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

Electronic Supplementary Information (ESI)

Chemical quenching of singlet oxygen by betanin

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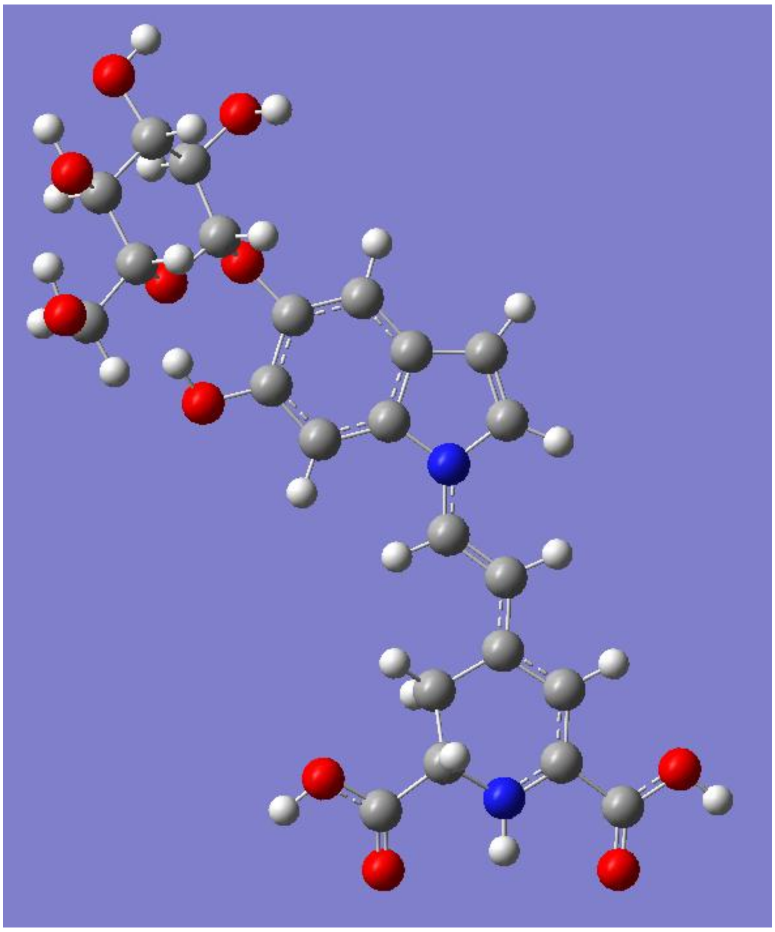
Table S1. TD-DFT of 2-decarboxy-2,3-dehydrobetanin at the B3LYP/6-311++G(d,p) level of theory with polarizable continuum model (PCM) for water.



Energy = -1828.85174750 Hartree

Wavelength (nm)	*f*
632.69	0.0658
487.50	1.0355
366.11	0.0808
336.21	0.0002
322.55	0.0001
309.81	0.0179
305.88	0.0331
301.32	0.0023
298.82	0.0019
291.11	0.0048

C	-0.075432000	-1.456483000	-0.251660000
N	-1.396855000	-1.858840000	0.071788000
C	-2.483034000	-1.059965000	0.012507000
H	-2.272229000	-0.060200000	-0.340971000
C	-3.765150000	-1.423648000	0.356592000
H	-3.955938000	-2.423260000	0.726609000
C	-4.875510000	-0.566383000	0.250415000
C	-6.148914000	-1.037702000	0.586343000
C	-4.779612000	0.825254000	-0.344512000
C	-7.271752000	-0.232764000	0.401294000
H	-6.290962000	-2.058127000	0.909411000
C	-5.896757000	1.732382000	0.191455000
H	-4.853342000	0.729086000	-1.434365000
N	-7.182335000	1.058084000	0.117413000
H	-8.026717000	1.602624000	-0.031104000
C	-8.687191000	-0.750266000	0.492826000
O	-9.641730000	-0.039414000	0.289649000
O	-8.738763000	-2.041278000	0.810606000
H	-9.667565000	-2.321956000	0.860191000
H	-3.827568000	1.302650000	-0.125359000
C	0.762197000	-2.571694000	-0.059708000

C	-1.349801000	-3.219194000	0.457160000
C	-0.074885000	-3.666000000	0.385804000
H	-2.247802000	-3.737568000	0.743913000
C	2.127345000	-2.447047000	-0.316816000
C	0.398248000	-0.223749000	-0.673737000
C	2.617634000	-1.221855000	-0.747174000
C	1.768239000	-0.105077000	-0.920996000
O	2.232653000	1.094866000	-1.353629000
H	3.192242000	1.151459000	-1.186630000
H	-0.231118000	0.645421000	-0.813409000
H	2.807668000	-3.282541000	-0.205430000
H	0.250453000	-4.667480000	0.621509000
O	3.957600000	-1.121724000	-1.113948000
C	6.271295000	-1.074337000	-0.522821000
C	4.855442000	-0.602277000	-0.172846000
C	7.307964000	-0.328791000	0.331079000
C	7.093858000	1.180467000	0.268403000
H	7.209392000	-0.648761000	1.378528000
C	5.646087000	1.528550000	0.632631000
H	7.287667000	1.522189000	-0.756253000
H	6.445461000	-0.848097000	-1.577424000
H	5.433019000	1.212174000	1.661770000
O	4.784955000	0.824913000	-0.277942000
O	7.954000000	1.868411000	1.179152000
O	8.634718000	-0.579645000	-0.123342000
O	6.423188000	-2.483250000	-0.403569000
H	6.252988000	-2.752780000	0.508609000
H	8.814641000	-1.524005000	-0.040853000
H	8.867968000	1.657685000	0.950354000
C	5.329101000	3.019659000	0.500248000
H	5.632279000	3.373535000	-0.493252000
H	4.251872000	3.161068000	0.600170000
O	5.945086000	3.785909000	1.530178000
H	6.882733000	3.542807000	1.547533000
H	4.563430000	-0.903262000	0.842574000
H	-5.688841000	1.956529000	1.248046000
C	-6.003666000	3.074527000	-0.521864000
O	-7.038357000	3.528443000	-0.945078000
O	-4.818907000	3.685769000	-0.581442000
H	-4.925173000	4.550454000	-1.011404000

Figure S1. (A) Transient absorption spectra of perinaphthenone (~ 9 × 10^{-5} M) in D_2O (λ_{exc} = 355 nm, E = 0.4 mJ per pulse), deoxygenated solution by 10 min of bubbling with argon. (B) The inverted stationary UV-vis spectrum of the studied sample. (C) Transient absorption kinetic traces at probe λ = 490 nm obtained for perinaphthenone (~6 × 10^{-5} M) in D_2O (λ_{exc} = 355 nm, E = 0.1 mJ per pulse). A long period (25 min) of bubbling with argon was used to obtain the triplet lifetime of perinaphthenone.

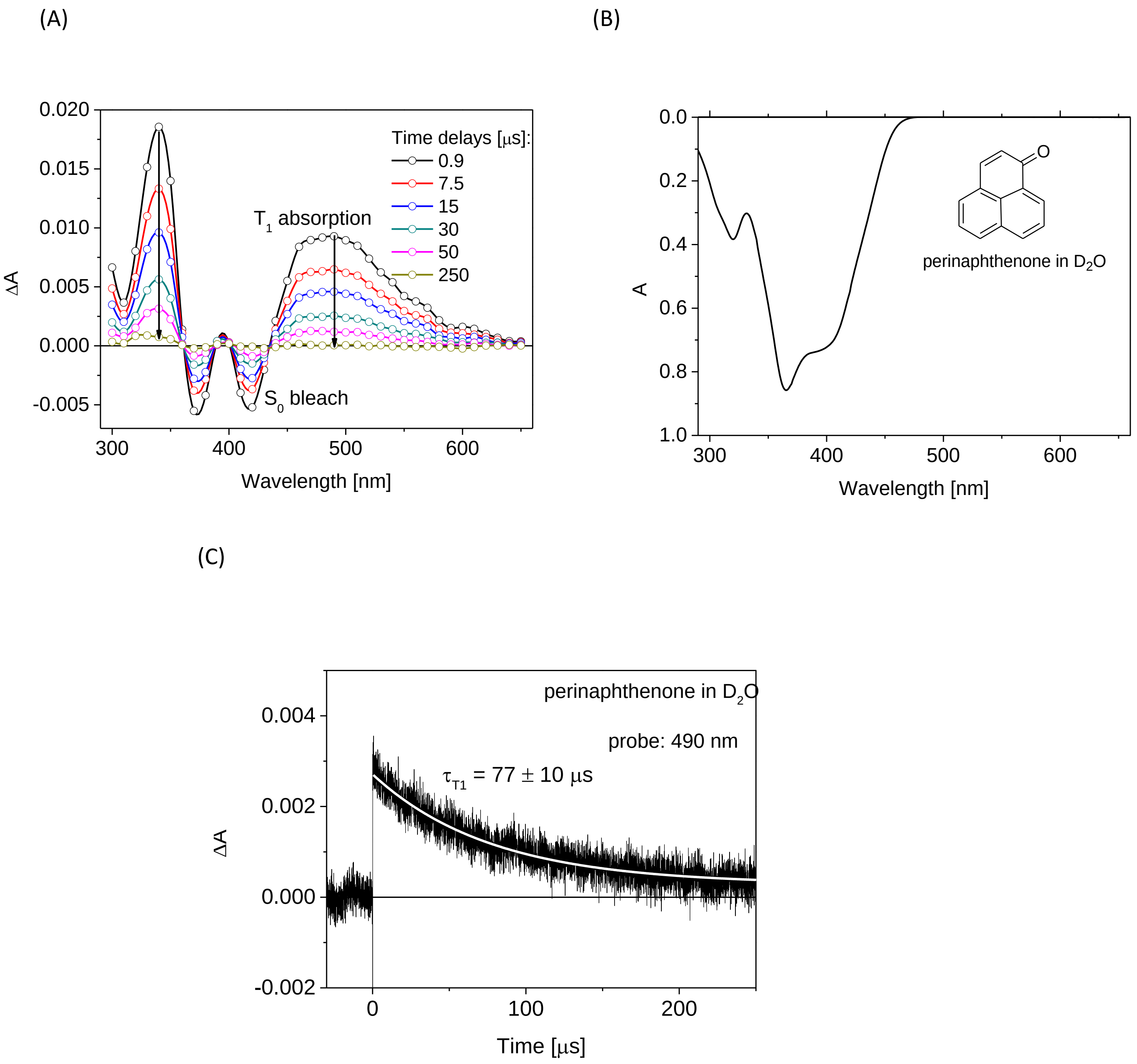


Figure S2. Signal comparison recorded in nanosecond transient absorption experiments (λ_{exc} = 355 nm, E = 0.4 mJ) for deoxygenated solutions of benzophenone (**bp**) in acetonitrile (ACN) and perinaphthenone (**pn**) in D_2O with the same absorbance [A(355 nm, 1 cm) = 0.71], so that the same number of photons would be absorbed by the two solutions. Two samples were measured one after the other under identical experimental conditions. The following relation can be used in comparative actinometric measurements:[1]

$$\frac{\varepsilon(\mathrm{T1}(\mathbf{pn}), 535\ \mathrm{nm})}{\Delta\mathrm{A}(\mathrm{T1}(\mathbf{pn}), 535\ \mathrm{nm})} = \frac{\varepsilon(\mathrm{T1}(\mathbf{bp}), 525\ \mathrm{nm})}{\Delta\mathrm{A}(\mathrm{T1}(\mathbf{bp}), 525\ \mathrm{nm})},$$

where the values $\Delta A(T_1(\mathbf{pn}), 535\ \mathrm{nm})$ and $\Delta A(T_1(\mathbf{bp}), 525\ \mathrm{nm})$ are taken from graph below, $\varepsilon(T_1(\mathbf{bp}), 525\ \mathrm{nm}) = 6500 \pm 400\ \mathrm{M^{-1}cm^{-1}}$ is given in report.[2] The calculated $\varepsilon(T_1(\mathbf{pn}), 535\ \mathrm{nm})$ is a value $1750 \pm 150\ \mathrm{M^{-1}cm^{-1}}$.

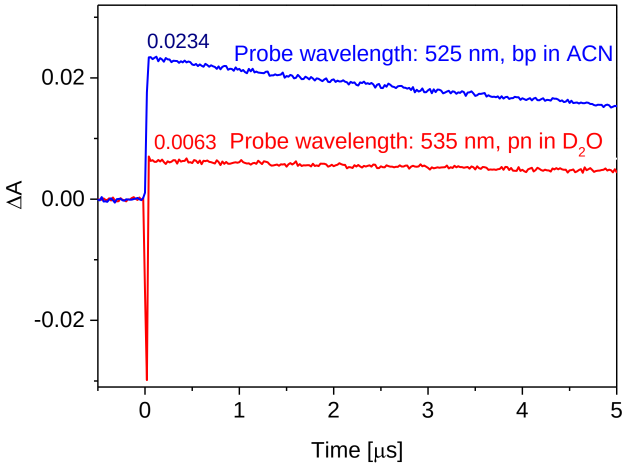
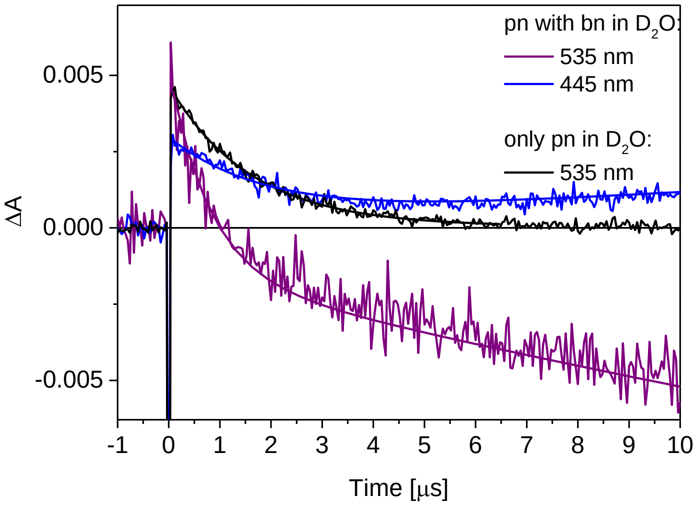


Figure S3. Transient absorption kinetic traces at early delays obtained for solution of perinaphthenone (6 × 10^{-5} M) with betanin (2.3 × 10^{-5} M) in D_2O and solution of only perinaphthenone (6 × 10^{-5} M) in D_2O (all air-equilibrated solutions). Fitting was performed with 2-exponential function ($\Delta A = A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)+\text{offset}$) for solution of betanin with perinaphthenone in D_2O, and a single-exponential function for perinaphthenone in D_2O.



Solution	Probe [nm]	A_1	τ_1[μs]	A_2	τ_2[μs]	Offset
pn with **bn**	535	0.0060	0.8±0.2	0.0205	50±3	-0.0220
pn with **bn**	445	0.0028	2.0±0.3	-0.0054	43±6	0.0055
pn	535	0.0044	1.6±0.2	–	–	0.00002

Perinaphthenone in D_2O has the triplet lifetime of 1.6 ± 0.2 μs (air equilibrated solutions). Similar time-constant should be obtained in solutions of perinaphthenone with added betanin, this is indeed true when we probe the mixture at 445 nm, however, at 535 nm the short component has the time-constant of 0.8 ± 0.2 μs. We believe that a relatively small fraction of betanin forms complexes with perinaphthenone (see also Figure S4). The laser excitation of such complex then localizes the excitation on perinaphthenone, which likely sensitizes betanin in the triplet excited state, and thus removes the betanin population from the ground state. The latter process would result in a fast transient absorption decay at 535 nm probe, being likely responsible for the observed 0.8 ± 0.2 μs component. A small fraction of the complexes (< 3 % vs. free perinaphthenone molecules) is needed to result in such shortening of τ_1, because of a huge difference between the triplet perinaphthenone and the ground-state betanin extinction coefficients (1750 vs. 65000 $M^{-1}cm^{-1}$). At longer delays, an important rise of the betanin bleaching with time-constant of 50 ± 3 μs reflects the reaction of betanin with $^1O_2$.

Figure S4. Transient absorption spectra of betanin (~2.1 × 10^{-5} M) and perinaphthenone (~1.1 × 10^{-4} M) in D_2O (λ_{exc} = 355 nm, E = 0.25 mJ per pulse), air-equilibrated solution. Bottom graph shows the inverted stationary UV-vis spectrum of the studied sample (solid black line) and contribution from betanin in D_2O (pink line). Inspection of the red side of spectra (around 600 nm) shows a weak discrepancy, the possible explanation can be that a part of betanin population forms a complex with perinaphthenone.

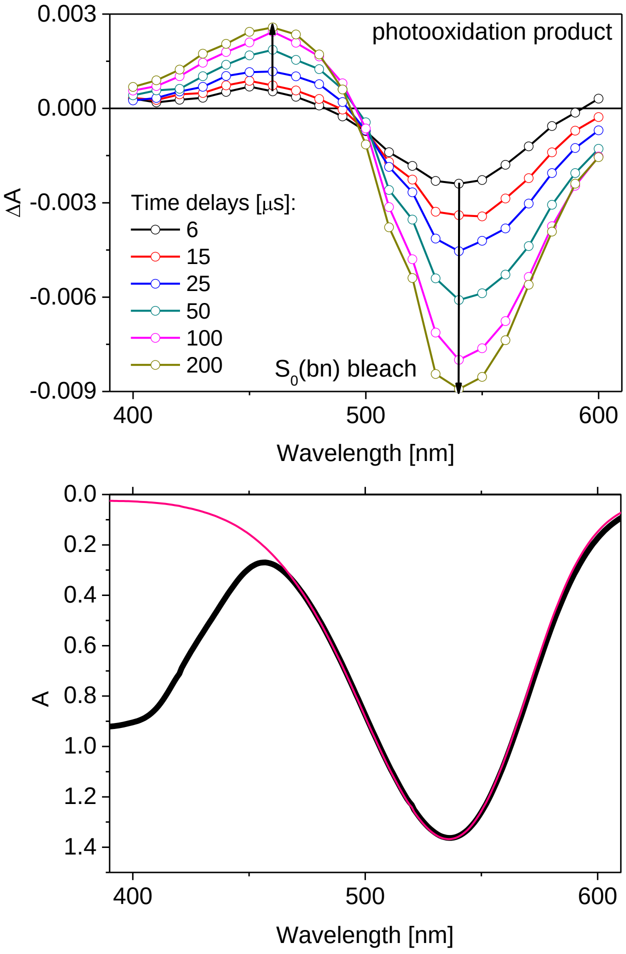
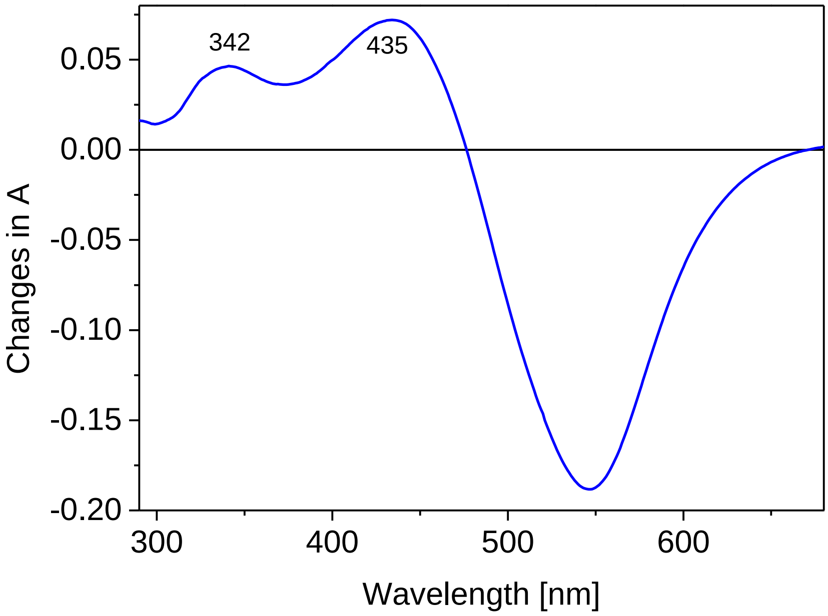
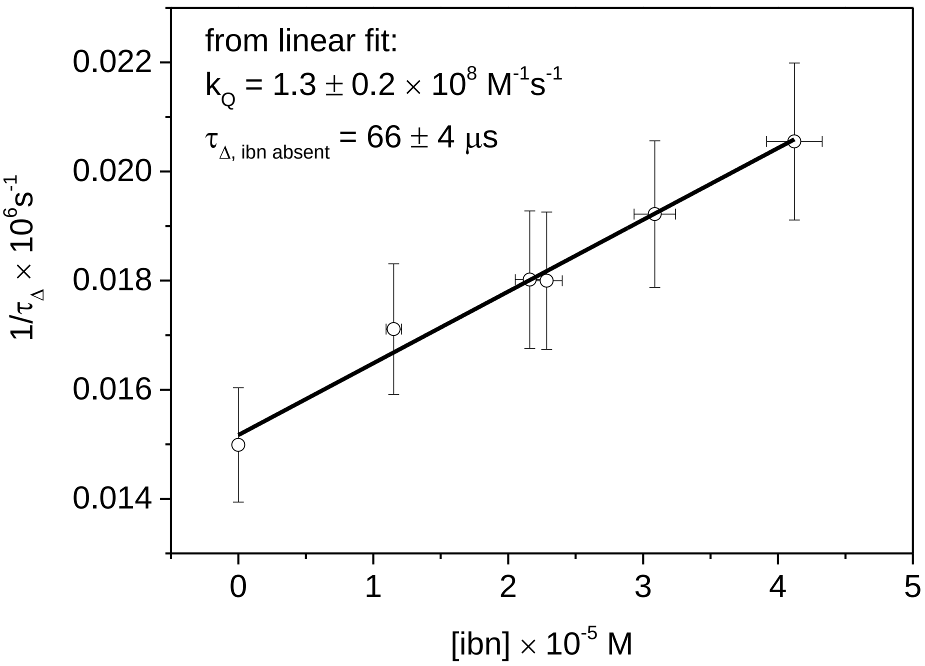


Figure S5. Changes in the stationary UV-vis spectra of solution of perinaphthenone and betanin in D_2O ([**bn**] = 2.3 × 10^{-5} M, [**pn**] = 6 × 10^{-5} M), as a result of laser flash photolysis LFP experiments (λ_{exc}= 355 nm).



The negative band at λ ~ 545 nm corresponds to the loss of betanin, the positive band at λ ~ 435 nm corresponds to the oxidation product, while the second band at 342 nm can be tentatively assigned to hydroxyperinaphthenyl radical accordingly to reference.[3]

Figure S6. Plot of the reciprocal singlet oxygen lifetime ($1/\tau_\Delta$), against the concentration of added isobetanin (**ibn**) to perinaphthenone D_2O solution (λ_{exc} = 394 nm).



References:

1. I. Carmichael and G. L. Hug, Triplet-triplet absorption spectra of organic molecules in condensed phases, *J. Phys. Chem. Ref. Data*, 1986, **15**, 1-250.
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3. N. A. Kuznetsova, A. V. Reznichenko, V. N. Kokin and O. L. Kaliya, Photolysis of 6-substituted phenalenones in deaerated alcohol media, *J. Org. Chem. USSR*, 1982, **18**, 540-544.