Chiral Platinum(II) Complexes Featuring Phosphine and Chloroquine Ligands as Cytotoxic and Monofunctional DNA-Binding Agents

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Supporting Information

Materials for synthesis

All manipulations were carried out under argon with standard Schlenk techniques. Solvents were purified by standard procedures immediately prior to use. [K_2PtCl_4] was purchased from Precmet. The ligands triphenylphosphine (PPh_3), 1,3-bis(diphenylphosphine)propane (dppp), 1,4-bis(diphenylphosphine)butane (dppb), 1,1'-bis(diphenylphosphine)ferrocene (dppf), quinoline, 4,7-dichloroquinoline, CQDP, calf thymus DNA (CT-DNA) and buffers were used as received from Sigma-Aldrich. Reagent grade solvents were appropriately distilled and dried before use. The extraction of the CQ base was described previously.[1] The synthesis of the ligands N-benzyl-7-chloroquinolin-4-amine (Q-MOD-I) and 7-chloro-N-(1-phenylethyl)quinolin-4-amine (Q-MOD-II) was carried out as reported.[2] All other commercial reagents were used without further purification.

Instrumentation

The infrared spectra were recorded on an FTIR Bomen-Michelson 102 spectrometer in the 4000-200 cm^{-1} region. Ultraviolet-visible (UV-vis) spectra were recorded on an HP 8452A diode array spectrophotometer. All NMR experiments were performed at 298 K on a Bruker DRX 400 MHz spectrometer, at 9.4 T, observing ^{1}H at 400.13, $^{13}C\{^{1}H\}$ at 100.62, $^{31}P\{^{1}H\}$ at 161.98 and $^{195}Pt\{^{1}H\}$ at 85.65 MHz. The NMR spectra were recorded in dichloromethane-d_2, acetone-d_6 and DMSO-d_6, with TMS (^{1}H and $^{13}C\{^{1}H\}$), 85% H_3PO_4 ($^{31}P\{^{1}H\}$) and [K_2PtCl_4] ($^{195}Pt\{^{1}H\}$ δ -1628 ppm) as the internal and external references, respectively. In all NMR spectra, multiplicity is indicated as follows: bs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), quint (quintuplet), sept (septet), or m (multiplet). Coupling constant values (in Hertz) and the number of protons for each signal are also indicated. When the two axial configurations present in CQ-Pt complexes **5-8** were clearly observed, they were labeled as X and X´, at a ratio of approximately 50:50 ± 10.

The electrochemical experiments were performed with a BAS-100B/W MF-9063 Bioanalytical Systems Instrument under an argon atmosphere at room temperature with tetrabutylammoniumperchlorate (TBAP Fluka Purum) as the supporting electrolyte. The electrochemical cell was equipped with platinum working and auxiliary electrodes and Ag/AgCl as the reference electrode in a Luggin capillary probe, a medium in which ferrocene is oxidized at 0.43 V (Fc+/Fc). The voltammogram was performed at a scan rate of 0.100 V s^{-1}. ESI(+) Mass spectra were obtained by direct infusion in a Waters Synapt Mass Spectrometer in positive ion mode, utilizing CH_3OCH_3 (LC/MS grade from Honeywell; B&J Brand) as the solvent. The circular dichroism experiments were performed on a JASCO J720 spectropolarimeter with a cylindrical cuvette with an optical path of 1 cm at 25ºC.

The diffraction experiment was carried out in a single crystal of complex **7a**, grown by the slow evaporation method in a mixture of solvents (dichlomethane/ether). The single crystal in a colorless prism form was mounted on an Enraf-Nonius Kappa-CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The dimensions and the symmetry of the unit cell were measured based on all reflections. Data collection was performed at room temperature (293 K) and a low temperature (100 K) after the unit cell dimensions were determined with the aid of the COLLECT program.[3] For the low temperature (100 K) measurements, an Oxford Cryosystem cryogenic device was used. Integration and scaling of the reflections were carried out with the HKL Denzo-Scalepack software package.[4] The structure was solved through direct methods of phase retrieval with SHELXS-2013[5] and the refinement by full-matrix least-squares on F^2 with SHELXL-2013[5] within the WinGX-v.2013.3[6] program package. Absorption correction was performed by the Gaussian method.[7] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated positions and refined using riding mode. The constrained positions and fixed isotropic thermal parameters for C–H hydrogen atoms were the bond lengths of 0.93

and 0.97 Å for C_{sp}^2–H (aromatic rings) and C_{sp}^3–H (methylene groups), respectively, considering $U_{iso}(H) = 1.2U_{eq}(C)$. Positional disorder was observed in the C121-C126 phenyl ring and in the PF6- anion, which can be reliably modeled. In both cases, the disorders were refined over two site occupancy factors (SOF) with 50% occupancy for each C-H group (phenyl ring) and fluorine atom (PF_6^- anion), respectively. Once the refinement was concluded, structure analysis and preparation of artwork were performed using MERCURY and ORTEP-3 software. WinGX was used to prepare the material for publication (CIF file).

Characterization of complexes 1-8

***Cis*-$[PtCl_2(PPh_3)_2].^1/_2H_2O$ (1)**

A white solid was obtained with a yield of 96.4%. Elemental analysis (%) Calc. for $C_{36}H_{30}Cl_2P_2Pt.^1/_2H_2O$: C 54.28; H 3.88. Found: C 54.37; H 4.05. IR ν (C-H) 3053 cm^{-1}, (overtones aromatics) 1970-1827cm^{-1}, (C-C aromatic) 1586 cm^{-1}, ν (C=C) 1481 cm^{-1}, ν (P-C) 1097 cm^{-1}, (Ph-P-Ph) 696 cm^{-1}, ν (*cis*-Pt-P) 518 and 527 cm^{-1}, (*cis*-Pt-Cl) 319 and 294 cm^{-1}. UV-Vis [ε, λ (assignation)]: 33500 M^{-1} cm^{-1}, 236 nm (π–π*); 10300 M^{-1} cm^{-1}, 272 nm (M-L); 8270 M^{-1} cm^{-1}, 280 nm (L-M); 587 M^{-1} cm^{-1}, 332 nm (d-d). NMR-^{1}H (CH_2Cl_2-d_2) [δ ppm, (integral; multiplicity; assignation, *J* Hz)]: 7.20 (2H, dt, Hc, $^3J_{metha}$ = 1.76 Hz and $^4J_{ortho}$ = 7.72 Hz), 7.36 (1H, m, Hd), 7.47 (2H, m, Hb). NMR-^{13}C{^{1}H} (CH_2Cl_2-d_2) [δ ppm (multiplicity, assignation, *J* Hz)]: 128.29;128.35 (d, Cc, ^3J C-P = 5.70;5.66 Hz), 130.14;129.46 (dd, Ca, ^1J C-P = 67.56 Hz and ^3J C-P = 2.60 Hz), 131.25 (Cd), 135.13;135.18 (d, Cb, ^2J C-P = 5.24;5.26 Hz). NMR-^{31}P{^{1}H} (CH_2Cl_2-d_2) [δ ppm, (assignation, multiplicity)]: 13.72 (PPh_3, s, ^1J P-Pt = 3681.55 Hz). NMR-^{195}Pt{^{1}H} (CH_2Cl_2-d_2) [δ ppm, (multiplicity, *J* Hz)]: -4414.02 (t, ^1J Pt-P = 3670.24 Hz).

[$PtCl_2$(dppp)].$^1/_2H_2O$ (2)

A white solid was obtained with a yield of 83.2%. Elemental analysis (%) Calc. for $C_{27}H_{26}Cl_2P_2Pt.^1/_2H_2O$: C 47.17; H 3.96. Found: C 47.28; H 4.04. IR ν (C-H) 3053 cm^{-1}, (overtones aromatics) 1971-1813 cm^{-1}, (C-C aromatic) 1586 cm^{-1}, ν (C=C) 1481 cm^{-1}, ν (P-C) 1101 cm^{-1}, (Ph-P-Ph) 675 cm^{-1}, ν (Pt-P) 515 cm^{-1}, (Pt-Cl) 309 and 291 cm^{-1}. UV-Vis [ε, λ (assignation)]: 33000 M^{-1} cm^{-1}, 236 nm (π–π*); 16070 M^{-1} cm^{-1}, 252 nm (M-L); 10275 and 6666 M^{-1} cm^{-1}, 268 and 276 nm (L-M); 1403 M^{-1} cm^{-1}, 300 nm (d-d). NMR-^{1}H (CH_2Cl_2-d_2) [δ ppm, (integral; multiplicity; assignation, *J* Hz)]: 2.01 (2H, m, Hf), 2.52 (4H, m, He), 7.45 (8H, m, Hc), 7.49 (4H, m, Hd), 7.75 (8H, m, Hb). NMR-^{13}C{^{1}H} (CH_2Cl_2-d_2) [δ ppm (multiplicity, assignation, *J* Hz)]: 73.20 (d, Ce, ^1J C-P = 70.56 Hz), 76.23;76.28 (d, Cf, ^2J C-P = 5.09;5.11 Hz), 128.33;128.39 (d, Cc, ^3J C-P = 5.66;5.64 Hz), 131.44 (d, Ca, ^1J C-P = 67.34 Hz), 131.66 (Cd), 135.28;135.33 (d, Cb, ^2J C-P = 5.42;5.39 Hz). NMR-^{31}P{^{1}H} (CH_2Cl_2-d_2) [δ ppm, (assignation, multiplicity)]: -7.61 (dppp, s, ^1J P-Pt = 3418.50 Hz).

[$PtCl_2$(dppb)].$2H_2O$ (3)

A white solid was obtained with a yield of 96.3%. Elemental analysis (%) Calc. for $C_{28}H_{28}Cl_2P_2Pt.2H_2O$: C 46.08; H 3.87. Found: C 46.16; H 4.43. IR ν (C-H) 3053 cm^{-1}, (overtones aromatics) 1967-1813 cm^{-1}, (C-C aromatic) 1587 cm^{-1}, ν (C=C) 1473 cm^{-1}, ν (P-C) 1103 cm^{-1}, (Ph-P-Ph) 700 cm^{-1}, ν (Pt-P) 536 cm^{-1}, (*cis*-Pt-Cl) 312 and 291 cm^{-1}. UV-Vis [ε, λ (assignation)]: 31220 M^{-1} cm^{-1}, 234 nm (π–π*); 16076 M^{-1} cm^{-1}, 252 nm (M-L); 9333 and 6978 M^{-1} cm^{-1}, 268 and 276 nm respectively (L-M); 871 M^{-1} cm^{-1}, 306 nm (d-d). NMR-^{1}H (CH_2Cl_2-d_2) [δ ppm, (integral; multiplicity; assignation, *J* Hz)]: 1.83 (4H, m, Hf), 2.61 (4H, m, He), 7.51 (8H, dt, Hc, $^3J_{metha}$ = 1.60 Hz and $^4J_{ortho}$ = 7.60 Hz), 7.57 (4H, m, Hd), 7.76 (8H, m, Hb). NMR-^{13}C{^{1}H} (CH_2Cl_2-d_2) [δ ppm (multiplicity, assignation, *J* Hz)]: 73.20 (d, Ce, ^1J C-P = 70.56 Hz), 76.23;76.28 (d, Cf, ^2J C-P = 5.09;5.11 Hz), 128.33;128.39 (d, Cc, ^3J C-P =

5.66;5.64 Hz), 131.44 (d, Ca, ^{1}J C-P = 67.34 Hz), 131.66 (Cd), 135.28;135.33 (d, Cb, ^{2}J C-P = 5.42;5.39 Hz). NMR-$^{31}P\{^{1}H\}$ (CH_2Cl_2-d_2) [δ ppm, (assignation, multiplicity)]: 9.81 (dppb, s, ^{1}J P-Pt = 3545.33 Hz).

[$PtCl_2$(dppf)]. $2H_2O$ (4)

A yellow solid was obtained with a yield of 83.2%. Elemental analysis (%) Calc. for $C_{34}H_{28}Cl_2FeP_2Pt.2H_2O$: C 47.68; H 3.77. Found: C 47.37; H 3.52. IR ν (C-H) 3053 cm^{-1}, (overtones aromatics) 1973-1814 cm^{-1}, (C-C aromatic) 1587 cm^{-1}, ν (C=C) 1481 cm^{-1}, ν (P-C) 1097 cm^{-1}, (Ph-P-Ph) 695 cm^{-1}, ν (Pt-P) 520 cm^{-1}, (*cis*-Pt-Cl) 318 and 295 cm^{-1}. UV-Vis [ε, λ (assignation)]: 33423 M^{-1} cm^{-1}, 234 nm (π–π*); 10345 M^{-1} cm^{-1}, 268 nm (M-L); 7960 M^{-1} cm^{-1}, 276 nm (L-M); 1138 M^{-1} cm^{-1}, 320 nm (d-d) and 300 M^{-1} cm^{-1}, 432 nm (d-d Fe). NMR-^{1}H (CH_2Cl_2-d_2) [δ ppm, (integral; multiplicity; assignation, *J* Hz)]: 4.20;4.21 (2H, d, Hg, ^{3}J = 1.80;1.84 Hz), 4.39 (2H, bs, Hf), 7.42 (4H, m, Hc), 7.51 (2H, m, Hd), 7.86 (4H, m, Hb). NMR-$^{13}C\{^{1}H\}$ (CH_2Cl_2-d_2) [δ ppm (multiplicity, assignation, *J* Hz)]: 73.20 (d, Ce, ^{1}J C-P = 70.56 Hz), 74.41;74.45 (d, Cg, ^{3}J C-P = 3.66;3.64 Hz), 76.23;76.28 (d, Cf, ^{2}J C-P = 5.09;5.11 Hz), 128.33;128.39 (d, Cc, ^{3}J C-P = 5.66;5.64 Hz), 131.44 (d, Ca, ^{1}J C-P = 67.34 Hz), 131.66 (Cd), 135.28;135.33 (d, Cb, ^{2}J C-P = 5.42;5.39 Hz). NMR-$^{31}P\{^{1}H\}$ (CH_2Cl_2-d_2) [δ ppm, (assignation, multiplicity)]: 12.63 (dppf, s, ^{1}J P-Pt = 3779.58 Hz). NMR-$^{195}Pt\{^{1}H\}$ (CH_2Cl_2-d_2) [δ ppm, (multiplicity, *J* Hz)]: -4363.30 (t, ^{1}J Pt-P = 3772.92 Hz).

***Cis*-[$Pt(PPh_3)_2$(CQ)Cl]PF_6.$^{1}/_{3}CH_2Cl_2$ (5)**

A yellow solid was obtained with a yield of 83.1%. Elemental analysis (%) Calc. for $C_{54}H_{56}Cl_2F_6N_3P_3Pt.^{1}/_{3}CH_2Cl_2$: C 52.28; H 4.58; N 3.37. Found: C 51.92; H 4.57; N 3.75. IR: ν (N-H) 3407 cm^{-1}, ν (C-H aromatic) 3057 cm^{-1}, ν (C-H aliphatic) 2970 cm^{-1}, (overtones aromatics) 1971-1813 cm^{-1}, (C-C aromatic) 1586 cm^{-1}, ν (C=C) 1612 cm^{-1}, ν (C=N) 1547 cm^{-1}, ν (P-C) 1095 cm^{-1}, (PF_6) 865 cm^{-1}, (Ph-P-Ph) 693 cm^{-1}, ν (Pt-P) 527 cm^{-1}, (Pt-Cl) 312 cm^{-1}.

UV-Vis [ε, λ (assignation)]: 44800 M^{-1} cm^{-1}, 238 nm (π–π* PPh_3); 27170 M^{-1} cm^{-1}, 262 nm (n–π* CQ); 16622 and 17092 M^{-1} cm^{-1}, 348 and 358 nm, respectively (π–π* CQ). NMR-^{1}H (CH_2Cl_2-d_2) [δ ppm (isomer 5:5`), (integral; multiplicity; assignation, *J* Hz)]: 1.00:1.03 (6H, t, H6´, ^{3}J = 7.16:7.12 Hz), 1.22:1.26 (3H, d, H1´´, ^{3}J = 6.36:6.40 Hz), 1.60 (2H, m, H3´), 1.75 (2H, m, H2´), 2.48 (2H, m, H4´), 2.55 (4H, m, H5´), 3.59 (1H, m, H1´), 6.17:6.22 (1H, d, H3, $^{3}J_{ortho}$ = 6.52:6.76 Hz), 6.73:7.08 (1H, d, NH, ^{3}J = 6.88 Hz), 7.13;7.28 (12H, m, Hc), 7.35 (6H, m, Hd), 7.50 (12H, m, Hb), 7.40 (1H, m, H6), 7.75:7.77 (1H, d, H5, $^{3}J_{ortho}$ = 9.16:9.04 Hz), 8.19:8.22 (1H, d, H2, $^{3}J_{ortho}$ = 6.52:6.76 Hz), 9.02:9.00 (1H, d, H8, $^{4}J_{metha}$ = 1.84 Hz). NMR-^{13}C{^{1}H} (CH_2Cl_2-d_2) [δ ppm (isomer 5:5`), (multiplicity, assignation, *J* Hz)]: 11.19:11.41 (C6´), 19.44:19.56 (C1´´), 23.65:23.85 (C3´), 34.06:34.33 (C2´), 47.40:47.42 (C5´), 49.46:49.58 (C1´), 52.51:52.65 (C4´), 101.42:101.51 (d, C3, ^{4}J C-P = 3.21:3.18 Hz), 118.56:118.75 (d, C10, ^{4}J C-P = 3.57:3.71 Hz), 124.03:124.25 (C5), 125.74:125.80 (C8), 126.16:126.26 (C6), 126.61:127.25 (d, Ca, ^{1}J C-P = 64.13:64.73 Hz), 128.85:129.07 (d, Cc, ^{3}J C-P = 11.27:11.49 Hz), 132.02:132.31 (d, Cd, ^{4}J C-P = 2.47:2.39 Hz), 134.08:135.34 (d, Cb, ^{2}J C-P = 10.87:9.98 Hz), 136.96:136.99 (C7), 145.53:145.59 (C9), 151.58: 151.70 (C4), 152.53:152.57 (C2). NMR-^{31}P{^{1}H} (CH_2Cl_2-d_2) [δ ppm, (assignation, multiplicity, *J* Hz)]: -144.5 (PF_6, sept, ^{1}J P-F = 711.24 Hz), 4.65 (PPh_3^{b}, d, ^{2}J P-P = 18.47 Hz, ^{1}J P-Pt = 3196.44 Hz), 15.03 (PPh_3^{a}, d, ^{2}J P-P = 18.47 Hz, ^{1}J P-Pt = 3792.85 Hz). NMR-^{195}Pt{^{1}H} (CH_2Cl_2-d_2) [δ ppm, (multiplicity, *J* Hz)]: -4320.66; -4283.25 (dd, ^{1}J Pt-P_a = 3707.86 Hz, ^{1}J Pt-P_b = 3204.17 Hz). High resolution ESI(+)-MS (acetone): $[M+H]^+$ (1220.3352 m/z, 8.34%), $[M-PF_6]^+$ (1074.3475 m/z, 15.42%), $[M-CQ-PF_6]^+$ (755.1503 m/z, 100%), $[CQ+H]^+$ (320.2032 m/z, 52.50%). Cyclic voltammetry (acetonitrile): 880 mV (CQ) and 1886 mV (Pt^{II}/Pt^{III}).

[Pt(dppp)(CQ)Cl]PF_6.$^1/_4CH_2Cl_2$ (6)

A white solid was obtained with a yield of 81.6%. Elemental analysis (%) Calc. for $C_{45}H_{52}Cl_2F_6N_3P_3Pt.^1/_4CH_2Cl_2$: C 48.14; H 4.69; N 3.72. Found: C 48.06; H 4.66; N 4.06. IR ν (N-H) 3413 cm^{-1}, ν (C-H aromatic) 3057 cm^{-1}, ν (C-H aliphatic) 2970 cm^{-1}, (overtones aromatics) 1970-1815 cm^{-1},, ν (C=C) 1612 cm^{-1}, ν (C=N) 1547 cm^{-1} (P-C) 1103, (PF_6) 846 cm^{-1}, (Ph-P-Ph) 695 cm^{-1}, (Pt-P) 517 cm^{-1}, (Pt-Cl) 306 cm^{-1}. UV-Vis [ε, λ (assignation)]: 41750 M^{-1} cm^{-1}, 234 nm (π–π* dppp); 20070 M^{-1} cm^{-1}, 262 nm (n–π* CQ); 14570 and 14800 M^{-1} cm^{-1}, 348 and 358 nm respectively (π–π* CQ). NMR-^{1}H (CH_2Cl_2-d_2) [δ ppm (isomer 6:6´), (integral; multiplicity; assignation, *J* Hz)]: 0.97:1.00 (6H, t, H6´, ^3J = 7.16 Hz), 1.23 (3H, d, H1´´, ^3J = 6.36 Hz), 1.55 (2H, m, H3´), 1.71 (2H, m, H2´), 2.09 (2H, m, Hf), 2.40 (2H, m, H4´), 2.52 (4H, m, H5´), 2.60;2.78 (4H, m, He), 3.57 (1H, m, H1´), 6.13:6.18 (1H, d, H3, $^3J_{ortho}$ = 6.56:6.64 Hz), 6.59:6.85 (1H, d, NH, ^3J = 7.04:6.24 Hz), 6.96;7.20;7.58 (8H, m, Hc), 7.11;7.41 (4H, m, Hd), 7.27 (1H, m, H6), 7.64;7.85 (8H, m, Hb), 7.64 (1H, m, H5), 7.97;7.98:7.99;8.00 (1H, d, H2, $^3J_{ortho}$ = 6.52:6.76 Hz), 8.55:8.51 (1H, d, H8, $^4J_{metha}$ = 1.84:1.92 Hz). NMR-^{13}C{^{1}H} (CH_2Cl_2-d_2) [δ ppm (isomer 6:6´), (multiplicity, assignation, *J* Hz)]: 11.19:11.40 (C6´), 18.81 (Cf), 19.40:19.47 (C1´´), 23.60:23.79 (C3´), 24.31;24.37:24.61;24.65 (d, Ce, ^1J C-P = 40.80;40.96:40.89;40.62 Hz), 33.97:34.23 (C2´), 47.26 (C5´), 49.30:49.38 (C1´), 52.41:52.48 (C4´), 101.00:101.03 (d, C3, ^4J C-P = 2.88:2.95 Hz), 118.27:118.41 (d, C10, ^4J C-P = 3.74:3.75 Hz), 123.36:123.54 (C5), 126.05:126.09 (C8), 126.09:126.14 (C6), 128.56;128.58:129.36;129.37;129.41;129.49;129.53 (d, Cc, ^3J C-P = 11.02:11.72 Hz), 127.29:128.10 (d, Ca, ^1J C-P = 65.51:60.37 Hz), 131.86:131.99 (d, Cd, ^4J C-P = 2.81:2.47 Hz), 132.31;132.37;132.61;133.32;133.35;133.50;133.56;132.45;132.62 (d, Cb, ^2J C-P = 10.24 Hz), 136.44:136.49 (C7), 145.23:145.30 (C9), 151.44: 151.53 (C4), 151.81 (C2). NMR-^{31}P{^{1}H} (CH_2Cl_2-d_2) [δ ppm (isomer 6:6´), (assignation, multiplicity, *J* Hz)]: -144.5 (PF_6, sept, ^1J P-F = 711.24 Hz), -14.56:-14.46 (P^b, d, ^2J P-P = 28.10 Hz, ^1J P-Pt =

2971.06 Hz), -5.53 (P^a, d, ^2J P-P = 28.10 Hz, ^1J P-Pt = 3342.59 Hz). NMR-^{195}Pt{^{1}H} (CH_2Cl_2-d_2) [δ ppm, (multiplicity, *J* Hz)]: -4399.40; -4364.23 (dd, ^1J Pt-P_a = 3351.82 Hz, ^1J Pt-P_b = 3012.65 Hz). High resolution ESI(+)-MS (acetone): $[M+H]^+$ (1108.3545 m/z, 3.77%), $[M-PF_6]^+$ (963.3629 m/z, 6.60%), $[M-CQ-PF_6]^+$ (643.1437 m/z, 70.75%), $[CQ+H]^+$ (320,2136 m/z, 100%). Cyclic voltammetry (acetonitrile): 890 mV (CQ) and 1860 mV (Pt^{II}/Pt^{III}).

$[Pt(dppb)(CQ)Cl]PF_6.{}^1/_3CH_2Cl_2$ (7)

A white solid was obtained with a yield of 81.9%. Elemental analysis (%) Calc. for $C_{46}H_{54}Cl_2F_6N_3P_3Pt.{}^1/_3CH_2Cl_2$: C 48.38; H 4.79; N 3.65. Found: C 48.14; H 4.65; N 3.98. IR ν (N-H) 3410 cm^{-1}, ν (C-H aromatic) 3057 cm^{-1}, ν (C-H aliphatic) 2968 cm^{-1}, (overtones aromatics) 1969-1815 cm^{-1}, ν (C=C) 1612 cm^{-1}, ν (C=N) 1548 cm^{-1}, (P-C) 1100 cm^{-1}, (PF_6) 863 cm^{-1}, (Ph-P-Ph) 695 cm^{-1}, (Pt-P) 534 cm^{-1}, (Pt-Cl) 308 cm^{-1}. UV-Vis [ε, λ (assignation)]: 40850 M^{-1} cm^{-1}, 234 nm (π–π* dppb); 20460 M^{-1} cm^{-1}, 262 nm (n–π* CQ); 14880 and 15064 M^{-1} cm^{-1}, 348 and 358 nm respectively (π–π* CQ). NMR-^{1}H (CH_2Cl_2-d_2) [δ ppm (isomer 7:7´), (integral; multiplicity; assignation, *J* Hz)]: 0.97:1.02 (6H, t, H6´, ^3J = 7.14 Hz), 1.25:1.24 (3H, d, H1´´, ^3J = 6.28:6.32 Hz), 1.53;2.47 (4H, m, Hf), 1.63 (2H, m, H3´), 1.73 (2H, m, H2´), 2.42 (2H, m, H4´), 2.39;2.91 (4H, m, He), 2.56 (4H, m, H5´), 3.60 (1H, m, H1´), 6.21:6.26 (1H, d, H3, $^3J_{ortho}$ = 6.52 Hz), 6.57:6.93 (1H, d, NH, ^3J = 6.88:6.76 Hz), 7.07;7.16;7.53;7.61 (8H, m, Hc), 7.37;7.67 (4H, m, Hd), 7.31 (1H, m, H6), 7.30;7.75;7.90 (8H, m, Hb), 7.33 (1H, m, H5), 8.09:8.11 (1H, d, H2, $^3J_{ortho}$ = 6.52 Hz), 8.54:8.57 (1H, d, H8, $^4J_{metha}$ = 1.92 Hz). NMR-^{13}C{^{1}H} (CH_2Cl_2-d_2) [δ ppm (isomer 7:7´), (multiplicity, assignation, *J* Hz)]: 11.30:11.52 (C6´), 19.35:19.51 (C1´´), 22.38:25.83 (Cf), 23.67:23.83 (C3´), 26.52;26.60:29.00;29.04 (d, Ce, ^1J C-P = 39.52;36.88:36.77;37.33 Hz), 34.02:34.33 (C2´), 47.32 (C5´), 49.35:49.44 (C1´), 52.44:52.58 (C4´), 101.24:101.33 (d, C3, ^4J C-P = 3.54:3.61 Hz), 118.20:118.39 (d, C10, ^4J C-P = 3.36:2.80 Hz), 123.76:123.96 (C5),

125.72:125.79 (C8), 126.11:126.18 (C6), 128.24:128.30 (d, Ca, ^{1}J C-P = 65.20:63.39 Hz), 128.96;129.03;129.22;129.33 (d, Cc, ^{3}J C-P = 10.94;11.22;11.08;11.20 Hz), 132.34;132.52 (d, Cd, ^{4}J C-P = 2.37 Hz), 132.97;133.05;134.20;134.45 (d, Cb, ^{2}J C-P = 9.60;10.05;9.70;9.47 Hz), 136.65:136.70 (C7), 145.35:145.43 (C9), 151.43: 151.55 (C4), 152.30 (C2). NMR-$^{31}P\{^{1}H\}$ (CH_2Cl_2-d_2) [δ ppm (isomer 7:7´), (assignation, multiplicity, *J* Hz)]: -144.5 (PF_6, sept, ^{1}J P-F = 711.24 Hz), -9.20:-9.50 (P^b, d, ^{2}J P-P = 23.11:22.68 Hz, ^{1}J P-Pt = 3002.29 Hz), 18.88:19.02 (P^a, d, ^{2}J P-P = 23.11:22.68 Hz, ^{1}J P-Pt = 3589.83 Hz). NMR-$^{195}Pt\{^{1}H\}$ (CH_2Cl_2-d_2) [δ ppm, (multiplicity, *J* Hz)]: -4384.07; -4348.73 (dd, ^{1}J Pt-P_a = 3644.15 Hz, ^{1}J Pt-P_b = 3026.69 Hz). High resolution ESI(+)-MS (acetone): $[M+H]^+$ (1122.3516 m/z, 6.66%), $[M-PF_6]^+$ (976.3547 m/z, 100%), $[M-CQ-PF_6]^+$ (656.1428 m/z, 78.75%), $[CQ+H]^+$ (320,2122 m/z, 89.16%). Cyclic voltammetry (acetonitrile): 900 mV (CQ) and 1861 mV (Pt^{II}/Pt^{III}).

[Pt(dppb)(quinoline)Cl]PF_6.$^{1}/_{2}C_4H_{10}O$ (7a)

A white solid was obtained with a yield of 83.2 %. Elemental analysis (%) Calc. for $C_{37}H_{35}ClF_6NP_3Pt.^{1}/_{2}C_4H_{10}O$: C 48.38; H 4.16; N 1.45. Found: C 48.81; H 3.69; N 1.10. NMR-^{1}H (Acetone-d_6) [δ ppm (integral; multiplicity; assignation, *J* Hz)]: 1.71;2.49 (4H, m, Hf), 2.61;3.28 (4H, m, He), 7.00;7.21;7.43 (4H, m, Hd), 7.25;7.62;8.05 (8H, m, Hc), 7.47 (1H, m, H3), 7.60;7.93 (8H, m, Hb), 7.63 (1H, m, H5), 7.70 (1H, m, H6), 7.99 (1H, m, H7), 8.35 (1H, d, H4, $^{3}J_{ortho}$ = 8.40 Hz), 9.02 (1H, d, H8, $^{3}J_{ortho}$ = 8.40 Hz), 9.21 (1H, m, H2). NMR-$^{13}C\{^{1}H\}$ (Acetone-d_6) [δ ppm (multiplicity, assignation, *J* Hz)]: 22.44;26.34 (s;d, Cf, ^{2}J C-P = 5.03 Hz), 26.85;28.28 (d, Ce, ^{1}J C-P = 39.24;36.22 Hz), 123.39 (d, C3, ^{4}J C-P = 3.02 Hz), 130.76 (d, C10, ^{4}J C-P = 3.02 Hz), 128.03 (C8), 129.13 (C6), 129.13;132.83 (Cd), 129.25;129.59;134.04;135.05 (d, Cb, ^{2}J C-P = 10.06 Hz), 129.94;130.26;132.33;135.16 (d, Cc, ^{3}J C-P = 10.06 Hz), 132.33 (C7), 140.96 (C4), 145.45 (C9), 154.24 (C2). NMR-$^{31}P\{^{1}H\}$ (Acetone-d_6) [δ ppm, (assignation, multiplicity, *J* Hz)]: -144.5 (PF_6, sept), -8.60 (P^b, d, ^{2}J P-P = 23.49 Hz, ^{1}J P-Pt = 3099.41 Hz), 17.54 (P^a, d, ^{2}J P-P = 23.49 Hz, ^{1}J P-Pt = 3521.36 Hz).

[Pt(dppb)(4,7-dichloroquinoline)Cl]PF_6.$^1/_2C_4H_{10}O$ (7b)

A pink pale solid was obtained with a yield of 82.4 %. Elemental analysis (%) Calc. for $C_{37}H_{33}Cl_3F_6NP_3Pt.^1/_2C_4H_{10}O$: C 45.17; H 3.69; N 1.35. Found: C 45.14; H 3.83; N 0.92. NMR-^{1}H (Acetone-d_6) [δ ppm (integral; multiplicity; assignation, *J* Hz)]: 1.72;2.36;2.456;2.58 (4H, m, Hf), 2.75;3.31 (4H, m, He), 7.21;7.59;7.67 (8H, m, Hc), 7.39;7.97;8.06 (8H, m, Hb), 7.49;7.58;7.73 (4H, m, Hd), 7.72:7.73 (1H, d, H3, $^3J_{ortho}$ = 5.60 Hz), 7.84 (1H, dd, H6, $^3J_{ortho}$ = 8.80 Hz , $^4J_{metha}$ = 2.00 Hz), 8.18 (1H, d, H5, $^3J_{ortho}$ = 8.80 Hz), 8.98 (1H, d, H8, $^4J_{metha}$ = 2.00 Hz), 9.24:9.25 (1H, d, H2, $^3J_{ortho}$ = 5.60 Hz). NMR-^{13}C{^{1}H} (Acetone-d_6) [δ ppm (multiplicity, assignation, *J* Hz)]: 22.36;26.17 (s;d, Cf, ^2J C-P = 4.03 Hz), 26.88;28.57 (d, Ce, ^1J C-P = 40.25;36.22 Hz), 124.65 (d, C3, ^4J C-P = 3.01 Hz), 127.12 (d, C10, ^4J C-P = 3.01 Hz), 127.25 (C8), 128.18 (C5), 129.20;129.80 (d, Cc, ^3J C-P = 12.07 Hz), 131.25 (C6), 132.82;133.62 (m, Cd), 133.09;134.97;135.24 (d, Cb, ^2J C-P = 10.06 Hz), 138.99 (C7), 146.19 (C9), 147.37 (C4), 155.53 (C2). NMR-^{31}P{^{1}H} (Acetone-d_6) [δ ppm, (assignation, multiplicity, *J* Hz)]: -144.5 (PF_6, sept), -7.10 (P^b, d, ^2J P-P = 23.49 Hz, ^1J P-Pt = 3160.23 Hz), 17.28 (P^a, d, ^2J P-P = 23.49 Hz, ^1J P-Pt = 3485.81 Hz.

[Pt(dppb)(Q-MOD-I)Cl]PF_6.$^1/_2C_4H_{10}O$ (7c)

A beige pale solid was obtained with a yield of 81.7 %. Elemental analysis (%) Calc. for $C_{44}H_{41}Cl_2F_6N_2P_3Pt.^1/_2C_4H_{10}O$: C 49.87; H 4.19; N 2.53. Found: C 50.00; H 3.71; N 2.08. NMR-^{1}H (Acetone-d_6) [δ ppm (integral; multiplicity; assignation, *J* Hz)]: 1.68;2.35;2.53 (4H, m, Hf), 2.44;2.64 (4H, m, He), 4.64 (2H, d, H1´, ^3J = 6.00 Hz), 6.41 (1H, d, H3, $^3J_{ortho}$ = 6.80 Hz), 7.11;7.55;7.63 (8H, m, Hc), 7.33;7.64;7.71 (4H, m, Hd), 7.35;7.92;8.04 (8H, m, Hb), 7.40-7.42 (5H, m, H3´- H5´), 7.45 (1H, dd, H6, $^3J_{ortho}$ = 8.80 Hz , $^4J_{metha}$ = 2.00 Hz), 8.07 (1H, d, H5, $^3J_{ortho}$ = 8.80 Hz), 8.09 (1H, t, NH, ^3J = 6.00 Hz), 8.42:8.43 (1H, d, H2, $^3J_{ortho}$ = 6.80 Hz), 8.67 (1H, d, H8, $^4J_{metha}$ = 2.00 Hz). NMR-^{13}C{^{1}H} (Acetone-d_6) [δ ppm (multiplicity, assignation, *J* Hz)]: 22.49;26.19 (s;d, Cf, ^2J C-P = 5.03 Hz), 26.66;28.68 (d, Ce, ^1J C-P =

39.24;37.23 Hz), 47.27 (C1´), 102.23 (d, C3, ^{4}J C-P = 4.02 Hz), 118.99 (d, C10, ^{4}J C-P = 3.22 Hz), 124.89 (C5), 126.49 (C8), 126.73 (C6), 128.35-128.53 (C3´-C5´), 129.30;132.80 (Cd), 129.43;129.58;129.63 (d, Cc, ^{3}J C-P = 11.06 Hz), 132.57;133.54;134.99;135.15 (d, Cb, ^{2}J C-P = 10.06 Hz), 136.54 (C7), 138.20 (C2´), 145.96 (C9), 152.94 (C4), 153.79 (C2). NMR-$^{31}P\{^{1}H\}$ Acetone-d_6) [δ ppm, (assignation, multiplicity, *J* Hz)]: -144.5 (PF_6, sept), -7.69 (P^b, d, ^{2}J P-P = 24.30 Hz, ^{1}J P-Pt = 3044.41 Hz), 17.71 (P^a, d, ^{2}J P-P = 24.30 Hz, ^{1}J P-Pt = 3558.70 Hz).

[Pt(dppb)(Q-MOD-II)Cl]PF_6.$^{3}/_{2}C_4H_{10}O$ (7d)

A beige pale was obtained with a yield of 78.2 %. Elemental analysis (%) Calc. for $C_{45}H_{43}Cl_2F_6N_2P_3Pt.^{3}/_{2}C_4H_{10}O$: C 51.22; H 4.89; N 2.34. Found: C 51.11; H 5.41; N 1.78. NMR-^{1}H (Acetone-d_6) [δ ppm (isomer 7d:7d`), (integral; multiplicity; assignation, *J* Hz)]: 1.66:1.69 (3H, d, H1´´, ^{3}J = 6.84 Hz), 1.68;2.41 (4H, m, Hf), 2.61;3.21 (4H, m, He), 4.88 (1H, m, H1´), 6.34:6.23 (1H, d, H3, $^{3}J_{ortho}$ = 6.48:6.44 Hz), 6.87;7.04;7.57;7.65 (8H, m, Hc), 7.23;7.39 (4H, m, Hd), 7.46 (1H, m, H6), 7.50-7.57 (5H, m, H3´- H5´), 7.75 (1H, m, NH), 7.92;8.04 (8H, m, Hb), 8.21:8.22 (1H, d, H5, $^{3}J_{ortho}$ = 9.04:8.84 Hz), 8.36 (1H, m, H2), 8.63:8.65 (1H, d, H8, $^{4}J_{metha}$ = 2.08:2.00 Hz). NMR-$^{13}C\{^{1}H\}$ (Acetone-d_6) [δ ppm (isomer 7d:7d`), (multiplicity, assignation, *J* Hz)]: 22.55 (Cf), 24.02:23.94 (C1´´), 26.42 (m, Ce), 54.24:54.41 (C1´), 102.81:103.12 (d, C3, ^{4}J C-P = 3.35:3.22 Hz), 118.85:119.14 (C10), 125.32:125.29 (C5), 126.56:126.35 (C6), 126.77:126.61 (C8), 129.10;129.50 (m, Cc), 129.61-129.83 (m, C3´-C5´), 133.10;133.60 (m, Cd), 135.00 (m, Cb), 136.51 (C2´), 143.87 (C7), 144.43 (C9), 152.07:152.24 (C4), 153.70:153.64 (C2). NMR-$^{31}P\{^{1}H\}$ (Acetone-d_6) [δ ppm (Isomer 7b:7b´), (assignation, multiplicity, *J* Hz)]: -144.5 (PF_6, sept), -8.33:-7.04 (P^b, d, ^{2}J P-P = 22.70:23.26 Hz, ^{1}J P-Pt = 3051.70 Hz), 17.96:17.29 (P^a, d, ^{2}J P-P = 22.70:23.26 Hz, ^{1}J P-Pt = 3558.47 Hz).

[Pt(dppf)(CQ)Cl]PF_6.$^1/_2CH_2Cl_2$ (8)

A yellow solid was obtained with a yield of 92.3%. Elemental analysis (%) Calc. for $C_{52}H_{54}Cl_2F_6FeN_3P_3Pt.^1/_2CH_2Cl_2$: C 48.80; H 4.29; N 3.25. Found: C 48.39; H 4.21; N 3.47. IR ν (N-H) 3409 cm^{-1}, ν (C-H aromatic) 3057 cm^{-1}, ν (C-H aliphatic) 2970 cm^{-1}, (overtones aromatics) 1971-1813 cm^{-1}, ν (C=C) 1612 cm^{-1}, ν (C=N) 1548 cm^{-1}, ν (P-C) 1098 cm^{-1}, ν (PF_6) 848 cm^{-1}, (Ph-P-Ph) 697 cm^{-1}, ν (Pt-P) 519 cm^{-1}, (Pt-Cl) 313 cm^{-1}. UV-Vis [ε, λ (assignation)]: 46815 M^{-1} cm^{-1}, 234 nm (π–π* dppf); 22895 M^{-1} cm^{-1}, 260 nm (n–π* CQ); 15150 e 15690 M^{-1} cm^{-1}, 348 e 358 nm respectively (π–π* CQ). NMR-^{1}H (CH_2Cl_2-d_2) [δ ppm (isomer 8:8´), (integral; multiplicity; assignation, *J* Hz)]: 1.02:1.06 (6H, t, H6´, ^3J = 7.08 Hz), 1.23:1.24 (3H, d, H1´´, ^3J = 6.12:6.24 Hz), 1.64 (2H, m, H3´), 1.79 (2H, m, H2´), 2.52 (2H, m, H4´), 2.61 (4H, m, H5´), 3.58 (1H, m, H1´), 3.63;3.67;4.73;4.79 (4H, s, Hg), 4.33;4.88;5.06 (4H, s, Hf), 6.13:6.17 (1H, d, H3, $^3J_{ortho}$ = 6.60:6.76 Hz), 6.65:6.97 (1H, d, NH, ^3J = 6.72:7.16 Hz), 7.04;7.61;7.67 (8H, m, Hc), 7.27 (4H, m, Hd), 7.35 (1H, m, H6), 7.60;7.69;8.01 (8H, m, Hd),7.79:7.74 (1H, d, H5, $^3J_{ortho}$ = 8.76:9.12 Hz), 8.02 (1H, m, H2), 8.83:8.82 (1H, d, H8, $^4J_{metha}$ = 1.76:1.80 Hz). NMR-^{13}C{^{1}H} (CH_2Cl_2-d_2) [δ ppm (isomer 8:8´), (multiplicity, assignation, *J* Hz)]: 10.97:11.23 (C6´), 19.53:19.59 (C1´´), 23.44:23.70 (C3´), 33.98:34.18 (C2´), 47.51 (C5´), 49.45:49.57 (C1´), 52.57:52.73 (C4´), 70.65:71.61 (d, Ce, ^1J C-P = 74.19:71.38 Hz), 74.25;74.55;75.97;76.53;76.86 (Cf), 77.67:76.97 (Cg), 101.44 (C3), 118.52:118.68 (d, C10, ^4J C-P = 4.36:4.21 Hz), 123.99:124.24 (C5), 125.62:125.69 (C8), 126.21:126.28 (C6), 128.59;128.89:132.34;132.52 (d, Cc, ^3J C-P = 11.38:7.63 Hz), 129.11;129.41:134.75;134.82;135.06;135.13 (d, Cb, ^2J C-P = 11.73:10.10 Hz), 131.70 (Cd), 136.92 (C7), 145.44 (C9), 151.60:151.72 (C4), 152.34 (C2). NMR-^{31}P{^{1}H} (CH_2Cl_2-d_2) [δ ppm (isomer 8:8´), (assignation, multiplicity, *J* Hz)]: -144.5 (PF_6, sept, ^1J P-F = 711.24 Hz), 4.92 (P^b, d, ^2J P-P = 15.42 Hz, ^1J P-Pt = 3310.21 Hz), 15.26:15.28 (P^a, d, ^2J P-P = 15.42 Hz, ^1J P-Pt = 3757.99 Hz). NMR-^{195}Pt{^{1}H} (CH_2Cl_2-d_2) [δ ppm, (multiplicity, *J* Hz)]: -4216.27;-

4255.16 (dd, ^{1}J Pt-P_a = 3776.26 Hz, ^{1}J Pt-P_b = 3330.50 Hz). High resolution ESI(+)-MS (acetone): $[M+H]^+$ (1250.1364 m/z, 8.66%), $[M-PF_6]^+$ (1108.2703 m/z, 8.75%), $[M-CQ-PF_6]^+$ (784.0406 m/z, 39.16%), $[CQ+H]^+$ (320,1958 m/z, 100%). Cyclic voltammetry (acetonitrile): 880 mV (CQ), 1886 mV (Pt^{II}/Pt^{III}), $E_{1/2}$ = 1048 mV and ΔE = 72 mV (redox pair Fe^{II}/Fe^{III}).

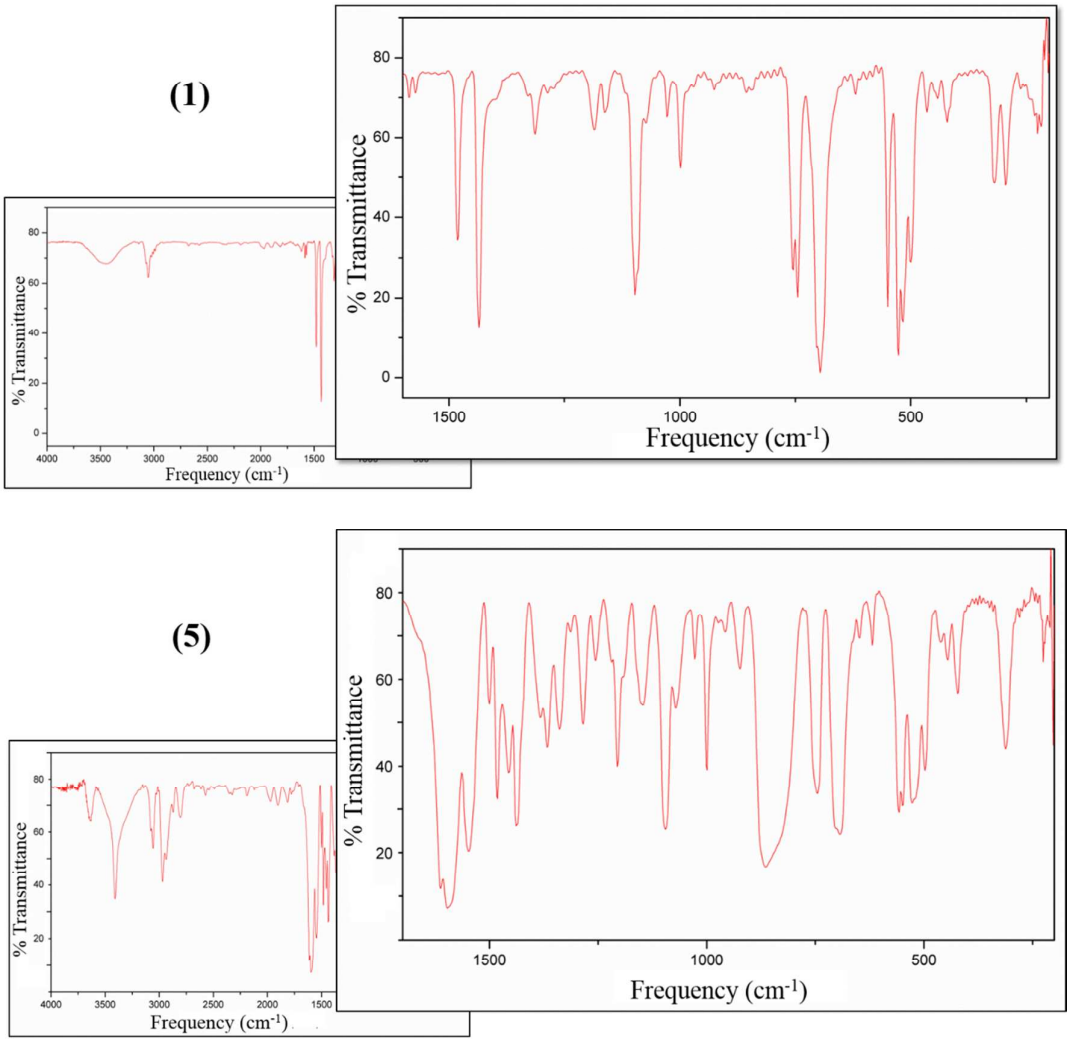

Figure S1. IR spectrum of complexes $[Pt(PPh_3)_2Cl_2]$ (**1**) and $[Pt(PPh_3)_2(CQ)Cl]PF_6$ (**5**) in KBr.

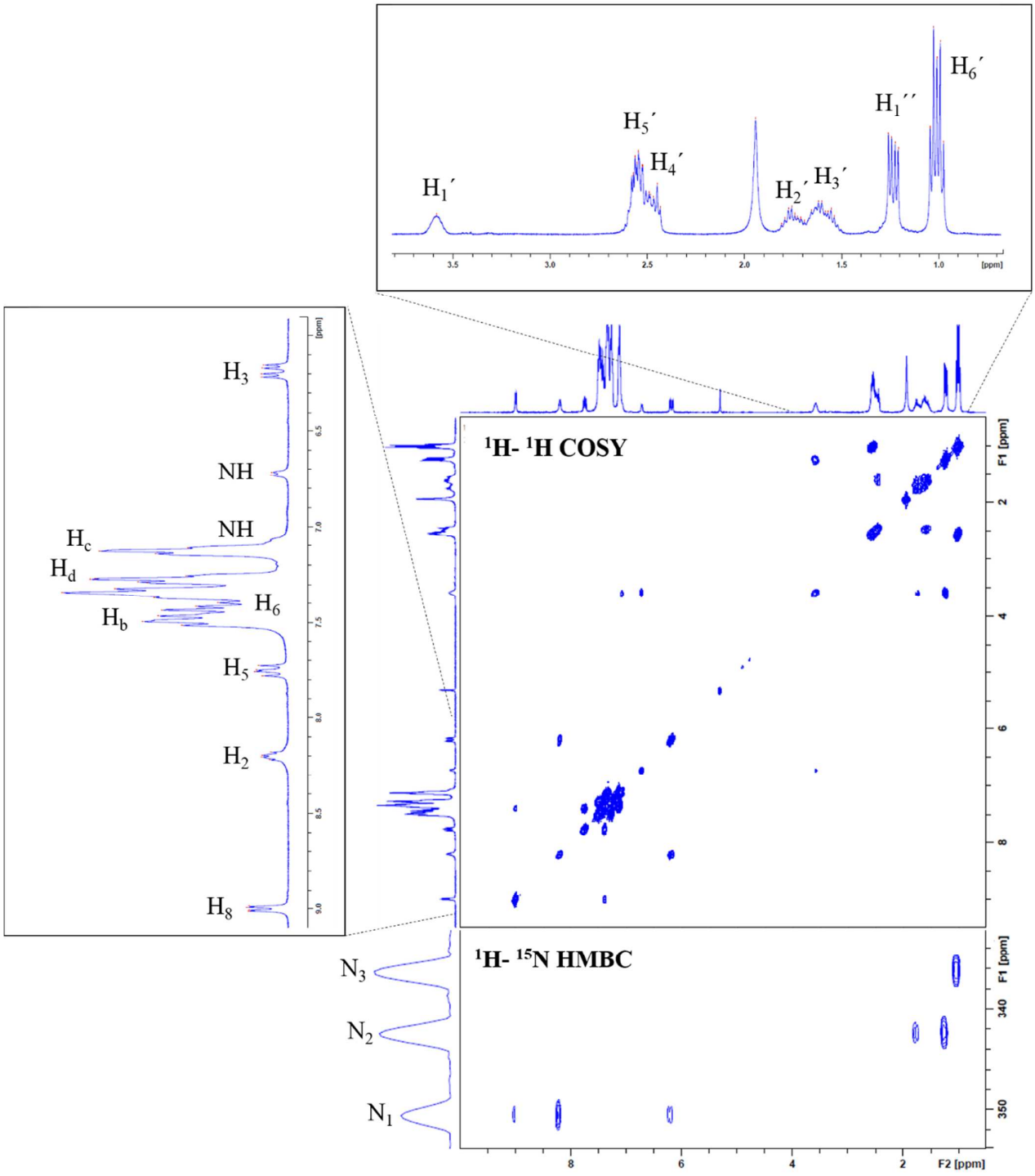

Figure S2. The 2D homonuclear ^{1}H-^{1}H COSY (top) and heteronuclear ^{1}H-^{15}N HMBC NMR spectra of $[Pt(PPh_3)_2(CQ)Cl]PF_6$ (**5**) in CD_2Cl_2 at 298 K.

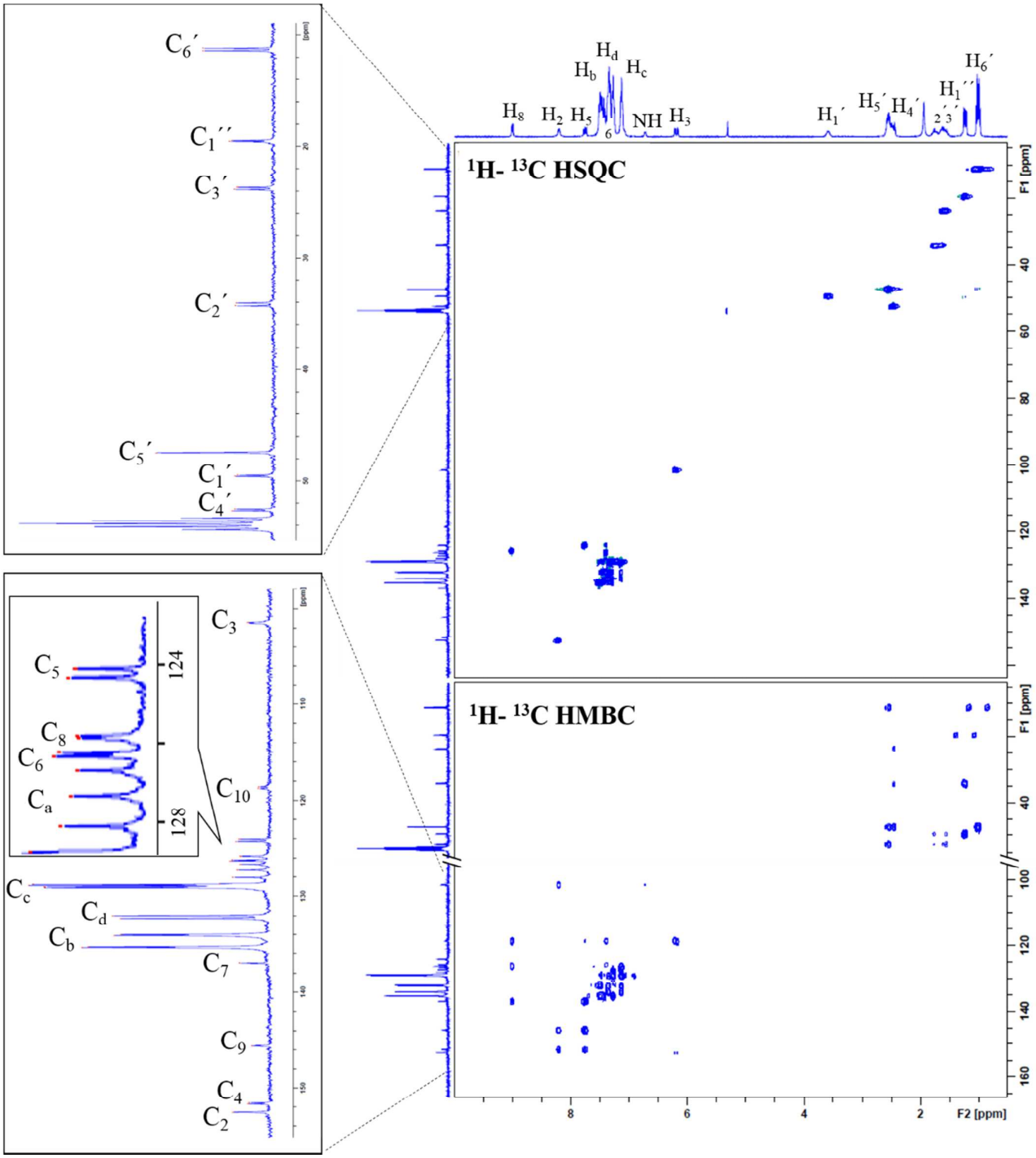

Figure S3. The 2D heteronuclear ^{1}H-^{13}C HSQC (top) and heteronuclear ^{1}H-^{13}C HMBC NMR spectra of $[Pt(PPh_3)_2(CQ)Cl]PF_6$ (**5**) in CD_2Cl_2 at 298 K.

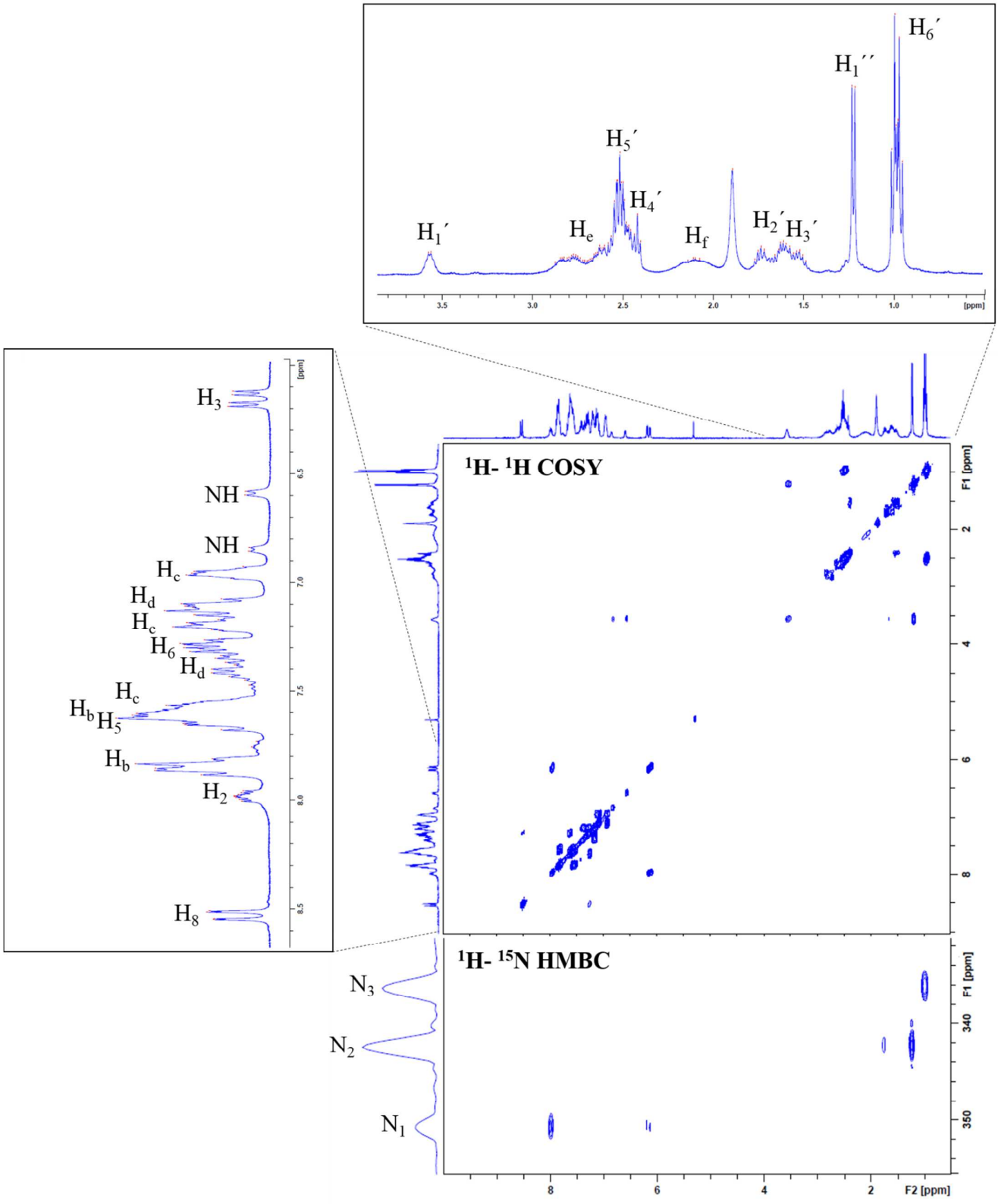

Figure S4. The 2D homonuclear ^{1}H-^{1}H COSY (top) and heteronuclear ^{1}H-^{15}N HMBC NMR spectra of [Pt(dppp)(CQ)Cl]PF6 (**6**) in CD_2Cl_2 at 298 K.

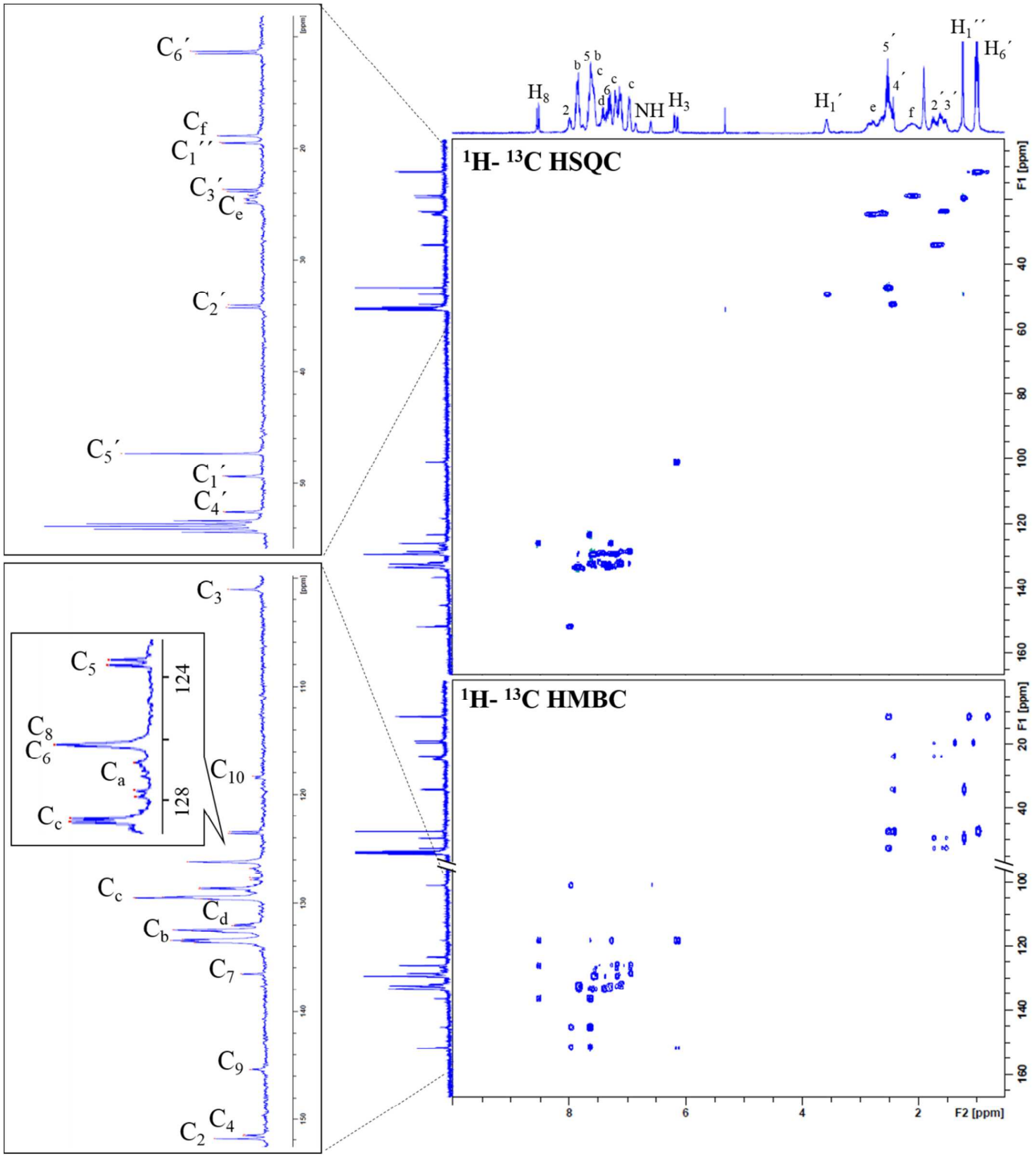

Figure S5. The 2D heteronuclear ^{1}H-^{13}C HSQC (top) and heteronuclear ^{1}H-^{13}C HMBC NMR spectra of [Pt(dppp)(CQ)Cl]PF_6 (**6**) in CD_2Cl_2 at 298 K.

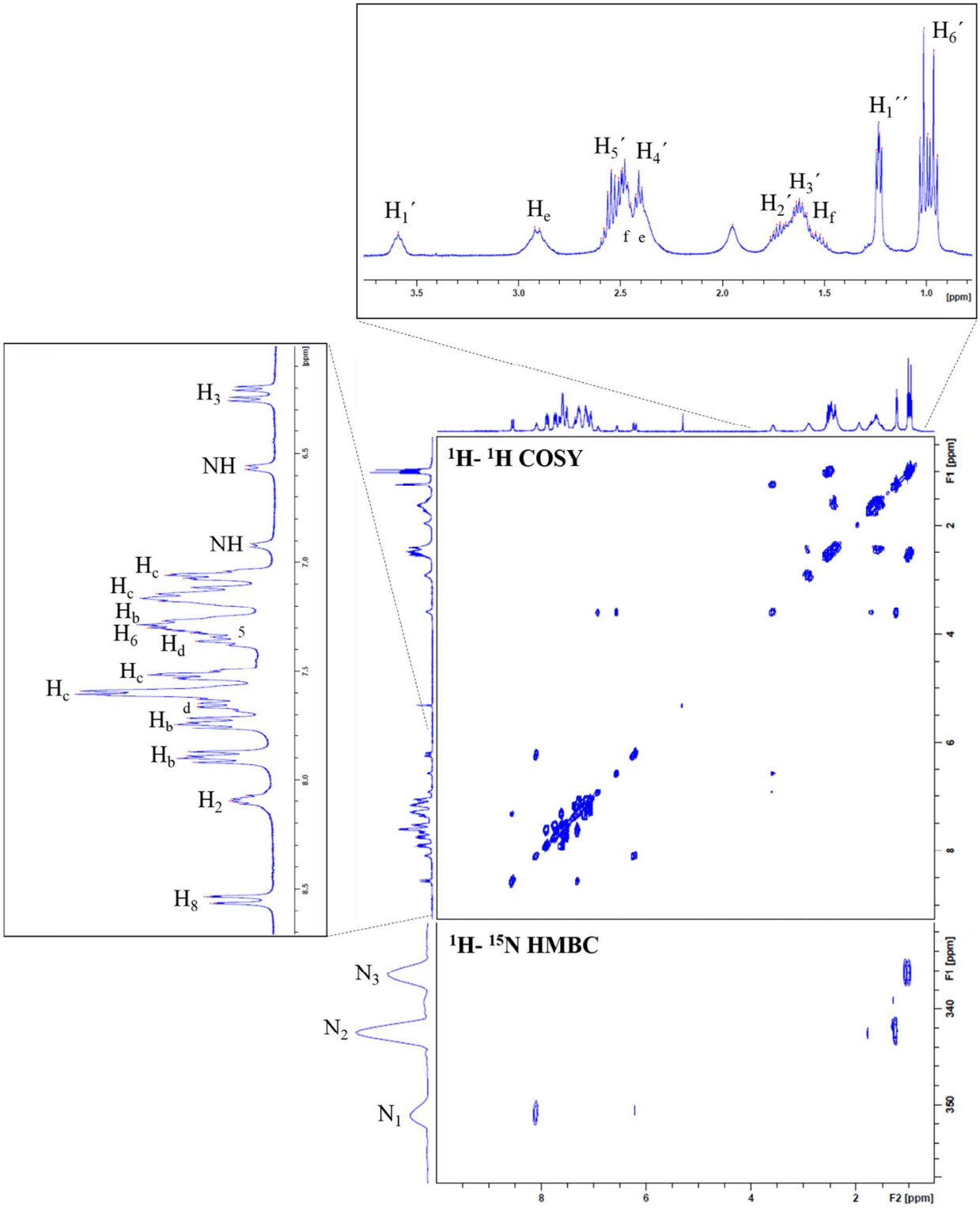

Figure S6. The 2D homonuclear ^{1}H-^{1}H COSY (top) and heteronuclear ^{1}H-^{15}N HMBC NMR spectra of [Pt(dppb)(CQ)Cl]PF6 (**7**) in CD_2Cl_2 at 298 K.

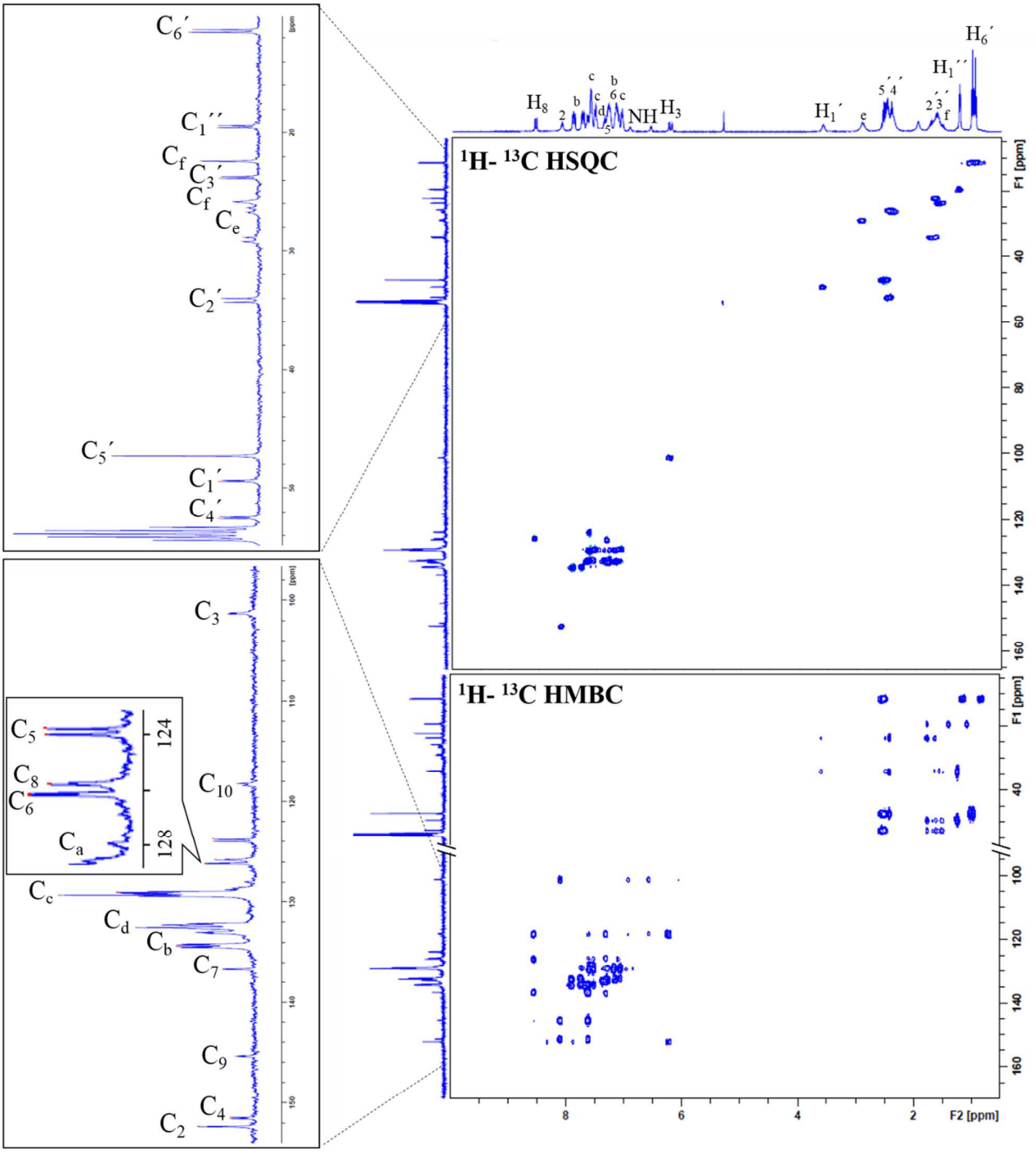

Figure S7. The 2D heteronuclear ^{1}H-^{13}C HSQC (top) and heteronuclear ^{1}H-^{13}C HMBC NMR spectra of [Pt(dppb)(CQ)Cl]PF_6 (**7**) in CD_2Cl_2 at 298 K.

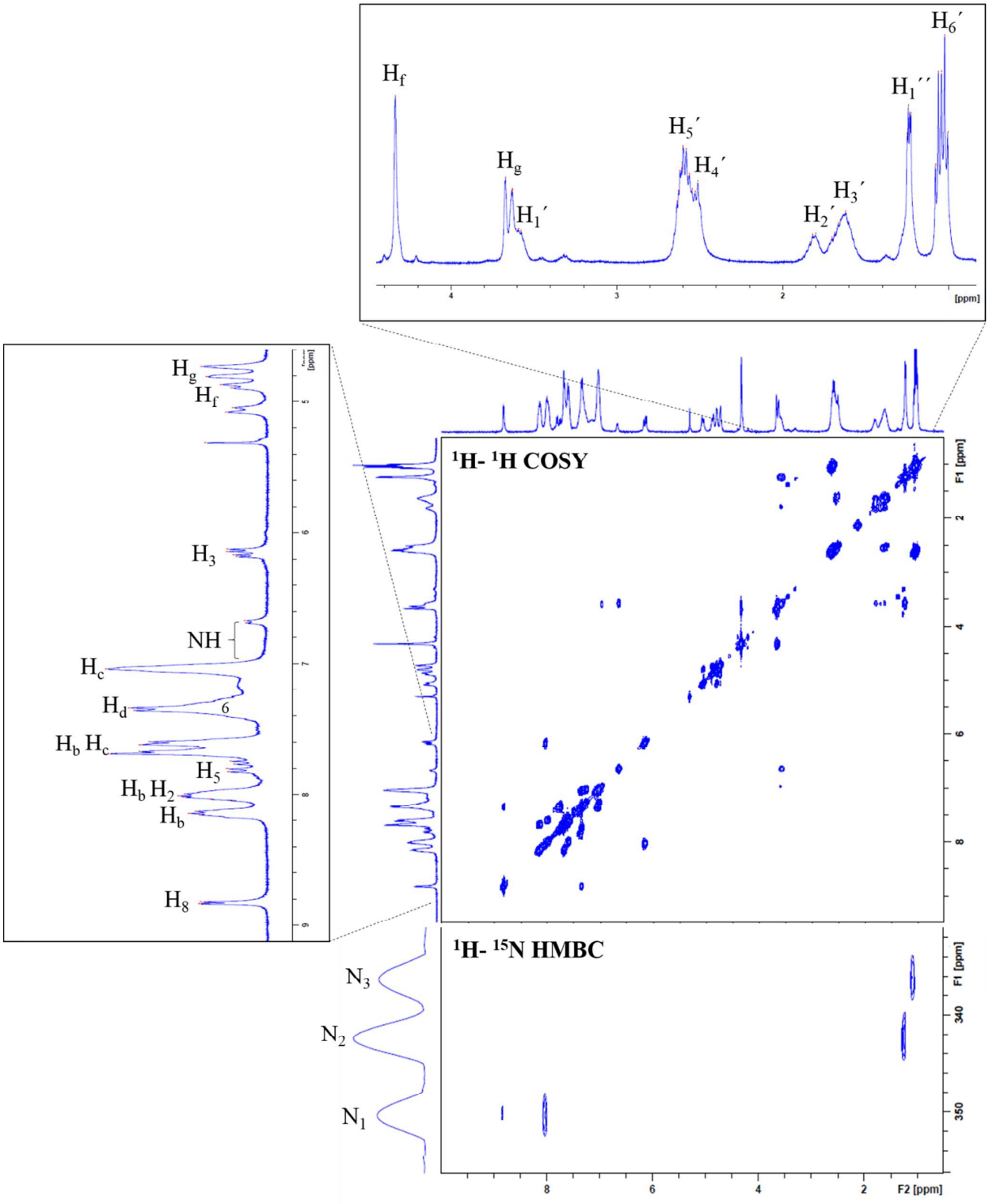

Figure S8. The 2D homonuclear ^{1}H-^{1}H COSY (top) and heteronuclear ^{1}H-^{15}N HMBC NMR spectra of [Pt(dppf)(CQ)Cl]PF6 (**8**) in CD_2Cl_2 at 298 K.

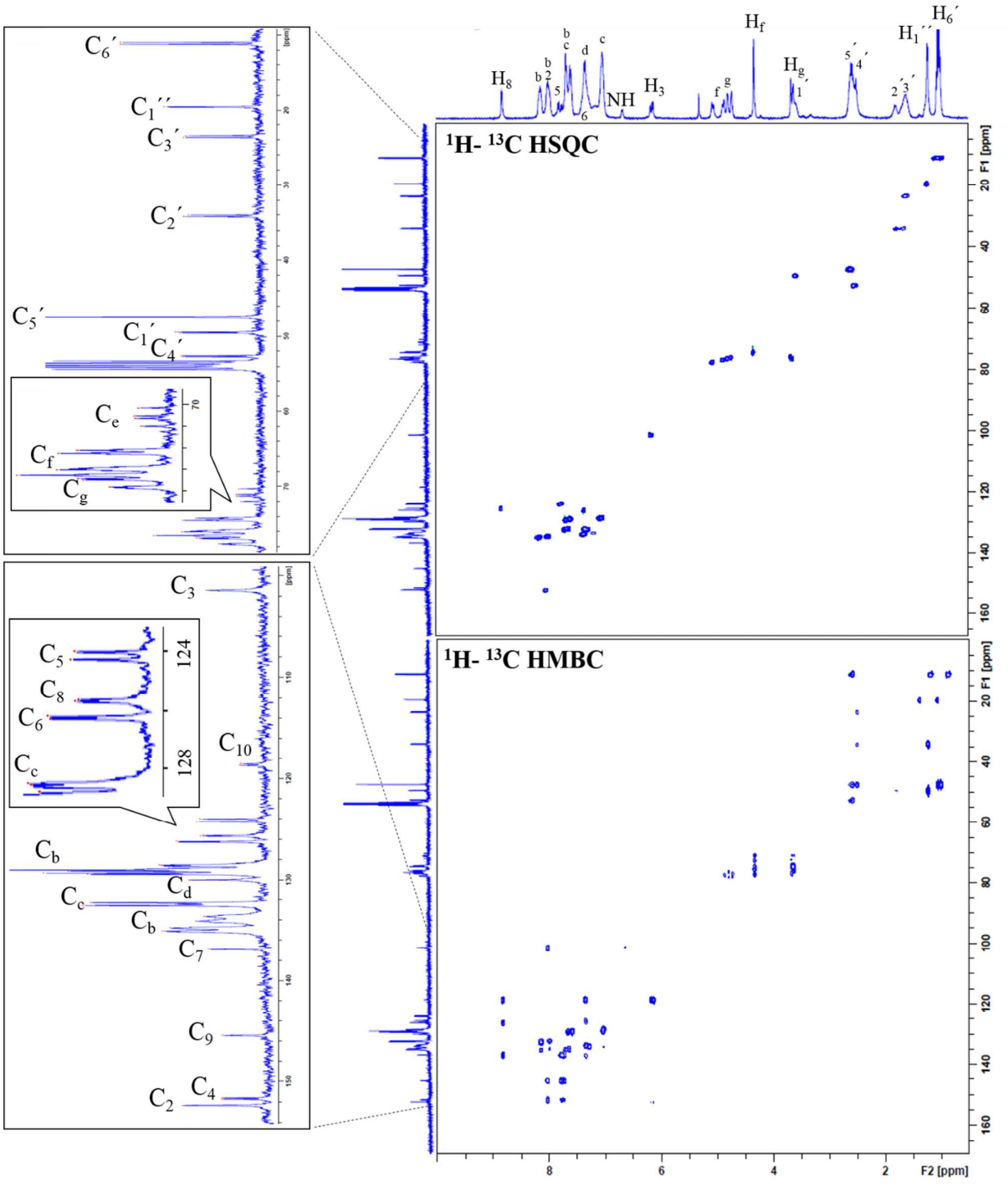

Figure S9. The 2D heteronuclear ^{1}H-^{13}C HSQC (top) and heteronuclear ^{1}H-^{13}C HMBC NMR spectra of [Pt(dppf)(CQ)Cl]PF_6 (**8**) in CD_2Cl_2 at 298 K.

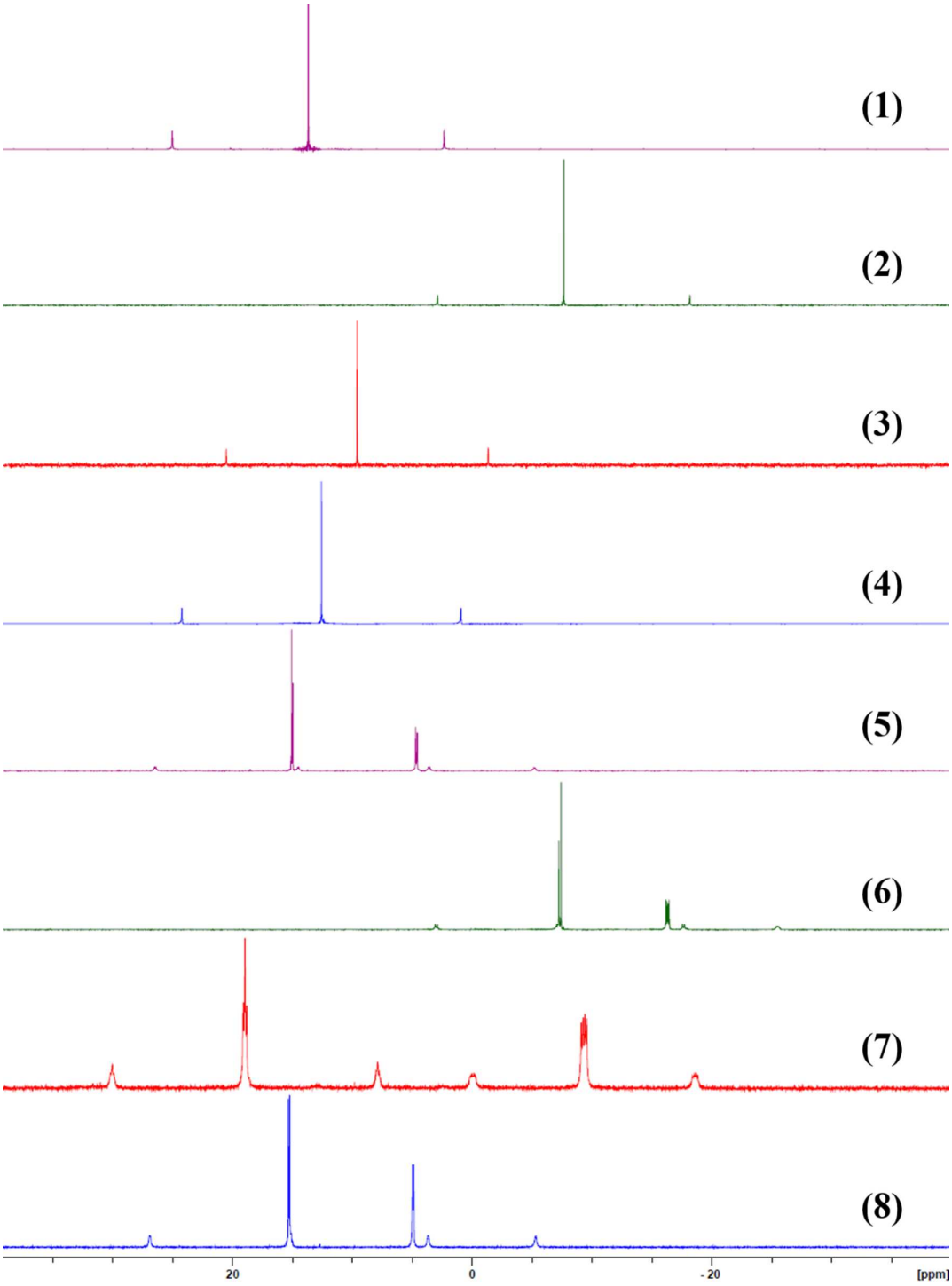

Figure S10. $^{31}P\{^{1}H\}$ NMR spectra of phosphine platinum(II) complexes (**1-8**) in CD_2Cl_2 at 298 K.

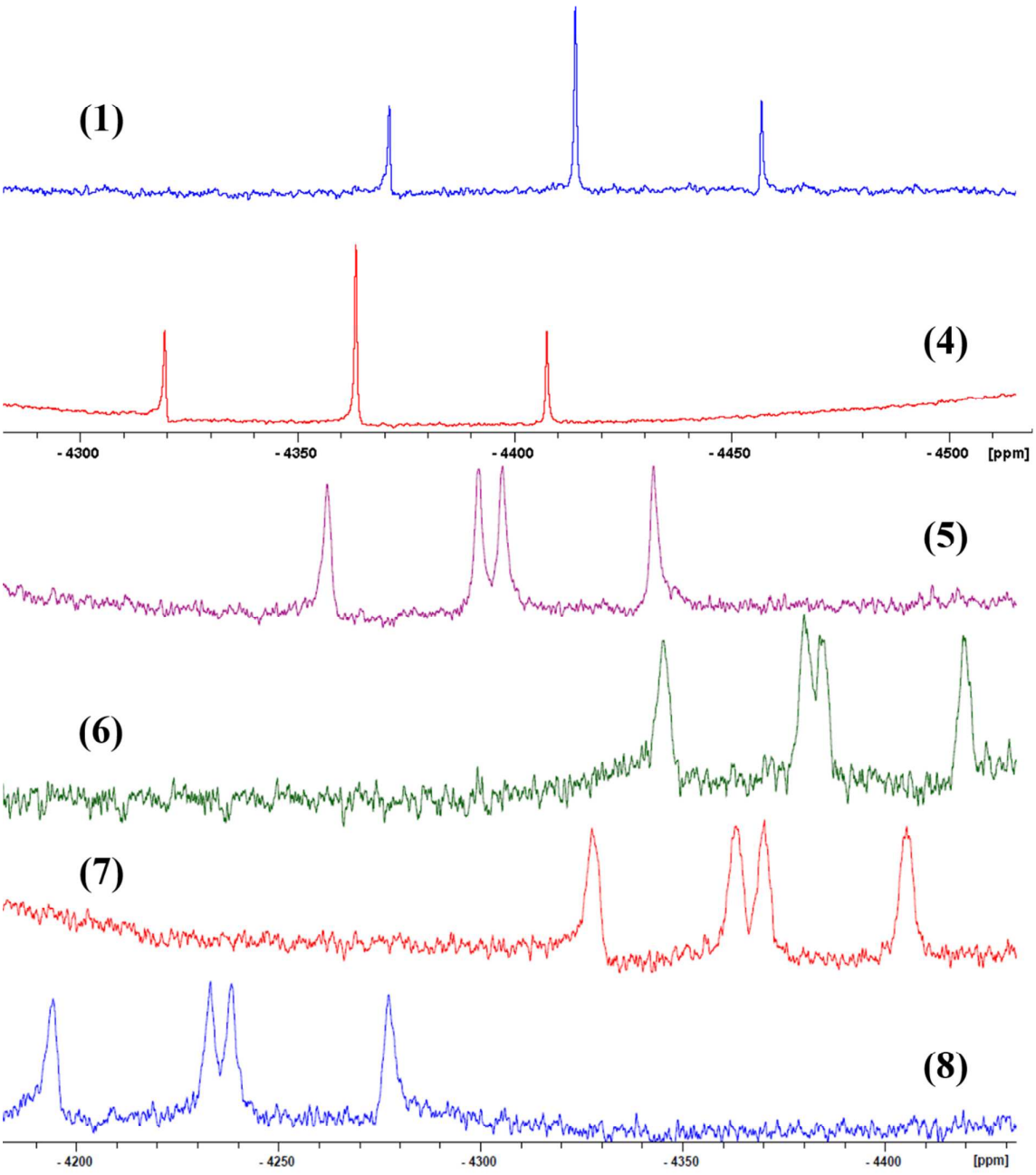

Figure S11. $^{195}Pt\{^{1}H\}$ NMR spectra of phosphine platinum(II) complexes (**1,4-8**) in CD_2Cl_2 at 298 K.

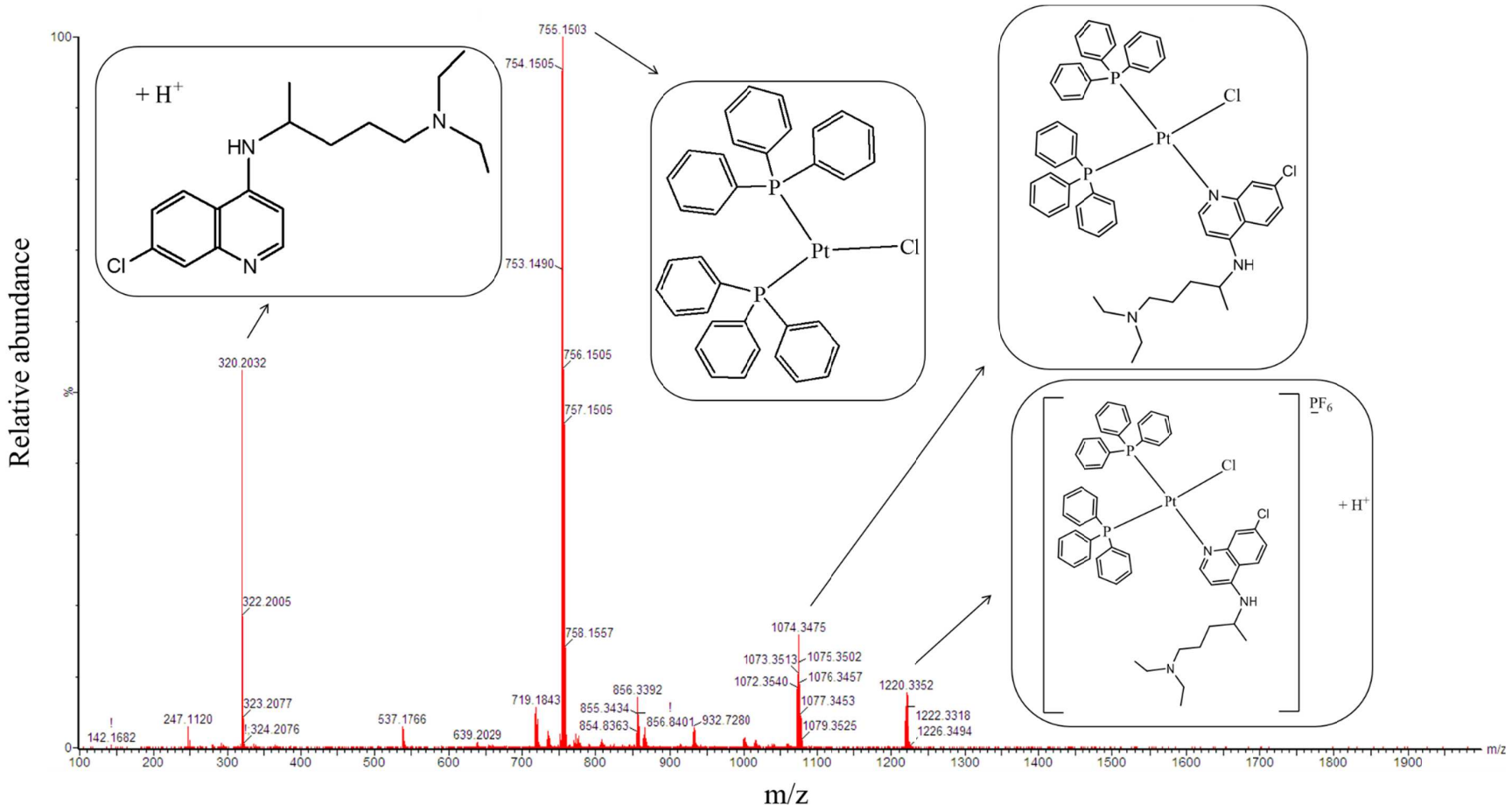

Figure S12. ESI(+)-MS spectrum of *cis*-[PtCl(CQ)(PPh_3)$_2$]PF_6 **(5)** in Acetone.

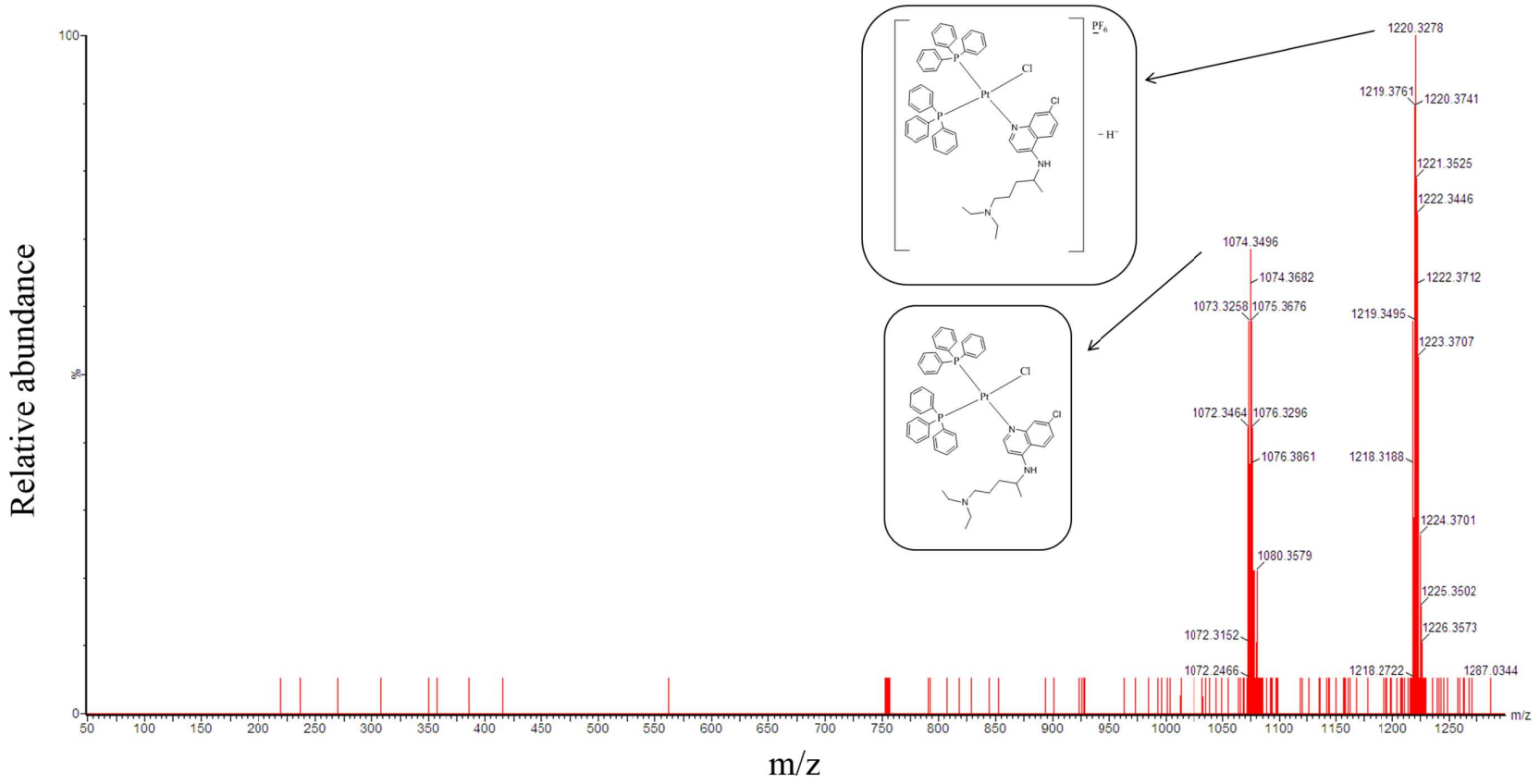

Figure S13. ESI(+)-MS-MS spectrum of *cis*-[PtCl(CQ)(PPh_3)$_2$]PF_6 **(5)** in Acetone.

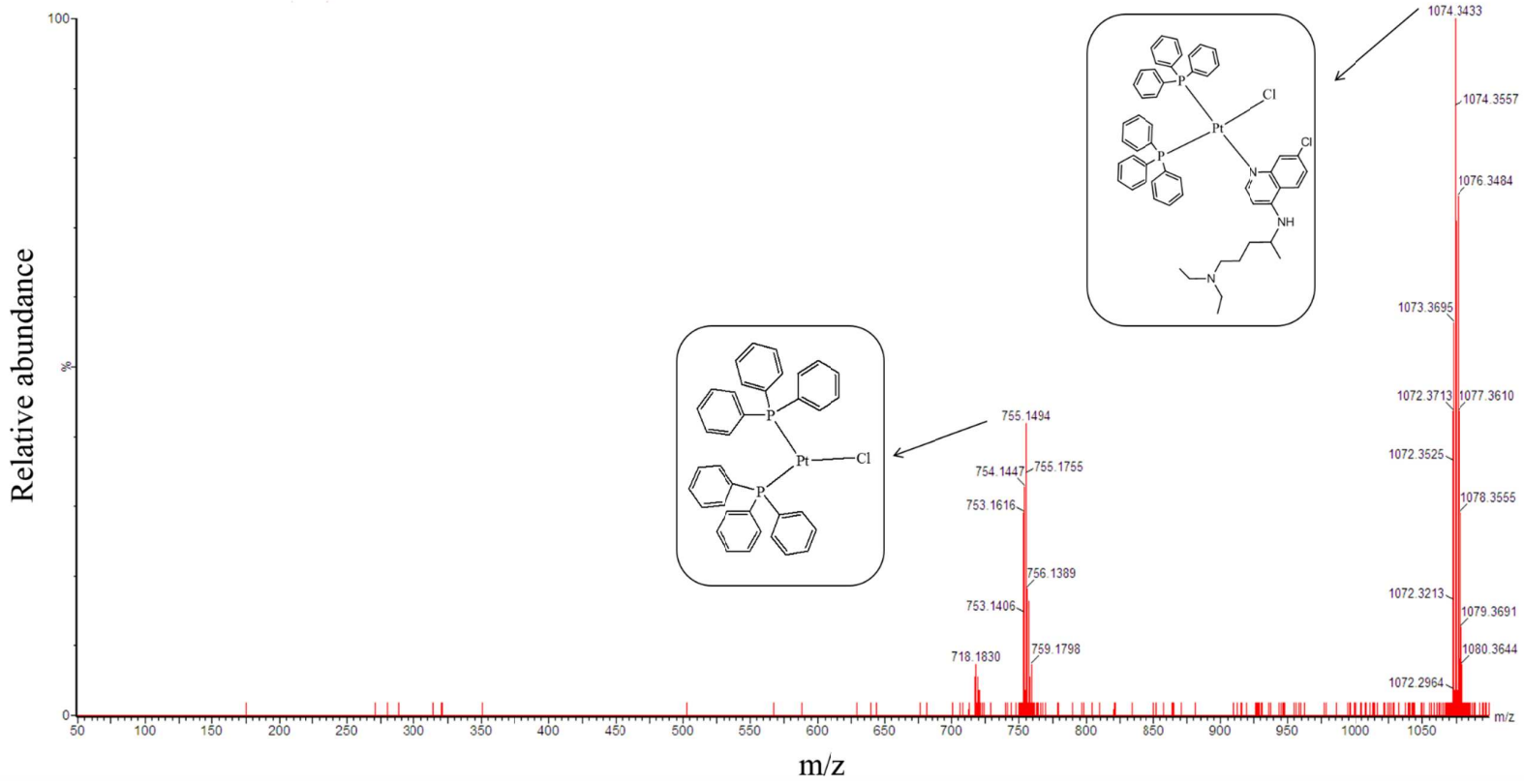

Figure S14. ESI(+)-MS-MS spectrum of *cis*-[PtCl(CQ)(PPh_3)$_2$]PF_6 **(5)** in Acetone.

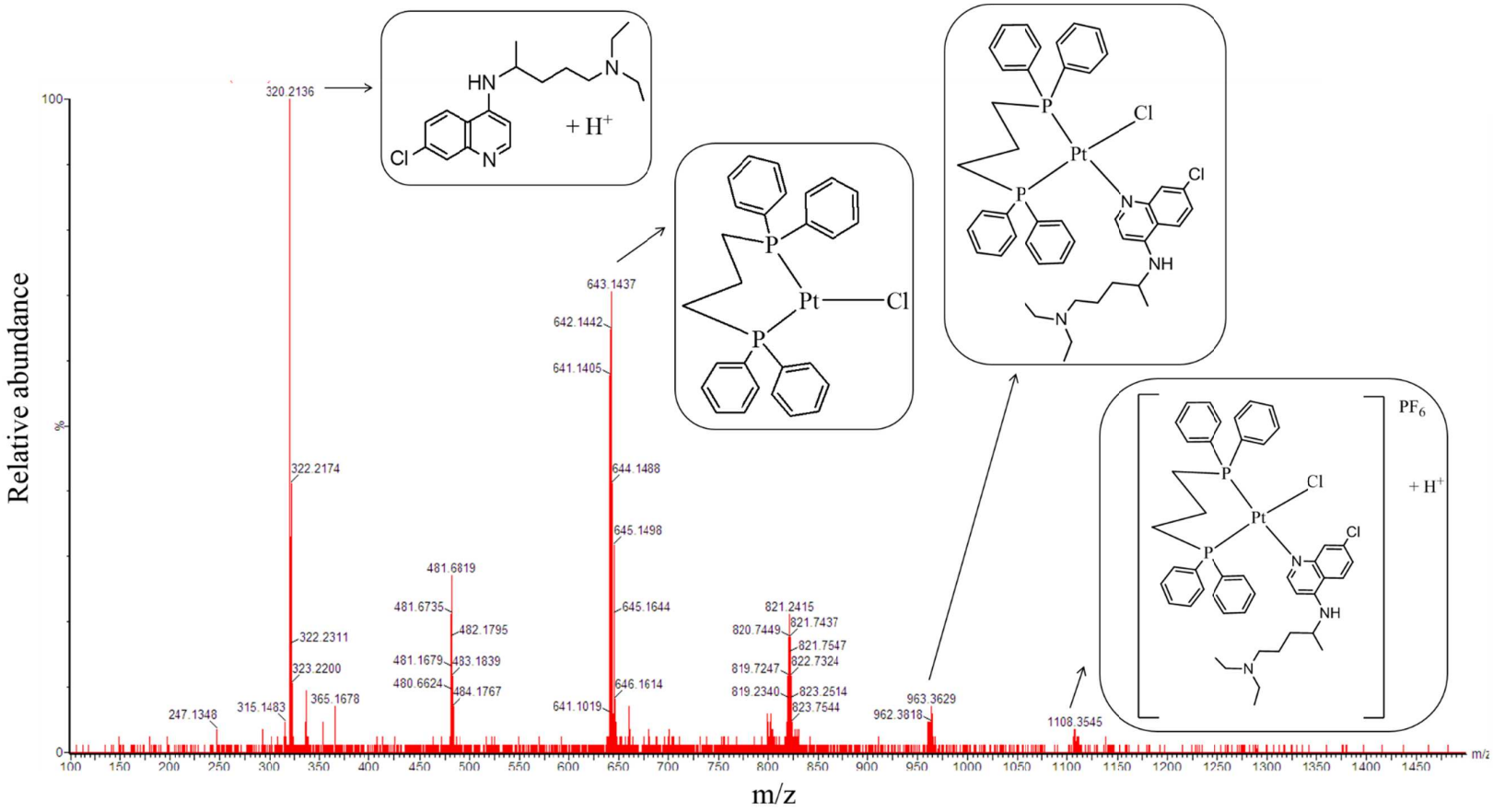

Figure S15. ESI(+)-MS spectrum of [PtCl(CQ)(dppp)]PF_6 **(6)** in Acetone.

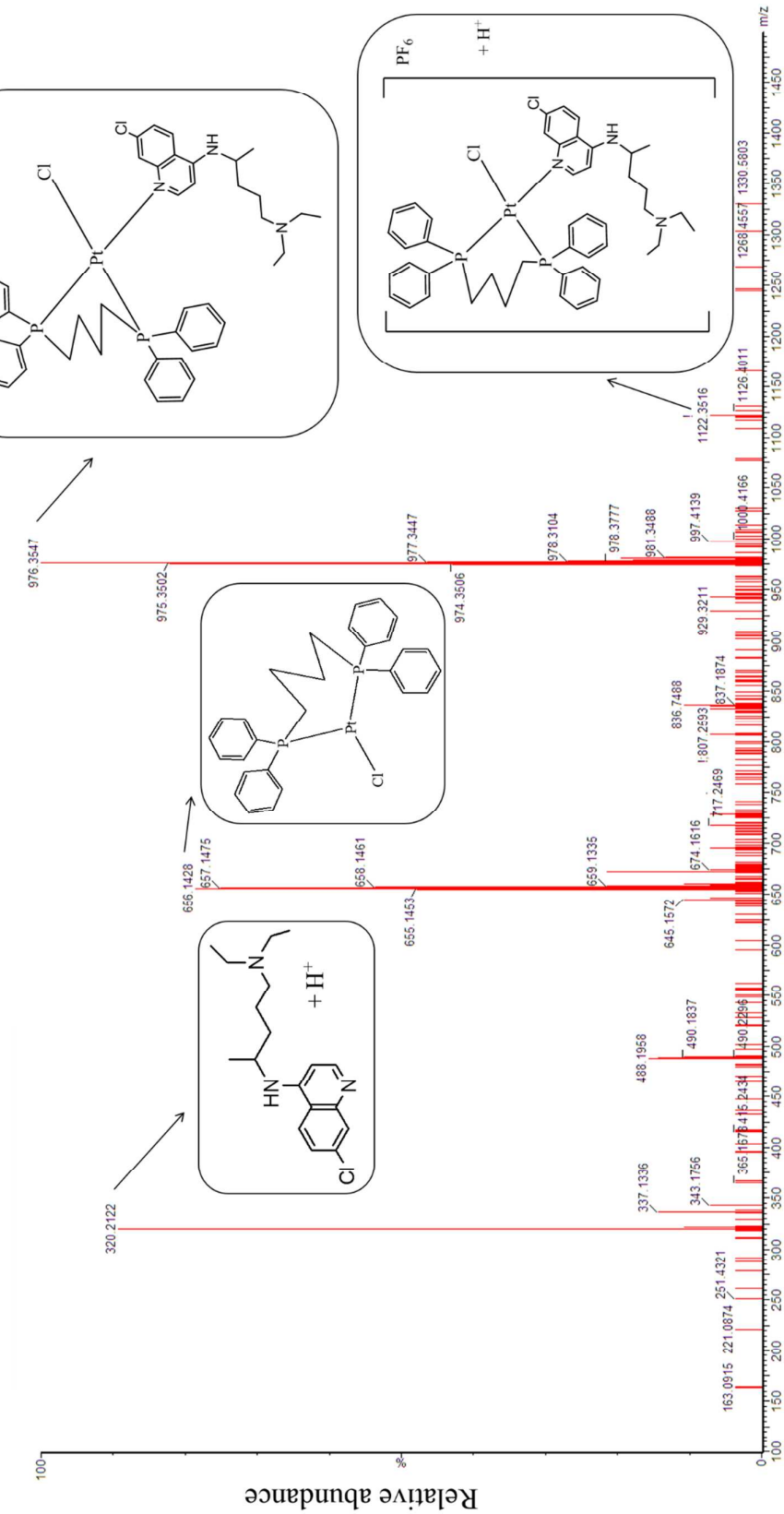

Figure S16. ESI(+)-MS spectrum of [PtCl(CQ)(dppb)]PF_6 (**7**) in Acetone.

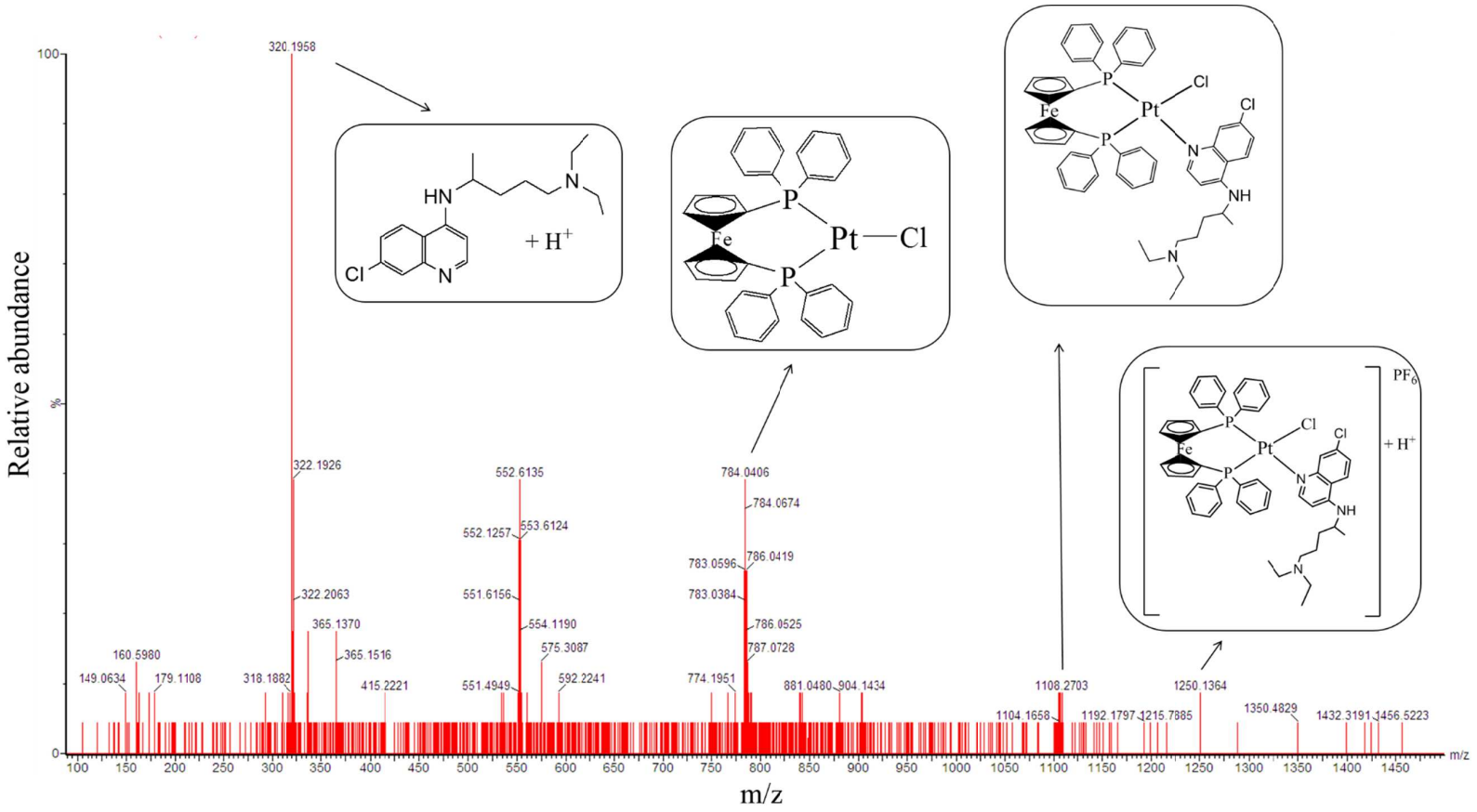

Figure S17. ESI(+)-MS spectrum of $[PtCl(CQ)(dppf)]PF_6$ **(8)** in Acetone.

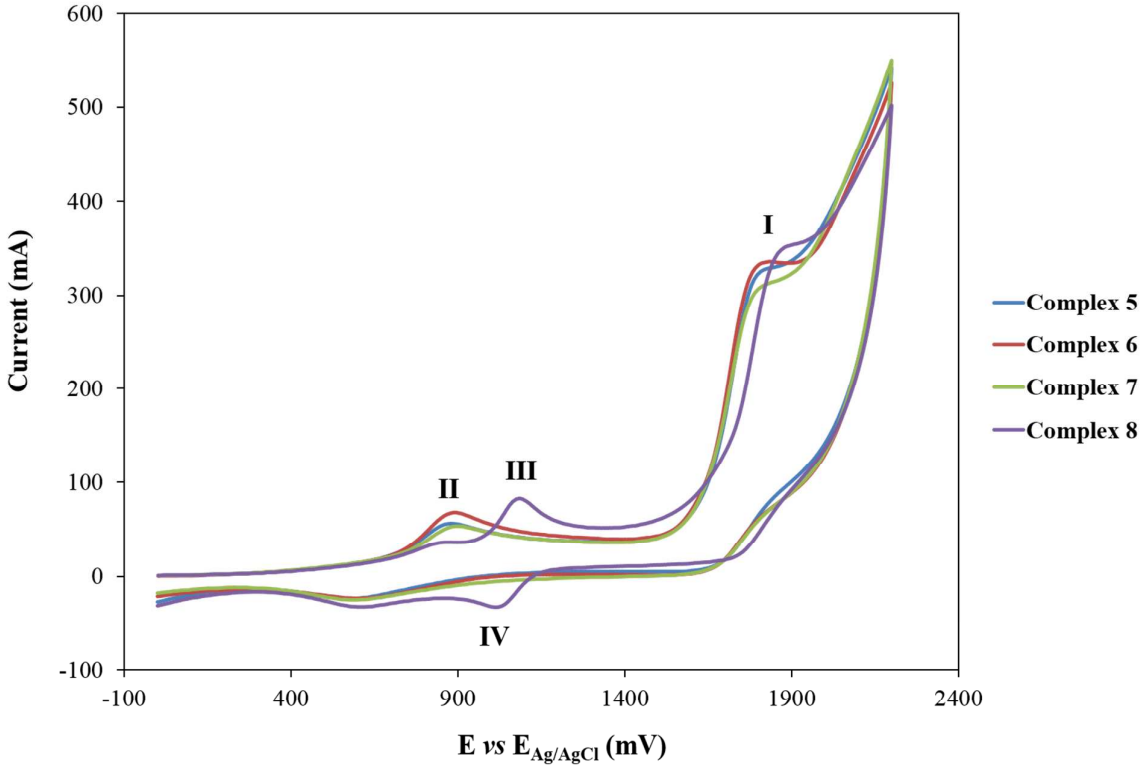

Figure S18. Cyclic voltammograms of the complexes **5-8** in acetonitrile, showed an oxidation wave **(I)** corresponding to oxidation of $Pt^{II} \rightarrow Pt^{III}$, an irreversible oxidation wave **(II)** corresponding to oxidation of the amino-alkyl chain of chloroquine and a reversible process **(III/IV)** referent to ferrocene ($Fe^{II} \rightarrow Fe^{III}$) present in **8**.

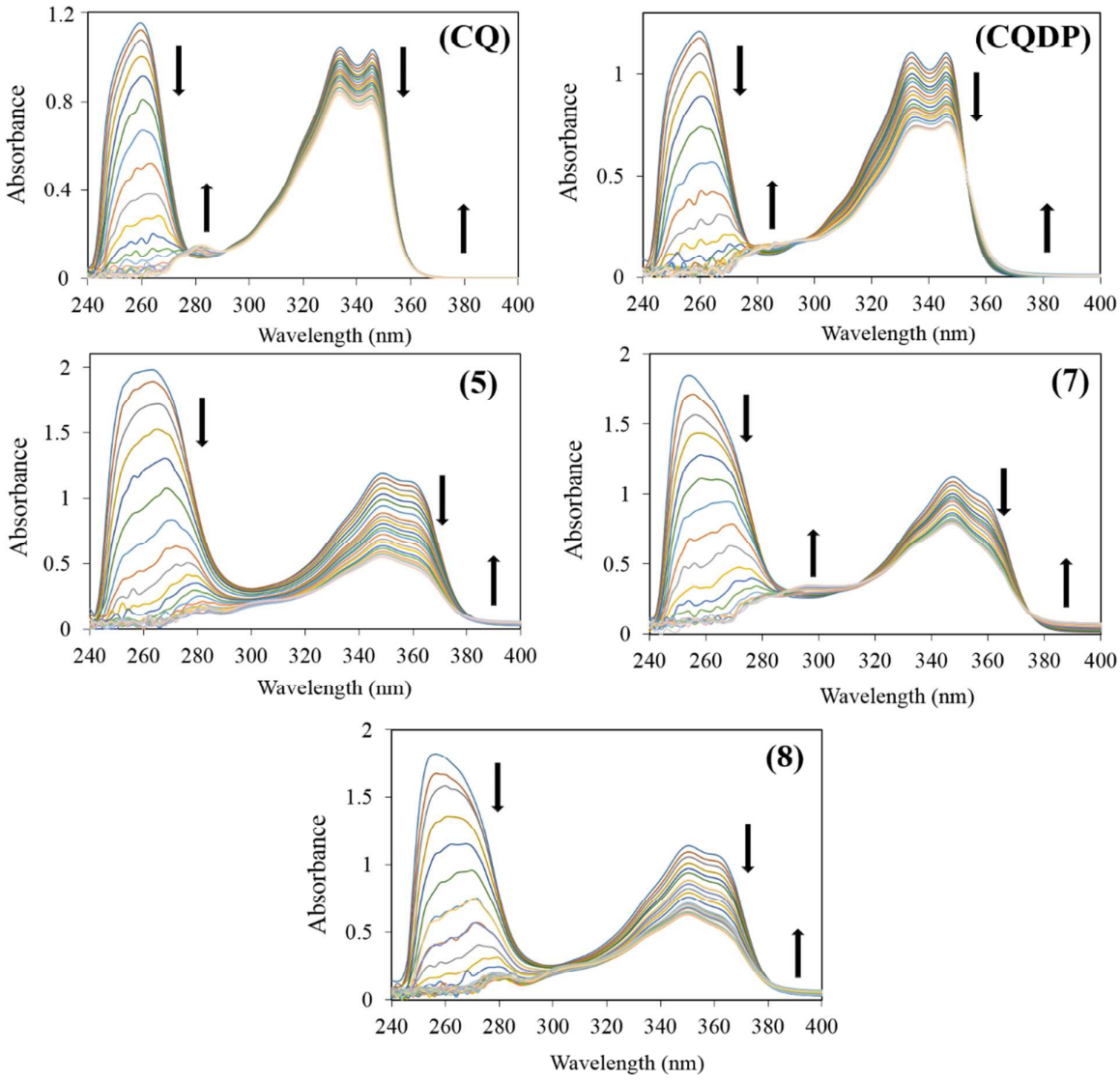

Figure S19. Spectrophotometric titration spectra of compounds with CT-DNA.

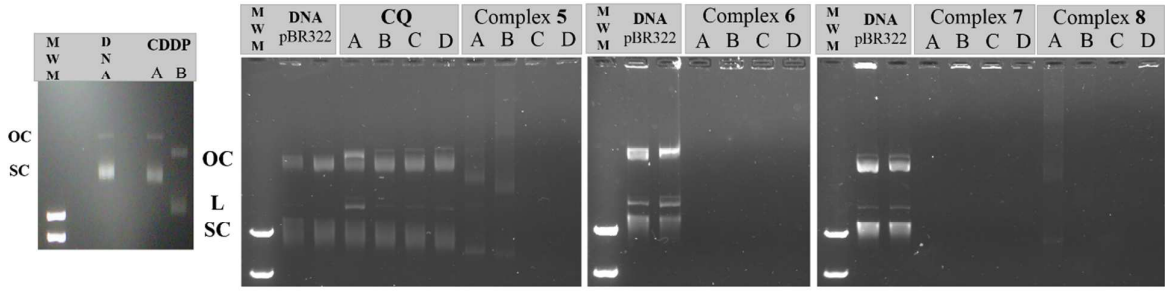

Figure S20. Effects of the concentration of complexes **5-8,** CQ and CDDP on the conformation of pBR322 plasmid DNA. The Ri values of the complex:DNA ratio are 0.5 (A), 1.0 (B), 2.0 (C) and 4.0 (D). Molecular weight marker (MWM) and DNA in DMSO (10%).

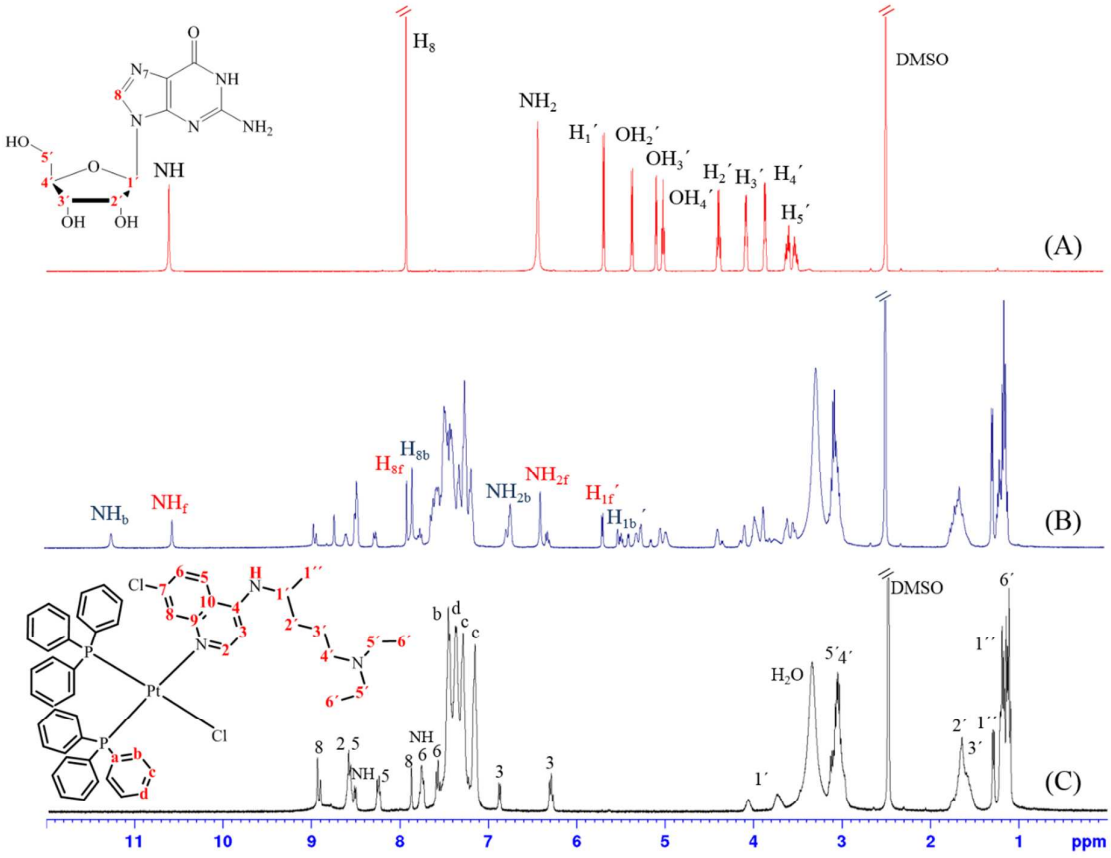

Figure S21. (A) ^{1}H NMR spectrum of guanosine in DMSO; (B) spectrum of a mixture of **(5)** and an excess of guanosine (1:1.2) immediately after sample preparation, only resonances of free (X_f) and bound (X_b) guanosine are assigned; (C) the ^{1}H NMR spectra of **(5)** in DMSO.

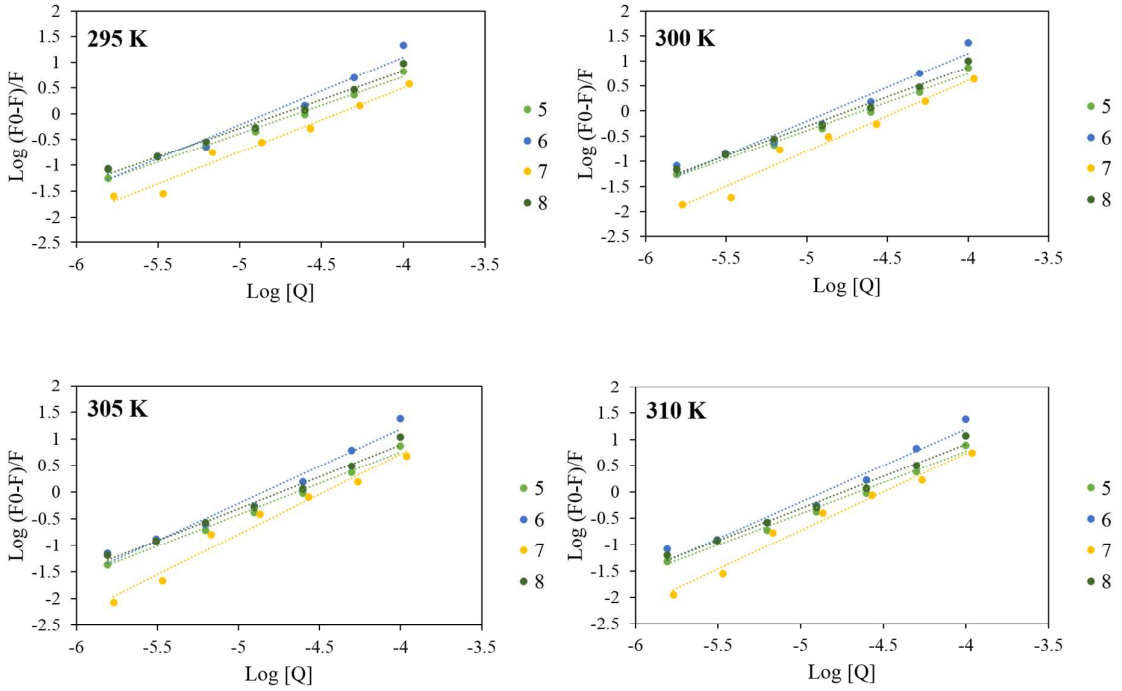

Figure S22. Plots of log(F_o-F)/F vs. log[Q] for the complexes **5-8**.

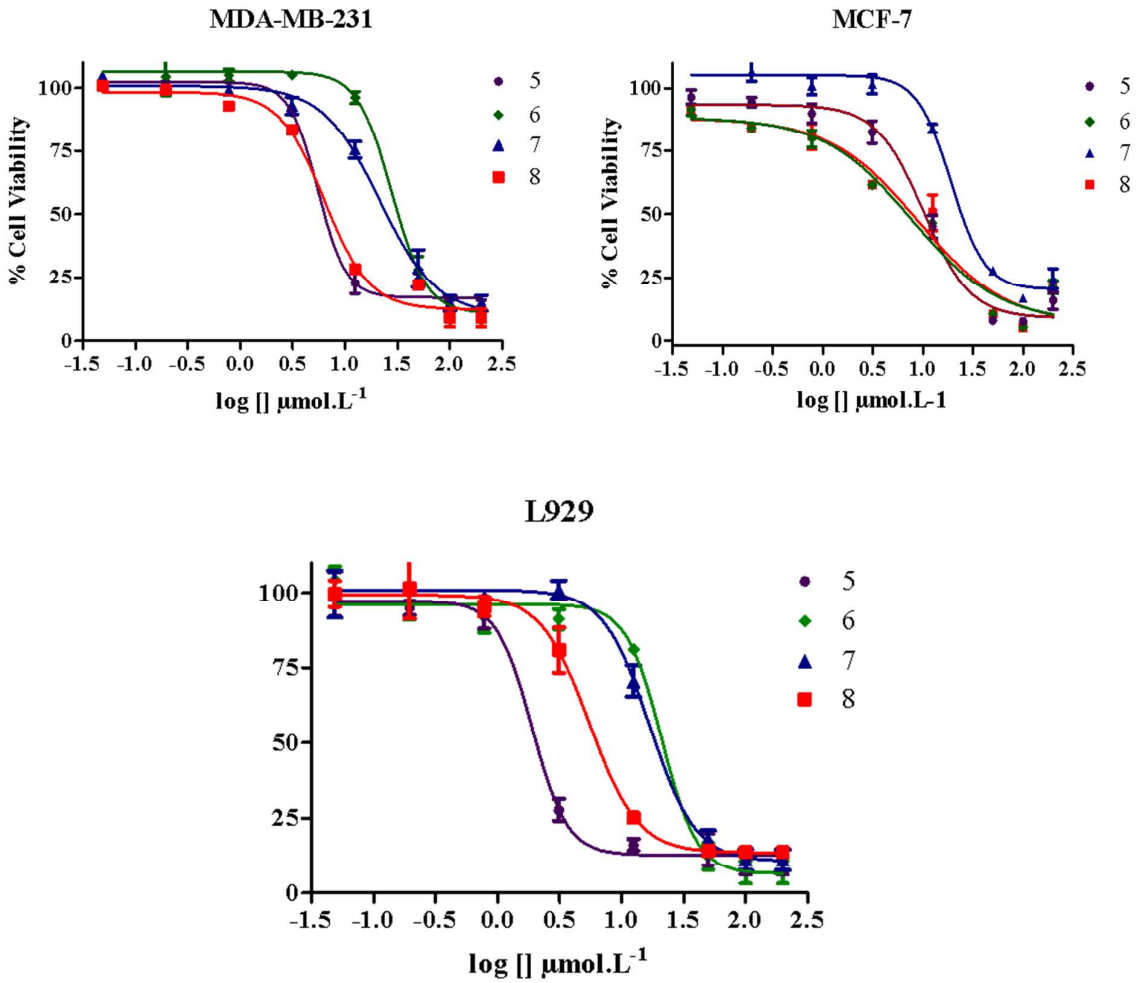

Figure S23. MTT colorimetric cell viability assay for MDA-MB-231 and MCF-7 tumor cell line of human breast, and L929 non-tumor cell line from mouse, treated with complexes **5-8** for 48 h.

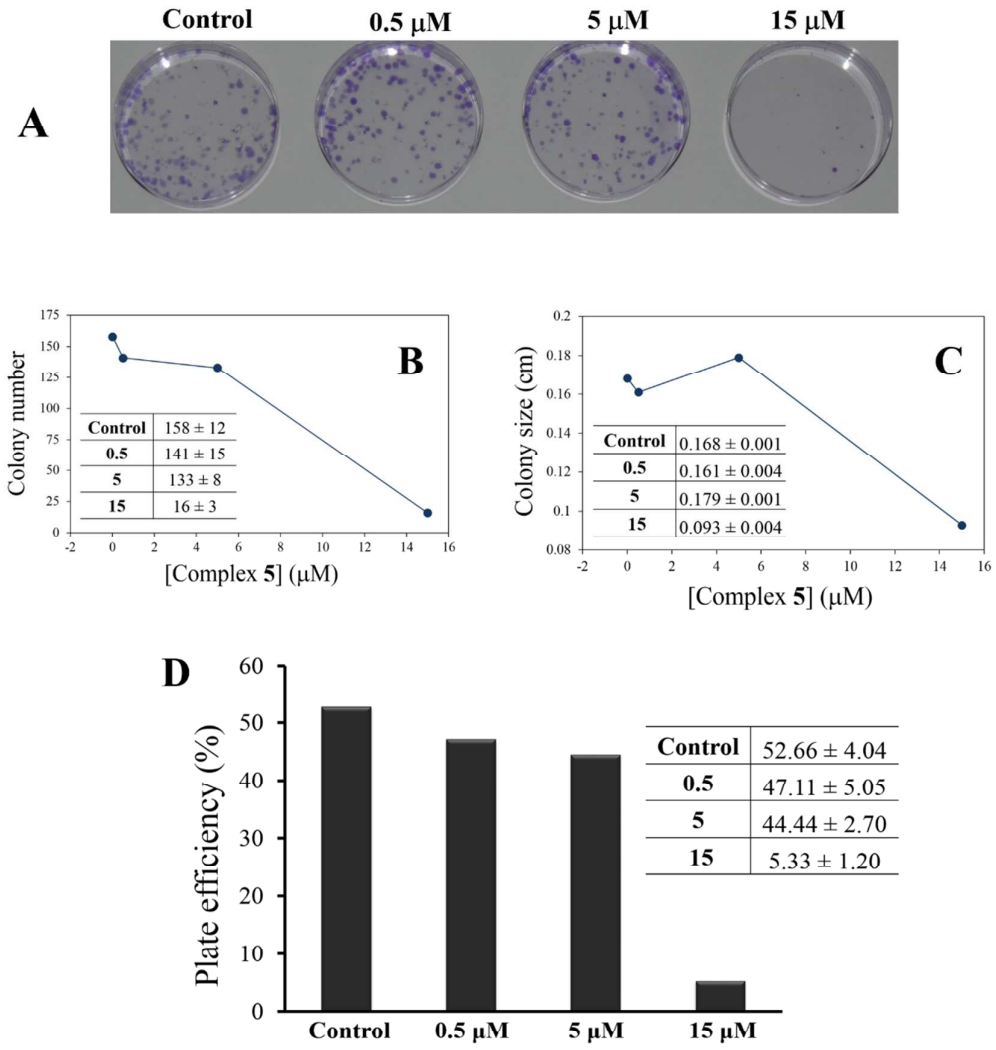

Figure S24. Effects of complex **5** on MDA-MB-231 colony formation. (A) Clonogenic assay of untreated MDA-MB-231 cells (control) or treated with complex **5** in 0.5, 5 and 15 µM, a photograph of Petri-dishes in a representative experiment is shown. (B) Quantification of colony number. (C) Quantification of colony size. (D) Plate efficiency. Quantification of colony number and size was performed using Image J public domain software.

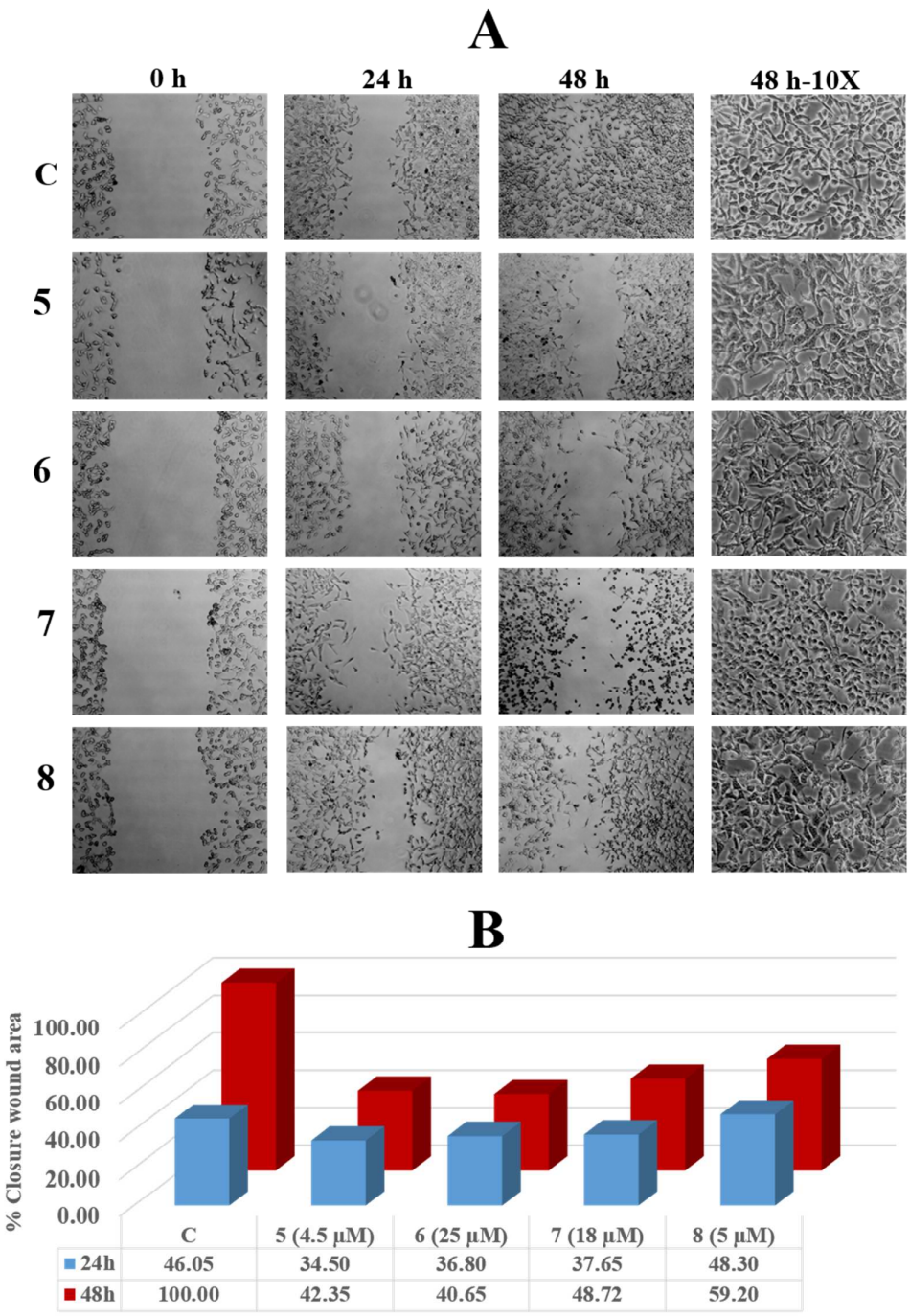

Figure S25. Effects of platinum complexes **5-8** on MDA-MB-231 cell migration (A) Wound-healing assay on MDA-MB-231 cells scratched using a pipette tip to make gaps between cells before complexes treatment, at 0, 24 and 48 hours of treatment, the plates were photographed under a light microscope. (B) Graphical representation of the quantitative values of the wound size.

Table S1. X-Ray crystallographic data collection and refinement parameters for complex **7a.**

Formula	$[PtC_{37}ClH_{35}NP_2]PF_6$	
Molecular weight	931.11	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Wavelength	0.71073 Å	
Temperature	293(2)	100(2)
a (Å)	16.9550(2)	16.9650(3)
b (Å)	13.7020(2)	13.5500(2)
c (Å)	16.9720(3)	16.7870(2)
β (°)	110.8500(10)	111.8020(10)
Cell volume (Å^3)	3684.69(10)	3582.91(10)
Z	4	4
D_{calc} (g/cm^3)	1,678	1,732
F(0 00)	1832	1839
μ (mm^{-1})	4,069	4,185
Crystal size (mm^3)	0.29 × 0.21 × 0.17	0.35 x 0.18 x 0.17
θ_{min}, θ_{max} (°)	2.97–26.37	2.915 - 25.690
Reflections collected	84029	*35283*
Independent reflections (R_{int})	7515 (0.080)	6714 (0.104)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0398$, $wR_2 = 0.0999$	$R_1 = 0.0491$, $wR_2 = 0.1291$
R indices (all data)	$R_1 = 0.0517$, $wR_2 = 0.1050$	$R_1 = 0.0624$, $wR_2 = 0.1370$
Minimum and maximum residual density (e Å^{-3})	−1.362 , 1.185	−2.014 , 1.884

Table S2. Selected interatomic distances (Å) and angles (deg) for complex **7a**[*].

	293 (2) K	100 (2) K
Pt(1)-N(1)	2.118(5)	2.114(6)
Pt(1)-P(1)	2.2518(14)	2.2515(18)
Pt(1)-P(2)	2.2562(13)	2.2528(18)
Pt(1)-Cl(1)	2.3284(15)	2.3296(17)
C(111)-C(116)	1.396(8)	1.415(16)
C(121)-C(126)	1.37(5)	1.396(10)
C(221)-C(226)	1.391(8)	1.397(11)
N(1)-Pt(1)-P(1)	92.75(14)	92.61(17)
N(1)-Pt(1)-P(2)	169.60(14)	169.72(18)
P(1)-Pt(1)-P(2)	95.32(5)	95.17(7)
N(1)-Pt(1)-Cl(1)	84.40(14)	84.94(17)
P(1)-Pt(1)-Cl(1)	176.29(5)	176.50(7)
P(2)-Pt(1)-Cl(1)	87.79(5)	87.56(6)

[*]Atoms are labeled as indicated in Figure 4. The numbers in the parentheses are the estimated standard deviations of the last significant figures.

Table S3. Assignments in ^{1}H, $^{13}C\{^{1}H\}$ and $^{15}N\{^{1}H\}$ NMR for CQ free in CH_2Cl_2-d_2.

^{1}H			$^{13}C\{^{1}H\}$		$^{15}N\{^{1}H\}$	
Assignments	δ (ppm)	*J* Hz	Assignments	δ (ppm)	Assignments	δ (ppm)
H_6'	0.97	7.12	C_6'	11.62	N_1	358.65
H_1''	1.29	6.32	C_1''	20.20	N_2	340.60
H_3'	1.58	m	C_3'	24.19	N_3	335.99
H_2'	1.72	m	C_2'	34.77		
H_4'	2.41	6.78	C_5'	47.18		
H_5'	2.48	7.12	C_1'	48.75		
H_1'	3.69	m	C_4'	52.86		
NH	5.46	6.40	C_3	99.67		
H_3	6.45	5.44	C_{10}	117.88		
H_6	7.33	2.10-8.94	C_5	122.14		
H_5	7.75	8.94	C_6	125.00		
H_8	7.89	2.10	C_8	128.81		
H_2	8.46	5.44	C_7	134.80		
			C_9	149.65		
			C_4	149.81		
			C_2	152.28		

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