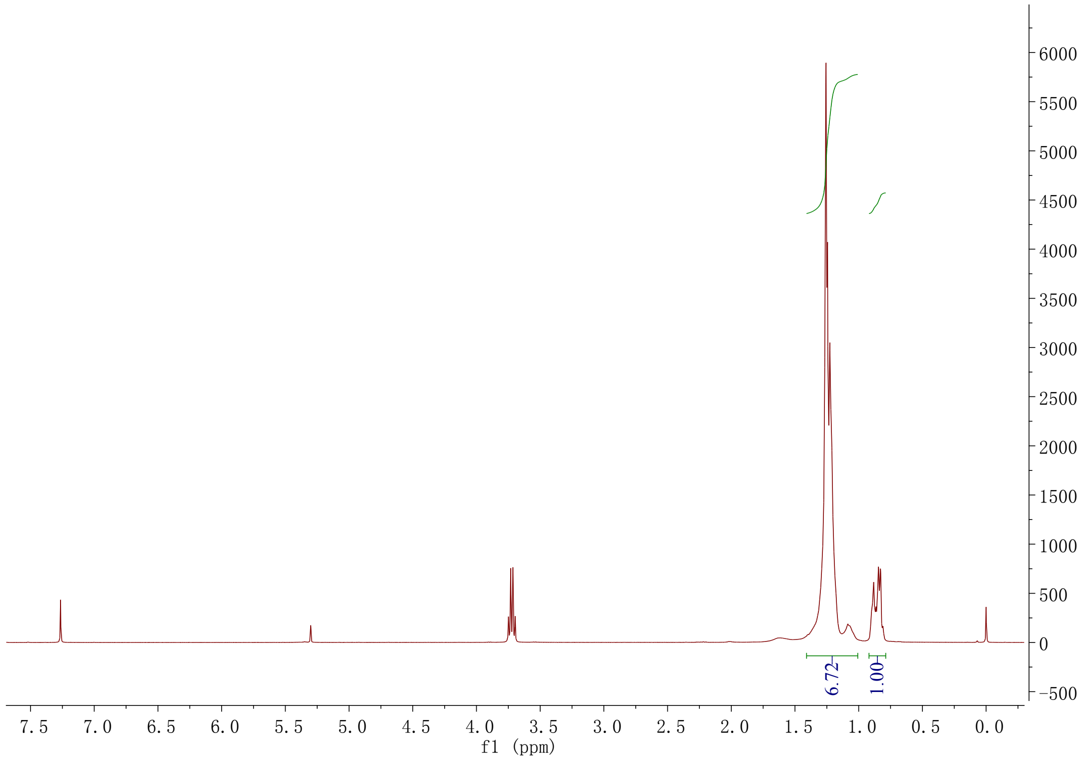


Figure S29. ^{1}H NMR spectrum of polyethylene obtained from **Pd-Ph** at 20 ^{o}C.

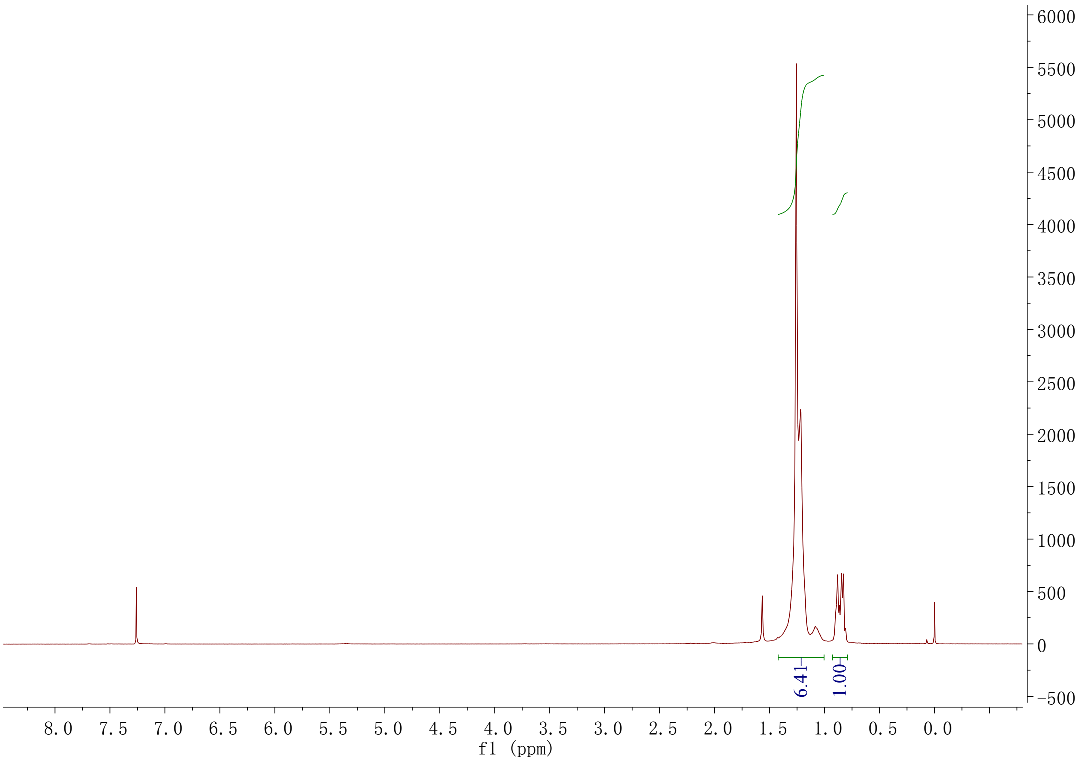


Figure S30. ^{1}H NMR spectrum of polyethylene obtained from **Pd-CF$_3$** at 20 ^{o}C.

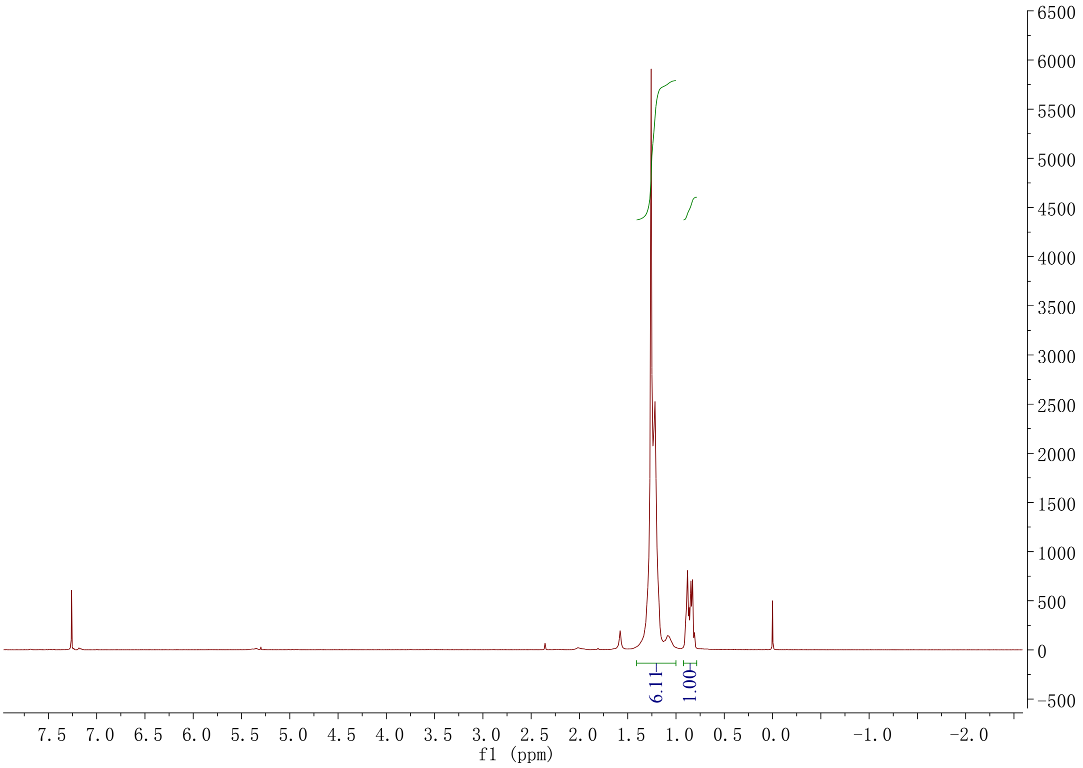


Figure S31. ^{1}H NMR spectrum of polyethylene obtained from **Pd-NO$_2$** at 20 ^{o}C.

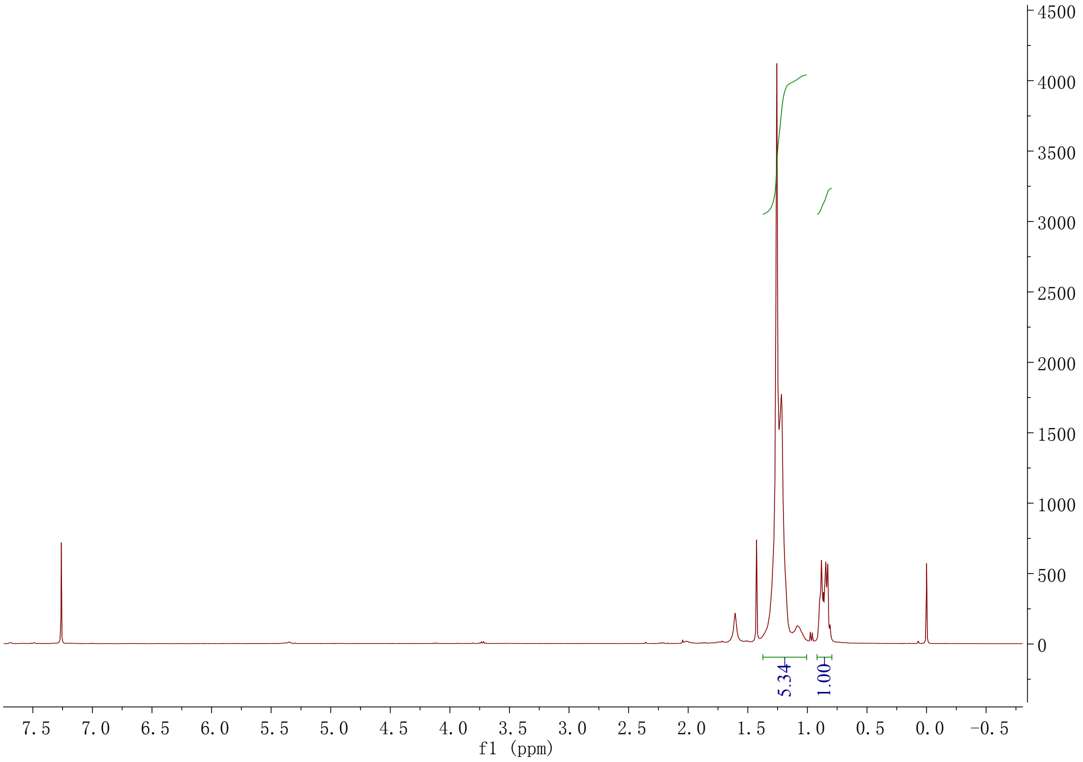


Figure S32. ^{1}H NMR spectrum of polyethylene obtained from **Pd-OMe** at 20 ^{o}C.

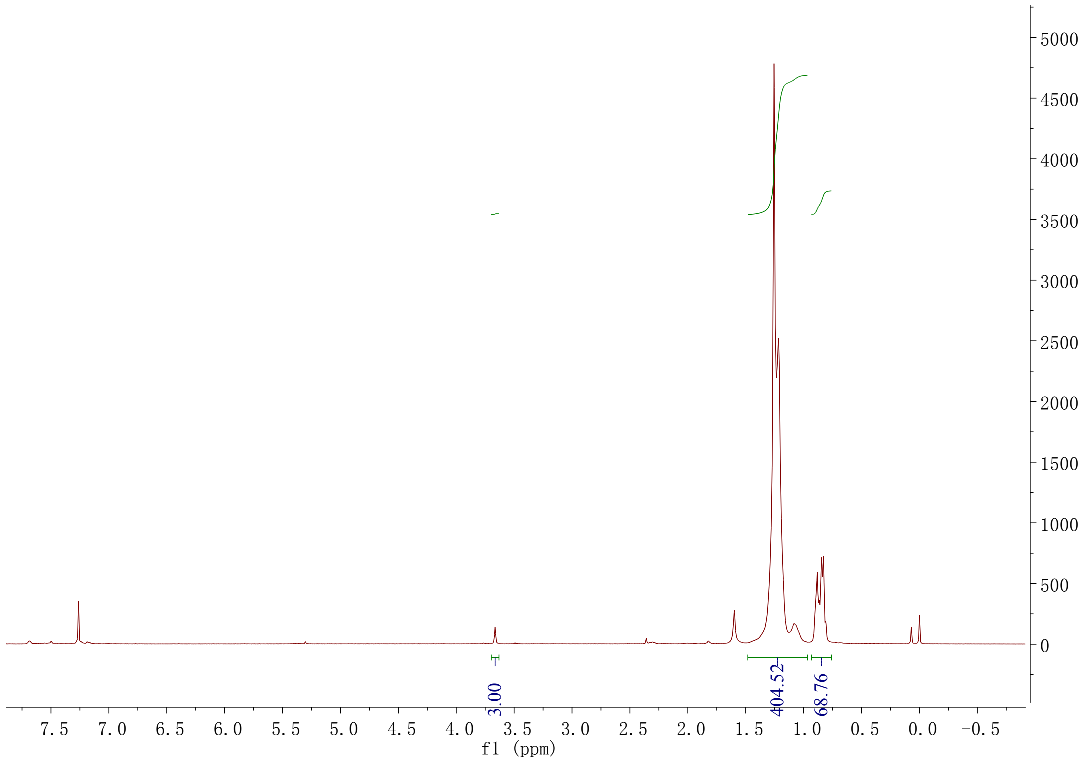


Figure S33. ^{1}H NMR spectrum of polyethylene-co-MA obtained from **Pd-OMe** at 20 ^{o}C.

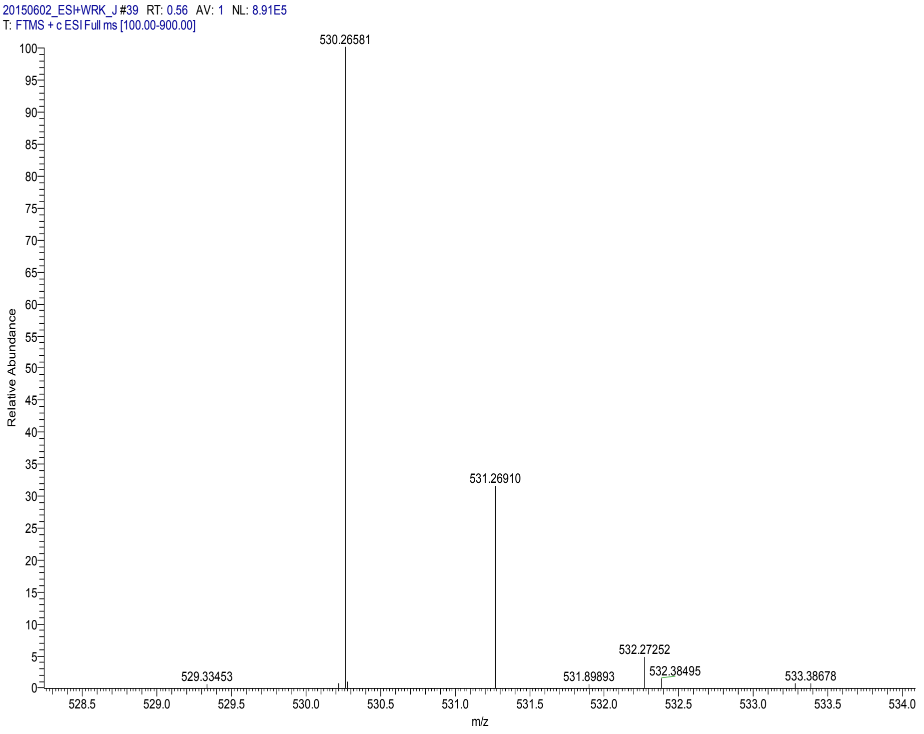


Figure S34. HRMS (m/z) of 4-(2,6-diisopropylaniline)-5-(4-trifluoridephenyl)-(9,9- dimethylxanthene-4,5-diyl)**.**

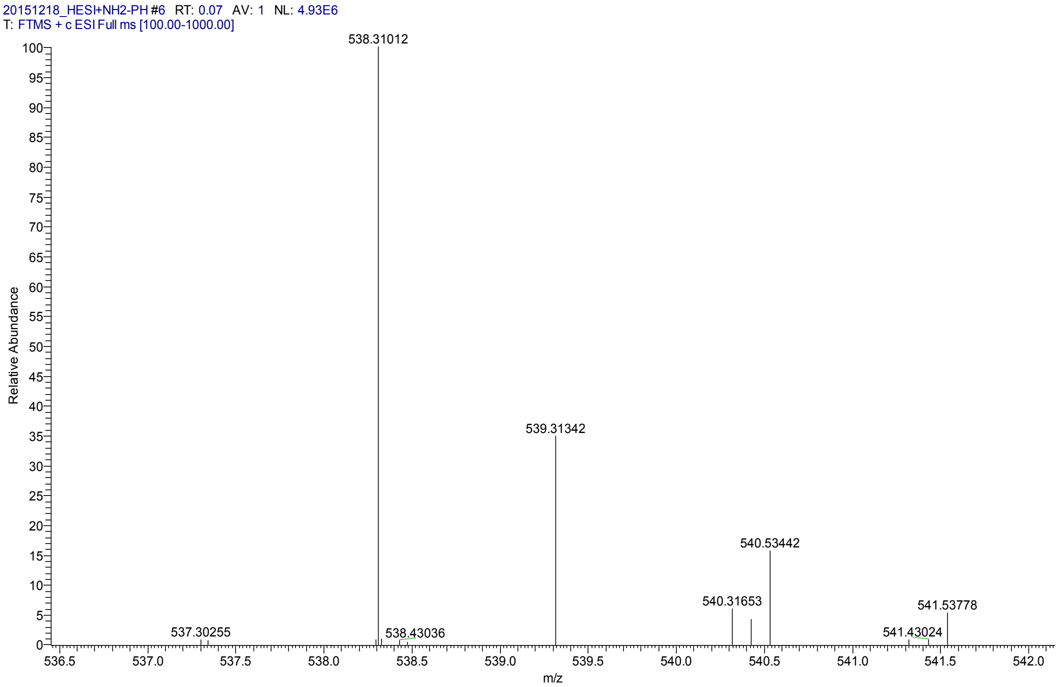


Figure S35. HRMS (m/z) of 4-(2,6-diisopropylaniline)-5-(4-biphenyl)-(9,9-dimethy lxanthene-4,5-diyl).

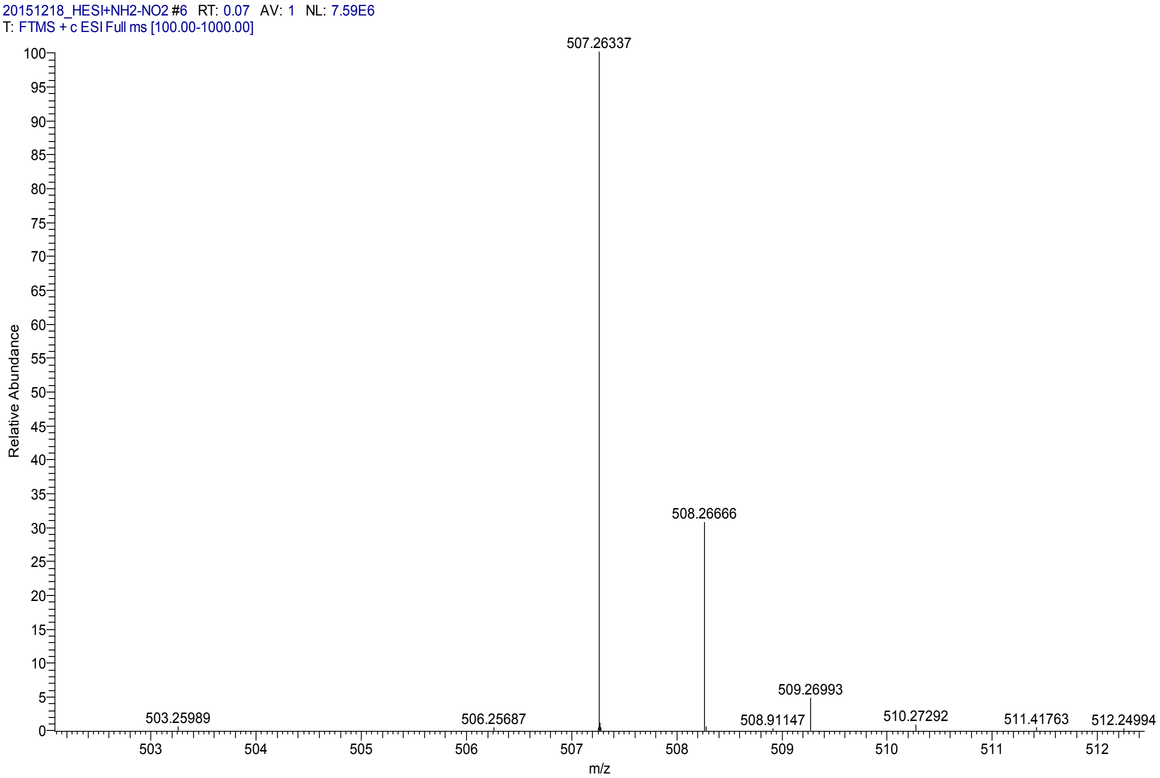
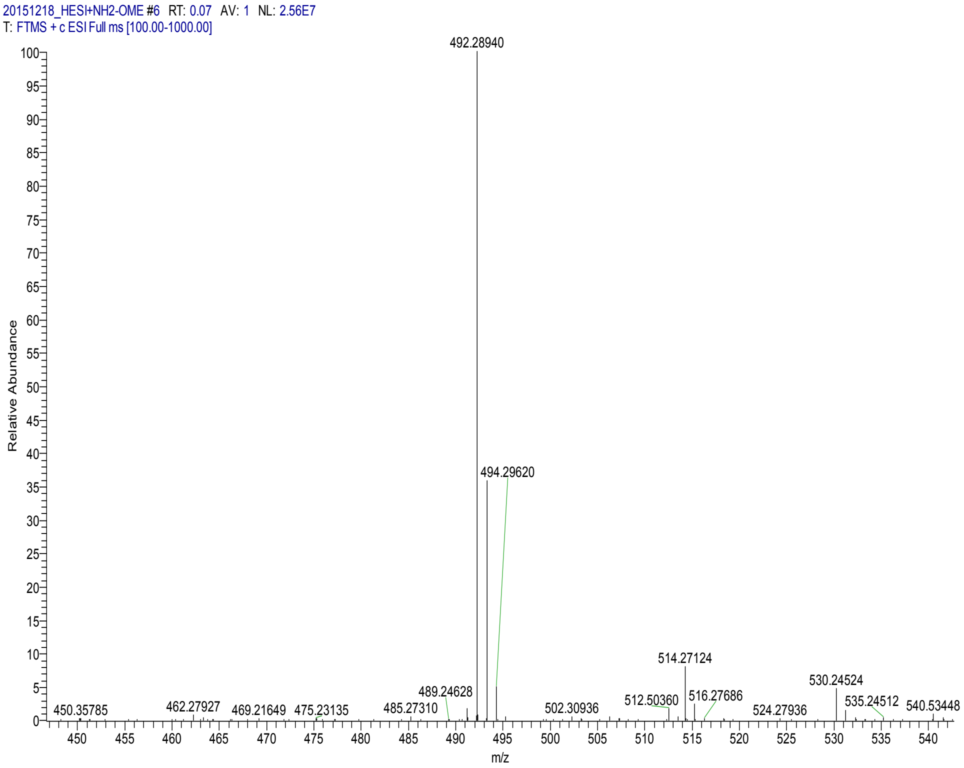


Figure S36. HRMS (m/z) of 4-(2,6-diisopropylaniline)-5-(4-nitrobenzene)-(9,9-di methylxanthene-4,5-



diyl).

Figure S37. HRMS (m/z) of 4-(2,6-diisopropylaniline)-5-(4-methoxybenzene)-(9,9- dimethylxanthene-4,5-diyl).

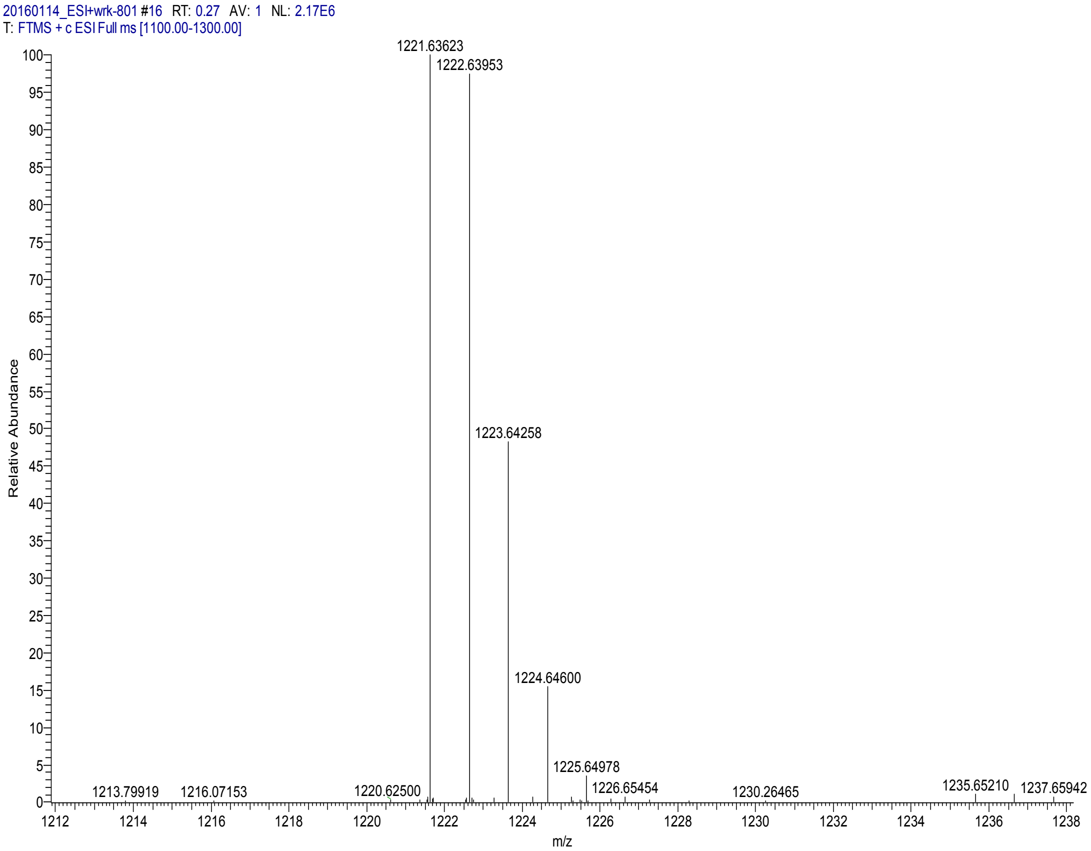


Figure S38. HRMS (m/z) of **L-Ph.**

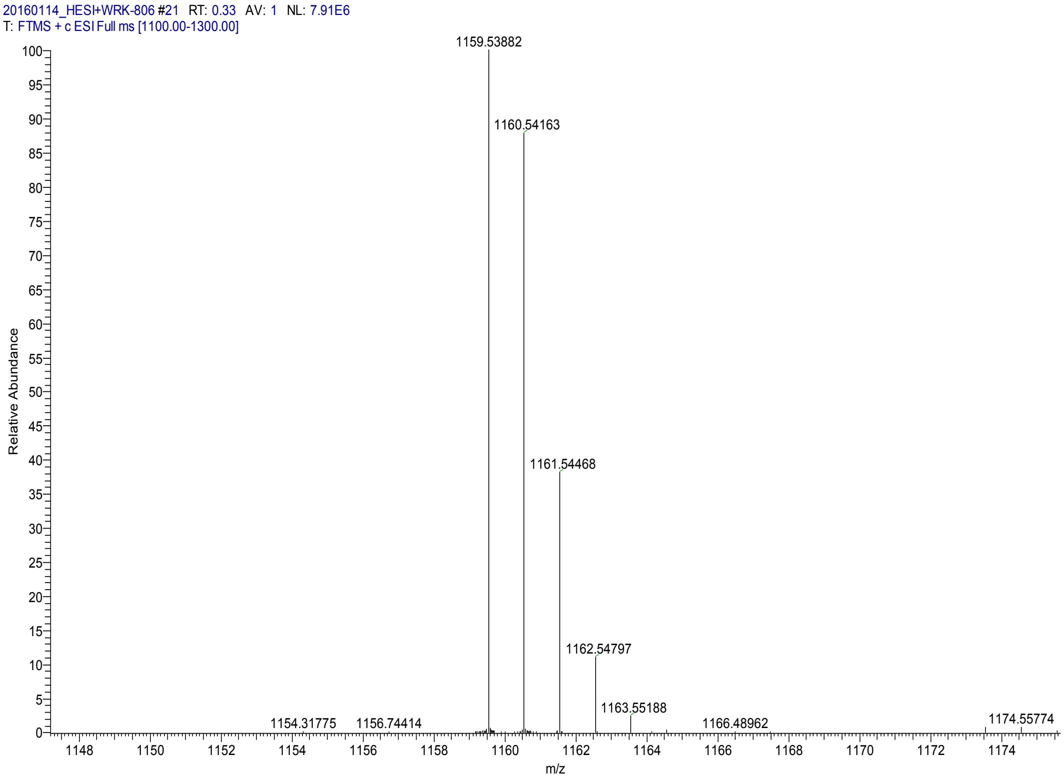


Figure S39. HRMS (m/z) of **L-NO$_2$.**

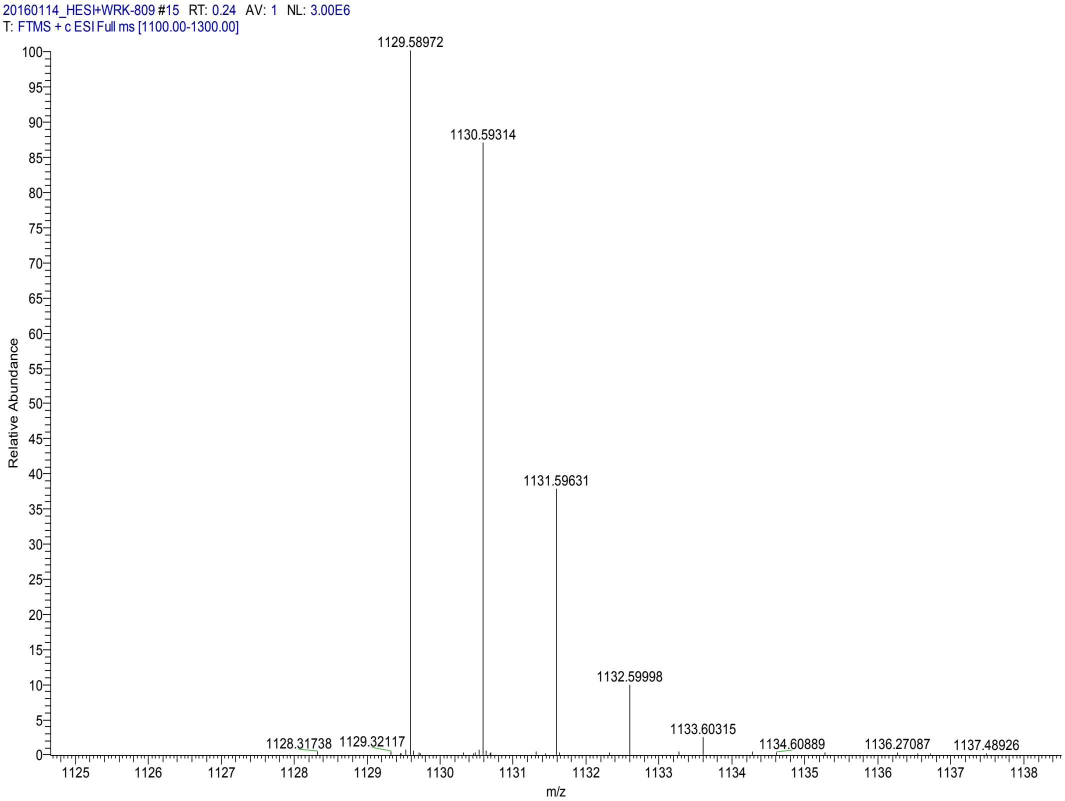


Figure S40. HRMS (m/z) of **L-OMe.**

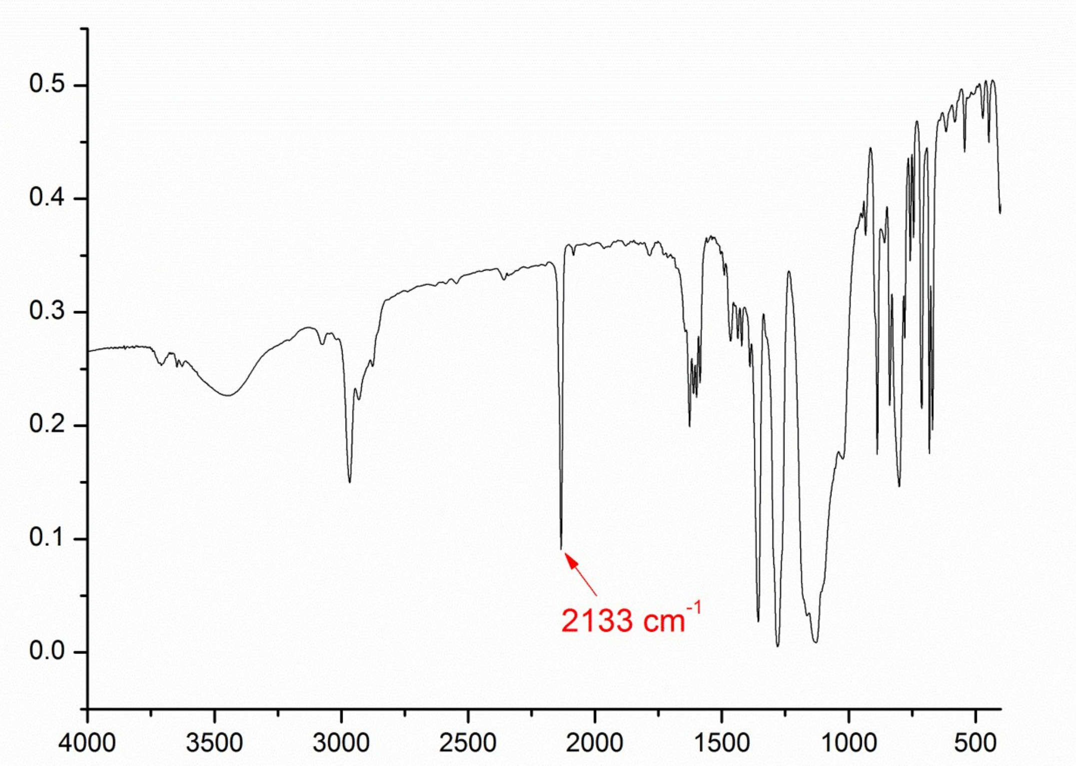


Figure S41. IR of **Pd-A-CO**.

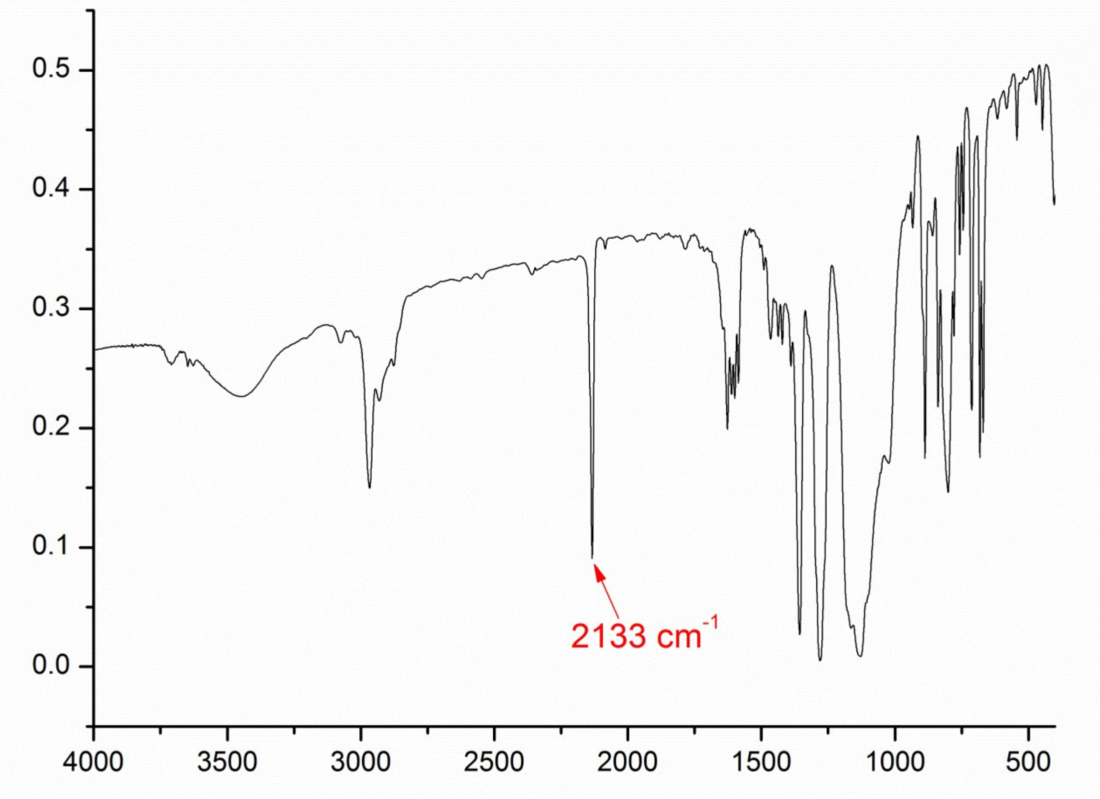


Figure S42. IR of **Pd-Ph-CO**.

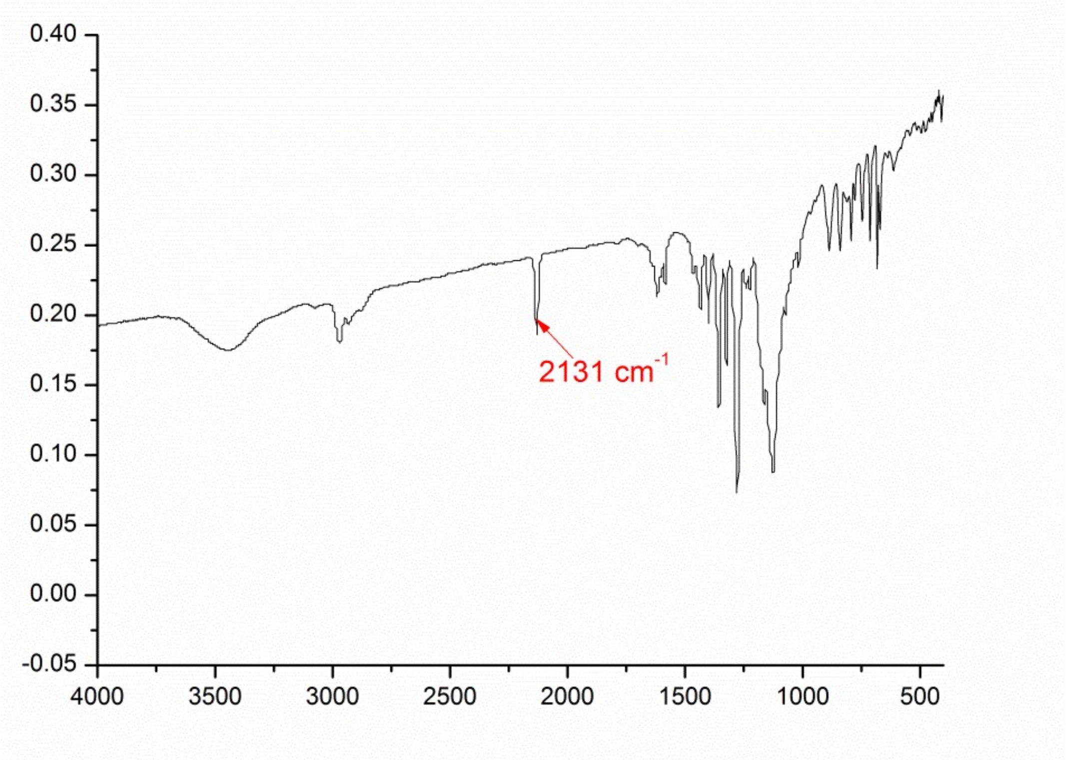


Figure S43. IR of **Pd-CF$_3$-CO**.

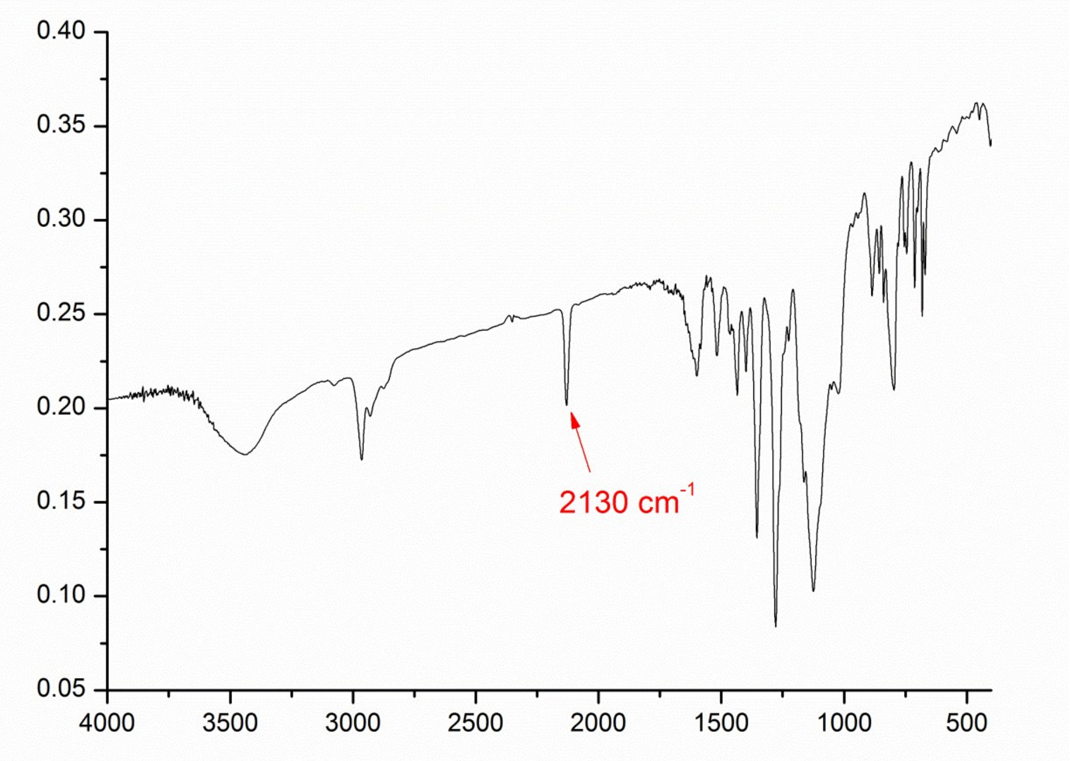


Figure S44. IR of **Pd-NO$_2$-CO**.

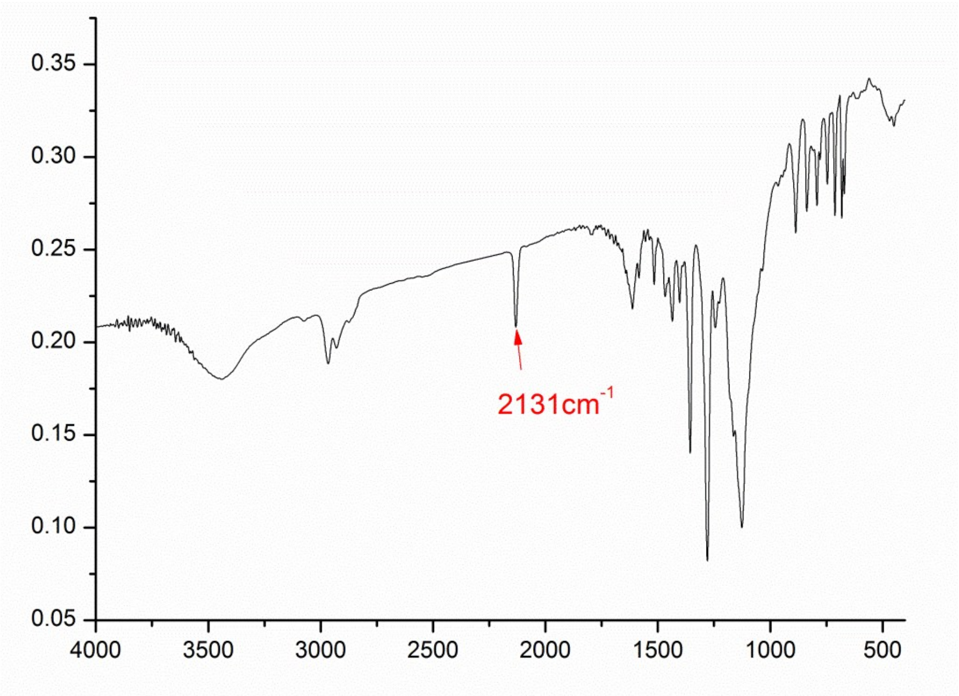


Figure S45. IR of **Pd-OMe-CO**.

4. X-ray crystallography of Pd-CF$_3$.

Table S1. Crystal data and structure refinement for **Pd-CF$_3$**.

Bond precision: C-C = 0.0159 A Wavelength=0.71073

Cell: a=30.455(3) b=12.1571(11) c=11.0990(9)
alpha=90 beta=90 gamma=90

Temperature: 298 K

	Calculated	Reported
Volume	4109.3(6)	4109.4(6)
Space group	P m n 21	Pmn2(1)
Hall group	P 2ac -2	?
Moiety formula	C81 H73 Cl F6 N2 O2 Pd, 2(C0.50 H Cl), C H2 Cl2	?
Sum formula	C83 H77 Cl5 F6 N2 O2 Pd	C83 H77 Cl5 F6 N2 O2 Pd
Mr	1532.12	1532.12
Dx,g cm-3	1.238	1.238
Z	2	2
Mu (mm-1)	0.446	0.446
F000	1580.0	1580.0
F000'	1580.15	
h,k,lmax	36,14,13	36,14,13

Nref	7410[3915]	7202
Tmin,Tmax	0.837,0.867	0.842,0.870
Tmin'	0.837	

Correction method= # Reported T Limits: Tmin=0.842 Tmax=0.870 AbsCorr = MULTI-SCAN

Data completeness= 1.84/0.97 Theta(max)= 25.020

R(reflections)= 0.0822(4923) wR2(reflections)= 0.2468(7202)

S = 1.039 Npar= 525

References

S1 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

S2 T. Wiedemann, G. Voit, A. Tchernook, P. Roesle, I. Göttker-Schnetmann and S. Mecking, *J. Am. Chem. Soc.*, 2014, **136**, 2078

S3 M. Hirotsu, N. Ohno, T. Nakajima, C. Kushibe, K. Ueno, I. Kinoshita, *Dalton Trans*., 2010, **39**, 139.