SUPPORTING INFORMATION

Tetranuclear Coordination Assemblies Based on Half-sandwich Ruthenium(II) Complexes. Non Covalent Binding to DNA and Cytotoxicity

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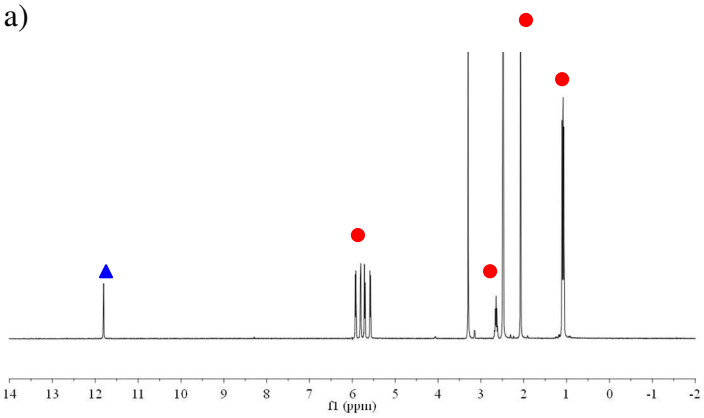
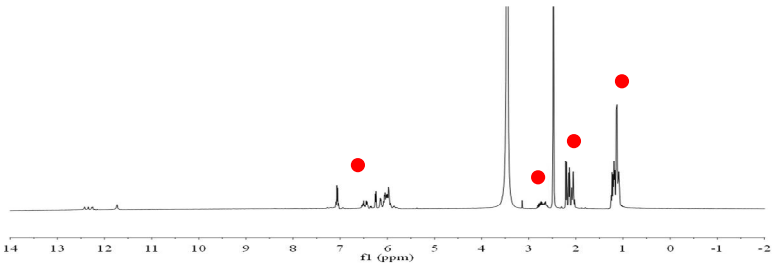
A) ^{1}H NMR Spectra

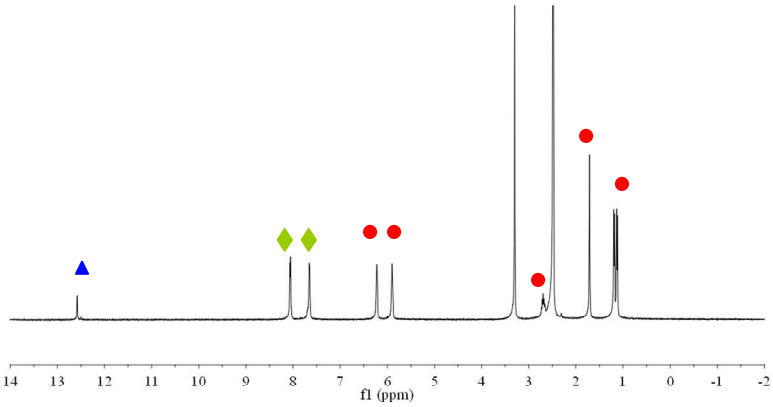
a)



b)



c)



d)

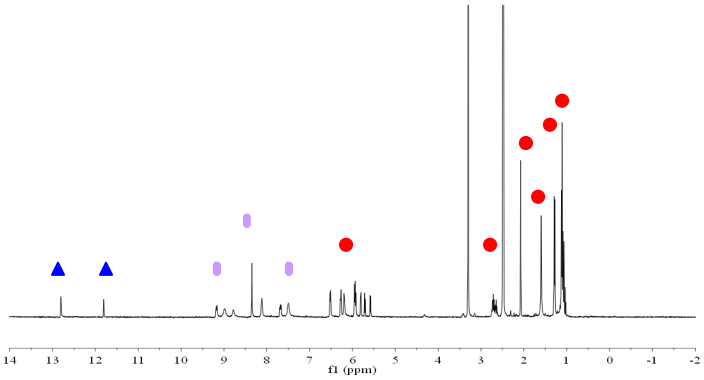


Figure S1. ^{1}H-NMR of a) $[(Cymene)_2Ru_2Cl_2(Hoxonate)]$ (1a), b) $[(Cymene)_2Ru_2(H_2O)_2(Hoxonate)](CF_3SO_3)_2$ (1b), c) $[(Cymene)_4Ru_4(Hoxonate)_2(4,4'\text{-}bpy)_2](CF_3SO_3)_4(H_2O)_3$ (2a), d) $[(Cymene)_4Ru_4(Hoxonate)_2(4,7\text{-}phen)_2](CF_3SO_3)_4$ (2b) . (Relevant signals corresponding to Cymene peaks (●) , Oxonic acid (▲) ; 4,4-bypirydine group (♦) and 4,7-Phenantroline group (▮) are marked).

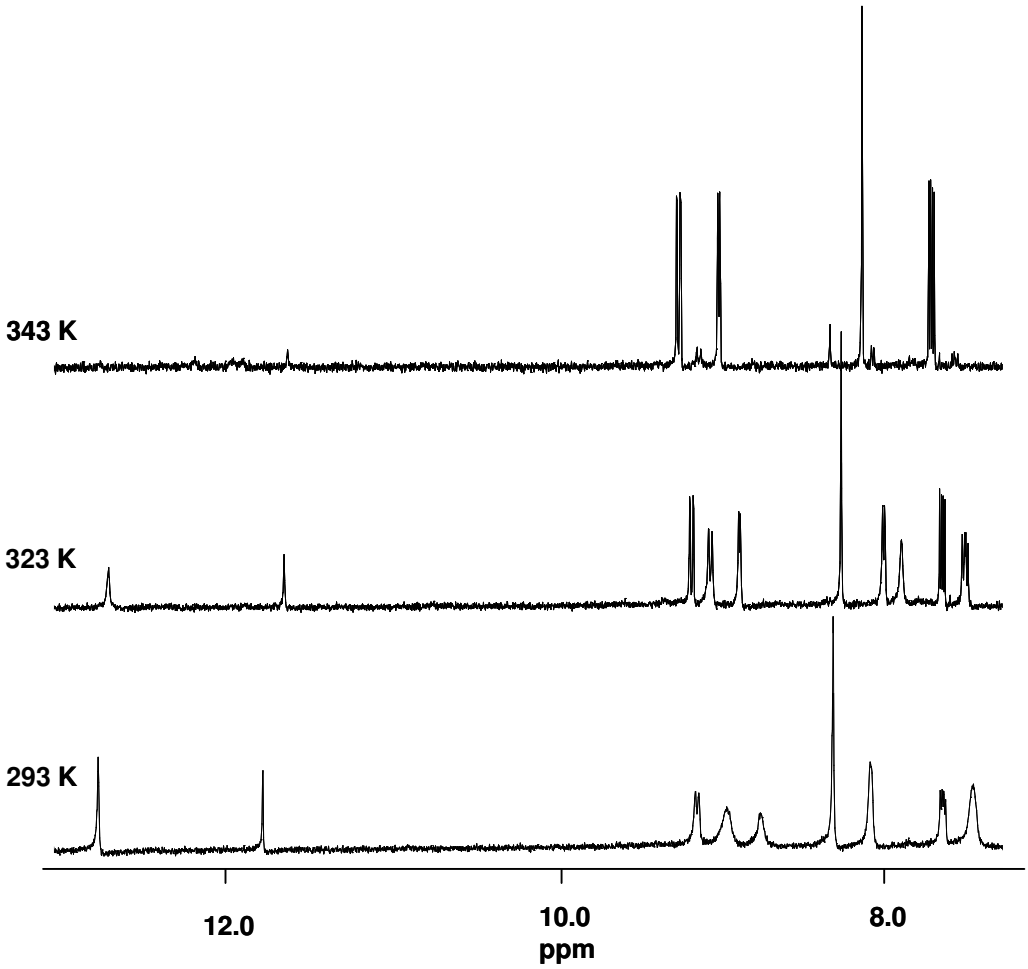
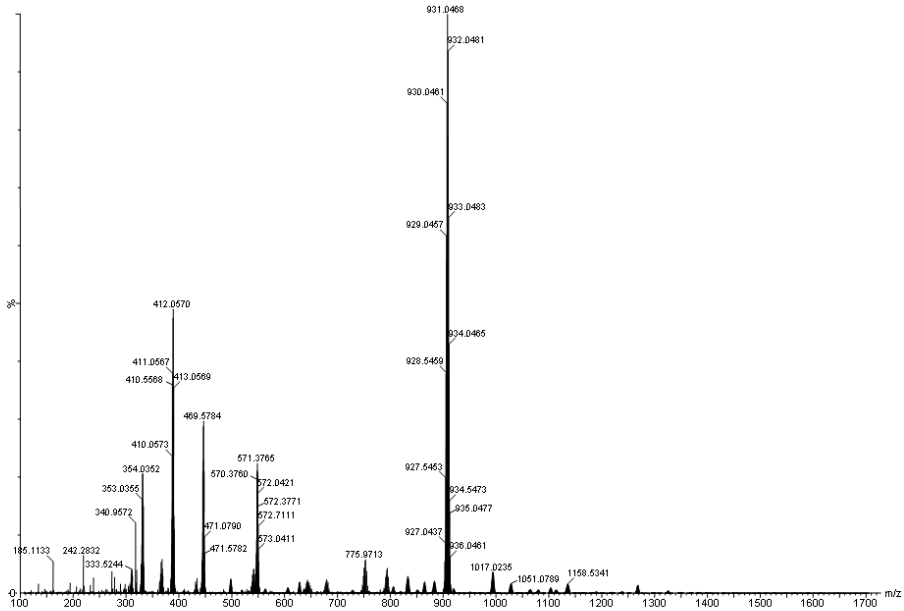


Figure S2. Temperature variable ^{1}H NMR experiment of $[(Cymene)_4Ru_4(Hoxonate)_2(4,7\text{-}Phen)_2](CF_3SO_3)_4$ (2b) in DMSO-d_6.

B) ESI-MS

a)



b)

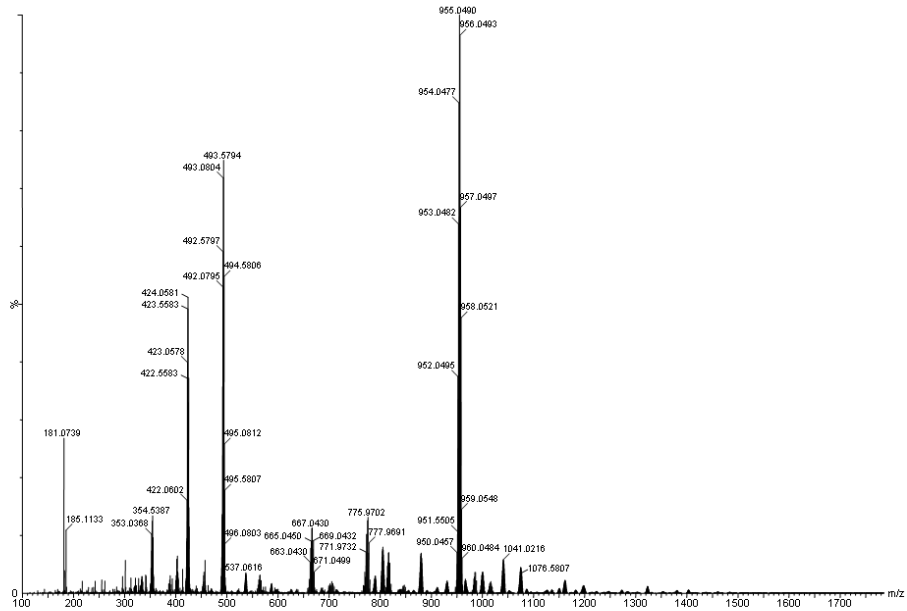
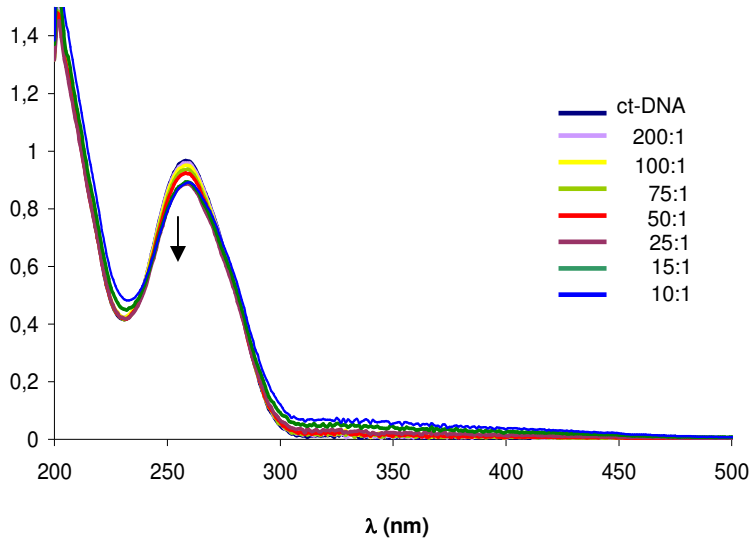


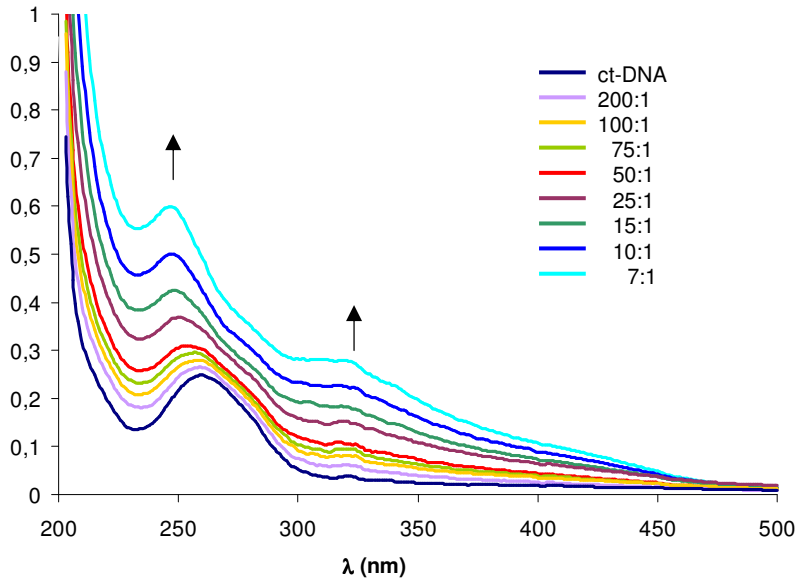
Figure S3. ESI-MS of a) $[(Cymene)_4Ru_4(Hoxonate)_2(4,4'\text{-}bpy)_2](CF_3SO_3)_4$ (2a) and $[(Cymene)_4Ru_4(Hoxonate)_2(4,7\text{-}phen)_2](CF_3SO_3)_4$ (2b).

C) UV/Vis and Fluorescence Spectra of the interaction of DNA with water soluble compounds 1b, 2a and 2b.

a)



b)



c)

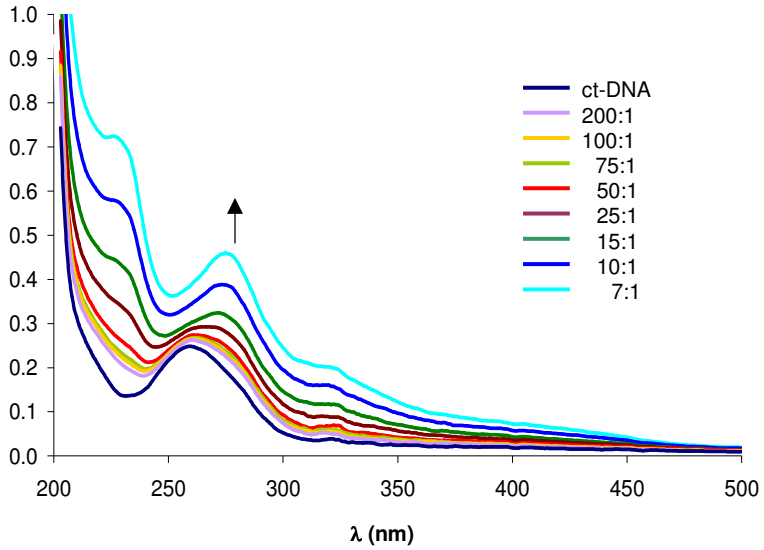


Figure S4. UV-vis spectra of mixtures of a) $[(cymene)_2Ru_2(oxonatoH)(CF_3SO_3)_2]$ (**1b**), b) $[(cymene)_4Ru_4(oxonatoH)_2(4,4'\text{-bpy})_2](CF_3SO_3)_4$ (**2a**) and c) $[(cymene)_4Ru_4(oxonatoH)_2(4,7\text{-phen})_2](CF_3SO_3)_4$ (**2b**) with *CT*-DNA in 1mM sodium cacodylate buffer and 20 mM NaCl.

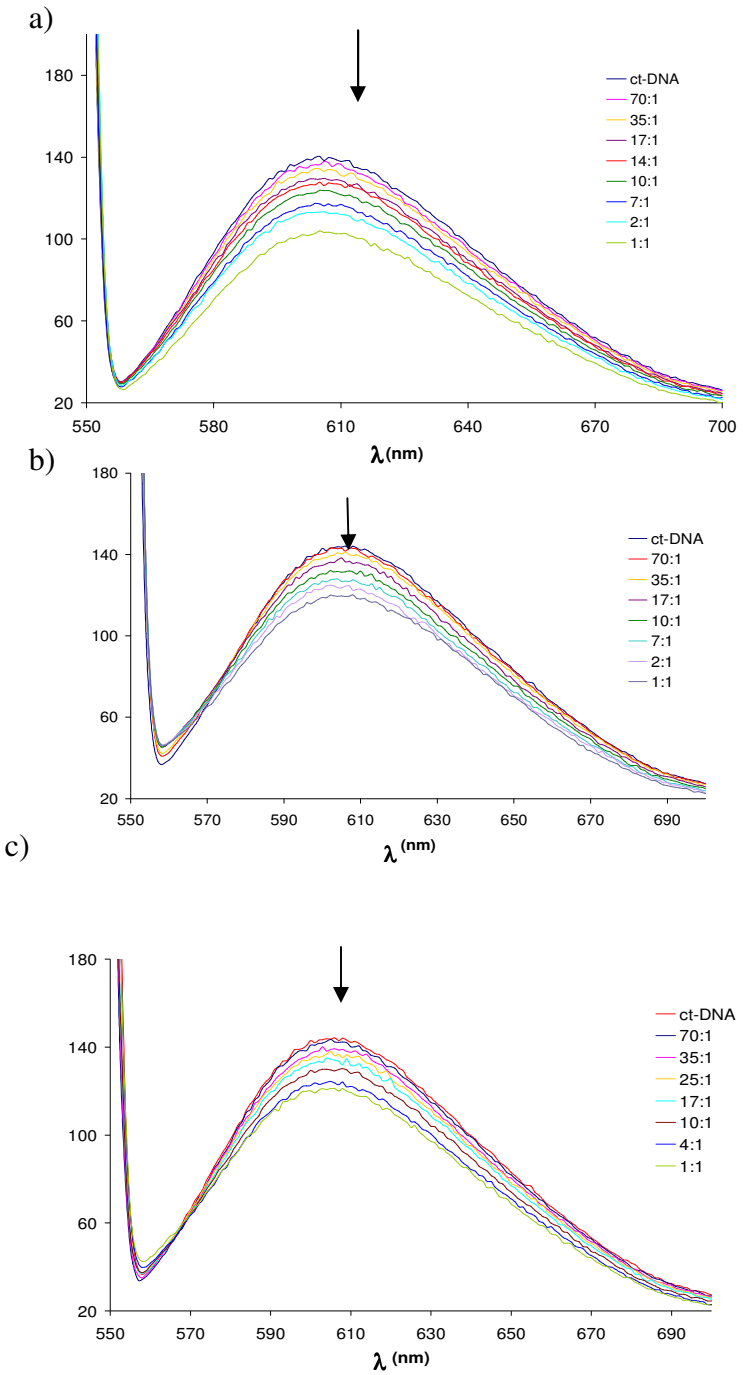


Figure S5. Competitive binding assays: Fluorescence spectra of intercalated ethidium bromide (5 μM) in DNA (4 μM) upon addition of increasing amounts of a) **1b**, b) **2a** and c) **2b** in 1mM sodium cacodylate buffer and 20mM NaCl.

D) Circular Dichroism

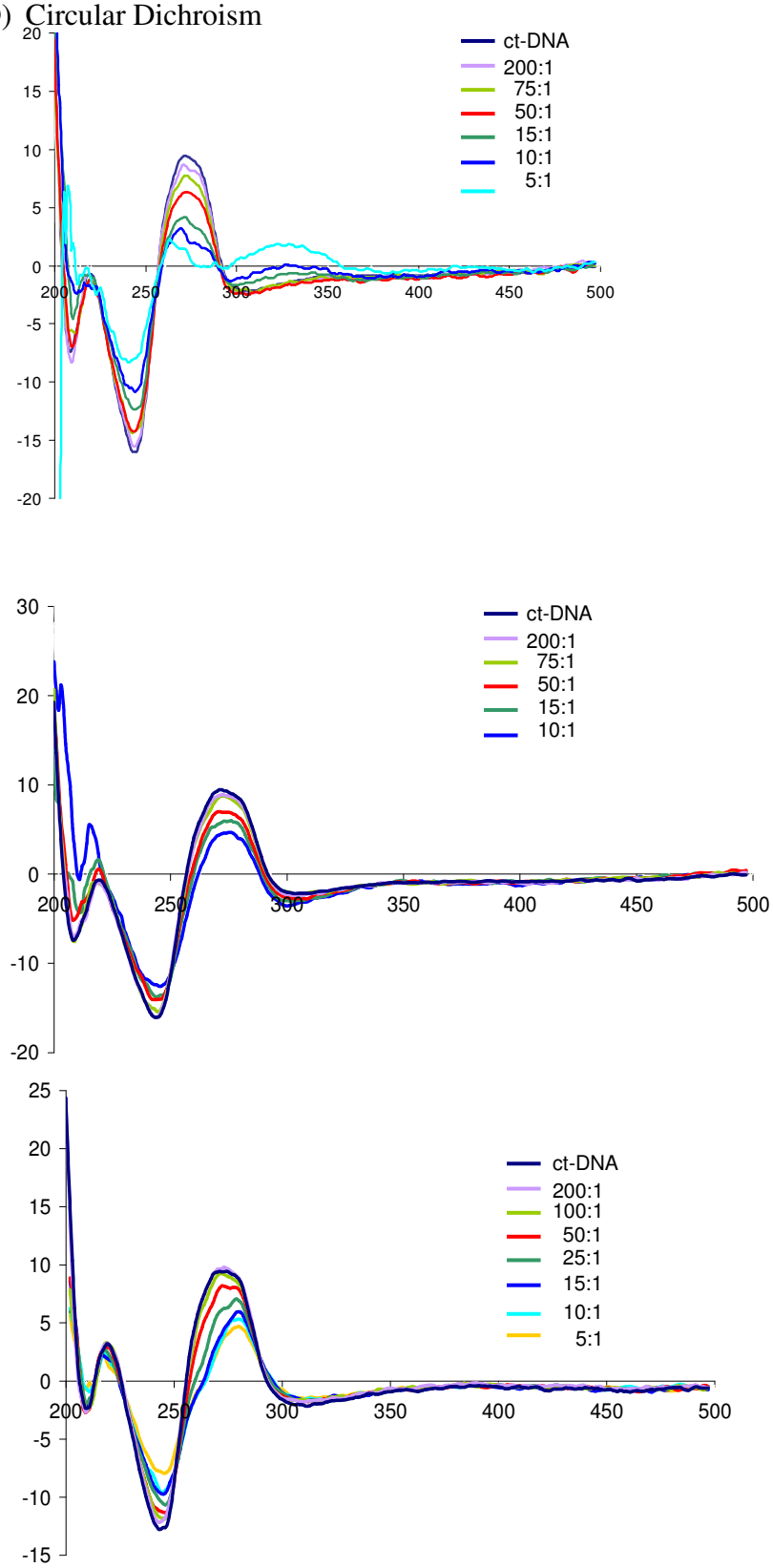


Figure S6. CD spectra of free ct-DNA (300 μM) in the presence of a) **1b**, b) **2a** and c) **2b** with ct-DNA (from r = 200:1 to r = 10:1) in a 1 mM sodium cacodylate buffer and 20 mM NaCl.

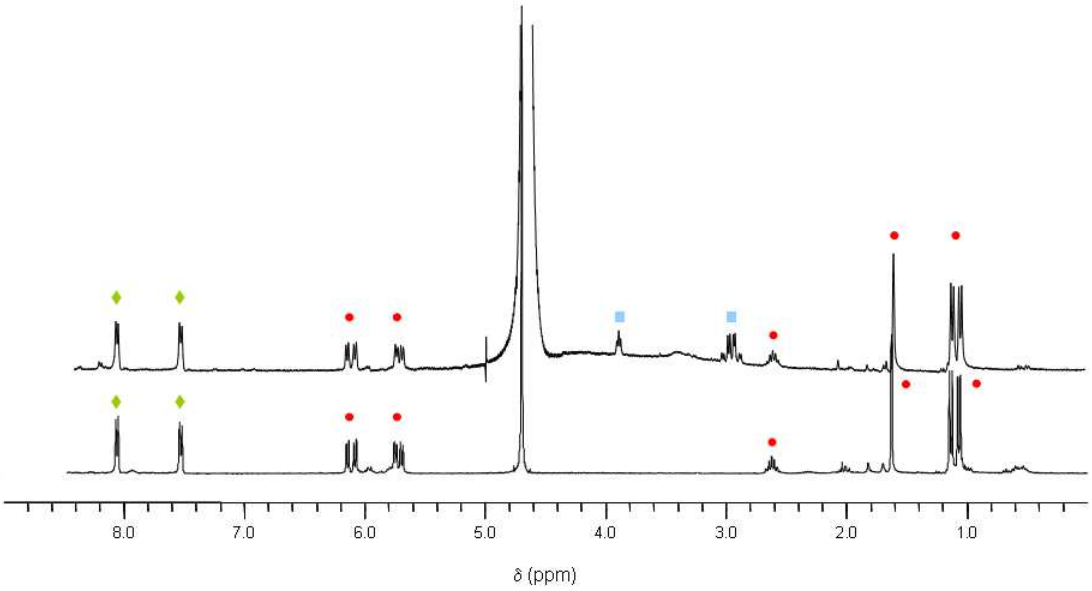


Figure S7. NMR spectra of free $[(cymene)_4Ru_4(oxonatoH)_2(4,4'\text{-}bpy)_2](CF_3SO_3)_4$ (**2a**) (down) and **2a** incubated at 37 ºC (during two hours) with 4 equivalents of cysteine (up). (Relevant signals corresponding to Cymene peaks (●); 4,4-bypirydine group (♦) and cysteine (■) are marked).