Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Photophysics and Photochemistry of the β-Lapachone Derived Diphenyldihydrodioxin: Generation and Characterization of Its Cation Radical

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Electronic Supplementary Information

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*Synthesis of 2,3-diphenyl-1,4-dioxene (**2**)*

This olefin was synthesized following a procedure from the literature.[1] Briefly, 10.6 g (0.05 mol) of benzoin and 0.2 g of *para*-toluenesulfonic acid were heated under reflux with 125 ml of ethylene glycol for 20 h in a dry atmosphere using a calcium chloride tube. The solution was cooled, filtered and washed with an ethylene glycol/water mixture and then dried at low pressure. Yellowish crystals were obtained and TLC analysis showed only one spot, distinct from the substrate. The yield of the crude product was 28%, m.p. = 94-5°C.

IR (KBr, cm^{-1}): 3078, 3052 (aromatic C-H), 2981, 2925, 2878 (C-H), 1634 (C=C), 1598 (aromatic C=C), 1287, 1258 (C-O-C=), 759 e 693 (monosubstituted aromatic ring). RMN ^1H ($CDCl_3$) δ (ppm): 7.33 (m, 10H), 4.4 (s, 4H).

*Synthesis of the diphenyldihydrodioxin **3***

The synthesis of **3** was already described in the literature.[2] Briefly: β-lapachone (1 mmol) was dissolved in benzene (20 mL) and 2.5 mmol of 2,3-diphenyl-1,4-dioxene was added. After deoxygenating with N_2, the tubes were irradiated with a 500 W Hg lamp. This mixture was filtered under reduced pressure, the colorless solid was collected and recrystallized from ethanol; m.p.: 209–211 ^oC, yield 69%. Spectra (IR, MS, ^1H NMR and ^{13}C NMR) for this compound are shown in Supporting Information (Figures 1S-4S).

UV (acetonitrile, λ_{max} nm (ε, $Lmol^{-1}cm^{-1}$): 212 ($3.9x10^4$), 245.5 ($3.08x10^4$), and a broad band from 270 to 360 nm, with maximum at 317 ($5.8x10^3$) (Figure 5S)

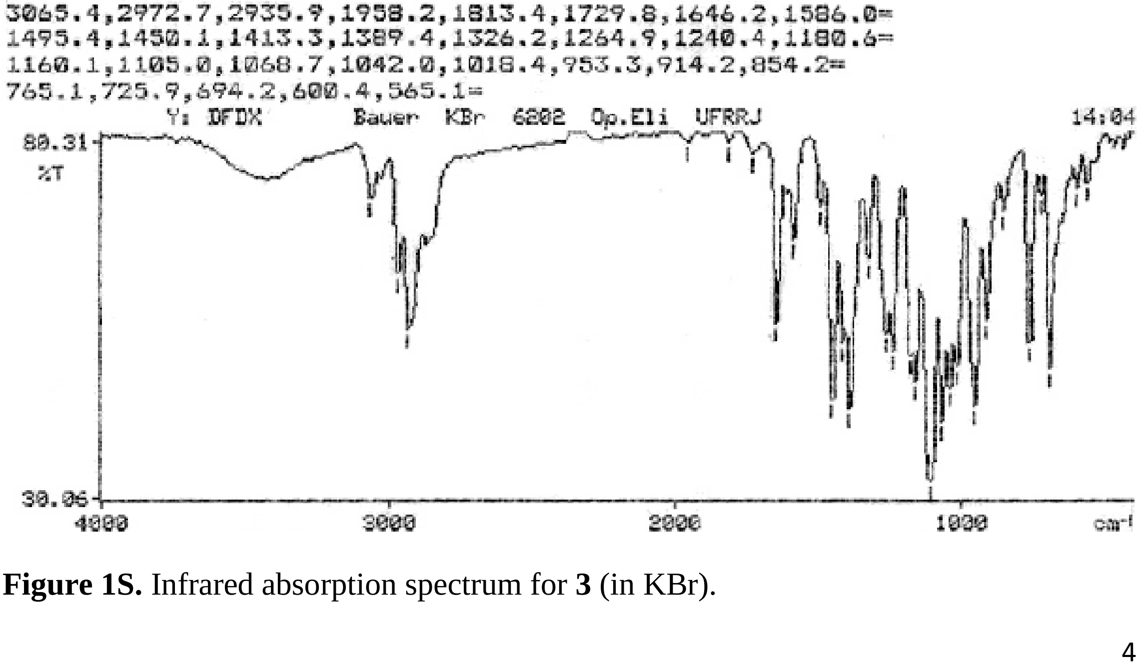
IR (KBr) (cm^{-1}): 3065.4, 2972.7, 2935.9, 1646.2, 1586.0, 1495.4, 1450.1, 1413.3, 1389.4, 1326.2, 1264.9, 1240.4, 1180.6, 1160.1, 1105.0, 1068.7, 1042.0, 1018.4, 953.3, 914.2, 854.2, 765.1, 725.9.

MS *m*/*z* (abundance): 480 (<1%), 238 (11%), 214 (1%), 199 (1%), 181 (1%), 159 (1%), 130(1%), 105 (100%), 77 (17%), 51 (2%).

HRMS: *m/z* 480.2020 (theoretical 480.2036)

^{1}H NMR ($CDCl_3$) δ (ppm): 8.16 (1*H*, m); 8.12 (1*H*, m); 7.77–7.68 (4*H*, m); 7.44 (1*H*, dt, J = 7.02 and 1.36 Hz); 7.32 (1*H*, dt, J = 6.20 and 1.36 Hz); 7.24– 7.18 (6*H*, m); 4.34–4.14 (2*H*, m); 3.96–3.89 (2*H*, m); 3.02–2.76 (2*H*, m), 1.87 (2*H*, J = 6.48 and 1.62 Hz); 1.42 (3*H*, s); 1.38 (3*H*, s).

^{13}C NMR ($CDCl_3$) δ (ppm): 17.39; 26.63; 26.82; 32.09; 61.41; 61.78; 74.03; 94.43; 95.10; 106.6; 119.75; 121.54; 123.27; 123.99; 125.57; 127.27; 127.67; 128.52; 134.46; 137.46; 137.79; 144.10.



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765.1,725.9,694.2,600.4,565.1=
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Figure 1S. Infrared absorption spectrum for **3** (in KBr).

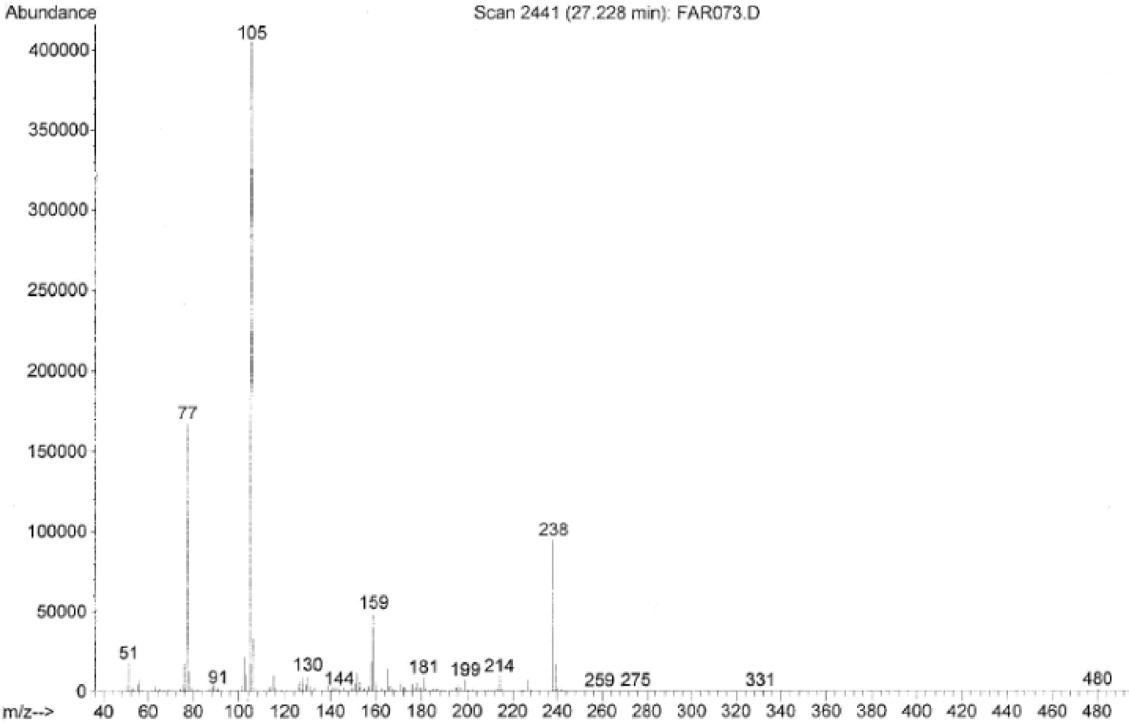

Figure 2S. Mass spectrum for **3.**

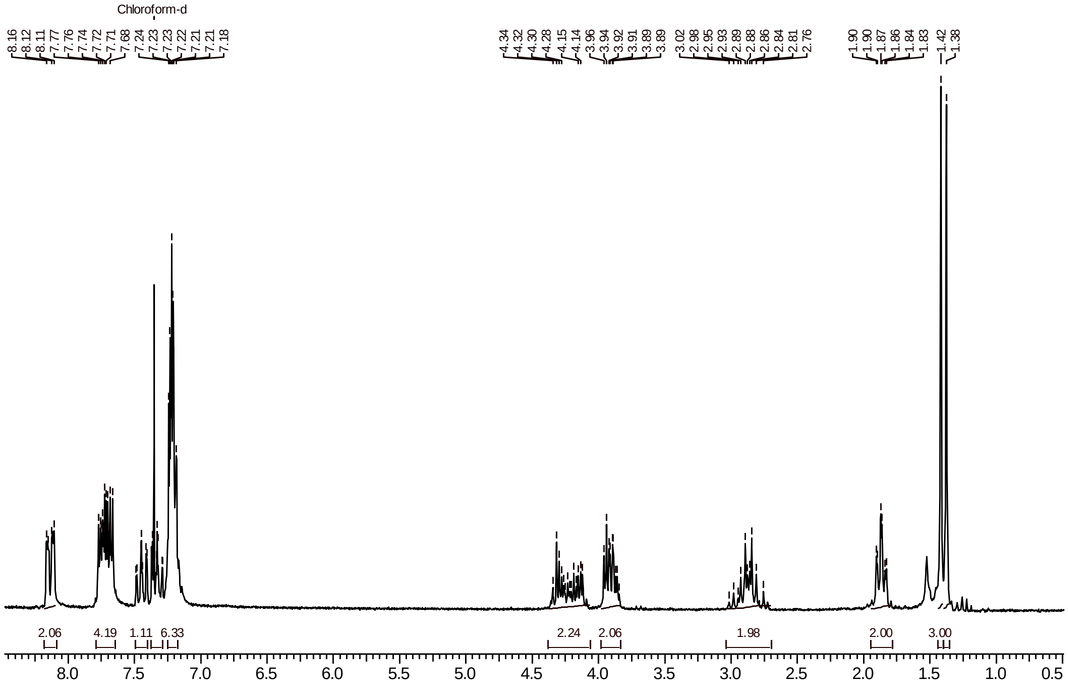

Figure 3S. ^{1}H Nuclear Magnetic Resonance for **3**, in $CDCl_3$

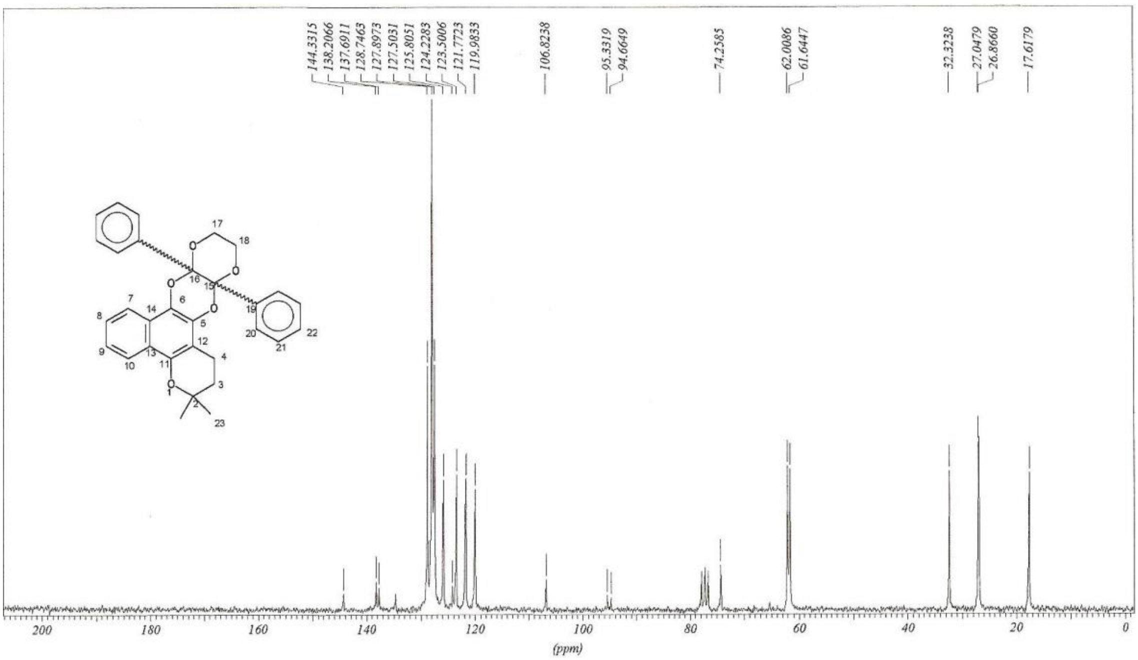

Figure 4S. ^{13}C Nuclear Magnetic Resonance for **3**, in CDCl$_3$.

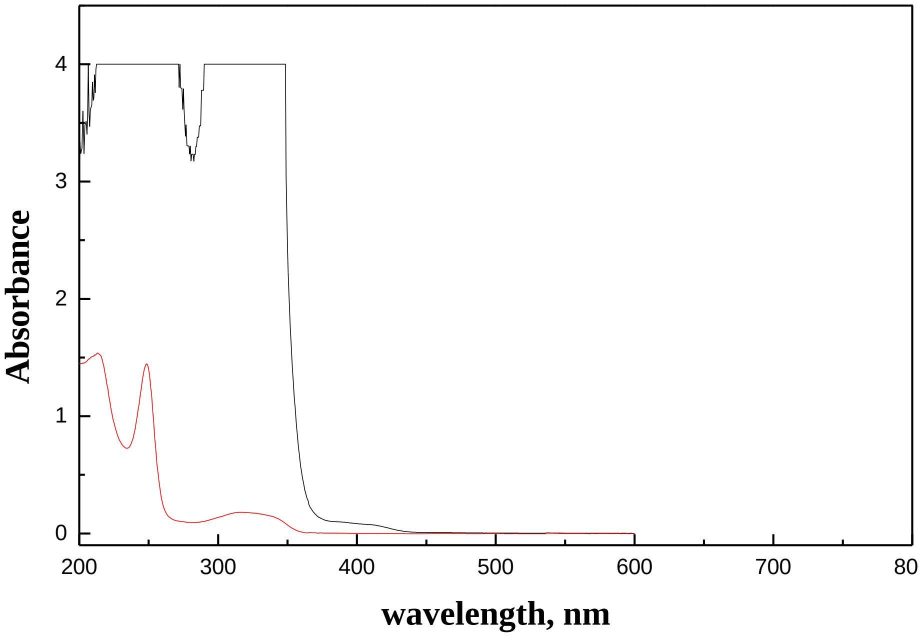

Figure 5S. UV-visible absorption spectra for **3**, in acetonitrile: (—) 1.2x10^{-3} mol/L; (—) 3.1x10^{-5} mol/L.

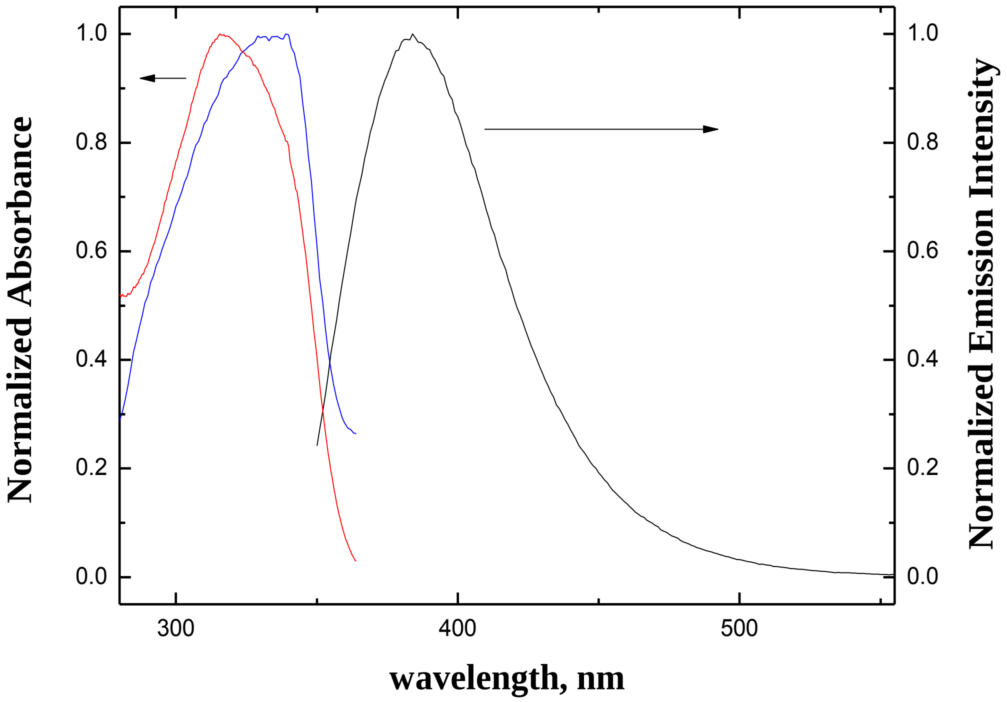

Figure 6S. Normalized absorption (—), excitation (—) and fluorescence emission (—) spectra for **3**, in acetonitrile.

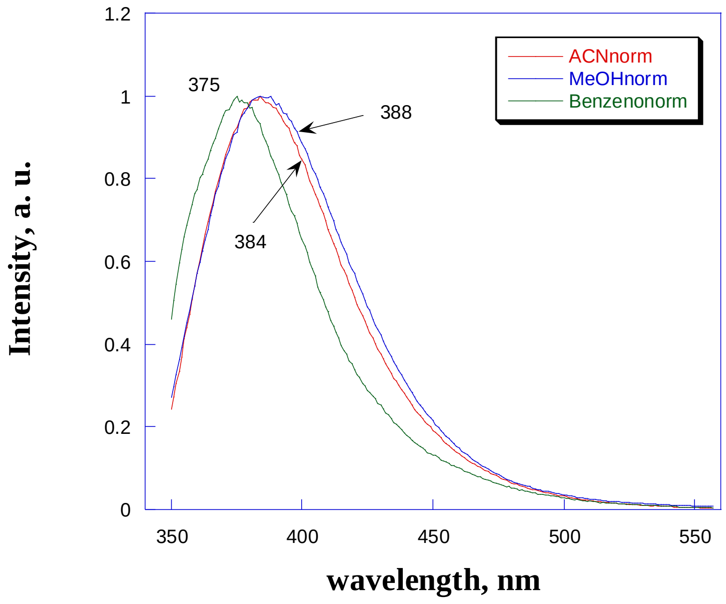

Figure 7S. Normalized fluorescence emission spectra for **3** in different solvents.

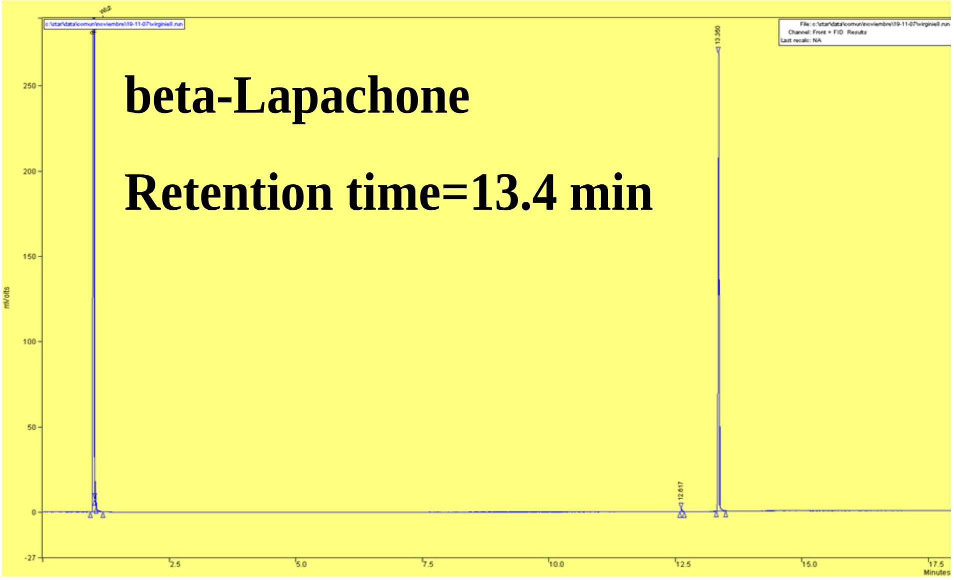

Figure 8S. Chromatogram (GC) for a solution of β-lapachone (**1**), in ACN.

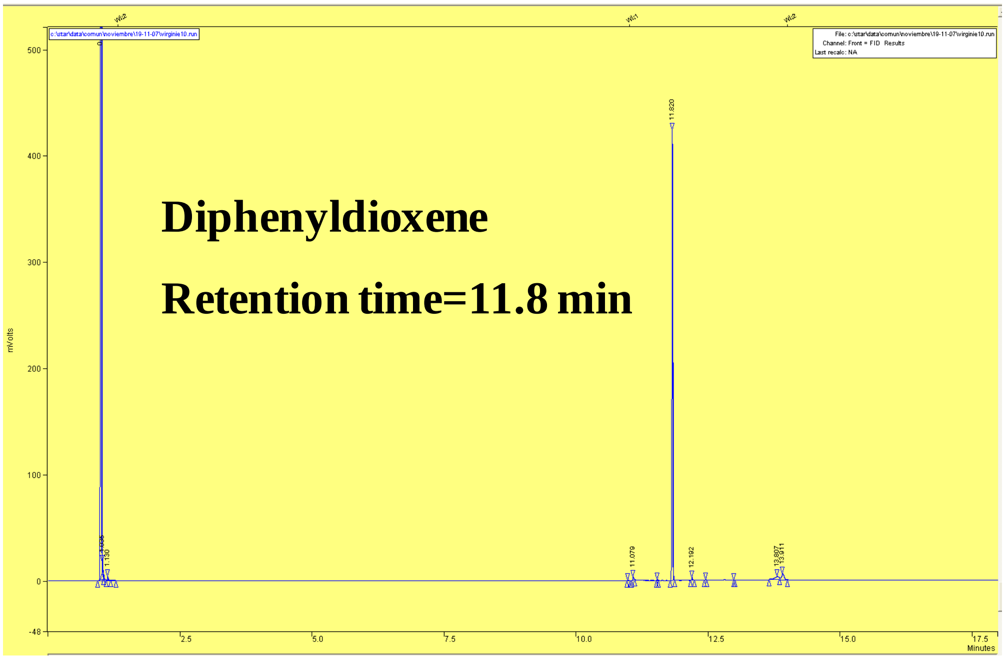

Figure 9S. Chromatogram (GC) for a solution of 2,3-diphenyldioxene (**2**), in ACN.

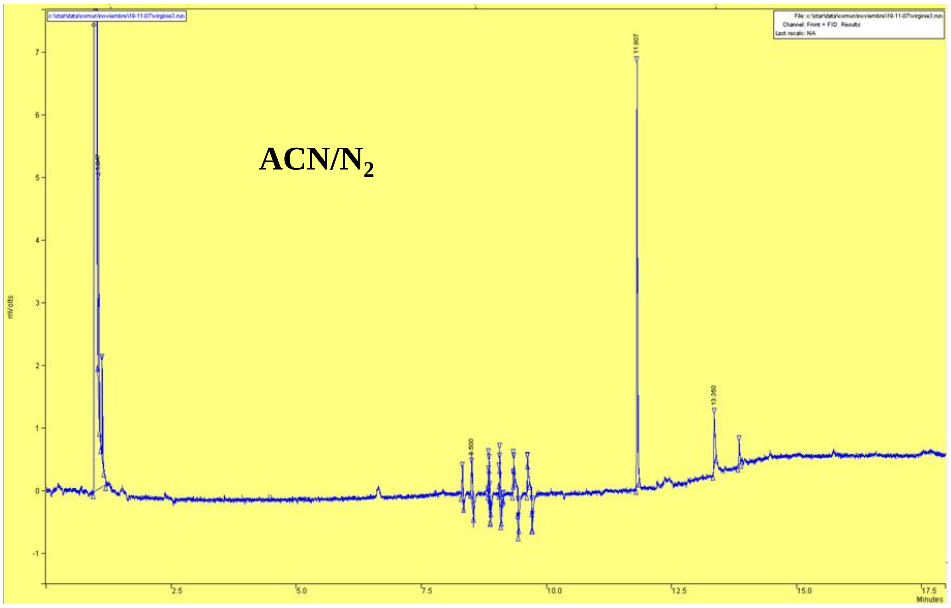

Figure 10S. Chromatogram (GC)for the irradiation of a solution of **3** under N_2, in ACN.

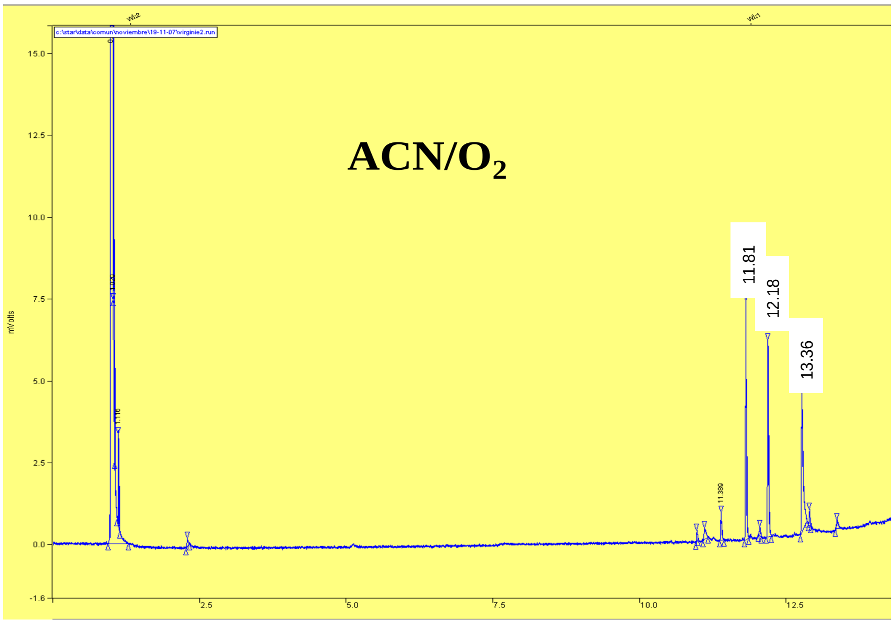

Figure 11S. Chromatogram (GC) for the irradiation of an oxygenated solution of **3**, in ACN, showing the formation of a new product with retention time at 12.18 min.

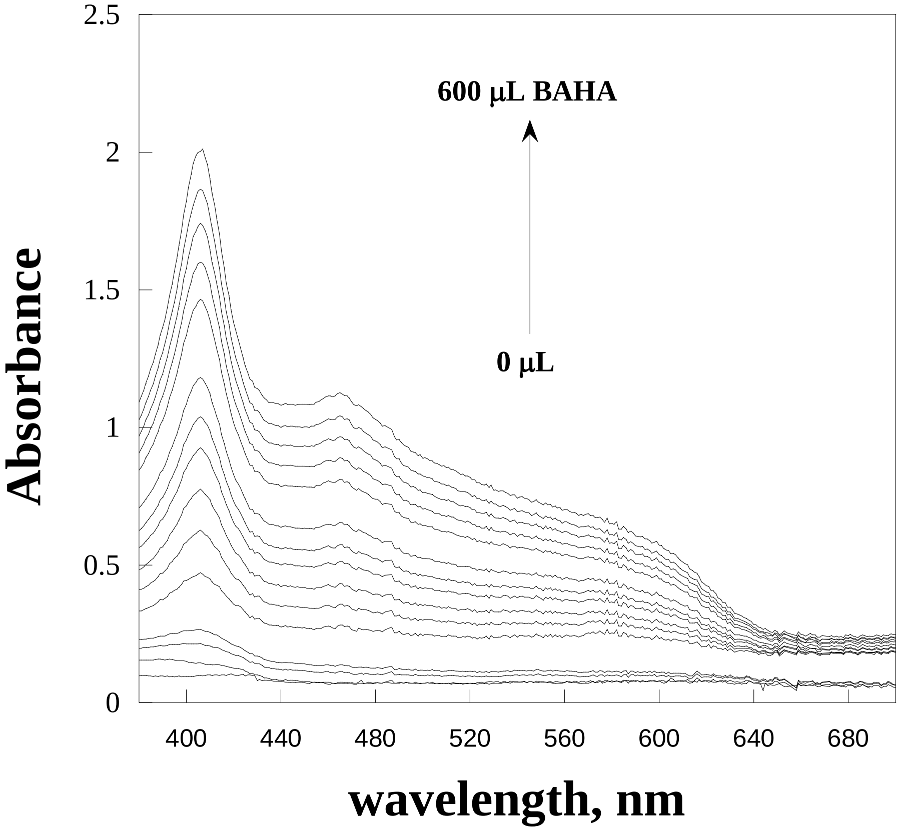

Figure 12S. Absorption spectra for the thermal generation of the diphenyldihydrodioxin cation radical **4** upon successive additions of μL aliquots (from 0 to 600 μL) of a 1.0 mmol L^{-1} solution of BAHA to a 1.0 mmol L^{-1} solution of diphenyldihydrodioxin **3,** in dichloromethane.

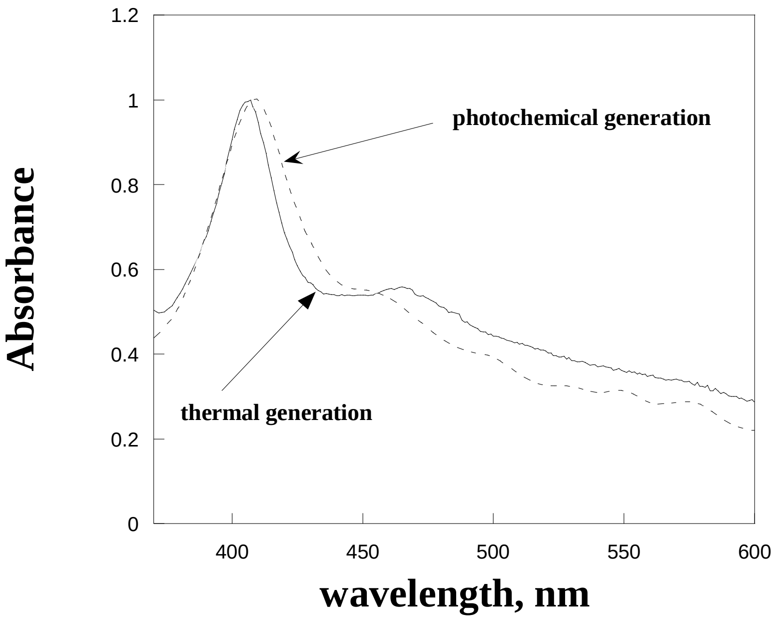

Figure 13S. Superposition of the absorption spectra for thermal and photochemically generated **4**.

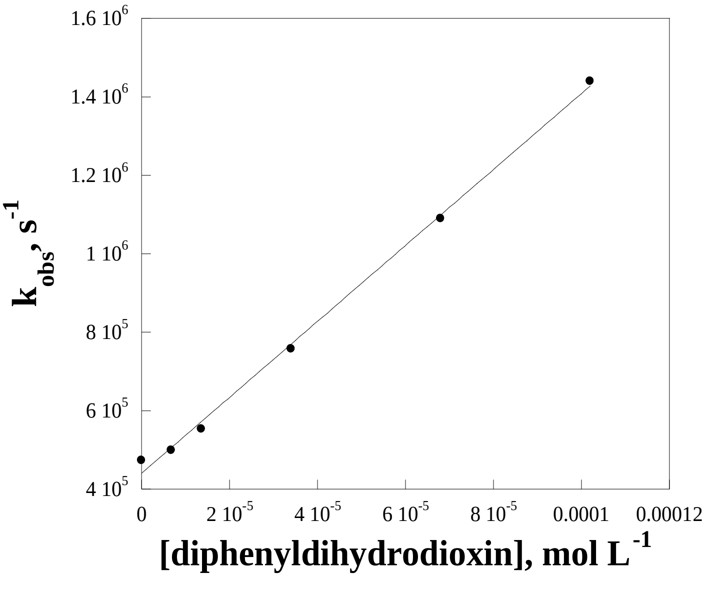

Figure 14S. Stern-Volmer plot for the quenching of benzophenone triplet by diphenyldihydrodioxin **3**, in acetonitrile.

References

1. R. K. Summerbell, D. R. Berger, *J. Am. Chem. Soc.* 1959, **81**, 633.
2. B. O. Bernardes, A. B. B. Ferreira, J. L. Wardell, S. M. S. V. Wardell, J. C. Netto-Ferreira, E. R. T. Tiekink, *Acta Cryst.* 2013, **E69**, o1487.