ON/OFF Photostimulation of Isatin Bipyridyl Hydrazones. Photochemical and Spectral Study.

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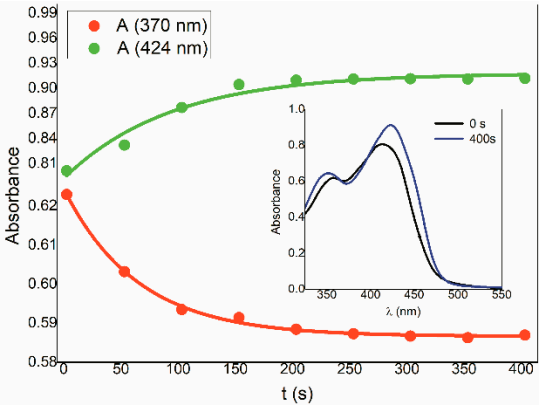


Figure S1. Hydrazone **4** kinetics of heat-stimulated *E-Z* isomerization (5×10^{-5} mol dm^{-3}) at 80 °C in DMF. In set hydrazone **4** UV-Vis spectra during isomerization.

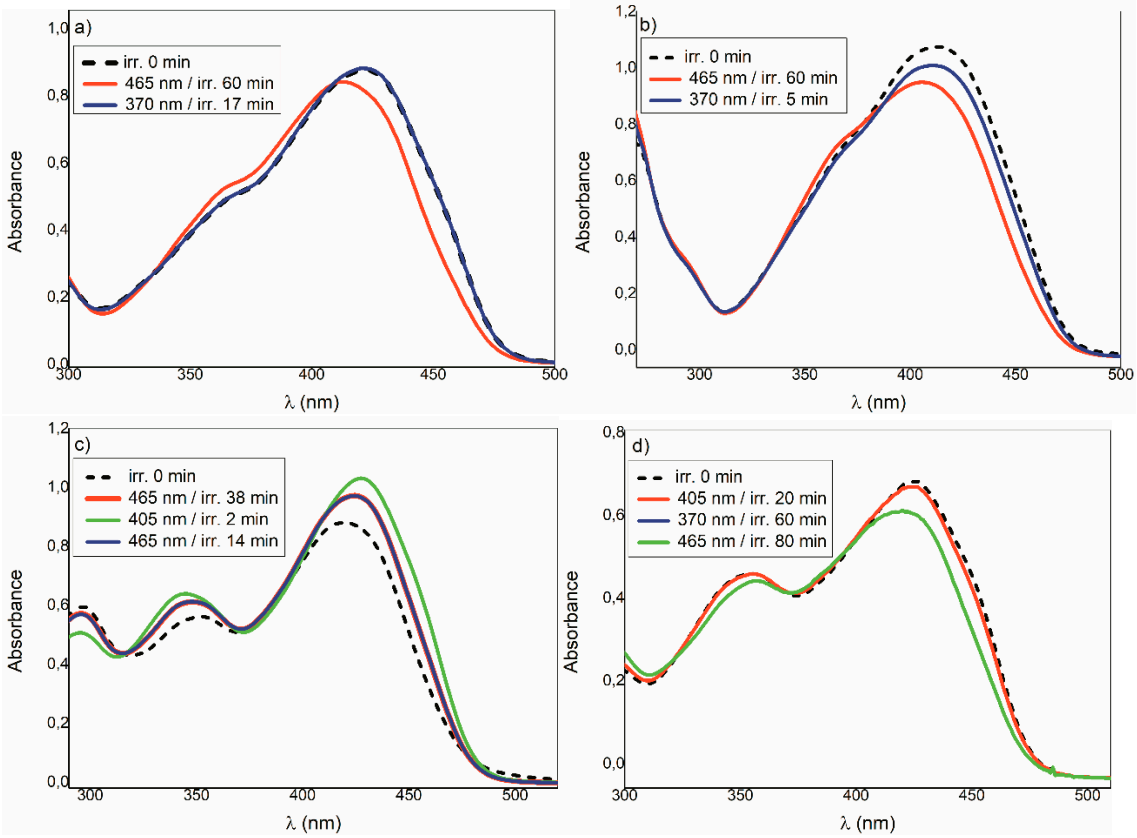


Figure S2. UV-Vis spectra change during irradiation: (**a**) hydrazone **3** (5×10^{-5} mol dm^{-3}) in $CHCl_3$; (**b**) hydrazone **3** (5×10^{-5} mol dm^{-3}) in DMF; (**c**) hydrazone **4** (1×10^{-4} mol dm^{-3}) in $CHCl_3$; (**d**) hydrazone **4** (1×10^{-4} mol dm^{-3}) in DMF.

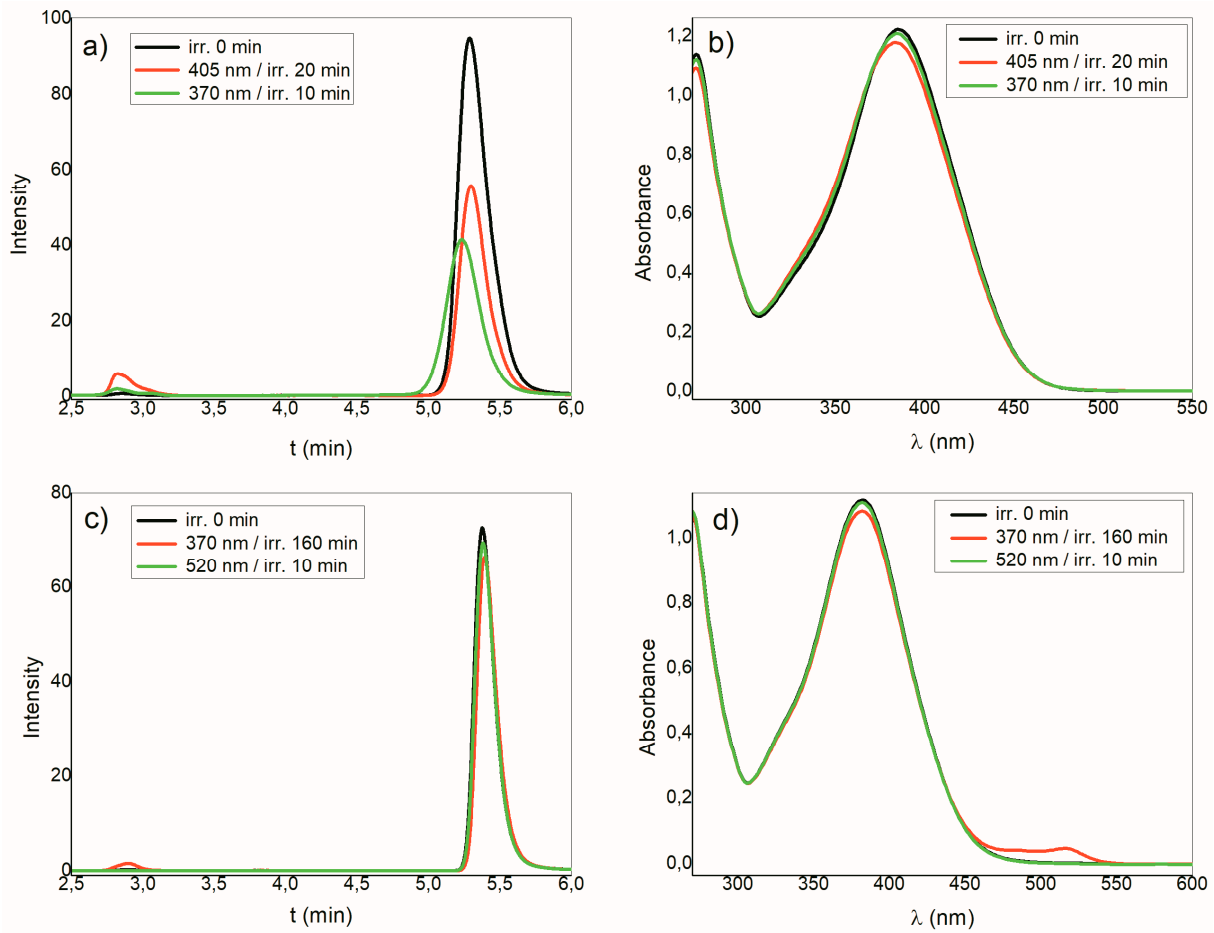


Figure S3. UV-Vis spectra and chromatograms change during hydrazone **2** (5×10^{-5} mol dm^{-3}) photolysis: (**a**) and (**b**) photolysis in $CHCl_3$;(**c**) and (**d**) photolysis in DMF.

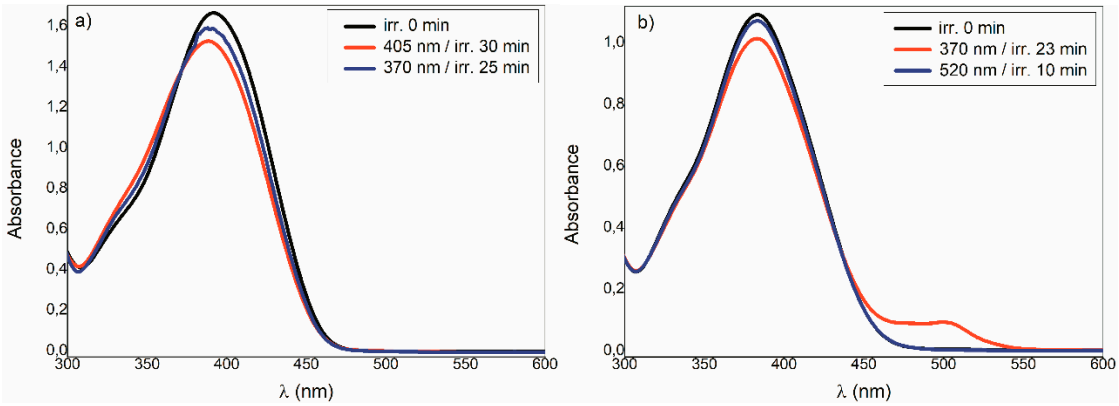


Figure S4. UV-Vis spectrum change: (**a**) hydrazone **1** (1×10^{-4} mol dm^{-3}) a light-stimulated change in $CHCl_3$; (**b**) hydrazone **1** (5×10^{-5} mol dm^{-3}) reversible light-stimulated change in DMF.

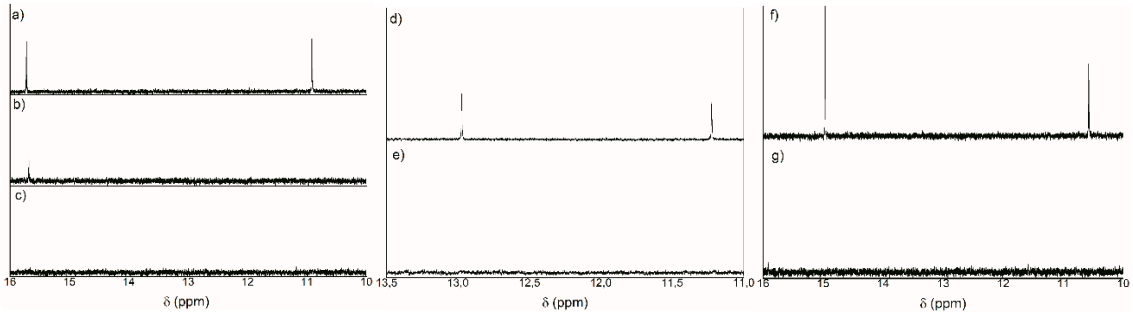


Figure S5. H-D exchange in DMSO: (**a**) hydrazone **3**; (**b**) solution a + D_2O; (**c**) solution b after 24 h; (**d**) hydrazone **1**; (**e**) solution d + D_2O; (**f**) hydrazone **4**; (**g**) solution f + D_2O.

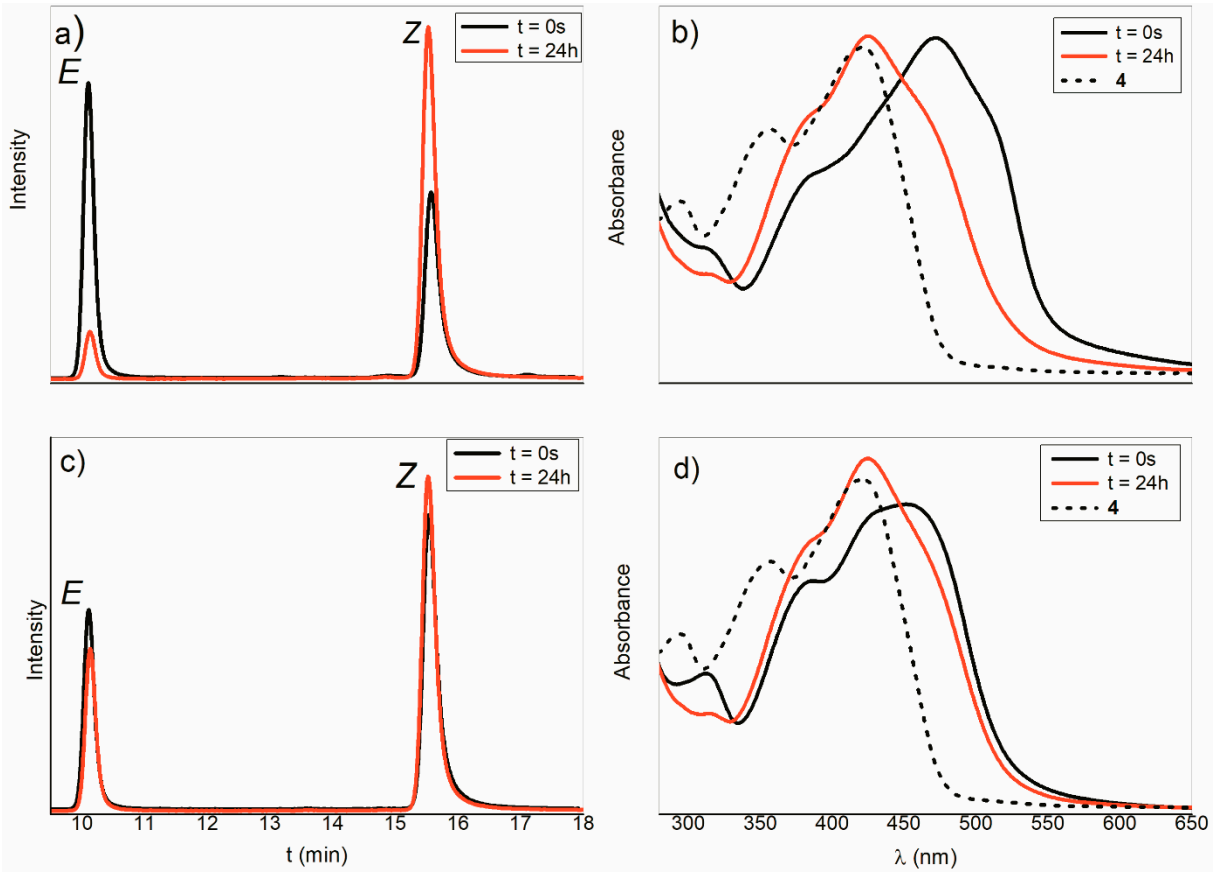


Figure S6. Thermic change of hydrazone **4** (1×10^{-4} mol dm^{-3}) in the TBAF presence: (**a**), (**c**) chromatogram - c_{TBAF} = 5×10^{-3} mol dm^{-3}; (**b**), (**d**) UV-Vis spectra - c_{TBAF} = 4×10^{-4} mol dm^{-3} in DMF.

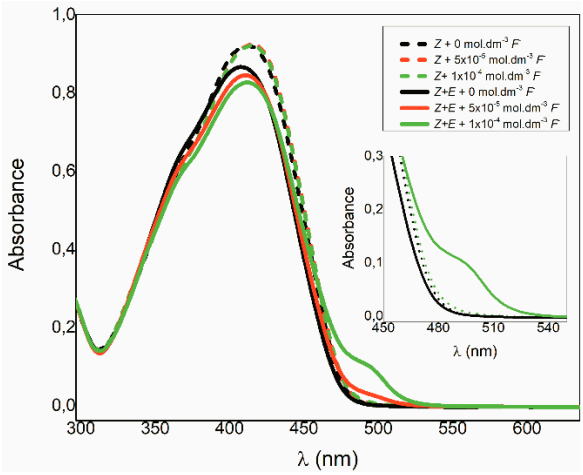


Figure S7. UV Vis spectra change of the *Z*-isomer and an *E* and *Z*-isomers mixture of the hydrazone **3** (5×10^{-5} mol dm^{-3}) depending on the TBAF concentration in DMF.

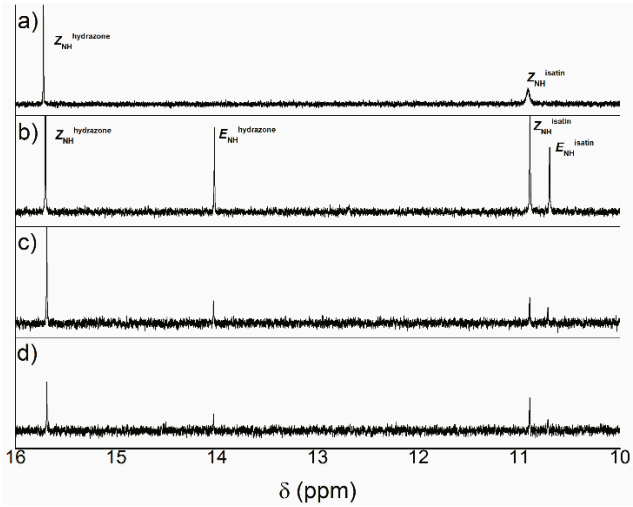


Figure S8. Hydrazone **3** *E* and *Z* isomers (1×10^{-3} mol dm^{-3}) ^{1}H-NMR spectrum change during H-D hydrogen exchange in DMSO: (**a**) *Z*-isomer from hydrazone **3**; (**b**) a mixture of *Z* and *E* isomers from hydrazone **3**; (**c**) solution b + 3 drops of D_2O; (**d**) solution c after 1 h.

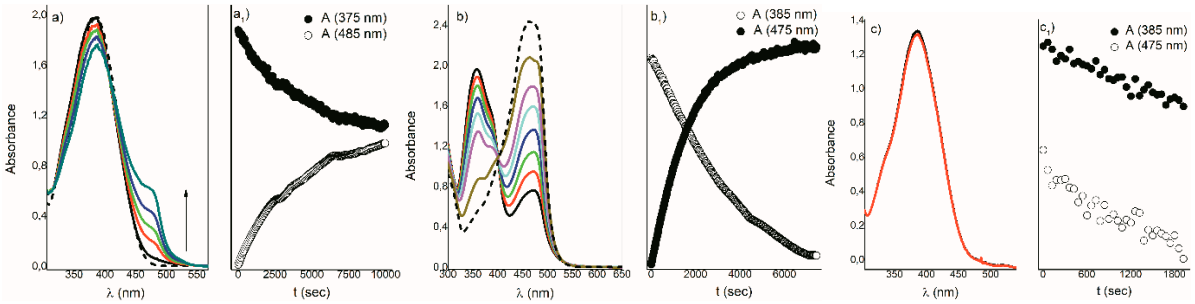


Figure S9. Hydrazone **1** reaction kinetics in the TBAF presence in DMSO: (**a**), (**a**$_1$) initial concentration TBAF c_{TBAF} = 1×10^{-3} mol dm^{-3}; (**b**), (**b**$_1$) TBAF concentration increased to c_{TBAF} = 5×10^{-2} mol dm^{-3}; (**c**), (**c**$_1$) -TBAF diluted to c_{TBAF} = 1×10^{-3} mol dm^{-3}.

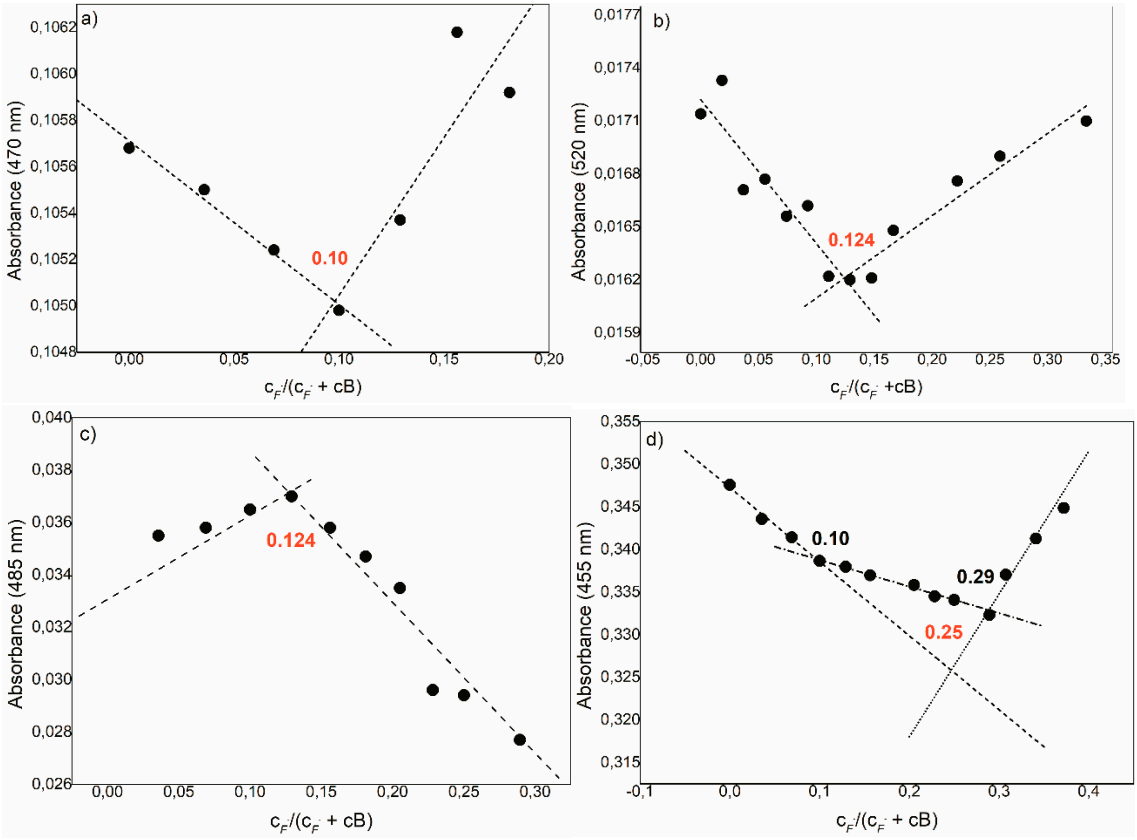


Figure S10. Job's plots for: (**a**) hydrazone **1**; (**b**) hydrazone **2**; (**c**) hydrazone **3**; (**d**) hydrazone **4** in DMF. Titration with TBAF.

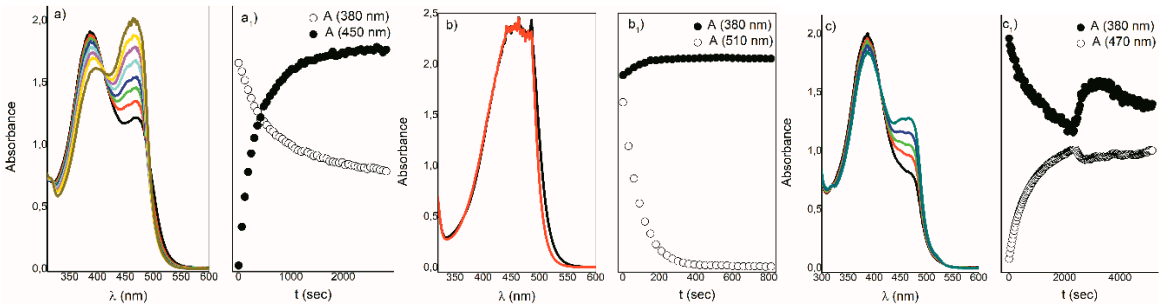


Figure S11. Hydrazone **2** reaction kinetics in the TBAF presence in DMSO: (**a**), (**a1**) - initial concentration TBAF c_{TBAF} = 1 × 10^{-3} mol dm^{-3}; (**b**), (**b1**) -TBAF concentration increased to c_{TBAF} = 2 × 10^{-2} mol dm^{-3}; (**c**), (**c1**) -TBAF diluted to c_{TBAF} = 1 × 10^{-3} mol dm^{-3}.

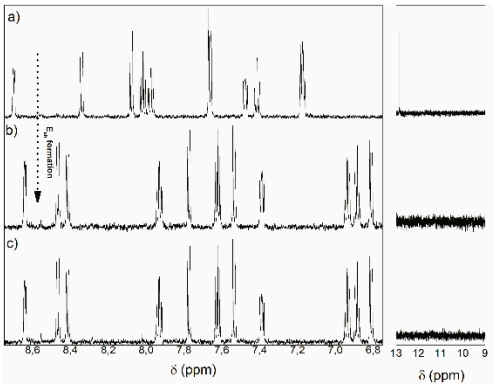


Figure S12. *Z*-isomer of hydrazone **2** (1×10^{-3} mol dm^{-3}) ^{1}H-NMR spectra change in DMSO at TBAF (2×10^{-2} mol dm^{-3}) presence: (**a**) hydrazone **2** *Z*-isomer; (**b**) immediately after TBAF addition - *E*-isomer of hydrazone **2** formation from E_{mah}; (**c**) after 3 h since TBAF addition.

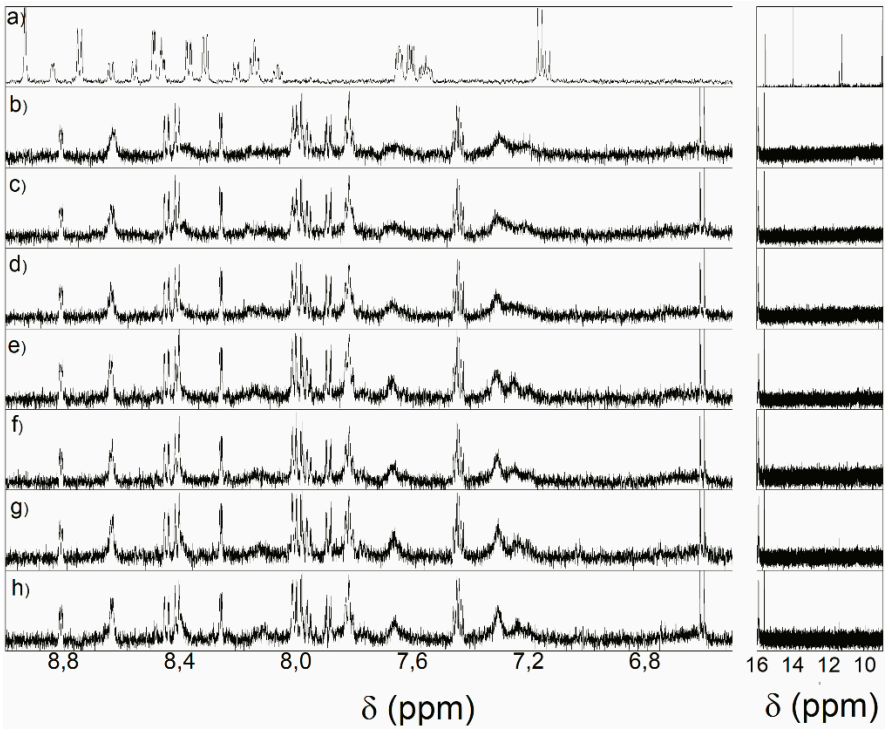


Figure S13. System hydrazone **4** (1×10^{-3} mol dm^{-3}) + TBAF (1×10^{-3} mol dm^{-3}) ^{1}H-NMR spectra changes as the time function in DMSO.

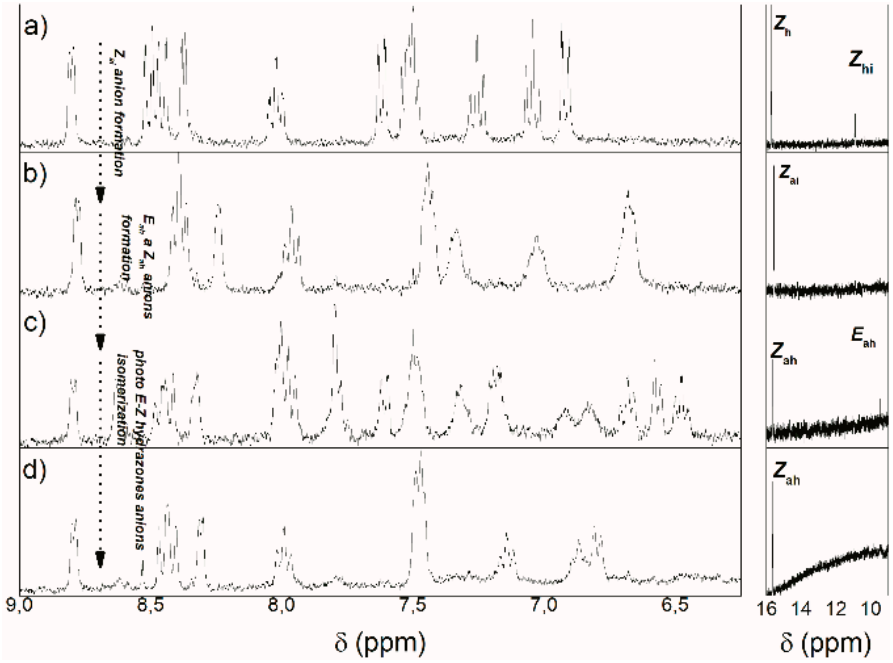
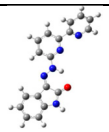
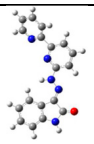
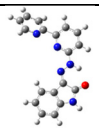
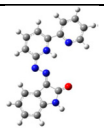
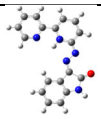
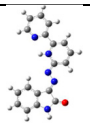
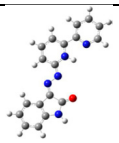
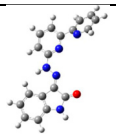
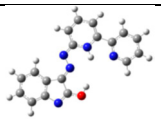
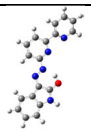
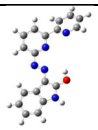
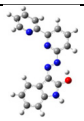
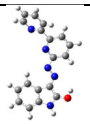
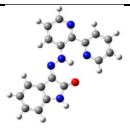
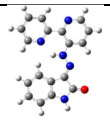
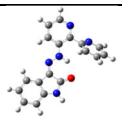
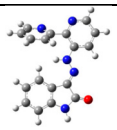
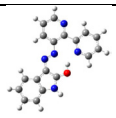
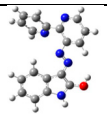


Figure S14. Hydrazone **3** thermally and photochemically stimulated change of ^{1}H-NMR spectrum (1×10^{-3} mol dm^{-3}) + TBAF in DMF: (**a**) without TBAF; (**b**) with TBAF (1×10^{-3} mol dm^{-3}); (**c**) solution b) after 3 h; (**d**) solution c) irradiated 20 min. with light 465 nm.

Table S1. Calculated Gibbs energies [M062x 6-31+g(dp)] level (T = 298.15 K) for *E* and Z isomers of studied hydrazones and their tautomeric forms.

Z_{isomer}	Compound 1	$\Delta G/\Delta G_{DMF}$ $kJ.mol^{-1}$	$\Delta G/\Delta G_{DMF}$ $kJ.mol^{-1}$	Compound 1	E_{isomer}
Z-1		**0/0**	**19.7/10.7**		*E-1*
Z-1-c₁		**16.7/8.6**	**21.5/13.6**		*E-1-t₁*
Z-1-t₁		**40.0**	***31.2***		*E-1-t₂*
Z-1-t₂		**45.3**	***55.1***		*E-1-c₁*
			74.1		*E-1-t₃*
Z-1-t₃		**57.9**	***78.0***		*E-1-t₄*
Z-1-t₄		**69.2**	***83.4***		*E-1-t₅*

	3			3	
Z-3		**0/0**	**14.8/3.4**		*E-3*
Z-3-c₁		**34.7/18.7**	**57.4**		*E-3-c₁*
Z-3-t₁		**56.3**	**90.8**		*E-3-t₁*

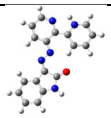
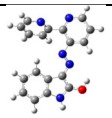
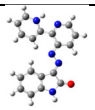
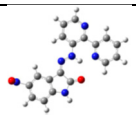
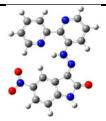
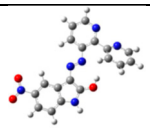
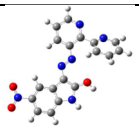
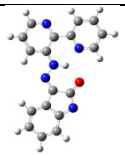
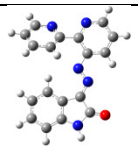
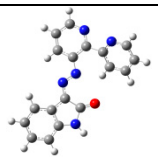
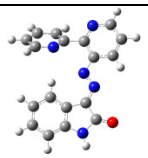
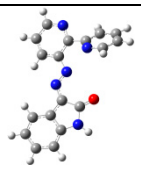
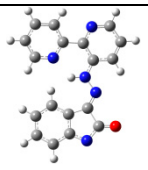
Z-3-t$_2$		**99.9**	**96.9**		*E-3-t*$_2$
-	-	-	**113.7**		*E-3-t*$_3$
	4			**4**	
Z-4		**21.3**	**0.0**		*E-4*
Z-4-t$_1$		**68.3**			
Z-4-t$_2$		**127.2**			

Table S2. Calculated Gibbs energies [M062x 6-31+g(dp)] level (T = 298.15 K) for *E* and *Z* isomers anions of studied hydrazones.

Anion Z$_{isomer}$	**Compound**	**ΔG/ΔG**$_{DMF}$ *kJ.mol*$^{-1}$	**ΔG/ΔG**$_{DMF}$ *kJ.mol*$^{-1}$	**Compound**	*Anion E*$_{isomer}$
	3			**3**	
Z-3-A$_1$*i*		**3.6/5.0**	**0.0/0.0**		*E-3-A*$_1$*h*
Z-3-A$_1$*h*		**14.4/21.5**	**5.6/39.5**		*E-3-A*$_2$*h*
Z-3-A$_2$*h*		**31,4/16.1**	**34.7/15.9**		*E-3-A*$_1$*i*