

SUPPORTING INFORMATION

Selective coordination mode of acylthiourea ligands in half sandwich Ru(II) complexes and their selectivity against anticancer cells

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(175 μM) ($\lambda_{\text{ex}} = 480 \text{ nm}$) at different concentrations (0-50 μM) of complexes **5m** and **5b** at 25 °C.

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Tables S1-S3. Crystal data and structure refinement parameters obtained for the complexes **1m-6m**, **1b**, **2b** and **4b-6b**.

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Table S6: Characteristic $^{13}\text{C}\{^1\text{H}\}$ NMR signals experimental and theoretical (ppm) for acylthiourea ligand and complexes early reported.

Measurements

All solvents used in reactions were purified by standard methods. Reactions were performed under inert atmosphere of argon. The ^1H (400 MHz), $^{13}\text{C}\{^1\text{H}\}$ (100 MHz) and $^{31}\text{P}\{^1\text{H}\}$ (162 MHz) NMR spectra were recorded on a Bruker 9.4 T equipment, AVANCE III model, using deuterated solvent for ^1H and $^{13}\text{C}\{^1\text{H}\}$ and a D_2O capillary (external reference) for $^{31}\text{P}\{^1\text{H}\}$ experiments. IR spectra were recorded on a FT-IR Bomem-Michelson 102 Spectrometer in the range 4000-250 cm^{-1} using KBr pellets, at room temperature. Elemental analysis was carried out by the microanalytical laboratory at the Chemistry Department of the Federal University of São Carlos using an EA 1108 CHNS microanalyser (Fisons Instruments). Conductivity analyses were performed in a Micronal model B-330 connected to a Pt with constant cell equal to 0.089 cm^{-1} , using 1mM solutions of the complexes in acetone. Circular dichroism measures were carried out in a spectropolarimeter JASCO J720. The HSA interaction and Hoechst displacement analysis were performed in a fluorimeter BioTeK SYNERGY/H1 microplate reader. Cell cycle and apoptosis assays were performed in Accuri C6 flow cytometer (BD Biosciences) and fluorescence was quantified by CellQuest software (BD Biosciences).

Characterization of complexes

1.1.1 [Ru(η^6 -p-cymene)(PPh_3)(N',N'-dimethyl-N'-benzoylthiourea)Cl](PF₆) (1m)

Elemental analysis (%) calc. for [RuC₃₈H₄₁N₂OPSCl]PF₆: exp. (calc.) C, 51.38 (51.50); H, 4.60 (4.66); N, 3.17 (3.16); S 3.33 (3.62)%. Molar conductance (acetone): 129 S cm² mol⁻¹. IR (KBr, cm^{-1}): (ν N-H) 3206; (ν C-H_{cym, PPh₃, T) 3055, 2962, 2871 ; (ν C=O) 1697; (ν C=S) 1282; (ν C-P) 1094; (ν P-F) 837; (ν Ru-P) 557; (ν Ru-S) 501. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 28.80 (s). ^1H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 0.83 (d, 3H, ^3J =}

6.9 CH₃ isopropyl of p-cymene); 1.02 (d, 3H, ³J= 6.9 CH₃ isopropyl of p-cymene); 1.95 (s, 3H, CH₃ p-cymene); 2.34 (hept, ³J= 6.9 Hz, 1H, CH isopropyl of p-cymene); 3.43 (s, 3H, CH₃ acylthiourea); 3.70 (s, 3H, CH₃ acylthiourea); 4.97 (d, 1H, ³J= 6.0 Hz, CH aromatic near methyl of p-cymene); 5.05 (d, 1H, ³J= 6.2 Hz, CH aromatic near isopropyl of p-cymene); 5.48 (d, 1H, ³J= 6.0 Hz, CH aromatic near isopropyl of p-cymene); 5.75 (d, 1H, ³J= 6.2 Hz, CH aromatic near methyl of p-cymene); 7.55 (m, 9H, H_{meta} and para triphenylphosphine); 7.69 (m, 8H, H₅ and H₇ acylthiourea and 6H_{ortho} triphenylphosphine); 7.82 (m, 1H, H₆ acylthiourea), 8.15 (d, 2H, ³J= 7.5 Hz, H₄ and H₈ acylthiourea), 11.37 (s, 1H, NH). ¹³C{¹H} NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 17.49 (CH₃ p-cymene); 22.03 and 22.25 (2 CH₃ isopropyl p-cymene); 31.49 (CH isopropyl p-cymene); 44.48 and 45.76 (C₉ and C₁₀); 89.66 and 90.53 (d, ²J_{CP}= 6.5; 2.3 Hz, 2 CH aromatic near isopropyl of p-cymene); 92.72 and 96.22 (d, ²J_{CP}= 1.9; 4.0 Hz, 2 CH aromatic near methyl of p-cymene); 100.26 (C adjacent CH₃ of p-cymene); 115.34 (C adjacent of isopropyl of p-cymene); 129.48 (d, ³J_{CP}= 10.3 Hz, C_{meta} triphenylphosphine); 129.98 (C₄ and C₈); 130.24 (C₅ and C₇); 132.10 (C_{para} triphenylphosphine); 133.46 (d, J_{CP}= 48.5 Hz C_{quaternary} triphenylphosphine); 134.95 (d, ²J_{CP}= 9.6 Hz, C_{ortho} triphenylphosphine); 135. 19 (C₃ and C₆); 165.18 (C₂); 181.00 (d, J_{CP}= 9.5 Hz, C₁).

1.1.2 [Ru(*η*⁶-p-cymene)(PPh₃)(N',N'-dimethyl-N'-benzoylthiourea)](PF₆) (1b)

Elemental analysis (%) calc. for [RuC₃₈H₄₀N₂OPS]PF₆: exp. (calc.) C, 53.36 (53.71); H, 4.90 (4.74); N, 3.40 (3.30); S 4.01 (3.77)%. Molar conductance (acetone): 132 S cm² mol⁻¹. IR (KBr, cm⁻¹): (ν C-H cym, PPh₃, T) 3057, 2964, 2929, 2873 ; (ν C=O) 1507; (ν C=S) 1286; (ν C-P) 1094; (ν P-F) 840; (ν Ru-P) 557; (ν Ru-S) 500; (ν Ru-O) 374. ³¹P{¹H} NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 35.24 (s). ¹H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 1.19 (d, 3H, ³J= 6.9 CH₃ isopropyl p-cymene); 1.20 (d, 3H, ³J= 6.9 CH₃ isopropyl p-cymene); 1.94 (s,

3H, CH₃ p-cymene); 2.78 (hept, ³J= 6.9 Hz, 1H, CH isopropyl p-cymene); 3.22 (s, 3H, CH₃ acylthiourea); 3.38 (s, 3H, CH₃ acylthiourea); 5.30 (d, 1H, ³J= 6.1 Hz, CH aromatic near methyl of p-cymene); 5.80 (d, 1H, ³J= 6.1 Hz, CH aromatic near methyl of p-cymene); 5.85 (d, 1H, ³J= 6.2 Hz, CH aromatic near isopropyl of p-cymene); 6.02 (d, 1H, ³J= 6.2 Hz, CH aromatic near isopropyl of p-cymene); 7.35 (m, 2H, H₅ and H₇ acylthiourea); 7.50 (m, 10H, 1H₆ acylthiourea and 9H_{meta} and para triphenylphosphine); 7.59 (m, 6H, H_{ortho} triphenylphosphine); 7.92 (m, 2H, H₄ and H₈ acylthiourea). ¹³C{¹H} NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 18.24 (CH₃ p-cymene); 21.78 and 22.89 (2 CH₃ isopropyl p-cymene); 31.57 (CH isopropyl p-cymene); 40.77 and 41.99 (C₉ and C₁₀); 89.58 and 92.38 (CH aromatic near methyl of p-cymene); 90.39 and 94.31 (d, ²J_{CP}= 4.1; 3.9 Hz, CH aromatic near isopropyl of p-cymene); 104.91 (C adjacent of CH₃ of p-cymene); 115.74 (d, ²J_{CP}= 6.2 Hz C adjacent of isopropyl of p-cymene); 128.79 (C₅ and C₇); 129.55 (d, ³J_{CP}= 10.1 Hz, C_{meta} triphenylphosphine); 129.91 (C₄ and C₈); 131.86 (d, J_{CP}= 48.5 Hz C_{quaternary} triphenylphosphine); 131.96 (C_{para} triphenylphosphine); 132.52 (C₆); 135.13 (d, ²J_{CP}= 9.6 Hz, C_{ortho} triphenylphosphine); 137.78 (C₃); 172.40 (C₂); 174.86 (C₁).

1.1.3 [Ru(η⁶-p-cymene)(PPh₃)(N',N'-diethyl-N'benzoylthiourea)Cl](PF₆) (2m)

Elemental analysis (%) calc. for [RuC₄₀H₄₅N₂OPSCl]PF₆: exp. (calc.) C, 52.40 (52.54); H, 4.94 (4.96); N, 3.08 (3.06); S 3.25 (3.51)%. Molar conductance (acetone): 140 S cm² mol⁻¹. IR (KBr, cm⁻¹): (vN-H) 3142; (vC-H cym, PPh₃, T) 3058, 2987, 2935, 2870 ; (vC=O) 1699; (vC=S) 1262; (vC-P) 1095; (vP-F) 839; (vRu-P) 557; (vRu-S) 501. ³¹P{¹H} NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 29.10 (s). ¹H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 0.83 (d, 3H, ³J= 6.9 CH₃ isopropyl p-cymene); 1.05 (d, 3H, ³J= 6.9 CH₃ isopropyl p-cymene); 1.29 (t, 3H, ³J= 7.1 Hz, CH₃ acylthiourea); 1.37 (t, 3H, J= 7.1 Hz, CH₃ acylthiourea); 1.94 (s, 3H, CH₃ p-cymene); 2.36 (hept, J= 6.9 Hz, 1H, CH isopropyl p-cymene); 3.81 (m, 2H,

CH_2 acylthiourea); 4.15 (m, 2H, CH_2 acylthiourea); 4.84 (d, 1H, $J = 6.1$ Hz, CH aromatic near methyl p-cymene); 4.94 (d, 1H, $J = 6.4$ Hz, CH aromatic near isopropyl p-cymene); 5.64 (d, 1H, $J = 6.1$ Hz, CH aromatic near isopropyl p-cymene); 5.82 (d, 1H, $J = 6.4$ Hz, CH aromatic near methyl p-cymene); 7.55 (m, 9H, H_{meta} and para triphenylphosphine); 7.68 (m, 8H, H_5 and H_7 acylthiourea and 6H_{ortho} triphenylphosphine); 7.82 (m, 1H, H_6 acylthiourea); 8.16 (m, 2H, H_4 and H_8 acylthiourea); 11.18 (s, 1H, NH). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 12.25 and 12.78 (C_{10} and C_{12}); 17.50 (CH_3 p-cymene); 21.78 and 22.29 (2 CH_3 isopropyl p-cymene); 31.40 (CH isopropyl p-cymene); 48.74 and 51.12 (C_9 and C_{11}); 89.78 and 90.12 (d,s, $^2J_{\text{CP}} = 6.3$, CH aromatic near group of p-cymene); 93.34 and 95.75 (s,d, $^2J_{\text{CP}} = 3.5$ Hz, CH aromatic near methyl group of p-cymene); 100.39 (C adjacent of CH_3 of p-cymene); 115.08 (C adjacent of isopropyl of p-cymene); 129.50 (d, $^3J_{\text{CP}} = 10.2$ Hz, C_{meta} triphenylphosphine); 129.92 (C_4 and C_8); 130.29 (C_5 and C_7); 132.15 (C_{para} of triphenylphosphine); 133.25 (d, $J_{\text{CP}} = 48.5$ Hz $\text{C}_{\text{quaternary}}$ triphenylphosphine); 134.98 (d, $^2J_{\text{CP}} = 9.5$ Hz, C_{ortho} triphenylphosphine); 135.20 (C_3 and C_6); 165.67 (C_2); 180.73 (d, $J_{\text{CP}} = 9.8$ Hz, C_1).

1.1.4 [Ru(η^6 -p-cymene)(PPh₃)(N',N'-diethyl-N'-benzoylthiourea)](PF₆) (2b)

Elemental analysis (%) calc. for [RuC₄₀H₄₄N₂OPS]PF₆: exp. (calc.) C, 54.75 (54.73); H, 5.37 (5.05); N, 3.16 (3.19); S 3.82 (3.65)%. Molar conductance (acetone): 139 S cm² mol⁻¹. IR (KBr, cm⁻¹): (ν C-H_{cym, PPh₃, T) 3059, 2971, 2932, 2873; (ν C=O) 1503; (ν C=S) 1248; (ν C-P) 1095; (ν P-F) 839; (ν Ru-P) 557; (ν Ru-S) 501; (ν Ru-O) 341. $^{31}\text{P}\{\text{H}\}$ NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 35.45 (s). ^1H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 1.20 (m, 9H, 2 CH_3 isopropyl p-cymene and 1 CH_3 acylthiourea); 1.29 (t, 3H, $^3J = 7.1$, CH_3 acylthiourea); 1.95 (s, 3H, CH_3 p-cymene); 2.80 (hept, $^3J = 6.9$ Hz, 1H, CH isopropyl p-cymene); 3.73 (m, 2H, CH_2 acylthiourea); 3.94 (m, 2H, CH_2 acylthiourea); 5.43 (d, 1H,}

$^3J = 6.1$ Hz, CH aromatic near isopropyl of p-cymene); 5.70 (d, 1H, $^3J = 6.2$ Hz, CH aromatic near isopropyl of p-cymene); 5.89 (d, 1H, $^3J = 6.1$ Hz, CH aromatic near methyl of p-cymene); 6.02 (d, 1H, $^3J = 6.2$ Hz, CH aromatic near methyl of p-cymene); 7.34 (m, 2H, H₅ and H₇ acylthiourea); 7.47 (m, 10H, H₆ acylthiourea and 9H_{meta} and para triphenylphosphine); 7.57 (m, 6H, H_{ortho} triphenylphosphine); 7.85 (m, 2H, H₄ and H₈ acylthiourea). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 13.08 and 13.66 (C₁₀ and C₁₂); 18.18 (CH₃ p-cymene); 21.91 and 22.75 (2 CH₃ isopropyl p-cymene); 31.68 (CH isopropyl p-cymene); 46.56 and 47.54 (C₉ and C₁₁); 89.82 and 92.88 (CH aromatic near isopropyl of p-cymene); 90.89 and 94.82 (d, $^2J_{\text{CP}} = 4.6$, 3.1 Hz, CH aromatic near methyl of p-cymene); 104.15 (C adjacent of CH₃ of p-cymene); 115.98 (d, $^2J_{\text{CP}} = 5.9$ Hz, C adjacent of isopropyl of p-cymene); 128.74 (C₅ and C₇); 129.58 (d, $^3J_{\text{CP}} = 10.1$ Hz, C_{meta} triphenylphosphine); 129.87 (C₄ and C₈); 131.89 (d, $J_{\text{CP}} = 47.2$ Hz C_{quaternary} triphenylphosphine); 131.97 (C_{para} triphenylphosphine); 132.48 (C₆); 135.10 (d, $^2J_{\text{CP}} = 9.6$ Hz, C_{ortho} triphenylphosphine); 137.94 (C₃); 172.72 (C₂); 173.70 (C₁).

1.1.5 [Ru(η^6 -p-cymene)(PPh₃)(N',N'-dimethyl-N'-2-furoylthiourea)Cl](PF₆) (3m)

Elemental analysis (%) calc. for [RuC₃₆H₃₉N₂O₂PSCl]PF₆: exp. (calc.) C, 49.34 (49.35); H, 4.63 (4.49); N, 3.60 (3.20); S 3.55 (3.66)%. Molar conductance (acetone): 135 S cm² mol⁻¹. IR (KBr, cm⁻¹): (ν N-H) 3146; (ν C-H_{cym, PPh₃, T}) 3058, 2963, 2931, 2870; (ν C=O) 1706; (ν C=S) 1263; (ν C-P) 1096; (ν P-F) 838; (ν Ru-P) 557; (ν Ru-S) 500. $^{31}\text{P}\{\text{H}\}$ NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 28.74 (s). ^1H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 0.99 (d, 3H, $^3J = 6.9$ CH₃ isopropyl p-cymene); 1.07 (d, 3H, $^3J = 6.9$ CH₃ isopropyl p-cymene); 2.02 (s, 3H, CH₃ p-cymene); 2.47 (hept, $^3J = 6.9$ Hz, 1H, CH isopropyl p-cymene); 3.41 (s, 3H, CH₃ acylthiourea); 3.67 (s, 3H, CH₃ acylthiourea); 5.07 (d, 1H, $^3J = 6.0$ Hz, CH aromatic near methyl of p-cymene); 5.10 (d, 1H, $^3J = 6.3$ Hz, CH aromatic near isopropyl of p-cymene); 5.57 (d, 1H, $^3J = 6.0$ Hz, CH aromatic near isopropyl of p-cymene); 5.77 (d,

1H, 3J = 6.3 Hz, CH aromatic near methyl of p-cymene); 6.87 (dd, 1H, 3J = 3.4, 3J = 1.5 Hz, H₅); 7.56 (m, 10H, H₄ and 9H_{meta} and para triphenylphosphine); 7.70 (m, 6H, H_{ortho} triphenylphosphine); 8.06 (m, 1H, H₆), 11.23 (s, 1H, NH). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 17.52 (CH₃ p-cymene); 21.94 and 22.10 (2 CH₃ isopropyl p-cymene); 31.43 (CH isopropyl p-cymene); 44.45 and 45.79 (C₇ and C₈); 89.77 and 90.41 (d,s, $^2J_{\text{CP}}$ = 6.1 Hz, CH aromatic near isopropyl of p-cymene); 93.20 and 95.87 (s,d, $^2J_{\text{CP}}$ = 3.5 Hz, CH aromatic near methyl of p-cymene); 100.63 (C adjacent of CH₃ p-cymene); 114.02 (C₅); 114.87 (C adjacent of isopropyl of p-cymene); 120.21 (C₄); 129.39 (d, $^3J_{\text{CP}}$ = 10.3 Hz, C_{meta} triphenylphosphine); 132.03 (C_{para} triphenylphosphine); 133.41 (d, J_{CP} = 48.4 Hz C_{quaternary} triphenylphosphine); 134.89 (d, $^2J_{\text{CP}}$ = 9.5 Hz, C_{ortho} triphenylphosphine); 146.15 (C₃); 148.99 (C₆) 155.14 (C₂); 180.05 (d, J_{CP} = 9.7 Hz, C₁).

1.1.6 [Ru(η^6 -p-cymene)(PPh₃)(N',N'-dimethyl-N'-2-furoylthiourea)](PF₆) (3b)

Elemental analysis (%) calc. for [RuC₃₆H₃₈N₂O₂PS]PF₆: exp. (calc.) C, 51.31 (51.49); H, 4.46 (4.56); N, 4.20 (3.81); S 3.69 (3.82)%. Molar conductance (acetone): 129 S cm² mol⁻¹. IR (KBr, cm⁻¹): (ν C-H cym, PPh₃, T) 3056, 2966, 2930, 2873; (ν C=O) 1578; (ν C=S) 1263; (ν C-P) 1096; (ν P-F) 839; (ν Ru-P) 557; (ν Ru-S) 495; (ν Ru-O) 340. $^{31}\text{P}\{\text{H}\}$ NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 33.54 (s). ^1H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 1.22 (d, 3H, 3J = 6.9 CH₃ isopropyl p-cymene); 1.23 (d, 3H, 3J = 6.9 CH₃ isopropyl p-cymene); 1.95 (s, 3H, CH₃ of p-cymene); 2.75 (hept, 3J = 6.9 Hz, 1H, CH isopropyl p-cymene); 3.14 (s, 3H, CH₃ acylthiourea); 3.34 (s, 3H, CH₃ acylthiourea); 5.49 (d, 1H, 3J = 6.0 Hz, CH aromatic near isopropyl of p-cymene); 5.63 (d, 1H, 3J = 6.1 Hz, CH aromatic near methyl of p-cymene); 5.83 (d, 1H, 3J = 6.1 Hz, CH aromatic near methyl of p-cymene); 5.97 (d, 1H, 3J = 6.0 Hz, CH aromatic near methyl of p-cymene); 6.52 (m, H₅); 7.01 (m, 1H, H₄); 7.48 (m, 6H, H_{meta} triphenylphosphine); 7.57 (m, 9H, H_{ortho} and para

triphenylphosphine); 7.68 (m, 1H, H₆). ¹³C{¹H} NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 17.79 (CH₃ p-cymene); 21.88 and 22.71 (2 CH₃ isopropyl of p-cymene); 31.51 (CH isopropyl of p-cymene); 40.44 and 41.62 (C₇ and C₈); 90.90 and 91.59 (CH aromatic near isopropyl of p-cymene); 90.53 and 94.91 (d, ²J_{CP}= 4.5, 3.4 Hz, CH aromatic near methyl of p-cymene); 104.08 (C adjacent of CH₃ of p-cymene); 112.68 (C₅); 114.64 (d, ²J_{CP}= 4.7 Hz, C adjacent of isopropyl group of p-cymene); 116.71 (C₄); 129.39 (d, ³J_{CP}= 9.9 Hz, C_{meta} triphenylphosphine); 131.86 (C_{para} triphenylphosphine); 131.89 (d, J_{CP}= 47.1 Hz C_{quaternary} triphenylphosphine); 134.98 (d, ²J_{CP}= 9.4 Hz, C_{ortho} triphenylphosphine); 146.70 (C₆); 151.62 (C₃) 164.07 (C₂); 174.00 (C₁).

1.1.7 [Ru(η⁶-p-cymene)(PPh₃)(N',N'-diethyl-N'-2-furoylthiourea)Cl](PF₆) (4m)

Elemental analysis (%) calc. for [RuC₃₈H₄₃N₂O₂PSCl]PF₆: exp. (calc.) C, 50.54 (50.47); H, 4.92 (4.79); N, 3.07 (3.10); S 3.27 (3.55)%. Molar conductance (acetone): 136 S cm² mol⁻¹. IR (KBr, cm⁻¹): (vN-H) 3116; (vC-H cym, PPh₃, T) 2979, 2936, 2876 ; (vC=O) 1693; (vC=S) 1284; (vC-P) 1093; (vP-F) 841; (vRu-P) 557; (vRu-S) 499. ³¹P{¹H} NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 29.61 (s). ¹H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 0.99 (d, 3H, ³J= 6.9 CH₃ isopropyl p-cymene); 1.10 (d, 3H, ³J= 6.9 CH₃ isopropyl p-cymene); 1.26 (t, 3H, ³J= 7.1 Hz, CH₃ acylthiourea); 1.35 (t, 3H, ³J= 7.1 Hz, CH₃ acylthiourea); 2.01 (s, 3H, CH₃ p-cymene); 2.48 (hept, ³J= 6.9 Hz, 1H, CH isopropyl p-cymene); 3.78 (m, 2H, CH₂ acylthiourea); 4.10 (m, 2H, CH₂ acylthiourea); 4.96 (d, 1H, ³J= 6.1 Hz, CH aromatic near methyl of p-cymene); 5.00 (d, 1H, ³J= 6.3 Hz, CH aromatic near methyl of p-cymene); 5.71 (d, 1H, ³J= 6.1 Hz, CH aromatic near isopropyl of p-cymene); 5.84 (d, 1H, J= 6.3 Hz, CH aromatic near isopropyl of p-cymene); 6.87 (dd, ³J= 3.5, ³J= 1.7 Hz, 1H, H₅); 7.55 (m, 10H, H₄ and 9H_{meta} and para triphenylphosphine); 7.69 (m, 6H, H_{ortho} triphenylphosphine); 8.06 (m, 1H, H₆); 11.05 (s, 1H, NH).). ¹³C{¹H} NMR (100

MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 12.15 and 12.74 (C₈ and C₁₀); 17.56 (CH₃ p-cymene); 22.04 and 22.20 (2CH₃ isopropyl of p-cymene); 31.49 (CH isopropyl of p-cymene); 48.73 and 51.12 (C₇ and C₉); 89.95 and 93.82 (d, ²J_{CP}= 5.9, 3.0 Hz, CH aromatic near methyl of p-cymene); 90.15 and 95.41 (d, ²J_{CP}= 2.6, 3.4 Hz, CH aromatic near isopropyl of p-cymene); 100.91 (C adjacent of CH₃ of p-cymene); 114.09 (C₅); 114.63 (C adjacent of isopropyl of p-cymene); 120.11 (C₄); 129.46 (d, ³J_{CP}= 10.2 Hz, C_{meta} triphenylphosphine); 132.10 (C_{para} triphenylphosphine); 133.25 (d, J_{CP}= 48.6 Hz C_{quaternary} triphenylphosphine); 134.97 (d, ²J_{CP}= 9.5 Hz, C_{ortho} triphenylphosphine); 146.34 (C₃); 148.95 (C₆); 155.76 (C₂); 179.81 (d, J_{CP}= 9.9 Hz, C₁).

1.1.8 [Ru(η⁶-p-cymene)(PPh₃)(N',N'-diethyl-N'-2-furoylthiourea)](PF₆)(4b)

Elemental analysis (%) calc. for [RuC₃₈H₄₂N₂O₂PS]PF₆: exp. (calc.) C, 53.02 (52.59); H, 4.66 (4.88); N, 3.74 (3.23); S 3.54 (3.69)%. Molar conductance (acetone): 136 S cm² mol⁻¹. IR (KBr, cm⁻¹): (νC-H_{cym, PPh₃, T}) 3055, 2970, 2932, 2872; (νC=O) 1577; (νC=S) 1258; (νC-P) 1095; (νP-F) 840; (νRu-P) 557; (νRu-S) 498; (νRu-O) 336. ³¹P{¹H} NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 33.56 (s). ¹H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 1.13 (t, ³J=7.0 Hz, 3H, CH₃ acylthiourea); 1.27 (m, 9H, CH₃ acylthiourea and 2CH₃ isopropyl of p-cymene); 1.97 (s, 3H, CH₃ p-cymene); 2.79 (hept, ³J= 6.9 Hz, 1H, CH p-cymene); 3.66 (m, 2H, CH₂ acylthiourea); 3.90 (m, 2H, CH₂ acylthiourea); 5.57 (d, 1H, ³J= 6.2 Hz, CH aromatic near methyl of p-cymene); 5.61 (d, 1H, J= 6.2 Hz, CH aromatic near methyl of p-cymene); 5.89 (d, 1H, ³J= 6.2 Hz, CH aromatic near isopropyl of p-cymene); 5.98 (d, 1H, ³J= 6.2 Hz, CH aromatic near isopropyl of p-cymene); 6.52 (dd, ³J= 3.4, ³J= 1.7 Hz, 1H, H₅); 6.92 (dd, ³J= 3.4, ⁴J= 0.8 Hz, 1H, H₄); 7.48 (m, 6H, H_{meta} triphenylphosphine); 7.57 (m, 9H, H_{ortho} and _{para} triphenylphosphine); 7.71 (dd, ³J= 1.7, ⁴J= 0.8 Hz, 1H, H₆). ¹³C{¹H} NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 12.96 and 13.61 (C₈ and C₁₀); 17.78 (CH₃ p-cymene); 22.03 and

22.64 (2 CH₃ isopropyl of p-cymene); 31.65 (CH isopropyl of p-cymene); 46.44 and 47.23 (C₇ and C₉); 90.95 and 92.04 (CH aromatic near methyl of p-cymene); 90.95 and 95.04 (s,d, ²J_{CP}= 3.3 Hz, CH aromatic near isopropyl of p-cymene); 103.73 (C adjacent of CH₃ of p-cymene); 112.67 (C₅); 114.97 (d, ²J_{CP}= 4.8 Hz, C adjacent of isopropyl of p-cymene); 116.61 (C₄ of acylthiourea); 129.44 (d, J³_{CP}= 10.0 Hz, C_{meta} triphenylphosphine); 131.90 (C_{para} triphenylphosphine); 131.96 (d, J_{CP}= 47.0 Hz C_{quaternary} triphenylphosphine); 135.01 (d, ²J_{CP}= 9.5 Hz, C_{ortho} triphenylphosphine); 146.77 (C₆); 151.89 (C₃); 164.44 (C₂); 172.62 (C₁).

1.1.9 [Ru(η⁶-p-cymene)(PPh₃)(N',N'-dimethyl-N'-2-tiophenocarbonylthiourea)Cl](PF₆) (5m)

Elemental analysis (%) calc. for [RuC₃₆H₃₉N₂OPS₂Cl]PF₆: exp. (calc.) C, 48.35 (48.46); H, 4.54 (4.41); N, 3.15 (3.14); S 7.01 (7.19)%. Molar conductance (acetone): 139 S cm² mol⁻¹. IR (KBr, cm⁻¹): (vN-H) 3179 (vC-H cym, PPh₃, T) 3059, 2961, 2939, 2865; (vC=O) 1683; (vC=S) 1256; (vC-P) 1090; (vP-F) 838; (vRu-P) 557; (vRu-S) 501. ³¹P{¹H} NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 28.91 (s). ¹H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 0.93 (d, 3H, ³J= 6.9 CH₃ isopropyl of p-cymene); 1.05 (d, 3H, ³J= 6.9 CH₃ isopropyl of p-cymene); 2.00 (s, 3H, CH₃ of p-cymene); 2.43 (hept, ³J= 6.9 Hz, 1H, CH isopropyl of p-cymene); 3.41 (s, 3H, CH₃ acylthiourea); 3.69 (s, 3H, CH₃ acylthiourea); 5.07 (d, 1H, ³J= 6.2 Hz, CH aromatic near methyl of p-cymene); 5.13 (d, 1H, J= 6.4 Hz, CH aromatic near isopropyl of p-cymene); 5.55 (d, 1H, ³J= 6.2 Hz, CH aromatic near isopropyl of p-cymene); 5.78 (d, 1H, ³J= 6.4 Hz, CH aromatic near methyl of p-cymene); 7.40 (dd, 1H, ³J= 5.0, ³J= 3.9 Hz, H₅); 7.56 (m, 9H, H_{meta} and para triphenylphosphine); 7.69 (m, 6H, H_{ortho} triphenylphosphine); 8.09 (dd, ³J= 3.9, ⁴J= 1.1 Hz, 1H, H₄); 8.12 (dd, ³J= 5.0, ⁴J= 1.1 Hz, 1H, H₆); 11.33 (s, 1H, NH). ¹³C{¹H} NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 17.49 (CH₃ p-cymene); 21.80 and 22.04 (2

CH_3 isopropyl of p-cymene); 31.37 (CH isopropyl of p-cymene); 44.42 and 45.69 (C_7 and C_8); 89.59 and 90.56 (d, s , $^2\text{J}_{\text{CP}} = 6.2$ Hz, CH aromatic near isopropyl of p-cymene); 92.80 and 96.09 (s, d , $^2\text{J}_{\text{CP}} = 3.7$ Hz, CH aromatic near methyl of p-cymene); 100.49 (C adjacent of CH_3 of p-cymene); 115.10 (C adjacent of isopropyl of p-cymene); 129.42 (d , $^3\text{J}_{\text{CP}} = 10.1$ Hz, C_{meta} triphenylphosphine); 129.80 (C_5); 132.05 (C_{para} triphenylphosphine); 133.35 (d , $\text{J}_{\text{CP}} = 48.4$ Hz $\text{C}_{\text{quaternary}}$ triphenylphosphine); 133.95 (C_4); 134.87 (d , $^2\text{J}_{\text{CP}} = 9.6$ Hz, C_{ortho} triphenylphosphine); 136.41 (C_6); 136.56 (C_3) 159.56 (C_2); 180.28 (d , $\text{J}_{\text{CP}} = 9.6$ Hz, C_1).

1.1.10 [Ru(η^6 -p-cymene)(PPh₃)(N',N'-dimethyl-N'-2-

tiophenocarbonylthiourea)](PF₆) (5b)

Elemental analysis (%) calc. for [RuC₃₆H₃₈N₂OPS₂]PF₆: exp. (calc.) C, 50.69 (50.52); H, 4.18 (4.48); N, 3.76 (3.32); S 7.85 (7.49)%. Molar conductance (acetone): 138 S cm² mol⁻¹. IR (KBr, cm⁻¹): (ν C-H_{cym, PPh₃, T}) 3056, 2963, 2929, 2870; (ν C=O) 1500; (ν C=S) 1263; (ν C-P) 1095; (ν P-F) 839; (ν Ru-P) 558; (ν Ru-S) 496; (ν Ru-O) 352. ³¹P{¹H} NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 34.54 (s). ¹H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 1.21 (d, 3H, $^3\text{J} = 6.9$ CH_3 isopropyl of p-cymene); 1.23 (d, 3H, $^3\text{J} = 6.9$ CH_3 isopropyl of p-cymene); 1.94 (s, 3H, CH_3 p-cymene); 2.78 (hept, $^3\text{J} = 6.9$ Hz, 1H, CH isopropyl of p-cymene); 3.14 (s, 3H, CH_3 acylthiourea); 3.34 (s, 3H, CH_3 acylthiourea); 5.38 (d, 1H, $^3\text{J} = 6.0$ Hz, CH aromatic near isopropyl of p-cymene); 5.72 (d, 1H, $^3\text{J} = 6.0$ Hz, CH aromatic near methyl of p-cymene); 5.85 (d, 1H, $^3\text{J} = 6.0$ Hz, CH aromatic near methyl of p-cymene); 6.01 (d, 1H, $^3\text{J} = 6.0$ Hz, CH aromatic near methyl of p-cymene); 7.07 (m, H₅); 7.48 (m, 6H, H_{meta} triphenylphosphine); 7.59 (m, 12H, H₄, H₆ and 9H_{ortho} and para triphenylphosphine). ¹³C{¹H} NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 18.03 (CH_3 p-cymene); 21.80 and 22.86 (2 CH_3 isopropyl of p-cymene); 31.47 (CH isopropyl of p-cymene); 40.55 and 41.69 (CH_3 acylthiourea); 90.13

and 92.00 (CH aromatic near isopropyl of p-cymene); 90.50 and 94.98 (d, $^2J_{CP}$ = 4.2, 3.5 Hz, CH aromatic near methyl of p-cymene); 104.57 (C adjacent of CH_3 of p-cymene); 115.20 (d, $^2J_{CP}$ = 5.6 Hz, C adjacent of isopropyl of p-cymene); 128.69 (C_5); 129.45 (d, $^3J_{CP}$ = 10.0 Hz, C_{meta} triphenylphosphine); 131.73 (d, J_{CP} = 46.9 Hz $C_{quaternary}$ triphenylphosphine); 131.91 (C_{para} triphenylphosphine); 132.26 (C_4); 132.48 (C_6); 135.05 (d, $^2J_{CP}$ = 9.5 Hz, C_{ortho} triphenylphosphine); 143.54 (C_3); 167.97 (C_2); 173.85 (C_1).

1.1.11 [Ru(η^6 -p-cymene)(PPh₃)(N',N'-diethyl-N'-2-tiophenocarbonylthiourea)Cl](PF₆) (6m)

Elemental analysis (%) calc. for [RuC₃₆H₃₉N₂OPS₂Cl]PF₆: exp. (calc.) C, 49.63 (49.59); H, 4.91 (4.71); N, 3.29 (3.04); S 6.79 (6.97)%.
 Molar conductance (acetone): 138 S cm² mol⁻¹. IR (KBr, cm⁻¹): (ν N-H) 3170 (ν C-H_{cym, PPh3, T}) 3054, 2961, 2965, 2872; (ν C=O) 1685; (ν C=S) 1267; (ν C-P) 1092; (ν P-F) 840; (ν Ru-P) 557; (ν Ru-S) 500. ³¹P{¹H} NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 29.23 (s). ¹H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 0.93 (d, 3H, 3J = 6.9 CH_3 isopropyl of p-cymene); 1.09 (d, 3H, 3J = 6.9 CH_3 isopropyl of p-cymene); 1.28 (t, 3H, 3J = 7.2 CH_3 acylthiourea); 1.36 (t, 3H, 3J = 7.2 CH_3 acylthiourea); 2.00 (s, 3H, CH_3 p-cymene); 2.45 (hept, 3J = 6.9 Hz, 1H, CH isopropyl of p-cymene); 3.79 (m, 2H, CH_2 acylthiourea); 4.14 (q, 3J = 7.2 Hz, 2H, CH_2 acylthiourea); 4.96 (d, 1H, 3J = 6.2 Hz, CH aromatic near methyl of p-cymene); 5.04 (d, 1H, 3J = 6.4 Hz, CH aromatic near isopropyl of p-cymene); 5.71 (d, 1H, J = 6.2 Hz, CH aromatic near isopropyl of p-cymene); 5.87 (d, 1H, J = 6.4 Hz, CH aromatic near methyl of p-cymene); 7.42 (dd, 1H, 3J = 5.0, 3J = 3.9 Hz, H_5); 7.56 (m, 9H, H_{meta} and $para$ triphenylphosphine); 7.68 (m, 6H, H_{ortho} triphenylphosphine); 8.09 (dd, 3J = 3.9, 4J = 1.1 Hz, 1H, H_4); 8.13 (dd, $3J$ = 5.0, 4J = 1.1 Hz, 1H, H_6); 11.14 (s, 1H, NH). ¹³C{¹H} NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 12.16 and 12.66 (C_8 and C_{10}); 17.51 (CH_3 p-

cymene); 21.85 and 22.17 (2 CH₃ isopropyl of p-cymene); 31.42 (CH isopropyl of p-cymene); 48.65 and 51.04 (C₇ and C₉); 89.76 and 90.20 (d, ²J_{CP}= 6.0 Hz, CH aromatic near isopropyl of p-cymene); 93.43 and 95.64 (d, ²J_{CP}= 3.5 Hz, CH aromatic near methyl of p-cymene); 100.66 (C adjacent of CH₃ of p-cymene); 114.91 (C adjacent of isopropyl of p-cymene); 129.47 (d, ³J_{CP}= 10.2 Hz, C_{meta} triphenylphosphine); 129.86 (C₅); 132.13 (C_{para} triphenylphosphine); 133.16 (d, J_{CP}= 48.6 Hz C_{quaternary} triphenylphosphine); 133.36 (C₄); 134.94 (d, ²J_{CP}= 9.5 Hz, C_{ortho} triphenylphosphine); 136.36 (C₆); 136.76 (C₃) 160.15 (C₂); 180.02 (d, J_{CP}= 10.0 Hz, C₁).

1.1.12 [Ru(η^6 -p-cymene)(PPh₃)(N',N'-diethyl-N-2-tiophenocarbonylthiourea)](PF₆)

(6b)

Elemental analysis (%) calc. for [RuC₃₈H₄₂N₂O₂PS]PF₆: exp. (calc.) C, 51.70 (51.64); H, 4.49 (4.79); N, 3.66 (3.17); S 7.21 (7.26)%. Molar conductance (acetone): 135 S cm² mol⁻¹. IR (KBr, cm⁻¹): (vC-H_{cym, PPh₃, T}) 3056, 2972, 2933, 2871; (vC=O) 1496; (vC=S) 1252; (vC-P) 1095; (vP-F) 840; (vRu-P) 557; (vRu-S) 500; (vRu-O) 346. ³¹P{¹H} NMR (162 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity)]: 35.01 (s). ¹H NMR (400 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, integral, J (Hz), assignation)]: 1.13 (t, ³J=7.0 Hz, 3H, CH₃ acylthiourea); 1.25 (m, 9H, CH₃ acylthiourea and 2CH₃ isopropyl of p-cymene); 1.94 (s, 3H, CH₃ p-cymene); 2.81 (hept, ³J= 6.9 Hz, 1H, CH isopropyl of p-cymene); 3.61 (m, 2H, CH₂ acylthiourea); 3.88 (m, 2H, CH₂ acylthiourea); 5.46 (d, 1H, ³J= 6.0 Hz, CH aromatic near methyl of p-cymene); 5.65 (d, 1H, ³J= 6.1 Hz, CH aromatic near methyl of p-cymene); 5.88 (d, 1H, ³J= 6.0 Hz, CH aromatic near isopropyl of p-cymene); 6.02 (d, 1H, ³J= 6.1 Hz, CH aromatic near isopropyl of p-cymene); 7.06 (m, 1H, H₅); 7.46 (m, 6H, H_{meta} triphenylphosphine); 7.58 (m, 11H, H₄ and H₆; 9H_{ortho} and para triphenylphosphine). ¹³C{¹H} NMR (100 MHz, Acetone-d₆, 298 K) [ppm, (multiplicity, J (Hz), assignation)]: 12.97 and 13.82 (C₈ and C₁₀); 18.06 (CH₃ p-cymene); 21.93 and 22.81 (2 CH₃ isopropyl group of p-cymene); 31.63 (CH isopropyl

group of p-cymene); 46.58 and 47.33 (C_7 and C_9); 90.10 and 92.63 (d, $^2J_{CP} = 2.2, 1.5$ Hz, CH aromatic near methyl of p-cymene); 90.94 and 95.07 (d, $^2J_{CP} = 4.8, 3.8$ Hz, CH aromatic near isopropyl of p-cymene); 104.18 (C adjacent of CH_3 of p-cymene); 115.60 (d, $^2J_{CP} = 5.5$ Hz, C adjacent of isopropyl of p-cymene); 128.75 (C_5); 129.52 (d, $^3J_{CP} = 10.1$ Hz, C_{meta} triphenylphosphine); 131.82 (d, $J_{CP} = 47.0$ Hz, $C_{quaternary}$ triphenylphosphine); 131.96 (C_{para} triphenylphosphine); 132.30 (C_4); 132.51 (C_6); 135.08 (d, $^2J_{CP} = 9.3$ Hz, C_{ortho} triphenylphosphine); 143.92 (C_3); 168.30 (C_2); 172.50 (C_1).

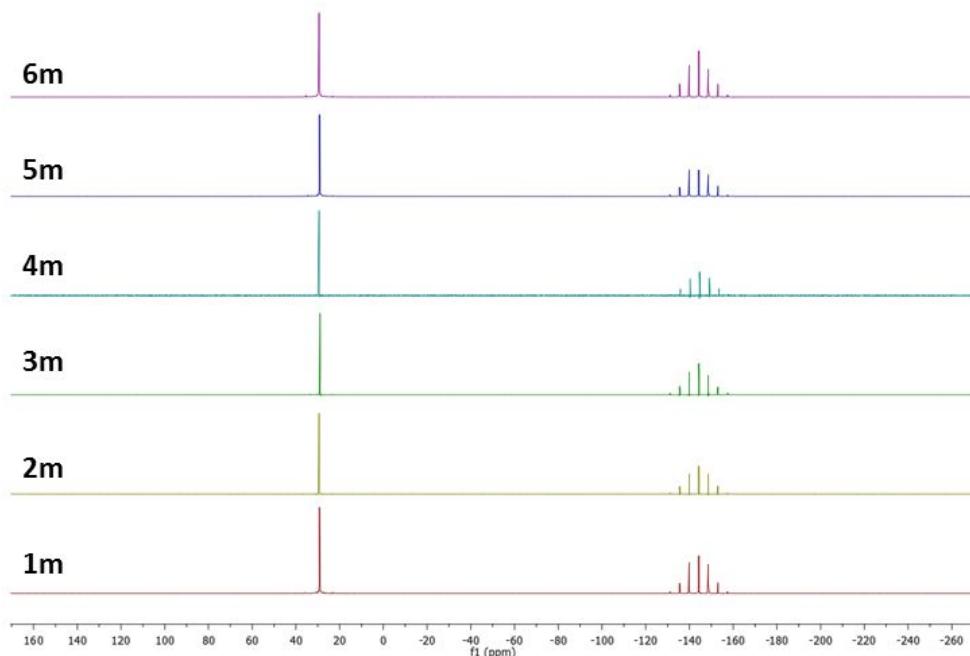


Figure S1: ^{31}P NMR spectra of complexes **1m-6m**.

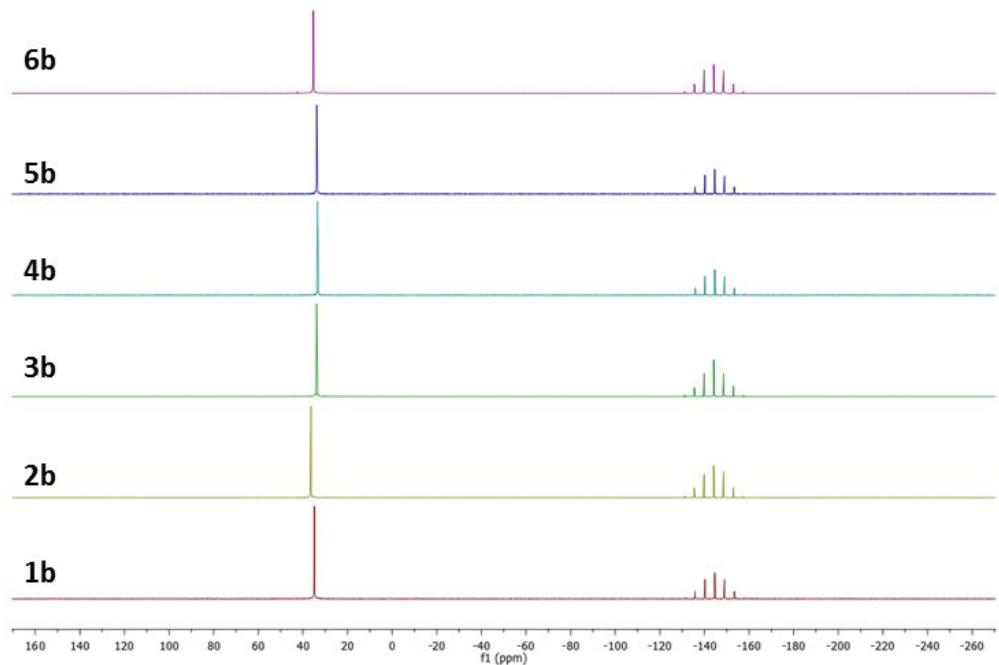


Figure S2: ^{31}P NMR spectra of complexes **1b**-**6b**.

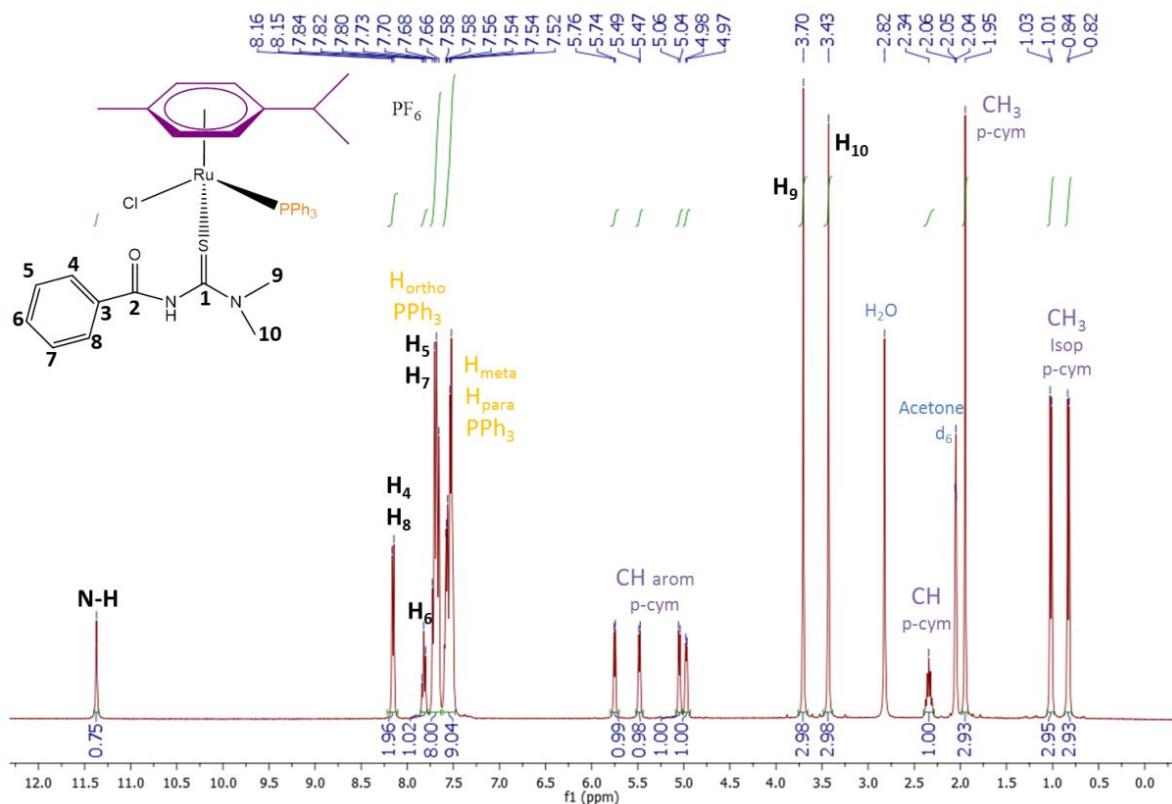


Figure S3: ^1H NMR spectrum of complex **1m**.

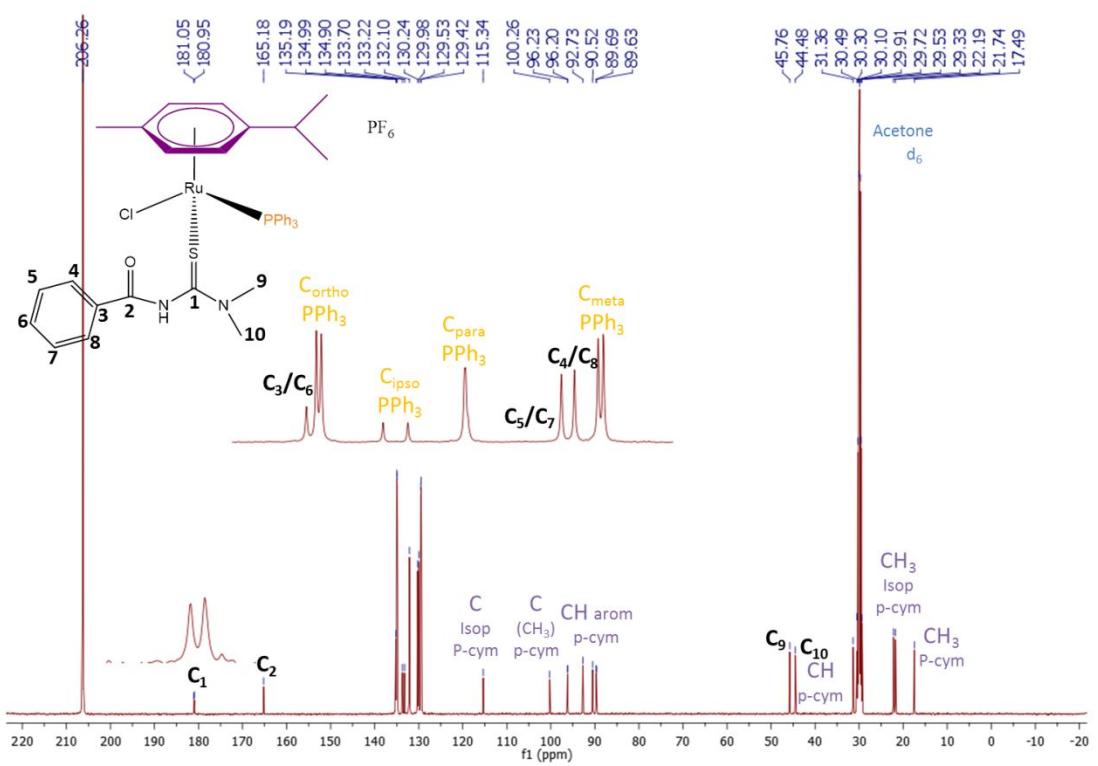


Figure S4: ^{13}C NMR spectrum of complex **1m**.

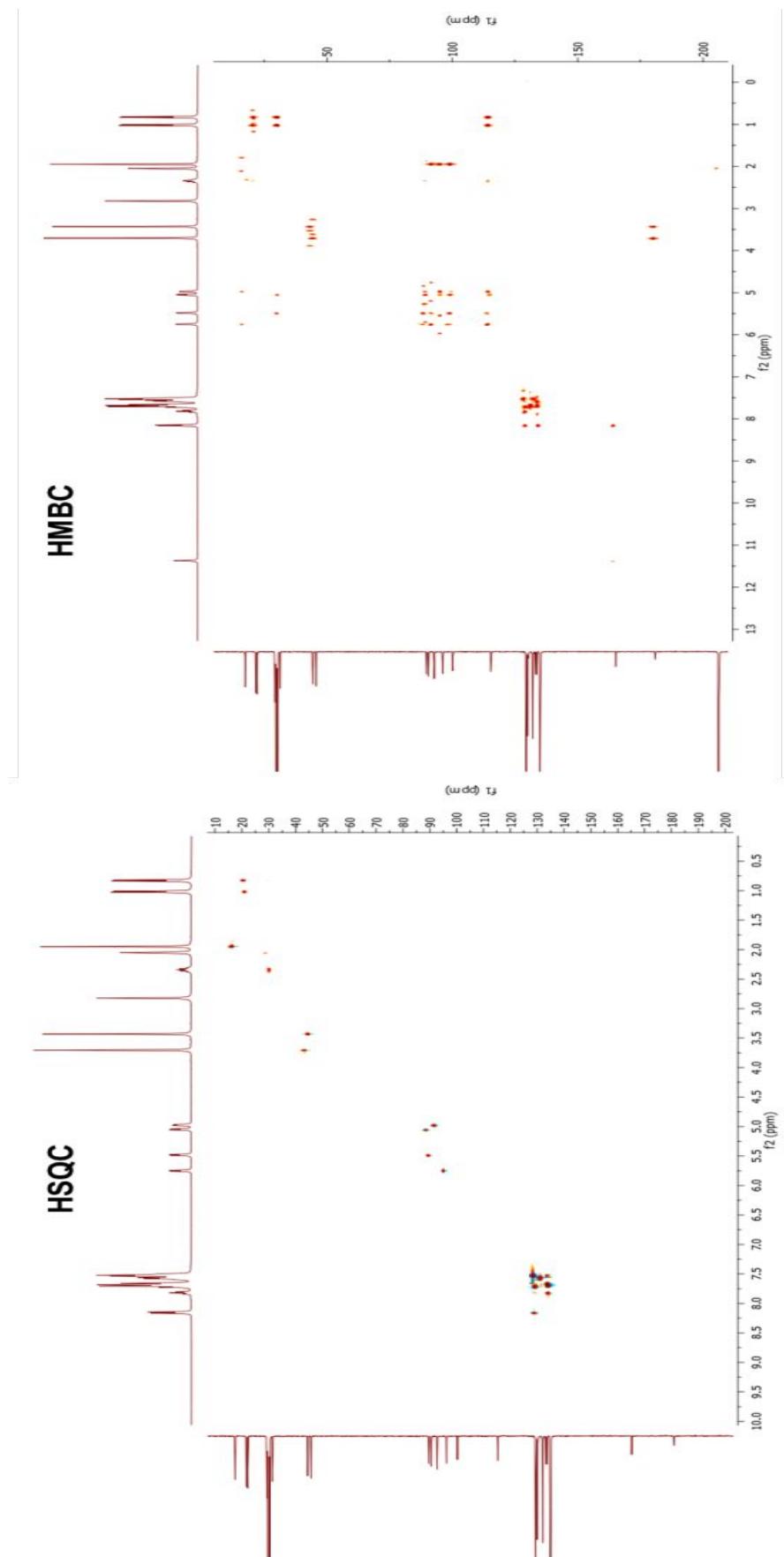


Figura S5: HSQC and HMBC spectra of complex **1m**

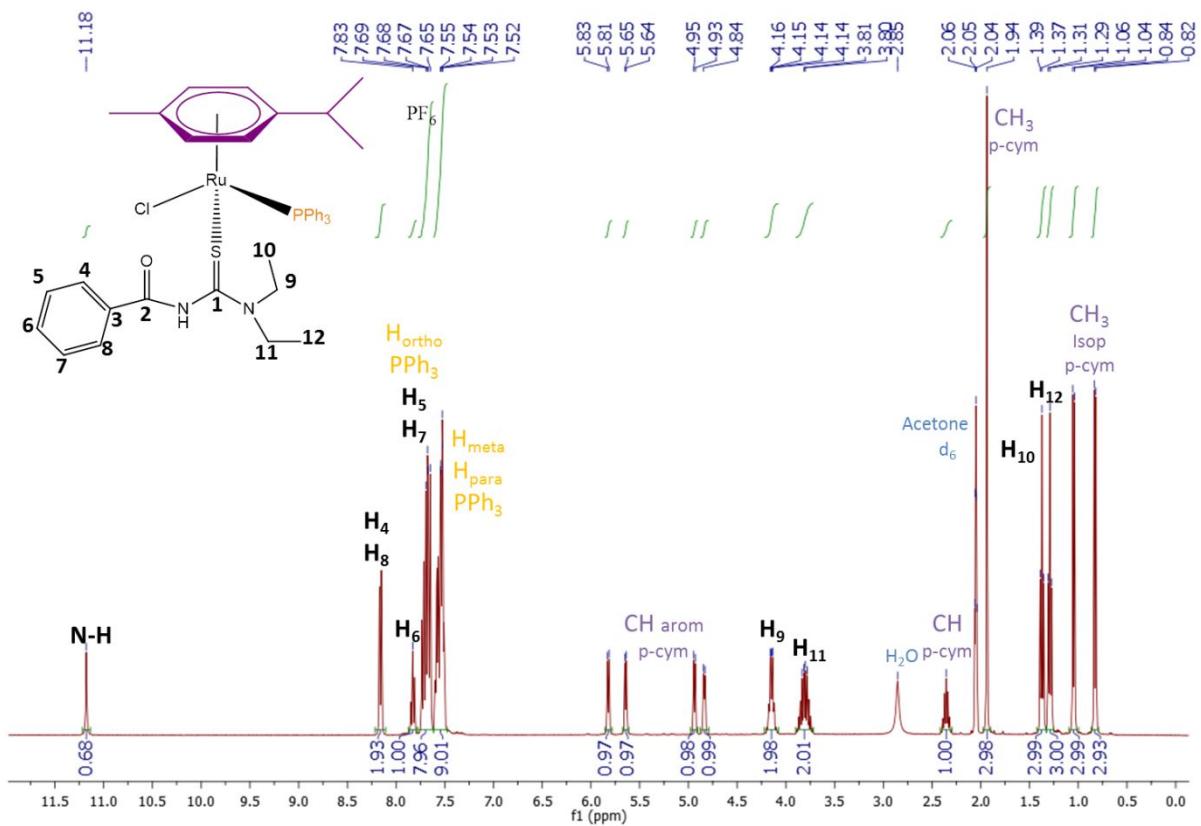


Figure S6: ^1H NMR spectrum of complex **2m**

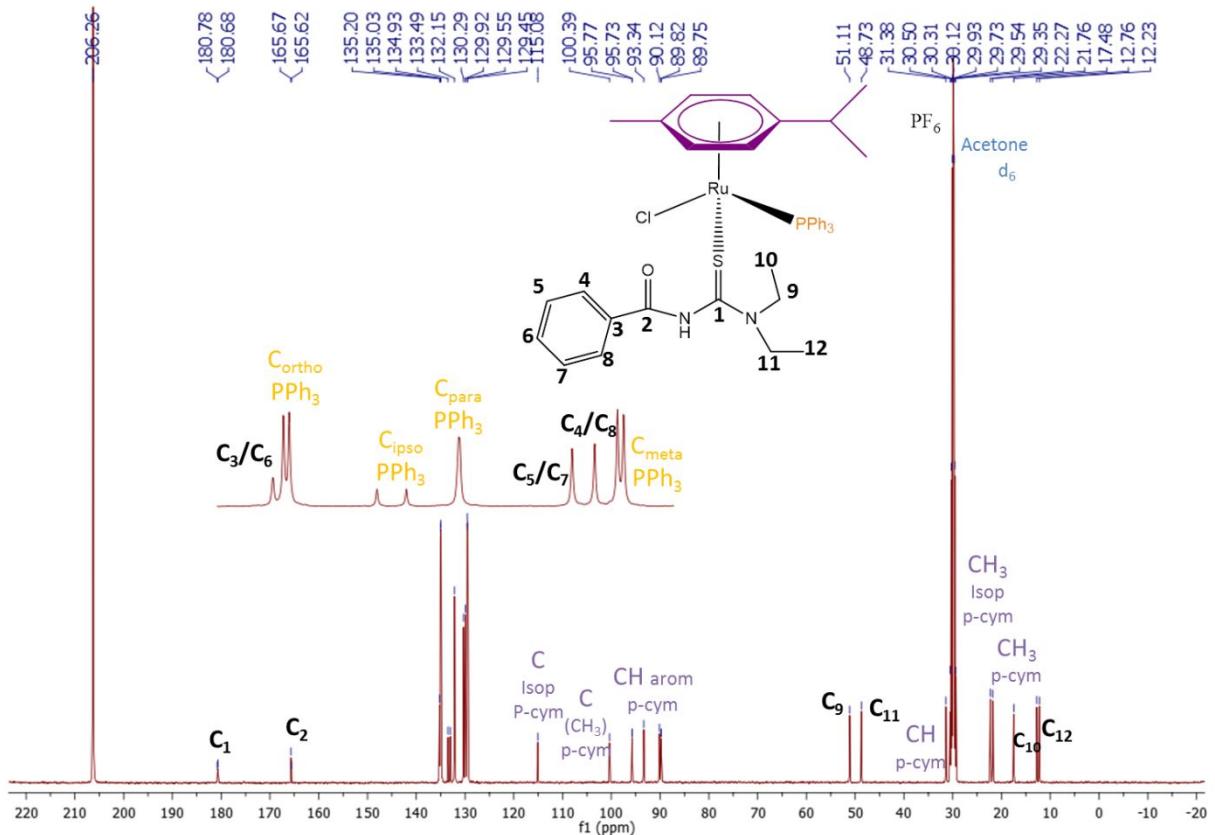


Figure S7: ^{13}C NMR spectrum of complex **2m**

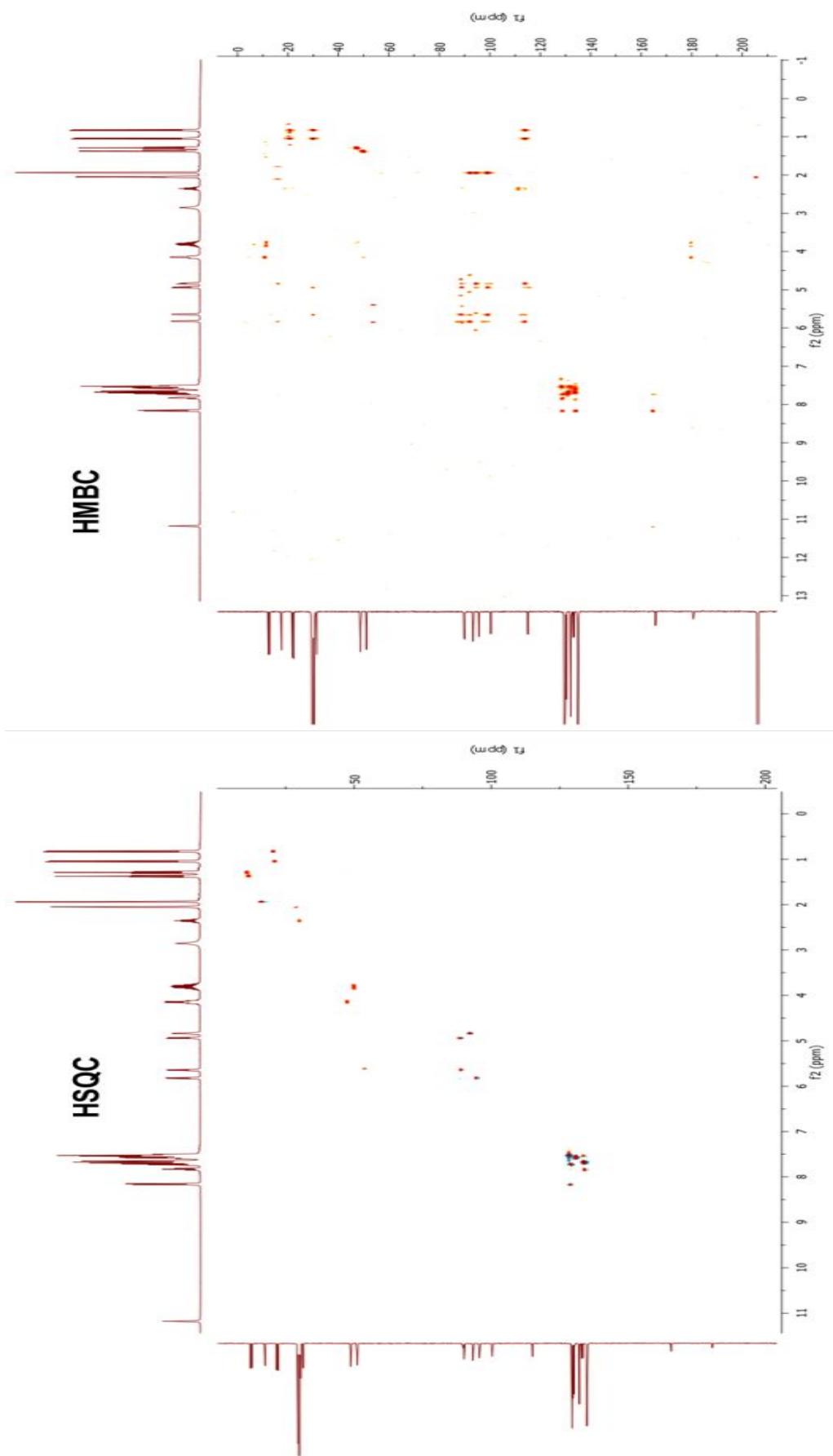


Figure S8: HSQC and HMBC spectra of complex **2m**

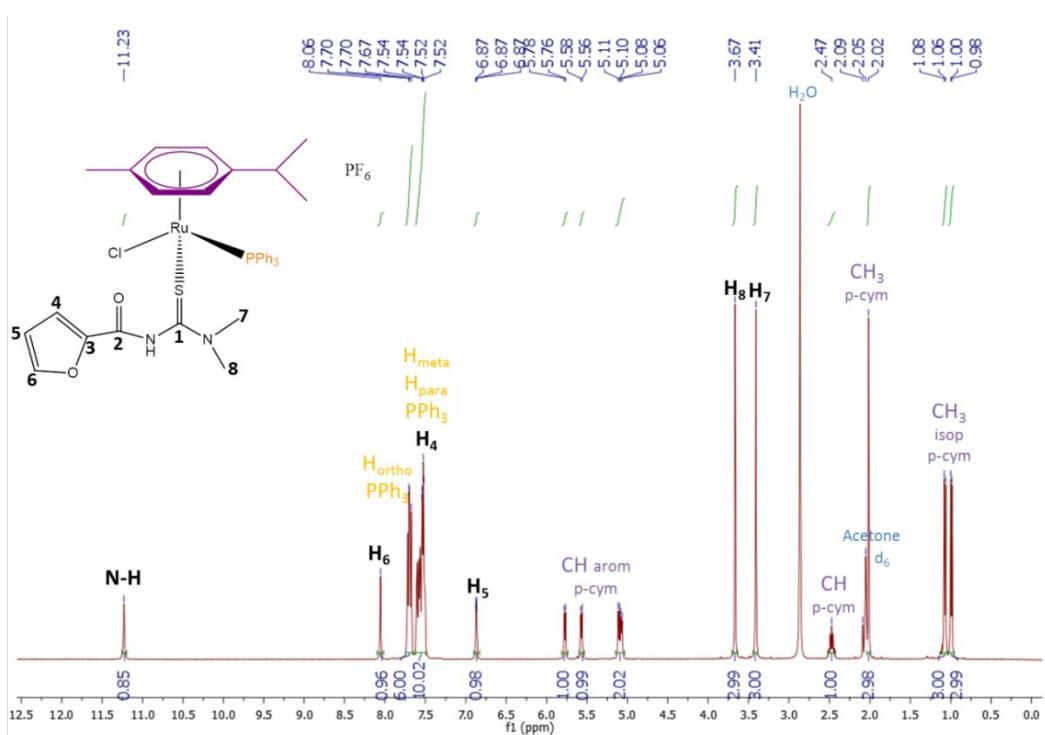


Figure S9: ¹H NMR spectrum of complex **3m**

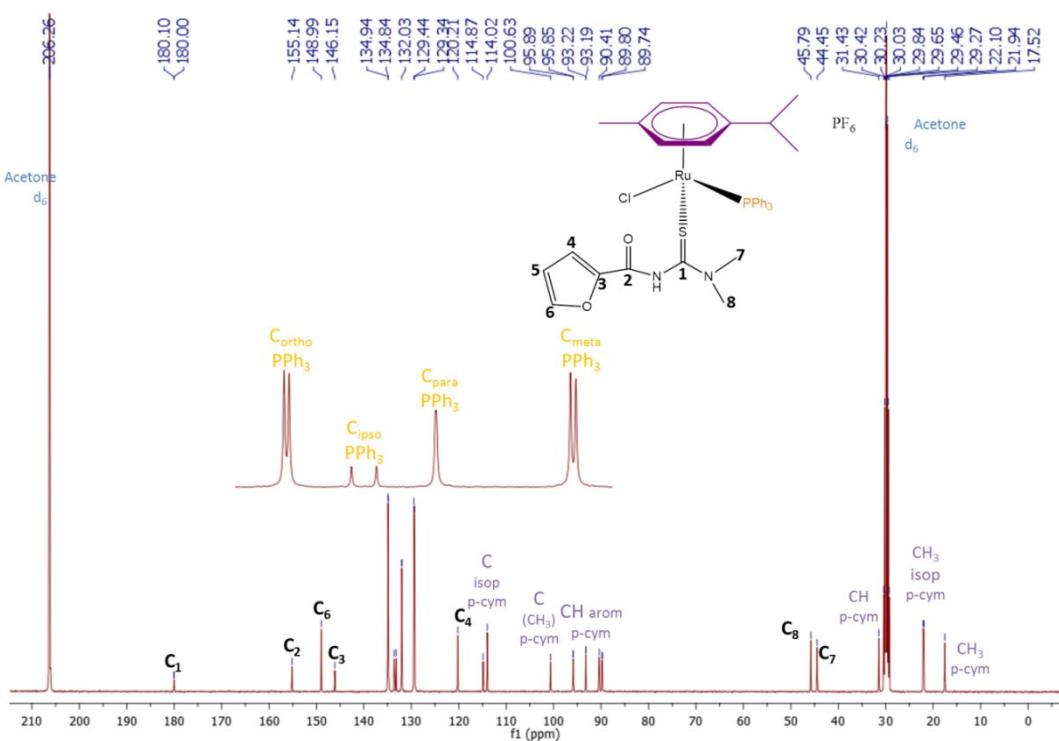


Figure S10: ¹³C NMR spectrum of complex **3m**

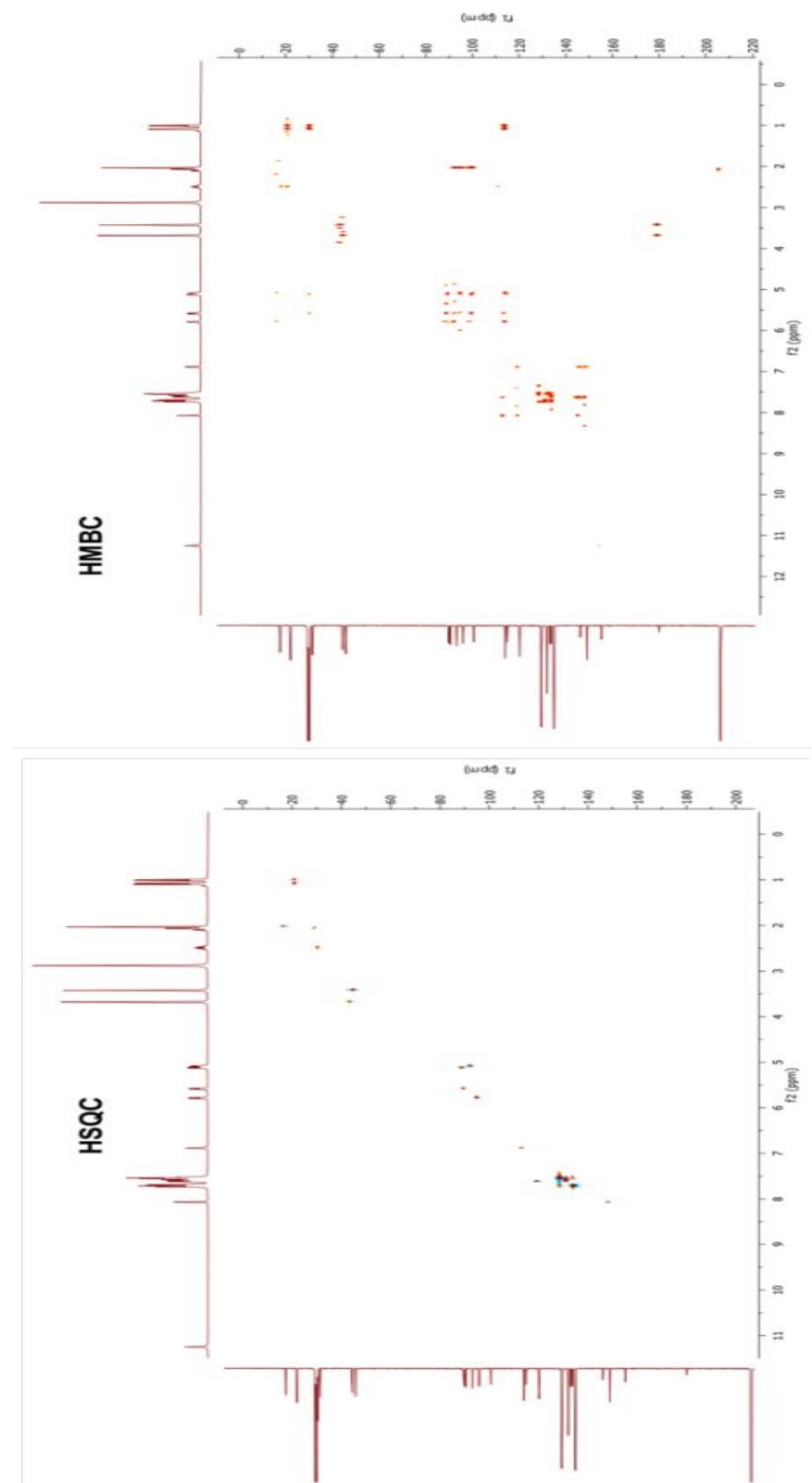


Figure S11: HSQC and HMBC spectra of complex **3m**

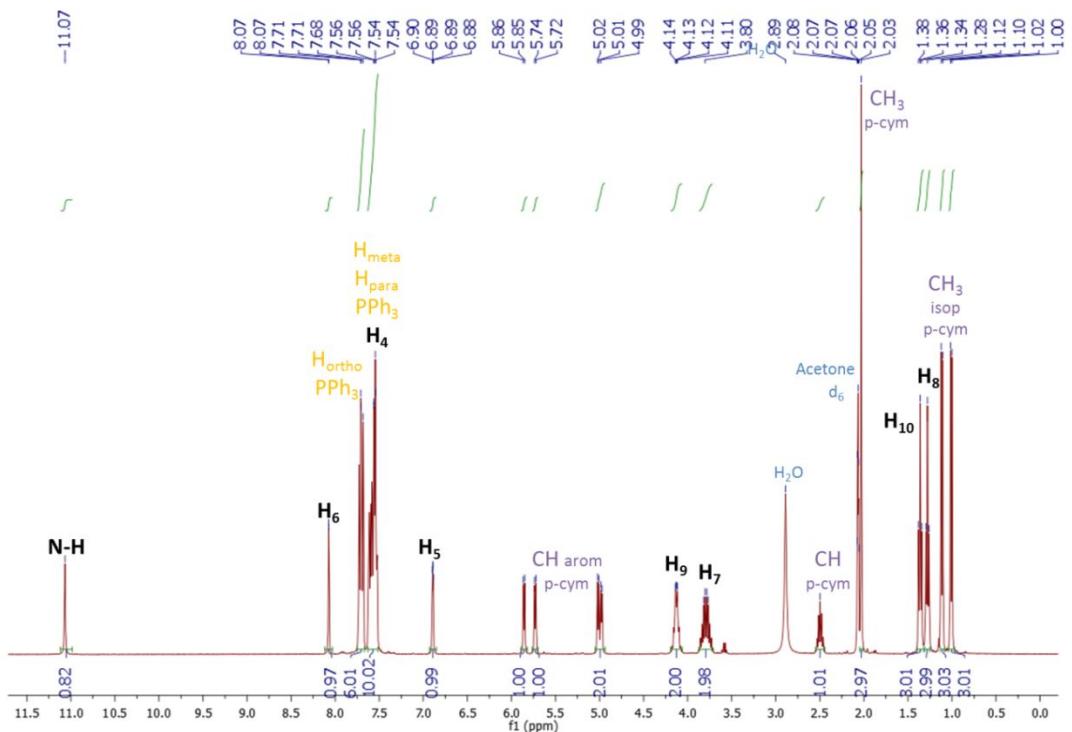


Figure S12: ^1H NMR spectrum of complex **4m**

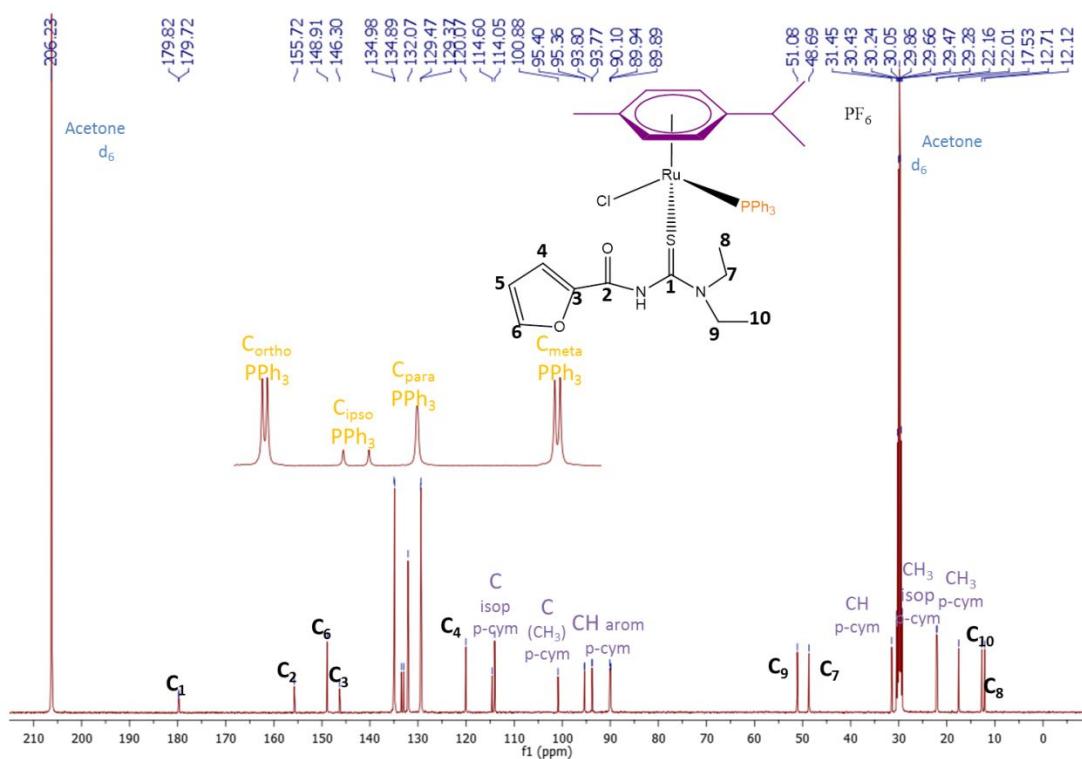


Figure S13: ^{13}C NMR spectrum of complex **4m**

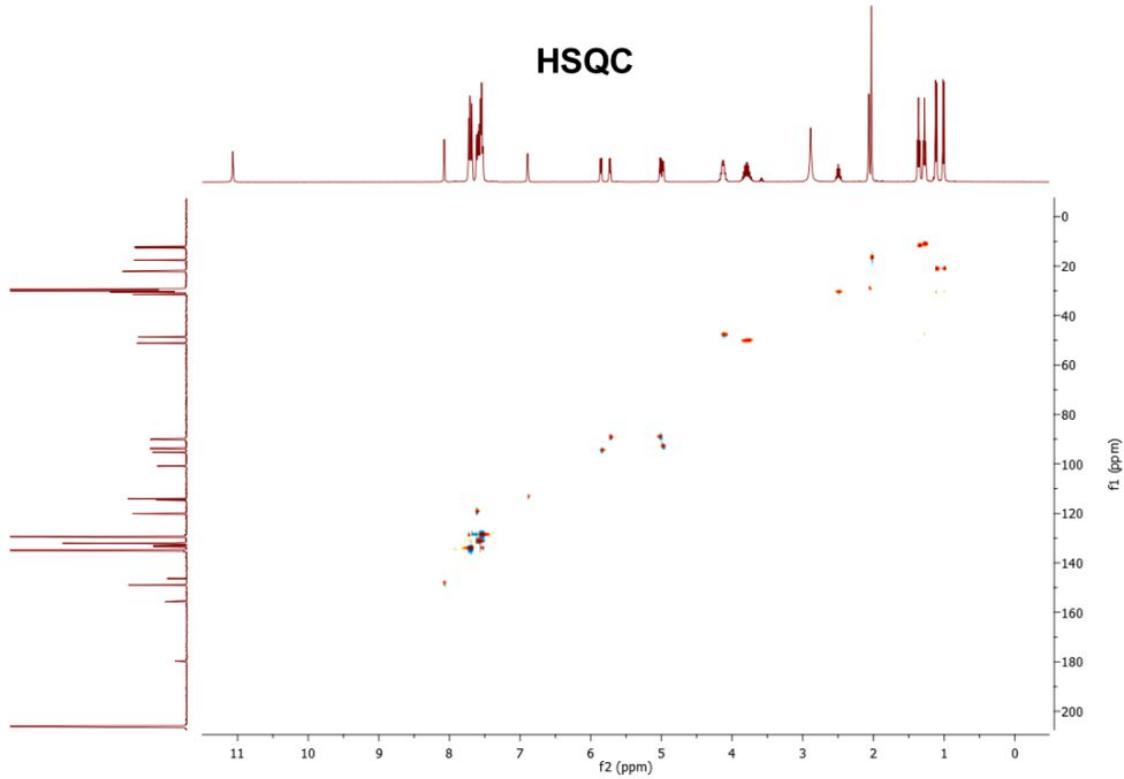


Figure S14: HSQC spectrum of complex **4m**

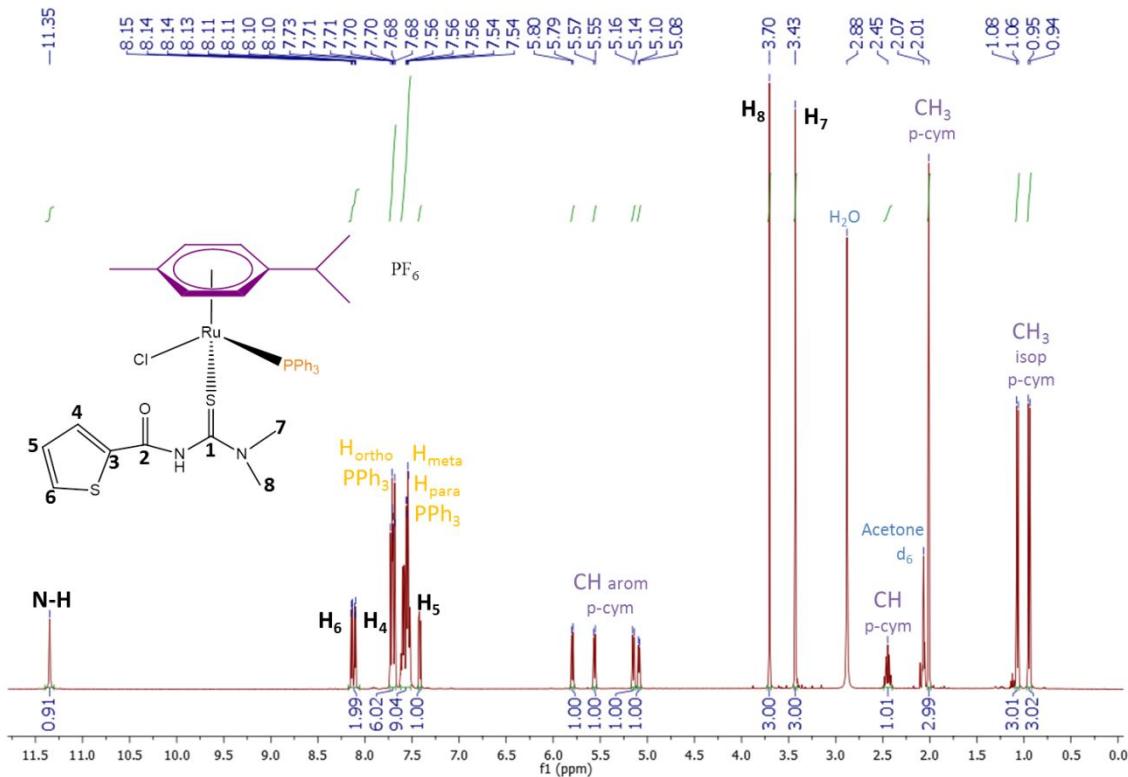


Figure S15: ^1H NMR spectrum of complex **5m**

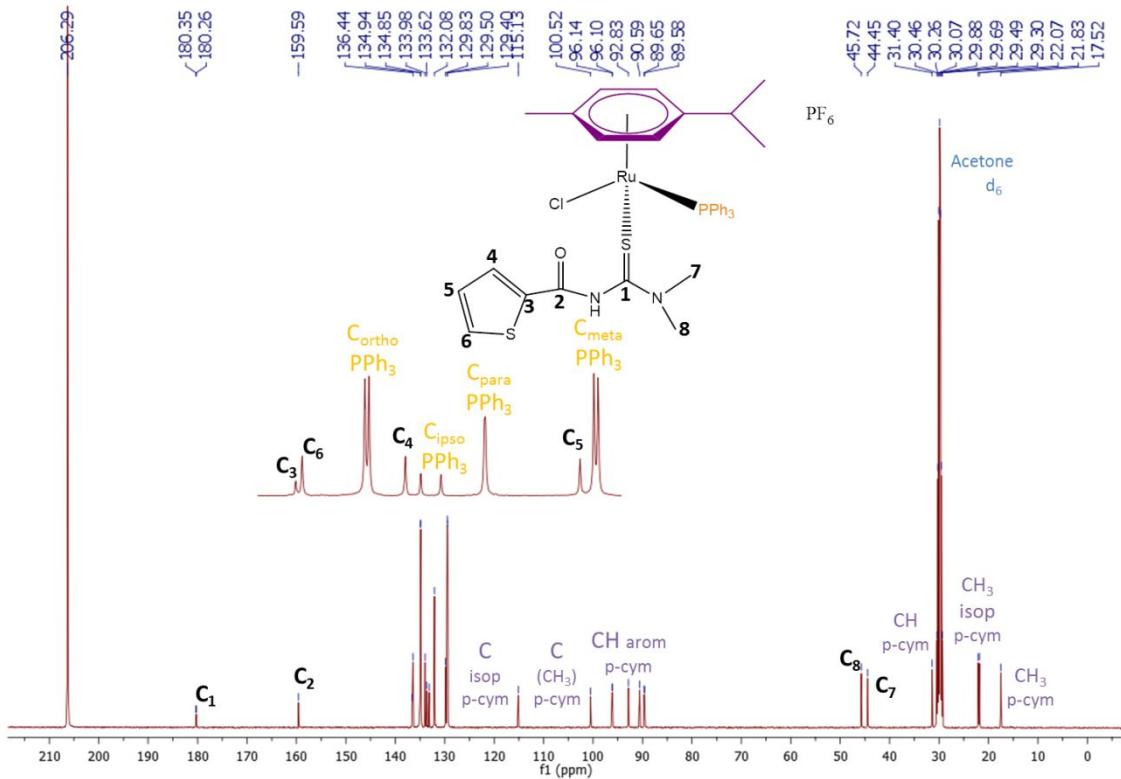


Figure S16: ^{13}C NMR spectrum of complex **5m**

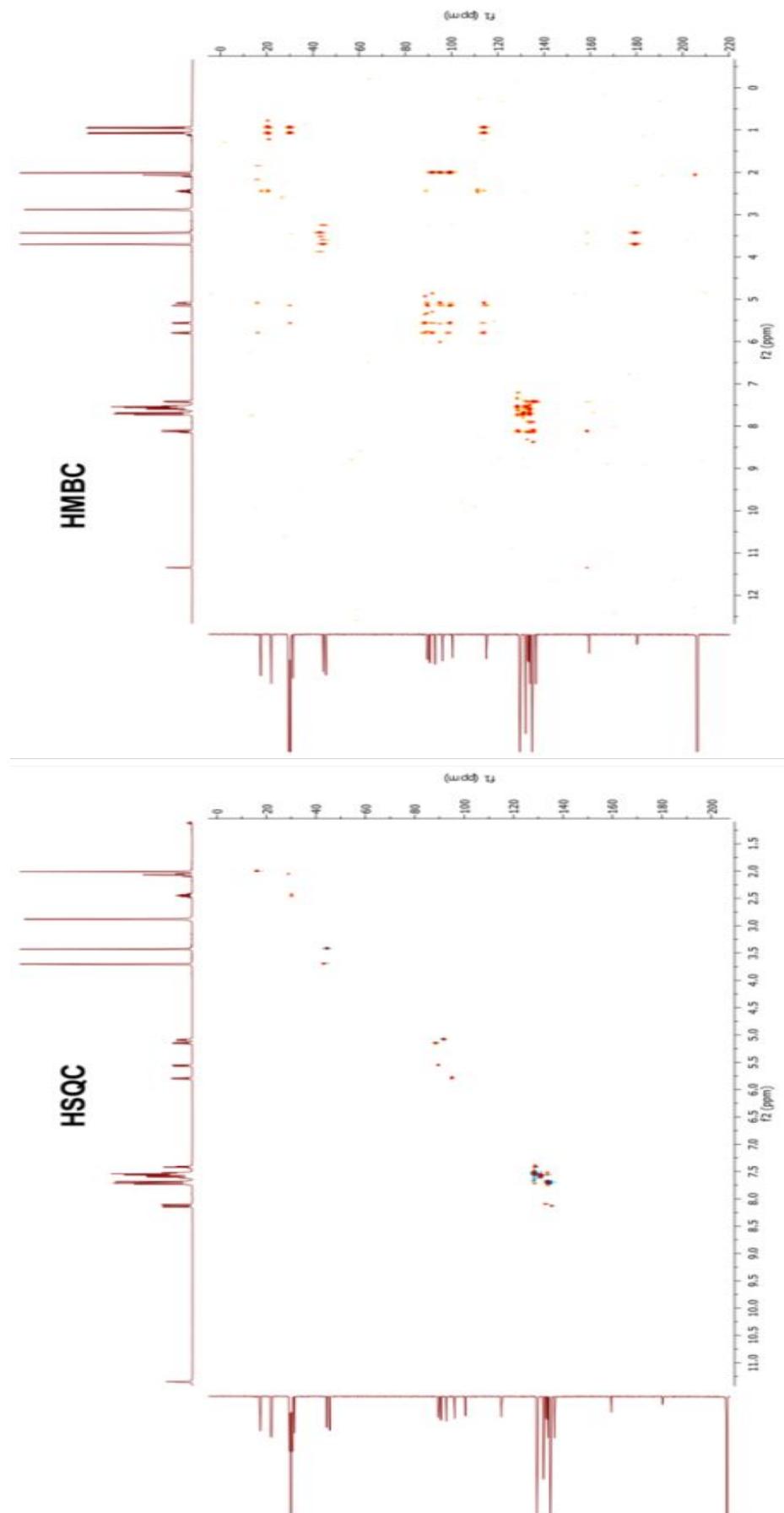


Figure S17: HSQC and HMBC spectra of complex **5m**

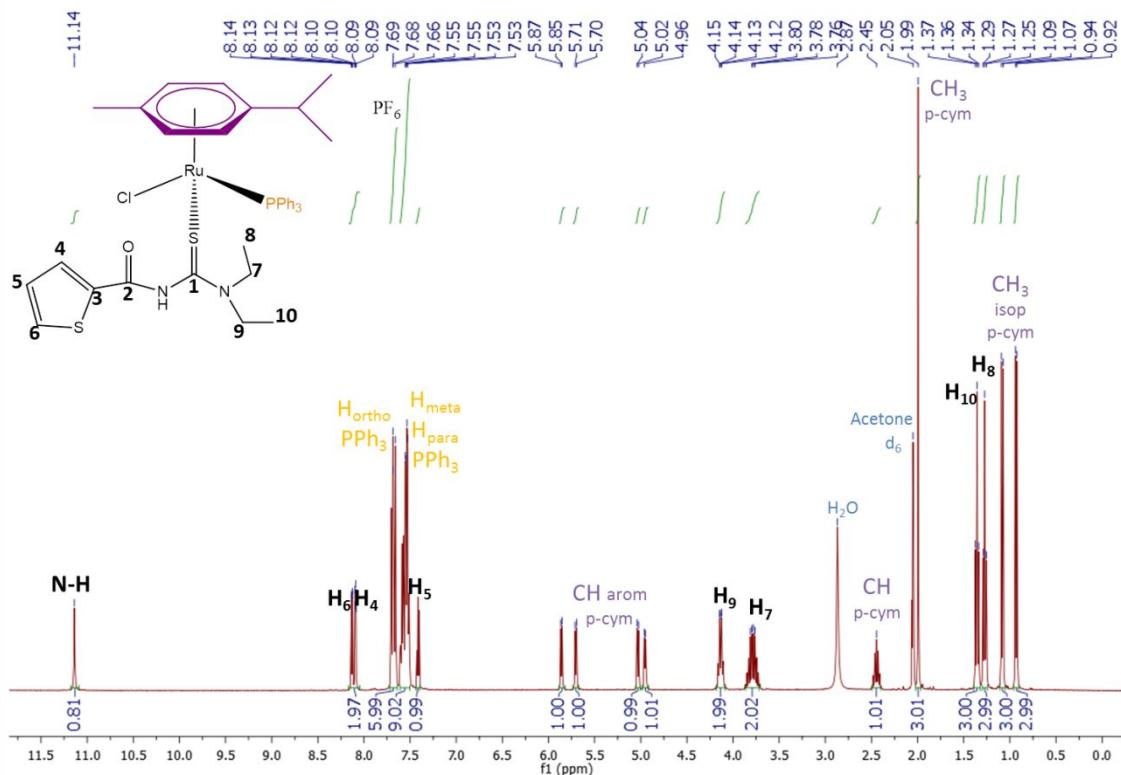


Figure S18: ¹H NMR spectrum of complex **6m**

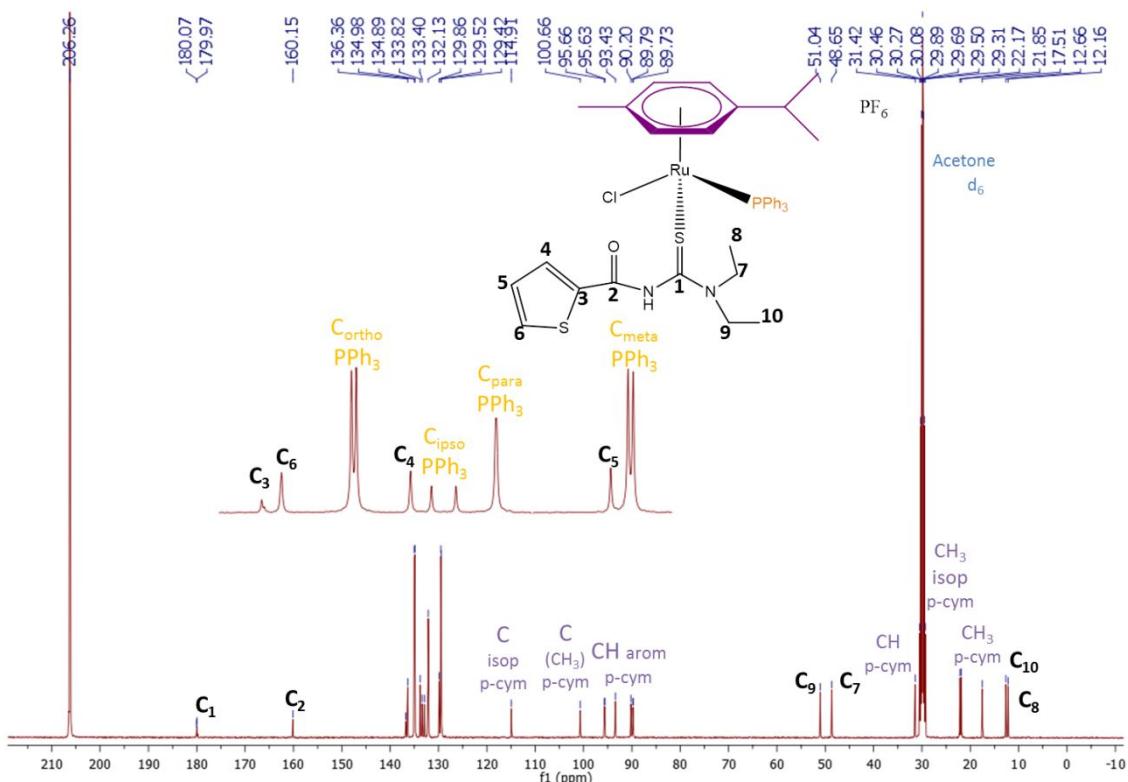


Figure S19: ¹³C NMR spectrum of complex **6m**

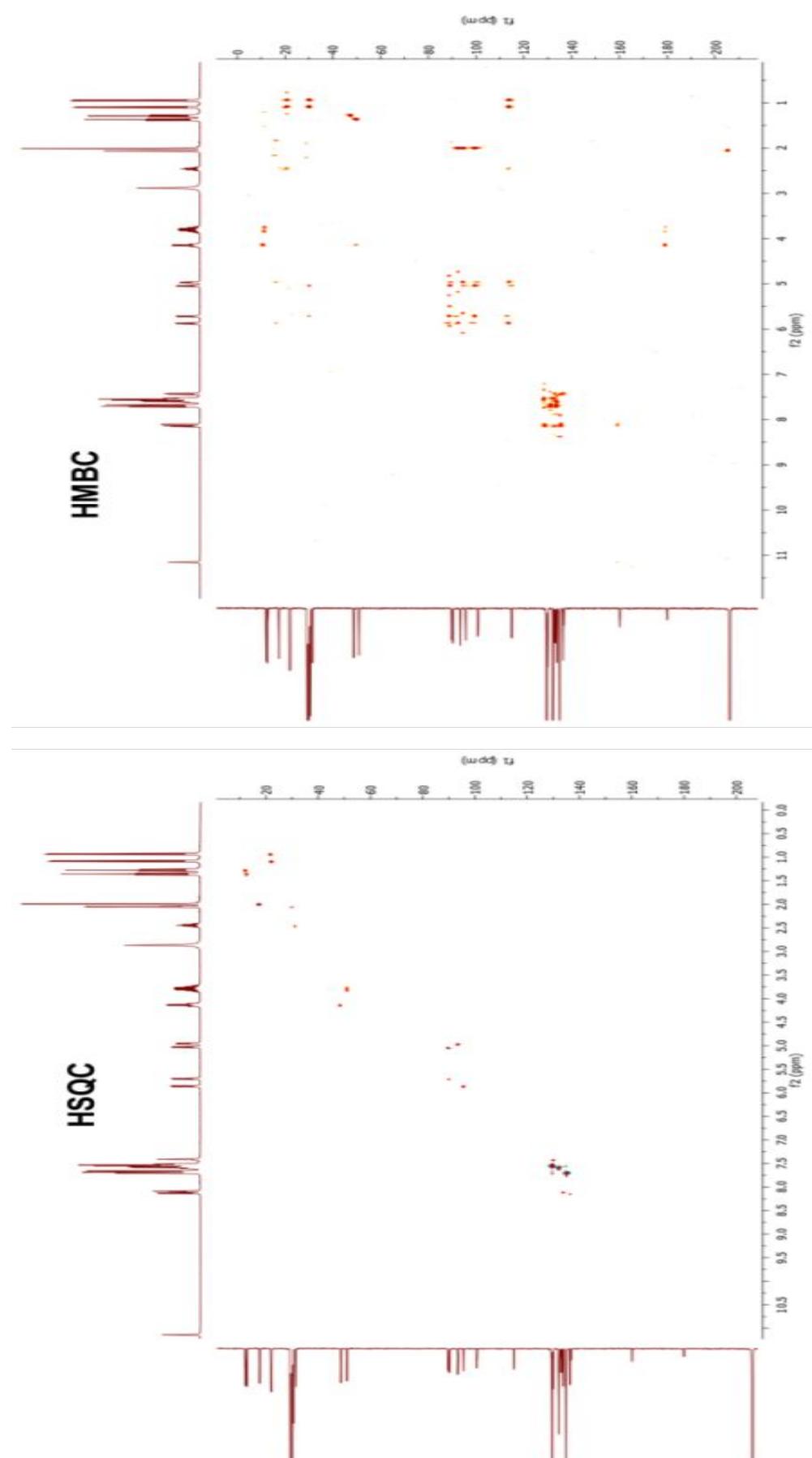


Figure S20: HSQC and HMBC spectra of complex **6m**

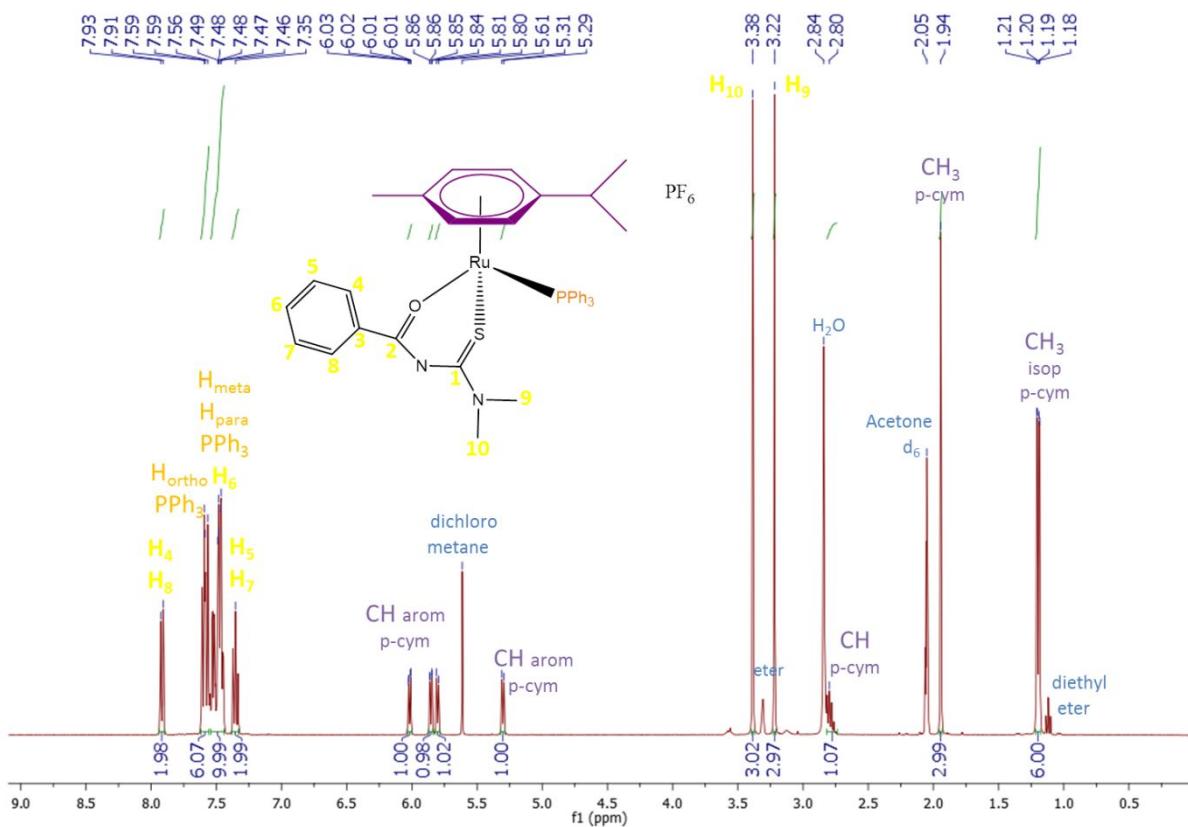


Figure S21: ¹H NMR spectrum of complex **1b**

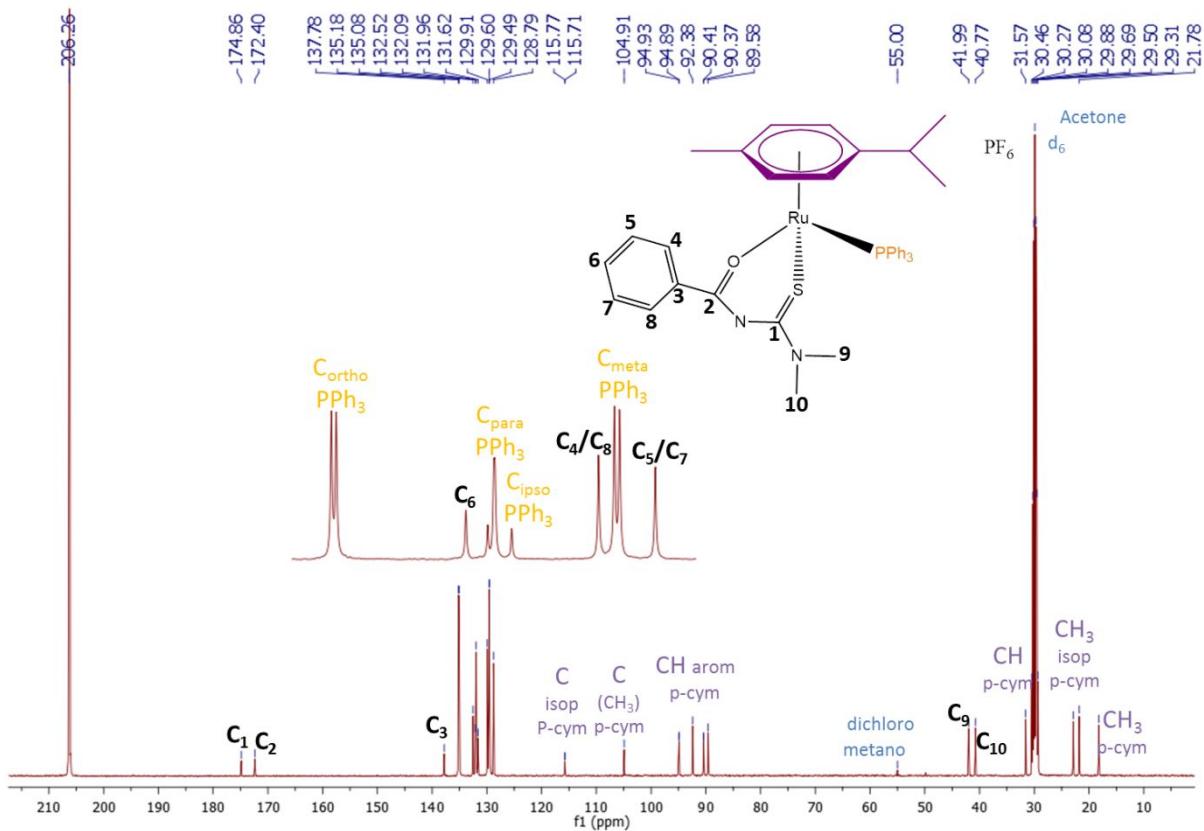


Figure S22: ^{13}C NMR spectrum of complex **1b**

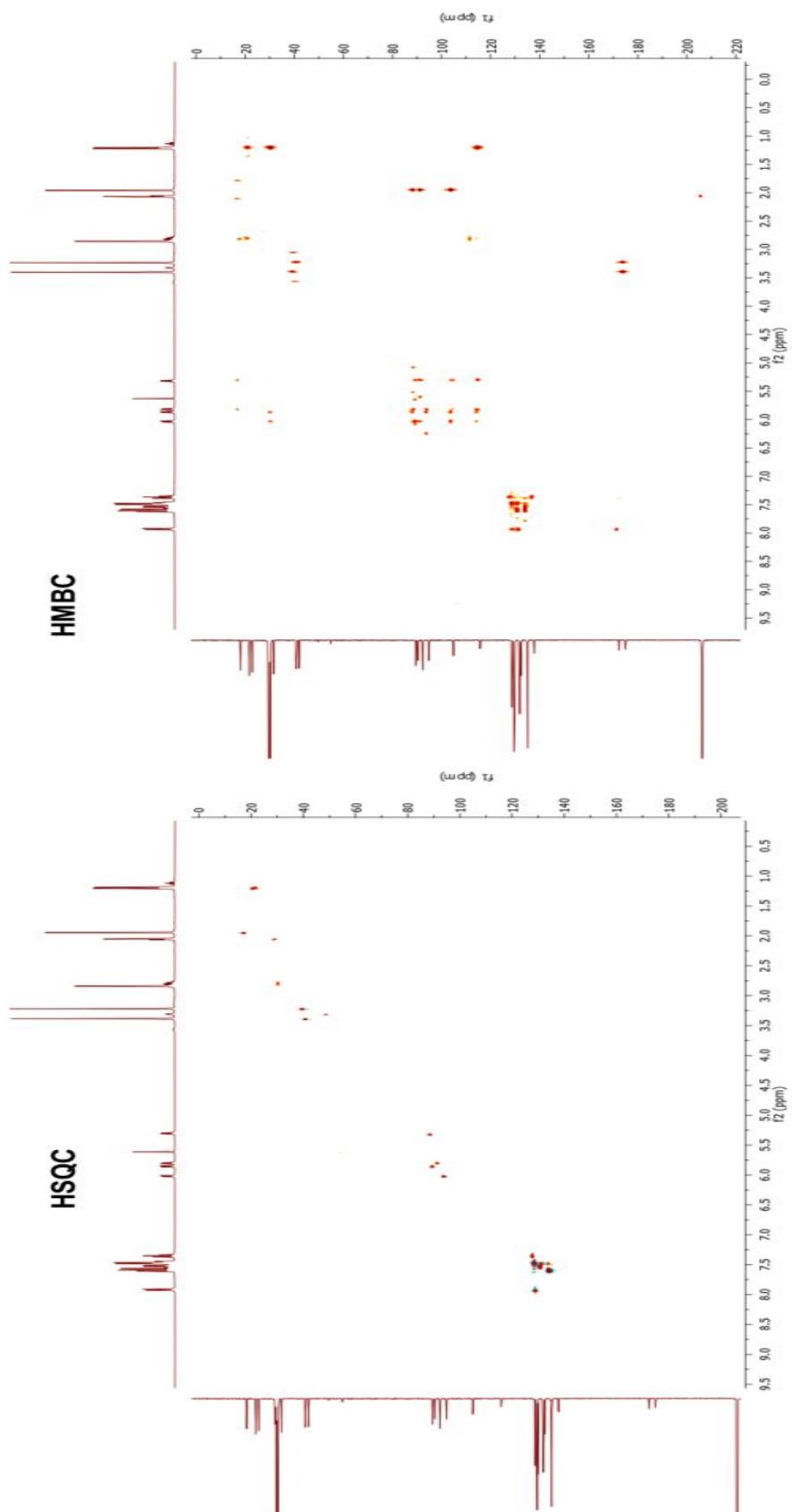


Figure S23: HSQC and HMBC spectra of complex **1b**

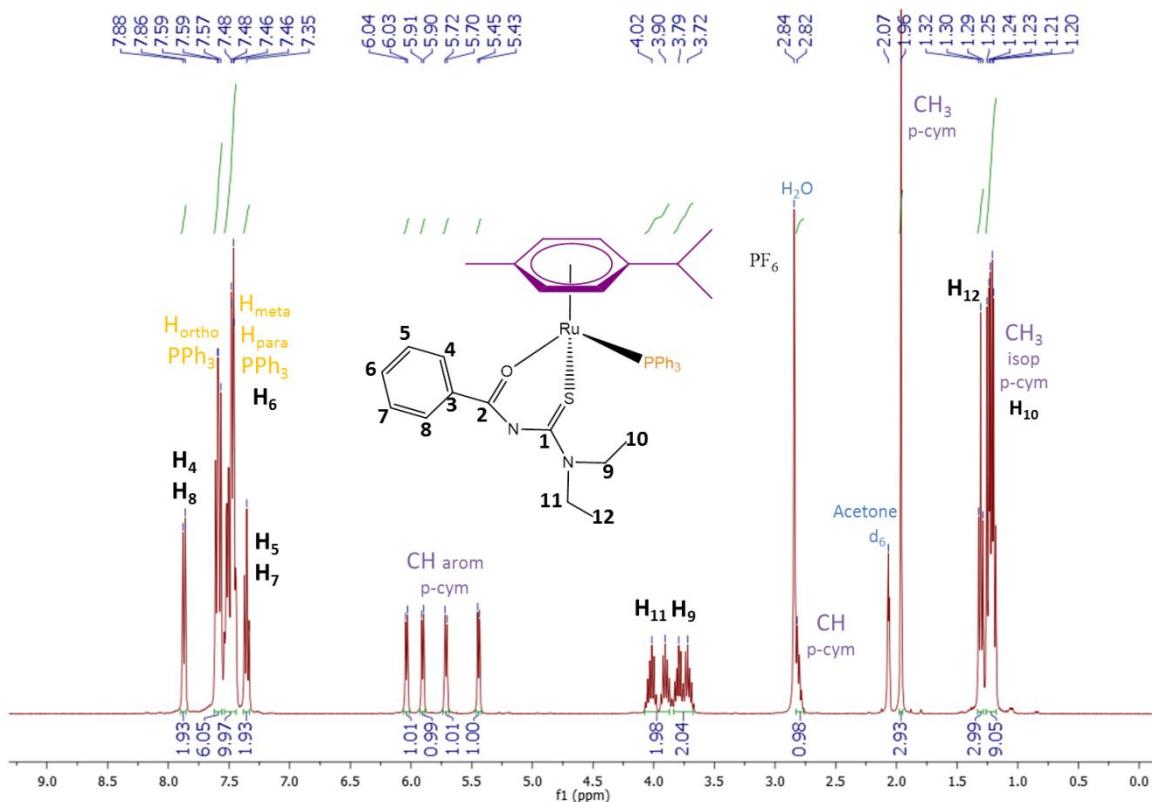


Figure S24: ^1H NMR spectrum of complex **2b**

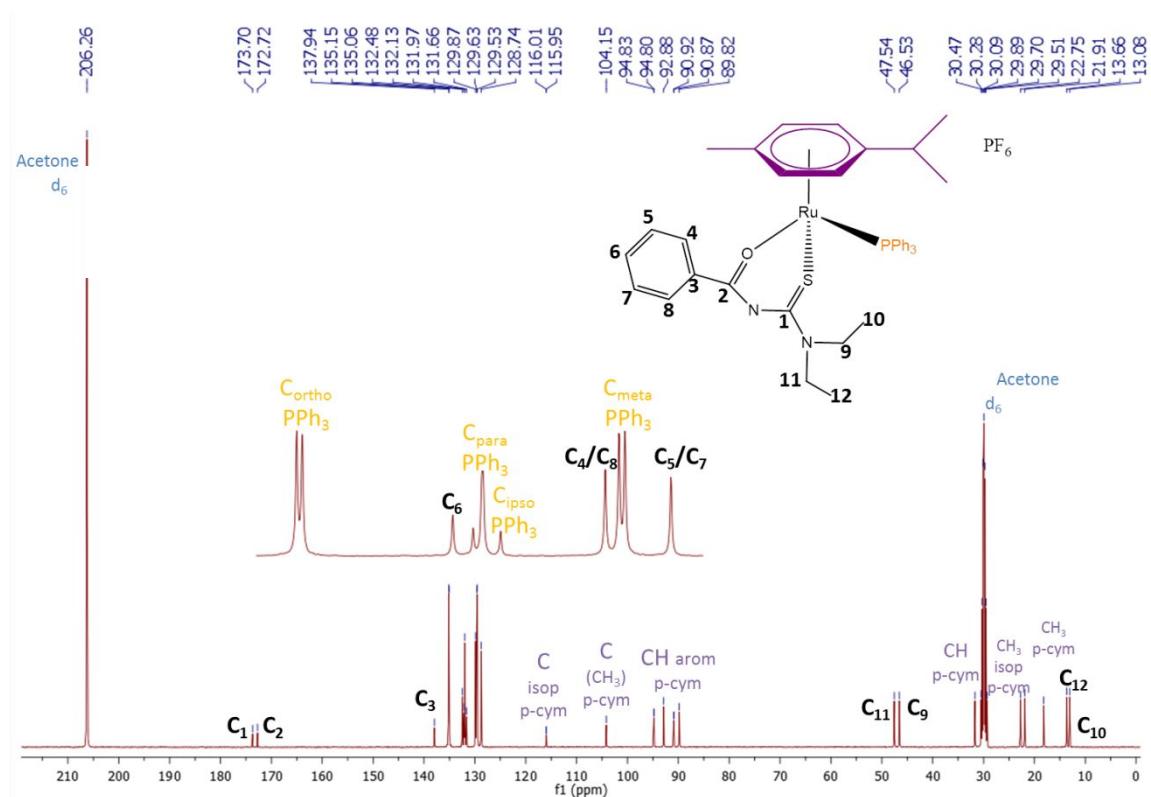


Figure S25: ^{13}C NMR spectrum of complex **2b**

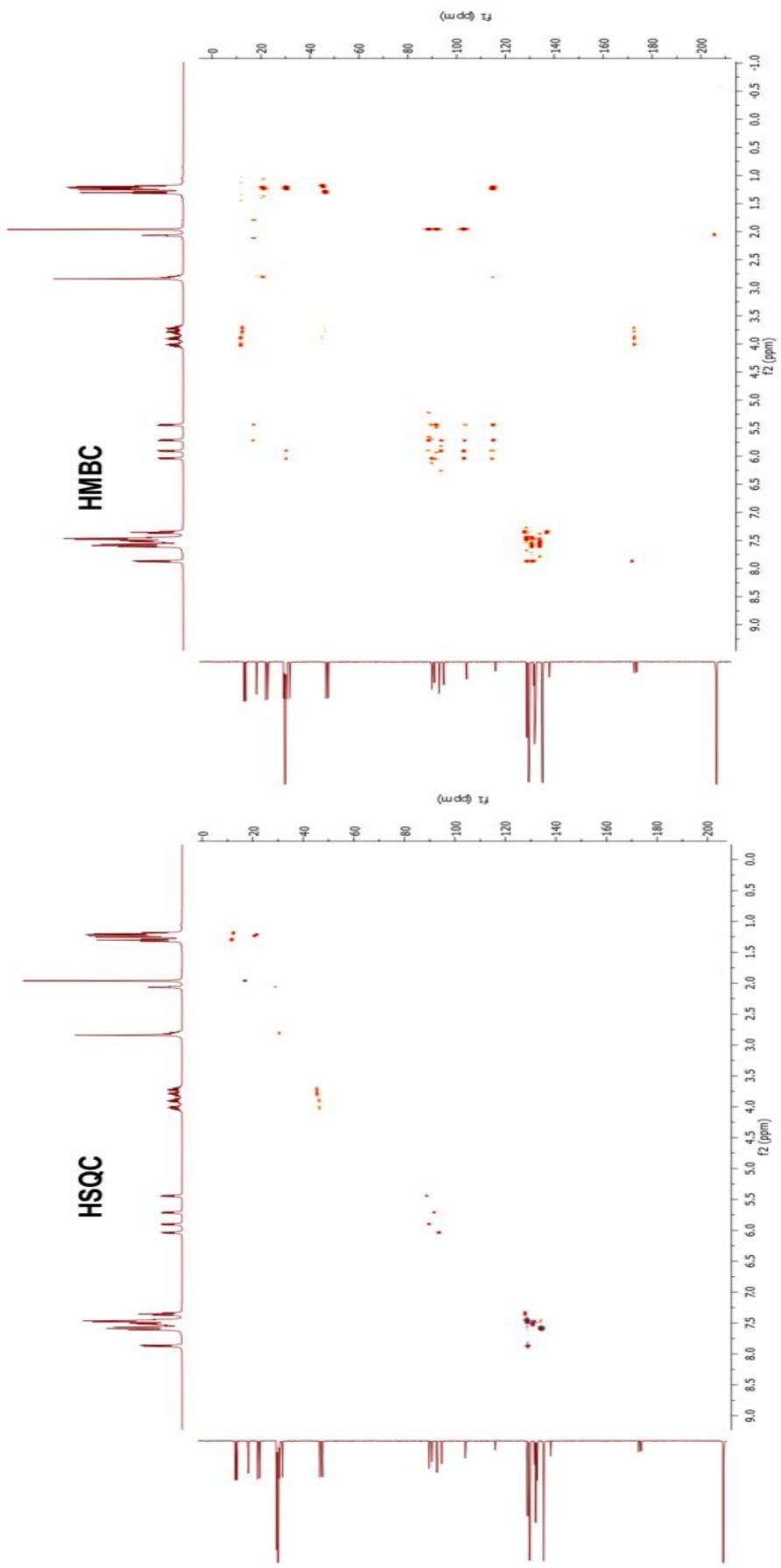


Figure S26: HSQC and HMBC spectra of complex **2b**

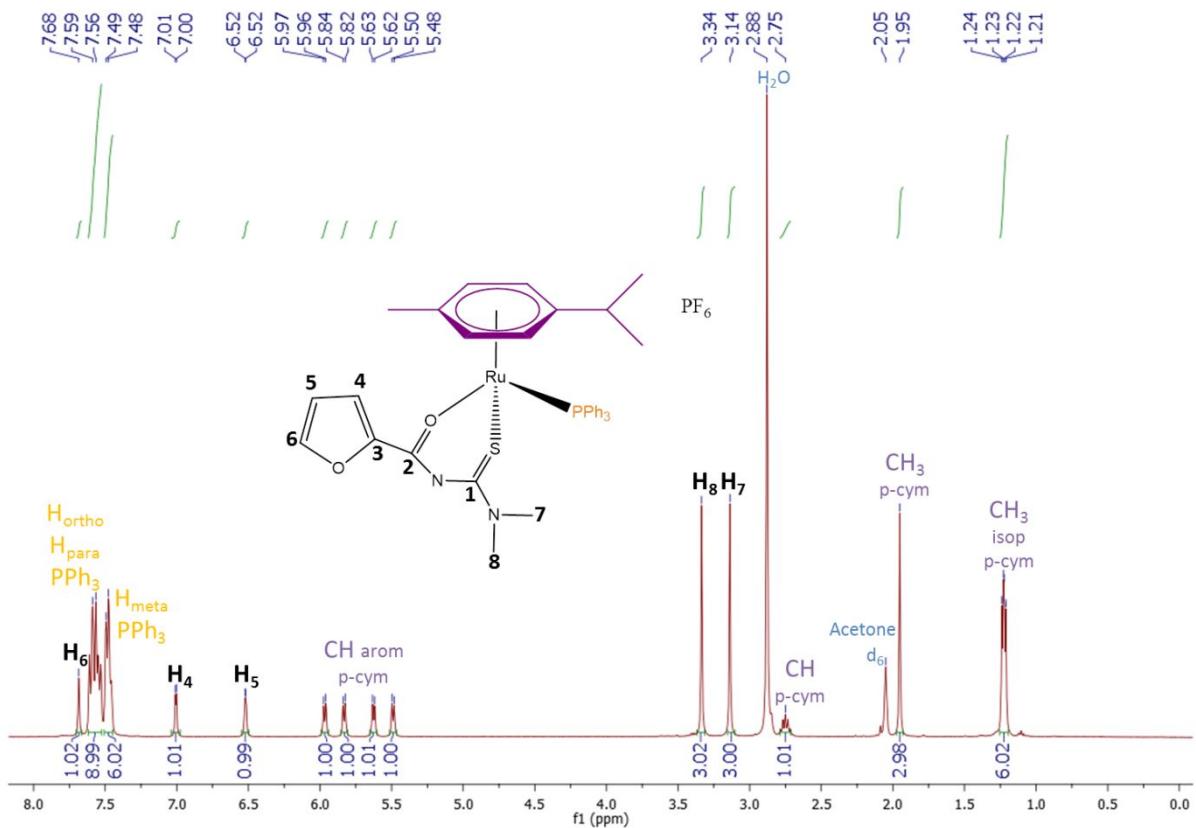


Figure S27: ¹H NMR spectrum of complex **3b**

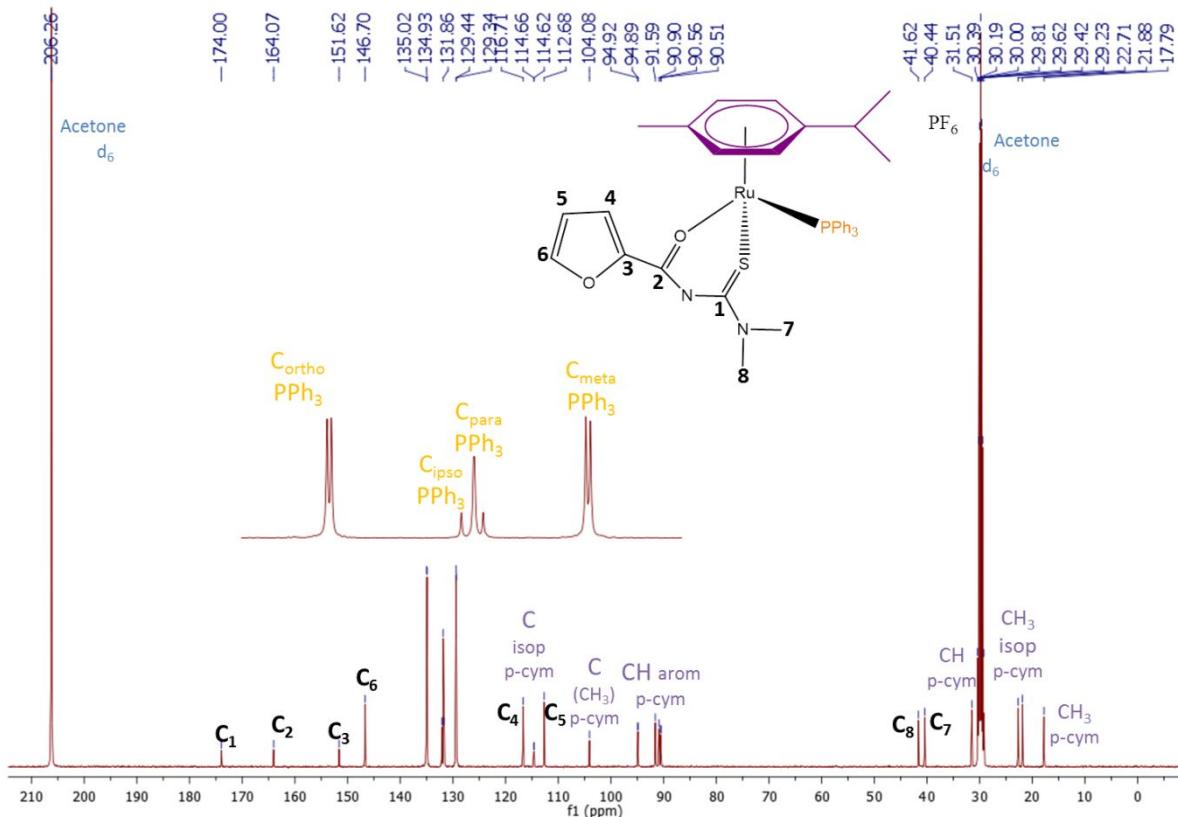


Figure S28: ¹³C NMR spectrum of complex **3b**

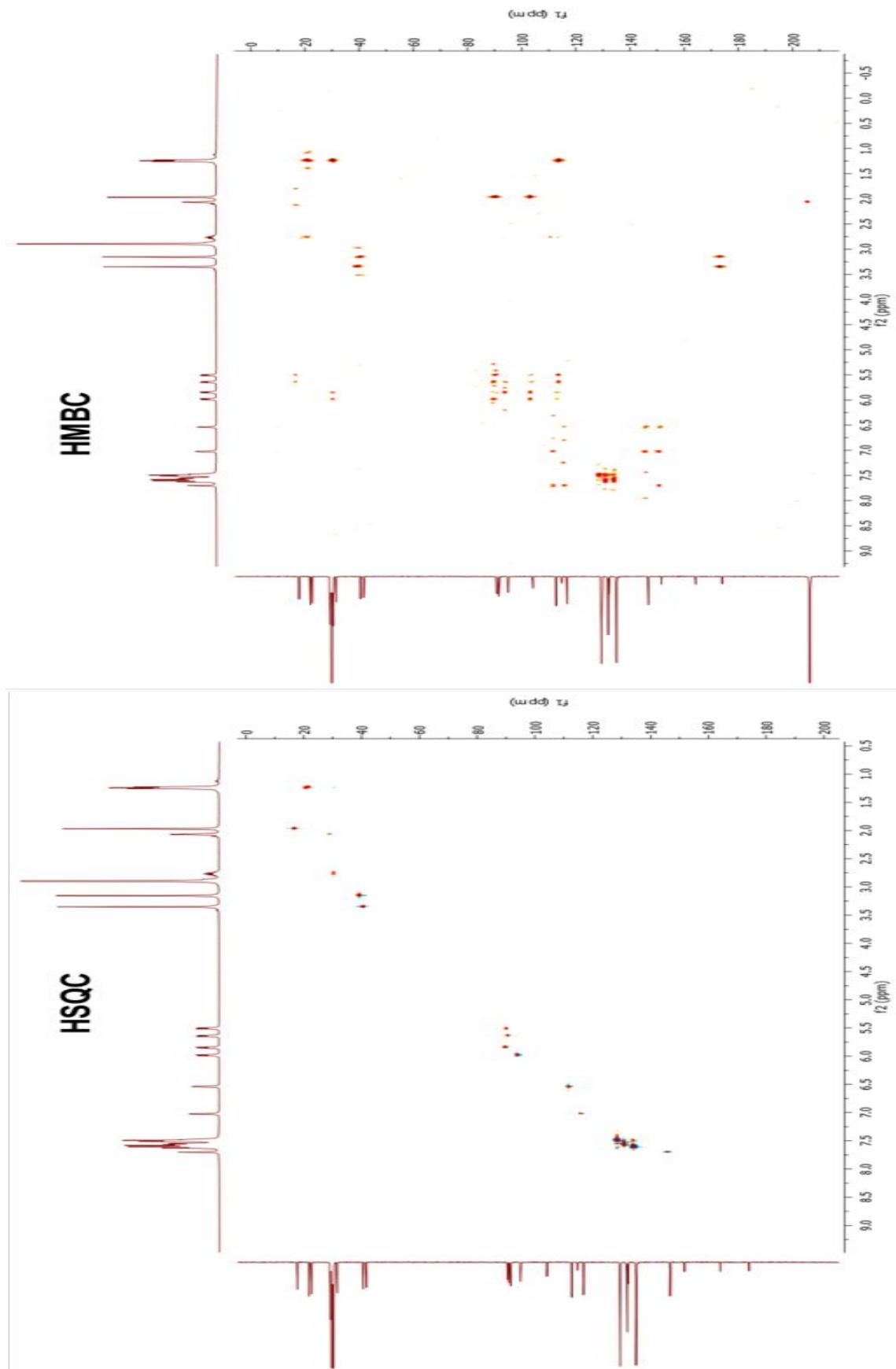


Figure S29: HSQC and HMBC spectra of complex 3b

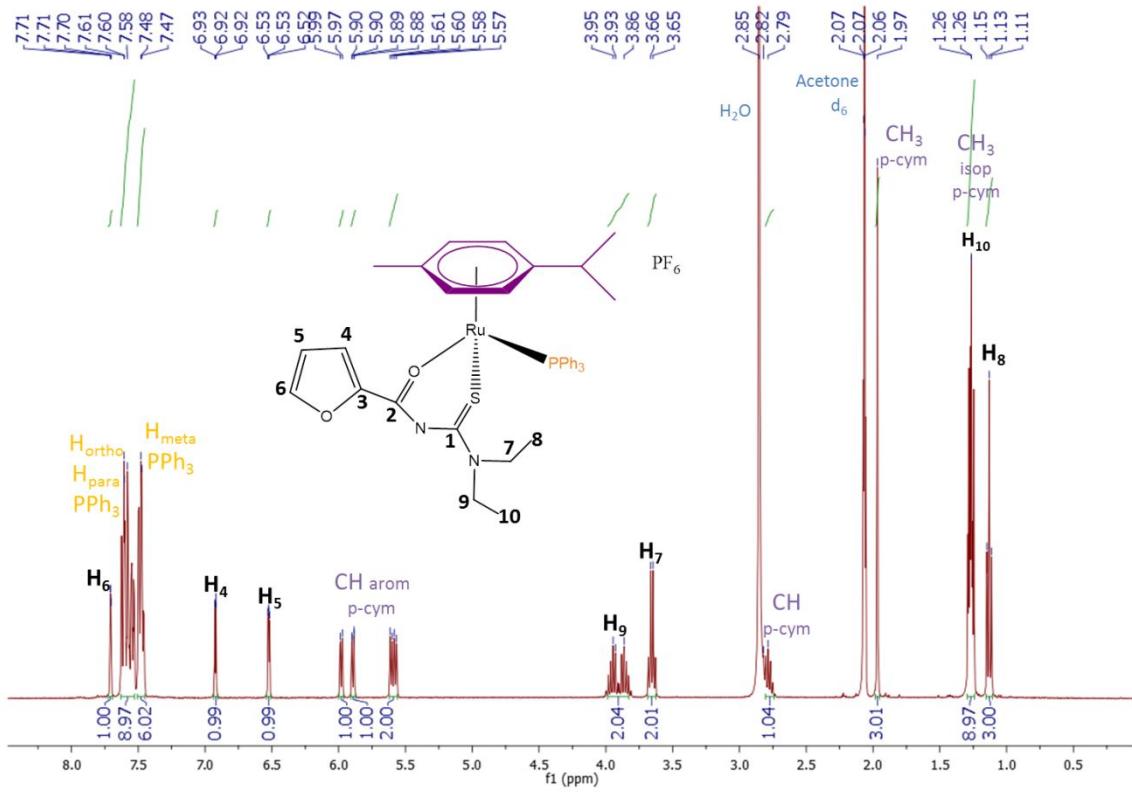


Figure S30: ¹H NMR spectrum of complex **4b**

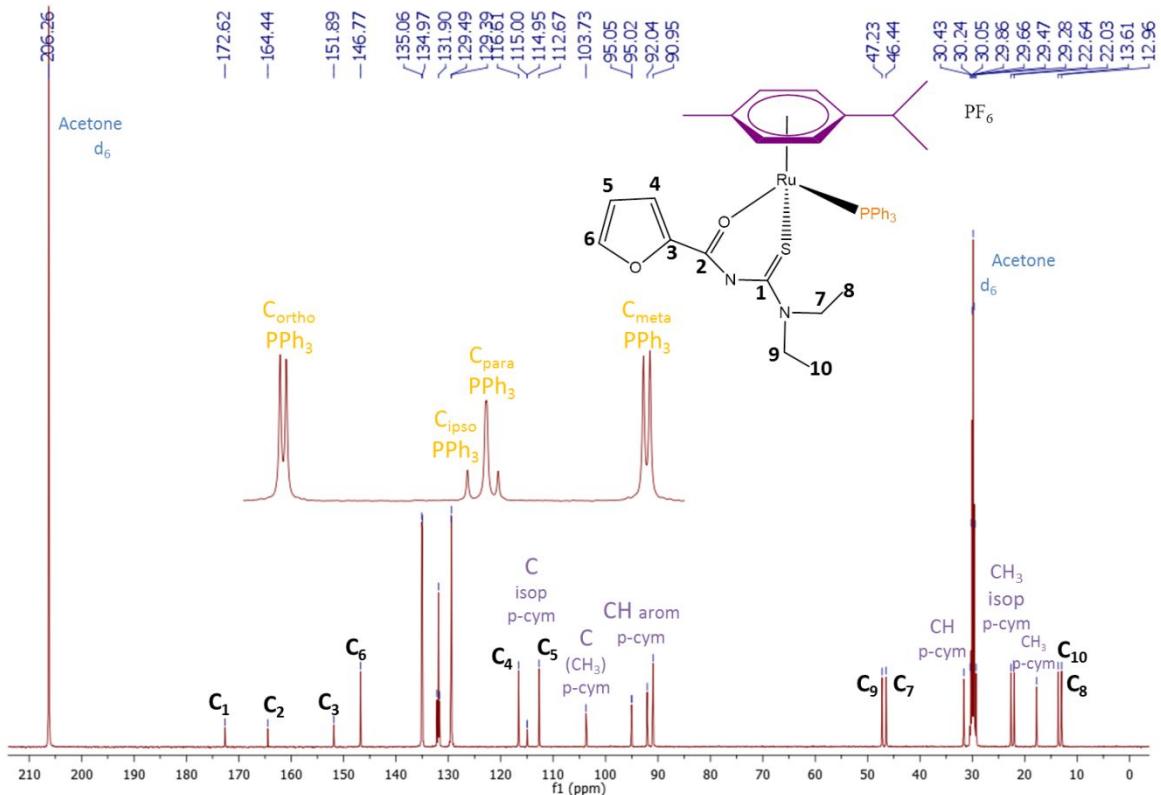


Figure S31: ¹³C NMR spectrum of complex **4b**

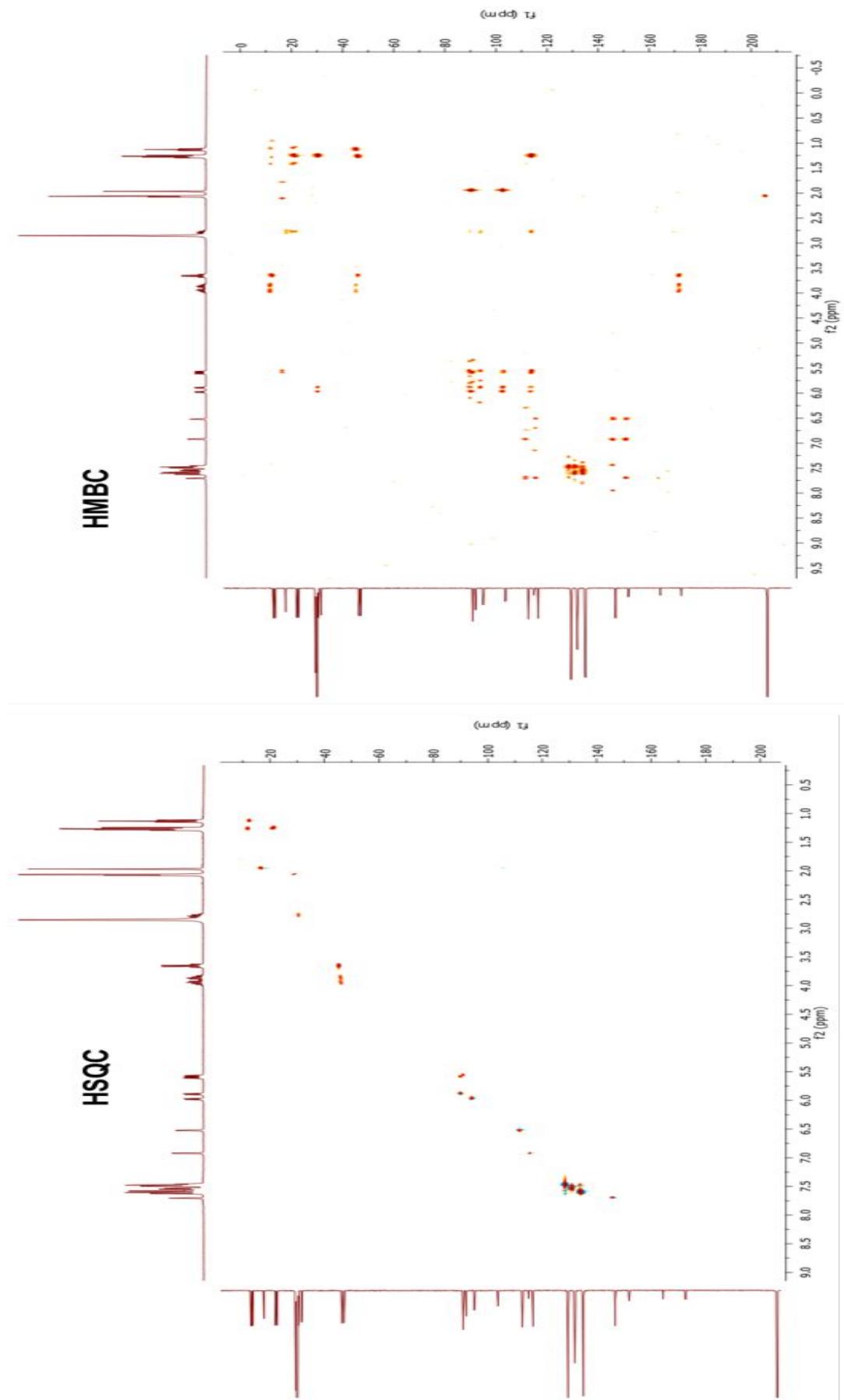


Figure S32: HSQC and HMBC spectra of complex 4b

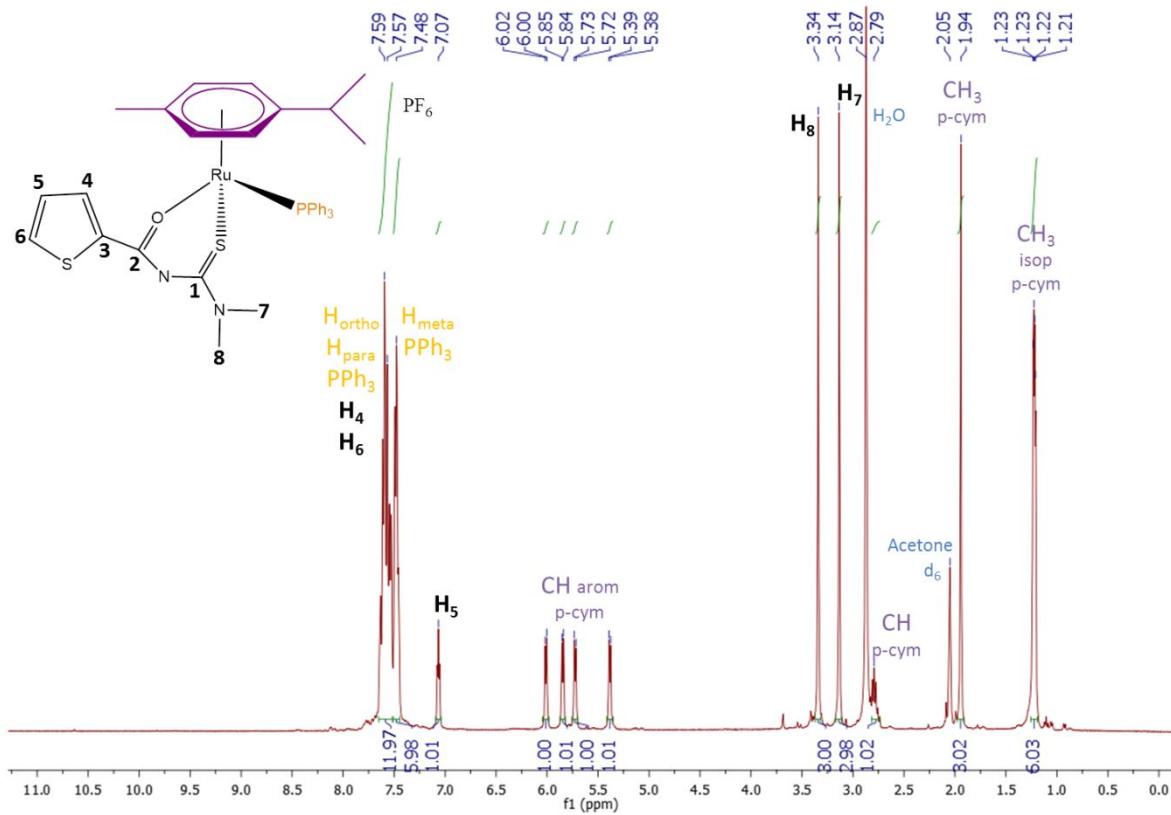


Figure S33: ^1H NMR spectrum of complex **5b**

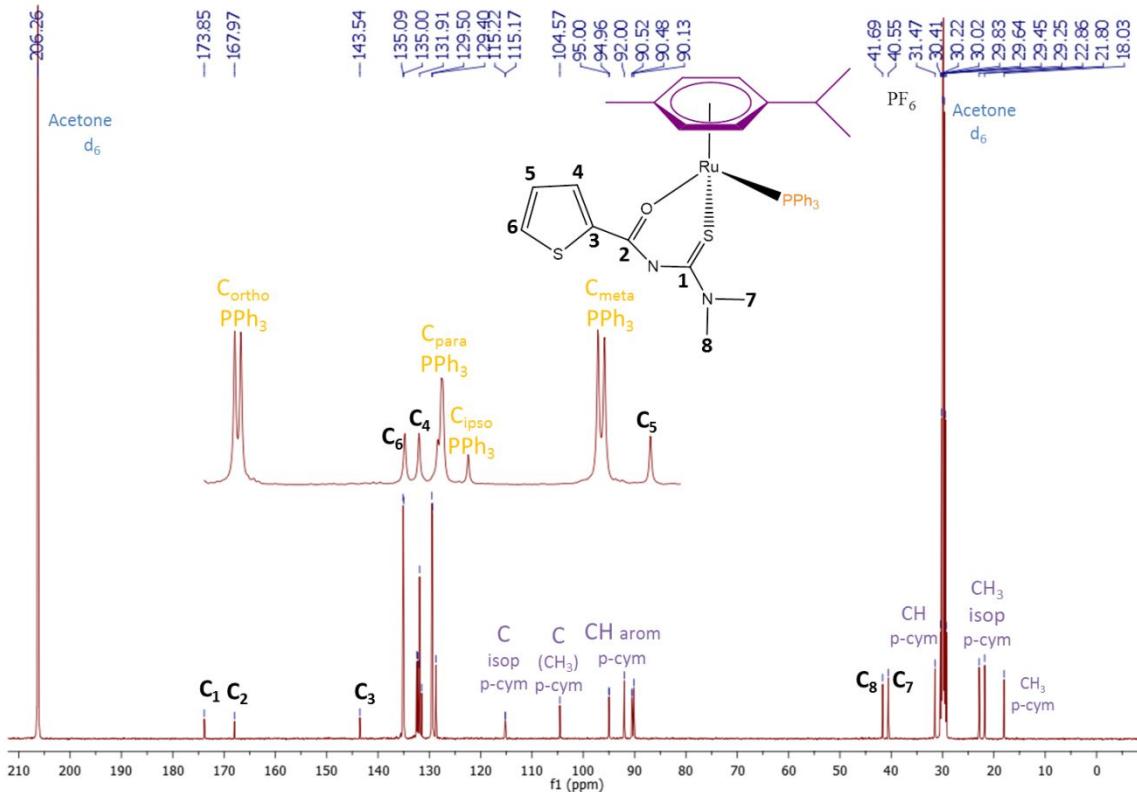


Figure S34: ^{13}C NMR spectrum of complex **5b**

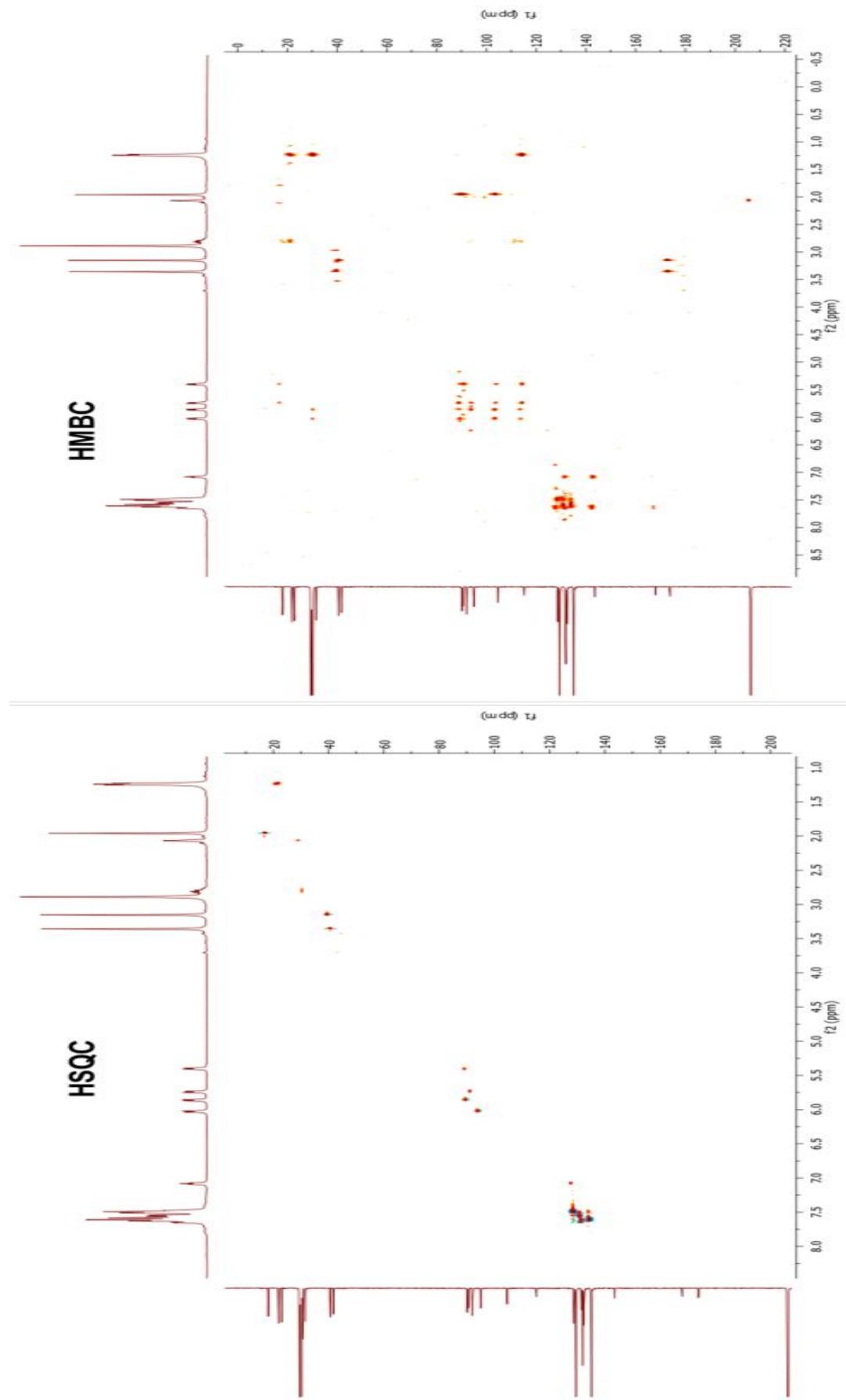


Figure S35: HSQC and HMBC spectra of complex **5b**

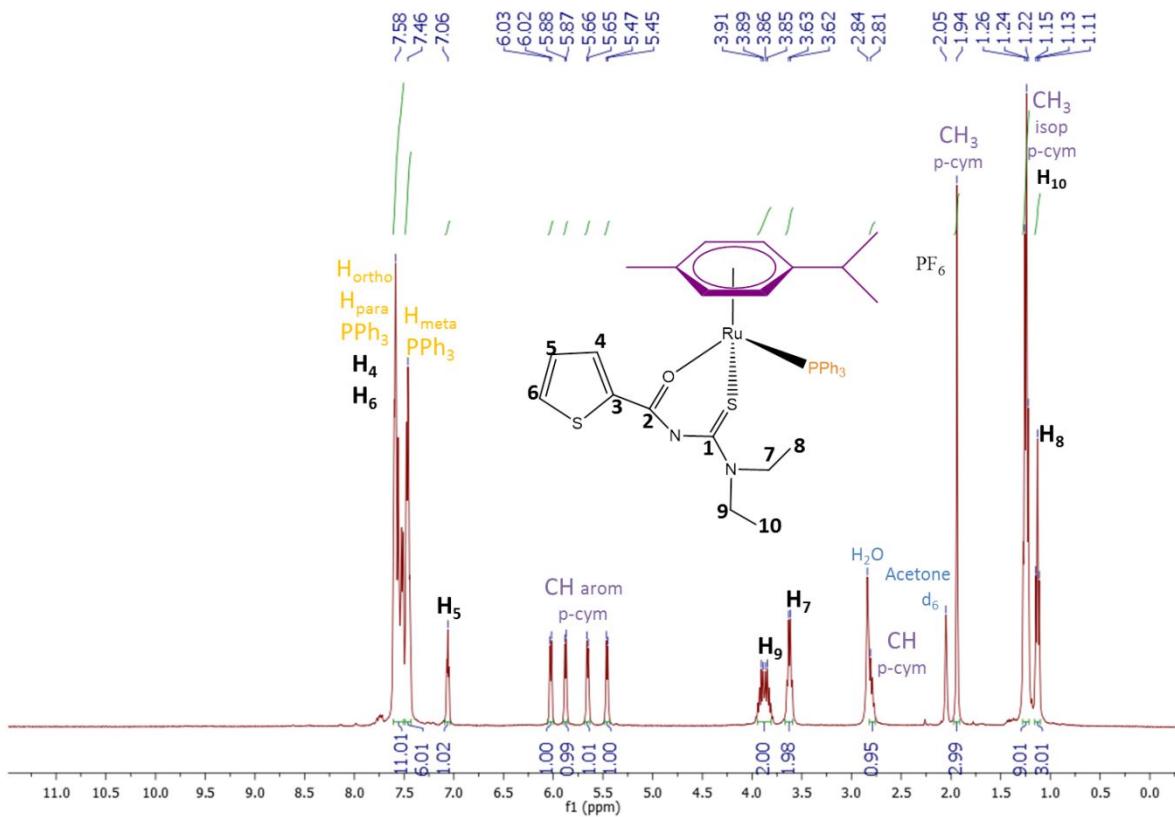


Figure S36: ¹H NMR spectrum of complex 6b

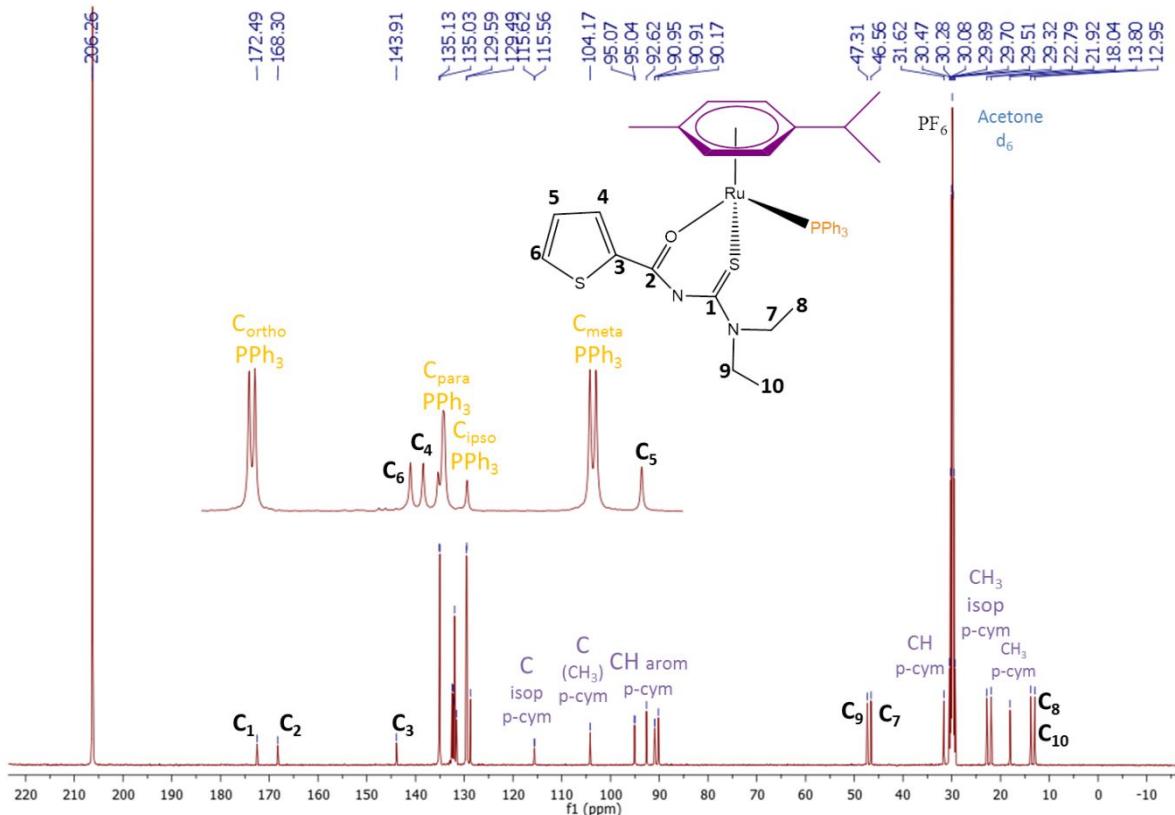


Figure S37: ¹³C NMR spectrum of complex 6b

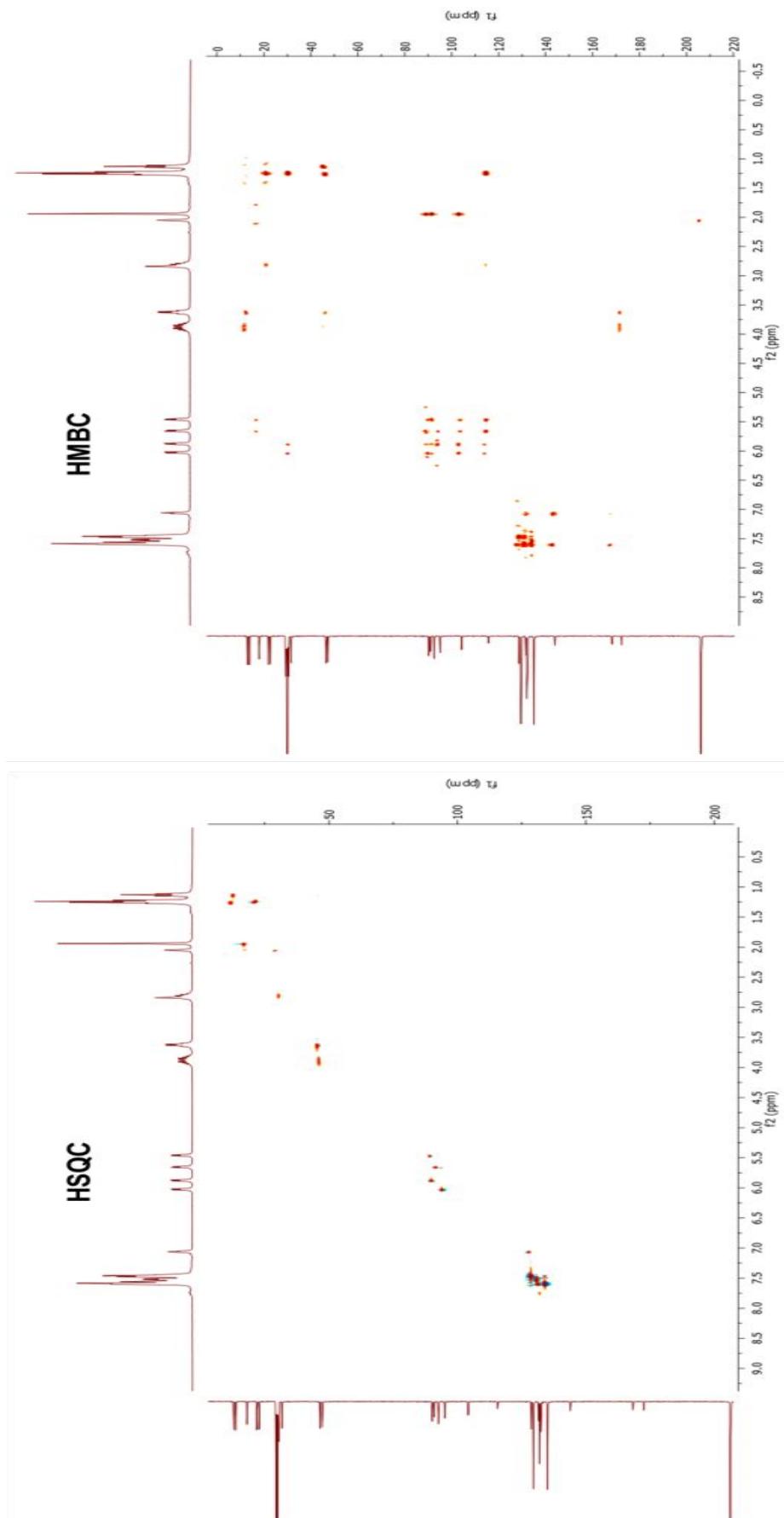


Figure S38: HSQC and HMBC spectra of complex **6b**

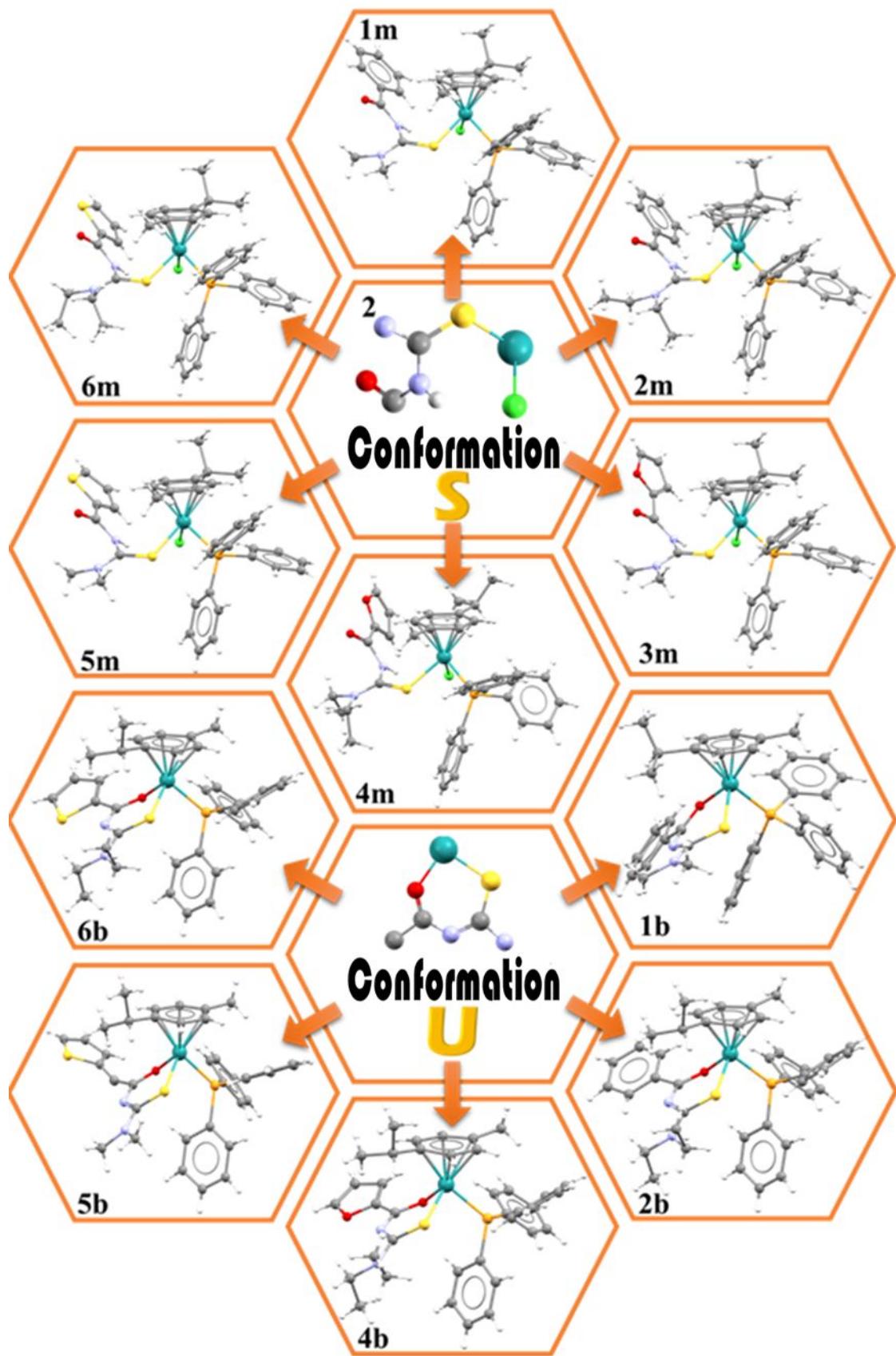


Figure S39: Crystal structures of the complexes **1m-6m**, **1b**, **2b**, and **4b-6b**. For the sake of clarity, the PF_6^- counterions are not included.

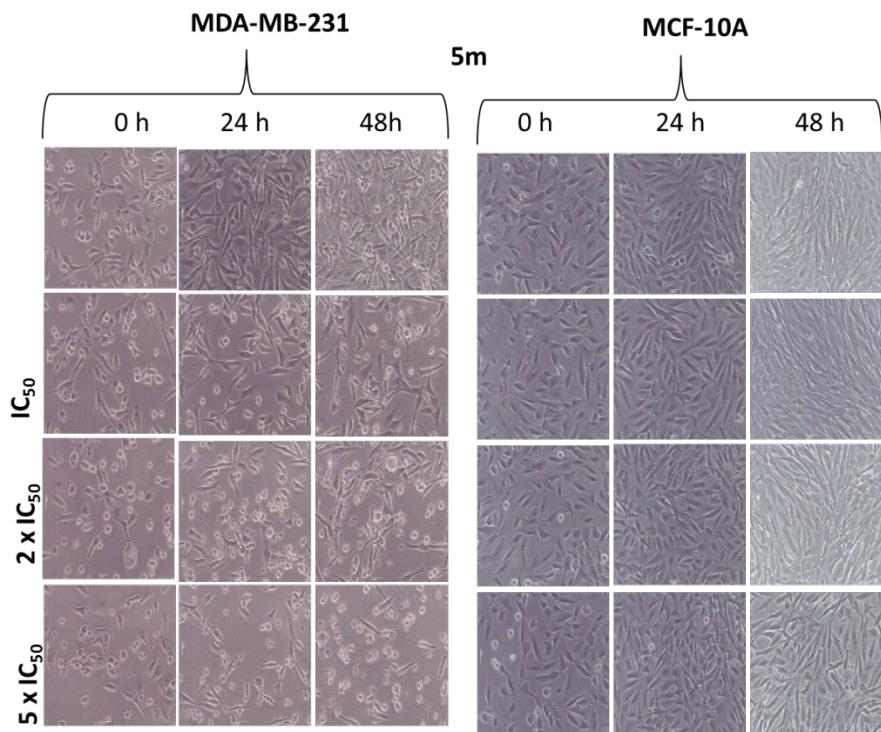


Figure S40: Effect of complex **5m** at IC_{50} , $2 \times IC_{50}$ and $5 \times IC_{50}$ concentrations in the morphology on MDA-MB-231 and MFC-10A breast cells at 0, 24 and 48 h.

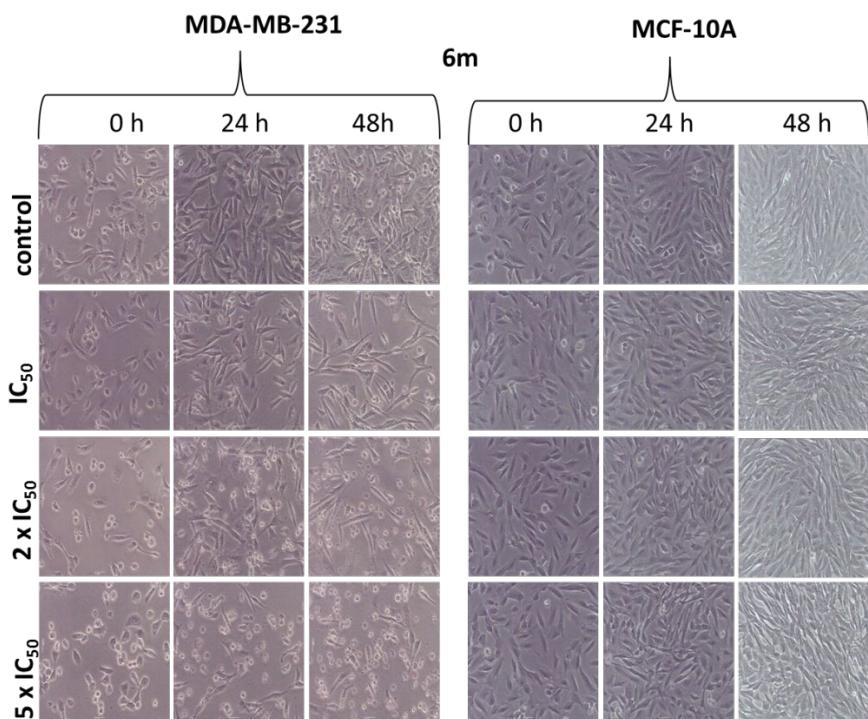


Figure S41: Effect of complex **6m** at IC_{50} , $2 \times IC_{50}$ and $5 \times IC_{50}$ concentrations in the morphology on MDA-MB-231 and MFC-10A breast cells at 0, 24 and 48 h.

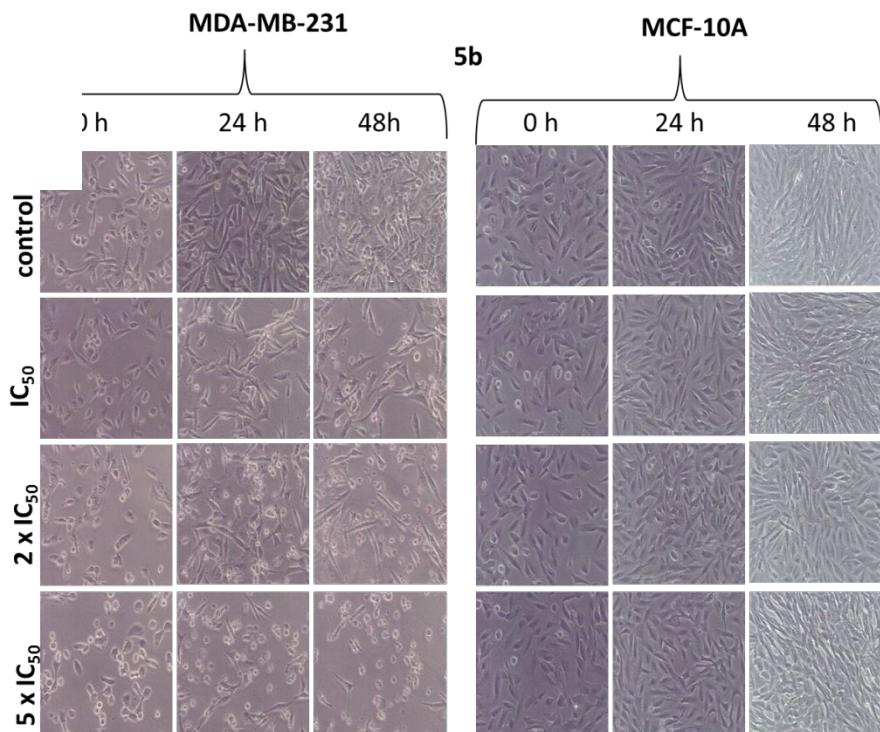


Figure S42: Effect of complex **5b** at IC_{50} , $2 \times IC_{50}$ and $5 \times IC_{50}$ concentrations in the morphology on MDA-MB-231 and MFC-10A breast cells at 0, 24 and 48 h.

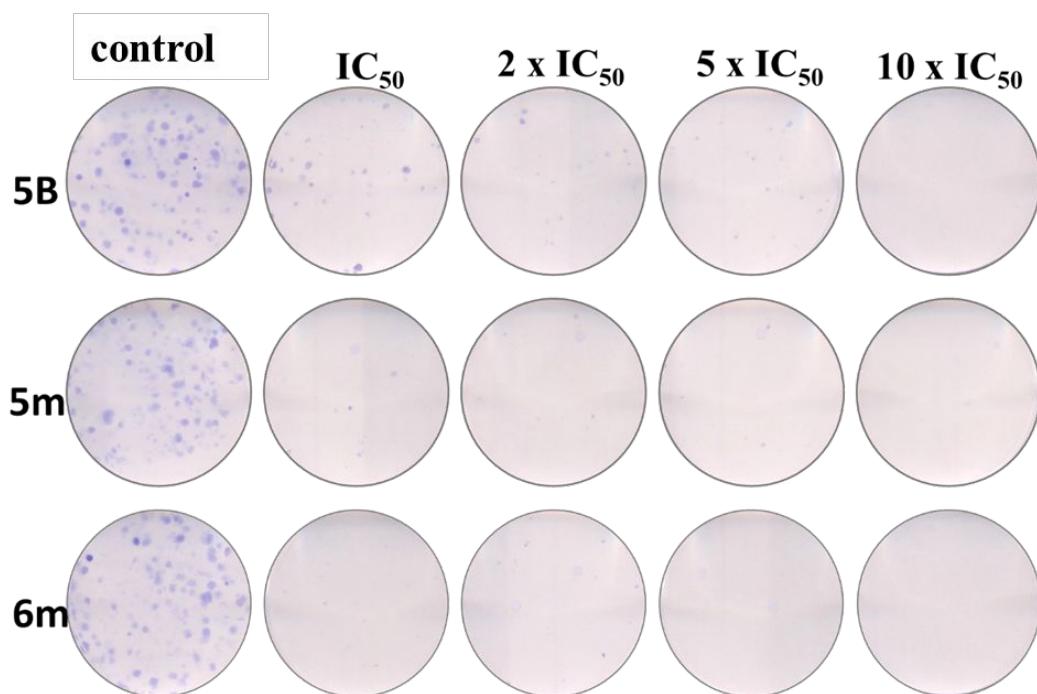


Figure S43: Effect of complexes **5m**, **6m** and **5b** at IC_{50} , $2 \times IC_{50}$, $5 \times IC_{50}$ and $10 \times IC_{50}$ concentrations in the colony formation on MDA-MB-231 and MFC-10A breast cells.

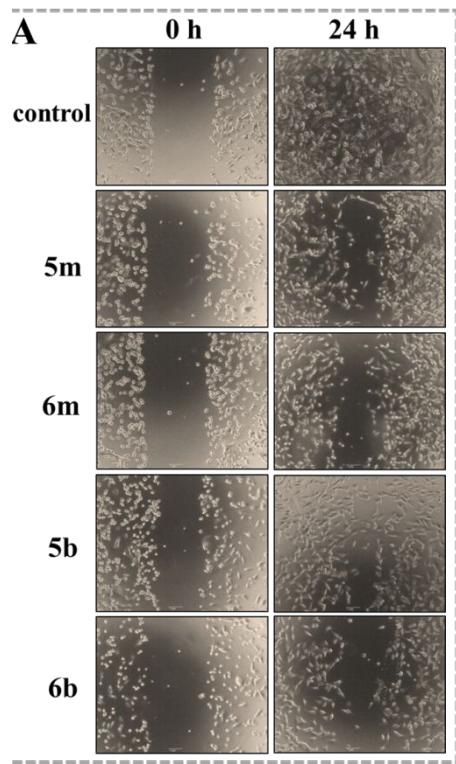


Figure S44: Effects of complexes **5m**, **6m**, **5b** and **6b** on MDA-MB-231 cells in Wound healing assay at respective IC₅₀ (48 h) concentration.

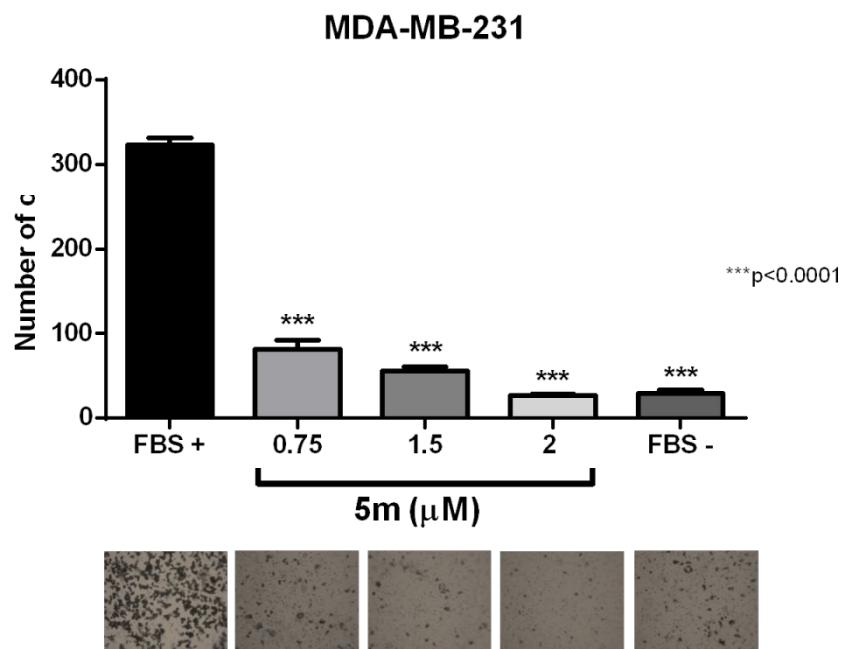


Figure S45: Effect of complexes **5m** at different concentrations and controls with FBS (FBS +) and without FBS (FBS -) in the Boyden chamber assay.

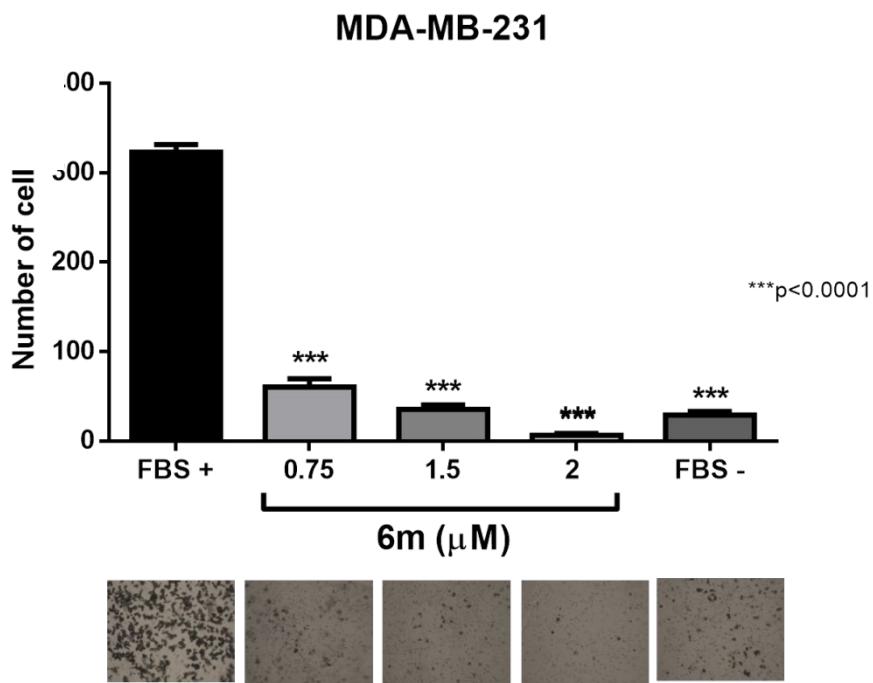


Figure S46: Effect of complexes **6m** at different concentrations and controls with FBS (FBS +) and without FBS (FBS -) in the Boyden chamber assay.

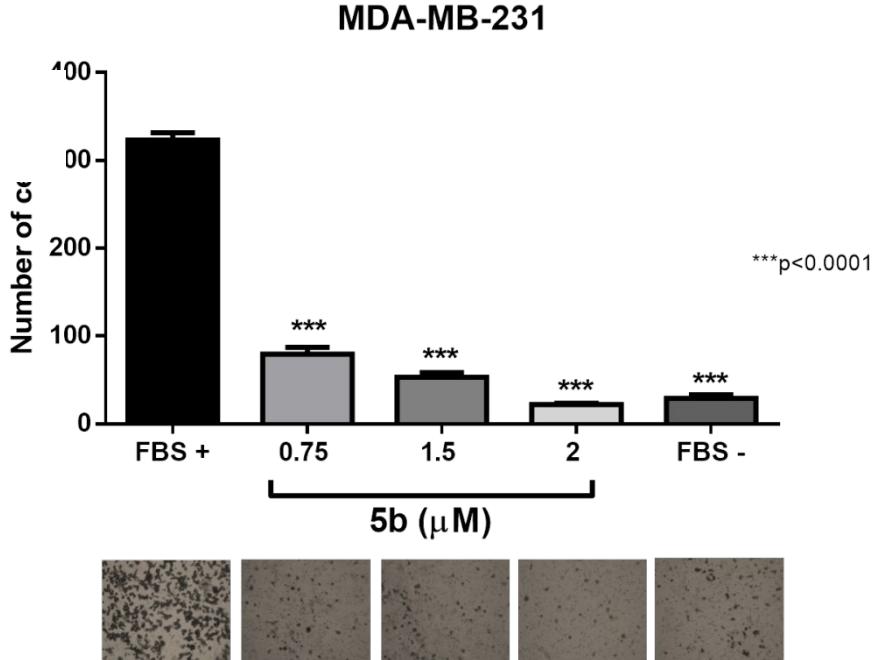
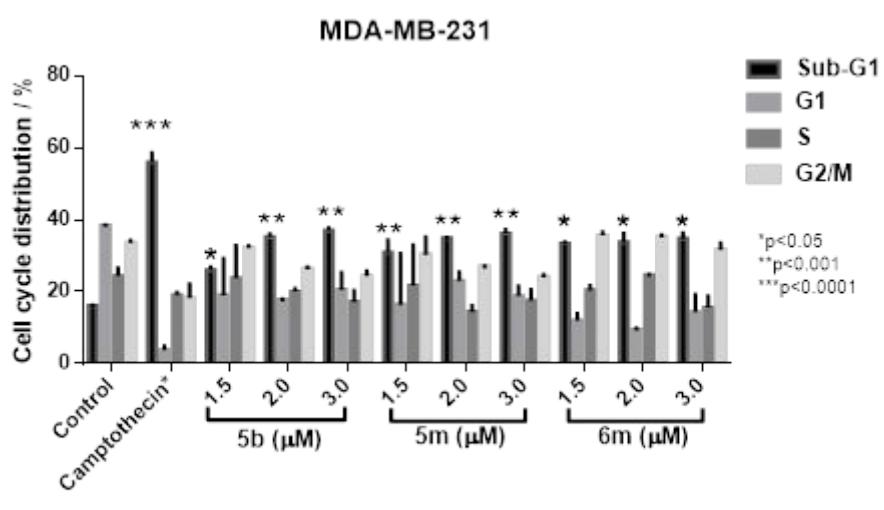
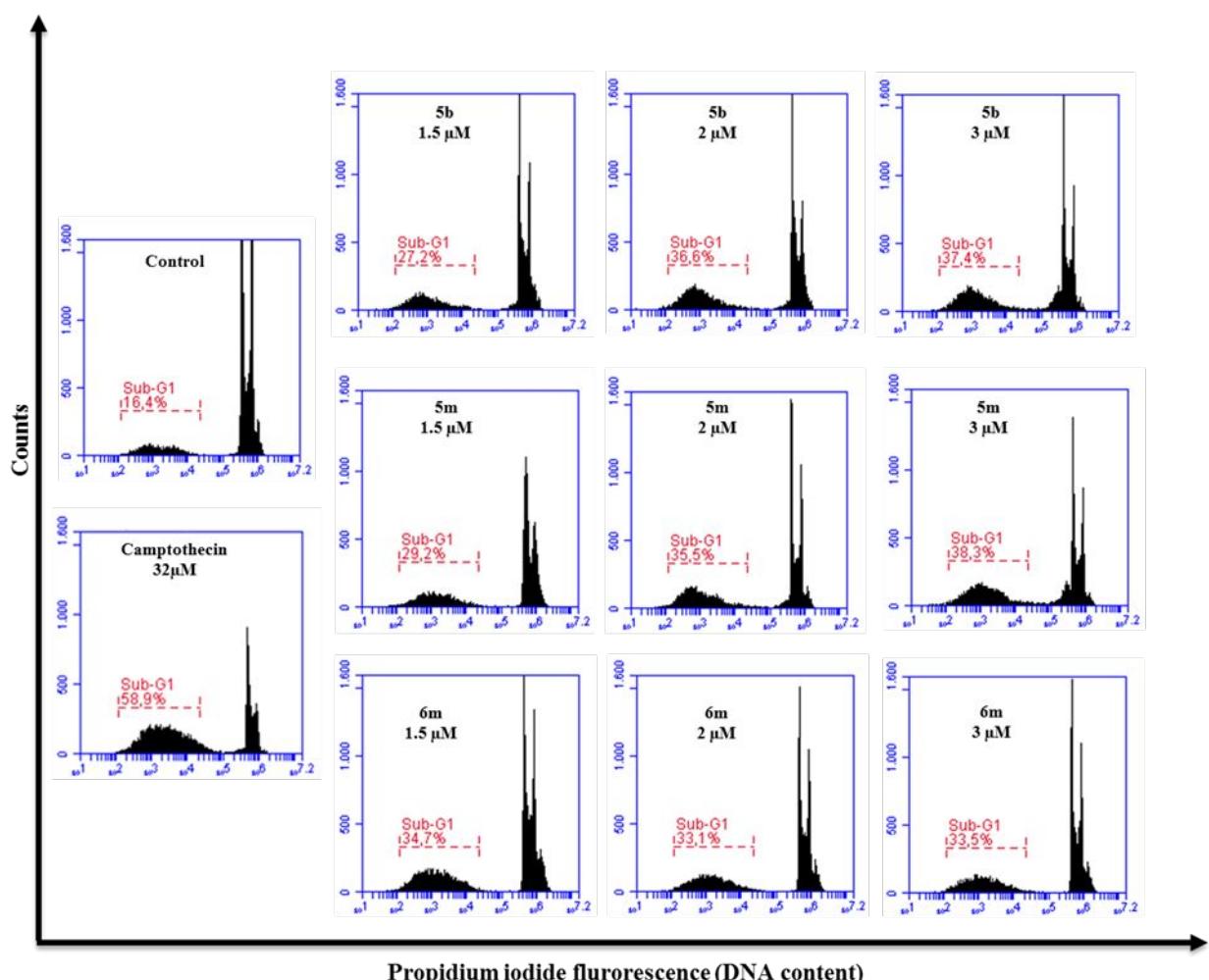


Figure S47: Effect of complexes **5b** at different concentrations and controls with FBS (FBS +) and without FBS (FBS -) in the Boyden chamber assay.



*Camptothecin 32 μM

Figure S48: Effects of the complexes **5m**, **6m** and **5b** at different concentrations on MDA-MB-231) in the cell cycle distribution for 24 h. Control corresponds to untreated cells and camptothecin was used as positive control.

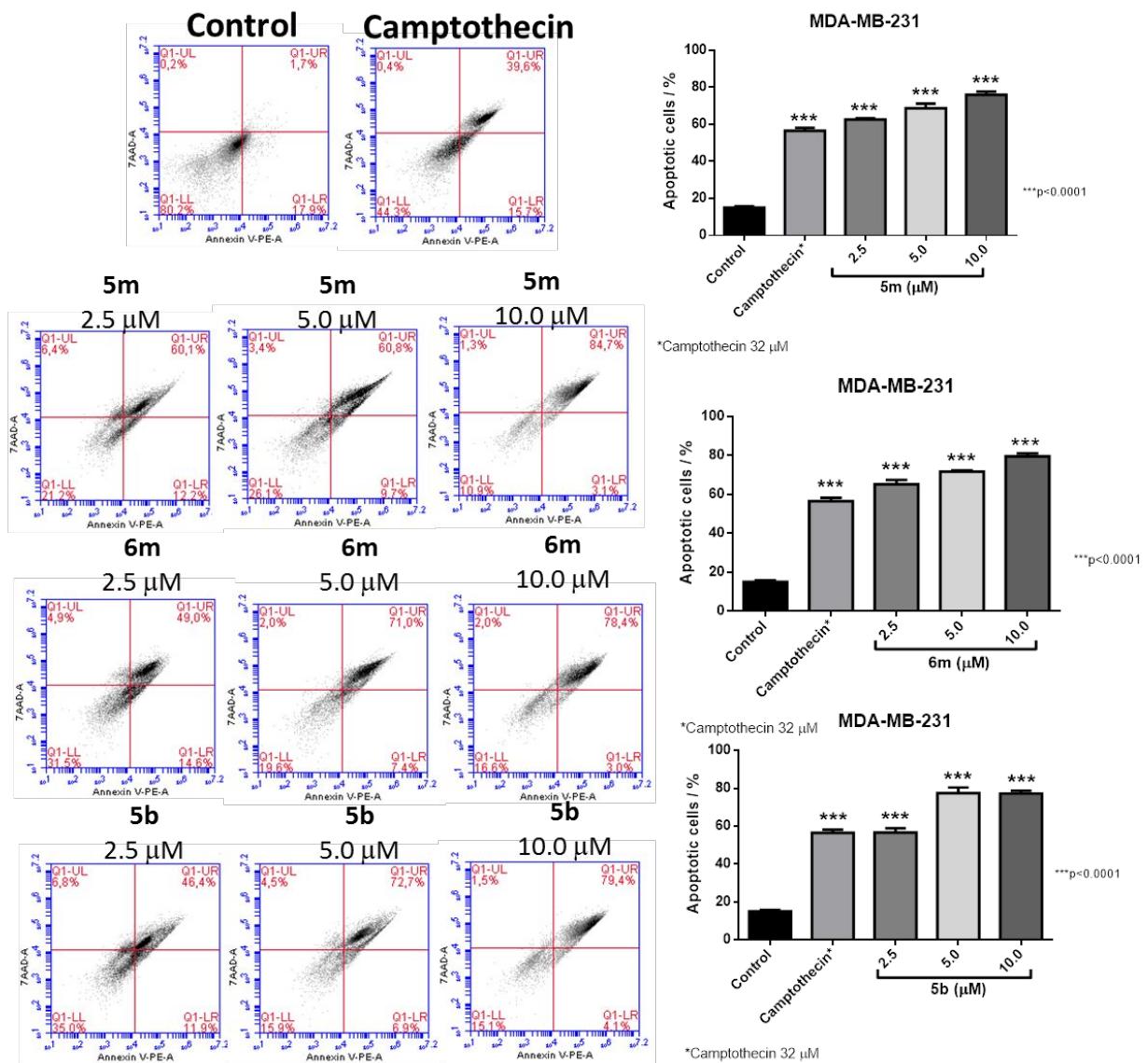
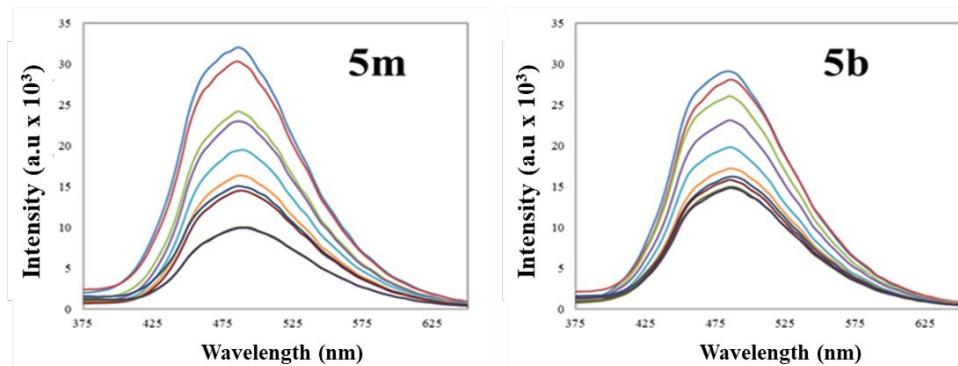


Figure S49: Effects of the complexes **5m**, **6m** and **5b** at different concentrations on MDA-MB-231)in the Apoptosis by PE-Annexin V – 7AAD assay for 24 h. Control corresponds to untreated cells and camptothecin was used as positive control.

Hoechst



TO

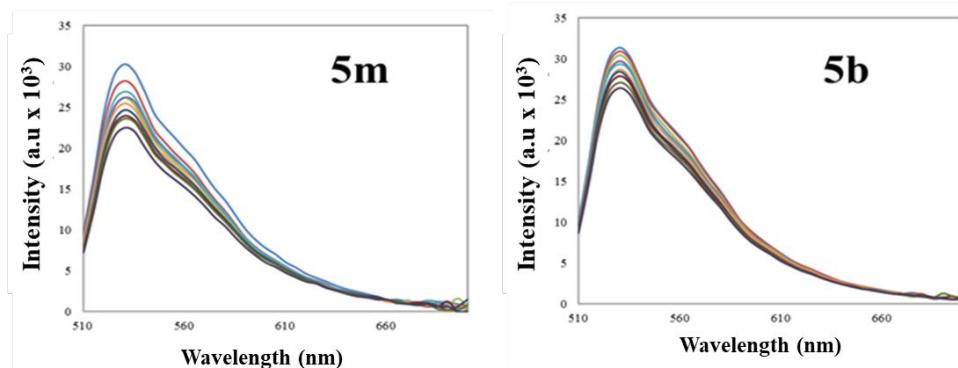


Figure S50: Displacement assay. (A) Emission spectra of Hoechst 33258 (5.0 μM) – CT-DNA (175 μM) ($\lambda_{\text{ex}} = 343 \text{ nm}$) at different concentrations (0-50 μM) of complexes **5m** and **5b** at 25 $^{\circ}\text{C}$. (B) Emission spectra of Thiazole orange (TO) (5.0 μM) – CT-DNA (175 μM) ($\lambda_{\text{ex}} = 480 \text{ nm}$) at different concentrations (0-50 μM) of complexes **5m** and **5b** at 25 $^{\circ}\text{C}$.

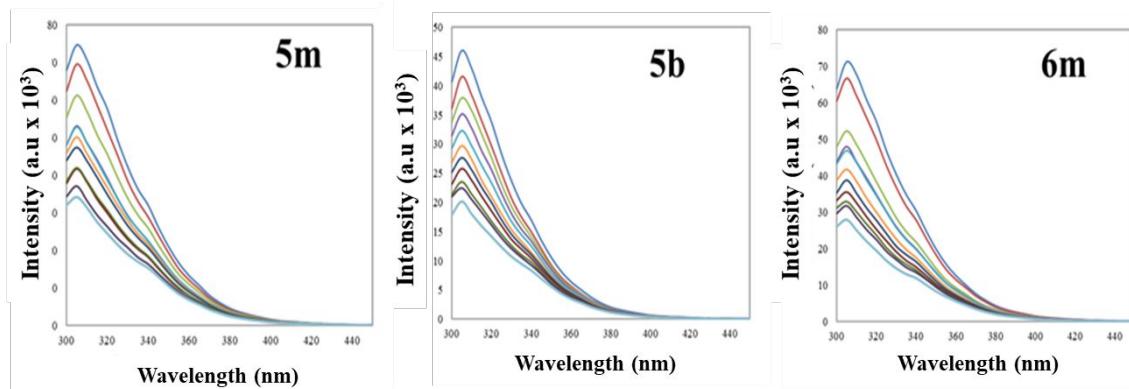


Figure S51: Fluorescence quenching spectra of HSA at different concentrations of complexes **5m**, **6m** and **5b** at 298 K.

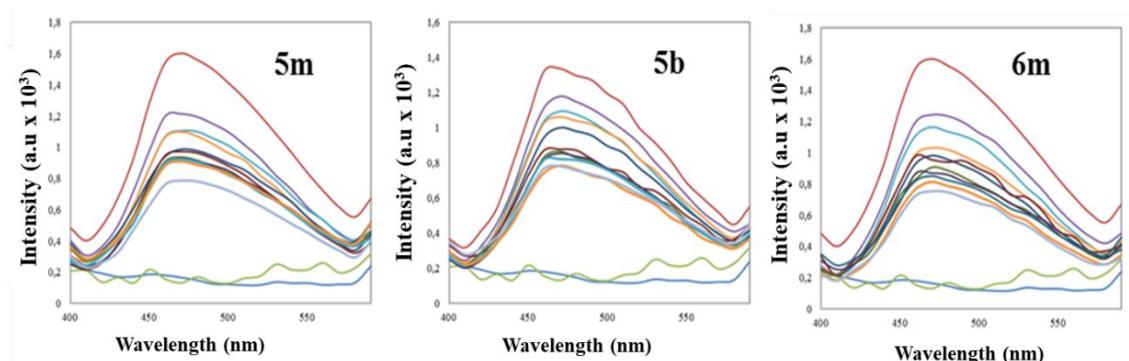


Figure S52: Fluorescence spectra of HSA-dansylglycine (DG) titrated with complexes **5m**, **6m** and **5b** at 298 K.

Table S1: Crystal data and structure refinement parameters obtained for the complexes **1m-4m**.

	1m	2m	3m	4m
Empirical formula	[RuC ₃₈ H ₄₁ N ₂ OPSCl] PF ₆	[RuC ₄₀ H ₄₅ N ₂ OPSCl]PF ₆	[RuC ₃₆ H ₃₉ N ₂ O ₂ PSCl]PF ₆	[RuC ₃₈ H ₄₃ N ₂ O ₂ PSCl]PF ₆
Formula weight	886.25	914.30	976.21	904.26
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P 2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	P2 ₁ /c
Unit cell dimensions				
a (Å)	9.3594(3)	20.7893(7)	9.2240(3)	9.6348(2)
b (Å)	20.8852(7)	20.7893(7)	20.7510(5)	24.8600(6)
c (Å)	20.0263(7)	9.5473(4)	19.9470(7)	17.2413(4)
α (°)	90	90	90	90
β (°)	94.7530(10)	90	95.045(2)	100.6520(10)
γ (°)	90	90	90	90
Volume (Å ³)	3901.1(2)	4126.3(3)	3803.2(2)	4058.49(16)
Z	4	4	4	4
Density calculated (Mg/m ³)	1.509	1.472	1.530	1.480
μ (mm ⁻¹)	0.668	0.634	0.686	0.645
F(000)	1808	1872	1780	1848
Crystal size (mm ³)	0.240 x 0.221 x 0.187	0.155 x 0.144 x 0.124	0.192 x 0.096 x 0.033	0.120 x 0.112 x 0.098
θ range (°)	1.411 to 25.999	1.385 to 25.993	2.839 to 27.101	1.454 to 25.999
Index ranges	-11 ≤ h ≤ 11, -25 ≤ k ≤ 21, -24 ≤ l ≤ 23	-25 ≤ h ≤ 25, -25 ≤ k ≤ 24, -11 ≤ l ≤ 11	-11 ≤ h ≤ 11, -22 ≤ k ≤ 26, -25 ≤ l ≤ 25	-11 ≤ h ≤ 9, -30 ≤ k ≤ 29, -21 ≤ l ≤ 21
Reflections collected	32383	37019	37791	32750
Independent reflections	7663 [R(int) = 0.0269]	6594 [R(int) = 0.0470]	8367 [R(int) = 0.0698]	7963 [R(int) = 0.0311]
Completeness to θ (%)	99.9	80.0	99.8	99.8
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	7663 / 0 / 474	6594 / 0 / 492	8367 / 0 / 468	7963 / 0 / 420
Goodness-of-fit on F ²	1.053	1.065	0.975	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0942	R1 = 0.0472, wR2 = 0.1201	R1 = 0.0451, wR2 = 0.1131	R1 = 0.0413, wR2 = 0.1084
R indices (all data)	R1 = 0.0402, wR2 = 0.0986	R1 = 0.0556, wR2 = 0.1232	R1 = 0.0786, wR2 = 0.1268	R1 = 0.0515, wR2 = 0.1167
Δρ _{max} and Δρ _{min} (e.Å ⁻³)	0.900 and -0.452	0.821 and -0.591	0.680 and -0.630	0.802 and -0.674

Table S2: Crystal data and structure refinement parameters obtained for the complexes **5m-6m** and **1b-2b**. For complex **1b** there are two independent structures, but stereochemically similar, in the asymmetric unit.

	5m	6m	1b	2b
Empirical formula	[RuC ₃₆ H ₃₉ N ₂ OPS ₂ Cl]PF ₆	[RuC ₃₈ H ₄₃ N ₂ OPS ₂ Cl]PF ₆	[RuC ₃₈ H ₄₀ N ₂ OPS] PF ₆	[RuC ₄₀ H ₄₄ N ₂ OPS]PF ₆
Formula weight	892.27	920.62	849.79	877.84
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P21/c	P21/c	P -1	C c
Unit cell dimensions				
a (Å)	9.3660(2)	9.5180(3)	10.8500(2)	21.7794(7)
b (Å)	20.7810(5)	20.6020(7)	16.7790(4)	16.5045(9)
c (Å)	19.9750(4)	20.7300(6)	22.5750(6)	11.3004(5)
α (°)	90	90	78.9320(10)	90
β (°)	94.7800(10)	90.223(2)	76.2940(10)	101.154(2)
γ (°)	90	90	88.1130(10)	90
Volume (Å ³)	3874.31(15)	4064.9(2)	3918.19(16)	3985.3(3)
Z	4	4	4	4
Density calculated (Mg/m ³)	1.530	1.502	1.441	1.463
μ (mm ⁻¹)	0.725	0.693	0.596	0.588
F(000)	1816	1870	1736	1800
Crystal size (mm ³)	0.285 x 0.255 x 0.112	0.235 x 0.124 x 0.101	0.301 x 0.211 x 0.187	0.306 x 0.086 x 0.066
θ range (°)	2.834 to 25.024	2.551 to 26.000	2.218 to 25.999	3.077 to 23.526
Index ranges	-11 ≤ h ≤ 11, -24 ≤ k ≤ 24, -23 ≤ l ≤ 22	-11 ≤ h ≤ 11, -23 ≤ k ≤ 25, -25 ≤ l ≤ 24	-13 ≤ h ≤ 13, -20 ≤ k ≤ 20, -27 ≤ l ≤ 20	-24 ≤ h ≤ 24, -15 ≤ k ≤ 18, -12 ≤ l ≤ 11
Reflections collected	39851	31791	37332	10220
Independent reflections	6822 [R(int) = 0.1082]	7941 [R(int) = 0.0568]	15189 [R(int) = 0.0319]	5184 [R(int) = 0.1440]
Completeness to θ (%)	97.4	99.6	98.8	82.1
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	6822 / 0 / 466	7941 / 0 / 484	15189 / 36 / 929	5184 / 2 / 483
Goodness-of-fit on F ²	1.101	1.098	1.082	1.096
Final R indices				
[I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1196	R1 = 0.0691, wR2 = 0.1796	R1 = 0.0564, wR2 = 0.1573	R1 = 0.0620, wR2 = 0.1625
R indices (all data)	R1 = 0.0634, wR2 = 0.1307	R1 = 0.1006, wR2 = 0.1988	R1 = 0.0755, wR2 = 0.1732	R1 = 0.0665, wR2 = 0.1655
Δρ _{max} and Δρ _{min} (e.Å ⁻³)	0.871 and -0.910	2.729 and -0.643	1.170 and -1.162	0.849 and -0.844

Table S3: Crystal data and structure refinement parameters obtained for the complexes **4b**-**6b**.

	4b	5b	6b
Empirical formula	[RuC ₃₈ H ₄₂ N ₂ O ₂ PS]PF ₆	[RuC ₃₆ H ₃₈ N ₂ OPS ₂] PF ₆	[RuC ₃₈ H ₄₂ N ₂ OPS ₂]PF ₆
Formula weight	867.80	885.81	883.86
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C c	P21/a	C c
Unit cell dimensions			
a (Å)	21.3545(5)	14.1630(4)	21.6907(6)
b (Å)	16.5342(4)	18.9980(5)	16.4995(6)
c (Å)	11.2997(2)	15.3060(5)	11.2879(3)
α (°)	90	90	90
β (°)	101.3400(10)	110.307(2)	100.501(2)
γ (°)	90	90	90
Volume (Å ³)	3911.80(15)	3862.4(2)	3972.1(2)
Z	4	4	4
Density calculated (Mg/m ³)	1.474	1.472	1.478
μ (mm ⁻¹)	0.600	0.657	0.641
F(000)	1776	1744	1808
Crystal size (mm ³)	0.200 x 0.154 x 0.121	0.301 x 0.211 x 0.187	0.224 x 0.210 x 0.133
θ range (°)	1.569 to 26.000	1.871 to 25.997	2.272 to 27.480
Index ranges	-26 ≤ h ≤ 22, -20 ≤ k ≤ 19, -10 ≤ l ≤ 13	17 ≤ h ≤ 17, -23 ≤ k ≤ 22, -18 ≤ l ≤ 18	-28 ≤ h ≤ 28, -21 ≤ k ≤ 21, -14 ≤ l ≤ 14
Reflections collected	15381	40112	16871
Independent reflections	6213 [R(int) = 0.0218]	7583 [R(int) = 0.0487]	8191 [R(int) = 0.0233]
Completeness to θ (%)	99.9	99.9	99.8
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	6213 / 2 / 474	7583 / 0 / 458	8191 / 2 / 475
Goodness-of-fit on F ²	0.780	1.127	1.121
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0860	R1 = 0.0623, wR2 = 0.1618	R1 = 0.0392, wR2 = 0.1059
R indices (all data)	R1 = 0.0313, wR2 = 0.0876	R1 = 0.0868, wR2 = 0.1954	R1 = 0.0442, wR2 = 0.1114
Δρ _{max} and Δρ _{min} (e.Å ⁻³)	0.658 and -0.537	1.048 and -0.954	0.712 and -1.258

Table S4: Selected interatomic distances [\AA] for complexes **1m-6m**, **1b-2b** and **4b-6b**

Complexes	1m	2m	3m	4m	5m	6m	1b	2b	4b	5b	6b
Bound lenghts											
Ru-P	2.3814(7)	2.383(2)	2.3786(9)	2.3774(8)	2.3799(11)	2.3799(15)	2.3653(12)	2.346(3)	2.3430(12)	2.3670(12)	2.3459(13)
Ru-S	2.3796(7)	2.366(2)	2.3763(10)	2.3856(9)	2.3843(11)	2.3696(15)	2.3691(13)	2.351(3)	2.3486(12)	2.3564(13)	2.3507(13)
Ru-Cl	2.4193(7)	2.420(2)	2.4173(9)	2.4106(8)	2.4201(11)	2.4208(16)	-	-	-	-	-
Ru-O	-	-	-	-	-	-	2.059(3)	2.075(9)	2.094(3)	2.073(3)	2.091(4)
Ru-C(4')	2.284(3)	2.297(8)	2.276(4)	2.291(3)	2.286(5)	2.290(6)	2.258(5)	2.304(13)	2.292(6)	2.274(5)	2.293(6)
Ru-C(5')	2.246(3)	2.230(8)	2.236(4)	2.244(3)	2.242(5)	2.219(6)	2.222(5)	2.195(12)	2.249(5)	2.187(5)	2.255(5)
Ru-C(6')	2.205(3)	2.192(9)	2.202(4)	2.222(3)	2.242(5)	2.229(6)	2.214(5)	2.223(13)	2.245(6)	2.217(5)	2.256(7)
Ru-C(7')	2.229(3)	2.216(9)	2.231(4)	2.232(4)	2.239(4)	2.240(6)	2.267(5)	2.298(13)	2.310(5)	2.296(5)	2.313(6)
Ru-C(8')	2.233(3)	2.177(7)	2.229(4)	2.196(4)	2.208(4)	2.210(6)	2.248(5)	2.241(15)	2.206(5)	2.246(6)	2.202(5)
Ru-C(9')	2.236(3)	2.237(9)	2.233(4)	2.245(4)	2.251(4)	2.261(6)	2.215(5)	2.263(12)	2.185(5)	2.239(6)	2.192(5)
S(1)-C(1)	1.706(3)	1.702(8)	1.697(4)	1.702(4)	1.698(4)	1.709(6)	1.722(5)	1.727(12)	1.732(5)	1.716(5)	1.720(5)
O(1)-C(2)	1.210(4)	1.221(11)	1.217(5)	1.216(4)	1.217(6)	1.204(8)	1.275(6)	1.268(14)	1.278(6)	1.276(6)	1.269(7)
N(1)-C(1)	1.384(4)	1.399(11)	1.396(5)	1.384(5)	1.392(6)	1.388(8)	1.357(7)	1.342(16)	1.341(7)	1.347(6)	1.345(7)
N(2)-C(1)	1.310(4)	1.295(11)	1.311(5)	1.325(5)	1.303(6)	1.307(8)	1.326(6)	1.341(16)	1.340(6)	1.324(7)	1.345(7)
N(1)-C(2)	1.390(4)	1.363(12)	1.392(5)	1.380(4)	1.382(6)	1.398(8)	1.317(6)	1.328(16)	1.308(6)	1.313(7)	1.320(7)

Table S5: Selected bond angles [deg] for complexes **1m-6m**, **1b-2b** and **4b-6b**

Complexes	1m	2m	3m	4m	5m	6m	1b	2b	4b	5b	6b
Bound angles											
P-Ru-Cl	92.63(2)	91.30(7)	92.83(3)	85.69(3)	92.42(4)	91.36(6)	-	-	-	-	-
S-Ru-Cl	90.47(3)	92.47(8)	90.32(4)	89.56(3)	90.51(4)	91.18(6)	-	-	-	-	-
S-Ru-P	82.70(2)	81.84(7)	82.67(3)	86.80(3)	82.77(4)	82.81(5)	84.87(5)	87.06(11)	87.03(4)	88.36(5)	87.05(5)
S-Ru-O	-	-	-	-	-	-	88.69(10)	88.7(3)	88.93(10)	89.21(10)	89.14(11)
P-Ru-O	-	-	-	-	-	-	84.57(10)	89.0(3)	88.58(10)	87.49(10)	88.67(11)
C(4')-Ru-S	154.65(8)	151.0(2)	155.02(11)	149.36(10)	155.57(13)	155.36(17)	101.77(17)	88.5(4)	88.41(15)	90.87(16)	88.45(17)
C(5')-Ru-S	153.75(8)	155.4(3)	153.53(11)	112.96(11)	118.34(14)	118.3(2)	86.41(18)	90.6(4)	112.68(14)	86.31(16)	112.08(15)
C(6')-Ru-S	116.75(8)	118.2(3)	91.62(10)	89.15(12)	91.63(14)	91.37(18)	100.07(18)	120.0(4)	149.23(16)	111.65(16)	149.16(17)
C(7')-Ru-S	89.79(8)	89.9(3)	114.30(11)	91.95(12)	89.66(13)	88.61(17)	94.38(15)	155.6(4)	155.61(16)	147.74(16)	156.57(19)
C(8')-Ru-S	91.18(9)	148.7(2)	151.08(12)	121.27(12)	115.69(13)	114.47(17)	106.54(16)	149.0(4)	119.29(16)	155.54(17)	120.1(2)
C(9')-Ru-S	117.63(9)	113.8(3)	159.31(11)	157.79(12)	152.87(13)	151.86(16)	137.43(16)	112.5(3)	90.45(15)	119.79(16)	90.80(17)
C(4')-Ru-O	-	-	-	-	-	-	98.58(19)	117.6(4)	118.46(18)	109.45(17)	118.24(19)
C(5')-Ru-O	-						131.2(2)	154.6(4)	91.86(17)	146.59(18)	91.56(18)
C(6')-Ru-O						163.63(17)	151.3(5)	90.15(18)	158.60(19)	89.3(2)	
C(7')-Ru-O						138.17(19)	115.3(5)	115.10(19)	123.03(19)	113.9(2)	
C(8')-Ru-O						103.64(16)	90.8(5)	151.77(19)	93.86(18)	150.8(2)	
C(9')-Ru-O						87.14(17)	91.5(4)	154.97(17)	88.07(18)	155.11(19)	

Table S6: Characteristic ^{13}C { ^1H } NMR signals experimental and theoretical (ppm) for acylthiourea ligand and complexes early reported.

13C NMR experimental						13C NMR theoretical					
Ligands			Complexes			Ligands			Complexes		
C=O	C=S		C=O	C=S		C=O	C=S		C=O	C=S	
1	158.0	181.1	1	158.8	180.6	1	157.3	179.2	1	156.8	177.2
			1a	166.4	190.1				1a	164.1	184.7