Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Sawhorse-type ruthenium complexes with triazolopyrimidine ligands - what do they represent in terms of cytotoxic and CORM compounds?

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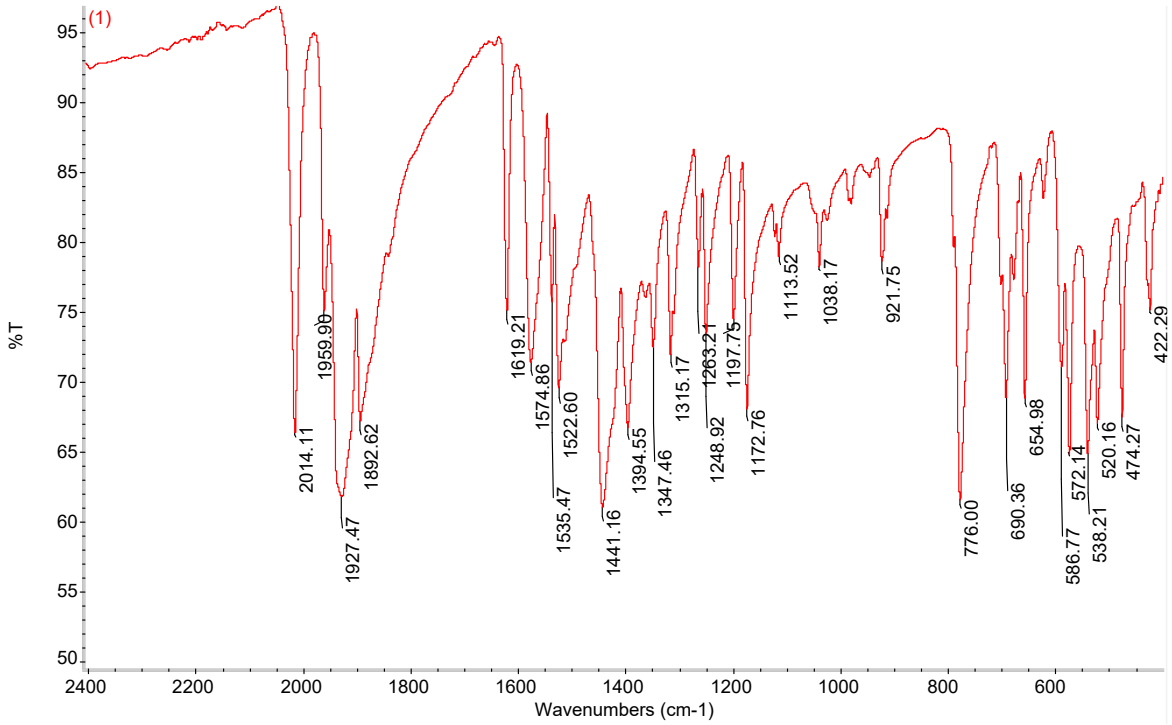

Fig. S1 FT-IR spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(tp)_2]$ (**1**).

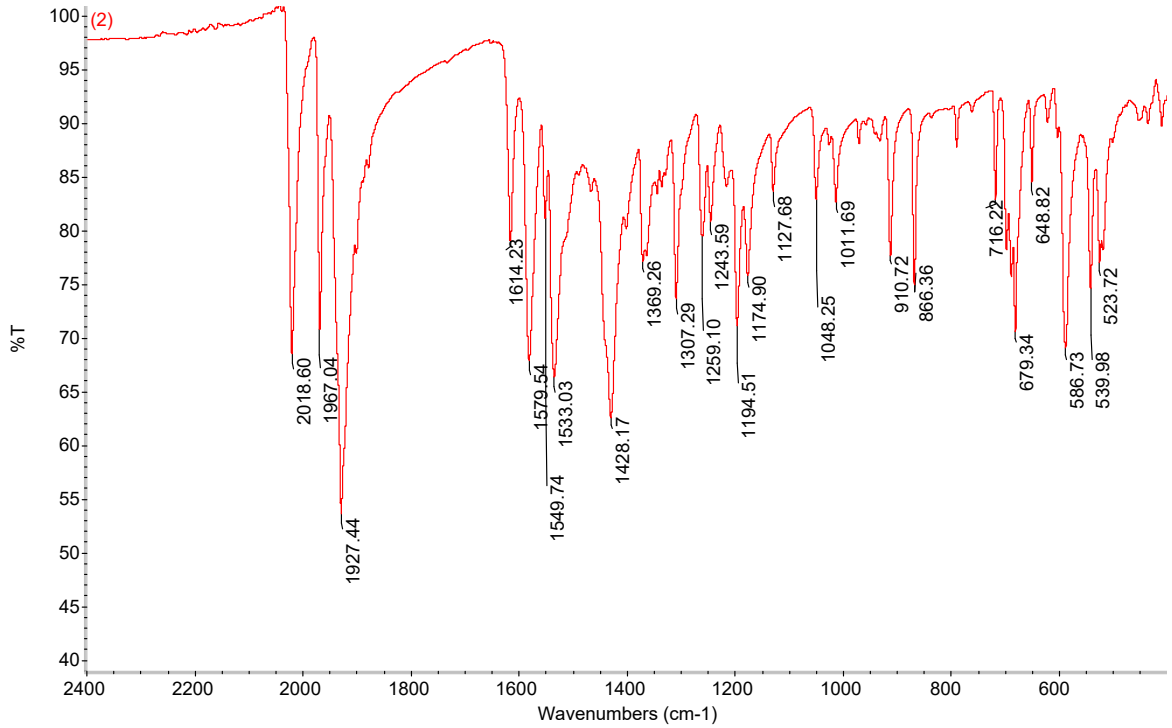

Fig. S2 FT-IR spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**).

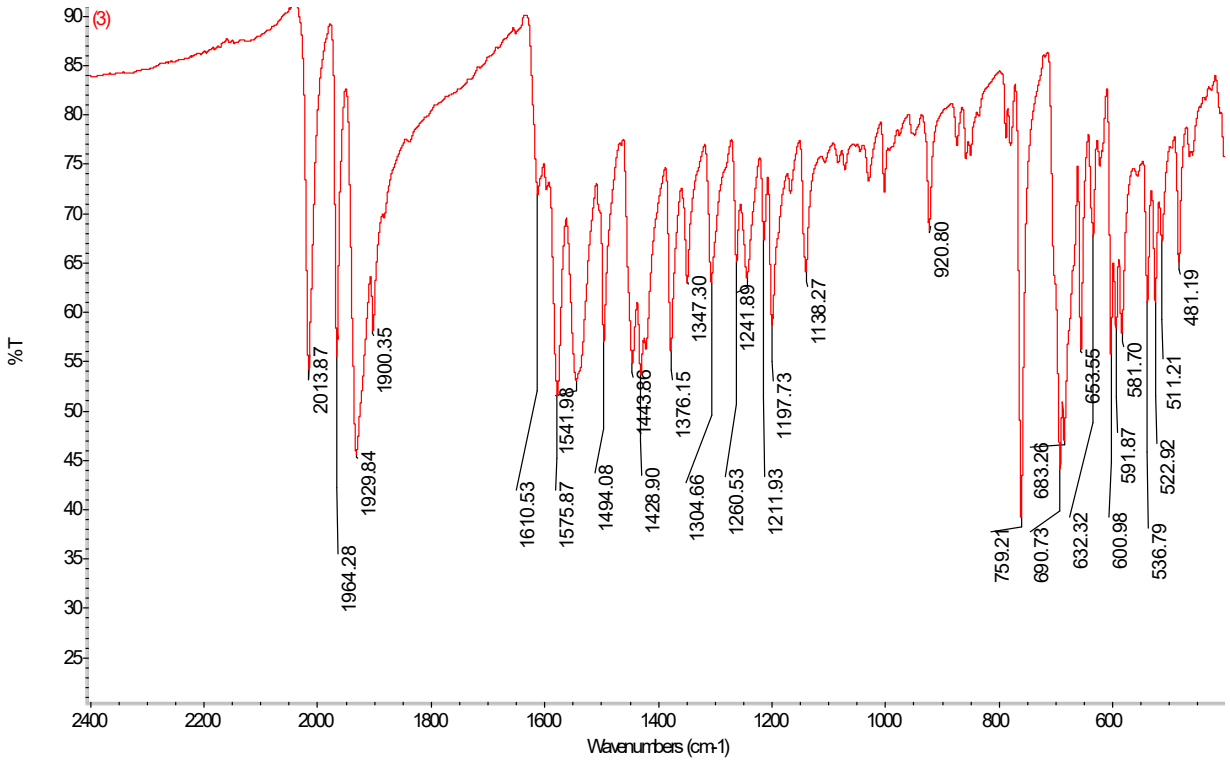

Fig. S3 FT-IR spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dptp)_2]$ (**3**).

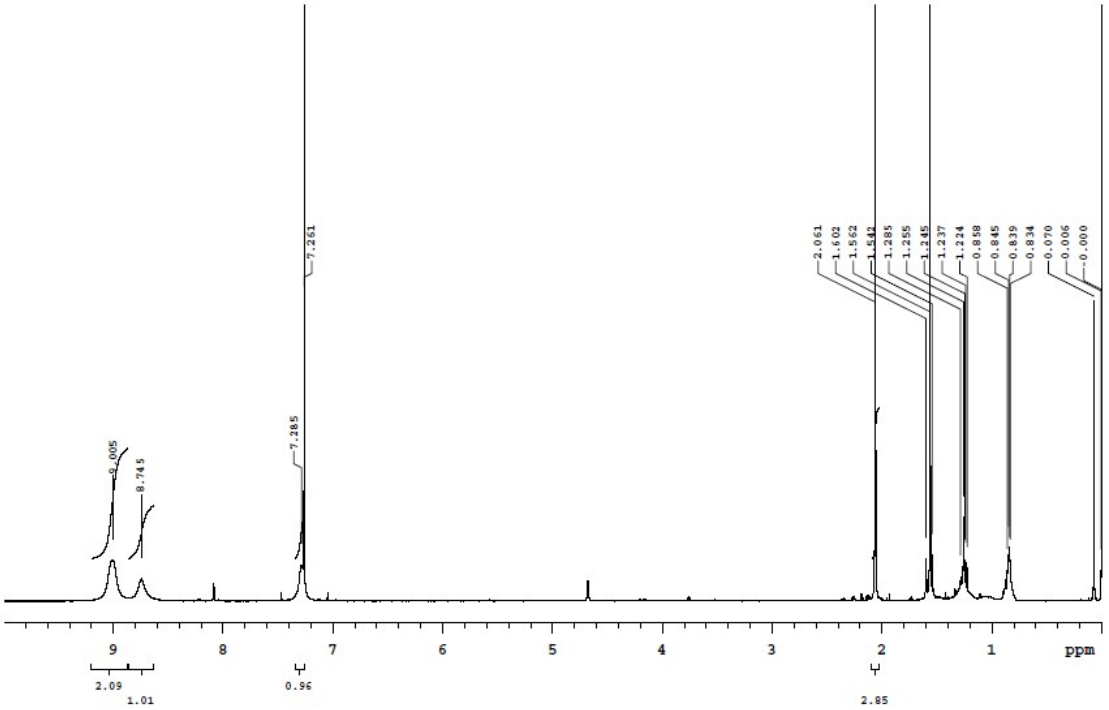

Fig. S4 ^{1}H NMR spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(tp)_2]$ (**1**) in $CDCl_3$.

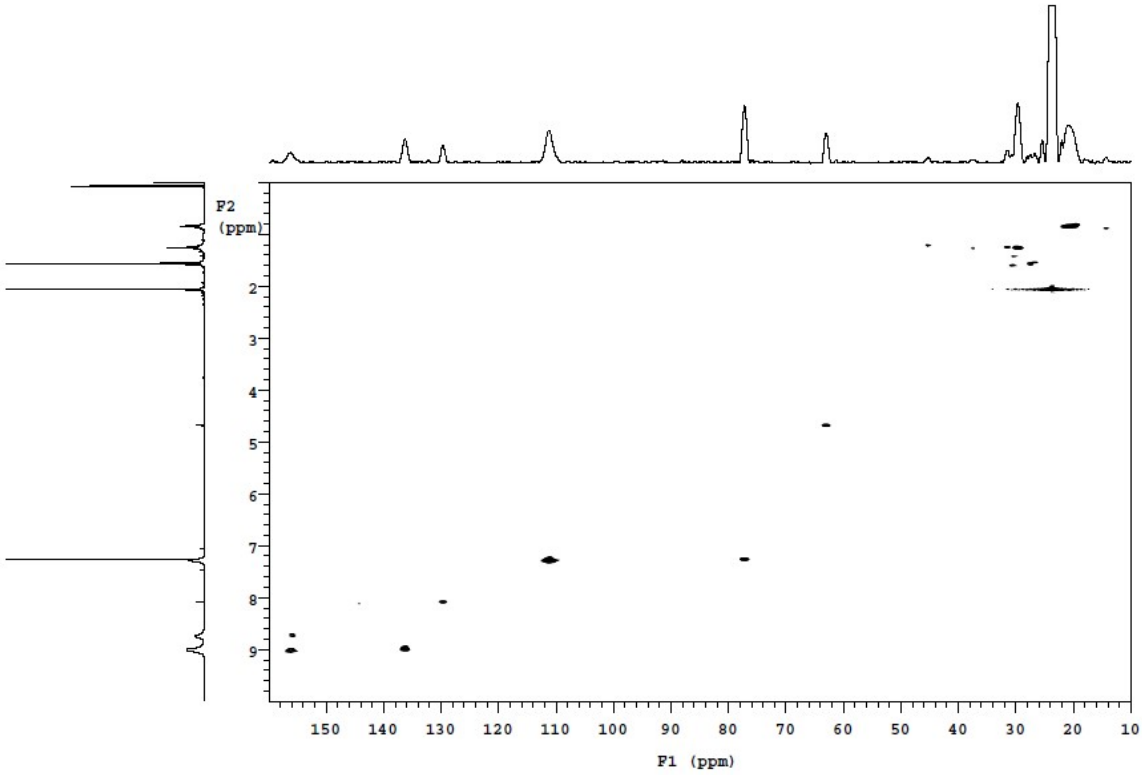

Fig. S5 ^{1}H-^{13}C HMBC spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(tp)_2]$ (**1**) in $CDCl_3$.

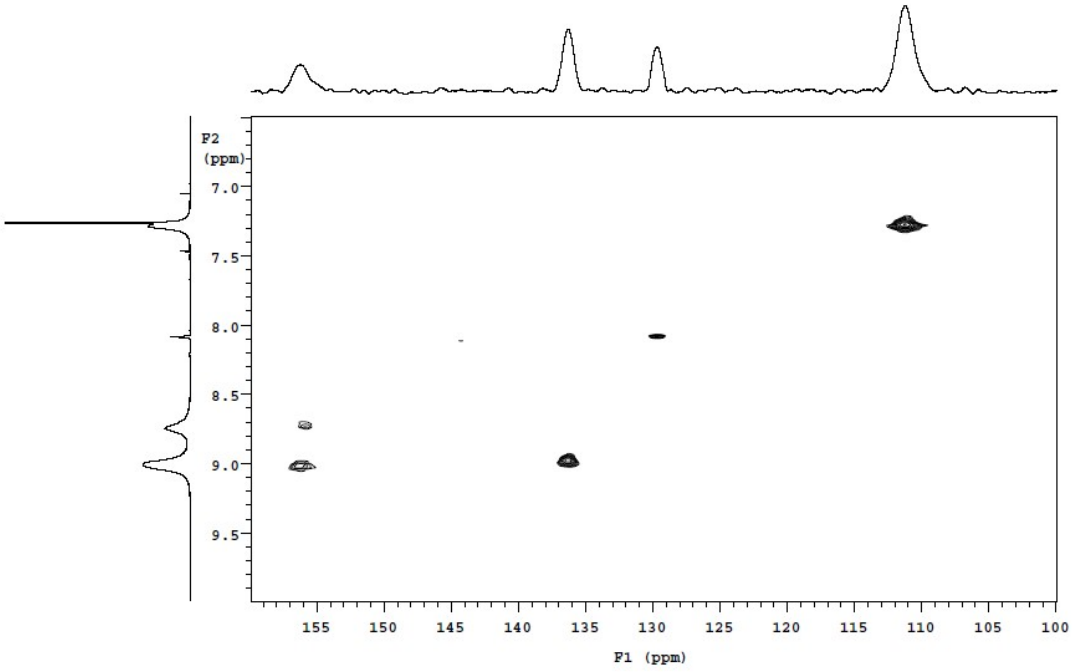

Fig. S6 Selected range of ^{1}H-^{13}C HMBC spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(tp)_2]$ (**1**) in $CDCl_3$.

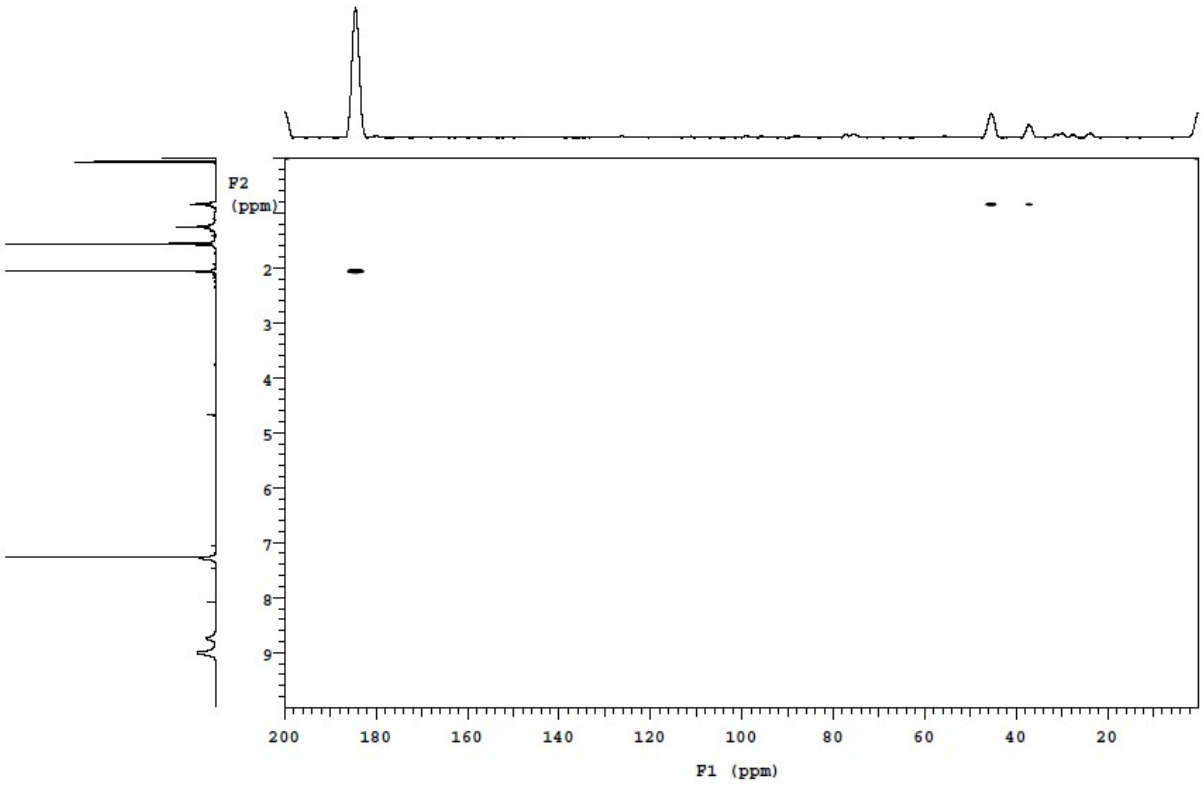

Fig. S7 ^{1}H-^{13}C HMBC spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(tp)_2]$ (**1**) in $CDCl_3$.

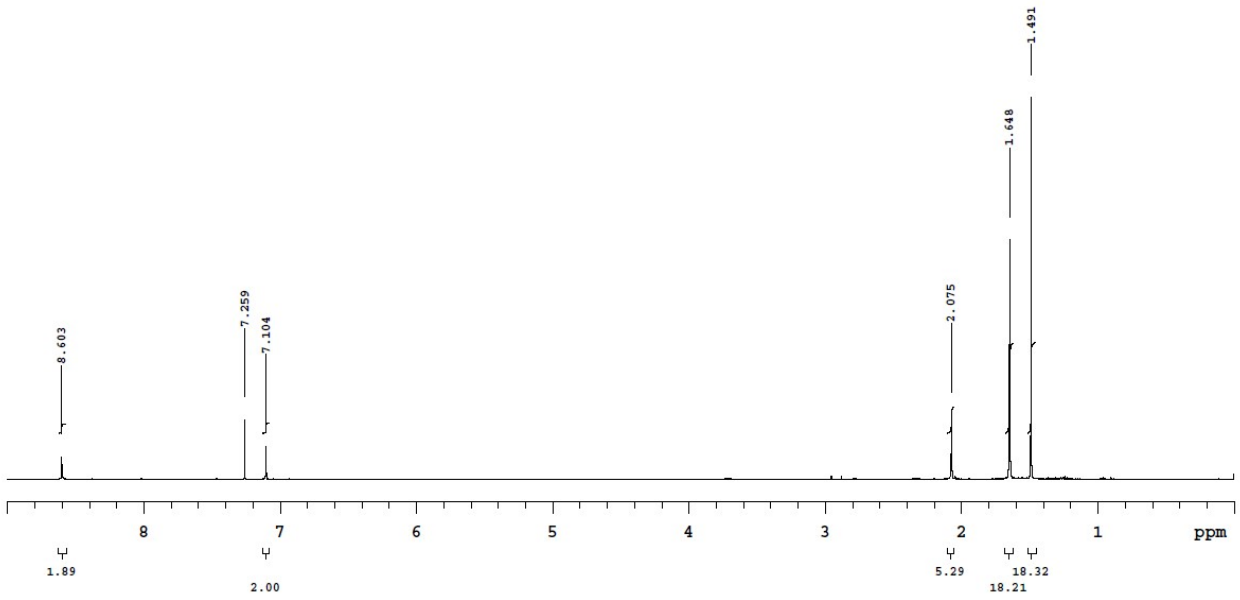

Fig. S8 ^{1}H NMR spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in $CDCl_3$.

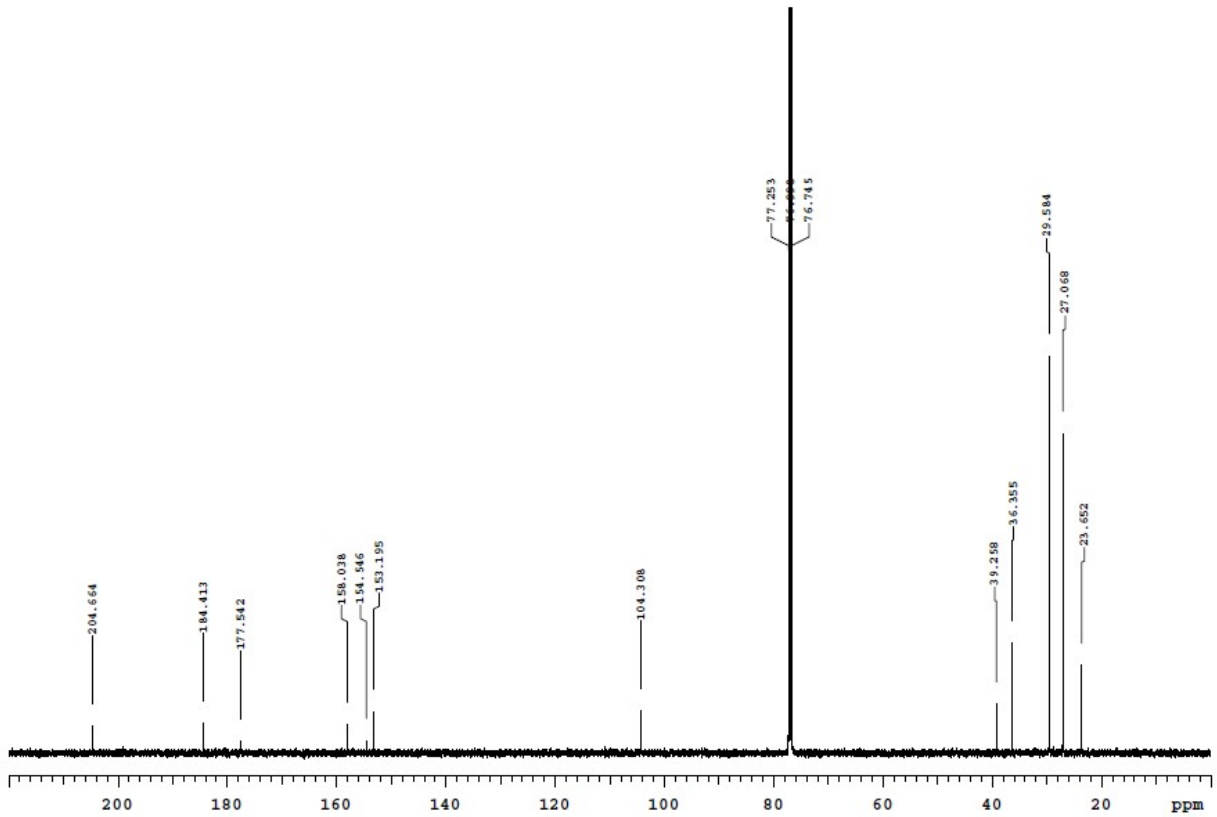

Fig. S9 ^{13}C NMR spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in $CDCl_3$.

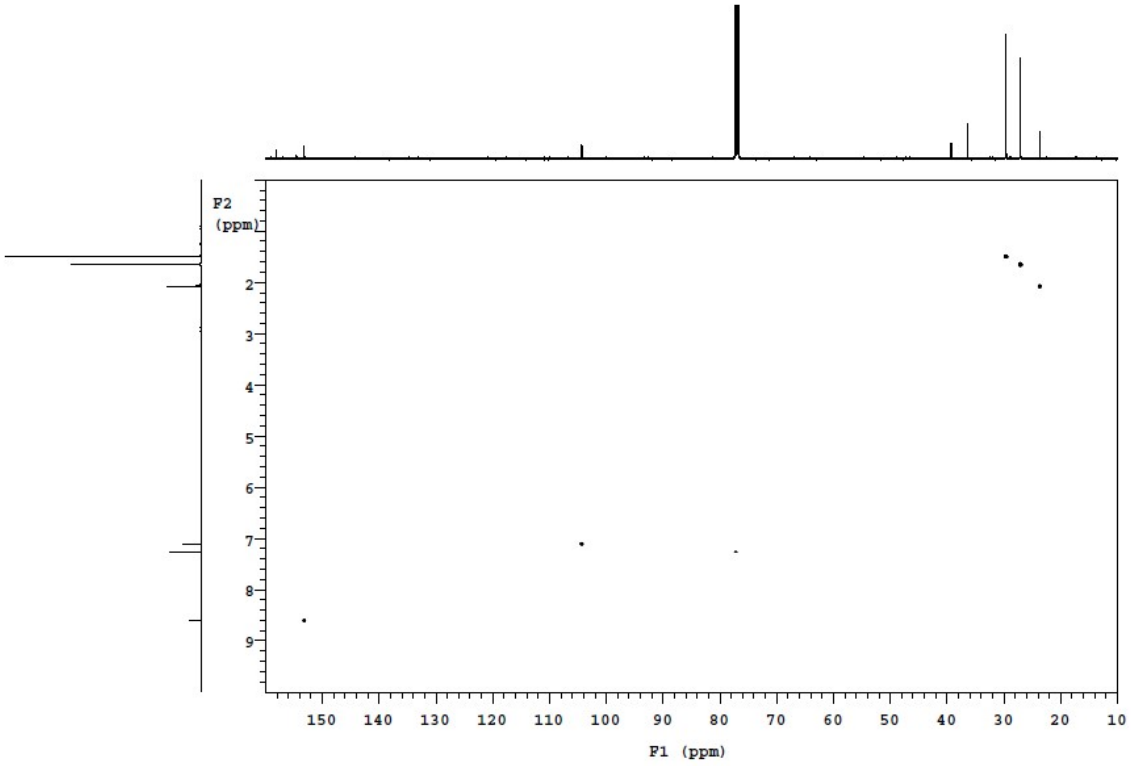

Fig. S10 ^{1}H-^{13}C HSQC spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in $CDCl_3$.

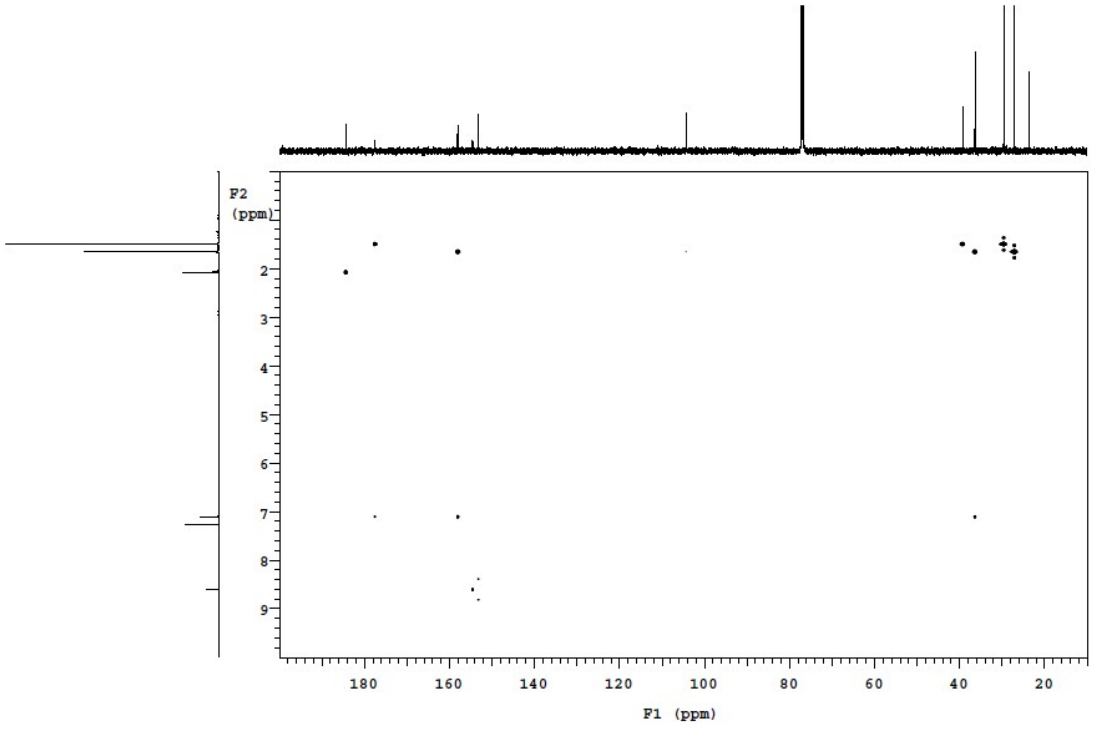

Fig. S11 ^{1}H-^{13}C HMBC spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in $CDCl_3$.

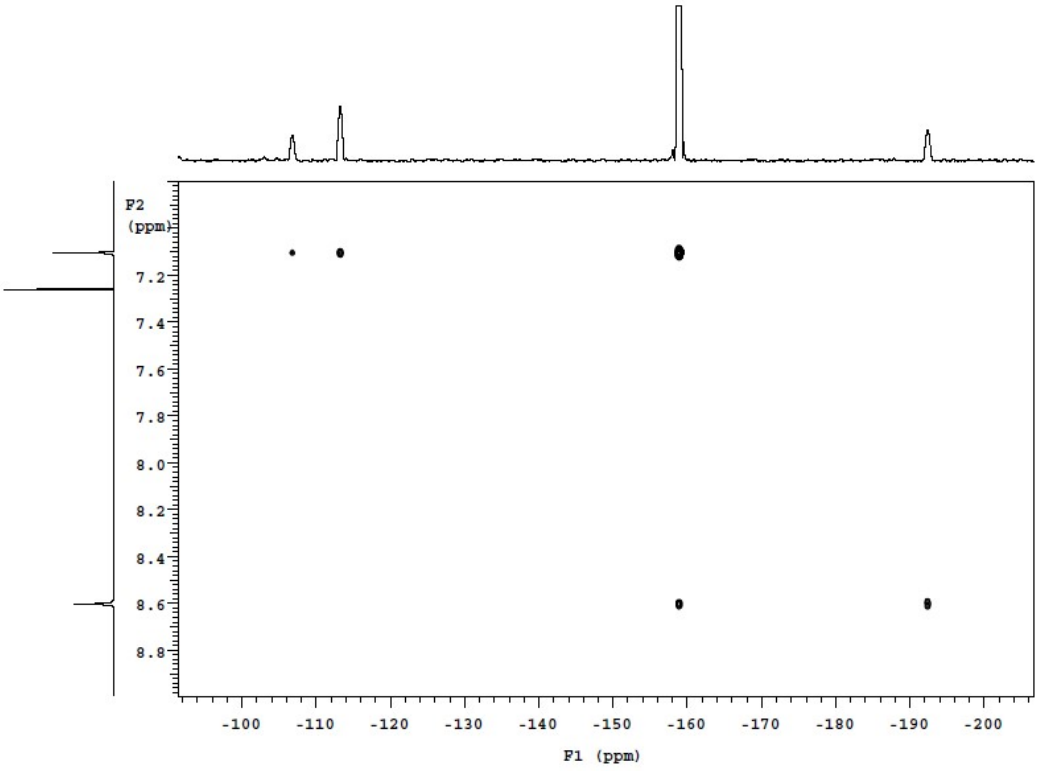

Fig. S12 ^{1}H-^{13}C HMQC spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in $CDCl_3$.

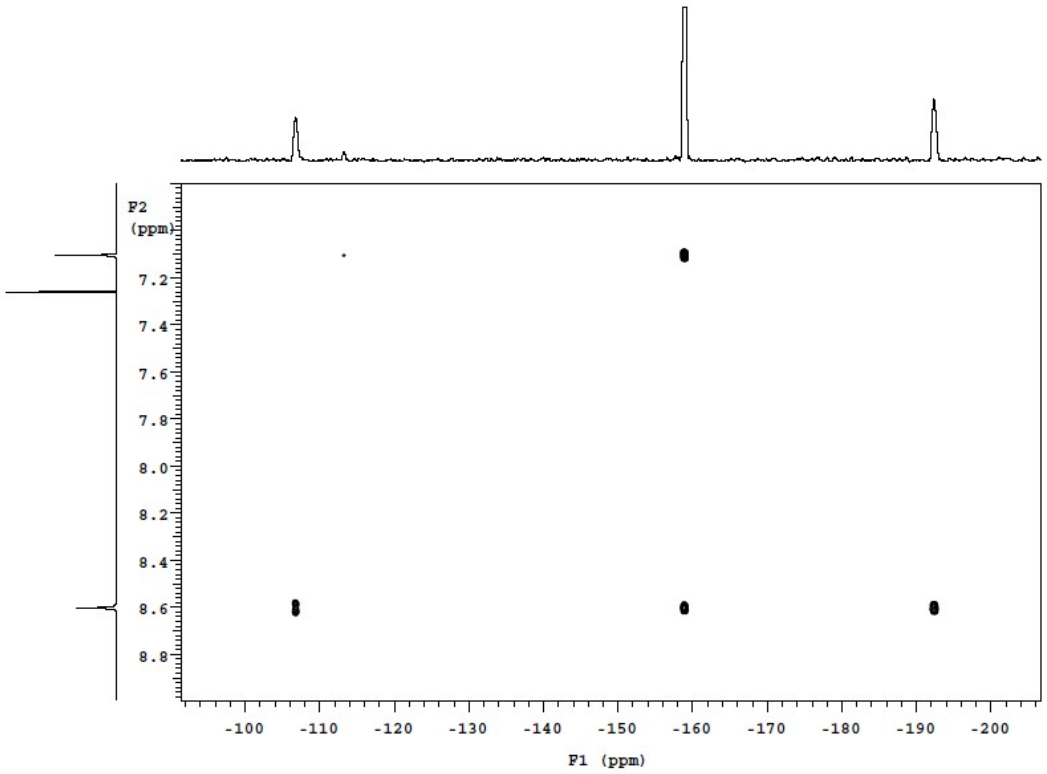

Fig. S13 ^{1}H-^{13}C HMQC spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in $CDCl_3$.

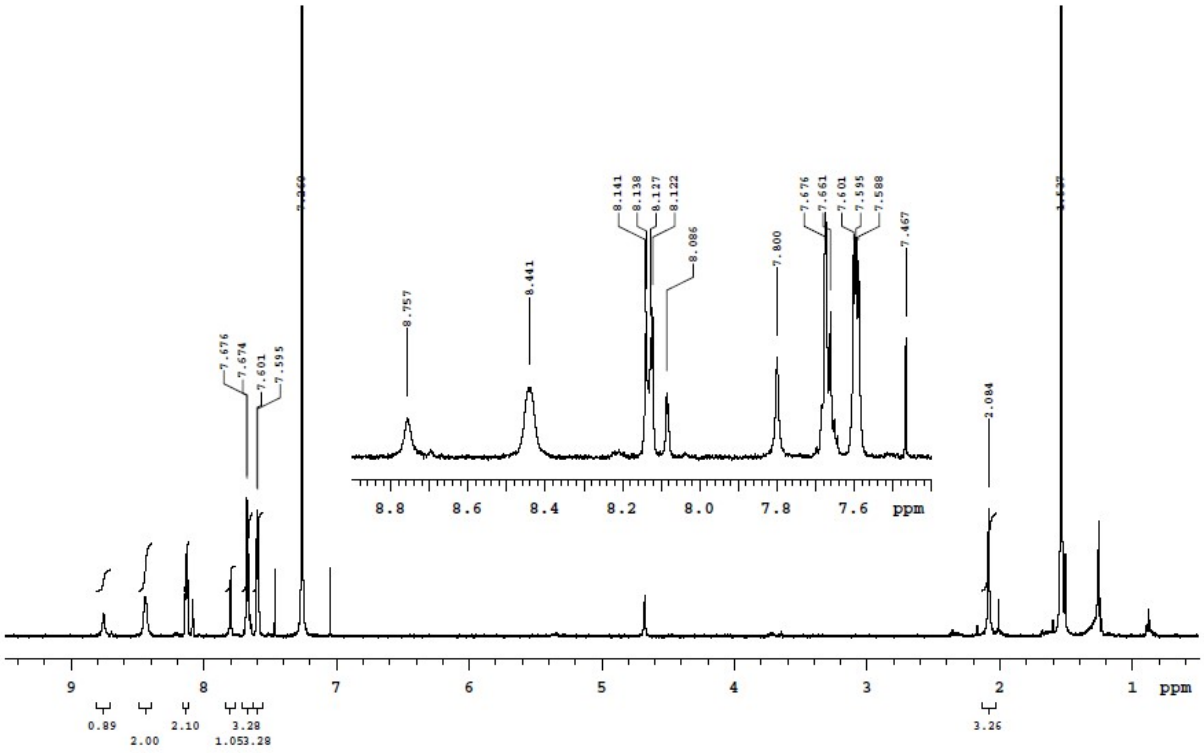

Fig. S14 ^{1}H NMR spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dptp)_2]$ (**3**) in $CDCl_3$.

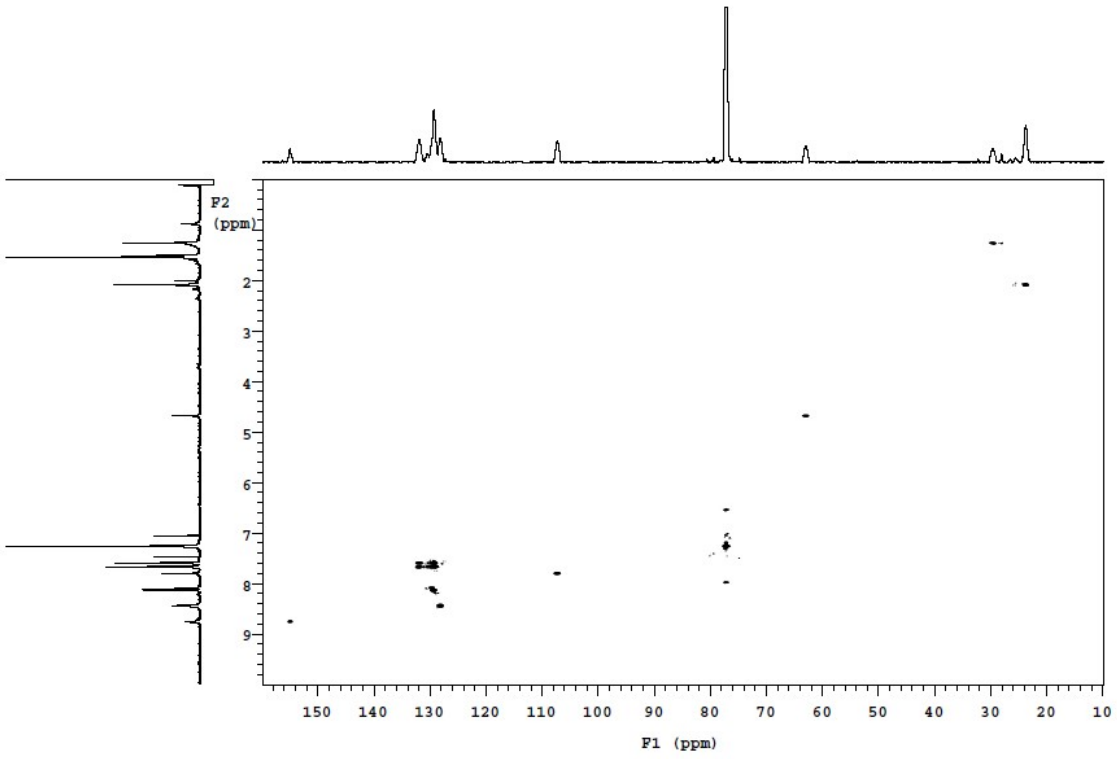

Fig. S15 ^{1}H-^{13}C HSQC spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dptp)_2]$ (**3**) in $CDCl_3$.

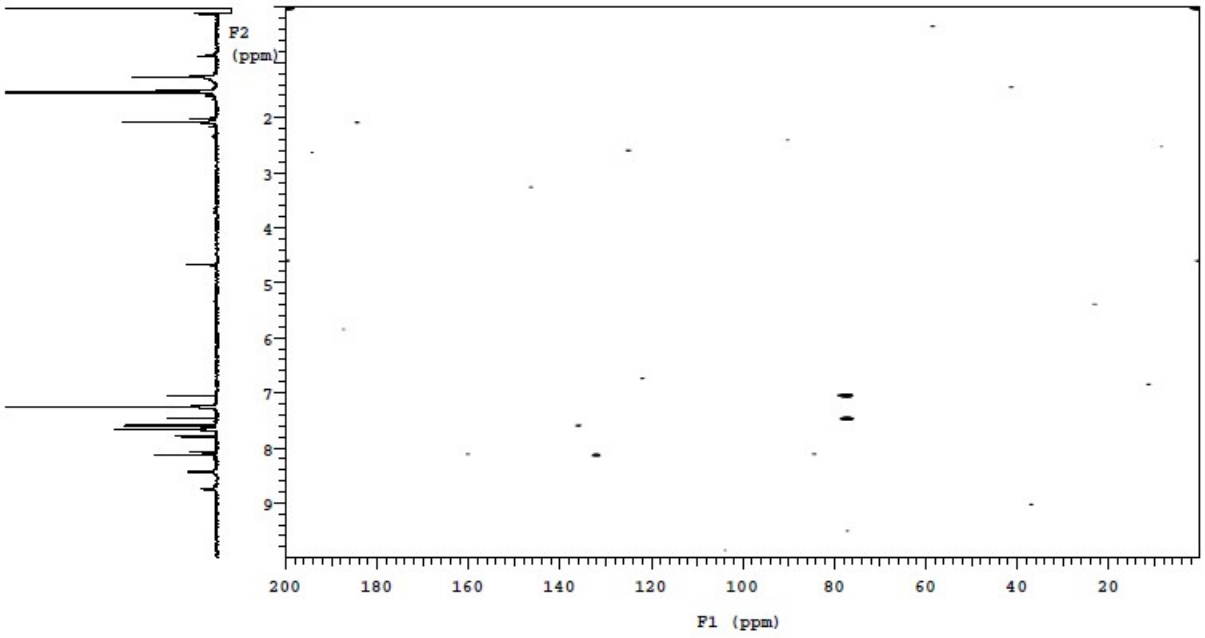

Fig. S16 ^{1}H-^{13}C HMBC spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dptp)_2]$ (**3**) in $CDCl_3$.

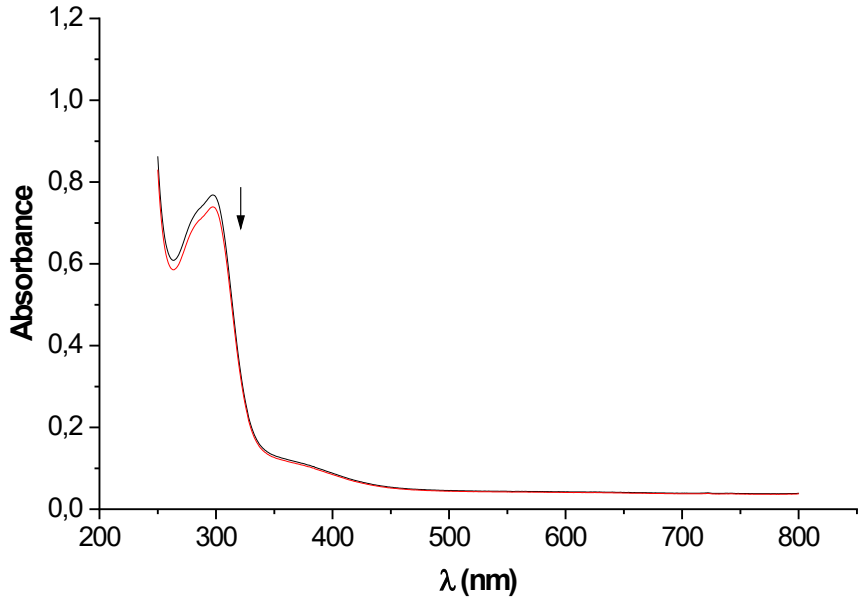

Fig. S17 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(tp)_2]$ (**1**) not irradiated with UV light. Experimental conditions: chloroform, $[Ru^I] = 50$ μmol L^{-1}, t = 0 min and after t = 120 min in dark.

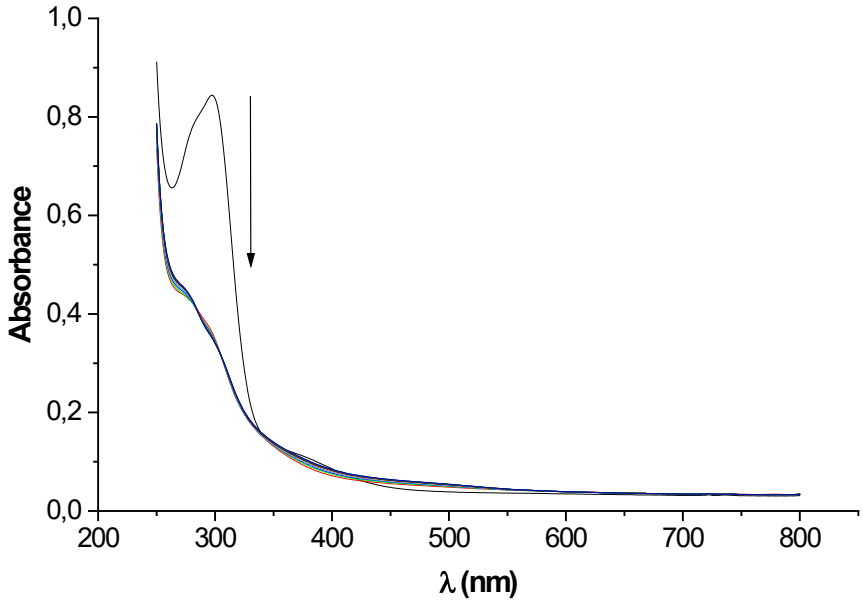

Fig. S18 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(tp)_2]$ (**1**) irradiated with UV light. Experimental conditions: LED lamp, λ_{irr} = 254 nm, chloroform, $[Ru^I] = 50$ μmol L^{-1}, Δt = 5 min, t = 0 – 5 min irradiation, t = 5 – 65 min without irradiation.

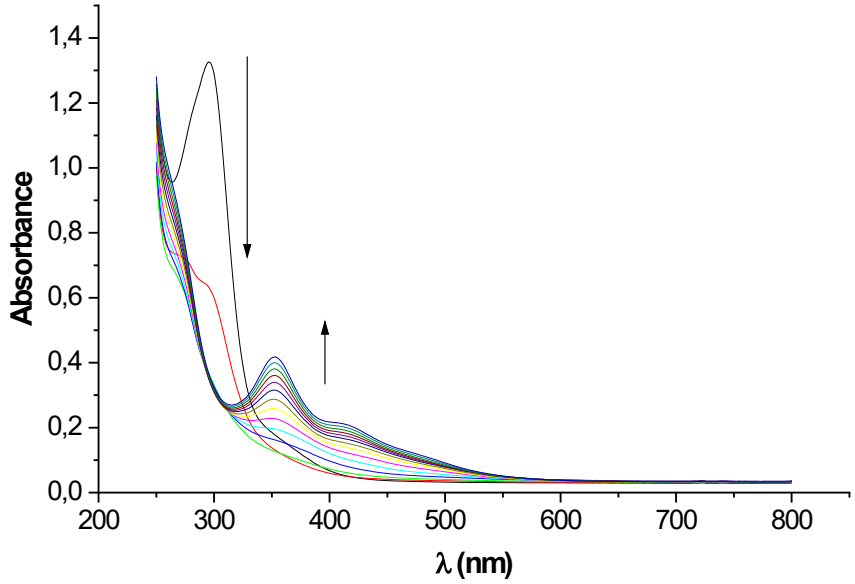

Fig. S19 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) irradiated with UV light. Experimental conditions: LED lamp, λ_{irr} = 254 nm, chloroform, $[Ru^I]$ = 50 μmol L^{-1}, Δt = 5 min, t_{total} = 65 min.

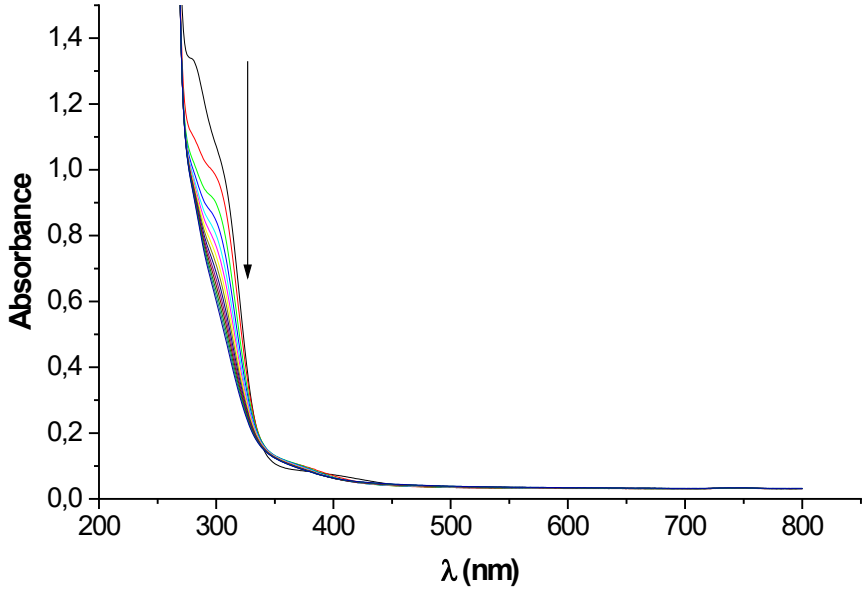

Fig. S20 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) irradiated with UV light. Experimental conditions: LED lamp, λ_{irr} = 254 nm, DMF, $[Ru^I]$ = 50 μmol L^{-1}, Δt = 5 min, t_{total} = 65 min.

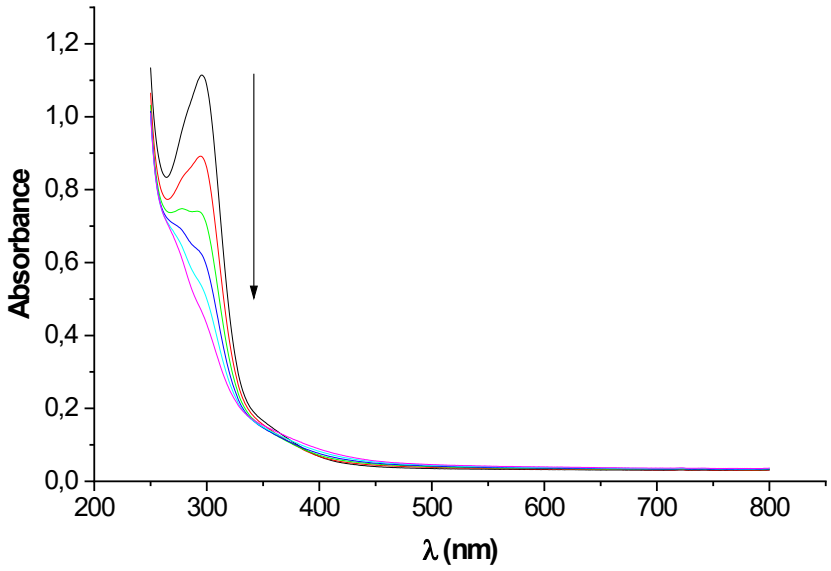

Fig. S21 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) irradiated with near UV light. Experimental conditions: LED lamp, λ_{irr} = 365 nm, chloroform, $[Ru^I]$ = 50 μmol L^{-1}, Δt = 30 min, t_{total} = 150 min.

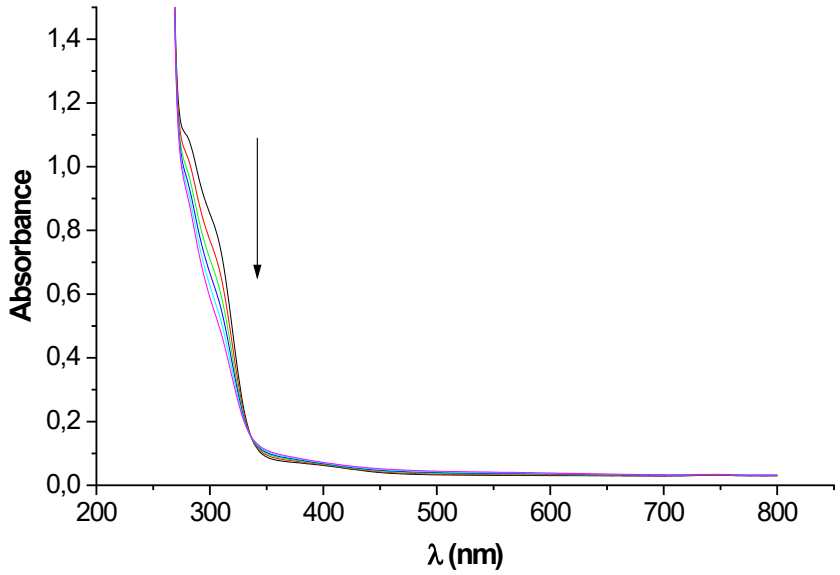

Fig. S22 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) irradiated with near UV light. Experimental conditions: LED lamp, λ_{irr} = 365 nm, DMF, $[Ru^I]$ = 50 μmol L^{-1}, Δt = 30 min, t_{total} = 150 min.

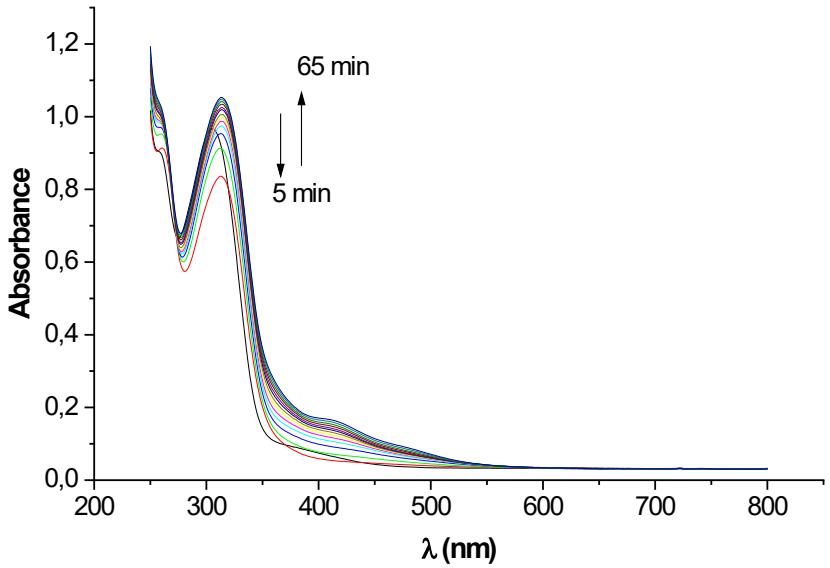

Fig. S23 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dptp)_2]$ (**3**) irradiated with UV light. Experimental conditions: LED lamp, λ_{irr} = 254 nm, chloroform, $[Ru^I]$ = 25 μmol L^{-1}, Δt = 5 min, t_{total} = 65 min.

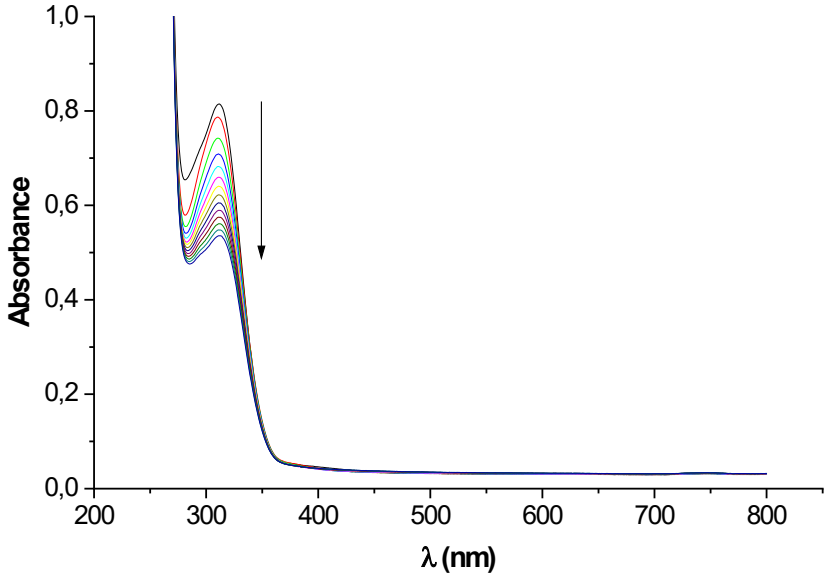

Fig. S24 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dptp)_2]$ (**3**) irradiated with UV light. Experimental conditions: LED lamp, λ_{irr} = 254 nm, DMF, $[Ru^I]$ = 25 μmol L^{-1}, Δt = 5 min, t_{total} = 65 min.

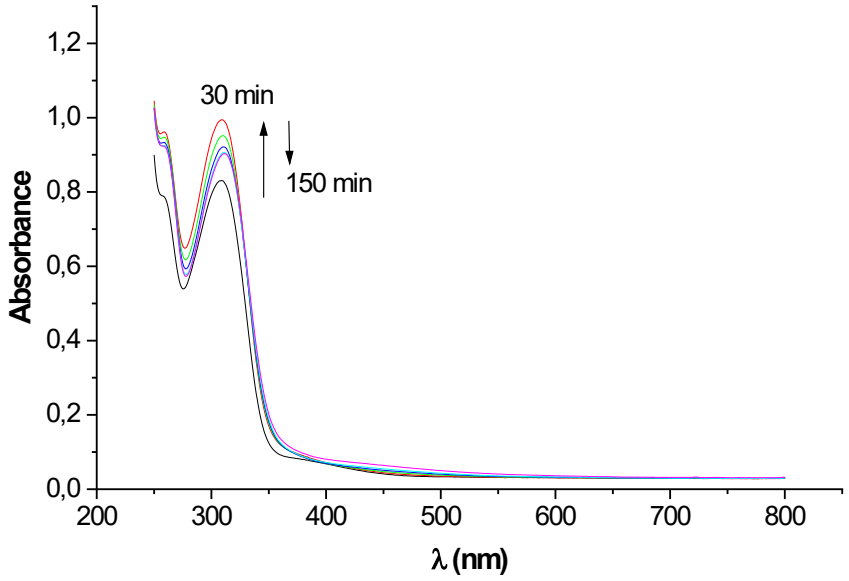

Fig. S25 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dptp)_2]$ (**3**) irradiated with near UV light. Experimental conditions: LED lamp, λ_{irr} = 365 nm, chloroform, $[Ru^I]$ = 25 μmol L^{-1}, Δt = 30 min, t_{total} = 150 min.

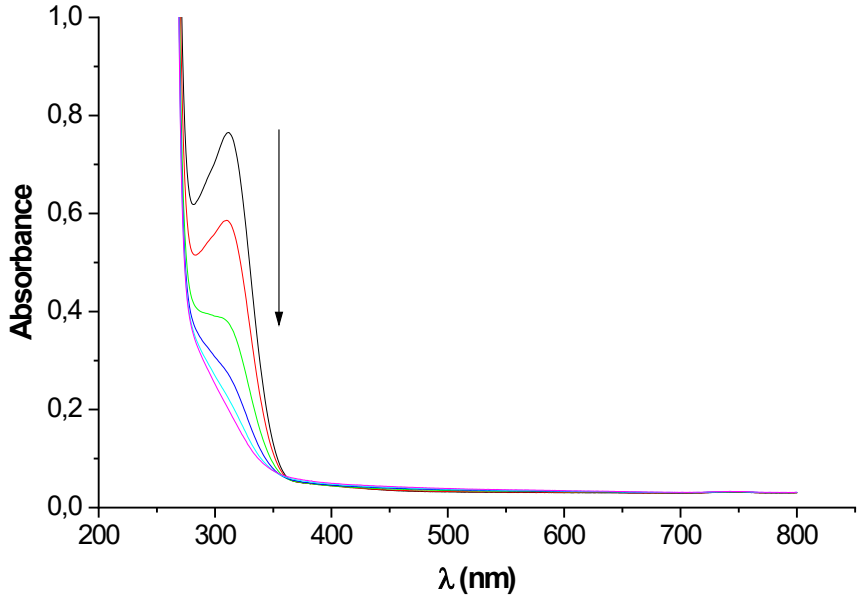

Fig. S26 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dptp)_2]$ (**3**) irradiated with near UV light. Experimental conditions: LED lamp, λ_{irr}= 365 nm, DMF, $[Ru^I]$ = 25 μmol L^{-1}, Δt = 30 min, t_{total} = 150 min.

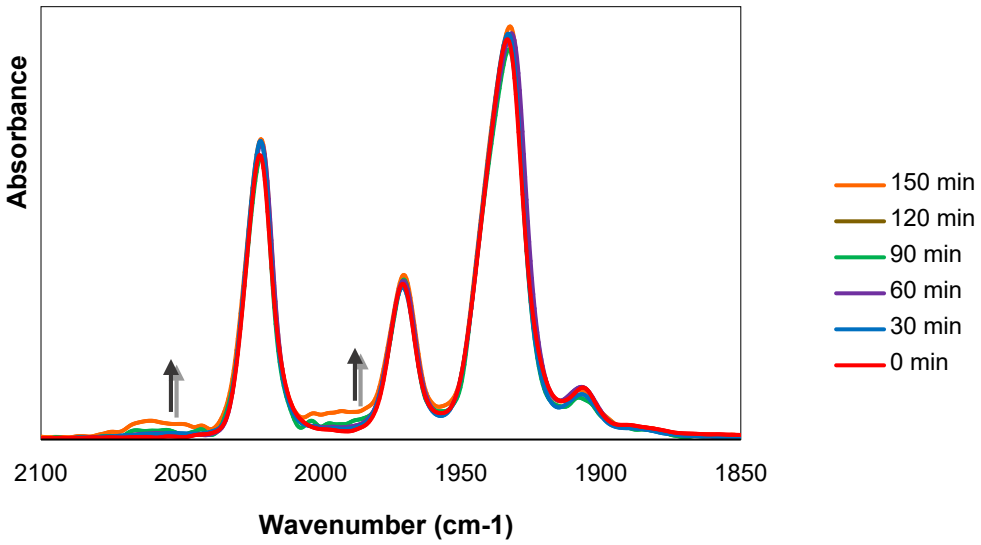

Fig. S27 FT-IR (ν(CO) region) of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in chloroform and the changes that occur during photolysis. Experimental conditions: LED lamp, λ_{irr} = 365 nm, $[Ru^I]$ = 0.038 mol L^{-1}.

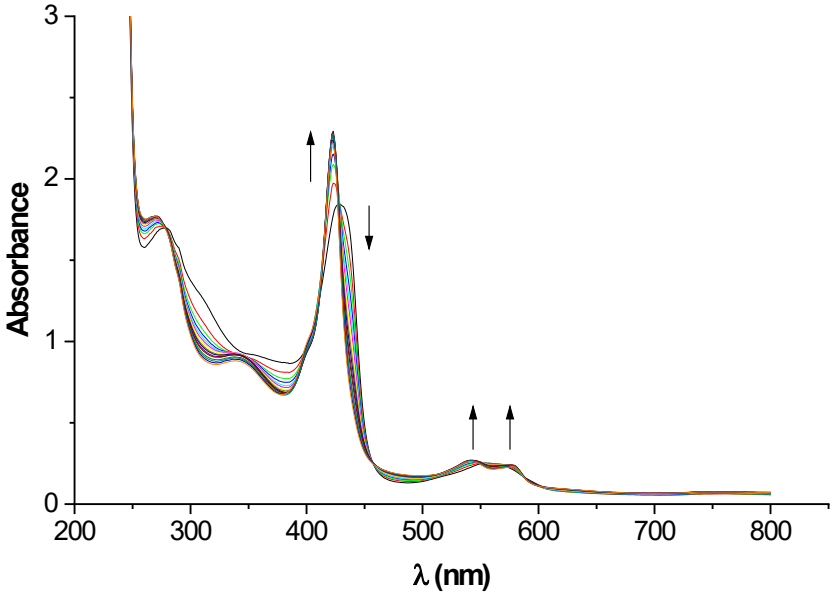

Fig. S28 The UV–Vis spectra of freshly reduced myoglobin in DMF/phosphate buffer solution pH 7.4 (1:9), after adding the $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(tp)_2]$ (**1**) irradiated with UV light. Experimental conditions: LED lamp, λ_{irr} = 365 nm, [Mb] = 20 μmol L^{-1}, $[Ru^I]$ = 50 μmol L^{-1}, Δt = 2.5 min, t_{total} = 30 min.

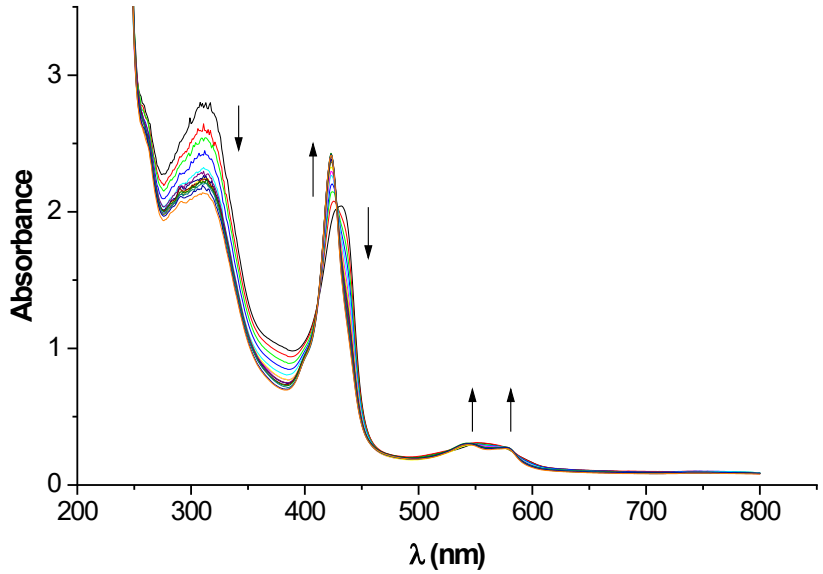

Fig. S29 The UV–Vis spectra of freshly reduced myoglobin in DMF/phosphate buffer solution pH 7.4 (1:9), after adding the $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dptp)_2]$ (**3**) irradiated with UV light. Experimental conditions: LED lamp, λ_{irr} = 365 nm, [Mb] = 20 μmol L^{-1}, [Ru^I] = 50 μmol L^{-1}, Δt = 2.5 min, t_{total} = 30 min.

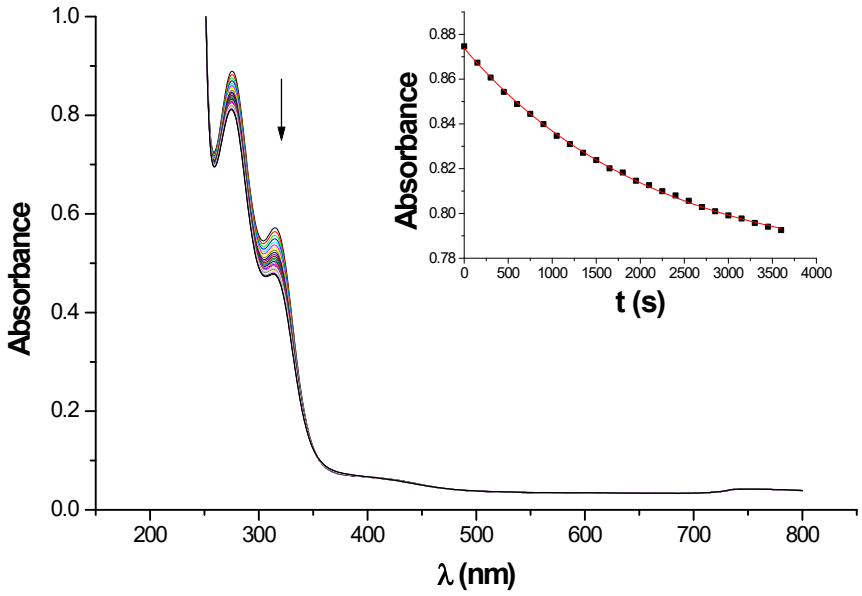

Fig. S30 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(tp)_2]$ (**1**) without UV light irradiation. Experimental conditions: λ_{obs} = 280 nm, DMF : buffer, [Ru^I] = 50 μmol L^{-1}, Δt = 2.5 min, t_{total} = 60 min, 25 cycles. Inset: the kinetic trace at 278 nm.

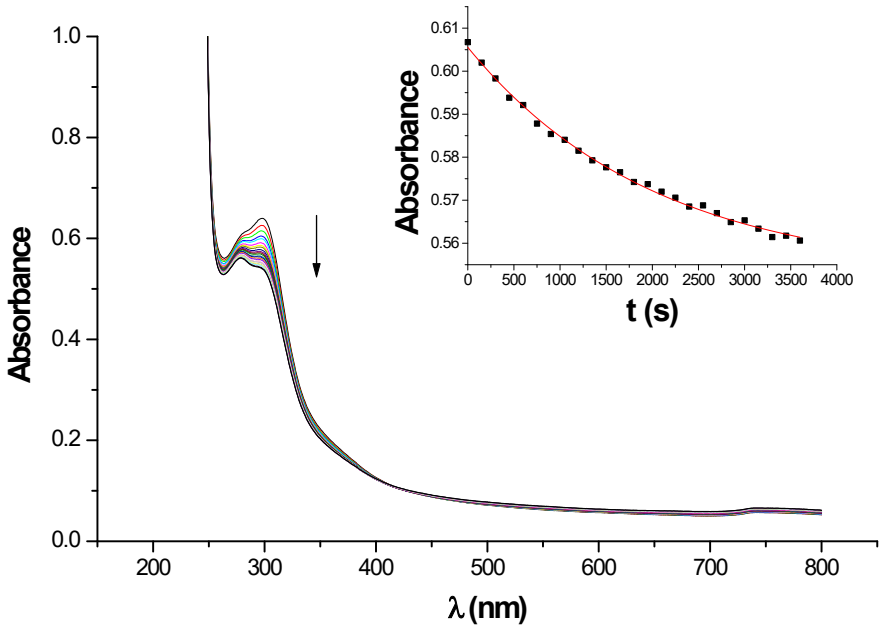

Fig. S31 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) without UV light irradiation. Experimental conditions: λ_{obs} = 298 nm, DMF : buffer, $[Ru^I]$ = 30 μmol L^{-1}, Δt = 2.5 min, t_{total} = 60 min, 25 cycles. Inset: the kinetic trace at 278 nm.

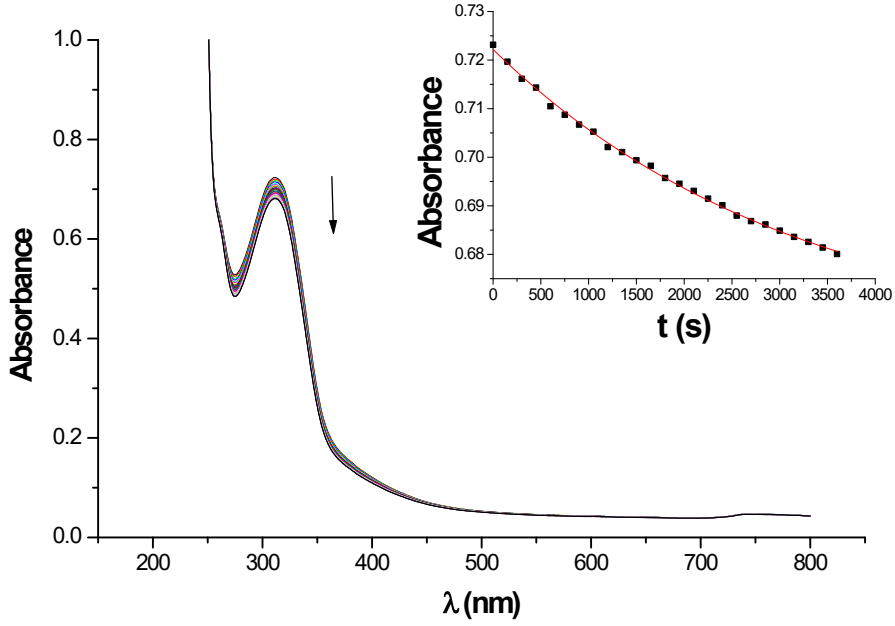

Fig. S32 The UV-Vis spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dptp)_2]$ (**3**) without UV light irradiation. Experimental conditions: λ_{obs} = 320 nm, DMF : buffer, $[Ru^I]$ = 20 μmol L^{-1}, Δt = 2.5 min, t_{total} = 60 min, 25 cycles. Inset: the kinetic trace at 320 nm.

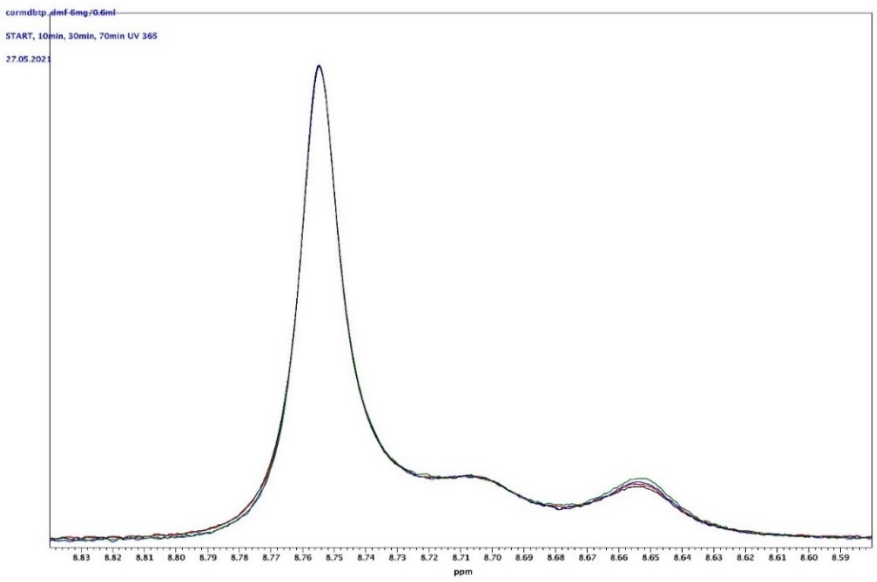

Fig. S33 Selected range of ^{1}H NMR spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in dmf-d_7 before and after 10 min, 30 min, and 70 min UV irradiation at 365 nm.

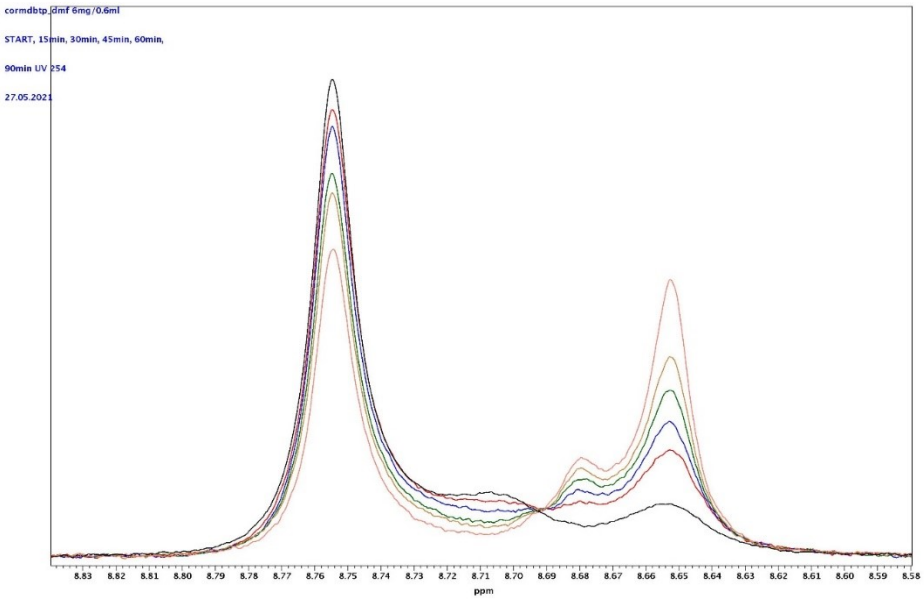

Fig. S34 Selected range of ^{1}H NMR spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in dmf-d_7 before and after 15 min, 30 min, 45 min, 60 min, and 90 min UV irradiation at 254 nm.

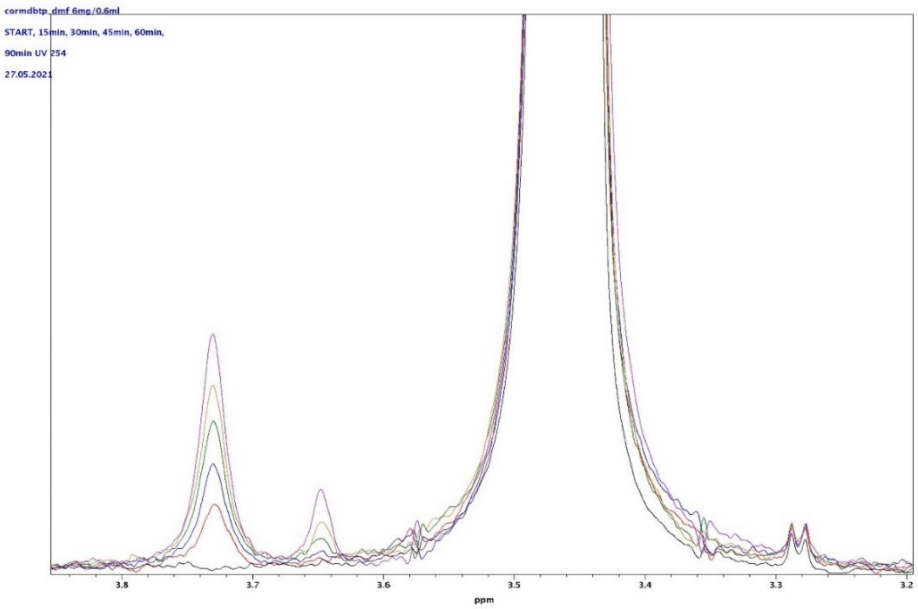

Fig. S35 Selected range of ^{1}H NMR spectra of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in dmf-d_7 before and after 15 min, 30 min, 45 min, 60 min, and 90 min UV irradiation at 254 nm.

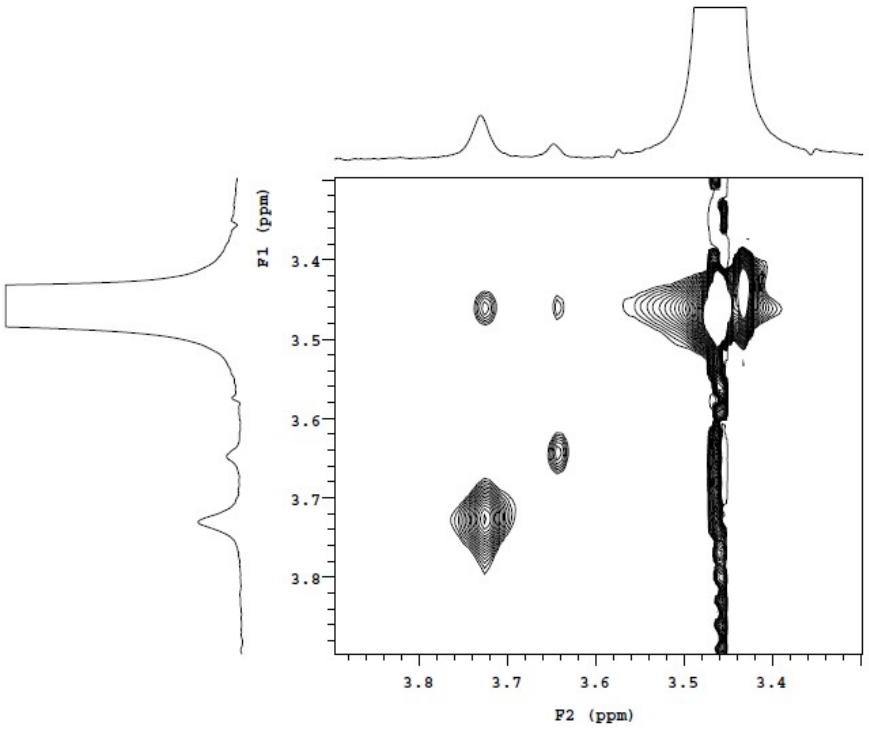

Fig. S36 Part of the NOESY spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in dmf-d_7 after 90 min UV irradiation at 254 nm.

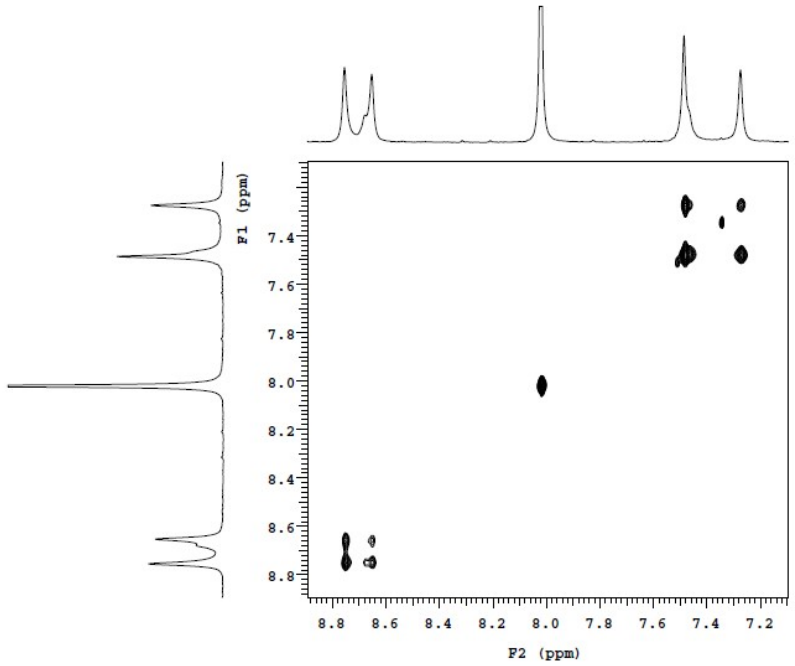

Fig. S37 Part of the NOESY spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in dmf-d_7 after 90 min UV irradiation at 254 nm.

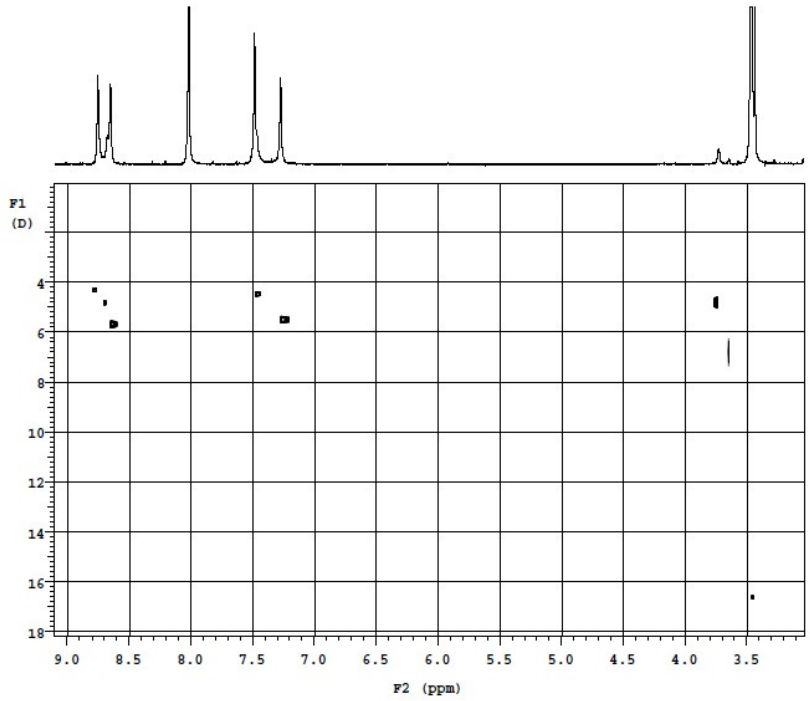

Fig. S38 Part of the DOSY spectrum of $[Ru_2(CO)_4(\mu\text{-}OOCCH_3)_2(dbtp)_2]$ (**2**) in dmf-d_7 after 90 min UV irradiation at 254 nm.