Supplementary Information

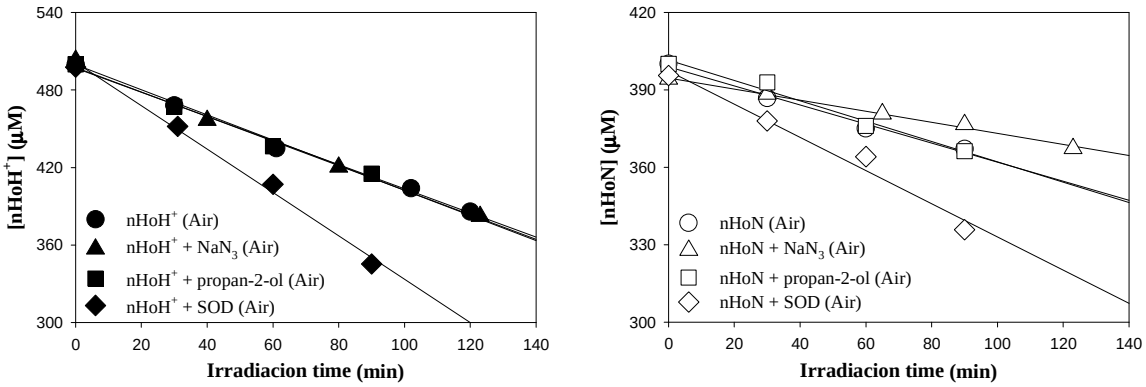

Fig. 1 HPLC analysis of $nHoH^+$ and nHoN concentration evolution as a function of irradiation time (UV-A (350 nm)). Experiments performed from air-equilibrated aqueous solutions in the presence and in the absence of different ROS scavengers.

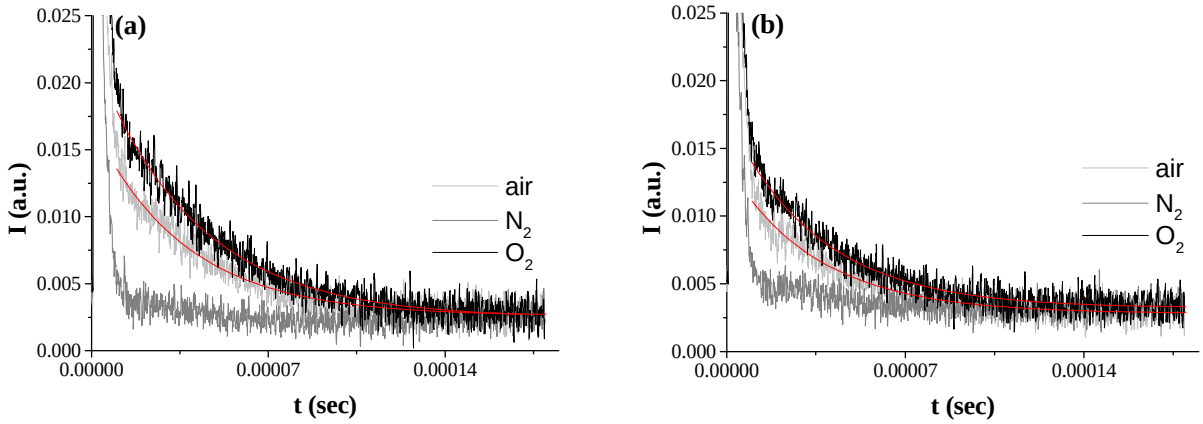

Fig. 2 Phosphorescence decay traces of $^1O_2$, observed at 1270 nm after excitation of norharmane D_2O solutions, under different atmospheres. Red line: fit to a first-order decay kinetic. Experiments carried out at **(a)** pH 5 and **(a)** pH 10.

Electron Ionization–Mass Spectrometry (EI-MS). An air-equilibrated aqueous solution (pH = 5) of norharmane was over night irradiated and analyzed by EI-MS. As it is shown in the spectrum obtained, several peaks with different m/z ratio were detected. The signal with m/z = 334 corresponds to the dimmer molecular ion. The signal with m/z ratio of 167 is characteristic of norharmane dimers[1], which suffer as main fragmentation M-167 yielding the ion with m/z = 167 (norharmane m.w., 168 Da; norharmane – H = 167 Da). Other signals can be assigned taking into account the characteristic fragmentation pattern of β-carbolines previously described[2]. The major fragmentation pathway of these molecules is the successive loss of CN^- and HCN moieties to give abundant ions at m/z = 308 and 281.

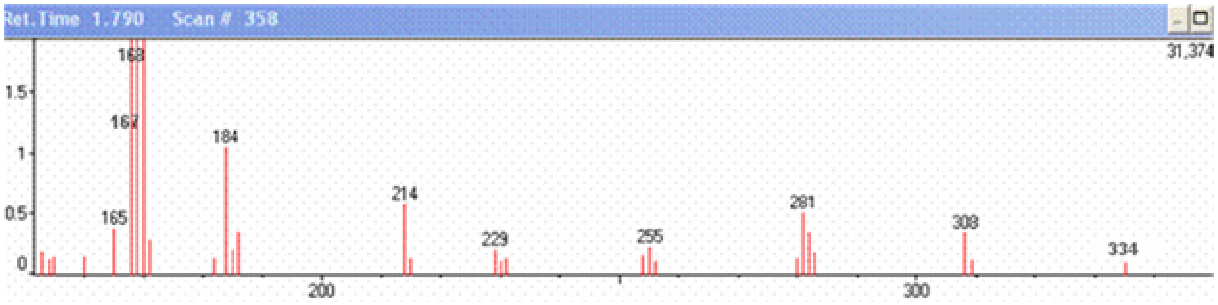

Fig. 3 EI-MS of the solid residue obtained after irradiation of aqueous solution of norharmane (pH = 5).

[1] R. Erra-Balsells and A.R. Frasca, *Tetrahedron*, 1983, **39** 33-39.
[2] R.T. Coutts, R.A. Locock and G.W.A.Slywka, *Organic Mass Spectrometry*, 1970, **3**, 879-889