Supporting Information *for*

Internal Conversion and Intersystem Crossing in α,β-Enones: A Combination of Electronic Structure Calculations and Dynamics Simulations

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Table S1. Relative Energies of Stationary and Intersection structures for *trans*-acrolein (AC) in the gas phase without zero-point correction. All relative energies are calculated based on two-state average calculations, except the S_0 and S_1 minima and vertical excitation energy of the S_1 state of AC. Unit is kcal/mol.

		CAS(6,5)/6-31G*	CASPT2//CAS(6,5)/6-31G*	CASPT2/ANO-S//CAS(6,5)/6-31G*
AC_S_0		0.0	0.0	0.0
$E_{ver}(S_1)$		91.2	91.3	89.6
E_{ver}(T): two-state-average (SA2)	T_1	88.4	83.5	78.4
	T_2	93.1	93.5	89.1
AC_S_1		72.4	76.0	73.1
T at AC_S_1: SA2	T_1	70.6	72.3	75.3
	T_2	77.1	81.3	81.9
AC_$T_1(\pi\pi^*)$: SA2	T_1	63.4	62.7	61.8
	T_2	101.7	101.0	97.1
AC_$T_1(n\pi^*)$: SA2	T_1	70.5	72.0	69.5
	T_2	78.1	82.3	80.1
AC_T_2T_1: SA2	T_1	74.2	75.6	72.8
	T_2	74.2	77.1	74.9
AC_S_1T_2:	S_1	75.7	76.5	73.6

SA2	T_2	74.9	78.6	71.3
	T_1	72.0	73.9	76.4
AC_T_1S_0: SA2	S_0	63.5	64.4	59.5
	T_1	63.6	62.1	61.8
AC_S_1S_0: SA2	S_0	91.9	93.6	91.2
	S_1	92.0	95.1	92.7

Table S2. Relative Energies of Stationary and Intersection structures for 2-cyclopentenone (CPO) in the gas phase without zero-point correction. In relative energy calculations, the state-average method was applied when necessary. Unit is kcal/mol.

		CAS(8,7)/6-31G*	CASPT2//CAS(8,7)/6-31G*	CASPT2/ANO-S//CAS(6,5)/6-31G*
CPO_S_0		0.0	0.0	0.0
$E_{ver}(S_1)$		90.0	89.5	87.3
$E_{ver}(T_1)$		100.8	84.7	82.9
E_{ver}(T): two-state-average (SA2)	T_1	103.8	83.7	81.9
	T_2	109.4	93.9	92.5
CPO_S_1		90.3	78.5	78.4
TS_S_1		106.1	91.2	87.3
CK_S_0		43.1	33.4	
CPO_S_1S_0: SA2	S_0	101.2	85.6	82.1
	S_1	101.2	89.4	85.8
CPO_$T_1(\pi\pi^*)$: SA2	T_1	87.7	73.7	73.8
	T_2	117.5	98.8	97.8
CPO_$T_1(n\pi^*)$: SA2	T_1	89.4	75.6	75.9
	T_2	96.2	84.8	85.4
CPO_T_2T_1:SA2	T_1	92.6	78.6	78.3
	T_2	92.6	78.9	80.4
CPO_S_1T_2: SA2	S_1	95.9	80.4	80.1
	T_1	92.1	78.7	78.6
	T_2	93.0	79.3	79.5
CPO_T_1S_0: SA2	S_0	92.6	79.1	78.4
	T_1	93.0	81.4	80.9

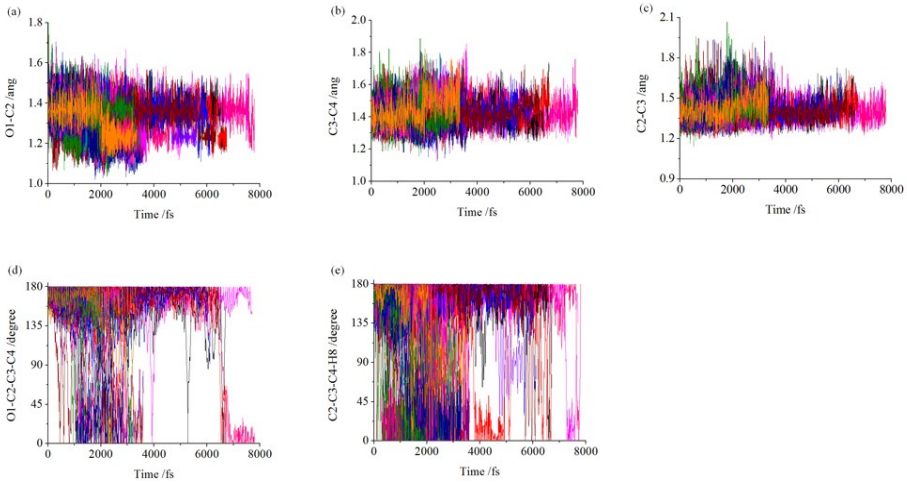

Figure S1. Time evolution of the selected structural parameters, (a) O1-C2, (b) C3-C4, (c) C2-C3, (d) O1-C2-C3-C4, (e) C2-C3-C4-H8 of AC.

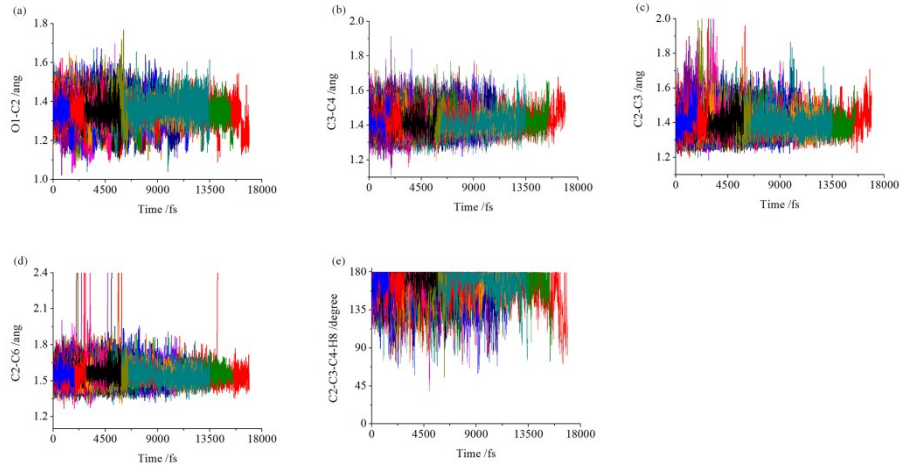

Figure S2. Time evolution of the selected structural parameters, (a) O1-C2, (b) C3-C4, (c) C2-C3, (d) C2-C6, (e) C2-C3-C4-H8 of CPO.

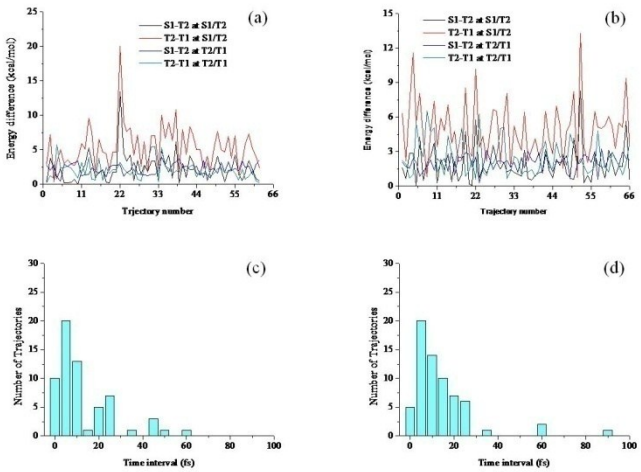

Figure S3: Distribution of the energy difference and time interval for those trajectories which undergo a $S_1 \rightarrow T_2$ or T_1 hop. The energy difference between S_1 and T_2, and between T_2 and T_1 at the geometries of the S_2/T_1 and T_2/T_1 hop was shown in (a) for AC and (b) for CPO. The time interval between the S_1/T_2 and T_2/T_1 hop was shown in (c) for AC, and (d) for CPO.

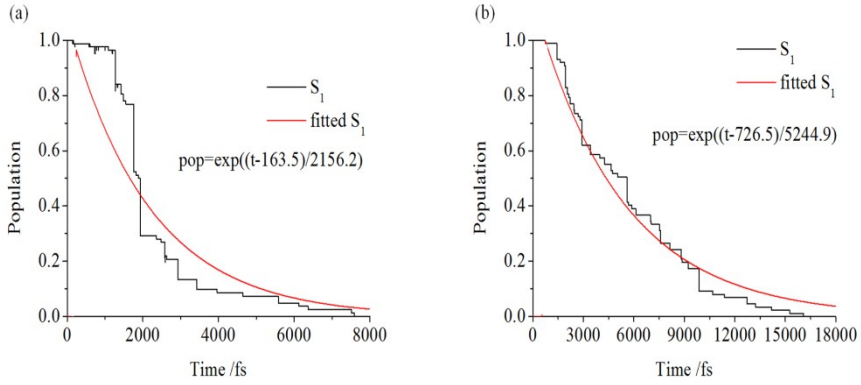

Figure S4. Fitting the S_1 state lifetime. (a) Fitting curve of the S_1 state of AC. The latency time τ_0 is 163.5 fs, and the delay constant τ_1 is 2156.2 fs. (b) Fitting curve of the S_1 state of CPO. The latency time τ_0 is 726.5 fs, and the delay constant τ_1 is 5244.9 fs.

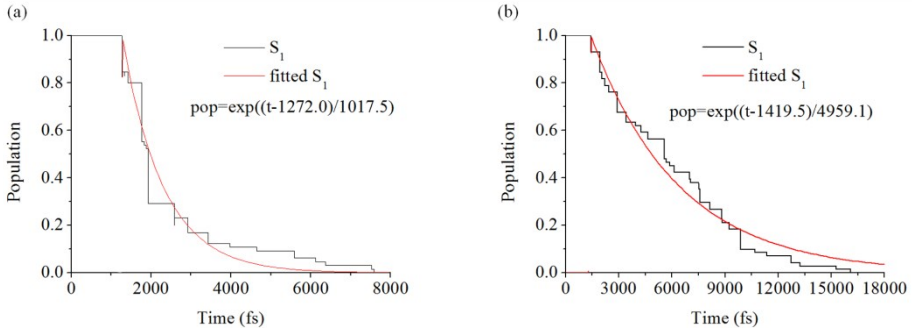

Figure S5. Fitting the ISC time for trajectories that have a $S_1 \rightarrow T_2$ or T_1 hop. (a) Fitting curve of the S_1 state of AC. The latency time τ_0 is 1272.0 fs, and the delay constant τ_1 is 1017.5 fs. (b) Fitting curve of the S_1 state of CPO. The latency time τ_0 is 1419.5 fs, and the delay constant τ_1 is 4959.1 fs.

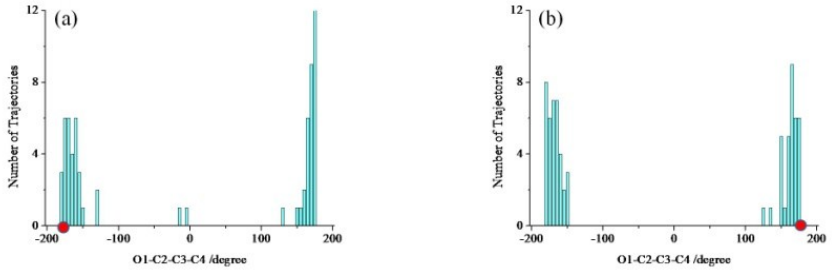

Figure S6. Distribution of the O1-C2-C3-C4 bond angle at a $S_1 \rightarrow T_2$ or T_1 hop. (a) for AC, and (b) for CPO. The values corresponding to the MECP geometries are marked by the red circles.

S1. Cartesian coordinates of the optimized structures of *trans*-acrolein.

a. a minimum of trans-acrolein in the ground state optimized at the CAS(6,5)/6-31G* level : AC_S_0

C	-0.003415000	0.074209000	0.703580000
C	0.051310000	-0.073285000	-0.764073000
C	0.031828000	0.986371000	-1.586791000
O	0.011065000	-0.864809000	1.462822000
H	-0.061010000	1.093102000	1.088595000
H	0.107373000	-1.080079000	-1.138561000
H	-0.024795000	1.992211000	-1.207498000
H	0.071292000	0.875762000	-2.654440000

b. a minimum of trans-acrolein in the S1 state optimized at the CAS(6,5)/6-31G* level : AC_S_1

C	-0.003464000	0.104994000	0.648498000
C	0.048145000	-0.047914000	-0.716143000
C	0.031554000	1.018915000	-1.622851000
O	0.014323000	-0.947971000	1.500397000
H	-0.061603000	1.046536000	1.162177000
H	0.104638000	-1.052231000	-1.100074000
H	-0.023954000	2.038457000	-1.288990000
H	0.074010000	0.842697000	-2.679380000

c. a CI between S1 and S0 optimized at the CAS(6,5)/6-31G* level : AC_S_1S_0

C	0.129331000	-0.002078000	0.556255000
C	0.315993000	-0.012926000	-0.728909000
C	-0.059191000	1.134522000	-1.595204000
O	0.361489000	-0.889450000	1.609018000
H	-0.291281000	0.781427000	1.182742000
H	0.744784000	-0.883523000	-1.199991000

H	0.706058000	1.798369000	-1.956721000
H	-0.959700000	1.086742000	-2.181493000

d. a ISC between S1 and T2 optimized at the CAS(6,5)/6-31G* level : AC_S_1T_2

C	-0.003389925	0.094184879	0.659206327
C	0.048012634	-0.061461264	-0.693323475
C	0.031170571	1.034934020	-1.632083741
O	0.015162733	-0.959482858	1.488716564
H	-0.061190355	1.055051337	1.140600799
H	0.104476878	-1.064361231	-1.078133499
H	-0.024396907	2.052001432	-1.294658217
H	0.073802425	0.852616366	-2.686690688

e. a CI between T1 and T2 optimized at the CAS(6,5)/6-31G* level : AC_T_2T_1

C	-0.003266000	0.082527000	0.672872000
C	0.048149000	-0.072118000	-0.684096000
C	0.030970000	1.044644000	-1.639275000
O	0.015112000	-0.953893000	1.481315000
H	-0.060854000	1.056370000	1.133484000
H	0.104510000	-1.073844000	-1.070059000
H	-0.024896000	2.059601000	-1.297579000
H	0.073923000	0.860196000	-2.693027000

f. a minimum of trans-acrolein in the T1(ππ*) state optimized at the CAS(6,5)/6-31G* level : AC_T_1(ππ*)

C	0.389819000	-0.057711000	0.807238000
C	0.105461000	-0.172617000	-0.601692000
C	-0.096548000	0.988907000	-1.478500000
O	0.555911000	-1.031842000	1.526235000
H	0.455469000	0.944269000	1.225917000
H	0.043587000	-1.172131000	-0.999275000
H	-1.091591000	1.301171000	-1.742274000
H	0.703164000	1.335763000	-2.108851000

g. a minimum of trans-acrolein in the T1(nπ*) state optimized at the CAS(6,5)/6-31G* level : AC_T_1(nπ*)

C	-0.0037381129	0.1082287302	0.6526340146
C	0.0481907171	-0.0433537641	-0.7231548823
C	0.0317706971	1.0135689512	-1.6207858628
O	0.0143591911	-0.9460558653	1.4953842544
H	-0.0618546649	1.0469102394	1.1705018066
H	0.1046349159	-1.0485385802	-1.1045282999
H	-0.0238251280	2.0339830947	-1.2885843108
H	0.0741104384	0.8387398772	-2.6778326498s

h. a ISC between T1 and S0 optimized at the CAS(6,5)/6-31G* level: AC_T_1S_0

C	0.002613472	0.049798491	0.735616689
C	0.047315575	-0.062833880	-0.692483886
C	0.031779608	1.098584298	-1.593879115
O	0.009476843	-0.934662857	1.471779926
H	-0.037312718	1.045821244	1.167707099
H	0.090808652	-1.060847065	-1.095750413
H	-0.897836296	1.462623895	-1.993615598
H	0.932105559	1.405518688	-2.095020256

S2. Cartesian coordinates of the optimized structures of 2-cyclopentenone.

a. a minimum of 2-cyclopentenone in the ground state optimized at the CAS(8,7)/6-31G* level : CPO_S_0

O	0.044410000	1.743774000	-0.043270000
C	-0.004657000	0.521077000	-0.015645000
C	-1.275513000	-0.316229000	0.068218000
C	1.145884000	-0.409564000	-0.057256000
C	-0.796434000	-1.782972000	0.073879000
C	0.711786000	-1.677851000	-0.007602000
H	-1.823835000	-0.052270000	0.965068000
H	-1.914613000	-0.088622000	-0.777071000
H	-1.100479000	-2.310022000	0.972884000
H	-1.191216000	-2.346113000	-0.765989000
H	2.163468000	-0.074988000	-0.117910000
H	1.342681000	-2.547672000	-0.022661000

b. a minimum of 2-cyclopentenone in the S1 state optimized at the CAS(8,7)/6-31G* level : CPO_S_1

O	0.023154000	1.756465000	-0.052505000
C	0.070040000	0.418358000	-0.026261000
C	-1.244711000	-0.394123000	0.005320000
C	1.172325000	-0.395064000	-0.049509000
C	-0.729878000	-1.858682000	0.042688000
C	0.776284000	-1.746262000	-0.023662000
H	-1.838896000	-0.135121000	0.874736000
H	-1.841996000	-0.183163000	-0.875303000
H	-1.050063000	-2.359114000	0.952169000
H	-1.128879000	-2.435102000	-0.786518000
H	2.186825000	-0.046953000	-0.084218000
H	1.440287000	-2.586966000	-0.013796000

c. a transition state for C-C bond cleavage in the S1 state optimized at the CAS(8,7)/6-

31G* level : TS_S_1

O	0.011739000	1.762735000	0.200279000
C	0.275504000	0.586159000	0.093365000
C	-1.370065000	-0.479168000	-0.029173000
C	1.195692000	-0.402585000	-0.077350000
C	-0.753595000	-1.860572000	0.113803000
C	0.717577000	-1.729796000	-0.181709000
H	-2.014850000	-0.124143000	0.756169000
H	-1.706743000	-0.199225000	-1.013588000
H	-0.910353000	-2.232539000	1.124210000
H	-1.244651000	-2.558918000	-0.559188000
H	2.235135000	-0.137070000	-0.123674000
H	1.371049000	-2.579725000	-0.183672000

d. a ISC between S1 and T2 optimized at the CAS(8,7)/6-31G* level : CPO_S_1T_2

O	0.064438203	1.740941223	0.105037244
C	0.062971616	0.436319956	0.007576792
C	-1.242748363	-0.401909034	-0.032138153
C	1.166556636	-0.364613023	-0.079796284
C	-0.734693645	-1.861834442	0.043100700
C	0.759748921	-1.777154829	-0.167995127
H	-1.897248930	-0.137401866	0.790074460
H	-1.777918213	-0.201682140	-0.954725988
H	-0.952696551	-2.288561108	1.020150466
H	-1.216042586	-2.501877808	-0.689331137
H	2.177878323	-0.008692453	-0.091895662
H	1.424246589	-2.599261476	0.013083688

e. a minimum of a cyclopropylketene species in the S0 state optimized at the CAS(8,7)/6-31G* level : CK_S_0

O	0.123855000	1.656248000	0.888660000
C	0.567285000	0.750117000	0.321854000
C	-0.255582000	-2.355940000	-1.219949000
C	1.076466000	-0.274623000	-0.334765000
C	-0.864087000	-1.962906000	0.088746000
C	0.590125000	-1.673818000	-0.142727000
H	-0.513677000	-1.776254000	-2.088310000
H	-0.083804000	-3.400997000	-1.410598000
H	-1.553975000	-1.136812000	0.093829000
H	-1.114310000	-2.739751000	0.789676000
H	1.889801000	-0.058725000	-1.002607000
H	1.277258000	-2.322068000	0.377120000

f. a minimum of 2-cyclopentenone in the T1($\pi\pi^*$) state optimized at the CAS(8,7)/6-

31G* level : CPO_T_1($\pi\pi^*$)

O	0.000885000	1.724485000	0.332844000
C	-0.000689000	0.506252000	0.130041000
C	-1.242180000	-0.356083000	-0.085715000
C	1.161088000	-0.366299000	0.114478000
C	-0.757701000	-1.796411000	0.212421000
C	0.703331000	-1.761927000	-0.197987000
H	-2.059648000	-0.028808000	0.544246000
H	-1.563836000	-0.260383000	-1.119740000
H	-0.839339000	-1.992055000	1.278794000
H	-1.327752000	-2.554949000	-0.308612000
H	2.149058000	-0.059867000	0.393296000
H	0.946719000	-2.148587000	-1.178347000

g. a minimum of 2-cyclopentenone in the T1($n\pi^*$) state optimized at the CAS(8,7)/6-31G* level : CPO_T_1($n\pi^*$)

O	0.025299751	1.756125043	-0.076613262
C	0.065862430	0.417063186	-0.042088894
C	-1.246067400	-0.392444495	0.011969442
C	1.172790412	-0.401067040	-0.048487693
C	-0.729365109	-1.856796931	0.038082493
C	0.778270078	-1.740835746	-0.003248984
H	-1.820854093	-0.136307949	0.895466168
H	-1.864107096	-0.182823643	-0.854432070
H	-1.065568701	-2.373444076	0.932236232
H	-1.109807944	-2.420152444	-0.808881625
H	2.186996762	-0.052283338	-0.083249383
H	1.441042911	-2.582759569	0.002388577

h. a CI between T1 and T2 optimized at the CAS(8,7)/6-31G* level : CPO_T_2T_1

O	0.049909	1.787655	-0.085622
C	0.024745	0.482351	-0.117902
C	-1.290817	-0.335815	-0.033396
C	1.116942	-0.340639	-0.172788
C	-0.801263	-1.799476	0.105712
C	0.691593	-1.743949	-0.117490
H	-1.889155	-0.007587	0.808456
H	-1.879731	-0.184964	-0.932090
H	-1.023831	-2.180776	1.100185
H	-1.293874	-2.464040	-0.597087
H	2.132271	-0.001335	-0.234114
H	1.351496	-2.576011	0.023529

i. a ISC between T1 and S0 optimized at the CAS(8,7)/6-31G* level : CPO_T_1S_0

O	0.007793125	1.728087658	0.095179258
C	0.029455116	0.533934302	-0.014159352
C	-1.202620531	-0.383607896	-0.097723015
C	1.239144145	-0.402636597	0.073910334
C	-0.665265086	-1.797876037	0.261475016
C	0.711997755	-1.713878675	-0.371653240
H	-1.991011632	-0.024213696	0.553057022
H	-1.586090729	-0.370799448	-1.114692314
H	-0.600953732	-1.907645620	1.340375573
H	-1.280165998	-2.599017112	-0.128534688
H	1.836388218	-0.331068830	0.967801322
H	0.671265232	-1.825912386	-1.449315927

k. a CI between S1 and S0 optimized at the CAS(8,7)/6-31G* level : CPO_S_1S_0

O	0.299583000	1.899750000	0.384005000
C	0.568526000	0.775847000	0.181324000
C	-1.637813000	-0.691546000	-0.104431000
C	1.242898000	-0.386345000	-0.062107000
C	-0.790653000	-1.910721000	0.129090000
C	0.665003000	-1.656306000	-0.159893000
H	-2.415663000	-0.434450000	0.590461000
H	-1.759805000	-0.333520000	-1.111180000
H	-0.901556000	-2.244813000	1.159605000
H	-1.139767000	-2.735621000	-0.491255000
H	2.304783000	-0.266470000	-0.186889000
H	1.314699000	-2.494197000	-0.328767000

S3: the fitting details to obtain the S_1 lifetime and ISC time

To obtain the lifetime, the range from τ_0 to 8000 or 16000 fs of the decay curves in Figure 10 of the manuscript text has been fitted to the formula

$$P(t) = \exp\left(-\frac{t - \tau_0}{\tau_1}\right),$$

where τ_0 is the initial delay or latency time and τ_1 is the delay constant. The decay constants τ_1 reflects the reaction rate of the nonadiabatic $S_1 \rightarrow S_0$ or T_2 deactivation after the first trajectories reached the intersection or crossing point. Here, we make an assumption of a purely exponential decay with complete depletion of the excited state in the long time limit.