"Dibromo-isonitrile and N-acyclic carbene complexes of platinum(II). Synthesis and reactivity"

Supplementary Information

Synthesis of *cis*-[$PtCl_2(CNCH_2COOEt)(PPh_3)$].

A sample of *trans*-[$Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$ (0.159 g, $1.505\cdot10^{-4}$ mol) was suspended in 10 ml of dried 1,2-DCE. A DCE solution of ethylisocyanoacetate (0.042 g, $3.713\cdot10^{-4}$ mol, Pt/isocyanide= 1/1 molar ratio) was added dropwise at 0°C. The orange mixture was stirred at 25 °C for 1h. ^{31}P NMR analysis showed a single signal at 8.4 ppm($^1J_{PPt}$=3360 Hz). The mixture's volume was reduced to 5 ml and heptane (20 mL) was added. The pale brown solid was filtered and dried under vacuum. Yield: 0.151 g, 74%.

El. Anal. Calcd $C_{23}H_{22}Cl_2NO_2PPt\cdot H_2O$, % : C 41.9, H 3.7, N 2.1, Found, % : C 42.3, H 3.7, N 2.5

I.R. (ATR, $\tilde{\nu}$, cm^{-1}): 2240 s, 1757 s, 1481 m, 1435 m, 1369 w, 1337 m, 1234 w, 1216 s, 1097 m, 1051 w, 998 w, 653 w, 755 m, 708 m, 690 s.

^1H NMR:7.8-7.7(m, 6H, H_{arom}),7.5-7.4(m, 9H, H_{arom}),4.1(q, J = 7.0 Hz, 2H, $COOCH_2$),3.9 (s, 2H, $^4J_{H\text{-}Pt}$ = 17 Hz, CH_2CO), 1.25(t, J = 7.0 Hz, 3H, CH_3)

^{31}P NMR: 8.41 ($^1J_{P\text{-}Pt}$= 3355 Hz)

^{195}Pt NMR: -4120 ($^1J_{P\text{-}Pt}$= 3355 Hz)

^{13}C NMR:160.7, 134.5 (d, J=10 Hz), 131.7, 128.5 (d, J=11 Hz), 128.2 (d, J=65 Hz), 63.2, 41.0, 14.0

Synthesis of *cis*-[$PtCl_2(CNtBu)(PPh_3)$]

A sample of *trans*-[$Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$ (0.700 g, $6.602\cdot10^{-4}$ mol) was suspended in 15 ml of dried 1,2-DCE. A DCE solution of tert-butylisocyanide (168 µL, $1.46\cdot10^{-4}$ mol, tert-Butyl isocyanide/[Pt] = 1.1 molar ratio) was added dropwise at 0°C. The orange mixture was stirred at 25 °C for 2h. ^{31}P NMR analysis showed a single signal at 7.98 ppm($^1J_{PPt}$=3391 Hz). The mixture's volume was reduced to 5 ml and heptane (20 mL) was added. The pale brown solid was filtered and dried under vacuum. Yield: 0.790 g, 92%.

El. Anal. Calcd $C_{22}H_{24}Cl_2NPPt$, % : C 45.2, H 3.9, N 2.3, Found, % : C 44.9, H 3.5, N 2.7.

I.R. (ATR, $\tilde{\nu}$, cm^{-1}): 3051 v-w, 2985 v-w, 2937 v-w, 2229 s, 1482 w-m, 1435 m-s, 1403 w, 1375 w, 1195 w-m, 1096 s, 1029 w, 997 w-m, 752 s.

^{31}P NMR: 8.30 ($^1J_{P\text{-}Pt}$ = 3423 Hz)

^{195}Pt NMR: -4120 ($^1J_{P\text{-}Pt}$ = 3423 Hz).

^{13}C NMR: 134.6 (d, $J_{C\text{-}P}$ = 12 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2 Hz), 128.7 (d, $J_{C\text{-}P}$ = 66 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11 Hz), 110.8, 59.0, 29.4.

Synthesis of $[PtBr_2(NCMe)_2]$

A mixture of $[Pt(Cl_2)(NCMe)_2]$ (1.0341g, 2.27mmol), 6.84mL (59.4mmol, 1.189gml^{-1}) of tBuBr (tBuBr/Pt = 20 molar ratio) and CH_3CN (5ml) was introduced, under Ar atmosphere, into a 80 mL Carius tube equipped with a magnetic stirrer. The mixture was heated and stirred (T=130°C, 16 h), then was cooled at room temperature. A deep orange solid was obtained, that was recovered by filtration and washed with water in air, until a brilliant yellow solid was obtained. The product was dried under vacuum. Yield: 0.932g (72%).

IR (ATR, ν, cm^{-1}): 2918 w, 2335 m, 2032 w, 1401 w, 1351 w, 1015 m. The spectrum was in good agreement with previously reported data (see ref. [45])

Synthesis of *trans*-[$Pt(\mu\text{-}Br)Br(PPh_3)]_2$

A Caurius tube equipped with a magnetic stirrer was charged, under Ar atmosphere, with [$Pt(Br_2)(NCMe)_2$] (0.932g, 2.13mmol), PPh_3 (0.559g, 2.13mmol, P/Pt = 1 molar ratio) and CH_3CN (10ml). The temperature was raised (T=135°C) and the mixture was stirred (6h), then it was cooled to room temperature. A yellow precipitate ([$Pt(Br_2)(NCMe)(PPh_3)$]) was obtained. The suspension was transferred into a Schlenk tube and the solvent was completely removed under vacuum. The residue was suspended in toluene and refluxed (2h). A brilliant orange solid precipitated, which, after cooling the mixture, was recovered by filtration in air, washed with pentane and dried under vacuum. Yield: 1.239g (94%).

IR (ATR, ν, cm^{-1}): 3073 w, 3053 w, 2680 w, 2577 w, 2321 w, 2191 w, 1961 w, 1906 w, 1808 w, 1670 w, 1570 w, 1480 m, 1432 s, 1314 w, 1184 w, 1094 s, 996 w, 741 s, 686 s. In good agreement with previously reported data (see ref. [24]).

^{31}P-NMR (ppm) (DMSO): 18.34 ($^1J_{P\text{-}Pt}$=3761 Hz). In good agreement with previously reported data (see ref. [45]).

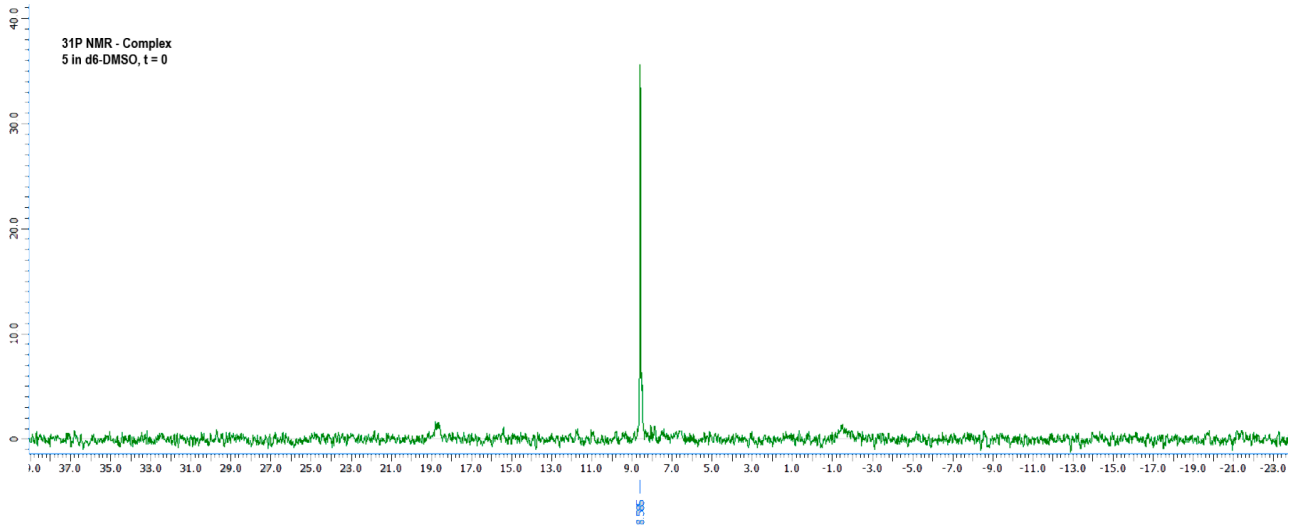

Figure S1. ^{31}P NMR spectrum: Complex **5** in d6-DMSO, t = 0

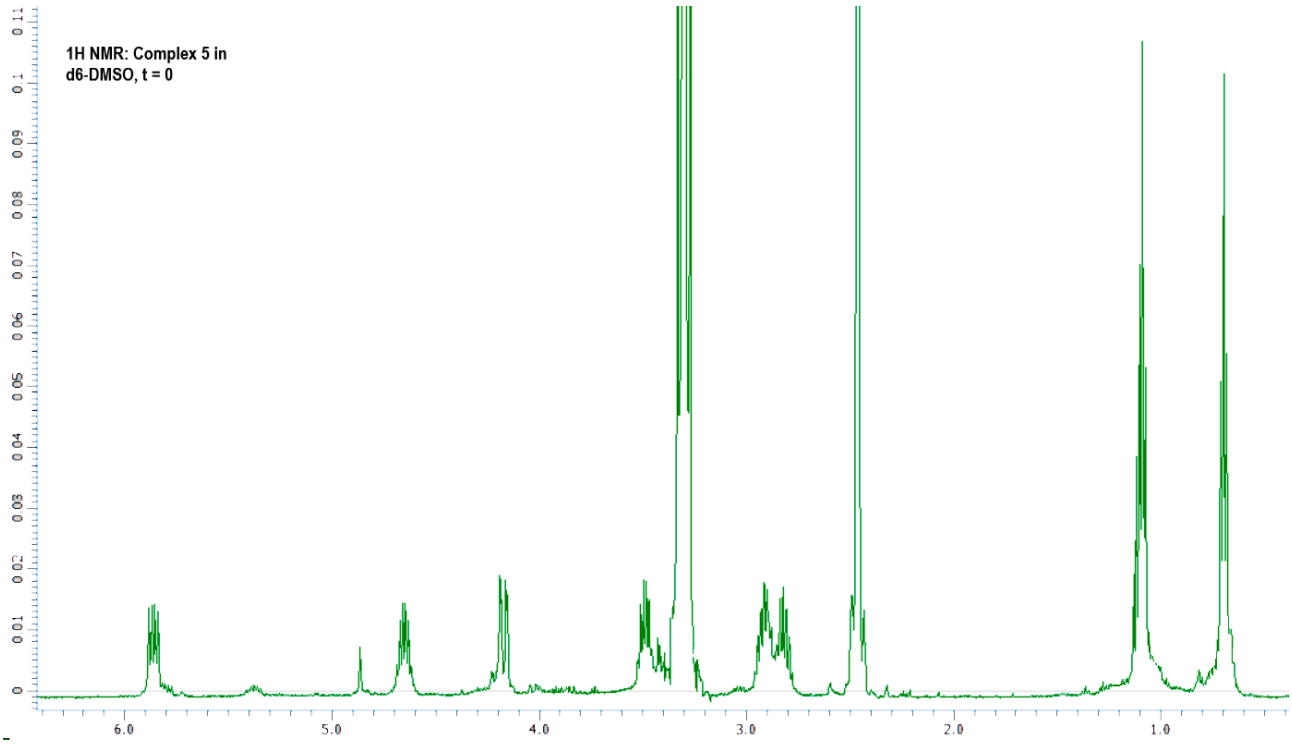

Figure S2. ^{1}H NMR spectrum: Complex **5** in d6-DMSO, t = 0. Signals due to aromatic hydrogen atoms are omitted.

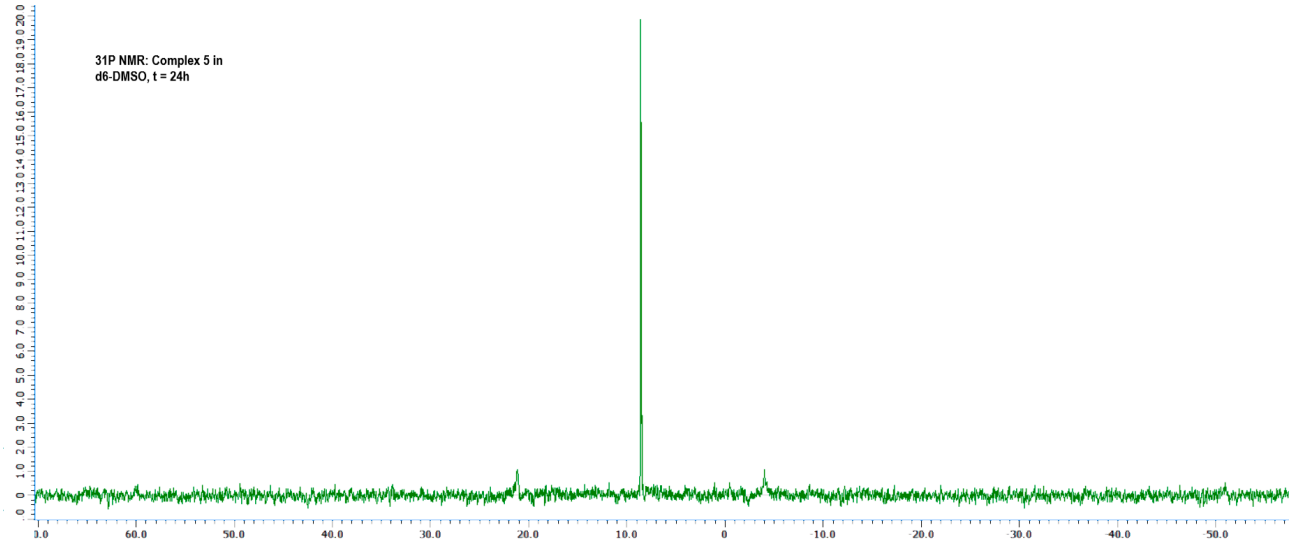

Figure S3. ^{31}P NMR spectrum: Complex **5** in d6-DMSO, t = 24h

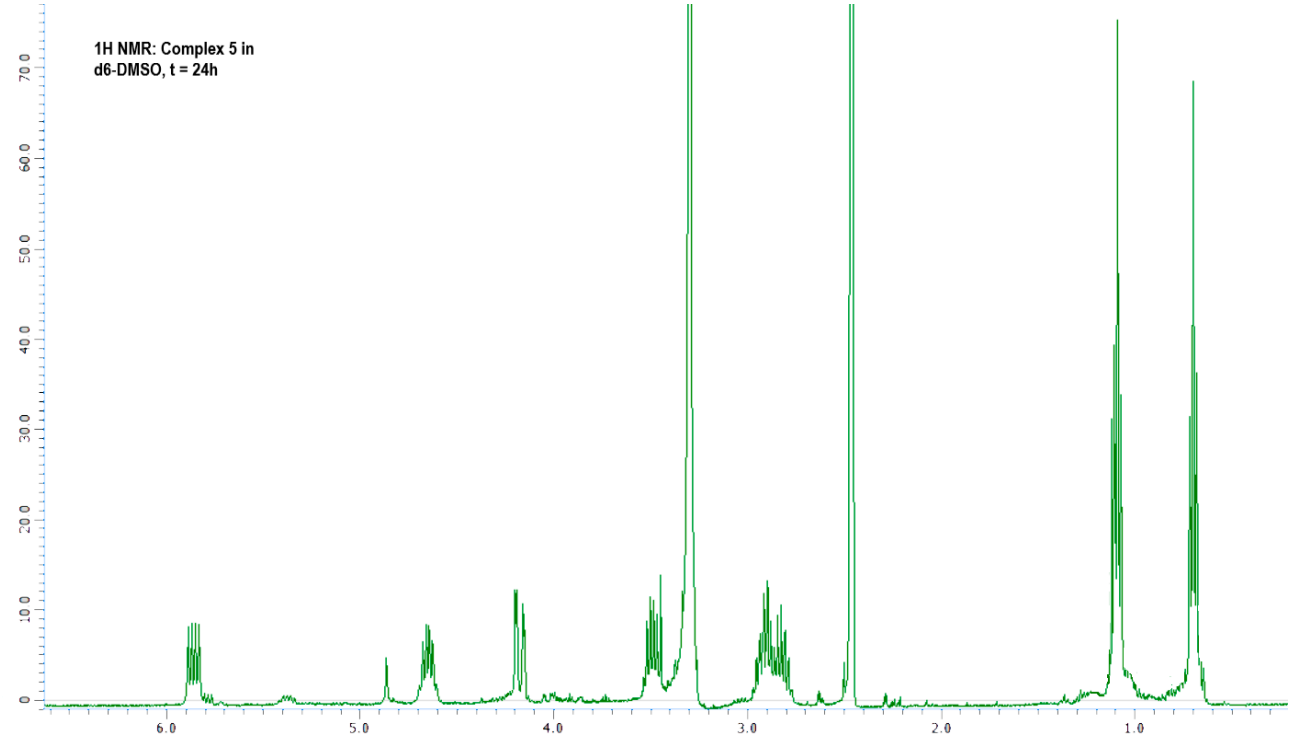

Figure S4. ^{1}H NMR spectrum: Complex **5** in d6-DMSO, t = 24h. Signals due to aromatic hydrogen atoms are omitted.

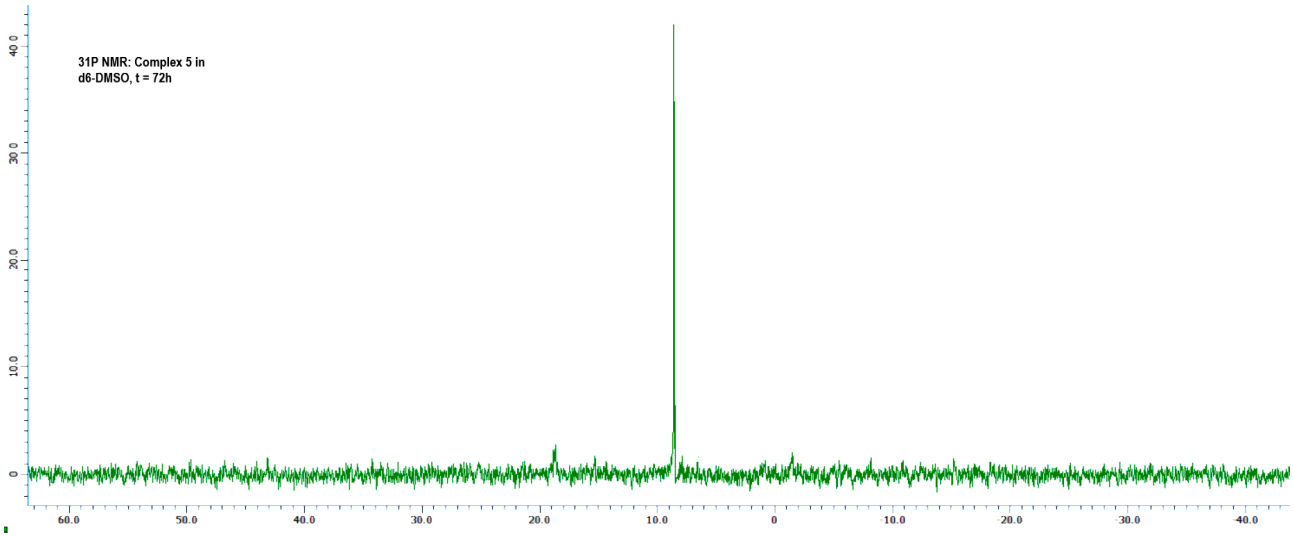

Figure S5. ^{31}P NMR spectrum: Complex **5** in d6-DMSO, t = 72h

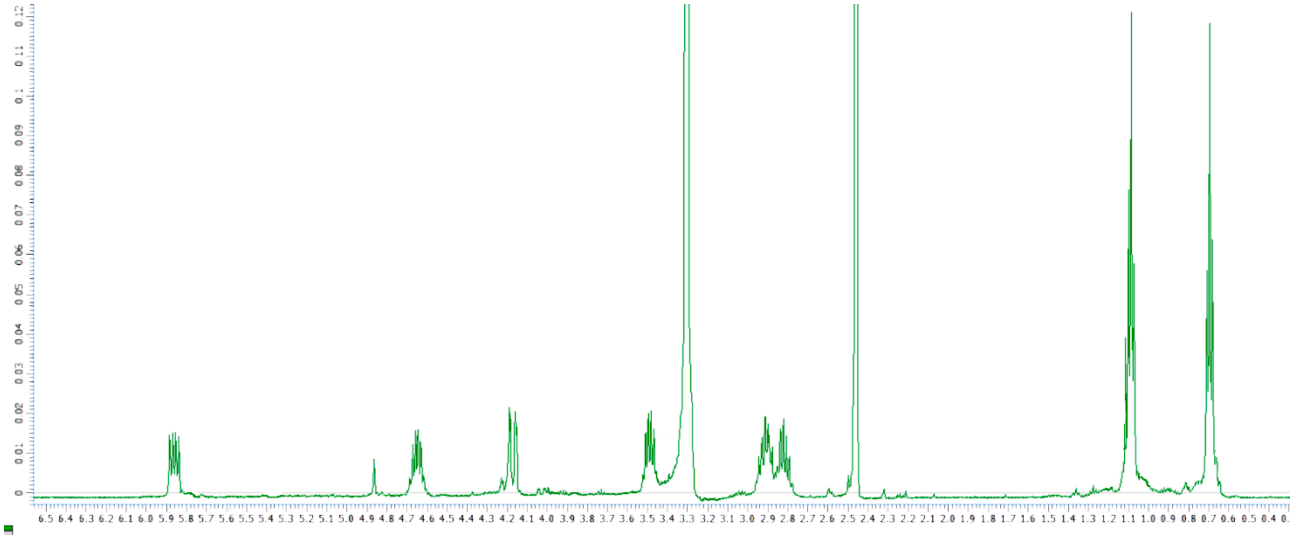

Figure S6. ^{1}H NMR spectrum: Complex **5** in d6-DMSO, t = 72h. Signals due to aromatic hydrogen atoms are omitted.

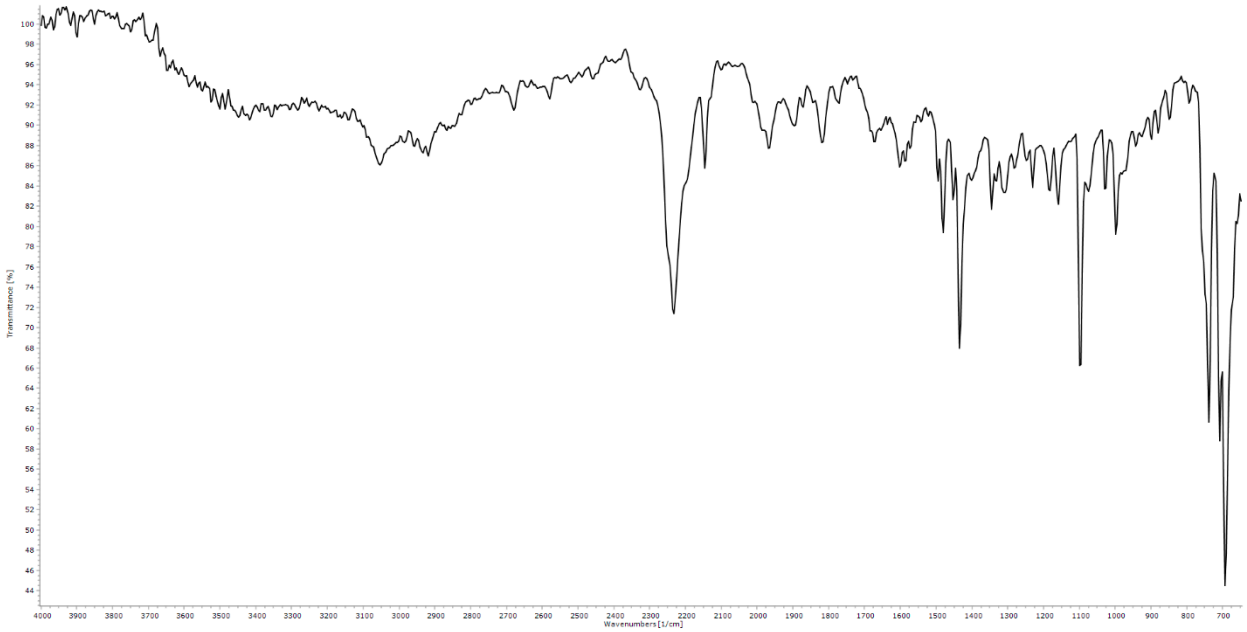

Figure S7. IR spectrum of complex **1**.

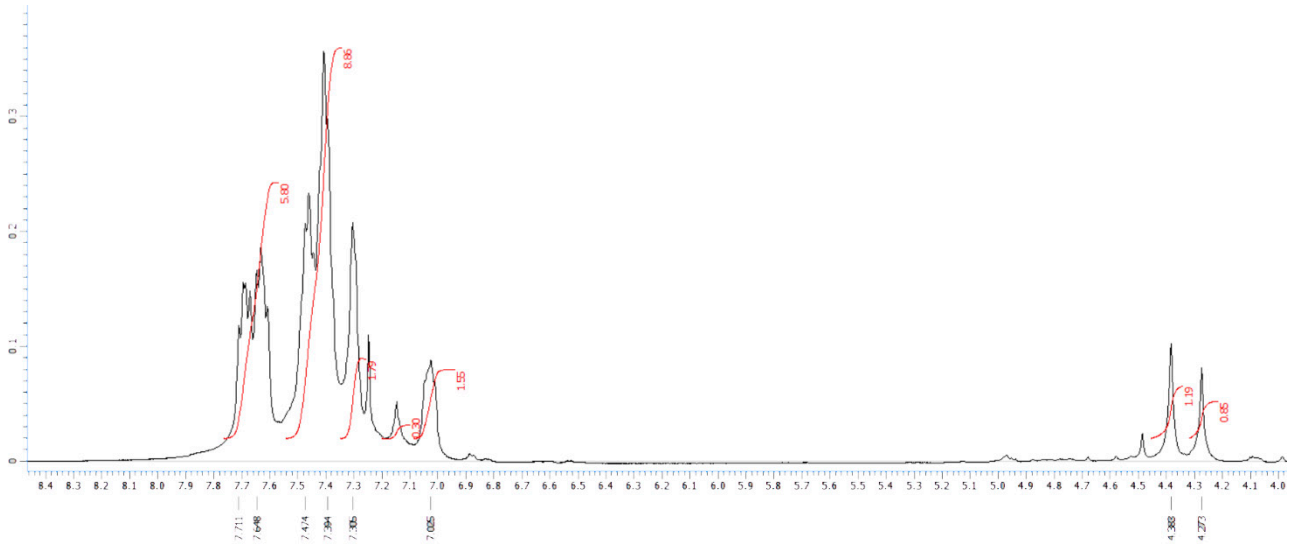

Figure S8. ^{1}H NMR of complex **1**.

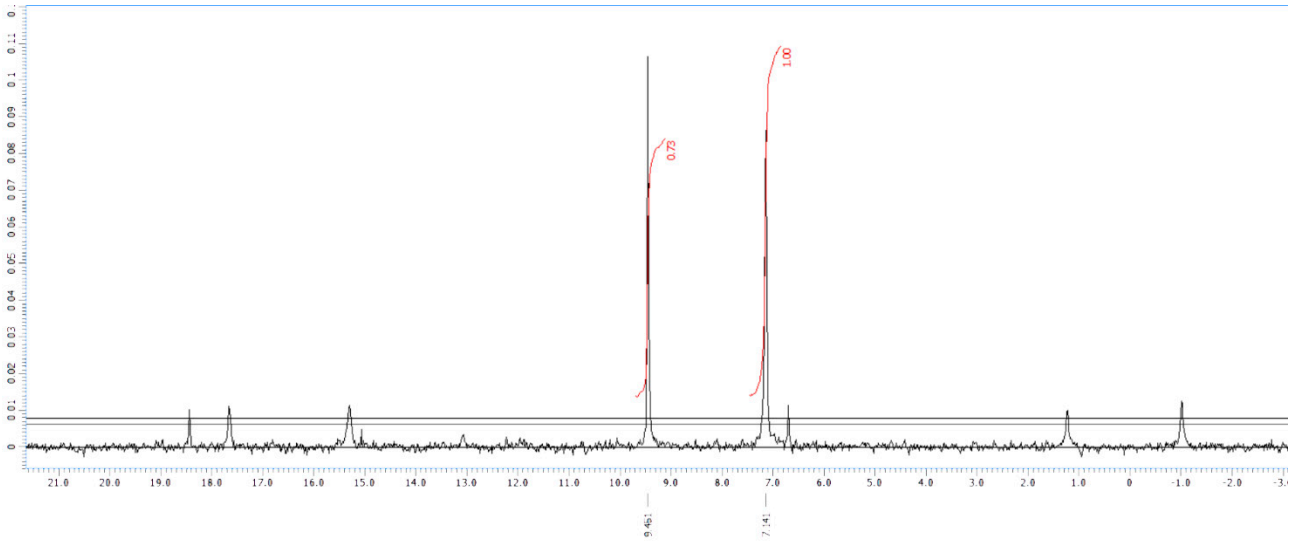

Figure S9. ^{31}P NMR of complex **1**.

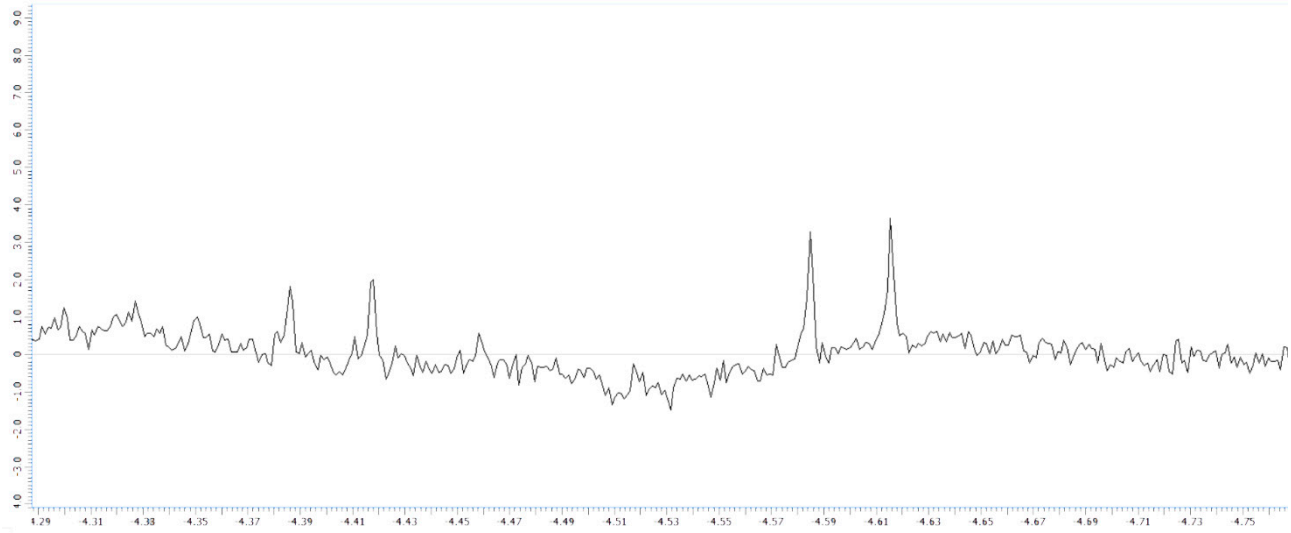

Figure S10. ^{195}Pt NMR of complex **1**.

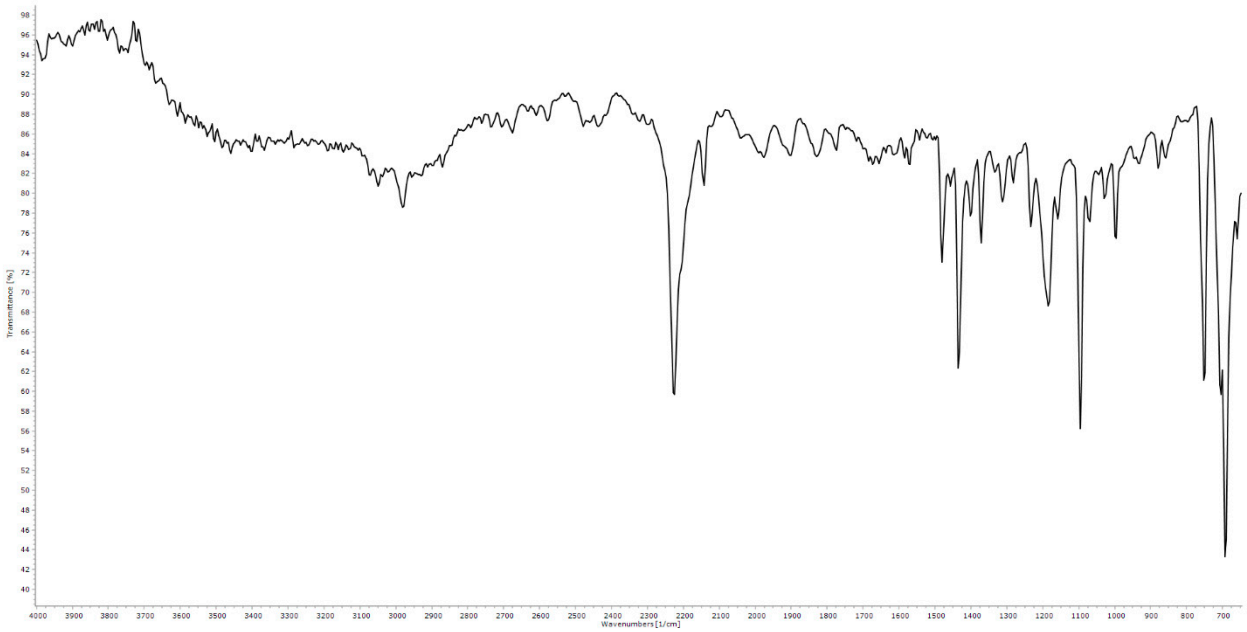

Figure S11. IR spectrum of complex **2**.

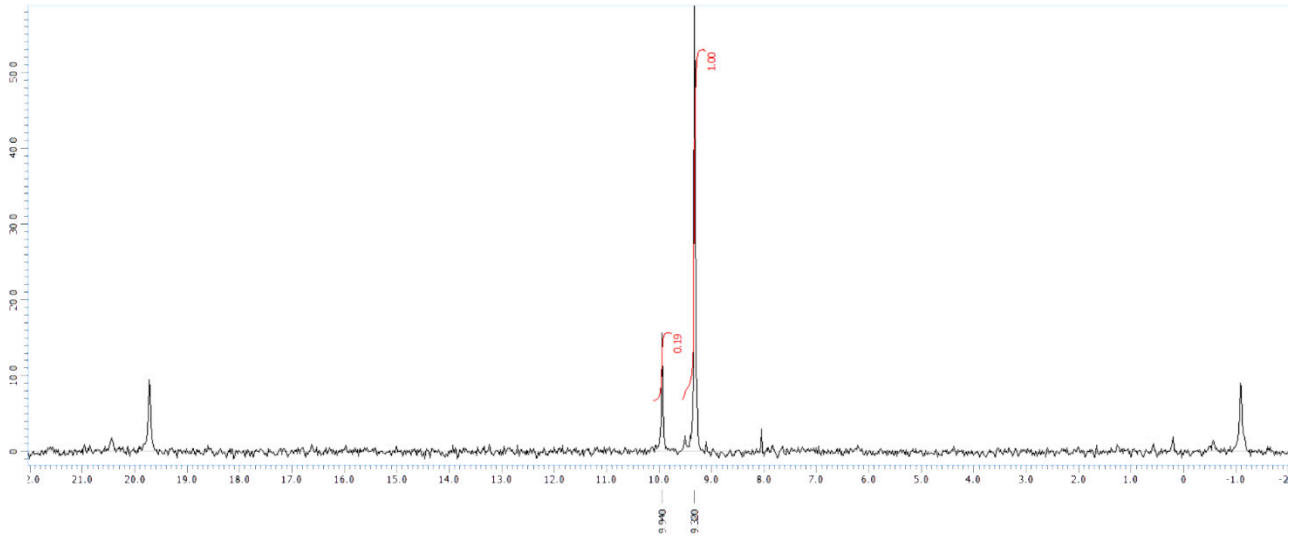

Figure S12. ^{31}P NMR of complex **2**.

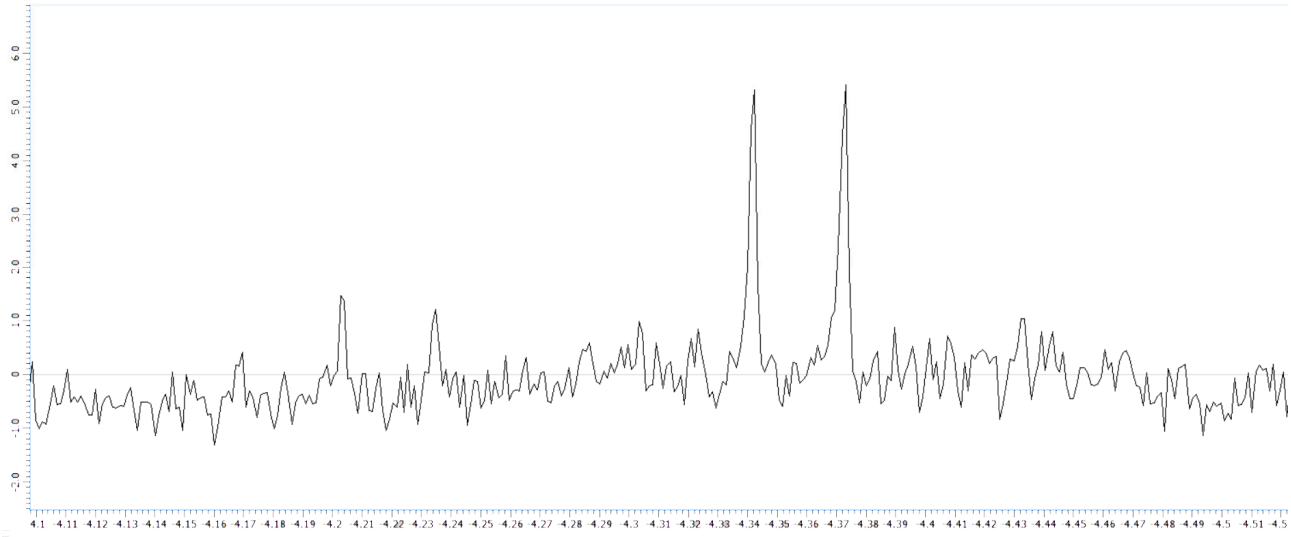

Figure S13. ^{195}Pt NMR of complex **2**.

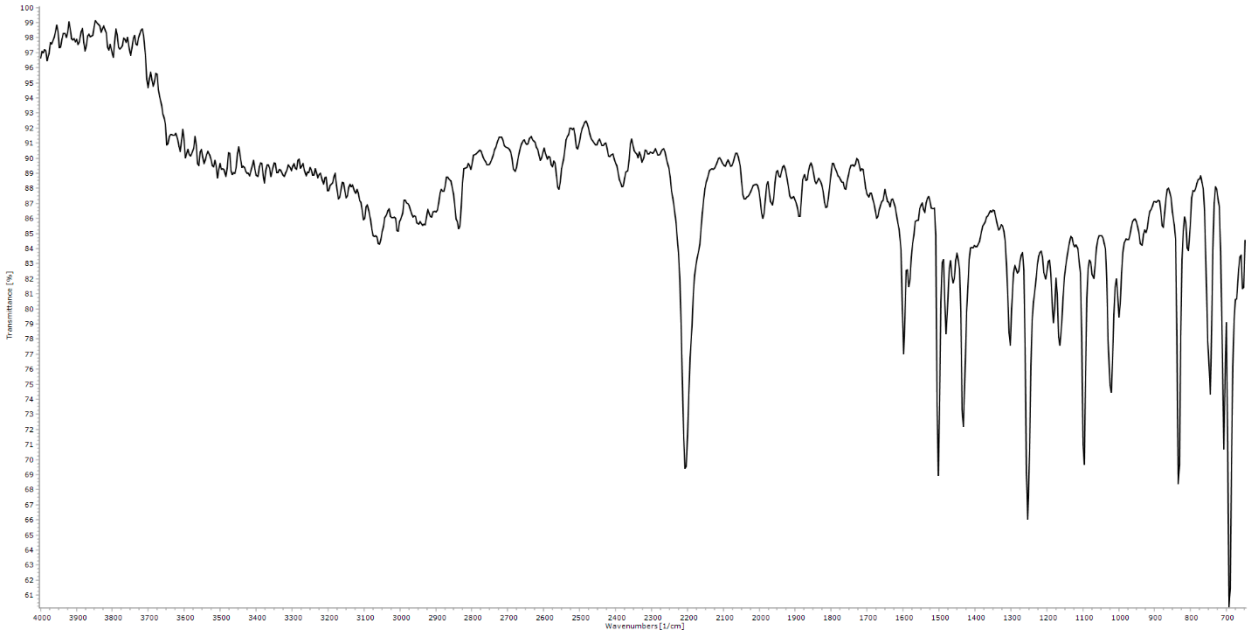

Figure S14. IR spectrum of complex **3**.

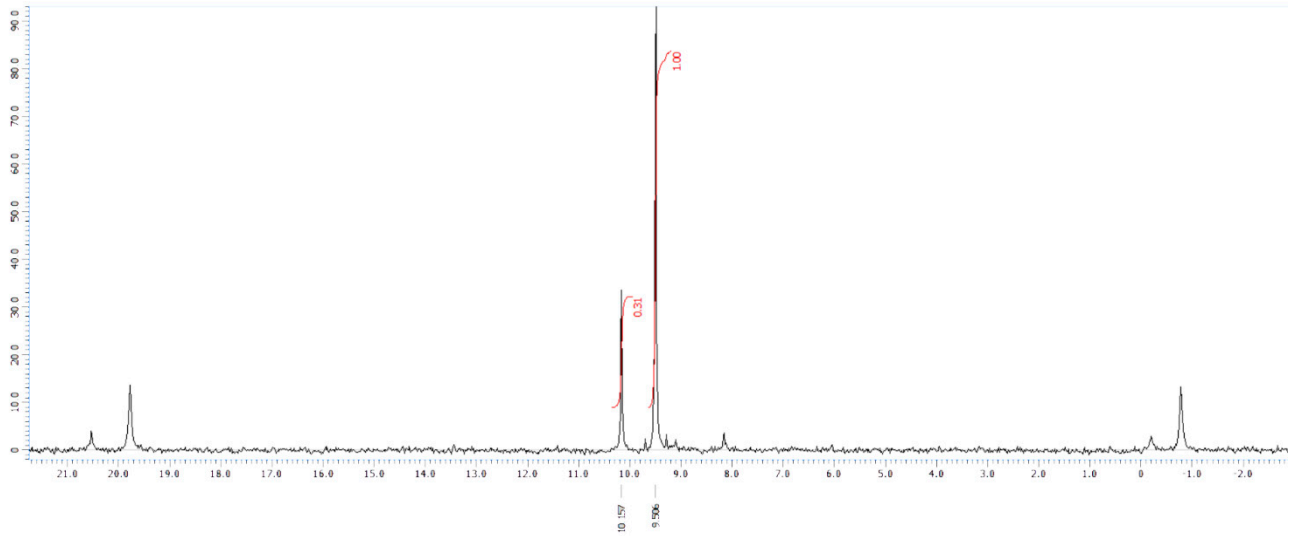

Figure S15. ^{31}P NMR of complex **3**.

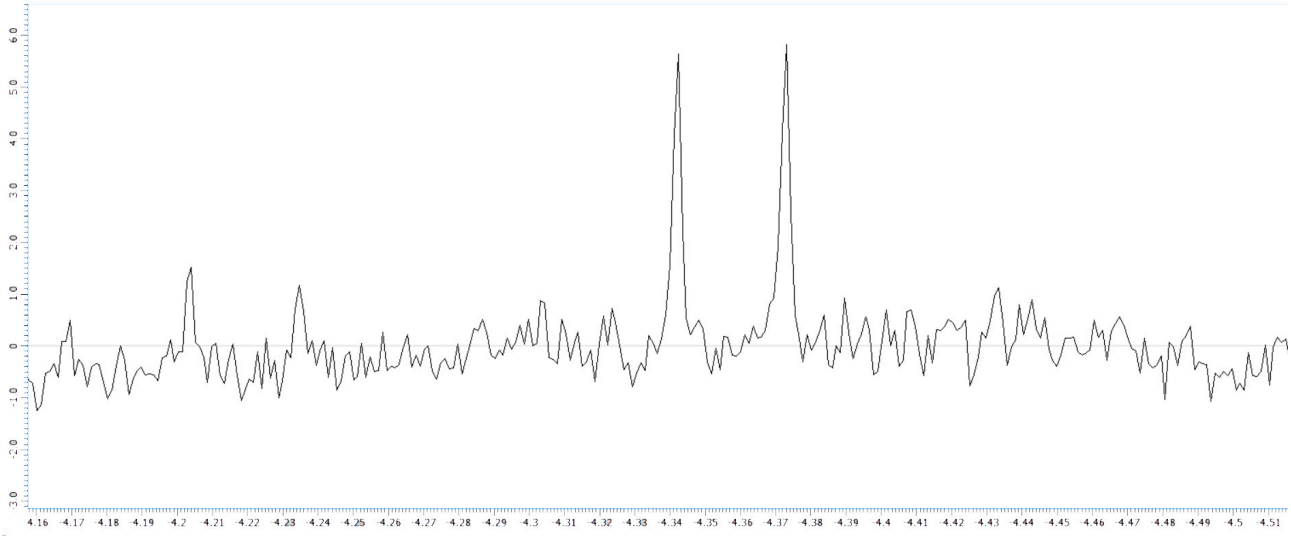

Figure S16. ^{195}Pt NMR of complex **3**.

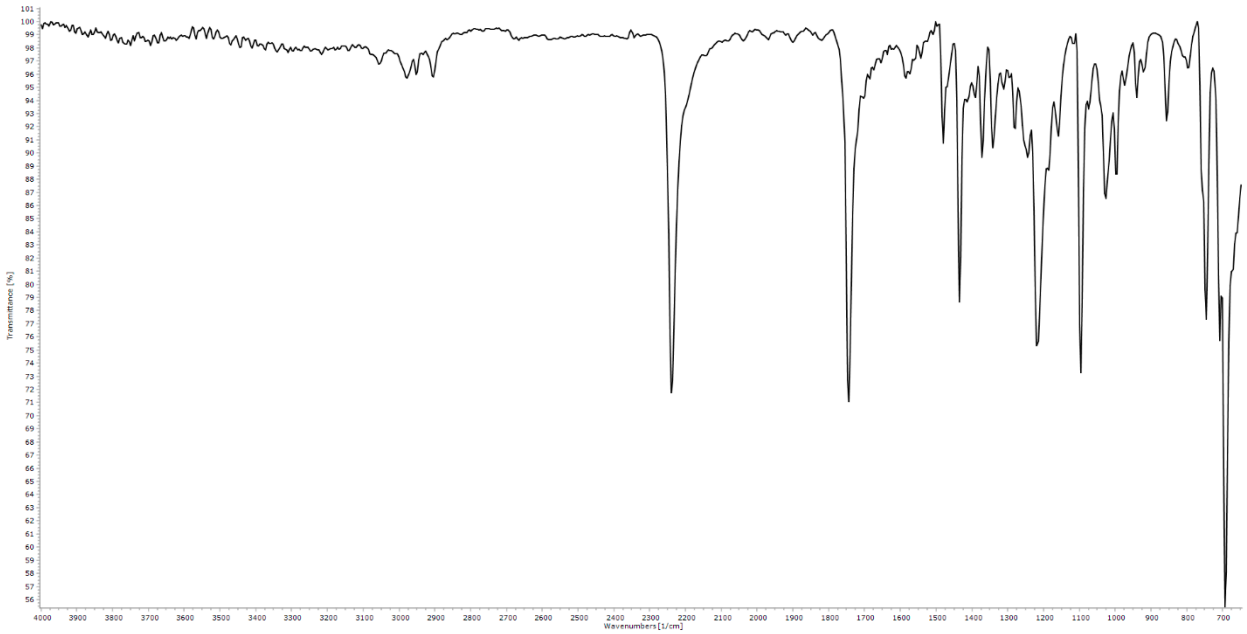

Figure S17. IR spectrum of complex **4**.

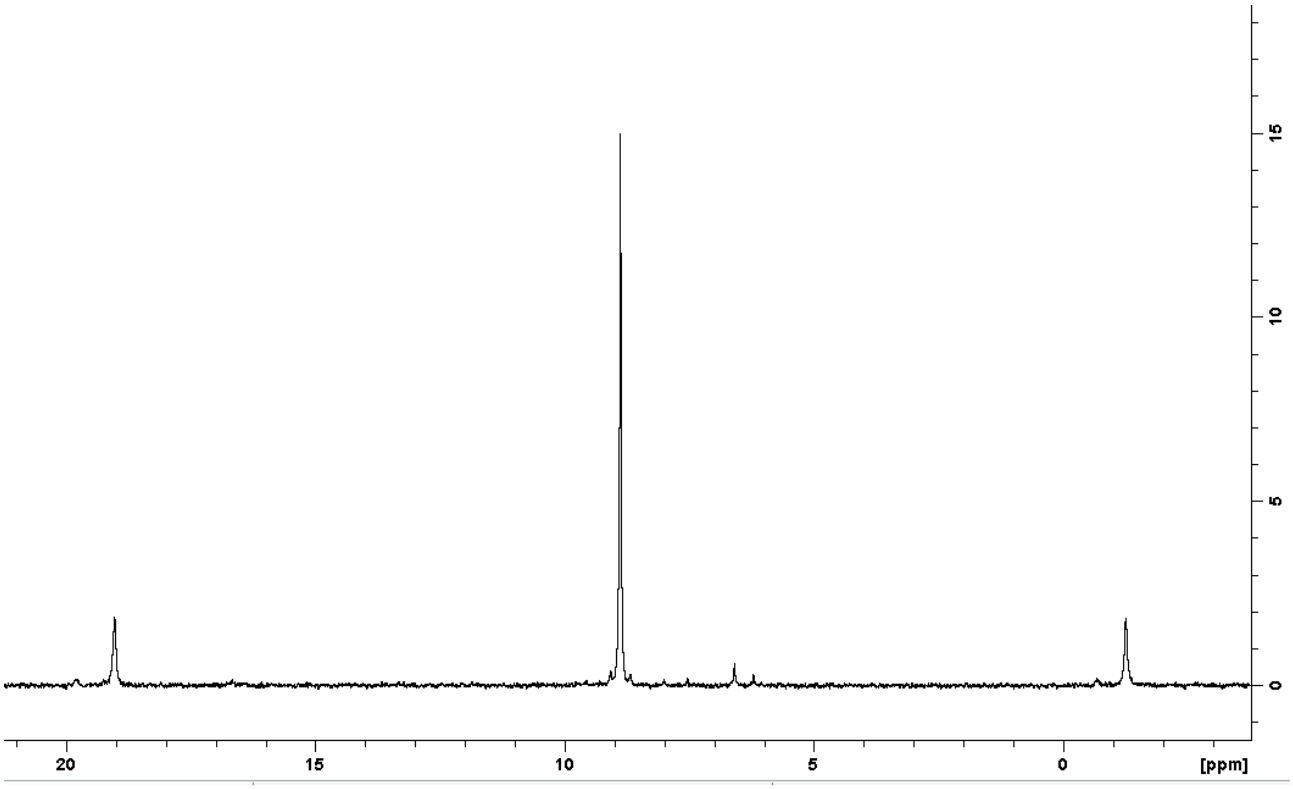

Figure S18. ^{31}P NMR of complex **4**.

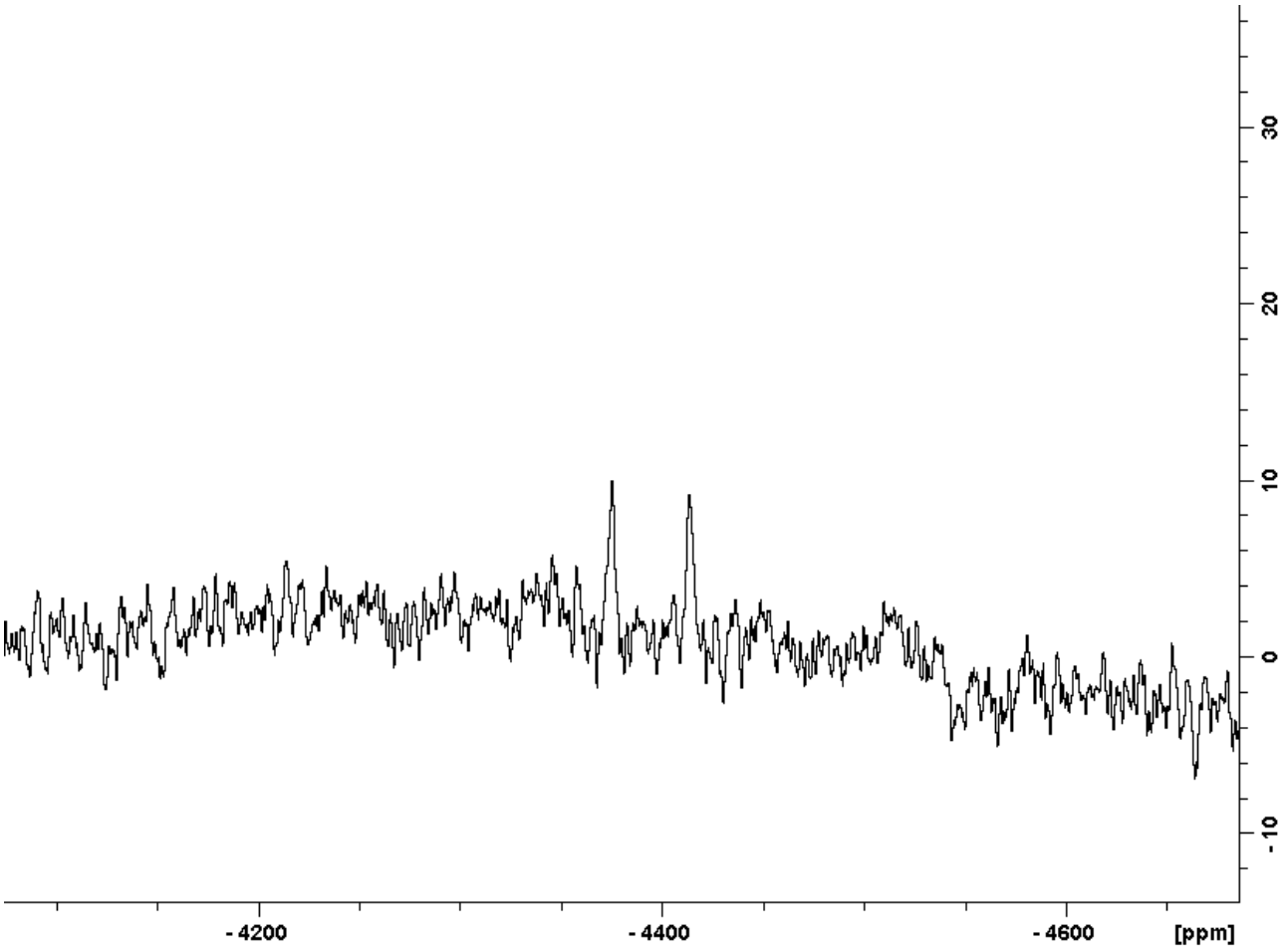

Figure S19. ^{195}Pt NMR of complex **4**.

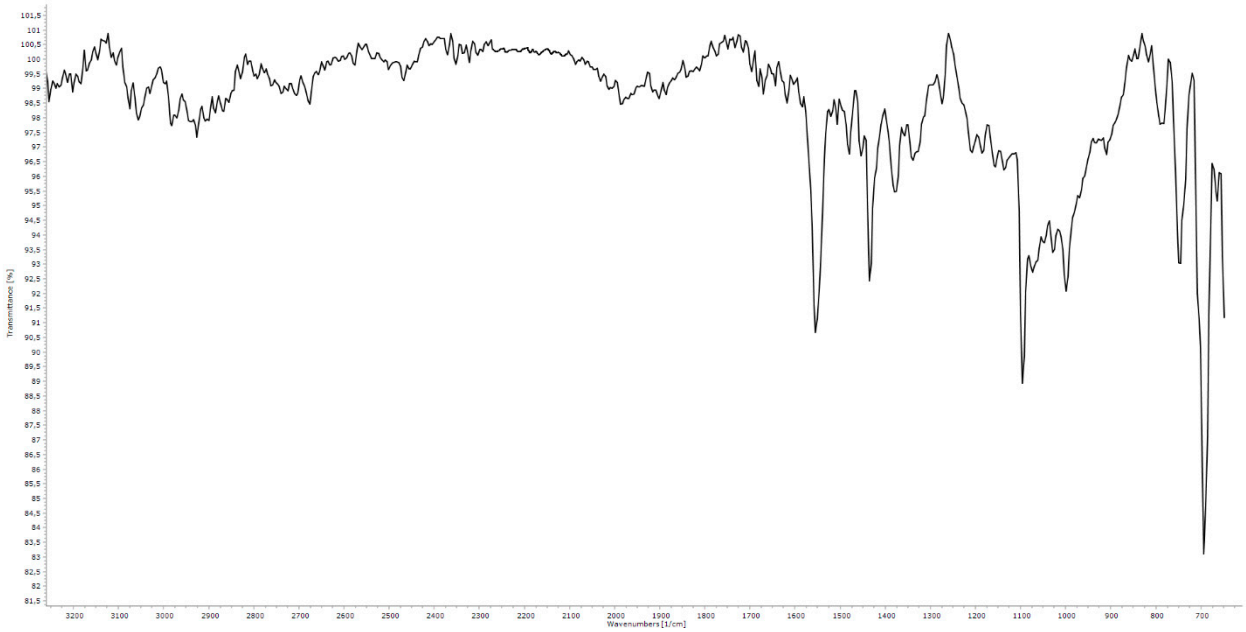

Figure S20. IR spectrum of complex **5**.

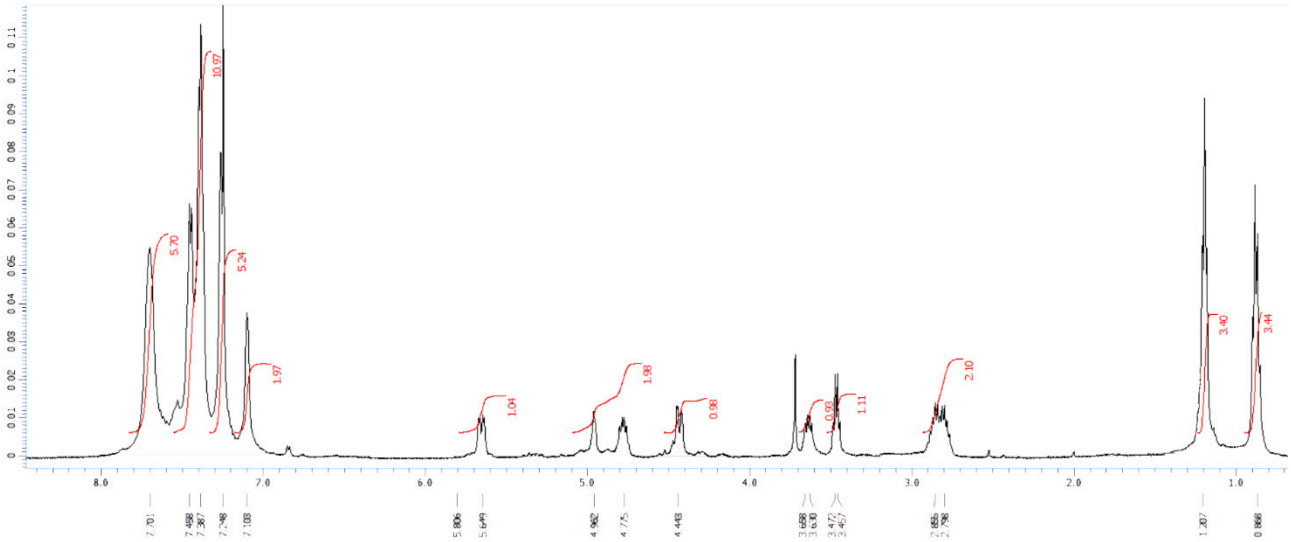

Figure S21. ^{1}H NMR of complex **5**.

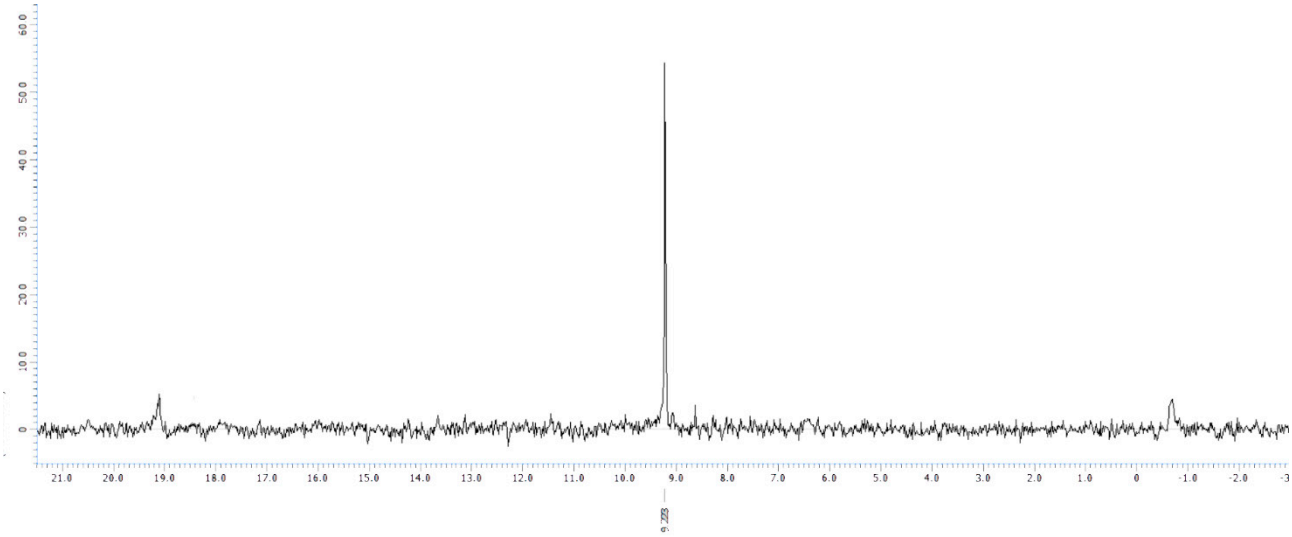

Figure S22. ^{31}P NMR of complex **5**.

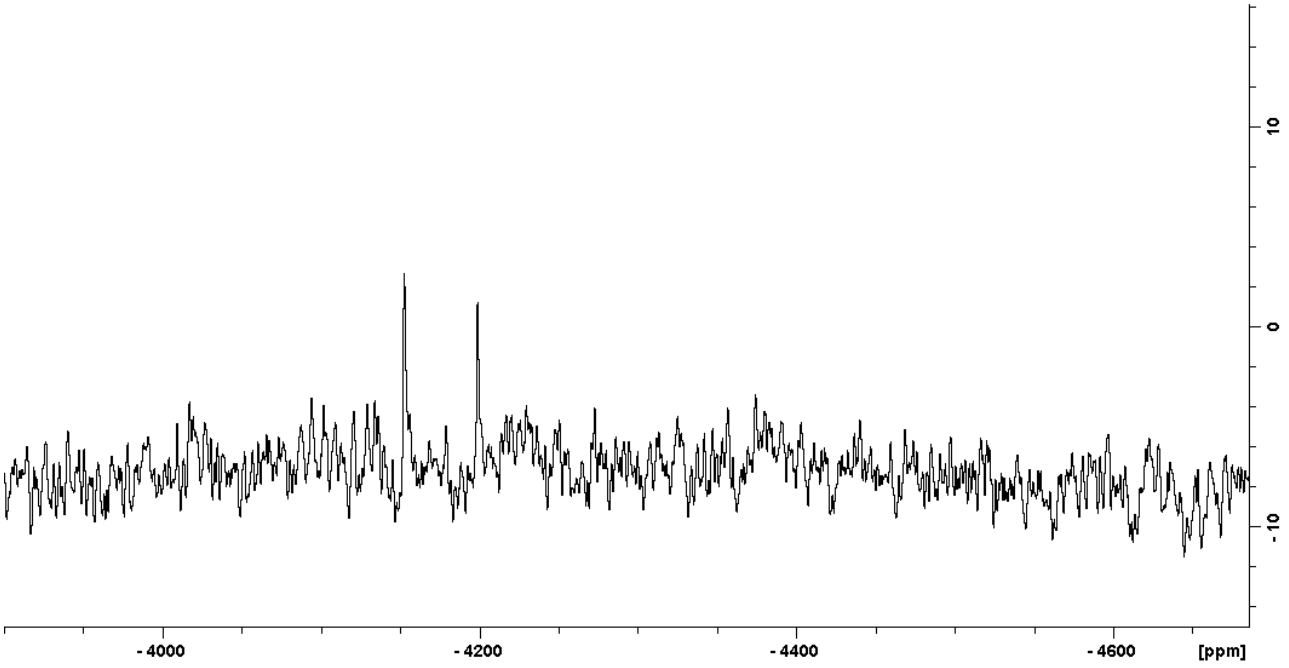

Figure S23. ^{195}Pt NMR of complex **5**.

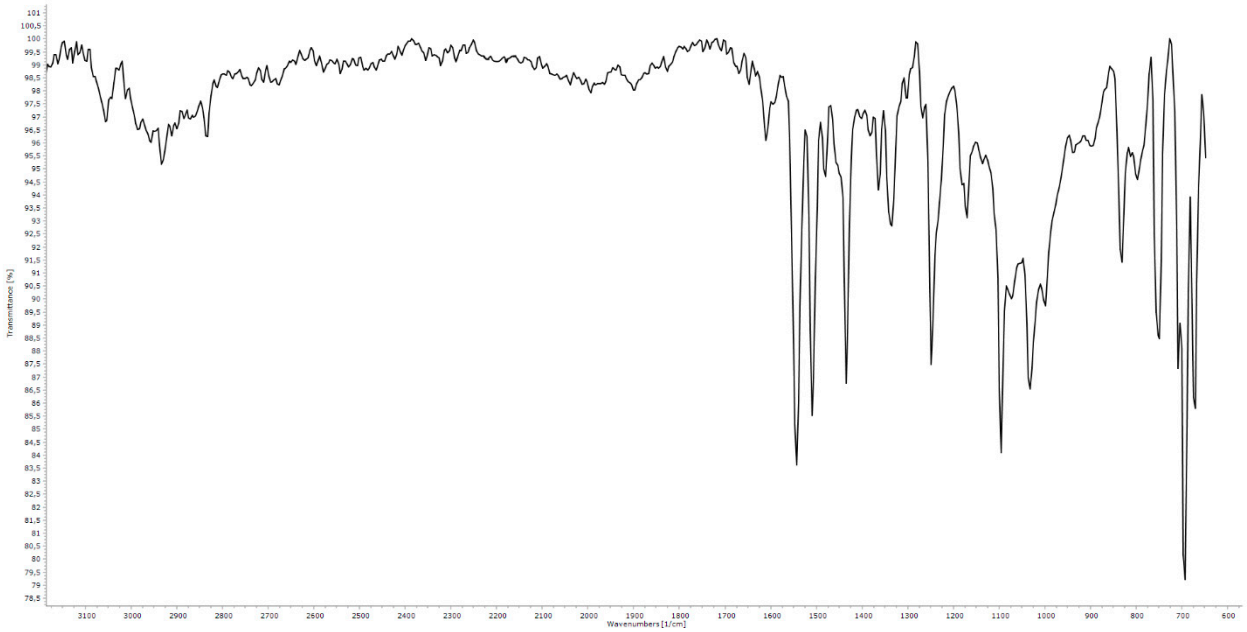

Figure S24. IR spectrum of complex **6**.

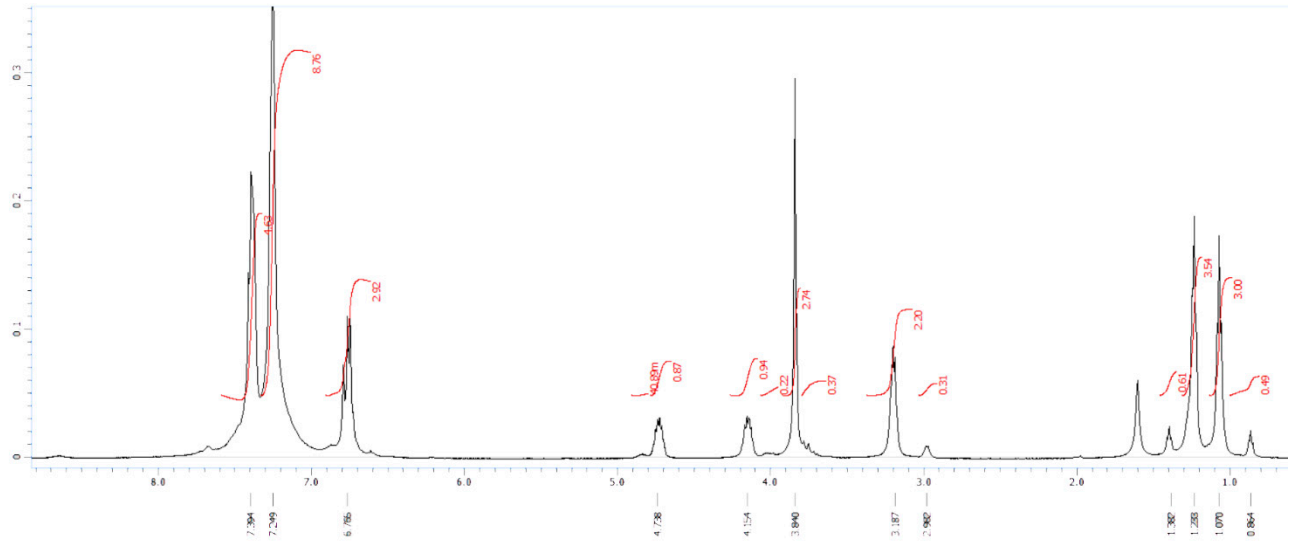

Figure S25. 1H NMR of complex **6**.

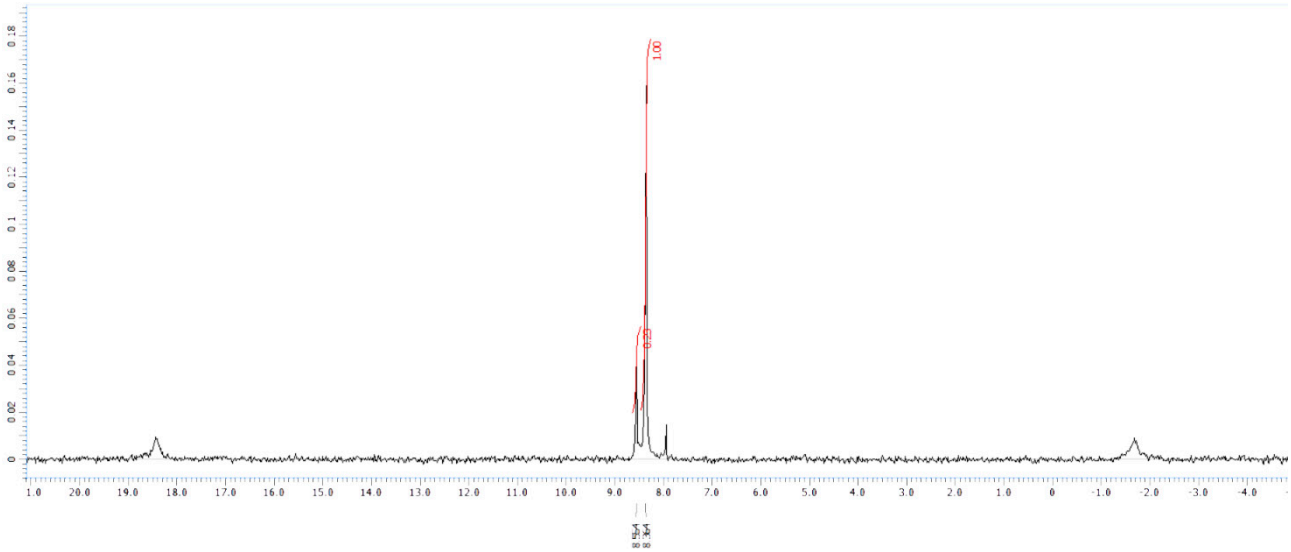

Figure S26. ^{31}P NMR of complex **6**.

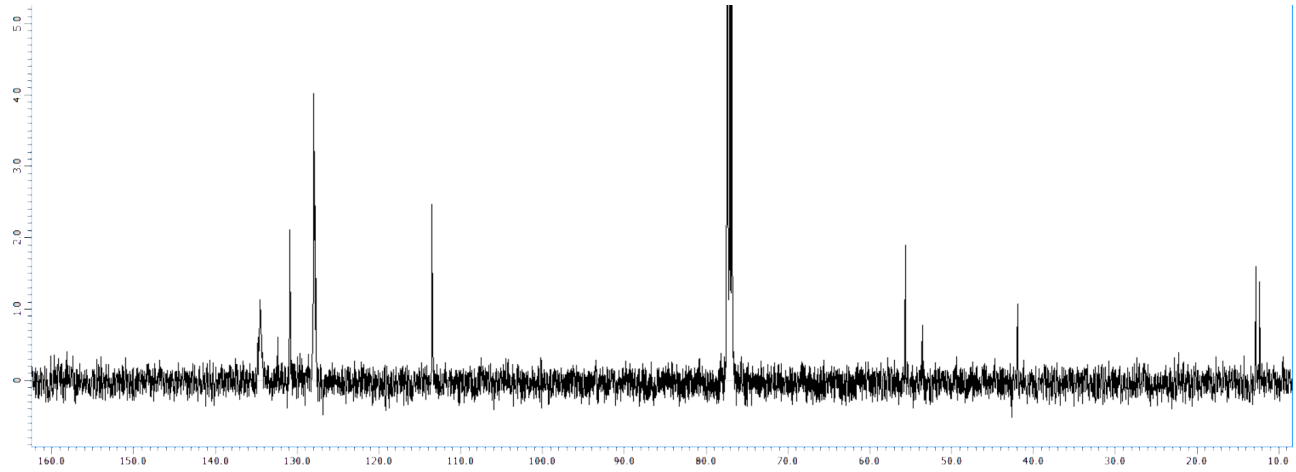

Figure S27. ^{13}C NMR of complex **6**.

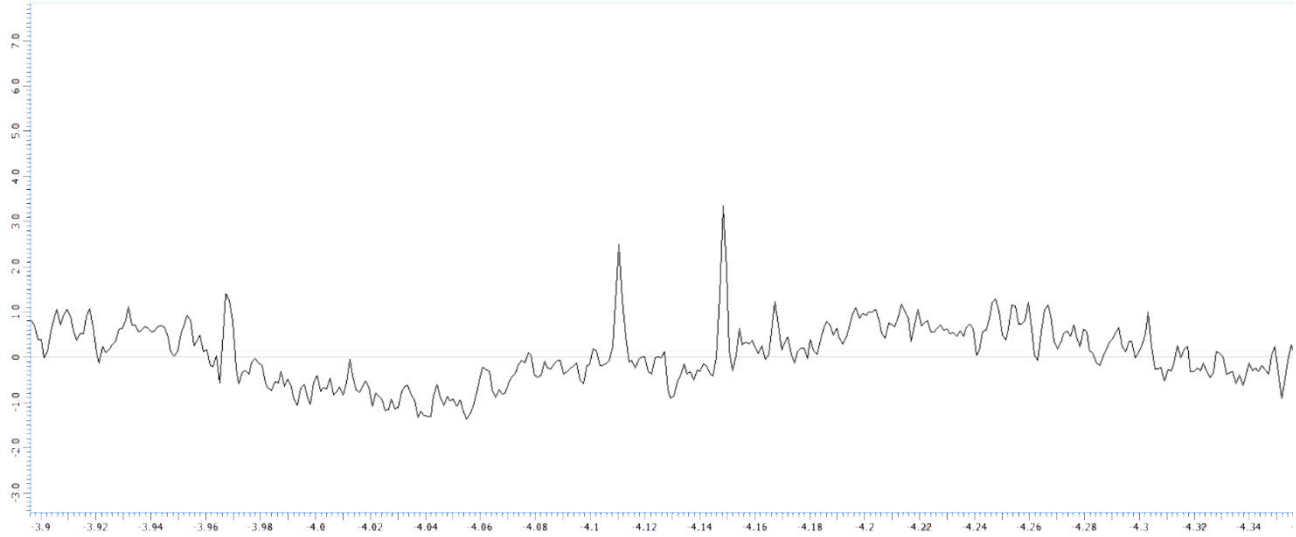

Figure S28. 195Pt NMR of complex **6**.