Supporting Information for

The Chiral Potential of Phenanthriplatin and Its Influence on Guanine Binding

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Contents

Experimental Section

Materials and Methods. All chemicals were reagent grade and used as received from commercial vendors without further purification. Enantiomerically pure *R*,*R*-1,2-diamino–cyclohexane (DACH) was obtained from Strem Chemicals. [Pt(*R*,*R*-DACH)Cl_2] was prepared as previously reported.[1] Solvents were used as received without further purification.

Physical Measurements. ^{1}H, $^{13}C\{^{1}H\}$, and $^{195}Pt\{^{1}H\}$ NMR spectroscopic measurements were performed on a Varian Inova-500 spectrometer equipped with a 5 mm broadband-style 'switchable' probe with z-axis pulsed field gradient capability in the MIT Department of Chemistry Instrumentation Facility. NMR chemical shifts (δ) are reported in ppm with respect to tetramethylsilane (^{1}H and ^{13}C) or Na_2PtCl_6 (^{195}Pt) and referenced to residual deuterated solvent peaks (^{1}H and ^{13}C) or an external standard of K_2PtCl_4 in D_2O (^{195}Pt, -1628 ppm). Samples prepared in D_2O for ^{1}H and ^{13}C NMR spectroscopic measurements contained dioxane for use as an internal chemical shift reference (^{1}H: 3.75 ppm, ^{13}C: 67.19 ppm). Full NMR spectra and peak assignments are presented in Figures S1–S18. Unless otherwise specified, NMR data were collected at room temperature. During super-ambient variable temperature (VT) experiments, the sample temperature was regulated using an Oxford VT controller driving an in-probe heater coil. During sub-ambient VT experiments, the sample temperature was regulated with 10-15 L min^{-1} of nitrogen gas passed through a heat exchanging coil inside a styrofoam bucket filled with liquid nitrogen. Temperature accuracy is ±2 °C, deemed sufficient to prevent significant error in the extraction of activation parameters from dynamic NMR data.[2] An internal chemical shift thermometer was therefore not used. Electrospray ionization mass spectrometry (ESI-MS) measurements were performed on an Agilent Technologies 1100 series LC/MSD ion trap. Elemental analyses were provided by a commercial vendor.

Synthesis. *cis-[Pt(NH_3)$_2$(phenanthridine)Cl]OTf (**1**)*. Cisplatin (500 mg, 1.67 mmol) was dissolved in DMF (15 mL) and combined with a solution of silver triflate (426 mg, 1.66 mmol) in DMF (1 mL). The mixture was stirred in the dark at room temperature overnight and the resulting suspension was filtered through a plug of Celite. Phenanthridine (299 mg, 1.67 mmol) was added to the pale yellow filtrate and the mixture was stirred overnight at room temperature

in the dark. The mixture was then concentrated to approximately 3 mL in vacuo and acetone (6 mL) was added. Unreacted cisplatin forms a yellow precipitate, which was removed by filtration. The filtrate was layered with ether (70 mL) and allowed to stand at room temperature overnight. Colorless needles formed and were collected by filtration, washed with ether, and allowed to dry under vacuum. Yield: 637 mg (64%); m.p., gradual decomposition after 216 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$) 4.37 (s, 3H), 4.62 (s, 3H), 7.88 (m, 2H), 7.99 (t, 1H, 8 Hz), 8.10 (t, 1H, 8 Hz), 8.38 (d, 1H, 8 Hz), 8.81 (d, 1H, 8.5 Hz), 8.85 (d, 1H, 8.5 Hz), 9.94 (d, 1H, 8.5 Hz), 9.97 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $(CD_3)_2CO$) 123.18, 123.86, 126.54, 127.51, 133.19, 135.03, 143.67, 161.28, 129.76, 129.79, 130.34, 130.40, 130.98; ^{195}Pt{^{1}H} NMR (108 MHz, $(CD_3)_2CO$) -2289; ESI-MS (+) mode *m/z* $[M–NH_4–Cl]^+$ 390.0 (calc. 390.1), $[M–NH_3]^+$ 426.9 (calc. 427.0), $[M]^+$ 444.0 (calc. 444.1); Anal. Calc. for $C_{14}H_{15}ClF_3N_3O_3PtS$: C 28.36, H 2.55, N 7.09. Found: C 28.18, H 2.54, N 7.00.

*cis-[Pt(R,R-DACH)(phenanthridine)Cl]OTf (**2**)*. A 100 mg portion of [Pt(*R*,*R*-DACH)Cl_2] (0.26 mmol) was dissolved in DMF (7 mL). A solution of silver triflate (68 mg, 0.26 mmol) in DMF (1 mL) was added and the mixture was stirred at room temperature in the dark overnight. The resulting suspension was filtered through Celite and phenanthridine (47 mg, 0.26 mmol) was added to the filtrate. The mixture was stirred at room temperature for 4 h and then stripped of solvent in vacuo. The residue was taken up in acetone (6 mL) and filtered through Celite to remove unreacted starting material. The filtrate was reduced in volume to 1 mL and ether (20 mL) was added to precipitate a white solid. The solid was collected by filtration, washed with ether, and dried under vacuum. Yield: 145 mg (85%); m.p., decomposition to black liquid at 290–303 °C. ^{1}H NMR spectral data were collected at 100 °C so that all peaks arising from interconverting diastereomers had coalesced. The spectra collected at intermediate temperatures are provided in Fig. S19. ^{1}H NMR (500 MHz, DMF-d_7) 1.26 (m, 2H), 1.53 (m, 1H), 1.66 (m, 3H), 2.07 (d, 1H, 12 Hz), 2.29 (d, 1H, 12 Hz), 2.81 (s, 2H), 5.46 (s, 2H), 5.96 (s, 1H), 6.21 (s, 1H), 7.92–8.02 (m, 3H), 8.17 (t, 1H, 8 Hz), 8.40 (d, 1H, 8 Hz), 8.90 (d, 1H, 8 Hz), 8.94 (d, 1H, 8 Hz), 9.85 (d, 1H, 8 Hz), 10.00 (s, 1H); ESI-MS (+) mode *m/z* $[M]^+$ 524.0 (calc. 524.1); Anal. Calc. for $C_{20}H_{23}ClF_3N_3O_3PtS$: C 35.69, H 3.44, N 6.24. Found: C 35.55, H 3.28, N 6.32.

*cis-[Pt(R,R-DACH)(phenanthridine)$_2$]OTf$_2$ (**3**)*. Potassium tetrachloroplatinate(II) (200 mg, 0.48 mmol) and potassium iodide (800 mg, 4.8 mmol) were dissolved in water (10 mL) and stirred at 70 °C for 10 min. A solution of *R,R*-DACH (55 mg, 0.48 mmol) in water (1 mL) was added to the deep purple tetraiodoplatinate(II) solution. The yellow solid that immediately formed was collected by filtration, washed with water (40 mL in portions), and dissolved in DMF (15 mL). Silver triflate (247 mg, 0.96 mmol) was added to the yellow solution, which was then stirred at 70 °C for 3 h. The resulting mixture was filtered through a plug of Celite. Phenanthridine (173 mg, 0.96 mmol) was added to the filtrate and the mixture was stirred at 50 °C for 5 h. The mixture was then concentrated to 1 mL in vacuo. The residue was taken up in acetone (3 mL) and added in a dropwise manner to rapidly stirring ether (100 mL). The beige solid that precipitated was collected by filtration, washed with ether, and dried under vacuum. Yield: 213 mg (46%); m.p., phase change at 170 °C and gradual decomposition starting at 175 °C. The ^{1}H NMR spectral data presented here were collected at 120 °C so that all peaks arising from interconverting diastereomers have coalesced. The spectra collected at intermediate temperatures are shown in Fig. S20. ^{1}H NMR (500 MHz, DMF-d_7) 1.34 (m, 2H), 1.70 (m, 4H), 2.22 (d, 2H, 11.7 Hz), 3.17 (s, 2H), 5.98 (s, 2H), 6.76 (s, 2H), 7.92 (m, 4H), 8.12 (t, 4H, 7.6 Hz), 8.42 (d, 2H, 7.7 Hz), 8.83 (t, 4H, 7.4 Hz), 10.16 (s, 2H), 10.50 (s, 2H); ESI-MS (+) mode *m/z* $[M]^{2+}$ 333.6 (calc. 333.6), $[M–NC_{13}H_9–Cl]^+$ 486.0 (calc. 486.1), $[M–H]^+$ 666.1 (calc. 666.2), $[M+SO_3CF_3]^+$ 817.1 (calc. 817.2); Anal. Calc. for $C_{34}H_{32}F_6N_2O_6PtS_2$: C 42.28, H 3.34, N 5.80. Found: C 42.33, H 3.31, N 5.42.

*cis-[Pt(NH$_3$)$_2$(phenanthridine)$_2$]OTf$_2$ (**4**)*. Cisplatin (200 mg, 0.67 mmol) and silver triflate (343 mg, 1.33 mmol) were combined in DMF (8 mL) and stirred at room temperature in the dark overnight. The resulting suspension was filtered through a plug of Celite. Phenanthridine (239 mg, 1.33 mmol) was added to the filtrate, which was stirred at 75 °C for 1 h and then stripped of solvent in vacuo. The residue was taken up in acetone (4 mL), layered with ether (80 mL), and left to stand at room temperature for 3 days. The colorless crystals that formed were isolated by filtration, washed with ether, and dried under vacuum. Yield: 312 mg (53%); m.p., phase change at 150 °C and gradual decomposition starting at 178 °C. The ^{1}H NMR spectral data presented here were collected at 130 °C so that all peaks arising from interconverting diastereomers had coalesced. The spectra collected at intermediate temperatures are presented in Fig. S21. ^{1}H NMR

(500 MHz, DMF-d_7) 5.16 (s, 6H), 7.91 (m, 4H), 8.11 (m, 4H), 8.40 (m, 2H), 8.82 (d, 4H, 8 Hz), 10.23 (s, 2H), 10.45 (s, 2H); ESI-MS (+) mode *m/z* $[M–NH_3]^{2+}$ 285.0 (calc. 285.1), $[M]^{2+}$ 293.5 (calc. 293.6), $[M–NH_3–NH_4–C_{13}H_9N]^+$ 373.0 (calc. 373.1), $[M–NH_4–C_{13}H_9N]^+$ 391.0 (calc. 391.1), $[M–NH_3–NH_4]^+$ 552.0 (calc. 552.1), $[M–NH_4]^+$ 569.0 (calc. 569.1), $[M–H]^+$ 586.0 (calc. 586.2), $[M–NH_3+SO_3CF_3]^+$ 719.0 (calc. 719.1), $[M+SO_3CF_3]^+$ 736.0 (calc. 736.1); Anal. Calc. for $C_{28}H_{24}F_6N_4O_6PtS_2·C_3H_7NO$: C 38.83, H 3.26, N 7.30. Found: C 38.74, H 3.20, N 7.50.

*cis-[Pt(NH$_3$)$_2$(phenanthridine)(9-ethylguanine)]OTf$_2$ (**5**).* *cis*-[Pt(NH$_3$)$_2$(phenanthridine)Cl]OTf, **1**, (100 mg, 0.169 mmol) and silver triflate (43 mg, 0.169 mmol) were dissolved in methanol (6 mL) and stirred overnight at room temperature in the dark. The resulting suspension was filtered through Celite and 9-ethylguanine (30 mg, 0.169 mmol) was added to the filtrate. The mixture was stirred for 3 h at room temperature and stripped of solvent in vacuo. The residue was taken up in acetone (2 mL), filtered through Celite, and added in a dropwise manner to rapidly stirring ether (50 mL). The white solid that precipitated was collected by filtration, washed with ether, and dried under vacuum. Yield 115 mg (77%); m.p., gradual decomposition after 177 °C. ^{1}H NMR (500 MHz, D_2O) 0.75 (t, 3H, 7.5 Hz), 3.01 (m, 2H), 6.27 (s, 2H), 6.63 (s, 1H), 6.84 (s, 1H), 7.51 (t, 1H, 7.5 Hz), 7.74 (t, 1H, 8.5 Hz), 8.11 (s, 1H), 8.14 (d, 1H, 8.0 Hz), 9.70 (d, 1H, 8.5 Hz), 9.88 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, D_2O) 14.07, 40.21, 114.45, 118.96, 120.68, 121.48, 121.94, 125.30, 126.50, 128.65, 129.49, 130.09, 130.93, 131.23, 131.93, 134.80, 140.98, 142.10, 150.62, 154.32, 156.95, 161.20; ^{195}Pt{^{1}H} NMR (108 MHz, D_2O) -2449; ESI-MS (+) mode *m/z* $[M–NH_3]^{2+}$ 285.0 (calc. 285.1); Anal. Calc. for $C_{22}H_{24}F_6N_8O_7PtS_2·H_2O$: C 29.24, H 2.90, N 12.40. Found: C 29.08, H 2.60, N 12.14.

*cis-[Pt(NH$_3$)$_2$(phenanthridine)(9-methylguanine)]OTf$_2$ (**6**).* *cis*-[Pt(NH$_3$)$_2$(phenanthridine)Cl]OTf, **1**, (200 mg, 0.34 mmol) and silver triflate (87 mg, 0.34 mmol) were dissolved in methanol (4 mL) and stirred at room temperature in the dark overnight. The resulting suspension was filtered through Celite and a solution of 9-methylguanine (56 mg, 0.34 mmol) in DMF (2 mL) was added to the filtrate. The solution was stirred at 60 °C for 5 h and then stripped of solvent in vacuo. The residue was taken up in acetone (2 mL) and added in a dropwise manner to rapidly stirring ether (100 mL). The resulting white solid was collected by filtration, washed with ether, and dried under vacuum. Yield: 255 mg (86%); m.p., gradual decomposition after 186 °C. ^{1}H NMR (500

MHz, DMF-d_7) 3.54 (s, 3H), 5.22 (s, 3H), 5.34 (s, 3H), 7.40 (s, 2H), 7.93 (t, 1H, 7.1 Hz), 8.00 (m, 2H), 8.22 (t, 1H, 8.0 Hz), 8.42 (d, 1H, 8.0 Hz), 8.64 (s, 1H), 8.98 (d, 1H, 7.5 Hz), 9.03 (d, 1H, 7.5 Hz), 9.98 (d, 1H, 8.0 Hz), 10.38 (s, 1H) 11.92 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, DMF-d_7) 15.96, 66.34, 114.88, 123.70, 124.48, 126.77, 127.69, 129.63, 130.10, 130.20, 130.98, 131.60, 133.50, 135.59, 142.38, 143.48, 152.18, 156.47, 156.77; Anal. Calc. for $C_{21}H_{22}F_6N_8O_7PtS_2$: C 28.94, H 2.54, N 12.86. Found: C 29.23, H 2.73, N 13.28.

*cis-[Pt(NH$_3$)$_2$(pyridine)Cl]OTf (**7**).* Cisplatin (300 mg, 1.00 mmol) was dissolved in DMF (26 mL) and combined with a solution of silver triflate (257 mg, 1.0 mmol) in DMF (4 mL). The mixture was stirred in the dark at room temperature overnight and the resulting suspension was filtered through a plug of Celite. Pyridine (79 mg, 1.00 mmol) was added to the filtrate and the mixture was stirred overnight at room temperature in the dark. The mixture was stripped of solvent. The residue was taken up in acetone (4 mL) and filtered to remove any unreacted cisplatin. The filtrate was layered with ether (70 mL) and allowed to stand at room temperature for 4 days. The colorless crystals that formed were collected by filtration, washed with ether, and allowed to dry under vacuum. Yield: 320 mg (65%); m.p., gradual browning starting at 169 °C. ^1H NMR (500 MHz, $(CD_3)_2CO$) 4.18 (2, 3H), 4.60 (s, 3H), 7.58 (t, 2H, 7.1 Hz), 8.06 (t, 1H, 7.7 Hz), 8.84 (d, 2H, 5.1 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $(CD_3)_2CO$) 127.2, 140.1, 154.1; $^{195}Pt\{^1H\}$ NMR (108 MHz, $(CD_3)_2CO$) -2283; ESI-MS (+) mode *m/z* $[M]^+$ 344.0 (calc. 343.7), $[M–NH_3]^+$ 327.0 (calc. 327.0), $[M–NH_3–Cl–H]^+$ 290.0 (calc. 290.0); Anal. Calc. for $C_6H_{11}ClF_3N_3O_3PtS$: C 14.62, H 2.25, N 8.53. Found: C 14.90, H 2.18, N 8.43.

*cis-[Pt(NH$_3$)$_2$(pyridine)(9-methylguanine)]OTf$_2$ (**8**).* *cis*-[Pt(NH$_3$)$_2$(pyridine)Cl]OTf, **7**, (100 mg, 0.20 mmol) and silver triflate (52 mg, 0.20 mmol) were dissolved in DMF (3 mL) and the mixture was stirred in the dark at room temperature overnight. The resulting suspension was filtered through Celite and 9-methylguanine (33 mg, 0.20 mmol) was added to the filtrate. The reaction mixture was stirred at 50 °C overnight and then stripped of solvent in vacuo. The residue was taken up in methanol (2 mL), filtered through Celite, and layered with ether (80 mL). After standing at room temperature overnight, a white solid formed which was collected by filtration, washed with ether, and dried in vacuo. Yield: 102 mg (66%); m.p., 232–235 °C (dec). ^1H NMR (500 MHz, DMSO-d_6) 3.58 (s, 3H), 4.46 (s, 3H), 4.73 (s, 3H), 6.87 (s, 2H), 7.56 (t, 2H,

6.5 Hz), 8.02 (t, 1H, 8.0 Hz), 8.36 (s, 1H), 8.68 (d, 2H, 5.0 Hz), 11.26 (s, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) 30.42, 113.24, 126.58, 139.79, 141.11, 150.68, 152.64, 154.50, 155.09; $^{195}Pt\{^{1}H\}$ NMR (108 MHz, DMSO-d_6) -2448; ESI-MS (+) mode *m/z* $[M–NH_3]^{2+}$ 227.9 (calc. 228.1), $[M–NH_4–NH_3–C_6H_7N_5O]^+$ 272.9 (calc. 273.0), $[M–NH_4–C_6H_7N_5O]^+$ 306.0 (calc. 306.1), $[M–NH_4–C_6H_5N]^+$ 376.0 (calc. 376.1), $[M–NH_4–NH_3]^+$ 438.0 (calc. 438.1), $[M–NH_4]^+$ 455.0 (calc. 455.1), $[M–H]^+$ 472.1 (calc. 472.0), $[M–NH_3+SO_3CF_3]^+$ 605.0 (calc. 605.1), $[M+SO_3CF_3]^+$ 623.0 (calc. 623.0); Anal. Calc. for $C_{13}H_{18}F_6N_8O_7PtS_2·0.5(C_3H_7NO)$: C 21.55, H 2.68, N 14.73. Found: C 21.16, H 2.56, N 14.42.

X-ray Crystallography. Crystals of **1**, **7**, and **8** were grown at room temperature by vapor diffusion of diethyl ether into DMF solutions of the compounds. Crystals of **5** were grown by slow evaporation of an acetone solution of the compound at –40 °C. Samples suitable for X-ray diffraction were selected under crossed-polarizers, mounted on a nylon cryoloop in Paratone oil, and cooled to 100 K under a stream of nitrogen. A Bruker APEX CCD X-ray diffractometer controlled by the *APEX2* software was used to record the diffraction of graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).[3] The data were integrated with *SAINT*[4] and absorption, Lorentz, and polarization corrections were calculated by *SADABS*.[5] Space group determination was carried out by analyzing the Laue symmetry and the systematically absent reflections with *XPREP*.[6] Structure solution via direct methods and refinement were performed with the *SHELX-97* program suite.[7] Refinement was carried out against F^2 using standard procedures.[8] Non-hydrogen atoms were located in difference Fourier maps during refinement and refined anisotropically. Hydrogen atoms were placed at calculated positions and refined using a riding model. For coordinated NH_3 and terminal CH_3 groups, hydrogen atom isotropic displacement parameters (U_{iso}) were set equal to 1.5 times the U_{iso} of the atom to which they were attached. For other hydrogen atoms, U_{iso} = 1.2 U_{iso} of the attached atom. All structures were checked for missed higher symmetry and twinning with *PLATON*[9] and were further validated using *CheckCIF*.

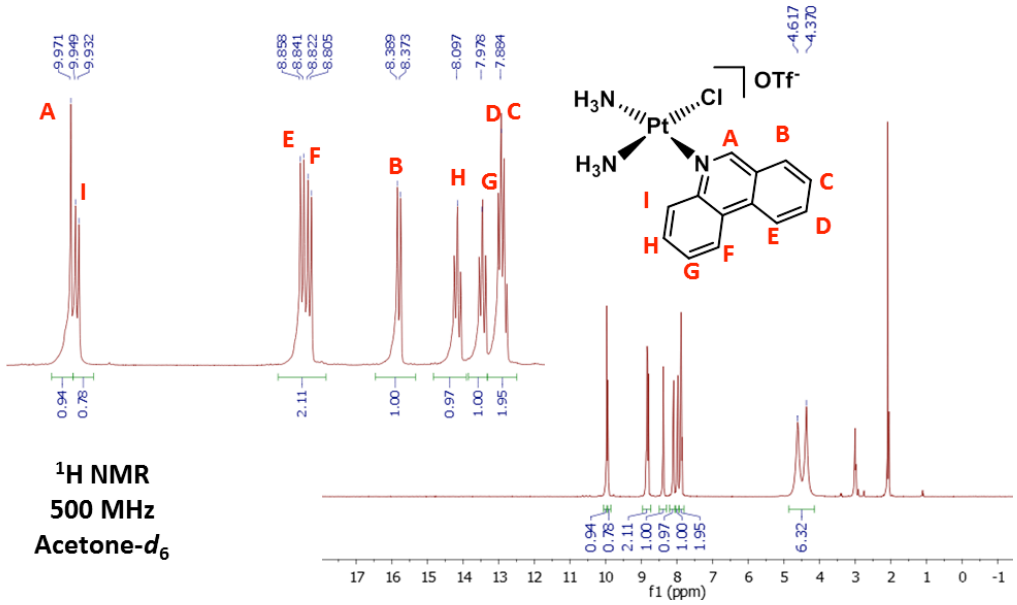

Figure S1. ^{1}H NMR spectrum of **1** (assignments made in accordance with Fig. S4)

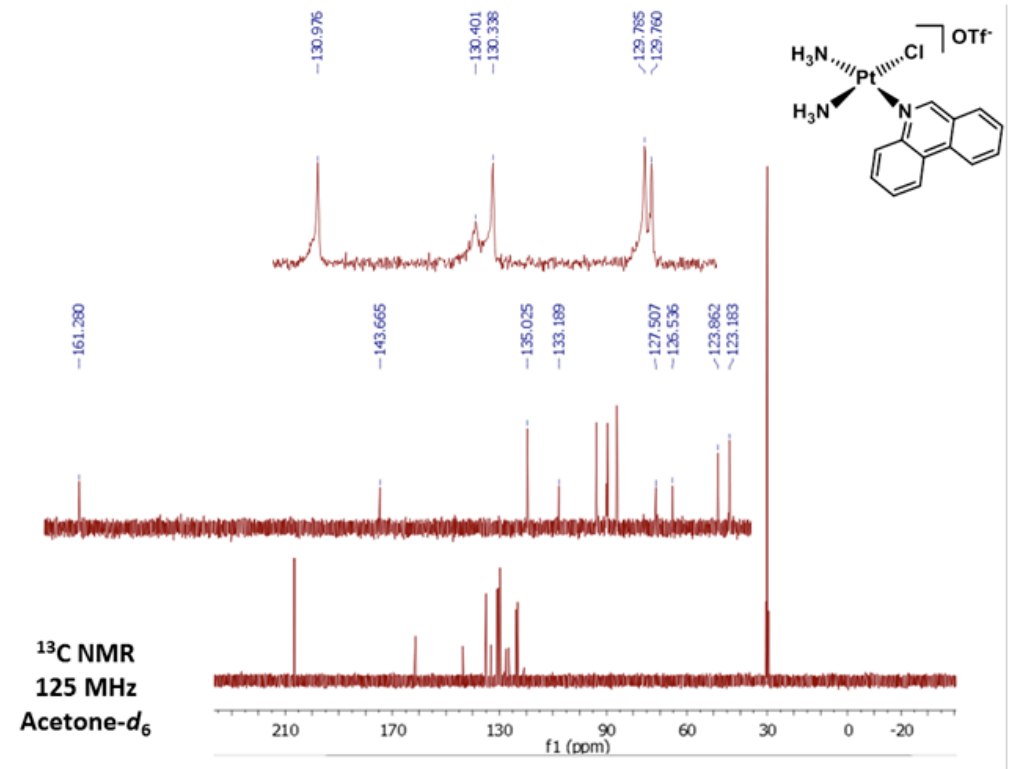

Figure S2. ^{13}C NMR spectrum of **1**

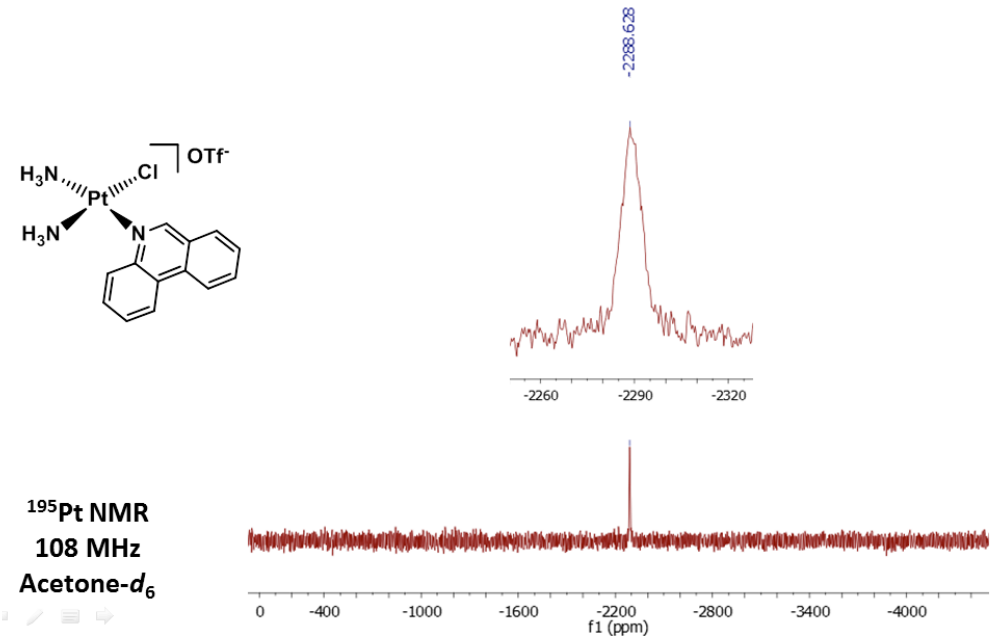

Figure S3. ^{195}Pt NMR spectrum of **1**

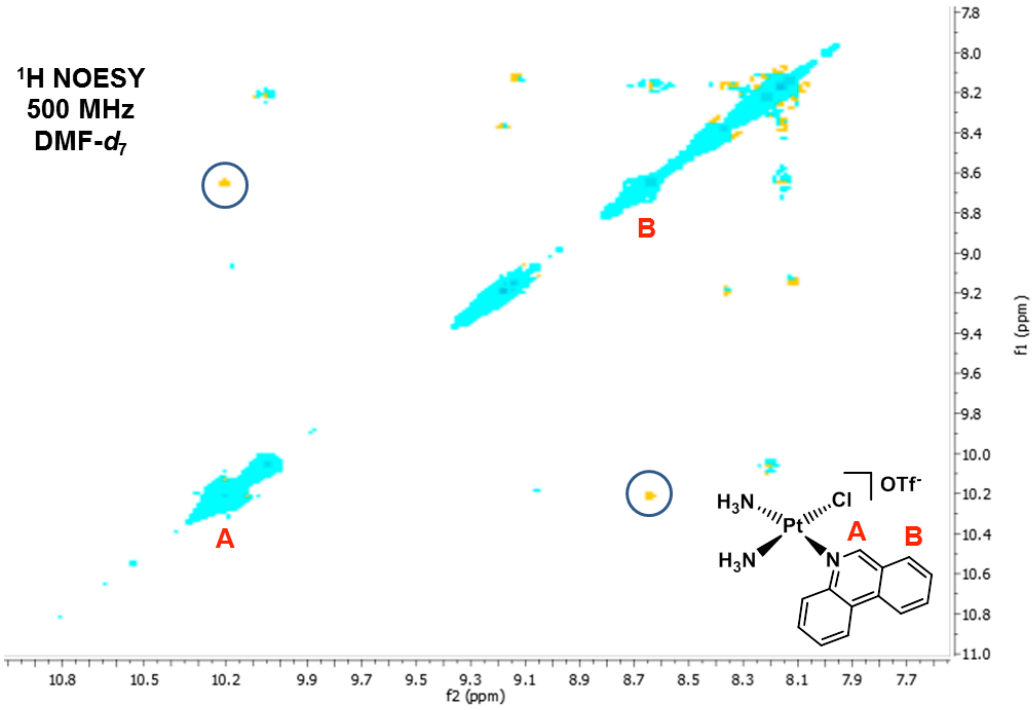

Figure S4a. ^{1}H NOESY spectrum of **1**

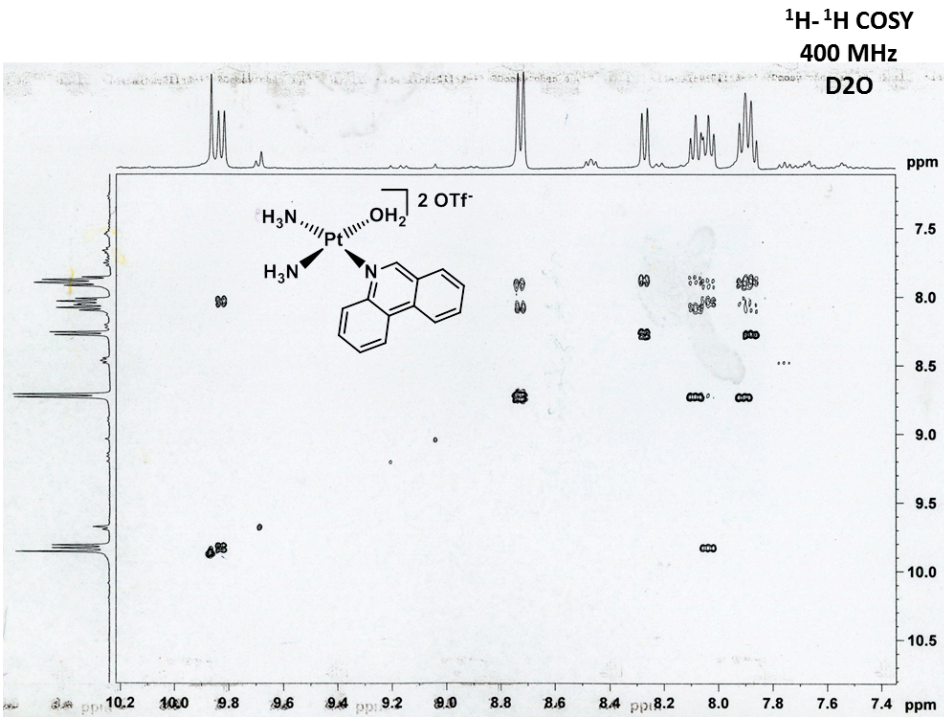

Figure S4b. ^{1}H COSY spectrum of **1**

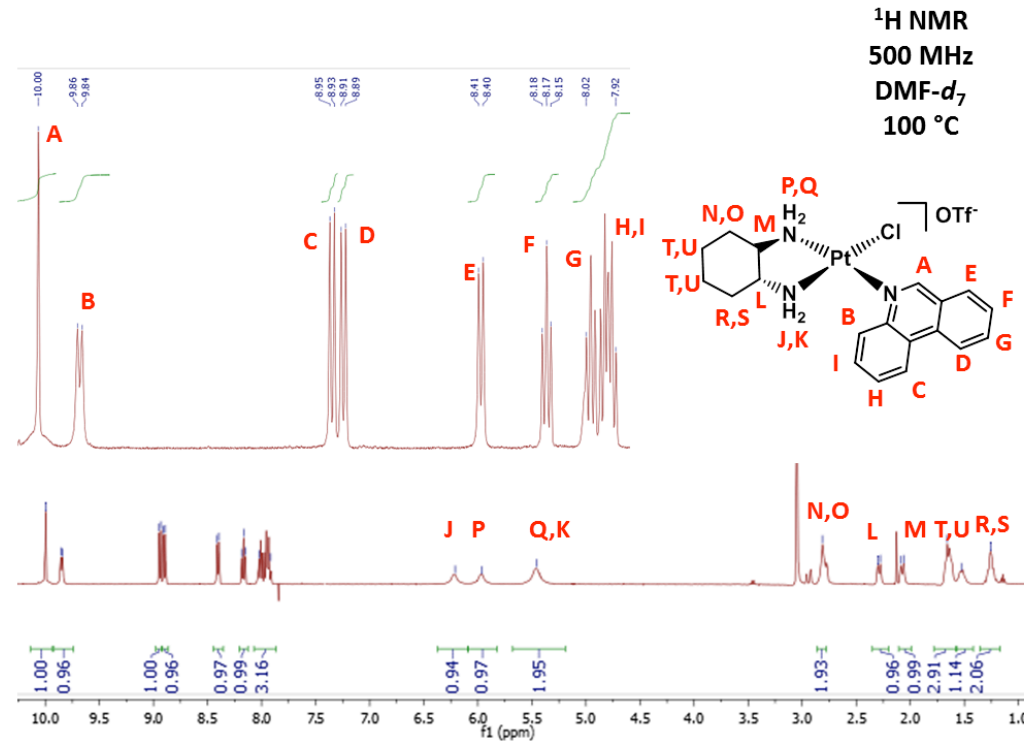

Figure S5. ^{1}H NMR spectrum of **2**

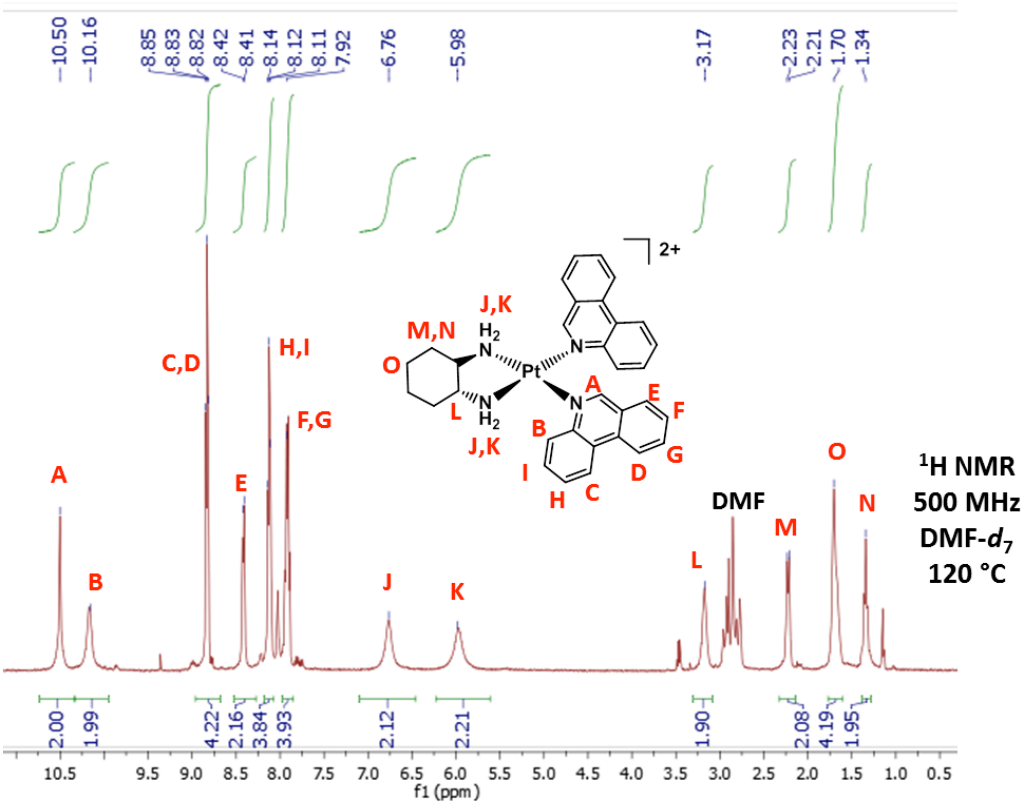

Figure S6. ^{1}H NMR spectrum of **3**

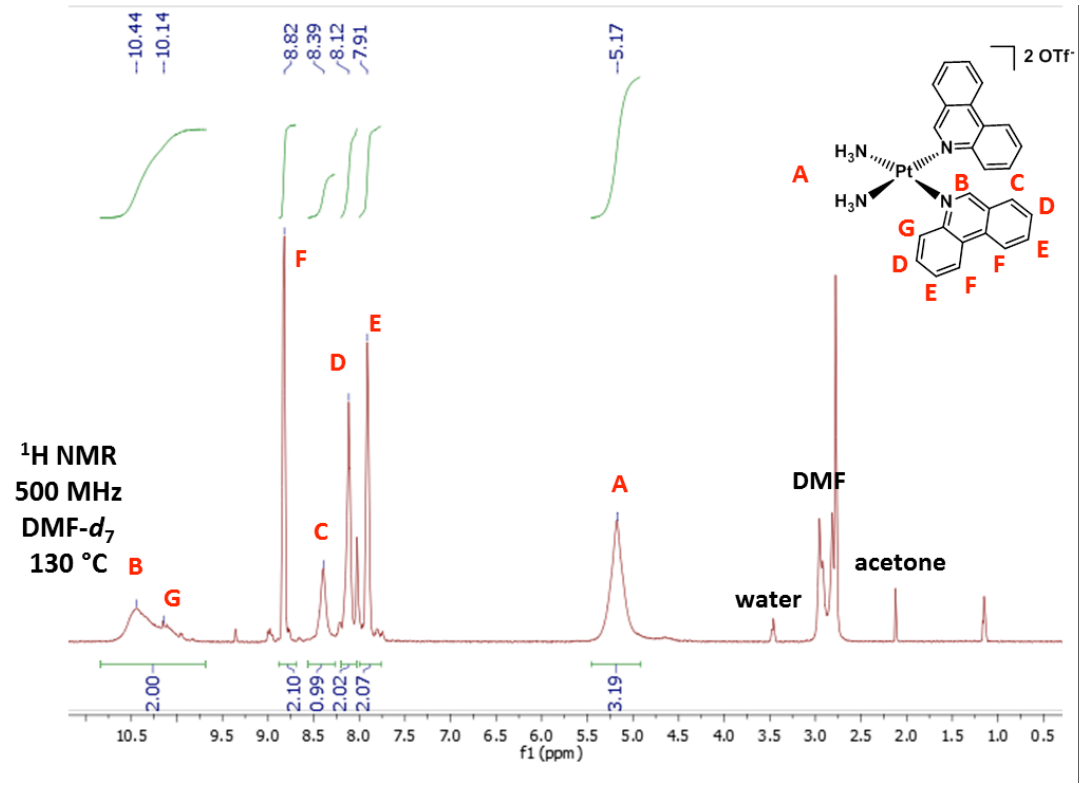

Figure S7. ^{1}H NMR spectrum of **4**

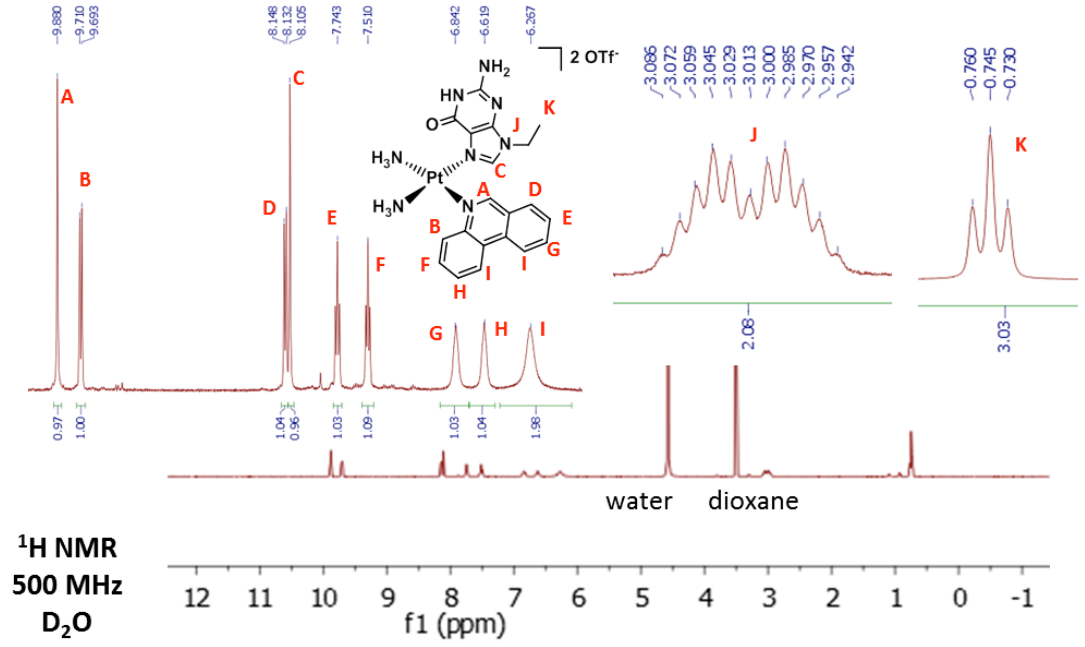

Figure S8. ^{1}H NMR spectrum of **5**

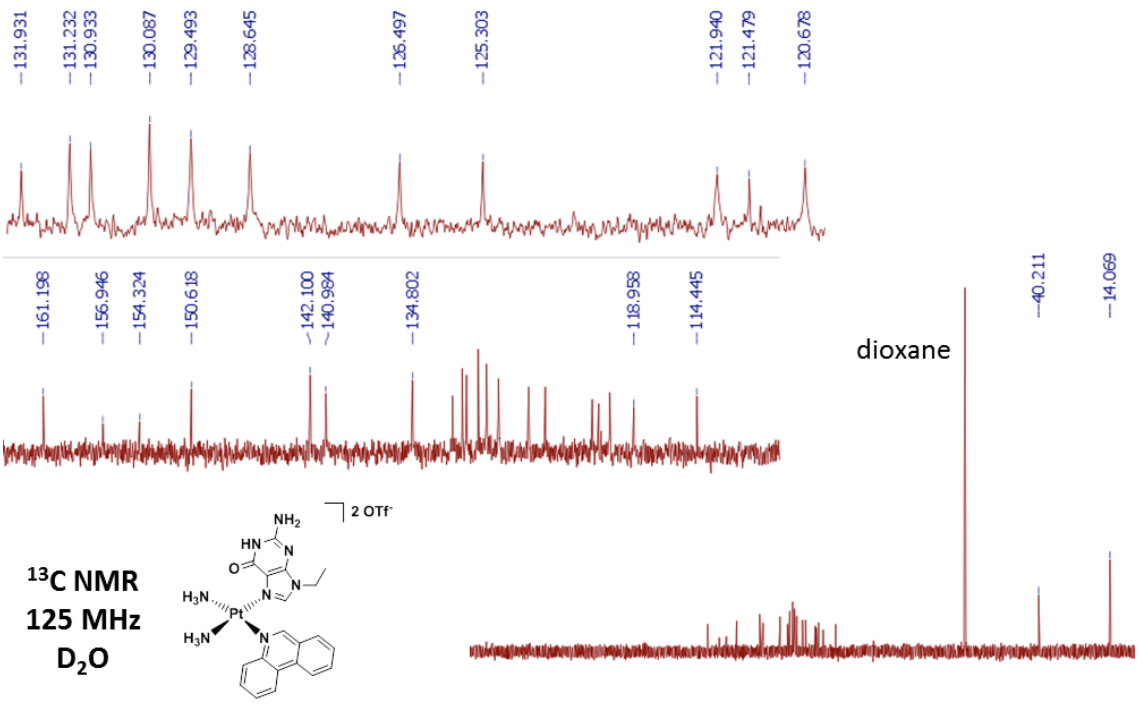

Figure S9. ^{13}C NMR spectrum of **5**

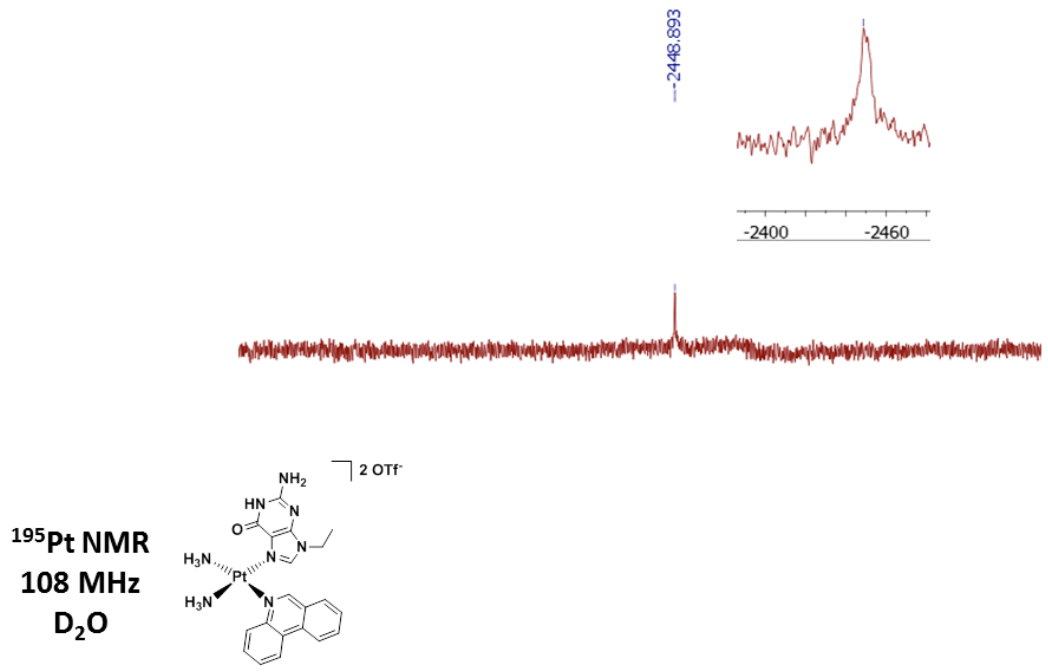

Figure S10. ^{195}Pt NMR spectrum of **5**

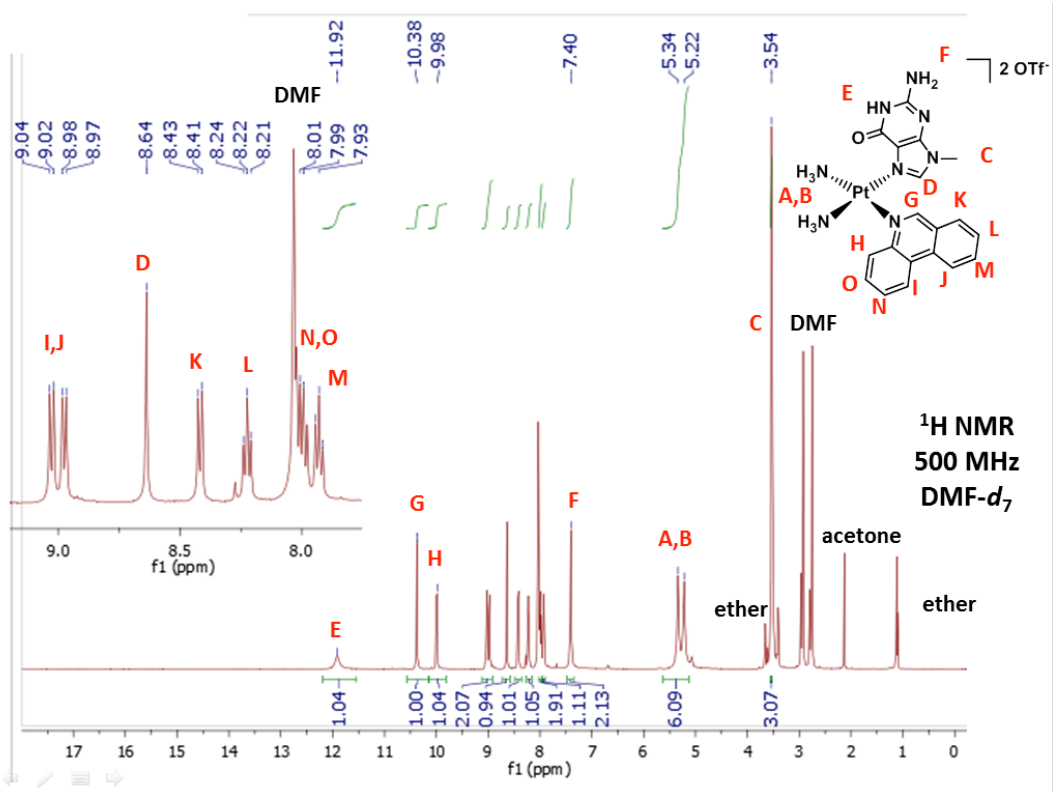

Figure S11. ^{1}H NMR spectrum of **6**

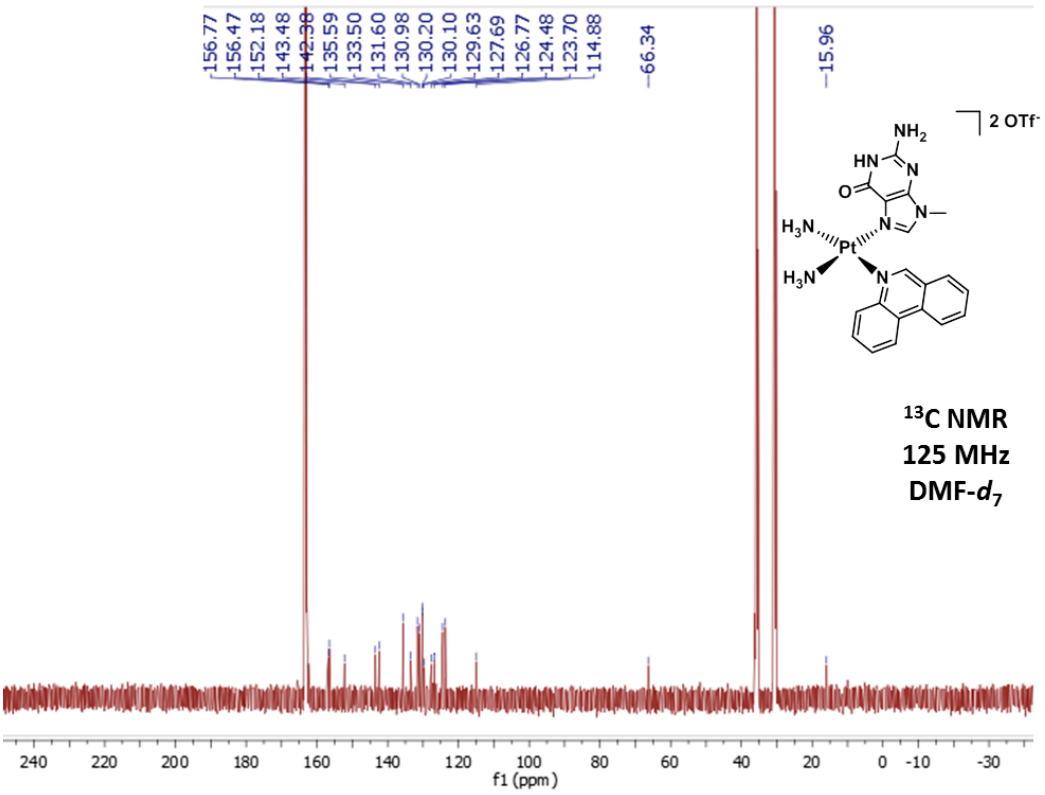

Figure S12. ^{13}C NMR spectrum of **6**

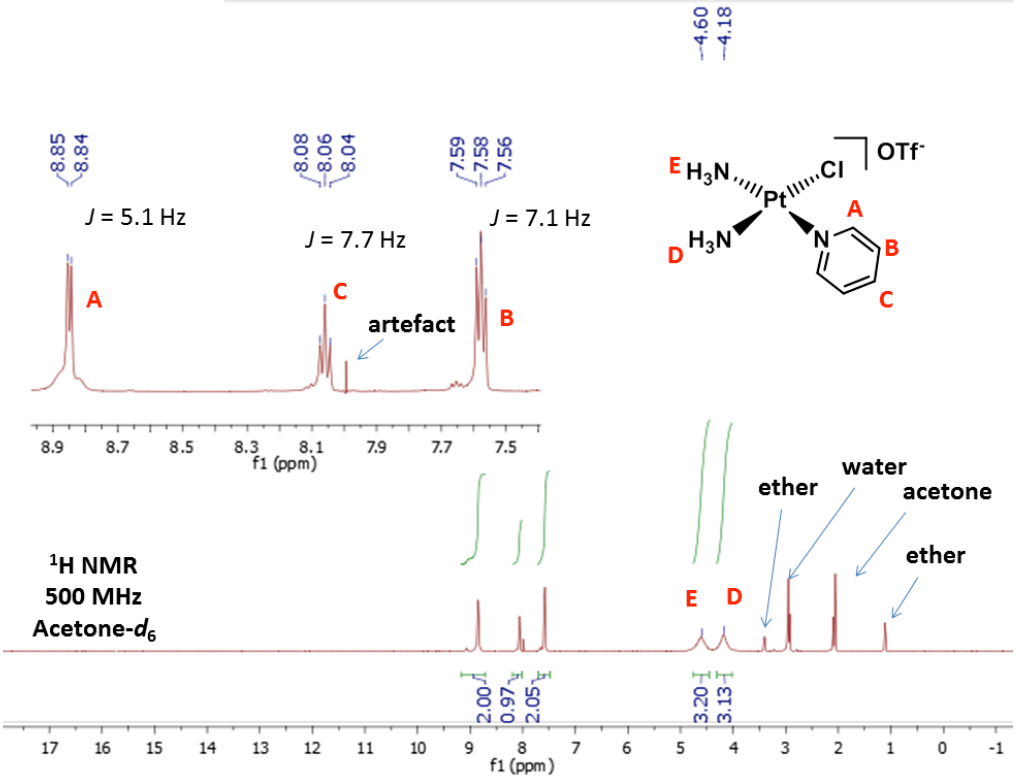

Figure S13. ^{1}H NMR spectrum of **7**

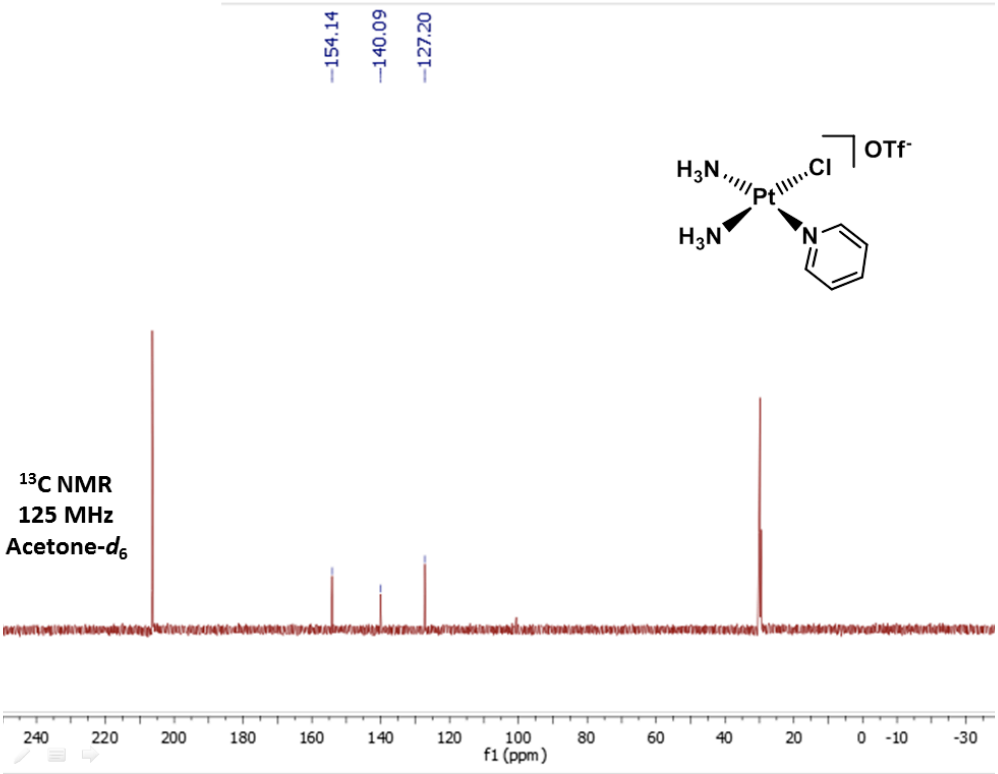

Figure S14. ^{13}C NMR spectrum of **7**

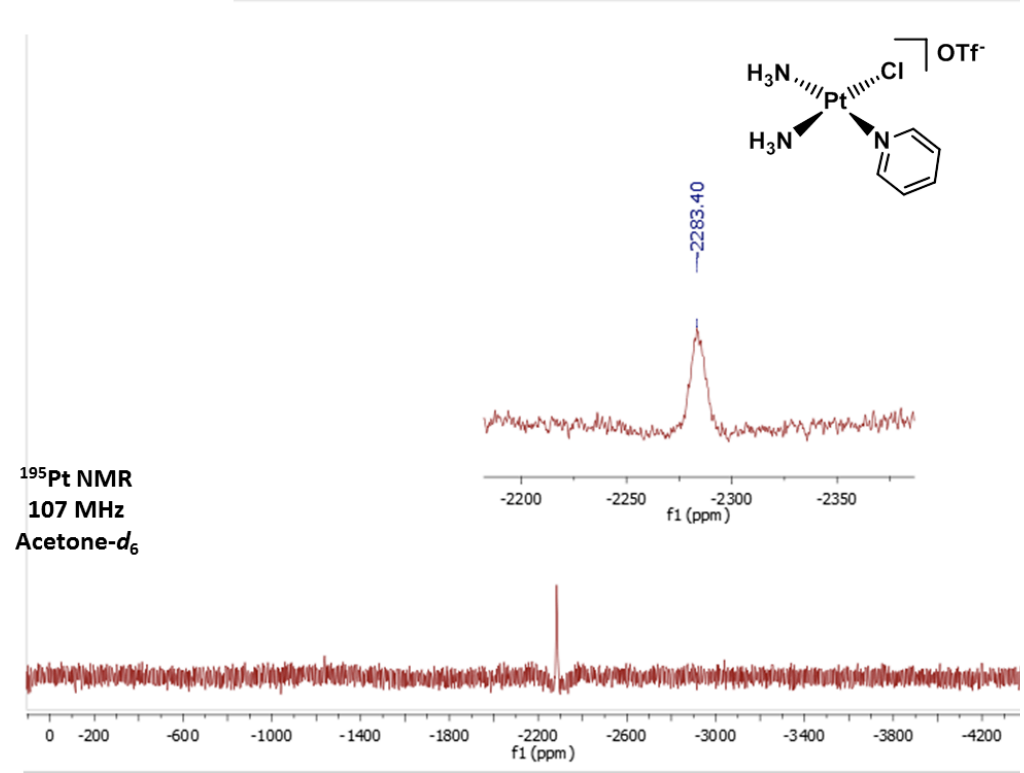

Figure S15. ^{195}Pt NMR spectrum of **7**

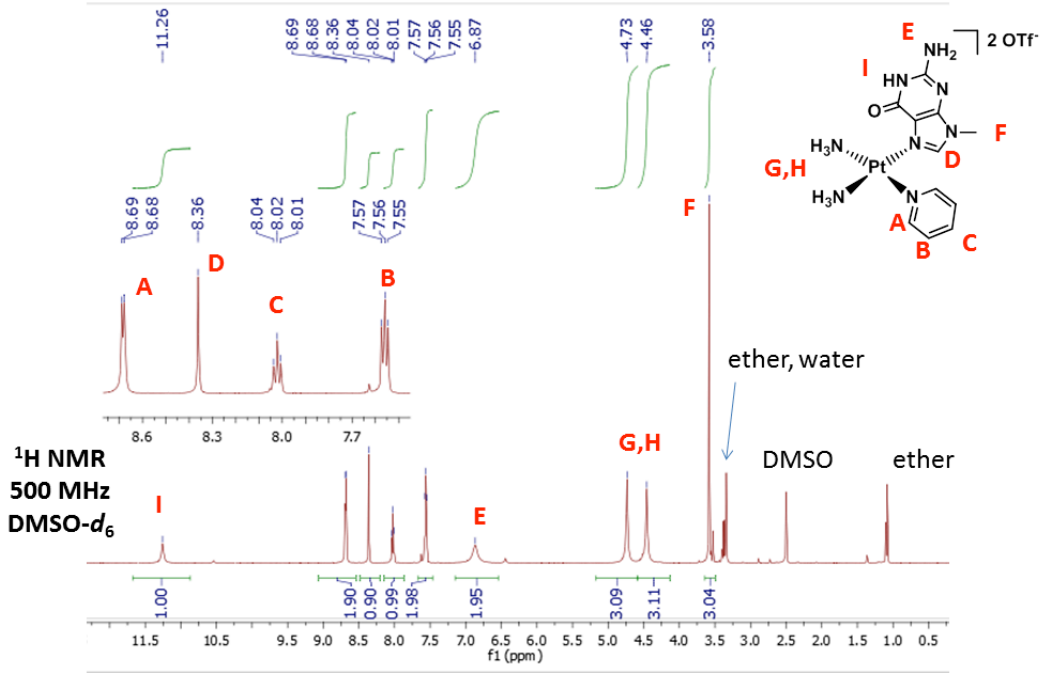

Figure S16. [1]H NMR spectrum of **8**

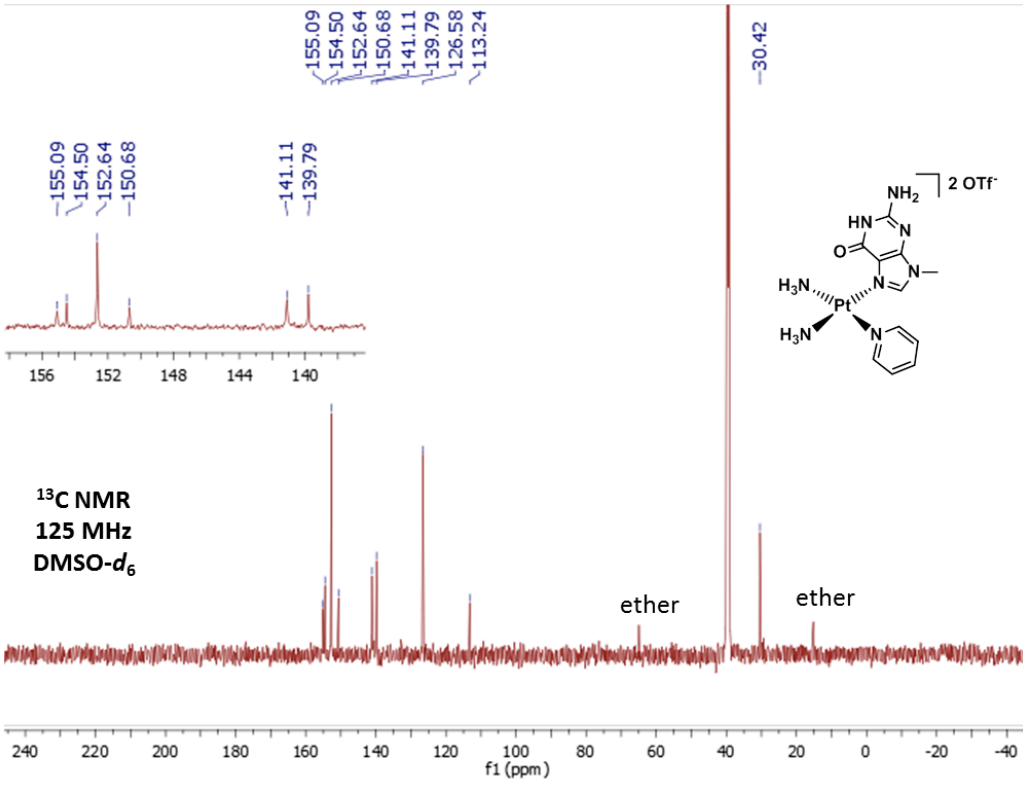

Figure S17. [13]C NMR spectrum of **8**

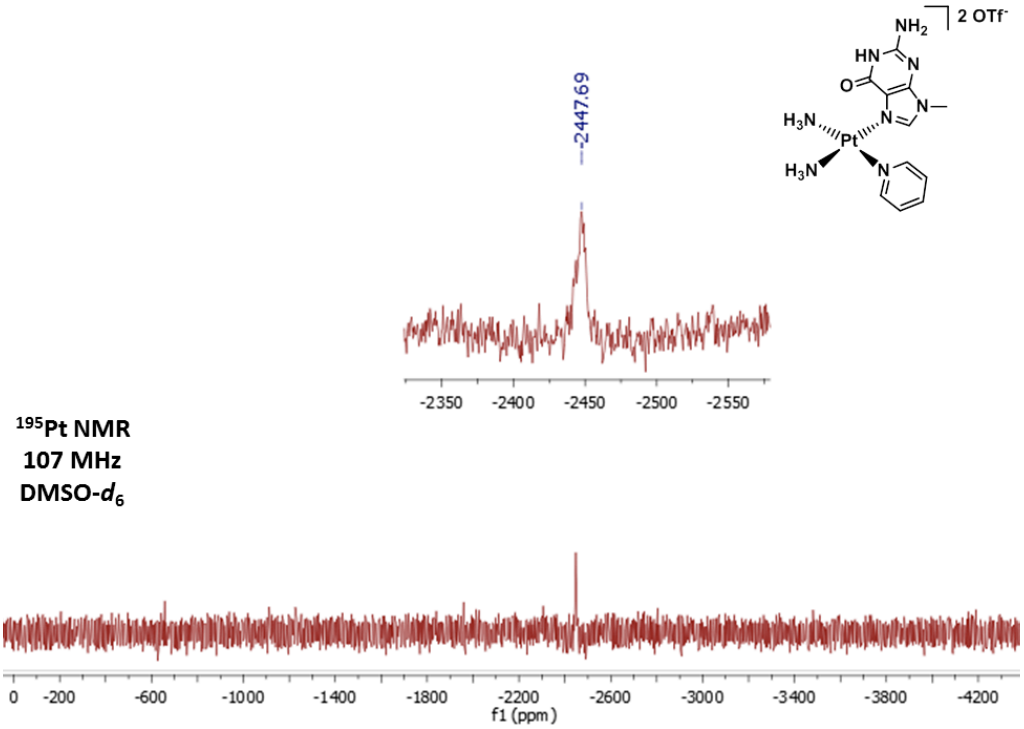

Figure S18. ^{195}Pt NMR spectrum of **8**

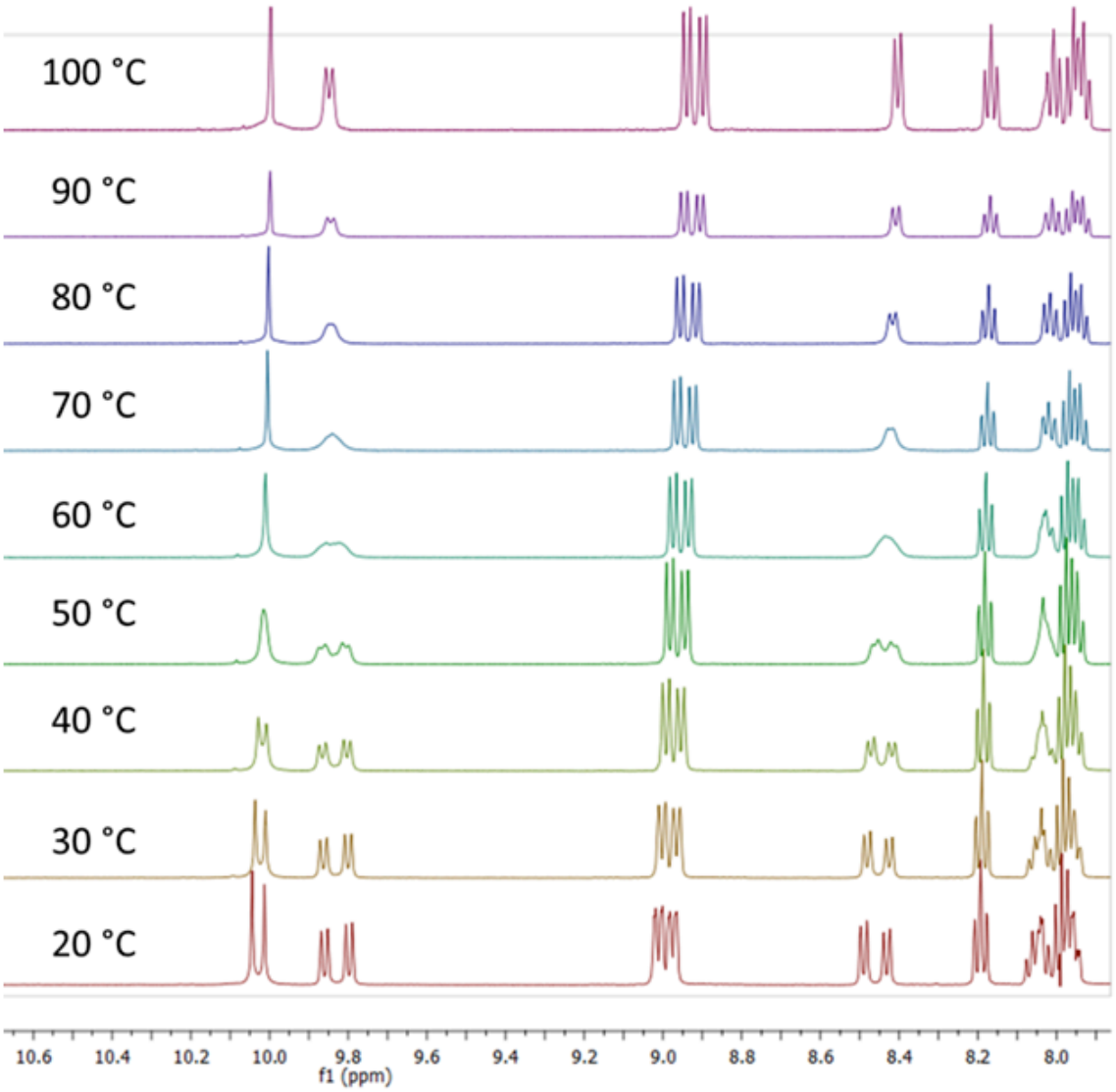

Figure S19. VT ^{1}H NMR spectra of **2** in DMF-d_7 (500 MHz)

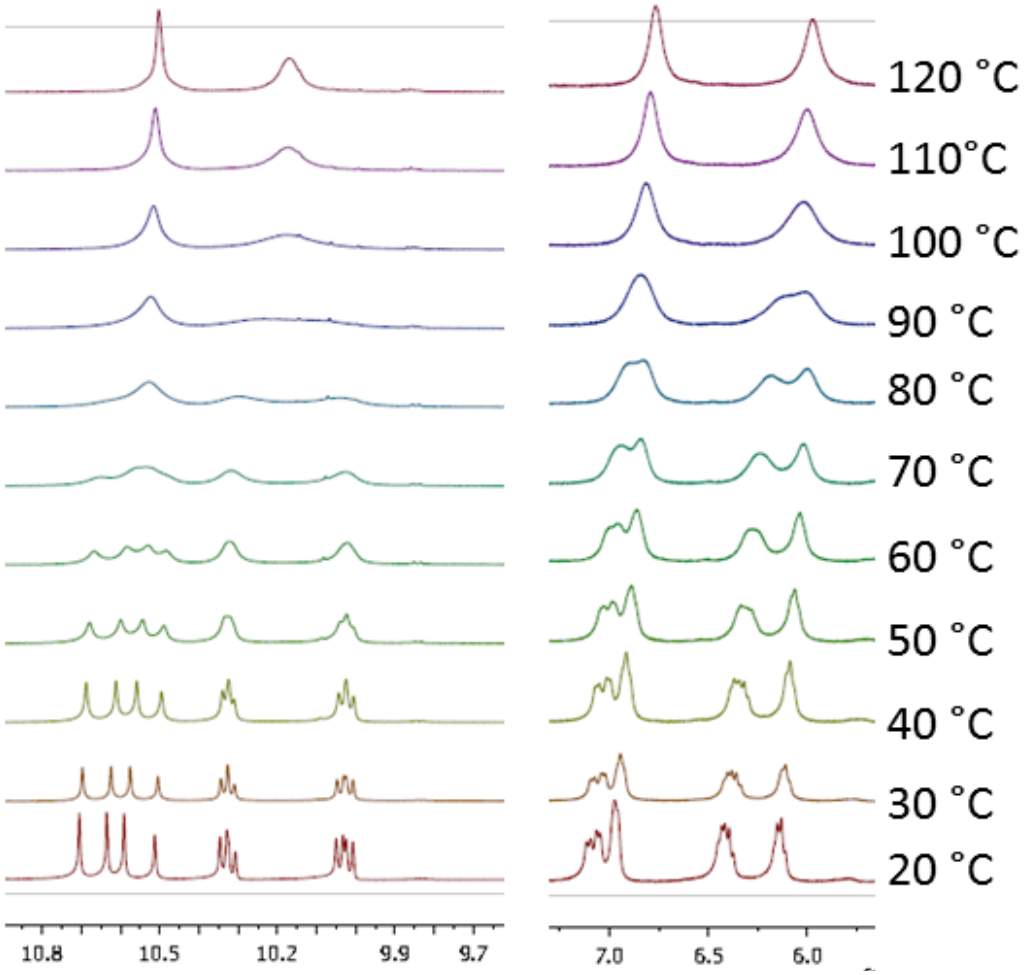

Figure S20. VT ^{1}H NMR spectra of **3** in DMF-d_7 (500 MHz)

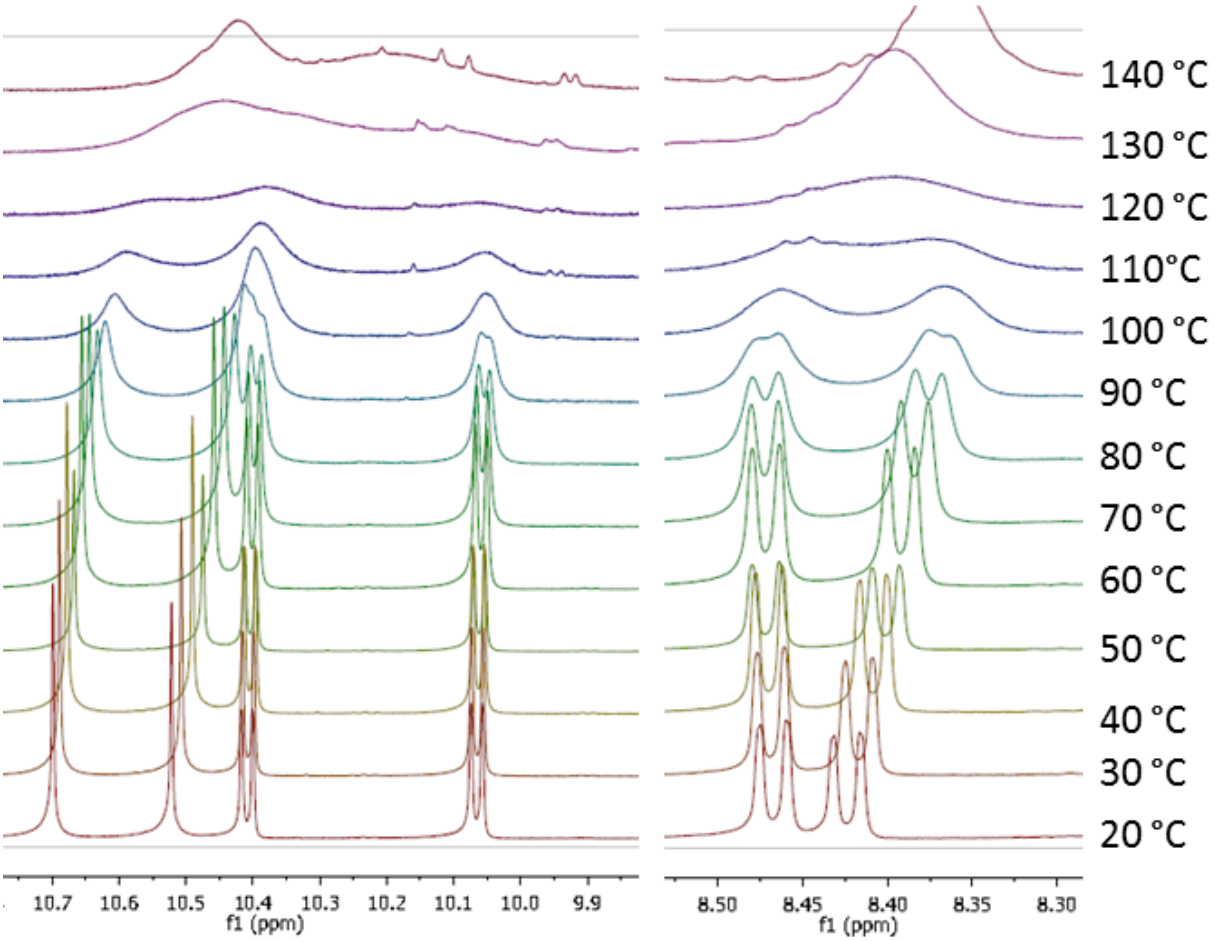

Figure S21. VT ^{1}H NMR spectra of **4** in DMF-d_7 (500 MHz)

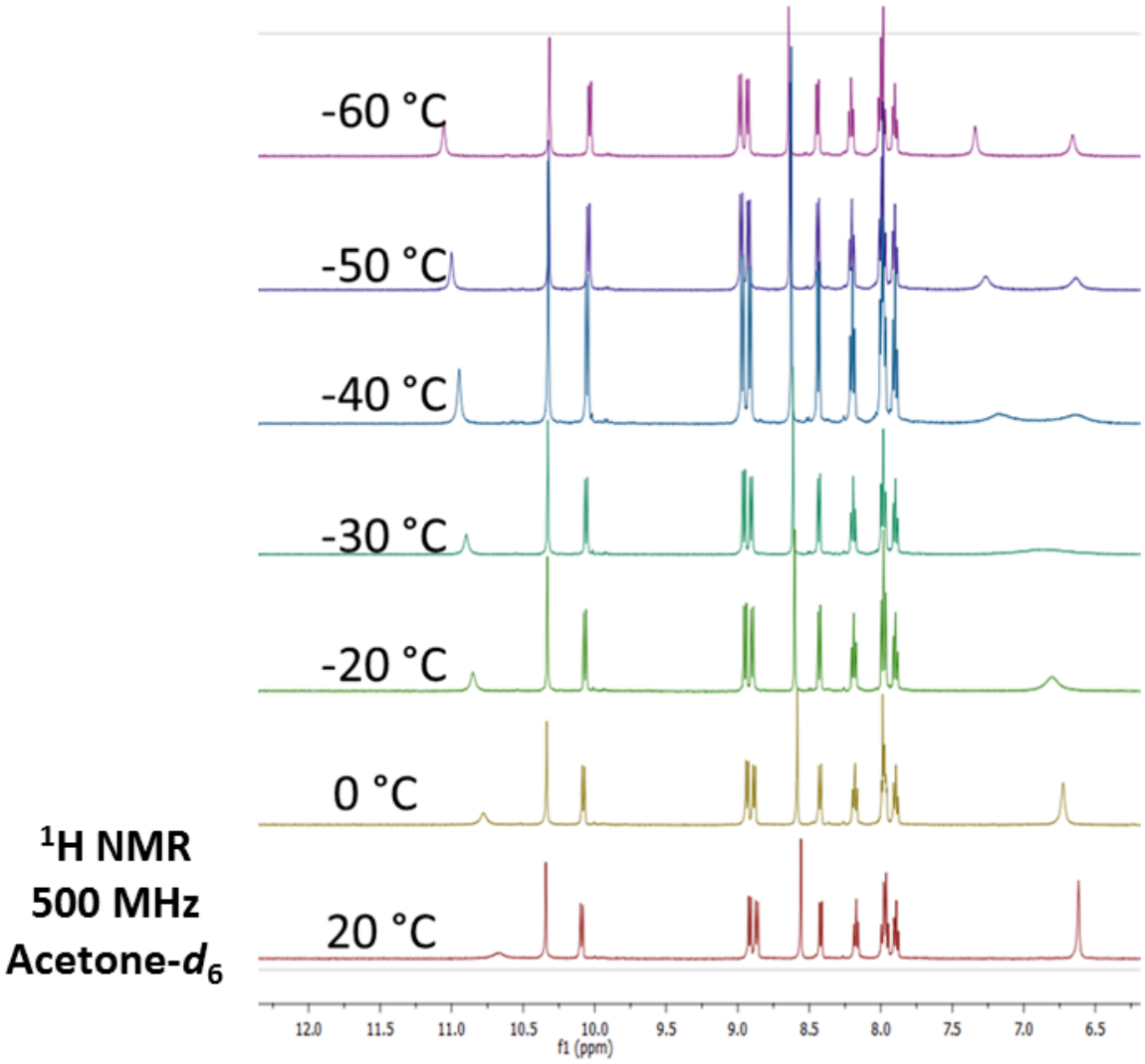

Figure S22. VT ^{1}H NMR spectra of **5** in acetone-d_6 (500 MHz). The signal that decoalesces at approximately 6.6 ppm is from the NH_2 protons of the guanine.

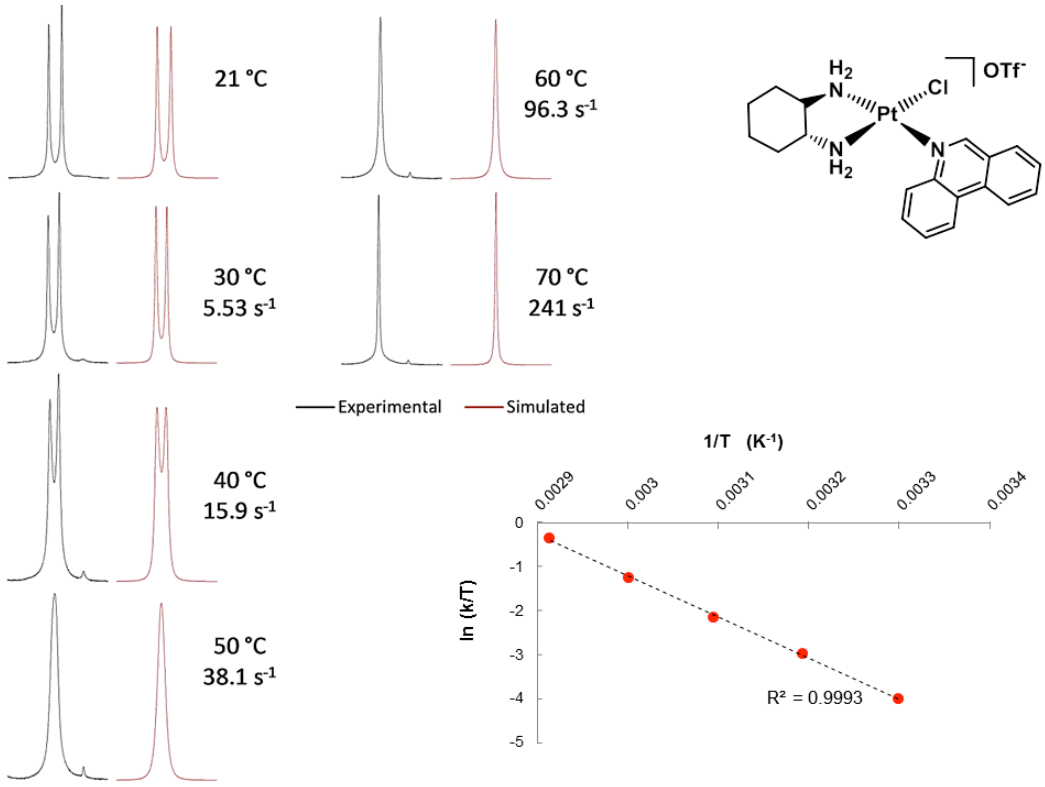

Figure S23. Lineshape analysis of ^{1}H VT NMR spectra of **2** in DMF-d_7 (500 MHz)

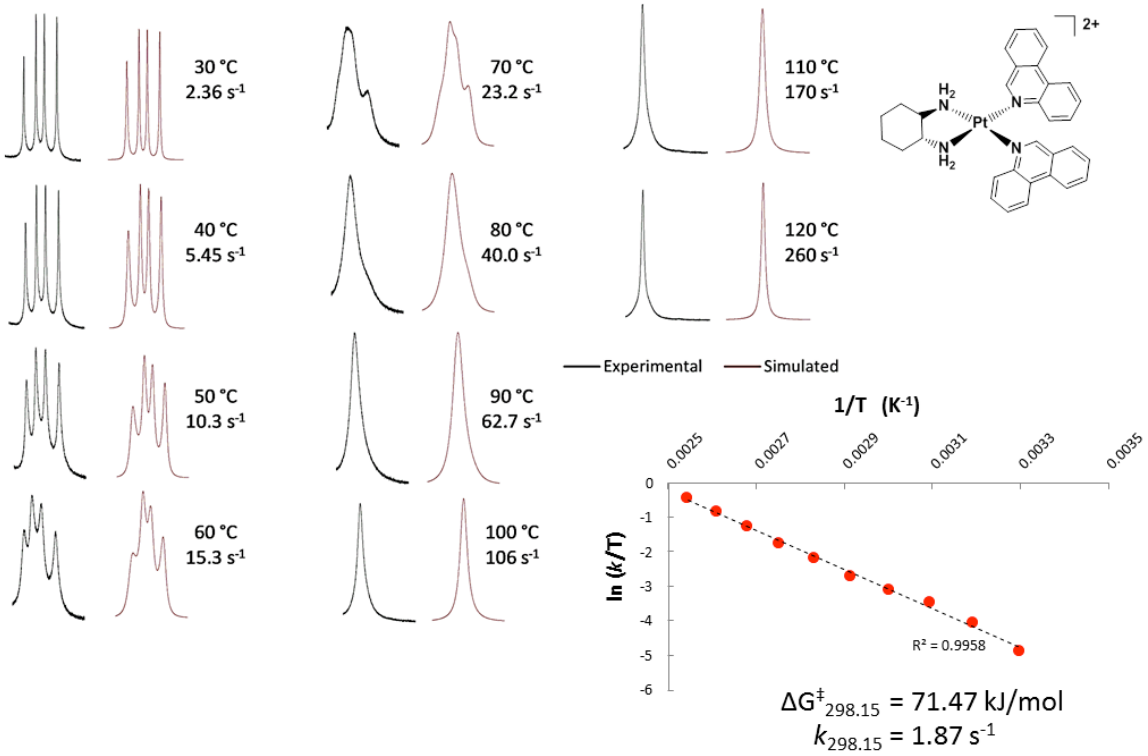

Figure S24. Lineshape analysis of ^{1}H VT NMR spectra of **3** in DMF-d_7 (500 MHz)

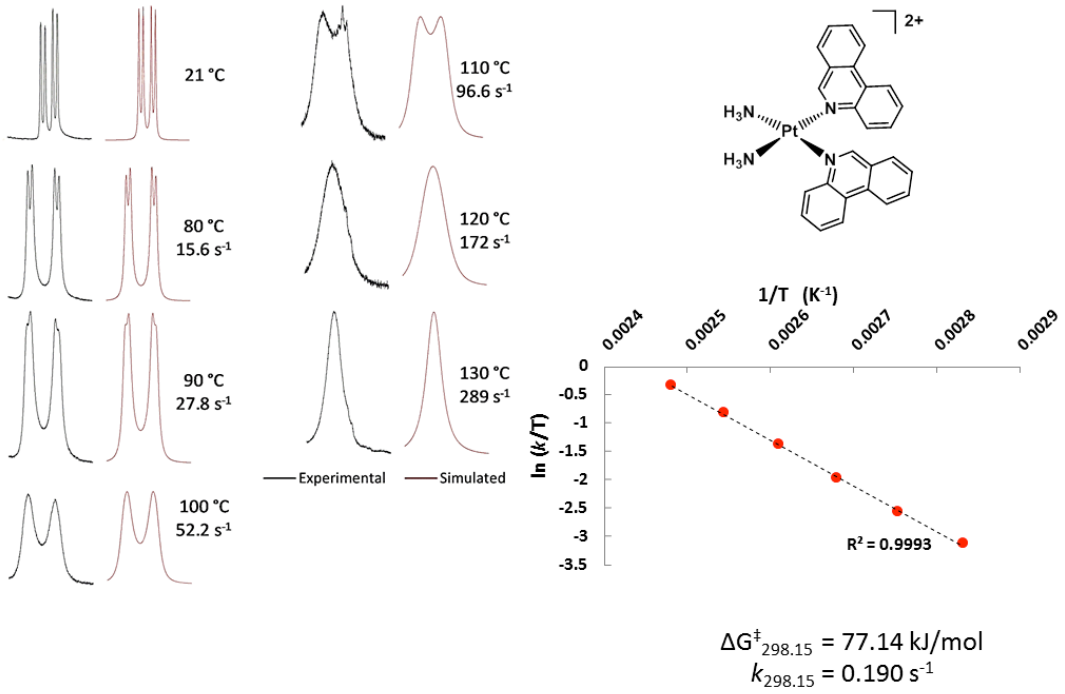

Figure S25. Lineshape analysis of ^{1}H VT NMR spectra of **4** in DMF-d_7 (500 MHz)

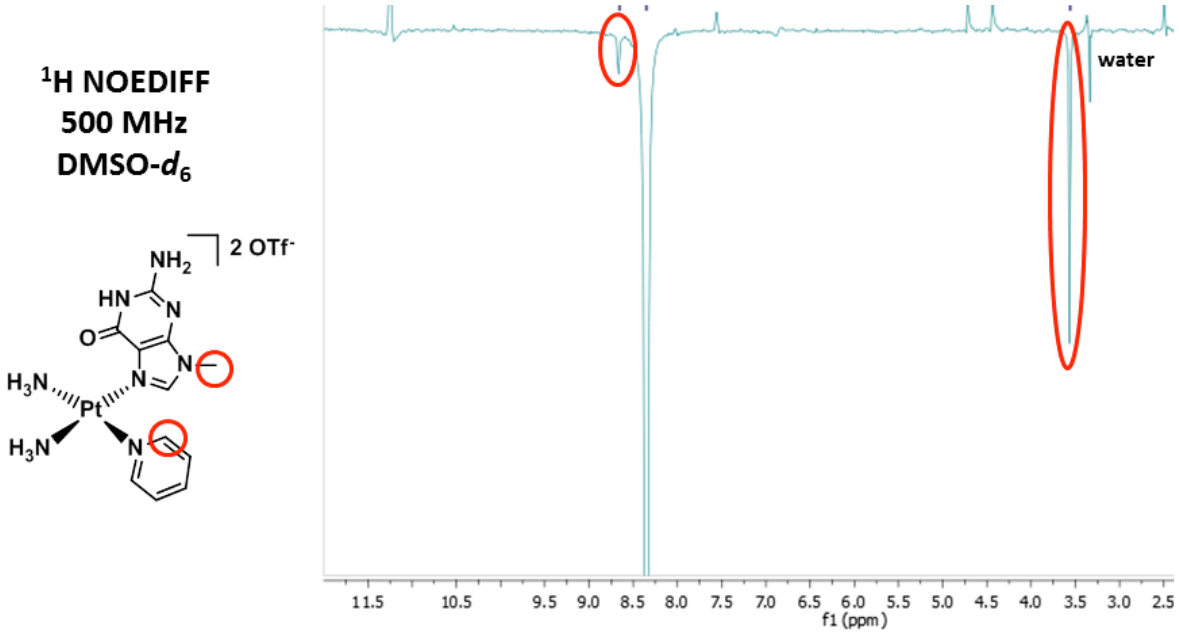

Figure S26. Difference spectrum of a ^{1}H NMR saturation transfer experiment using **8** in DMSO-d_6 (500 MHz)

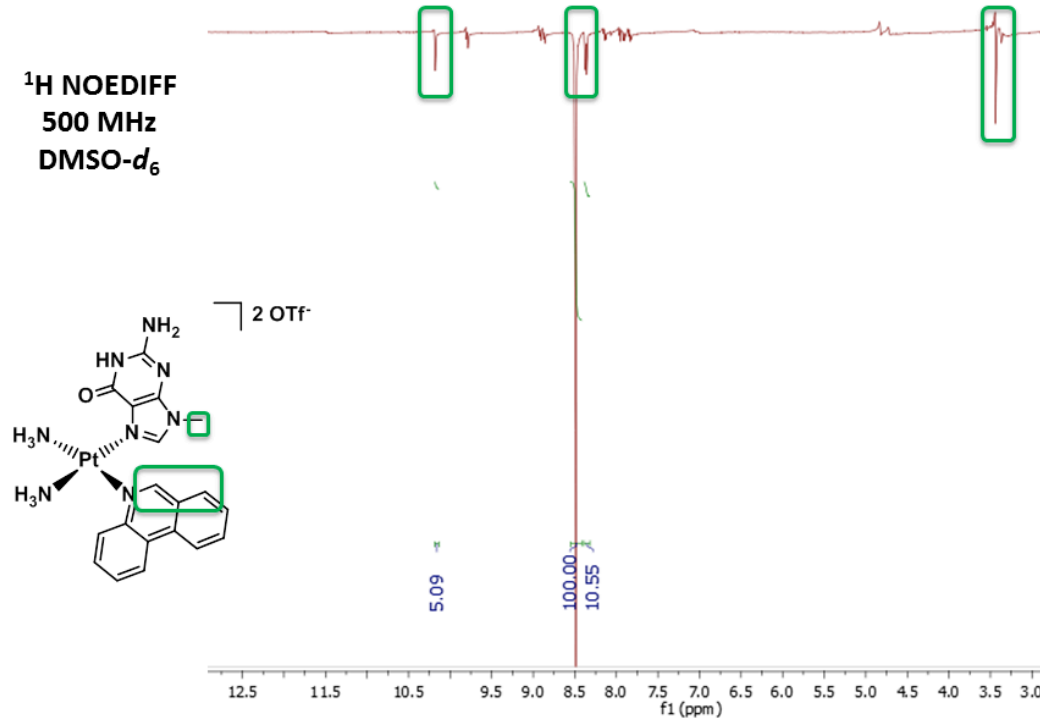

Figure S27. Difference spectrum of a ^{1}H NMR saturation transfer experiment using **6** in DMSO-d_6 (500 MHz)

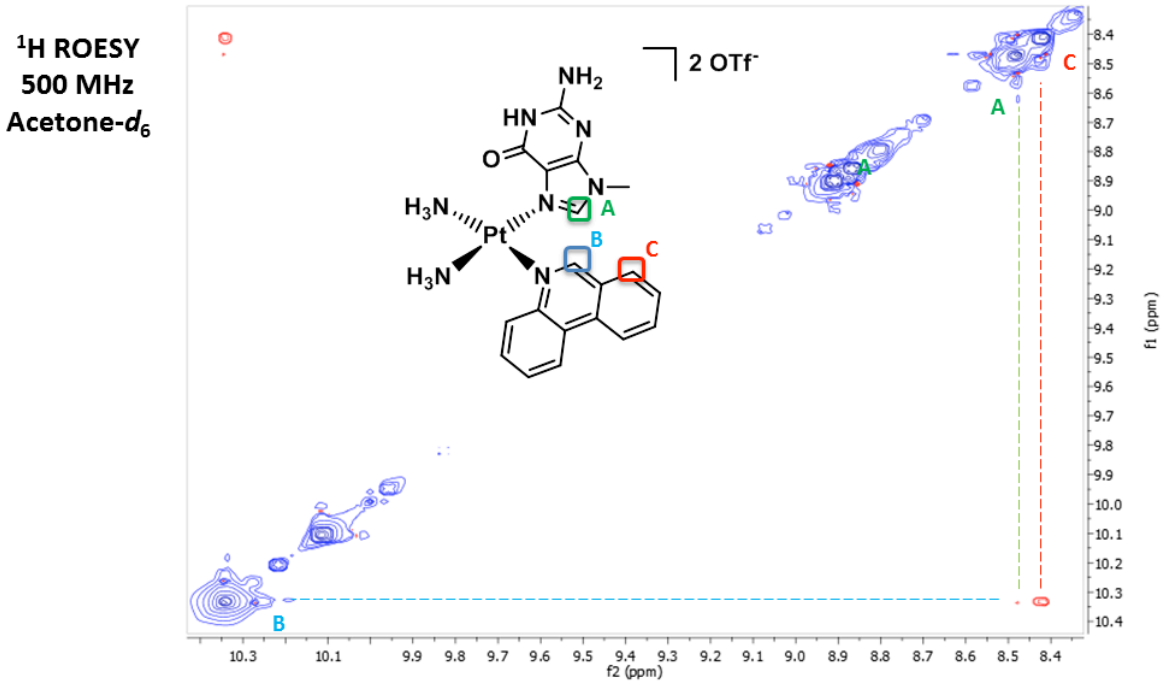

Figure S28. ^{1}H ROESY NMR spectrum of **6** in acetone-d_6 (500 MHz)

Table S1. Crystallographic parameters for 1, 5, 7, and 8

	1	5	7	8
Formula	$C_{14}H_{15}ClF_3N_3O_3PtS$	$C_{23.5}H_{28}F_6N_8O_8PtS_2$	$C_6H_{11}ClF_3N_3O_3PtS$	$C_{13}H_{18}F_6N_8O_7PtS_2$
Formula weight	592.89	923.75	492.78	771.56
Space group	*Pbca*	*C*2/*c*	$P2_1/c$	*C*2/*c*
a, Å	12.8700(12)	22.1704(19)	11.8226(7)	24.6325(9)
b, Å	9.8433(9)	12.2581(10)	4.9998(3)	11.4033(4)
c, Å	28.980(3)	27.389(3)	23.0652(13)	19.3606(7)
β, °		110.7160(10)	101.8880(10)	92.3990(10)
V, Å^3	3671.3(6)	6962.2(11)	1334.16(14)	5433.5(3)
Z	8	8	4	8
T, K	100(2)	100(2)	100(2)	100(2)
μ(Mo Kα), mm^{-1}	7.952	4.237	10.912	5.406
θ range, °	1.41 to 28.74	1.93 to 28.27	1.76 to 28.61	1.65 to 28.67
total no. of data	55588	63291	50604	53900
no. of unique data	4763	8601	3420	6996
no. of parameters	237	574	165	337
completeness (%)	99.9	99.8	99.9	99.9
R_1[a] (%)	2.02	6.19	1.43	2.16
wR_2[b] (%)	3.98	13.95	3.65	4.56
GOF[c]	1.116	1.265	1.158	1.042

[a]$R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[c]$GOF=\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

X-ray Crystal Structure of *trans*-[Pt(pyridine)$_2$Cl$_2$]

The data were collected and processed as described above with the exception that the unit cell was indexed using *CELLNOW*. Three distinct crystalline domains were identified and integration of the detwinned data permitted solution of the structure using the heavy atom method. Prior to detwinning, no reasonable solution could be obtained. The final structure was refined using only data from the major domain. Inclusion of the other two domains resulted in no improvement of the model. The present data set provides a higher resolution structure than that which was previously reported.[10]

Table S2. Crystallographic parameters for *trans*-[Pt(pyridine)$_2$Cl$_2$]

Formula	$C_{10}H_{10}Cl_2N_2Pt$
Formula weight	424.19
Space group	$P\bar{1}$
a, Å	5.4655(3)
b, Å	6.9612(4)
c, Å	7.6303(5)
α, °	79.8420(9)
β, °	84.5790(10)
Y, °	89.1230(9)
V, Å^3	284.48(3)
Z	1
T, K	100(2)
μ(Mo Kα), mm^{-1}	12.766
θ range, °	2.72 to 28.75
total no. of data	1478
no. of unique data	1478
no. of parameters	70
completeness (%)	99.9
R_1[a] (%)	1.28
wR_2[b] (%)	3.01
GOF[c]	1.047

[a]$R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[c]$GOF=\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

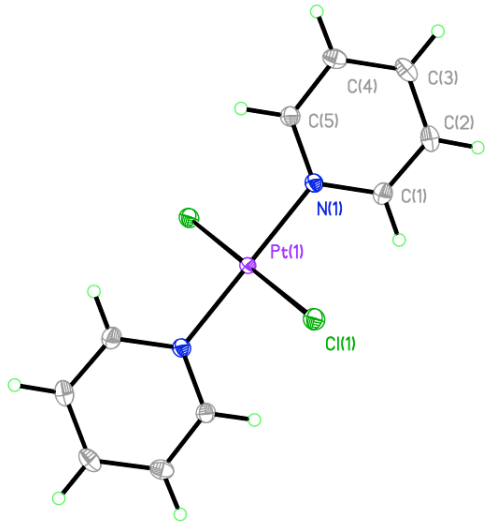

Figure S29. Molecular diagrams of the platinum complexes from the crystal structures of *trans*-[Pt(pyridine)$_2$Cl$_2$] with thermal ellipsoids drawn at the 50% probability level.

Table S3. Select bond lengths and angles for *trans*-[Pt(pyridine)$_2$Cl$_2$]

Pt(1)-N(1)	2.021(2)
Pt(1)-Cl(1)	2.3050(6)
N(1)-C(5)	1.345(3)
N(1)-C(1)	1.349(3)
C(5)-C(4)	1.382(3)
C(1)-C(2)	1.389(4)
C(4)-C(3)	1.393(4)
C(3)-C(2)	1.386(4)
N(1)-Pt(1)-Cl(1)	89.93(6)
C(5)-N(1)-C(1)	118.9(2)
C(5)-N(1)-Pt(1)	120.87(16)
C(1)-N(1)-Pt(1)	120.18(16)
N(1)-C(5)-C(4)	121.9(2)

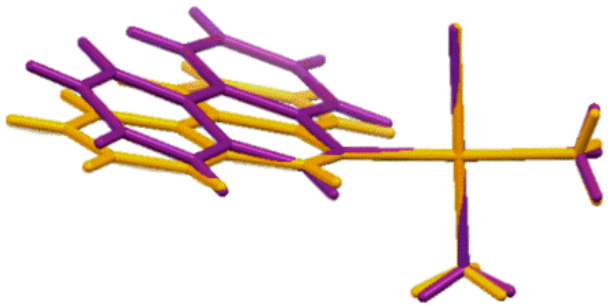

Figure S30. Overlay of the complex cations present in the crystal structures of *cis*-$[Pt(NH_3)_2(phenanthridine)Cl]X$, X = nitrate (purple) or triflate (yellow)

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