

**Multi-state nonadiabatic deactivation mechanism of coumarin revealed by  
ab initio on-the-fly trajectory surface hopping dynamic simulation**

**Supporting Information**

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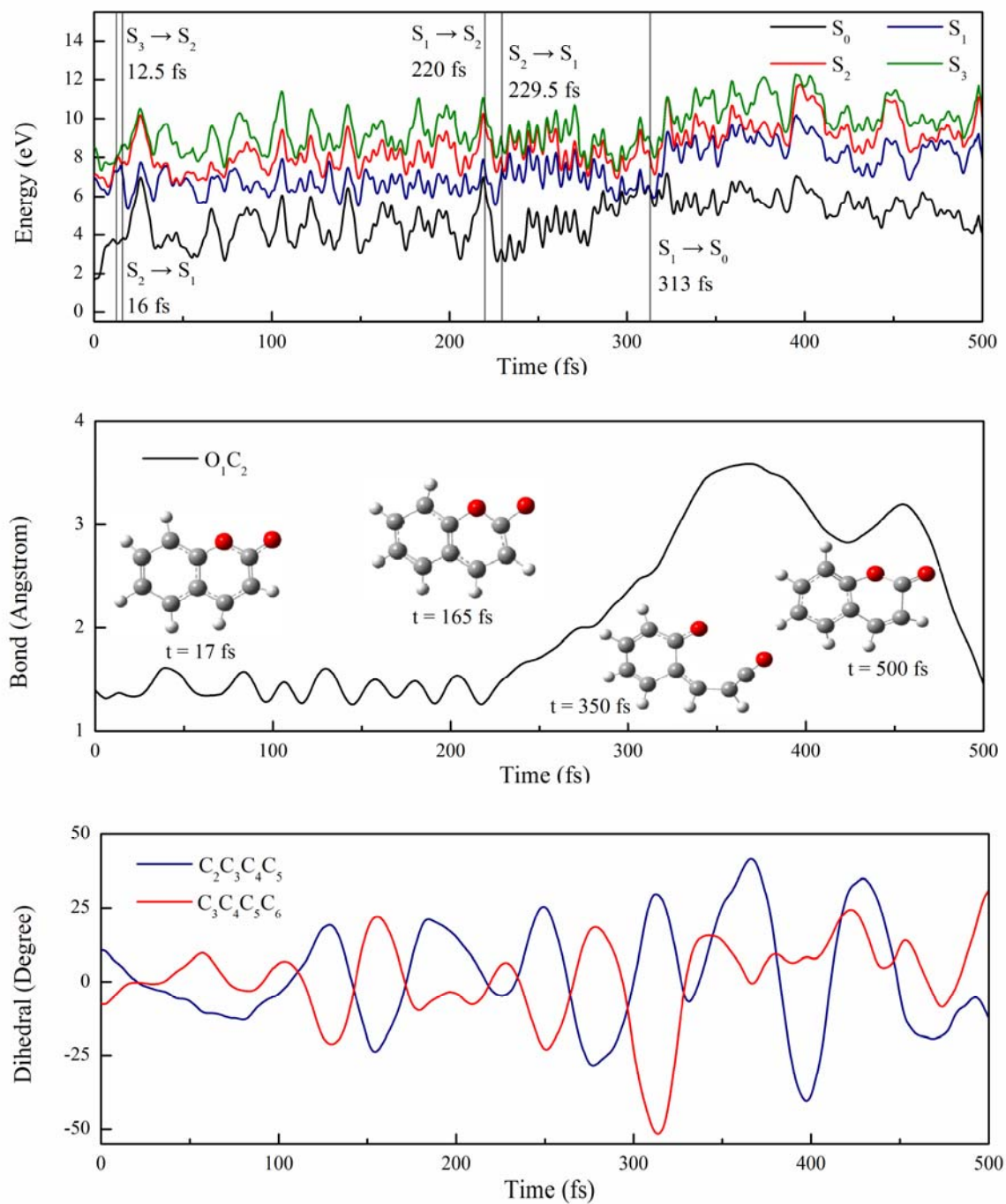
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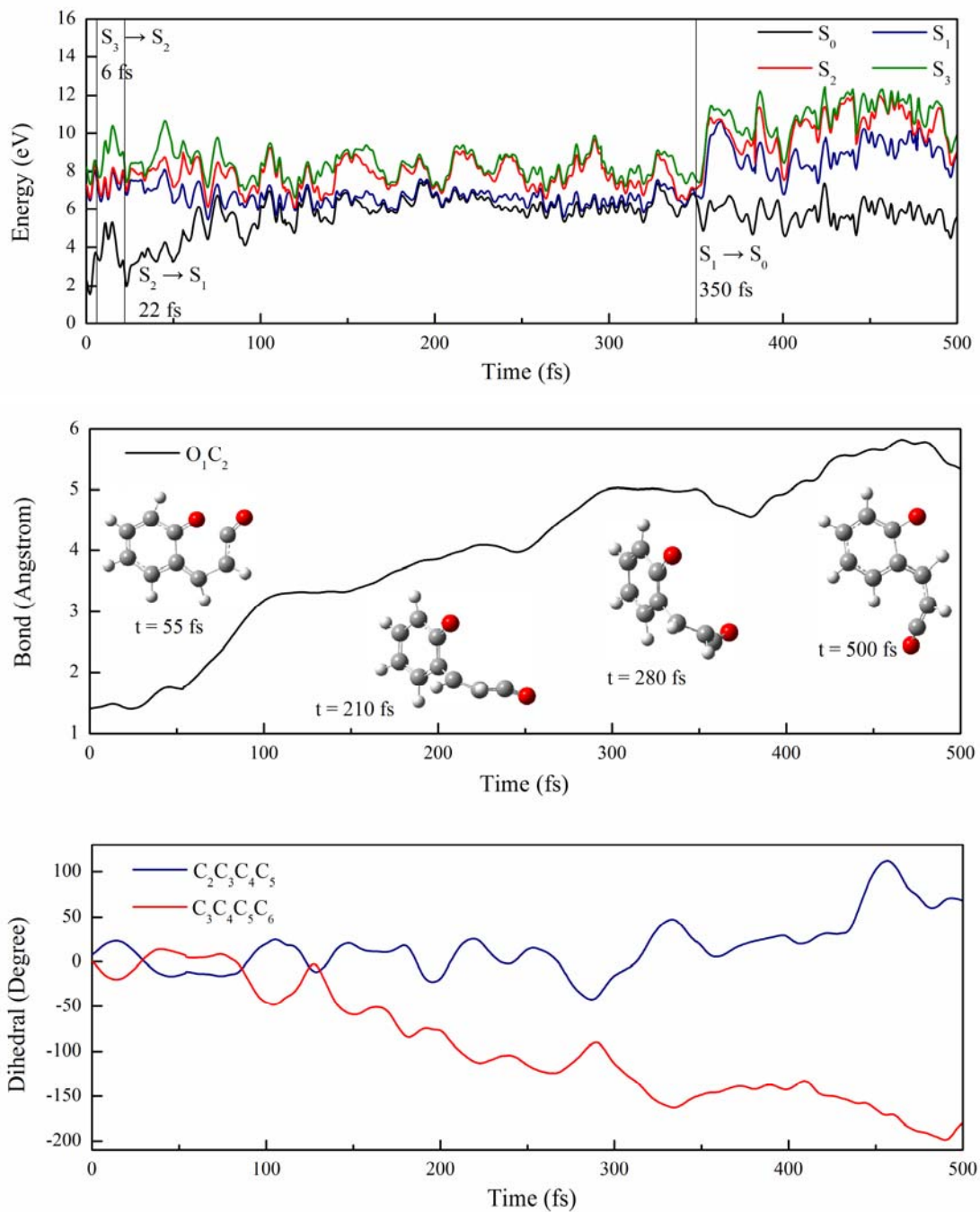
**Table S1.** Comparison of MP2, B3LYP, and CASSCF (12, 10) geometry optimizations with experimental crystal data for ground state of coumarin (bond lengths in Angstroms and bond angles in Degrees).

	MP2	B3LYP	CASSCF(12,10)	Expt. <sup>a</sup>
O <sub>1</sub> -C <sub>2</sub>	1.396	1.398	1.366	1.374
O <sub>1</sub> -C <sub>6</sub>	1.375	1.365	1.355	1.378
C <sub>2</sub> -C <sub>3</sub>	1.462	1.460	1.468	1.454
C <sub>2</sub> =O <sub>11</sub>	1.217	1.208	1.186	1.213
C <sub>3</sub> =C <sub>4</sub>	1.355	1.352	1.344	1.347
C <sub>4</sub> -C <sub>5</sub>	1.442	1.442	1.440	1.438
C <sub>5</sub> =C <sub>6</sub>	1.405	1.409	1.383	1.397
C <sub>5</sub> -C <sub>10</sub>	1.408	1.407	1.406	1.405
C <sub>6</sub> -C <sub>7</sub>	1.398	1.396	1.394	1.394
C <sub>7</sub> =C <sub>8</sub>	1.392	1.391	1.372	1.383
C <sub>8</sub> -C <sub>9</sub>	1.405	1.403	1.405	1.397
C <sub>9</sub> =C <sub>10</sub>	1.390	1.388	1.384	1.380
C <sub>2</sub> -O <sub>1</sub> -C <sub>6</sub>	122.1	122.8	123.5	121.9
O <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	116.3	115.9	115.9	117.4
O <sub>1</sub> -C <sub>2</sub> =O <sub>11</sub>	118.2	117.9	119.0	116.8
C <sub>2</sub> -C <sub>3</sub> =C <sub>4</sub>	121.9	121.7	121.2	121.4
C <sub>3</sub> =C <sub>4</sub> -C <sub>5</sub>	120.4	120.8	120.4	120.1
C <sub>4</sub> -C <sub>5</sub> =C <sub>6</sub>	117.5	117.3	117.6	118.1
O <sub>1</sub> -C <sub>6</sub> =C <sub>5</sub>	121.8	121.4	121.4	121.1

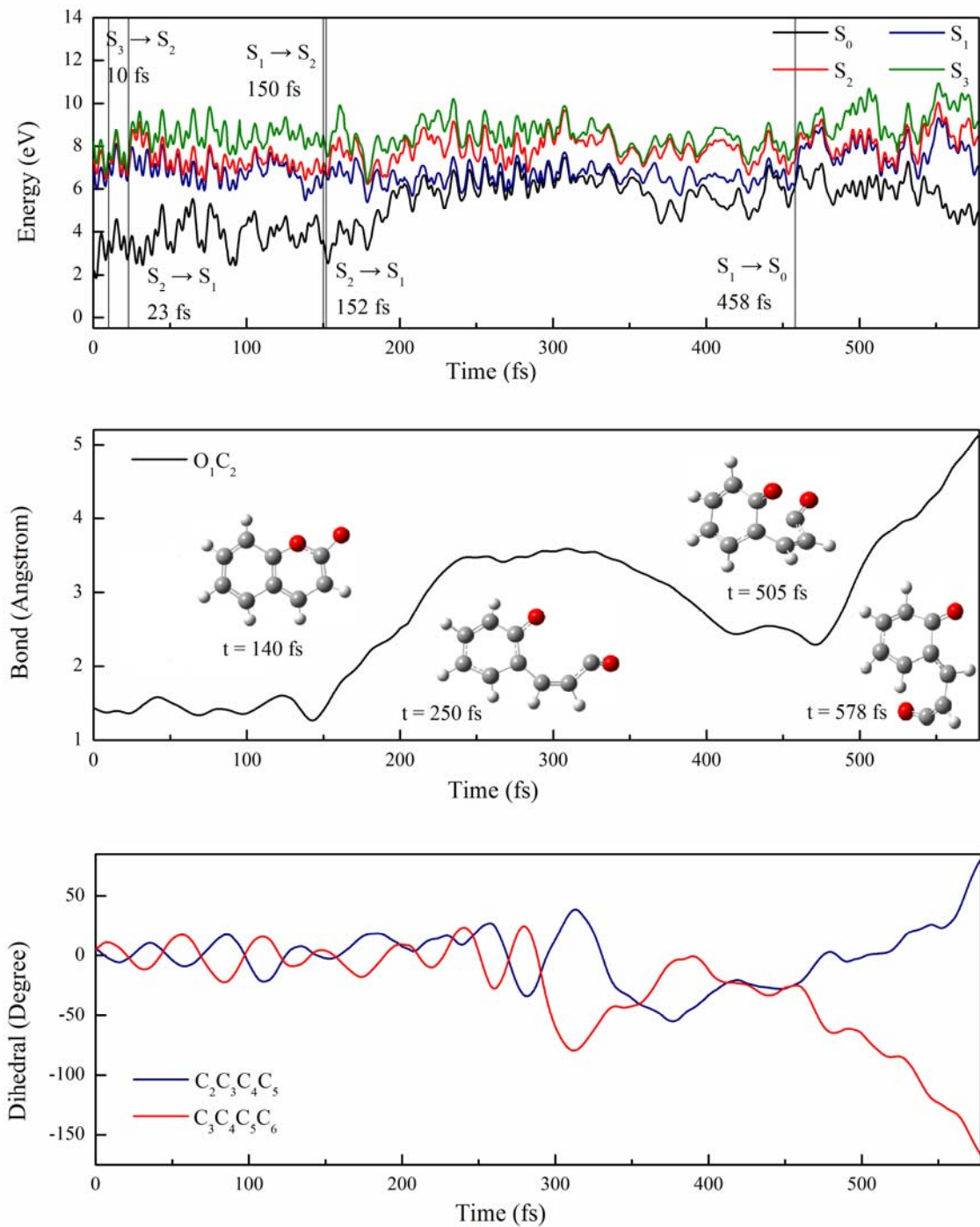
<sup>a</sup> X-ray structure from Ref. 24.



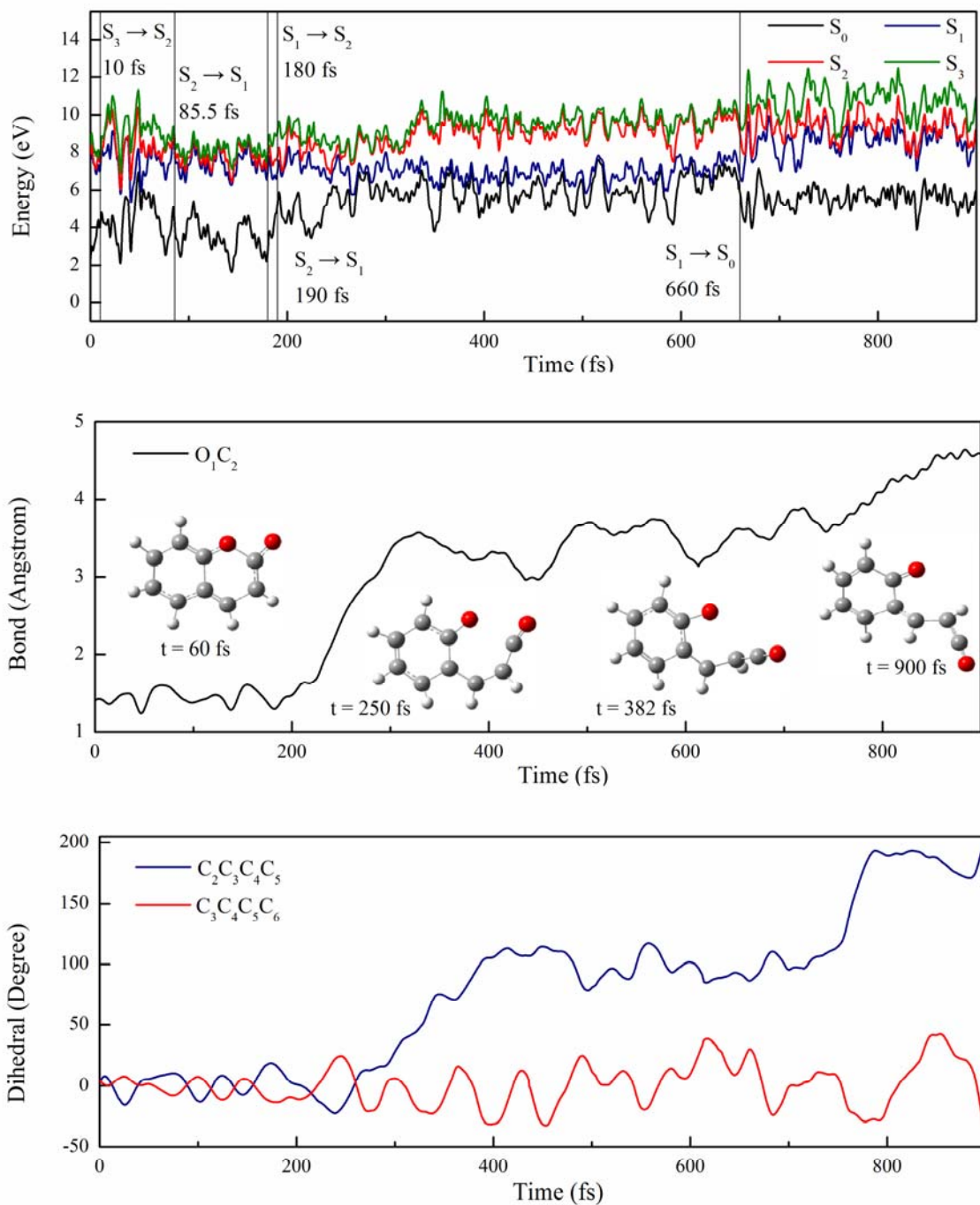
**Fig. S1** Trajectory has ring opening reaction on ground state, but close again. The upper panel is for potential energy profiles against the time, the middle panel is evolution for bond length  $O_1C_2$  and the bottom panel is for two dihedrals  $C_2C_3C_4C_5$  and  $C_3C_4C_5C_6$  (see Fig.6).



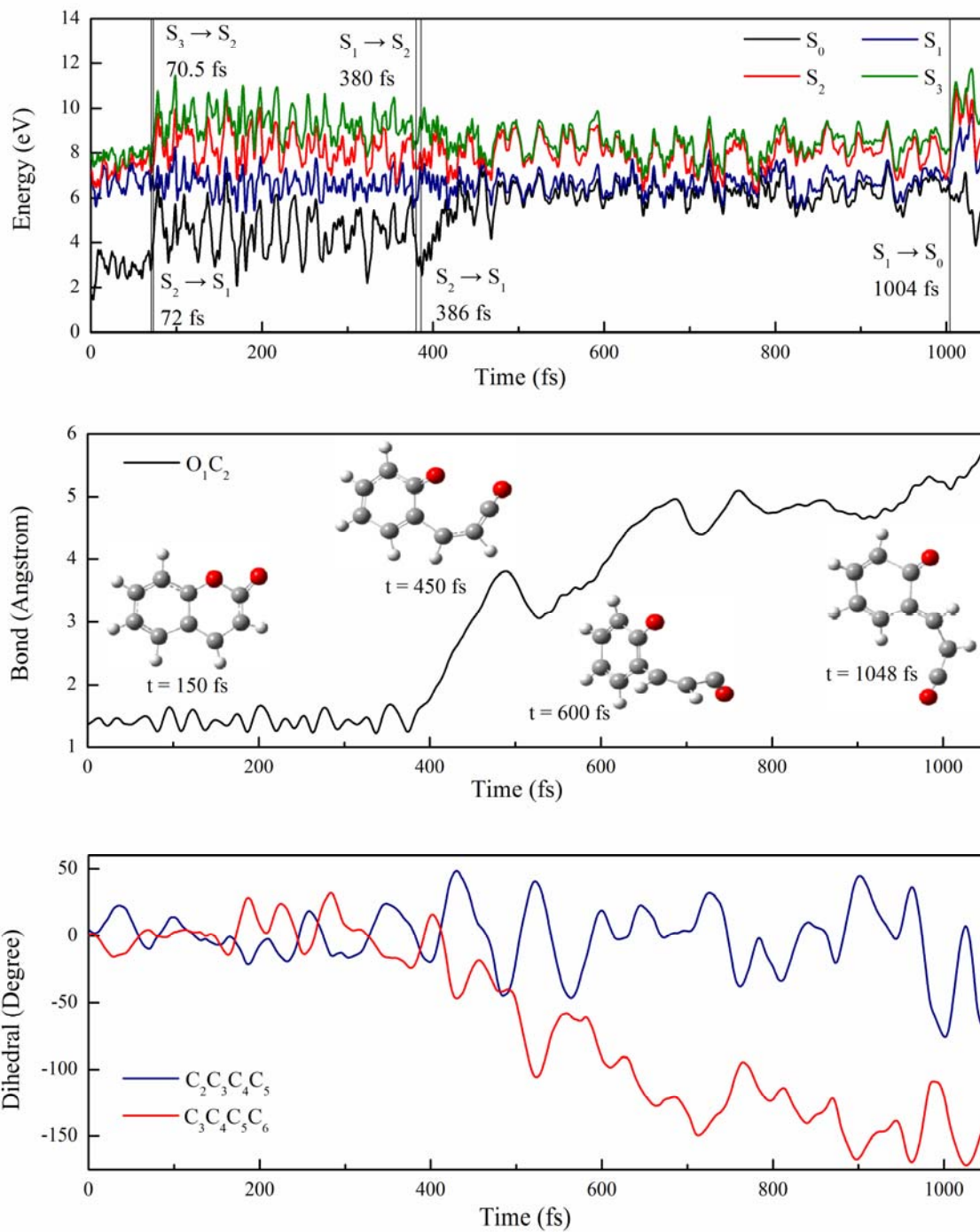
**Fig. S2** The same as Fig. S1 except for the trajectory to evolve  $S_3(\pi\pi^*L_b) \rightarrow S_3/S_2 \rightarrow S_2/S_1 \rightarrow S_1(\pi\pi^*L_a)/S_0 \rightarrow S_0 \rightarrow TS_0(E) \rightarrow S_0(E)$  (see Fig.6).



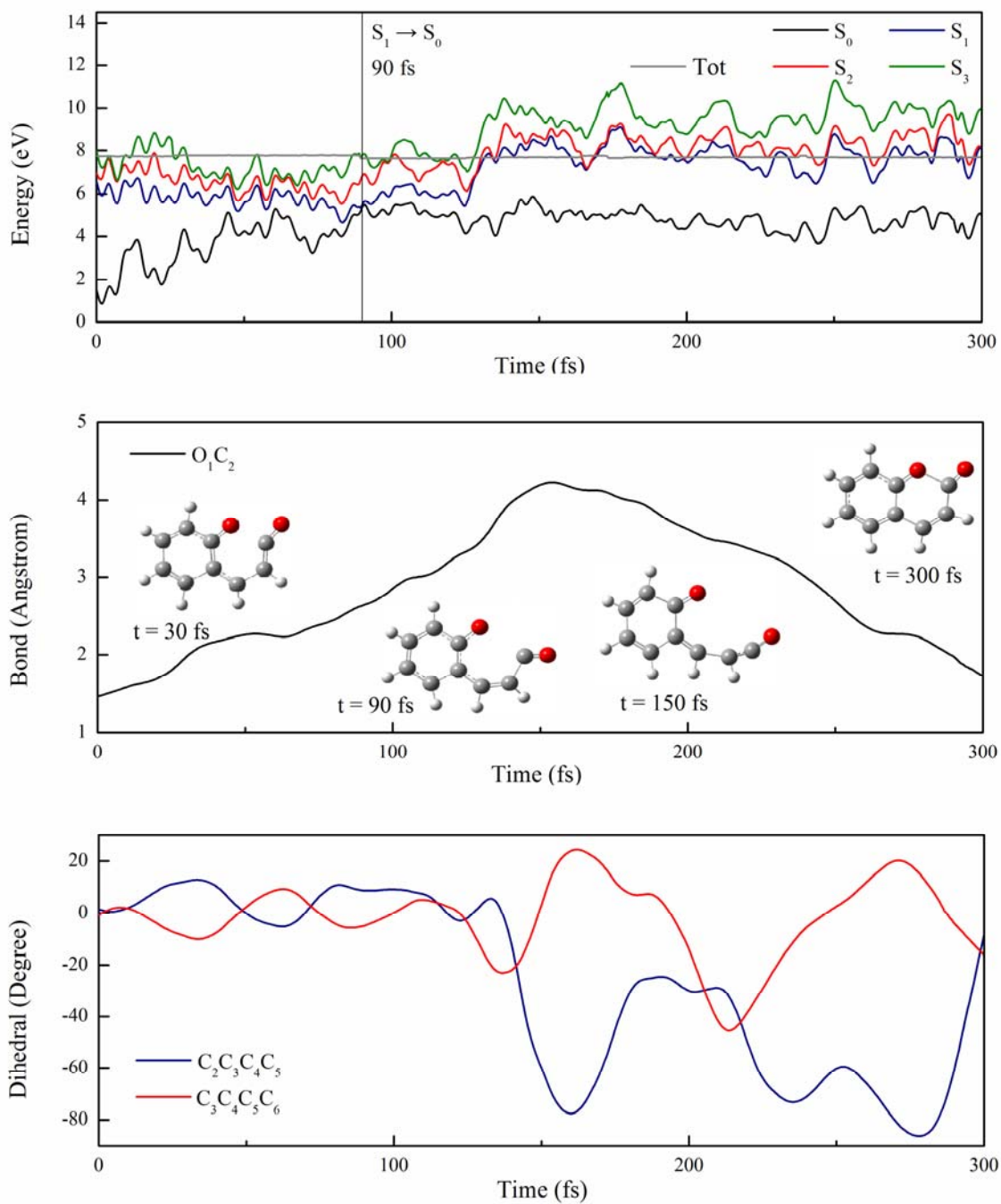
**Fig. S3** The same as Fig. S1 except for the trajectory to evolve  $S_3(\pi\pi^*L_b) \rightarrow S_3/S_2 \rightarrow S_2/S_1 \rightarrow S_1(\pi\pi^*L_a)/S_0 \rightarrow S_0 \rightarrow TS_0(E) \rightarrow S_0(E)$  (see Fig.6).



**Fig. S4** The same as Fig. S1 except for the trajectory to evolve  $S_3(\pi\pi^*L_b) \rightarrow S_3/S_2 \rightarrow S_2/S_1 \rightarrow S_1(\pi\pi^*L_a) \rightarrow TS_1(Z) \rightarrow S_1(Z) \rightarrow S_1(Z)/S_0(Z) \rightarrow S_0(Z)$  (see Fig.6).



**Fig. S5** The same as Fig. S1 except for the trajectory to evolve  $S_3(\pi\pi^*L_b) \rightarrow S_3/S_2 \rightarrow S_2/S_1 \rightarrow S_1(\pi\pi^*L_a) \rightarrow TS_1(E) \rightarrow S_1(E) \rightarrow S_1(E)/S_0(E) \rightarrow S_0(E)$  (see Fig.6).



**Fig. S6** The same as Fig. S1 except for the trajectory starting from  $S_1(\pi\pi^*L_a)$  state to evolve  $S_1(\pi\pi^*L_a) \rightarrow S_1(\pi\pi^*L_a)/S_0 \rightarrow S_0$ .



Table S2. Cartesian coordinates (in angstrom) of all geometries optimized at the SA4-CASSCF (12, 10) /6-31G\* level.

Table S1.1:  $(S_0)_{\min}$

	X	Y	Z
C	-2.85367460	0.37016600	0.00033860
C	-1.80119750	1.26856450	0.00032090
C	-0.47302070	0.80637460	-0.00015950
C	-0.24136750	-0.55745030	-0.00041790
C	-1.29370060	-1.47119330	-0.00050720
C	-2.58509590	-1.00860120	-0.00018000
H	0.52092600	2.74208550	-0.00008500
H	-3.86835730	0.72226810	0.00079120
H	-1.98662610	2.32765530	0.00068210
C	0.67376680	1.67775580	-0.00020330
H	-1.06889550	-2.52098450	-0.00103510
H	-3.39941280	-1.70999650	-0.00027290
C	2.14040330	-0.28444050	0.00038740
C	1.91634370	1.16610220	-0.00006960
H	2.79832220	1.77495850	0.00041260
O	1.01703260	-1.06076860	-0.00088450
O	3.20350990	-0.81065660	0.00135320

Table S1.2:  $TS_0$  (Z)

	X	Y	Z
C	-2.70827060	-0.97733390	0.33825300
C	-1.46396070	-1.46439430	0.09982630
C	-0.32276060	-0.58554010	-0.17954890
C	-0.59295780	0.88859460	-0.20002380
C	-1.98173600	1.33929850	0.10406540
C	-2.95371600	0.48151610	0.34733840
H	0.91167550	-2.23699950	-0.44690870
H	-3.52984440	-1.64151420	0.53164800
H	-1.29099350	-2.52518170	0.09517610
C	0.88779630	-1.15887250	-0.45179600
H	-2.13465380	2.40252030	0.10051530
H	-3.95053880	0.82710210	0.55706670
C	2.96894910	-0.06476530	0.17818230
C	2.17848710	-0.49208650	-0.76469230
H	2.49283410	-0.34595560	-1.78022280
O	0.25155440	1.71187900	-0.48052480
O	3.64654480	0.28473900	1.05554470

Table S1.3: TS<sub>0</sub>(E)

	X	Y	Z
C	-2.26638320	0.58540530	-0.64719610
C	-1.18422570	1.21337740	-0.05841030
C	-0.27331430	0.52342220	0.71462250
C	-0.45793040	-0.92808130	0.93078230
C	-1.62060160	-1.55106130	0.28028720
C	-2.48485940	-0.81080910	-0.47690990
C	0.90160310	1.18663980	1.31844470
C	2.41804430	0.65180440	-0.52950030
C	2.17433860	1.16920290	0.68436390
O	0.30518230	-1.57390230	1.60484690
O	2.67645670	0.22652880	-1.59164310
H	0.84839570	1.52646280	2.33438170
H	-2.95058810	1.15695650	-1.24645430
H	-1.04131940	2.26824810	-0.21163850
H	-1.74604750	-2.60627610	0.43172450
H	-3.33082890	-1.27375800	-0.95054940
H	3.03785080	1.58017230	1.17390580

Table S1.4: S<sub>0</sub>(Z)

	X	Y	Z
C	-2.79685470	0.45274490	0.00003010
C	-1.71883330	1.25758820	0.00181310
C	-0.34292200	0.72589650	0.00226260
C	-0.19342120	-0.77034450	0.00066970
C	-1.43981690	-1.57681640	-0.00123510
C	-2.63645570	-1.01100570	-0.00156050
H	0.44525700	2.62753670	0.00521360
H	-3.78955560	0.86340450	-0.00024760
H	-1.83856150	2.32661090	0.00296970
C	0.68326920	1.57632200	0.00424520
H	-1.30706660	-2.64298390	-0.00238900
H	-3.52422110	-1.61865470	-0.00300740
C	3.01767640	2.21396000	0.00696720
C	2.09795880	1.25755920	0.00479080
H	2.44910050	0.24808820	0.00345090
O	0.89176640	-1.33107960	0.00088060
O	3.82661600	3.03933470	0.00887890

Table S1.5:  $S_0$  (E)

	X	Y	Z
C	-2.90582800	0.30449360	0.00346100
C	-1.88465690	1.19588190	0.00482720
C	-0.48891540	0.76184320	0.00210440
C	-0.22651050	-0.70926170	0.00028990
C	-1.40607420	-1.61921690	-0.00192640
C	-2.63883520	-1.14894480	-0.00078690
H	1.55103240	1.11277290	0.00163890
H	-3.92524850	0.64231960	0.00617230
H	-2.11367660	2.24352770	0.00912290
C	0.59289550	1.59510120	0.00131660
H	-1.18725160	-2.67100950	-0.00455240
H	-3.48099740	-1.81811840	-0.00253380
C	-0.28094790	3.94086590	-0.02149770
C	0.68750150	3.05462640	0.00033670
H	1.66714990	3.49336820	0.01703720
O	0.89514250	-1.17235980	0.00006580
O	-1.09728940	4.75820920	-0.04064220

Table S1.6:  $S_1(\pi\pi^*L_a)_{\min}$ 

	X	Y	Z
C	-2.85424740	0.46080290	-0.04973160
C	-1.71892980	1.17835950	-0.00881600
C	-0.42275640	0.55848460	0.05674030
C	-0.37377440	-0.89799550	0.10230180
C	-1.64535430	-1.62617270	0.03213800
C	-2.81388790	-0.98340430	-0.03500600
H	0.42806860	2.48034080	0.07956780
H	-3.80635780	0.95721690	-0.09871750
H	-1.76545010	2.25234050	-0.02743990
C	0.71585490	1.44309610	0.05837980
H	-1.57744490	-2.69785410	0.05803550
H	-3.73841880	-1.53116100	-0.07746390
C	2.83138560	0.02907840	-0.08382590
C	2.07522660	1.26464180	-0.00323360
H	2.67700120	2.16039370	0.01115900
O	0.67945900	-1.52844330	0.21960460
O	4.00858190	-0.08788530	-0.23322140

Table S1.7: TS<sub>1</sub> (Z)

	X	Y	Z
C	-2.73853680	-0.94741430	0.35698290
C	-1.49197580	-1.44555400	0.10294530
C	-0.38921050	-0.60949120	-0.18826440
C	-0.66595960	0.77735860	-0.21399070
C	-1.92699660	1.30101490	0.03179700
C	-2.97563180	0.43767080	0.32553130
H	0.97988930	-2.25139000	-0.41214370
H	-3.54551650	-1.62329640	0.58423080
H	-1.32630860	-2.50904080	0.13288370
C	0.90827940	-1.17848510	-0.42262500
H	-2.06911560	2.36608480	0.01375470
H	-3.95369070	0.82826840	0.53523750
C	2.95768950	-0.03681670	0.19382450
C	2.12137980	-0.39616690	-0.75168100
H	2.39832650	-0.12411120	-1.75266550
O	0.38074650	1.69638210	-0.43633820
O	3.67931670	0.26954240	1.02520030

Table S1.8: TS<sub>1</sub> (E)

	X	Y	Z
C	-2.23069850	0.58020550	-0.68463800
C	-1.16926200	1.23327710	-0.06051740
C	-0.28885080	0.49663850	0.73419010
C	-0.51468290	-0.85827840	0.92030160
C	-1.56067670	-1.52871930	0.28902940
C	-2.40804990	-0.79343370	-0.51315390
C	0.95724930	0.97270560	1.40254330
C	2.32690050	0.66587670	-0.57383950
C	2.19845470	1.08004850	0.67028080
O	0.35205900	-1.46148720	1.75106220
O	2.39378830	0.39660950	-1.68750160
H	0.89533070	1.50503540	2.32941540
H	-2.90607850	1.13169640	-1.31139340
H	-1.01862300	2.28898150	-0.20090260
H	-1.69593220	-2.58517020	0.43221500
H	-3.21593270	-1.29009640	-1.02124950
H	3.08052090	1.49519310	1.12302900

Table S1.9:  $S_1$  (Z)

	X	Y	Z
C	-2.82192220	0.40751920	-0.00043770
C	-1.71925040	1.20337080	0.00128990
C	-0.39443350	0.67610070	0.00204120
C	-0.30382190	-0.71271110	0.00105450
C	-1.43209050	-1.54612900	-0.00083370
C	-2.67896790	-0.99330370	-0.00159300
H	0.45494680	2.64518950	0.00677130
H	-3.80292200	0.84627630	-0.00087530
H	-1.83436780	2.27262870	0.00216460
C	0.71798310	1.60412400	0.00417180
H	-1.29144680	-2.61131080	-0.00144610
H	-3.54708060	-1.62641960	-0.00301960
C	3.06885290	2.21996490	0.00742300
C	2.11222070	1.28440720	0.00388110
H	2.47976070	0.27864120	0.00130330
O	0.91140960	-1.33936040	0.00205230
O	3.90506560	3.02917300	0.00978530

Table S1.10:  $S_1$  (E)

	X	Y	Z
C	-2.80236560	0.15866570	0.44885850
C	-1.74260120	1.03803240	0.59200530
C	-0.41916110	0.67591220	0.23738210
C	-0.26569460	-0.63470200	-0.27011050
C	-1.31788260	-1.52106720	-0.41503110
C	-2.58616130	-1.12986070	-0.05908690
H	1.69976360	1.09550500	0.25072030
H	-3.79174980	0.46523640	0.73409480
H	-1.93106170	2.00895710	1.00680910
C	0.72987970	1.53056540	0.38289550
H	-1.12842020	-2.50245220	-0.80981080
H	-3.40749490	-1.81325780	-0.17156950
C	-0.23648960	3.81247310	0.53258450
C	0.74437080	2.95165340	0.68421560
H	1.66356420	3.39762970	1.01495870
O	0.98064330	-1.06249700	-0.65210610
O	-1.08484530	4.59560580	0.43034360

Table S1.11:  $S_1(n\pi^*)_{\min}$ 

	X	Y	Z
C	2.84688060	0.34040790	-0.00011380
C	1.82860130	1.24407190	0.00017390
C	0.47177830	0.82577900	0.00042640
C	0.23976950	-0.54655510	0.00021280
C	1.28183950	-1.48279630	-0.00007880
C	2.57293400	-1.04254240	-0.00015840
H	-0.49369940	2.79418410	-0.00015010
H	3.86685610	0.67972290	-0.00031330
H	2.03841620	2.29887330	0.00024710
C	-0.64250010	1.73357930	0.00068300
H	1.03823770	-2.52879470	-0.00002650
H	3.38203140	-1.74960780	-0.00027120
C	-2.06809650	-0.18315160	-0.00022620
C	-1.94898010	1.16470510	0.00009110
H	-2.83517660	1.76872510	-0.00065930
O	-1.03077080	-1.07448030	0.00047270
O	-3.23678510	-0.86673740	-0.00068830

Table S1.12:  $S_3(\pi\pi^*L_b)_{\min}$ 

	X	Y	Z
C	-2.87159320	0.39380390	-0.00000030
C	-1.82918460	1.31706510	0.00023950
C	-0.45112810	0.88118420	0.00019510
C	-0.21149550	-0.58953930	-0.00009570
C	-1.28452260	-1.48091200	-0.00031040
C	-2.56921150	-1.03275780	-0.00027360
H	0.49428840	2.75661750	0.00057240
H	-3.89081360	0.72670840	0.00001280
H	-2.02922450	2.37277400	0.00044430
C	0.60978300	1.68745360	0.00035540
H	-1.06521740	-2.53276850	-0.00048270
H	-3.38140460	-1.73443860	-0.00046090
C	2.14352160	-0.26898250	0.00001940
C	1.95064180	1.12250420	0.00026740
H	2.82021660	1.74527750	0.00014150
O	1.04097290	-1.08901550	0.00000000
O	3.22332720	-0.84313500	-0.00015330

Table S1.13:  $S_3(\pi\pi^*L_b)/S_2(\pi\pi^*L_a)$ 

	X	Y	Z
C	-2.87721350	0.41612949	-0.00009631
C	-1.83255491	1.32041113	0.00104410
C	-0.46135247	0.88024605	0.00109719
C	-0.20766480	-0.61104546	0.00178064
C	-1.27626267	-1.48672159	-0.00050966
C	-2.56305640	-1.03019893	-0.00134694
H	0.48244516	2.75222354	0.00020176
H	-3.89696996	0.74443404	-0.00013163
H	-2.01931817	2.37968266	0.00171822
C	0.59395568	1.68205513	0.00020917
H	-1.07067978	-2.54171931	-0.00137074
H	-3.37606406	-1.73095000	-0.00295220
C	2.14402992	-0.27929082	0.00075406
C	1.94609311	1.11806860	-0.00061662
H	2.81280460	1.74418221	-0.00261039
O	1.06148245	-1.10813342	0.00523799
O	3.23928170	-0.81753412	-0.00193774

Table S1.14:  $S_3(\pi\pi^*L_b)/S_2(n\pi^*)$ 

	X	Y	Z
C	-2.86598350	0.38334090	-0.00034490
C	-1.81574500	1.33067750	-0.00098310
C	-0.42116000	0.90082300	-0.00079140
C	-0.17079100	-0.59305190	-0.00132400
C	-1.26557630	-1.49180250	0.00033880
C	-2.53694550	-1.04583140	0.00082470
H	0.49447080	2.78022620	0.00152380
H	-3.88817340	0.70314460	-0.00051630
H	-2.02220910	2.38426770	-0.00116680
C	0.61841130	1.71177130	0.00061900
H	-1.04767630	-2.54400660	0.00091310
H	-3.34597060	-1.75216550	0.00205010
C	2.20249490	-0.24956990	-0.00094640
C	1.96436070	1.16118890	0.00146930
H	2.82899140	1.79125440	0.00377610
O	1.07025500	-1.10118850	-0.00409060
O	3.27097080	-0.78201290	-0.00086570

Table S1.15:  $S_2(n\pi^*)/S_1(\pi\pi^*L_a)$ 

	X	Y	Z
C	2.84426390	0.36728970	0.00035150
C	1.84511420	1.25981920	0.00017200
C	0.46010700	0.83865110	-0.00050520
C	0.21368070	-0.58120970	-0.00034370
C	1.30249240	-1.50985750	-0.00026090
C	2.56596860	-1.05186180	-0.00002560
H	-0.46226380	2.77348550	0.00002530
H	3.86752210	0.69460190	0.00085340
H	2.04759230	2.31538140	0.00051270
C	-0.61692950	1.71244650	-0.00101680
H	1.07058820	-2.55802650	-0.00078490
H	3.38853900	-1.74300480	-0.00020090
C	-2.21104500	-0.16451370	0.00008600
C	-1.97421820	1.17198340	-0.00053780
H	-2.82371780	1.82423110	0.00109670
O	-0.98411230	-1.09154760	-0.00119240
O	-3.22224550	-0.88248570	0.00139190

Table S1.16:  $S_1(\pi\pi^*L_a)/S_0$ 

	X	Y	Z
C	-2.86240270	0.45540380	-0.11075890
C	-1.70488110	1.19424470	-0.03347580
C	-0.42287370	0.58321020	0.08378750
C	-0.36879090	-0.90354490	0.22251410
C	-1.64695330	-1.63561620	0.08808130
C	-2.80508600	-1.00117150	-0.05994550
H	0.44846820	2.48771330	0.19880230
H	-3.81336400	0.94164350	-0.21666300
H	-1.75953120	2.26660470	-0.08519950
C	0.71973800	1.44898950	0.11147190
H	-1.57493190	-2.70547150	0.14258130
H	-3.72440400	-1.55347390	-0.13844790
C	2.81840220	0.03771570	-0.24257370
C	2.07831890	1.25856930	0.00006440
H	2.69622370	2.13800830	0.06731040
O	0.64648300	-1.49313900	0.46349070
O	3.97454070	-0.08784680	-0.49056850



Table S1.17:  $S_1(n\pi^*)/S_0$ 

	X	Y	Z
C	2.85517641	0.32398644	-0.03116405
C	1.87711523	1.26395175	0.02318275
C	0.49796974	0.89888467	0.00738420
C	0.22648740	-0.47122445	-0.02017171
C	1.23278160	-1.45241184	-0.07971927
C	2.53158511	-1.05453174	-0.09237464
H	-0.54828923	2.66914982	0.73881310
H	3.88814825	0.62236663	-0.02967227
H	2.12573913	2.30963728	0.06668298
C	-0.59139508	1.84354247	0.04991346
H	0.95192216	-2.48849461	-0.10380410
H	3.31766037	-1.78565796	-0.13598780
C	-2.02157356	-0.02586351	-0.21067922
C	-1.92962757	1.25602087	-0.36278894
H	-2.66284407	1.82568824	-0.89020381
O	-1.06437729	-0.92277695	0.16579143
O	-2.79687403	-1.12577468	-0.66447537

Table S1.18:  $[S_1(Z)/S_0(Z)]$ 

	X	Y	Z
C	-2.68607430	-0.90622870	-0.11273120
C	-1.36923430	-1.37381630	-0.14369650
C	-0.33409800	-0.48985190	0.13571840
C	-0.62522590	0.83173810	0.44604880
C	-1.93018190	1.31799530	0.45932410
C	-2.95390920	0.41876050	0.18382990
H	1.56546670	-1.22361240	1.00508340
H	-3.49583630	-1.57894510	-0.32923440
H	-1.15977460	-2.40041140	-0.38612670
C	1.13181380	-0.75203620	0.14146020
H	-2.12999480	2.34876500	0.68571650
H	-3.97218870	0.76383030	0.19722270
C	3.12112180	-1.20892200	-1.16512970
C	1.89004500	-0.74872320	-1.08200100
H	1.48298910	-0.33575830	-1.98450430
O	0.44985420	1.57470160	0.73716280
O	4.19826100	-1.61993480	-1.24073230

Table S1.19:  $[S_1(E)/S_0(E)]$ 

	X	Y	Z
C	-2.81814120	-0.97078200	0.25809380
C	-1.61194620	-1.55574520	-0.08316310
C	-0.49193020	-0.75293030	-0.25576850
C	-0.59705120	0.62201870	-0.10381470
C	-1.79832950	1.23287120	0.27194760
C	-2.91060310	0.41376220	0.43577820
H	1.15793440	-1.37677370	-1.60570390
H	-3.68916160	-1.58395730	0.40058820
H	-1.53952580	-2.62219470	-0.20563310
C	0.90269210	-1.16040500	-0.58409710
H	-1.85293790	2.29668570	0.40888500
H	-3.85351190	0.85044690	0.71077420
C	1.46317880	-1.80572050	1.69296670
C	1.79605990	-1.67533570	0.42338680
H	2.80232230	-1.96445350	0.17680390
O	0.52510870	1.29169130	-0.36444230
O	1.20180050	-1.94430840	2.79645230