Electronic Supplementary Information
Photodecarbonylation of π–Extended Flavonol: Mechanistic Insights for PDT

by

Phorntep Promma

Department of Chemical Engineering,

Faculty of Engineering,

Chulalongkorn University,

Bangkok 10330, Thailand

Charoensak Lao-Ngam

· Chemistry Program, Faculty of Science and Technology,

Nakhon Ratchasima Rajabhat University,

Nakhon Ratchasima 30000, Thailand

Pannipa Panajapo

Siramol Photiganit

Ananda Thongyu

and

Kritsana Sagarik[*]

School of Chemistry,

Institute of Science,

Suranaree University of Technology,

Nakhon Ratchasima 30000, Thailand

*Corresponding author: *kritsana@sut.ac.th*

Tel./Fax: (6681) 8783994

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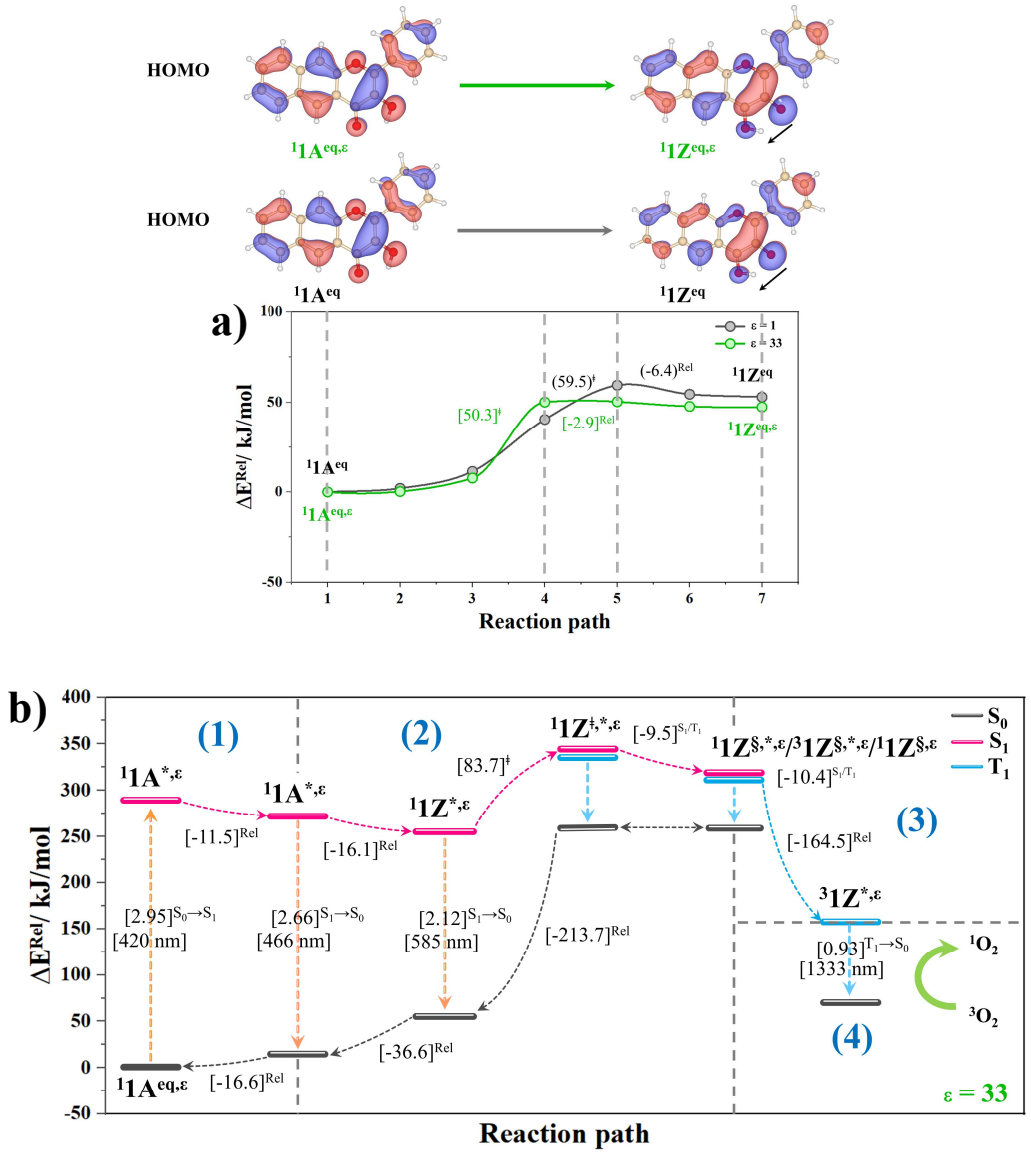


Figure S1 a) The S_0 PES for the $^1\mathbf{1A}^{eq} \rightarrow {}^1\mathbf{1Z}^{eq}$ isomerization (the proton/hydrogen transfer) with ε = 1 and 33. b) The S_1, T_1 and S_0 potential energy profiles for the successive ESIPTs [E**(1)**–E**(2)** in Path **(I)**] and the energy transfer to the $^3O_2 \rightarrow {}^1O_2$ reaction [E**(3)**–E**(4)** in Path **(II)**] with ε = 33. The symbols used are explained in the text. The dashed lines in Figure S1b denote the energies calculated with ε = 33 using the geometries with ε = 1 (Figure 4). The symbols used are explained in the text. ΔE^{Rel} = relative energy with respect to the precursor in kJ/mol; $(\ldots)^{Rel}$ and $(\ldots)^{\ddagger}$ = relaxation energy and energy barrier on PES; $^{\varepsilon}$ and […] = structure and energy computed with ε = 33, respectively; → = proton/hydrogen transfer direction.

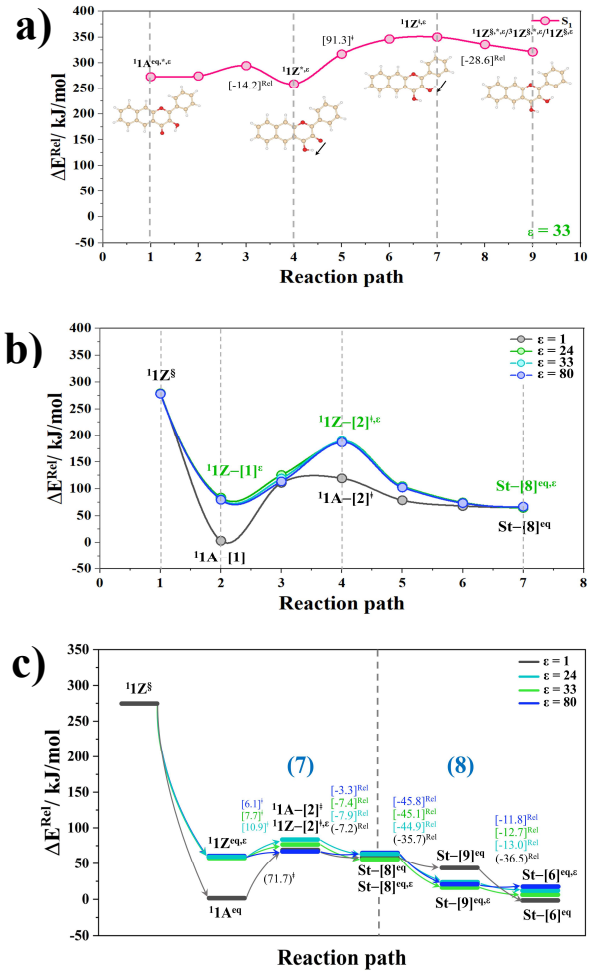


Figure S2 a) The S_1 PES for formation of $^1\mathbf{1Z}^{\S,*,\varepsilon}$, $^3\mathbf{1Z}^{\S,*,\varepsilon}$ and $^1\mathbf{1Z}^{\S,\varepsilon}$ at the S_1/T_1 and T_1/S_0 intersections via successive ESIPTs and ISC ($^1\mathbf{1A}^{eq,*,\varepsilon} \rightarrow {}^1\mathbf{1Z}^{\S,*,\varepsilon}/{}^3\mathbf{1Z}^{\S,*,\varepsilon}/{}^1\mathbf{1Z}^{\S,\varepsilon}$), obtained based on the NEB method with ε = 33 [E**(2)** in Path **(I)** in Figure 1b]. b) The S_0 PESs for the $^1\mathbf{1Z}^{\S} \rightarrow \mathbf{St–[8]}^{eq}$ reaction [E**(7)** in Path **(IV)**] in different local dialectic environment (ε = 1–80). c) The refined potential energy profiles for the $^1\mathbf{1Z}^{\S} \rightarrow \mathbf{St–[6]}^{eq}$ reaction [E**(7)**–E**(8)** in Path **(IV)**] in different local dialectic environment (ε = 1–80). The symbols used are explained in the text. ΔE^{Rel} = relative energy with respect to the precursor in kJ/mol; $(\ldots)^{Rel}$ and $(\ldots)^{\ddagger}$ = relaxation energy and energy barrier on PES; $^{\varepsilon}$ and […] = structure and energy computed with ε = 33, respectively; → = proton/hydrogen transfer direction.

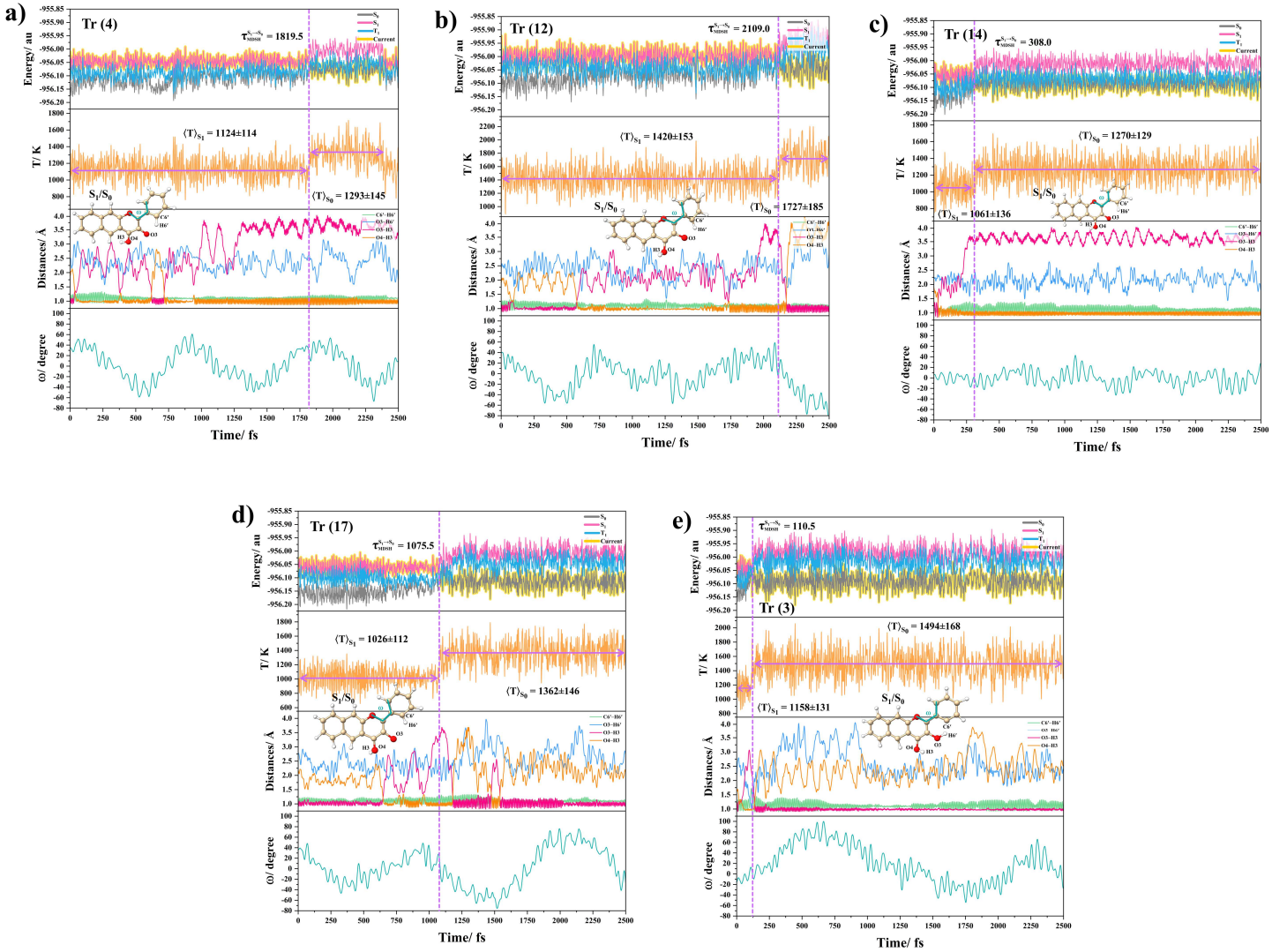


Figure S3 a)–d) Time evolutions of single ESIPT, obtained from NVE-MDSH simulations. e) Time evolutions of consecutive ESIPTs, obtained from NVE-MDSH simulations. $\tau^{S_1\rightarrow S_0}_{MDSH}$ = $S_1\rightarrow S_0$ surface hopping time; $\langle T\rangle_{S_1}$ = average temperature in the S_1 state; $\langle T\rangle_{S_0}$ = average temperature in the S_0 state; Tr (*n*) = NVE-MDSH trajectory number *n*.

Table S1 Equilibrium structures and energies of the precursors, intermediates and products in the proposed elementary reactions [E**(1)**–E**(8)** in Figure 1c] obtained from the DFT and TD-DFT/B3LYP/def2-TZVP geometry optimizations with ε = 1. The symbols used are explained in the text. E^{Tot} = total energy in au; $\Delta E^{S_0 \rightarrow S_1}$ and $\Delta E^{S_1 \rightarrow S_0}$ = $S_0 \rightarrow S_1$ vertical excitation and $S_1 \rightarrow S_0$ relaxation energies in eV, respectively; $\Delta E^{S_1 \rightarrow T_1}$ and $\Delta E^{T_1 \rightarrow S_0}$ = $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ ISC energies, respectively; k_F, k_P and k_{ISC} = fluorescence, phosphorescence and ISC rate constants in s^{-1}, respectively; […] = value computed with ε = 33; ^{eq} and * = equilibrium and excited structures, respectively; § = structure at the intersection of electronic states.

Table S1

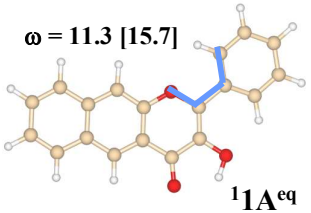
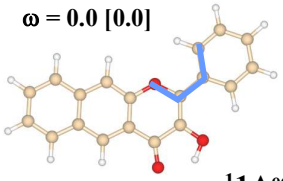
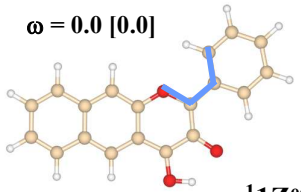
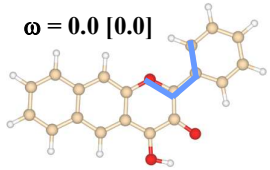
Structure	Energy	Rate constant
 $^{1}1A^{eq}$	E^{Tot} = -956.7391519 [-956.7534171] $\Delta E^{S_0 \rightarrow S_1}$ = 3.17 [2.95]	-
 $^{1}1A^{eq,*}$	E^{Tot} = -956.6279860 [-956.6431487] $\Delta E^{S_1 \rightarrow S_0}$ = -2.87 [-2.66]	k_F = 8.58×10^{7} [1.45×10^{8}]
 $^{1}1Z^{eq}$	E^{Tot} = -956.7189847 [-956.7353621] $\Delta E^{S_0 \rightarrow S_1}$ = 2.49 [2.25]	-
 $^{1}1Z^{eq,*}$	E^{Tot} = -956.6305519 [-956.6553497] $\Delta E^{S_1 \rightarrow S_0}$ = -2.31 [-2.12]	k_F = 9.30×10^{7} [1.36×10^{8}]

Table S1 (Cont.)

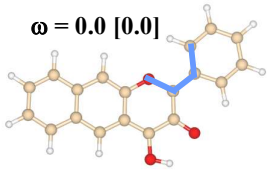
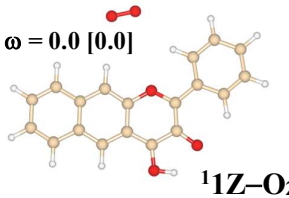
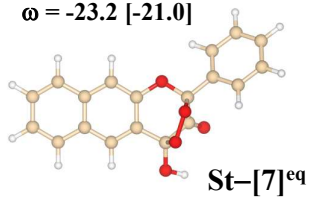
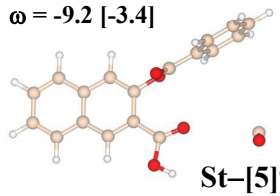
Structure	Energy	Rate constant
 ω = 0.0 [0.0] $^{3}1Z^{eq,*}$	E^{Tot} = -956.6851572 [-956.6962951] $\Delta E^{T_1 \rightarrow S_0}$ = -0.79 [-0.93]	k_P = 1.27×10^{1} [2.14×10^{-1}]
 ω = 0.0 [0.0] $^{1}1Z–O_2^{eq}$	E^{Tot} = -1106.9890196 [-1107.0045429]	-
 ω = -23.2 [-21.0] $St–[7]^{eq}$	E^{Tot} = -1107.0589047 [-1107.0755615] $\Delta E^{S_0 \rightarrow S_1}$ = 3.44 [3.34]	-
 ω = -9.2 [-3.4] $St–[5]^{eq}$	E^{Tot} = -1107.2092940 [-1107.228154] $\Delta E^{S_0 \rightarrow S_1}$ = 3.94 [3.82]	-

Table S1 (Cont.)

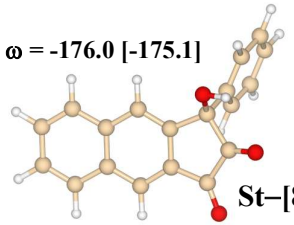
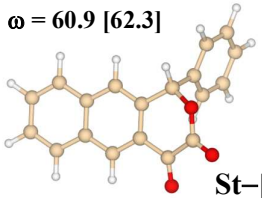
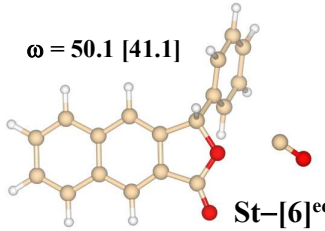
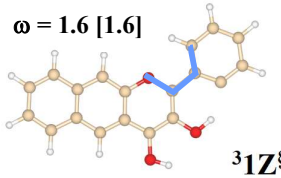
Structure	Energy	Rate constant
 ω = -176.0 [-175.1] **St–[8]^{eq}**	E^{Tot} = -956.7145222 [-956.7341361] $\Delta E^{S_0 \rightarrow S_1}$ = 2.21 [2.31]	-
 ω = 60.9 [62.3] **St–[9]^{eq}**	E^{Tot} = -956.7287006 [-956.7515922] $\Delta E^{S_0 \rightarrow S_1}$ = 3.01 [2.92]	-
 ω = 50.1 [41.1] **St–[6]^{eq}**	E^{Tot} = -956.7396325 [-956.7564214] $\Delta E^{S_0 \rightarrow S_1}$ = 4.07 [3.86]	-
 ω = 1.6 [1.6] **$^{3}1Z^{\S,*}$**	E^{Tot} = -956.6308845 [-956.6297020] $\Delta E^{S_1 \rightarrow S_0}$ = -0.06 [-0.65] $\Delta E^{S_1 \rightarrow T_1}$ = -0.12 [-0.11] $\Delta E^{T_1 \rightarrow S_0}$ = -0.06 [-0.54]	k_{ISC} = 1.40×10^{9} [2.94×10^{7}] k_{P} = 3.09×10^{0} [1.66×10^{0}]

Table S2 Characteristic structures and energies of the chemical species on the S_0, S_1 and T_1 PESs obtained from DFT and TD-DFT/B3LYP/def2-TZVP and double-ended structure path optimizations.

a) Photoexcitation and acid-base reactions, E**(1)** and E**(2)** in Path **(I)**.

b) Aerobic pathway to transfer energy to the $^3O_2 \rightarrow {}^1O_2$ reaction, E**(3)** and E**(4)** in Path **(II)**.

c) Aerobic pathway for the decarbonylation in E**(3)**–E**(6)** in Path **(III)**.

d) Anerobic pathway for the decarbonylation in E**(7)**–E**(8)** in Path **(IV)** with $\varepsilon = 1$.

e) Anerobic pathway for the decarbonylation in E**(7)**–E**(8)** in Path **(IV)** with $\varepsilon = 33$.

E^{Tot} = total energy in au; $\Delta E^{S_0 \rightarrow S_1}$ and $\Delta E^{S_1 \rightarrow S_0} = S_0 \rightarrow S_1$ vertical excitation and $S_1 \rightarrow S_0$ relaxation energies, respectively; $\Delta E^{S_1 \rightarrow T_1}$ and $\Delta E^{T_1 \rightarrow S_0} = S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ ISC energies, respectively; k_F, k_P and k_{ISC} = fluorescence, phosphorescence and ISC rate constants in s^{-1}, respectively; […] = value computed with $\varepsilon = 33$; […]$^{\varepsilon}$ = structure obtained with $\varepsilon = 33$.

Table S2

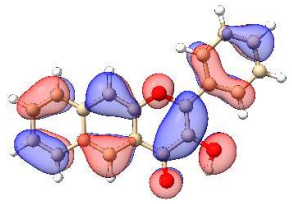
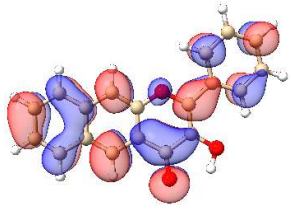
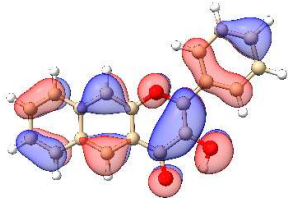
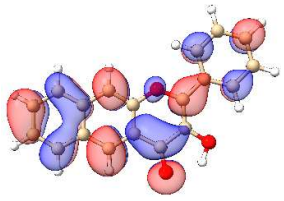
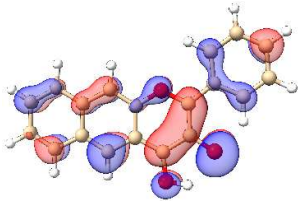
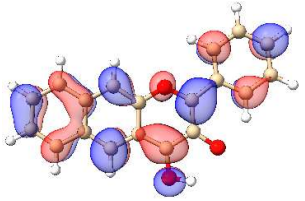
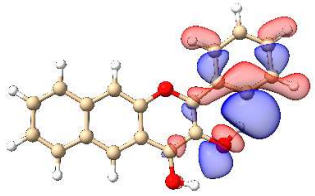
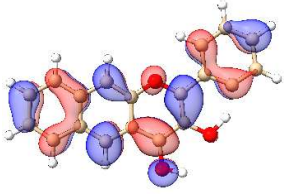
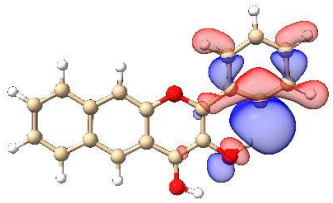
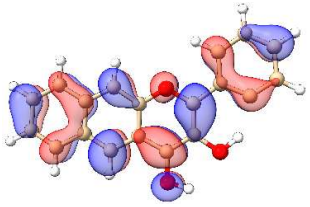
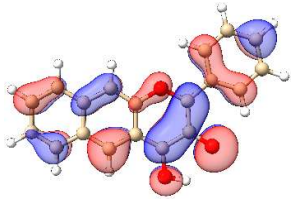
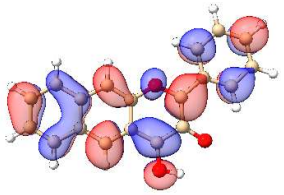
a)	Path (I)		ω	E^{Tot}		
	HOMO	LUMO		S_1	S_0	T_1
^{1}1A*			11.3 [15.7]	-956.6227059 [-956.6399679]	-956.7391519 [-956.7534171]	-956.6596534 [-956.6741423]
^{1}1A^{eq,*}			0.0 [0.0]	-956.6279860 [-956.6431487]	-956.7332610 [-956.7470397]	-956.6657117 [-956.6793172]
^{1}1Z*			0.0 [0.0]	-956.6202166 [-956.6411906]	-956.7090987 [-956.7294164]	-956.6713283 [-956.687125]
^{1}1Z‡,*			0.0 [0.0]	-956.6102801 [-956.6231474]	-956.6479531 [-956.6565077]	-956.6139957 [-956.6267764]

Table S2 (Cont.)

	Path (I)		ω	E^{Tot}		
	HOMO	LUMO		T_1	S_0	S_1
^{3}**1Z**§,*			1.6 [1.6]	-956.6352341 [-956.6336758]	-956.633150 [-956.633149]	-956.6308845 [-956.6297020]
^{3}**1Z**^{eq,*}			0.0 [0.0]	-956.6851572 [-956.6962951]	-956.7141621 [-956.7305884]	-956.6305519 [-956.6553497]

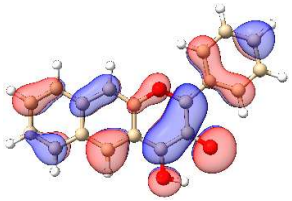
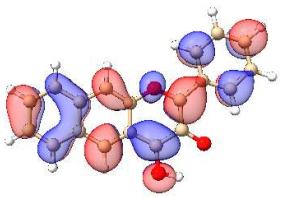
b)	Path (II)		ω	E^{Tot}		
	HOMO	LUMO		T_1	S_0	S_1
^{3}**1Z**^{eq,*}			0.0 [0.0]	-956.6851572 [-956.6962951]	-956.7141621 [-956.7305884]	-956.6305519 [-956.6553497]

Table S2 (Cont.)

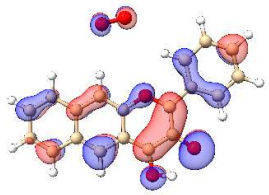
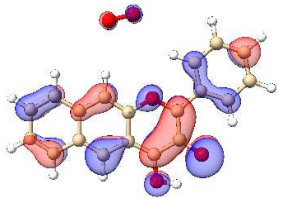
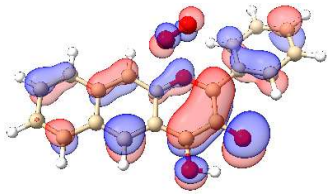
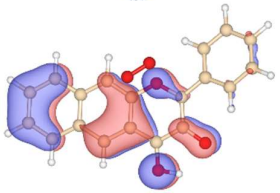
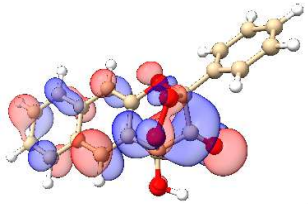
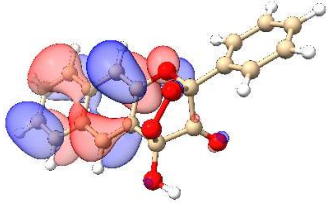
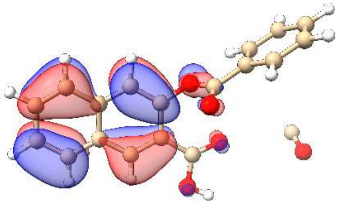
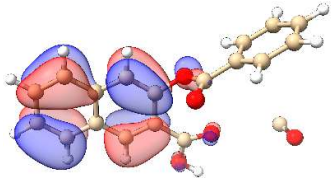
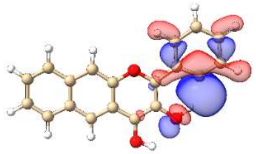
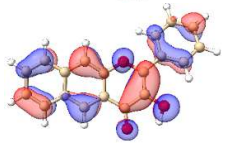
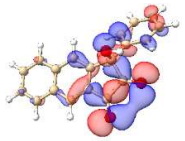
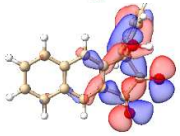
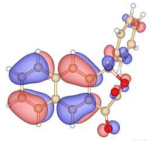
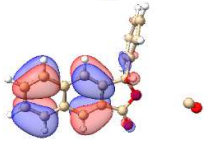
c)	Path (III) Aerobic		ω	E^{Tot}		
	HOMO	HOMO (ε)		S_0	S_1	T_1
^{1}**1Z–O$_2$^{eq}**			0.0 [0.0]	-1106.9890196 [-1107.0060920]	-	-
^{1}**1Z–O$_2$‡**			-18.5 [-19.4]	-1106.9862249 [-1107.0047111]	-	-
St–[7]^{eq}			-23.2 [-21.0]	-1107.0589047 [-1107.0755615]	-	-
St–[5]^{eq}			-9.2 [-3.4]	-1107.2092940 [-1107.228154]	-	-

Table S2 (Cont.)

d)	Path (IV) Anaerobic HOMO	ω	E^{Tot} S_0
^{1}1Z§,*		1.6	-956.6331404
^{1}1A–[1]		-14.5	-956.7378506
^{1}1A–[2]‡		-116.2	-956.6936197
St–[8]^{eq}		-176.0	-956.7145222
St–[9]‡		-65.8	-956.7000901
St–[6]^{eq}		50.1	-956.7396325

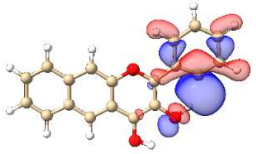
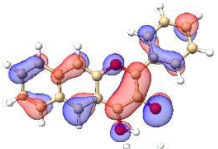
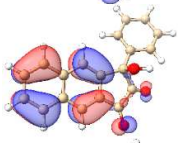
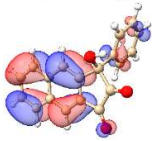
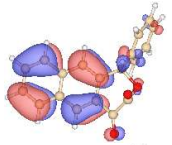
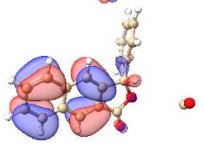
e)	Path (IV) Anaerobic HOMO (ε)	ω	E^{Tot} S_0
^{1}1Z^{§,*,ε}		[1.6]	[-956.6535430]
^{1}1Z–[1]^ε		[-16.1]	[-956.7335492]
^{1}1Z–[2]^{‡,ε}		[-115.4]	[-956.7173583]
St–[8]^{eq,ε}		[-175.1]	[-956.7341361]
St–[9]^{‡,ε}		[-66.1]	[-956.7177000]
St–[6]^{eq,ε}		[41.1]	[-956.7564214]

Table S3 Thermodynamic and kinetic properties on the ESIPT pathways with ε = 1 [E**(1)**–E**(3)** in Path **(I)** in the S_1 state]. Rate constants, temperatures and energies are in s^{-1}, K and kJ/mol, respectively.

$\Delta E^{\ddagger}$ = energy barrier on the PES; $\Delta E^{\ddagger,ZPC}$ = zero-point energy-corrected $\Delta E^{\ddagger}$, obtained by including the zero-point correction energy to $\Delta E^{\ddagger}$; $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ = activation enthalpy, entropy and Gibbs free energies, respectively; T_c = crossover temperature; T = temperature; $k_{f/r}^{Q\text{-}vib}$ = rate constant obtained with quantized vibrations including the zero-point vibrational energy; f/r = forward or reverse direction.

Table S3

E(1) and E(2)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
$^1\mathbf{1A}^{*}\leftarrow{}^1\mathbf{1A}^{eq,*}$	13.9	-3.1	10.7	13.3	61	273	6.35×10^{11}	4.9	3.06×10^{-2}
						298	1.05×10^{12}	4.4	3.25×10^{-2}
						307	1.23×10^{12}	4.2	3.32×10^{-2}
						338	2.00×10^{12}	3.5	3.56×10^{-2}
						350	2.35×10^{12}	3.3	3.65×10^{-2}
						392	3.85×10^{12}	2.4	3.96×10^{-2}
						408	4.54×10^{12}	2.1	4.08×10^{-2}
						465	7.50×10^{12}	1.0	4.49×10^{-2}
						488	8.88×10^{12}	0.6	4.65×10^{-2}
						573	1.48×10^{13}	-1.0	5.23×10^{-2}
$^1\mathbf{1A}^{eq,*}\rightarrow{}^1\mathbf{1Z}^{eq,*}$	6.7	-1.9	4.9	5.5	1	273	1.26×10^{11}	8.6	-1.17×10^{-2}
						298	1.53×10^{11}	9.2	-1.36×10^{-2}
						307	1.63×10^{11}	9.4	-1.43×10^{-2}
						338	1.99×10^{11}	10.0	-1.68×10^{-2}
						350	2.12×10^{11}	10.3	-1.77×10^{-2}
						392	2.59×10^{11}	11.2	-2.12×10^{-2}
						408	2.77×10^{11}	11.6	-2.25×10^{-2}
						465	3.39×10^{11}	13.0	-2.76×10^{-2}
						488	3.62×10^{11}	13.5	-2.96×10^{-2}
						573	4.44×10^{11}	15.7	-3.75×10^{-2}

Table S3 (Cont.)

E(2)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
$^1\mathbf{1Z}^{eq,*} \rightarrow {}^1\mathbf{1Z}^{\ddagger,*}$	24.1	-4.2	19.9	19.9	7	273	1.54×10^{8}	23.9	-1.45×10^{-2}
						298	3.18×10^{8}	24.4	-1.66×10^{-2}
						307	4.06×10^{8}	24.4	-1.74×10^{-2}
						338	8.40×10^{8}	24.7	-2.01×10^{-2}
						350	1.07×10^{9}	25.4	-2.12×10^{-2}
						392	2.21×10^{9}	25.7	-2.51×10^{-2}
						408	2.82×10^{9}	26.8	-2.66×10^{-2}
						465	5.80×10^{9}	27.2	-3.22×10^{-2}
						488	7.38×10^{9}	29.3	-3.46×10^{-2}
						573	1.52×10^{10}	31.8	-4.34×10^{-2}
$^1\mathbf{1Z}^{\ddagger,*} \leftarrow {}^1\mathbf{1Z}^{\S,*}$	25.2	-12.8	12.3	10.9	7	273	2.27×10^{9}	17.8	-2.51×10^{-2}
						298	3.42×10^{9}	18.6	-2.80×10^{-2}
						307	3.91×10^{9}	18.9	-2.92×10^{-2}
						338	5.86×10^{9}	19.9	-3.31×10^{-2}
						350	6.70×10^{9}	20.4	-3.46×10^{-2}
						392	9.97×10^{9}	21.8	-4.01×10^{-2}
						408	1.14×10^{10}	22.4	-4.22×10^{-2}
						465	1.68×10^{10}	24.6	-5.02×10^{-2}
						488	1.91×10^{10}	25.5	-5.34×10^{-2}
						573	2.82×10^{10}	28.8	-6.56×10^{-2}

Table S3 (Cont.)

E(3)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
$^3\mathbf{1Z}^{\S,*}\leftarrow{}^3\mathbf{1Z}^{eq,*}$	130.9	1.4	132.2	132.0	3	273	1.67×10^{-14}	138.7	-2.43×10^{-2}
						298	2.04×10^{-12}	139.5	-2.73×10^{-2}
						307	1.01×10^{-11}	139.8	-2.84×10^{-2}
						338	1.24×10^{-9}	140.9	-3.24×10^{-2}
						350	6.15×10^{-9}	141.3	-3.39×10^{-2}
						392	7.54×10^{-7}	142.8	-3.93×10^{-2}
						408	3.75×10^{-6}	143.3	-4.14×10^{-2}
						465	4.61×10^{-4}	145.4	-4.90×10^{-2}
						488	2.29×10^{-3}	146.3	-5.21×10^{-2}
						573	2.82×10^{-1}	149.5	-6.39×10^{-2}

Table S4 a)–b) Thermodynamic and kinetic properties for formation of salicylic ester and CO on the aerobic pathway [E**(5)** and E**(6)** in Path **(III)** in Figure 5c] computed with ε = 1 and 33, respectively. Rate constants, temperatures and energies are in s^{-1}, K and kJ/mol, respectively. $\Delta E^{\ddagger}$ = energy barrier on the PES; $\Delta E^{\ddagger,ZPC}$ = zero-point energy-corrected $\Delta E^{\ddagger}$, obtained by including the zero-point correction energy to $\Delta E^{\ddagger}$; $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ = activation enthalpy, entropy and Gibbs free energies, respectively; T_c = crossover temperature; T = temperature; $k_{f/r}^{Q\text{-}vib}$ = rate constant obtained with quantized vibrations including the zero-point vibrational energy; f/r = forward or reverse direction; $^{\varepsilon}$ = structure obtained with ε = 33.

Table S4a

E(5)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
^{1}1Z–O_2^{eq} →^{1}1Z–$O_2^{\ddagger}$	5.5	-0.8	4.7	5.2	7	273	6.07×10^{8}	20.8	-5.69×10^{-2}
						298	7.34×10^{8}	22.4	-6.28×10^{-2}
						307	7.82×10^{8}	23.0	-6.51×10^{-2}
						338	9.45×10^{8}	25.1	-7.27×10^{-2}
						350	1.01×10^{9}	25.9	-7.57×10^{-2}
						392	1.22×10^{9}	28.7	-8.60×10^{-2}
						408	1.30×10^{9}	29.8	-9.00×10^{-2}
						465	1.49×10^{9}	33.8	-1.05×10^{-1}
						488	1.59×10^{9}	35.4	-1.10×10^{-1}
						573	1.94×10^{9}	41.1	-1.32×10^{-1}
^{1}1Z–$O_2^{\ddagger}$←St–[7]^{eq}	191.3	-9.3	182.0	188.5	7	273	1.64×10^{-20}	170.1	6.75×10^{-2}
						298	1.54×10^{-17}	168.7	7.26×10^{-2}
						307	1.51×10^{-16}	168.1	7.46×10^{-2}
						338	1.43×10^{-13}	166.4	8.11×10^{-2}
						350	1.41×10^{-12}	165.7	8.36×10^{-2}
						392	1.36×10^{-9}	163.3	9.22×10^{-2}
						408	1.34×10^{-8}	162.4	9.55×10^{-2}
						465	1.30×10^{-6}	159.2	1.07×10^{-1}
						488	1.29×10^{-5}	158.0	1.12×10^{-1}
						573	1.25×10^{-2}	153.3	1.29×10^{-1}

Table S4a (Cont.)

E(6)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
St–[7]^{eq}←St–[5]^{eq}	394.8	10.2	405.1	394.0	3	273	2.37×10^{-76}	461.9	-2.49×10^{-1}
						298	4.25×10^{-70}	468.1	-2.71×10^{-1}
						307	5.15×10^{-68}	470.5	-2.80×10^{-1}
						338	9.02×10^{-62}	478.5	-3.09×10^{-1}
						350	1.08×10^{-59}	481.6	-3.21×10^{-1}
						392	1.85×10^{-52}	492.3	-3.60×10^{-1}
						408	2.20×10^{-51}	496.5	-3.75×10^{-1}
						465	3.67×10^{-45}	511.6	-4.31×10^{-1}
						488	4.33×10^{-43}	517.6	-4.53×10^{-1}
						573	7.04×10^{-37}	540.0	-5.35×10^{-1}

Table S4b

E(5)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
^{1}1Z–O$_2^{\varepsilon}$←^{1}1Z–O$_2^{\ddagger,\varepsilon}$	4.7	-0.8	3.9	4.4	10	273	2.68×10^{8}	22.6	-6.68×10^{-2}
						298	3.14×10^{8}	24.5	-7.36×10^{-2}
						307	3.32×10^{8}	25.2	-7.61×10^{-2}
						338	3.89×10^{8}	27.6	-8.49×10^{-2}
						350	4.10×10^{8}	28.5	-8.83×10^{-2}
						392	4.82×10^{8}	31.7	-1.00×10^{-1}
						408	5.08×10^{8}	33.0	-1.05×10^{-1}
						465	5.96×10^{8}	37.5	-1.21×10^{-1}
						488	5.97×10^{8}	39.3	-1.28×10^{-1}
						573	7.09×10^{8}	46.2	-1.53×10^{-1}
^{1}1Z–O$_2^{\ddagger,\varepsilon}$←St–[7]$^{eq,\varepsilon}$	189.0	-8.9	180.1	186.3	10	273	5.08×10^{-21}	172.7	4.96×10^{-2}
						298	4.39×10^{-18}	171.8	5.31×10^{-2}
						307	4.18×10^{-17}	171.4	5.44×10^{-2}
						338	3.66×10^{-14}	170.2	5.88×10^{-2}
						350	3.51×10^{-13}	169.7	6.05×10^{-2}
						392	3.10×10^{-10}	168.1	6.64×10^{-2}
						408	2.98×10^{-9}	167.5	6.86×10^{-2}
						465	2.67×10^{-6}	165.4	7.66×10^{-2}
						488	2.57×10^{-5}	164.5	7.98×10^{-2}
						573	2.32×10^{-2}	161.4	9.12×10^{-2}

Table S4b (Cont.)

E(6)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
St–[7]$^{eq,\varepsilon}$←St–[5]$^{eq,\varepsilon}$	400.0	10.4	410.4	399.4	3.5	273	9.94×10^{-80}	479.6	-2.94×10^{-1}
						298	2.17×10^{-73}	486.9	-3.20×10^{-1}
						307	2.81×10^{-71}	489.6	-3.30×10^{-1}
						338	5.99×10^{-65}	499.1	-3.65×10^{-1}
						350	7.68×10^{-63}	502.7	-3.78×10^{-1}
						392	1.60×10^{-56}	515.3	-4.24×10^{-1}
						408	2.03×10^{-54}	520.2	-4.42×10^{-1}
						465	4.12×10^{-48}	537.8	-5.07×10^{-1}
						488	5.20×10^{-46}	544.9	-5.33×10^{-1}
						573	1.03×10^{-39}	571.1	-6.29×10^{-1}

Table S5 Thermodynamic and kinetic properties for formation of lactone and CO on the anaerobic pathway [E**(7)** and E**(8)** in Path **(IV)** in Figure 6c] computed with ε = 1. Rate constants, temperatures and energies are in s^{-1}, K and kJ/mol, respectively. $\Delta E^{\ddagger}$ = energy barrier on the PES; $\Delta E^{\ddagger,ZPC}$ = zero-point energy-corrected $\Delta E^{\ddagger}$, obtained by including the zero-point correction energy to $\Delta E^{\ddagger}$; $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ = activation enthalpy, entropy and Gibbs free energies, respectively; T_c = crossover temperature; T = temperature; $k_{f/r}^{Q\text{-}vib}$ = rate constant obtained with quantized vibrations including the zero-point vibrational energy; f/r = forward or reverse direction.

Table S5

E(7)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
^{1}1Z§←^{1}1A–[1]	278.3	-11.2	267.1	269.5	148	273	1.12×10^{-38}	265.0	1.63×10^{-2}
						298	2.08×10^{-34}	264.8	1.71×10^{-2}
						307	5.53×10^{-33}	264.7	1.75×10^{-2}
						338	1.04×10^{-28}	264.4	1.86×10^{-2}
						350	2.78×10^{-27}	264.3	1.90×10^{-2}
						392	5.31×10^{-23}	263.9	2.04×10^{-2}
						408	1.42×10^{-21}	263.7	2.10×10^{-2}
						465	2.77×10^{-17}	263.2	2.29×10^{-2}
						488	7.48×10^{-16}	263.0	2.37×10^{-2}
						573	1.49×10^{-11}	262.2	2.65×10^{-2}
^{1}1A–[1]→^{1}1A–[2]‡	71.7	-4.7	66.9	69.3	3	273	2.21×10^{-1}	70.1	-2.96×10^{-3}
						298	2.71×10^{0}	70.4	-4.19×10^{-3}
						307	6.24×10^{0}	70.5	-4.65×10^{-3}
						338	7.70×10^{1}	71.0	-6.25×10^{-3}
						350	1.78×10^{2}	71.2	-6.86×10^{-3}
						392	2.22×10^{3}	71.7	-9.03×10^{-3}
						408	5.15×10^{3}	72.0	-9.88×10^{-3}
						465	6.49×10^{4}	72.8	-1.30×10^{-3}
						488	1.51×10^{5}	73.2	-1.42×10^{-2}
						573	1.94×10^{6}	74.5	-1.91×10^{-2}

Table S5 (Cont.)

E(7)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
^{1}**1A–[2]‡←St–[8]^{eq}**	7.1	0.3	7.4	7.4	3	273	2.03×10^{10}	13.4	-2.19×10^{-2}
						298	2.95×10^{10}	14.2	-2.46×10^{-2}
						307	3.34×10^{10}	14.4	-2.57×10^{-2}
						338	4.84×10^{10}	15.4	-2.93×10^{-2}
						350	5.49×10^{10}	15.8	-3.07×10^{-2}
						392	7.98×10^{10}	17.2	-3.57×10^{-2}
						408	9.05×10^{10}	17.7	-3.76×10^{-2}
						465	1.32×10^{11}	19.7	-4.48×10^{-2}
						488	1.50×10^{11}	20.5	-4.77×10^{-2}
						573	2.18×10^{11}	23.5	-5.88×10^{-2}

Table S5 (Cont.)

E(8)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
St–[8]^{eq}←St–[9]^{eq}	35.7	-3.4	32.3	34.0	3	273	1.45×10^{2}	55.4	-7.85×10^{-2}
						298	4.86×10^{2}	57.6	-8.66×10^{-2}
						307	7.28×10^{2}	58.4	-8.96×10^{-2}
						338	2.46×10^{3}	61.2	-1.00×10^{-1}
						350	3.71×10^{3}	62.3	-1.04×10^{-1}
						392	1.27×10^{4}	66.0	-1.18×10^{-1}
						408	1.93×10^{4}	67.5	-1.23×10^{-1}
						465	6.75×10^{4}	72.7	-1.42×10^{-1}
						488	1.03×10^{5}	74.7	-1.49×10^{-1}
						573	3.68×10^{5}	82.4	-1.77×10^{-1}
St–[9]^{eq}←St–[6]^{eq}	29.6	11.0	40.5	33.2	4	273	1.60×10^{-3}	81.3	-1.76×10^{-1}
						298	5.58×10^{-3}	85.7	-1.92×10^{-1}
						307	8.43×10^{-3}	87.4	-1.99×10^{-1}
						338	2.89×10^{-2}	93.2	-2.20×10^{-1}
						350	4.34×10^{-2}	95.4	-2.28×10^{-1}
						392	1.46×10^{-1}	103.1	-2.56×10^{-1}
						408	2.17×10^{-1}	106.1	-2.67×10^{-1}
						465	7.13×10^{-1}	117.0	-3.07×10^{-1}
						488	1.05×10^{0}	121.4	-3.23×10^{-1}
						573	3.37×10^{0}	137.7	-3.83×10^{-1}

Table S6 Thermodynamic and kinetic properties for formation of lactone and CO on the anaerobic pathway [E**(7)** and E**(8)** in Path **(IV)** in Figure 6c] computed with ε = 33. Rate constants, temperatures and energies are in s^{-1}, K and kJ/mol, respectively. $\Delta E^{\ddagger}$ = energy barrier on the PES; $\Delta E^{\ddagger,ZPC}$ = zero-point energy-corrected $\Delta E^{\ddagger}$, obtained by including the zero-point correction energy to $\Delta E^{\ddagger}$; $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ = activation enthalpy, entropy and Gibbs free energies, respectively; T_c = crossover temperature; T = temperature; $k_{f/r}^{Q\text{-}vib}$ = rate constant obtained with quantized vibrations including the zero-point vibrational energy; f/r = forward or reverse direction; $^{\varepsilon}$ = structure obtained in ε = 33.

Table S6

E(7)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
^{1}1Z§←^{1}1Z–[1]$^{\varepsilon}$	214.6	-6.8	207.7	210.3	37	273	7.49×10^{-28}	208.4	6.85×10^{-3}
						298	1.55×10^{-24}	208.5	6.49×10^{-3}
						307	1.99×10^{-23}	208.6	6.36×10^{-3}
						338	4.17×10^{-20}	208.7	5.89×10^{-3}
						350	5.34×10^{-19}	208.7	5.71×10^{-3}
						392	1.14×10^{-15}	208.9	5.08×10^{-3}
						408	1.46×10^{-14}	209.0	4.83×10^{-3}
						465	3.16×10^{-11}	209.2	3.89×10^{-3}
						488	4.10×10^{-10}	209.3	3.50×10^{-3}
						573	9.10×10^{-7}	209.8	1.96×10^{-5}
^{1}1Z–[1]$^{\varepsilon}$→^{1}1Z–[2]$^{\ddagger,\varepsilon}$	7.8	-3.2	4.6	7.7	9	273	8.86×10^{11}	4.8	1.08×10^{-2}
						298	1.18×10^{11}	4.8	1.08×10^{-2}
						307	1.29×10^{11}	4.8	1.08×10^{-2}
						338	1.71×10^{12}	4.8	1.08×10^{-2}
						350	1.88×10^{12}	4.8	1.08×10^{-2}
						392	2.50×10^{12}	4.8	1.07×10^{-2}
						408	2.74×10^{12}	4.8	1.07×10^{-2}
						465	3.64×10^{12}	4.9	1.05×10^{-2}
						488	4.00×10^{12}	4.9	1.04×10^{-2}
						573	5.30×10^{12}	5.0	9.84×10^{-3}

Table S6 (Cont.)

E(7)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
^{1}**1Z–[2]$^{\ddagger,\varepsilon}$←St–[8]$^{eq,\varepsilon}$**	7.5	-0.6	6.8	7.4	9	273	3.65×10^{7}	27.1	-7.24×10^{-2}
						298	4.77×10^{7}	29.1	-7.97×10^{-2}
						307	5.21×10^{7}	29.9	-8.25×10^{-2}
						338	6.81×10^{7}	32.5	-9.19×10^{-2}
						350	7.45×10^{7}	33.5	-9.55×10^{-2}
						392	9.74×10^{7}	36.9	-1.08×10^{-1}
						408	1.07×10^{8}	38.3	-1.13×10^{-1}
						465	1.40×10^{8}	43.1	-1.31×10^{-1}
						488	1.53×10^{8}	45.1	-1.38×10^{-1}
						573	2.01×10^{8}	52.4	-1.65×10^{-1}

Table S6 (Cont.)

E(8)	$\Delta E^{\ddagger}$	ΔE^{ZPE}	$\Delta E^{\ddagger,ZPC}$	$\Delta H^{\ddagger}$	T_c	T	$k_{f/r}^{Q\text{-}vib}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
St–[8]$^{eq,\varepsilon}$←St–[9]$^{eq,\varepsilon}$	45.1	-4.2	40.8	43.3	9	273	1.33×10^{1}	60.2	-6.22×10^{-2}
						298	6.84×10^{1}	62.1	-6.89×10^{-2}
						307	1.18×10^{2}	62.7	-7.14×10^{-2}
						338	6.11×10^{2}	65.1	-7.99×10^{-2}
						350	1.06×10^{3}	65.9	-8.31×10^{-2}
						392	5.45×10^{3}	69.0	-9.44×10^{-2}
						408	9.42×10^{3}	70.2	-9.87×10^{-2}
						465	4.86×10^{4}	74.4	-1.14×10^{-1}
						488	8.40×10^{4}	76.1	-1.20×10^{-1}
						573	4.34×10^{5}	82.4	-1.43×10^{-1}
St–[9]$^{eq,\varepsilon}$←St–[6]$^{eq,\varepsilon}$	12.7	10.8	23.6	16.1	8	273	1.05×10^{-3}	82.2	-2.42×10^{-1}
						298	1.96×10^{-3}	88.3	-2.64×10^{-1}
						307	2.41×10^{-3}	90.6	-2.73×10^{-1}
						338	4.44×10^{-3}	98.4	-3.02×10^{-1}
						350	5.42×10^{-3}	101.4	-3.13×10^{-1}
						392	9.76×10^{-3}	111.9	-3.51×10^{-1}
						408	1.18×10^{-2}	116.0	-3.66×10^{-1}
						465	2.08×10^{-2}	130.7	-4.20×10^{-1}
						488	2.50×10^{-2}	136.6	-4.41×10^{-1}
						573	4.29×10^{-2}	158.5	-4.21×10^{-1}

Table S7 The equilibrium constants and Gibbs free energies of the proposed elementary reactions obtained based on the analysis of the rate constants

a) The values for E**(5)** and E**(6)** calculated from the data in Table S4† (ε = 1 and 33).

b) The values for E**(7)** and E**(8)** calculated from the data in Table S5† (ε = 1).

c) The values for E**(7)** and E**(8)** calculated from the data in Table S6† (ε = 33).

The symbols used are explained in the text. K = equilibrium constant; $k_{f/r}^{Q\text{-}vib}$ = rate constant obtained with quantized vibrations including the zero-point vibrational energy; f/r = forward or reverse direction; $^{\varepsilon}$ = structure obtained in ε = 33. $\Delta G^{\circ,E(7)}$ and $\Delta G^{\circ,E(8)}$ = Gibbs free energies of E**(7)** and E**(8)**, respectively. $\Delta G^{\circ,(IV)}$ = total Gibbs free energy for reaction Path **(IV)**.

Table S7a

a) T	E(5) / E(6): $^{1}1Z–O_2^{eq} \leftrightharpoons {}^{1}1Z–O_2^{\ddagger} \rightarrow St–[7]^{eq} \rightarrow St–[5]^{eq}$			
	$\Delta G^{\circ,Tot,(III)}$	$K^{(III)}$	$\Delta G^{\circ,Tot,(III),\varepsilon}$	$K^{(III),\varepsilon}$
273	-611.2	8.98×10^{116}	-629.7	3.06×10^{120}
298	-614.4	3.88×10^{112}	-634.2	1.62×10^{116}
307	-615.6	1.40×10^{111}	-635.9	6.37×10^{114}
338	-619.8	7.54×10^{106}	-641.7	4.54×10^{110}
350	-621.4	2.98×10^{105}	-643.9	2.01×10^{109}
392	-627.0	2.21×10^{101}	-651.7	2.22×10^{105}
408	-629.2	9.99×10^{99}	-654.8	1.18×10^{104}
465	-637.0	1.23×10^{96}	-665.7	2.59×10^{100}
488	-640.2	6.93×10^{94}	-670.1	1.84×10^{99}
573	-652.0	2.05×10^{91}	-686.3	1.31×10^{96}

Table S7b

b) T	E(7) ^{1}1A–[1] ⇋ ^{1}1A–[2]‡ → St–[8]^{eq}		E(8) St–[8]^{eq} → St–[9]^{eq} → St–[6]^{eq}		Path (IV) ^{1}1A–[1]^{eq} → St–[6]^{eq}	
	$K = k_f^{Q\text{-}vib}/k_r^{Q\text{-}vib}$	$\Delta G^{\circ,E(7)}$	$K = e^{-\Delta G^{\circ}/RT}$	$\Delta G^{\circ,E(8)}$	$\Delta G^{\circ,Tot,(IV)}$	$K^{(IV)}$
273	1.43×10^{-11}	56.7	1.40×10^{26}	-136.6	-80.0	2.00×10^{15}
298	1.34×10^{-10}	56.3	1.42×10^{25}	-143.3	-87.0	1.90×10^{15}
307	2.81×10^{-10}	56.1	6.68×10^{24}	-145.8	-89.7	1.88×10^{15}
338	2.64×10^{-9}	55.5	6.99×10^{23}	-154.4	-98.9	1.85×10^{15}
350	5.59×10^{-9}	55.3	3.31×10^{23}	-157.7	-102.4	1.85×10^{15}
392	5.31×10^{-8}	54.6	3.60×10^{-22}	-169.2	-114.6	1.91×10^{15}
408	1.13×10^{-7}	54.3	1.73×10^{22}	-173.6	-119.4	1.94×10^{15}
465	1.08×10^{-6}	53.1	1.96×10^{21}	-189.7	-136.5	2.12×10^{15}
488	2.31×10^{-6}	52.7	9.57×10^{20}	-196.1	-143.4	2.21×10^{15}
573	2.25×10^{-5}	51.0	1.15×10^{20}	-220.1	-169.1	2.59×10^{15}

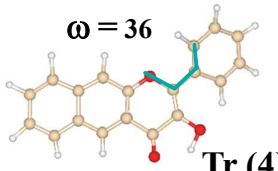
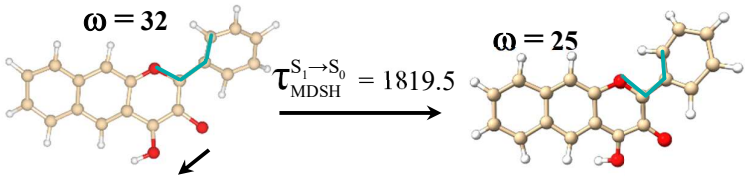
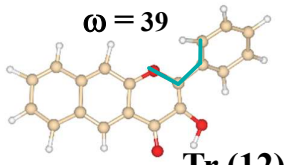
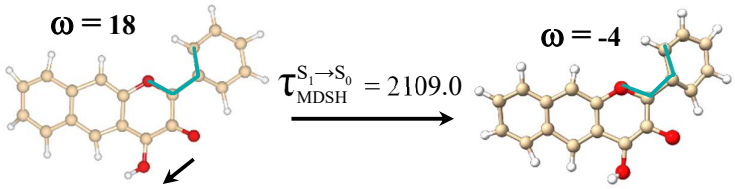
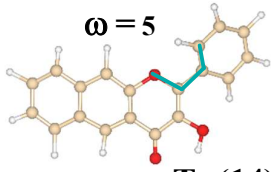
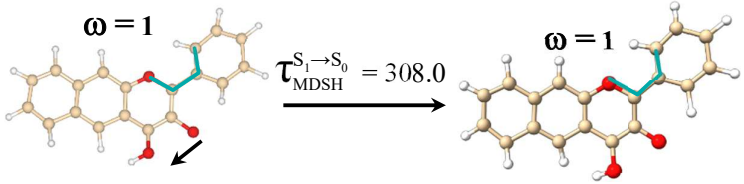
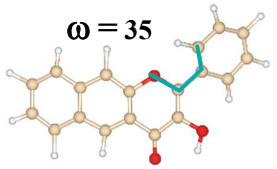
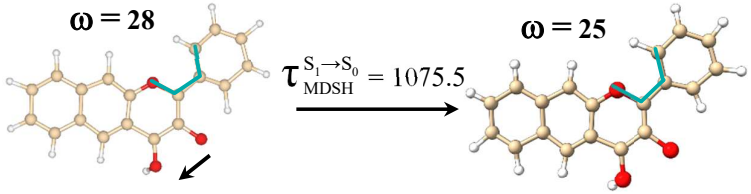
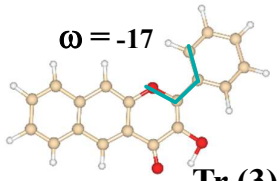
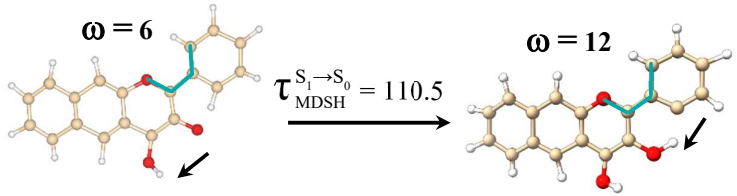
Table S7c

c) T	E(7) ^{1}1Z–[1]$^{\varepsilon} \leftrightharpoons {}^1$1Z–[2]$^{\ddagger,\varepsilon} \rightarrow$ St–[8]$^{eq,\varepsilon}$		E(8) St–[8]$^{eq,\varepsilon} \rightarrow$ St–[9]$^{eq,\varepsilon} \rightarrow$ St–[6]$^{eq,\varepsilon}$		Path (IV) ^{1}1Z–[1]$^{eq,\varepsilon} \rightarrow$ St–[6]$^{eq,\varepsilon}$	
	$K = k_f^{Q\text{-}vib}/k_r^{Q\text{-}vib}$	$\Delta G^{\circ,E(7),\varepsilon}$	$K = e^{-\Delta G^{\circ}/RT}$	$\Delta G^{\circ,E(8),\varepsilon}$	$\Delta G^{\circ,Tot,(IV),\varepsilon}$	$K^{(IV),\varepsilon}$
273	1.91×10^{4}	-22.4	1.83×10^{27}	-142.5	-164.9	3.49×10^{31}
298	1.90×10^{4}	-24.4	2.47×10^{26}	-150.4	-174.7	4.69×10^{30}
307	1.89×10^{4}	-25.1	1.28×10^{26}	-153.3	-178.5	2.42×10^{30}
338	1.89×10^{4}	-27.7	1.78×10^{25}	-163.5	-191.2	3.37×10^{29}
350	1.90×10^{4}	-28.7	9.26×10^{24}	-167.4	-196.1	1.76×10^{29}
392	1.92×10^{4}	-32.1	1.33×10^{24}	-180.9	-213.0	2.56×10^{28}
408	1.93×10^{4}	-33.5	7.04×10^{23}	-186.2	-219.7	1.36×10^{28}
465	1.98×10^{4}	-38.3	1.06×10^{23}	-205.1	-243.4	2.09×10^{27}
488	2.00×10^{4}	-40.2	5.68×10^{22}	-212.7	-252.9	1.13×10^{27}
573	2.07×10^{4}	-47.3	9.05×10^{21}	-240.9	-288.2	1.87×10^{26}

Table S8 Characteristic dynamic results for E**(1)** and E**(2)** in Path **(I)**, obtained from the NVE-MDSH simulations with ε = 1.

$\Delta E^{S_0 \rightarrow S_1}$ = excitation energy; $\tau_{MDSH}^{S_1 \rightarrow S_0}$ = surface hopping time; $\langle T \rangle_{S_1}$ and $\langle T \rangle_{S_0}$ = average temperatures in the S_1 and S_0 states, respectively; $\langle KE \rangle_{S_1}$ and $\langle KE \rangle_{S_0}$ = average kinetic energies in the S_1 and S_0 states, respectively; Tr (*n*) = NVE-MDSH trajectory number *n*.

Table S8

Initial structure	$\Delta E^{S_0 \rightarrow S_1}$	$S_1 \rightarrow S_0$ Hopping	$\langle T \rangle_{S_1}$	$\langle T \rangle_{S_0}$	$\langle KE \rangle_{S_1}$	$\langle KE \rangle_{S_0}$
	3.07 (404 nm)		1124±114	1293±145	452±46	516±60
	3.06 (405 nm)		1420±153	1727±185	572±61	697±69
	3.06 (405 nm)		1061±136	1270±129	427±55	520±59
	3.06 (405 nm)		1026±112	1362±146	413±45	551±58
	3.06 (405 nm)		1158±131	1494±168	466±53	600±65