

Electronic Supplementary Information

A Redox-Active Binucleating Ligand Combines a PCP Pincer Site with a Bidentate N-N Donor in Opposition

Derek W. Leong[‡], Yanwu Shao[‡], Nattamai Bhuvanesh and Oleg V. Ozerov

*Department of Chemistry, Texas A&M University,
3255 TAMU, College Station, TX 77842*

[‡] These authors contributed equally.

ozero@chem.tamu.edu

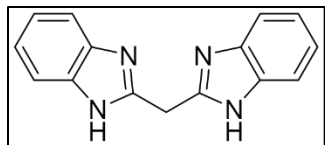
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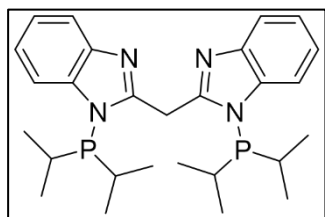
I. General Considerations

Unless otherwise specified, all manipulations were performed under an argon atmosphere using standard Schlenk line or glove box techniques. Toluene, THF, diethyl ether, pentane, and isooctane were dried and deoxygenated (by purging) using a solvent purification system and stored over molecular sieves in an Ar-filled glove box. C₆D₆ was dried over and distilled from NaK/Ph₂CO/18-crown-6 and stored over molecular sieves in an Argon-filled glove box. CDCl₃, dichloromethane, and 1,2-dichlorobenzene were dried with and then distilled from CaH₂ and stored over molecular sieves in Ar-filled glove box. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Bruker Avance Neo 400 (¹H NMR, 399.535 MHz; ¹³C NMR, 100.582 MHz; ³¹P NMR, 161.734 MHz), a Bruker Avance Neo 500 (¹H NMR, 500.13 MHz; ¹³C NMR, 125.77 MHz; ³¹P NMR, 202.45 MHz) and Varian Inova 500 (¹H NMR, 499.703 MHz; ¹³C NMR, 125.77 MHz) spectrometer. For ¹H and ¹³C NMR spectra, the residual solvent peak was used as an internal reference. (¹H NMR: δ 7.16 for C₆D₆, 7.24 for CDCl₃, 5.32 for CD₂Cl₂, 2.50 for (CD₃)₂SO; ¹³C NMR: δ 128.06 for C₆D₆, 77.16 for CDCl₃, 53.84 for CD₂Cl₂, 39.52 for (CD₃)₂SO). ³¹P NMR spectra were referenced externally using 85% H₃PO₄ at δ 0 ppm. ¹⁹F NMR spectra were referenced externally using CF₃CO₂H at -78.5 ppm. ¹¹B NMR spectra were referenced externally using BF₃•Et₂O at 0 ppm. Electrochemical studies were conducted using a CH Instruments Model 700 D Series. Electrochemical Analyzer and Workstation in conjunction with a three electrode cell: the working electrode was a CHI 104 glassy carbon disk with a 3.0 mm diameter, the auxiliary electrode was composed of platinum wire and the reference electrode, was a Ag/AgNO₃ electrode, which was prepared as a bulk solution composed of 0.01 M AgNO₃ and 0.1 M [*n*-Bu₄N][PF₆] or 0.1 M [*n*-Bu₄N][BArF₂₄]¹ that was made following a literature procedure in dichloromethane. A fine porosity frit was used for separation from solution. CVs were conducted in dichloromethane with 0.1 M supporting electrolyte and the scan rate is 100 mV/s. The concentration of the analyte solutions was approximately 1 mM. CVs were referenced to ferrocene/ferrocenium redox couple as recommended by IUPAC.^{2,3} Ultraviolet-visible (UV-vis) spectra were collected on a UV-2450 UV-Vis spectrophotometer (Shimadzu, Japan).

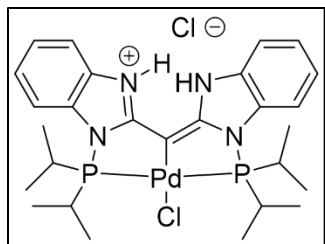
II. Synthesis of Compounds



Synthesis of bis(benzimidazolyl)methane (1). This synthesis was modified from the published procedure.⁴ In a 50 mL culture tube, 1,2-diaminobenzene (1.00 g, 9.24 mmol) and malonamide (0.472 g, 4.62 mmol) were dissolved in 85% H₃PO₄ (5 mL). The reaction was stirred for 48 h at 150 °C and the color of the mixture changed to a deep blue. 3M NaOH was added into the mixture to adjust the pH to 7, changing the color to pink. The solution was then filtered through a Büchner funnel and the pink solid was collected on the filter paper. The pink solids were washed with water and CH₂Cl₂, then dried under vacuum, yielding the product as pink powder (1.13 g, 99% yield). ¹H NMR ((CD₃)₂SO, 400 MHz): δ 12.49 (s, 2H, NH), 7.53 (dd, *J* = 3.2, 6.0 Hz, 4H, Ar-*H*), 7.17 (dd, *J* = 3.2, 6.0 Hz, 4H, Ph-*H*), 4.52 (s, 2H, CH₂); ¹³C{¹H} NMR ((CD₃)₂SO, 125 MHz): δ 150.3 (C=N), 143.2 (Ar), 134.5 (Ar), 121.5 (Ar, 2 overlapping signals), 118.2 (Ar), 111.3 (Ar), 29.5 (CH₂).

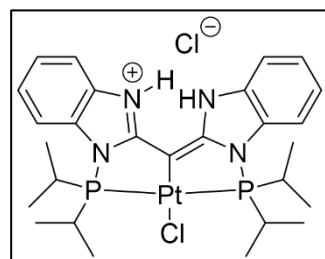


Synthesis of (P^NC^NP^{iPr})H (2). In a Schlenk flask, **1** (4.50 g, 18.1 mmol), ClPⁱPr₂ (6.95 g, 43.5 mmol), and triethylamine (4.61 g, 43.5 mmol) were combined and dissolved in THF. After stirring over night at RT, the reaction mixture was filtered through a pad of Celite and the volatiles were removed in vacuo to give a pink solid. The pink solid was then redissolved in THF and layered with pentane in a 1:1 ratio and left in a -35 °C freezer overnight to recrystallize. The precipitate was washed with cold pentane several times and further dried under vacuum to yield a pink solid (8.53 g, 98% yield, >95% pure by ¹H NMR spectroscopy). ³¹P{¹H} NMR (C₆D₆, 202 MHz): δ 68.2 (s); ¹H NMR (C₆D₆, 400 MHz): δ 7.91 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.37 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.17 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 7.13 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 5.21 (s, CH₂), 2.48 (m, 4H, CHMe₂), 0.89 (dd, *J* = 6.9, 18.4, 12H, CH(CH₃)₂), 0.77 (q, *J* = 7.1 Hz, 12 H, CH(CH₃)₂); ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 158.0 (dd, *J*_{P1-C} = 20.3 Hz, *J*_{P2-C} = 2.3 Hz, C=N), 146.0 (s, Ar), 137.9 (d, *J*_{P-C} = 9.8 Hz, Ar), 122.7 (s, Ar), 122.5 (s, Ar), 120.8 (s, Ar), 113.1 (s, Ar), 31.8 (t, *J*_{P-C} = 17.4 Hz, CH₂), 26.2 (d, *J*_{P-C} = 14.3 Hz, CHMe₂), 20.0 (d, *J*_{P-C} = 10.5 Hz, CHMe₂), 20.0 (d, *J*_{P-C} = 29.8 Hz, CHMe₂).



Synthesis of (^HP^NC^NPⁱPr)PdCl•HCl (3-Pd). In a 50 mL Schlenk tube, **2** (3.79 g, 7.88 mmol), Pd(COD)Cl₂ (2.25 g, 7.88 mmol) were dissolved in a minimum amount of 1,2-dichlorobenzene under argon. The reaction mixture was stirred overnight at around 180 °C. The yellow mixture was diluted with CH₂Cl₂ and filtered, with the

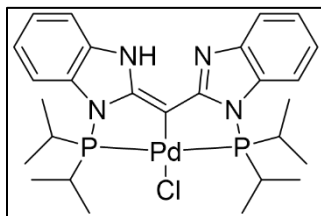
resultant filtrate layered with pentane in a 1:1 ratio and then placed in a -35 °C freezer. The precipitate formed overnight was washed with cold pentane several times and further dried under vacuum to yield a yellow solid (4.67 g, 90%) that was 97% pure by ³¹P{¹H} and ¹H NMR spectroscopy. ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ 110.7k (s); ¹H NMR (CDCl₃, 400 MHz): δ 13.60 (s, 2H, NH), 7.68 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.20 (td, *J* = 7.2 Hz, 2 Hz, 2H, Ar-*H*), 7.13-7.08 (4H, Ar-*H*), 3.04 (m, 4H, CHMe₂), 1.58 (dvt, *J* = 8.0 Hz, 12 H, CHMe₂), 1.33 (dvt, *J* = 8.0 Hz, 12 H, CHMe₂). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 161.5 (vt, *J*_{P-C} = 17.5 Hz, C=N), 139.9 (s, Ar), 130.1 (vt, *J*_{P-C} = 2.3 Hz, Ar), 124.6 (s, Ar), 122.9 (s, Ar), 113.5 (s, Ar), 110.6 (s, Ar), 70.2 (s, Pd-C), 27.8 (vt, *J*_{P-C} = 10.4 Hz, CHMe₂), 19.2 (s, CHMe₂), 18.2 (vt, *J*_{P-C} = 3.5 Hz, CHMe₂).



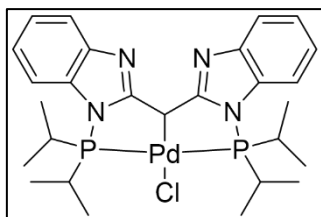
Synthesis of (^HP^NC^NPⁱPr)PtCl•HCl (3-Pt). In a 50 mL Schlenk tube, **2** (416 mg, 0.866 mmol) and Pt(COD)Cl₂ (324 mg, 0.866 mmol) were dissolved in 30 mL of toluene. The reaction mixture was stirred for 48 h at 120 °C. The yellow mixture was then filtered through a pad of Celite with the help of additional CH₂Cl₂. The volatiles were removed

under vacuum from the filtrate to yield a yellow powder that was dissolved in CH₂Cl₂ and layered with pentane in a 1:2 ratio and then left in a -35 °C freezer. The yellow precipitate formed overnight was washed with cold pentane several times and further dried under vacuum to yield a yellow solid (490 mg, 76% yield) that was 95% pure by ³¹P{¹H} and ¹H NMR spectroscopy. ³¹P{¹H} NMR (CDCl₃, 202 MHz): δ 102.6 (s, *J*_{Pt-P} = 3077.3 Hz); ¹H NMR (CDCl₃, 400 MHz): δ 13.66 (s, 2H, NH), 7.66 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.20 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.16-7.09 (m, 4H, Ar-*H*), 3.23 (m, 4H, CHMe₂), 1.57 (m, 12 H, CHMe₂), 1.29 (m, 12 H, CHMe₂). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 161.4 (vt, *J*_{P-C} = 15.2 Hz, C=N), 139.8 (Ar), 130.1 (Ar), 124.5 (Ar), 122.8 (Ar), 113.6 (Ar), 110.4 (Ar), 59.4 (t, *J*_{P-C} = 5.1 Hz, Pt-C), 28.3 (vt, *J*_{P-C} = 14.2 Hz, CHMe₂), 19.0 (CHMe₂), 17.8 (vt, *J*_{P-C} = 3.0 Hz, CHMe₂).

Synthesis of (¹H^NC^NP^{iPr})PdCl (4-Pd**).** In a 25 mL Teflon stoppered Schlenk flask with a stir bar, **2** (185 mg, 0.385 mmol), Pd(COD)Cl₂ (99.5 mg 0.350 mmol), and Et₃N (100 μL, 0.70 mmol) were dissolved in ca. 10 mL of toluene. The reaction mixture was stirred for 12 h at 120 °C. The resulting orange mixture was filtered through a pad of Celite and the volatiles were removed in vacuo from the filtrate. The remaining orange solid was redissolved in THF and this solution was layered with pentane in a 1:1 ratio and then placed in a -35 °C freezer overnight. The precipitate appeared to consist of two different solids: a fine orange powder and red crystals. This precipitate was washed with pentane (3 × 5 mL) then dried under vacuum (194 mg, 90% yield). Upon dissolution in C₆D₆ the **4a-Pd**: **4b-Pd** ratio was 95:5. Anal. Calcd for C₂₇H₃₇ClN₄P₂Pd: C: 52.18; H: 6.00; N: 9.02. Found: C: 51.92; H: 5.79; N: 8.95.



Data for **4a-Pd**: ³¹P{¹H} NMR (C₆D₆, 202 MHz): δ 108.4 (s), ¹H NMR (C₆D₆, 400 MHz): δ 10.23 (br s, NH, 1H), 6.94 (m, Ar-H, 4H), 6.82 (t, *J* = 8.0 Hz, Ar-H, 2H), 6.71 (d, *J* = 8.2 Hz, Ar-H, 2H), 2.56 (m, (CH₃)₂CH, 4H), 1.45 (m, (CH₃)₂CH, 12H), 1.04 (m, (CH₃)₂CH, 12H); ¹³C{¹H} NMR (C₆D₆, 100 MHz): δ 166.3 (C=N), 147.2 (Ar), 133.3 (Ar), 123.0 (Ar), 120.3 (Ar), 113.5 (Ar), 110.2 (Ar), 75.2 (Pd-C), 27.7 (vt, *J*_{C-P} = 11.0 Hz, CH(CH₃)₂), 18.9 (CH(CH₃)₂), 18.4 (t, *J*_{C-P} = 3.8 Hz, CH(CH₃)₂). ³¹P{¹H} NMR (CDCl₃, 202 MHz): δ 108.9 (s). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ Resonances for the arenes of **4a-Pd** could not be seen at the achievable concentration, 68.0 (Pd-C), 27.1 (vt, *J*_{C-P} = 11.8 Hz, CH(CH₃)₂), 18.3 (s, CH(CH₃)₂), 17.4 (s, CH(CH₃)₂). Total concentration of Pd in solution for the CDCl₃ solution was 50 mM and ca. 8 mM for **4a-Pd**.



Data for **4b-Pd**: ³¹P{¹H} NMR (C₆D₆, 202 MHz): δ 93.1 (s), ¹H NMR (C₆D₆, 400 MHz): δ 7.93 (br s, Ar-H, 2H), Other aryl peaks overlap with **4a-Pd** in solution, 5.74 (s, α-CH, 1H), 2.73 (m, (CH₃)₂CH, 2H), 2.37 (m, (CH₃)₂CH, 2H), 1.35 (m, (CH₃)₂CH, 12H), 0.90 (m, (CH₃)₂CH, overlaps with residual pentane). The achievable concentration of **4b-Pd** in C₆D₆ solution was not sufficient to observe its resonances in the ¹³C{¹H} NMR spectrum. ³¹P{¹H} NMR (CDCl₃, 202 MHz): δ 93.1 (s). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 166.2 (vt, *J*_{C-P} = 12.7 Hz, C=N), 150.9 (Ar), 137.9 (Ar), 123.31 (Ar), 122.9 (Ar), 122.0 (Ar), 111.6 (Ar), 45.9 (Pd-C), 28.2 (vt, *J*_{C-P} = 10.1 Hz, CH(CH₃)₂), 19.1 (m, CH(CH₃)₂ Overlaps with other methyl of the

isopropyl arm), 18.8 (CH(CH₃)₂ Overlaps with other methyl of the isopropyl arm). Total concentration of Pd in solution for the C₆D₆ solution is ca. 50 mM and for **4b-Pd** is ca. 3 mM.

Tautomer equilibrium experiment with 4-Pd. **4-Pd** (61.4 mg, 0.098 mmol) was added to a J. Young tube, dissolved in 625 μL of toluene-*d*₈ and analyzed by ³¹P NMR spectroscopy (**Fig S1**). The ratio was found to be 91% **4a-Pd** and 9% **4b-Pd**. The volatiles were removed from this solution under vacuum, and the residue was then redissolved in 625 μL CDCl₃. Analysis by ³¹P NMR spectroscopy revealed the ratio of 15% **4a-Pd** to 85% **4b-Pd**. The volatiles were removed from this solution under vacuum, and the residue was then redissolved in 625 μL toluene-*d*₈. Analysis by ³¹P NMR spectroscopy revealed the ratio returned to favor **4a-Pd** with 90% **4a-Pd** to 10% **4b-Pd**.

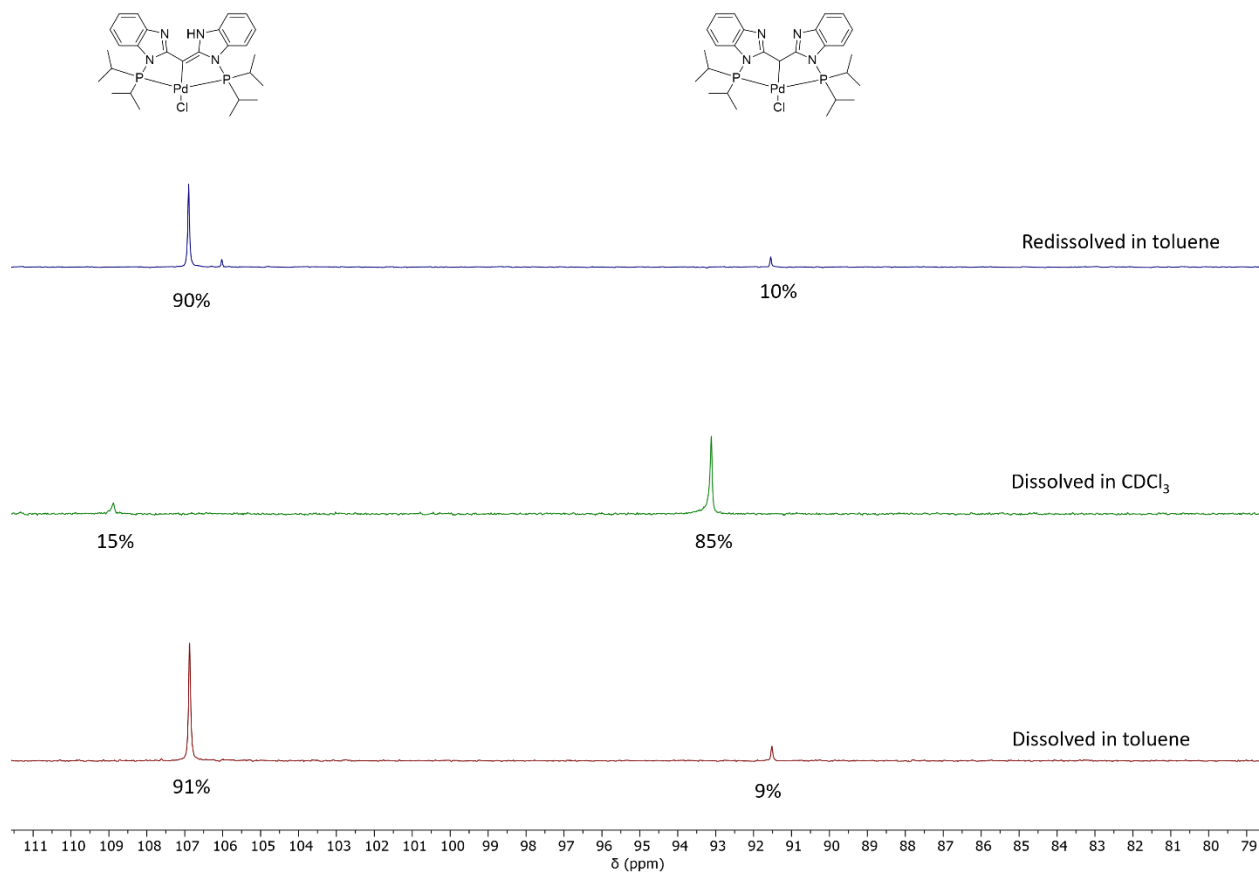
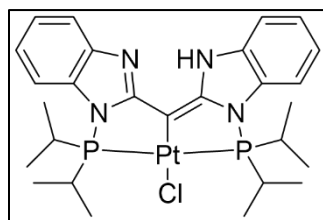
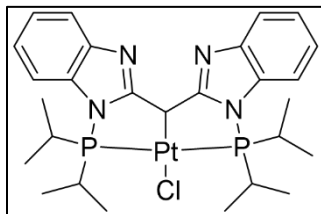


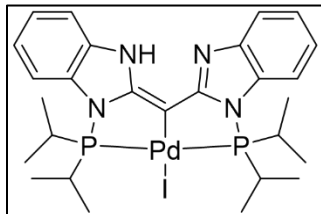
Figure S1. ³¹P{¹H} NMR (202 MHz) spectra of the mixture of **4a-Pd** and **4b-Pd** in toluene-*d*₈ and in CDCl₃.



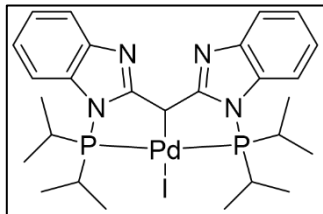
Synthesis of (HPNCNPiPr)PtCl (4-Pt). In a 25 mL Schlenk flask with a stir bar, **3-Pt** (150 mg, 0.201 mmol) and Et₃N (42 μL, 0.301 mmol) were dissolved in 10 mL of toluene in the dark. The reaction mixture



was stirred for 12 h at room temperature. The resulting yellow mixture was filtered through a pad of Celite and the volatiles were removed in vacuo from the filtrate. The resultant yellow solid was redissolved in toluene, layered with pentane in a 1:2 ratio, and then left in a -35 °C freezer overnight. The resultant yellow solid was washed with pentane and then dried under vacuum (199 mg, 82% yield). Only **4a-Pt** was observed when the product was dissolved in C₆D₆. When CDCl₃ was used to dissolve **4-Pt**, both **4a-Pt** and **4b-Pt** were observed by NMR spectroscopy in a 53:47 ratio. Anal. Calcd for C₂₇H₃₇ClN₄P₂Pd: C: 45.67; H: 5.25; N: 7.89. Found: C: 46.28; H: 5.37; N: 7.18. Data for **4a-Pt**: ³¹P{¹H} NMR (C₆D₆, 162 MHz): 98.9 (s, *J*_{Pt-P} = 3184.0 Hz); ¹H NMR (C₆D₆, 400 MHz): δ 9.90 (br s, *NH*, 1H), 6.95 (d *J* = 7.9 Hz, *Ar-H*, 4H), 6.83 (m, *Ar-H*, 2H), 6.73 (d *J* = 7.9 Hz, *Ar-H*, 2H), 2.76, (m, (CH₃)₂CH, 4H), 1.45 (m, (CH₃)₂CH, 12H), 1.03 (m, (CH₃)₂CH, 12H). ¹³C{¹H} NMR (C₆D₆, 125 MHz): 165.5 (C=N), 147.3 (Ar), 133.3 (Ar), 122.9 (Ar), 120.3 (Ar), 113.7 (Ar), 110.0 (Ar), 64.0 (Pt-C), 28.3 (t, *J*_{C-P} = 14.7 Hz, CH(CH₃)₂), 18.7 ((CH₃)₂CH), 17.9 ((CH₃)₂CH). ³¹P{¹H} NMR (CDCl₃, 202 MHz): 100.9 ppm (s, *J*_{Pt-P} = 3177.5 Hz, 53%). ¹H NMR (CDCl₃, 500 MHz): 10.02 (br s, *NH*, 1H). Data for **4b-Pt**: ³¹P{¹H} NMR (CDCl₃, 202 MHz): 90.3 ppm (s, *J*_{Pt-P} = 3048.2 Hz, 47%). ¹H NMR (CDCl₃, 500 MHz): Resonances for the arene peaks overlap with **4a-Pt**. 5.51 (s, *J*_{Pt-P} = 155.3 Hz, α-*CH*, 1H). Resonances for the isopropyl arms overlap with **4a-Pt**.



Synthesis of (^HP^NC^NPⁱPr)₂PdI (5-Pd). **4-Pd** (581 mg, 0.935 mmol) was added to a 50 mL Schlenk flask and dissolved in ca. 20 mL of toluene and Me₃SiI (200 μL, 1.40 mmol) was then added to the solution. The mixture was allowed to stir for 12 h before the volatiles were removed in vacuo. The yellow solid was dissolved in THF and recrystallized by layering in a 1:1 fashion with pentane. The solid was washed with pentane and dried under vacuum (554 mg, 82% yield). Data for **5a**: ³¹P{¹H} NMR (CDCl₃, 202 MHz): δ 114.6; ¹H NMR (CDCl₃, 400 MHz): δ 12.06 (br s, *NH*, 1H), 7.95 (d, *J* = 7.7 Hz, *Ar-H*, 2H), 7.17 (m, *Ar-H*, 6H overlaps with solvent peak), 3.12 (m, CH(CH₃)₂, 4H), 1.57 (dvt, *J* = 10.2 Hz, CH(CH₃)₂), 1.32 (dvt, *J* = 8.2 Hz, CH(CH₃)₂); ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 160.9 (vt, *J*_{P-C} = 17.5 Hz, C=N), 139.5 (Ar), 130.0 (t, *J* = 2.4 Hz, Ar), 124.6 (Ar), 123.1 (Ar), 113.6 (Ar), 111.2 (Ar), 68.0 (Pd-C), 28.4 (vt, *J*_{P-C} = 11.2 Hz, CHMe₂), 19.3 (vt, *J*_{P-C} = 2.8 Hz, CHMe₂), 19.2 (CHMe₂). ³¹P{¹H} NMR (C₇D₈, 202 MHz): δ 118.2 (s).



$^{31}\text{P}\{^1\text{H}\}$ NMR (C_7D_8 , 202 MHz): δ 97.8 (s).

Tautomer equilibrium experiment with compound **5-Pd**.

Compound 5-Pd (78 mg, 0.110 mmol) was added to a J. Young tube, dissolved in 625 μL of toluene- d_8 and analyzed by ^{31}P NMR spectroscopy (**Fig S2. 1**). The only tautomer in solution was determined by ^{31}P NMR spectroscopy to be **5a-Pd**. The volatiles were removed from this solution under vacuum, and the residue was then redissolved in 625 μL CDCl_3 . Analysis by ^{31}P NMR spectroscopy revealed the ratio favored **5b-Pd** as the major tautomer (56%) and **5a-Pd** being the minor tautomer (44%). The volatiles were removed from this solution under vacuum, and the residue was then redissolved in 625 μL toluene- d_8 . Analysis by ^{31}P NMR spectroscopy revealed the composition returned to **5a-Pd** only.

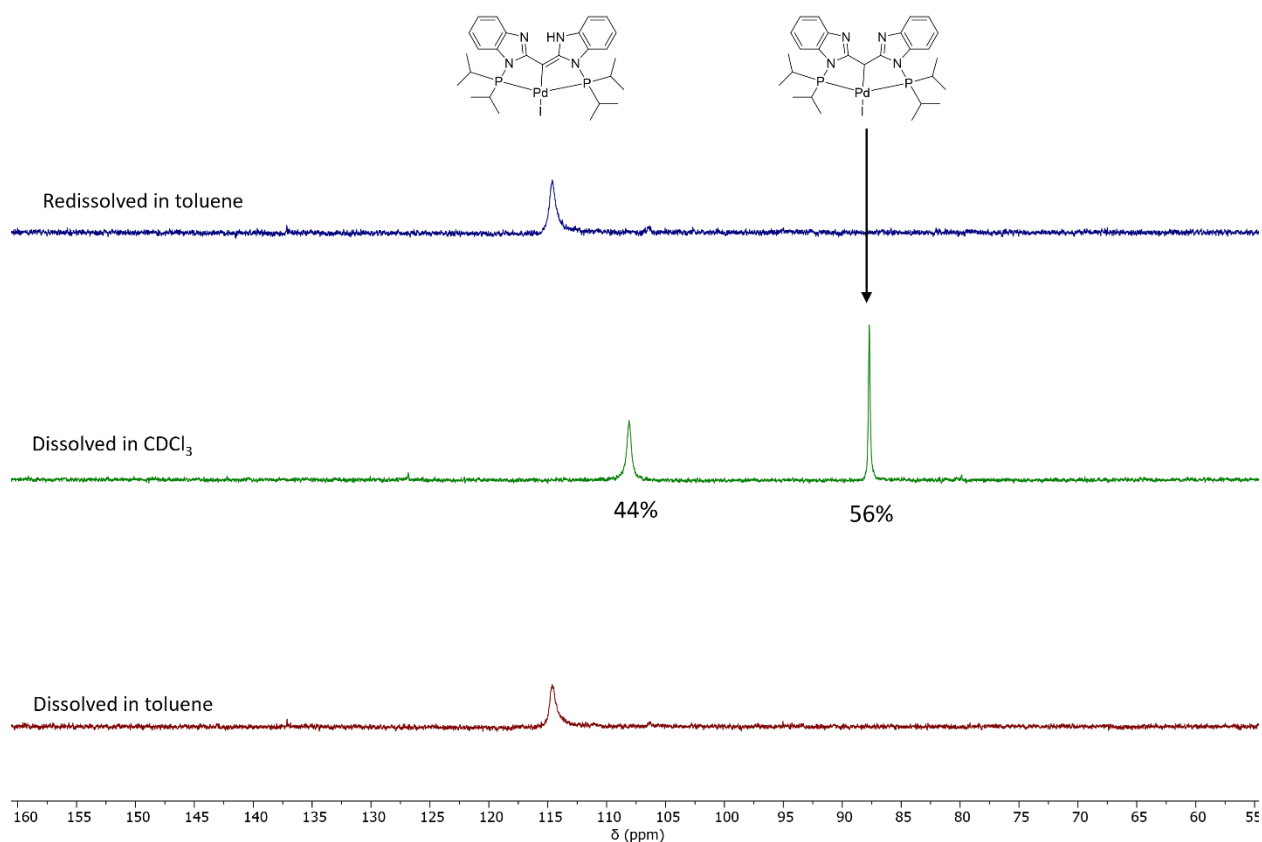
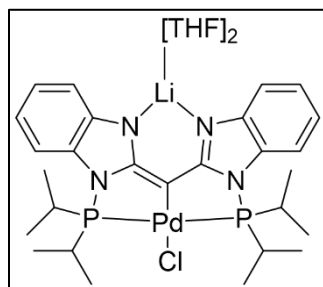


Figure S2. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectra of the mixture of **5a** and **5b** in CDCl_3 and in toluene- d_8 .



Synthesis of $(\text{LiP}^{\text{N}}\text{C}^{\text{N}}\text{P}^{\text{iPr}})\text{PdCl}\cdot 2\text{THF}$ (6-Pd**).** In a 50 mL Schlenk flask, $\text{HN}(\text{SiMe}_3)_2$ (120 μL , 0.573 mmol) was dissolved in ca. 20 mL of THF, then $n\text{BuLi}$ (200 μL , 0.500 mmol) was added. The mixture was allowed to stir for 2 h. **4-Pd** (194 mg, 0.312 mmol) was added to the mixture and it was stirred for 12 h. The mixture was then filtered through a pad of Celite and the volatiles were removed in vacuo from the filtrate to yield a brown solid. It was recrystallized by dissolving in minimal THF (ca. 2 mL), layering with 5 mL of pentane, and placing it in a $-35\text{ }^\circ\text{C}$ freezer overnight to give a brown powder. The supernatant was decanted from the brown powder which was then washed with pentane ($3 \times 10\text{ mL}$) and dried. (192 mg, 80% yield) $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz): δ 99.1 (s);

^1H NMR (C_6D_6 , 400 MHz): δ 7.39 (d, $J = 7.6$ Hz, 2H, Ar- H), 7.16 (br s, 2H, Ar- H), 6.86 (br s, 4H, Ar- H), 3.58 (br s, 8H, OCH_2), 2.74 (m, 4H, CHMe_2), 1.28 (br s, 8H, CH_2CH_2), 1.53 (m, 12H, $\text{CH}(\text{CH}_3)_2$), 1.18 (m, 12H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 172.2 (vt, $J_{\text{P-C}} = 16.1$ Hz, C=N), 152.6 (Ar), 133.1 (vt, $J_{\text{P-C}} = 2.3$ Hz, Ar), 120.1 (Ar), 115.5 (Ar), 111.4 (Ar), 107.4 (Ar), 76.6 (Pd-C), 66.3 (OCH_2CH_2), 25.5 (vt, $J_{\text{P-C}} = 11.3$ Hz, CHMe_2), 23.5 (s, $\text{CH}_2\text{CH}_2\text{O}$), 17.2 (s, CHMe_2), 18.2 (vt, $J_{\text{P-C}} = 3.8$ Hz, CHMe_2).

Chloride Test of 6-Pd: Compound **6-Pd** (14 mg, 0.018 mmol) was dissolved in 600 μL of C_6D_6 in a J. Young tube, and then Me_3SiI (5 μL , 0.035 mmol) was added to it. The solution was allowed to age for 30 min before the reaction mixture was analyzed by NMR spectroscopy, which evinced the formation of one equivalent of Me_3SiCl .

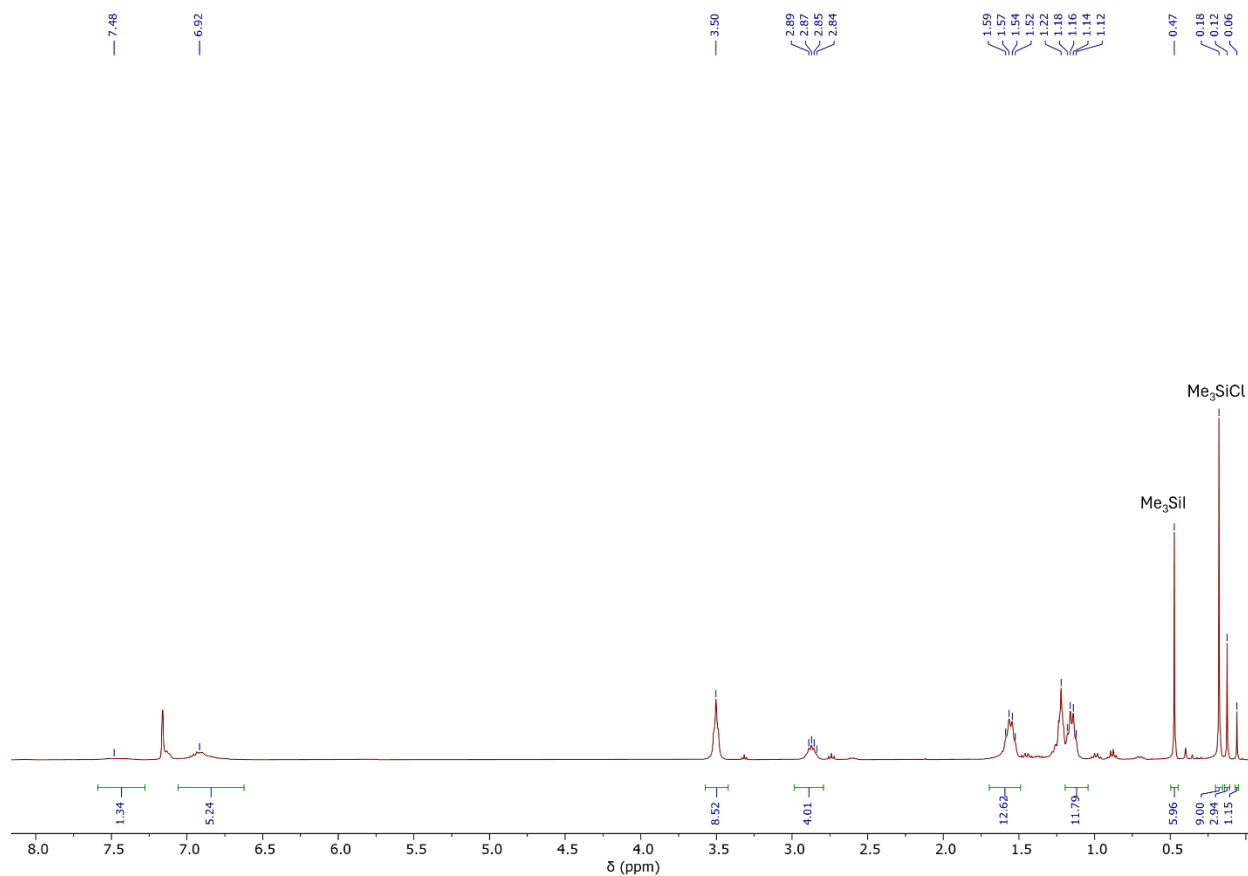
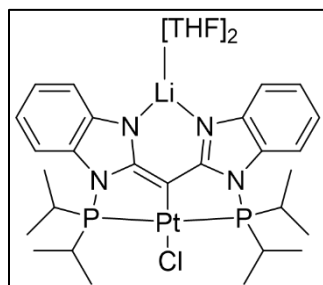


Figure S3. ^1H NMR (400 MHz, C_6D_6) NMR spectrum of the reaction between **6-Pd** and Me_3SiI after 30 min.



Synthesis of $(\text{LiP}^{\text{N}}\text{C}^{\text{N}}\text{P}^{\text{iPr}})\text{PtCl}\cdot 2\text{THF}$ (6-Pt**).** In a 50 mL Schlenk flask, $\text{HN}(\text{SiMe}_3)_2$ (50 μL , 0.240 mmol) was dissolved in ca. 20 mL

of THF, then n BuLi (90 μ L, 0.225 mmol) was added. The mixture was allowed to stir for 2 h. **4-Pt** (100 mg, 0.141 mmol) was added to the mixture and it was stirred for 12 h in the dark. The mixture was then filtered through a pad of Celite and the volatiles were removed in vacuo to yield a brown solid. The brown solid was redissolved in minimal THF (ca. 2 mL), then layered with 8 mL of pentane, and placed in a -35 $^{\circ}$ C freezer overnight to give a brown powder. The supernatant was decanted from the brown solid which was then washed with pentane (3×10 mL) and dried to give 84 mg (69%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz): δ 92.9 (s, $J_{\text{P-Pt}} = 3214.1$ Hz); ^1H NMR (C_6D_6 , 400 MHz): δ 7.22 (s, 2H, Ar-*H*), 6.90 (s, 4H, Ar-*H*), 3.57 (br s, 8H, OCH₂), 2.57 (s, 4H, CHMe₂), 1.56 (s, 12 H, CH(CH₃)₂), 1.26 (s, CH₂CH₂, 8H), 1.16 (s, 12 H, CH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): 173.2 (C=N), 154.5 (Ar), 135.2 (Ar), 122.1 (Ar), 117.6 (Ar), 113.4 (Ar), 109.3 (Ar), 68.4 (OCH₂), 64.9 (Pt-C), 28.2 (t, $J = 13.8$ Hz, CH(CH₃)₂), 25.4 (OCH₂CH₂), 19.0 (CH(CH₃)₂), 18.3 (CH(CH₃)₂).

Chloride Test of 6-Pt: Compound **6-Pd** (14 mg, 0.018 mmol) was dissolved in 600 μ L of C_6D_6 in a J. Young tube, and then Me₃SiI (5 μ L, 0.035 mmol) was added to it. The solution was allowed to age for 30 min before the reaction mixture was analyzed by NMR spectroscopy. By ^1H NMR analysis, 1 equivalent of Me₃SiCl was formed from the 2 equivalents of Me₃SiI added to the reaction.

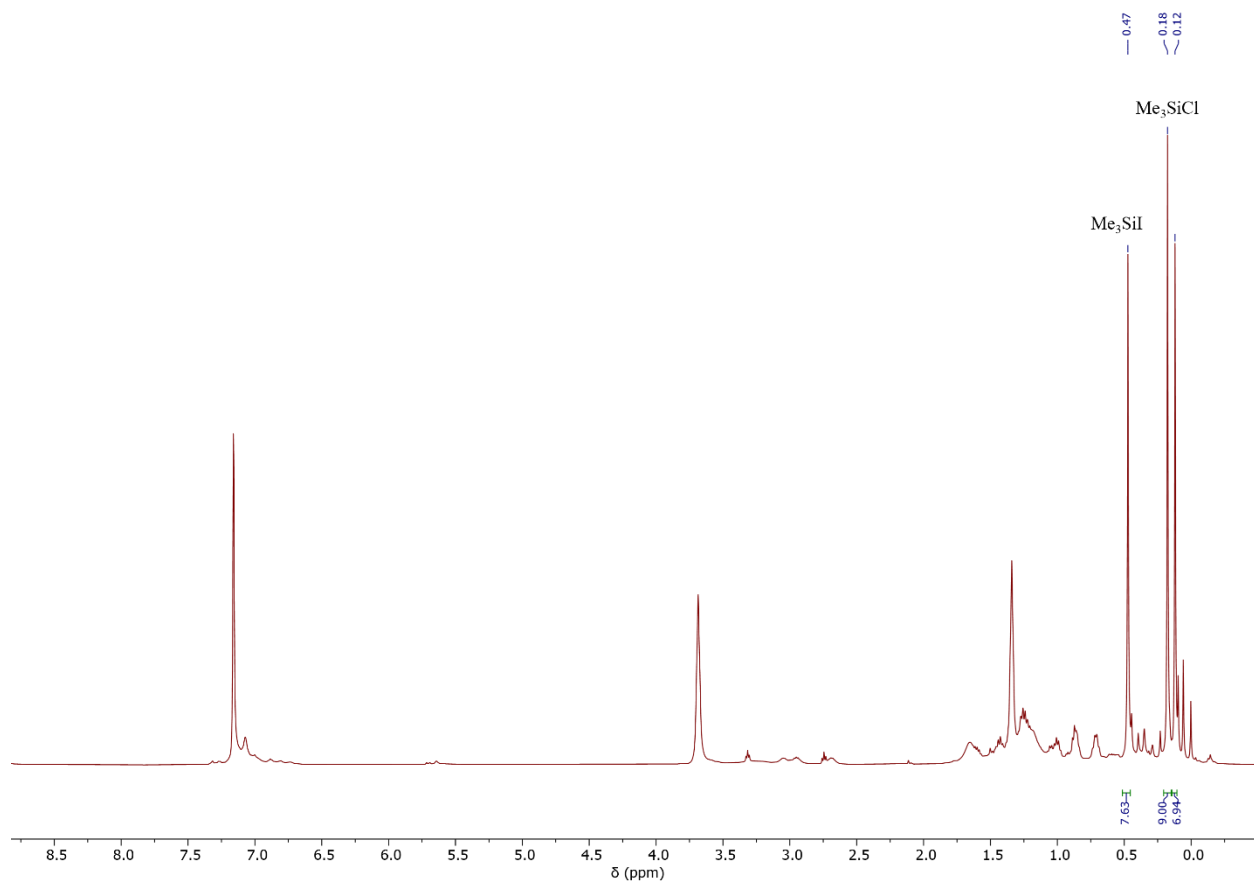
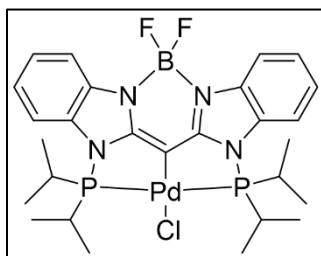
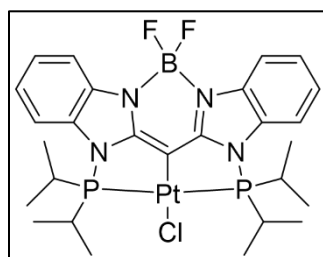


Figure S4. ^1H NMR (500 MHz, C_6D_6) NMR spectrum of the reaction between **6-Pt** and Me_3SiI after 30 min.



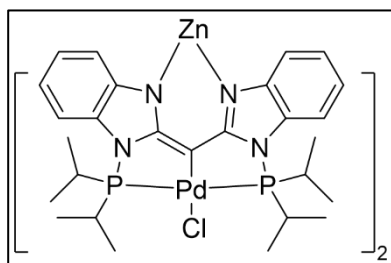
Synthesis of $(\text{BF}_2\text{PNCNPiPr})\text{PdCl}$ (7-Pd**).** **6-Pd** (192 mg, 0.306 mmol) was added to a 50 mL Schlenk flask and dissolved in ca. 20 mL of toluene, then $\text{BF}_3\cdot\text{OEt}_2$ (52 μL , 0.428 mmol) was added to give a yellow solution. The solution was stirred for 16 h. The solution was then filtered through a pad of Celite. The volatiles were removed from the filtrate in vacuo to yield a yellow solid. The yellow solid was then recrystallized by dissolving in toluene, layering with pentane in a 1:1 ratio, and placing in a freezer at $-35\text{ }^\circ\text{C}$

overnight. The resulting yellow solid was washed with pentane and dried (111 mg, 54%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz): δ 124.4 (s). ^1H NMR (C_6D_6 , 400 MHz): δ 7.97 (d, $J = 7.9$ Hz, 2H, Ar-*H*), 6.97 (td, $J = 7.9$ Hz, 2H, Ar-*H*), 6.82 (d, $J = 7.8$ Hz, 2H, Ar-*H*), 6.61 (d, $J = 8.0$ Hz, 2H, Ar-*H*), 2.35 (m, 4H, CHMe_2), 1.27 (m, 12 H, $\text{CH}(\text{CH}_3)_2$), 0.86 (m, 12 H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 166.2 (vt, $J_{\text{P-C}} = 21.6$ Hz, C=N), 141.6 (Ar), 132.4 (Ar), 124.0 (Ar), 122.0 (Ar), 114.1 (Ar), 110.8 (Ar), 64.7 (Pd-C), 27.8 (vt, $J_{\text{P-C}} = 9.6$ Hz, CHMe_2), 18.9 (CHMe_2), 18.2 (vt, $J_{\text{P-C}} = 3.8$ Hz, CHMe_2). ^{19}F NMR (C_6D_6 , 472 MHz): δ -138.1 (q, $J_{\text{B-F}} = 29.7$ Hz); ^{11}B NMR (C_6D_6 , 128 MHz): δ 3.1 (t, $J_{\text{F-B}} = 29.4$ Hz). Anal. Calcd for $\text{C}_{27}\text{H}_{36}\text{BClF}_2\text{N}_4\text{P}_2\text{Pd}$: C: 48.46; H: 5.42; N: 8.37. Found: C: 48.73; H: 5.48; N: 8.20.



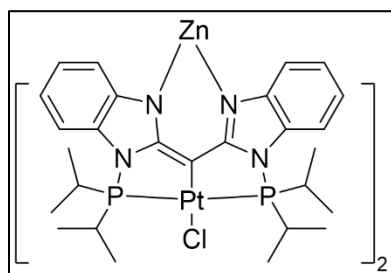
Synthesis of $(\text{BF}_2\text{P}^{\text{N}}\text{C}^{\text{N}}\text{P}^{\text{iPr}})\text{PtCl}$ (7-Pt). **6-Pt** (100.0 mg, 0.140 mol) and $\text{BF}_3\cdot\text{OEt}_2$ (21.8 mg, 0.154 mmol) were added to a PTFE stoppered Schlenk flask and dissolved in toluene to give a yellow solution. The solution was then heated at 110 °C for 16 h and the flask was brought back into a glovebox. The solution was then filtered

through a pad of Celite, the solvent was removed from the filtrate under vacuum to yield a yellow solid. The solid was then redissolved in THF and layered with pentane (1:2) and placed in a -35 °C freezer overnight to give a yellow powder. The supernatant was decanted and then yellow powder was then washed with pentane (3×10 mL) and dried under vacuum (70.2 mg, 42%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz): δ 115.3 (s, $J_{\text{P-Pt}} = 3267.5$ Hz); ^1H NMR (C_6D_6 , 400 MHz): δ 7.95 (d, $J = 7.6$ Hz, 2H, Ar-*H*), 6.97 (td, $J = 8.1$ Hz, 2H, Ar-*H*), 6.83 (d, $J = 7.7$ Hz, 2H, Ar-*H*), 6.63 (d, $J = 7.6$ Hz, 2H, Ar-*H*), 2.53 (m, $J = 7.2$ Hz, 4H, CHMe_2), 1.26 (m, 12 H, $\text{CH}(\text{CH}_3)_2$), 0.84 (m, 12 H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 166.6 (C=N), 142.7 (Ar), 133.0 (Ar), 124.2 (Ar), 121.7 (Ar), 115.0 (Ar), 110.8 (Ar), 55.3 (Pt-C), 28.5 (vt, $J_{\text{P-C}} = 13.4$ Hz, CHMe_2), 18.2 (CHMe_2), 17.5 (vt, $J = 3.6$ Hz, CHMe_2). ^{19}F NMR (C_6D_6 , 472 MHz): δ -138.2 (q, $J_{\text{B-F}} = 29.4$ Hz); ^{11}B NMR (C_6D_6 , 128 MHz): δ 3.4 (t, $J_{\text{F-B}} = 29.6$ Hz).



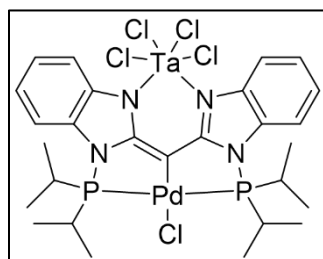
Synthesis of $\text{Zn}[(\text{P}^{\text{N}}\text{C}^{\text{N}}\text{P}^{\text{iPr}})\text{PdCl}]_2$ (8-Pd). **6-Pd** (100.0 mg, 0.1596 mmol) and ZnCl_2 (11 mg, 0.080 mmol) were added to a Schlenk flask and dissolved in toluene to give an initial brown solution. ^{31}P NMR spectroscopy was used to monitor the reaction conversion. After stirring for 12 h the solution turned orange. The solution was filtered through a pad of Celite and the volatiles were removed from

the filtrate under vacuum to yield an orange solid. It was recrystallized by dissolving the solid in THF, layering with pentane in a 1:1 ratio, and left in a freezer at $-35\text{ }^{\circ}\text{C}$ overnight. Orange precipitate formed overnight. The supernatant was decanted from the resultant solid which was then washed with pentane ($3 \times 5\text{ mL}$) and dried under vacuum to yield an orange solid (91 mg, 43% yield). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz): δ 106.2 (s); ^1H NMR (C_6D_6 , 400 MHz): δ 7.10 (m, 4H, Ar-*H*), 6.73 (m, 12H, Ar-*H*), 2.61 (m, 8H, *CHMe*₂), 1.51 (m, 24H, *CHMe*₂), 1.10 (m, 24H, *CHMe*₂); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 171.9 (C=N), 150.2 (Ar), 133.5 (Ar), 123.3 (Ar), 119.7 (Ar), 113.9 (Ar), 110.0 (Ar), 74.3 (s, Pd-C), 27.6 (vt, $J_{\text{P-C}} = 10.8\text{ Hz}$, *CHMe*₂), 19.0 (*CHMe*₂), 18.4 (vt, $J_{\text{P-C}} = 3.7\text{ Hz}$, *CHMe*₂). Anal. Calcd for $\text{C}_{54}\text{H}_{72}\text{Cl}_2\text{N}_8\text{P}_4\text{Pd}_2\text{Zn}$: C: 49.65; H: 5.56; N: 8.58; Found: C: 49.41; H: 5.29; N: 8.12



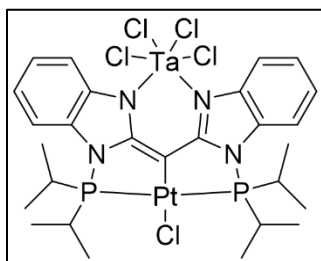
Synthesis of $\text{Zn}[(\text{P}^{\text{N}}\text{C}^{\text{N}}\text{P}^{\text{iPr}})\text{PtCl}]_2$ (8-Pt). 6-Pt (107.4 mg, 0.149 mmol) and ZnCl_2 (10.1 mg, 0.070 mmol) were added to a Schlenk flask and dissolved in toluene in the dark to give an initial brown solution. ^{31}P NMR spectroscopy was used to monitor the reaction conversion. After stirring for 12 h the

solution turned yellow. The solution was filtered through a pad of Celite and the volatiles were removed to yield a yellow solid. The solid was recrystallized by dissolving the solid in THF, layering with pentane in a 1:1 ratio, and left in a freezer at $-35\text{ }^{\circ}\text{C}$ overnight. Yellow precipitate formed overnight. The supernatant was decanted from the resultant solid which was then washed with pentane ($3 \times 5\text{ mL}$) and dried under vacuum to yield a yellow solid (88.4 mg, 40%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz): δ 99.0 (s, $J_{\text{P-Pt}} = 3181.5\text{ Hz}$); ^1H NMR (C_6D_6 , 400 MHz): δ 7.08 (m, 4H, Ar-*H*), 6.74 (m, 12H, Ar-*H*), 2.79 (m, 8H, *CHMe*₂), 1.50 (m, 24H, *CHMe*₂), 1.08 (m, 24H, *CHMe*₂); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 171.1 (t, $J = 13.7\text{ Hz}$), 150.3 (Ar), 133.6 (Ar), 123.27 (Ar), 119.7 (Ar), 114.1 (Ar), 109.9 (Ar), 62.4 (Pt-C), 28.4 (vt, $J = 13.5\text{ Hz}$, *CHMe*₂), 18.8 (*CHMe*₂), 18.0 (vt, $J = 2.8\text{ Hz}$). $\text{C}_{54}\text{H}_{72}\text{Cl}_2\text{N}_8\text{P}_4\text{Pt}_2\text{Zn}$: C: 43.72; H: 4.89; N: 7.55; Found: C: 43.75; H: 5.07; N: 6.73



Synthesis of $(\text{TaCl}_5\text{P}^{\text{N}}\text{C}^{\text{N}}\text{P}^{\text{iPr}})\text{PdCl}$ (9-Pd). 6-Pd (20.0 mg, 0.0319 mmol) and TaCl_5 (12.3 mg, 0.0319 mmol) were added to a J. Young tube and dissolved in C_6D_6 . After heating at $80\text{ }^{\circ}\text{C}$ overnight, the solution became purple blue and ^{31}P NMR analysis confirmed the

completion of the reaction. The solution was filtered and the volatiles were removed from the filtrate under vacuum. The solid was dissolved in CH₂Cl₂ and layered with pentane in 1:1 ration and left in a -35 °C freezer. Purple precipitate formed overnight. The supernatant was removed and the solid was washed with pentane several times and then dried. (16.0 mg, 53%). ³¹P{¹H} NMR (C₆D₆, 202 MHz): δ 114.4 (s); ¹H NMR (C₆D₆, 400 MHz): δ 8.42 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.11 (td, *J* = 7.8 Hz, 2H, Ar-*H*), 6.74 (td, *J* = 7.8 Hz, 2H, Ar-*H*), 6.67 (d, *J* = 8.3 Hz, Ar-*H*), 2.46 (bs, 4H, CHMe₂), 1.33 (m, 12 H, CH(CH₃)₂), 0.78 (m, 12 H, CH(CH₃)₂); ¹³C{¹H} NMR (C₆D₆, 100 MHz): δ 164.7 (vt, *J*_{P-C} = 17.7 Hz, C=N), 145.8 (Ar), 132.6 (vt, *J* = 3 Hz, Ar), 125.3 (Ar), 123.9 (d, *J* = 2.4 Hz, Ar), 109.5 (Ar), 102.7 (Ar), 30.2 (CHMe₂), 18.2 (CHMe₂). Anal. Calcd for C₂₇H₃₆Cl₅N₄P₂PdTa: C: 52.27; H: 5.85; N: 9.03. Found: C: 51.92; H: 5.79; N: 8.95.



Synthesis of (TaCl₄P^{Nc}N^{Pr})PtCl (9-Pt). 6-Pt (73.3 mg, 0.098 mmol) and TaCl₅ (35.2 mg, 0.098 mmol) were added to a 25 mL PTFE stoppered Schlenk flask, dissolved in toluene in the dark, and stirred for 12 h at 110 °C. During stirring, the solution turned blue and was then filtered through a pad of Celite. The volatiles were removed from

the filtrate to yield a blue solid. The solid was dissolved in CH₂Cl₂ and layered with pentane in 1:1 ratio and left in a -35 °C freezer. Blue precipitate formed overnight. The supernatant was removed and the solid was washed with pentane several times and then dried. (44.9 mg, 44%). ³¹P{¹H} NMR (C₆D₆, 202 MHz): δ 106.8 (s, *J*_{P-Pt} = 3074.4 Hz); ¹H NMR (C₆D₆, 400 MHz): δ 8.44 (d, *J* = 3.7 Hz, 2H, Ar-*H*), 7.12 (m, 2H, Ar-*H*, overlaps with solvent) 6.70 (m, 4H, Ar-*H*) 2.6 (br s, 4H, CHMe₂), 1.30 (m, 12 H, CH(CH₃)₂), 0.75 (m, 12 H, CH(CH₃)₂); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ 161.7 (C=N), 144.3 (Ar), 132.5 (Ar), 128.6 (Ar), 126.4 (Ar), 123.9 (Ar), 123.6 (Ar), 109.9 (Ar), Pt-C not observed with achievable concentration, 22.8 (CH(CH₃)₂), 18.7 (CH(CH₃)₂), 14.2 (CH(CH₃)₂).

Table S1. ¹³C{¹H} NMR Data for Palladium and Platinum Compounds, δ ppm.

	C=N ^c	CAr	CAr	CAr	CAr	CAr	CAr	CH ^c	CH(Me) ₂	CH(Me) ₂ ^c
3-Pd^a	161.5 (<i>J</i> = 17.5)	139.9	130.1	124.6	122.9	113.5	110.6	27.8 (<i>J</i> = 10.4)	19.2	18.2 (<i>J</i> = 3.5)
3-Pt^a	161.4 (<i>J</i> = 15.2)	139.8	130.1	124.5	122.8	113.6	110.4	28.3 (<i>J</i> = 14.2)	19.0	17.8 (<i>J</i> = 3.0)
4a-Pd	166.3	147.2	133.3	123.0	120.3	113.5	110.2	27.7 (<i>J</i> = 11.0)	18.9	18.4 (<i>J</i> = 3.8)

4b-Pd^a	166.2 (<i>J</i> = 12.7)	150.9	137.9	123.31	122.9	122.0	111.6	28.2 (<i>J</i> = 10.1)	19.1	18.8
4a-Pt	165.5	147.4	133.3	122.9	120.3	113.7	110.0	28.3 (<i>J</i> = 14.7)	18.7	17.9
5a	160.9 (<i>J</i> = 17.5)	139.5	130.0	124.6	123.1	113.6	111.2	28.4 (<i>J</i> = 11.2)	19.3 (<i>J</i> = 2.8 Hz)	19.2
6-Pd	172.2	152.6	133.1	120.1	115.5	111.4	107.4	25.5 (<i>J</i> = 11.3)	17.2	18.2 (<i>J</i> = 3.8)
6-Pt	173.2	154.5	135.2	122.1	117.6	113.4	109.3	28.2 (<i>J</i> = 13.8)	19.0	18.3
7-Pd	166.2 (<i>J</i> = 21.6)	141.6	132.4	124.0	122.0	114.1	110.8	27.8 (<i>J</i> = 9.6)	18.9	18.2 (<i>J</i> = 3.8)
7-Pt	166.6	142.7	133.0	124.2	121.7	115	110.8	28.5 (<i>J</i> = 13.4)	18.2	17.5 (<i>J</i> = 3.6)
8-Pd	171.9	150.2	133.5	123.3	119.7	113.9	110.0	27.6 (<i>J</i> = 10.8)	19.0	18.4 (<i>J</i> = 3.7)
8-Pt	171.1 (<i>J</i> = 13.7)	150.3	133.6	123.3	119.7	114.1	109.9	28.4 (<i>J</i> = 13.5)	18.8	18.0 (<i>J</i> = 2.8)
9-Pd	164.7 (<i>J</i> = 17.7)	145.8	132.6	125.3	123.9	109.5	102.7	30.2	18.2	
9-Pt^b	161.7	144.3	132.5	128.6	126.4	123.9	109.9	22.8	18.7	14.2

NMR spectra collected in C₆D₆ unless otherwise noted. ^aSpectra collected in CDCl₃. ^bSpectra collected in CD₂Cl₂.

^cCoupling to phosphorus was not seen in all compounds due to signal broadness and low achievable concentration of compounds.

Table S2. ¹H NMR Data for Palladium and Platinum Compounds, δ ppm.

	NH	CHAr	CHAr	CHAr	CHAr	α-CH	CH	CH(Me)₂	CH(Me)₂
3-Pd^a	13.60	7.68 (2H)	7.20 (2H)	7.13-7.08 (4H)	-	-	3.04	1.58	1.33
3-Pt^a	13.66	7.66 (2H)	7.20 (2H)	7.16-7.09 (4H)	-	-	3.23	1.57	1.29
4a-Pd	10.23	6.94 (4H)	6.82 (2H)	6.71 (2H)	-	-	2.56	1.45	1.04
4b-Pd	-	-	-	-	-	5.74 (s)	-	-	-
4a-Pt	9.90	6.95 (4H)	6.83 (2H)	6.73 (2H)	-	-	2.76	1.45	1.03
4b-Pt^a	-	-	-	-	-	5.51 (<i>J</i> _{Pt-P} = 155 Hz).	-	-	-
5a^a	12.06	7.95 (2H)	7.17 (6H)	-	-	-	3.12	1.57	1.32

6-Pd	-	7.39 (2H)	7.16 (2H)	6.86 (4H)	-	-	2.74	1.53	1.18
6-Pt	-	7.22 (4H)	6.9 (4H)	-	-	-	2.57	1.56	1.26
7-Pd	-	7.97 (2H)	6.97 (2H)	6.82 (2H)	6.61 (2H)	-	2.35	1.27	0.86
7-Pt	-	7.95 (2H)	6.97 (2H)	6.83 (2H)	6.63 (2H)	-	2.53	1.26	0.84
8-Pd	-	7.10 (4H)	6.73 (12H)	-	-	-	2.61	1.51	1.10
8-Pt	-	7.08 (4H)	6.74 (12H)	-	-	-	2.79	1.50	1.08
9-Pd	-	8.42 (2H)	7.11 (2H)	6.74 (2H)	6.67 (2H)	-	2.46	1.33	0.78
9-Pt	-	8.44 (2H)	7.12 (2H)	6.70 (4H)	-	-	2.60	1.30	0.75

NMR spectra collected in C₆D₆ unless otherwise noted. ^a Spectra collected in CDCl₃. Some aryl peaks contain overlapping multiplets which accounts for some compounds having fewer signals observed in the arene region.

III. NMR Spectra

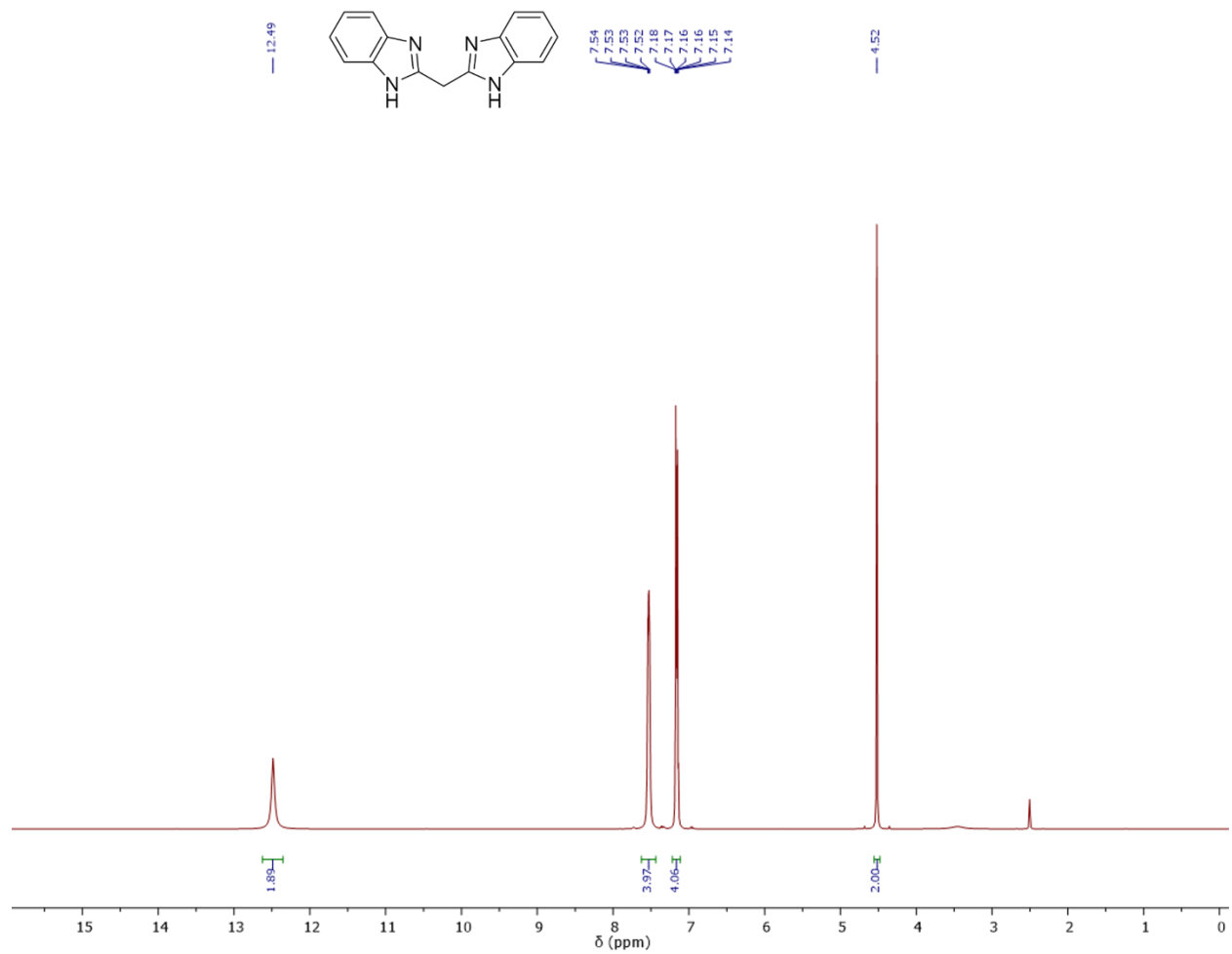


Figure S5. ¹H NMR (400 MHz) spectrum of **1** in (CD₃)₂SO.

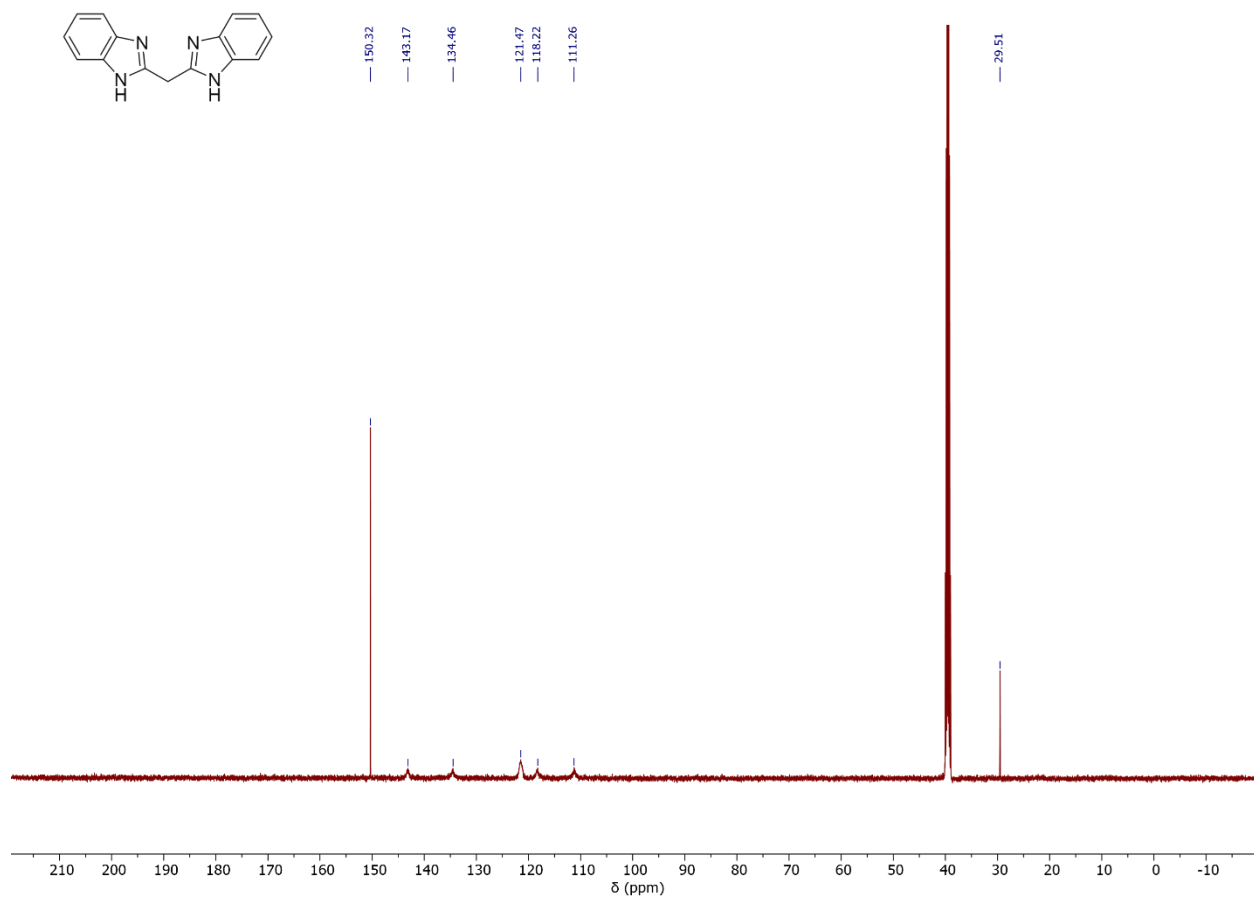


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) spectrum of **1** in $(\text{CD}_3)_2\text{SO}$.

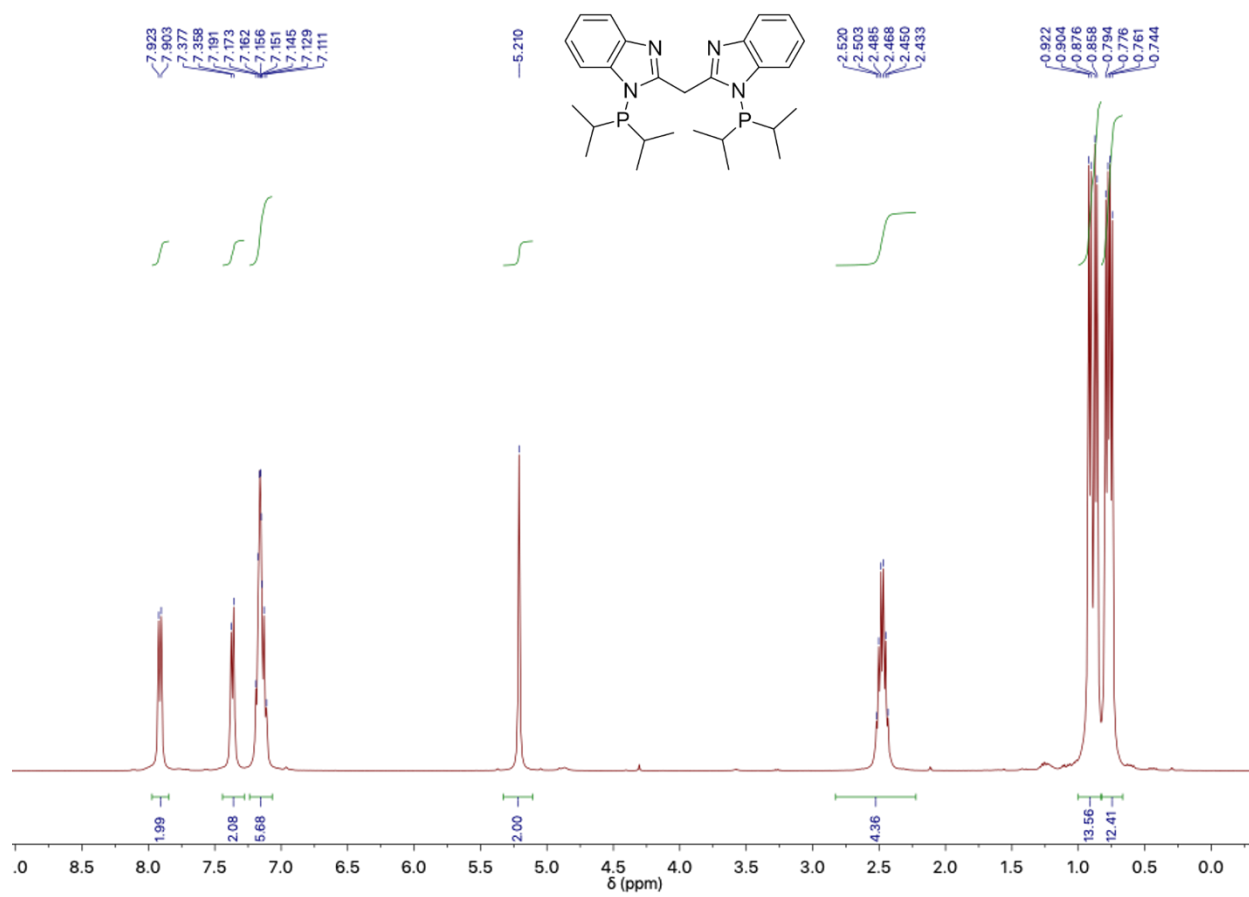


Figure S7. $^1\text{H NMR}$ (400 MHz) spectrum of **2** in C_6D_6 .

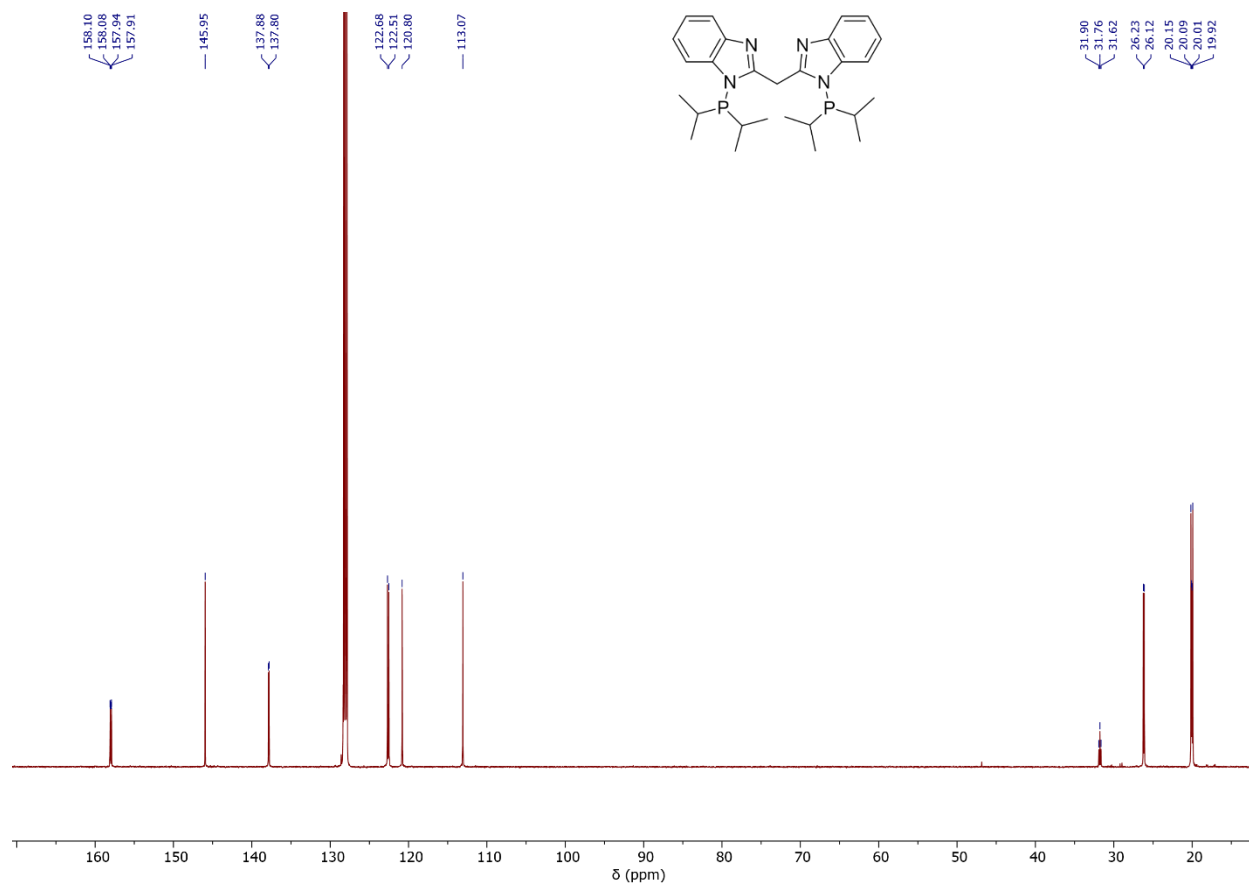


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) spectrum of **2** in C_6D_6 .

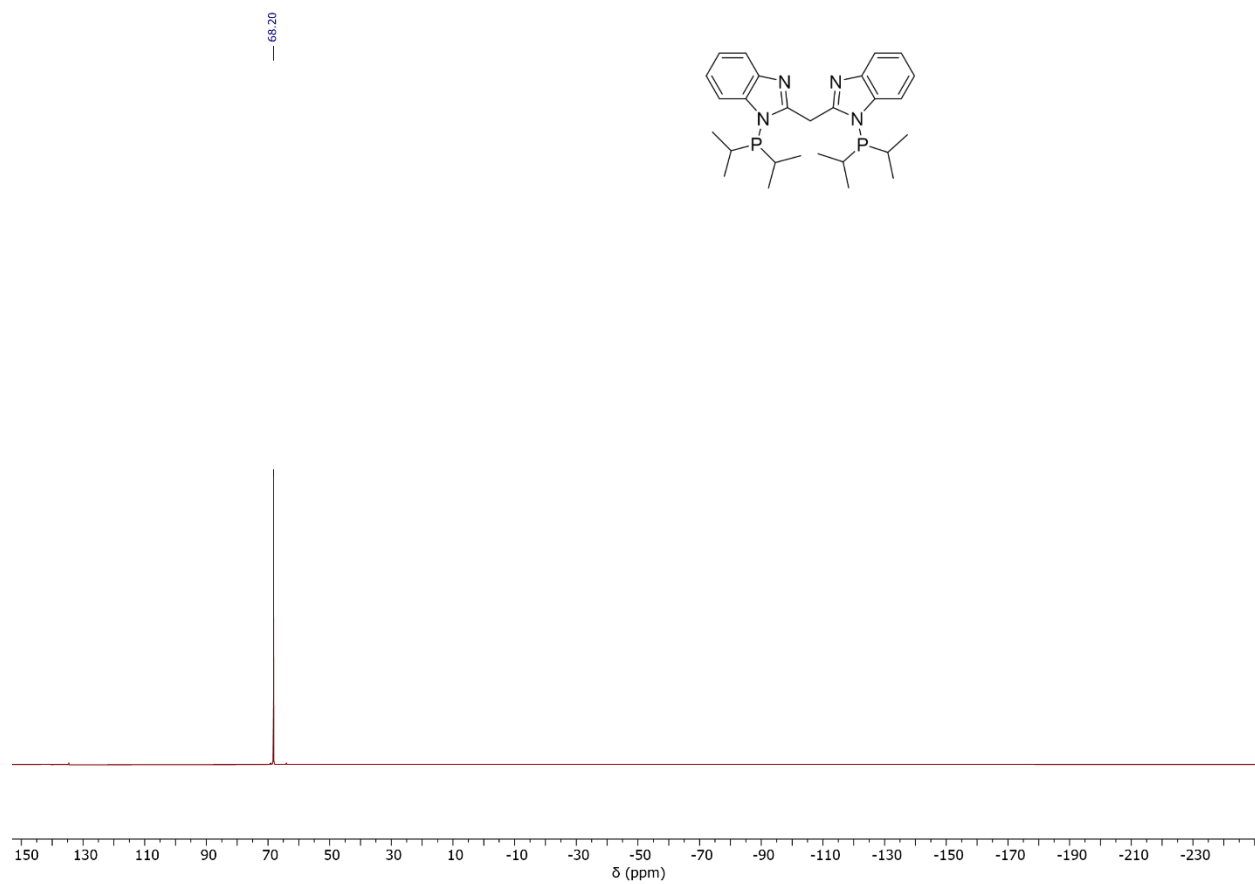


Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **2** in C_6D_6 .

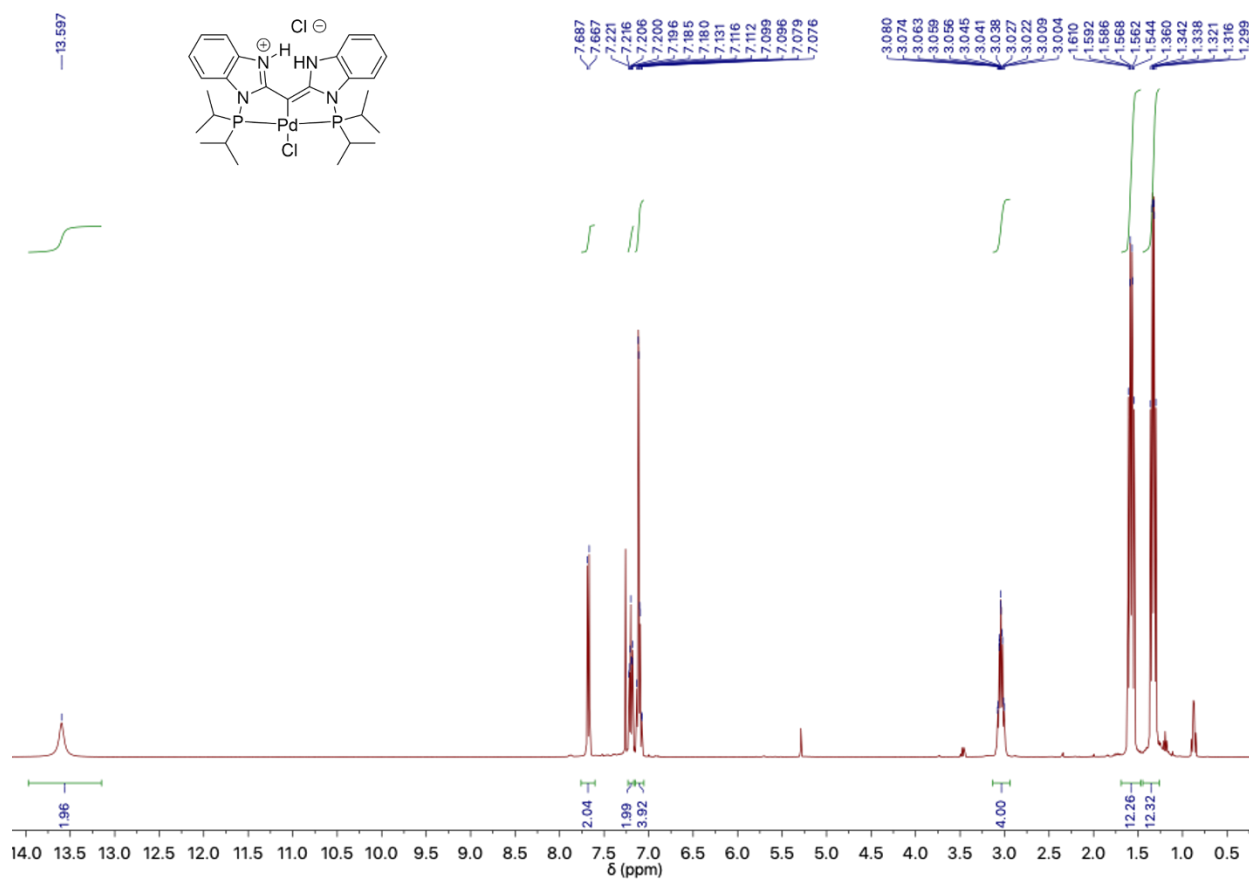


Figure S10. ^1H NMR (400 MHz) spectrum of **3-Pd** in CDCl_3 . The sample contains residuals CH_2Cl_2 (s, 5.30 ppm), diethyl ether (q, 3.27 ppm; t, 1.12 ppm), pentane (m, 1.27 ppm; t, 0.88 ppm).

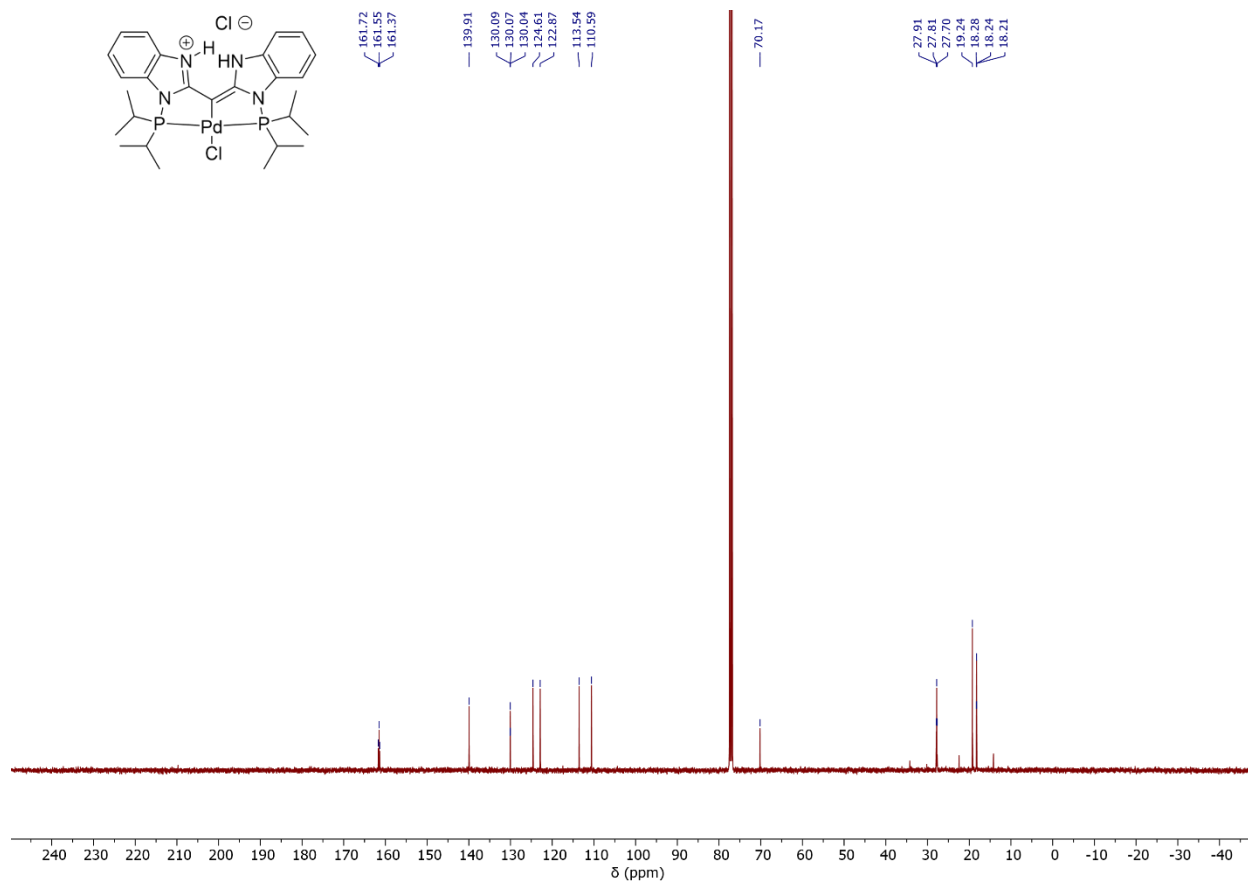


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **3-Pd** in CDCl_3 .

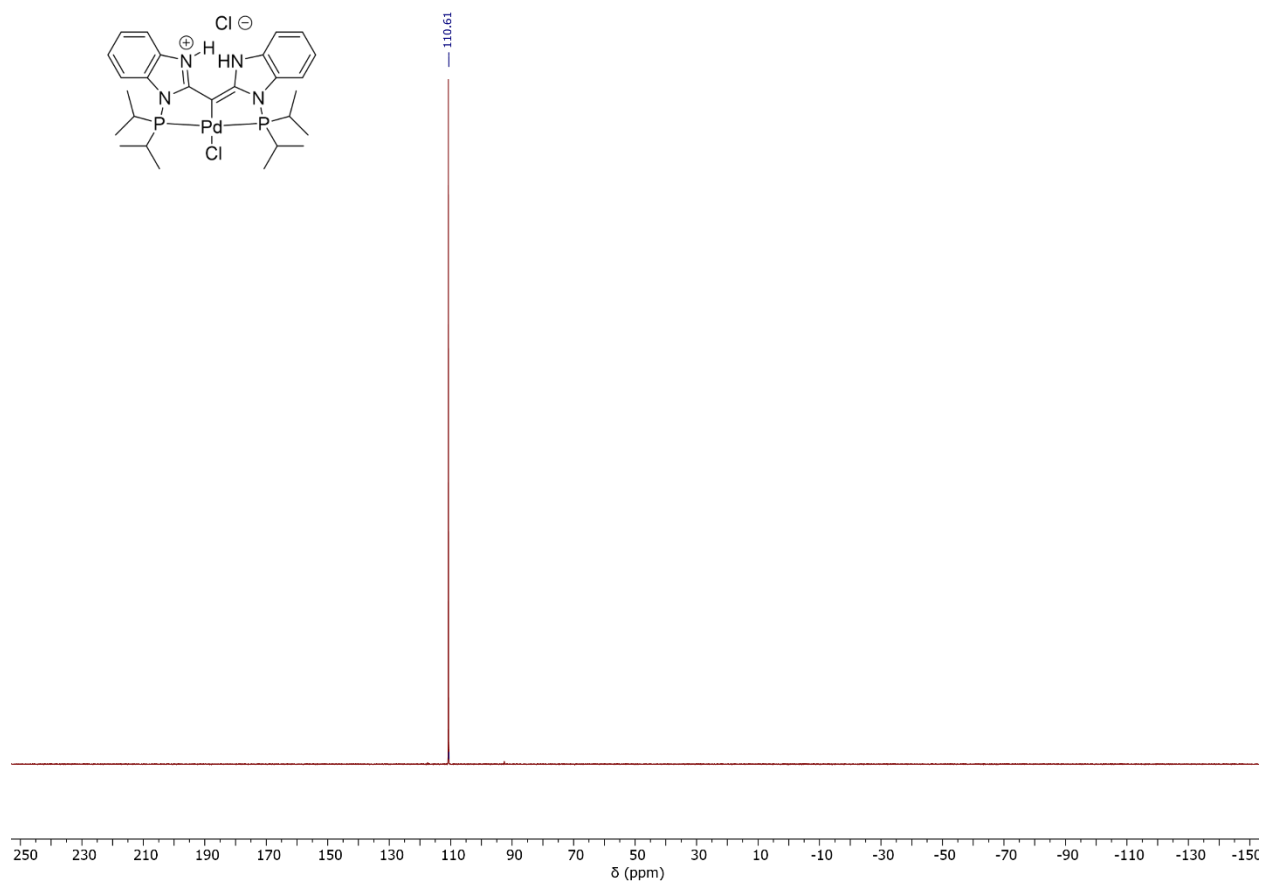


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ (162 MHz) NMR spectrum of **3-Pd** in CDCl_3 .

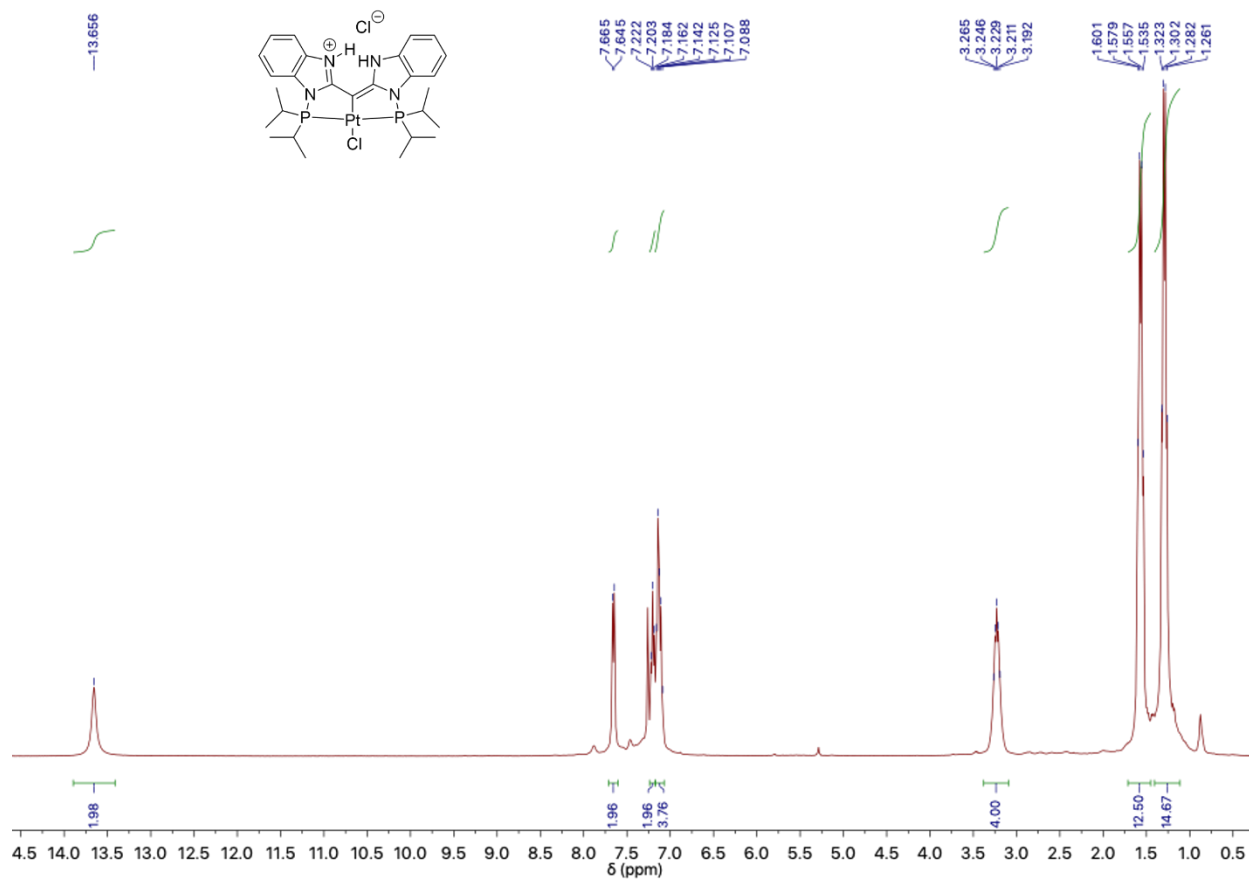


Figure S13. ¹H NMR (400 MHz) spectrum of **3-Pt** in CDCl₃. The sample contains residuals CH₂Cl₂ (s, 5.30 ppm), pentane (m, 1.27 ppm; t, 0.88 ppm).

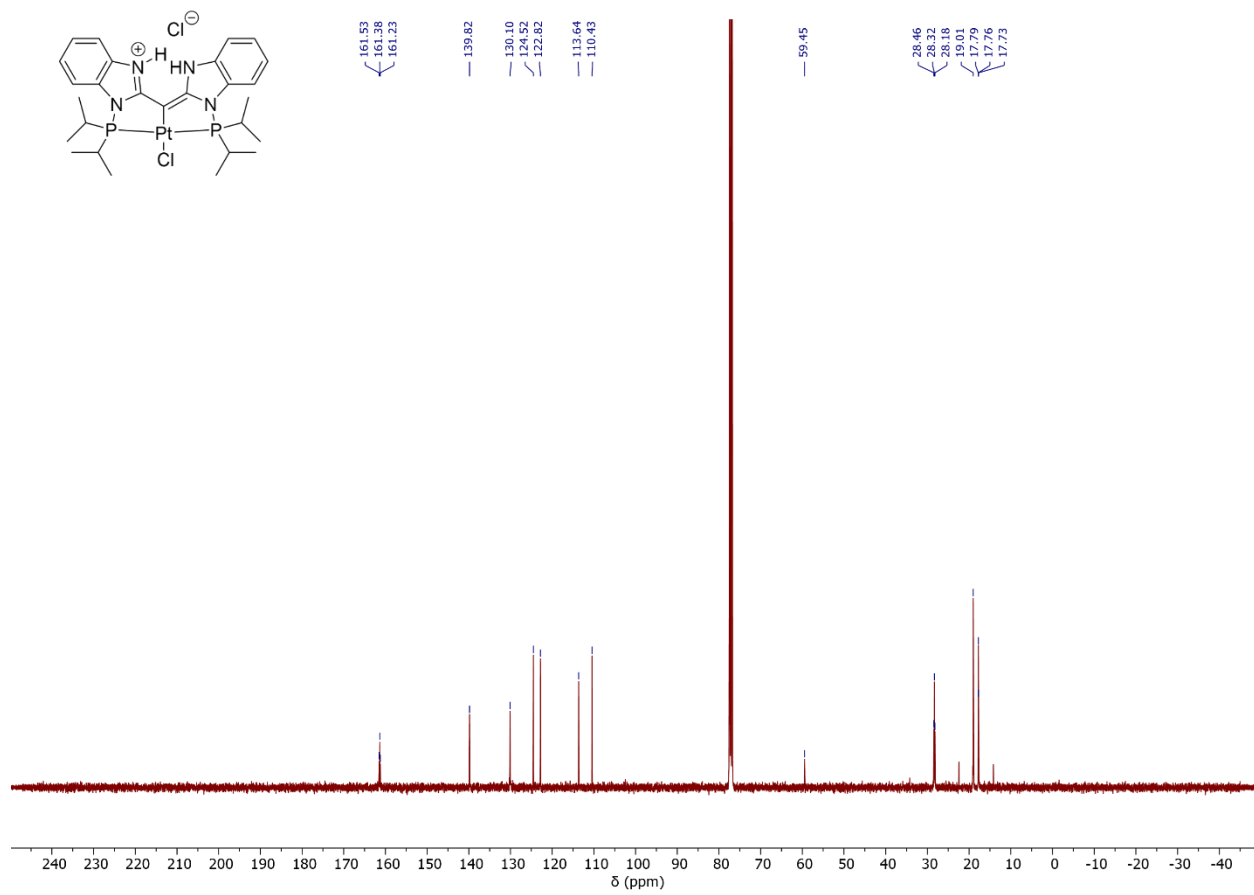


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **3-Pt** in CDCl_3 .

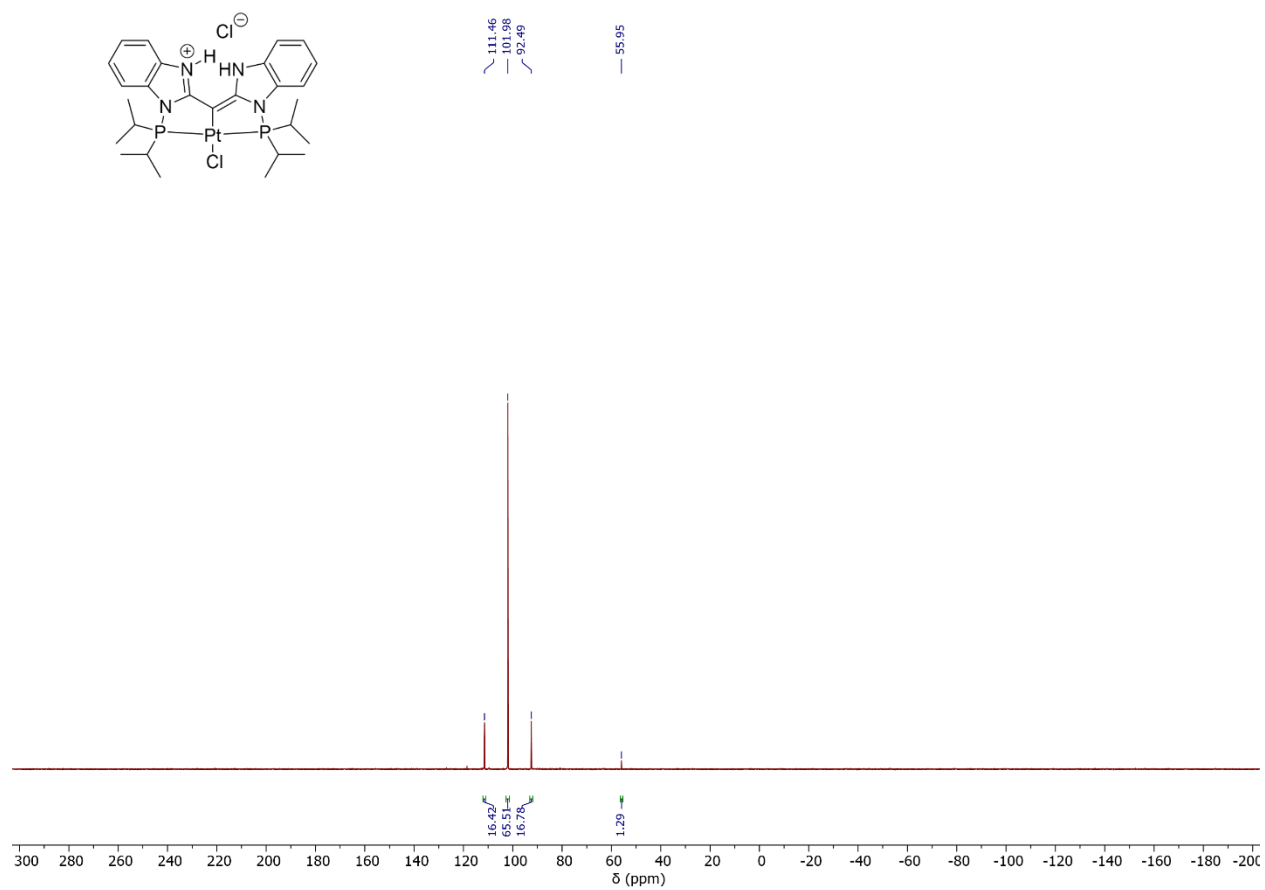


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **3-Pt** in CDCl_3 . Free ligand at 55.95 ppm.

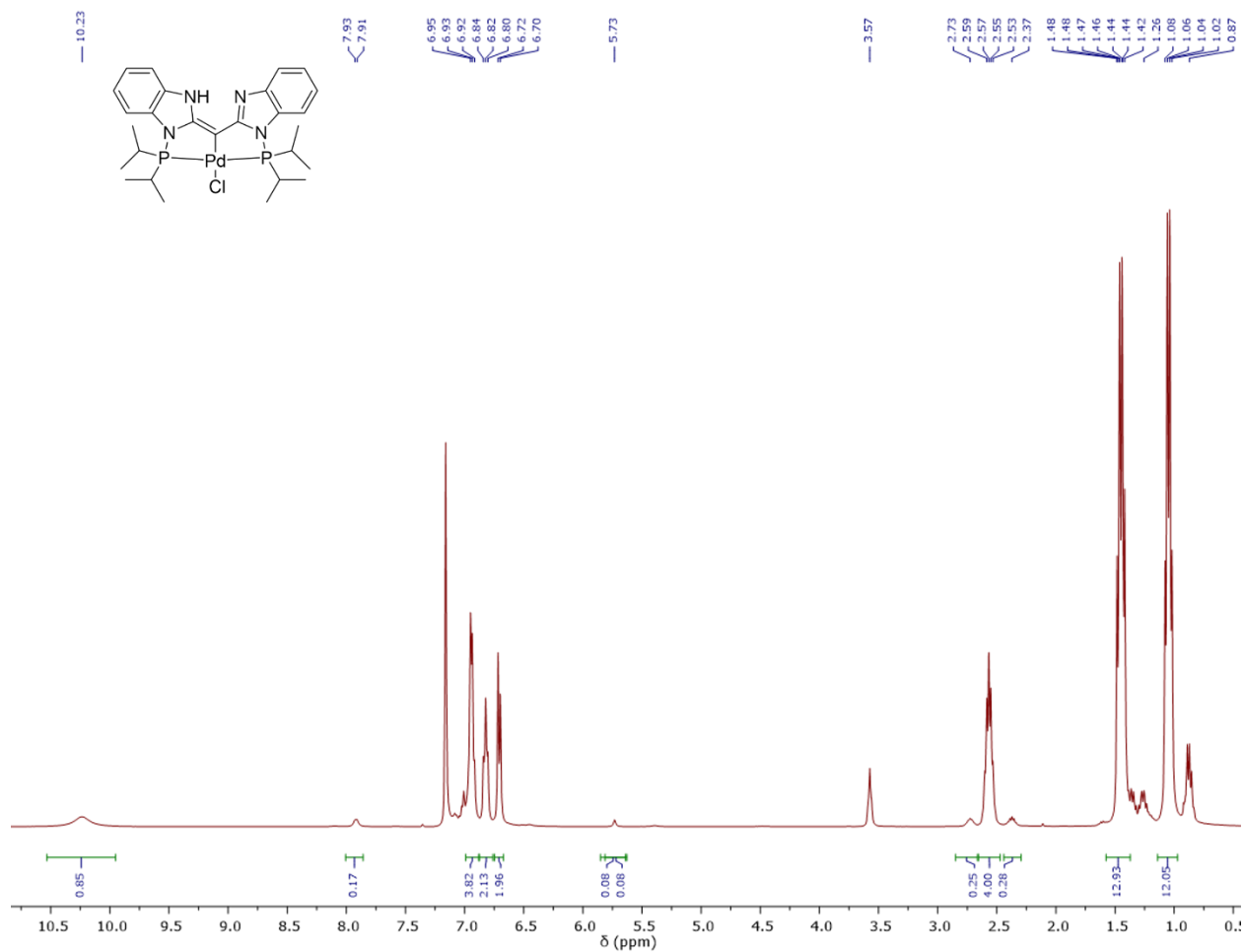


Figure S16. ¹H NMR (400 MHz) spectrum of **4a-Pd** and **4b-Pd** in C₆D₆. Both tautomers can be seen upon dissolution with **4a-Pd** being the major tautomer (95%) and **4b-Pd** the minor tautomer (5%). Contains residual THF (t, 3.57), and pentane (m 1.27, t 0.87).

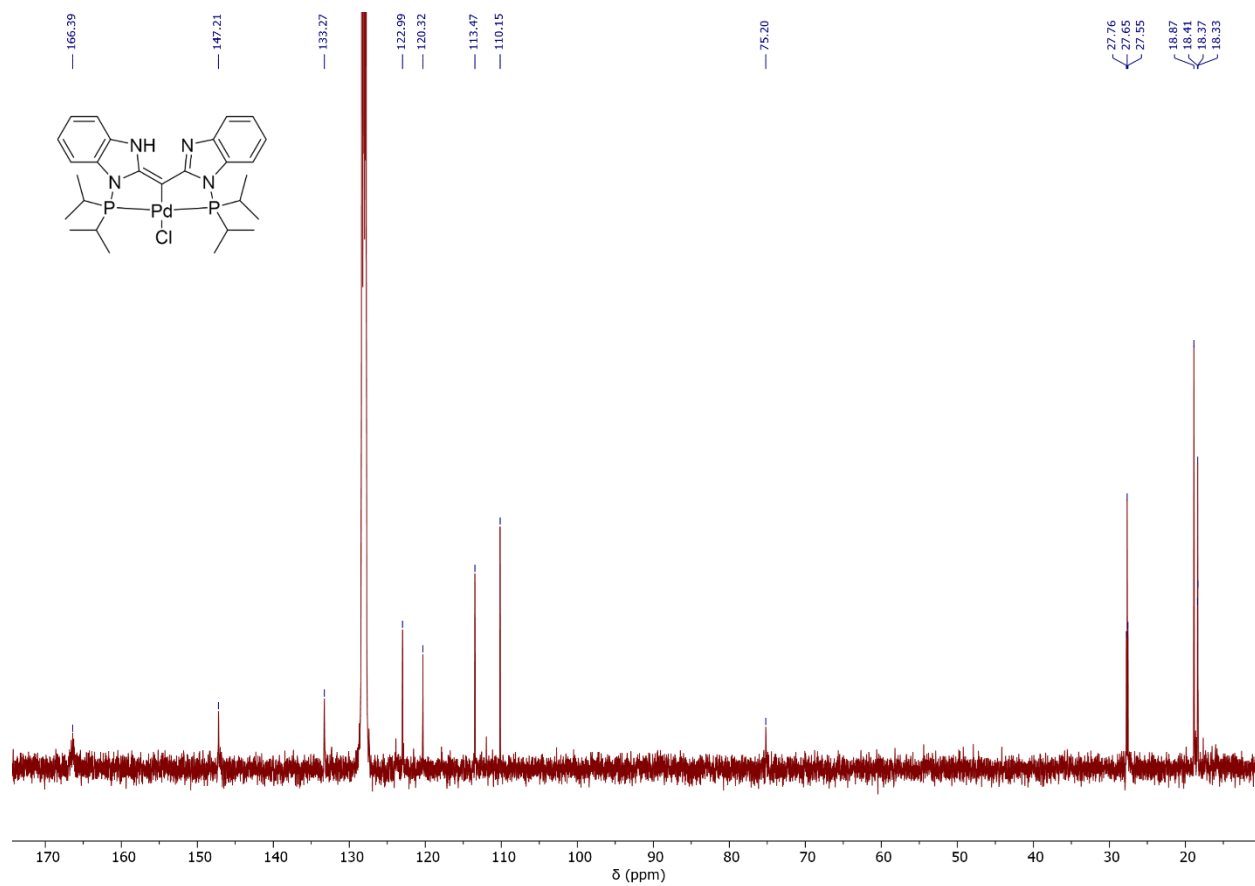


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ (100 MHz) NMR spectrum of **4a-Pd** in C_6D_6 .

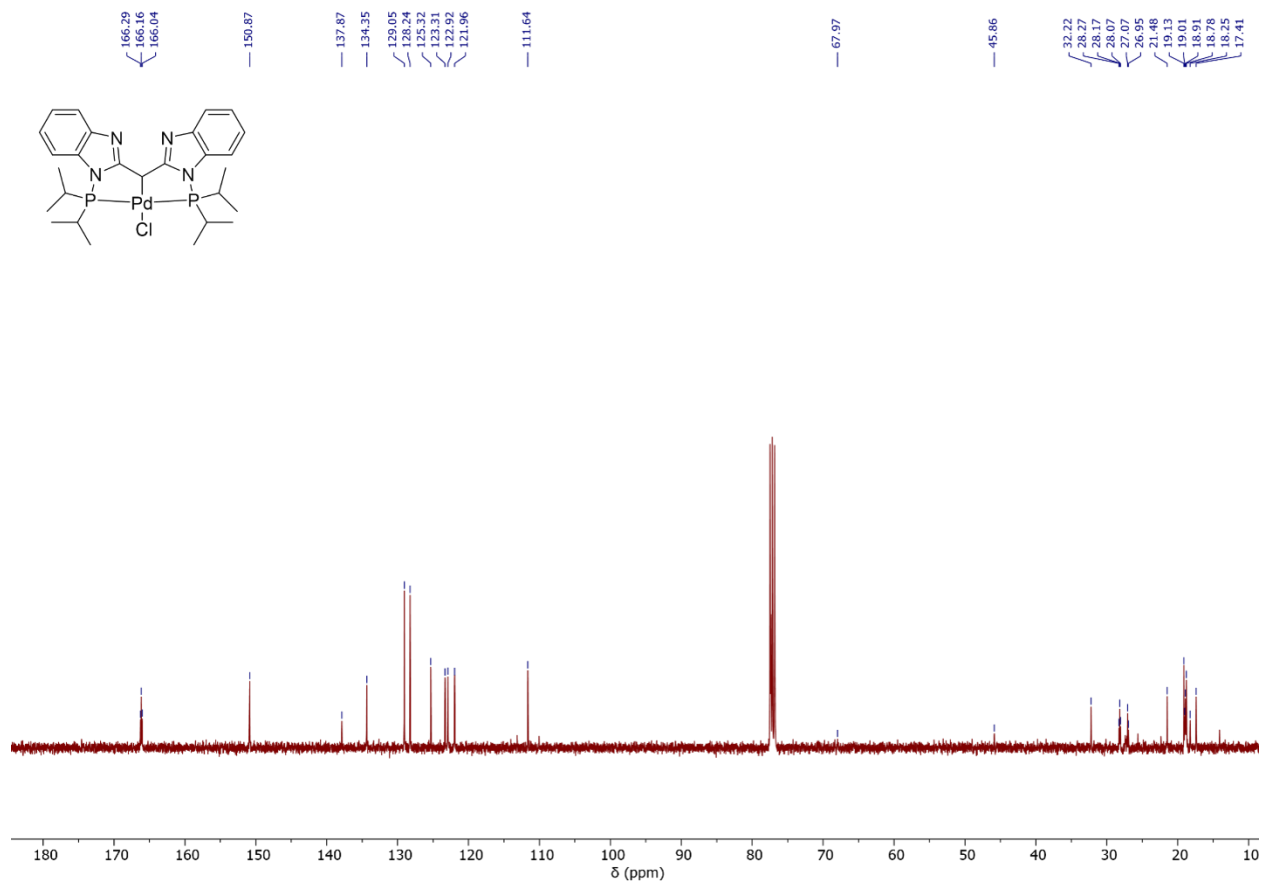


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ (100 MHz) NMR spectrum of **4b-Pd** in CDCl_3 . Sample contains residual toluene (s, 137.9, 129.1, 128.2, 125.3, 21.5 ppm).

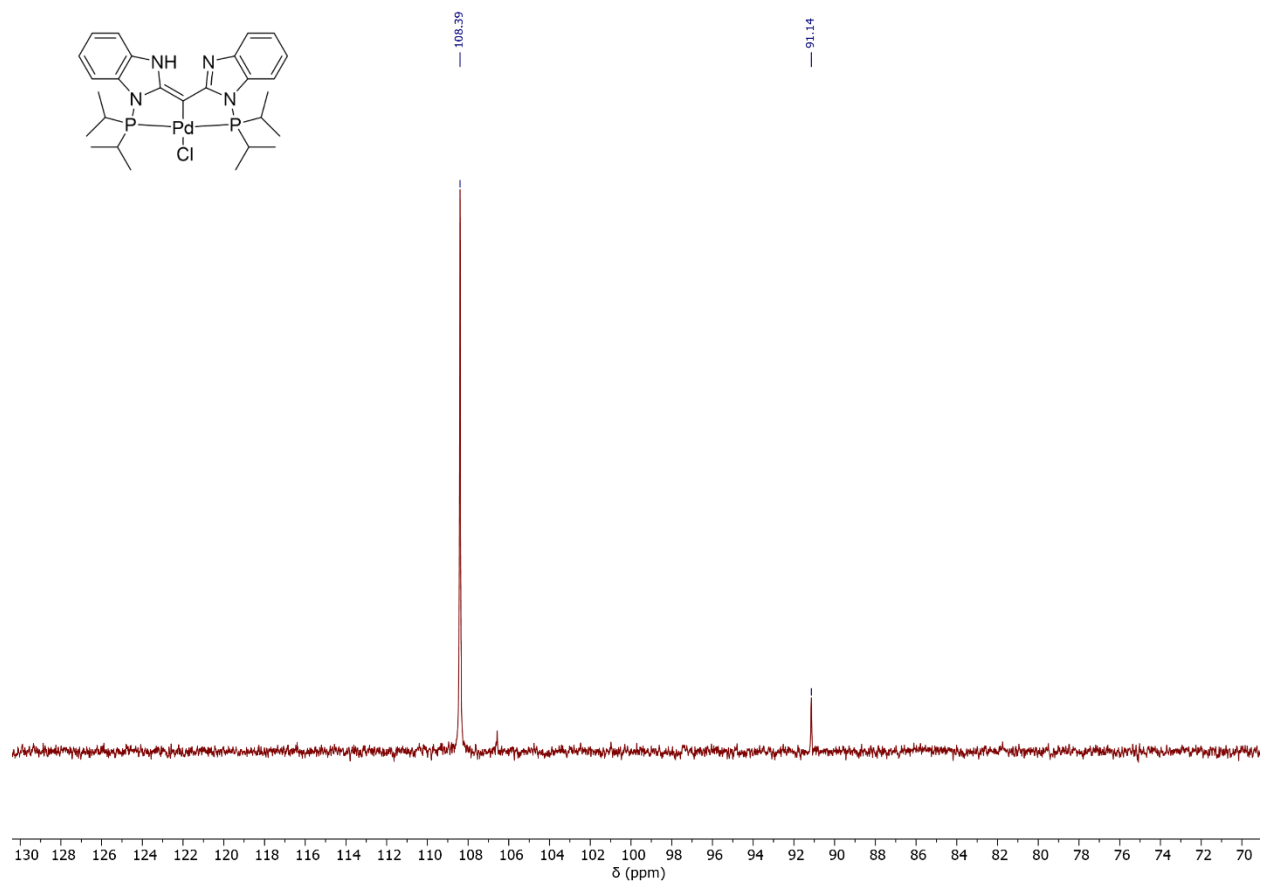


Figure S19. $^{31}\text{P}\{^1\text{H}\}$ (202 MHz) NMR spectrum of **4a-Pd** (108.4 ppm, major tautomer, 95%) and **4b-Pd** (91.1 ppm, minor tautomer, 5%) in C_6D_6 .

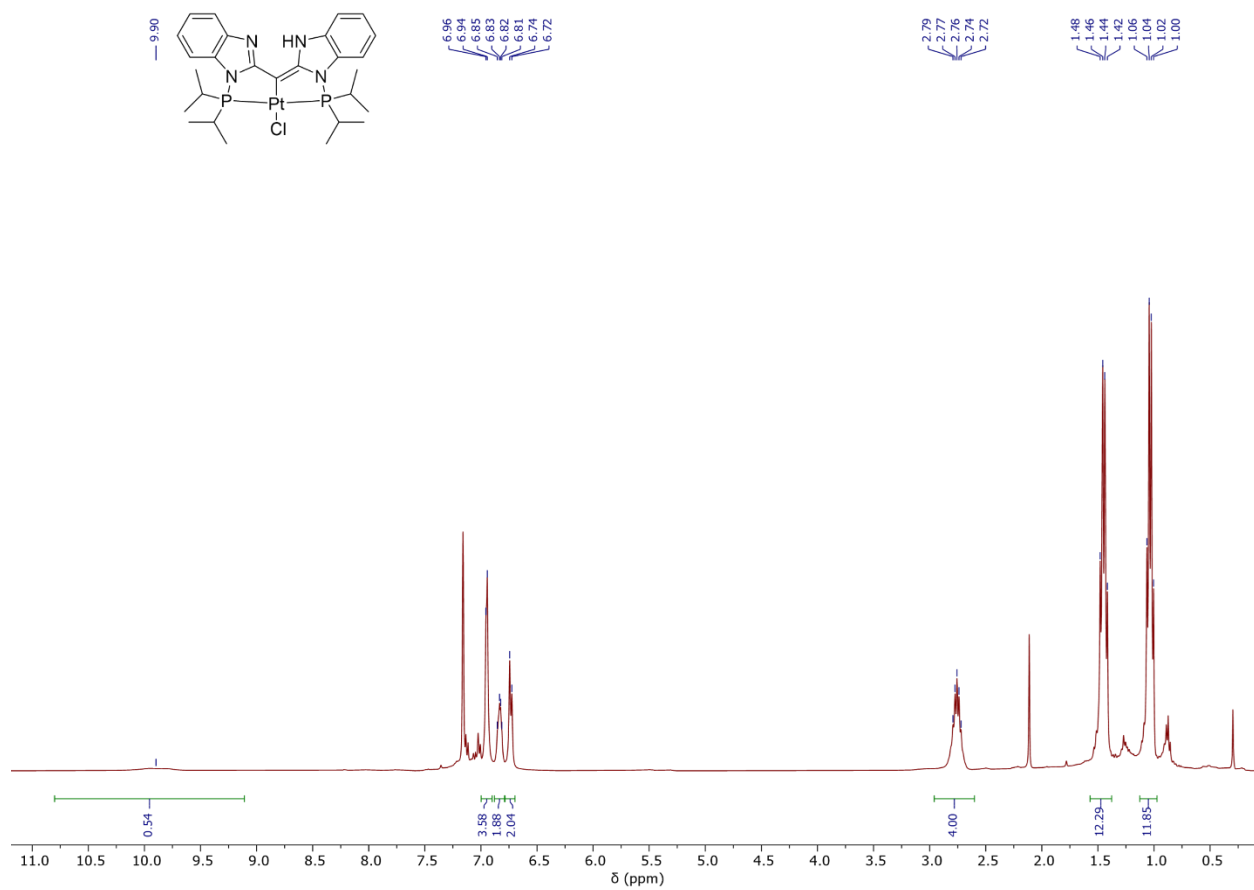


Figure S20. $^1\text{H NMR}$ (400 MHz) spectrum of **4-Pt** in C_6D_6 . Contains residual toluene (s, 2.11).

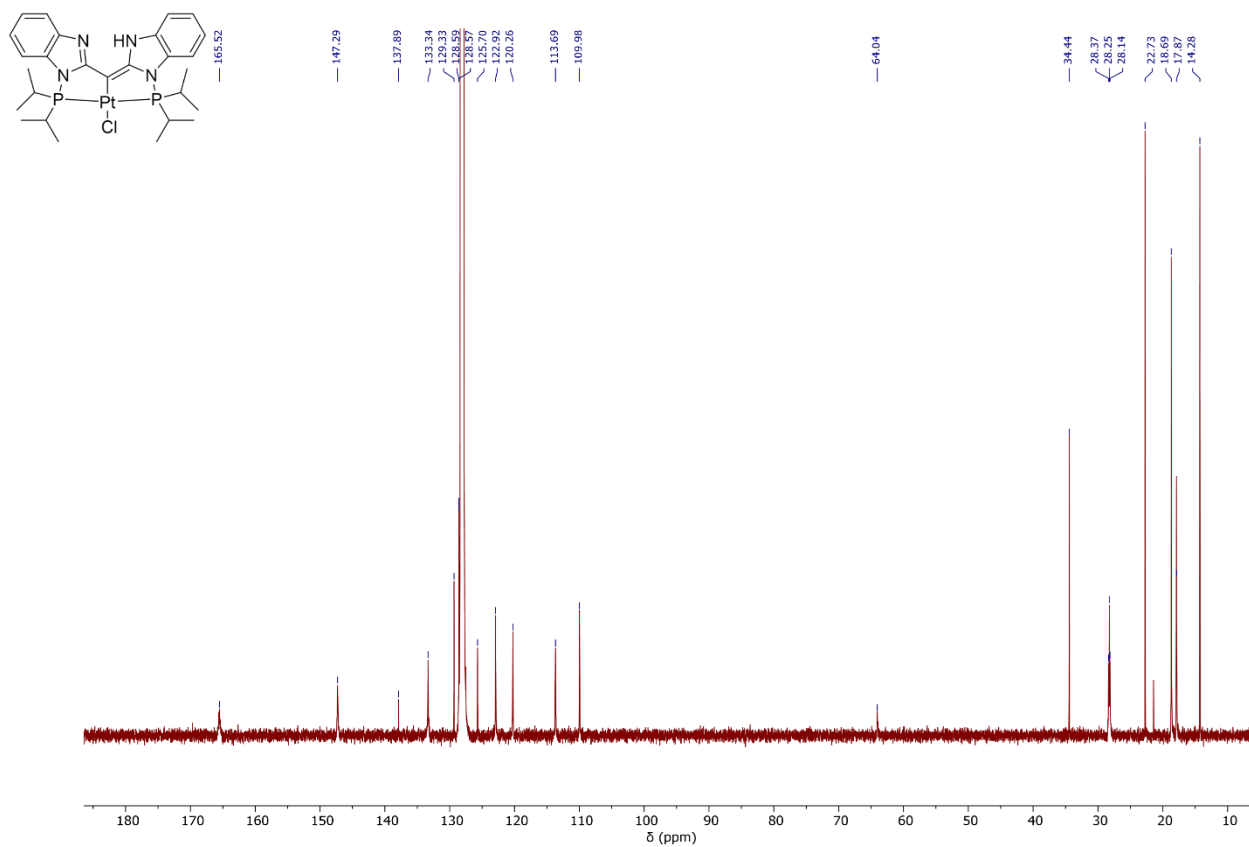


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) spectrum of **4-Pt** in C_6D_6 . Contains residual toluene (s: 137.9, 129.3, 128.6, 125.7, 21.1) and pentane (s: 34.4, 22.7, 14.3).

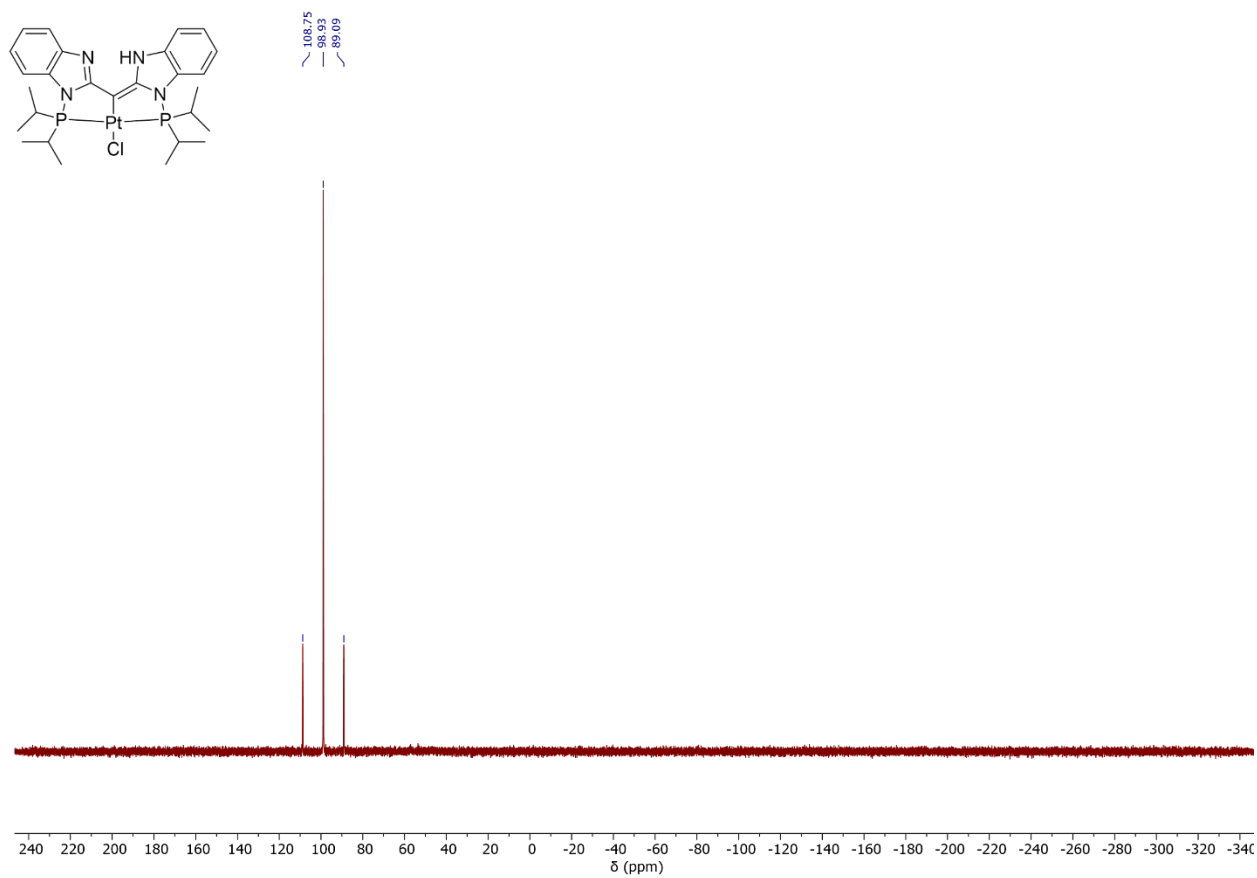


Figure S22. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectrum of **4-Pt** in C_6D_6 .

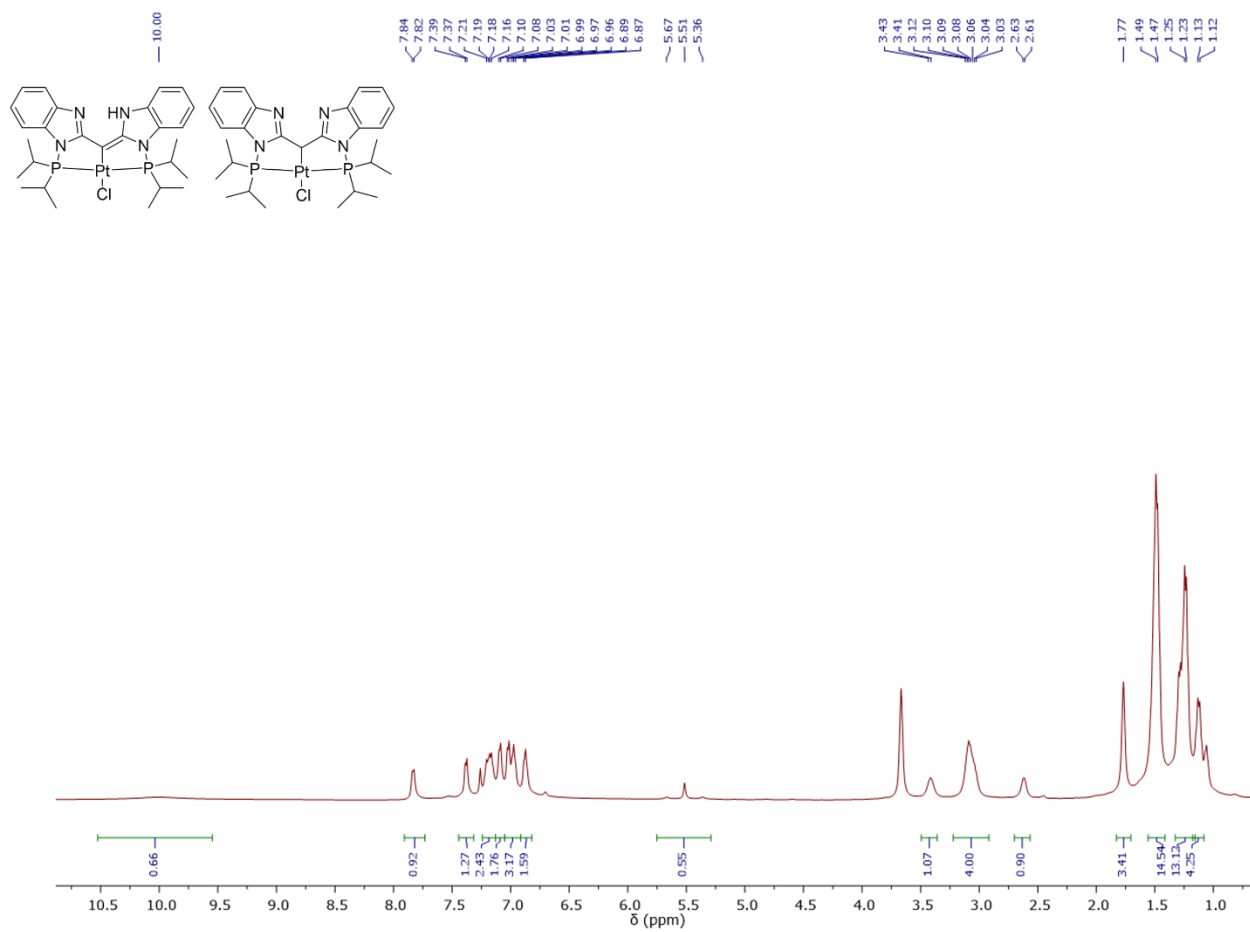


Figure S23. ^1H NMR (500 MHz) spectrum of **4-Pt** in CDCl_3 .

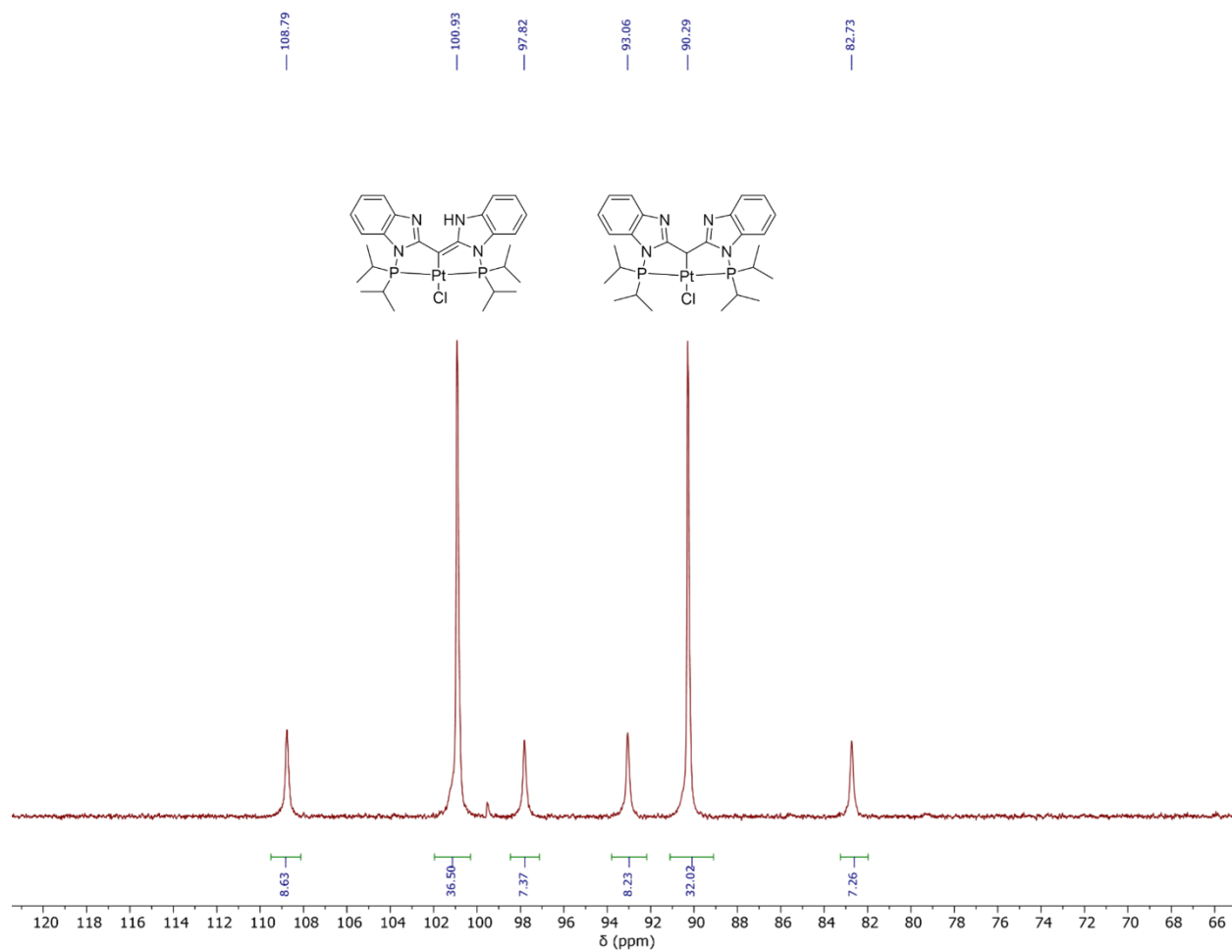


Figure S24. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **4-Pt** in CDCl_3 . **4a-Pt** (53%) at 100.9 ppm and **4b-Pt** (47%) at 90.3 ppm.

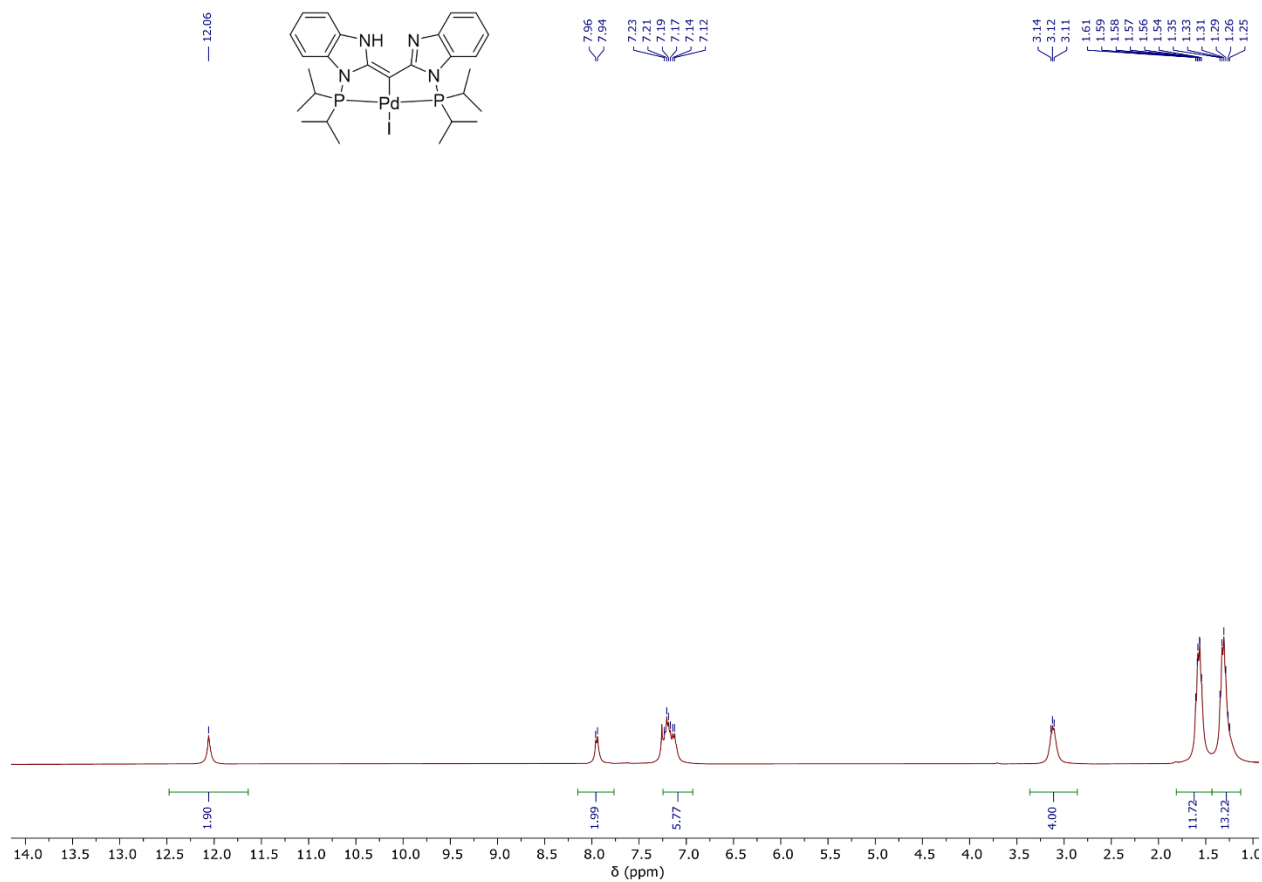


Figure S25. $^1\text{H NMR}$ (400 MHz) spectrum of **5** in CDCl_3 .

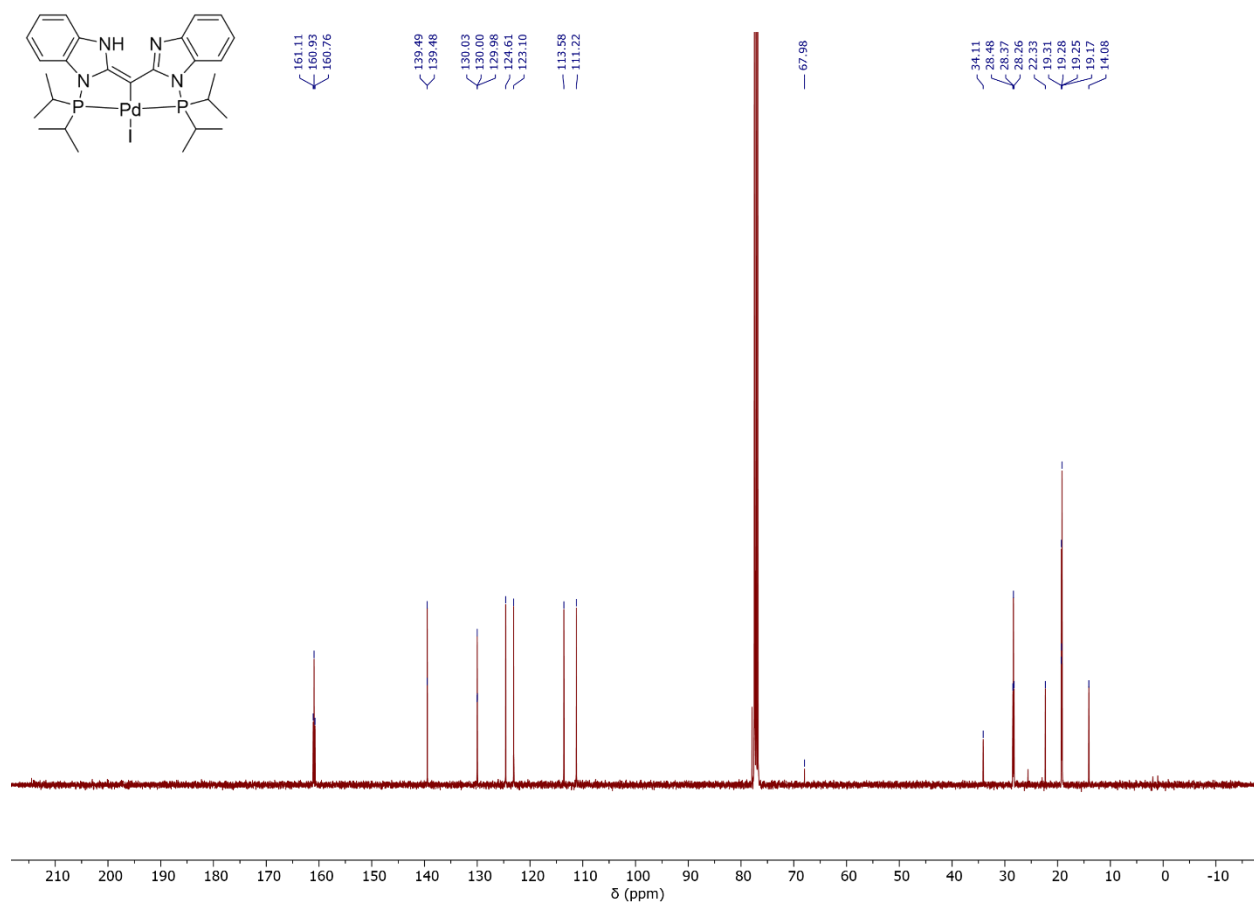


Figure S26. $^{13}\text{C}\{^1\text{H}\}$ (100 MHz) NMR spectrum of **5** in CDCl_3 .

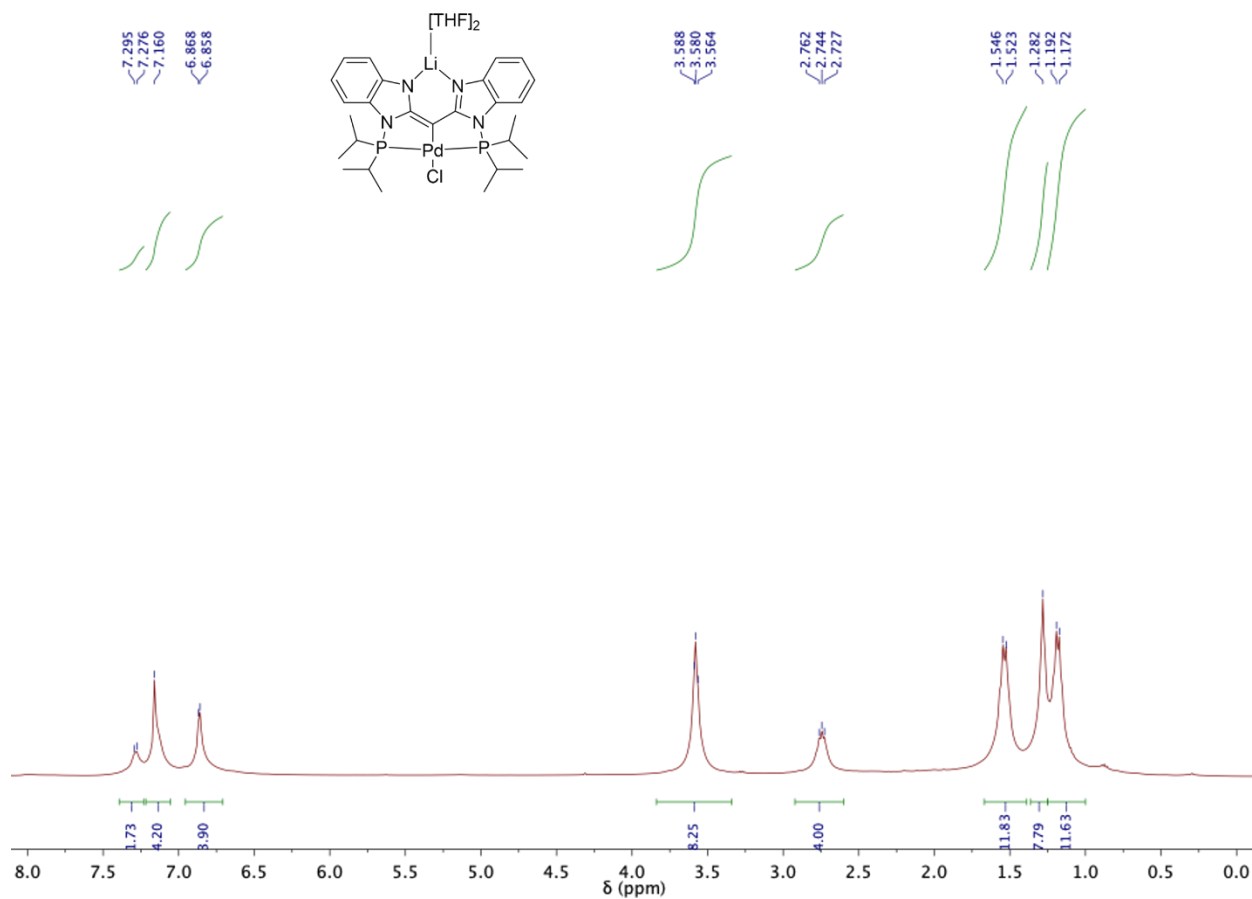


Figure S28. ^1H NMR (400 MHz) spectrum of **6-Pd** in C_6D_6 .

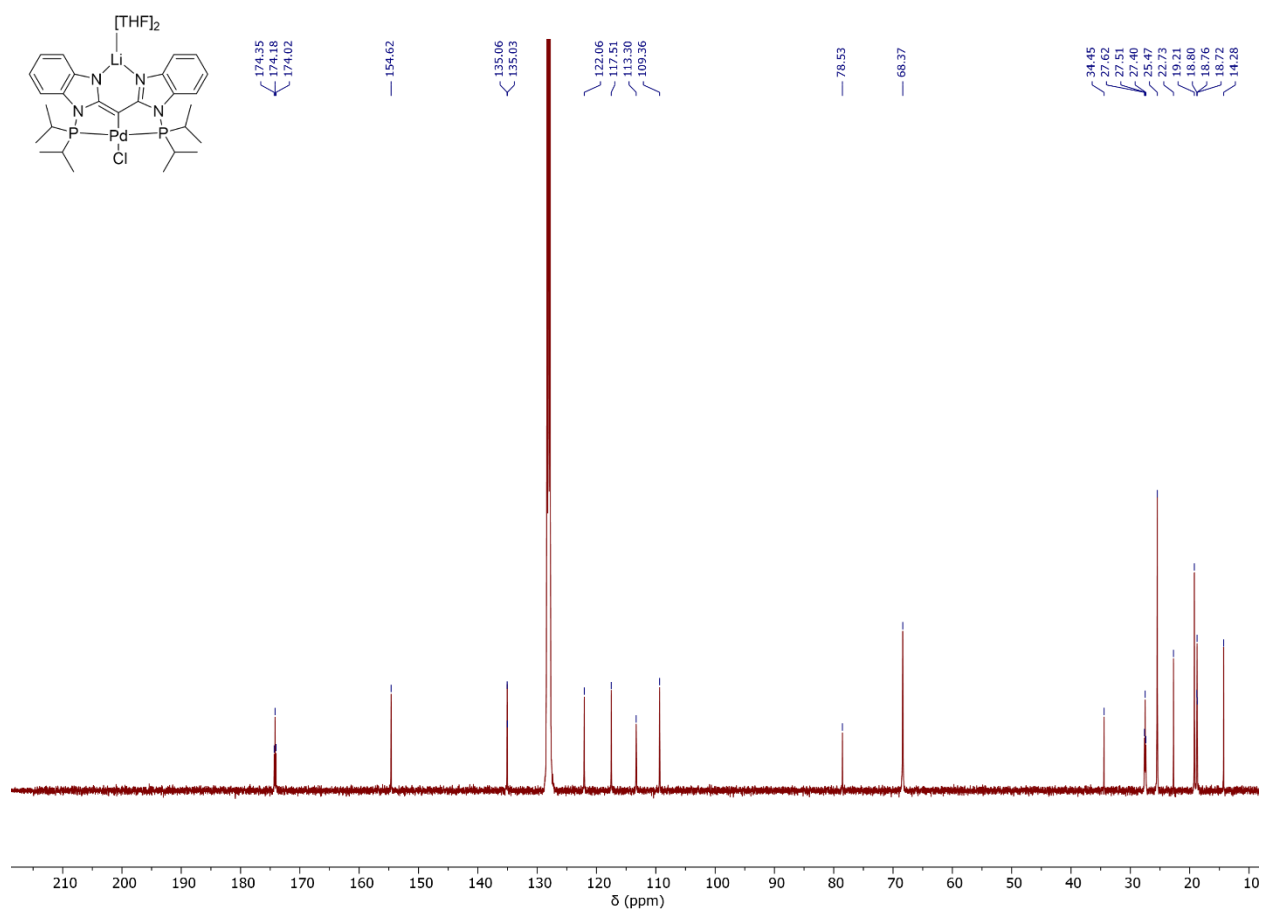


Figure S29. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **6-Pd** in C_6D_6 .

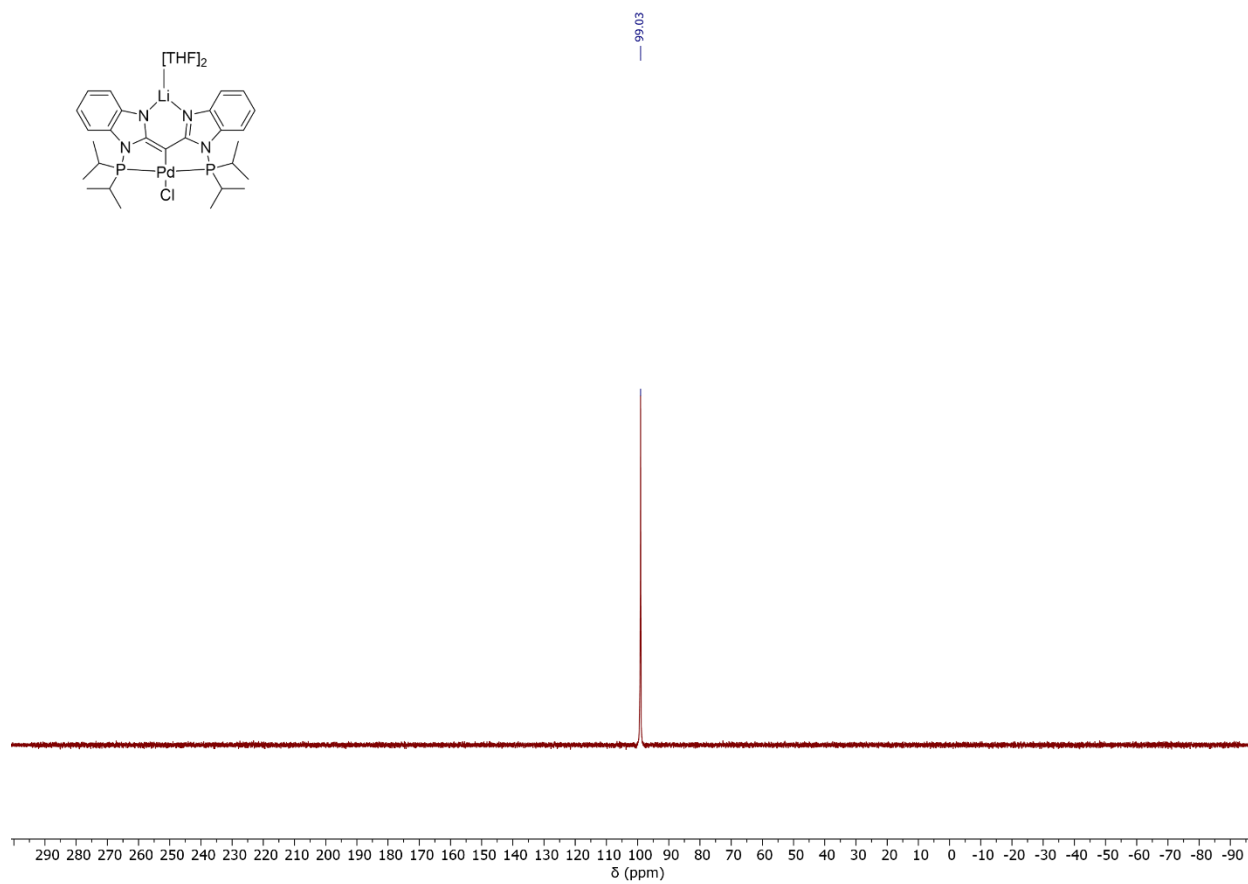


Figure S30. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **6-Pd** in C_6D_6 .

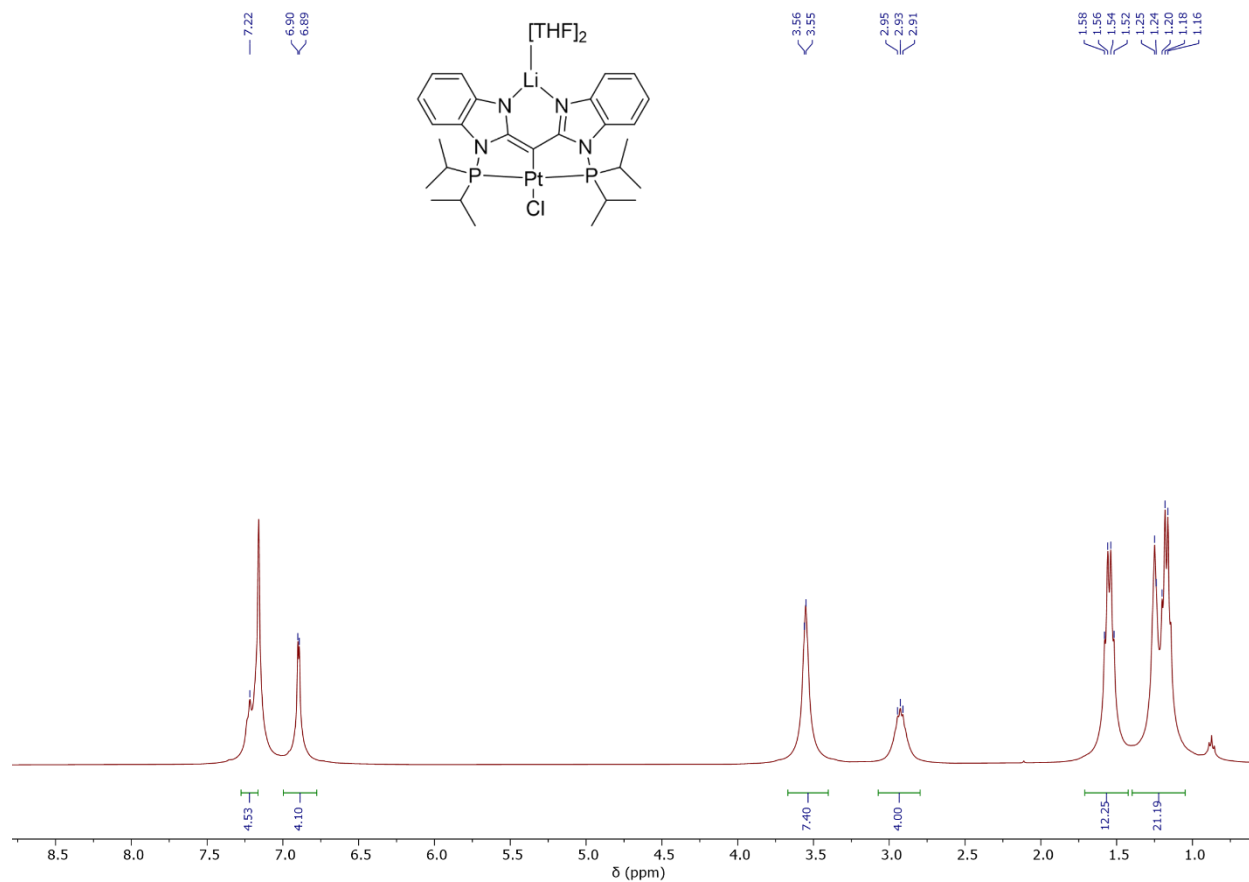


Figure S31. ^1H NMR (400 MHz) spectrum of **6-Pt** in C_6D_6 . The sample contains residual $\text{HN}(\text{Me}_3\text{Si})_2$ at 0.10 ppm.

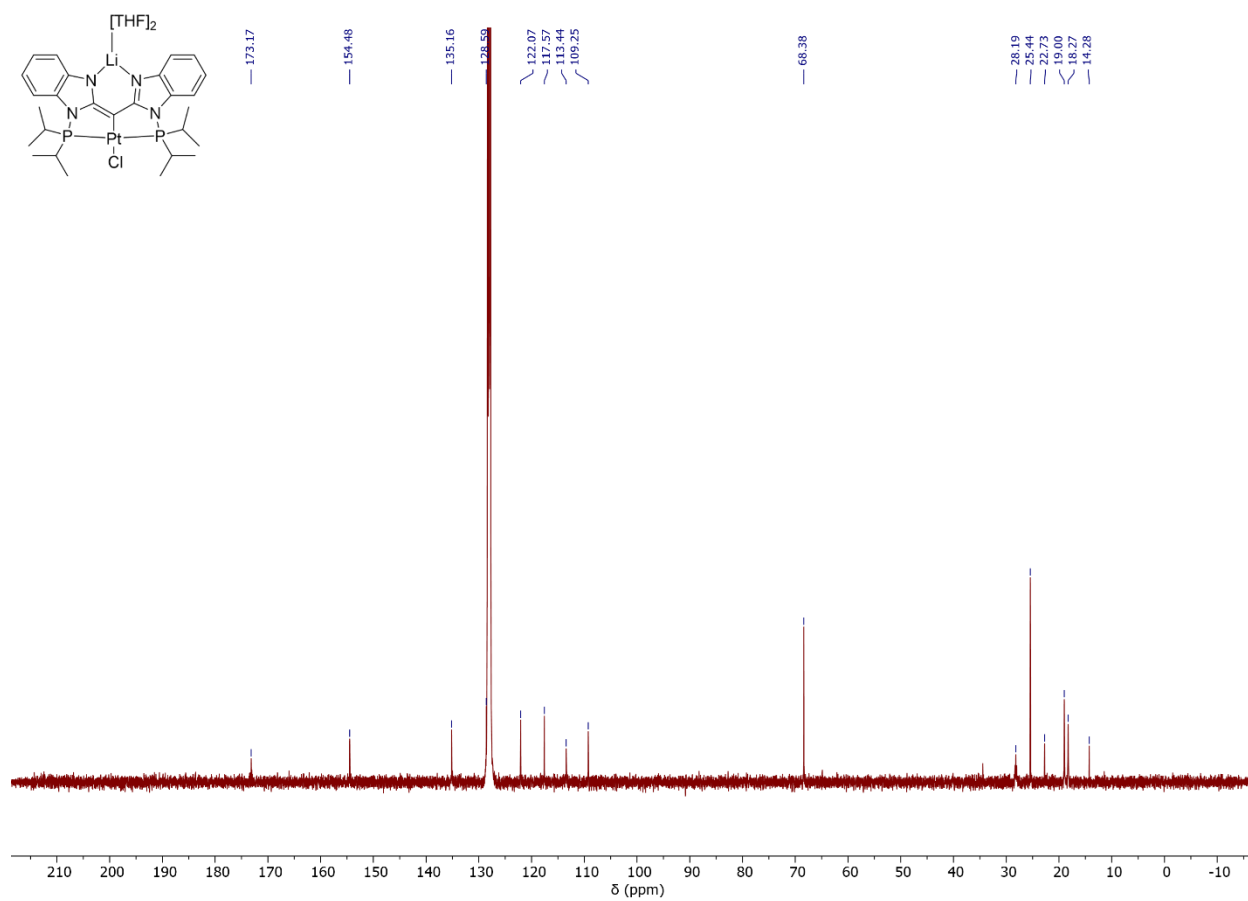


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **6-Pt** in C_6D_6 .

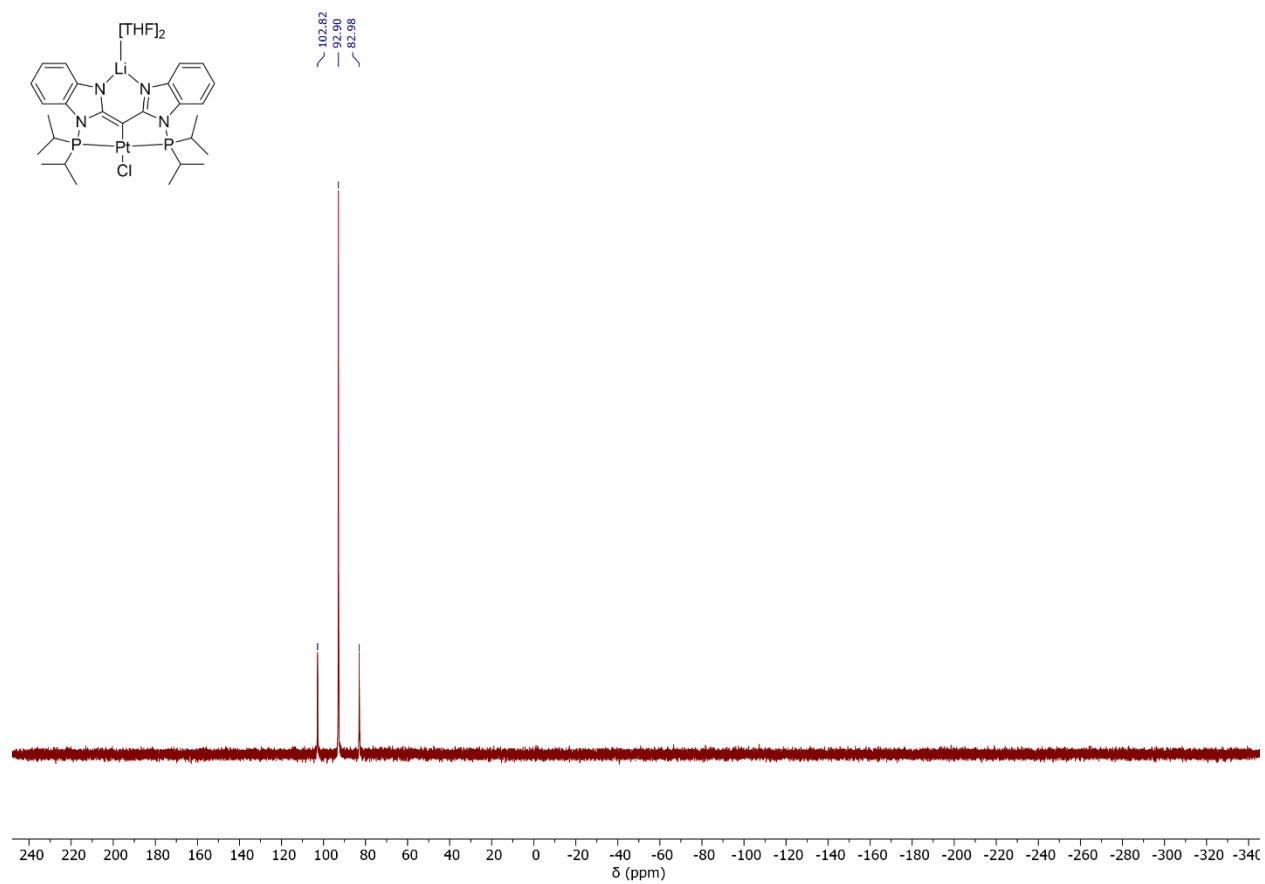


Figure S33. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **6-Pt** in C_6D_6 .

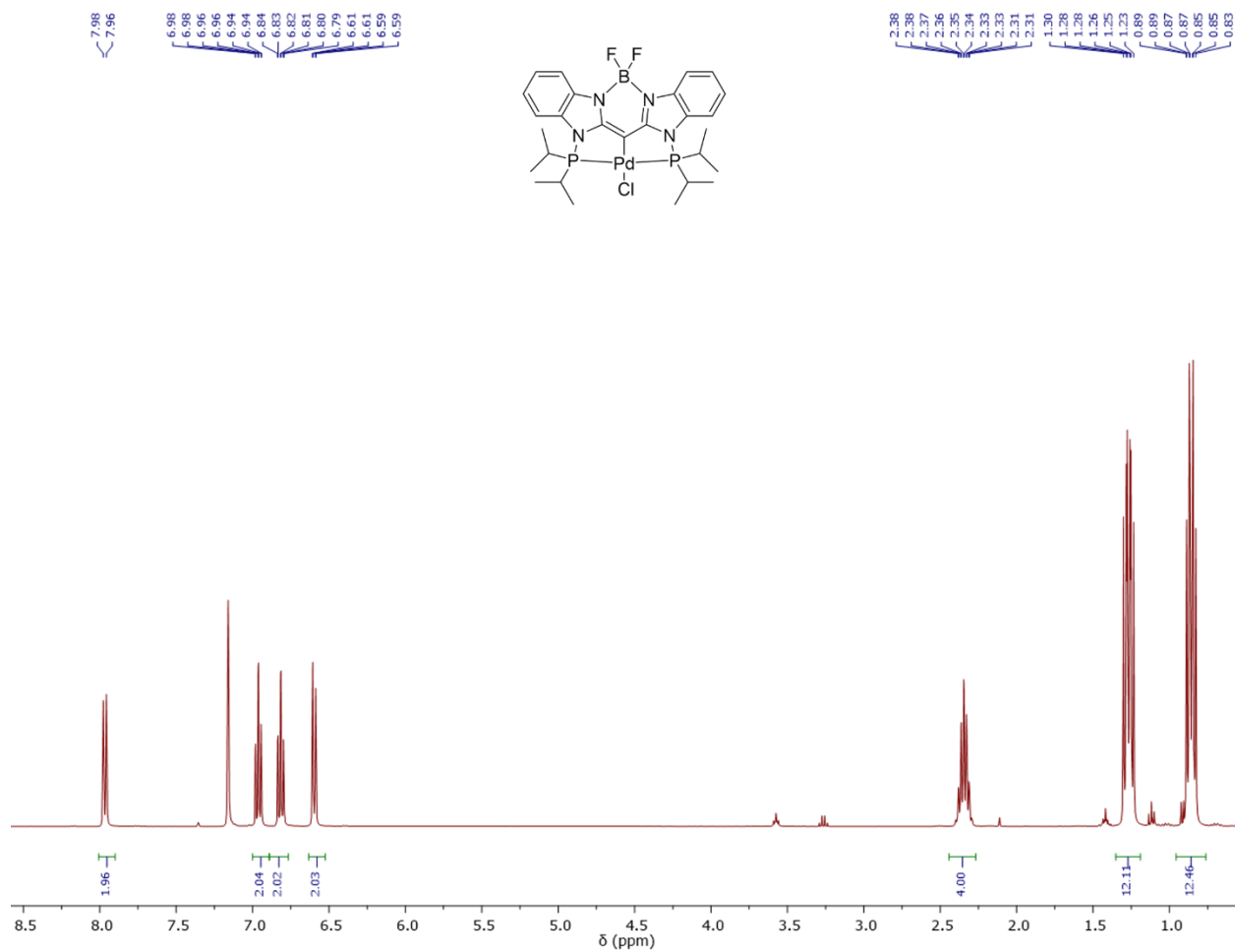


Figure S34. ¹H NMR spectrum (400 MHz) of **7-Pd** in C₆D₆. The sample contains residual THF (m, 3.58 ppm; m, 1.42 ppm) and diethyl ether (q, 3.27 ppm; t, 1.11 ppm).

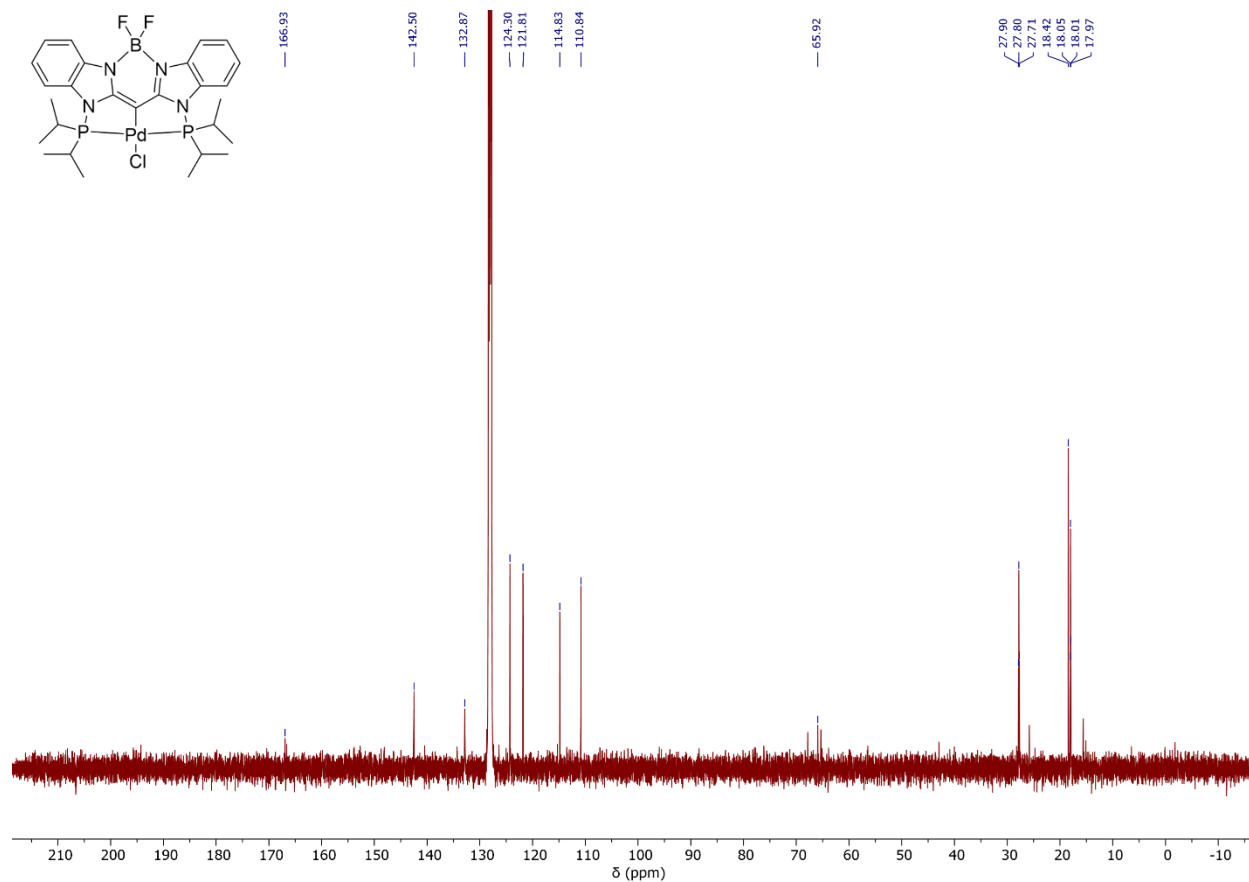


Figure S35. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **7-Pd** in C_6D_6 . Sample contains residual THF (s: 67.8, 25.8 ppm) and diethyl ether (s: 65.3, 15.6 ppm)

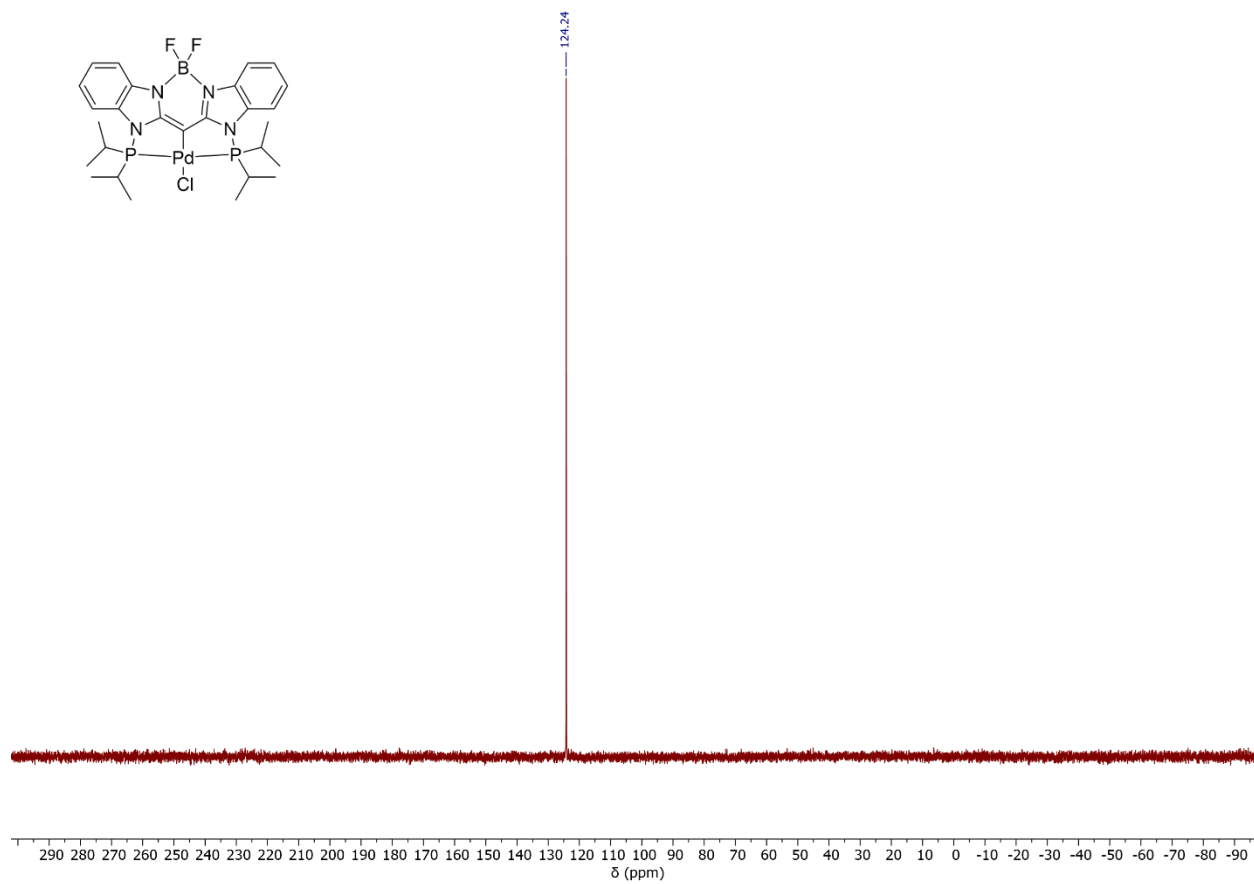


Figure S36. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **7-Pd** in C_6D_6 .

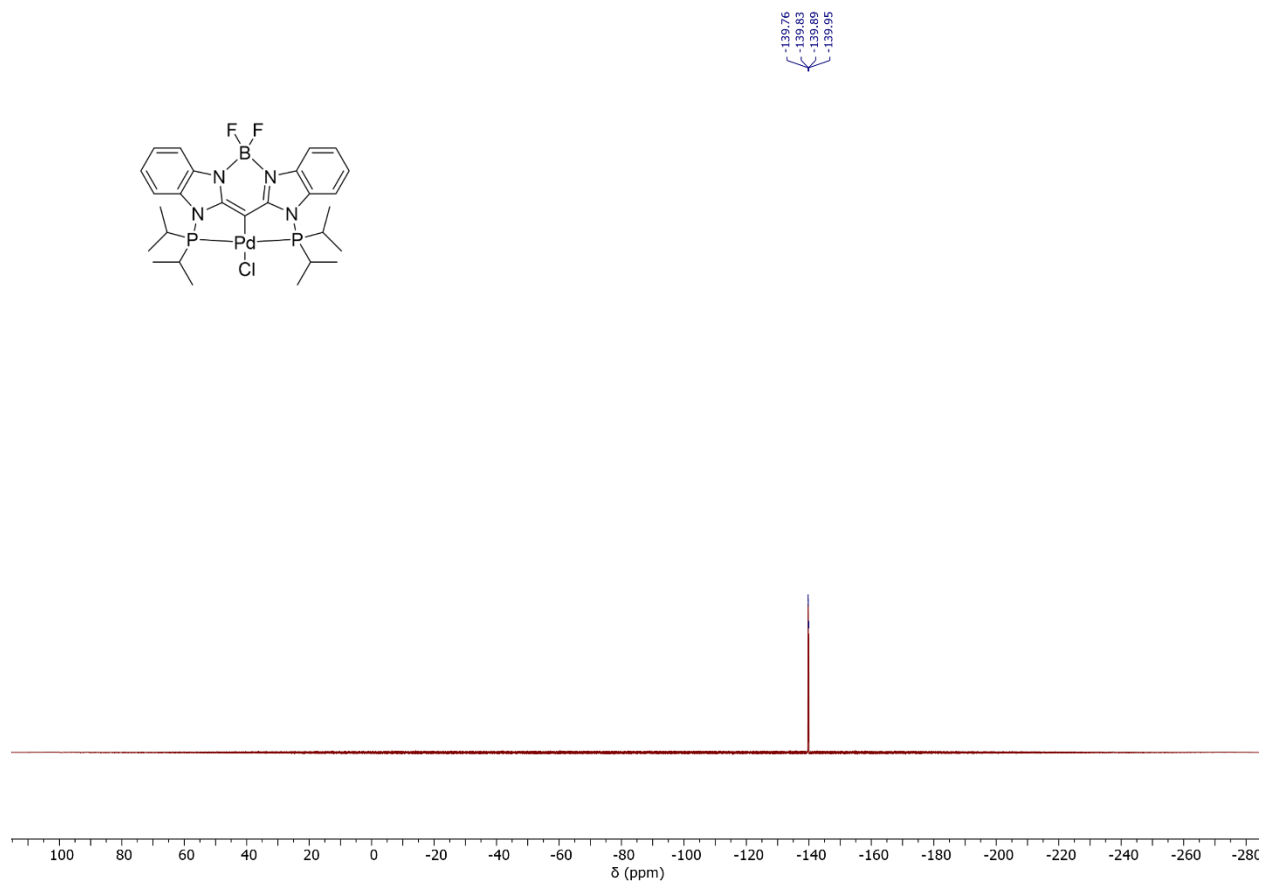


Figure S37. ^{19}F NMR (472 MHz) spectrum of **7-Pd** in C_6D_6 .

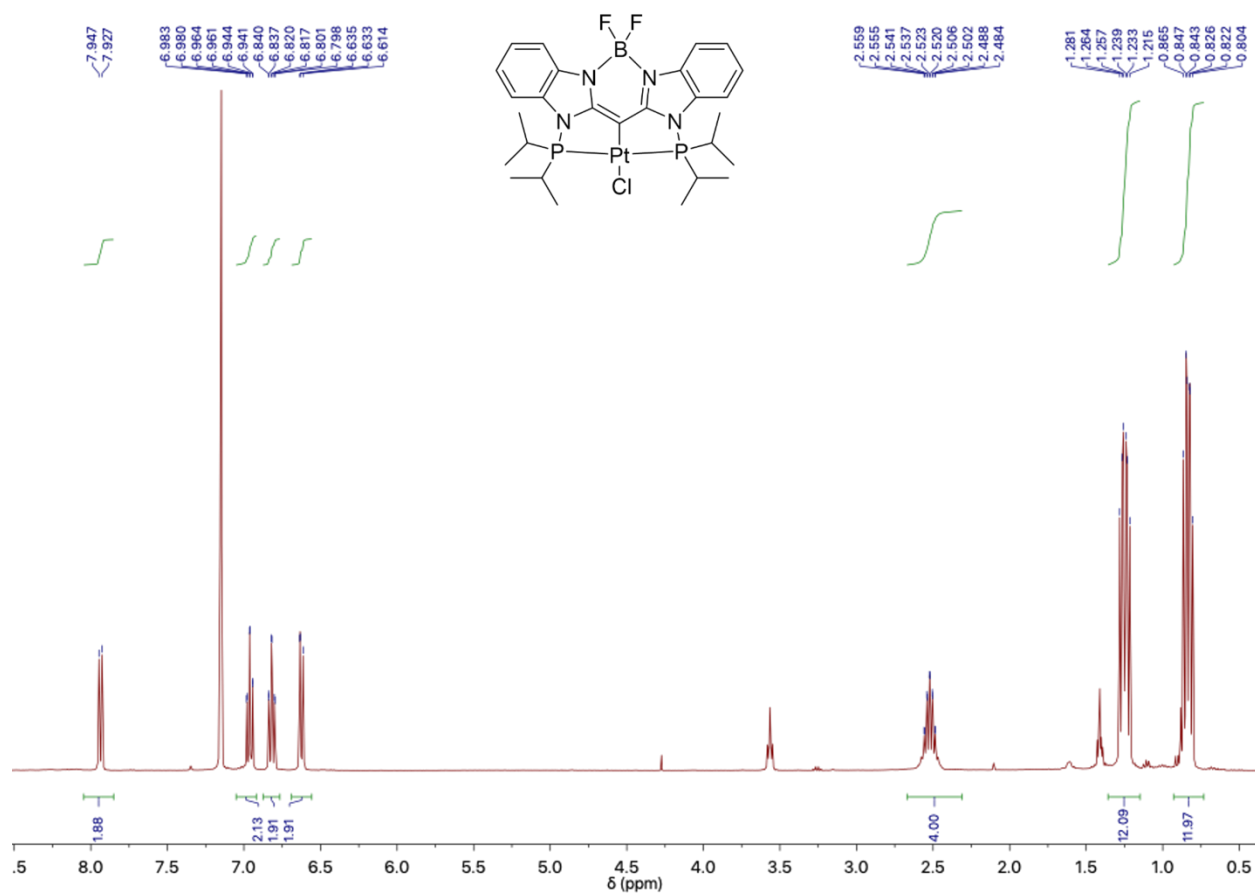


Figure S38. ^1H NMR (400 MHz) spectrum of **7-Pt** in C_6D_6 . The sample contains residuals CH_2Cl_2 (s, 4.27 ppm) and THF (m, 3.56 ppm; m, 1.41 ppm).

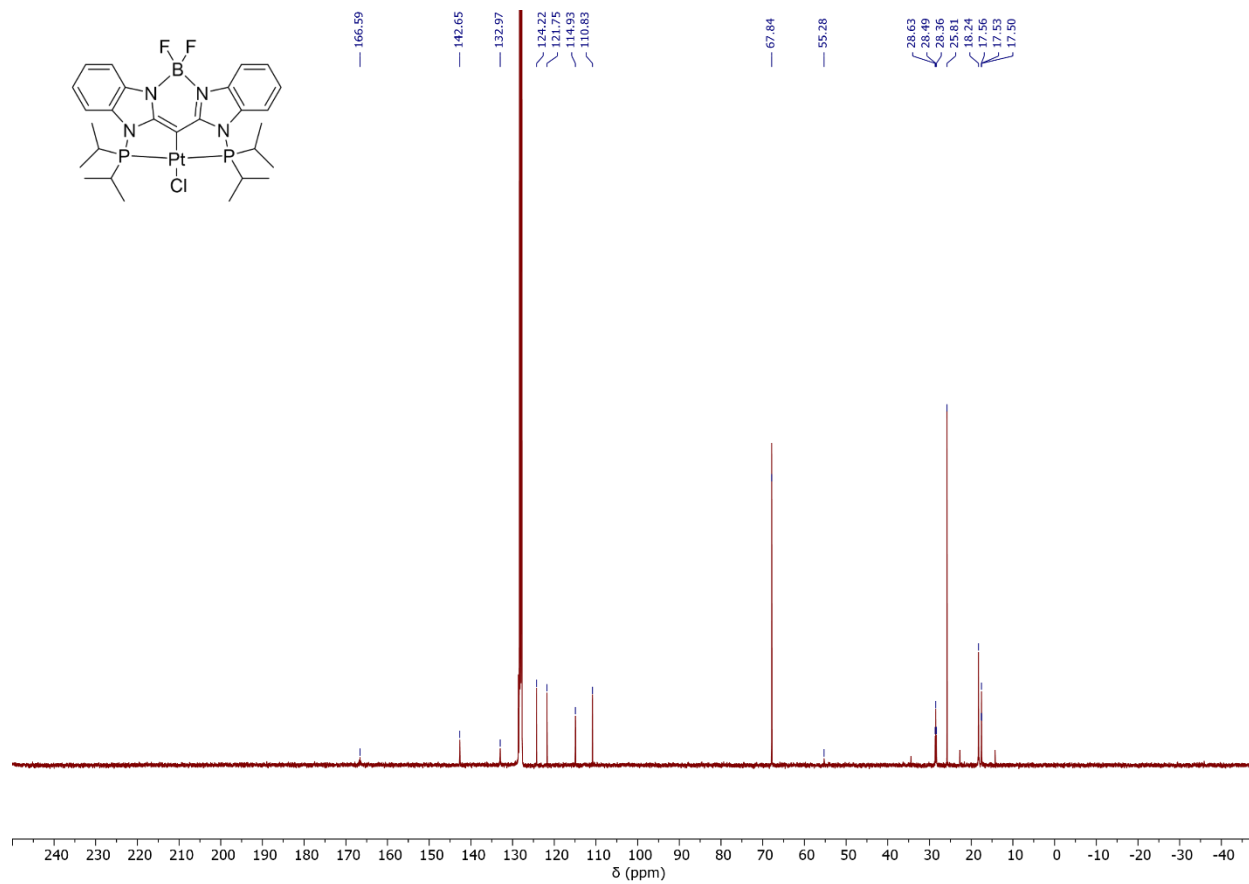


Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **7-Pt** in C_6D_6 . Sample contains residual THF (s: 67.8, 25.8 ppm)

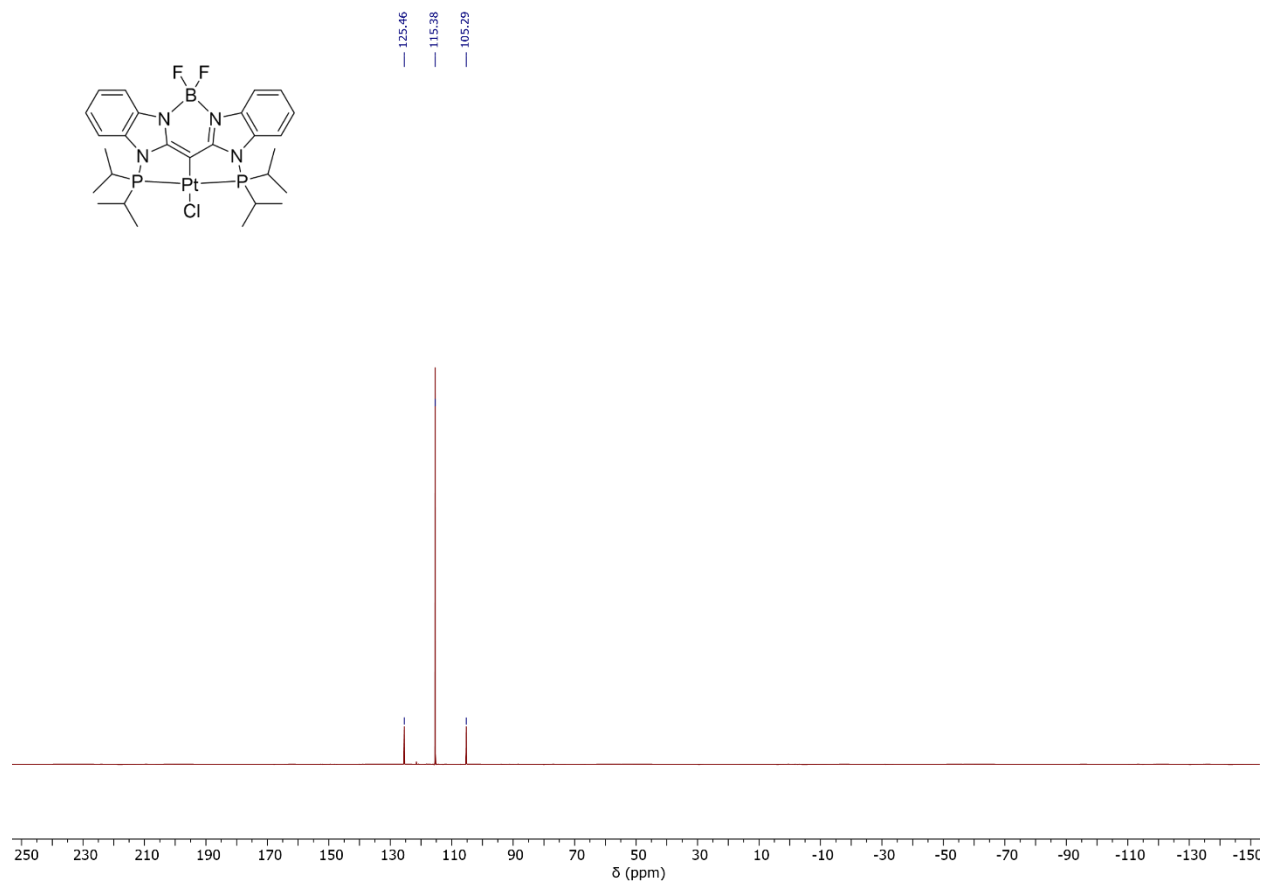


Figure S40. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **7-Pt** in C_6D_6 .

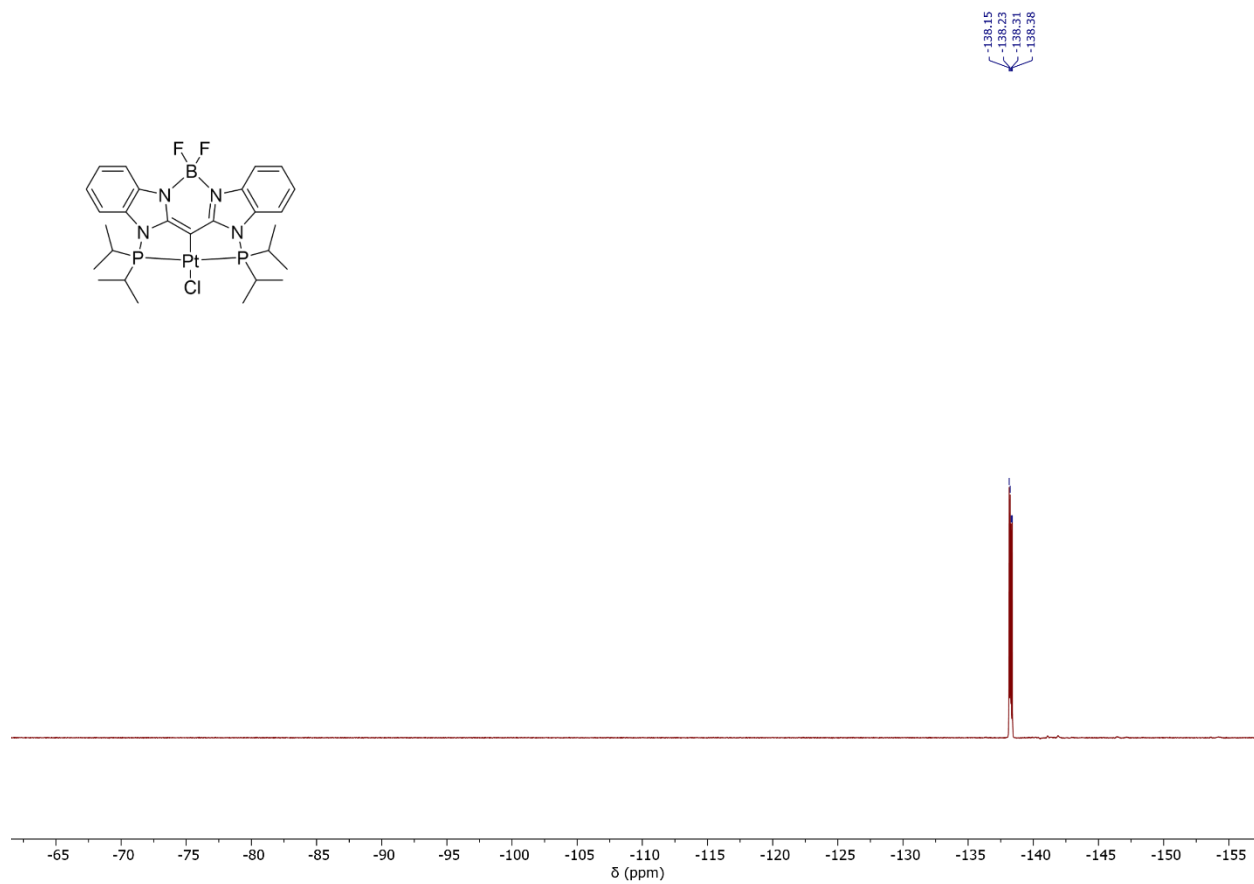


Figure S41. ^{19}F NMR (472 MHz) spectrum of **7-Pt** in C_6D_6

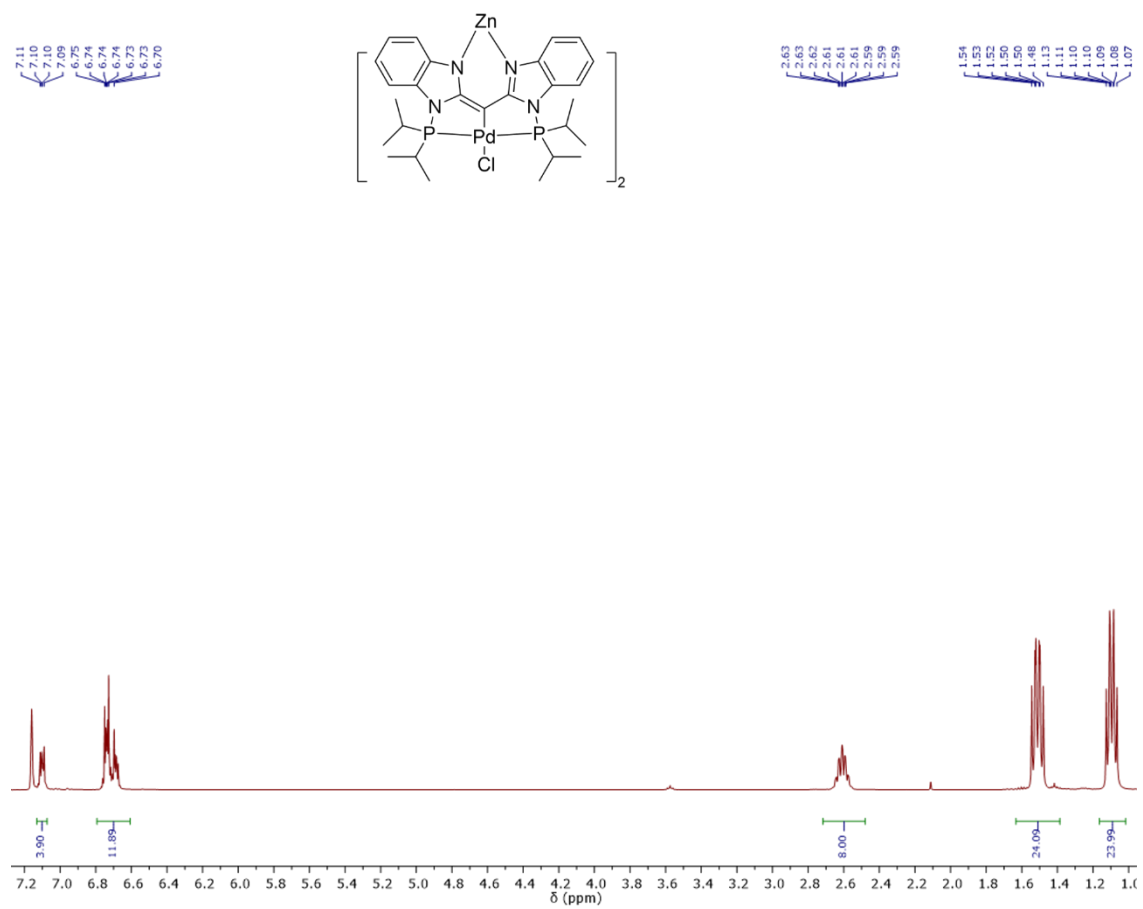


Figure S42. ^1H NMR (400 MHz) spectrum of **8-Pd** in C_6D_6 .

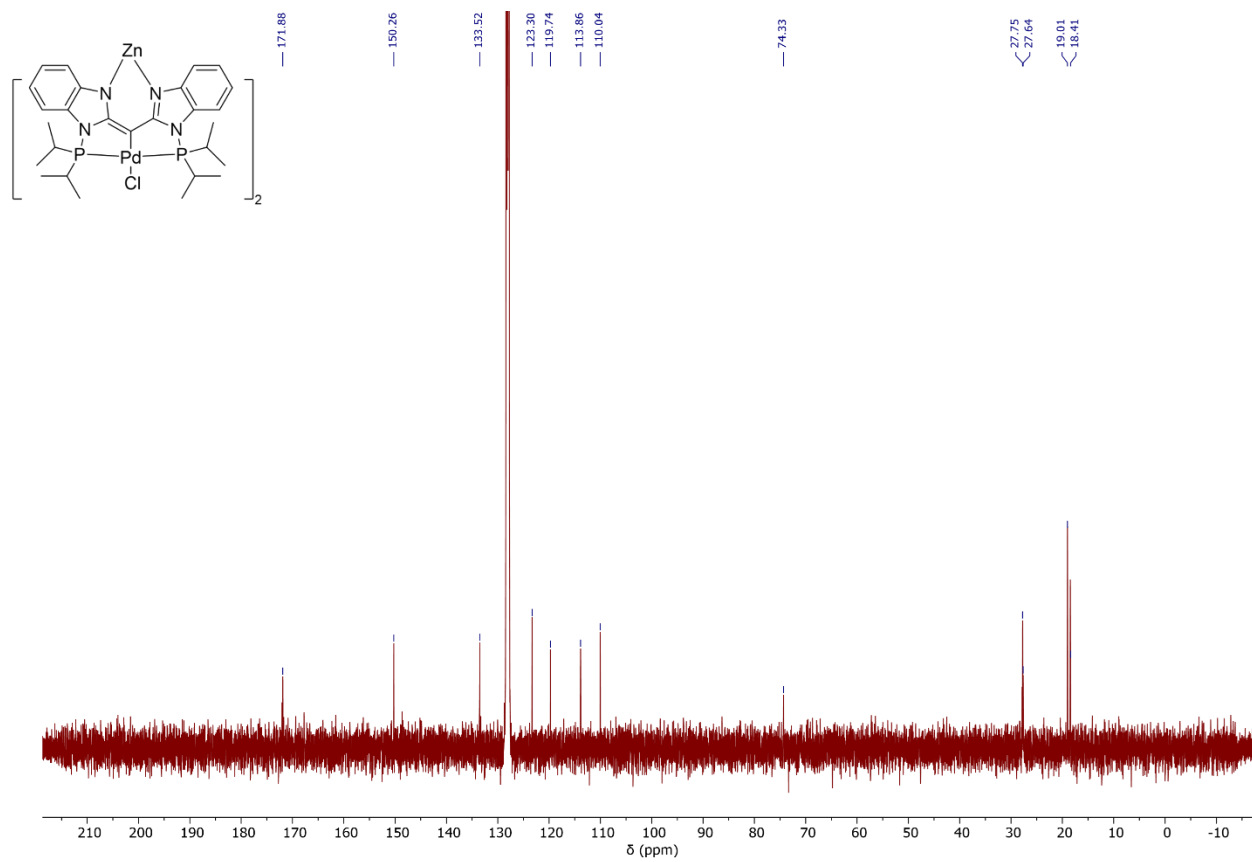


Figure S43. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **8-Pd** in C_6D_6 .

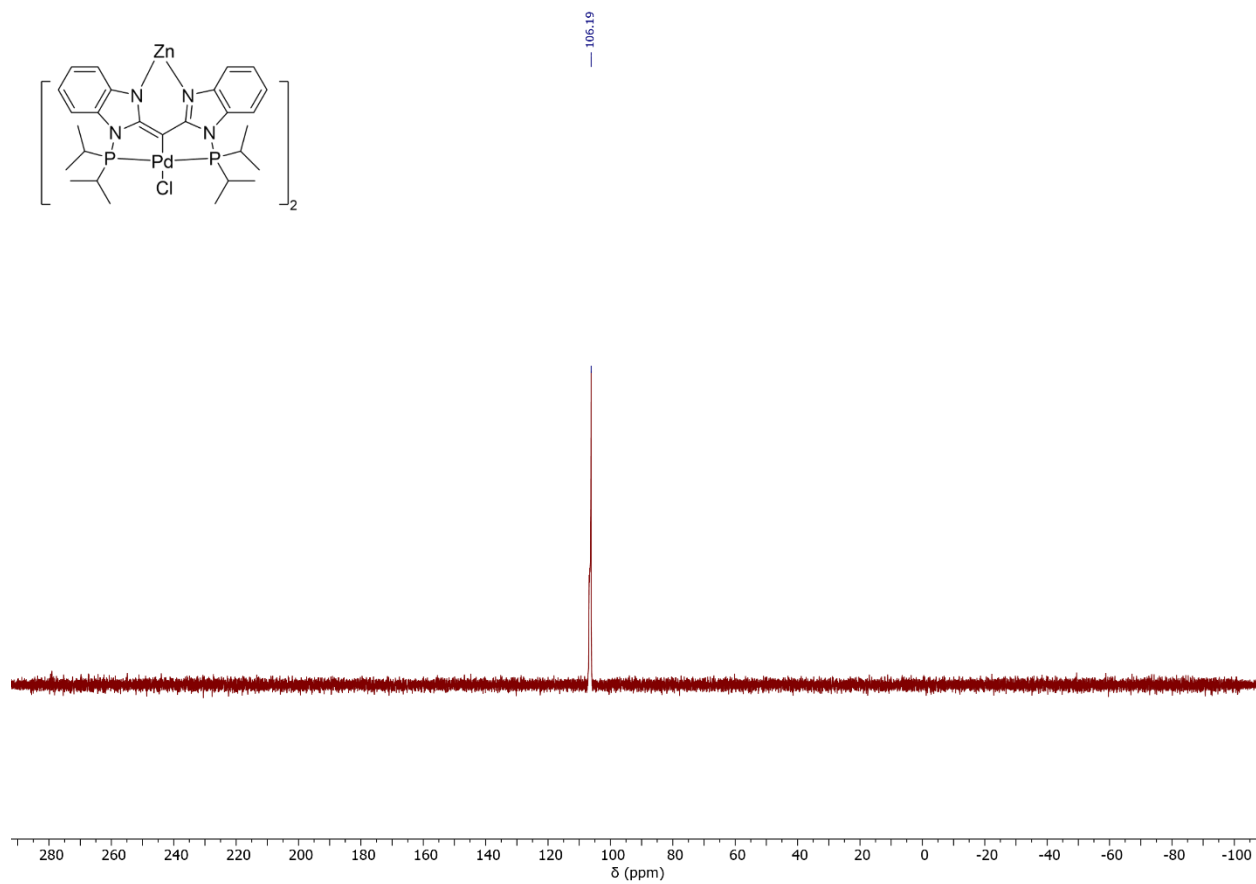


Figure S44. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **8-Pd** in C_6D_6 .

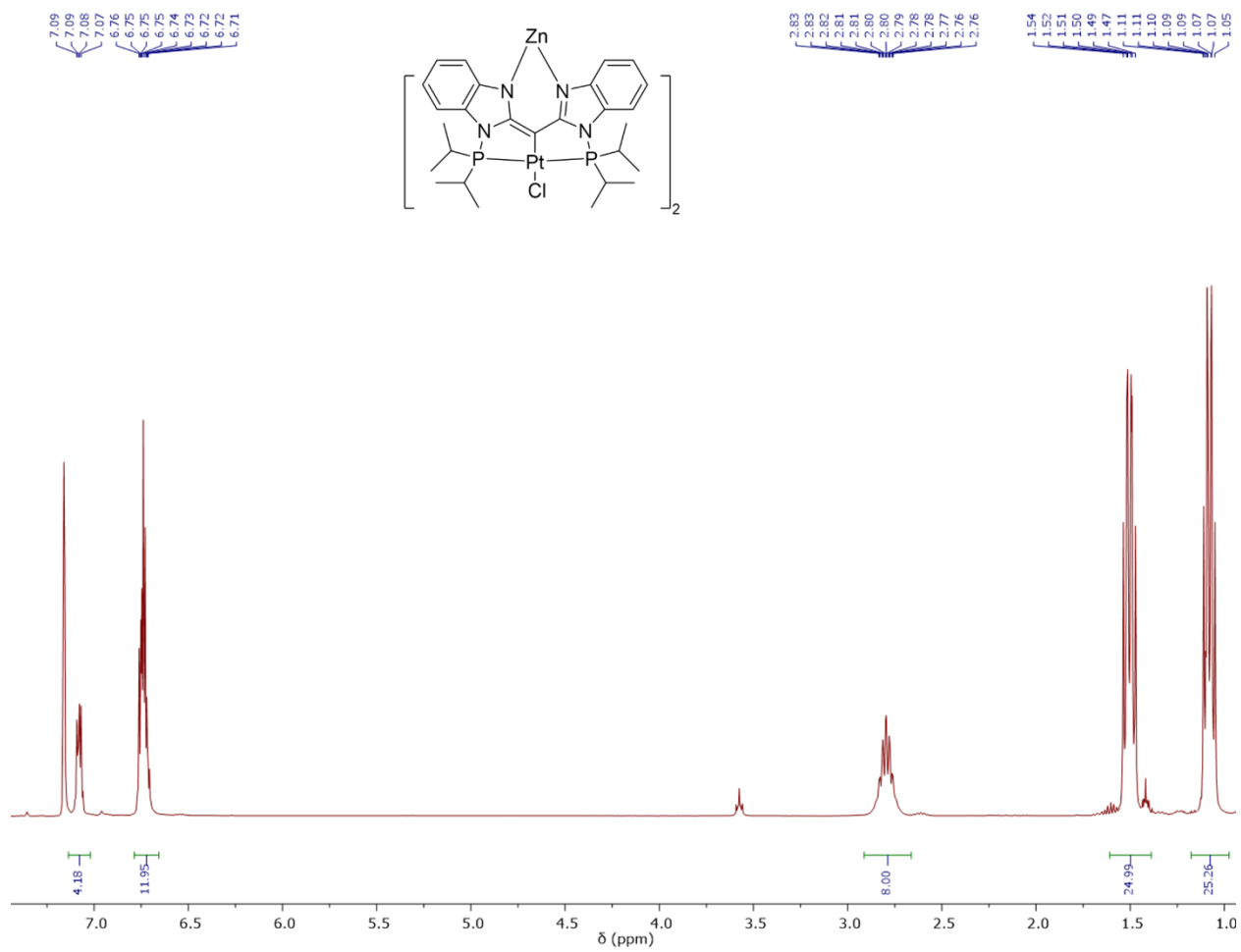


Figure S45. ¹H NMR (400 MHz) spectrum of **8-Pt** in C₆D₆.

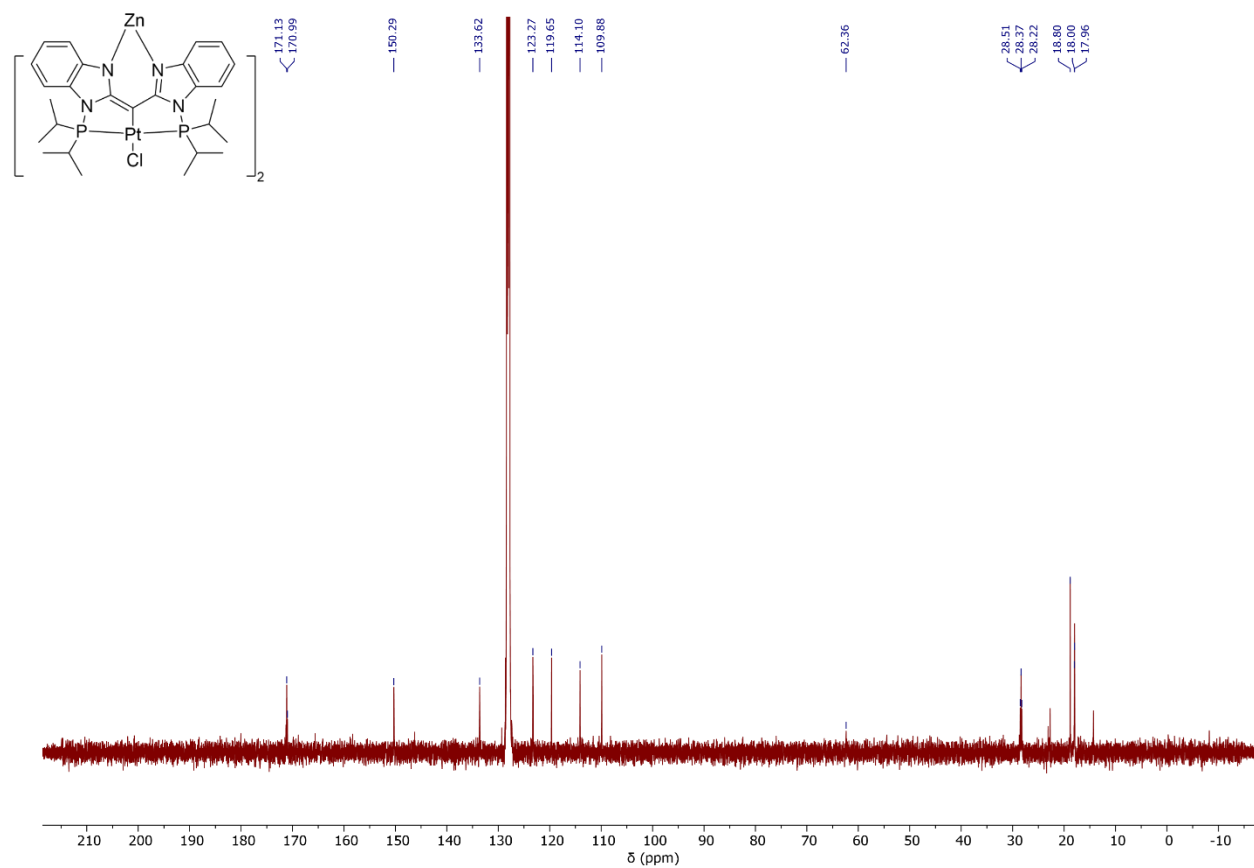


Figure S46. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **8-Pt** in C_6D_6 .

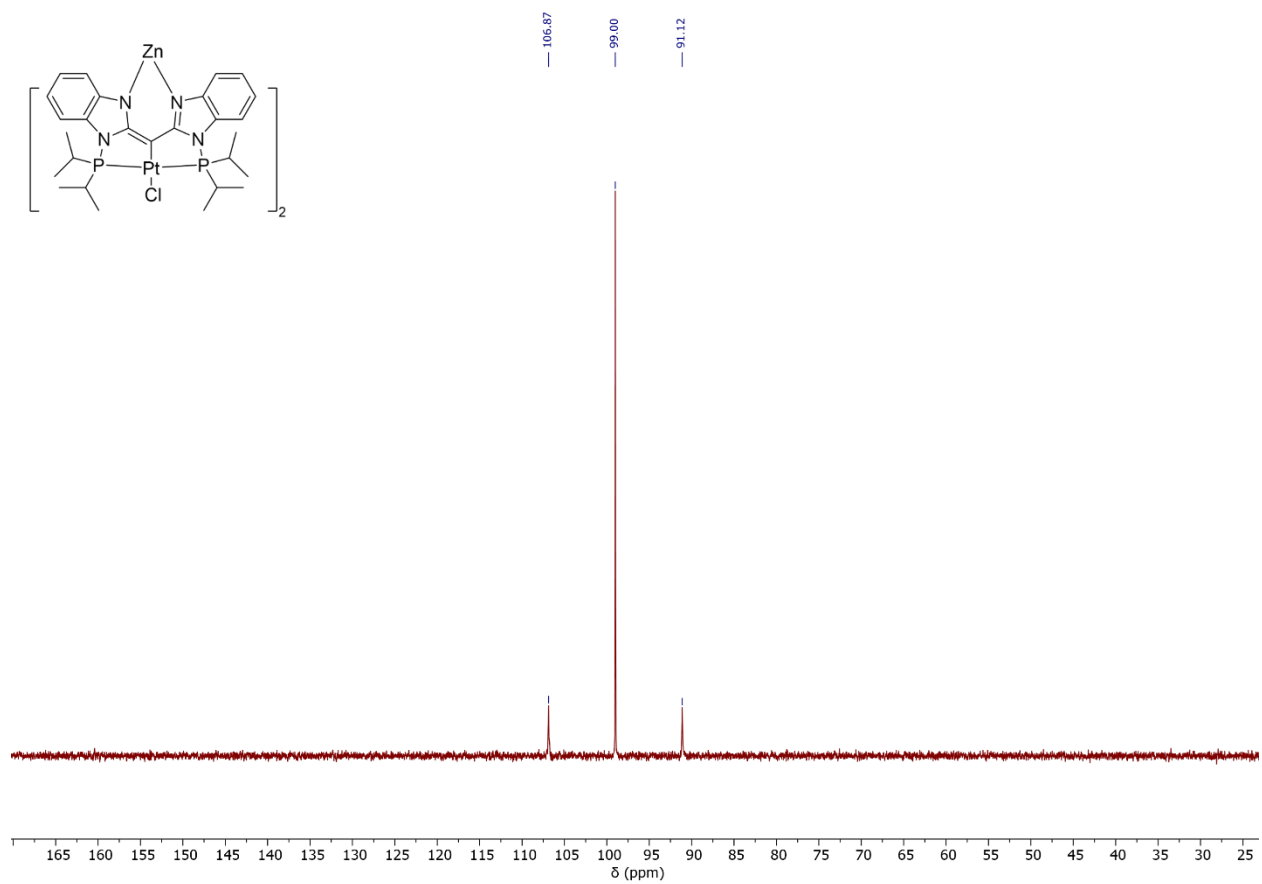


Figure S47. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **8-Pt** in C_6D_6 .

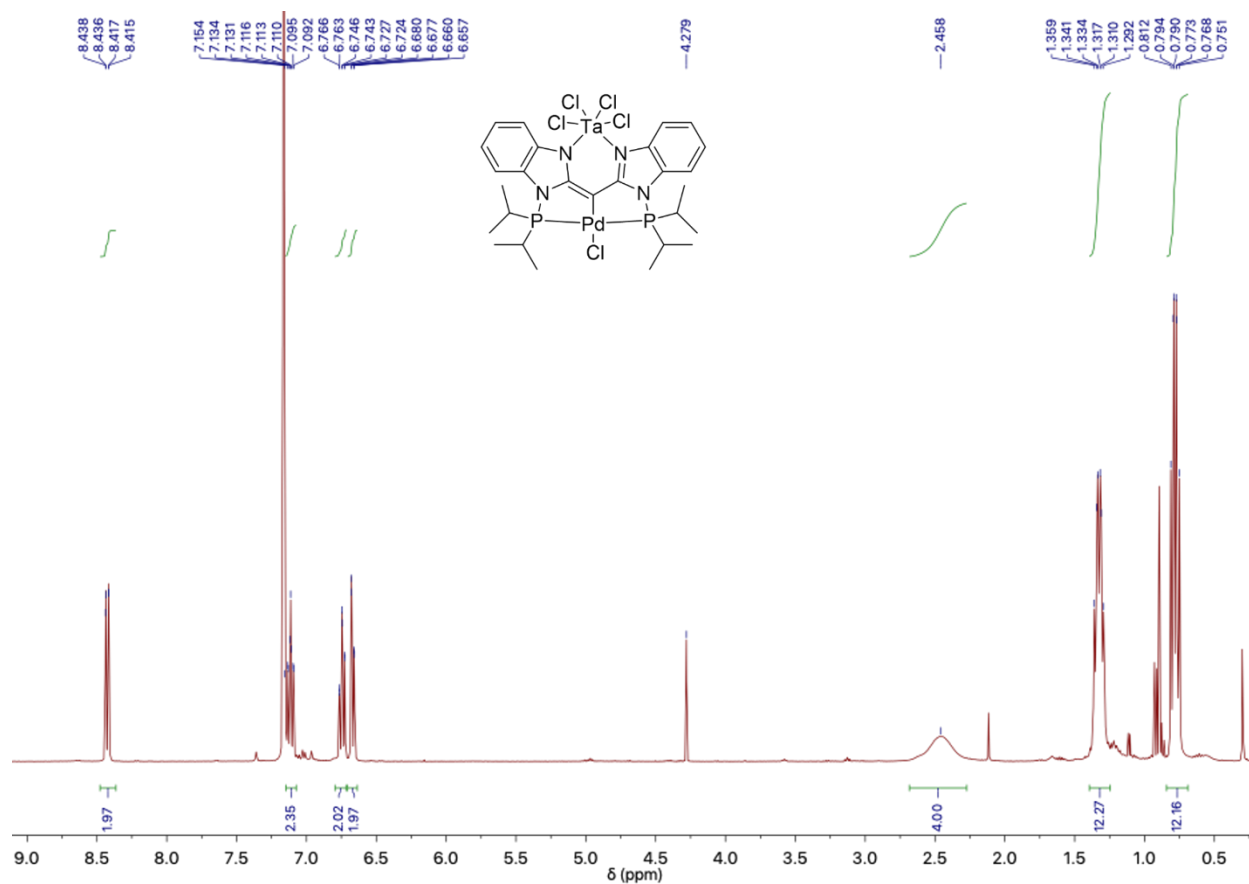


Figure S48. ^1H NMR (400 MHz) spectrum of **9-Pd** in C_6D_6 . The sample contains residuals CH_2Cl_2 (s, 4.28 ppm), pentane (t, 0.87 ppm) and silicone grease (s, 0.30 ppm).

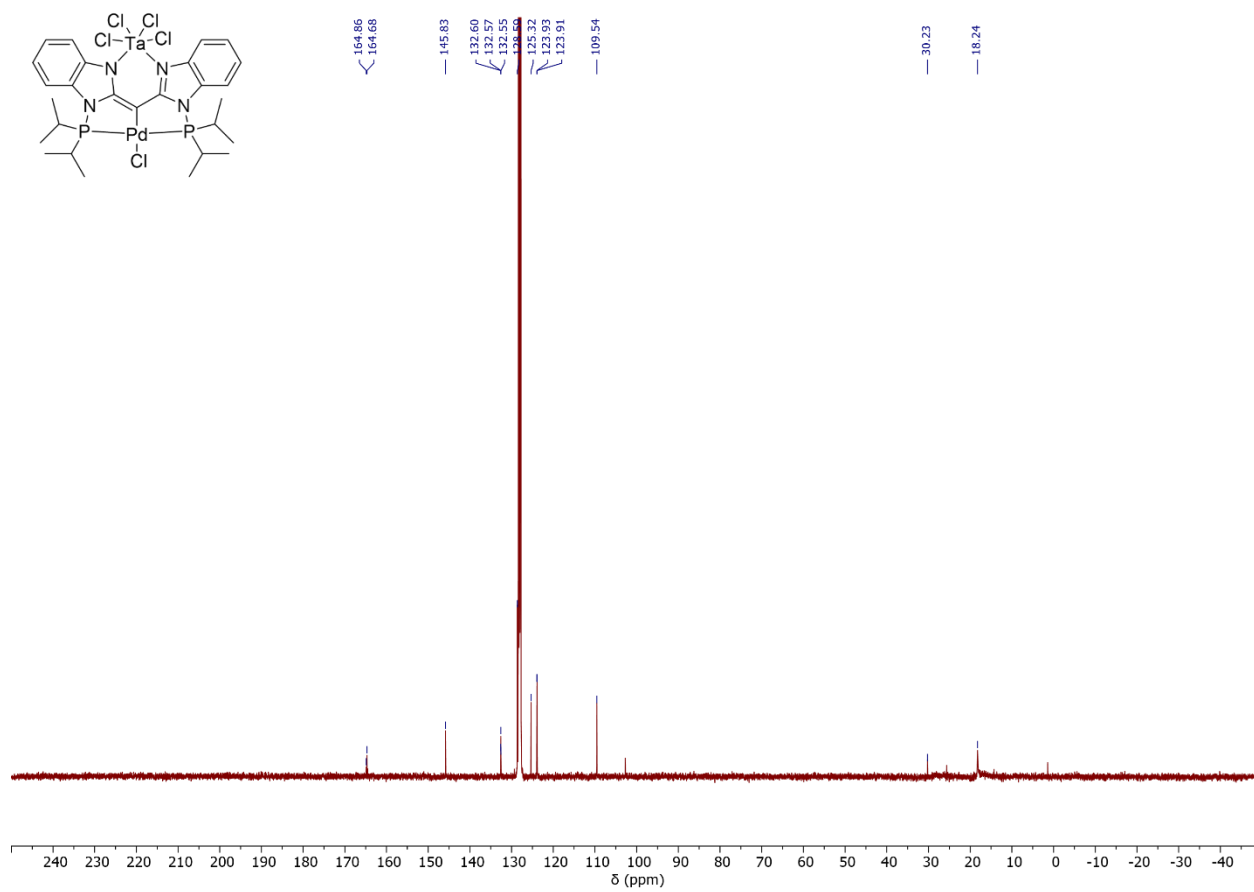


Figure S49. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **9-Pd** in C_6D_6 .

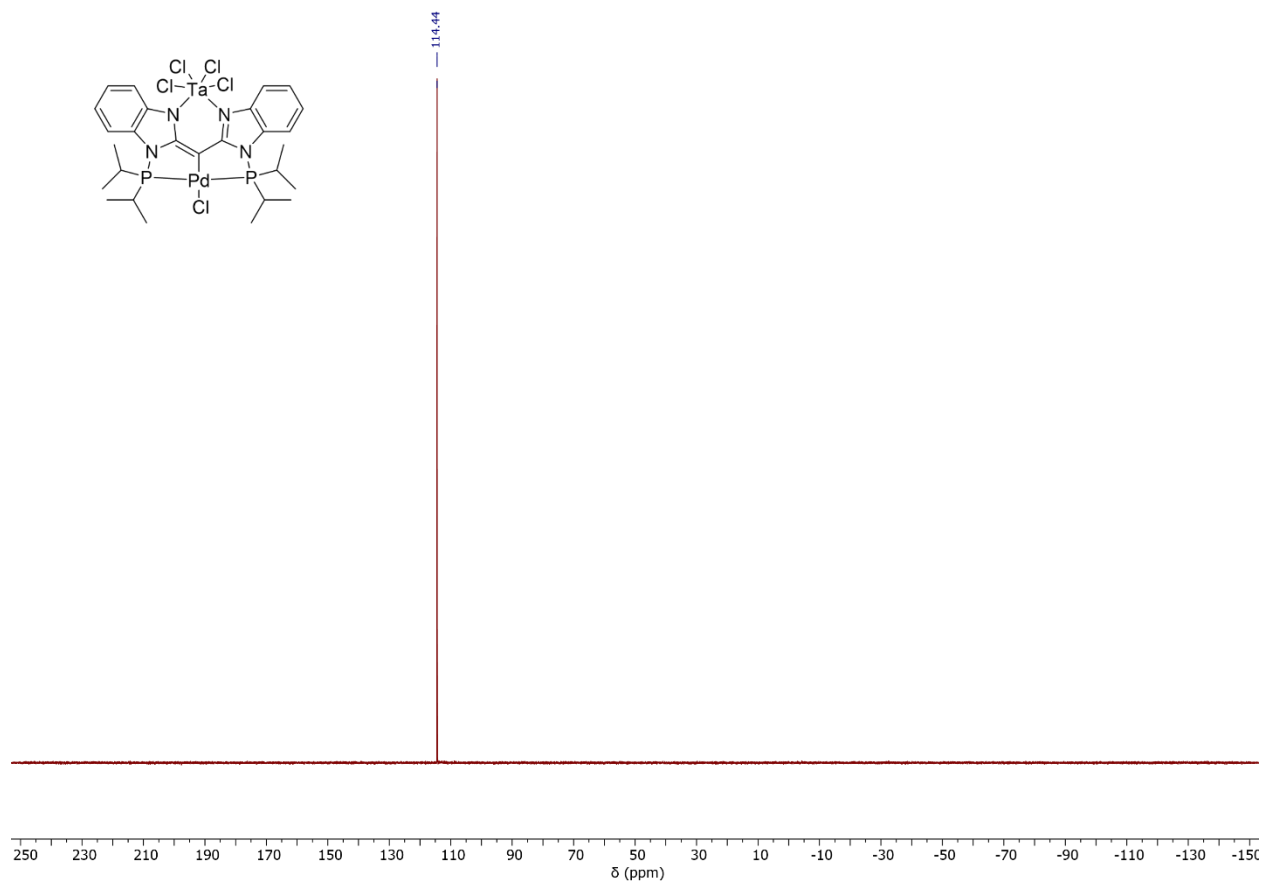


Figure S50. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **9-Pd** in C_6D_6 .

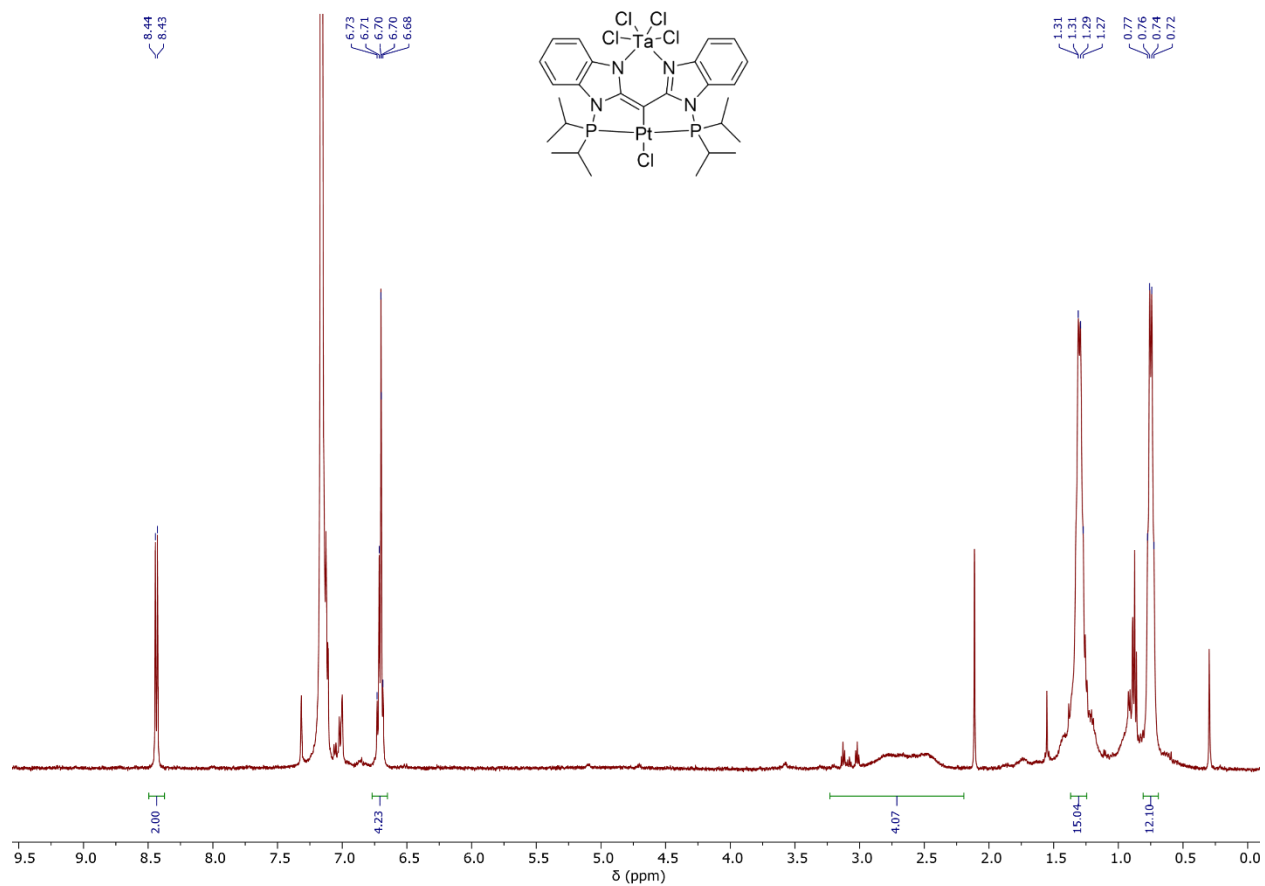


Figure S51. ¹H NMR (400 MHz) spectrum of **9-Pt** in C₆D₆. Sample contains residual toluene (m, 7.1 and overlapping with solvent peak, s 2.11 ppm) and residual pentane (m, 1.23 ppm) and silicone grease (s, 0.3 ppm).

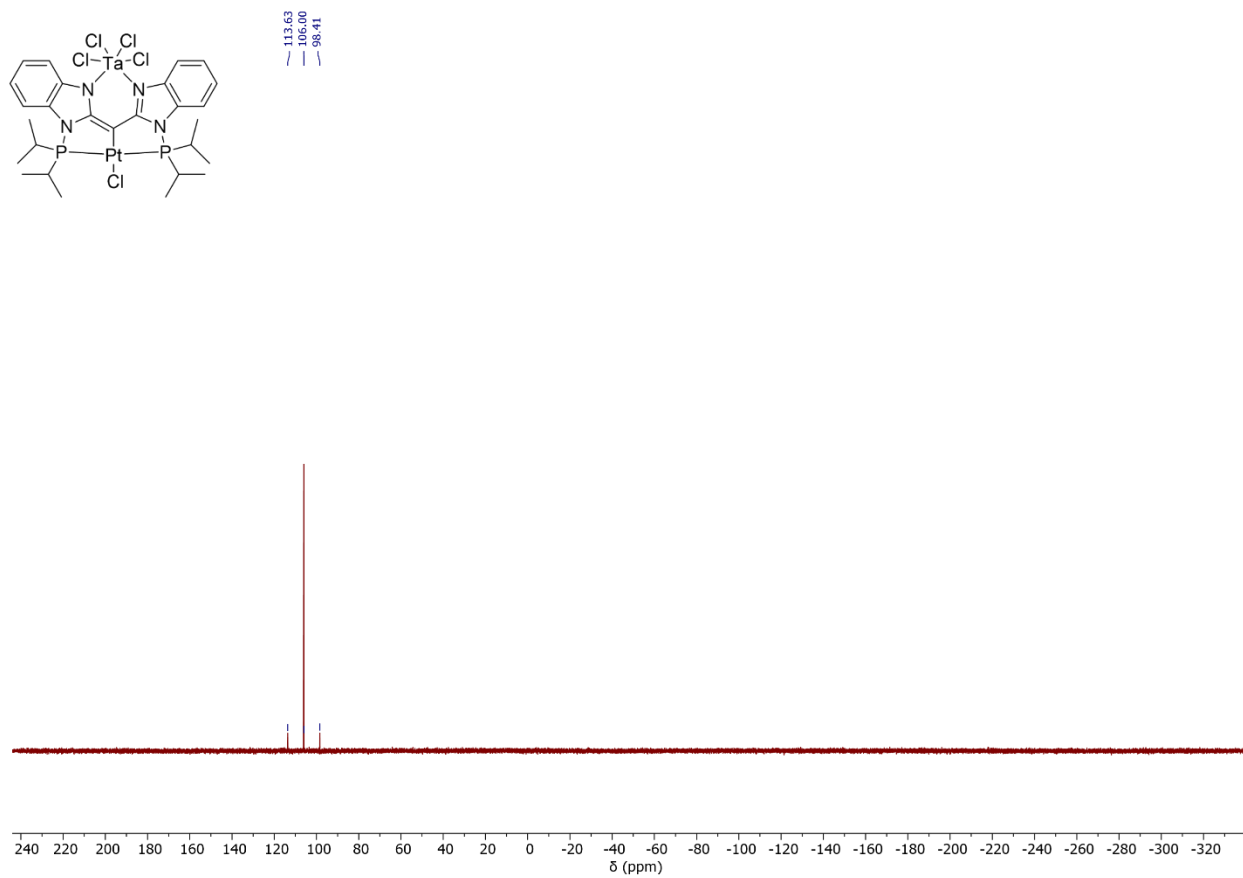


Figure S52. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz) spectrum of **9-Pt** in C_6D_6

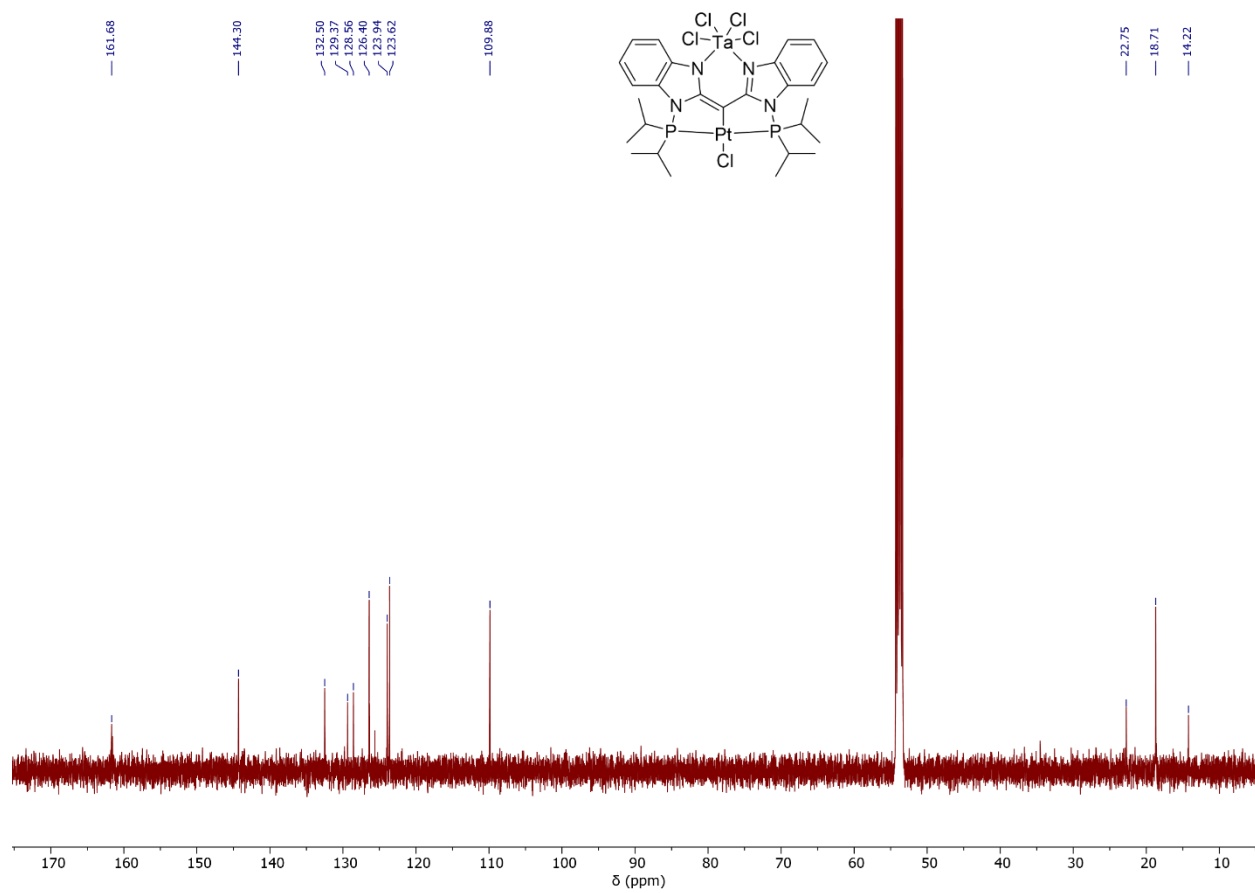


Figure S53. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **9-Pt** in CD_2Cl_2 .

IV. X-ray Diffractometry Details

3-Pd (CCDC 2351193)

Data Collection

A Leica MZ 75 microscope was used to identify a suitable orange block with very well defined faces with dimensions (max, intermediate, and min) $0.102 \times 0.085 \times 0.074 \text{ mm}^3$ from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER Quest X-ray (fixed-Chi geometry) diffractometer with a PHOTON II detector was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite.⁵ The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The X-ray radiation employed was generated from a Mo-I μ s X-ray tube ($K_{\alpha} = 0.71073 \text{ \AA}$).

45 data frames were taken at widths of 1° . These reflections were used to determine the unit cell. The unit cell was verified by examination of the $h k l$ overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, an extended data collection procedure (2 sets) was initiated using omega scans.

Data Reduction, Structure Solution, and Refinement

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.⁵ The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. The

absorption correction program SADABS⁶ was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group $P2_12_12_1$. A solution was obtained readily using XT/XS in APEX3.^{5,7} Three molecules of dichloromethane were found solvated. Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Elongated thermal ellipsoids on one of the CH_2Cl_2 and all the four $-\text{CH}(\text{CH}_3)_2$ groups suggested disorder, which were modeled successfully between two positions each with an occupancy ratio of 0.58:0.42 (the occupancy ratio of the disordered groups were restrained to the same value as the independently refined values were very close to the reported value). Appropriate restraints and / or constraints were used to keep the bond distances, angles, and thermal ellipsoids meaningful. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).⁸ The structure was refined (weighted least squares refinement on F^2) to convergence.^{7,9}

7-Pt (CCDC 2351194)

Data Collection

A Leica MZ 75 microscope was used to identify a suitable colorless block with very well defined faces with dimensions (max, intermediate, and min) $0.351 \times 0.216 \times 0.172 \text{ mm}^3$ from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER Quest X-ray (fixed-Chi geometry) diffractometer with a PHOTON II detector was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite.⁵ The sample was optically centered

with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The X-ray radiation employed was generated from a Mo-I μ s X-ray tube ($K_{\alpha} = 0.71073\text{\AA}$).

45 data frames were taken at widths of 1° . These reflections were used to determine the unit cell. The unit cell was verified by examination of the $h k l$ overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, an extended data collection procedure (6 sets) was initiated using omega and phi scans.

Data Reduction, Structure Solution, and Refinement

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.⁵ The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS⁴ was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group $P-1$. A solution was obtained readily ($Z=4$; $Z'=2$) using XT/XS in APEX3.^{5,7} Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Residual electron ($4.2 e^{-}/\text{\AA}^3$), which could not be attributed to any solvent (reaction was carried out in water free reaction conditions), was MASKed using OLEX2. Assuming the electron density as partially occupied water molecule, the occupancy refines to 0.165 water molecules per Pt complex. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).⁸ The structure was refined (weighted least squares refinement on F^2) to convergence.^{7,9}

8-Pd (CCDC 2351196)

Data Collection

A Leica MZ 75 microscope was used to identify a suitable red block with very well defined faces with dimensions (max, intermediate, and min) $0.128 \times 0.054 \times 0.023 \text{ mm}^3$ from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER Venture X-ray (kappa geometry) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite.⁵ The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The X-ray radiation employed was generated from a Cu-I μ s X-ray tube ($K_{\alpha} = 1.5418\text{\AA}$ with a potential of 50 kV and a current of 1.0mA).

45 data frames were taken at widths of 1° . These reflections were used to determine the unit cell. The unit cell was verified by examination of the $h k l$ overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, an extended data collection procedure (17 sets) was initiated using omega and phi scans.

Data Reduction, Structure Solution, and Refinement

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.⁵ The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. The

absorption correction program SADABS⁶ was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/c$. A solution was obtained readily using XT/XS in APEX3.^{5,7} Two molecules of toluene and a molecule of isooctane were found solvated. Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Elongated thermal ellipsoids and residual electron density peaks near the solvent molecules indicated possible disorder. No efforts were made to model this disorder. Absence of additional symmetry or void were confirmed using PLATON (ADDSYM).⁸ The structure was refined (weighted least squares refinement on F^2) to convergence.^{7,9}

9-Pd (CCDC 2351195)

Data Collection

A Leica MZ 75 microscope was used to identify a dark brown block with very well defined faces with dimensions (max, intermediate, and min) $0.452 \times 0.272 \times 0.248 \text{ mm}^3$ from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER APEX 2 Duo X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite.⁵ The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector (Bruker - PHOTON) was set at 6.0 cm from the crystal sample. The X-ray radiation employed was generated from a Mo sealed X-ray tube ($K_\alpha = 0.71073 \text{ \AA}$ with a potential of 40 kV and a current of 40 mA).

45 data frames were taken at widths of 1.0° . These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the $h k l$ overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, an extended data collection procedure (6 sets) was initiated using omega scans.

Data Reduction, Structure Solution, and Refinement

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.⁵ The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS⁴ was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/n$. A solution was obtained readily using XT/XS in APEX2.^{5,7} A molecule of dichloromethane was found solvated. Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Elongated ellipsoids on the solvent atoms suggested disorder which was successfully modeled between two positions which refined to an occupancy ratio very close to 0.5. For the final refinement cycles the occupancy of the disordered solvent molecule were fixed to 0.5. Appropriate restraints were added to keep the bond distances, and thermal ellipsoids meaningful. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).⁷ The structure was refined (weighted least squares refinement on F^2) to convergence.^{7,9}

V. Electrochemical Analysis

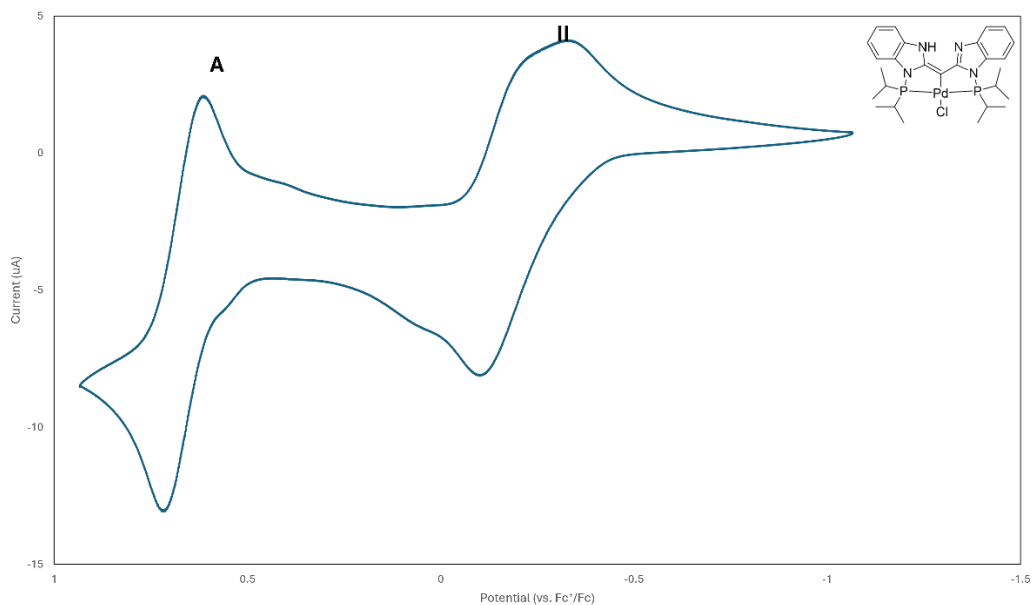


Figure S54. Cyclic voltammogram of **4-Pd** in CH₂Cl₂ (1 mM) with [Bu₄N][PF₆] (0.1 M) as the supporting electrolyte. $E_{1/2} = 0.67$ V (**A**), Irreversible redox event = -0.21V (**II**).

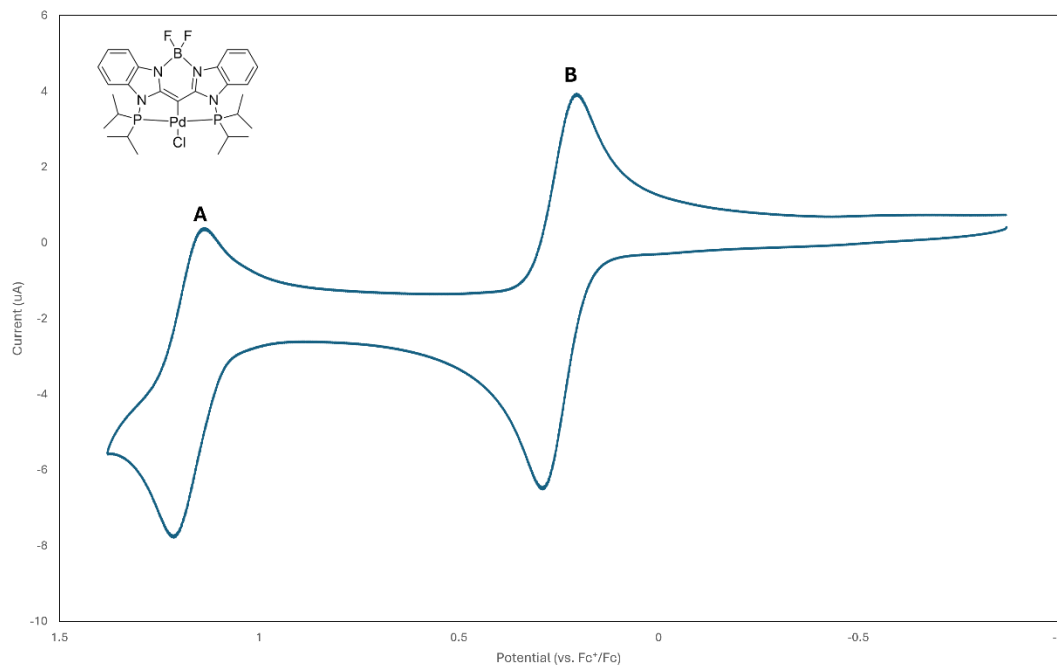


Figure S55. Cyclic voltammogram of **7-Pd** in CH₂Cl₂ (1 mM) with [Bu₄N][PF₆] (0.1 M) as the supporting electrolyte. $E_{1/2} = 1.18$ V (**A**), 0.25 V (**B**).

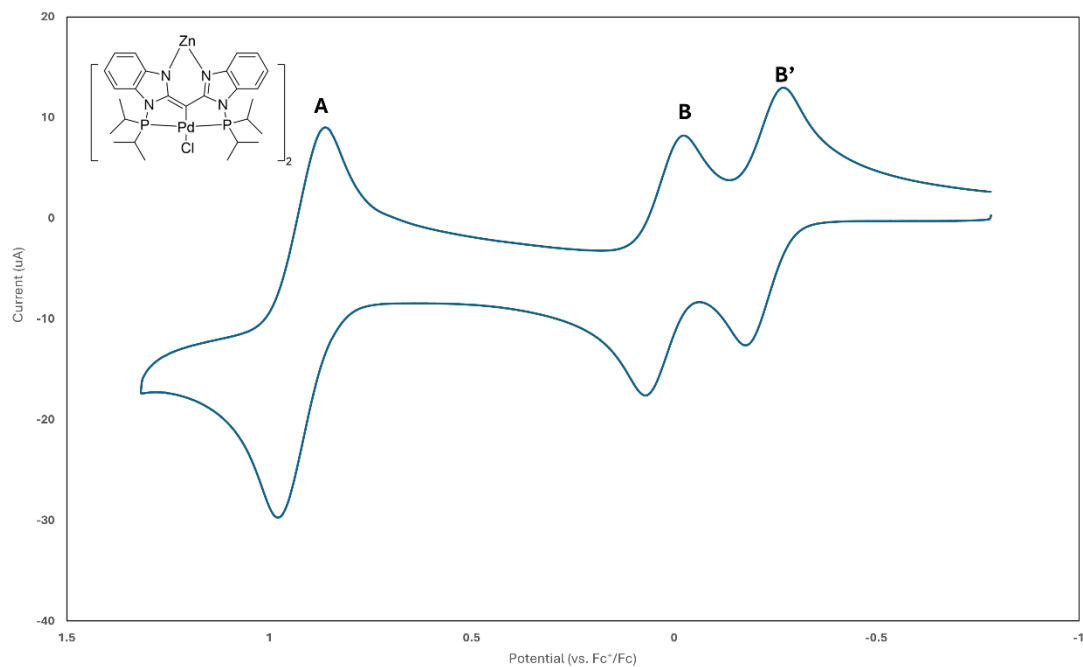


Figure S56. Cyclic voltammogram of **8-Pd** in CH_2Cl_2 (1 mM) with $[\text{Bu}_4\text{N}][\text{PF}_6]$ (0.1 M) as the supporting electrolyte. $E_{1/2} = 0.92$ V (A), 0.02 V (B), -0.22 V (C).

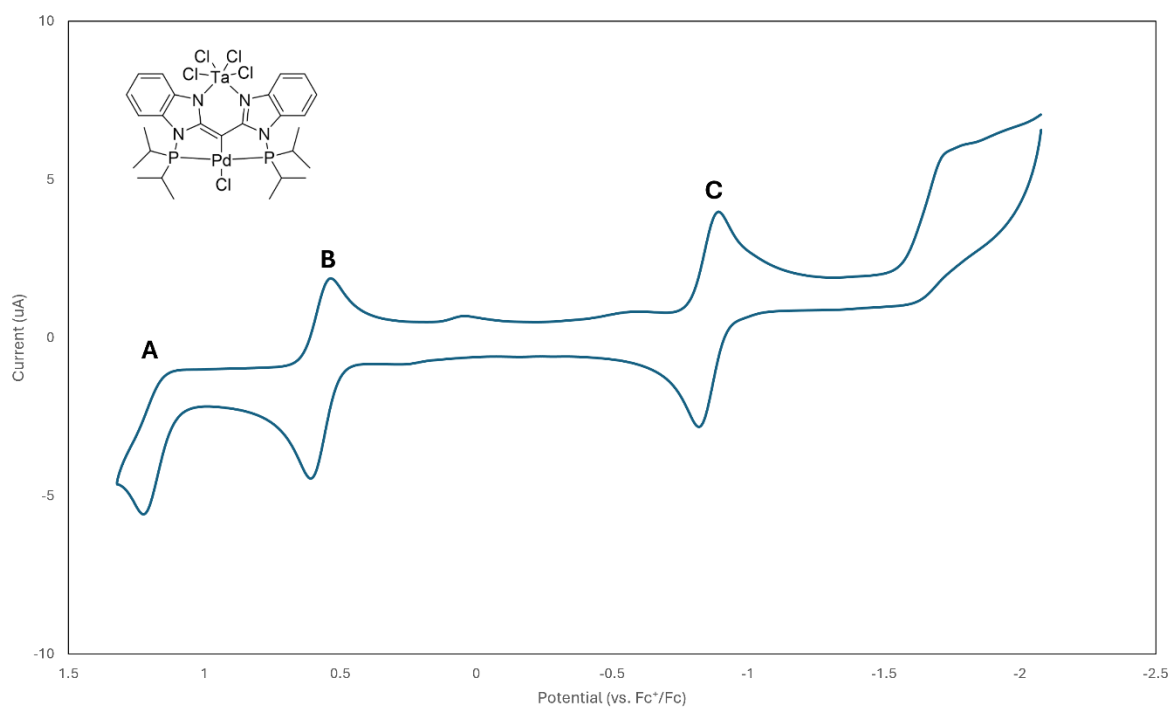


Figure S57. Cyclic voltammogram of **9-Pd** in CH_2Cl_2 (1 mM) with $[\text{Bu}_4\text{N}][\text{BArF}_{24}]$ (0.1 M) as the supporting electrolyte. Ligand oxidation = 1.18 V (A), $E_{1/2} = 0.57$ V (B), -0.87 V (C).

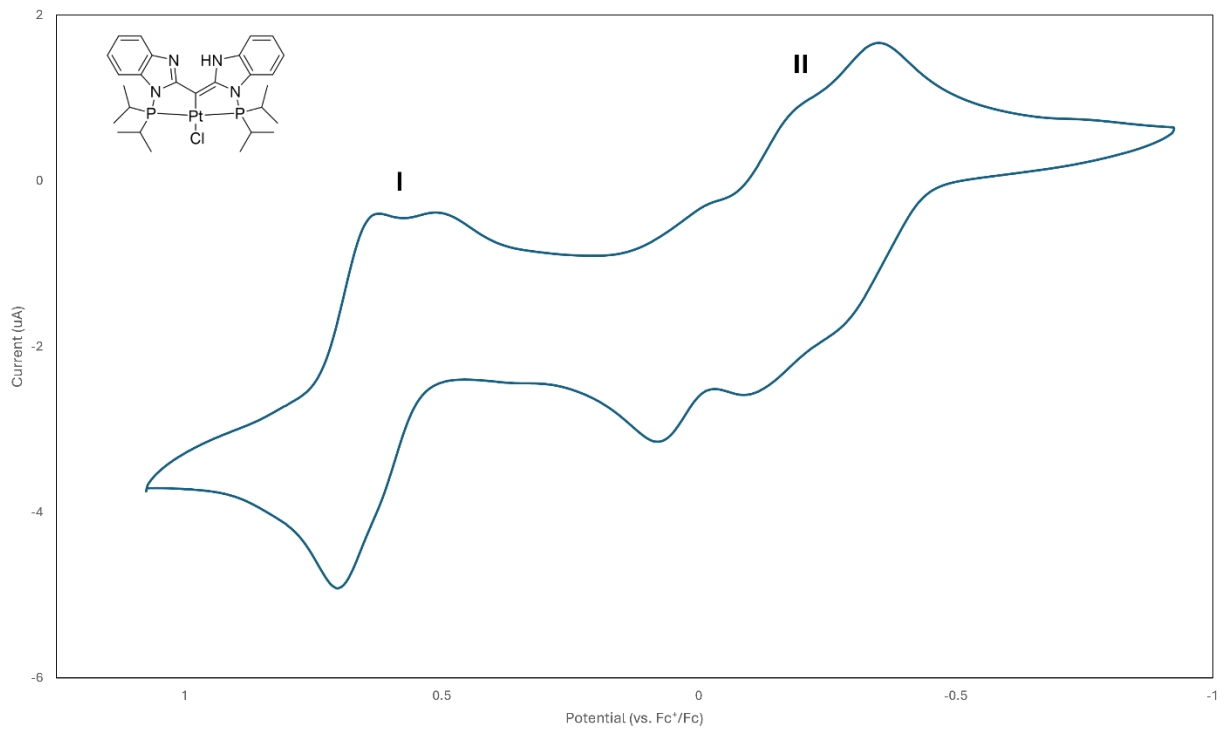


Figure S58. Cyclic voltammogram of **4-Pt** in CH₂Cl₂ (1 mM) with [Bu₄N][PF₆] (0.1 M) as the supporting electrolyte. Irreversible redox events = 0.62 V (**I**), -0.14 V (**II**).

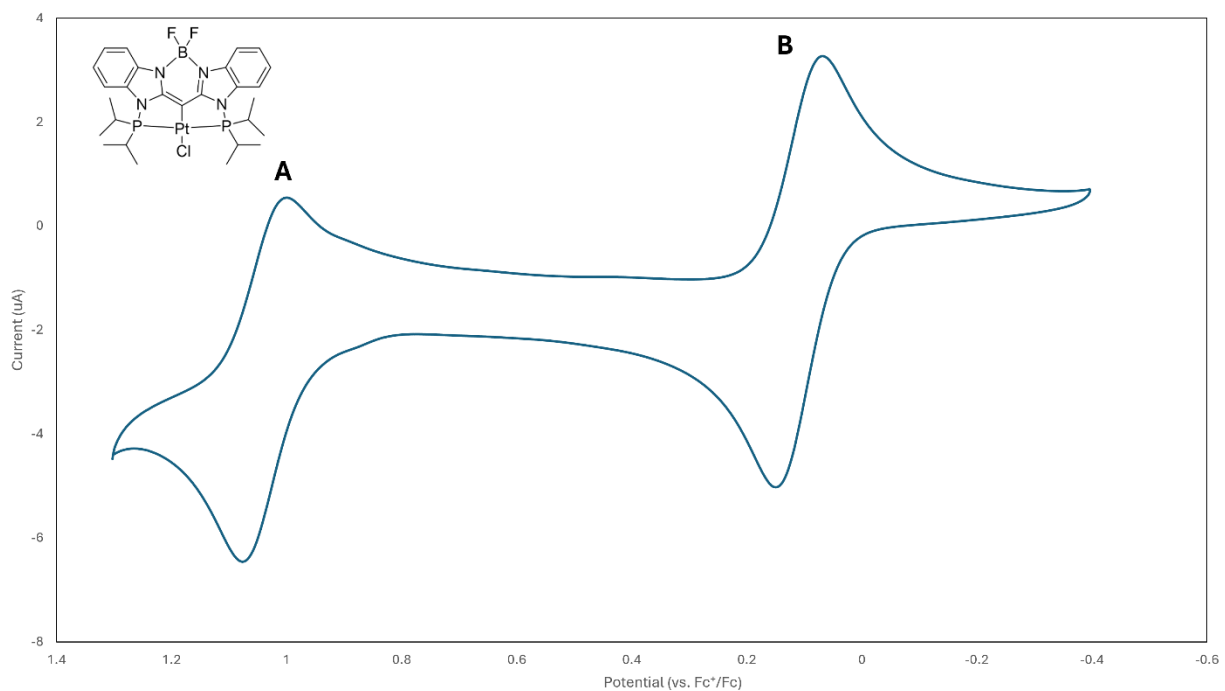


Figure S59. Cyclic voltammogram of **7-Pt** in CH₂Cl₂ (1 mM) with [Bu₄N][PF₆] (0.1 M) as the supporting electrolyte. $E_{1/2}$ = 1.03 V (**A**), 0.11 V (**B**).

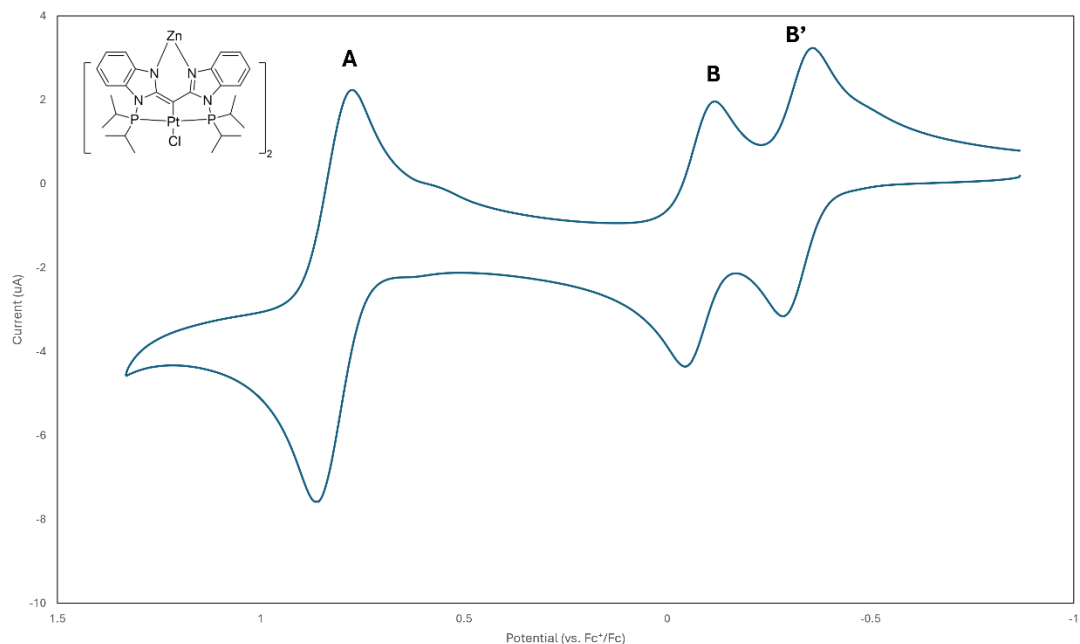


Figure S60. Cyclic voltammogram of **8-Pt** in CH_2Cl_2 (1 mM) with $[\text{Bu}_4\text{N}][\text{PF}_6]$ (0.1 M) as the supporting electrolyte. $E_{1/2} = 0.82$ V (**A**), -0.09 V (**B**), -0.32 V (**C**).

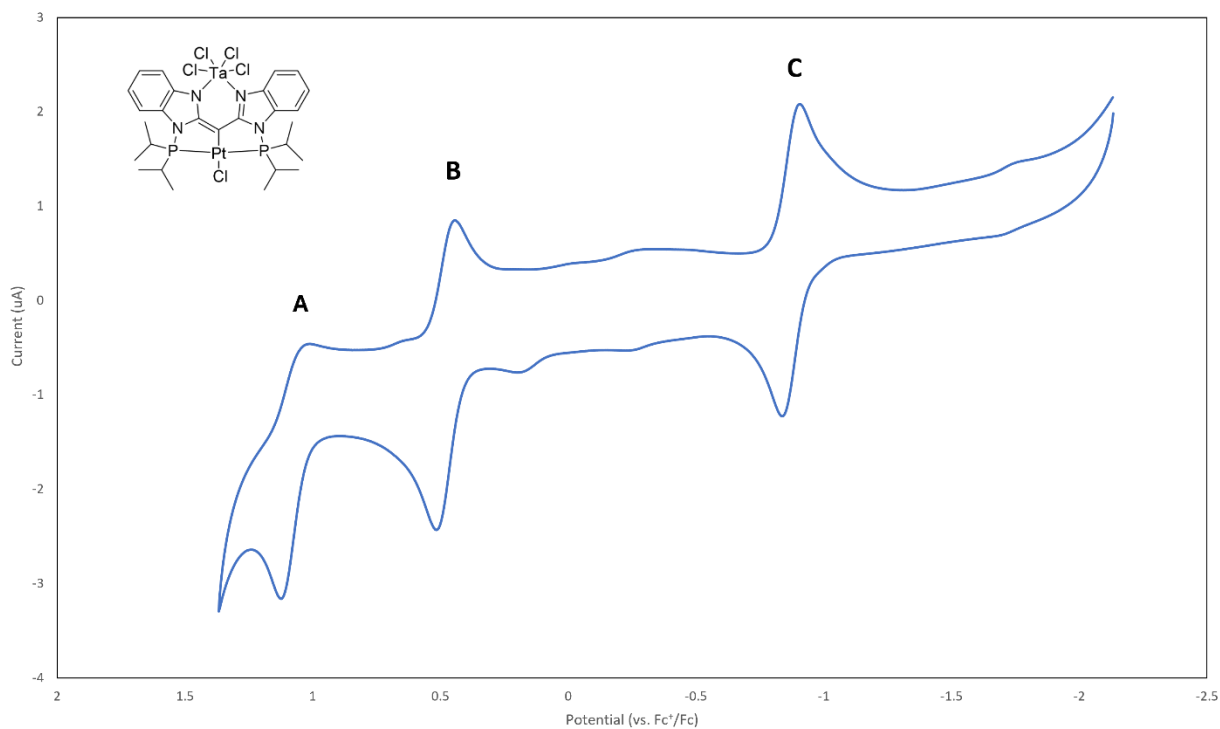


Figure S61. Cyclic voltammogram of **9-Pt** in CH_2Cl_2 (1 mM) with $[\text{Bu}_4\text{N}][\text{BARF}_{24}]$ (0.1 M) as the supporting electrolyte. Ligand oxidation = 1.07 V (**A**), $E_{1/2} = 0.47$ V (**A**), -0.88 V (**B**).

VI. UV-Vis Data.

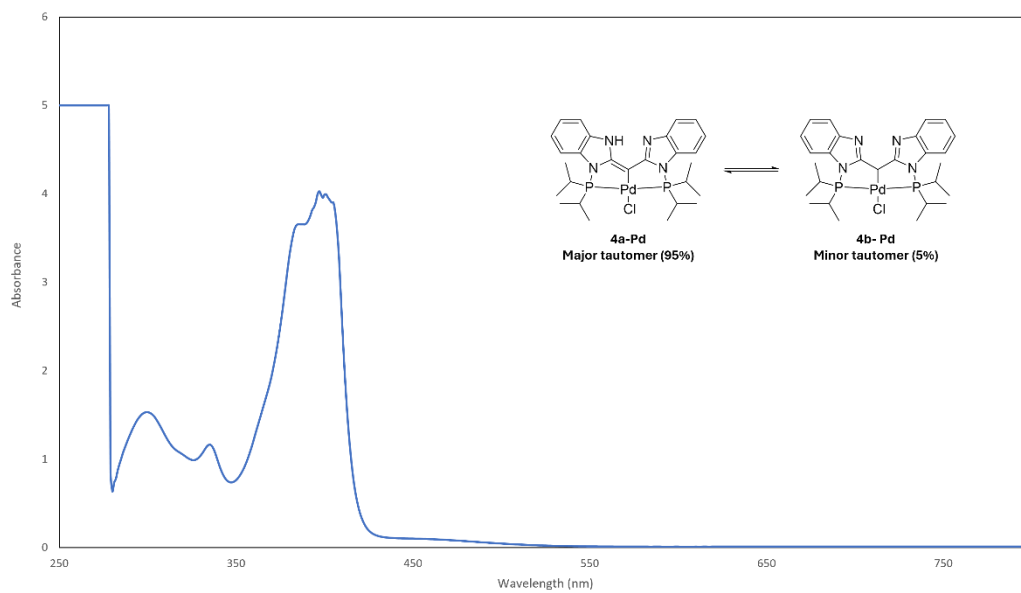


Figure S62. UV-Vis of **4-Pd** in toluene (0.05 mM).

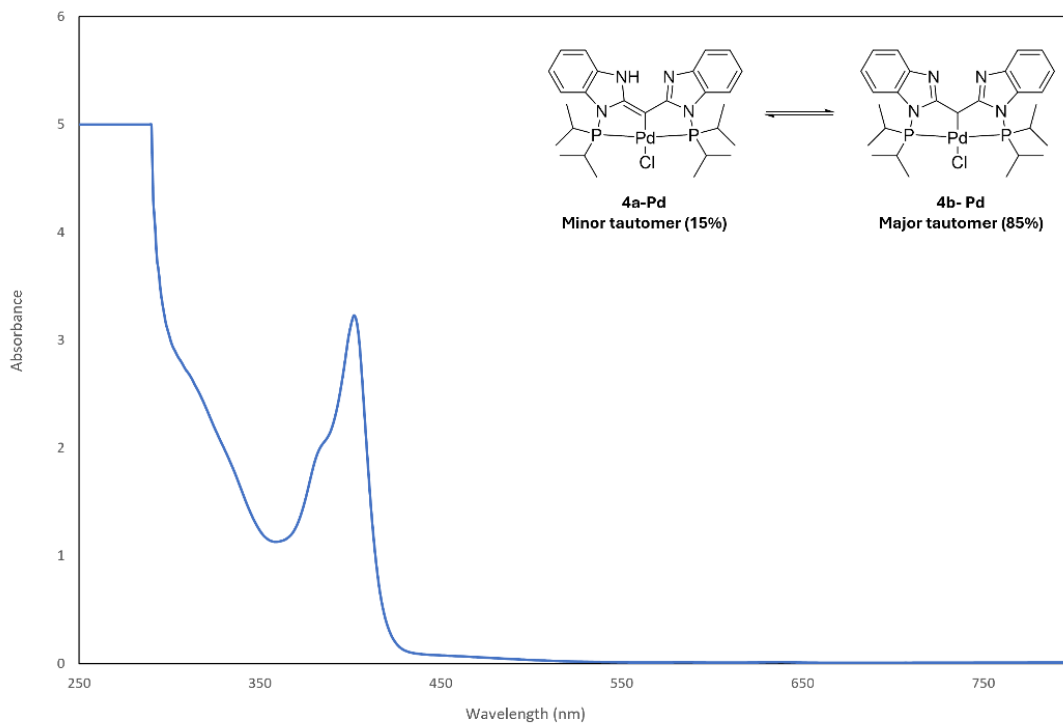


Figure S63. UV-Vis of **4-Pd** in CDCl₃ (0.25 mM).

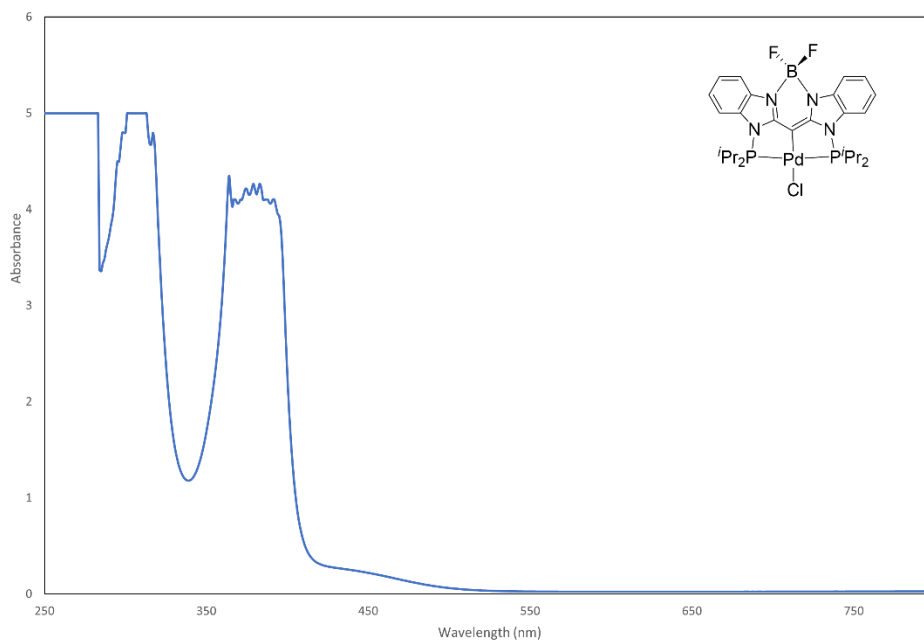


Figure S64. UV-Vis of **7-Pd** in toluene (0.05 mM).

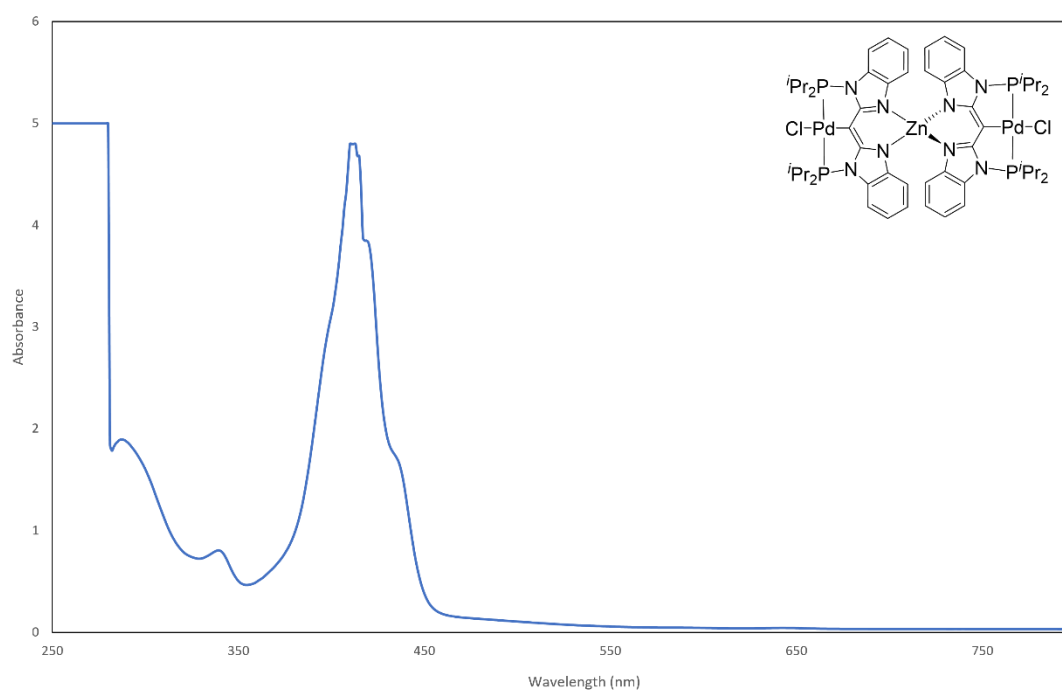


Figure S65. UV-Vis of **8-Pd** in toluene (0.05 mM).

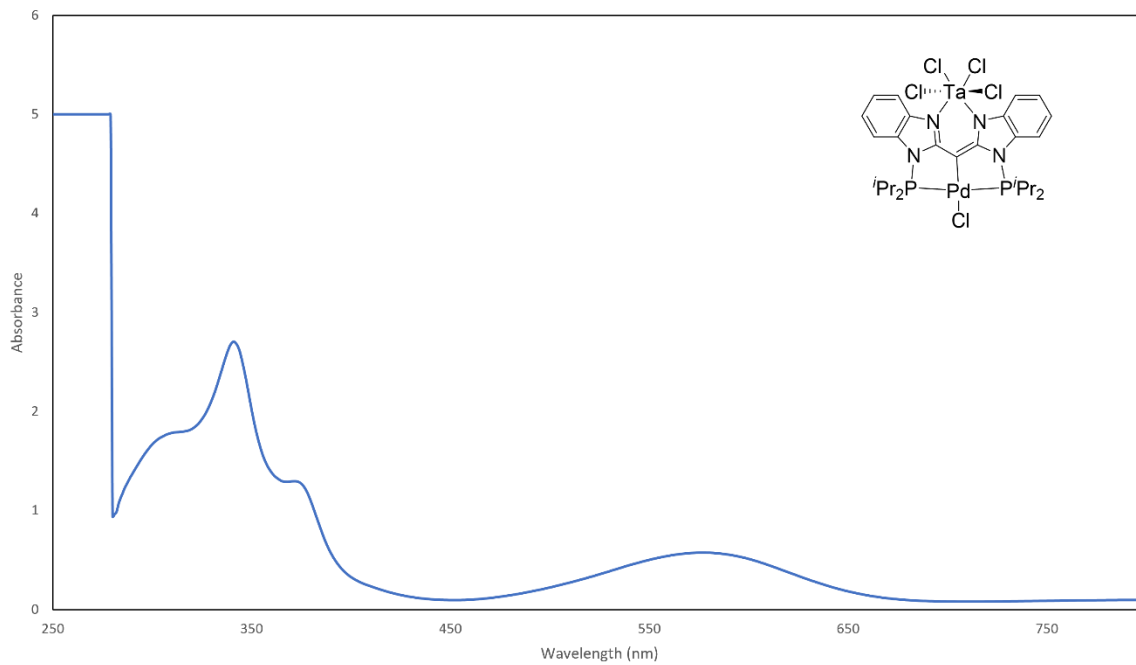


Figure S66. UV-Vis of **9-Pd** in toluene (0.025 mM).

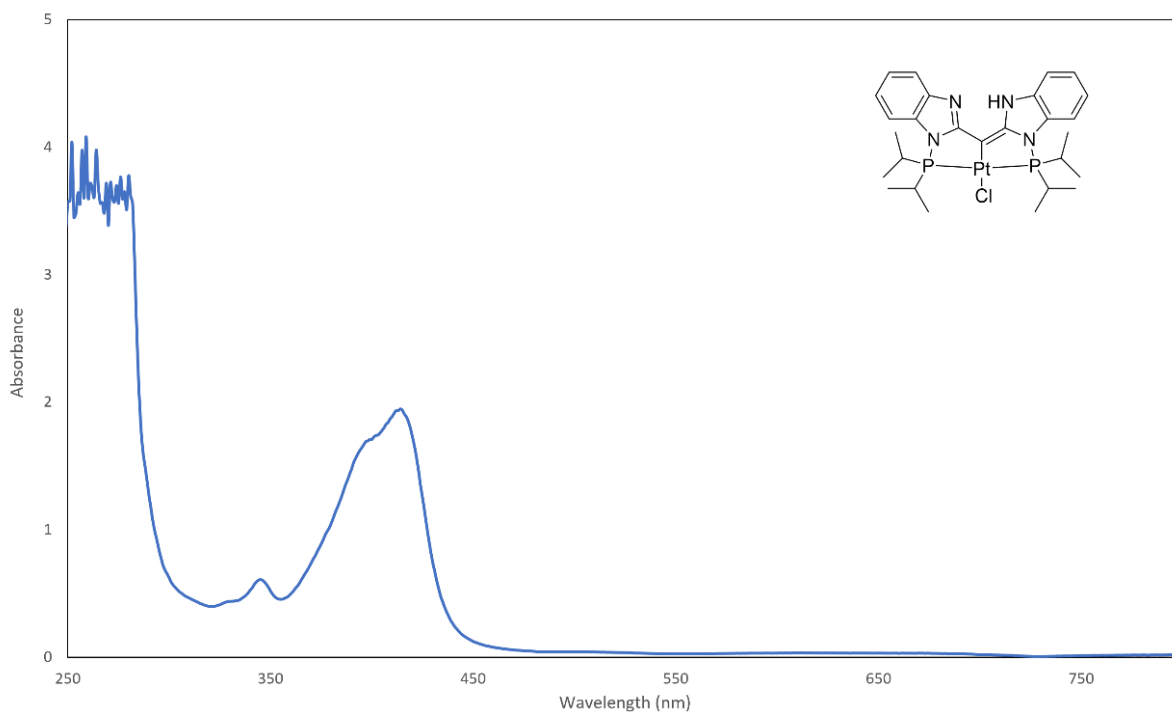


Figure S67. UV-Vis of **4-Pt** in toluene (0.25 mM).

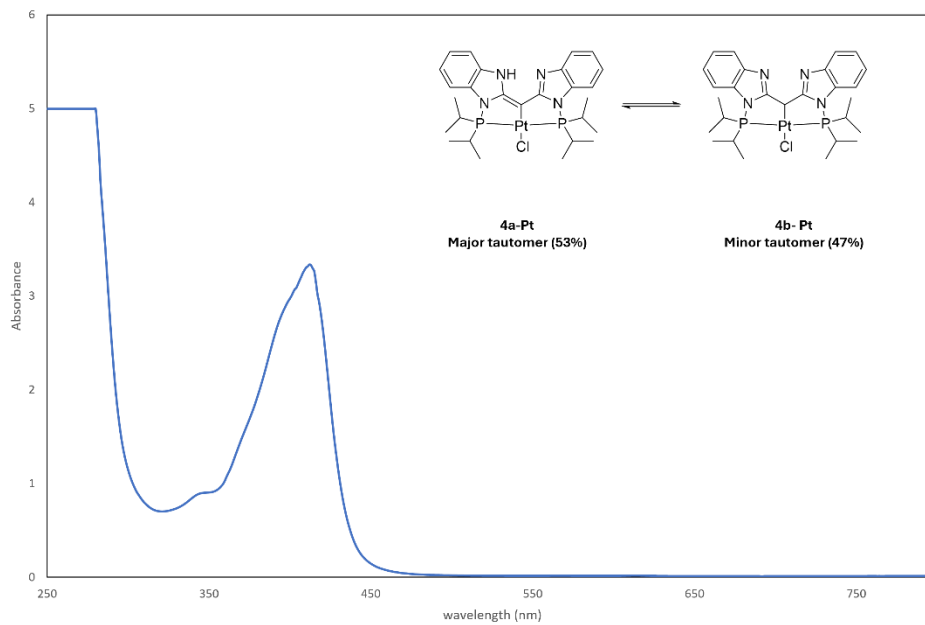


Figure S 68. UV-Vis of **4-Pt** in CDCl₃ (0.28 mM).

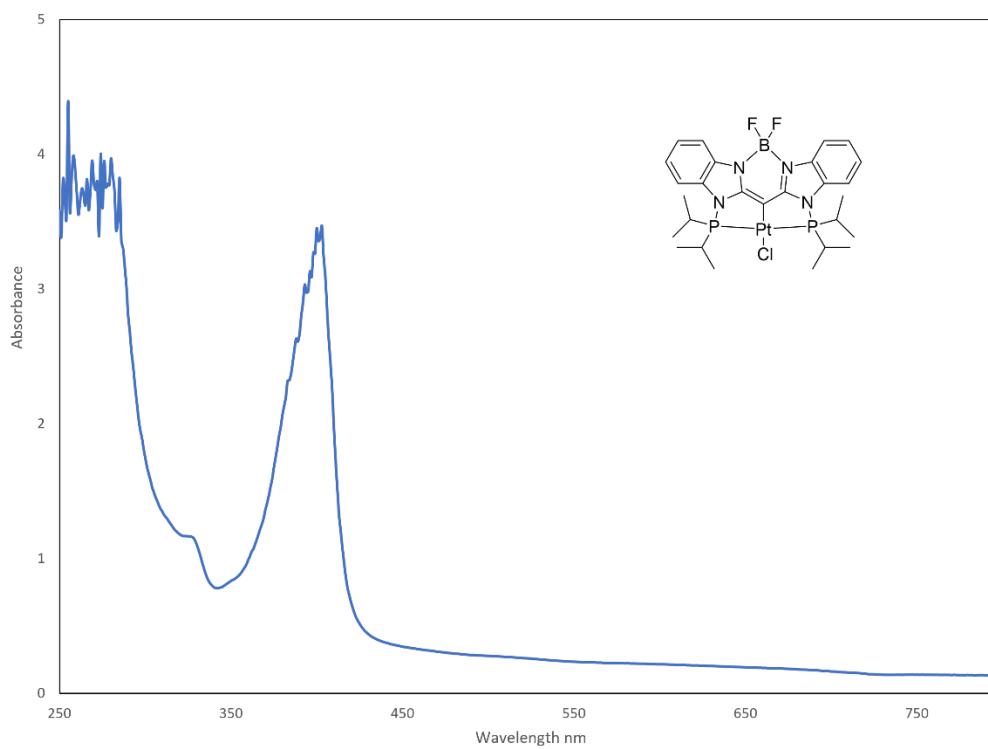


Figure S69. UV-Vis of **7-Pt** in toluene (0.06 mM).

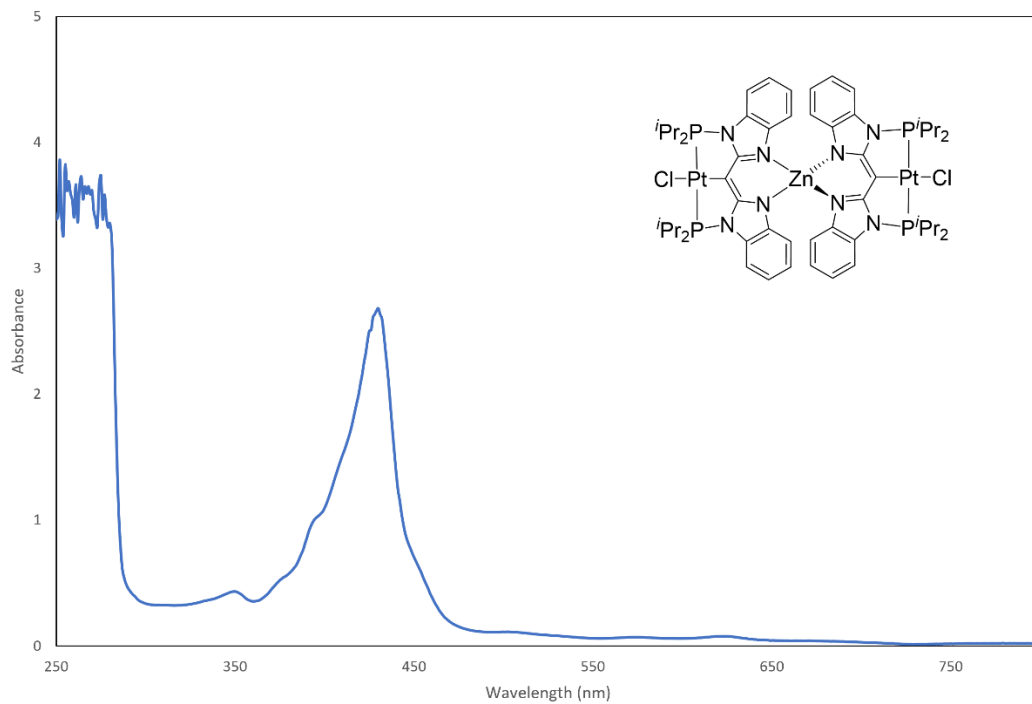


Figure S70. UV-Vis of **8-Pt** in toluene (0.03 mM).

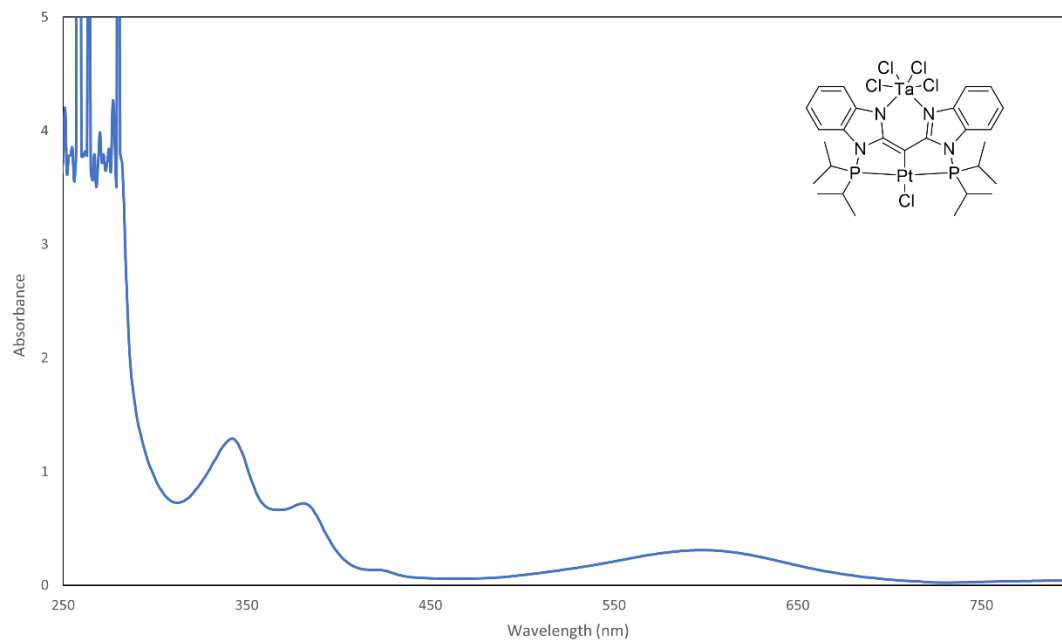


Figure S71. UV-Vis of **9-Pt** in toluene (0.09 mM).

V. References

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- ⁸ (a) A. L. Spek, PLATON - A Multipurpose Crystallographic Tool. *J. Appl. Cryst.*, 2003, **36**, 7-13. (b) Spek, A. L. Utrecht University, Utrecht, The Netherlands 2008.
- ⁹ O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, OLEX2: a complete structure solution, refinement, and analysis program. *J. Appl. Cryst.*, 2009, **42**, 339-341.