Supporting Information

Synthesis and photophysical studies of an indigo derivative: *N*-octyl-7,7´-diazaindigo

Gustavo de Miguel*[a], Andrés Garzón-Ruiz[b], Amparo Navarro[c], and Eva M. Garcia-Frutos*[d]

[a]*Institute of Fine Chemistry and Nanochemistry, Department of Physical Chemistry and Applied Thermodynamics, University of Cordoba, Campus Universitario de Rabanales, Edificio Marie Curie, Córdoba, E-14014, Spain, E-mail: q62mirog@uco.es*

[b] *Department of Physical Chemistry, Faculty of Pharmacy, Universidad de Castilla-La Mancha, Cronista Francisco Ballesteros Gómez, 1, E02071 Albacete, Spain*

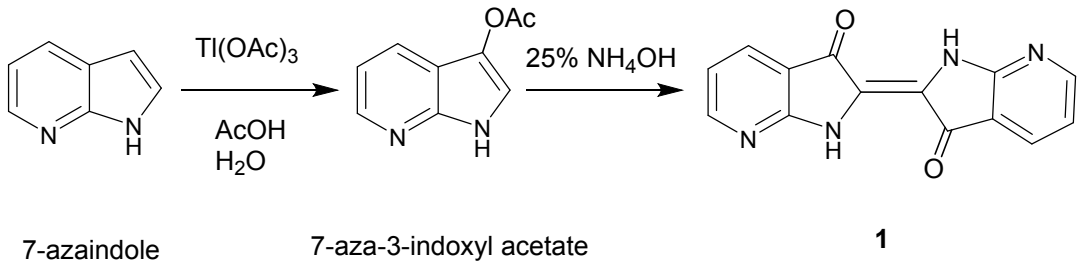
[c] *Department of Physical and Analytical Chemistry, Faculty of Experimental Sciences, Universidad de Jaén, Campus Las Lagunillas, E23071 Jaén, Spain.*

[d]*Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, Cantoblanco, Madrid, E-28049, Spain. E-mail: emgfrutos@icmm.csic.es; phone: +34 91 334 9038*

Table of contents:

1. Experimental Section

7-aza-3-indoxyl acetate and **1** were synthesized based on the reported methods.[1]



Scheme S1. Synthesis of 7,7'-diazaindigo **(1)**.

Synthesis of 2 (E)-1-octyl-[2,2'-bipyrrolo[2,3-b]pyridinylidene]-3,3'(1H,1'H)-dione (2) A mixture of **1** (36 mg, 0,15 mmol), K_2CO_3 (42 mg, 0.031 mmol) and 1-iodooctane (0.07 mL) in dimethylformamide (DMF) (4 mL) was heated at 100 ºC conditions for 2 h. The mixture was cooled to room temperature, the solvent was evaporated. The blue-brown residue was partioned between CH_2Cl_2 and H_2O and dried ($MgSO_4$) and evaporated. The solvent was evaporated and the residue chromatographed on silica gel (hexane:acetone, 3:1) to give a blue solid of compound **2** (20 mg, 37%): ^{1}H NMR (300 MHz, $CDCl_3$,) δ 11,12 (s, 1H), 8,5 (dd, *J* = 1,7 Hz, *J* = 5,0 Hz, 1H), 8,41 (dd, *J* = 1,7 Hz, *J* = 5,0 Hz, 1H), 8,03-7,98 (m, 2H), 7,00-6,94 (m, 2H), 4,70 (t, *J* = 7,6 Hz, 2H), 1,64 (m, 2H), 1,31 (m, 4H), 1,21 (m, 6H), 0,85 (t, *J* = 6,5 Hz, 3H); ^{13}C NMR (76 MHz, $CDCl_3$) δ 187.72, 184.51, 162.67, 162.31, 155.27, 154.78, 133.56, 132.78, 124.02, 121.97, 116.72, 113.53, 113.05,45.08, 31.76, 29.34, 29.17, 29.00, 26.46, 22.59, 14.04. UV-vis (CH_2Cl_2, 25 ºC) λ_{max} (ε) 317 (31066), 601 (10933); MALDI-TOF MS m/z 377 ($M+H^+$); HRMS (MALDI-TOF) calculated for $C_{22}H_{24}N_4O_2$: 377,1972, found: 377,1967.

2. Single crystal X-ray diffraction data for 2

Crystal X-ray diffraction data collections were done at 296(2) K on a Bruker Kappa Apex II diffractometer using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). The structure was solved and refined using the Bruker SHELXTL Software Package. Relevant data acquisition and refinement parameters are gathered in Figure S1 and Tables S1, S2. The crystal structure has been deposited at the CSD with deposition number CCDC 2013556

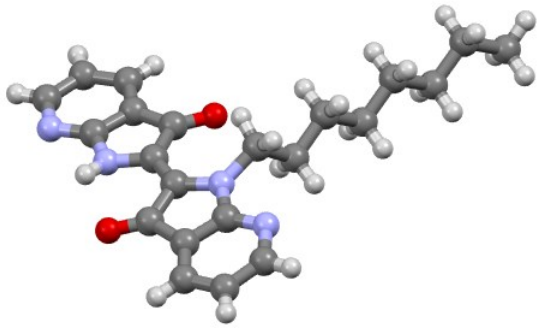


Figure S1. Molecule **2** extracted from X-ray crystal structure

A blue needle-like specimen of $C_{22}H_{24}N_4O_2$, approximate dimensions 0.010 mm x 0.028 mm x 0.233 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 39.96 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 11012 reflections to a maximum θ angle of 25.34° (0.83 Å resolution), of which 3428 were independent (average redundancy 3.212, completeness = 99.9%, R_{int} = 8.83%, R_{sig} = 13.71%) and 2026 (59.10%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.5359(14) Å, b = 5.1353(6) Å, c = 13.931(2) Å, β = 103.691(5)°, volume = 940.8(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 885 reflections above 20 σ(I) with 6.085° < 2θ < 38.18°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.835. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9800 and 0.9990. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21 1, with Z = 2 for the formula unit, $C_{22}H_{24}N_4O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 258 variables converged at R1 = 6.40%, for the observed data and wR2 = 16.40% for all data. The goodness-of-fit was 1.041. The largest peak in the final difference electron density synthesis was 0.240 $e^-/Å^3$ and the largest hole was -0.295 $e^-/Å^3$ with an RMS deviation of 0.067 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.329 g/cm^3 and F(000), 400 e^-.

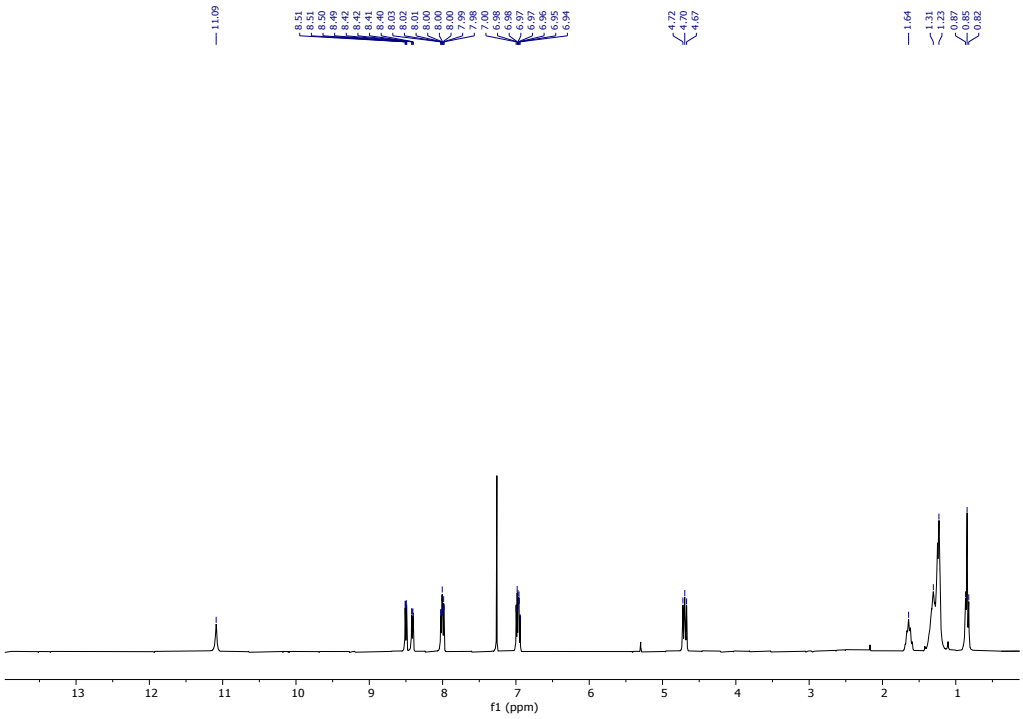
Table S1. Sample and crystal data for **2**

Chemical formula	$C_{22}H_{24}N_4O_2$	
Formula weight	376.45 g/mol	
Temperature	200(2) K	
Wavelength	0,71073 Å	
Crystal size	0.010 x 0.028 x 0.233 mm	
Crystal habit	Blue needle	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 13.5359(14) Å	α = 90°
	b = 5.1353(6) Å	β = 103.691(5)°
	c = 13.931(2) Å	γ = 90°
Volume	940.8(2) $Å^3$	
Z	2	
Density (calculated)	1.329 g/cm^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	400	

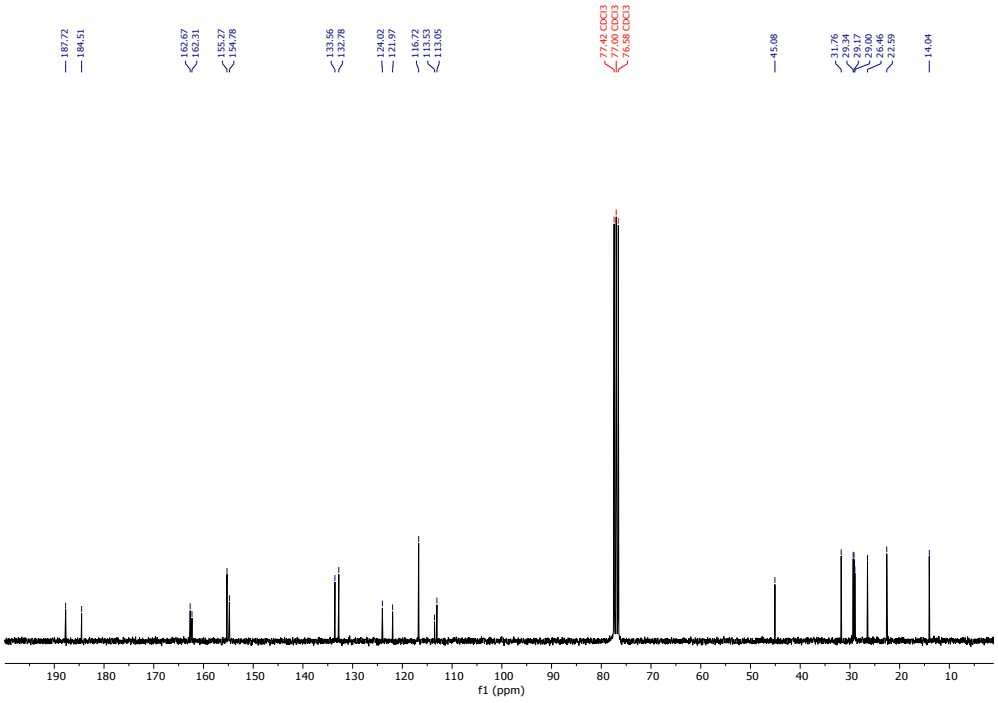
Table S2. Data collection and structure refinement

Theta range for data collection	1.55 to 25.34°	
Index ranges	-16<=h<=16, -6<=k<=6, -16<=l<=16	
Reflections collected	11012	
Independent reflections	3428 [R(int) = 0.0883]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9990 and 0.9800	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3428 / 1 / 258	
Goodness-of-fit on F^2	1.041	
Final R indices	2026 data; I>2σ(I)	$R_1 = 0.0640$, $wR_2 = 0.1181$
	all data	$R_1 = 0.1391$, $wR_2 = 0.1640$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0,0707P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.1(10)	
Largest diff. peak and hole	0.240 and -0.295 $eÅ^{-3}$	
R.M.S. deviation from mean	0.067 $eÅ^{-3}$	

3. Copy ^{1}H NMR and ^{13}C NMR spectrum of compound 2



^{1}H-NMR (300 MHz, $CDCl_3$) (compound **2**)



^{13}C-NMR (75.4 MHz, $CDCl_3$) (compound **2**)

4. UV-Vis absorption, transient absorption and fluorescence emission spectra recorded for compound 1

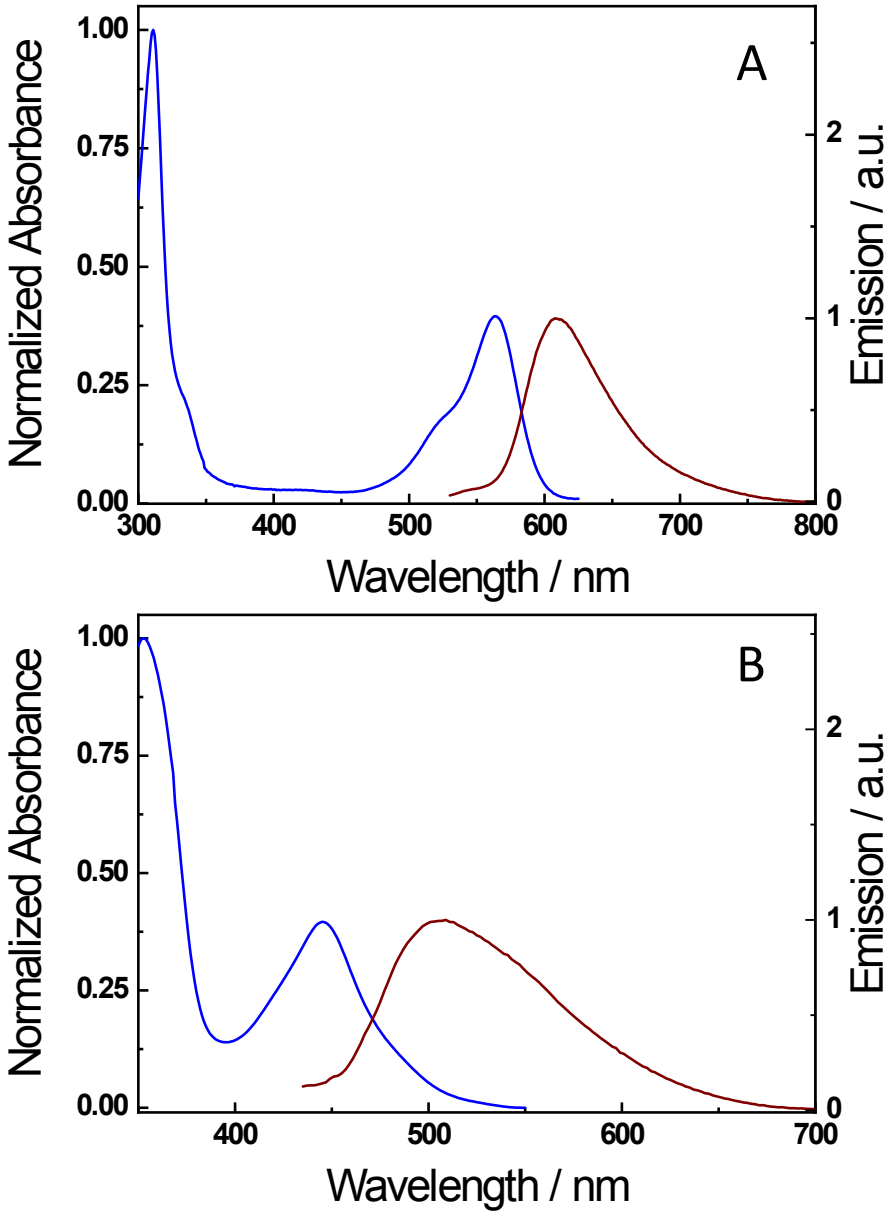


Figure S2. Normalized absorption and emission spectra of the keto (A) and leuco (B) forms of compound **1** in DMF.

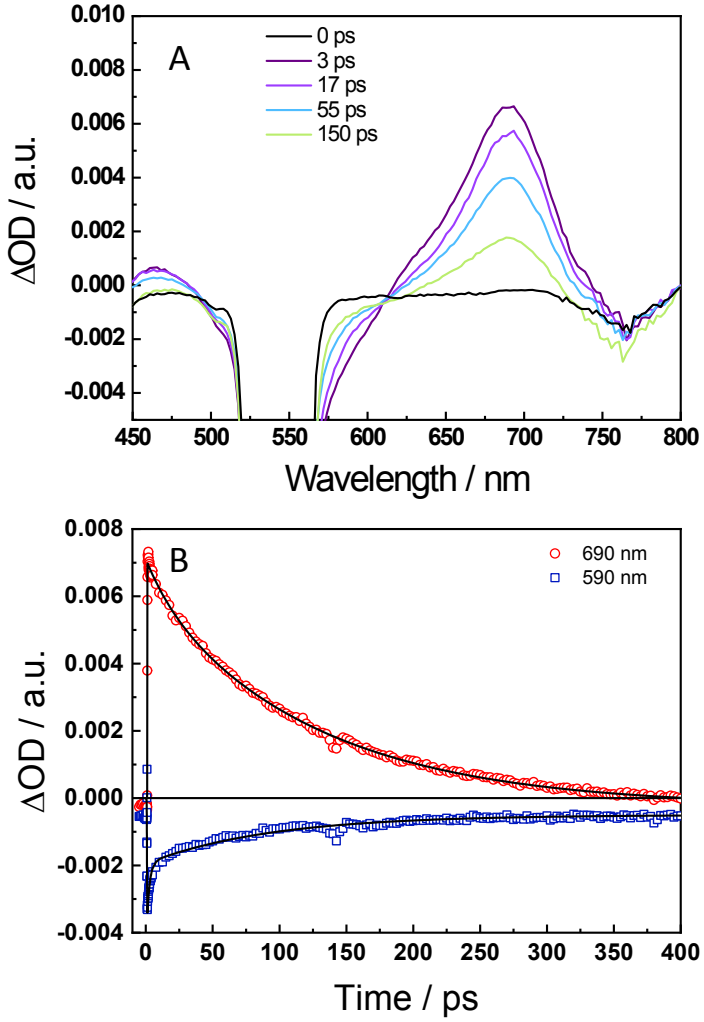


Figure S3. Transient absorption spectra at different time delays (A) and time decays at λ_{probe} = 690 nm and 590 nm (B) for the keto form of **1** in DMF with λ_{exc} = 540 nm. The solid lines in (B) are the best fits of the experimental data obtained from the global analysis.

5. Additional computational data

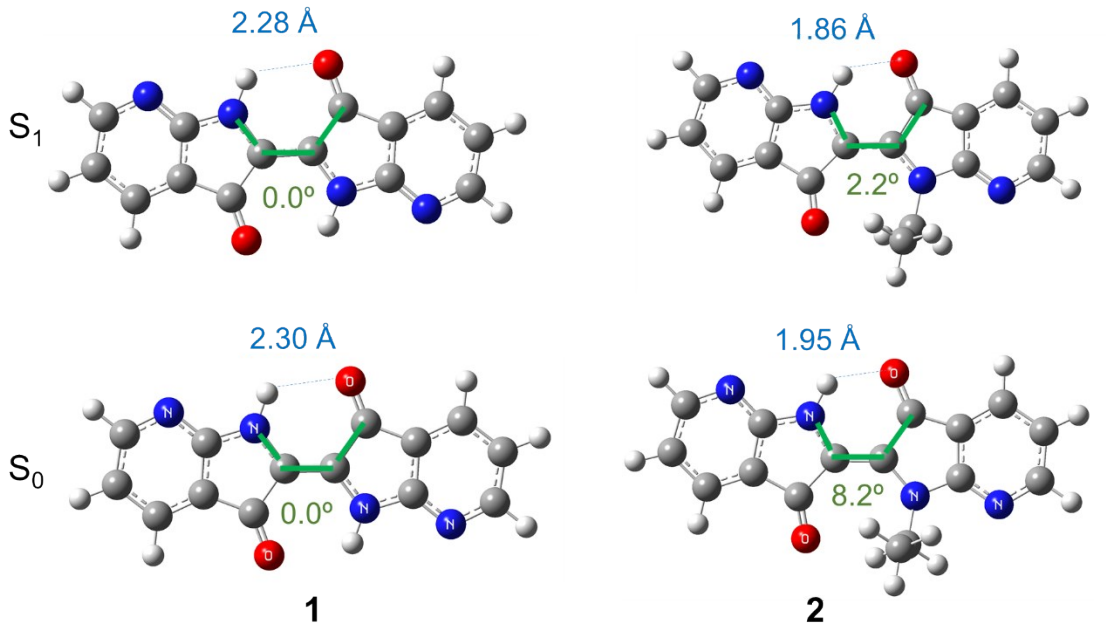


Figure S4. Molecular structure calculated for the ground state (S_0) and first excited state (S_1) of compounds **1** and **2** (in the keto form) at the PBE0/6-31+G* level of theory in DMF solution.

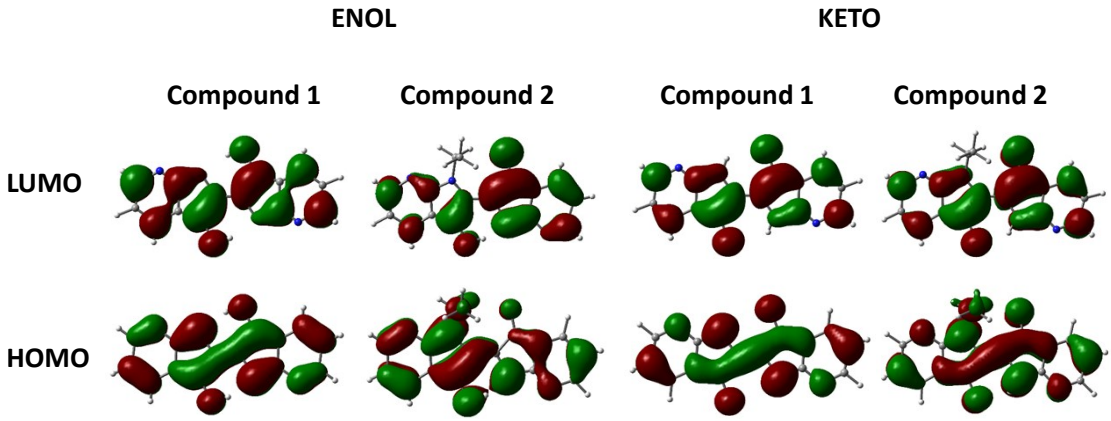


Figure S5. Shapes of frontier molecular orbitals for compounds **1** and **2** calculated at the PBE0/6-31+G* level of theory in DMF solution (isocontour plots (0.02 au)).

Table S3. Calculated vertical electronic transition energies, oscillator strength (*f*), and main component of the transition (% contribution). Calculations were performed at the TD-PBE0/6-31+G* level of theory in DMF solution.

Compound	Form	$\Delta E(S_0 \rightarrow S_1)$ / eV (nm)	Transition	*f*	% Contr.
1	keto	2.32 (535)	$S_0 \rightarrow S_1$	0.31	H → L (100)
		3.95 (314)	$S_0 \rightarrow S_6$	0.34	H-4→ L (94)
1	enol	1.42 (873)	$S_0 \rightarrow S_1$	0.17	H → L (100)
		2.97 (417)	$S_0 \rightarrow S_5$	0.62	H-3 → L (96)
2	keto	2.19 (566)	$S_0 \rightarrow S_1$	0.27	H→L (100)
		3.91 (317)	$S_0 \rightarrow S_6$	0.28	H-4 → L (100)
2	enol	2.00 (620)	$S_0 \rightarrow S_1$	0.23	H→L (100)
		3.62 (342)	$S_0 \rightarrow S_5$	0.39	H-3→L (77); H → L+1 (17)

6. Reference:

1. X. Cheng, K.-H. Merz, S. Vatter, J. Christ, S. Wölfl and G. Eisenbrand, *Bioorganic & Medicinal Chemistry*, 2014, **22**, 247-255.