Supporting information

Phototransformation of Tetrazoline oxime ethers: Photoisomerization *vs* photodegradation

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1. Irradiations

1.1 Emission spectrum of polychromatic tubes

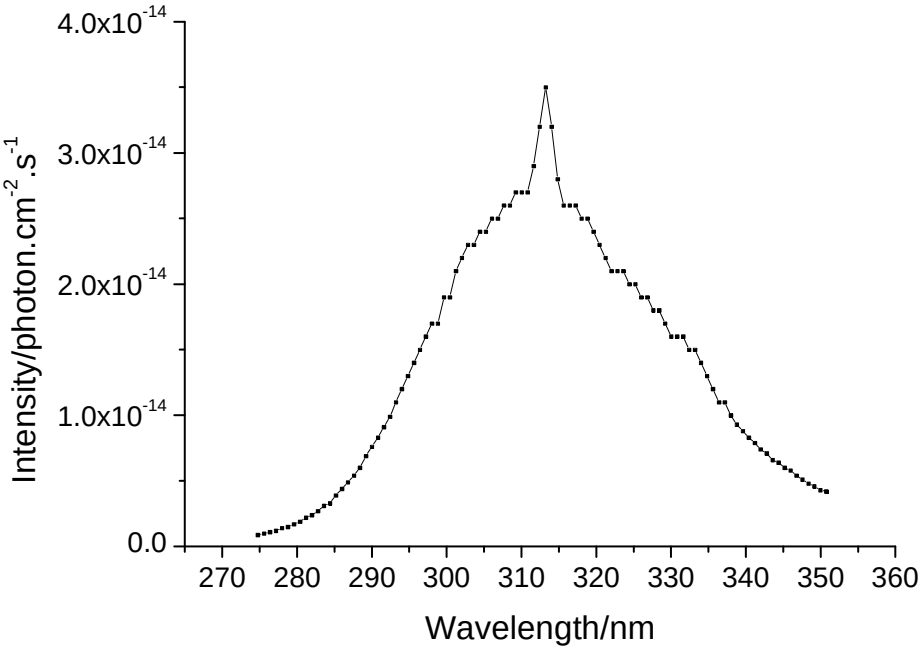


Figure SI-1: Emission spectrum of polychromatic tubes

1.2 Polychromatic quantum yields

Polychromatic quantum yields were obtained using the following expression,

$$\Phi = \frac{R_{1-Z}}{R_{Ia}} \qquad (eq.1)$$

where $R_{1\text{-}Z}$ is the rate of photolysis of **1-Z**, R_{Ia} is the rate of light absorption,

$$R_{Ia} = \sum_{280}^{350} (1 - 10^{-A_\lambda})\, I_\lambda\, l^{-1}\, \Delta\lambda \qquad (eq.2)$$

In equation 2, A_λ is the absorption of the sample and I_λ is the photon fluence rate at wavelength λ at the front face of the reactor, as measured with an Ocean Optics spectroradiometer. $\Delta\lambda$ was set at 5 nm and A_λ and I_λ were averaged within the 5-nm wavelength ranges. l is the averaged path length. R_{Ia} was found to be 2.25x10^{-6} Einstein/L/s.

2. Formation and identification of 1-E

2.1 UPLC analysis of irradiated 1-Z at very low conversion extent

a) b)

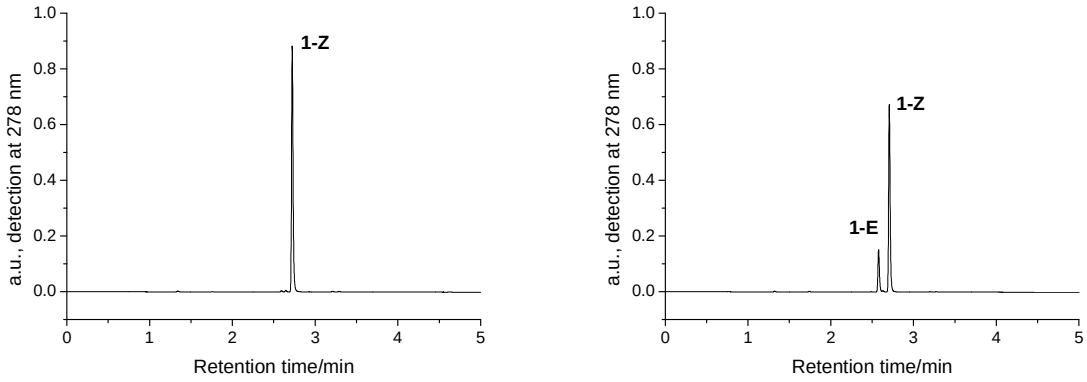


Figure SI-2: Evolution of the chromatogram of **1-Z** during its polychromatic irradiation in acetonitrile. **a)** Only the **Z** isomer is present initially. **b)** After 60 s, **1-E** is the only photoproduct

2.2 HPLC-MS of 1-E

The HPLC-MS data below confirmed that **1-Z** and **1-E** show the same m/z.

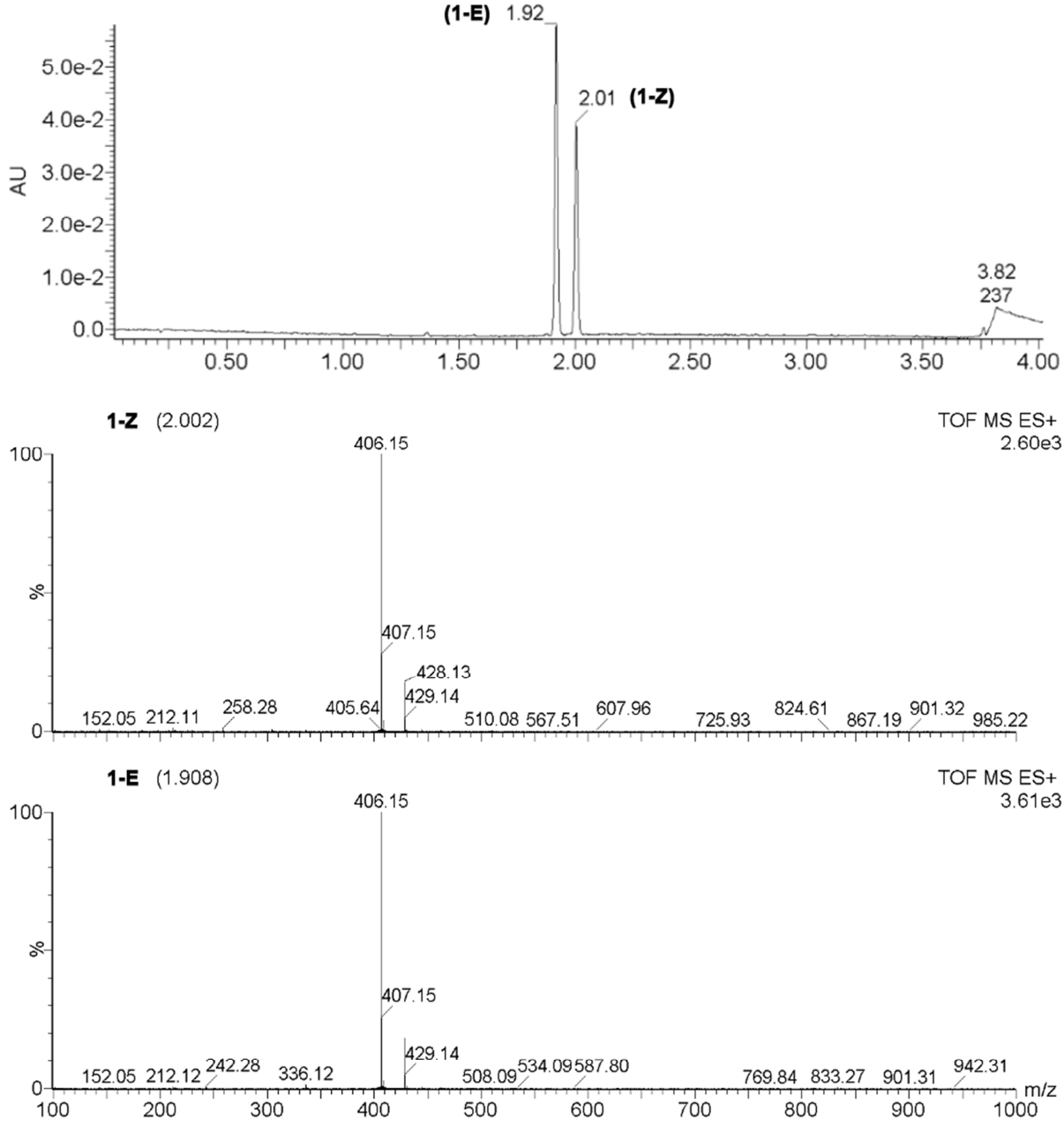


Figure SI-3: HPLC-MS data of a mixture of **1-Z** (retention time 2.01 min) and **1-E** (retention time 1.98 min) obtained after irradiation of **1-Z**.

2.3 UV spectra of 1-Z and 1-E

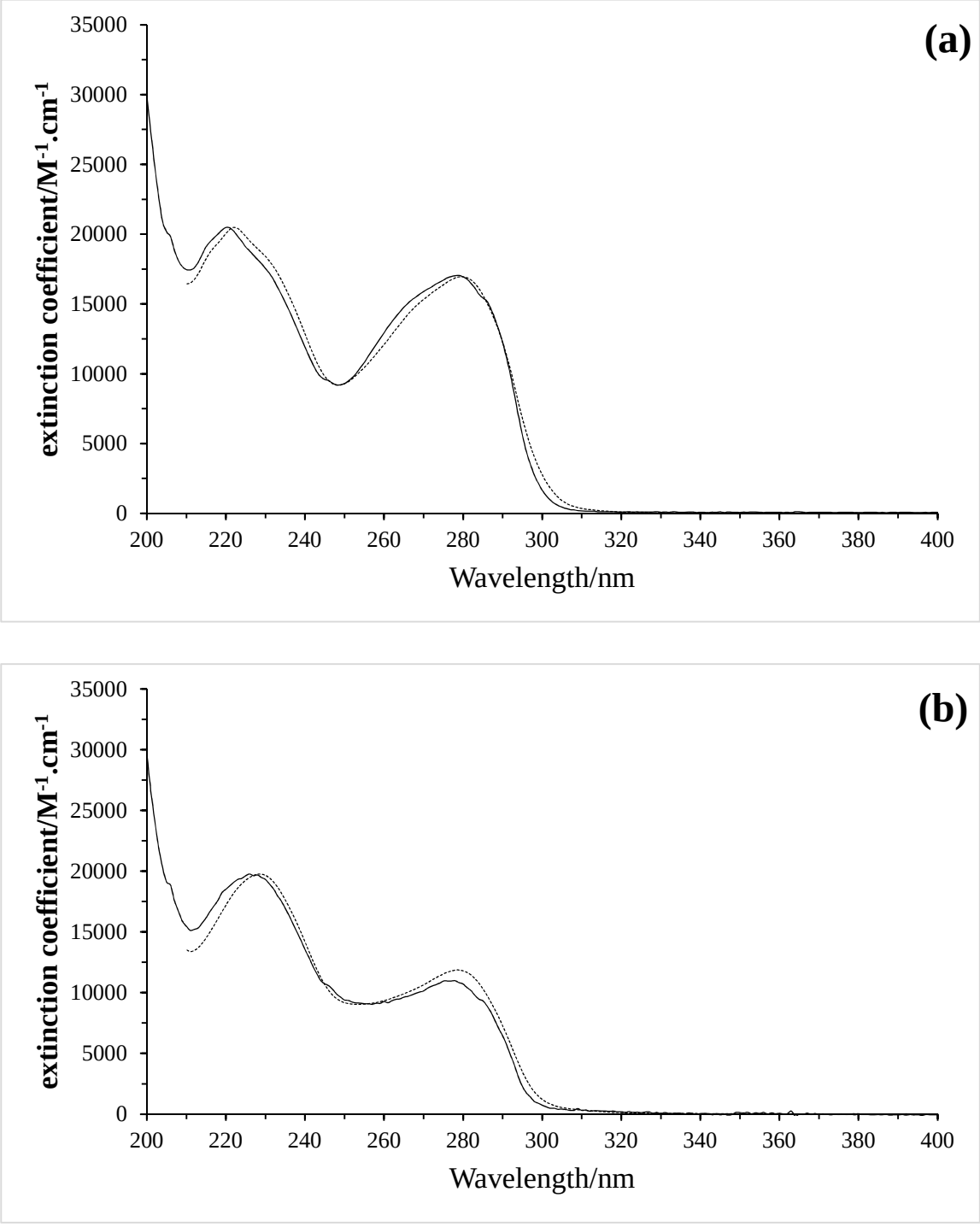


Figure SI-4: UV spectra of isomers **1-Z (a)** and **1-E (b)**. Comparison of spectra obtained by HPLC (dotted line) with those obtained by conventional UV spectrophotometry (solid line) for **1-Z** and after subtraction for **1-E**.

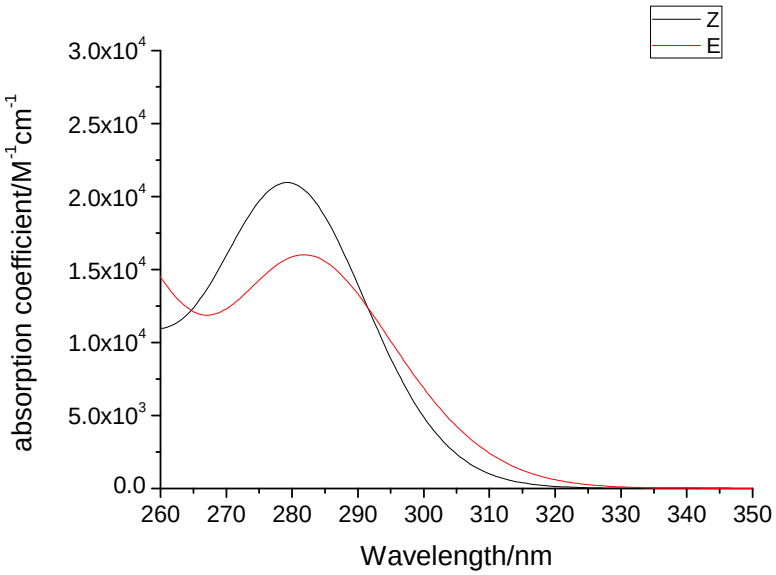


Figure SI-5: Theoretical absorption spectra of **1-Z** and **1-E**

3. Irradiation of 1-Z in polychromatic light

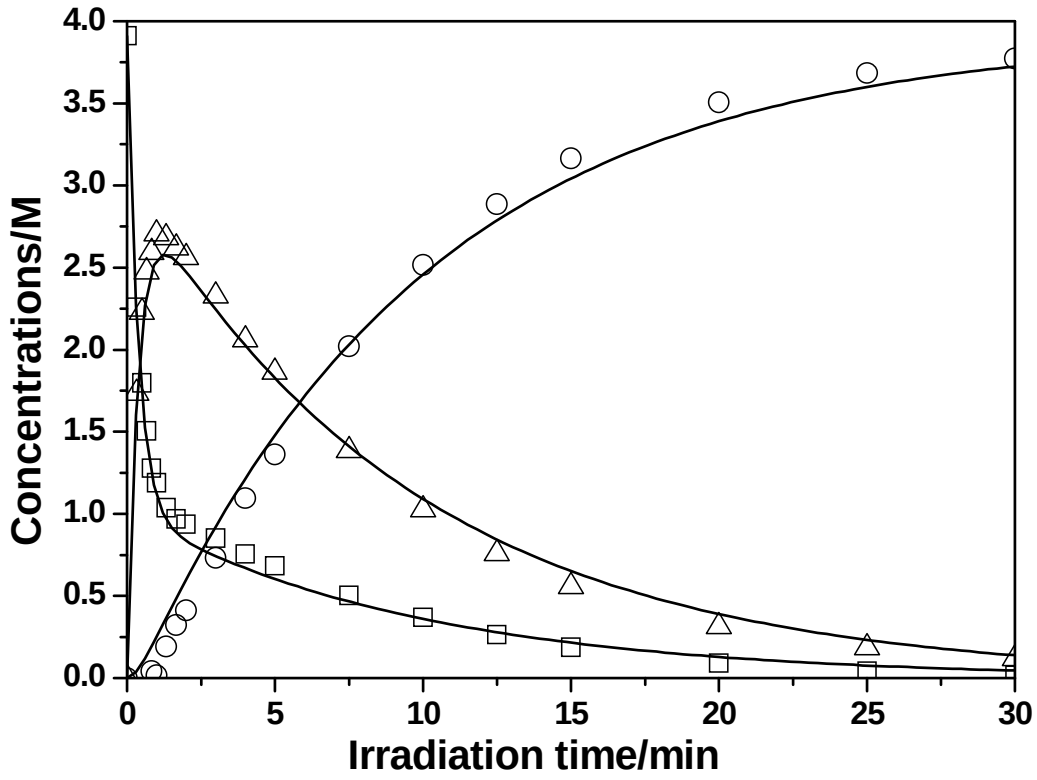


Figure SI-6: Consumption profile of **1-Z** (□) and formation profile of **1-E** (△), and degradation photoproducts (○) upon polychromatic irradiation. The irreversible photodegradation is obtained by subtracting the amounts of **1-Z** and **1-E** from the initial concentration of **1-Z**. Solid lines were obtained by the fitting procedure.

4. Irradiation of 2-Z in polychromatic light

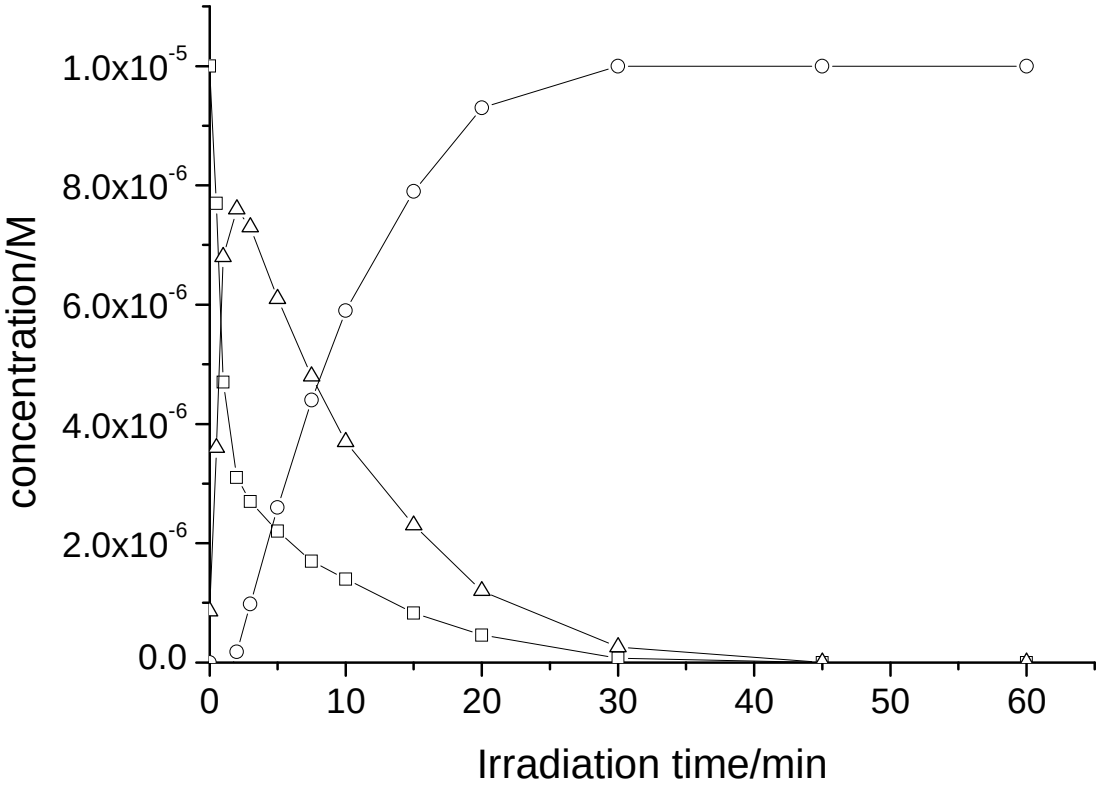


Figure SI-7: Consumption profile of **2-Z** (□) and formation profile of **2-E** (△), and degradation photoproducts (○) upon polychromatic irradiation. The irreversible photodegradation is obtained by subtracting the amounts of **2-Z** and **2-E** from the initial concentration of **1-Z**. Solid lines were obtained by the fitting procedure.

5. UV spectra of 4 and 5

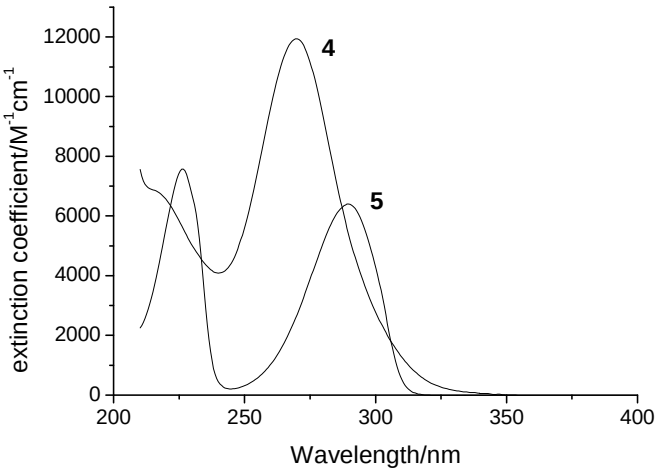
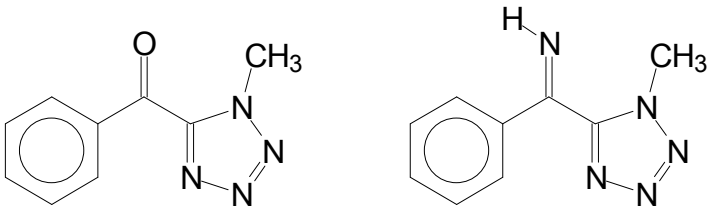


Figure SI-8: UV spectra of **4** and **5** in acidic water -acetonitrile mixture (55:45, v/v)

6. Calculation of the electronic absorption spectra of species 4 and 6

Time-Dependent Density Functional Theory (TD-DFT) calculations were performed at the B3LYP/6-31(d,p) level to obtain the electronic absorption spectra of species **4** and **6**. These are shown below in the most stable conformation.



4 **6**

The theoretical UV absorption spectra are shown below. This Figure shows that both species **4** and **6** absorb in the same regions at ~230 nm and ~280 nm. However, the carbonyl species **4** is a stronger UV absorbant (x3) than the imine **6** at 280 nm.

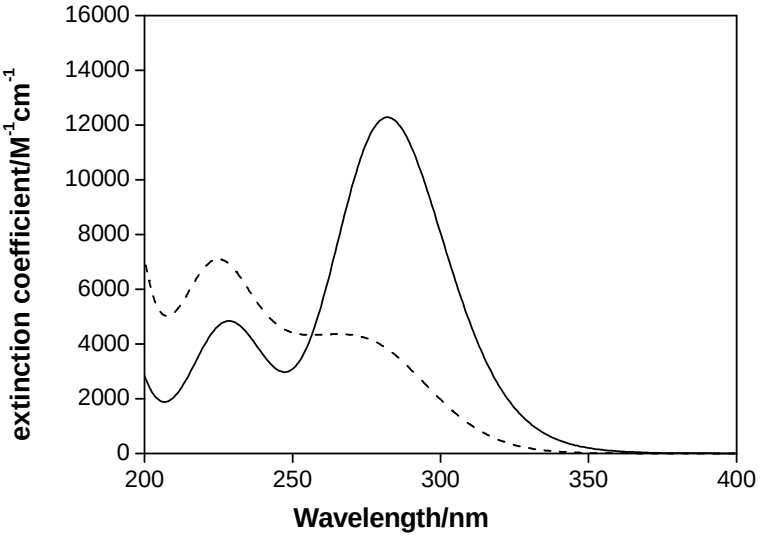


Figure SI-9: Theoretical absorption spectra of **4** (solid line) and **6** (dotted line)

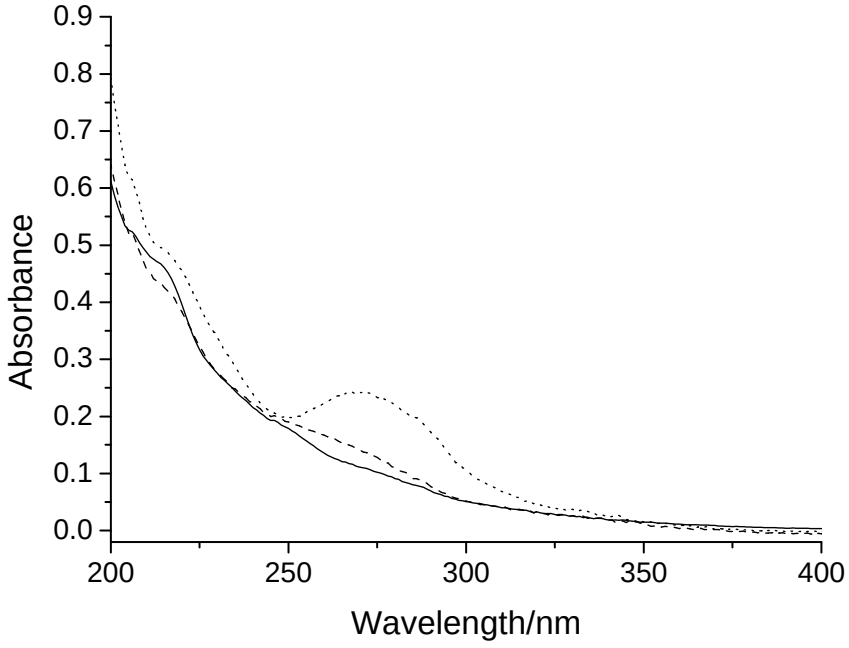


Figure SI-10: Changes of the absorption spectrum of an irradiated solution of **1-Z** upon acidification. Solid line: pure acetonitrile; dashed line: addition of pure water; dotted line: addition of acidified water with orthophosphoric acid (0.1%)

6. Data on 3-Z and 3-E

6.1 Photoisomerization of 3-Z into 3-E

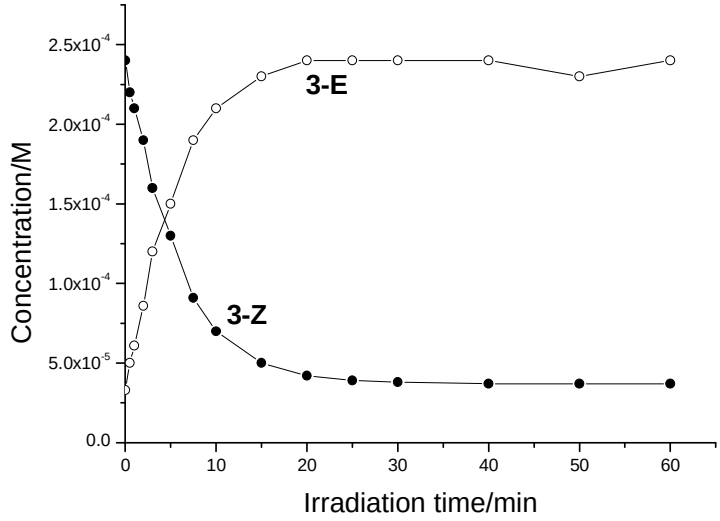


Figure SI-11: Concentrations evolution of isomers **3-Z** and **3-E** during the polychromatic irradiation of **3-Z**. After establishment of the photostationary state, [**3-E**]/[**3-Z**] = 6.2.

6.2 Absorption spectra of 3-Z and 3-E

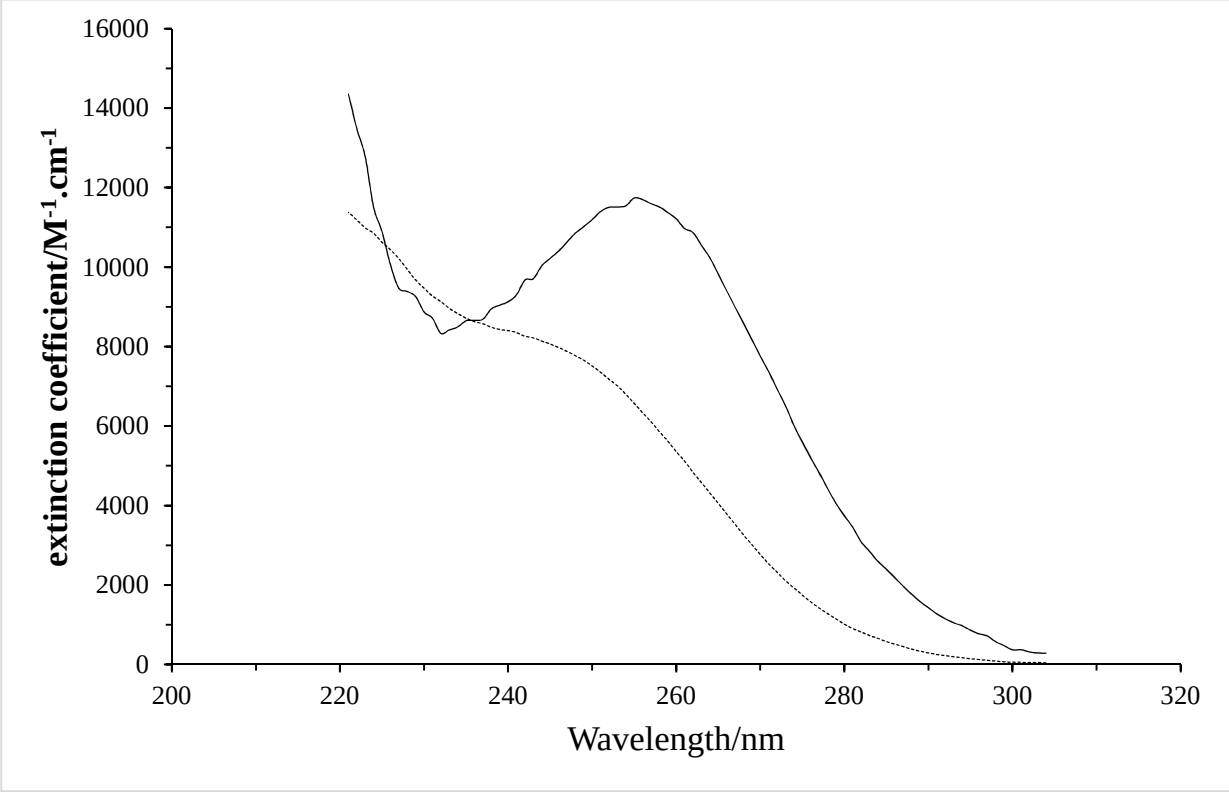
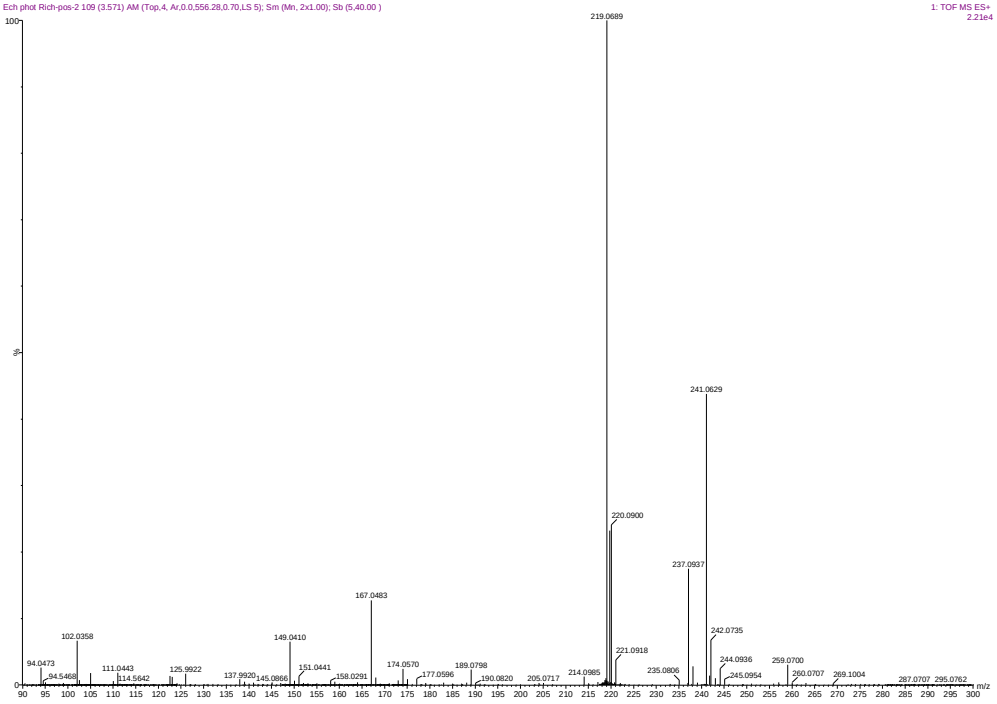


Figure SI-12: Experimental absorption spectra of isomers **3-Z** (solid line) and **3-E** (dotted line), determined by spectrum subtraction.

7. MS data on 7 and 8

a)



b)

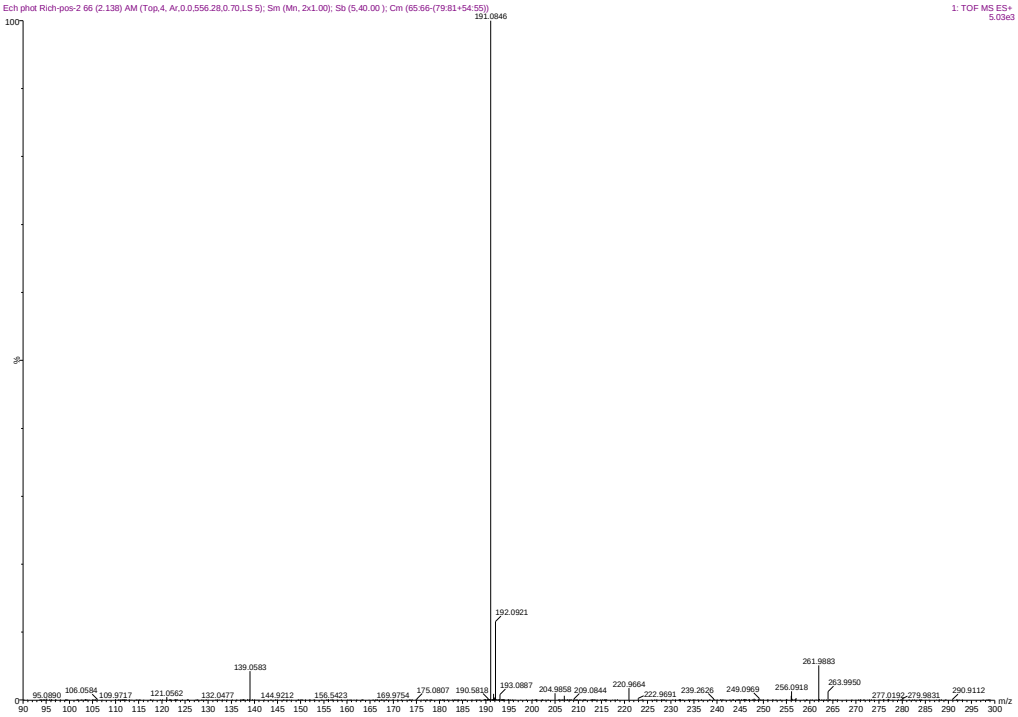


Figure SI-13: MS data of **7** (a) and **8** (b)

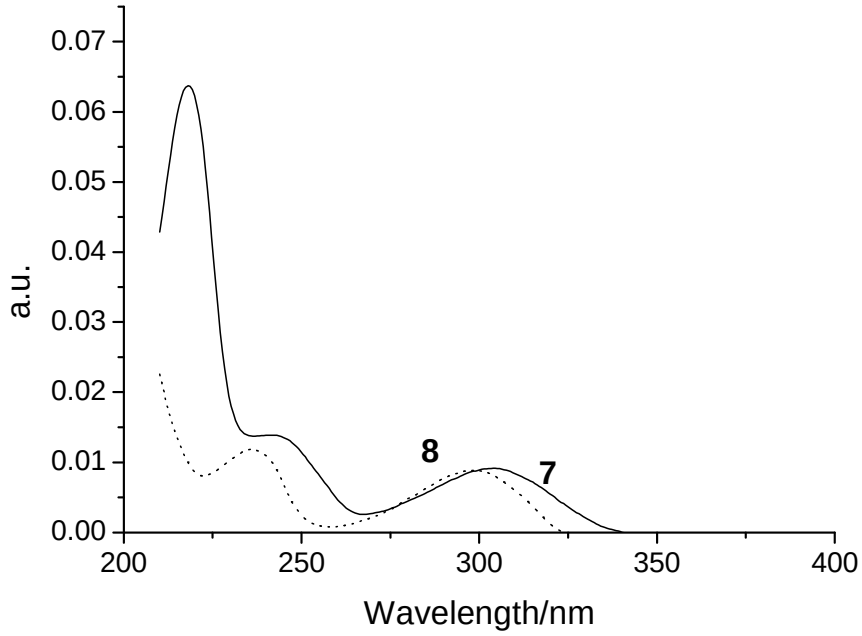


Figure SI-14: Experimental UV spectra of **7** (solid line) and **8** (dotted line)

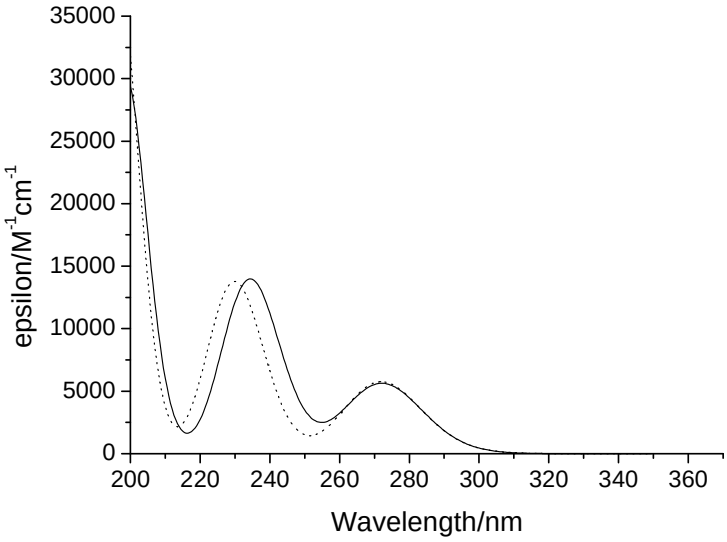


Figure SI-15: Theoretical UV spectra of **8** (dotted line) and **M8** (solid line)

8. Phototransformation of 4 in polychromatic irradiation

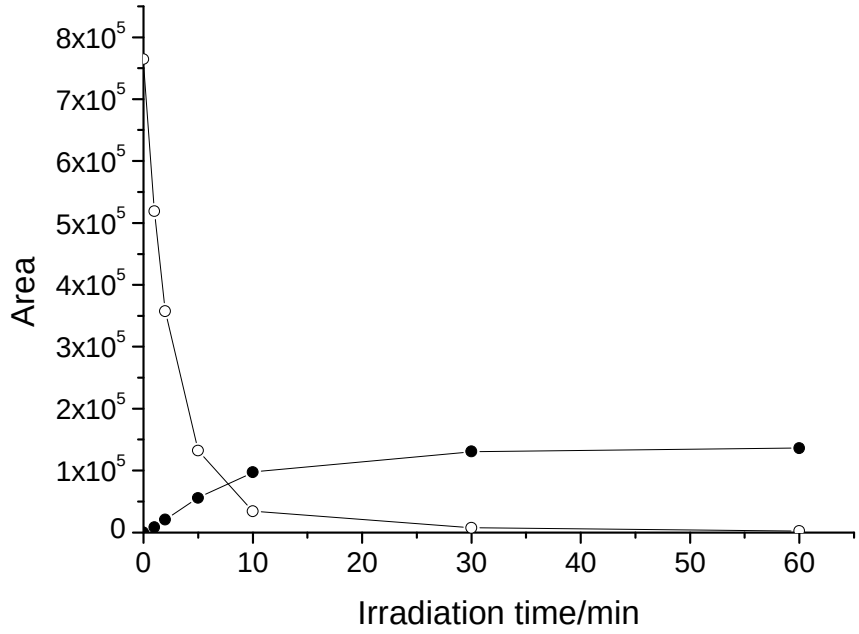


Figure SI-16: Concentration profile of **4** (○) during its polychromatic irradiation. Only one photoproduct (●) is detected by HPLC.

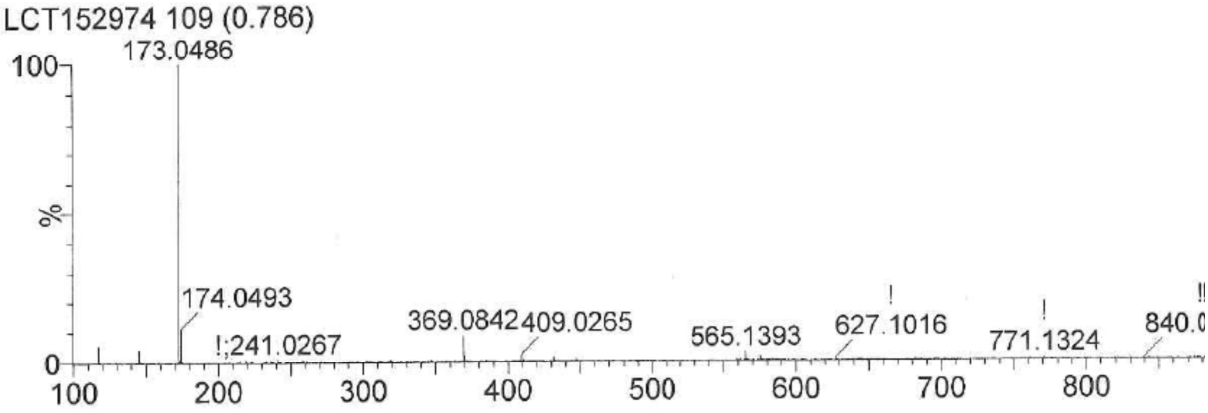


Figure SI-17: MS data of photoproduct **9** in ES^-, m/z=173.

9. Phototransformation of M8 in polychromatic irradiation

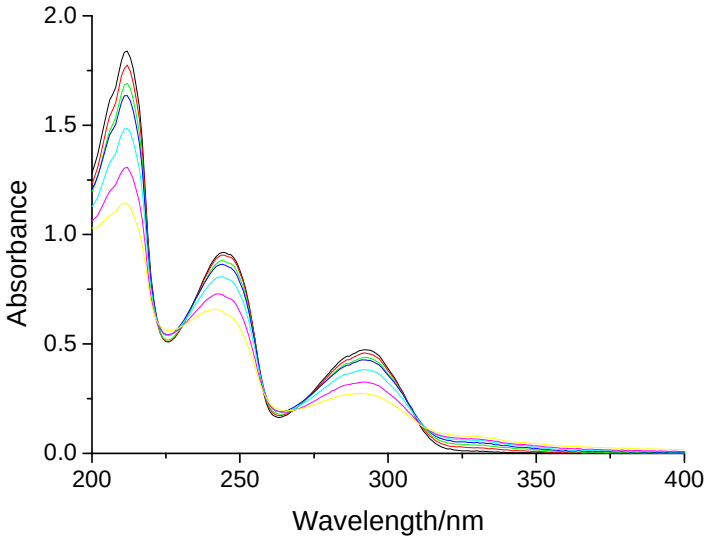


Figure SI-18: Absorbance evolution of a solution of **M8** in acetonitrile during its polychromatic irradiation. Irradiation times: 0, 5, 10, 15, 25, 40, 60 min