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Electronic Supplementary Information

Cyclometallation of the NNN Pincer Ligand in Complexes of Platinum

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I. NMR Specta for Pt Complexes

(NNN)PtCl (1)

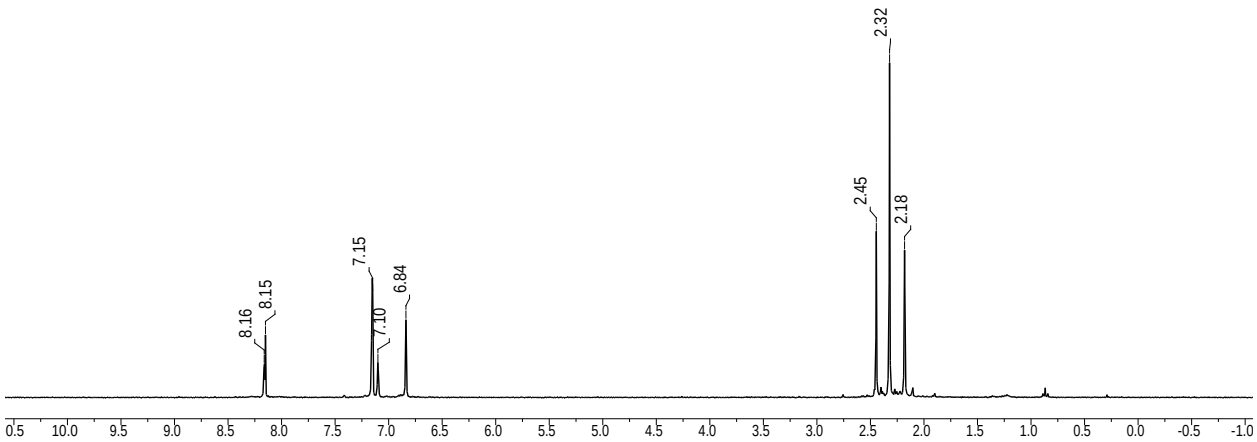

Figure S1. ^{1}H NMR spectrum of **1** in C_6D_6 at 23°C measured on a 300 MHz Varian iNova.

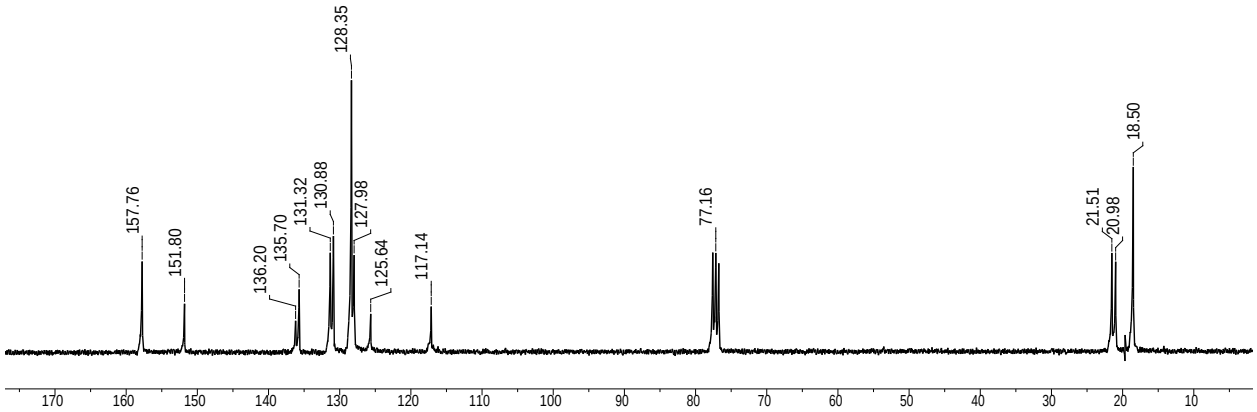

Figure S2. ^{13}C{^{1}H} NMR spectrum of **1** in $CDCl_3$ at 23°C measured on a 300 MHz Varian iNova.

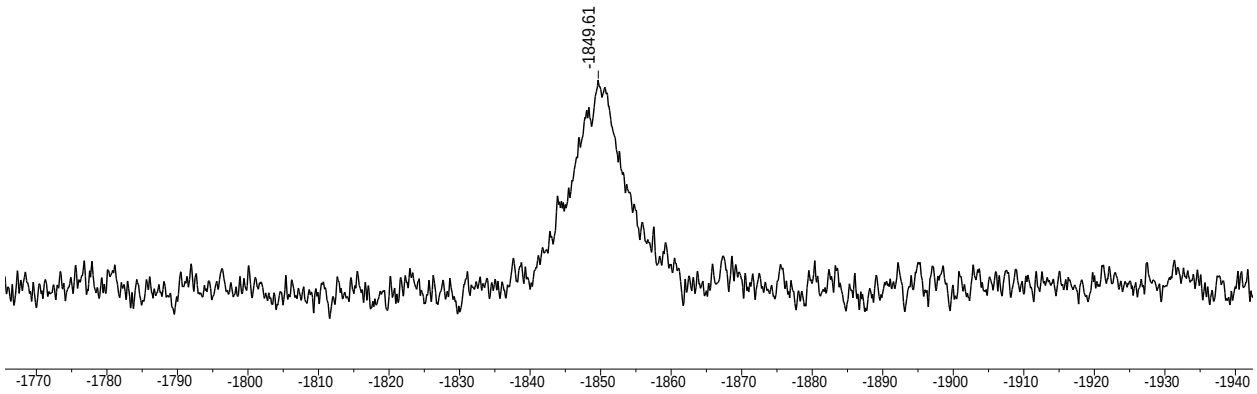

Figure S3. $^{195}Pt\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$ at 23°C measured on a 400 MHz Varian iNova.

(NNN)PtMe (2)

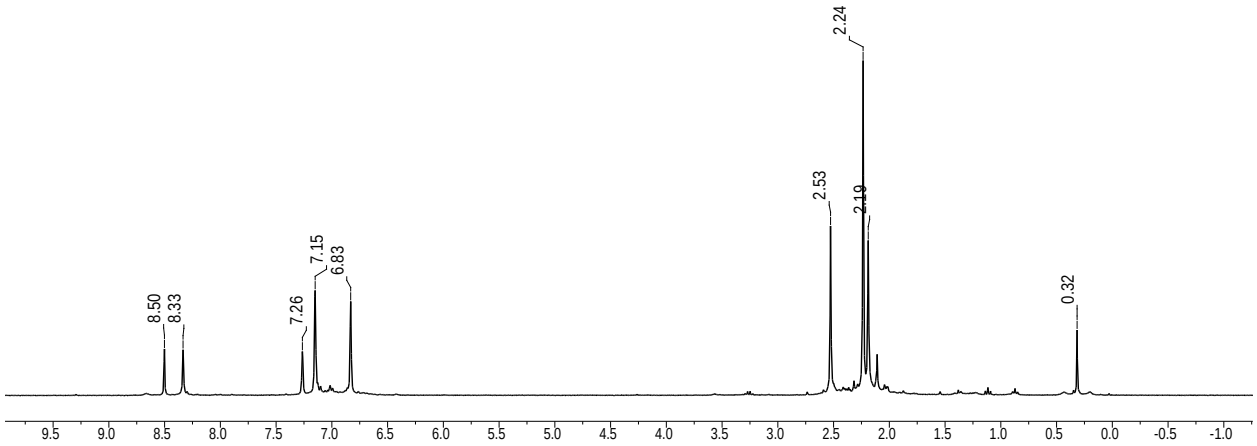

Figure S4. ^{1}H NMR spectrum of **2** in C_6D_6 at 23°C measured on a 300 MHz Varian iNova.

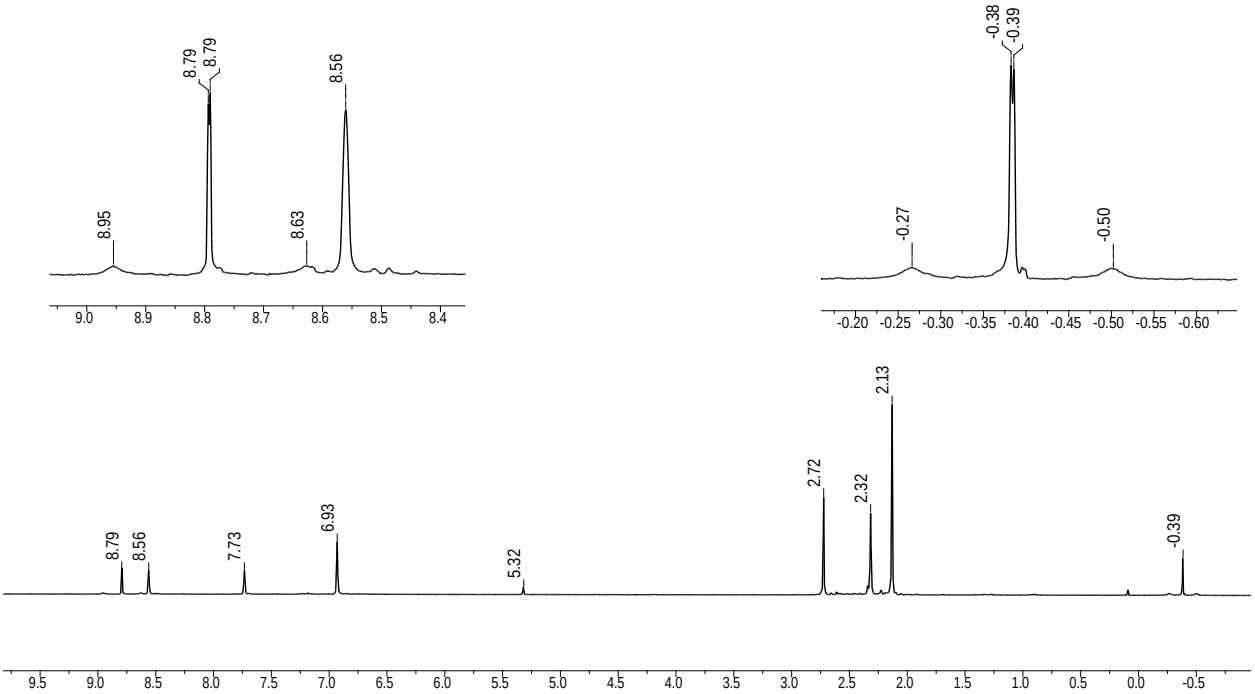

Figure S5. ^{1}H NMR spectrum of **2** in CD_2Cl_2 at 23°C measured on a 300 MHz Varian iNova with insets showing 195Pt coupling for N=C*H* and Pt-CH_3.

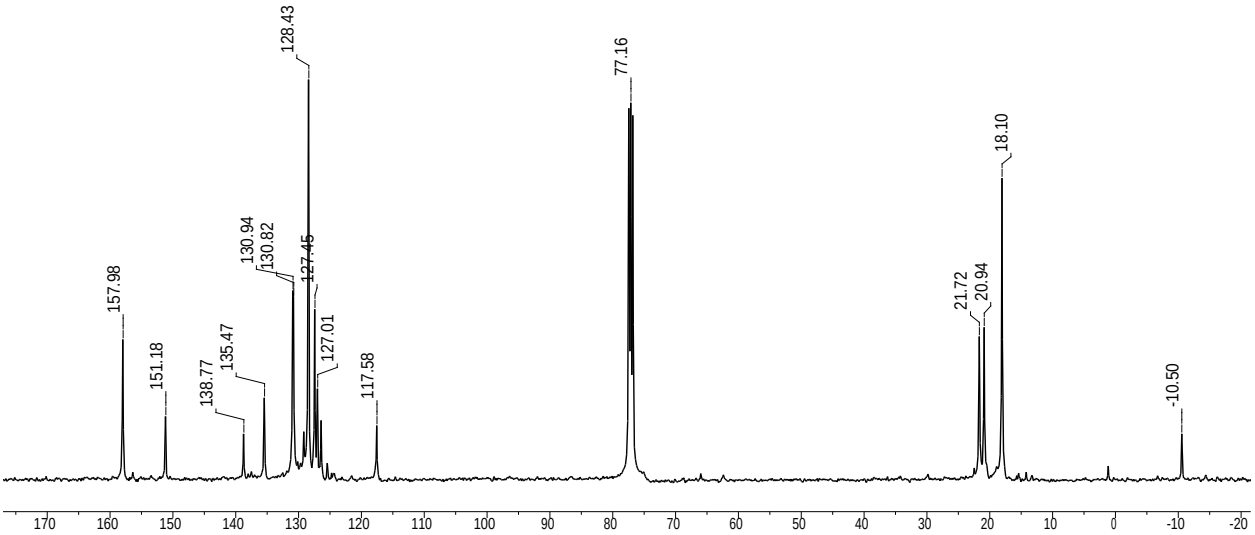

Figure S6. ^{13}C{^{1}H} NMR spectrum of **2** in $CDCl_3$ at 23°C measured on a 300 MHz Varian iNova.

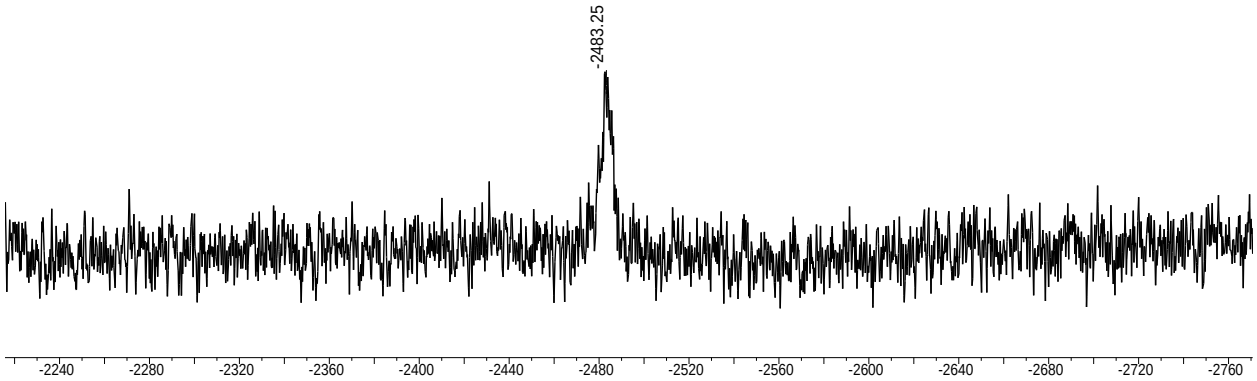

Figure S7. $^{195}Pt\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ at 23°C measured on a 400 MHz Varian iNova.

(NNN)PtOTf (3)

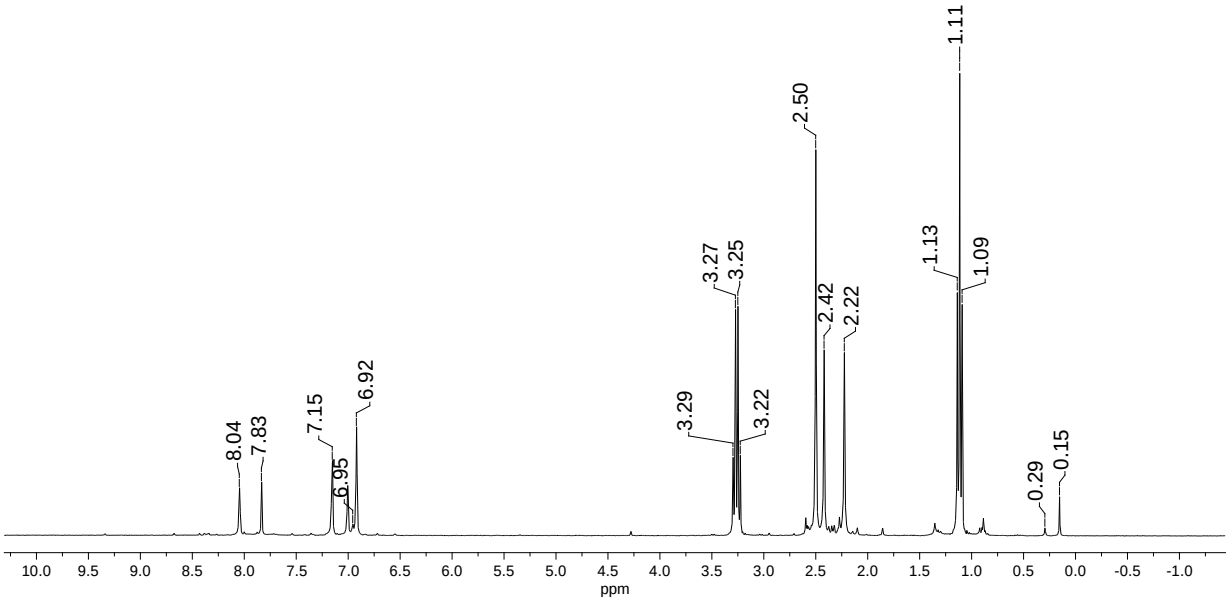

Figure S8. In situ ^{1}H NMR spectrum of **3** in C_6D_6 at 23°C measured on a 500 MHz Varian iNova.

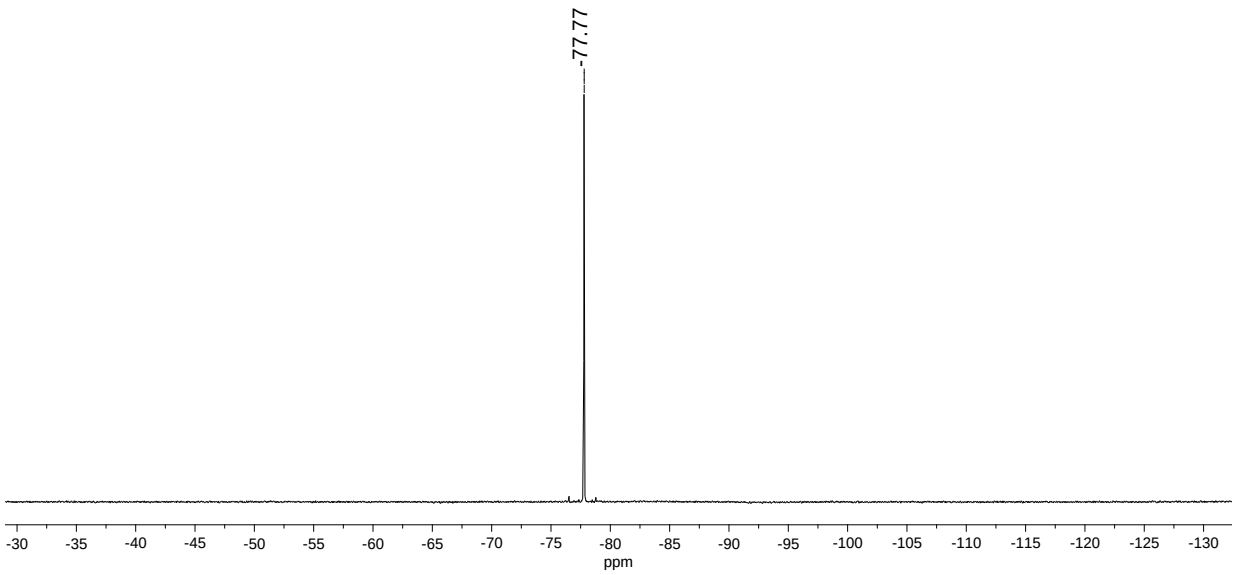

Figure S9. In situ ^{19}F NMR spectrum of **3** in C_6D_6 at 23°C measured on a 300 MHz Varian iNova.

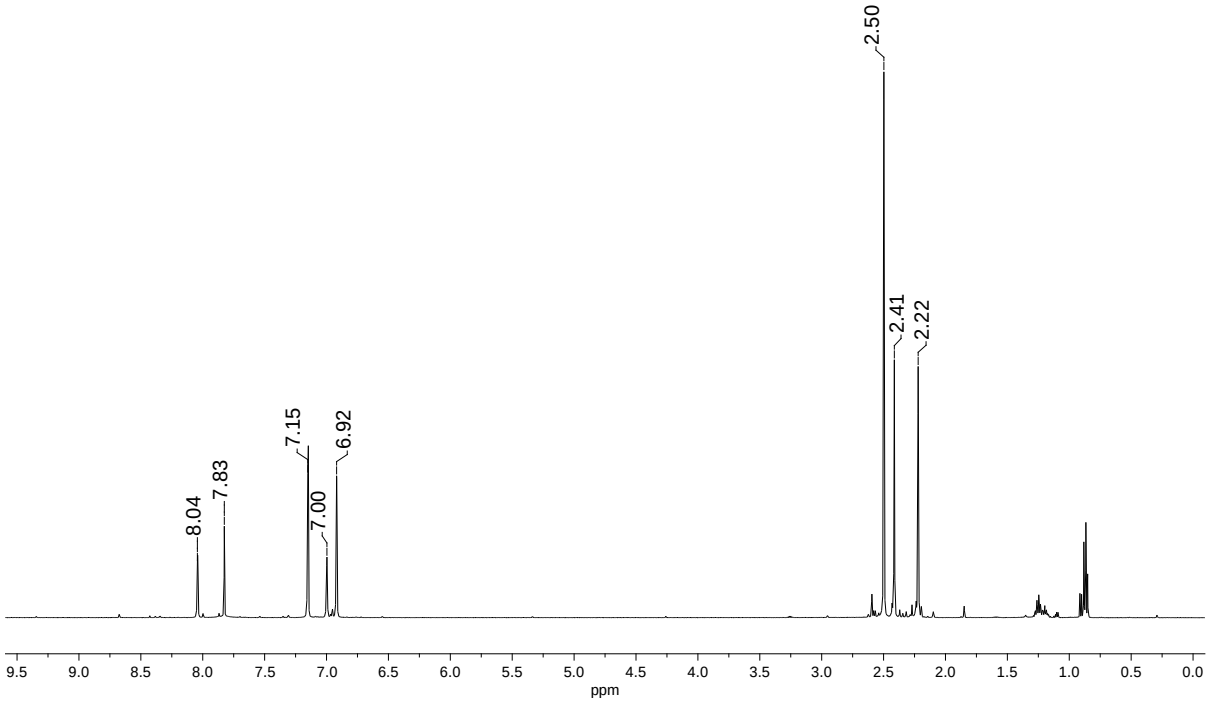

Figure S10. ^{1}H NMR spectrum of **3** in C_6D_6 at 23°C measured on a 500 MHz Varian iNova.

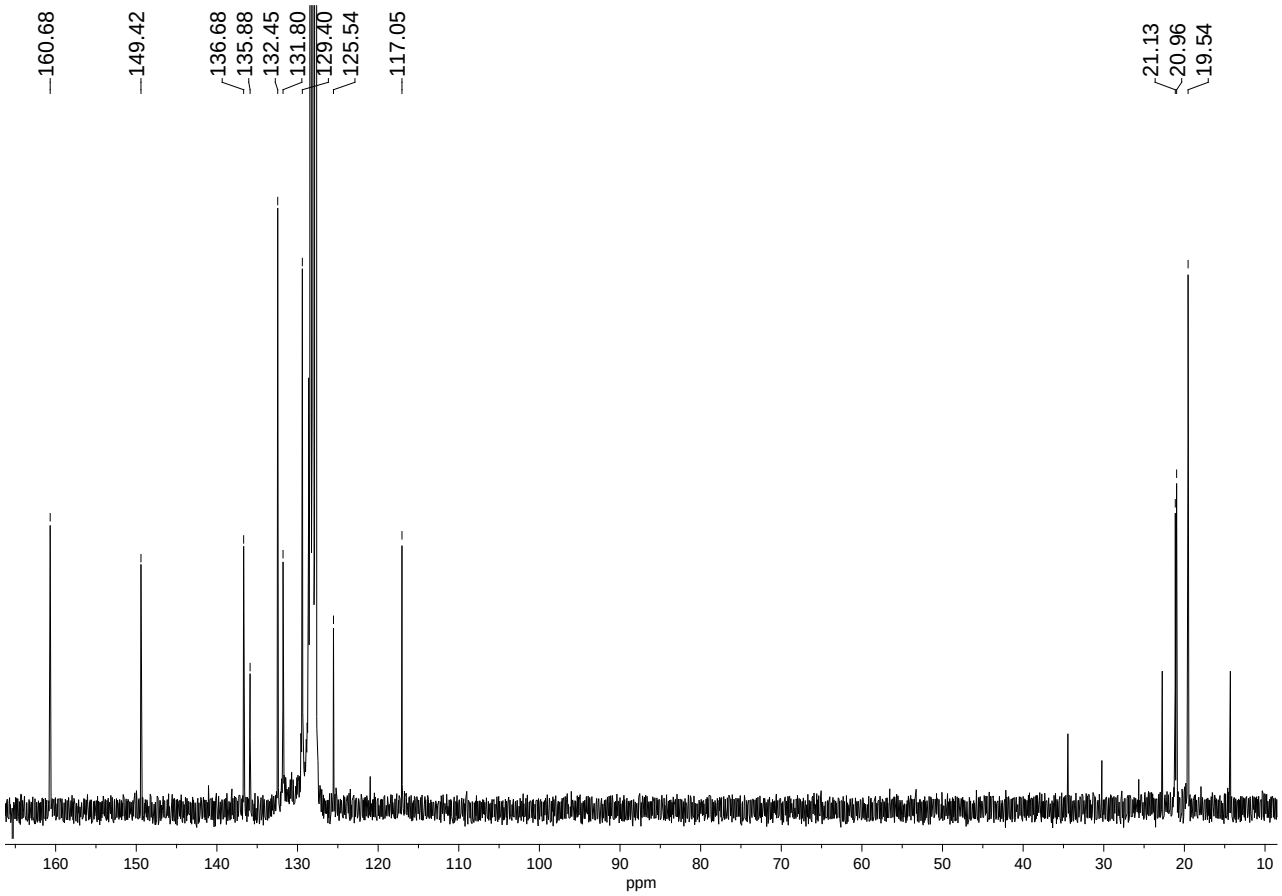

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ at 23°C measured on a 300 MHz Varian iNova.

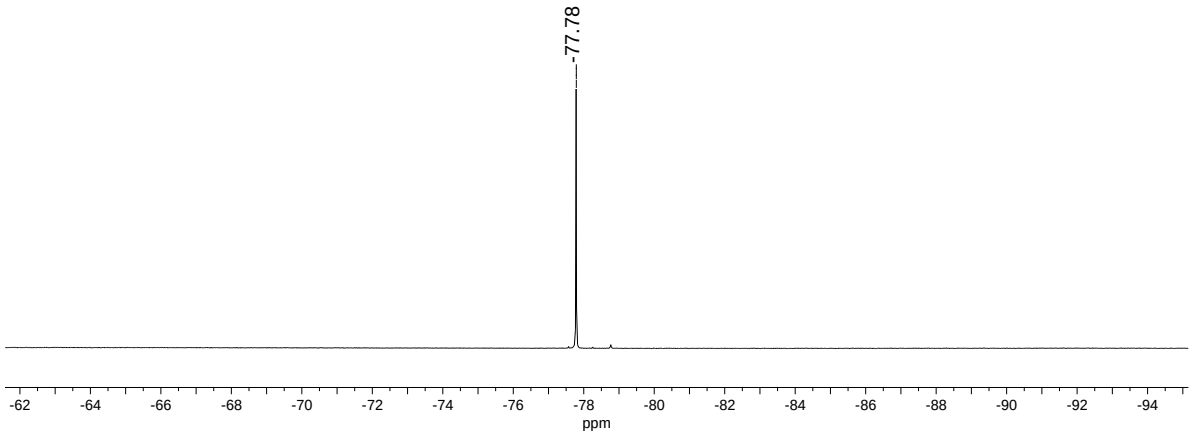

Figure S12. In situ ^{19}F NMR spectrum of **3** in C_6D_6 at 23°C measured on a 300 MHz Varian iNova.

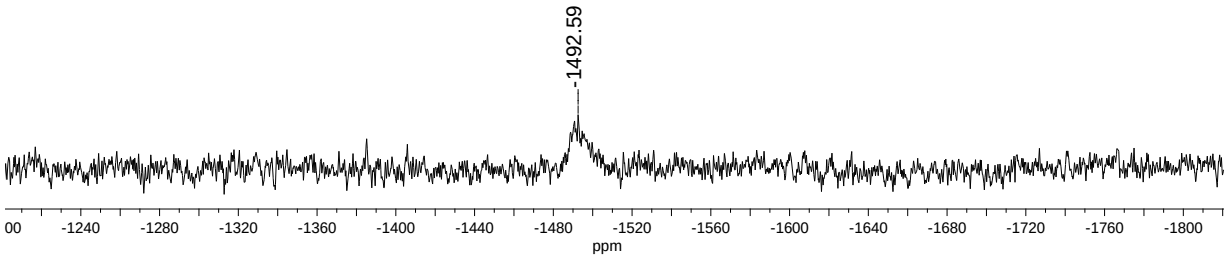

Figure S13. $^{195}Pt\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ at 23°C measured on a 400 MHz Varian iNova.

[(NNN)PtOH$_2$]OTf (4)

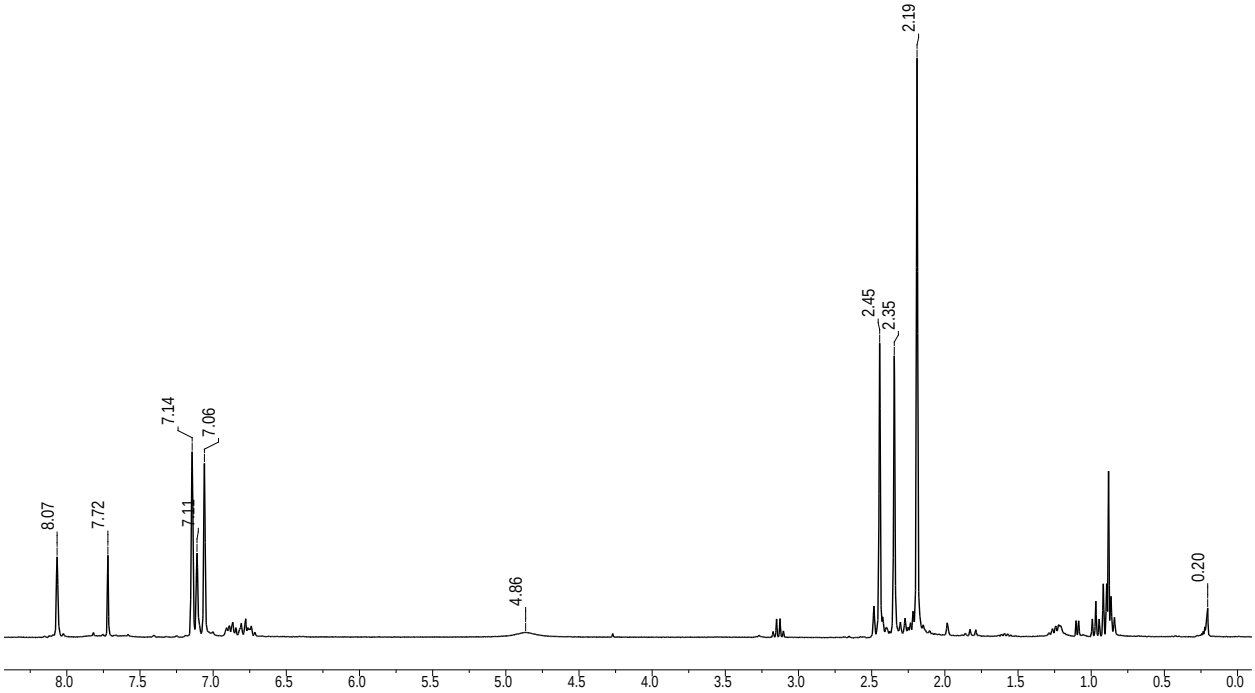

Figure S14. ^{1}H NMR spectrum of **4** in C_6D_6 at 23°C measured on a 300 MHz Varian iNova

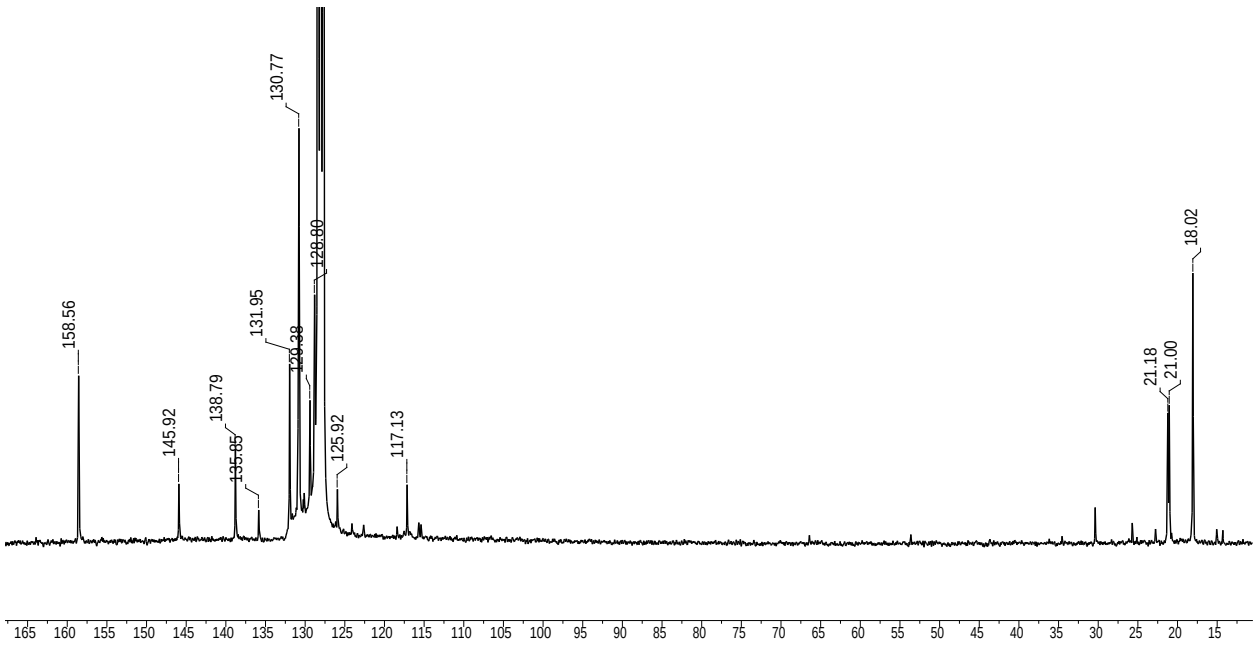

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 23°C measured on a 300 MHz Varian iNova

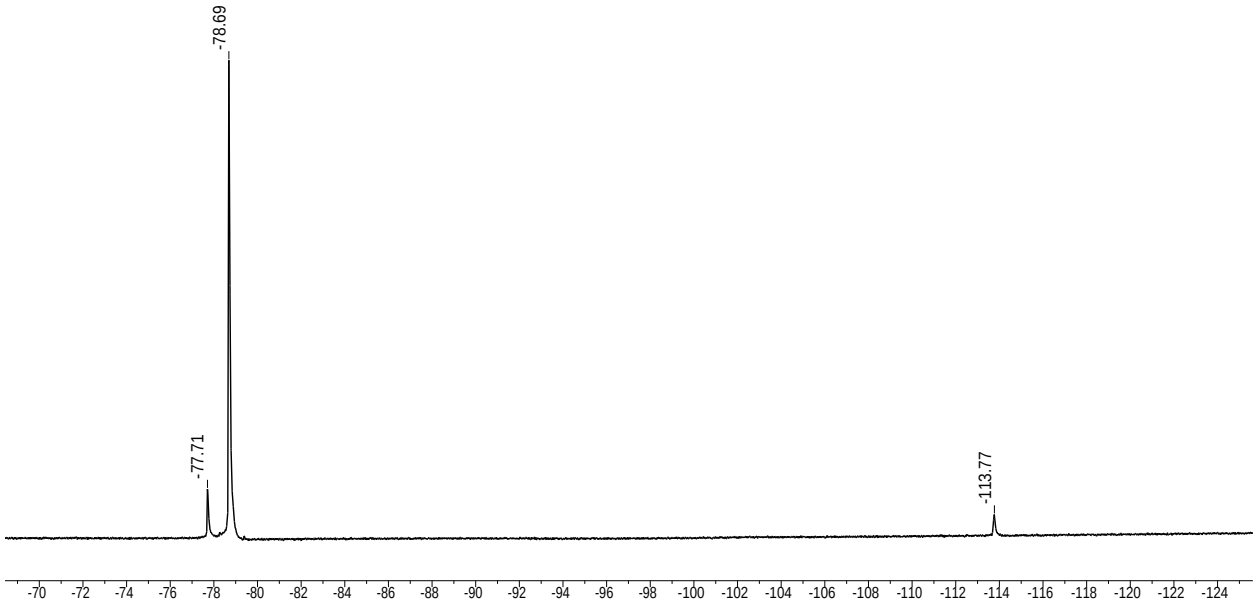

Figure S16. $^{19}F\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 23°C measured on a 300 MHz Varian iNova

Cyclometallated (NNN)Pt(II) (5)

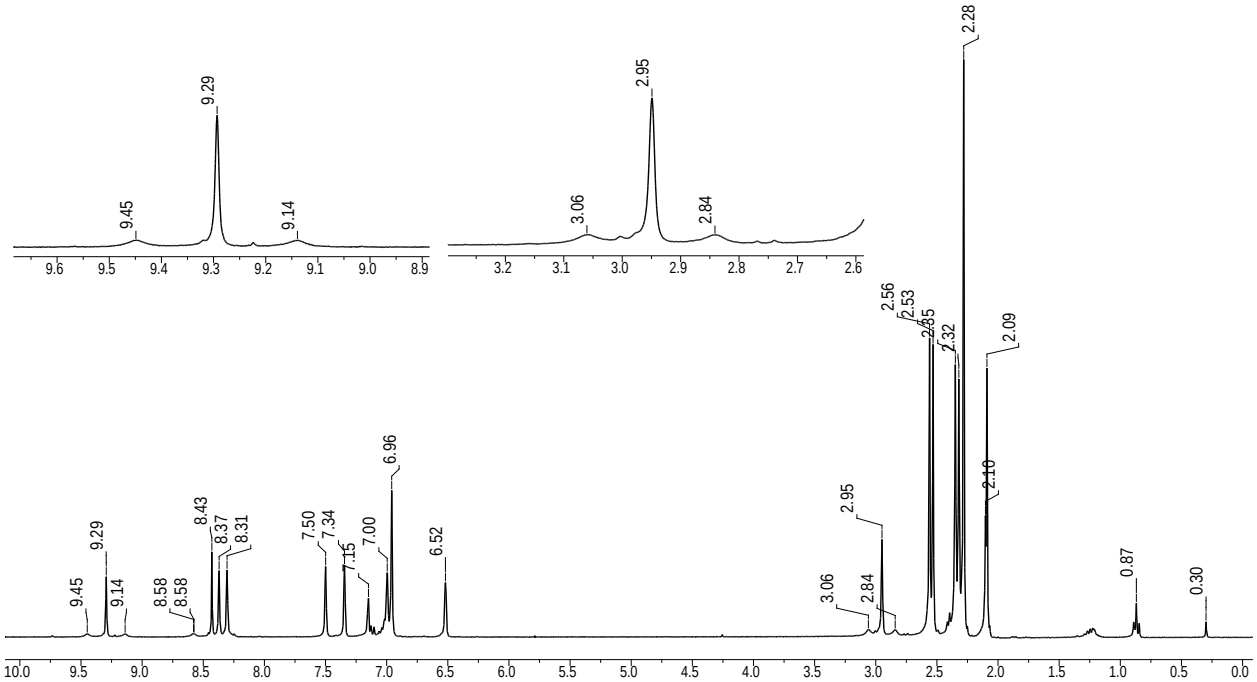

Figure S17. ^{1}H NMR spectrum of **5** in C_6D_6 at 23°C measured on a 500 MHz Varian iNova with insets showing coupling to ^{195}Pt.

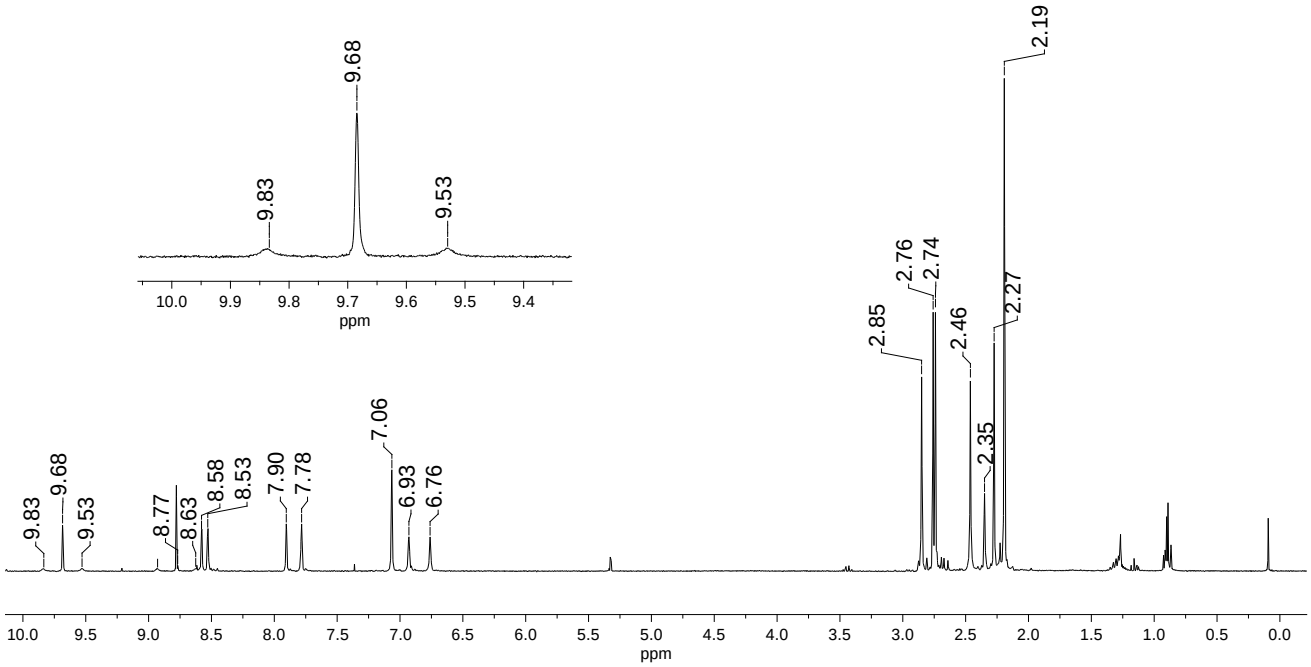

Figure S18. ^{1}H NMR spectrum of **5** in CD_2Cl_2 at 23°C measured on a 300 MHz Varian iNova with inset showing coupling to ^{195}Pt.

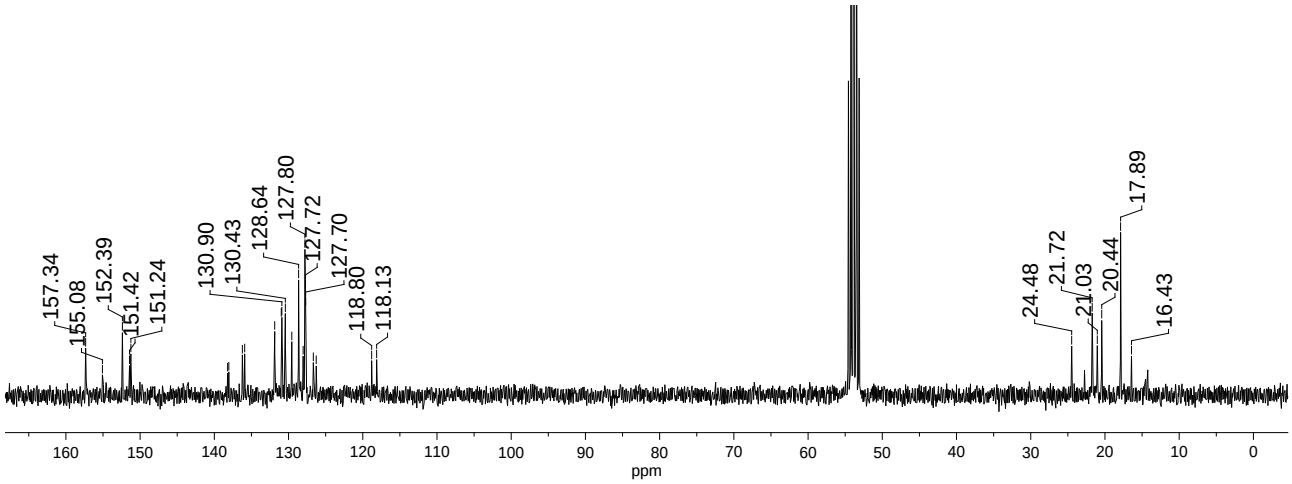

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in CD_2Cl_2 at 23°C measured on a 300 MHz Varian iNova.

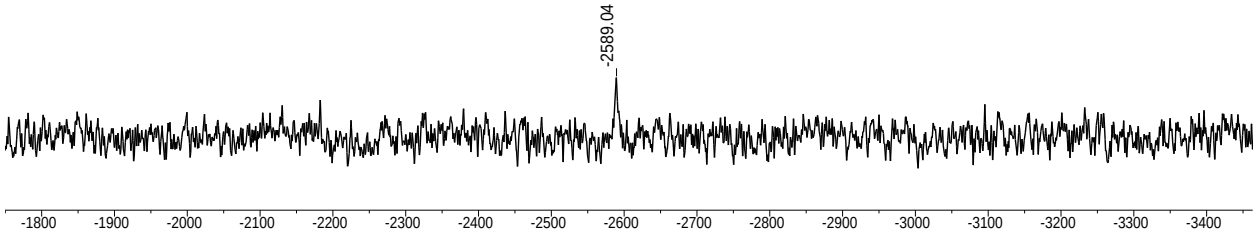

Figure S20. $^{195}Pt\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 at 23°C measured on a 400 MHz Varian iNova.

II. NMR spectrum and table for reactivity studies.

Attempt to remove H_2O from **4**. A sample of **4** as a yellow powder was transferred to a 25 mL Schlenk flask and heated at 130 °C under vacuum for 48 h. After 48 h, the discolored solid was redissolved in C_6D_6 forming a red solution. ^{1}H NMR analysis shows a mixture of 53% **3** and 47% **5** was formed.

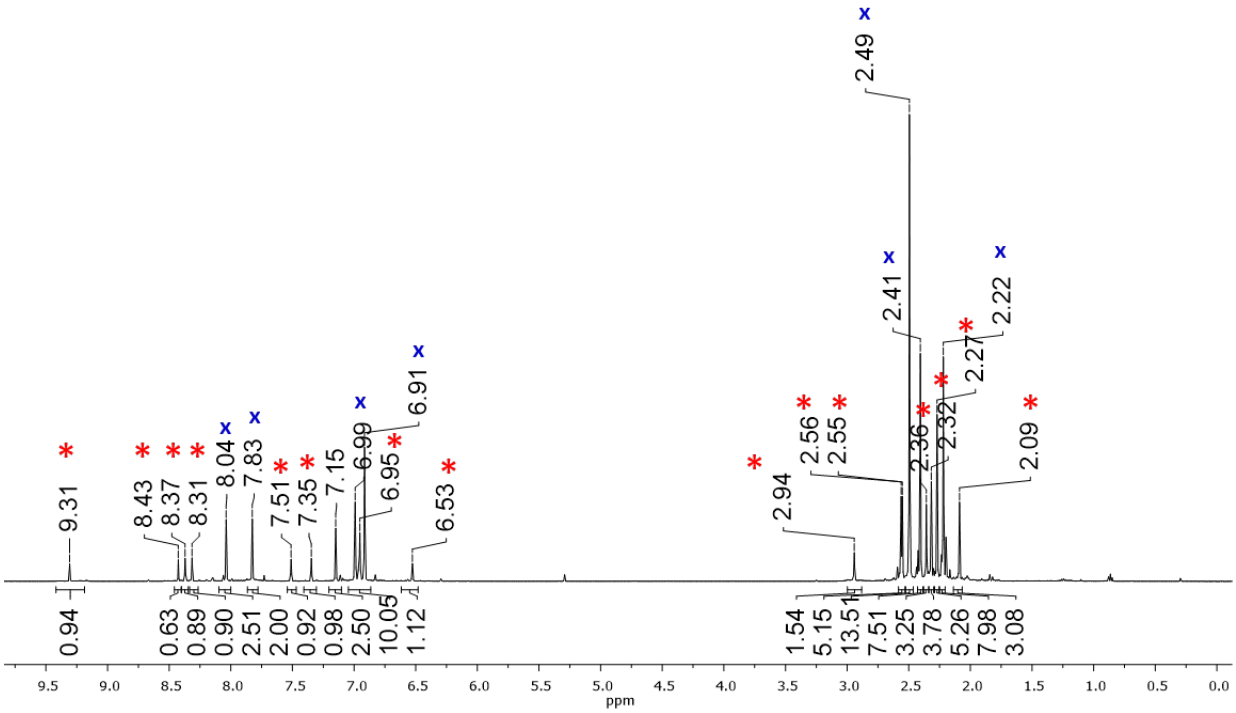

Figure S21. ^{1}H NMR spectrum measured on a 500 MHz Varian iNova of product mixture (**3**, **x**; **5**, *) in C_6D_6 after heating at 130 °C for 48 h under vacuum.

Reaction of (NNN)PtMe with 5 mol% (NNN)PtOTf

Table 1. Summary of relative ratios of Pt species in solution over time for reaction of **2** with 5 mol% **3** in C_6D_6.

Time	2	5	3
5 min	80%	15%	5%
1 h 45 min	71 %	24%	5%
3 h 15 min	57%	38%	5%
6 h	45%	50%	5%
18 h	15%	80%	5%

V. X-ray diffractometry details.

X-Ray data collection, solution, and refinement for 4·HOTf·1/2C_6H_5F. Crystals were grown from fluorobenzene layered with pentane. An orange block of suitable size and quality (0.47 × 0.24 × 0.14 mm) was selected from a representative sample of crystals of the same habit using an optical microscope, mounted onto a nylon loop, and placed in a cold stream of nitrogen (150 K). Low-temperature X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEX2 software.[1] An absorption correction was applied using SADABS.[2] The space group was determined on the basis of systematic absences and intensity statistics. The structure was solved by direct methods in the monoclinic I2/a space group using SHELXS.[3] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bound to carbon were placed in idealized positions and refined using a riding model. The hydrogen atoms on the metal-bound water were located in the difference map, and refined with restraints. The hydrogen atom on the triflic acid moiety was not observed in the difference map, but placed in an idealized position and refined using a riding model in order to obtain the correct charge balance. The structure was brought to convergence by weighted full-matrix least-squares refinement on $|F|^2$ using SHELXL.[3] A check for missed symmetry was run using the ADDSYM program within PLATON,[4] revealing no apparent higher symmetry. Disordered solvent was satisfactorily modeled using PLATON's SQUEEZE functionality – 4 voids were located in the unit cell, each containing 30 e^- with volume 175 $Å^3$.

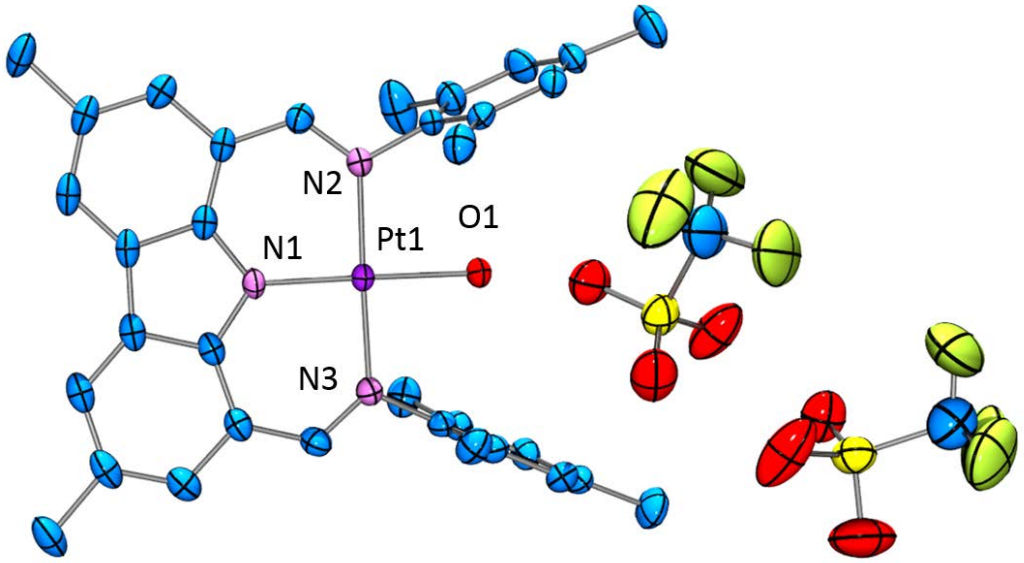

Figure S22. ORTEP drawing (50% probability ellipsoids) of **4·HOTf·1/2C_6H_5F.** Omitted for clarity: H atoms and C_6H_5F. Selected distance (Å) and angles (deg) follow: Pt1-O1, 2.088(2); Pt1-N1, 1.938(3); Pt1-N2, 2.021(3); Pt1-N3, 2.012(3); N2-Pt1-N3, 178.35(11); N1-Pt1-O1, 178.63(11); N1-Pt1-N2, 90.84(12); N1-Pt1-N3, 90.82(12); N2-Pt1-O1, 90.16(10); N3-Pt1-O1, 88.18(11).

X-Ray data collection, solution, and refinement for 4·C_6D_6. Crystals were grown from a solution of deuterobenzene/fluorobenzene layered with pentane. An orange block of suitable size and quality (0.15 × 0.07 × 0.04 mm) was selected from a representative sample of crystals of the same habit using an optical microscope, mounted onto a nylon loop, and placed in a cold stream of nitrogen (150 K). Low-temperature X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEX2 software.[1] An absorption correction was applied using SADABS.[2] The space group was determined on the basis of systematic absences and intensity statistics. The structure was solved by direct methods in the monoclinic $P2_1/c$ space group using SHELXS.[3] All non-hydrogen atoms

were refined with anisotropic thermal parameters. Hydrogen atoms bound to carbon were placed in idealized positions and refined using a riding model. The hydrogen atoms associated with the coordinated water molecule were located in the difference map after down-weighting (truncating) high-angle reflections to enhance the contribution from hydrogen, and refined with restraints.[5] The structure was brought to convergence by weighted full-matrix least-squares refinement on $|F|^2$. PLATON's ADDSYM and NEWSYM features were used to check for missed symmetry.[4] Structure manipulations were performed with the aid of shelXle.[6]

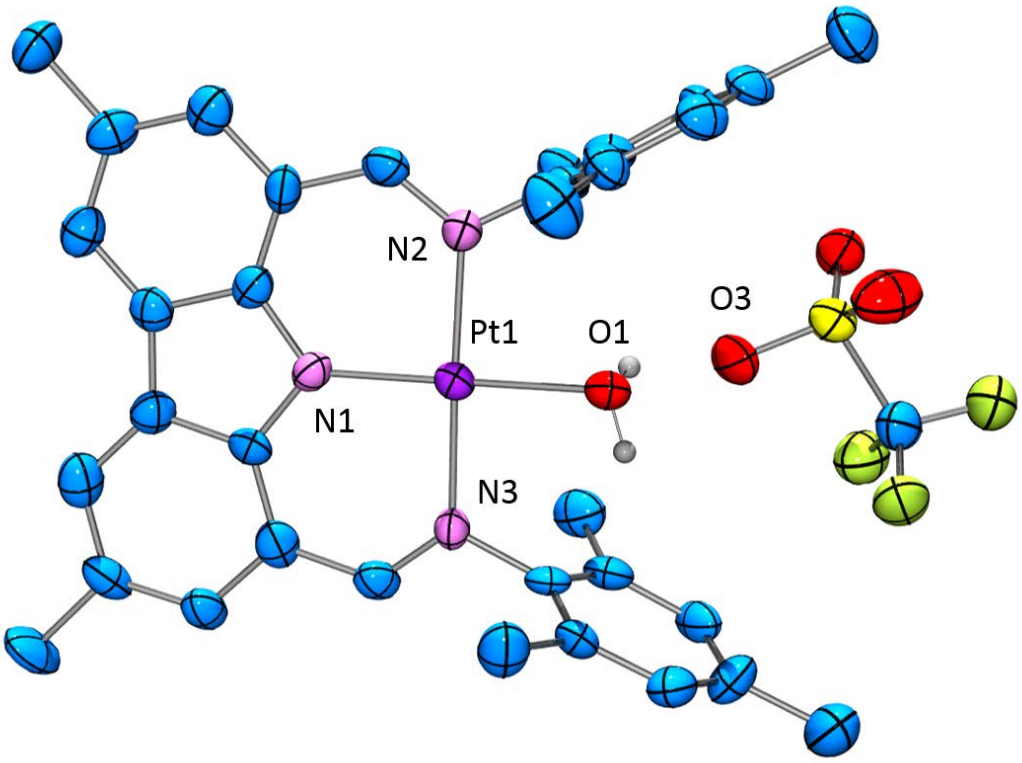

Figure S23. ORTEP drawing (50% probability ellipsoids) of **4·C_6D_6.** Omitted for clarity: H atoms and C_6D_6. Selected distance (Å) and angles (deg) follow: Pt1-O1, 2.078(6); Pt1-N1, 1.933(6); Pt1-N2, 2.018(6); Pt1-N3, 2.023(6); N2-Pt1-N3, 177.1(2); N1-Pt1-O1, 175.7(2); N1-Pt1-N2, 91.0(3); N1-Pt1-N3, 90.5(3); N2-Pt1-O1, 87.9(2); N3-Pt1-O1, 90.8(2).

X-Ray data collection, solution, and refinement for 5. Crystals were grown from a solution of deuterobenzene/fluorobenzene layered with pentane. An orange block of suitable size and quality (0.11 × 0.09 × 0.03 mm) was selected from a representative sample of crystals of the same habit using an optical microscope, mounted onto a nylon loop, and placed in a cold stream of nitrogen (150 K). Low-temperature X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, $K_\alpha = 0.71073$ Å). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEX2 software.[1] An absorption correction was applied using SADABS.[2] The space group was determined on the basis of systematic absences and intensity statistics. The structure was initially solved by direct methods in the triclinic P1 space group using SHELXS,[3] and converted into the centrosymmetric P–1 space group with PLATON's ADDSYM feature after locating all heavy atoms.[4] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bound to carbon were placed in idealized positions and refined using a riding model. PLATON's SQUEEZE feature was utilized to account for partial occupancy and disorder of solvent in the crystal structure, which appeared to be benzene based on the difference map (total void volume 205 $Å^3$, 37 e^-). The structure was brought to convergence by weighted full-matrix least-squares refinement on $|F|^2$. Structure manipulations were performed with the aid of shelXle.[6]

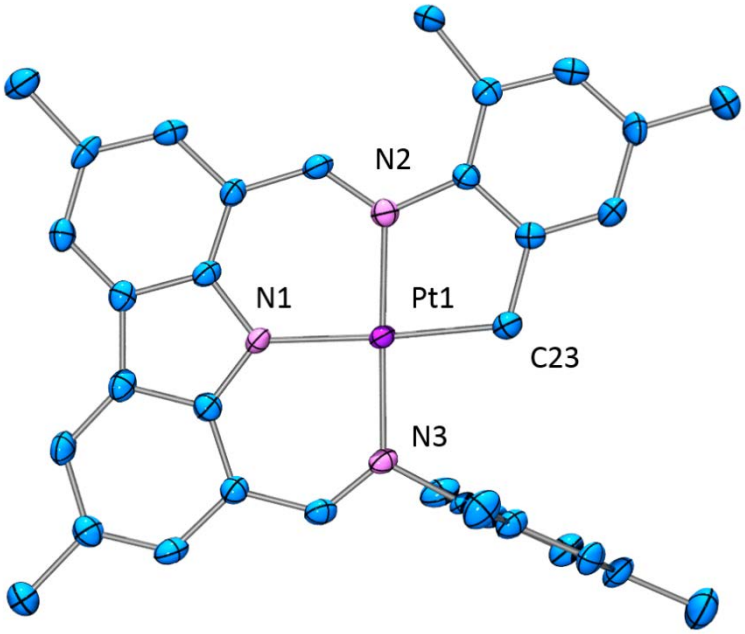

Figure S24. ORTEP drawing (50% probability ellipsoids) of **5.** Omitted for clarity: H atoms. Selected distance (Å) and angles (deg) follow: Pt1-C23, 2.027(5); Pt1-N1, 2.007(4); Pt-N2, 2.011(4); Pt-N3, 2.012(4); N2-Pt1-N3, 178.37(15); N1-Pt1-C23, 176.43(16); N1-Pt1-N2, 92.89(16); N1-Pt1-N3, 88.70(16); N2-Pt1-C23, 83.59(18); N3-Pt1-C23, 94.82(18).

IV. Cyclic voltammogram for Compound 1

A BAS-100A electroanalyzer utilizing a three-electrode system with glassy carbon working electrode, platinum wire counter electrode, and a vycor-tipped $Ag/AgNO_3$ reference electrode was used for electrochemical measurements. Cyclic voltammogram was obtained from 2 mM solution of compound 1 in CH_2Cl_2, using 10 mM $[Bu_4N][PF_6]$ supporting electrolyte at a scan rate of 200 mV/s. Solutions were degassed by a purge of Ar, and a blanket of Ar was maintained over the solution while the measurement was made. Cyclic voltammogram was referenced to Fc/Fc^+ ($E_{½}$ = 0 V).

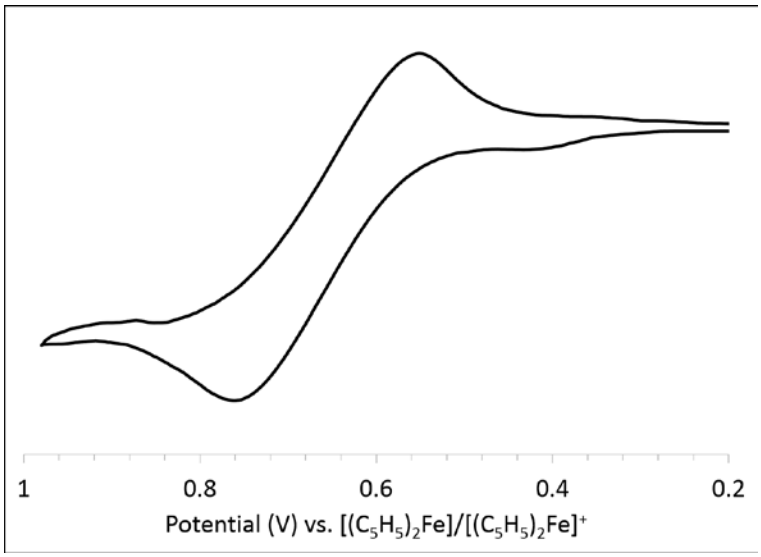

Figure S25. Cyclic voltammogram of **1** in CH_2Cl_2 at 23 °C. The scan rate was 200 mV/s in the positive direction. The cyclic voltammogram was obtained with 2 mM solution of Compound **1** in CH_2Cl_2 and 10 mM $[Bu_4N][PF_6]$ as the supporting electrolyte and resulted in a measured potential (E½) equal to 0.65 V (vs Fc/Fc^+).

V. SI References

[1] APEX2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.

[2] SADABS, Program for Absorption Correction for Data from Area Detector Frames, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.

[3] Sheldrick, G.M. *Acta Cryst*. 2008, **A64**, 112.

[4] Spek, A. L. (2006) PLATON – A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. Spek, A. L. *Acta Cryst*. 1990, **A46**, C34.

[5] Cooper, R.I.; Thompson, A.L.; Watkin, D.J. *J. Appl. Cryst.* 2010, **43**, 1100-1107.

[6] Hübschle, C.B.; Sheldrick, G.M. *J. Appl. Cryst.* 2011, **44**, 1281–1284.