Electronic Supplementary Material (ESI) for RSC Advances.

From iridoids to dyes: a theoretical study on genipin reactivity - Supporting information

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Table S1. Activation enthalpies ($\Delta H^{\neq}$, kcal/mol) and products stabilization (ΔH, kcal/mol) calculated for the water assisted open-ring reaction and tautomerization in gas phase and in solvent (PCM, solvent=ethanol).

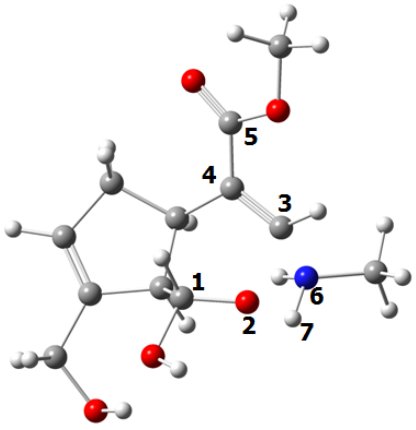
	GAS PHASE		SOLVENT	
REACTION	$\Delta H^{\neq}$	ΔH	$\Delta H^{\neq}$	ΔH
1→2' (H_2O assisted)	16.8	5.6	16.6	5.6
2'→2 (H_2O assisted)	19.2	4.1	16.5	2.3

Table S2 and **S3.** Activation barriers ($\Delta G^{\neq}$, kcal/mol) and products stabilization (ΔG, kcal/mol) calculated in the gas phase for each step of the reaction pathway producing **7** and starting from nucleophilic attack of methylamine on genipin in the open-ring form **2** dubbed **C** and **D** in Figure 2. Activation barriers and products stabilizations are also reported for the same reactions catalyzed by one or two water molecules.

REACTIONS	$\Delta G^{\neq}$	ΔG
C	**32.1**	**0.5**
2A → 3 + H_2O	58.7	2.9
+ H_2O	29.4	1.6
+ 2 H_2O	**24.9**	**3.4**
3 → 4	76.5	6.7
+ H_2O	30.5	-1.2
+ 2 H_2O	**27.2**	**1.4**
4 → 5*cis*	33.6	-22.6
+ H_2O	3.7	-17.2
+ 2 H_2O	**2.6**	**-14.8**
5*cis* → 7 + H_2O + H_2O	44.5	3.9

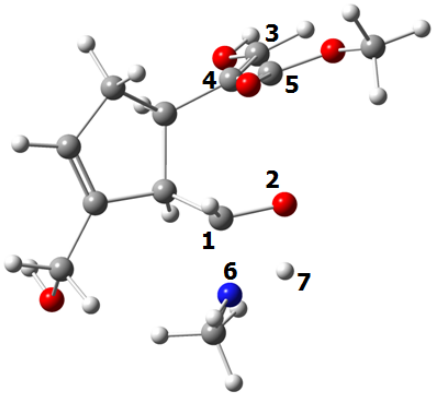
REACTIONS	$\Delta G^{\neq}$	ΔG
D	**33.7**	**4.3**
2A' → 3' + H_2O	49.6	2.0
+ 2 H_2O	**22.7**	**0.5**
3' → 4'	57.3	3.8
+ 2 H_2O	**31.2**	**4.8**
4' → 5'*cis*	23.2	-10.8
+ H_2O	5.2	-14.6
+ 2 H_2O	**3.0**	**-13.9**
5'*cis* → 7 + H_2O + H_2O	36.5	5.1

Figure S1. Optimized structure of the transition states involved in the reactions described in the paper.



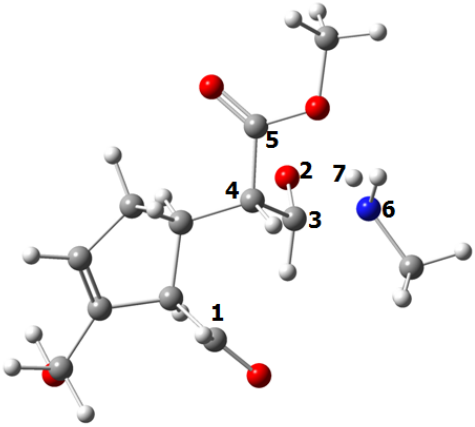
reaction A

C3-N6= 1.50Å
O2-H7= 1.69 Å
C5-C4-C3-N6= -147.7°
C1-O2-C3-N6= -110.7 °



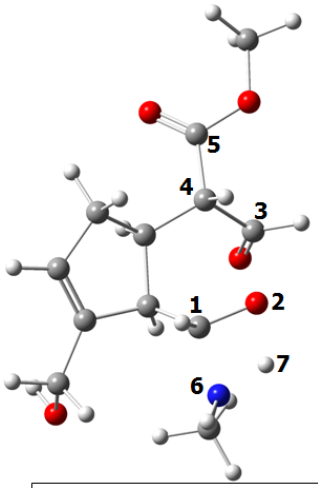
reaction B

C1-N6= 1.56 Å N6-H7= 1.21 Å
O2-H7= 1.38 Å O2-C3= 3.56 Å
N6-C1-O2= 95.4°
C1-O2-H7= 75.2 °
C3-C4-C5-O2= -106.8 °



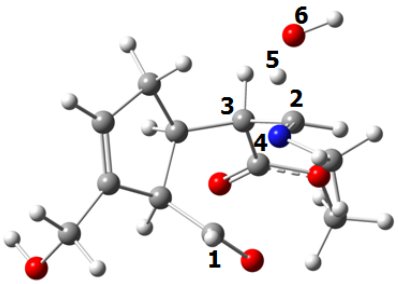
reaction C

C3-N6= 1.53 Å N6-H7= 1.22 Å
O2-H7= 1.37 Å C1-O2= 4.51 Å
N6-C3-O2= 97.2°
C3-O2-H7= 75.4 °
C5-C4-C3-N6= 67.5 °



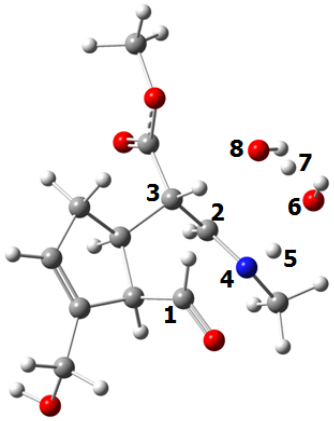
reaction D

C1-N6= 1.54 Å N6-H7= 1.22 Å
O2-H7= 1.35 Å O2-C3= 2.45 Å
N6-C1-O2= 95.4°
C1-O2-H7= 76.0 °
C5-C4-C3-O2= 162.4 °



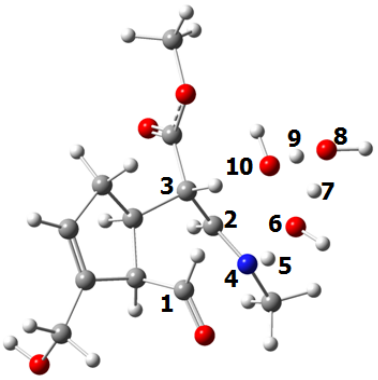
2A → 3 + H_2O

C1-N4= 2.64 Å N4-H5= 1.28 Å
H5-O6= 1.27 Å C2-O6= 1.93 Å
C2-N4-H5= 81.1°
N4-H5-O6= 129.9°
C3-C2-N4-H5= -96.0°



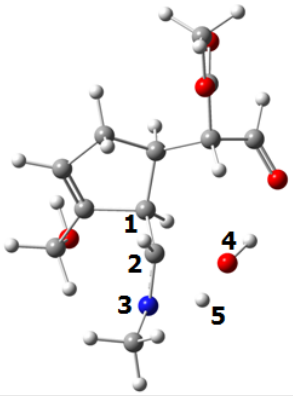
2A → 3 + H_2O (+ H_2O)

C1-N4= 3.16 Å N4-H5= 1.10 Å
H5-O6= 1.51 Å O6-H7= 1.29 Å
H7-O8= 1.15 Å C2-O8= 2.19 Å
C2-N4-H5-O6= -59.1°
H5-O6-H7-O8= -2.0°



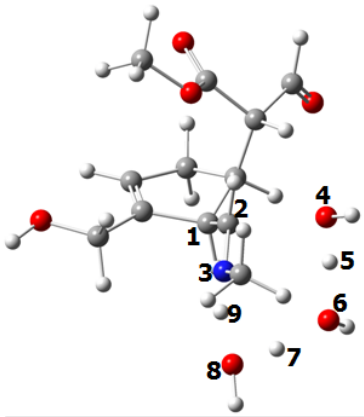
2A → 3 + H_2O (+ $2H_2O$)

C1-N4= 3.16 Å N4-H5= 1.07 Å
H5-O6= 1.60 Å O6-H7= 1.13 Å
H7-O8= 1.32 Å O8-H9= 1.38 Å
H9-O10= 1.09 Å C2-O10= 2.18 Å
C2-N4-H5-O6= -31.4°
O6-H7-O8-H9= -20.5°
H5-N4-C2-O10= 83.1°



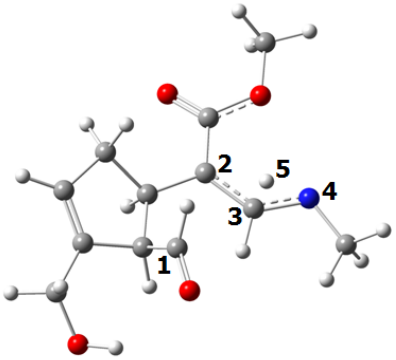
2A' → 3' + H_2O

C2-N3= 1.35 Å C2-O4= 1.82 Å
N3-H5= 1.34 Å O4-H5= 1.22 Å
C1-C2-N3-H5= 100.4°
C2-N3-H5-O4= 16.0°



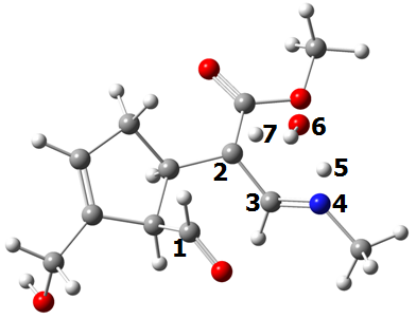
2A' → 3' + H_2O (+ $2H_2O$)

C2-N3= 1.29 Å C2-O4= 2.29 Å
N3-H9= 1.07 Å O4-H5= 1.09 Å
H5-O6= 1.38 Å O6-H7= 1.35 Å
H7-O8= 1.10 Å O8-H9= 1.59 Å
C1-C2-N3-H9= 21.3°
C2-N3-H9-O8= 47.4°
N3-H9-O8-H7= 18.4°
H9-O8-H7-O6= -5.1°
O8-H7-O6-H5= -16.1°
H7-O6-H5-O4= 22.7°



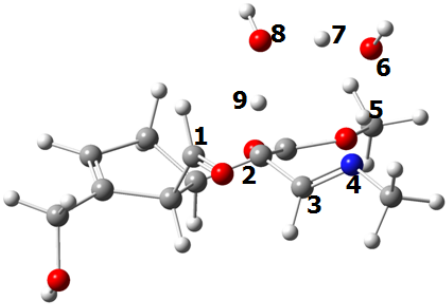
3 → 4

C1-C3= 3.07 Å N4-H5= 1.64 Å
C2-H5= 1.84 Å C3-H5= 1.17 Å
C2-C3-N4-H5= 81.1°



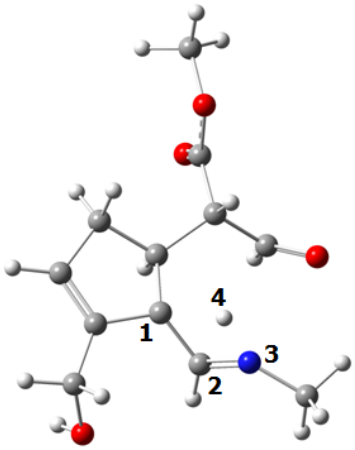
3 → 4 (+ H_2O)

C1-C3= 3.05Å N4-H5= 1.12 Å
H5-O6= 1.46 Å O6-H7= 1.31 Å
C2-H7= 1.34 Å
C2-C3-N4-H5= 9.2°
N4-H5-O6-H7= -10.3°



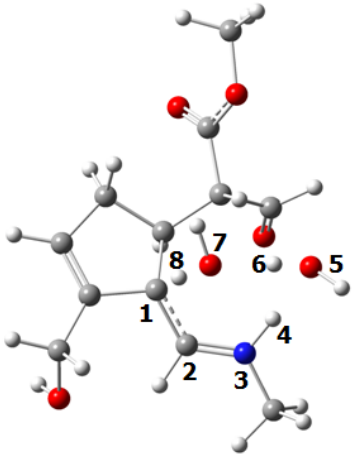
3 → 4 (+ $2H_2O$)

C1-C3= 2.95 Å N4-H5= 1.09 Å
H5-O6= 1.53 Å O6-H7= 1.10 Å
H7-O8= 1.36 Å O8-H9= 1.48 Å
C2-H9= 1.22 Å
C2-C3-N4-H5= 6.4°
N4-H5-O6-H7= -44.1°
O6-H7-O8-H9= -22.1°



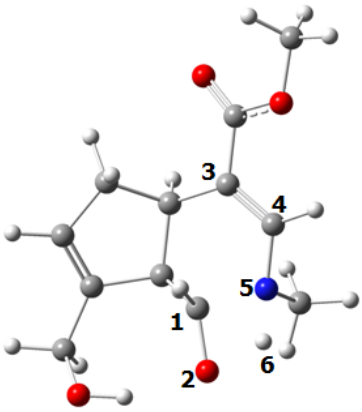
3' → 4'

C1-C2= 1.47 Å C2-N3= 1.29 Å
N3-H4= 1.25 Å C1-H4= 1.63 Å
C1-C2-N3-H4= 2.3°



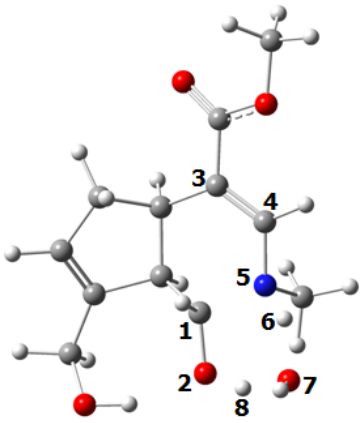
3' → 4' (+ $2H_2O$)

C1-C2= 1.44 Å C2-N3= 1.30 Å
N3-H4= 1.04 Å H4-O5= 1.81 Å
O5-H6= 1.03 Å H6-O7= 1.55 Å
C1-H8= 1.29 Å
C1-C2-N3-H4= 4.6°
C2-N3-H4-O5= 71.4°
N3-H4-O5-H6= -33.8°
H4-O5-H6-O7= -21.4°
O5-H6-O7-H8= -7.3°



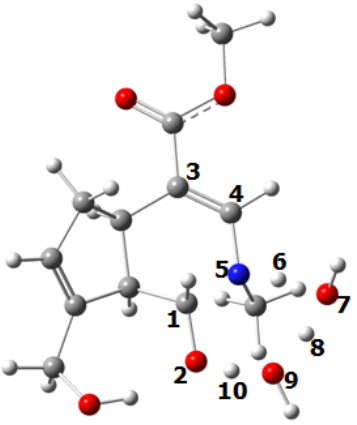
4 → 5*cis*

C1-N5= 1.52 Å N5-H6= 1.25 Å
O2-H6= 1.42 Å
C1-O2-H6= 72.9°
C4-N5-H6= 139.8°
C3-C4-N5-H6= -122.7°



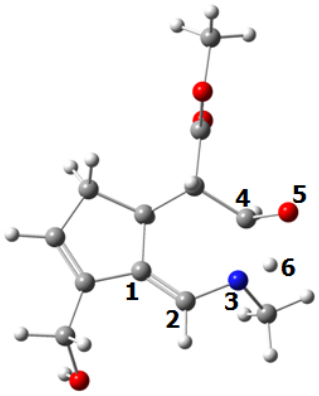
4 → 5*cis* (+ H_2O)

C1-N5= 1.55 Å N5-H6= 1.15 Å
H6-O7= 1.42 Å O7-H8= 1.24 Å
H8-O2= 1.20 Å
C1-O2-H8= 101.4°
C4-N5-H6= 116.7°
C3-C4-N5-H6= -139.1°
C4-N5-H6-O7= 162.6°
N5-H6-O7-H8= -18.1°



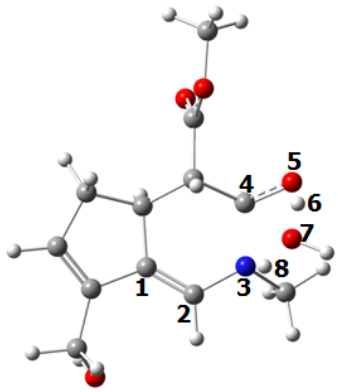
4 → 5*cis* (+ $2H_2O$)

C1-N5= 1.55 Å N5-H6= 1.14 Å
H6-O7= 1.41 Å O7-H8= 1.16 Å
H8-O9= 1.26 Å O9-H10= 1.26 Å
H10-O2= 1.17 Å
C1-O2-H10= 109.7°
C4-N5-H6= 107.3°
C3-C4-N5-H6= -138.3°
C4-N5-H6-O7= -167.0°
N5-H6-O7-H8= -49.1°
H6-O7-H8-O9= -4.5°
O7-H8-O9-H10= 16.1°



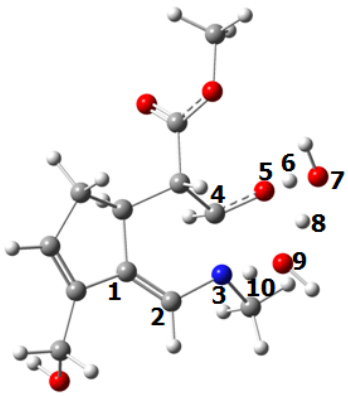
4' → 5'*cis*

C2-N3= 1.43 Å N3-C4= 1.56 Å
C4-O5= 1.35 Å N3-H6= 1.21 Å
O5-H6= 1.39 Å
C4-O5-H6= 75.8°
C1-C2-N3-H6= 105.4°



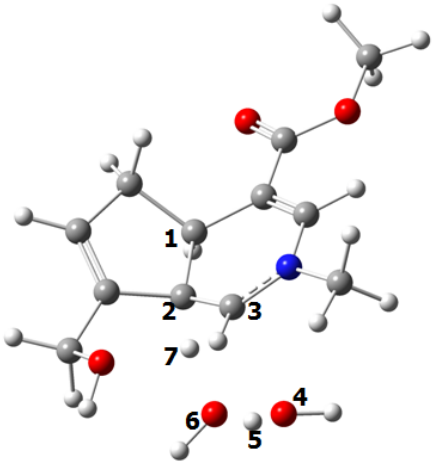
4' → 5'*cis* (+ H_2O)

C2-N3= 1.44 Å N3-C4= 1.57 Å
C4-O5= 1.34 Å O5-H6= 1.21 Å
H6-O7= 1.23 Å O7-H8= 1.46 Å
N3-H8= 1.12 Å
C4-O5-H6= 103.9°
C1-C2-N3-H8= 104.2°
C2-N3-H8-O7= -133.3°
N3-H8-O7-H6= -13.8°



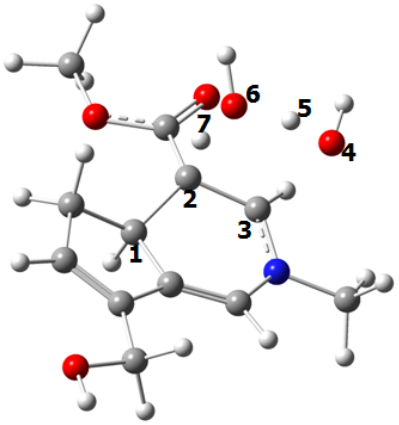
4' → 5'*cis* (+ $2H_2O$)

C2-N3=1.45 Å N3-C4= 1.56 Å
C4-O5= 1.34 Å O5-H6= 1.15 Å
H6-O7= 1.28 Å O7-H8= 1.27 Å
H8-O9= 1.15 Å O9-H10= 1.47 Å
N3-H10= 1.12 Å
C4-O5-H6= 113.4°
C1-C2-N3-H10= 98.5°
C2-N3-H10-O9= -85.4°
N3-H10-O9-H8= -60.9°
H10-O9-H8-O7= 0.1°
O9-H8-O7-H6= 1.3°



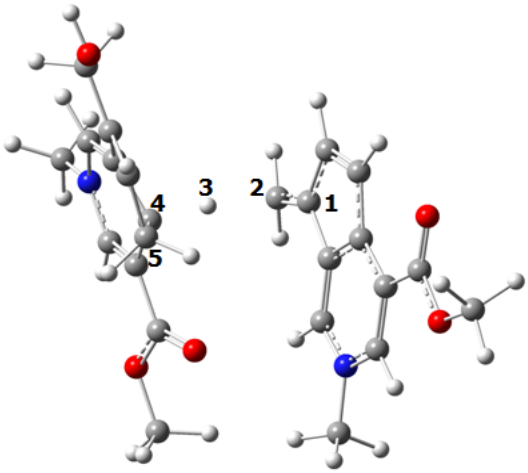
5*cis* → 7 + H_2O (+ H_2O)

C2-C3= 1.45 Å C3-O4= 2.31 Å
O4-H5= 1.14 Å H5-O6= 1.28 Å
O6-H7= 1.55 Å C2-H7= 1.19 Å
C1-C2-C3-O4= -118.0°
C2-C3-O4-H5= 0.9°
C3-O4-H5-O6= 15.2°
O4-H5-O6-H= -19.7°



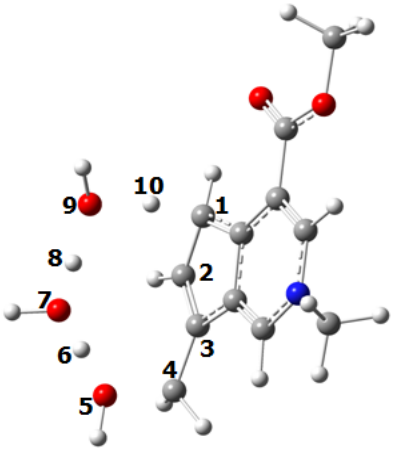
5'*cis* → 7 + H_2O (+ H_2O)

C2-C3= 1.47 Å C3-O4= 2.17 Å
O4-H5= 1.15 Å H5-O6= 1.27 Å
O6-H7= 1.48 Å C2-H7= 1.22 Å
C1-C2-C3-O4= -129.3°
C2-C3-O4-H5= 20.0°
C3-O4-H5-O6= -2.4°
O4-H5-O6-H= -12.4°



7 + 8Me

C1-C2= 1.39 Å C2-H3= 1.46 Å
H3-C4= 1.25 Å C4-C5= 1.48 Å
C1-C2-H3= 112.2°
C1-C2-H3-C4= -97.7°



7ox → 8Me (+ 2 H_2O)

C1-H10= 1.23 Å C3-C4= 1.47 Å
C4-O5= 1.60 Å O5-H6= 1.29 Å
H6-O7= 1.14 Å O7-H8= 1.10 Å
H8-O9= 1.43 Å O9-H10= 1.39 Å
C2-C3-C4-O5= -85.2°
C3-C4-O5-H6= -7.2°
C4-O5-H6-O7= 176.5°
O5-H6-O7-H8= -144.4°
H6-O7-H8-O9= 52.8°
O7-H8-O9-H10= -86.5°

Figure S2. UV-visible spectrum simulated (PBE0/6-31+G(d)) for the intermediate 7. Optimized structure of the intermediate and his calculated emission color are also reported.

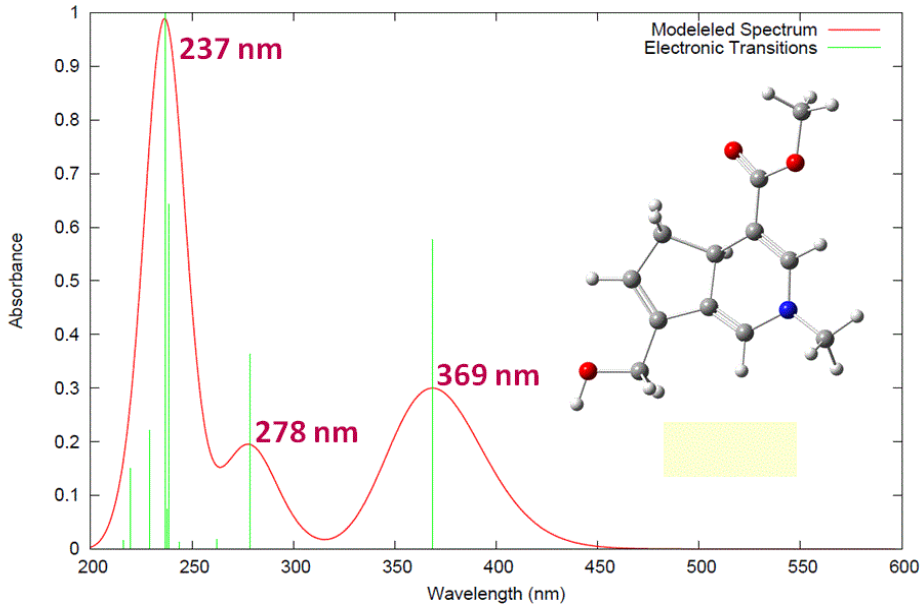


Figure S3. Orbitals involved in the HOMO-LUMO electronic transition of **8** intermediate.