SUPPLEMENTARY DATA

COUPLING APPROCHES FOR [Pt(1,10-PHENANTHROLINE)(1*S*,2*S*-DIAMMINOCYCLOHEXANE)DIHYDROXIDE]$^{2+}$ USING HYDRAZONE AND OXIME LIGATION

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A. Experimental details

Synthesis of tosylhydrazine

Tosylhydrazine was synthesised based on a modified literature method.[1] *p*-Toluenesulfonyl chloride (2.0 g, 10.5 mmol) was dissolved in of tetrahydrofuran (20 mL) and placed in an ice bath. Hydrazine hydrate (1.2 g, 37.4 mmol) was added dropwise to the reaction and left to stir for 30 minutes, forming a white suspension. The solution was then rotary evaporated to collect a white solid which was then extracted with ethyl acetate and washed three times with brine. The organic layer was then dried to collect a white solid which was recrystallised from ethanol. Yield (1.7 g, 71.3%). ^{1}H NMR (400 MHz, DMSO-d_6): δ8.29 (s, 1H), 7.69 (d, 2H, *J* = 8.1 Hz), 7.41 (d, 2H, *J* = 8.1 Hz), 4.05 (s, 2H), 2.40 (s, 3H).

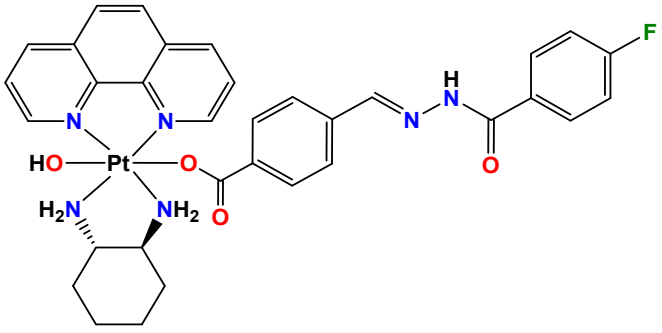
Synthesis of palmitic acid hydrazide

Palmitoyl chloride (0.90 g, 3.3 mmol) was added dropwise to methanol (10 mL) and allowed to stir for 5 minutes to form methyl palmitate. The reaction mix was dried, dissolved in chloroform and washed with excess 1 M NaOH. The organic layer was dried then redissolved in methanol (15 mL). Excess hydrazine hydrate (0.50 g, 15.6 mmol) was added dropwise, and the reaction refluxed for 4 hours. The reaction was allowed to cool to room temperature, forming a white suspension. The solid was filtered, washed with water, then then recrystallised from ethanol. Yield (0.61 g, 64.3%). ^{1}H NMR (400 MHz, DMSO-d_6): δ8.92 (s, 1H), 4.23 (s, 2H), 1.99 (t, 2H, *J* = 7.4 Hz), 1.47 (t, 2H, *J* = 7.2 Hz), 1.24 (m, 24H), 0.86 (t, 2H, *J* = 6.9 Hz).

Synthesis of Pt^{IV}PhenSS mono succinate $(NO_3)_2$ complex

Pt^{IV}PhenSS (300 mg, 0.46 mmol) was dissolved in 2.5 mL of H_2O at 45 °C. Succinic anhydride (190 mg, 1.9 mmol) was then added to the reaction and allowed to stir for 1 hour. The reaction mix was then diluted with methanol (15 mL) and excess ether added to precipitate a white solid which was collected by vacuum filtration and with cold methanol and diethyl ether. Yield (284.2 mg, 82.0 %). ^{1}H NMR (400 MHz, D_2O): ^{1}H NMR (400 MHz, D_2O) δ δ9.30 (d, *J* = 5.6 Hz, 1H) 9.25 (d, *J* = 5.6 Hz, 1H), 9.07 (d, *J* = 8.5 Hz, 2H), 8.32 (s, 2H), 8.25 (dd, *J* = 8.5, 5.6 Hz, 2H), 3.18 (m, 2H), 2.39 (d, *J* = 12.0 Hz, 2H), 2.19 (m, 4H), 1.68 (m, 4H), 1.30 (m, 2H).

Synthesis of Complex 2 - Pt^{IV}PhenSS(4fBz)(OH) 4-fluorobenzhydrazide hydrazone $(NO_3)_2$

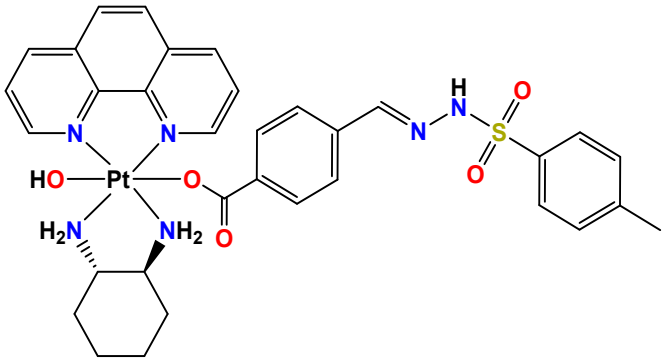


Pt^{IV}PhenSS(4-formyl-benzoate)(OH) (53.4 mg, 0.068 mmol) was suspended in methanol (0.5 mL). 4-Fluorobenzhydrazide (55.4 mg, 0.355 mmol) was dissolved in methanol (1.5 mL) and added dropwise, forming a yellow suspension. The reaction was left to stir for 30 minutes at room temperature with no visible change. The product was collected by vacuum filtration, washed with excess ethyl acetate, and dried with diethyl ether. Yield (55.8 mg, 89.0%). ^{1}H NMR (400 MHz, DMSO-d_6): δ11.94 (s, 1H), 9.46 (d, *J* = 5.2 Hz, 2H), 9.30 (d, *J* = 8.3 Hz, 2H), 9.04 (m, 2H), 8.52 (m, 2H), 8.37 (m, 3H), 7.97 (t, *J* = 6.3 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.37 d, (*J* = 8.1 Hz, 2H), 3.14 (m, 2H), 2.33 (m, 2H), 1.73 (m, 4H), 1.37 (m, 2H). ^{19}F NMR (376 MHz): δ109.09 (s). ^{13}C NMR (100 MHz, DMSO-d_6): δ170.80, 165.93, 163.45, 162.68, 152.05, 151.79, 147.29, 146.94, 146.88, 143.49, 137.71, 134.00, 131.79, 131.75, 130.89, 130.80, 130.58, 130.13, 128.95, 127.57, 127.50, 126.99, 116.12, 115.90, ~~61.70, 61.59, 31.50, 31.21, 24.14, 2~~3.99. ^{1}H-^{195}Pt HMQC (400 / 86 MHz, DMSO-d_6): δ9.46, 9.04, 8.33 / 489 ppm.

[1]. G. Zhang, Q. Fan, H. Wang, Y. Zhao and C. Ding, *Adv. Synth. & Catal.*, 2021, **363**, 833-837.

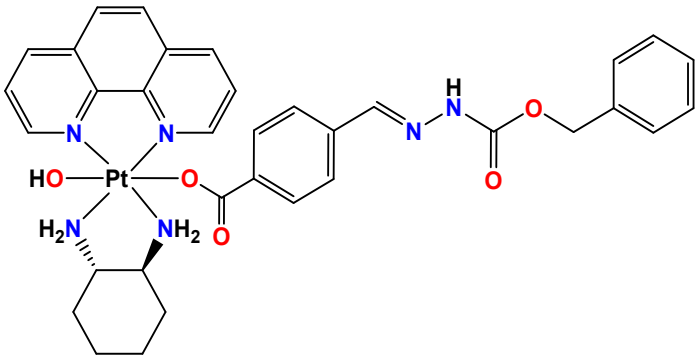
RP-HPLC Phenomenex C18 150 × 4.6 mm, 0 – 100% B over 15 min, R_t: 7.17 mins. Electronic spectrum λ_{max} nm (ε/mol^{-1}.dm^3.cm^{-1}, H_2O): 306 (41780 ± 150), 277 (44307 ± 420). SRCD spectrum λ_{max} nm (mdeg.mol.L^{-1}, H_2O): 198 (-2.97), 273 (-0.53).HRMS (ESI): m/z calcd for $C_{33}H_{32}FN_6O_4Pt$ [M-H]$^+$: 790.2117 [M-H]$^+$; found: 790.2118.

Synthesis of Complex 3 - Pt^{IV}PhenSS(4fBz)(OH) tosylhydrazine hydrazone $(NO_3)_2$



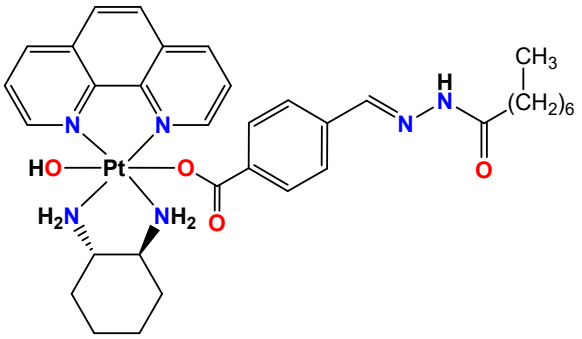
Pt^{IV}PhenSS(4-formyl-benzoate)(OH) (41.5 mg, 0.053 mmol) was suspended in methanol (0.5 mL). Tosylhydrazine (14.9 mg, 0.080 mmol) was dissolved in methanol (1.5 mL) and added dropwise. The reaction was left to stir for 15 minutes at room temperature, forming a clear solution. The solution was diluted with diethyl ether (10 mL), forming a white precipitate which was collected by vacuum filtration and washed with ether (15 mL) to remove excess tosylhydrazine. Yield (47.2 mg, 93.5%). ^{1}H NMR (400 MHz, DMSO-d_6): δ11.59 (s, 1H), 9.42 (m), 9.29 (d, *J* = 8.3 Hz, 2H), 9.00 (m, 2H), 8.50 (m, 4H), 8.30 (m, 2H), 7.85 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 3.10 (m, 2H), 2.34 (m, 5H), 1.72 (m, 4H), 1.36 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ170.70, 152.02, 151.78, 146.91, 146.86, 146.45, 144.06, 143.46,136.99, 136.49, 133.95, 131.77, 131.73, 130.54, 130.16, 128.93, 127.65, 127.56, 127.48, 126.62, 61.68, 61.59, 31.49, 31.17, 24.12, 23.97, 21.45. ^{1}H-^{195}Pt HMQC (400 / 86 MHz, DMSO-d_6): δ9.42, 9.00, 8.30 / 489 ppm. RP-HPLC Phenomenex C18 150 × 4.6 mm, 0 – 100% B over 15 min, R_t: 7.63 mins. Electronic spectrum λ_{max} nm (ε/mol^{-1}.dm^3.cm^{-1}, H_2O): 280 (46650 ± 130). SRCD spectrum λ_{max} nm (mdeg.mol.L^{-1}, H_2O): 189 (-3.45), 210 (-3.13), 270 (-0.79). HRMS (ESI): m/z calcd for $C_{33}H_{35}N_6O_5PtS$ [M-H]$^+$: 822.2037 [M-H]$^+$; found: 822.2032.

Synthesis of Complex 4 - Pt^{IV}PhenSS(4fBz)(OH) benzyl carbazate hydrazone $(NO_3)_2$



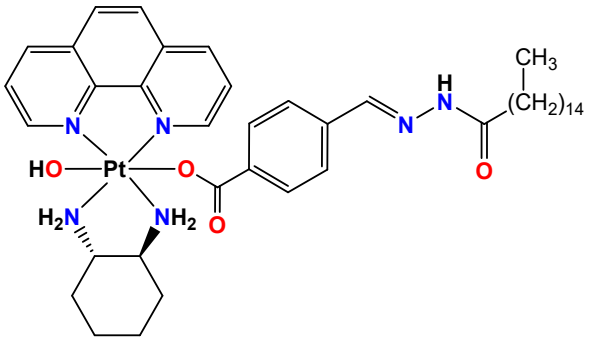
Pt^{IV}PhenSS(4-formyl-benzoate)(OH) (44.1 mg, 0.057 mmol) was suspended in methanol (0.5 mL). Benzyl carbazate (24.3 mg, 0.146 mmol) was dissolved in methanol (1.5 mL) and added dropwise. The reaction was left to stir for 30 minutes at room temperature, gradually forming a white suspension. The solid was then collected by vacuum filtration and washed with excess cold methanol and dried with diethyl ether. Yield (48.5 mg, 92.4%). ^{1}H NMR (400 MHz, DMSO-d_6): δ11.34 (s, 1H), 9.44 (m, 2H), 9.29 (d, *J* = 8.3 Hz, 2H), 9.01 (m, 2H), 8.50 (m, 4H), 8.30 (m, 2H), 7.96 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.37 (m, 5H), 5.16 (s, 2H), 3.11 (m, 2H), 2.32 (m, 2H), 1.72 (m, 4H), 1.36 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ170.85, 153.77, 152.05, 151.79, 146.92, 146.86, 143.47, 137.74, 136.92, 133.56, 131.78, 131.74, 130.52, 128.94, 128.58, 128.47, 127.56, 127.49, 126.51, 66.52, 61.69, 61.59, 31.50, 31.19, 24.14, 23.98. ^{1}H-^{195}Pt HMQC (400 / 86 MHz, DMSO-d_6): δ9.44, 9.01, 8.30 / 488 ppm. RP-HPLC Phenomenex C18 150 × 4.6 mm, 0 – 100% B over 15 min, R_t: 7.90 mins. Electronic spectrum λ_{max} nm (ε/mol^{-1}.dm^3.cm^{-1}, H_2O): 205 (91300 ± 1000), 280 (47900 ± 400), 300 (36100 ± 600). SRCD spectrum λ_{max} nm (mdeg.mol.L^{-1}, H_2O): 206 (-1.83), 276 (-0.36).HRMS (ESI): m/z calcd for $C_{34}H_{35}N_6O_5Pt$ [M-H]$^+$: 802.2317 [M-H]$^+$; found: 802.2319.

Synthesis of Complex 5 - Pt^{IV}PhenSS(4fBz)(OH) octanoic hydrazide hydrazone $(NO_3)_2$



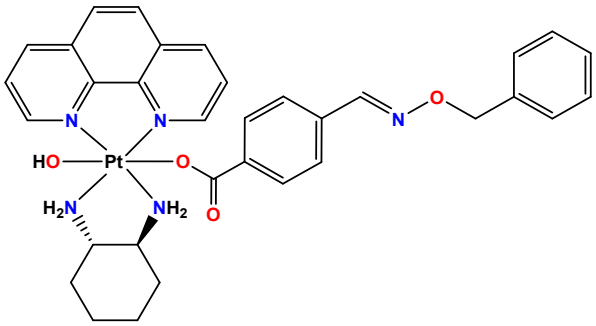
Pt^{IV}PhenSS(4-formyl-benzoate)(OH) (46.0 mg, 0.059 mmol) was suspended in methanol (0.5 mL). Octanoic hydrazide (18.0 mg, 0.114 mmol) was dissolved in methanol (1.5 mL) and added dropwise. The reaction was left to stir for 15 minutes at room temperature, where it gradually formed a white suspension. The solid was then collected by vacuum filtration and washed with excess cold methanol. Yield (44.7 mg, 82.4%). ^{1}H NMR (400 MHz, DMSO-d_6): δ11.38 (s, C=N-H, *cis*-amide isomer), 11.26 (s, C=N-H, *trans*-amide isomer), 9.44 (m, 2H), 9.29 (d, *J* = 8.3 Hz, 2H), 9.02 (m, 2H), 8.51 (m, 4H), 8.31 (m, 2H), 8.09 (s, H-C=N, *cis*-amide isomer), 7.91 (s, H-C=N, *trans*-amide isomer), 7.67 (m, 2H), 7.55 (m, 2H), 3.11 (m, 2H), 2.57 (t, *J* = 7.5 Hz, O=C-CH_2, *cis*-amide isomer), 2.32 (d, *J* = 11.5 Hz, 2H), 2.17 (t, *J* = 7.3 Hz, O=C-CH_2, *trans*-amide isomer), 1.72 (m, 4H), 1.54 (m, 2H), 1.36 (m, 2H), 1.25 (m, 8H), 0.84 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ174.99, 170.84, 170.77, 169.36, 152.03, 151.79, 146.93, 146.88, 145.17, 143.47, 141.95, 137.86, 137.77, 133.75, 133.55, 131.78, 131.74, 130.56, 130.49, 128.94, 127.57, 127.49, 126.79, 126.42, 61.71, 61.59, 34.62, 32.20, 31.60, 31.57, 31.49, 31.20, 29.11, 29.03, 28.89, 28.87, 25.42, 24.64, 24.13, 23.99, 22.50, 14.39. ^{1}H-^{195}Pt HMQC (400 / 86 MHz, DMSO-d_6): δ9.44, 9.02, 8.31 / 490 ppm. RP-HPLC Phenomenex C18 150 × 4.6 mm, 0 – 100% B over 15 min, R_t: 8.99 mins. Electronic spectrum λ_{max} nm (ε/mol^{-1}.dm^3.cm^{-1}, H_2O): 280 (49800 ± 300), 305 (40200 ± 300). CD spectrum λ_{max} nm (mdeg.mol.L^{-1}, 2,2,2-trifluoroethanol): 213 (-1.78), 222 (-2.01), 256 (-0.21).HRMS (ESI): m/z calcd for $C_{34}H_{43}N_6O_4Pt$ $[M-H]^+$: 794.2994 $[M-H]^+$; found: 794.2990.

Synthesis of Complex 6 - Pt^{IV}PhenSS(4fBz)(OH) palmitic hydrazide hydrazone $(NO_3)_2$



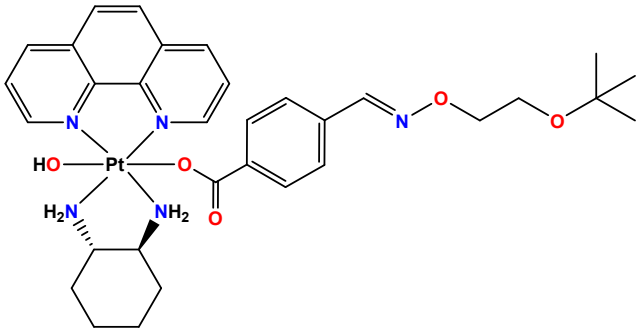
Pt^{IV}PhenSS(4-formyl-benzoate)(OH) (42.7 mg, 0.055 mmol) was suspended in methanol (0.5 mL). Palmitic acid hydrazide (73.6 mg, 0.272 mmol) was suspended in methanol (1.5 mL) and added dropwise to form a white suspension. The reaction was left to stir for two hours at room temperature with no discernible colour change. The suspension was then filtered to collect a white solid which was identified to be excess hydrazide by NMR. The product was then isolated from the filtrate using flash chromatography through a C_{18} column. Yield (30.1 mg 53.3%).^{1}H NMR (400 MHz, DMSO-d_6): δ11.38 (s, C=N-H, *cis*-amide isomer), 11.26 (s, C=N-H, *trans*-amide isomer), 9.45 (m, 2H), 9.29 (d, *J* = 8.3 Hz, 2H), 9.03 (m, 2H), 8.51 (m, 4H), 8.32 (m, 2H), 8.09 (s, H-C=N, *cis*-amide isomer), 7.91 (s, H-C=N, *trans*-amide isomer), 7.68 (m, 2H), 7.55 (m, 2H), 3.12 (m, 2H), 2.56 (m, O=C-CH_2, *cis*-amide isomer), 2.32 (d, *J* = 11.5 Hz, 2H), 2.16 (t, *J* = 7.3 Hz, O=C-CH_2, *trans*-amide isomer), 1.72 (m, 4H), 1.54 (m, 2H), 1.37 (d, *J* = 11.5 Hz, 2H), 1.21 (m, 24H), 0.84 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ174.95, 170.85, 170.80, 169.35, 152.06, 151.82, 146.89, 146.84, 145.17, 143.47, 141.95, 137.85, 137.76, 133.75, 133.54, 131.79, 131.75, 130.56, 130.49, 128.94, 127.57, 127.50, 126.78, 126.39, 61.72, 61.58, 34.61, 32.19, 31.73, 31.49, 31.19, 29.49, 29.45, 29.42, 29.39, 29.36, 29.32, 29.24, 29.20, 29.15, 29.07, 25.42, 24.60, 24.13, 24.00, 22.55, 14.41. ^{1}H-^{195}Pt HMQC (400 / 86 MHz, DMSO-d_6): δ9.45, 9.03, 8.32 / 486 ppm. RP-HPLC Phenomenex C18 150 × 4.6 mm, 0 – 100% B over 15 min, R_t: 13.60 mins. Electronic spectrum λ_{max} nm (ε/mol^{-1}.dm^3.cm^{-1}, MeOH): 280 (50500 ± 500), 303 (43400 ± 100). SRCD spectrum λ_{max} nm (mdeg.mol.L^{-1}, H_2O): 202 (-1.04).HRMS (ESI): m/z calcd for $C_{42}H_{59}N_6O_4Pt$ $[M-H]^+$: 906.4246 $[M-H]^+$; found: 906.4249.

Synthesis of Complex 7- Pt^{IV}PhenSS (4fBz)(OH) *O*-benzylhydroxylamine oxime $(NO_3)_2$



Pt^{IV}PhenSS(4-formyl-benzoate)(OH) (46.8 mg, 0.060 mmol) was suspended in methanol (0.5 mL). *O*-Benzylhydroxylamine (15.0 mg, 0.122 mmol) was dissolved in methanol (0.5 mL) and added dropwise to form a white suspension which dissolved after 5 minutes. The solution was left to stir for an additional 30 minutes to form a white suspension. The solid was then collected by vacuum filtration and washed with excess cold methanol. Yield (50.7 mg, 95.5%). ^{1}H NMR (400 MHz, DMSO-d_6): δ9.43 (d, 2H, *J* = 5.1 Hz), 9.29 (d, 2H, *J* = 8.3 Hz), 9.00 (2H, m), 8.51 (m, 4H), 8.29 (m, 3H), 7.67 (d, 2H, *J* = 8.2 Hz), 7.50 (d, 2H, *J* = 8.2 Hz), 7.35 (m, 5H), 5.14 (s, 2H), 3.11 (m, 2H), 2.13 (d, 2H, *J* = 11.3 Hz), 1.72 (m, 4H), 1.37 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ170.70, 152.02, 151.77, 149.10, 146.93, 146.88, 143.46, 137.87, 135.26, 133.97, 131.77, 131.73, 130.55, 128.93, 128.88, 128.83, 128.77,128.39, 127.56, 127.48, 126.77, 76.13, 61.68, 61.60, 31.49, 31.18, 24.13, 23.96. ^{1}H-^{195}Pt HMQC (400 / 86 MHz, DMSO-d_6): δ9.43, 9.00, 9.29 / 485 ppm. RP-HPLC Phenomenex C18 150 × 4.6 mm, 0 – 100% B over 15 min, R_t: 9.01 mins. Electronic spectrum λ_{max} nm (ε/mol^{-1}.dm^3.cm^{-1}, H_2O): 279 (48900 ± 500). SRCD spectrum λ_{max} nm (mdeg.mol.L^{-1}, H_2O: 210 (-2.90), 271 (-0.64).HRMS (ESI): m/z calcd for $C_{33}H_{34}N_5O_4Pt$ $[M-H]^+$: 759.2259 $[M-H]^+$; found: 759.2255.

Synthesis of Complex 8 - Pt^{IV}PhenSS(4fBz)(OH) *O*-(2-(tert-butoxy)ethyl)hydroxylamine oxime $(NO_3)_2$



Pt^{IV}PhenSS(4-formyl-benzoate)(OH) (40.3 mg, 0.052 mmol) was suspended in methanol (0.5 mL). *O*-(2-(tert-butoxy)ethyl)-hydroxylamine (34.1 mg, 0.256 mmol) was dissolved in methanol (1.5 mL) and added dropwise. The reaction was left to stir for 15 minutes at room temperature, forming a clear solution. The complex was then isolated using flash chromatography through a C_{18} column. Yield (19.2 mg 41.5%). ^{1}H NMR (400 MHz, DMSO-d_6): δ9.43, (d, *J* = 5.92 Hz, 2H), 9.29 (d, *J* = 8.3 Hz, 2H), 9.00 (m, 2H), 8.51 (m, 4H), 8.30 (m, 2H), 8.24 (s, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 4,13 (t, *J* = 5.0 Hz, 2H), 3.54 (t, *J* = 5.0 Hz, 2H), 3.11 (m, 2H), 2.32 (d, *J* = 12.4 Hz, 2H), 1.72 (m, 4H), 1.36, (m, 2H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ170.74, 152.01, 151.77, 148.58, 146.92, 146.86, 143.47, 135.43, 133.87, 131.77, 131.73, 130.53, 128.94, 127.56, 127.49, 126.69, 74.40, 73.02, 61.68, 61.58, 60.14, 31.49, 31.19, 27.76, 27.72, 27.64, 24.13, 23.97. ^{1}H-^{195}Pt HMQC (400 / 86 MHz, DMSO-d_6): δ9.43, 9.00, 8.30 / 489 ppm. RP-HPLC Phenomenex C18 150 × 4.6 mm, 0 – 100% B over 15 min, R_t: 8.18 mins. Electronic spectrum λ_{max} nm (ε/mol^{-1}.dm^3.cm^{-1}, H_2O): 279 (54500 ± 700). SRCD spectrum λ_{max} nm (mdeg.mol.L^{-1}, H_2O): 206 (-3.55), 266 (-0.74). HRMS (ESI): m/z calcd for $C_{32}H_{40}N_5O_5Pt$ $[M-H]^+$: 769.2677 $[M-H]^+$; found: 769.2670.

B. NMR spectra

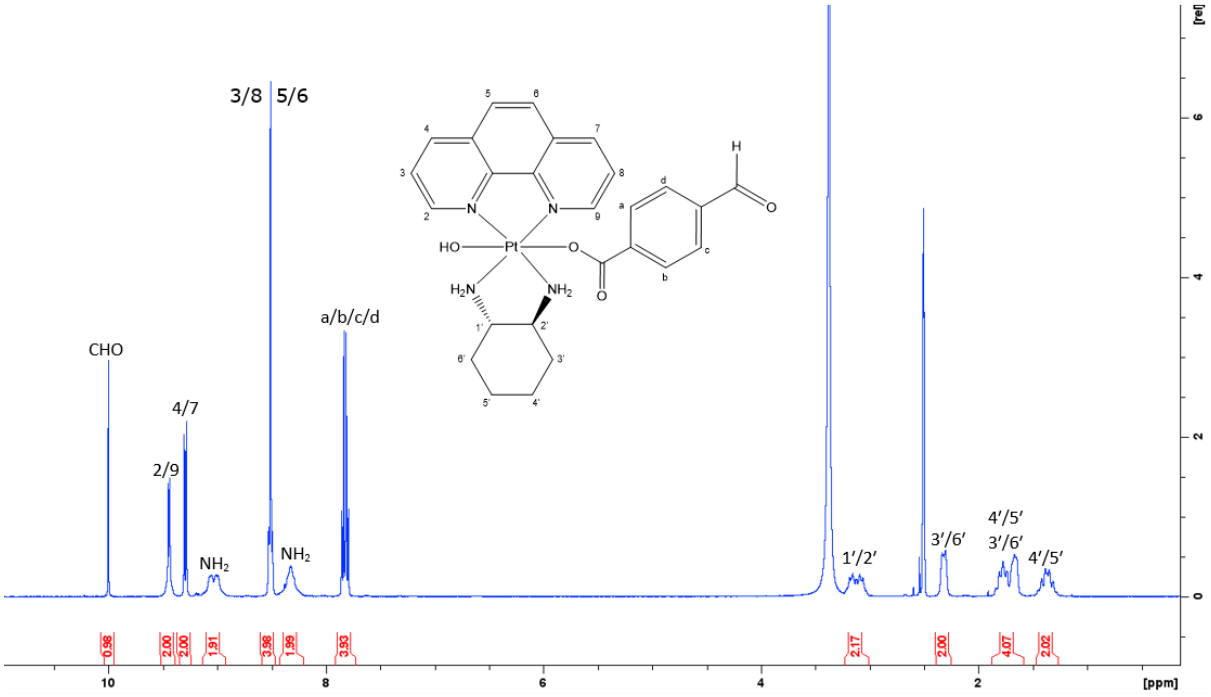


Figure B.1 ^{1}H spectra of complex **1** in DMSO-d_6 at 298 K. Inset: structure and proton numbering scheme.

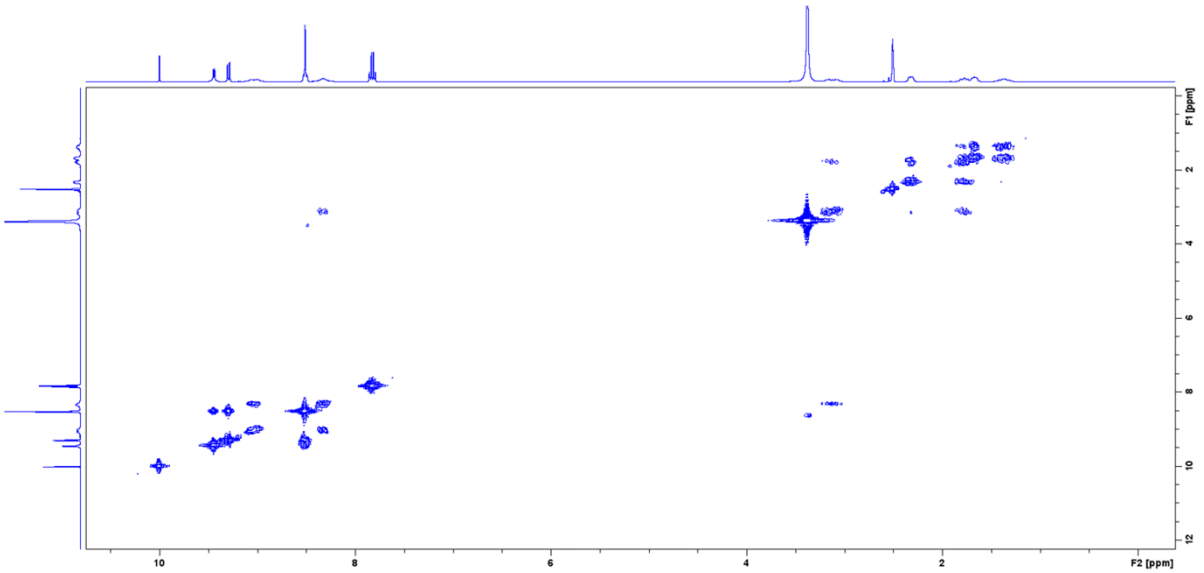


Figure B.2 COSY spectra of Complex **1** in DMSO-d_6 at 298 K

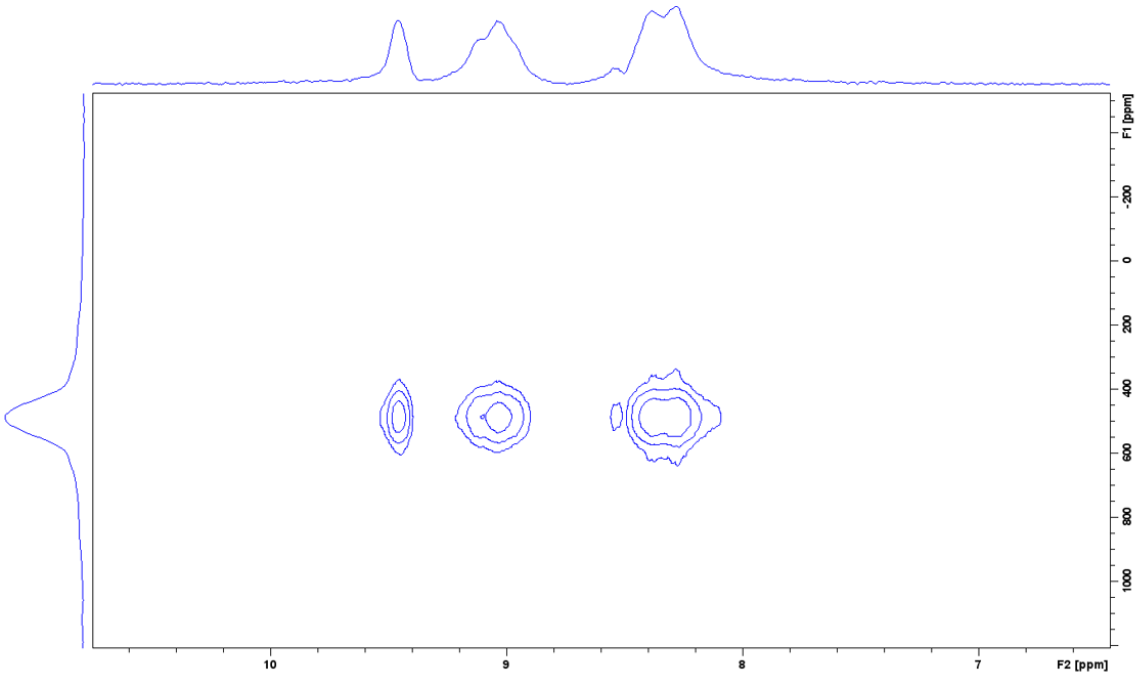


Figure B.3 ^{1}H-^{195}Pt spectra of Complex **1** in DMSO-d_6 at 298 K.

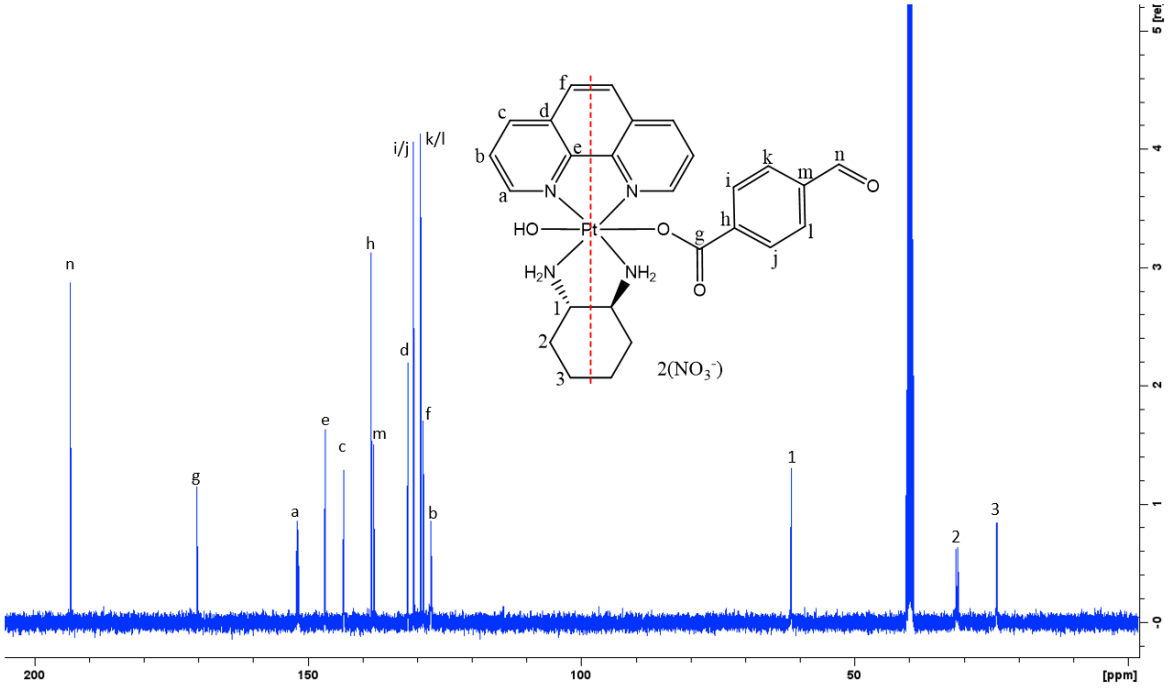


Figure B.4 ^{13}C spectra of Complex **1** in DMSO-d_6 at 298 K. Inset: structure and carbon numbering scheme.

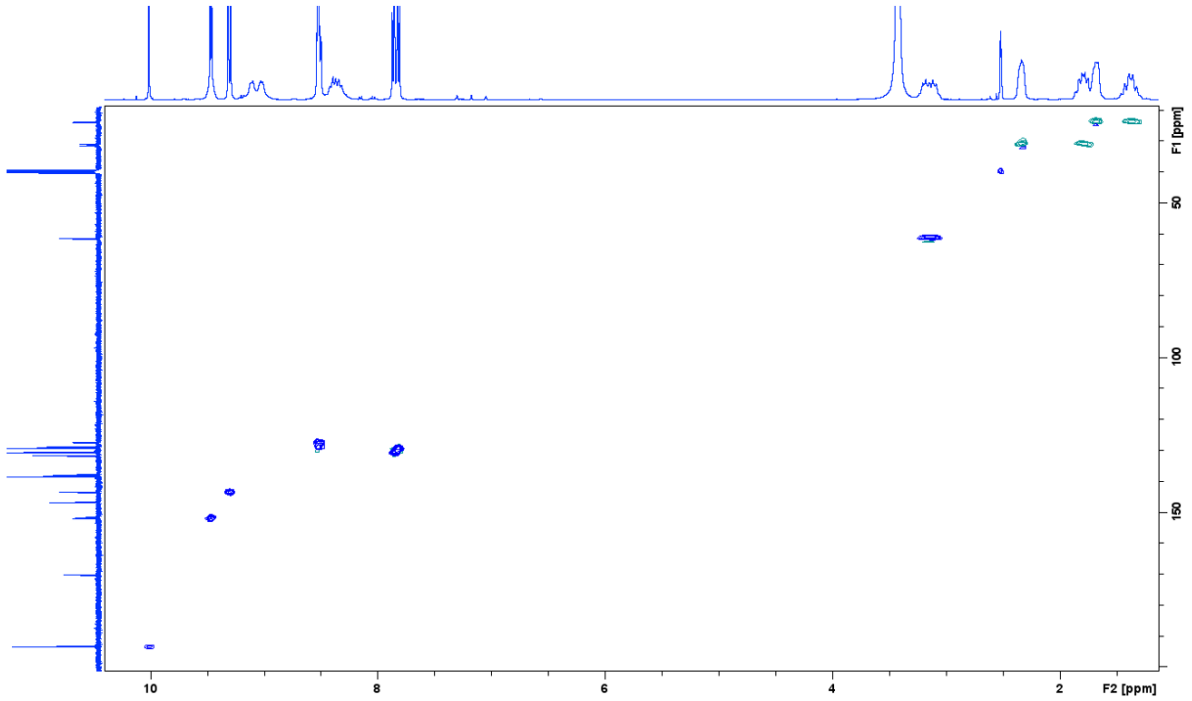


Figure B.5 HSQC spectra of Complex **1** in DMSO-d_6 at 298 K.

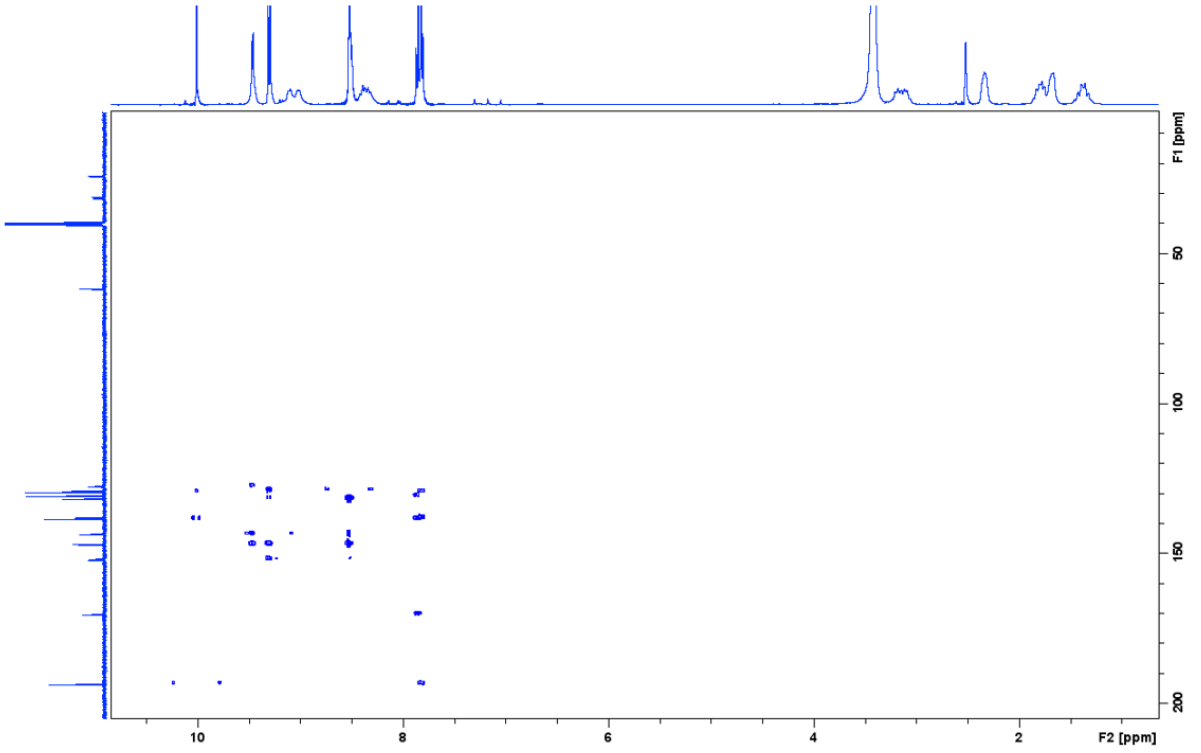


Figure B.6 HMBC spectra of Complex **1** in DMSO-d_6 at 298 K.

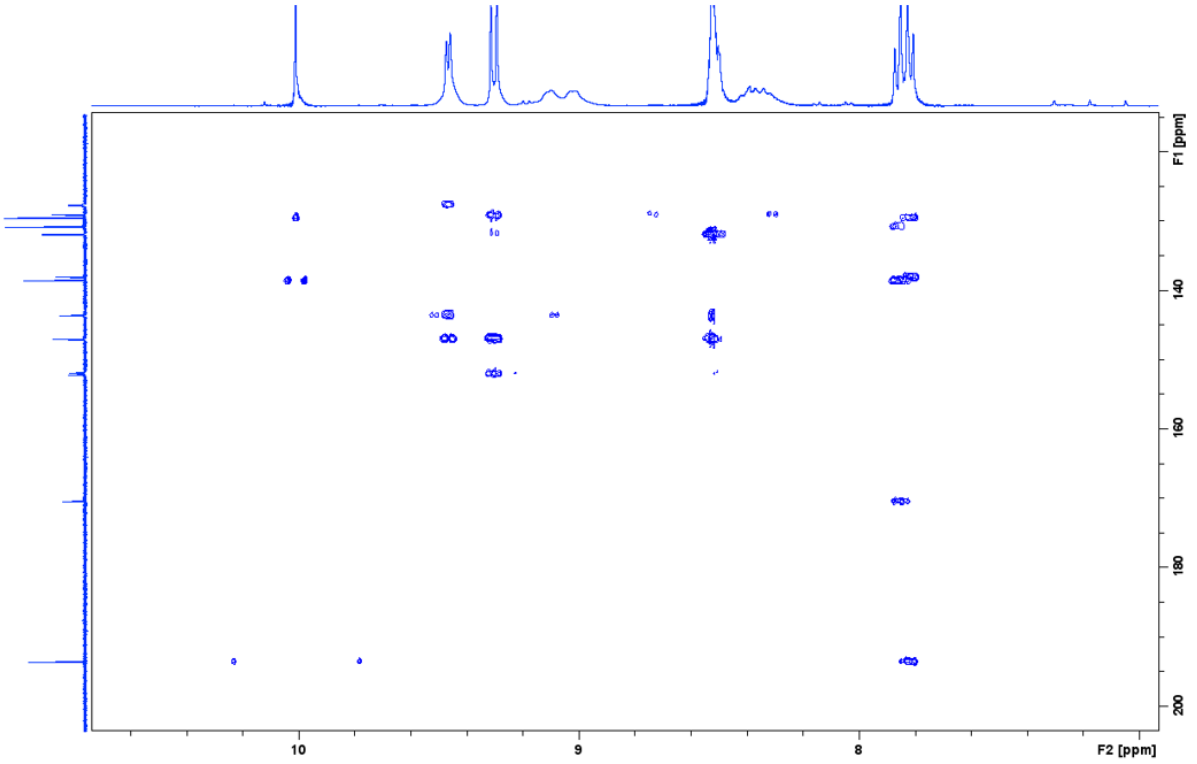


Figure B.7 Zoomed aromatic region of HMBC spectra of Complex **1** in DMSO-d_6 at 298 K.

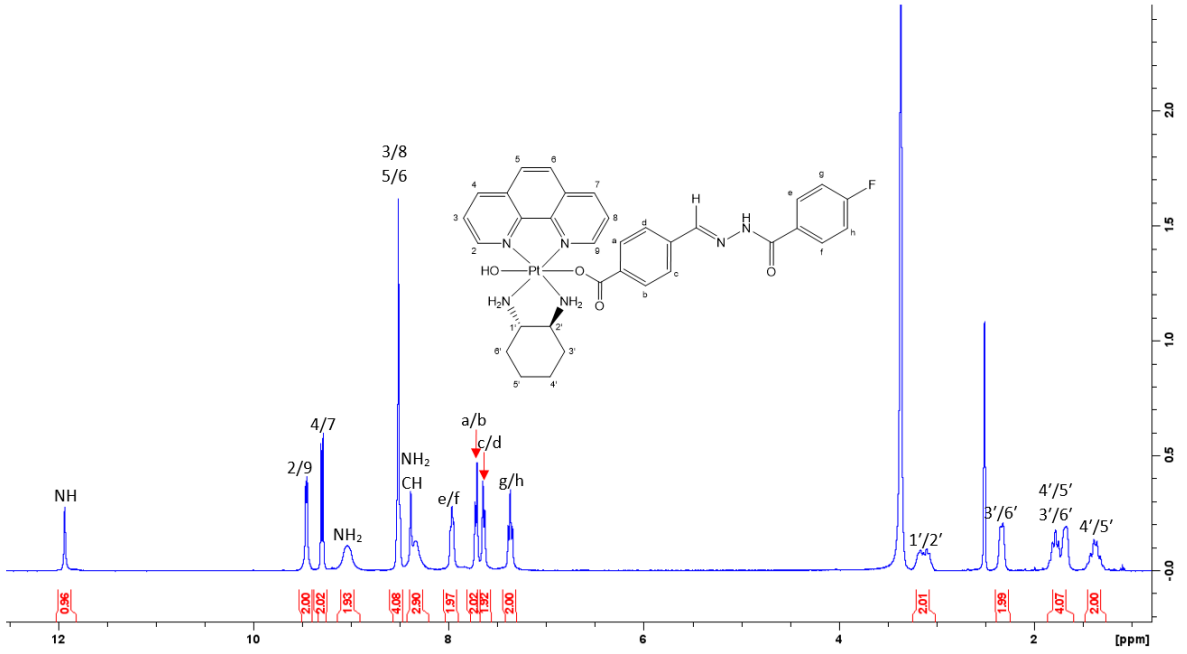


Figure B.8 ^{1}H spectra of Complex **2** in DMSO-d_6 at 298 K. Inset: structure and proton numbering scheme.

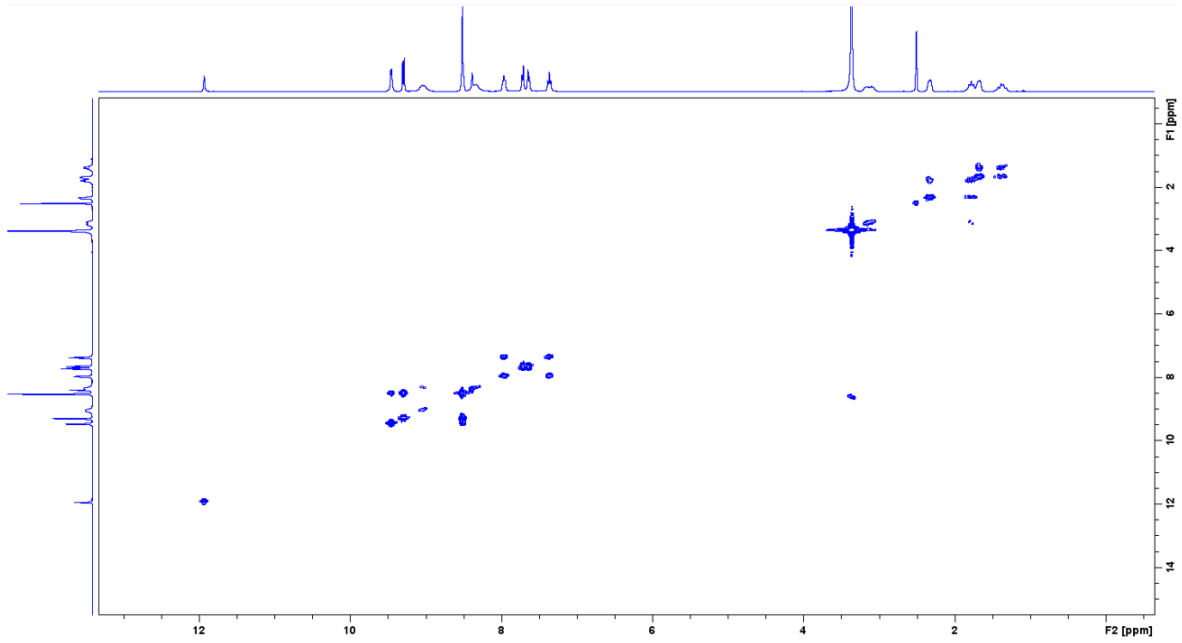


Figure B.9 COSY spectra of Complex **2** in DMSO-d_6 at 298 K.

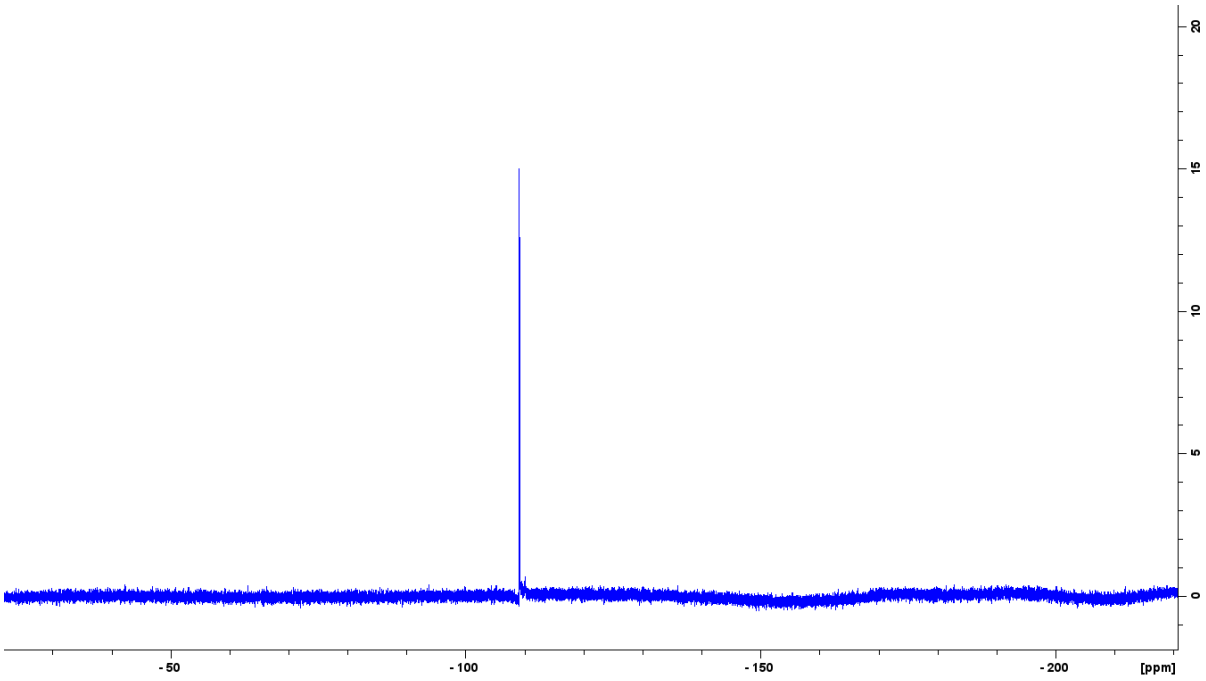


Figure B.10 ^{19}F spectra of Complex **2** in DMSO-d_6 at 298 K.

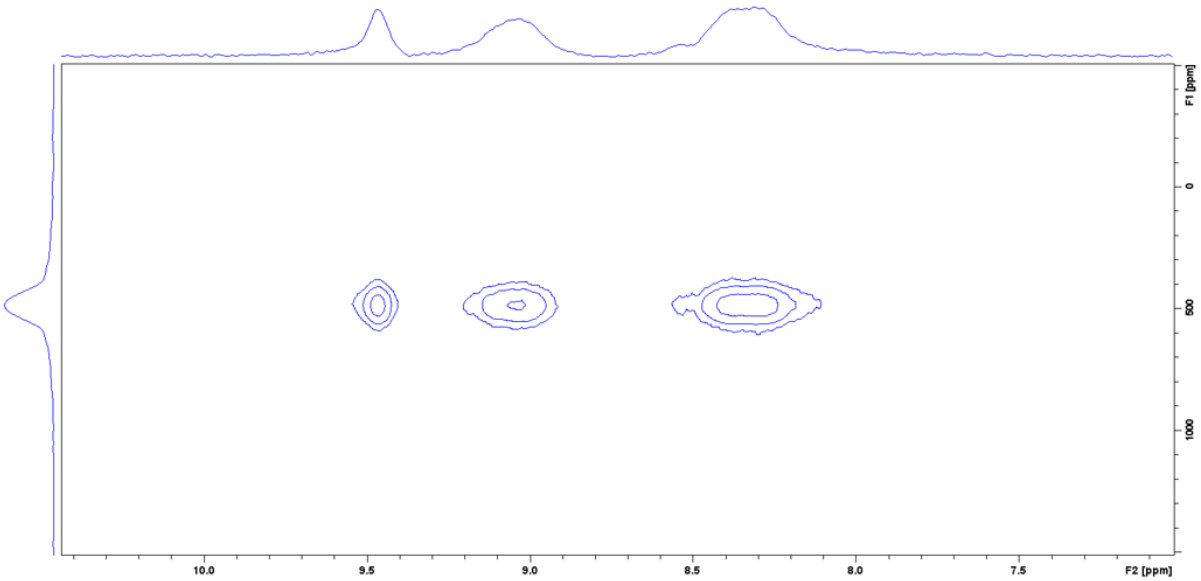


Figure B.11 ^{1}H-^{195}Pt spectra of Complex **2** in DMSO-d_6 at 298 K.

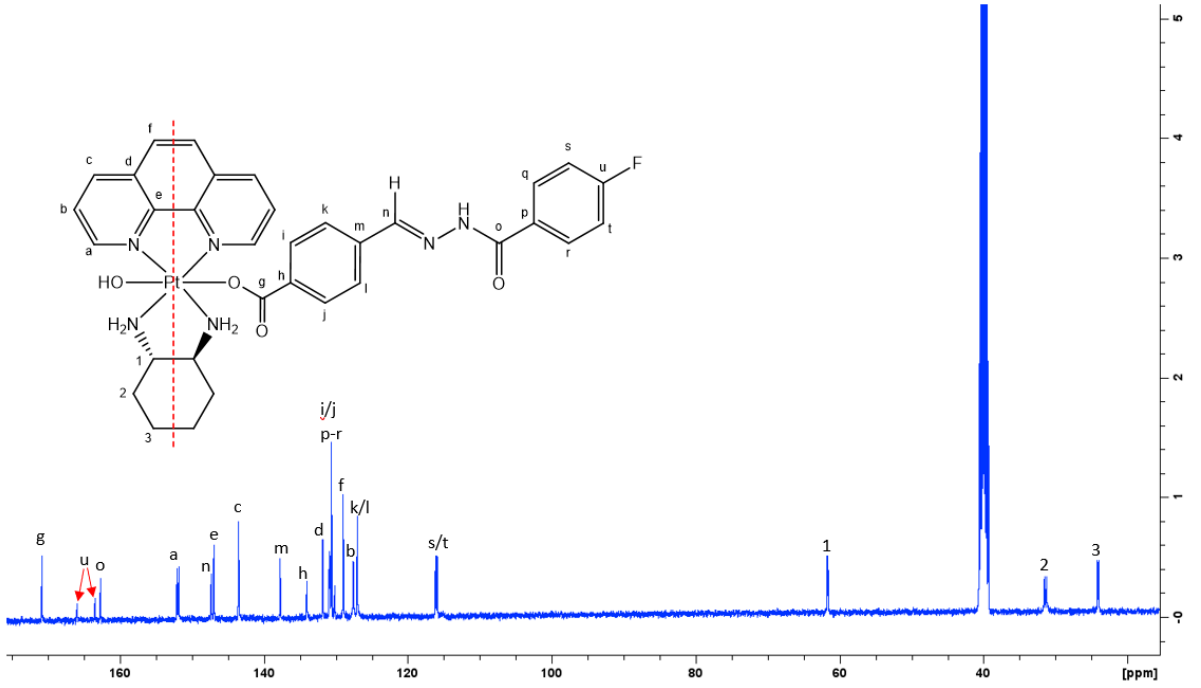


Figure B.12 ^{13}C spectra of Complex **2** in DMSO-d_6 at 298 K. Inset: structure and carbon numbering scheme.

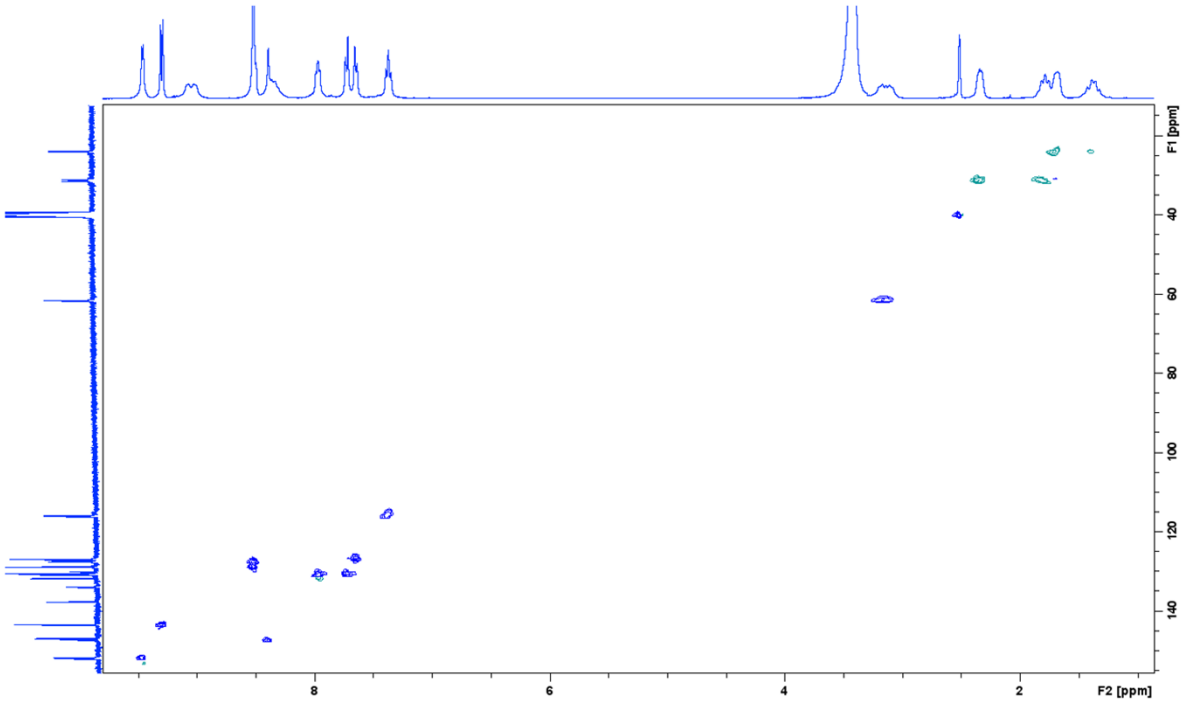


Figure B.13 HSQC spectra of Complex **2** in DMSO-d_6 at 298 K.

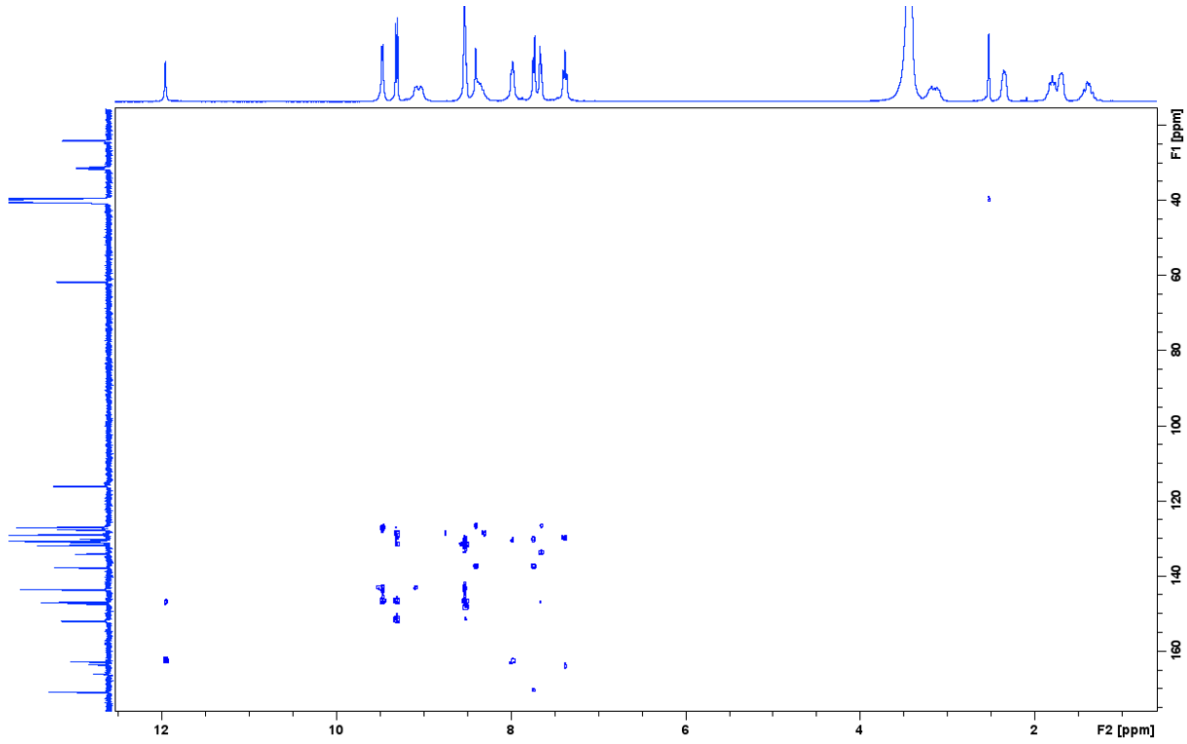


Figure B.14 HMBC spectra of Complex **2** in DMSO-d_6 at 298 K.

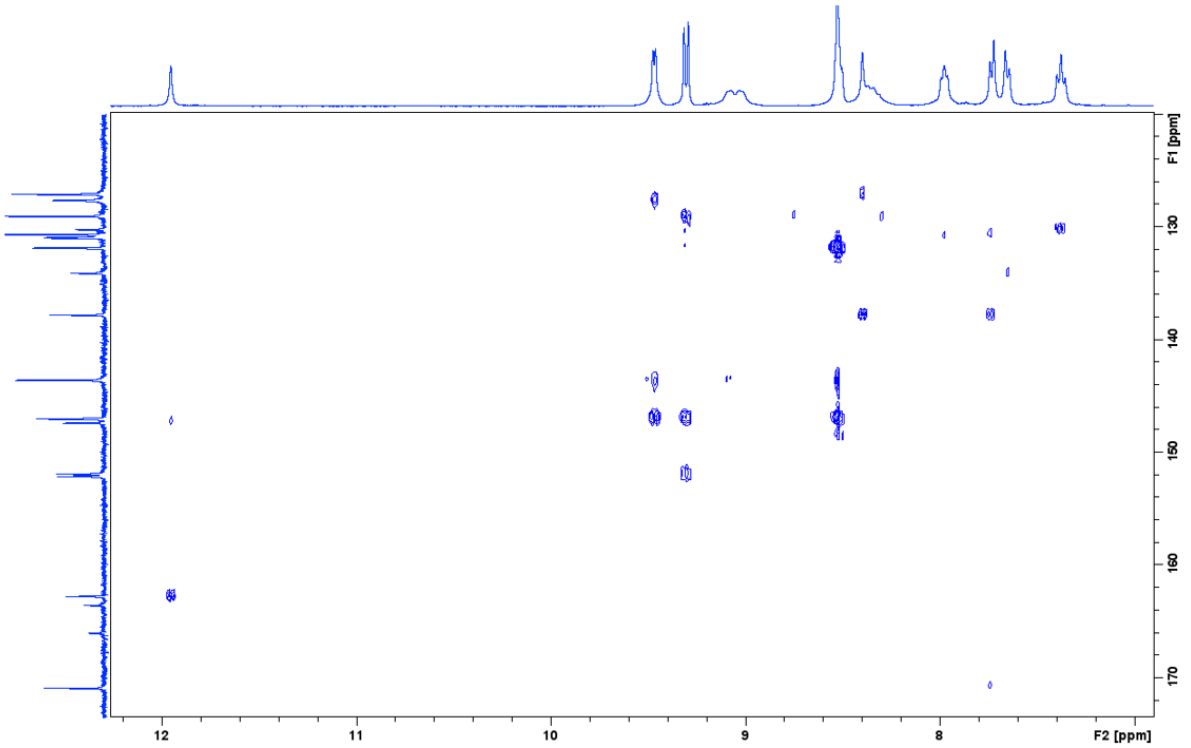


Figure B.15 Zoomed aromatic region of HMBC spectra of Complex **2** in DMSO-d_6 at 298 K.

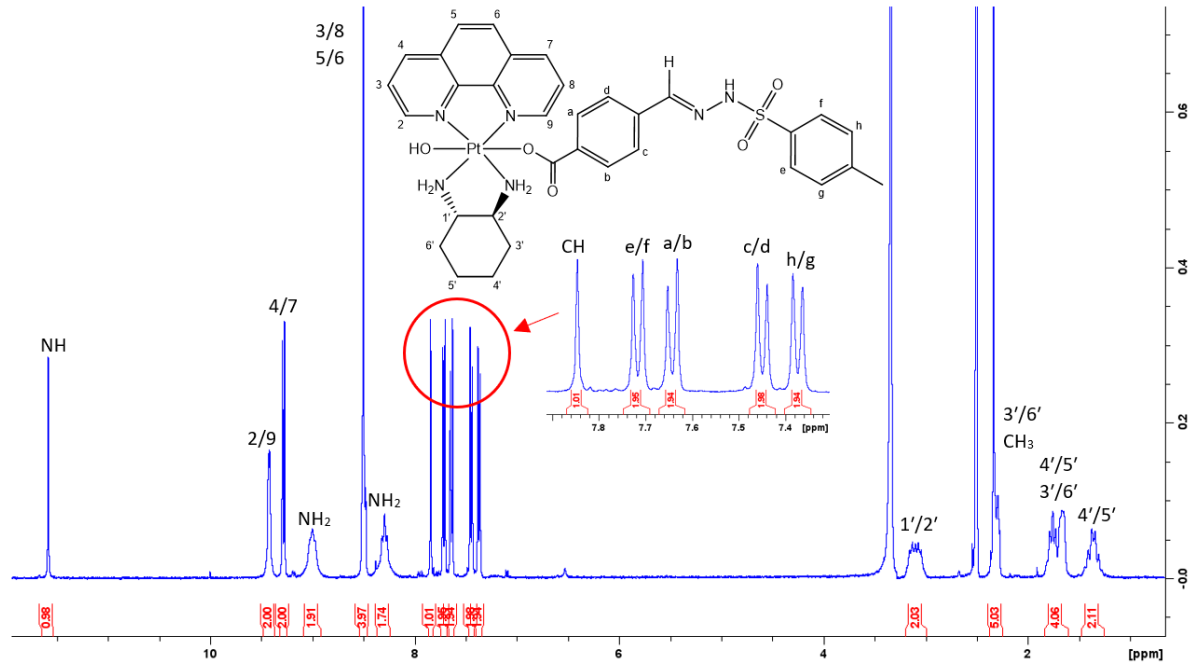


Figure B.16 ^{1}H spectra of Complex **3** in DMSO-d_6 at 298 K. Inset: structure and proton numbering scheme and zoomed region between 7.3-7.9 ppm.

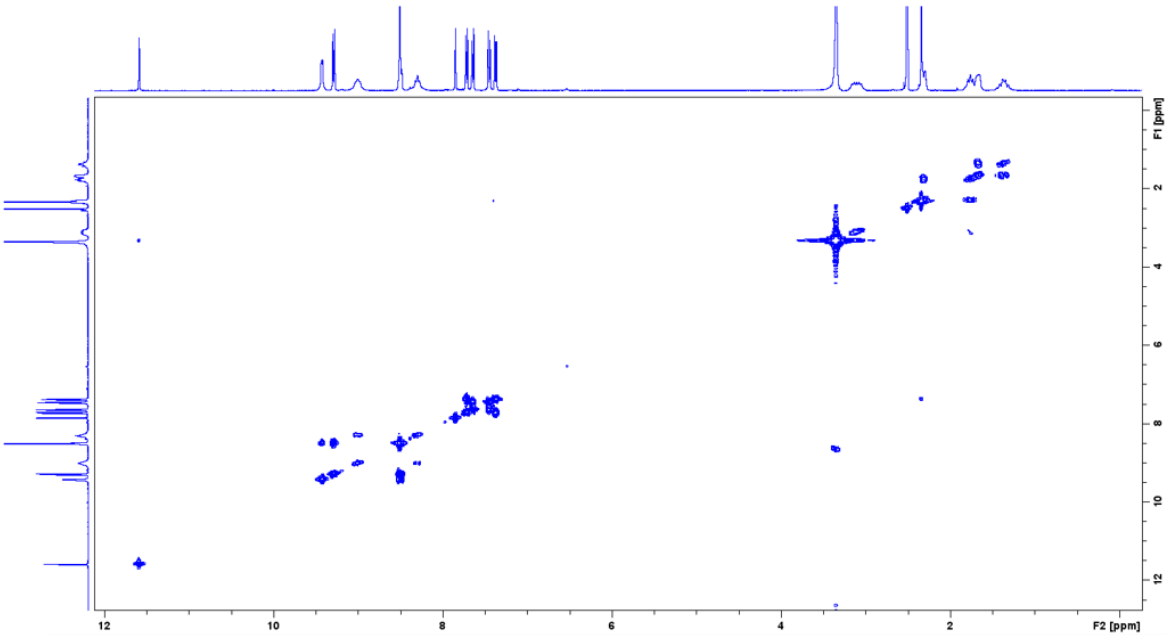


Figure B.17 COSY spectra of Complex **3** in DMSO-d_6 at 298 K.

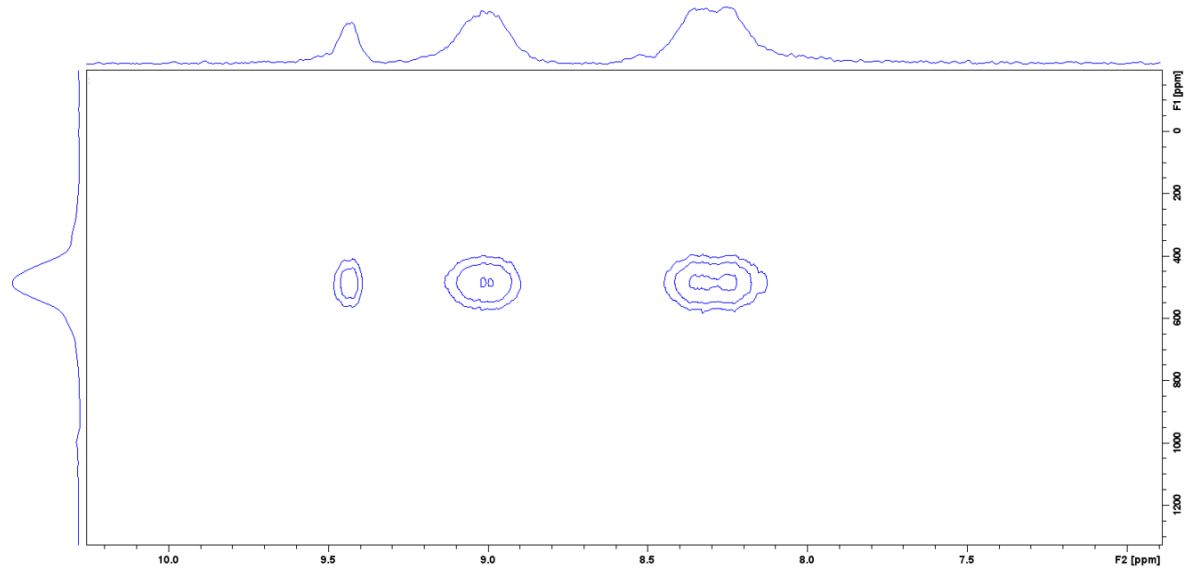


Figure B.18 ^{1}H-^{195}Pt spectra of Complex **3** in DMSO-d_6 at 298 K.

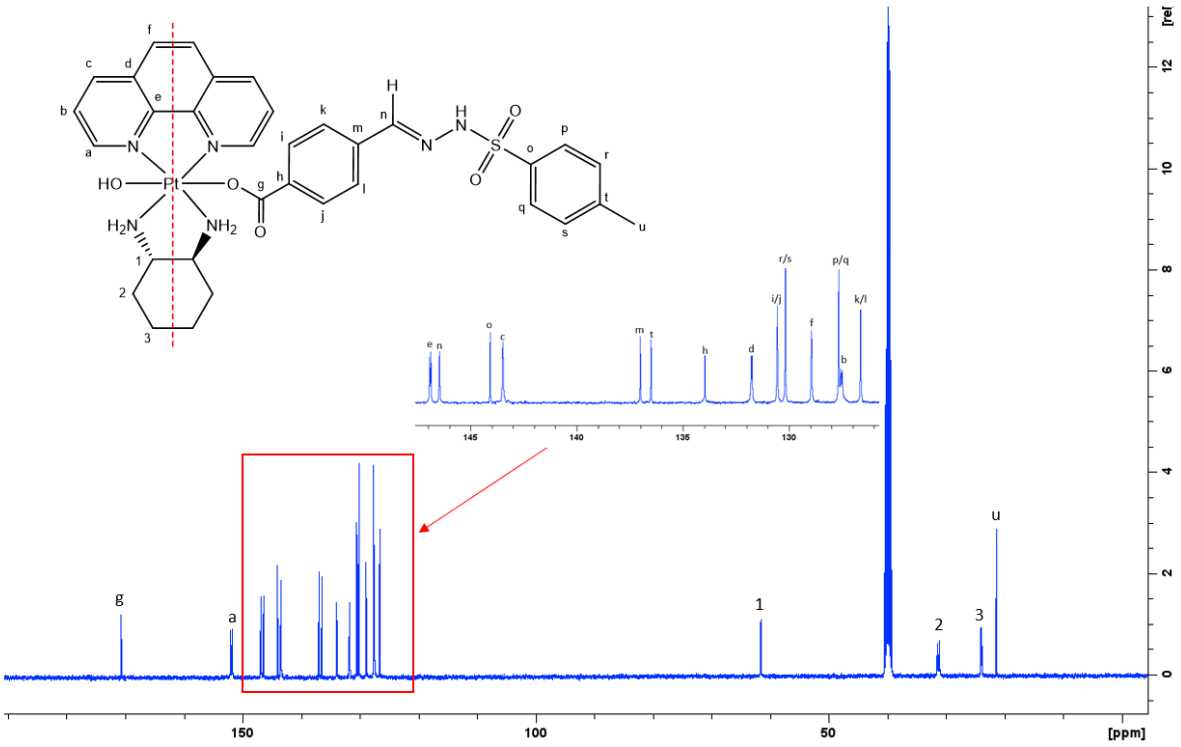


Figure B.19 ^{13}C spectra of Complex **3** in DMSO-d_6 at 298 K.

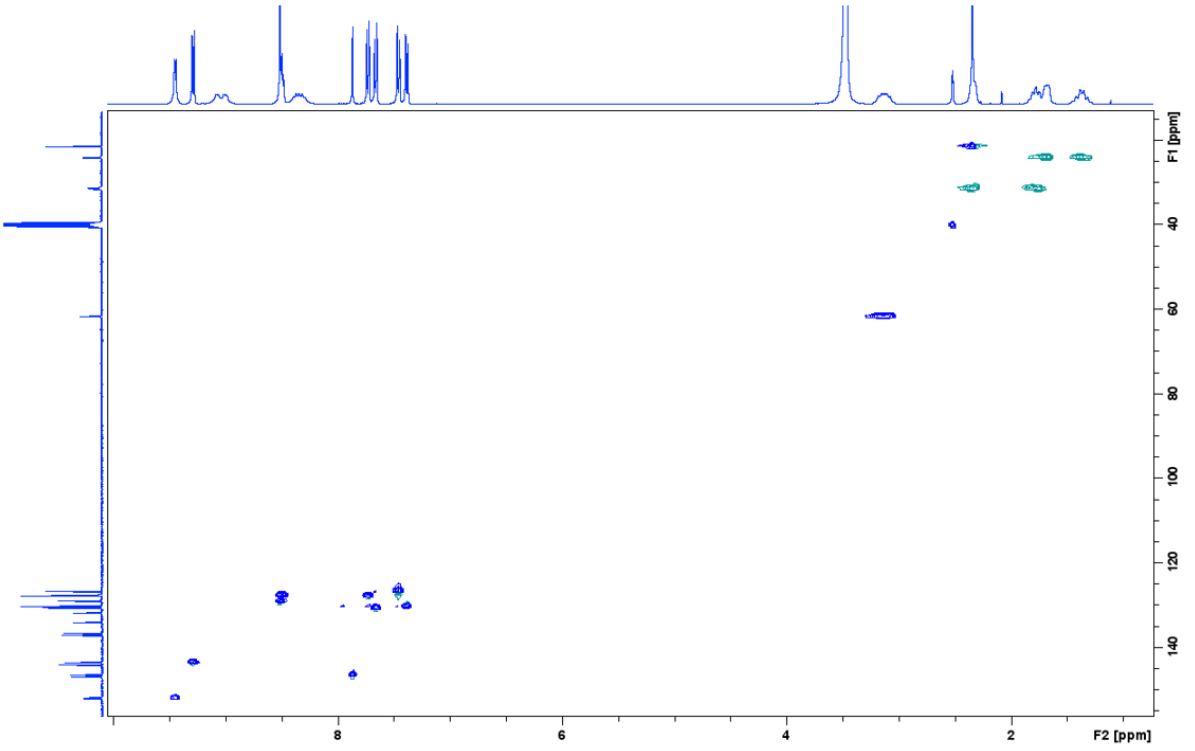


Figure B.20 HSQC spectra of Complex **3** in DMSO-d_6 at 298 K.

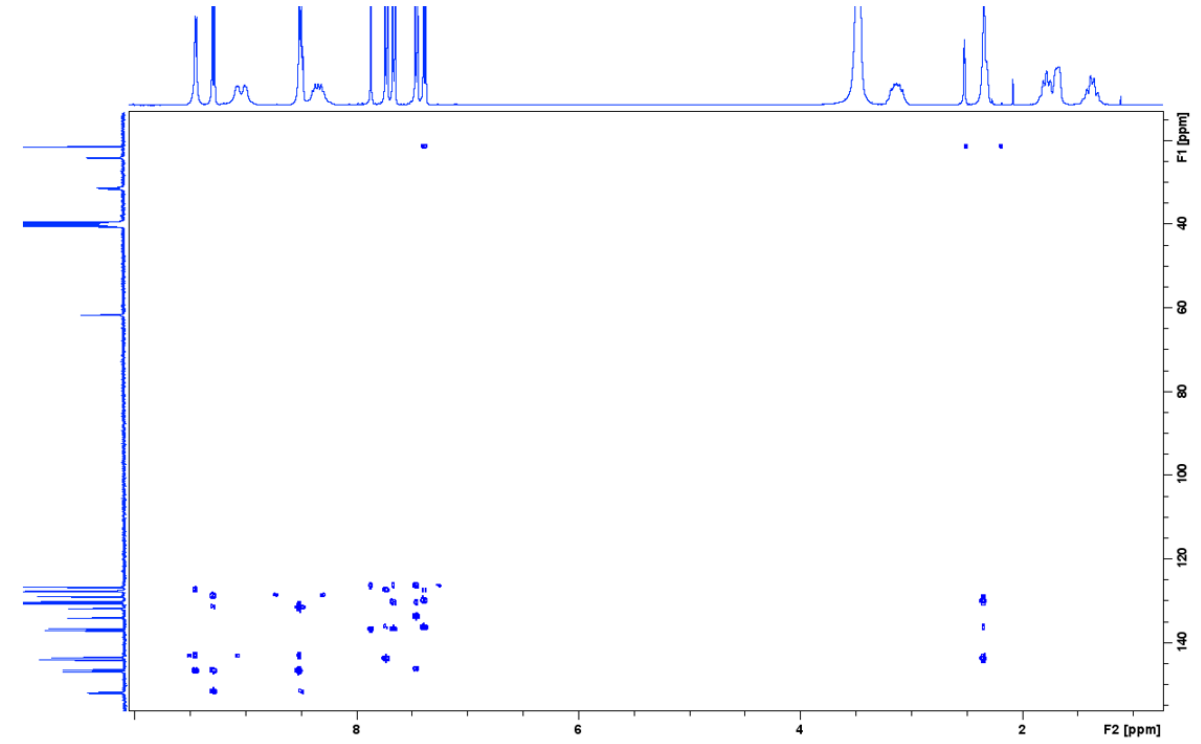


Figure B.21 HMBC spectra of Complex **3** in DMSO-d_6 at 298 K.

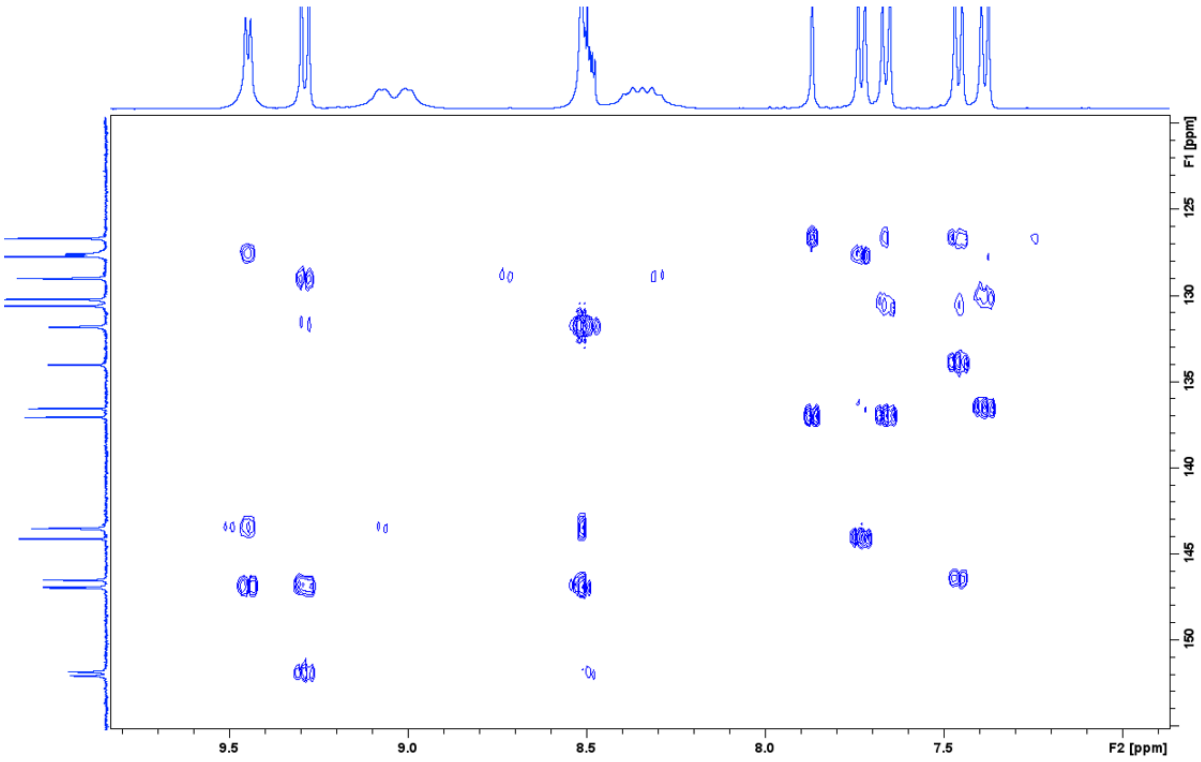


Figure B.22 Zoomed aromatic region of HMBC spectra of Complex **3** in DMSO-d_6 at 298 K.

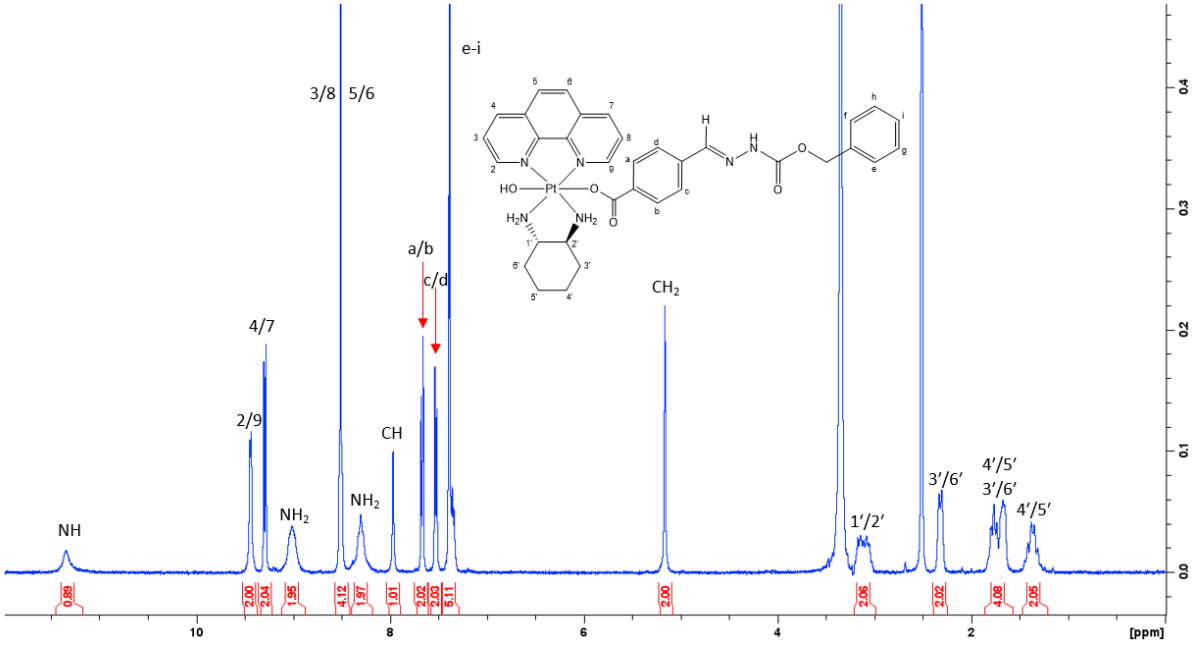


Figure B.23 ^{1}H spectra of Complex **4** in DMSO-d_6 at 298 K. Inset: structure and proton numbering scheme.

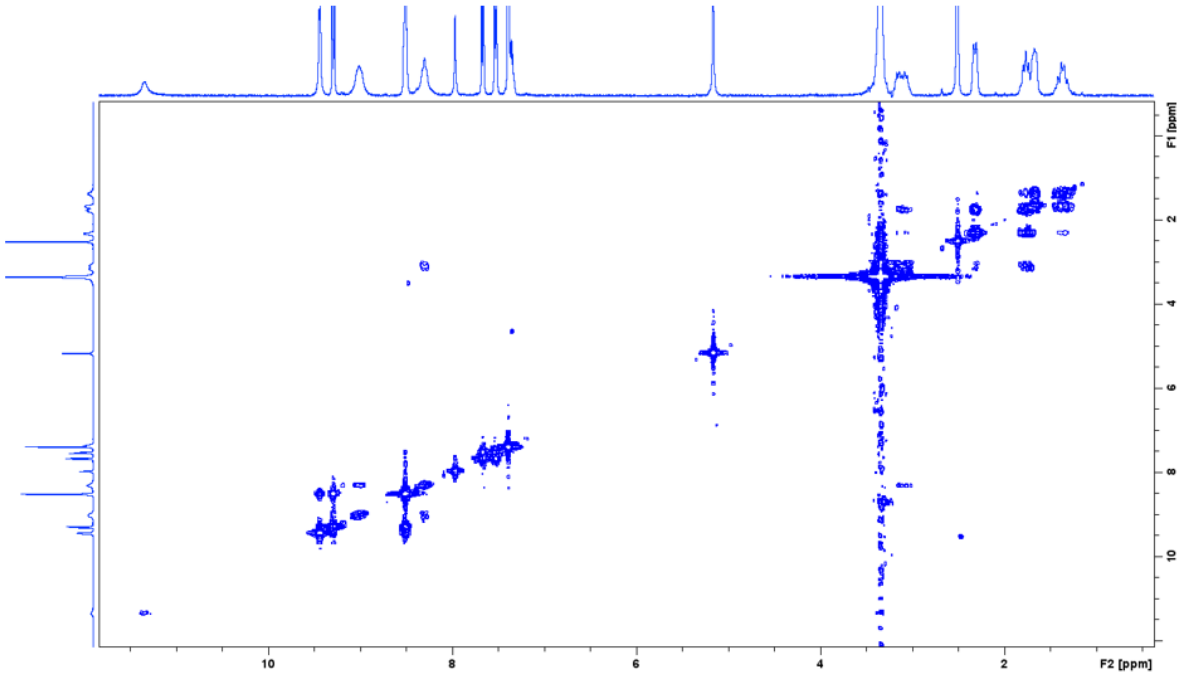


Figure B.24 COSY spectra of Complex **4** in DMSO-d_6 at 298 K.

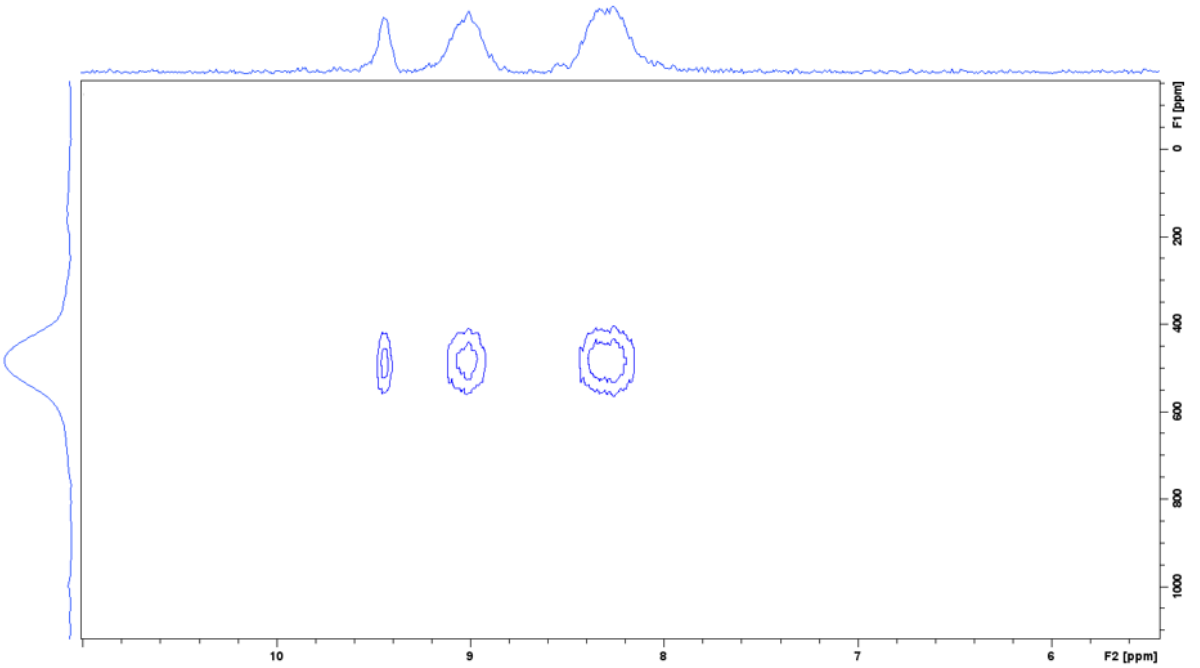


Figure B.25 ^{1}H-^{195}Pt spectra of Complex **4** in DMSO-d_6 at 298 K.

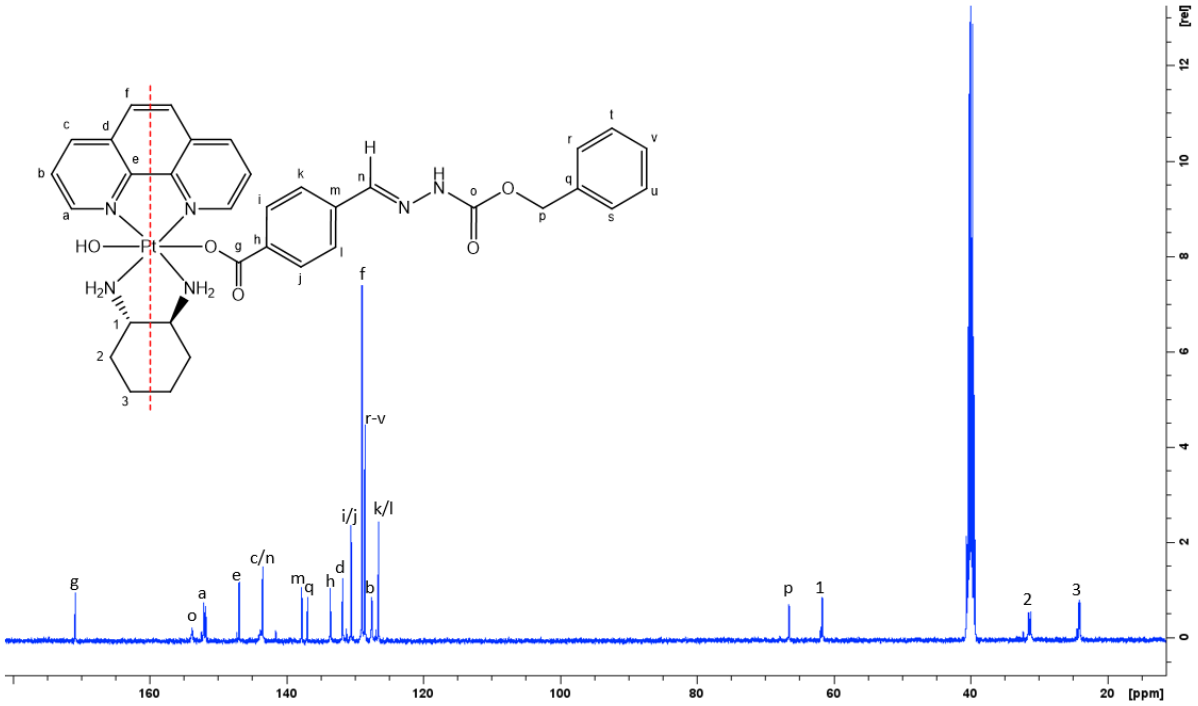


Figure B.26 ^{13}C spectra of Complex **4** in DMSO-d_6 at 298 K. Inset: structure and carbon numbering scheme.

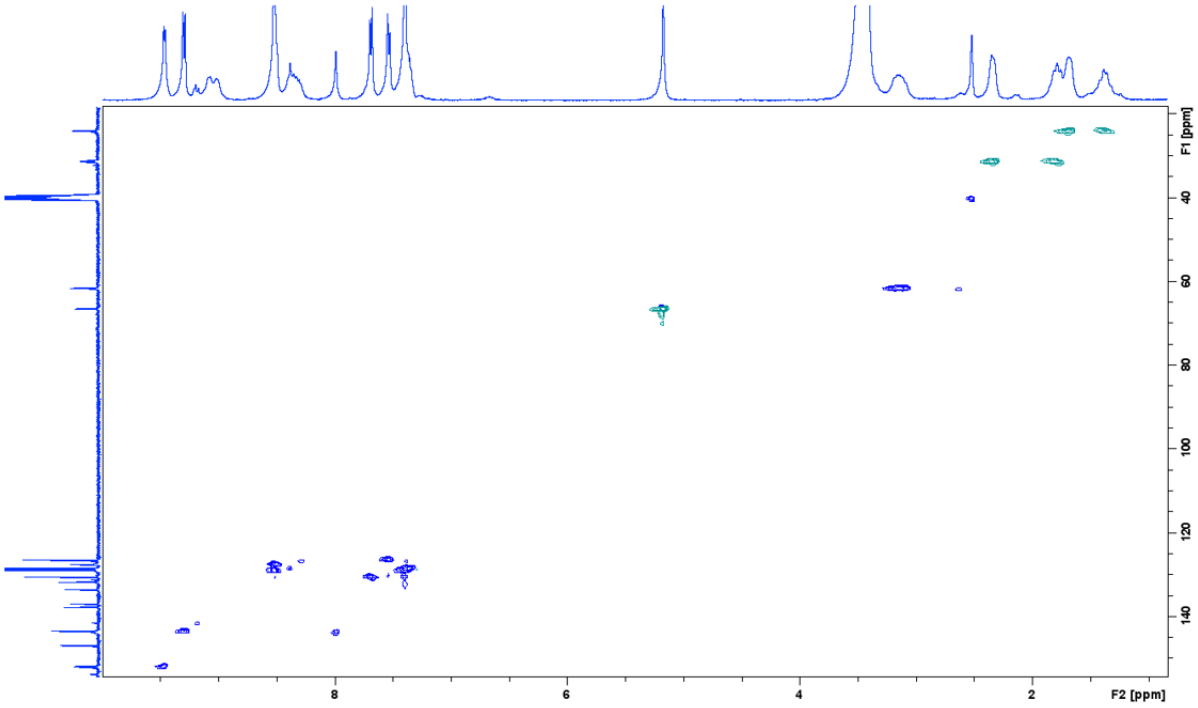


Figure B.27 HSQC spectra of Complex **4** in DMSO-d_6 at 298 K.

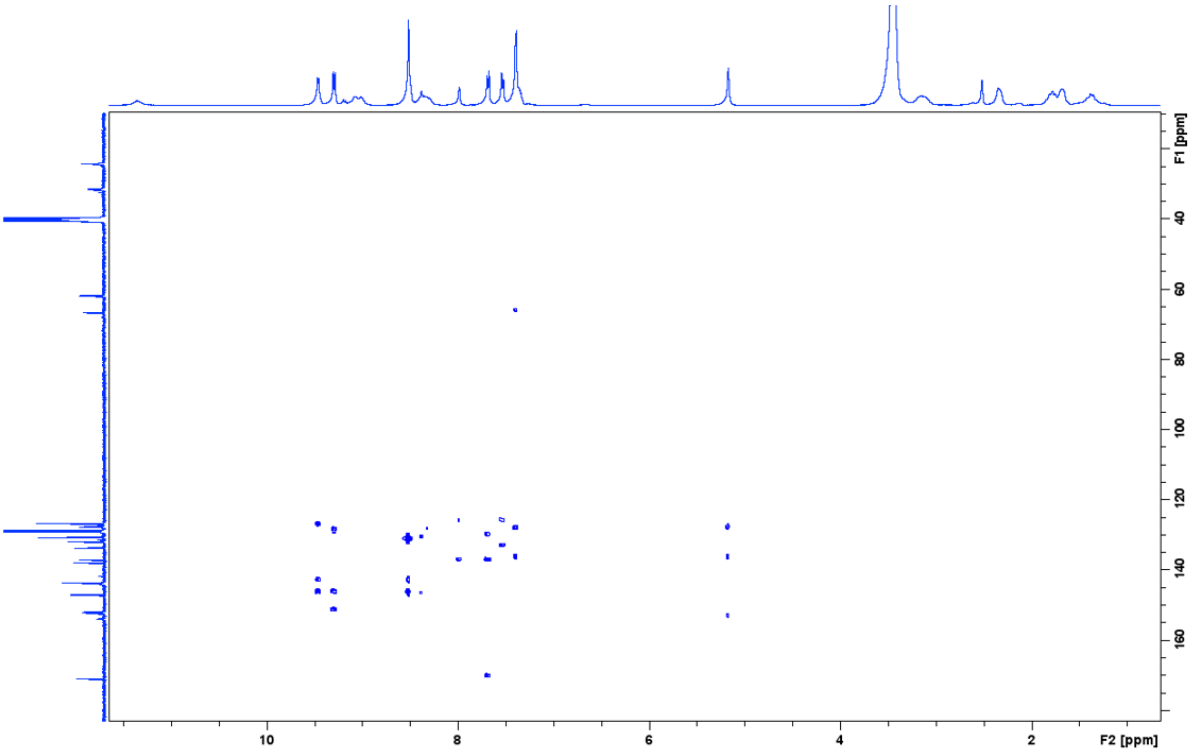


Figure B.28 HMBC spectra of Complex **4** in DMSO-d_6 at 298 K.

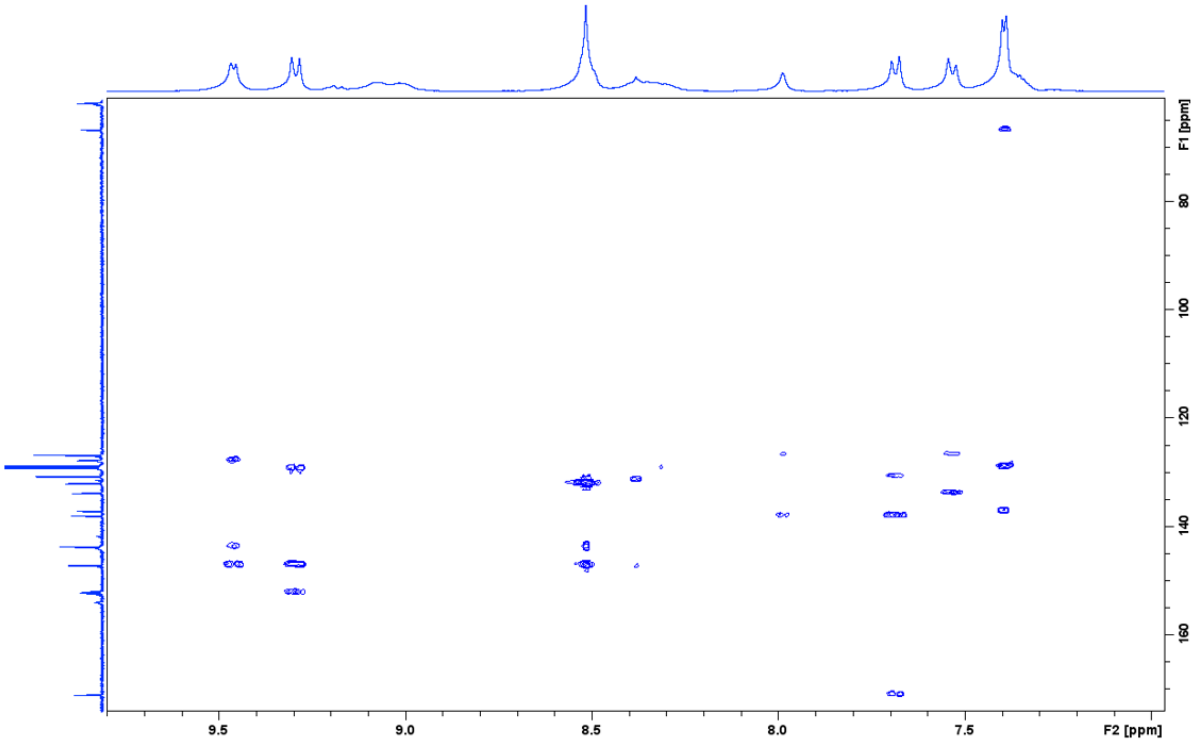


Figure B.29 Zoomed aromatic region of HMBC spectra of Complex **4** in DMSO-d_6 at 298 K.

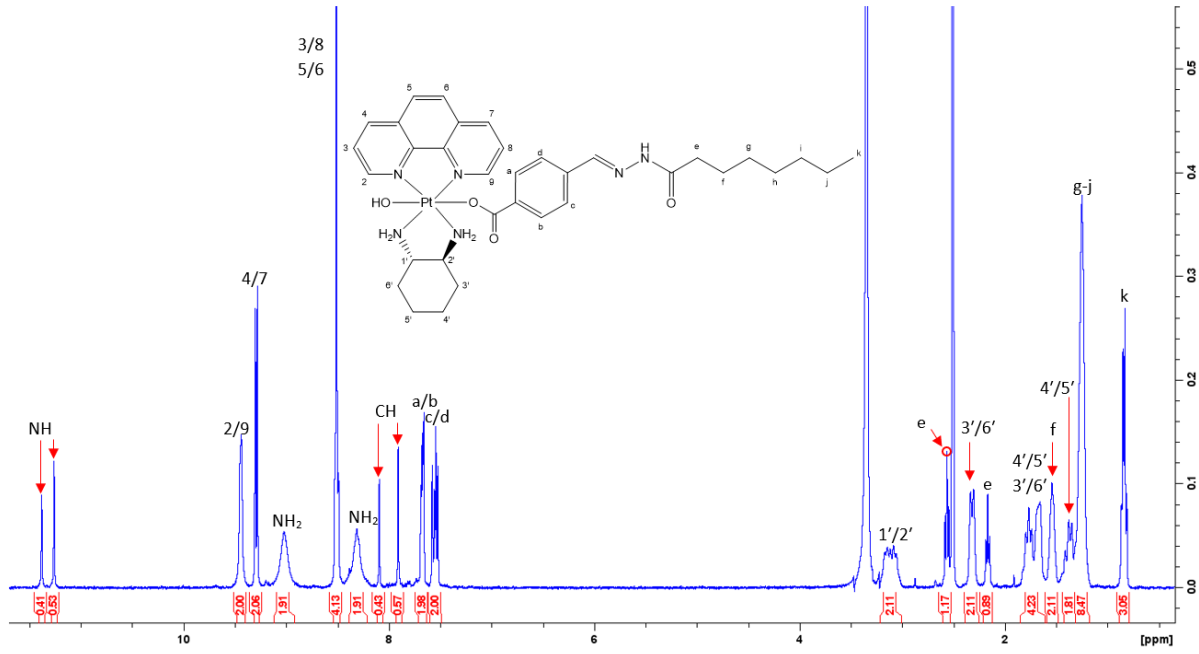


Figure B.30 ^{1}H spectra of Complex **5** in DMSO-d_6 at 298 K.

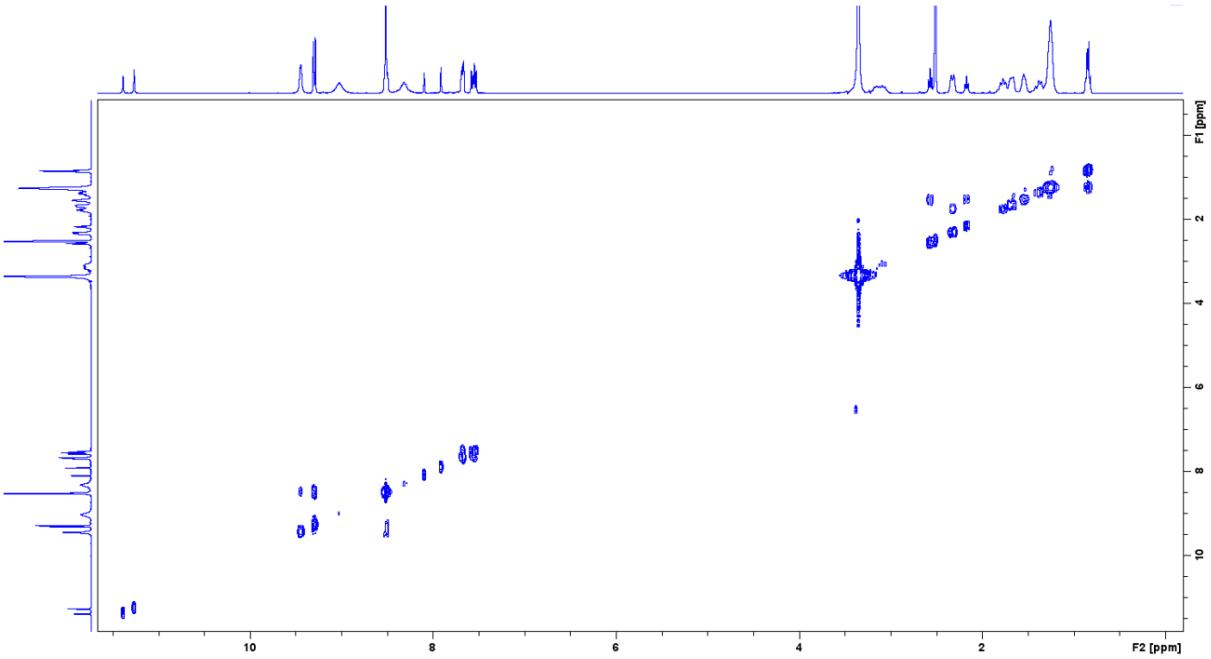


Figure B.31 COSY spectra of Complex **5** in DMSO-d_6 at 298 K.

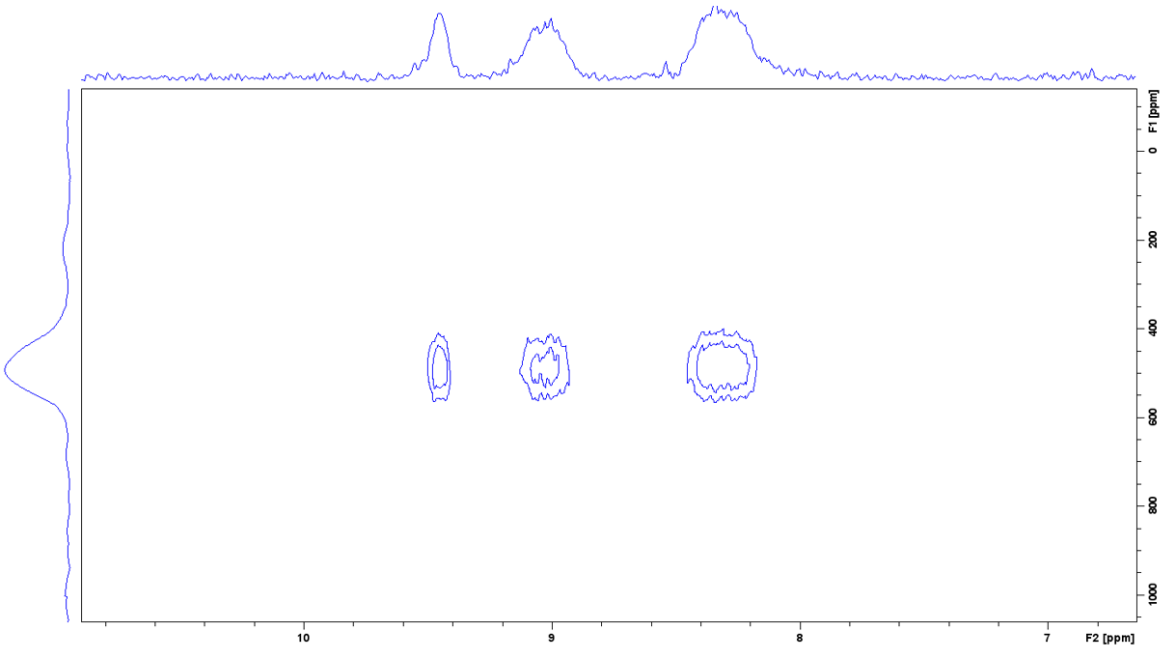


Figure B.32 ^{1}H-^{195}Pt spectra of Complex **5** in DMSO-d_6 at 298 K.

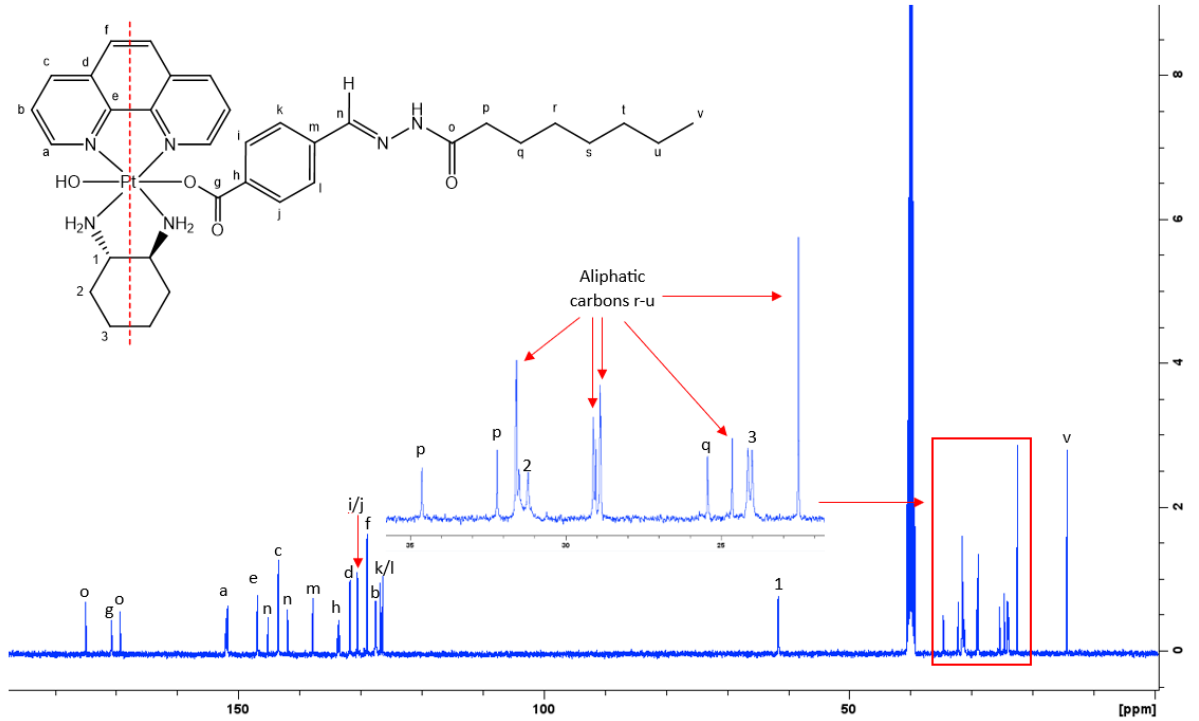


Figure B.33 ^{13}C spectra of Complex **5** in DMSO-d_6 at 298 K. Inset: structure, carbon numbering scheme and zoomed region between 22-35 ppm.

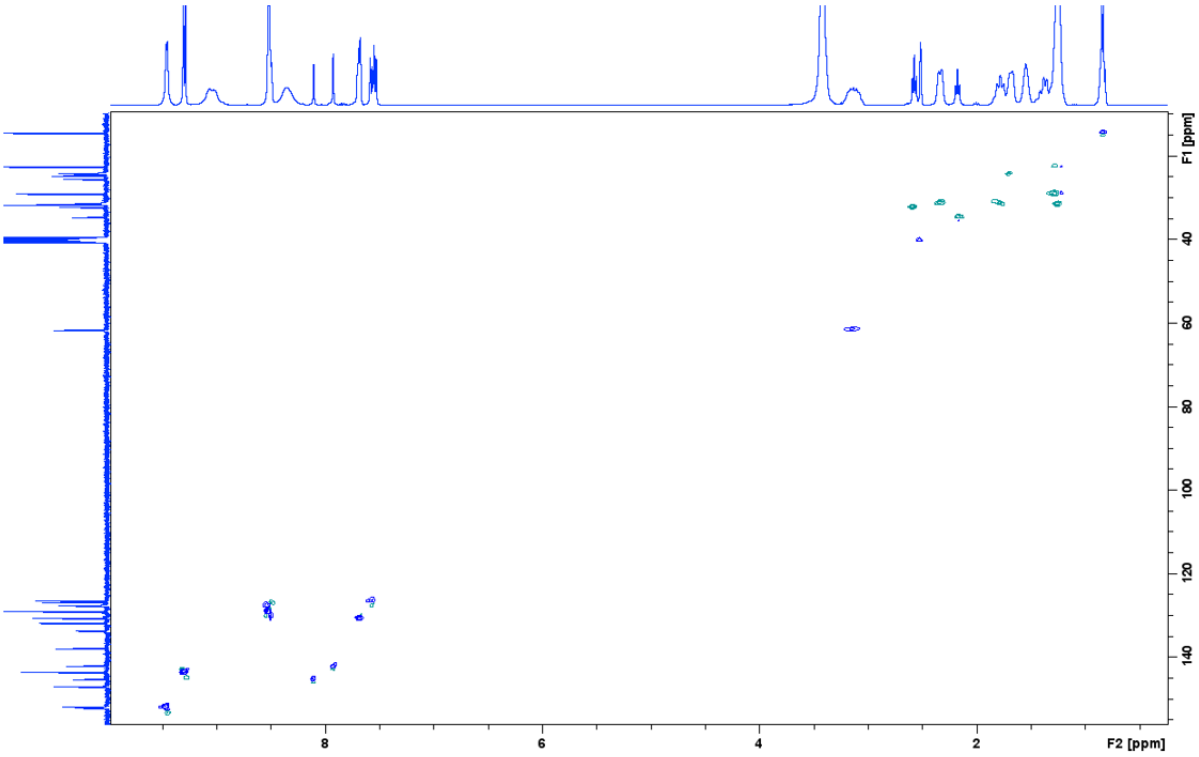


Figure B.34 HSQC spectra of Complex **5** in DMSO-d_6 at 298 K.

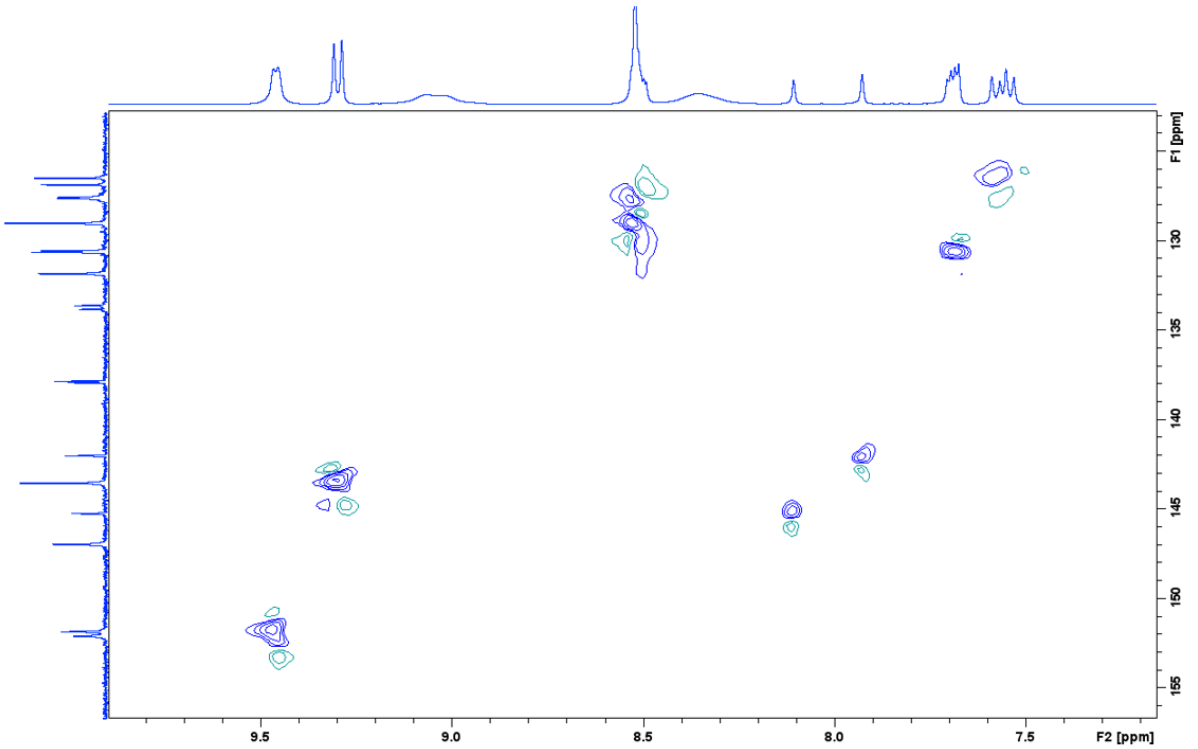


Figure B.35 Zoomed aromatic region of HSQC spectra of Complex **5** in DMSO-d_6 at 298 K.

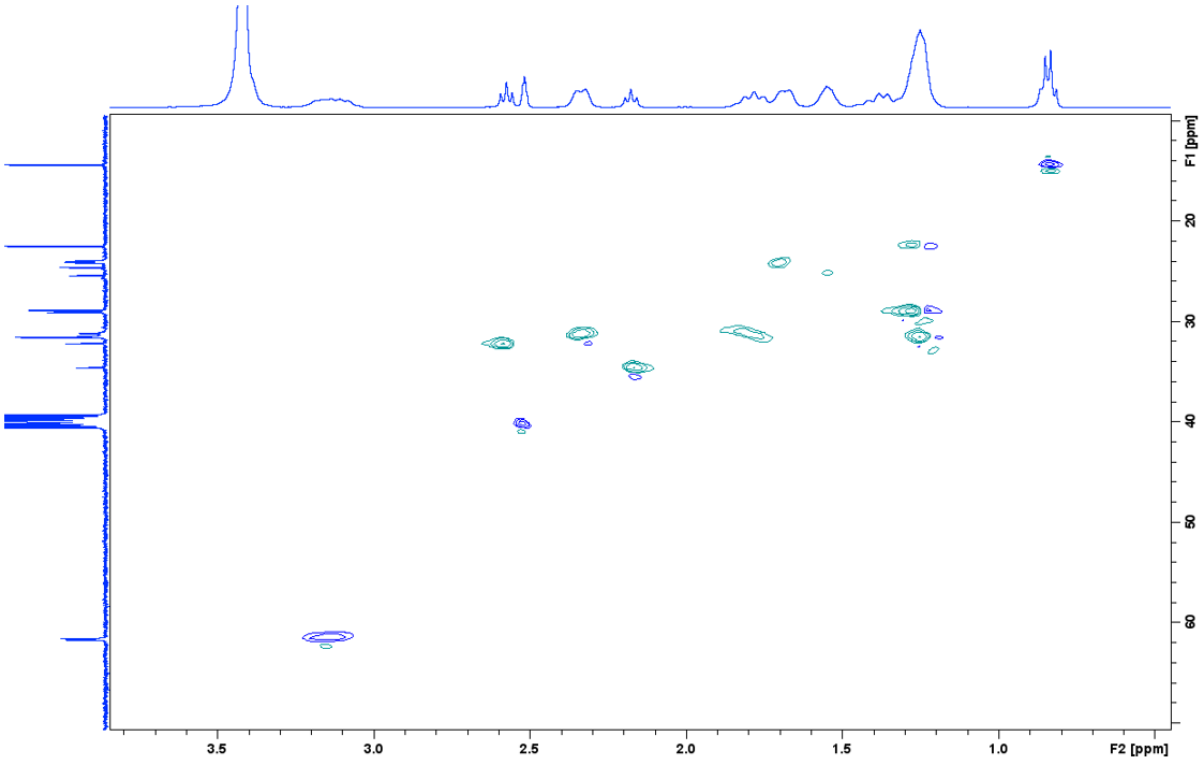


Figure B.36 Zoomed aliphatic region of HSQC spectra of Complex **5** in DMSO-d_6 at 298 K.

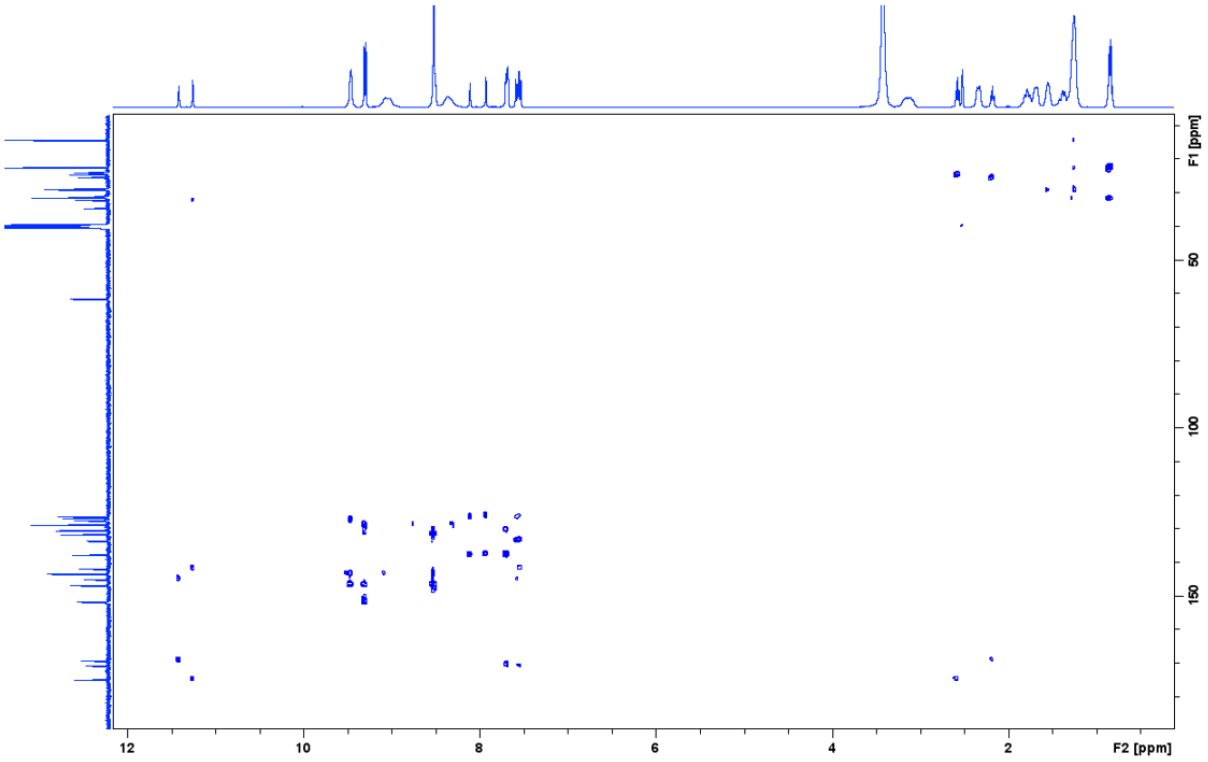


Figure B.37 HMBC spectra of Complex **5** in DMSO-d_6 at 298 K.

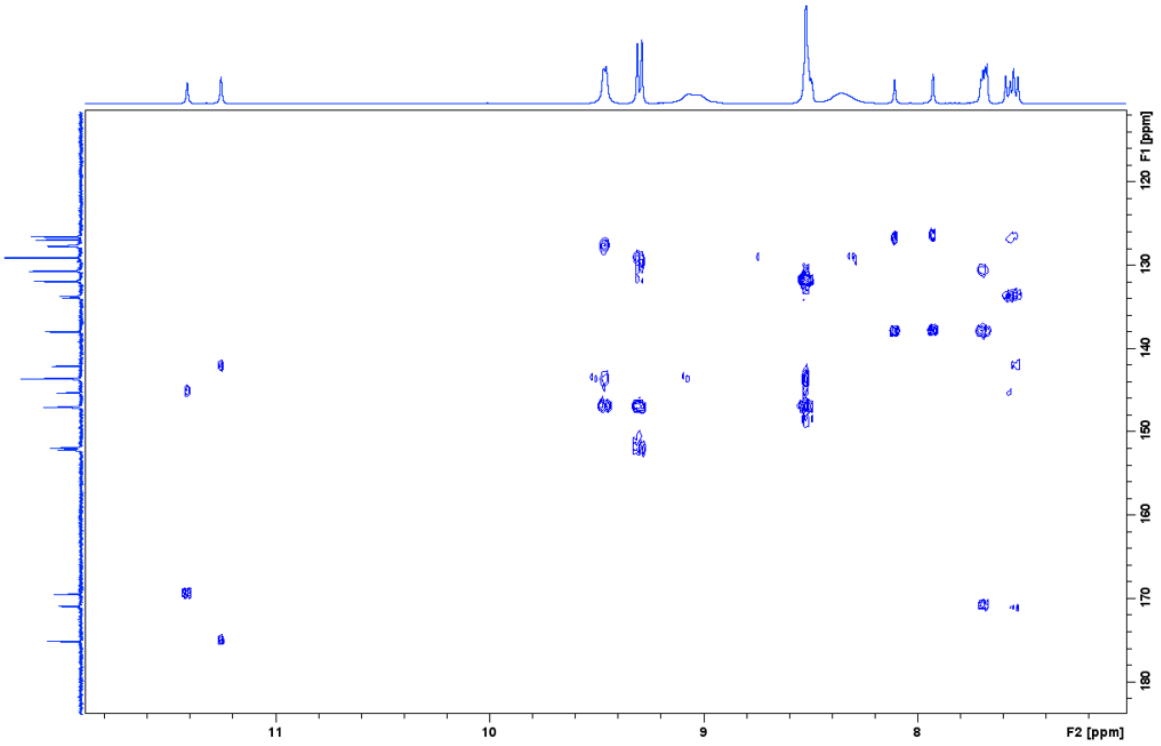


Figure B.38 Zoomed aromatic region of HMBC spectra of Complex **5** in DMSO-d_6 at 298 K.

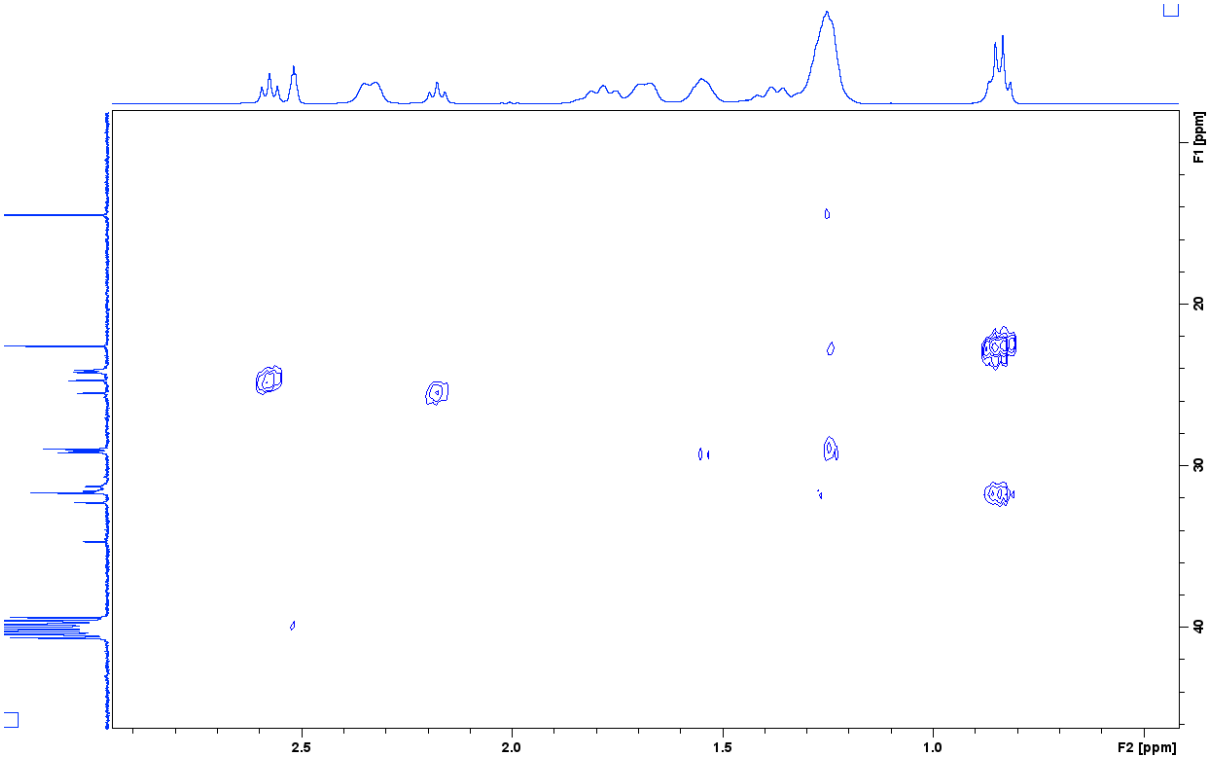


Figure B.39 Zoomed aliphatic region of HMBC spectra of Complex **5** in DMSO-d_6 at 298 K.

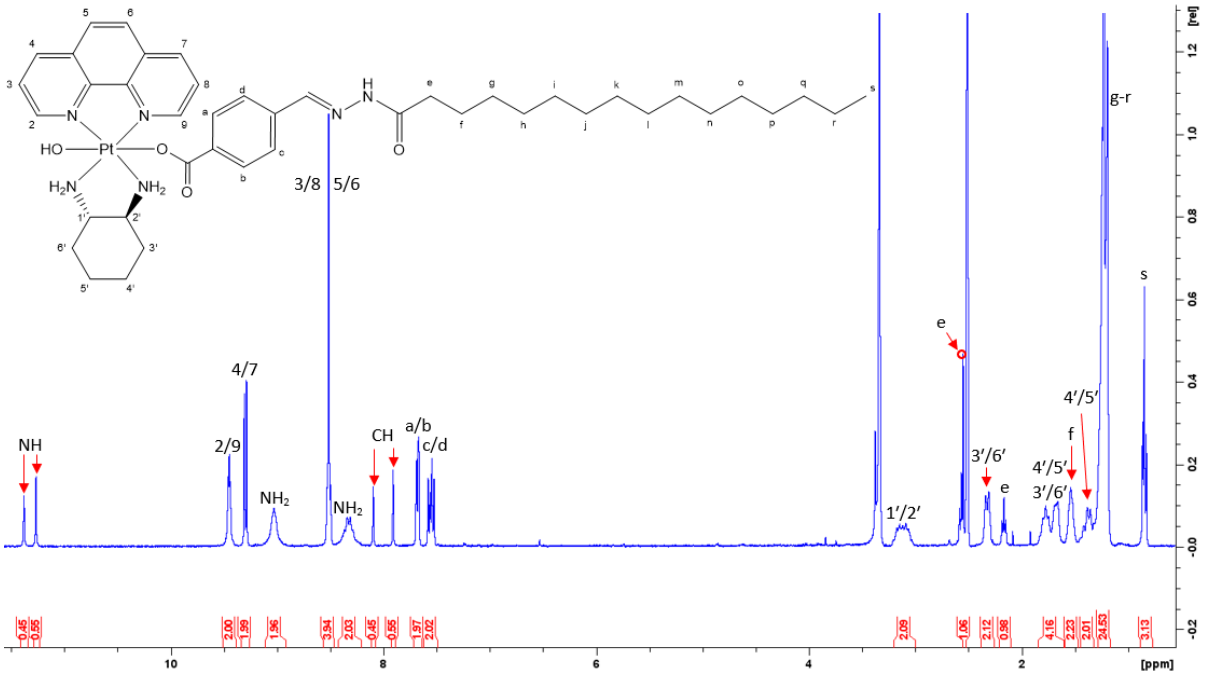


Figure B.40 ^{1}H spectra of Complex **6** in DMSO-d_6 at 298 K. Inset: structure and proton numbering scheme.

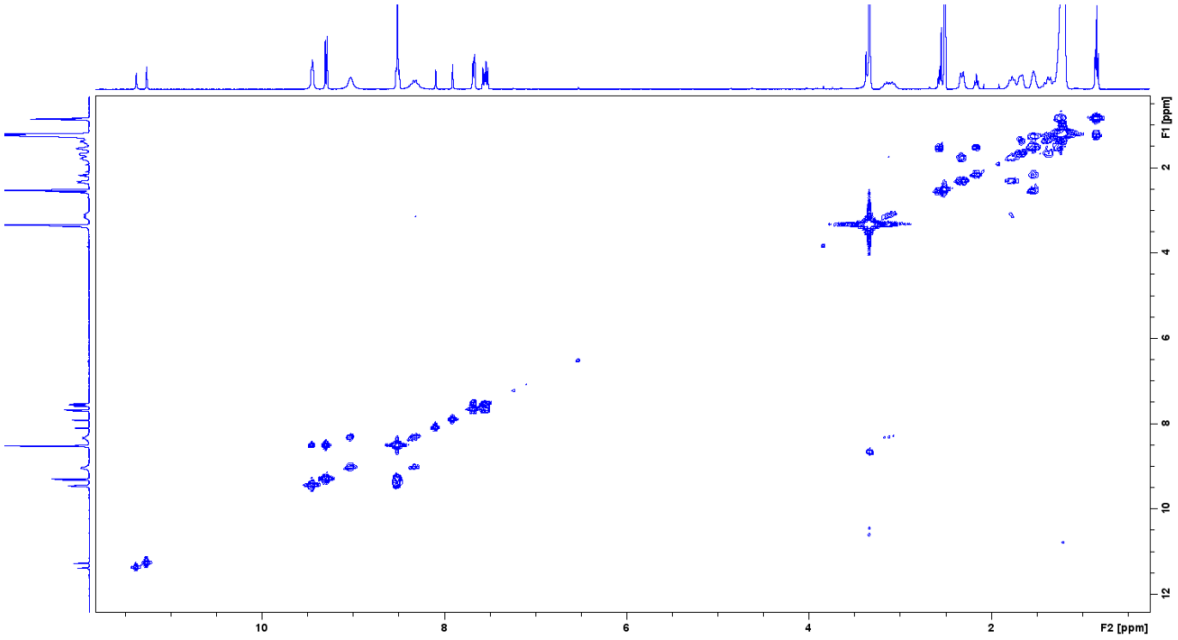


Figure B.41 COSY spectra of Complex **6** in DMSO-d_6 at 298 K.

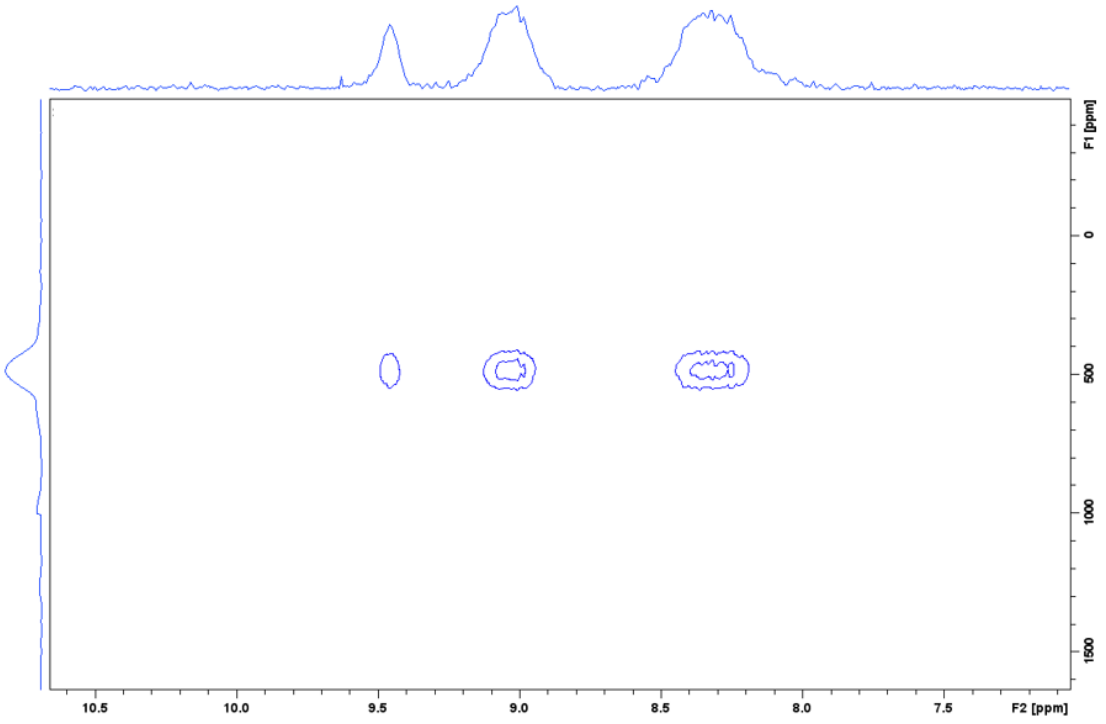


Figure B.42 ^{1}H-^{195}Pt spectra of Complex **6** in DMSO-d_6 at 298 K.

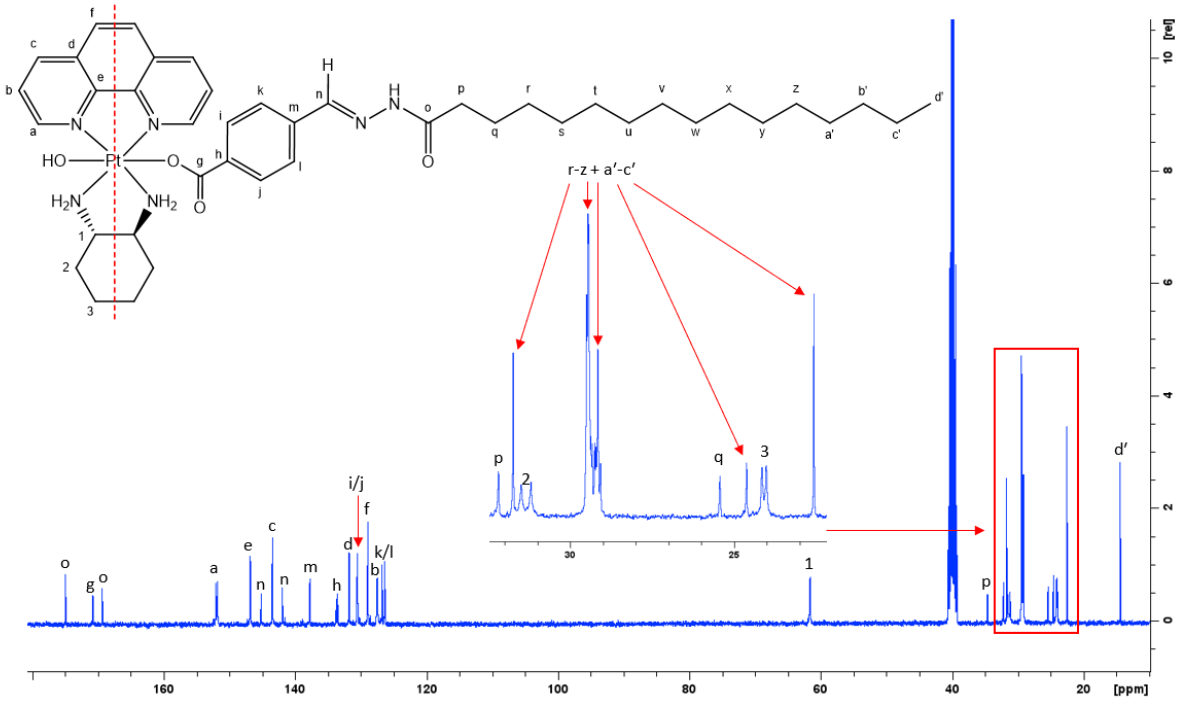


Figure B.43 ^{13}C spectra of Complex **6** in DMSO-d_6 at 298 K. Inset: structure, carbon numbering scheme and zoomed region between 22-33 ppm.

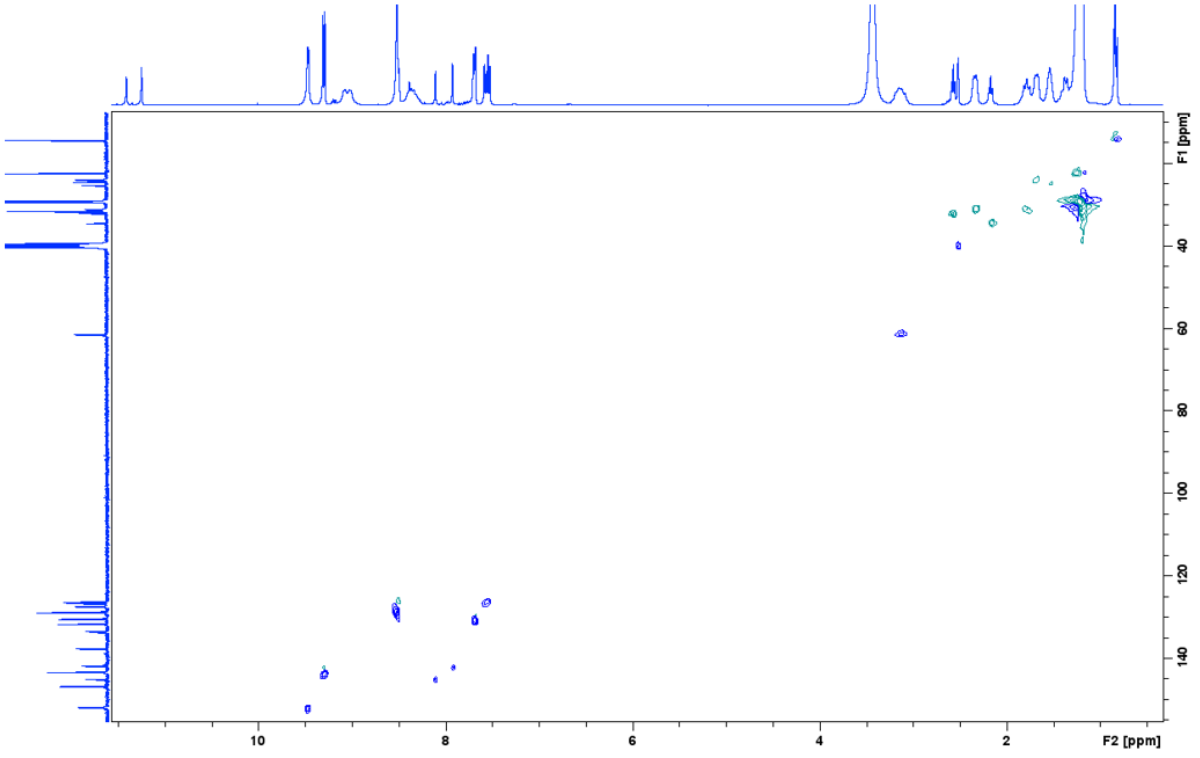


Figure B.44 HSQC spectra of Complex **6** in DMSO-d_6 at 298 K.

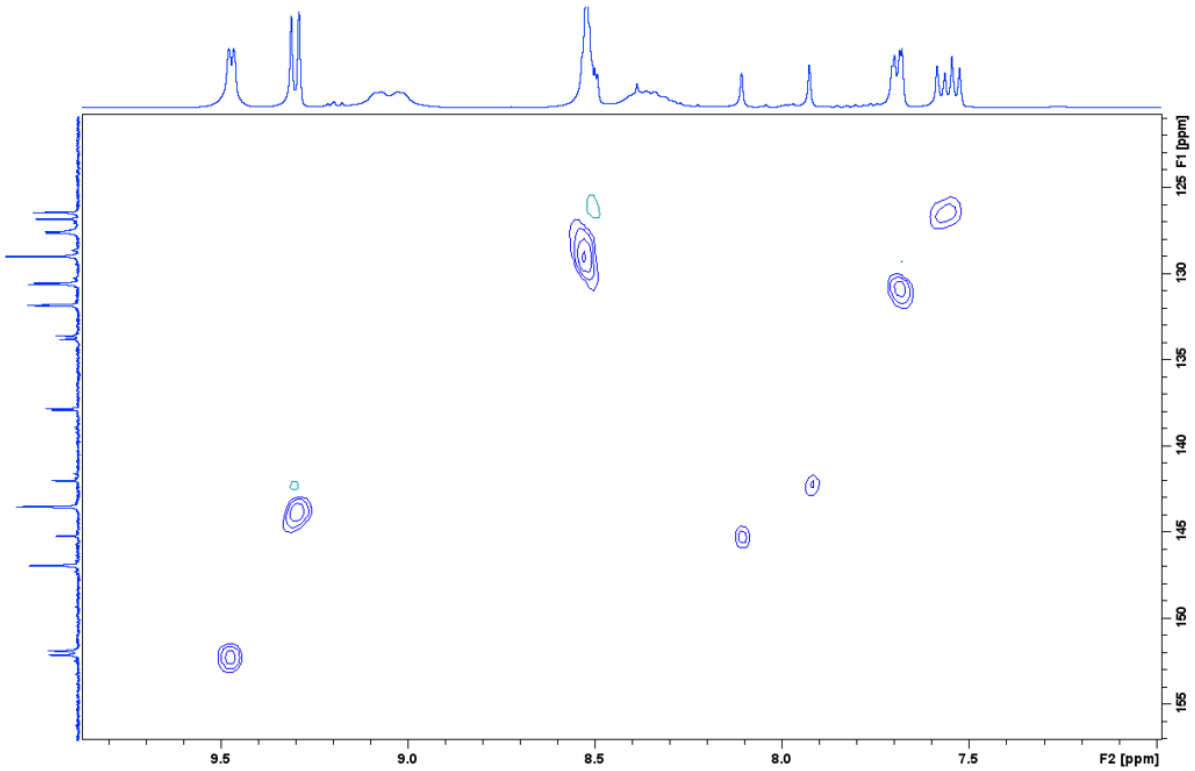


Figure B.45 Zoomed aromatic region of HSQC spectra of Complex **6** in DMSO-d_6 at 298 K.

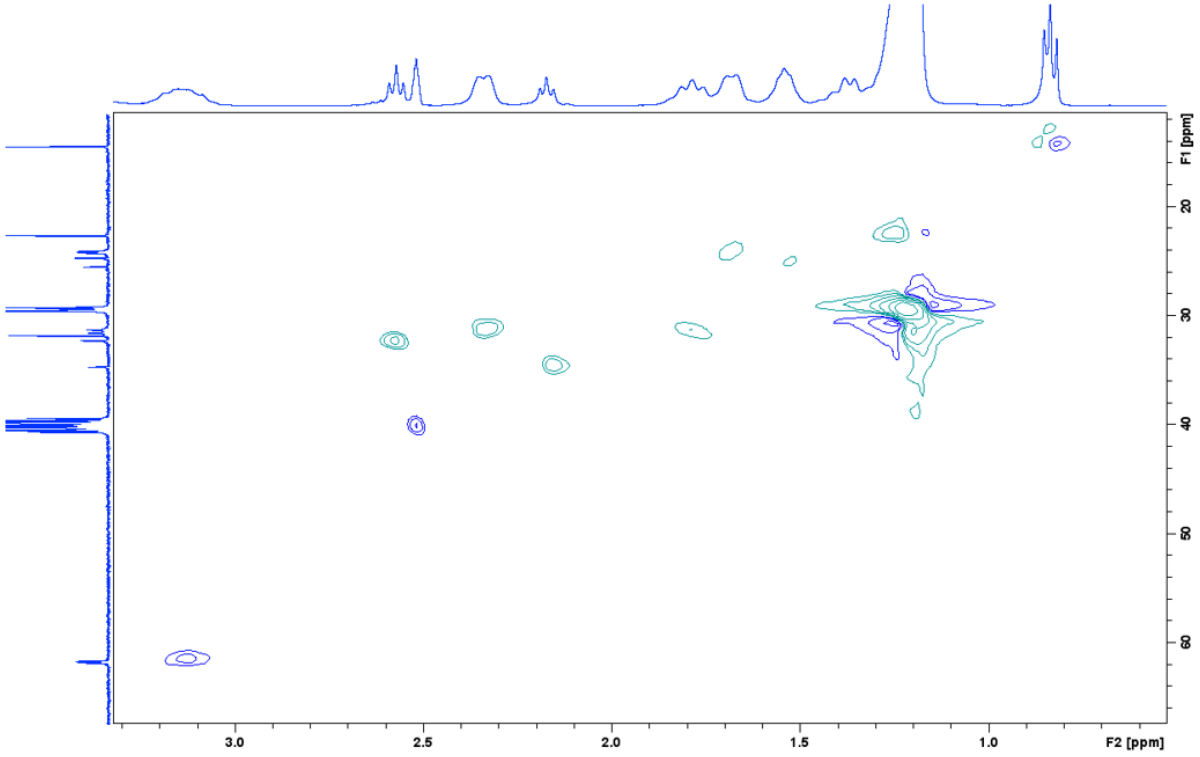


Figure B.46 Zoomed aliphatic region of HSQC spectra of Complex **6** in DMSO-d_6 at 298 K.

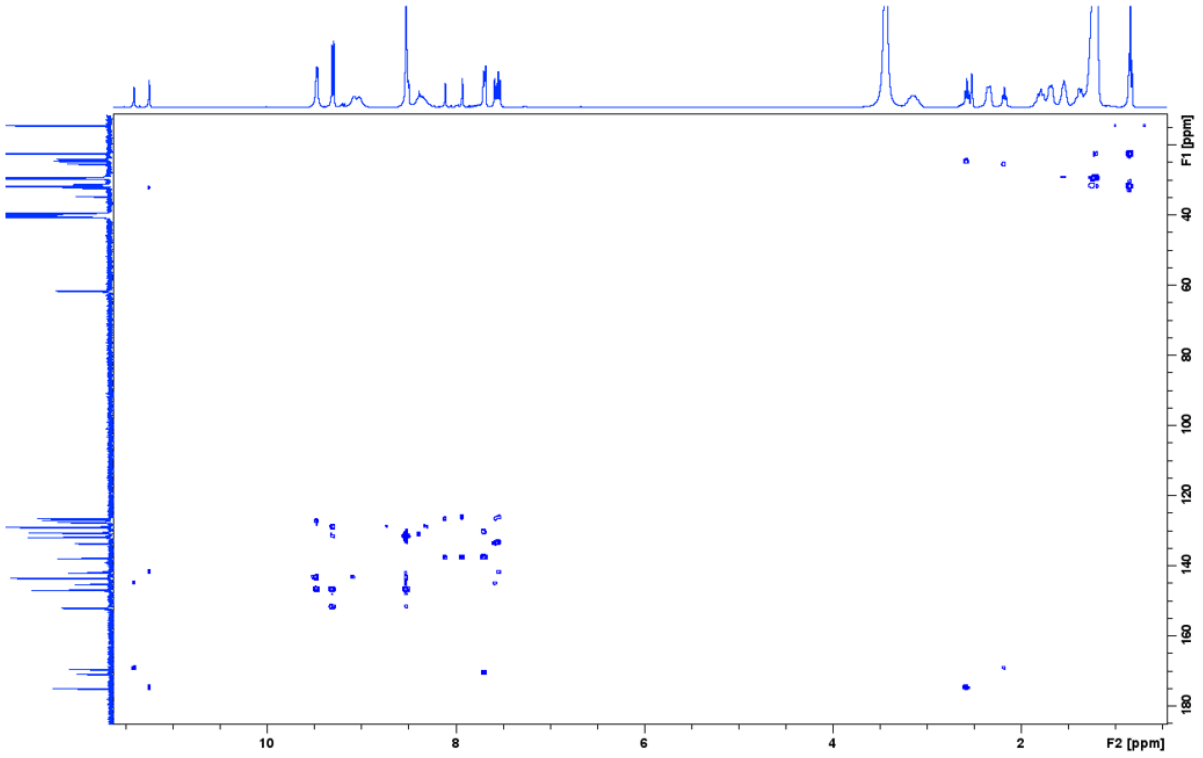


Figure B.47 HMBC spectra of Complex **6** in DMSO-d_6 at 298 K.

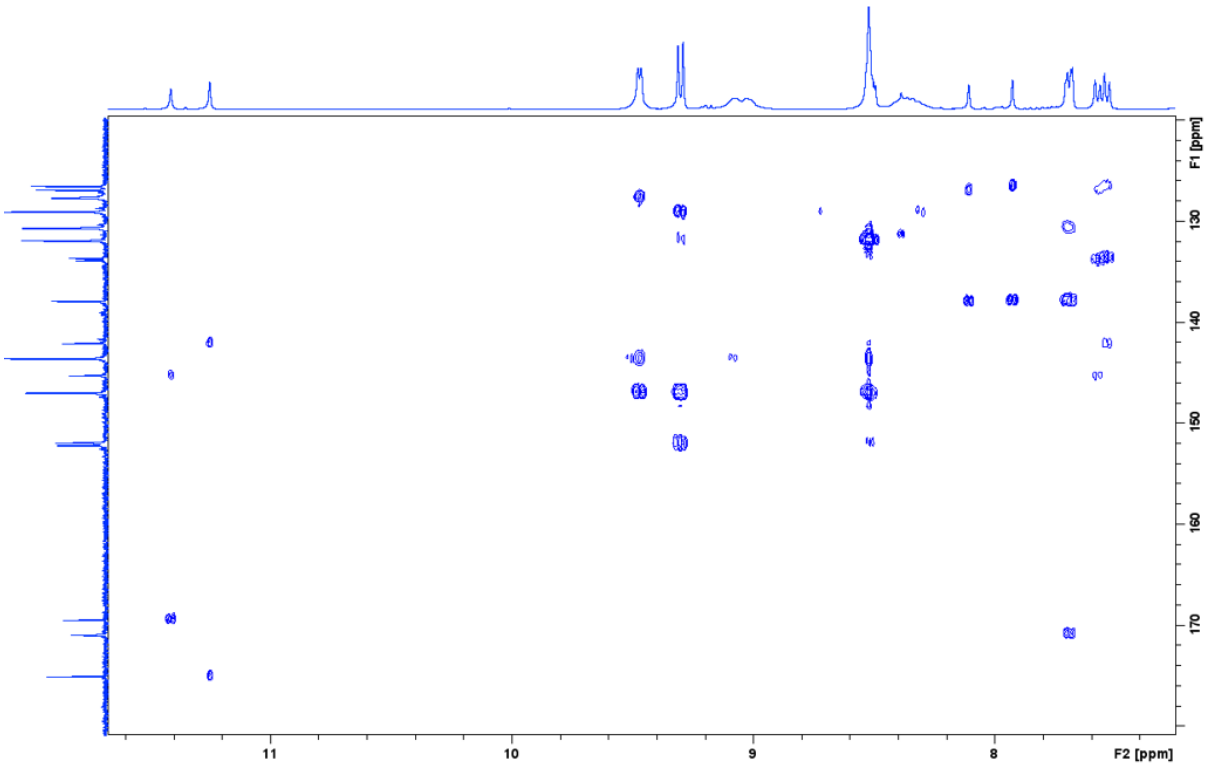


Figure B.48 Zoomed aromatic region of HMBC spectra of Complex **6** in DMSO-d_6 at 298 K.

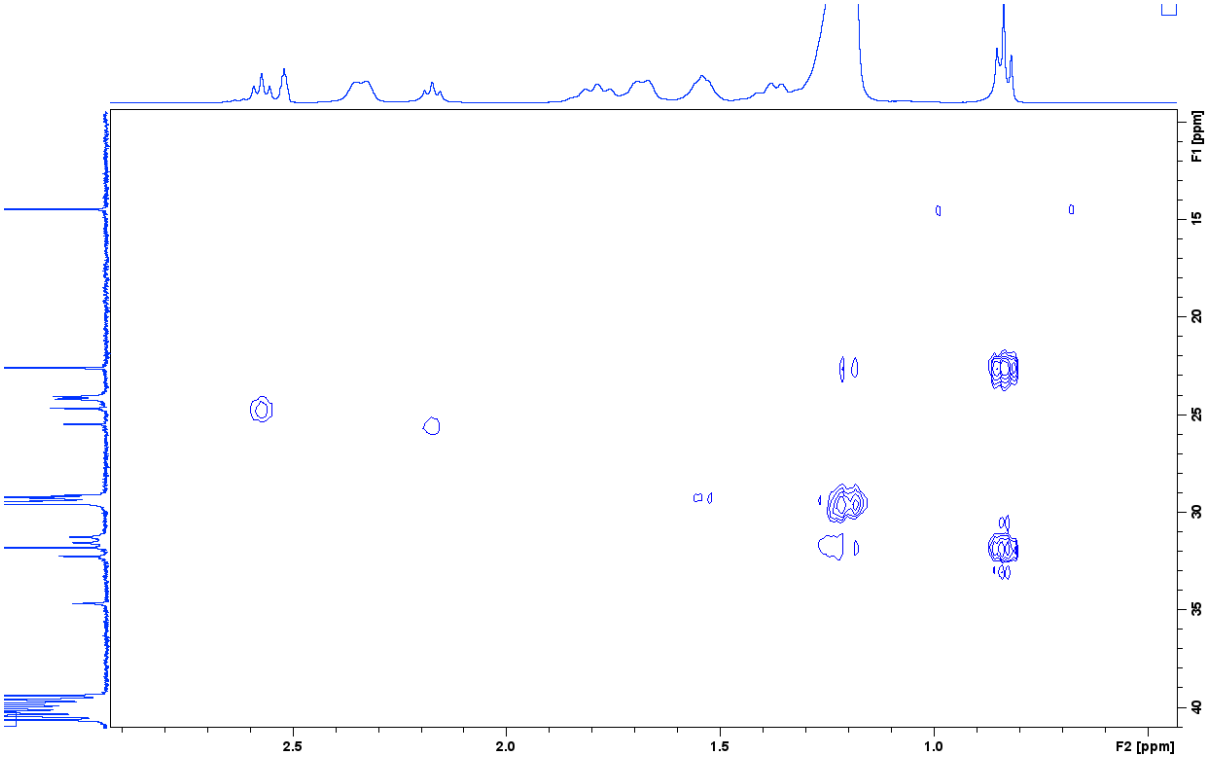


Figure B.49 Zoomed aliphatic region of HMBC spectra of Complex **6** in DMSO-d_6 at 298 K.

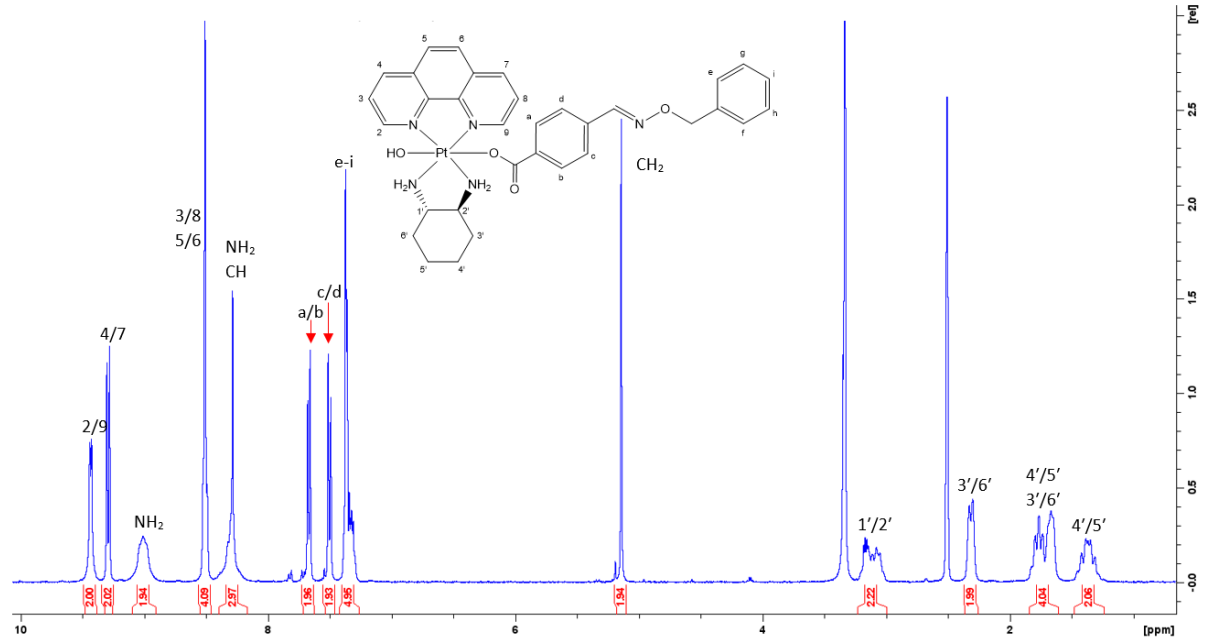


Figure B.50 ^{1}H spectra of Complex **7** in DMSO-d_6 at 298 K. Inset: structure and proton numbering scheme.

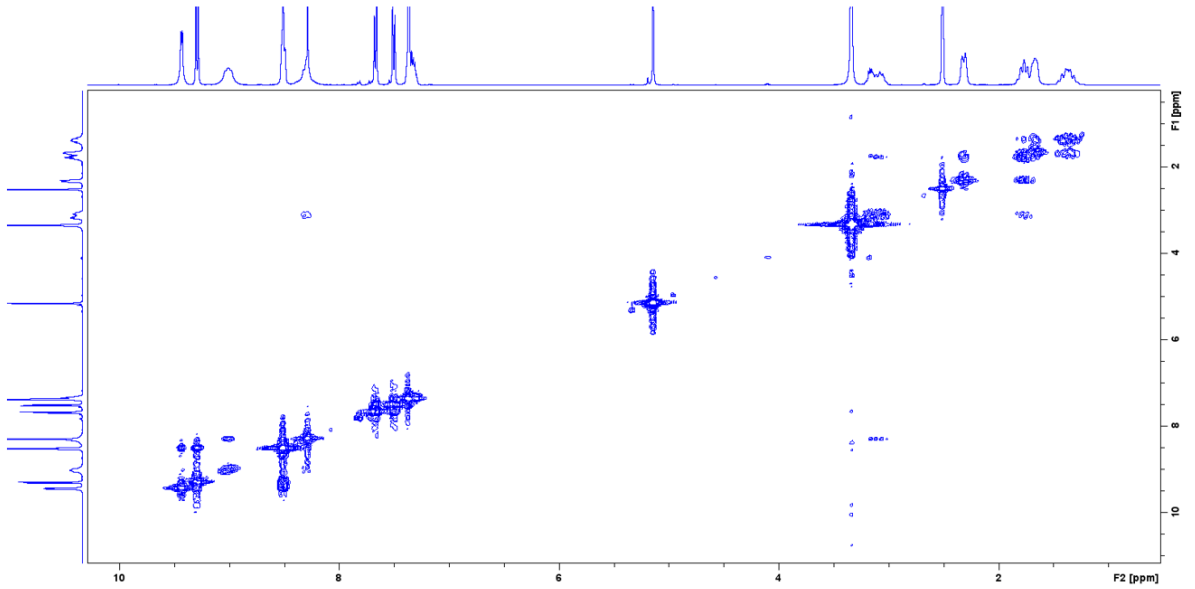


Figure B.51 COSY spectra of Complex **7** in DMSO-d_6 at 298 K.

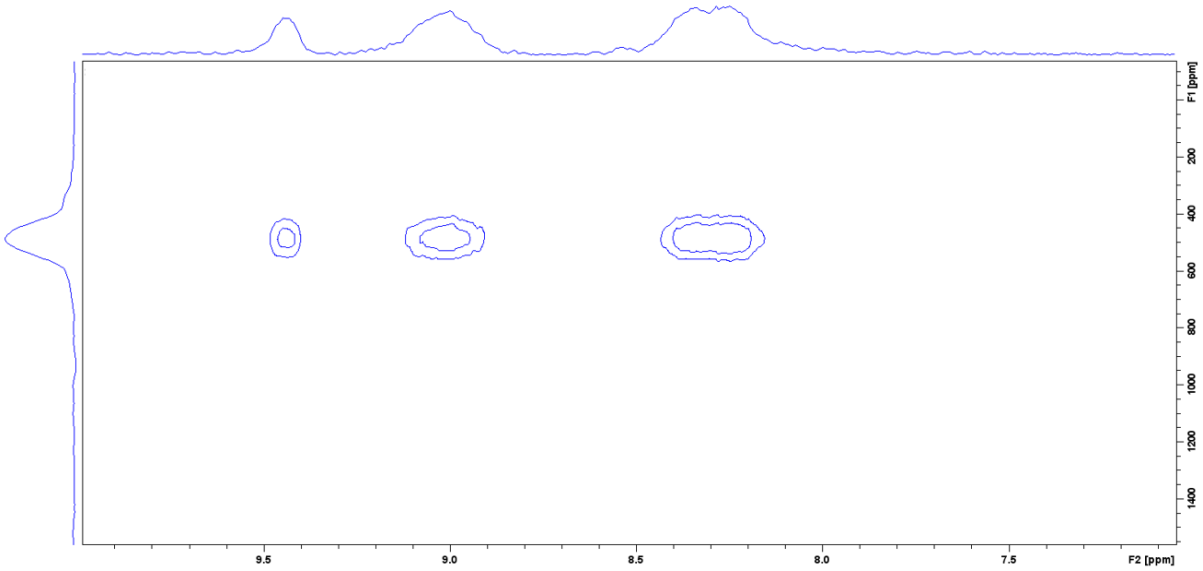


Figure B.52 ^{1}H-^{195}Pt spectra of Complex **7** in DMSO-d_6 at 298 K.

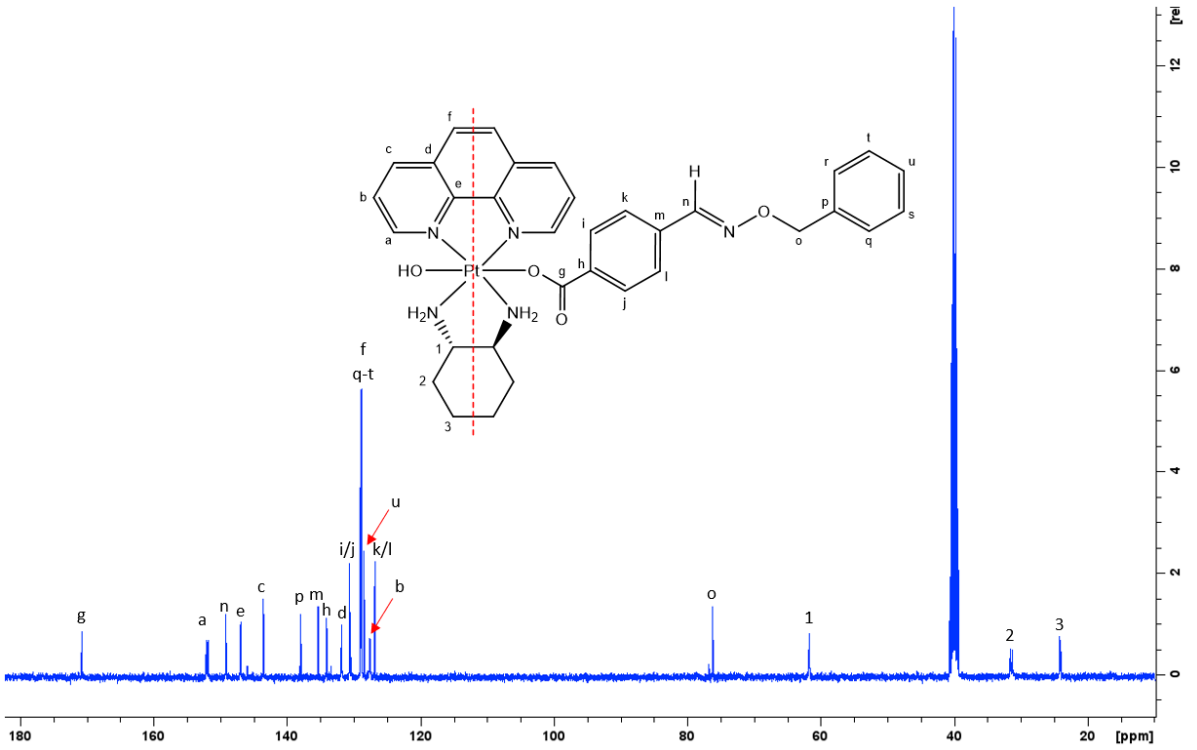


Figure B.53 ^{13}C spectra of Complex **7** in DMSO-d_6 at 298 K. Inset: structure and carbon numbering scheme.

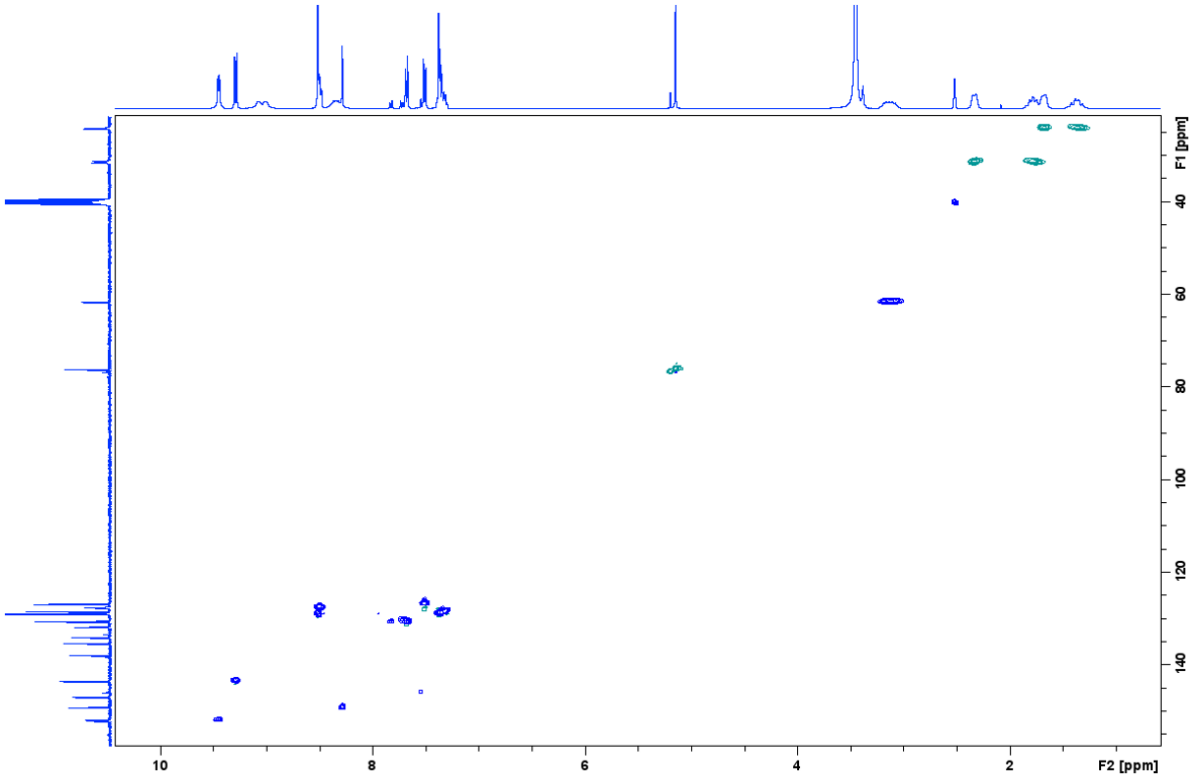


Figure B.54 HSQC spectra of Complex **7** in DMSO-d_6 at 298 K.

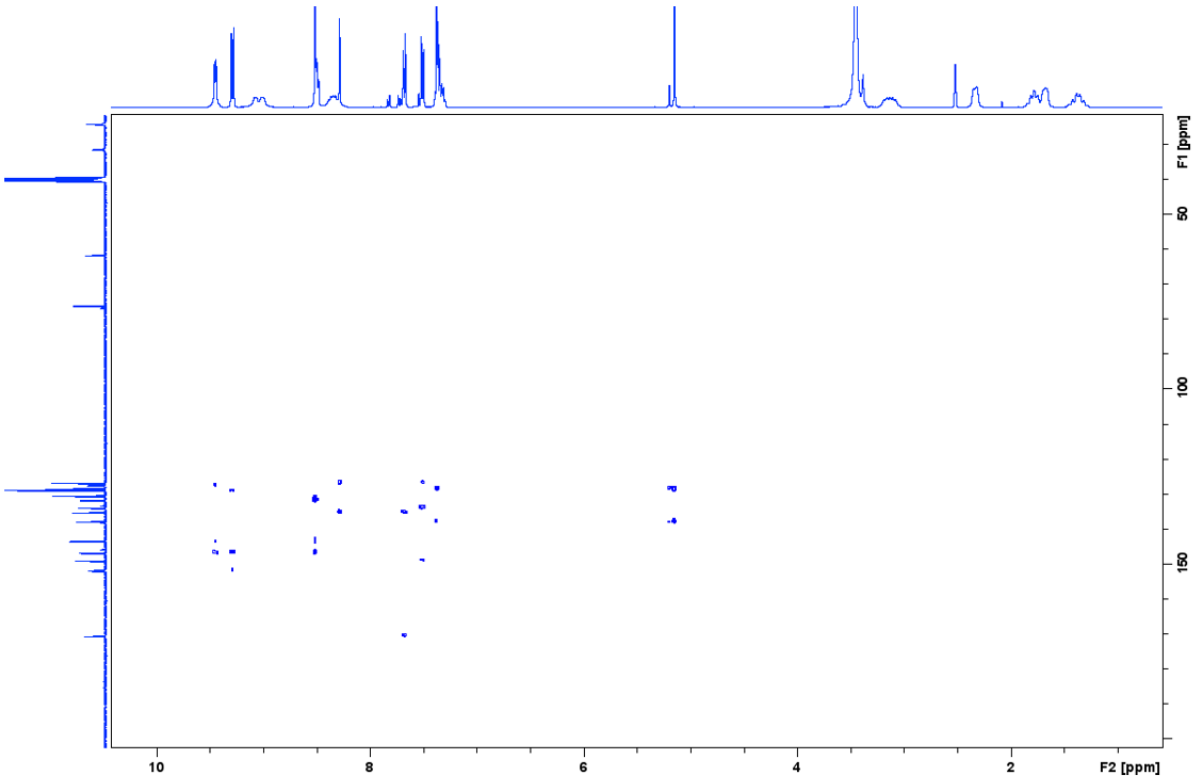


Figure B.55 HMBC spectra of Complex **7** in DMSO-d_6 at 298 K.

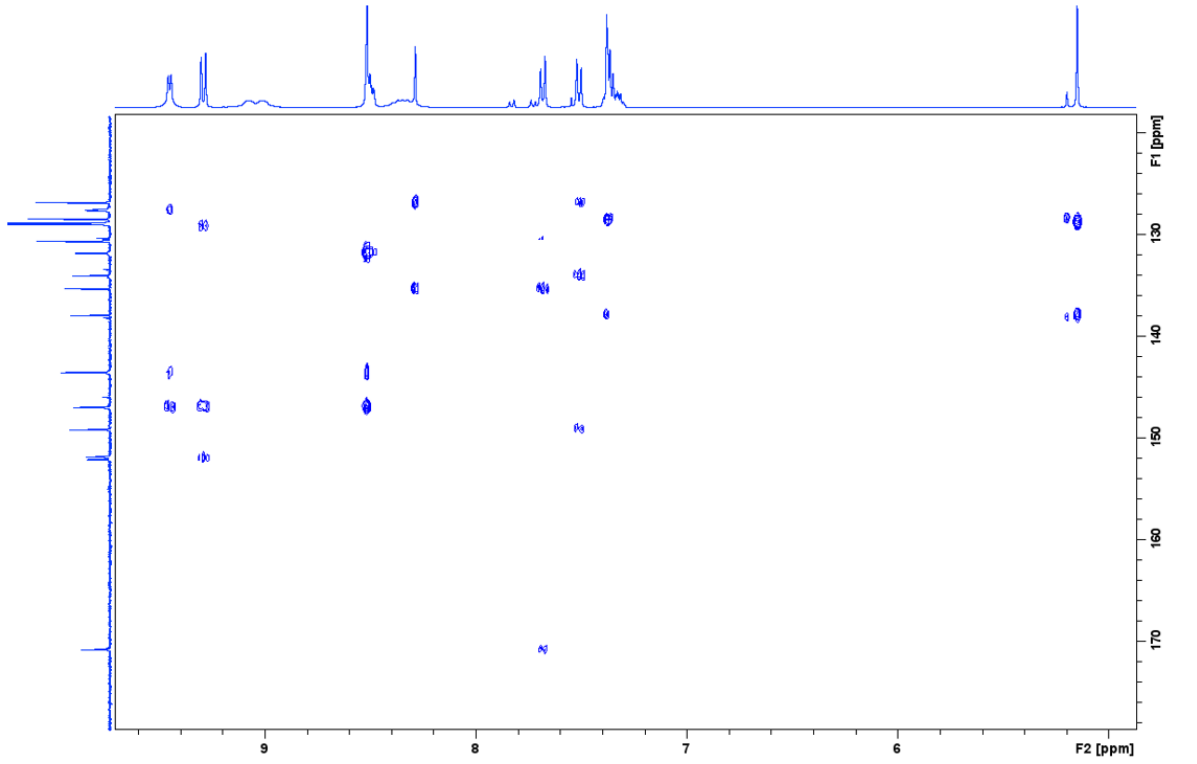


Figure B.56 Zoomed aromatic region of HMBC spectra of Complex **7** in DMSO-d_6 at 298 K.

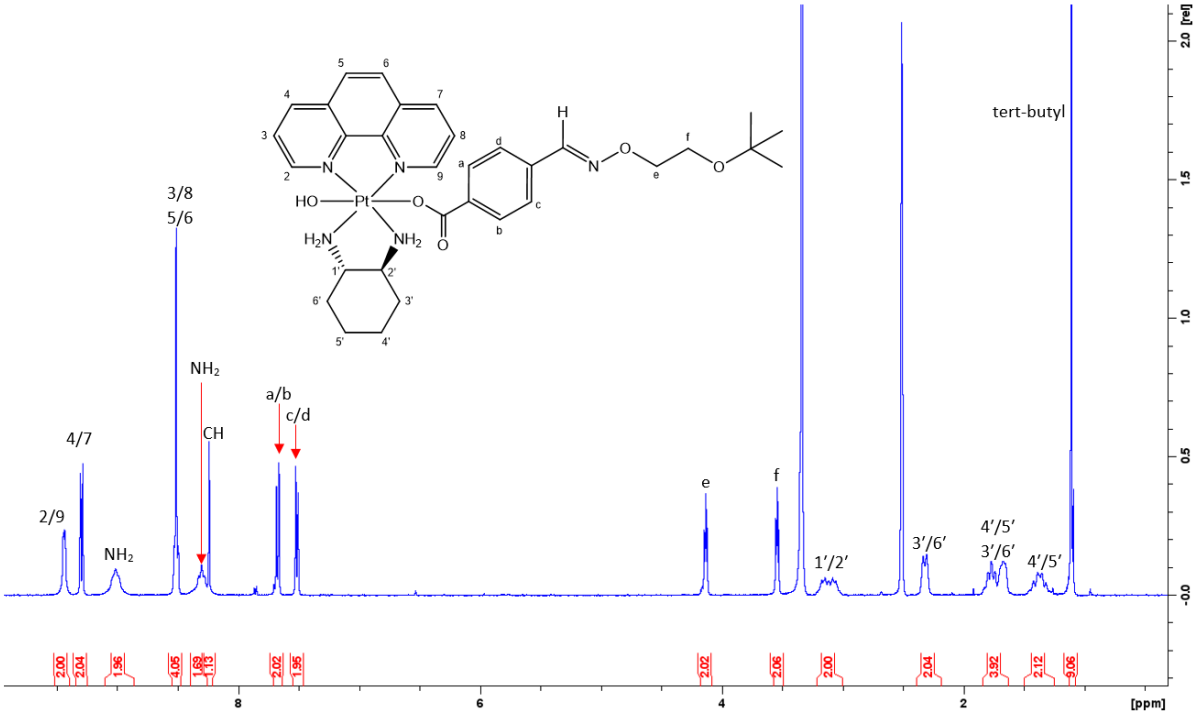


Figure B.57 ^{1}H spectra of Complex **8** in DMSO-d_6 at 298 K. Inset: structure and proton numbering scheme.

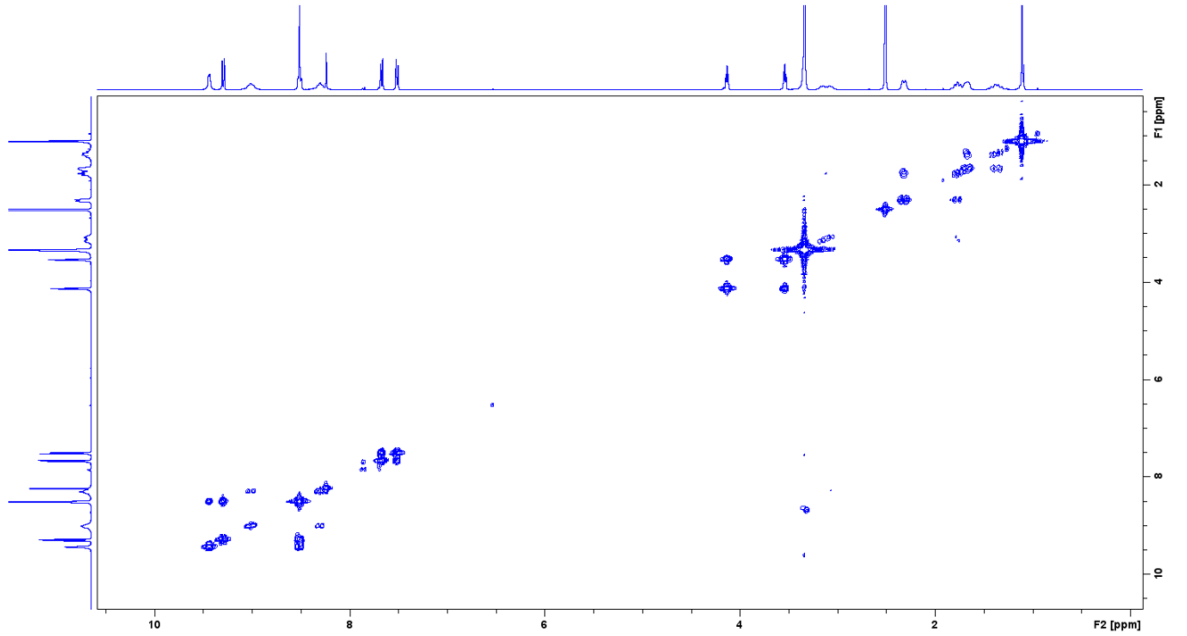


Figure B.58 COSY spectra of Complex **8** in DMSO-d_6 at 298 K.

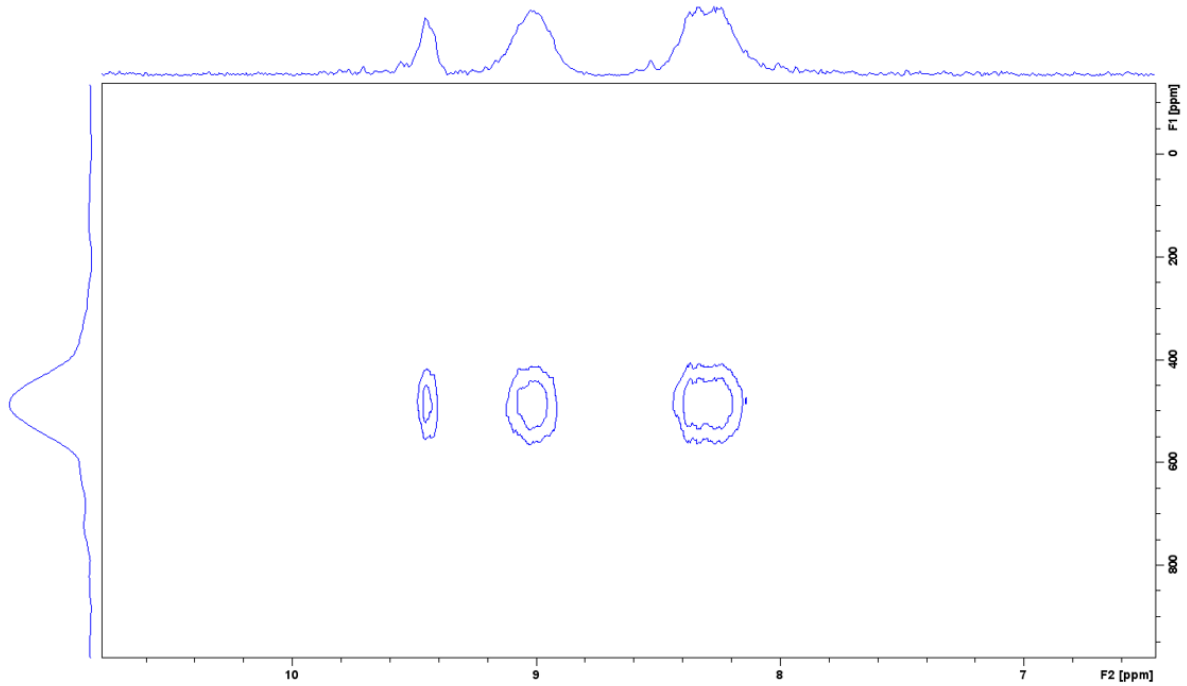


Figure B.59 ^{1}H-^{195}Pt spectra of Complex **8** in DMSO-d_6 at 298 K.

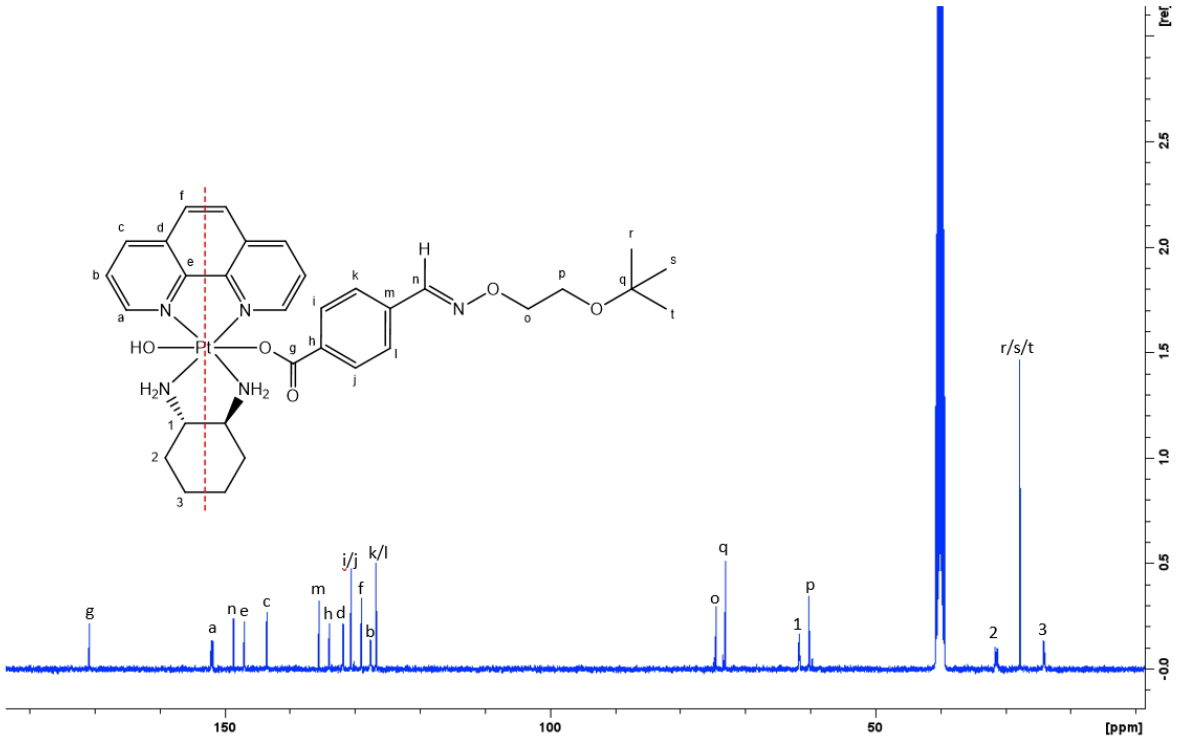


Figure B.60 ^{13}C spectra of Complex **8** in DMSO-d_6 at 298 K. Inset: structure and carbon numbering scheme.

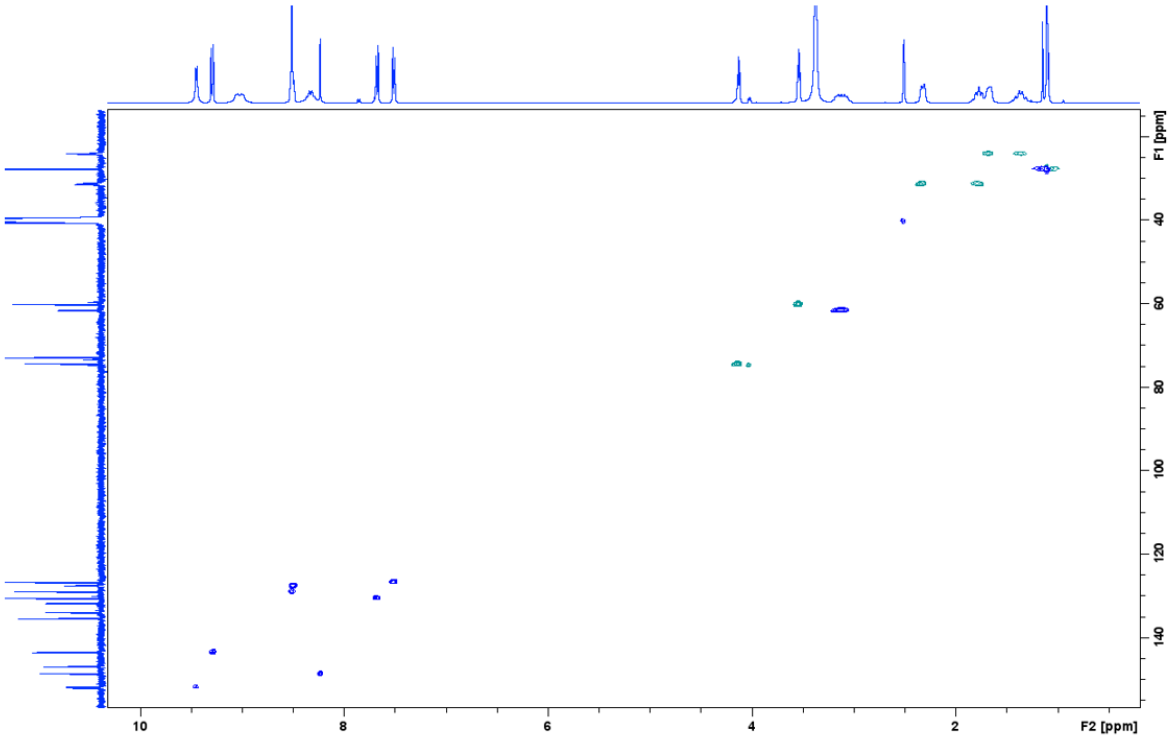


Figure B.61 HSQC spectra of Complex **8** in DMSO-d_6 at 298 K.

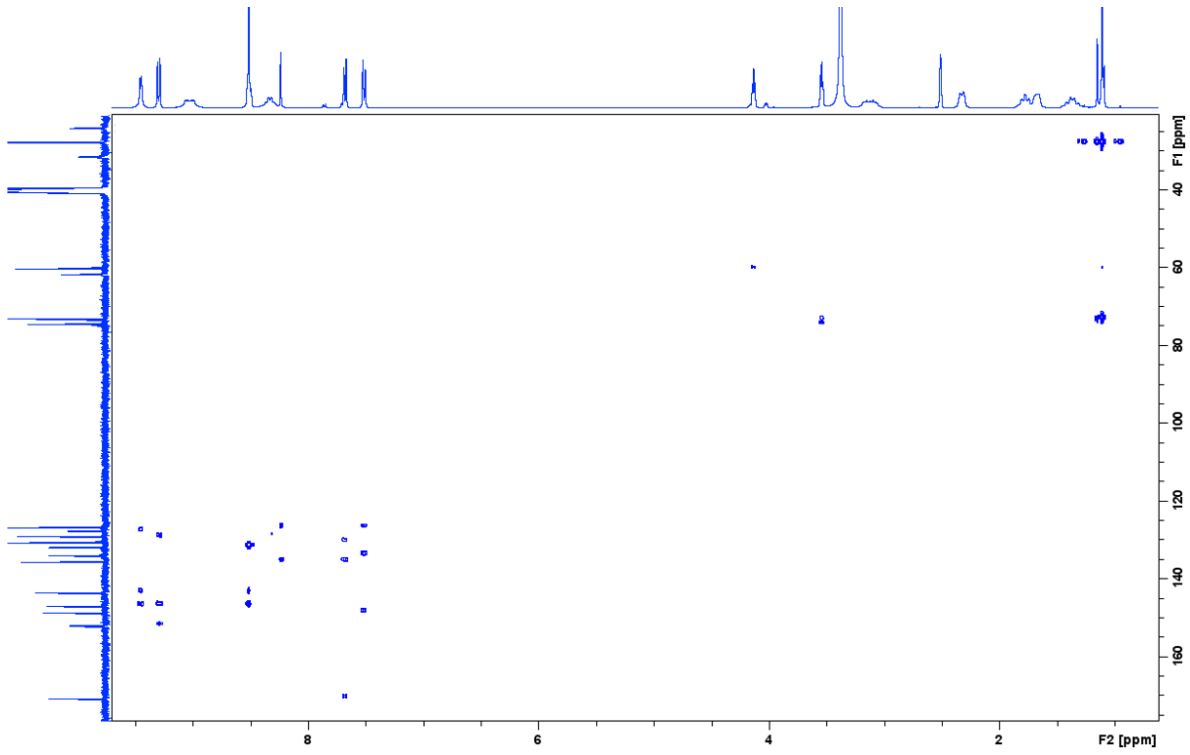


Figure B.62 HMBC spectra of Complex **8** in DMSO-d_6 at 298 K.

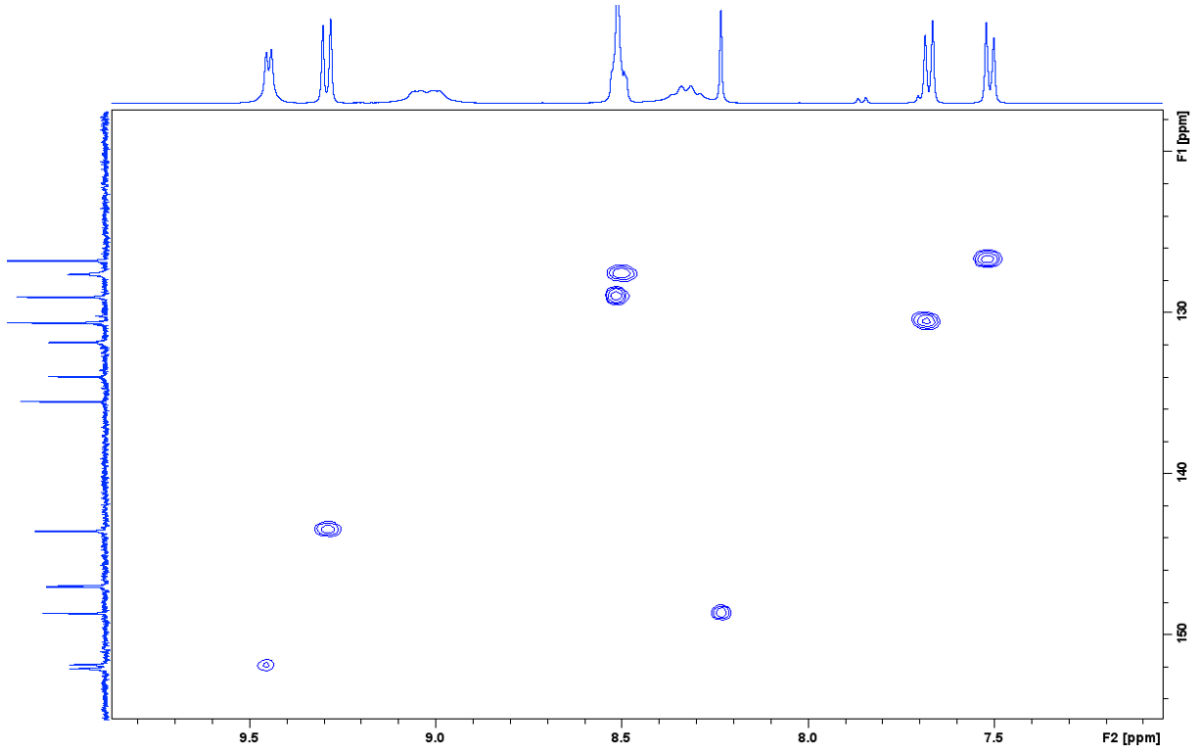


Figure B.63 Zoomed aromatic region of HMBC spectra of Complex **8** in DMSO-d_6 at 298 K.

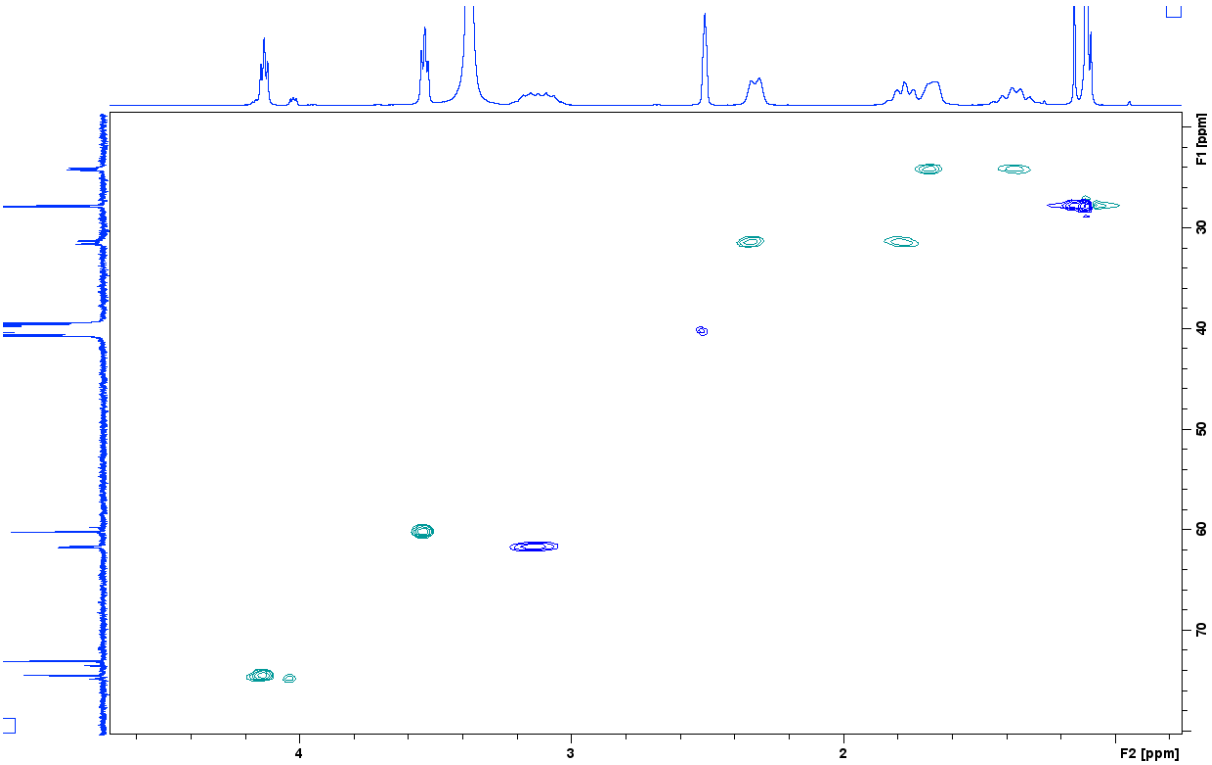


Figure B.64 Zoomed aliphatic region of HMBC spectra of Complex **8** in DMSO-d_6 at 298 K.

C. ESI-MS

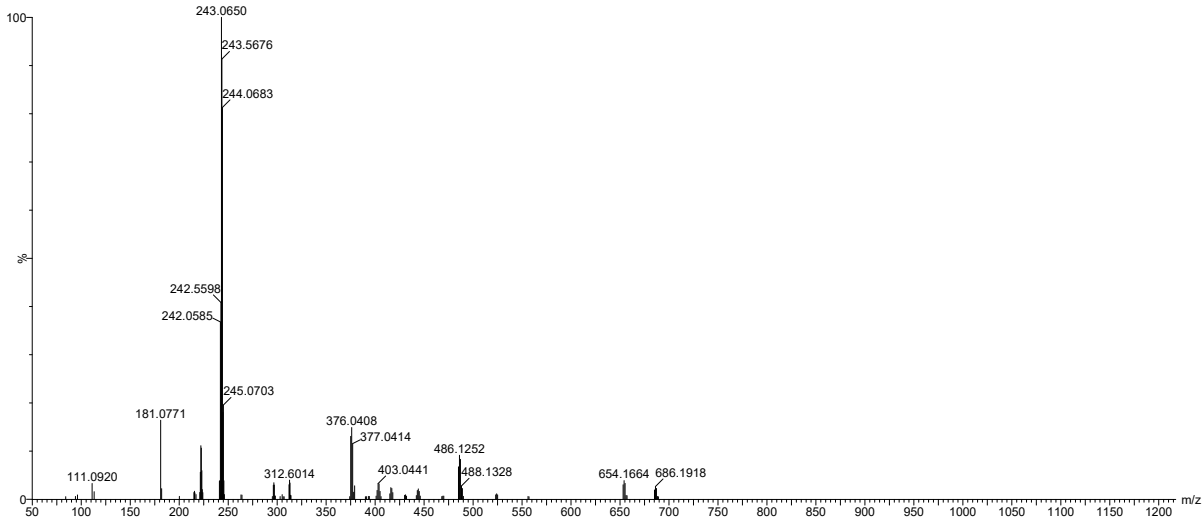


Figure C.1 Full ESI MS spectrum of Complex **1**

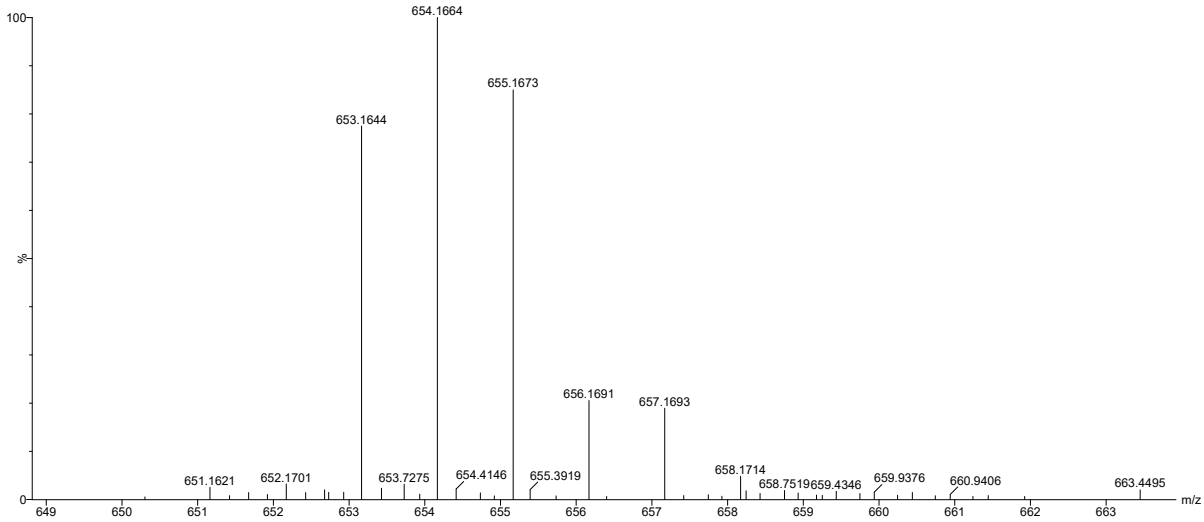


Figure C.2 Expanded $[M-H]^+$ peak for Complex **1**

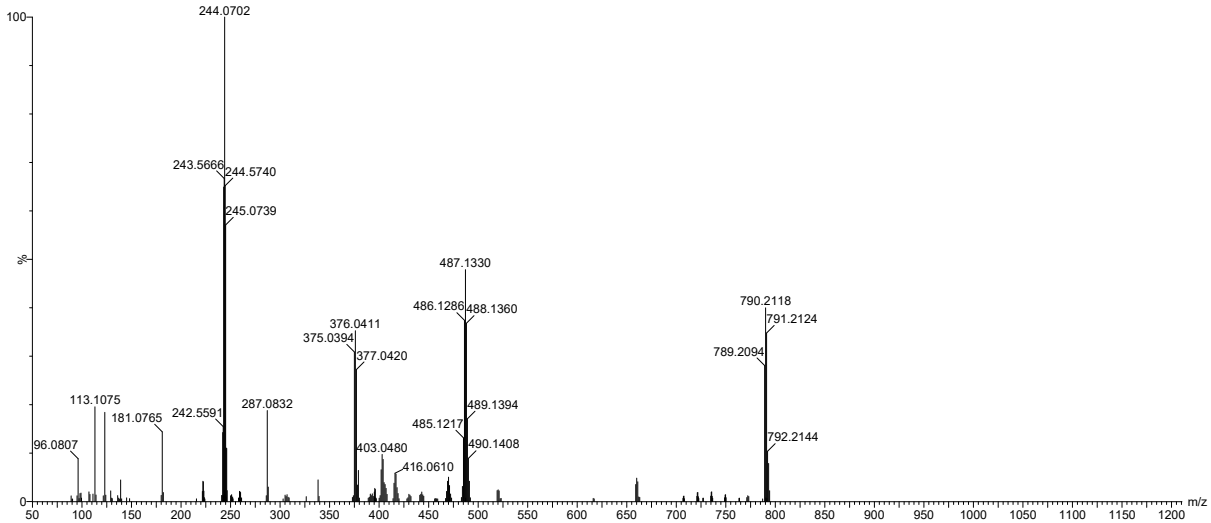


Figure C.3 Full ESI MS spectrum of Complex **2**

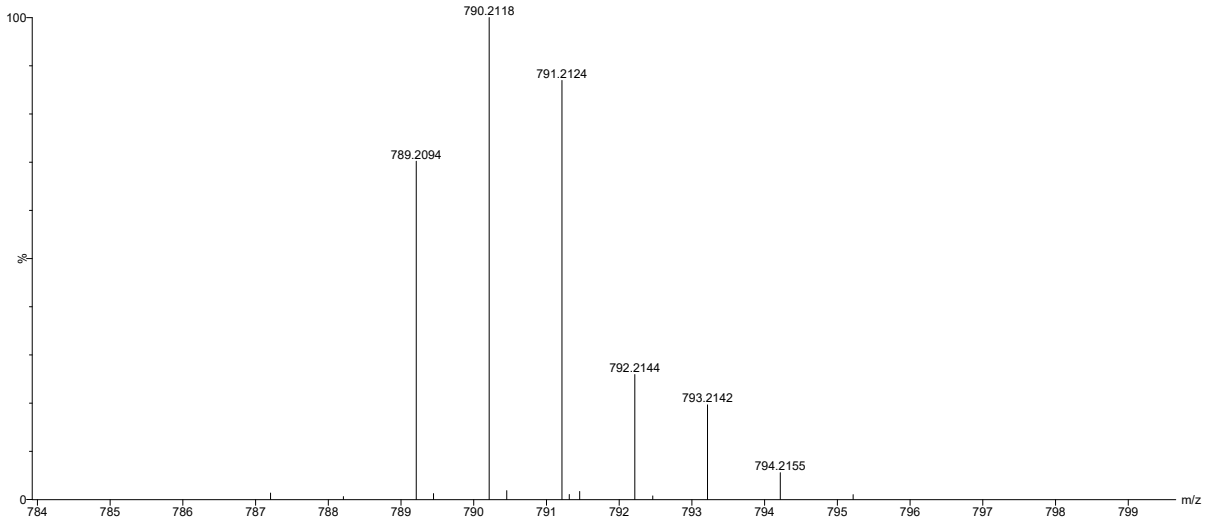


Figure C.4 Expanded $[M-H]^+$ peak for Complex **2**

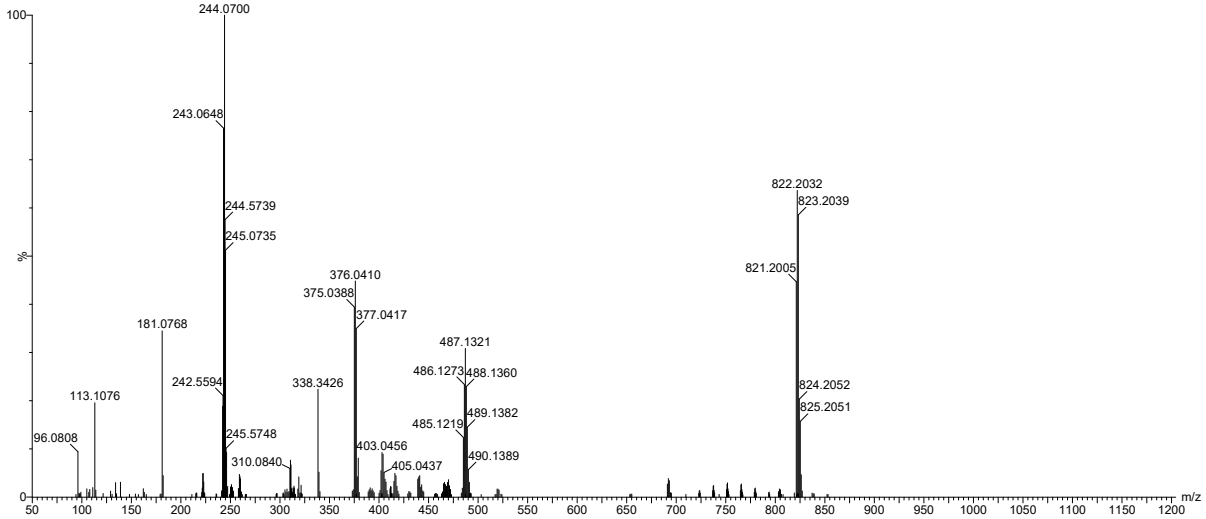


Figure C.5 Full ESI MS spectrum of Complex **3**

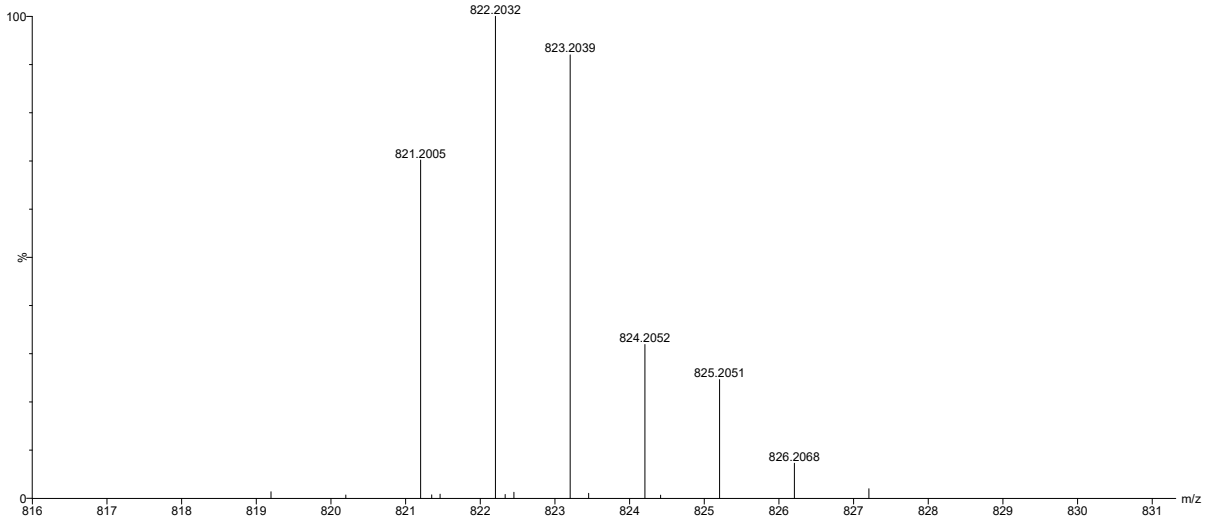


Figure C.6 Expanded $[M-H]^+$ peak for Complex **3**

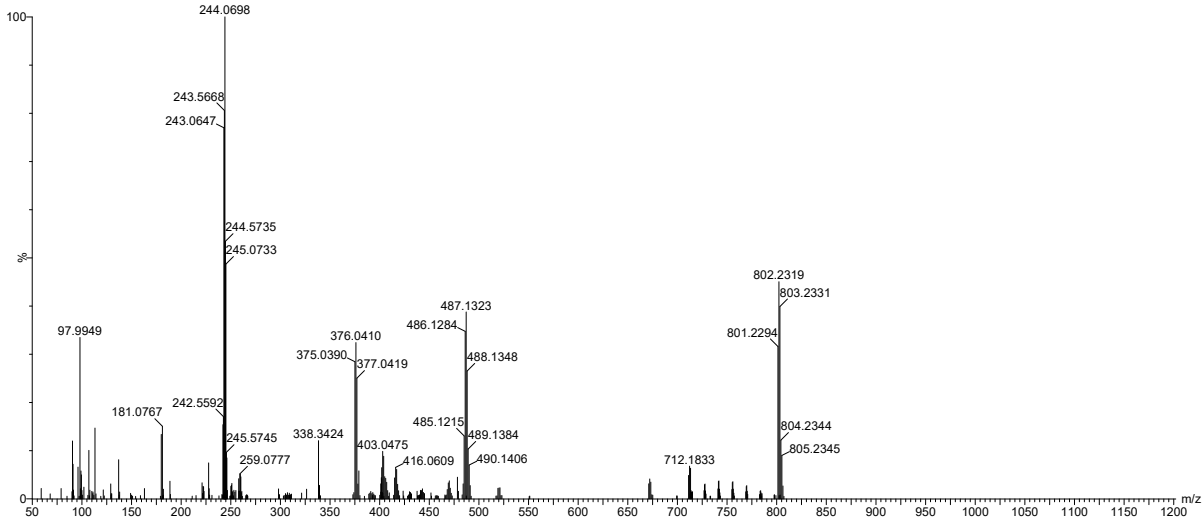


Figure C.7 Full ESI MS spectrum of Complex **4**

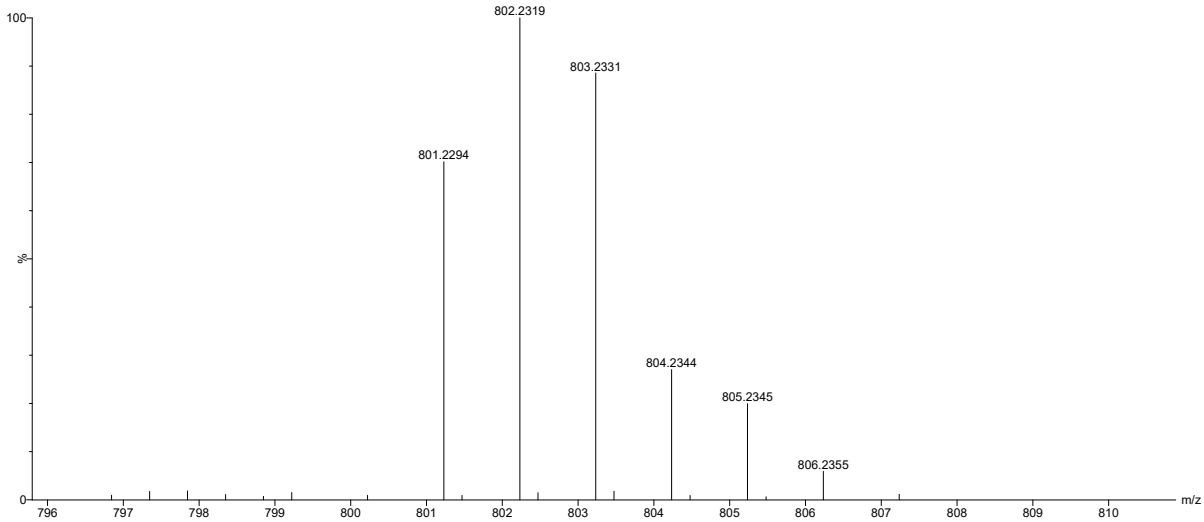


Figure C.8 Expanded $[M-H]^+$ peak for Complex **4**

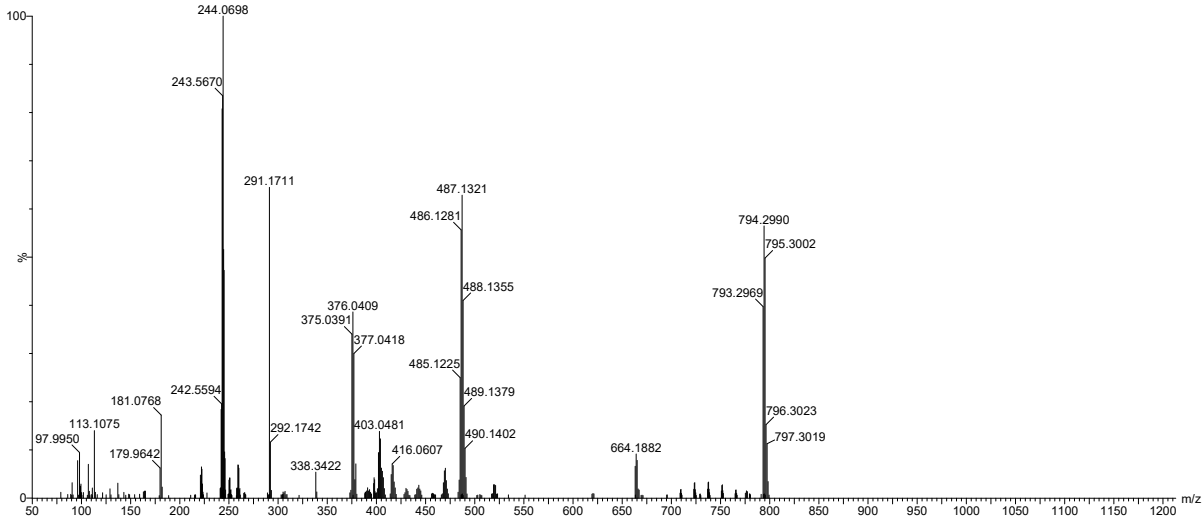


Figure C.9 Full ESI MS spectrum of Complex **5**

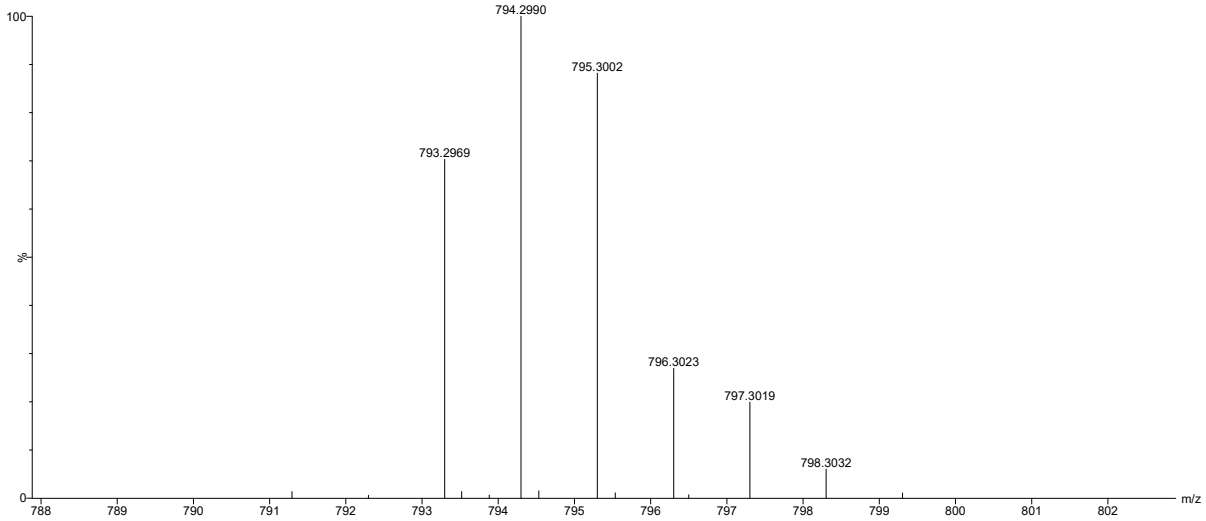


Figure C.10 Expanded $[M-H]^+$ peak for Complex **5**

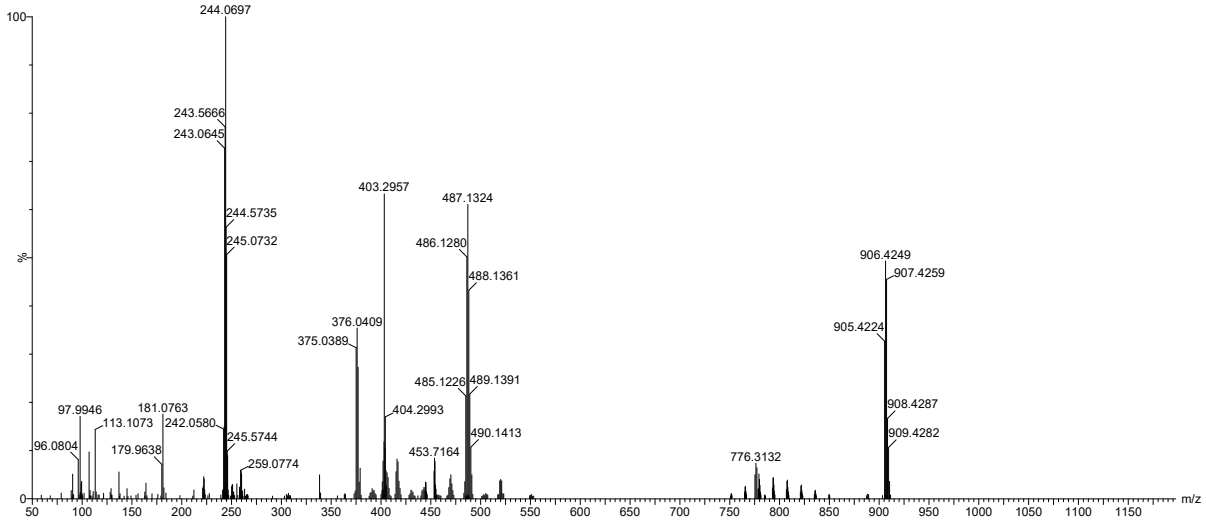


Figure C.11 Full ESI MS spectrum of Complex **6**

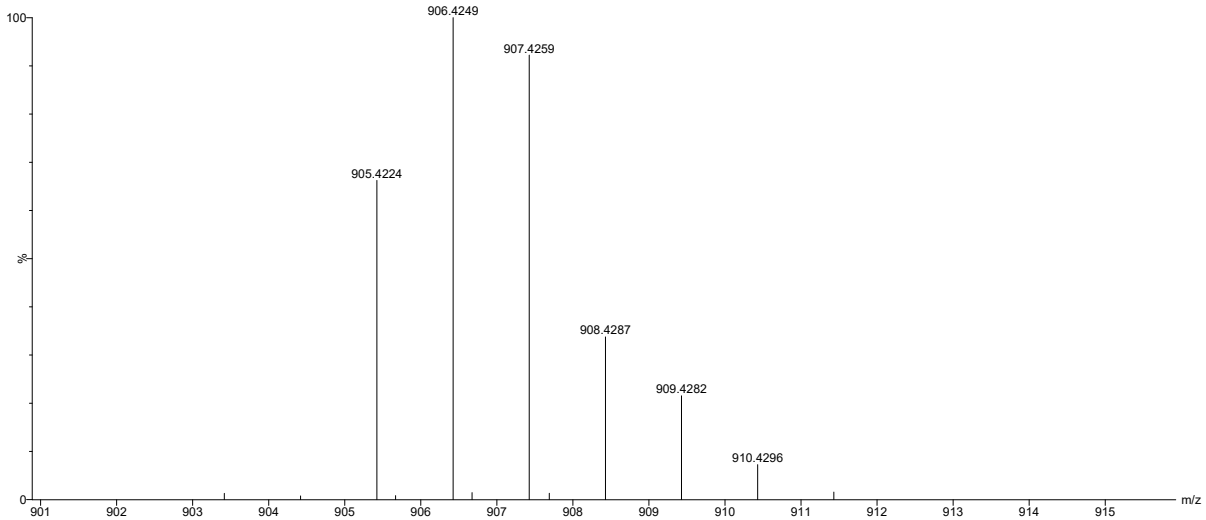


Figure C.12 Expanded $[M-H]^+$ peak for Complex **6**

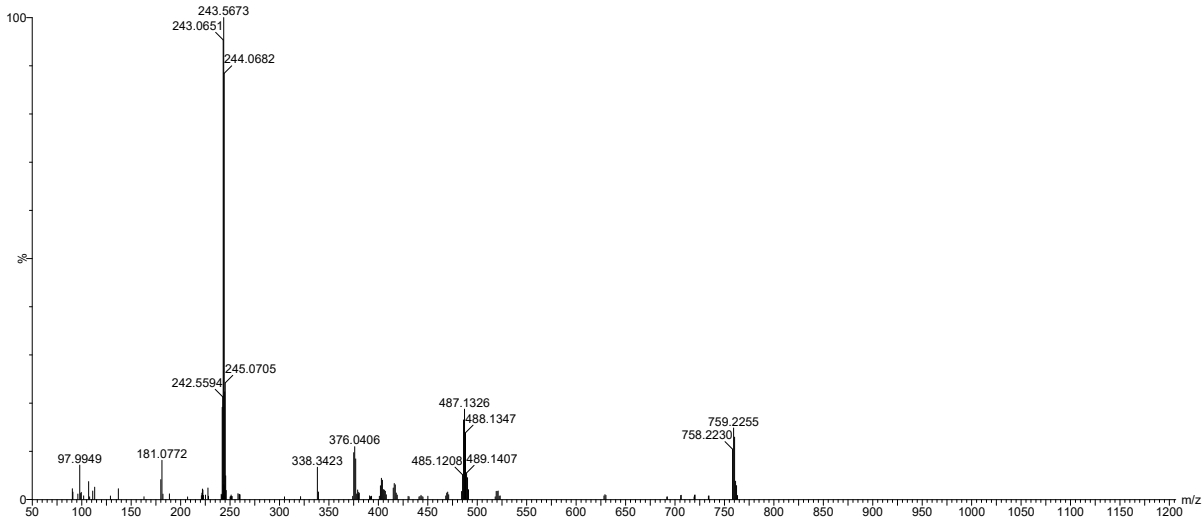


Figure C.13 Full ESI MS spectrum of Complex **7**

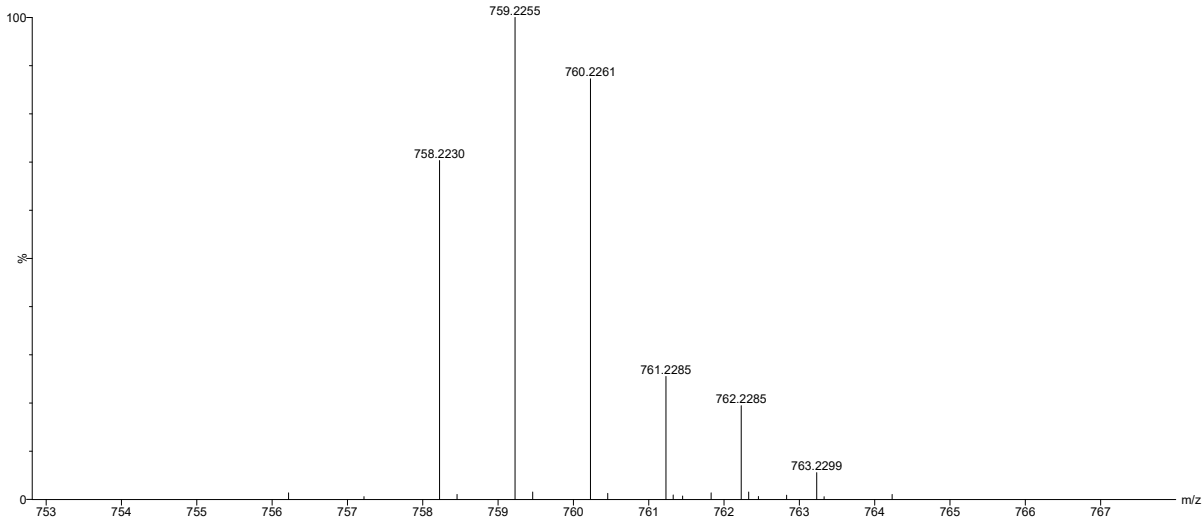


Figure C.14 Expanded $[M-H]^+$ peak for Complex **7**

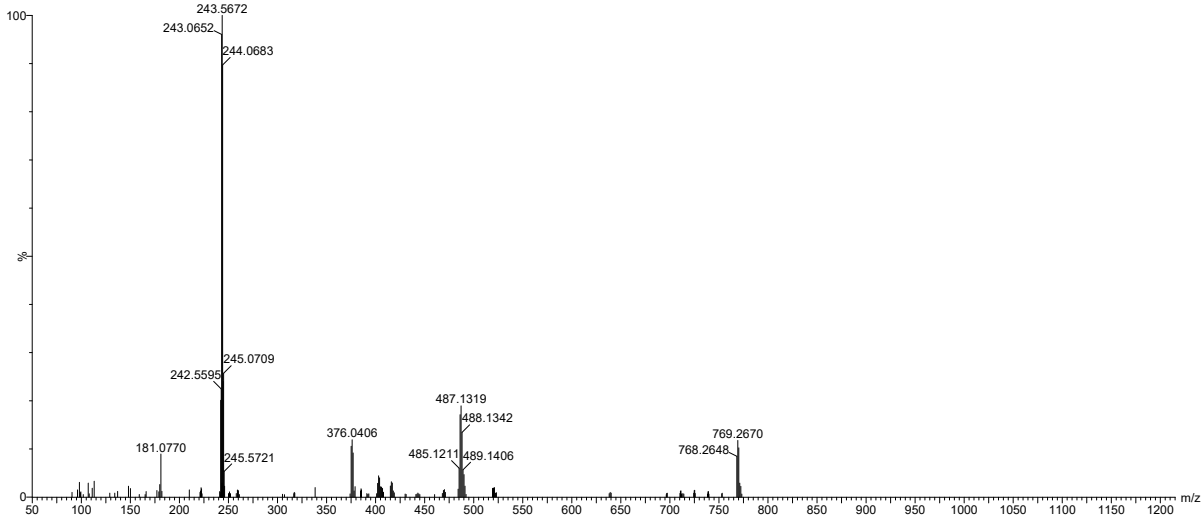


Figure C.15 Full ESI MS spectrum of Complex **8**

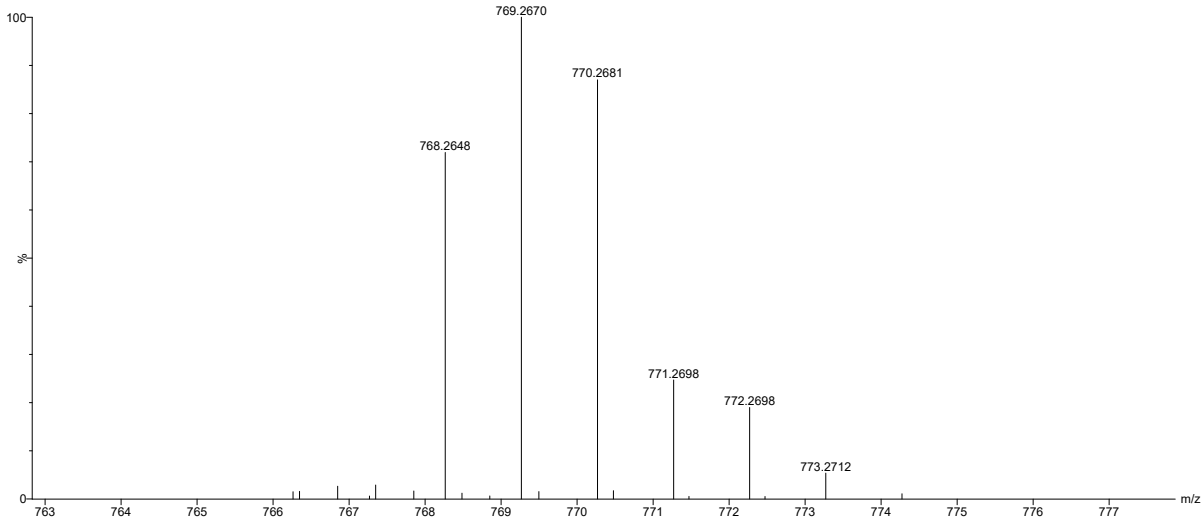


Figure C.16 Expanded $[M-H]^+$ peak for Complex **8**

D. HPLC

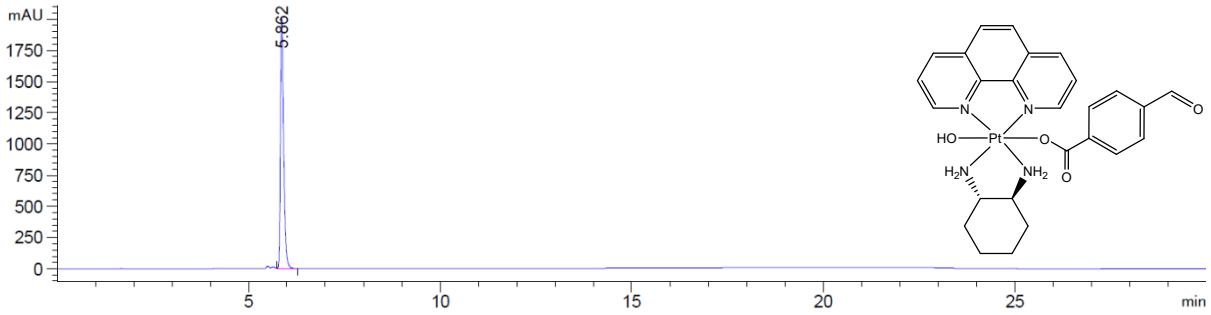


Figure D.1 Complex **1** - Pt^{IV}PhenSS(4-formyl-benzoate)(OH). Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

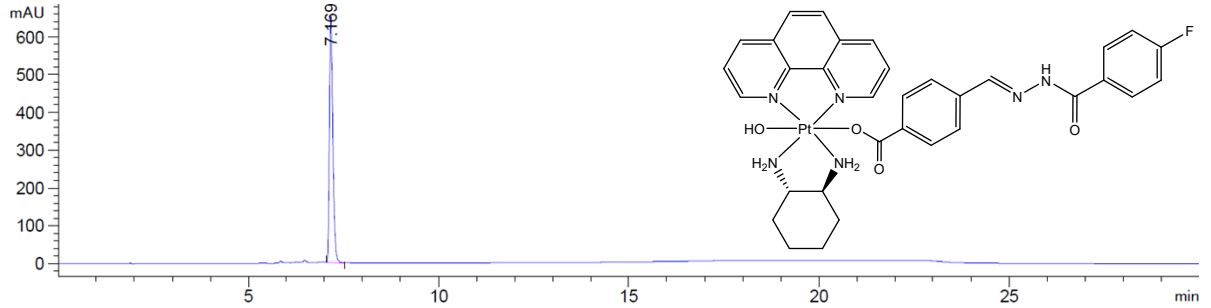


Figure D.2 Complex **2** - Pt^{IV}PhenSS(4-formyl-benzoate)(OH) 4-fluoro-benzoic hydrazide hydrazone complex. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

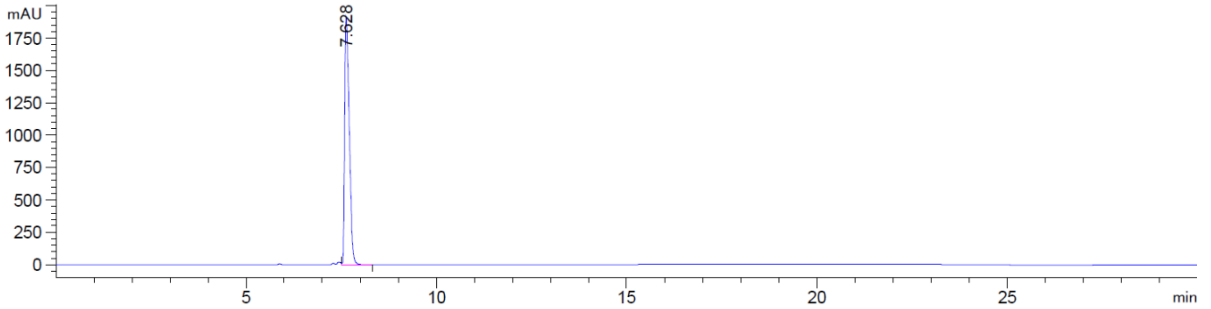


Figure D.3 Complex **3** - Pt^{IV}PhenSS(4-formyl-benzoate)(OH) tosylhydrazine hydrazone complex. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

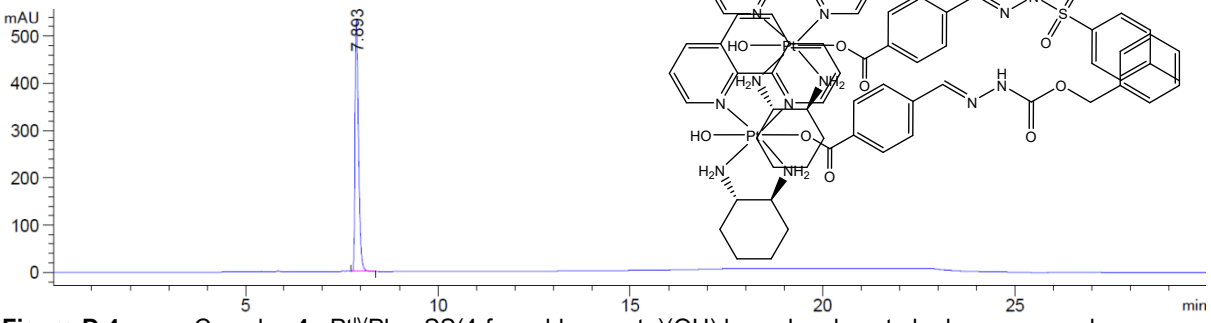


Figure D.4 Complex **4** - Pt^{IV}PhenSS(4-formyl-benzoate)(OH) benzyl carbazate hydrazone complex. Gradient 0-100 solvent B (15 mins). B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

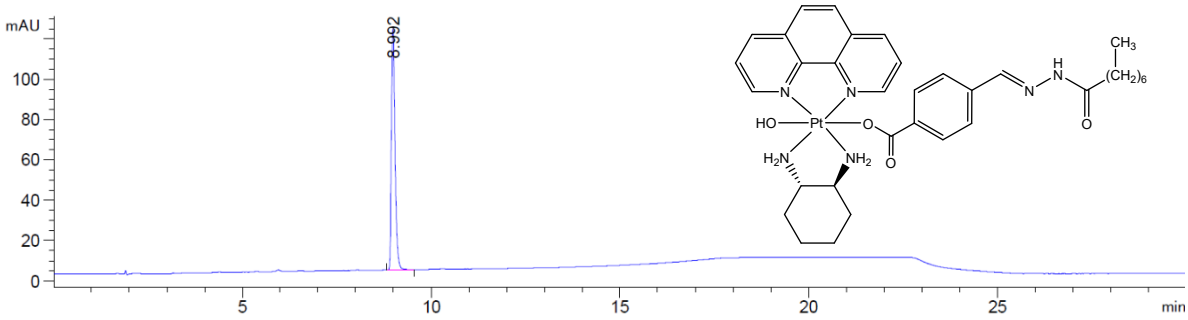


Figure D.5 Complex **5** - Pt^{IV}PhenSS(4-formyl-benzoate)(OH) octanoic hydrazide hydrazone complex. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

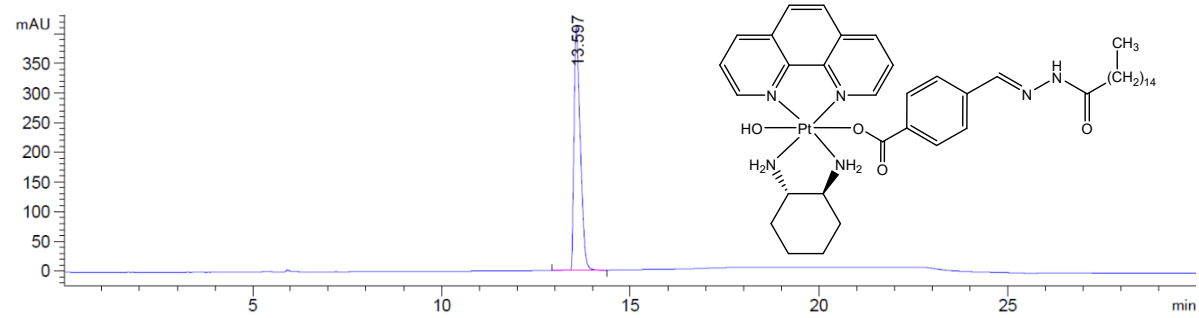


Figure D.6 Complex **6** - Pt^{IV}PhenSS(4-formyl-benzoate)(OH) palmitic acid hydrazide hydrazone complex. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

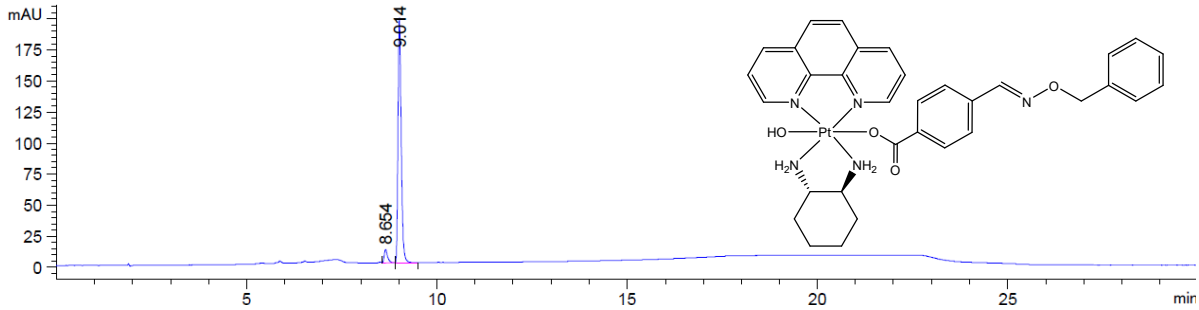


Figure D.7 Complex **7** - Pt^{IV}PhenSS(4-formyl-benzoate)(OH) *O*-benzylhydroxylamine oxime complex. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

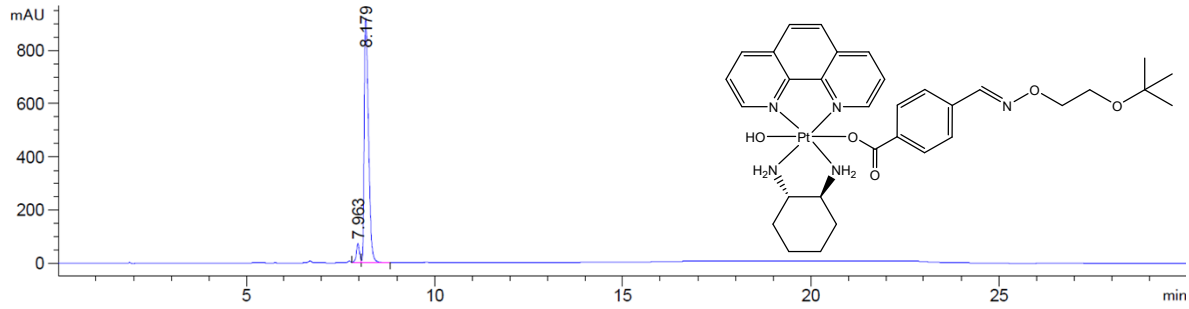


Figure D.8 Complex **8** - Pt^{IV}PhenSS(4-formyl-benzoate)(OH) *O*-(2-(tert-butoxy)ethyl)hydroxylamine oxime complex. Gradient 0-100 solvent A = 0.06% TFA in H_2O. B (15 mins). B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

E. UV-Vis spectra

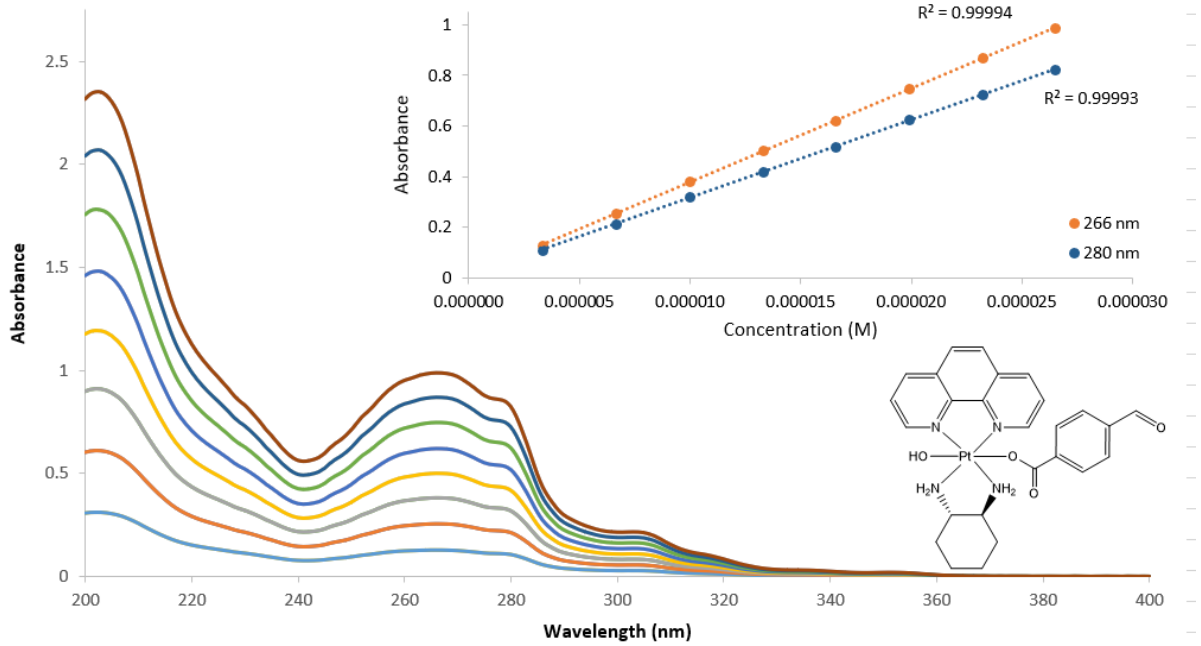


Figure E.1 Exemplar UV of Complex **1** in H_2O.

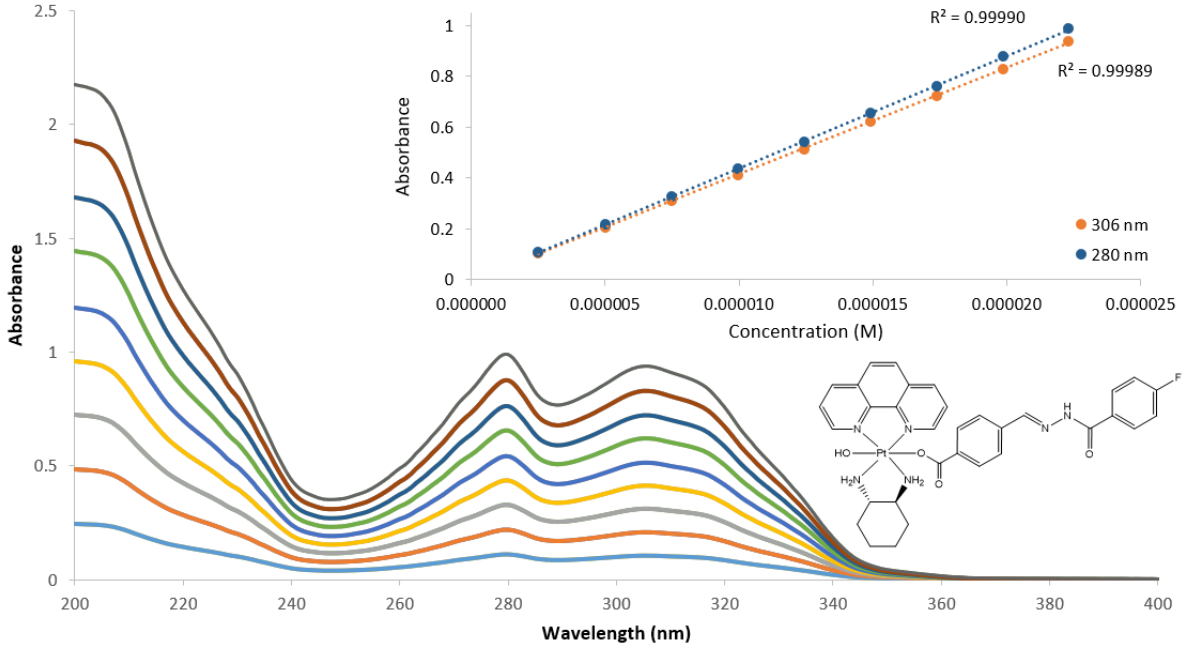


Figure E.2 Exemplar UV spectrum of Complex **2** in H_2O.

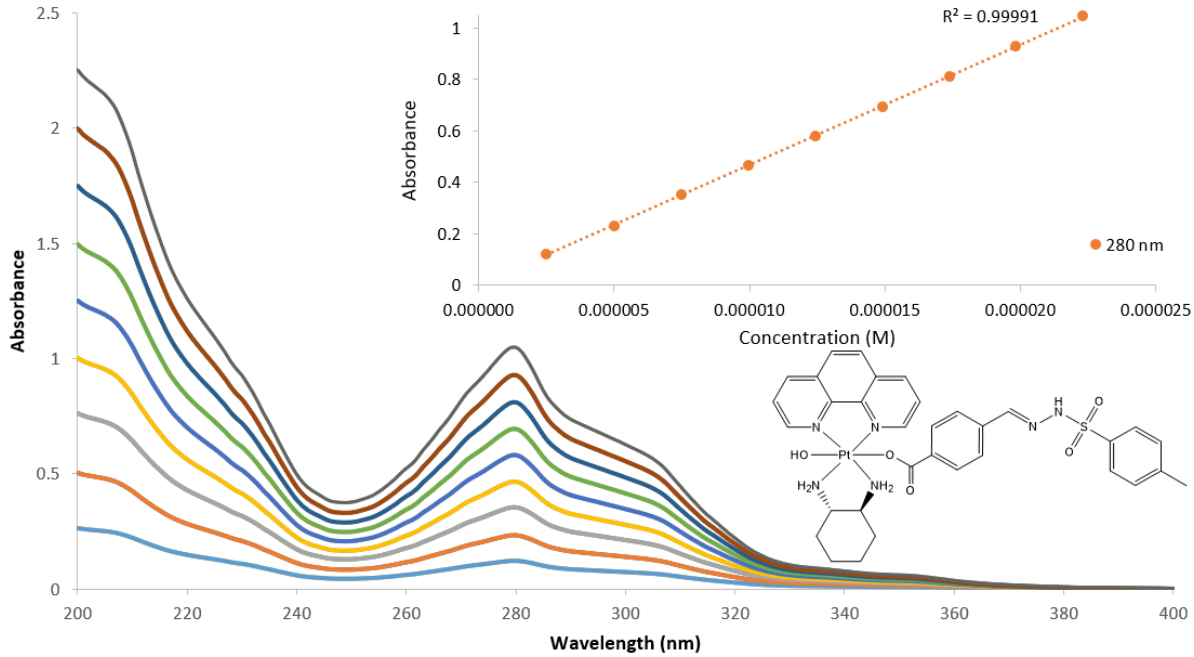


Figure E.3 Exemplar UV spectrum of Complex **3** in H_2O.

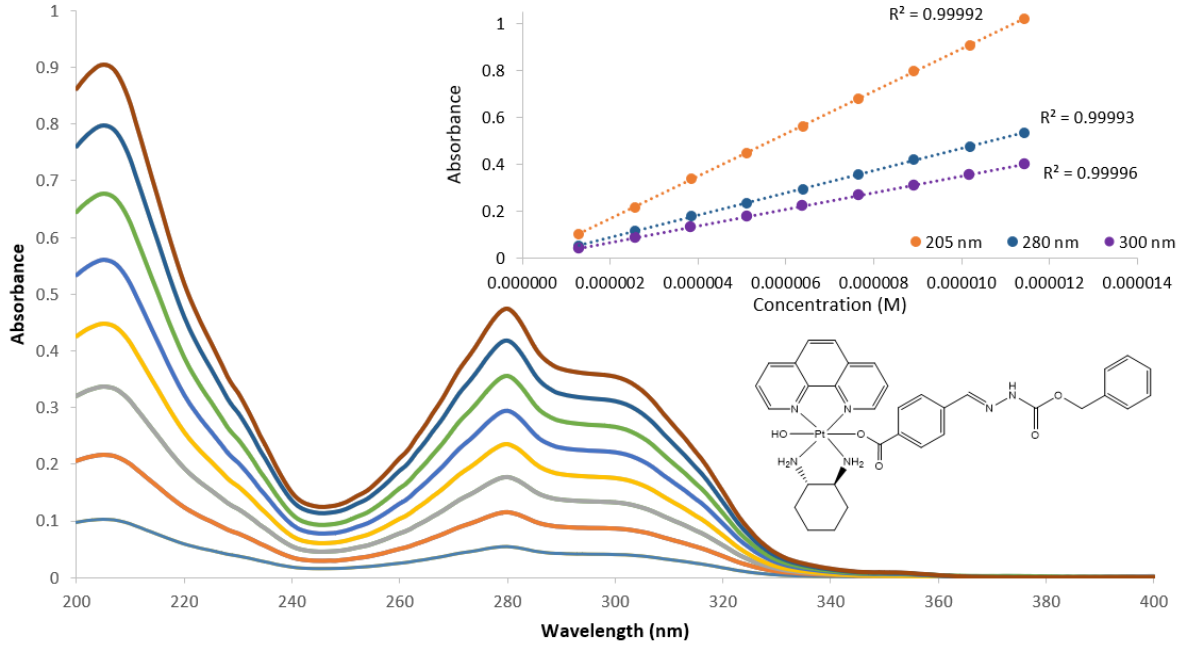


Figure E.4 Exemplar UV spectrum of Complex **4** in H_2O.

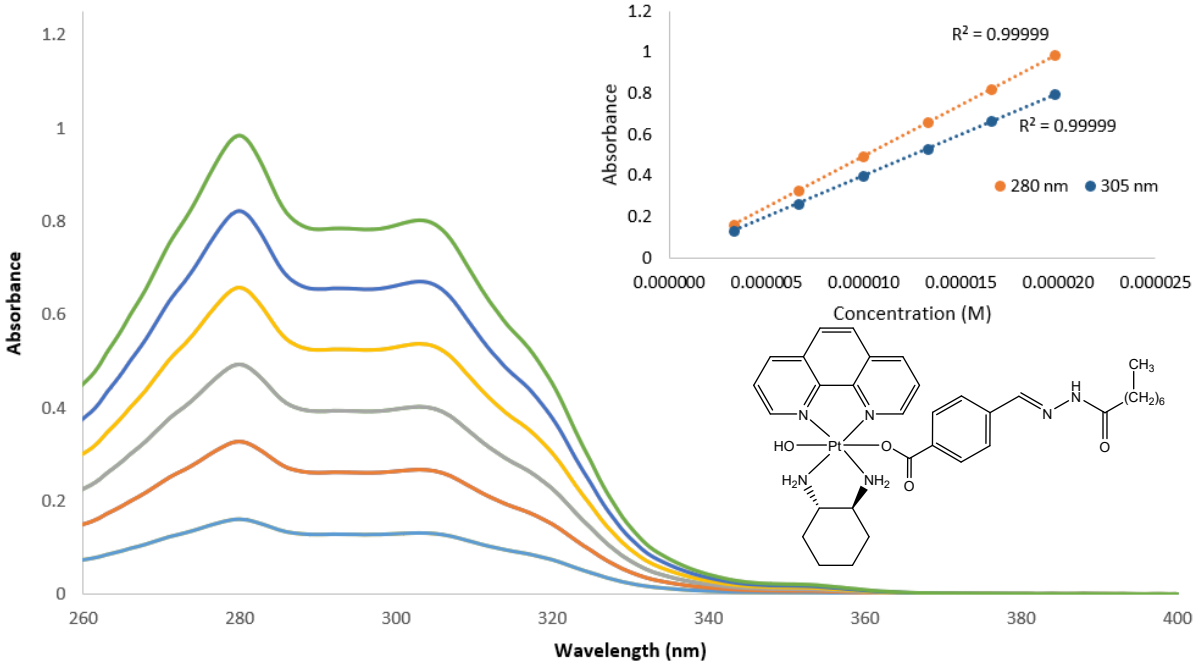


Figure E.5 Exemplar UV spectrum of Complex **5** in H_2O. Data limited between 260-400 nm due to interference from titration of complex **5** in DMSO.

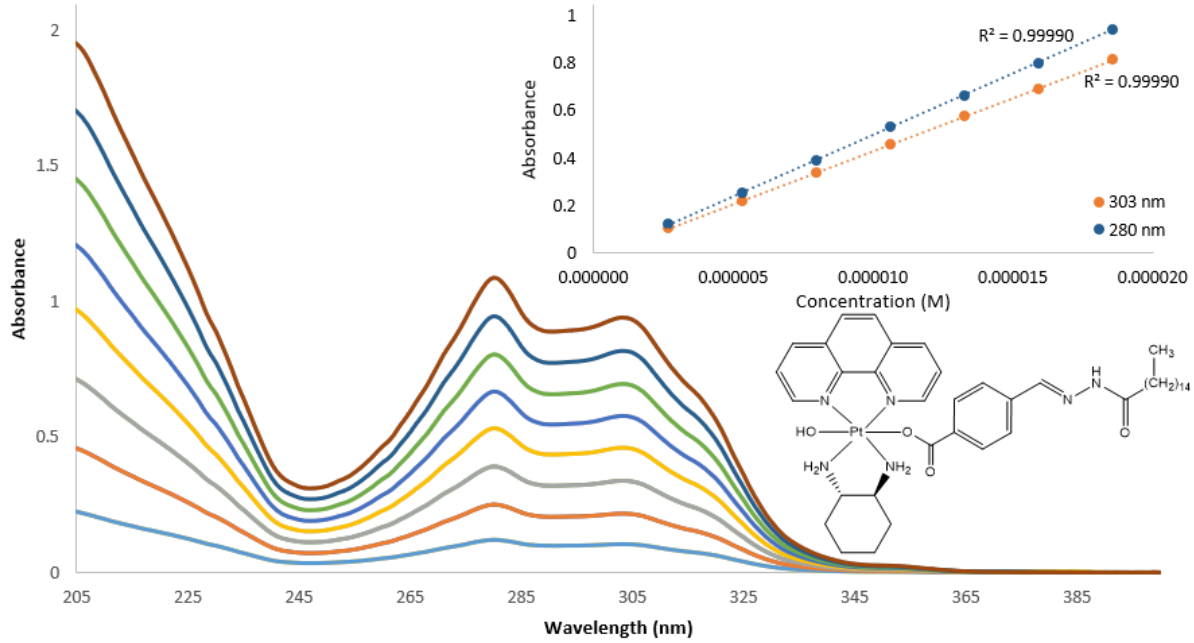


Figure E.6 Exemplar UV spectrum of Complex **6** in Methanol. Data cut off at 205 nm due to interference from methanol.

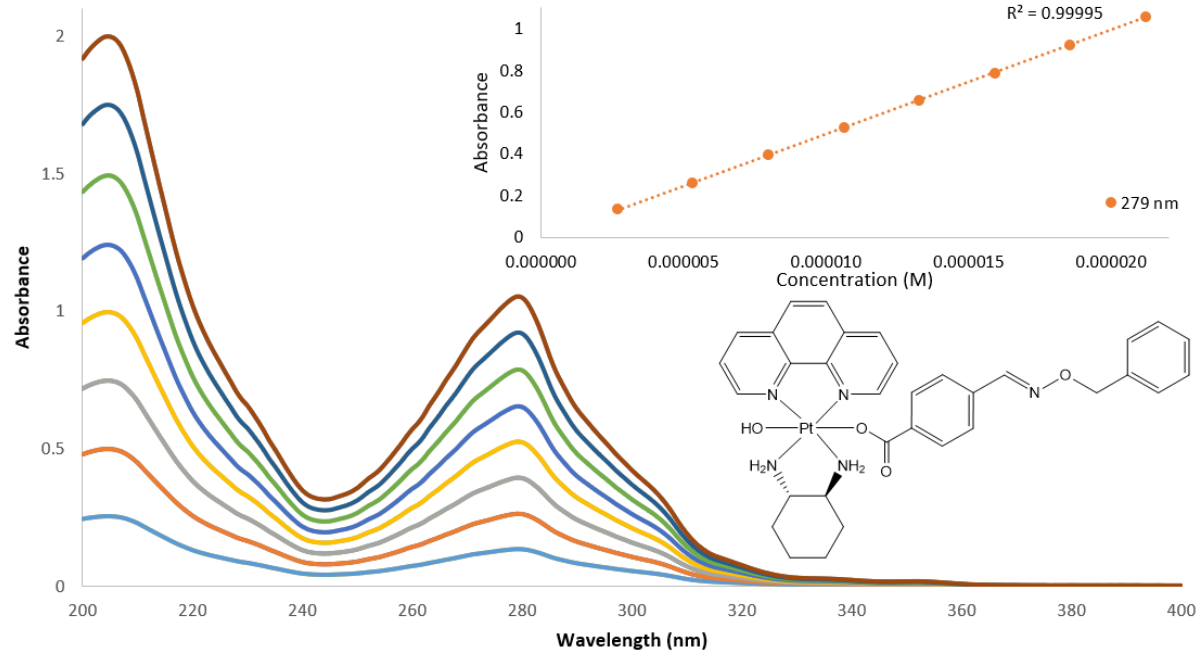


Figure E.7 Exemplar UV spectrum of Complex **7** in H_2O.

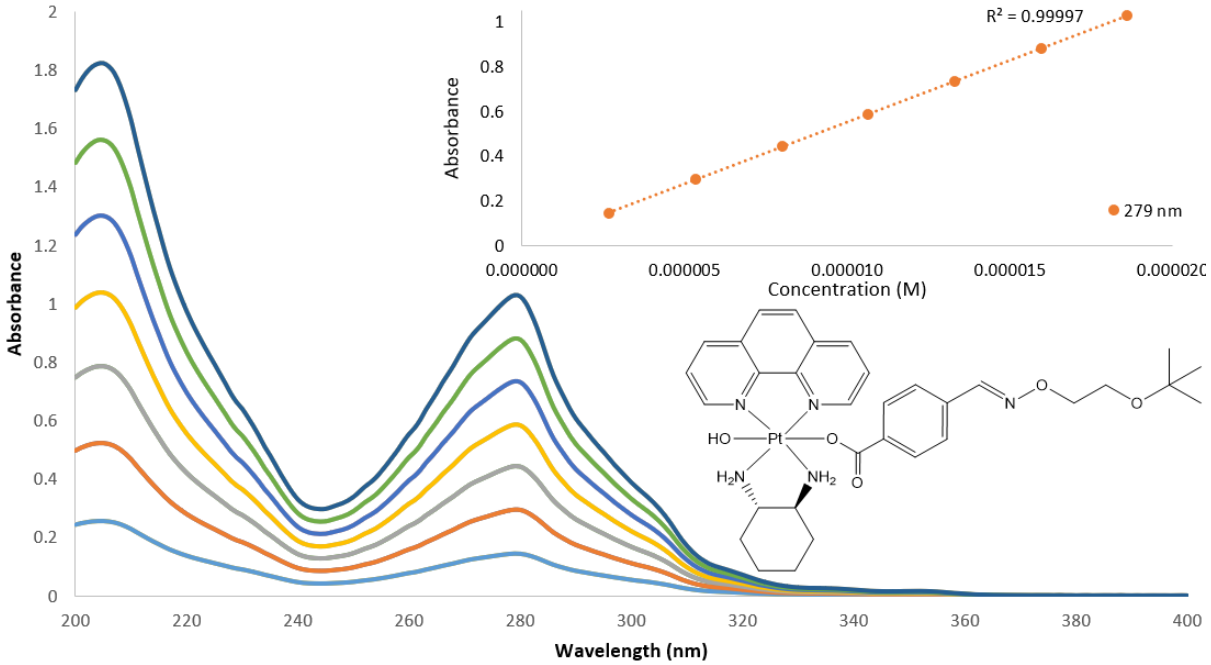


Figure E.8 Exemplar UV spectrum of Complex **8** in H_2O.

F. SRCD and CD spectra

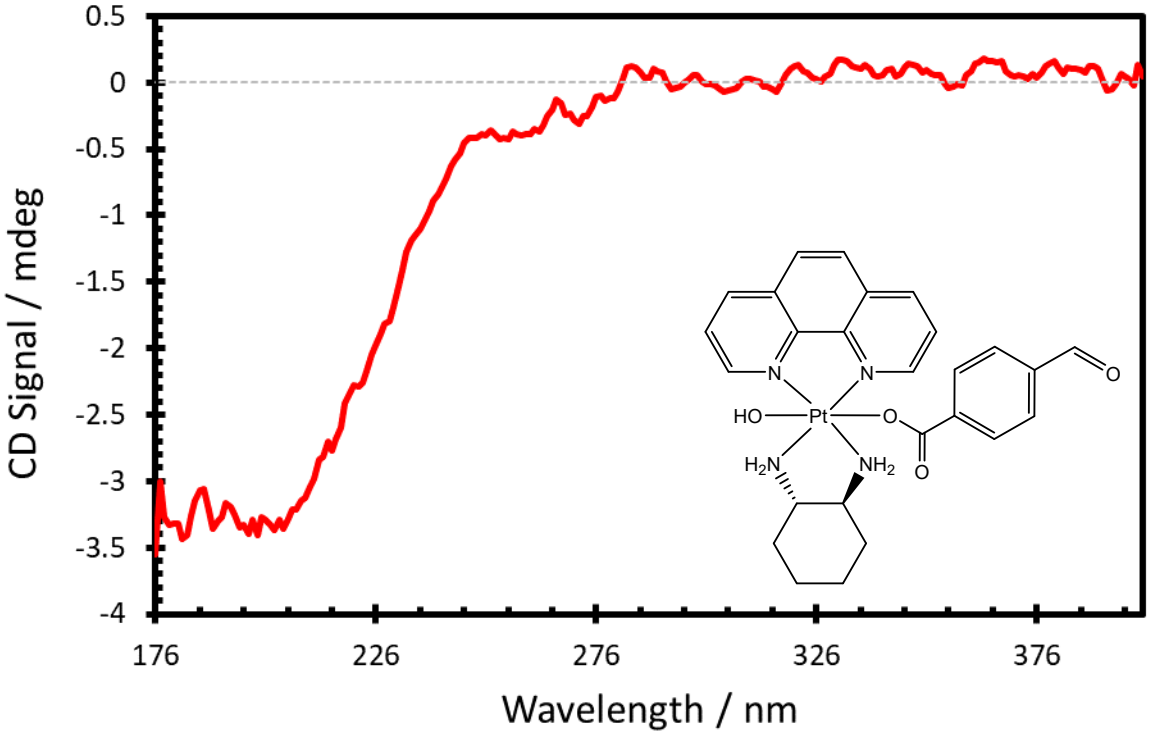


Figure F.1 SRCD spectrum of 1 mM Complex **1** in H_2O

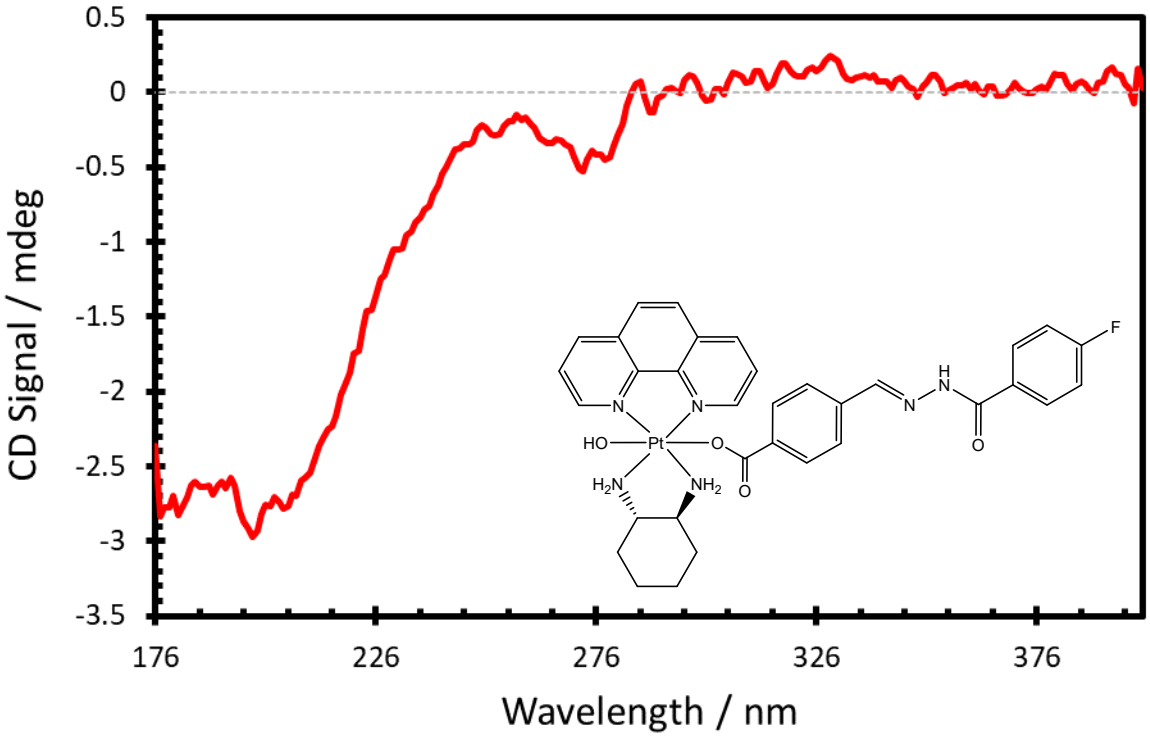


Figure F.2 SRCD spectrum of 1 mM Complex **2** in H_2O

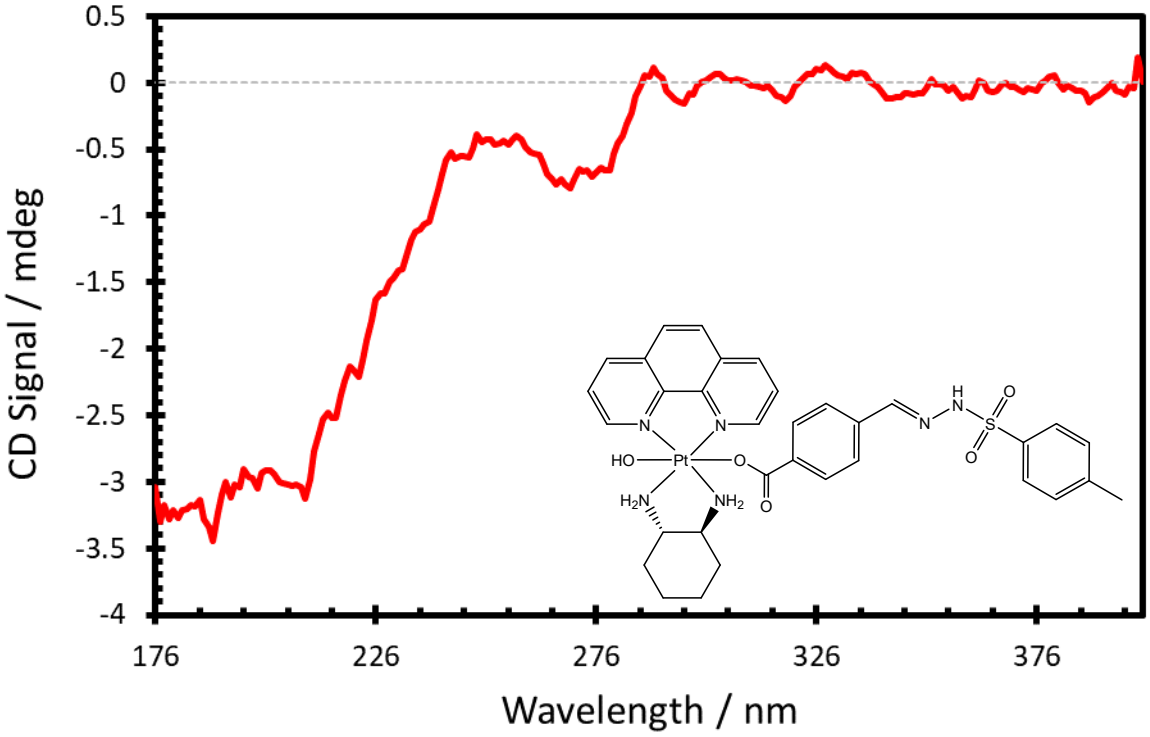


Figure F.3 SRCD spectrum of 1 mM Complex **3** in H_2O

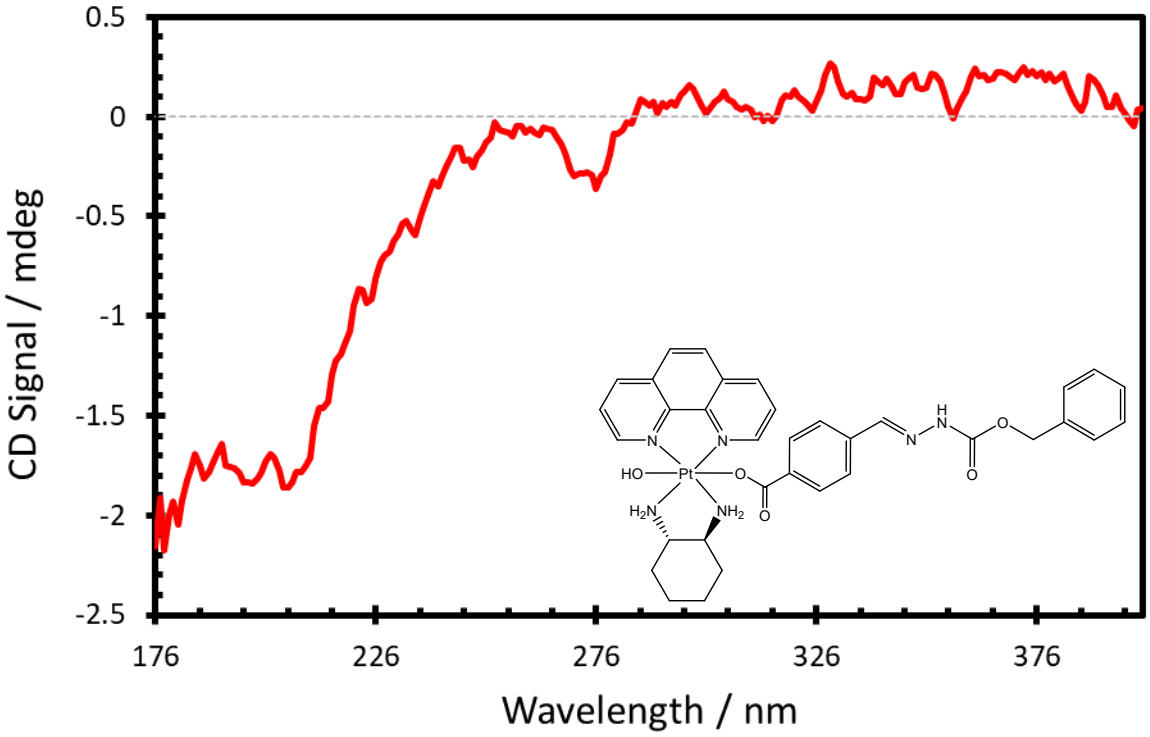


Figure F.4 SRCD spectrum of 1 mM Complex **4** in H_2O

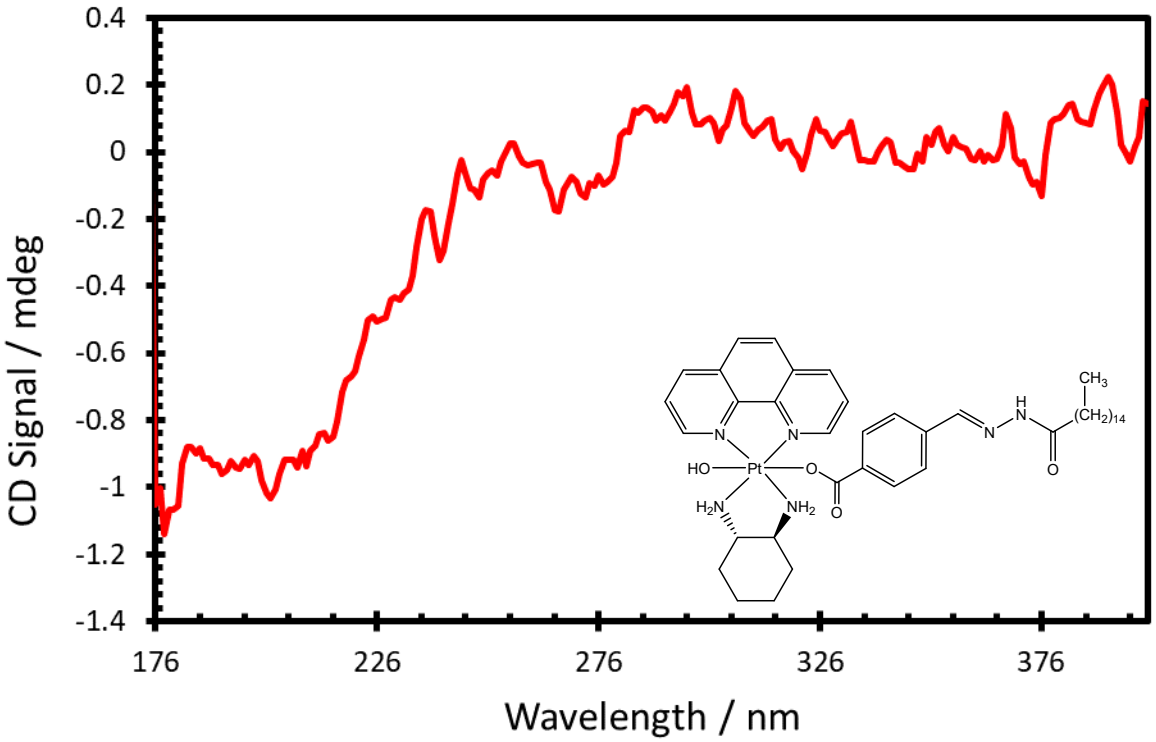


Figure F.5 SRCD spectrum of 0.4 mM Complex **6** in H_2O

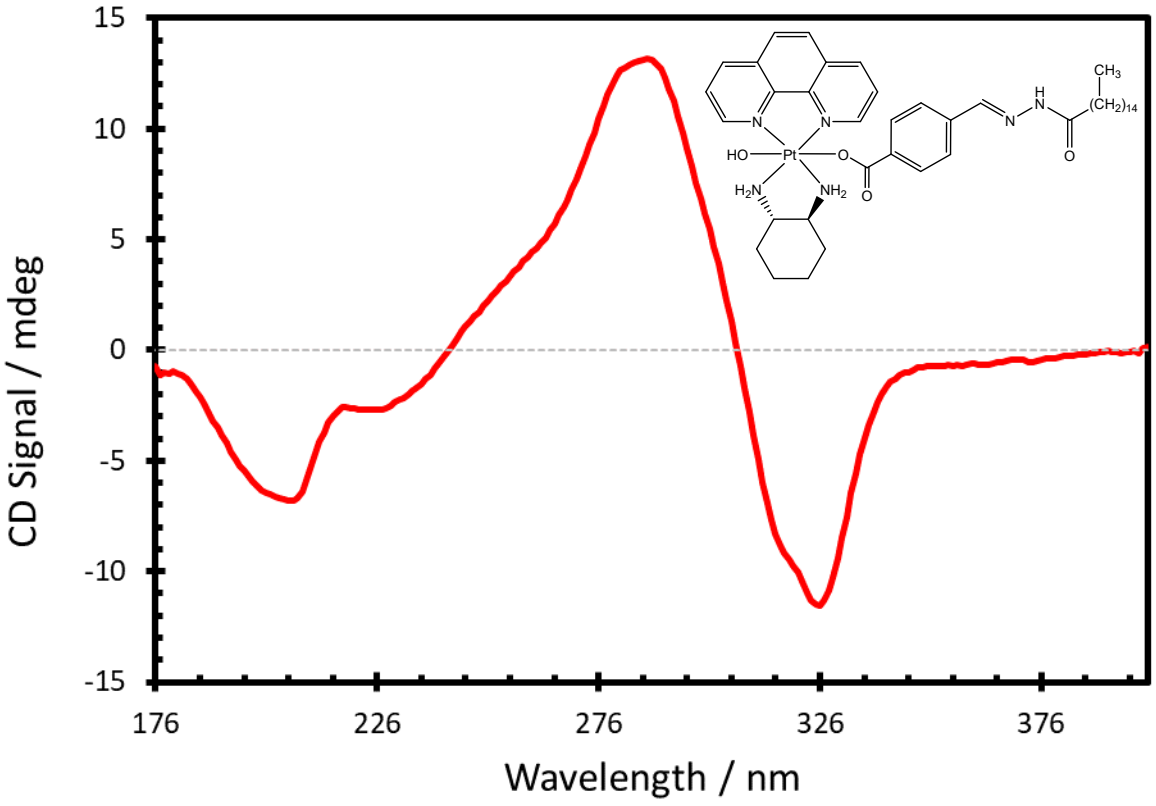


Figure F.6 SRCD spectrum of 1 mM Complex **6** in H_2O

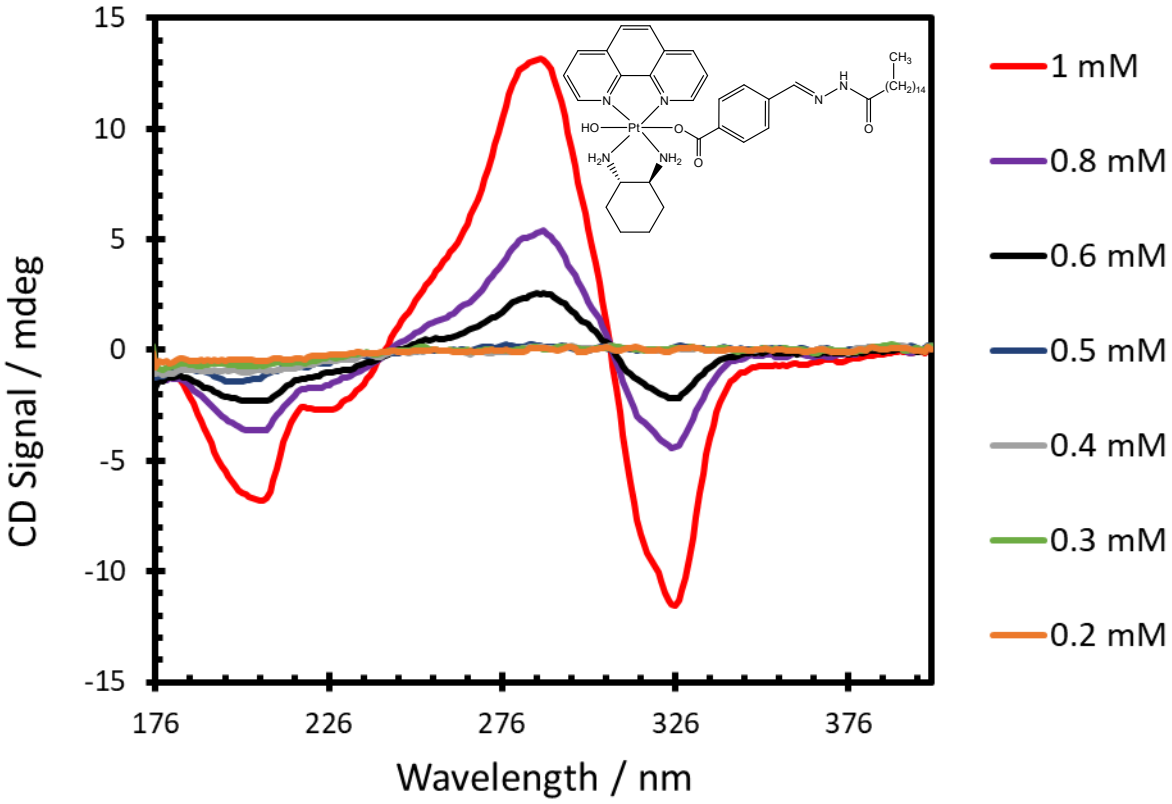


Figure F.7 SRCD spectrum of Complex **6** in H_2O between 0.2 to 1 mM

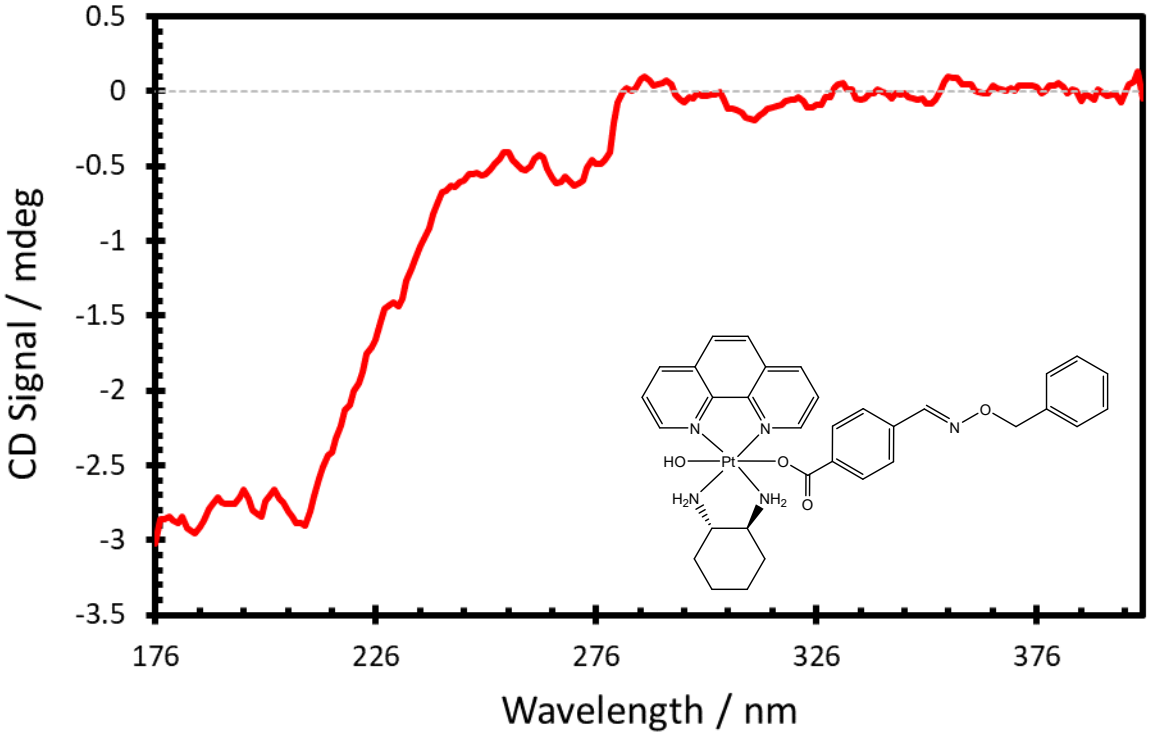


Figure F.8 SRCD spectrum of 1 mM Complex **7** in H_2O

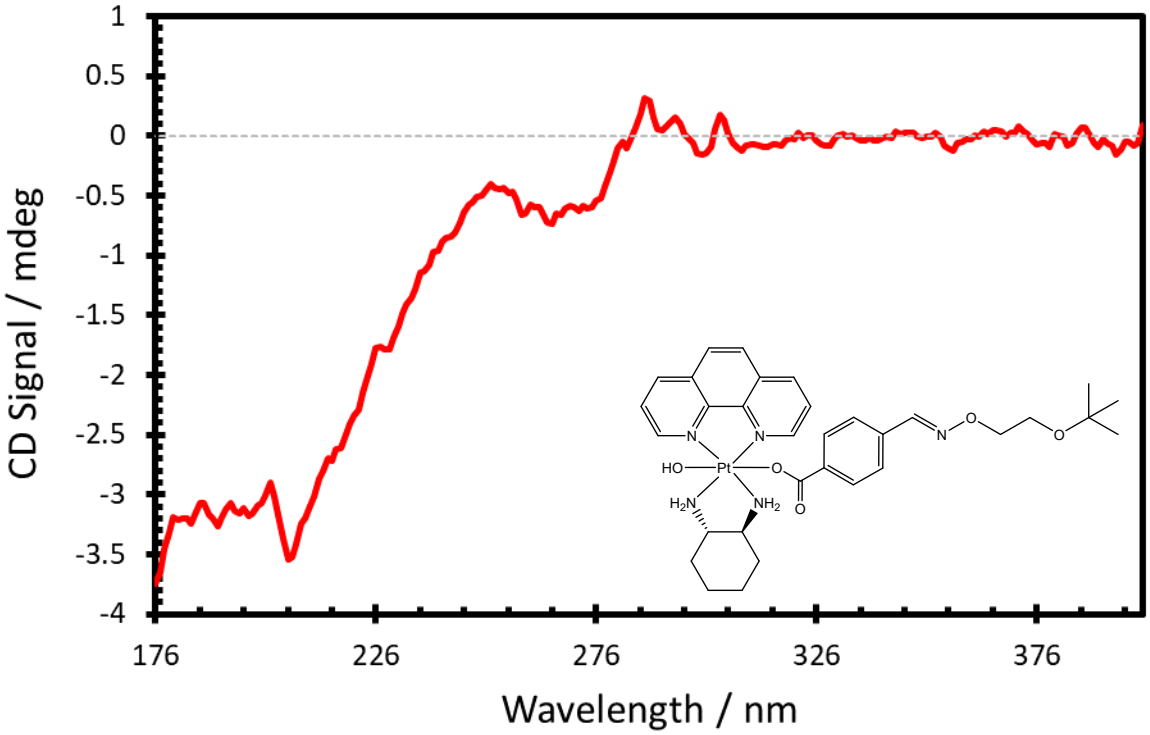


Figure F.9 SRCD spectrum of 1 mM Complex **8** in H_2O

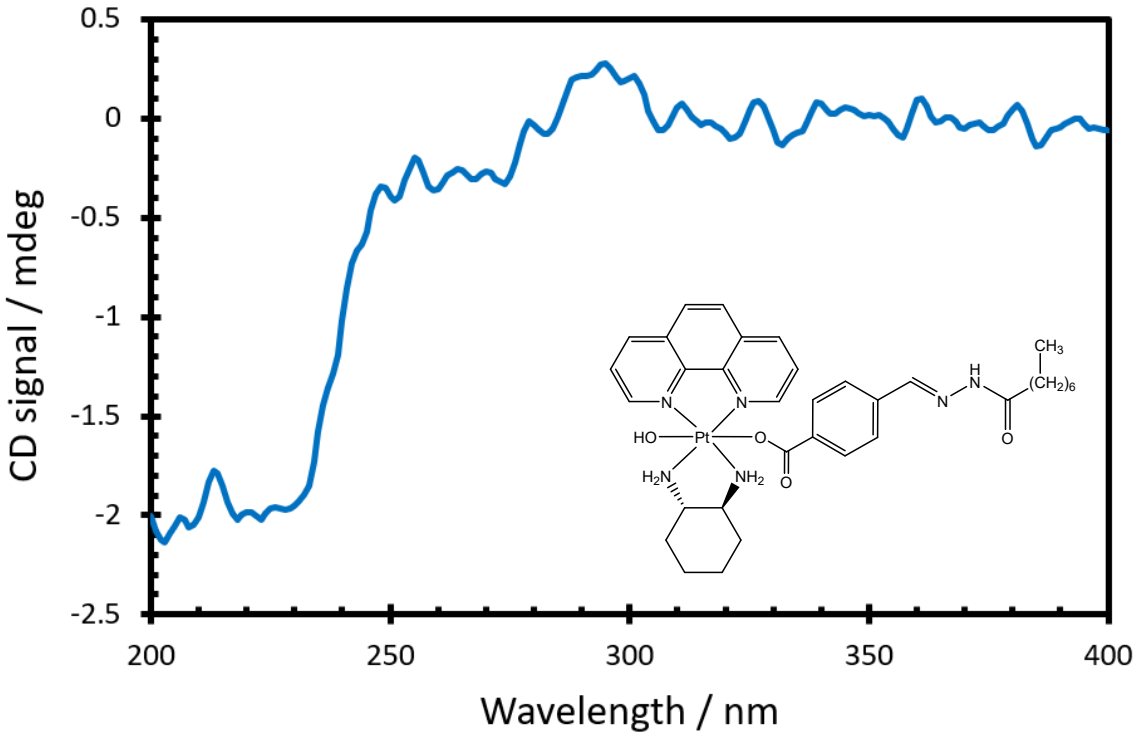


Figure F.10 CD spectrum of 1 mM Complex **5** in 2,2,2-Trifluoroethanol. 7-point smoothing applied.

G. Reaction monitoring HPLC

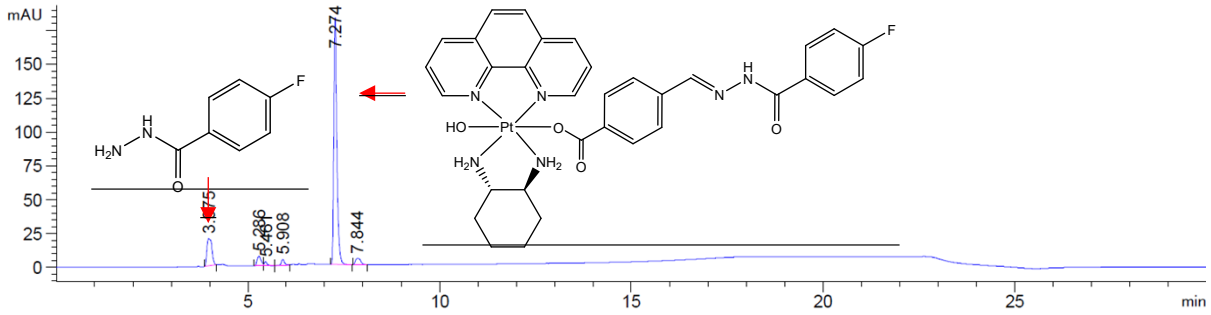


Figure G.1 Complex **1** + 4-fluoro-benzoic hydrazide reaction after 30 minutes. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

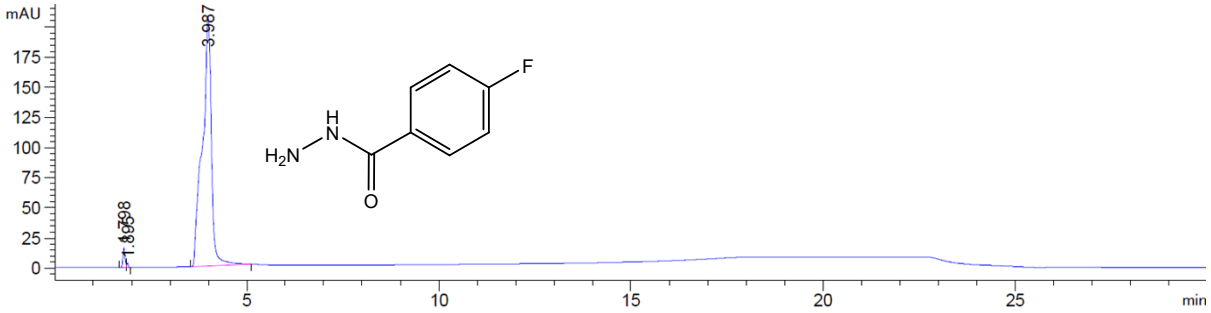


Figure G.2 4-fluoro-benzoic hydrazide. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

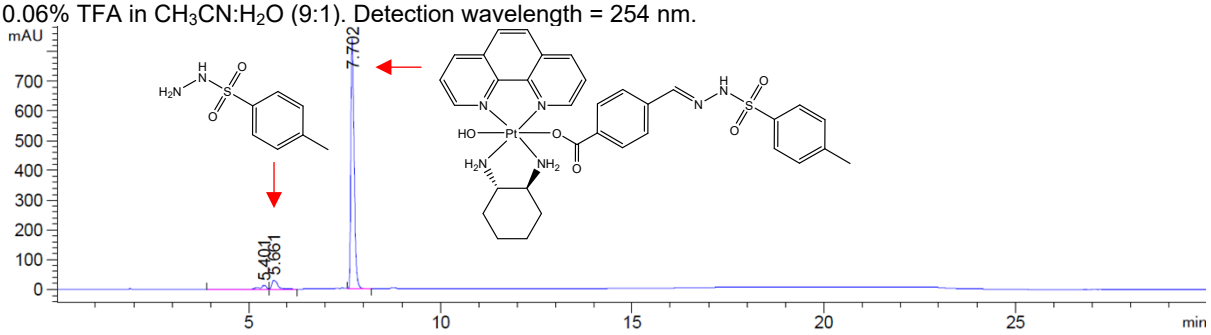


Figure G.3 Complex **1** + tosylhydrazine reaction after 15 minutes. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

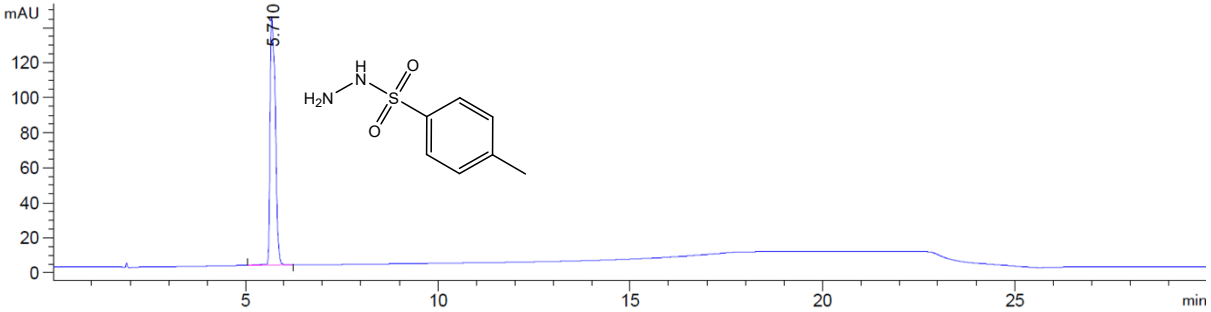


Figure G.4 Tosylhydrazine. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

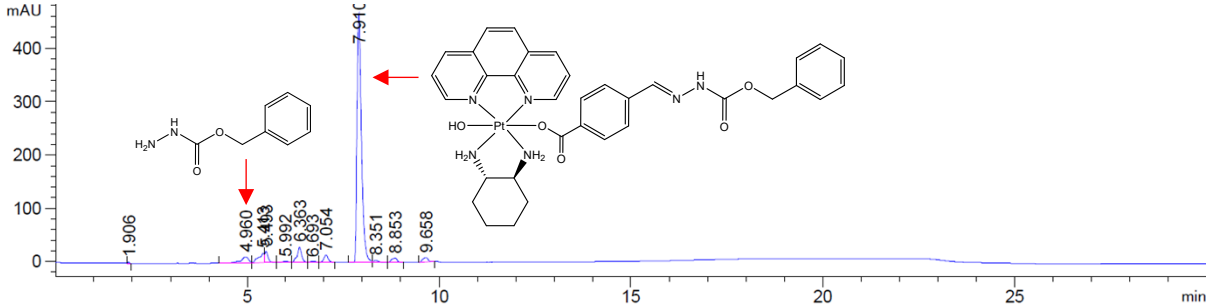


Figure G.5 Complex **1** + benzyl carbazate reaction after 30 minutes. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

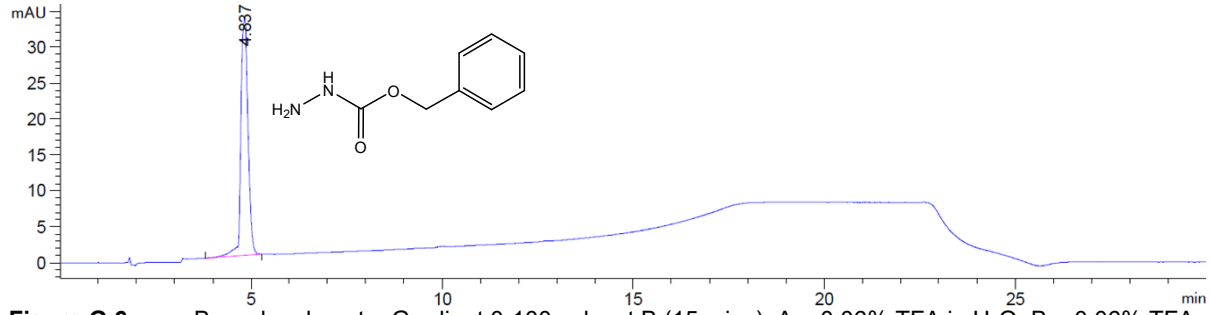


Figure G.6 Benzyl carbazate. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

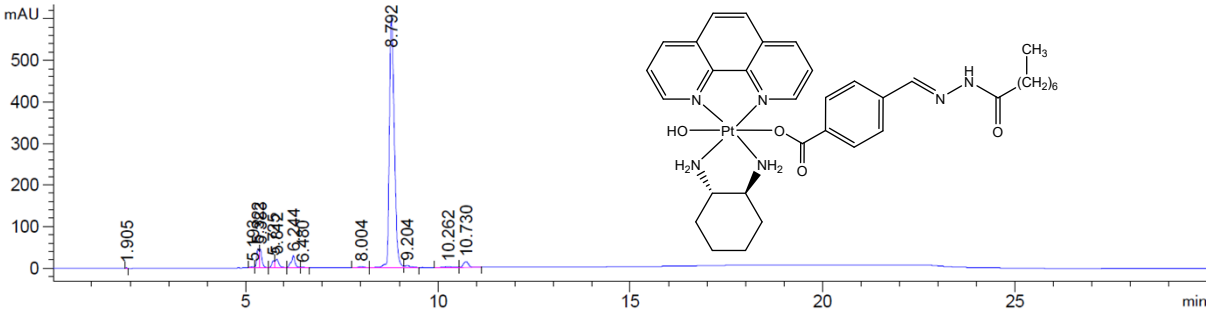


Figure G.7 Complex **1** + octanoic acid hydrazide reaction after 15 minutes. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm. Note octanoic acid hydrazide is non-UV active.

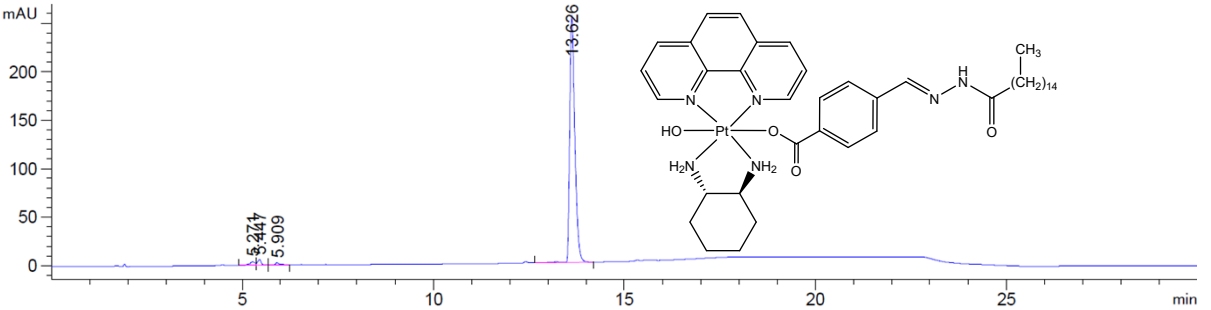


Figure G.8 Complex **1** + palmitic acid hydrazide reaction after 2 hours. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm. Note palmitic acid hydrazide is non-UV active.

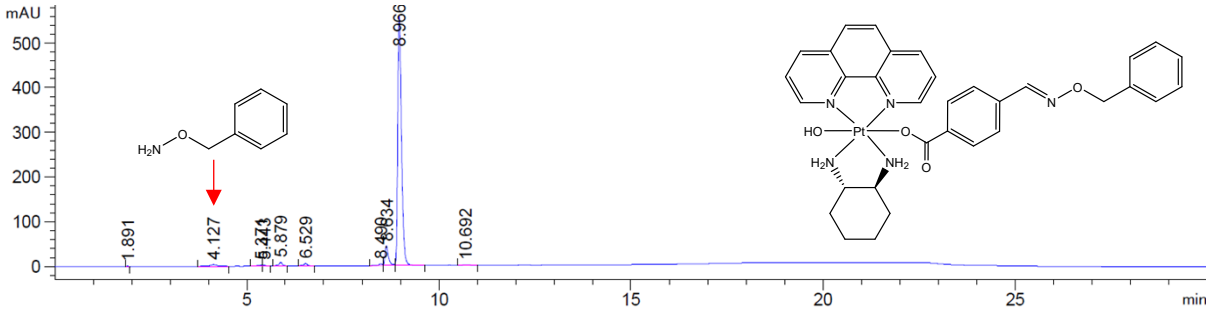


Figure G.9 *O*-benzylhydroxylamine reaction after 30 minutes. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

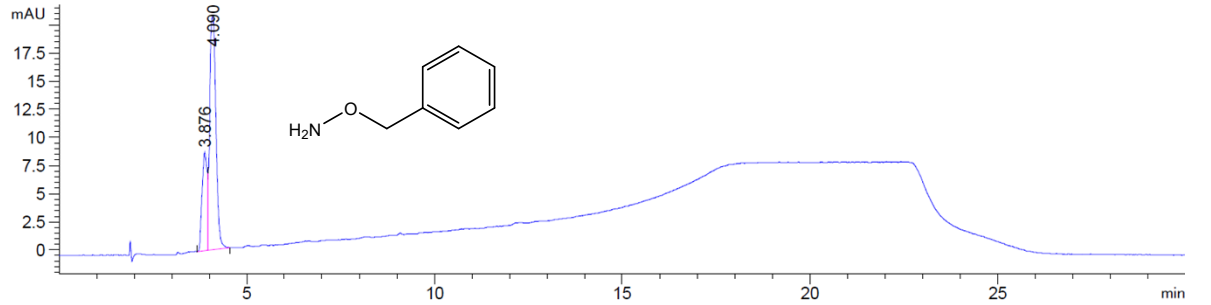


Figure G.10 *O*-benzylhydroxylamine reagent. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

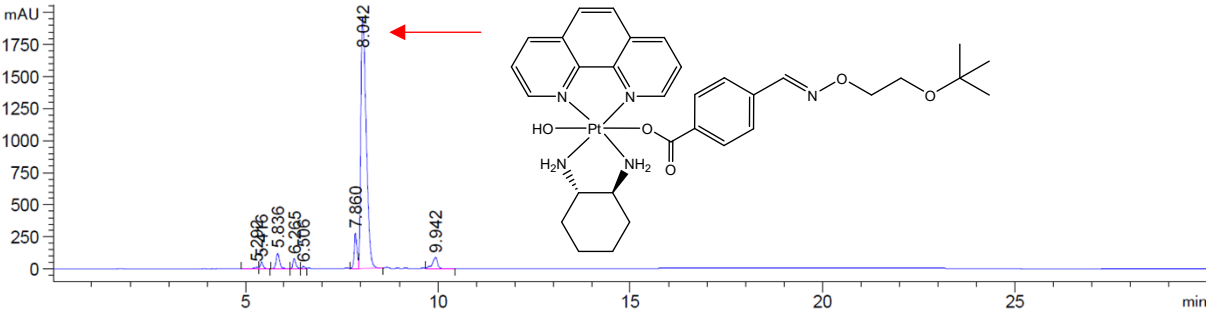


Figure G.11 Complex **1** + *O*-(2-(tert-butoxy)ethyl)hydroxylamine reaction after 2 hours. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm. Note *O*-(2-(tert-butoxy)ethyl)hydroxylamine reagent is non-UV active.

H. HPLC stability studies

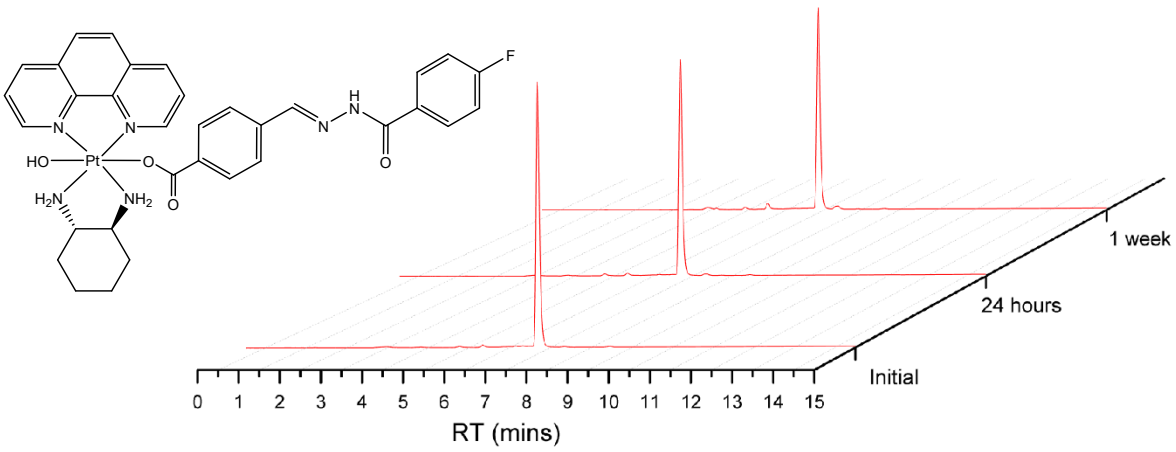


Figure H.1 Complex **2** (1 mM) in 10 mM PBS. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

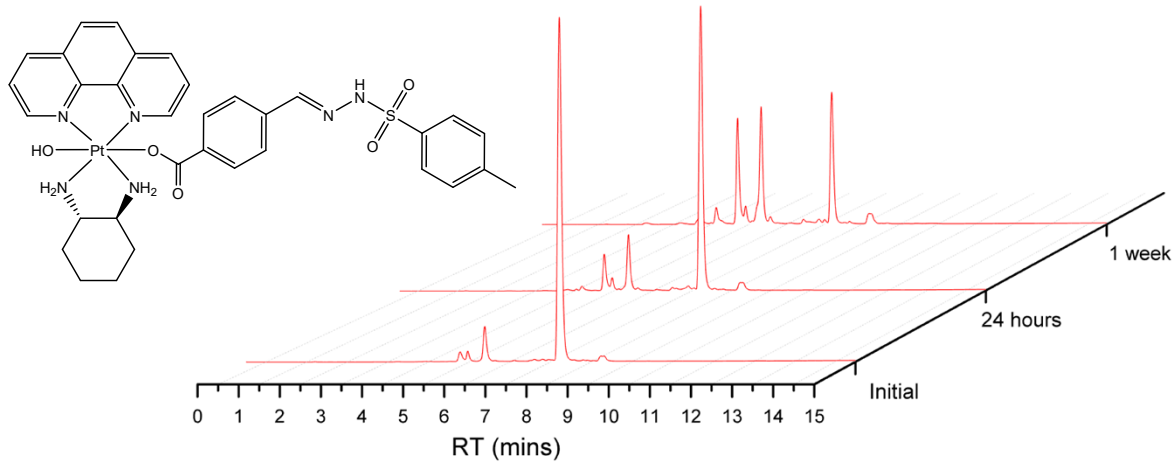


Figure H.2 Complex **3** (1 mM) in 10 mM PBS. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

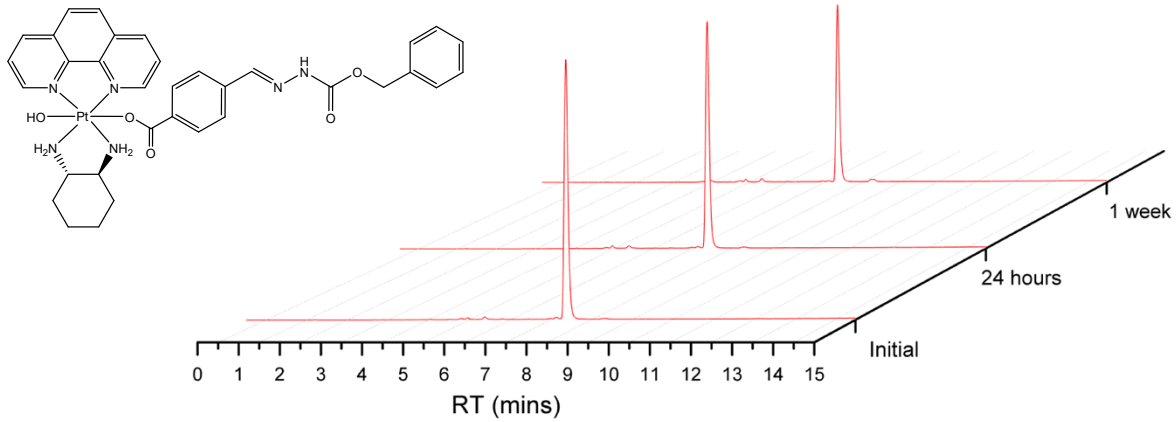


Figure H.3 Complex **4** (1 mM) in 10 mM PBS. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

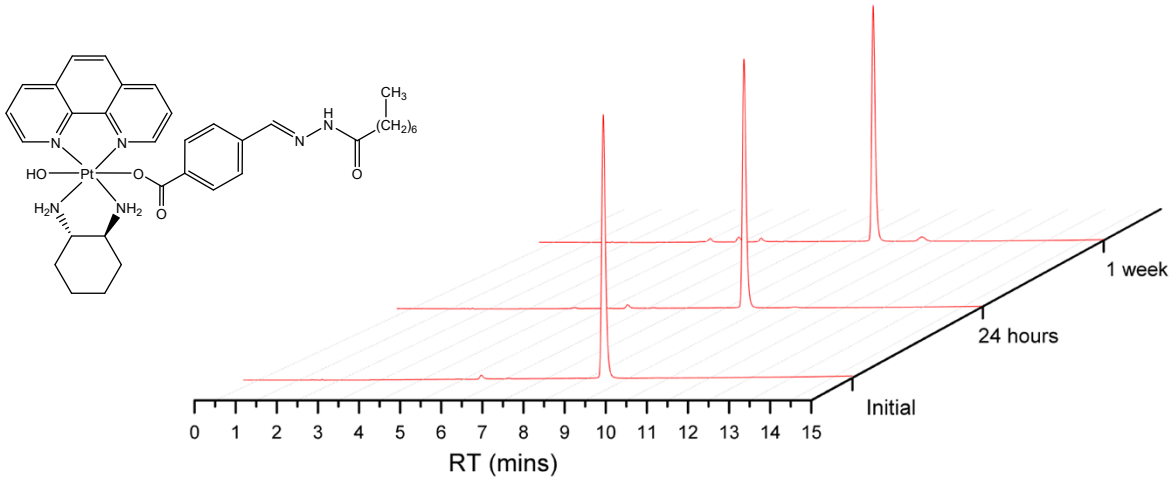


Figure H.4 Complex **5** (1 mM) in 10 mM PBS in 25% methanol. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

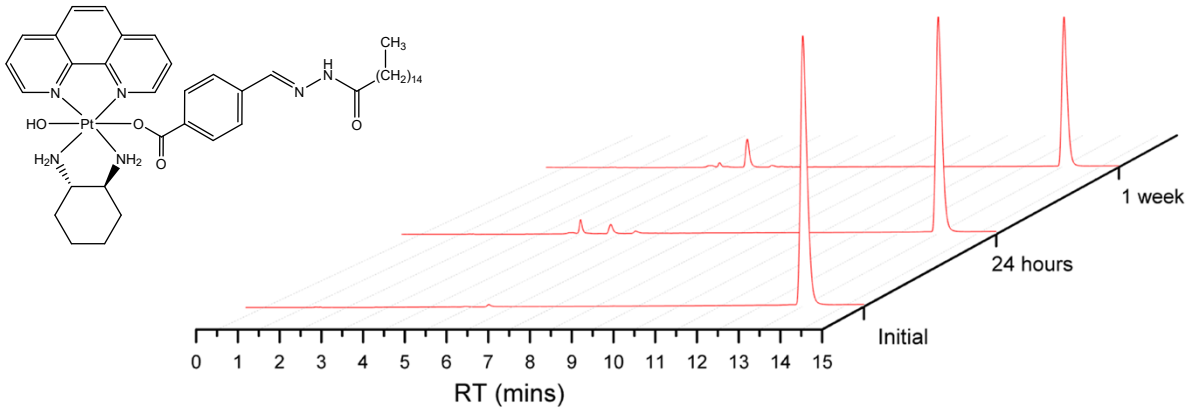


Figure H.5 Complex **6** (1mM) in 10 mM PBS. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

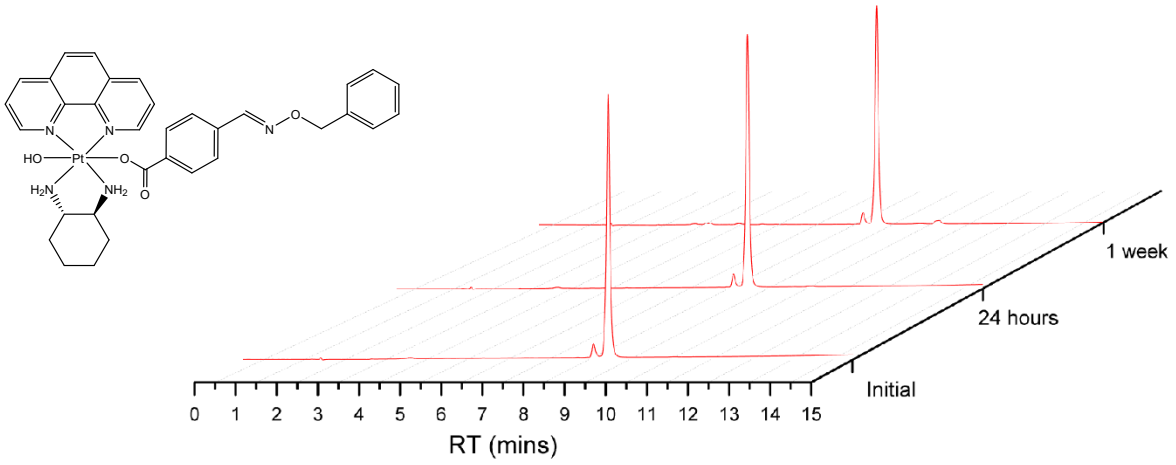


Figure H.6 Complex **7** (1 mM) in 10 mM PBS. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

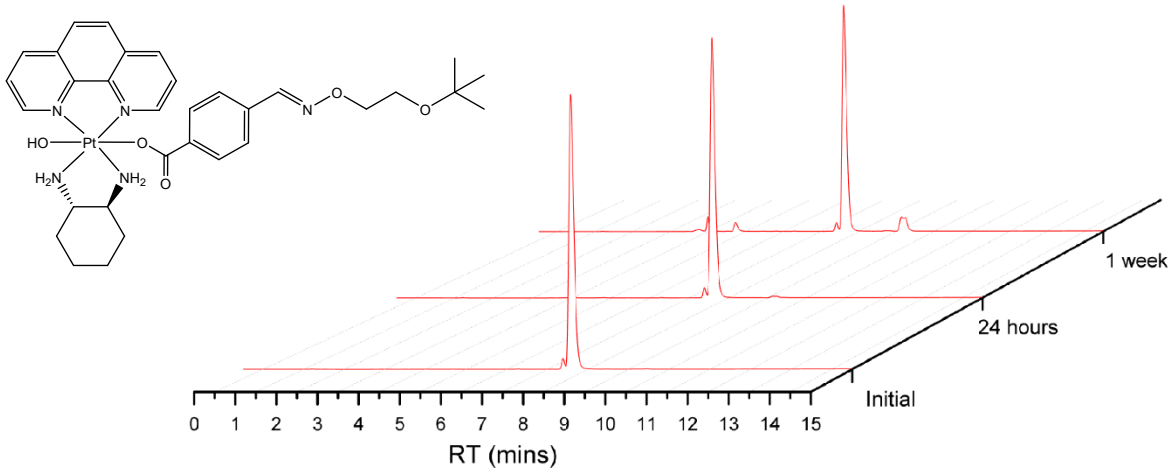


Figure H.7 Complex **8** (1 mM) in 10 mM PBS. Gradient 0-100 solvent B (15 mins). A = 0.06% TFA in H_2O. B = 0.06% TFA in CH_3CN:H_2O (9:1). Detection wavelength = 254 nm.

I. ^{195}Pt NMR stability studies

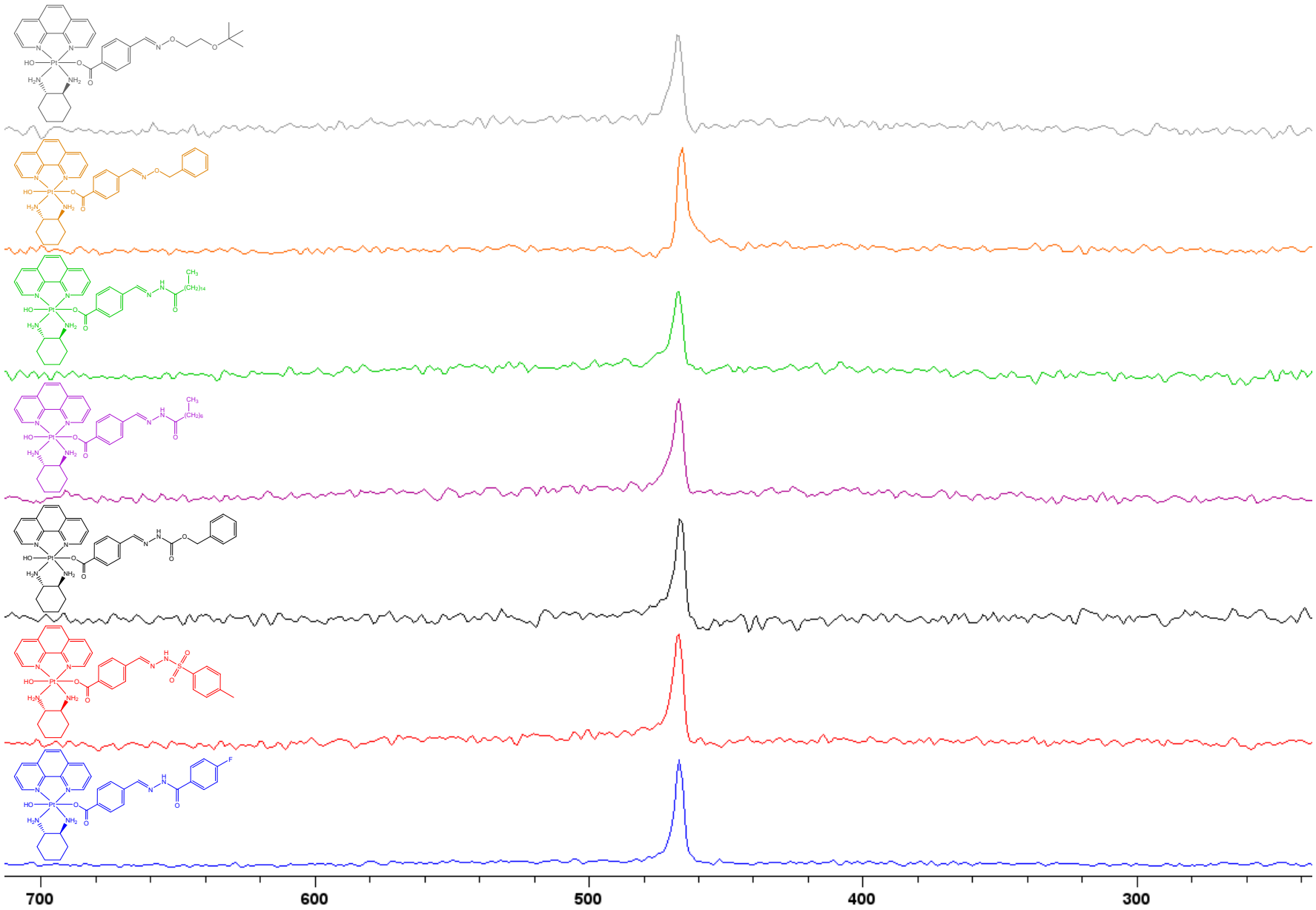


Figure I.1 ^{195}Pt NMR of Pt(IV) region for Complexes **2-8** after 100 days in DMSO-d_6.

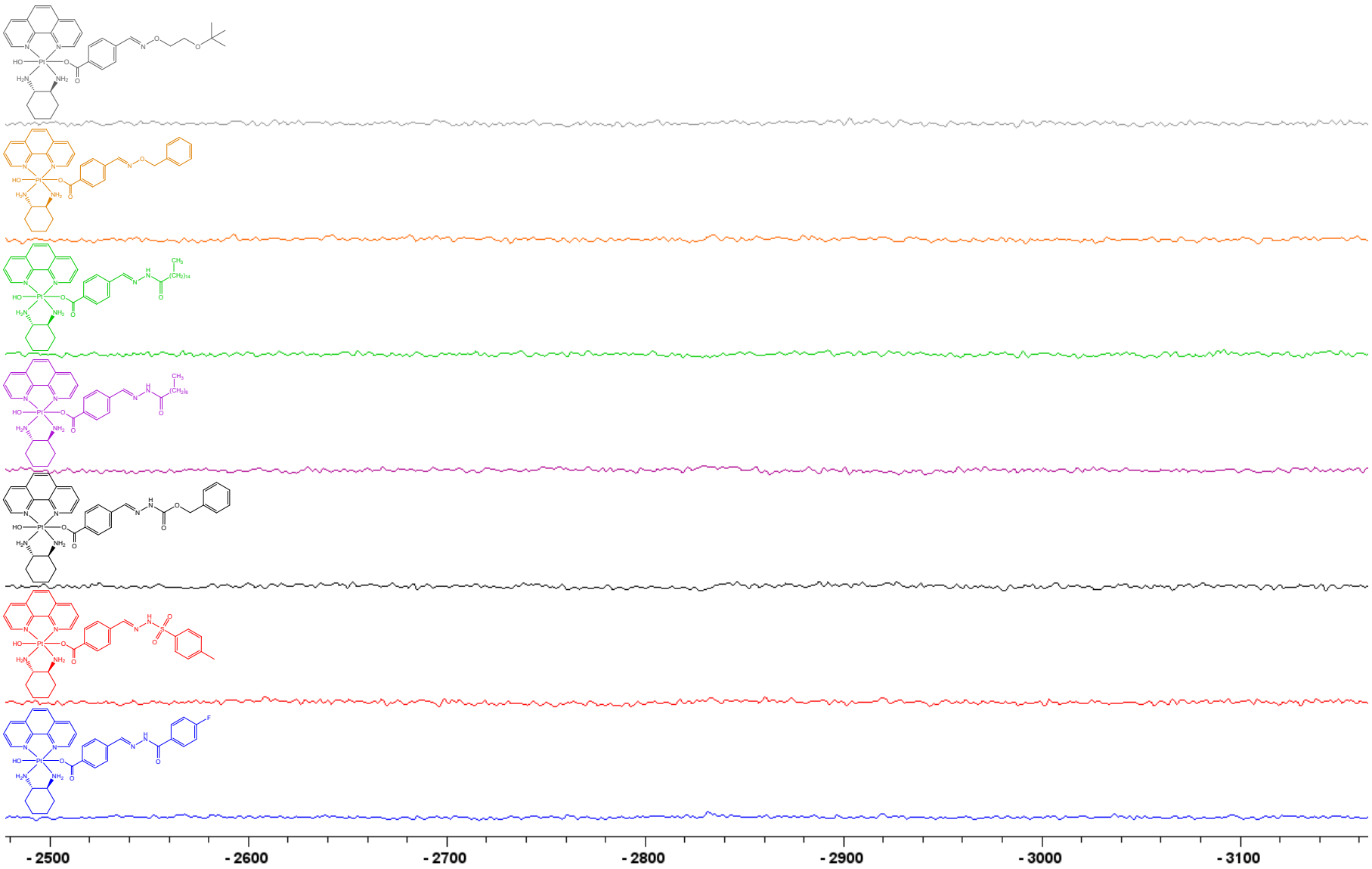


Figure I.2 ^{195}Pt NMR of Pt(II) region for Complexes **2-8** after 100 days in DMSO-d_6.