Palladium Complexes of Azomethine Derivatives of Porphyrins as Potential Photosensitizers

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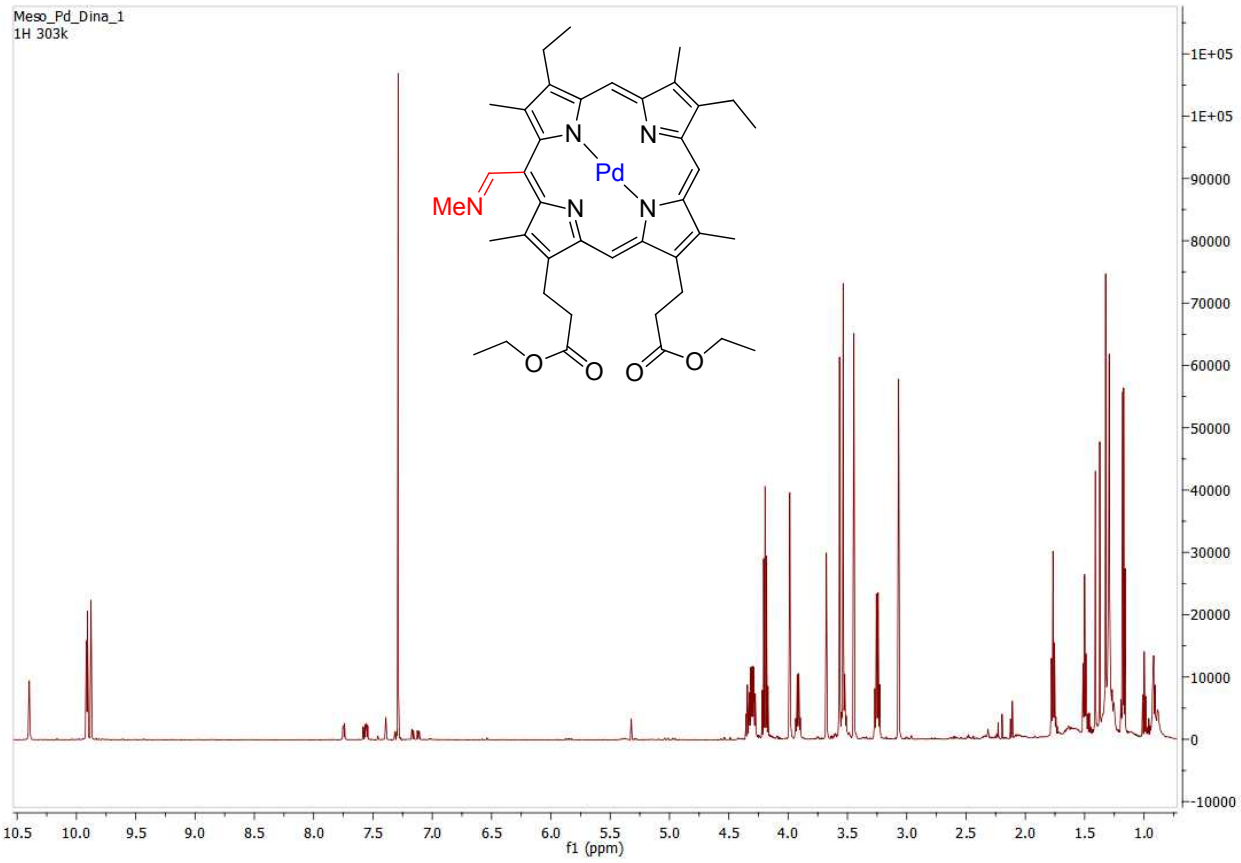
Supporting Information

NMR spectra

In the ^{1}H NMR spectrum of compound **3a** (Figure 1), the signals of three *meso*-H (9.91; 9.91; for 9.88) and one proton signal of the azomethine group (10.40) are in low field.



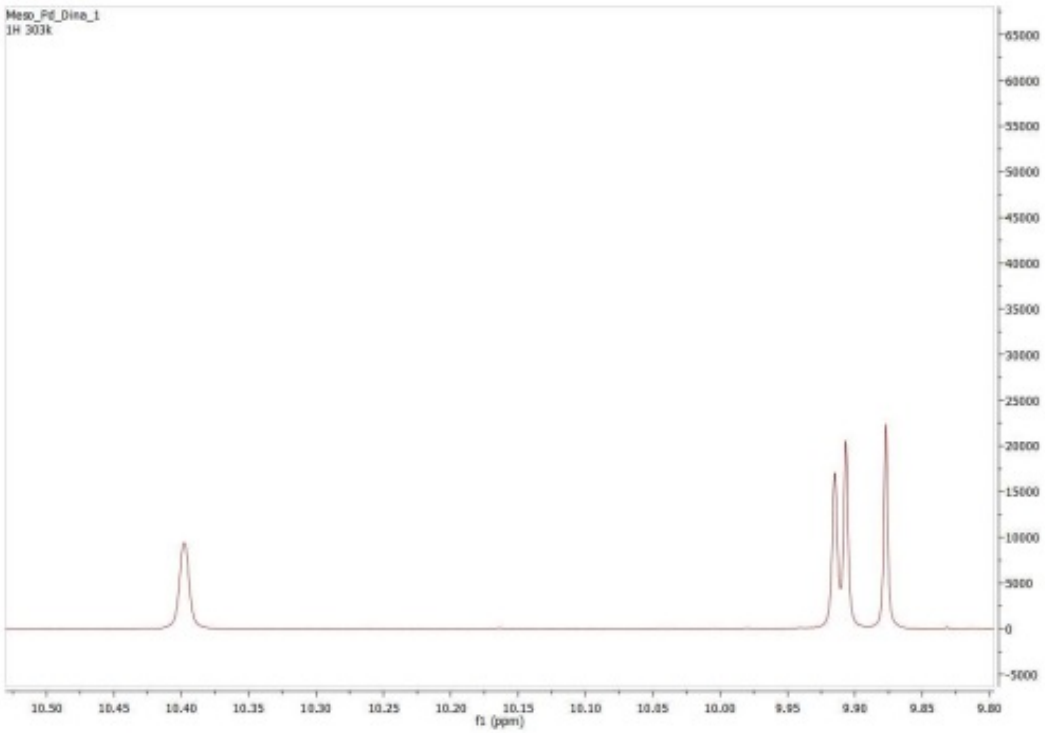


Figure 1.[1]H NMR spectrum of **3a** and the low field fragment.

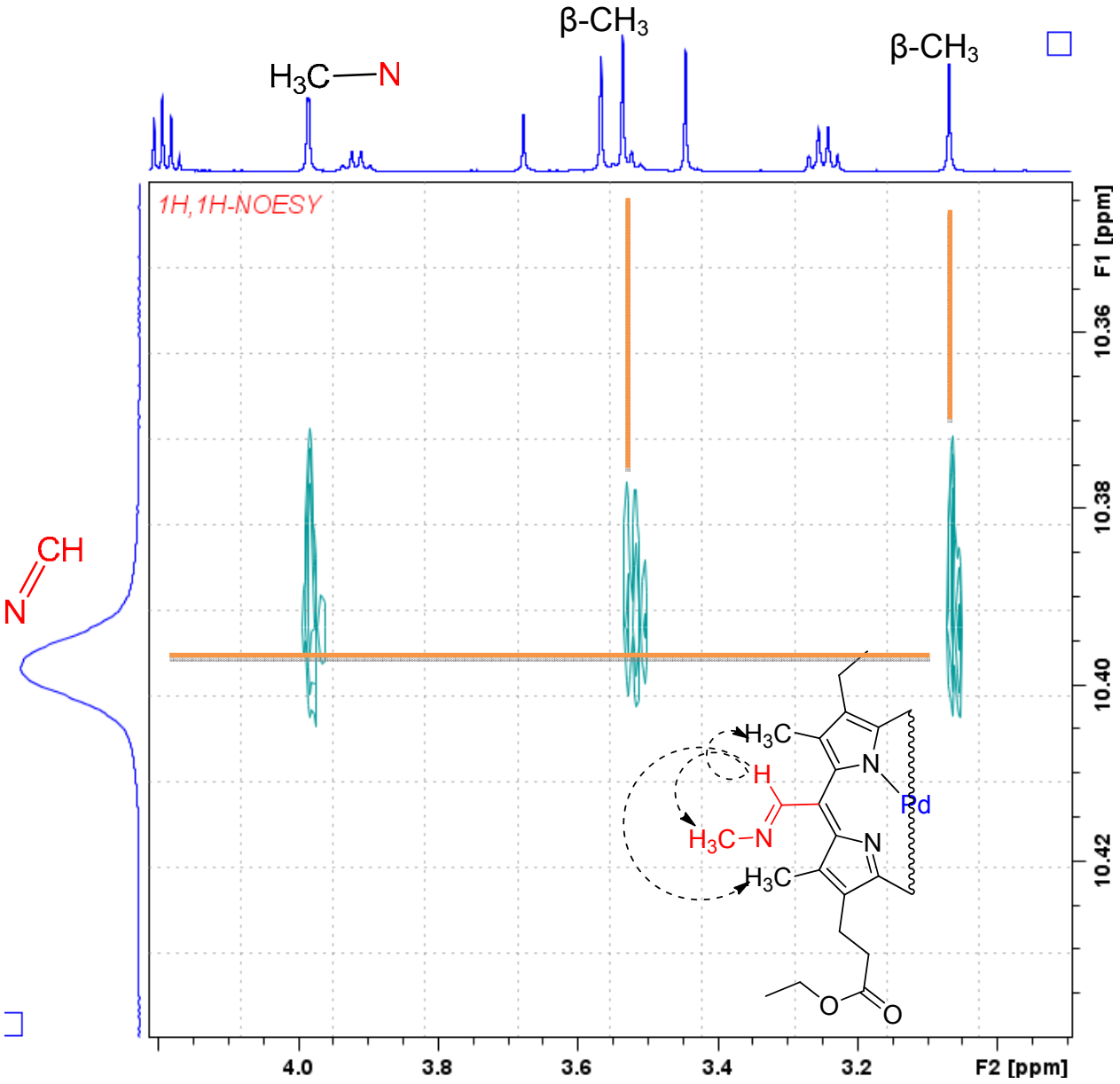


Figure 2.Fragment of NOESY spectrum of **3a.**

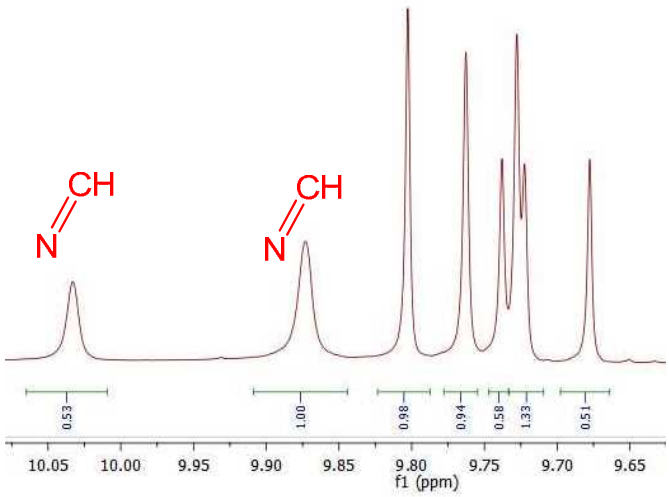


Figure 3. Fragment of [1]HNMR spectrum of isomers **3b** + **3c**.

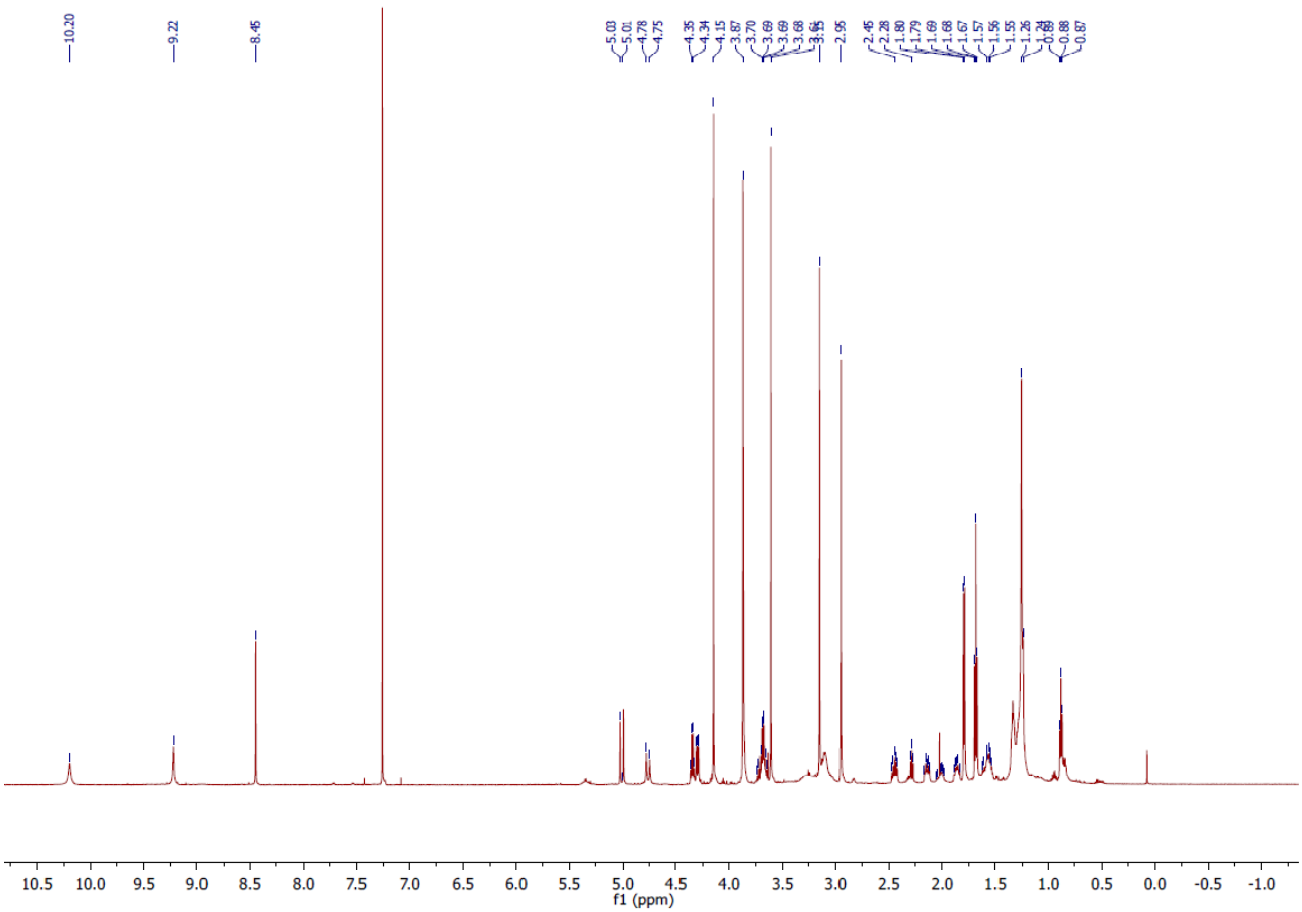


Figure 4.[1]HNMR spectrum **5**.

Mass spectra

On the mass spectra of the four isomers of **3a-d** two molecular ions are present, one corresponds to the Schiff base (M=768), and the other corresponds to cyclopentane derivative molecular ion (M=736) (Figure 5).

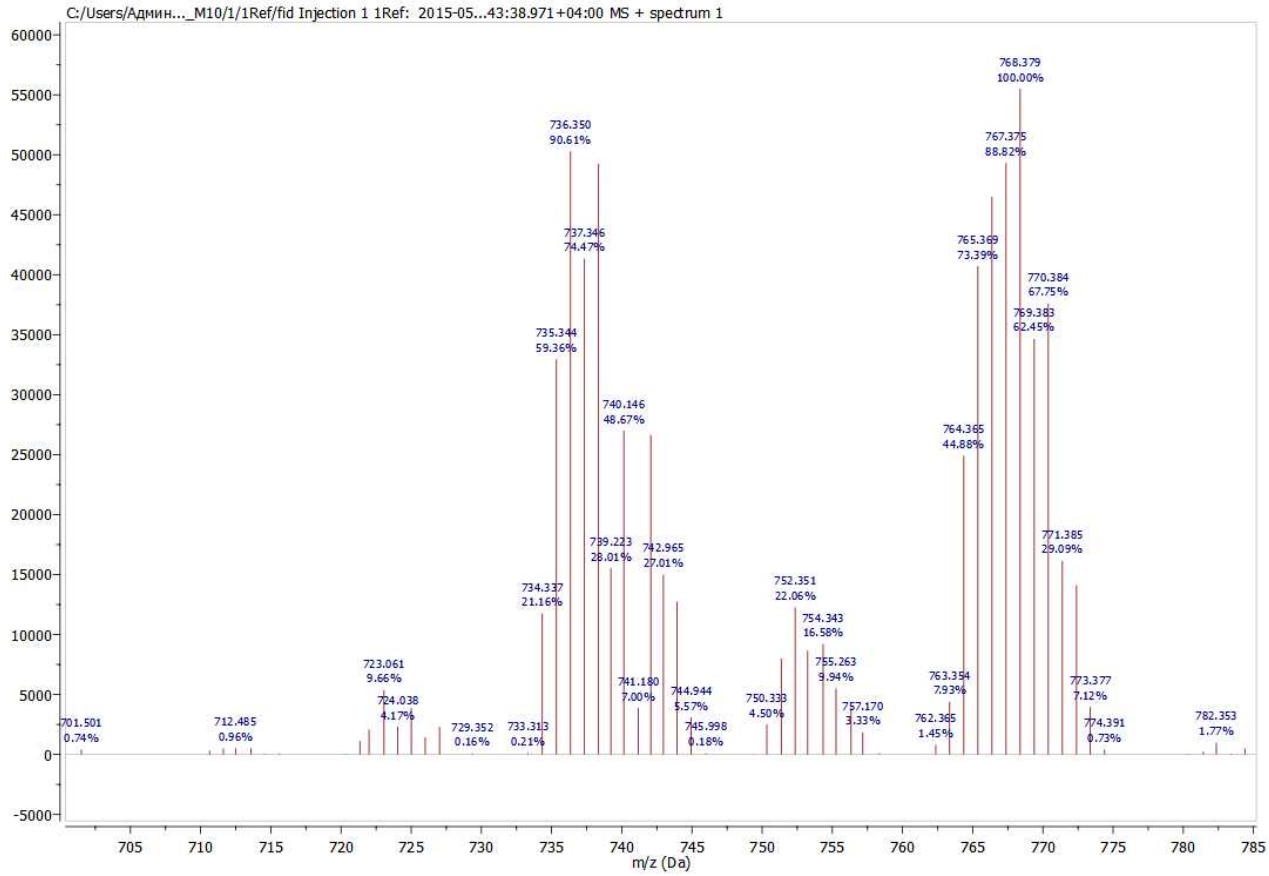


Figure 5. Fragment of the mass spectrum of isomers **3a-d**.

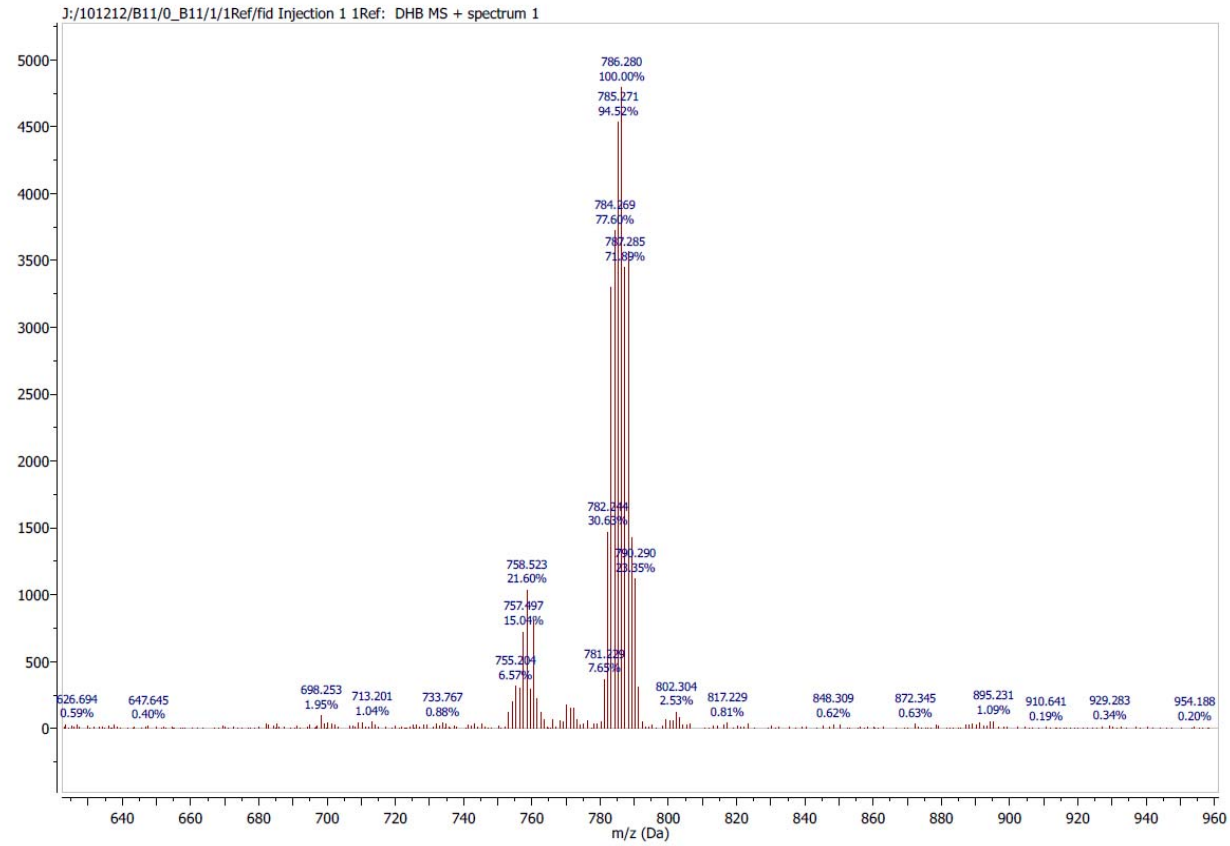


Figure 6.Fragment of the mass spectrum of **4**.

Electronic absorption spectra.

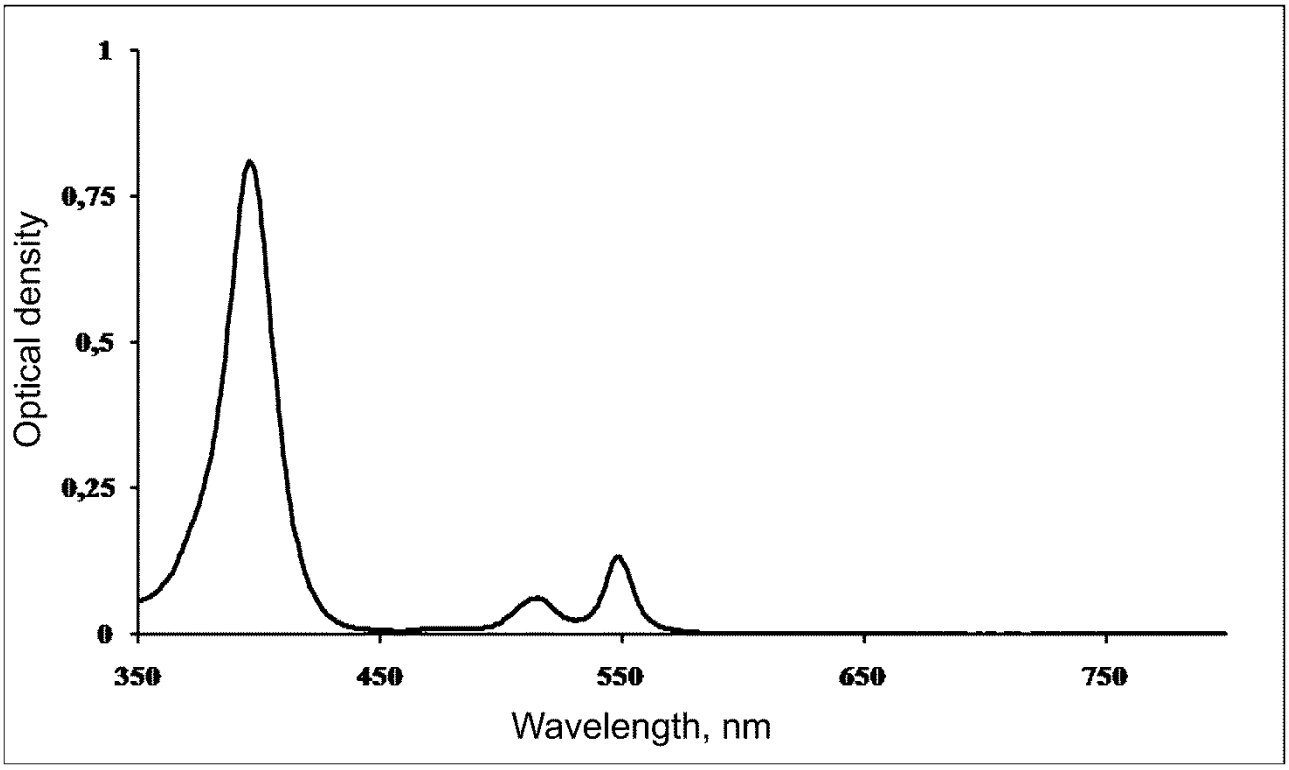


Figure 7. UV-Vis absorption spectra of **8** in acetone.

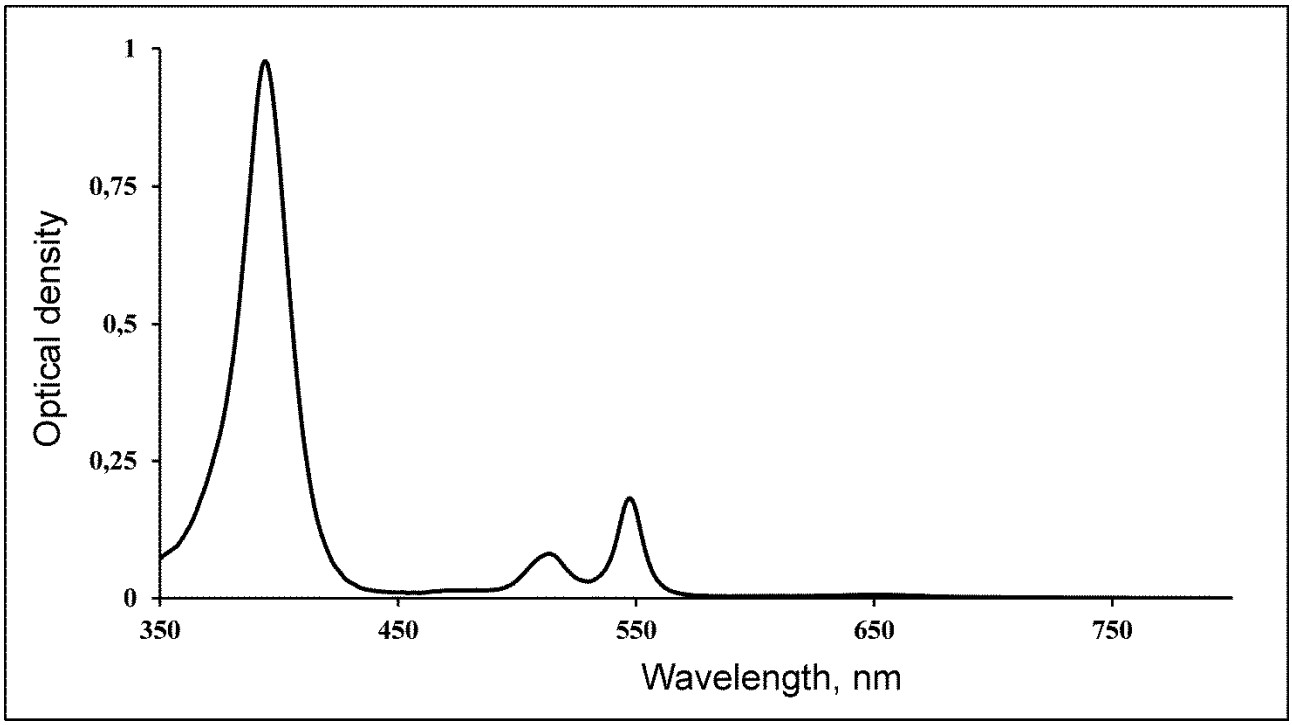


Figure 8. UV-Vis absorption spectra of **9** in acetone.

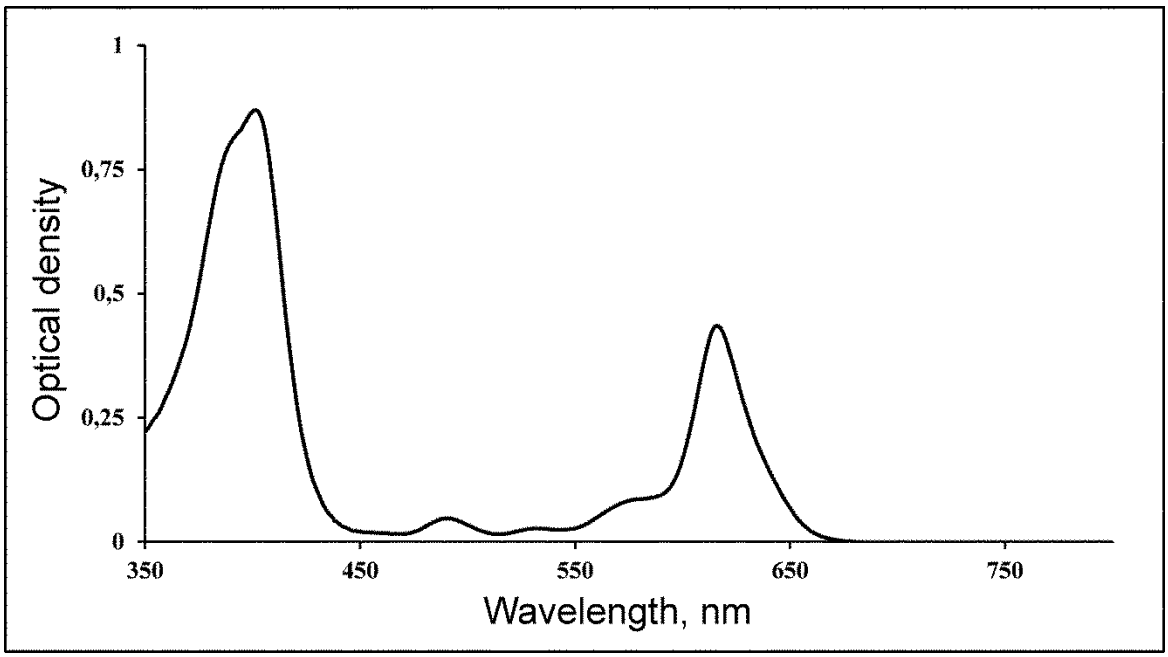


Figure 9. UV-Vis absorption spectra of **5** in acetone.

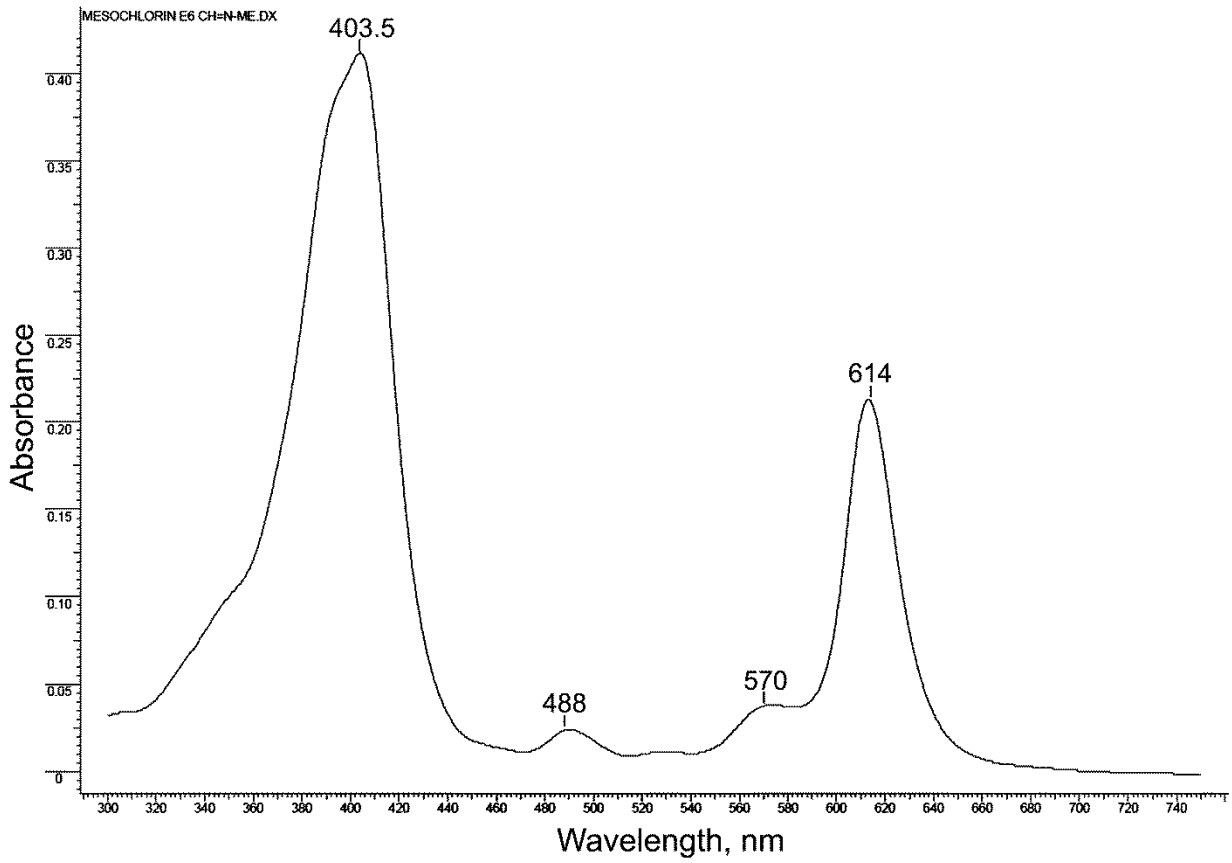


Figure 10. UV-Vis absorption spectra of **4** in acetone.

Photoluminescence spectra.

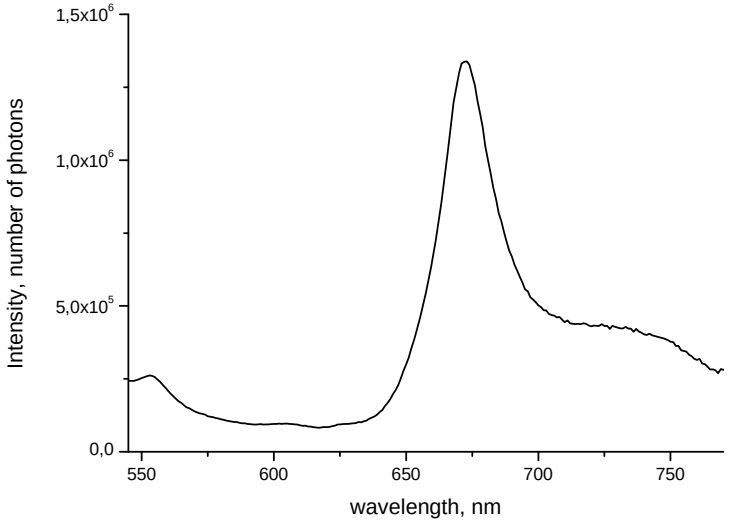


Figure 11. Corrected photoluminescence spectrum of **3a** in polystyrene film. Excitation at 397 nm.

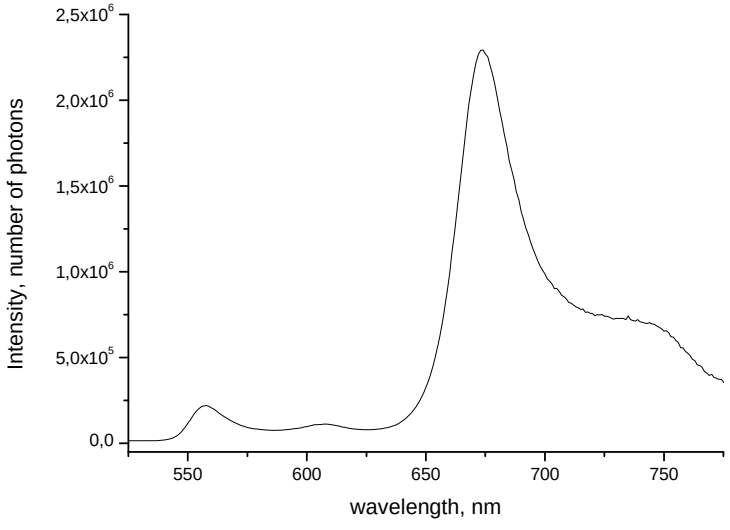


Figure 12. Corrected photoluminescence spectrum of **3b**+**3c** in polystyrene film. Excitation at 397 nm.

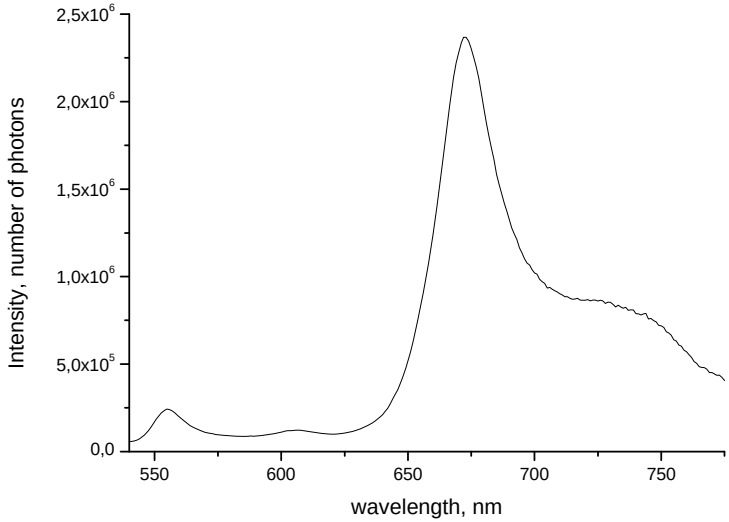


Figure 13. Corrected photoluminescence spectrum of **3d** in polystyrene film. Excitation at 397 nm.

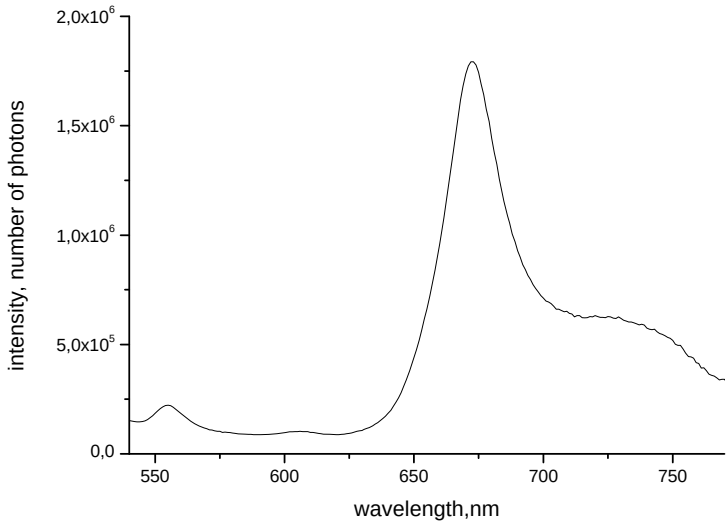


Figure 14. Corrected photoluminescence spectrum of **7** in polystyrene film. Excitation at 397 nm.

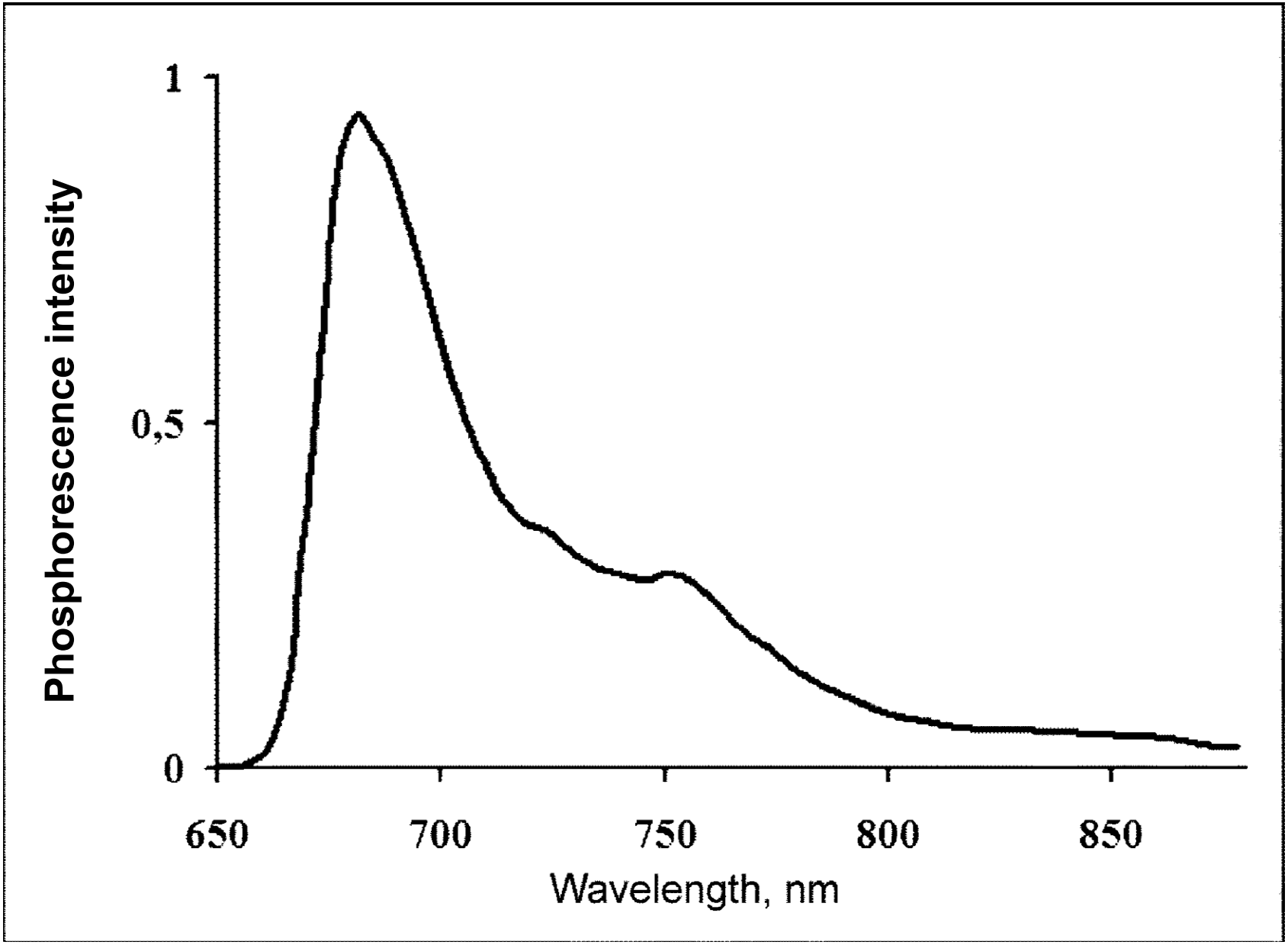


Figure 15. Phosphorescence spectrum of 8 in acetone at 77K

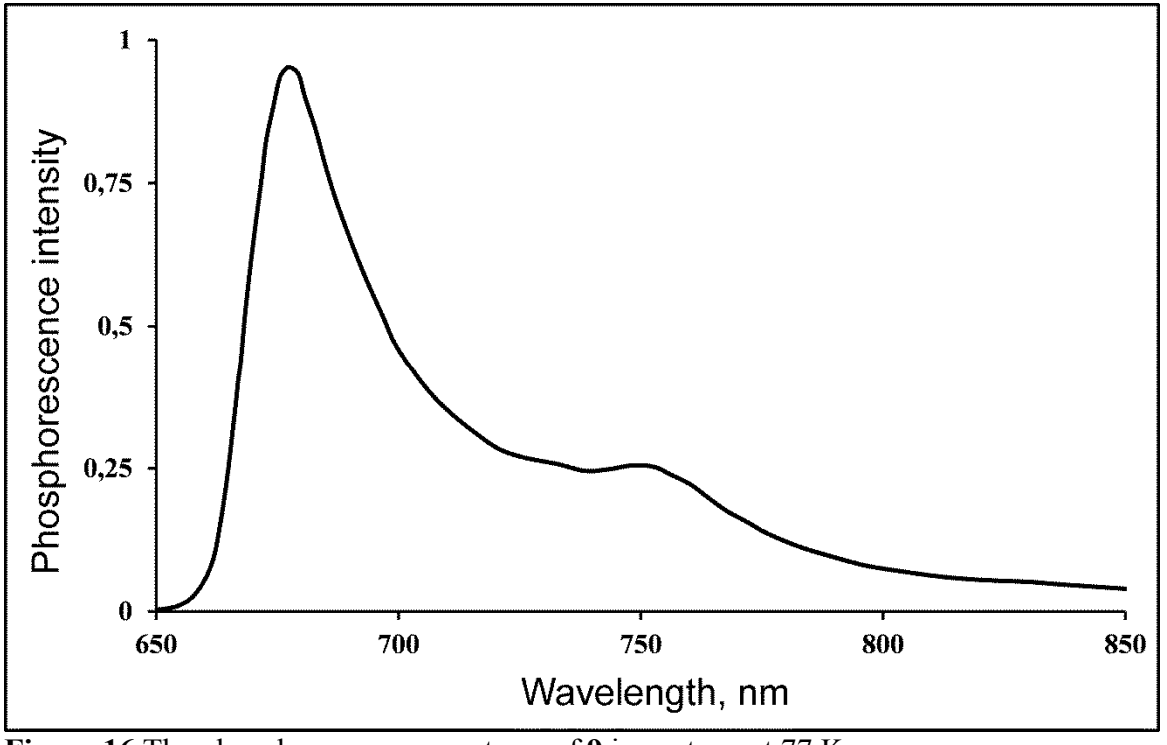


Figure 16.The phosphorescence spectrum of **9** in acetone at 77 K.

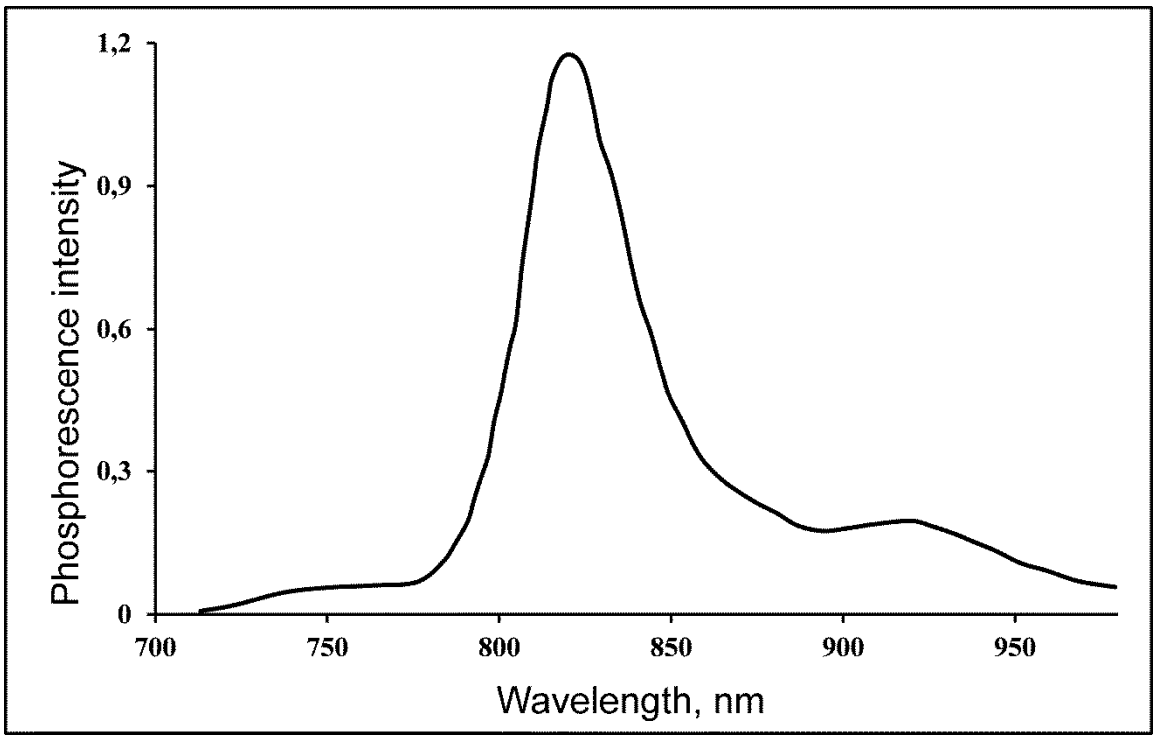


Figure 17.The phosphorescence spectrum of **5** in acetone at 77 K.

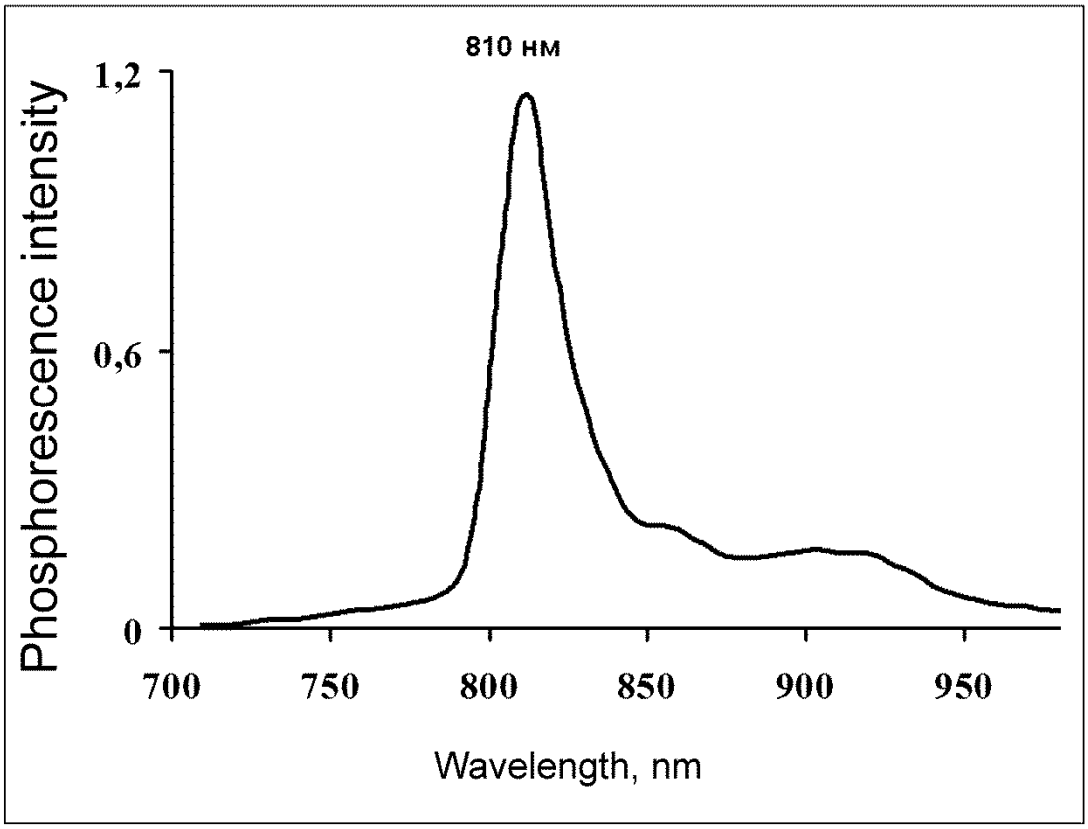


Figure 18.The phosphorescence spectrum of **4** in acetone at 77 K.

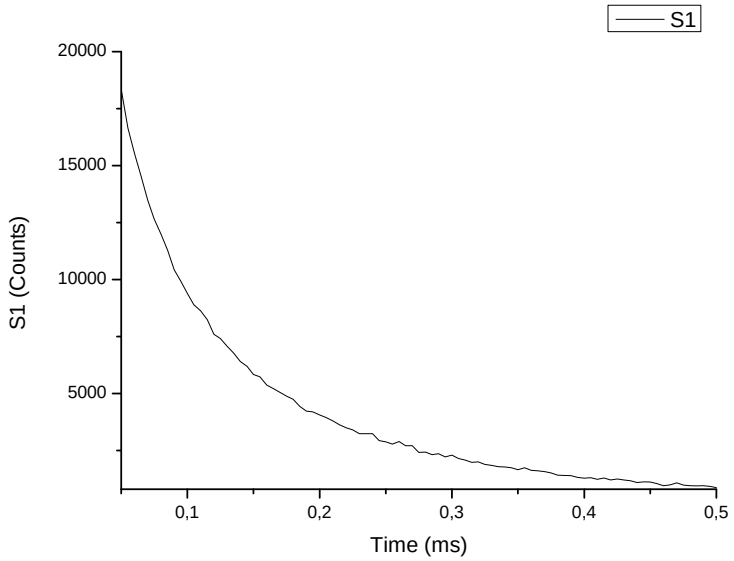


Figure 19.The phosphorescence decay curve for **3a** at 298K(excitation at 397 nm, emission at 670nm) .

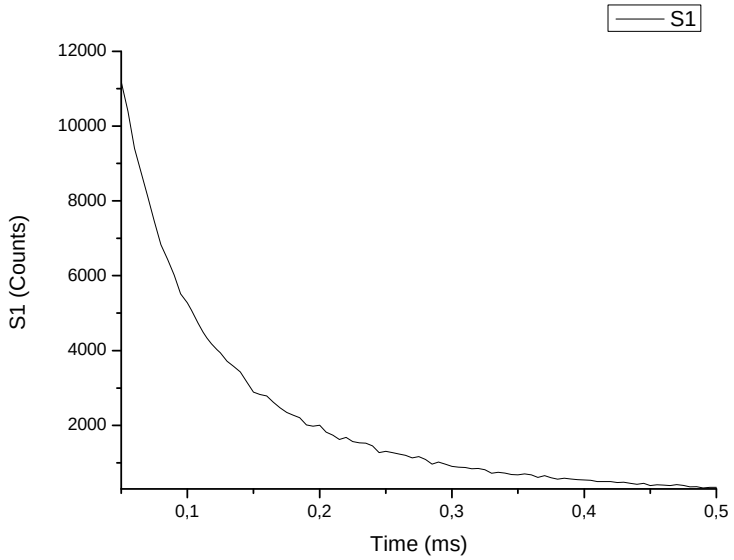


Figure 20.The phosphorescence decay curve for **3b**+**c** at 298K(excitation at 397 nm, emission at 670nm) .

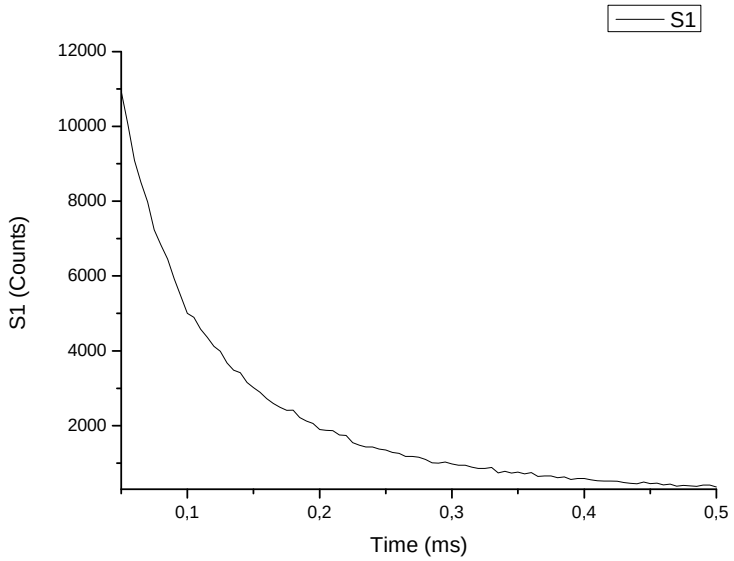


Figure 21.The phosphorescence decay curve for **3d** at 298K(excitation at 397 nm, emission at 670nm) .

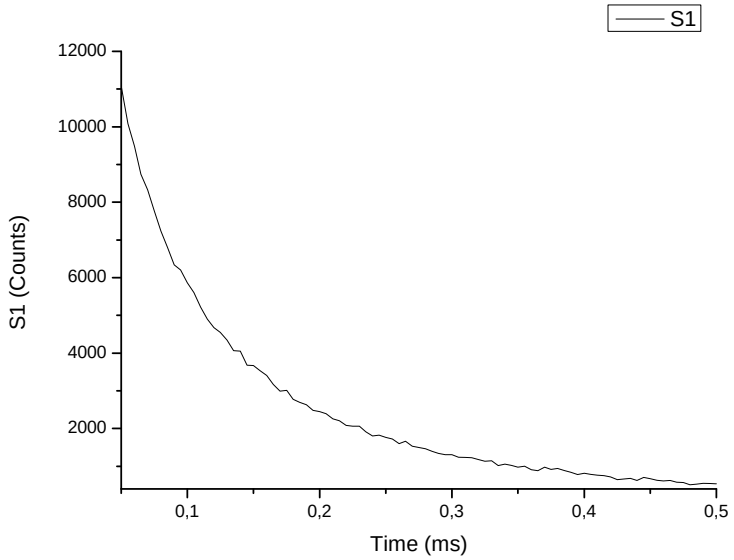
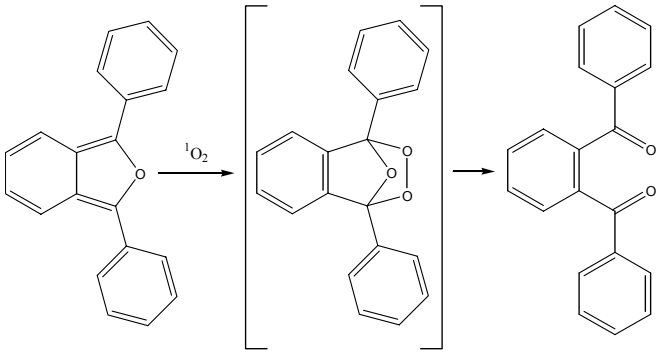


Figure 22.The phosphorescence decay curve for **7** at 298K(excitation at 397 nm, emission at 670nm).

Calculation of singlet oxygen yield

Quantum yield of singlet oxygen generation by the studied compounds was determined by the relative method using chemical traps. The standard compound was TPP (*meso*-tetraphenylporphin). According to literature data, the most probable value of the quantum yield of singlet oxygen generation by TPP in acetone was 0.65 ± 0.05.[1,2] 1,3-Diphenylisobenzofuran (DPIBF) was used as a chemical trap. The interaction of this trap with singlet oxygen proceeds by chemical reaction is shown on the scheme below.[3] The products of the reaction have no absorption bands in the visible spectrum. Therefore, the amount of singlet oxygen formed during the photoreaction can be measured by loss of optical density in the maximum absorption DPIBF.



Solutions of the investigated compounds and DPIBF in a fixed volume of solvent were prepared for the determination of quantum yields of singlet oxygen generation. Measurements were performed in square quartz fluorescence cuvettes with optical path length 1 cm. The solutions were irradiated for a certain time with the light from a xenon lamp fluorimeter Perkin Elmer MPF-44B passing through the monochromator. Light intensity was measured using a ThorLabs unit PM-100D with sensor head S120VC (Germany). Samples were irradiated with the wavelength of light, selected based on the position of the maximum wavelength of the green band of compound (550 nm). The spectral slit width of the monochromator of the fluorimeter corresponds to 5 nm. Not only the change of optical density at the maximum of absorption of DPIBF, but also at the wavelength of the exciting light was controlled at irradiation. During the irradiation the absorption band of the sensitizer do not fade, i.e. the optical density of sensitizer at the wavelength of the exciting light did not change. The optical density was determined using a two-beam spectrophotometer Hitachi U-3400. DPIBF concentration in the sample was selected so that its optical density in the maximum absorption was 0.80-1.10.

When calculating quantum yield by relative method the comparison of the loss of DPIBF optical density and the irradiation time in the experiments performed for the compound under investigation and standard compound. Three experiments were carried out with standard compound and four experiments were carried out with compound under investigation. The calculation was performed according to the following formula

$$\varphi_{\Delta} = \varphi_{\Delta St} \cdot \frac{\Delta D_C \cdot t_{irrSt} \cdot I_{St} \cdot (1-10^{-D_{St}}) \cdot \lambda_{St}}{\Delta D_{St} \cdot t_{irrC} \cdot I_C \cdot (1-10^{-D_C}) \cdot \lambda_C},$$

Where $\varphi_{\Delta St}$ is the quantum yield of generation of singlet oxygen standard compound; ΔD_C is the average loss of optical density of DPIBF in the experiments with the test compound, ΔD_{St} is the average loss of optical density DPIBF in experiments with the standard compound, t_{irrC} is the duration of irradiation of the mixture DPIBF with compound under investigation in sec, t_{irrSt} isthe duration of irradiation of the mixture CFIBF with standard compound in sec, I_C and I_{St} are intensities of the light flux from the xenon lamp in the experiments with the test connection and the standard compound in μw, D_C and D_{St} are optical densities of the compound under investigation and standard compound corresponding to the wavelengths of the exciting light λ_C and λ_{St} (in nm).

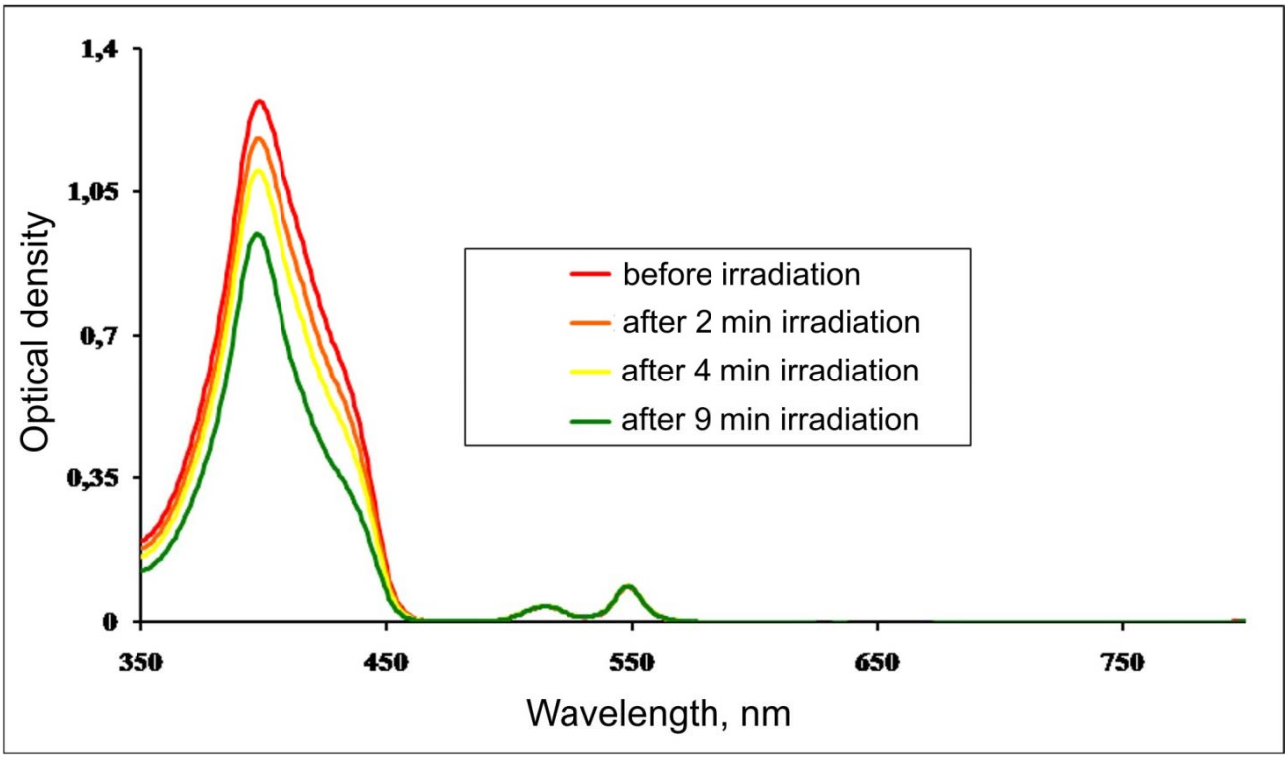


Figure 23.Absorption spectra of mixtures of **8** and DPIBF in acetone before and after irradiation at 550 nm in the presence of oxygen.

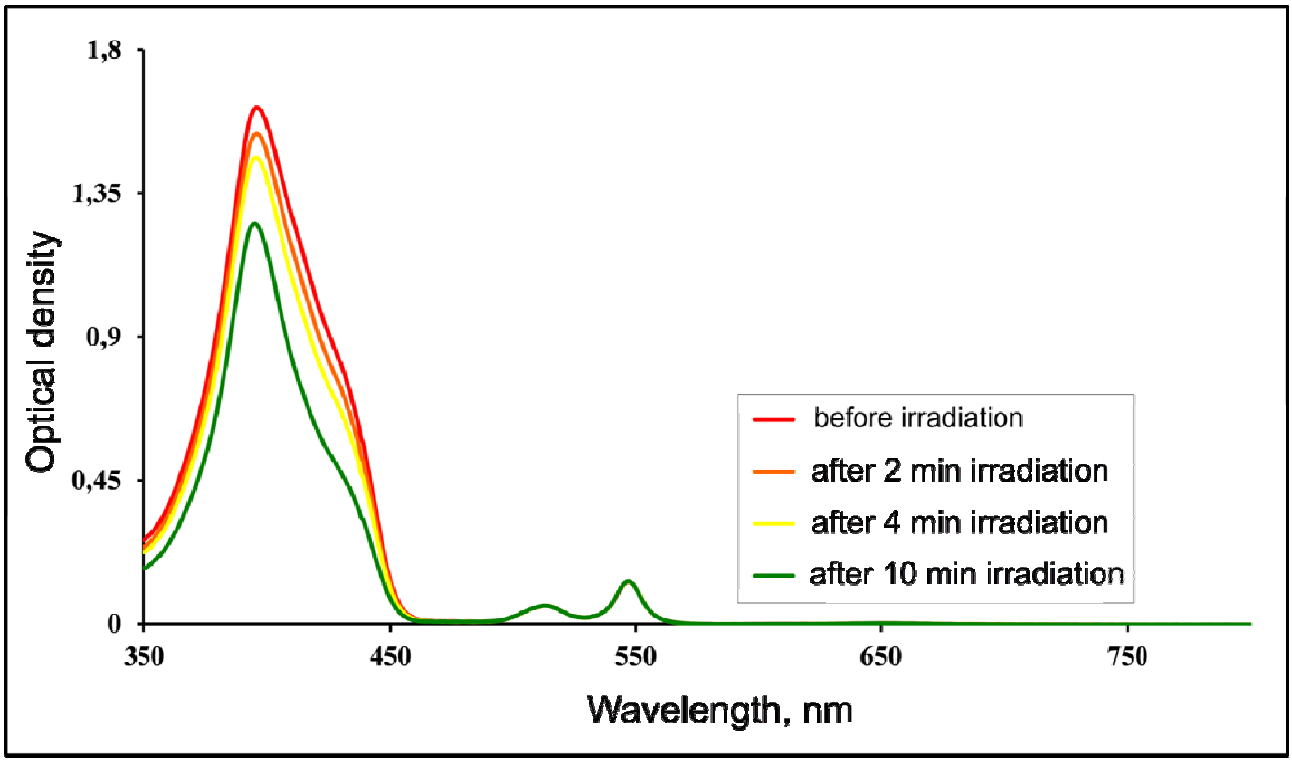


Figure 24.Absorption spectra of mixtures of **9** and DPIBF in acetone before and after irradiation at 550 nm in the presence of oxygen.

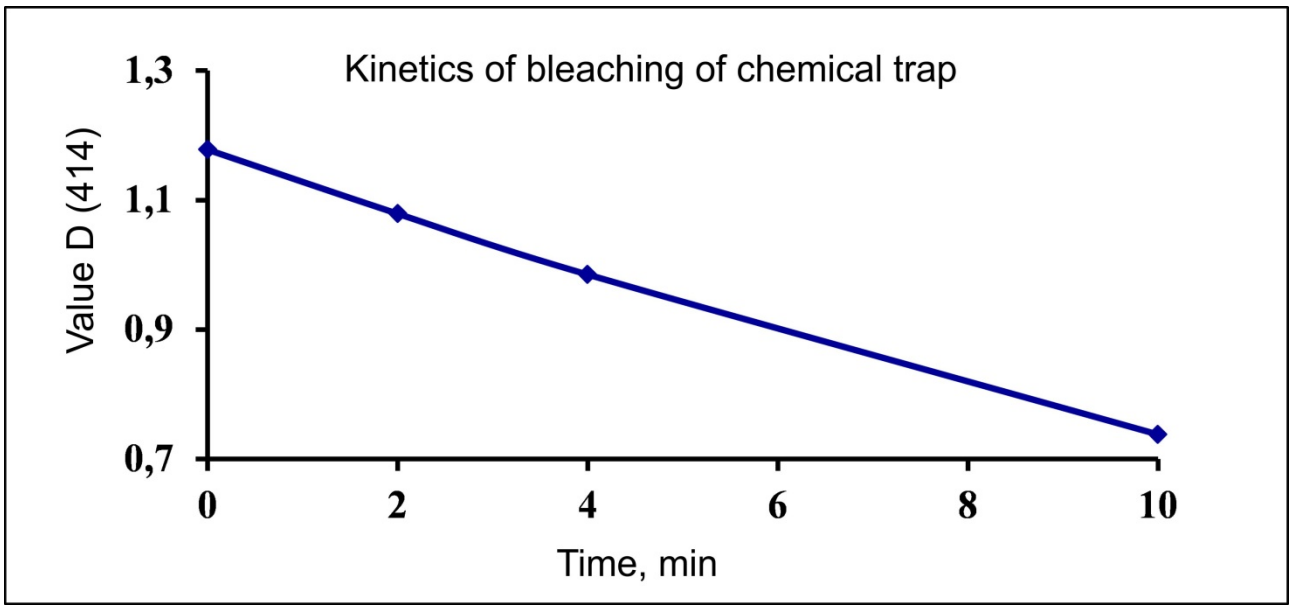


Figure 25.The kinetics of bleaching of DPIBF upon irradiation of the mixture with **9**.

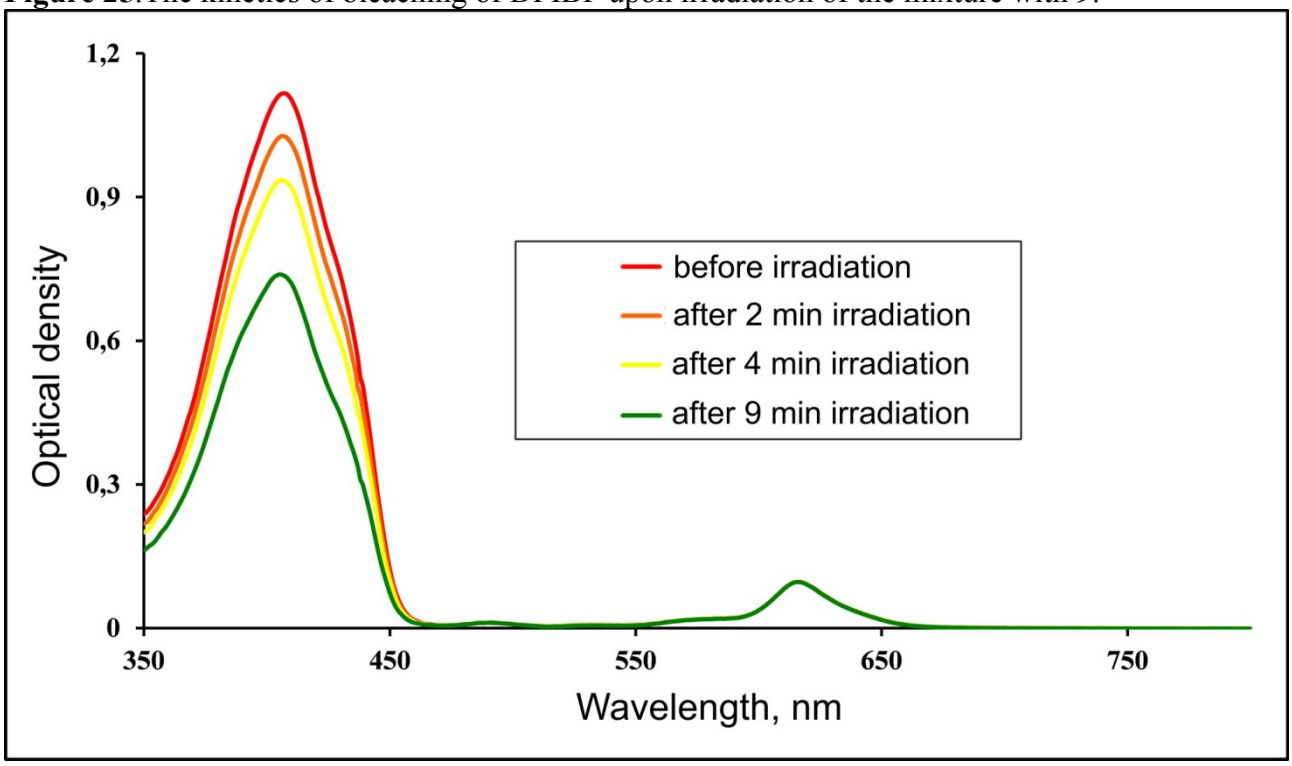


Figure 26.The UV-Vis absorption spectra of the mixture **5** and DPIBF in acetone before and after irradiation at 615 nm in the presence of oxygen.

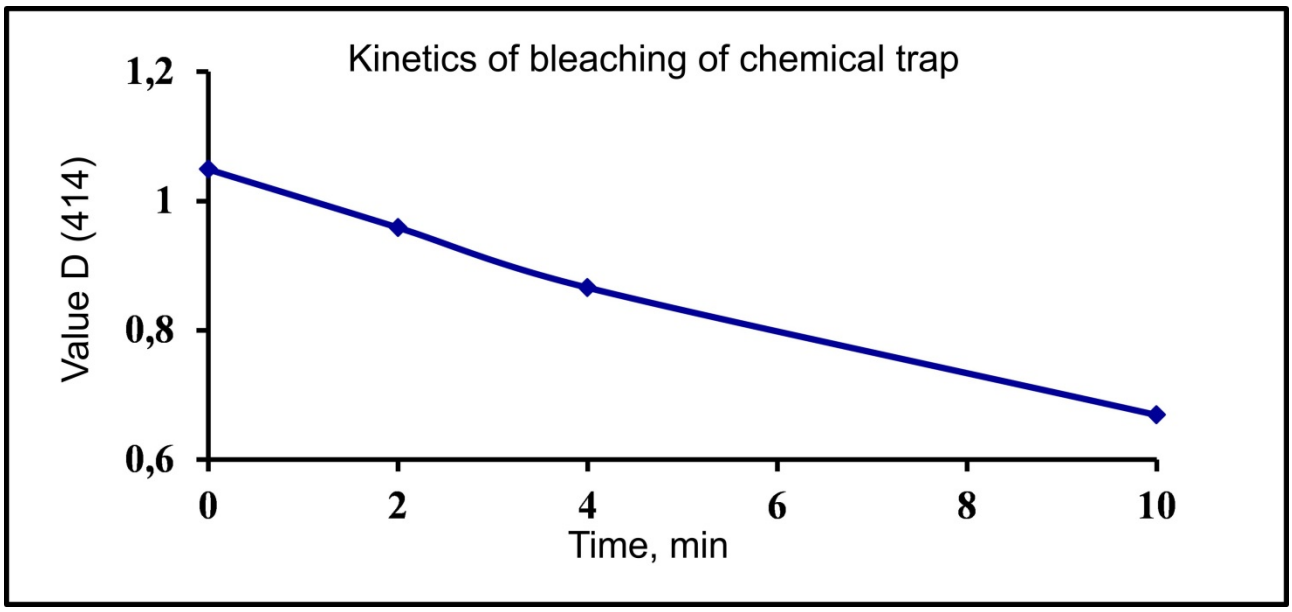


Figure 27.The kinetics of bleaching of DPIBF upon irradiation of the mixture with **5**.

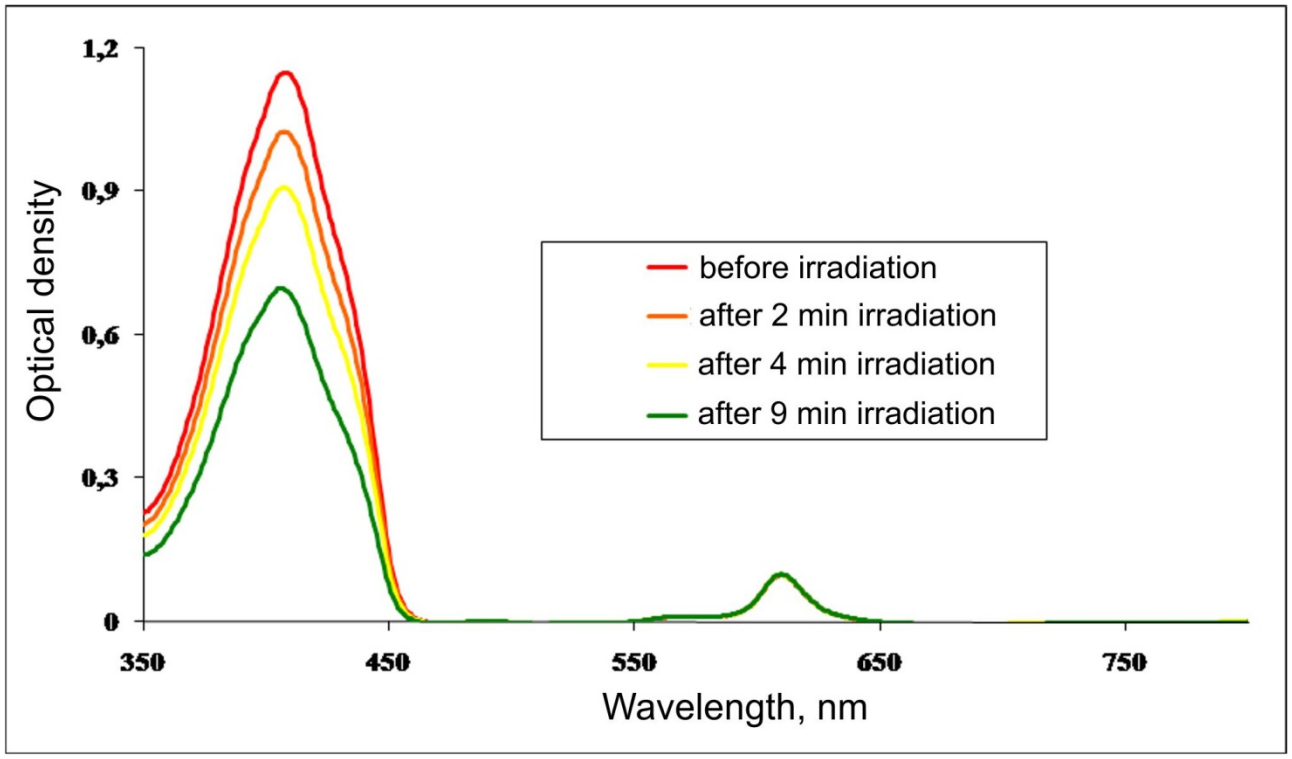


Figure 28.The UV-Vis absorption spectra of the mixture **4** and DPIBF in acetone before and after irradiation at 613 nm in the presence of oxygen.

Table 1.Irradiation data of palladium complexes in the presence of DPIBF and oxygen in acetone.

	Compounds	λ, nm	I, μw	T_{irr}, s	ΔD_c, ΔD_{St}*	D_c or D_{st}*	φ
1	**8** +DPIBF	550	94	120	0.136	0.115	1.00±0.07
	TPP+DPIBF	512	105	600	0.112	0.026	0.65±0.05
2	**9** +DPIBF	545	97	120	0.14	0.114	1.00 ± 0.05
	TPP+DPIBF	512	105	600	0.112	0.026	0.65 ± 0.05
3	**5** +DPIBF	615	107	120	0.176	0.116	1.00 ± 0.05
	TPP+DPIBF	512	105	600	0.112	0.026	0.65 ± 0.05
4	**4** +DPIBF	613	98	120	0.18	0.134	1.00±0.07
	TPP+DPIBF	512	105	600	0.113	0.026	0.65±0.05

* Averaged values across multiple experiments.

References:

1. KrasnovskyA.A. *Jr*., KozlovA.S., RoumbalYa.V.*Photochem. Photobiol. Sci.* **2012**, *11*, 988-997. http://dx.doi.org/10.1039/c2pp05350k
2. WilkinsonF., HelmanW.P., RossA.B.*J. Phys. Chem. Ref. Data***1993**, *22*, 113-262. http://dx.doi.org/10.1063/1.555934
3. YoungR.H., Brewer D., KellerR.A.*J. Am. Chem. Soc.* **1973**, *95*, 375-379. http://dx.doi.org/10.1021/ja00783a012