

***Electronic Supplementary Information (ESI)***

***Mechanisms of photoisomerization of the prenylated flavin  
mononucleotide cofactor: A theoretical study†***

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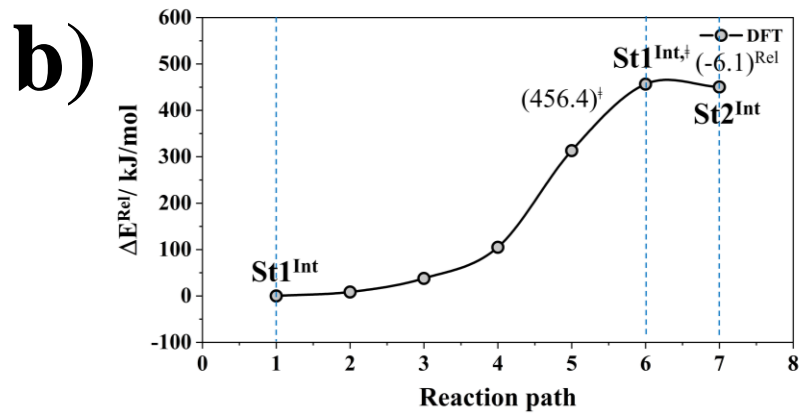
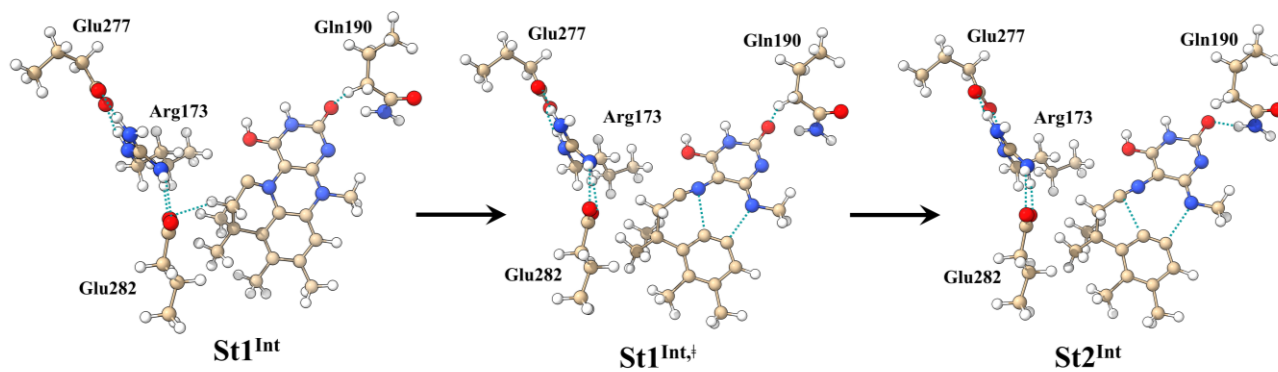
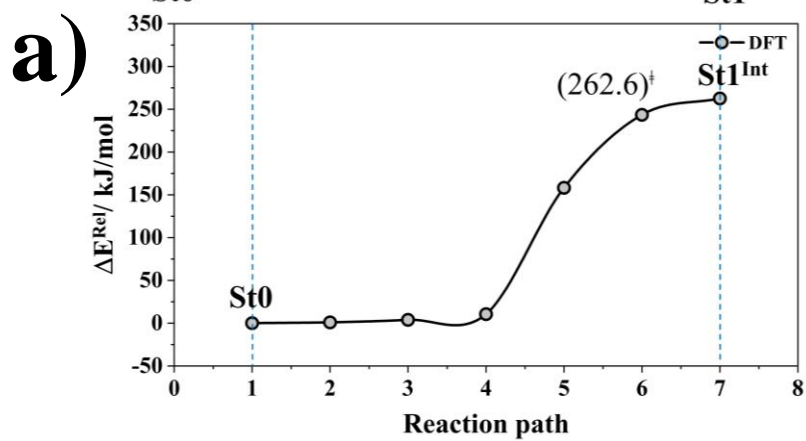
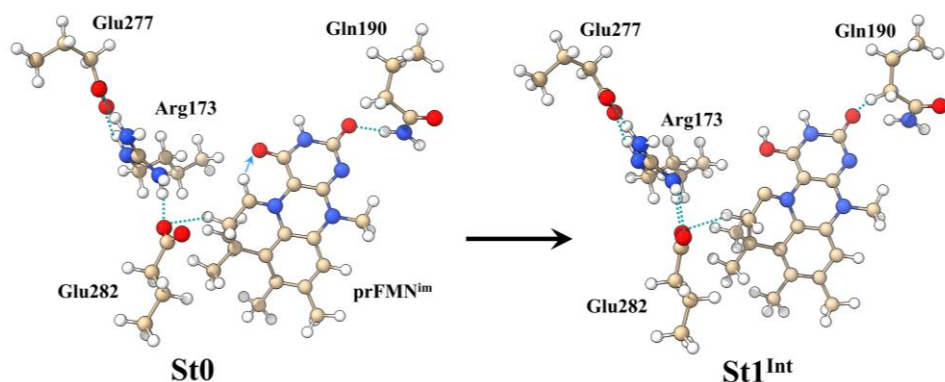
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**Figure S1** The  $S_0$  PESs for the intramolecular proton transfer and concerted covalent bond dissociations ( $St0 \rightarrow St1^{Int} \rightarrow St2^{Int}$ ) in Type **(1)** mechanism<sup>5</sup> (Figure 1), obtained from the DFT/B3LYP/DZP reaction path optimizations.

a)  $C_{1'}^{prFMN} - H \dots O^{prFMN^{im}}$  intramolecular proton transfer in **prFMN<sup>im</sup>** ( $St0 \rightarrow St1^{Int}$ ).

b) Concerted  $N_5^{prFMN} - C_{5a}^{prFMN}$  and  $N_{10}^{prFMN} - C_{9a}^{prFMN}$  covalent bond dissociations in **prFMN<sup>im</sup>** ( $St1^{Int} \rightarrow St2^{Int}$ ).

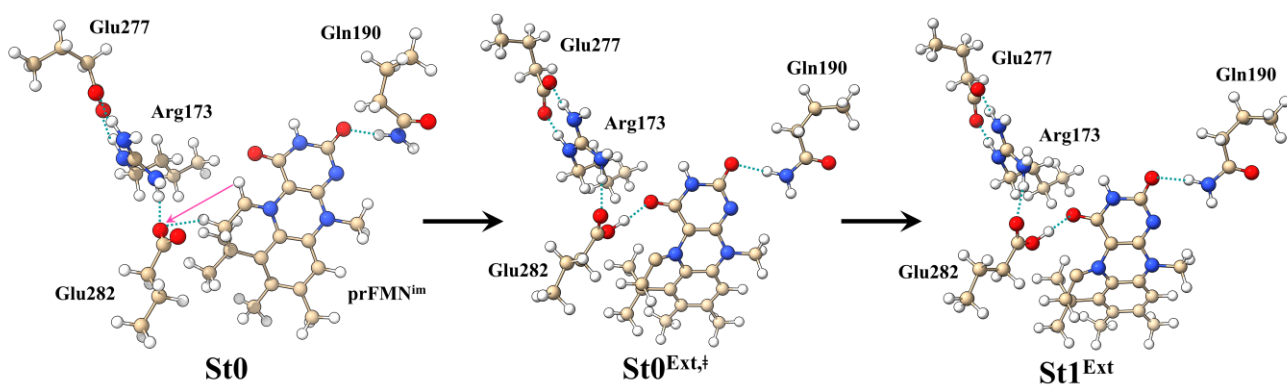


**Figure S1**

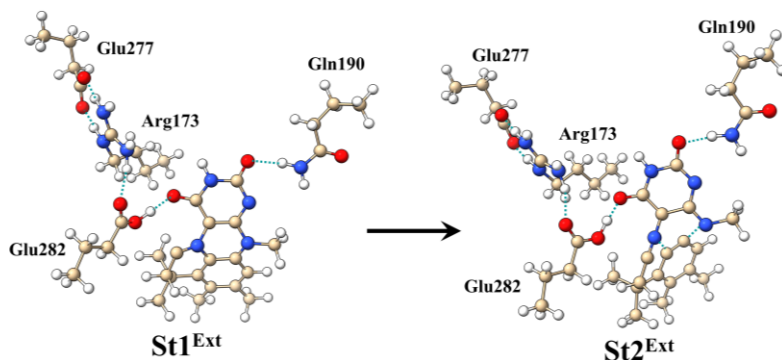
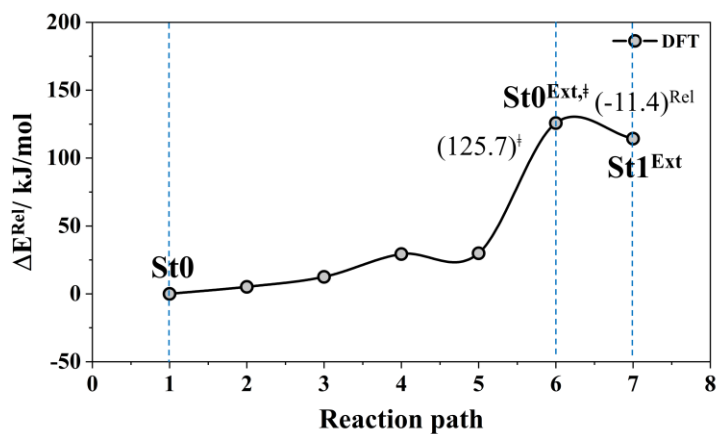
**Figure S2** The  $S_0$  PESs for the intermolecular proton transfer and concerted covalent bond dissociations ( $St0 \rightarrow St1^{Ext} \rightarrow St2^{Ext}$ ) in Type (2) mechanism<sup>5</sup> (Figure 1), obtained from the DFT/B3LYP/DZP reaction path optimizations.

a) Intermolecular proton transfer in the  $C_{1'}^{prFMN} - H \rightarrow O^{Glu282}$  H-bond between **prFMN<sup>im</sup>** and **Glu282** ( $St0 \rightarrow St1^{Ext}$ ).

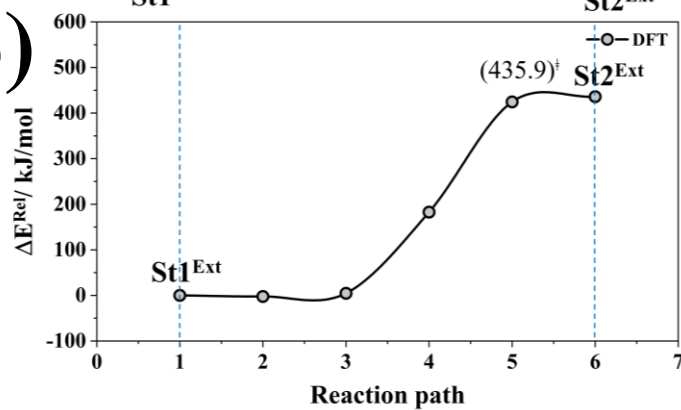
b) Concerted  $N_5^{prFMN} - C_{5a}^{prFMN}$  and  $N_{10}^{prFMN} - C_{9a}^{prFMN}$  covalent bond dissociations in **prFMN<sup>im</sup>** ( $St1^{Ext} \rightarrow St2^{Ext}$ ).



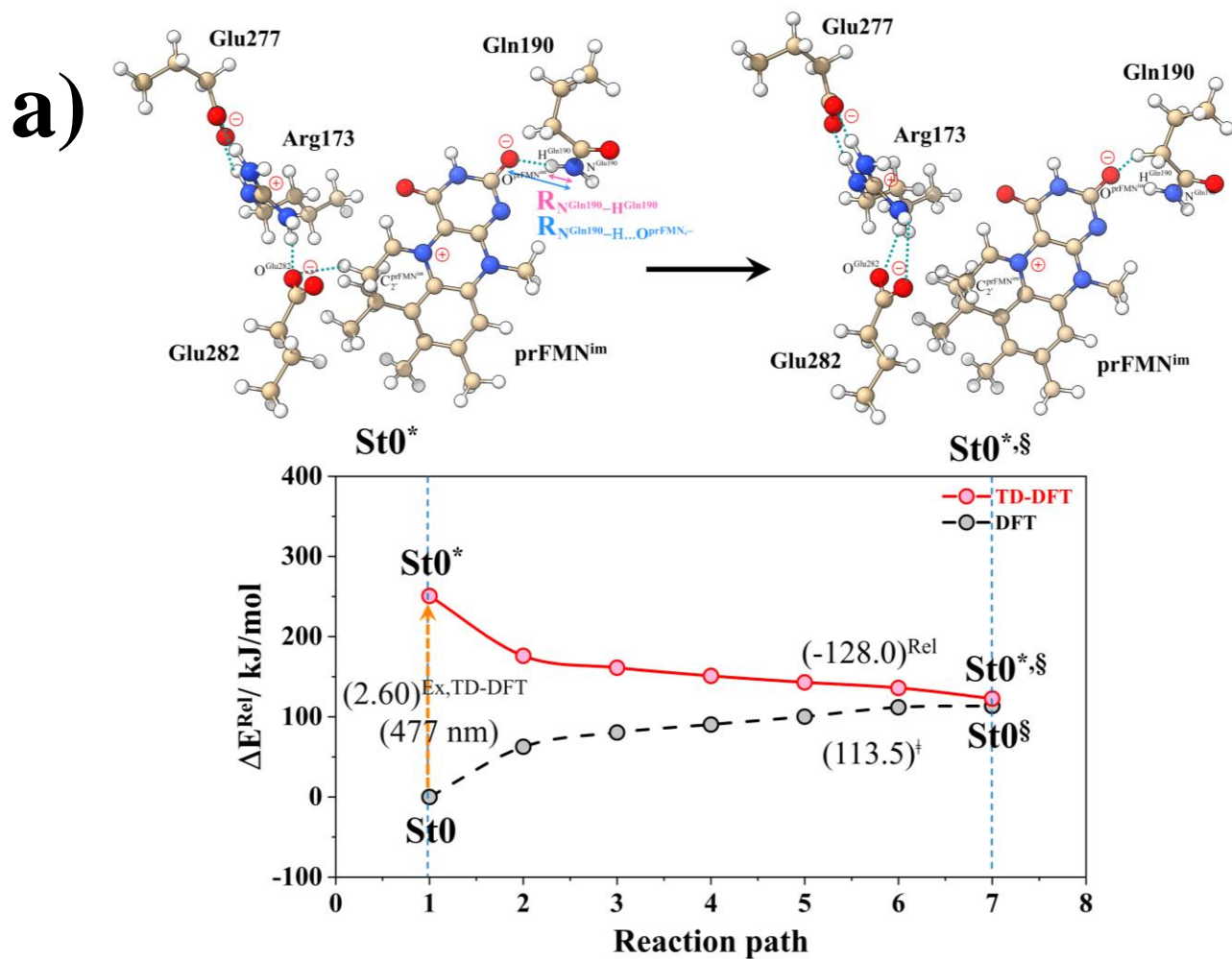
**a)**



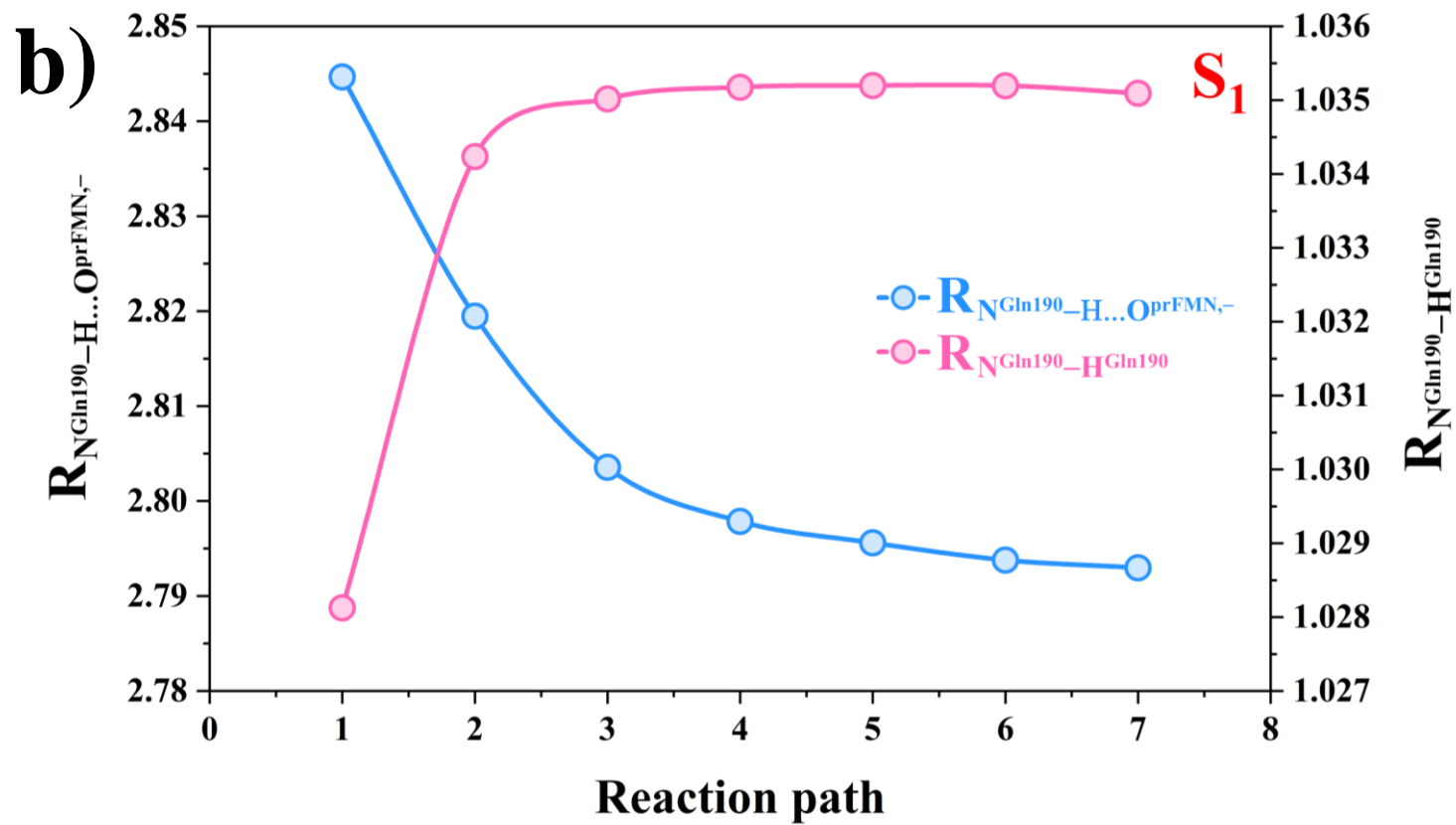
**b)**



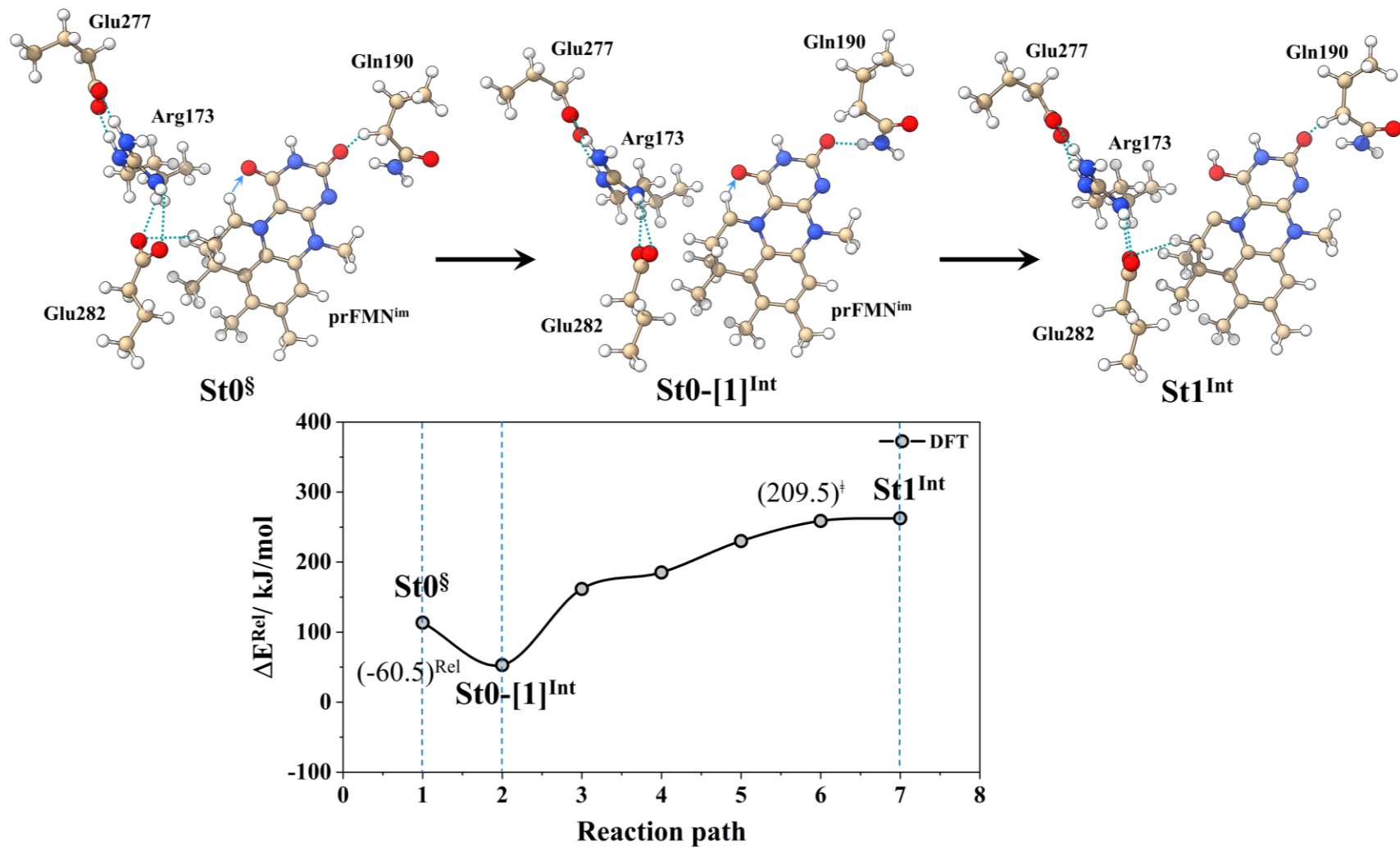
**Figure S2**



**Figure S3** a) The  $S_1$  PES (solid line) for the relaxation of the  $S_0 \rightarrow S_1$  vertically excited active site cluster to the structure at the  $S_0/S_1$  intersection ( $St0^* \rightarrow St0^{*,§}$ ), obtained from TD-DFT/B3LYP/DZP reaction path optimizations; dash line =  $S_0$  PES computed using the geometry on the  $S_1$  PES and DFT/B3LYP/DZP method. b) The variation of the  $N^{\text{Gln190}}-\text{H}\dots\text{O}^{\text{prFMN,-}}$  H-bond distances on the  $S_1$  PES, which reflects an increase in the  $N^{\text{Gln190}}-\text{H}\dots\text{O}^{\text{prFMN,-}}$  H-bond strength (red-shift) in the  $S_1$  state towards the  $S_0/S_1$  intersection.



**Figure S3 (Cont.)**



**Figure S4** The S<sub>0</sub> PES for the C<sub>1</sub><sup>prFMN</sup>-H → O<sup>prFMN<sup>im</sup></sup> intramolecular proton transfer after the S<sub>1</sub> → S<sub>0</sub> nonradiative relaxation (St0<sup>S</sup> → St1<sup>Int</sup>), obtained from DFT/B3LYP/DZP reaction path optimizations.



**Figure S5** The  $S_0$  PESs for formation of **prFMN<sup>ket</sup>** after the  $S_1 \rightarrow S_0$  nonradiative relaxation in Type (3) mechanism ( $St0^S \rightarrow St4$ ), obtained from DFT/B3LYP/DZP reaction path optimizations.

- a)  $C_1^{prFMN}-H \rightarrow O^{Glu282}$  intermolecular proton transfer ( $St0^S \rightarrow St1^{Ext}$ ).
- b) Ring expansion ( $St1^{Ext} \rightarrow St3^{Ext}$ )
- c) Reverse protonation ( $St3^{Ext} \rightarrow St4$ ).

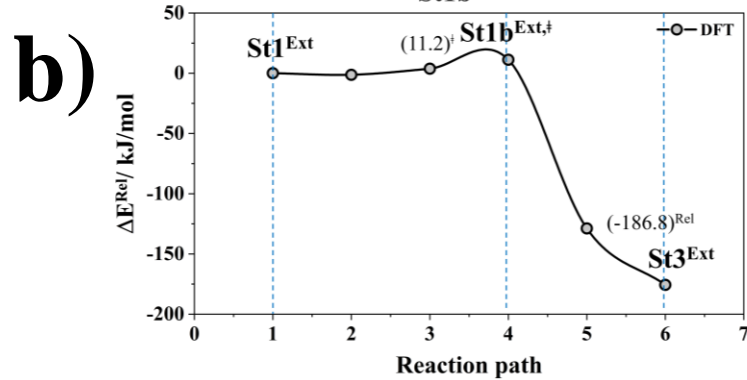
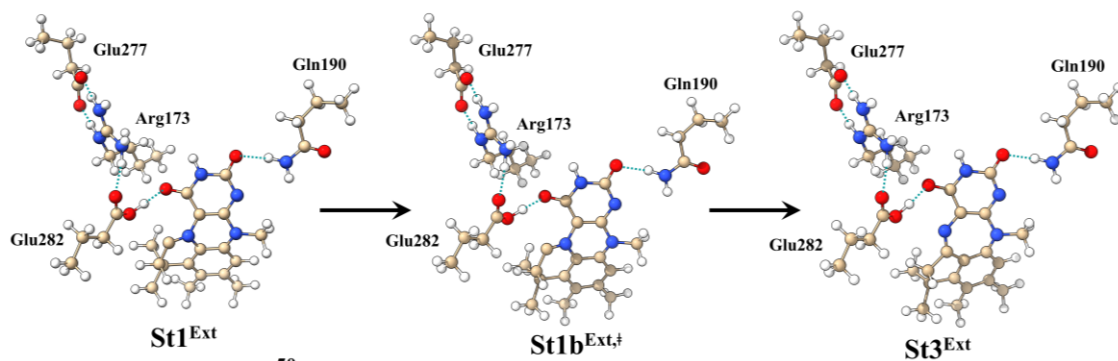
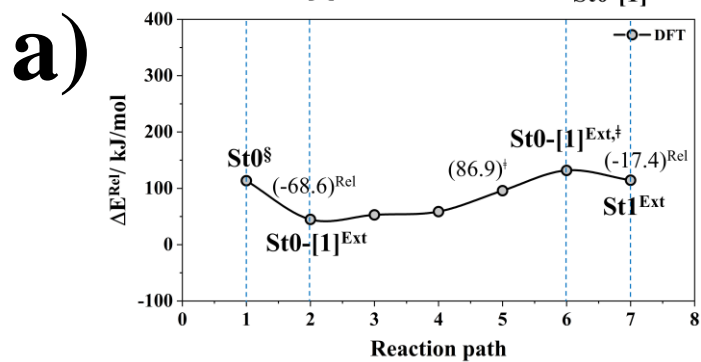
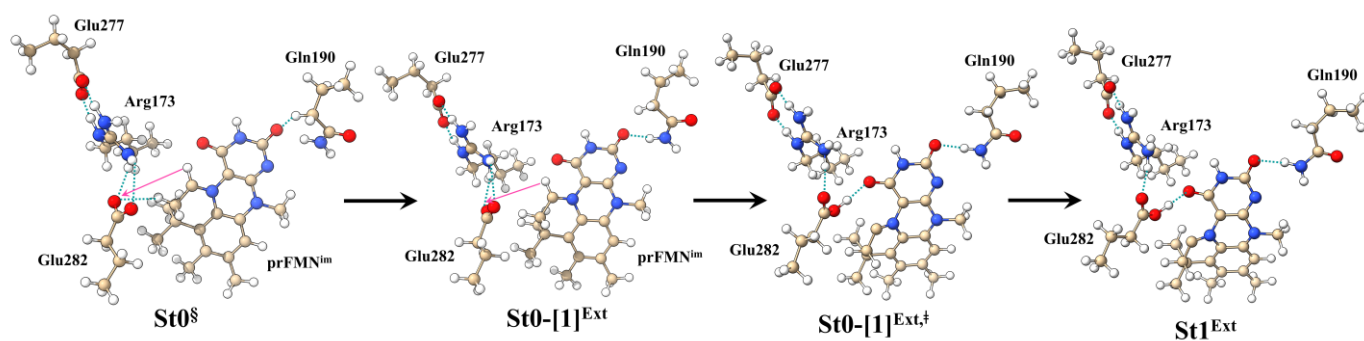
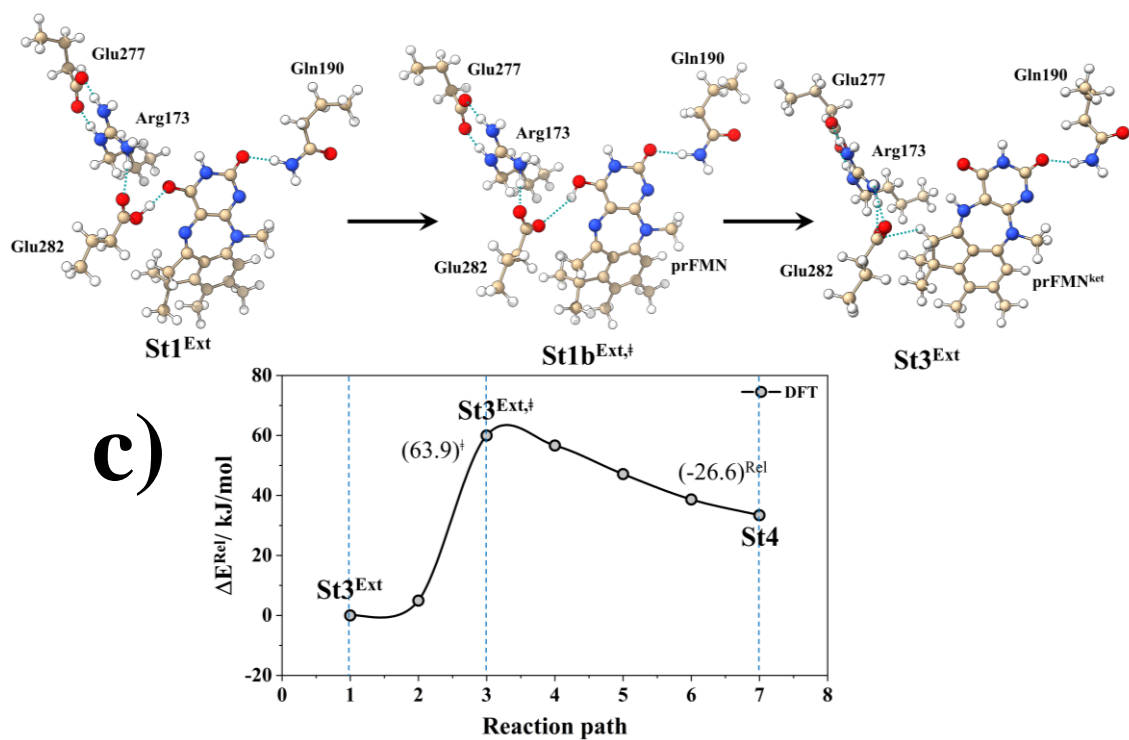
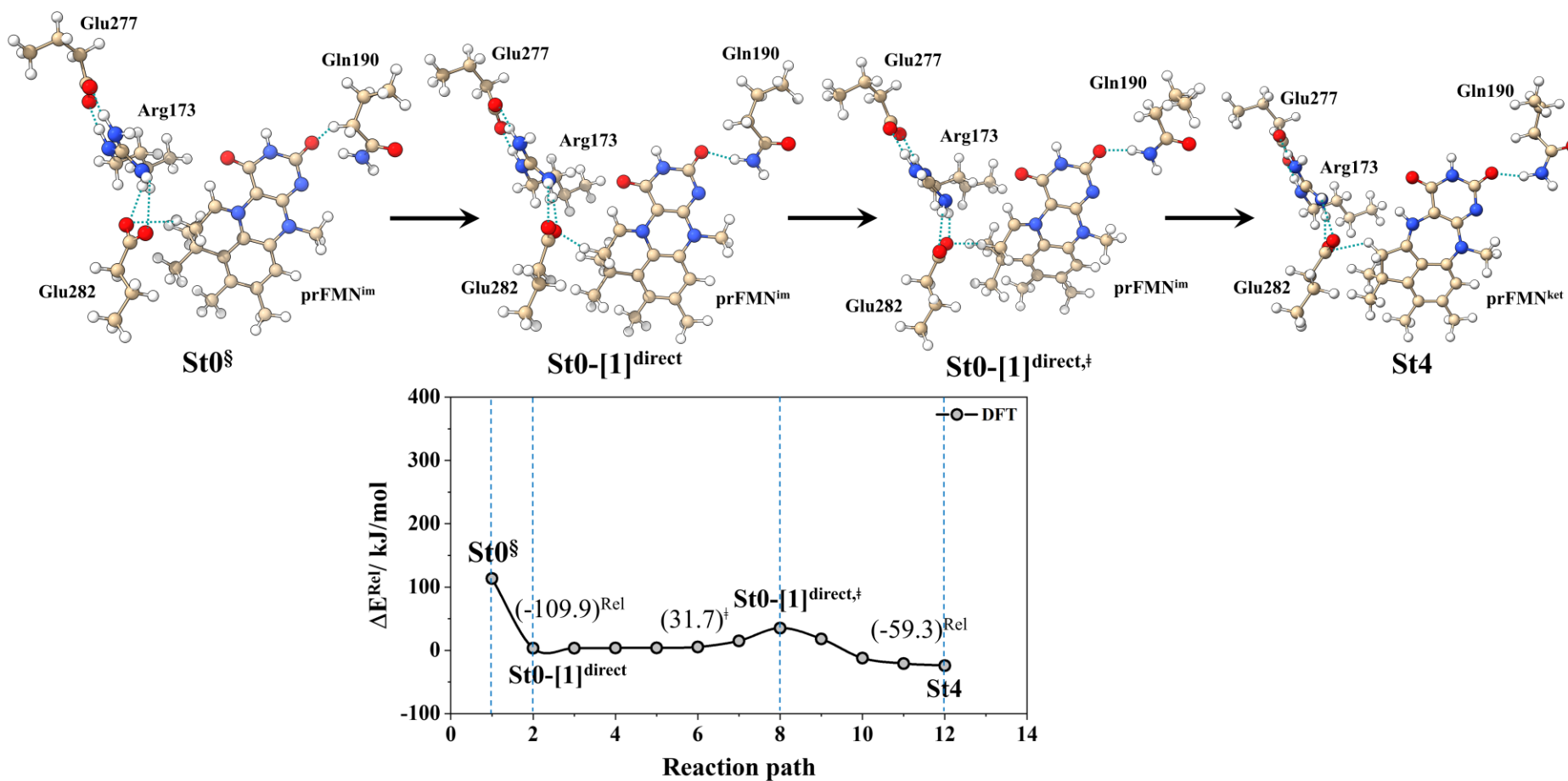


Figure S5

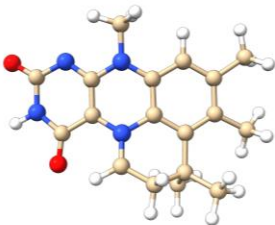
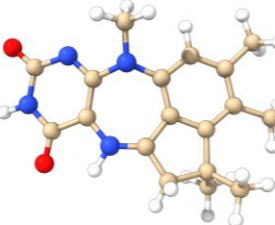
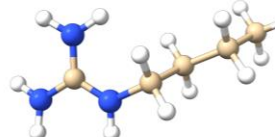
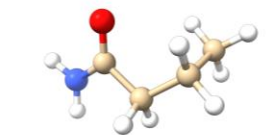
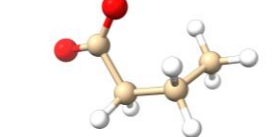
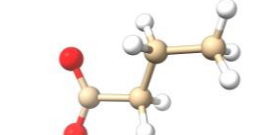


**Figure S5**



**Figure S6** The S<sub>0</sub> PES for formation of prFMN<sup>ket</sup> after the S<sub>1</sub>→S<sub>0</sub> nonradiative relaxation in Type (4) mechanism (St0<sup>S</sup>→St4). The S<sub>1</sub>→S<sub>0</sub> nonradiative relaxation is followed by concerted C<sub>1</sub><sup>prFMN</sup>-H→N<sub>5</sub><sup>prFMN</sup> intramolecular proton transfer and ring expansion (St0<sup>S</sup>→St4), obtained from DFT/B3LYP/DZP reaction path optimization.

**Table S1** Equilibrium structures and energies of molecules involved in the  $\text{prFMN}^{\text{im}} \rightarrow \text{prFMN}^{\text{ket}}$  photoisomerization obtained from DFT/B3LYP/DZP geometry optimizations.  $E^{\text{Tot}}$  = total energy in au;  $\Delta E^{\text{Ex}}$  = the  $S_0 \rightarrow S_1$  energy in eV; (...) = absorption wavelength in nm.

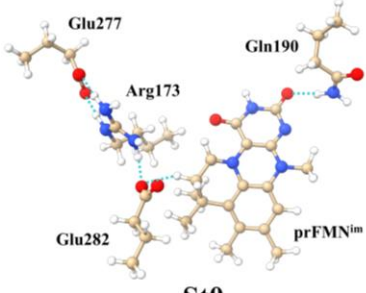
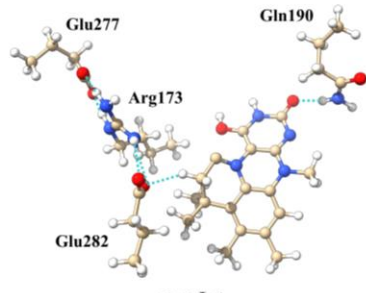
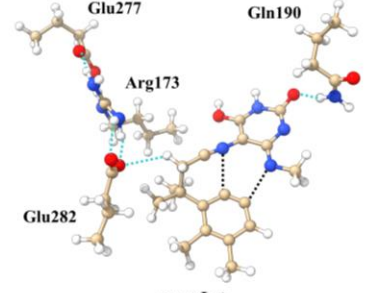
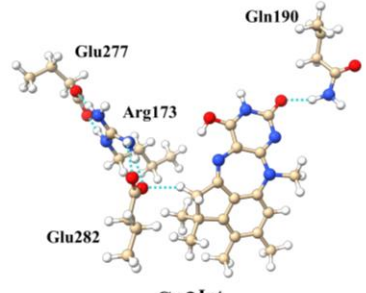
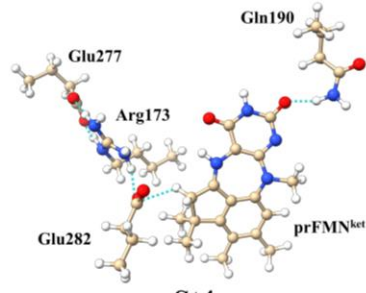
Structures	$E^{\text{Tot}}$ / au	$\Delta E^{\text{Ex}}$ / eV
 <b>prFMN<sup>im</sup></b>	-1066.743681	3.15 (394 nm)
 <b>prFMN<sup>ket</sup></b>	-1066.756385	2.25 (551 nm)
 <b>Arg173</b>	-362.765659	7.17 (173 nm)
 <b>Gln190</b>	-287.647485	5.75 (215 nm)
 <b>Glu277</b>	-306.937343	5.23 (237 nm)
 <b>Glu282</b>	-306.935420	4.79 (259 nm)

**Table S2** a) Equilibrium structures, energies and residue-to-residue (R-to-R) distances in the active site clusters on the **prFMN<sup>im</sup>→prFMN<sup>ket</sup>** photoisomerization pathways obtained from DFT/B3LYP/DZP geometry optimizations.


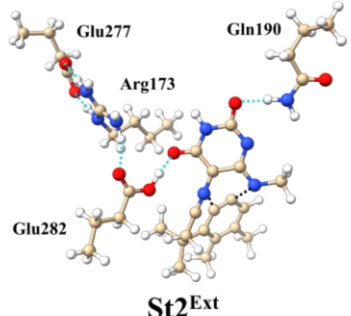
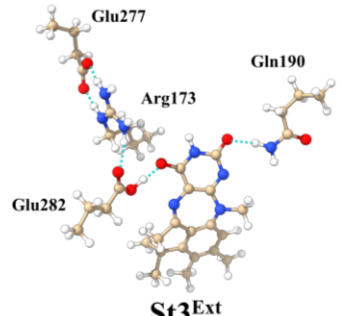
b) The average residue-to-residue distances and standard deviation (SD) for all the equilibrium structures of the active site clusters.

$E^{\text{Tot}}$  = total energy in au;  $\Delta E^{\text{Ex}}$  = the  $S_0 \rightarrow S_1$  energy in eV; (...) = absorption wavelength in nm; sp = single point calculation.

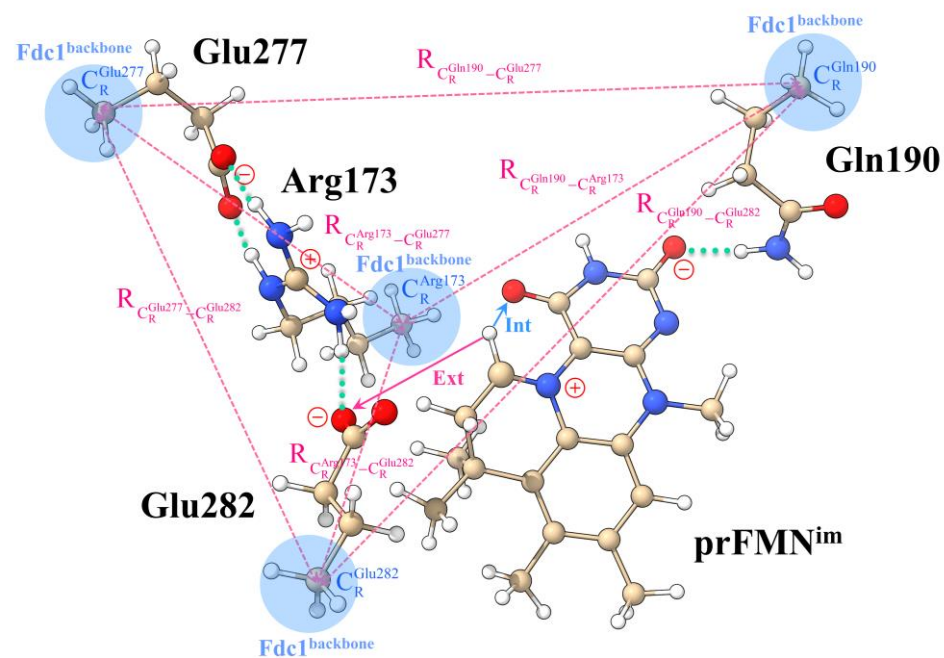
**Table S2a**

Model molecular cluster	$E^{\text{Tot}}/ \text{au}$	$\Delta E^{\text{Ex}}/ \text{eV}$	R-to-R/ Å
 <p><b>St0</b></p>	-2331.560638	2.60 (477 nm)	$R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Arg173}}} = 12.40$ $R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Glu277}}} = 17.47$ $R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 17.13$ $R_{\text{C}_{\text{R}}^{\text{Arg173}}-\text{C}_{\text{R}}^{\text{Glu277}}} = 9.79$ $R_{\text{C}_{\text{R}}^{\text{Arg173}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 10.11$ $R_{\text{C}_{\text{R}}^{\text{Glu277}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 13.25$
 <p><b>St1Int</b></p>	-2331.460634	2.69 (462 nm)	$R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Arg173}}} = 12.42$ $R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Glu277}}} = 17.48$ $R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 17.14$ $R_{\text{C}_{\text{R}}^{\text{Arg173}}-\text{C}_{\text{R}}^{\text{Glu277}}} = 9.82$ $R_{\text{C}_{\text{R}}^{\text{Arg173}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 10.10$ $R_{\text{C}_{\text{R}}^{\text{Glu277}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 13.26$
 <p><b>St2Int</b></p>	-2331.289127 <sup>sp</sup>	2.96 (419 nm)	$R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Arg173}}} = 12.40$ $R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Glu277}}} = 17.47$ $R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 17.14$ $R_{\text{C}_{\text{R}}^{\text{Arg173}}-\text{C}_{\text{R}}^{\text{Glu277}}} = 9.80$ $R_{\text{C}_{\text{R}}^{\text{Arg173}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 10.11$ $R_{\text{C}_{\text{R}}^{\text{Glu277}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 13.74$
 <p><b>St3Int</b></p>	-2331.559782	2.70 (460 nm)	$R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Arg173}}} = 12.58$ $R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Glu277}}} = 17.60$ $R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 17.20$ $R_{\text{C}_{\text{R}}^{\text{Arg173}}-\text{C}_{\text{R}}^{\text{Glu277}}} = 10.00$ $R_{\text{C}_{\text{R}}^{\text{Arg173}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 10.05$ $R_{\text{C}_{\text{R}}^{\text{Glu277}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 13.34$
 <p><b>St4</b></p>	-2331.569793	2.27 (546 nm)	$R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Arg173}}} = 12.48$ $R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Glu277}}} = 17.52$ $R_{\text{C}_{\text{R}}^{\text{Gln190}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 17.11$ $R_{\text{C}_{\text{R}}^{\text{Arg173}}-\text{C}_{\text{R}}^{\text{Glu277}}} = 9.98$ $R_{\text{C}_{\text{R}}^{\text{Arg173}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 10.04$ $R_{\text{C}_{\text{R}}^{\text{Glu277}}-\text{C}_{\text{R}}^{\text{Glu282}}} = 13.35$

**Table S2a (Cont.)**

Model molecular cluster	$E^{\text{Tot}}/ \text{au}$	$\Delta E^{\text{Ex}}/ \text{eV}$	<b>R-to-R/ Å</b>
 <p><b>St1<sup>Ext</sup></b></p>	-2331.560638	3.21 (386 nm)	$R_{C_{\text{R}}^{\text{Gln190}}-C_{\text{R}}^{\text{Arg173}}} = 12.48$ $R_{C_{\text{R}}^{\text{Gln190}}-C_{\text{R}}^{\text{Glu277}}} = 17.52$ $R_{C_{\text{R}}^{\text{Gln190}}-C_{\text{R}}^{\text{Glu282}}} = 17.11$ $R_{C_{\text{R}}^{\text{Arg173}}-C_{\text{R}}^{\text{Glu277}}} = 9.98$ $R_{C_{\text{R}}^{\text{Arg173}}-C_{\text{R}}^{\text{Glu282}}} = 10.04$ $R_{C_{\text{R}}^{\text{Glu277}}-C_{\text{R}}^{\text{Glu282}}} = 13.35$
 <p><b>St2<sup>Ext</sup></b></p>	-2331.351063 <sup>SP</sup>	1.88 (658 nm)	$R_{C_{\text{R}}^{\text{Gln190}}-C_{\text{R}}^{\text{Arg173}}} = 12.39$ $R_{C_{\text{R}}^{\text{Gln190}}-C_{\text{R}}^{\text{Glu277}}} = 17.47$ $R_{C_{\text{R}}^{\text{Gln190}}-C_{\text{R}}^{\text{Glu282}}} = 17.11$ $R_{C_{\text{R}}^{\text{Arg173}}-C_{\text{R}}^{\text{Glu277}}} = 9.79$ $R_{C_{\text{R}}^{\text{Arg173}}-C_{\text{R}}^{\text{Glu282}}} = 10.08$ $R_{C_{\text{R}}^{\text{Glu277}}-C_{\text{R}}^{\text{Glu282}}} = 13.22$
 <p><b>St3<sup>Ext</sup></b></p>	-2331.582516	2.67 (465 nm)	$R_{C_{\text{R}}^{\text{Gln190}}-C_{\text{R}}^{\text{Arg173}}} = 12.41$ $R_{C_{\text{R}}^{\text{Gln190}}-C_{\text{R}}^{\text{Glu277}}} = 17.43$ $R_{C_{\text{R}}^{\text{Gln190}}-C_{\text{R}}^{\text{Glu282}}} = 17.02$ $R_{C_{\text{R}}^{\text{Arg173}}-C_{\text{R}}^{\text{Glu277}}} = 9.93$ $R_{C_{\text{R}}^{\text{Arg173}}-C_{\text{R}}^{\text{Glu282}}} = 9.96$ $R_{C_{\text{R}}^{\text{Glu277}}-C_{\text{R}}^{\text{Glu282}}} = 13.21$





**Table S2b**

Model molecular cluster	$R_{C_{R}^{Gln190}-C_{R}^{Arg173}}$	$R_{C_{R}^{Gln190}-C_{R}^{Glu277}}$	$R_{C_{R}^{Gln190}-C_{R}^{Glu282}}$	$R_{C_{R}^{Arg173}-C_{R}^{Glu277}}$	$R_{C_{R}^{Arg173}-C_{R}^{Glu282}}$	$R_{C_{R}^{Glu277}-C_{R}^{Glu282}}$
St0	12.40	17.47	17.13	9.79	10.11	13.25
St1 <sup>Int</sup>	12.42	17.48	17.14	9.82	10.10	13.26
St3 <sup>Int</sup>	12.58	17.60	17.20	10.00	10.05	13.34
St4	12.48	17.52	17.11	9.98	10.04	13.35
St1 <sup>Ext</sup>	12.80	17.51	17.06	9.92	9.91	13.12
St3 <sup>Ext</sup>	12.41	17.43	17.02	9.93	9.96	13.21
<b>Average±SD</b>	<b>12.52±0.15</b>	<b>17.50±0.06</b>	<b>17.11±0.06</b>	<b>9.91±0.08</b>	<b>10.03±0.08</b>	<b>13.26±0.09</b>

**Table S3** Thermodynamics and kinetics of the elementary reactions for the **prFMN<sup>im</sup>→prFMN<sup>ket</sup>** photoisomerization (Type **(3)** mechanism), obtained from DFT/B3LYP/DZP reaction path optimizations and TST methods. Rate constants, temperatures and energies are in s<sup>-1</sup>, K and kJ/mol, respectively;  $\Delta E^\ddagger$  = energy barriers;  $\Delta E^{\ddagger, \text{ZPC}}$  = energy barrier with the zero-point vibrational energy;  $\Delta H^\ddagger$  = activation enthalpy;  $T_c$  = crossover temperature;  $T$  = temperature;  $k_{f/r}^{\text{Q-Vib}}$  = rate constant obtained with quantized vibration correction;  $\Delta G^\ddagger$  = activation free energy;  $\Delta S^\ddagger$  = activation entropy; f/r = forward or reverse direction.

Table S3

<b>S<sub>1</sub>→S<sub>0</sub> relaxation</b>	<b>ΔE<sup>‡</sup></b>	<b>ΔE<sup>‡,ZPC</sup></b>	<b>ΔH<sup>‡</sup></b>	<b>T</b>	<b>k<sub>f/r</sub><sup>Q-Vib</sup></b>	<b>ΔG<sup>‡</sup></b>	<b>ΔS<sup>‡</sup></b>
<b>St0* ← St0*,§</b>	119.7	107.6	111.6	273	1.61×10 <sup>-7</sup>	102.2	3.46×10 <sup>-2</sup>
				277	3.22×10 <sup>-7</sup>	102.1	3.44×10 <sup>-2</sup>
				298	1.03×10 <sup>-5</sup>	101.5	3.37×10 <sup>-2</sup>
				303	2.05×10 <sup>-5</sup>	101.4	3.36×10 <sup>-2</sup>
				353	1.06×10 <sup>-2</sup>	100.2	3.24×10 <sup>-2</sup>
<b>Intermolecular proton transfer</b>	<b>ΔE<sup>‡</sup></b>	<b>ΔE<sup>‡,ZPC</sup></b>	<b>ΔH<sup>‡</sup></b>	<b>T</b>	<b>k<sub>f/r</sub><sup>Q-Vib</sup></b>	<b>ΔG<sup>‡</sup></b>	<b>ΔS<sup>‡</sup></b>
<b>St0<sup>§</sup> ← St0-[1]<sup>Ext</sup></b>	68.6	66.1	66.8	273	4.33×10 <sup>0</sup>	63.3	1.26×10 <sup>-2</sup>
				277	6.56×10 <sup>0</sup>	63.3	1.25×10 <sup>-2</sup>
				298	5.22×10 <sup>1</sup>	63.2	1.18×10 <sup>-2</sup>
				303	7.91×10 <sup>1</sup>	63.2	1.17×10 <sup>-2</sup>
				353	3.32×10 <sup>3</sup>	63.1	1.05×10 <sup>-2</sup>
<b>St0-[1]<sup>Ext</sup> → St0-[1]<sup>Ext,‡</sup></b>	86.9	78.7	78.7	273	1.89×10 <sup>-4</sup>	86.1	-2.74×10 <sup>-2</sup>
				277	3.08×10 <sup>-4</sup>	86.3	-2.75×10 <sup>-2</sup>
				298	3.53×10 <sup>-3</sup>	87.0	-2.82×10 <sup>-2</sup>
				303	5.76×10 <sup>-3</sup>	87.2	-2.83×10 <sup>-2</sup>
				353	4.71×10 <sup>-1</sup>	89.1	-2.95×10 <sup>-2</sup>
<b>St0-[1]<sup>Ext,‡</sup> ← St1<sup>Ext</sup></b>	17.4	17.4	16.3	273	2.17×10 <sup>16</sup>	-18.7	1.28×10 <sup>-1</sup>
				277	2.44×10 <sup>16</sup>	-19.2	1.28×10 <sup>-1</sup>
				298	4.39×10 <sup>16</sup>	-22.0	1.28×10 <sup>-1</sup>
				303	4.93×10 <sup>16</sup>	-22.6	1.28×10 <sup>-1</sup>
				353	1.60×10 <sup>17</sup>	-29.8	1.28×10 <sup>-1</sup>

Table S3 (Cont.)

Ring expansion	$\Delta E^\ddagger$	$\Delta E^{\ddagger, ZPC}$	$\Delta H^\ddagger$	T	$k_{f/r}^{Q-Vib}$	$\Delta G^\ddagger$	$\Delta S^\ddagger$
$St1^{Ext} \rightarrow St1^{Ext, \ddagger}$	11.2	10.3	11.2	273	$4.87 \times 10^{10}$	10.8	$1.53 \times 10^{-3}$
				277	$5.22 \times 10^{10}$	10.8	$1.41 \times 10^{-3}$
				298	$7.40 \times 10^{10}$	11.0	$7.85 \times 10^{-4}$
				303	$7.94 \times 10^{10}$	11.0	$6.56 \times 10^{-4}$
				353	$1.49 \times 10^{11}$	11.4	$-6.04 \times 10^{-4}$
$St1^{Ext, \ddagger} \leftarrow St3^{Ext}$	186.8	186.2	186.0	273	$1.84 \times 10^{-25}$	195.9	$-3.66 \times 10^{-2}$
				277	$5.84 \times 10^{-25}$	196.1	$-3.67 \times 10^{-2}$
				298	$1.89 \times 10^{-22}$	197.1	$-3.73 \times 10^{-2}$
				303	$6.00 \times 10^{-22}$	197.3	$-3.74 \times 10^{-2}$
				353	$1.98 \times 10^{-17}$	199.6	$-3.87 \times 10^{-2}$
Reverse protonation	$\Delta E^\ddagger$	$\Delta E^{\ddagger, ZPC}$	$\Delta H^\ddagger$	T	$k_{f/r}^{Q-Vib}$	$\Delta G^\ddagger$	$\Delta S^\ddagger$
$St3^{Ext} \rightarrow St3^{Ext, \ddagger}$	63.9	62.8	61.8	273	$6.10 \times 10^7$	26.0	$1.31 \times 10^{-1}$
				277	$9.11 \times 10^7$	25.5	$1.31 \times 10^{-1}$
				298	$6.75 \times 10^8$	22.6	$1.31 \times 10^{-1}$
				303	$1.01 \times 10^9$	22.0	$1.31 \times 10^{-1}$
				353	$3.73 \times 10^{10}$	15.5	$1.31 \times 10^{-1}$
$St3^{Ext, \ddagger} \leftarrow St4$	26.6	17.2	19.6	273	$1.75 \times 10^{11}$	7.9	$4.27 \times 10^{-2}$
				277	$1.97 \times 10^{11}$	7.8	$4.26 \times 10^{-2}$
				298	$3.61 \times 10^{11}$	7.1	$4.19 \times 10^{-2}$
				303	$4.07 \times 10^{11}$	6.9	$4.18 \times 10^{-2}$
				353	$1.22 \times 10^{12}$	5.3	$4.05 \times 10^{-2}$

**Table S4** Thermodynamics and kinetics of the elementary reactions for the **prFMN<sup>im</sup>→prFMN<sup>ket</sup>** photoisomerization (Type (4) mechanism), obtained from DFT/B3LYP/DZP reaction path optimizations and TST methods. Rate constants, temperatures and energies are in s<sup>-1</sup>, K and kJ/mol, respectively;  $\Delta E^\ddagger$  = energy barriers;  $\Delta E^{\ddagger,ZPC}$  = energy barrier with the zero-point vibrational energy;  $\Delta H^\ddagger$  = activation enthalpy;  $T_c$  = crossover temperature;  $T$  = temperature;  $k_{f/r}^{Q-Vib}$  = rate constant obtained with quantized vibration correction;  $\Delta G^\ddagger$  = activation free energy;  $\Delta S^\ddagger$  = activation entropy; f/r = forward or reverse direction.

**Table S4**

<b>Intramolecular proton transfer and ring expansion</b>								
	$\Delta E^\ddagger$	$\Delta E^{\ddagger,ZPC}$	$\Delta H^\ddagger$	<b>T</b>	$k_{f/r}^{Q-Vib}$	$\Delta G^\ddagger$	$\Delta S^\ddagger$	
<b>St0<sup>§</sup> ← St0-[1]<sup>direct</sup></b>				273	$3.05 \times 10^{-7}$	100.7	$3.23 \times 10^{-2}$	
				277	$6.01 \times 10^{-7}$	100.6	$3.22 \times 10^{-2}$	
		109.9	107.0	109.5	298	$1.81 \times 10^{-5}$	100.1	$3.16 \times 10^{-2}$
					303	$3.57 \times 10^{-5}$	100.0	$3.14 \times 10^{-2}$
					353	$1.64 \times 10^{-2}$	98.9	$3.02 \times 10^{-2}$
<b>St0-[1]<sup>direct</sup> → St0-[1]<sup>direct,‡</sup></b>				273	$1.08 \times 10^0$	66.5	$-1.35 \times 10^{-1}$	
				277	$1.30 \times 10^0$	67.0	$-1.35 \times 10^{-1}$	
		31.7	29.0	29.7	298	$3.26 \times 10^0$	70.1	$-1.36 \times 10^{-1}$
					303	$3.92 \times 10^0$	70.8	$-1.36 \times 10^{-1}$
					353	$2.07 \times 10^1$	78.0	$-1.37 \times 10^{-1}$
<b>St0-[1]<sup>direct,‡</sup> ← St4</b>				273	$1.91 \times 10^{-5}$	91.3	$-1.26 \times 10^{-1}$	
				277	$2.73 \times 10^{-5}$	91.8	$-1.26 \times 10^{-1}$	
		59.3	57.2	56.9	298	$1.60 \times 10^{-4}$	94.7	$-1.27 \times 10^{-1}$
					303	$2.28 \times 10^{-4}$	95.4	$-1.27 \times 10^{-1}$
					353	$5.51 \times 10^{-3}$	102.1	$-1.28 \times 10^{-1}$

**Table S5** Thermodynamic properties of the elementary reactions in Type (3) and Type (4) mechanisms, obtained based on the hypothesized photo-to-thermal pathway in Figure 4 and from the DFT/B3LYP/DZP, TD-DFT/B3LYP/DZP and TST methods.

<b>a)</b> Type (3)	$\text{St0}^* \rightarrow \text{St0-[1]}^{\text{Ext}}$ (I)* $\rightarrow$ (III)		$\text{St0}^* \rightarrow \text{St0-[1]}^{\text{Ext},\ddagger}$ (I)* $\rightarrow$ (IV) $\ddagger$		$\text{St0}^* \rightarrow \text{St1}^{\text{Ext}}$ (I)* $\rightarrow$ (V)		$\text{St0}^* \rightarrow \text{St3}^{\text{Ext}}$		$\text{St0}^* \rightarrow \text{St4}$	
	T	$\Delta G^\circ$	$\Delta S^\circ$	$\Delta G^\circ$	$\Delta S^\circ$	$\Delta G^\circ$	$\Delta S^\circ$	$\Delta G^\circ$	$\Delta S^\circ$	$\Delta G^{\circ,\text{Tot}}$
273	-165.5	$-4.72 \times 10^{-2}$	-79.4	$-7.45 \times 10^{-2}$	-60.66	$-2.03 \times 10^{-1}$	-245.8	$-1.65 \times 10^{-1}$	-227.7	$-7.61 \times 10^{-2}$
277	-165.4	$-4.69 \times 10^{-2}$	-79.1	$-7.44 \times 10^{-2}$	-59.90	$-2.03 \times 10^{-1}$	-245.2	$-1.65 \times 10^{-1}$	-227.5	$-7.59 \times 10^{-2}$
298	-164.8	$-4.56 \times 10^{-2}$	-77.7	$-7.37 \times 10^{-2}$	-55.75	$-2.02 \times 10^{-1}$	-241.9	$-1.64 \times 10^{-1}$	-226.3	$-7.45 \times 10^{-2}$
303	-164.6	$-4.53 \times 10^{-2}$	-77.4	$-7.36 \times 10^{-2}$	-54.85	$-2.02 \times 10^{-1}$	-241.1	$-1.64 \times 10^{-1}$	-226.0	$-7.43 \times 10^{-2}$
353	-163.3	$-4.28 \times 10^{-2}$	-74.2	$-7.24 \times 10^{-2}$	-45.26	$-2.01 \times 10^{-1}$	-233.4	$-1.63 \times 10^{-1}$	-223.2	$-7.18 \times 10^{-2}$

<b>b)</b> Type (4)	$\text{St0}^* \rightarrow \text{St0-[1]}^{\text{Ext}}$ (I)* $\rightarrow$ (III)		$\text{St0}^* \rightarrow \text{St0-[1]}^{\text{Ext},\ddagger}$ (I)* $\rightarrow$ (IV) $\ddagger$		$\text{St0}^* \rightarrow \text{St1}$ (I)* $\rightarrow$ (V)	
	T	$\Delta G^\circ$	$\Delta S^\circ$	$\Delta G^\circ$	$\Delta S^\circ$	$\Delta G^{\circ,\text{Tot}}$
273	-202.9	$-6.69 \times 10^{-2}$	-136.4	$-2.02 \times 10^{-1}$	-227.7	$-7.59 \times 10^{-2}$
277	-202.7	$-6.66 \times 10^{-2}$	-135.7	$-2.02 \times 10^{-1}$	-227.5	$-7.56 \times 10^{-2}$
298	-201.7	$-6.53 \times 10^{-2}$	-131.6	$-2.01 \times 10^{-1}$	-226.3	$-7.43 \times 10^{-2}$
303	-201.4	$-6.50 \times 10^{-2}$	-130.7	$-2.01 \times 10^{-1}$	-226.0	$-7.40 \times 10^{-2}$
353	-199.1	$-6.26 \times 10^{-2}$	-121.1	$-2.00 \times 10^{-1}$	-223.2	$-7.15 \times 10^{-2}$

$\Delta G^\circ$  and  $\Delta H^\circ$  = Gibbs free energy and enthalpy in kJ/mol;  $\Delta S^\circ$  = entropy in kJ/mol·K;  $\Delta G^{\circ,\text{Tot}}$  = total reaction Gibbs free energy for  $\text{prFMN}^{\text{im}} \rightarrow \text{prFMN}^{\text{ket}}$  and;  $\Delta S^{\circ,\text{Rx}}$  = reaction entropy of all the elementary processes; T = temperature in K.