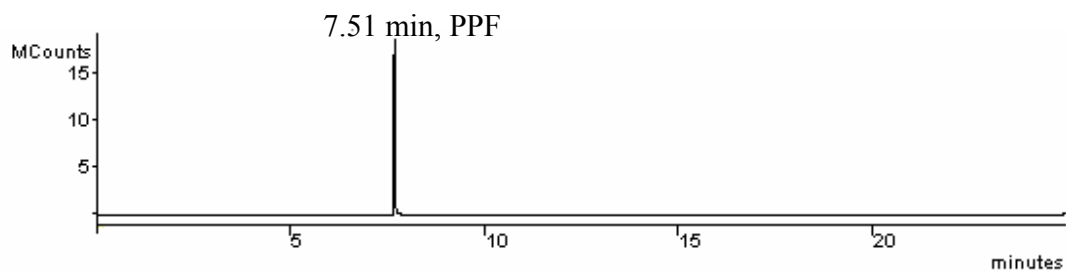


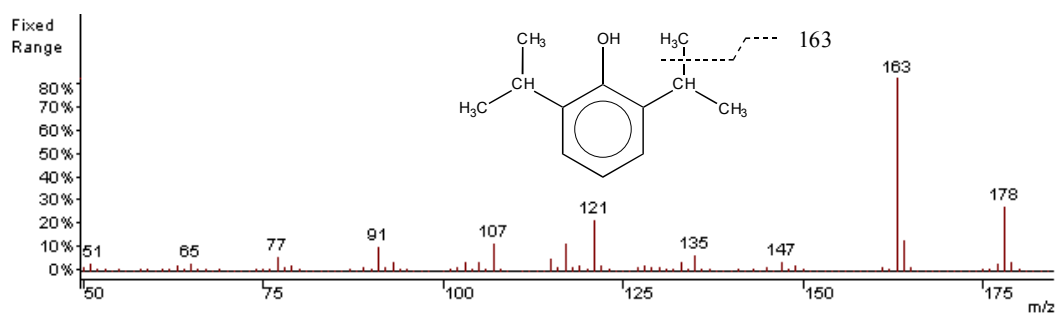
## Continuous irradiation

Chromatogram of PPF in cyclohexane:

a)



b)

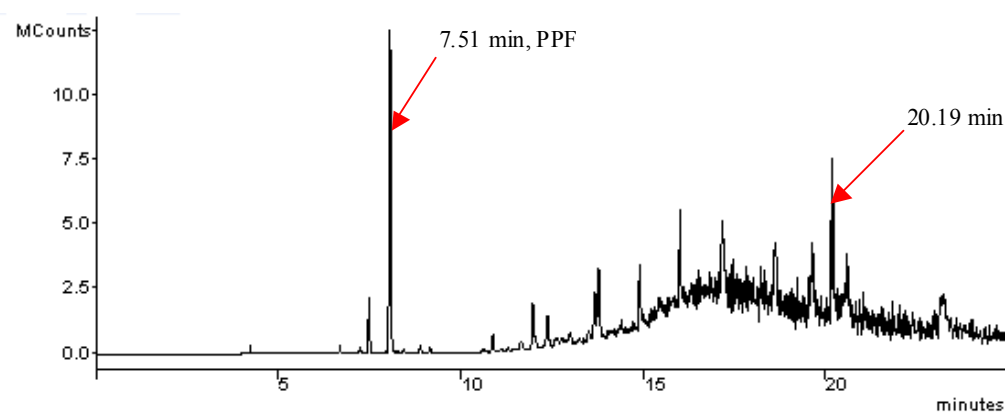


**Figure S.I. 1:** GC chromatogram (a) and mass spectrum (b) of a PPF ( $10^{-4}$  M) solution in cyclohexane. The retention time of PPF is 7 min 51. The molecular ion is characterized by  $m/z$  178 and the major fragment,  $m/z$  163, is due to the loss of a methyl group.

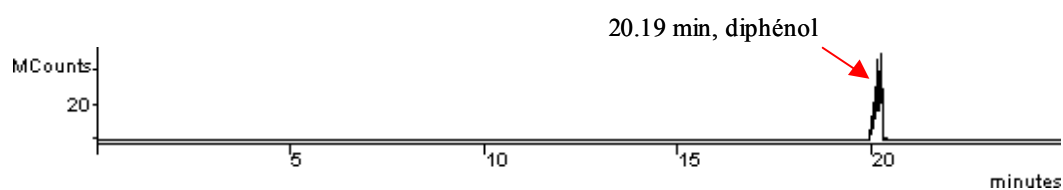
## Chromatogram of irradiated solution of PPF

*In the absence of oxygen:*

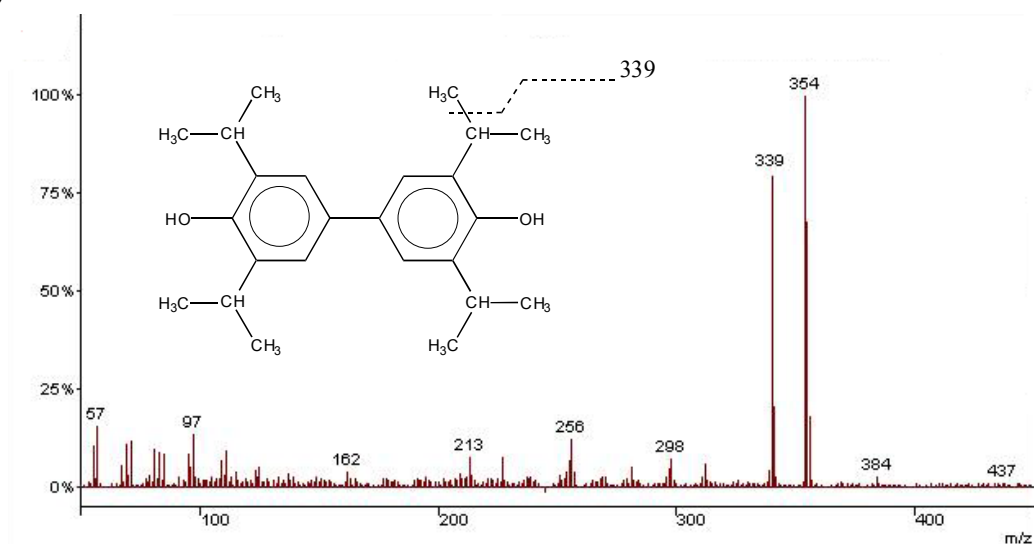
a)



b)



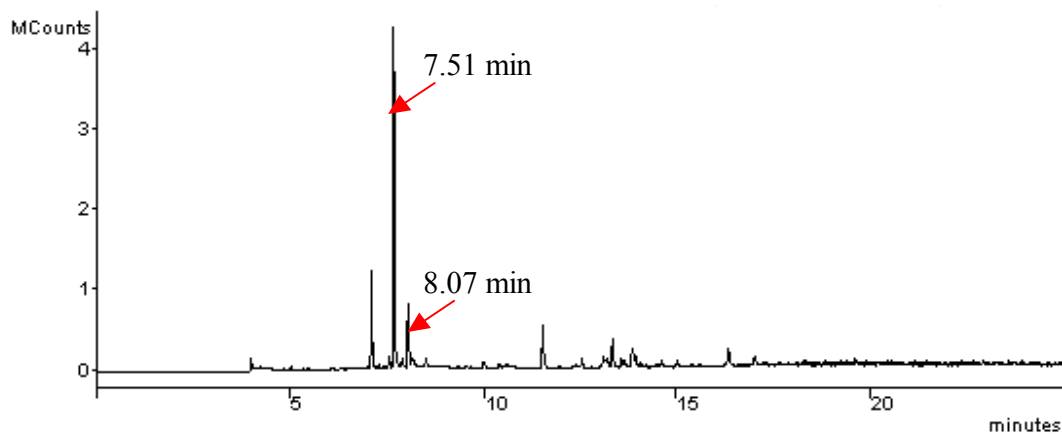
c)



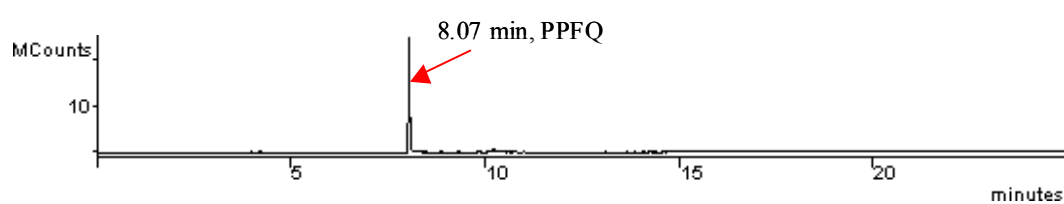
**Figure S.I. 2** : GC chromatogram of a) PPF  $10^{-4}$  M solution in cyclohexane irradiated in the absence of oxygen for 20 min, b) Diphenol solution in cyclohexane. c) Mass spectrum of diphenol with the molecular ion at m/z 354 and the major fragment, m/z 339, due to the loss of a methyl group.

*In the presence of oxygen*

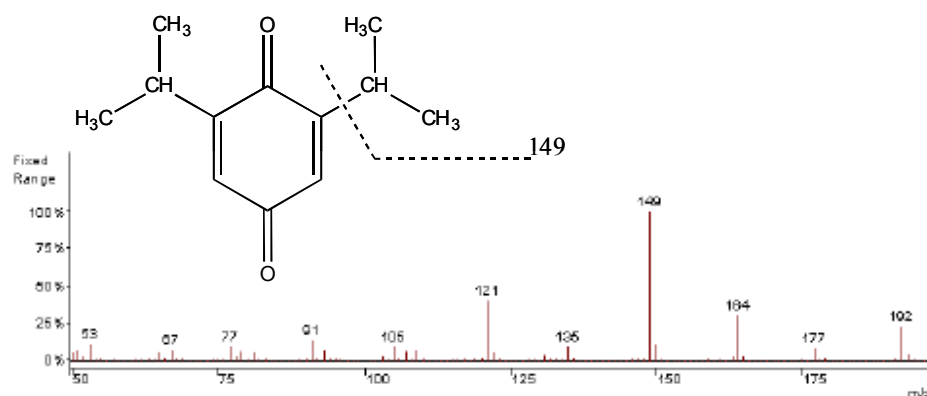
a)



b)

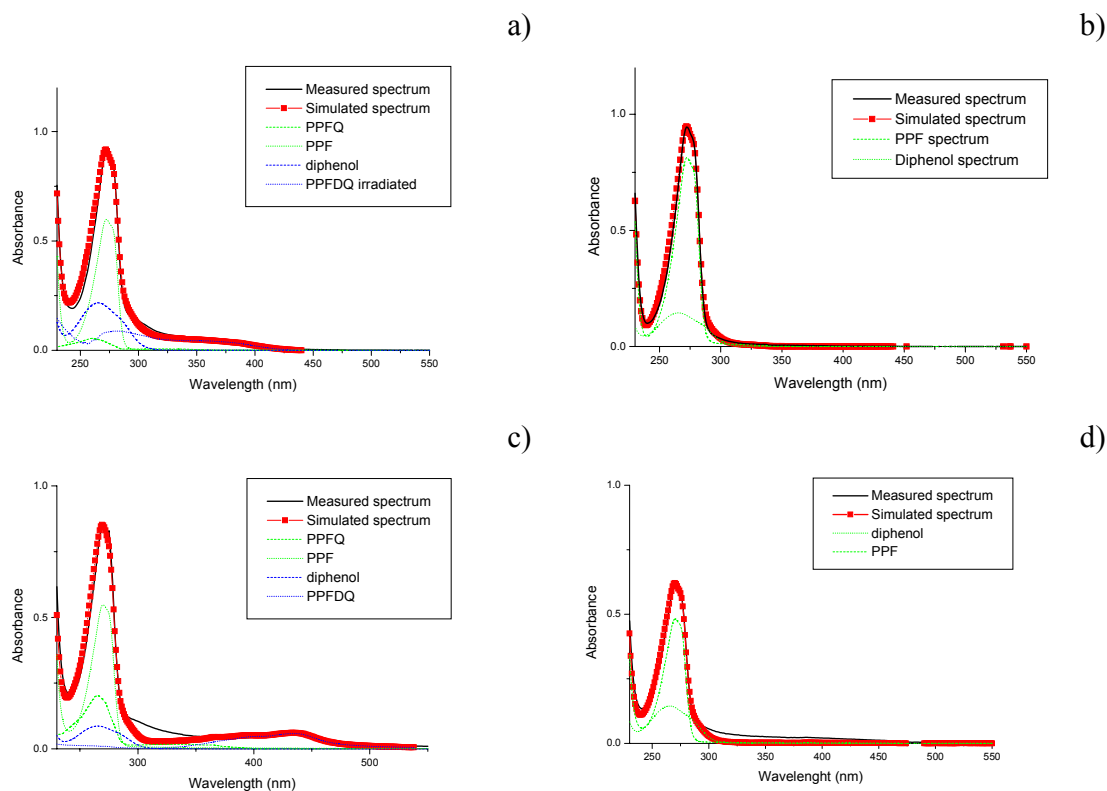


c)



**Figure SI 3** : GC chromatogram of a) a PPF  $10^{-4}$  M solution in cyclohexane irradiated in the presence of oxygen for 20 min, b) PPFQ solution in cyclohexane. c) Mass spectrum of PPFQ with the molecular ion at  $m/z$  192 and the major fragment,  $m/z$  149, due to the loss of the propyl group.

UV/Vis modelization of the photoproduct of PPF in methanol and phosphate buffer.



**Figure SI 4:** Measured and simulated absorption spectrum of an irradiated solution ( $\lambda_{exc} = 254 \text{ nm}$  of PPF in the presence (a,c) and in the absence (b,d) of oxygen:  $10^{-3} \text{ M}$  in methanol (a,b) and  $5 \times 10^{-4} \text{ M}$  in phosphate buffer pH 7 (c,d). The irradiation time is 80 min.

## Laser flash photolysis

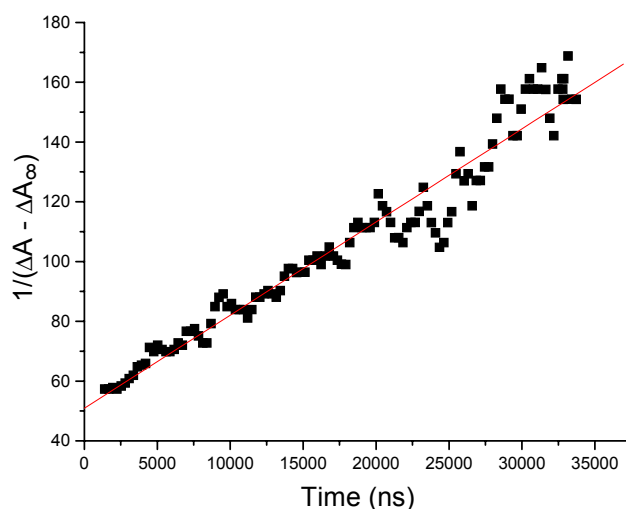
In cyclohexane

In figure 4 from the paper, the decay of the transient species measured at 300 nm in the absence of oxygen was assigned to a second order kinetic.

As known, a second order kinetic should be represented by the following equation:

$$\frac{1}{\text{Abs}_t} = \frac{1}{\text{Abs}_{t,0}} + \frac{2k}{\epsilon_{\text{PPF}} \cdot l} t, \quad (1)$$

where  $Abs_t$  represents the absorbance, the  $Abs_{t,0}$  is the absorbance at the initial time,  $k$  is the decay rate constant of the transient,  $\epsilon_{PPF}$  corresponds to the molar extinction coefficient of the transient species and  $l$  is the optical path length (1 cm in our case).

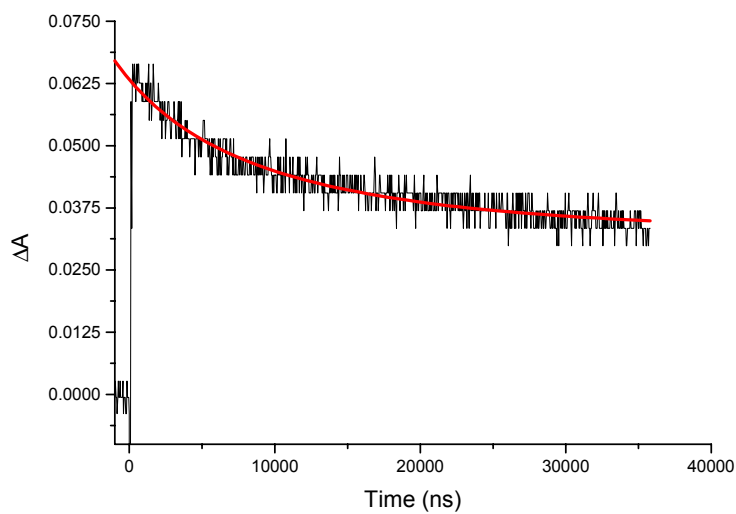


**Figure SI 5:** Kinetic measured at 300 nm of a PPF ( $10^{-4}$  M) solution irradiated with an excitation laser set at 266 nm in the absence of oxygen (1 atm argon). The kinetic is plotted as the reverse of the absorbance.

As shown in figure SI 5, the reverse of the absorbance variation is linear in function of the time, proving that the decay of the transient observed in figure 4 (paper) in the absence of oxygen follows a second order kinetic.

In the presence of oxygen, the decay of the transient species measured at 300 nm follows a mixed second and first order kinetic. Indeed, the decay is well fitted by the equation:

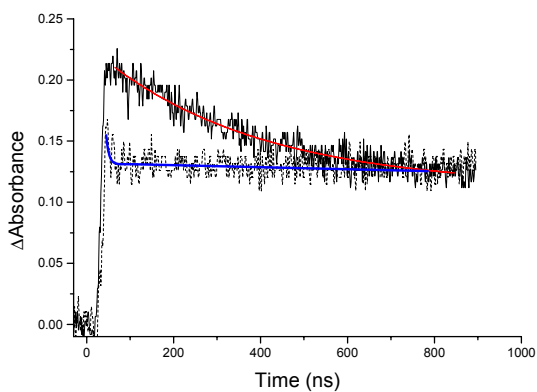
$$A = A_{\infty} + \frac{A_0 k_{3O_2} [^3O_2]}{\left( k_{3O_2} [^3O_2] + \frac{2k_{dim}}{\epsilon_{PPF} \cdot l} A_0 \right)} e^{-k_{3O_2} [^3O_2] t} - \frac{2k_{dim}}{\epsilon_{PPF} \cdot l} A_0 \quad (2)$$



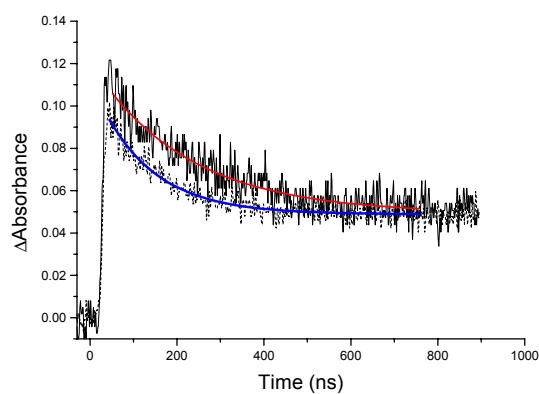
**Figure SI 6** : Decay measured at 300 nm of a solution of PPF ( $10^{-4}$  M) in cyclohexane in the presence of oxygen (1 atm) after a laser pulse excitation at 266nm. The red curve is the fit according to the equation given in the text above.

In polar solvent:

a)



b)



**Figure SI 7:** Kinetics measured at 250 nm in the absence (straight) and in the presence (dot) of 1 atm of oxygen after the laser pulse excitation ( $\lambda=266$  nm) of a PPF solution: a)  $10^{-3}$  M in methanol, b)  $5 \times 10^{-4}$  M in phosphate buffer. The plain lines on the experimental data represent the fit by a monoexponential decay.