Electronic Supplementary Information

Theoretical Study on the Excited-State Deactivation Paths for A-5FU Dimer

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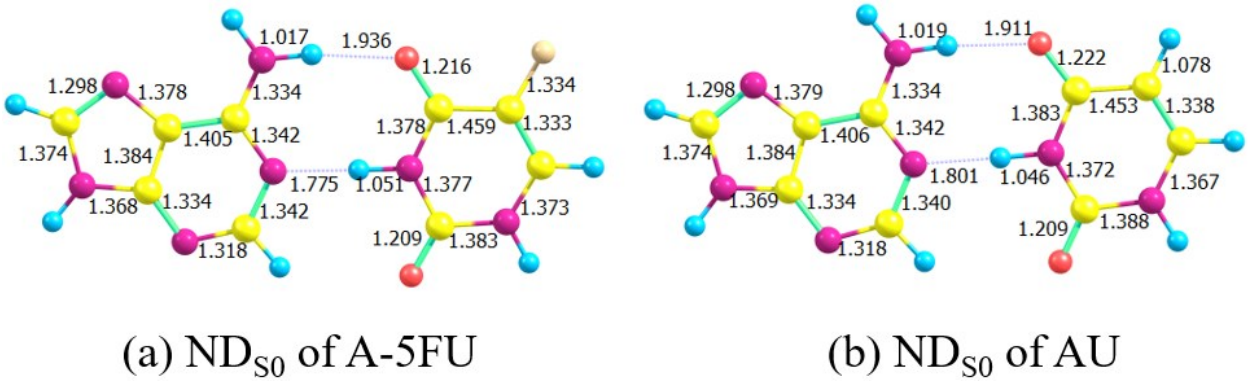
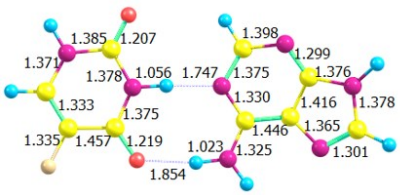
Figure S1. Equilibrium geometries in the S_0 state optimized at the CAM-B3LYP/TZVP level: (a) ND_{S0} of A-5FU dimer and (b) ND_{S0} of AU dimer. Bond lengths are in angstroms.

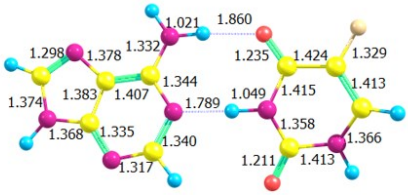


(a) ND_{S0} of A-5FU (b) ND_{S0} of AU

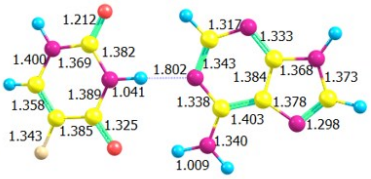
Figure S2. Equilibrium geometries in the S_1 state optimized at the (TD-)CAM-B3LYP/TZVP level: (a) ND_{ALE}, (b) ND_{ULE}, (c) $ND_{n\pi^*}$, (d) INT_{LE} and (e) INT_{CT}. Bond lengths are in angstroms.



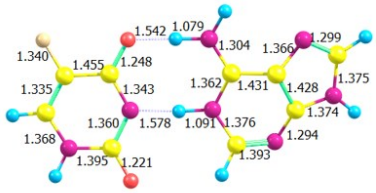
(a) ND_{ALE}



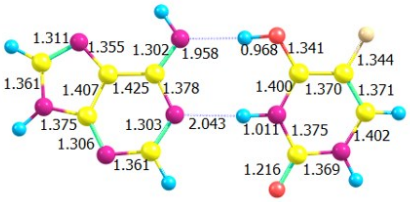
(b) ND_{ULE}



(c) $ND_{n\pi^*}$



(d) INT_{LE}



(e) INT_{CT}

Figure S3. The involved frontier orbitals for (a) ND_{ALE}, (b) ND_{ULE}, (c) $ND_{n\pi^*}$, (d) INT_{LE} and (e) INT_{CT}. Bond lengths are in angstroms.

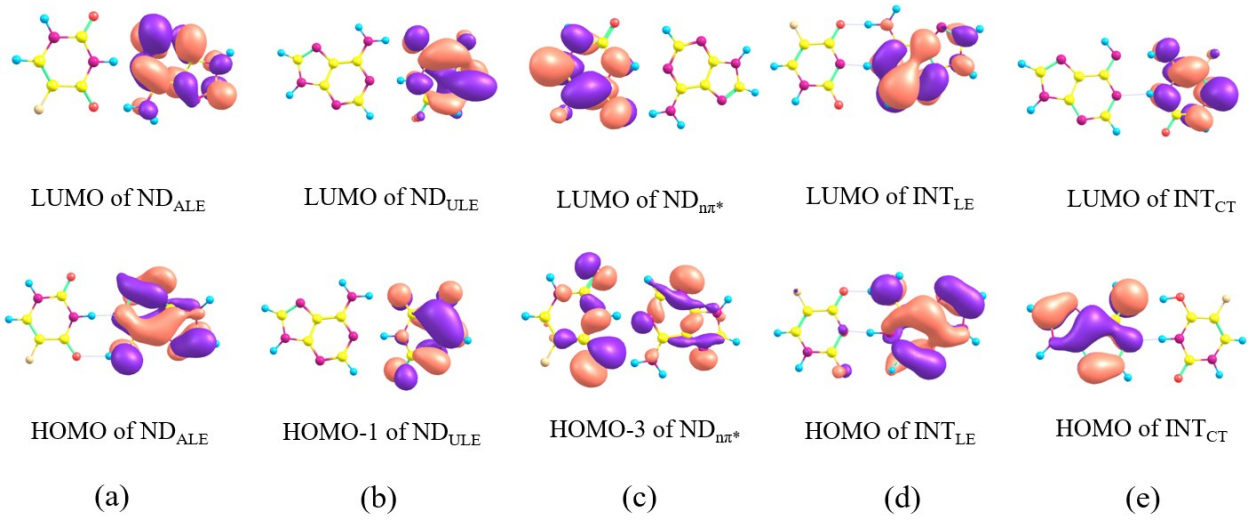
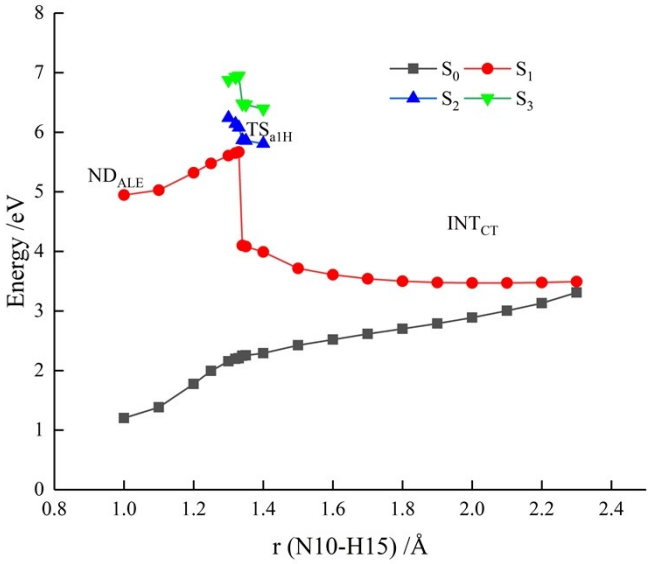
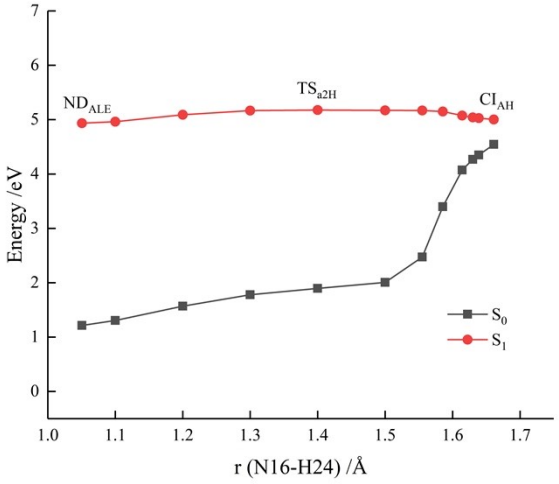


Figure S4. The potential energy profiles as a function of r(N-H) along (a) N-H···O, (b) N-H···N in ND_{ALE}, (c) N-H···O and (d) N-H···N in ND_{ULE} calculated at the (TD-)CAM-B3LYP/6-31g(d) level as well as (e) N-H···O in ND_{ALE} calculated at the (TD-)CAM-B3LYP/def2-SV(P) level.

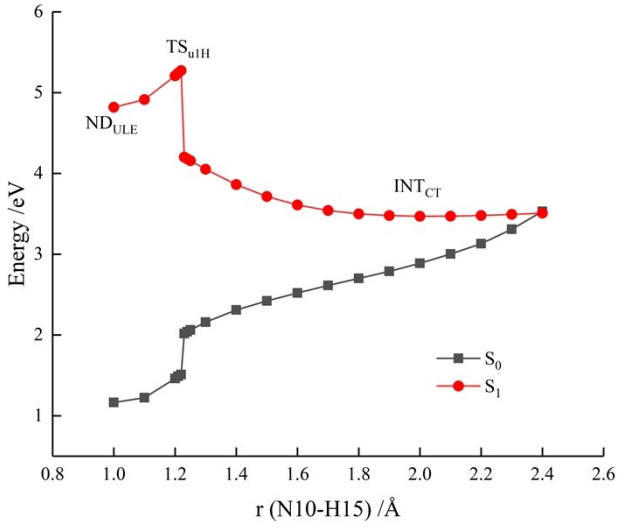
(a)



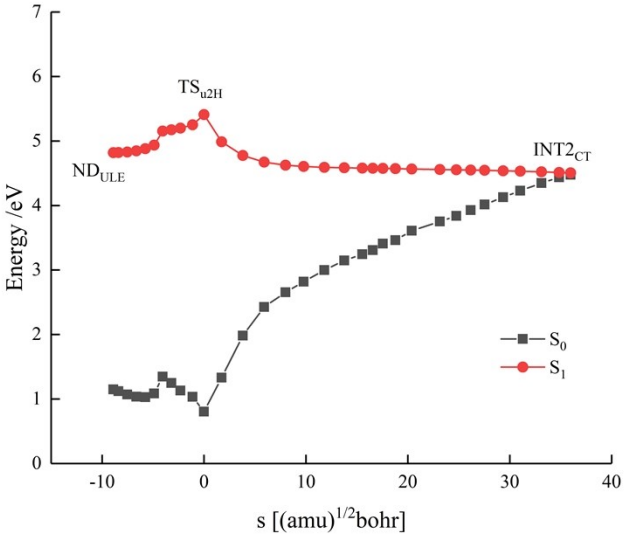
(b)



(c)


TS$_{u1H}$
ND$_{ULE}$
INT$_{CT}$
S$_0$
S$_1$
Energy /eV
r (N10-H15) /Å

(d)


TS$_{u2H}$
ND$_{ULE}$
INT2$_{CT}$
S$_0$
S$_1$
Energy /eV
s [(amu)$^{1/2}$bohr]

(e)

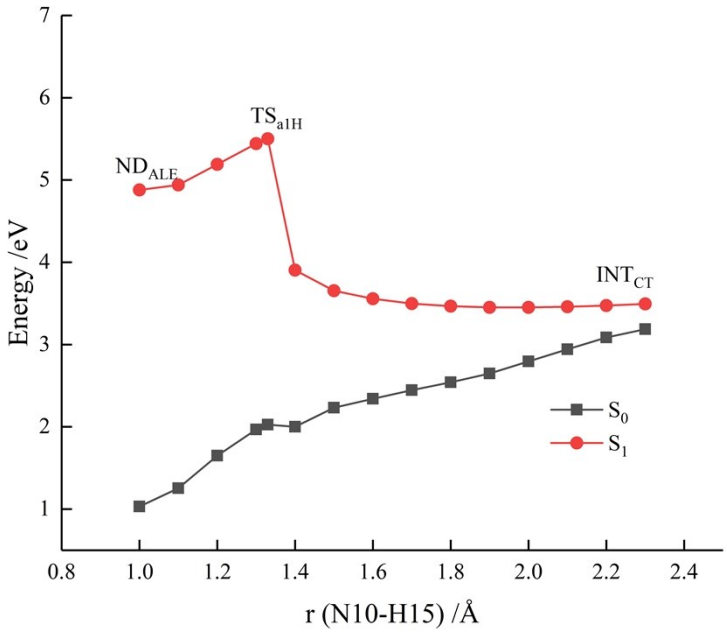
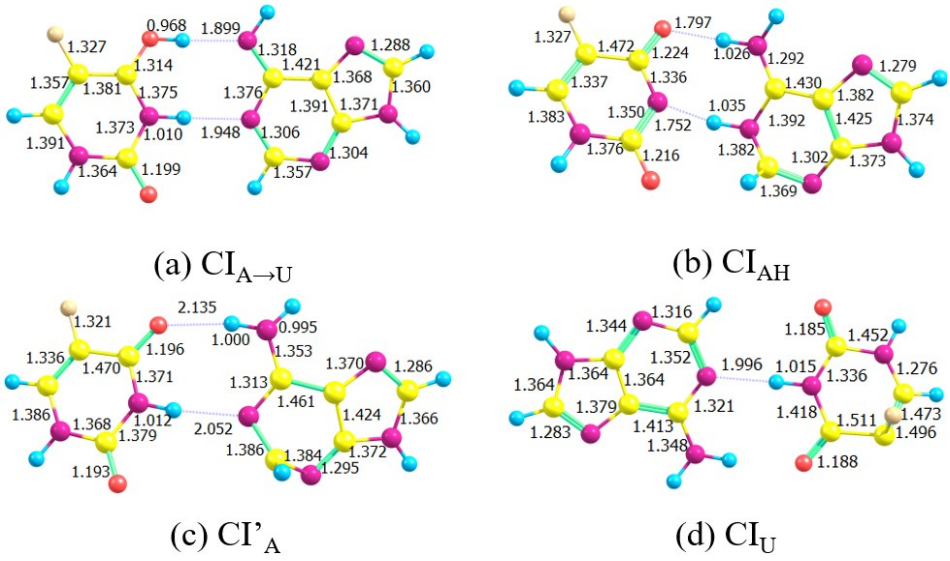

Energy /eV
r (N10-H15) /Å
ND_ALE
TS_a1H
INT_CT
S0
S1
7
6
5
4
3
2
1
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4

Figure S5. The equilibrium geometries of CIs: (a) $CI_{A\rightarrow U}$, (b) CI_{AH}, (c) CI'_{A} and (d) CI_{U} calculated at the CASSCF(6,6)/6-31G(d) level. Bond lengths are in angstroms.

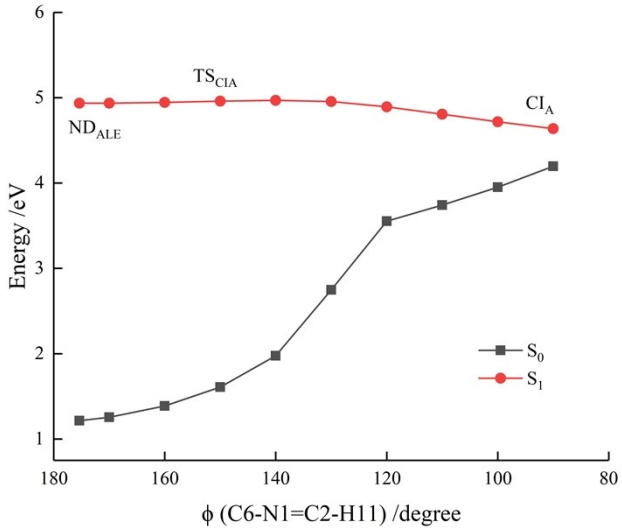


(a) $CI_{A\rightarrow U}$ (b) CI_{AH}

(c) CI'_{A} (d) CI_{U}

Figure S6. The potential energy profiles as a function of dihedral angles (a) ϕ (C6-N1=C2-H11) and (b) δ (F27-C20=C19-N18) calculated at the (TD-)CAM-B3LYP/6-31G(d) level.

(a)



(b)

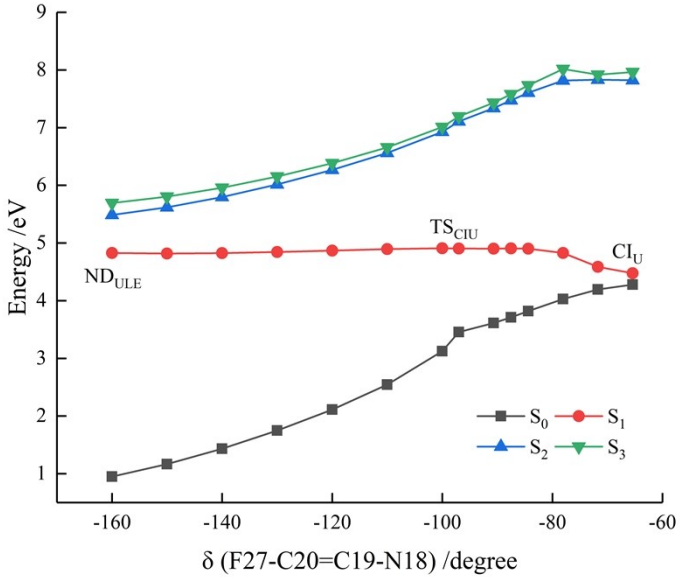
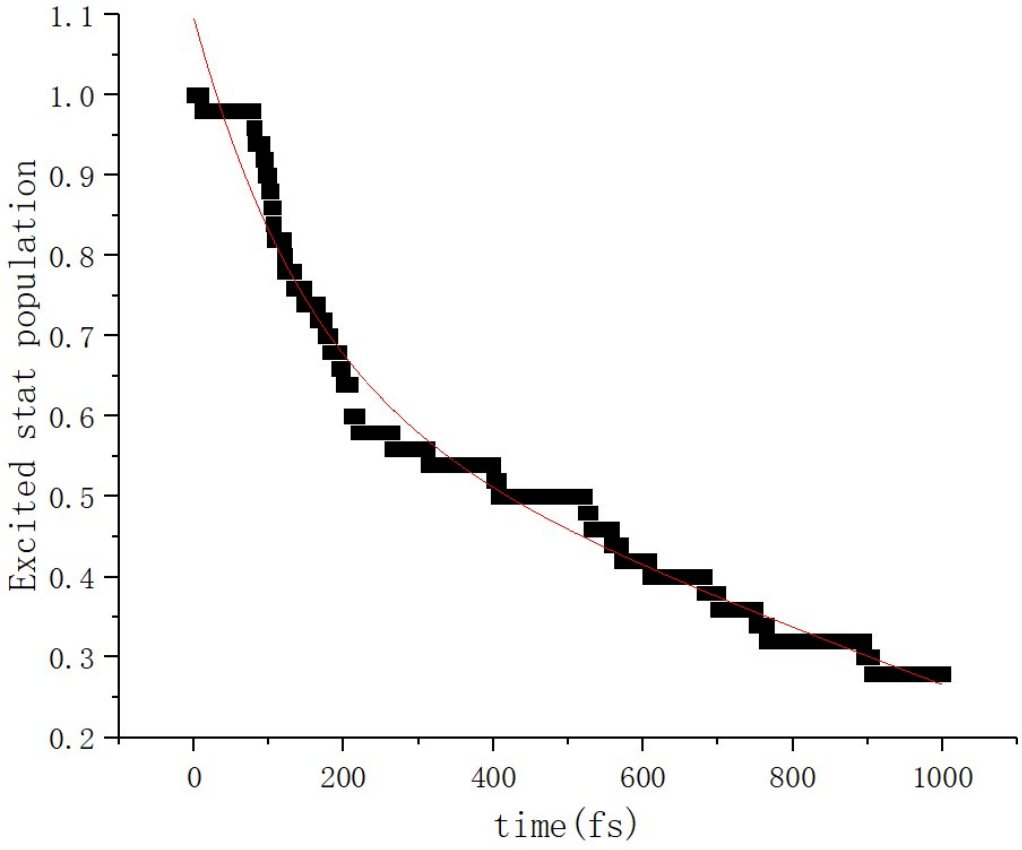


Figure S7. The excited state population as a function of time and the exponential fit.



2. Double proton transfer processes in the locally excited state

We investigated the ESDPT in A-5FU dimer to check whether the tautomerization could induce DNA mutation. **Figure S8a, b** show the reaction diagram for the ESDPT processes in monomer 5FU and monomer A locally excited states determined at (TD-)CAM-B3LYP/TZVP level, respectively. The ESDPT from ND_{ULE} to TD_{ULE} is a single-step process via a single transition state (TS_U) occurring in monomer 5FU locally excited state. This process is a direct DPT, without forming any intermediate. Energetically, TD_{ULE} and TS_U lie about 0.33 and 0.38

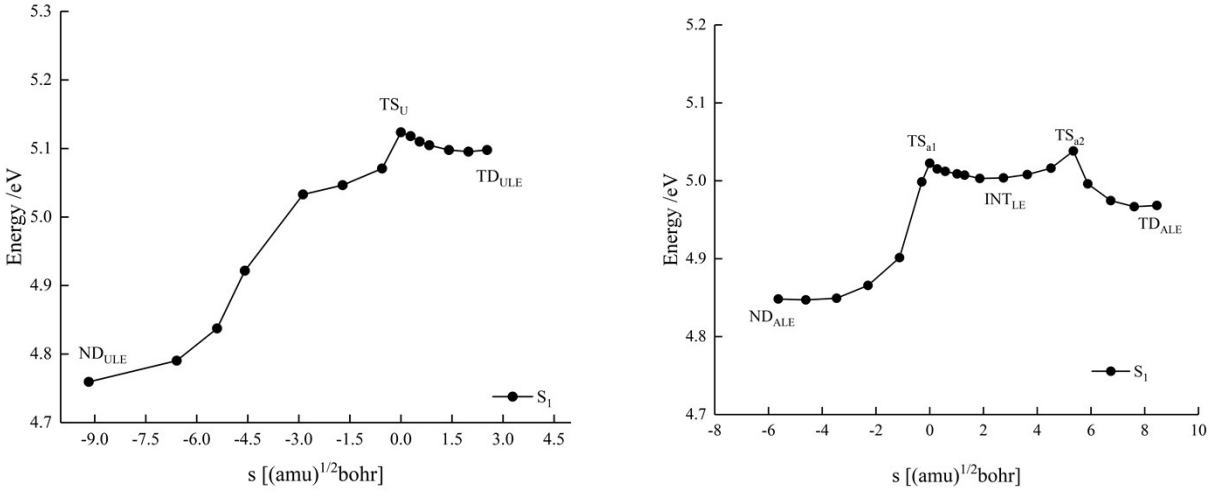


Figure S8 The IRC paths for the ESDPT process from (a) ND_{ULE} to TD_{ULE} and (b) ND_{ALE} to TD_{ALE} calculated at the (TD-)CAM-B3LYP/TZVP level.

eV higher than ND_{ULE} at (TD-)CAM-B3LYP/TZVP level, and TS_U is closer to TD_{ULE} side, thus, the forward DPT process is very difficult to occur compared to the reverse proton transfer from TD_{ULE} to ND_{ULE}. The corresponding values at the (TD-)CAM-B3LYP/6-31G(d) level are also similar, calculated to be 0.37 and 0.44 eV. The shape of potential energy profile for the ESDPT in ND_{ALE} is different from that in ND_{ULE}. The ESDPT in A locally excited state is a three-step process via two transition states (TS_{a1} and TS_{a2}). An intermediate of locally excited state (INT_{LE}) is formed after the first SPT process from A to 5FU via TS_{a1}, followed by the other proton transfer from INT_{LE} to ND_{ALE} via TS_{a2}. Energetically, TD_{ALE}, TS_{a1} and TS_{a2} lie about 0.13 (0.31), 0.20 (0.35) and 0.22 (0.40) eV higher than ND_{ALE} at the (TD-)CAM-B3LYP/TZVP(6-31G(d)) level, respectively. Similarly, the reverse proton transfer is more favorable to occur than the

forward DPT. One should mention that for the AT dimer, the step wise reaction path has also been found in the previous work[1].

3. The second SPT in the S_1 state

As discussed above, INT_{CT} was located at 1.34 (1.46) eV lower than ND_{ULE} (ND_{ALE}), and 1.72 (1.65) eV lower than TD_{ULE} (TD_{ALE}) at the (TD-)CAM-B3LYP/6-31G(d) level. In this case, the second SPT from INT_{CT} to TD_{ULE} (TD_{ALE}) is very unlikely to happen. In contrast, the reversed proton transfer from TD_{ULE} (and TD_{ALE}) to INT_{CT} is possible, thus the second SPT process is also discussed in this section.

We located two transition states for the second SPT processes, namely $TS_{aINT/TD}$ and $TS_{uINT/TD}$, respectively. $TS_{aINT/TD}$ and $TS_{uINT/TD}$ have imaginary frequencies of -3459.6 and -

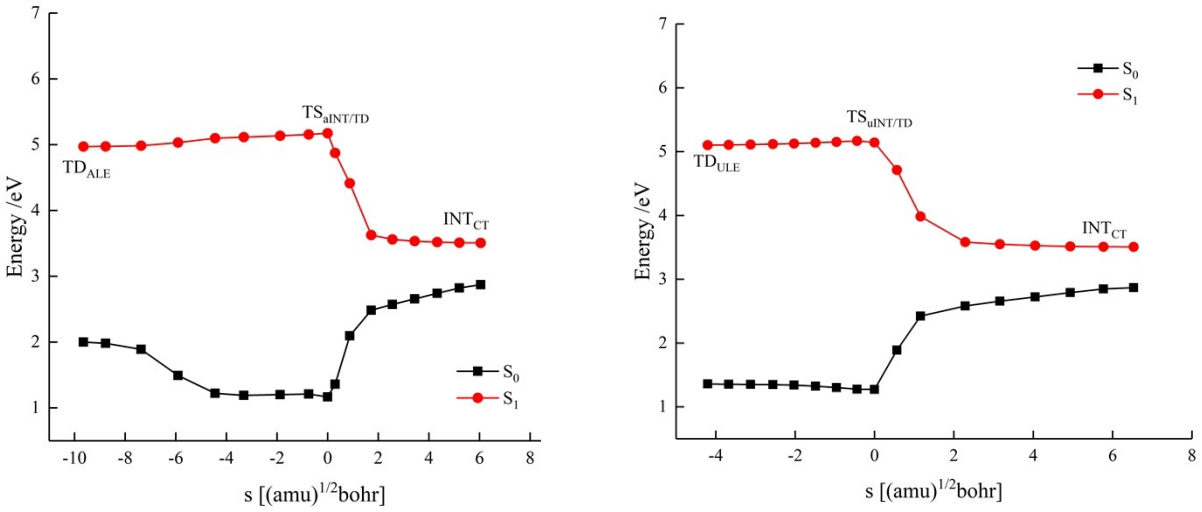


Figure S9 The IRC paths for the ESPT process from INT_{CT} to (a) TD_{ALE} and (b) TD_{ULE} calculated at the (TD-)CAM-B3LYP/TZVP level.

8760.2 cm^{-1}, respectively, with the vibration modes of two hydrogen atoms transferring along the hydrogen bonds. The IRC calculations confirm the connection of INT_{CT} and TD_{ALE} via $TS_{aINT/TD}$ as well as the connection of INT_{CT} and TD_{ULE} via $TS_{uINT/TD}$. In both transition states, the structure parameters are very different from each other. The transition state in $TS_{aINT/TD}$ is quasi-planar while the structure is nonplanar in $TS_{uINT/TD}$. Figure S9 show the potential energy profiles for the second SPT from INT_{CT}, forming TD_{ALE} and TD_{ULE} determined at the (TD-)CAM-B3LYP/TZVP levels. The shapes of both potential energy profiles are very similar with each other. The energies of the S_1 state increase sharply as proton transfer, and once passing through the $TS_{aINT/TD}$ ($TS_{uNT/TD}$), the energy decreases slowly accompanied by the bond r(N16-H24)

stretching from 1.679 Å in $TS_{uINT/TD}$ to 1.818 Å and structure deformation on 5FU in TD_{ULE}, and the bond r(N16-H24) stretching from 1.682 Å in $TS_{aINT/TD}$ to 1.864 Å and structure deformation on monomer A in TD_{ALE}, finally forming the tautomer dimers (TD_{ULE} and TD_{ALE}). Obviously, the proton transfer for the second SPT from 5FU to A is very unfavorable to occur. In contrast, the reverse proton transfer is very likely to occur due to the small energy barrier. Once the double proton transferred tautomers (TD_{ALE} and TD_{ULE}) are formed, they could go to INT_{CT} by passing through the corresponding energy barriers, then followed by internal conversion to the S_0 state.

4. Decay path from the nπ* state

4.1 SPT in the nπ* state

The energy for the minimum in the nπ* state ($ND_{n\pi^*}$) is very similar with the one (ND_{ULE}) in the ππ* state, and $ND_{n\pi^*}$ is located at 0.088 eV lower than ND_{ULE} at (TD-)CAM-B3LYP/6-31G(d) level, and about 0.005 eV higher than ND_{ULE} at the (TD-)CAM-B3LYP/TZVP level, thus proton transfer process in nπ* is also very important. **Figure S10** shows the potential energy

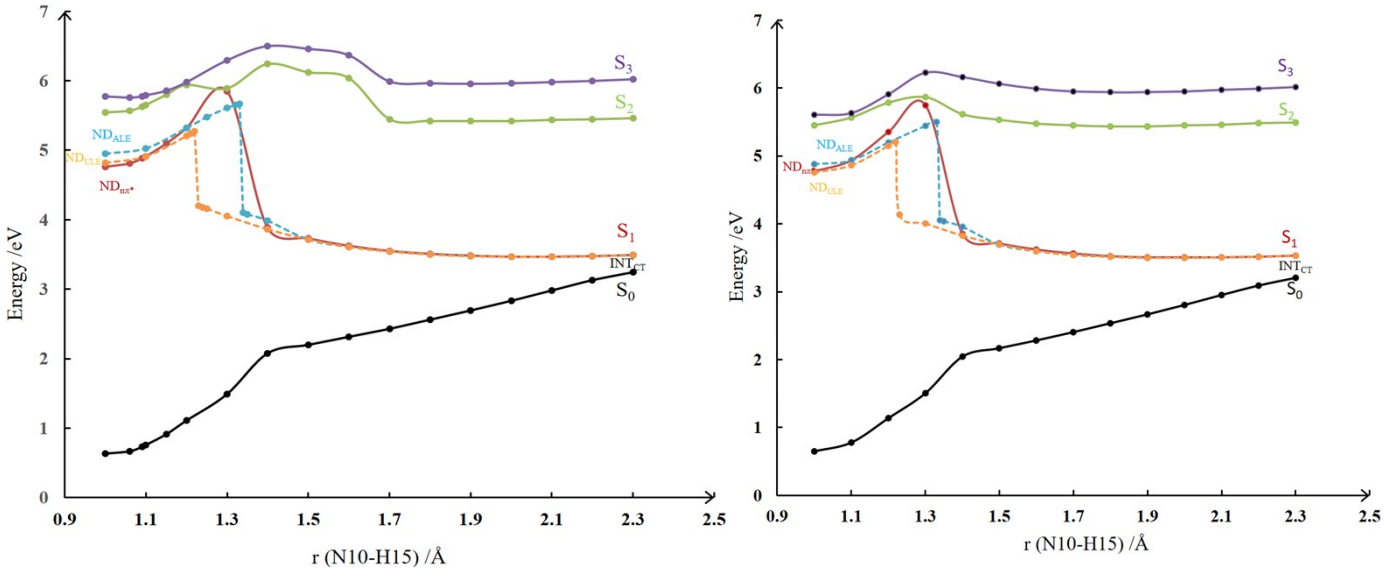


Figure S10 The potential energy profiles as a function of r(N-H) along N-H···O in the lowest 4 states calculated (a) at the (TD-)CAM-B3LYP/6-31G(d) level and (b) at the (TD-)CAM-B3LYP/TZVP level.

profiles of the lowest 4 states along proton transfer from A to 5FU at the (TD-)CAM-B3LYP/6-31G(d) level. In this calculation, the nπ* state was relaxed along proton transfer reaction path, and the energies of the other states were obtained with single-point energy calculation based on the S_1 optimized geometries. The energy curve of the relaxed ππ* state of 5FU locally excited state and A locally excited state are also shown by orange and blue dotted lines, respectively. The shapes of the potential curves for the S_1 and S_0 are very similar to the ones in ND_{ULE}, and the energy gap between S_1 and S_0 becomes smaller towards to INT_{CT}. The highest point of the S_1 state appears at r(N-H) = 1.3 Å along the proton transfer coordinate. At this point, the energies of S_1 and S_2 states are almost degenerate, with the electronic characters of S_1 and S_2 state are nπ*

and CT state, respectively. The energy barrier for proton transfer process in the nπ* state is estimated to be 1.1 eV with respect to $ND_{n\pi^*}$, such high energy barrier prohibits the direct proton transfer process along this path. However, there are several crossings between nπ* state and A locally and 5FU locally excited states along proton transfer channel. For example, crossing occurs between nπ* state and the U locally excited state at r(N-H) = 1.1 Å, and with A locally excited state at r(N-H) = 1.2 Å. These crossings could provide additional decay paths for nπ* state. Once nπ* state is populated, proton transfer occurs on the relaxed nπ* state until crossing at r(N-H) = 1.1 Å, then U locally excited state is populated, followed by proton transfer in U locally excited state as is shown by orange dotted line. Another possible decay path for nπ* state is through crossing with A locally excited state at r(N-H) = 1.2 Å, then followed by proton transfer on A locally excited state as is shown in blue dotted line. These two additional paths exhibit smaller energy barriers than the direct decay path from nπ* state shown in red line, especially from the former decay path via 5FU locally excited state. At the (TD-)CAM-B3LYP/TZVP level shown in Figure S10b, the S_1 energy of the relaxed nπ* state lies between the relaxed ππ* state of monomer A LE, and the relaxed ππ* state of monomer 5FU LE in the first point at r (N-H) =1.0 Å. The energy of nπ* state increases sharply, and becomes degenerates with the one for the relaxed ππ* state of monomer A LE when proton transfer occurs. In the meanwhile, the potential energy for the proton transfer in 5FU locally excited state becomes lower than the one in nπ* state. Energetically, the energy barrier for proton in the nπ* state (1.0 eV with respect to $ND_{n\pi^*}$) is higher than that in the ππ* state, thus the direct proton transfer in the nπ* state is also less likely to occur. Instead, once nπ* state is populated, A locally excited state could be switched on owing to the crossing between nπ* and ππ* states at r(N-H) = 1.2 Å, from where proton transfer follows on A locally excited state.

We also investigated the reaction path between nπ* minimum $ND_{n\pi^*}$ and U locally excited state minimum ND_{ULE} to check whether $ND_{n\pi^*}$ or ND_{ULE} could be populated. **Figure S11** shows the potential energy profiles connecting ND_{ULE} with $ND_{n\pi^*}$ along the LIIC path at the (TD-)CAM-B3LYP/TZVP, and the one at the (TD-)CAM-B3LYP/6-31G(d) level is very similar with the one at the (TD-)CAM-B3LYP/TZVP level. The S_1 energy for $ND_{n\pi^*}$ and ND_{ULE} are very similar, and these two minimums are separated by a small energy barrier from a crossing between the nπ* and ππ* states at both levels. At the (TD-)CAM-B3LYP/TZVP(6-31G(d)) level, the energy barriers for reaching $ND_{n\pi^*}$ from ND_{ULE} as well as the one for reaching ND_{ULE} from

$ND_{n\pi^*}$ are very small, calculated to be only 0.26 (0.24) eV and 0.26(0.32) eV, respectively. Furthermore, such small energy barriers could be overcome upon excitation on U locally excited state at the Franck–Condon geometry. Thus nπ* state could be populated via this path, and also could be switched to ππ* via the reverse path.

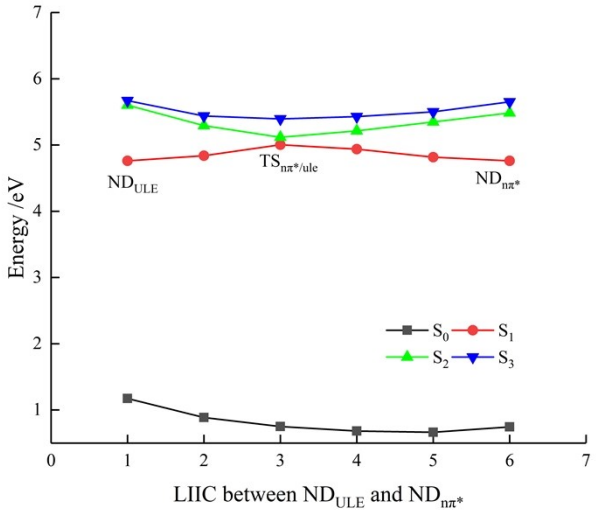


Figure S11 The potential energy profiles of the LIIC between ND_{ULE} and $ND_{n\pi^*}$ at the (TD-)CAM-B3LYP/TZVP level.

4.2 Monomer-like decay in the nπ* state

To check whether the monomer-like decay path occurs via the nπ* state directly, we have

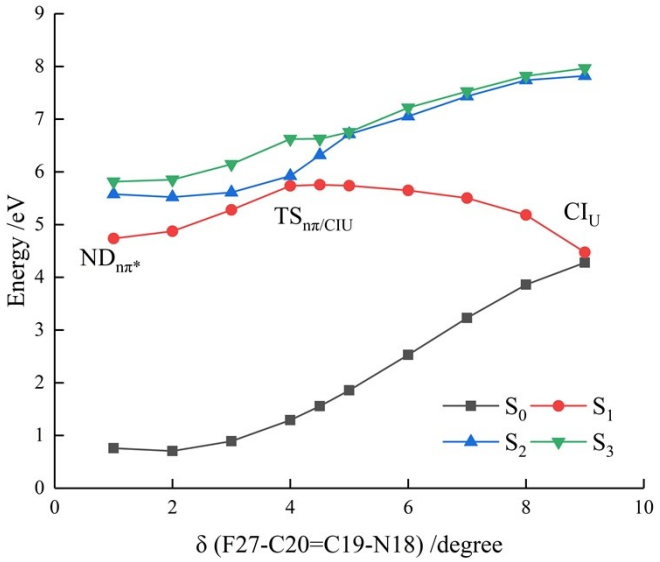


Figure S12 The potential energy profiles of the LIIC between $ND_{n\pi^*}$ and CI_U at the (TD-)CAM-B3LYP/6-31G(d) level

investigated the nonradiative decay path from nπ* minimum $ND_{n\pi^*}$. **Figure S12** shows the potential energy profiles connecting it with CI_U along the LIIC path at the (TD-)CAM-B3LYP/6-31G(d) level. The energy barrier for reaching CI_U is estimated to be 1.00 eV, such a high barrier makes the direct nonradiative decay path from $ND_{n\pi^*}$ less favorable. At the (TD-)CAM-B3LYP/TZVP level, the energy barrier is estimated to be 0.87 eV. One should mention, that this barrier could be overestimated because this path is not the minimum energy path. The similar energy barrier for reaching CI_U from nπ* minimum was also found in the monomer U, T, 5FU in the previous study at MS-CASPT2 level[2]. Another decay path for $ND_{n\pi^*}$ to CI_U is a two-step process involving ππ* minimum ND_{ULE} as an intermediate, discussed above. In the first step, nπ* minimum $ND_{n\pi^*}$ switched to ππ* minimum ND_{ULE} via a small barrier of 0.26 eV as shown in Figure S11, and then ND_{ULE} could further reach CI_U via the out-of-plane deformation by overcoming the tiny energy barrier of 0.11 eV at the (TD-)CAM-B3LYP/TZVP level. The total energy barrier for the two-step processes is much smaller than the single-step process, thus nπ* decay path is likely to occur through this two-step process through an intermediate ND_{ULE}.

5. Cartesian Coordinates of All Optimized Structures

ND_{S0} for A-5FU dimer optimized at the CAM-B3LYP/TZVP level

N	-0.981555000000	0.368599000000	0.000000000000
C	-1.578016000000	1.570211000000	0.000000000000
N	-2.870030000000	1.828628000000	0.000000000000
C	-3.599394000000	0.711177000000	0.000000000000
C	-3.122373000000	-0.587513000000	0.000000000000
C	-1.726083000000	-0.747772000000	0.000000000000
N	-4.961396000000	0.581149000000	0.000000000000
C	-5.228325000000	-0.766355000000	0.000000000000
N	-4.156777000000	-1.498308000000	0.000000000000
N	-1.136458000000	-1.944920000000	0.000000000000
H	-0.901316000000	2.417655000000	0.000000000000
H	-5.625202000000	1.337696000000	0.000000000000
H	-6.239139000000	-1.142993000000	0.000000000000
H	-1.711844000000	-2.768928000000	0.000000000000
H	-0.122777000000	-2.026658000000	0.000000000000
N	1.844050000000	0.370046000000	0.000000000000
C	2.457950000000	1.602226000000	0.000000000000
N	3.840066000000	1.541853000000	0.000000000000
C	4.545881000000	0.364628000000	0.000000000000
C	3.906846000000	-0.804915000000	0.000000000000
C	2.449653000000	-0.867896000000	0.000000000000
O	1.809519000000	-1.902233000000	0.000000000000
O	1.856239000000	2.650692000000	0.000000000000
H	0.793350000000	0.378262000000	0.000000000000

H	4.314946000000	2.429925000000	0.000000000000
H	5.624145000000	0.431303000000	0.000000000000
F	4.571869000000	-1.961655000000	0.000000000000

ND_{S0} for A-U dimer optimized at the CAM-B3LYP/TZVP level

N	0.000000000000	0.725287000000	0.000000000000
C	0.905610000000	1.713593000000	0.000000000000
N	0.682476000000	3.012956000000	0.000000000000
C	-0.622446000000	3.291084000000	0.000000000000
C	-1.662690000000	2.378901000000	0.000000000000
C	-1.309515000000	1.018170000000	0.000000000000
N	-1.233719000000	4.515490000000	0.000000000000
C	-2.587057000000	4.280022000000	0.000000000000
N	-2.884695000000	3.016969000000	0.000000000000
N	-2.212222000000	0.035843000000	0.000000000000
H	1.940019000000	1.387809000000	0.000000000000
H	-0.766289000000	5.406753000000	0.000000000000
H	-3.301959000000	5.087826000000	0.000000000000
H	-3.188323000000	0.274801000000	0.000000000000
H	-1.919455000000	-0.939866000000	0.000000000000
N	0.993184000000	-1.942994000000	0.000000000000
C	2.356615000000	-2.094483000000	0.000000000000
N	2.775761000000	-3.417284000000	0.000000000000
C	1.911794000000	-4.476815000000	0.000000000000
C	0.585339000000	-4.301575000000	0.000000000000
C	0.047242000000	-2.952355000000	0.000000000000
O	-1.145123000000	-2.687022000000	0.000000000000

O	3.140152000000	-1.173585000000	0.000000000000
H	0.639420000000	-0.958430000000	0.000000000000
H	3.773748000000	-3.553252000000	0.000000000000
H	2.372715000000	-5.454916000000	0.000000000000
H	-0.104965000000	-5.129001000000	0.000000000000

ND_{ALE} optimized at the (TD-)CAM-B3LYP/TZVP level

N	-0.785668000000	-0.649951000000	0.101169000000
C	-2.138538000000	-0.787356000000	0.307604000000
N	-2.763313000000	-1.915732000000	-0.232375000000
C	-2.134774000000	-3.027339000000	0.005576000000
C	-0.770439000000	-3.038208000000	0.382569000000
C	-0.086611000000	-1.774167000000	0.225306000000
N	-2.412875000000	-4.335768000000	-0.315778000000
C	-1.250139000000	-5.048434000000	-0.119280000000
N	-0.253710000000	-4.293138000000	0.240789000000
N	1.237902000000	-1.757605000000	0.187608000000
H	-2.733036000000	0.092457000000	0.495669000000
H	-3.305561000000	-4.698767000000	-0.604295000000
H	-1.211044000000	-6.118848000000	-0.241699000000
H	1.732413000000	-2.629497000000	0.292222000000
H	1.743037000000	-0.875674000000	0.067564000000
N	0.383630000000	1.893801000000	-0.017102000000
C	-0.439968000000	2.997729000000	0.027425000000
N	0.234117000000	4.205734000000	-0.049509000000
C	1.597601000000	4.306998000000	-0.152007000000
C	2.353264000000	3.209379000000	-0.183621000000

C	1.755564000000	1.882720000000	-0.109272000000
O	2.399526000000	0.847275000000	-0.124808000000
O	-1.641828000000	2.937062000000	0.124871000000
H	-0.091764000000	0.951909000000	0.023155000000
H	-0.345426000000	5.028757000000	-0.018369000000
H	2.021267000000	5.299480000000	-0.203736000000
F	3.682551000000	3.281551000000	-0.281024000000

ND_{ULE} optimized at the (TD-)CAM-B3LYP/TZVP level

N	0.947518000000	0.282698000000	0.092152000000
C	1.492241000000	1.509464000000	0.142990000000
N	2.771204000000	1.822421000000	0.103709000000
C	3.546054000000	0.742452000000	0.001221000000
C	3.123016000000	-0.573893000000	-0.063421000000
C	1.737759000000	-0.791811000000	-0.015576000000
N	4.910579000000	0.671668000000	-0.064586000000
C	5.231588000000	-0.659980000000	-0.163747000000
N	4.192047000000	-1.437064000000	-0.166558000000
N	1.205992000000	-2.019542000000	-0.082663000000
H	0.781784000000	2.325163000000	0.223383000000
H	5.542869000000	1.454692000000	-0.043503000000
H	6.255837000000	-0.991728000000	-0.230462000000
H	1.818587000000	-2.815205000000	-0.125472000000
H	0.209836000000	-2.159769000000	-0.005373000000
N	-1.890228000000	0.380764000000	0.210450000000
C	-2.527304000000	1.593275000000	0.026811000000
N	-3.876634000000	1.509096000000	-0.190630000000

C	-4.590446000000	0.310032000000	-0.297556000000
C	-3.912979000000	-0.851696000000	-0.109085000000
C	-2.550465000000	-0.838911000000	0.137868000000
O	-1.821870000000	-1.859960000000	0.565758000000
O	-1.920776000000	2.642145000000	0.052127000000
H	-0.849686000000	0.373973000000	0.194700000000
H	-4.345670000000	2.391245000000	-0.308393000000
H	-5.629622000000	0.354436000000	-0.572992000000
F	-4.551434000000	-2.032684000000	-0.149458000000

$ND_{n\pi^*}$ optimized at the (TD-)CAM-B3LYP/TZVP level

N	0.023567000000	0.197494000000	-0.067423000000
C	0.006150000000	0.036750000000	1.266039000000
N	1.038035000000	0.000738000000	2.084054000000
C	2.193684000000	0.147982000000	1.435963000000
C	2.359171000000	0.323853000000	0.073030000000
C	1.190964000000	0.348935000000	-0.703744000000
N	3.463687000000	0.162269000000	1.944056000000
C	4.311947000000	0.342908000000	0.879166000000
N	3.691665000000	0.444118000000	-0.256403000000
N	1.220683000000	0.525406000000	-2.031364000000
H	-0.980516000000	-0.072266000000	1.703283000000
H	3.711278000000	0.059243000000	2.914338000000
H	5.381665000000	0.390783000000	1.009571000000
H	2.109768000000	0.599578000000	-2.494194000000
H	0.373399000000	0.499529000000	-2.578543000000
N	-2.596951000000	0.189785000000	-1.167077000000

C	-3.680505000000	0.312541000000	-0.318188000000
N	-4.869827000000	0.590973000000	-0.937097000000
C	-5.017189000000	0.812619000000	-2.311096000000
C	-3.918164000000	0.679754000000	-3.097598000000
C	-2.687293000000	0.376463000000	-2.540314000000
O	-1.602380000000	-0.007160000000	-3.197792000000
O	-3.567313000000	0.187381000000	0.881882000000
H	-1.648450000000	0.162996000000	-0.739702000000
H	-5.663310000000	0.664724000000	-0.323098000000
H	-5.977889000000	1.126860000000	-2.679919000000
F	-4.005109000000	0.830671000000	-4.429383000000

INT_{LE} optimized at the (TD-)CAM-B3LYP/TZVP level

N	-0.865792000000	-0.584496000000	-0.120215000000
C	-2.201545000000	-0.744557000000	0.169703000000
N	-2.800060000000	-1.903280000000	-0.318790000000
C	-2.119497000000	-2.964144000000	-0.024525000000
C	-0.748221000000	-2.905679000000	0.368760000000
C	-0.077169000000	-1.662126000000	0.146027000000
N	-2.342532000000	-4.297571000000	-0.271396000000
C	-1.162686000000	-4.954075000000	-0.009574000000
N	-0.193791000000	-4.153409000000	0.319886000000
N	1.221207000000	-1.542497000000	0.153231000000
H	-2.786286000000	0.117181000000	0.449356000000
H	-3.218425000000	-4.709289000000	-0.548278000000
H	-1.085671000000	-6.028091000000	-0.072710000000
H	1.756896000000	-2.371801000000	0.369453000000

H	1.715492000000	-0.596802000000	-0.006124000000
N	0.381104000000	1.769480000000	0.004606000000
C	-0.414625000000	2.867986000000	0.097497000000
N	0.229801000000	4.103714000000	0.049006000000
C	1.585925000000	4.223503000000	-0.080428000000
C	2.337939000000	3.124094000000	-0.165773000000
C	1.717807000000	1.809051000000	-0.118840000000
O	2.405279000000	0.770188000000	-0.186883000000
O	-1.628412000000	2.817359000000	0.216448000000
H	-0.402106000000	0.403257000000	-0.101237000000
H	-0.360844000000	4.915961000000	0.119884000000
H	2.005643000000	5.218779000000	-0.108430000000
F	3.669753000000	3.204927000000	-0.291325000000

INT_{CT} optimized at the (TD-)CAM-B3LYP/TZVP level

N	1.077992000000	0.528952000000	0.222623000000
C	1.747700000000	1.644520000000	0.287429000000
N	3.095891000000	1.811964000000	0.198908000000
C	3.731097000000	0.683847000000	0.026384000000
C	3.154508000000	-0.595993000000	-0.068626000000
C	1.734673000000	-0.668163000000	0.034881000000
N	5.081536000000	0.459045000000	-0.104384000000
C	5.235455000000	-0.883654000000	-0.264855000000
N	4.103971000000	-1.546018000000	-0.248771000000
N	1.015902000000	-1.750947000000	-0.042119000000
H	1.173125000000	2.551320000000	0.424145000000
H	5.803755000000	1.160875000000	-0.084956000000

H	6.206350000000	-1.335344000000	-0.391154000000
H	1.623160000000	-2.558031000000	-0.181132000000
H	-0.917571000000	-1.826909000000	0.254891000000
N	-1.967907000000	0.416995000000	0.125952000000
C	-2.636485000000	1.603167000000	-0.064813000000
N	-3.985424000000	1.471987000000	-0.257504000000
C	-4.670476000000	0.248724000000	-0.266365000000
C	-3.931280000000	-0.888721000000	-0.064763000000
C	-2.574993000000	-0.844104000000	0.124918000000
O	-1.854708000000	-1.917670000000	0.479516000000
O	-2.072173000000	2.680134000000	-0.060480000000
H	-0.964376000000	0.491886000000	0.219455000000
H	-4.483287000000	2.336418000000	-0.375429000000
H	-5.721506000000	0.249680000000	-0.484699000000
F	-4.555502000000	-2.079021000000	-0.051275000000

TD_{ALE} optimized at the (TD-)CAM-B3LYP/TZVP level

N	-1.028313000000	-0.643823000000	-0.038923000000
C	-2.347448000000	-0.873937000000	0.246165000000
N	-2.917438000000	-2.057338000000	-0.238054000000
C	-2.138192000000	-3.065125000000	-0.029500000000
C	-0.760679000000	-2.956952000000	0.356206000000
C	-0.140143000000	-1.686282000000	0.175826000000
N	-2.300872000000	-4.403133000000	-0.307462000000
C	-1.089810000000	-5.012971000000	-0.063093000000
N	-0.155385000000	-4.184675000000	0.287987000000
N	1.129735000000	-1.446266000000	0.160029000000

H	-2.978112000000	-0.036031000000	0.493271000000
H	-3.158623000000	-4.845028000000	-0.592042000000
H	-0.967249000000	-6.080845000000	-0.157098000000
H	1.657509000000	-2.291930000000	0.361281000000
H	1.882521000000	-0.044581000000	-0.023826000000
N	0.429390000000	1.855041000000	0.037642000000
C	-0.341661000000	2.988679000000	0.083451000000
N	0.348392000000	4.202003000000	-0.001540000000
C	1.701367000000	4.281650000000	-0.122076000000
C	2.420303000000	3.153321000000	-0.163388000000
C	1.730407000000	1.896129000000	-0.078344000000
O	2.446218000000	0.816678000000	-0.118059000000
O	-1.549071000000	2.979489000000	0.188577000000
H	-0.632734000000	0.307320000000	-0.034468000000
H	-0.219370000000	5.034290000000	0.032766000000
H	2.152828000000	5.261494000000	-0.180104000000
F	3.752089000000	3.174219000000	-0.279999000000

TD_{ULE} optimized at the (TD-)CAM-B3LYP/TZVP level

N	0.193223000000	-0.048120000000	-0.155333000000
C	1.537479000000	0.022129000000	-0.288688000000
N	2.238823000000	1.110762000000	-0.282753000000
C	1.464841000000	2.211838000000	-0.121528000000
C	0.097827000000	2.266415000000	0.028104000000
C	-0.646628000000	1.044438000000	0.018457000000
N	1.878626000000	3.510643000000	-0.069766000000
C	0.753466000000	4.275248000000	0.106425000000

N	-0.331132000000	3.561064000000	0.169420000000
N	-1.910818000000	0.858368000000	0.144495000000
H	2.033761000000	-0.933715000000	-0.404916000000
H	2.831134000000	3.827560000000	-0.147291000000
H	0.800134000000	5.349905000000	0.180525000000
H	-2.404440000000	1.735688000000	0.263254000000
H	-2.706496000000	-0.477313000000	0.115387000000
N	-1.305681000000	-2.476016000000	-0.089999000000
C	-0.668046000000	-3.594441000000	0.209461000000
N	-1.419283000000	-4.781303000000	0.458902000000
C	-2.675882000000	-4.891937000000	-0.059774000000
C	-3.359035000000	-3.665922000000	-0.150693000000
C	-2.678485000000	-2.451825000000	-0.031868000000
O	-3.323396000000	-1.321139000000	0.084081000000
O	0.556052000000	-3.726720000000	0.274996000000
H	-0.269705000000	-0.975644000000	-0.170727000000
H	-0.864452000000	-5.595992000000	0.680677000000
H	-3.064572000000	-5.840895000000	-0.398207000000
F	-4.672305000000	-3.690257000000	-0.346834000000

ND_{ALE} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

N	-0.771749515652	-0.667770279674	0.012094170974
C	-2.137917359034	-0.739162671648	0.214777768922
N	-2.761546610747	-1.910420451123	-0.219406780880
C	-2.128002669013	-3.033029808629	0.004244205006
C	-0.741728489671	-3.056696613589	0.289406018865
C	-0.069082937944	-1.790831021192	0.138653772919

N	-2.453641106871	-4.349732636043	-0.219786380888
C	-1.288840532395	-5.086041513684	-0.037925179964
N	-0.257095967900	-4.330298378049	0.213268580914
N	1.265564004440	-1.753778446203	0.125841065920
H	-2.701687722800	0.182640299909	0.222174965914
H	-3.377701737488	-4.710356732879	-0.400128882796
H	-1.286005606415	-6.164931588183	-0.095714752982
H	1.771362695190	-2.623491625803	0.212407299908
H	1.762635363186	-0.863028145592	0.030755773986
N	0.411360454795	1.884147806147	-0.039611297962
C	-0.439893998825	2.969636761634	0.036154867009
N	0.212048658918	4.193852230111	0.011209817999
C	1.578143726299	4.326375393053	-0.079450417948
C	2.361081097930	3.241947441548	-0.144308099930
C	1.787031179181	1.899773170130	-0.115596679953
O	2.457980784872	0.875426948615	-0.153576635954
O	-1.647195527242	2.877504676691	0.117735219944
H	-0.050772963001	0.940610799578	-0.034285704960
H	-0.388346714833	5.003259131717	0.065694581992
H	1.981804543111	5.330803927598	-0.094395056944
F	3.688376029342	3.337959142502	-0.231579528908

TD_{ALE} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

N	-1.012005697523	-0.642501813722	-0.039325049001
C	-2.339927371918	-0.850630132630	0.261167054897
N	-2.942515624650	-2.045918063077	-0.157493787935
C	-2.148304317047	-3.055870573618	0.013524476011

C	-0.745418001665	-2.960338815633	0.325114920847
C	-0.128831860953	-1.691815776214	0.127914191931
N	-2.334922914945	-4.400260417995	-0.240763769906
C	-1.117496877517	-5.021073059717	-0.035172244972
N	-0.152748036935	-4.197988045116	0.256849505872
N	1.152091821491	-1.455734921320	0.063535984966
H	-2.951664183649	0.018818750980	0.452212046807
H	-3.215682781539	-4.840521569785	-0.457302407769
H	-1.014698534544	-6.095265965232	-0.115168052943
H	1.671378315263	-2.318402801929	0.228529004898
H	1.948309181094	-0.014184012001	-0.087669086948
N	0.457508583797	1.829201317171	-0.056358779973
C	-0.345663987820	2.944574612685	-0.003529837998
N	0.320826243839	4.177335712114	-0.003678772977
C	1.679976391227	4.294354472048	-0.044031158963
C	2.433200372906	3.181138852581	-0.089514172966
C	1.764403096190	1.907236798130	-0.092260198967
O	2.512653984862	0.841897484617	-0.130200799950
O	-1.561263442283	2.902685080669	0.041824603978
H	-0.607762068703	0.304413921847	-0.094494303978
H	-0.272785131874	4.994007693728	0.034155155980
H	2.109430925061	5.288256421618	-0.035719284969
F	3.767570382283	3.227979595543	-0.126920637939

ND_{ULE} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

N	-0.001921015016	-0.026310369969	-0.126840770963
C	1.340249252382	-0.019937494974	-0.184938722922

N	2.155540775022	1.020873364530	-0.166193120906
C	1.474491594305	2.170712075027	-0.073126213978
C	0.096999650959	2.322613649930	0.003339235020
C	-0.670278617670	1.138930493472	-0.023655947989
N	1.966000311132	3.450140412422	-0.025304649980
C	0.878155803608	4.286540731067	0.076495396991
N	-0.259710243901	3.652657409337	0.097729361937
N	-2.004959810099	1.136097049506	0.044823224961
H	1.797976362200	-1.004184021530	-0.249826554883
H	2.940384002645	3.708986799335	-0.057892161965
H	0.994480299556	5.360582471545	0.131620144933
H	-2.483961730891	2.016812273067	0.149771583928
H	-2.526432181837	0.255530501892	0.084968433980
N	-1.341619546391	-2.528453641839	-0.259797308905
C	-0.587342659734	-3.586987458376	0.150301408943
N	-1.295671825438	-4.794195186844	0.328257098833
C	-2.578957890855	-4.975022458769	-0.122864133956
C	-3.343276146480	-3.785194095298	-0.081808651960
C	-2.745437420746	-2.487615554854	-0.076479782981
O	-3.339317658506	-1.421206861382	0.146352898924
O	0.616715484702	-3.570591838383	0.336197963853
H	-0.847272335607	-1.604884203281	-0.253806357905
H	-0.699673486681	-5.574669571498	0.590561715743
H	-2.851596047717	-5.903683343313	-0.622899734731
F	-4.659669892894	-3.859221684242	0.109040604958

TD_{ULE} optimized at the (TD)-CAM-B3LYP/6-31G(d) level

N	0.179656227914	-0.045959461967	-0.136482548930
C	1.530862720301	0.008389954997	-0.223888029882
N	2.250507096956	1.091305974498	-0.209293400890
C	1.475983337350	2.202685372989	-0.091525486946
C	0.100621496952	2.277156603977	0.011021326015
C	-0.658029065703	1.058335544511	-0.003137047983
N	1.902339398160	3.501277846412	-0.044916025981
C	0.778155816657	4.280907127061	0.081597344976
N	-0.321903310838	3.579757247392	0.119056333966
N	-1.930803902128	0.878261548622	0.088661602959
H	2.016210040094	-0.959662031565	-0.309011607836
H	2.862823658719	3.806432517293	-0.094639729982
H	0.836848019638	5.358924059575	0.140910691925
H	-2.414706825899	1.768160615187	0.178938928894
H	-2.765018063772	-0.505165762745	0.105909132969
N	-1.331448171379	-2.455134210907	-0.108721419953
C	-0.669053146721	-3.571937297362	0.143663688937
N	-1.362409006364	-4.779134791807	0.364759762826
C	-2.672556021785	-4.906233455768	-0.024209139990
C	-3.374428616445	-3.687233935349	-0.088765220944
C	-2.709695757770	-2.461004430858	-0.017142226014
O	-3.377026763493	-1.336229612368	0.114751739940
O	0.574770543753	-3.666641844361	0.181642061905
H	-0.295446816879	-0.968003873554	-0.161099931916
H	-0.782858713666	-5.580431727475	0.580120112718
H	-3.061017275605	-5.857519180346	-0.365512038822

F	-4.697367093880	-3.728482327323	-0.216882691923

$ND_{n\pi^*}$ optimized at the(TD-)CAM-B3LYP//6-31G(d) level

N	-0.833446095634	-0.753733011669	-0.188511536939
C	-2.136982375014	-0.864734720629	-0.201932435923
N	-2.877070893695	-2.006014249109	-0.113021994930
C	-2.125936629057	-3.076606116621	-0.000684862995
C	-0.715970968689	-3.121859196600	0.034950413975
C	-0.036725175988	-1.870008719178	-0.061862785984
N	-2.510029259886	-4.394623343009	0.111953807948
C	-1.361507519370	-5.125114541650	0.205987200924
N	-0.266363544896	-4.398228163994	0.164075787905
N	1.260839610452	-1.686377693253	-0.031130230973
H	-2.696774781794	0.060451162968	-0.289705425871
H	-3.459792787428	-4.735963615831	0.123266868958
H	-1.378929851391	-6.201500658205	0.305030656870
H	1.723352872206	-2.593885091820	0.065428150984
H	2.167212701022	0.129916216946	-0.179199168899
N	0.492877550782	1.912078835153	-0.135744757944
C	-0.392247846820	2.961099919681	-0.018481763976
N	0.198607203885	4.188411127082	0.140899666941
C	1.588120715298	4.401359448020	0.190673812911
C	2.404943569897	3.300535345492	0.063121415973
C	1.887073625146	2.036475149074	-0.096209326960
O	2.658670662818	0.954315775567	-0.301219728860
O	-1.603762844252	2.805529099744	-0.055292912957
H	0.062677995972	1.001964689560	-0.227485270880

H	-0.443716060777	4.959131685725	0.219377985912
H	1.949060058104	5.400873192560	0.357963291815
F	3.737671070297	3.459913476407	0.101130141965

INT_{LE} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

N	-0.820880912600	-0.575820358800	-0.123110926000
C	-2.169341753600	-0.700525247400	0.154877748600
N	-2.788951995400	-1.860218066400	-0.308381586200
C	-2.124544519400	-2.940364956000	-0.013664420100
C	-0.741993128100	-2.908676331500	0.354885509100
C	-0.056198581200	-1.669964831900	0.133688360700
N	-2.377561075000	-4.272913634300	-0.252060158300
C	-1.205081833200	-4.954374370500	0.003536592100
N	-0.210499838000	-4.169899616300	0.310378970800
N	1.253824523700	-1.568368841700	0.140319930700
H	-2.730708863600	0.192984744300	0.388436747200
H	-3.271547078100	-4.670477310200	-0.498557991700
H	-1.155442818400	-6.033377130300	-0.049949860900
H	1.783336261200	-2.408105528000	0.341399778900
H	1.751898357200	-0.637786073800	-0.008854721500
N	0.416089050900	1.735491900600	-0.014657421100
C	-0.421129747000	2.805967006700	0.086654875600
N	0.183912118600	4.063700724300	0.058660855000
C	1.540713401000	4.230026235200	-0.063774823300
C	2.335333593500	3.154211787400	-0.154812283700
C	1.758499469000	1.813770432400	-0.121984656400
O	2.484254586300	0.799172373500	-0.188193515600

O	-1.638814765600	2.710732730700	0.196740742600
H	-0.328133161600	0.418755121900	-0.111471732400
H	-0.437630291300	4.854934097100	0.132838739500
H	1.926648259600	5.241696021800	-0.080714925600
F	3.663136484100	3.277093760600	-0.272901565700

INT_{CT} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

N	-0.833446095634	-0.753733011669	-0.188511536939
C	-2.136982375014	-0.864734720629	-0.201932435923
N	-2.877070893695	-2.006014249109	-0.113021994930
C	-2.125936629057	-3.076606116621	-0.000684862995
C	-0.715970968689	-3.121859196600	0.034950413975
C	-0.036725175988	-1.870008719178	-0.061862785984
N	-2.510029259886	-4.394623343009	0.111953807948
C	-1.361507519370	-5.125114541650	0.205987200924
N	-0.266363544896	-4.398228163994	0.164075787905
N	1.260839610452	-1.686377693253	-0.031130230973
H	-2.696774781794	0.060451162968	-0.289705425871
H	-3.459792787428	-4.735963615831	0.123266868958
H	-1.378929851391	-6.201500658205	0.305030656870
H	1.723352872206	-2.593885091820	0.065428150984
H	2.167212701022	0.129916216946	-0.179199168899
N	0.492877550782	1.912078835153	-0.135744757944
C	-0.392247846820	2.961099919681	-0.018481763976
N	0.198607203885	4.188411127082	0.140899666941
C	1.588120715298	4.401359448020	0.190673812911
C	2.404943569897	3.300535345492	0.063121415973

C	1.887073625146	2.036475149074	-0.096209326960
O	2.658670662818	0.954315775567	-0.301219728860
O	-1.603762844252	2.805529099744	-0.055292912957
H	0.062677995972	1.001964689560	-0.227485270880
H	-0.443716060777	4.959131685725	0.219377985912
H	1.949060058104	5.400873192560	0.357963291815
F	3.737671070297	3.459913476407	0.101130141965

TS_{ULE} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

Imaginary frequency : -930.51

N	0.144991857315	-0.095752576561	-0.132646700323
C	1.496293917208	-0.036763365493	-0.219547126889
N	2.212402382498	1.050750677400	-0.205917707303
C	1.439058149825	2.157522845344	-0.090339619147
C	0.060573287657	2.225173527916	0.012254609102
C	-0.675477695081	1.003724763465	-0.002243727782
N	1.855682938952	3.458363000349	-0.044802595197
C	0.725424191489	4.230925021893	0.080979181545
N	-0.370855582151	3.525427654519	0.119181245567
N	-1.962300498703	0.842357299006	0.091758676151
H	1.982410980820	-1.004432330439	-0.302341005867
H	2.814100107338	3.770885084805	-0.094307967968
H	0.778003864944	5.309340896902	0.139242186852
H	-2.474035803580	1.713413812409	0.182291096107
H	-2.584583102640	-0.257433578275	0.104625150945
N	-1.275722056938	-2.430774344303	-0.136641503139
C	-0.624165233335	-3.551336706464	0.142151900129

N	-1.372134965795	-4.740392996255	0.416456257498
C	-2.659958463915	-4.853777639899	-0.037511972491
C	-3.341227904659	-3.618823562162	-0.099252083336
C	-2.659079246076	-2.387651862317	-0.035142151985
O	-3.275650966337	-1.265496000930	0.118448385667
O	0.606642338534	-3.687625247214	0.168737586310
H	-0.337679274644	-1.039912311402	-0.161205575539
H	-0.800175043757	-5.557558973403	0.591744282006
H	-3.017487970617	-5.780465196393	-0.478679723974
F	-4.668679344160	-3.636719437863	-0.206520749918

TS_{a1} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

Imaginary frequency : -567.8

N	-0.760960399863	-0.563006579541	-0.077894299062
C	-2.120195259321	-0.666507243702	0.159768165715
N	-2.750181415671	-1.816062359750	-0.317400439230
C	-2.116861776827	-2.914810240157	-0.017831670308
C	-0.740742334741	-2.911716467284	0.364008926933
C	-0.034646438688	-1.678949094247	0.154443209420
N	-2.394026711514	-4.240775157792	-0.268565492758
C	-1.236030515650	-4.946635366130	-0.009220302787
N	-0.230671809106	-4.181183199921	0.310951862678
N	1.282384517410	-1.623024722757	0.153139351339
H	-2.675463230784	0.240945401795	0.351028044441
H	-3.293212792231	-4.619769577210	-0.524856052673
H	-1.206266344738	-6.025926635355	-0.069066833387
H	1.789479326176	-2.480373459871	0.332414022243

H	1.790063262264	-0.713920920998	0.004123958313
N	0.406024930936	1.724044859938	-0.022870844483
C	-0.441091842806	2.790757029841	0.082196028387
N	0.159884999215	4.048321682369	0.054224499065
C	1.516202091106	4.222868481161	-0.067200405650
C	2.317733211942	3.153130680645	-0.160012456106
C	1.754639509982	1.806348158162	-0.129439166460
O	2.483082863791	0.800381966455	-0.195268936200
O	-1.655830698425	2.686999462085	0.195017157105
H	-0.225927464289	0.499869235068	-0.075294703867
H	-0.465985419909	4.835913244900	0.131982796663
H	1.895143763564	5.237120389841	-0.081894868375
F	3.644000362126	3.282518998516	-0.276481549790

TS_{a2} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

Imaginary frequency : -907.7

N	-0.995683072452	-0.577228704740	-0.184552564926
C	-2.310862805133	-0.801547982329	0.156398470829
N	-2.889473504202	-1.990504904115	-0.302192766280
C	-2.132272961822	-3.010051006854	-0.023521337310
C	-0.748705949355	-2.884865004688	0.332645646458
C	-0.129230087259	-1.617194138658	0.087362990136
N	-2.299760367252	-4.360604606913	-0.238507463370
C	-1.085417319282	-4.960844189241	0.025603858862
N	-0.140103717629	-4.113766215411	0.318726215832
N	1.156634404570	-1.409243570547	0.082972553559
H	-2.922277879796	0.030266637304	0.475409974689

H	-3.166515533768	-4.817785426630	-0.477489886657
H	-0.968046793851	-6.035580387862	-0.012518701887
H	1.701942849618	-2.234868060991	0.317396736154
H	1.727533914509	-0.323307458273	-0.083158625139
N	0.392323702527	1.794165587811	-0.025256741183
C	-0.368579545347	2.926692080188	0.074797063254
N	0.329489339652	4.139830595219	0.059959902274
C	1.691826750715	4.213251350894	-0.047861255995
C	2.406834135207	3.080928106608	-0.139751922023
C	1.718019859610	1.805341548996	-0.122303871459
O	2.397732140789	0.731792338761	-0.197441045292
O	-1.586566263480	2.921619861857	0.172644594440
H	-0.579170143563	0.389181498347	-0.168328942726
H	-0.235883051984	4.973072529350	0.131484196916
H	2.150713234016	5.194080538143	-0.052969421866
F	3.740569641219	3.099412128477	-0.242982007484

$TS_{aINT/TD}$ optimized at the (TD-)CAM-B3LYP/6-31G(d) level

Imaginary frequency : -3459.6

N	-0.838615317606	-0.654420705687	-0.000251174987
C	-2.204207180022	-0.725393757658	-0.000166785980
N	-2.899324759681	-1.906064749159	0.000010679009
C	-2.143590094004	-2.958805856665	0.000057996980
C	-0.696974966667	-2.996583268645	-0.000060580000
C	-0.027725378979	-1.763897837224	-0.000205182022
N	-2.492394978884	-4.301814365062	0.000240005007
C	-1.314376028383	-5.018723775732	0.000218485009

N	-0.234712993884	-4.282964689069	0.000040218000
N	1.275241738413	-1.555378388276	-0.000287255985
H	-2.725232064768	0.220604979886	-0.000225681979
H	-3.431564011445	-4.667943730897	0.000389130014
H	-1.316706825401	-6.100813832258	0.000341636991
H	1.760513718183	-2.454368488888	-0.000248605990
H	2.158343786004	0.043110058967	-0.000229032993
N	0.525758296761	1.713328668213	-0.000239295010
C	-0.372498368840	2.746975568772	-0.000145085003
N	0.168489344923	4.033594419174	0.000097518001
C	1.520406768317	4.284854467070	0.000255203983
C	2.372854539918	3.232919499559	0.000176920994
C	1.835695023176	1.919649250116	-0.000069704974
O	2.670615584800	0.895392341602	-0.000110761984
O	-1.585838389275	2.586811704842	-0.000257178026
H	-0.354553213825	0.279984172889	-0.000281908014
H	-0.501815797757	4.788333431824	0.000156595984
H	1.852556832185	5.313591729588	0.000448374000
F	3.699800384318	3.411493906451	0.000345468022

$TS_{uINT/TD}$ optimized at the (TD-)CAM-B3LYP/6-31G(d) level

Imaginary frequency : -8760.2

N	0.215703994899	0.100172886939	-0.074089478975
C	1.560586203303	0.102085790938	-0.105400598978
N	2.321140429941	1.170200628485	-0.094536529941
C	1.592219300303	2.304809665964	-0.046886244003
C	0.209280212893	2.433429935870	-0.004363818008

C	-0.584131504711	1.237909794456	-0.011201296975
N	2.061083900068	3.590174757348	-0.024354464974
C	0.961919610561	4.409462760983	0.030769818985
N	-0.166592629938	3.748537365318	0.044894961975
N	-1.865823613164	1.091509007531	0.034349652961
H	2.012587128074	-0.884679222598	-0.140869671957
H	3.032923367641	3.862161958247	-0.043307477960
H	1.054936816527	5.486303884510	0.058659049973
H	-2.324800413950	1.999786211091	0.073575985958
H	-2.766116067722	-0.449430083797	0.094745341961
N	-1.197085556463	-2.240527727982	-0.055693366994
C	-0.429194377810	-3.317800746507	0.069515949981
N	-0.997378457560	-4.582898118903	0.165691726945
C	-2.349642017909	-4.791494990821	-0.032147995988
C	-3.139082191573	-3.632457915373	-0.047433869959
C	-2.572977867842	-2.367509316927	0.008471241014
O	-3.325006890510	-1.277807090443	0.123191461941
O	0.822956379602	-3.267873692494	0.099122937946
H	-0.300507014843	-0.820771945602	-0.085956664978
H	-0.349438132825	-5.346857888586	0.297660899887
H	-2.713826060760	-5.776414152355	-0.283437342894
F	-4.463073676963	-3.776037033266	-0.113554106943

TS_{a1H} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

N	-0.003463000000	0.001795000000	0.000696000000
C	-0.001255000000	-0.000752000000	1.378442000000
N	1.233100000000	0.001797000000	2.064878000000

C	2.088965000000	0.826689000000	1.540542000000
C	1.939084000000	1.398465000000	0.241859000000
C	0.925992000000	0.792784000000	-0.581501000000
N	3.387689000000	1.150056000000	1.897829000000
C	3.909813000000	1.899163000000	0.863102000000
N	3.096471000000	2.018001000000	-0.150587000000
N	0.904330000000	0.964009000000	-1.888054000000
H	-0.846271000000	-0.454160000000	1.879400000000
H	3.824084000000	0.950830000000	2.784310000000
H	4.897825000000	2.335218000000	0.924469000000
H	1.628640000000	1.577794000000	-2.246286000000
N	-1.924475000000	-1.018985000000	-1.522397000000
C	-2.942894000000	-1.713431000000	-0.882822000000
N	-3.891026000000	-2.250733000000	-1.746623000000
C	-3.844093000000	-2.114232000000	-3.107458000000
C	-2.840715000000	-1.429090000000	-3.678118000000
C	-1.810918000000	-0.835042000000	-2.856272000000
O	-0.874098000000	-0.187995000000	-3.384166000000
O	-3.012845000000	-1.848514000000	0.316725000000
H	-1.152733000000	-0.615157000000	-0.871028000000
H	-4.640267000000	-2.759145000000	-1.298471000000
H	-4.634842000000	-2.571970000000	-3.688180000000
F	-2.757106000000	-1.268418000000	-4.997980000000
H	-0.006831000000	0.369503000000	-2.653069000000

TS_{a2H} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

N	-0.050540000000	0.080747000000	-0.029172000000

C	-0.045533000000	0.039046000000	1.353457000000
N	1.206094000000	0.010333000000	1.969754000000
C	2.025860000000	0.910528000000	1.506583000000
C	1.818054000000	1.543334000000	0.242882000000
C	0.811625000000	0.956009000000	-0.595260000000
N	3.321871000000	1.238796000000	1.837882000000
C	3.802748000000	2.040935000000	0.822881000000
N	2.956523000000	2.190833000000	-0.157087000000
N	0.731813000000	1.222405000000	-1.882418000000
H	-0.930120000000	-0.324302000000	1.857202000000
H	3.795062000000	0.991951000000	2.694110000000
H	4.785953000000	2.488239000000	0.873747000000
H	1.394031000000	1.884364000000	-2.266923000000
H	-0.018001000000	0.794735000000	-2.486815000000
N	-2.137639000000	-0.624654000000	-1.360194000000
C	-3.119746000000	-1.198198000000	-0.604563000000
N	-4.243587000000	-1.640585000000	-1.300942000000
C	-4.375772000000	-1.509056000000	-2.660975000000
C	-3.395681000000	-0.932394000000	-3.369099000000
C	-2.193699000000	-0.443186000000	-2.701000000000
O	-1.281240000000	0.111135000000	-3.340308000000
O	-3.052952000000	-1.332232000000	0.610761000000
H	-0.994198000000	-0.269585000000	-0.634611000000
H	-4.968781000000	-2.064117000000	-0.741700000000
H	-5.284048000000	-1.880953000000	-3.118459000000
F	-3.488952000000	-0.782486000000	-4.695562000000

TS_{u1H} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

N	-0.008051000000	0.002982000000	0.009140000000
C	-0.001543000000	-0.004883000000	1.351006000000
N	1.037009000000	-0.009328000000	2.167987000000
C	2.190257000000	-0.002577000000	1.481488000000
C	2.345403000000	0.011867000000	0.103834000000
C	1.161981000000	0.019308000000	-0.674722000000
N	3.469867000000	-0.003575000000	1.974366000000
C	4.311405000000	0.010783000000	0.886146000000
N	3.678809000000	0.021060000000	-0.252714000000
N	1.151510000000	0.042174000000	-1.999797000000
H	-0.987397000000	-0.003123000000	1.810695000000
H	3.725225000000	-0.010955000000	2.950122000000
H	5.386723000000	0.012900000000	1.003317000000
H	2.043543000000	0.057650000000	-2.472017000000
H	0.108378000000	0.087320000000	-2.630857000000
N	-2.396034000000	-0.049669000000	-1.412420000000
C	-3.489136000000	0.429015000000	-0.761693000000
N	-4.647081000000	0.586534000000	-1.553427000000
C	-4.778956000000	0.023175000000	-2.797339000000
C	-3.550772000000	-0.092179000000	-3.482554000000
C	-2.293113000000	-0.027654000000	-2.817860000000
O	-1.191997000000	0.116766000000	-3.402342000000
O	-3.547618000000	0.695783000000	0.425832000000
H	-1.493540000000	-0.054789000000	-0.851589000000
H	-5.451248000000	0.917269000000	-1.028933000000

H	-5.719817000000	-0.435588000000	-3.092668000000
F	-3.556863000000	-0.164058000000	-4.807816000000

TS_{u2H} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

Imaginary frequency: -3828.4

N	0.421551490806	0.327471233840	0.023972962998
C	1.776855564190	0.367339423808	0.050474660970
N	2.511369717876	1.442478945347	0.049446118995
C	1.752690635213	2.573850141817	0.016965499969
C	0.366586148832	2.662699913803	-0.013536275976
C	-0.367990397816	1.460793456344	-0.010622124012
N	2.186639926991	3.869742229242	0.005878267996
C	1.068919599512	4.664356838860	-0.030132526009
N	-0.045603031985	3.974987670222	-0.042820870956
N	-1.700661149248	1.342064100366	-0.039019280968
H	2.249540268955	-0.609880868743	0.072545911962
H	3.150937729590	4.165640193116	0.021418904987
H	1.137075806486	5.742880187387	-0.045675680983
H	-2.240332603979	2.193096359021	-0.062605332950
H	-2.180676575020	0.426503234792	-0.034433494958
N	-0.855445769635	-2.109886786019	0.035286506987
C	-0.104373518961	-3.203414336569	-0.039995349991
N	-0.729067976694	-4.490072585963	-0.093377583981
C	-2.064780352063	-4.664232968891	0.015810807006
C	-2.822768638702	-3.477873009432	0.048483669989
C	-2.241726845957	-2.162312321996	0.018907753990
O	-2.950498678643	-1.132011956511	-0.016392336978

O	1.130714113482	-3.238577197534	-0.061420801958
H	-0.048338987002	-0.613229876714	0.032299351001
H	-0.084611971982	-5.269289164610	-0.149057433936
H	-2.488320388892	-5.653675307410	0.112203156956
F	-4.133028541124	-3.607085540389	0.095494866976

TS_{CIA} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

N	0.914608000000	0.475155000000	0.068500000000
C	1.596141000000	1.666228000000	-0.100605000000
N	2.889215000000	1.762161000000	0.415134000000
C	3.654572000000	0.757482000000	0.062994000000
C	3.093784000000	-0.475367000000	-0.353323000000
C	1.661360000000	-0.604785000000	-0.151902000000
N	4.977867000000	0.465550000000	0.309730000000
C	5.151224000000	-0.872654000000	0.017265000000
N	4.038533000000	-1.464423000000	-0.324545000000
N	1.117150000000	-1.818090000000	-0.163680000000
H	1.069302000000	2.551073000000	-0.427767000000
H	5.689475000000	1.123353000000	0.589046000000
H	6.123526000000	-1.342729000000	0.066553000000
H	1.716194000000	-2.613752000000	-0.333110000000
H	0.108675000000	-1.936920000000	-0.019488000000
N	-1.886851000000	0.378790000000	0.015350000000
C	-2.559307000000	1.580431000000	-0.095692000000
N	-3.941142000000	1.451155000000	-0.095628000000
C	-4.592432000000	0.243583000000	-0.006316000000
C	-3.894279000000	-0.894688000000	0.087696000000

C	-2.434725000000	-0.881960000000	0.095406000000
O	-1.752612000000	-1.897945000000	0.164165000000
O	-2.009443000000	2.657796000000	-0.186859000000
H	-0.834532000000	0.443844000000	0.044176000000
H	-4.454647000000	2.316227000000	-0.176308000000
H	-5.674889000000	0.258196000000	-0.017373000000
F	-4.496706000000	-2.082200000000	0.172073000000

TS_{CIU} optimized at the (TD-)CAM-B3LYP/6-31G(d) level

N	-0.940159000000	0.378456000000	-0.140380000000
C	-1.524717000000	1.587414000000	-0.089465000000
N	-2.813837000000	1.869248000000	-0.007038000000
C	-3.554802000000	0.754165000000	0.028238000000
C	-3.096574000000	-0.555639000000	-0.007632000000
C	-1.700358000000	-0.731447000000	-0.093584000000
N	-4.918404000000	0.639963000000	0.114818000000
C	-5.201250000000	-0.706336000000	0.127709000000
N	-4.139630000000	-1.457754000000	0.056763000000
N	-1.120624000000	-1.935962000000	-0.133323000000
H	-0.834763000000	2.427270000000	-0.113662000000
H	-5.572453000000	1.406524000000	0.162835000000
H	-6.218416000000	-1.068798000000	0.191487000000
H	-1.701833000000	-2.755893000000	-0.056346000000
H	-0.103416000000	-2.023956000000	-0.120105000000
N	1.893826000000	0.298227000000	-0.348229000000
C	2.501352000000	1.453343000000	0.076929000000
N	3.927066000000	1.399044000000	0.121879000000

C	4.560988000000	0.354910000000	-0.466426000000
C	3.929098000000	-0.903992000000	-0.202546000000
C	2.487367000000	-0.972385000000	-0.252829000000
O	1.807281000000	-1.983766000000	-0.114444000000
O	1.932683000000	2.489935000000	0.338685000000
H	0.846306000000	0.325342000000	-0.319286000000
H	4.353687000000	2.312031000000	0.272614000000
H	5.396559000000	0.549558000000	-1.139573000000
F	4.476701000000	-1.693353000000	0.772700000000

CI_{AH} optimized at the CASSCF(6,6)/6-31G(d) level

N	0.417019991100	-0.296957059900	-0.207911112100
C	0.112582347200	-0.157934303000	1.133183098900
N	1.174817974800	-0.044628707600	1.989167944400
C	1.620396878300	1.149998026300	1.723484964000
C	1.318928156500	1.798379817600	0.490880729000
C	0.804954591000	0.989722476400	-0.570337277700
N	2.541881839500	1.977211973900	2.317195000400
C	2.706928266900	3.043742999400	1.467607622300
N	2.025190136000	2.982324866900	0.387508624900
N	0.648718015900	1.406767594700	-1.783438360400
H	-0.908695709600	-0.050398186200	1.452759469500
H	2.976132781900	1.847534549600	3.201922744300
H	3.369952713500	3.846181796800	1.720670612600
H	0.883801566400	2.355028431700	-1.989002529000
H	0.166753147800	0.858512635000	-2.503890590000
N	-1.837141885600	-0.611936592200	-1.766521790200

C	-2.860509761400	-1.118084935600	-1.045696447500
N	-4.002655752600	-1.478160585200	-1.723514880500
C	-4.126448218000	-1.334620596600	-3.093474076300
C	-3.104759317900	-0.818123905100	-3.784810692500
C	-1.875301130000	-0.407973489200	-3.086526366600
O	-0.946001534700	0.103727187800	-3.696466900400
O	-2.806259867100	-1.260652029100	0.160487268600
H	-0.378109254200	-0.601076343700	-0.797073870200
H	-4.744716439000	-1.853041257400	-1.179173798200
H	-5.047185079500	-1.640972328800	-3.547084350200
F	-3.177206456900	-0.648725037000	-5.099200036800

$CI_A \rightarrow_U$ optimized at the CASSCF(6,6)/6-31G(d) level

N	-0.888266288100	-0.721901185800	-0.231955712000
C	-2.182930981400	-0.878442682400	-0.300144372900
N	-2.878357640700	-2.041037245100	-0.213682976800
C	-2.103962331600	-3.075702325100	-0.040063352700
C	-0.716265986300	-3.070244330500	0.058471959900
C	-0.067445721900	-1.810038538300	-0.040409153800
N	-2.446719873700	-4.397060219500	0.089751113100
C	-1.283749697800	-5.082097691400	0.254038565100
N	-0.232922008500	-4.336735034800	0.242321109100
N	1.228974347000	-1.589464494000	0.042771419000
H	-2.766771963200	0.011226479000	-0.435776995000
H	-3.368351873000	-4.769687539500	0.069214861500
H	-1.274492098900	-6.145419587500	0.379359943400
H	1.725539832500	-2.453364815500	0.180702215400

H	2.057371366700	0.087033774000	-0.286383354400
N	0.443265511800	1.914694926900	-0.139854636600
C	-0.390551567300	2.980943025300	0.090047833900
N	0.252206861300	4.171764538700	0.262189929800
C	1.634121059900	4.326279489200	0.222467514500
C	2.399496791500	3.228189278400	-0.003178050400
C	1.815367838200	1.990834882100	-0.190993911100
O	2.521143750900	0.916919926400	-0.466301672200
O	-1.583254797800	2.869961556500	0.130667728400
H	-0.019053230500	1.021906680600	-0.239137476600
H	-0.339003389700	4.954608725800	0.424388763800
H	2.034855473700	5.304559431100	0.375036948300
F	3.721607617000	3.335677975500	-0.050173240700

CI'$_A$ optimized at the CASSCF(6,6)/6-31G(d) level

N	-0.856077076100	-0.712971332200	0.329263322200
C	-2.185584753000	-1.085146451500	0.445527967800
N	-2.768191996400	-1.891013953700	-0.517245364200
C	-2.162751643700	-3.006187742600	-0.258448409500
C	-0.896980412200	-3.070403526400	0.390857777400
C	-0.157385347800	-1.814175249800	0.484221140200
N	-2.403309166100	-4.301508317000	-0.642051695000
C	-1.328951884300	-5.037797384800	-0.229138235600
N	-0.418182308400	-4.353278954500	0.368068635400
N	1.186158077700	-1.824637042900	0.639889919100
H	-2.589610970500	-1.104365734800	1.449255333100
H	-3.205744736700	-4.631249714600	-1.127141855600

H	-1.278805681200	-6.092880637600	-0.406044640900
H	1.655443874000	-2.680652376000	0.446000570500
H	1.679516108900	-0.983336491900	0.418067162500
N	0.390842968800	2.061001913100	0.008458391800
C	-0.402470020300	3.188672527900	0.010135099400
N	0.280925224200	4.359443148800	-0.171319845400
C	1.654418483300	4.429469110700	-0.342463851700
C	2.382847198100	3.309617942500	-0.332640576800
C	1.751974947200	1.995609443300	-0.142524685800
O	2.361234203200	0.966564335100	-0.119886120200
O	-1.585794630500	3.147016003100	0.158793072900
H	-0.095007881300	1.181762009500	0.127218734300
H	-0.273516820700	5.185028908200	-0.173464302600
H	2.084490412000	5.400497669900	-0.477148690600
F	3.694321982000	3.330310738500	-0.490334903100

CI_U optimized at the CASSCF(6,6)/6-31G(d) level

N	1.068665234400	-0.082707852400	0.367841909700
C	1.665197763900	0.192179363900	1.549456687300
N	2.950375896800	0.348713260500	1.784844969900
C	3.682047749500	0.204330941100	0.666203888200
C	3.205852191200	-0.075888057500	-0.581384299100
C	1.807856520800	-0.228554669900	-0.716912002900
N	5.034183791300	0.305109240800	0.519804421600
C	5.289923954200	0.083485528500	-0.801806254200
N	4.235540830400	-0.147079062700	-1.495628775800
N	1.237173709900	-0.544761889200	-1.897063477900

H	1.001034495000	0.292569870800	2.386359462200
H	5.692828278600	0.504440118400	1.237195759400
H	6.288072801500	0.107789616000	-1.188418819900
H	1.792233575200	-0.453649410800	-2.717225263500
H	0.247755007500	-0.447169149400	-1.997758102000
N	-1.941251789200	-0.133141929700	0.305937057500
C	-2.572308326900	-0.167841609600	1.483061772000
N	-3.999748942200	-0.411142669600	1.375037148900
C	-4.633713292800	-0.350829884700	0.268954751900
C	-4.048816525200	0.210472793400	-0.961455449200
C	-2.567295027200	-0.086620845200	-0.965703487100
O	-1.877245990400	-0.219889597900	-1.923664640000
O	-2.115421302800	-0.117449279300	2.574784670700
H	-0.927062221700	-0.122319387600	0.341907261200
H	-4.435489523300	-0.648580106700	2.247255747200
H	-5.664688285400	-0.665033960600	0.309782574000
F	-3.971850473800	1.588503878200	-0.383988148500

6. Cartesian Coordinates of the last point in typical MD trajectories

MD_dihedral_last.xyz

N	-0.985834510000	0.467145460000	0.254525850000
C	-1.647966370000	1.524201970000	-0.405695660000
N	-2.988050780000	1.982068600000	0.001973480000
C	-3.634863570000	0.780562480000	-0.110202820000
C	-3.016280840000	-0.543680240000	-0.117266410000
C	-1.568348720000	-0.710654940000	-0.065942880000
N	-5.044777350000	0.470539700000	0.220067810000

C	-5.064710590000	-0.855530300000	0.114632720000
N	-3.979734890000	-1.486788900000	-0.200153270000
N	-1.090544940000	-2.002305670000	-0.022895370000
H	-1.707269900000	1.405548890000	-1.589115500000
H	-5.784399060000	1.077996260000	0.191066860000
H	-6.030059750000	-1.304401350000	0.616950510000
H	-1.522999990000	-2.620756840000	0.598269270000
H	-0.092673850000	-2.042543970000	0.082369400000
N	1.849017920000	0.492018220000	0.107212160000
C	2.605904840000	1.609138500000	0.166506420000
N	3.954198790000	1.417364230000	0.017883870000
C	4.511410640000	0.217994560000	-0.217484780000
C	3.726177650000	-0.926520810000	-0.131698090000
C	2.285363730000	-0.826467420000	0.061255220000
O	1.612657940000	-1.776457280000	0.297479010000
O	2.143525760000	2.824293580000	0.174043100000
H	0.844619880000	0.797227110000	0.077391750000
H	4.516216120000	2.274364920000	0.097395560000
H	5.467984760000	0.301801220000	-0.445621550000
F	4.373077560000	-2.113724820000	-0.225158910000

MD_SPT_last.xyz

N	-1.109580370000	0.503196430000	-0.089338210000
C	-1.811761560000	1.692166040000	-0.032899630000
N	-3.167864570000	1.797342270000	-0.028521150000
C	-3.800972410000	0.638435770000	-0.010677830000
C	-3.203665540000	-0.663508380000	0.005957050000

C	-1.766549860000	-0.678049070000	0.027424000000
N	-5.134363760000	0.399060460000	-0.106090220000
C	-5.319880150000	-0.919135710000	0.044168510000
N	-4.176162050000	-1.540957230000	0.038796720000
N	-1.172147070000	-1.858178810000	0.289533230000
H	-1.187737850000	2.567040610000	0.070336730000
H	-5.667984890000	1.214920080000	-0.057007300000
H	-6.376250640000	-1.381784980000	0.295874440000
H	-1.744473990000	-2.525074410000	0.056557130000
H	0.752572940000	-1.715644540000	-0.341719640000
N	2.181534080000	0.553527350000	-0.026286600000
C	2.830485650000	1.766965520000	0.100613840000
N	4.096126070000	1.522089760000	-0.033077160000
C	4.707247060000	0.207233900000	0.064169590000
C	3.893786290000	-0.959433490000	-0.084404200000
C	2.543145980000	-0.778646070000	-0.167877070000
O	1.739397500000	-1.927462390000	-0.281188370000
O	2.039826220000	2.789628780000	0.064059980000
H	1.120498550000	0.955811360000	-0.080216000000
H	4.711573380000	2.314092370000	0.327769020000
H	5.477636170000	0.123513210000	0.753372510000
F	4.502379800000	-2.092801960000	0.128314850000

7. References

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