# Supporting Information (SI) For:

# Design and Nonadiabatic Photoisomerization Dynamics Study of a Three-Stroke Light Driven Molecular Rotary Motor

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## 1. Optimized geometries and potential energy surfaces of three-stroke LDMRM DDIY

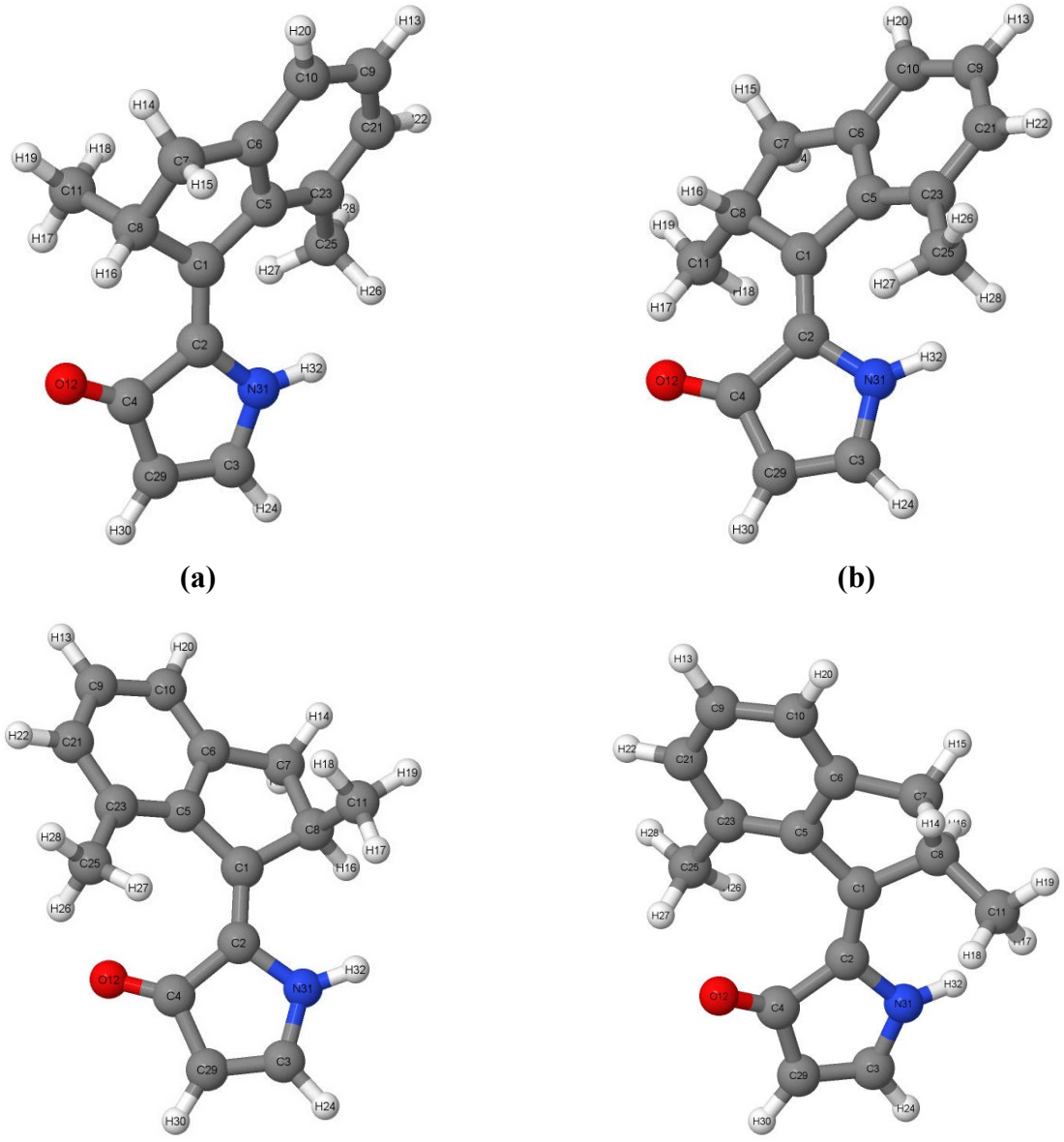



**Figure S1.** Optimized geometries of (a) *ZP*, (b) *ZM*, (c) *EP* and (d) *EM* isomers calculated with OM2/MRCI method implemented in the development version of the MNDO program[S1].

**Table S1.** Optimized geometrical parameters of ground state three-stroke LDMRM DDIY, obtained from different methods. OM2/MRCI method is implemented in the development version of the MNDO program[S1].; while CAM-B3LYP/6-311G(d) and BH&HLYP/6-31G(d) method are implemented in Gaussian 09[S2] program. The lengths are in angstroms; the dihedral angles and bond angles are in degrees.

| | | CAM-B3LYP/ 6-31G(d) | BH&HLYP/ 6-31G(d) | OM2/MRCI |
|---|---|---|---|---|
| *ZP* | C1-C2 | 1.35 | 1.34 | 1.37 |
| | C5-C1-C2 | 129.7 | 129.5 | 130.3 |
| | C1-C2-C4 | 126.6 | 126.7 | 125.4 |
| | C5-C1-C2-C4 | 178.4 | 178.3 | 181.4 |
| | C5-C1-C2-N31 | 2.1 | 1.9 | -1.2 |
| | C2-N31-C4-C1 | -1.5 | -1.4 | 1.0 |
| | C2-C1-C5-C23 | 32.8 | 33.5 | 32.1 |
| *ZM* | C1-C2 | 1.35 | 1.35 | 1.37 |
| | C5-C1-C2 | 125.3 | 125.3 | 126.5 |
| | C1-C2-C4 | 131.0 | 130.9 | 129.6 |
| | C5-C1-C2-C4 | 167.1 | 167.4 | 166.2 |
| | C5-C1-C2-N31 | -10.8 | -10.6 | -8.6 |
| | C2-N31-C4-C1 | -0.8 | -0.8 | -2.1 |
| | C2-C1-C5-C23 | -35.5 | -35.6 | -31.9 |
| *EP* | C1-C2 | 1.35 | 1.34 | 1.37 |
| | C5-C1-C2 | 131.1 | 131.1 | 130.2 |
| | C1-C2-C4 | 131.2 | 131.1 | 131.9 |
| | C5-C1-C2-C4 | 14.6 | 14.1 | 13.6 |
| | C5-C1-C2-N31 | -177.0 | -177.5 | -174.9 |
| | C2-N31-C4-C1 | 4.6 | 4.6 | 3.4 |
| | C2-C1-C5-C23 | 35.0 | 35.4 | 28.1 |
| *EM* | C1-C2 | 1.35 | 1.35 | 1.37 |
| | C5-C1-C2 | 127.9 | 128.0 | 127.3 |
| | C1-C2-C4 | 129.2 | 129.2 | 129.9 |
| | C5-C1-C2-C4 | -18.0 | -18.0 | -19.9 |
| | C5-C1-C2-N31 | 172.8 | 172.8 | 169.5 |
| | C2-N31-C4-C1 | -4.3 | -4.3 | -3.8 |
| | C2-C1-C5-C23 | -36.2 | -36.1 | -25.5 |

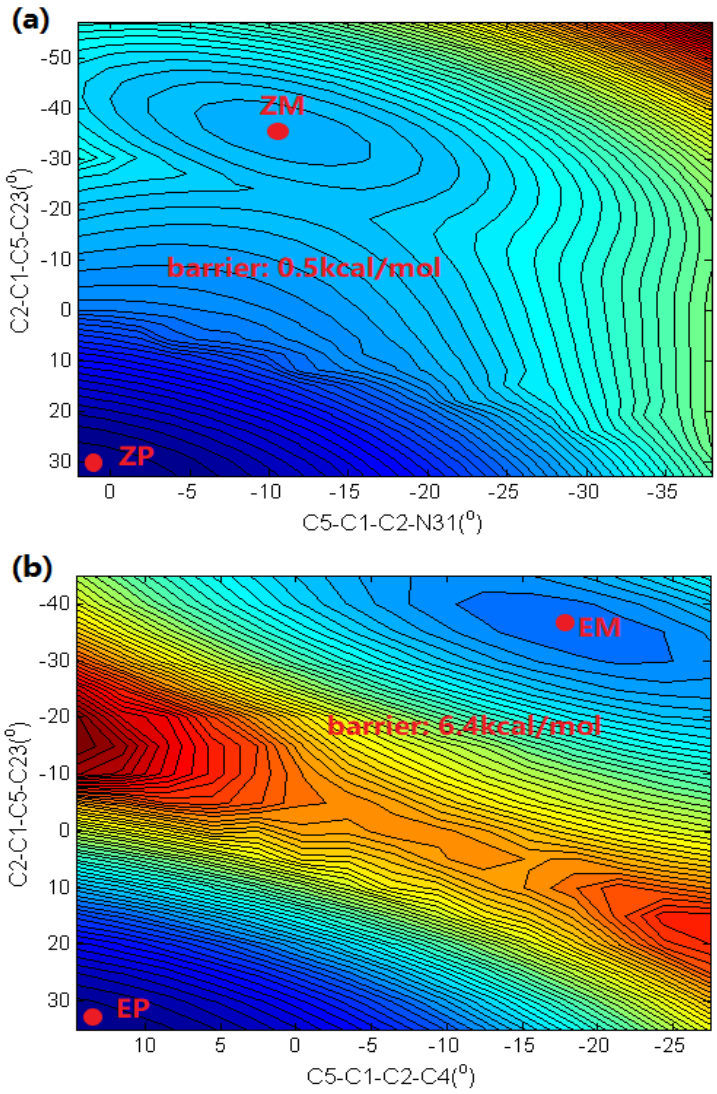



**Figure S2.** Two-dimensional contours of ground state potential energy surface of DDIY (a) near *ZP* and *ZM* geometries corresponding to dihedral angles C5-C1-C2-N31 and C2-C1-C5-C23; (b) near *EP* and *EM* geometries corresponding to dihedral angles C5-C1-C2-C4 and C2-C1-C5-C23. Corresponding potential energy surfaces were obtained with relaxed scan method at the CAM-B3LYP/6-31G(d) level, as implemented in Gaussian 09[S2] program. The energy barrier from *ZM* to *ZP* isomer, together with energy barrier from *EM* to *EP* isomer, are shown in subfigures (a) and (b), respectively.

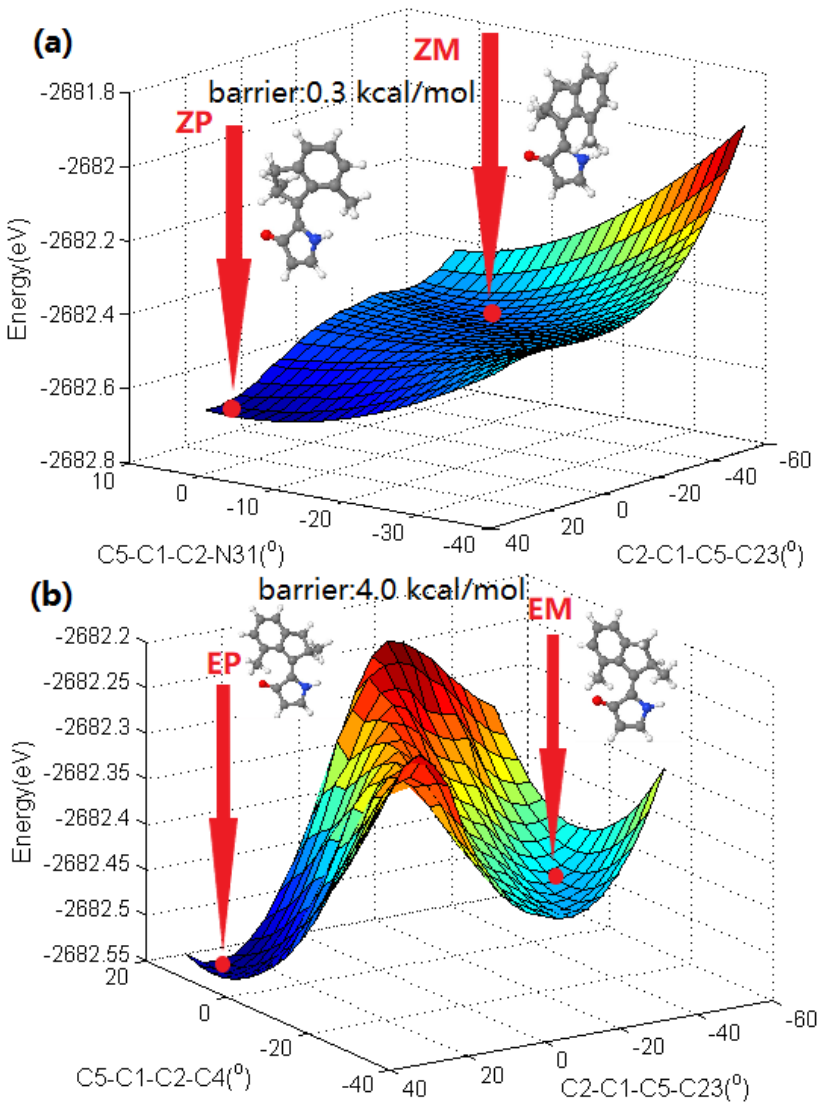



**Figure S3.** Ground state potential energy surface of DDIY (a) near *ZP* and *ZM* geometries corresponding to dihedral angles C5-C1-C2-N31 and C2-C1-C5-C23; (b) near *EP* and *EM* geometries corresponding to dihedral angles C5-C1-C2-C4 and C2-C1-C5-C23. Above potential energy surfaces were obtained with relaxed scan method at the OM2/MRCI level, as implemented in the development version of the MNDO program[S1]. The energy barrier from *ZM* to *ZP* isomer, together with energy barrier from *EM* to *EP* isomer, are shown in subfigures (a) and (b), respectively.

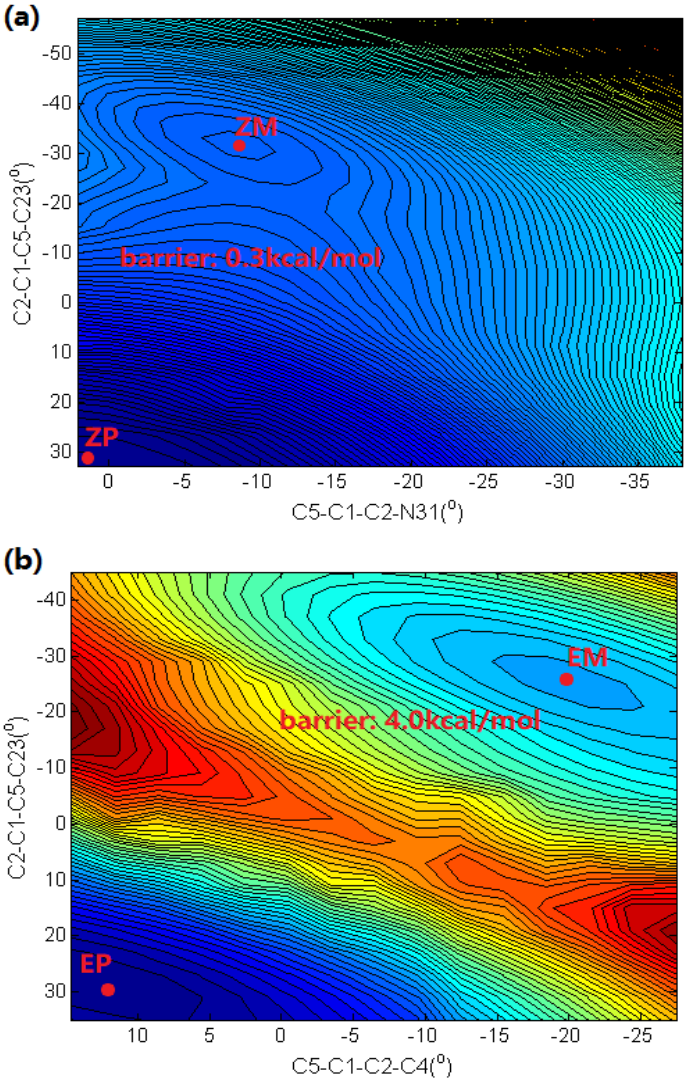



**Figure S4.** Two-dimensional contours of ground state potential energy surface of DDIY (a) near *ZP* and *ZM* geometries corresponding to dihedral angles C5-C1-C2-N31 and C2-C1-C5-C23; (b) near *EP* and *EM* geometries corresponding to dihedral angles C5-C1-C2-C4 and C2-C1-C5-C23. Corresponding potential energy surfaces were obtained with relaxed scan method at the OM2/MRCI level, as implemented in the development version of the MNDO program[S1]. The energy barrier from *ZM* to *ZP* isomer, together with energy barrier from *EM* to *EP* isomer, are shown in subfigures (a) and (b), respectively.

## 2. Optimized geometries of three isomers in Filatov's two-stroke LDMRM DTPN

Based on the CAM-B3LYP/6-31G(d) and BH&HLYP/6-31G(d) levels of theory, three local minima structures of Filatov's two-stroke LDMRM DTPN[S3] were obtained using Gaussian 09 program[S2], which are named as *EP*, *ZP* and *ZM* isomers, respectively.

The optimized geometries for three isomers of Filatov's two-stroke LDMRM DTPN[S3] calculated with CAM-B3LYP/6-31G(d) method are presented in Figure S2, while the corresponding geometrical parameters obtained with CAM-B3LYP/6-311G(d) and BH&HLYP/6-31G(d) methods implemented in Gaussian 09 program[S2] are summarized in Table S2. For comparison, optimized ground state geometrical parameters of *EP* and *ZP* isomers obtained by Filatov *et al.* [S3] are also presented.

The ground state potential energy surfaces near *EP* and *ZP* isomers obtained with relaxed scan method at CAM-B3LYP/6-311G(d) level are presented in Figure S3(a) and S3(b), respectively. As we can see, Figure S3(b) confirms the exsitence of *ZM* isomer of Filatov's two-stroke LDMRM DTPN. But the energy barrier from *ZM* to *ZP* isomer is only about 0.8 kcal/mol. Due to the low energy barrier and large kinetic energy of the molecules after nonadiabatic decay, photoisomerization trajectory starting from *EP* isomer can exceed the barrier and arrive at more stable *ZP* isomer at room temperature. Filatov *et al.* did observe direct *EP-ZP*

photoisomerization process, metastable *ZM* geometry was not observed during the working cycle of their LDMRM DTPN.

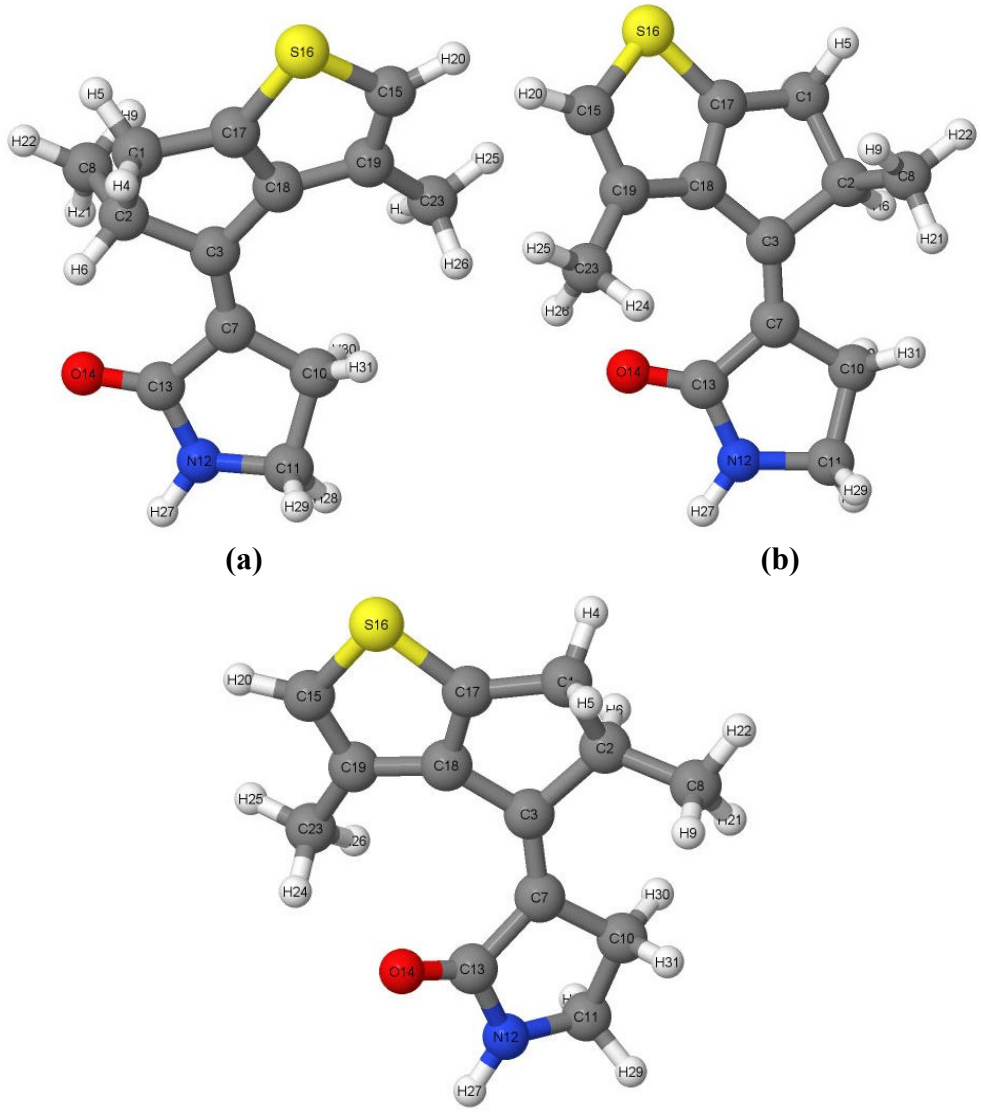



**Figure S5.** Optimized geometries for three isomers of Filatov's two-stroke LDMRM DTPN[S3] calculated with CAM-B3LYP/6-31G(d) method implemented in Gaussian 09[S2] program. (a) *EP*, (b) *ZP* and (c) *ZM* isomers. All atoms are labeled.

**Table S2.** Optimized ground state geometrical parameters of Filatov's two-stroke LDMRM DTPN[S3], obtained from DFT methods. CAM-B3LYP/6-31G(d) and BH&HLYP/6-31G(d) methods are implemented in Gaussian 09 program[S2]. For comparison, optimized ground state geometrical parameters of *EP* and *ZP* isomers obtained by Filatov *et al.* are also presented. The lengths are in angstroms; the dihedral angles and bond angles are in degrees.

| | | CAM-B3LYP/ 6-31G(d) | BH&HLYP/ 6-31G(d) | SSR-BH&HLYP/ 6-31G(d)[S3] |
|---|---|---|---|---|
| *EP* | C3-C7 | 1.34 | 1.34 | 1.34 |
| | C18-C3-C7 | 129.8 | 129.8 | 129.8 |
| | C3-C7-C13 | 123.4 | 123.6 | 123.6 |
| | C18-C3-C7-C13 | 177.4 | 177.3 | 177.3 |
| | C18-C3-C7-C10 | 2.3 | 2.2 | 2.2 |
| | C7-C10-C13-C3 | -2.0 | -2.0 | -2.0 |
| | C19-C18-C3-C7 | 22.1 | 22.5 | 22.7 |
| *ZP* | C3-C7 | 1.34 | 1.34 | 1.34 |
| | C18-C3-C7 | 133.1 | 133.1 | 133.3 |
| | C3-C7-C13 | 127.9 | 127.9 | 128.0 |
| | C18-C3-C7-C13 | 8.2 | 8.0 | 8.2 |
| | C18-C3-C7-C10 | -178.6 | -178.7 | -178.7 |
| | C7-C10-C13-C3 | 2.8 | 2.7 | 2.8 |
| | C19-C18-C3-C7 | 30.0 | 30.0 | 29.9 |
| *ZM* | C3-C7 | 1.35 | 1.34 | |
| | C18-C3-C7 | 129.7 | 129.9 | |
| | C3-C7-C13 | 125.7 | 125.9 | |
| | C18-C3-C7-C13 | -15.2 | -15.2 | |
| | C18-C3-C7-C10 | 168.3 | 168.2 | |
| | C7-C10-C13-C3 | -1.4 | -1.3 | |
| | C19-C18-C3-C7 | -28.0 | -27.8 | |

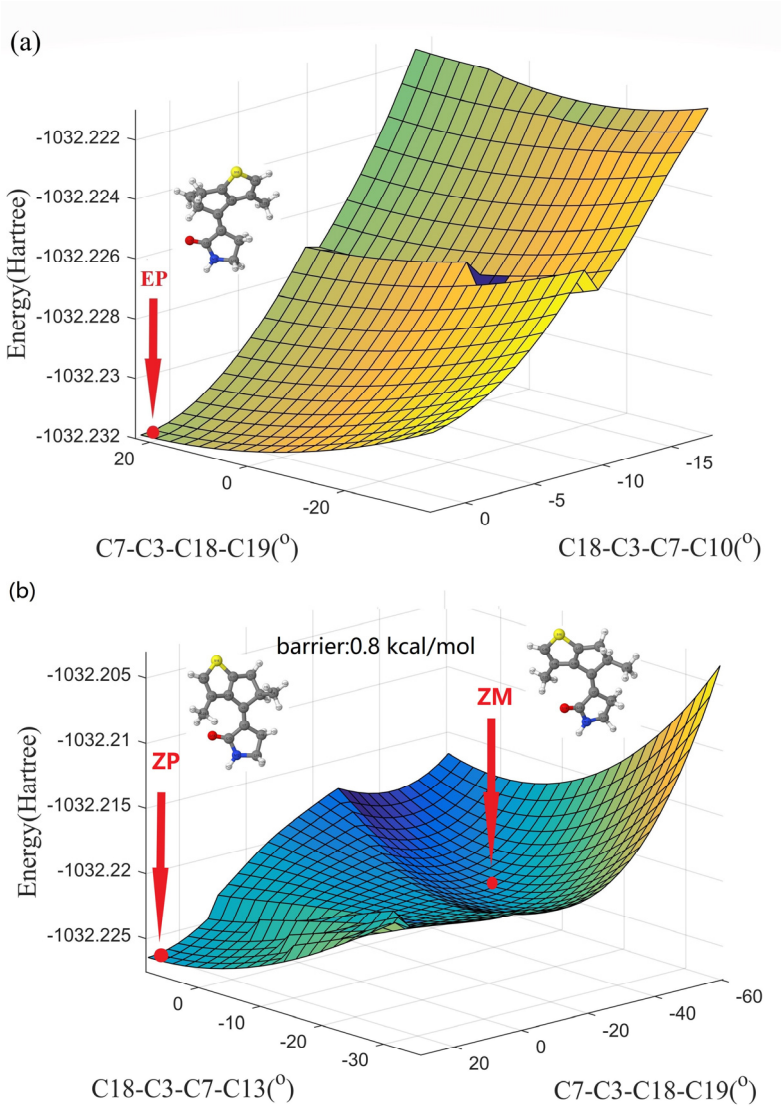
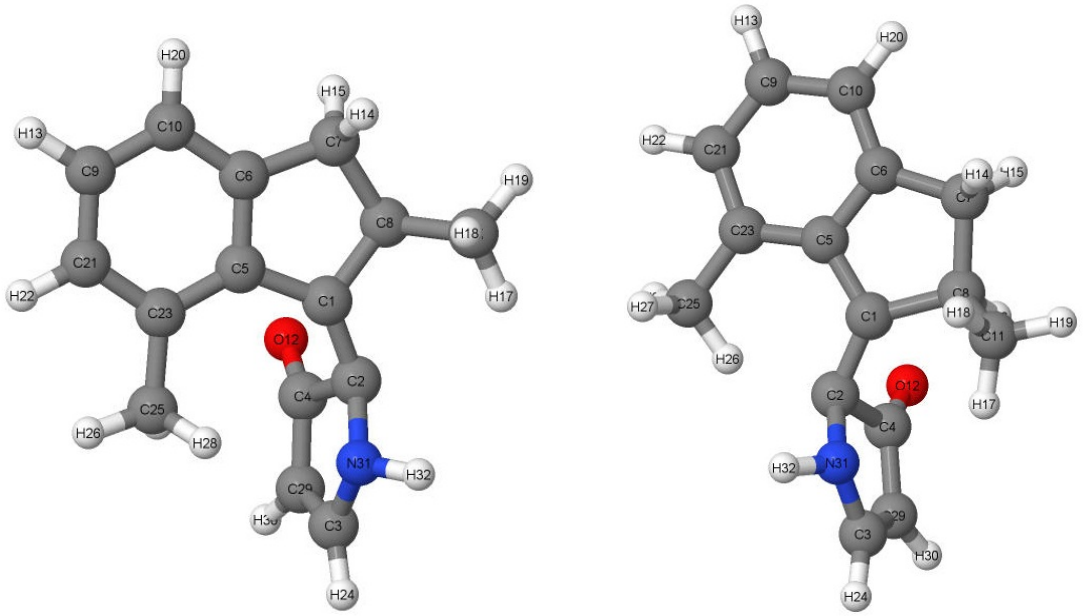


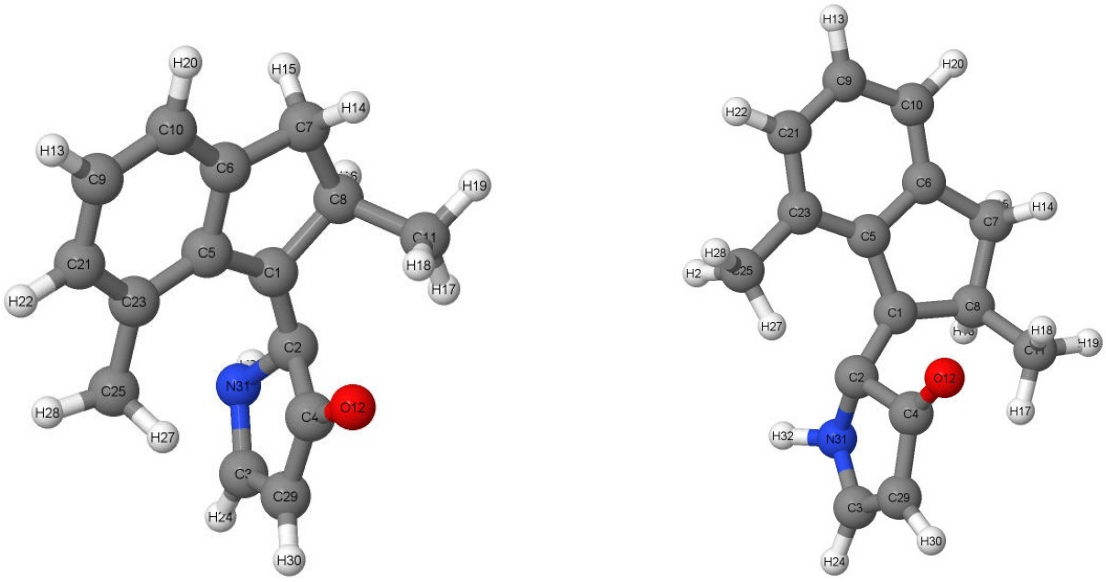

**Figure S6.** With dihedral angles (a) C7-C3-C18-C19 and C18-C3-C7-C10, (b) C7-C3-C18-C19 and C18-C3-C7-C13 as degrees of freedom respectively, the ground state potential energy surfaces near (a) *EP* and (b) *ZP* isomers of Filatov's two-stroke LDMRM DTPN[S3] were obtained from relaxed scan method at CAM-B3LYP/6-31G(d) level implemented in Gaussian 09[S2] program. The energy barrier from *ZM* to *ZP* isomer is also presented in the figure.

## 3. Optimized geometries of conical intersection in the *EP-ZP* and *ZP-EM* photoisomerization processes of three-stroke LDMRM DDIY




**(a)** **(b)**

**Figure S7.** Optimized geometries of two $S_0/S_1$ conical intersections (a) *ECI(1)* and (b) *ECI(2)* in the *EP-ZP* photoisomerization process calculated with OM2/MRCI method implemented in MNDO99[S1] program.




**(a)** **(b)**

**Figure S8.** Optimized geometries of two $S_0/S_1$ conical intersections (a) *ZCI(1)* and (b) *ZCI(2)* in the *ZP-EM* photoisomerization process calculated with OM2/MRCI method implemented in MNDO99[S1] program.

**Table S3.** Optimized geometrical parameters of two $S_0/S_1$ conical intersections *ECI(1)* and *ECI(2)* in the *EP-ZP* photoisomerization process calculated with OM2/MRCI method implemented in MNDO99[S1] program. The lengths are in angstroms; the dihedral angles and bond angles are in degrees.

| | | OM2/MRCI |
|---|---|---|
| *ECI(1)* | C1-C2 | 1.39 |
| | C5-C1-C2 | 132.7 |
| | C1-C2-C4 | 104.1 |
| | C5-C1-C2-C4 | 55.8 |
| | C5-C1-C2-N31 | -67.9 |
| | C2-N31-C4-C1 | -25.8 |
| | C2-C1-C5-C23 | 12.7 |
| *ECI(2)* | C1-C2 | 1.42 |
| | C5-C1-C2 | 122.0 |
| | C1-C2-C4 | 104.2 |
| | C5-C1-C2-C4 | 111.9 |
| | C5-C1-C2-N31 | -132.2 |
| | C2-N31-C4-C1 | 31.1 |
| | C2-C1-C5-C23 | 6.2 |

**Table S4.** Optimized geometrical parameters of two $S_0/S_1$ conical intersections *ZCI(1)* and *ZCI(2)* in the *ZP-EM* photoisomerization process calculated with OM2/MRCI method implemented in MNDO99[S1] program.. The lengths are in angstroms; the dihedral angles and bond angles are in degrees.

| | | OM2/MRCI |
|---|---|---|
| *ZCI(1)* | C1-C2 | 1.40 |
| | C5-C1-C2 | 133.4 |
| | C1-C2-C4 | 105.1 |
| | C5-C1-C2-C4 | -55.0 |
| | C5-C1-C2-N31 | 66.4 |
| | C2-N31-C4-C1 | 27.6 |
| | C2-C1-C5-C23 | -9.7 |
| *ZCI(2)* | C1-C2 | 1.41 |
| | C5-C1-C2 | 121.2 |
| | C1-C2-C4 | 105.6 |
| | C5-C1-C2-C4 | -113.5 |
| | C5-C1-C2-N31 | 129.7 |
| | C2-N31-C4-C1 | -30.8 |
| | C2-C1-C5-C23 | -6.1 |

## 4. Time-dependent evolution of geometrical parameters in several typical trajectories of three-stroke LDMRM DDIY

In order to explore the reaction dynamics of three-stroke LDMRM DDIY in detail, time dependent evolution of geometrical parameters in five typical trajectories for both *EP-ZP* and *ZP-EM* photoisomerization processes are presented in the following.

Time dependence of central bond length C1-C2, central dihedral angle C5−C1−C2−C4, central dihedral angle C5−C1−C2−N31, side dihedral angle C2−C1−C5−C23 and pyramid dihedral angle C2−N31−C4−C1 in five typical trajectories (named as trajectory 1-5, respectively) of *EP-ZP* photoisomerization process are shown in Figure S6-S10. The correpongding geometrical parameters in reaction product *ZP* isomer are also shown in the figures with red lines.

Time dependence of central bond length C1-C2, central dihedral angle C5−C1−C2−C4, central dihedral angle C5−C1−C2−N31, side dihedral angle C2−C1−C5−C23 and pyramid dihedral angle C2−N31−C4−C1 in five typical trajectories (named as trajectory 1-5, respectively) of *ZP-EM* photoisomerization process are shown in Figure S11-S15. The correpongding geometrical parameters in reaction product *EM* isomer are also shown in the figures with red lines.

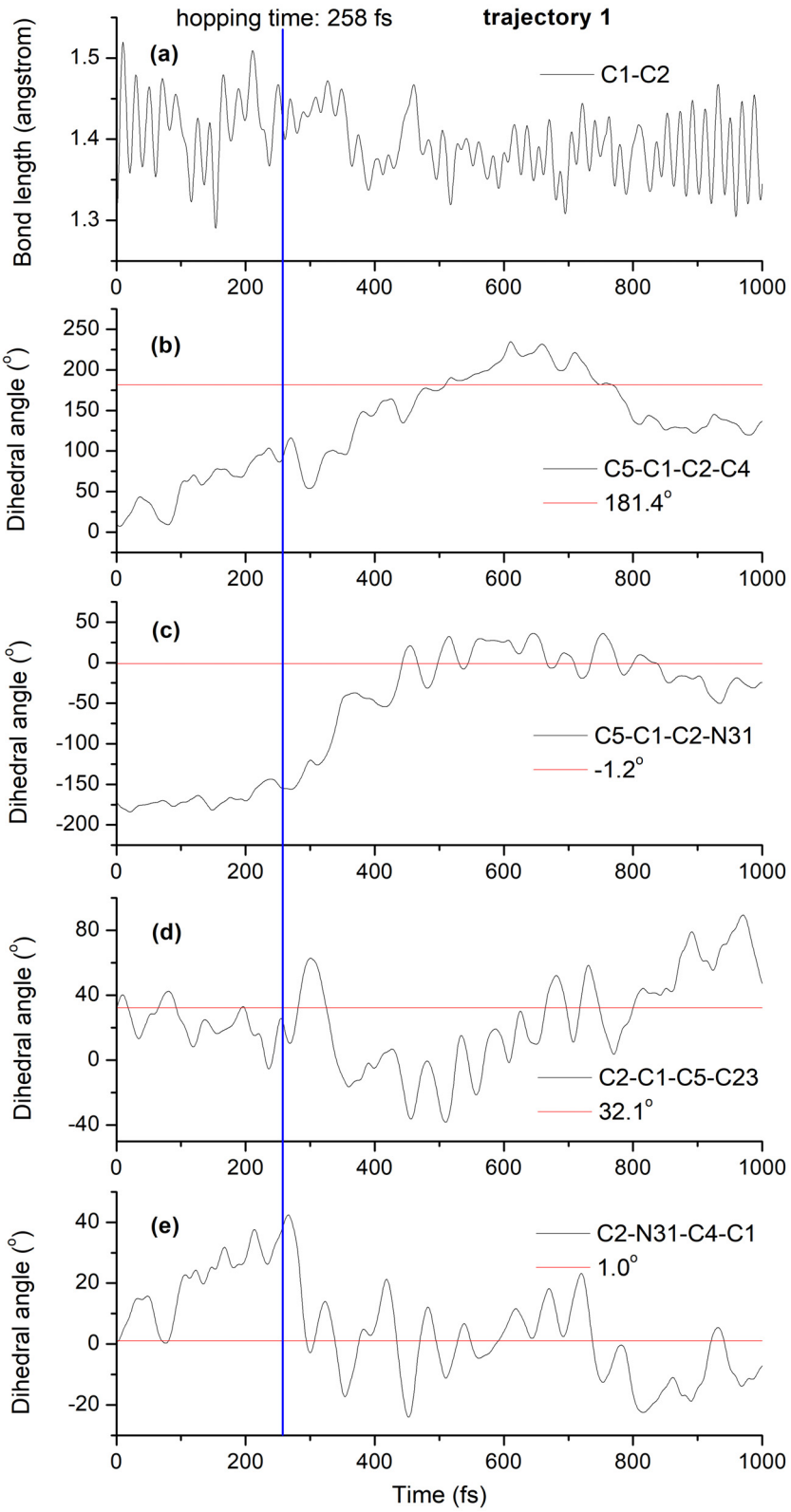



**Figure S9.** Time dependence of (a) central bond length C1-C2, (b) central dihedral angle C5−C1−C2−C4, (c) central dihedral angle C5−C1−C2−N31, (d) side dihedral angle C2−C1−C5−C23 and (e) pyramid dihedral angle C2−N31−C4−C1 in a representative trajectory (named as trajectory 1) of *EP-ZP* photoisomerization process.

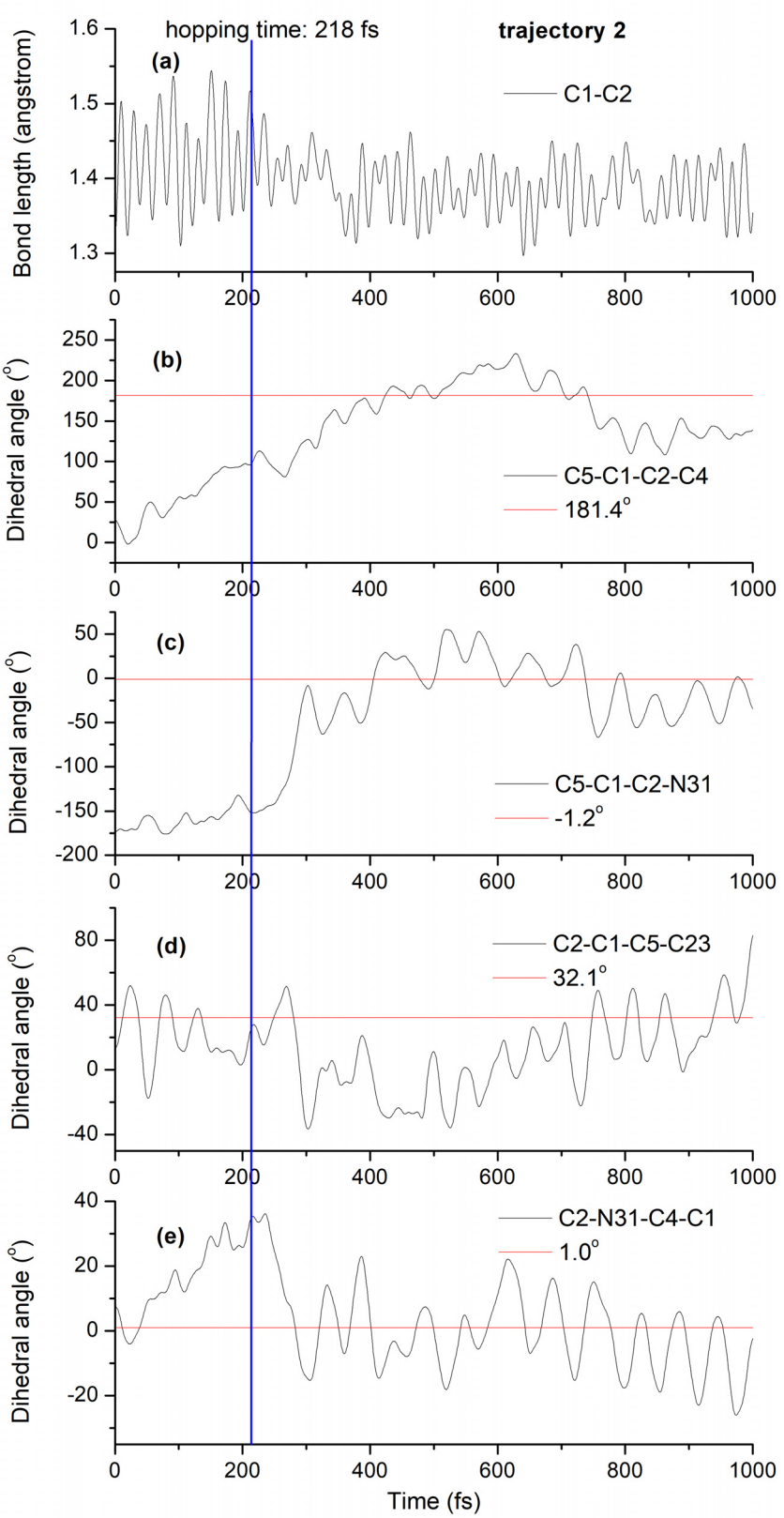



**Figure S10.** Time dependence of (a) central bond length C1-C2, (b) central dihedral angle C5−C1−C2−C4, (c) central dihedral angle C5−C1−C2−N31, (d) side dihedral angle C2−C1−C5−C23 and (e) pyramid dihedral angle C2−N31−C4−C1 in a representative trajectory (named as trajectory 2) of *EP-ZP* photoisomerization process.

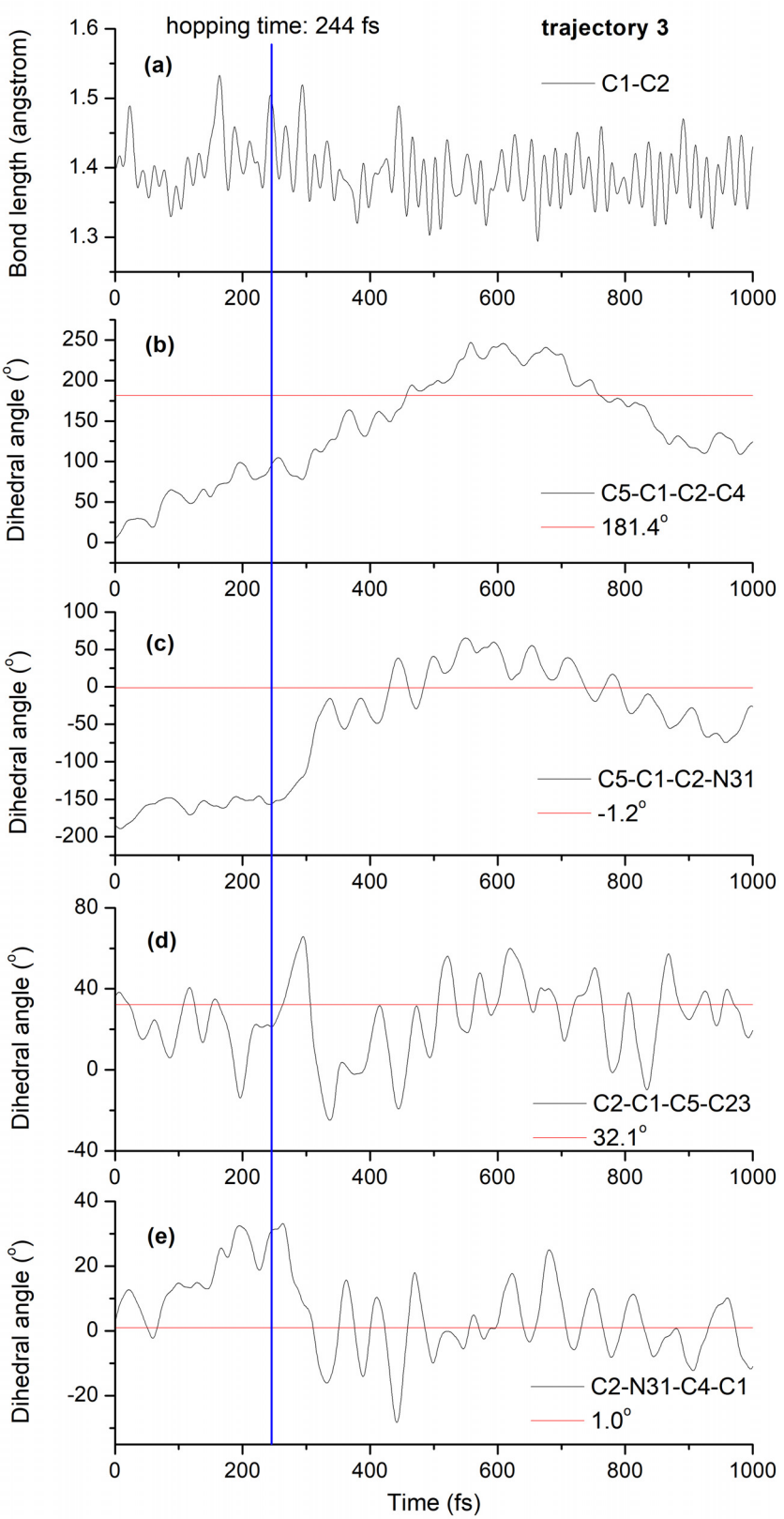



**Figure S11.** Time dependence of (a) central bond length C1-C2, (b) central dihedral angle C5−C1−C2−C4, (c) central dihedral angle C5−C1−C2−N31, (d) side dihedral angle C2−C1−C5−C23 and (e) pyramid dihedral angle C2−N31−C4−C1 in a representative trajectory (named as trajectory 3) of *EP-ZP* photoisomerization process.

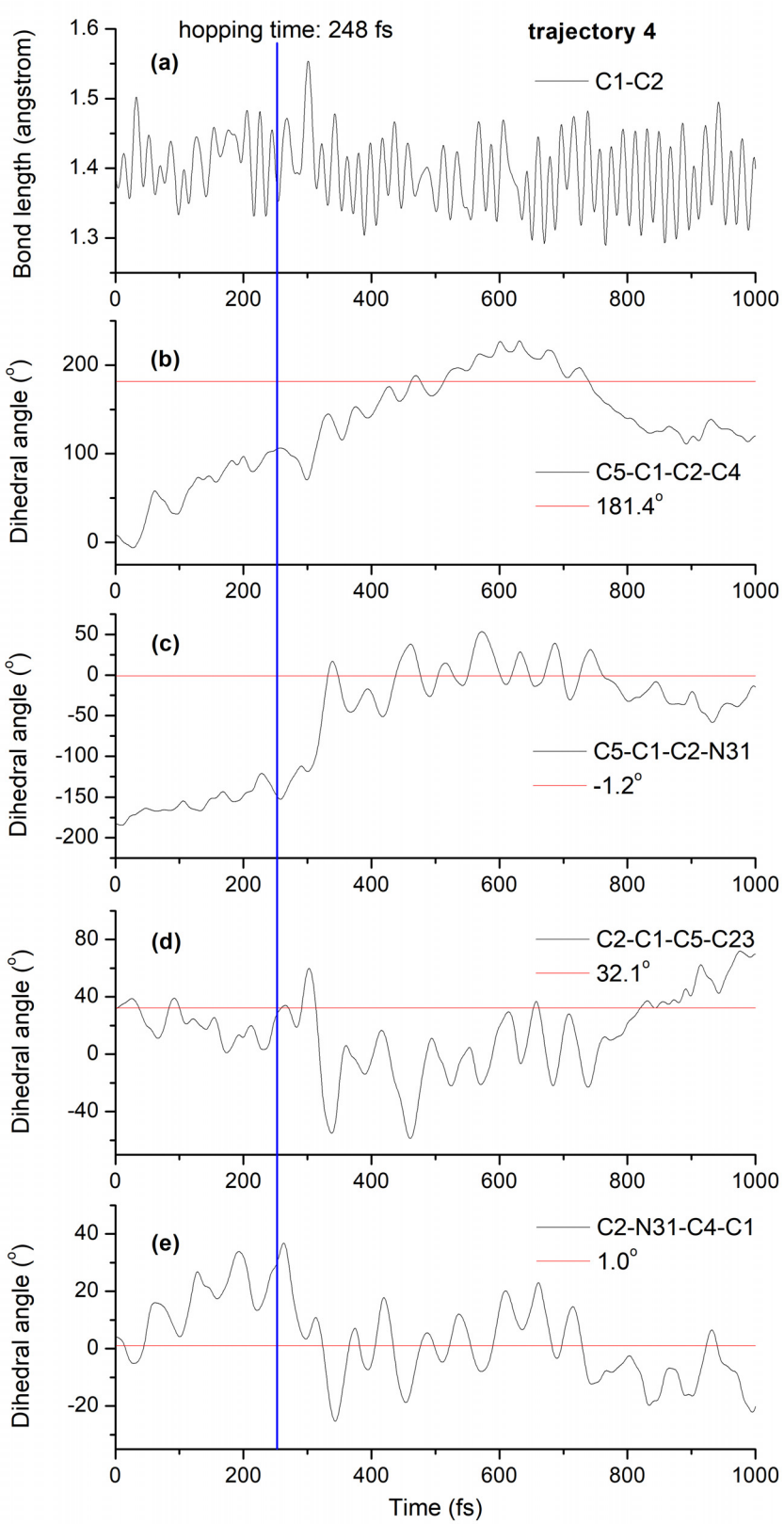



**Figure S12.** Time dependence of (a) central bond length C1-C2, (b) central dihedral angle C5−C1−C2−C4, (c) central dihedral angle C5−C1−C2−N31, (d) side dihedral angle C2−C1−C5−C23 and (e) pyramid dihedral angle C2−N31−C4−C1 in a representative trajectory (named as trajectory 4) of *EP-ZP* photoisomerization process.

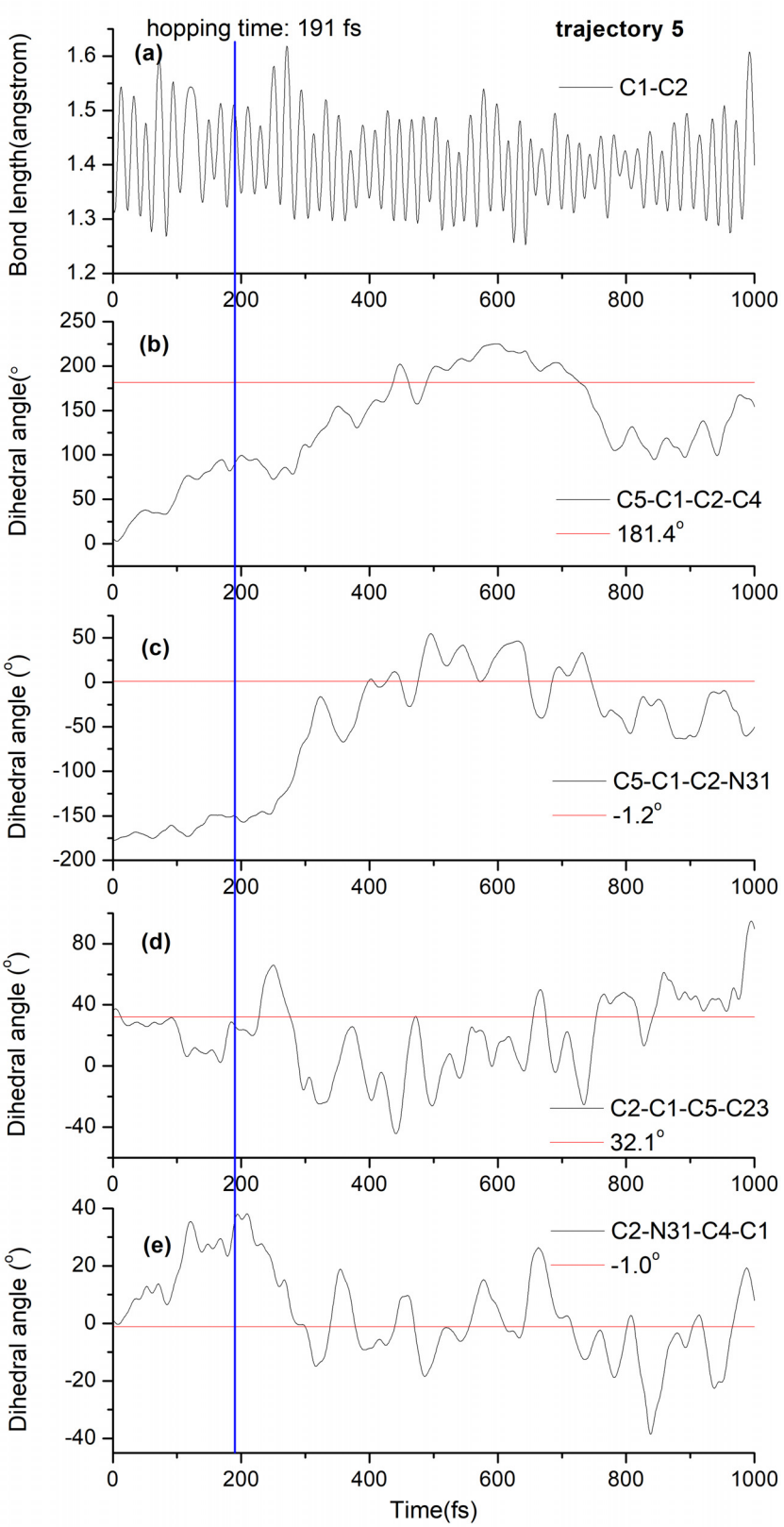



**Figure S13.** Time dependence of (a) central bond length C1-C2, (b) central dihedral angle C5−C1−C2−C4, (c) central dihedral angle C5−C1−C2−N31, (d) side dihedral angle C2−C1−C5−C23 and (e) pyramid dihedral angle C2−N31−C4−C1 in a representative trajectory (named as trajectory 5) of *EP-ZP* photoisomerization process.

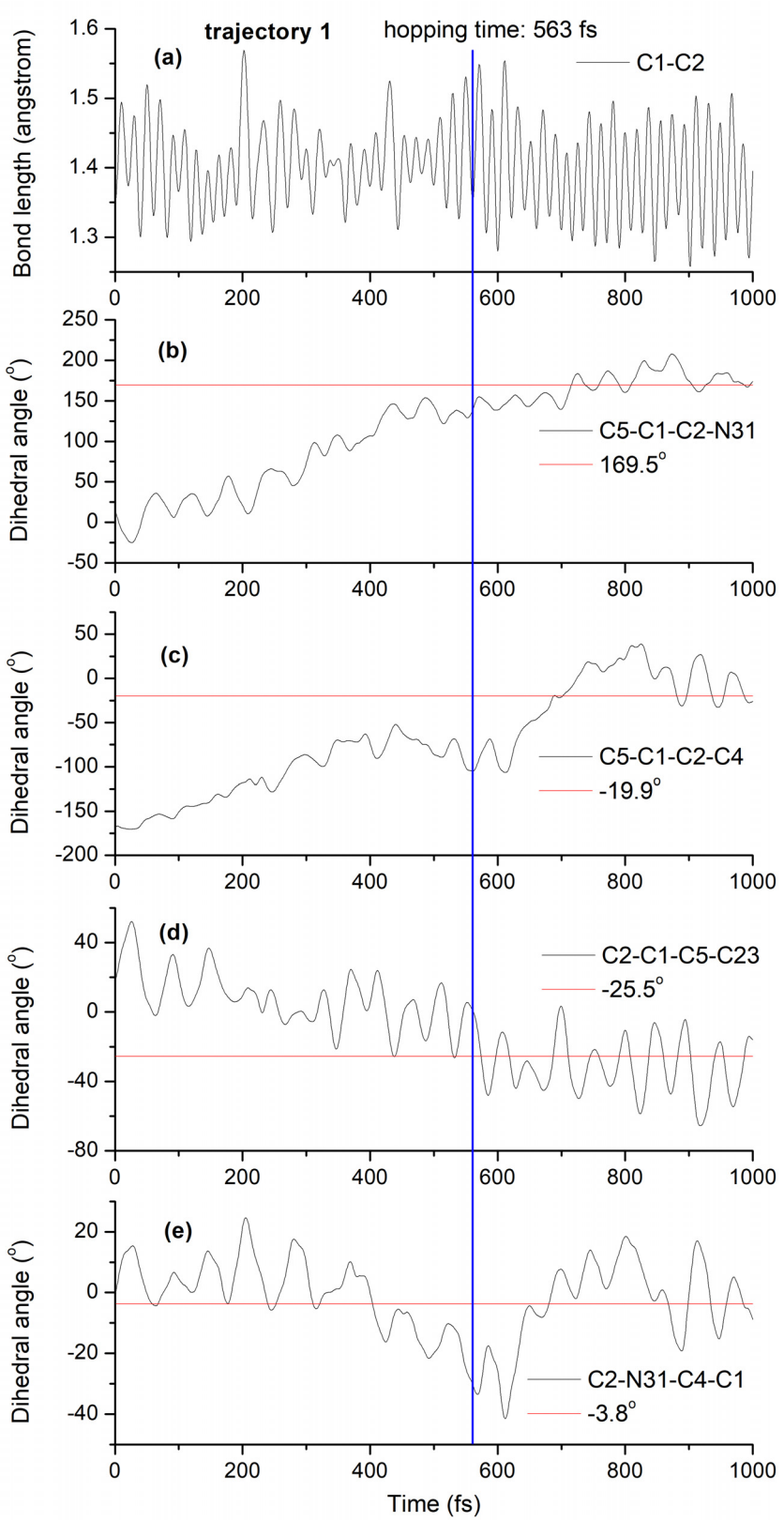



**Figure S14.** Time dependence of (a) central bond length C1-C2, (b) central dihedral angle C5−C1−C2−C4, (c) central dihedral angle C5−C1−C2−N31, (d) side dihedral angle C2−C1−C5−C23 and (e) pyramid dihedral angle C2−N31−C4−C1 in a representative trajectory (named as trajectory 1) of *ZP-EM* photoisomerization process.

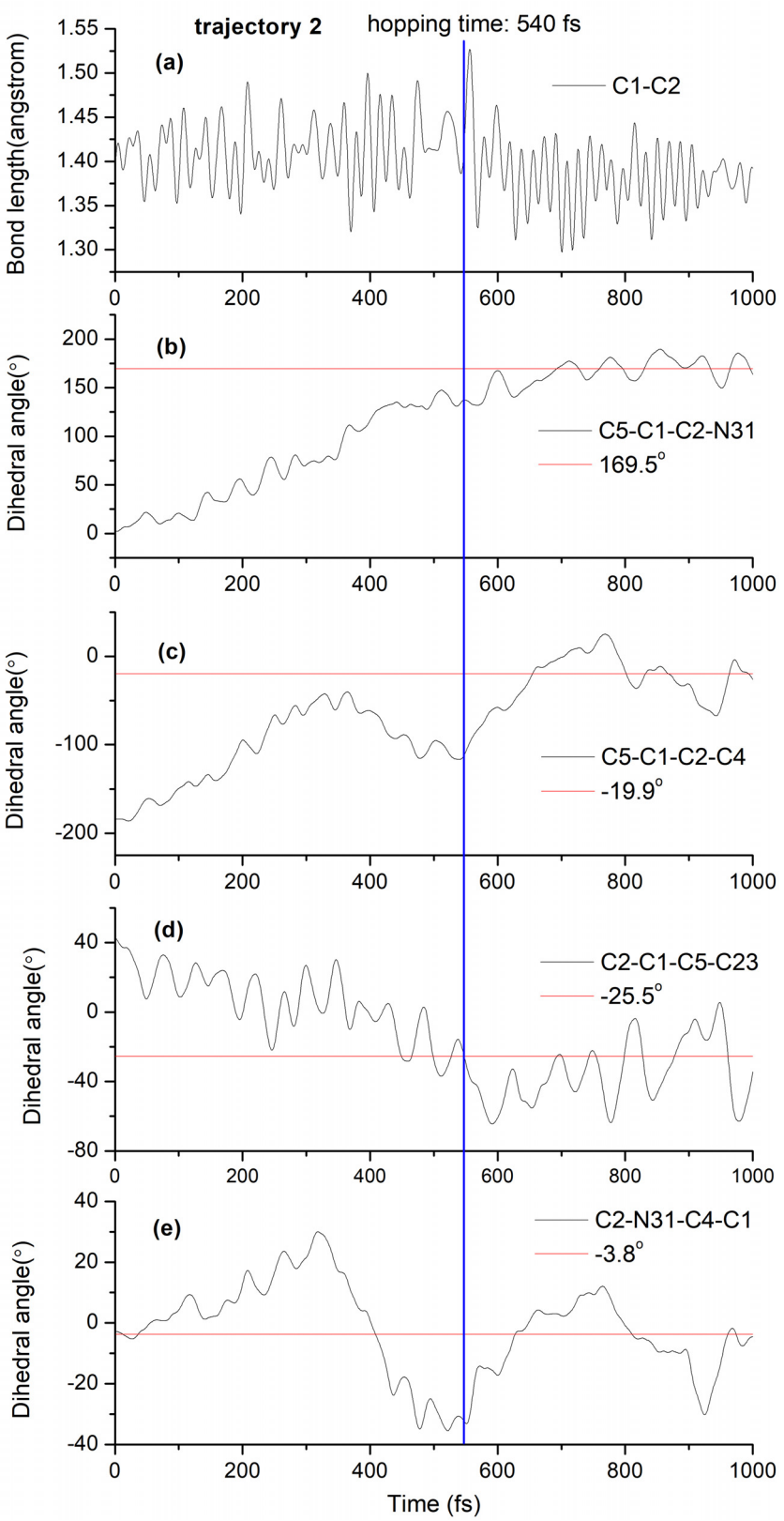



**Figure S15.** Time dependence of (a) central bond length C1-C2, (b) central dihedral angle C5−C1−C2−C4, (c) central dihedral angle C5−C1−C2−N31, (d) side dihedral angle C2−C1−C5−C23 and (e) pyramid dihedral angle C2−N31−C4−C1 in a representative trajectory (named as trajectory 2) of *ZP-EM* photoisomerization process.

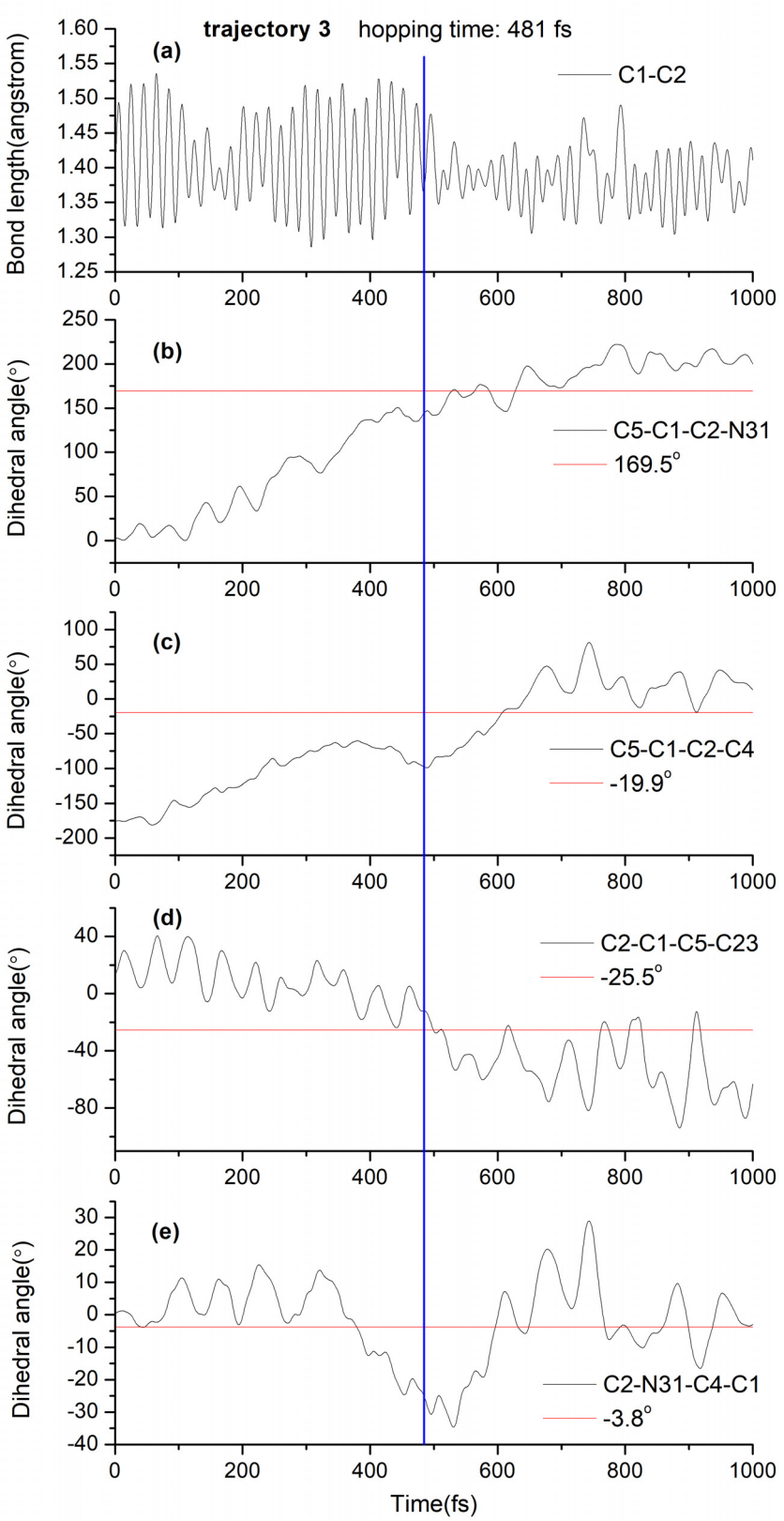



**Figure S16.** Time dependence of (a) central bond length C1-C2, (b) central dihedral angle C5−C1−C2−C4, (c) central dihedral angle C5−C1−C2−N31, (d) side dihedral angle C2−C1−C5−C23 and (e) pyramid dihedral angle C2−N31−C4−C1 in a representative trajectory (named as trajectory 3) of *ZP-EM* photoisomerization process.

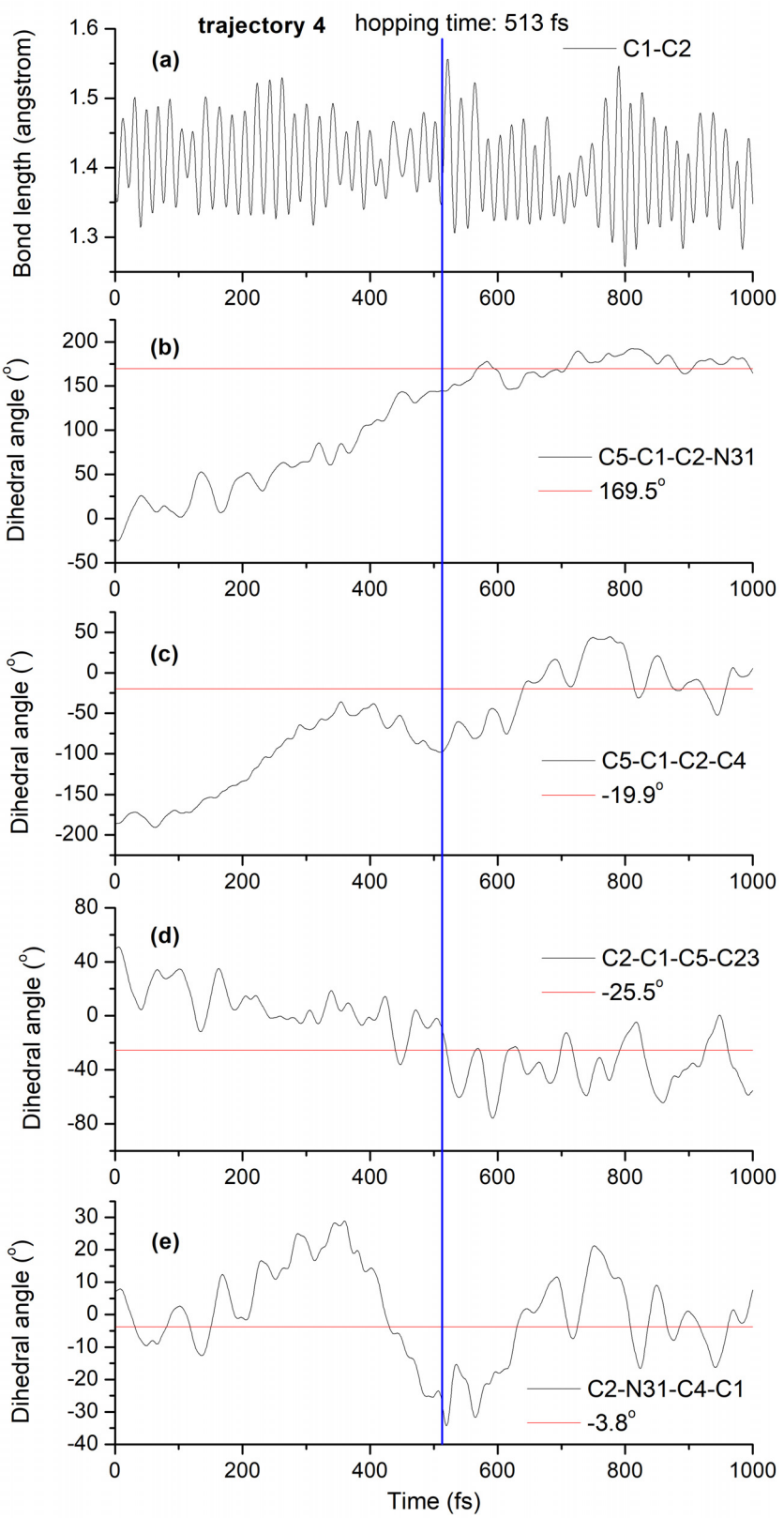



**Figure S17.** Time dependence of (a) central bond length C1-C2, (b) central dihedral angle C5−C1−C2−C4, (c) central dihedral angle C5−C1−C2−N31, (d) side dihedral angle C2−C1−C5−C23 and (e) pyramid dihedral angle C2−N31−C4−C1 in a representative trajectory (named as trajectory 4) of *ZP-EM* photoisomerization process.

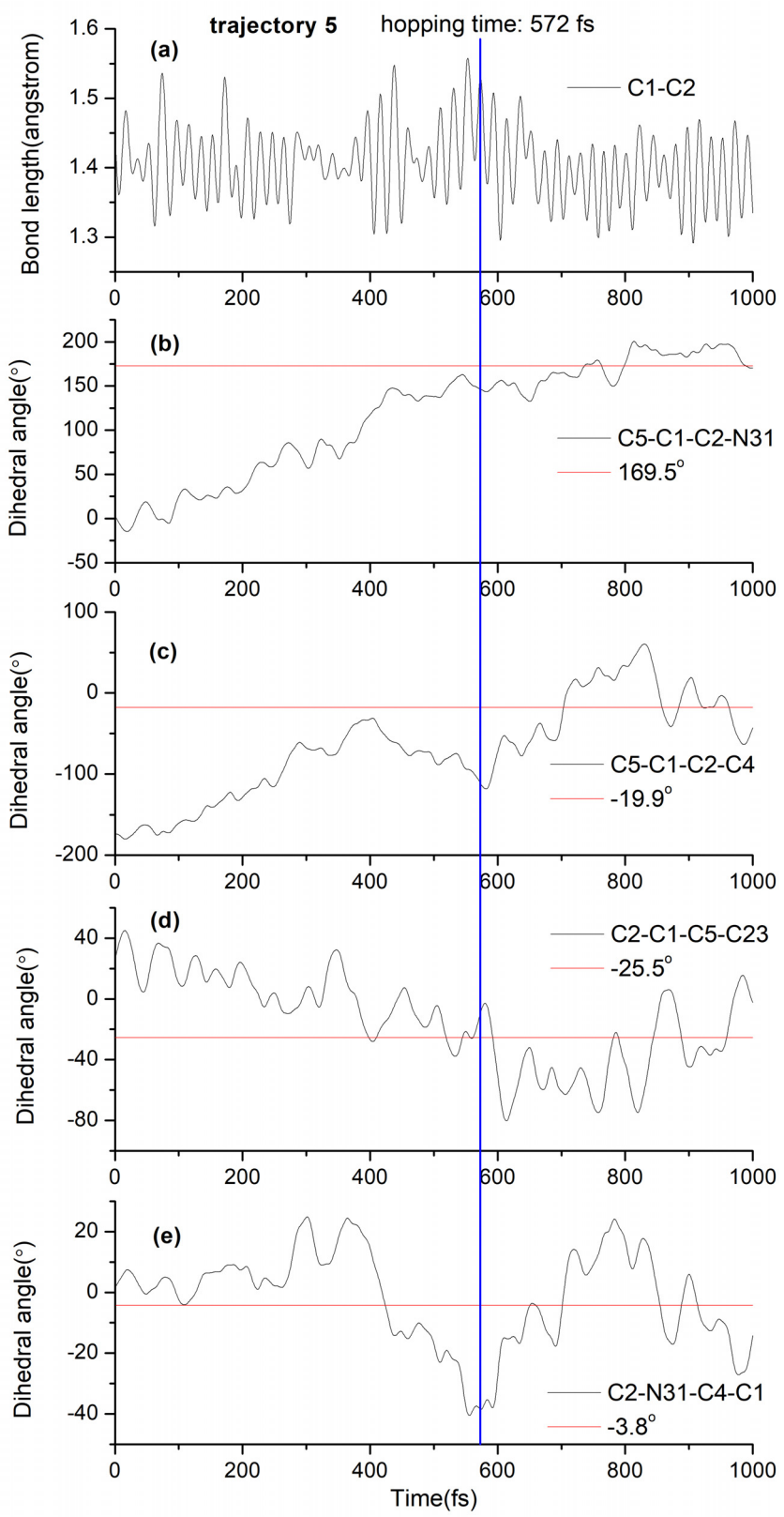



**Figure S18.** Time dependence of (a) central bond length C1-C2, (b) central dihedral angle C5−C1−C2−C4, (c) central dihedral angle C5−C1−C2−N31, (d) side dihedral angle C2−C1−C5−C23 and (e) pyramid dihedral angle C2−N31−C4−C1 in a representative trajectory (named as trajectory 5) of *ZP-EM* photoisomerization process.

## 5. Cartesian coordinates for several structures of three-stroke LDMRM DDIY optimized with the OM2/MRCI method

Unit of the Cartesian coordinate below is angstrom.

(1) *ZP* geometry at ground state.

| | | | |
|---|---|---|---|
| C | 0.2750443351 | 0.3700125800 | -0.0202993675 |
| C | 1.4643832762 | -0.2892385988 | -0.1616219784 |
| C | 3.0425486914 | -1.9186262367 | -0.3649515743 |
| C | 2.8327543141 | 0.3508440060 | -0.1109143091 |
| C | -1.1051069040 | -0.1444545098 | -0.0241349823 |
| C | -1.9374362037 | 0.9118537016 | -0.4687985311 |
| C | -1.1510166444 | 2.1694069165 | -0.7074108653 |
| C | 0.2055790061 | 1.8862783101 | -0.0325166523 |
| C | -3.8667377742 | -0.4925782290 | -0.2880902994 |
| C | -3.3100698777 | 0.7457410877 | -0.6194041726 |
| C | 0.2306329987 | 2.3848234884 | 1.4015476089 |
| O | 3.0412751010 | 1.5569600595 | 0.0048942225 |
| H | -4.9438450248 | -0.6549901702 | -0.4099749403 |
| H | -1.6609248625 | 3.0463198481 | -0.2601329244 |
| H | -1.0279894232 | 2.3352229781 | -1.7984445784 |
| H | 1.0495880083 | 2.3322868363 | -0.6112757127 |
| H | 1.2003755053 | 2.1507413737 | 1.8594875823 |
| H | -0.5701266943 | 1.9177906259 | 1.9957653868 |
| H | 0.0901060238 | 3.4782047684 | 1.4145932058 |
| H | -3.9366521031 | 1.5625746604 | -0.9855687437 |
| C | -3.0710836506 | -1.5088923384 | 0.2397328461 |
| H | -3.5409925428 | -2.4461343442 | 0.5620691117 |
| C | -1.6818026782 | -1.3522269077 | 0.3906798915 |
| H | 3.4369089335 | -2.9331228467 | -0.4555798625 |
| C | -0.9204201047 | -2.4447438961 | 1.0699273849 |
| H | -0.6023779552 | -3.2005242395 | 0.3294361101 |
| H | -0.0489670590 | -2.0349073144 | 1.5972573529 |
| H | -1.5681162396 | -2.9420203427 | 1.8083048076 |
| C | 3.7779040437 | -0.7584313707 | -0.2293558463 |
| H | 4.8459954022 | -0.6577862495 | -0.2342124817 |
| N | 1.6892707987 | -1.6620573609 | -0.3289078297 |
| H | 0.9743913779 | -2.3674192789 | -0.3950541704 |

(2) *ZM* geometry at ground state.

| | | | |
|---|---|---|---|
| C | -0.2356184253 | 0.4332587176 | 0.1566298098 |
| C | -1.3808045932 | -0.2752903724 | -0.1093054657 |
| C | -2.7111300226 | -2.0088287163 | -0.7764354352 |
| C | -2.8179428018 | 0.0606221415 | 0.2121306733 |
| C | 1.1491566252 | -0.0722851925 | 0.0721839795 |
| C | 2.0034268936 | 1.0367817890 | -0.1301524907 |
| C | 1.2279952308 | 2.3180348567 | -0.1376188612 |
| C | -0.1703138630 | 1.9308559184 | 0.3854984644 |
| C | 3.9164932383 | -0.3981443472 | -0.1681653626 |
| C | 3.3800416123 | 0.8884485499 | -0.2647238664 |
| C | -1.2349223591 | 2.7148002201 | -0.3689254206 |
| O | -3.2067169262 | 1.0569722464 | 0.8192718424 |
| H | 4.9936045342 | -0.5517235712 | -0.2995726330 |
| H | 1.1667436515 | 2.7120257640 | -1.1740648679 |
| H | 1.7142899526 | 3.0752759709 | 0.5092083267 |
| H | -0.2630070907 | 2.1278376066 | 1.4888006166 |
| H | -2.2114672752 | 2.5590384279 | 0.0850858501 |
| H | -1.2606368560 | 2.4039307344 | -1.4249971832 |
| H | -0.9875258055 | 3.7883530168 | -0.3275158475 |
| H | 4.0228634916 | 1.7549111003 | -0.4371126328 |
| C | 3.0981708356 | -1.4826170058 | 0.1489388086 |
| H | 3.5531480076 | -2.4653260029 | 0.3213574825 |
| C | 1.7062873120 | -1.3396478556 | 0.2931417888 |
| H | -2.9528349769 | -2.9943545053 | -1.1766180840 |
| C | 0.9369718993 | -2.5197287800 | 0.7954695088 |
| H | 1.5501404153 | -3.0609843789 | 1.5318158558 |
| H | 0.0115820298 | -2.1996459468 | 1.2884001721 |
| H | 0.7055924370 | -3.2121663087 | -0.0323763496 |
| C | -3.5945217203 | -1.0958214796 | -0.2367714406 |
| H | -4.6611439916 | -1.1807105089 | -0.1657953059 |
| N | -1.4136882842 | -1.5597563253 | -0.6744452722 |
| H | -0.6097627966 | -2.0541458807 | -1.0243118814 |

(3) *EP* geometry at ground state.

| | | | |
|---|---|---|---|
| C | -0.2522189976 | 0.6044405751 | 0.0383053531 |
| C | -1.5454394664 | 0.1449868929 | 0.0579829789 |
| C | -3.8282497139 | 0.2919406201 | -0.0050040244 |

| | | | |
|---|---|---|---|
| C | -2.1249760796 | -1.2108117478 | 0.3535847348 |
| C | 1.0146220324 | -0.1332392095 | 0.0426166042 |
| C | 2.0158152520 | 0.7498841581 | 0.5156489872 |
| C | 1.4523481242 | 2.1077552781 | 0.8133275625 |
| C | 0.0832551499 | 2.0815144563 | 0.1020724560 |
| C | 3.6610932978 | -0.9613801476 | 0.2851390559 |
| C | 3.3348837763 | 0.3414160284 | 0.6771662965 |
| C | 0.1848916250 | 2.6580084735 | -1.3011856187 |
| O | -1.4969295498 | -2.1927335761 | 0.7460799230 |
| H | 4.6979005372 | -1.3067778392 | 0.3812352530 |
| H | 2.1041321788 | 2.9142084391 | 0.4225673091 |
| H | 1.3218395692 | 2.2360128440 | 1.9076773791 |
| H | -0.6799998712 | 2.6477261921 | 0.6997881751 |
| H | -0.7825930340 | 2.5787978066 | -1.8222702391 |
| H | 0.9383569063 | 2.1067541019 | -1.8785192593 |
| H | 0.4753009872 | 3.7190224817 | -1.2551409080 |
| H | 4.0876531774 | 1.0110018288 | 1.0990812019 |
| C | 2.7033771904 | -1.8021476932 | -0.2784386878 |
| H | 3.0046323246 | -2.7894352575 | -0.6488862935 |
| C | 1.3566863931 | -1.4089499708 | -0.4267141740 |
| H | -4.8065296685 | 0.7643881709 | -0.1154485952 |
| C | 0.4063714827 | -2.3178521257 | -1.1216630598 |
| H | -0.1447445774 | -2.9007496594 | -0.3795330997 |
| H | -0.3090915296 | -1.7333881889 | -1.7209358677 |
| H | 0.9553267265 | -2.9969115282 | -1.7958557250 |
| C | -3.5760493985 | -1.0418611407 | 0.2507922109 |
| H | -4.2928500586 | -1.8233213930 | 0.4052575116 |
| N | -2.6545159004 | 1.0126966174 | -0.0565437766 |
| H | -2.6065778604 | 1.9816556721 | -0.3193283252 |

(4) *EM* geometry at ground state.

| | | | |
|---|---|---|---|
| C | -0.2528633741 | 0.6315776011 | 0.2397745895 |
| C | -1.4773437466 | 0.0175339273 | 0.1271773688 |
| C | -3.7443394648 | -0.2544042086 | 0.2433041293 |
| C | -1.8411288924 | -1.3041675450 | -0.4973907603 |
| C | 1.0698168018 | 0.0015617782 | 0.1429024801 |
| C | 2.0173933359 | 1.0206492982 | -0.1136258912 |
| C | 1.3586978646 | 2.3626814613 | -0.1878944577 |
| C | -0.0334405608 | 2.1205278681 | 0.4397982625 |
| C | 3.7821814366 | -0.5817290139 | -0.1285543224 |

| | | | |
|---|---|---|---|
| C | 3.3689180610 | 0.7457153600 | -0.2844125322 |
| C | -1.0647445784 | 3.0084708681 | -0.2383390920 |
| O | -1.0843847548 | -2.0277586799 | -1.1426791769 |
| H | 4.8444349783 | -0.8310441452 | -0.2432208565 |
| H | 1.2584830406 | 2.6750220428 | -1.2484373600 |
| H | 1.9295382910 | 3.1310515067 | 0.3686311984 |
| H | -0.0024015377 | 2.3433361446 | 1.5433241485 |
| H | -1.9830085970 | 3.0984443080 | 0.3681609633 |
| H | -1.3266483151 | 2.6051449061 | -1.2244169012 |
| H | -0.6513980314 | 4.0221604482 | -0.3623796357 |
| H | 4.0800915686 | 1.5353168042 | -0.5365536997 |
| C | 2.8730414553 | -1.5769860525 | 0.2230136910 |
| H | 3.2372634079 | -2.5925583905 | 0.4197478380 |
| C | 1.4967644080 | -1.3133400992 | 0.3816196583 |
| H | -4.7778591368 | -0.0005745623 | 0.4866739138 |
| C | 0.6090445575 | -2.4089925006 | 0.8546885945 |
| H | -0.2119434924 | -2.0035375124 | 1.4669276213 |
| H | 0.1866705490 | -2.9267091025 | -0.0119384575 |
| H | 1.1846214302 | -3.1216275618 | 1.4693238600 |
| C | -3.2937859643 | -1.4169938271 | -0.3467982816 |
| H | -3.8762682130 | -2.2601899431 | -0.6603324825 |
| N | -2.7063913289 | 0.6345917810 | 0.4379773588 |
| H | -2.7940795737 | 1.4573616649 | 1.0076894021 |

(5) Four different $S_1$ /$S_0$ CIs for the three-stroke LDMRM DDIY.

*ZCI(1)*

| | | | |
|---|---|---|---|
| C | 0.2732282810 | 0.6018458157 | -0.7314016296 |
| C | 1.6141843364 | 0.2082438660 | -0.7532900973 |
| C | 3.0699455772 | -1.5495358737 | -0.6576926578 |
| C | 1.9769574727 | -0.0382743507 | 0.6927659786 |
| C | -0.9444008209 | -0.0034750013 | -0.1881775168 |
| C | -2.0005386594 | 0.9422771598 | -0.2588917041 |
| C | -1.5509969324 | 2.2406458143 | -0.8642419031 |
| C | -0.0416052700 | 2.0483172450 | -1.0640775747 |
| C | -3.5052604849 | -0.6391884783 | 0.7066462175 |
| C | -3.2831253106 | 0.6365266619 | 0.1785652906 |
| C | 0.7782210042 | 2.9022237310 | -0.1034312460 |
| O | 1.6354917810 | 0.6831617346 | 1.6474289053 |
| H | -4.5081245919 | -0.9031517765 | 1.0673024200 |
| H | -1.7760265954 | 3.0773046686 | -0.1781882845 |

| | | | |
|---|---|---|---|
| H | -2.0717396511 | 2.4046172119 | -1.8281929948 |
| H | 0.2706579387 | 2.2542314341 | -2.1157131336 |
| H | 1.8379027770 | 2.6910423910 | -0.2569051148 |
| H | 0.5223826714 | 2.6646756758 | 0.9345302931 |
| H | 0.5701008571 | 3.9657034997 | -0.3061434432 |
| H | -4.0904461537 | 1.3666787832 | 0.1174041719 |
| C | -2.4797541297 | -1.5814078593 | 0.7856072526 |
| H | -2.6892783355 | -2.5679839974 | 1.2088518288 |
| C | -1.1793540311 | -1.2876316293 | 0.3453548531 |
| H | 3.7634938994 | -2.2886119557 | -1.0422948786 |
| C | -0.1049503529 | -2.3105966011 | 0.4781791735 |
| H | 0.4534380858 | -2.3940544812 | -0.4561002346 |
| H | 0.5682776079 | -1.9957466809 | 1.2796196938 |
| H | -0.5380335052 | -3.2917646685 | 0.7314270202 |
| C | 3.0208572950 | -1.0609730400 | 0.6243067111 |
| H | 3.4916559108 | -1.4716742572 | 1.5072585037 |
| N | 2.1330272903 | -0.9275103158 | -1.4691294377 |
| H | 2.4894515860 | -0.6633139275 | -2.3977022965 |

*ZCI(2)*

| | | | |
|---|---|---|---|
| C | 0.2537939023 | 0.2482710856 | -0.5712551904 |
| C | 1.3568111731 | -0.6276492260 | -0.4488251291 |
| C | 3.5463098107 | -0.7924017087 | -1.1395022050 |
| C | 2.2694682336 | 0.0051239598 | 0.5931742396 |
| C | -1.0691368349 | -0.1529646620 | -0.1556138898 |
| C | -1.9441325600 | 0.9651108874 | -0.1512754206 |
| C | -1.2389613072 | 2.2067079463 | -0.6147038743 |
| C | 0.2000667244 | 1.7415433399 | -0.9033512025 |
| C | -3.6893876821 | -0.4270894034 | 0.6950990350 |
| C | -3.2646248037 | 0.8333036061 | 0.2506328058 |
| C | 1.2235844860 | 2.5496934111 | -0.1322425157 |
| O | 1.8917908945 | 0.4017474212 | 1.7059270914 |
| H | -4.7264613535 | -0.5452830552 | 1.0383294576 |
| H | -1.2642279964 | 2.9655781774 | 0.1896320510 |
| H | -1.7294096962 | 2.6129786828 | -1.5206195637 |
| H | 0.4248929209 | 1.7938025450 | -2.0018762264 |
| H | 2.2340756960 | 2.2054604223 | -0.3819549097 |
| H | 1.0676858478 | 2.4326567549 | 0.9437740697 |
| H | 1.1301728178 | 3.6121368871 | -0.4103704342 |
| H | -3.9495398460 | 1.6813190317 | 0.2416036512 |

| | | | |
|---|---|---|---|
| C | -2.8317595465 | -1.5259883696 | 0.7252312745 |
| H | -3.1986001081 | -2.4859170089 | 1.0965592130 |
| C | -1.4995361000 | -1.4219300116 | 0.2917397360 |
| H | 4.3724363609 | -1.1465157126 | -1.7483304996 |
| C | -0.5587788091 | -2.5733279672 | 0.3076843357 |
| H | -0.7553254853 | -3.1926153208 | -0.5820421407 |
| H | 0.4596461770 | -2.1693126986 | 0.2645943325 |
| H | -0.7274387796 | -3.1818547315 | 1.2078377511 |
| C | 3.6294849743 | -0.2873701440 | 0.1353768941 |
| H | 4.5168769255 | 0.0468887929 | 0.6518324180 |
| N | 2.2335104041 | -0.8661975517 | -1.5718739875 |
| H | 1.9936739720 | -1.7130081830 | -2.1005636238 |

*ECI(1)*

| | | | |
|---|---|---|---|
| C | -0.1869416250 | 0.7022061102 | 0.0481793943 |
| C | -1.5554859397 | 0.4815922237 | -0.0856311629 |
| C | -3.2342182515 | -0.8076937309 | -0.9287870272 |
| C | -1.8487715719 | -0.6255953920 | 0.9044297167 |
| C | 0.9780570701 | -0.1804520099 | -0.0661909103 |
| C | 2.1179340455 | 0.4940718534 | 0.4419351903 |
| C | 1.7852669184 | 1.8824832552 | 0.9084594021 |
| C | 0.2566579343 | 1.9453835956 | 0.7976600305 |
| C | 3.4783280339 | -1.4058366564 | -0.0467323236 |
| C | 3.3714048691 | -0.1053057209 | 0.4558501239 |
| C | -0.2515417462 | 3.1992851810 | 0.1172968182 |
| O | -1.3531826806 | -0.6781527530 | 2.0444530725 |
| H | 4.4562688638 | -1.9047807452 | -0.0395993403 |
| H | 2.2687525379 | 2.6238516743 | 0.2421357974 |
| H | 2.1358393803 | 2.0357485955 | 1.9454425907 |
| H | -0.2191903745 | 1.8304823023 | 1.8032225442 |
| H | -1.3333641743 | 3.1151614984 | -0.0180356296 |
| H | 0.2313403086 | 3.3283584818 | -0.8650669486 |
| H | -0.0254459076 | 4.0770436127 | 0.7404596821 |
| H | 4.2440638927 | 0.4180048834 | 0.8478814754 |
| C | 2.3695976995 | -2.0811643496 | -0.5576216311 |
| H | 2.4904693849 | -3.0989679900 | -0.9400542385 |
| C | 1.0975744192 | -1.4880660234 | -0.5780359341 |
| H | -4.0465784616 | -1.0749292416 | -1.5939137134 |
| C | -0.0695964481 | -2.2506978881 | -1.1038730955 |
| H | 0.2703082625 | -3.1513821399 | -1.6400176837 |

| | | | |
|---|---|---|---|
| H | -0.6937716048 | -2.5489447923 | -0.2572422960 |
| H | -0.6526582359 | -1.6255660829 | -1.7836297643 |
| C | -3.0201437049 | -1.2910729778 | 0.3404320570 |
| H | -3.4668046243 | -2.1642428877 | 0.7966665034 |
| N | -2.2914576770 | 0.1506237100 | -1.2653400025 |
| H | -2.6673335261 | 0.9783657061 | -1.7447149746 |

*ECI(2)*

| | | | |
|---|---|---|---|
| C | -0.2096525352 | 0.4239157833 | -0.0839894233 |
| C | -1.4007473556 | -0.2467471545 | -0.4541746827 |
| C | -3.6370078311 | 0.1814560352 | -0.7573781220 |
| C | -2.1407681408 | -0.4488965577 | 0.8641796835 |
| C | 1.0849378433 | -0.2050799880 | -0.1821842624 |
| C | 2.0636518825 | 0.5981074696 | 0.4613223829 |
| C | 1.4603551591 | 1.8702600795 | 0.9846272485 |
| C | -0.0510981846 | 1.6828276657 | 0.7601779769 |
| C | 3.7094095339 | -1.0654849102 | -0.0150891560 |
| C | 3.3840935848 | 0.1808529629 | 0.5387260639 |
| C | -0.6946086269 | 2.8625901222 | 0.0594192991 |
| O | -1.6180650066 | -0.8589153671 | 1.9114076403 |
| H | 4.7480324750 | -1.4180957314 | 0.0479985045 |
| H | 1.8505329584 | 2.7327963910 | 0.4089001856 |
| H | 1.7056311066 | 2.0005915823 | 2.0551868468 |
| H | -0.5714933462 | 1.4739502583 | 1.7261474689 |
| H | -1.7460139829 | 2.6428076177 | -0.1492729069 |
| H | -0.1776277571 | 3.0745745816 | -0.8894222683 |
| H | -0.6306430320 | 3.7522263005 | 0.7036876801 |
| H | 4.1462608696 | 0.7919926059 | 1.0228747548 |
| C | 2.7527391511 | -1.8706895111 | -0.6339789591 |
| H | 3.0467915458 | -2.8428627566 | -1.0375223637 |
| C | 1.4143263770 | -1.4599098449 | -0.7386531722 |
| H | -4.5472081424 | 0.3583715069 | -1.3202610479 |
| C | 0.3662172710 | -2.2972401849 | -1.3832783968 |
| H | -0.6120674625 | -1.9039629414 | -1.0850998229 |
| H | 0.4883227235 | -2.2275848380 | -2.4758362653 |
| H | 0.4903432590 | -3.3459949145 | -1.0778696537 |
| C | -3.5531590986 | -0.2995056689 | 0.5288908606 |
| H | -4.3477110596 | -0.3832276902 | 1.2535375688 |
| N | -2.3838180658 | 0.3837768857 | -1.3015835066 |
| H | -2.2794052528 | 0.1639977777 | -2.2968099759 |

## 6. Cartesian coordinates for three isomers of Filatov's two-stroke LDMRM DTPN optimized with the CAM-B3LYP/6-31G(d) method

Unit of the Cartesian coordinate below is angstrom.

(1) *EP* geometry at ground state.

| | | | |
|---|---|---|---|
| C | 1.29495100 | -2.07075300 | -0.67219500 |
| C | -0.11258600 | -1.88041700 | -0.04312400 |
| C | -0.30571200 | -0.36080900 | 0.01465300 |
| H | 1.22670000 | -2.27033300 | -1.74859600 |
| H | 1.83984300 | -2.90634000 | -0.22138800 |
| H | -0.89210200 | -2.33619200 | -0.65271400 |
| C | -1.50479900 | 0.24471200 | -0.00508800 |
| C | -0.18666700 | -2.49575100 | 1.35787800 |
| H | 0.56276400 | -2.05251700 | 2.02288700 |
| C | -1.83162500 | 1.71757200 | -0.09693400 |
| C | -3.28344000 | 1.74854000 | -0.61740600 |
| N | -3.78087800 | 0.43884300 | -0.24713200 |
| C | -2.79955000 | -0.49594600 | -0.04054000 |
| O | -3.00606700 | -1.69257600 | 0.09097100 |
| C | 3.04389200 | 1.37393200 | 0.09575900 |
| S | 3.54542900 | -0.18744300 | -0.47243900 |
| C | 1.92691700 | -0.74497700 | -0.40432300 |
| C | 1.04717200 | 0.22390900 | -0.00212800 |
| C | 1.70362000 | 1.47158700 | 0.31617700 |
| H | 3.78485400 | 2.14274300 | 0.26952800 |
| H | -1.17974800 | -2.33781800 | 1.78129500 |
| H | -0.00400200 | -3.57426700 | 1.30905400 |
| C | 1.08941000 | 2.71178000 | 0.90108100 |
| H | 0.42096100 | 2.46846900 | 1.73198200 |
| H | 1.86984100 | 3.37367800 | 1.28486500 |
| H | 0.50994200 | 3.27961500 | 0.16815800 |
| H | -4.71317600 | 0.12002700 | -0.46628400 |
| H | -3.87324300 | 2.54455700 | -0.15446200 |
| H | -3.31066400 | 1.89648700 | -1.70554500 |
| H | -1.78427300 | 2.20095700 | 0.88453500 |
| H | -1.15937000 | 2.25846200 | -0.76501000 |

(2) *ZP* geometry at ground state.

| | | | |
|---|---|---|---|
| C | -1.50826600 | 2.04532900 | -0.74478500 |
| C | -0.11165300 | 2.07012200 | -0.06460500 |
| C | 0.31212300 | 0.59838300 | -0.03996300 |
| H | -1.42198000 | 2.21430500 | -1.82497400 |
| H | -2.17967300 | 2.81249400 | -0.34562800 |
| H | 0.59572100 | 2.66235600 | -0.65309800 |
| C | 1.60491900 | 0.24665300 | -0.12567500 |
| C | -0.19976800 | 2.65712200 | 1.34849300 |
| H | -0.93369800 | 2.10704600 | 1.94571200 |
| C | 2.77301800 | 1.21274300 | -0.10726700 |
| C | 3.99442700 | 0.31180800 | 0.16112300 |
| N | 3.53087500 | -0.98069500 | -0.29753600 |
| C | 2.17026200 | -1.10574300 | -0.39290100 |
| O | 1.59423800 | -2.13093800 | -0.71368700 |
| C | -2.77052900 | -1.55228600 | 0.23233300 |
| S | -3.48326300 | -0.10892800 | -0.42103500 |
| C | -1.95009000 | 0.65136200 | -0.43497900 |
| C | -0.94153000 | -0.17542000 | -0.01400900 |
| C | -1.42373700 | -1.46861000 | 0.41658100 |
| H | -3.40402400 | -2.39390300 | 0.47759500 |
| H | 0.76222900 | 2.60167500 | 1.86634500 |
| H | -0.50623000 | 3.70746900 | 1.31246500 |
| C | -0.64155400 | -2.55806700 | 1.08676200 |
| H | 0.00284900 | -2.14507600 | 1.87024300 |
| H | -1.32000000 | -3.27810600 | 1.55249100 |
| H | 0.01129700 | -3.07032700 | 0.38131000 |
| H | 4.11603300 | -1.79764200 | -0.38301100 |
| H | 4.88099000 | 0.63605800 | -0.39100300 |
| H | 4.24883300 | 0.29506800 | 1.22960000 |
| H | 2.88533600 | 1.70530400 | -1.08161800 |
| H | 2.67877200 | 1.99812200 | 0.64574300 |

(3) *ZM* geometry at ground state.

| | | | |
|---|---|---|---|
| C | 1.57204600 | 2.15808300 | -0.21544200 |
| C | 0.14131800 | 2.07999100 | 0.39055800 |
| C | -0.28036900 | 0.61834200 | 0.15487800 |
| H | 2.21981700 | 2.84600700 | 0.33663900 |
| H | 1.52069000 | 2.51911200 | -1.25112900 |
| H | 0.24342100 | 2.22395200 | 1.47544900 |
| C | -1.55133400 | 0.19648600 | 0.02850500 |

| | | | |
|---|---|---|---|
| C | -0.75076000 | 3.18111000 | -0.17617900 |
| H | -0.98563000 | 2.99054900 | -1.22844000 |
| C | -2.82223800 | 0.95439500 | 0.36011700 |
| C | -3.87697400 | -0.16020700 | 0.51133300 |
| N | -3.32882000 | -1.21325600 | -0.31566200 |
| C | -1.98272800 | -1.11187400 | -0.54609600 |
| O | -1.32799100 | -1.91825600 | -1.18375500 |
| C | 2.80290500 | -1.54937900 | 0.18447400 |
| S | 3.54137000 | -0.01841900 | -0.17231500 |
| C | 2.00591200 | 0.73531400 | -0.14467900 |
| C | 0.97988200 | -0.14469000 | 0.06890500 |
| C | 1.44747700 | -1.49406600 | 0.30370400 |
| H | 3.42707000 | -2.42225300 | 0.31956400 |
| H | -1.68859500 | 3.29552200 | 0.36856500 |
| H | -0.22551000 | 4.14032300 | -0.12055800 |
| C | 0.64448700 | -2.68193000 | 0.74379100 |
| H | 0.09903600 | -3.12590900 | -0.08854400 |
| H | 1.29952900 | -3.43301400 | 1.19389100 |
| H | -0.09988300 | -2.39129000 | 1.49269700 |
| H | -3.82314500 | -2.05267600 | -0.57607100 |
| H | -3.97547800 | -0.47485400 | 1.55941700 |
| H | -4.86369100 | 0.15185000 | 0.15830700 |
| H | -2.74250100 | 1.55382200 | 1.26937500 |
| H | -3.11913700 | 1.62296300 | -0.45566100 |

## 7. References

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