Supporting Information

Photoisomerization mechanism associated excited-state hydrogen transfer in 2`-hydroxychalcone revealed by on-the-fly trajectory surface hopping molecular dynamics simulation

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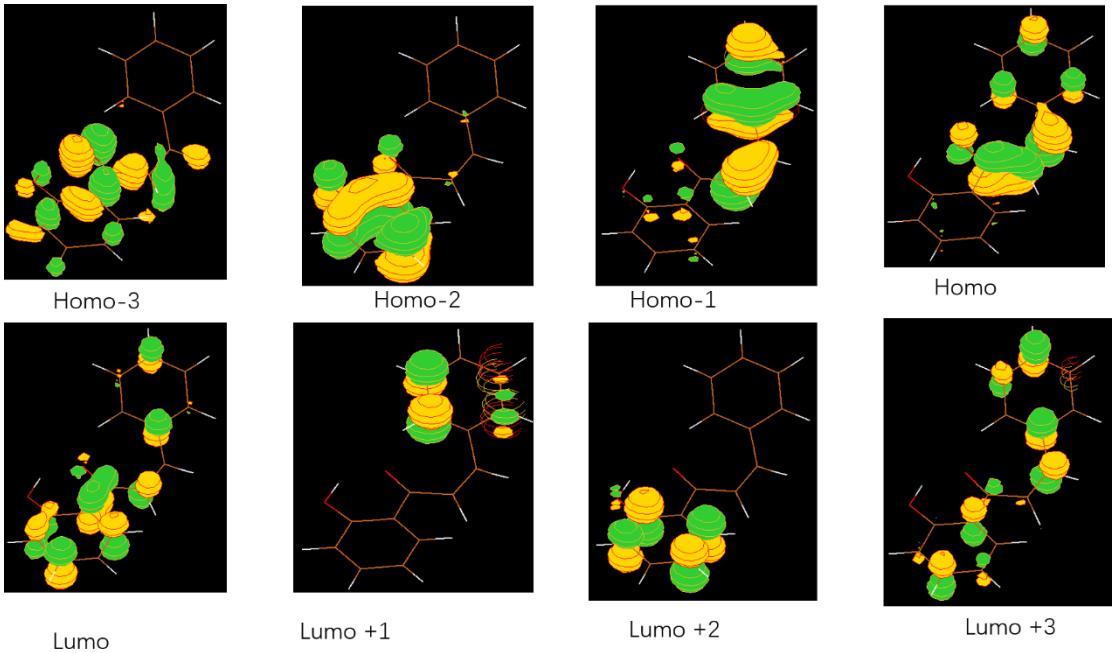
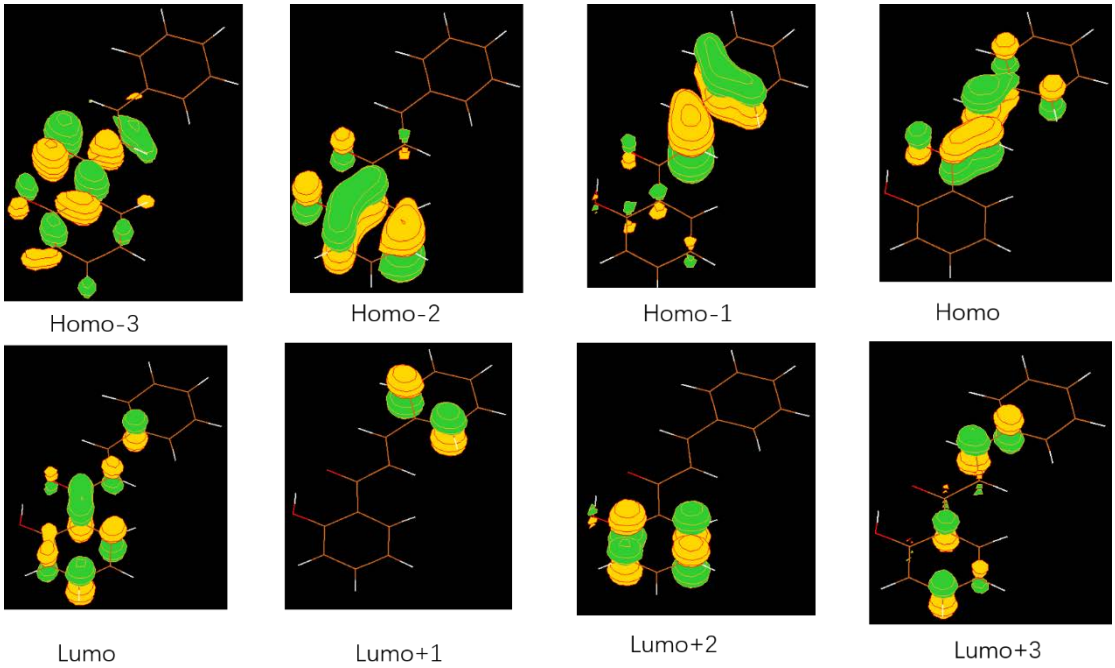
Table S1 Vertical excitation/de-excitation energies (in eV) for optimized geometries in Table 1 at OM2/MRCI(14, 15) level for nine conical intersections, three minima and two transition states in ground state S_0 and low-lying singlet excited S_1, S_2 and S_3 states. Numbers in parentheses are calcuated by (TD)-B3LYP/6-31g method at OM2/MRCI(14, 15) optimized geometires (trans-S_0 energy is taken as zero point reference for both OM2/MRCI and (TD)-B3LYP methods).

Geometry	S0(DFT)	T1	S1(TD-DFT)	S2(TD-DFT)	S3(TD-DFT)
Trans-S_0	0.00(0.00)	3.12	4.42(3.20)	4.56(3.46)	4.92(3.94)
trans-K-S_1	2.40(2.42)	2.77	2.90(3.16)	5.26(4.58)	5.77(5.10)
CI-trans-K-S_1/S_0	2.76(2.73)	2.81	2.76(3.13)	5.06(3.82)	5.58(5.13)
CI-trans-S_3/S_2	0.56(0.58)	2.84	4.14(3.21)	4.63(3.69)	4.63(4.06)
CI-cis-S_3/S_2	0.92(1.02)	3.27	4.36(3.48)	4.98(3.99)	4.98(4.45)
Cis-S_0	0.28(0.31)	3.34	4.51(3.54)	4.81(3.73)	5.09(4.11)
CI-cis-K-S_1/S_0	2.98(3.18)	2.96	2.98(3.60)	5.28(4.25)	5.79(5.53)
$CI_{H\text{-}shift}$-cis-S_2/S_1	0.76(0.76)	3.55	4.21(3.56)	4.21(3.58)	4.92(4.34)
CI-cis-S_1/S_0- H_{24}	2.82(2.84)	3.07	2.82(3.22)	5.62(5.49)	5.95(5.58)
CI_{rot}-cis-S_2/S_1	0.80(0.75)	3.48	4.00(3.06)	4.00(3.40)	5.00(4.28)
CI-E_{rot}-S_1/S_0	2.66(3.00)	2.65	2.66(3.19)	5.29(4.08)	5.33(4.43)
TS-S_0	2.72(2.35)	3.69	4.93(5.10)	7.36(6.14)	7.53(6.36)
TS-trans-S_1	1.71(1.82)	2.41	3.51(3.81)	5.26(4.13)	5.35(4.20)
$CI_{H\text{-}shift}$-trans-S_2/S_1	0.24(0.20)	3.12	3.96(3.03)	3.96(3.18)	4.78(3.93)



(A)



(B)

Fig. S1 Active space of 14 electrons in 15 orbitals within the MO2/MRCI(14,15) method in which four π orbitals and 4 π* orbitals are shown up consistently at both (A) cis-2HC minimum and (B) trans-2HC minimum. Thus, they could be utilized for on-the-fly potential energies and its gradients via whole potential energy surfaces for trajectory surface hopping dynamics.

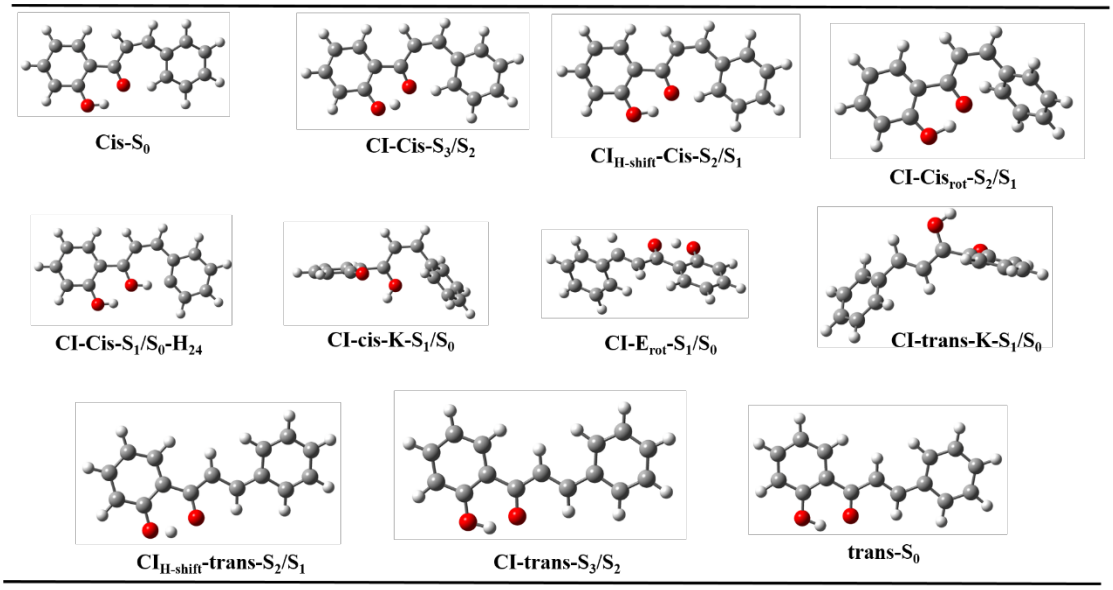


Fig. S2 Geometry structures for two minima on S_0 and nine conical intersections.

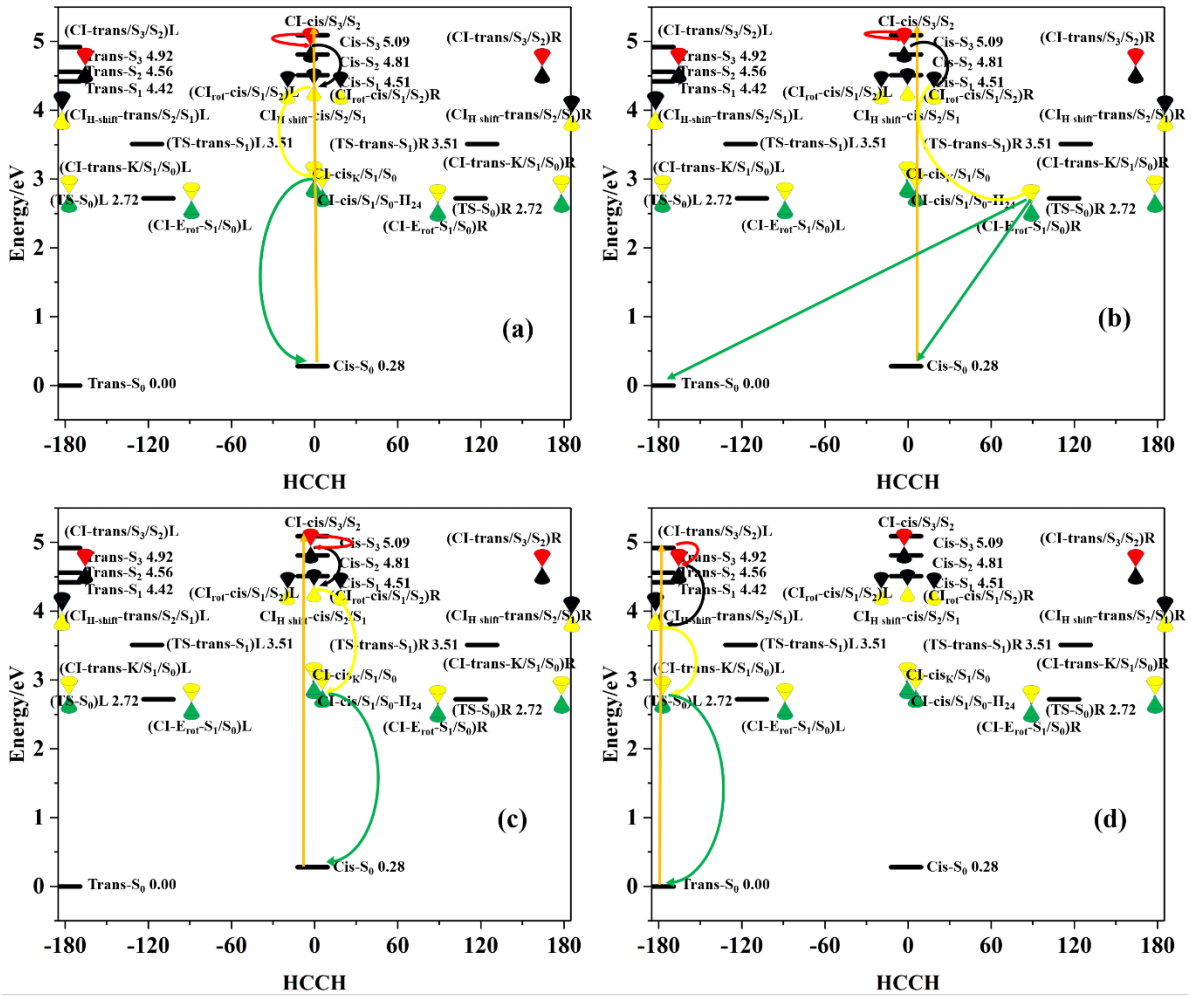


Fig. S3 Potential energy surface profiles computed by OM2/MRCI(14, 15) method for minima, transition states and conical intersections (see Table 1) among the S_3, S_2, S_1 and S_0 excited states via scaled dihedral angle $H_{17}C_{16}$ $C_{14}H_{15}$ from -180° to +180° (i.e., from L-hand to R-hand enantiomers). (a) H_{12} transferred of cis-2HC: CI-cis-S_3/S_2 →$CI_{H\text{-}shift}$-cis-S_2/S_1 → CI-cis-K-S_1/S_0→cis-S_0, (b) rotation of $H_{17}C_{16}C_{14}H_{15}$ of cis-2HC: CI-cis-S_3/S_2 →CI_{rot}-cis-S_2/S_1 → CI-E_{rot}-S_1/S_0→trans-S_0 (cis-S_0), (c) H_{24} transferred of cis-2HC: CI-S_3/S_2 →$CI_{H\text{-}shift}$-cis-S_2/S_1 → CI-cis-S_1/S_0-H_{24}→ cis-S_0, and (d)H_{12} transferred of trans-2HC: CI-trans-S_3/S_2 →$CI_{H\text{-}shift}$-trans-S_2/S_1→ CI-trans-K-S_1/S_0→ trans-S_0.

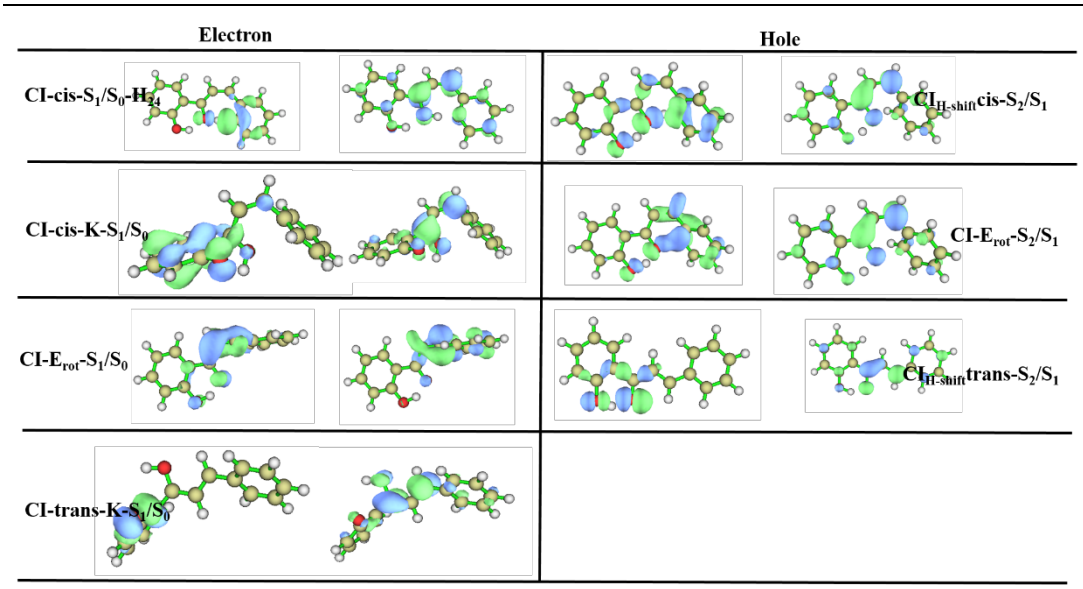


Fig. S4 Calculated natural transition orbitals of $S_0 \rightarrow S_1$ from TDDF-T-B3LYP/6-31g* calculation. Vertical excitations based on conical intersection geometries between S_1 and S_0 states, and between S_2 and S_1 states within OM2/MRCI.

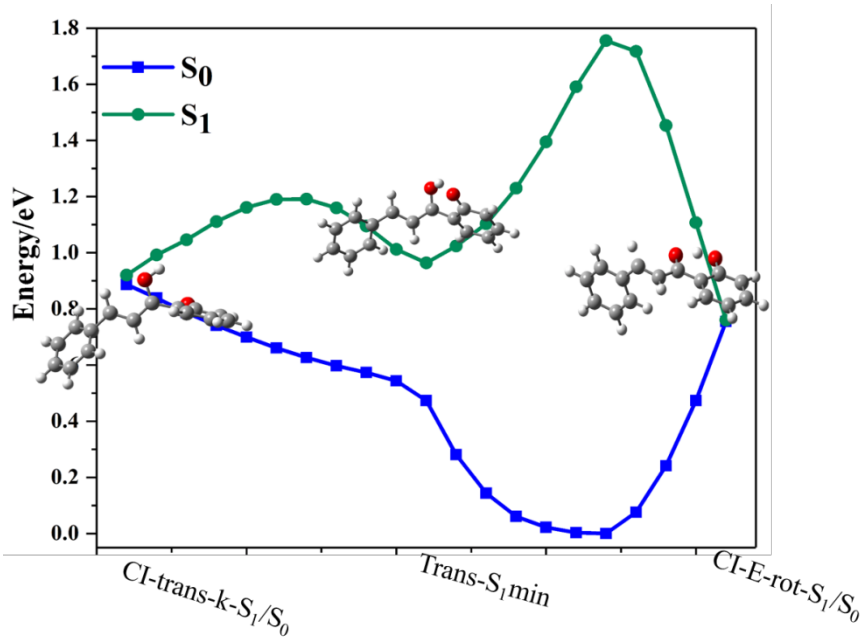


Fig. S5 Energy profiles along the intrinsic reaction coordinate (IRC) connecting three points; CI-trans-K-S_1/S_0, Trans-K-S_1 and CI-E_{rot}-S_1/S_0.

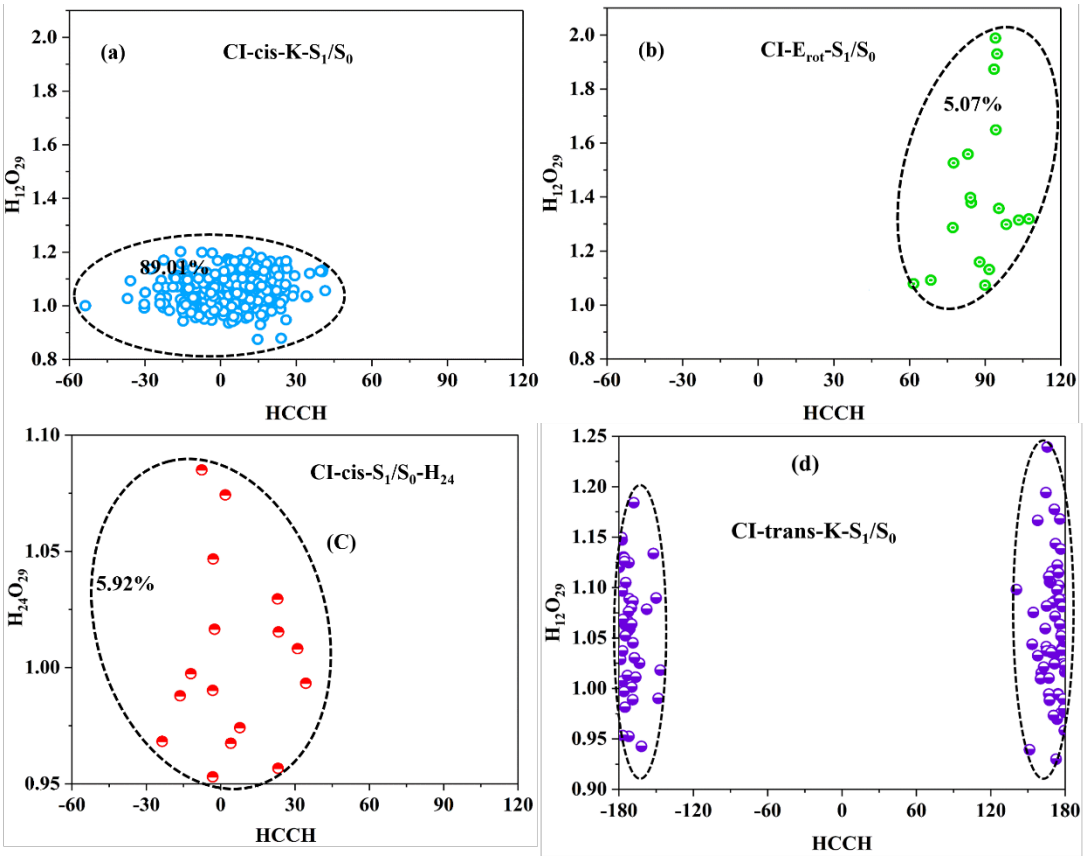


Fig. S6 Hopping spot distributions at conical intersections between S_1 and S_0 states in terms of hydrogen transfer bond and dihedral angle $H_{17}C_{16}C_{14}H_{15}$ (a) at CI-cis-K-S_1/S_0 for H_{12} transferred case of cis-2HC, (b) at CI-E_{rot}-S_1/S_0 for rotation of $H_{17}C_{16}C_{14}H_{15}$ of cis-2HC case, (c) at CI-cis-S_1/S_0-H_{24} for H_{24} transferred of cis-2HC case, and (d) at CI-trans-K-S_1/S_0 for H_{12} transferred of trans-2HC case. The percentage number means ratio of such events from total sampling trajectories.

Table S2 Cartesian coordinates (in angstrom) of optimized geometries at the OM2/MRCI(14,15) level for two minima on S_0 and one on S_1, and one transition state on S_0 and one on S_1, and nine conical intersections.

Table S2.1: Trans-S_0-L

	X	Y	Z
C	-4.7094599573	1.4608044570	0.0007140160
C	-4.6913377263	0.0756872329	-0.0068063158
C	-3.4442198789	-0.5886231946	-0.0080071180
C	-2.2295823119	0.1422725469	-0.0016687169
C	-2.2915987651	1.5434921177	0.0058568327
C	-3.5178955339	2.1962191004	0.0070414986
H	-5.6689191684	1.9923320555	0.0017519591
H	-5.6051312683	-0.5158872907	-0.0118046486
H	-1.3668892304	2.1344496982	0.0108770234
H	-3.5554418264	3.2891975194	0.0129358868
O	-3.5120617412	-1.9295396208	-0.0154382796
H	-2.5869544563	-2.3333794189	-0.0158529441
C	-0.9644692943	-0.6155060338	-0.0033663866
C	0.3487818625	0.0469566917	0.0027325794
H	0.4000562968	1.1360601979	0.0087653744
C	1.4553250956	-0.7385668713	0.0005332769
H	1.3362140224	-1.8325038729	-0.0056594303
C	2.8211522614	-0.2243168779	0.0059057935
C	3.8753669482	-1.1559025506	0.0027942797
C	3.1100196777	1.1499585363	0.0139519349
C	5.1941441842	-0.7148225657	0.0076724645
H	3.6545665482	-2.2295267110	-0.0034827560
C	4.4335627385	1.5803407985	0.0187840141
H	2.2990108404	1.8881002836	0.0164646532
C	5.4752173350	0.6523387127	0.0156655713
H	6.0134887738	-1.4396395383	0.0052457447
H	4.6587826495	2.6517994395	0.0250613138
H	6.5136963742	0.9966250178	0.0194896737
O	-1.0168764538	-1.8554996865	-0.0102139266

Table S2.2: trans-K-S_1-L

	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38794103
C	1.25236118	0.00000000	2.09805765
C	2.48857408	-0.02386267	1.31001353
C	2.43228904	-0.10911383	-0.06171933
C	1.19036634	-0.06478532	-0.71721744
H	-0.94132060	0.02029023	-0.54465814
H	-0.91396194	0.17673938	1.96447979
H	3.34444617	-0.20931522	-0.65063563
H	1.16035048	-0.08560457	-1.80649997
O	1.35807996	-0.16113174	3.34375499
C	3.69662491	-0.18832005	2.16193063
O	3.57960852	-1.11140483	3.10662818
H	2.63550930	-1.00169323	3.56514424
C	4.54824812	0.94437170	2.40116790
H	4.52736449	1.77382722	1.69032047
C	5.44659324	0.90903284	3.43650039
H	5.45163190	0.06578141	4.13640607
C	6.43535635	1.97196547	3.63094002
C	6.74885721	2.39674087	4.92801901
C	7.06769144	2.56034589	2.52299460
C	7.67335090	3.41729514	5.12853404
H	6.24791340	1.93758585	5.78850148
C	7.99744052	3.57496181	2.73432252
H	6.84123544	2.20940005	1.51094043
C	8.30423803	4.00502184	4.02568743
H	7.90846165	3.76584775	6.13830043
H	8.50083522	4.03523414	1.87463077
H	9.04654427	4.79450352	4.1849506

Table S2.3: CI-trans-K-S_1/S_0

	X	Y	Z
C	-0.0547095131	0.0763293717	0.2163437362
C	0.0143867815	-0.4831901088	1.4674825410
C	1.2970457713	-0.6857342613	2.1151248408
C	2.4971204873	-0.2902583175	1.3564859824
C	2.3729593804	0.2896960166	0.1003816926
C	1.1140166729	0.4720120668	-0.4652550709
H	-1.0281071167	0.2213871007	-0.2611372770
H	-0.8768025038	-0.7992046184	2.0059582415
H	3.2651263417	0.5911865737	-0.4394699722
H	1.0281953923	0.9241629399	-1.4600925169
O	1.4036906050	-1.1334656424	3.2693732732
H	3.6452307298	1.0390591470	3.0389809328
C	3.8102678062	-0.5236127878	1.9448461594
C	4.5335882067	-1.7477536403	1.8604245005
H	4.1110587028	-2.5367446872	1.2427768376
C	5.7285093695	-1.9032374684	2.5275563271
H	6.1267058845	-1.1134970521	3.1700923301
C	6.4941551502	-3.1475590331	2.3973248169
C	6.9978637365	-3.7649237452	3.5474989322
C	6.7052249570	-3.7008321641	1.1270772939
C	7.7124015901	-4.9569773396	3.4325204038
H	6.8181479360	-3.3302124092	4.5360004045
C	7.4251984900	-4.8913003152	1.0232848989
H	6.3284107612	-3.2004917714	0.2301430767
C	7.9232146405	-5.5140350127	2.1676440918
H	8.1044425101	-5.4520702774	4.3251031714
H	7.6065124279	-5.3266093002	0.0354495093
H	8.4913401363	-6.4476548448	2.0790739715
O	4.3633040248	0.4327682762	2.7095133057

Table S2.4: CI-trans-S_3/S_2-L

	X	Y	Z
C	-4.7659830600	1.3813650684	0.0030655200
C	-4.6390403380	0.0071424046	0.1577335890
C	-3.3492311685	-0.5645076606	0.1029097881
C	-2.1967812647	0.2578917743	-0.0364258644
C	-2.3638078727	1.6383997291	-0.1688755228
C	-3.6424126308	2.1948861965	-0.1692289679
H	-5.7636149989	1.8365828989	0.0068387796
H	-5.5079052057	-0.6450272738	0.2399646068
H	-1.4854417486	2.2942424674	-0.2447817793
H	-3.7649262490	3.2789429709	-0.2617494212
O	-3.2570726283	-1.8925183212	0.1510120805
H	-2.2479366193	-2.1469796464	0.3152500960
C	-0.9053822402	-0.4278539703	0.0277929229
C	0.3387529237	0.1675595821	-0.3578652069
H	0.4528299061	1.2334617054	-0.5590126321
C	1.4544793957	-0.7125991579	-0.2725210774
H	1.2303911021	-1.7871884566	-0.3340830076
C	2.7789836786	-0.2769693357	-0.0648904844
C	3.8463823823	-1.2294260377	-0.1146494494
C	3.0882722924	1.1029075319	0.1633256352
C	5.1537331604	-0.7994777133	-0.0570269379
H	3.6071902308	-2.2924340530	-0.2308896202
C	4.4092514235	1.5057119138	0.2146530709
H	2.2786364687	1.8306800338	0.2675432820
C	5.4396277459	0.5662098450	0.1051462016
H	5.9762771122	-1.5221715549	-0.0943916108
H	4.6541490965	2.5604269398	0.3883514636
H	6.4846474896	0.8983458762	0.1410672143
O	-0.8772391246	-1.6622757366	0.3557164546

Table S2.5: CI-cis-S_3/S_2-L

	X	Y	Z
C	4.8451875827	0.1107043116	-0.1605984045
C	4.0524809351	-1.0339015486	-0.2239239839
C	2.6485391027	-0.8987073904	-0.0486329157
C	2.0508217091	0.3816522820	0.2126834903
C	2.8899994778	1.4816339001	0.3291386288
C	4.2739782403	1.3504793588	0.1024793286
H	5.9257863661	0.0328535259	-0.3360867841
H	4.4750834876	-2.0128939477	-0.4496493199
H	2.4857874481	2.4665405234	0.6089232245
H	4.9042992315	2.2371348325	0.1595996199
O	1.9068056545	-1.9839900763	-0.1591795220
H	0.9473691241	-1.7672619587	0.2883014360
C	0.5909013177	0.3714997289	0.4305635703
C	-0.1958436533	1.5300863115	0.1088044634
H	0.3892003210	2.4559024118	-0.0258730837
C	-1.5770800562	1.7010669384	-0.0340408006
H	-1.9118337632	2.7388537385	-0.2085776352
C	-2.6138374982	0.7262576741	-0.0482185443
C	-3.9276702419	1.1843653207	-0.3595198810
C	-2.4017750192	-0.6696820659	0.2229164985
C	-4.9936924983	0.3186938068	-0.2697810711
H	-4.0936192392	2.2415991187	-0.5930386165
C	-3.5078949960	-1.5017166065	0.3418860098
H	-1.3715970420	-1.0186861971	0.3870050620
C	-4.7893423929	-1.0379811126	0.0689144921
H	-6.0112122236	0.6739255356	-0.4619288260
H	-3.3550959520	-2.5593451179	0.5733539666
H	-5.6475713116	-1.7189004325	0.1032090788
O	0.1171031960	-0.7582315578	0.8056479685

Table S2.6: Cis-S_0-L

	X	Y	Z
C	4.847856	0.331743	0.401334
C	4.263115	-0.903515	0.173871
C	2.860861	-0.972674	-0.022687
C	2.064306	0.201658	-0.009997
C	2.695789	1.434234	0.236109
C	4.069031	1.500341	0.441763
H	5.931907	0.401736	0.553893
H	4.842686	-1.825120	0.150764
H	2.101519	2.355176	0.293434
H	4.549096	2.463695	0.636768
O	2.378619	-2.197902	-0.241065
H	1.377181	-2.175947	-0.302778
C	0.614722	0.073049	-0.288257
C	-0.166310	1.288116	-0.571366
H	0.454446	2.146877	-0.870688
C	-1.508472	1.494807	-0.509554
H	-1.832877	2.531808	-0.751785
C	-2.625234	0.627727	-0.146795
C	-3.865564	1.285307	0.018902
C	-2.551973	-0.769675	-0.023518
C	-5.014104	0.556794	0.315448
H	-3.929054	2.382253	-0.068453
C	-3.716354	-1.482816	0.279421
H	-1.602072	-1.285741	-0.163900
C	-4.941937	-0.834523	0.445313
H	-5.974408	1.072330	0.450359
H	-3.663824	-2.575854	0.375966
H	-5.847717	-1.409759	0.671300
O	0.128249	-1.074705	-0.318034

Table S2.7: CI-cis-K-S_1/S_0-L

	X	Y	Z
C	4.6889899845	0.1351653955	0.5595328202
C	4.0304786434	-0.9432578664	0.0196187274
C	2.6016052263	-0.8880640377	-0.2348058502
C	1.9200186235	0.3695663156	0.0901702054
C	2.6306777855	1.4314385513	0.6481405116
C	3.9948315190	1.3136659861	0.8794750188
H	5.7639985841	0.0937406431	0.7497725042
H	4.5454284580	-1.8686944873	-0.2359359251
H	2.1173654268	2.3625310293	0.8973866300
H	4.5407119805	2.1464722257	1.3121350946
O	1.9709306701	-1.8616031740	-0.6818474277
H	0.0328612996	-0.4762476147	1.4155739240
C	0.4910362601	0.4780918663	-0.1907684532
C	-0.0291011078	0.8942865006	-1.4527148815
H	0.6989596237	1.2515100706	-2.1851366609
C	-1.3717012085	0.8794985967	-1.7470755947
H	-1.7244414135	1.2415126222	-2.7204583431
C	-2.3995537295	0.3674189887	-0.8303655484
C	-3.2403227622	1.2655423177	-0.1651412909
C	-2.5380413992	-1.0162469081	-0.6703745104
C	-4.2357288535	0.7677380827	0.6765579755
H	-3.1146676411	2.3462230747	-0.2893885778
C	-3.5394137578	-1.4994324863	0.1728923730
H	-1.8698594756	-1.7060756507	-1.1922285265
C	-4.3827628994	-0.6102513708	0.8386397675
H	-4.8983814462	1.4606647548	1.2070989701
H	-3.6604810000	-2.5803277977	0.3061249862
H	-5.1688913332	-0.9966795129	1.4995009120
O	-0.3833493942	0.1699762234	0.7752839749

Table S2.8: $CI_{H\text{-}shift}$-cis-S_2/S_1

	X	Y	Z
C	4.8646682275	0.1059304798	0.0895786523
C	4.1324199749	-1.0637538751	0.1848395957
C	2.7242929261	-0.9905532509	0.1631552535
C	2.0659412833	0.2667413719	0.0451224019
C	2.8338309495	1.4278455584	-0.0489938800
C	4.2209699867	1.3428278926	-0.0264870586
H	5.9586171625	0.0631970954	0.1051731140
H	4.6032683181	-2.0396502555	0.2760176807
H	2.3544959489	2.4085285748	-0.1406820632
H	4.8179017524	2.2567661859	-0.1006468469
O	2.0668819066	-2.1427219516	0.2576783504
H	1.0387835342	-1.9609326306	0.2305372880
C	0.5787888210	0.2510755257	0.0303990059
C	-0.1587190139	1.4511269918	-0.0834837132
H	0.4523513574	2.3642016858	-0.1574144251
C	-1.5360597623	1.6398248456	-0.1150831577
H	-1.8555698902	2.6942293736	-0.2115735123
C	-2.6190702743	0.6985907052	-0.0437978410
C	-3.9370490465	1.2190253105	-0.1040605722
C	-2.4501951406	-0.6933882187	0.0808975062
C	-5.0251586905	0.3671217373	-0.0407147580
H	-4.0879056649	2.3022993267	-0.2013032358
C	-3.5463447353	-1.5386757842	0.1435898565
H	-1.4182211412	-1.0942167398	0.1274937806
C	-4.8368744714	-1.0132729999	0.0831710856
H	-6.0424837188	0.7728257651	-0.0875931219
H	-3.4001516952	-2.6191012673	0.2405581828
H	-5.7036832986	-1.6826378736	0.1328180723
O	0.0672339805	-0.9382447967	0.1297987320

Table S2.9: CI-cis-S_1/S_0-H_{24}-R

	X	Y	Z
C	4.8569455774	0.1466492846	0.0900746205
C	4.1243648389	-1.0309155118	0.1356238201
C	2.7167015613	-0.9679389743	0.1164791937
C	2.0343985076	0.2750913065	0.0480970610
C	2.8137462112	1.4436774501	0.0139152445
C	4.2033739794	1.3799109317	0.0307896283
H	5.9524937798	0.1093327432	0.1008165230
H	4.6049781880	-2.0067975684	0.1834186296
H	2.3336529216	2.4299659959	-0.0268381085
H	4.7879126722	2.3048869306	0.0048876146
O	2.1258174693	-2.1793468142	0.1569151000
H	1.1318085430	-2.0864367583	0.1732200177
C	0.5704413982	0.3426775867	0.0248809636
C	-0.1631175241	1.5338553065	-0.1548225013
H	0.4500305085	2.4390695812	-0.2705517386
C	-1.5292537598	1.7517641295	-0.2030507158
H	-1.8654235357	2.7873082302	-0.3511645293
C	-2.6040202815	0.7904042627	-0.0828871369
C	-3.9542282978	1.1993596121	-0.1422399449
C	-2.4629076485	-0.5764933981	0.0901528628
C	-4.9918493683	0.2739190277	-0.0287225054
H	-4.1759810517	2.2639710978	-0.2794501272
C	-3.4140258410	-1.5507082644	0.2086137138
H	-0.9917982112	-0.8612537094	0.1316311079
C	-4.7360036748	-1.0868225938	0.1431443159
H	-6.0266217786	0.6217204486	-0.0737919295
H	-3.1721931209	-2.5994792366	0.3444913983
H	-5.5582356159	-1.8040129799	0.2283675421
O	0.0264326002	-0.8828875901	0.1652436133

Table S2.10: CI_{rot}-cis-S_2/S_1-R

	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38794103
C	1.25236118	0.00000000	2.09805765
C	2.48857408	-0.02386267	1.31001353
C	2.43228904	-0.10911383	-0.06171933
C	1.19036634	-0.06478532	-0.71721744
H	-0.94132060	0.02029023	-0.54465814
H	-0.91396194	0.17673938	1.96447979
H	3.34444617	-0.20931522	-0.65063563
H	1.16035048	-0.08560457	-1.80649997
O	1.35807996	-0.16113174	3.34375499
C	3.69662491	-0.18832005	2.16193063
O	3.57960852	-1.11140483	3.10662818
H	2.63550930	-1.00169323	3.56514424
C	4.54824812	0.94437170	2.40116790
H	4.52736449	1.77382722	1.69032047
C	5.44659324	0.90903284	3.43650039
H	5.45163190	0.06578141	4.13640607
C	6.43535635	1.97196547	3.63094002
C	6.74885721	2.39674087	4.92801901
C	7.06769144	2.56034589	2.52299460
C	7.67335090	3.41729514	5.12853404
H	6.24791340	1.93758585	5.78850148
C	7.99744052	3.57496181	2.73432252
H	6.84123544	2.20940005	1.51094043
C	8.30423803	4.00502184	4.02568743
H	7.90846165	3.76584775	6.13830043
H	8.50083522	4.03523414	1.87463077
H	9.04654427	4.79450352	4.18495064

Table S2.11: CI-E_{rot}-S_1/S_0-R

	X	Y	Z
C	-0.0459692487	0.0752909465	0.0168531378
C	0.1049629315	0.7240647308	1.2337880916
C	1.3523147522	0.6730449387	1.8964441102
C	2.4334349556	-0.0397029034	1.3090807146
C	2.2542821743	-0.6762254484	0.0845257870
C	1.0203884158	-0.6227983367	-0.5609326353
H	-1.0110500057	0.1110855070	-0.5044627698
H	-0.7140359533	1.2711246618	1.6986640767
H	3.0871732388	-1.2229551486	-0.3786115149
H	0.8832939092	-1.1290879283	-1.5215127887
O	1.4591726651	1.3024760812	3.0627311159
H	2.4598218927	1.1999680074	3.4028145069
C	3.7075716159	-0.0180882247	2.0837383332
C	4.8125003277	-0.7406267441	1.6231693322
H	4.7530998728	-1.2580011675	0.7030328078
C	5.9521004843	-0.6542606997	2.3827504634
H	6.7189146653	0.1841666700	2.2554351957
C	6.2298090368	-1.5672673755	3.4766675749
C	7.4453098916	-1.4958967299	4.1865107957
C	5.2309526807	-2.4894162346	3.8403083511
C	7.6657058666	-2.3685055572	5.2419532916
H	8.2123349741	-0.7674482405	3.8946362785
C	5.4627572067	-3.3433698183	4.9160238530
H	4.2896096379	-2.4856039794	3.2886662593
C	6.6722730768	-3.2850660575	5.6048281536
H	8.6047664001	-2.3355843936	5.7974569696
H	4.6907227011	-4.0498129035	5.2262708304
H	6.8485285781	-3.9594668619	6.4516818217
O	3.7384187179	0.6416367228	3.1808992534

Table S2.12: TS-S_0-R

	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38973800
C	1.23648431	0.00000000	2.06605974
C	2.45316959	-0.01216352	1.33536023
C	2.42291900	-0.01449928	-0.06500147
C	1.19857090	-0.00735398	-0.72520824
H	-0.95312651	0.01331689	-0.53897025
H	-0.92152195	0.00095606	1.96783247
H	3.36032021	-0.02540286	-0.62697436
H	1.16939774	-0.01275897	-1.81845558
O	1.18953916	0.03331081	3.40635935
H	2.12745557	-0.04651083	3.79247660
C	3.68588342	-0.04247047	2.08595464
C	5.06881911	-0.10267652	1.87483716
H	5.71306148	-0.41970336	1.08633423
C	5.36493489	0.35010538	3.21357879
H	5.17628767	1.40445073	3.53234959
C	6.35073521	-0.38796755	4.03761535
C	7.10837570	0.28383234	4.99983327
C	6.48108346	-1.76438797	3.83812760
C	8.04137133	-0.42895433	5.75390806
H	6.99002411	1.36235986	5.15687799
C	7.41919062	-2.47182124	4.59506251
H	5.85479165	-2.27772235	3.10476312
C	8.18563869	-1.80101812	5.54609347
H	8.64609738	0.08756997	6.50350893
H	7.54162074	-3.54686020	4.43779098
H	8.90933587	-2.36312330	6.15025880
O	3.67539848	-0.02291426	3.42497539

Table S2.13: TS-trans-S_1-R

	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38758129
C	1.23026616	0.00000000	2.07507153
C	2.44618036	-0.05677838	1.34404906
C	2.42321367	-0.01704155	-0.05106309
C	1.20230891	0.00295982	-0.72041189
H	-0.95893622	-0.00238970	-0.53063431
H	-0.91778184	0.00752357	1.97182911
H	3.36404378	-0.00178647	-0.60491156
H	1.17769820	0.01765514	-1.81433812
O	1.17030644	0.00732669	3.40780460
H	2.12986969	0.08472136	3.78613319
C	3.65492154	-0.20465329	2.18957510
C	4.92412586	-0.56826373	1.64574145
H	5.02305327	-0.94455569	0.63999868
C	5.99946944	-0.31302430	2.53646785
H	6.15805359	0.70137194	2.95011113
C	6.83520978	-1.34958775	3.06310198
C	7.87959875	-1.01523580	3.96074998
C	6.76386764	-2.65194417	2.52708937
C	8.79497588	-1.98460337	4.34368224
H	7.95757857	0.00195878	4.35608326
C	7.68605840	-3.61048118	2.92719485
H	5.97062571	-2.89314173	1.82429905
C	8.68219235	-3.28971466	3.85097234
H	9.58873666	-1.73528015	5.05443242
H	7.60144914	-4.62488224	2.52829293
H	9.38948484	-4.05480369	4.17788015
O	3.56581690	0.19363197	3.39220588

Table S2.14: $CI_{H\text{-}shift}$-trans-S2/S1-R

	X	Y	Z
C	-4.6832914528	1.4374149448	0.0154908501
C	-4.6397450608	0.0476330068	-0.0006114554
C	-3.4000634957	-0.5963646429	-0.0059717502
C	-2.2175929782	0.1762519994	0.0050680553
C	-2.2692154216	1.5728826037	0.0212368022
C	-3.5104430664	2.1916309997	0.0262924577
H	-5.6547610417	1.9403037490	0.0196672312
H	-5.5425340165	-0.5592225082	-0.0092317104
H	-1.3497363657	2.1655088209	0.0297207590
H	-3.5679970295	3.2833089365	0.0389050689
O	-3.3983491314	-1.9399675896	-0.0216183193
H	-2.4283942729	-2.2979486469	-0.0241086838
C	-0.9577732145	-0.5964003695	-0.0017521307
C	0.3156567102	0.0110023667	0.0075186990
H	0.3576722483	1.1024093985	0.0203045440
C	1.4477363829	-0.7954475593	0.0000967723
H	1.3425543780	-1.8841956505	-0.0127626842
C	2.7813043661	-0.2519115127	0.0087301079
C	3.8652316323	-1.1572413157	0.0000907992
C	3.0508581852	1.1313301400	0.0252874763
C	5.1692354327	-0.6895206154	0.0078013320
H	3.6668558228	-2.2364945369	-0.0128034314
C	4.3604982692	1.5857349740	0.0328522094
H	2.2261694347	1.8561662847	0.0322866572
C	5.4226803632	0.6817185911	0.0241783786
H	6.0066165321	-1.3960576864	0.0010463279
H	4.5656557229	2.6626225189	0.0457355524
H	6.4547734252	1.0492421527	0.0302458220
O	-1.0749986547	-1.8860739999	-0.0169750640