SUPPORTING INFORMATION

Exploring Structural and Optical Properties of a New Series of Soft Salts Based on Cyclometalated Platinum Complexes

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EXPERIMENTAL SECTION

1- General Procedures

In air- and moisture-sensitive reactions, all glassware was flame-dried. All reactions under a dry nitrogen atmosphere were conducted using Schlenk techniques. The starting materials were purchased from Sigma-Aldrich, TCI, or Alfa-Aesar and were used as received. Thin layer chromatography (TLC) was conducted on pre-coated aluminum sheets with 0.20 mm Merck Alugram SIL G/UV254, with fluorescent indicator UV254 and 0.25 mm Merck silica gel (60-F254). Column chromatography was carried out using Macherey Nagel silica gel 60 (particle size 63-200 μm) and Macherey Nagel Aluminum neutral oxide 40 (particle size 40-160 μm). Nuclear magnetic resonance (NMR) spectra were acquired at room temperature on a Bruker AC-300 spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz,) and referenced as follows: ^{1}H NMR, residual $CHCl_3$ (δ = 7.26 ppm); $^{13}C\{^1H\}$ NMR, internal $CDCl_3$ (δ = 77.2 ppm). The chemical shifts δ are reported in parts per million relatives to TMS (^{1}H, 0.0 ppm) and $CDCl_3$ (^{13}C, 77.2 ppm). The coupling constant *J* is given in Hz. In the ^{1}H NMR data, the following abbreviations are used to describe the peak pattern: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quadruplet) and m (multiplet). Acidic impurities in $CDCl_3$ were removed by treatment with anhydrous K_2CO_3. UV-Vis and fluorescence spectra were recorded using standard 1 cm quartz cells on a Jasco V-650 spectrophotometer and a Horiba Fluoromax spectrometer, respectively. Complexes were excited at their absorption maxima (band of lowest energy) to record the emission spectra in degassed DMSO. Fluorescence quantum yields in solution were calculated relative to 9,10-bis(phenylethynyl)anthracene in cyclohexane (Φ_{PL} =1) as the reference. Fluorescence quantum yields in solution were calculated relative to 9,10-bis(phenylethynyl)anthracene in cyclohexane (Φ_{PL} =1) as the reference using solutions with absorbance below 0.1 at excitation wavelength. Five solutions of different concentration were used for each compound and the standard. Solid-state emission spectra were registered at 1 wt% in a KBr matrix. The phosphorescence lifetimes measurements in the solid state were performed on the same spectrometer in the phosphorimeter mode. Fluorescence quantum yields of solid samples (powder) were calculated using a Jasco FP-8300 spectrofluorometer equipped with a Jasco ILF-835/100 mm integrating sphere. High Resolution Mass Spectrometry (HRMS) analyses were performed at the "Centre Régional de Mesures Physiques de l'Ouest" (CRMPO, University of Rennes, France) using a Thermo scientific Orbitrap Exploris 480 apparatus. Vapochromism tests were performed by depositing a small quantity of product (powder) on a glass plate, which was then introduced into a slope closed test tube containing a small volume of the selected solvent for 10 min (heating is possible for less volatile solvents). Reversible solid-state emission quenching was observed using the same procedure as vapochromism tests, by replacing the solvents with HCl or NH_3 vapors. In solution, reactions were performed by bubbling (N_2) a solution of HCl/NH_3, and the acid/basic vapors were introduced directly into the analytical quartz cells via cannulas for 10 min.

A. Synthesis of Ligands

In an oven-dried Schlenk tube under a N_2 atmosphere 2-bromopyridine or 2-chloropyrimidine (1 eq.) and aryl phenyl boronic acid (1.3 eq.) were added. A mixture of 2 M Na_2CO_3 aqueous solution/toluene/ethanol (8/30/8) was poured into the flask and $Pd(PPh_3)_4$ (0.05 eq.) was added. The mixture was heated to reflux for 24 h. After completion of the reaction, the reaction mixture was cooled to room temperature and the crude compound was extracted with EtOAc. The organic phase was washed with a saturated NH_4Cl solution and dried over $MgSO_4$. The crude product was purified by column chromatography over silica gel using petroleum ether/EtOAc as eluent.

B. Synthesis of cyclometalated Platinum (II) dimers

Platinum(II) dimers $[Pt(C\hat{}N)_2Cl]_2$ were prepared using 1.5 eq. of the C^N ligand vs K_2PtCl_4. The two reactants were placed in the reaction flask in a deoxygenated mixture of 15 mL of 2-ethoxyethanol and 5 mL of water. The mixture was stirred at 80 °C for 16 h under a nitrogen atmosphere. After cooling down, the mixture was poured into 30 mL of cold water. Yellow solids were obtained by filtration and vacuum drying.

C. Synthesis of cationic Platinum complexes

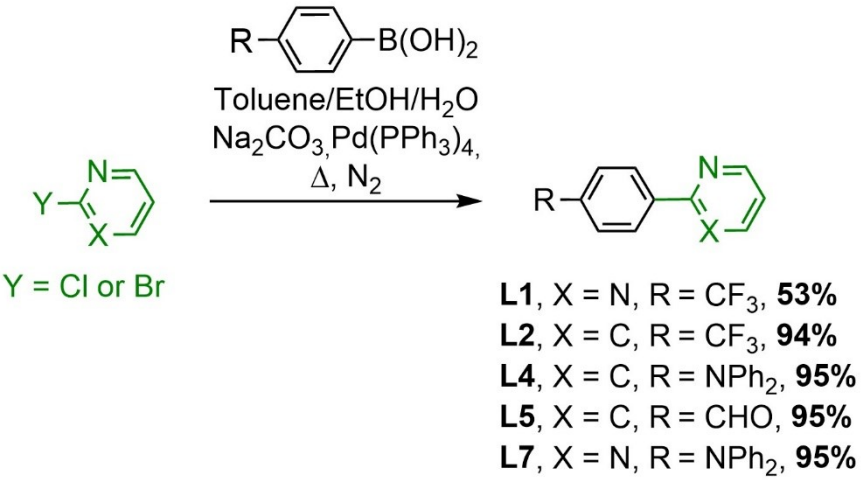
Platinum(II) dimers $[Pt(C\hat{}N)_2Cl]_2$ were added to a solution of 3 eq. of ethylenediamine in 15 mL of dichloromethane. Under a nitrogen atmosphere, the mixture was stirred at room temperature for 3 h until yellow solid suspensions were observed. Yellow solids were obtained by filtration, which were washed with water (3 × 10 mL) and dichloromethane (3 × 10 mL).

D. Synthesis of anionic platinum complexes

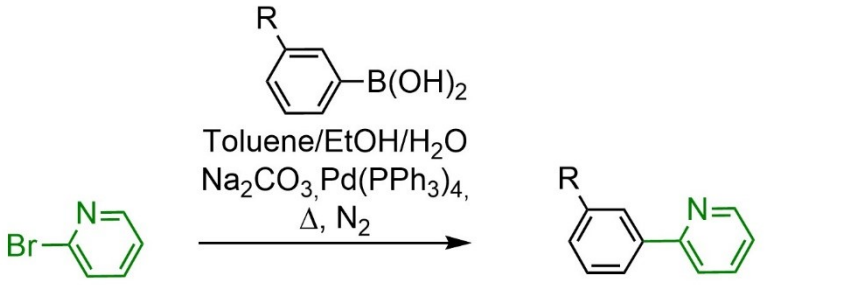
Platinum(II) dimers $[Pt(C\hat{}N)_2Cl_2]$ and 4 eq. of tetrabutylammonium cyanide were refluxed at 50 °C in dichloromethane for 5 h. After cooling, the crude compound was extracted three times with dichloromethane and the organic phase was washed with water. Finally, the desired solid product was obtained by column chromatography over alumina, eluting with dichloromethane/methanol (20/1).

E. Synthesis of Soft Salts

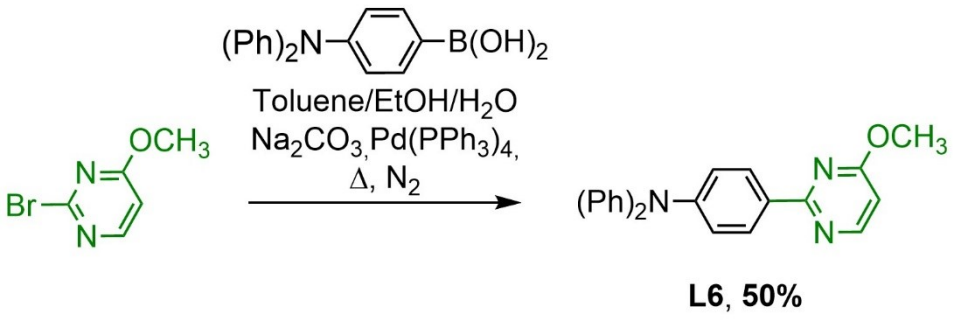
All soft salts were prepared by metathesis reaction. 1 eq. of anionic complex and 1.1 eq. of cationic complex were dissolved in 5 mL ethanol. The yellow solution turned red after ultrasonic treatment for 10 min. Deionized water (50 mL) was then added to the mixture and the ultrasonic treatment was extended for 30 min., until the formation of a solid suspension was observed. Finally, the residue was filtered, washed with 10 mL of deionized water and 10 mL of dichloromethane to provide the desired soft salt.



L1, X = N, R = CF_3, **53%**
L2, X = C, R = CF_3, **94%**
L4, X = C, R = NPh_2, **95%**
L5, X = C, R = CHO, **95%**
L7, X = N, R = NPh_2, **95%**



L3, X = C, R = CHO, **94%**
L8, X = C, R = NPh_2, **54%**

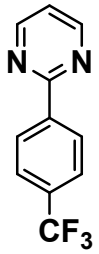


L6, **50%**

2- Synthesis of ligands L1-L8

Scheme S1 : Synthesis of the C^N ligands **1-8**.

Ligand 1

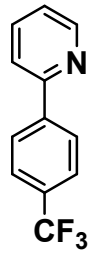


2-(4-(trifluoromethyl)phenyl)pyrimidine

Synthesized using general procedure **A** from 2-chloropyridimine (139 mg, 1.22mmol, 1 eq.), (4-(trifluoromethyl)phenyl)boronic acid (300 mg, 1.58mmol, 1.3 eq.), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol, 0.05 eq.). The crude material was purified by column chromatography (Petroleum ether /EtOAc: 8/2) to yield the product as a white solid (145 mg, 53 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (d, J = 4.8 Hz, 2H), 8.57 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.29 – 7.21 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 158.0, 141.4, 132.7 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 129.0, 126.11 (q, $^3J_{C\text{-}F}$ = 3.74 Hz), 124.3 (q, $^3J_{C\text{-}F}$ = 272.4 Hz), 120.4. Spectroscopic data were similar to literature.[2]

Ligand 2

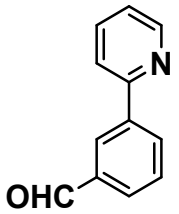


2-(4-(trifluoromethyl)phenyl)pyridine

Synthesized using general procedure **A** from 2-bromopyridine (166 mg, 100 mmL, 1.05mmol, 1 eq.), (4-(trifluoromethyl)phenyl)boronic acid (300 mg, 1.58 mmol, 1.5 eq.), $Pd(PPh_3)_4$ (60 mg, 0.053 mmol, 0.05 eq.). The crude material was purified by column chromatography (Petroleum ether /EtOAc: 9/1) to yield the product as a white solid (225 mg, 94 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (d, J = 5.0 Hz, 1H), 8.11 (d, J = 8.1 Hz, 2H), 7.84 – 7.70 (m, 4H), 7.37 – 7.27 (m, 1H). Spectroscopic data were similar to literature.[3]

Ligand 3

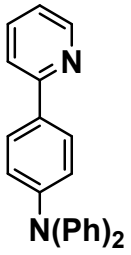


3-(pyridin-2-yl)benzaldehyde

Synthesized using general procedure **A** from 2-bromopyridine (243 mg, 146 μL, 1.54mmol, 1 eq.), (3-formylphenyl)boronic acid (300 mg, 2 mmol, 1.3 eq.), $Pd(PPh_3)_4$ (89 mg, 0.077 mmol, 0.05 eq.). The crude material was purified by column chromatography (Petroleum ether /EtOAc: 8/2) to yield the product as a white solid (270 mg, 94 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.66 (dt, *J* = 4.9, 1.5 Hz, 1H), 8.45 (t, *J* = 1.8 Hz, 1H), 8.23 (m, 1H), 7.87 (m, 1H), 7.77 – 7.70 (m, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.20 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 155.2, 149.4, 139.8, 136.6, 136.5, 132.2, 129.3, 129.0, 127.9, 122.4, 120.1. Spectroscopic data were similar to literature.[4]

Ligand 4

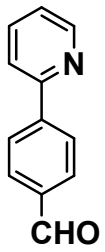


N, N-diphenyl-4-(pyridin-2-yl)aniline

Synthesized using general procedure **A** from 2-bromopyridine (150 mg, 90 L, 0.949 mmol, 1 eq.), (4-(diphenylamino)phenyl)boronic acid (400 mg, 1.38 mmol, 1.5 eq.), $Pd(PPh_3)_4$ (53 mg, 0.046 mmol, 0.05 eq.). The crude material was purified by column chromatography (Petroleum ether /EtOAc: 8/2) to yield the product as a white solid (285 mg, 95 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 – 8.61 (m, 1H), 7.90 – 7.83 (m, 2H), 7.76 – 7.65 (m, 2H), 7.31 – 7.27 (m, 3H), 7.25 (s, 1H), 7.16 (m, 5H), 7.13 (d, *J* = 2.6 Hz, 2H), 7.09 – 7.01 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 149.8, 148.9, 147.7, 136.8, 133.3, 129.5, 127.9, 124.9, 123.4, 123.4, 121.6, 120.0. Spectroscopic data were similar to literature.[5]

Ligand 5

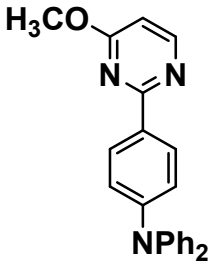


4-(pyridin-2-yl)benzaldehyde

Synthesized using general procedure **A** from 2-bromopyridine (260 mg, 156 μL, 1.65mmol, 1 eq.), (4-formylphenyl)boronic acid (800 mg, 5.34 mmol, 3 eq.), $Pd(PPh_3)_4$ (237 mg, 0.205 mmol, 0.05 eq.). The crude material was purified by column chromatography (Petroleum ether /EtOAc: 8/2) to yield the product as a white solid (652 mg, 87 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.76 (dt, *J* = 4.8, 1.4 Hz, 1H), 8.24 – 8.14 (m, 2H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.88 – 7.79 (m, 2H), 7.37 – 7.31 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 156.1, 150.1, 145.1, 137.1, 136.6, 130.3, 127.6, 123.3, 121.3. Spectroscopic data were similar to literature.[3]

Ligand 6

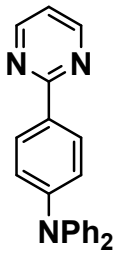


4-(4-methoxypyrimidin-2-yl)-N,N-diphenylaniline

Synthesized using general procedure **A** from 2-bromo-4-methoxypyrimidine (436 mg, 2.31 mmol, 1 eq.), (4-(diphenylamino)phenyl)boronic acid (1 g, 3.46 mmol, 1.5 eq.), $Pd(PPh_3)_4$ (133 mg, 0.115 mmol, 0.05 eq.). The crude material was purified by column chromatography (Petroleum ether /EtOAc: 9/1) to yield the product as a yellow-white solid (407 mg, 50 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.7 Hz, 1H), 8.33 – 8.26 (m, 2H), 7.32 – 7.26 (m, 4H), 7.18 – 7.04 (m, 8H), 6.56 (d, *J* = 5.7 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.51, 164.29, 157.5, 150.4, 147.4, 131.1, 129.5, 129.4, 125.5, 123.7, 122.2, 105.4, 53.5.

Ligand 7

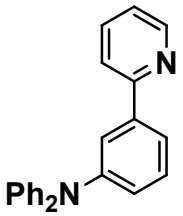


N,N-diphenyl-4-(pyrimidin-2-yl)aniline

Synthesized using general procedure **A** from 2-chloropyrimidine (213 mg, 1.86 mmol, 1 eq.), (4-(diphenylamino)phenyl)boronic acid (700 mg, 2.42 mmol, 1.5 eq.), $Pd(PPh_3)_4$ (108 mg, 0.093 mmol, 0.05 eq.). The crude material was purified by column chromatography (Petroleum ether /EtOAc: 9/1) to yield the product as a white solid (400 mg, 66 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.8 Hz, 2H), 8.36 – 8.26 (m, 2H), 7.36 – 7.27 (m, 5H), 7.18 – 7.04 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 157.3, 150.5, 147.4, 131.0, 129.5, 129.3, 125.4, 123.8, 122.3, 118.4. Spectroscopic data were similar to literature.[6]

Ligand 8



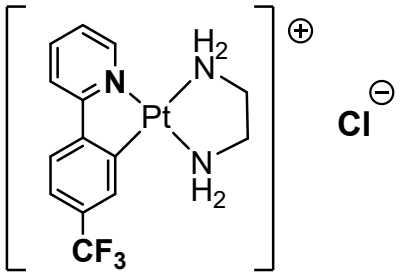
N,N-diphenyl-3-(pyridin-2-yl)aniline

Synthesized using general procedure **A** from 2-bromopyridine (374 mg, 226 μL, 2.37 mmol, 1 eq.), (3-(diphenylamino)phenyl)boronic acid (891 mg, 3.08 mmol, 1.3 eq.), $Pd(PPh_3)_4$ (27 mg, 0.118 mmol, 0.05 eq.). The crude material was purified by column chromatography (Petroleum ether /EtOAc: 7/3) to yield the product as a yellow-white solid (535 mg, 54 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 – 8.63 (m, 1H), 7.77 – 7.59 (m, 4H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.32 – 7.23 (m, 5H), 7.18 – 7.11 (m, 5H), 7.07 – 7.00 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 149.7, 148.5, 148.0, 140.9, 136.8, 129.8, 129.40, 128.4, 125.0, 124.4, 122.9, 122.3, 121.7, 120.8. Mass spectroscopic date were similar to literature.[7]

3- Synthesis of precursors C1-2 and A1-7

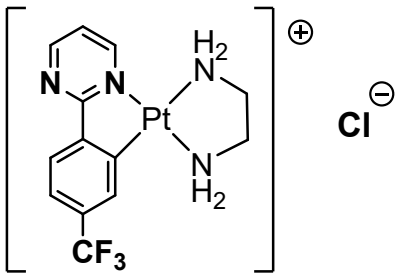
Cationic platinum complex C1



Synthesized using general procedure **C** from platinum (II) dimers $[Pt(C\hat{}N)_2Cl]_2$ (650 mg, 0.718 mmol, 1 eq.), ethylenediamine (129 mg, 144 μL, 2.15 mmol, 3 eq.). Yellow solid (298 mg, 86%).

^{1}H NMR (300 MHz, DMSO) δ 8.71 (d, *J* = 5.8 Hz, 1H), 8.20 (d, *J* = 4.6 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.61 (s, 1H), 7.55 – 7.41 (m, 2H), 6.27 (s, 2H), 5.48 (s, 2H), 2.68 (s, 4H). Spectroscopic data were similar to literature.[1a,8]

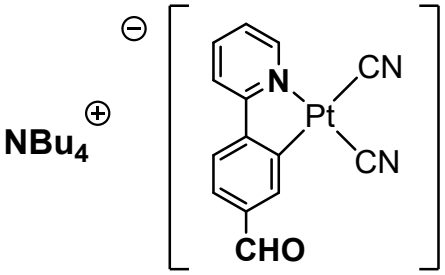
Cationic platinum complex C2



Synthesized using general procedure **C** from platinum (II) dimers $[Pt(C\hat{}N)_2Cl]_2$ (220 mg, 0,242 mmol, 1 eq.), ethylenediamine (44 mg, 49 μL, 0.727 mmol, 3 eq.). Yellow solid (193 mg, 77%).

^{1}H NMR (300 MHz, DMSO) δ 9.22 – 9.04 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.58 (t, *J* = 5.3 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 6.42 (s, 2H), 5.60 (s, 2H), 2.68 (s, 4H).^{13}C NMR (75 MHz, DMSO) δ 172.8, 159.3, 158.7, 145.9, 144.5, 131 (q, $^2J_{C\text{-}F}$ = 31 Hz), 129.8 (q, $^3J_{C\text{-}F}$ = 3.62 Hz), 126.6, 124.3 (q, $^3J_{C\text{-}F}$ = 271.3 Hz), 120.5, 120.3, 47.9, 43.7. HRMS (ESI) *m/z* calculated for C^+ ($C_{13}H_{14}N_4F_3{}^{195}Pt$) = 478.0818, found = 478.0812.

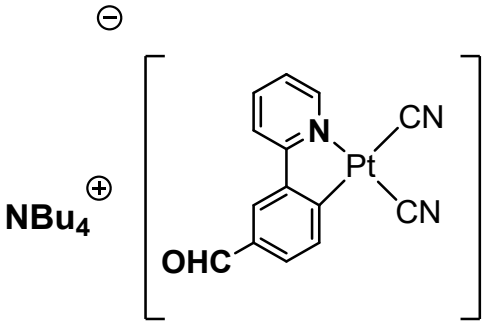
Anionic platinum complex A1



Synthesized using general procedure **D** from platinum (II) dimers $[Pt(C\hat{}N)_2Cl]_2$ (157 mg, 0.190 mmol, 1eq.), tetrabutylammonium cyanide (204 mg, 0.761mmol, 4 eq). Yellow solid (54 mg, 42 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.07 (s, 1H), 9.60 – 9.46 (m, 1H), 8.77 – 8.57 (m, 1H), 7.97 – 7.87 (m, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.73 – 7.61 (m, 2H), 7.26 – 7.19 (m, 1H), 3.51 – 3.34 (m, 8H), 1.80 – 1.69 (m, 8H), 1.56 – 1.41 (m, 8H), 1.01 (t, *J* = 7.3 Hz, 12H). Spectroscopic data were similar to literature.[7]

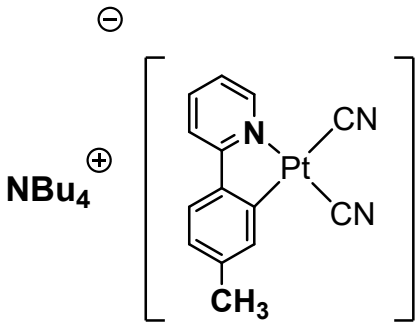
Anionic platinum complex A2



Synthesized using general procedure **D** from platinum (II) dimers $[Pt(C\hat{}N)_2Cl]_2$ (250 mg, 0.303 mmol, 1eq), tetrabutylammonium cyanide (285 mg, 1.06, 4 eq). Yellow solid (90 mg, 44 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.94 (s, 1H), 9.49 (d, *J* = 5.6 Hz, 1H), 8.41 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 1.6 Hz, 1H), 7.97 – 7.80 (m, 2H), 7.61 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.23 – 7.14 (m, 1H), 3.48 – 3.27 (m, 8H), 1.79 – 1.66 (m, 8H), 1.53 – 1.39 (m, 8H), 0.98 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (75 MHz, DMSO) δ 192.8, 168.6, 166.9, 153.5, 147.9, 146.1, 139.5, 139.0, 132.8, 132.7, 123.6, 122.8, 119.1, 117.7, 59.3, 24.3, 19.9, 13.8. HRMS (ESI) *m/z* calculated for A^- ($C_{14}H_8N_3O^{195}Pt$) = 429.0315, found = 429.0321.

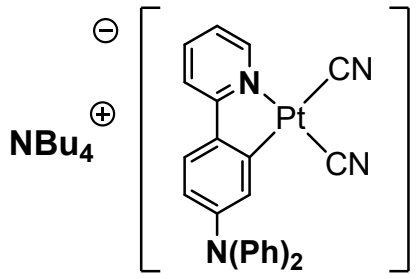
Anionic platinum complex A3



Synthesized using general procedure **D** from platinum (II) dimers $[Pt(C^N)_2Cl]_2$ (92 mg, 0.115 mmol, 1eq.), tetrabutylammonium cyanide (123 mg, 0.459 mmol, 4 eq.). Yellow solid (31 mg, 65 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.41 (d, *J* = 5.7 Hz, 1H), 8.02 (s, 1H), 7.76 (t, *J* = 7.9 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.03 (t, *J* = 6.6 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 3.44 – 3.33 (m, 8H), 2.32 (s, 3H), 1.77 – 1.65 (m, 8H), 1.50 – 1.41 (m, 8H), 0.98 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 157.4, 153.1, 144.1, 140.5, 139.6, 138.24, 124.6, 123.1, 122.1, 122.0, 118.7, 118.1, 59.1, 24.1, 21.7, 19.7, 13.7.* HRMS (ESI) *m/z* calculated for A^- ($C_{14}H_{10}N_3{}^{195}Pt$) = 415.0523, found = 415.0528.

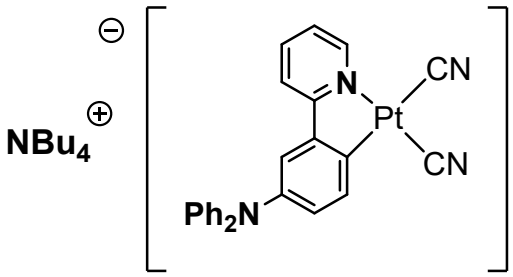
Anionic platinum complex A4



Synthesized using general procedure **D** from platinum (II) dimers $[Pt(C^N)_2Cl]_2$ (300mg, 0.272 mmol, 1eq.), tetrabutylammonium cyanide (292 mg, 1.09 mmol, 4 eq.). Yellow solid (149 mg, 67 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.40 (d, *J* = 6.0 Hz, 1H), 7.97 (d, *J* = 2.3 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 4H), 7.12 (d, *J* = 8.1 Hz, 4H), 6.99 (dt, *J* = 14.6, 6.7 Hz, 3H), 6.81 – 6.73 (m, 1H), 3.37 (q, *J* = 11.4 Hz, 8H), 1.71 (d, *J* = 10.1 Hz, 8H), 1.46 (h, *J* = 7.4 Hz, 8H), 0.99 (t, *J* = 7.3 Hz, 12H).^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 158.9, 153.2, 149.7, 148.1, 147.3, 141.9, 138.3, 134.6, 129.1, 124.3, 122.4, 121.7, 120.5, 120.5, 118.2, 59.3, 24.3, 19.9, 13.8.* HRMS (ESI) *m/z* calculated for A^- ($C_{25}H_{17}N_4{}^{195}Pt$) = 568.1101, found = 568.1106.

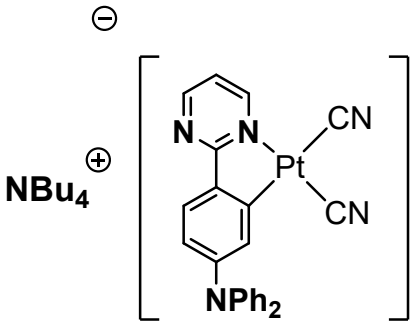
Anionic platinum complex A5



Synthesized using general procedure **D** from platinum (II) dimers $[Pt(C\hat{}N)_2Cl]_2$ (200 mg, 0.172 mmol, 1 eq.), tetrabutylammonium cyanide (184 mg, 0.686 mmol, 4 eq.). Yellow solid (128 mg, 89 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.43 (d, *J* = 5.7 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 6.9 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 2.5 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 5H), 7.05 (s, 5H), 7.00 – 6.89 (m, 3H), 3.45 – 3.32 (m, 8H), 1.73 – 1.62 (m, 8H), 1.52 – 1.38 (m, 8H), 0.97 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 153.4, 153.0, 148.3, 147.4, 144.0, 140.6, 139.0, 129.9, 129.1, 125.4, 123.2, 122.9, 121.9, 121.2, 118.8, 118.2, 59.3, 24.3, 19.9, 13.9. HRMS (ESI) *m/z* calculated for A^- ($C_{25}H_{17}N_4{}^{195}Pt$) = 568.1101, found = 568.1107.

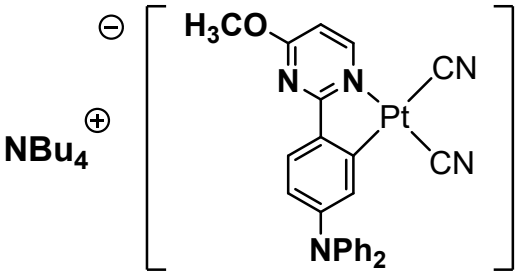
Anionic platinum complex A6



Synthesized using general procedure **D** from platinum (II) dimers $[Pt(C\hat{}N)_2Cl]_2$ (250 mg, 0.226 mmol, 1 eq.), tetrabutylammonium cyanide (243 mg, 0.904 mmol, 4 eq.). Yellow solid (104 mg, 56 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.46 (dd, *J* = 5.8, 2.3 Hz, 1H), 8.80 – 8.67 (m, 1H), 7.93 – 7.83 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.26 – 7.17 (m, 4H), 7.17 – 7.05 (m, 4H), 7.04 – 6.87 (m, 3H), 6.79 – 6.71 (m, 1H), 3.37 – 3.24 (m, 8H), 1.71 – 1.60 (m, 8H), 1.50 – 1.38 (m, 8H), 0.98 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 159.8, 158.6, 158.1, 152.1, 148.2, 146.3, 138.4, 133.24, 129.6, 128.9, 126.7, 125.4, 123.4, 120.3, 117.6, 60.7, 26.4, 19.8, 13.1.* HRMS (ESI) *m/z* calculated for A^- ($C_{24}H_{16}N_5{}^{195}Pt$) = 569.1054, found = 569.1062.

Anionic platinum complex A7

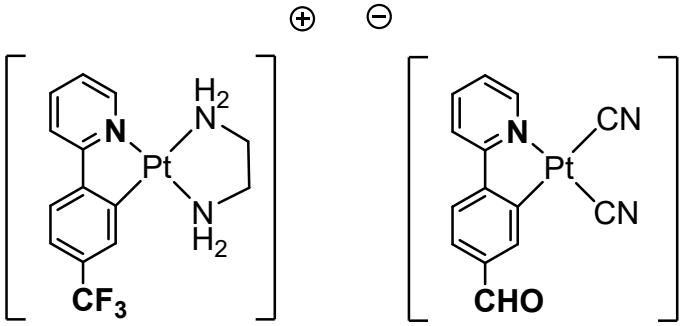


Synthesized using general procedure **D** from platinum (II) dimers $[Pt(C\hat{}N)_2Cl]_2$ (200 mg, 0.171 mmol, 1eq.), tetrabutylammonium cyanide (184 mg, 0.686 mmol, 4 eq. Yellow solid (94 mg, 65 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (d, *J* = 6.6 Hz, 1H), 7.87 (d, *J* = 2.3 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.24 – 7.17 (m, 4H), 7.15 – 7.08 (m, 4H), 6.97 (t, *J* = 7.2 Hz, 2H), 6.73 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.38 (d, *J* = 6.5 Hz, 1H), 4.05 (s, 3H), 3.39 – 3.29 (m, 8H), 1.75 – 1.65 (m, 8H), 1.45 (q, *J* = 7.4 Hz, 8H), 0.98 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 169.3, 159.2, 151.6, 147.9, 145.5, 138.6, 133.0, 129.2, 128.4, 128.2, 124.8, 124.0, 122.9, 119.8, 104.4, 59.3, 54.2, 24.3, 19.9, 13.9. HRMS (ESI) *m/z* calculated for A^- ($C_{25}H_{18}N_5O^{195}Pt$) = 599.1159, found =569.1166.

4- Synthesis of soft salts S1-9

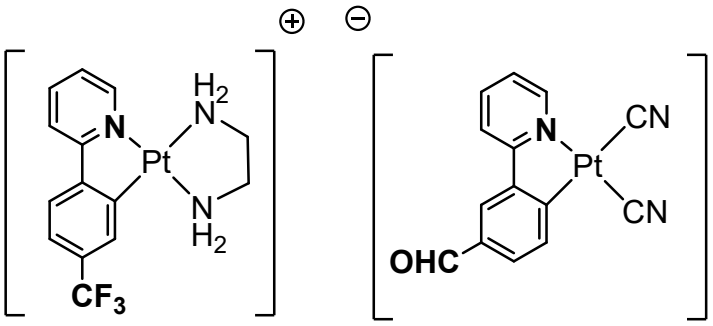
Soft Salt S0



Synthesized using general procedure **E** from **C1** (20 mg, 0.039 mmol, 1.1 eq), **A1** (24 mg, 0.036 mmol, 1 eq.). Red solid (24 mg, 75 %).

^{1}H NMR (300 MHz, DMSO) δ 9.96 (s, 1H), 9.29 (d, *J* = 5.8 Hz, 1H), 8.66 (d, *J* = 5.7 Hz, 1H), 8.43 (d, *J* = 23.9 Hz, 1H), 8.25 – 8.12 (m, 4H), 7.99 – 7.87 (m, 2H), 7.58 (d, *J* = 6.5 Hz, 2H), 7.54 – 7.40 (m, 3H), 6.22 (s, 2H), 5.38 (s, 2H), 2.68 (s, 4H). Spectroscopic data were similar to literature.[7]

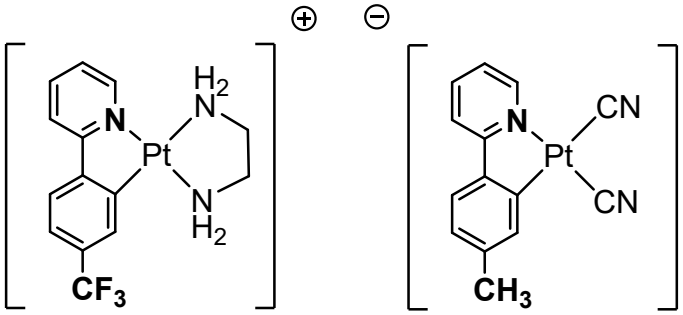
Soft Salt S1



Synthesized using general procedure **E** from **C1** (30 mg, 0.059 mmol, 1.1 eq.), **A2** (36 mg, 0.053 mmol, 1 eq.). Red solid (18 mg, 56 %).

^{1}H NMR (300 MHz, DMSO) δ 9.93 (s, 1H), 9.27 (d, *J* = 5.8 Hz, 1H), 8.66 (d, *J* = 5.8 Hz, 1H), 8.18 (dt, *J* = 15.9, 8.0 Hz, 6H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 3H), 6.22 (s, 2H), 5.38 (s, 2H). ^{13}C NMR (75 MHz, DMSO) δ 193.1, 166.1, 165.2, 163.0, 159.3, 152.8, 151.8, 149.7, 148.1, 145.2, 144.1, 140.8, 140.8, 140.2, 138.9, 132.9, 130.6 (q, $^{2}J_{C\text{-}F}$ = 30.5 Hz), 130.2, 129.6, 125.0, 124.5 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 123.5, 122.3 (q, $^{1}J_{C\text{-}F}$ = 276.7 Hz), 121.0, 120.8, 120.4, 48.2, 44.1.* HRMS (ESI) *m/z* calculated for C^{+} ($C_{14}H_{15}N_3F_3{}^{195}Pt$) = 477.0866, found = 477.0859; A^{-} ($C_{14}H_8N_3O{}^{195}Pt$) = 429.0315, found = 429.0321.

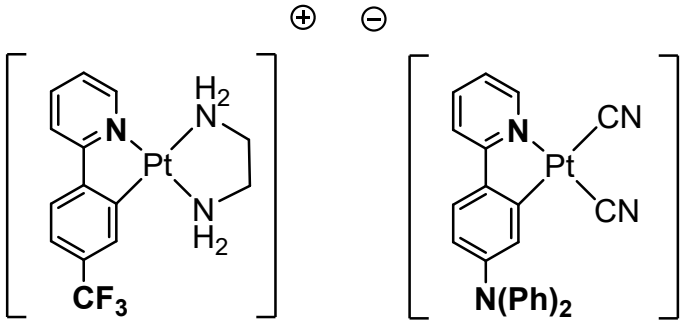
Soft Salt S2



Synthesized using general procedure **E** from **C1** (20 mg, 0.039 mmol, 1.1 eq.), **A3** (23 mg, 0.035 mmol, 1 eq.). Red solid (20 mg, 63 %).

^{1}H NMR (300 MHz, DMSO) δ 9.18 (d, *J* = 5.6 Hz, 1H), 8.66 (d, *J* = 5.8 Hz, 1H), 8.20 (d, *J* = 4.5 Hz, 2H), 8.05 – 7.89 (m, 3H), 7.72 (s, 1H), 7.62 – 7.54 (m, 2H), 7.53 – 7.41 (m, 2H), 7.32 (t, *J* = 6.8 Hz, 1H), 6.91 – 6.81 (m, 1H), 6.22 (s, 2H), 5.38 (s, 2H), 2.68 (s, 4H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 167.3, 164.7, 157.9, 152.0, 151.3, 149.2, 144.7, 144.4, 144.1, 140.3, 139.4, 139.1, 138.7, 129.7 (q, $^{3}J_{C\text{-}F}$ =3.75 Hz), 128.9 (q, $^{2}J_{C\text{-}F}$ =30.7 Hz), 124.6, 124.3 (q, $^{1}J_{C\text{-}F}$ =273 Hz), 124.2, 124.1, 123.5, 123.0, 120.5, 120.4, 118.9, 115.8, 47.8, 43.66, 21.4. HRMS (ESI) *m/z* calculated for C^{+} ($C_{14}H_{15}N_3F_3{}^{195}Pt$) = 477.0866, found = 477.0858; A^{-} ($C_{14}H_{10}N_3{}^{195}Pt$) = 415.0523, found = 415.0528.

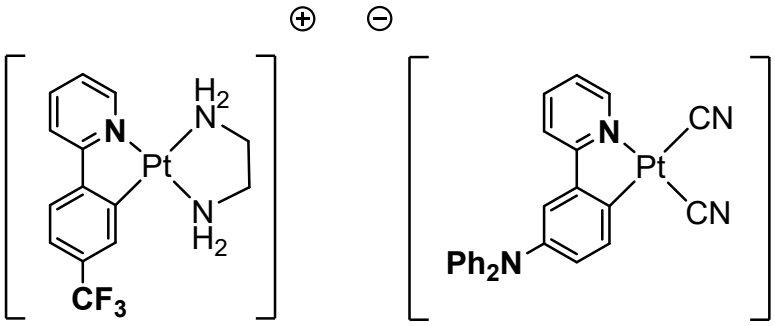
Soft Salt S3



Synthesized using general procedure **E** from **C1** (20 mg, 0.039 mmol, 1.1 eq.), **A4** (29 mg, 0.035 mmol, 1 eq.). Yellow solid (35 mg, 94 %).

^{1}H NMR (300 MHz, DMSO) δ 9.16 (d, *J* = 5.7 Hz, 1H), 8.66 (d, *J* = 5.8 Hz, 1H), 8.20 (d, *J* = 4.5 Hz, 2H), 8.11 – 7.76 (m, 4H), 7.75 – 7.63 (m, 2H), 7.61 (d, *J* = 6.2 Hz, 1H), 7.55 – 7.41 (m, 2H), 7.40 – 7.19 (m, 5H), 7.12 – 6.96 (m, 5H), 6.66 – 6.55 (m, 1H), 6.23 (s, 2H), 5.38 (s, 2H), 2.68 (s, 4H). ^{13}C NMR (75 MHz, DMSO) δ 166.7, 164.7, 159.5, 151.9, 151.4, 149.3, 148.6, 147.3, 144.7, 143.8, 141.5, 140.4, 139.3, 133.0, 129.7 (q, $^{3}J_{C\text{-}F}$=3.75 Hz), 129.4, 129.0 (q, $^{2}J_{C\text{-}F}$=30.3Hz), 124.9, 124.6 (q, $^{1}J_{C\text{-}F}$ = 252.1 Hz), 124.6, 124.1, 123.8, 122.7, 122.6, 120.6, 120.4, 119.3, 118.9, 115.2, 47.8, 43.7. HRMS (ESI) *m/z* calculated for C^{+} ($C_{14}H_{13}N_3F_3{}^{195}Pt$) = 477.0866, found = 477.0858; A^{-} ($C_{25}H_{17}N_4{}^{195}Pt$) = 568.1101, found = 568.1106.

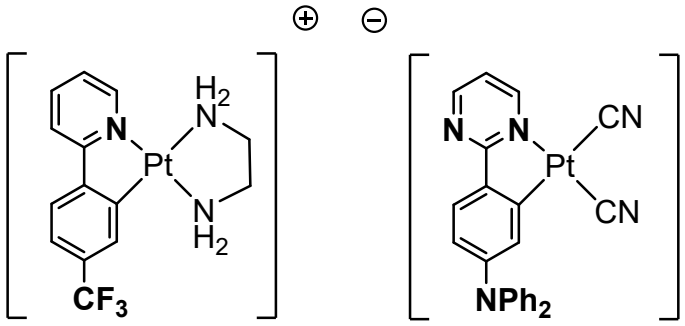
Soft Salt S4



Synthesized using general procedure **E** from **C1** (30 mg, 0.059 mmol, 1.1 eq.), **A7** (43 mg, 0.053 mmol, 1 eq.). Yellow solid (48 mg, 86 %).

^{1}H NMR (300 MHz, DMSO) δ 9.31 – 9.12 (m, 1H), 8.79 – 8.58 (m, 1H), 8.29 – 8.13 (m, 2H), 8.05 – 7.78 (m, 4H), 7.65 – 7.56 (m, 1H), 7.52 – 7.40 (m, 3H), 7.40 – 7.34 (m, 1H), 7.30 – 7.16 (m, 4H), 7.12 – 6.79 (m, 7H), 6.22 (s, 2H), 5.38 (s, 2H), 2.69 (s, 4H). ^{13}C NMR (75 MHz, DMSO) δ 166.4, 164.7, 154.2, 152.2, 151.3, 149.2, 148.2, 147.5, 144.7, 144.0, 143.0, 140.3, 139.6, 139.3, 129.77 (q, $^{3}J_{C\text{-}F}$ =3.75 Hz), 129.4 (q, $^{2}J_{C\text{-}F}$ =38.07 Hz), 129.2, 128.4, 124.9, 124.0, 123.9, 123.1 (q, $^{1}J_{C\text{-}F}$ = 237 Hz), 122.2, 121.8, 120.5, 120.3, 120.3, 119.4, 115.1, 47.8, 43.7. HRMS (ESI) *m/z* calculated for C^{+} ($C_{14}H_{15}N_3F_3{}^{195}Pt$) = 477.0866, found = 477.0860; A^{-} ($C_{25}H_{17}N_4{}^{195}Pt$) = 568.1101, found =568.1107.

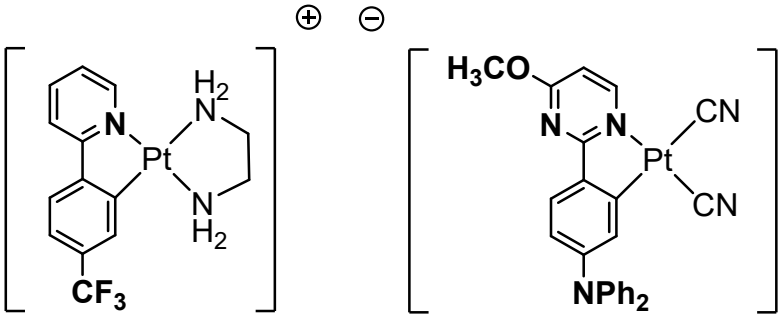
Soft Salt S5



Synthesized using general procedure **E** from **C1** (30 mg, 0.059 mmol, 1.1 eq.), **A6** (43 mg, 0.053 mmol, 1 eq.). Yellow solid (43 mg, 77 %).

^{1}H NMR (300 MHz, DMSO) δ 9.26 (d, *J* = 5.7 Hz, 1H), 8.94 (s, 1H), 8.66 (s, 1H), 8.19 (s, 2H), 7.97 – 7.89 (m, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 5.8 Hz, 2H), 7.55 – 7.42 (m, 3H), 7.39 – 7.27 (m, 5H), 7.09 – 7.01 (m, 5H), 6.61 (d, *J* = 8.6 Hz, 1H), 6.21 (s, 2H), 5.37 (s, 2H), 2.68 (s, 4H). ^{13}C NMR (75 MHz, DMSO) δ 174.2, 164.7, 158.9, 158.7, 158.3, 151.3, 150.5, 149.2, 147.0, 144.7, 142.3, 140.3, 137.5, 131.3, 129.4, 129.4 (q, $^{2}J_{C\text{-}F}$ =31.4 Hz), 129.2 (q, $^{3}J_{C\text{-}F}$ =3.75 Hz), 127.8, 126.3, 124.6, 124.5, 123.3, 122.5, 122.3 (q, $^{1}J_{C\text{-}F}$ =262.1 Hz), 120.5, 120.3, 118.6, 118.4, 47.8, 43.7.* HRMS (ESI) *m/z* calculated for C^{+} ($C_{14}H_{15}N_3F_3{}^{195}Pt$) = 477.0866, found = 477.0860; A^{-} ($C_{24}H_{16}N_5{}^{195}Pt$) = 569.1054, found =569.1062.

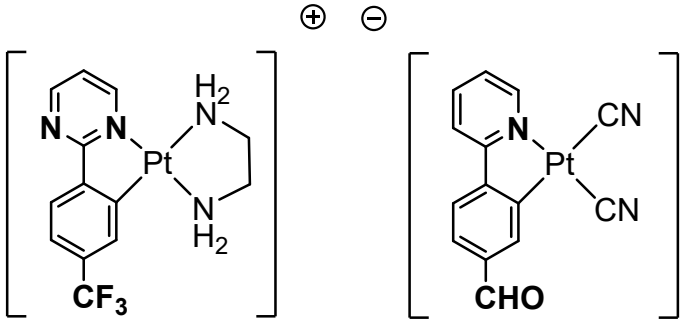
Soft Salt S6



Synthesized using general procedure **E** from **C1** (30 mg, 0.059 mmol, 1.1 eq.), **A5** (45 mg, 0.053 mmol, 1 eq.). Yellow solid (30 mg, 52 %).

^{1}H NMR (300 MHz, DMSO) δ 9.16 (d, *J* = 5.7 Hz, 1H), 8.66 (d, *J* = 5.9 Hz, 1H), 8.19 (d, *J* = 4.5 Hz, 2H), 7.99 (t, *J* = 7.7 Hz, 1H), 7.91 (t, *J* = 9.8 Hz, 2H), 7.65 (s, 1H), 7.60 (d, *J* = 6.0 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.34 – 7.23 (m, 5H), 7.04 – 6.97 (m, 5H), 6.60 (d, *J* = 8.3 Hz, 1H), 6.22 (s, 2H), 5.37 (s, 2H), 3.50 (s, 3H), 2.68 (s, 4H). ^{13}C NMR (75 MHz, DMSO) δ 167.2, 165.2, 156.0, 152.4, 151.8, 149.7, 149.0, 147.8, 145.2, 144.2, 142.0, 140.8, 139.7, 133.5, 132.7, 130.1 (q, $^{3}J_{C\text{-}F}$ =3.9 Hz), 129.8, 125.3, 124.8 (q, $^{2}J_{C\text{-}F}$ = 40 Hz), 124.2, 123.1, 123.0, 121.2 (q, $^{1}J_{C\text{-}F}$ =278.4 Hz), 121.0, 120.8, 119.7, 115.5, 100.4, 85.0, 48.3, 44.1.* HRMS (ESI) *m/z* calculated for C^{+} ($C_{14}H_{15}N_3F_3{}^{195}Pt$) = 477.0866, found = 477.0859; A^{-} ($C_{25}H_{18}N_5O^{195}Pt$) = 599.1159, found =599.1166.

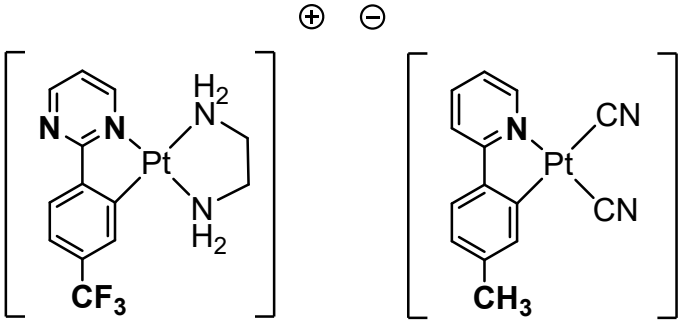
Soft Salt S7



Synthesized using general procedure **E** from **C2** (20 mg, 0.039 mmol, 1.1 eq.), **A1** (24 mg, 0.036 mmol, 1 eq.). Red solid (23 mg, 48 %).

^{1}H NMR (300 MHz, DMSO) δ 9.95 (s, 1H), 9.28 (s, 1H), 9.12 (s, 1H), 8.98 (s, 1H), 8.34 (d, *J* = 23.1 Hz, 1H), 8.17 (s, 2H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 27.5 Hz, 5H), 6.34 (s, 2H), 5.38 (s, 2H), 2.70 (s, 4H). ^{13}C NMR (75 MHz, DMSO) δ 194.2, 173.3, 165.9, 163.3, 159.9, 158.9, 158.9, 158.5, 153.1, 153.0, 146.4, 144.6, 140.4, 140.0, 139.4, 136.7, 131.3 (q, $^{2}J_{C\text{-}F}$ =31 Hz), 130.1 (q, $^{3}J_{C\text{-}F}$ =3.37 Hz), 127.2, 125.5, 125.4, 122.6 (q, $^{1}J_{C\text{-}F}$ = 245.01 Hz) 121.2, 121.1, 120.8, 48.3, 44.2.* HRMS (ESI) *m/z* calculated for C^{+} ($C_{13}H_{14}N_4F_3{}^{195}Pt$) = 478.0818, found = 478.0812; A^{-} ($C_{14}H_8N_3O^{195}Pt$) = 429.0315, found = 429.0320.

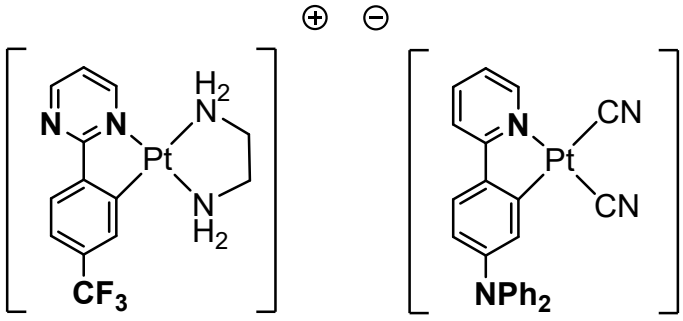
Soft Salt S8



Synthesized using general procedure **E** from **C2** (20 mg, 0.039 mmol, 1.1 eq.), **A1** (23 mg, 0.035 mmol, 1 eq.). Red solid (25 mg, 79 %).

^{1}H NMR (300 MHz, DMSO) δ 9.25 – 9.08 (m, 2H), 8.99 (d, *J* = 5.8 Hz, 1H), 8.08 – 7.88 (m, 3H), 7.78 – 7.44 (m, 5H), 7.31 (t, *J* = 6.5 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.35 (s, 2H), 5.40 (s, 2H), 2.70 (s, 4H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 173.3, 167.8, 159.9, 158.9, 158.4, 152.4, 146.4, 144.9, 144.7, 144.5, 139.8, 139.5, 139.2, 131.3 (q, $^{2}J_{C\text{-}F}$ =31 Hz), 130.2 (q, $^{3}J_{C\text{-}F}$ =3.9l Hz), 127.2, 124.7 (q, $^{1}J_{C\text{-}F}$ =271.6 Hz) 124.6, 123.9, 123.5, 121.0, 120.8, 119.3, 116.2, 48.3, 44.2, 21.9. HRMS (ESI) *m/z* calculated for C^{+} ($C_{13}H_{14}N_4F_3{}^{195}Pt$) = 478.0818, found = 478.0814; A^{-} ($C_{14}H_{10}N_3{}^{195}Pt$) = 415.0523, found = 415.0528.

Soft Salt S9



Synthesized using general procedure **E** from **C2** (20 mg, 0.039 mmol, 1.1 eq), **A4** (29 mg, 0.035 mmol, 1 eq). Yellow solid (29 mg, 78 %).

^{1}H NMR (300 MHz, DMSO) δ 9.30 – 9.07 (m, 2H), 9.07 – 8.88 (m, 1H), 8.12 – 7.82 (m, 3H), 7.77 – 7.44 (m, 5H), 7.42 – 7.19 (m, 5H), 7.13 – 6.87 (m, 6H), 6.67 – 6.51 (m, 1H), 6.46 – 6.19 (m, 2H), 5.38 (s, 2H), 2.69 (s, 4H). ^{13}C NMR (75 MHz, DMSO) δ 172.8, 166.7, 159.5, 159.4, 158.4, 151.9, 148.5, 147.3, 145.9, 144.2, 143.7, 141.5, 139.2, 133.0, 130.8 (q, $^{2}J_{C\text{-}F}$ =30.2 Hz) 129.7 (q, $^{3}J_{C\text{-}F}$ =3.9 Hz), 129.3, 126.7, 124.8, 124.1, 124.2 (q, $^{1}J_{C\text{-}F}$ =271.5 Hz), 123.7, 122.6, 122.5, 120.6, 120.4, 119.2, 118.8, 115.1, 47.8, 43.7. HRMS (ESI) *m/z* calculated for C^{+} ($C_{13}H_{14}N_4F_3{}^{195}Pt$) = 478.0818, found = 478.0814; A^{-} ($C_{14}H_{10}N_3{}^{195}Pt$) = 568.1101, found = 568.1109

5- ^{1}H and ^{13}C NMR Spectra

A- L1-L8 ligands

L1

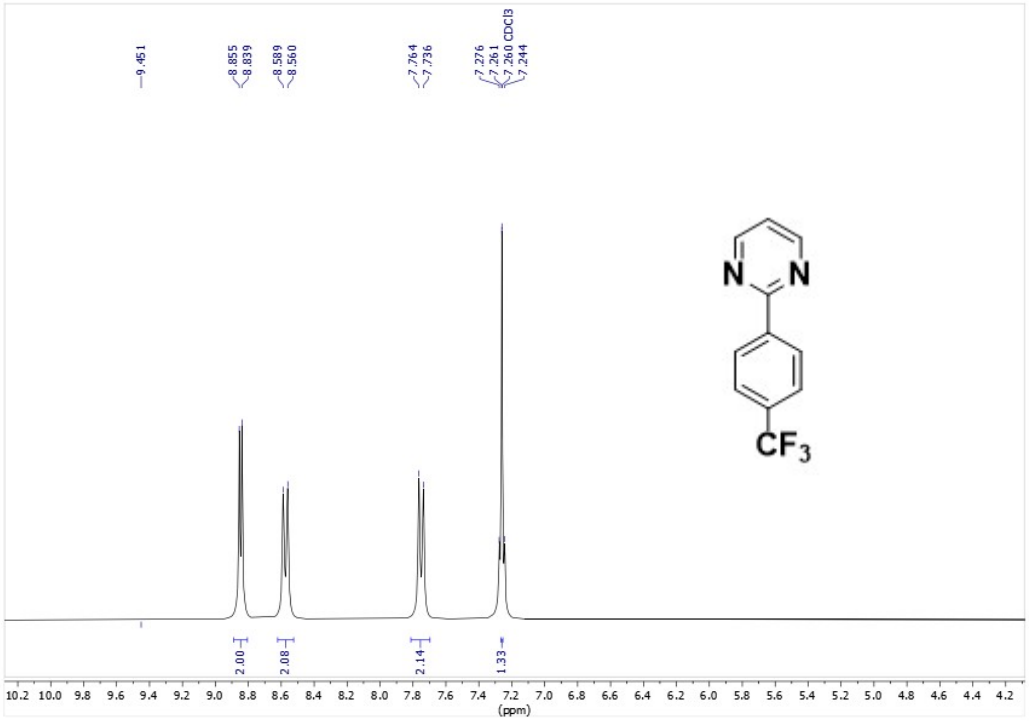


Figure S1 *: ^{1}H NMR spectrum for ligand **L1** in $CDCl_3$*

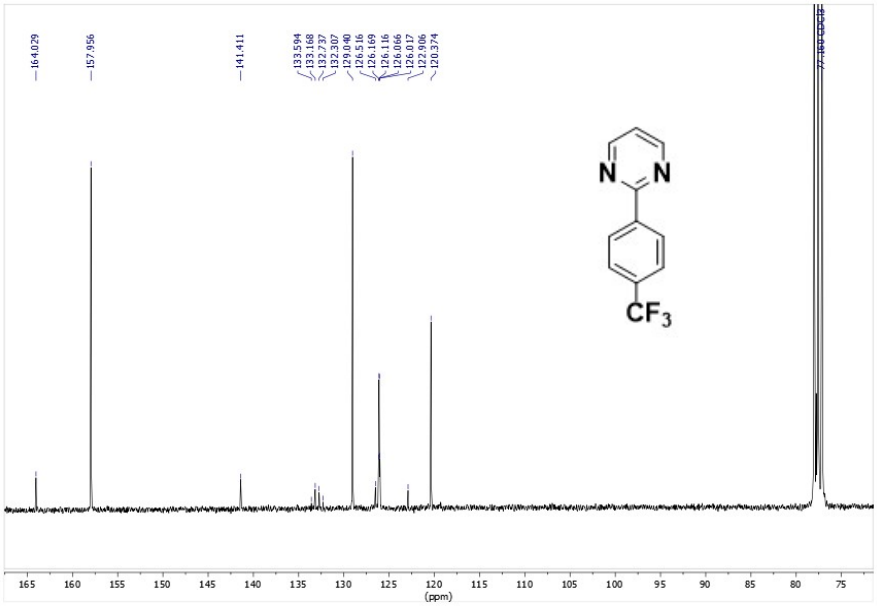


Figure S2 : *^{13}C NMR spectrum for ligand **L1** in $CDCl_3$*

L2

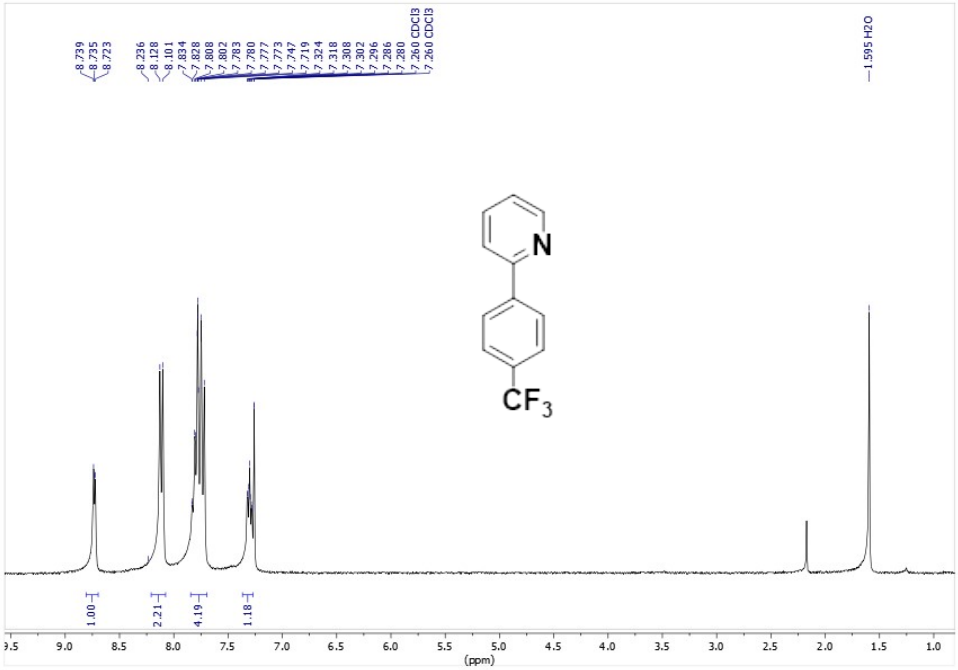


Figure S3 : ^1H NMR spectrum for ligand **L2** in $CDCl_3$

L3

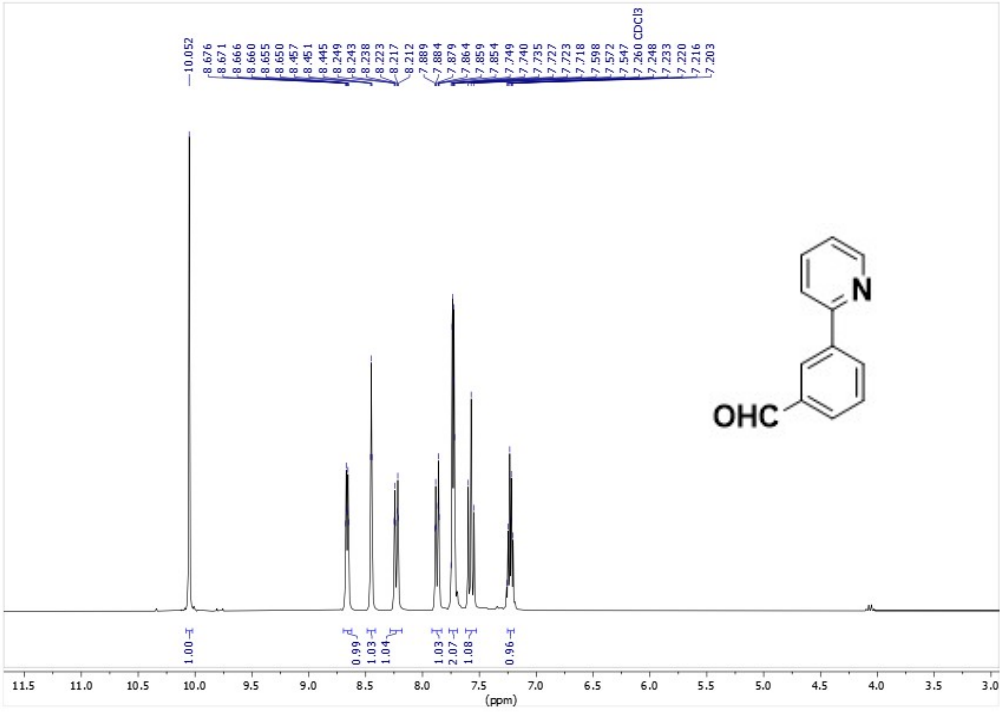


Figure S4 : ^1H NMR spectrum for ligand **L3** in $CDCl_3$

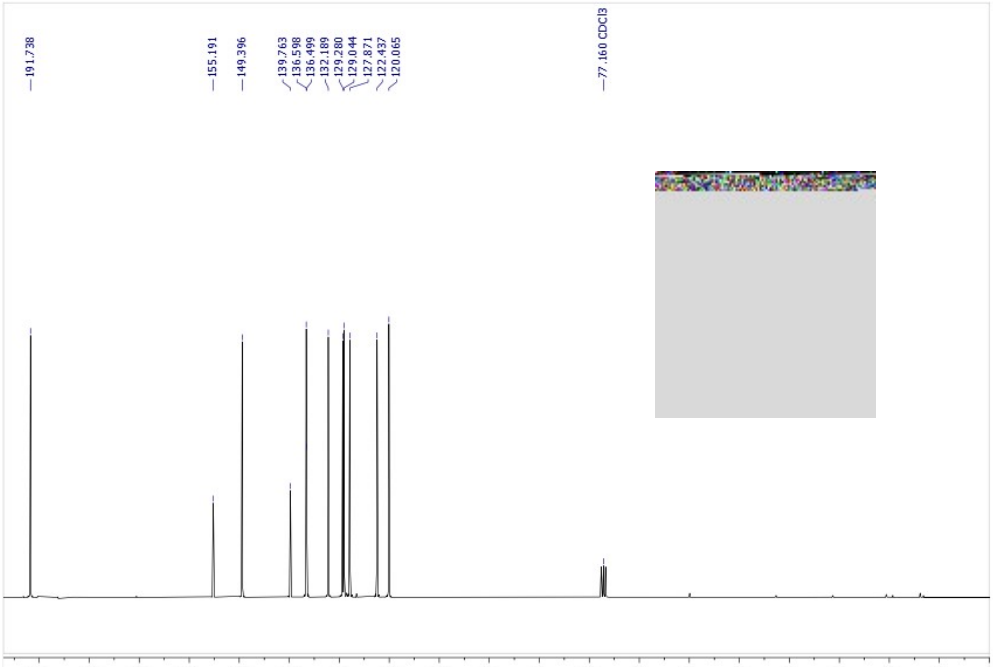


Figure S5 : ^{13}C NMR spectrum for ligand **L3** in $CDCl_3$

L4

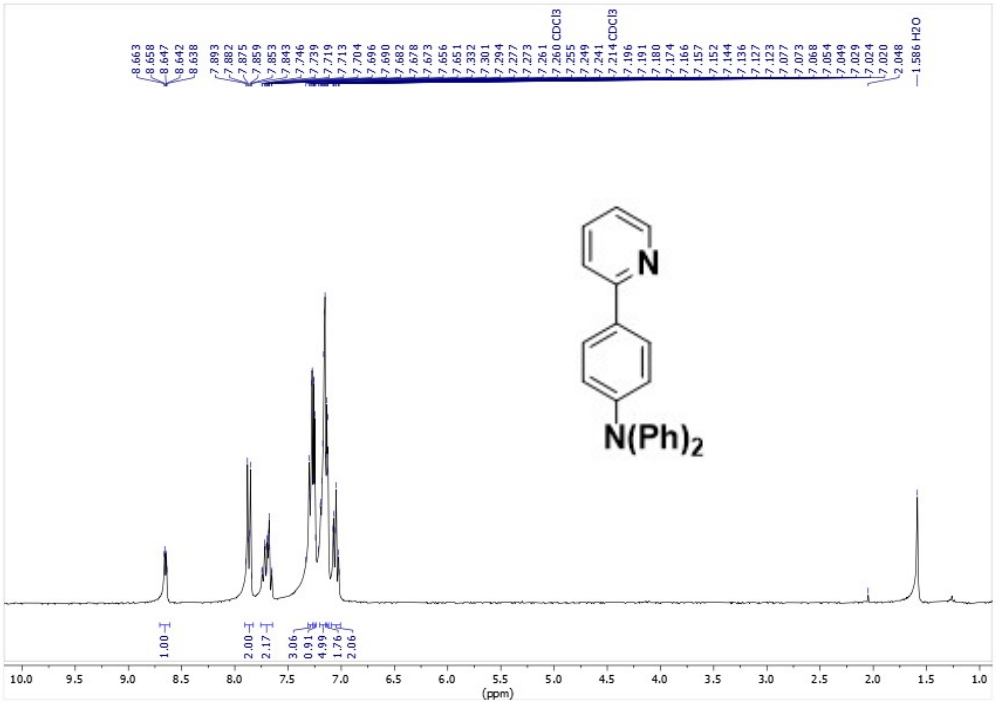


Figure S6 : ^{1}H NMR spectrum for ligand **L4** in $CDCl_3$

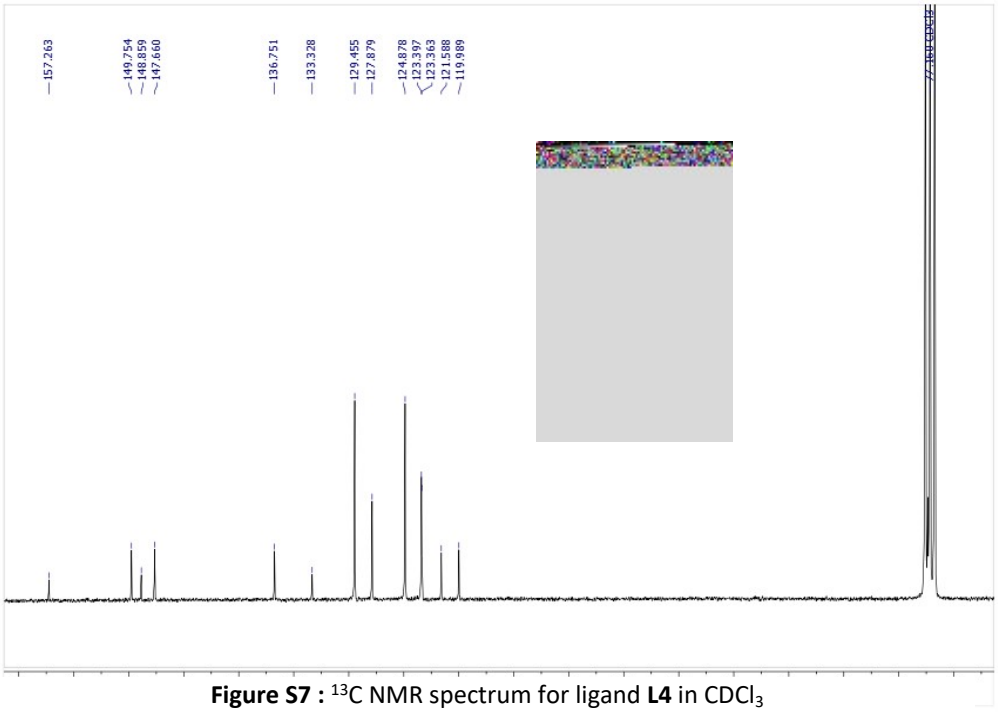


Figure S7 : ^{13}C NMR spectrum for ligand **L4** in $CDCl_3$

L5

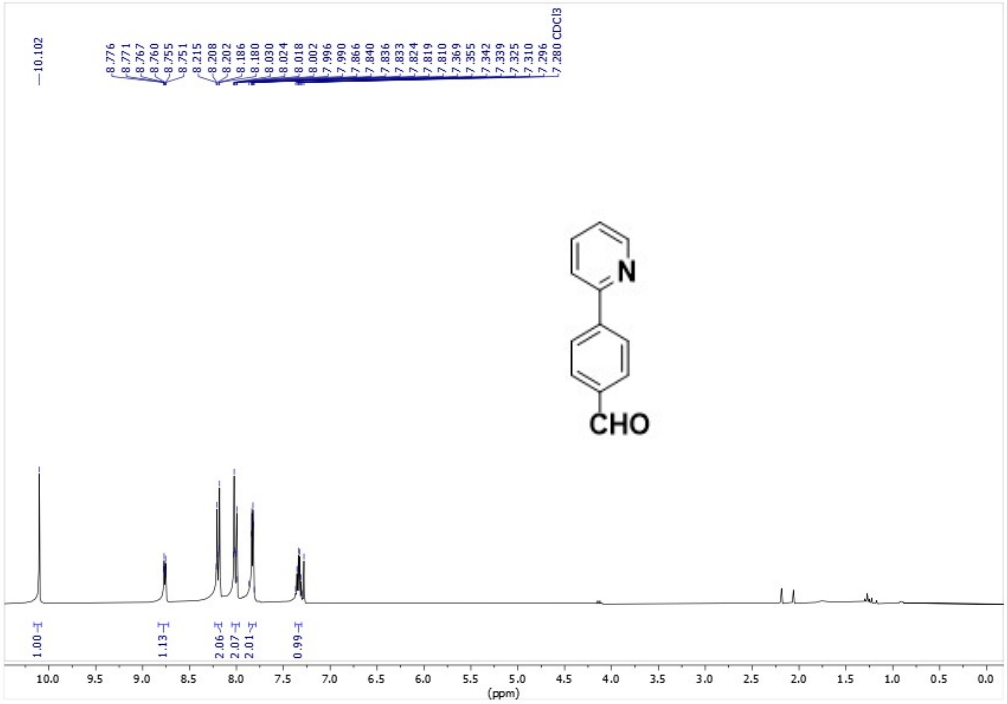


Figure S8 : ^{1}H NMR spectrum for ligand **L5** in $CDCl_3$

L6

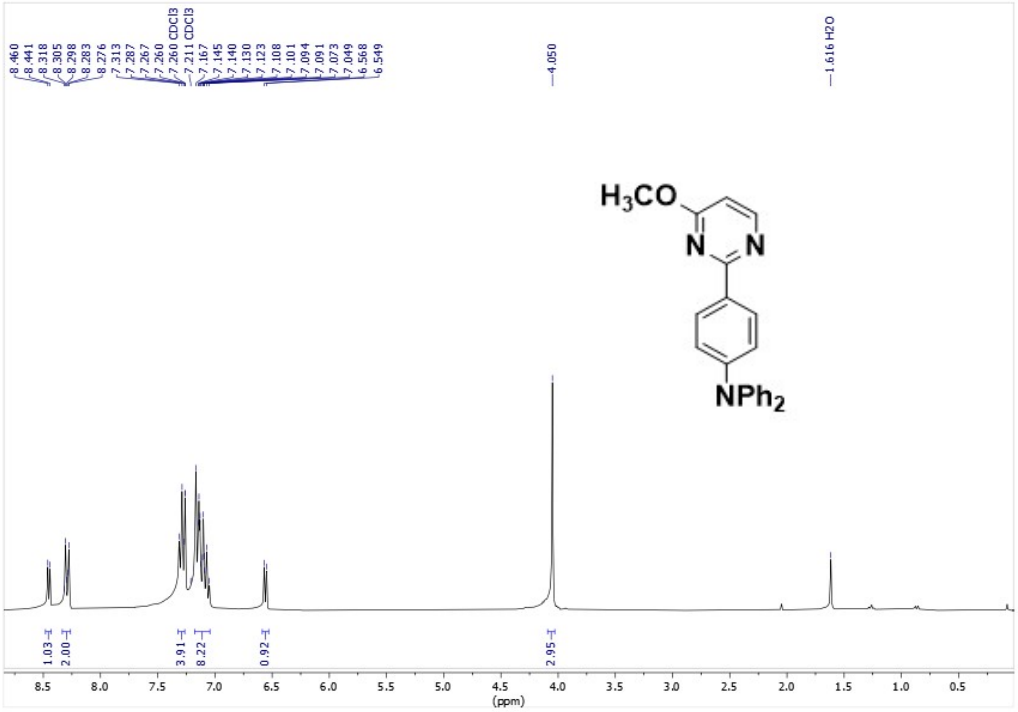


Figure S9 : ^{1}H NMR spectrum for ligand **L6** in $CDCl_3$

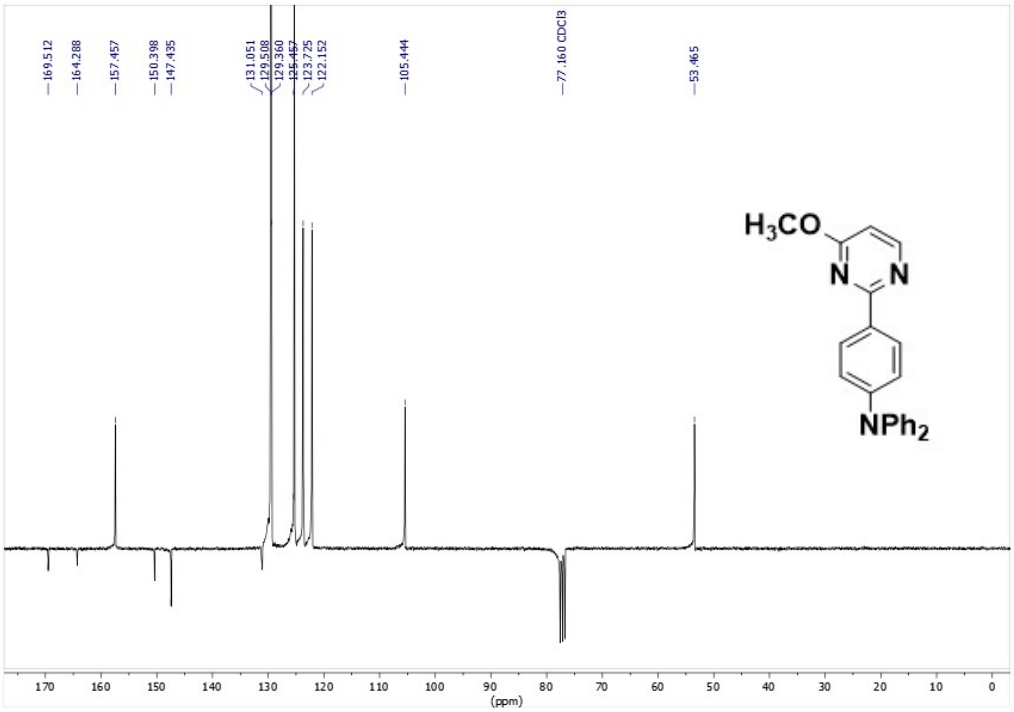


Figure S10 : J-mod ^{13}C NMR spectrum for ligand **L6** in $CDCl_3$

L7

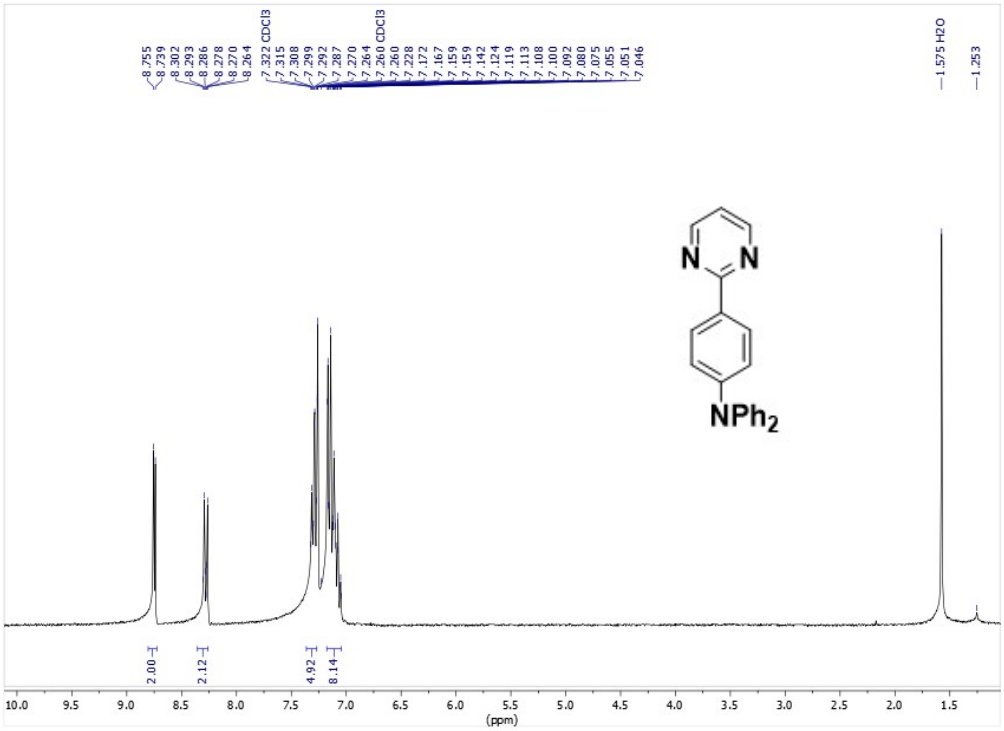


Figure S11 : ^{1}H NMR spectrum for ligand **L7** in $CDCl_3$

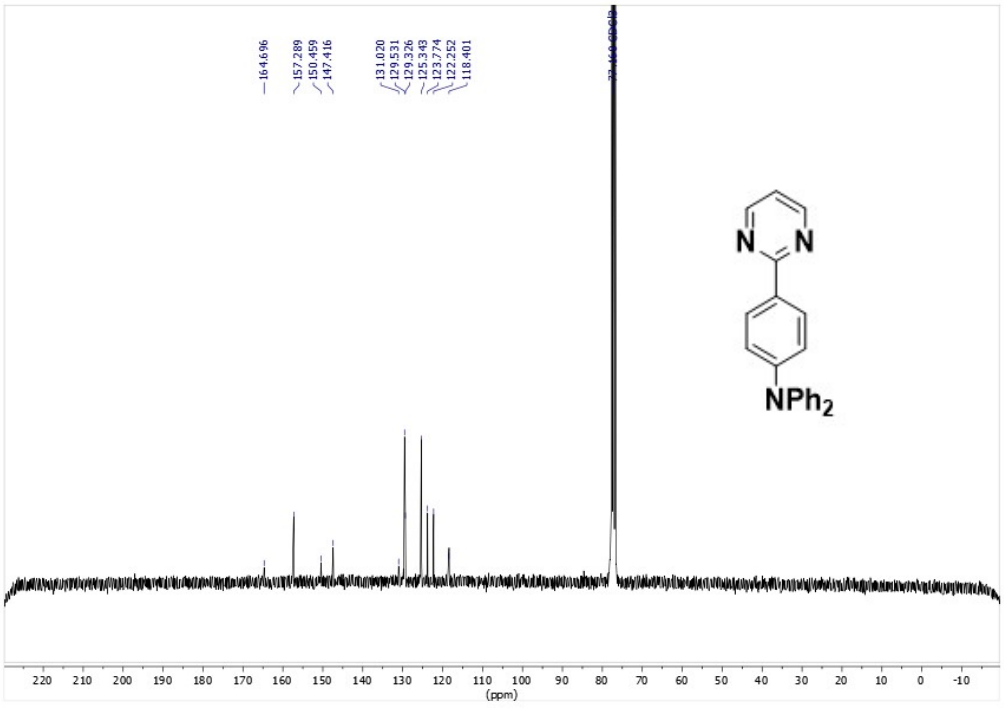


Figure S12 : ^{13}C NMR spectrum for ligand **L7** in $CDCl_3$

L8

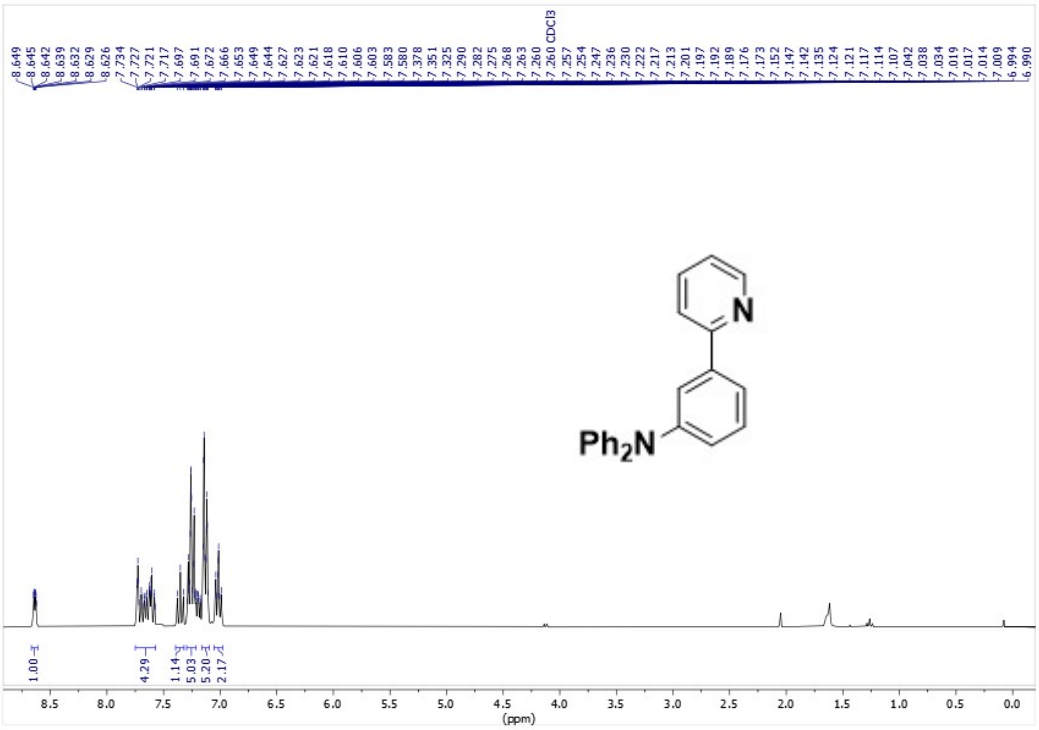


Figure S13 : ^{1}H NMR spectrum for ligand **L8** in $CDCl_3$

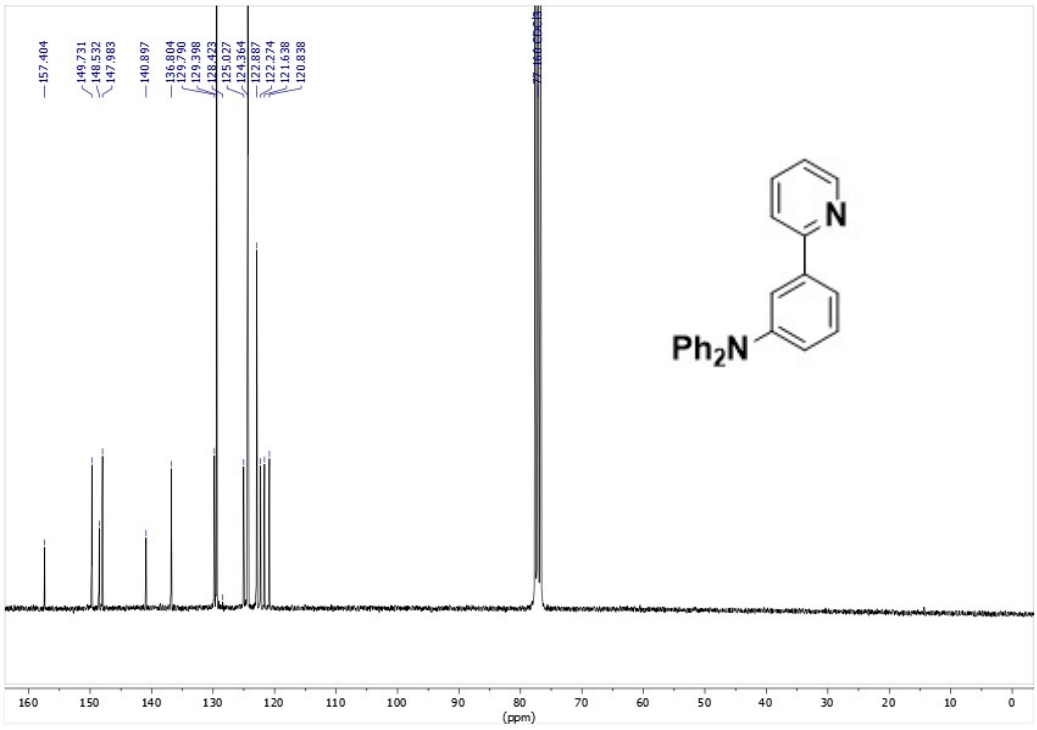


Figure S14 : ^{13}C NMR spectrum for ligand **L8** in $CDCl_3$

B- C1-C2 cationic precursors

C1

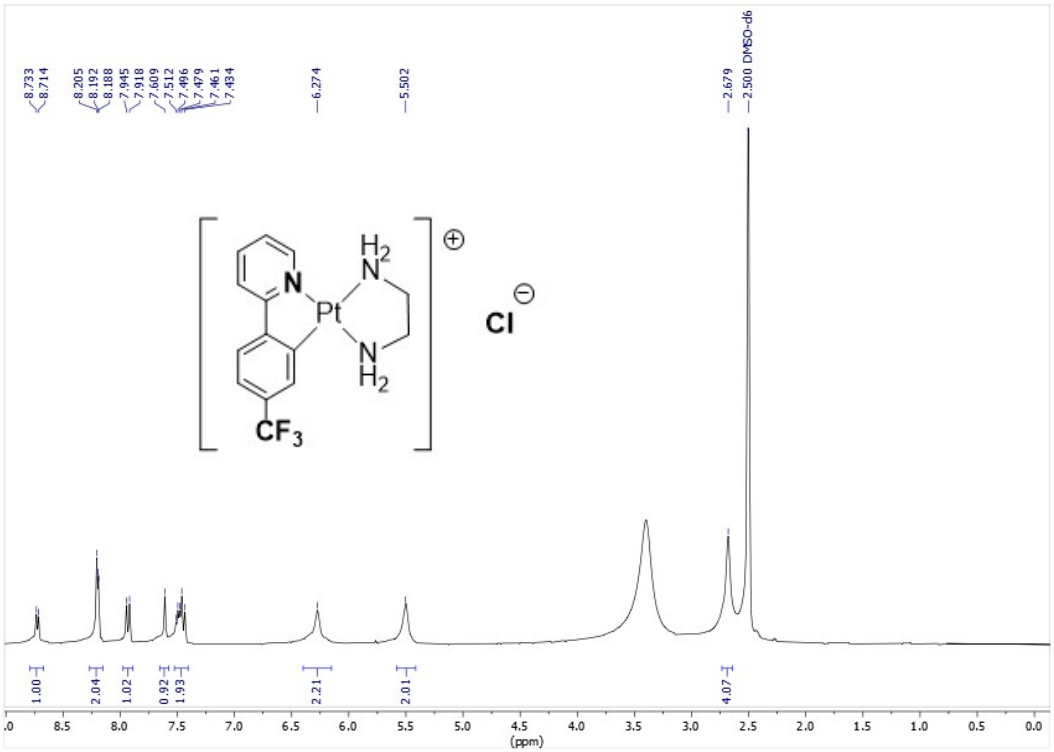


Figure S15 : ^{1}H NMR spectrum for cationic platinum complex **C1** in DMSO-d6

C2

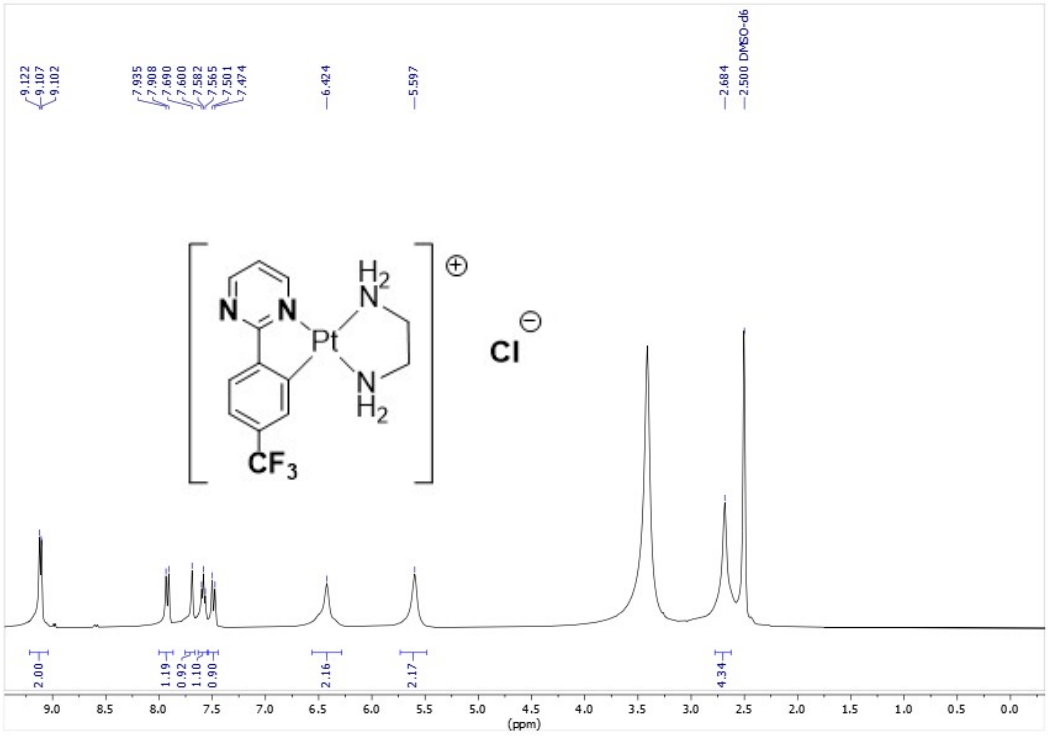


Figure S16 : ^{1}H NMR spectrum for cationic platinum complex **C2** in DMSO-d6

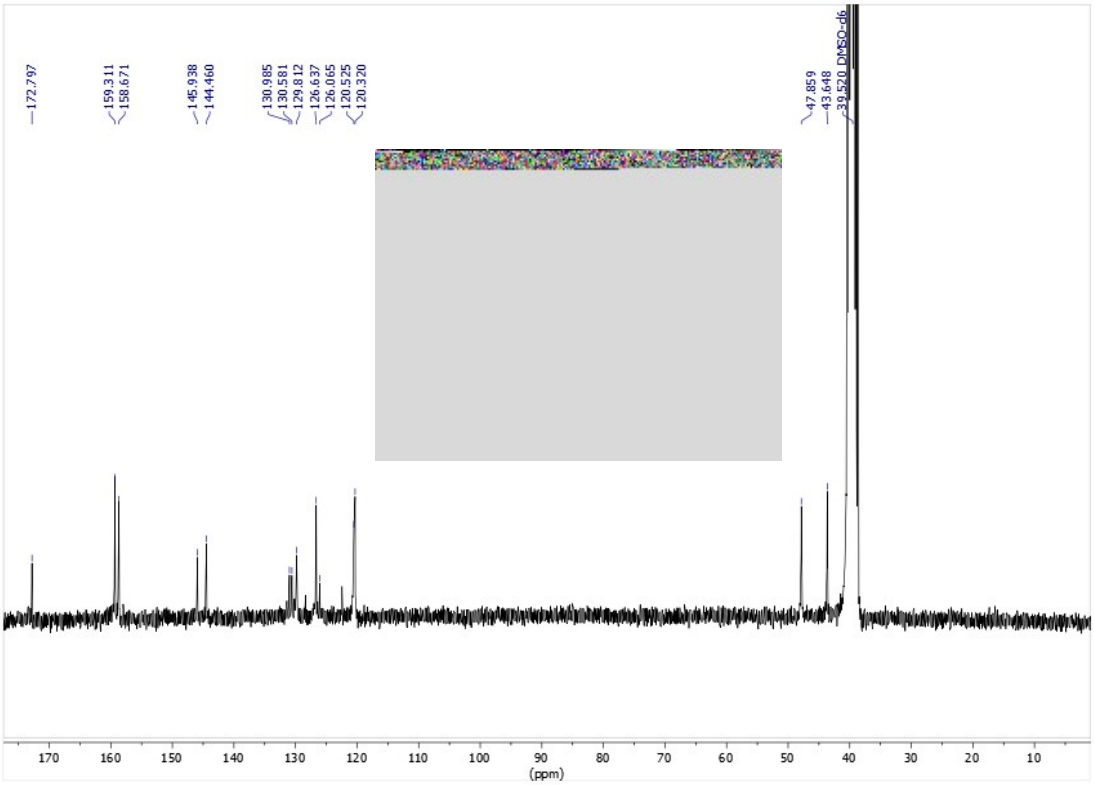


Figure S17 : ^{13}C NMR spectrum for cationic platinum complex **C2** in DMSO-d6

C- A1-A7 anionic precursors

A1

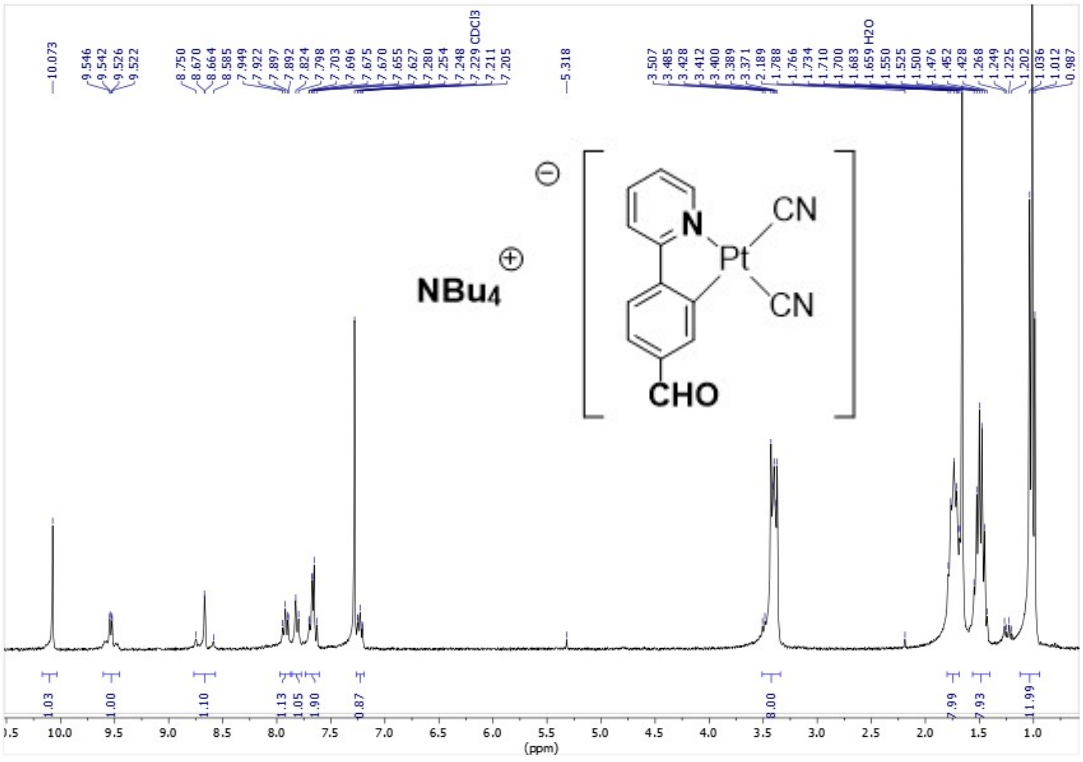


Figure S18 : ^{1}H NMR spectrum for anionic platinum complex **A1** in $CDCl_3$

A2

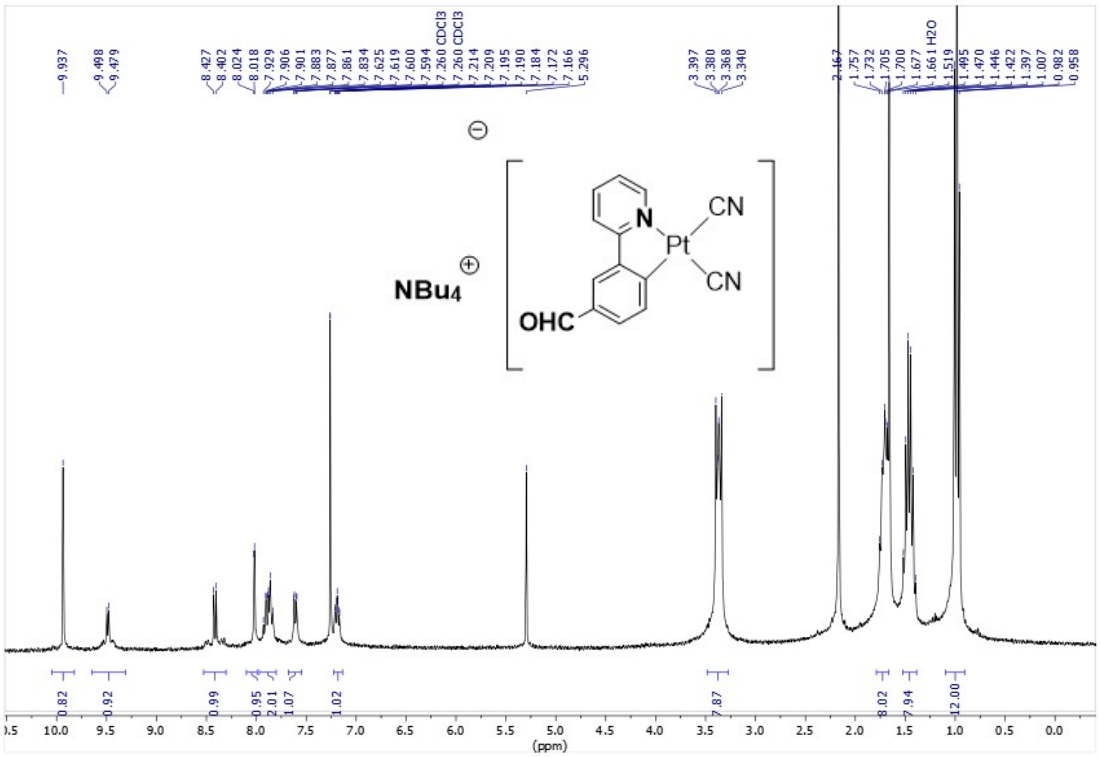


Figure S19 : ^{1}H NMR spectrum for anionic platinum complex **A2** in $CDCl_3$

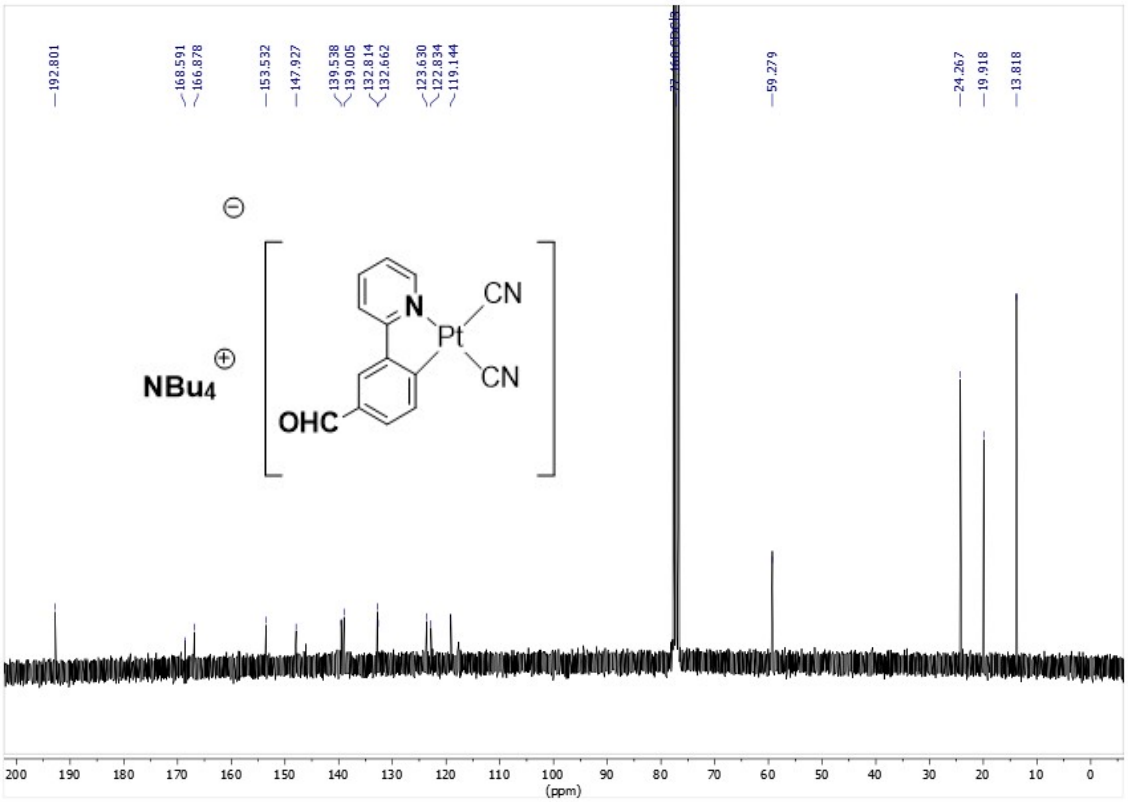


Figure S20 : ^{13}C NMR spectrum for anionic platinum complex **A2** in $CDCl_3$

A3

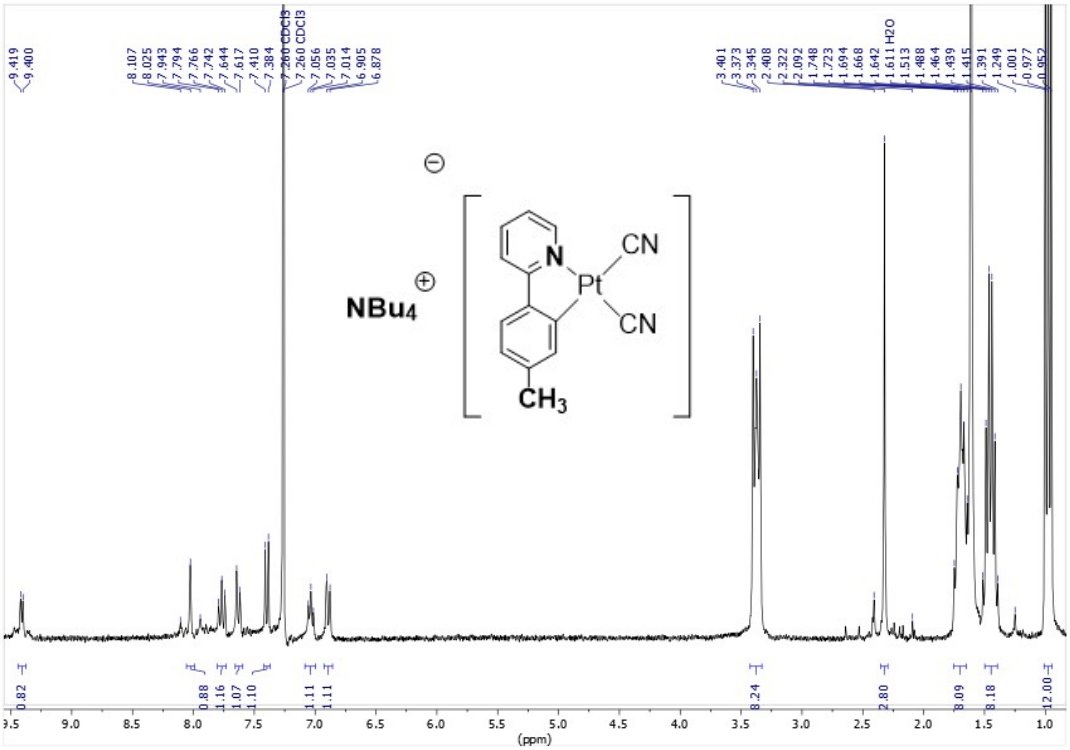


Figure S21 : ^{1}H NMR spectrum for anionic platinum complex **A3** in $CDCl_3$

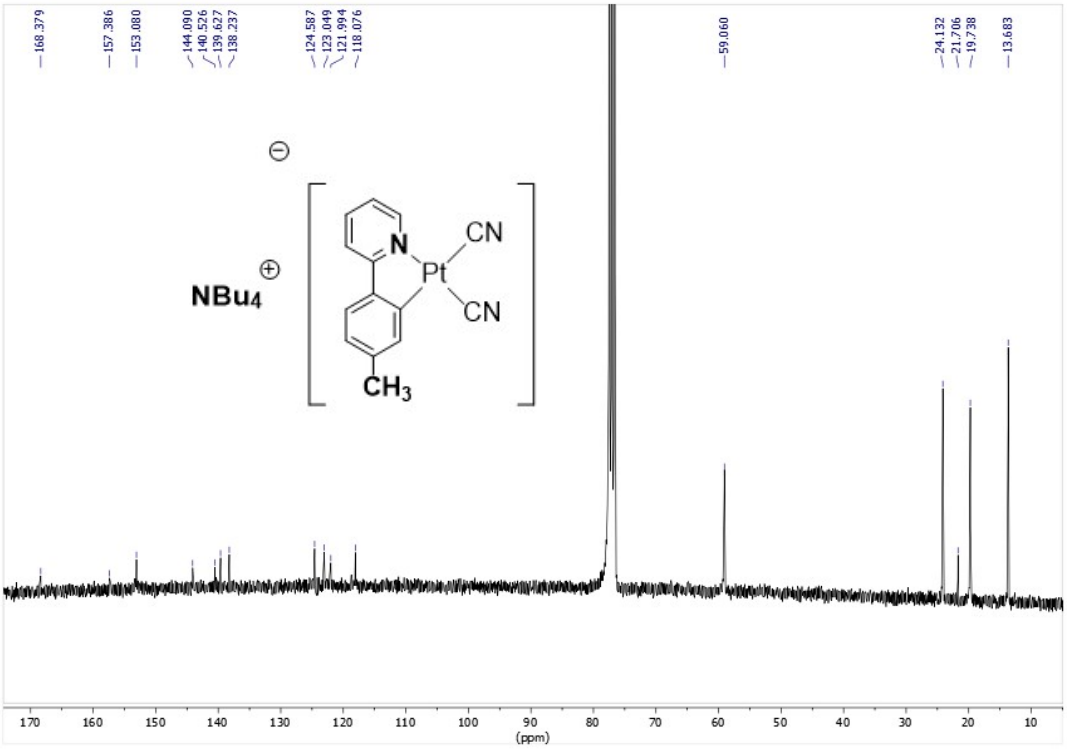


Figure S22 : ^{13}C NMR spectrum for anionic platinum complex **A3** in $CDCl_3$

A4

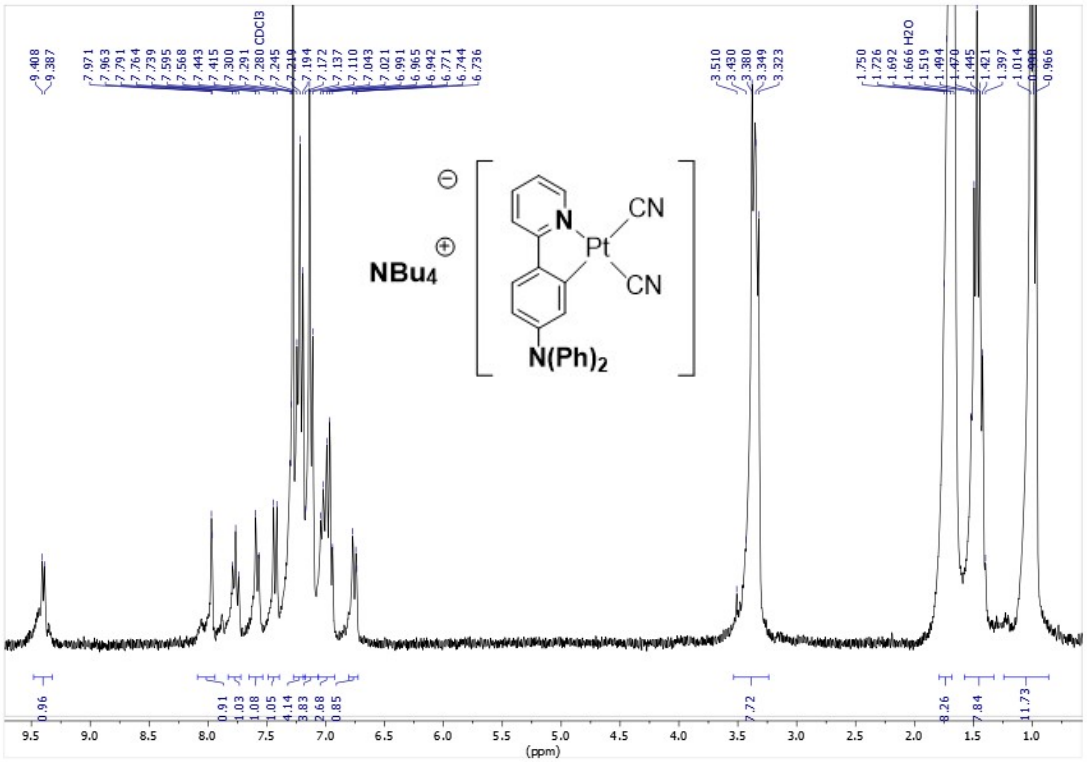


Figure S23 : ^{1}H NMR spectrum for anionic platinum complex **A4** in $CDCl_3$

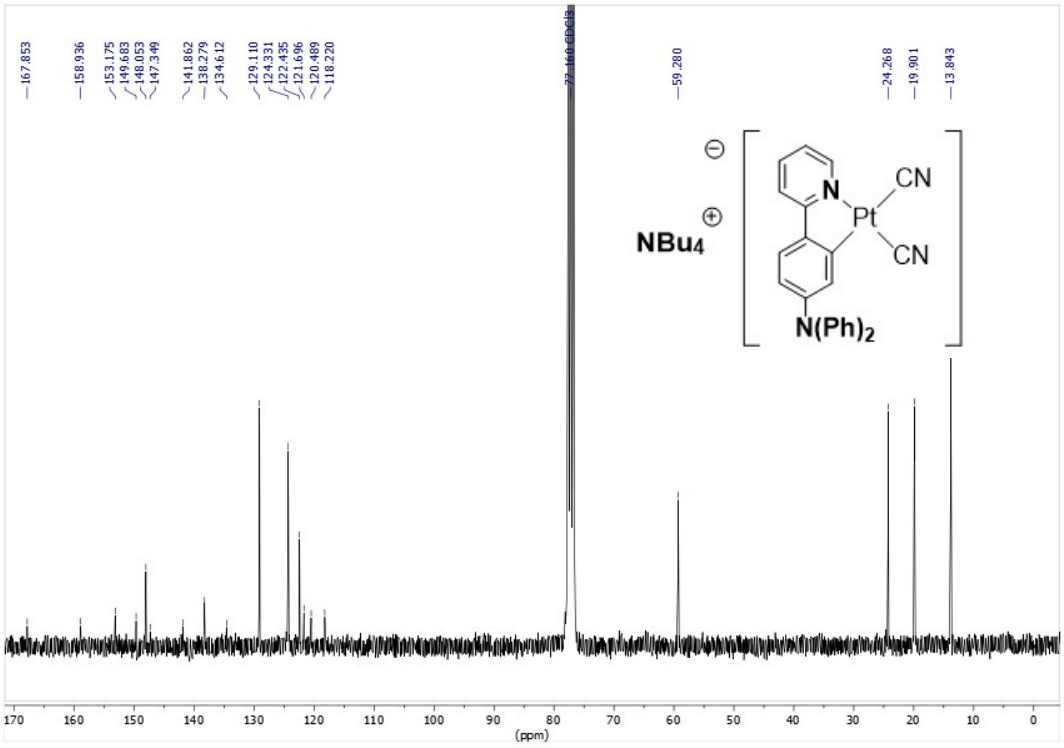


Figure S24 : ^{13}C NMR spectrum for anionic platinum complex **A4** in $CDCl_3$

A5

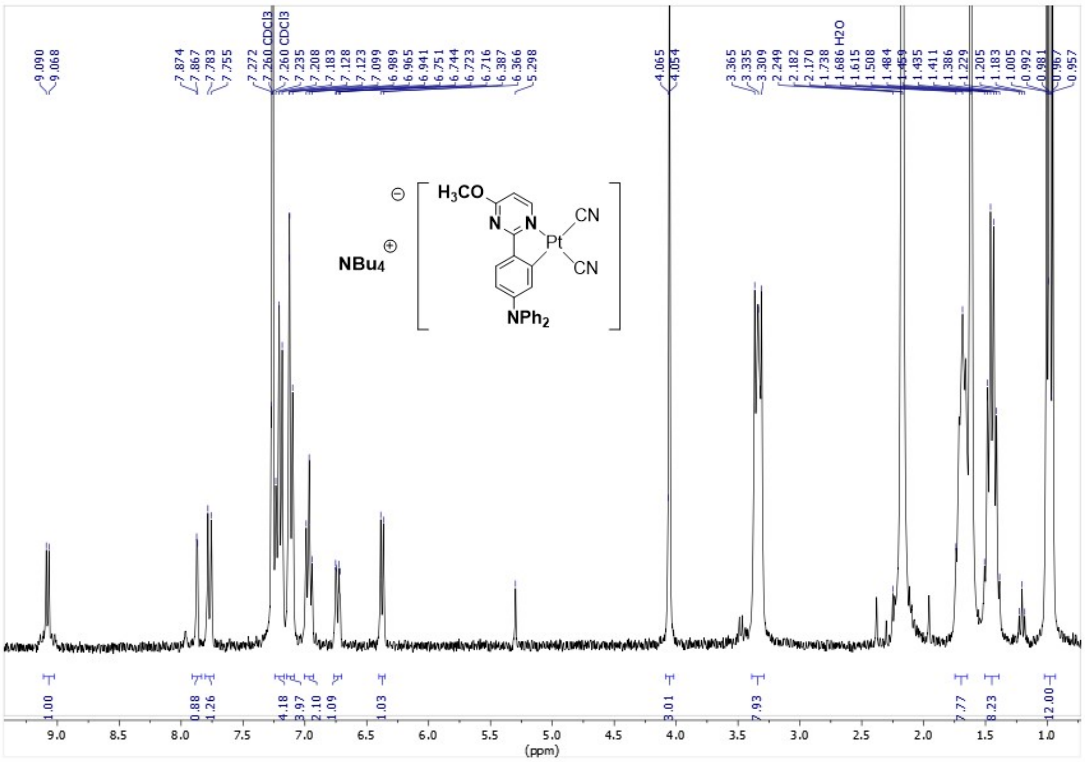


Figure S25 : ^{1}H NMR spectrum for anionic platinum complex **A5** in $CDCl_3$

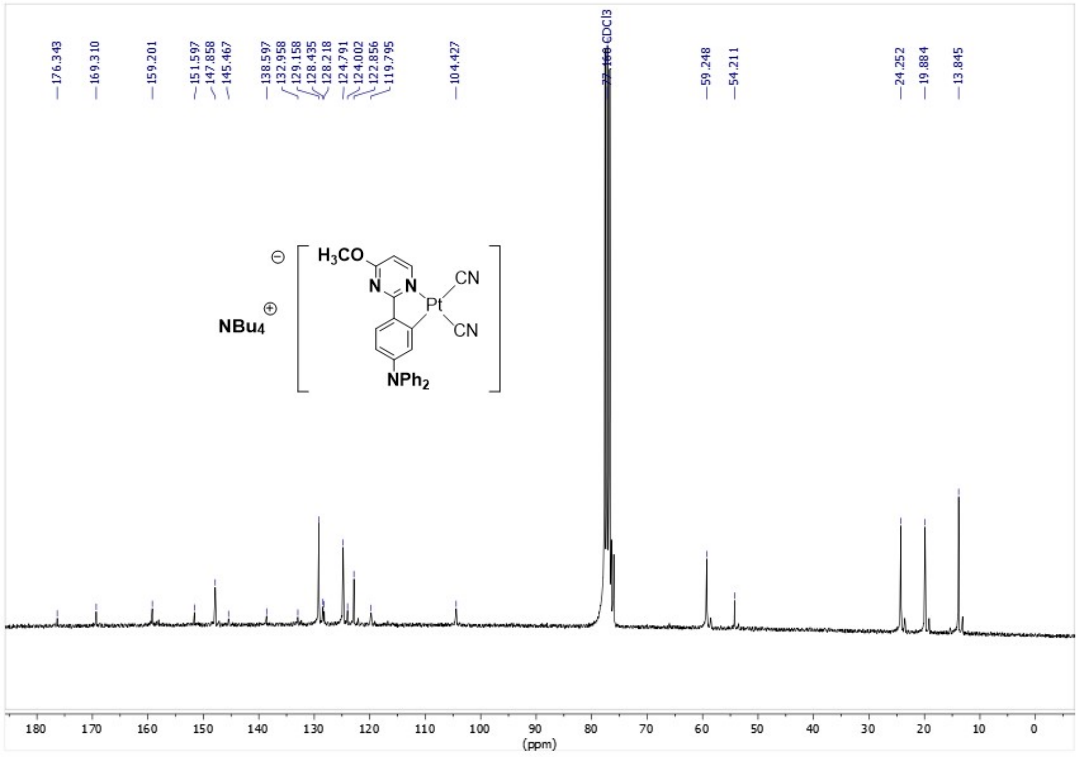


Figure S26 : ^{13}C NMR spectrum for anionic platinum complex **A5** in $CDCl_3$

A6

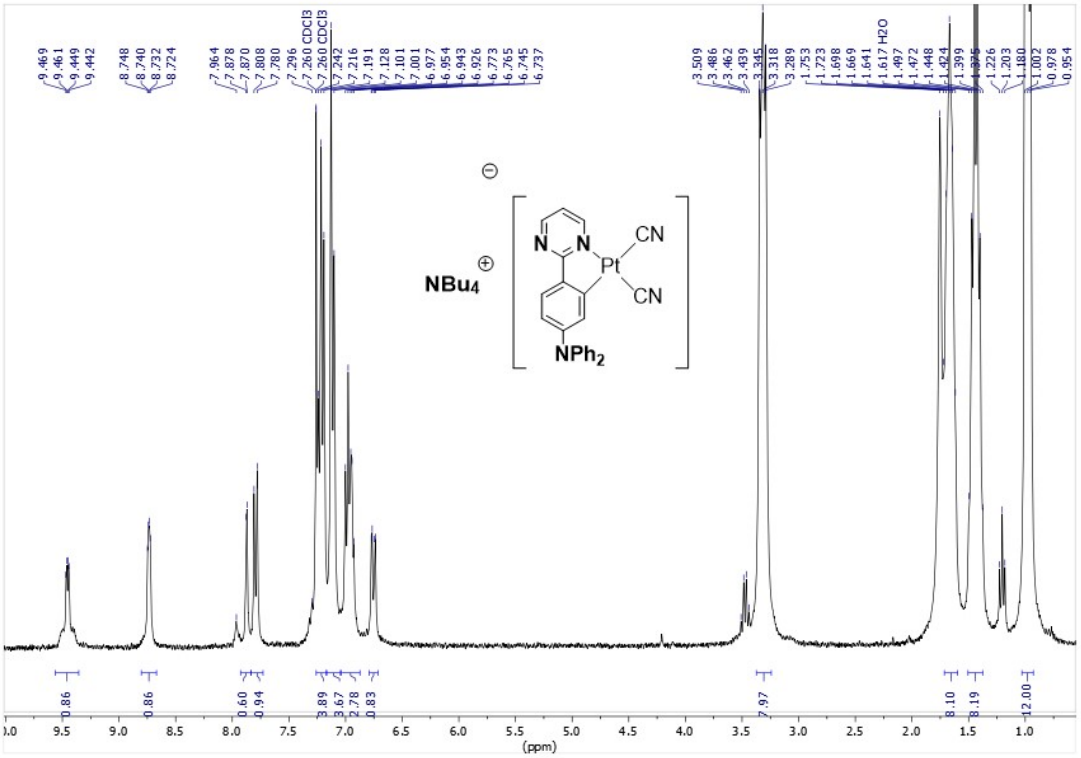


Figure S27 : ^{1}H NMR spectrum for anionic platinum complex **A6** in $CDCl_3$

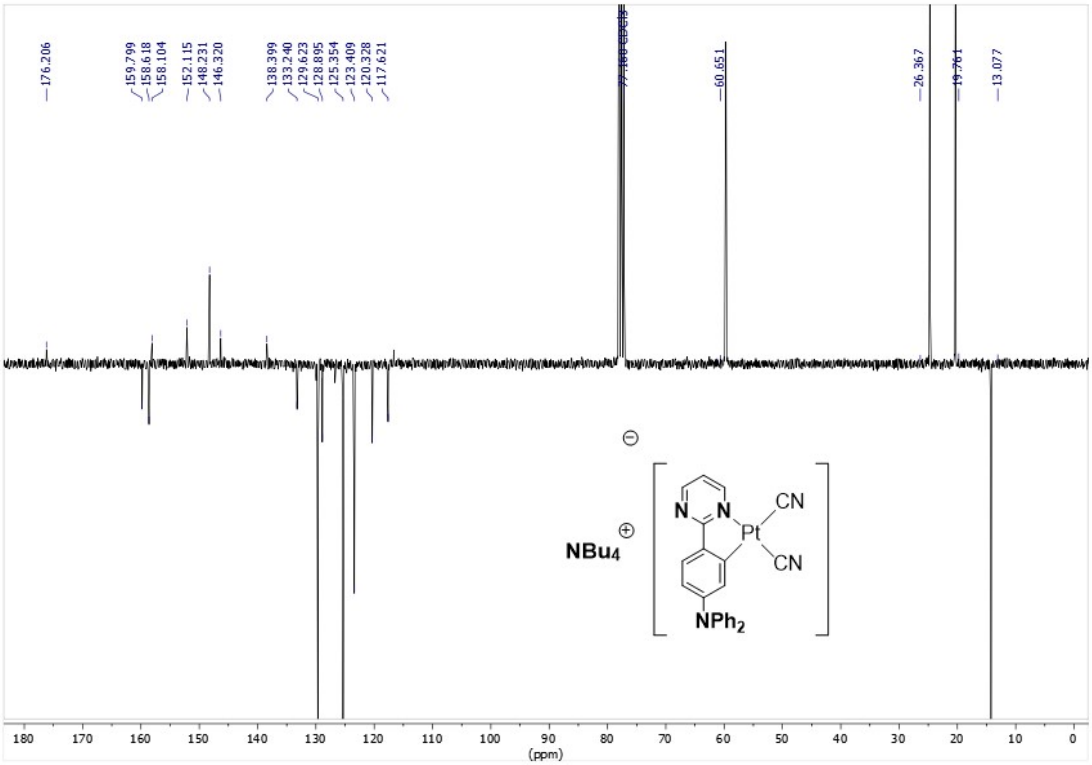


Figure S28 : J-mod ^{13}C NMR spectrum for anionic platinum complex **A6** in $CDCl_3$

A7

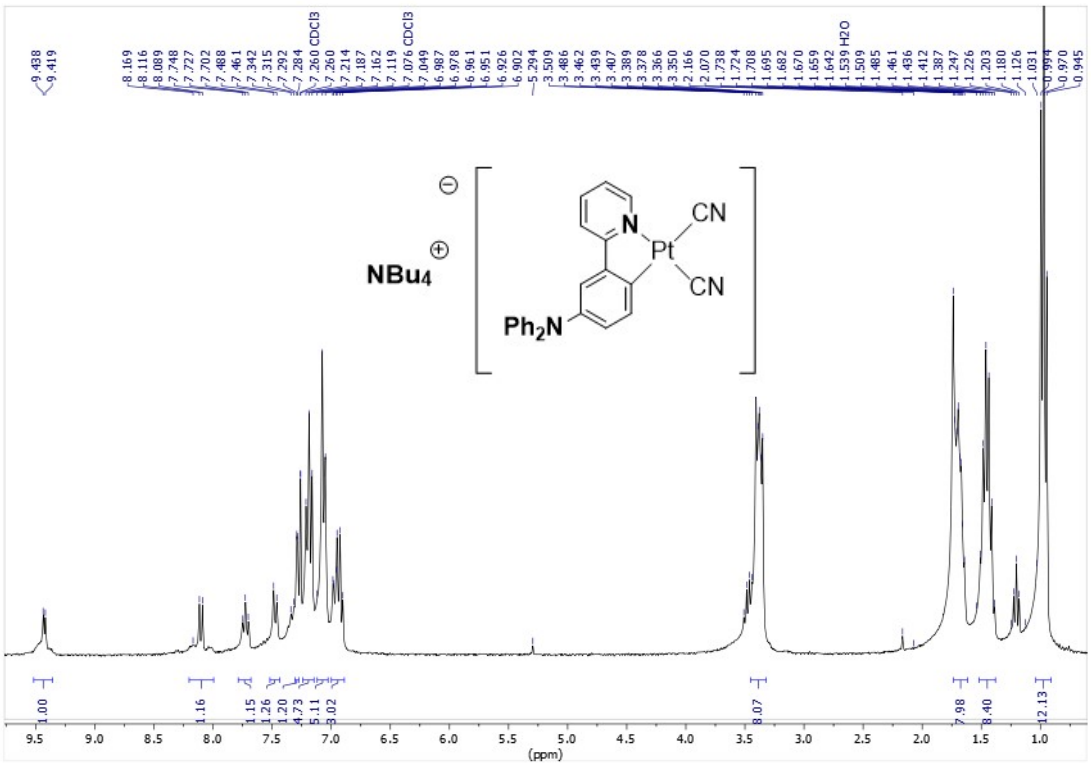


Figure S29 : ^{1}H NMR spectrum for anionic platinum complex **A7** in $CDCl_3$

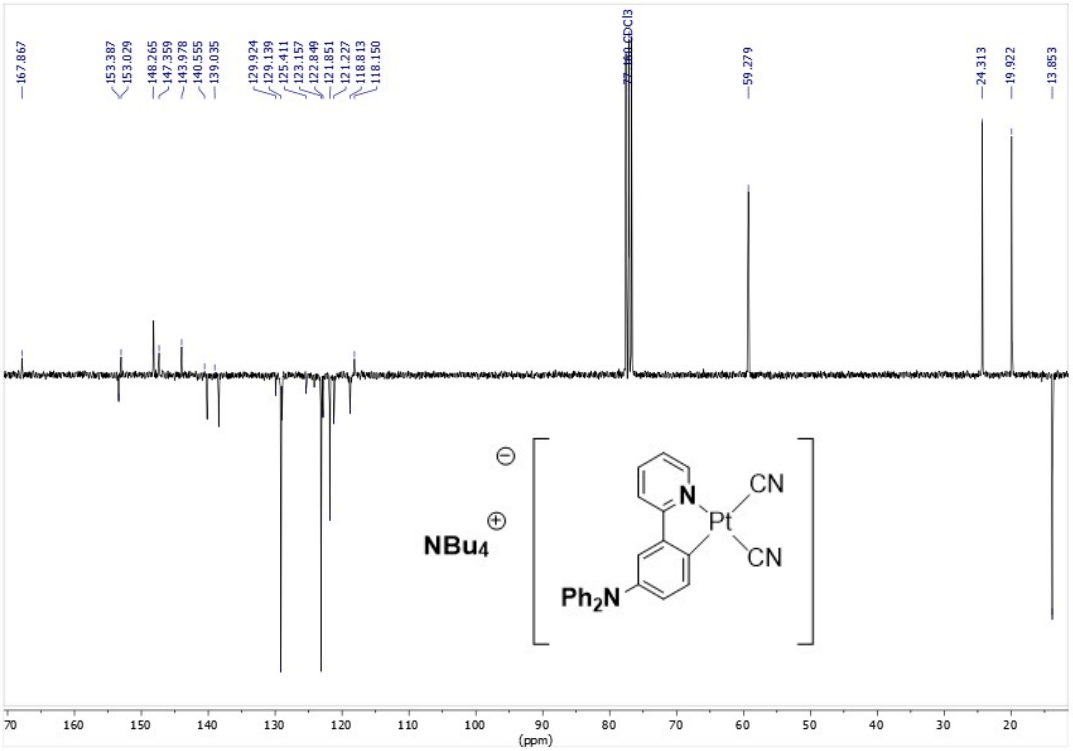


Figure S30 : J-mod ^{13}C NMR spectrum for anionic platinum complex **A7** in $CDCl_3$

D- S0-S9 soft salts

S0

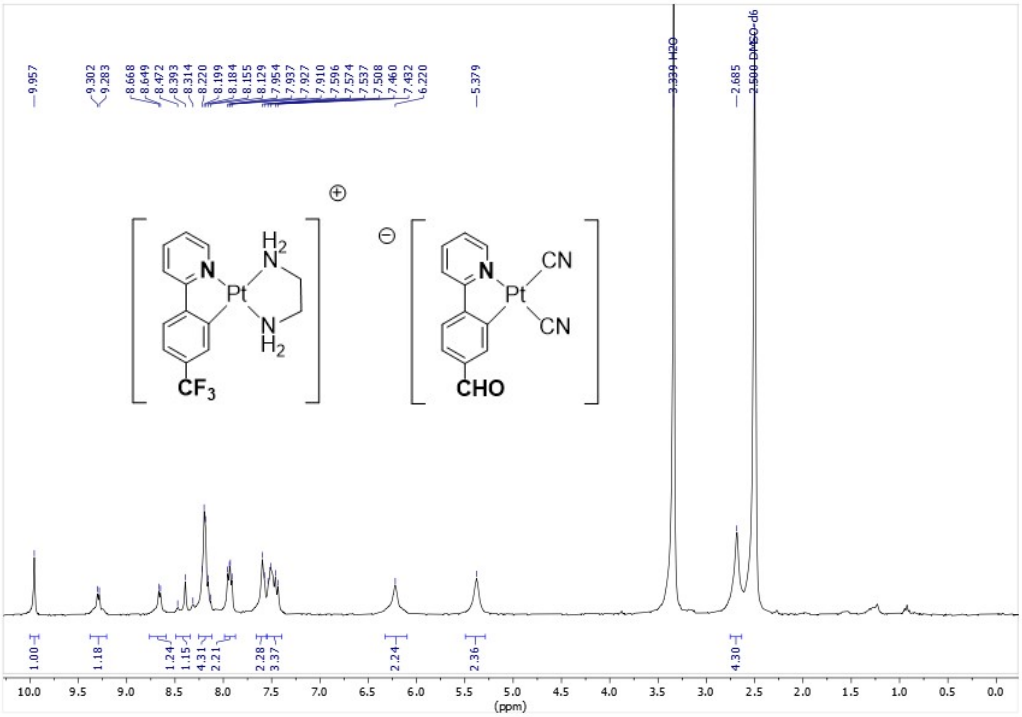


Figure S31 : ^{1}H NMR spectrum soft salt **S0** in DMSO-d6

S1

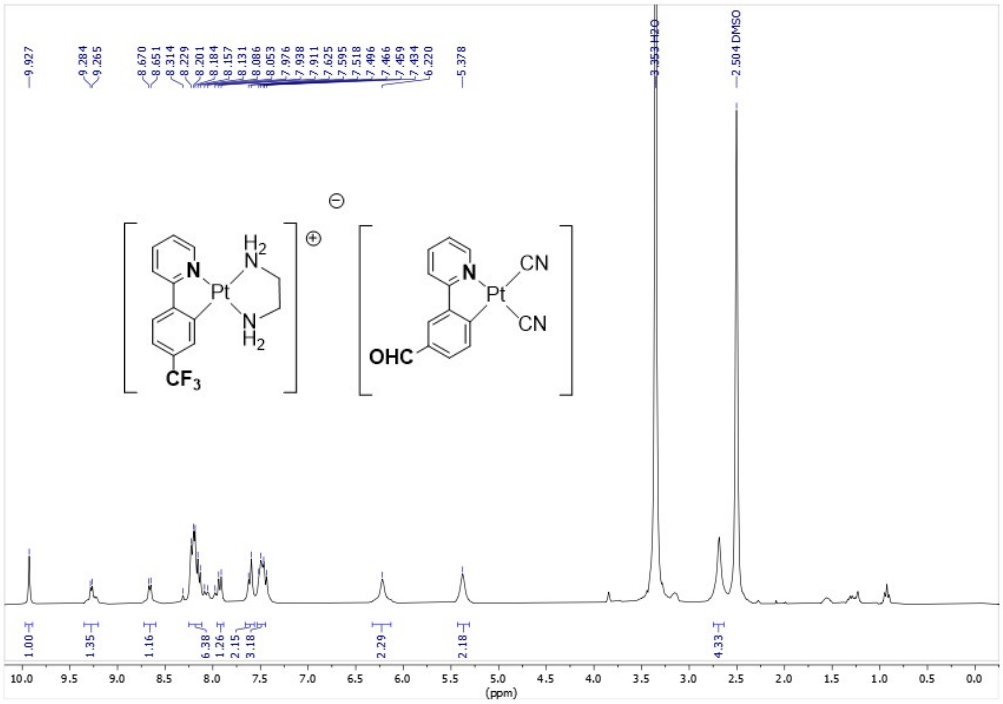


Figure S32 : ^{1}H NMR spectrum soft salt **S1** in DMSO-d6

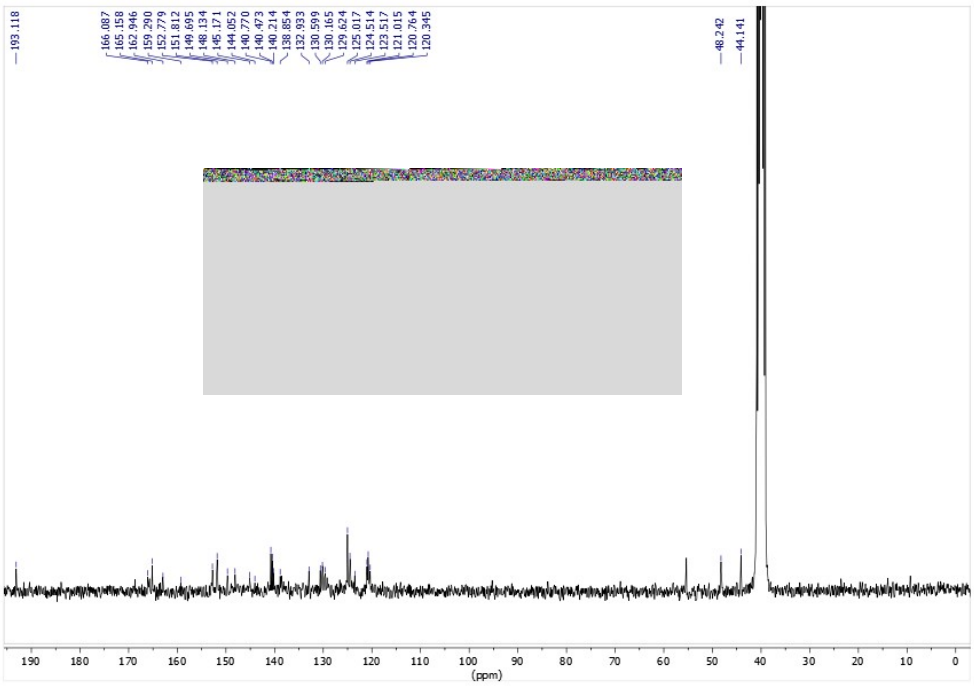


Figure S33 : ^{13}C NMR spectrum for soft salt **S1** in DMSO-d6

S2

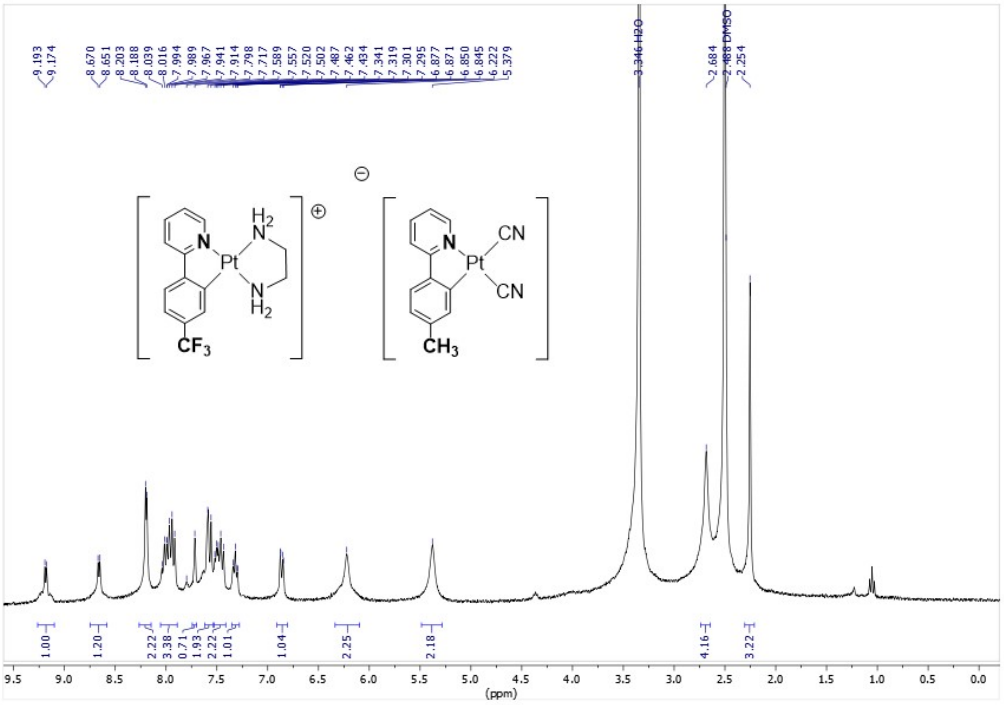


Figure S34 : ^{1}H NMR spectrum soft salt **S2** in DMSO-d6

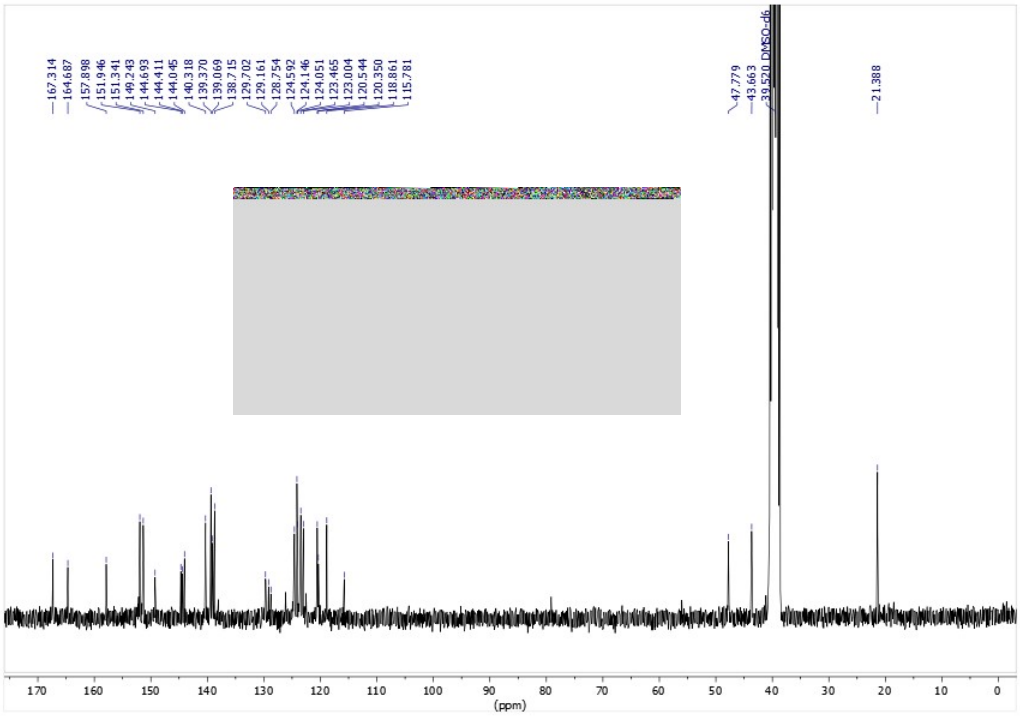


Figure S35 : ^{13}C NMR spectrum for soft salt **S2** in DMSO-d6

S3

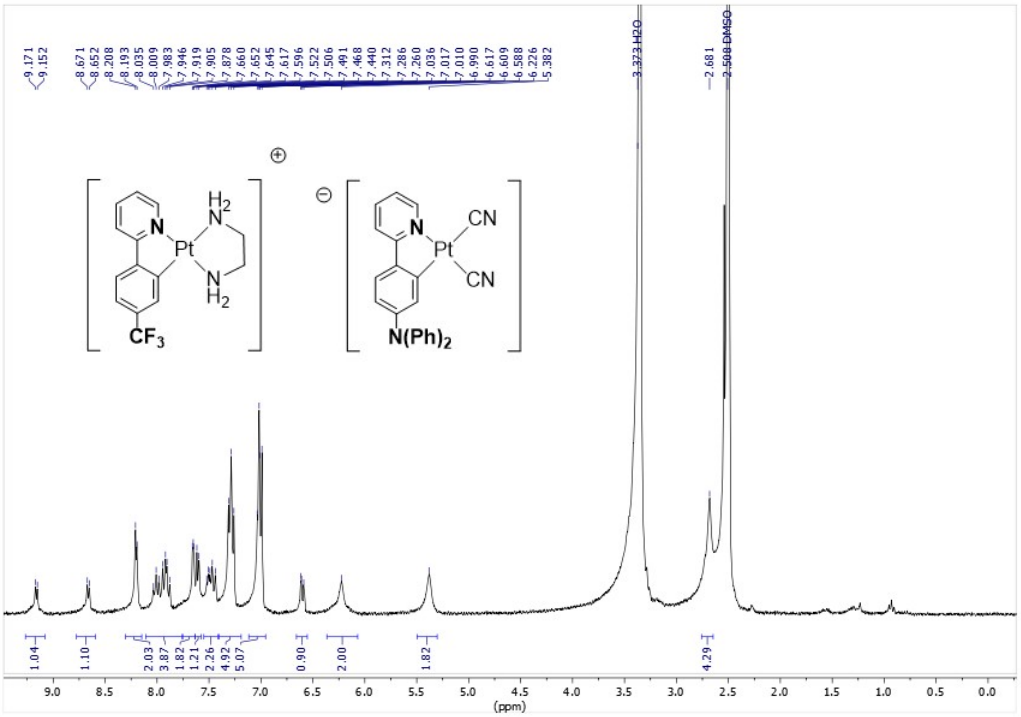


Figure S36 : ^{1}H NMR spectrum for soft salt **S3** in DMSO-d6

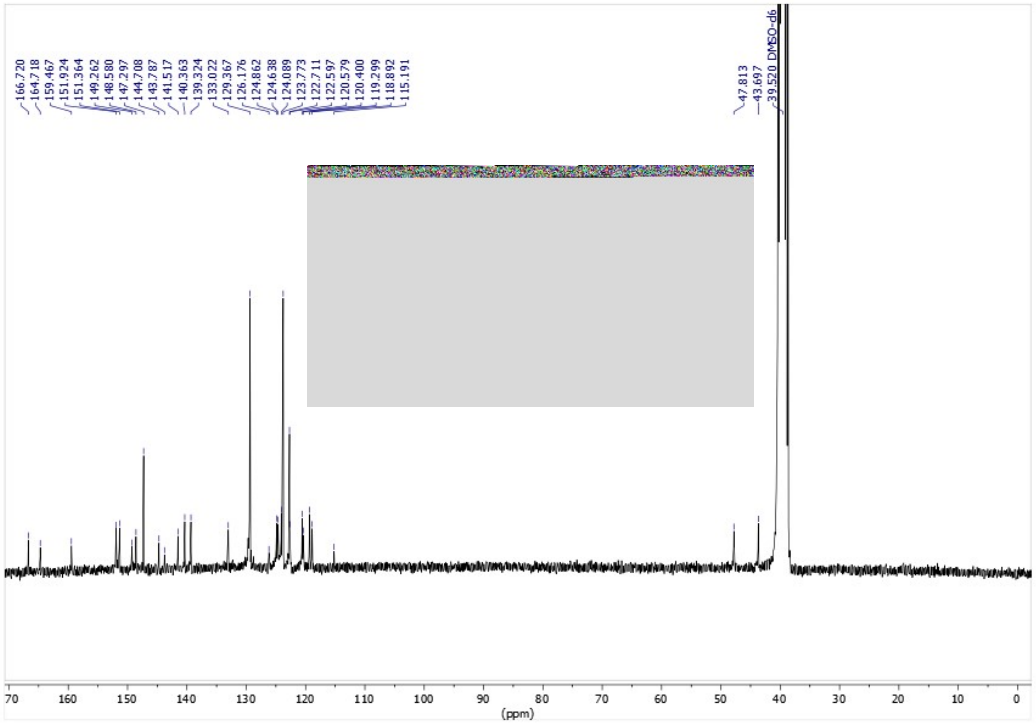


Figure S37 : ^{13}C NMR spectrum for soft salt **S3** in DMSO-d6

S4

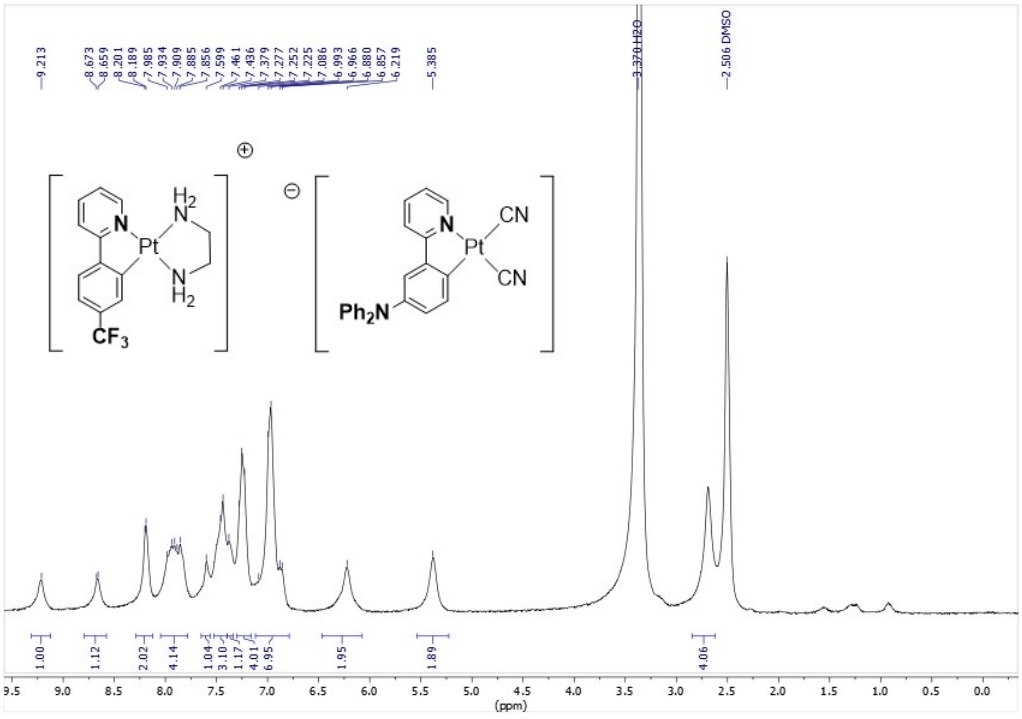


Figure S38 : ^{1}H NMR spectrum for soft salt **S4** in DMSO-d6

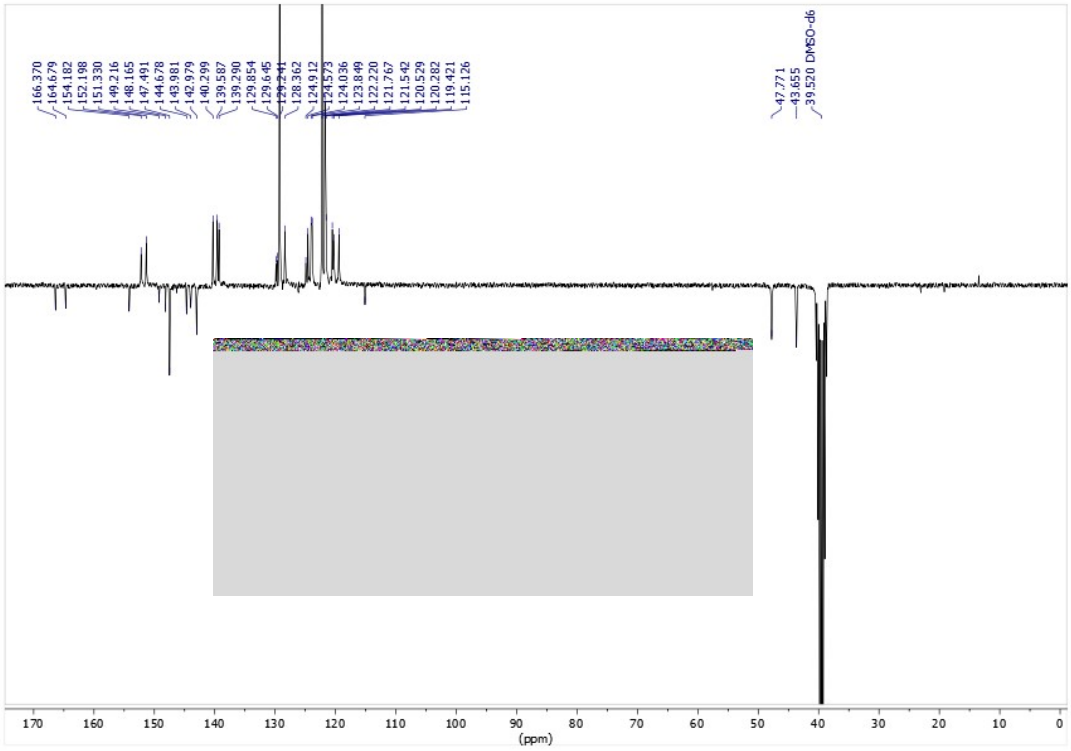


Figure S39 : J-mod ^{13}C NMR spectrum for soft salt **S4** in DMSO-d6

S5

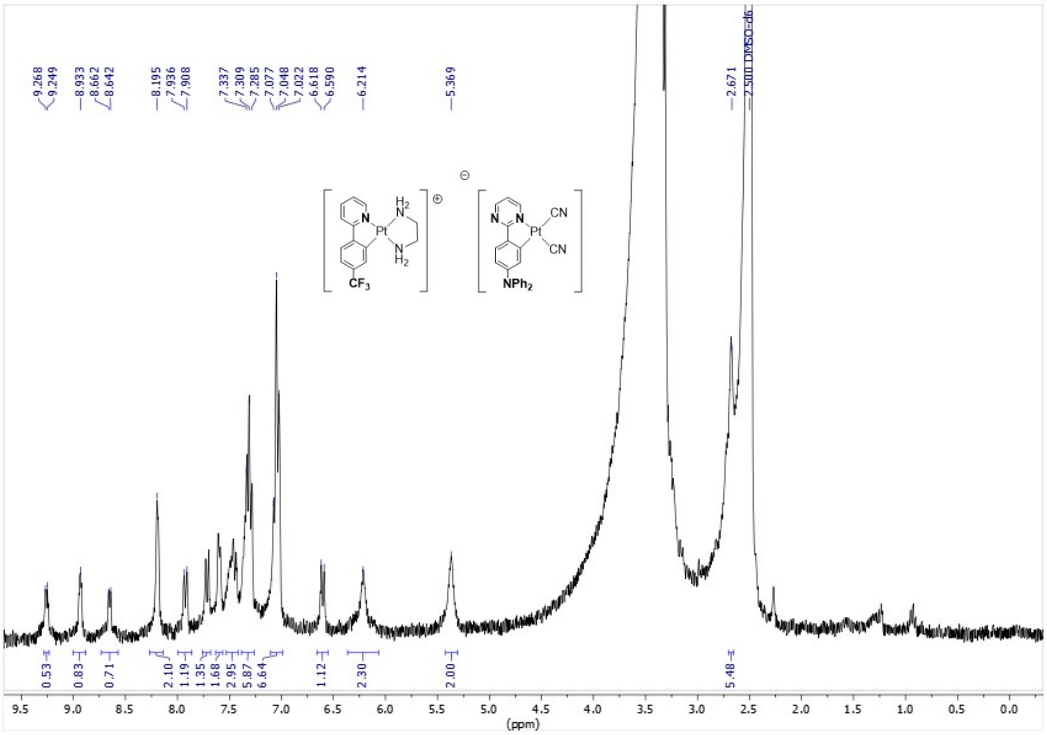


Figure S40 : ^{1}H NMR spectrum for soft salt **S5** in DMSO-d6

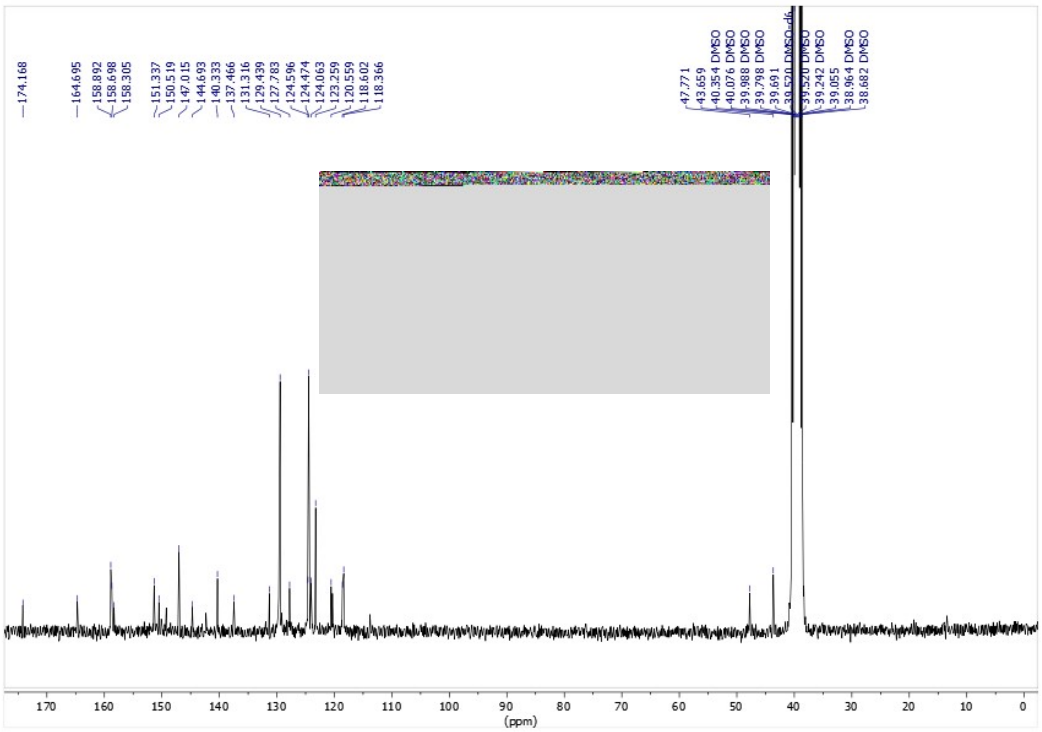


Figure S41 : ^{13}C NMR spectrum for soft salt **S5** in DMSO-d6

S6

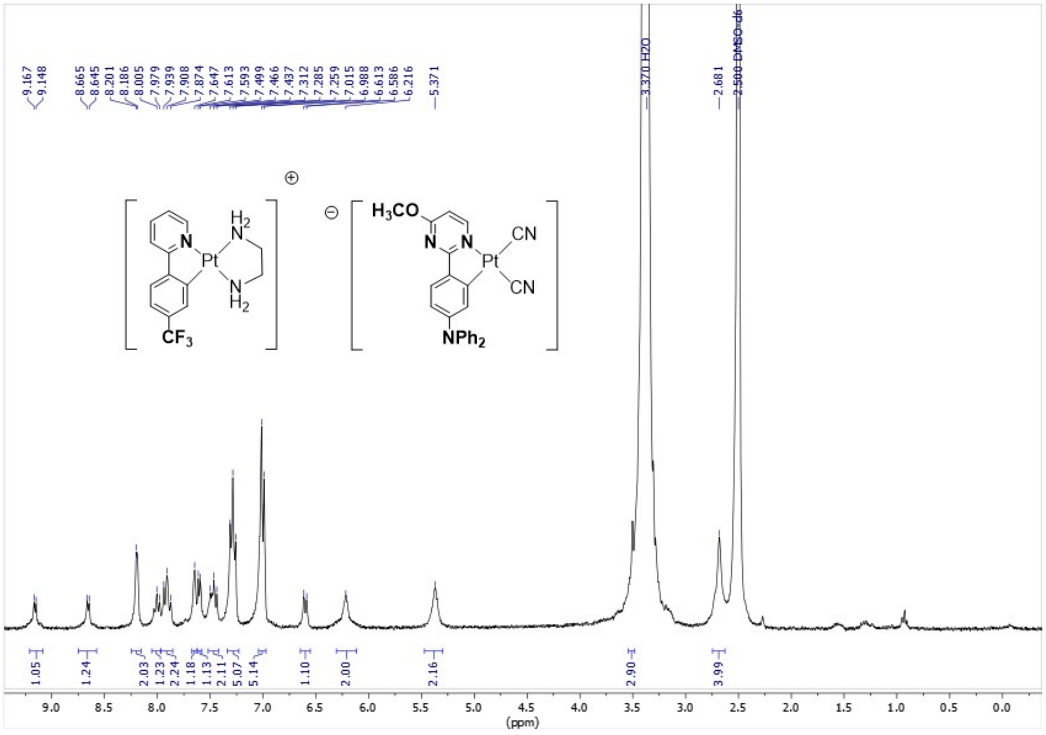


Figure S42 : ^{1}H NMR spectrum for soft salt **S6** in DMSO-d6

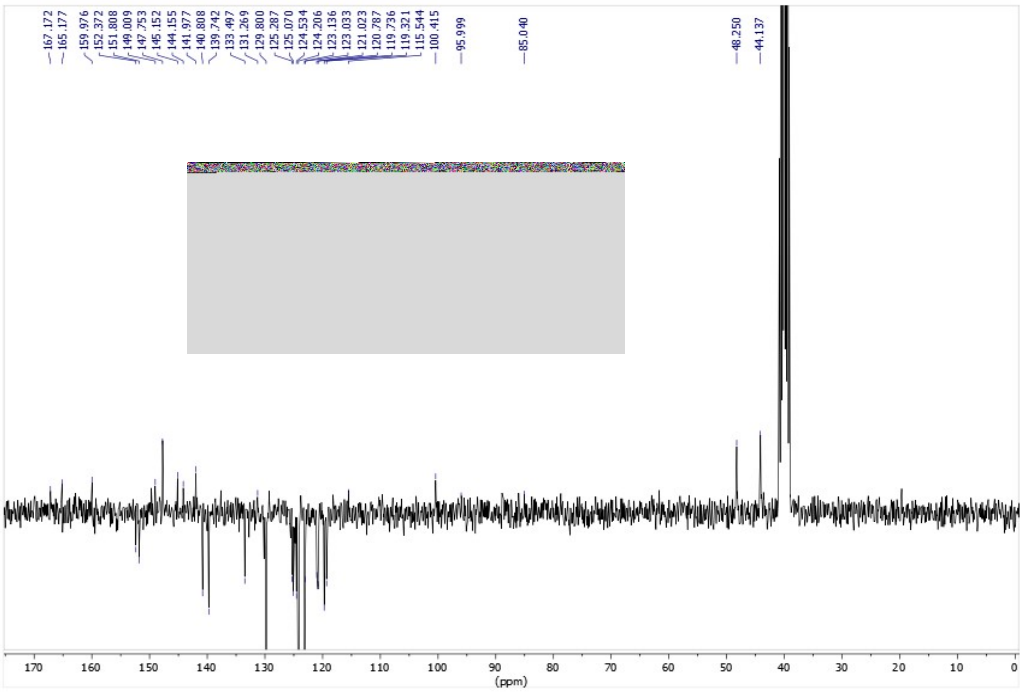


Figure S43 : J-mod ^{13}C NMR spectrum for soft salt **S6** in DMSO-d6

S7

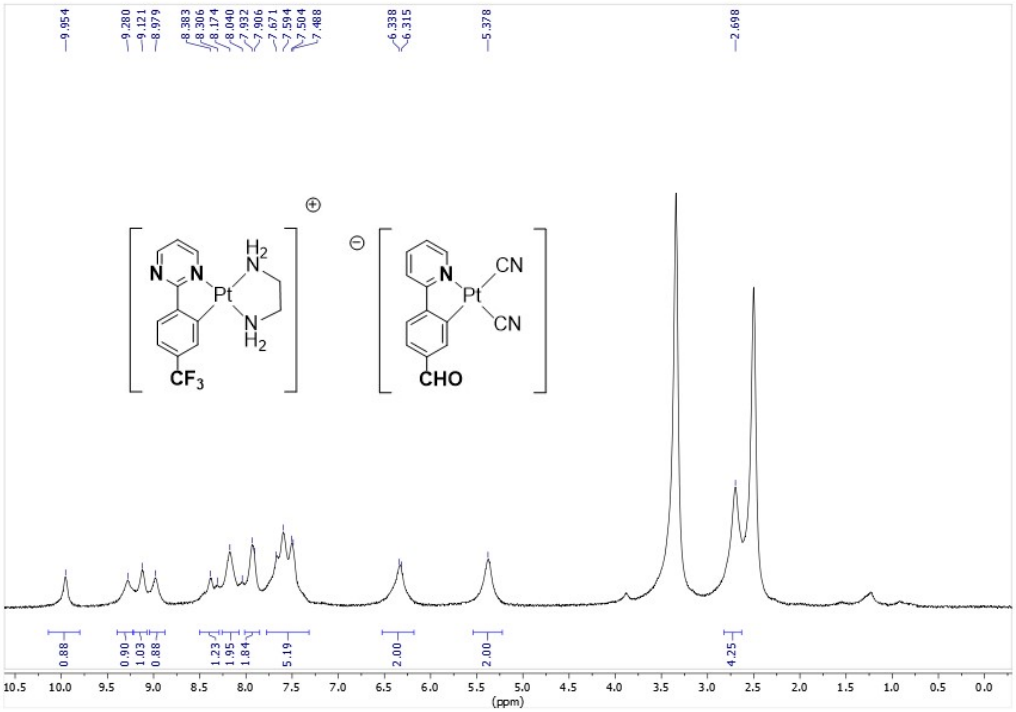


Figure S44 : ^{1}H NMR spectrum for soft salt **S7** in DMSO-d6

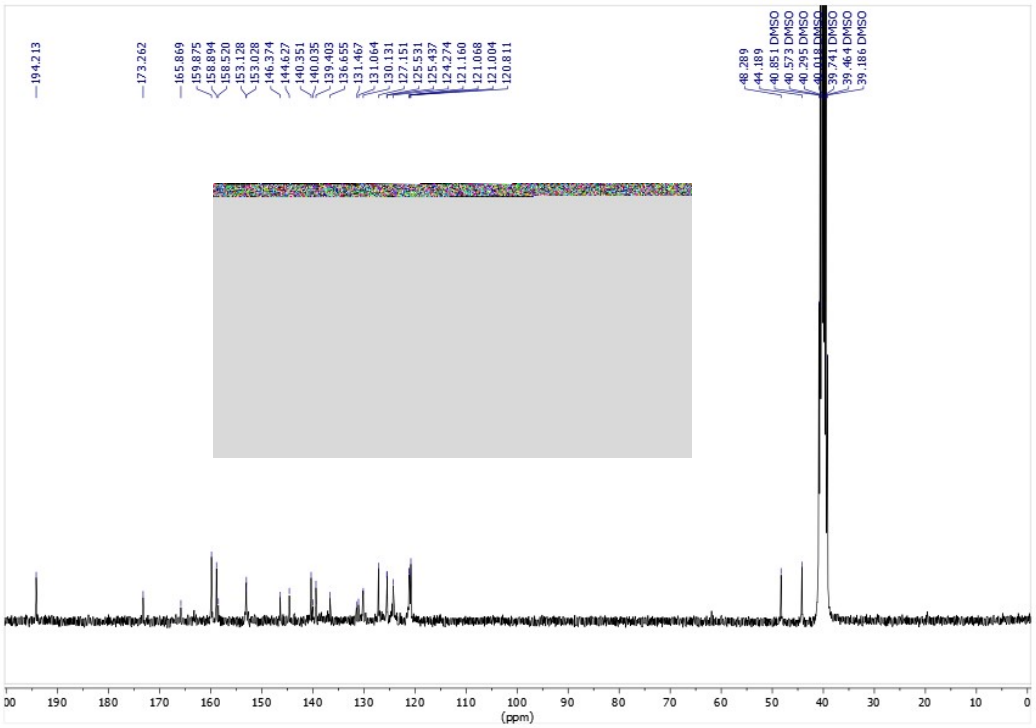


Figure S45 : ^{1}H NMR spectrum for soft salt **S7** in DMSO-d6

S8

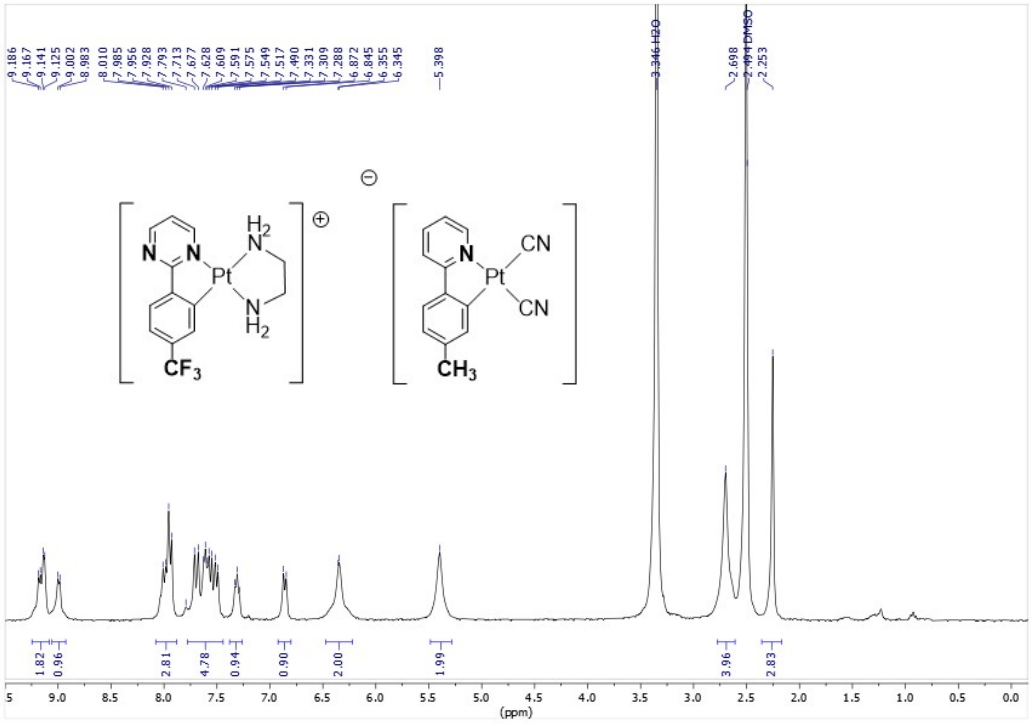


Figure S46 : ^{1}H NMR spectrum soft salt **S8** in DMSO-d6

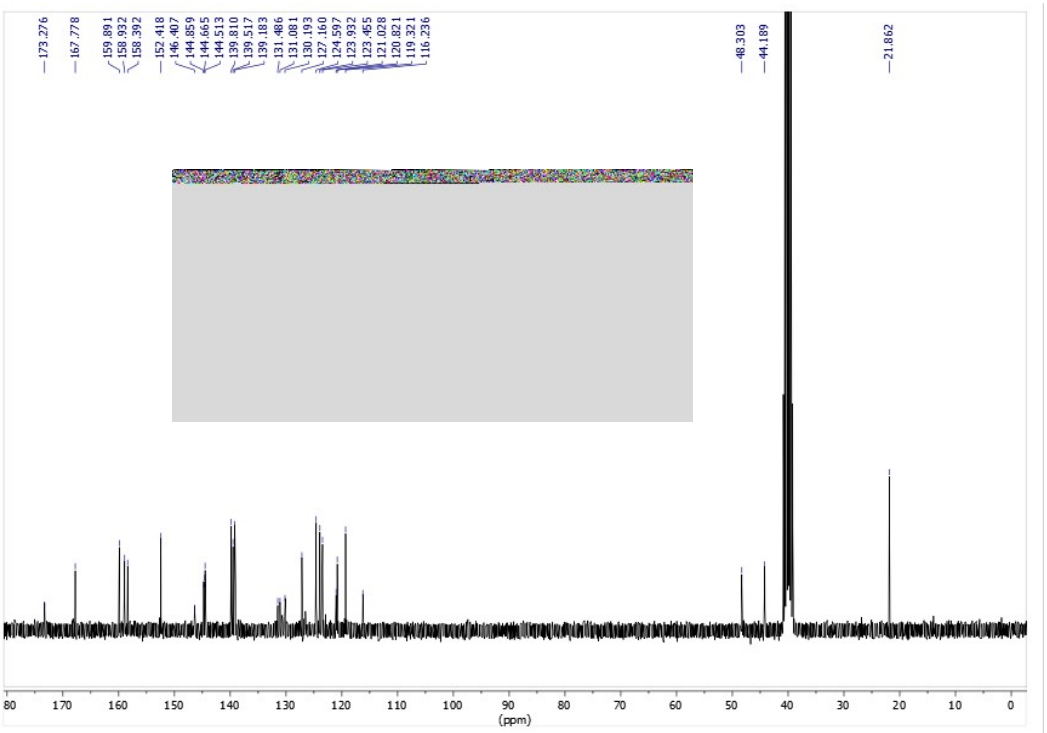


Figure S47 : ^{13}C NMR spectrum for soft salt **S8** in DMSO-d6

S9

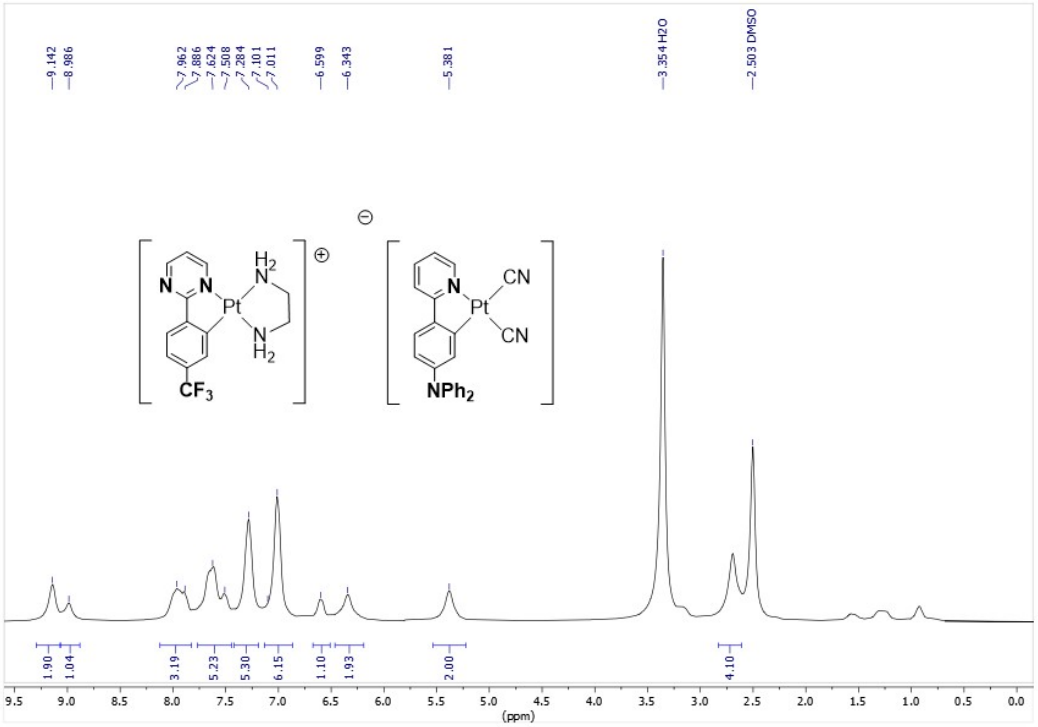


Figure S48 : ^{1}H NMR spectrum soft salt **S9** in DMSO-d6

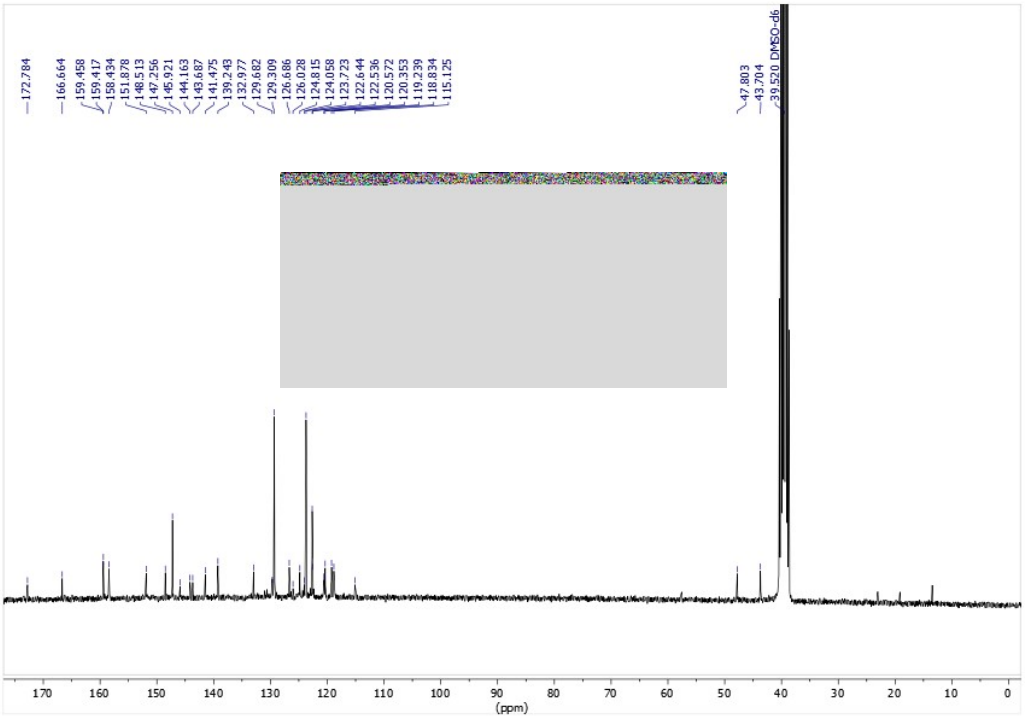


Figure S49 : ^{13}C NMR spectrum for soft salt **S9** in DMSO-d6

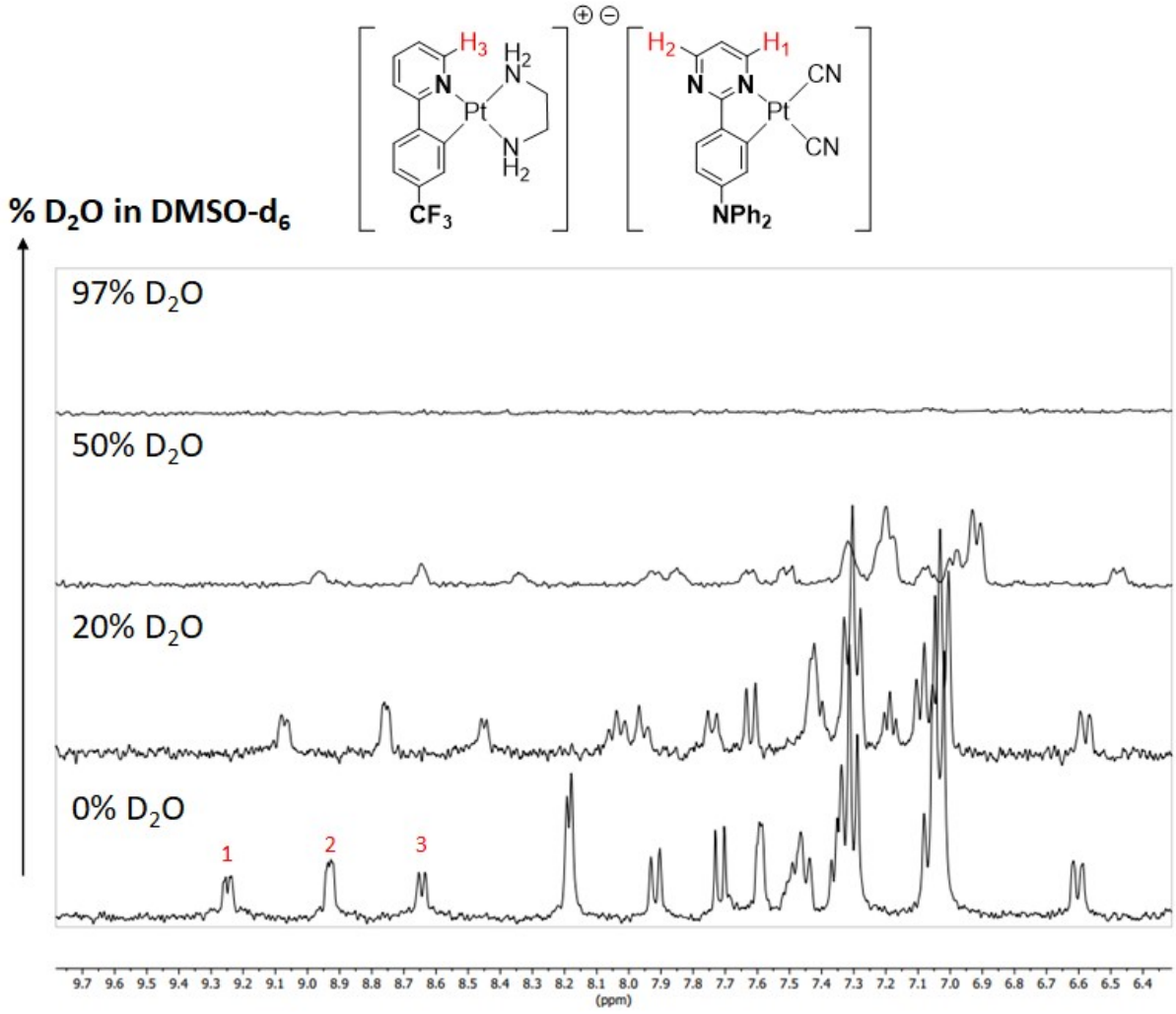


Figure S50 : ^{1}H NMR of **S5** in the DMSO-D_2O mixture (10^{-3} M) with different D_2O fractions

6- Photophysical data in solution

Complexes	*Absorption λ_{max} / nm (ε / mM $^{-1}$ cm $^{-1}$)*	*Emission λ_{max} / nm[a]*	*Φ_{Pl}[a,b]*
C1	334 (6.5), 341 (7.3), 371 (4.4), 390 (3.1)	**490, 524,** 566sh	< 0.01
C2	320 (14.6), 330 (14.6), 354 (11.3), 388 (4.2)	**490, 523**	< 0.01
A1	292 (19.9), 321 (12.1), 334 (11850), 392 (2.8)	**480, 512,** 566sh	< 0.01
A2	316 (8.6), 329 (5.3), 351 (4.5), 388 (11.3)	**480, 512,** 549sh	< 0.01
A3	321 (15.5), 332 (16.8), 361 (5.4), 385 (4.2)	**486, 513,** 560sh	< 0.01
A4	306 (31.9), 340 (26.2), 411 (23)	**511**	0.073
A5	372 (1.8), 411 (2.4)	**620**	0.19
A6	343 (19.2), 369 (22.2), 412 (24)	**573**	0.46
A7	309 (30.3), 339 (20.5), 410 (35)	495sh**, 543**	0.27

Table S1 : Photophysical properties of **C1-2** and **A1-7** complexes in DMSO solution (10^{-5} M).

[a] *All analysis was performed in degassed DMSO solution* [b] *PLQY (±10%) measured relative to 9-10-bisphenylethynylanthracene in cyclohexane (Φ_{PL} = 1.00).*

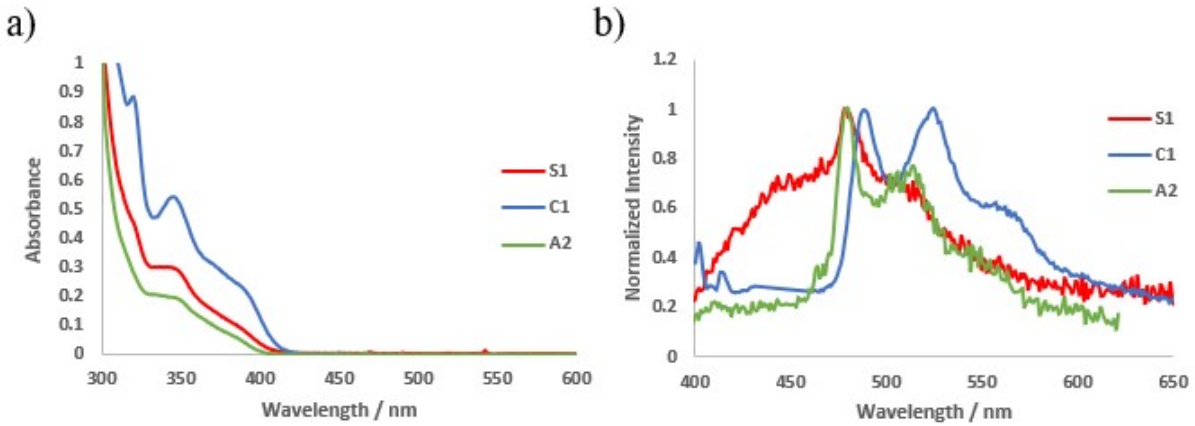


Figure S51 : a) UV-Vis absorption spectra of **S1**, **C1**, and **A2** in DMSO solution (10^{-5} M); b) PL spectra of **S1**, **C1**, and **A2** in DMSO solution (10^{-5} M).

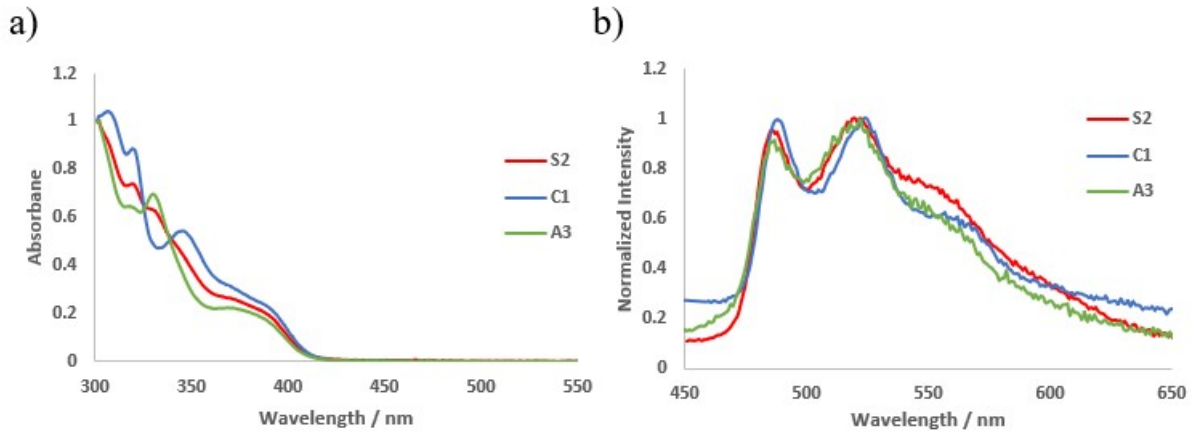


Figure S52 : a) UV-Vis absorption spectra of **S2**, **C1**, and **A3** in DMSO solution (10^{-5} M); b) PL spectra of **S2**, **C1**, and **A3** in DMSO solution (10^{-5} M).

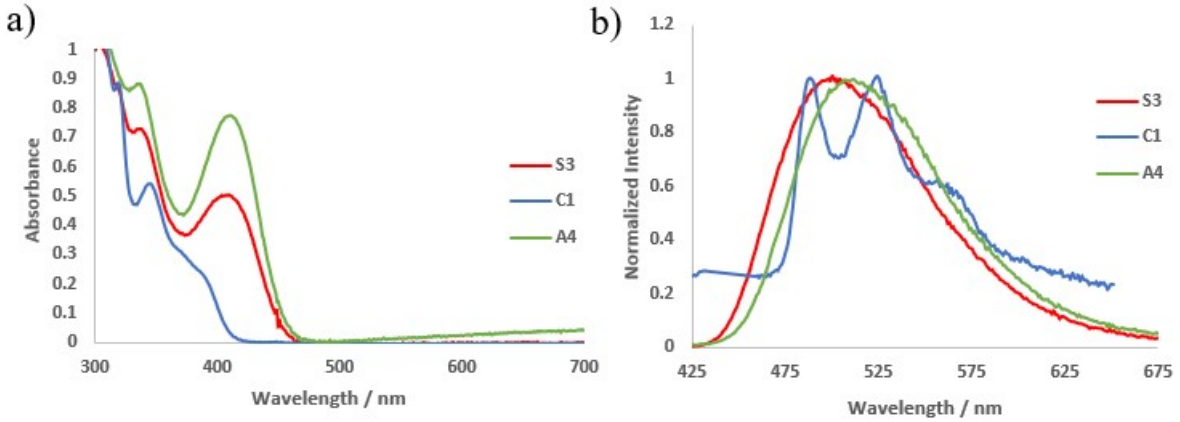


Figure S53 : a) UV-Vis absorption spectra of **S3**, **C1**, and **A4** in DMSO solution (10^{-5} M); b) PL spectra of **S3**, **C1**, and **A4** in DMSO solution (10^{-5} M).

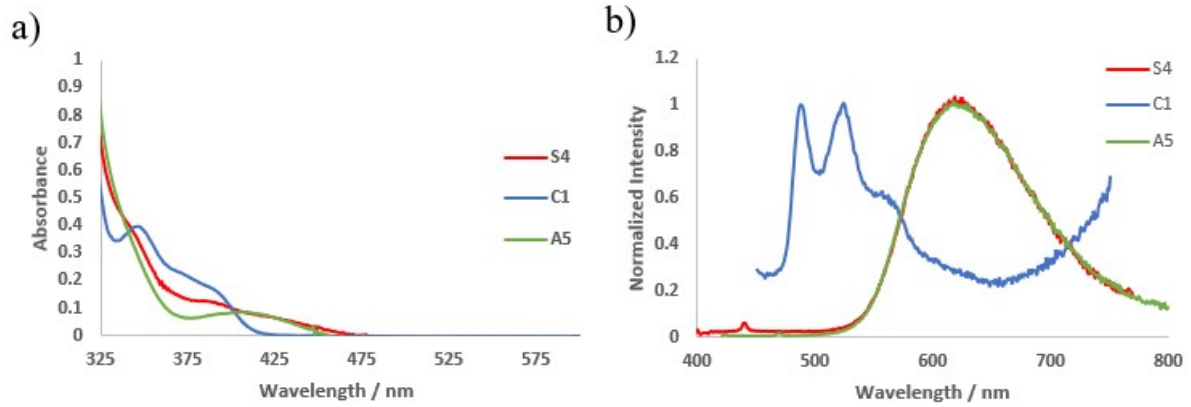


Figure S54 : a) UV-Vis absorption spectra of **S4**, **C1**, and **A5** in DMSO solution (10^{-5} M); b) PL spectra of **S4**, **C**1, and **A5** in DMSO solution (10^{-5} M).

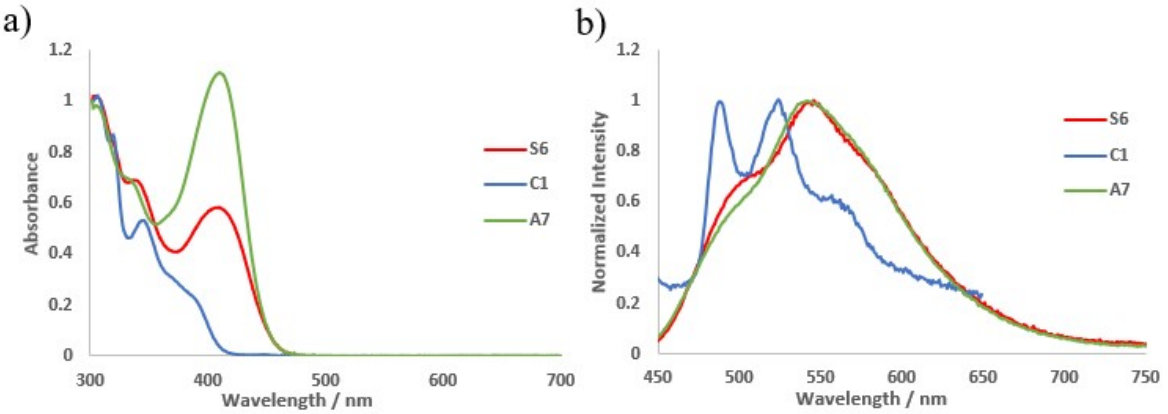


Figure S55 : a) UV-Vis absorption spectra of **S6**, **C1**, and **A7** in DMSO solution (10^{-5} M); b) PL spectra of **S6**, **C1**, and **A7** in DMSO solution (10^{-5} M).

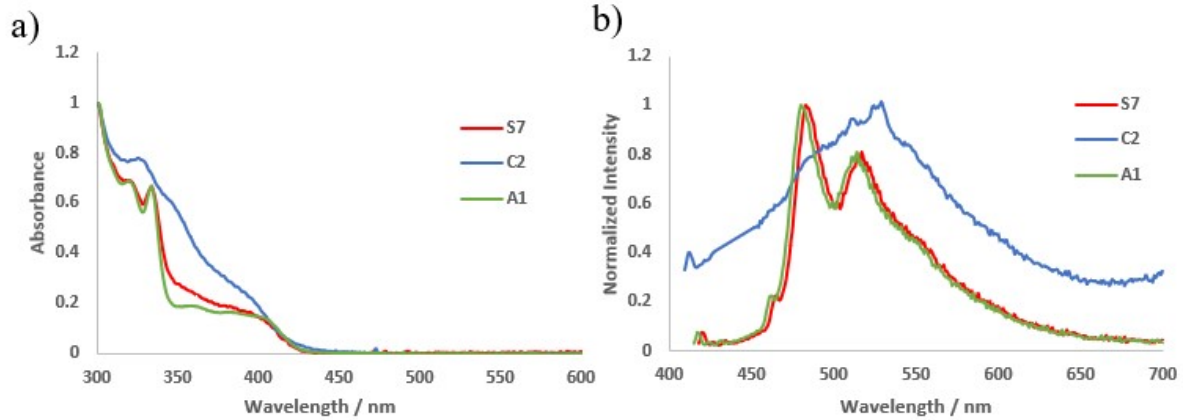


Figure S56 : a) UV-Vis absorption spectra of **S7**, **C2**, and **A1** in DMSO solution (10^{-5} M); b) PL spectra of **S7**, **C2**, and **A1** in DMSO solution (10^{-5} M).

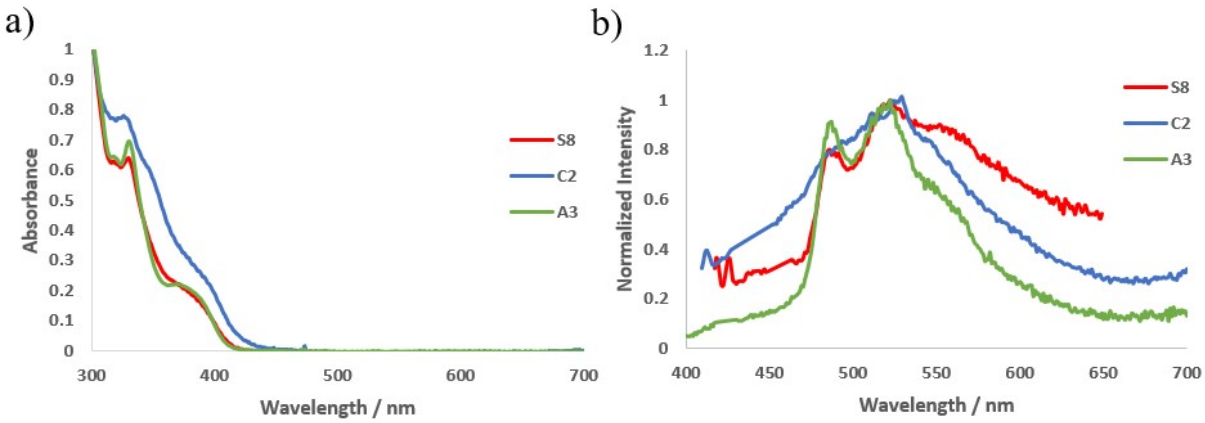


Figure S57 : a) UV-Vis absorption spectra of **S8**, **C2**, and **A3** in DMSO solution (10^{-5} M); b) PL spectra of **S8**, **C2**, and **A3** in DMSO solution (10^{-5} M).

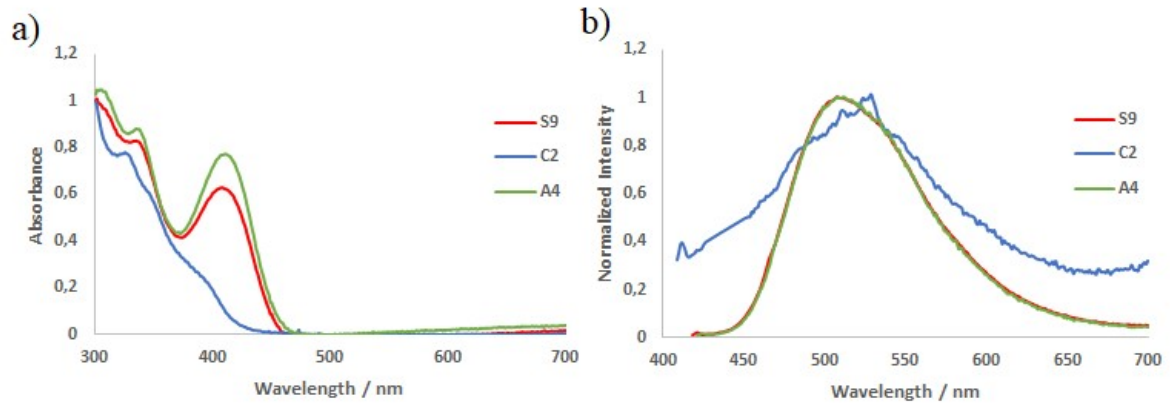


Figure S58 : a) UV-Vis absorption spectra of **S9**, **C2** and **A4** in DMSO solution (10^{-5} M); b) PL spectra of **S9**, **C2**, and **A4** in DMSO solution (10^{-5} M).

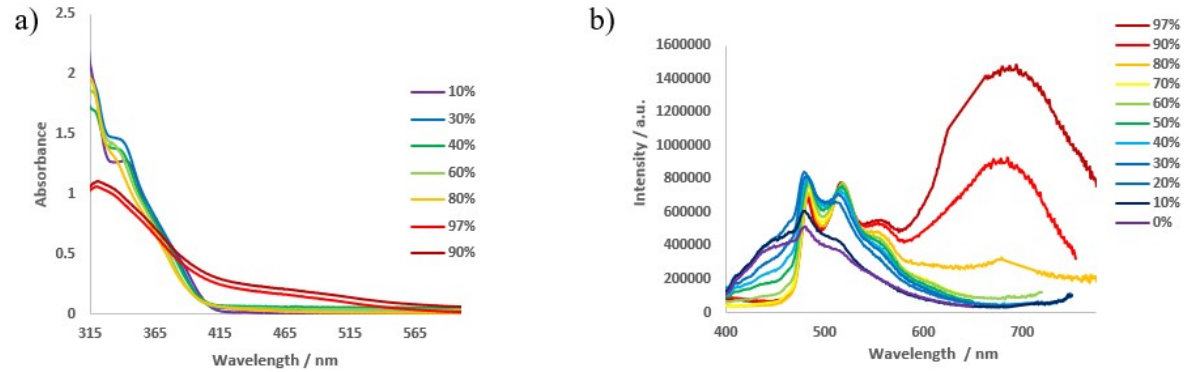


Figure S59 : a) UV-Vis absorption spectra of **S1** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions; b) PL spectra of **S1** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions.

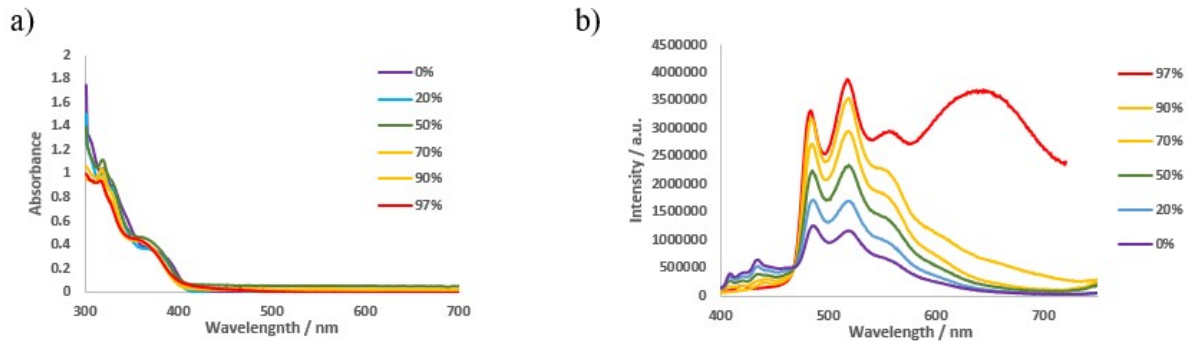


Figure S60 : a) UV-Vis absorption spectra of **S2** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions; b) PL spectra of **S2** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions.

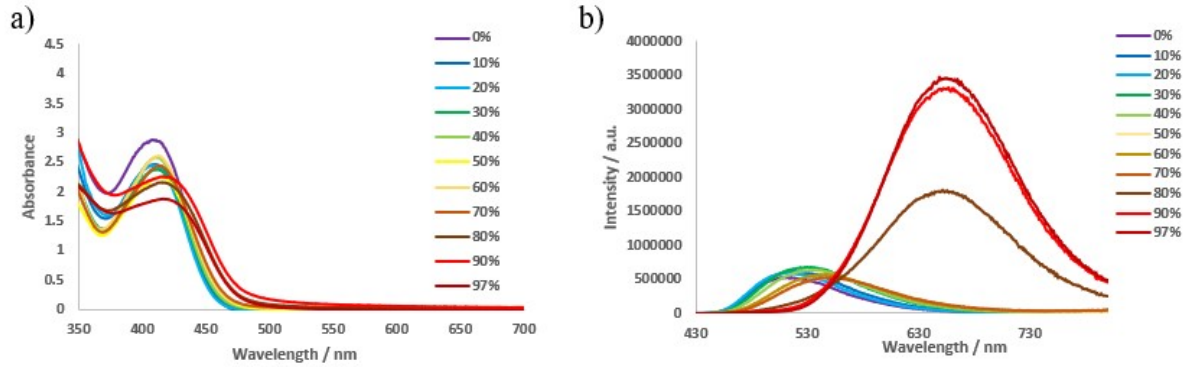


Figure S61 : a) UV-Vis absorption spectra of **S3** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions; b) PL spectra of **S3** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions.

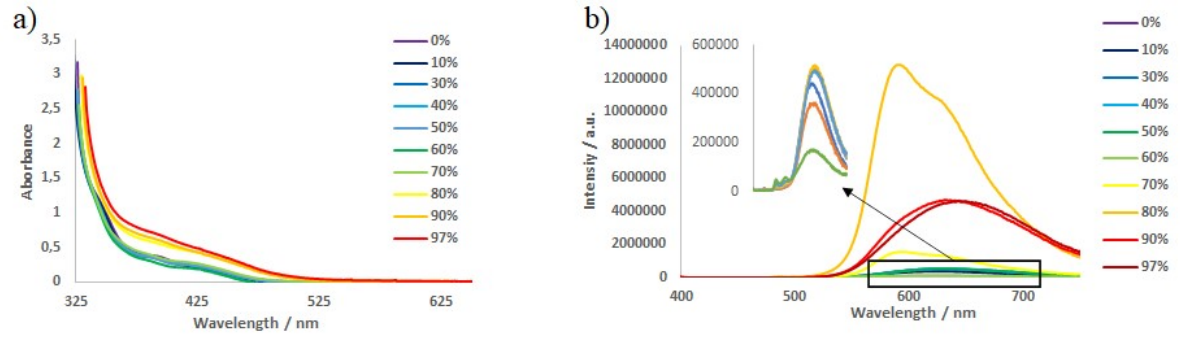


Figure S62 : a) UV-Vis absorption spectra of **S4** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions; b) PL spectra of **S4** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions.

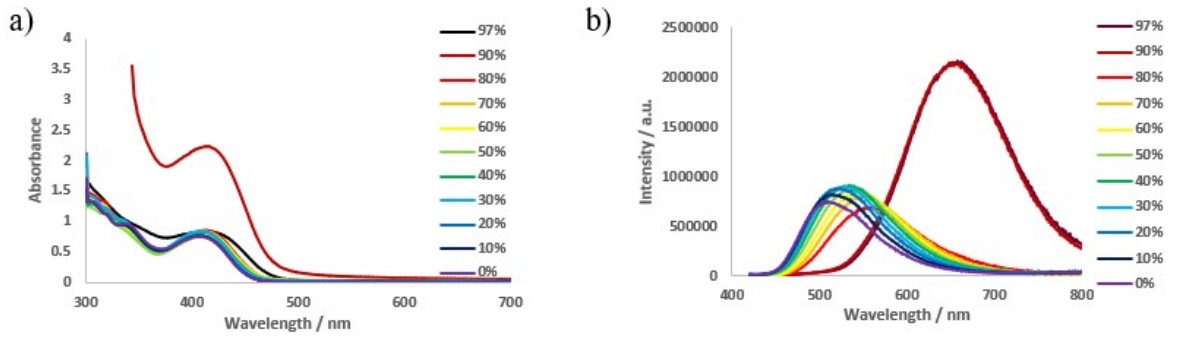


Figure S63 : a) UV-Vis absorption spectra of **S6** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions; b) PL spectra of **S6** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions.

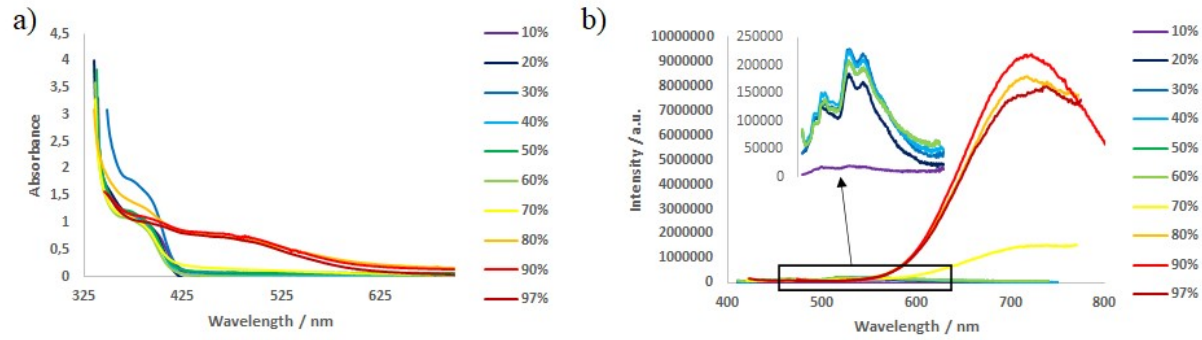


Figure S64 : a) UV-Vis absorption spectra of **S7** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions; b) PL spectra of **S7** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions.

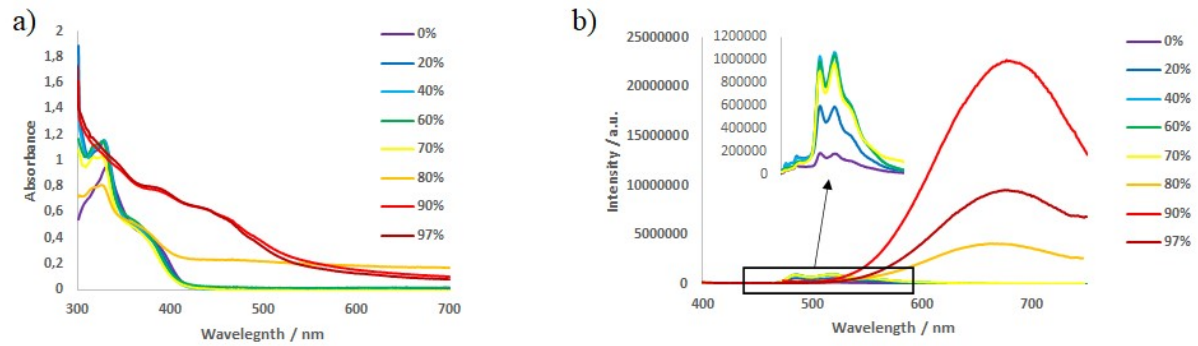


Figure S65 : a) UV-Vis absorption spectra of **S8** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions; b) PL spectra of **S8** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions.

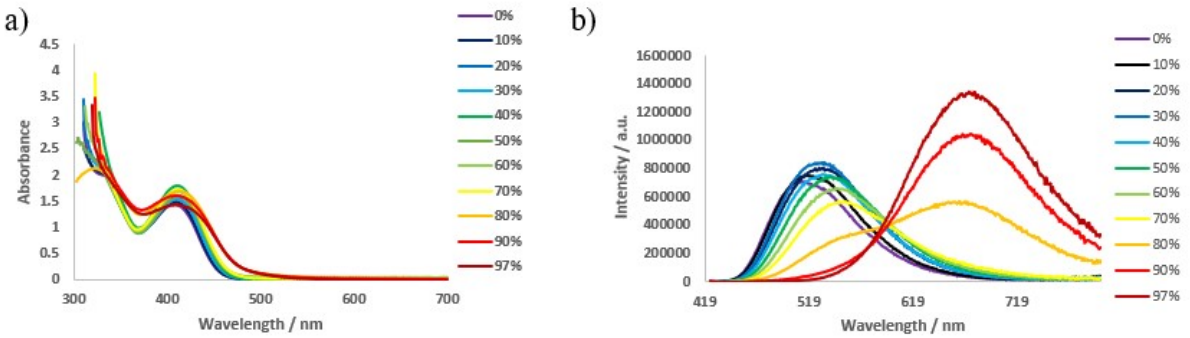


Figure S66 : a) UV-Vis absorption spectra of **S9** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions; b) PL spectra of **S9** in the DMSO-H_2O mixture (10^{-3} M) with different H_2O fractions.

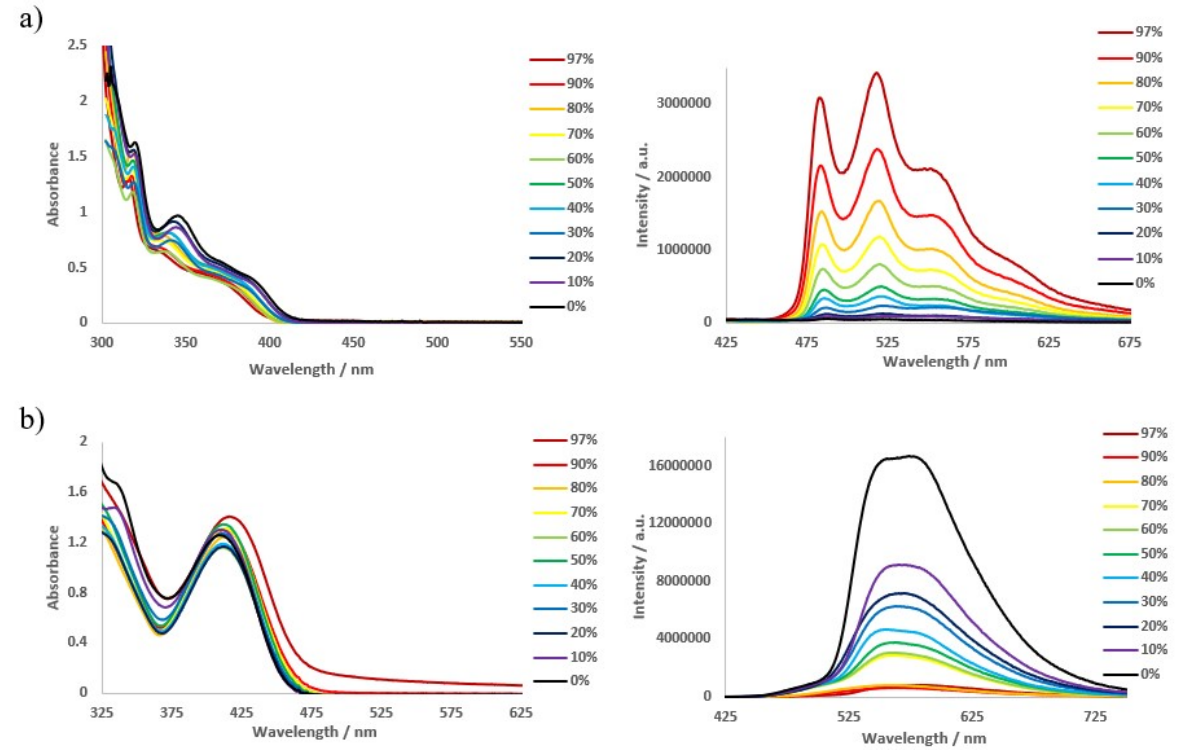


Figure S67 : a) Uv-Vis absorption and emission spectra of **C1** in DMSO-water mixtures (10^{-3} M) with different water ratio; b) Uv-Vis absorption and emission spectra of **A4** in DMSO-water mixtures (10^{-3} M) with different water ratio.

7- Photophysical data in the solid state

Table S2 : Photophysical properties of **C1-2** and **A0-7** complexes in solid state.

Complexes	*Emission* λ_{max} */ nm*	$\Phi_{PL}{}^{a}$ $(\tau_0 / \mu s)$	k_r (s^{-1})	k_{nr} (s^{-1})	*Chromaticity coordinates (x ; y)*
C1	532	0.04 (12.9)	3.1×10^3	7.4×10^4	(0.35 ; 0.55)
C2	567	0.07 (18.4)	3.8×10^3	5.0×10^4	(0.44 ; 0.501)
A1	620	0.31 (10.1)	3.1×10^4	6.8×10^4	(0.43 ; 0.52)
A2	478	0.53 (31.8)	1.7×10^4	1.5×10^4	(0.24 ; 0.50)
A3	558	0.57 (17.9)	3.2×10^4	2.4×10^4	(0.29 ; 0.56)
A4	579	0.09 (27.5)	3.3×10^3	3.3×10^4	(0.42 ; 0.49)
A5	644	0.25 (18)	1.4×10^4	4.2×10^4	(0.54 ; 0.45)
A6	589	0.35 (37.3)	9.4×10^3	1.7×10^4	(0.48 ; 0.48)
A7	614	0.06 (24.4)	2.5×10^3	6.9×10^4	(0.49 ; 0.43)

[a] *Measured as powder with an integrating sphere*

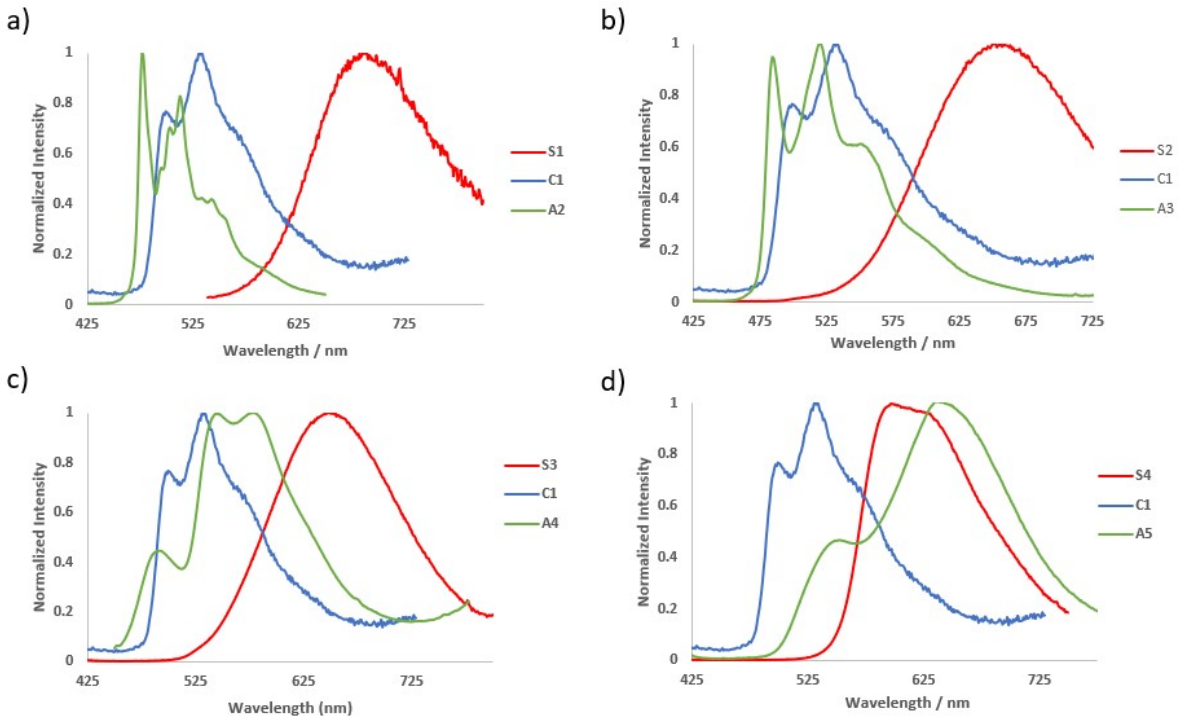
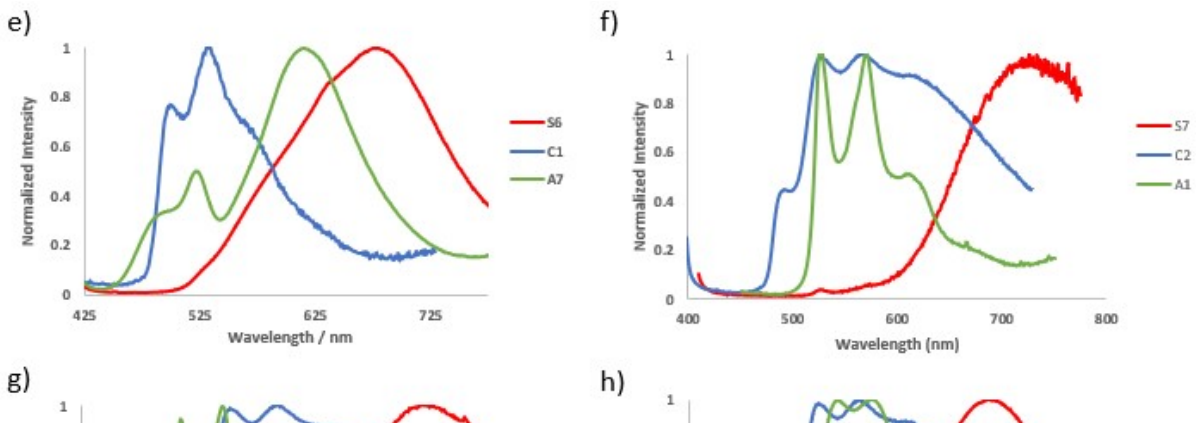


Figure S68 : a) PL spectra in solid state of **S1**, **C1**, and **A2** at 298 K; b) PL spectra in solid state of **S2**, **C1**, and **A3** at 298 K; c) PL spectra in solid state of **S3**, **C1**, and **A4** at 298 K; d) PL spectra in solid state of **S4**, **C1**, and **A5** at 298 K; e) PL spectra in solid state of **S6**, **C1**, and **A7** at 298 K; f) PL spectra in solid state of **S7**, **C2**, and **A1** at 298 K; g) PL spectra in solid state of **S8**, **C2**, and **A3** at 298 K; a) PL spectra in solid state of **S9**, **C2**, and **A4** at 298 K.



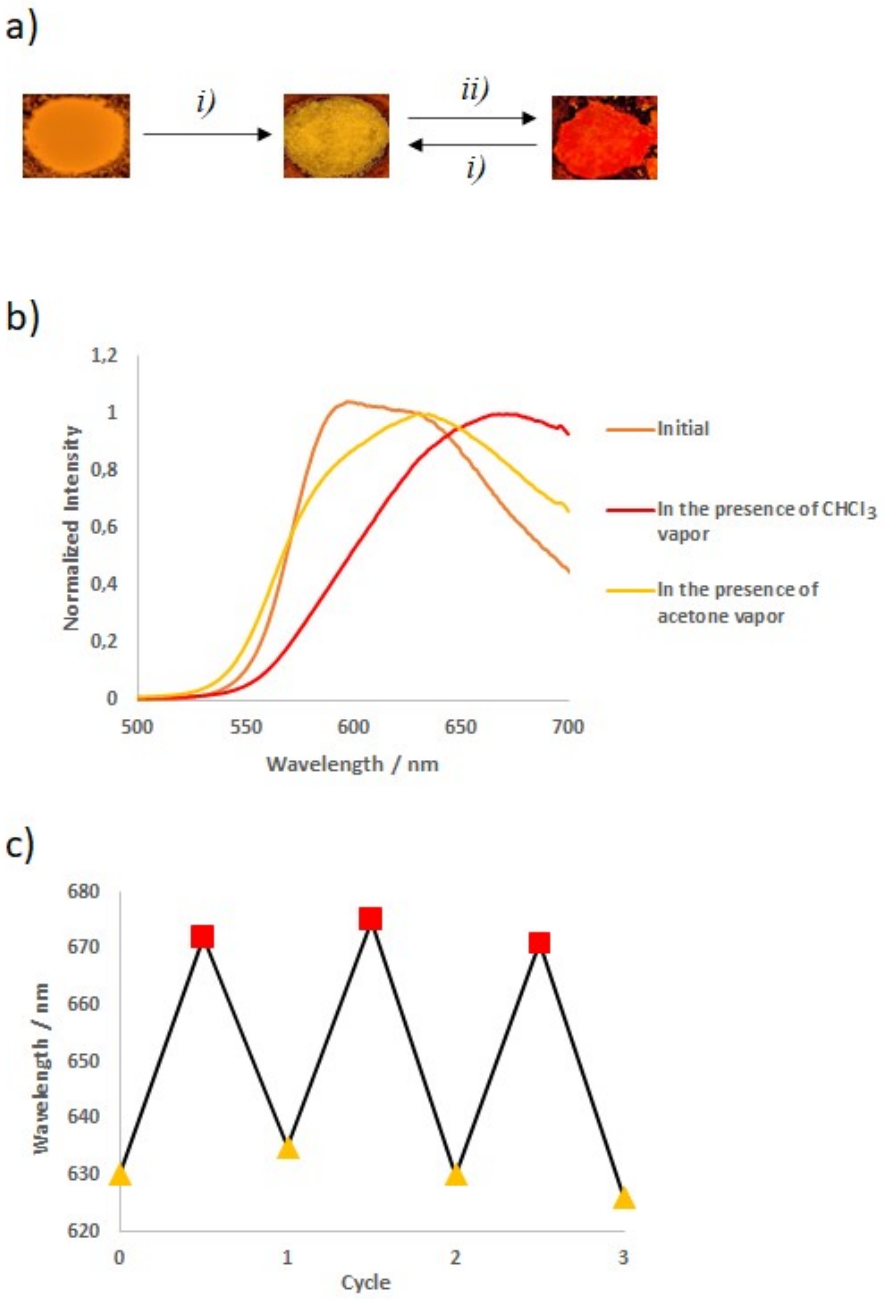


Figure S69 : a) Vapochromic behavior of **S4** in solid state. Pictures were taken in the dark upon irradiation with a handheld UV lamp (λ_{exc} = 365 nm). Conditions: i) Acetone vapors, ii) $CHCl_3$ vapors; b) Normalized Pl spectra of S3 in the initial and in presence of $CHCl_3$/Acetone vapors; c) 3 cycles of emission wavelength variations measured after repeated fuming with $CHCl_3$/Acetone.

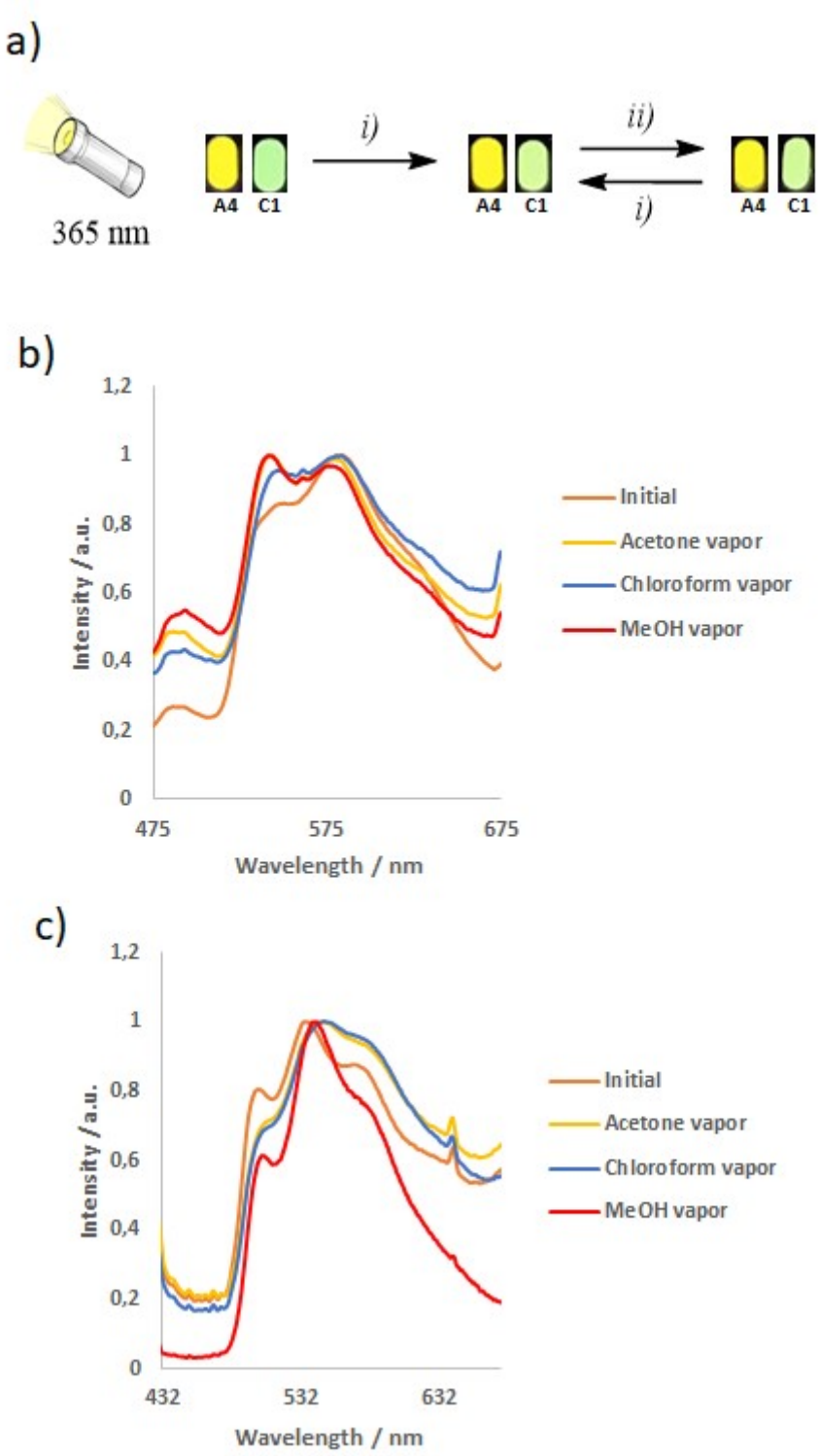


Figure S70 : a) Vapochromic behavior of **C1** and **A4** in solid state. Pictures were taken in the dark upon irradiation with a handheld UV lamp (λ_{exc} = 365 nm). Conditions: i) MeOH vapors, ii) Acetone vapors; Normalized PL spectra of **C1** b) and **A4** c) in the initial and in presence of MeOH/Acetone/ $CHCl_3$ vapor.

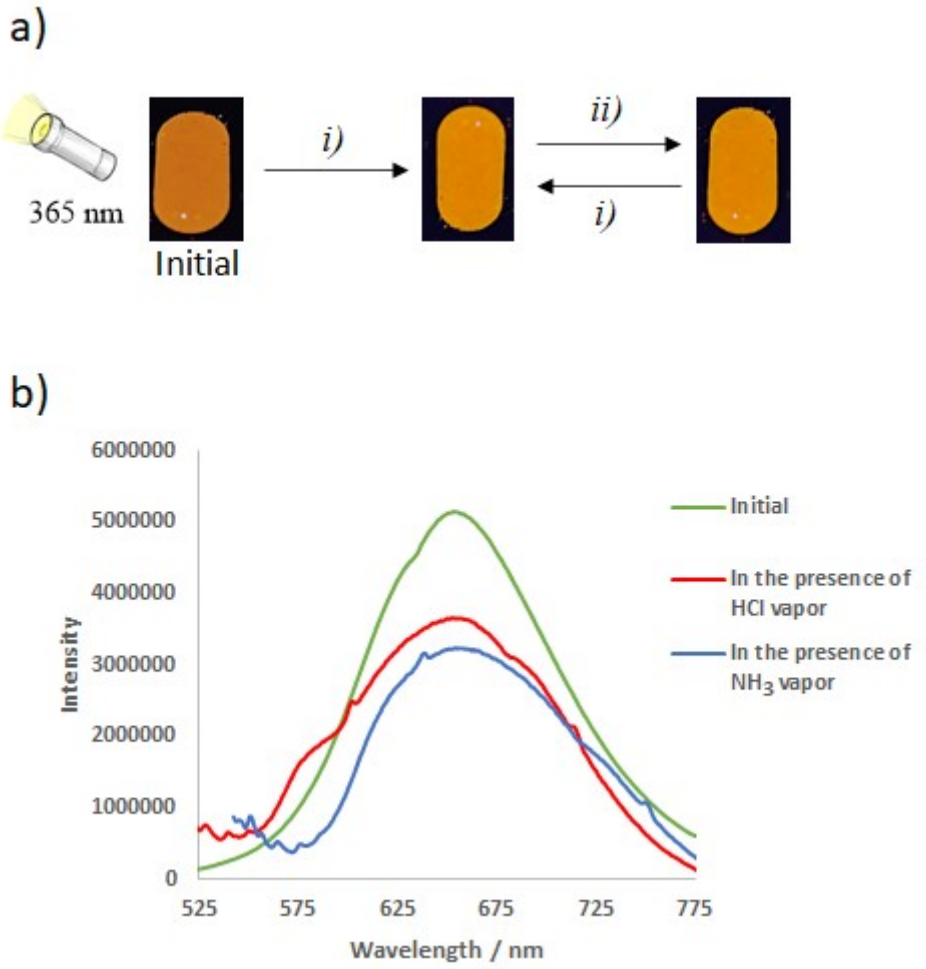


Figure S71 : a) Pictures of **S3** taken in the dark upon irradiation with a handheld UV lamp (λ_{exc} = 365 nm). Conditions : i) HCl vapors, ii) NH_3 vapors; b) PL spectra of **S3** in the initial and in presence of HCl/NH_3 vapors.

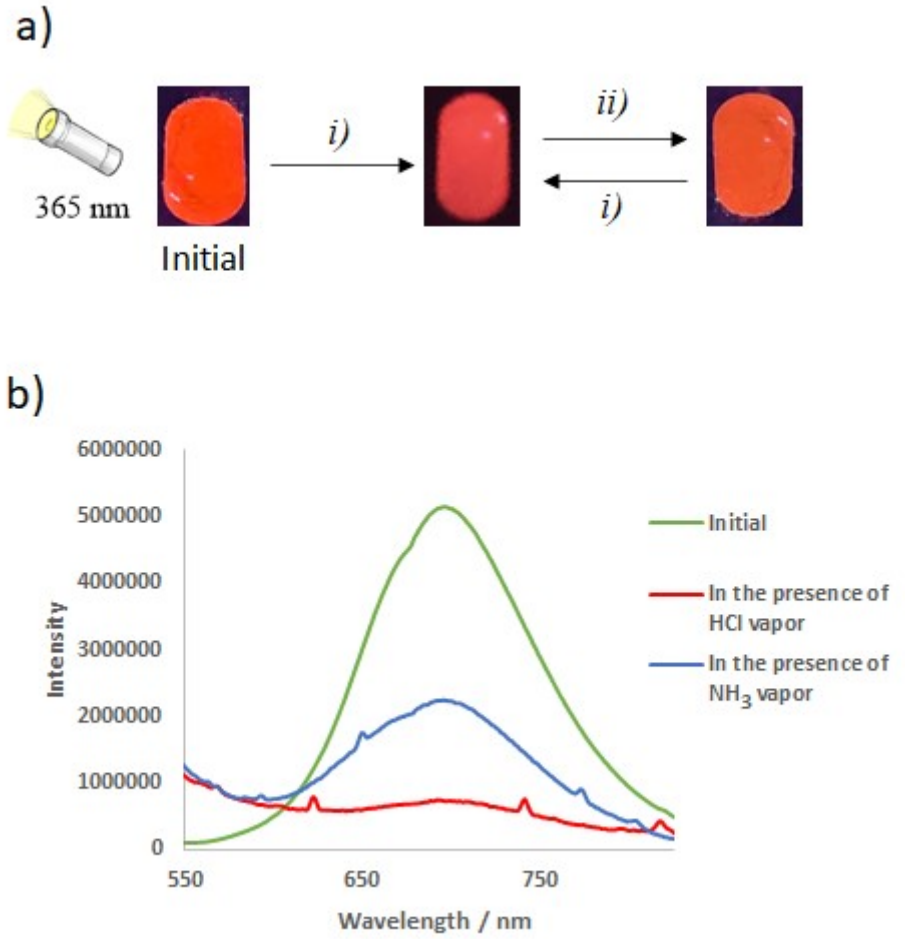


Figure S72 : a) Pictures of **S9** taken in the dark upon irradiation with a handheld UV lamp (λ_{exc} = 365 nm). Conditions : i) HCl vapors, ii) NH_3 vapors; b) PL spectra of **S9** in the initial and in presence of HCl/NH_3 vapors.

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[2] (a) J. Li, K. Chen, J. Wei, Y. Ma, R. Zhou, S. Liu, Q. Zhao, W.-Y. Wong, *J. Am. Chem. Soc.* 2021, **143**, 18317. (b) X. Hong, H. Wang, B. Liu, B. Xu, *Chem. Commun.* 2014, **50**, 14129.

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