SUPPORTING INFORMATION

Synthesis, Characterisation and Potent Cytotoxicity of Unconventional Platinum(IV) Complexes with Modified Lipophilicities

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A. NMR Spectra

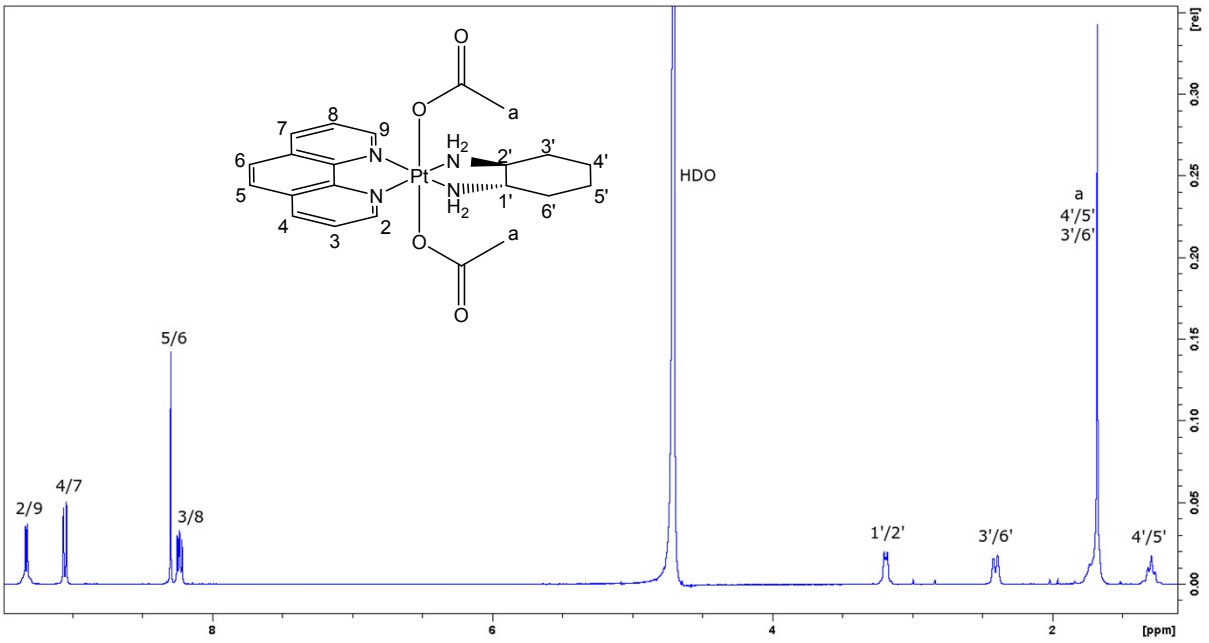


Figure A.1 ^{1}H NMR of **[Pt(PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** in D_2O at 298 K. Inset: Structure and proton numbering scheme of **[Pt(PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$**.

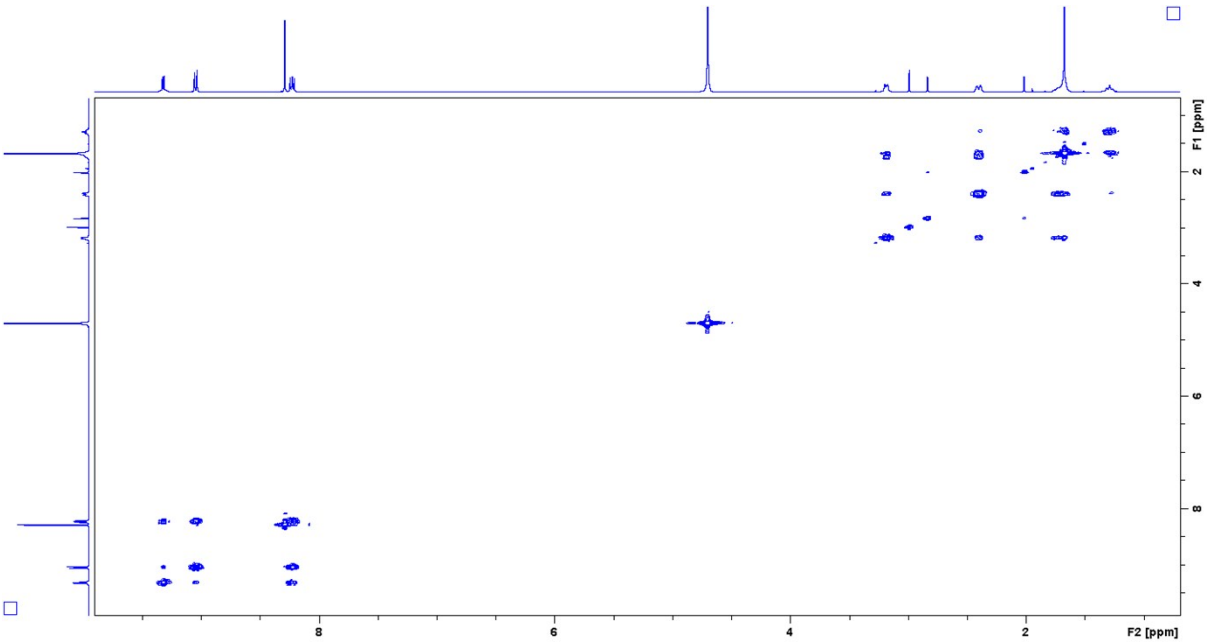


Figure A.2 COSY NMR of **[Pt(PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** in D_2O at 298 K.

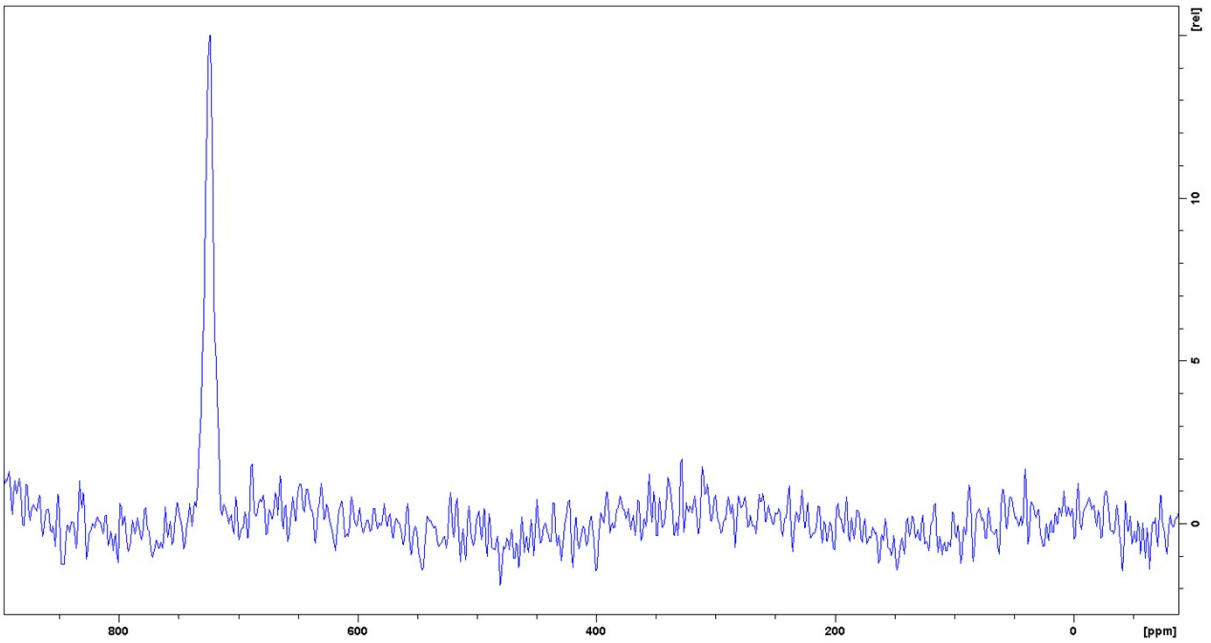


Figure A.3 ^{195}Pt NMR of **[Pt(PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** in D_2O at 298 K, showing a peak at 724 ppm.

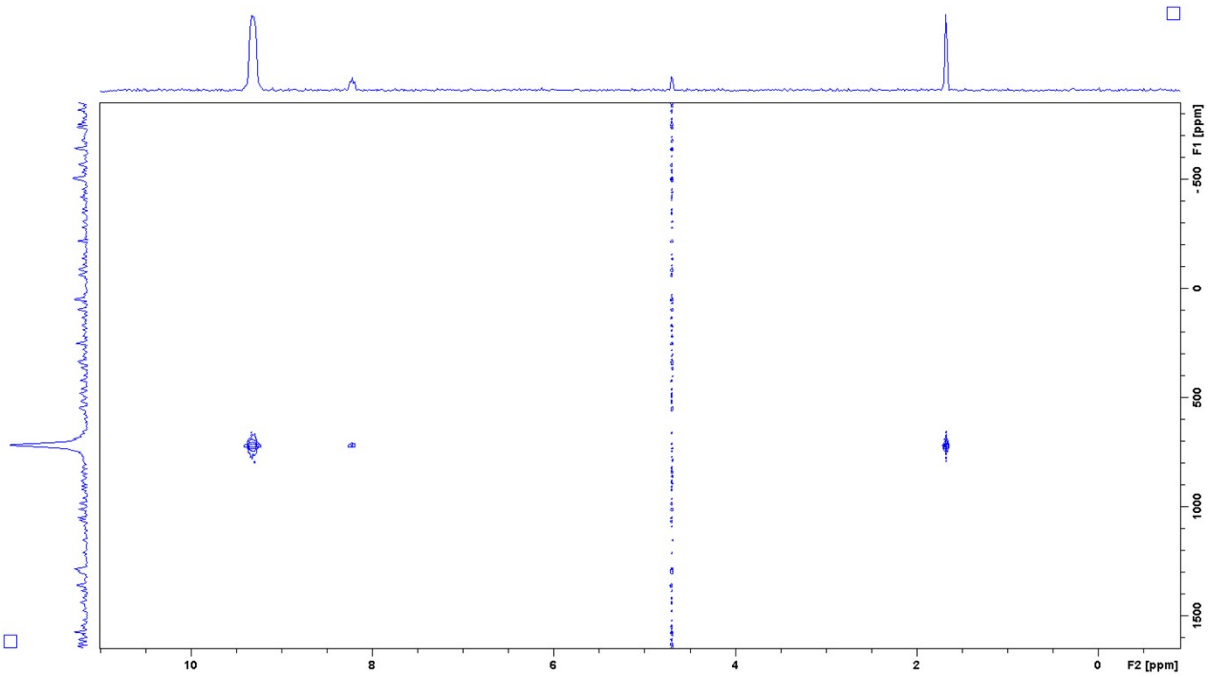


Figure A.4 ^{1}H-^{195}Pt HMQC NMR of **[Pt(PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** showing proton and platinum coupling resonances, in D_2O at 298 K.

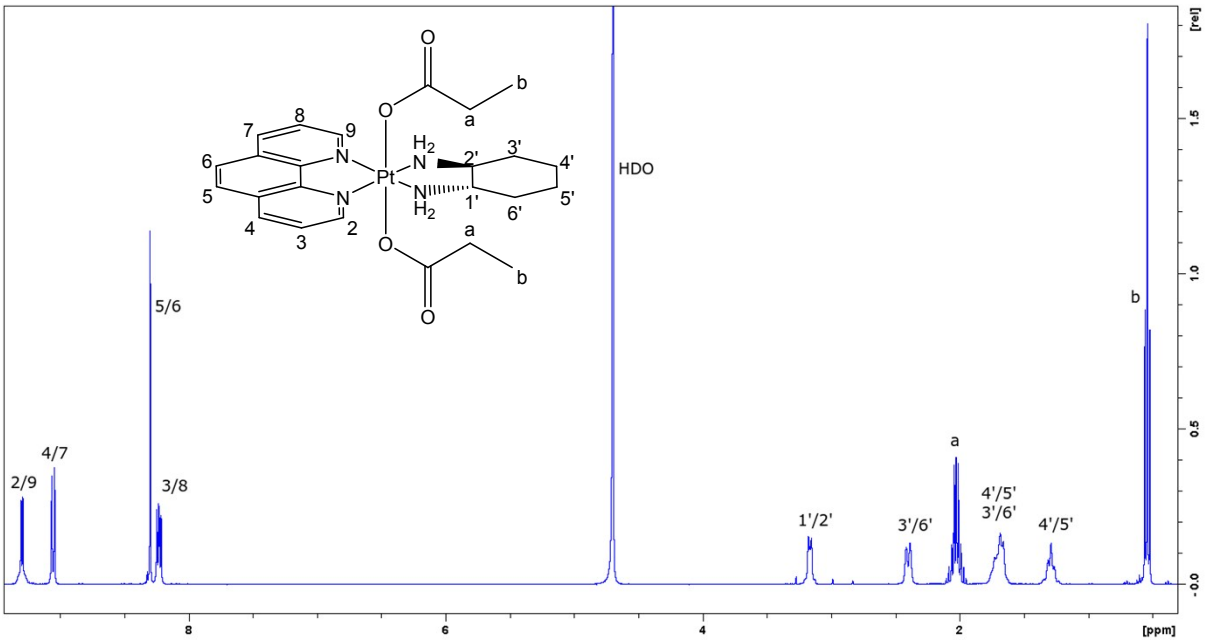


Figure A.5 ^{1}H NMR of **[Pt(PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K. Inset: Structure and proton numbering scheme of **[Pt(PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$**.

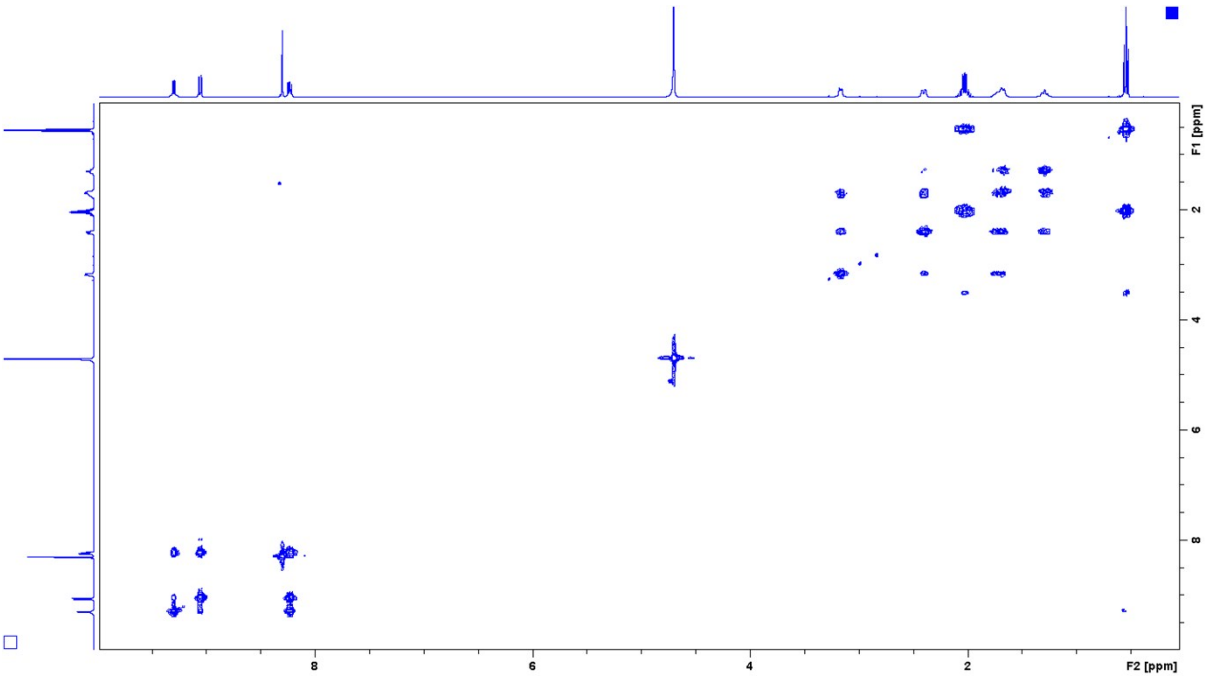
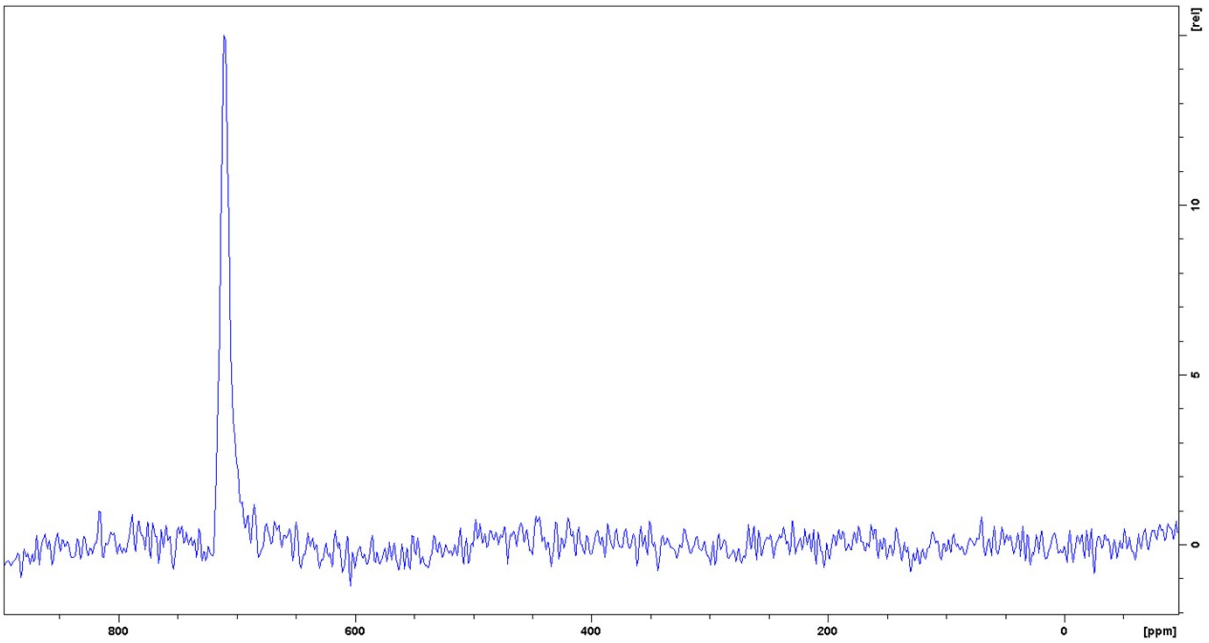


Figure A.6 COSY NMR of **[Pt(PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K.



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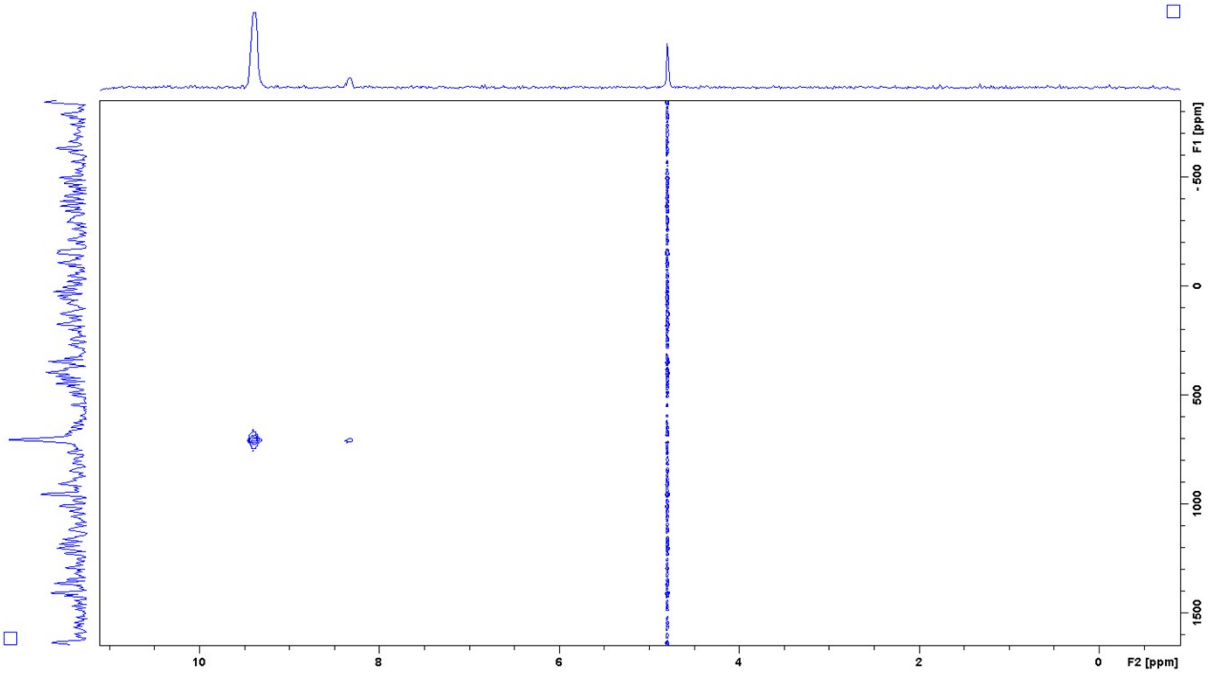

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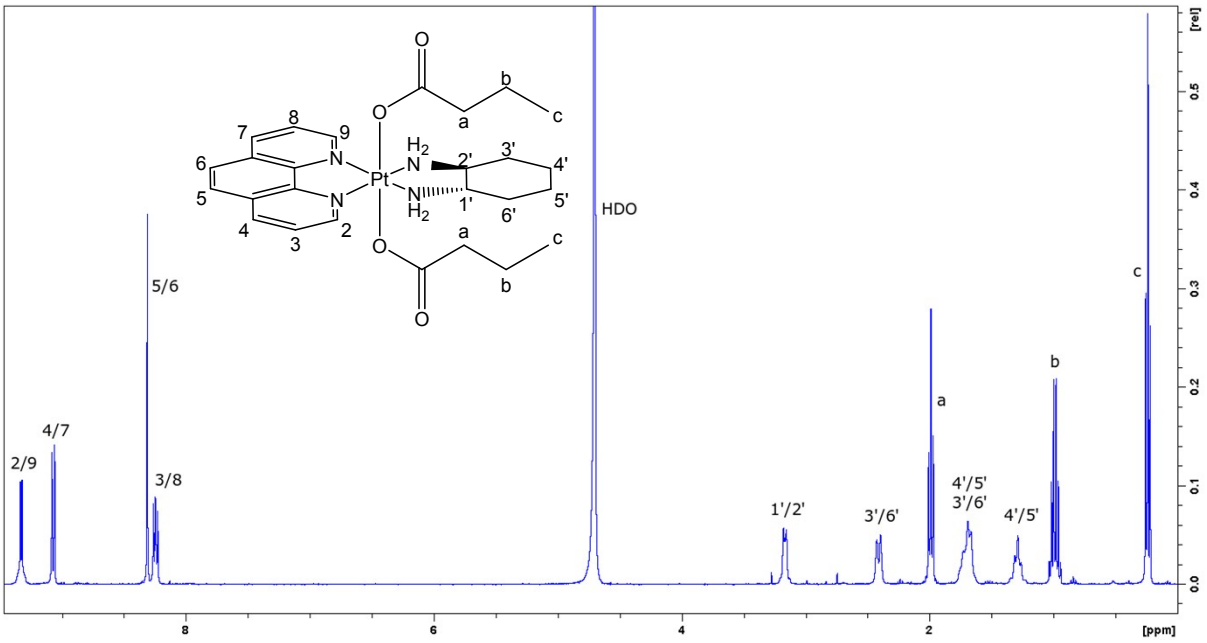

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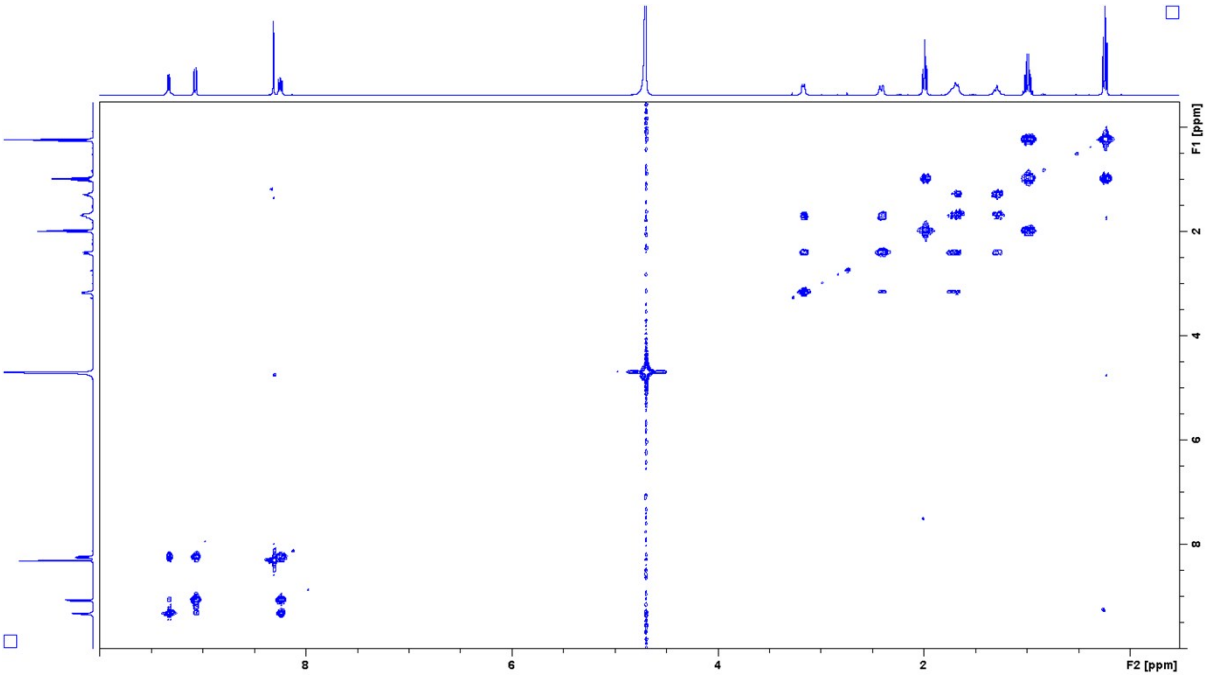

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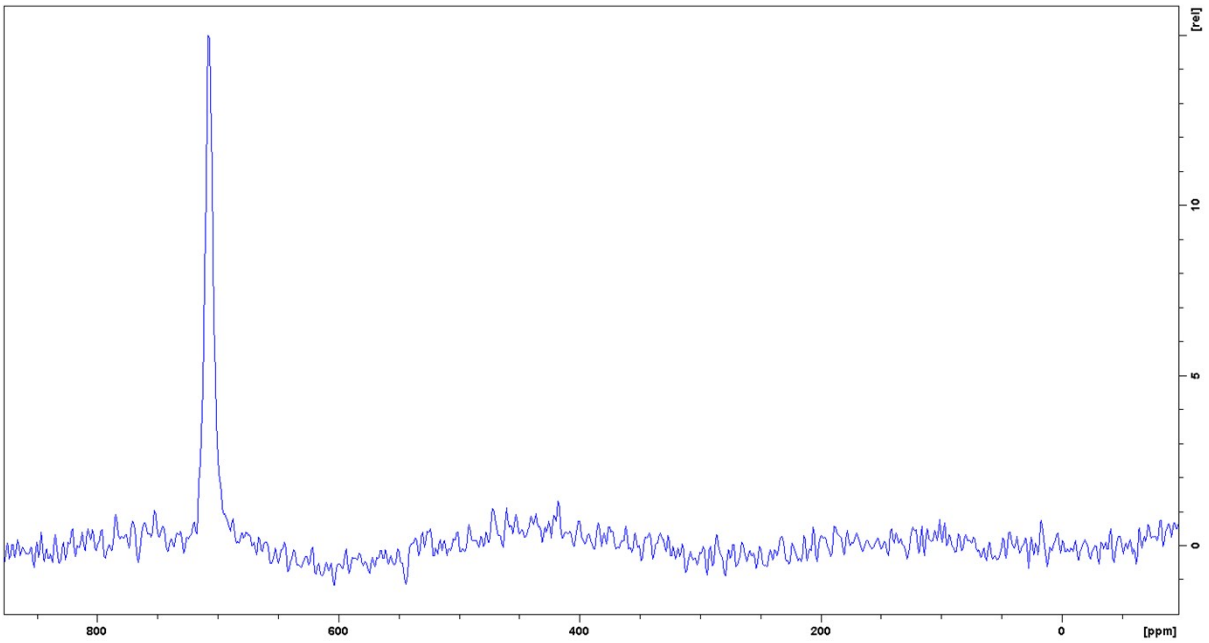
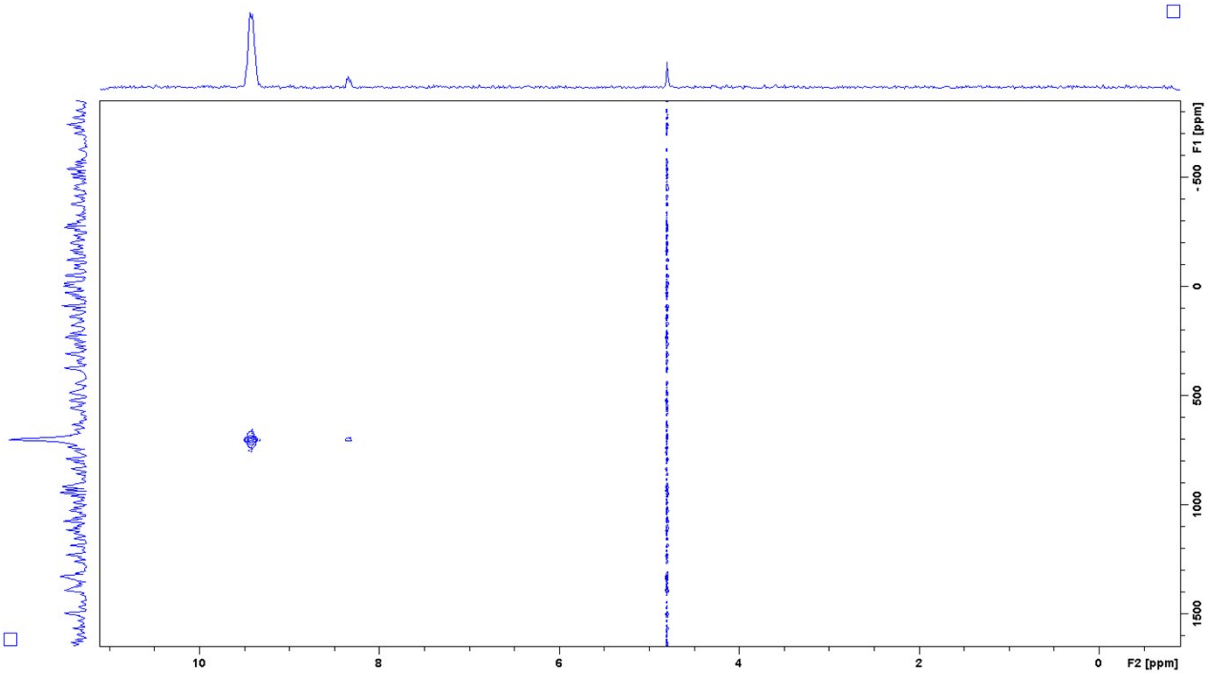


Figure A.11 ^{195}Pt NMR of **[Pt(PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K, showing a peak at 707 ppm.



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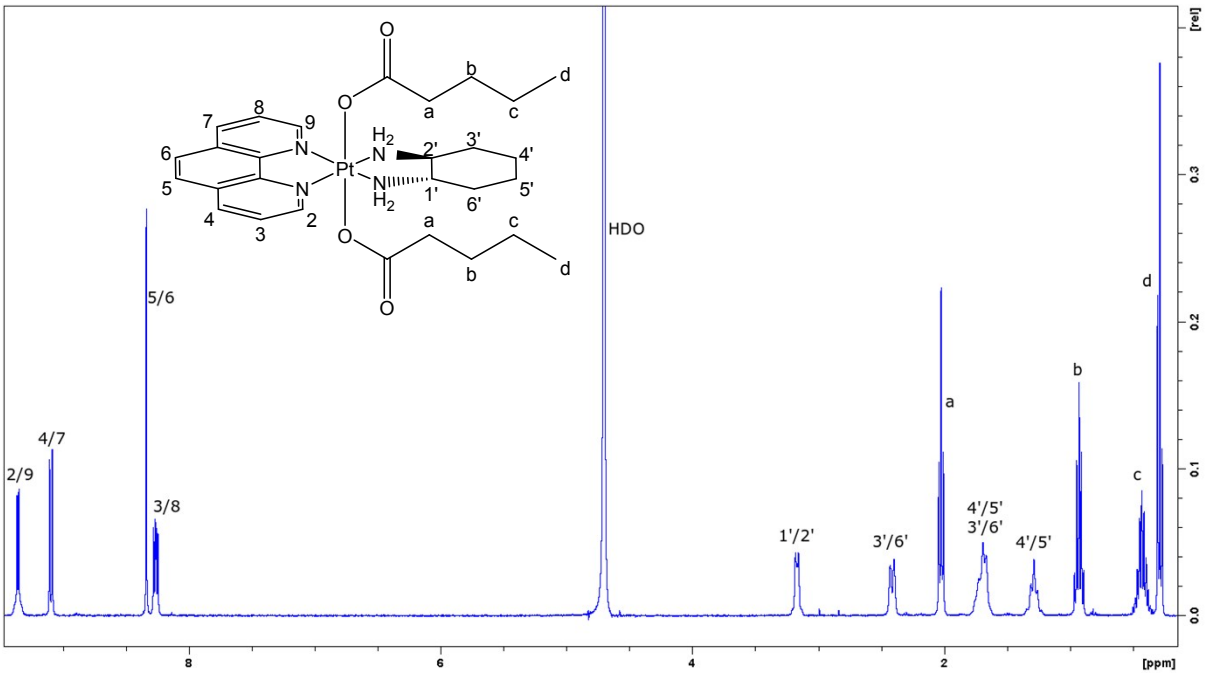

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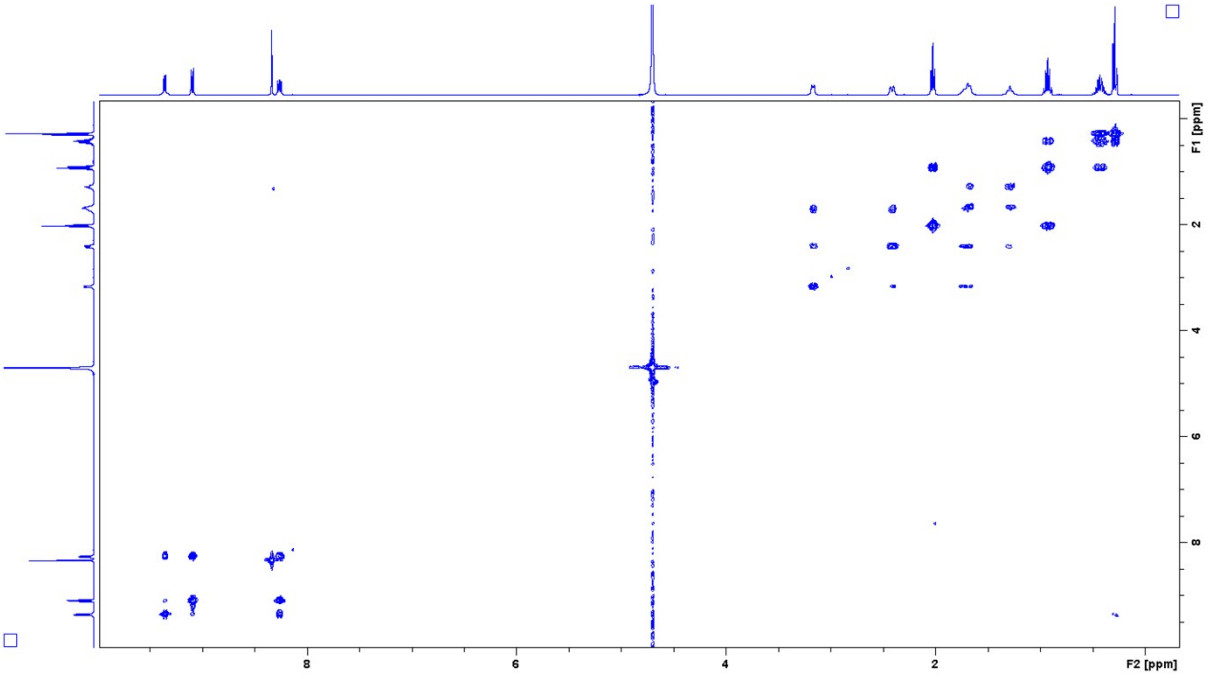

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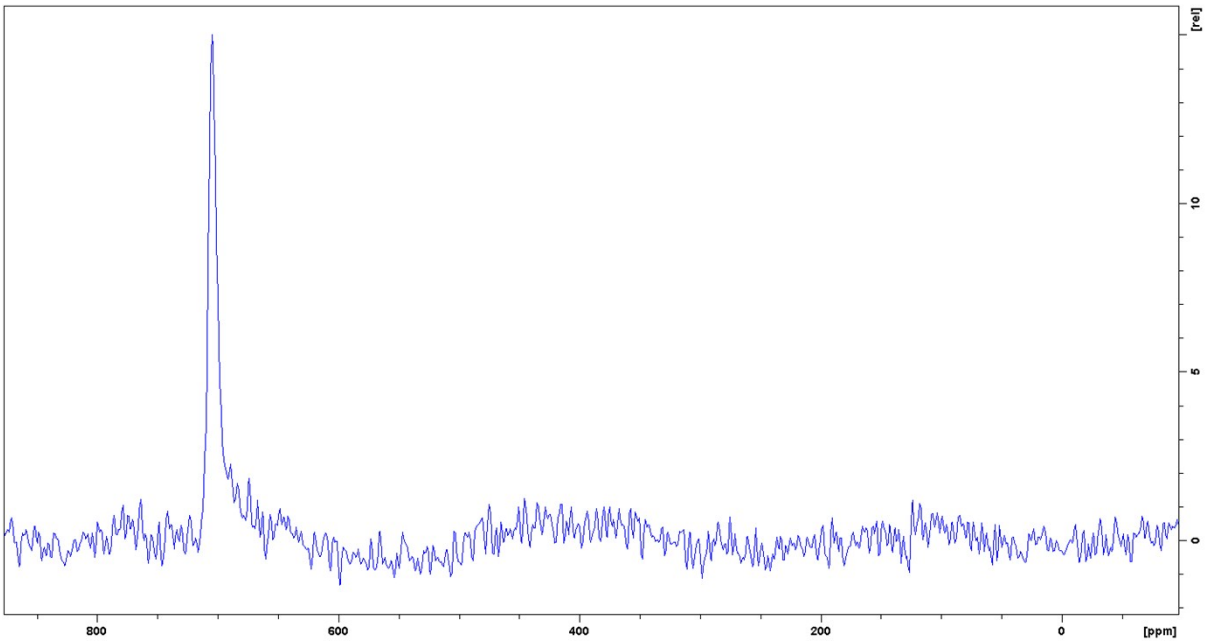
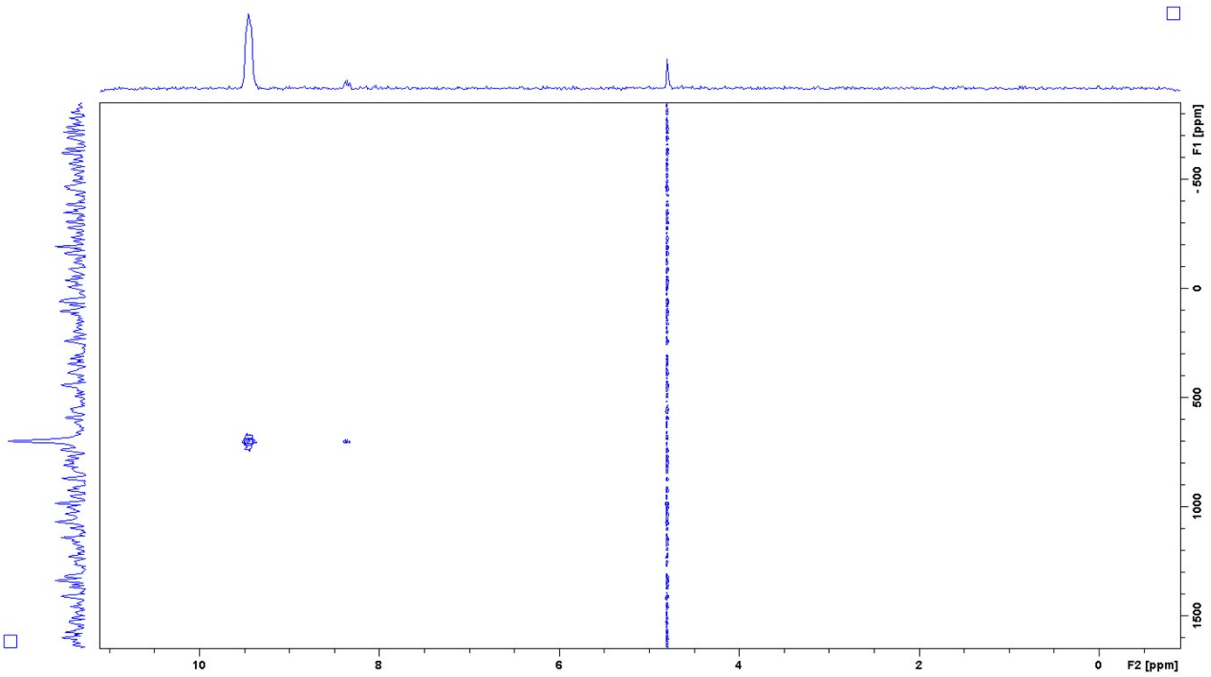


Figure A.15 ^{195}Pt NMR of **[Pt(PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K, showing a peak at 705 ppm.



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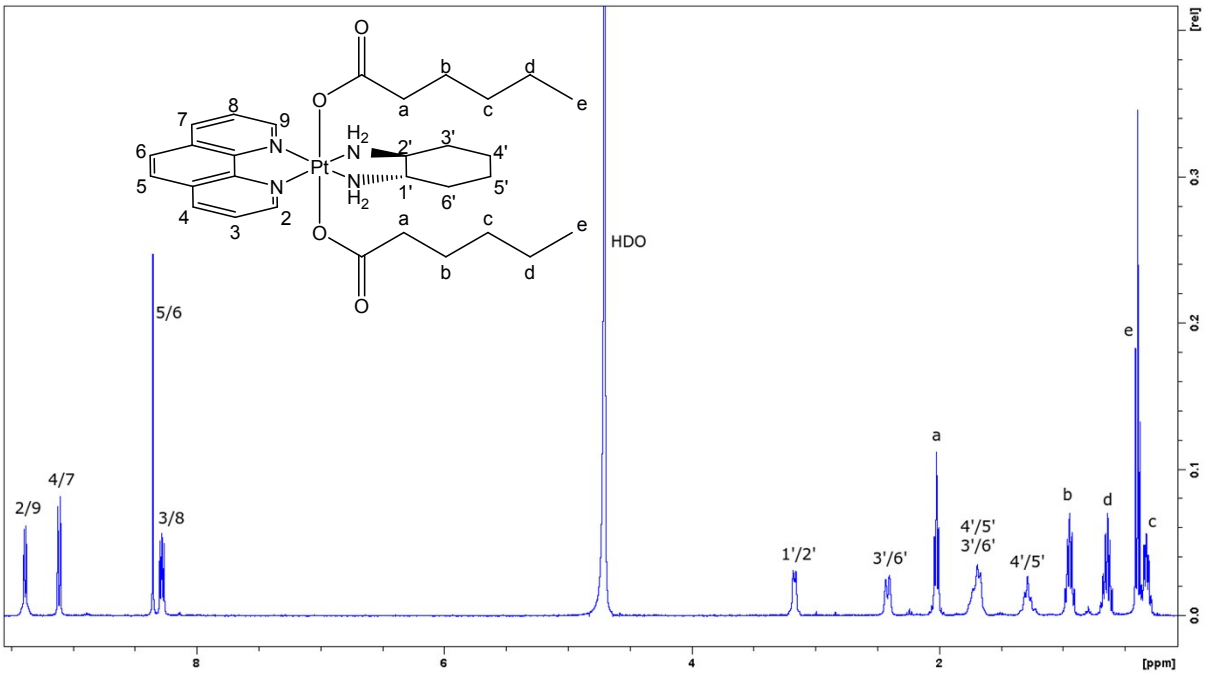


Figure A.17 ^{1}H NMR of **[Pt(PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K. Inset: Structure and proton numbering scheme of **[Pt(PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$**.

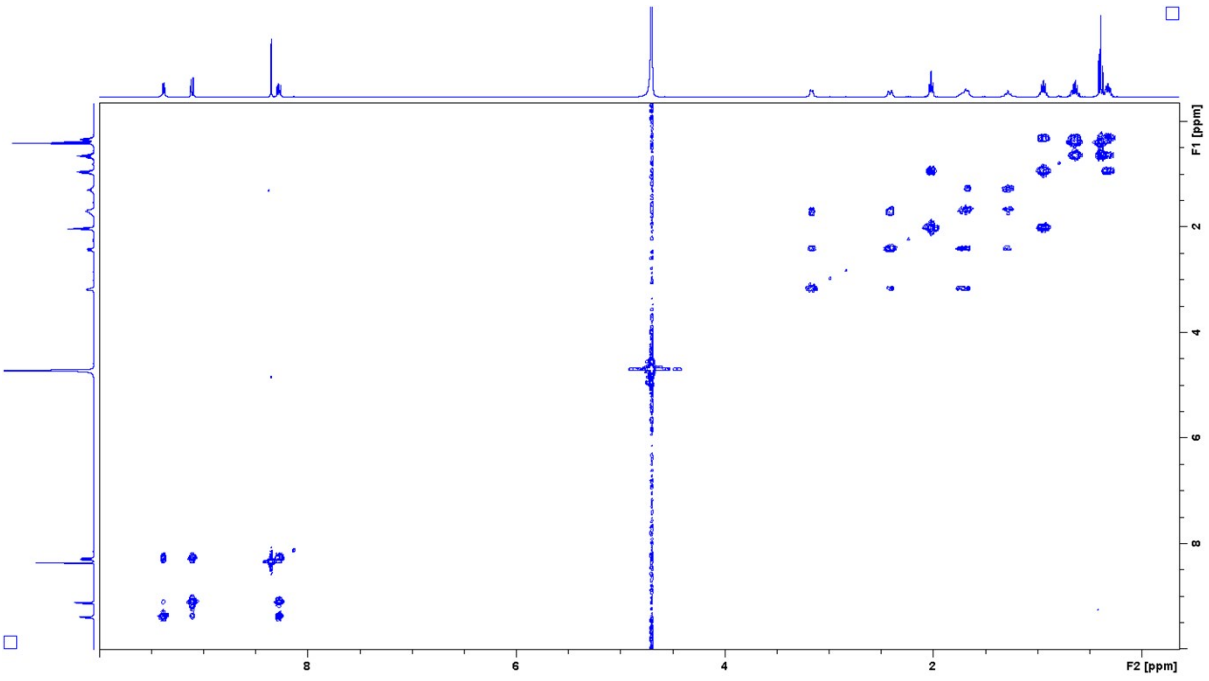


Figure A.18 COSY NMR of **[Pt(PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K.

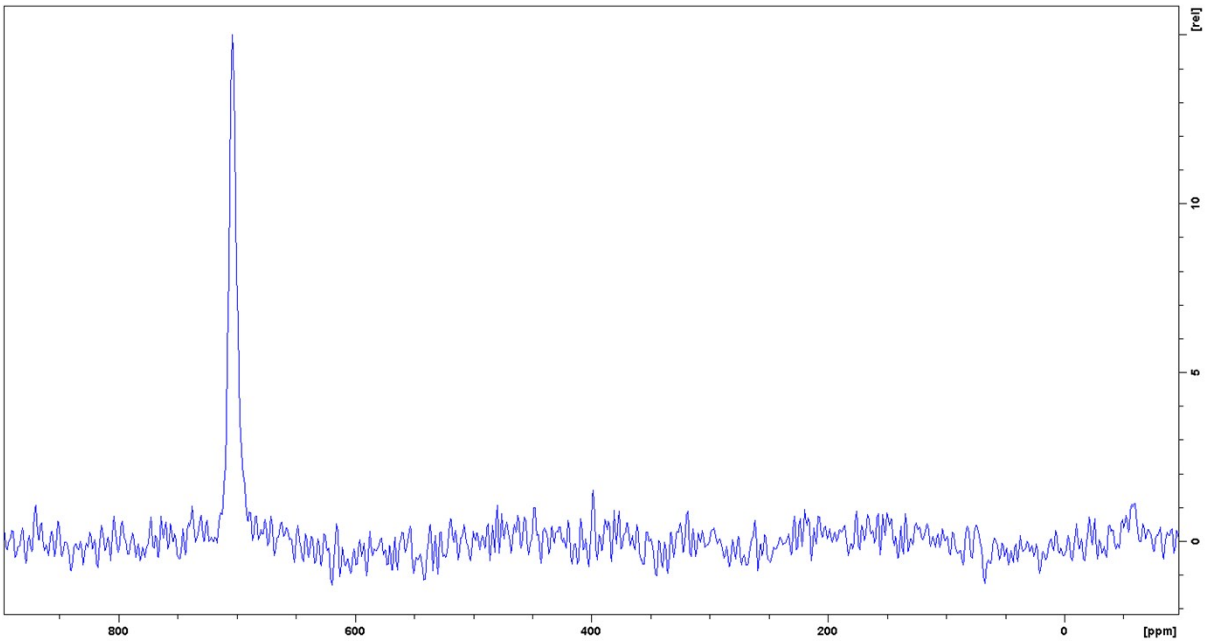


Figure A.19 ^{195}Pt NMR of **[Pt(PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K, showing a peak at 703 ppm.

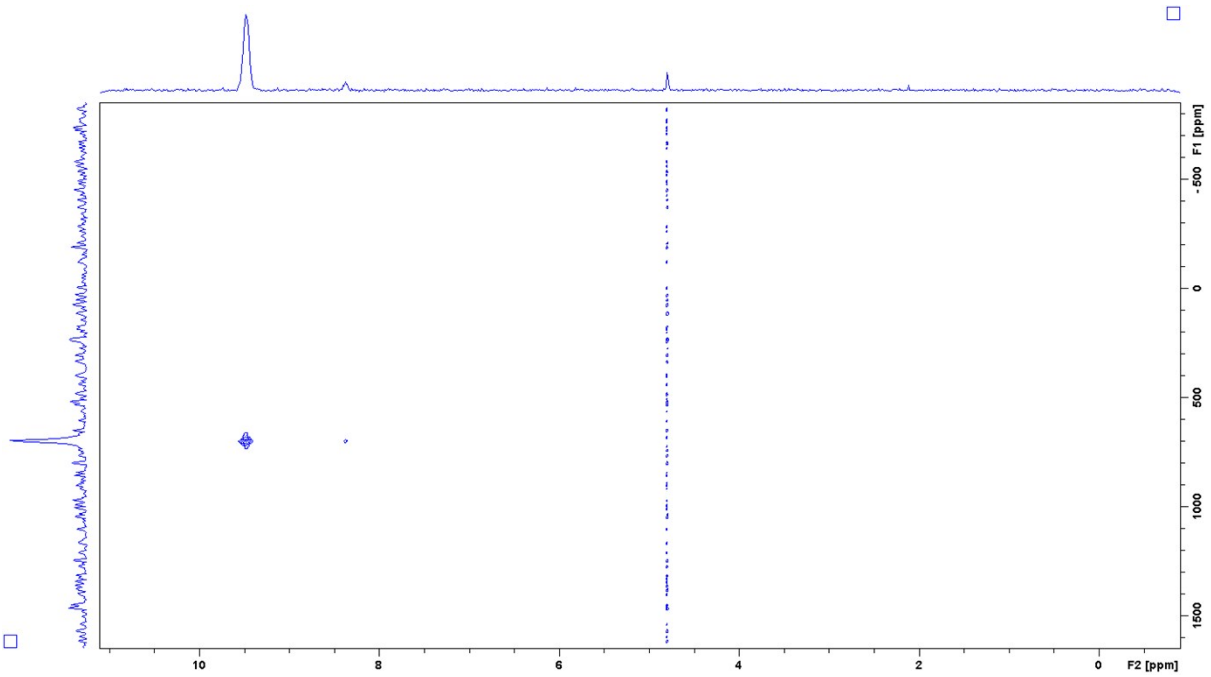


Figure A.20 ^{1}H-^{195}Pt HMQC NMR of **[Pt(PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** showing proton and platinum coupling resonances, in D_2O at 298 K.

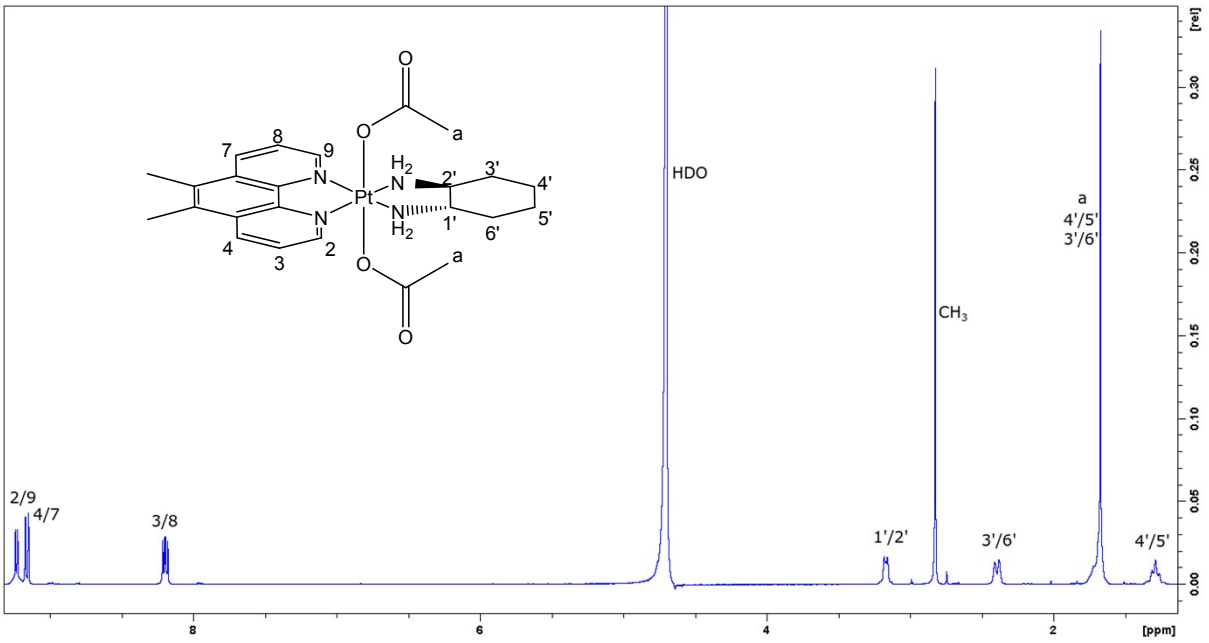


Figure A.21 ^{1}H NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** in D_2O at 298 K. Inset: Structure and proton numbering scheme of **[Pt(56Me$_2$PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$**.

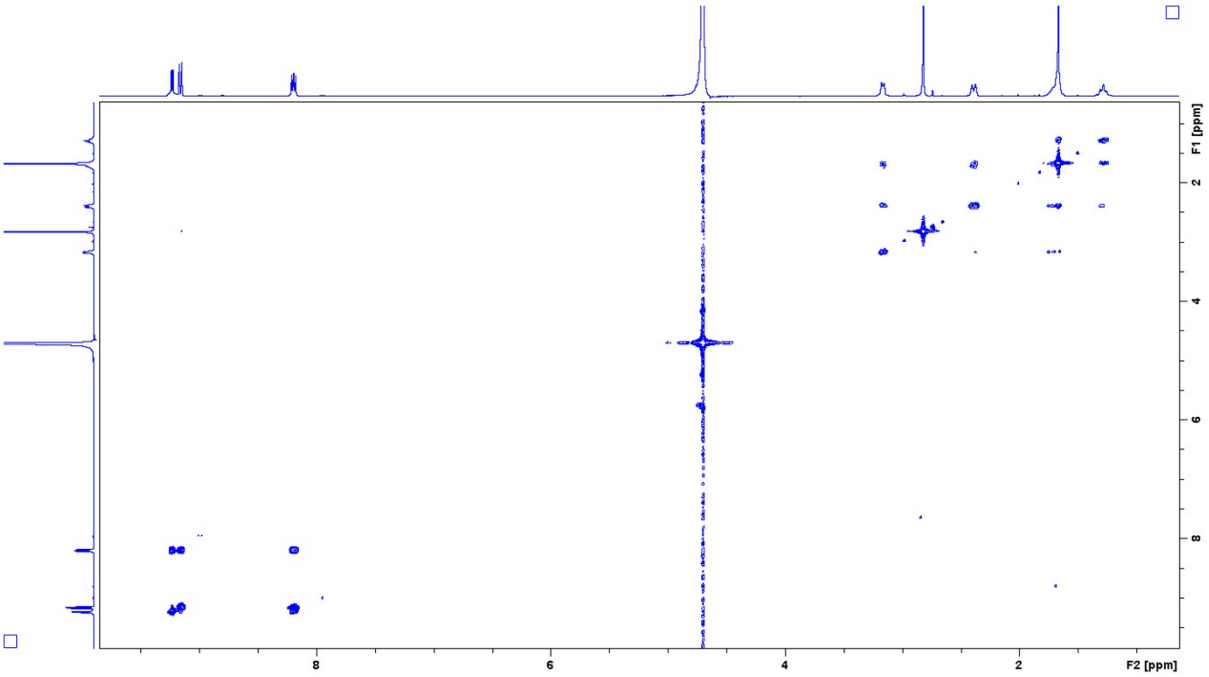


Figure A.22 COSY NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** in D_2O at 298 K.

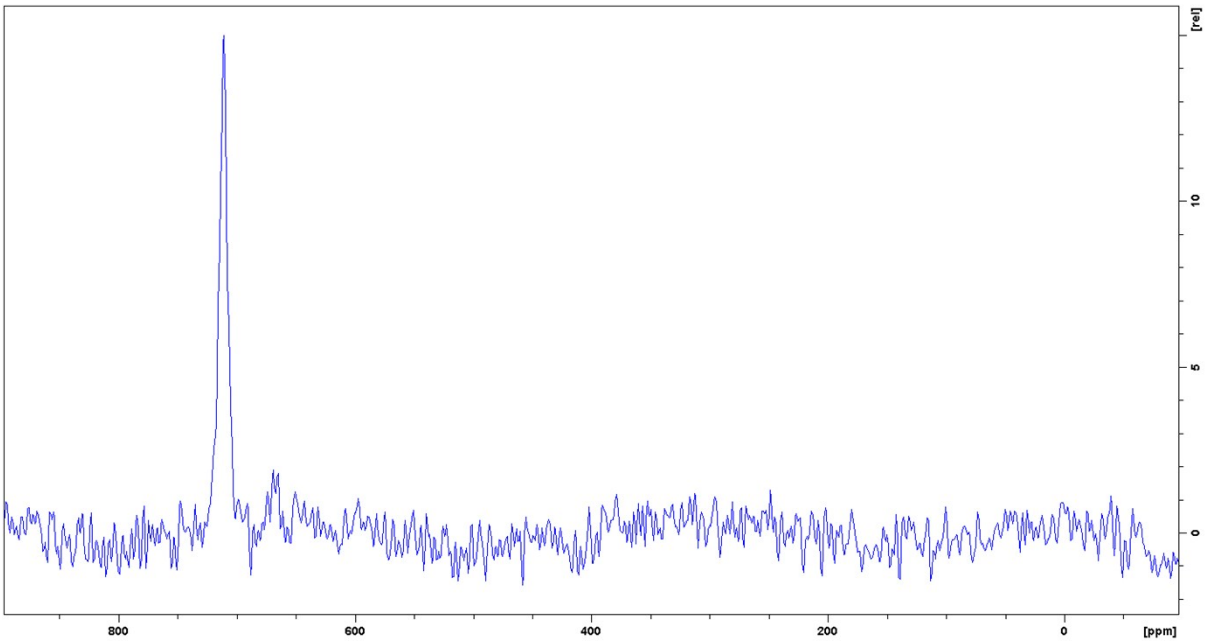


Figure A.23 ^{195}Pt NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** in D_2O at 298 K, showing a peak at 711 ppm.

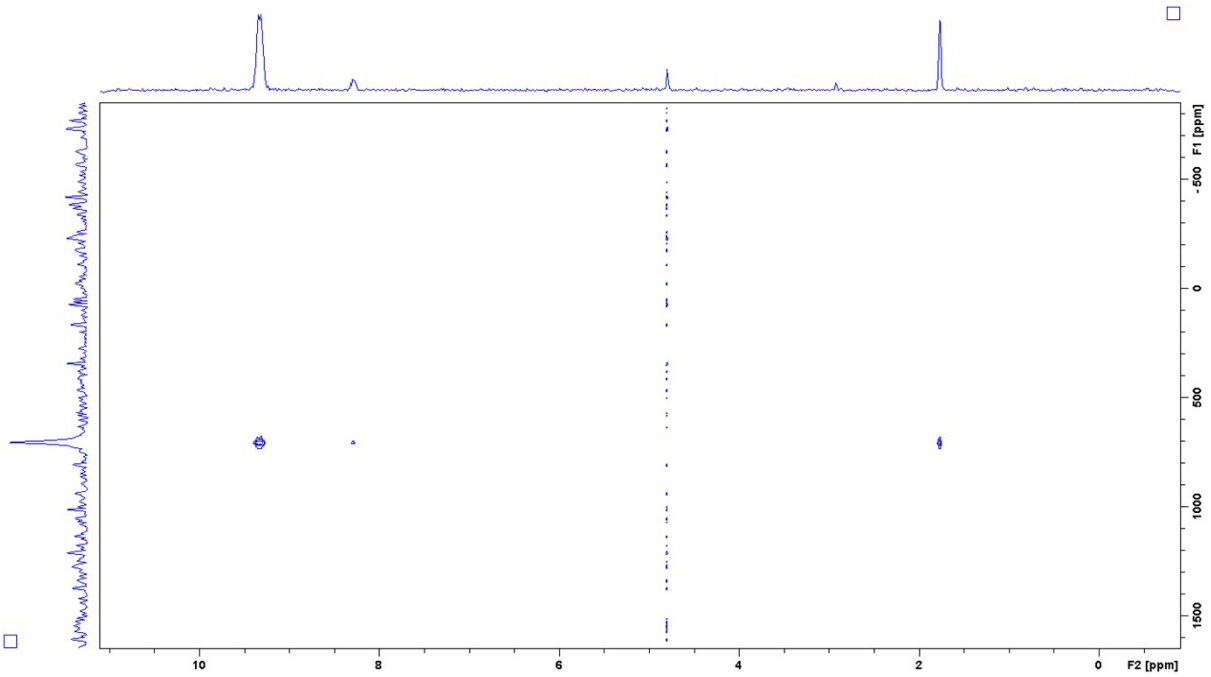


Figure A.24 ^{1}H-^{195}Pt HMQC NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** showing proton and platinum coupling resonances, in D_2O at 298 K.

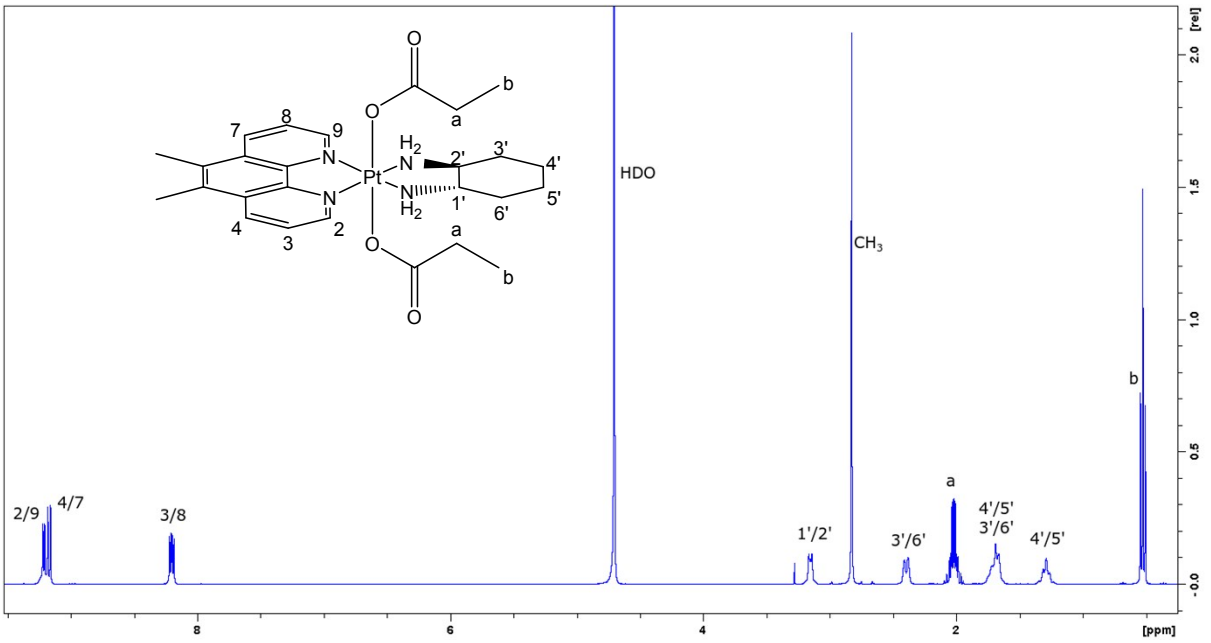


Figure A.25 ^{1}H NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K. Inset: Structure and proton numbering scheme of **[Pt(56Me$_2$PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$**.

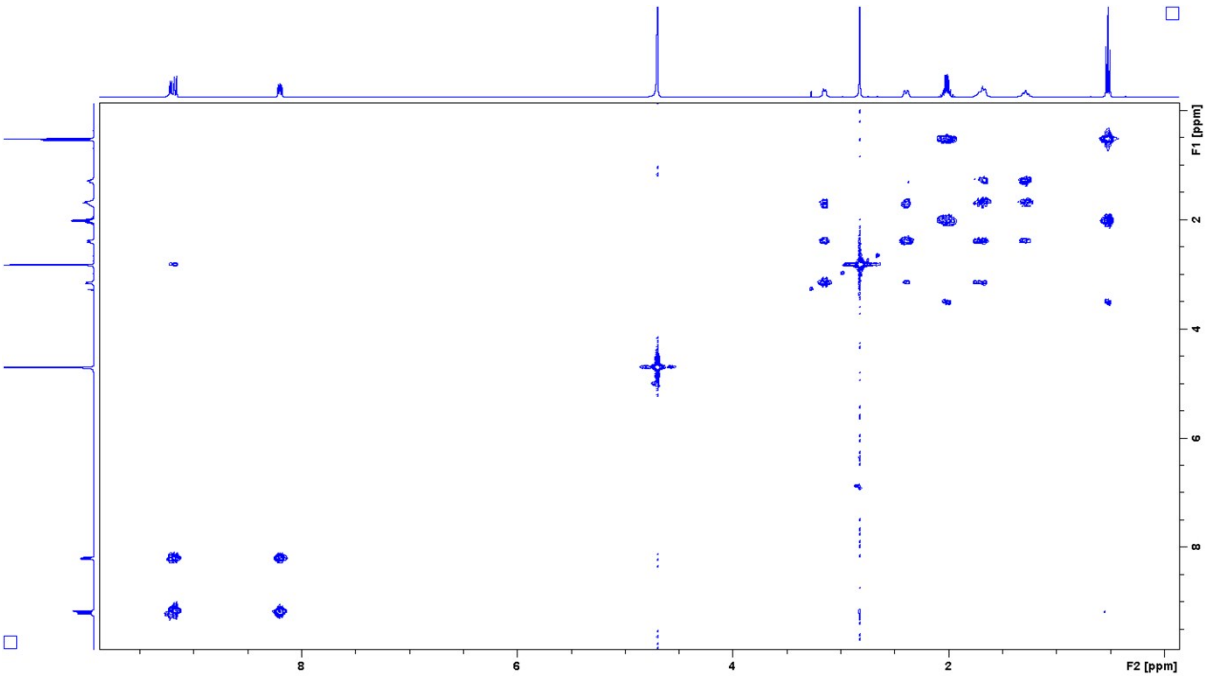


Figure A.26 COSY NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K.

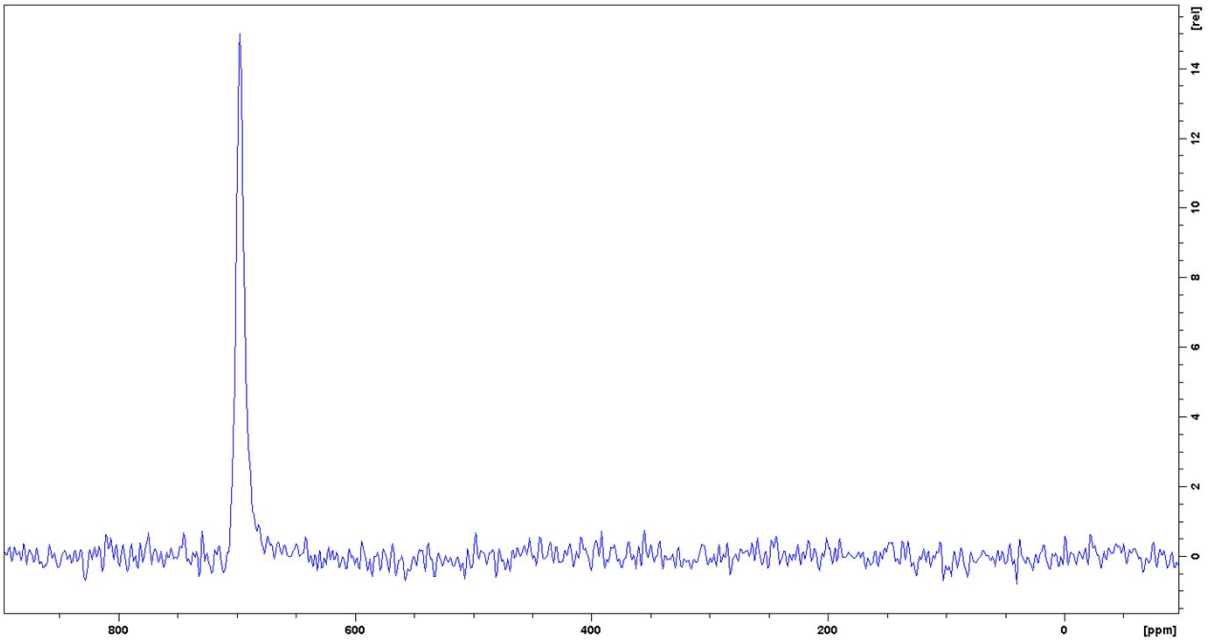
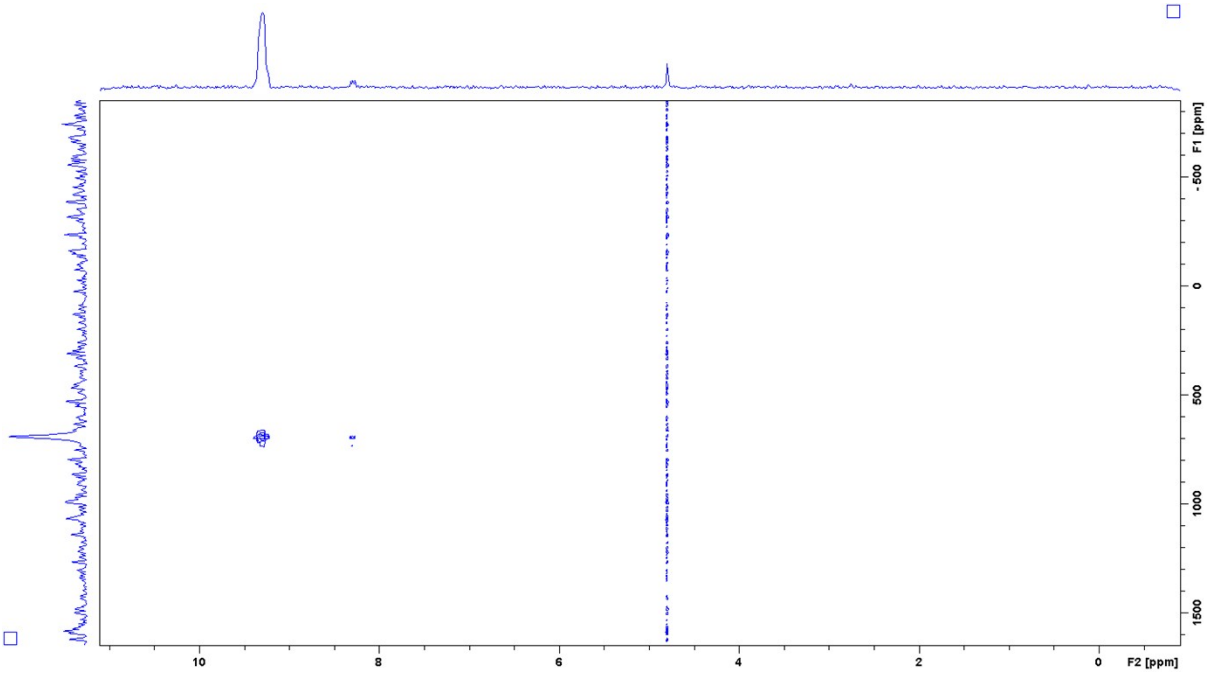


Figure A.27 ^{195}Pt NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K, showing a peak at 697 ppm.



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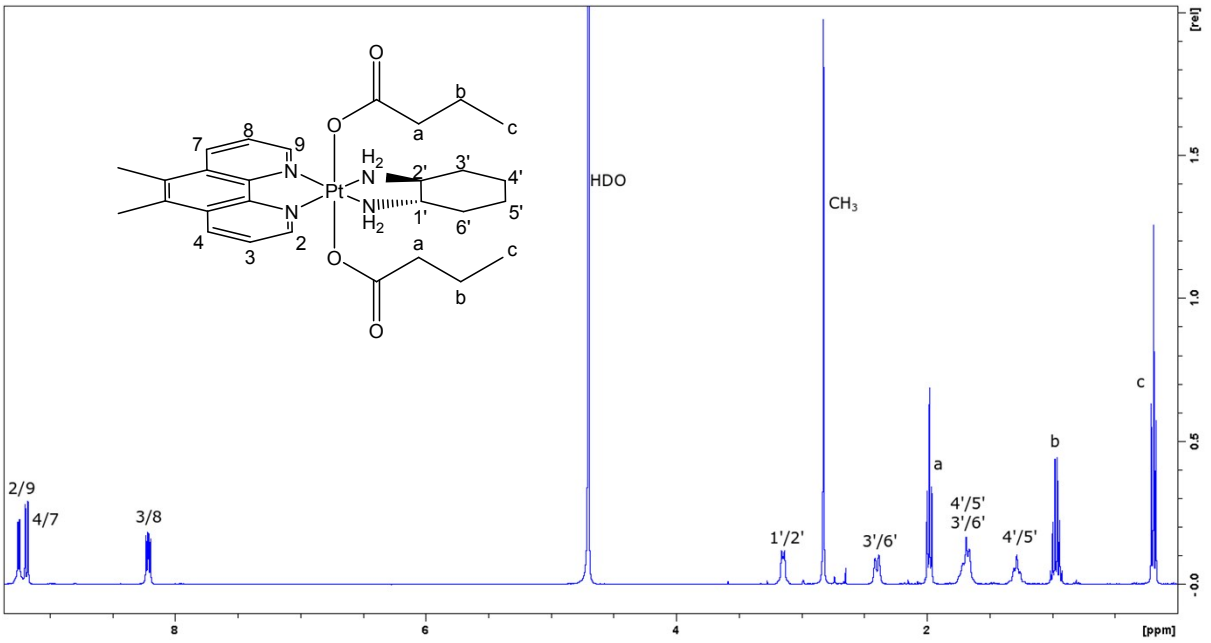

Figure A.29 ^{1}H NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K. Inset: Structure and proton numbering scheme of **[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$**.

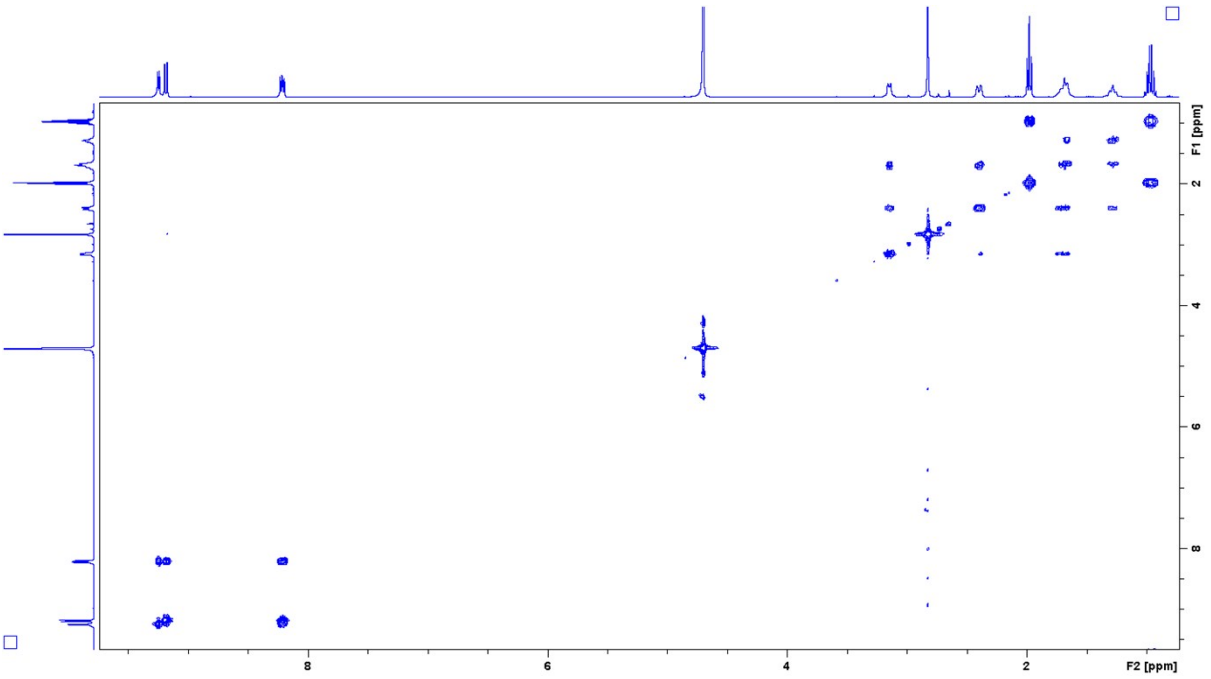

Figure A.30 COSY NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K. Inset: Structure and proton numbering scheme of **[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$**.

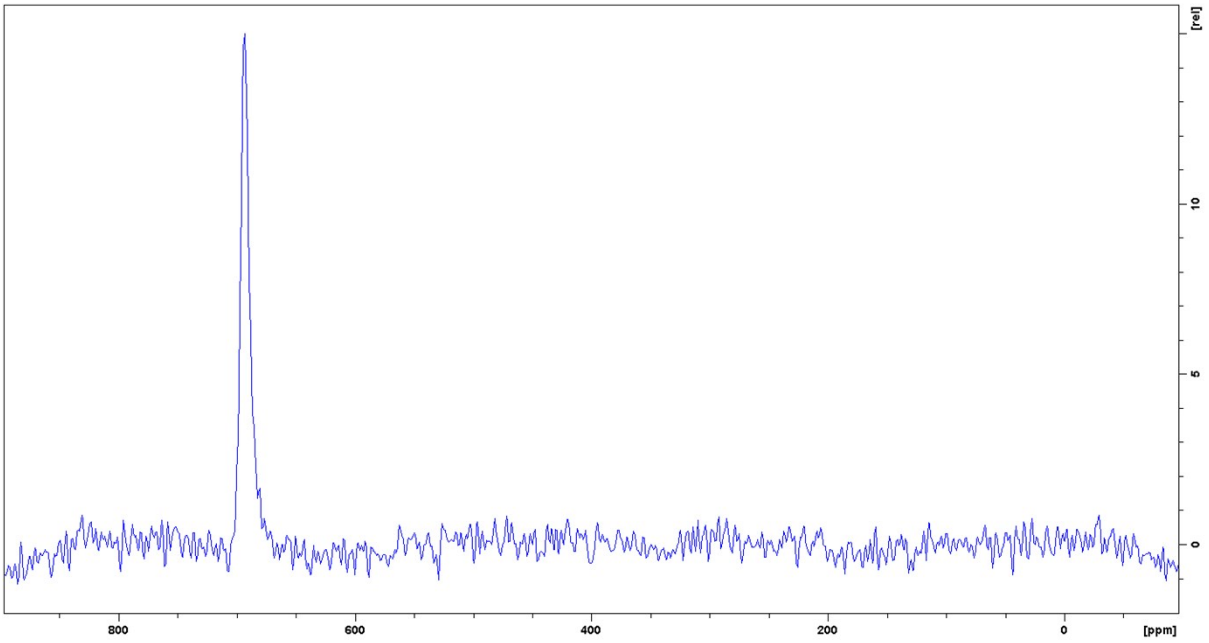

Figure A.31 ^{195}Pt NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K, showing a peak at 692 ppm.

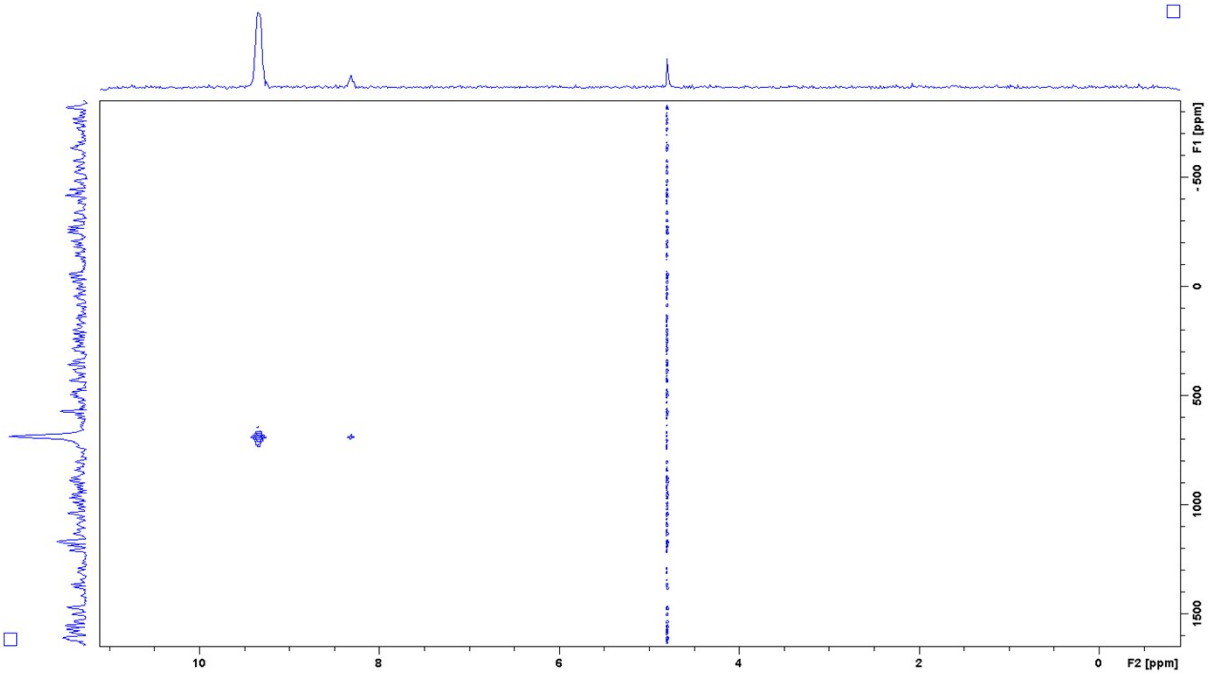

Figure A.32 ^{1}H-^{195}Pt HMQC NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** showing proton and platinum coupling resonances, in D_2O at 298 K.

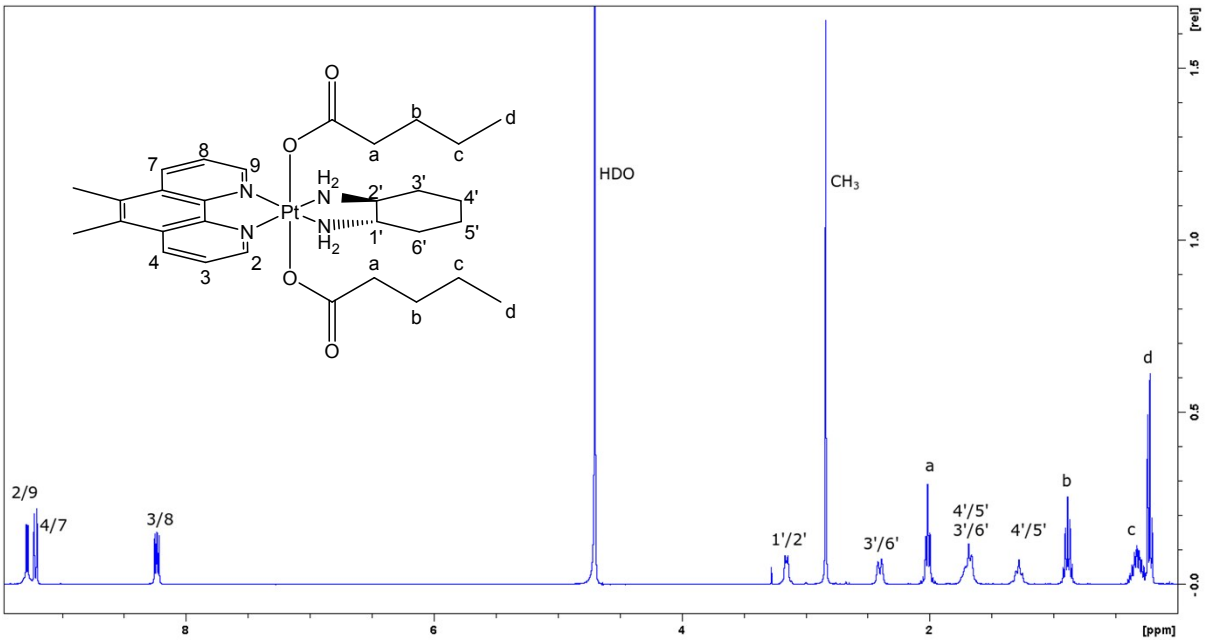

Figure A.33 ^{1}H NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K. Inset: Structure and proton numbering scheme of **[Pt(56Me$_2$PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$**.

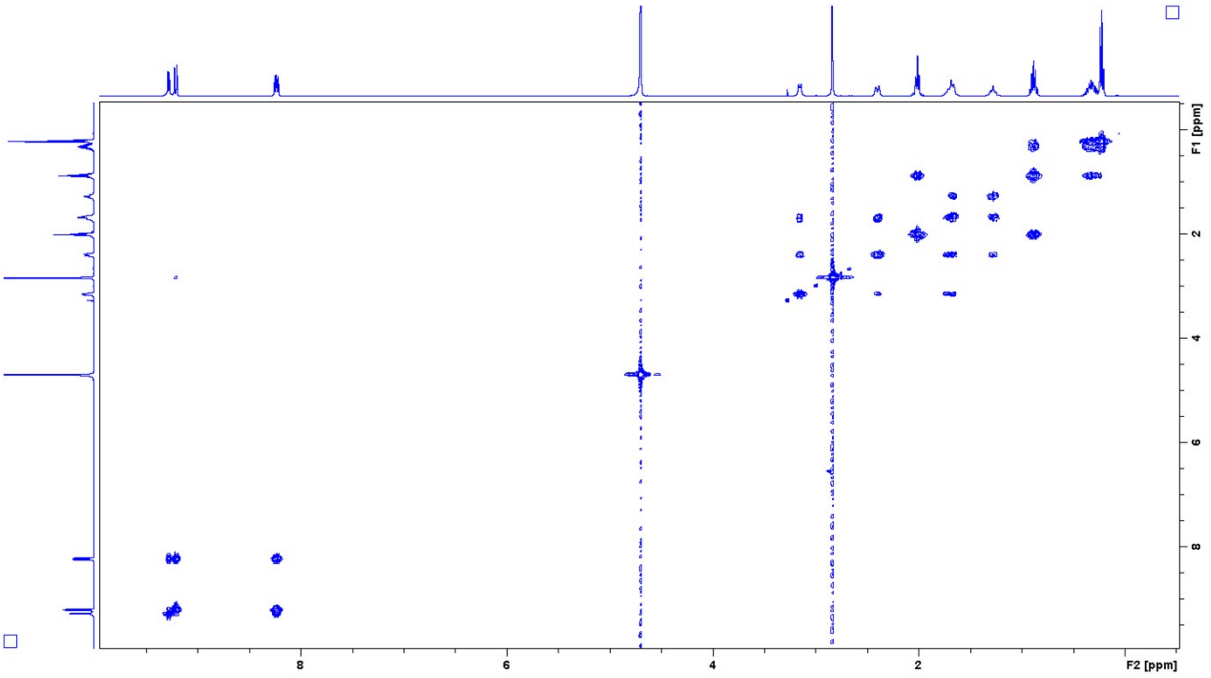

Figure A.34 COSY NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K.

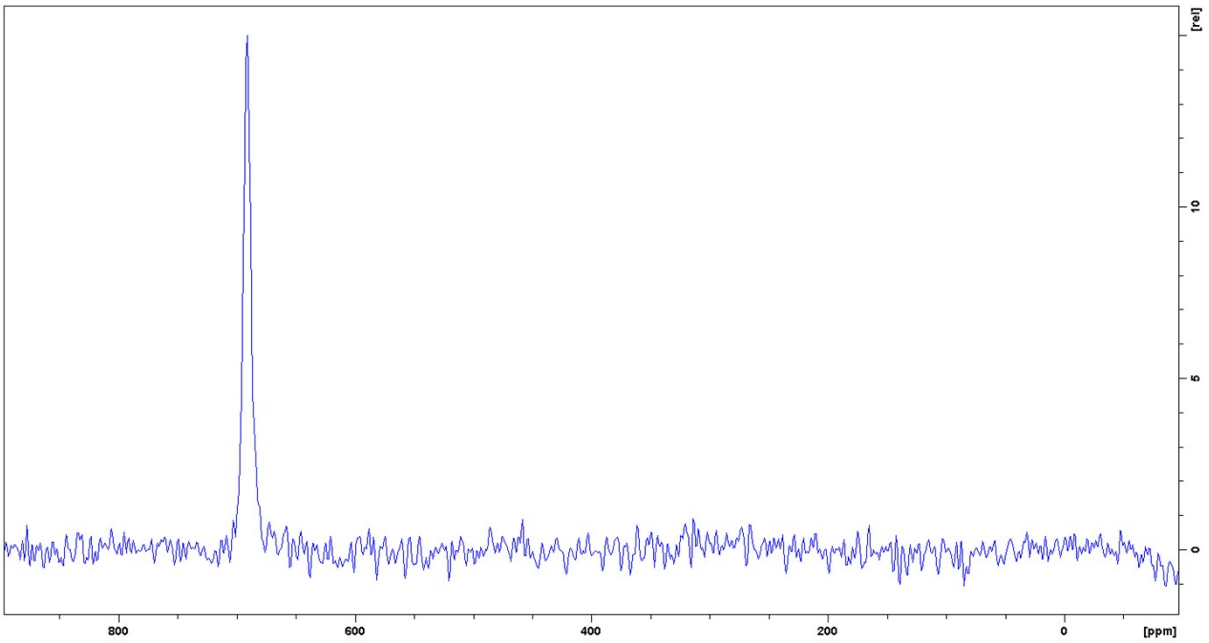

Figure A.35 ^{195}Pt NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K, showing a peak at 691 ppm.

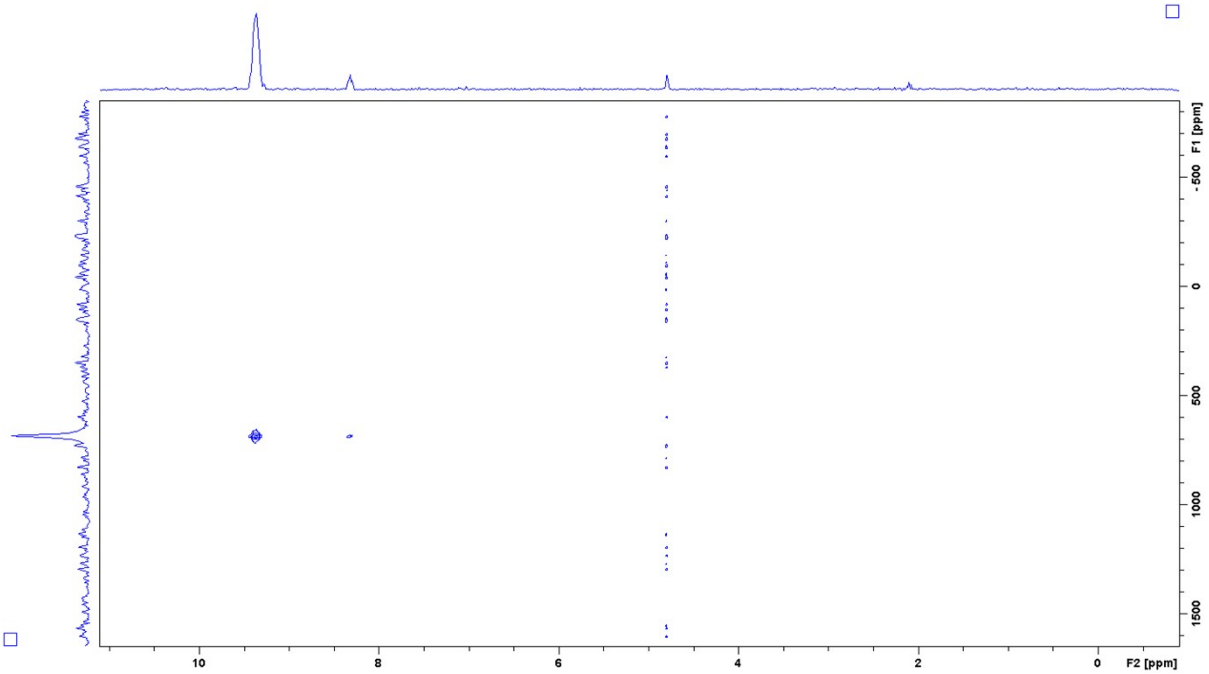

Figure A.36 ^{1}H-^{195}Pt HMQC NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** showing proton and platinum coupling resonances, in D_2O at 298 K.

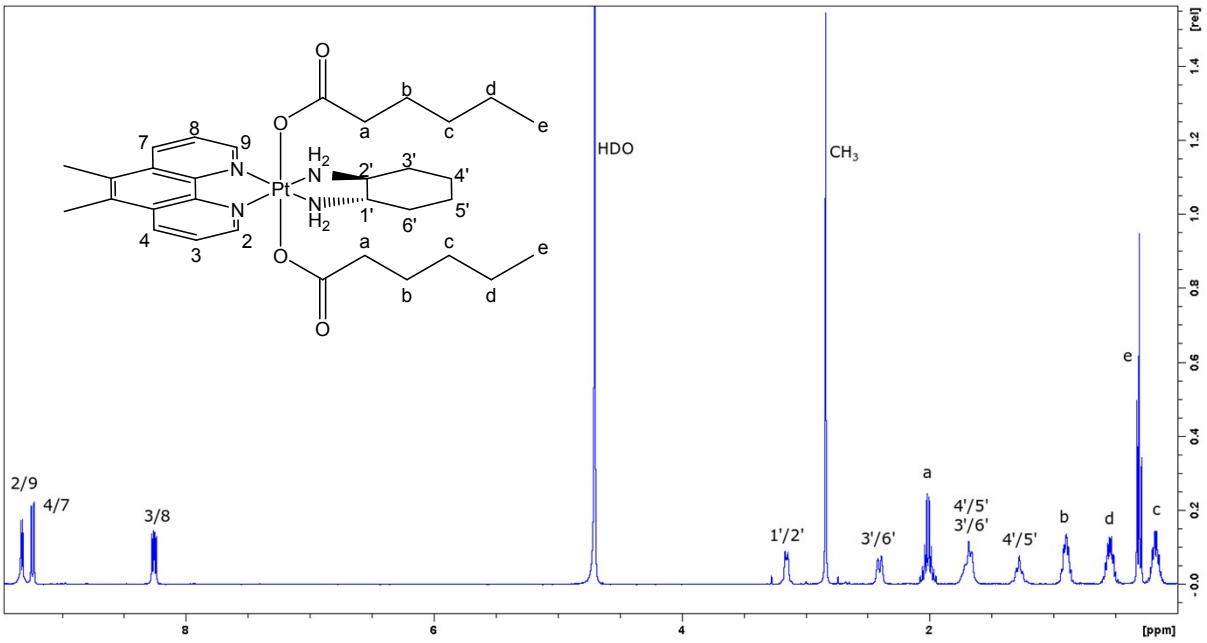

Figure A.37 ^{1}H NMR of **$[Pt(56Me_2PHEN)(SSDACH)(Hexanoate)_2](NO_3)_2$** in D_2O at 298 K. Inset: Structure and proton numbering scheme of **$[Pt(56Me_2PHEN)(SSDACH)(Hexanoate)_2](NO_3)_2$**.

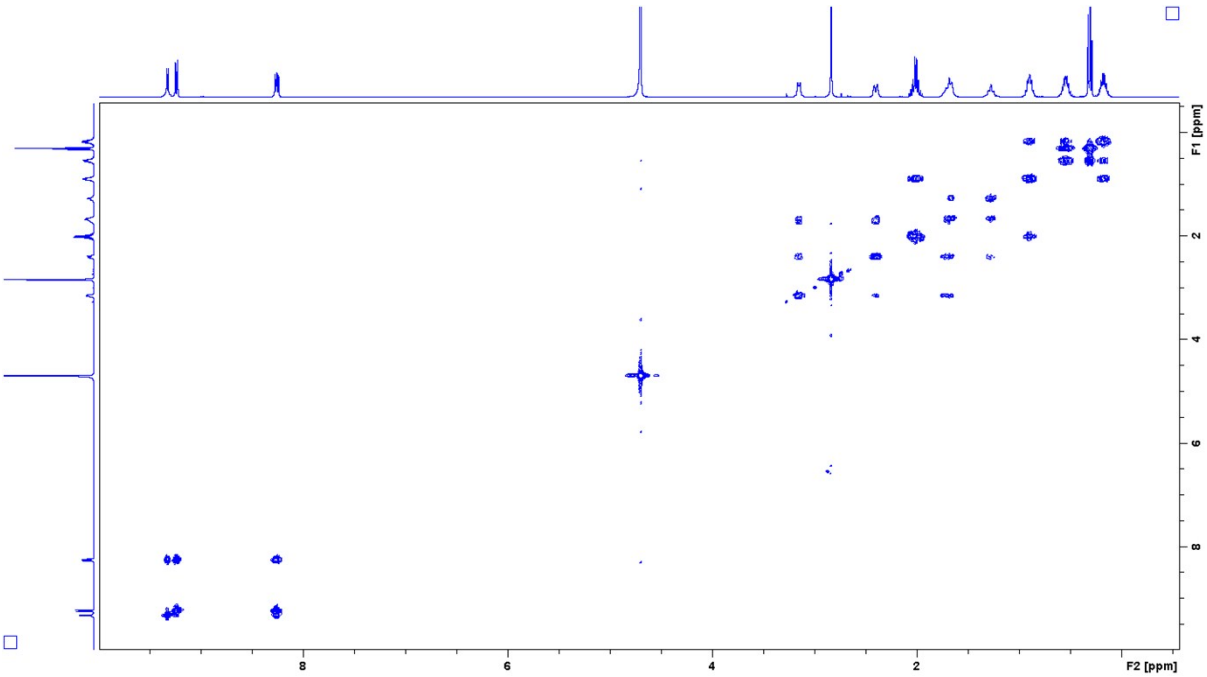

Figure A.38 COSY NMR of **$[Pt(56Me_2PHEN)(SSDACH)(Hexanoate)_2](NO_3)_2$** in D_2O at 298 K.

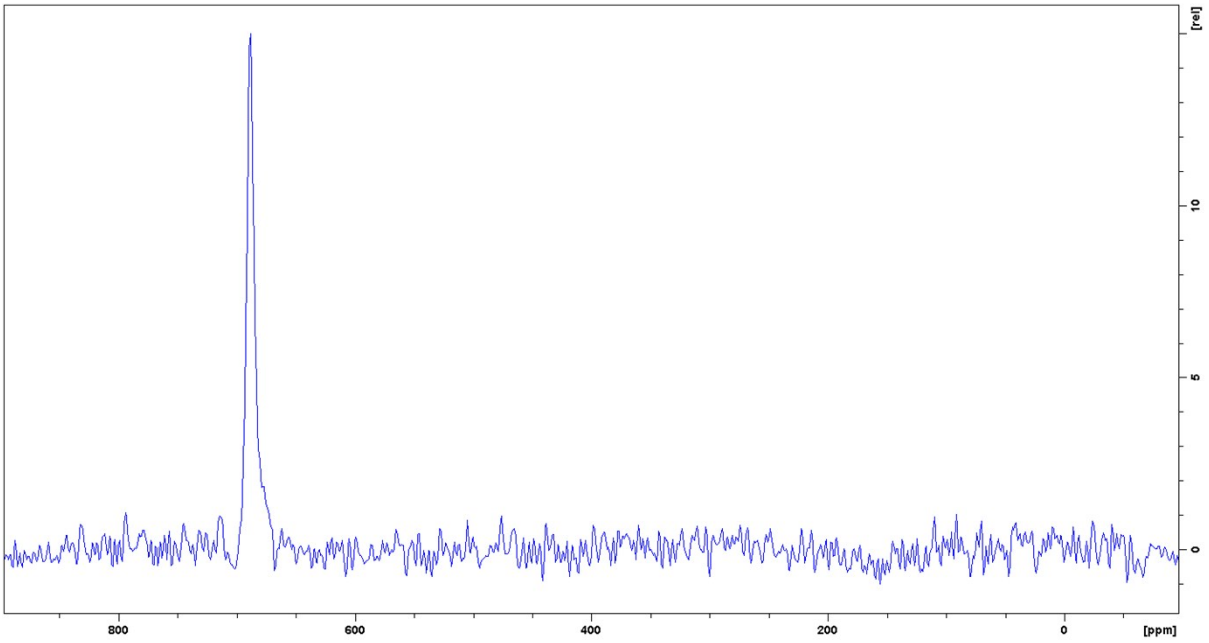

Figure A.39 ^{195}Pt NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** in D_2O at 298 K, showing a peak at 689 ppm.

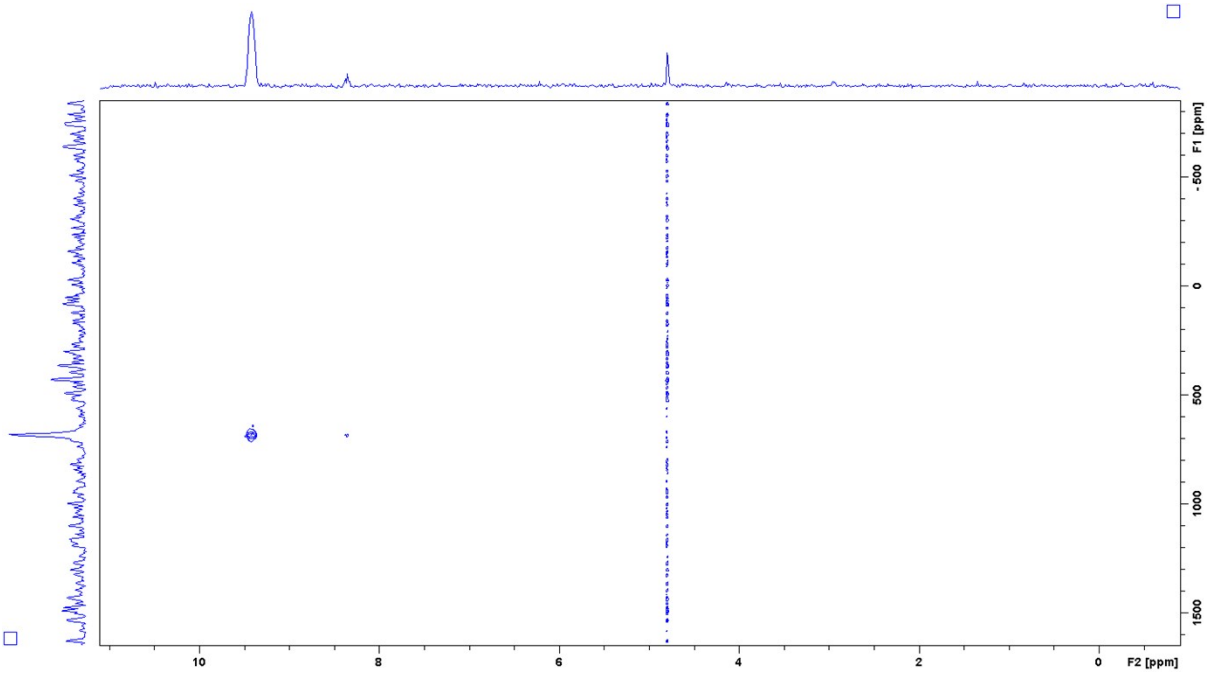

Figure A.40 ^{1}H-^{195}Pt HMQC NMR of **[Pt(56Me$_2$PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** showing proton and platinum coupling resonances, in D_2O at 298 K.

Table A.1 Summary of NMR spectroscopy data of **1-10** in D_2O, showing chemical shift (ppm), integration, multiplicity and coupling constants.

Label	**Complex**									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
H2/9	9.32 (d, J = 5.52 Hz, 2 H)	9.21 (d, J = 5.56 Hz, 2 H)	9.33 (d, J = 5.48 Hz, 2 H)	9.36 (d, J = 5.60 Hz, 2 H)	9.39 (d, J = 5.52 Hz, 2 H)	9.23 (d, J = 5.52 Hz, 2 H)	9.21 (d, J = 5.48 Hz, 2 H)	9.25 (d, J = 5.48 Hz, 2 H)	9.28 (d, J = 5.56 Hz, 2 H)	9.32 (d, J = 5.24 Hz, 2 H)
H3/8	8.22 (dd, J_1 = 8.30 Hz, J_2 = 5.66 Hz, 2 H)	8.23 (dd, J_1 = 8.30 Hz, J_2 = 5.62 Hz, 2 H)	8.24 (dd, J_1 = 8.30 Hz, J_2 = 5.66 Hz, 2 H)	8.26 (dd, J_1 = 8.40 Hz, J_2 = 5.80 Hz, 2 H)	8.28 (dd, J_1 = 8.36 Hz, J_2 = 5.68 Hz, 2 H)	8.20 (dd, J_1 = 8.60 Hz, J_2 = 5.60 Hz, 2 H)	8.20 (dd, J_1 = 8.62 Hz, J_2 = 5.58 Hz, 2 H)	8.21 (dd, J_1 = 8.60 Hz, J_2 = 5.60 Hz, 2 H)	8.23 (dd, J_1 = 8.70 Hz, J_2 = 5.50 Hz, 2 H)	8.26 (dd, J_1 = 8.60 Hz, J_2 = 5.60 Hz, 2 H)
H4/7	9.05 (d, J = 8.24 Hz, 2 H)	9.05 (d, J = 8.56 Hz, 2 H)	9.07 (d, J = 8.24 Hz, 2 H)	9.10 (d, J = 8.32 Hz, 2 H)	9.11 (d, J = 8.28 Hz, 2 H)	9.16 (d, J = 8.32 Hz, 2 H)	9.17 (d, J = 8.56 Hz, 2 H)	9.18 (d, J = 8.52Hz, 2 H)	9.21 (d, J = 8.68 Hz, 2 H)	9.24 (d, J = 8.44 Hz, 2 H)
H5/6	8.29 (s, 2 H)	8.29 (s, 2 H)	8.31 (s, 2 H)	8.34 (s, 2 H)	8.35 (s, 2H)	-	-	-	-	-
CH_3	-	-	-	-	-	2.82 (s, 6 H)	2.83 (s, 6 H)	2.82 (s, 6 H)	2.84 (s, 6 H)	2.84 (s, 6 H)
H1′/2′	3.19 (m, 2 H)	3.17 (m, 2 H)	3.17 (m, 2 H)	3.17 (m, 2 H)	3.17 (m, 2 H)	3.17 (m, 2 H)	3.15 (m, 2 H)	3.15 (m, 2 H)	3.15 (m, 2 H)	3.15 (m, 2 H)
H3′/6′	2.40 (m, 2 H)	2.40 (m, 2 H)	2.41 (m, 2 H)	2.41 (m, 2 H)	2.42 (m, 2 H)	2.39 (m, 2 H)	2.39 (m, 2 H)	2.40 (m, 2 H)	2.40 (m, 2 H)	2.40 (m, 2 H)
H4′/5′	1.68 (m, 10 H)	1.69 (m, 4 H)	1.70 (m, 4 H)	1.72 (m, 4 H)	1.70 (m, 4 H)	1.67 (m, 10 H)	1.69 (m, 4 H)	1.69 (m, 4 H)	1.69 (m, 4 H)	1.69 (m, 4 H)
H3′/6′	1.68 (m, 10 H)	1.69 (m, 4 H)	1.70 (m, 4 H)	1.72 (m, 4 H)	1.70 (m, 4 H)	1.67 (m, 10 H)	1.69 (m, 4 H)	1.69 (m, 4 H)	1.69 (m, 4 H)	1.69 (m, 4 H)
H4′/5′	1.29 (m, 2 H)	1.29 (m, 2 H)	1.29 (m, 2 H)	1.29 (m, 2 H)	1.29 (m, 2 H)	1.29 (m, 2 H)	1.29 (m, 2 H)	1.28 (m, 2 H)	1.28 (m, 2 H)	1.27 (m, 2 H)
a	1.68 (m, 10 H)	2.03 (m, 4 H)	1.99 (t, J = 7.24 Hz, 4 H)	2.02 (t, J = 7.14 Hz, 4 H)	2.02 (t, J = 7.14 Hz, 4 H)	1.67 (m, 10 H)	2.02 (m, 4 H)	1.97 (t, J = 7.22 Hz, 4 H)	2.00 (td, J_1 = 7.14 Hz, J_2 = 1.79 Hz, 4 H)	2.01 (oct, J = 7.23 Hz, 4 H)
b	-	0.54 (t, J = 7.54 Hz, 6 H)	0.99 (sxt, J = 7.51 Hz, 4 H)	0.93 (pnt, J = 7.30 Hz, 4 H)	0.95 (pnt, J = 7.55 Hz, 4 H)	-	0.52 (t, J = 7.54 Hz, 6H)	0.97 (sxt, J = 7.30, 4 H)	0.89 (pnt, J = 7.24, 4 H)	0.90 (m, 4 H)
c	-	-	0.24 (t, J = 7.42 Hz, 6 H)	0.43 (m, 4 H)	0.39 (m, 6 H)	-	-	0.19 (t, J = 7.42 Hz, 6 H)	0.33 (m, 4 H)	0.17 (m, 4 H)
d	-	-	-	0.29 (t, J = 7.16 Hz, 6 H)	0.65 (m, 4 H)	-	-	-	0.22 (m, 6 H)	0.55 (m, 4 H)
e	-	-	-	-	0.32 (m, 4 H)	-	-	-	-	0.31 (t, J = 7.34 Hz, 6 H)
$^{1}H/^{195}Pt$	9.31, 8.22, 1.69/720	9.29, 8.22/708	9.35, 8.26/701	9.35, 8.26/701	9.38, 8.28/700	9.22, 8.18, 1.68/708	9.20, 8.20/694	9.24, 8.22/690	9.27, 8.22/687	9.32, 8.26/685

B. HPLC

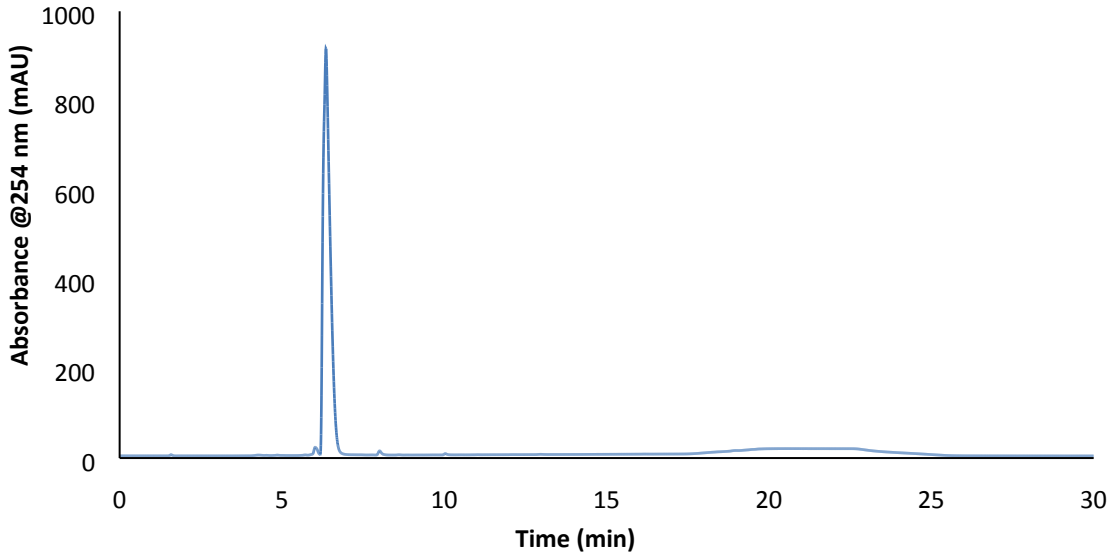

Figure B.1 HPLC trace of **[Pt(PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** using a gradient of 0–30 % (H_2O:ACN/H_2O (90:10)) over 15 min, T_R = 6.4 min.

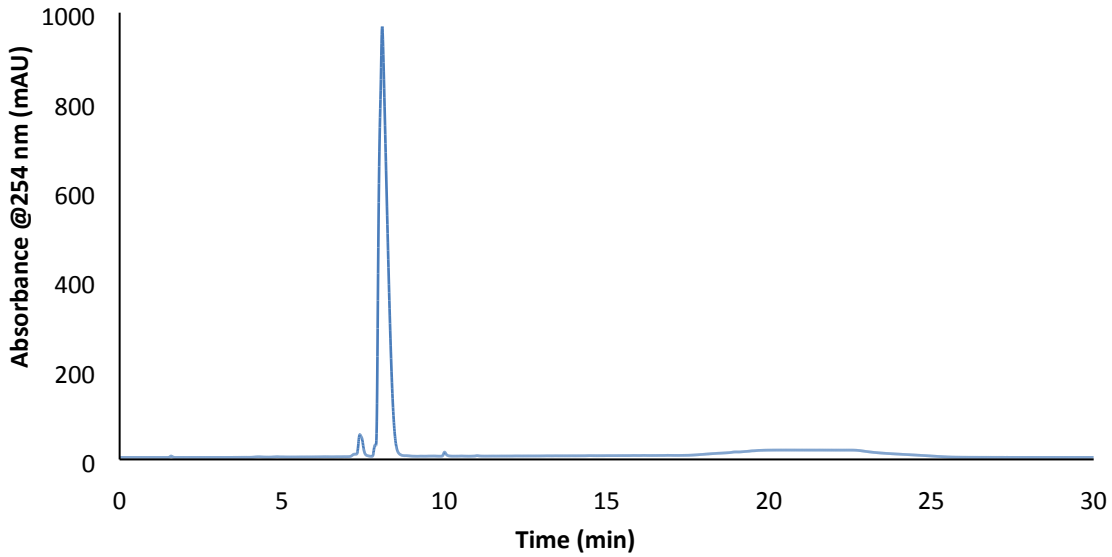

Figure B.2 HPLC trace of **[Pt(PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** using a gradient of 0–30 % (H_2O:ACN/H_2O (90:10)) over 15 min, T_R = 8.1 min.

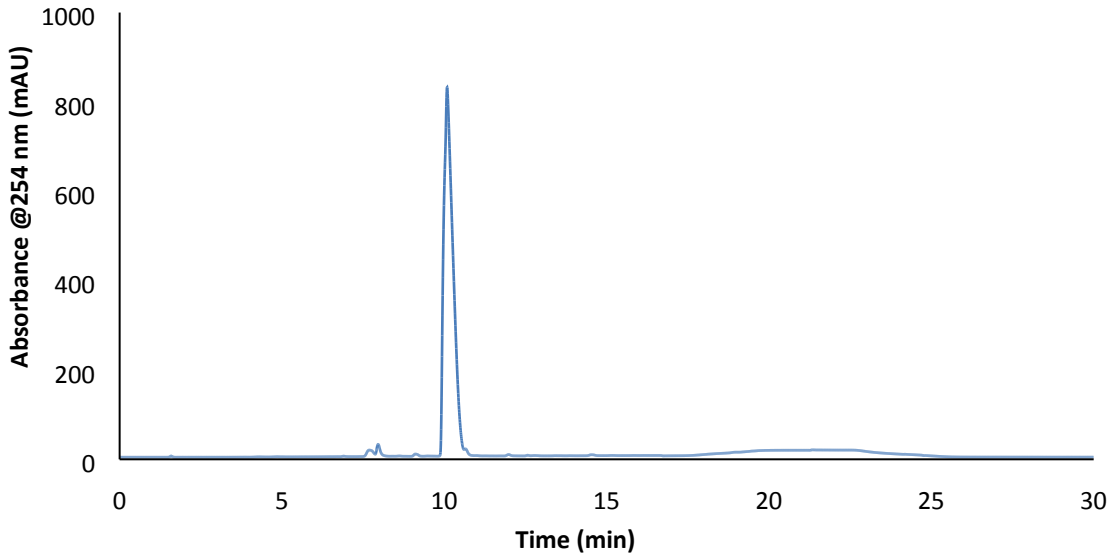

Figure B.3 HPLC trace of **[Pt(PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** using a gradient of 0–30 % (H_2O:ACN/H_2O (90:10)) over 15 min, T_R = 10.1 min.

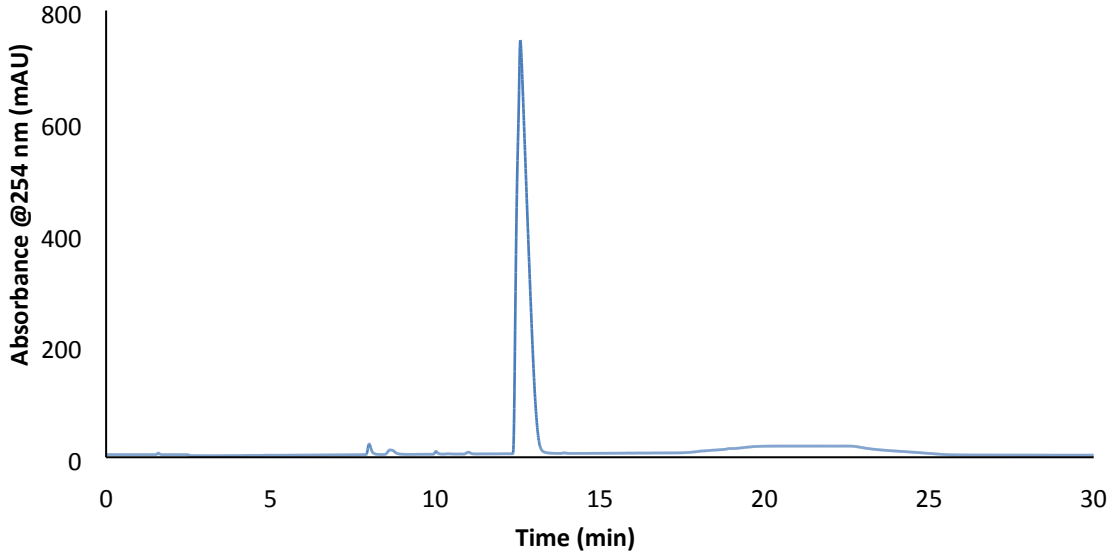

Figure B.4 HPLC trace of **[Pt(PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** using a gradient of 0–30 % (H_2O:ACN/H_2O (90:10)) over 15 min, T_R = 12.6 min.

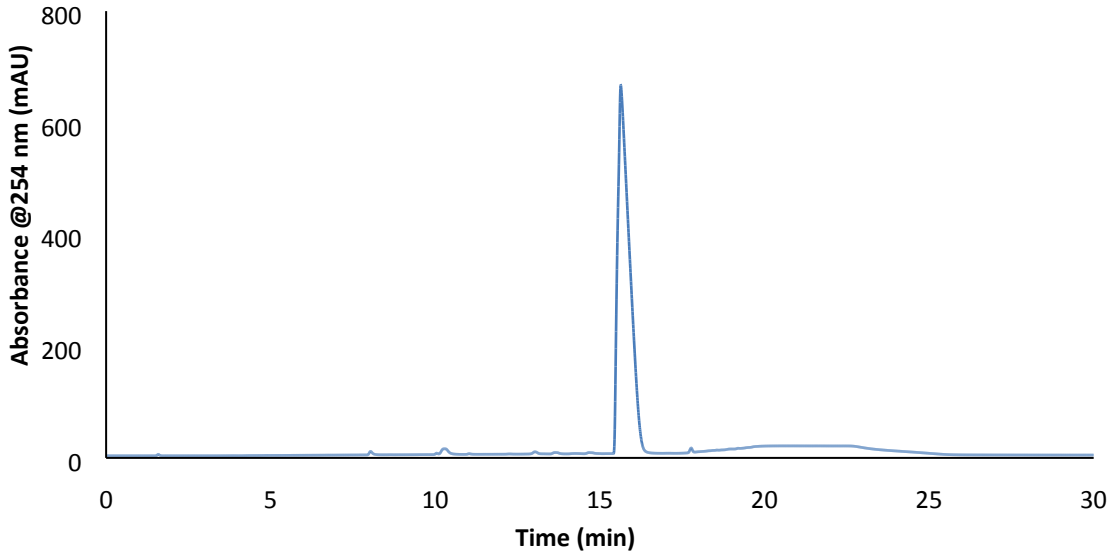

Figure B.5 HPLC trace of **[Pt(PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** using a gradient of 0–30 % (H_2O:ACN/H_2O (90:10)) over 15 min, T_R = 15.6 min.

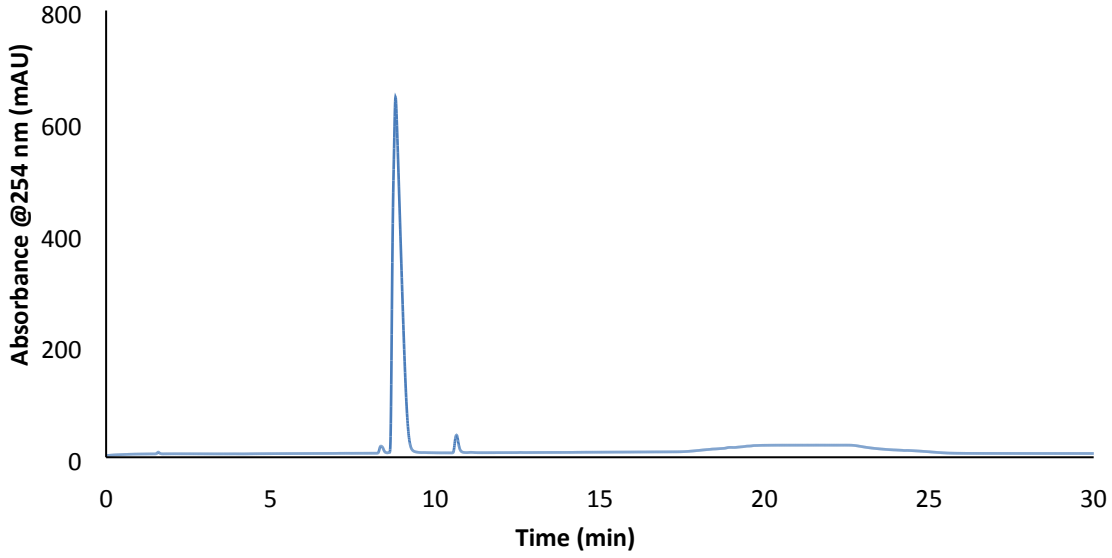

Figure B.6 HPLC trace of **[Pt(56Me$_2$PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** using a gradient of 0–30 % (H_2O:ACN/H_2O (90:10)) over 15 min, T_R = 8.8 min.

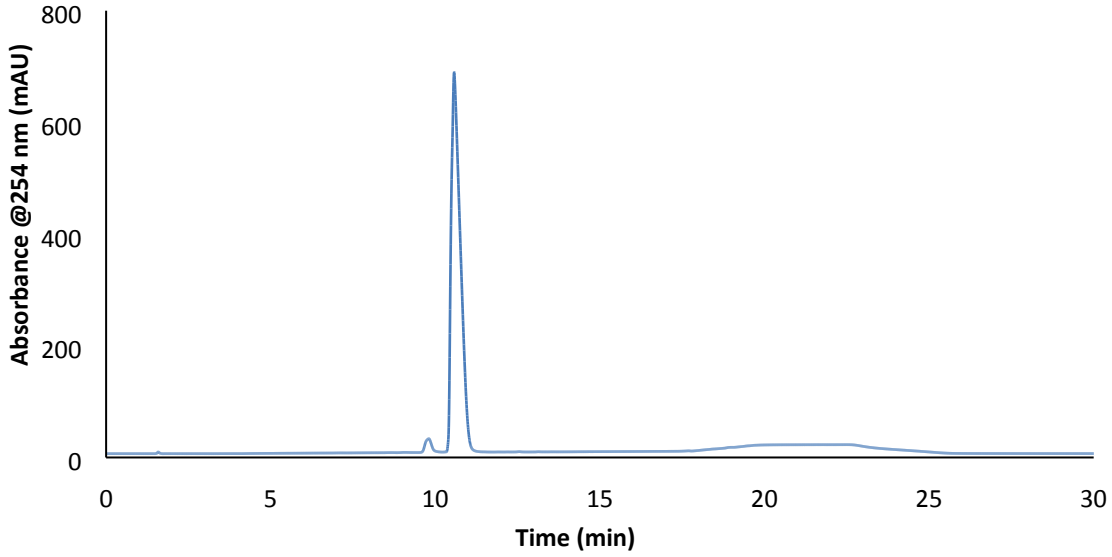

Figure B.7 HPLC trace of **[Pt(56Me$_2$PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** using a gradient of 0–30 % (H_2O:ACN/H_2O (90:10)) over 15 min, T_R = 10.6 min.

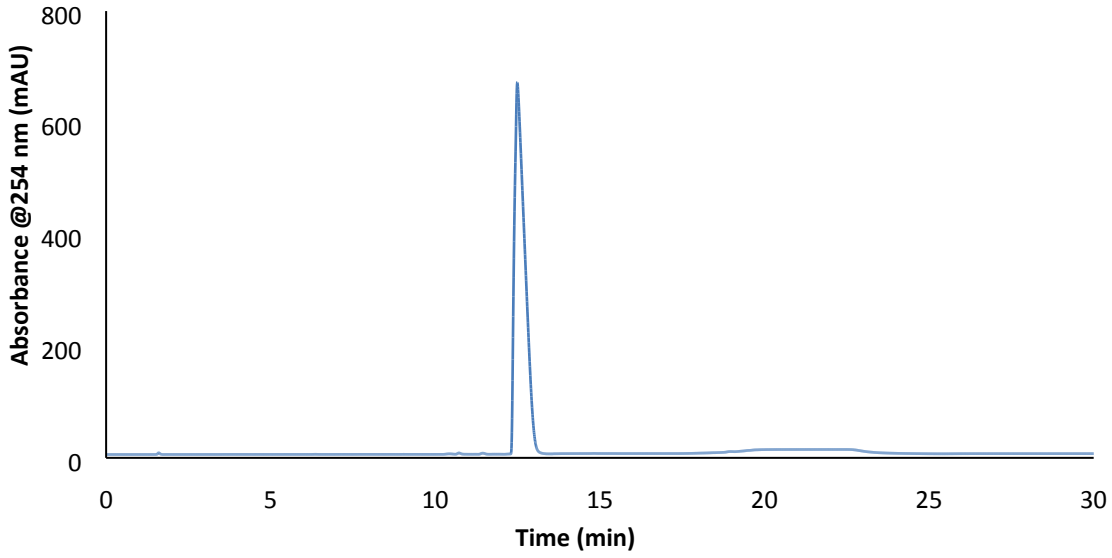

Figure B.8 HPLC trace of **[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** using a gradient of 0–30 % (H_2O:ACN/H_2O (90:10)) over 15 min, T_R = 12.5 min.

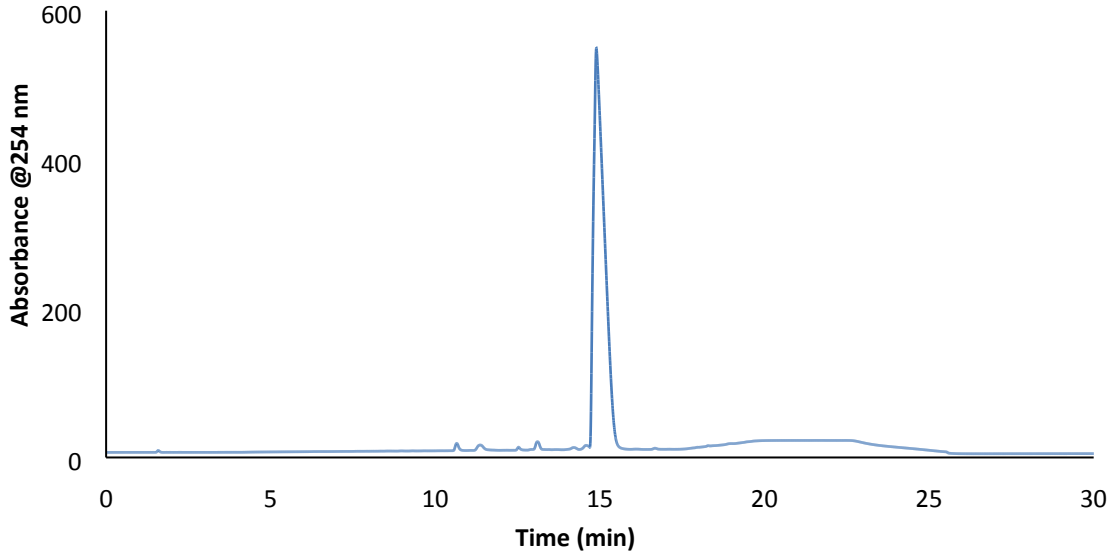

Figure B.9 HPLC trace of **[Pt(56Me$_2$PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** using a gradient of 0–30 % (H_2O:ACN/H_2O (90:10)) over 15 min, T_R = 14.9 min.

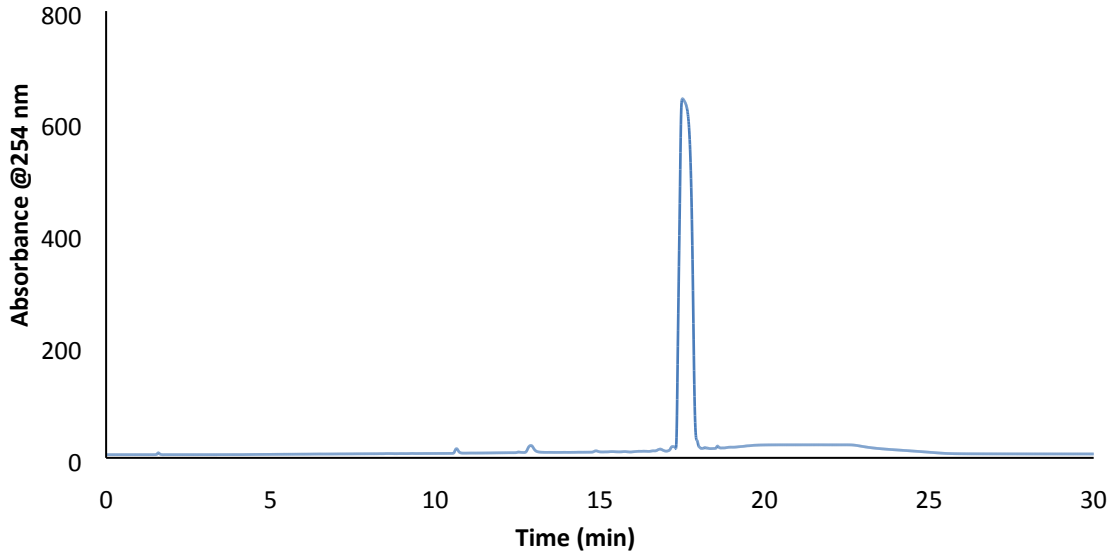

Figure B.10 HPLC trace of **[Pt(56Me$_2$PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** using a gradient of 0–30 % (H_2O:ACN/H_2O (90:10)) over 15 min, T_R = 17.5 min.

C. ESI-MS

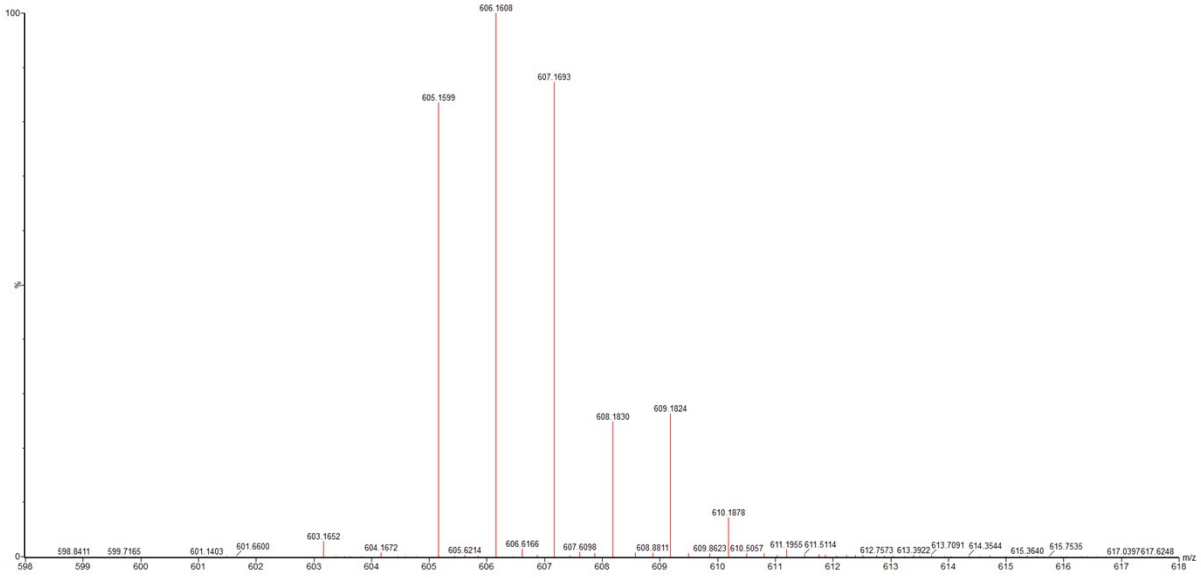

Figure C.1 ESI-MS spectrum of **[Pt(PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$**.

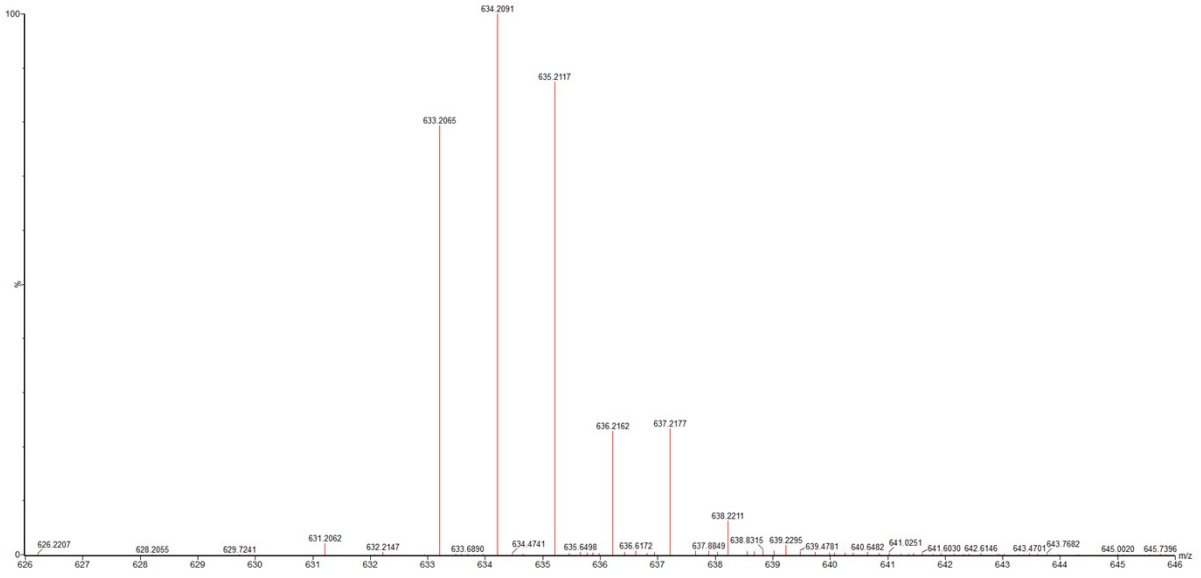

Figure C.2 ESI-MS spectrum of **[Pt(PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$**.

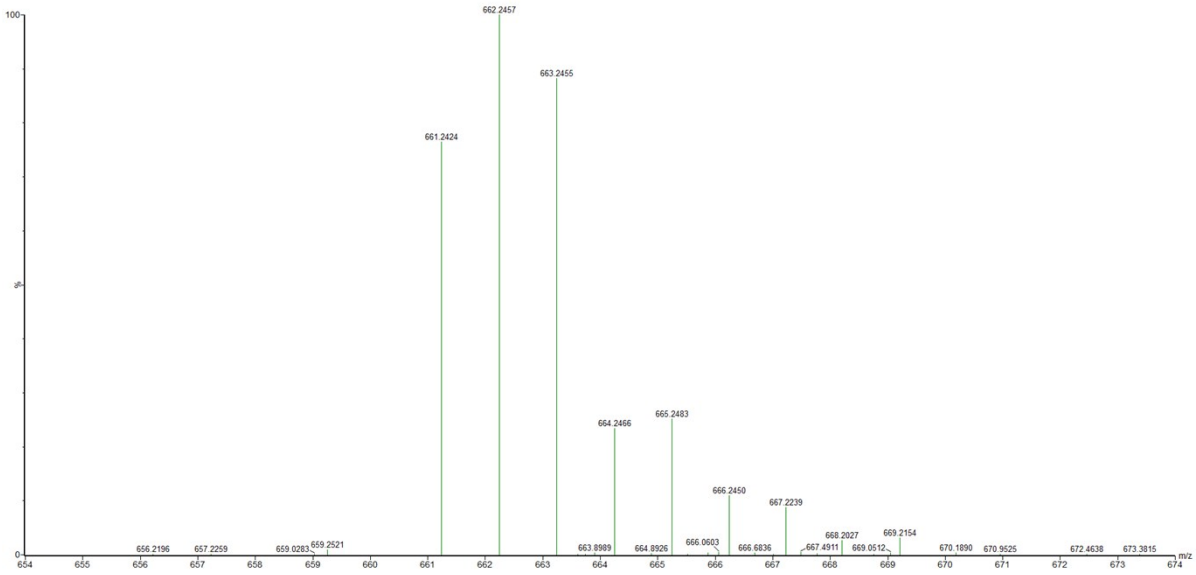

Figure C.3 ESI-MS spectrum of **[Pt(PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$**.

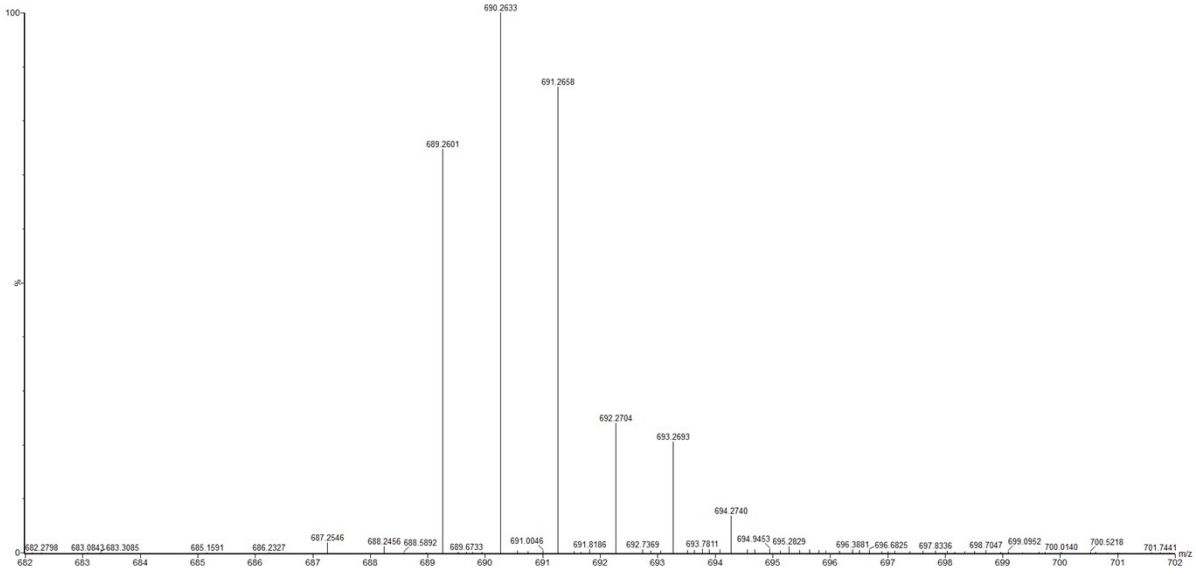

Figure C.4 ESI-MS spectrum of **[Pt(PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$**.

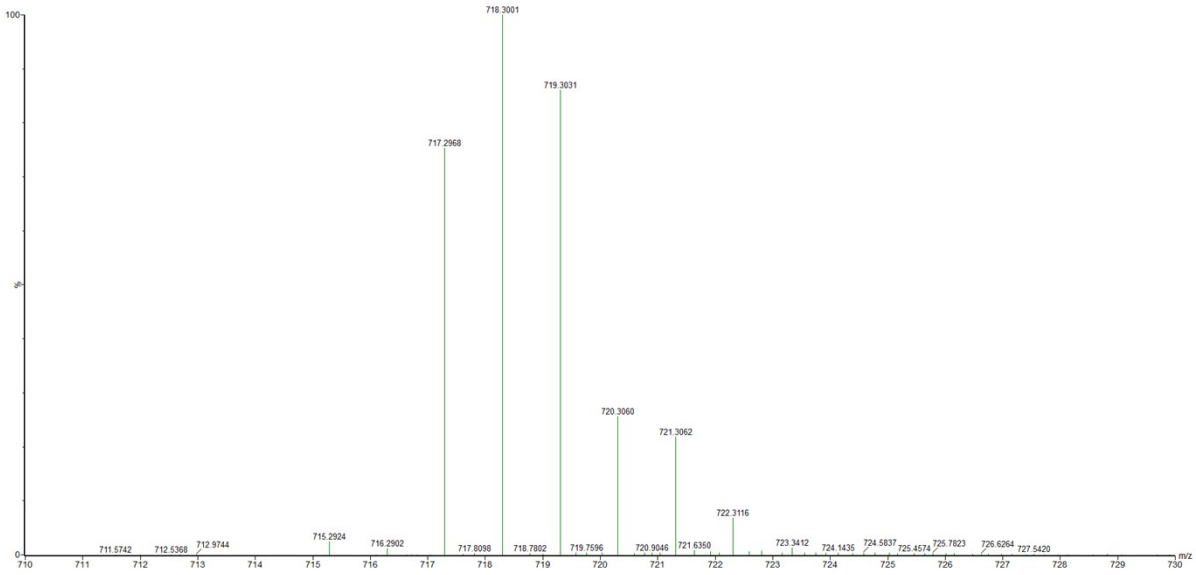

Figure C.5 ESI-MS spectrum of **[Pt(PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$**.

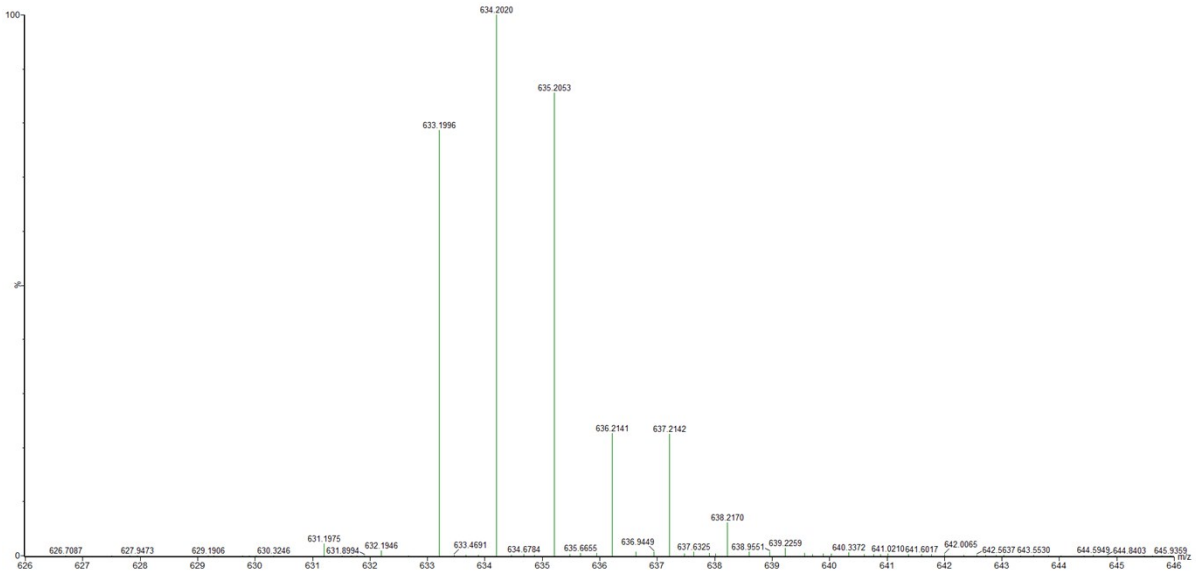

Figure C.6 ESI-MS spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$**.

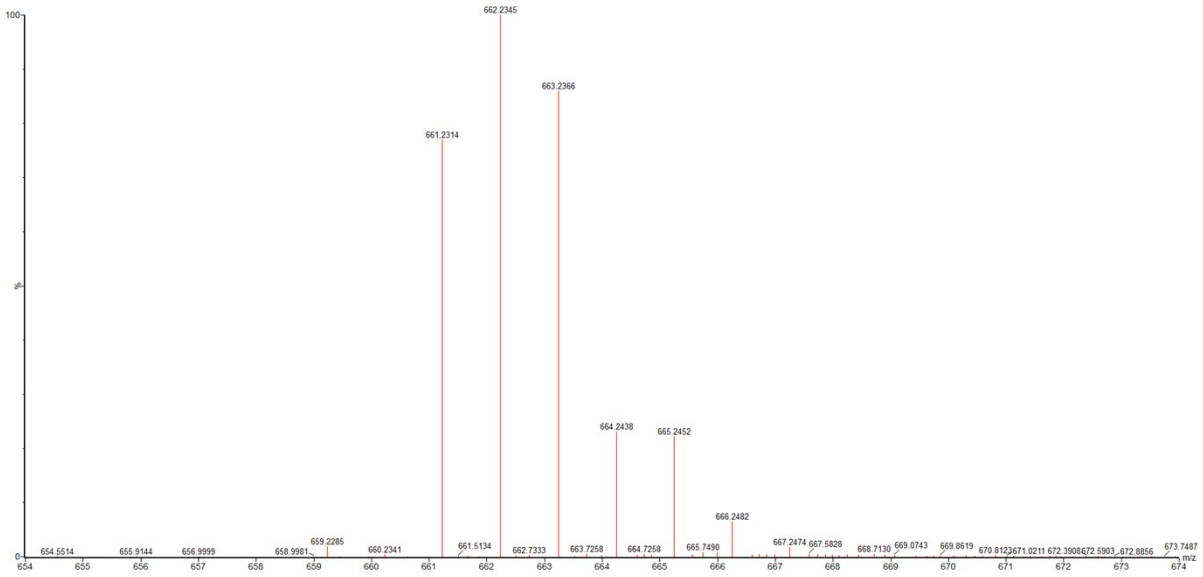

Figure C.7 ESI-MS spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$**.

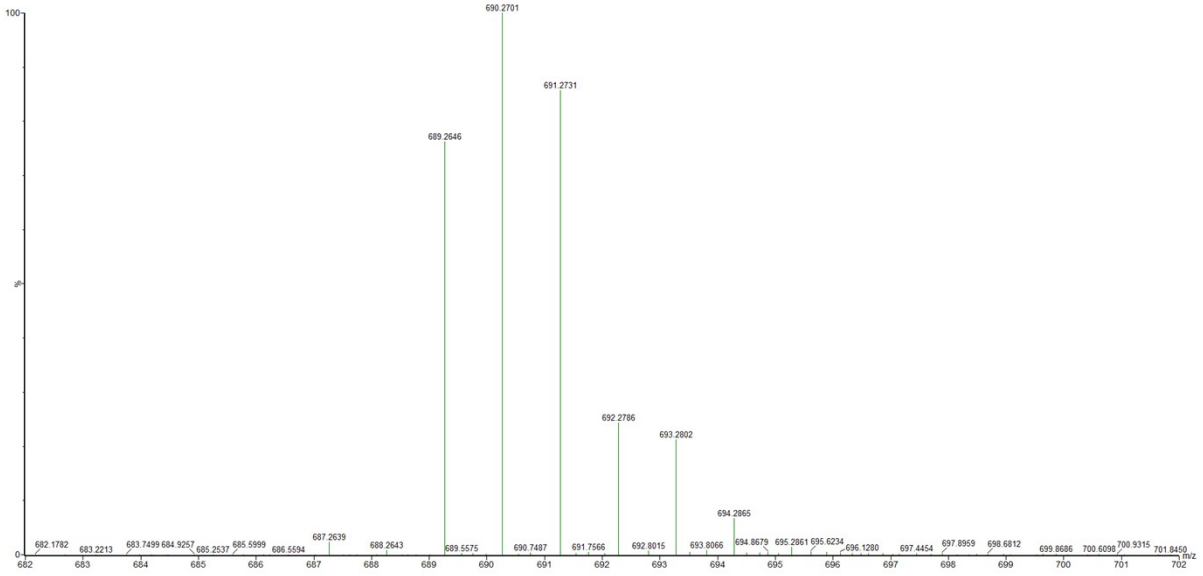

Figure C.8 ESI-MS spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$**.

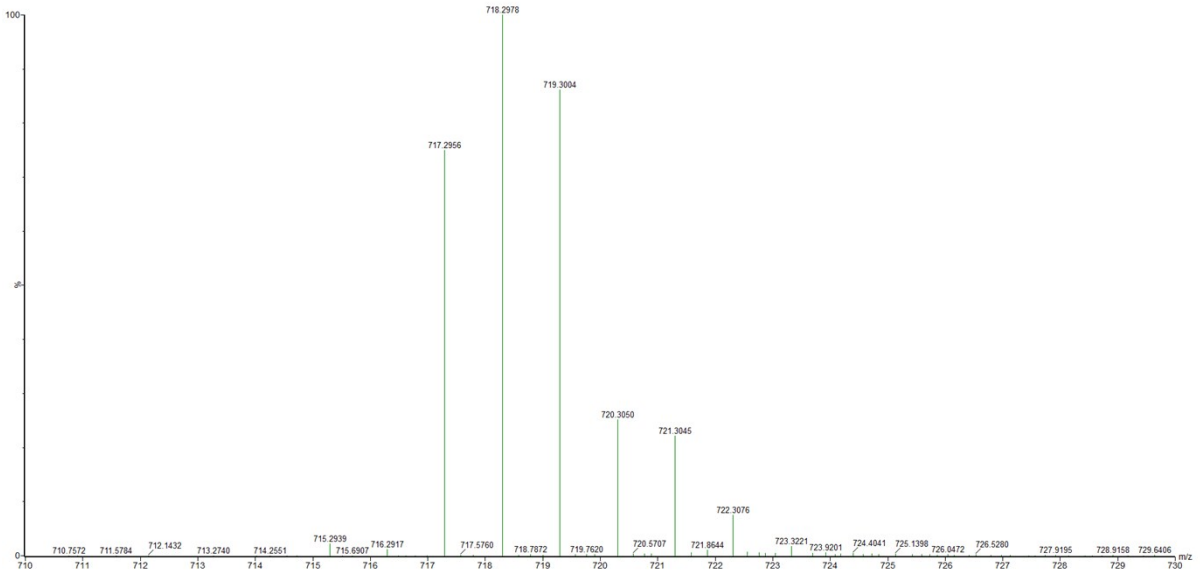

Figure C.9 ESI-MS spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$**.

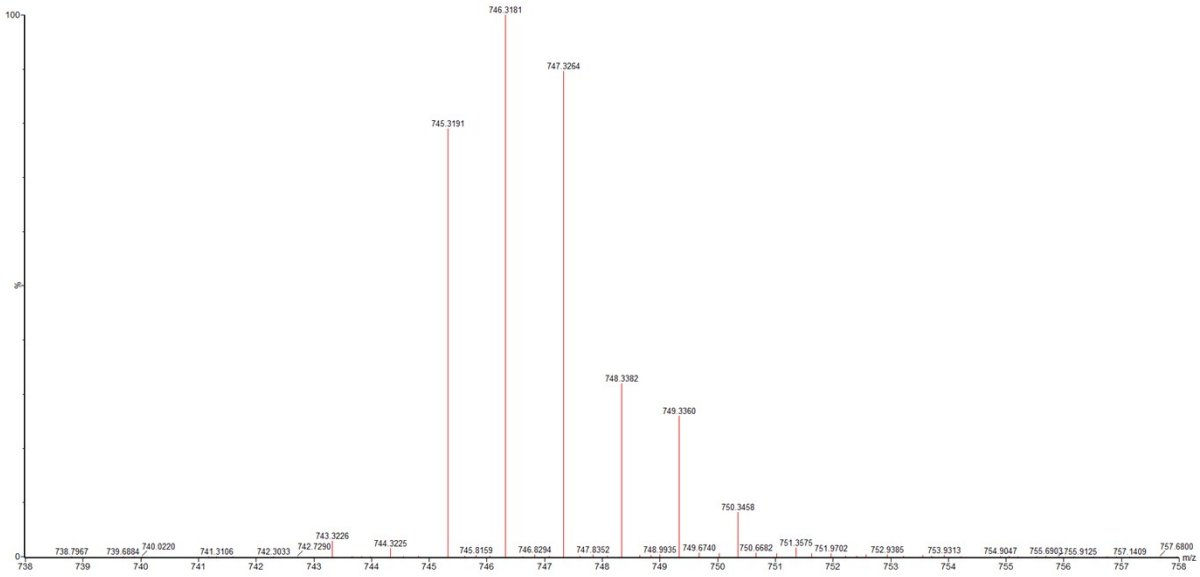

Figure C.10 ESI-MS spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$**.

D. UV-Vis Spectra

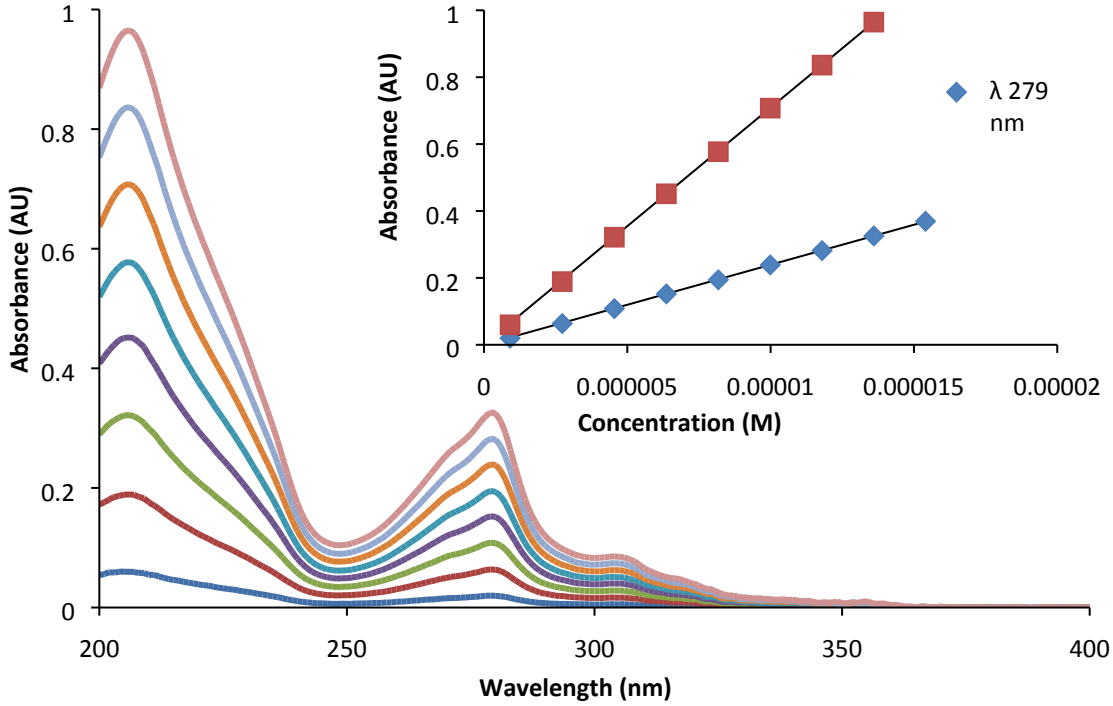

Figure D.1 Exemplar of a replicate of the UV spectrum of **[Pt(PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** in water.

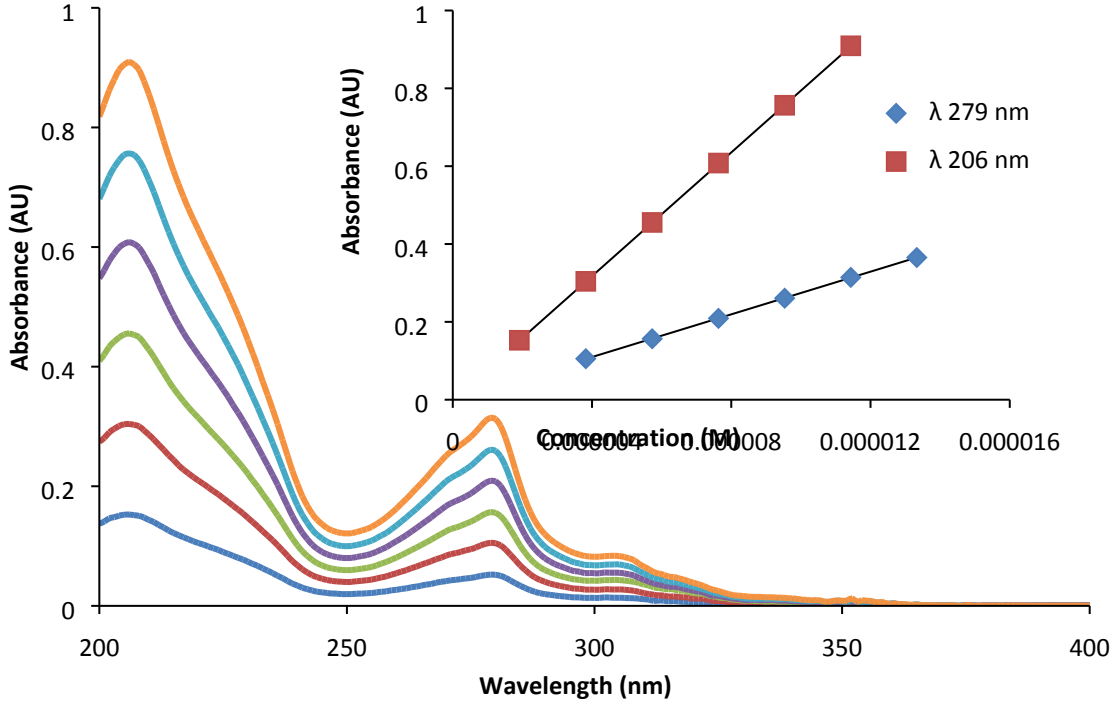

Figure D.2 Exemplar of a replicate of the UV spectrum of **[Pt(PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** in water.

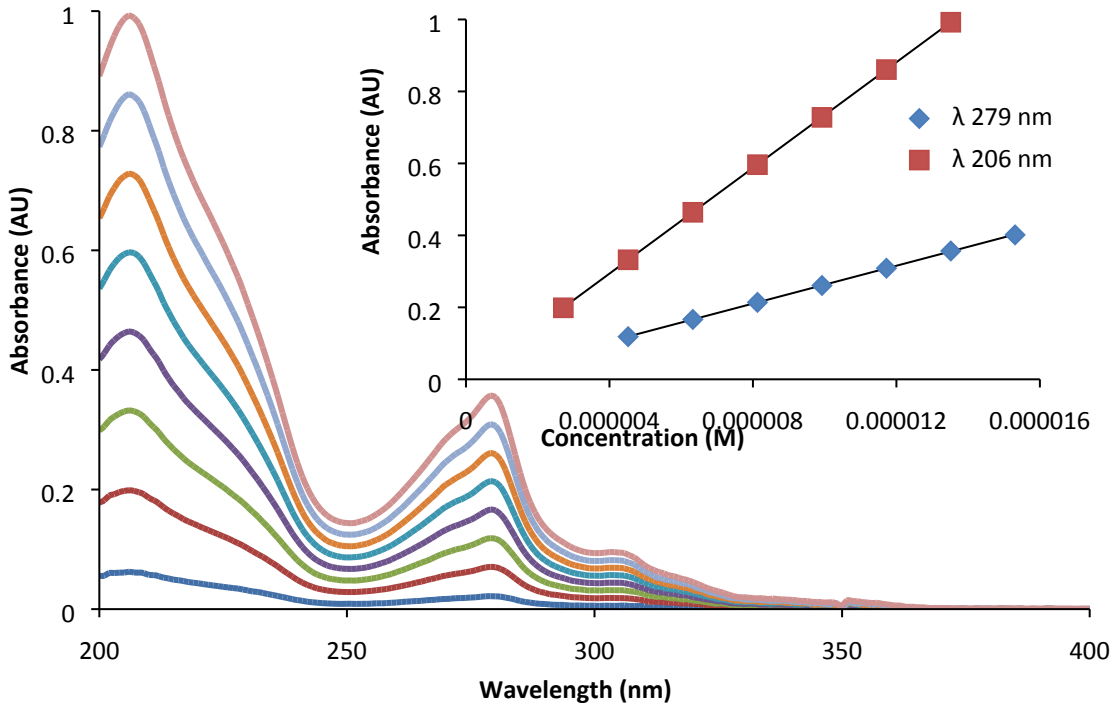

Figure D.3 Exemplar of a replicate of the UV spectrum of **[Pt(PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** in water.

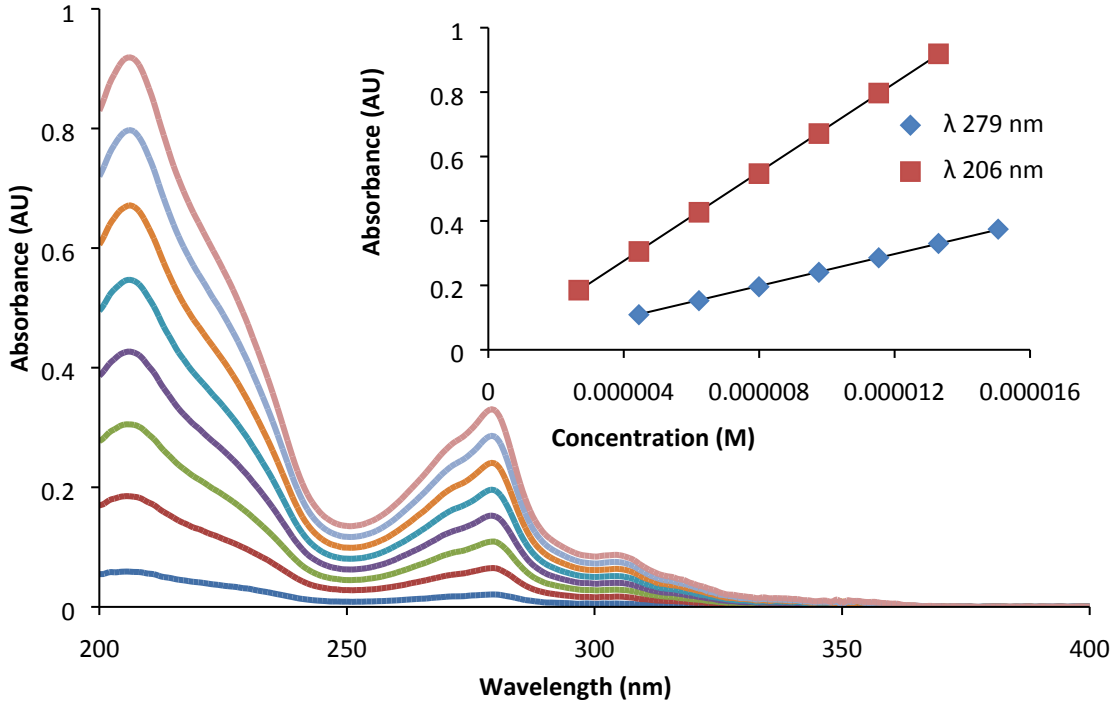

Figure D.4 Exemplar of a replicate of the UV spectrum of **[Pt(PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** in water.

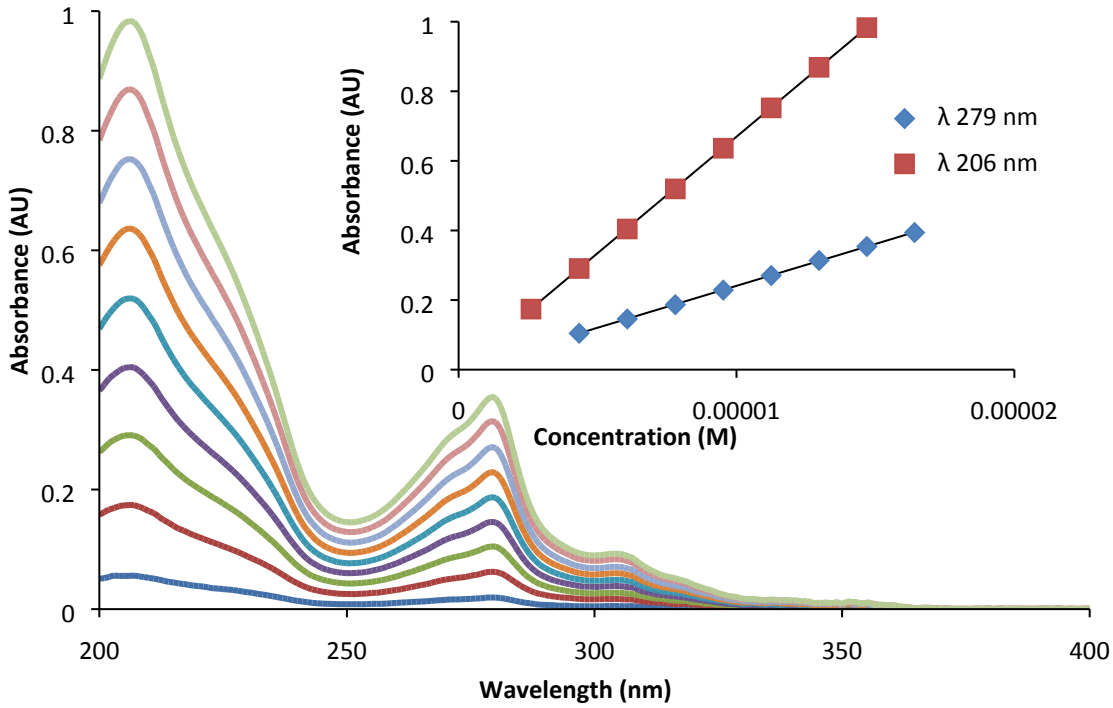

Figure D.5 Exemplar of a replicate of the UV spectrum of **[Pt(PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** in water.

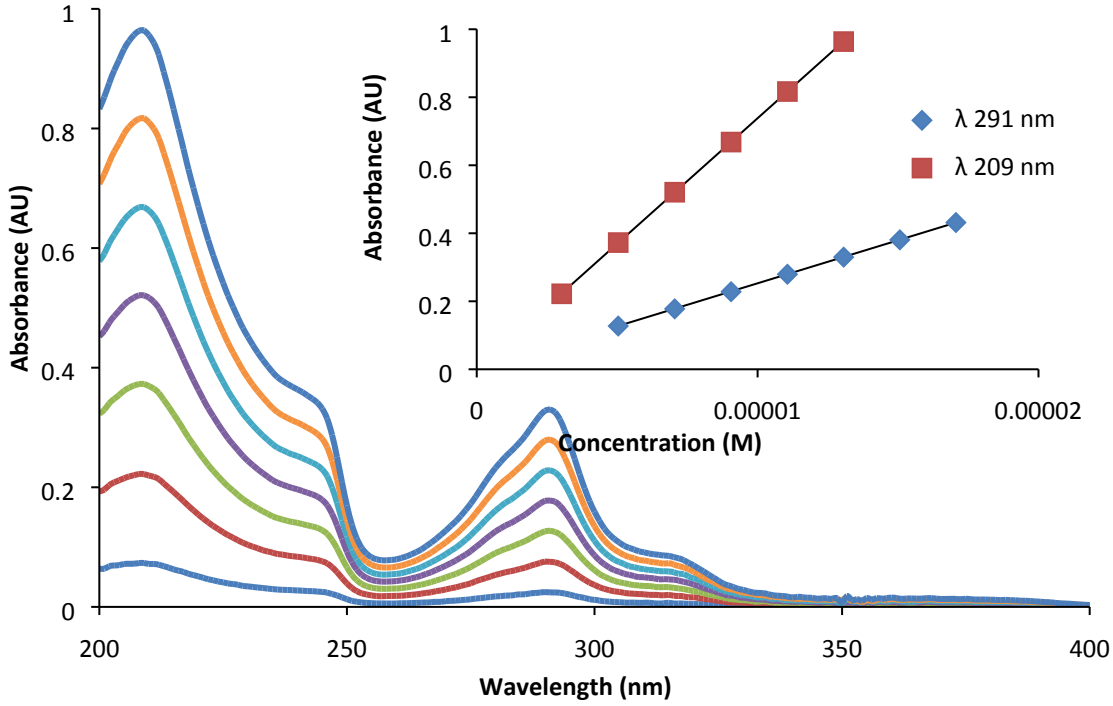

Figure D.6 Exemplar of a replicate of the UV spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** in water.

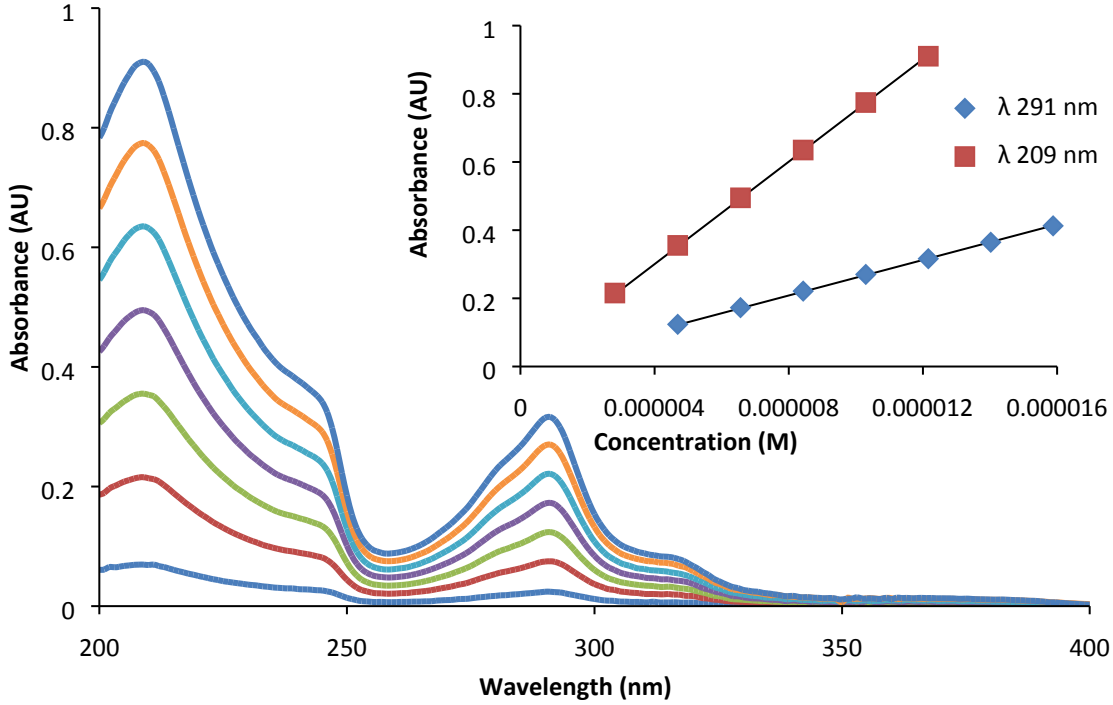

Figure D.7 Exemplar of a replicate of the UV spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** in water.

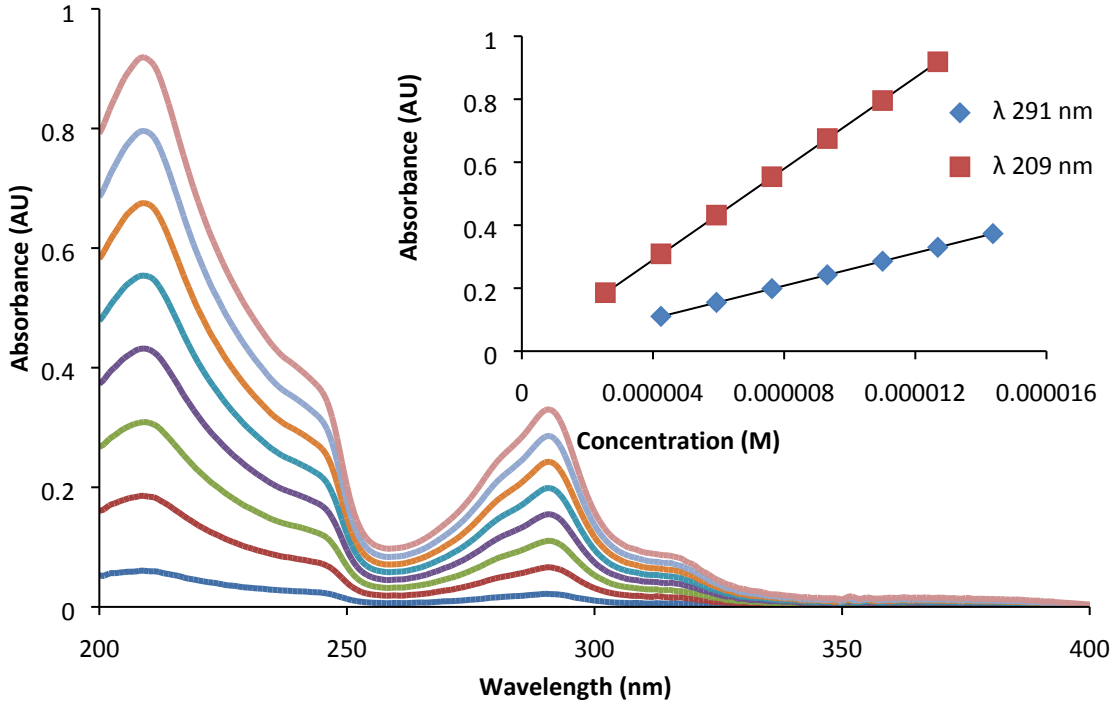

Figure D.8 Exemplar of a replicate of the UV spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** in water.

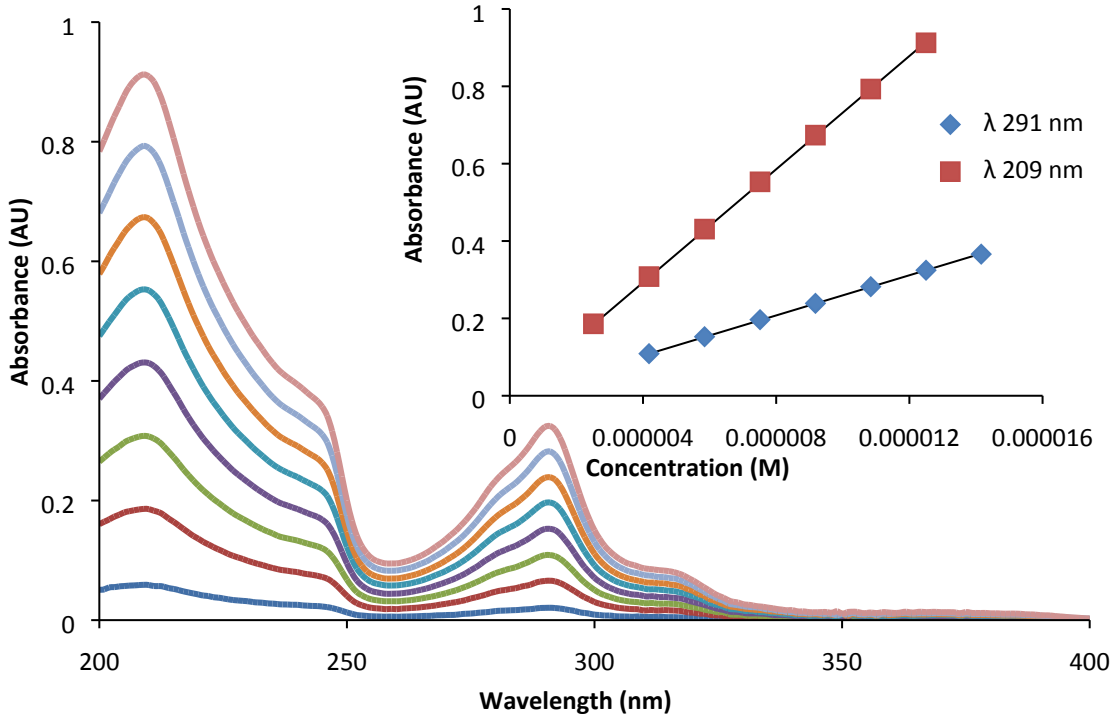

Figure D.9 Exemplar of a replicate of the UV spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** in water.

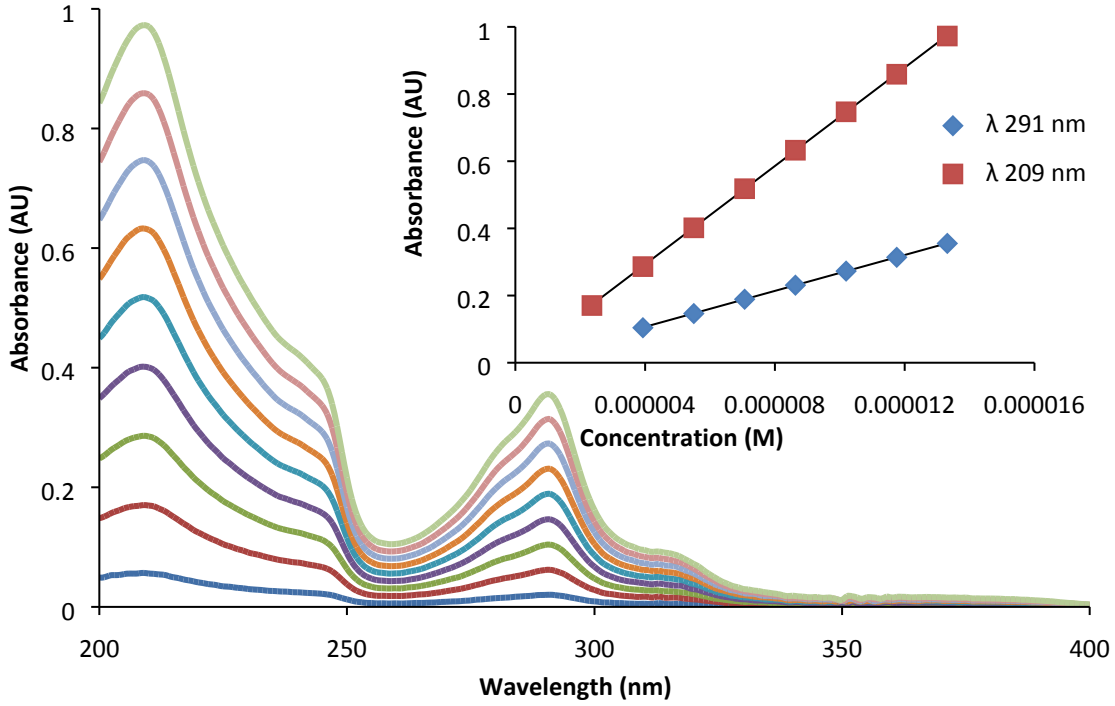

Figure D.10 Exemplar of a replicate of the UV spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** in water.

E. CD Spectra

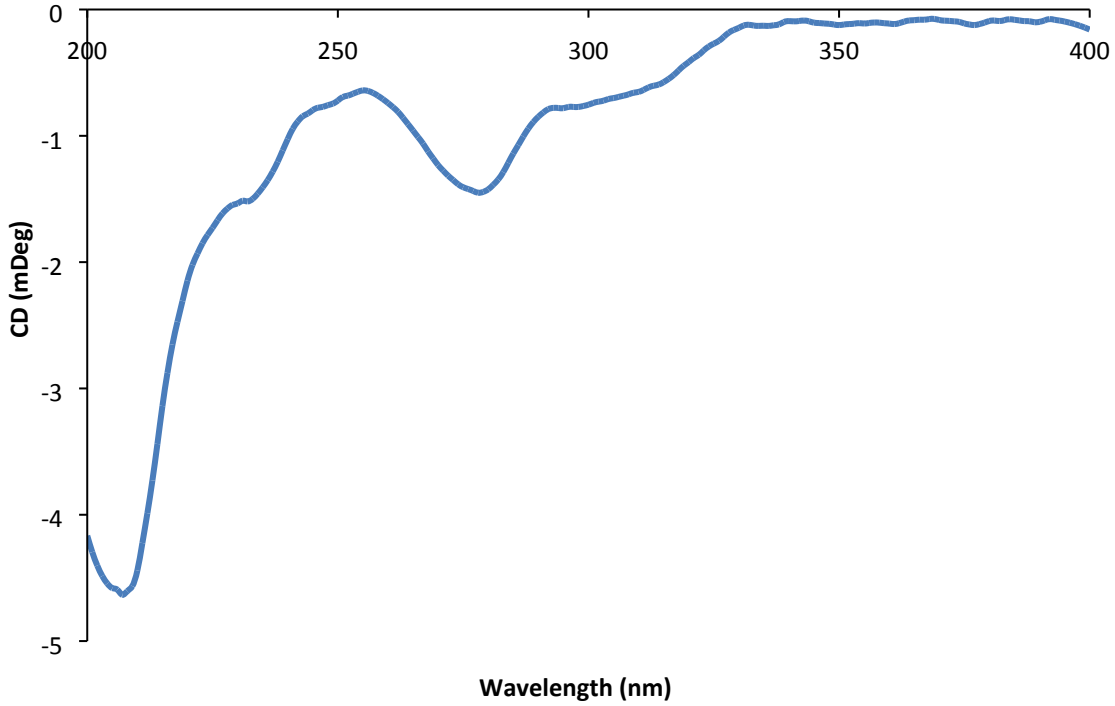

Figure E.1 CD spectrum of **[Pt(PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** in water. 13pt smoothing applied.

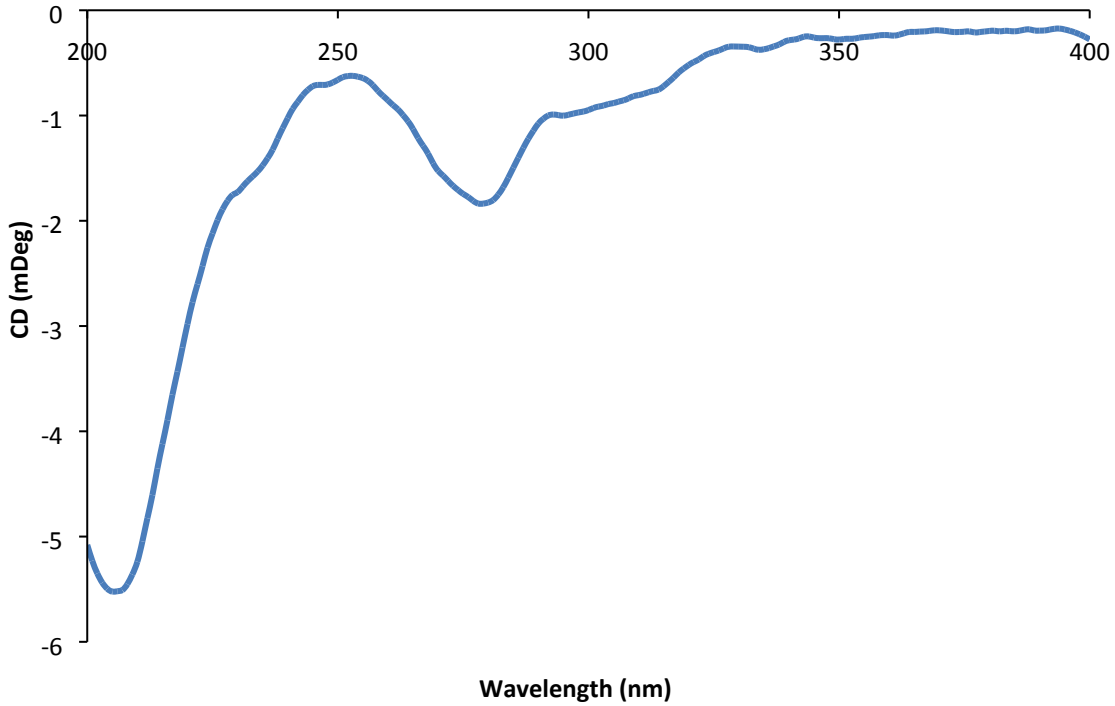

Figure E.2 CD spectrum of **[Pt(PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** in water. 13pt smoothing applied.

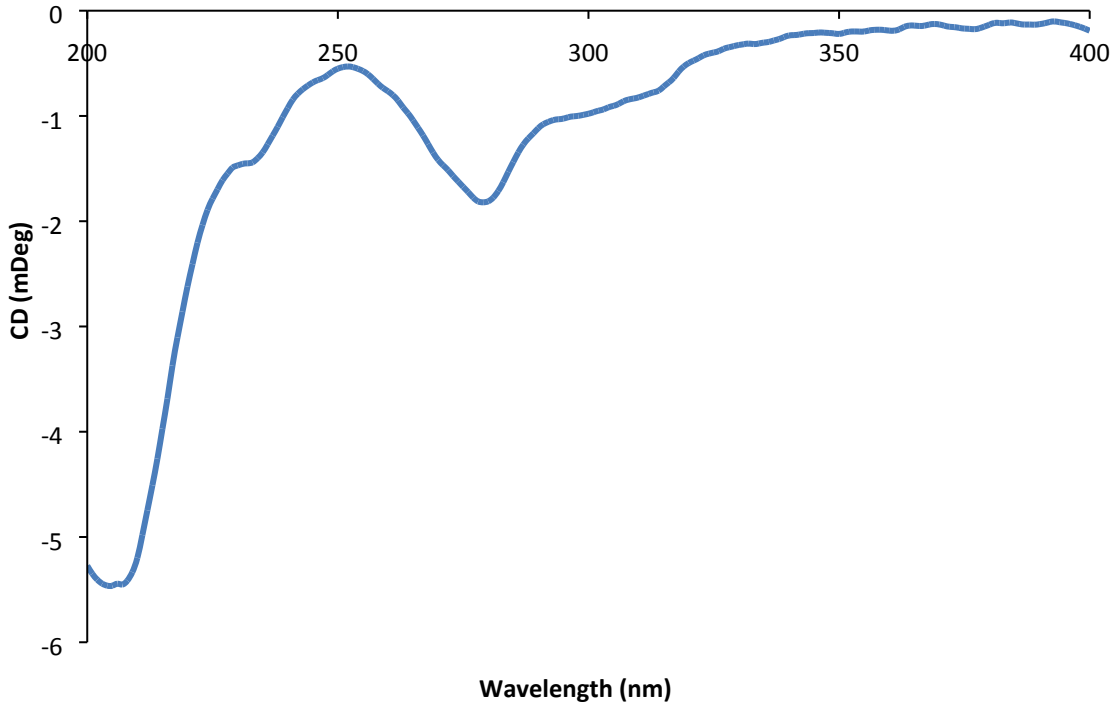

Figure E.3 CD spectrum of **[Pt(PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** in water. 13pt smoothing applied.

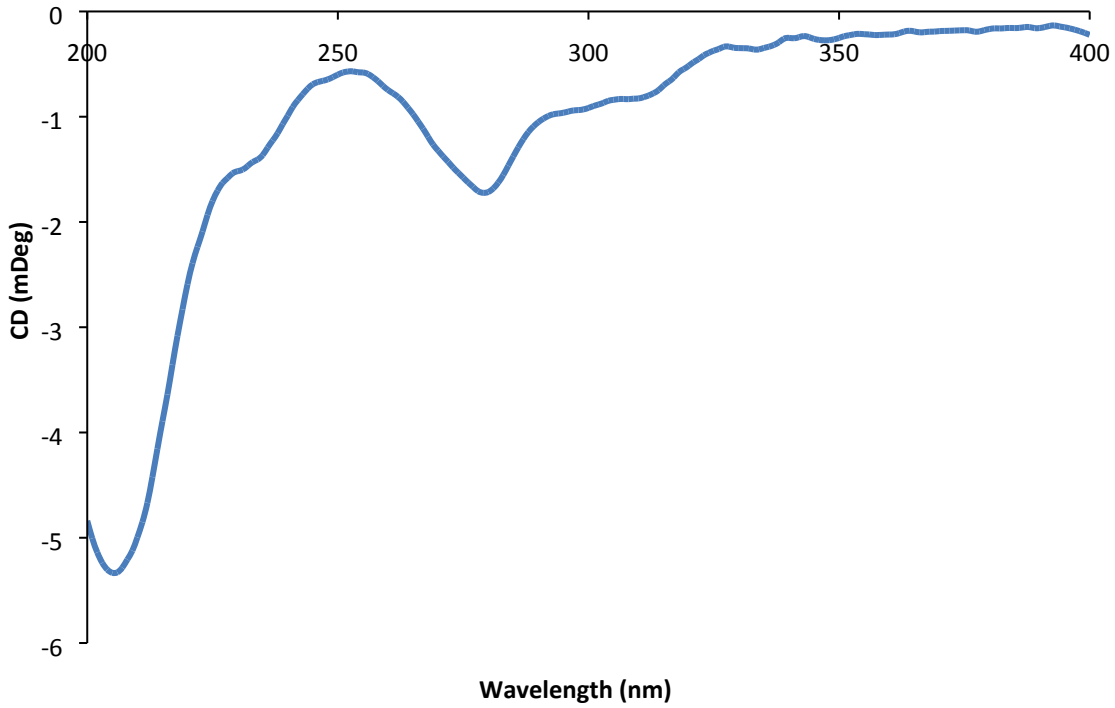

Figure E.4 CD spectrum of **[Pt(PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** in water. 13pt smoothing applied.

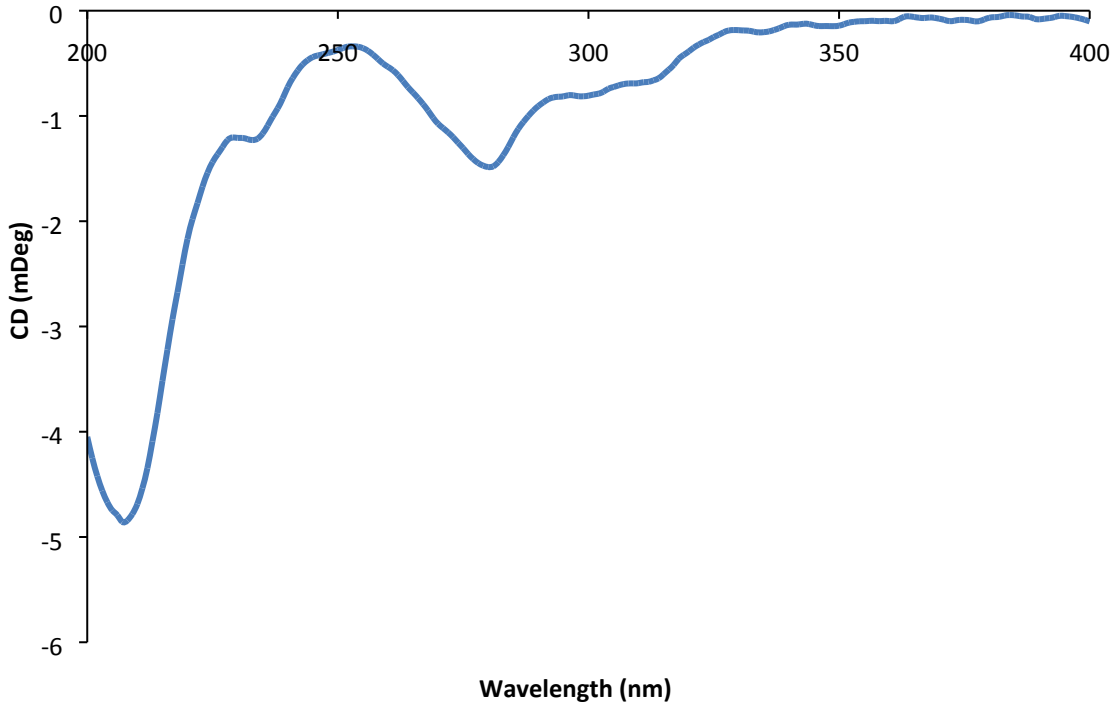

Figure E.5 CD spectrum of **[Pt(PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** in water. 13pt smoothing applied.

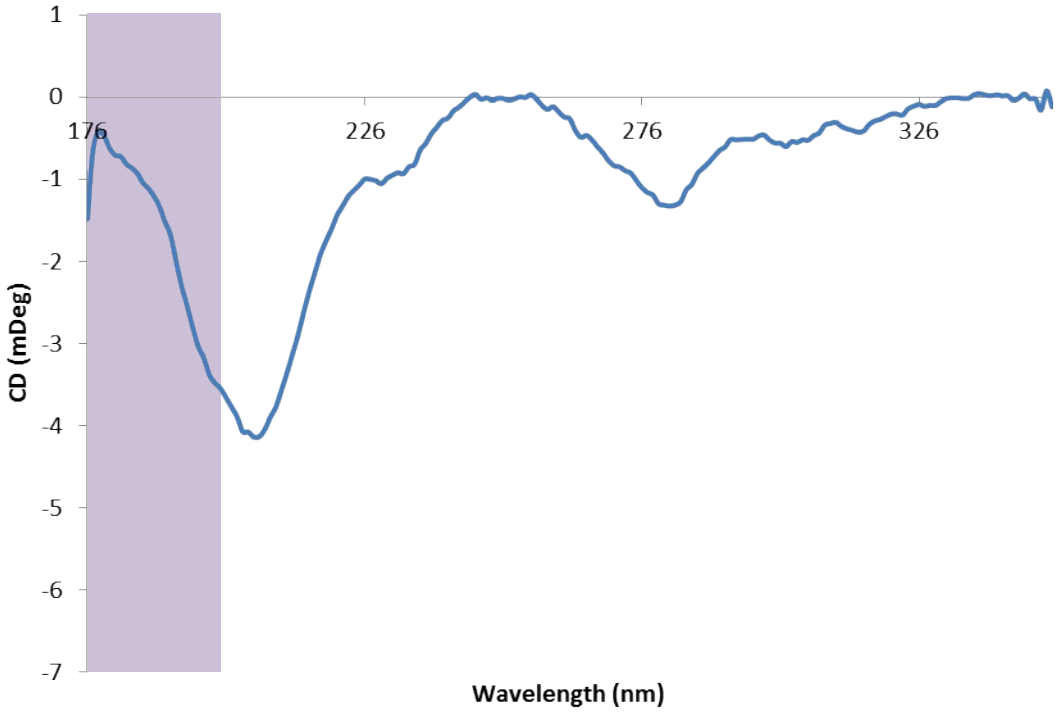

Figure E.5 SRCD spectrum of **[Pt(PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** in water, with additional spectral information highlighted in purple. 7pt smoothing applied.

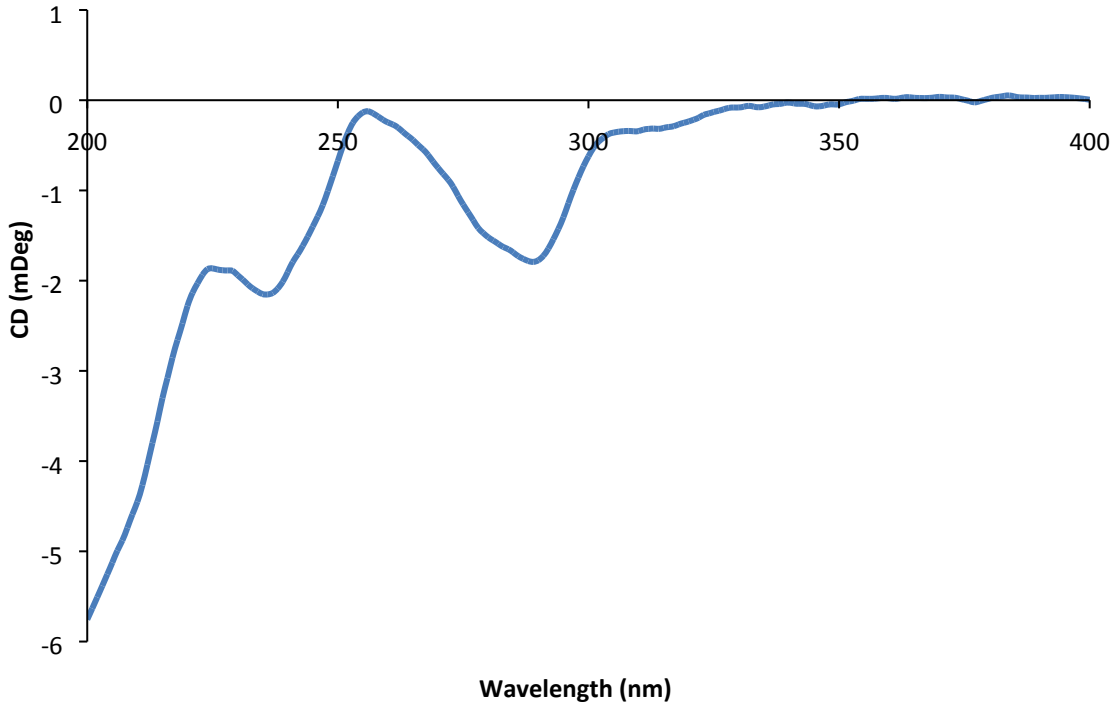

Figure E.6 CD spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$** in water. 13pt smoothing applied.

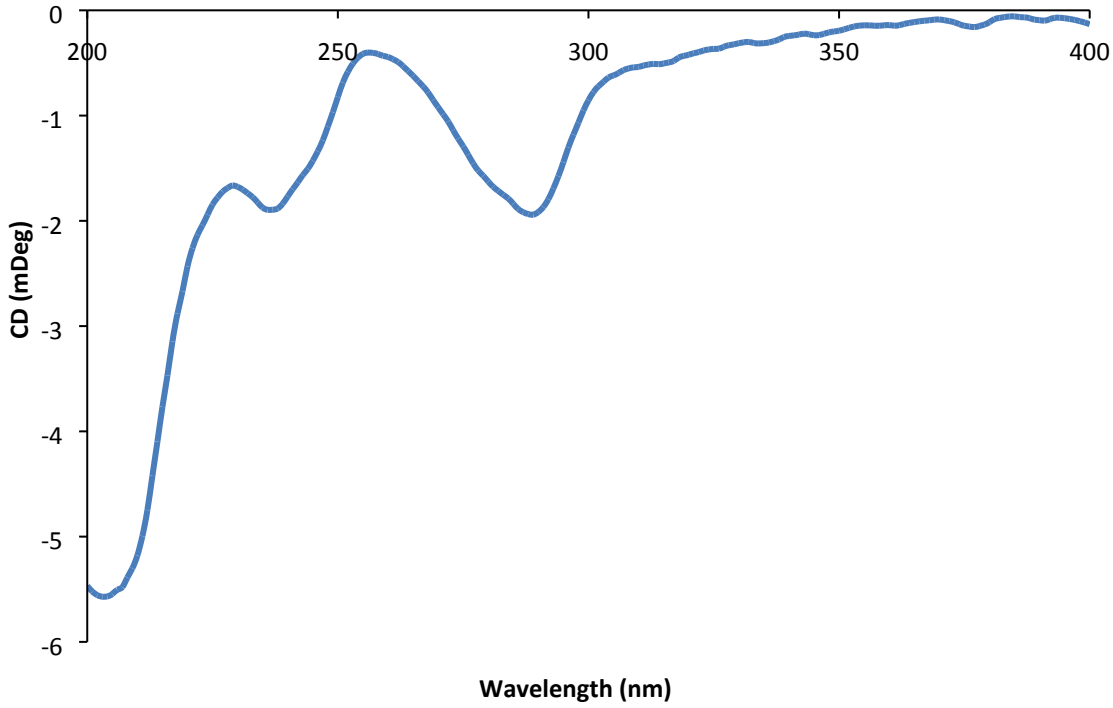

Figure E.7 CD spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$** in water. 13pt smoothing applied.

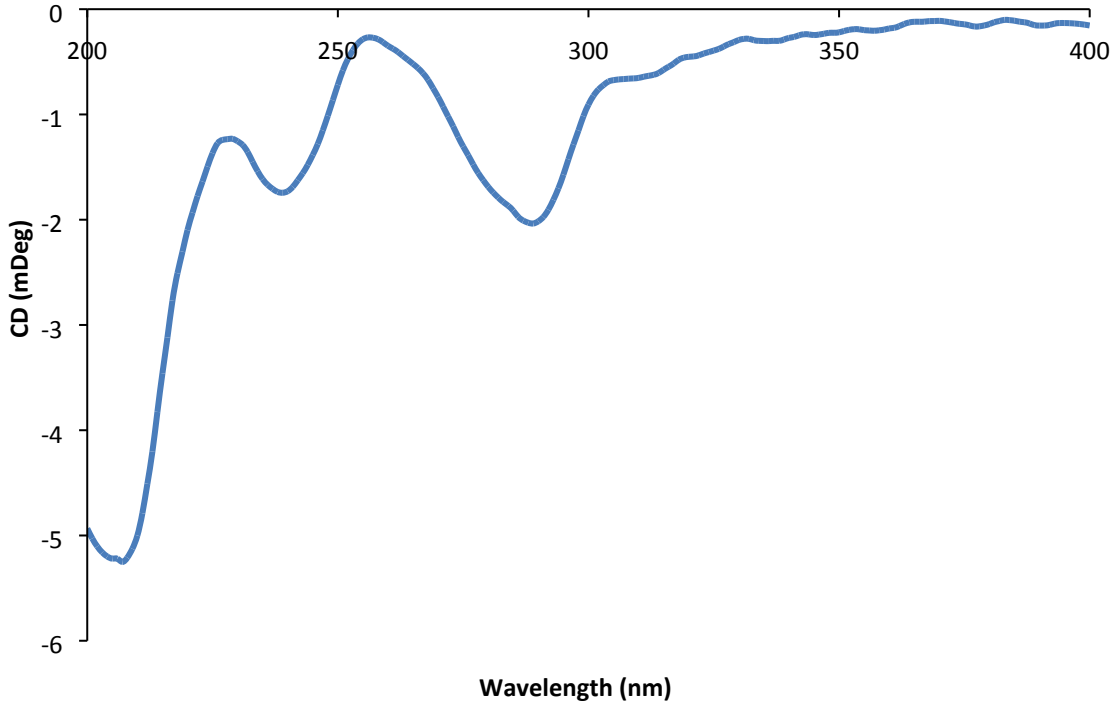

Figure E.8 CD spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$** in water. 13pt smoothing applied.

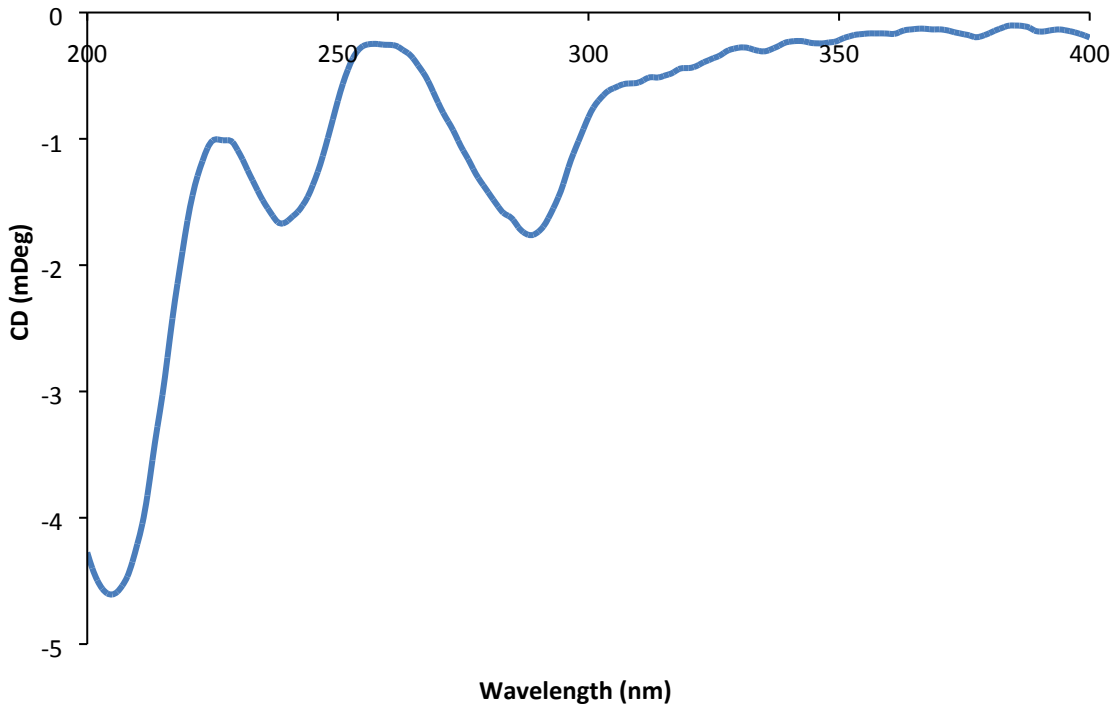

Figure E.9 CD spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$** in water. 13pt smoothing applied.

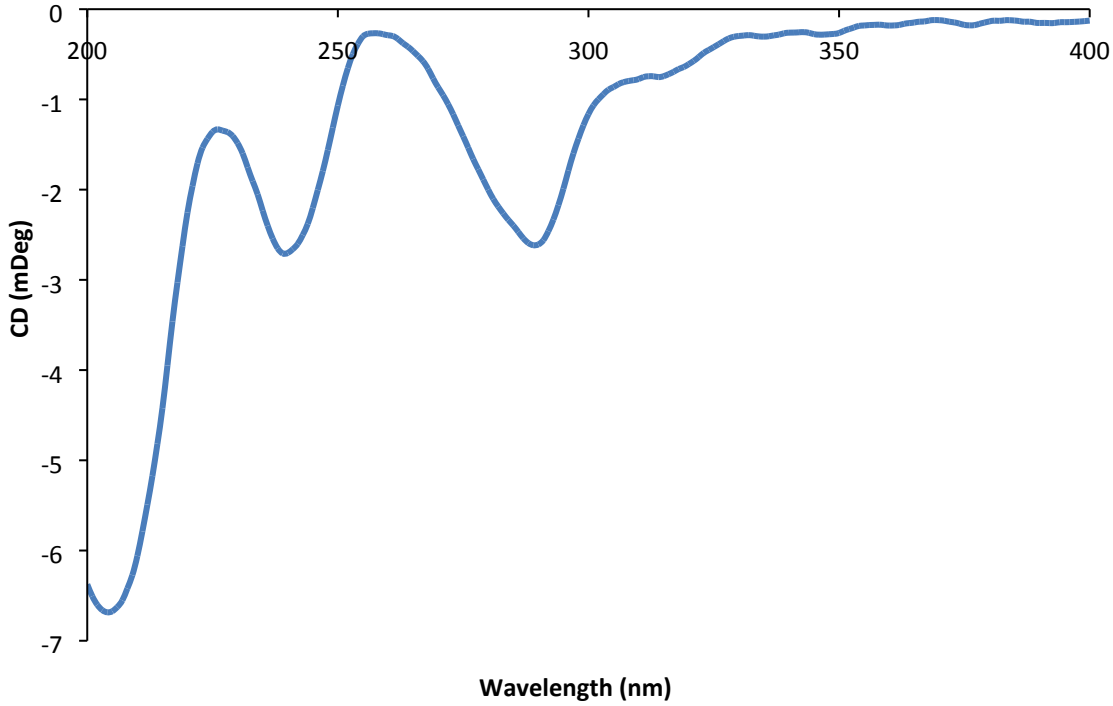

Figure E.10 CD spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** in water. 13pt smoothing applied.

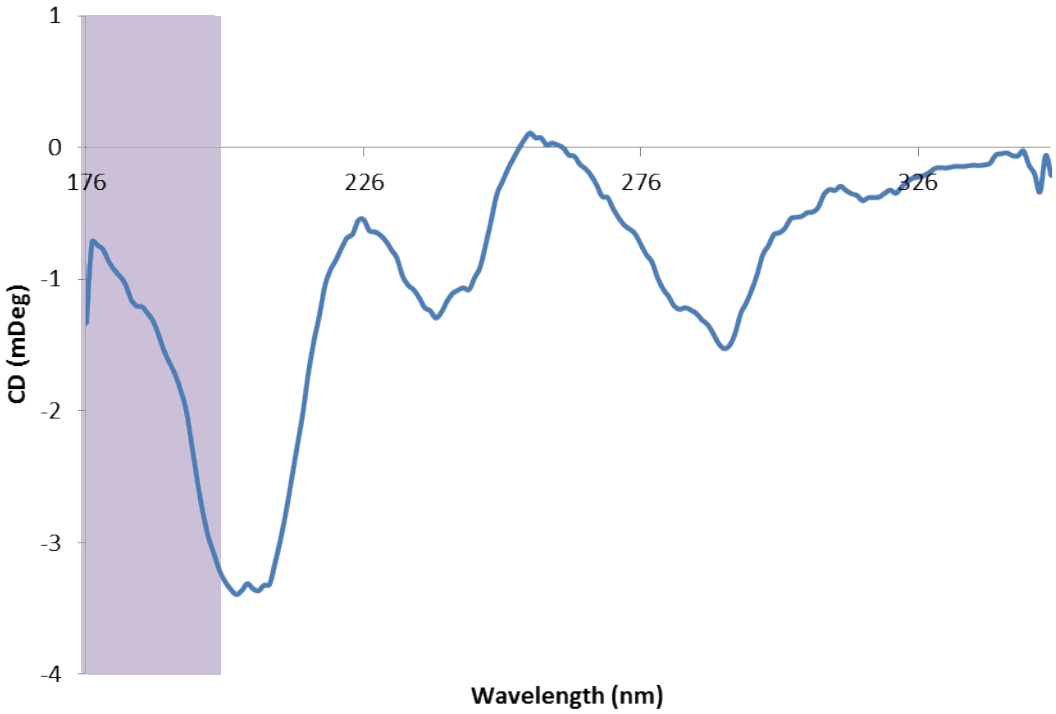

Figure E.10 SRCD spectrum of **[Pt(56Me$_2$PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$** in water, with additional spectral information highlighted in purple. 7pt smoothing applied.

F. Flash Chromatography Details

Table E.1 Flash chromatography gradients, flowrates and elution times of **56MESS(IV)** derivatives (complexes **6**–**10**)

Complex	**Gradient (H_2O:MeOH)**	**Flowrate**	**Elution time (min)**
[Pt(56Me$_2$PHEN)(SSDACH)(Acetate)$_2$](NO$_3$)$_2$ (6)	100:0 over 22 min	10 mL/min	16 – 22
[Pt(56Me$_2$PHEN)(SSDACH)(Propanoate)$_2$](NO$_3$)$_2$ (7)	100:0 over 42 min	8 mL/min for 33 min 15 mL/min for 9 min	33 – 42
[Pt(56Me$_2$PHEN)(SSDACH)(Butanoate)$_2$](NO$_3$)$_2$ (8)	100:0 over 42 min 90:10 over 13 min	8 mL/min	47 – 55
[Pt(56Me$_2$PHEN)(SSDACH)(Pentanoate)$_2$](NO$_3$)$_2$ (9)	100:0 over 95 min	8 mL/min	79 – 95
[Pt(56Me$_2$PHEN)(SSDACH)(Hexanoate)$_2$](NO$_3$)$_2$ (10)	100:0 over 72 min 95:5 over 2 min 85:15 over 2 min 75:25 over 8 min 0:100 over 28 min	8 mL/min for 61 min 15 mL/min for 10 min 25 mL/min for 2 min 15 mL/min for 10 min 25 mL/min for 8 min 15 mL/min for 20 min	92 – 112

G. Lipophilicity Studies

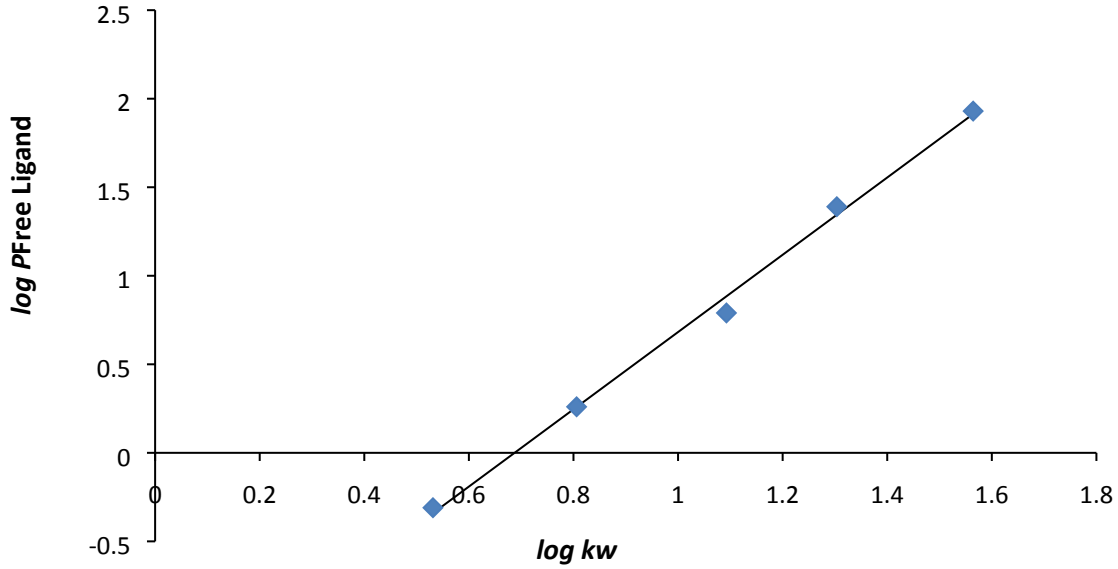

Figure G.1 Plot of *log P* values of carboxylic acid ligands vs. *log* k_w values of synthesised **PHENSS(IV)** derivatives, complexes **1–5**.

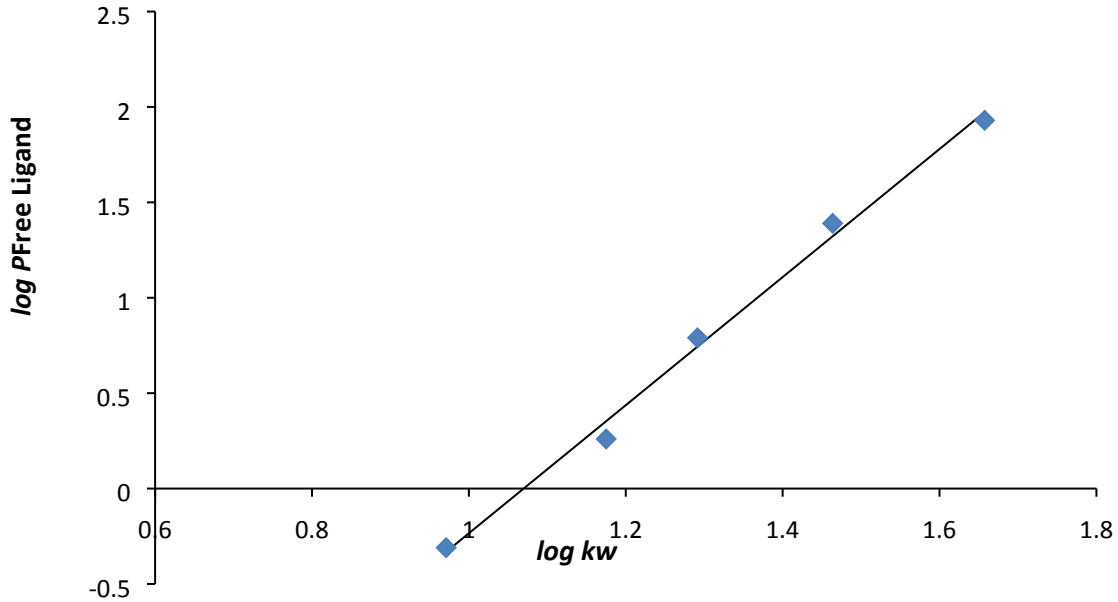

Figure G.2 Plot of *log P* values of carboxylic acid ligands vs. *log* k_w values of synthesised **56MESS(IV)** derivatives, complexes **6–10**.

Log P values of carboxylic acids used to construct the plots against *log* k_w were obtained from literature.[1, 2]

H. *In vitro* cytotoxicity

Table H.1 *In vitro* cytotoxicity of synthesised complexes. Cisplatin, oxaliplatin and carboplatin values are shown for comparison. IC_{50} values [nM] are reported with standard error; produced from duplicate experiments that were conducted on 3-4 separate occasions (n = 3-4); n.d. = not determined. [α]data taken from ref [3].

	IC_{50} ± Std Dev (nM)										
Complex	**HT29**	**U87**	**MCF-7**	**A2780**	**H460**	**A431**	**Du145**	**BE2-C**	**SJ-G2**	**MIA**	**MCF10A**
1	100 ± 19	1400 ± 250	1400 ± 340	310 ± 72	320 ± 37	650 ± 150	140 ± 29	510 ± 52	340 ± 47	200 ± 30	290 ± 60
2	87 ± 21	1000 ± 20	1200 ± 600	200 ± 6	300 ± 17	430 ± 120	200 ± 72	410 ± 38	290 ± 20	190 ± 22	270 ± 12
3	120 ± 24	570 ± 40	790 ± 100	290 ± 21	290 ± 80	560 ± 31	73 ± 33	340 ± 120	330 ± 55	210 ± 36	350 ± 23
4	130 ± 34	670 ± 130	840 ± 490	270 ± 27	380 ± 57	680 ± 93	100 ± 49	1100 ± 460	330 ± 33	210 ± 20	330 ± 45
5	150 ± 17	740 ± 35	930 ± 220	300 ± 50	540 ± 130	540 ± 52	110 ± 3.3	1000 ± 530	340 ± 62	190 ± 15	380 ± 13
6	16 ± 2	93 ± 0	100 ± 35	29 ± 2	24 ± 3	160 ± 120	25 ± 7	90 ± 19	91 ± 20	18 ± 1	29 ± 4
7	13 ± 5	80 ± 30	110 ± 35	28 ± 10	22 ± 9	21 ± 5	28 ± 20	72 ± 21	80 ± 24	13 ± 5	24 ± 10
8	27 ± 9	140 ± 30	350 ± 50	44 ± 4	38 ± 1	75 ± 29	19 ± 1	180 ± 34	200 ± 55	26 ± 4	38 ± 5
9	15 ± 6	100 ± 30	160 ± 24	31 ± 7	22 ± 2	44 ± 6	14 ± 4	130 ± 15	140 ± 26	20 ± 6	28 ± 2
10	13 ± 6	79 ± 20	150 ± 17	29 ± 4	20 ± 5	18 ± 9	10 ± 0	100 ± 27	140 ± 32	13 ± 6	25 ± 4
PHENSS(II)	160 ± 45	980 ± 270	1500 ± 500	230 ± 30	360 ± 35	480 ± 170	100 ± 38	380 ± 46	330 ± 66	200 ± 57	300 ± 58
PHENSS(IV)	710 ± 300	4900 ± 610	16000 ± 4500	800 ± 84	1700 ± 200	4300 ± 530	310 ± 92	3000 ± 530	1700 ± 350	3400 ± 2200	1700 ± 200
56MESS(II)[α]	76 ± 61	76 ± 14	50 ± 4	30 ± 4	37 ± 9	51 ± 21	7 ± 2	100 ± 16	74 ± 18	15 ± 2	20 ± 5
56MESS(IV)[α]	22 ± 4	140 ± 23	140 ± 0	63 ± 16	53 ± 10	100 ± 15	9 ± 3	320 ± 61	110 ± 9	27 ± 2	30 ± 3
Cisplatin[α]	11300 ± 1900	3800 ± 1100	6500 ± 800	1000 ± 100	900 ± 200	2400 ± 300	1200 ± 100	1900 ± 200	400 ± 100	7500 ± 1300	n.d.
Oxaliplatin[α]	900 ± 200	1800 ± 200	500 ± 100	160 ± 0	1600 ± 100	4100 ± 500	2900 ± 400	900 ± 200	3000 ± 1200	900 ± 200	n.d.
Carboplatin[α]	>50000	>50000	>50000	9200 ± 2900	14000 ± 1000	24300 ± 2200	14700 ± 1200	18700 ± 1200	5700 ± 200	>50000	n.d.

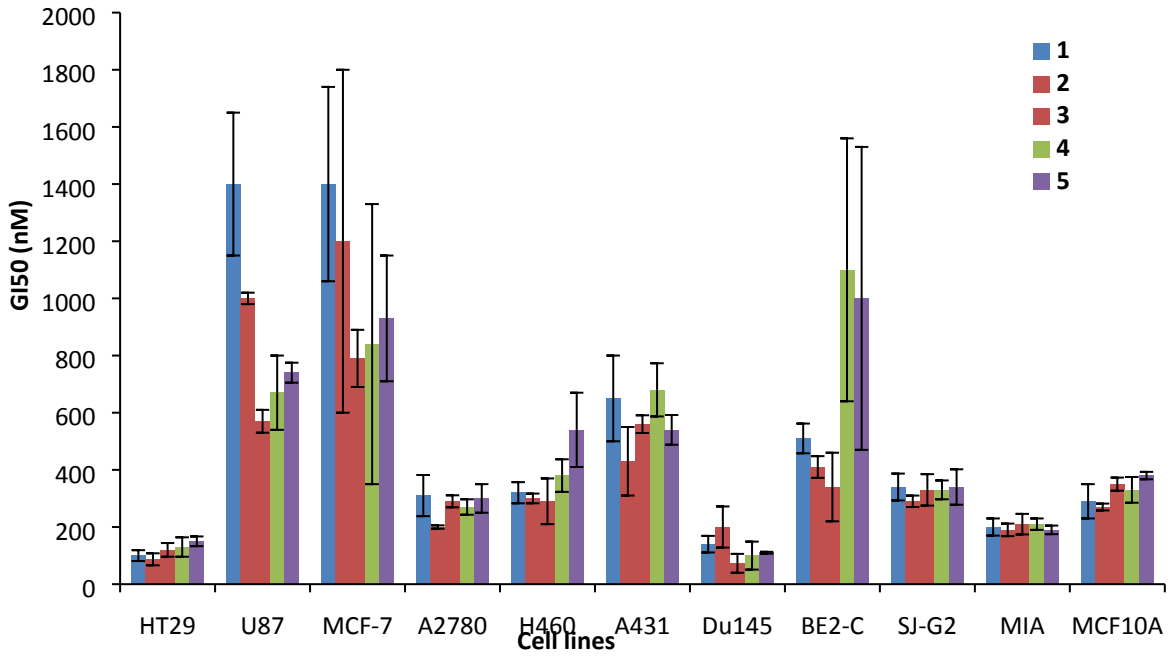

Figure H.1 *In vitro* cytotoxicity of **PHENSS(IV)** derivatives (**1**–**5**).

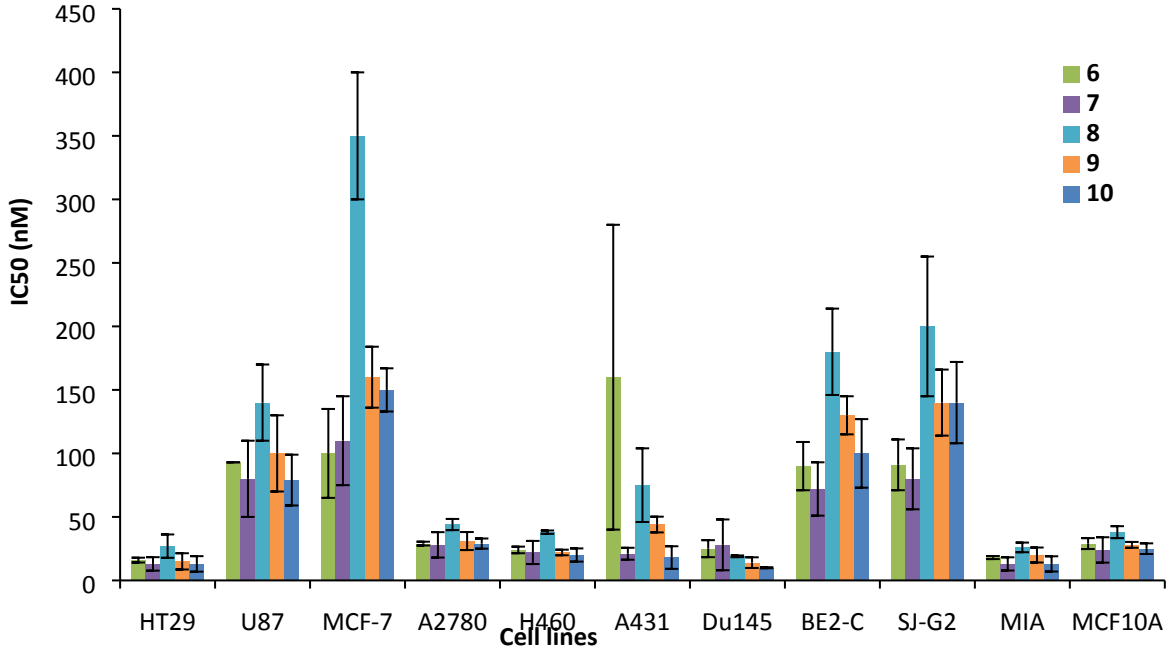

Figure H.2 *In vitro* cytotoxicity of **56MESS(IV)** derivatives (**6**–**10**).

I. Crystallographic Data

Table I.1 Calculated hydrogen bonds for complex **3** using PLATON.

Donor---H…Acceptor	**D - H**	**H...A**	**D...A**	**D - H...A**
N(3)---H(3A)…O(10)	0.89	1.99	2.86(2)	167
N(3)---H(3B)…O(8)	0.89	2.52	3.35(3)	157
N(3)---H(3B)…O(9)	0.89	2.12	2.95(3)	156'
N(4)---H(4A)…O(6)	0.89	2.00	2.80(2)	149
N(4)---H(4B)…O(5)	0.89	2.26	3.04(2)	145
N(4)---H(4B)…O(7)	0.89	2.34	3.19(3)	160'

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2. P. E. Keane, J. Simiand, E. Mendes, V. Santucci and M. Morre, *Neuropharmacology*, 1983, **22**, 875-879.
3. F. J. Macias, K. M. Deo, B. J. Pages, P. Wormell, J. K. Clegg, Y. Zhang, F. Li, G. Zheng, J. Sakoff, J. Gilbert and J. R. Aldrich-Wright, *Chem. Eur. J.*, 2015, **21**, 16990-17001.