**Supplementary Information for**

# Excited-State Dynamics of 3-Hydroxychromone in Gas Phase

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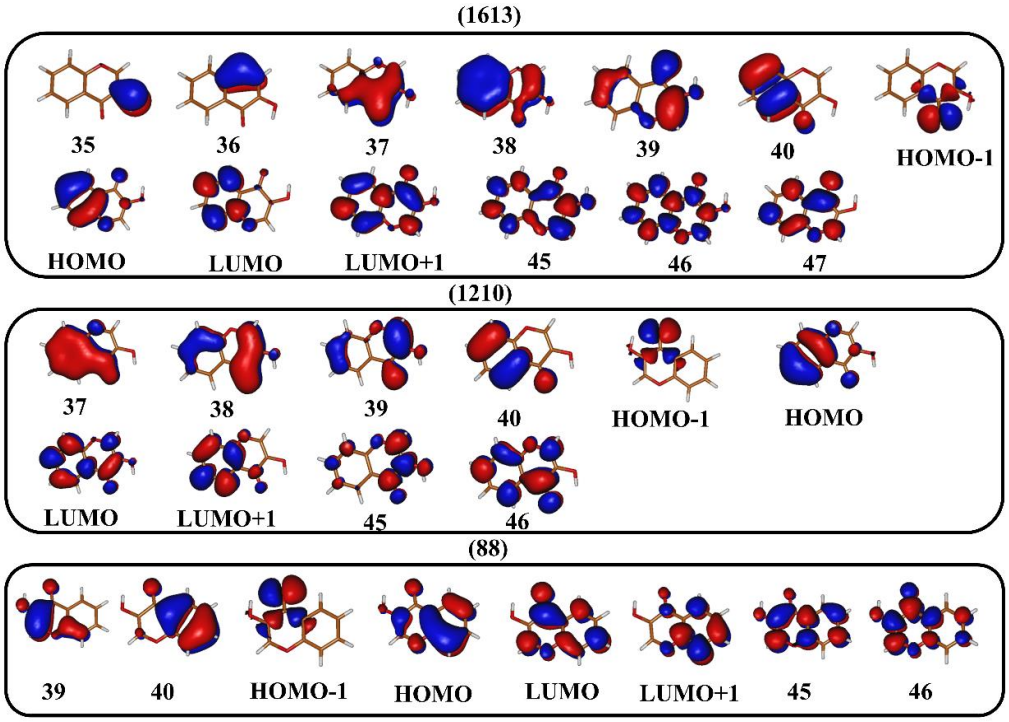


**Figure S1** The active spaces included in the SA3-CASSCF(16,13)//6-31G** (top), SA3-CASSCF(12,10)//6-31G* (middle) and SA3-CASSCF(8,8) //6-31G (bottom) calculation levels for the most stable ground-state conformation of 3-HC system.

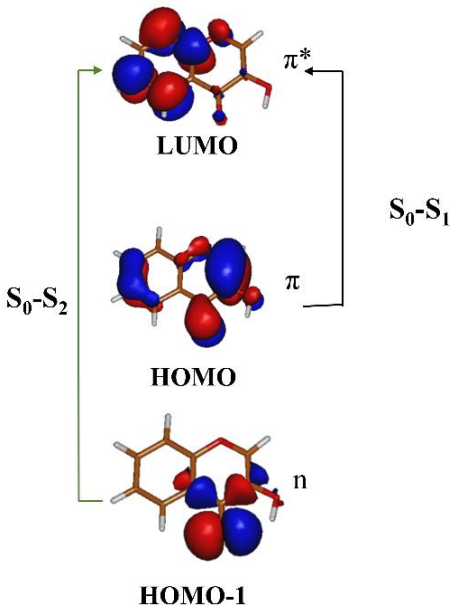


**Figure S2** Orbitals and orbital promotions involved in forming the first two excited singlet states of 3-HC system.

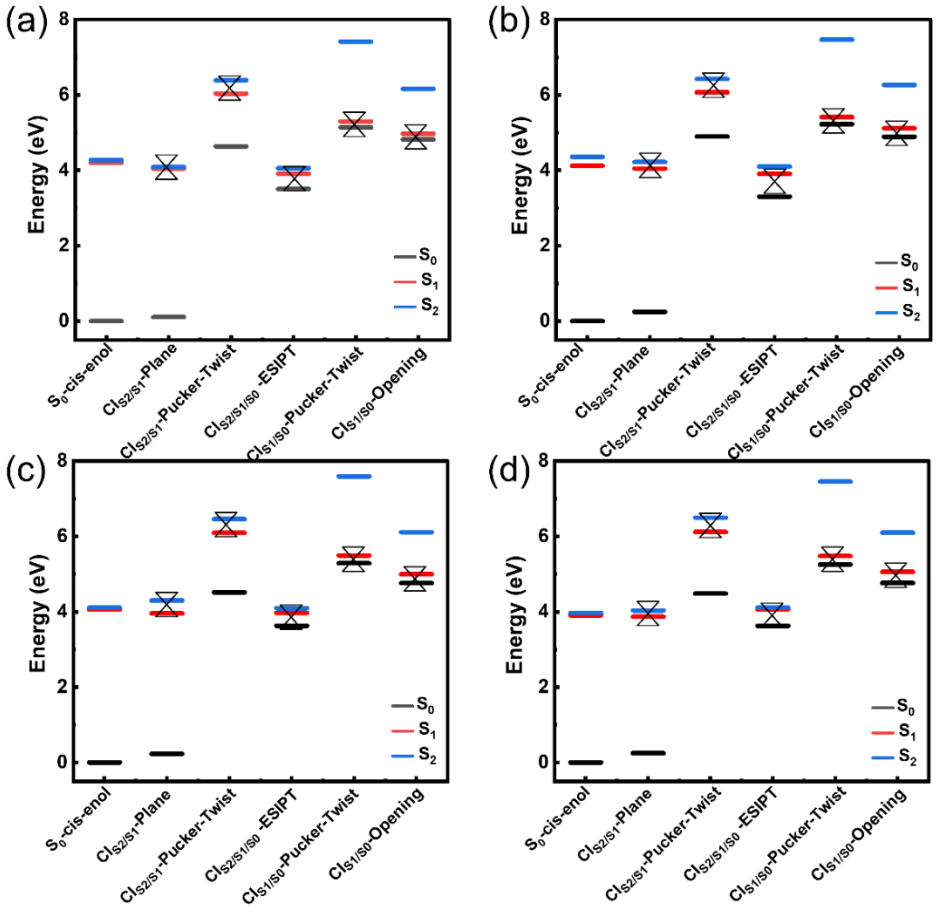


**Figure S3** The three low-lying electronic states energies relative to the ground state minimum of different optimized geometries at CASPT2//SA3-CASSCF(12,10)//6-31G* level (a), CASPT2//SA3-CASSCF(16,13)//6-31G** level (b), CASPT2//SA3-CASSCF(12,10)//cc-pVDZ (c) and CASPT2//SA3-CASSCF(12,10)//cc-pVTZ (d).

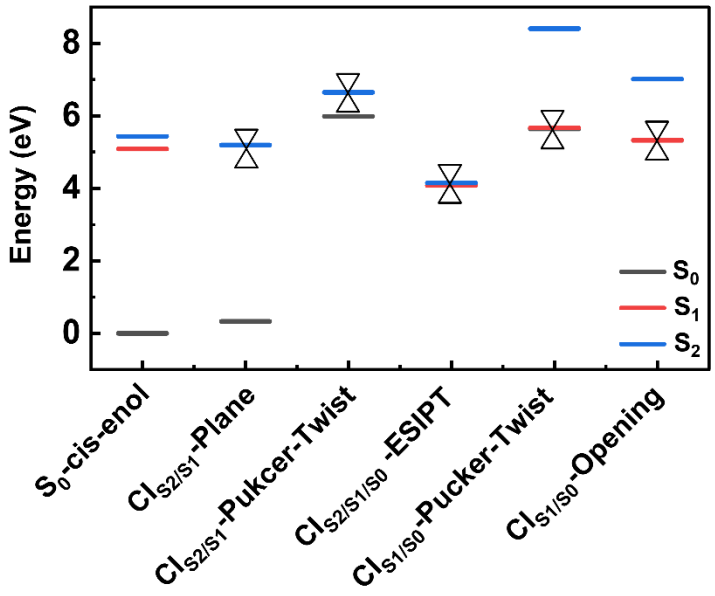

**Figure S4** The three low-lying electronic states energies relative to the ground state minimum of different optimized geometries at SA3-CASSCF(12,10)//6-31G* level.

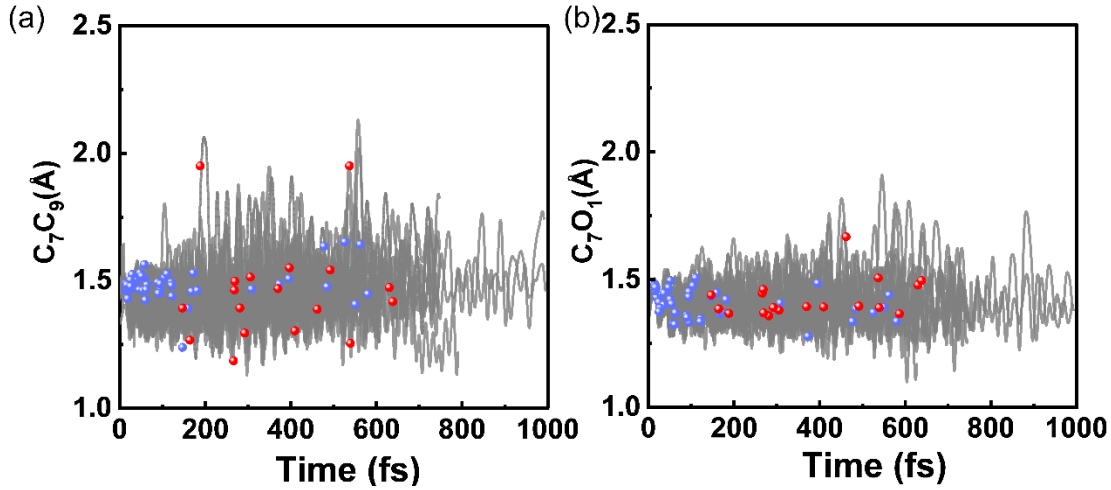


**Figure S5** The variation of (a) $C_7C_9$ and (b) $C_7O_1$ bond lengths as functions of the simulation time.

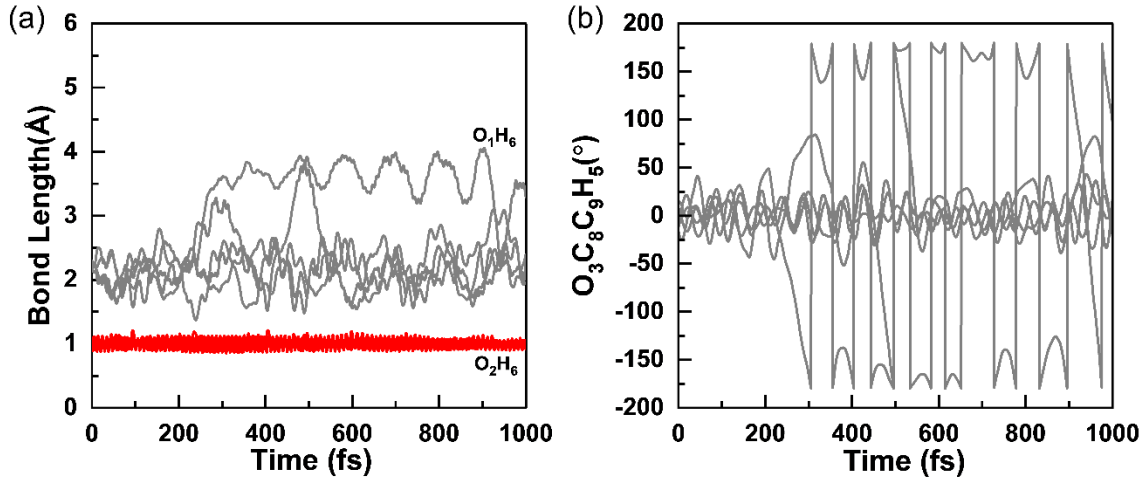


**Figure S6** The variation of (a) $O_2H_6$ and $O_1H_6$ bond lengths; (b) dihedral angle $C_7C_9O_2H_67$ as functions of the simulation time. The trajectories were run using Newton-X package interfaced with Gaussian 09 software.

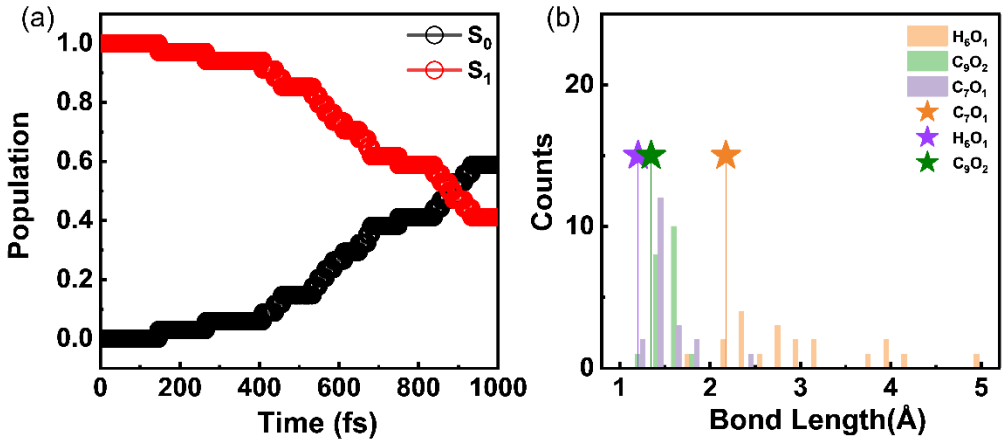


**Figure S7** (a)The time-dependent occupation of the $S_1$ and $S_0$ state of 3-HC system; (b) key bond lengths of the $S_1 \rightarrow S_0$ hopping points. Abscissa value of green, orange and purple star represents the $C_9O_2$, $O_1H_6$ and $C_7O_1$ bond length of FC point, respectively. Their ordinate values are meaningless.

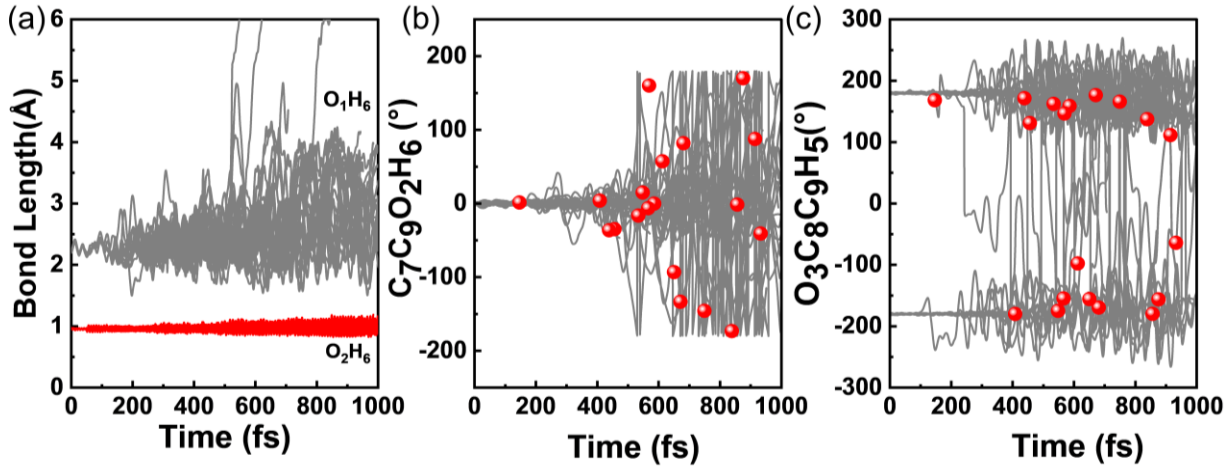


**Figure S8** The variation of (a) $O_2H_6$ and $O_1H_6$ bond lengths; (b) dihedral angle $C_7C_9O_2H_6$ and (c) $O_3C_8C_9H_5$ as functions of the simulation time. The rosy balls represent the $S_1 \rightarrow S_0$ hopping events.

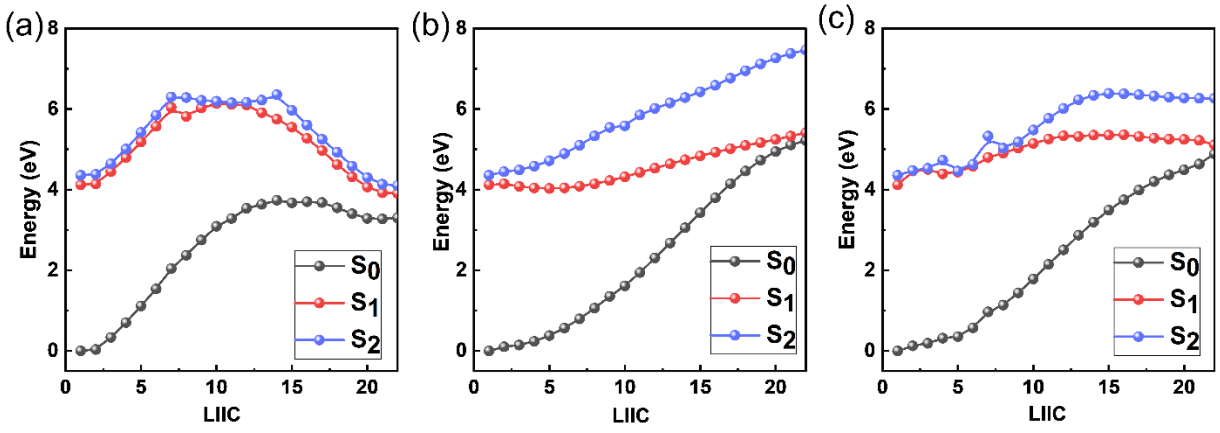

**Figure S9** The energy profiles constructed by LIIC method connecting the Franck-Condon geometry and (a) $CI_{S2/S1/S0}$-ESIPT; (b) $CI_{S1/S0}$-Pucker-Twist; and (c) $CI_{S1/S0}$-Opening computed at CASPT2//SA3-CASSCF(16,13)//6-31G** level.

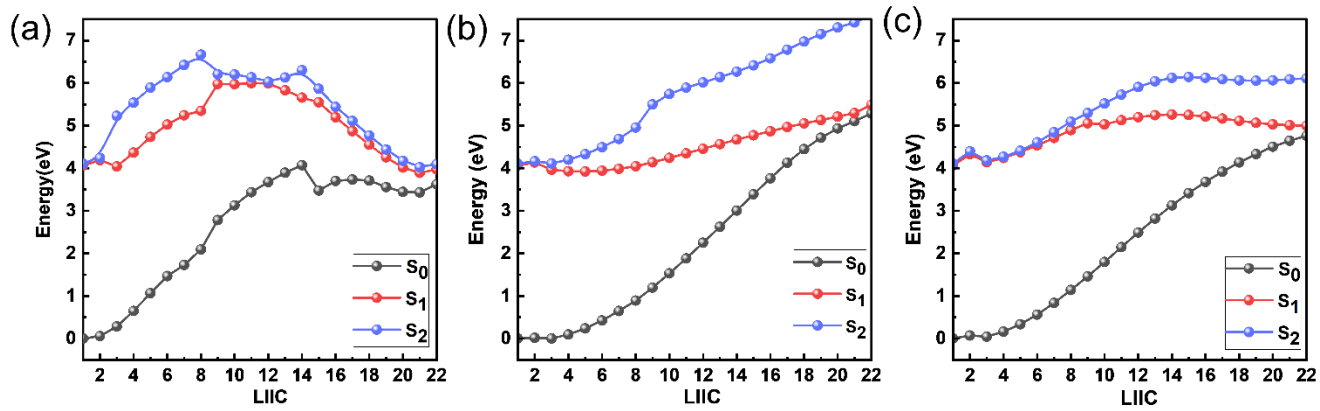


**Figure S10** The energy profiles constructed by LIIC method connecting the Franck-Condon geometry and (a) $CI_{S2/S1/S0}$-ESIPT; (b) $CI_{S1/S0}$-Pucker-Twist; and (c) $CI_{S1/S0}$-Opening computed at CASPT2//SA3-CASSCF(12,10)//cc-pVDZ level.

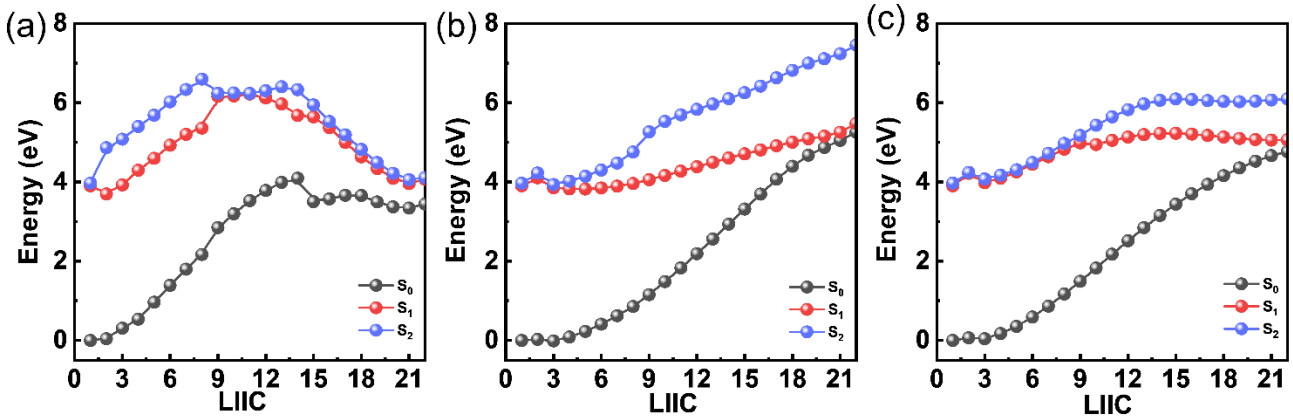


**Figure S11** The energy profiles constructed by LIIC method connecting the Franck-Condon geometry and (a) $CI_{S2/S1/S0}$-ESIPT; (b) $CI_{S1/S0}$-Pucker-Twist; and (c) $CI_{S1/S0}$-Opening computed at CASPT2//SA3-CASSCF(12,10)//cc-pVTZ level.

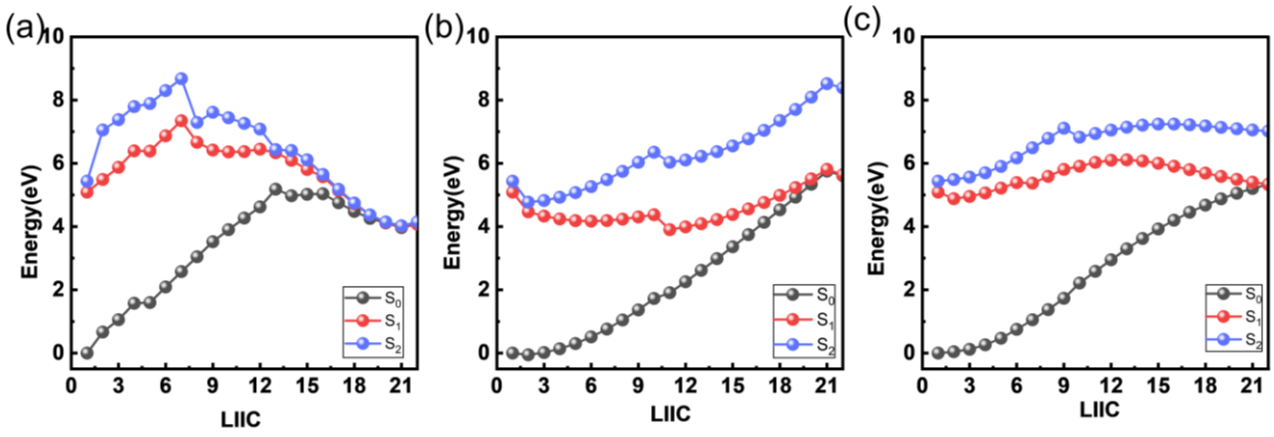


**Figure S12** The energy profiles constructed by LIIC method connecting the Franck-Condon geometry and (a) $CI_{S2/S1/S0}$-ESIPT; (b) $CI_{S1/S0}$-Pucker-Twist; and (c) $CI_{S1/S0}$-Opening computed at SA3-CASSCF(12,10)// 6-31G* level.

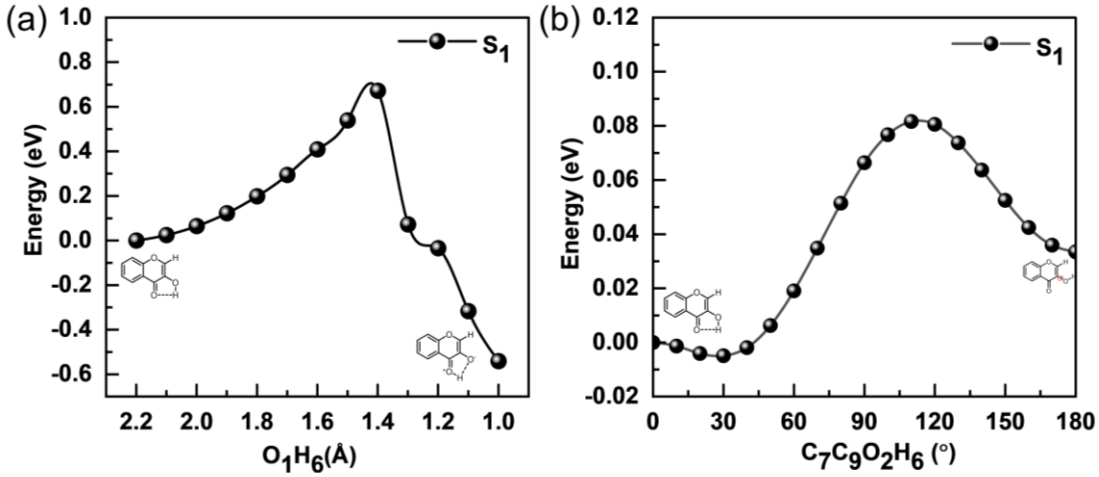


**Figure S13** The energy potential curve of the $S_1$ state constructed by scanning (a) the O1H6 bond length from 2.199 Å to 0.999 Å and (b) $C_7C_9O_2H_6$ dihedral angle from 0° to 180° computed at TDDFT//B3LYP//6-31G* level.

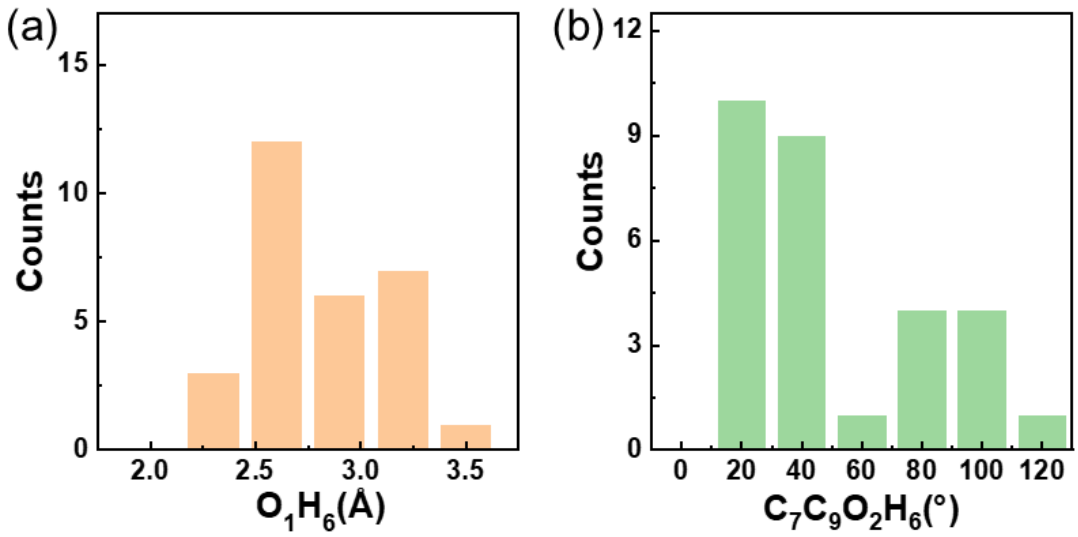


**Figure S14** The distributions of the $O_1H_6$ (a) and $C_7C_9O_2H_6$ (b) of the final structures of the trajectories remain in the $S_1$ state at the end of simulations.

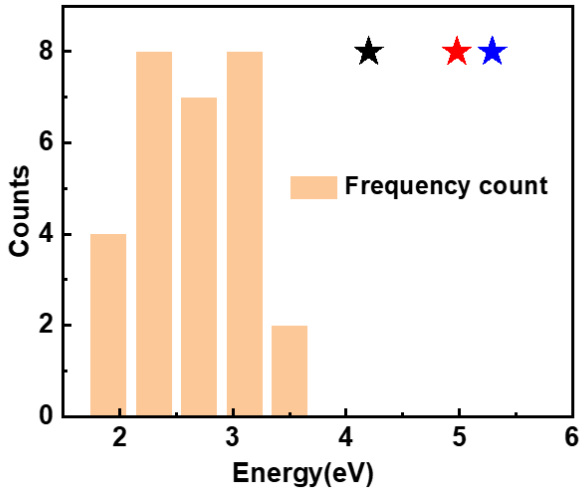


**Figure S15** The distributions of the $S_1$ energies of the final structures of the trajectories remain in the $S_1$ state at the end of simulations. The black, red and blue star indicates the $S_1$ energy of FC point, energy barrier along the ESIPT process (in Figure 6(a)), and the $S_1$ energy of $CI_{S1/S0}$-Pucker-Twist, respectively.

**Table S1** The vertical excitation energies and relative energies (in eV) of critical points calculated at the CASPT2//SA3-CASSCF(12,10)//6-31G* and SA3-CASSCF(12,10)//6-31G* level.

| Geo. | $S_0 \rightarrow S_1$ | $S_0 \rightarrow S_2$ | $S_0 \rightarrow S_3$ |
|---|---|---|---|
| $S_0$-cis-enol[a] | 4.13 | 4.19 | 5.35 |
| $S_0$-cis-enol[b] | 5.09 | 5.43 | |
| $S_1$-cis-enol[a] | 3.78 | 3.96 | |
| $S_1$-cis-keto[a] | 1.63 | 1.79 | |
| $S_1$-trans-enol[a] | 2.73 | 3.94 | |

[a] CASPT2//SA4-CASSCF(12,10)//6-31G*;[b] SA3-CASSCF(12,10)//6-31G*

**Table S2** The vertical excitation energies and relative energies (in eV) of critical points calculated at the CASPT2//SA3-CASSCF(16,13)//6-31G**, CASPT2//SA3-CASSCF(12,10)//cc-pVDZ and CASPT2//SA3-CASSCF(12,10)//cc-pVTZ level.

| Geo. | (16,13)//6-31G** | | (12,10)//cc-pVDZ | | (12,10)//cc-pVTZ | |
|---|---|---|---|---|---|---|
| | $S_0 \rightarrow S_1$ | $S_0 \rightarrow S_2$ | $S_0 \rightarrow S_1$ | $S_0 \rightarrow S_2$ | $S_0 \rightarrow S_1$ | $S_0 \rightarrow S_2$ |
| $S_0$-cis-enol | 4.12 | 4.35 | 4.06 | 4.11 | 3.90 | 3.97 |
| $CI_{S2/S1}$-Plane | 3.77 | 4.03 | 3.72 | 4.06 | 3.61 | 3.78 |
| $CI_{S2/S1}$-Pukcer-Twist | 1.17 | 1.52 | 1.58 | 1.94 | 1.63 | 2.01 |
| $CI_{S2/S1/S0}$ -ESIPT | 0.45 | 0.80 | 0.34 | 0.47 | 0.42 | 0.66 |
| $CI_{S1/S0}$-Pucker-Twist | 0.19 | 2.24 | 0.20 | 2.30 | 0.22 | 2.19 |
| $CI_{S1/S0}$-Opening | 0.22 | 1.37 | 0.23 | 1.35 | 0.29 | 1.33 |

**Table S3** Key geometrical parameters (bond lengths in Å, angles in degree) obtained at the SA3-CASSCF(12,10)//6-31G*, SA3-CASSCF(10,8)//6-31G*, SA3-CASSCF(8,8)//6-31G* and SA3-CASSCF(6,6)//6-31G levels for several critical structures of the 3-HC system.

| Geo. | Method | $C_9O_2$ | $O_2H_6$ | $O_1H_6$ | $C_7C_9$ | $C_7O_1$ | $C_7C_9O_2H_6$ | $O_3C_8C_9H_5$ |
|---|---|---|---|---|---|---|---|---|
| $S_0$-cis-enol | CASSCF(12,10)[a] | 1.349 | 0.952 | 2.199 | 1.461 | 1.235 | 0.0 | 180.0 |
| | CASSCF(10,8)[a] | 1.352 | 0.952 | 2.198 | 1.462 | 1.198 | 0.0 | 180.0 |
| | CASSCF(8,8)[a] | 1.371 | 0.953 | 2.297 | 1.467 | 1.239 | 0.0 | 180.0 |
| | CASSCF(6,6)[b] | 1.358 | 0.973 | 2.128 | 1.445 | 1.235 | 0.0 | 180.0 |
| $S_1$-cis-enol | CASSCF(12,10)[a] | 1.344 | 0.953 | 2.147 | 1.480 | 1.248 | 0.0 | 180.0 |
| | CASSCF(10,8)[a] | 1.347 | 0.953 | 2.164 | 1.474 | 1.206 | 0.0 | 180.0 |
| | CASSCF(8,8)[a] | 1.379 | 0.949 | 2.431 | 1.439 | 1.242 | 0.0 | 180.0 |
| | CASSCF(6,6)[b] | 1.368 | 0.954 | 2.257 | 1.465 | 1.233 | 0.0 | 180.0 |
| $S_0$-cis-keto | CASSCF(12,10)[a] | 1.212 | 2.153 | 0.957 | 1.490 | 1.323 | 0.0 | 180.0 |
| | CASSCF(10,8)[a] | 1.220 | 2.120 | 0.957 | 1.444 | 1.323 | 0.0 | 180.0 |
| | CASSCF(8,8)[a] | 1.246 | 2.246 | 0.957 | 1.448 | 1.347 | 0.0 | 180.0 |
| | CASSCF(6,6)[b] | 1.258 | 2.119 | 0.961 | 1.437 | 1.328 | 0.0 | 180.0 |
| $S_1$-cis-keto | CASSCF(12,10)[a] | 1.384 | 2.349 | 0.949 | 1.472 | 1.347 | 0.0 | 180.0 |
| | CASSCF(10,8)[a] | 1.391 | 2.326 | 0.949 | 1.393 | 1.347 | 0.0 | 180.0 |
| | CASSCF(8,8)[a] | 1.417 | 2.410 | 0.951 | 1.391 | 1.368 | 0.0 | 180.0 |
| | CASSCF(6,6)[b] | 1.401 | 2.401 | 0.952 | 1.391 | 1.365 | 0.0 | 180.0 |
| $S_0$-trans-enol | CASSCF(12,10)[a] | 1.350 | 0.947 | 3.655 | 1.472 | 1.209 | 180.0 | 180.0 |
| | CASSCF(10,8)[a] | 1.348 | 0.948 | 3.650 | 1.481 | 1.209 | 180.0 | 180.0 |
| | CASSCF(8,8)[a] | 1.370 | 0.950 | 3.667 | 1.476 | 1.233 | 180.0 | 180.0 |
| | CASSCF(6,6)[b] | 1.369 | 0.950 | 3.668 | 1.469 | 1.216 | 180.0 | 180.0 |
| $S_1$-trans-enol | CASSCF(12,10)[a] | 1.356 | 0.947 | 3.666 | 1.399 | 1.359 | 180.0 | 180.0 |
| | CASSCF(10,8)[a] | 1.351 | 0.948 | 3.640 | 1.436 | 1.372 | 180.0 | 180.0 |
| | CASSCF(8,8)[a] | 1.372 | 0.950 | 3.646 | 1.437 | 1.396 | 180.0 | 180.0 |
| | CASSCF(6,6)[b] | 1.367 | 0.950 | 3.692 | 1.484 | 1.242 | 180.0 | 180.0 |

[a] 6-31G* basis set; [b] 6-31G basis set;

**Table S4** Cartesian coordinates of $S_0$-min (left) and $S_1$-min (right) of 3-HC cis-enol tautomer optimized at SA3-CASSCF(12,10)//6-31G* level.

| SA3-CASSCF(12,10)//6-31G* | | | | SA3-CASSCF(12,10)//6-31G* | | | |
|---|---|---|---|---|---|---|---|
| | X | Y | Z | | X | Y | Z |
| C | -4.0453510459 | -1.4426837932 | 0.0000000000 | C | -4.0757499855 | -1.4563057200 | 0.0000000000 |
| C | -2.6597570914 | -1.4883127248 | 0.0000000000 | C | -2.6253831535 | -1.5161645904 | 0.0000000000 |
| C | -1.9133134093 | -0.2932926067 | 0.0000000000 | C | -1.8729466724 | -0.3120159534 | 0.0000000000 |
| C | -2.5802578110 | 0.9221085045 | 0.0000000000 | C | -2.5916544523 | 0.9299596434 | 0.0000000000 |
| C | -3.9693421990 | 0.9817150969 | 0.0000000000 | C | -3.9723529695 | 0.9999647740 | 0.0000000000 |
| C | -4.6971790872 | -0.1990811222 | 0.0000000000 | C | -4.7518539722 | -0.1907381395 | 0.0000000000 |
| H | -4.6187068417 | -2.3508385544 | 0.0000000000 | H | -4.6385658328 | -2.3692552517 | 0.0000000000 |
| H | -2.1312638162 | -2.4219237431 | 0.0000000000 | H | -2.1130272367 | -2.4560733933 | 0.0000000000 |
| C | -0.4475827261 | -0.2999540281 | 0.0000000000 | C | -0.4401107297 | -0.3004669583 | 0.0000000000 |
| H | -4.4499322715 | 1.9414774687 | 0.0000000000 | H | -4.4312039591 | 1.9692694659 | 0.0000000000 |
| H | -5.7708041177 | -0.1556634528 | 0.0000000000 | H | -5.8218917395 | -0.1428807396 | 0.0000000000 |
| C | -0.5748435023 | 2.1110509880 | 0.0000000000 | C | -0.5559109374 | 2.1261693057 | 0.0000000000 |
| C | 0.1752311022 | 1.0194712536 | 0.0000000000 | C | 0.1904140450 | 1.0388008756 | 0.0000000000 |
| H | -0.1783026712 | 3.1047635693 | 0.0000000000 | H | -0.1904020756 | 3.1299647542 | 0.0000000000 |
| O | 0.2502277746 | -1.3197411033 | 0.0000000000 | O | 0.2916718460 | -1.3122089591 | 0.0000000000 |
| O | 1.5233870179 | 1.0795887774 | 0.0000000000 | O | 1.5299428583 | 1.0771981057 | 0.0000000000 |
| H | 1.8527588031 | 0.1867051134 | 0.0000000000 | H | 1.8401335569 | 0.1755182323 | 0.0000000000 |
| O | -1.9219905622 | 2.0950087328 | 0.0000000000 | O | -1.9281310450 | 2.0796629245 | 0.0000000000 |

**Table S5** Cartesian coordinates of $S_0$-min (left) and $S_1$-min (right) of 3-HC trans-enol tautomer optimized at SA3-CASSCF(12,10)//6-31G* level.

| SA3-CASSCF(12,10)//6-31G* | | | | SA3-CASSCF(12,10)//6-31G* | | | |
|---|---|---|---|---|---|---|---|
| | X | Y | Z | | X | Y | Z |
| C | -4.1263159459 | 0.8536014735 | 2.2990757314 | C | -2.6799145415 | -1.0848151493 | 0.0252561511 |
| C | -2.7457379962 | 0.9068138159 | 2.3843454510 | C | -1.3363579318 | -1.4520979579 | 0.0294807565 |
| C | -1.9607969248 | 0.9370682281 | 1.2195171862 | C | -0.3302140510 | -0.4760568966 | 0.0033062231 |
| C | -2.5887405392 | 0.9128650966 | -0.0143382153 | C | -0.7166627544 | 0.8796009387 | -0.0156080475 |
| C | -3.9751118454 | 0.8594294826 | -0.1155300087 | C | -2.0378907971 | 1.2434498931 | -0.0187801681 |
| C | -4.7407792055 | 0.8299179248 | 1.0372256067 | C | -3.0308925640 | 0.2620606047 | -0.0007803209 |
| H | -4.7243554802 | 0.8305508928 | 3.1911477800 | H | -3.4417440262 | -1.8425784233 | 0.0470031567 |
| H | -2.2472558743 | 0.9260270628 | 3.3343224568 | H | -1.0528991392 | -2.4868310207 | 0.0656645020 |
| C | -0.4854853845 | 0.9939318728 | 1.2976688633 | C | 1.0752583119 | -0.7863914128 | -0.0054559839 |
| H | -4.4229647299 | 0.8421676909 | -1.0912067198 | H | -2.2866606524 | 2.2882863519 | -0.0337413679 |
| H | -5.8118408937 | 0.7886354278 | 0.9598857522 | H | -4.0646676310 | 0.5549778976 | -0.0034613915 |
| C | -0.5450091339 | 0.9916375774 | -1.1452683608 | C | 1.5364707702 | 1.5895963182 | -0.0004425182 |
| C | 0.1809050879 | 1.0196168065 | -0.0154134275 | C | 1.9771090407 | 0.2870162693 | 0.0138295289 |
| H | -0.1269794076 | 1.0077498739 | -2.1318483641 | H | 2.1612593267 | 2.4545354422 | 0.0173592210 |
| O | 0.1264559621 | 1.0175183042 | 2.3407283169 | O | 1.5252705606 | -2.0718571408 | 0.0352790027 |
| O | 1.5305053585 | 1.0716349822 | 0.0163155671 | O | 3.3130528170 | 0.0333175567 | 0.0433629187 |
| H | 1.8911645105 | 1.0855359894 | -0.8602256789 | O | 0.2065683493 | 1.8796458780 | -0.0312705311 |
| O | -1.8989947567 | 0.9394503406 | -1.1756165117 | H | 1.5639355223 | -2.4378955488 | -0.8408358415 |

**Table S6** Cartesian coordinates of $S_0$-min (left) and $S_1$-min (right) of 3-HC cis-keto tautomer optimized at SA3-CASSCF(12,10)//6-31G* level.

| SA3-CASSCF(12,10)//6-31G* | | | | SA3-CASSCF(12,10)//6-31G* | | | |
|---|---|---|---|---|---|---|---|
| | X | Y | Z | | X | Y | Z |
| C | -2.6591481345 | -1.0986636540 | 0.0000000000 | C | -4.1263159459 | 0.8536014735 | 2.2990757314 |
| C | -1.3648267361 | -1.4763884886 | 0.0000000000 | C | -2.7457379962 | 0.9068138159 | 2.3843454510 |
| C | -0.3249935572 | -0.4859293631 | 0.0000000000 | C | -1.9607969248 | 0.9370682281 | 1.2195171862 |
| C | -0.7044550595 | 0.8599739022 | 0.0000000000 | C | -2.5887405392 | 0.9128650966 | -0.0143382153 |
| C | -2.0687153594 | 1.2481407699 | 0.0000000000 | C | -3.9751118454 | 0.8594294826 | -0.1155300087 |
| C | -3.0179584059 | 0.2870018376 | 0.0000000000 | C | -4.7407792055 | 0.8299179248 | 1.0372256067 |
| H | -3.4378088828 | -1.8390548180 | 0.0000000000 | H | -4.7243554802 | 0.8305508928 | 3.1911477800 |
| H | -1.0838152366 | -2.5118796928 | 0.0000000000 | H | -2.2472558743 | 0.9260270628 | 3.3343224568 |
| C | 1.0448237582 | -0.7763975656 | 0.0000000000 | C | -0.4854853845 | 0.9939318728 | 1.2976688633 |
| H | -2.3085649314 | 2.2946364940 | 0.0000000000 | H | -4.4229647299 | 0.8421676909 | -1.0912067198 |
| H | -4.0572657791 | 0.5596817303 | 0.0000000000 | H | -5.8118408937 | 0.7886354278 | 0.9598857522 |
| C | 1.5148863166 | 1.5890269808 | 0.0000000000 | C | -0.5450091339 | 0.9916375774 | -1.1452683608 |
| C | 2.0885839342 | 0.2877493661 | 0.0000000000 | C | 0.1809050879 | 1.0196168065 | -0.0154134275 |
| H | 2.0987871654 | 2.4841376665 | 0.0000000000 | H | -0.1269794076 | 1.0077498739 | -2.1318483641 |
| O | 1.4878605059 | -2.0233517868 | 0.0000000000 | O | 0.1264559621 | 1.0175183042 | 2.3407283169 |
| O | 3.2687172271 | 0.0079667586 | 0.0000000000 | O | 1.5305053585 | 1.0716349822 | 0.0163155671 |
| O | 0.2080513133 | 1.8229704043 | 0.0000000000 | H | 1.8911645105 | 1.0855359894 | -0.8602256789 |
| H | 2.4441728017 | -1.9809655554 | 0.0000000000 | O | -1.8989947567 | 0.9394503406 | -1.1756165117 |

**Table S7** Cartesian coordinates of $CI_{S2/S1}$-Plane (left) and $CI_{S2/S1/S0}$–ESIPT (right) optimized at SA3-CASSCF(12,10)//6-31G* level.

| SA3-CASSCF(12,10)//6-31G* | | | | SA3-CASSCF(12,10)//6-31G* | | | |
|---|---|---|---|---|---|---|---|
| | X | Y | Z | | X | Y | Z |
| C | -1.9961203031 | -0.2998239579 | 0.0000000000 | C | -4.0379640567 | -1.1738602189 | 0.0008113185 |
| C | -1.0628783276 | 0.8687678666 | 0.0000000000 | C | -2.6198635835 | -1.1478615190 | 0.0015461200 |
| C | 0.3235167989 | 0.5299274178 | 0.0000000000 | C | -1.9385579455 | 0.0266483784 | 0.0020599984 |
| C | 1.3470921099 | 1.5114154364 | 0.0000000000 | C | -2.6762102068 | 1.2403665004 | -0.0000211128 |
| C | 2.7460888072 | 1.1060899850 | 0.0000000000 | C | -4.0428810001 | 1.2246460925 | -0.0006135448 |
| C | 3.1037568663 | -0.2841228350 | 0.0000000000 | C | -4.7349233905 | -0.0107690673 | -0.0000102883 |
| C | 2.0608905589 | -1.2508399184 | 0.0000000000 | H | -4.5464876364 | -2.1210411108 | 0.0009202890 |
| C | 0.7266889554 | -0.8478151304 | 0.0000000000 | H | -2.0712234116 | -2.0703094231 | 0.0016435586 |
| O | -0.1794618552 | -1.8000272655 | 0.0000000000 | C | -0.4527685911 | 0.0975454837 | -0.0006607971 |
| C | -1.5355629556 | -1.5350609383 | 0.0000000000 | H | -4.5739295981 | 2.1581430118 | -0.0016498808 |
| O | -3.2961371406 | -0.0012698858 | 0.0000000000 | H | -5.8100870705 | -0.0112598308 | -0.0002995566 |
| O | -1.5273521785 | 1.9974901439 | 0.0000000000 | C | -0.6837536040 | 2.5524864155 | -0.0003659134 |
| H | -3.3513767031 | 0.9539471205 | 0.0000000000 | C | 0.0195241352 | 1.3741772551 | 0.0008268992 |
| H | -2.1142205688 | -2.4322590357 | 0.0000000000 | H | -0.2911597368 | 3.5427973872 | -0.0003975705 |
| H | 2.2678038250 | -2.3028916995 | 0.0000000000 | O | 0.2115966005 | -1.1169555441 | -0.0033708168 |
| H | 4.1312976759 | -0.5860267462 | 0.0000000000 | O | 1.5667981577 | 1.6001260961 | 0.0057487168 |
| H | 3.5085019573 | 1.8602839995 | 0.0000000000 | H | 1.1522061171 | -1.0503428978 | -0.0045503348 |
| H | 1.0757244876 | 2.5467057529 | 0.0000000000 | O | -2.0702695088 | 2.4838312202 | -0.0016170845 |

**Table S8** Cartesian coordinates of $CI_{S2/S1}$-Pukcer-Twist (left) and $CI_{S1/S0}$-Pucker-Twist (right) of cytidine optimized at SA3-CASSCF(12,10)//6-31G* level

| SA3-CASSCF(12,10)//6-31G* | | | | SA3-CASSCF(12,10)//6-31G* | | | |
|---|---|---|---|---|---|---|---|
| | X | Y | Z | | X | Y | Z |
| C | -0.8975184862 | 2.5481052812 | 0.3171163683 | C | -0.8592715185 | 2.3415533796 | -1.2336595165 |
| C | 0.2988456475 | 1.8453565580 | 0.3427975284 | C | 0.1994044262 | 1.8542197370 | -0.4448754222 |
| C | 0.3039861305 | 0.4857952363 | 0.0091612345 | C | 0.3877846105 | 0.4902037742 | -0.3198888239 |
| C | -0.8687173885 | -0.1192700260 | -0.4015468202 | C | -0.5336732389 | -0.4268531577 | -0.8999464918 |
| C | -2.0801715193 | 0.5596173597 | -0.4140085314 | C | -1.5852929218 | 0.0589319345 | -1.6214619366 |
| C | -2.0855624504 | 1.9004204700 | -0.0502210271 | C | -1.7203171614 | 1.4487196813 | -1.8081431492 |
| H | -0.9132325711 | 3.5898076661 | 0.5794300765 | H | -0.9966140673 | 3.3987015055 | -1.3614684969 |
| H | 1.2145561568 | 2.3323643177 | 0.6221403686 | H | 0.8597978901 | 2.5564285626 | 0.0873197172 |
| C | 1.4472833148 | -0.4138530237 | 0.0776967031 | C | 1.5796925373 | -0.1086937788 | 0.3148223779 |
| H | -2.9705675718 | 0.0543664708 | -0.7370471361 | H | -2.3028485506 | -0.6227719291 | -2.0357236266 |
| H | -3.0078995575 | 2.4512348435 | -0.0784237808 | H | -2.5467252276 | 1.8085533408 | -2.3941152346 |
| C | 0.4816834998 | -1.9263051740 | -0.8112709642 | C | 0.1409981673 | -1.8698059491 | 0.6514463275 |
| C | 1.2860935763 | -1.7193630891 | 0.4662292569 | C | 1.5077656273 | -1.3163921339 | 0.8179078442 |
| H | 0.9610843934 | -1.9504091865 | -1.7805420868 | H | -0.6016033415 | -1.5810233721 | 1.3803237249 |
| O | 2.8164944161 | 0.1982916188 | -0.0164011048 | O | 2.5368504835 | 0.6971881817 | -0.2284072343 |
| O | 2.3355406789 | -2.5207263866 | 0.7548842706 | O | 2.5784204178 | -2.1919481965 | 0.6276568031 |
| H | 2.0083494953 | -3.3973949898 | 0.9112084934 | H | 2.7857976779 | -2.5782199544 | 1.4652055218 |
| O | -0.7770984546 | -1.3906998166 | -0.8501778789 | O | -0.4069377803 | -1.7461174154 | -0.6362887640 |

**Table S9** Cartesian coordinates of $CI_{S1/S0}$-Opening optimized at SA3-CASSCF(12,10)//6-31G* level

| SA3-CASSCF(12,10)//6-31G* | | | |
|---|---|---|---|
| | X | Y | Z |
| C | -0.0208325707 | -1.1131421378 | 2.0333830316 |
| C | -0.1619198245 | 0.1615155380 | 1.4946206905 |
| C | -0.8926411737 | 0.3532963602 | 0.3181315035 |
| C | -1.4677410593 | -0.7531478342 | -0.3134355809 |
| C | -1.3360410719 | -2.0153121984 | 0.2196131330 |
| C | -0.6111965168 | -2.1983731497 | 1.3890241367 |
| H | 0.5349177191 | -1.2567561083 | 2.9414497540 |
| H | 0.2824699513 | 1.0138119803 | 1.9738771870 |
| C | -0.9978952138 | 1.6773519304 | -0.3049794266 |
| H | -1.7949175356 | -2.8427666840 | -0.2879446105 |
| H | -0.5087537331 | -3.1872242927 | 1.7970300423 |
| C | -2.8217354239 | 0.4690690300 | -1.8245432773 |
| C | -3.5029222364 | 1.2149516122 | -0.9382587114 |
| H | -2.8086235610 | 0.6617127280 | -2.8826877783 |
| O | -0.7489608178 | 2.7537974968 | 0.1192552288 |
| O | -4.3121026710 | 2.1740022562 | -1.3843025592 |
| H | -4.4976332471 | 2.7867196664 | -0.6850881686 |
| O | -2.1166530442 | -0.6385263036 | -1.5055194950 |