

## Supporting Information to paper

### Mechanism of Photochromic Transformations and Photodegradation of an Asymmetrical 2,3-Diarylcyclopentenone

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\*Numbering of references corresponds to the main paper.

#### Part S1. Determination of parameters of diarylethene photochromic transformations

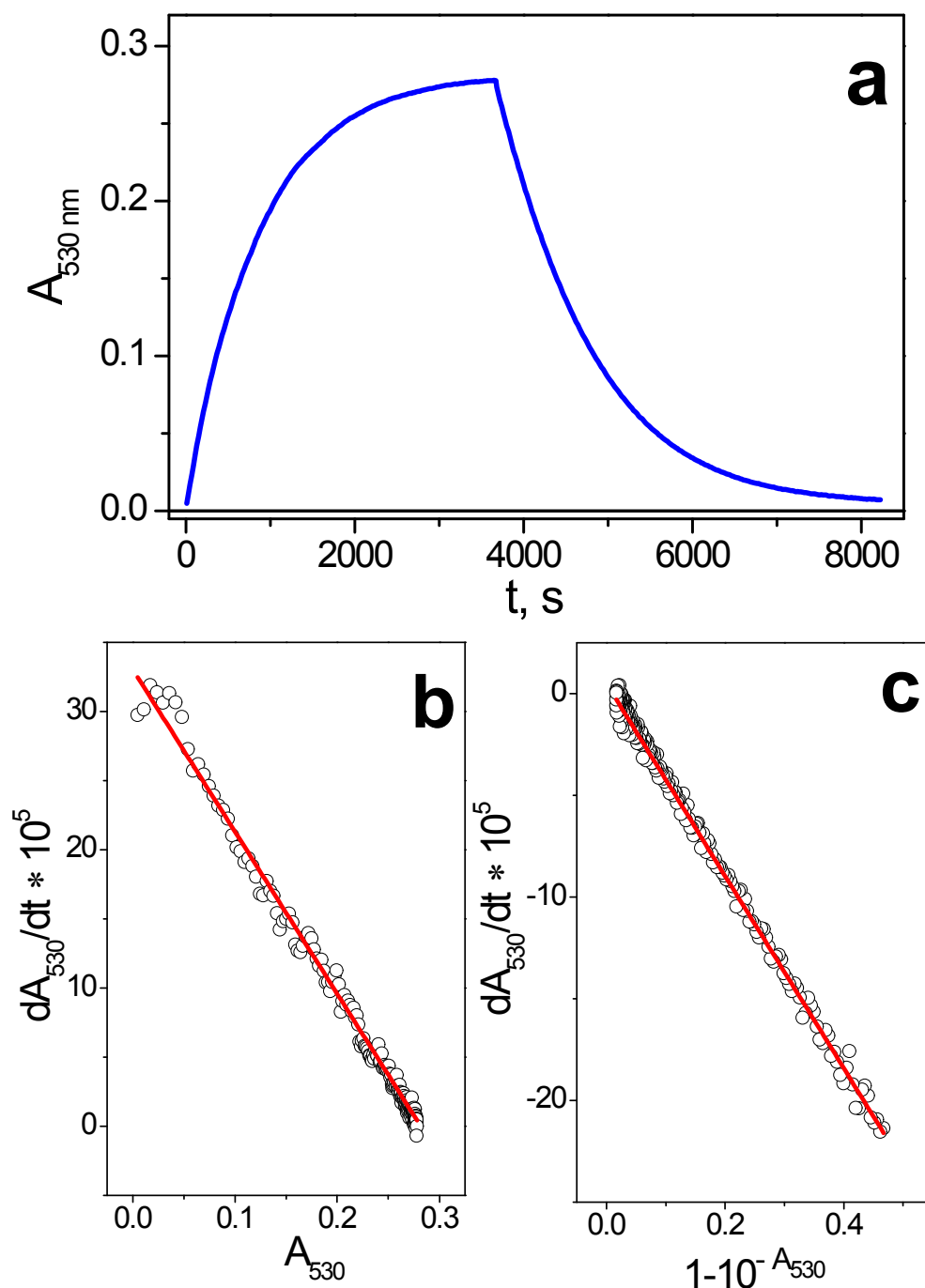
Quantum yields of compound **1** ring closure ( $\varphi_{AB}$ ) and opening ( $\varphi_{BA}$ ) and molar absorption coefficient ( $\varepsilon_B$ ) of the closed form in the maximum of its absorption band (540 nm) were determined spectrophotometrically using photokinetic method described in [38]. The equations (1) and (2) were used for analysis of the kinetic curves of photocoloration (irradiation at 313 nm, which correspond to the isosbestic point of **1A** and **1B** spectra), and photobleaching (irradiation at 530 nm, Fig. S1a).

$$\frac{dA_{530}}{dt} = \varphi_{AB} \varepsilon_{313} L C_0 \varepsilon_{530} L I_{313} F_{313} - (\varphi_{AB} + \varphi_{BA}) \varepsilon_{313} L I_{313} F_{313} A_{530} \quad (S1)$$

$$\frac{dA_{530}}{dt} = -\varphi_{BA} \varepsilon_{530} L I_{530} (1 - 10^{-A_{530}}) \quad (S2)$$

In equations (S1, S2)  $\varepsilon_{313}$  is the molar absorption coefficient at the isosbestic point (313 nm),  $\varepsilon_{530}$  is the molar absorption coefficient of the B-form at 530 nm,  $L$  is the optical path length,  $C_0$  is the initial concentration of **1**,  $I_\lambda$  is the incident light intensity,  $A_\lambda$  and  $F_\lambda = (1 - 10^{-A_\lambda}) / A_\lambda$  are absorption and photokinetic factor at the wavelength  $\lambda$ . Difference between molar absorption coefficients of the closed form at wavelengths 540 nm (maximum of the absorption band) and 530 nm (irradiation wavelength) is less than 2%.

Equation (S1) describes increase in maximal absorption of the closed form band (530 nm) upon the UV irradiation of a sample. The change in absorption caused by photobleaching caused by the visible irradiation (Eq. S2) was recorded at the wavelength of 530 nm upon irradiation of the sample at the same wavelength. Equations (S1, S2) were obtained in assumption that the quantum yield of the reverse reaction does not depend of irradiation wavelength; this is usually performed for diarylethenes.



**Figure S1.** Determination of photochromic parameters for compound 1 in  $\text{CH}_3\text{CN}$ . Concentration  $4.4 \times 10^{-5}$  M, 1 cm cell, air-saturated solutions, sample volume 3 mL. a – photokinetic curves (ascending part of the curve corresponds to photocoloration caused by irradiation at 313 nm; descending part corresponds to photobleaching caused by irradiation at 530 nm). (b), (c) – data treatment according Eqs. (S1) and (S2). Data points are the experimental results, red lines are the best fits. Parameters or linear dependencies  $y = ax + b$ : panel (b):  $a = -117.4 \pm 0.8$ ;  $b = 33.04 \pm 0.2$ . Panel (c):  $a = -47.3 \pm 0.2$ ;  $b = 0.49 \pm 0.04$ .

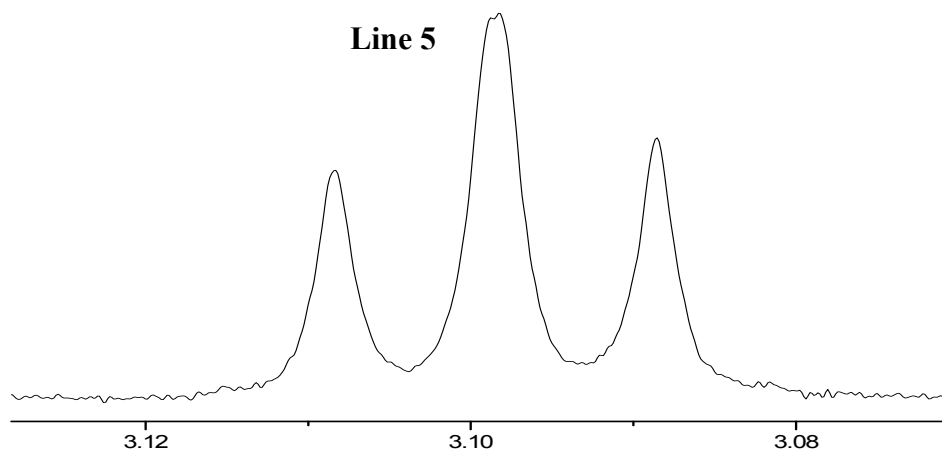
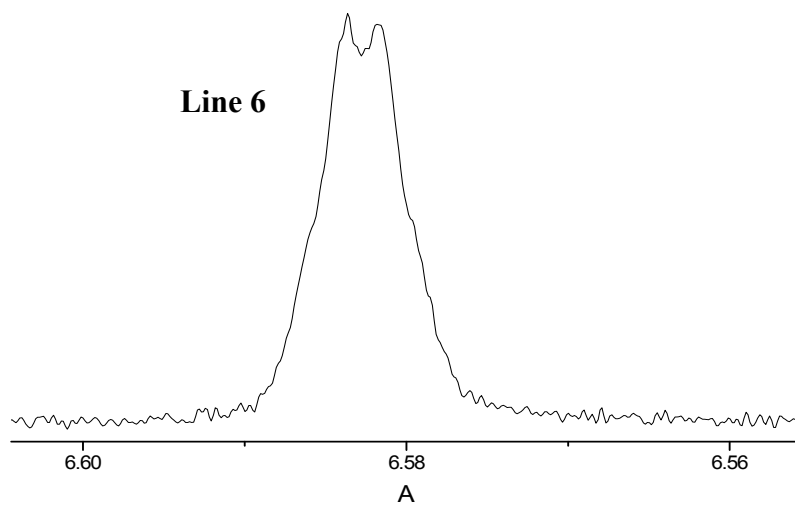
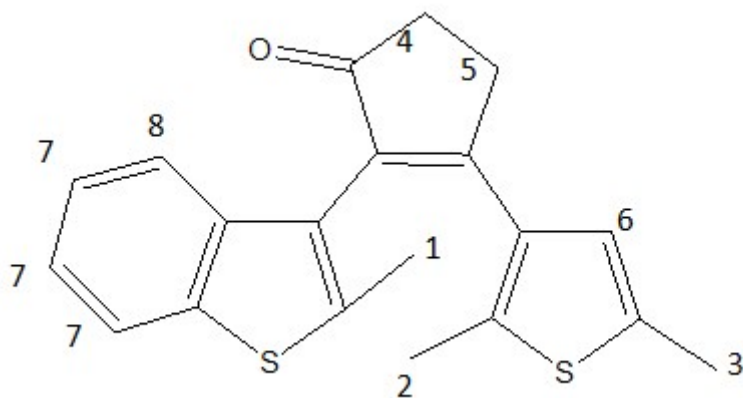
Equations (S1, S2) were linearised by plotting the dependence of the derivative  $\frac{dA_{530}}{dt}$  on the value of  $A_{530}$  for photocoloration and  $(1-10^{-A_{530}})$  for photobleaching (Figs. 1S b, c). The tangent of the inclination angle and cutoff of the linearized form were extracted from the Eq. S1 plot, and the tangent of the inclination angle was extracted from the Eq. S2 plot. Three unknown parameters  $\varphi_{AB}$ ,  $\varphi_{BA}$  and  $\varepsilon_{530}$  were calculated from the three parameters of the two linear dependencies (Eqs. S1, S2). The results were averaged over three independent experiments. The values obtained are shown in Table. 1 of the main text.

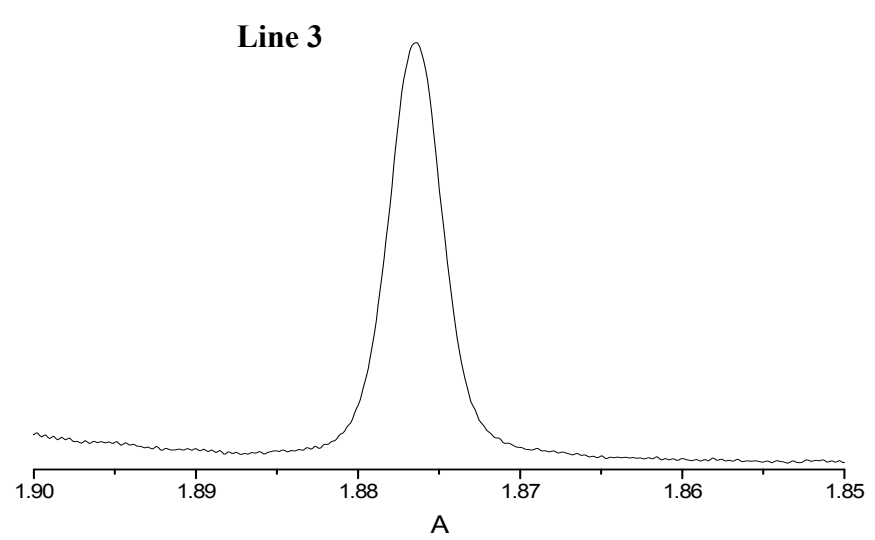
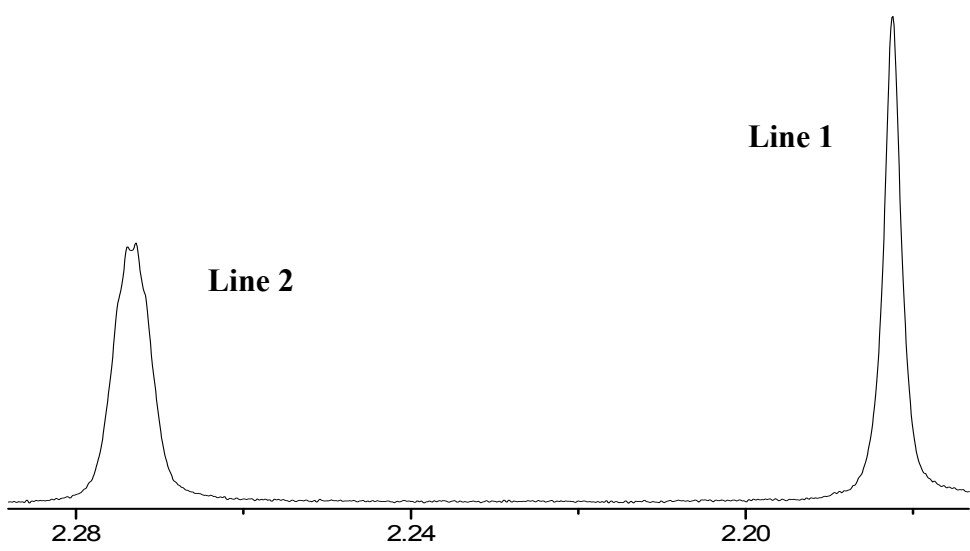
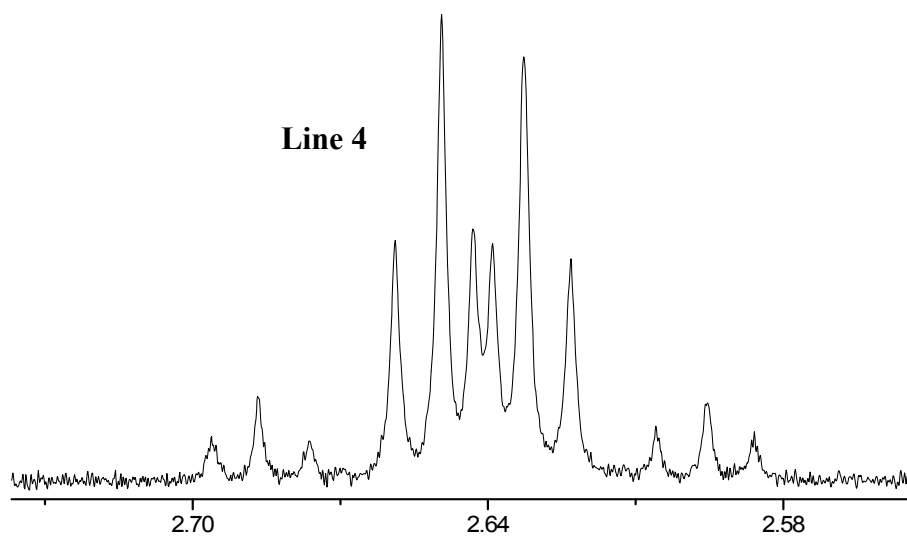
### Reference

[38] S. Delbaere, G. Vermeersch, J.C. Micheau, *J. Photochem. Photobiol. C: Photochem. Rev.* **2011**, *12*, 74.

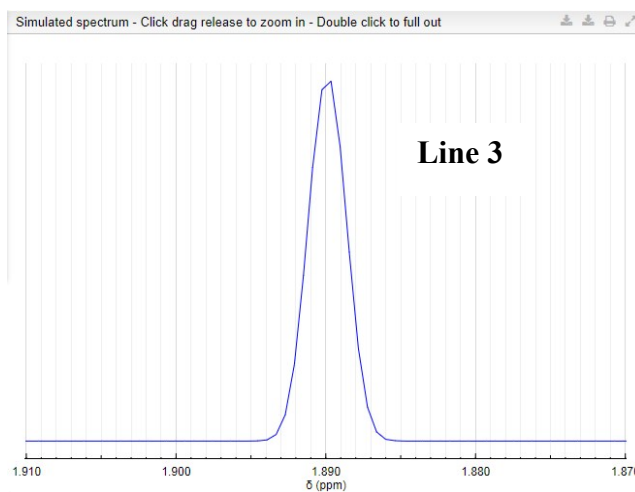
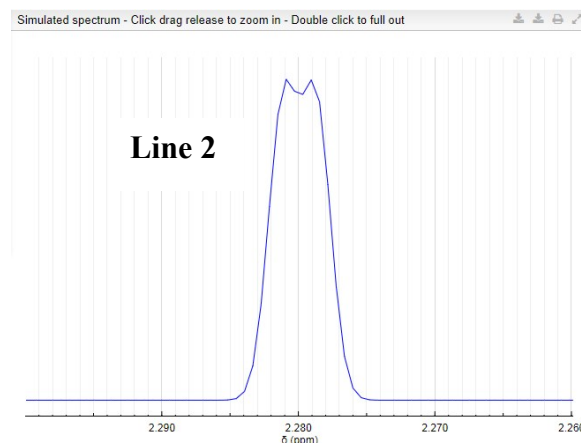
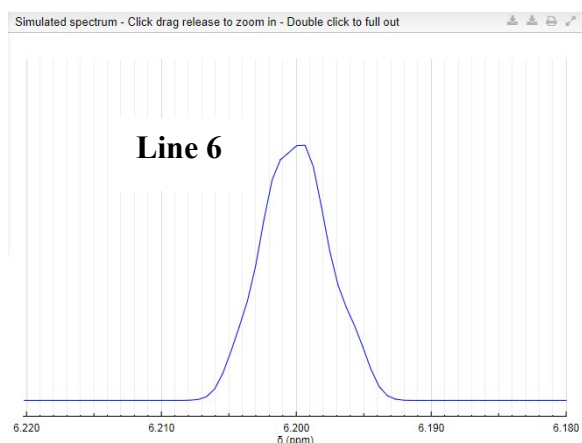
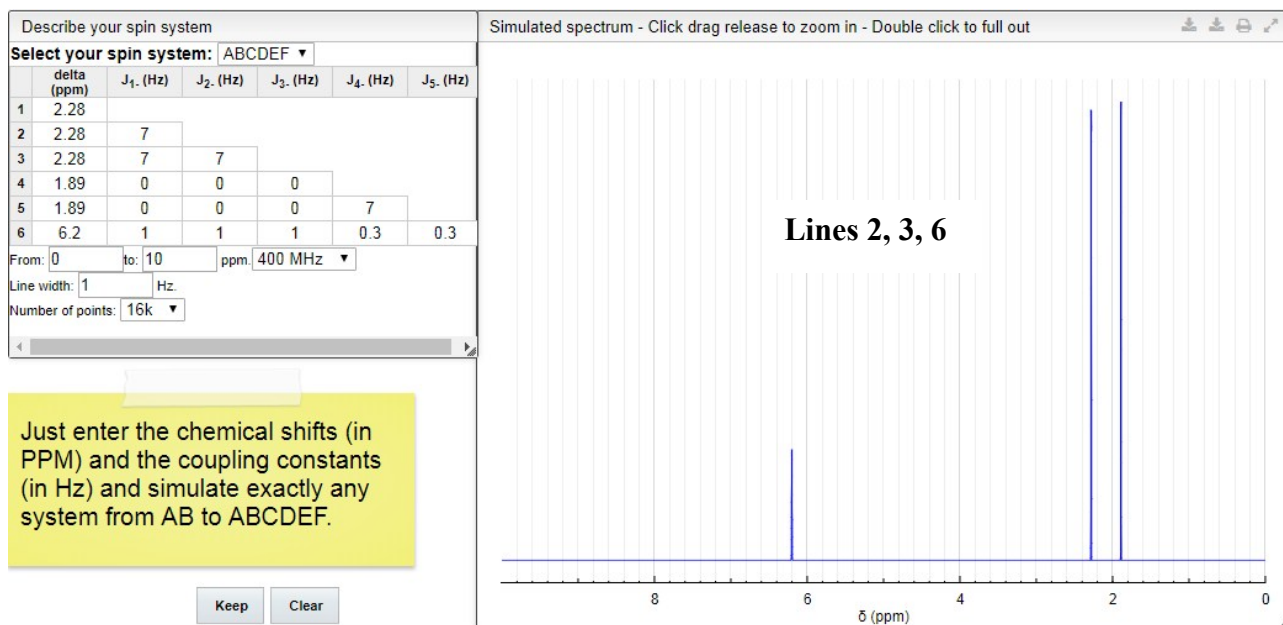
**Part S2. Description of the  $^1\text{H}$  NMR spectrum of the initial compound 1A.**

<b>№</b>	<b><math>\delta</math>, ppm</b>	<b>Multiplicity</b>	<b>Split at lines</b>	<b>Integral (number of protons)</b>
1	2.18	1	-	3
2 COSY	2.27	4	6, 2	3
3	1.88	1	6 (broadened)	3
4	2.65	2/2/3	At 4', 5	2
5	3.1	2/2	At 4	2
6 COSY	6.58	4	At 2, 3	1



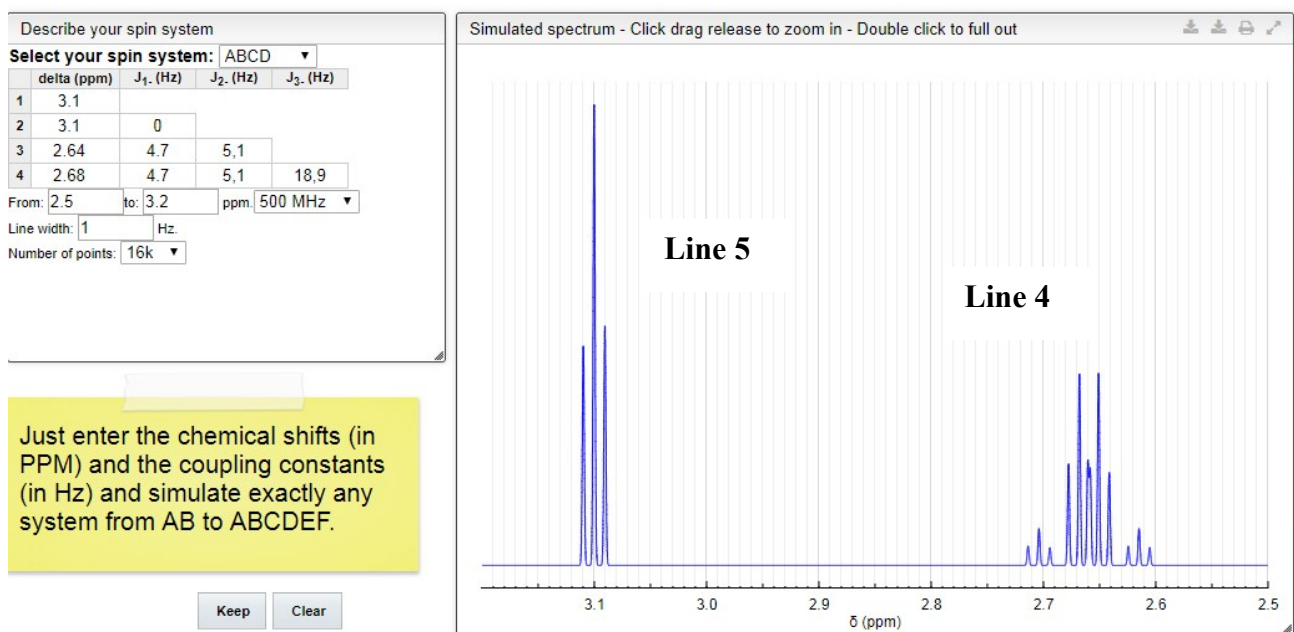


## Simulation of lines 2, 3, 6 (complicated $A_3M_3X$ system). Simulated according to [37].



Splitting at the bound lines does not coincide.

## Simulation of lines 4, 5 (AA'XY system). Simulated according to [37]

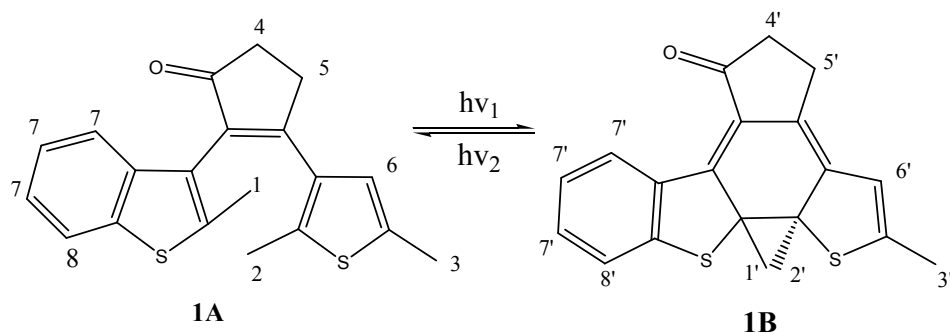
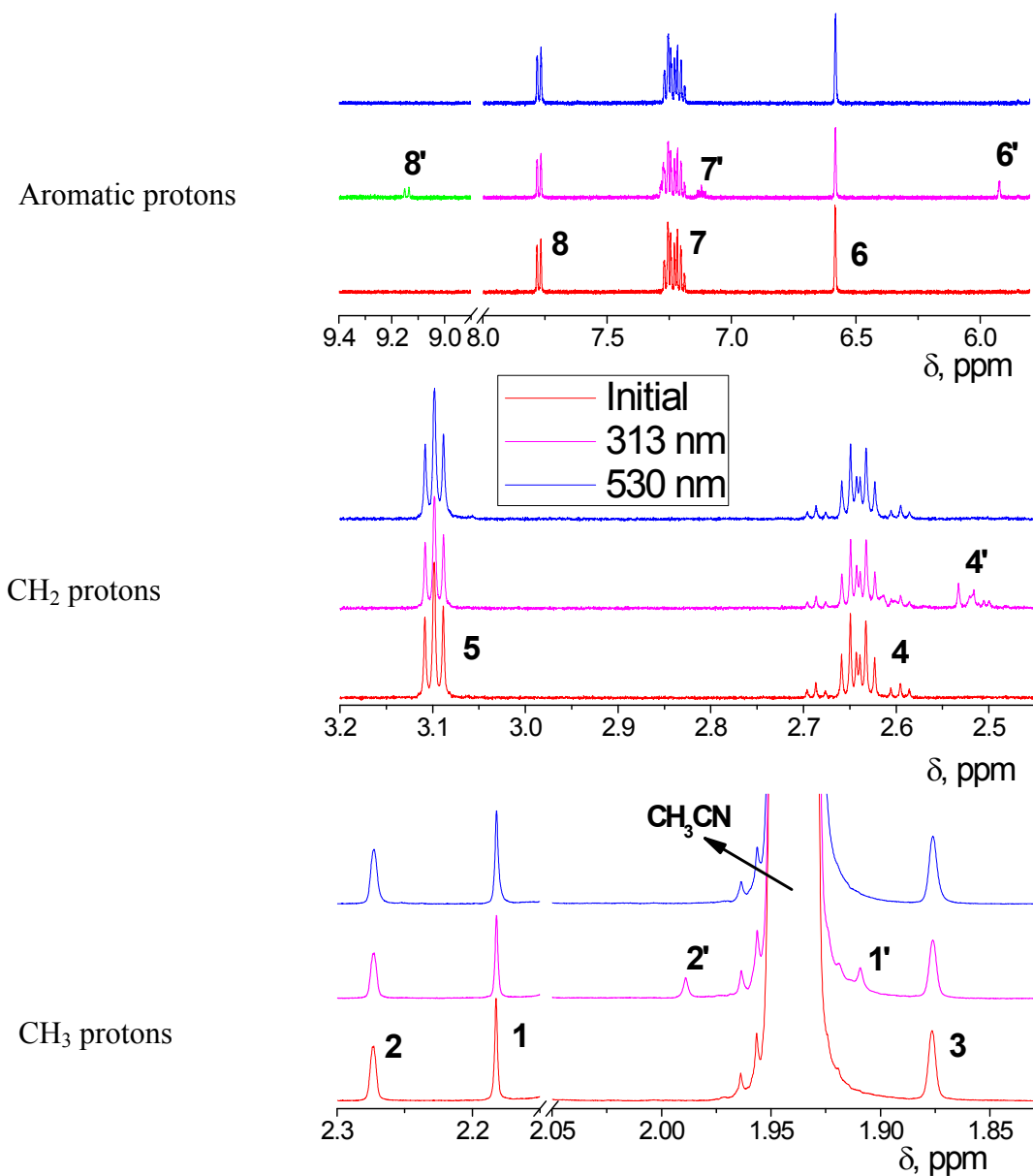


Reference

## Reference

[37] A.M. Castillo, L. Patiny, J. Wist, *J. Magn. Resonance*. **2011**, 209, 123-130.

**Part S3. Changes in the  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_3\text{CN}$  caused by photochemical cyclization (313 nm), cycloreversion (530 nm) and deep photolysis.**

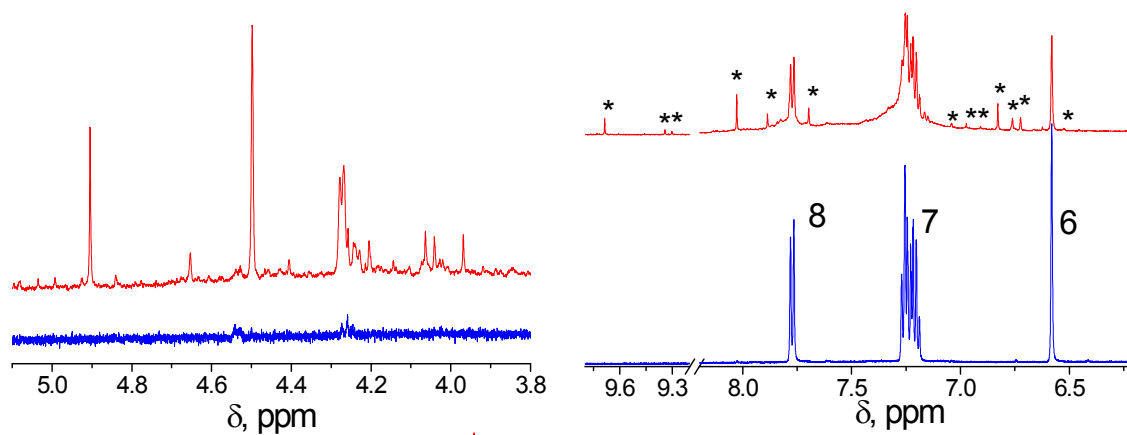


**Figure S2.** Changes in the  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_3\text{CN}$  caused by photochemical cyclization (313 nm) and reversion (530 nm).

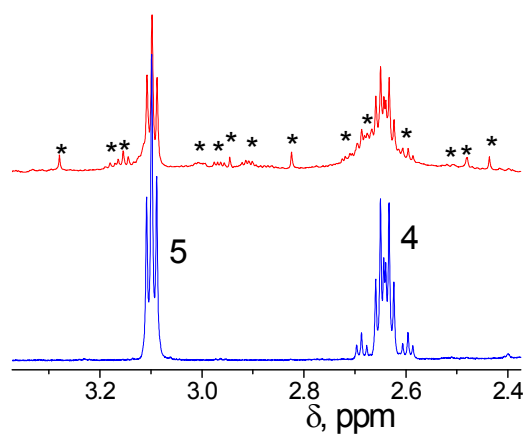


Range  $\delta$  3.8÷5.0

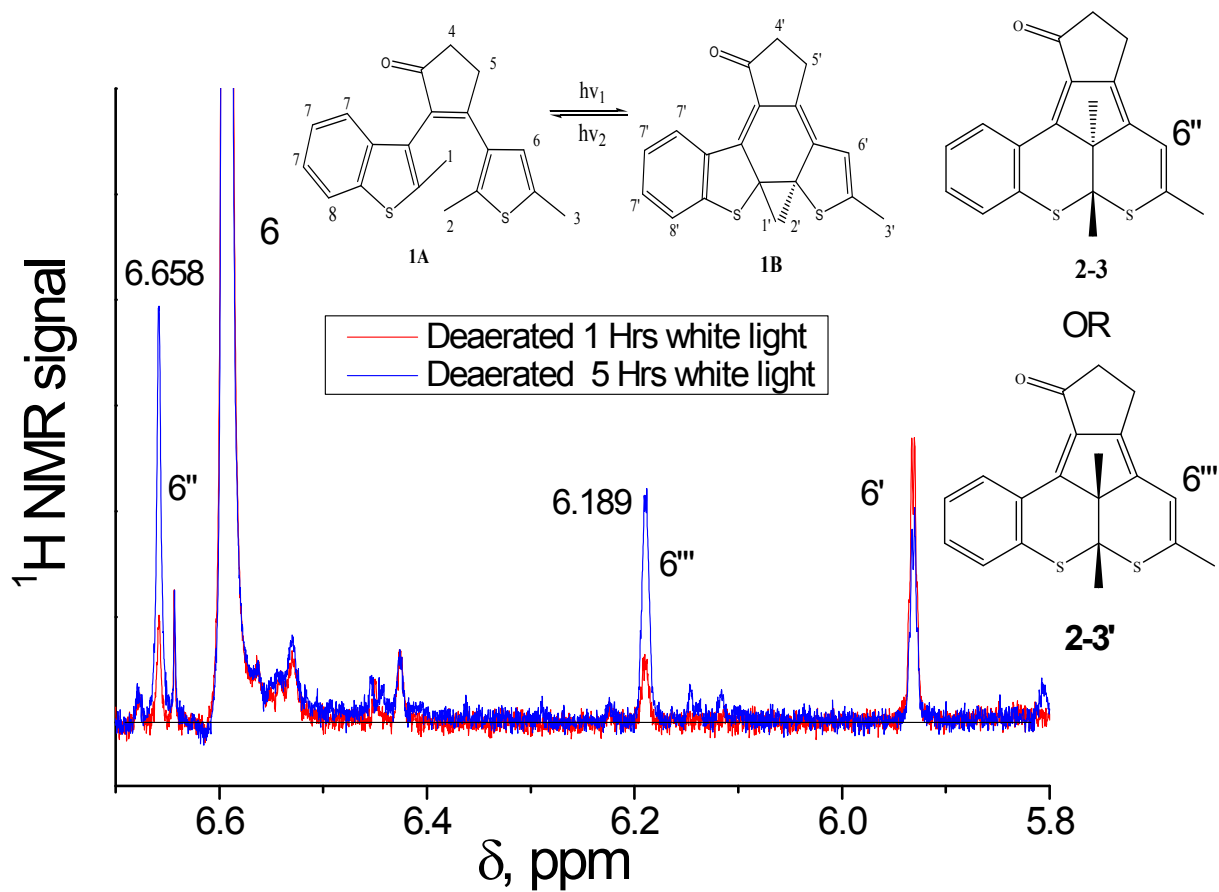
Aromatic protons



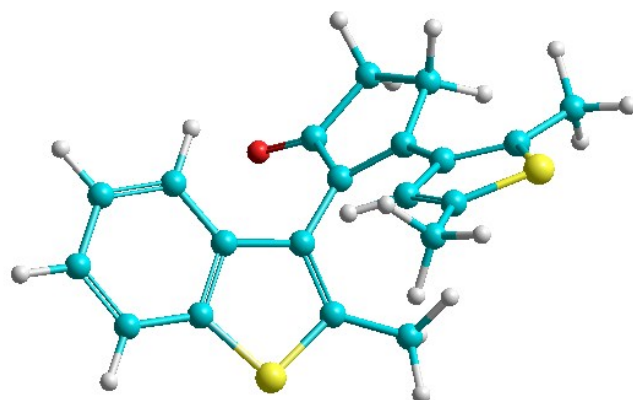
CH<sub>2</sub> protons



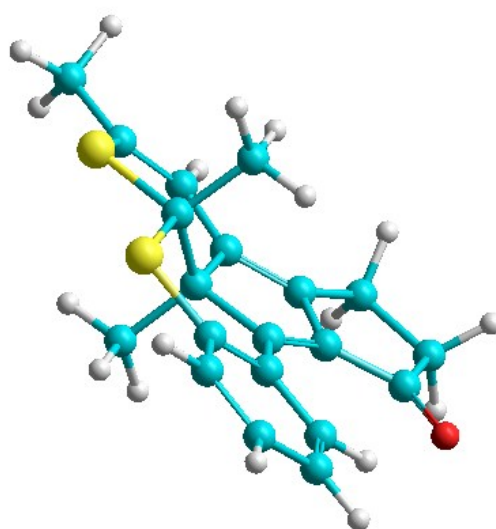
**Figure S3.** Changes in the <sup>1</sup>H NMR spectrum of **1** in CD<sub>3</sub>CN caused by deep photolysis in air-saturated solution (30 min of irradiation by a high-pressure mercury lamp). Blue lines – before irradiation; red lines – after irradiation.



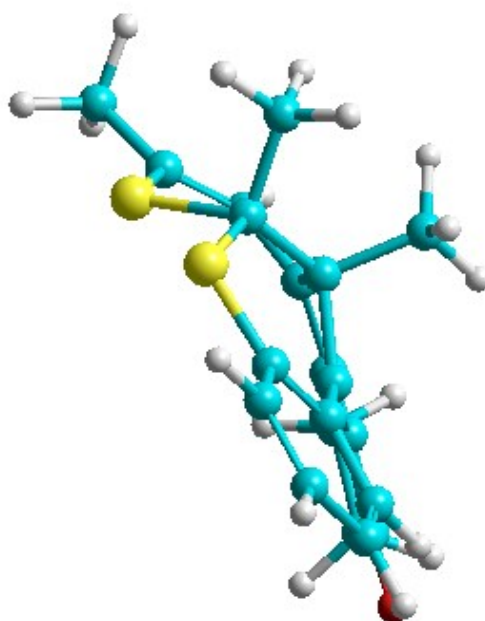
**Figure S4.** Changes in the  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_3\text{CN}$  caused by deep photolysis in solution deaerated by five freeze-pump-thaw cycles at 77 K. Red and blue curves correspond to 1 and 5 hrs of irradiation by a high-pressure mercury lamp.



1A



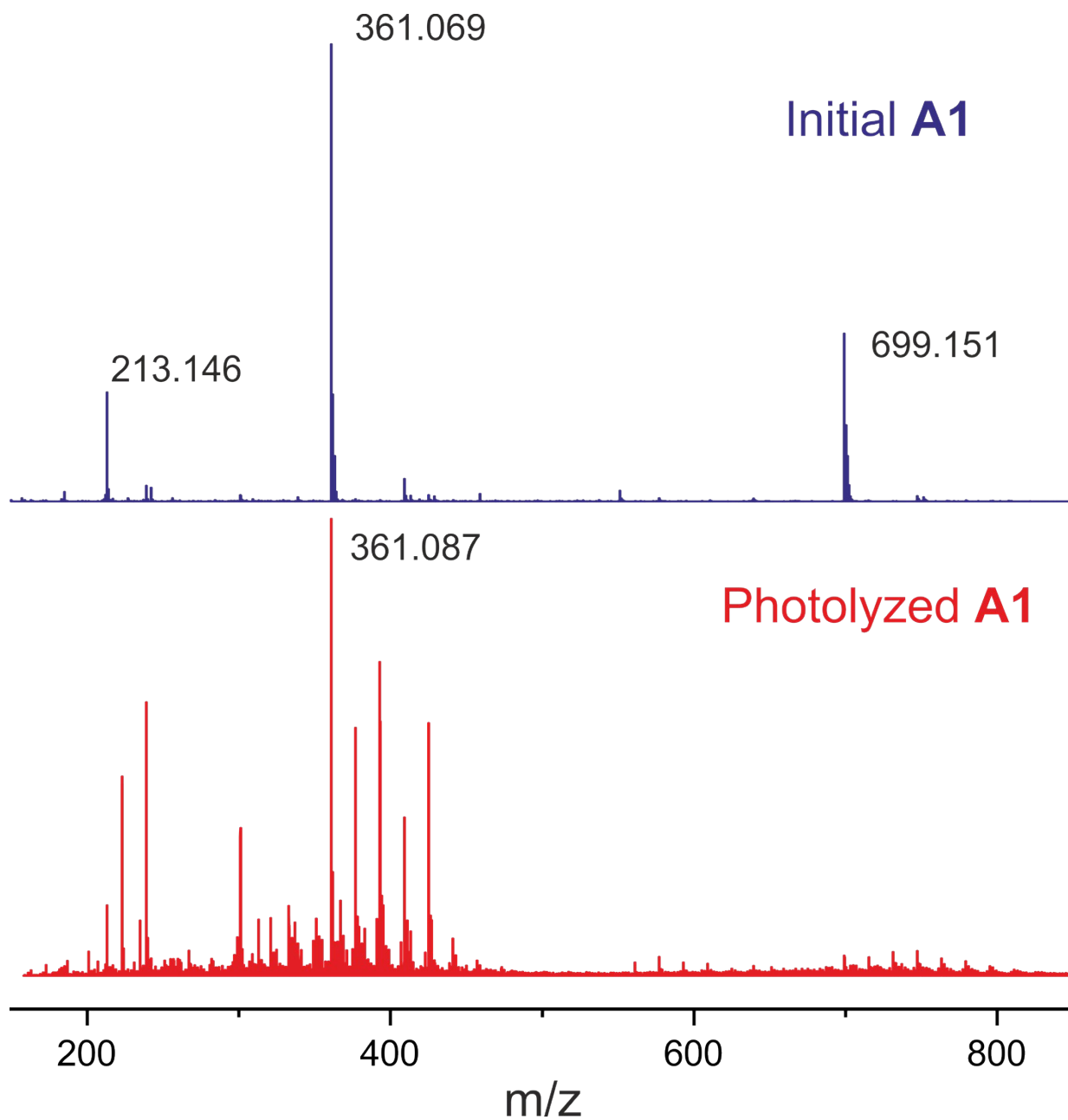
3-2 (*trans*)



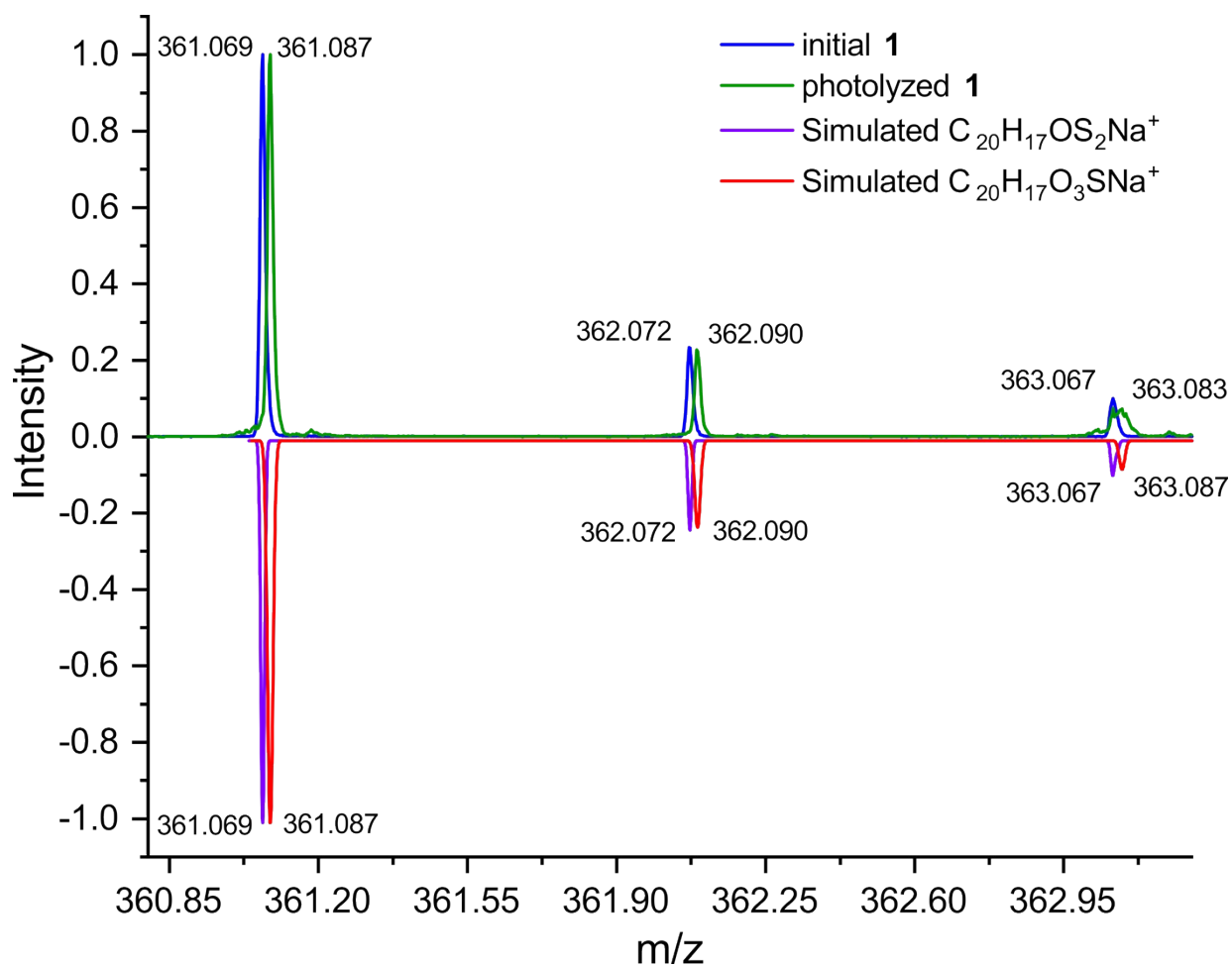
3-2' (*cis*)

**Figure S5.** Spatial structures of 1A, *trans*-isomer 2-3 and *cis*-isomer 2-3' obtained by quantum chemical calculations using unrestricted Hartree–Fock (UHF) AM1 method (Hyperchem 7.5).

Part S4. MS spectra of A1 and products of its photodegradation

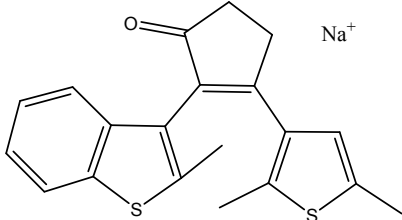
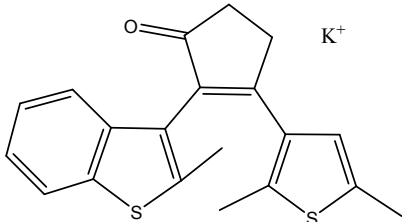
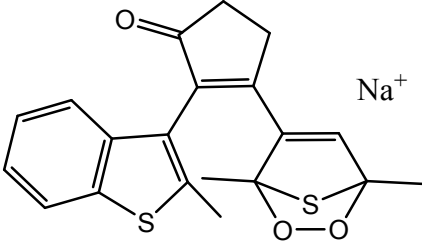
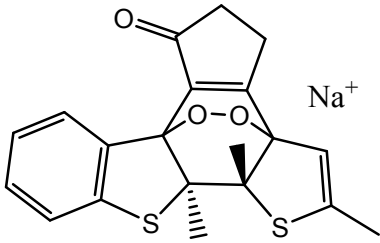
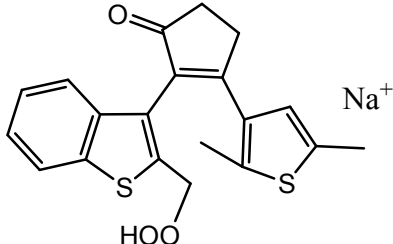


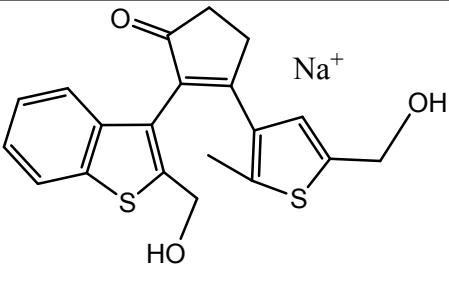
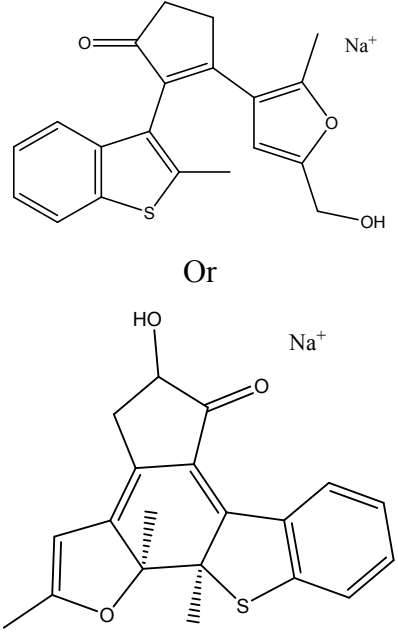
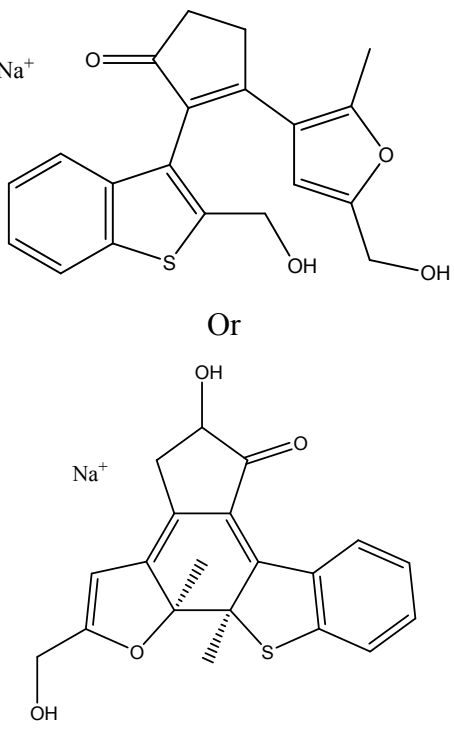
**Figure S6.** Mass-spectra of initial Compound **1** (top) in CH<sub>3</sub>CN and its products (bottom) caused by deep photolysis in air-saturated acetonitrile (30 min of irradiation by a high-pressure mercury lamp).

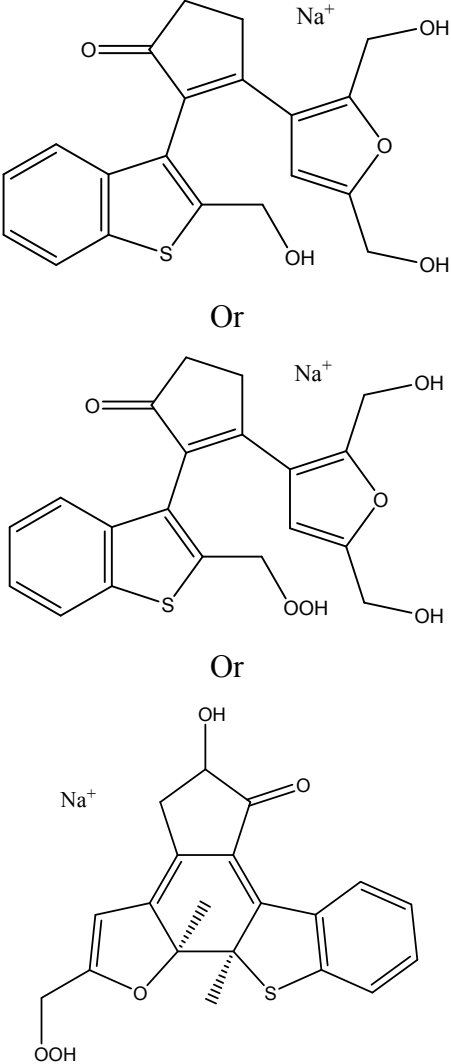
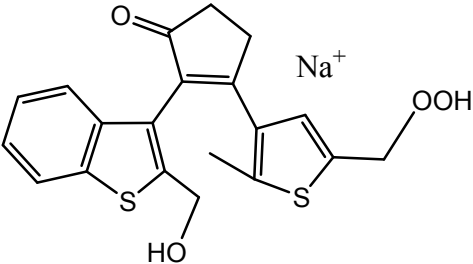
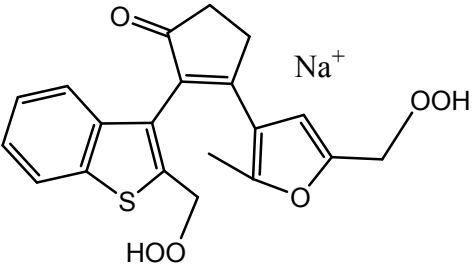


**Figure S7.** Fragment of high-resolution mass-spectra of initial (blue) and irradiated (green) solutions of Compound **1** (top) in acetonitrile and simulated spectra (bottom) of initial compound ( $[\text{C}_{20}\text{H}_{18}\text{OS}_2]\text{H}^+$ , violet) and product ( $[\text{C}_{20}\text{H}_{18}\text{O}_3\text{S}]\text{H}^+$ , red) ions. Theoretical ratio of isotope content for initial compound – 100/23.45/11.78, measured 100/23.38/9.96 and product 100/22.74/7.55, measured 100/22.74/7.24.

**Table S1.** Products of deep photolysis of **1** CH<sub>3</sub>CN detected by mass-spectrometry and their putative structures. Air-saturated solutions.

Species, formula	Structure	m/z, exp	m/z. calc.	Comments
C <sub>20</sub> H <sub>18</sub> OS <sub>2</sub> Na <sup>+</sup> <b>1A Na<sup>+</sup></b>		361.069	361.069	Initial + Na <sup>+</sup>
C <sub>20</sub> H <sub>18</sub> OS <sub>2</sub> K <sup>+</sup> <b>1A K<sup>+</sup></b>		377.042	377.043	Initial + K <sup>+</sup>
C <sub>20</sub> H <sub>18</sub> OS <sub>2</sub> Na <sup>+</sup> <b>2×1A Na<sup>+</sup></b>		699.153	699.149	2×Initial + Na <sup>+</sup>
C <sub>20</sub> H <sub>18</sub> O <sub>3</sub> S <sub>2</sub> Na <sup>+</sup> <b>2a</b>		393.058	393.059	
<b>2b</b>	Or 			
<b>2c</b>	Or 			

<p><b>2d</b></p>				
<p><math>C_{20}H_{18}O_3SNa^+</math></p> <p><b>3a</b></p> <p><b>3b</b></p>		<p>361.088</p>	<p>361.087</p>	<p><math>C_{20}H_{18}O_3SNa^+</math></p> <p><b>3a</b></p> <p><b>3b</b></p>
<p><math>C_{20}H_{18}O_4SNa^+</math></p> <p><b>4a</b></p> <p><b>4b</b></p>		<p>377.082</p>	<p>377.082</p>	<p><math>C_{20}H_{18}O_4SNa^+</math></p> <p><b>4a</b></p> <p><b>4b</b></p>

<p><math>C_{20}H_{18}O_5SNa^+</math></p> <p><b>5a</b></p> <p><b>5b</b></p> <p><b>5c</b></p>	 <p>Or</p> <p>Or</p>	<p>393.076</p>	<p>393.077</p>	
<p><math>C_{20}H_{18}O_4S_2Na^+</math></p> <p><b>6</b></p> <p>(example)</p>		<p>409.055</p>	<p>409.054</p>	
<p><math>C_{20}H_{18}O_6S_2Na^+</math></p> <p><b>7</b></p> <p>(example)</p>		<p>409.067</p>	<p>409.072</p>	



$C_{20}H_{18}O_5S_2Na^+$ <b>8</b> (example)		425.048	425.049	
$C_{20}H_{18}O_7SNa^+$ <b>9</b> (example)		425.056	425.066	
<b>10</b>		425.285		Minor; not identified
<b>11</b>		213.145		Impurity in the initial compound (not identified)
<b>12</b>		223.035	223.035	
$C_{12}H_8O_2SNa^+$ <b>13</b>		239.014	239.014	
<b>14</b>		301.141		Not identified