Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information: **Substitution effect on the nonradiative decay and *trans* → *cis* photoisomerization route: a guideline to develop efficient cinnamate based sunscreens**

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Contents:

1. Energy diagram and spin-orbit coupling (SOC) values of minimum energy seam of crossings (MESXs) between the singlet ($^1\pi\pi^*$ or $^1n\pi^*$) and triplet (T_2, T_3) states

We found several low-lying MESXs between 1 singlet ($^1\pi\pi^*$ or $^1n\pi^*$) and triplet (T_2, T_3) states as displayed in Figure S1. MESXs 4 and 5 have very small SOC values due to the El-Sayed's rule and they have minor contributions to the triplet mediated photoisomerization root. The MESX 1 is the dominant ISC channel.

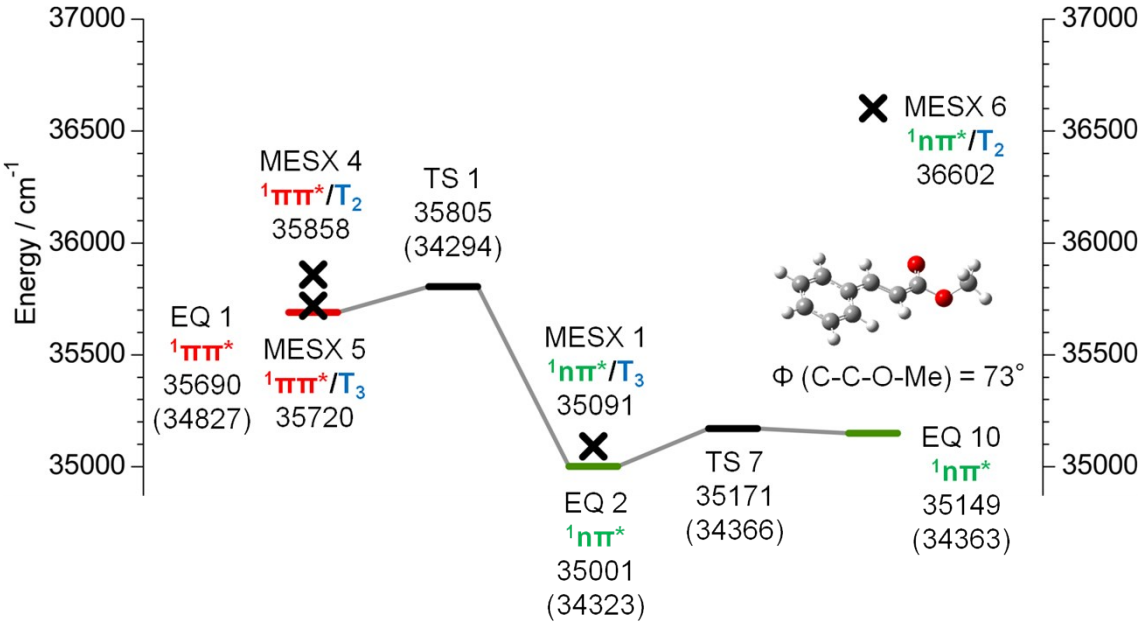


Figure S1 The energy diagram of the EQs, TSs and MESXs between the singlet ($^1\pi\pi^*$ or $^1n\pi^*$) and triplet (T_2, T_3) state of methylcinnamate (MC). The values in parentheses are the zero-point vibrational energy corrected ones. MESXs are indicated as crosses.

Table S1. The calculated SOC values (cm^{-1}) of MESXs at the ωB97XD/6-311G(d,p) level.

Structure	Character	SOC value / cm^{-1}
MESX 4	$^1\pi\pi^*/^3\pi\pi^*$ (T_2)	0.07443
MESX 5	$^1\pi\pi^*/^3\pi\pi^*$ (T_3)	0.2572
MESX 1	$^1n\pi^*/^3\pi\pi^*$ (T_3)	24.09
MESX 6	$^1n\pi^*/^3\pi\pi^*$ (T_2)	26.37

2. The energy and geometric structures of minimum energy conical intersections (MECIs) between T_2 and T_1 states, and decay route from MECI 5 (T_2/T_1)

We also searched the MECI between T_2 and T_1 states using SC-AFIR method as explained in section 2.1 of the main text. The resultant nine MECIs are summarized in Figure S2.

We found that the MECI 5, which is basically the mirror inversion structure of the MECI 3, can be accessible from the EQ 11 (mirror inversion structure of EQ 6). The small deviations in energy among these mirror inversion structures may be originated from the numerical errors in the TD-DFT calculations and/or geometry optimization. The methoxy tilted T_1/T_2 MECI like MECIs 3 and 5 is also energetically preferable for *p*-MMC.[18] The structural change on the T_2 state from EQ 3 to MECI 5 is essentially same as those to MECI 3 since the MC molecule at EQ 3 belongs to C_s point group. After the $T_2 \rightarrow T_1$ IC, MC molecule reaches the EQ 8. EQ 8 and EQ 7 co-exist due to large excess energy in the T_1 state.

We also tried to search intermediates and TSs between the other low-lying T_2/T_1 MECI and other EQs in the T_2 and T_1 states by using meta-IRC and SC-AFIR methods. However, it was unsuccessful due to serious SCF convergence problems on the TD-DFT calculations.

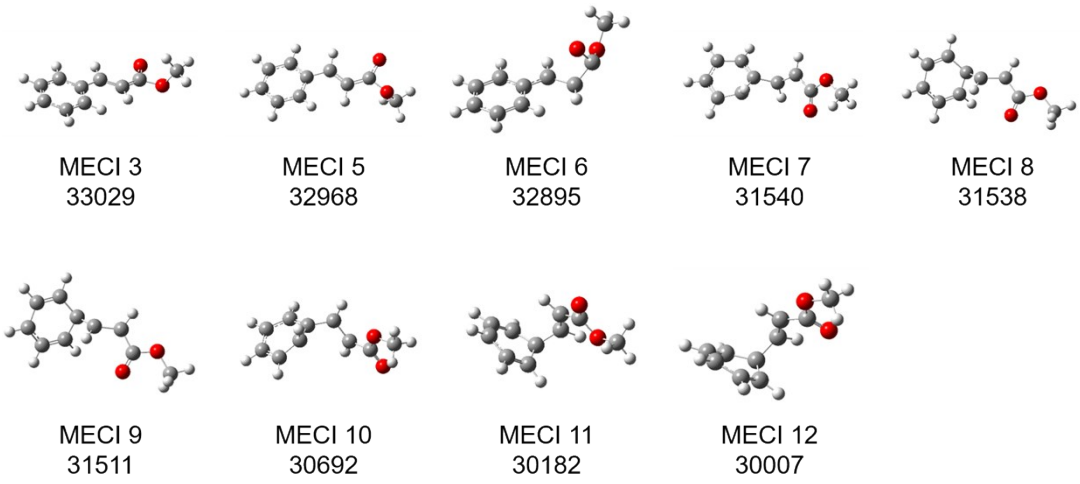


Figure S2 The energies (cm^{-1}) and structures of MECIs (T_2/T_1) in the region around 30000-33000 cm^{-1} obtained by SC-AFIR/TD-DFT calculation at ωB97XD/6-311G(d,p) level.

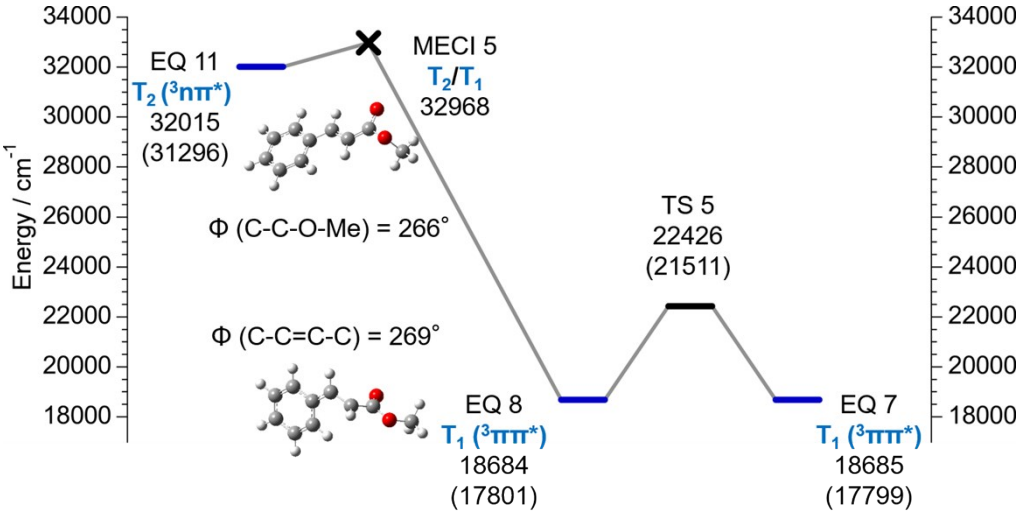


Figure S3 The T_2/T_1 pathway which competes with the main pathway of Figure 1 in the text. The values in parentheses are the zero-point vibrational energy corrected ones.

3. Energy diagram of isomerization on the S_0 state

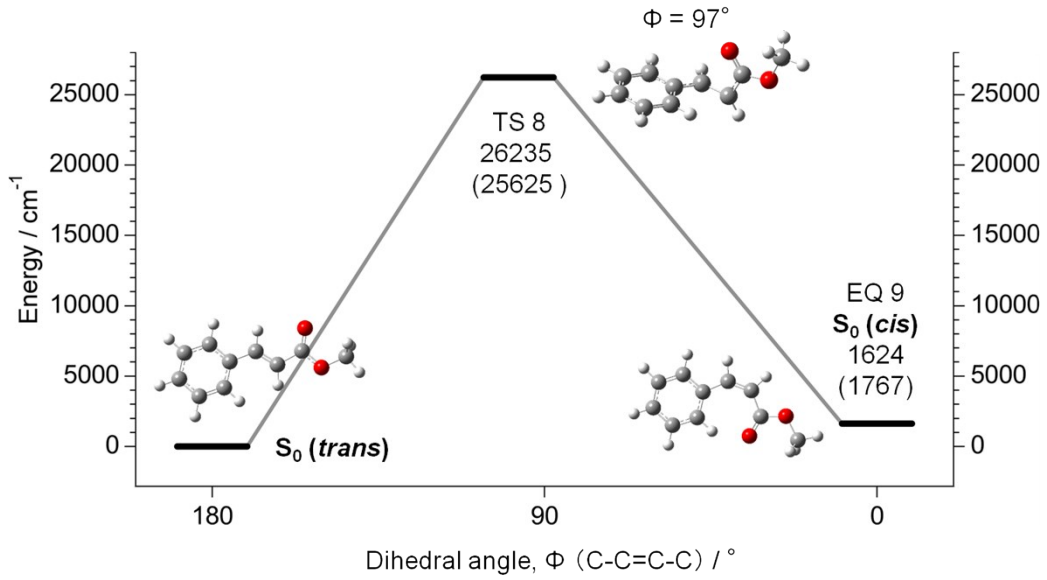


Figure S4 Energy diagram for the isomerization on the S_0 state. The values in parentheses are the zero-point vibrational energy corrected ones. The x-axis represents dihedral angle, Φ (C-C=C-C), where Φ of *trans*-form is set as 180°. TS 8 is TS between S_0 (*trans*) and S_0 (*cis*)

4. Vertical transition energies and their characters of MC and *para*-substituted MC

Table S2. The vertical transition energies in cm^{-1} of (a) MC, (b) *para*-hydroxy MC (*p*-HMC) and (c) *para*-methoxy MC (*p*-MMC) at the $^1\pi\pi^*$ minima calculated at ωB97XD/6-311G(d,p) level. Characters of their transitions are also listed.

(a) MC

State	Character	*Energy* / cm^{-1}
T_1	ππ*	14026
T_2	ππ*	31259
T_3	ππ*	33183
T_4	nπ*	33632
T_5	ππ*	38174
S_1	ππ*	32605
S_2	nπ*	36295
S_3	ππ*	38322

(b) *p*-HMC

State	Character	*Energy* / cm^{-1}
T_1	ππ*	14673
T_2	ππ*	31494
T_3	ππ*	33021
T_4	nπ*	34650
T_5	ππ*	36002
S_1	ππ*	31879
S_2	nπ*	37336
S_3	ππ*	38289

(c) *p*-MMC

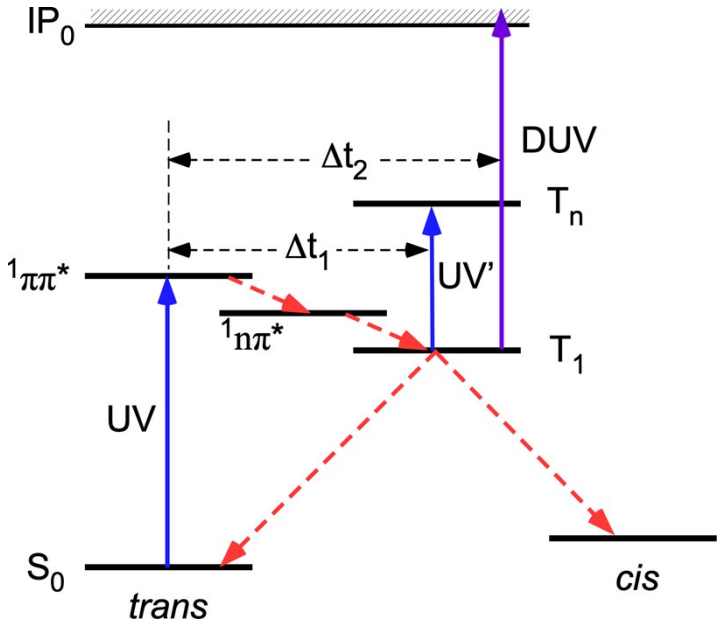
State	Character	*Energy* / cm^{-1}
T_1	ππ*	14819
T_2	ππ*	31609
T_3	ππ*	33108
T_4	nπ*	34729
T_5	ππ*	35864
S_1	ππ*	31691
S_2	nπ*	37425
S_3	ππ*	38242

Table S3. The major electron configurations of $^1\pi\pi^*$ (1) and $^1\pi\pi^*$ (2) states at $^1\pi\pi^*$ (1) minmum for MC, *p*-HMC, *p*-MMC, *m*-HMC, and *o*-HMC calculated at the ωB97XD/6-311G(d,p) level at the $^1\pi\pi^*$ minimum of each molecule.

	Electron configuration	
Molecule	$^1\pi\pi^*$ (1)	$^1\pi\pi^*$ (2)
MC	0.70 HOMO→LUMO	0.58 HOMO-1→LUMO 0.36 HOMO→LUMO+1
p-HMC	0.70 HOMO→LUMO	0.39 HOMO-2→LUMO 0.56 HOMO→LUMO+1
p-MMC	0.70 HOMO→LUMO	0.40 HOMO-2→LUMO 0.56 HOMO→LUMO+1
m-HMC	0.67 HOMO→LUMO	0.63 HOMO-1→LUMO -0.26 HOMO→LUMO+1
o-HMC	0.69 HOMO→LUMO	0.64 HOMO-1→LUMO -0.24 HOMO→LUMO+1

5. Detection of transient absorption from the T_1 ($^3\pi\pi^*$) state

Transient absorption spectroscopy (TAS) is a possible experimental set-up to examine the generation and decay of T_1 ($^3\pi\pi^*$) state, and its time constant. Since T_1 decays in the time scale of a few tens of nanoseconds, we can apply nanosecond pump-probe spectroscopy with UV-UV'-DUV setup. In this scheme (Scheme S1), a tunable UV' laser pulse is introduced with the timing between the UV and DUV pulses, where the UV' pulse excites the T_1 state molecule to T_n. By scanning the UV' frequency we will observe the $T_1 \rightarrow T_n$ transition as the modulation (either depletion or enhancement) of the ion intensity monitored by DUV pulse.



Scheme S1. Energy levels of cinnamates and the UV-UV'-DUV pump-probe-probe scheme to measure the $T_1 \rightarrow T_n$ transient absorption spectrum.

In order to assess the feasibility of the TAS experiment for the T_1 ($^3\pi\pi^*$) state, we simulated the excited state absorption from the T_1 ($^3\pi\pi^*$) state at the multi-state multi-reference complete active space second order perturbation theory (MS-CASPT2).[75] We computed the 20 low-lying triplet (T_n) states both at the of EQs 7 and 8 in the T_1 state optimized at the ωB97X-D/6-311G(*d,p*) level of theory. We used OpenMOLCAS 18.09 quantum chemistry package.[76] We chose the ANO-RCC-VTZP basis set[77] for the all atoms and used Cholesky decomposition technique (threshold: 1.0×10^{-4}) to reduce the computational costs[78] of two-electron integral

and subsequent calculations. The reference wave function of MS-CASPT2 calculations were constructed by the state-averaged complete active state self-consistent field (SA-CASSCF) theory.[79] The averaged energy of T_n (n = 1-20) were minimized with the equal-weight. Base on the molecular orbital energies evaluated at the Hartree-Fock/ANO-RCC-TZVP level of theory, we included four π orbitals, three π^* orbitals, one lone-pair n orbital on CO group, and the lowest 3*s* Rydberg orbital (in total 9 orbitals) to our active space for the SA-CASSCF and subsequent MS-CASPT2 calculations as shown in Figure S5. The 10 electrons in the four π and one n active orbitals are treated as the active electrons. Hereafter, we call our active space as the [10e, 9o] active space. For the MS-CASPT2 calculations, we used 0.25 au of the IP-EA shift to avoid intruder state problems.[80] The oscillator strength *f* and transition energy D_0 were evaluated by the complete-active space state interaction method.[81]

The averaged absorption spectra at EQs 7 and 8 were convoluted by a normalized Gaussian function with FWHM = 1000 cm^{-1} and averaged over the Boltzmann weight at temperature of 742 K (EQ 7:8 = 1:1), which corresponds to the excess energy in the T_1 state.

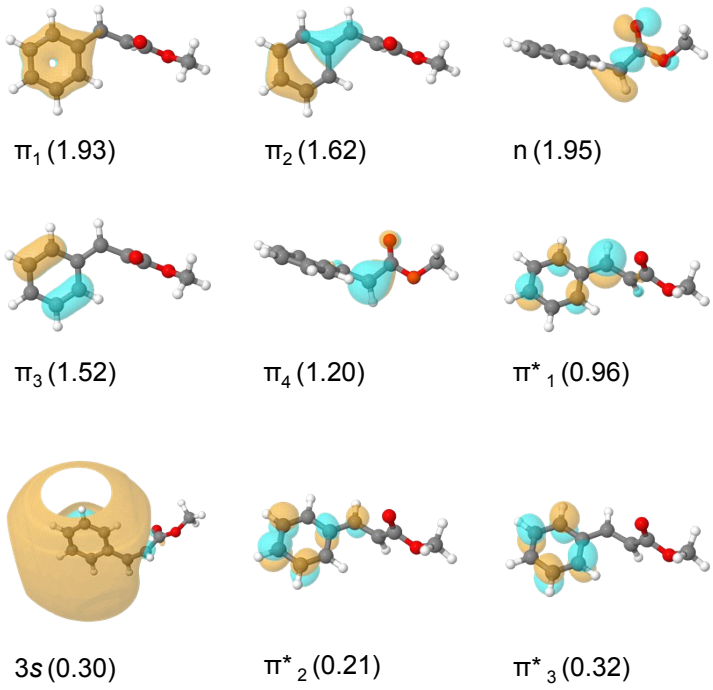


Figure S5 The 9 natural orbitals and their characters at the EQ 7 obtained at the 20 states SA-CASSCF/ANO-RCC-VTZP. The occupation numbers are written in the paraeneses.

The calculated one-photon $T_1 \rightarrow T_n$ excited state UV-DUV absorption spectra at the [10e, 9o]-MS-CASPT2/ANO-RCC-VTZP//ωB97X-D/6-311G(*d,p*) level of theory are displayed in Figure S6. The assignment of pronounced absorption bands A, B and C were summarized in Table S3 and S4 for EQ 7 and 8, respectively. We found that the line shape of the spectra at EQs 7 and 8 are quite similar each other. Hereafter, we discuss the spectrum at EQ7 in detail.

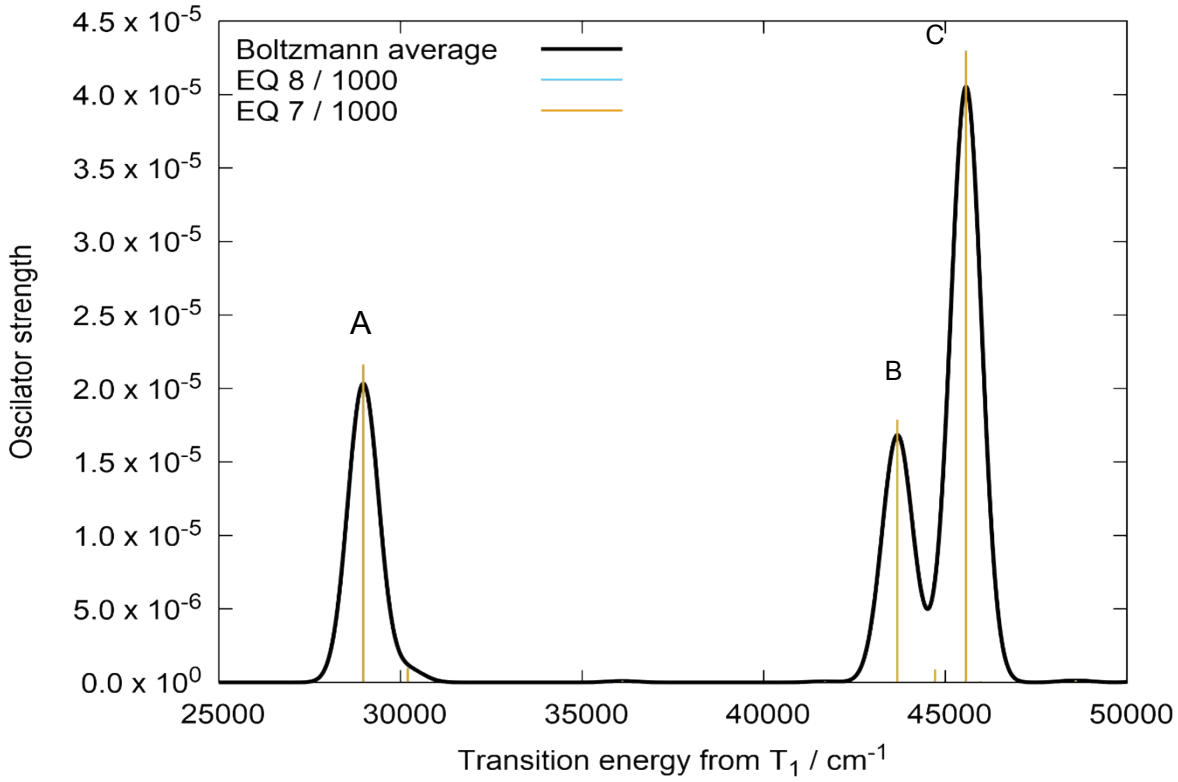


Figure S6 The calculated $T_1 \rightarrow T_n$ absorption spectra at the EQ 7 (orange) and 8 (blue), and its Boltzmann average (black) at 742 K (EQ 7:8 = 1:1). Bar graphs indicate the peak positions in cm^{-1} and oscillator strengths (scaled by 1/1000). Bold line-spectra are the convolution of the bar spectra using a normalized Gaussian function with FWHM = 1000 cm^{-1}. Result at the [10e, 9o]-MS-CASPT2/ANO-RCC-VTZP//ωB97X-D/6-311G(*d,p*) level of theory.

In Figure S6, the lowest band A is located around 29000 cm^{-1} (Figure S6 and table S2), which consists of $T_1 \rightarrow T_2$ ($\pi_2 \rightarrow \pi^*_1$) transition. The second lowest band B is located around 44000 cm^{-1}. The $T_1 \rightarrow T_7$ ($\pi^*_1 \rightarrow \pi^*_3$) transition contributes to this band. The highest

energy band C located locates at around 46000 cm^{-1}, which comes from $T_1 \rightarrow T_9$($\pi_2 \rightarrow \pi_4$) transition. The oscillator strengths of these bands are the order of 10^{-2}. This indicates that strong pump and probe pulses and long data accumulation time are essential to obtain TAS of the T_1 state with sufficient signal to noise ratio. UV-DUV time-resolved photo-ion spectroscopy that we reported and/or UV-DUV time-resolved photoelectron spectroscopy will be alternative choices. A DUV probe pulse generated by synchrotron radiation[82] or free electron laser[83] will be helpful to obtain strong signal for these proposed experiments. In addition, time-resolved vibrational spectroscopy of the T_1 state[84] with nanosecond laser will also be feasible.

Table S4 The assignment of $T_1 \rightarrow T_n$ absorption bands A, B and C at EQ 7 at the [10e, 9o]-MS-CASPT2/ANO-RCC-VTZP//ωB97X-D/6-311G(*d,p*) level of theory. The main electron configurations are written in energetical order of active molecular orbital: [π_1, π_2, n, π_3, π_4, π^*_1, 3*s*, π^*_2, π^*_3]. The "u" and "d" indicate an electron with up and down spin, respectively.

Final state	**Transition energy D_0 /cm^{-1}**	***f***	**Band**	**Main electron configuration [π_1, π_2, n, π_3, π_4, π^*_1, 3s, π^*_2, π^*_3]**	**Coefficient of main configuration**
T_1	0	---	---	[2, 2, 2, 2, u, u, 0, 0, 0]	−0.95
T_2	28975	0.022	A	[2, u, 2, 2, u, 2, 0, 0, 0]	0.72
T_7	43678	0.018	B	[2, 2, 2, 2, u, 0, 0, 0, u]	0.56
T_9	45570	0.043	C	[2, u, 2, 2, 2, u, 0, 0, 0]	0.89

Table S5. The assignment of $T_1 \rightarrow T_n$ absorption bands A, B and C at EQ 11 at the [10e, 9o]-MS-CASPT2/ANO-RCC-VTZP//ωB97X-D/6-311G(*d,p*) level of theory. The main electron configurations are written in energetical order of active molecular orbital: [π_1, π_2, n, π_3, π_4, π^*_1, 3*s*, π^*_2, π^*_3]. The "u" and "d" indicate an electron with up and down spin, respectively.

Final state	**Transition energy D_0 /cm^{-1}**	***f***	**Band**	**Main electron configuration [π_1, π_2, n, π_3, π_4, π^*_1, 3s, π^*_2, π^*_3]**	**Coefficient of main configuration**
T_1	0	---	---	[2, 2, 2, 2, u, u, 0, 0, 0]	0.95
T_2	28973	0.022	A	[2, u, 2, 2, u, 2, 0, 0, 0]	−0.73
T_7	43678	0.018	B	[2, 2, 2, 2, u, 0, 0, 0, u]	0.56
T_9	45571	0.043	C	[2, u, 2, 2, 2, u, 0, 0, 0]	0.88

6. Computational detail for Spin-orbit coupling (SOC) constant between T_1 and S_0 states at T_1/S_0 MESXs

The Spin-orbit coupling (SOC) constant between T_1 and S_0 states at T_1/S_0 MESXs 2 and 3 were evaluated at the [10e, 9o]-MS-CASPT2/ANO-RCC-VTZP//ωB97X-D/6-311G(*d,p*) level of theory as described for the TAS calculation. The reference wave function of MS-CASPT2 calculations were constructed by the SA-CASSCF theory. The averaged energy of the two-lowest energy states in singlet (S_0 and S_1) and triplet (T_1 and T_2) states were minimized in each spin state with equal-weight. We used mean field spin-orbit Hamiltonian and SOC between the T_1 and S_0 states.[85] The SOC values were evaluated by using restricted active space state interaction approach.[86]

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7. Appendix: Cartesian coordinates, energies and lowest frequency vibrations for the optimized structures

All of the optimized structures were calculated at (TD-, U)ωB97XD/6-311G(d,p) level. The cartesian coordinates (Å), absolute energies (Abs. E / Hartree), relative energies (Rel. E / cm^{-1}) and lowest frequency vibrations (Freq. / cm^{-1}) of each optimized structure are listed. It is noted that the value of freq. of the transient state (TS) is negative. The value in parentheses is the zero-point vibrational energy corrected one (ZPE).

S_0 (*trans*)
Abs. E = -537.479702475512 (ZPE = -537.301589)
Rel. E = 0 (ZPE = 0)
Freq. = 18.67935258

C	3.728143186654	0.702063625575	-0.000000001047
C	2.386078703425	1.057267030441	-0.000000000419
C	1.383827435939	0.082994449442	0.000000000562
C	1.764203225912	-1.264242492737	0.000000001050
C	3.102831275290	-1.619834390665	0.000000000459
C	4.089991004765	-0.638262331716	-0.000000000620
H	4.490541881855	1.472470001127	-0.000000001852
H	2.104710616893	2.105220027437	-0.000000000746
H	1.009076993473	-2.041767704967	0.000000001990
H	3.380780407387	-2.667591624705	0.000000000866
H	5.136634093323	-0.920288171134	-0.000000001089
C	-0.016417066597	0.516869618583	0.000000000992
C	-1.105046434644	-0.255448110807	0.000000000292
H	-0.185201652433	1.591706664015	0.000000001821
H	-1.071515242652	-1.338081154840	-0.000000000770
C	-2.445318555112	0.365546812063	0.000000000677
O	-2.677918072481	1.548221308997	0.000000002050
O	-3.404496248809	-0.575344484082	-0.000000000822
C	-4.743987107294	-0.085541189189	-0.000000000836
H	-4.931193881652	0.521400212348	-0.887743792000
H	-4.931193882401	0.521400210315	0.887743791556
H	-5.380343488282	-0.967716612617	-0.000000002112

Figure 1
EQ 1: $^1\pi\pi^*$
Abs. E = -537.317084959649 (ZPE = -537.1429074)
Rel. E = 35690 (ZPE = 34827)
Freq. = 23.33250821

C	3.744252223376	0.680779144166	-0.000000367064
C	2.448630567502	1.111416302198	-0.000004104760
C	1.355645384125	0.175790785849	-0.000003154361
C	1.689032810548	-1.238797205233	0.000001810081

C	3.005386295479	-1.642525610734	0.000005534091
C	4.038972865478	-0.705196704538	0.000004496317
H	4.556062001090	1.398676599861	-0.000001157182
H	2.215980182916	2.170814810633	-0.000008024016
H	0.894696381571	-1.974104845867	0.000003710911
H	3.242643506105	-2.700375170190	0.000009442791
H	5.071381164133	-1.035343902644	0.000007208902
C	0.031988507645	0.622462873348	-0.000006133055
C	-1.091035931471	-0.235831085139	-0.000008602182
H	-0.174227290048	1.688067797298	-0.000005353572
H	-1.002106713175	-1.314658668668	-0.000019039221
C	-2.415844279330	0.331493363185	-0.000000217486
O	-2.668479023912	1.526085956672	0.000012424895
O	-3.377840546213	-0.623984901779	-0.000007692847
C	-4.712695114731	-0.136238077885	0.000002177523
H	-4.904625305375	0.472830024867	-0.886778697143
H	-4.904621198726	0.472804787235	0.886801328310
H	-5.351034002537	-1.017984426199	-0.000008737380

TS 1
Abs. E = -537.316561283721 (ZPE = -537.1453323)
Rel. E = 35805 (ZPE = 34294)
Freq. = -454.39879413

C	3.727797347747	0.693153815272	0.060244689126
C	2.420886388512	1.103995963264	0.085061329336
C	1.349165356777	0.158845377157	0.015805633711
C	1.698835774369	-1.229295186803	-0.124892209346
C	3.021691121297	-1.620409562231	-0.139148480119
C	4.042793369457	-0.676449355123	-0.043456200928
H	4.526486633365	1.423316266800	0.122731432684
H	2.175494093103	2.157117035623	0.172279941989
H	0.914100827097	-1.967027328143	-0.239619500739
H	3.269517190301	-2.671368265825	-0.237510848002
H	5.079336773436	-0.992945136401	-0.058175568833
C	0.012769001295	0.582938865561	0.108245243469
C	-1.094448676208	-0.293929032472	0.194306255890
H	-0.203442925130	1.646953034178	0.115311991855
H	-0.987686836223	-1.359526768214	0.362714538550
C	-2.392141541714	0.237840793934	-0.015201069906
O	-2.576969308848	1.377951025550	-0.471858076167
O	-3.417899678970	-0.581636073887	0.283126220024
C	-4.719524379052	-0.076690528110	0.001633307491
H	-4.850070480443	0.086190345359	-1.070728214769
H	-4.892744238059	0.866046020314	0.525743379230
H	-5.411783327671	-0.838889459354	0.353383059011

MECI 1: $^1\pi\pi^*/^1n\pi^*$
Abs. E = -537.313481916336
Rel. E = 36481

C	3.743190869339	0.683508521045	-0.000037958499
C	2.430512653110	1.088840626283	-0.000667815635
C	1.363513557530	0.142986250875	-0.000518292572
C	1.718891730717	-1.243931179877	-0.000048910586
C	3.042821476975	-1.632942085628	0.000817892609
C	4.064775099372	-0.683856387173	0.000687493754
H	4.536923046805	1.423128693298	-0.000055624261
H	2.185630375291	2.146651279636	-0.000889225758
H	0.941379138780	-1.999248175113	-0.000161650538
H	3.290289985004	-2.689527599760	0.001182718038
H	5.102610828280	-0.998885053831	0.001108867738
C	0.021256455701	0.589592103084	-0.000722315450
C	-1.103980038704	-0.252064467348	-0.001063853146
H	-0.157800538353	1.660098885003	-0.001371011260
H	-1.030742093860	-1.333557691183	-0.000493591998
C	-2.409095885171	0.278551539596	-0.000540350182
O	-2.668301764324	1.507494575967	0.001034932640
O	-3.413769640727	-0.619270208055	-0.001466213100
C	-4.738393009977	-0.096098483516	0.000430004981
H	-4.918542638919	0.512710586222	-0.887974810361
H	-4.917689918245	0.507978096865	0.892260399275
H	-5.391317204458	-0.965977980375	-0.001513832076

EQ 2: $^1n\pi^*$
Abs. E = -537.320228232678 (ZPE = -537.1452014)
Rel. E = 35001 (ZPE = 34323)
Freq. = 4.66132613

C	3.748901047951	0.694109909007	-0.000042594103
C	2.416749107383	1.072451851260	-0.000059999075
C	1.382520706346	0.117956220794	0.000027283347
C	1.756454208973	-1.239190706308	0.000161154986
C	3.089537830611	-1.612957975113	0.000172757463
C	4.097158093443	-0.652471826107	0.000067354927
H	4.522140786598	1.454578641147	-0.000121036916
H	2.157738881783	2.126510632964	-0.000157081118
H	0.996042229560	-2.011745587348	0.000268128410
H	3.347796004588	-2.666416416273	0.000271044657
H	5.138986078212	-0.950737235741	0.000076162158
C	0.010942014823	0.564209521170	-0.000051803834
C	-1.109674058815	-0.257637735837	-0.000195882185

H	-0.133095528423	1.638960889298	-0.000051377628
H	-1.046955609774	-1.339124576350	-0.000305008645
C	-2.394758351754	0.230511031490	-0.000281888992
O	-2.689486848065	1.505779120432	-0.000033300601
O	-3.454126677448	-0.583748510534	-0.000715421916
C	-4.771318080130	-0.020988848100	0.000120335883
H	-4.938213429311	0.582454861506	-0.894306667006
H	-4.937578358422	0.581234814099	0.895489010214
H	-5.441342880188	-0.876396296736	-0.000231981326

MESX 1: $^{1}n\pi^*/T_3$ ($^{3}\pi\pi^*$)
Abs. E = -537.319818171334
Rel. E = 35091

C	3.751630643959	0.693812388432	-0.001179784033
C	2.417123599607	1.073847500675	-0.000726568268
C	1.383467819150	0.120452696236	0.000486034422
C	1.754920764625	-1.243634080158	0.001412575248
C	3.090580663205	-1.619999530141	0.000910808510
C	4.100038445861	-0.660069868147	-0.000401063040
H	4.525903731783	1.452889562027	-0.002145935501
H	2.159210642354	2.128049474191	-0.001395254608
H	0.992213121512	-2.013550474815	0.002761395792
H	3.347246878194	-2.673687334491	0.001660110584
H	5.141650057035	-0.958363767250	-0.000731371087
C	0.007179525409	0.570758090154	0.000750268356
C	-1.111343459401	-0.243471660866	-0.000500978391
H	-0.136763299299	1.645698866403	0.001857514371
H	-1.050973137925	-1.325340433495	-0.002373457004
C	-2.403508723883	0.254886614950	0.000316749278
O	-2.690021808539	1.521730669358	0.002932204817
O	-3.447917356156	-0.581657063607	-0.001801105062
C	-4.769031369646	-0.032480201936	-0.000617161798
H	-4.940469535988	0.572719337314	-0.893013242539
H	-4.940643969782	0.568404053358	0.894660285484
H	-5.432076064129	-0.893653059457	-0.002762836836

MECI 2: T_3/T_2
Abs. E = -537.328987627220
Rel. E = 33078

C	3.760658317960	0.686735671849	-0.002232397934
C	2.409125992875	1.071580882044	-0.001931599201
C	1.384885553528	0.132338955276	0.001159411551
C	1.749347305054	-1.247715701316	0.004329234214
C	3.100646234672	-1.630553535434	0.003951229182

C	4.106605666300	-0.680611716347	0.000677151716
H	4.534695969199	1.444997744313	-0.004734959450
H	2.158454663969	2.127509991352	-0.004278269492
H	0.984014123123	-2.013881960617	0.007378018652
H	3.350905411018	-2.685601241625	0.006379563719
H	5.147897737618	-0.979171728959	0.000419444001
C	0.002143025983	0.595473735646	0.000945615581
C	-1.113698938441	-0.204521301486	0.001139763422
H	-0.137682339360	1.671302460228	0.000385956933
H	-1.055340748810	-1.287083544613	0.001178951556
C	-2.426842349746	0.302383690174	0.001116122738
O	-2.703787141344	1.544168553602	0.001183012672
O	-3.437271666501	-0.585686033889	0.001018802930
C	-4.765332792192	-0.065619459640	0.000961468672
H	-4.949024444241	0.537560288412	-0.891135258252
H	-4.949126665295	0.537504750706	0.893078993036
H	-5.415371484402	-0.937326537369	0.000901611824

EQ 3: T_2 ($^3\pi\pi^*$)
Abs. E = -537.341495281967 (ZPE = -537.1696881)
Rel. E = 30333 (ZPE = 28949)
Freq. = 13.92410091

C	3.793393697448	0.698844606379	0.059751635398
C	2.368478068273	1.071345122809	0.045405581000
C	1.384847409522	0.133014806360	-0.009906612163
C	1.757391637578	-1.255431124886	-0.060239713576
C	3.173425777574	-1.626139491335	-0.040582191641
C	4.149061126703	-0.669289751250	0.017111997758
H	4.546386106852	1.474174837214	0.104075758762
H	2.108775961226	2.123892613909	0.082327130261
H	1.008045066150	-2.032061388284	-0.125005142480
H	3.434562163799	-2.677201473556	-0.073888823118
H	5.194840694097	-0.953000475755	0.030478947721
C	-0.011617607767	0.583961427953	-0.012340417139
C	-1.127113588978	-0.223360294351	-0.012798869120
H	-0.182300209037	1.656354471818	-0.010411309124
H	-1.068579172812	-1.304339815829	-0.007283888114
C	-2.458744146160	0.373865265756	-0.015859245242
O	-2.696708170186	1.561874639143	-0.019210411393
O	-3.420792487697	-0.569801165540	-0.014118871837
C	-4.757849861840	-0.078157737389	-0.016221931561
H	-4.945776068388	0.526686239820	-0.905637839241
H	-4.946634676269	0.531950647252	0.869403638675
H	-5.396135481031	-0.959179168488	-0.013915111985

TS 2

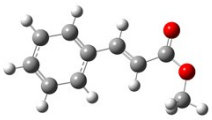
Abs. E = -537.322865070967 (ZPE = -537.1521798)

Rel. E = 34422 (ZPE = 32792)

Freq. = -107.8402207

C	3.651382045713	0.627279168666	-0.192999125342
C	2.285048588314	1.081963530696	0.099276288948
C	1.244231464056	0.212643187260	0.179880932385
C	1.501420175670	-1.195933418012	-0.017790787953
C	2.859084493348	-1.646017100690	-0.319294276293
C	3.892217628647	-0.757026529957	-0.400794859773
H	4.453729845403	1.350571165620	-0.248598123543
H	2.114699976933	2.142831790420	0.249199934750
H	0.710767068549	-1.926137781970	0.084664326284
H	3.031084013262	-2.704604257049	-0.474278138946
H	4.895948296520	-1.099167634847	-0.622880948574
C	-0.092579890671	0.747768943009	0.459601878931
C	-1.266023888276	0.033723636547	0.488247438321
H	-0.161465133573	1.812413179589	0.663156934392
H	-1.295441817404	-1.032517272609	0.297128816603
C	-2.528363339051	0.693211437156	0.794823850083
O	-2.644041666219	1.861140864344	1.080300149815
O	-3.617403114624	-0.143860369895	0.778474449339
C	-4.166040578610	-0.367078157952	-0.510734970204
H	-3.428165397900	-0.812291123303	-1.190490580615
H	-4.536551390927	0.568432072811	-0.942418001923
H	-4.996581140107	-1.059342538087	-0.383340874845

EQ 4: T_2 ($^3\pi\pi^*$)



Abs. E = -537.329210201935 (ZPE = -537.1576413)

Rel. E = 33029 (ZPE = 31593)

Freq. = 16.97254129

C	3.647402011862	0.560732025216	-0.017114934183
C	2.297762030063	1.027419230221	0.329093509388
C	1.212839148789	0.214005448559	0.228591512846
C	1.407253909320	-1.146501151478	-0.209328102980
C	2.746544276550	-1.603150312330	-0.577405801378
C	3.824031650359	-0.769003059749	-0.478096742820
H	4.486248423763	1.236851173074	0.079219002395
H	2.174372036868	2.051926638199	0.663667349535
H	0.586929578074	-1.851414924016	-0.213566272717
H	2.869694218268	-2.621663690993	-0.926275557194
H	4.814105145831	-1.115721842849	-0.749273087076
C	-0.107006657059	0.765485373879	0.556573141881
C	-1.317866799279	0.161555373374	0.306270624171

H	-0.132471560628	1.742062953465	1.029679007880
H	-1.356399110802	-0.796986621766	-0.193570537154
C	-2.550982880653	0.846377194881	0.701130620747
O	-2.556721946156	1.931680633591	1.236403450288
O	-3.742757960325	0.251091482242	0.459748607229
C	-3.817621509684	-1.022848098755	-0.155476136260
H	-3.317149707086	-1.791847987048	0.441626182373
H	-3.401540911650	-1.009670080668	-1.167927915721
H	-4.878550868196	-1.258371345804	-0.214371443759

TS 3

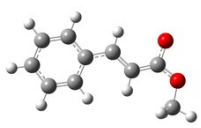
Abs. E = -537.325560580169 (ZPE = -537.1572511)

Rel. E = 33830 (ZPE = 31679)

Freq. = -1329.29545534

C	3.546145345305	0.615257338126	-0.242649087980
C	2.318163316881	1.079250324334	0.196103554487
C	1.220777882595	0.192033585604	0.359741718496
C	1.426551546483	-1.197591618084	0.084644592473
C	2.651501934645	-1.654493753612	-0.375702492456
C	3.728290290920	-0.761011797014	-0.548674596943
H	4.374118279776	1.304869472631	-0.358381882426
H	2.179100559648	2.132624262273	0.413029917574
H	0.613343657000	-1.893651447797	0.256465528581
H	2.787950990987	-2.708927361612	-0.586727848422
H	4.688148785886	-1.119292567902	-0.898798362181
C	-0.086109779009	0.702110136016	0.777474485821
C	-1.275294468465	0.246672895900	0.268214779814
H	-0.115599387272	1.466799841540	1.549801367950
H	-1.279123031584	-0.474779736850	-0.541105364331
C	-2.523148048738	0.761150946088	0.739464701025
O	-2.568404035680	1.761916313988	1.486516562155
O	-3.711728976922	0.248135871484	0.371784405229
C	-3.746408104981	-0.987641058669	-0.322951381494
H	-3.181669981856	-1.759786599478	0.207773253355
H	-3.362156917975	-0.881660077744	-1.342095984287
H	-4.796337339395	-1.269976557995	-0.364331388943

EQ 5: T_2 ($^3n\pi^*$)



Abs. E = -537.333746072318 (ZPE = -537.1578952)

Rel. E = 32034 (ZPE = 31537)

Freq. = 26.57390013

C	3.634196247498	0.497061692823	0.160174520624
C	2.370602373647	0.981930361023	0.456523374161
C	1.215647581278	0.219767769623	0.208549452578

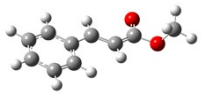
C	1.394000104466	-1.057019083508	-0.353330558502
C	2.658137374421	-1.539052617238	-0.648519799388
C	3.788687754057	-0.768031913240	-0.395089207105
H	4.504870376929	1.110595935035	0.363877284806
H	2.263458632192	1.971218963555	0.889776098820
H	0.535409981773	-1.684856791773	-0.563854740611
H	2.764568696470	-2.527797258404	-1.081451509456
H	4.775918663244	-1.149500640753	-0.627771909379
C	-0.078647103520	0.776816545958	0.538063344290
C	-1.297294410987	0.147372327716	0.350895722019
H	-0.063483889636	1.772727649019	0.966257708073
H	-1.342681957828	-0.846684043496	-0.074634611215
C	-2.514561291431	0.715821081048	0.680162947060
O	-2.572134687082	1.920923161600	1.203779693035
O	-3.738933170126	0.204649438548	0.544356281201
C	-3.853717357079	-1.097261644142	-0.008435414038
H	-3.340283978428	-1.833039644373	0.616922316447
H	-3.453896903631	-1.125446020723	-1.025983975277
H	-4.919722329529	-1.310142190799	-0.026410408439

TS 4
Abs. E = -537.332827268186 (ZPE = -537.1576366)
Rel. E = 32235 (ZPE = 31594)
Freq. = -69.30910037

C	3.649362847482	0.583630737996	-0.027197551050
C	2.375371556023	1.051189689741	0.253338030373
C	1.251658435048	0.212006920462	0.167059565081
C	1.468830319625	-1.121373328551	-0.222026136567
C	2.743114019687	-1.586796210287	-0.499815129846
C	3.843691507416	-0.740099366375	-0.404739974810
H	4.496427825580	1.256369807225	0.049789232049
H	2.236529003104	2.086104381273	0.549317852591
H	0.632263564308	-1.804869102374	-0.314785283982
H	2.880835348039	-2.620684433408	-0.797180450745
H	4.838922596417	-1.108240555189	-0.624647127637
C	-0.056449957344	0.752925725461	0.476926452081
C	-1.236454744194	0.040243384337	0.509875730089
H	-0.082605071432	1.812531851653	0.707805925923
H	-1.247217546976	-1.024985244537	0.309161909905
C	-2.471511567318	0.593589617211	0.791728042552
O	-2.655960249298	1.862243508016	1.063031421639
O	-3.658131776784	-0.040326765025	0.842591128433
C	-3.960209894189	-0.930964331559	-0.229577988754
H	-3.363404865931	-1.843523162731	-0.154763112649
H	-3.782401612094	-0.449182575426	-1.193744873909

H	-5.014549099190	-1.177781154968	-0.122549912566

EQ 6: T_2 ($^3n\pi^*$)



Abs. E = -537.333887121861 (ZPE = -537.1591003)
Rel. E = 32003 (ZPE = 31273)
Freq. = 30.21772185

C	3.665205277058	0.655279670579	-0.216132124669
C	2.373132208731	1.084768442911	0.043076626461
C	1.310185184724	0.174931355685	0.163038118842
C	1.606296457967	-1.190808532448	0.016579535492
C	2.897761433609	-1.617655900913	-0.243582967839
C	3.937083613007	-0.699740295772	-0.362891008107
H	4.464835654229	1.382438379389	-0.303796479325
H	2.172300198625	2.145455946543	0.155091031878
H	0.820423407379	-1.931211933109	0.113800345488
H	3.098188683779	-2.678050178254	-0.350900138539
H	4.946470154951	-1.038526875934	-0.564807303887
C	-0.023198137044	0.680625971541	0.429226303323
C	-1.170737771831	-0.074025291606	0.504139001156
H	-0.097951119109	1.753657630418	0.571384289680
H	-1.155619621925	-1.149003264467	0.357096645120
C	-2.427346674865	0.426371735670	0.780095979786
O	-2.737294422153	1.665681879091	1.038603199531
O	-3.557153138999	-0.324037667674	0.847754102732
C	-4.314614618621	-0.401996950692	-0.369318319174
H	-3.697443334142	-0.824570326220	-1.166150289167
H	-4.681290487993	0.583474077619	-0.661651573270
H	-5.155305569224	-1.058407329598	-0.153408321898

MECI 3: T_2/T_1

Abs. E = -537.3292091
Rel. E = 33029

C	3.677310429740	0.614105997798	-0.206852262992
C	2.384343823332	1.078936061737	-0.002036872161
C	1.303360624498	0.199705025618	0.102863828307
C	1.567538983191	-1.169071365283	-0.008399506341
C	2.857179822519	-1.634950943004	-0.214074884195
C	3.921547767009	-0.746601260352	-0.314214542117
H	4.495855764851	1.321587229469	-0.281501695455
H	2.207139521741	2.146612210992	0.081572485760
H	0.758739646020	-1.887820970807	0.063985426925
H	3.032785548633	-2.701969549074	-0.297331721593
H	4.928749799207	-1.113688866620	-0.473808628663
C	-0.040045545424	0.747878422765	0.318270361297

C	-1.175562811508	0.032194364363	0.482504017127
H	-0.094044485809	1.831619991379	0.345354185644
H	-1.171193437859	-1.053307992553	0.473472373146
C	-2.426019781782	0.568236769585	0.717339962933
O	-2.879616735358	1.773899053985	0.842604366760
O	-3.604630019694	-0.124119010740	0.806530969114
C	-4.325473580887	-0.324866635682	-0.425978248641
H	-3.710187680114	-0.032818619434	-1.276611162039
H	-5.247605770797	0.252839992833	-0.393733274188
H	-4.553215643053	-1.390397115522	-0.468820866784

EQ 7: T_1 ($^3\pi\pi^*$)
Abs. E = -537.394569423274 (ZPE = -537.2204894)
Rel. E = 18685 (ZPE = 17799)
Freq. = 41.41680816

C	3.552921624768	0.571933870471	-0.170783499007
C	2.459181726371	1.079618389871	0.500579070905
C	1.242377631860	0.355331278549	0.564007840059
C	1.189545697599	-0.901610382869	-0.088724051242
C	2.291041048769	-1.399172307382	-0.756633564120
C	3.479256543375	-0.670010699824	-0.803425483980
H	4.473789265874	1.143021117689	-0.207731882769
H	2.520104637272	2.046639363846	0.988690838085
H	0.267621108739	-1.472879636303	-0.061354542674
H	2.229319954878	-2.362326627861	-1.250671178883
H	4.340067421284	-1.064621158002	-1.330335175879
C	0.129369534953	0.883339100778	1.254079366915
C	-1.151554444511	0.201938760561	1.385341575757
H	0.225276551753	1.864100870261	1.715996038335
H	-1.354539445878	-0.458809094755	2.224254519453
C	-2.220302271810	0.404926626675	0.417740554005
O	-2.157301101137	1.128065362544	-0.549688282958
O	-3.311722846821	-0.324062701318	0.732261258716
C	-4.411206653255	-0.187618009635	-0.163886781169
H	-4.128497753123	-0.498003419413	-1.171860693000
H	-4.753752564118	0.848544199291	-0.199414386154
H	-5.193505325370	-0.833853593721	0.228275384049

TS 5
Abs. E = -537.377523110556 (ZPE = -537.203579)
Rel. E = 22426 (ZPE = 21511)
Freq. = -137.62018103

C	3.666429296756	0.288119595990	0.114390064364
C	2.589516559048	0.920844586649	0.669020625303

C	1.233325372554	0.474210808426	0.419858113716
C	1.085230352211	-0.674189754612	-0.442234583263
C	2.187228924071	-1.289371509256	-0.983866738166
C	3.484354651984	-0.828261273360	-0.722689837924
H	4.668024109047	0.649283319265	0.319389239359
H	2.736370602686	1.781162556433	1.313515743174
H	0.089558079579	-1.039253686273	-0.650413154565
H	2.047010119499	-2.150414656193	-1.628033572500
H	4.341326191937	-1.325631611740	-1.160903215251
C	0.210427859846	1.174733210768	1.019276089667
C	-1.265725369332	1.039708292750	1.008649784737
H	0.523435632381	2.011635057065	1.636363860435
H	-1.782195963759	1.783813368852	1.603826606424
C	-2.168426623935	0.113239499703	0.365030119012
O	-1.913036181596	-0.825785143088	-0.363832666272
O	-3.445346614898	0.434750874594	0.690807525956
C	-4.447592337618	-0.395456919582	0.116138243918
H	-4.303068812656	-1.437766256159	0.407757212891
H	-4.424977378496	-0.331004633948	-0.974075441031
H	-5.394378132220	-0.019874416619	0.498742907723

EQ 8: T_1 ($^3\pi\pi^*$)
Abs. E = -537.394570529635 (ZPE = -537.2204825)
Rel. E = 18684 (ZPE = 17801)
Freq. = 41.35240776

C	3.543578223163	0.566869511786	0.179369613552
C	2.449783598213	1.079850165400	-0.487863448838
C	1.242043281904	0.343731456562	-0.581361364687
C	1.198209316491	-0.930696411557	0.037224916740
C	2.299672613334	-1.433382007799	0.701331536339
C	3.478929304622	-0.692312518115	0.778000398231
H	4.457426548870	1.147166992999	0.239641618313
H	2.503653203308	2.060228275499	-0.949437385988
H	0.283244178438	-1.511475659659	-0.013398597656
H	2.244902896381	-2.410061996569	1.168933424304
H	4.339736878609	-1.091124528388	1.301743094660
C	0.128970661139	0.877315533872	-1.267029109049
C	-1.142807285870	0.185204804521	-1.427903530705
H	0.217475659637	1.871135886954	-1.701713207538
H	-1.330988616469	-0.454788067325	-2.286134712802
C	-2.222059482873	0.349721829869	-0.464663616643
O	-2.175651603653	1.046816658584	0.522611842916
O	-3.302312086921	-0.382590877993	-0.808666828625
C	-4.411069396861	-0.282995937916	0.080872989810
H	-4.765059189815	0.748093391041	0.142352113990

H	-4.133973142016	-0.618711585468	1.082273225562
H	-5.182859052418	-0.926134501285	-0.336415158905

Figure 2

MESX 2: T_1/S_0

Abs. E = -537.390674453927

Rel. E = 19534

C	3.775576956946	0.641880385671	-0.176852910877
C	2.654839849196	1.173618471327	0.413417763579
C	1.462682560420	0.398321617950	0.537359825703
C	1.481190312251	-0.930052457194	0.018016350421
C	2.616948831940	-1.447643832482	-0.571076175652
C	3.769945643943	-0.670317584528	-0.674877371091
H	4.673023860801	1.243467790531	-0.265808332636
H	2.660520468559	2.189658628039	0.792636335874
H	0.563499334516	-1.514271673200	0.111022846983
H	2.611633619505	-2.460632369005	-0.957128667164
H	4.659585208642	-1.076413393358	-1.141041148661
C	0.327760269725	0.880272646751	1.142100134676
C	-0.930522200606	0.136159766740	1.166549093269
H	0.225952273931	1.901990911917	1.457781265938
H	-1.205266750758	-0.378636369815	2.066720137430
C	-1.901183408290	0.293827551569	0.120171941771
O	-1.798397276481	1.045168566043	-0.825480389983
O	-2.956067298267	-0.535741222518	0.300496685708
C	-3.933765649331	-0.514558415620	-0.735030015338
H	-3.465423276002	-0.639212782837	-1.713039215840
H	-4.484456589505	0.428329681956	-0.727571075711
H	-4.605169040239	-1.344453374115	-0.524471477429

MESX 3: T_1/S_0

Abs. E = -537.379298899026

Rel. E = 22036

C	3.577724965638	0.663696112705	-0.273144986825
C	2.433708659460	1.159303837777	0.313283017465
C	1.310361066113	0.316201902504	0.508005617727
C	1.384221646116	-1.018243134506	0.042987011702
C	2.531781277353	-1.498905365149	-0.560373758325
C	3.635141158075	-0.664672423803	-0.713987704155
H	4.442233281749	1.306244413283	-0.396563122957
H	2.392569581153	2.189592787052	0.650332413344
H	0.503996290765	-1.642130897428	0.197203088158
H	2.574728457938	-2.526991111080	-0.901095626332
H	4.540765664366	-1.043020208508	-1.173426881977

C	0.164922131548	0.712660869606	1.195783286802
C	-1.109419436516	-0.014371851359	1.193155391299
H	-0.164418063107	1.742465345370	1.200312841889
H	-1.501554289410	-0.280526759523	2.156277147809
C	-2.067340102171	0.183191847938	0.135921692426
O	-1.886118193001	0.774752661438	-0.905338500264
O	-3.234652542659	-0.435768106972	0.442602236464
C	-4.234445798265	-0.404031032520	-0.569223051965
H	-3.856030681239	-0.820953795354	-1.504639340430
H	-4.569801279939	0.619399328006	-0.749868182438
H	-5.055814671968	-1.008589496571	-0.188952662085

EQ 9: S_0 (*cis*)
Abs. E = -537.472302527711 (ZPE = -537.293537)
Rel. E = 1624 (ZPE = 1767)
Freq. = 19.56774361

C	3.721418693476	0.354546893144	0.302601471821
C	2.547794309980	0.784567532267	0.900445248217
C	1.293051226308	0.356855382459	0.439568770551
C	1.253084538463	-0.523642649107	-0.649572798205
C	2.430536861035	-0.952071606984	-1.245669760210
C	3.664926331837	-0.518717018822	-0.776748404575
H	4.677767203318	0.700042798707	0.677932857848
H	2.599132934031	1.466746015344	1.743234495382
H	0.297948581556	-0.865412694075	-1.020285517551
H	2.380802964939	-1.633404859793	-2.087488636214
H	4.578919376138	-0.859741663478	-1.249979962217
C	0.127922841478	0.885917958031	1.159586321336
C	-1.206607046544	0.754763430937	1.070778327194
H	0.429860255545	1.550926088506	1.967102899472
H	-1.796233222044	1.309791371109	1.791183188764
C	-2.045310958487	-0.029934548651	0.144848335616
O	-1.708417884422	-0.748729600892	-0.764634140659
O	-3.340196598503	0.164482688706	0.457624752855
C	-4.280668302150	-0.533322281787	-0.354878768544
H	-4.124115201939	-1.611424592400	-0.285635012751
H	-4.186856349558	-0.230146740812	-1.399339244449
H	-5.260461183936	-0.264583302483	0.033558880855

Figure 3
TS 6
Abs. E = -537.316808446002 (ZPE = -537.1429699)
Rel. E = 35751 (ZPE = 34813)
Freq. = -51.39693178

C	3.733565275812	0.664453332494	-0.083084884971
C	2.458418103861	1.119964397906	0.110393099910
C	1.353664180487	0.207332834478	0.173338911969
C	1.639537763894	-1.200594375165	0.020439929071
C	2.932160813725	-1.631105565717	-0.188296101765
C	3.983961869894	-0.717377923472	-0.234745621011
H	4.559869147338	1.364574978576	-0.123945858619
H	2.258472858890	2.180494545265	0.219285560464
H	0.821786553892	-1.910073104229	0.069606242211
H	3.135143165707	-2.689802563672	-0.303274626724
H	5.000280042002	-1.067082930452	-0.375363960611
C	0.044588246621	0.663956641328	0.347825756289
C	-1.085456928729	-0.194616655303	0.402260455114
H	-0.146664022844	1.734655939865	0.365190974328
H	-1.024827682611	-1.205790462930	0.790783194560
C	-2.378588847210	0.311146742445	0.020639251100
O	-2.596385450327	1.444995586627	-0.376556529704
O	-3.354760471749	-0.618418375552	0.167668043261
C	-4.660457065141	-0.182241515856	-0.185708372940
H	-4.702256314772	0.108478278767	-1.238338267317
H	-4.962907060473	0.673771053295	0.422367011208
H	-5.316981693823	-1.030539012250	-0.000487352272

MECI 4: $^{1}\pi\pi^{*}/S_{0}$
Abs. E = -537.362312425183
Rel. E = 25764

C	3.352175381431	0.563744291697	-0.627910261528
C	2.192286142959	1.141870968916	-0.149558006944
C	1.162143290332	0.340310812558	0.377806233199
C	1.326440701805	-1.056519202191	0.408422062316
C	2.489245410364	-1.629201722449	-0.072492725416
C	3.500438679627	-0.821910941132	-0.588613273697
H	4.143335496003	1.183064739488	-1.033456336409
H	2.060621519592	2.218261261020	-0.182210875339
H	0.521861385583	-1.657083546746	0.816878610565
H	2.615656688365	-2.705132678048	-0.048334050130
H	4.411223249681	-1.274840016122	-0.964209622701
C	-0.031114641424	0.946723017590	0.874972716399
C	-1.164489957151	0.230105484734	1.451165033896
H	-0.022639892043	2.041423871631	0.880805478891
H	-1.358420502863	0.072589601063	2.500695091388
C	-2.020744181597	0.131936735055	0.367823333486
O	-1.598450404297	0.610104642101	-0.719365684292
O	-3.232892267174	-0.434394420525	0.471921177193
C	-4.009808963652	-0.440873972239	-0.720238538494

H	-4.185956252615	0.574990900646	-1.080738108416
H	-4.953066875184	-0.914455370215	-0.453613812317
H	-3.513656815664	-1.009672764240	-1.509748441786

Figure S1

EQ 10: OMe twisted $^1n\pi^*$

Abs. E = -537.319550034209 (ZPE = -537.1450208)

Rel. E = 35149 (ZPE = 34363)

Freq. = 32.97060025

C	3.771679097673	0.761328188498	0.048555689969
C	2.426039079166	1.088835827111	0.025333849233
C	1.430761034584	0.095479070812	-0.002235622921
C	1.854657081398	-1.246069391577	-0.005973049795
C	3.200575416460	-1.569674146309	0.017884140118
C	4.169913042054	-0.571042955890	0.045104477656
H	4.515456636985	1.550168418515	0.070062440532
H	2.126419874070	2.131961669463	0.029270640421
H	1.124182315550	-2.046652936388	-0.027244561487
H	3.499118242720	-2.612302964360	0.015206773533
H	5.222167510385	-0.829478460115	0.063524794285
C	0.041901680166	0.491039359778	-0.024356644092
C	-1.047309226669	-0.364550700552	-0.049006558448
H	-0.145756228851	1.559398432906	-0.022404425027
H	-0.939370100443	-1.442926717781	-0.034841655850
C	-2.345784347351	0.077409892885	-0.079105212103
O	-2.804682446998	1.281230273203	-0.101616080596
O	-3.422855009842	-0.760324259621	-0.044432392735
C	-4.145287424040	-0.913470957636	-1.278404685765
H	-3.444683705616	-1.043620795620	-2.106123743945
H	-4.791829278730	-0.054608146188	-1.456111784037
H	-4.749052465476	-1.809380503779	-1.146857533595

TS 7

Abs. E = -537.319453801946 (ZPE = -537.1450077)

Rel. E = 35171 (ZPE = 34366)

Freq. = -44.65132806

C	3.723021917412	0.646424341399	-0.120615584499
C	2.414217150286	1.075239414511	0.026607412653
C	1.346518343505	0.161745135443	0.086009504908
C	1.658380821105	-1.206690654364	-0.011814033013
C	2.967887818964	-1.631592085218	-0.157789304821
C	4.010501388422	-0.710934819581	-0.213626800592
H	4.524869772139	1.375267641686	-0.162779440419
H	2.201349450289	2.136994197327	0.099460029086

H	0.867937690743	-1.947492490153	0.025867529278
H	3.179863773721	-2.692761409422	-0.229980441962
H	5.033771261985	-1.048698808626	-0.328636830212
C	0.000559387104	0.660879186117	0.243215391818
C	-1.147047570134	-0.110971694379	0.331779849339
H	-0.099499431192	1.739727047518	0.294149186109
H	-1.125087726585	-1.194203092095	0.316384169136
C	-2.403399231165	0.428183503812	0.458096330218
O	-2.721710404066	1.684974777507	0.482039541192
O	-3.507686656517	-0.329850802592	0.654516332969
C	-4.590658938666	-0.180089877870	-0.281490501040
H	-4.203717703699	-0.139661966838	-1.302112832076
H	-5.178577904279	0.710307209560	-0.061116881730
H	-5.203076041428	-1.069452975021	-0.148063437639

MESX 4: $^{1}\pi\pi^{*}/T_{2}$ ($^{3}\pi\pi^{*}$)
Abs. E = -537.316320117953
Rel. E = 35858

C	3.744808436354	0.675902905113	-0.001129259428
C	2.462839737965	1.122504336685	0.001160727773
C	1.345573776206	0.189753670367	0.002078353975
C	1.666827829435	-1.223893459654	0.001698278818
C	2.976576495374	-1.635295435701	-0.000897840276
C	4.017338170722	-0.705488384471	-0.002416033161
H	4.567428497703	1.381660088054	-0.001942682610
H	2.237594962606	2.183488623264	0.001826607660
H	0.867570799737	-1.953693428275	0.003430139038
H	3.207967636285	-2.694554535000	-0.001428778839
H	5.045718089949	-1.049782948176	-0.004200261984
C	0.044607034992	0.636418057873	0.002534242679
C	-1.080181566448	-0.235382982550	0.001993934113
H	-0.171106712547	1.700113277144	0.002907351256
H	-0.983026385162	-1.313471695753	0.002945035195
C	-2.405780984105	0.326076552670	0.000189316281
O	-2.662272189560	1.520206004122	-0.001495213849
O	-3.364776329611	-0.633878313227	0.000493837833
C	-4.700633330153	-0.149868985217	-0.001553109344
H	-4.893161688277	0.457659123347	-0.889467935385
H	-4.894747263441	0.460831467710	0.883830277260
H	-5.337002533577	-1.033122091885	-0.000560133452

MESX 5: $^{1}\pi\pi^{*}/T_{3}$ ($^{3}\pi\pi^{*}$)
Abs. E = -537.316948301376
Rel. E = 35720

C	3.749886672568	0.679235797039	0.012084978626
C	2.448972889558	1.107740884151	-0.004370126060
C	1.353880924114	0.168829471943	-0.014447760328
C	1.692002761316	-1.237970417805	-0.016470934873
C	3.012125553408	-1.640192069660	0.000232936489
C	4.050033910773	-0.700767105296	0.016317492976
H	4.557266650664	1.402133731849	0.022190100280
H	2.216012513615	2.167005586606	-0.007852780120
H	0.900611687617	-1.976489401731	-0.032123093322
H	3.249318114337	-2.698091061141	0.000363531110
H	5.081842273895	-1.030959390683	0.030678668140
C	0.026708314606	0.613706188098	-0.015827547455
C	-1.095329116855	-0.237688182703	-0.012647470116
H	-0.176941882773	1.680035984193	-0.014730928082
H	-1.010013120634	-1.316917535187	-0.013849487497
C	-2.419356886999	0.332960103401	-0.005929620066
O	-2.672245933675	1.526925505952	-0.009793663395
O	-3.382700494521	-0.621548531624	0.005248232699
C	-4.716871918159	-0.132297854243	0.013560556160
H	-4.915502944425	0.472813978078	-0.874407595126
H	-4.901306905315	0.481014091806	0.899001022465
H	-5.356230578659	-1.013297926607	0.022770341051

MESX 6: OMe twisted $^{1}n\pi^{*}/T_{2}$ ($^{3}\pi\pi^{*}$)
Abs. E = -537.312930461772
Rel. E = 36602

C	3.782762620916	0.698065194097	0.060945451591
C	2.443691879710	1.062524851763	0.017131860228
C	1.428422829216	0.102094000774	-0.027320546187
C	1.810194998850	-1.243724328119	-0.032980332964
C	3.147236293442	-1.609007217709	0.012943578650
C	4.143203036688	-0.641196661773	0.060680461365
H	4.546592820772	1.467174066064	0.096296307762
H	2.174983689912	2.114262192456	0.020778822518
H	1.056923187091	-2.022543584745	-0.079452314058
H	3.414042901325	-2.660363007081	0.008069977984
H	5.187310455397	-0.929846195097	0.094878961479
C	0.035057461788	0.543021146286	-0.066337906661
C	-1.061997704594	-0.258288767544	-0.019620824742
H	-0.109432779136	1.616501160464	-0.130983088279
H	-0.987566655245	-1.336027922218	0.072943324341
C	-2.344377211356	0.218096245916	-0.064204556026
O	-2.963535756825	1.324378945769	-0.180106385935
O	-3.496908792152	-0.559163799355	0.004242724205
C	-4.064353303421	-0.946136345618	-1.262177071086

H	-3.558982365536	-0.431888483222	-2.076401253775
H	-5.125315792641	-0.710576703167	-1.239937527938
H	-3.911691036815	-2.024606590609	-1.333160807150

Figure S2

MECI 5: T_2/T_1

Abs. E = -537.3294914

Rel. E = 32968

C	3.604121387104	0.617405328455	0.474120971266
C	2.323390828261	1.069854336412	0.185631899013
C	1.310464234152	0.185390710937	-0.195015475610
C	1.634365804599	-1.170905522675	-0.298558362413
C	2.911960867917	-1.625139691746	-0.004791042766
C	3.904444185830	-0.734457429650	0.385493107259
H	4.369708814610	1.326395771163	0.769615144038
H	2.098451771620	2.128925168028	0.263772555158
H	0.886640116190	-1.880431316855	-0.635963830103
H	3.137650965432	-2.682132164334	-0.095290111545
H	4.903744466758	-1.090561556765	0.607713831309
C	-0.032687597103	0.706646196850	-0.472001477768
C	-1.165792468483	-0.030461473737	-0.489201395525
H	-0.090479511362	1.774900855942	-0.654711066722
H	-1.150820218490	-1.092939644807	-0.265202395816
C	-2.428015309336	0.447651595928	-0.784855113298
O	-2.893456845424	1.609519834037	-1.113128798131
O	-3.594873821053	-0.268017518148	-0.733934561401
C	-4.319868793171	-0.220306304561	0.512284385372
H	-5.144262389244	0.485848817586	0.426339113875
H	-3.650604390124	0.058586943106	1.326430974253
H	-4.707125859731	-1.227770143680	0.662385961280

MECI 6: T_2/T_1

Abs. E = -537.3298202

Rel. E = 32895

C	3.259794248395	0.892221188296	0.443140212950
C	1.899090736191	0.870656641143	0.669004851002
C	1.099471752299	-0.221327115733	0.235791977439
C	1.750385913296	-1.278462710517	-0.454755483755
C	3.109807059585	-1.239609681015	-0.684623340632
C	3.875958158907	-0.160878061864	-0.235571770686
H	3.851283950204	1.731152955133	0.791399504335
H	1.420984441919	1.690258497331	1.194885687948
H	1.173131542949	-2.119045039401	-0.819208928944
H	3.587092369952	-2.053286647246	-1.218836103321

H	4.944211577584	-0.140821146382	-0.416478186594
C	-0.276951237880	-0.226718496055	0.531078290349
C	-1.264679799577	-1.317712991330	0.192106982270
H	-0.695475863738	0.635293411532	1.039110025179
H	-0.904137482355	-2.213808531161	-0.298869712668
C	-2.532306328165	-0.773619380646	-0.280947752911
O	-1.978988906578	-0.129433492000	-1.370462812823
O	-3.197764167870	0.005859628805	0.630772569128
C	-4.121707706653	0.927963471823	0.075077994430
H	-3.624404175005	1.618574713897	-0.611099452458
H	-4.541052770770	1.484122419940	0.911874307197
H	-4.926787073605	0.406623157118	-0.452254545341

MECI 7: T_2/T_1
Abs. E = -537.3359958
Rel. E = 31540

C	3.169922317547	1.009733823398	0.364536766140
C	1.706596541647	0.687343227570	0.404548613367
C	1.299707982648	-0.532531672320	-0.363877224998
C	2.166095637407	-1.564117227173	-0.386404147043
C	3.510242507623	-1.381977755541	0.126941159474
C	4.011447136934	-0.052388347664	0.355425824811
H	3.522443043970	2.033578575969	0.402340273904
H	1.222178027554	0.788338167321	1.379847868340
H	1.906265238574	-2.500429702019	-0.870872199229
H	4.184720674633	-2.227705525049	0.174401317039
H	5.084001991224	0.091000305868	0.438755038423
C	-0.005303526410	-0.460739542823	-1.053881588226
C	-1.297571743505	-0.752923236498	-0.363803218513
H	-0.067859515610	0.184526945884	-1.926584297214
H	-1.471160820087	-1.724259594447	0.086462064376
C	-2.359725507176	0.235771682674	-0.318185073807
O	-2.300438068901	1.339614065190	-0.813387271715
O	-3.437592855587	-0.221118234873	0.349422117647
C	-4.525976047527	0.694129031323	0.448132712241
H	-4.889072186388	0.970523970522	-0.543720812523
H	-4.221387372685	1.600074122006	0.976025442430
H	-5.300577216851	0.171559712236	1.005010947451

MECI 8: T_2/T_1
Abs. E = -537.3360068
Rel. E = 31538

C	3.654317104335	0.640675278246	0.402427040467
C	2.634766351923	0.600202430587	1.278673821047

C	1.383965515323	-0.124251362625	0.864598162701
C	1.606579771221	-1.256440464887	-0.108066676994
C	2.624169759004	-1.126215544891	-1.018477549272
C	3.622973201367	-0.139344852562	-0.829042683049
H	4.554131186850	1.201991897831	0.632159791916
H	2.676733488309	1.108282751410	2.235598383421
H	0.892349575256	-2.070815880000	-0.148460566714
H	2.720847229114	-1.826808892101	-1.841021908676
H	4.441829142505	-0.053442925241	-1.532537899841
C	0.240514488389	0.647304564539	0.321905523739
C	-1.172732377217	0.494964450922	0.816717212863
H	0.327024963893	0.955462622801	-0.717876666059
H	-1.425405183129	0.751581363252	1.839742662944
C	-2.251988564774	0.116117894782	-0.080949546374
O	-2.121402027339	-0.129032970154	-1.258961252715
O	-3.434821995352	0.067205381738	0.562172908020
C	-4.552481787916	-0.299908314634	-0.243597148803
H	-4.403054846809	-1.287213490934	-0.684841065046
H	-4.702516111176	0.425250642199	-1.045951661227
H	-5.408842644686	-0.307561788660	0.426923429498

MECI 9: T_2/T_1
Abs. E = -537.3361285
Rel. E = 31511

C	3.656200982701	0.566084813311	0.484014201588
C	2.616438841544	0.538199758008	1.336427344245
C	1.362613642337	-0.163010729509	0.890578384442
C	1.588177884620	-1.293452329021	-0.085753744808
C	2.627565210493	-1.173340518429	-0.971683727735
C	3.640251876692	-0.206122162592	-0.752176027486
H	4.559503564796	1.111373718577	0.737515429660
H	2.644385564827	1.040816641832	2.296654742292
H	0.861314906596	-2.094996818742	-0.148477378108
H	2.731411262237	-1.869683260358	-1.797059515108
H	4.478053468384	-0.132715215936	-1.434318578546
C	0.246988580349	0.634749969289	0.329409681411
C	-1.178817888583	0.518294164037	0.789156103249
H	0.369484506607	0.965043054576	-0.699913872138
H	-1.448981153337	0.778023047162	1.807241839509
C	-2.247804567735	0.169999392578	-0.133265431622
O	-2.099317406254	-0.073617844372	-1.309355492496
O	-3.443991913162	0.144552987507	0.486437490618
C	-4.551750705036	-0.203730641713	-0.340982551332
H	-4.428645962045	-1.210396892130	-0.745423102279
H	-4.648918166754	0.498956830784	-1.170675269138

H	-5.427206290099	-0.157025173128	0.302783785685

MECI 10: T_2/T_1
Abs. E = -537.3398577
Rel. E = 30692

C	3.600565620142	0.331702391745	0.051592165435
C	2.427208339752	1.095214720628	-0.239824381896
C	1.233481513993	0.463579899718	-0.408834496253
C	1.271111163291	-1.031404171194	-0.535916452338
C	2.318189707472	-1.717930888771	0.284861513890
C	3.483444767167	-1.055662383245	0.445728930466
H	4.556766788942	0.832260753977	0.142824971452
H	2.482027337361	2.179576006907	-0.231587402397
H	1.152967632484	-1.400245475945	-1.558056522470
H	2.161273296551	-2.718665380249	0.670369691457
H	4.325004112899	-1.524473355639	0.945019394894
C	-0.089388341138	1.113988620653	-0.424840166858
C	-0.951416242431	0.948159178135	0.770128914230
H	-0.550414877325	1.401202918934	-1.365598824928
H	-0.555983815319	1.187696313308	1.750900360709
C	-2.291057577439	0.394863197649	0.750348278618
O	-2.990129764866	0.266777449122	1.731591904777
O	-2.688386660505	0.042418881222	-0.491108812225
C	-4.001970418869	-0.502101009999	-0.578556650955
H	-4.743939685664	0.220394190258	-0.232676574810
H	-4.085613474465	-1.407771532845	0.025446708723
H	-4.156783183102	-0.731577532785	-1.630678237461

MECI 11: T_2/T_1
Abs. E = -537.3421821
Rel. E = 30182

C	2.079722940037	0.874910869262	0.638260952438
C	1.423605847850	0.983411067412	-0.550388350186
C	1.233275196745	-0.275680999815	-1.362429740566
C	2.384771787318	-1.241530057038	-1.268554807102
C	3.051599584444	-1.293978896006	-0.100612134509
C	2.822123938131	-0.304592578746	0.938262852398
H	2.116047441111	1.710312240918	1.329391879219
H	0.933298336310	1.898219487513	-0.863105734016
H	2.618782558006	-1.895428584621	-2.100937356962
H	3.838297664318	-2.026209037744	0.050145451740
H	3.345913174273	-0.390982694432	1.881952762059
C	-0.160349875292	-0.781951286143	-1.253977287475
C	-0.700858634645	-1.035680039918	0.100999954939

H	-0.862140413989	-0.542037378288	-2.047711264785
H	-0.140765052598	-1.661318313309	0.787082002032
C	-1.882816258166	-0.404740830261	0.657186073287
O	-2.317952357556	-0.630389702242	1.764863791829
O	-2.460020965124	0.463702516732	-0.200370158759
C	-3.633283248963	1.109812416362	0.284824562492
H	-3.959433685891	1.769744755721	-0.516168624906
H	-3.412875348466	1.684322052780	1.186610829817
H	-4.409986388825	0.378087783791	0.515808658960

MECI 12: T_2/T_1
Abs. E = -537.3429812
Rel. E = 30007

C	2.082814187624	0.113422182948	1.098326799050
C	1.767677373386	1.042905554822	0.153958042068
C	1.575827792280	0.561475498083	-1.263223122747
C	2.493109691553	-0.566260849669	-1.653433571535
C	2.832768901799	-1.444540629834	-0.691111889526
C	2.520603842187	-1.184867701332	0.703249789749
H	2.088550141358	0.373798275436	2.151500470333
H	1.525987023464	2.069376681088	0.404733791508
H	2.814956556119	-0.678839389760	-2.682511538031
H	3.426530301282	-2.320580381810	-0.931916994210
H	2.777047311971	-1.922797397581	1.453137259744
C	0.135274312759	0.497551123550	-1.628111019082
C	-0.775181445580	-0.265662716572	-0.744091327092
H	-0.292107910112	1.330117855934	-2.181052347497
H	-0.533221480561	-1.288250756637	-0.476623107243
C	-1.906446214780	0.375169842307	-0.097423602175
O	-2.201879526483	1.543616695234	-0.223101209653
O	-2.606245777359	-0.487822966416	0.663902447083
C	-3.740624718428	0.064707090776	1.325979708763
H	-4.454223890743	0.463764087858	0.602277348724
H	-3.439623533319	0.867860846020	2.001678711647
H	-4.184636699735	-0.756140152291	1.884989671870

Figure S3
EQ 11: T_2 ($^3n\pi^*$)
Abs. E = -537.333829811114 (ZPE = -537.1589957)
Rel. E = 32015 (ZPE = 31296)
Freq. = 28.00399086

C	3.677495934812	0.706612190208	0.326367741364
C	2.362702871839	1.104199457994	0.140810357385
C	1.343809762104	0.169950126919	-0.106388029326

C	1.707258759094	-1.186288419530	-0.162181851522
C	3.021316858575	-1.581430004738	0.024928125086
C	4.016452712613	-0.640042505805	0.270624094701
H	4.441861398777	1.452227450365	0.515225708534
H	2.109892554616	2.158660794912	0.187462312970
H	0.956555411995	-1.943510572412	-0.357771339203
H	3.273466880208	-2.635084892884	-0.024488939110
H	5.043650212435	-0.953751128927	0.415478165878
C	-0.015097622016	0.643920882277	-0.289072184597
C	-1.121851586508	-0.143090939295	-0.508203202815
H	-0.146266010784	1.719836034174	-0.239386147230
H	-1.049965092362	-1.224408139684	-0.562857343332
C	-2.403298331772	0.333993033738	-0.697788553452
O	-2.777910874816	1.582077722083	-0.726481158581
O	-3.491364055090	-0.449413888151	-0.913015857325
C	-4.249241111006	-0.782060900639	0.260200523323
H	-4.695383331136	0.111392486802	0.700268258058
H	-3.606297822061	-1.279919581681	0.990319590352
H	-5.033018989263	-1.457996902959	-0.076010839778

Figure S4

TS 8

Abs. E = -537.360166172021 (ZPE = -537.1848321)

Rel. E = 26235 (ZPE = 25625)

Freq. = -228.20803949

C	3.432720344270	0.574983753573	-0.548688312625
C	2.266041374980	1.154727163047	-0.093423240257
C	1.206473503141	0.349024779171	0.373668237121
C	1.348253196602	-1.053093283839	0.362396831599
C	2.518144028145	-1.626415969551	-0.097139837637
C	3.556786727146	-0.814879789858	-0.549898986548
H	4.247208166448	1.192327097999	-0.907776758041
H	2.149239678867	2.233300377086	-0.093516904391
H	0.515092554028	-1.647936940569	0.719303640049
H	2.629044855989	-2.704008619545	-0.109414159339
H	4.473491351579	-1.268809031443	-0.909931160592
C	0.006365148403	0.947268550609	0.841090039595
C	-1.151904811899	0.232191124221	1.336644169407
H	0.007963439324	2.044588849313	0.822359721312
H	-1.378319544442	0.095193602014	2.384473785706
C	-2.041758001860	0.139243370670	0.266850465870
O	-1.702774616674	0.556383676409	-0.859427516047
O	-3.259300625056	-0.404448956728	0.487688502774
C	-4.113591154880	-0.457242070516	-0.646180119075
H	-4.304267580303	0.542154080837	-1.044156680963

H	-5.042073793496	-0.904852080344	-0.294483640086
H	-3.678647048235	-1.068657989960	-1.440438077968