Supplementary information

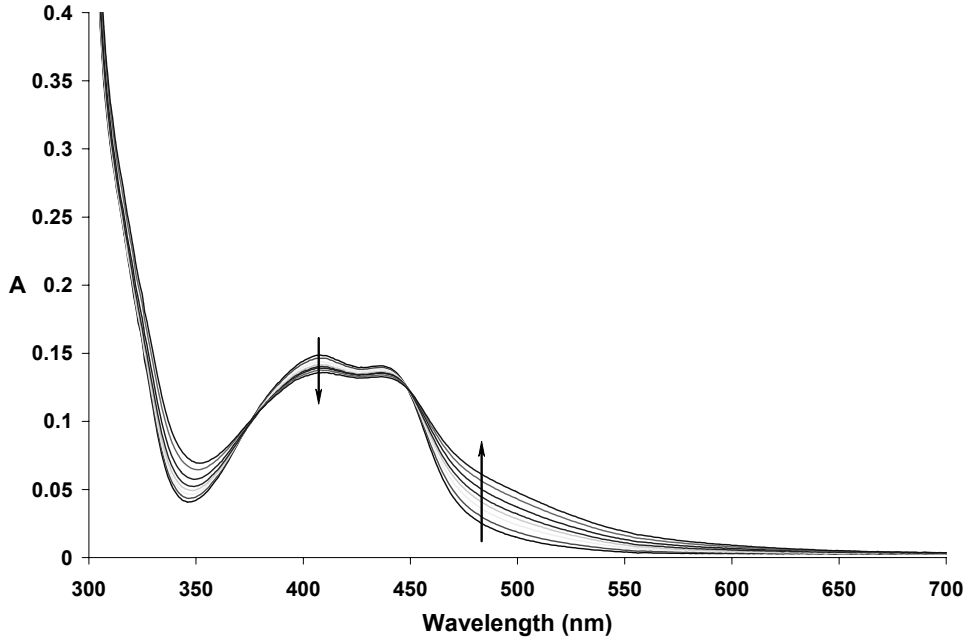
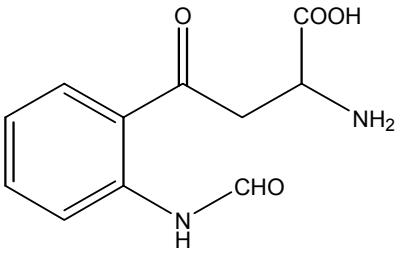
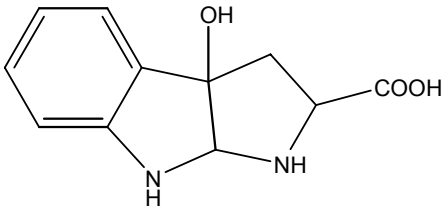


Fig. 1 Variation of the absorption spectra of $Ru(TAP)_3^{2+}$ (10^{-5} M) in presence of Trp (10^{-3} M) in 10 mM TRIS buffer (pH 7) in deaerated solution as a function of the illumination time (0 to 30 min).



N-FK



HPI

Fig. 2 Structure of N-FK and HPI.

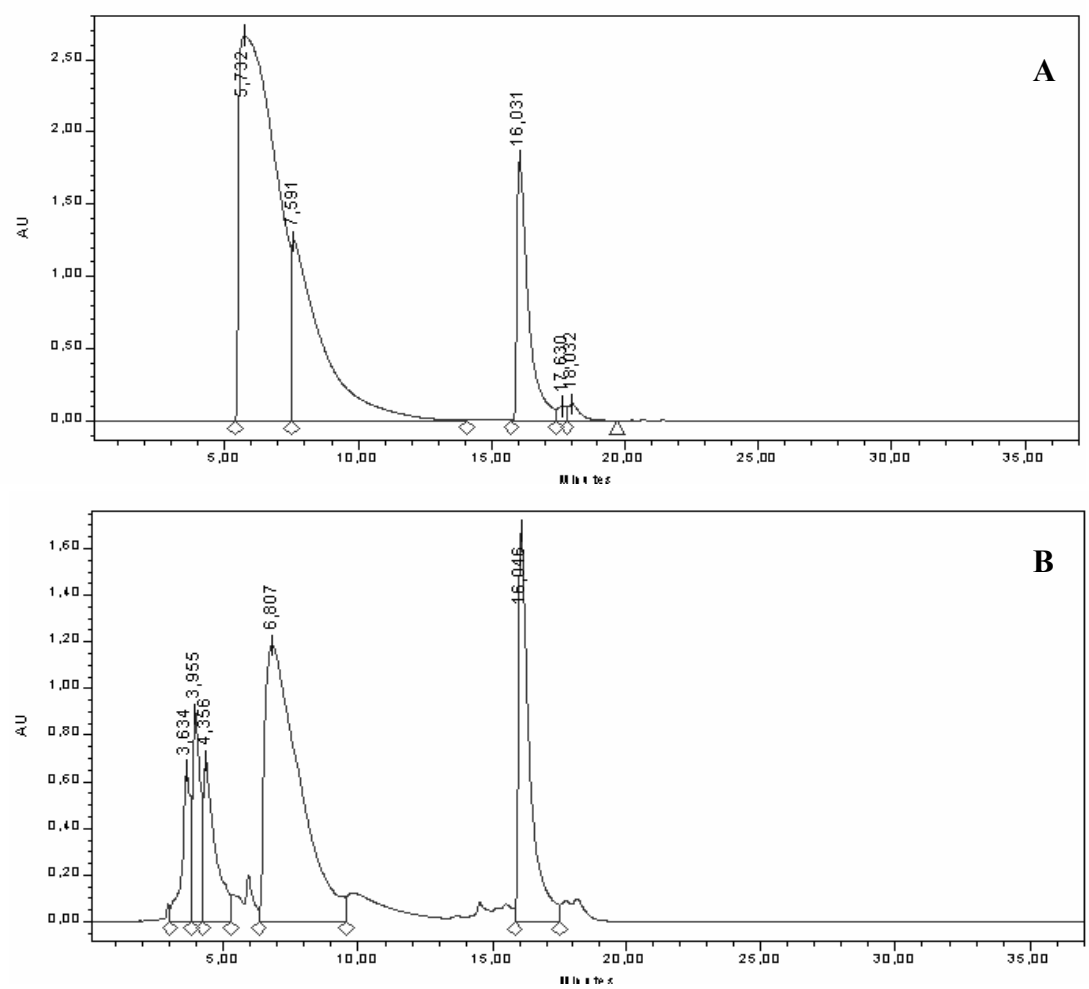


Fig. 3 HPLC chromatograms at 280 nm of A) an aerated solution containing $Ru(bpy)_3^{2+}$ (10^{-5} M) and Trp (10^{-3} M), B) the same solution illuminated 2h. The HPLC gradient is different from the previous one to improve the separation of peaks at low t_R, hence t_R is slightly different for Trp, N-FK and HPI.

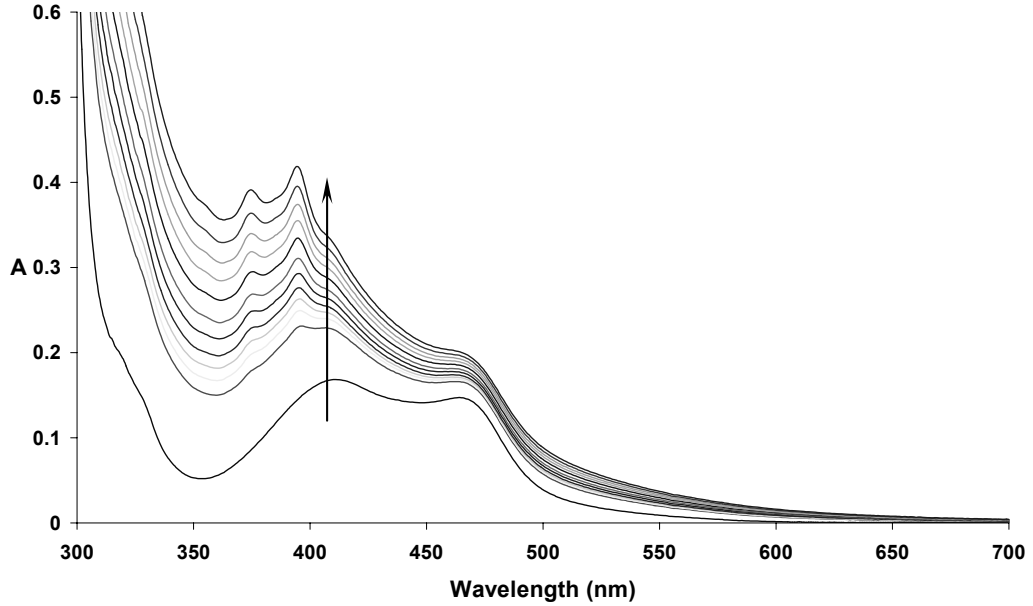


Fig. 4 Variation of the absorption spectra of $Ru(TAP)_2phen^{2+}$ (10^{-5} M) in presence of Trp (10^{-3} M) in 10 mM TRIS buffer (pH 7) in presence of O_2 as a function of the illumination time (0 to 30 min).

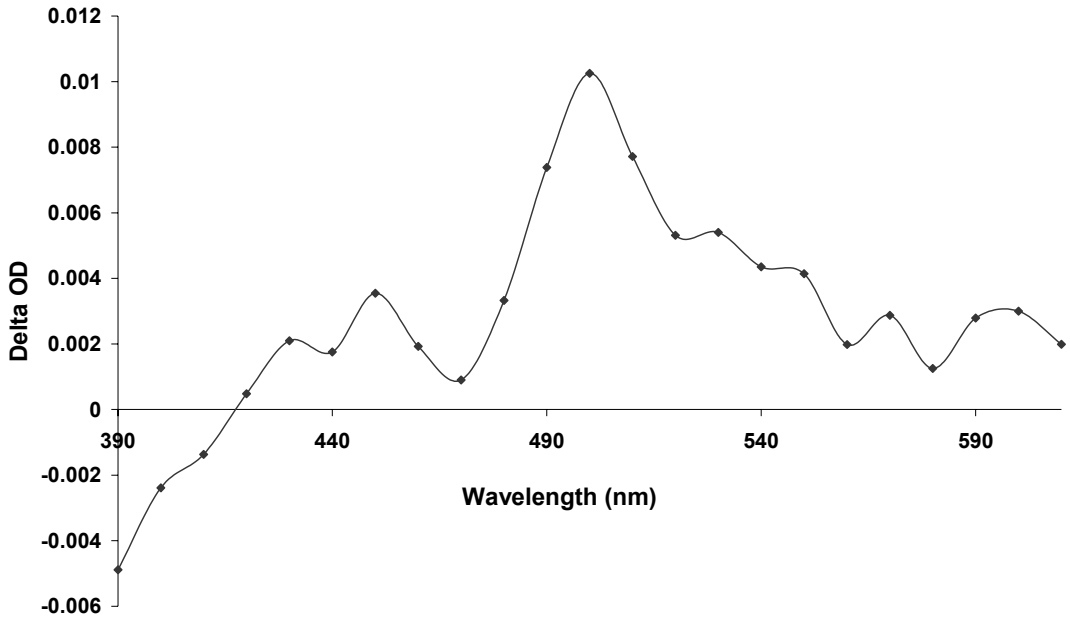


Fig. 5 Transient differential absorption spectrum of a solution containing $Ru(TAP)_2phen^{2+}$ (10^{-4} M) and Trp (10^{-2} M) illuminated with a laser pulse and measured 10 μs after the pulse.

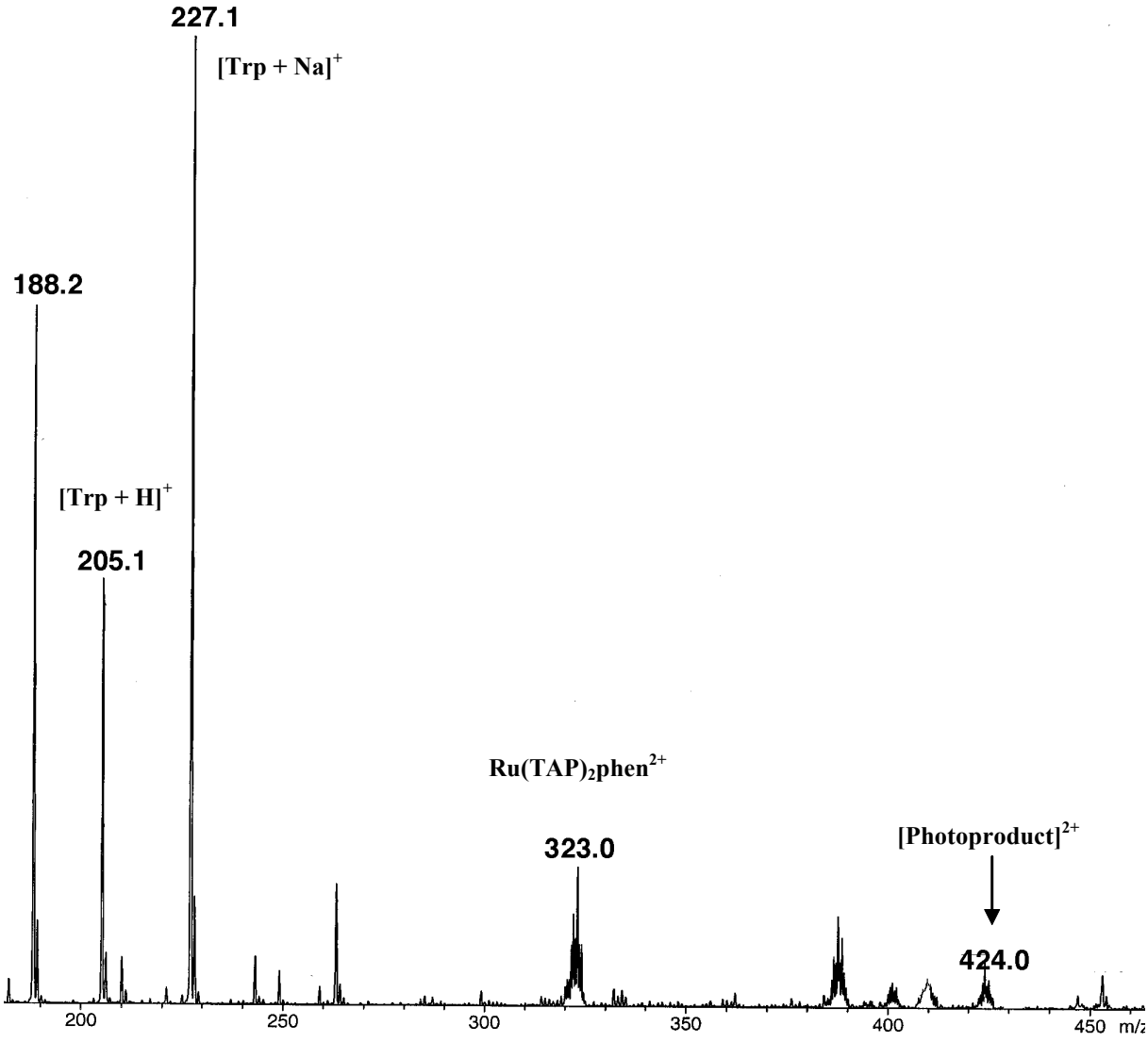


Fig. 6 ESMS analysis of the illuminated mixture of $Ru(TAP)_2phen^{2+}$ (10^{-5} M) + Trp (10^{-3} M), concentrated before injection. ElectroSpray Mass Spectra were recorded on an Esquire spectrometer (Bruker). The analysis was performed on the positive mode. The eluent was 50% aqueous acetonitrile and the flow rate was 8µL/min. The HPLC t_R of the photoadduct was indeed too close to that of the starting complex to allow a good separation of the mixture.

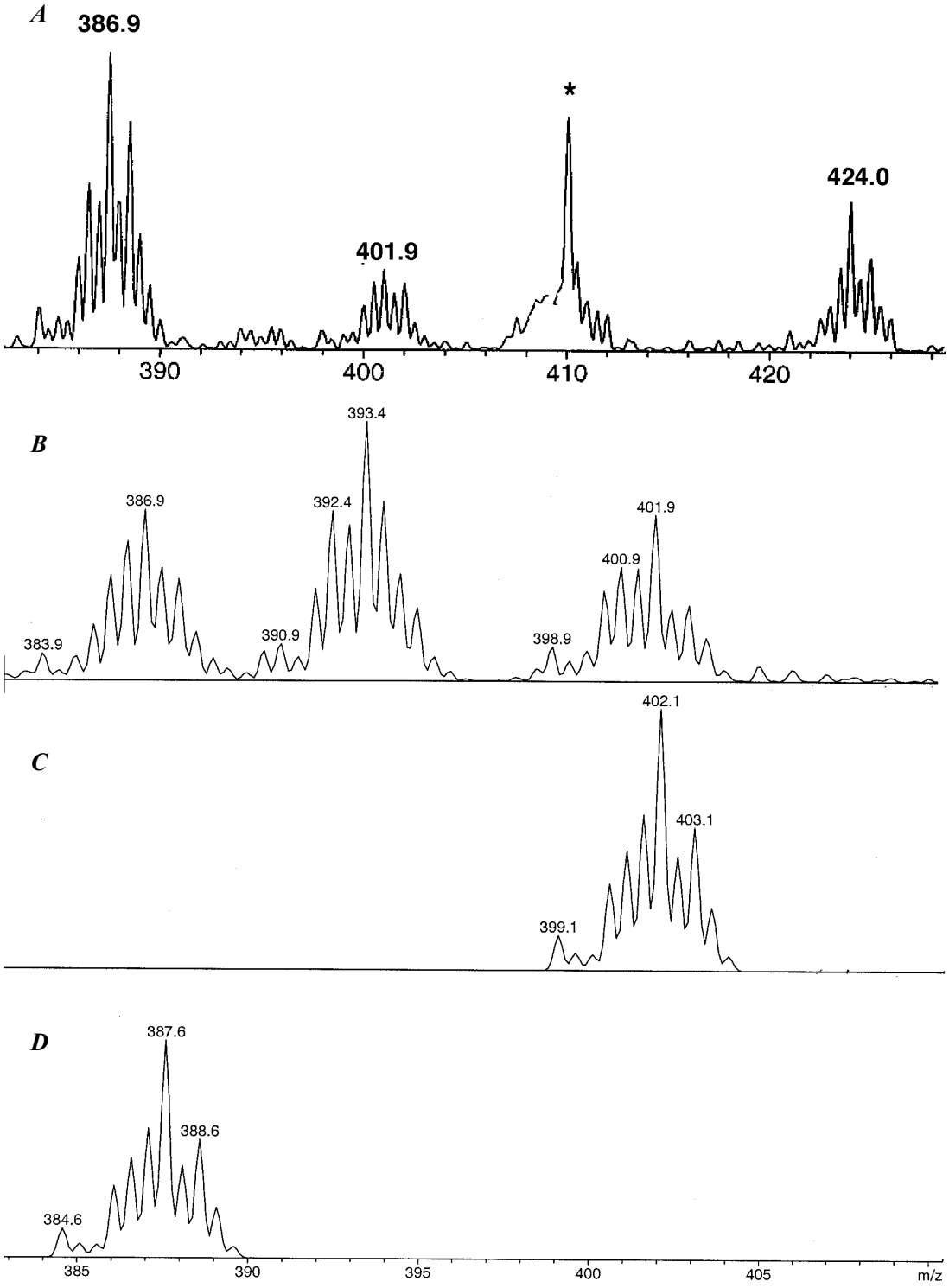


Fig. 7 ESMS analysis of the illuminated mixture of $Ru(TAP)_2phen^{2+}$ (10^{-5} M) + Trp (10^{-3} M), concentrated before injection (region 380-430) : (A) Experimental spectrum, (B) MS^2 of the peak at 424, (C) theoretical spectrum corresponding to the loss of CO_2 (Calcd mass = 804.2), (D) theoretical spectrum corresponding to the loss of $–CH(NH_2)COOH$ (Calcd mass = 775.2). * Impurity of the solvent.

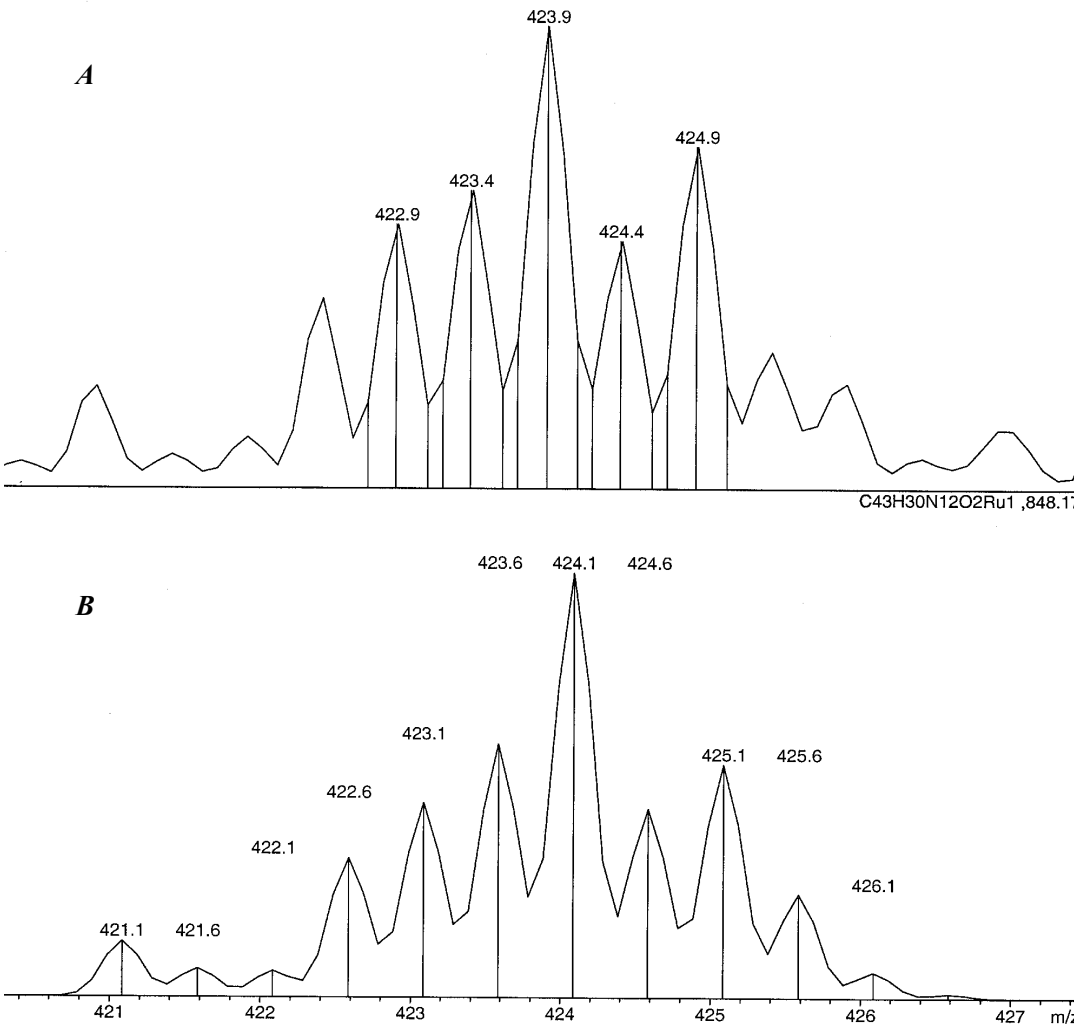


Fig. 8 ESMS analysis of the illuminated mixture of $Ru(TAP)_2phen^{2+}$ + Trp : (A) Experimental spectrum, (B) Theoretical spectrum $C_{43}H_{30}N_{12}O_2Ru$ (Calcd mass = 848.17).