Supporting Information

For

"Mechanistic Investigations on the role of Excited state Aromaticity during Photochemical Ring Opening Reaction"

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Contents

I.   Static Quantum Computational Details:

After the reaction path was traced out by the surface hopping molecular dynamics trajectory, comparison of S_0 to S_1 vertical excitation energies with B3LYP functional with 6-31++g(d,p) basis by using G09 program were conducted. The energetics and the structural parameters were computed using the B3LYP functional with 6-31++g(d,p) basis. All computations were carried out in the gas phase.

II.   Excited state dynamics using SHARC

Excited state dynamics studies were performed with the help of SHARC interfaced with MOLPRO. For the dynamics, the nuclei were considered as classical particles and Newton's laws of motion were integrated with the velocity Verlet algorithm. A 0.5 fs time step integration was used. A [2, 2] CAS space, and [4, 4] CAS space ware used for the excited state dynamics computations. The CASSCF were performed with MOLPRO in a State Averaged framework with equal weightage on each state. The probability of hopping from one state to the other was computed using Tully's surface hopping algorithm. The dynamics were carried out in a microcanonical ensemble. Ten different dynamics runs were performed from different initial conditions.

2.   Additional Supporting Material

I. S_0 to S_1 vertical excitation energy using the B3LYP, CAM-B3LYP, wB97x-D functionals with 6-31++g(d,p) basis Computed UV-VIS spectra for computation.
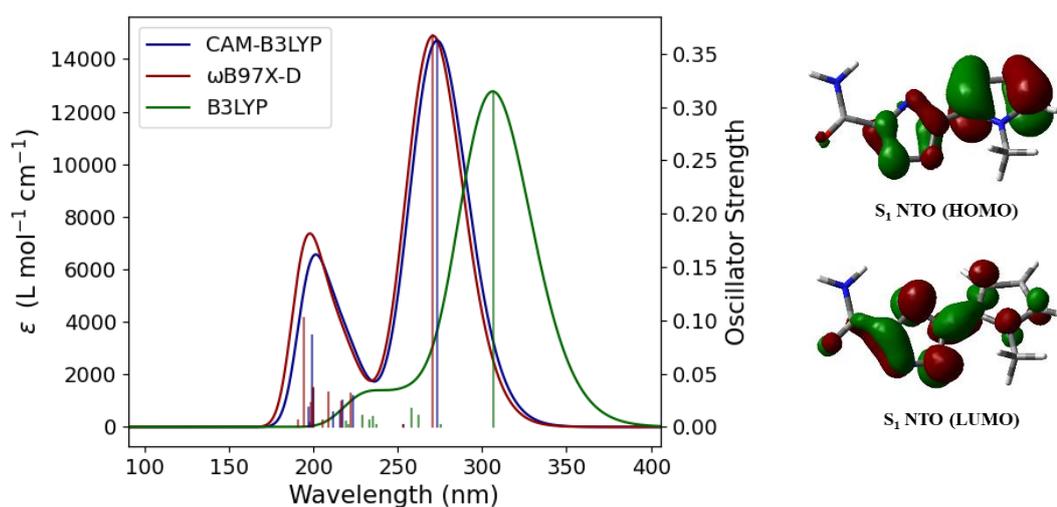

Figure S1: Vertical absorption spectra using TD-DFT level. The natural transition orbitals (NTOs) are also shown in case of S_1 state (bright state) which remains same across the three functionals.

II. More results from dynamics ([2, 2] CAS space)

The dynamics were carried out from ten different dynamic runs. Each run was executed from different initial condition. Dynamics were initiated from the first excited state (S_1) because S_1 is the brightest state. The black ball in section a (see Figure S2-S5) signifies the molecule at that particular time. We have included excited state dynamics results from product yielding trajectory in the main article. We have performed different dynamic run and we got the other successful trajectory also. From S2-S5 we have plotted potential energy, dipole moment, N-N and C-N bond distance and change in C-N-N angle with time. All these parameters together explain the photochemical event here how N_2 release from the system.
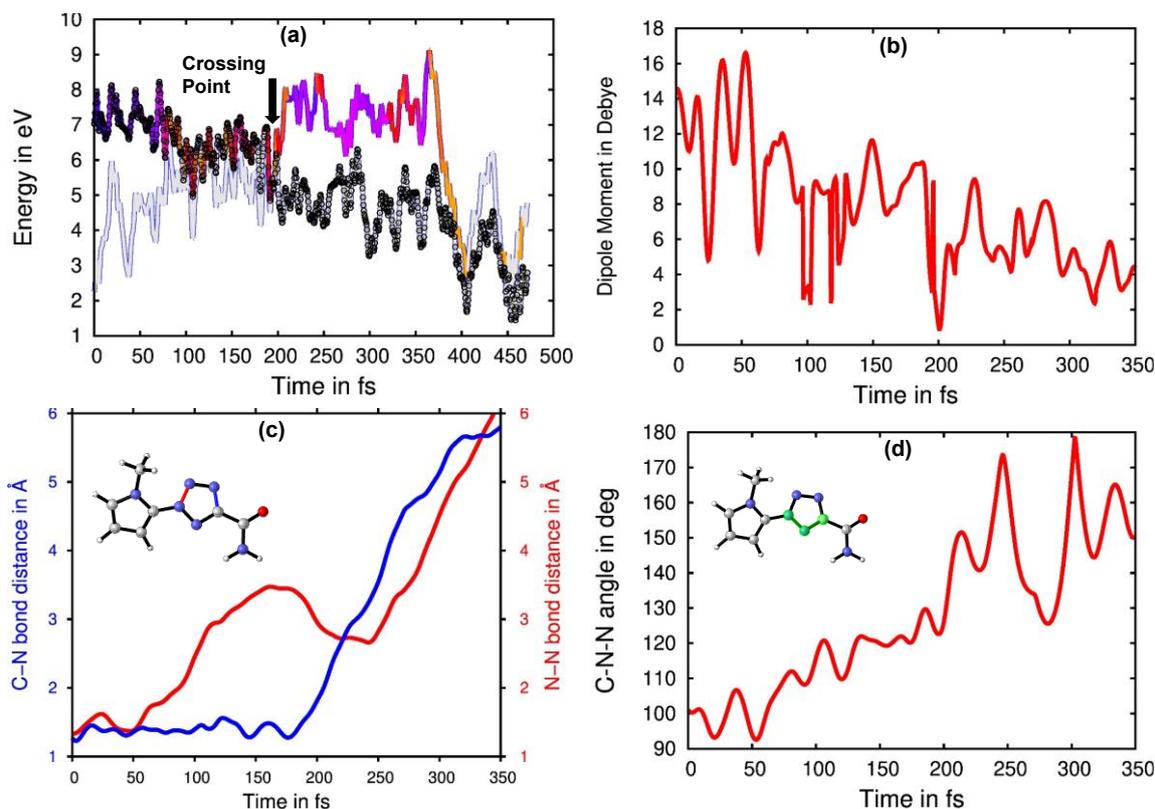

Figure S2: (a) Plot of the potential energies for molecule (A), trajectory with two singlet states. (b) Change of dipole moment during dynamics. (c) Plot of N-N bond (red) and C-N bond (blue) distance with time. (d) Change in C-N-N angle (highlighted) with time.

Figure S3: (a) Plot of the potential energies for molecule (A), trajectory with two singlet states. (b) Change of dipole moment during dynamics. (c) Plot of N-N bond (red) and C-N bond (blue) distance with time. (d) Change in C-N-N angle (highlighted) with time.
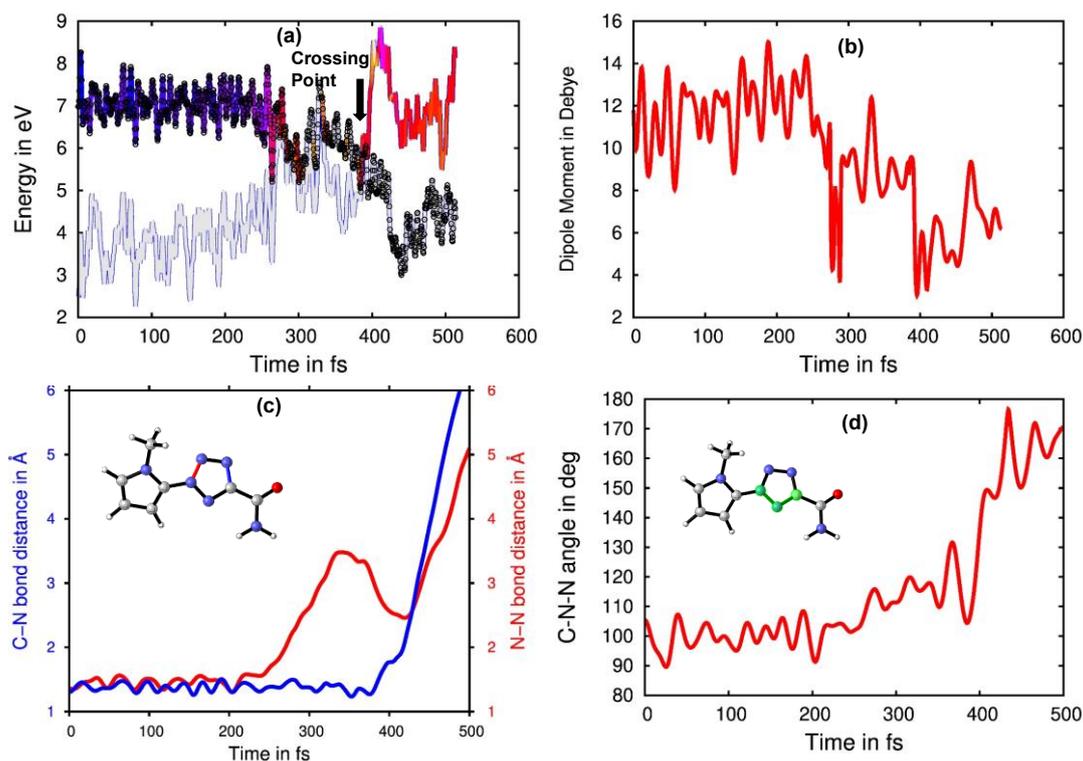

Figure S4: (a) Plot of the potential energies for molecule (A), trajectory with two singlet states. (b) Change of dipole moment during dynamics. (c) Plot of N-N bond (red) and C-N bond (blue) distance with time. (d) Change in C-N-N angle (highlighted) with time.
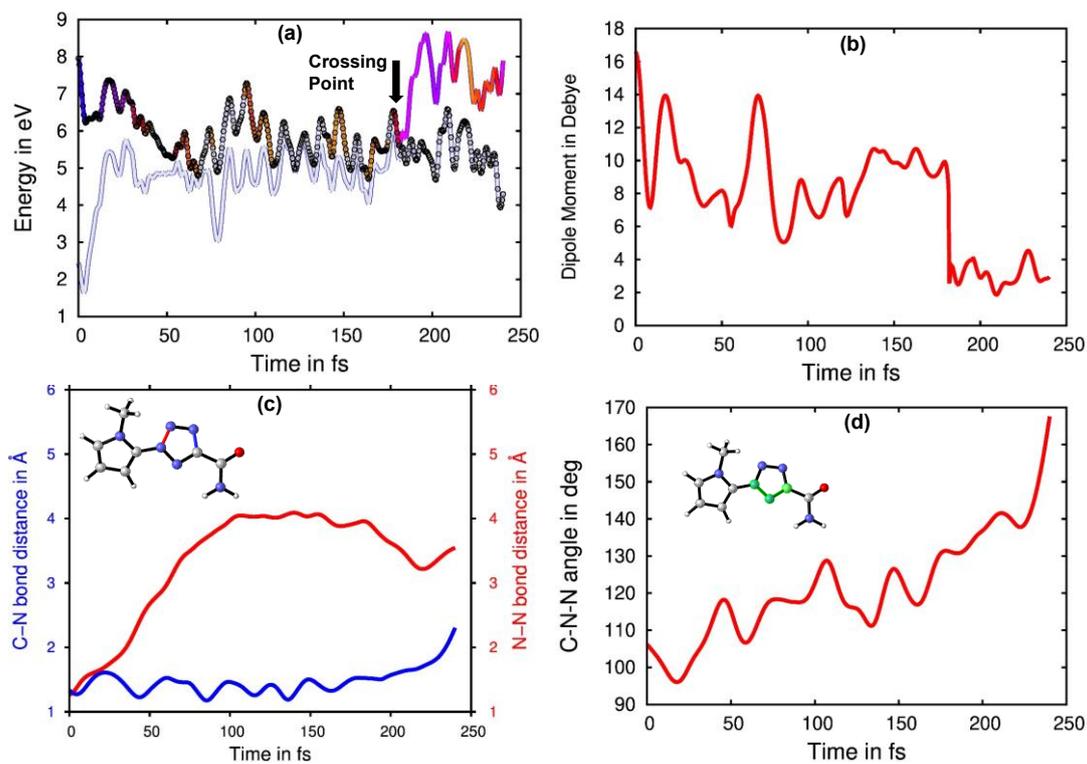
Figure S5: (a) Plot of the potential energies for molecule (A), trajectory with two singlet states. (b) Change of dipole moment during dynamics. (c) Plot of N-N bond (red) and C-N bond (blue) distance with time. (d) Change in C-N-N angle (highlighted) with time.
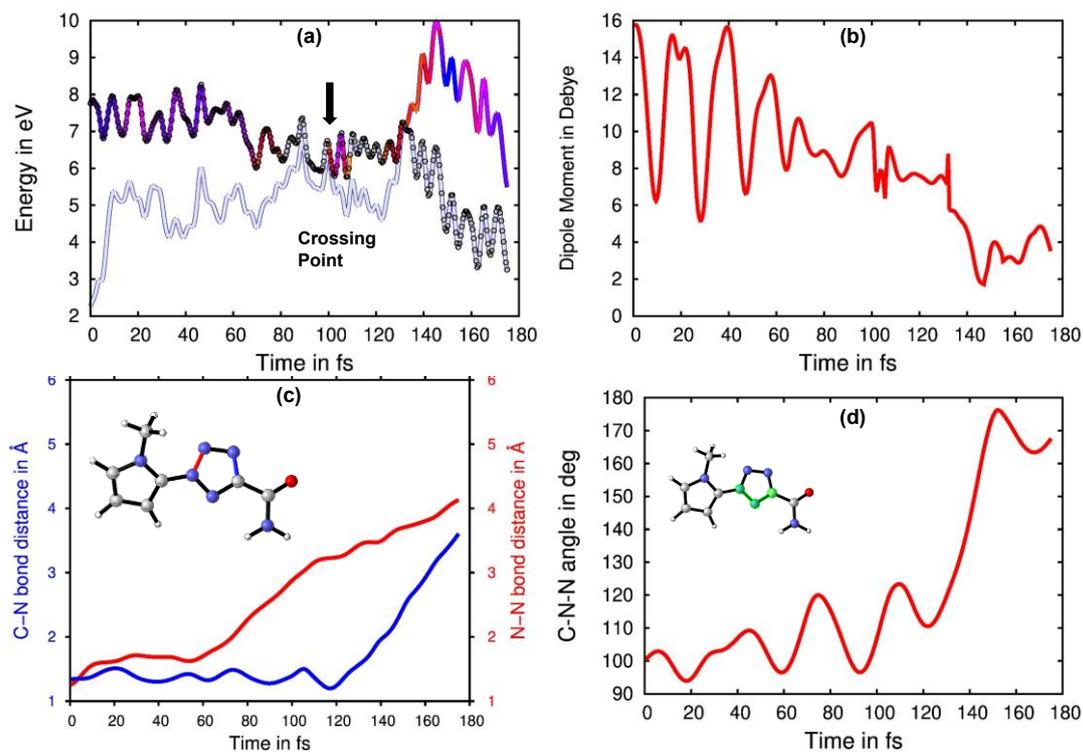
III.   More results from dynamics ([4, 4] CAS space)
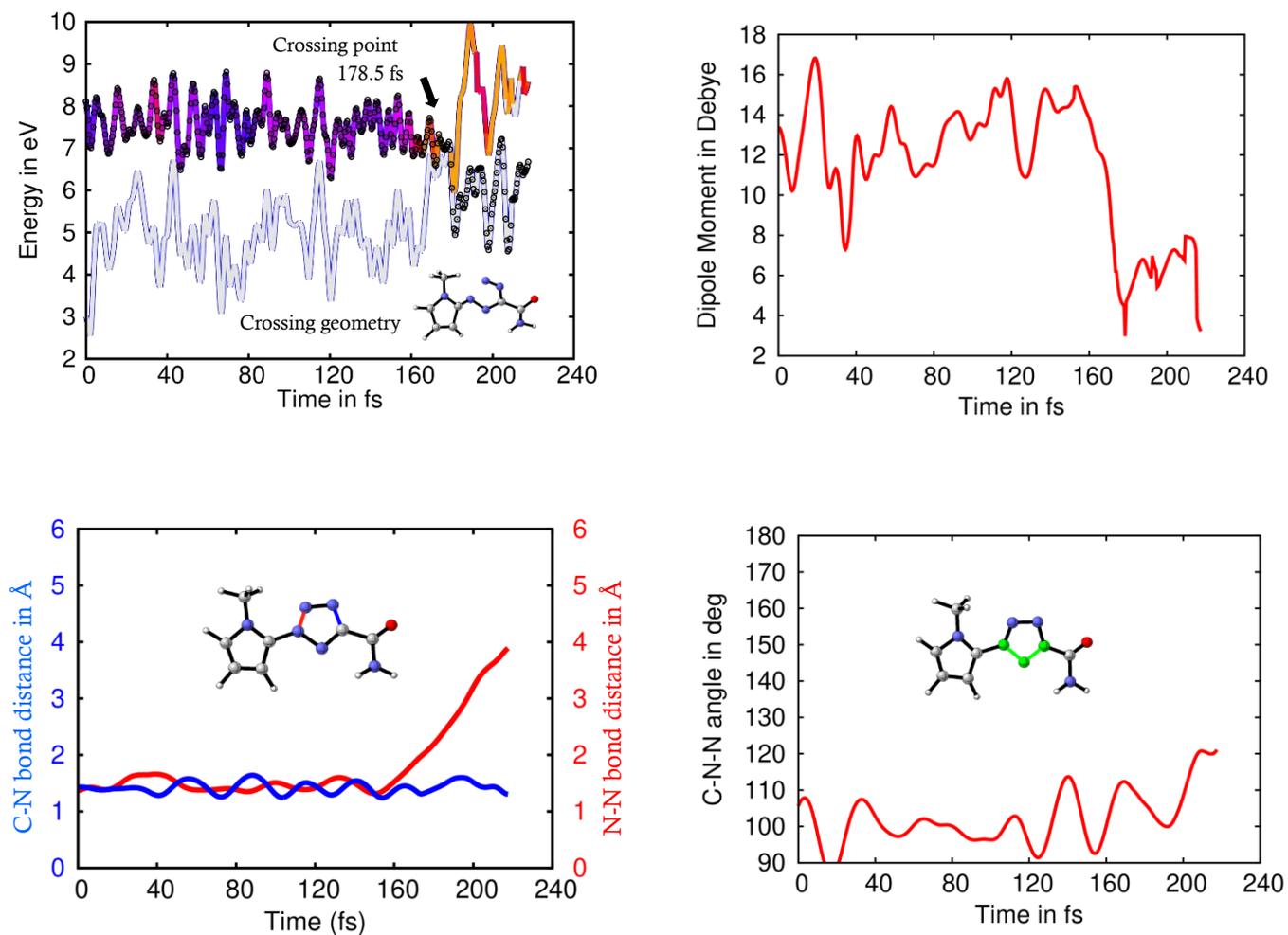
Figure S6: Results from [4,4] CAS space dynamics (a) Plot of the potential energies for molecule (A), trajectory with two singlet states. (b) Change of dipole moment during dynamics. (c) Plot of N-N bond (red) and C-N bond (blue) distance with time. (d) Change in C-N-N angle (highlighted) with time.

Figure S7**:** Molecular orbital analysis throughout the trajectory ([4,4] CAS space).
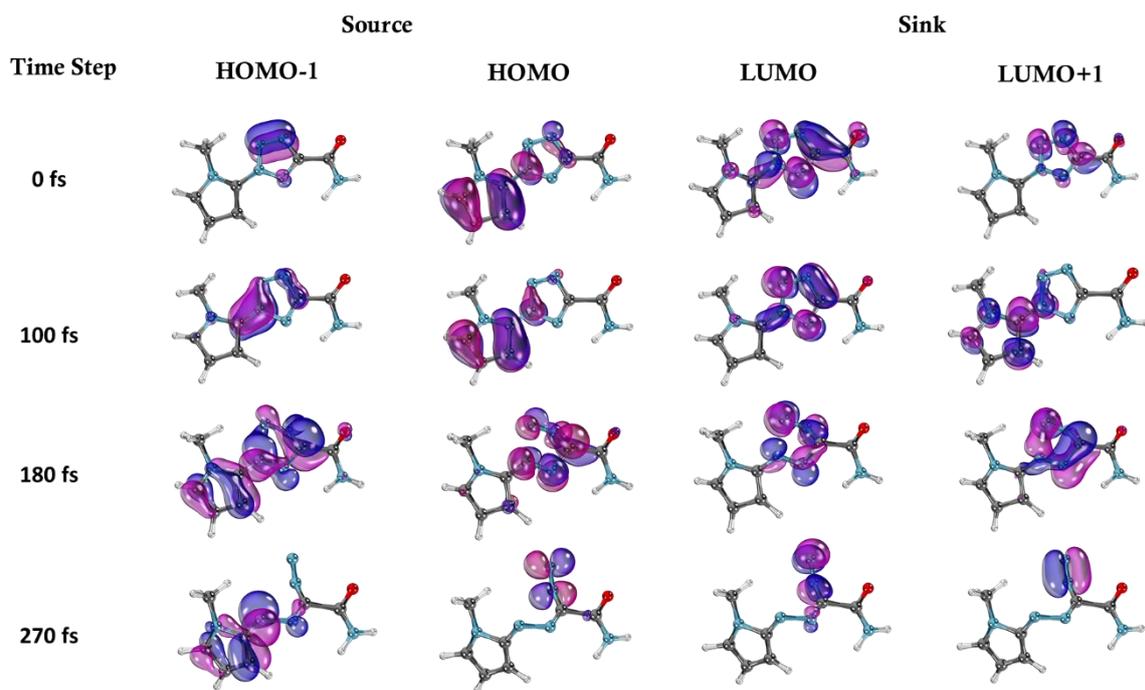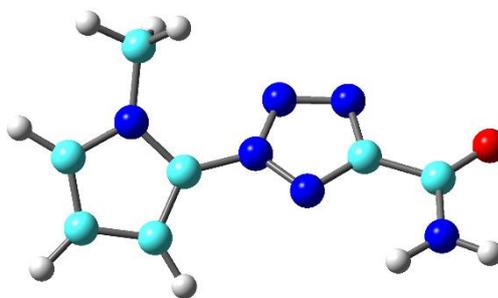
IV.   Optimized geometry and co-ordinates

Blue=N, Red=O, White=H, Sky Blue=C

Figure S8: Optimized geometry of our model (A)

Optimized energy: -675.269378198

Cartesian Coordinates in Angstroms:

|			
C	1.49665100	0.34270900	-0.12200600
C	1.95311500	1.62070200	-0.38882800
C	3.35876400	1.58557400	-0.21246300
C	3.69752800	0.29479100	0.15145300
N	2.55712200	-0.47087900	0.21523600
H	1.33729100	2.45909700	-0.67788700
H	4.04670900	2.40855200	-0.34221000
H	4.65875200	-0.14602000	0.37115800
N	0.17132900	-0.12762200	-0.15470300
C	-1.89736800	-0.19369000	-0.08503100
N	-0.17930700	-1.36655900	-0.55412800
N	-1.48298100	-1.41677400	-0.49754200
N	-0.87626400	0.63497200	0.14639000
C	-3.33350400	0.19070300	0.10656900
O	-4.24790500	-0.59211400	-0.10339700
C	2.52253100	-1.88368000	0.58762100
H	1.76501700	-2.05785800	1.35504800
H	2.29628500	-2.51313100	-0.27519700
H	3.50146600	-2.14622800	0.99135400
N	-3.50869000	1.47554100	0.52913700
H	-2.72624000	2.08797300	0.70476100
H	-4.45080800	1.80112300	0.68552800
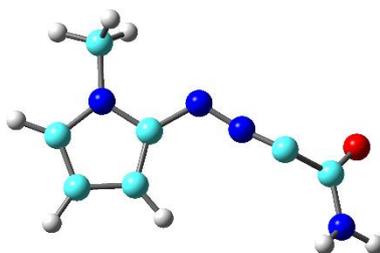
Figure S9: Optimized geometry of photoproduct

Optimized energy: -863.454058999

Cartesian Coordinates in Angstroms:

|			
C	1.23612300	0.04413900	0.07097600
C	1.25197400	1.43598500	0.02024100
C	2.60472600	1.82034100	-0.15888200
C	3.36389000	0.66279000	-0.21553500
N	2.52723300	-0.41872600	-0.08062500
H	0.38919700	2.08253000	0.09172200
H	2.98409700	2.82868300	-0.24718700
H	4.42701200	0.52239800	-0.34555300
N	0.23387600	-0.90448300	0.23684800
C	-2.04990600	-0.20715700	0.70668900
N	-0.92647700	-0.49815000	0.39473500
C	-3.31366000	-0.09212500	-0.06813600
O	-3.79893000	-1.04935400	-0.65430000
C	2.93047100	-1.81704100	-0.03708800
H	2.86516900	-2.21392600	0.98106800
H	2.28784500	-2.41479800	-0.68691000
H	3.96219100	-1.89095000	-0.38538900
N	-3.88137900	1.14819900	-0.01858700
H	-3.54682400	1.84446100	0.63014400
H	-4.79173400	1.26696400	-0.43968500
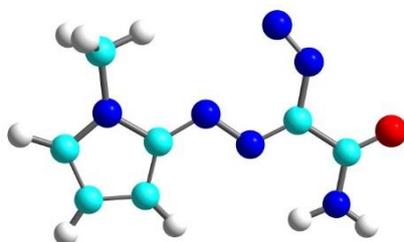
Figure S10: Optimized geometry of conical intersection geometry using MRSF-TDDFT level of theory with BHHLYP functional and 6-31+G* basis set.

Cartesian Coordinates in Angstroms:

C	1.406845428	0.293152071	0.032213708

C	1.676582019	1.672282730	-0.124136950
C	3.050754117	1.819393373	-0.159577859
C	3.608689442	0.551988071	-0.027497935
N	2.623923283	-0.358748896	0.082836455
H	0.926250641	2.431594012	-0.205526767
H	3.604088930	2.730963163	-0.273917180
H	4.639329236	0.255072720	-0.009522890
N	0.305326473	-0.431823090	0.120763869
C	-1.926228054	-0.367347252	0.111847783
N	-1.248742049	-2.602556266	0.231357104
N	-2.081384410	-1.785609487	0.172539088
N	-0.808937217	0.271409736	0.073647094
C	-3.218557308	0.376905255	0.078902476
O	-4.279330808	-0.199919178	0.114638521
C	2.787176679	-1.783293646	0.287465258
H	2.973414486	-2.003760827	1.334318318
H	1.876764938	-2.280909107	-0.016163967
H	3.619116675	-2.139015862	-0.309240964
N	-3.087300526	1.717440143	0.008596926
H	-2.184892826	2.142048993	-0.005661553
H	-3.918274598	2.269737665	-0.003457306

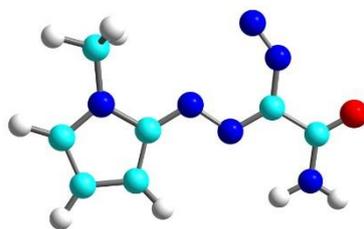**Figure S11**: Optimized geometry of conical intersection using [4,4] CASSCF with 6-31G* basis set.

Cartesian Coordinates in Angstroms:

C	0.943674280	0.192546651	-0.045971759
C	1.237672132	1.563102889	-0.203366674

C	2.619377128	1.687233114	-0.253420128
C	3.147118907	0.415469914	-0.128567536
N	2.151927047	-0.476258760	-0.004830367
H	0.507978099	2.341135063	-0.269023422
H	3.186189476	2.587983819	-0.366676826
H	4.170365461	0.102362160	-0.121446081
N	-0.159661258	-0.505497639	0.059315306
C	-2.388664865	-0.473846544	0.114803142
N	-1.734358104	-2.701311100	0.341102963
N	-2.470486731	-1.819640656	0.264193770
N	-1.265030922	0.193690359	0.012179951
C	-3.700679131	0.244997232	0.071250535
O	-4.737166718	-0.346591299	0.165535512
C	2.289011553	-1.911090155	0.147569450
H	1.843365382	-2.234930793	1.077365733
H	1.799824271	-2.424564212	-0.667961628
H	3.341567124	-2.156592546	0.147973561
N	-3.606068665	1.579273503	-0.080195911
H	-2.727818027	2.035906080	-0.149460788
H	-4.448136441	2.106622918	-0.110368804