Supplementary Materials for "Theoretical studies on the photochemistry of 2-nitrofluorene in the gas phase and acetonitrile solution"

Li Bo,[1] Teng-Shuo Zhang,[2] Jiadan Xue,[3] Bin-Bin Xie,[1*], Wei-Hai Fang,[1,2] and Lin Shen[2*]

1) *Hangzhou Institute of Advanced Studies, Zhejiang Normal University, 1108 Gengwen Road, Hangzhou 311231, Zhejiang, P. R. China.*

2) *Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China.*

3) *Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, China.*

---

[*]Author to whom correspondence should be addressed.

Email: *binbinxie@mail.bnu.edu.cn, lshen@bnu.edu.cn.*

Table of Contents

Molecular orbitals in the gas phase

49 [1.87]   **50 [1.99]**   **51 [2.00]**   **52 [2.00]**

53 [1.93]   **54 [1.93]**   **55 [1.96]**   **56 [0.14]**

57 [0.04]   **58 [0.07]**   **59 [0.07]**

Figure S1. Molecular orbitals in the active space for SA5-CASSCF and MS-CASPT2 computations in the gas phase. The occupation numbers corresponding to natural orbitals in the ground state are shown in brackets.

Critical structures in the gas phase
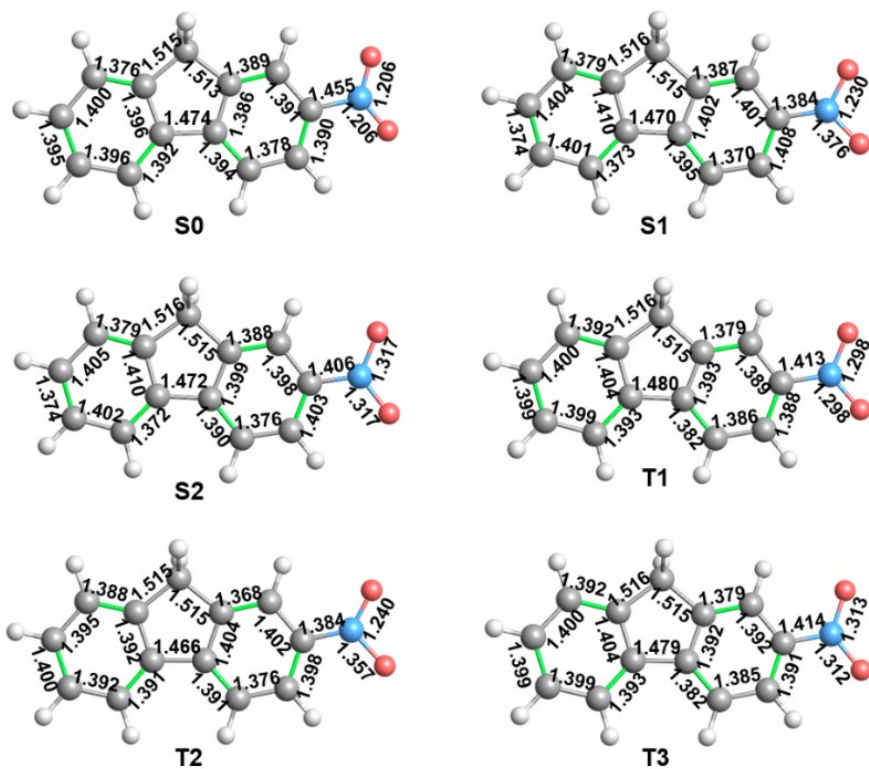
Figure S2. SA5-CASSCF(14,11) optimized minimum-energy structures in the lowest six electronically singlet and triplet states in the gas phase. Also shown are the selected bond lengths.
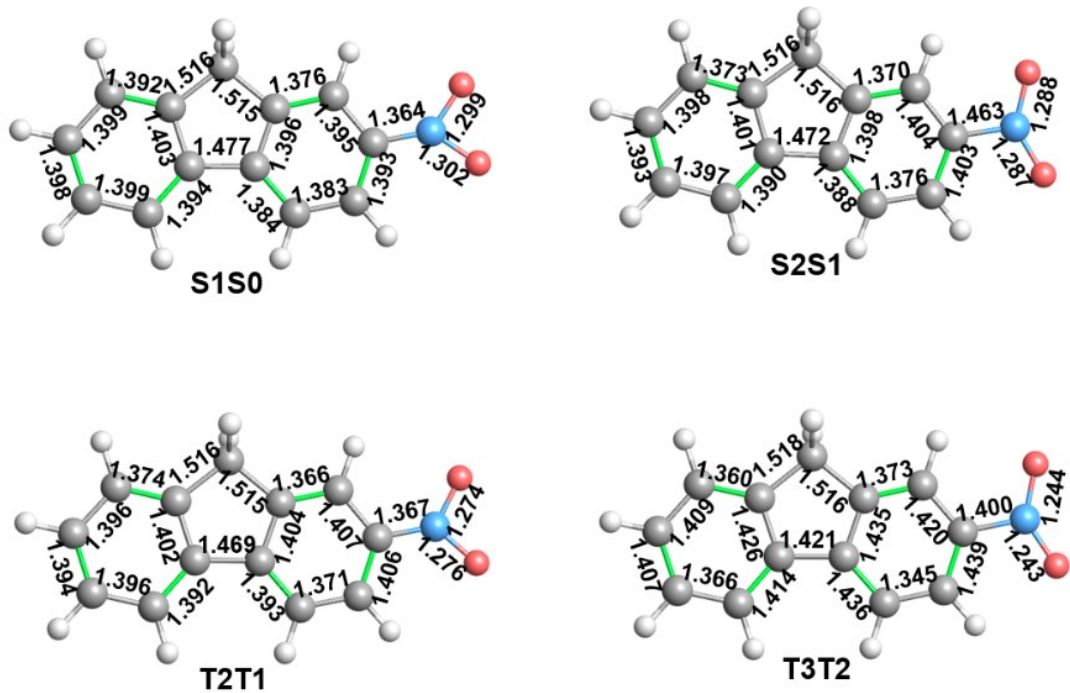
Figure S3. Minimum-energy conical intersections of 2-NF in the gas phase between excited singlet and triplet states optimized at the SA5-CASSCF(14,11) level. Also shown are the selected bond lengths.
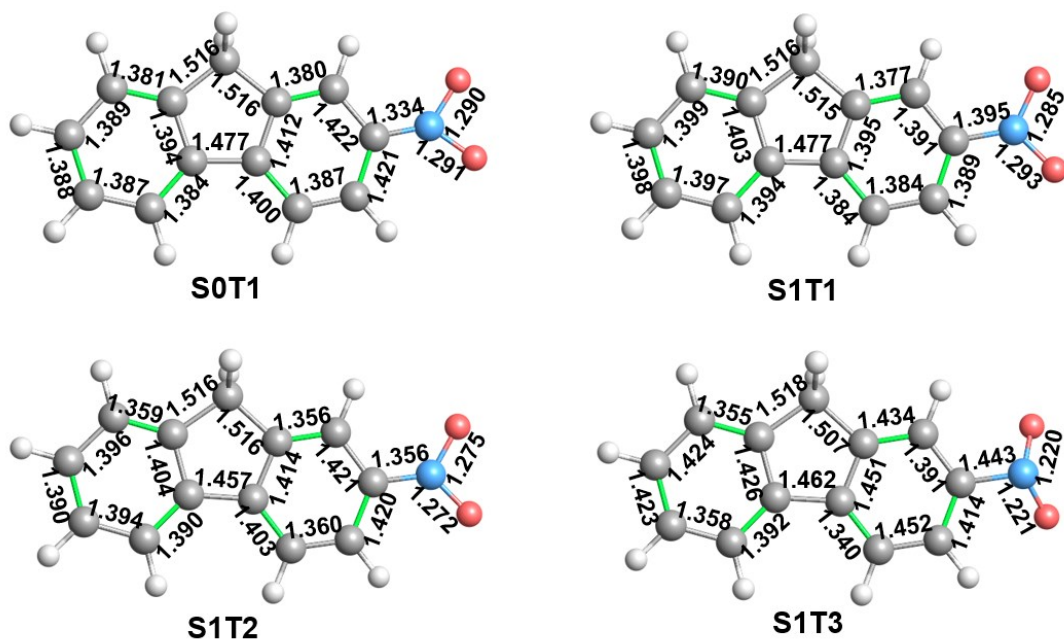
Figure S4. Minimum-energy crossing points of 2-NF in the gas phase between different excited singlet and triplet states optimized at the SA5-CASSCF(14,11) level. Also shown are the selected bond lengths.

LIIC paths in the gas phase and acetonitrile solution
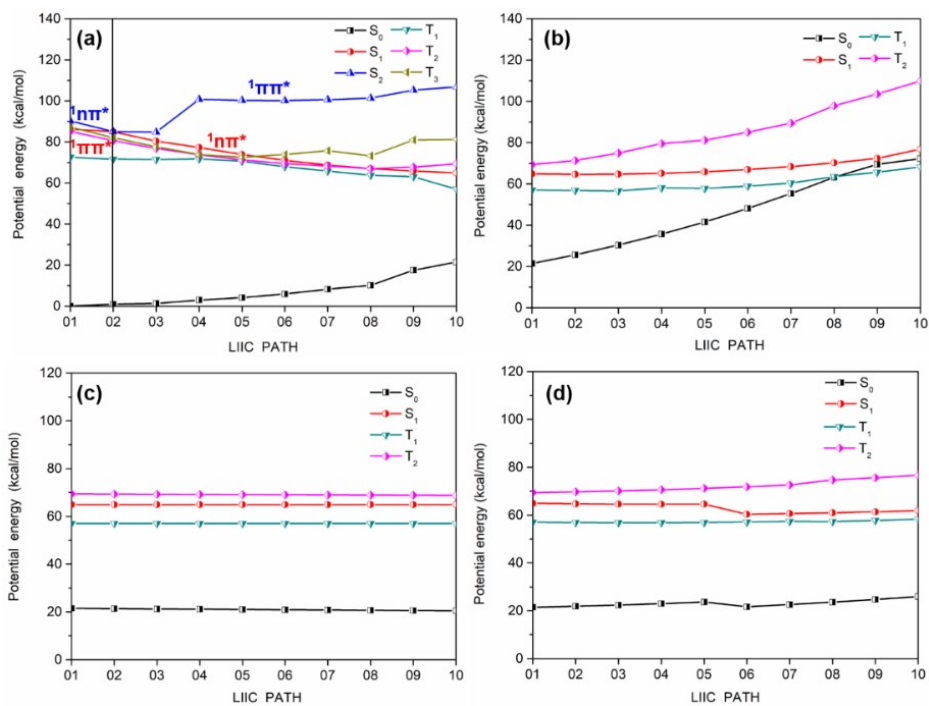
Figure S5. MS-CASPT2 computed linearly interpolated internal coordinate (LIIC) paths in the gas phase connecting (a) the S_1-FC point and S_1 minimum; (b) S_1 minimum and the S_1/S_0 conical intersection; (c) the S_1 minimum and the S_1/T_2 crossing point; (d) the S_1 minimum and the S_1/T_1 crossing point.
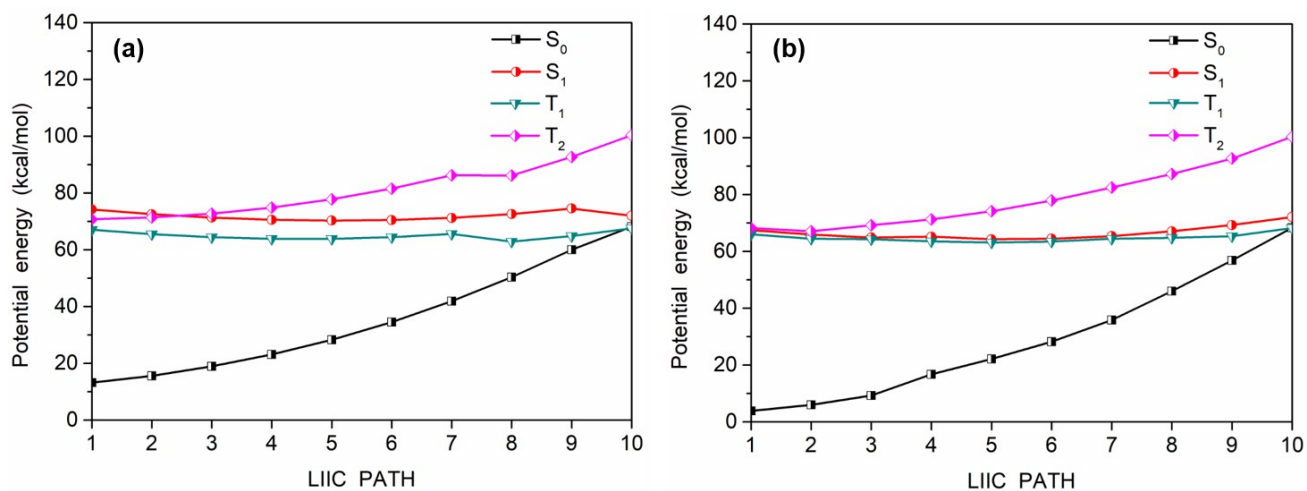
Figure S6. MS-CASPT2 and QM(MS-CASPT2)/MM computed linearly interpolated internal coordinate (LIIC) paths connecting the T_1 minimum and S_0/T_1 crossing point in the gas phase (a) and acetonitrile solution (b).

PES scanned along selected reaction coordinates in the gas phase
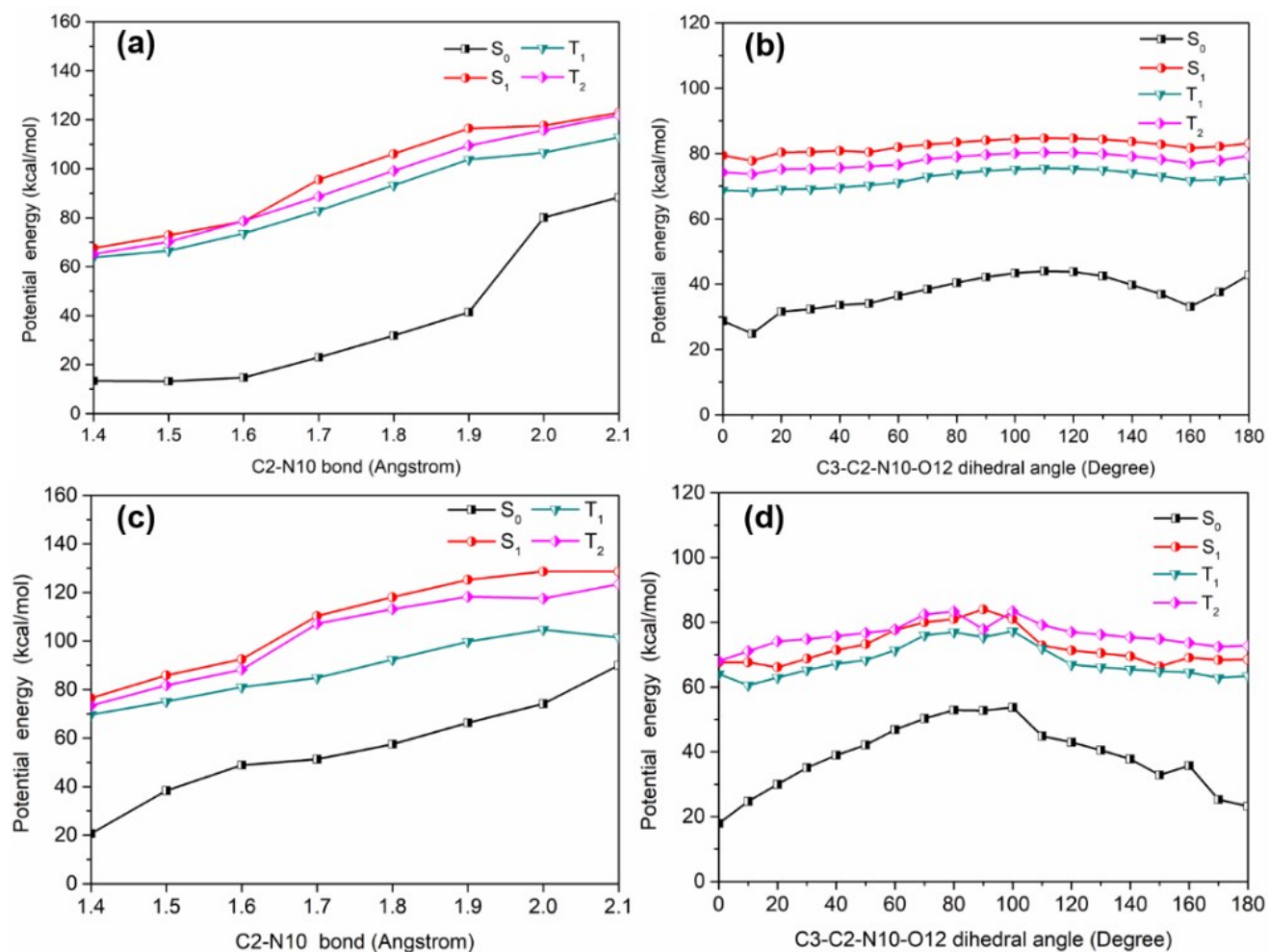
Figure S7. PESs scanned along the C_2-N_{10} bond and the C_3-C_2-N_{10}-O_{12} dihedral angle in the T_1 (a,b) and S_1 (c,d) states in the gas phase at MS-CASPT2 level.

Reaction process related to intramolecular rearrangement mechanism in gas phase
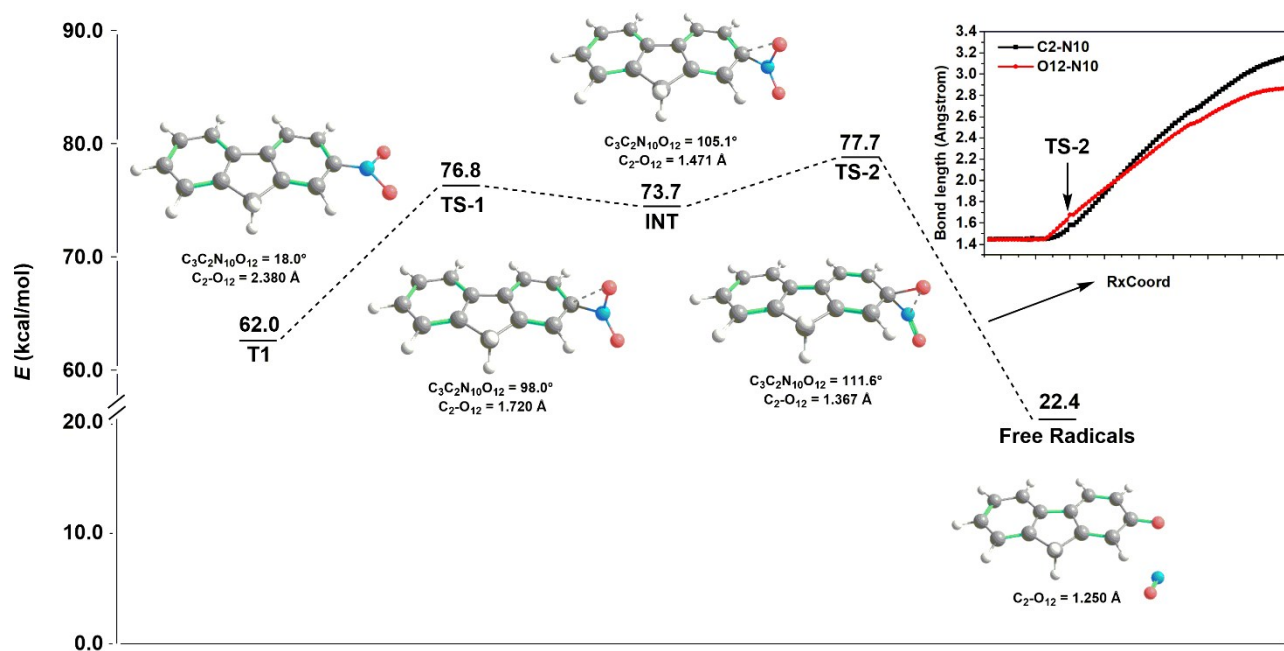
Figure S8. MN15 computed intramolecular rearrangement reaction mechanism of the 2-NF system in the T_1 state in the gas phase.

Active space choice

Table S1. Vertical excitation energies and electronic configurations obtained using different computational models [units: kcal/mol].

active space	5-state-averaged				8-state-averaged
	I (14,11)	II (14,11)	III (14,11)	IV (16,12)	IV (16,12)
S_1-FC	331.7 $(\pi_H\pi^*_L)$	324.1 $(n_{H-4}\pi^*_L)$	330.8 $(n_{H-4}\pi^*_L)$	327.1 $(n_{H-4}\pi^*_L)$	331.8 $(n_{H-4}\pi^*_L)$
S_2-FC	316.9 $(n_{H-4}\pi^*_L)$	278.9 $(n_{H-3}\pi^*_L)$	311.7 $(\pi_H\pi^*_L)$	287.1 $(n_{H-3}\pi^*_L)$	319.6 $(\pi_H\pi^*_L)$
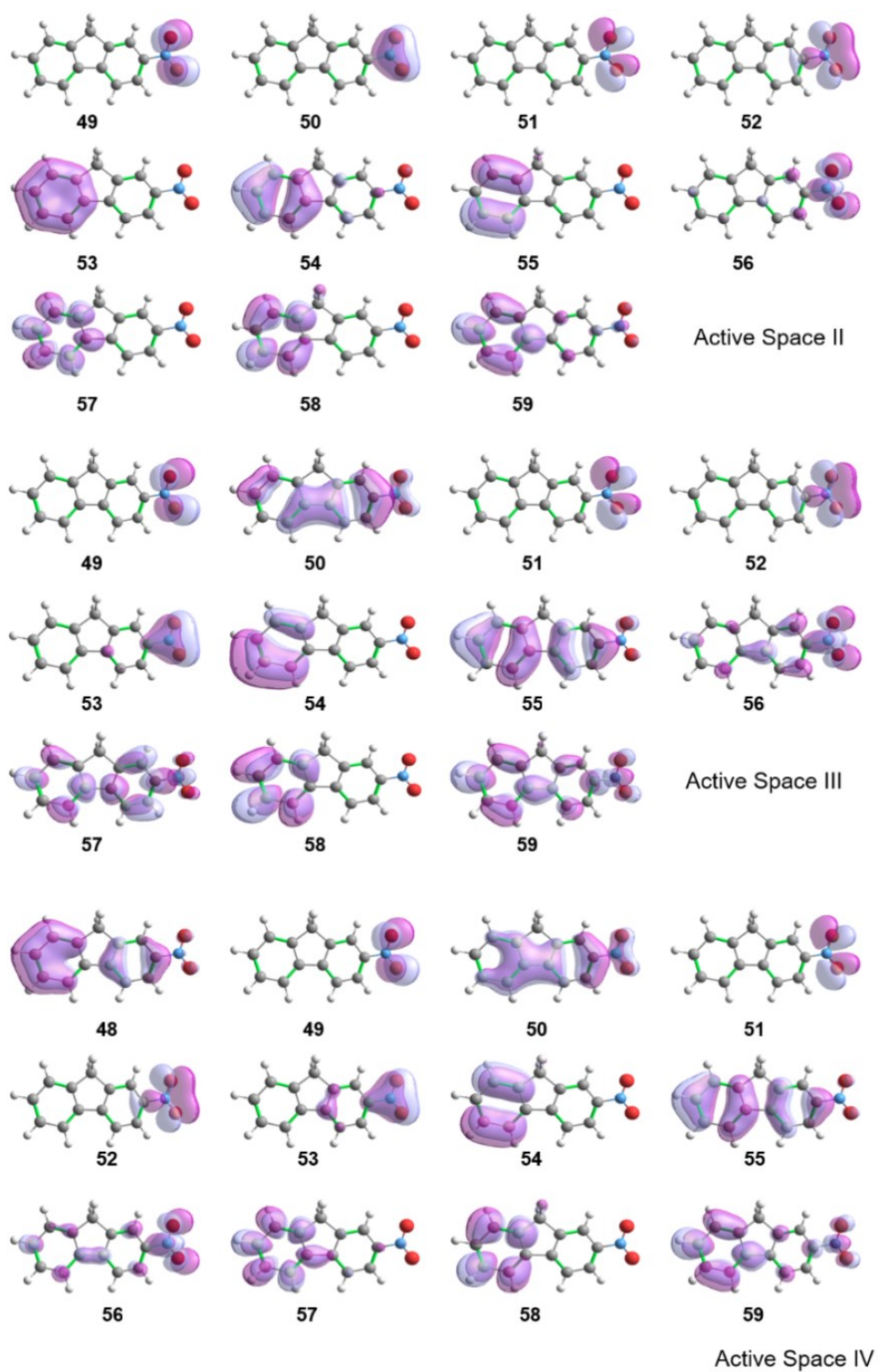
Figure S9. Different molecular orbitals included in active spaces II, III and IV.
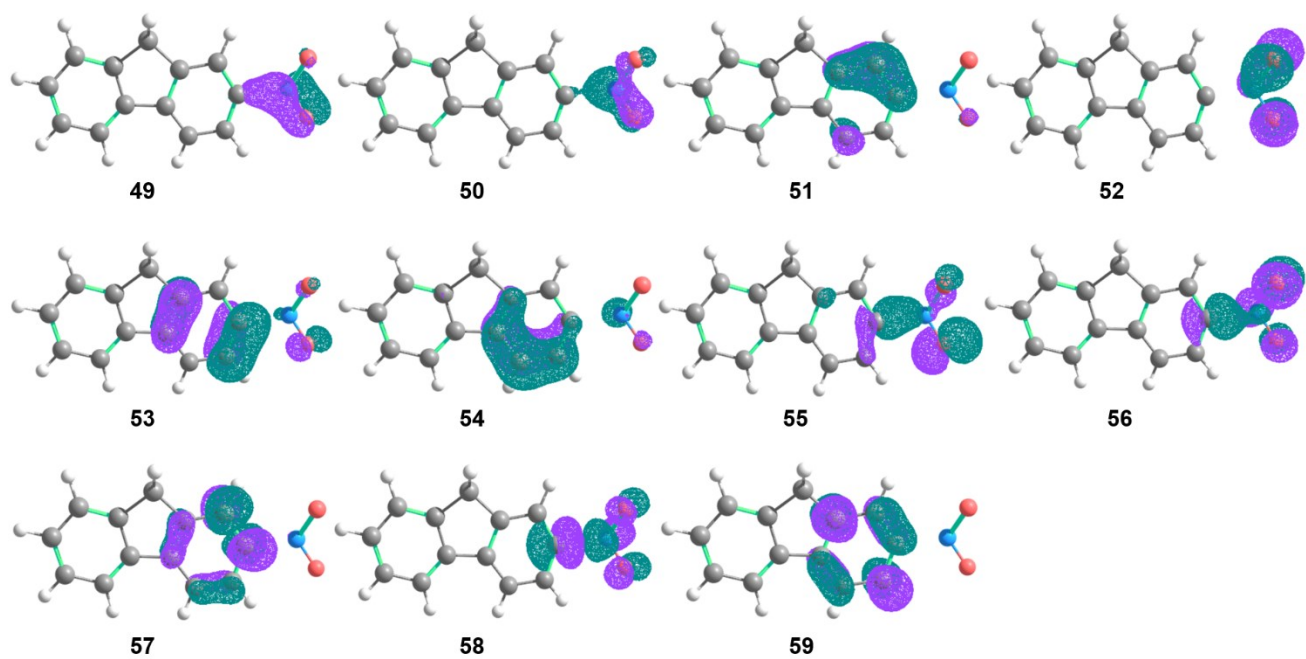
Figure S10. Active space including the σ and σ* orbitals with the elongation of the C-N bond during photodegradation reaction.

Number of CI roots in SA-CASSCF method

Table S2. Vertical excitation energies and electronic configurations obtained using different computational models [units: kcal/mol (nm)].

	MS-CASPT2//CASSCF/MM			MN15/MM	Exp.
	3-state-averaged	4-state-averaged	5-state-averaged		
S_1-FC	90.9 (314.5) $^1n\pi^*$	90.2 (317.2) $^1n\pi^*$	85.1 (336.1) $^1\pi\pi^*$	84.3 (339.3)	85.9 (333.0)
S_2-FC	103.5 (276.3) $^1n\pi^*$	98.2 (291.3) $^1\pi\pi^*$	91.6 (312.2) $^1n\pi^*$	89.7 (318.7)	

Inclusion of solvent in QM subsystem

Table S3. QM(MS-CASPT2)/MM vertical and adiabatic excitation energies [units: kcal/mol].

	S_0-min	S_1-FC	S_2-FC	S_1-min	T_1-min
no CH$_3$CN in QM	0.0	85.1	91.6	71.2	65.9
one CH$_3$CN in QM	0.0	84.3	91.7	73.0	65.6
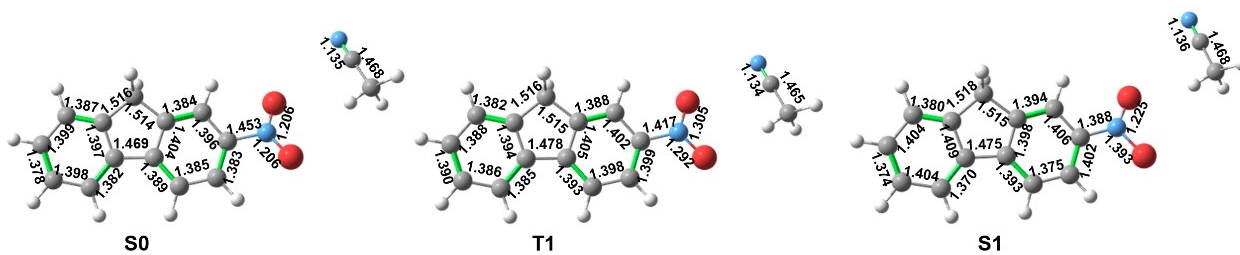
Figure S11. The S_0, T_1 and S_1 minimum structures that involves one acetonitrile molecule in QM subsystem optimized at the QM(SA5-CASSCF(14,11))/MM level.

Solvent configurations in QM/MM calculation

Table S4. QM(MS-CASPT2)/MM vertical excitation energies from the snapshots at 30, 40 and 50 ps [units: kcal/mol].

	S_0-min	S_1-FC	S_2-FC	T_1-FC	T_2-FC	T_3-FC
30 ps	0.0	87.1	89.7	66.9	81.7	85.6
40 ps	0.0	84.9	90.5	62.9	83.3	83.5
50 ps	0.0	85.1	91.6	65.8	84.3	84.7
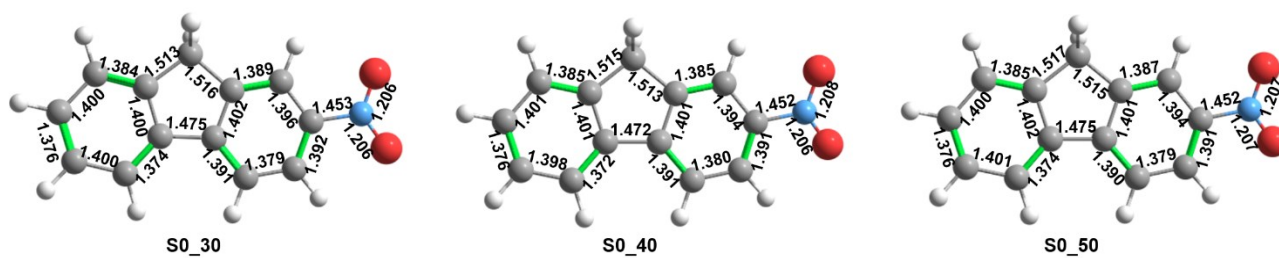
Figure S12. QM(SA5-CASSCF(14,11))/MM optimized S_0 minimum-energy structures from different snapshots at 30, 40 and 50 ps in acetonitrile solvent. Also shown are the selected bond lengths.

Comparison on scanned PESs between different computational models
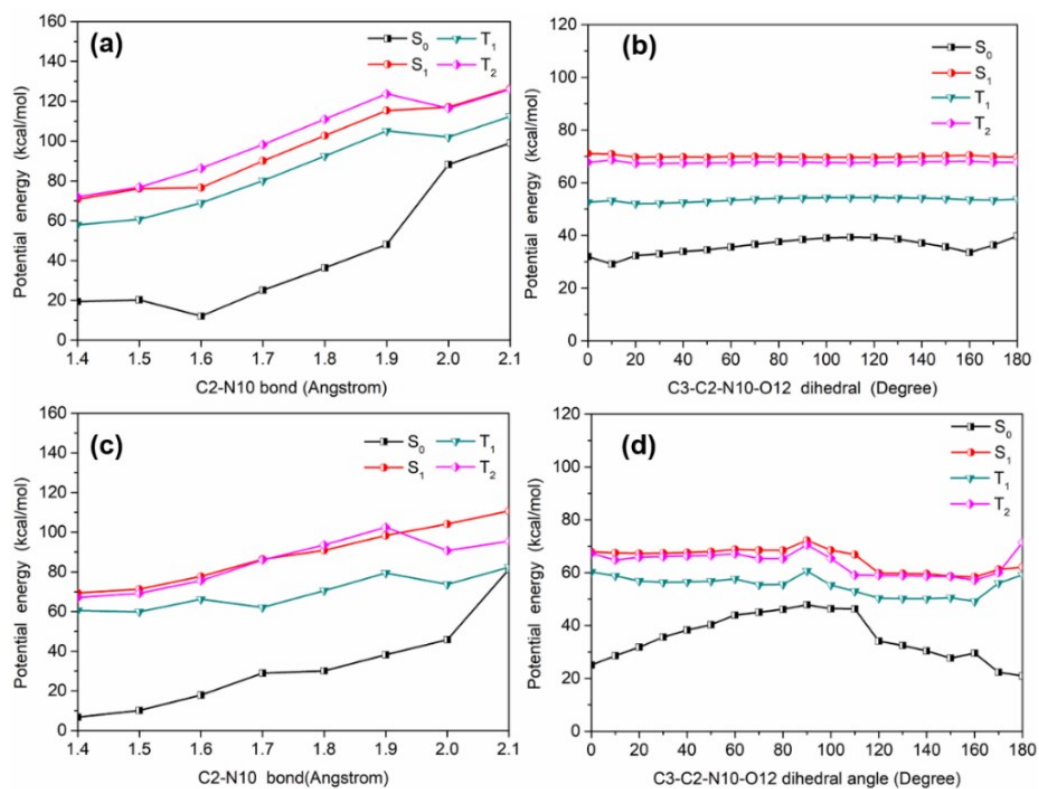
Figure S13. PESs scanned along the C_2-N_{10} bond and the C_3-C_2-N_{10}-O_{12} dihedral angle in the T_1 (a,b) and S_1 (c,d) states in the gas phase at SA5-CASSCF level.
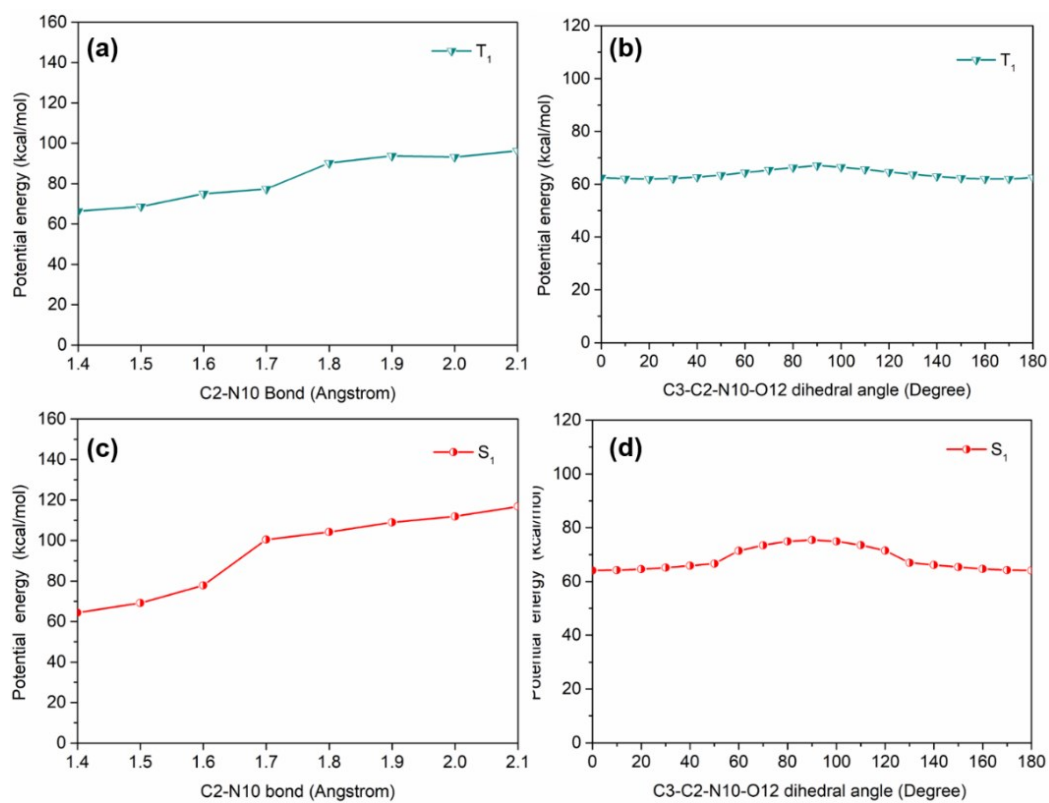
Figure S14. PESs scanned along the C_2-N_{10} bond and the C_3-C_2-N_{10}-O_{12} dihedral angle in the T_1 (a,b) and S_1 (c,d) states in the gas phase at MN15 level.
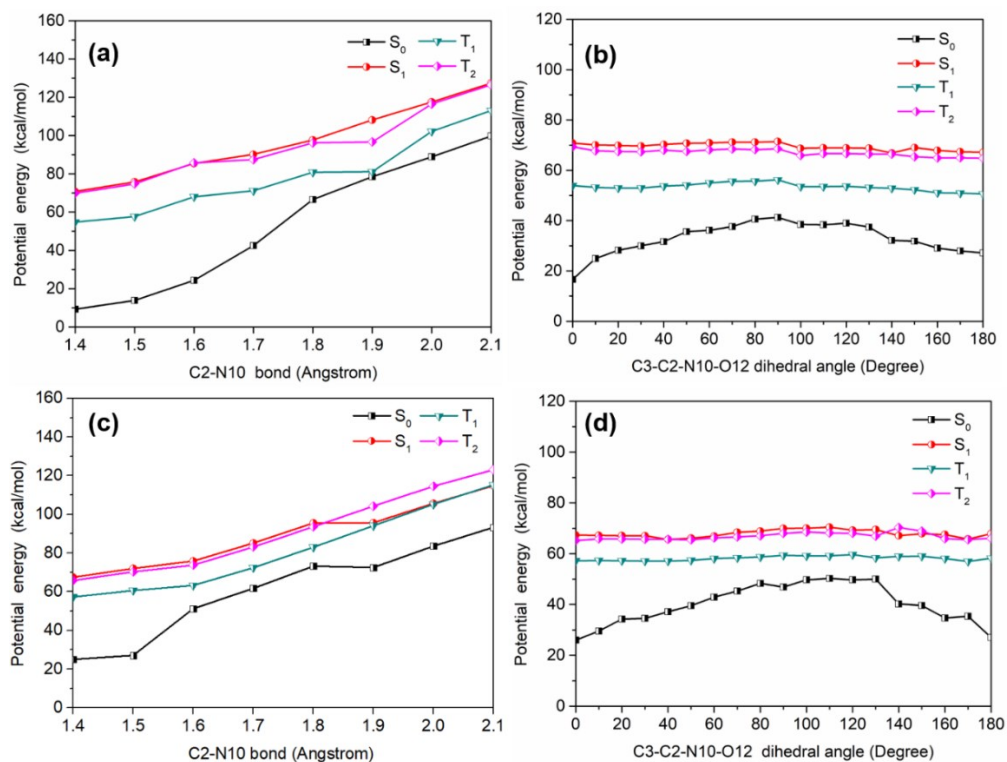
Figure S15. PESs scanned along the C_2-N_{10} bond and the C_3-C_2-N_{10}-O_{12} dihedral angle in the T_1 (a,b) and S_1 (c,d) states in acetonitrile solution at QM(SA5- CASSCF)/MM level.
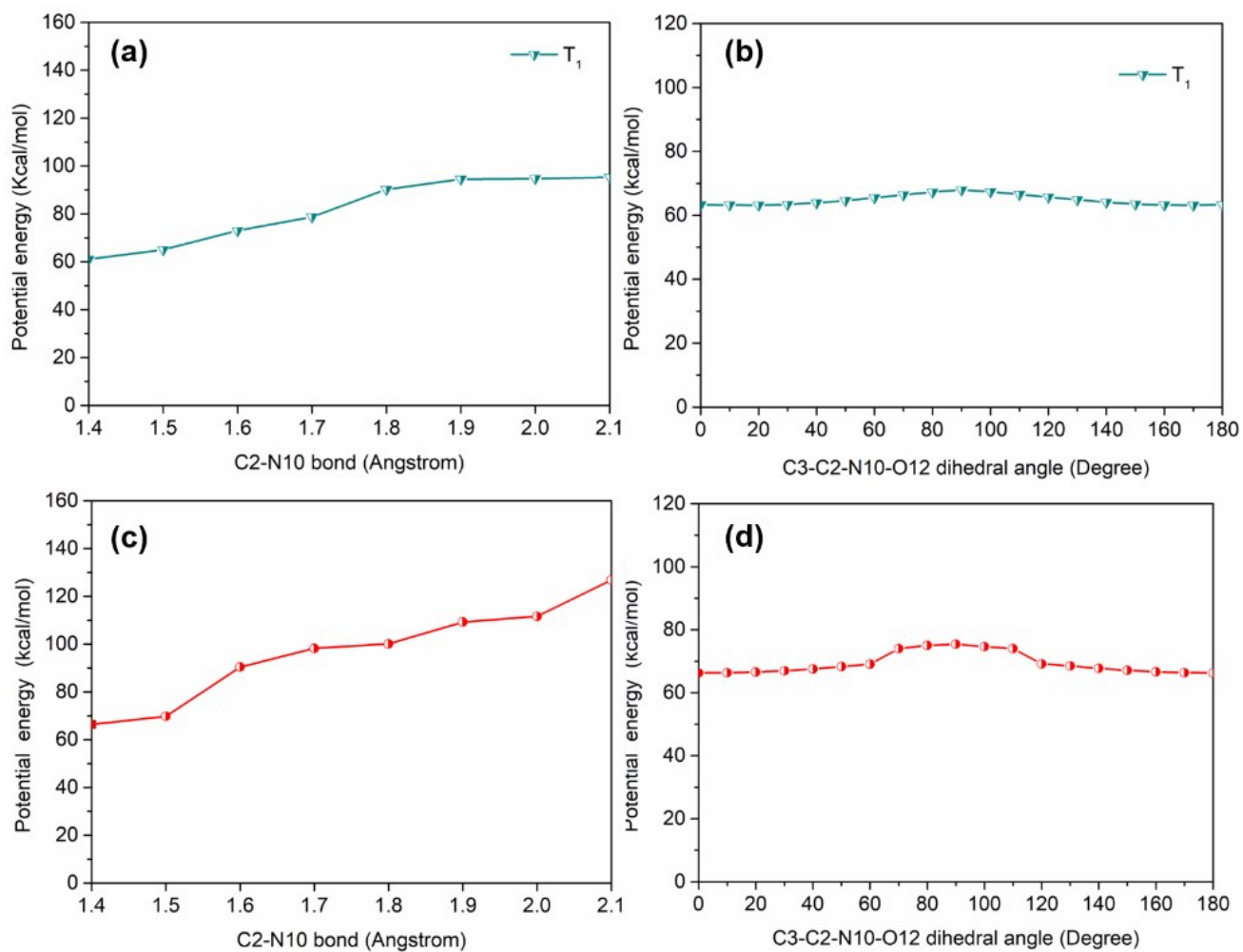
Figure S16. PESs scanned along the C_2-N_{10} bond and t the C_3-C_2-N_{10}-O_{12} dihedral angle in the T_1 (a,b) and S_1 (c,d) states in acetonitrile solution at MN15/PCM level.

Resonant structure of nitro group
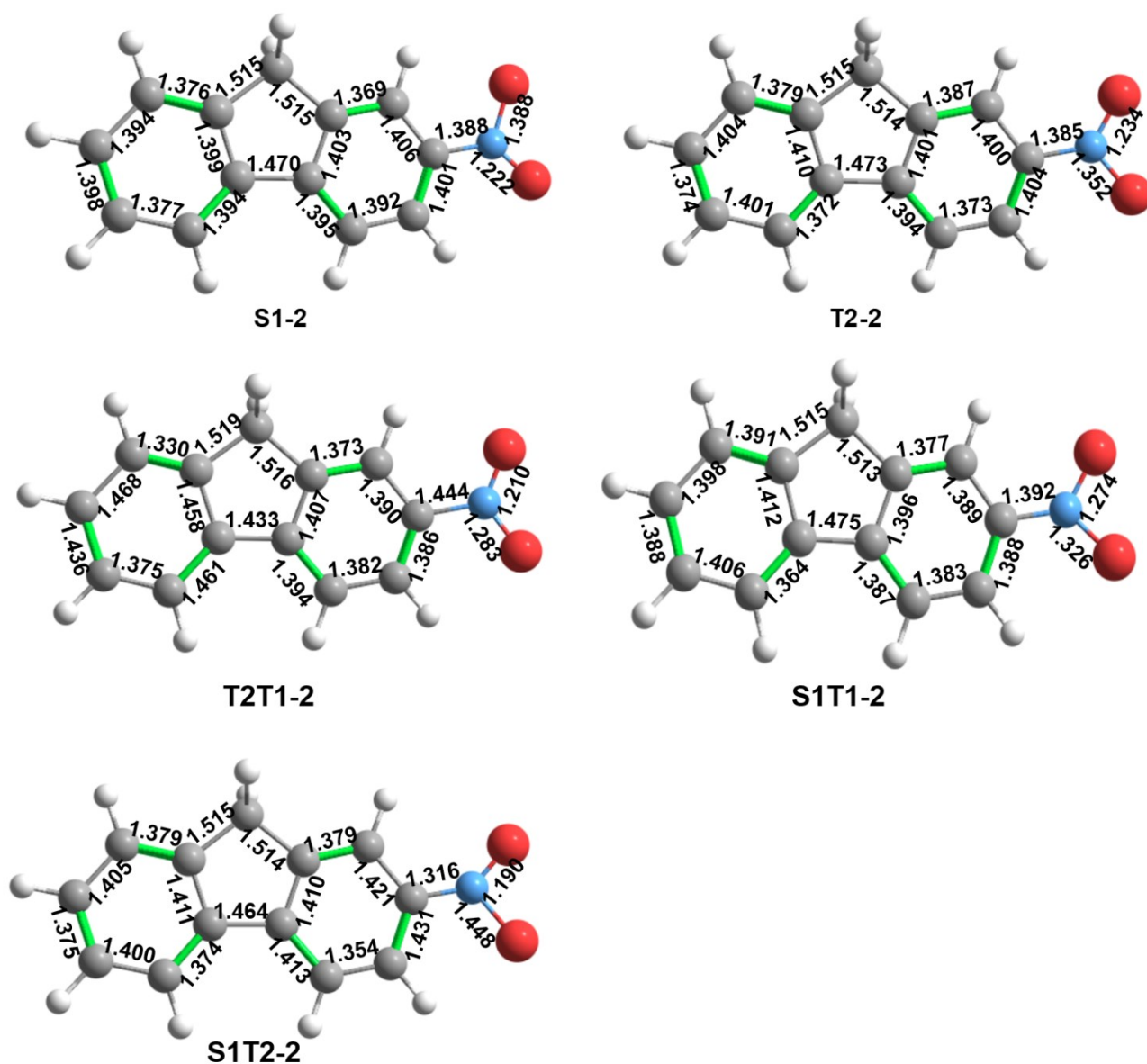
Figure S17. QM(SA5-CASSCF(14,11))/MM optimized additional minimum and surface-crossing structures in acetonitrile solution.

Table S5. QM(MS-CASPT2)/MM computed adiabatic excitation energies of additional minimum and surface-crossing structures in acetonitrile solution relative to their S_0 minima [units: kcal/mol].

Structures	Energies	Structures	Energies
S1	71.2	T2T1-2	71.9/73.0
S1-2	72.4	S1T1	76.8/73.5
T2	71.3	S1T1-2	70.3/74.4
T2-2	71.2	S1T2	73.2/72.8
T2T1	72.5/76.7	S1T2-2	76.3/79.1
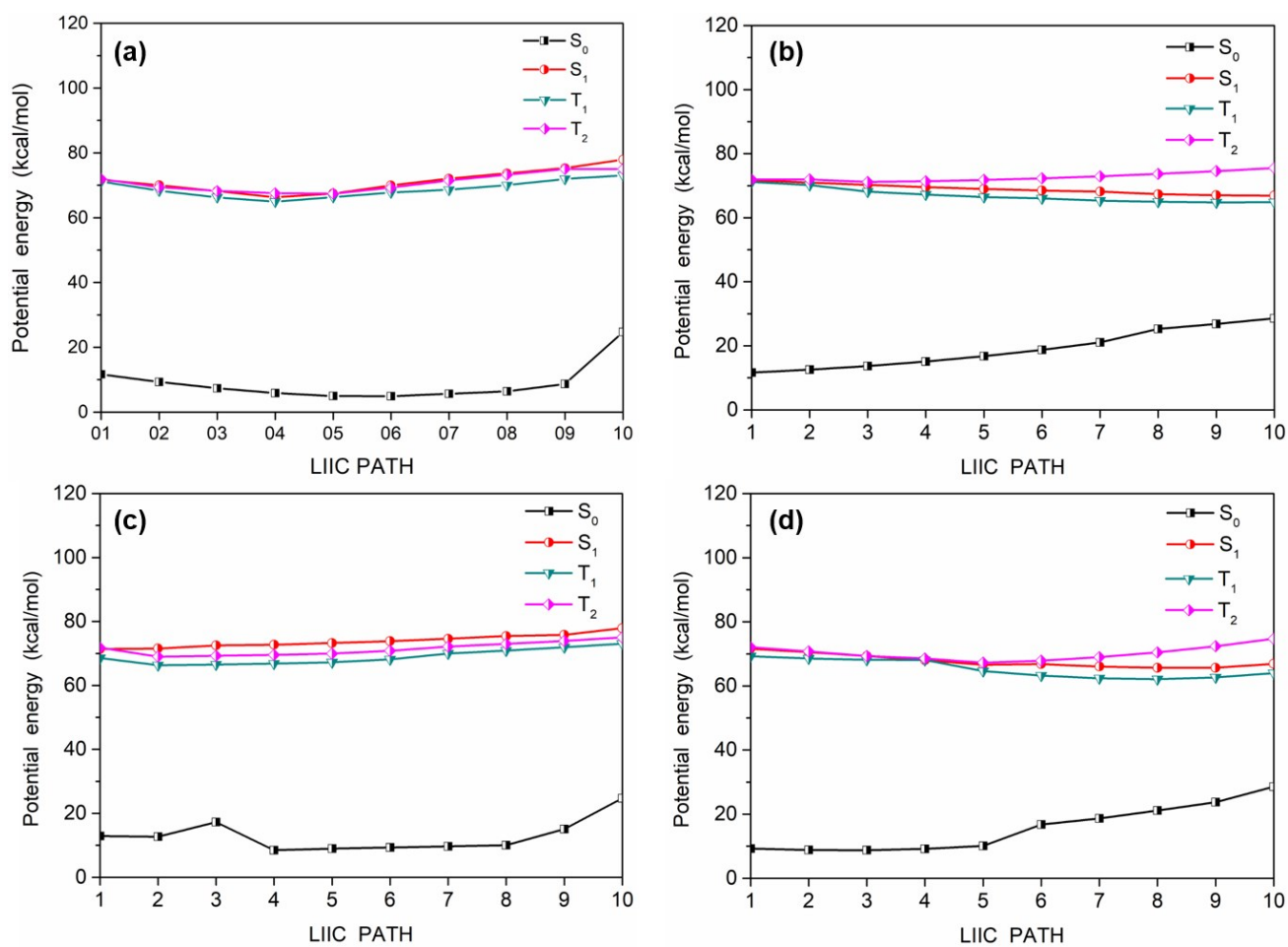
Figure S18. QM(MS-CASPT2)/MM computed linearly interpolated internal coordinate (LIIC) paths connecting the S_1 minimum and the S_1/T_1 crossing point (a); the S_1 minimum and the S_1/T_1-2 crossing point (b); the S_1-2 minimum and the S_1/T_1 crossing point (c); the S_1-2 minimum and the S_1/T_1-2 crossing point (d).

Discussion on the active space choice

A series of active spaces have been tested previously at the FC region and shown in Figs. 2 and S9. Only the active space (14e,11o) in Fig. 2, which includes five π and four π* orbitals on the aromatic ring and nitro group and two non-bonding n orbitals of the oxygen atoms, can give the reasonable vertical excitation energies and also the correct properties of electronic states in comparison to the experiments as well as TD-MN15 calculations. We finally employed this active space and denoted it as (I), to make a good balance between computational accuracy and efficiency. In contrast, the active spaces (II, III and IV) including the bonding π orbital of NO_2 group cannot give the correct electronic configurations of the S_1 state (see Table S1 and Fig. S9).

When we simulated the photodegradation reaction and performed CASSCF(14,11) and MS-CASPT2 calculations along the reaction path of the cleavage of the C_2-N_{10} bond, the σ and σ* orbitals of the C-N bond are involved in the active space. It is reasonable because the energy of the σ orbital increase and that of the σ* orbital decreases with the bond elongation. The updated active space (14e,11o) is shown in Fig. S10 and applied in the CASSCF and MS-CASPT2 calculations in Section 3.2. However, compared with photochemical reactions, the change on the geometry of 2-NF is not so large during the whole photophysical process. Therefore, the active space shown in Fig. 2 was applied to all the calculations in Section 3.1.

Discussion on comparison between CASPT2 and CASSCF results

The PESs scanned along the selected reaction coordinates at the CASSCF level were reported in Figs. S13 and S15. On one hand, the SA5-CASSCF calculations can provide at least qualitatively correct results in comparison with the MS-CASPT2. On the other hand, the influence of dynamical correlation is remarkable when the molecular structure changes along the selected reaction coordinate during photochemical processes. For example, the scanned PES along the C_2-N_{10} cleavage at the MS-CASPT2 level is smoother than that at the CASSCF level; The PESs along the rotation of the C_3-C_2-N_{10}-O_{12} dihedral angle in the lowest three excited states, T_1 state in particular, were underestimated at the CASSCF level.

Discussion on resonant structure of the nitro group

On account of the resonant structure of the nitro group, there would be some additional minimum and intersection structures due to the asymmetry in two N-O bond lengths. We have located two S_1 minimum structures in acetonitrile solution. As shown in Figs. 3 and S17, the N_{10}-O_{11} and N_{10}-O_{12} bond lengths of the minimum structure S1 are computed as 1.234 and 1.361 Å, respectively. In another optimized minimum structure denoted as S1-2, the N_{10}-O_{11} bond is elongated to 1.388 Å and the N_{10}-O_{12} bond is shortened to 1.222 Å. The adiabatic excitation energies of the two S_1 minima are calculated as 71.2 and 72.4 kcal/mol. The differences between other critical structures such as T2, T2T1, S1T1, S1T2 and their corresponding resonant geometries are found to be small in structures and energies. As shown in Fig. S18, the influence of the resonant structure on the LIIC path connecting S_1 minima and S1T1 is insignificant and suggests the same deactivation process. The small difference on the curves may originate from the flip of two N-O bonds.

Cartesian coordinates of all reported structures (Unit: Angstrom)

I. gas phase

S0

H	-0.932340599	-2.427751773	-0.875018172
C	-4.122952760	1.099740450	-0.000143439
C	-4.496666554	-0.244641690	-0.000454108
C	-3.524344445	-1.251912973	-0.000444858
C	-2.195413496	-0.896250314	-0.000167871
C	-1.817669943	0.448163144	0.000134268
C	-2.774082371	1.459389756	0.000152980
H	-4.879600024	1.863641296	-0.000187392
H	-5.538682800	-0.509139947	-0.000702462
H	-3.820288398	-2.286514964	-0.000720882
H	-2.488771842	2.496152928	0.000305552
C	-0.968798890	-1.784646457	-0.000139782
H	-0.932494457	-2.427814714	0.874702581
C	0.157573670	-0.775137527	0.000073788
C	1.527384572	-1.005442875	0.000113032
C	2.366311151	0.103697658	0.000172009
C	1.874918163	1.403562694	0.000402688
C	0.513075708	1.614444305	0.000541010
C	-0.345159856	0.516590578	0.000290571
H	1.936549760	-1.995789185	-0.000169702
H	2.558063433	2.228648362	0.000433761
H	0.129054028	2.617988232	0.000727719
O	4.521249997	0.868436445	-0.005413298
O	4.215397755	-1.238222422	0.005045239
N	3.806927234	-0.103411887	-0.000010420

S1

C	-2.118195190	-3.228322230	-0.124932060
C	-0.779561250	-3.497411030	0.220119340
C	0.140881110	-2.463316030	0.432558850
C	-0.308095580	-1.158533690	0.293009300
C	-1.639760490	-0.884571450	-0.049749000
C	-2.539344970	-1.931028270	-0.256922190
C	-0.583256060	1.182761090	0.178030240
C	-0.468701220	2.557049790	0.180657100
C	-1.600814430	3.331158270	-0.121371440
C	-2.801216040	2.730010840	-0.414341000
C	-2.921706470	1.334066950	-0.418013020
C	-1.817852900	0.573036350	-0.123261540
H	1.303617180	0.190994690	-0.227724410
H	-2.807210610	-4.036209210	-0.283421230
H	1.154781350	-2.696079320	0.694588070
H	-3.562833080	-1.733195520	-0.519898220
C	0.469298270	0.130464130	0.464944320
H	0.874395450	0.223788330	1.468292050
H	0.467411100	3.036016350	0.408951500
H	-1.525169160	4.403907710	-0.122681200
H	-3.660356090	3.334799160	-0.643891060
H	-3.868045870	0.877933190	-0.649273720
O	0.772079890	-5.221142710	0.654431920
O	-1.231357140	-5.829782230	0.165738700
N	-0.346092510	-4.805593220	0.352671390

S2

C	-2.126416000	-3.234069000	-0.134189000

C	-0.795645000	-3.508861000	0.213087000
C	0.119222000	-2.473368000	0.426796000
C	-0.327441000	-1.166074000	0.287864000
C	-1.654817000	-0.888037000	-0.055510000
C	-2.549487000	-1.931330000	-0.265026000
C	-0.592250000	1.176787000	0.176920000
C	-0.472532000	2.550389000	0.183242000
C	-1.601630000	3.330109000	-0.116748000
C	-2.803937000	2.733832000	-0.410333000
C	-2.929720000	1.337912000	-0.417108000
C	-1.828924000	0.571908000	-0.125735000
H	1.289377000	0.177745000	-0.233813000
H	-2.813813000	-4.041603000	-0.291755000
H	1.136399000	-2.689177000	0.690839000
H	-3.573358000	-1.736497000	-0.529478000
C	0.456305000	0.119355000	0.460982000
H	0.864725000	0.210622000	1.463371000
H	0.465568000	3.025128000	0.412792000
H	-1.521796000	4.402602000	-0.115805000
H	-3.660969000	3.342176000	-0.638836000
H	-3.877642000	0.885810000	-0.649959000
O	0.870713000	-5.111242000	0.668093000
O	-1.237970000	-5.825504000	0.165262000
N	-0.377036000	-4.845146000	0.343199000

T1

H	-0.923266289	-2.417924656	-0.875386373
C	-4.144864561	1.095162512	0.000003270
C	-4.514469210	-0.254192218	0.000334001

C	-3.540104275	-1.258967281	0.000178100
C	-2.197254388	-0.893147202	-0.000251349
C	-1.828210572	0.461058193	-0.000517213
C	-2.795297531	1.463530304	-0.000429438
H	-4.905203736	1.855507074	0.000135882
H	-5.556226021	-0.520799310	0.000746002
H	-3.831116460	-2.294982239	0.000452891
H	-2.518744214	2.502962053	-0.000621630
C	-0.964336539	-1.775308611	-0.000436211
H	-0.923233316	-2.418518985	0.874061954
C	0.160455580	-0.760416557	-0.000269388
C	1.520173108	-0.992805254	0.000145508
C	2.374077621	0.103097847	0.000246380
C	1.881449364	1.400646690	-0.000159520
C	0.512347666	1.614948849	-0.000546540
C	-0.350366717	0.535381471	-0.000539920
H	1.917051071	-1.989599742	0.000506862
H	2.559600656	2.230895762	-0.000131628
H	0.139611008	2.623669220	-0.000786601
O	4.627705235	0.867187264	0.001639470
O	4.298249349	-1.294857585	0.000307611
N	3.771212214	-0.108748486	0.000840730
T2			
H	-0.941129138	-2.429409347	-0.874393044
C	-4.126249021	1.103020132	-0.000491198
C	-4.506343968	-0.244379356	-0.000731021
C	-3.538939397	-1.249789612	-0.000392120
C	-2.198051599	-0.892353484	0.000109069

C	-1.821374141	0.447991024	0.000278982
C	-2.779837332	1.456412854	0.000023628
H	-4.879772081	1.870066407	-0.000779811
H	-5.549510084	-0.504837704	-0.001227321
H	-3.832834519	-2.285003644	-0.000583831
H	-2.492247981	2.492825382	0.000137089
C	-0.974812899	-1.786397298	0.000392470
H	-0.941416777	-2.429200587	0.875348506
C	0.159580760	-0.782812418	0.000483832
C	1.507287669	-1.014917042	0.000371033
C	2.368176591	0.091980917	0.000228610
C	1.869904897	1.398540421	0.000470222
C	0.510294395	1.609754704	0.000605109
C	-0.357424708	0.522300056	0.000542989
H	1.916732517	-2.007142995	0.000235140
H	2.542834844	2.235261173	0.000471873
H	0.134303328	2.616966010	0.000721538
O	4.614374403	0.897871475	-0.002062310
O	4.352539024	-1.208325516	-0.000665477
N	3.733154231	-0.134642441	0.000428829

T3

H	-0.918716126	-2.419281567	-0.874104113
C	-4.139945869	1.095609608	-0.000709251
C	-4.510095025	-0.253363098	-0.000881599
C	-3.536198158	-1.258957550	-0.000334001
C	-2.193353489	-0.894109464	0.000265462
C	-1.823807431	0.460305163	0.000396618
C	-2.789984523	1.463196017	-0.000031920

H	-4.899743574	1.856477003	-0.001113680
H	-5.552008902	-0.519316126	-0.001430678
H	-3.828181728	-2.294708056	-0.000402291
H	-2.512660210	2.502407740	0.000149731
C	-0.960158457	-1.776405310	0.000593599
H	-0.918971915	-2.419091396	0.875449256
C	0.164709234	-0.761052035	0.000609570
C	1.523769561	-0.995028820	0.000216142
C	2.381415352	0.101114178	0.000115578
C	1.885385427	1.400215632	0.000557038
C	0.516782918	1.612745778	0.000775832
C	-0.346577167	0.534098740	0.000689370
H	1.914864219	-1.993831583	-0.000072571
H	2.558614153	2.234063513	0.000676670
H	0.144891980	2.621742432	0.001077082
O	4.586526450	0.924877485	-0.003925860
O	4.242931287	-1.338140215	0.001465048
N	3.779751056	-0.109788928	-0.000508248

S1S0

H	-0.935835778	-2.420419816	-0.875364836
C	-4.152090968	1.095550960	-0.000035121
C	-4.523333288	-0.252029730	-0.000094061
C	-3.550961378	-1.257649889	-0.000282792
C	-2.207276941	-0.893345427	-0.000244702
C	-1.835694101	0.459348141	-0.000197669
C	-2.802165384	1.463276076	0.000021807
H	-4.911288613	1.856992014	0.000051669
H	-5.565421582	-0.517116670	0.000023421

H	-3.842859671	-2.293340959	-0.000352750
H	-2.525243500	2.502505183	0.000298938
C	-0.976765479	-1.778095698	-0.000279623
H	-0.936096159	-2.420828426	0.874453355
C	0.150243142	-0.765993926	-0.000067661
C	1.506466719	-0.999336804	0.000504100
C	2.355846470	0.107640018	0.000418452
C	1.865849574	1.412095704	0.000052828
C	0.498605208	1.618597298	-0.000006990
C	-0.360846014	0.533369359	0.000003080
H	1.912688036	-1.994199885	0.000820902
H	2.548632135	2.240836643	-0.000086388
H	0.119793050	2.624731083	-0.000111408
O	4.752178625	0.680698709	-0.001928412
O	4.479811555	-1.136168414	0.000499400
N	3.705003367	-0.093336447	0.001427281

S2S1

H	-0.922618385	-2.420716732	-0.874712233
C	-4.127939726	1.092527484	-0.000282157
C	-4.493002156	-0.251657205	-0.000182937
C	-3.515721576	-1.250918183	-0.000050166
C	-2.190045776	-0.892021960	-0.000014288
C	-1.816257527	0.458759082	-0.000113445
C	-2.780464746	1.460366856	-0.000248047
H	-4.888627825	1.852629742	-0.000384495
H	-5.533445358	-0.522910171	-0.000207803
H	-3.807032709	-2.287214203	0.000024787
H	-2.502822250	2.499529063	-0.000320073

C	-0.959708927	-1.777883773	0.000121182
H	-0.922704345	-2.420569901	0.875066570
C	0.169412450	-0.766587182	0.000089833
C	1.519282487	-1.002880281	0.000141476
C	2.390881190	0.097477720	0.000103354
C	1.883374278	1.405259210	0.000015976
C	0.523302032	1.614544187	-0.000097295
C	-0.346060865	0.532819867	-0.000049298
H	1.906978007	-2.000491819	0.000184974
H	2.553640310	2.238352796	0.000064062
H	0.151842840	2.623721286	-0.000182227
O	4.498734463	0.983917452	0.002304969
O	4.141171946	-1.371979639	-0.002058404
N	3.837071202	-0.120294588	0.000308500

T2T1

H	-0.937943078	-2.425628137	-0.875034815
C	-4.134204190	1.095122972	-0.000051193
C	-4.502041969	-0.249360798	0.000022262
C	-3.527871565	-1.249818971	-0.000009668
C	-2.200839929	-0.893404663	-0.000111148
C	-1.823435811	0.456368916	-0.000191102
C	-2.786709820	1.460573753	-0.000157578
H	-4.893676716	1.856316763	-0.000029242
H	-5.543077982	-0.518082106	0.000107910
H	-3.820850215	-2.285554814	0.000039540
H	-2.507359183	2.499178240	-0.000223001
C	-0.973724191	-1.783069218	-0.000129961
H	-0.937900627	-2.425598255	0.874794663

C	0.159111502	-0.776684868	-0.000166903
C	1.505011482	-1.009209505	-0.000076138
C	2.366241782	0.103555156	0.000017378
C	1.864935944	1.417286753	-0.000166648
C	0.509040076	1.621354735	-0.000300562
C	-0.356325723	0.529494697	-0.000234029
H	1.910929390	-2.003759213	-0.000064819
H	2.546890644	2.246177475	-0.000151678
H	0.127050621	2.626351561	-0.000425691
O	4.649940559	0.777261925	0.000783780
O	4.356953315	-1.199104057	0.000787612
N	3.719094727	-0.095989218	0.000493802

T3T2

C	-2.159594840	-3.237434860	-0.133267030
C	-0.792908180	-3.522723150	0.213498110
C	0.150078190	-2.483697230	0.429165050
C	-0.283333140	-1.187245560	0.296320540
C	-1.643829550	-0.887162950	-0.048994810
C	-2.570489360	-1.963427920	-0.260155490
C	-0.567101950	1.155919240	0.181926930
C	-0.459220200	2.511922310	0.184020320
C	-1.591728620	3.295873540	-0.112963660
C	-2.820087050	2.676415350	-0.408310530
C	-2.942046810	1.316169520	-0.414038880
C	-1.809277910	0.523020120	-0.116550720
H	1.322400310	0.171632540	-0.230121060
H	-2.834887780	-4.055436030	-0.286420390
H	1.162528330	-2.724945020	0.686753030

H	-3.592291600	-1.753492580	-0.518948260
C	0.491116120	0.105505580	0.465478820
H	0.899007320	0.203154630	1.467149960
H	0.477375640	2.992159540	0.409142210
H	-1.518608670	4.367494960	-0.114149460
H	-3.674800410	3.289549370	-0.632786830
H	-3.886670380	0.855451090	-0.641310700
O	0.782426520	-5.148850960	0.638941470
O	-1.187193350	-5.794190380	0.159337430
N	-0.389395870	-4.857613840	0.339773580

S0T1

H	0.852189000	0.231989000	1.483035000
C	-2.784702000	2.757209000	-0.433424000
C	-1.566470000	3.347656000	-0.128923000
C	-0.461117000	2.565799000	0.179089000
C	-0.591394000	1.190953000	0.178404000
C	-1.815835000	0.598924000	-0.127526000
C	-2.918596000	1.376731000	-0.435118000
H	-3.632282000	3.375404000	-0.669872000
H	-1.478184000	4.419413000	-0.131577000
H	0.480882000	3.030182000	0.414428000
H	-3.866456000	0.926516000	-0.671869000
C	0.455008000	0.135837000	0.476660000
H	1.295245000	0.193229000	-0.209218000
C	-0.323642000	-1.153019000	0.302612000
C	0.120202000	-2.451839000	0.447658000
C	-0.816148000	-3.499241000	0.227337000
C	-2.163887000	-3.223268000	-0.128726000

C	-2.575143000	-1.905313000	-0.265712000
C	-1.659809000	-0.867711000	-0.052073000
H	1.133233000	-2.685488000	0.717443000
H	-2.846288000	-4.036430000	-0.287160000
H	-3.594562000	-1.697252000	-0.535075000
O	-1.018340000	-5.904459000	0.230791000
O	0.699881000	-5.324192000	0.664053000
N	-0.421059000	-4.766645000	0.353732000

S1T1

H	-0.927972765	-2.421624753	-0.874930112
C	-4.142006199	1.096394600	-0.000154202
C	-4.513402939	-0.251457430	-0.000267520
C	-3.540500295	-1.257167899	-0.000249258
C	-2.198826409	-0.894185956	-0.000127362
C	-1.826800732	0.458487863	-0.000019950
C	-2.793532323	1.463227408	-0.000029009
H	-4.901334345	1.857754257	-0.000178259
H	-5.555419073	-0.516735847	-0.000368821
H	-3.832964337	-2.292754397	-0.000347421
H	-2.515686983	2.502227444	0.000036392
C	-0.967976929	-1.778927411	-0.000080329
H	-0.928095126	-2.421682407	0.874732945
C	0.158582790	-0.766250154	0.000045530
C	1.516411759	-0.997914164	0.000009091
C	2.365658099	0.104105998	0.000137771
C	1.876246938	1.404419041	0.000251952
C	0.508359215	1.615789764	0.000116980
C	-0.351955148	0.532148468	0.000067761

H	1.918963999	-1.993439135	-0.000270140
H	2.556497074	2.234331922	0.000518509
H	0.132075751	2.622923688	0.000172612
O	4.648386556	0.821130788	-0.002635483
O	4.339551914	-1.243050069	0.002869099
N	3.744978549	-0.103972508	0.000222059

S1T2

H	-0.942918037	-2.429831255	-0.874903171
C	-4.125789790	1.093547939	-0.000253180
C	-4.491329977	-0.247419146	-0.000170141
C	-3.514085222	-1.244971829	-0.000064671
C	-2.200686070	-0.894723124	-0.000064422
C	-1.816778861	0.455786963	-0.000099469
C	-2.779940511	1.458632027	-0.000208358
H	-4.885403585	1.854758796	-0.000363143
H	-5.531481428	-0.519187489	-0.000190689
H	-3.807774266	-2.280846443	0.000004800
H	-2.500157123	2.497165520	-0.000275431
C	-0.975388782	-1.787264011	0.000004932
H	-0.942967076	-2.429736146	0.874986554
C	0.161930821	-0.784765606	0.000003662
C	1.497689129	-1.017337715	0.000009388
C	2.373147741	0.102414689	0.000099951
C	1.858243815	1.426304822	0.000124838
C	0.512674089	1.626904789	0.000027401
C	-0.361171177	0.528639256	-0.000021590
H	1.902789479	-2.012142365	-0.000145540
H	2.539375523	2.255692675	0.000323592

H	0.128490687	2.631187072	0.000071439
O	4.627049785	0.793897168	0.000287608
O	4.328930183	-1.210139895	0.000150429
N	3.714789690	-0.092787569	0.000188048

S1T3

C	-2.133032830	-3.264719860	-0.124545180
C	-0.787257490	-3.529322320	0.217866410
C	0.143192540	-2.516814890	0.429880110
C	-0.308654740	-1.163238770	0.289125900
C	-1.689782240	-0.890910680	-0.061673760
C	-2.565193460	-1.885291900	-0.260490630
C	-0.575151180	1.175407770	0.175346870
C	-0.446282400	2.523816560	0.180651100
C	-1.579406650	3.332968280	-0.118295420
C	-2.827505210	2.718833160	-0.417710950
C	-2.958299670	1.366999060	-0.423605410
C	-1.828053470	0.563638010	-0.125396660
H	1.307905180	0.176625320	-0.235183890
H	-2.816437960	-4.071787890	-0.278530710
H	1.156524290	-2.746045600	0.688360660
H	-3.590103190	-1.694380950	-0.520680620
C	0.472441060	0.113799090	0.458375230
H	0.884490510	0.210891500	1.460252430
H	0.495475310	2.992647200	0.406404160
H	-1.493937350	4.402870720	-0.118101660
H	-3.674301100	3.342618050	-0.641425920
H	-3.904455150	0.909958170	-0.650786010
O	0.793774160	-5.124671140	0.646189540

O	-1.181910160	-5.782205820	0.166877240
N	-0.369150320	-4.903948990	0.350829770

TS-1(MN15/6-31G*)

C	1.865806000	1.561088000	-0.125343000
C	2.442853000	0.248014000	-0.021775000
C	1.612059000	-0.922287000	0.010719000
C	0.256250000	-0.748202000	0.014348000
C	-0.315049000	0.558144000	-0.048994000
C	0.501157000	1.707686000	-0.125827000
C	-2.097479000	-0.935063000	0.034462000
C	-3.429637000	-1.326446000	0.059235000
C	-4.422569000	-0.343151000	0.018172000
C	-4.088036000	1.016120000	-0.047211000
C	-2.756075000	1.416853000	-0.072927000
C	-1.760043000	0.433538000	-0.032297000
H	-0.785601000	-2.390328000	0.979198000
H	2.545119000	2.404958000	-0.185372000
H	2.102722000	-1.890949000	0.036560000
H	0.052890000	2.695952000	-0.192249000
C	-0.846339000	-1.781099000	0.068355000
H	-0.794742000	-2.475032000	-0.780432000
H	-3.699742000	-2.378671000	0.110085000
H	-5.469010000	-0.636169000	0.037495000
H	-4.877657000	1.762097000	-0.077688000
H	-2.494076000	2.471325000	-0.122954000
O	3.688303000	0.222826000	1.164879000
O	4.404166000	-0.901510000	-0.751371000
N	3.843280000	0.079302000	-0.214028000

TS-2(MN15/6-31G*)

H	-0.717642000	-2.510335000	-0.572241000
C	-4.042066000	1.019870000	-0.234112000
C	-4.384655000	-0.336675000	-0.139665000
C	-3.398067000	-1.318067000	0.013654000
C	-2.068479000	-0.929714000	0.071331000
C	-1.718720000	0.439620000	-0.025315000
C	-2.712619000	1.420791000	-0.177830000
H	-4.825909000	1.763271000	-0.352579000
H	-5.430322000	-0.629143000	-0.185557000
H	-3.674690000	-2.367331000	0.087021000
H	-2.445386000	2.472429000	-0.251631000
C	-0.825874000	-1.774659000	0.234644000
H	-0.832899000	-2.336656000	1.177135000
C	0.286375000	-0.747126000	0.207478000
C	1.623094000	-0.926749000	0.317875000
C	2.522853000	0.250916000	0.291700000
C	1.884623000	1.587141000	0.149785000
C	0.538014000	1.724970000	0.041796000
C	-0.290569000	0.566170000	0.058062000
H	2.098182000	-1.894211000	0.452798000
H	2.566567000	2.431573000	0.161224000
H	0.088126000	2.711904000	-0.043228000
O	3.693155000	0.172773000	0.992133000
O	4.112501000	-0.964058000	-1.082026000
N	3.749324000	0.118550000	-0.658603000

INT(MN15/6-31G*)

H	-0.866798000	-2.278220000	1.167265000

C	-4.127791000	1.009402000	-0.295772000
C	-4.434856000	0.039180000	0.667952000
C	-3.425678000	-0.728550000	1.259833000
C	-2.109066000	-0.515534000	0.878615000
C	-1.796567000	0.462724000	-0.094090000
C	-2.811223000	1.230465000	-0.685248000
H	-4.928081000	1.593942000	-0.741884000
H	-5.470127000	-0.118151000	0.958794000
H	-3.673687000	-1.479046000	2.006972000
H	-2.572224000	1.983232000	-1.433086000
C	-0.848042000	-1.197659000	1.357497000
H	-0.694915000	-1.068459000	2.436358000
C	0.233757000	-0.507907000	0.553598000
C	1.574215000	-0.708989000	0.567111000
C	2.426961000	0.108740000	-0.309225000
C	1.779930000	1.109332000	-1.176273000
C	0.428130000	1.276550000	-1.163000000
C	-0.370460000	0.477190000	-0.302872000
H	2.072665000	-1.443994000	1.192765000
H	2.438562000	1.697228000	-1.807529000
H	-0.039543000	2.021004000	-1.803489000
O	3.732139000	0.494500000	0.249306000
O	4.051477000	-1.659607000	-0.621739000
N	3.650029000	-0.495476000	-0.794977000

Free Radical(MN15/6-31G*)

H	-0.749901000	-2.155863000	1.263222000
C	-4.173050000	0.829445000	-0.448024000
C	-4.467051000	-0.137814000	0.522380000

C	-3.445065000	-0.818072000	1.191554000
C	-2.124869000	-0.516454000	0.883662000
C	-1.828148000	0.461322000	-0.089996000
C	-2.853435000	1.136493000	-0.764061000
H	-4.984536000	1.344771000	-0.954994000
H	-5.504373000	-0.361379000	0.757758000
H	-3.684118000	-1.566379000	1.943760000
H	-2.622263000	1.890899000	-1.512760000
C	-0.848070000	-1.080414000	1.461914000
H	-0.796615000	-0.954447000	2.550875000
C	0.223186000	-0.282879000	0.750159000
C	1.580350000	-0.303344000	0.910217000
C	2.413810000	0.602994000	0.132293000
C	1.751438000	1.465881000	-0.841386000
C	0.388762000	1.468521000	-0.990488000
C	-0.388686000	0.607306000	-0.183135000
H	2.086979000	-0.957754000	1.614995000
H	2.399129000	2.113010000	-1.425671000
H	-0.094860000	2.128213000	-1.707962000
O	3.653691000	0.642891000	0.287523000
O	3.965429000	-2.114494000	-0.844530000
N	4.102133000	-1.367579000	-1.718251000

II. QM/MM

S0

C	-2.989498215	-2.913140214	-0.274237018
C	-1.729723124	-3.423861247	0.022040000
C	-0.625610045	-2.601629188	0.239364015

C	-0.814396060	-1.231548089	0.128129010
C	-2.080395149	-0.705479053	-0.162335011
C	-3.168652231	-1.548747113	-0.356443026
C	-0.641371044	1.119771079	0.015737001
C	-0.258447020	2.450149179	-0.017723003
C	-1.229437090	3.420525250	-0.294768021
C	-2.538259186	3.063863224	-0.526678040
C	-2.927619212	1.718979127	-0.490881035
C	-1.975733145	0.764013057	-0.225923019
H	1.005915075	-0.216391018	-0.449265034
H	-3.808271275	-3.585750257	-0.432039034
H	0.329590022	-3.029350220	0.473378032
H	-4.141213301	-1.150361086	-0.580489043
C	0.199798014	-0.115912006	0.271587020
H	0.648824045	-0.106526010	1.260495090
H	0.762715054	2.743480198	0.147449012
H	-0.943850067	4.456283324	-0.334267023
H	-3.271358238	3.822088278	-0.737257051
H	-3.953772285	1.451389104	-0.672111051
O	-0.552105039	-5.286996385	0.617537043
O	-2.439939175	-5.564045403	-0.330440023
N	-1.562346111	-4.863258354	0.111232010
S1			
C	-2.113399151	-3.231683232	-0.147664011
C	-0.780360057	-3.499366252	0.215255017
C	0.137348008	-2.463134178	0.431061029
C	-0.313096022	-1.158906087	0.288601021
C	-1.644029118	-0.885870063	-0.054293004

C	-2.537925185	-1.932315141	-0.276830018
C	-0.585572044	1.182767086	0.178834012
C	-0.466717035	2.556611186	0.179012011
C	-1.598391115	3.333961240	-0.116767008
C	-2.801654204	2.735608200	-0.401459029
C	-2.925747211	1.338893096	-0.403769030
C	-1.822917132	0.575557042	-0.116816010
H	1.293275091	0.185469011	-0.244326020
H	-2.799715203	-4.040587295	-0.313164021
H	1.149936082	-2.693773193	0.698840053
H	-3.559466256	-1.736576128	-0.548996038
C	0.466448033	0.127877010	0.456972035
H	0.882389066	0.218561015	1.455837104
H	0.472136032	3.033108220	0.401015028
H	-1.519445109	4.406551320	-0.119761008
H	-3.660855268	3.341895242	-0.626839043
H	-3.874463279	0.885547063	-0.631187044
O	0.768955054	-5.215854378	0.686708051
O	-1.213569086	-5.840645425	0.197837016
N	-0.350273026	-4.802895348	0.370414025
S2			
C	-2.123382154	-3.236540232	-0.152127013
C	-0.796465058	-3.510283253	0.208353016
C	0.118984007	-2.473781177	0.426335032
C	-0.329846022	-1.165567084	0.285450019
C	-1.656460121	-0.888368065	-0.056654002
C	-2.550244183	-1.937798142	-0.280504022
C	-0.594010045	1.177050087	0.178590014

C	-0.470880035	2.551340183	0.180292012
C	-1.599422116	3.332639244	-0.114835009
C	-2.804197202	2.737599198	-0.400496027
C	-2.932384210	1.341203098	-0.404322031
C	-1.831617134	0.574180043	-0.117747007
H	1.282185092	0.175096015	-0.245201020
H	-2.807758205	-4.045462293	-0.316699021
H	1.134820081	-2.688971195	0.693816049
H	-3.572591260	-1.745292127	-0.551945042
C	0.454821035	0.118260008	0.455881035
H	0.870989064	0.207574015	1.454994103
H	0.469569036	3.024513218	0.403213029
H	-1.517263110	4.405059321	-0.116591009
H	-3.661799267	3.346448241	-0.625617046
H	-3.882151282	0.890411065	-0.632534048
O	0.867934060	-5.103180370	0.696512049
O	-1.233620088	-5.826920419	0.182169014
N	-0.378287029	-4.845742349	0.357819025
T1			
C	-2.128703153	-3.227683234	-0.149252009
C	-0.802853059	-3.498440255	0.211314017
C	0.112851007	-2.469792181	0.425974033
C	-0.330437023	-1.160462085	0.283088021
C	-1.658155118	-0.882403063	-0.059878004
C	-2.552896187	-1.925078139	-0.281068019
C	-0.590326040	1.182190087	0.173873012
C	-0.467356032	2.558290186	0.174104014
C	-1.596221118	3.338038244	-0.122249009

C	-2.801510204	2.742668197	-0.407821030
C	-2.930286213	1.347424095	-0.410237032
C	-1.831779131	0.579711041	-0.122967008
H	1.284078091	0.176424012	-0.249121017
H	-2.810199205	-4.039557294	-0.309935024
H	1.126828081	-2.693723196	0.693894050
H	-3.574637260	-1.728866126	-0.552515040
C	0.456799031	0.122059008	0.452096031
H	0.873209063	0.211267016	1.451007107
H	0.472749036	3.031948221	0.396869030
H	-1.514487109	4.410481319	-0.125136010
H	-3.658607265	3.351873244	-0.633784044
H	-3.880578282	0.897440063	-0.638221048
O	0.822940061	-5.157579373	0.699488052
O	-1.188918088	-5.843341424	0.205064016
N	-0.387606026	-4.838546353	0.366015028
T2			
C	-2.154050156	-3.223394231	-0.147091013
C	-0.821025058	-3.500773255	0.212035016
C	0.105013008	-2.475497177	0.423492033
C	-0.335011025	-1.164219084	0.279927023
C	-1.661730118	-0.881949066	-0.059347006
C	-2.566558188	-1.924014139	-0.277815018
C	-0.588173040	1.178818084	0.169442010
C	-0.459706034	2.552032183	0.169024013
C	-1.586332113	3.336751242	-0.124960011
C	-2.794403200	2.746061197	-0.407596030
C	-2.928464213	1.350714096	-0.409004027

C	-1.830341135	0.579850040	-0.123441008
H	1.281645093	0.166758012	-0.258208017
H	-2.832766207	-4.038951290	-0.302858019
H	1.121683081	-2.696568196	0.689361049
H	-3.587237261	-1.719109125	-0.546613041
C	0.456304033	0.115920007	0.445553030
H	0.875632065	0.204278013	1.443312103
H	0.482683037	3.022329218	0.389276030
H	-1.500329110	4.408778320	-0.128318011
H	-3.649802263	3.358111244	-0.631887045
H	-3.880657283	0.903781067	-0.634430048
O	0.829910061	-5.133477371	0.707479052
O	-1.118068081	-5.846634426	0.239756019
N	-0.438367030	-4.822879351	0.361063024

T3

C	-2.119114154	-3.238213237	-0.146216013
C	-0.790902056	-3.507786256	0.211813015
C	0.120607009	-2.470243177	0.425214028
C	-0.329449023	-1.164667086	0.283611023
C	-1.658504121	-0.889876067	-0.056641005
C	-2.547462187	-1.936109141	-0.275882018
C	-0.595900044	1.177689085	0.174774011
C	-0.476473037	2.554009184	0.174633011
C	-1.608008118	3.330880243	-0.119270006
C	-2.812229203	2.732191197	-0.402132031
C	-2.937373214	1.336478095	-0.404328027
C	-1.836712132	0.571541042	-0.119514010
H	1.280097091	0.176497012	-0.252106016

H	-2.802491203	-4.048145295	-0.308264020
H	1.137299081	-2.684045195	0.690522048
H	-3.570860257	-1.745857124	-0.545404041
C	0.454534030	0.120263007	0.450939033
H	0.872550063	0.210351015	1.449056105
H	0.462915034	3.030091222	0.395242027
H	-1.529082109	4.403532316	-0.122428009
H	-3.671514268	3.339055243	-0.626170046
H	-3.887068281	0.884157063	-0.630351044
O	0.872707064	-5.093003371	0.703182053
O	-1.225897090	-5.820101420	0.188729013
N	-0.368098028	-4.844530353	0.361419028

S1S0

C	-2.171808159	-3.202377232	-0.141456011
C	-0.816473060	-3.504590253	0.227997018
C	0.128753010	-2.459116178	0.437078034
C	-0.310411024	-1.156006084	0.287639019
C	-1.643059120	-0.862380065	-0.049573002
C	-2.564049185	-1.913578139	-0.266888021
C	-0.561121039	1.191321088	0.176018011
C	-0.430077030	2.562416186	0.174728015
C	-1.556888114	3.351332245	-0.117325010
C	-2.765740198	2.763233200	-0.396937029
C	-2.904074211	1.367711100	-0.397373029
C	-1.807028130	0.592291045	-0.113820010
H	1.303446095	0.173321012	-0.258865017
H	-2.860060206	-4.010994290	-0.300442024
H	1.140716084	-2.696102197	0.706067053

H	-3.582605262	-1.696576122	-0.534507038
C	0.481623037	0.125483007	0.448608034
H	0.904713064	0.212386014	1.444521103
H	0.513963038	3.030718218	0.392344030
H	-1.467887105	4.423066318	-0.121073008
H	-3.620342262	3.376930242	-0.619957045
H	-3.858365278	0.924097065	-0.620465045
O	0.661655048	-5.336660384	0.708352051
O	-1.048585076	-5.898830427	0.280749020
N	-0.451940035	-4.759775345	0.382370028

S2S1

C	-2.007866147	-3.347425245	-0.218072018
C	-0.692401051	-3.606062260	0.191392012
C	0.194745012	-2.566445188	0.460560031
C	-0.272057019	-1.259204093	0.348242028
C	-1.586617117	-0.989222073	-0.041584002
C	-2.455800178	-2.030109144	-0.334232023
C	-0.557554040	1.080402081	0.266569017
C	-0.442895031	2.457213177	0.291218020
C	-1.549753111	3.229934232	-0.029986003
C	-2.755364202	2.630871190	-0.370628025
C	-2.872324206	1.249713093	-0.399258027
C	-1.766154130	0.481085033	-0.081155004
H	1.347054100	0.106039008	-0.089245007
H	-2.665739192	-4.162829303	-0.430779031
H	1.208039088	-2.770552203	0.733558055
H	-3.468054252	-1.844967133	-0.644374045
C	0.489715036	0.029499002	0.572860042

H	0.859717065	0.109094007	1.591001118
H	0.487377035	2.929614210	0.555626041
H	-1.474043108	4.302778312	-0.014782000
H	-3.604435263	3.243598234	-0.615865044
H	-3.808188274	0.791958056	-0.667449047
O	0.993837070	-5.044116368	0.618261043
O	-1.273032093	-5.718574415	0.684545049
N	-0.260638020	-5.012973361	0.261867018

T2T1

C	1.525689109	1.464212106	-0.228473018
C	2.088104150	0.199901013	-0.414223027
C	1.309944095	-0.968699071	-0.474264034
C	-0.058933004	-0.842247061	-0.335150024
C	-0.638808048	0.428822033	-0.159033009
C	0.136298009	1.560826113	-0.112285009
C	-2.400615172	-1.097191081	-0.206922015
C	-3.711742270	-1.531218112	-0.165057015
C	-4.721772344	-0.599420041	0.028204004
C	-4.423287318	0.749266057	0.168614012
C	-3.110301226	1.188698088	0.116195010
C	-2.103100150	0.256707016	-0.070291006
H	-1.005469074	-2.639541193	0.417343030
H	2.159012156	2.326277167	-0.179747012
H	1.764044126	-1.931445142	-0.672510050
H	-0.309847022	2.529721181	0.021167000
C	-1.131637080	-1.908766140	-0.375804029
H	-1.117827083	-2.462807178	-1.334916096

H	-3.951400285	-2.574928185	-0.270481018
H	-5.745665417	-0.924241065	0.073966004
H	-5.217685379	1.457896106	0.319960023
H	-2.885577207	2.234931162	0.223688017
O	3.705583271	-1.401080102	-0.445585035
O	4.418029318	0.639130047	-0.401679029
N	3.426738246	-0.002518000	-0.529744040

T3T2

C	-2.162299156	-3.242907235	-0.163376014
C	-0.789783058	-3.526408257	0.206928016
C	0.154911009	-2.477016180	0.424736033
C	-0.282862020	-1.187088088	0.289916021
C	-1.650101120	-0.889315065	-0.054354002
C	-2.574880189	-1.974476142	-0.286018022
C	-0.574058042	1.157073085	0.182105015
C	-0.466017034	2.511514182	0.180582011
C	-1.601467117	3.296839239	-0.109661010
C	-2.812023204	2.705661197	-0.391299027
C	-2.945779215	1.317407098	-0.396742027
C	-1.821958131	0.530184040	-0.109923005
H	1.309912096	0.175917012	-0.251400019
H	-2.830178207	-4.065286294	-0.324274024
H	1.166399083	-2.718467196	0.683594049
H	-3.593821258	-1.764822128	-0.556196039
C	0.487706035	0.107531008	0.454132030
H	0.908188066	0.204600017	1.450397103
H	0.472224034	2.992381215	0.397681031
H	-1.516011108	4.368610317	-0.110106005

H	-3.667070264	3.319835240	-0.611300044
H	-3.895155284	0.865565061	-0.620411047
O	0.778160055	-5.131672374	0.691736050
O	-1.185486088	-5.791169421	0.192884012
N	-0.387919029	-4.857122353	0.364731027

S0T1

C	-2.157084156	-3.224739236	-0.163116014
C	-0.813447060	-3.500751252	0.213416015
C	0.120604009	-2.451692175	0.435615034
C	-0.323635021	-1.154262085	0.289151022
C	-1.660448123	-0.867555063	-0.063425005
C	-2.570481186	-1.907890140	-0.295454020
C	-0.591839043	1.190169085	0.178632014
C	-0.460556036	2.565165188	0.182487012
C	-1.567092112	3.348773245	-0.116412010
C	-2.787944200	2.759759199	-0.414777028
C	-2.923239212	1.379419099	-0.419513032
C	-1.818657134	0.599193045	-0.122712008
H	1.287317095	0.191032013	-0.234192017
H	-2.840182208	-4.037313291	-0.324475021
H	1.132308082	-2.683263193	0.712449052
H	-3.588681259	-1.701719122	-0.572223040
C	0.456333032	0.132637007	0.462371034
H	0.867003063	0.224162017	1.463531108
H	0.483215035	3.028608219	0.412329028
H	-1.477633105	4.420502322	-0.117278008
H	-3.636329262	3.379083247	-0.645379048
H	-3.872476282	0.930634066	-0.653859045

O	0.690517047	-5.316435383	0.719805050
O	-1.019258073	-5.905725427	0.288853021
N	-0.425588030	-4.762808346	0.383146030

S1T1

C	-2.181011154	-3.233284231	-0.159005010
C	-0.848929062	-3.513154251	0.201924016
C	0.090976004	-2.504640180	0.421647030
C	-0.333720023	-1.186174087	0.283183019
C	-1.666276121	-0.898133063	-0.060830004
C	-2.583454188	-1.947301139	-0.286191021
C	-0.576143042	1.160103085	0.176786011
C	-0.443206034	2.540713182	0.177833015
C	-1.577059112	3.327260242	-0.120074006
C	-2.779246199	2.736565196	-0.403993031
C	-2.911023208	1.332170095	-0.406052028
C	-1.830799132	0.569385041	-0.123056010
H	1.290254092	0.136676011	-0.246697020
H	-2.854283204	-4.052554294	-0.316498023
H	1.106679081	-2.739356198	0.689551050
H	-3.601741258	-1.733819125	-0.557052042
C	0.463440036	0.091104007	0.454346035
H	0.877587063	0.172580010	1.453939104
H	0.498042037	3.011156218	0.400212028
H	-1.492168106	4.399222316	-0.123089009
H	-3.636483263	3.344758239	-0.630060044
H	-3.864737276	0.889238064	-0.634637046
O	0.885078064	-5.004920363	0.717839051
O	-1.120101080	-5.824184420	0.224778017

N	-0.467875033	-4.833897346	0.347718026

S1T2

C	-2.155141155	-3.237178235	-0.159792013
C	-0.807890059	-3.516795255	0.209290015
C	0.130857009	-2.471318180	0.427891030
C	-0.309400021	-1.171855086	0.287170020
C	-1.657153121	-0.879737062	-0.060296006
C	-2.570715188	-1.936120142	-0.288706021
C	-0.583332042	1.171184084	0.176504013
C	-0.460414031	2.543547186	0.177185011
C	-1.584135117	3.325536241	-0.117433010
C	-2.795235204	2.732207199	-0.404310029
C	-2.926088212	1.342991098	-0.407444029
C	-1.820350131	0.567488041	-0.118828011
H	1.295981092	0.175477012	-0.247738017
H	-2.826292204	-4.056235294	-0.319412023
H	1.144659084	-2.698431196	0.692877051
H	-3.589560260	-1.730411123	-0.561738038
C	0.470226036	0.116245007	0.454390031
H	0.886412062	0.208848014	1.452786106
H	0.480779036	3.015220219	0.399857029
H	-1.499848109	4.397563319	-0.119551010
H	-3.649970266	3.344642243	-0.629524046
H	-3.875968280	0.892669064	-0.634997046
O	0.812983056	-5.090012371	0.703709050
O	-1.182508085	-5.802867419	0.204073015
N	-0.427653033	-4.852360350	0.359730027

S1T3

C	-2.120703152	-3.262064234	-0.151538012
C	-0.787277054	-3.524090254	0.211380016
C	0.142378012	-2.515635181	0.434598029
C	-0.310521025	-1.158207086	0.287923023
C	-1.685660122	-0.881214065	-0.063388005
C	-2.561149187	-1.881838135	-0.282426020
C	-0.572074040	1.178115083	0.177733011
C	-0.444531030	2.527104183	0.175913012
C	-1.581102116	3.330616242	-0.117826008
C	-2.832222207	2.715332197	-0.405939027
C	-2.965258214	1.365898101	-0.406426029
C	-1.828412130	0.561268039	-0.113969010
H	1.302263093	0.173749010	-0.251185020
H	-2.802384204	-4.070272297	-0.308817021
H	1.151615082	-2.746905198	0.704881051
H	-3.584172261	-1.694244123	-0.549812040
C	0.474649037	0.114759008	0.451607035
H	0.898468064	0.209366015	1.448592106
H	0.497654039	2.999071217	0.392384031
H	-1.497848110	4.400875318	-0.122748008
H	-3.679152264	3.340432242	-0.625759045
H	-3.912248281	0.907072068	-0.625788044
O	0.780409059	-5.123095369	0.680312049
O	-1.188031087	-5.778786420	0.183503012
N	-0.371566028	-4.905418355	0.367503026

TS-1(MN15/6-31G*/PCM)

| C | 1.861517000 | 1.566221000 | -0.112558000 |
| C | 2.444881000 | 0.247596000 | 0.004375000 |

C	1.608451000	-0.927873000	0.023197000
C	0.256179000	-0.752704000	0.023096000
C	-0.318292000	0.558038000	-0.041331000
C	0.500217000	1.710653000	-0.118192000
C	-2.095403000	-0.937862000	0.033593000
C	-3.427845000	-1.328940000	0.051898000
C	-4.419254000	-0.342964000	0.007633000
C	-4.084922000	1.018730000	-0.054461000
C	-2.753839000	1.420435000	-0.073825000
C	-1.757766000	0.433349000	-0.030007000
H	-0.788486000	-2.396397000	0.979654000
H	2.537544000	2.412129000	-0.179809000
H	2.091202000	-1.900383000	0.048465000
H	0.052628000	2.698113000	-0.192368000
C	-0.845980000	-1.784930000	0.070851000
H	-0.790468000	-2.477000000	-0.778407000
H	-3.698891000	-2.380554000	0.099730000
H	-5.465831000	-0.635090000	0.021737000
H	-4.875107000	1.763596000	-0.087522000
H	-2.490735000	2.474311000	-0.121565000
O	3.670647000	0.210911000	1.149938000
O	4.422409000	-0.889071000	-0.761828000
N	3.839433000	0.084010000	-0.228632000

TS-2(MN15/6-31G*/PCM)

H	-0.713773000	-2.512712000	-0.561832000
C	-4.043458000	1.019204000	-0.243197000
C	-4.383928000	-0.339993000	-0.148466000
C	-3.398239000	-1.322542000	0.009952000

C	-2.069115000	-0.932262000	0.072414000
C	-1.721712000	0.439342000	-0.024877000
C	-2.715464000	1.422680000	-0.182335000
H	-4.828556000	1.760213000	-0.365358000
H	-5.429073000	-0.632979000	-0.198065000
H	-3.674648000	-2.371320000	0.083477000
H	-2.448322000	2.473999000	-0.255755000
C	-0.826935000	-1.775296000	0.242042000
H	-0.835845000	-2.335671000	1.184876000
C	0.281725000	-0.746304000	0.216775000
C	1.619769000	-0.923074000	0.332902000
C	2.507342000	0.253467000	0.297237000
C	1.878053000	1.588545000	0.165936000
C	0.531192000	1.727381000	0.051519000
C	-0.296461000	0.567462000	0.063463000
H	2.090544000	-1.892512000	0.468394000
H	2.556671000	2.435661000	0.178993000
H	0.083082000	2.714447000	-0.033321000
O	3.709951000	0.171697000	0.961119000
O	4.131429000	-0.964706000	-1.085212000
N	3.756040000	0.119039000	-0.661265000

INT(MN15/6-31G*/PCM)

H	-0.879055000	-2.285501000	1.159360000
C	-4.127716000	1.027654000	-0.281984000
C	-4.434839000	0.055775000	0.682475000
C	-3.428358000	-0.720937000	1.268548000
C	-2.111981000	-0.514907000	0.880305000
C	-1.800034000	0.464569000	-0.092752000

C	-2.812159000	1.242034000	-0.678746000
H	-4.927241000	1.617531000	-0.721741000
H	-5.469426000	-0.095343000	0.978339000
H	-3.677222000	-1.471166000	2.015022000
H	-2.571894000	1.994636000	-1.425870000
C	-0.853474000	-1.205878000	1.350922000
H	-0.692963000	-1.080973000	2.428639000
C	0.226385000	-0.520664000	0.542966000
C	1.566324000	-0.730671000	0.547830000
C	2.413897000	0.091510000	-0.323850000
C	1.772959000	1.087839000	-1.196627000
C	0.421849000	1.263637000	-1.176271000
C	-0.376099000	0.470442000	-0.309360000
H	2.058564000	-1.472415000	1.170474000
H	2.428372000	1.667787000	-1.838370000
H	-0.043356000	2.007186000	-1.818665000
O	3.722944000	0.501135000	0.257410000
O	4.100327000	-1.639624000	-0.607536000
N	3.661225000	-0.485854000	-0.780092000

Free Radical(MN15/6-31G*/PCM)

H	-0.598409000	-2.214063000	0.848354000
C	-4.204662000	0.835692000	-0.279036000
C	-4.417929000	-0.308969000	0.503893000
C	-3.343852000	-1.032353000	1.031411000
C	-2.050891000	-0.598433000	0.766916000
C	-1.835359000	0.553442000	-0.022224000
C	-2.913887000	1.277835000	-0.549661000
H	-5.057149000	1.380289000	-0.675006000

H	-5.434593000	-0.636743000	0.703978000
H	-3.521067000	-1.917071000	1.637602000
H	-2.744535000	2.163655000	-1.155529000
C	-0.732076000	-1.185700000	1.208602000
H	-0.641179000	-1.221656000	2.302119000
C	0.275227000	-0.243676000	0.589572000
C	1.639838000	-0.267041000	0.646372000
C	2.410172000	0.754900000	-0.046573000
C	1.672706000	1.783037000	-0.775699000
C	0.302890000	1.793510000	-0.819535000
C	-0.410175000	0.778127000	-0.138281000
H	2.190037000	-1.025771000	1.196328000
H	2.267045000	2.538103000	-1.282583000
H	-0.232881000	2.565543000	-1.367415000
O	3.664731000	0.755816000	-0.025152000
O	3.759016000	-2.464792000	-0.544311000
N	4.172959000	-1.713522000	-1.321545000