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Journal:	*The Journal of Physical Chemistry*
Manuscript ID	jp-2022-01105s.R2
Manuscript Type:	Article
Date Submitted by the Author:	21-Mar-2022
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Photochromism of a Spiropyran in Low-Temperature Matrices. Unprecedented Bidirectional Switching Between a Merocyanine and an Allene Intermediate

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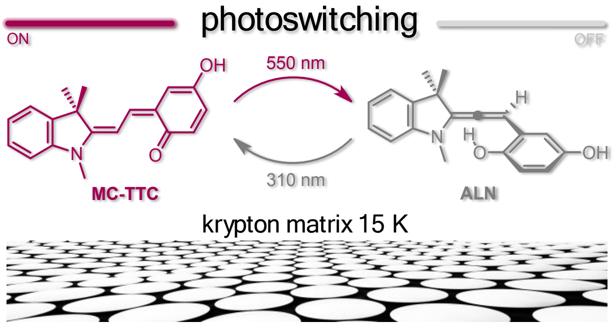

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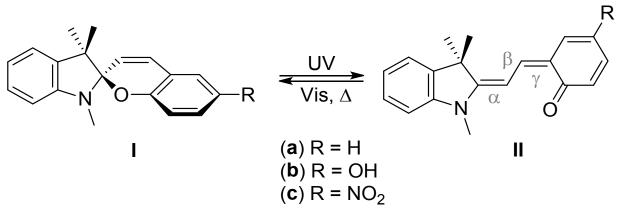
ABSTRACT:

Photochromism of spiropyrans has attracted much attention due to its potential in many light-controlled systems applications. However, several fundamental aspects regarding the structure, energetics, and mechanistic details of the transformations of spiropyrans are still not well understood. Here, we report the study of the photochromism of a 6-hydroxy-spiropyran (**HBPS**) under conditions of matrix isolation, where monomers of the compound are frozen in a solidified noble gas (krypton, at 15 K). The structure of the matrix-isolated **HBPS** was first elucidated by IR spectroscopy supported by DFT computations. Then, the photochromism of **HBPS**, from the colorless spiropyran to the colored merocyanine, was induced by UV-irradiation at 310 nm. The analysis of the IR spectrum of the photoproduced species revealed the exclusive formation of the most stable merocyanine **MC-TTC** stereoisomer. Subsequent visible-light (550 nm) irradiation of **MC-TTC** generated a new colorless allenic isomeric species **ALN**, where the UV-irradiation (310 nm) of **ALN** was found to convert this species back to **MC-TTC**. This constitutes an unprecedented bidirectional transformation between a colored merocyanine and a colorless allene species. The newly observed photoswitching reaction (or photocromism) occurs along an intramolecular hydrogen bond existing in both, merocyanine and allenic species, thus suggesting that it might be generally feasible in the chemistry of spiropyrans. On the other hand, the usual assumption that as a general rule merocyanines photochemically revert to spiropyrans is not supported in this work.

1. INTRODUCTION

Photochromism of spiropyrans was first reported by Fischer and Hirshberg seven decades ago.[1–3] These authors found that UV-irradiation of the naphtho-derivative spiropyran **I** (Scheme 1; with R = fused benzene ring) in solution leads to an intense violet-red color due to the formation of the merocyanine **II**, which can be reverted back to the colorless spiropyran **I** by subsequent visible light irradiation. The use of low-temperature conditions was key to discover this bidirectional photochromic behavior, since above −50 ºC the irradiated solution quickly losses its color (thermochromism).



Scheme 1. The isomerization between a colorless spiropyran **I** and a colored merocyanine **II**.

The closed spiropyran form **I** is essentially constituted by independent and orthogonal indoline and chromene structural units, which results in absorption in the UV region. On the other hand, the opened merocyanine form **II** has a skeleton that is essentially planar and bears a π-system that is conjugated throughout the entire structure, which results in intense absorption in the 500−600 nm visible region. The interconversion between **I** and **II** results in important changes in the molecular features, e.g., geometry, energy, dipole moment, polarizability, conformational flexibility, vibrational and electronic spectra, as well as in significantly different macroscopic properties of the corresponding materials. Consequently, photoswitches built on spiropyran-based molecular systems have attracted enormous attention in the last few decades, and many applications for these systems have been explored, such as the photocontrol of optical and magnetic properties of materials, permeability across biologic membranes, activity of enzymes, properties of polymers, among others.[4–7]

The knowledge about the structure, energetics and mechanistic details of the chemical transformations of spiropyrans is instrumental both to improve and discover suitable light-controlled systems and materials based on these molecules.[4–7] In this context, several studies have been conducted on the fundamental aspects of the photochromism of spiropyrans, but the lack of a general picture on the reactivity of this type of systems is noticeable. For instance, time-resolved spectroscopic studies on spiropyrans **Ia** (R = H), **Ib** (R = OH), and **Ic** (R = NO_2) in solution indicated the formation of merocyanines **IIa**, **IIb**, and **IIc**, respectively.[5] However, the processes observed for the three compounds have received rather distinct interpretations and are not completely understood.

Conversion of **Ia** into **IIa** was observed to take place in a few picoseconds from the S_1-excited state.[8,9] The main decay channel from the **Ia** S_1-excited state was found to be the internal conversion back to the ground state, with a quantum yield (Φ) of 90 %, whereas the ring-opening to **IIa** occurs only with $\Phi \approx 10$ %.[9] It shall be pointed out that merocyanines **II** have a dimethine bridge with three conjugated CC bonds, which result in the possible existence of several stereoisomers (the relevant dihedral angles are labeled as α, β, and γ for the **TTC** stereoisomer shown in Scheme 1; **T** = *trans* and **C** = *cis*). Noteworthy, although the picoseconds merocyanine photoproduct **IIa** was considered to exhibit the *trans* conformation around the central CC bond (β-*trans*), the number and precise nature of stereoisomers formed could not been determined.[9–11] Additionally, femtosecond UV-IR pump-probe results suggested the existence of an intermediate formed in less than one picosecond.[9] This intermediate can be intuitively postulated to be a β-*cisoid* **IIa** form, but its nature could not be established hitherto.

In the case of the 6-hydroxy-spiropyran **Ib**, transient-absorption spectroscopy studies indicated that the C_{spiro}–O bond cleaves in less than 100 fs (upon excitation at 310 nm).[12] The generated metastable species then either reestablishes the C_{spiro}–O bond in 200 fs (minor fraction) or vibrationally relaxes, in a few picoseconds (major fraction), and then isomerizes to merocyanine **IIb** in ~100 ps. Although like for the **Ia** → **IIa** process, it was suggested that the metastable intermediate species observed in the **Ib** → **IIb** phototransformation could be a β-*cisoid* **IIb** form and the picoseconds photoproduct species a β-*trans* **IIb** form,[5] their nature still remains unknown, while the time scale of the ring-opening photoprocess was found to be substantially different for the two spiropyrans, **Ib** and **Ib**.

In the case of the 6-nitro-spiropyran **Ic**, time-resolved spectroscopic studies revealed that its UV-induced ring-opening to **IIc** involves a triplet state and takes place with a much higher quantum efficiency compared to the transformations of **Ia** into **IIa**.[13–15] A first stereoisomer of **IIc** was found to be formed in the T_1-excited state, in ~17 ps, and then quantitatively converted into a second stereoisomer in ~350 ps (also in the T_1-excited state).[16] The steady-state IR spectrum of **IIc**, generated by UV-irradiation of spiropyran **Ic** in an argon matrix at 8 K, was found to be only compatible with the computed IR spectrum of the **TTC** stereoisomer.[17]

It is interesting to point out that the **TTC** stereoisomer of the merocyanines has been consistently suggested as being the experimentally most relevant species. For example, investigations using NMR spectroscopy showed that the **TTC** and **TTT** stereoisomers of **IIc** exist in equilibrium in solution at room temperature,[18] with a free energy difference of ~4.7 kJ mol^{-1} measured for the 6-nitro-8-bromo and 6,8-dinitro derivatives.[19,20] **TTC** has been found as the most stable form in all these cases, in agreement with results from DFT computations.[17,21,22]

If the situation regarding the phototransformation of the spiropyrans into the merocyanines is still far from being well understood, the degree of understanding of the putative inverse reaction is still even more limited. It has been generically assumed that merocyanines **II** photochemically revert back to the close-ring spiropyrans **I**, as showed for the naphtho-derivative by Fischer and Hirshberg,[2,3] although supporting evidences are still lacking.[23-26] Actually, time-resolved experiments demonstrated that nitro-merocyanine **IIc** does not photochemically reverts to **Ic**.[27,28] Instead, the most recent study concluded that **TTC**, assigned as dominant **IIc** stereoisomer resulting from ring-opening of **Ic**, photoisomerizes to **TTT**, whereas this later does not photoisomerize at all but relaxes to its ground-state.[28] Moreover, studies with 6-hydroxy-spiropyran **Ib** in solid films showed that UV-irradiations generated a colored species, characteristic of a merocyanine, which does not return back to **Ib** but, instead, isomerizes to a third species upon visible-light irradiation or thermal heating.[29,30] Although merocyanines β-*cisoid* structures aggregated with different neighboring molecules have been proposed for such products,[30] there is no convincing evidence supporting such assignment.

In the light of the current data, it is evident that there are still many knowledge to acquire about the fundamental aspects of the photochromism of spiropyrans and merocyanines. In this realm, we reported here investigations on the photochromism of 6-hydroxy-spiropyran **Ib** isolated in cryogenic matrices. Matrix isolation is a powerful technique for structural characterization and for generation of reactive species.[31–33] Under matrix isolation conditions, a chemical species can be frozen in a solidified noble gas in enough low concentration to guarantee the absence of intermolecular interactions. Since interactions with the noble gas are usually very weak, the results obtained might constitute a reference data similar to gas-phase experiments, thus allowing direct comparison with results obtained by quantum chemistry. Moreover, as temperatures are close to the absolute zero, matrix isolation provides ideal conditions for stabilization of reactive species, allowing to perform their spectroscopic characterization and to probe their light-induced reactivity in great detail. As it will be shown, we provide a detailed structural characterization of spiropyran **Ib** and of its photochemical ring-opening merocyanine **IIb** product, using matrix isolation and IR spectroscopy, complemented by DFT computations. Noteworthy, we discovered that light induces bidirectional switching between the colored merocyanine **IIb** and a colorless new allene isomeric species. To the best of our knowledge, the experimental characterization of an allene intermediate and its reversible photochromism with a merocyanine is unprecedented in the chemistry of spiropyrans.

2. EXPERIMENTAL METHODS

2.1 Synthesis

Commercially available high-grade reagents were used as acquired. Reaction monitoring was conducted by TLC analysis, on SiO_2 60 F_{254}-coated aluminum plates. Flash column chromatography was performed using SiO_2 60 (35–70 μm) as the stationary phase. NMR spectra were recorded with a Bruker Avance III spectrometer, operating at 400 MHz (^{1}H) and 100 MHz (^{13}C). Tetramethylsilane (TMS) was used as internal standard. Chemical shifts (δ) are expressed in parts per million related to TMS and coupling constants (J) are converted into hertz (Hz). Synthesis of 1’,3’,3’-trimethyl-6-hydroxyspiro[2*H*-1-benzopyran-2,2’-indoline] (spiropyran **Ib**, from now on abbreviated by **HBPS**) was carried out adapting a procedure described in the literature.[34] A solution of 2,5-dihydroxybenzaldehyde (0.7 g, 5 mmol) and 1,3,3-trimethyl-2-methyleneindoline (0.88 mL, 5 mmol) in ethanol (10 mL) was stirred and heated to reflux for 3 h hours. After cooling to room temperature, the solvent was evaporated and the resulting residue was purified by flash column chromatography, using hexane:ethyl acetate (3:1) as an eluent. After evaporation of the solvents, **HBPS** was obtained as a pale-yellow solid in 48 % yield (0.7 g, 2.4 mmol). Spectral data (Figure S1) are in accordance with literature.[34] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.16 (td, J = 7.6, 1.2 Hz, 1H), 7.06 (dd, J = 7.2, 0.8 Hz, 1H), 6.83 (td, J = 7.5, 0.8 Hz, 1H), 6.76 (d, J = 10.2 Hz, 1H), 6.59-6.56 (m, 2H), 6.54-6.53 (m, 1H), 6.51 (d, J = 7.7 Hz, 1H), 5.69 (d, J = 10.2 Hz, 1H), 4.54 (s, 1H), 2.71 (s, 3H), 1.30 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 148.7, 148.6, 148.2, 136.8, 129.0, 127.6, 121.5, 120.5, 119.3, 119.1, 116.4, 115.6, 112.9, 106.8, 103.9, 51.7, 29.0, 25.9, 20.3.

2.2 Theoretical Computations

All quantum chemical calculations were performed with Gaussian 16.[35] Geometry optimizations were carried at the DFT level of theory using the functionals ωB97X-D[36] (a hybrid GGA functional with dispersion correction, which has been showed a solid performance on the calculation of thermochemistry[37,38] and energy barriers’ heights[38]) and B3LYP[39–41] (a hybrid GGA functional which has been showed a reliable performance on the calculation of vibrational frequencies and IR intensities of organic molecules[42–44]) in conjugation with the 6-311+G(2d,p)[45] basis set. Harmonic vibrational calculations at both levels were carried out for the respective optimized geometries. The nature of the stationary points on the potential energy surfaces (true minima or first-order transition states) was confirmed through the analysis of the corresponding Hessian matrices. For the purpose of interpretation of the experimental IR spectra, the B3LYP/6-311+G(2d,p) computed harmonic frequencies and IR intensities were used. The calculated frequencies scaled by a factor of 0.979 (except for the ν(OH) modes, which were scaled by 0.950),[46] together with the computed IR intensities, were used to simulate the IR spectra by convoluting each peak with a Lorentzian function having a full-width at half-maximum (FWHM) equal to 4 cm^{-1}. The integral band intensities correspond to the calculated IR absolute intensities and are presented in the arbitrary units of "Relative Intensity". The assignments of the vibrational modes were made with help of the ChemCraft vibrational modes' animation module.[47] Vertical electronic excitation energies were calculated at the B3LYP/6-311+G(2d,p) level of theory using the time-dependent density functional theory (TD-DFT).[48–50] For the simulation of the UV-Vis spectra, the calculated peaks were convoluted with a Lorentzian function having a half-width at half-maximum (HWHM) equal to 1250 cm^{-1}.

2.3 Matrix-Isolation IR Spectroscopy

For preparing the low-temperature matrices of **HBPS**, a solid sample of the compound was slowly sublimated (~340 K) using a miniature glass oven placed in the vacuum chamber of the cryostat (10^{-6}-10^{-5} mbar). The vapors of the compound were deposited simultaneously with a large excess of krypton gas (N48, Air Liquide) onto a cesium iodide (CsI) window kept at 22 K. The window was then cooled to 15 K to collect the IR spectra and to perform the irradiation experiments. The temperature of the CsI window was measured directly by a silicon diode sensor, connected to a digital controller (Scientific Instruments, model 9650-1), with an accuracy of 0.1 K. In all experiments, an APD Cryogenics closed-cycle helium refrigeration system with a DE-202A expander was used. IR spectra were recorded using a Thermo Nicolet 6700 Fourier transform infrared (FTIR) spectrometer, equipped with a deuterated triglycine sulfate (DGTS) detector and a potassium bromide (KBr) beam splitter, for the mid-IR region (4000−400 cm^{-1}; resolution 0.5 cm^{-1}), or with a thermoelectrically cooled indium gallium arsenide (InGaAs) detector and a calcium fluoride (CaF_2) beam splitter, for the near-IR range (7500−4000 cm^{-1}; resolution 2.0 cm^{-1}). The sample compartment of the FTIR spectrometer was modified to accommodate the cryostat head and allow purging of the instrument by a stream of filtered dry air to avoid interference from atmospheric H_2O and CO_2.

2.4 Irradiation experiments

The matrix-isolated species were irradiated (through the outer quartz window of the cryostat) using tunable narrowband (~0.2 cm^{-1} spectral width) light provided by a Spectra Physics Quanta-Ray MOPO-SL optical parametric oscillator (OPO) pumped with a pulsed Nd:YAG laser (repetition rate = 10 Hz, duration = 10 ns). For UV-irradiations the frequency-doubled beam (signal or idler) was used (pulse energy ∼1 mJ). For Vis-irradiations the signal beam was used (pulse energy ∼10 mJ). For near-IR-irradiations the idler beam was used (pulse energy ∼10 mJ). The outcome of those irradiations (consumption of a reactant and generation of a photoproduct) was monitored by collecting IR spectra.

3. RESULTS AND DISCUSSION

3.1 Structure and IR spectrum of matrix-isolated spiropyran HBPS

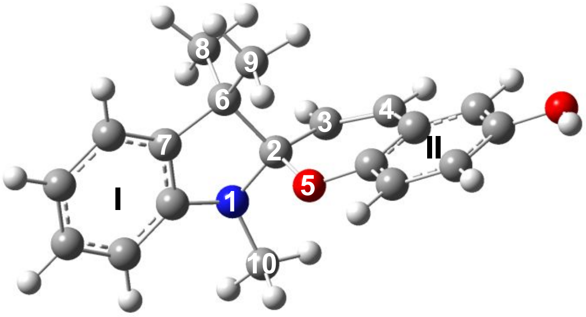
The structure of spiropyrans is known to comprise a chromene and an indoline unit linked by a chiral spiro carbon and oriented almost perpendicular to each other.[22,51–54] The relative energies of the different stereoisomers of the spiropyran **HBPS** (labeled here as **SP-x**) and the transition states for interconversion between them (labeled here as **TS-x**), calculated at the *ω*B97X-D/6-311+G(2d,p) and B3LYP/6-311+G(2d,p) levels of theory, are given in Table 1. The *ω*B97X-D optimized geometry of most stable stereoisomer **SP-1a** is shown in Figure 1.

In **HBPS**, the chromene unit can adopt a bent-up and bent-down orientation regarding the perpendicular alignment relative to the indoline unit (Scheme S1), which give rise to the **SP-1a** [angle between the mean-planes of the chromene and indoline rings (Ω) = 100.9º; $\tau_I = -138.6^o$; all structural data indicated in the text were taken from the *ω*B97X-D computations] and the **SP-2a** [Ω = 77.1º; $\tau_I = -104.2^o$] conformers, respectively. Both **SP-1a** and **SP-2a** conformers may exist with two different orientations of the OH substituent in the chromene moiety, where the OH group are aligned with the ring-plane and points towards or away from C4 (see Figure 1). These four forms are almost isoenergetic, with the higher energy OH forms of **SP-1a** and **SP-2a**, which correspond to the forms with the OH group pointing towards C4 being here notated as **SP-1a*** and **SP-2a***, respectively (Table 1). The transitions states **TS(1a-2a)** and **TS(1a*-2a*)** separating **SP-1a** from **SP-2a** and **SP-1a*** from **SP-2a***, respectively, are characterized by having the chromene and the indoline units essentially perpendicular to each other (Scheme S1) [Ω ≈ 89º; $\tau_I \approx -121^o$] and a very low energy (~2 kJ mol^{-1}). Consequently, the movement of distortion between **SP-1a** and **SP-2a** and that between **SP-1a*** and **SP-2a*** should be practically free, even when the **HBPS** molecules are isolated in low-temperature matrix conditions.[55]

Table 1. Relative Zero-point Corrected Energies (ΔE_0) and Geometric Parameter (τ_{I} and τ_{II}) Computed at the ωB97X-D/6-311+G(2d,p) and B3LYP/6-311+G(2d,p) Levels of Theory for the Spiropyran Forms of **HBPS** and Corresponding Transition States.[a]

	ωB97X-D/6-311+G(2d,p)				B3LYP/6-311+G(2d,p)		
Structure[b]	ΔE_0	τ_{I}	Ω	τ_{II}	ΔE_0	τ_{I}	τ_{II}
SP-1a	0.0	−138.6°	100.9°	29.4°	0.0	−127.5°	28.0°
SP-1a*	0.7	−138.6°	100.7°	29.4°	[c]	[c]	[c]
SP-2a	1.0	−104.2°	77.1°	29.8°	−0.1[d]	−109.6°	28.1°
SP-2a*	1.6	−104.2°	77.2°	29.8°	0.4	−109.6°	28.1°
SP-1b	9.5	−139.5°	93.9°	−29.6°	[c]	[c]	[c]
SP-1b*	10.0	−139.6°	94.0°	−29.6°	[c]	[c]	[c]
SP-2b	8.7	−106.0°	83.2°	−31.4°	8.0	−109.8°	−29.5°
SP-2b*	9.1	−106.0°	83.1°	−31.4°	8.4	−109.7°	−29.6°
TS(1a-2a)	1.9	−120.9°	88.7°	29.6°	−0.1	−125.6°	28.1°
TS(1a*-2a*)	2.5	−121.2°	88.9°	29.5°	[c]	[c]	[c]
TS(1a-1b)	16.5	−139.4°	94.4°	−3.1°	[c]	[c]	[c]
TS(1a*-1b*)	17.0	−139.5°	94.4°	−3.2°	[c]	[c]	[c]
TS(2a-2b)	18.1	−105.2°	88.8°	−5.1°	13.6	−109.1°	−6.0°
TS(2a*-2b*)	18.6	−105.2°	88.9°	−5.2°	14.1	−108.9°	−6.0°
TS(1b-2b)	9.7	−124.9°	90.3°	−30.5°	[c]	[c]	[c]
TS(1b*-2b*)	10.2	−125.2°	90.2°	−30.5°	[c]	[c]	[c]
TS(1a-1a*)	8.7	−138.1°	100.1°	29.3°	[c]	[c]	[c]
TS(2a-2a*)	9.6	−104.9°	77.2°	29.7°	8.6	−110.6°	28.0°
TS(1b-1b*)	18.4	−138.8°	93.7°	−29.6°	[c]	[c]	[c]
TS(2b-2b*)	17.5	−106.4°	83.5°	−31.4°	17.1	−110.3°	−29.5°

[a] Calculated energies (kJ mol^{-1}) are relative to the **SP-1a** form. The optimized structure of the spiropyran **SP-1a** is given in Figure 1. [b] In the names of the structures, **1** and **2** designates differences in the $\tau_{\mathrm{I}(1\text{-}2\text{-}3\text{-}4)}$ dihedral angle, whereas **a** and **b** designates differences in the $\tau_{\mathrm{II}(1\text{-}2\text{-}6\text{-}7)}$ dihedral angle (see Figure 1). The symbol Ω indicates the angle between the mean-planes of the indoline and chromene rings. The asterisk symbol (*) designates the most energetic OH conformation. [c] Not found. [d] B3LYP/6-311+G(2d,p) computed relative Gibbs energy at 298.15 K for **SP-2a** is 2.4 kJ mol^{-1} higher than for **SP-1a**.



SP-1a: $\tau_{\mathrm{I}(1\text{-}2\text{-}3\text{-}4)} = -138.6^{\circ}$; $\tau_{\mathrm{II}(1\text{-}2\text{-}6\text{-}7)} = 29.4^{\circ}$

Figure 1. ωB97X-D/6-311+G(2d,p) optimized geometry of the most stable spiropyran form of **HBPS**. Values of selected dihedral angles, which allow to differentiate between the spiropyran stereoisomers, are provided. **I** = indoline phenyl ring; **II** = chromene phenyl ring. Color code: light gray – H atom; gray – C atom; blue – N atom, red – O atom.

An additional isomerization degree of freedom in spiropyran **HBPS** (typically not considered in the analysis of the structure of spiropyrans) is the nitrogen atom inversion,[56] which makes the indoline unit to adopt a bent-right and bent-left orientation in relation to the plane of the N1-C2-C6 atoms. The indoline bent-right orientation is the most stable one and characterizes the **SP-1a/SP-1a*** [τ_{II} = 29.4º] and **SP-2a/SP-2a*** [τ_{II} = 29.8º] structures. The indoline bent-left orientation was found in the **SP-1b/SP-1b*** [τ_{II} = −29.6º] and **SP-2b/SP-2b*** [τ_{II} = −31.4º] forms which are 8−10 kJ mol^{-1} higher in energy than the forms possessing the indoline bent-right orientation (Table 1). The **SP-1b** and **SP-2b** forms can be obtained from **SP-1a** and **SP-2a**, respectively, through transition states **TS(1a-1b)** [τ_{II} = −3.1º] and **TS(2a-2b)** [τ_{II} = −5.1º], which are characterized by possessing the indoline unit close to the plane of the N1-C2-C6 atoms and have a relative energy of ~17 kJ mol^{-1} (similar situation for the **SP-1b*** and **SP-2b*** forms). In the case of the indoline bent-left orientation, the potential energy surface (PES) around the perpendicularity of chromene and indoline units was found to be even more flat than for the indoline bent-right orientation, with the transition states **TS(1b-2b)/TS(1b*-2b*)** [$\tau_I \approx -125$º] having a relative energy ≤ 1 kJ mol^{-1}. Based on the computed energies, the **SP-1b/SP-1b*** and **SP-2b/SP-2b*** forms should have essentially negligible equilibrium populations (Boltzmann distribution) in the sublimated gas-phase vapor of **HBPS** (~340 K), priory to the quench in a krypton matrix at low-temperature.

It shall also be pointed out that, though as mentioned the OH group in the **HBPS** chromene unit can adopt two different orientations, with those having the OH group pointing towards C4 being slightly more energetic than the corresponding forms having the OH group pointing away from C4, the OH rotamerization barriers amount to only ~8 kJ mol^{-1} (Table 1). Therefore, as it has been reported for phenol derivatives studied in noble-gas matrices,[57–61] even if the high-energy OH conformers are populated in the gas phase equilibrium prior to matrix deposition, they should undergo fast rotamerization tunneling to the corresponding most stable forms during matrix deposition, which precludes their isolation and characterization in low-temperature matrix conditions.

In conclusion, the theoretical data points (although acknowledging some uncertainties) to the existence in the cryogenic matrices of only the most stable **SP-1a** structure of the investigated spiropyran (Scheme S2). This is because: (i) All **SP-b** forms should have negligible populations in the gas phase equilibrium prior to deposition; (ii) the higher-energy OH forms **SP-1a*** and **SP-2a*** should convert into the corresponding lower-energy forms **SP-1a** and **SP-2a** respectively, by tunneling during matrix deposition; and (iii) **SP-2a** can convert into **SP-1a** during matrix deposition, considering the very small energy barrier separating these two forms (conformational cooling effect).[62]

The **HBPS** was synthesized by standard procedures and monomers of this species were isolated is a krypton matrix at 15 K, as described in the Experimental Methods Section. The prepared **HBPS** krypton matrix is colorless, which excludes the presence of any open merocyanine form. The corresponding IR spectrum is presented in Figure 2a (1700−600 cm^{-1} region) and Figure S2 (7200−6900 and 3700−3575 cm^{-1} regions). Two factors that are associated with the large size of the molecule make difficult to undertake a detailed spectra analysis: (i) the appearance of many overlapping bands; and (ii) the possible contribution to the spectrum of a substantial number of bands due to overtones and combination modes (resulting from the electric anharmonicity). Nevertheless, the comparison between the experimental IR spectrum and the B3LYP/6-311+G(2d,p) computed harmonic IR spectrum of the most stable **SP-1a** form shows a very good match (Figure 2). Note that the computed IR spectra of **SP-1a** and **SP-2a** forms of **HBPS** are very similar, except in the 1050–900 cm^{-1} region, where the agreement with the experimental data is better for the **SP-1a** form (Figure S3), in consonance with the expectation extracted from the PES analysis indicating the possible occurrence of **SP-2a** → **SP-1a** conversion during matrix deposition. Also, as anticipated based on the computational results, the calculated IR spectrum of **SP-2b** does not agree with the experimental spectrum, indicating that this species is most probably not present in the matrix-isolated **HBPS** sample (Figure S3).

In addition to the 7097 and 3635 cm^{-1} absorptions (Figure S2), easily identified as the 2ν(OH) and ν(OH) modes, a few other characteristic IR bands can be assigned to vibrational modes of **SP-1a**. In the high frequency region of the experimental IR spectrum, bands appear at 1652, 1614 and 1587 cm^{-1}, which have good correspondence with the computed IR bands at 1660 [ν(C3=C4)], 1607 [$\nu(CC)_{ring\text{-}I}$] and 1581 [$\nu(CC)_{ring\text{-}II}$] cm^{-1} (Figure 2). The strongest experimental IR band is observed at 1487 cm^{-1}, which is well reproduced by the intense computed IR bands at 1485 [$\nu(CC)_{ring\text{-}II}$] and 1479 [$\delta(C10H_3)_{as}$] cm^{-1}. Other distinctive experimental bands appear at 1303, 1282, 1254 and 1180 cm^{-1}, which are in good agreement with the computed IR bands at 1301 [approx. ν(C−N)],[63] 1274 [ν(C−OH)], 1245 [ν(C−O5)] and 1172 [δ(C3H) + δ(OH)] cm^{-1}. Finally, the strong experimental bands comprising the pairs 975 and 965 cm^{-1} plus 942 and 937 cm^{-1}, and the band at 742 cm^{-1}, compare well with the corresponding intense computed IR bands comprising the pairs 969 [$\nu(C_{spiro}-C6)$] and 962 [ν(C_{spiro}−O)] cm^{-1} plus 935 [aprox. γ($C8H_3$) + γ($C9H_3$)] and 932 [aprox. ν(N−C−O)] cm^{-1}, and the band at 734 [γ$(CH)_{ring\text{-}I}$] cm^{-1}. The assignment of a few characteristic IR bands previously reported for other spiropyran derivatives (in solution or solid phases) in general agree with the IR spectral assignment described here for the matrix-isolated **HBPS**.[64–66] A detailed comparison between the experimental IR spectrum of **HBPS** and the computed IR spectrum of **SP-1a** is provided in Table S1.

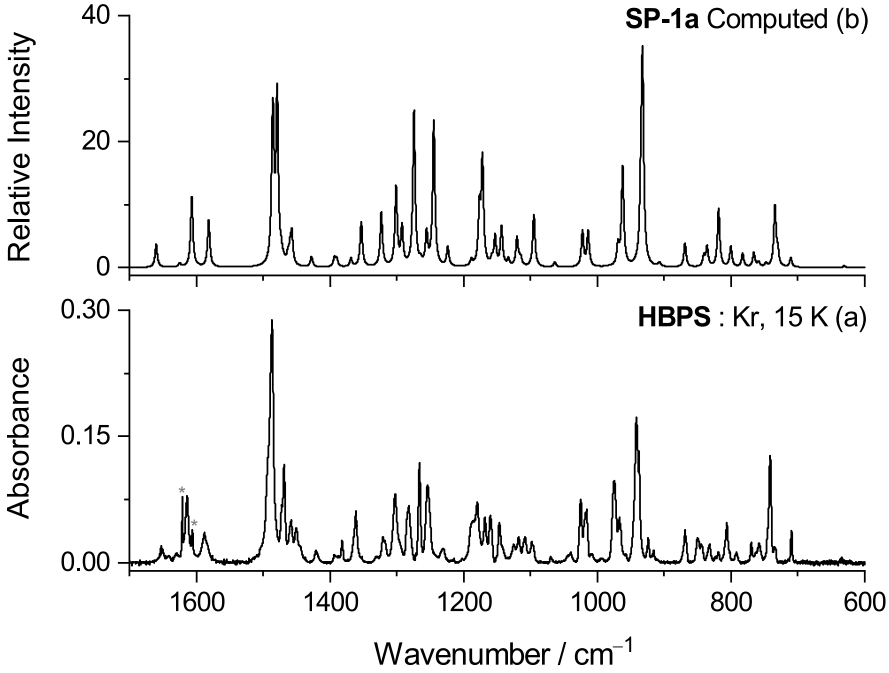


Figure 2. (a) Experimental IR spectrum of **HBPS** isolated in a krypton matrix at 15 K. Asterisk symbols (∗) indicate bands due to monomeric water. (b) B3LYP/6-311+G(2d,p) computed IR spectrum of the spiropyran form **SP-1a** (details are given in Experimental Methods Section).

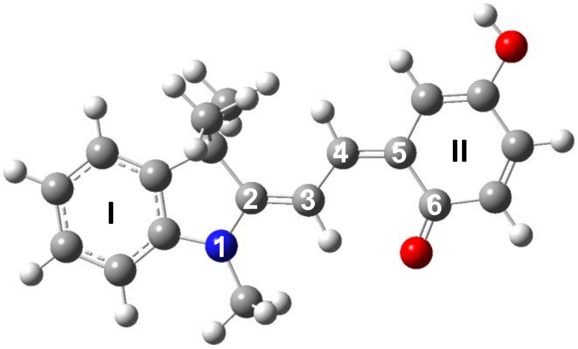
3.2 Structure and IR spectrum of matrix-isolated merocyanine form of HBPS

As already mentioned in the Introduction section, the merocyanines resulting from the ring-opening of spiropyrans have different stereoisomers due to the existence of three isomerizationally-relevant internal coordinates associated with the central −C=CH−CH=C− fragment (α, β and γ dihedral angles; see Figure 1). The relative energies of the merocyanine forms of **HBPS** and the corresponding relevant transitions states for their interconversion, found at the ωB97X-D/6-311+G(2d,p) and B3LYP/6-311+G(2d,p) levels of theory, are given in Table 2. The ωB97X-D optimized geometry of the most stable merocyanine stereoisomer **MC-TTC** is shown in Figure 3.

Table 2. Relative Zero-point Corrected Energies (ΔE_0) and Geometric Parameter (α, β and γ) Computed at the *ω*B97X-D/6-311+G(2d,p) and B3LYP/6-311+G(2d,p) Levels of Theory for the Merocyanine Forms of **HBPS** and the Corresponding Relevant Transitions States.[a]

	*ω*B97X-D/6-311+G(2d,p)				B3LYP/6-311+G(2d,p)			
Structure[b]	ΔE_0	α	β	γ	ΔE_0	α	β	γ
MC-CCC	17.1	−28.8º	−26.5º	−13.6º	30.8	−27.7º	−27.6º	−12.5º
MC-TCC	53.1	−171.1º	51.6º	17.3º	65.0	−165.6º	45.0º	16.9º
MC-CTC	12.1	−11.4º	178.2º	−2.9º	10.5	−10.0º	179.3º	−2.5º
MC-TTC	0.0	180.0º	180.0º	0.0º	0.0	180.0º	180.0º	0.0º
MC-CCT	20.6	−14.7º	−41.4º	177.5º	36.7	−16.8º	−38.4º	178.2º
MC-TCT	35.8	−179.9º	72.5 º	−178.0º	55.5	−178.7º	58.6 º	−176.1º
MC-CTT	8.5	−8.7º	177.9º	178.0º	8.7	−7.1º	179.0º	178.3º
MC-TTT	0.5	180.0º	180.0º	180.0º	2.9	180.0º	180.0º	180.0º
TS(1a-CCC)	26.7	−61.6º	−14.9º	−17.1º	46.0	−66.8º	−14.9º	−14.3º
TS(2a-TCC)	53.4	−159.0º	38.8 º	18.3º	65.4	−153.9º	35.0 º	15.9º
TS(CCC-CTC)	57.9	−0.6º	−91.5º	1.6º	74.6	1.3º	−94.5º	3.0º
TS(TCC-TTC)	53.1	−177.9º	79.5º	4.7º	72.9	−179.8º	88.6º	1.3º

[a] Calculated energies (kJ mol^{-1}) are relative to the merocyanine **MC-TTC** form. The optimized structure of the **MC-TTC** is given in Figure 3. [b] In the names of the structures, **C** and **T** designates *cisoid* and *transoid* dihedral angles; the first letter relative to the dihedral $\alpha_{(1\text{-}2\text{-}3\text{-}4)}$; the second letter relative to the dihedral $\beta_{(2\text{-}3\text{-}4\text{-}5)}$; the third letter relative to the dihedral $\gamma_{(3\text{-}4\text{-}5\text{-}6)}$ (see Figure 3). Only data of the most stable OH conformation are given, which in all species correspond to the OH orientation towards the C4 atom. The capture of high-energy OH conformers under noble-gas matrices conditions should be impossible due to their fast decay by H-tunneling (rotamerization barriers ~9 kJ mol^{-1}), as mentioned in Section 3.1.



MC-TTC: $\alpha_{(1\text{-}2\text{-}3\text{-}4)}$ = 180.0º; $\beta_{(2\text{-}3\text{-}4\text{-}5)}$ = 180.0º; $\gamma_{(3\text{-}4\text{-}5\text{-}6)}$ = 0.0º

Figure 3. *ω*B97X-D/6-311+G(2d,p) optimized geometry of the most stable merocyanine form of **HBPS**. Values of selected dihedral angles, which allow to differentiate between the merocyanine stereoisomers, are provided. **I** = indoline phenyl ring; **II** = *o*-quinonemethide ring. Color code: light gray – H atom; gray – C atom; blue – N atom, red – O atom.

As found for other derivatives,[17,21,22,53] the most stable stereoisomers of the merocyanine form of **HBPS** have a central β dihedral angle with *trans* orientation, i.e. **MC-CTC**, **MC-TTC**, **MC-CTT**, and **MC-TTT**. The **MC-TTC** and **MC-TTT** are the only truly planar forms, with the latter being more energetic by 1−3 kJ mol^{-1}. The **MC-CTC** and **MC-CTT** forms are 9−12 kJ mol^{-1} more energetic than **MC-TTC**. The structural features accounting for those energy differences have been analyzed in more detail elsewhere for a similar derivative.[17] The most stable merocyanine **MC-TTC** is more energetic than the most stable spiropyran **SP-1a**, although the magnitude varies significantly with the theoretical method; ~62 *vs.* ~17 kJ mol^{-1} at ωB97X-D and B3LYP levels, respectively. Those results are in line with our experimental observation regarding the absence of any merocyanine after deposition of **HBPS** in a krypton matrix.

The ring-opening of spiropyran **HBPS** should occur by the cleavage of the relatively weak C_{spiro}–O bond. On the ground-state PES, computations show that the C_{spiro}–O cleavage leads first to the merocyanine stereoisomer **MC-CCC** or **MC-TCC**. The formation of **MC-CCC** [r($C_{spiro}\cdots$O) = 2.70 Å, ~17 kJ mol^{-1}; all data were taken from the ωB97X-D computations] occurs by a transition state **TS(1a-CCC)** [r($C_{spiro}\cdots$O) = 2.21 Å, ~88 kJ mol^{-1} relative to the **SP-1a** species] characterized by having the O atom closer to the methyl group bound to the nitrogen atom of the indole moiety, which resembles more the spiropyran **SP-1a** than **SP-2a**. The formation of **MC-TCC** [r($C_{spiro}\cdots$O) = 2.97 Å, ~53 kJ mol^{-1}] occurs by a transition state **TS(2a-TCC)** [r($C_{spiro}\cdots$O) = 2.68 Å, ~115 kJ mol^{-1} relative to the **SP-2a** species] characterized by having the O atom closer to the two geminal methyl groups bound to the indole carbon atom, which resembles more the spiropyran **SP-2a** than **SP-1a**. These higher energy merocyanine forms can then undergone *cis* → *trans* isomerization at the β dihedral angle to the most stable **MC-CTC** and **MC-TTC** forms, through an energy barrier of ~41 kJ mol^{-1} (relative to the **MC-CCC** species) [**TS(CCC-CTC)**] and <0.1 kJ mol^{-1} (relative to the **MC-TCC** species) [**TS(TCC-TTC)**], respectively. The *cis* → *trans* isomerization at the γ dihedral angle (to **MC-CCT** and **MC-TCT**, respectively) is significantly more energetic due to the more pronounced double character of the rotating bond and the steric repulsion that arises between the methyl groups of the indoline unit and the *o*-quinonemethide unit (Figure S4). These findings indicate that the most favorable route on the ground-state to a β-*trans* merocyanine is the pathway to **MC-TTC**. The corresponding **MC-TCC** intermediate is situated in the very flat PES region, with a very small energy barrier separating this form from the **MC-TTC** form, which awards the **MC-TCC** species a very elusive nature.

Computations on the excited state are beyond the scope of our work. Nevertheless, it is relevant to mention two recent computational studies on this subject. One work carried at the CASPT2//CASSCF level, for the unsubstituted spiro[2*H*-1-benzopyran-2,2'-indoline],[53] indicated that the ring-opening on the S_1 surface occurs by C_{spiro}–O cleavage, leading to **MC-CCC** and **MC-TCC** intermediates by a barrierless process. Another work carried out at the TD-DFT ωB97X-D/cc-pVDZ and RI-CC2 levels, for the 1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'-indoline],[54] indicated that the excitation into a bright state leads to a barrierless C_{spiro}–O cleavage and to a conical intersection with the ground state, resulting in the **MC-TCC** species (or in the starting spiropyran form). In the context of the electronic excitation of the **HBPS** molecule, the hypothetic generation of **MC-TCC** should result in the subsequent formation of **MC-TTC** or in the recovery of the spiropyran **SP-1a**. On the other hand, the hypothetic generation of **MC-CCC** is unlikely to result in the formation of **MC-CTC** (unless driven by a secondary photoprocess). The **MC-CCC** is situated in a potential energy well separated by 9.5 kJ mol^{-1} from **SP-1a** and by ~41 kJ mol^{-1} from **MC-CTC** (values relative to the **MC-CCC** energy at the ωB97X-D level). This makes **MC-CCC** a reactive intermediate difficult to capture even under low-temperature matrix isolation conditions, which most likely converts back promptly to the spiropyran **SP-1a**.

The UV-induced photochemistry of matrix-isolated spiropyran **HBPS** was investigated experimentally using narrowband irradiation at 310 nm (UV-Vis spectrum of **HBPS** in 1-propanol: λ_{max} = ~300 and 340 nm).[12] Figure 4a (1700−600 cm^{-1} region) and Figure S5 (7200−6900 and 3700−3575 cm^{-1} regions) show the difference IR spectrum after the consumption of spiropyran **HBPS** promoted by the performed UV-irradiation. The appearance of a red-purple color in the matrix sample indicates the occurrence of the ring-opening reaction and formation of a merocyanine species.[5,6,12] Due to the large size of the molecule, it is expected that many IR bands of the consumed spiropyran (negative in the difference spectrum) will appear overlapped with those of the photoproduced merocyanine (positive in the difference spectrum), which makes more difficult the identification of the stereoisomer(s) of the latter. Nevertheless, the comparison between the experimental difference IR spectrum (positive bands) and the B3LYP/6-311+G(2d,p) computed harmonic IR spectrum of the most stable merocyanine **MC-TTC** form shows a reasonable good correspondence (Figure 4). The computed IR spectra of the others β-*trans* merocyanine stereoisomers (**MC-CTC**, **MC-CTT** and **MC-TTT**) do not reproduce so well the experimental IR data (Figure S6). In addition, the computed IR spectra of **MC-TCC** and **MC-CCC** also do not agree well with the experimental IR data (Figure S7).

These finding suggest that **MC-TTC** is the predominant or the exclusively produced merocyanine stereoisomer resulting from the UV-irradiation of the matrix-isolated **HBPS**, in consonance with the indications extracted from the computational data presented above. Note that a previous study on the UV-irradiation of the matrix-isolated 6-nitro-substituted spiropyran derivative has also suggested the sole formation of the merocyanine **MC-TTC** stereoisomer.[17] Nevertheless, for such a nitro substituted spiropyran, the reaction would involve a triplet pathway instead of occurring in the singlet manifold, as expected for the **HBPS** and other non-nitro derivatives.[5,13,14]

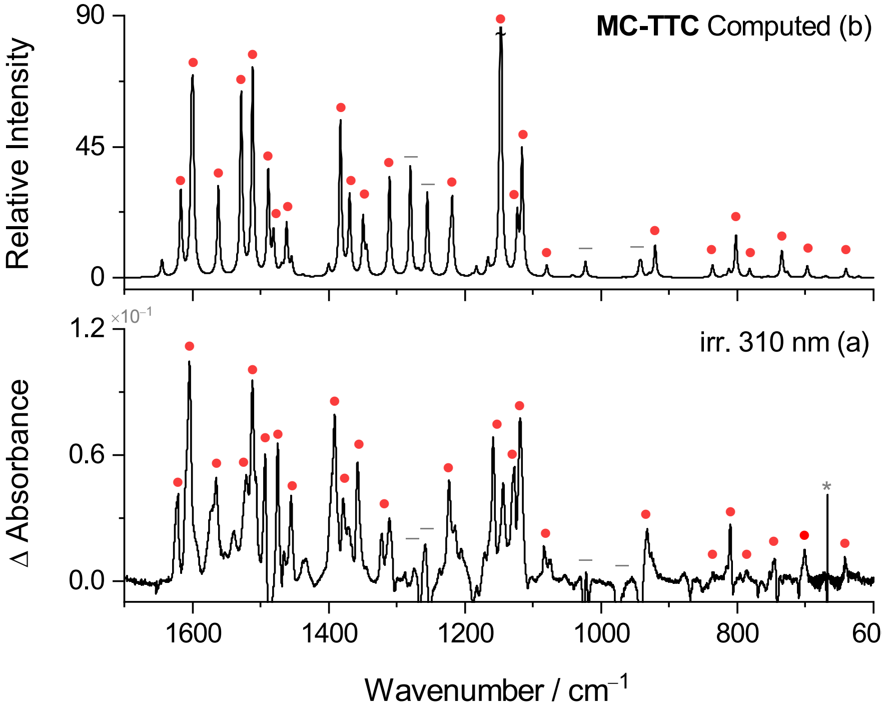


Figure 4. (a) Experimental difference IR spectrum showing changes after irradiation at 310 nm of **HBPS** isolated in a krypton matrix at 15 K. The growing IR bands are assigned to the photoproduct **MC-TTC** (closed circles). The decreasing truncated IR bands are due to **HBPS**. Horizontal bars indicate overlap of IR bands and the asterisk symbol indicates an IR band due to atmospheric CO_2. (b) B3LYP/6-311+G(2d,p) computed IR spectrum of the merocyanine **MC-TTC**.

The easily identified 2ν(OH) and ν(OH) modes of the merocyanine photoproduct are observed at 7080 and 3627 cm^{-1}, slightly red-shifted in relation to the same modes of the initial spiropyran form. For the ν(OH) mode, the observed shift is -8 cm^{-1}, which is well reproduced by computations, which estimate the ν(OH) mode of **MC-TTC** shifted by −8 cm^{-1} in relation to that of **SP-1a**. Some of the strongest experimental IR absorptions of the merocyanine appear between 1640 and 1480 cm^{-1}, a region that comprises the bands at 1621, 1604, 1565, 1521, 1512 and 1493 cm^{-1}, which have a good correspondence with the intense computed IR bands of **MC-TTC** at 1617, 1601, 1562, 1528, 1512 and 1489 cm^{-1}, respectively. Except for the computed band at 1489 cm^{-1} that corresponds mainly to a $\nu(CC)_{\text{ring-I}}$ mode, the other bands correspond to different degrees of coupling between ν(C=O), ν(C=C) and $\nu(CC)_{\text{ring-I}}$ modes. The ν(C=O) absorption has been reported at 1656 cm^{-1} for the parent *o*-quinonemethide molecule.[67] In the merocyanine **MC-TTC** planar structure, the *o*-quinonemethide unit is conjugated with an extra C=C bond and its C=O moiety involved in an intramolecular hydrogen bond with the dimethine C3 atom, which justifies a further decrease in the ν(C=O) frequency[68,69] and its coupling with the ν(C=C) and $\nu(CC)_{\text{ring-I}}$ modes. Other strong IR absorptions are observed at 1391, 1357, 1223, 1159/1144 and 1119 cm^{-1} in good agreement with intense computed IR bands of **MC-TTC** at 1383 [ν(N1−C) − ν(C2−C) + ν(C5−C6)], 1349 [ν(N1−C2), $\nu(CC)_{\text{ring-I}}$], 1219 [ν(C3C4) + ν(C−OH), ν(CC)], 1147 [δ(OH), ν(C−OH) – ν(HOC−C)] and 1116 [$\delta(CH)_{\text{ring-I}}$] cm^{-1}, respectively. A detailed comparison between the experimental growing IR band, resulting from UV-irradiation of spiropyran **HBPS**, and the computed IR spectrum of **MC-TTC** is provided in Table S2.

3.3 Bidirectional photoswitching between the merocyanine and a novel allene intermediate

The photochemistry of the merocyanine form of **HBPS**, generated in krypton matrix at 15 K, was investigated using visible-light narrowband irradiation at 550 nm (or 600 nm). This species exhibits purple-red color (i.e. the absorption maximum is expected at ~550 nm), which correlates reasonably well with the computed UV-Vis spectrum of **MC-TTC** with a λ_{max} = 523 nm (f = 0.4990) (Figure S8). Although, the performed irradiation resulted into the fade of the purple-red color, indicating the formation of a colorless species, the occurrence of ring-closure back to the spiropyran **HBPS** could be clearly exclude by analysis of the IR spectroscopy data (Figure 5a and S9b),[70] while the appearance of a characteristic IR band at ~1930 cm^{-1} doubtlessly indicates the formation of an allene moiety.[68,71] The most likely candidate was found to be the allelic species **ALN** shown in Figure 6. The B3LYP/6-311+G(2d,p) computed harmonic IR spectrum of **ALN** shows a remarkable good match with the experimental IR spectral data of the new phtotoproduced species (Figure 5 and S9).

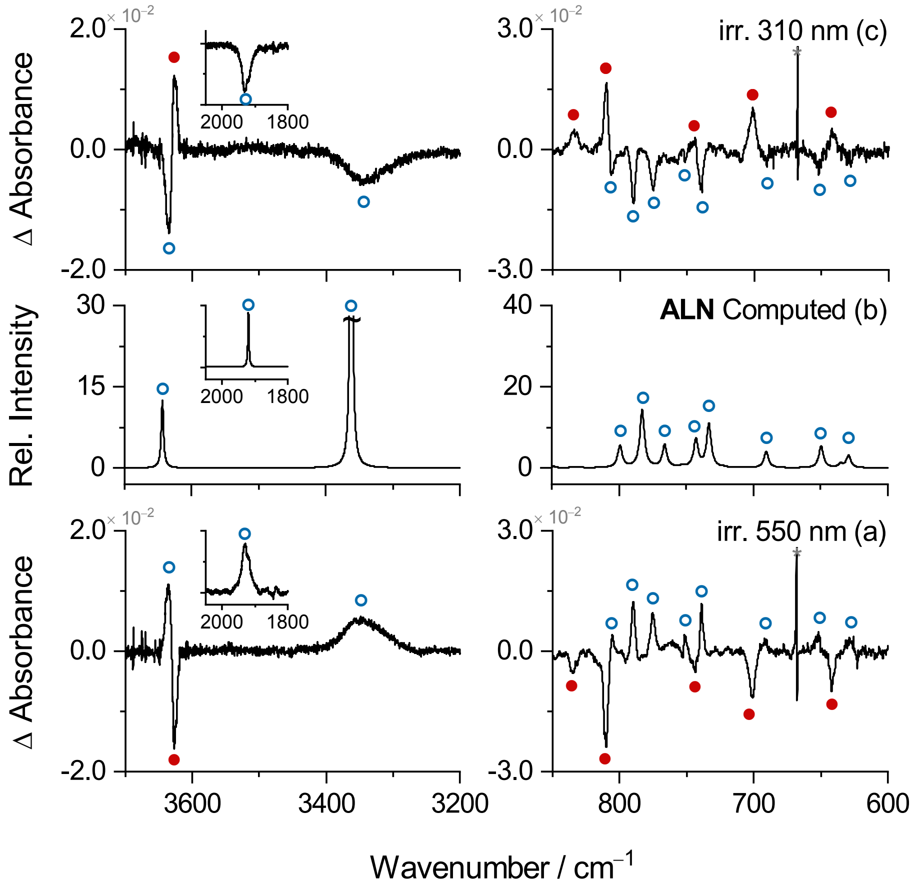
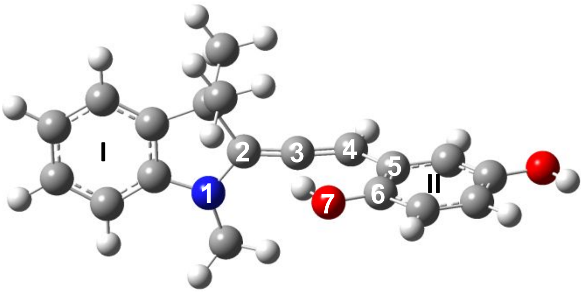


Figure 5. Selected regions of the experimental difference IR spectrum (krypton matrix at 15 K) showing changes after: (a) irradiation of the merocyanine form of **HBPS** at 550 nm; (c) subsequent irradiation at 310 nm. The positive IR bands in panel (a) and negative in panel (c) are assigned to the allenic species **ALN** (open circles). The negative IR bands in panel (a) and positive in panel (c) are due to **MC-TTC** (closed circles). The asterisk symbol indicates an IR band due to atmospheric CO_2. (b) B3LYP/6-311+G(2d,p) computed IR spectrum of **ALN**.

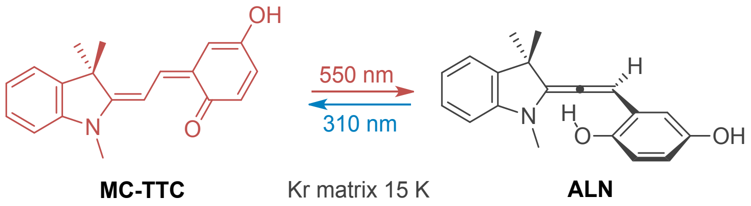


ALN: $\tau_{a\,(1\text{-}2\text{-}3\text{-}4)} = 121.1^{\circ}$; $\tau_{b\,(4\text{-}5\text{-}6\text{-}7)} = 0.0^{\circ}$

Figure 6. ωB97X-D/6-311+G(2d,p) optimized geometry of the allenic derivative **ALN**. **I** = indoline phenyl ring; **II** = diol phenyl ring. Color code: light gray – H atom; gray – C atom; blue – N atom, red – O atom.

In addition to the mentioned characteristic allenic IR band readily assigned to the ν(C=C=C)$_{as}$ mode (computed at 1920 cm^{-1}), some other characteristic bands also identify the **ALN** species. Very distinctive is the broad IR band observed at 3348 cm^{-1}, which correlates well with the characteristic computed IR band of **ALN** at 3362 cm^{-1}, ascribable to the stretching vibration of the newly formed OH group. This "new" OH moiety in the **ALN** species results from the [1,5]-H shift from C3 to C=O in the merocyanine **MC-TTC** (Figure 3). In the **ALN** structure, this OH group is forming an intramolecular hydrogen bond with the allenic fragment [r(O7H···C3) = 1.99 Å, at the ωB97X-D level], which is the reason for its significant low-frequency stretching vibration. The absorption observed at 3636 cm^{-1} is easily assigned to the "inherited" ν(OH) mode of **ALN**, which appears blue-shifted by +9 cm^{-1} in relation to the same mode of the merocyanine **MC-TTC**, in agreement with the computations that estimate a blue-shift of +9 cm^{-1}. The 1650−1100 cm^{-1} region is mostly dominated by intense IR bands of the merocyanine **MC-TTC**, which obscure the less intense IR bands of **ALN**. Some of the exceptions are the bands appearing at 1485 and ~1280 cm^{-1}, which are in good agreement with the most intense computed IR bands of **ALN** at 1484 [δ(CH_3)$_{as}$, ν(CC)$_{\text{rings-I-II}}$] and 1274 [ν(C−OH) + ν(C4−C5), ν(N1−C2)] cm^{-1}. Also worth mention is the observed band at 1410 cm^{-1}, which matches well the computed band of **ALN** at 1411 cm^{-1}, corresponding mainly to the ν(C=C=C)$_s$ mode. The 810−600 cm^{-1} region is particularly free of band-overlappings, which offer a clear signature that characterize well the **ALN** species. The most intense IR bands in this region are those observed at 790, 775, 739 and 652 cm^{-1}, which correlated well with the computed bands of **ALN** at 783 [δ(C4C5C), δ(CC)$_{\text{rings-I-II}}$], 766 [δ(CCC2), δ(CC)$_{\text{ring-I}}$], 733 [γ(CH)$_{\text{ring-I}}$], and 650 [δ(C3C4C5), δ(CC)$_{\text{rings-I-II}}$] cm^{-1}. A detailed comparison between the experimental IR bands growing due to the visible-light irradiation of merocyanine **MC-TTC** and the computed IR spectrum of **ALN** is provided in Table S3.

The computed UV-Vis spectrum of **ALN** indicates this species to be colorless, with λ_{max} = 375 (f = 0.0005) and 321 nm (f = 0.1581) (Figure S8), in agreement with the experimental observations. Interestingly, subsequent UV-irradiations (310 nm) were found to induce the conversion of **ALN** back to the purple-red merocyanine **MC-TTC**. The resulting difference IR spectrum nicely mirrors the inverse difference IR spectrum corresponding to the **MC-TTC** → **ALN** transformation previously induced by visible-light irradiation (550 or 600 nm) (Figures 5c and 5a). The IR bands previously assigned to the formation of **ALN** are now consumed, whereas those previously evidencing the consumption of **MC-TTC** are now growing, indicating now the occurrence of the **ALN** → **MC-TTC** transformation. A subsequent cycle of irradiations (550 and 310 nm) confirms the bidirectional photoswitching between the colored merocyanine **MC-TTC** and the colorless allene **ALN** in a clean fashion (Scheme 2).[72]



Scheme 2. Summary of the experimental observation of bidirectional photoswitching (or photochromism) between merocyanine **MC-TTC** and allene **ALN** in a krypton matrix at 15 K.

The allenic **ALN** structure shown in Figure 6 is the most stable conformer of this species, with the "new" and the "inherited" OH groups adopting respectively *syn* and *anti* orientation in relation to the C4 allenic fragment. The conformer with the "inherited" OH adopting the *syn* orientation is more energetic by ~0.5 kJ mol^{-1}, whereas the conformer with the "new" OH adopting the *anti* orientation is more energetic by ~23 kJ mol^{-1}, due to the disruption of the intramolecular hydrogen bond with the allenic moiety (Table S5). In both cases, the OH-rotamerization barrier to the most stable conformer is only ~7 kJ mol^{-1}, which makes inaccessible the capture of these higher-energy conformers under noble-gas matrices conditions due to tunneling to the lowest energy form, in a similar way as described for the high-energy OH conformers of spiropyran forms in Section 3.1.

To the best of our knowledge, the experimental observation of an allenic species involved in the chemistry of spiropyrans is unprecedented. The only previous reference to an allene-type intermediate on the photoreactivity of this kind of compounds was the suggestion made in the theoretical study of Minkin and co-workers about the possible existence of an allenic species as an intermediate in the equilibrium between the merocyanine stereoisomers **MC-TTC** and **MC-CTC** of 1′,3′,3′-trimethyl-1,2-tetramethylenespiro-[7*H*-furo(3,2-*f*)-(2*H*-1)-benzopyran-7,2′-indolines].[51] An allenic-type intermediate was also detected in the photochromic reaction of the 2,2-di(4-fluorophenyl)-6-methoxy-2*H*-1-chromene using NMR and low-temperature (−45 ºC) solutions.[73,74] This compound shares common structural features with spiropyrans, in particular a chromene moiety bearing substituents in the α-carbon to the heterocyclic ring oxygen atom.

Our ωB97X-D computations for the **HBPS** derivative indicate the **ALN** species to be ~25 kJ mol^{-1} more energetic than the most stable merocyanine **MC-TTC** form. On the ground-state PES, **ALN** was predicted to interconvert with **MC-TTC** via 1,5-H shift (along the intramolecular hydrogen bond) through a barrier of ~53 kJ mol^{-1} (relative to **ALN**) or ~78 kJ mol^{-1} (relative to **MC-TTC**). The alternative possible ground state conversion of **ALN** to **MC-CTC** can occur by a similar mechanism, but through a slightly more energetic barrier of ~54 kJ mol^{-1}. Although computations on the excited state are beyond the scope of our work, a more favorable process for the interconversion between **ALN** and **MC-TTC**, compared to between **ALN** and **MC-CTC**, seems also to characterize the relevant excited-state PES, since the experimental data obtained in cryogenic matrices indicate the sole photo-induced interconversion between **ALN** and **MC-TTC**.

Following our recent advances in triggering bond-breaking/bond-forming reactions by IR vibrational excitation (ground-state chemistry),[61,75,76] we investigated also the possibility to transform **ALN** into the merocyanine by irradiating the matrix-isolated **ALN** species with near-IR light tuned at the frequencies of its 2ν(OH) modes, at 7079 cm^{-1} and at 6550/6500/6450 cm^{-1} (Figure S10). Nevertheless, no changes in the sample were observed upon monitoring the effect of those irradiation by IR spectroscopy. It is conceivable that the energy deposited in the **ALN** excited vibrational modes likely ends up in the low-energy OH torsional coordinates associated with the rotamerization of these groups, instead of being channeled into the much more energetic 1,5-H shift reaction coordinate (leading either to **MC-TTC** or **MC-CTC**). In this scenario, a high-energy OH conformer of **ALN** would be produced, following the vibrational excitation, which, as mentioned before, should decay very fast by H-tunneling back to the most stable **ALN** form, justifying the non-observation of any spectral changes during the experiments performed using steady-state spectroscopy.

4. CONCLUSION

In conclusion, we have presented here new insights to better understand the photochromism of spiropyrans, in particular for the case of 6-hydroxy-spiropyran, **HBPS**, and the nature of the species involved. DFT computations demonstrated that the **HBPS** chromene unit can adopt a bent-up and bent-down orientation regarding its perpendicular alignment relative to the indoline unit, and that nitrogen atom inversion is in fact a structurally relevant degree of freedom in spite of being frequently not included in the structural analysis of this type of compounds. The analysis of the IR spectrum of the matrix-isolated **HBPS**, carried out with the support of the B3LYP/6-311+G(2d,p) computations, suggests that only the most stable stereoisomer (**SP-1a** most likely) exists after the vapor of the compound being quenched with large excess of krypton at 15 K.

The UV-irradiation of the colorless spiropyran **HBPS** was found to generate the corresponding merocyanine, which exhibits a characteristic purple-red color. Computations on the merocyanine form of **HBPS** show the existence of several possible stereoisomers with distinct dihedral angles in the dimethine bridge. The comparison of the corresponding calculated IR spectra with the experimental data indicates the main or exclusive formation of the most stable merocyanine **MC-TTC** stereoisomer, after UV-irradiation of the studied spiropyran. The formation of a first **MC-CCC** or **MC-TCC** intermediate, upon C_{spiro}–O bond cleavage of a spiropyran, has been predicted theoretically and speculated in some experimental studies.[5,50,51] No evidence of these stereoisomers were found in our cryogenic matrix UV-irradiation experiments on **HBPS**, and hints for the sole observation of **MC-TTC** were obtained based on ground-state PES computations.

Noteworthy, we discovered that visible-light irradiation of matrix-isolated **MC-TTC** generates a new allenic **ALN** species. The IR spectral signature of such new photoproduct allowed the unequivocal identification of the most stable conformer of **ALN**, which is structurally characterized by having an OH intramolecular hydrogen bond involving the allenic fragment. Remarkably, the UV-irradiation of **ALN** converts this species back to **MC-TTC**. The bidirectional photoswitching between the colored merocyanine **MC-TTC** and the colorless allene **ALN** occurs in a clean and repeatable fashion. Such photoswitching reaction might be generally feasible in the chemistry of spiropyrans, since it occurs along an intramolecular hydrogen bond existing in both involved species. Although it has been generally assumed that open merocyanines photochemically revert to the close-ring spiropyrans, this work disproves such view, highlighting the key role that the allenic species can have in the photochemistry of this type of chemical systems. Whether the photoswitching (or photochromism) between a merocyanine and an intermediate allene species, demonstrated here experimentally for the first time, constitutes a limitation or an opportunity to develop suitable spiropyran-based light-controlled systems is a matter that is now open to investigation.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: xxx.xxx.xxx. Detailed vibrational analysis and assignments, additional experimental data and computational results (PDF).

AUTHOR INFORMATION

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Author Contributions

C.M.N. conceived the original working hypothesis, performed the computations, analyzed the data and wrote the first draft of the manuscript. C.M.N. and N.A.M.P. performed the experiments. R.F. analyzed the data and wrote the final draft of the manuscript. All authors discussed and co-wrote the final version of the article.

Notes

The authors declare no competing interests.

ACKNOWLEDGMENTS

This work was supported by Projects POCI-01-0145-FEDER-028973 funded by FEDER, via Portugal 2020-POCI, and by National Funds via the Portuguese Foundation for Science and Technology (FCT). The Coimbra Chemistry Centre – Institute of Molecular Sciences (CQC-IMS) is supported by FCT through projects UIDB/00313/2020 and UIDP/00313/2020 co-funded by COMPETE and the IMS special complementary funds provided by FCT. C.M.N. acknowledges FCT for an Auxiliary Researcher grant. N.A.M.P. acknowledges the Project POCI-01-0145-FEDER-028973 for a Junior Researcher grant. The authors acknowledge the Laboratory for Advanced Computing at University of Coimbra (UC-LCA) for providing computing resources that have contributed to the research results reported within this paper, and LaserLab Coimbra for experimental facilities.

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structure was only considered in the work reported in the ref. 17.

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Supporting Information

Photochromism of a Spiropyran in Low-Temperature Matrices. Unprecedented Bidirectional Switching Between a Merocyanine and an Allene Intermediate

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1. Figures

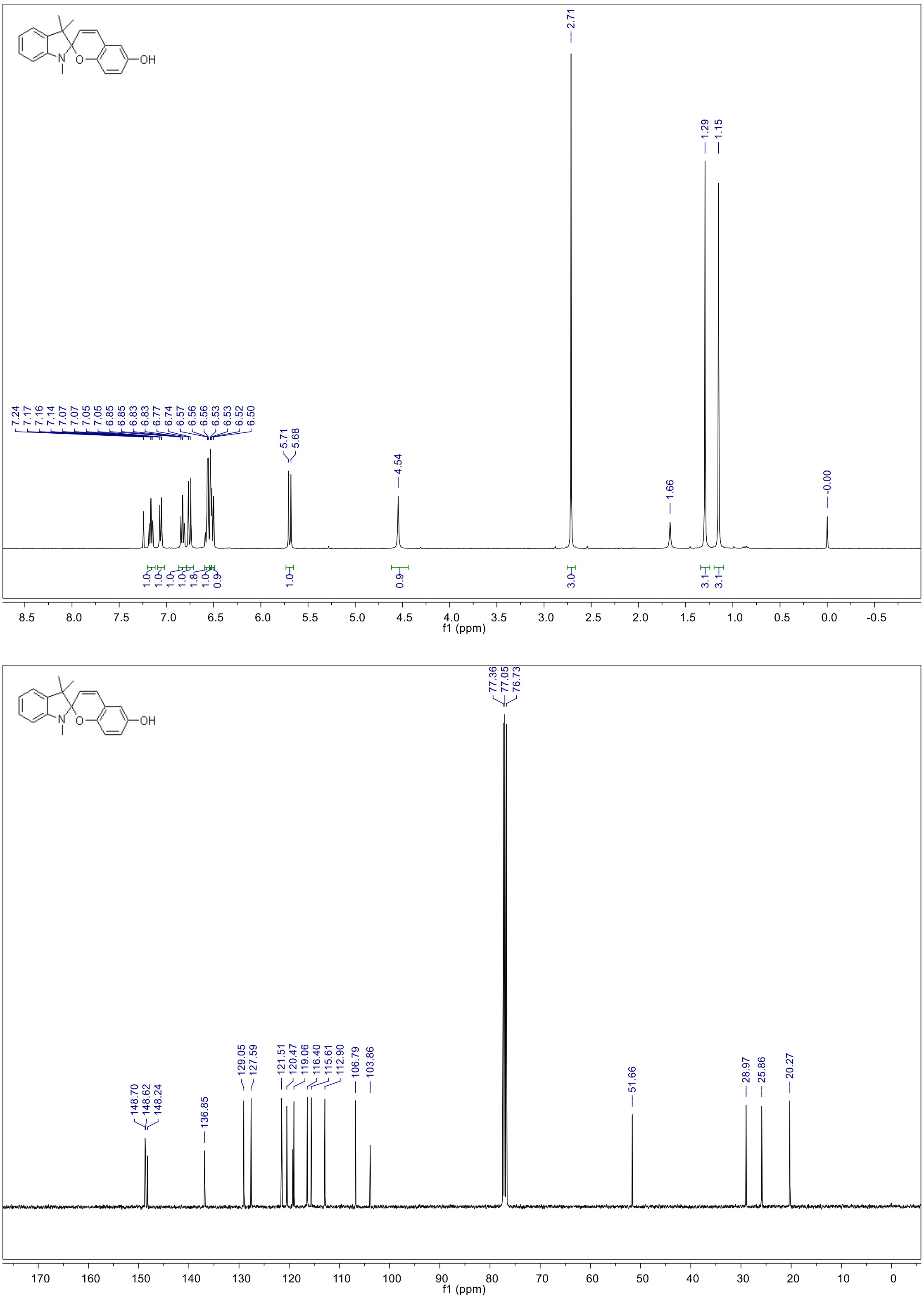


Figure S1. ^{1}H (top) and ^{13}C (down) NMR spectra of 1',3',3'-trimethyl-6-hydroxyspiro[2*H*-1-benzopyran-2,2'-indoline] (**HBPS**) in $CDCl_3$.

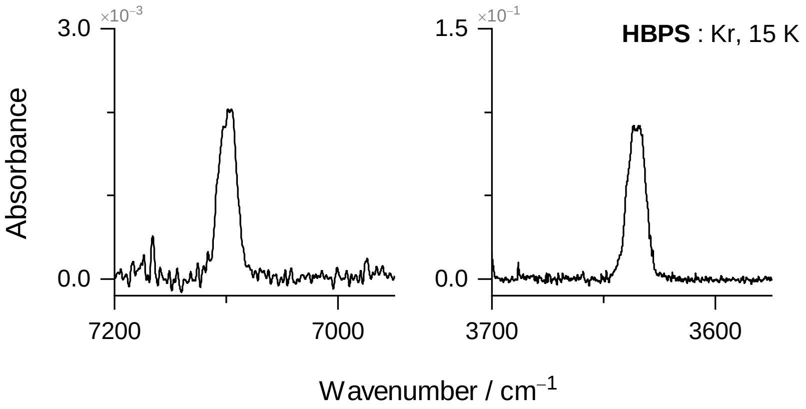


Figure S2. Selected regions of the experimental near-IR (left) and mid-IR (right) spectrum of **HBPS** in a krypton matrix at 15 K. The IR bands correspond to the 2ν(OH) (left) and ν(OH) (right) modes.

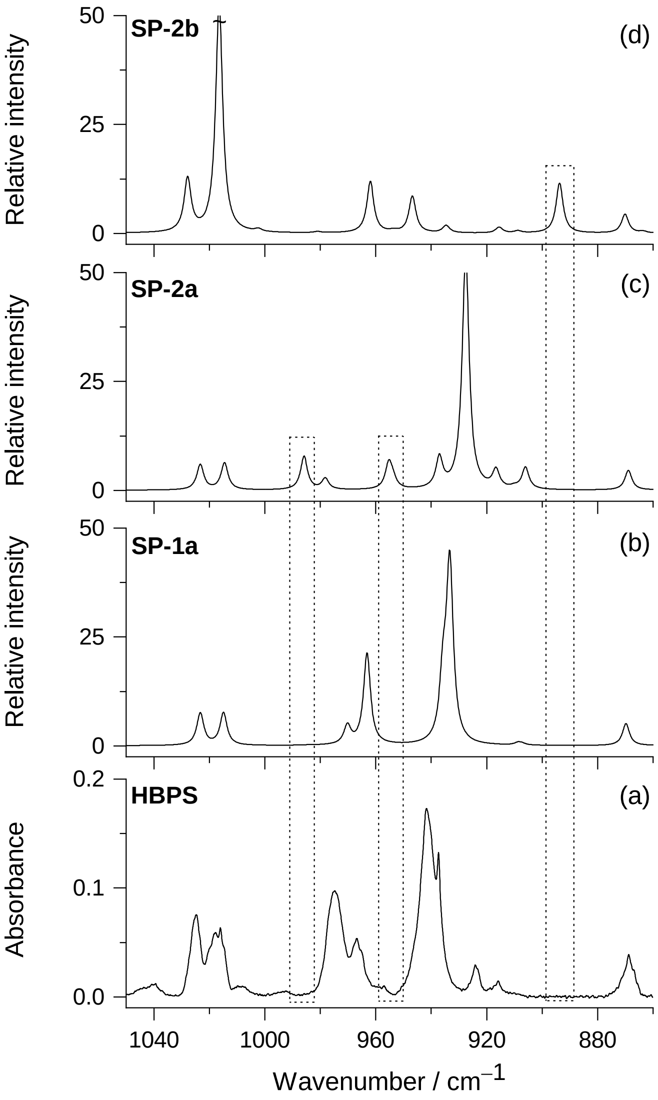


Figure S3. (a) Selected region of the experimental IR spectrum of **HBPS** in a krypton matrix at 15 K. B3LYP/6-311+G(2d,p) computed IR spectrum of the spiropyran forms: (b) **SP-1a**; (c) **SP-2a**; (d) **SP-2b**. The dotted rectangles are centred at selected IR bands of **SP-2a** or **SP-2b** that do not have a good correspondence with the experimental IR spectrum.

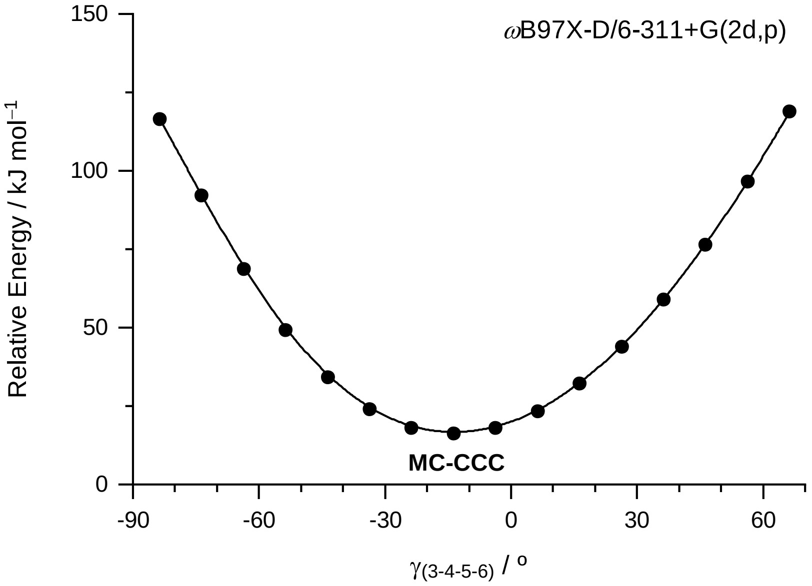


Figure S4. ωB97X-D/6-311+G(2d,p) relaxed potential energy scan as a function of the dihedral angle $\gamma_{(3\text{-}4\text{-}5\text{-}6)}$ for the merocyanine **MC-CCC** form of **HBPS.** The γ dihedral angle was incrementally fixed with a step of 10° and the remaining parameters were optimized. Calculated energies (kJ mol^{-1}) are relative to the merocyanine **MC-TTC** form.

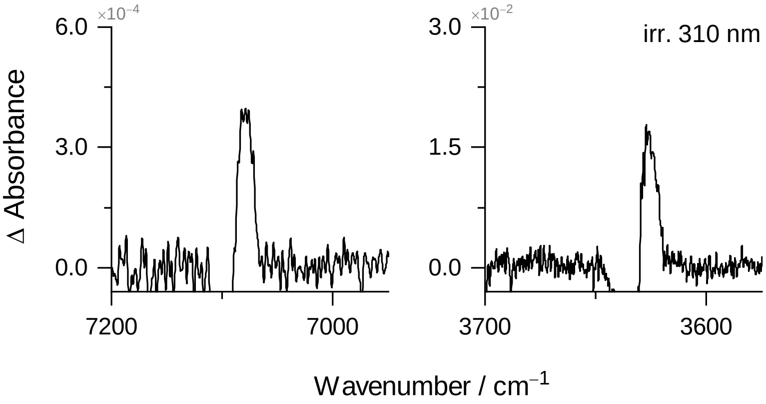


Figure S5. Selected regions of the experimental difference near-IR (left) and mid-IR (right) spectrum showing changes after irradiation at 310 nm of **HBPS** isolated in a krypton matrix at 15 K. The growing IR bands are assigned to the 2ν(OH) (left) and ν(OH) modes of the merocyanine photoproduct **MC-TTC**. The decreasing truncated IR bands are due to **HBPS**.

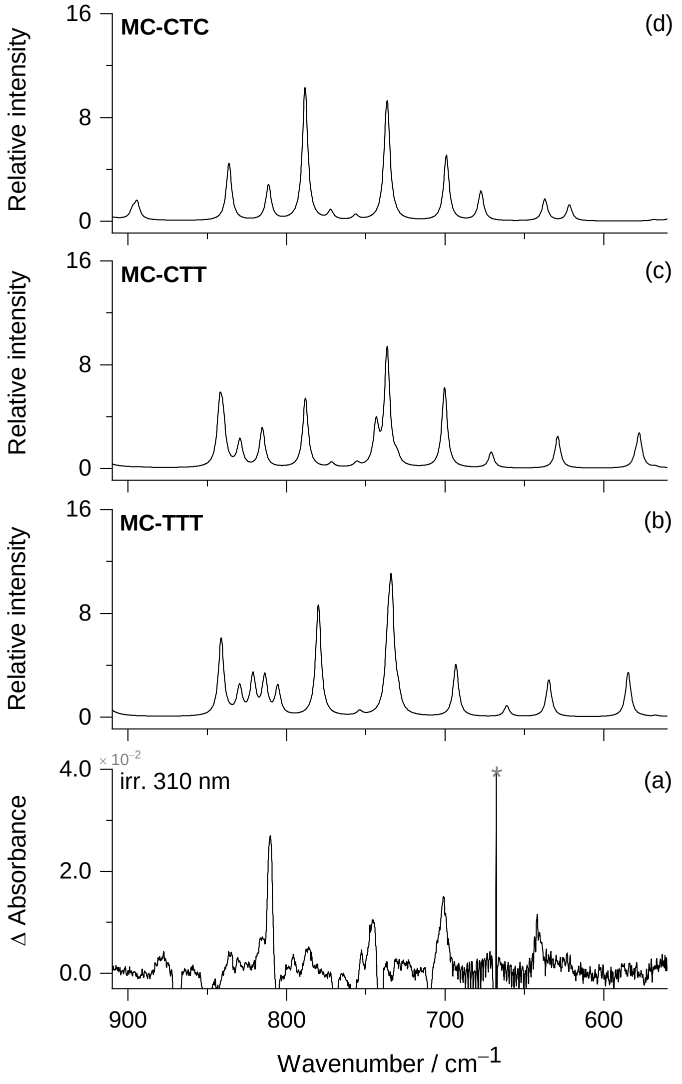


Figure S6. (a) Selected region of the experimental difference IR spectrum showing changes after irradiation at 310 nm of **HBPS** isolated in a krypton matrix at 15 K. Asterisk symbol indicates an IR band due to atmospheric CO_2. B3LYP/6-311+G(2d,p) computed IR spectrum of the merocyanine forms: (b) **MC-TTT**; (c) **MC-CTT**; (d) **MC-CTC**.

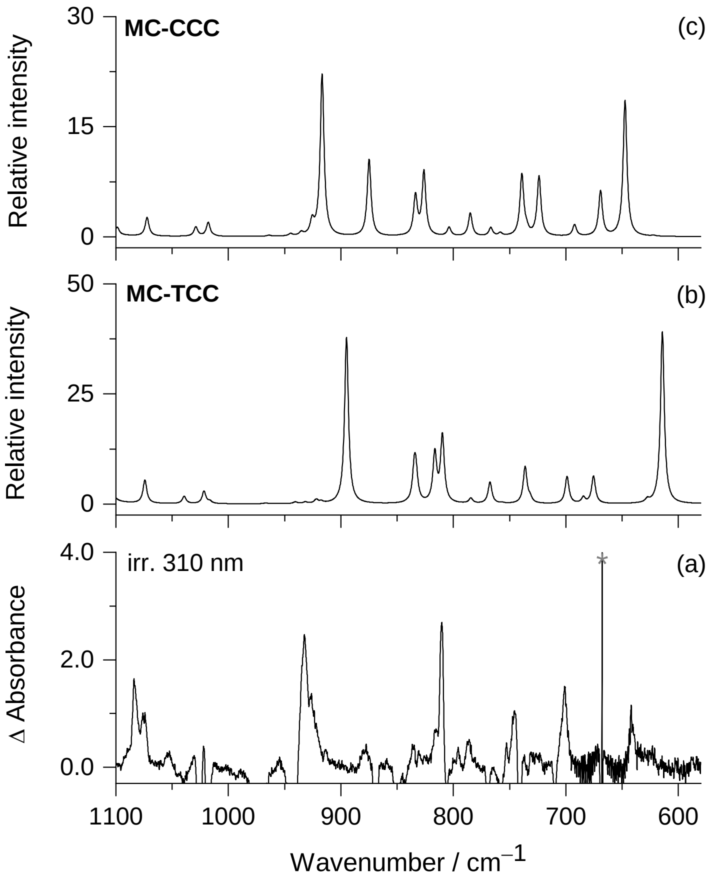


Figure S7. (a) Selected region of the experimental difference IR spectrum showing changes after irradiation at 310 nm of **HBPS** isolated in a krypton matrix at 15 K. Asterisk symbol indicates an IR band due to atmospheric CO_2. B3LYP/6-311+G(2d,p) computed IR spectrum of the merocyanine forms: (b) **MC-TCC**; (c) **MC-CCC**.

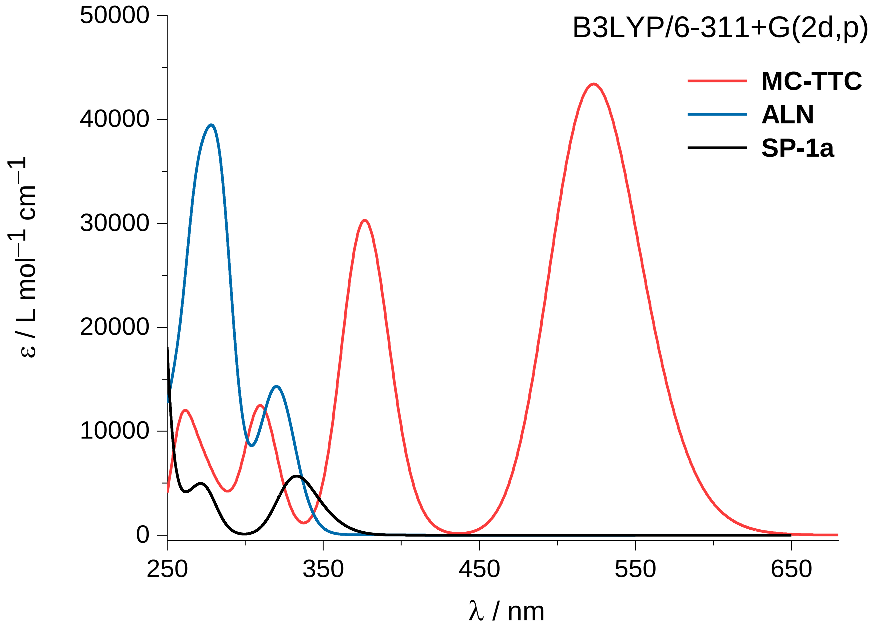


Figure S8. B3LYP/6-311+G(2d,p) computed UV-Vis spectra of merocyanine **MC-TTC** (red), allene **ALN** (blue), and spiropyran **SP-1a** (black), considering the fifteen lowest singlet and triplet excited states (details are given in Experimental Methods Section). The calculated vertical transition wavelengths and oscillator strengths are given in Table S4.

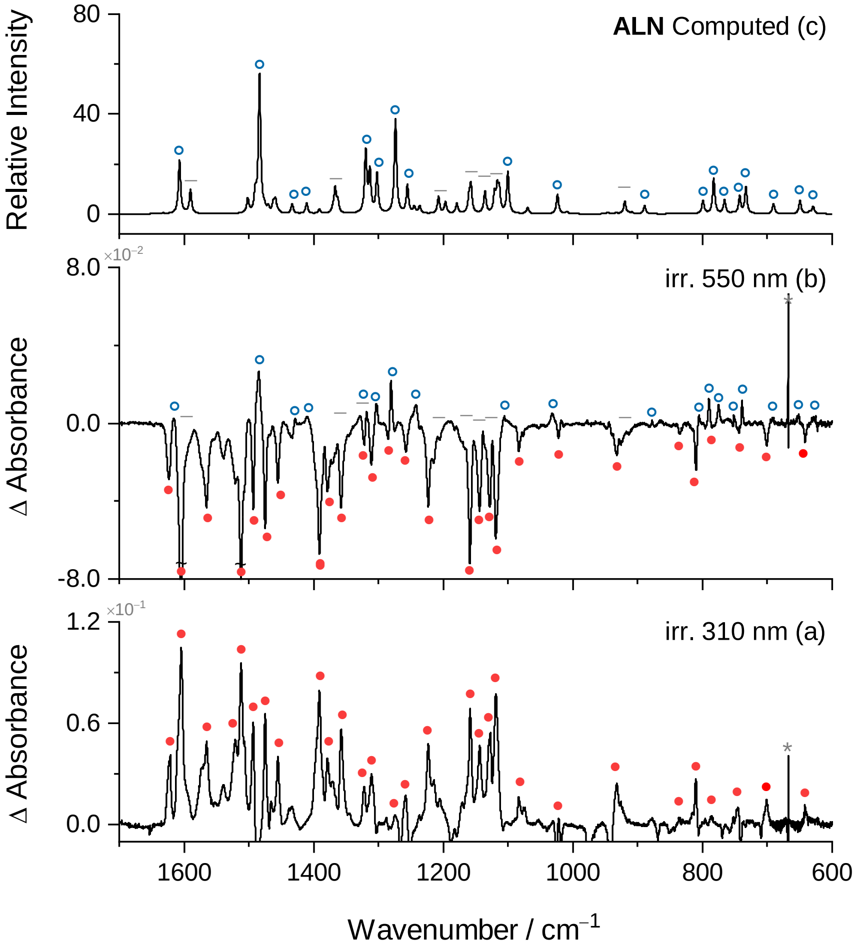


Figure S9. Experimental difference IR spectrum (krypton matrix at 15 K) showing: (a) the production merocyanine **MC-TTC**, after irradiation of spiropyran **HBPS** at 310 nm (negative bands truncated); (b) the consumption of merocyanine **MC-TTC** (closed circles) and production of an allene species **ALN** (open circles), after irradiation at 550 nm. Horizontal bars indicate overlap of IR bands and the asterisk symbol indicates an IR band due to atmospheric CO_2. (c) B3LYP/6-311+G(2d,p) computed IR spectrum of **ALN**.

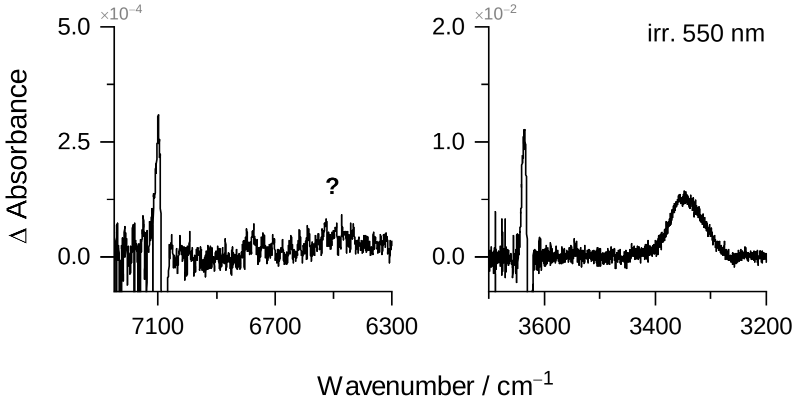
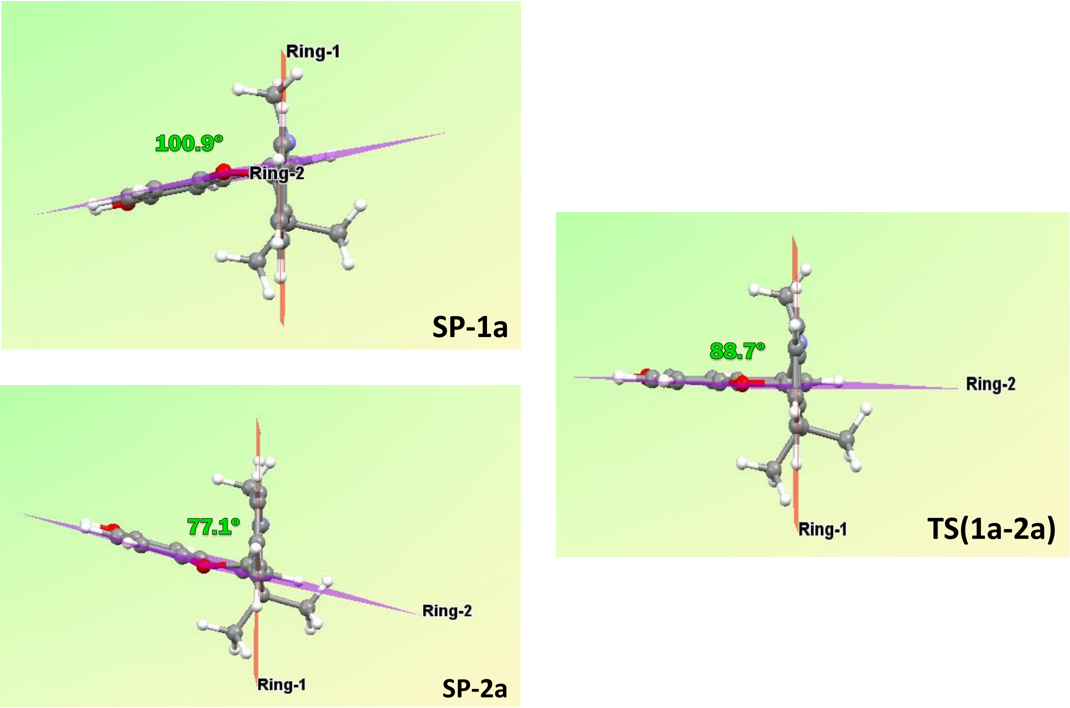
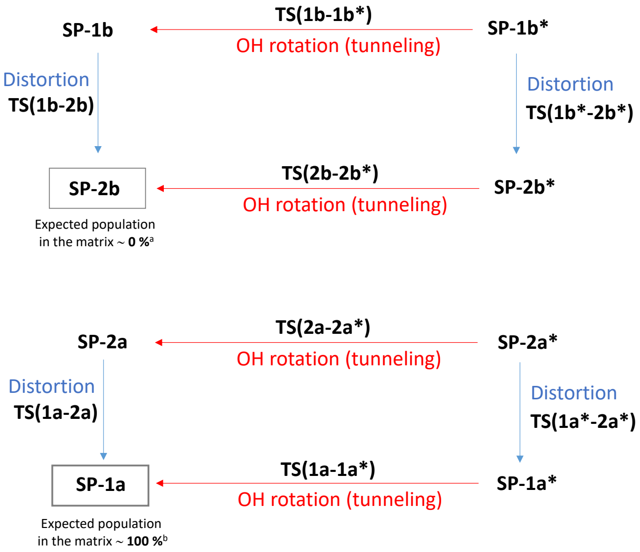


Figure S10. Selected regions of the experimental difference near-IR (left) and mid-IR (right) spectrum showing changes after irradiation at 550 nm of merocyanine **HBPS** in a krypton matrix at 15 K. The growing IR bands are assigned to the 2ν(OH) (left) and ν(OH) modes of the allene photoproduct **ALN**. The decreasing truncated IR bands are due to the merocyanine stereoisomer **MC-TTC**.

2. Schemes



Scheme S1. Visualization of the **HBPS** stereoisomers with the chromene unit adopting a bent-up [100.9º; **SP-1a**] and bent-down [77.1º; **SP-2a**] orientation regarding the perpendicular alignment relative to the indoline unit [88.7º; **TS(1a-2a)**]. The angles provided are those between the mean-planes of the indoline and chromene rings.



Scheme S2. Illustration of the processes of conversion between stereoisomers of the spiropyran form of **HBPS**, leading to the expected existence of only the most stable **SP-1a** stereoisomer in the cryogenic matrices. [a] Population sum of **SP-1b**, **SP-2b**, **SP-1b*** and **SP-2b***. [b] Population sum of **SP-1a**, **SP-2a**, **SP-1a*** and **SP-2a***.

3. Tables

Table S1. Experimental IR spectral data (krypton matrix at 15 K), and B3LYP/6-311+G(2d,p) calculated harmonic vibrational frequencies (ν, cm^{-1}) and absolute infrared intensities (Ath, km mol^{-1}) of spiropyran **HBPS**.

Kr matrix[a]		Calculated[b]		Kr matrix[a]		Calculated[b]	
ν	I	ν	Ath	ν	I	ν	Ath
7097	vw	–		1147	m	1143	39.4
3635	s	3643	77.2	1141	w	1133	7.2
1652	w	1660	22.8	1125	w	1120	27.9
1629	w	1625	3.9	1118	w	1117	3.7
1614	m	1607	70.0			1114	7.3
–		1597	0.8	1109	w	–	
1587	m	1581	46.9	1098	w	1095	52.3
1487	s	1486	49.6	1069	vw	1064	4.9
		1485	114.5	1039	w	–	
		1482	2.1	1025	m	1022	35.0
		1479	166.9	1018/1016	m/m	1014	35.2
1469	m	1473	8.9	–		983	0.4
–		1469	2.4	975	m	969	20.1
–		1463	8.8	967	w	962	99.2
–		1460	2.8	–		953	0.2
1458	w	1460	11.2	942	s	935	62.6
1450	w	1457	30.6	937	m	932	194.2
1421	vw	1428	10.1	–		916	0.1
1393	vw	1393	8.8	924/916	w/vw	908	2.5
–		1390	7.9	–		906	1.7
1382	vw	1369	8.2	869	w	869	23.8
1361	m	1353	44.8	850	w	841	10.3
1321	w	1323	53.7	845	w	836	19.5
1303	m	1301	78.4	819	vw	819	57.9
1295	sh	1292	37.9	806	w	800	20.1
1282	m	1274	154.6	792	vw	783	13.0
1272	vw	1264	4.2	770	w	766	14.1
1266	m	1255	32.0	758	w	759	4.8
1254	m	1245	144.4	–		748	3.3
1231	vw	1224	19.2	742	s	734	59.8
1188	br	1188	6.2	735	w	730	12.9
		1176	54.2	710	w	711	9.2
1180	m	1172	105.0	–		646	0.1
1168	m	1158	6.2	634	vw	631	1.4
1160	m	1153	29.2				

[a] Experimental intensities are presented in qualitative terms: s = strong, m = medium, w = weak, vw = very weak, br = broad, and ov = overlapped. The spectral range in 1700−600 cm^{-1} region plus the ν(OH) and 2ν(OH) bands are reported. [b] B3LYP/6-311+G(2d,p) computed data for the spiropyran **SP-1a** stereoisomer with frequencies scaled by a factor of 0.979 [ν(O-H) frequency scaled by 0.950].

Table S2. Experimental IR spectral data (krypton matrix at 15 K), and B3LYP/6-311+G(2d,p) calculated harmonic vibrational frequencies (ν, cm^{-1}) and absolute infrared intensities (Ath, km mol^{-1}) of merocyanine **HBPS**.

Kr matrix[a]		Calculated[b]		Kr matrix[a]		Calculated[b]	
ν	I	ν	Ath	ν	I	ν	Ath
7080	vw	–		1171	w	1166	35.7
3627	m	3635	67.6			1161	7.1
–		1645	36.7	1159/1144	s/m	1147	691.3
1621	m	1617	180.8	–		1128	2.8
1604	s	1601	268.8	1127	m	1123	125.2
–		1599	310.6	1119	s	1116	266.7
1565	m	1562	193.2	–		1112	9.5
1539	w	–		1084/1074	w/w	1080	24.9
1521	m	1528	393.6	–		1042	5.7
1512	s	1512	447.3	1022	ov	1023	35.4
1493	m	1489	224.0	–		1015	0.5
1474	m	1481	87.9	–		967	0.6
		1473	3.4	–		958	0.1
1466	w	1469	17.7	–	ov	943	27.3
1455	m	1462	112.1	–	ov	941	23.5
		1456	0.2	–	ov	929	6.8
		1454	12.7	932	m	921	69.0
		1453	23.5	–		917	0.6
1433	w	1438	5.1	–		902	1.7
–		1400	24.3	–		838	0.2
1391	s	1383	334.4	836	vw	836	27.2
1378/1372	m/w	1374	6.6	–		820	3.0
		1369	172.0	816	sh	813	15.8
1357	m	1349	124.9	810	m	802	91.3
1345	vw	1344	52.0	786	vw	782	18.0
1321/1310	m/w	1311	215.4	–		755	2.5
1274	ov	1280	236.8	746	w	735	55.8
–		1268	9.6	–	ov	733	4.9
1258	ov	1255	181.1	–		726	9.3
1223	m	1222	62.0	701	w	697	25.5
1214	w	1219	159.8	–		670	4.2
–		1189	4.4	642	w	640	18.9
1183	vw	1183	20.0	–		622	3.0

[a] The merocyanine **HBPS** was generated by UV-irradiation (λ = 310 nm) of spiropyran **HBPS** isolated in a krypton matrix at 15 K. Experimental intensities are presented in qualitative terms: s = strong, m = medium, w = weak, vw = very weak, br = broad, and ov = overlapped. The spectral range in 1700−600 cm^{-1} region plus the ν(OH) and 2ν(OH) bands are reported. [b] B3LYP/6-311+G(2d,p) computed data for merocyanine **MC-TTC** stereoisomer with frequencies scaled by a factor of 0.979 [ν(O-H) frequency scaled by 0.950].

Table S3. Experimental IR spectral data (krypton matrix at 15 K), and B3LYP/6-311+G(2d,p) calculated harmonic vibrational frequencies (ν, cm^{-1}) and absolute infrared intensities (A^{th}, km mol^{-1}) of the allenic species **ALN**.

Kr matrix[a]		Calculated[b]		Kr matrix[a]		Calculated[b]	
ν	I	ν	A^{th}	ν	I	ν	A^{th}
7079	vw	–		1180 (?)	ov	1179	24.8
3636	m	3644	78.2	–	ov	1160	36.9
3348	br	3362	525.0	–	ov	1157	66.9
1930	m	1920	333.0	–		1140	1.8
–		1632	1.9	1139 (?)	ov	1136	54.8
1616 (?)	ov	1607	135.5	–	m	1121	47.2
–		1598	2.7	–	ov	1117	59.0
–	ov	1590	58.9	–	ov	1114	54.0
1499 (?)	ov	1502	35.6	1106	ov	1100	104.5
1485	s	1490	45.9	–		1070	15.3
		1484	346.9	1032	ov	1024	49.7
–		1477	1.5	–		1012	1.7
–		1476	9.2	–		1009	3.9
–		1470	13.7	–		953	0.0
1463 (?)	ov	1462	23.5	–		946	4.2
		1459	32.2	–		933	2.7
–		1455	1.7	940	ov	920	31.5
–		1454	3.0	–		913	2.1
1430	w	1433	23.4	–		909	3.4
1410	w	1411	26.4	878	vw	889	20.1
–		1391	11.1	–		849	2.2
–	m	1370	9.2	–		835	0.8
–		1367	61.5	–		830	1.6
–		1363	29.5	806	ov	799	33.4
1327/1318 (?)	ov	1320	154.9	790	m	783	88.6
		1313	103.1	775	w	766	34.8
1302	m	1302	98.3	–		753	2.4
1280 (?)	ov	1274	236.7	751	ov	743	43.4
1242 (?)	ov	1255	70.6	739	m	733	66.7
–		1245	16.5	–		722	0.9
–		1236	18.6	690	vw	690	25.1
–	ov	1207	42.3	652	w	650	33.7
–	ov	1207	42.3	630	vw	635	5.6
–	ov	1197	29.8			629	18.7

[a] The allenic species **ALN** was generated by visible-light irradiation (λ = 550 nm) of merocyanine **MC-TTC** in a krypton matrix at 15 K. Experimental intensities are presented in qualitative terms: s = strong, m = medium, w = weak, vw = very weak, br = broad, and ov = overlapped. The question mark symbol (?) indicates that the band frequency is uncertain due to overlap. The spectral range in 2000−600 cm^{-1} region plus the ν(OH) and 2ν(OH) bands are reported. [b] B3LYP/6-311+G(2d,p) computed data for **ALN** with frequencies scaled by a factor of 0.979 [ν(O-H) frequency scaled by 0.950].

Table S4. Wavelengths (WL, nm) and oscillator strengths (*f*) of the low-energy electronic excited singlet states computed at the B3LYP/6-311+G(2d,p) level using the time-dependent density functional theory (TD-DFT) for the most relevant species identified in this work.

MC-TTC		**ALN**		**SP-1a**	
WL	*f*	WL	*f*	WL	*f*
523.28	0.4989	375.52	0.0005	349.83	0.0147
471.01	0.0000	320.86	0.1581	331.36	0.0601
376.62	0.3474	302.34	0.0289	273.64	0.0491
353.11	0.0034	283.39	0.3581	264.69	0.0045
310.09	0.1399	278.99	0.0028	263.92	0.0043
301.13	0.0028	268.79	0.3085	259.09	0.0056
295.04	0.0018	264.39	0.0029	257.57	0.0131
286.77	0.0209	262.54	0.0020	254.92	0.0065
280.92	0.0073	261.72	0.0002	252.26	0.0003
280.08	0.0003	254.96	0.1222	248.83	0.0025
272.68	0.0575	249.73	0.0026	245.04	0.0014
266.68	0.0052	248.53	0.0041	241.67	0.2835
259.69	0.1055	247.65	0.0003	239.86	0.1752
257.79	0.0138	245.73	0.0224	238.39	0.0901
255.57	0.0000	238.98	0.0799	236.00	0.0049

Table S5. Relative Zero-point Corrected Energies (ΔE_0) Computed at the ωB97X-D/6-311+G(2d,p) and B3LYP/6-311+G(2d,p) Levels of Theory for the Different Conformers of Allene **ALN** and the Corresponding Relevant Transitions States.[a]

Structure[b]		ωB97X-D/6-311+G(2d,p)	B3LYP/6-311+G(2d,p)
OH$_{\text{“new”}}$	OH$_{\text{“inherited”}}$	ΔE_0	ΔE_0
syn	***anti***	0.0	0.0
syn	***syn***	0.5	0.4
anti	***anti***	23.3	22.2
anti	***syn***	22.7	21.6
TS(*anti-syn*[OH$_{\text{“inherited”}}$]ANL)		7.9	8.3
TS(*syn-anti*[OH$_{\text{“new”}}$]ANL)		29.3	30.2
TS(ALN-TTC)		53.0	39.5
TS(ALN-CTC)		54.2	40.5

[a] Calculated energies (kJ mol^{-1}) are relative to the most stable **ALN** conformer having OH$_{\text{“new”}}$ = *syn* and OH$_{\text{“inherited”}}$ = *anti* (see structure in Figure 6). [b] The designation of OH “new” and “inherited” refers to the respective OH group in *ortho* and *meta* position relative to the allenic moiety substitution. The designation of *syn* and *anti* refers to the orientation of the OH group in respect to the allenic moiety substitution.

4. Computational Data

Table S6. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **SP-1a**.

SP-1a			
E_{elec} = -940.920558			
E_{ZPE} = 0.335471			
Coordinates (Angstroms)			
	x	y	z
C	-3.757174	-1.500128	-0.979952
C	-2.369097	-1.480757	-0.890526
C	-1.733133	-0.469421	-0.181766
C	-2.489304	0.522501	0.455182
C	-3.882050	0.492653	0.359692
C	-4.516937	-0.511617	-0.357271
C	-1.765083	1.522674	1.215975
C	-0.430981	1.532431	1.254483
C	0.425633	0.555886	0.505027
O	-0.371840	-0.501839	-0.116674
N	2.495482	-0.481084	0.605457
C	2.518630	0.229565	-0.599036
C	3.485832	-1.406812	0.911944
C	4.513050	-1.602917	-0.015007
C	4.544238	-0.901685	-1.214211
C	3.536041	0.024271	-1.509046
C	3.557926	0.567587	-2.447461
C	5.344468	-1.074653	-1.923138
H	5.292262	-2.323195	0.205751
H	3.467174	-1.971110	1.835605
H	0.101684	2.265150	1.845053
H	-2.333018	2.261703	1.771155
H	-4.478812	1.253372	0.849074
H	-4.246977	-2.289780	-1.540825
H	-1.772122	-2.245566	-1.371004
H	1.346766	1.194411	-0.620984
C	1.391563	-0.098780	1.375295
H	0.920593	-0.944648	2.456815
H	0.623578	-1.941794	2.110501
H	1.705594	-1.052393	3.207187
C	0.063332	-0.471749	2.934995
H	0.631663	1.294634	-1.970391
H	0.335301	0.316262	-2.343689
H	-0.259861	1.922369	-1.893142
C	1.293880	1.756856	-2.706088
H	1.846774	2.593418	-0.200286
H	2.581964	2.944623	-0.926583
H	1.028741	3.317114	-0.172589
O	2.330113	2.572086	0.777983
H	-5.890084	-0.481746	-0.415670
H	-6.206460	-1.226993	-0.937714

SP-1a			
E_{elec} = -940.615538			
E_{ZPE} = 0.339891			
Coordinates (Angstroms)			
	x	y	z
C	3.644168	-1.648475	-0.742047
C	2.273973	-1.486500	-0.886826
C	1.668919	-0.315155	-0.466054
C	2.436472	0.708486	0.089593
C	3.808570	0.537662	0.231683
C	4.414656	-0.638591	-0.178262
C	1.741474	1.930598	0.464660
C	0.414956	1.990300	0.426901
C	-0.432880	0.806931	0.062449
O	0.331288	-0.184922	-0.657052
N	-2.551731	0.239474	-0.618950
C	-2.379869	-0.432895	0.589729
C	-3.622652	-0.041436	-1.449269
C	-4.533934	-1.012219	-1.034113
C	-4.372832	-1.683365	0.167155
C	-3.282262	-1.390577	0.989344
C	-3.147857	-1.918336	1.927737
C	-5.088672	-2.439341	0.465564
H	-5.378168	-1.249680	-1.671059
H	-3.752430	0.465497	-2.397451
H	-0.119489	2.894179	0.689003
H	2.327650	2.793177	0.762620
H	4.416437	1.325832	0.660909
H	4.111729	-2.572187	-1.068312
H	1.664687	-2.267923	-1.323567
H	-1.155221	0.122398	1.281494
C	-1.532037	1.174585	-0.800901
H	-1.238958	1.674995	-2.124445
H	-0.980851	0.872854	-2.825674
H	-2.102253	2.220727	-2.509337
C	-0.399839	2.368969	-2.066899
H	-0.284239	-0.928386	1.960604
H	-0.029856	-1.740508	1.280714
H	0.641478	-0.482495	2.334409
C	-0.816871	-1.351018	2.815874
H	-1.599458	1.172609	2.311805
H	-2.222151	0.691903	3.068821
H	-0.738678	1.622127	2.813026
O	-2.188873	1.964243	1.844742
H	5.765127	-0.747013	-0.007587
H	6.062023	-1.599778	-0.330409

Table S7. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the ωB97X-D/6-311+G(2d,p) level of theory, for **SP-1a***

SP-1a*			
E_{elec} = -940.615302			
E_{ZPE} = 0.339904			
Coordinates (Angstroms)			
	x	y	z
C	3.637333	-1.668533	-0.745597
C	2.271402	-1.499897	-0.886680
C	1.668352	-0.323560	-0.466107
C	2.436852	0.697854	0.084049
C	3.812198	0.519428	0.223262
C	4.412794	-0.659453	-0.185166
C	1.747104	1.923313	0.455569
C	0.420626	1.987721	0.418396
C	-0.430949	0.805137	0.059558
O	0.330668	-0.192462	-0.654695
N	-2.551771	0.241426	-0.618976
C	-2.382054	-0.425666	0.592833
C	-3.623654	-0.039852	-1.447877
C	-4.538076	-1.005619	-1.028051
C	-4.379091	-1.671554	0.176403
C	-3.287530	-1.378519	0.997090
C	-3.154610	-1.902536	1.937776
C	-5.097217	-2.423954	0.478299
H	-5.382993	-1.243510	-1.663914
H	-3.751706	0.462724	-2.398603
H	-0.110497	2.894737	0.676183
H	2.335187	2.786385	0.749128
H	4.408407	1.319808	0.653059
H	4.118159	-2.585006	-1.063791
H	1.656955	-2.279070	-1.320423
H	-1.155378	0.128567	1.281803
C	-1.528817	1.172358	-0.805624
H	-1.233493	1.663691	-2.132142
H	-0.977289	0.856507	-2.828216
H	-2.094967	2.209560	-2.520863
C	-0.392396	2.355607	-2.078424
H	-0.287814	-0.922155	1.965406
H	-0.035769	-1.737937	1.289088
H	0.639265	-0.477619	2.337474
C	-0.821846	-1.339619	2.822328
H	-1.595831	1.185012	2.307337
H	-2.219918	0.709890	3.066708
H	-0.733453	1.633993	2.806376
O	-2.182731	1.976460	1.836778
H	5.753757	-0.888054	-0.066840
H	6.177614	-0.122846	0.326049

Table S8. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **SP-2a**.

SP-2a			
E_{elec} = -940.920738			
E_{ZPE} = 0.335616			
Coordinates (Angstroms)			
	x	y	z
C	-3.732419	-1.366870	-1.145133
C	-2.351243	-1.218172	-1.205831
C	-1.724711	-0.242545	-0.440317
C	-2.481817	0.590112	0.393949
C	-3.868520	0.429523	0.448917
C	-4.494060	-0.543793	-0.316400
C	-1.761847	1.580513	1.169405
C	-0.426675	1.627902	1.163579
C	0.422380	0.669108	0.383003
O	-0.376081	-0.095361	-0.572648
N	1.135411	-0.255344	1.258850
C	2.298447	-0.678074	0.606928
C	2.615151	0.196245	-0.437552
C	1.597326	1.322867	-0.460343
C	3.096846	-1.781057	0.886689
C	4.233073	-1.987679	0.099902
C	4.555565	-1.123944	-0.939700
C	3.737794	-0.020178	-1.210922
H	3.987073	0.650792	-2.025717
H	5.435777	-1.306743	-1.543576
H	4.865959	-2.844027	0.301946
H	2.850458	-2.471015	1.683620
H	0.100981	2.344454	1.776569
H	-2.330832	2.278846	1.774074
H	-4.466732	1.065227	1.091046
H	-1.752714	-1.851119	-1.848710
C	0.398074	-1.169400	2.110814
H	-0.453110	-0.648558	2.546988
H	0.034044	-2.049593	1.566517
H	1.037615	-1.505986	2.928642
C	1.152676	1.747916	-1.862272
H	0.342857	2.479726	-1.807537
H	1.988074	2.219813	-2.384882
H	0.810755	0.900863	-2.452934
C	2.200224	2.540768	0.273313
H	3.103442	2.859991	-0.249346
H	1.505742	3.384128	0.286036
H	2.479287	2.297906	1.300132
O	-5.860918	-0.651164	-0.217250
H	-6.171483	-1.355330	-0.796691
H	-4.216671	-2.129214	-1.747115

SP-2a			
E_{elec} = -940.615280			
E_{ZPE} = 0.340003			
Coordinates (Angstroms)			
	x	y	z
C	-3.636270	-1.396005	-1.111837
C	-2.269546	-1.188846	-1.214711
C	-1.671059	-0.166711	-0.496852
C	-2.440180	0.655803	0.326172
C	-3.810740	0.438228	0.425528
C	-4.410551	-0.584070	-0.289464
C	-1.742655	1.702669	1.052796
C	-0.413645	1.758140	1.049146
C	0.427185	0.750288	0.323178
O	-0.342196	0.042586	-0.668041
N	1.033876	-0.196295	1.244628
C	2.184008	-0.702940	0.637174
C	2.601207	0.143360	-0.387807
C	1.668641	1.332878	-0.444803
C	2.881558	-1.860158	0.938180
C	4.025286	-2.146450	0.193484
C	4.449712	-1.307362	-0.824176
C	3.729030	-0.148039	-1.118854
H	4.052498	0.508416	-1.919857
H	5.336184	-1.554112	-1.395413
H	4.584796	-3.048678	0.412125
H	2.552749	-2.532655	1.720773
H	0.112109	2.505336	1.626748
H	-2.325201	2.423920	1.615929
H	-4.419885	1.068122	1.063615
H	-1.657806	-1.814472	-1.852576
C	0.188576	-1.078377	2.016034
H	-0.649725	-0.513015	2.422401
H	-0.202638	-1.910544	1.417058
H	0.754294	-1.485714	2.855716
C	1.321998	1.797259	-1.855002
H	0.542536	2.563099	-1.825897
H	2.205989	2.237819	-2.322702
H	0.974085	0.974413	-2.476208
C	2.315930	2.490183	0.332866
H	3.276833	2.730917	-0.125438
H	1.694942	3.388912	0.301424
H	2.500019	2.220140	1.374828
O	-5.758764	-0.748622	-0.149319
H	-6.051600	-1.480045	-0.695984
H	-4.100543	-2.198600	-1.676377

Table S9. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **SP-2a*.**

SP-2a*			
E_{elec} = -940.920567			
E_{ZPE} = 0.335642			
Coordinates (Angstroms)			
	x	y	z
C	-3.725281	-1.376050	-1.164568
C	-2.347876	-1.220542	-1.219082
C	-1.723822	-0.245699	-0.445904
C	-2.482234	0.579977	0.389993
C	-3.871701	0.411646	0.439178
C	-4.491574	-0.559248	-0.332925
C	-1.767171	1.568534	1.171078
C	-0.431896	1.620359	1.167647
C	0.420483	0.666413	0.384611
O	-0.375475	-0.095108	-0.575443
N	1.133563	-0.260378	1.257878
C	2.299315	-0.677511	0.606728
C	2.616215	0.201962	-0.433226
C	1.595557	1.326044	-0.453959
C	3.099649	-1.779752	0.883648
C	4.238093	-1.980367	0.098551
C	4.560837	-1.111441	-0.936646
C	3.741064	-0.008537	-1.205083
H	3.990416	0.666238	-2.016695
H	5.442666	-1.289744	-1.539494
H	4.872401	-2.836209	0.298199
H	2.852952	-2.473913	1.676818
H	0.092593	2.336291	1.783987
H	-2.338035	2.263612	1.778148
H	-4.459356	1.052055	1.090866
H	-1.744453	-1.847545	-1.863354
C	0.395930	-1.180954	2.102619
H	-0.457369	-0.664258	2.539640
H	0.035045	-2.058657	1.552336
H	1.034033	-1.520926	2.920166
C	1.152548	1.754804	-1.855278
H	0.341347	2.485038	-1.799688
H	1.988019	2.229814	-2.374915
H	0.813111	0.909097	-2.449267
C	2.193777	2.542868	0.285277
H	3.097034	2.866440	-0.234604
H	1.497019	3.384360	0.299797
H	2.471733	2.297005	1.311696
O	-5.850137	-0.767239	-0.323394
H	-6.269084	-0.142992	0.279095
H	-4.221582	-2.129316	-1.763142

SP-2a*			
E_{elec} = -940.615103			
E_{ZPE} = 0.340057			
Coordinates (Angstroms)			
	x	y	z
C	-3.629244	-1.406615	-1.130465
C	-2.266788	-1.193136	-1.226648
C	-1.670499	-0.170823	-0.500927
C	-2.440590	0.644996	0.322480
C	-3.814196	0.419607	0.416046
C	-4.408390	-0.600582	-0.305574
C	-1.748371	1.690794	1.054341
C	-0.419362	1.751180	1.052638
C	0.425178	0.747574	0.324926
O	-0.341724	0.040487	-0.668752
N	1.033007	-0.199923	1.244557
C	2.185999	-0.701308	0.637499
C	2.602224	0.149157	-0.384271
C	1.665946	1.335759	-0.439965
C	2.886565	-1.857226	0.936340
C	4.032375	-2.137834	0.192749
C	4.455925	-1.294459	-0.821744
C	3.732164	-0.136610	-1.114338
H	4.054762	0.522967	-1.913115
H	5.343945	-1.536984	-1.392372
H	4.594084	-3.039135	0.409497
H	2.558308	-2.533308	1.716060
H	0.103008	2.498875	1.632579
H	-2.332866	2.409479	1.619180
H	-4.411790	1.055979	1.063146
H	-1.649874	-1.812871	-1.865434
C	0.188301	-1.087939	2.009890
H	-0.651747	-0.526282	2.417844
H	-0.200283	-1.917699	1.405959
H	0.753504	-1.498459	2.848346
C	1.319810	1.801884	-1.849718
H	0.538383	2.565725	-1.820230
H	2.203255	2.245504	-2.315531
H	0.974720	0.979324	-2.472852
C	2.308415	2.493472	0.341067
H	3.269154	2.738260	-0.115412
H	1.684682	3.390369	0.310636
H	2.492053	2.221773	1.382693
O	-5.746379	-0.866692	-0.250519
H	-6.175506	-0.241251	0.336248
H	-4.106808	-2.200501	-1.690931

Table S10. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the *ω*B97X-D/6-311+G(2d,p) level of theory, for **SP-1b.**

SP-1b			
E_{elec} = -940.611815			
E_{ZPE} = 0.339779			
Coordinates (Angstroms)			
	x	y	z
C	-4.220775	-0.243624	1.154280
C	-2.899160	-0.041542	1.527432
C	-1.951984	0.265333	0.568398
C	-2.320167	0.385171	-0.772530
C	-3.644794	0.180503	-1.137289
C	-4.595441	-0.136250	-0.179192
C	-1.269919	0.729638	-1.720359
C	-0.001807	0.711204	-1.329275
C	0.400771	0.341905	0.078507
O	-0.677942	0.512170	0.984733
N	1.473977	1.206186	0.556427
C	2.680474	0.611295	0.214234
C	2.498894	-0.748983	-0.045353
C	1.042626	-1.095939	0.172864
C	3.932497	1.196770	0.116940
C	5.010972	0.381875	-0.226457
C	4.841523	-0.970369	-0.475278
C	3.570157	-1.542385	-0.382732
H	3.430729	-2.599383	-0.583910
H	5.692318	-1.581840	-0.749272
H	5.998492	0.821368	-0.307313
H	4.077295	2.254355	0.300041
H	0.809793	0.932480	-2.013211
H	-1.542827	0.981855	-2.739261
H	-3.946817	0.268632	-2.174482
H	-4.959851	-0.489814	1.910049
H	-2.595497	-0.119713	2.563882
O	-5.877933	-0.329033	-0.603856
H	-6.437450	-0.536882	0.146765
C	1.309629	2.637105	0.474446
H	1.515175	3.034914	-0.529301
H	0.287238	2.889144	0.753058
H	1.981094	3.122957	1.184600
C	0.861936	-1.651302	1.593550
H	1.196862	-0.934321	2.343910
H	-0.185197	-1.890599	1.789154
H	1.453217	-2.563784	1.697655
C	0.478933	-2.086087	-0.841855
H	0.678766	-1.779890	-1.869087
H	0.931311	-3.068816	-0.688251
H	-0.601697	-2.194964	-0.719011

Table S11. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the ωB97X-D/6-311+G(2d,p) level of theory, for **SP-1b***

SP-1b*			
E_{elec} = -940.611639			
E_{ZPE} = 0.339803			
Coordinates (Angstroms)			
	x	y	z
C	-4.219261	-0.237567	1.174449
C	-2.899578	-0.031966	1.538439
C	-1.951930	0.267606	0.572915
C	-2.321191	0.377995	-0.765036
C	-3.651024	0.168772	-1.122600
C	-4.598039	-0.141092	-0.159475
C	-1.274647	0.717765	-1.717872
C	-0.005330	0.703698	-1.330078
C	0.400233	0.341501	0.078911
O	-0.677125	0.515785	0.985873
N	1.473897	1.208796	0.550178
C	2.679950	0.613293	0.207481
C	2.498646	-0.748396	-0.044918
C	1.043292	-1.095328	0.179385
C	3.931238	1.199225	0.103865
C	5.009386	0.383437	-0.238473
C	4.840262	-0.970132	-0.480186
C	3.569599	-1.542658	-0.381282
H	3.430529	-2.600822	-0.576483
H	5.690817	-1.582362	-0.753228
H	5.996386	0.823209	-0.323990
H	4.075811	2.257745	0.281648
H	0.804081	0.923802	-2.016888
H	-1.549200	0.965580	-2.737654
H	-3.937440	0.253168	-2.167318
H	-4.968692	-0.478423	1.917734
H	-2.591109	-0.101653	2.574163
O	-5.911432	-0.360153	-0.458061
H	-6.048374	-0.262889	-1.402230
C	1.308061	2.639189	0.463389
H	1.509103	3.033391	-0.542743
H	0.286711	2.891501	0.745562
H	1.982147	3.128212	1.168829
C	0.866794	-1.642975	1.603578
H	1.203254	-0.921653	2.349049
H	-0.179563	-1.881891	1.803522
H	1.458998	-2.554440	1.711127
C	0.477613	-2.091486	-0.828333
H	0.673890	-1.790382	-1.857800
H	0.931777	-3.072790	-0.671080
H	-0.602402	-2.201221	-0.700917

Table S12. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and *ω*B97X-D/6-311+G(2d,p) (right) levels of theory, for **SP-2b**.

SP-2b			
E_{elec} = -940.917423			
E_{ZPE} = 0.335399			
Coordinates (Angstroms)			
	x	y	z
C	-4.316162	0.246482	-1.164588
C	-2.976499	0.493738	-1.446963
C	-2.012948	0.279412	-0.471926
C	-2.381641	-0.183450	0.797033
C	-3.728759	-0.431222	1.068081
C	-4.694260	-0.217878	0.093894
C	-1.319908	-0.383560	1.765175
C	-0.045455	-0.185118	1.424145
C	0.386113	0.187196	0.030456
O	-0.714517	0.577304	-0.792308
N	1.097865	-0.949605	-0.597102
C	2.453249	-0.822704	-0.307152
C	2.750862	0.491418	0.082432
C	1.485412	1.326956	-0.003849
C	3.448821	-1.792777	-0.368179
C	4.756514	-1.417543	-0.048000
C	5.060777	-0.116709	0.333027
C	4.046451	0.847714	0.396113
H	4.283245	1.862894	0.695650
H	6.078892	0.150669	0.587229
H	5.543371	-2.161755	-0.090495
H	3.226326	-2.813374	-0.652605
H	0.755698	-0.357593	2.132088
H	-1.582611	-0.705481	2.767318
H	-4.031098	-0.791964	2.044095
H	-5.066153	0.415850	-1.930446
C	-2.672568	0.855633	-2.420982
H	-6.001058	-0.481169	0.426400
H	-6.570470	-0.289561	-0.326693
H	0.466966	-2.251055	-0.690780
C	0.513479	-2.825427	0.243907
H	-0.577147	-2.125082	-0.972921
H	0.952417	-2.831127	-1.477697
H	1.462064	2.052810	-1.366900
C	1.524340	1.347499	-2.195720
H	0.550455	2.639762	-1.484130
H	2.319972	2.725855	-1.424027
H	1.317930	2.357270	1.116354
O	1.428933	1.919582	2.108627
H	2.069553	3.143298	1.014162
H	0.335757	2.832603	1.059377

SP-2b			
E_{elec} = -940.612132			
E_{ZPE} = 0.339813			
Coordinates (Angstroms)			
	x	y	z
C	-4.276075	0.268198	-1.139656
C	-2.952003	0.587927	-1.400448
C	-1.986998	0.370826	-0.433048
C	-2.339543	-0.164879	0.805134
C	-3.669062	-0.485686	1.056166
C	-4.637487	-0.271510	0.089537
C	-1.272349	-0.367184	1.771473
C	-0.010485	-0.142084	1.424580
C	0.386827	0.263500	0.029362
O	-0.709355	0.743130	-0.722756
N	1.021786	-0.873050	-0.655528
C	2.377682	-0.829956	-0.353182
C	2.740159	0.449533	0.076349
C	1.522718	1.344103	0.008866
C	3.313797	-1.848241	-0.428915
C	4.632629	-1.552708	-0.083888
C	5.001299	-0.284831	0.334809
C	4.042990	0.729036	0.414535
H	4.324639	1.722833	0.746608
H	6.029580	-0.081389	0.606932
H	5.379165	-2.336765	-0.137287
H	3.037958	-2.847449	-0.742619
H	0.804984	-0.323164	2.114586
H	-1.526585	-0.715935	2.766567
H	-3.958005	-0.905812	2.012618
H	-5.029138	0.439442	-1.902309
C	-2.658574	1.008425	-2.354085
H	-5.923722	-0.608118	0.398115
H	-6.495453	-0.409052	-0.345608
H	0.330794	-2.138371	-0.731628
C	0.372692	-2.708549	0.205972
H	-0.713618	-1.963563	-0.988984
H	0.769771	-2.741806	-1.528044
H	1.528451	2.083926	-1.338681
C	1.546819	1.383138	-2.174189
H	0.646878	2.718327	-1.439343
H	2.421189	2.710654	-1.393479
H	1.404793	2.356213	1.143059
O	1.521163	1.897601	2.125681
H	2.176669	3.122283	1.038652
H	0.433150	2.855158	1.107620

Table S13. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **SP-2b***.

SP-2b*			
E_{elec} = -940.917304			
E_{ZPE} = 0.335434			
Coordinates (Angstroms)			
	x	y	z
C	-4.313732	0.258786	-1.181195
C	-2.975422	0.505506	-1.453902
C	-2.012452	0.284560	-0.476021
C	-2.382748	-0.184402	0.787285
C	-3.734898	-0.433262	1.049822
C	-4.696376	-0.213001	0.073760
C	-1.324668	-0.389900	1.757490
C	-0.048938	-0.189702	1.421516
C	0.385660	0.188557	0.030263
O	-0.713383	0.583644	-0.792160
N	1.097124	-0.946098	-0.601201
C	2.452077	-0.822478	-0.307993
C	2.750550	0.489463	0.088309
C	1.486381	1.327053	0.002906
C	3.446504	-1.793537	-0.371592
C	4.754008	-1.421487	-0.046935
C	5.059128	-0.122868	0.340889
C	4.045933	0.842593	0.406366
H	4.283470	1.856119	0.710865
H	6.077093	0.142034	0.598257
H	5.540046	-2.166438	-0.091566
H	3.223358	-2.812412	-0.661641
H	0.750083	-0.365306	2.131016
H	-1.589022	-0.716637	2.757898
H	-4.023365	-0.800891	2.030436
H	-5.072867	0.427232	-1.934258
C	-2.666350	0.872965	-2.424305
H	-6.035227	-0.440634	0.280834
H	-6.175156	-0.755805	1.180463
H	0.464417	-2.245803	-0.704882
C	0.506387	-2.825704	0.226686
H	-0.578269	-2.116359	-0.990713
H	0.952009	-2.822207	-1.493145
H	1.466357	2.058397	-1.357238
C	1.529728	1.356409	-2.188775
H	0.555428	2.646469	-1.474005
H	2.324874	2.731020	-1.409963
H	1.317885	2.352971	1.126956
O	1.426124	1.911089	2.117715
H	2.070866	3.138307	1.029642
H	0.336573	2.830045	1.069592

SP-2b*			
E_{elec} = -940.612004			
E_{ZPE} = 0.339829			
Coordinates (Angstroms)			
	x	y	z
C	-4.274251	0.283605	-1.155046
C	-2.951821	0.601832	-1.406088
C	-1.986688	0.375603	-0.436280
C	-2.340551	-0.167457	0.794609
C	-3.675410	-0.489089	1.036997
C	-4.640086	-0.265510	0.069459
C	-1.277018	-0.377168	1.762632
C	-0.013959	-0.149468	1.421252
C	0.386426	0.264082	0.029110
O	-0.708338	0.748225	-0.722143
N	1.022084	-0.868811	-0.660817
C	2.377240	-0.828807	-0.355014
C	2.739657	0.447953	0.082777
C	1.523075	1.343898	0.017090
C	3.312682	-1.847403	-0.434331
C	4.630896	-1.554948	-0.084273
C	4.999509	-0.289857	0.342749
C	4.041838	0.724368	0.425892
H	4.323546	1.716054	0.764147
H	6.027302	-0.088793	0.618439
H	5.376989	-2.339214	-0.140598
H	3.036887	-2.844452	-0.754868
H	0.799488	-0.334104	2.112612
H	-1.532818	-0.732057	2.755398
H	-3.948920	-0.917410	1.997388
H	-5.037397	0.454214	-1.903807
C	-2.653105	1.029400	-2.355022
H	-5.958979	-0.562992	0.255730
H	-6.087915	-0.919981	1.136415
H	0.329785	-2.132415	-0.749239
C	0.365874	-2.709078	0.184736
H	-0.712865	-1.954259	-1.011397
H	0.772295	-2.731129	-1.547222
H	1.532317	2.090799	-1.326524
C	1.552243	1.394465	-2.165687
H	0.651273	2.726099	-1.425961
H	2.425454	2.717384	-1.375960
H	1.403165	2.350050	1.156339
O	1.516595	1.886139	2.136854
H	2.176043	3.115890	1.058019
H	0.432157	2.850237	1.120880

Table S14. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(1a-2a)**.

TS(1a-2a)			
E_{elec} = -940.920555			
E_{ZPE} = 0.335440			
Coordinates (Angstroms)			
	x	y	z
C	-3.761508	-1.464670	-1.029893
C	-2.372684	-1.435627	-0.958476
C	-1.735874	-0.443994	-0.222786
C	-2.491908	0.518288	0.458083
C	-3.885670	0.478723	0.380419
C	-4.521430	-0.505844	-0.362374
C	-1.766308	1.499767	1.241119
C	-0.432003	1.511707	1.274355
C	0.424832	0.554390	0.501294
O	-0.373644	-0.462378	-0.183794
N	1.365188	-0.148757	1.362673
C	2.478257	-0.515738	0.598563
C	2.534051	0.242092	-0.575739
C	1.376444	1.224243	-0.580360
C	3.449628	-1.467553	0.885401
C	4.491308	-1.641426	-0.029759
C	4.554944	-0.893181	-1.198904
C	3.565532	0.058586	-1.474503
H	3.612635	0.638726	-2.389657
H	5.365928	-1.049327	-1.899467
H	5.256064	-2.381383	0.175963
H	3.405682	-2.068162	1.784992
H	0.100572	2.229095	1.883366
H	-2.333259	2.222730	1.818055
H	-4.482199	1.216633	0.903823
H	-4.252010	-2.238729	-1.611514
C	-1.775599	-2.177139	-1.474042
H	-5.895542	-0.487257	-0.400826
H	-6.212254	-1.216041	-0.945429
H	0.861983	-1.030879	2.399695
C	0.556493	-2.008204	2.007103
H	1.631448	-1.182116	3.158574
H	0.003666	-0.564426	2.882270
H	0.688656	1.389998	-1.937514
C	0.386819	0.432220	-2.356808
H	-0.196281	2.025724	-1.850167
H	1.370518	1.873714	-2.640740
H	1.888734	2.597385	-0.094308
O	2.643922	2.965109	-0.791292
H	1.081502	3.332564	-0.054403
H	2.351615	2.529798	0.891729

TS(1a-2a)			
E_{elec} = -940.614777			
E_{ZPE} = 0.339869			
Coordinates (Angstroms)			
	x	y	z
C	-3.712151	-1.466687	-1.028920
C	-2.328270	-1.393936	-0.994504
C	-1.705859	-0.385234	-0.276559
C	-2.470755	0.551076	0.416911
C	-3.858990	0.468968	0.378079
C	-4.482625	-0.534261	-0.343048
C	-1.756638	1.564305	1.174008
C	-0.428582	1.586569	1.198126
C	0.425305	0.607052	0.453310
O	-0.352468	-0.353038	-0.290484
N	1.291484	-0.129838	1.354756
C	2.408139	-0.544139	0.625768
C	2.543414	0.221604	-0.530865
C	1.439568	1.254733	-0.560188
C	3.309912	-1.549774	0.927878
C	4.367945	-1.766093	0.045672
C	4.512219	-1.006751	-1.104348
C	3.588701	-0.000813	-1.396720
H	3.692253	0.591165	-2.300061
H	5.337116	-1.197833	-1.779640
H	5.083805	-2.550474	0.262742
H	3.200672	-2.160079	1.815848
H	0.106147	2.316090	1.790994
H	-2.330203	2.293368	1.736293
H	-4.463292	1.190773	0.915485
H	-4.192384	-2.257511	-1.596676
C	-1.720055	-2.115070	-1.526038
H	-5.848253	-0.560270	-0.343522
H	-6.154974	-1.295929	-0.876648
H	0.680194	-1.034204	2.302114
C	0.363467	-1.974227	1.833923
H	1.383843	-1.258021	3.105520
H	-0.191727	-0.552019	2.745381
H	0.812389	1.478450	-1.931426
C	0.511253	0.539928	-2.393403
H	-0.066877	2.123674	-1.849064
H	1.529124	1.975606	-2.589442
H	1.996304	2.582479	-0.023064
O	2.810899	2.914637	-0.669415
H	1.229752	3.361457	-0.017567
H	2.395248	2.469733	0.987179

Table S15. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the ωB97X-D/6-311+G(2d,p) level of theory, for the transition state **TS(1a*-2a*)**.

TS(1a*-2a*)			
E_{elec} = -940.614586			
E_{ZPE} =0.339883			
Coordinates (Angstroms)			
	x	y	z
C	-3.704320	-1.479445	-1.046005
C	-2.324712	-1.402060	-1.003252
C	-1.704861	-0.392946	-0.277396
C	-2.470958	0.538256	0.415188
C	-3.862520	0.451044	0.367875
C	-4.480090	-0.550303	-0.359929
C	-1.762154	1.549222	1.179136
C	-0.434048	1.575226	1.206569
C	0.423512	0.601463	0.458139
O	-0.351631	-0.361184	-0.285481
N	1.294448	-0.133344	1.356452
C	2.412374	-0.540214	0.624841
C	2.542106	0.228917	-0.530084
C	1.432913	1.256372	-0.555526
C	3.319655	-1.541870	0.923438
C	4.377466	-1.750752	0.039230
C	4.516230	-0.988024	-1.109233
C	3.587242	0.013838	-1.398008
H	3.686347	0.608237	-2.300248
H	5.340955	-1.173543	-1.786270
H	5.097476	-2.532137	0.253302
H	3.214625	-2.155031	1.809940
H	0.097527	2.303498	1.803742
H	-2.337668	2.274842	1.744326
H	-4.455379	1.180382	0.913214
H	-4.197666	-2.259561	-1.612086
H	-1.710924	-2.119282	-1.533854
O	-5.837102	-0.680835	-0.441733
H	-6.258713	0.015024	0.065763
C	0.688773	-1.043566	2.301887
H	0.375158	-1.983322	1.831210
H	1.394866	-1.266907	3.103270
H	-0.184399	-0.566522	2.748302
C	0.802265	1.479640	-1.925242
H	0.504639	0.540632	-2.388481
H	-0.079862	2.120642	-1.840196
H	1.515450	1.981306	-2.583673
C	1.983420	2.585834	-0.016268
H	2.794978	2.923994	-0.663313
H	1.212686	3.360690	-0.007509
H	2.384878	2.472835	0.992961

Table S16. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the ωB97X-D/6-311+G(2d,p) level of theory, for the transition state **TS(1a-1b)**.

TS(1a-1b)			
E_{elec} = -940.608653			
E_{ZPE} = 0.339300			
Coordinates (Angstroms)			
	x	y	z
C	-4.024712	0.399181	-1.451791
C	-2.668144	0.182235	-1.645460
C	-1.875546	-0.220939	-0.585591
C	-2.439860	-0.425743	0.673763
C	-3.799567	-0.205811	0.859660
C	-4.592788	0.210152	-0.197497
C	-1.551073	-0.895504	1.725780
C	-0.238630	-0.905874	1.526746
C	0.394716	-0.419051	0.246014
O	-0.559753	-0.467643	-0.828015
N	1.476104	-1.278137	-0.153623
C	2.680528	-0.621493	-0.218575
C	2.520402	0.733315	0.066247
C	1.065703	1.029071	0.361653
C	3.928657	-1.151526	-0.513220
C	5.019116	-0.283293	-0.530125
C	4.869224	1.067334	-0.260393
C	3.604131	1.579246	0.039983
H	3.482558	2.635853	0.256175
H	5.730177	1.723821	-0.277326
H	6.002609	-0.677803	-0.758446
H	4.057137	-2.205849	-0.725563
H	0.447548	-1.246759	2.292643
H	-1.978390	-1.233385	2.663609
H	-4.251617	-0.362038	1.832329
H	-4.640366	0.722274	-2.285327
H	-2.215263	0.327640	-2.618171
O	-5.919416	0.414395	0.050679
H	-6.357953	0.693237	-0.755280
C	1.330986	-2.700037	-0.296042
H	1.839627	-3.249427	0.506242
H	0.271899	-2.953199	-0.276484
H	1.736636	-3.034880	-1.255279
C	0.492458	1.991613	-0.685267
H	0.596587	1.592961	-1.693635
H	-0.563955	2.198132	-0.500705
H	1.037801	2.936761	-0.631982
C	0.901886	1.647076	1.753459
H	1.344801	1.024379	2.532362
H	1.407449	2.615089	1.779132
H	-0.151581	1.806416	1.993677

Table S17. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the ωB97X-D/6-311+G(2d,p) level of theory, for the transition state **TS(1a*-1b*)**.

TS(1a*-1b*)			
E_{elec} = -940.608458			
E_{ZPE} = 0.339282			
Coordinates (Angstroms)			
	x	y	z
C	4.019520	-0.390528	-1.474162
C	2.666141	-0.169059	-1.657993
C	1.874517	0.225191	-0.589785
C	2.440094	0.417543	0.667389
C	3.803929	0.192024	0.844387
C	4.592232	-0.215061	-0.219177
C	1.556130	0.880696	1.725702
C	0.242991	0.895583	1.530506
C	-0.393832	0.417941	0.247765
O	0.558570	0.474635	-0.827626
N	-1.476272	1.279851	-0.142391
C	-2.680836	0.623637	-0.209520
C	-2.520095	-0.733009	0.065960
C	-1.064379	-1.031083	0.354152
C	-3.929490	1.155695	-0.498056
C	-5.020110	0.287714	-0.517821
C	-4.869759	-1.064584	-0.256918
C	-3.603990	-1.578630	0.036889
H	-3.481970	-2.636730	0.245363
H	-5.730806	-1.720877	-0.276154
H	-6.004050	0.683722	-0.741555
H	-4.058236	2.211295	-0.703797
H	-0.440407	1.233617	2.300073
H	1.985542	1.212487	2.665005
H	4.242365	0.343417	1.827013
H	4.646730	-0.706094	-2.298358
H	2.208136	-0.303406	-2.629997
O	5.930389	-0.455807	-0.099294
H	6.206845	-0.297506	0.805225
C	-1.330293	2.701855	-0.282487
H	-1.839176	3.249989	0.520484
H	-0.271094	2.954444	-0.261887
H	-1.735128	3.038715	-1.241385
C	-0.495027	-1.985175	-0.702635
H	-0.602566	-1.578378	-1.707347
H	0.561960	-2.193710	-0.523787
H	-1.040574	-2.930513	-0.655301
C	-0.895632	-1.660157	1.740355
H	-1.335577	-1.043644	2.525867
H	-1.401158	-2.628312	1.760129
H	0.158747	-1.821651	1.975201

Table S18. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(2a-2b)**.

TS(2a-2b)			
E_{elec} = -940.914922			
E_{ZPE} = 0.335022			
Coordinates (Angstroms)			
	x	y	z
C	-4.146146	-0.179028	-1.466402
C	-2.773995	-0.031066	-1.636511
C	-1.948254	0.102681	-0.527612
C	-2.493592	0.085639	0.762152
C	-3.873097	-0.068191	0.921130
C	-4.698411	-0.198717	-0.186230
C	-1.570145	0.219892	1.870437
C	-0.253739	0.298959	1.659661
C	0.380856	0.199962	0.298544
O	-0.613799	0.288343	-0.751820
N	1.095418	-1.063381	0.171956
C	2.451220	-0.890355	-0.014275
C	2.772085	0.468100	-0.107474
C	1.510910	1.307784	0.000324
C	3.437658	-1.870409	-0.103588
C	4.758970	-1.459152	-0.293442
C	5.087631	-0.112808	-0.391736
C	4.081655	0.858104	-0.301226
H	4.339235	1.908914	-0.379514
H	6.118190	0.186609	-0.535767
H	5.538994	-2.208454	-0.363881
H	3.194473	-2.922852	-0.030885
H	0.433481	0.363966	2.492425
H	-1.967449	0.239955	2.879768
H	-4.309125	-0.086203	1.912992
H	-4.786671	-0.280831	-2.336605
C	-2.336784	-0.013689	-2.626748
H	-6.046438	-0.345364	0.038168
H	-6.506828	-0.422621	-0.804518
H	1.246153	2.034541	-1.332596
C	1.171171	1.338335	-2.166241
H	0.325928	2.619301	-1.291451
H	2.077012	2.715383	-1.529839
H	1.620133	2.362137	1.114858
C	1.936878	1.932945	2.065693
H	2.364376	3.109760	0.832999
H	0.669100	2.878229	1.266098
H	0.480711	-2.354950	0.374551
O	-0.586360	-2.229508	0.543705
H	0.610097	-2.991367	-0.506824
H	0.904635	-2.876766	1.240725

TS(2a-2b)			
E_{elec} = -940.607963			
E_{ZPE} = 0.33922			
Coordinates (Angstroms)			
	x	y	z
C	-4.082756	-0.293551	-1.460285
C	-2.722015	-0.092313	-1.630947
C	-1.915989	0.147850	-0.530405
C	-2.470044	0.187639	0.748462
C	-3.836301	-0.020539	0.910698
C	-4.643628	-0.259612	-0.187810
C	-1.561117	0.431229	1.854051
C	-0.250747	0.506543	1.642377
C	0.377773	0.296076	0.290601
O	-0.599020	0.390535	-0.753277
N	1.018905	-1.000950	0.249066
C	2.373772	-0.915106	0.038326
C	2.764004	0.412294	-0.128259
C	1.553070	1.317075	-0.061451
C	3.299843	-1.947503	-0.007953
C	4.636555	-1.616462	-0.224858
C	5.034735	-0.300153	-0.392251
C	4.085043	0.724092	-0.347420
H	4.391740	1.756398	-0.481934
H	6.078712	-0.064988	-0.557569
H	5.375724	-2.408436	-0.262714
H	2.998664	-2.980336	0.117319
H	0.436028	0.638278	2.467662
H	-1.968116	0.526784	2.854940
H	-4.278902	0.003944	1.899827
H	-4.709537	-0.480814	-2.326491
C	-2.275697	-0.116041	-2.617130
H	-5.976163	-0.455615	0.036014
H	-6.423449	-0.605524	-0.798863
H	1.326642	1.980480	-1.426703
C	1.210910	1.241527	-2.218295
H	0.440022	2.616425	-1.416414
H	2.195648	2.599924	-1.660175
H	1.727608	2.415617	0.991817
C	2.046724	2.018676	1.956230
H	2.498322	3.113686	0.658053
H	0.801107	2.978095	1.131979
H	0.337775	-2.240114	0.507782
O	-0.706150	-2.042901	0.745992
H	0.367229	-2.896873	-0.367906
H	0.784804	-2.771784	1.355497

Table S19. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and *ω*B97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(2a*-2b*)**.

TS(2a*-2b*)			
E_{elec} = -940.914792			
E_{ZPE} = 0.33507			
Coordinates (Angstroms)			
	x	y	z
C	-4.141116	-0.178121	-1.486002
C	-2.771503	-0.028532	-1.647002
C	-1.947270	0.104553	-0.533448
C	-2.494052	0.085064	0.752705
C	-3.877679	-0.072108	0.903380
C	-4.698171	-0.200771	-0.207351
C	-1.575020	0.219178	1.863898
C	-0.257804	0.300458	1.657437
C	0.380062	0.201772	0.297668
O	-0.612695	0.292069	-0.754472
N	1.093434	-1.062156	0.172237
C	2.449888	-0.890711	-0.011279
C	2.772548	0.467449	-0.102182
C	1.511950	1.308408	0.002515
C	3.435196	-1.871904	-0.099796
C	4.757477	-1.462036	-0.285922
C	5.088037	-0.115965	-0.381440
C	4.083066	0.856099	-0.292203
H	4.342104	1.906662	-0.368926
H	6.119288	0.182351	-0.522753
H	5.536696	-2.212211	-0.355860
H	3.190450	-2.924155	-0.029589
H	0.426753	0.366375	2.492241
H	-1.974187	0.238332	2.872764
H	-4.301301	-0.091466	1.903504
H	-4.791972	-0.279725	-2.345076
H	-2.328797	-0.008636	-2.634836
O	-6.060560	-0.355991	-0.115648
H	-6.326386	-0.339074	0.810202
C	1.251315	2.035298	-1.331154
H	1.177584	1.339099	-2.164892
H	0.331644	2.621073	-1.292497
H	2.083451	2.715137	-1.526419
C	1.619189	2.362607	1.117326
H	1.933282	1.933189	2.068973
H	2.364619	3.109740	0.837363
H	0.668137	2.879437	1.266082
C	0.475582	-2.353515	0.366125
H	-0.591520	-2.226657	0.533991
H	0.604982	-2.985231	-0.518622
H	0.897002	-2.881114	1.230013

TS(2a*-2b*)			
E_{elec} = -940.607963			
E_{ZPE} = 0.33922			
Coordinates (Angstroms)			
	x	y	z
C	-4.079742	-0.286742	-1.480146
C	-2.721573	-0.086164	-1.641788
C	-1.915898	0.147349	-0.535468
C	-2.470726	0.180799	0.739741
C	-3.841599	-0.028628	0.893876
C	-4.644937	-0.259656	-0.208619
C	-1.565641	0.418121	1.849049
C	-0.254626	0.496330	1.641302
C	0.376984	0.292502	0.289848
O	-0.598284	0.388433	-0.755346
N	1.020611	-1.002987	0.245098
C	2.375951	-0.913962	0.038294
C	2.764234	0.414911	-0.120869
C	1.551144	1.316927	-0.055661
C	3.303890	-1.944509	-0.010431
C	4.640722	-1.610023	-0.221258
C	5.037111	-0.292177	-0.380571
C	4.085436	0.730145	-0.334070
H	4.390661	1.763585	-0.463077
H	6.081186	-0.054361	-0.541398
H	5.381367	-2.400514	-0.261018
H	3.004069	-2.978534	0.108069
H	0.429944	0.625422	2.468784
H	-1.973932	0.508560	2.850139
H	-4.270126	-0.006951	1.892173
H	-4.718788	-0.468823	-2.334983
H	-2.270210	-0.104301	-2.625889
O	-5.990601	-0.470074	-0.115189
H	-6.263174	-0.410302	0.802290
C	1.327680	1.982701	-1.420256
H	1.216471	1.245231	-2.213864
H	0.439473	2.616436	-1.411738
H	2.195977	2.604711	-1.649469
C	1.719340	2.413416	1.000678
H	2.036196	2.015103	1.965296
H	2.489330	3.114288	0.671179
H	0.790920	2.973256	1.138864
C	0.338796	-2.244858	0.488142
H	-0.705410	-2.049806	0.727031
H	0.369047	-2.891645	-0.394909
H	0.784532	-2.786215	1.330354

Table S20. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the ωB97X-D/6-311+G(2d,p) level of theory, for the transition state **TS(1b-2b)**.

TS(1b-2b)			
E_{elec} = -940.611407			
E_{ZPE} = 0.339473			
Coordinates (Angstroms)			
	x	y	z
C	-1.117265	-1.117265	-1.117265
C	-1.477183	-1.477183	-1.477183
C	-0.542405	-0.542405	-0.542405
C	0.759306	0.759306	0.759306
C	1.110914	1.110914	1.110914
C	0.179236	0.179236	0.179236
C	1.686450	1.686450	1.686450
C	1.302891	1.302891	1.302891
C	-0.082126	-0.082126	-0.082126
O	-0.963393	-0.963393	-0.963393
N	-0.666307	-0.666307	-0.666307
C	-0.290943	-0.290943	-0.290943
C	0.097218	0.097218	0.097218
C	-0.072189	-0.072189	-0.072189
C	-0.266927	-0.266927	-0.266927
C	0.135435	0.135435	0.135435
C	0.512571	0.512571	0.512571
C	0.491989	0.491989	0.491989
H	0.792411	0.792411	0.792411
H	0.830482	0.830482	0.830482
H	0.160263	0.160263	0.160263
H	-0.549536	-0.549536	-0.549536
H	1.976540	1.976540	1.976540
H	2.689740	2.689740	2.689740
H	2.119722	2.119722	2.119722
H	-1.854739	-1.854739	-1.854739
H	-2.484890	-2.484890	-2.484890
O	0.588850	0.588850	0.588850
H	-0.142456	-0.142456	-0.142456
C	-0.713186	-0.713186	-0.713186
H	0.245301	0.245301	0.245301
H	-0.995921	-0.995921	-0.995921
H	-1.478338	-1.478338	-1.478338
C	-1.439745	-1.439745	-1.439745
H	-2.250095	-2.250095	-2.250095
H	-1.607941	-1.607941	-1.607941
H	-1.469412	-1.469412	-1.469412
C	1.024355	1.024355	1.024355
H	2.022798	2.022798	2.022798
H	0.945445	0.945445	0.945445
H	0.920743	0.920743	0.920743

Table S21. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the ωB97X-D/6-311+G(2d,p) level of theory, for the transition state **TS(1b*-2b*)**.

TS(1b*-2b*)			
E_{elec} = -940.611260			
E_{ZPE} = 0.339499			
Coordinates (Angstroms)			
	x	y	z
C	-4.315221	0.285147	-1.135866
C	-2.978442	0.327072	-1.488744
C	-2.000468	0.034167	-0.549385
C	-2.358253	-0.309741	0.749585
C	-3.708094	-0.350345	1.096071
C	-4.684992	-0.053069	0.161275
C	-1.284591	-0.618024	1.679437
C	-0.019956	-0.492338	1.299014
C	0.390851	-0.064553	-0.085135
O	-0.707456	0.075100	-0.969294
N	1.298976	-1.056550	-0.666319
C	2.589876	-0.714887	-0.286988
C	2.645427	0.626591	0.100931
C	1.273127	1.238226	-0.073232
C	3.721269	-1.513890	-0.259089
C	4.922719	-0.933373	0.146941
C	4.988438	0.398035	0.523887
C	3.835820	1.187566	0.499325
H	3.880352	2.229326	0.799286
H	5.930830	0.824602	0.844449
H	5.819037	-1.542255	0.174620
H	3.681563	-2.558672	-0.541802
H	0.799321	-0.711813	1.974331
H	-1.536103	-0.946143	2.682472
H	-3.983224	-0.619793	2.112116
H	-5.086706	0.515121	-1.859825
H	-2.677602	0.587565	-2.495854
O	-6.019019	-0.075678	0.450039
H	-6.145918	-0.319550	1.368751
C	0.884599	-2.437302	-0.715792
H	1.011627	-2.958513	0.243060
H	-0.165771	-2.478819	-1.003699
H	1.460572	-2.964388	-1.478473
C	1.203603	1.932674	-1.441479
H	1.422138	1.234827	-2.250672
H	0.213958	2.359076	-1.613121
H	1.941811	2.737195	-1.469494
C	0.869683	2.220070	1.021478
H	1.012991	1.806954	2.020611
H	1.468624	3.130573	0.944254
H	-0.180898	2.503015	0.913847

Table S22. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the *ω*B97X-D/6-311+G(2d,p) level of theory, for the transition state **TS(1a-1a*)**.

TS(1a-1a*)			
E_{elec} = -940.611575			
E_{ZPE} = 0.339228			
Coordinates (Angstroms)			
	x	y	z
C	-3.639708	-1.384040	-1.143921
C	-2.271794	-1.188148	-1.229805
C	-1.673654	-0.179174	-0.487452
C	-2.441804	0.642033	0.337785
C	-3.816602	0.431023	0.415402
C	-4.412993	-0.581206	-0.313415
C	-1.744950	1.680969	1.074920
C	-0.416132	1.738239	1.072880
C	0.427679	0.738648	0.340363
O	-0.344445	0.015404	-0.641859
N	1.051805	-0.201933	1.254464
C	2.201583	-0.697316	0.635536
C	2.599644	0.152873	-0.393598
C	1.654200	1.332564	-0.442300
C	2.913849	-1.846967	0.930227
C	4.052916	-2.121834	0.174170
C	4.458341	-1.278861	-0.847979
C	3.722964	-0.127203	-1.135915
H	4.031508	0.531994	-1.940475
H	5.341418	-1.516870	-1.428039
H	4.623781	-3.018160	0.387438
H	2.599856	-2.522351	1.716403
H	0.108751	2.482056	1.655513
H	-2.328442	2.398234	1.642232
H	-4.430389	1.067689	1.043184
H	-1.655329	-1.803959	-1.872658
C	0.219207	-1.093599	2.028422
H	-0.621600	-0.536017	2.440634
H	-0.167577	-1.927823	1.429283
H	0.792954	-1.497951	2.863984
C	1.286363	1.790733	-1.849187
H	0.498015	2.547107	-1.812437
H	2.159521	2.241554	-2.327150
H	0.942066	0.962981	-2.465890
C	2.297306	2.498229	0.326285
H	3.250021	2.749011	-0.143520
H	1.665964	3.389856	0.300716
H	2.496691	2.231949	1.366385
O	-5.784883	-0.751448	-0.270852
H	-6.010148	-1.359529	0.435459
H	-4.123562	-2.159663	-1.725119

Table S23. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(2a-2a*)**.

TS(2a-2a*)			
E_{elec} = -940.916753			
E_{ZPE} = 0.334950			
Coordinates (Angstroms)			
	x	y	z
C	-3.728322	-1.382452	-1.145296
C	-2.347869	-1.237082	-1.198096
C	-1.725407	-0.258575	-0.428146
C	-2.482622	0.576104	0.404413
C	-3.871252	0.414698	0.446904
C	-4.492323	-0.551540	-0.328415
C	-1.763849	1.558474	1.190301
C	-0.428786	1.607238	1.187134
C	0.423169	0.657891	0.399129
O	-0.378312	-0.121715	-0.547500
N	1.153482	-0.259404	1.265111
C	2.314611	-0.669642	0.600980
C	2.611094	0.208258	-0.446246
C	1.580689	1.323562	-0.458282
C	3.127494	-1.763851	0.872591
C	4.257731	-1.958120	0.074159
C	4.560290	-1.090775	-0.968446
C	3.728098	0.004153	-1.231140
H	3.961908	0.677803	-2.048292
H	5.436152	-1.264096	-1.581347
H	4.901726	-2.807699	0.269397
H	2.896597	-2.456579	1.671731
H	0.097875	2.318508	1.807123
H	-2.333926	2.250633	1.801118
H	-4.470944	1.042360	1.096408
H	-1.742132	-1.874163	-1.830156
C	0.433066	-1.181688	2.123070
H	-0.419915	-0.669984	2.566573
H	0.073963	-2.065341	1.581326
H	1.082945	-1.511583	2.935339
C	1.114991	1.742462	-1.855223
H	0.297858	2.465459	-1.791537
H	1.938797	2.223328	-2.387848
H	0.776171	0.891144	-2.441605
C	2.177151	2.548936	0.268128
H	3.069468	2.879860	-0.265825
H	1.471929	3.383140	0.290190
H	2.472354	2.309335	1.291169
O	-5.867788	-0.744639	-0.234439
H	-6.319731	-0.187546	-0.877637
H	-4.224397	-2.146225	-1.731493

TS(2a-2a*)			
E_{elec} = -940.611365			
E_{ZPE} = 0.339357			
Coordinates (Angstroms)			
	x	y	z
C	3.637329	-1.690700	-0.669512
C	2.268927	-1.532042	-0.819023
C	1.669141	-0.339691	-0.442077
C	2.436561	0.704655	0.074039
C	3.809970	0.531240	0.217740
C	4.410559	-0.658328	-0.154824
C	1.743340	1.939420	0.406236
C	0.417063	2.001681	0.363281
C	-0.433152	0.808736	0.040161
O	0.334099	-0.218517	-0.630322
N	-2.547099	0.218375	-0.635857
C	-2.386894	-0.405075	0.600200
C	-3.611896	-0.092739	-1.463063
C	-4.529314	-1.043641	-1.016625
C	-4.379872	-1.666233	0.211987
C	-3.295255	-1.343547	1.030733
C	-3.169863	-1.833565	1.990560
C	-5.100228	-2.407826	0.534575
H	-5.369030	-1.304437	-1.650380
H	-3.732496	0.375949	-2.431912
H	-0.115638	2.915535	0.591905
H	2.330729	2.810572	0.675756
H	4.419291	1.329329	0.627631
H	4.117444	-2.622895	-0.941505
H	1.652045	-2.327918	-1.217348
H	-1.166292	0.174393	1.279148
C	-1.522798	1.143037	-0.846899
H	-1.217248	1.589204	-2.186833
H	-0.954328	0.758970	-2.852780
H	-2.076219	2.119792	-2.601313
C	-0.377784	2.284203	-2.149744
H	-0.302157	-0.849977	2.005785
H	-0.046571	-1.690493	1.361832
H	0.622791	-0.391461	2.366086
C	-0.840353	-1.235361	2.874948
H	-1.615668	1.265756	2.263427
H	-2.246202	0.816851	3.033297
H	-0.757714	1.731982	2.754085
O	-2.198651	2.040141	1.760718
H	5.766861	-0.842958	0.043446
H	6.246427	-0.547733	-0.732645

Table S24. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the ωB97X-D/6-311+G(2d,p) level of theory, for the transition state **TS(1b-1b*)**.

TS(1b-1b*)			
E_{elec} = -940.60768			
E_{ZPE} = 0.339056			
Coordinates (Angstroms)			
	x	y	z
C	-4.222562	-0.258646	1.164675
C	-2.900681	-0.064685	1.535154
C	-1.955580	0.243555	0.570203
C	-2.323305	0.371424	-0.769823
C	-3.653520	0.174945	-1.126413
C	-4.600783	-0.134511	-0.165144
C	-1.273533	0.712861	-1.718363
C	-0.004919	0.695136	-1.329091
C	0.400872	0.324730	0.076602
O	-0.681657	0.472538	0.985219
N	1.461790	1.200303	0.560728
C	2.676364	0.621918	0.216562
C	2.511676	-0.739034	-0.050103
C	1.059860	-1.105111	0.165674
C	3.920961	1.223375	0.123268
C	5.009620	0.423588	-0.223471
C	4.856955	-0.929343	-0.479330
C	3.592811	-1.517552	-0.390680
H	3.466579	-2.575157	-0.597186
H	5.715448	-1.528862	-0.755674
H	5.991723	0.875558	-0.301234
H	4.052660	2.281689	0.311945
H	0.805849	0.917529	-2.013556
H	-1.547060	0.965154	-2.737152
H	-3.956819	0.257619	-2.164280
H	-4.970640	-0.518456	1.903683
H	-2.588126	-0.155365	2.567945
O	-5.908790	-0.383190	-0.537798
H	-6.407738	0.435522	-0.520661
C	1.279741	2.629357	0.483602
H	1.478496	3.033075	-0.519119
H	0.254920	2.868309	0.765074
H	1.946355	3.120899	1.194338
C	0.885858	-1.669726	1.583614
H	1.211826	-0.952600	2.337776
H	-0.157976	-1.923683	1.778114
H	1.488677	-2.575098	1.682890
C	0.507527	-2.096628	-0.853839
H	0.704662	-1.783935	-1.879636
H	0.969980	-3.075190	-0.704185
H	-0.571949	-2.217831	-0.732112

Table S25. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(2b-2b*)**.

TS(2b-2b*)			
E_{elec} = -940.913313			
E_{ZPE} = 0.334753			
Coordinates (Angstroms)			
	x	y	z
C	-4.311447	0.229539	-1.184609
C	-2.971592	0.469509	-1.465511
C	-2.012489	0.263669	-0.480615
C	-2.382956	-0.185420	0.792784
C	-3.734775	-0.423936	1.057679
C	-4.694389	-0.210459	0.079874
C	-1.323609	-0.384635	1.763170
C	-0.048022	-0.190284	1.424191
C	0.387215	0.174536	0.030104
O	-0.715071	0.546639	-0.803261
N	1.108158	-0.959745	-0.587675
C	2.462489	-0.819460	-0.297929
C	2.748746	0.499552	0.082965
C	1.476400	1.323991	-0.009767
C	3.465991	-1.781624	-0.352052
C	4.770240	-1.393312	-0.033612
C	5.063390	-0.087429	0.338860
C	4.041131	0.868910	0.394914
H	4.269323	1.888031	0.687629
H	6.079100	0.190125	0.591722
H	5.563317	-2.131149	-0.070793
H	3.252205	-2.805842	-0.630001
H	0.751743	-0.360476	2.134234
H	-1.588898	-0.702045	2.766129
H	-4.040284	-0.786413	2.032624
H	-5.068333	0.373491	-1.945659
H	-2.657925	0.812423	-2.443367
O	-6.029205	-0.508707	0.336754
H	-6.475242	0.268831	0.690057
C	0.487511	-2.266882	-0.672687
H	0.538010	-2.834238	0.265977
H	-0.557368	-2.151350	-0.956566
H	0.977953	-2.848329	-1.455367
C	1.448779	2.041948	-1.376866
H	1.517515	1.332618	-2.201708
H	0.532949	2.621423	-1.498677
H	2.301498	2.721275	-1.436812
C	1.299200	2.358871	1.104720
H	1.411677	1.927108	2.099410
H	2.045232	3.149801	0.999628
H	0.313760	2.826980	1.043643

TS(2b-2b*)			
E_{elec} = -940.608114			
E_{ZPE} = 0.33912			
Coordinates (Angstroms)			
	x	y	z
C	-4.272260	0.255740	-1.158921
C	-2.948324	0.570417	-1.418256
C	-1.987340	0.356386	-0.442007
C	-2.340809	-0.171720	0.799062
C	-3.675211	-0.485075	1.043872
C	-4.638179	-0.266777	0.075081
C	-1.275673	-0.374789	1.766798
C	-0.012999	-0.150021	1.422836
C	0.387628	0.251940	0.028056
O	-0.710644	0.716796	-0.734366
N	1.032154	-0.881564	-0.650285
C	2.387358	-0.826417	-0.346030
C	2.738757	0.457474	0.079118
C	1.514295	1.342152	0.006031
C	3.331544	-1.837499	-0.416571
C	4.647380	-1.530077	-0.070615
C	5.005231	-0.257662	0.343780
C	4.038824	0.748817	0.418160
H	4.312093	1.746132	0.746645
H	6.031445	-0.044942	0.616560
H	5.400268	-2.308274	-0.120000
H	3.064139	-2.839957	-0.727142
H	0.801349	-0.329314	2.114581
H	-1.531923	-0.722634	2.761758
H	-3.967039	-0.910549	1.997725
H	-5.033230	0.404135	-1.915339
H	-2.645077	0.977664	-2.374589
O	-5.951475	-0.630311	0.309333
H	-6.423294	0.108114	0.698740
C	0.350408	-2.152230	-0.722270
H	0.395766	-2.718607	0.217387
H	-0.695086	-1.986308	-0.981324
H	0.794183	-2.755181	-1.516285
C	1.517158	2.077671	-1.343875
H	1.542343	1.374455	-2.177133
H	0.631414	2.705620	-1.448610
H	2.405426	2.710647	-1.398898
C	1.385970	2.356638	1.136947
H	1.502795	1.901575	2.121156
H	2.152721	3.127783	1.032405
H	0.411027	2.848899	1.097452

Table S26. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-CCC**.

MC-CCC			
E_{elec} = -940.90106			
E_{ZPE} = 0.334245			
Coordinates (Angstroms)			
	x	y	z
C	4.313825	-1.278382	0.887252
C	3.025608	-1.337354	1.306776
C	1.996900	-0.431293	0.815019
C	2.443956	0.580696	-0.161321
C	3.832623	0.614001	-0.531626
C	4.729945	-0.284010	-0.046446
C	1.622780	1.616221	-0.619111
C	0.243821	1.854812	-0.511211
C	-0.839578	1.000953	-0.376860
O	0.826216	-0.511211	1.236159
N	-0.937131	-0.275425	-0.809125
C	-2.183989	-0.833534	-0.469732
C	-2.968023	0.134323	0.154709
C	-2.171293	1.418462	0.261566
C	-2.644068	-2.122411	-0.696928
C	-3.941869	-2.424669	-0.284068
C	-4.741404	-1.466915	0.332639
C	-4.253999	-0.175699	0.554812
H	-4.880207	0.564982	1.039209
H	-5.744377	-1.725784	0.648513
H	-4.327358	-3.424688	-0.441550
H	-2.022444	-2.877979	-1.158787
H	-0.029309	2.906607	-0.521206
H	2.171432	2.452411	-1.051029
H	4.158439	1.379490	-1.231538
H	2.702760	-2.078766	2.027446
C	0.003752	-0.945087	-1.685014
H	0.543021	-0.196389	-2.261394
H	0.723669	-1.539936	-1.122367
H	-0.551323	-1.589357	-2.366499
C	-1.942740	1.821878	1.733428
H	-1.331393	2.724625	1.789672
H	-2.900487	2.022065	2.219528
H	-1.427173	1.029129	2.275010
C	-2.843174	2.568265	-0.517057
H	-3.813780	2.799135	-0.072831
H	-2.235017	3.474105	-0.478556
H	-3.002258	2.301243	-1.563109
O	6.063359	-0.312126	-0.386504
H	6.250890	0.404804	-1.002773
H	5.059793	-1.972562	1.257936

MC-CCC			
E_{elec} = -940.583921			
E_{ZPE} = 0.338309			
Coordinates (Angstroms)			
	x	y	z
C	4.185755	-1.308403	0.891051
C	2.902540	-1.325684	1.306640
C	1.906227	-0.377138	0.823327
C	2.388602	0.616177	-0.142180
C	3.782302	0.608263	-0.507091
C	4.642412	-0.318924	-0.031838
C	1.607092	1.672547	-0.601614
C	0.232033	1.918847	-0.512860
C	-0.826591	1.038239	-0.393260
O	0.741760	-0.425926	1.247977
N	-0.887252	-0.223634	-0.845920
C	-2.107238	-0.826887	-0.495370
C	-2.910382	0.104564	0.145323
C	-2.155367	1.404922	0.260952
C	-2.522020	-2.124463	-0.724943
C	-3.801048	-2.470836	-0.298981
C	-4.622465	-1.547103	0.332308
C	-4.176843	-0.246175	0.558781
H	-4.816056	0.473392	1.058589
H	-5.612193	-1.842436	0.657985
H	-4.155406	-3.482074	-0.458211
H	-1.879612	-2.855414	-1.198753
H	-0.053233	2.966847	-0.505221
H	2.177069	2.501294	-1.021032
H	4.133218	1.368429	-1.201012
H	2.551262	-2.062948	2.018462
C	0.068577	-0.856524	-1.717681
H	0.580963	-0.090344	-2.297202
H	0.813373	-1.423208	-1.155035
H	-0.464577	-1.522129	-2.396367
C	-1.913849	1.782889	1.729573
H	-1.330036	2.703719	1.791011
H	-2.869754	1.940444	2.235090
H	-1.360417	0.993712	2.238885
C	-2.866357	2.538808	-0.489905
H	-3.839859	2.728594	-0.032398
H	-2.286481	3.462796	-0.440708
H	-3.024659	2.280351	-1.538490
O	5.967885	-0.393878	-0.362333
H	6.184568	0.317521	-0.968359
H	4.905152	-2.033398	1.255680

Table S27. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and *ω*B97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-CCC***.

MC-CCC*			
E_{elec} = -940.89994			
E_{ZPE} = 0.333966			
Coordinates (Angstroms)			
	x	y	z
C	4.309587	-1.255893	0.885168
C	3.020779	-1.316205	1.311214
C	1.991420	-0.418868	0.811295
C	2.440556	0.585843	-0.170448
C	3.824579	0.622764	-0.543353
C	4.726054	-0.269993	-0.055710
C	1.617453	1.622240	-0.631890
C	0.240393	1.858081	-0.526618
C	-0.841359	1.000516	-0.383396
O	0.818493	-0.500644	1.230353
N	-0.938705	-0.274097	-0.816409
C	-2.182656	-0.835582	-0.470613
C	-2.964822	0.130052	0.159351
C	-2.169664	1.415302	0.262762
C	-2.641135	-2.125058	-0.697089
C	-3.935927	-2.430430	-0.277237
C	-4.733762	-1.474963	0.345307
C	-4.247895	-0.183033	0.566431
H	-4.872853	0.555718	1.055327
H	-5.734458	-1.736250	0.666388
H	-4.320512	-3.430896	-0.434027
H	-2.020680	-2.878507	-1.163920
H	-0.036936	2.908626	-0.547341
H	2.167302	2.458078	-1.061821
H	4.162438	1.377760	-1.244605
H	2.703058	-2.053745	2.037978
C	0.002953	-0.944940	-1.690923
H	0.546029	-0.197071	-2.264552
H	0.719311	-1.541728	-1.125868
H	-0.552011	-1.587022	-2.374549
C	-1.932605	1.818315	1.733467
H	-1.322885	2.722354	1.786097
H	-2.887813	2.016237	2.225427
H	-1.411608	1.026349	2.270906
C	-2.847613	2.564694	-0.511452
H	-3.816074	2.793386	-0.061532
H	-2.240857	3.471508	-0.475376
H	-3.012089	2.298324	-1.556828
O	6.036610	-0.204768	-0.478304
H	6.559206	-0.858815	-0.002663
H	5.043528	-1.959373	1.271820

MC-CCC*			
E_{elec} = -940.582601			
E_{ZPE} = 0.337889			
Coordinates (Angstroms)			
	x	y	z
C	4.177375	-1.288069	0.888943
C	2.892779	-1.304643	1.309866
C	1.897051	-0.364136	0.818361
C	2.383369	0.621572	-0.150092
C	3.772576	0.617251	-0.514880
C	4.636410	-0.306469	-0.038613
C	1.601166	1.681422	-0.613336
C	0.229141	1.924528	-0.532406
C	-0.828075	1.038613	-0.402035
O	0.728735	-0.414754	1.238933
N	-0.889295	-0.219291	-0.858217
C	-2.104866	-0.827863	-0.498938
C	-2.904515	0.099552	0.151466
C	-2.151429	1.401113	0.263843
C	-2.517437	-2.125786	-0.729473
C	-3.791641	-2.477105	-0.293393
C	-4.609943	-1.557507	0.348101
C	-4.166392	-0.256009	0.574923
H	-4.803252	0.460024	1.082679
H	-5.595962	-1.856752	0.681389
H	-4.144806	-3.488697	-0.452905
H	-1.877146	-2.852989	-1.211793
H	-0.061640	2.970977	-0.540348
H	2.174235	2.511361	-1.024940
H	4.137647	1.367507	-1.208108
H	2.545359	-2.038834	2.026658
C	0.068256	-0.853460	-1.727779
H	0.587437	-0.087752	-2.301467
H	0.806644	-1.424433	-1.161233
H	-0.464680	-1.514380	-2.411179
C	-1.897580	1.777334	1.730953
H	-1.315332	2.699401	1.788165
H	-2.849554	1.932158	2.244618
H	-1.337409	0.988626	2.233461
C	-2.870416	2.535167	-0.479447
H	-3.840710	2.721437	-0.013881
H	-2.292481	3.460406	-0.432275
H	-3.036326	2.278843	-1.527384
O	5.942982	-0.290196	-0.453006
H	6.443361	-0.940054	0.042715
H	4.880983	-2.025236	1.269536

Table S28. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-TCC**.

MC-TCC			
E_{elec} = -940.88744			
E_{ZPE} = 0.33368			
Coordinates (Angstroms)			
	x	y	z
C	-3.472627	-1.865837	0.012607
C	-2.605544	-0.798684	0.153571
C	-3.054339	0.494238	-0.108043
C	-4.362548	0.759215	-0.491363
C	-5.228667	-0.326575	-0.622217
C	-4.793872	-1.625065	-0.375656
C	-1.145687	-0.756407	0.570533
C	-0.846441	0.760089	0.463780
C	-1.991500	1.390321	0.071295
O	1.150913	0.427977	-1.646022
N	2.237899	0.227577	-1.084435
C	2.469662	0.414914	0.369075
C	1.570850	1.111108	1.169569
C	0.225866	1.479317	0.958477
C	3.771525	0.111467	0.905229
C	4.782425	-0.344738	0.123779
C	4.592814	-0.486561	-1.286270
C	3.405541	-0.180219	-1.860028
H	-3.140384	-2.880145	0.201442
H	-5.483168	-2.453338	-0.482868
H	-6.255401	-0.151066	-0.919775
H	-4.712241	1.765676	-0.680728
H	-0.026795	2.464849	1.343907
H	2.018013	1.564949	2.054705
H	3.931671	0.253002	1.970984
H	5.431369	-0.836235	-1.878173
C	3.253849	-0.279796	-2.927741
H	6.035210	-0.676898	0.583448
H	6.071515	-0.543747	1.537455
H	-2.089263	2.813794	-0.179363
C	-2.339038	3.369919	0.729902
H	-1.136500	3.172326	-0.567235
H	-2.862020	2.996352	-0.924455
H	-1.001504	-1.168640	2.055346
C	-1.310768	-2.208504	2.180699
H	0.037880	-1.073207	2.372520
H	-1.619849	-0.547095	2.705416
H	-0.305956	-1.703570	-0.304956
O	-0.318698	-1.407067	-1.350267
H	0.729256	-1.728740	0.030940
H	-0.717975	-2.711545	-0.213026

MC-TCC			
E_{elec} = -940.56950			
E_{ZPE} = 0.33758			
Coordinates (Angstroms)			
	x	y	z
C	-3.363772	-1.919978	-0.050731
C	-2.543673	-0.824585	0.105726
C	-3.056140	0.455071	-0.060901
C	-4.387591	0.676954	-0.366432
C	-5.208085	-0.437939	-0.515707
C	-4.708637	-1.722852	-0.361399
C	-1.069188	-0.745014	0.442082
C	-0.855184	0.781417	0.468350
C	-2.031555	1.383250	0.123805
O	1.220512	0.774289	-1.659495
N	2.242706	0.430344	-1.074359
C	2.415622	0.447717	0.400487
C	1.520212	1.073807	1.230437
C	0.185625	1.499351	0.982767
C	3.680302	0.010165	0.954531
C	4.686511	-0.426749	0.174803
C	4.547406	-0.425168	-1.256143
C	3.417829	0.005575	-1.841679
H	-2.972823	-2.924550	0.069482
H	-5.366345	-2.574971	-0.479715
H	-6.255249	-0.294520	-0.754025
H	-4.790836	1.675084	-0.481534
H	-0.055693	2.487721	1.365132
H	1.921584	1.374959	2.199573
H	3.795887	0.030568	2.035125
H	5.389824	-0.773194	-1.843751
C	3.306556	0.015357	-2.918955
H	5.891246	-0.877661	0.629859
H	5.904316	-0.842268	1.588802
H	-2.189656	2.806226	-0.019026
C	-2.381861	3.293832	0.942691
H	-1.280553	3.222983	-0.454724
H	-3.022210	3.013282	-0.690003
H	-0.801648	-1.313465	1.844532
C	-1.058509	-2.375135	1.867316
H	0.254521	-1.206300	2.099033
H	-1.396701	-0.798008	2.600575
H	-0.258982	-1.531524	-0.596968
O	-0.330559	-1.085901	-1.586824
H	0.791631	-1.578797	-0.313319
H	-0.648111	-2.552030	-0.636640

Table S29. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) level of theory, for **MC-TCC***.

MC-TCC*			
E_{elec} = -940.88620			
E_{ZPE} = 0.33338			
Coordinates (Angstroms)			
	x	y	z
C	-3.462084	-1.850510	0.002499
C	-2.588973	-0.791040	0.164881
C	-3.007471	0.500268	-0.147387
C	-4.290261	0.774668	-0.601543
C	-5.163319	-0.302772	-0.752785
C	-4.758187	-1.600912	-0.457534
C	-1.155170	-0.752955	0.660616
C	-0.823144	0.752940	0.505688
C	-1.940423	1.387456	0.064699
O	1.041177	0.350683	-1.555614
N	2.164661	0.191863	-1.043850
C	2.460957	0.396087	0.390245
C	1.587777	1.112566	1.213221
C	0.244890	1.470612	1.033686
C	3.779633	0.113794	0.878397
C	4.767121	-0.334743	0.060494
C	4.519392	-0.476401	-1.336973
C	3.303322	-0.185419	-1.867472
H	-3.153524	-2.864520	0.228759
H	-5.452288	-2.422650	-0.582790
H	-6.171291	-0.121505	-1.105695
H	-4.615300	1.781208	-0.830234
H	-0.020403	2.442080	1.445527
H	2.068283	1.595292	2.063864
H	3.995230	0.260322	1.930879
H	5.326070	-0.815319	-1.983141
C	3.113623	-0.289487	-2.928612
H	6.006200	-0.623990	0.590476
H	6.603074	-0.889159	-0.117013
H	-2.007340	2.805651	-0.229663
C	-2.321100	3.385286	0.643744
H	-1.024501	3.145390	-0.552699
H	-2.719803	2.972263	-1.036272
H	-1.110702	-1.080791	2.174856
C	-1.454254	-2.104302	2.338395
H	-0.089612	-0.989588	2.547467
H	-1.750205	-0.409316	2.750698
H	-0.281004	-1.764239	-0.100185
O	-0.253229	-1.551986	-1.164913
H	0.739600	-1.759313	0.279042
H	-0.697005	-2.762440	0.058054

Table S30. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-CTC**.

MC-CTC			
E_{elec} = -940.90895			
E_{ZPE} = 0.33442			
Coordinates (Angstroms)			
	x	y	z
C	4.670244	-0.843546	0.199716
C	3.355657	-0.434183	0.084322
C	3.058564	0.922032	-0.048990
C	4.052325	1.892417	-0.055167
C	5.375836	1.465269	0.063418
C	5.687612	0.115665	0.188029
C	2.065863	-1.228387	0.066472
C	1.013061	-0.113946	-0.056075
C	1.665974	1.088458	-0.162641
O	-2.514852	-2.226500	-0.307030
N	-3.264434	-1.247893	-0.159628
C	-2.780753	0.145299	0.006506
C	-1.434801	0.485093	0.024912
C	-0.333137	-0.391510	-0.055563
C	-3.751266	1.196755	0.162009
C	-5.084831	0.949117	0.162453
C	-5.569527	-0.388329	0.007732
C	-4.712763	-1.424819	-0.141571
H	4.916711	-1.894532	0.299649
H	6.721382	-0.192739	0.281022
H	6.169825	2.202227	0.062913
H	3.825883	2.947433	-0.136835
H	-0.591056	-1.440708	-0.082353
H	-1.242412	1.543574	0.161155
H	-3.388962	2.214820	0.283505
H	-6.643055	-0.540789	0.015273
C	-5.070126	-2.440327	-0.258736
H	-6.057766	1.910180	0.306356
H	-5.642642	2.774235	0.406982
H	1.058992	2.366728	-0.477061
C	0.253653	2.222572	-1.196483
H	0.659486	2.860749	0.413114
H	1.808032	3.015259	-0.927692
H	2.001656	-2.172043	-1.154625
C	2.793149	-2.921906	-1.086896
H	1.041405	-2.688520	-1.192835
H	2.133835	-1.620350	-2.086801
H	1.873165	-2.031152	1.368784
O	1.907939	-1.378813	2.242871
H	0.912832	-2.548643	1.363848
H	2.664478	-2.777596	1.468131

MC-CTC			
E_{elec} = -940.58599			
E_{ZPE} = 0.33846			
Coordinates (Angstroms)			
	x	y	z
C	-4.657172	0.816545	0.225013
C	-3.343809	0.422732	0.097733
C	-3.030847	-0.921667	-0.055949
C	-4.007658	-1.901282	-0.070211
C	-5.332649	-1.491933	0.060255
C	-5.659975	-0.152127	0.204737
C	-2.070178	1.231133	0.083240
C	-1.008447	0.136130	-0.050936
C	-1.640987	-1.069142	-0.177904
O	2.519045	2.218757	-0.357859
N	3.251895	1.243085	-0.187075
C	2.760337	-0.135840	0.016747
C	1.423227	-0.456189	0.047411
C	0.324253	0.430134	-0.045232
C	3.724782	-1.196859	0.197561
C	5.051141	-0.961717	0.187458
C	5.546064	0.372206	-0.004482
C	4.705727	1.407719	-0.177896
H	-4.910223	1.864829	0.340507
H	-6.697234	0.141398	0.307020
H	-6.117977	-2.238219	0.053680
H	-3.766882	-2.952465	-0.165873
H	0.575504	1.481069	-0.067138
H	1.214668	-1.508306	0.214553
H	3.351136	-2.207276	0.346430
H	6.621255	0.514219	-0.003678
C	5.072304	2.416492	-0.322742
H	6.017188	-1.913972	0.351391
H	5.602989	-2.769972	0.478584
H	-1.027181	-2.315401	-0.565093
C	-0.217226	-2.119320	-1.268344
H	-0.632896	-2.865607	0.293749
H	-1.768693	-2.936788	-1.066039
H	-2.023125	2.174207	-1.129252
C	-2.828428	2.909068	-1.056921
H	-1.070712	2.706077	-1.166116
H	-2.147173	1.619896	-2.061260
H	-1.885513	2.020502	1.385283
O	-1.905379	1.356927	2.251551
H	-0.933259	2.553604	1.379597
H	-2.689967	2.751828	1.493631

Table S31. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-CTC***.

	MC-CTC*		
	E_{elec} = -940.90799		
	E_{ZPE} = 0.33418		
	Coordinates (Angstroms)		
	x	y	z
C	4.670244	-0.843546	0.199716
C	3.355657	-0.434183	0.084322
C	3.058564	0.922032	-0.048990
C	4.052325	1.892417	-0.055167
C	5.375836	1.465269	0.063418
C	5.687612	0.115665	0.188029
C	2.065863	-1.228387	0.066472
C	1.013061	-0.113946	-0.056075
C	1.665974	1.088458	-0.162641
O	-2.514852	-2.226500	-0.307030
N	-3.264434	-1.247893	-0.159628
C	-2.780753	0.145299	0.006506
C	-1.434801	0.485093	0.024912
C	-0.333137	-0.391510	-0.055563
C	-3.751266	1.196755	0.162009
C	-5.084831	0.949117	0.162453
C	-5.569527	-0.388329	0.007732
C	-4.712763	-1.424819	-0.141571
H	4.916711	-1.894532	0.299649
H	6.721382	-0.192739	0.281022
H	6.169825	2.202227	0.062913
H	3.825883	2.947433	-0.136835
H	-0.591056	-1.440708	-0.082353
H	-1.242412	1.543574	0.161155
H	-3.388962	2.214820	0.283505
H	-6.643055	-0.540789	0.015273
C	-5.070126	-2.440327	-0.258736
H	-6.057766	1.910180	0.306356
H	-5.642642	2.774235	0.406982
H	1.058992	2.366728	-0.477061
C	0.253653	2.222572	-1.196483
H	0.659486	2.860749	0.413114
H	1.808032	3.015259	-0.927692
H	2.001656	-2.172043	-1.154625
C	2.793149	-2.921906	-1.086896
H	1.041405	-2.688520	-1.192835
H	2.133835	-1.620350	-2.086801
H	1.873165	-2.031152	1.368784
O	1.907939	-1.378813	2.242871
H	0.912832	-2.548643	1.363848
H	2.664478	-2.777596	1.468131

	MC-CTC*		
	E_{elec} = -940.58467		
	E_{ZPE} = 0.33815		
	Coordinates (Angstroms)		
	x	y	z
C	4.672589	-0.842477	0.197452
C	3.357717	-0.433655	0.082998
C	3.059868	0.922494	-0.048405
C	4.052804	1.893651	-0.053481
C	5.376529	1.467140	0.064185
C	5.689174	0.117485	0.186776
C	2.068207	-1.228032	0.065108
C	1.015466	-0.113870	-0.056502
C	1.666751	1.088091	-0.161345
O	-2.513971	-2.227560	-0.305785
N	-3.261577	-1.246118	-0.158277
C	-2.779053	0.146340	0.007584
C	-1.430672	0.484895	0.025721
C	-0.331806	-0.392227	-0.057010
C	-3.741250	1.201071	0.162704
C	-5.076031	0.961144	0.162705
C	-5.560681	-0.375667	0.008653
C	-4.709023	-1.419310	-0.140214
H	4.919782	-1.893416	0.296010
H	6.723192	-0.190321	0.279042
H	6.170059	2.204573	0.064587
H	3.825544	2.948576	-0.133522
H	-0.590085	-1.441366	-0.086505
H	-1.239036	1.542962	0.163012
H	-3.391062	2.220374	0.284293
H	-6.634770	-0.547364	0.012897
C	-5.072173	-2.432761	-0.256654
H	-5.954018	2.011831	0.312670
H	-6.857763	1.679822	0.299944
H	1.058523	2.367698	-0.470703
C	0.253279	2.225962	-1.190576
H	0.658567	2.857098	0.421544
H	1.807297	3.018332	-0.918480
H	2.003286	-2.171092	-1.156431
C	2.794848	-2.920921	-1.089275
H	1.043044	-2.687578	-1.194408
H	2.135097	-1.619035	-2.088439
H	1.875605	-2.031201	1.367293
O	1.910753	-1.379167	2.241573
H	0.915155	-2.548452	1.362353
H	2.666891	-2.777739	1.466010

Table S32. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-TTC**.

MC-TTC			
E_{elec} = -940.91266			
E_{ZPE} = 0.33413			
Coordinates (Angstroms)			
	x	y	z
C	-4.321075	-1.493742	-0.000063
C	-3.177609	-0.718687	-0.000022
C	-3.277015	0.673491	0.000035
C	-4.509175	1.316054	0.000041
C	-5.655841	0.521451	-0.000002
C	-5.570959	-0.866982	-0.000051
C	-1.711461	-1.120230	-0.000038
C	-1.020023	0.253669	0.000026
C	-1.989428	1.225106	0.000092
O	2.535423	2.376698	-0.000250
N	3.263067	1.369751	0.000103
C	2.747672	-0.021736	0.000074
C	1.393789	-0.326556	0.000049
C	0.315907	0.578830	0.000035
C	3.692748	-1.106972	0.000106
C	5.032042	-0.892143	0.000056
C	5.547501	0.442549	-0.000079
C	4.714994	1.509491	-0.000114
H	-4.258517	-2.576194	-0.000108
H	-6.474546	-1.463485	-0.000085
H	-6.627874	0.999677	0.000001
H	-4.595123	2.394571	0.000070
H	0.593175	1.622523	0.000053
H	1.165833	-1.387686	0.000058
H	3.306059	-2.123208	0.000150
H	6.624542	0.568115	-0.000173
C	5.096521	2.522978	-0.000260
H	5.982591	-1.885810	0.000065
H	5.547427	-2.745874	0.000132
H	-1.697205	2.646658	0.000160
C	-1.118490	2.920214	0.885173
H	-1.118975	2.920427	-0.885109
H	-2.627468	3.207207	0.000492
H	-1.377463	-1.928609	1.272765
C	-1.968323	-2.846977	1.292735
H	-0.323084	-2.201742	1.309889
H	-1.611183	-1.355955	2.171442
H	-1.377472	-1.928490	-1.272921
O	-1.611182	-1.355744	-2.171541
H	-0.323099	-2.201639	-1.310072
H	-1.968349	-2.846846	-1.292982

MC-TTC			
E_{elec} = -940.59007			
E_{ZPE} = 0.33793			
Coordinates (Angstroms)			
	x	y	z
C	4.273433	-1.514581	0.000069
C	3.150046	-0.718449	0.000015
C	3.272044	0.665807	-0.000033
C	4.510149	1.284713	-0.000016
C	5.639268	0.470308	0.000039
C	5.530730	-0.912495	0.000079
C	1.683970	-1.095846	0.000002
C	1.017775	0.283868	-0.000047
C	1.996918	1.236609	-0.000096
O	-2.545344	2.379188	0.000087
N	-3.252653	1.369373	-0.000041
C	-2.725284	-0.011000	-0.000028
C	-1.380124	-0.295385	-0.000031
C	-0.305844	0.621657	-0.000041
C	-3.660386	-1.112586	-0.000023
C	-4.992794	-0.913778	0.000015
C	-5.522740	0.420339	0.000074
C	-4.710227	1.492288	0.000072
H	4.185129	-2.595726	0.000105
H	6.423994	-1.524387	0.000122
H	6.619937	0.930761	0.000054
H	4.615501	2.361885	-0.000036
H	-0.580567	1.665914	-0.000047
H	-1.137216	-1.353879	-0.000031
H	-3.258971	-2.123273	-0.000043
H	-6.601477	0.532379	0.000128
C	-5.104073	2.501188	0.000134
H	-5.933260	-1.904897	0.000028
H	-5.496379	-2.759125	-0.000003
H	1.720225	2.652661	-0.000169
C	1.144353	2.931160	-0.885990
H	1.144687	2.931339	0.885816
H	2.655291	3.206423	-0.000410
H	1.345281	-1.892080	-1.270078
C	1.931253	-2.813848	-1.291697
H	0.288880	-2.157835	-1.310706
H	1.585684	-1.314447	-2.164011
H	1.345245	-1.892016	1.270112
O	1.585616	-1.314334	2.164023
H	0.288846	-2.157776	1.310721
H	1.931223	-2.813778	1.291798

Table S33. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-TTC***.

MC-TTC*			
E_{elec} = -940.91156			
E_{ZPE} = 0.33389			
Coordinates (Angstroms)			
	x	y	z
C	-4.322572	-1.494716	0.000007
C	-3.179087	-0.719612	0.000086
C	-3.278945	0.672386	0.000046
C	-4.510819	1.315259	-0.000150
C	-5.657467	0.520650	-0.000243
C	-5.572320	-0.867797	-0.000151
C	-1.712980	-1.120817	0.000133
C	-1.022303	0.253206	0.000189
C	-1.990792	1.223996	0.000197
O	2.534081	2.377322	0.000028
N	3.259891	1.367740	0.000007
C	2.746042	-0.023281	0.000055
C	1.389833	-0.327134	0.000123
C	0.314625	0.578897	0.000190
C	3.683144	-1.111154	-0.000010
C	5.023434	-0.903375	-0.000092
C	5.538338	0.430737	-0.000085
C	4.710724	1.504308	-0.000039
H	-4.259977	-2.577130	0.000077
H	-6.475897	-1.464326	-0.000207
H	-6.629549	0.998755	-0.000396
H	-4.596672	2.393785	-0.000242
H	0.592371	1.622543	0.000153
H	1.162638	-1.388056	0.000113
H	3.308976	-2.129114	0.000008
H	6.616303	0.576249	-0.000098
C	5.097670	2.515654	-0.000023
H	5.877413	-1.984103	-0.000165
H	6.788830	-1.673559	-0.000270
H	-1.698914	2.645854	0.000042
C	-1.120298	2.919448	0.885029
H	-1.120762	2.919409	-0.885263
H	-2.629395	3.206012	0.000319
H	-1.378513	-1.929148	1.272959
C	-1.969782	-2.847192	1.292889
H	-0.324451	-2.203142	1.309480
H	-1.611773	-1.356481	2.171780
H	-1.378533	-1.928837	-1.272963
O	-1.611821	-1.355912	-2.171609
H	-0.324466	-2.202805	-1.309557
H	-1.969818	-2.846862	-1.293103

MC-TTC*			
E_{elec} = -940.58862			
E_{ZPE} = 0.33761			
Coordinates (Angstroms)			
	x	y	z
C	-4.274886	-1.515777	-0.000023
C	-3.151423	-0.719576	-0.000028
C	-3.273922	0.664445	0.000012
C	-4.511647	1.283811	0.000049
C	-5.640784	0.469430	0.000055
C	-5.531990	-0.913421	0.000022
C	-1.685349	-1.096580	-0.000105
C	-1.020104	0.283321	-0.000048
C	-1.997910	1.235237	0.000029
O	2.543179	2.380164	-0.000230
N	3.248777	1.367567	0.000030
C	2.723701	-0.011860	0.000064
C	1.375923	-0.295658	0.000034
C	0.304809	0.621697	-0.000034
C	3.650959	-1.115663	0.000152
C	4.984274	-0.925019	0.000147
C	5.513055	0.408896	0.000023
C	4.705040	1.486952	-0.000066
H	-4.186578	-2.596878	-0.000060
H	-6.425288	-1.525279	0.000025
H	-6.621491	0.929768	0.000082
H	-4.616870	2.360994	0.000067
H	0.580192	1.665898	-0.000038
H	1.134163	-1.354092	0.000091
H	3.262644	-2.128648	0.000213
H	6.592586	0.543725	-0.000010
C	5.104625	2.493540	-0.000185
H	5.828326	-2.002794	0.000232
H	6.737417	-1.699543	0.000159
H	-1.721569	2.651676	0.000086
C	-1.145692	2.930038	0.885849
H	-1.146168	2.930229	-0.885929
H	-2.656834	3.205046	0.000409
H	-1.345950	-1.892582	1.270080
C	-1.932155	-2.814129	1.291758
H	-0.289822	-2.159078	1.310063
H	-1.585960	-1.314914	2.164132
H	-1.346079	-1.892442	-1.270415
O	-1.586128	-1.314651	-2.164376
H	-0.289972	-2.158994	-1.310517
H	-1.932335	-2.813955	-1.292164

Table S34. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-CCT**.

MC-CCT			
E_{elec} = -940.89859			
E_{ZPE} = 0.334063			
Coordinates (Angstroms)			
	x	y	z
C	-4.344342	1.449089	0.476411
C	-4.787180	0.357013	-0.181279
C	-3.897484	-0.756320	-0.518291
C	-2.482903	-0.627665	-0.059227
C	-2.083827	0.568083	0.637462
C	-2.974378	1.555086	0.900510
C	-1.672955	-1.724494	-0.244614
C	-0.286608	-1.910994	0.048199
C	0.790848	-1.078092	-0.061629
O	-4.305907	-1.726101	-1.160692
N	0.882265	0.090281	-0.787131
C	2.139718	0.689600	-0.607360
C	2.936296	-0.116682	0.206641
C	2.156194	-1.359604	0.592852
C	2.603387	1.893098	-1.123272
C	3.907502	2.275657	-0.805194
C	4.713991	1.480307	0.002157
C	4.226792	0.272139	0.511215
H	4.860652	-0.347155	1.136032
H	5.721437	1.798606	0.239149
H	4.292221	3.211566	-1.192113
H	1.980583	2.525493	-1.742644
H	-0.040837	-2.906007	0.410081
H	-2.209309	-2.610843	-0.575408
H	-1.066322	0.647645	1.005145
H	-5.818430	0.264114	-0.498201
C	-0.010696	0.465285	-1.871307
H	-0.466548	-0.433607	-2.284152
H	-0.810224	1.130344	-1.540358
H	0.571581	0.958238	-2.649338
C	2.021894	-1.503330	2.120172
H	1.398661	-2.362660	2.374609
H	3.004682	-1.648305	2.574563
H	1.571189	-0.613578	2.562689
C	2.805466	-2.626544	-0.005833
H	3.805231	-2.767214	0.411151
H	2.213466	-3.513880	0.227117
H	2.896613	-2.548538	-1.090189
O	-2.680011	2.703023	1.592356
H	-1.755478	2.686353	1.866204
H	-5.007964	2.272286	0.716586

MC-CCT			
E_{elec} = -940.58245			
E_{ZPE} = 0.33817			
Coordinates (Angstroms)			
	x	y	z
C	-4.178841	1.522501	0.471951
C	-4.677421	0.467048	-0.188071
C	-3.852977	-0.708814	-0.497873
C	-2.443335	-0.661959	-0.020639
C	-1.984097	0.507349	0.696491
C	-2.809432	1.542532	0.932580
C	-1.681327	-1.769976	-0.231020
C	-0.291696	-1.966713	0.082381
C	0.759876	-1.124793	-0.061658
O	-4.310874	-1.649940	-1.130364
N	0.811708	0.036319	-0.799503
C	2.046504	0.670610	-0.626952
C	2.867989	-0.104040	0.183812
C	2.132039	-1.363736	0.577990
C	2.469216	1.882513	-1.144639
C	3.759917	2.303100	-0.832556
C	4.591324	1.537326	-0.028808
C	4.143209	0.320076	0.483919
H	4.793165	-0.282421	1.109461
H	5.589640	1.886960	0.202838
H	4.115098	3.249343	-1.222918
H	1.823536	2.494267	-1.762168
H	-0.046411	-2.942871	0.491343
H	-2.225919	-2.630701	-0.612456
H	-0.968045	0.519748	1.076836
H	-5.705286	0.440360	-0.527961
C	-0.082755	0.366787	-1.885489
H	-0.506723	-0.551135	-2.292609
H	-0.905903	1.009704	-1.565827
H	0.486757	0.868564	-2.668278
C	2.013643	-1.500655	2.099445
H	1.422763	-2.380289	2.363023
H	3.004894	-1.605744	2.547021
H	1.532823	-0.622838	2.534977
C	2.809381	-2.603913	-0.024042
H	3.818000	-2.712454	0.381853
H	2.244687	-3.507515	0.215913
H	2.883703	-2.520168	-1.109567
O	-2.469267	2.668208	1.619913
H	-1.554146	2.605450	1.903795
H	-4.790766	2.389897	0.693923

Table S35. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-CCT***.

MC-CCT*			
E_{elec} = -940.89730			
E_{ZPE} = 0.33382			
Coordinates (Angstroms)			
	x	y	z
C	4.358672	1.424317	0.477859
C	4.800789	0.321194	-0.166895
C	3.900975	-0.778843	-0.513329
C	2.486194	-0.626736	-0.070342
C	2.091279	0.573386	0.613622
C	2.986665	1.554948	0.881965
C	1.666441	-1.722021	-0.252676
C	0.280599	-1.904957	0.021372
C	-0.798888	-1.066894	-0.072056
O	4.305400	-1.755831	-1.150680
N	-0.899475	0.104247	-0.783012
C	-2.160913	0.695134	-0.597422
C	-2.950789	-0.123835	0.209315
C	-2.157578	-1.359015	0.591188
C	-2.631851	1.899117	-1.104305
C	-3.939300	2.268359	-0.785304
C	-4.740790	1.459399	0.013728
C	-4.245039	0.251611	0.514863
H	-4.874334	-0.376764	1.135151
H	-5.751019	1.768015	0.251804
H	-4.330552	3.205026	-1.163646
H	-2.011394	2.542742	-1.714124
H	0.028040	-2.906252	0.360224
H	2.203713	-2.615364	-0.562785
H	1.077352	0.680660	0.976719
H	5.835687	0.215377	-0.467236
C	0.001460	0.515221	-1.846654
H	0.766187	1.209605	-1.494740
H	0.499234	-0.364715	-2.250676
H	-0.582844	0.988349	-2.635618
C	-2.800295	-2.634019	0.003725
H	-2.200184	-3.515843	0.236606
H	-3.795312	-2.780349	0.429875
H	-2.901225	-2.562285	-1.080231
C	-2.006906	-1.493492	2.118518
H	-2.984576	-1.643019	2.582360
H	-1.374959	-2.347200	2.370431
H	-1.558163	-0.598115	2.551188
O	2.572968	2.678009	1.560436
H	3.330694	3.243366	1.744188
H	5.048675	2.232381	0.710511

MC-CCT*			
E_{elec} = -940.58015			
E_{ZPE} = 0.33804			
Coordinates (Angstroms)			
	x	y	z
C	-4.211141	1.486359	0.474209
C	-4.698888	0.421474	-0.182955
C	-3.853247	-0.732848	-0.508696
C	-2.445622	-0.656522	-0.040381
C	-2.000025	0.518039	0.670637
C	-2.839118	1.538968	0.919926
C	-1.671117	-1.763265	-0.239767
C	-0.283813	-1.955658	0.061430
C	0.770266	-1.108242	-0.064935
O	-4.298504	-1.678634	-1.146729
N	0.833913	0.051635	-0.794329
C	2.075499	0.675146	-0.620465
C	2.887920	-0.109479	0.188489
C	2.134008	-1.355770	0.588618
C	2.509746	1.882685	-1.137348
C	3.805719	2.287502	-0.827588
C	4.629970	1.510523	-0.026959
C	4.168865	0.298794	0.486561
H	4.812124	-0.310801	1.112080
H	5.632619	1.848576	0.203294
H	4.170655	3.230817	-1.215932
H	1.868293	2.504364	-1.749037
H	-0.033174	-2.938796	0.449682
H	-2.215791	-2.633896	-0.598579
H	-0.986637	0.565059	1.048986
H	-5.730134	0.377075	-0.510438
C	-0.068092	0.410267	-1.864104
H	-0.517607	-0.495136	-2.271626
H	-0.871222	1.068381	-1.525472
H	0.501497	0.906183	-2.650458
C	1.994219	-1.468230	2.110931
H	1.389656	-2.337314	2.378608
H	2.978797	-1.577786	2.571958
H	1.517931	-0.578415	2.526288
C	2.803263	-2.611948	0.012172
H	3.806527	-2.723734	0.430114
H	2.228573	-3.506730	0.260975
H	2.889420	-2.546006	-1.073712
O	-2.394606	2.631020	1.609743
H	-3.124488	3.228851	1.779253
H	-4.860033	2.332015	0.691562

Table S36. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-TCT**.

MC-TCT			
E_{elec} = -940.89115			
E_{ZPE} = 0.33378			
Coordinates (Angstroms)			
	x	y	z
C	3.466591	-1.461974	1.138636
C	2.611089	-0.567662	0.525392
C	3.103811	0.331334	-0.420263
C	4.451246	0.368671	-0.759004
C	5.305671	-0.536686	-0.127486
C	4.826376	-1.444020	0.810742
C	1.108744	-0.378747	0.679660
C	0.860794	0.832448	-0.253055
C	2.050427	1.106951	-0.912595
O	-3.851863	1.728373	1.759840
N	-3.749181	0.856344	0.897272
C	-2.505371	0.666400	0.084898
C	-1.523904	1.608537	0.232779
C	-0.201862	1.684368	-0.331291
C	-2.460449	-0.405406	-0.877822
C	-3.519954	-1.228131	-1.055060
C	-4.721355	-1.071476	-0.276581
C	-4.841505	-0.082267	0.632276
H	3.096897	-2.168860	1.873022
H	5.507391	-2.134158	1.292702
H	6.360942	-0.524536	-0.372557
H	4.841832	1.075956	-1.478994
H	0.018340	2.658095	-0.763007
H	-1.838931	2.482950	0.800550
H	-1.584765	-0.497114	-1.510394
H	-5.531969	-1.766573	-0.465163
C	-5.745902	0.050855	1.212530
H	-3.575163	-2.237179	-1.982767
H	-2.745653	-2.269883	-2.473461
H	2.217832	2.180732	-1.863958
C	1.349277	2.228455	-2.522151
H	2.335952	3.152857	-1.370916
H	3.099608	1.991157	-2.473345
H	0.390015	-1.673082	0.245599
C	0.766309	-2.508946	0.839115
H	-0.684399	-1.602618	0.401884
H	0.580656	-1.899912	-0.805560
H	0.733518	-0.029671	2.133028
O	1.270125	0.856436	2.474732
H	-0.336430	0.159611	2.224145
H	0.991317	-0.860261	2.793866

MC-TCT			
E_{elec} = -940.57589			
E_{ZPE} = 0.33738			
Coordinates (Angstroms)			
	x	y	z
C	-3.408752	-1.410417	1.205220
C	-2.570524	-0.536378	0.551611
C	-3.063722	0.288708	-0.453758
C	-4.401436	0.269423	-0.812103
C	-5.241360	-0.615709	-0.139732
C	-4.759288	-1.449488	0.857123
C	-1.082309	-0.302501	0.721939
C	-0.851736	0.860425	-0.259277
C	-2.024962	1.053156	-0.976419
O	3.771369	1.534827	1.915301
N	3.680736	0.754198	0.983171
C	2.470118	0.679890	0.104320
C	1.489490	1.580611	0.321384
C	0.209069	1.680365	-0.374115
C	2.435035	-0.303995	-0.959301
C	3.468958	-1.136098	-1.159277
C	4.648066	-1.083100	-0.318592
C	4.760456	-0.194889	0.677565
H	-3.027902	-2.058238	1.987773
H	-5.431619	-2.126420	1.369147
H	-6.292358	-0.645639	-0.401949
H	-4.798261	0.919606	-1.581498
H	0.084015	2.588525	-0.957925
H	1.719613	2.350817	1.055751
H	1.562813	-0.329007	-1.603903
H	5.442791	-1.787642	-0.537971
C	5.641545	-0.146701	1.305055
H	3.537311	-2.074164	-2.142137
H	2.729272	-2.055149	-2.660520
H	-2.190542	2.096592	-1.947442
C	-2.261608	3.085835	-1.479021
H	-1.342882	2.099397	-2.636686
H	-3.094996	1.918430	-2.526300
H	-0.744354	0.107683	2.159886
C	-1.017455	-0.695877	2.848102
H	0.324016	0.300493	2.271764
H	-1.292231	1.006198	2.448036
H	-0.319229	-1.579582	0.340502
O	-0.488586	-1.841245	-0.706433
H	0.751134	-1.465450	0.505770
H	-0.674054	-2.409766	0.955703

Table S37. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and *ω*B97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-TCT***.

MC-TCT*			
E_{elec} = -940.88970			
E_{ZPE} = 0.33355			
Coordinates (Angstroms)			
	x	y	z
C	3.458744	1.473496	1.128845
C	2.605290	0.573385	0.521032
C	3.102411	-0.334262	-0.413230
C	4.450592	-0.375863	-0.747498
C	5.302879	0.534969	-0.121248
C	4.819684	1.451059	0.806617
C	1.101913	0.387932	0.667922
C	0.860154	-0.835330	-0.250707
C	2.050104	-1.116065	-0.900095
O	-3.862410	-1.761955	1.729494
N	-3.747903	-0.876478	0.879628
C	-2.500855	-0.675610	0.080854
C	-1.523969	-1.630839	0.216721
C	-0.195989	-1.702581	-0.316361
C	-2.440410	0.405499	-0.864712
C	-3.490909	1.240854	-1.039783
C	-4.695972	1.075128	-0.272062
C	-4.832883	0.070081	0.620585
H	3.086358	2.188510	1.853849
H	5.499104	2.145635	1.284504
H	6.359049	0.520678	-0.362167
H	4.842917	-1.089878	-1.459835
H	0.045886	-2.685484	-0.714048
H	-1.856810	-2.520572	0.749344
H	-1.571020	0.510025	-1.499392
H	-5.516295	1.769907	-0.438206
C	-5.744055	-0.065726	1.189405
H	-3.410659	2.237884	-1.983398
H	-4.251645	2.704137	-2.036823
H	2.221691	-2.191010	-1.850519
C	2.358994	-3.159311	-1.355330
H	1.346568	-2.251436	-2.498232
H	3.094232	-1.990575	-2.469782
H	0.716230	0.055877	2.122639
C	0.968004	0.895277	2.774548
H	-0.354230	-0.133131	2.207176
H	1.250703	-0.825398	2.479984
H	0.390672	1.680335	0.214340
O	0.573969	1.889566	-0.841131
H	-0.683194	1.621191	0.376331
H	0.777067	2.521765	0.793335

MC-TCT*			
E_{elec} = -940.57335			
E_{ZPE} = 0.33687			
Coordinates (Angstroms)			
	x	y	z
C	-3.384824	-1.419075	1.207046
C	-2.553391	-0.539683	0.551772
C	-3.057162	0.289491	-0.444027
C	-4.397394	0.271520	-0.791937
C	-5.230387	-0.618626	-0.117759
C	-4.738137	-1.457321	0.870116
C	-1.064121	-0.304126	0.710479
C	-0.845197	0.865119	-0.267760
C	-2.023636	1.059728	-0.969309
O	3.789972	1.599082	1.855754
N	3.677422	0.789190	0.949156
C	2.458983	0.692964	0.090403
C	1.494669	1.623742	0.278719
C	0.200718	1.710968	-0.375539
C	2.398620	-0.320641	-0.939546
C	3.417801	-1.172505	-1.130298
C	4.603612	-1.102408	-0.302171
C	4.742204	-0.180704	0.662342
H	-2.996530	-2.071776	1.981787
H	-5.405175	-2.138263	1.383803
H	-6.283527	-0.648850	-0.371093
H	-4.800608	0.926346	-1.554016
H	0.034134	2.640276	-0.913886
H	1.761125	2.434780	0.954765
H	1.532314	-0.361433	-1.587005
H	5.404372	-1.815358	-0.486213
C	5.632921	-0.123598	1.275282
H	3.348447	-2.105834	-2.122786
H	4.167036	-2.602872	-2.164681
H	-2.197802	2.088911	-1.954644
C	-2.304995	3.080690	-1.498962
H	-1.336472	2.105104	-2.625813
H	-3.085716	1.879442	-2.548835
H	-0.717533	0.109041	2.145897
C	-0.976630	-0.697664	2.835826
H	0.350021	0.312312	2.246325
H	-1.270865	1.002408	2.439672
H	-0.306253	-1.584415	0.329297
O	-0.459538	-1.840201	-0.720954
H	0.762228	-1.480247	0.510039
H	-0.676969	-2.413828	0.936112

Table S38. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-CTT**.

MC-CTT			
E_{elec} = -940.90963			
E_{ZPE} = 0.33442			
Coordinates (Angstroms)			
	x	y	z
C	4.611319	-1.095276	0.134648
C	3.318982	-0.614771	0.047336
C	3.087870	0.756940	-0.052887
C	4.132411	1.673106	-0.052679
C	5.433045	1.175279	0.037223
C	5.677423	-0.190765	0.128226
C	1.990346	-1.343158	0.035191
C	0.993522	-0.173169	-0.053821
C	1.705132	0.997473	-0.142412
O	-3.192302	2.700418	0.231708
N	-3.639038	1.550343	0.147195
C	-2.766221	0.350228	0.027134
C	-1.406760	0.585535	0.029780
C	-0.365911	-0.367326	-0.036885
C	-3.371367	-0.947640	-0.083732
C	-4.719456	-1.094202	-0.070904
C	-5.582626	0.046759	0.053856
C	-5.078903	1.295775	0.157551
H	4.803907	-2.159664	0.209433
H	6.694911	-0.554055	0.199236
H	6.263658	1.870684	0.040607
H	3.961854	2.739930	-0.108791
H	-0.654933	-1.411943	-0.038020
H	-1.165953	1.634859	0.126337
H	-2.740975	-1.825796	-0.183847
H	-6.651947	-0.132873	0.060107
C	-5.723498	2.160946	0.250144
H	-5.373259	-2.297227	-0.173080
H	-4.727418	-3.008499	-0.253567
H	1.156152	2.320118	-0.385123
C	0.376885	2.266755	-1.144521
H	0.734117	2.759456	0.521860
H	1.947475	2.968881	-0.753202
H	1.869864	-2.263163	-1.198441
C	2.631017	-3.045559	-1.157226
H	0.890363	-2.744164	-1.231695
H	2.007781	-1.702040	-2.123853
H	1.782681	-2.154557	1.329459
O	1.857447	-1.515972	2.210742
H	0.801793	-2.633364	1.337144
H	2.542075	-2.935753	1.408216

MC-CTT			
E_{elec} = -940.58733			
E_{ZPE} = 0.33845			
Coordinates (Angstroms)			
	x	y	z
C	4.595942	-1.074787	0.160921
C	3.305547	-0.605401	0.059190
C	3.062617	0.756104	-0.067630
C	4.093766	1.679016	-0.078845
C	5.395197	1.194270	0.025573
C	5.651033	-0.163683	0.142270
C	1.989871	-1.344104	0.054038
C	0.986573	-0.190002	-0.051172
C	1.682447	0.981682	-0.167823
O	-3.156826	2.682712	0.301466
N	-3.605925	1.545656	0.189702
C	-2.745621	0.346099	0.042546
C	-1.398170	0.568035	0.056516
C	-0.360419	-0.396877	-0.024748
C	-3.360047	-0.950500	-0.106244
C	-4.699998	-1.085196	-0.100169
C	-5.556285	0.063746	0.055235
C	-5.050977	1.300265	0.192025
H	4.791598	-2.137440	0.256171
H	6.671701	-0.515629	0.224634
H	6.220155	1.896506	0.020571
H	3.912221	2.743464	-0.152797
H	-0.648038	-1.442087	-0.014250
H	-1.144035	1.612337	0.184191
H	-2.732362	-1.827477	-0.231001
H	-6.626758	-0.110289	0.055260
C	-5.690925	2.166384	0.306637
H	-5.367030	-2.267230	-0.236086
H	-4.734329	-2.982088	-0.334123
H	1.128543	2.276738	-0.489011
C	0.331407	2.166028	-1.224358
H	0.729315	2.784200	0.392364
H	1.909501	2.895880	-0.927038
H	1.882369	-2.270090	-1.166581
C	2.655188	-3.040793	-1.117369
H	0.908285	-2.763027	-1.194981
H	2.013831	-1.711142	-2.094557
H	1.789281	-2.135656	1.352178
O	1.851616	-1.480776	2.222644
H	0.814652	-2.627743	1.361632
H	2.560912	-2.903724	1.443334

Table S39. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-CTT***.

MC-CTT*			
E_{elec} = -940.90852			
E_{ZPE} = 0.33413			
Coordinates (Angstroms)			
	x	y	z
C	4.610083	-1.103941	0.130120
C	3.319274	-0.618862	0.044934
C	3.093059	0.754043	-0.049249
C	4.140379	1.666908	-0.045238
C	5.439355	1.164442	0.042454
C	5.679038	-0.202846	0.127521
C	1.988260	-1.342451	0.030118
C	0.995983	-0.168926	-0.055071
C	1.710521	0.999179	-0.137270
O	-3.195909	2.705925	0.220061
N	-3.637549	1.552408	0.140043
C	-2.764390	0.353928	0.023921
C	-1.402939	0.592698	0.024809
C	-0.364942	-0.360266	-0.041468
C	-3.359299	-0.945811	-0.080584
C	-4.705808	-1.102673	-0.066339
C	-5.570229	0.036967	0.053937
C	-5.075273	1.292188	0.152110
H	4.799087	-2.169258	0.200222
H	6.695346	-0.569806	0.196730
H	6.272317	1.857008	0.048671
H	3.973426	2.734520	-0.097030
H	-0.657144	-1.403719	-0.047142
H	-1.163171	1.642543	0.118201
H	-2.739426	-1.828545	-0.176177
H	-6.645804	-0.125359	0.064043
C	-5.726082	2.152957	0.241313
H	-5.240736	-2.365857	-0.168691
H	-6.201972	-2.312926	-0.145069
H	1.164516	2.324950	-0.369122
C	0.390809	2.281003	-1.134916
H	0.735914	2.753462	0.539922
H	1.958977	2.977394	-0.723341
H	1.863576	-2.258200	-1.206325
C	2.621580	-3.043716	-1.167096
H	0.882316	-2.735158	-1.240850
H	2.004021	-1.695009	-2.130142
H	1.776634	-2.157078	1.322025
O	1.853921	-1.521589	2.205371
H	0.794020	-2.632042	1.327502
H	2.533010	-2.941416	1.398144

MC-CTT*			
E_{elec} = -940.58576			
E_{ZPE} = 0.33802			
Coordinates (Angstroms)			
	x	y	z
C	4.594595	-1.084011	0.158772
C	3.305892	-0.609834	0.057179
C	3.068146	0.753065	-0.063260
C	4.102081	1.672765	-0.068130
C	5.401703	1.183179	0.036133
C	5.652606	-0.176262	0.146459
C	1.987745	-1.343667	0.046419
C	0.989189	-0.185742	-0.055294
C	1.688168	0.983341	-0.164348
O	-3.158214	2.688570	0.287953
N	-3.602824	1.547929	0.181741
C	-2.744008	0.349559	0.038053
C	-1.394165	0.574184	0.047965
C	-0.359504	-0.390250	-0.033715
C	-3.349886	-0.948612	-0.102402
C	-4.688071	-1.093777	-0.093110
C	-5.544147	0.055261	0.058128
C	-5.045838	1.297458	0.187753
H	4.786449	-2.147753	0.249059
H	6.671966	-0.532036	0.228722
H	6.229048	1.882607	0.035986
H	3.924327	2.738171	-0.137326
H	-0.650162	-1.434397	-0.030077
H	-1.140954	1.619237	0.171411
H	-2.734330	-1.831582	-0.222738
H	-6.621289	-0.097626	0.064705
C	-5.691300	2.159842	0.299159
H	-5.238956	-2.337474	-0.228526
H	-6.194932	-2.272906	-0.205789
H	1.137544	2.282503	-0.474019
C	0.344948	2.180929	-1.215651
H	0.732939	2.779291	0.410985
H	1.921586	2.906279	-0.899492
H	1.877899	-2.263575	-1.178758
C	2.647430	-3.037627	-1.131326
H	0.901973	-2.752269	-1.210998
H	2.013628	-1.701054	-2.103987
H	1.781066	-2.140334	1.340617
O	1.844560	-1.489819	2.214320
H	0.804644	-2.628635	1.345536
H	2.549520	-2.911820	1.429332

Table S40. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-TTT**.

MC-TTT			
E_{elec} = -940.91154			
E_{ZPE} = 0.33411			
Coordinates (Angstroms)			
	x	y	z
C	-4.365945	-1.268168	-0.000004
C	-3.190731	-0.541863	-0.000005
C	-3.233398	0.852339	-0.000001
C	-4.437007	1.546234	0.000003
C	-5.616293	0.800360	0.000005
C	-5.588660	-0.590132	0.000002
C	-1.743654	-1.007847	-0.000019
C	-0.993784	0.336367	-0.000008
C	-1.922375	1.350530	0.000009
O	3.079315	-2.596315	-0.000034
N	3.565036	-1.459693	0.000119
C	2.733648	-0.224091	0.000049
C	1.367300	-0.407886	0.000035
C	0.357595	0.578607	0.000000
C	3.383501	1.057296	0.000023
C	4.735669	1.155809	-0.000005
C	5.559522	-0.020828	-0.000028
C	5.013302	-1.256079	-0.000003
H	-4.347891	-2.352130	-0.000011
H	-6.516088	-1.148841	0.000001
H	-6.567509	1.318749	0.000008
H	-4.479109	2.627548	0.000004
H	0.668305	1.616294	-0.000007
H	1.078888	-1.450871	0.000070
H	2.783424	1.962132	0.000011
H	6.634515	0.120915	-0.000080
C	5.628128	-2.147468	-0.000046
H	5.431063	2.339815	-0.000042
H	4.810387	3.077531	-0.000074
H	-1.577977	2.756503	0.000012
C	-0.994348	3.012875	0.888295
H	-0.994518	3.012932	-0.888370
H	-2.485513	3.353232	0.000122
H	-1.446821	-1.832174	1.272596
C	-2.089017	-2.715140	1.294353
H	-0.410882	-2.167667	1.303372
H	-1.645945	-1.247277	2.172053
H	-1.446848	-1.832166	-1.272643
O	-1.645961	-1.247253	-2.172093
H	-0.410920	-2.167690	-1.303433
H	-2.089068	-2.715114	-1.294407

MC-TTT			
E_{elec} = -940.58999			
E_{ZPE} = 0.33805			
Coordinates (Angstroms)			
	x	y	z
C	4.323970	-1.283879	0.000054
C	3.164892	-0.540384	-0.000004
C	3.224920	0.847445	-0.000078
C	4.433054	1.522607	-0.000086
C	5.598648	0.760815	-0.000024
C	5.552690	-0.625263	0.000044
C	1.718228	-0.987793	-0.000027
C	0.988389	0.360815	-0.000053
C	1.924414	1.360494	-0.000122
O	-3.033165	-2.583992	-0.000457
N	-3.524916	-1.459786	0.000510
C	-2.710560	-0.219261	0.000254
C	-1.356471	-0.387875	0.000140
C	-0.351255	0.612612	0.000014
C	-3.374175	1.062067	0.000266
C	-4.718171	1.144739	0.000170
C	-5.530582	-0.046285	-0.000090
C	-4.978891	-1.270335	-0.000118
H	4.284457	-2.367776	0.000103
H	6.472667	-1.196206	0.000090
H	6.557241	1.265637	-0.000029
H	4.490220	2.603599	-0.000133
H	-0.665129	1.649445	-0.000004
H	-1.055107	-1.428158	0.000199
H	-2.779395	1.970403	0.000283
H	-6.606984	0.086348	-0.000335
C	-5.585653	-2.167337	-0.000451
H	-5.430071	2.308263	0.000116
H	-4.825202	3.053342	0.000234
H	1.589412	2.760277	-0.000185
C	1.006917	3.018617	-0.889100
H	1.007045	3.018738	0.888779
H	2.499319	3.354566	-0.000295
H	1.418242	-1.801619	-1.269514
C	2.058797	-2.686057	-1.293203
H	0.381043	-2.134342	-1.302635
H	1.620820	-1.211015	-2.164668
H	1.418169	-1.801587	1.269462
O	1.620736	-1.210976	2.164614
H	0.380952	-2.134264	1.302546
H	2.058688	-2.686050	1.293187

Table S41. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for **MC-TTT***.

MC-TTT*			
E_{elec} = -940.91059			
E_{ZPE} = 0.33383			
Coordinates (Angstroms)			
	x	y	z
C	4.372785	-1.261074	-0.000042
C	3.194924	-0.539029	-0.000029
C	3.232551	0.855347	0.000030
C	4.433504	1.553784	0.000050
C	5.615442	0.812231	0.000039
C	5.592897	-0.578425	-0.000001
C	1.749542	-1.009767	-0.000123
C	0.995534	0.331783	-0.000043
C	1.919616	1.348639	0.000089
O	-3.086045	-2.601705	0.000145
N	-3.565080	-1.461203	0.000317
C	-2.732033	-0.228720	0.000096
C	-1.363675	-0.416156	0.000091
C	-0.357300	0.570960	-0.000037
C	-3.370659	1.054928	-0.000065
C	-4.721563	1.165433	-0.000098
C	-5.548035	-0.008535	-0.000020
C	-5.011505	-1.250182	0.000113
H	4.358728	-2.345100	-0.000099
H	6.522425	-1.133652	-0.000018
H	6.564766	1.334068	0.000052
H	4.471357	2.635221	0.000055
H	-0.671723	1.607188	-0.000088
H	-1.075572	-1.459284	0.000249
H	-2.780301	1.962823	-0.000192
H	-6.628619	0.116658	-0.000090
C	-5.633236	-2.136679	0.000124
H	-5.298396	2.414450	-0.000234
H	-6.257455	2.327604	-0.000500
H	1.569739	2.754211	0.000258
C	0.985669	3.008279	-0.888074
H	0.984443	3.007675	0.887945
H	2.475303	3.353850	0.001114
H	1.454888	-1.834746	-1.272799
C	2.099564	-2.715906	-1.294766
H	0.419800	-2.172962	-1.303288
H	1.652107	-1.249194	-2.172234
H	1.454729	-1.834903	1.272413
O	1.651942	-1.249504	2.171949
H	0.419596	-2.173009	1.302768
H	2.099314	-2.716133	1.294293

MC-TTT*			
E_{elec} = -940.58855			
E_{ZPE} = 0.33768			
Coordinates (Angstroms)			
	x	y	z
C	-4.330297	-1.277401	0.000199
C	-3.168792	-0.537634	0.000011
C	-3.224321	0.850341	-0.000135
C	-4.430104	1.529634	-0.000055
C	-5.598135	0.771680	0.000141
C	-5.556723	-0.614612	0.000262
C	-1.723549	-0.989194	-0.000097
C	-0.990179	0.357144	-0.000194
C	-1.921851	1.359011	-0.000336
O	3.037121	-2.589041	-0.000278
N	3.523286	-1.461185	0.000385
C	2.709085	-0.223194	0.000190
C	1.352612	-0.394276	0.000030
C	0.351057	0.606413	-0.000101
C	3.362900	1.059814	0.000264
C	4.705398	1.154164	0.000276
C	5.518965	-0.035594	0.000126
C	4.975354	-1.265320	0.000062
H	-4.294376	-2.361426	0.000299
H	-6.478635	-1.182449	0.000413
H	-6.555075	1.279624	0.000208
H	-4.483479	2.610785	-0.000116
H	0.668368	1.641918	-0.000092
H	1.051365	-1.434723	0.000032
H	2.779321	1.972300	0.000267
H	6.601186	0.076197	0.000016
C	5.588800	-2.157721	-0.000135
H	5.302072	2.383993	0.000284
H	6.255053	2.281749	0.000425
H	-1.582016	2.758547	-0.000557
C	-0.999004	3.014904	0.888263
H	-0.998161	3.014346	-0.888979
H	-2.490194	3.355391	-0.001203
H	-1.425359	-1.803636	1.269444
C	-2.068267	-2.686363	1.293402
H	-0.388968	-2.138910	1.302110
H	-1.625952	-1.212374	2.164597
H	-1.425596	-1.803699	-1.269658
O	-1.626327	-1.212468	-2.164801
H	-0.389224	-2.139009	-1.302491
H	-2.068535	-2.686407	-1.293470

Table S42. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(1a*-CCC)**.

TS(1a*-CCC)			
E_{elec} = -940.894629			
E_{ZPE} = 0.333621			
Coordinates (Angstroms)			
	x	y	z
C	-3.969755	-1.259012	-1.175764
C	-2.632996	-1.130831	-1.455799
C	-1.778358	-0.273749	-0.693863
C	-2.411367	0.530807	0.318060
C	-3.805209	0.397199	0.553354
C	-4.568281	-0.493798	-0.156213
C	-1.690623	1.602570	0.922981
C	-0.350730	1.841542	0.875062
C	0.681955	0.926886	0.460401
O	-0.518125	-0.228005	-0.938441
N	1.018974	-0.192441	1.126100
C	2.199435	-0.758686	0.598821
C	2.753061	0.124093	-0.325265
C	1.883967	1.363127	-0.393955
C	2.784830	-1.976844	0.903636
C	3.972796	-2.300268	0.245578
C	4.540278	-1.429987	-0.679511
C	3.930155	-0.205464	-0.968902
H	4.375388	0.465479	-1.694557
H	5.458138	-1.705797	-1.183783
H	4.452266	-3.248787	0.454736
H	2.339434	-2.666427	1.608510
H	-0.003541	2.839473	1.123015
H	-2.297008	2.384548	1.374558
H	-4.266229	1.022110	1.314514
H	-2.175244	-1.710952	-2.247705
C	0.174435	-0.885130	2.079079
H	-0.468204	-0.161795	2.574464
H	-0.449072	-1.622802	1.569051
H	0.800515	-1.380261	2.820879
C	1.489612	1.771976	-1.819446
H	0.811274	2.627089	-1.793864
H	2.382600	2.062324	-2.378211
H	0.986836	0.954153	-2.329362
C	2.606657	2.542580	0.309048
H	3.526446	2.770898	-0.231813
H	1.985166	3.439716	0.306451
H	2.871105	2.299178	1.339626
O	-5.920549	-0.685178	0.050737
H	-6.220817	-0.093033	0.748600
H	-4.591662	-1.944628	-1.740000

TS(1a-CCC*)			
E_{elec} = -940.579379			
E_{ZPE} = 0.337475			
Coordinates (Angstroms)			
	x	y	z
C	3.899008	-1.297116	1.126842
C	2.578168	-1.151857	1.435727
C	1.725795	-0.241967	0.730393
C	2.359763	0.580437	-0.258577
C	3.747007	0.429748	-0.521621
C	4.499448	-0.502186	0.130767
C	1.660974	1.688975	-0.816780
C	0.325408	1.929426	-0.784733
C	-0.700060	0.985377	-0.445323
O	0.483597	-0.180693	1.006637
N	-0.951997	-0.139715	-1.114262
C	-2.111810	-0.766487	-0.615197
C	-2.730251	0.084713	0.287666
C	-1.929985	1.359627	0.376411
C	-2.618074	-2.011961	-0.925898
C	-3.799715	-2.393331	-0.295525
C	-4.434946	-1.551802	0.606694
C	-3.900724	-0.298875	0.903331
H	-4.394184	0.354483	1.614155
H	-5.348940	-1.875105	1.089389
H	-4.222371	-3.367631	-0.508667
H	-2.116816	-2.680107	-1.614252
H	-0.024630	2.937833	-0.978574
H	2.280902	2.490025	-1.214240
H	4.206584	1.076009	-1.266297
H	2.120293	-1.754784	2.210695
C	-0.044700	-0.792222	-2.025833
H	0.559902	-0.038847	-2.525818
H	0.615941	-1.468504	-1.477677
H	-0.619109	-1.346658	-2.767374
C	-1.581215	1.776630	1.804179
H	-0.934540	2.656555	1.790646
H	-2.496851	2.029895	2.344409
H	-1.055836	0.974355	2.317276
C	-2.687232	2.496555	-0.342119
H	-3.633589	2.673423	0.171929
H	-2.112539	3.424459	-0.318635
H	-2.905478	2.239875	-1.380667
O	5.835359	-0.715014	-0.104221
H	6.137365	-0.103746	-0.778297
H	4.515074	-2.019966	1.650073

Table S43. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(1a-CCC*)**.

TS(1a-CCC*)			
E_{elec} = -940.894309			
E_{ZPE} = 0.333475			
Coordinates (Angstroms)			
	x	y	z
C	-3.983004	-1.240861	-1.157018
C	-2.645719	-1.119692	-1.451828
C	-1.783153	-0.268175	-0.696365
C	-2.410077	0.539390	0.320125
C	-3.798986	0.414852	0.567339
C	-4.572145	-0.474166	-0.134238
C	-1.682403	1.610021	0.922370
C	-0.342464	1.845669	0.872303
C	0.689942	0.930049	0.461284
O	-0.523876	-0.228293	-0.945949
N	1.017966	-0.194173	1.120918
C	2.197628	-0.763801	0.595172
C	2.757454	0.119583	-0.324507
C	1.893349	1.362065	-0.392202
C	2.776956	-1.985341	0.898011
C	3.965390	-2.311665	0.242341
C	4.539150	-1.440816	-0.678414
C	3.935047	-0.212890	-0.965807
H	4.385284	0.458501	-1.687948
H	5.457449	-1.718806	-1.180697
H	4.440494	-3.262685	0.450093
H	2.326770	-2.674993	1.599749
H	0.006364	2.843532	1.118828
H	-2.286660	2.393706	1.373118
H	-4.265727	1.034390	1.325358
H	-2.198859	-1.703247	-2.247314
C	0.169268	-0.885207	2.071735
H	-0.470751	-0.160468	2.568344
H	-0.457053	-1.618355	1.558863
H	0.792627	-1.385072	2.812604
C	1.499226	1.771683	-1.817777
H	0.825682	2.630556	-1.792000
H	2.393058	2.056394	-2.378095
H	0.990854	0.955970	-2.325598
C	2.620238	2.539107	0.310379
H	3.540247	2.764847	-0.231205
H	2.001377	3.438027	0.308579
H	2.884757	2.294673	1.340693
O	-5.915457	-0.576404	0.176063
H	-6.333560	-1.195872	-0.430913
H	-4.597649	-1.933130	-1.727216

TS(1a-CCC*)			
E_{elec} = -940.578971			
E_{ZPE} = 0.337338			
Coordinates (Angstroms)			
	x	y	z
C	3.913966	-1.279914	1.104364
C	2.593112	-1.142923	1.430041
C	1.731369	-0.236799	0.735860
C	2.357994	0.591495	-0.256613
C	3.739796	0.451600	-0.532731
C	4.503776	-0.479750	0.107553
C	1.651254	1.698775	-0.811649
C	0.315254	1.934750	-0.780138
C	-0.710059	0.989605	-0.446900
O	0.490755	-0.181920	1.019050
N	-0.949198	-0.141861	-1.106619
C	-2.108465	-0.772651	-0.610634
C	-2.735936	0.079503	0.284859
C	-1.942348	1.358513	0.372497
C	-2.606069	-2.022358	-0.918227
C	-3.788841	-2.407132	-0.292229
C	-4.433325	-1.564686	0.602678
C	-3.907596	-0.307538	0.896260
H	-4.408435	0.346492	1.601267
H	-5.348225	-1.890609	1.081899
H	-4.205289	-3.384598	-0.503059
H	-2.097616	-2.690723	-1.601048
H	-0.036603	2.942905	-0.972751
H	2.268843	2.502443	-1.206681
H	4.204939	1.094345	-1.272921
H	2.147569	-1.752328	2.207033
C	-0.036786	-0.791993	-2.015189
H	0.566478	-0.037317	-2.514677
H	0.624842	-1.464541	-1.463919
H	-0.607444	-1.349853	-2.757039
C	-1.594855	1.776421	1.800645
H	-0.954471	2.660919	1.787256
H	-2.511730	2.022421	2.342135
H	-1.062799	0.977136	2.311654
C	-2.704170	2.492097	-0.346230
H	-3.651020	2.665703	0.168035
H	-2.132930	3.422110	-0.323454
H	-2.921720	2.234088	-1.384593
O	5.830631	-0.601099	-0.229976
H	6.248672	-1.231132	0.358778
H	4.521815	-2.012361	1.630534

Table S44. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(2a*-TCC)**.

TS(2a*-TCC)			
E_{elec} = -940.887254			
E_{ZPE} = 0.333618			
Coordinates (Angstroms)			
	x	y	z
C	-3.439025	-1.822789	0.001120
C	-2.559743	-0.772642	0.189109
C	-2.928094	0.511744	-0.203285
C	-4.167088	0.791833	-0.761578
C	-5.047893	-0.275583	-0.937864
C	-4.691203	-1.568139	-0.565416
C	-1.173283	-0.731370	0.800526
C	-0.782377	0.749918	0.563397
C	-1.858914	1.388674	0.050677
O	0.886208	0.216759	-1.414134
N	2.058066	0.112945	-0.990983
C	2.451901	0.365557	0.403875
C	1.625462	1.111757	1.255899
C	0.283722	1.464050	1.124952
C	3.806629	0.114909	0.800520
C	4.741253	-0.333428	-0.081396
C	4.398783	-0.503325	-1.452123
C	3.138723	-0.245444	-1.891700
H	-3.168353	-2.832507	0.286832
H	-5.389731	-2.382238	-0.713986
H	-6.022561	-0.091307	-1.373044
H	-4.452405	1.794267	-1.052785
H	0.014386	2.426503	1.554551
H	2.150708	1.627276	2.059319
H	4.081529	0.296640	1.836535
H	5.173590	-0.835520	-2.134083
C	2.872543	-0.371239	-2.934022
H	6.048171	-0.618914	0.248332
H	6.178921	-0.466026	1.190773
H	-1.875079	2.791676	-0.319384
C	-2.282325	3.414438	0.482101
H	-0.857359	3.106907	-0.541485
H	-2.486376	2.920494	-1.211869
H	-1.283007	-0.912782	2.339284
C	-1.682671	-1.904197	2.561378
H	-0.297110	-0.818272	2.796299
H	-1.944929	-0.169501	2.787624
H	-0.261643	-1.830225	0.234191
O	-0.172304	-1.758469	-0.845122
H	0.734786	-1.771884	0.669691
H	-0.689605	-2.800811	0.498112

TS(2a*-TCC)			
E_{elec} = -940.569223			
E_{ZPE} = 0.33744			
Coordinates (Angstroms)			
	x	y	z
C	-3.362242	-1.867225	-0.031331
C	-2.514146	-0.797561	0.158207
C	-2.941653	0.484506	-0.152053
C	-4.212020	0.745113	-0.631510
C	-5.062305	-0.341866	-0.811732
C	-4.646622	-1.633134	-0.518475
C	-1.099097	-0.744399	0.685386
C	-0.790654	0.761786	0.556311
C	-1.895665	1.382231	0.097118
O	0.930508	0.475496	-1.478901
N	2.058000	0.270761	-1.008613
C	2.401518	0.387246	0.415043
C	1.583710	1.095573	1.286764
C	0.249193	1.479440	1.130389
C	3.731282	0.039967	0.844212
C	4.674349	-0.381243	-0.026472
C	4.380860	-0.430209	-1.423661
C	3.164250	-0.079856	-1.890161
H	-3.039371	-2.876939	0.196402
H	-5.326119	-2.463186	-0.667106
H	-6.064343	-0.172970	-1.187122
H	-4.545777	1.749656	-0.858394
H	-0.023382	2.437593	1.564986
H	2.091783	1.530471	2.147812
H	3.964425	0.121428	1.903082
H	5.169815	-0.747357	-2.096814
C	2.937432	-0.112382	-2.948873
H	5.944510	-0.754425	0.318580
H	6.048666	-0.682249	1.269496
H	-1.961184	2.793794	-0.192587
C	-2.288424	3.369369	0.677912
H	-0.971714	3.131836	-0.499912
H	-2.659403	2.961247	-1.011728
H	-1.085495	-1.077325	2.190964
C	-1.430783	-2.102458	2.341523
H	-0.070588	-0.983652	2.581413
H	-1.737931	-0.407453	2.754682
H	-0.203799	-1.739954	-0.059311
O	-0.177380	-1.533455	-1.125485
H	0.813645	-1.712357	0.328713
H	-0.604726	-2.743806	0.103948

Table S45. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) level of theory, for the transition state **TS(2a-TCC*)**.

TS(2a-TCC*)			
E_{elec} = -940.886204			
E_{ZPE} = 0.333369			
Coordinates (Angstroms)			
	x	y	z
C	-3.460693	-1.848432	0.001253
C	-2.586940	-0.789877	0.166260
C	-3.001651	0.501227	-0.151690
C	-4.281258	0.776634	-0.613979
C	-5.155074	-0.299828	-0.767774
C	-4.753617	-1.597876	-0.467089
C	-1.156517	-0.752202	0.671275
C	-0.820192	0.752192	0.510757
C	-1.934243	1.387350	0.064277
O	1.028778	0.341197	-1.544920
N	2.156309	0.186880	-1.039599
C	2.460174	0.393583	0.392013
C	1.590346	1.112018	1.217733
C	0.247589	1.469429	1.041984
C	3.781371	0.113514	0.873659
C	4.765432	-0.334150	0.050827
C	4.510659	-0.476377	-1.344998
C	3.291065	-0.187545	-1.869216
H	-3.155037	-2.862367	0.231705
H	-5.448213	-2.418850	-0.594606
H	-6.160656	-0.117910	-1.127093
H	-4.603285	1.783131	-0.847073
H	-0.018422	2.439774	1.455993
H	2.074505	1.597274	2.064796
H	4.002260	0.261353	1.924867
H	5.314420	-0.813994	-1.995463
C	3.096053	-0.292316	-2.929329
H	6.007732	-0.621061	0.574784
H	6.600826	-0.887584	-0.135363
H	-1.997172	2.804746	-0.235366
C	-2.317658	3.387452	0.633478
H	-1.011243	3.142124	-0.551234
H	-2.702645	2.969322	-1.048535
H	-1.124139	-1.069853	2.188265
C	-1.471956	-2.091223	2.356016
H	-0.105502	-0.978985	2.567595
H	-1.765860	-0.392704	2.754937
H	-0.278761	-1.770621	-0.075446
O	-0.246226	-1.568600	-1.141966
H	0.740042	-1.761890	0.308567
H	-0.695368	-2.767313	0.090640

Table S46. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(CCC-CTC)**.

TS(CCC-CTC)			
E_{elec} = -940.88191			
E_{ZPE} = 0.331793			
Coordinates (Angstroms)			
	x	y	z
C	4.878623	-0.322746	1.205814
C	3.773774	0.127245	1.826751
C	2.550316	0.473247	1.089138
C	2.609815	0.303694	-0.405626
C	3.846971	-0.182677	-0.991081
C	4.919752	-0.480806	-0.230295
C	1.561195	0.599449	-1.216706
C	0.250487	1.167822	-0.867742
C	-0.921338	0.574711	-0.599442
O	1.558748	0.877976	1.682643
N	-1.222577	-0.788502	-0.552402
C	-2.534037	-0.994803	-0.125364
C	-3.177851	0.232944	0.054379
C	-2.205703	1.358486	-0.253795
C	-3.193655	-2.197060	0.109106
C	-4.529531	-2.142887	0.513447
C	-5.183080	-0.928337	0.683680
C	-4.498393	0.271153	0.453723
H	-5.006046	1.219191	0.594809
H	-6.218260	-0.909093	1.000841
H	-5.060113	-3.068877	0.701944
H	-2.697297	-3.152089	-0.004424
H	0.239376	2.255344	-0.846177
H	1.756980	0.472024	-2.284355
H	3.888402	-0.298891	-2.070465
H	3.732916	0.251222	2.901531
C	-0.294215	-1.873586	-0.772743
H	0.444380	-1.588560	-1.518093
H	0.231925	-2.161929	0.144116
H	-0.834635	-2.740675	-1.154283
C	-1.991110	2.264397	0.973038
H	-1.265283	3.050246	0.754399
H	-2.932172	2.740891	1.259029
H	-1.617871	1.692527	1.822742
C	-2.685700	2.192270	-1.457984
H	-3.630491	2.689283	-1.223936
H	-1.951467	2.959914	-1.712862
H	-2.840738	1.562502	-2.335806
O	6.116984	-0.942082	-0.705762
H	6.079847	-1.016693	-1.666758
H	5.774809	-0.579070	1.759717

TS(CCC-CTC)			
E_{elec} = -940.56622			
E_{ZPE} = 0.33612			
Coordinates (Angstroms)			
	x	y	z
C	-4.681619	0.459724	1.258724
C	-3.587384	-0.040789	1.844108
C	-2.454382	-0.559688	1.060006
C	-2.565198	-0.415521	-0.429173
C	-3.804084	0.114584	-0.979185
C	-4.800970	0.530603	-0.183846
C	-1.549643	-0.732542	-1.257462
C	-0.231450	-1.277346	-0.902519
C	0.906034	-0.633008	-0.634228
O	-1.505369	-1.080756	1.615691
N	1.146103	0.737698	-0.631577
C	2.429016	1.012608	-0.170709
C	3.111450	-0.177445	0.071837
C	2.199206	-1.347448	-0.220547
C	3.033712	2.241322	0.043424
C	4.353200	2.250143	0.491545
C	5.044501	1.071773	0.723391
C	4.414115	-0.155681	0.513070
H	4.945862	-1.082528	0.701626
H	6.068562	1.103526	1.073957
H	4.842473	3.201528	0.665172
H	2.509270	3.174473	-0.118593
H	-0.197233	-2.359999	-0.817283
H	-1.753146	-0.606254	-2.322736
H	-3.894446	0.180003	-2.059910
H	-3.493862	-0.107735	2.920787
C	0.163895	1.753039	-0.901497
H	-0.431070	1.481400	-1.772974
H	-0.512211	1.909530	-0.054462
H	0.668145	2.691611	-1.128716
C	1.976382	-2.201104	1.033369
H	1.292442	-3.026440	0.824426
H	2.926386	-2.620353	1.375005
H	1.544541	-1.605397	1.838022
C	2.747920	-2.203950	-1.368211
H	3.702213	-2.653480	-1.081573
H	2.049728	-3.007712	-1.613925
H	2.907967	-1.600471	-2.263687
O	-5.982744	1.048573	-0.611721
H	-6.002652	1.061623	-1.571573
H	-5.518986	0.824598	1.843149

Table S47. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(CCC*-CTC*)**.

TS(CCC*-CTC*)			
E_{elec} = -940.87984			
E_{ZPE} = 0.33135			
Coordinates (Angstroms)			
	x	y	z
C	4.877260	-0.309771	1.188910
C	3.776638	0.146986	1.815209
C	2.549488	0.483841	1.079993
C	2.607471	0.301552	-0.411848
C	3.838611	-0.189660	-1.000344
C	4.916072	-0.483760	-0.245593
C	1.556796	0.594507	-1.223593
C	0.247563	1.165100	-0.874444
C	-0.923791	0.573032	-0.602101
O	1.560208	0.890759	1.676840
N	-1.224319	-0.790176	-0.551866
C	-2.534489	-0.996182	-0.121261
C	-3.178223	0.231697	0.058391
C	-2.207543	1.357075	-0.255234
C	-3.193175	-2.198288	0.116693
C	-4.527898	-2.143863	0.524801
C	-5.181264	-0.929244	0.695295
C	-4.497595	0.270116	0.461485
H	-5.005212	1.218220	0.602291
H	-6.215566	-0.909821	1.015312
H	-5.057774	-3.069733	0.715888
H	-2.696905	-3.153305	0.002669
H	0.237417	2.252800	-0.857187
H	1.751947	0.461008	-2.290183
H	3.889312	-0.320173	-2.075090
H	3.743383	0.280023	2.889082
C	-0.297708	-1.875230	-0.779992
H	0.436643	-1.589421	-1.529295
H	0.233680	-2.165868	0.133082
H	-0.840701	-2.741250	-1.160279
C	-1.990281	2.266665	0.968338
H	-1.265451	3.052255	0.745465
H	-2.930842	2.743545	1.255355
H	-1.614515	1.697488	1.818744
C	-2.691086	2.187060	-1.460662
H	-3.635618	2.684142	-1.225690
H	-1.957948	2.954377	-1.719644
H	-2.847836	1.554654	-2.336254
O	6.059054	-0.950955	-0.840735
H	6.743862	-1.089396	-0.177758
H	5.767167	-0.556549	1.763445

TS(CCC*-CTC*)			
E_{elec} = -940.56384			
E_{ZPE} = 0.33571			
Coordinates (Angstroms)			
	x	y	z
C	4.878623	-0.322746	1.205814
C	3.773774	0.127245	1.826751
C	2.550316	0.473247	1.089138
C	2.609815	0.303694	-0.405626
C	3.846971	-0.182677	-0.991081
C	4.919752	-0.480806	-0.230295
C	1.561195	0.599449	-1.216706
C	0.250487	1.167822	-0.867742
C	-0.921338	0.574711	-0.599442
O	1.558748	0.877976	1.682643
N	-1.222577	-0.788502	-0.552402
C	-2.534037	-0.994803	-0.125364
C	-3.177851	0.232944	0.054379
C	-2.205703	1.358486	-0.253795
C	-3.193655	-2.197060	0.109106
C	-4.529531	-2.142887	0.513447
C	-5.183080	-0.928337	0.683680
C	-4.498393	0.271153	0.453723
H	-5.006046	1.219191	0.594809
H	-6.218260	-0.909093	1.000841
H	-5.060113	-3.068877	0.701944
H	-2.697297	-3.152089	-0.004424
H	0.239376	2.255344	-0.846177
H	1.756980	0.472024	-2.284355
H	3.888402	-0.298891	-2.070465
H	3.732916	0.251222	2.901531
C	-0.294215	-1.873586	-0.772743
H	0.444380	-1.588560	-1.518093
H	0.231925	-2.161929	0.144116
H	-0.834635	-2.740675	-1.154283
C	-1.991110	2.264397	0.973038
H	-1.265283	3.050246	0.754399
H	-2.932172	2.740891	1.259029
H	-1.617871	1.692527	1.822742
C	-2.685700	2.192270	-1.457984
H	-3.630491	2.689283	-1.223936
H	-1.951467	2.959914	-1.712862
H	-2.840738	1.562502	-2.335806
O	6.116984	-0.942082	-0.705762
H	6.079847	-1.016693	-1.666758
H	5.774809	-0.579070	1.759717

Table S48. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levesl of theory, for the transition state **TS(TCC-TTC).**

TS(TCC-TTC)			
E_{elec} = -940.88281			
E_{ZPE} = 0.33203			
Coordinates (Angstroms)			
	x	y	z
C	3.607816	-1.820583	0.436490
C	2.725088	-0.820316	0.083062
C	3.175962	0.495912	-0.060761
C	4.513394	0.825023	0.134866
C	5.394995	-0.197955	0.490046
C	4.957070	-1.508298	0.641609
C	1.227052	-0.876350	-0.181810
C	0.936700	0.582029	-0.587834
C	2.107218	1.320540	-0.399956
O	-1.608515	1.422546	1.436767
N	-2.551349	0.826213	0.931197
C	-2.539146	0.293878	-0.477502
C	-1.483459	0.461050	-1.317245
C	-0.193741	1.118485	-1.076354
C	-3.734858	-0.369404	-0.968211
C	-4.825960	-0.528028	-0.191826
C	-4.850402	-0.029104	1.163888
C	-3.791133	0.611401	1.690218
H	3.266147	-2.843184	0.555066
H	5.658169	-2.286791	0.915235
H	6.440787	0.039747	0.645942
H	4.875830	1.837750	0.014032
H	-0.167552	2.158418	-1.394224
H	-1.659101	0.131643	-2.344030
H	-3.726606	-0.743298	-1.988145
H	-5.757505	-0.188186	1.736180
C	-3.800136	0.992316	2.703634
H	-5.983672	-1.146208	-0.579828
H	-5.900289	-1.452574	-1.490663
H	2.196368	2.739600	-0.634564
C	2.177885	2.980305	-1.704883
H	1.361557	3.250378	-0.149168
H	3.121726	3.123155	-0.209869
H	0.896207	-1.861023	-1.317470
C	1.196465	-2.873423	-1.036834
H	-0.176151	-1.876822	-1.521508
H	1.419994	-1.593546	-2.236673
H	0.472223	-1.272340	1.104998
O	0.637699	-0.544886	1.899643
H	-0.600188	-1.338189	0.922844
H	0.821274	-2.248444	1.450817

TS(TCC-TTC)			
E_{elec} = -940.56843			
E_{ZPE} = 0.33652			
Coordinates (Angstroms)			
	x	y	z
C	3.389165	-1.931850	0.274746
C	2.582980	-0.849855	0.007646
C	3.114571	0.437787	-0.002273
C	4.460336	0.661680	0.240871
C	5.266676	-0.442999	0.506975
C	4.746972	-1.727703	0.526041
C	1.095364	-0.788155	-0.279430
C	0.910756	0.708835	-0.564855
C	2.107434	1.352099	-0.273649
O	-1.532430	1.469485	1.473056
N	-2.419878	0.809017	0.965901
C	-2.470434	0.462626	-0.494355
C	-1.467061	0.758684	-1.347359
C	-0.158893	1.347400	-1.053547
C	-3.668960	-0.188485	-1.003091
C	-4.666354	-0.559457	-0.186556
C	-4.593172	-0.307706	1.238101
C	-3.547424	0.327217	1.780380
H	2.976828	-2.935514	0.288706
H	5.393602	-2.571346	0.732622
H	6.322238	-0.289216	0.698675
H	4.886739	1.656741	0.222016
H	-0.069222	2.401860	-1.299272
H	-1.676083	0.569886	-2.402441
H	-3.722762	-0.391983	-2.068981
H	-5.424946	-0.647969	1.844937
C	-3.489958	0.531558	2.842151
H	-5.806667	-1.189812	-0.575660
H	-5.793288	-1.326005	-1.525986
H	2.281271	2.771721	-0.378073
C	2.320671	3.103628	-1.422908
H	1.453270	3.281520	0.120457
H	3.205931	3.065457	0.115675
H	0.727258	-1.648315	-1.492625
C	0.967302	-2.695773	-1.293544
H	-0.342121	-1.584634	-1.704681
H	1.279503	-1.332253	-2.379274
H	0.306405	-1.246082	0.957833
O	0.456545	-0.565065	1.796035
H	-0.760915	-1.295245	0.740512
H	0.639949	-2.243891	1.253691

Table S49. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) leveld of theory, for the transition state **TS(TCC*-TTC*).**

TS(TCC*-TTC*)			
E_{elec} = -940.88067			
E_{ZPE} = 0.33157			
Coordinates (Angstroms)			
	x	y	z
C	3.613772	-1.819834	0.435760
C	2.729725	-0.820322	0.083546
C	3.178554	0.497012	-0.057063
C	4.515223	0.827915	0.140805
C	5.398147	-0.194328	0.494851
C	4.962272	-1.505719	0.643138
C	1.232151	-0.878452	-0.183378
C	0.939793	0.580246	-0.586302
C	2.108859	1.320552	-0.395890
O	-1.613661	1.424936	1.435015
N	-2.554107	0.828592	0.923853
C	-2.539174	0.290419	-0.481075
C	-1.479058	0.454887	-1.317836
C	-0.191794	1.115335	-1.073168
C	-3.728805	-0.374564	-0.977632
C	-4.825719	-0.532078	-0.210179
C	-4.853130	-0.025394	1.142809
C	-3.798174	0.618724	1.676662
H	3.273711	-2.843308	0.551353
H	5.664410	-2.283652	0.915710
H	6.443388	0.044799	0.652302
H	4.876163	1.841466	0.022381
H	-0.169399	2.156789	-1.386620
H	-1.650905	0.120094	-2.343068
H	-3.729063	-0.756756	-1.991758
H	-5.755890	-0.171705	1.731494
C	-3.815323	1.002608	2.688758
H	-5.925955	-1.174852	-0.716043
H	-6.627789	-1.196152	-0.056810
H	2.195889	2.739789	-0.629953
C	2.174671	2.980806	-1.700143
H	1.361611	3.249605	-0.142534
H	3.121778	3.124224	-0.207256
H	0.903867	-1.861377	-1.321261
C	1.205734	-2.873793	-1.042464
H	-0.168201	-1.879305	-1.526509
H	1.427898	-1.591114	-2.239482
H	0.476037	-1.277484	1.101771
O	0.641149	-0.552019	1.898368
H	-0.596211	-1.342724	0.918174
H	0.824377	-2.254599	1.445455

TS(TCC*-TTC*)			
E_{elec} = -940.56599			
E_{ZPE} = 0.33605			
Coordinates (Angstroms)			
	x	y	z
C	3.399748	-1.928858	0.284689
C	2.590938	-0.849942	0.013311
C	3.118998	0.439267	-0.000067
C	4.463844	0.667453	0.244233
C	5.272842	-0.434207	0.514868
C	4.756690	-1.720264	0.537229
C	1.103530	-0.793158	-0.275614
C	0.915459	0.701872	-0.567190
C	2.109861	1.349977	-0.275867
O	-1.541377	1.483123	1.459948
N	-2.427876	0.821651	0.951474
C	-2.472116	0.454852	-0.502243
C	-1.461127	0.737324	-1.352346
C	-0.156989	1.334639	-1.056045
C	-3.664040	-0.202244	-1.013232
C	-4.670555	-0.561905	-0.204521
C	-4.604874	-0.286330	1.216923
C	-3.564268	0.356080	1.762795
H	2.990139	-2.933609	0.300733
H	5.405395	-2.561518	0.747041
H	6.327757	-0.276916	0.707335
H	4.887653	1.663577	0.222767
H	-0.075695	2.390766	-1.297690
H	-1.661568	0.528326	-2.404888
H	-3.723219	-0.426871	-2.072026
H	-5.431855	-0.609454	1.845204
C	-3.518038	0.574272	2.822294
H	-5.761622	-1.200655	-0.712248
H	-6.404573	-1.357471	-0.018752
H	2.280266	2.769217	-0.389717
C	2.313983	3.094496	-1.436842
H	1.453646	3.280802	0.109404
H	3.206645	3.067923	0.097724
H	0.737391	-1.660654	-1.484041
C	0.980437	-2.706366	-1.279580
H	-0.332135	-1.602020	-1.696666
H	1.288546	-1.347785	-2.372468
H	0.313858	-1.244052	0.963858
O	0.466455	-0.559715	1.798997
H	-0.753661	-1.290948	0.746844
H	0.644750	-2.241528	1.263872

Table S50. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for ***syn*-*syn*-ALN**.

ss-ALN

E_{elec} = -940.89798

E_{ZPE} = 0.333075

Coordinates (Angstroms)

	x	y	z
C	4.387852	1.132274	0.504179
C	3.186968	0.593311	0.088441
C	3.098735	-0.770778	-0.208430
C	4.196486	-1.614349	-0.086766
C	5.404595	-1.054156	0.334978
C	5.507623	0.300645	0.627568
C	1.834502	1.251191	-0.137894
C	0.968101	0.025654	-0.522375
C	1.806486	-1.086111	-0.624444
O	-1.685144	-0.508360	1.761207
N	-2.827112	-0.315535	1.046162
C	-2.819207	0.001274	-0.325047
C	-1.586101	0.147148	-1.104812
C	-0.340528	0.031175	-0.687839
C	-4.053480	0.178277	-0.972826
C	-5.253255	0.049003	-0.294123
C	-5.244405	-0.266207	1.063449
C	-4.038990	-0.445840	1.721405
H	4.469974	2.188063	0.737912
H	6.453404	0.713335	0.955539
H	6.273819	-1.692832	0.438474
H	4.126386	-2.672525	-0.303867
H	-1.753716	0.371258	-2.161445
H	-4.054090	0.422459	-2.031529
H	-6.185321	-0.366832	1.589442
H	-4.016586	-0.690938	2.775935
C	-6.477625	0.217301	-0.898716
H	-6.350501	0.430255	-1.829566
H	1.350048	-2.425505	-0.915110
H	0.381755	-2.370474	-1.409165
C	2.053240	-2.925478	-1.584204
H	1.243715	-3.025655	-0.004083
H	1.303997	1.948647	1.124318
H	1.952247	2.785798	1.393434
C	0.298046	2.337560	0.953762
H	1.268307	1.262509	1.971949
H	1.880466	2.243175	-1.316840
H	2.251248	1.761633	-2.223346
O	0.883325	2.640725	-1.518539
H	2.543145	3.079051	-1.080976
H	-0.919412	-0.373082	1.170817

ss-ALN

E_{elec} = -940.57965

E_{ZPE} = 0.337232

Coordinates (Angstroms)

	x	y	z
C	4.268671	1.073535	0.695331
C	3.110404	0.581125	0.139650
C	3.038713	-0.749953	-0.267671
C	4.109867	-1.612851	-0.110922
C	5.276258	-1.102155	0.455545
C	5.363940	0.222595	0.853643
C	1.792459	1.271258	-0.145795
C	0.955126	0.089420	-0.662544
C	1.791038	-1.011456	-0.823985
O	-1.501613	-0.609823	1.603200
N	-2.681761	-0.382104	0.979154
C	-2.774350	0.028994	-0.356908
C	-1.601819	0.252192	-1.213144
C	-0.338144	0.117918	-0.885759
C	-4.046793	0.234531	-0.903906
C	-5.193965	0.041945	-0.159544
C	-5.087411	-0.367215	1.164848
C	-3.841905	-0.575444	1.721983
H	4.330424	2.108744	1.013895
H	6.280056	0.595790	1.293989
H	6.127589	-1.759067	0.589783
H	4.050947	-2.652093	-0.409321
H	-1.837252	0.557048	-2.234214
H	-4.121258	0.553291	-1.940340
H	-5.988568	-0.517791	1.746007
H	-3.744008	-0.893838	2.752482
C	-6.449807	0.234586	-0.663446
H	-6.388943	0.514956	-1.578415
H	1.305580	-2.325345	-1.147909
H	0.437245	-2.232585	-1.799979
C	2.076045	-2.885289	-1.679609
H	1.011343	-2.884943	-0.252020
H	1.172348	1.891394	1.107318
H	1.799781	2.707526	1.473376
C	0.181259	2.293170	0.883769
H	1.072962	1.153706	1.905591
H	1.942955	2.323965	-1.251704
H	2.373394	1.884360	-2.153411
O	0.968623	2.750497	-1.501808
H	2.600169	3.129830	-0.916174
H	-0.776742	-0.424064	0.986269

Table S51. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for ***syn-anti*-ALN** (mentioned only as **ALN** in the main text).

sa-ALN			
E_{elec} = -940.89811			
E_{ZPE} = 0.333046			
Coordinates (Angstroms)			
	x	y	z
C	4.389021	-1.134033	0.499686
C	3.188395	-0.592873	0.086134
C	3.099462	0.773500	-0.200170
C	4.196362	1.616972	-0.070010
C	5.404209	1.054504	0.349472
C	5.507886	-0.302449	0.631664
C	1.837048	-1.250249	-0.148473
C	0.970054	-0.022267	-0.523207
C	1.807819	1.090949	-0.615968
O	-1.685013	0.487967	1.761646
N	-2.827057	0.303002	1.044219
C	-2.818445	-0.000779	-0.332778
C	-1.582679	-0.139616	-1.111093
C	-0.338471	-0.027137	-0.689528
C	-4.046304	-0.170993	-0.986457
C	-5.248366	-0.047765	-0.309780
C	-5.242517	0.253274	1.050352
C	-4.037457	0.426702	1.717660
H	4.471665	-2.191612	0.725004
H	6.453476	-0.716934	0.957939
H	6.272744	1.693064	0.459364
H	4.125765	2.676717	-0.279168
H	-1.748975	-0.354668	-2.169379
H	-4.063231	-0.404313	-2.044658
H	-6.177629	0.353022	1.592332
H	-4.019609	0.660903	2.774665
C	-6.407952	-0.231192	-1.027754
H	-7.166670	-0.122126	-0.444407
H	1.350905	2.431884	-0.898537
H	0.383527	2.379492	-1.394652
C	1.242732	3.025990	0.016270
H	2.054840	2.936709	-1.563198
H	1.886173	-2.231071	-1.336673
H	2.549583	-3.068270	-1.107584
C	0.889892	-2.627857	-1.543886
H	2.257766	-1.740525	-2.237984
H	1.305282	-1.960278	1.106141
H	1.267488	-1.282291	1.960234
O	0.300077	-2.348659	0.930087
H	1.953976	-2.799317	1.368257
H	-0.919431	0.357861	1.169663

sa-ALN			
E_{elec} = -940.57968			
E_{ZPE} = 0.337078			
Coordinates (Angstroms)			
	x	y	z
C	4.358976	-1.207275	0.293301
C	3.153713	-0.600425	0.026459
C	3.078507	0.786475	-0.093296
C	4.202030	1.585783	0.033118
C	5.416939	0.957759	0.301676
C	5.502978	-0.419200	0.433800
C	1.779127	-1.203998	-0.175407
C	0.950364	0.055924	-0.480548
C	1.767930	1.172031	-0.340103
O	-1.625171	0.287470	1.736632
N	-2.769703	0.183999	1.019335
C	-2.789330	0.041364	-0.377480
C	-1.569806	-0.008662	-1.196551
C	-0.327455	0.065287	-0.780974
C	-4.023651	-0.056122	-1.022584
C	-5.211475	-0.014465	-0.318162
C	-5.179658	0.128130	1.063547
C	-3.966053	0.226165	1.721456
H	4.423423	-2.285978	0.389640
H	6.458597	-0.884361	0.640781
H	6.310319	1.562343	0.405228
H	4.148718	2.661839	-0.076012
H	-1.749645	-0.112386	-2.267562
H	-4.059648	-0.166820	-2.100482
H	-6.103822	0.162813	1.632079
H	-3.928566	0.336959	2.798034
C	-6.376042	-0.116680	-1.026817
H	-7.120961	-0.076018	-0.424492
H	1.348142	2.514935	-0.630680
H	0.270278	2.589407	-0.483565
C	1.836408	3.213357	0.051287
H	1.580942	2.803413	-1.661823
H	1.742272	-2.175732	-1.357345
H	2.372133	-3.044354	-1.150654
C	0.720898	-2.522889	-1.530173
H	2.105861	-1.697369	-2.268399
H	1.270770	-1.885847	1.100180
H	1.283712	-1.196117	1.946478
O	0.247605	-2.242551	0.959663
H	1.904944	-2.740374	1.347966
H	-0.867107	0.223989	1.135135

Table S52. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for ***anti*-*syn*-ALN**.

	as-ALN		
	E_{elec} = -940.88941		
	E_{ZPE} = 0.332563		
	Coordinates (Angstroms)		
	x	y	z
C	4.409779	1.179854	0.389405
C	3.188880	0.610466	0.090368
C	3.103964	-0.758573	-0.196194
C	4.237803	-1.565557	-0.204285
C	5.465764	-0.973276	0.099188
C	5.560678	0.381299	0.395426
C	1.802280	1.234865	0.019863
C	0.958962	0.023442	-0.445178
C	1.783851	-1.115617	-0.436918
O	-1.659762	-0.716157	1.616185
N	-2.838764	-0.431502	0.977665
C	-2.794355	-0.013634	-0.363414
C	-1.560482	0.149808	-1.148460
C	-0.309593	0.049192	-0.763490
C	-4.015363	0.258212	-0.998925
C	-5.232760	0.134711	-0.345474
C	-5.258296	-0.276757	0.982030
C	-4.062667	-0.556677	1.628515
H	4.485514	2.238297	0.614149
H	6.523477	0.820694	0.624491
H	6.360026	-1.585642	0.097292
H	4.181586	-2.620025	-0.442744
H	-1.751720	0.389610	-2.197320
H	-3.993953	0.578070	-2.036847
H	-6.206431	-0.375455	1.494530
H	-4.080986	-0.881365	2.664576
C	-6.435838	0.400867	-0.954174
H	-6.282826	0.677548	-1.864261
H	1.350777	-2.412013	-0.895944
H	0.289857	-2.529296	-0.676467
C	1.500032	-2.542095	-1.975373
H	1.899589	-3.194923	-0.370437
H	1.333668	1.715184	1.406950
H	1.976779	2.523049	1.765308
C	0.307247	2.083986	1.354991
H	1.367209	0.902769	2.134300
H	1.729937	2.386213	-0.995095
H	2.067009	2.062835	-1.981170
O	0.704286	2.751037	-1.084619
H	2.361368	3.218399	-0.673988
H	-1.851501	-0.997403	2.518231

	as-ALN		
	E_{elec} = -940.57061		
	E_{ZPE} = 0.33664		
	Coordinates (Angstroms)		
	x	y	z
C	4.321757	1.193449	0.487354
C	3.120037	0.624711	0.136024
C	3.056068	-0.725757	-0.212868
C	4.192871	-1.518026	-0.232281
C	5.404181	-0.927564	0.124051
C	5.477607	0.409084	0.482452
C	1.732671	1.232404	0.069235
C	0.933841	0.055472	-0.508722
C	1.747091	-1.081499	-0.495419
O	-1.518545	-0.956341	1.376942
N	-2.719262	-0.571444	0.859229
C	-2.752782	-0.011022	-0.422576
C	-1.561862	0.205786	-1.262346
C	-0.306100	0.104527	-0.910590
C	-3.996287	0.356809	-0.942310
C	-5.170084	0.194192	-0.226601
C	-5.120940	-0.357478	1.044175
C	-3.899670	-0.736079	1.572797
H	4.374804	2.242178	0.760765
H	6.430826	0.846467	0.752108
H	6.305646	-1.529290	0.113979
H	4.152594	-2.561197	-0.520310
H	-1.790700	0.489872	-2.290517
H	-4.030619	0.787018	-1.939724
H	-6.036529	-0.488109	1.606655
H	-3.863405	-1.172577	2.566574
C	-6.392678	0.552689	-0.717584
H	-6.290012	0.923637	-1.595965
H	1.337725	-2.337317	-1.056563
H	0.276305	-2.484624	-0.854248
C	1.497764	-2.377316	-2.141338
H	1.892309	-3.151119	-0.587215
H	1.212477	1.571378	1.472980
H	1.829010	2.352295	1.925849
C	0.179951	1.923630	1.417036
H	1.239157	0.691733	2.118294
H	1.670192	2.459963	-0.839020
H	2.046347	2.226930	-1.836438
O	0.639388	2.810493	-0.930685
H	2.273309	3.271130	-0.423008
H	-1.660644	-1.339967	2.244744

Table S53. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for ***anti-anti*-ALN**.

aa-ALN			
E_{elec} = -940.88916			
E_{ZPE} = 0.33253			
Coordinates (Angstroms)			
	x	y	z
C	4.410787	1.181674	0.383861
C	3.190088	0.610403	0.087702
C	3.104931	-0.760972	-0.187824
C	4.238613	-1.568356	-0.187760
C	5.466359	-0.974117	0.112718
C	5.561407	0.382765	0.398187
C	1.803993	1.235065	0.009382
C	0.960662	0.020151	-0.446194
C	1.785238	-1.119486	-0.427484
O	-1.658725	-0.699347	1.616431
N	-2.838259	-0.420641	0.976193
C	-2.793471	-0.013964	-0.371417
C	-1.557211	0.141677	-1.155200
C	-0.307440	0.043561	-0.766043
C	-4.008653	0.252205	-1.012634
C	-5.227680	0.134318	-0.360358
C	-5.255816	-0.264394	0.970423
C	-4.060078	-0.539836	1.626155
H	4.486637	2.241956	0.599763
H	6.524068	0.823675	0.624945
H	6.360407	-1.586807	0.116914
H	4.182387	-2.624641	-0.418055
H	-1.747090	0.372698	-2.205792
H	-4.004718	0.562957	-2.050646
H	-6.198091	-0.363852	1.498916
H	-4.082195	-0.854835	2.664973
C	-6.363088	0.422481	-1.079565
H	-7.138164	0.303683	-0.520006
H	1.352705	-2.418574	-0.879292
H	0.291309	-2.534220	-0.661203
C	1.503708	-2.555358	-1.957640
H	1.900378	-3.198379	-0.347972
H	1.333645	1.728371	1.391333
H	1.976817	2.539002	1.743339
C	0.307634	2.097574	1.334240
H	1.365427	0.922551	2.126097
H	1.734033	2.377308	-1.016020
H	2.072626	2.044871	-1.998531
O	0.708751	2.741743	-1.110844
H	2.365351	3.212041	-0.701300
H	-1.849089	-0.973204	2.520996

aa-ALN			
E_{elec} = -940.57036			
E_{ZPE} = 0.33664			
Coordinates (Angstroms)			
	x	y	z
C	4.327744	1.200782	0.453574
C	3.124831	0.623525	0.120755
C	3.059561	-0.735419	-0.193613
C	4.196429	-1.527925	-0.196913
C	5.408955	-0.928778	0.140310
C	5.483595	0.416455	0.464713
C	1.737409	1.229764	0.042667
C	0.937089	0.039248	-0.504433
C	1.749709	-1.098274	-0.462565
O	-1.523757	-0.875682	1.420211
N	-2.724622	-0.523021	0.880704
C	-2.753793	-0.015386	-0.426860
C	-1.557143	0.174683	-1.265532
C	-0.303194	0.079061	-0.905702
C	-3.991002	0.321598	-0.971799
C	-5.170033	0.179380	-0.259200
C	-5.127499	-0.317874	1.033362
C	-3.905890	-0.666461	1.591102
H	4.381744	2.256192	0.699759
H	6.437760	0.860490	0.719800
H	6.310415	-1.530614	0.142125
H	4.155282	-2.577974	-0.458640
H	-1.781488	0.431797	-2.301344
H	-4.040929	0.710606	-1.982375
H	-6.038416	-0.439113	1.610445
H	-3.876464	-1.060351	2.602569
C	-6.331226	0.541700	-0.879894
H	-7.071031	0.396390	-0.287415
H	1.341195	-2.364904	-0.999605
H	0.279282	-2.508016	-0.796882
C	1.503149	-2.426341	-2.083115
H	1.894556	-3.169483	-0.513187
H	1.221143	1.602890	1.439200
H	1.838060	2.395601	1.870598
C	0.187909	1.952069	1.377583
H	1.251103	0.739489	2.106018
H	1.672455	2.434898	-0.894943
H	2.045979	2.177631	-1.887362
O	0.641430	2.783061	-0.992650
H	2.276591	3.255988	-0.500389
H	-1.666403	-1.222755	2.303154

Table S54. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and *ω*B97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(sa-ALN-aa-ALN)**.

TS(sa-ALN-aa-ALN)			
E_{elec} = -940.88540			
E_{ZPE} = 0.33182			
Coordinates (Angstroms)			
	x	y	z
C	4.301575	1.054461	0.812330
C	3.133969	0.606535	0.228773
C	3.074723	-0.677292	-0.329562
C	4.173934	-1.530407	-0.293731
C	5.347321	-1.062263	0.301505
C	5.421073	0.213394	0.848632
C	1.791097	1.301580	0.054223
C	0.961405	0.175774	-0.609139
N	1.821756	-0.902941	-0.882705
O	-1.584338	-1.359014	1.211032
C	-2.764630	-0.769160	0.788130
C	-2.782977	0.011554	-0.381572
C	-1.588427	0.347732	-1.177990
C	-0.322281	0.217459	-0.859878
C	-4.017804	0.498635	-0.826519
C	-5.192352	0.250497	-0.129991
C	-5.158685	-0.513854	1.032128
C	-3.944043	-1.027304	1.472794
H	4.357676	2.047405	1.245415
H	6.340559	0.555144	1.307114
H	6.213826	-1.712229	0.338670
H	4.129117	-2.529644	-0.707608
H	-1.829239	0.776313	-2.153496
H	-4.066564	1.095109	-1.729833
H	-6.070697	-0.722639	1.581772
H	-3.905649	-1.652952	2.356732
O	-6.351545	0.781421	-0.636713
H	-7.093761	0.531259	-0.075525
C	1.369848	-2.172766	-1.399589
H	0.488046	-2.010582	-2.018006
H	2.148248	-2.620459	-2.019867
H	1.104915	-2.873444	-0.599266
C	1.179839	1.731653	1.397280
H	1.793555	2.504417	1.866755
H	0.176146	2.136238	1.248364
H	1.115918	0.887233	2.085948
C	1.902095	2.512837	-0.891634
H	2.326304	2.220679	-1.853606
H	0.916222	2.949018	-1.068320
H	2.546011	3.280134	-0.454484
H	-1.269946	-0.934070	2.016478

TS(sa-ALN-aa-ALN)			
E_{elec} = -940.567366			
E_{ZPE} = 0.335927			
Coordinates (Angstroms)			
	x	y	z
C	-4.113015	0.982047	-1.031071
C	-3.011860	0.605024	-0.297927
C	-2.983182	-0.634078	0.344684
C	-4.044333	-1.520073	0.241264
C	-5.151503	-1.126777	-0.507855
C	-5.196415	0.107449	-1.137136
C	-1.719753	1.349136	-0.025453
C	-0.937867	0.282900	0.755401
N	-1.798422	-0.781296	1.049199
O	1.375712	-1.537975	-0.787596
C	2.578987	-0.899506	-0.584818
C	2.716317	0.024488	0.459208
C	1.603163	0.456258	1.327609
C	0.325393	0.352360	1.073133
C	3.976132	0.571676	0.695153
C	5.066909	0.247376	-0.094755
C	4.916300	-0.656405	-1.136934
C	3.675522	-1.232292	-1.362619
H	-4.138632	1.945891	-1.528946
H	-6.067228	0.390051	-1.715407
H	-5.991416	-1.805555	-0.600646
H	-4.021139	-2.490931	0.720215
H	1.916599	0.931758	2.257451
H	4.113385	1.280828	1.503427
H	5.762623	-0.926417	-1.760301
H	3.552367	-1.967530	-2.149566
O	6.256608	0.844065	0.199939
H	6.931782	0.531775	-0.405409
C	-1.324213	-2.024416	1.595347
H	-0.558280	-1.813593	2.342342
H	-2.145167	-2.548908	2.085714
H	-0.884864	-2.669941	0.826949
C	-0.988792	1.740544	-1.311001
H	-1.566493	2.483065	-1.867318
H	-0.010501	2.167803	-1.077813
H	-0.843554	0.870930	-1.954789
C	-1.964615	2.583966	0.851218
H	-2.469218	2.307179	1.778599
H	-1.014909	3.062454	1.102293
H	-2.591212	3.306422	0.321709
H	1.017192	-1.292982	-1.642331

Table S55. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and *ω*B97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(sa-ALN-ss-ALN)**.

TS(sa-ALN-ss-ALN)			
E_{elec} = -940.894343			
E_{ZPE} = 0.332451			
Coordinates (Angstroms)			
	x	y	z
C	4.392422	1.129662	0.506519
C	3.190491	0.593081	0.090705
C	3.100333	-0.770199	-0.209099
C	4.197137	-1.615405	-0.090737
C	5.406315	-1.057658	0.331178
C	5.511230	0.296317	0.626951
C	1.838693	1.252970	-0.133693
C	0.970506	0.029225	-0.519345
N	1.807151	-1.083015	-0.624375
O	-1.689218	-0.506338	1.755801
C	-2.830068	-0.317968	1.043549
C	-2.818765	0.004721	-0.329315
C	-1.582660	0.152360	-1.104646
C	-0.338819	0.036199	-0.682416
C	-4.050959	0.176754	-0.977020
C	-5.250009	0.043067	-0.299398
C	-5.244681	-0.287381	1.053020
C	-4.040234	-0.462984	1.718060
H	4.476189	2.184859	0.742338
H	6.457867	0.707085	0.954863
H	6.274922	-1.697568	0.432128
H	4.125540	-2.672895	-0.310639
H	-1.748245	0.376912	-2.161216
H	-4.069559	0.411509	-2.035414
H	-6.186706	-0.410824	1.573061
H	-4.016515	-0.719872	2.769737
O	-6.457340	0.162651	-0.984058
H	-6.751782	1.079762	-0.965016
C	1.349988	-2.420837	-0.921704
H	0.379538	-2.363200	-1.411104
H	2.050417	-2.916220	-1.597095
H	1.248263	-3.026655	-0.013955
C	1.310067	1.949592	1.129733
H	1.959599	2.785559	1.399420
H	0.304552	2.340132	0.960167
H	1.274123	1.262451	1.976561
C	1.884993	2.246295	-1.311556
H	2.254554	1.765369	-2.218857
H	0.888207	2.645202	-1.512295
H	2.548885	3.081054	-1.075157
H	-0.923339	-0.368929	1.164428

TS(sa-ALN-ss-ALN)			
E_{elec} = -940.576166			
E_{ZPE} = 0.336588			
Coordinates (Angstroms)			
	x	y	z
C	4.272323	1.071075	0.698001
C	3.113385	0.580889	0.141760
C	3.039681	-0.749755	-0.266634
C	4.109493	-1.614427	-0.110653
C	5.276578	-1.105981	0.456410
C	5.366224	0.218270	0.855750
C	1.796677	1.273233	-0.144045
C	0.957435	0.092942	-0.660971
N	1.791589	-1.008797	-0.823115
O	-1.504647	-0.603887	1.597054
C	-2.684121	-0.383296	0.975985
C	-2.774147	0.031672	-0.362740
C	-1.598845	0.256263	-1.215163
C	-0.336203	0.122771	-0.883384
C	-4.044759	0.229986	-0.909517
C	-5.190688	0.033011	-0.165533
C	-5.087197	-0.388582	1.153450
C	-3.841637	-0.591313	1.717895
H	4.335769	2.105992	1.017196
H	6.282909	0.589673	1.296424
H	6.126945	-1.764258	0.590040
H	4.049011	-2.653259	-0.410145
H	-1.833273	0.559899	-2.236573
H	-4.139718	0.538190	-1.945220
H	-5.989642	-0.560649	1.727567
H	-3.741830	-0.919398	2.745099
O	-6.435401	0.189411	-0.750140
H	-6.725786	1.096819	-0.642429
C	1.305521	-2.321088	-1.152754
H	0.437289	-2.225225	-1.804464
H	2.075802	-2.879033	-1.686800
H	1.011191	-2.884417	-0.259250
C	1.177454	1.894872	1.108719
H	1.806306	2.709895	1.474797
H	0.187276	2.298609	0.884538
H	1.076532	1.157524	1.907144
C	1.949213	2.325347	-1.250289
H	2.379241	1.884704	-2.151658
H	0.975674	2.753266	-1.501095
H	2.607662	3.130234	-0.914827
H	-0.780414	-0.416509	0.978416

Table S56. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and *ω*B97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(ALN-CTC*)**.

TS(ALN-CTC*)			
E_{elec} = -940.87837			
E_{ZPE} = 0.32874			
Coordinates (Angstroms)			
	x	y	z
C	5.651495	-0.066501	0.056798
C	5.412585	1.248534	-0.328614
C	4.585477	-0.932034	0.323482
C	3.291514	-0.463701	0.198251
C	3.070528	0.857155	-0.191457
C	4.110647	1.735555	-0.458605
C	1.954786	-1.146690	0.406806
C	0.969278	-0.005883	0.104977
C	1.685834	1.103656	-0.237656
O	-2.791065	0.278228	0.131869
N	-3.025681	-0.907004	-0.641468
C	-2.029121	-1.620978	-1.107141
C	-3.882387	1.034928	0.602734
C	-5.410972	-0.516151	-0.409304
C	-4.364011	-1.294417	-0.861263
C	1.766447	-1.635969	1.856755
C	1.752622	-2.314428	-0.580530
C	-0.392419	-0.151982	0.071204
H	-1.442665	0.606843	0.490007
H	1.132079	2.372836	-0.671205
H	6.669850	-0.422189	0.152049
H	6.247124	1.909262	-0.529467
H	4.779674	-1.955663	0.622799
H	3.931963	2.762142	-0.751072
H	1.910814	-0.824122	2.571970
H	0.761391	-2.039316	1.989923
C	2.489142	-2.422681	2.083702
H	2.492389	-3.094288	-0.386536
H	0.756277	-2.742484	-0.466376
H	1.867668	-1.983769	-1.613896
C	-1.022848	-1.136221	-0.573139
H	-1.310376	1.413737	1.214101
H	0.074401	2.240384	-0.885266
H	1.247161	3.136867	0.101420
C	1.644240	2.706093	-1.575942
H	-5.175774	0.657472	0.324199
H	-6.205714	1.448912	0.791165
H	-6.433012	-0.817853	-0.621880
O	-4.549029	-2.202798	-1.420759
H	-3.706169	1.927831	1.192508
H	-7.047715	1.055266	0.539465

TS(ALN-CTC*)			
E_{elec} = -940.55465			
E_{ZPE} = 0.332697			
Coordinates (Angstroms)			
	x	y	z
C	5.628096	-0.072194	0.099381
C	5.397273	1.241456	-0.283096
C	4.561268	-0.935980	0.344923
C	3.275312	-0.463841	0.200165
C	3.063342	0.852554	-0.186932
C	4.101551	1.730245	-0.432086
C	1.939888	-1.141418	0.383332
C	0.970640	-0.003194	0.073994
C	1.680560	1.097381	-0.256877
O	-2.774082	0.281949	0.108432
N	-3.014872	-0.927901	-0.609797
C	-2.037036	-1.661283	-1.059133
C	-3.853293	1.058688	0.567232
C	-5.392377	-0.522500	-0.356911
C	-4.358753	-1.316399	-0.793513
C	1.724224	-1.634216	1.820033
C	1.746172	-2.290898	-0.616416
C	-0.389611	-0.155487	0.027577
H	-1.422402	0.622458	0.438236
H	1.133763	2.361383	-0.691394
H	6.644939	-0.428041	0.209405
H	6.236179	1.901557	-0.467022
H	4.744143	-1.962072	0.644042
H	3.925931	2.758596	-0.721930
H	1.862079	-0.825229	2.540065
H	0.713425	-2.030925	1.930505
C	2.439232	-2.426486	2.052393
H	2.484118	-3.072717	-0.422827
H	0.746725	-2.716555	-0.516923
H	1.872856	-1.944096	-1.643370
C	-1.013256	-1.151676	-0.560180
H	-1.274603	1.452434	1.133279
H	0.086145	2.220759	-0.950719
H	1.210331	3.113424	0.096856
C	1.678979	2.709791	-1.570571
H	-5.147117	0.677398	0.325958
H	-6.164589	1.482380	0.773982
H	-6.417765	-0.832501	-0.541480
O	-4.554711	-2.245514	-1.314317
H	-3.663855	1.973777	1.118642
H	-7.005959	1.082415	0.548778

Table S57. Electronic energies (E_{elec}, Hartree), zero-point energies (E_{ZPE}, Hartree), and optimized cartesian coordinates, calculated at the B3LYP/6-311+G(2d,p) (left) and ωB97X-D/6-311+G(2d,p) (right) levels of theory, for the transition state **TS(ALN-TTC*)**.

TS(ALN-TTC*)			
E_{elec} = -940.87859			
E_{ZPE} = 0.32855			
Coordinates (Angstroms)			
	x	y	z
C	-5.581082	-0.591212	0.305654
C	-5.566775	0.735626	-0.111820
C	-4.384575	-1.302589	0.446932
C	-3.189315	-0.669521	0.165847
C	-3.193030	0.663219	-0.246234
C	-4.366226	1.388519	-0.397346
C	-1.756659	-1.166512	0.214438
C	-0.975089	0.090599	-0.214735
C	-1.872871	1.086330	-0.461900
O	2.780770	-0.167187	-0.167514
N	2.996491	1.042158	0.573718
C	1.988502	1.774142	0.983928
C	3.884049	-0.943007	-0.576452
C	5.386024	0.636642	0.431399
C	4.328566	1.432862	0.823324
C	-1.520568	-2.315555	-0.787410
C	-1.347951	-1.604618	1.634291
C	0.384904	0.272701	-0.204713
H	1.444861	-0.506498	-0.559851
H	-1.532332	2.425728	-0.903784
H	-6.524515	-1.077375	0.520509
H	-6.500331	1.274596	-0.218505
H	-4.404141	-2.336896	0.771274
H	-4.361357	2.420917	-0.722126
H	-1.775117	-2.016641	-1.805607
H	-0.480890	-2.642843	-0.767236
C	-2.145349	-3.169993	-0.518646
H	-1.936910	-2.471908	1.941082
H	-0.291110	-1.873777	1.657797
H	-1.513423	-0.804737	2.357344
C	0.999838	1.268118	0.435048
H	1.342121	-1.340402	-1.255308
H	-1.977436	3.164566	-0.234221
H	-0.451166	2.534585	-0.889151
C	-1.897816	2.599634	-1.919150
H	5.169245	-0.560592	-0.269289
H	6.210287	-1.370212	-0.676010
H	6.402024	0.941856	0.666669
O	3.722871	-1.855381	-1.140052
H	4.499320	2.358519	1.358526
H	7.045318	-0.973180	-0.407011

TS(ALN-TTC*)			
E_{elec} = -940.55486			
E_{ZPE} = 0.33243			
Coordinates (Angstroms)			
	x	y	z
C	-5.556677	-0.609419	0.286809
C	-5.547170	0.717689	-0.118231
C	-4.361712	-1.314859	0.427985
C	-3.173914	-0.671999	0.158606
C	-3.183207	0.657168	-0.242341
C	-4.351940	1.378277	-0.392491
C	-1.744416	-1.156664	0.213820
C	-0.976245	0.099892	-0.203636
C	-1.865167	1.085658	-0.450241
O	2.764214	-0.166123	-0.151451
N	2.985121	1.058152	0.548787
C	1.995206	1.806403	0.943015
C	3.856386	-0.959375	-0.548761
C	5.367880	0.634325	0.399250
C	4.323317	1.443701	0.776588
C	-1.495488	-2.296231	-0.784236
C	-1.339982	-1.584240	1.630585
C	0.382550	0.285663	-0.181617
H	1.426292	-0.510552	-0.527911
H	-1.530872	2.427328	-0.866899
H	-6.499291	-1.100762	0.493474
H	-6.483419	1.252119	-0.224021
H	-4.372168	-2.352181	0.744118
H	-4.347123	2.413816	-0.708790
H	-1.729495	-1.989530	-1.805210
H	-0.458083	-2.629324	-0.742901
C	-2.131183	-3.146728	-0.528799
H	-1.924620	-2.455382	1.935109
H	-0.279941	-1.842109	1.656265
H	-1.516249	-0.781346	2.348060
C	0.987975	1.282197	0.415580
H	1.312093	-1.359029	-1.204192
H	-1.960993	3.150090	-0.170437
H	-0.448851	2.535131	-0.871958
C	-1.918819	2.620543	-1.869777
H	5.141822	-0.580007	-0.265150
H	6.171123	-1.400370	-0.653823
H	6.387226	0.942471	0.617360
O	3.682805	-1.886501	-1.084992
H	4.504492	2.383093	1.284152
H	7.005431	-1.000794	-0.403126