Supplementary Material for: Dynamical insights into denitrogenation of 1-pyrazoline: Exploring pathways via transition states and second-order saddle

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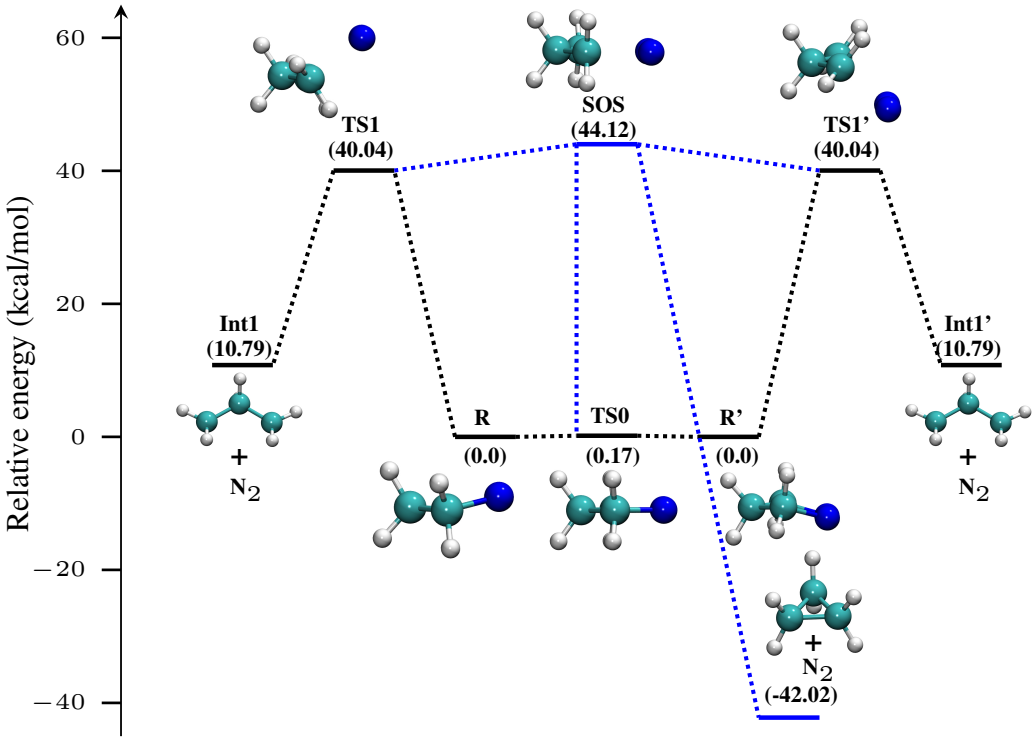

Fig. S1: Potential energy profile for the synchronous denitrogenation pathways obtained at the CASSCF(4,4)/6-31+G* level of theory. The numbers in the parentheses are relative energies in kcal/mol without zero-point-energy correction.[1] This data is reproduced from Ref.[1].

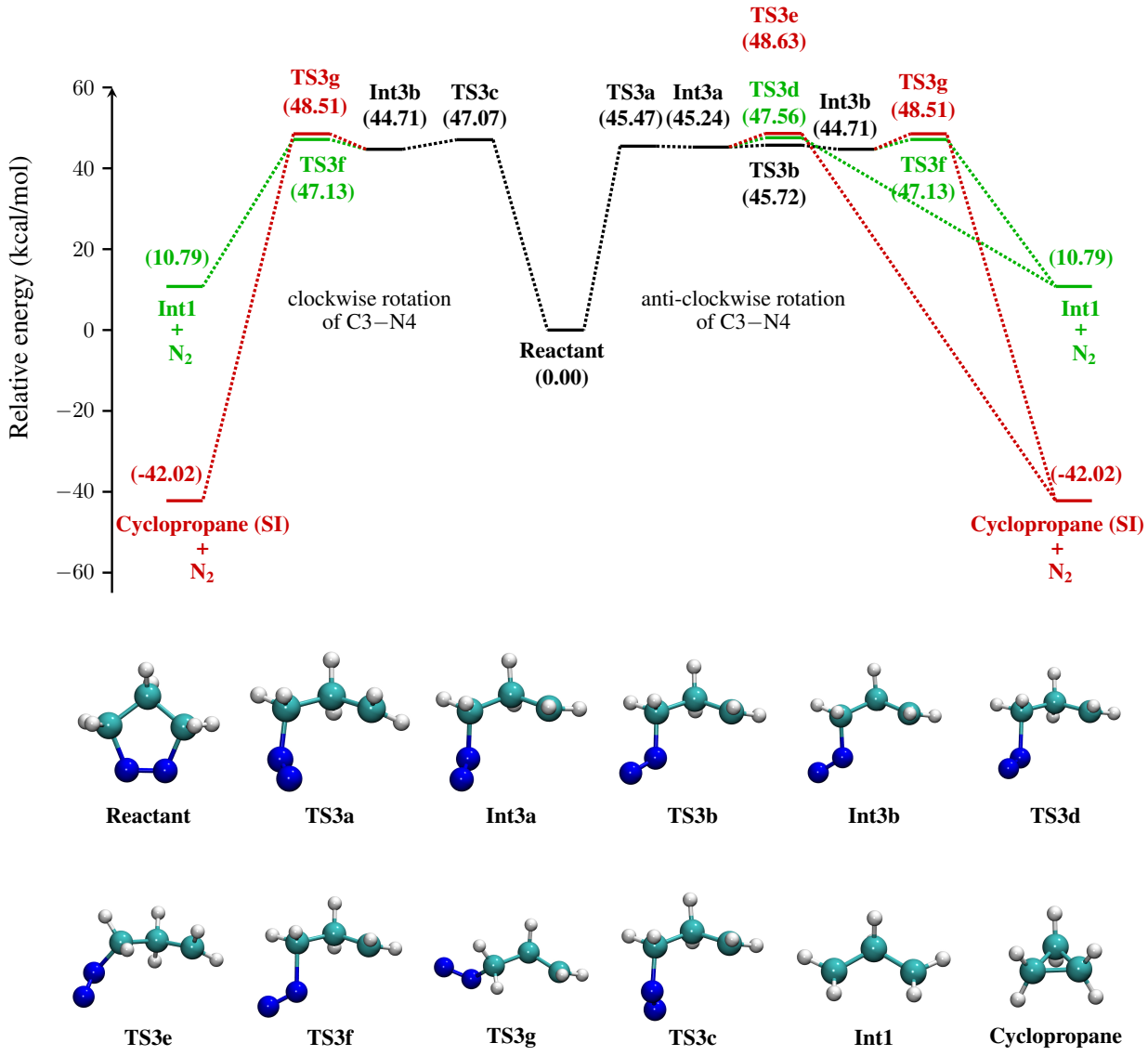

Fig. S2: Potential energy profile and the stationary point structures for the asynchronous step-wise denitrogenation pathway through the planar-like diazenyl diradicals obtained at CASSCF(4,4)/6-31+G* level of theory. The numbers in the parentheses are relative energies in kcal/mol without zero-point-energy correction.[2] This data is reproduced from Ref.[2].

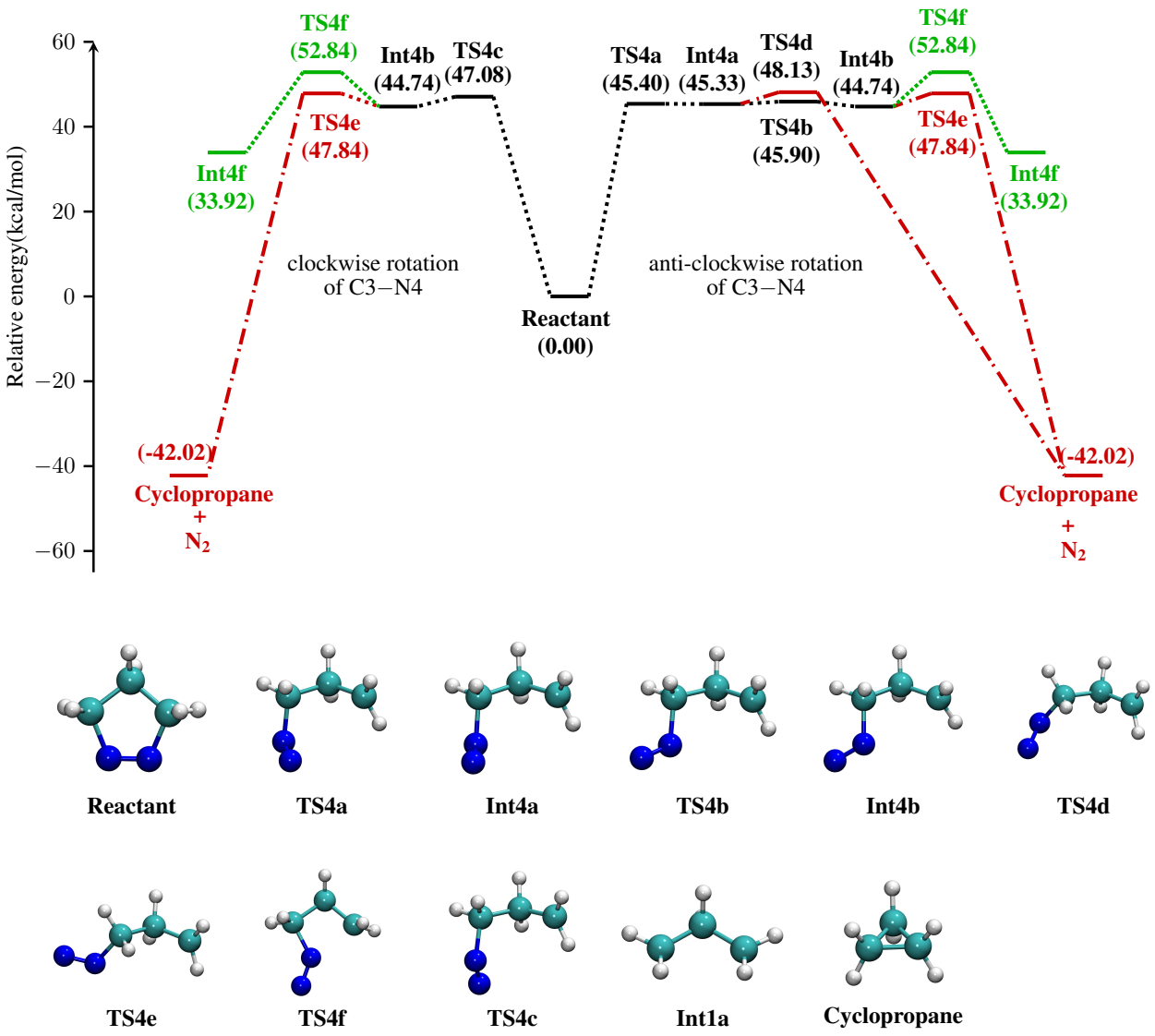

Fig. S3: Potential energy profile and the stationary point structures for the asynchronous stepwise denitrogenation pathway through the perpendicular-like diazenyl diradicals obtained at CASSCF(4,4)/6-31+G* level of theory. The numbers in the parentheses are relative energies in kcal/mol without zero-point-energy correction.[2] This data is reproduced from Ref.[2].

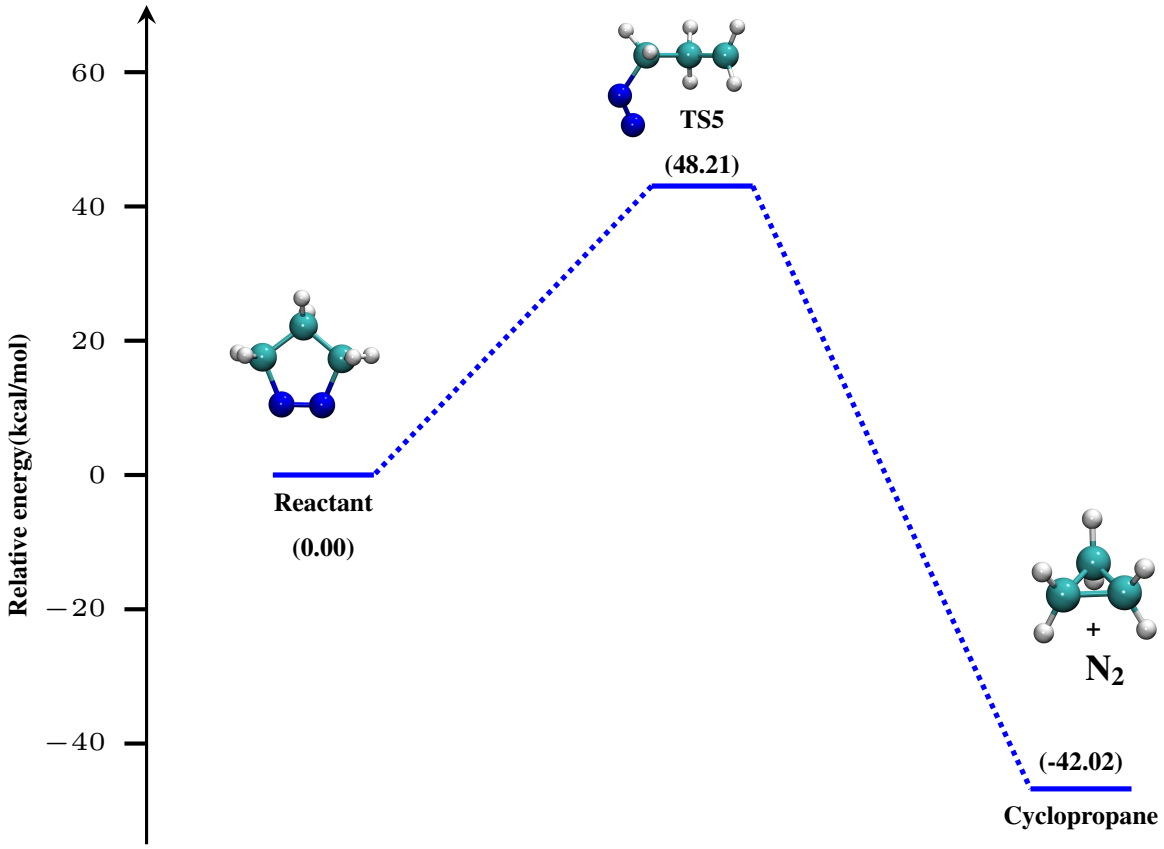

Fig. S4: Potential energy profile for the asynchronous concerted denitrogenation pathway obtained at CASSCF(4,4)/6-31+G* level of theory. The numbers in the parentheses are relative energies in kcal/mol without zero-point-energy correction.[2] This data is reproduced from Ref.[2].

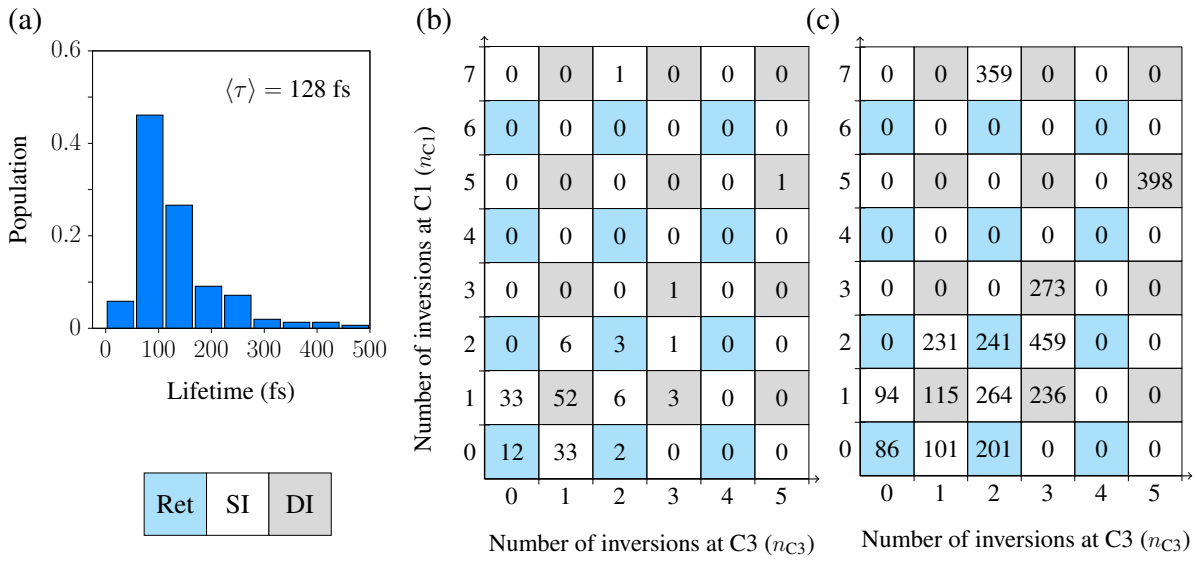

Fig. S5: (a) The lifetime distribution of trimethylene diradical intermediate (**Int1**) obtained for the synchronous trajectories. The average lifetime of **Int1** was found to be 128 fs. Matrix representing (b) the number of trajectories showing (n_{C1}, n_{C3}) inversions at the C1 and C3 atoms, respectively, and (c) the average lifetimes (fs) of the **Int1** for each (n_{C1}, n_{C3}) inversion.

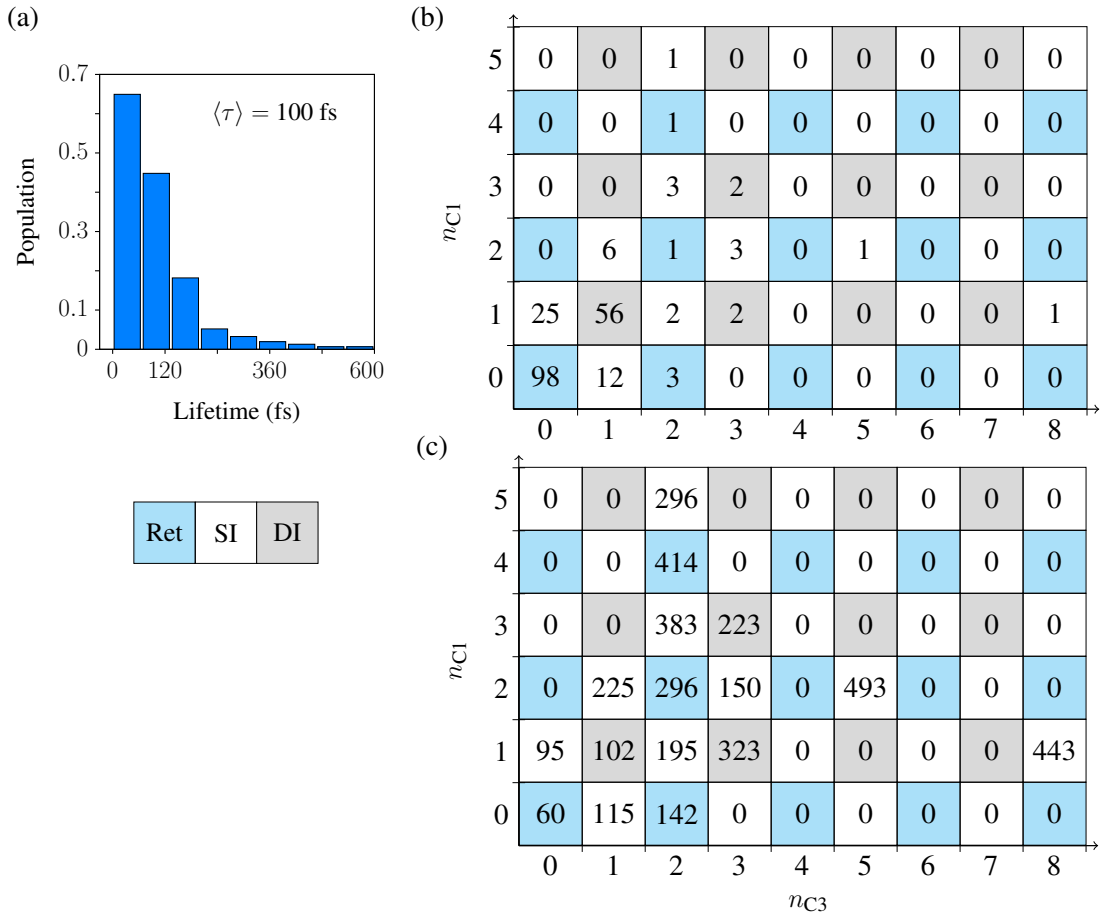

Fig. S6: (a) The lifetime distribution of diradicals obtained for the **SOS** trajectories. The average lifetime of diradicals was found to be 100 fs. Matrix representing (b) the number of trajectories howing (n_{C1}, n_{C3}) inversions at the C1 and C3 atoms, respectively, and (c) the average lifetime (fs) of the diradical for each (n_{C1}, n_{C3}) inversions.

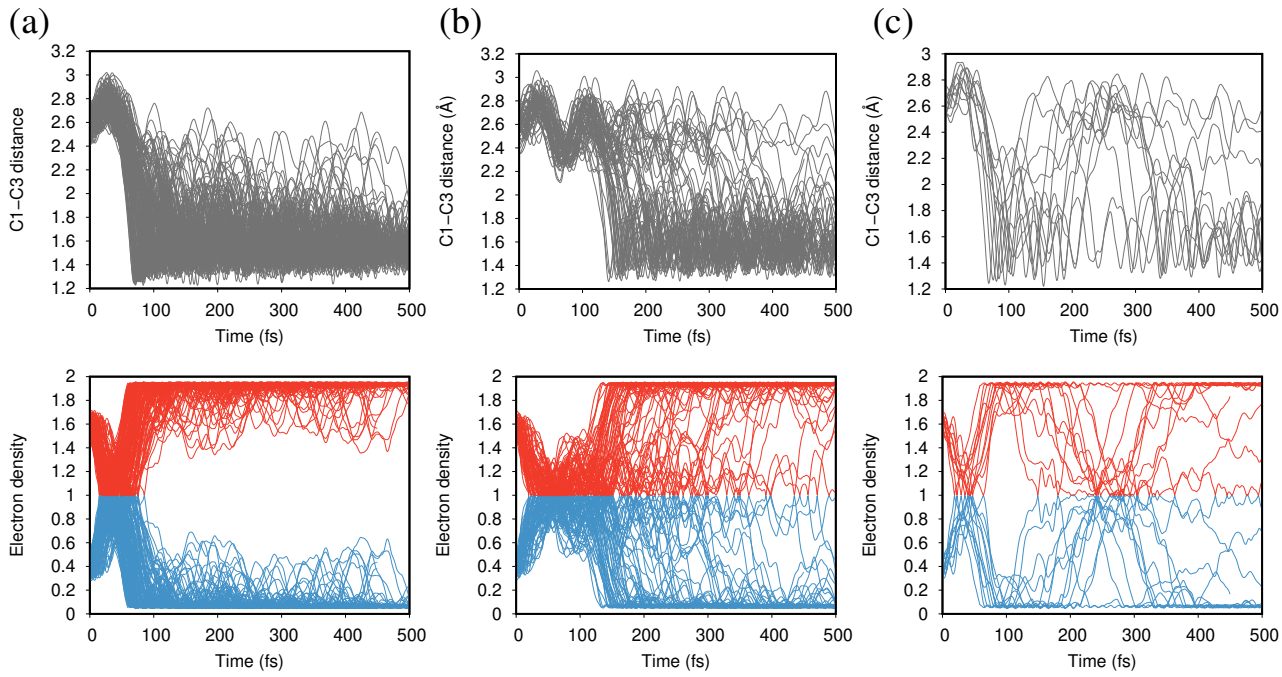

Fig. S7: Plot of C1−C3 bond distance (top panel) and electron densities (ρ_1 and ρ_2, bottom panel) in the $\sigma_{\text{C-N}}$ and $\sigma^*_{\text{C-N}}$ orbitals vs time for trajectories initiated at **SOS** region for (a) Type 1 trajectories with a short diradical lifetime, (b) Type 2 trajectories with a longer diradical lifetime, and (c) trajectories showing **Cp** isomerization.

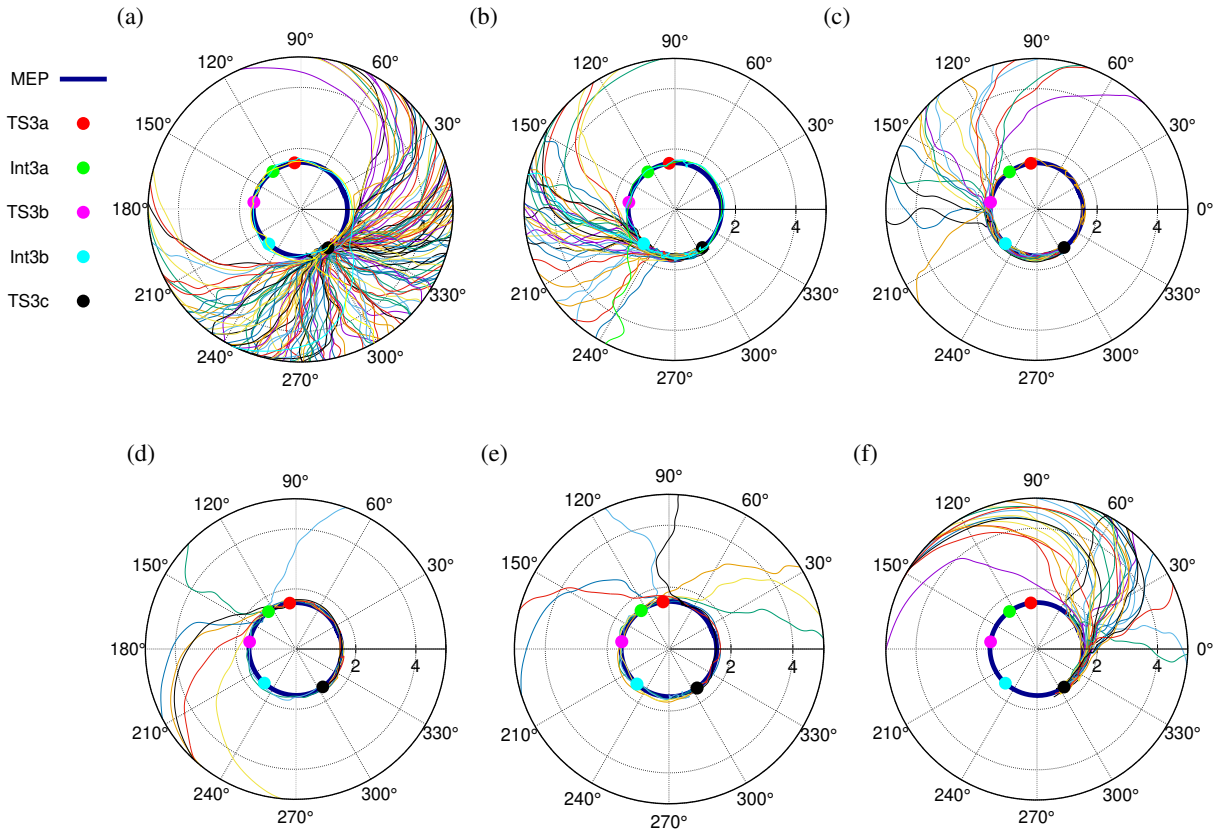

Fig. S8: Plot of ∠C2-C3-N4-N5 vs C3−N4 for minimum energy path, all the stationary points along the minimum energy path, and the 272 trajectories that form **Cp** from the transition state **TS3c**.

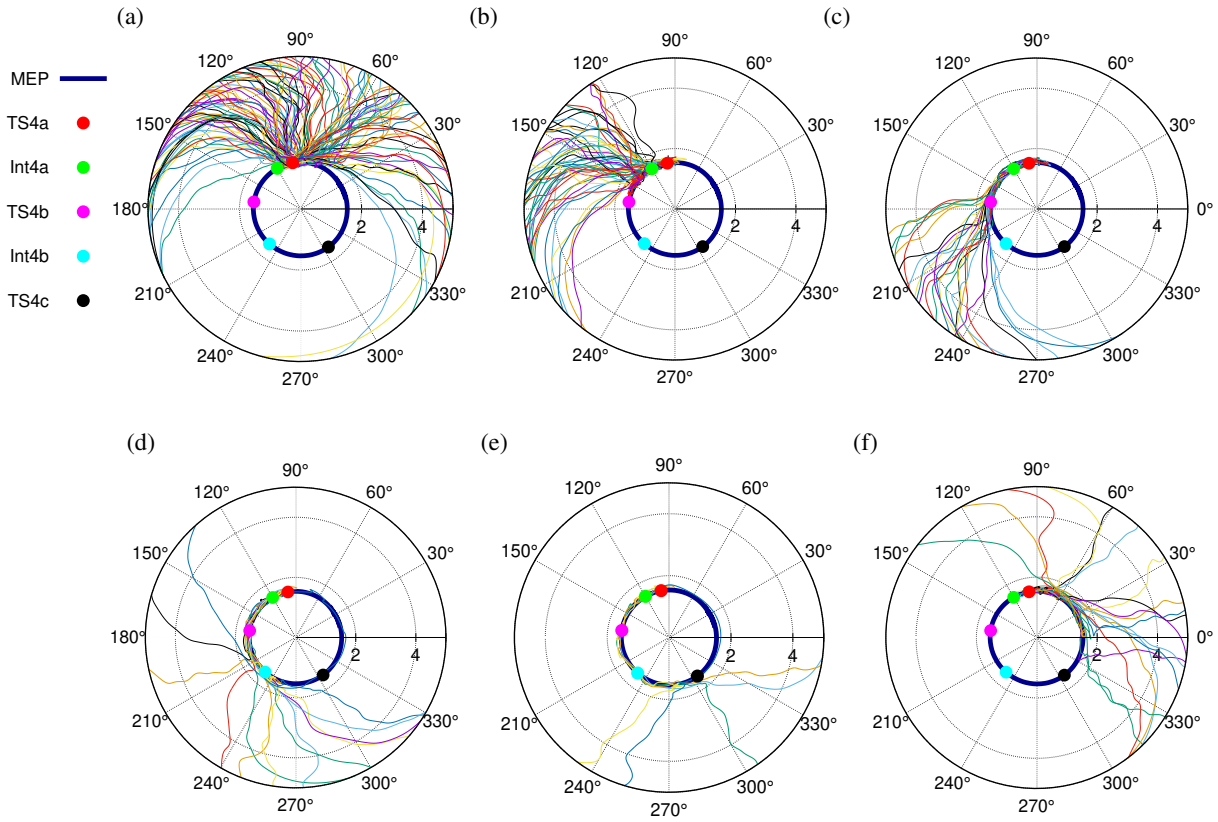

Fig. S9: Plot of ∠C2-C3-N4-N5 vs C3−N4 for minimum energy path, all the stationary points along the minimum energy path, and the 241 trajectories that form **Cp** from the transition state **TS4a**.

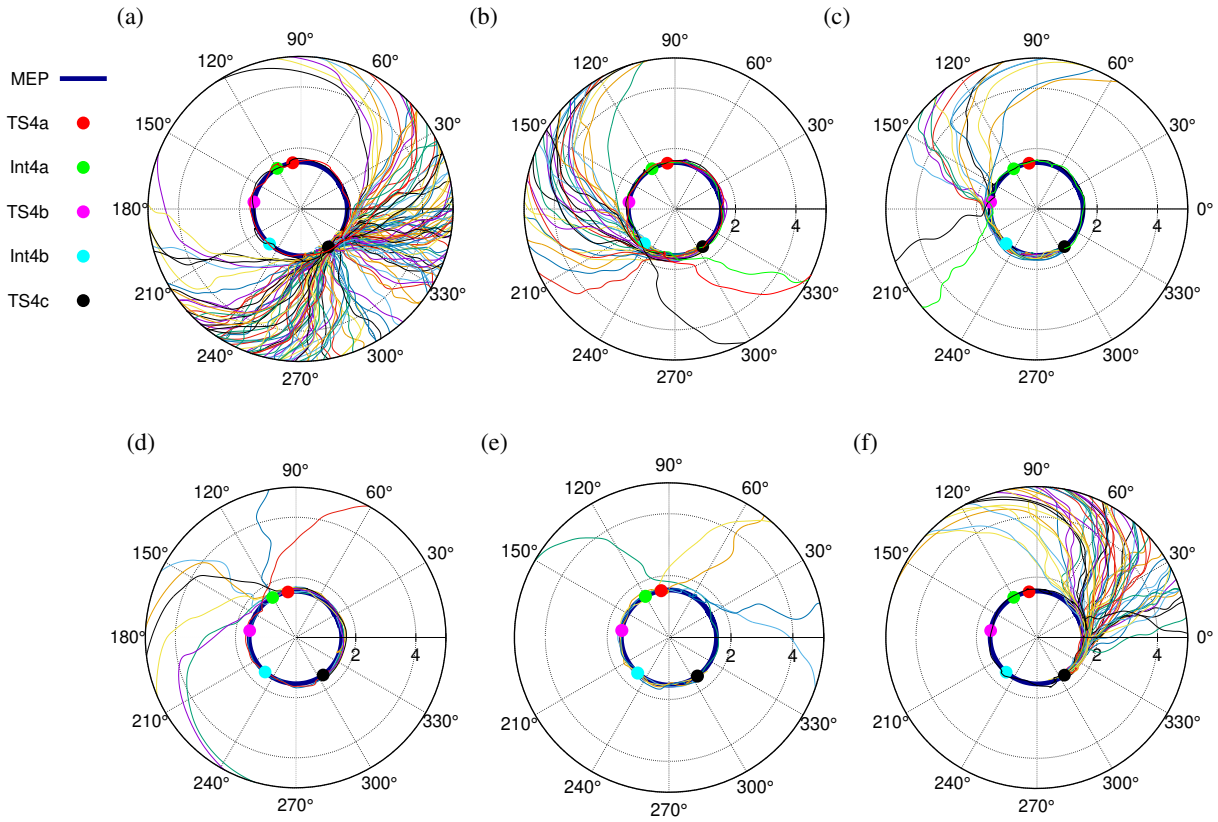

Fig. S10: Plot of ∠C2-C3-N4-N5 vs C3−N4 for minimum energy path, all the stationary points along the minimum energy path, and the 288 trajectories that form **Cp** from the transition state **TS4c**.

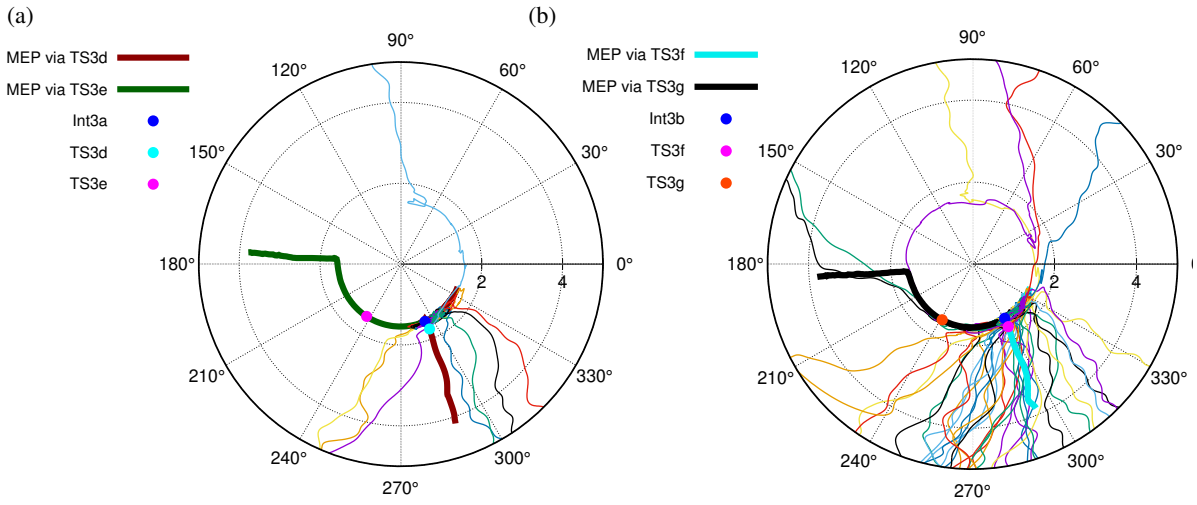

Fig. S11: Plot of ∠C1-C2-C3-N4 versus C3−N4 for the minimum energy path, all stationary points along the minimum energy path, and the 48 **TS3c** trajectories that dissociate from the **Int3a** or **Int3b** regions of the PES.

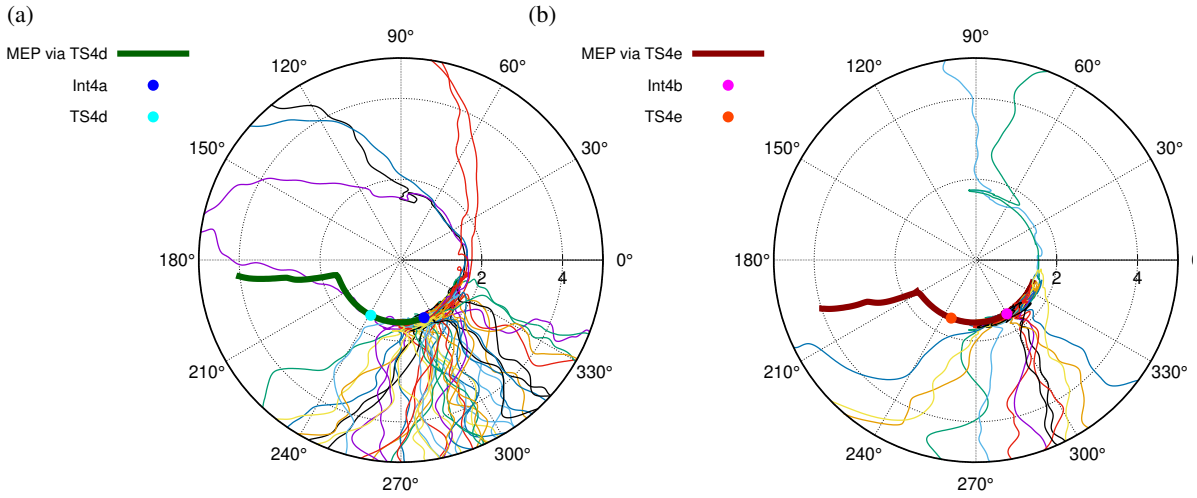

Fig. S12: Plot of ∠C1-C2-C3-N4 versus C3−N4 for the minimum energy path, all stationary points along the minimum energy path, and the 69 **TS4a** trajectories that dissociate from the **Int4a** or **Int4b** regions of the PES.

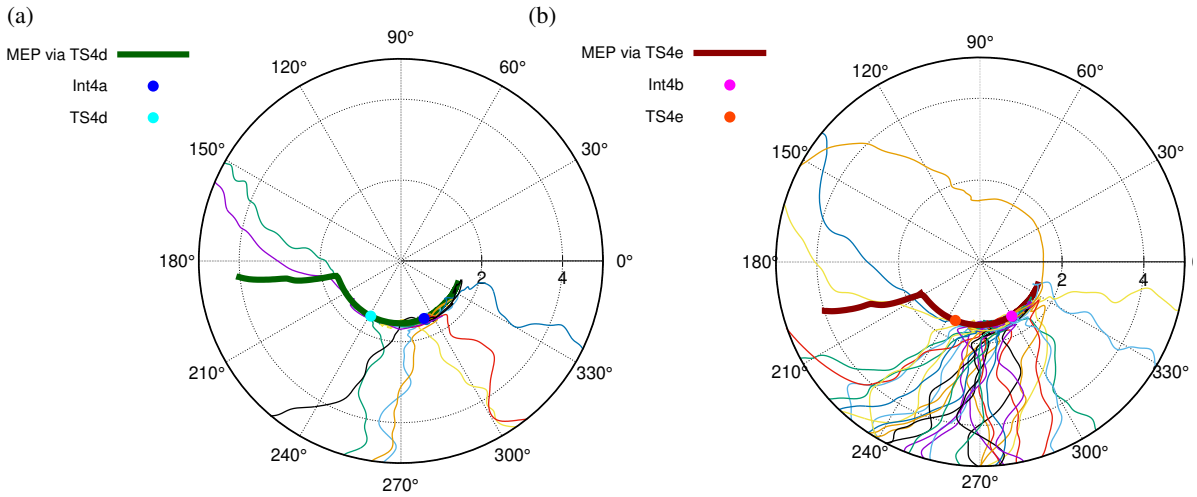

Fig. S13: Plot of ∠C1-C2-C3-N4 versus C3−N4 for the minimum energy path, all stationary points along the minimum energy path, and the 45 **TS4c** trajectories that dissociate from the **Int4a** or **Int4b** regions of the PES.

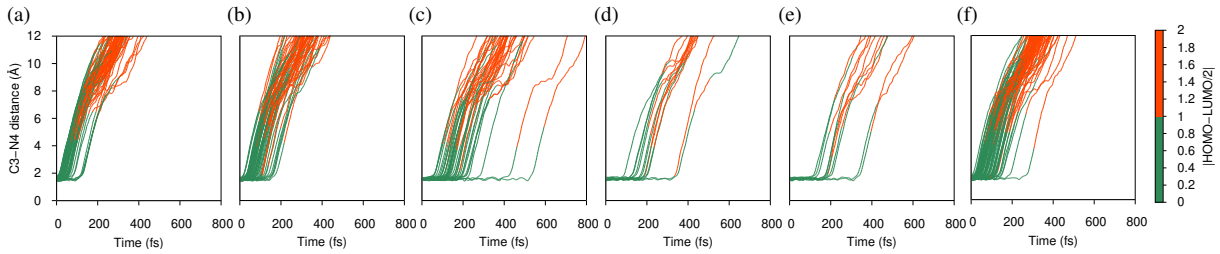

Fig. S14: Plot of the C3−N4 bond distance vs. time (fs) and the difference in the electron densities between the HOMO and LUMO orbitals during the dissociation process for the **TS3a** trajectories that follow different pathways. The orange colour indicates the formation of the **Cp**, whereas the green colour indicates the molecule is in the diradical region.

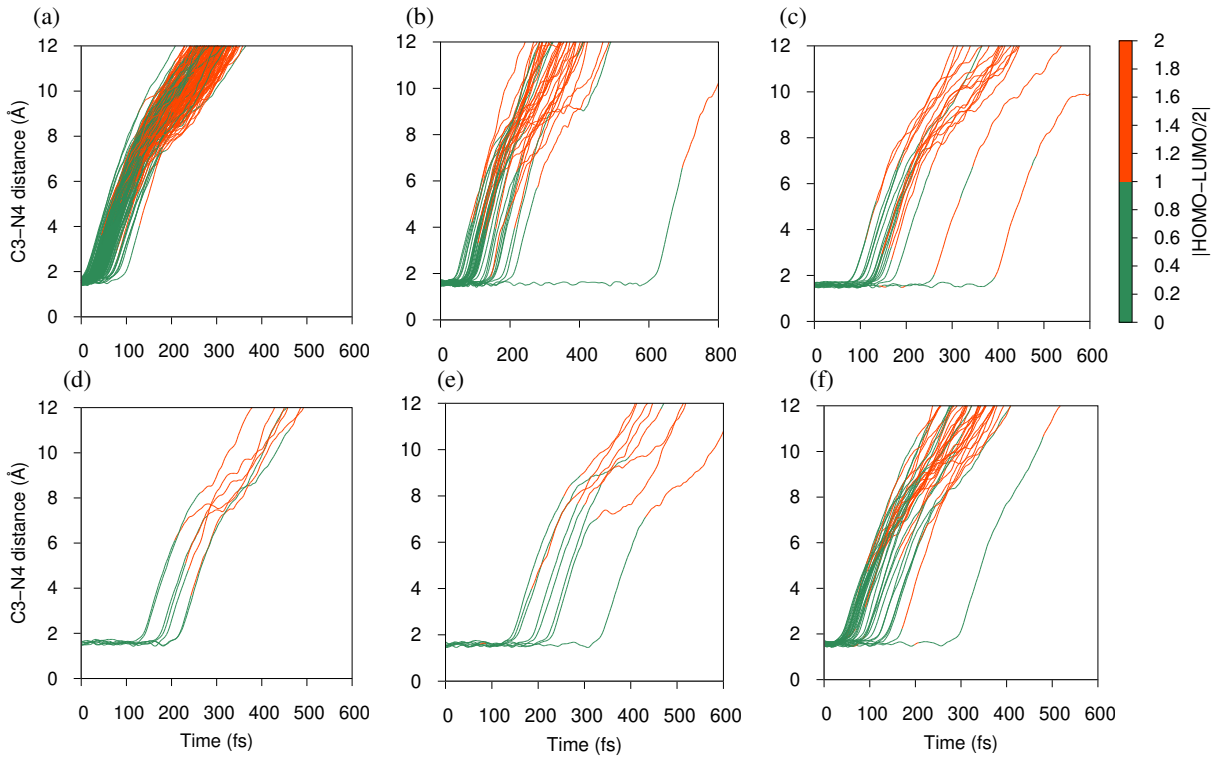

Fig. S15: Plot of the C3−N4 bond distance vs. time (fs) and the difference in the electron densities between the HOMO and LUMO orbitals during the dissociation process for the **TS3c** trajectories that follow different pathways. The orange colour indicates the formation of the **Cp**, whereas the green colour indicates the molecule is in the diradical region.

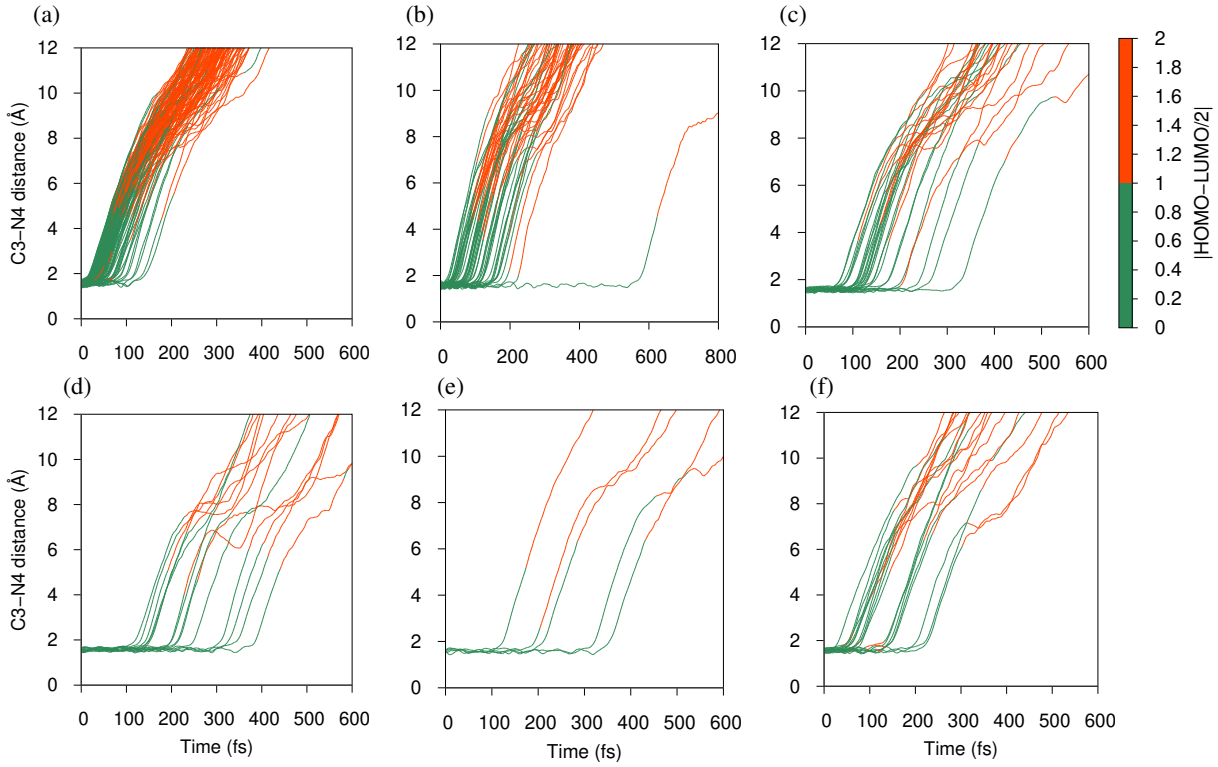

Fig. S16: Plot of the C3−N4 bond distance vs. time (fs) and the difference in the electron densities between the HOMO and LUMO orbitals during the dissociation process for the **TS4a** trajectories that follow different pathways. The orange colour indicates the formation of the **Cp**, whereas the green colour indicates the molecule is in the diradical region.

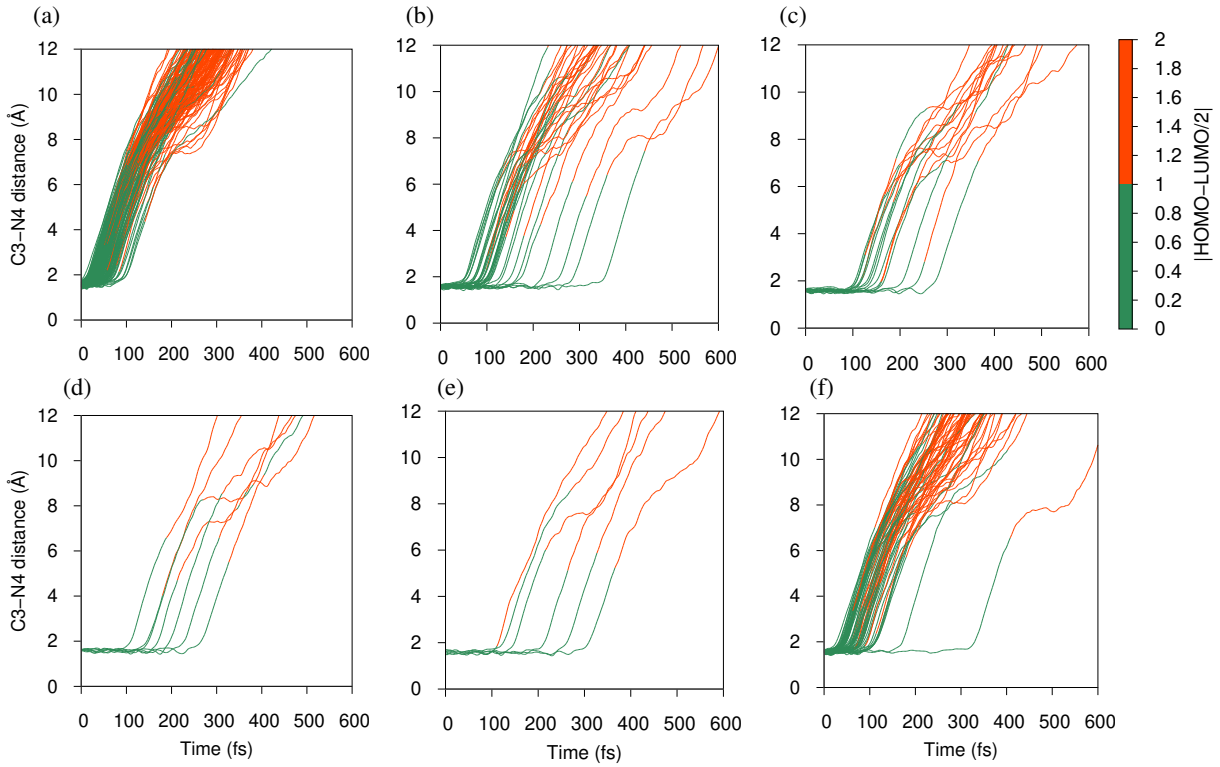

Fig. S17: Plot of the C3−N4 bond distance vs. time (fs) and the difference in the electron densities between the HOMO and LUMO orbitals during the dissociation process for the **TS4c** trajectories that follow different pathways. The orange colour indicates the formation of the **Cp**, whereas the green colour indicates the molecule is in the diradical region.

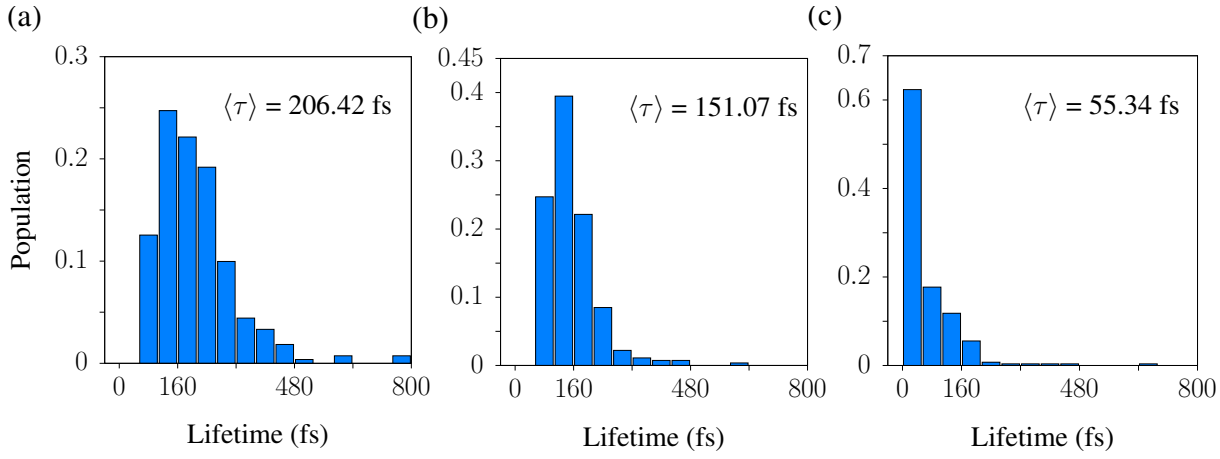

Fig. S18: Lifetime distributions of (a) total (**DZ + TMD**), (b) **DZ**, and (c) **TMD** diradicals obtained for the trajectories integrated from the transition state **TS3a**. The average lifetimes of **DZ** and **TMD** diradicals were found to be 151.1 and 55.3 fs, respectively.

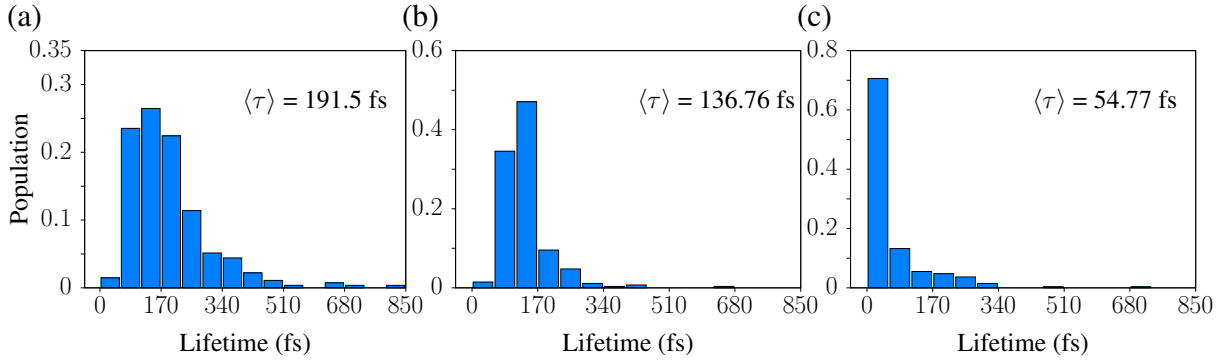

Fig. S19: Lifetime distribution of (a) total (**DZ** + **TMD**), (b) **DZ**, and (c) **TMD** diradicals obtained for the trajectories integrated from the transition state **TS3c**. The average lifetimes of **DZ** and **TMD** diradicals were found to be 136.76 and 54.77 fs, respectively.

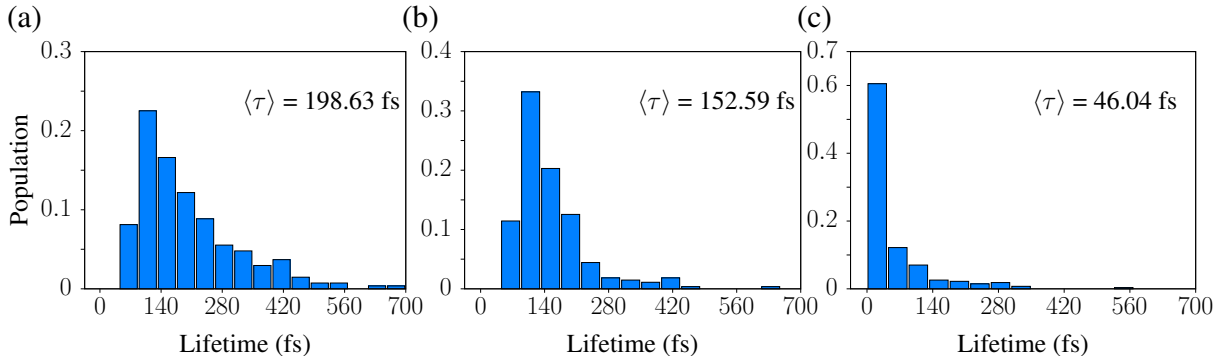

Fig. S20: Lifetime distribution of (a) total (**DZ** + **TMD**), (b) **DZ**, and (c) **TMD** diradicals obtained for the trajectories integrated from the transition state **TS4a**. The average lifetimes of **DZ** and **TMD** diradicals were found to be 152.59 and 46.04 fs, respectively.

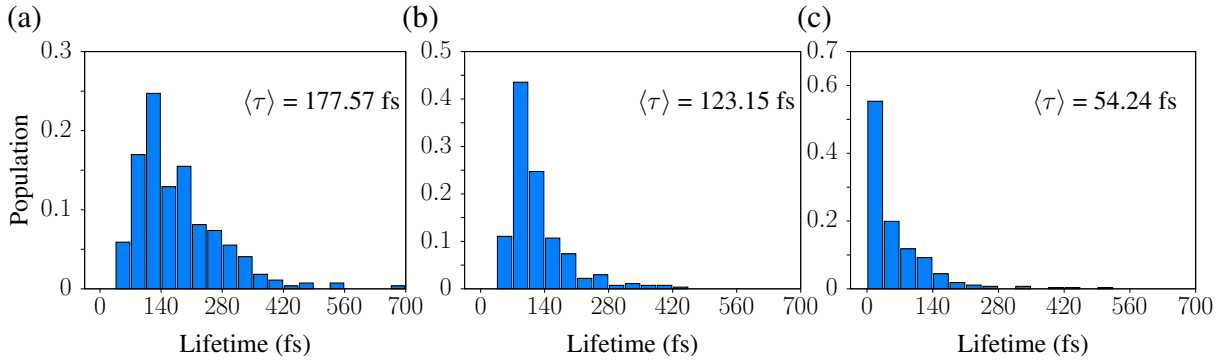

Fig. S21: Lifetime distribution of (a) total (**DZ** + **TMD**), (b) **DZ**, and (c) **TMD** diradicals obtained for the trajectories integrated from the transition state **TS4c**. The average lifetimes of **DZ** and **TMD** diradicals were found to be 123.15 and 54.24 fs, respectively.

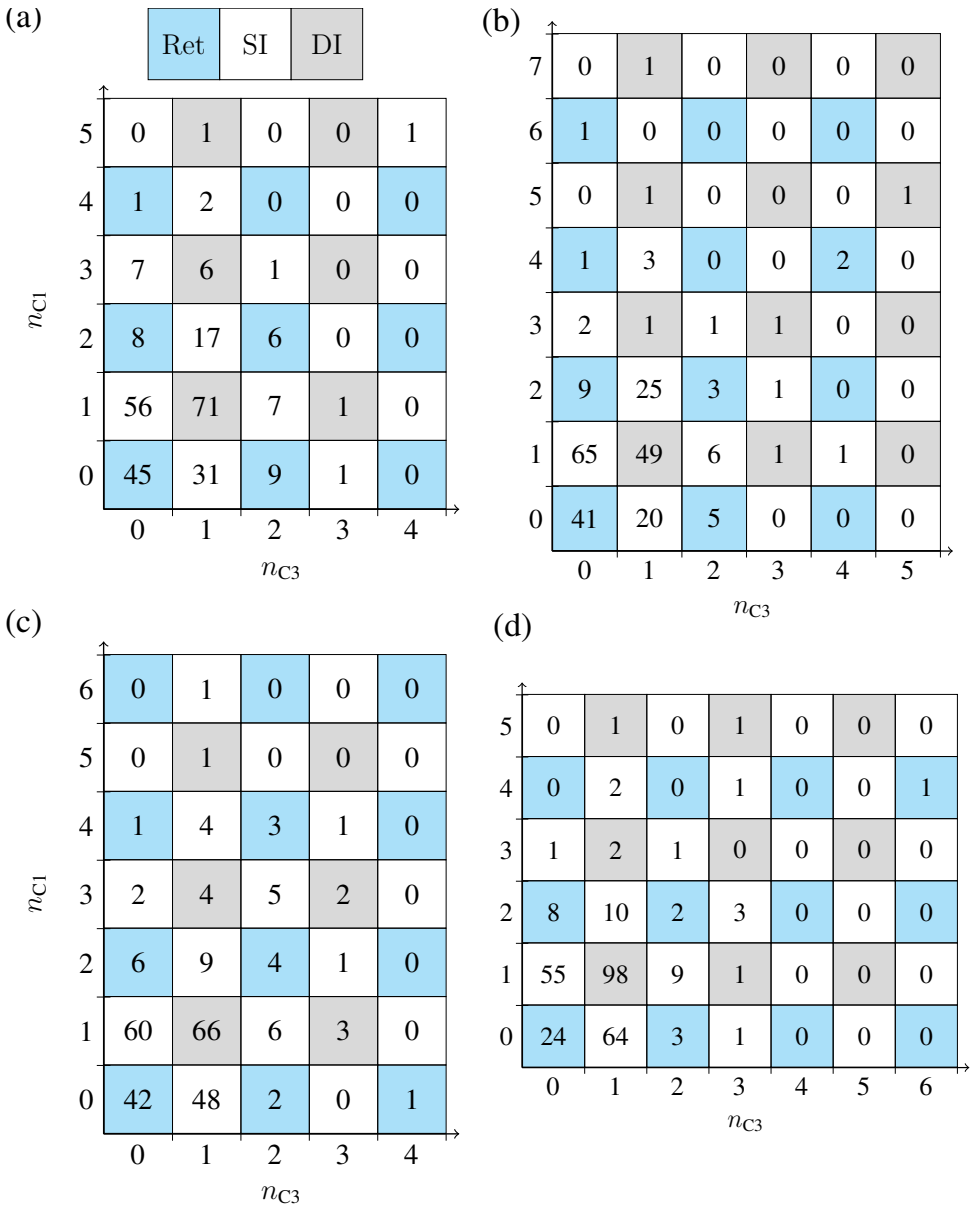

Fig. S22: Matrix exhibiting the number of trajectories displaying (n_{C1}, n_{C3}) inversions at the C1 and C3 atoms for trajectories integrated from the (a) **TS3a**, (b) **TS4a**, (c) **TS3c**, and (d) **TS4c** regions of the PES.

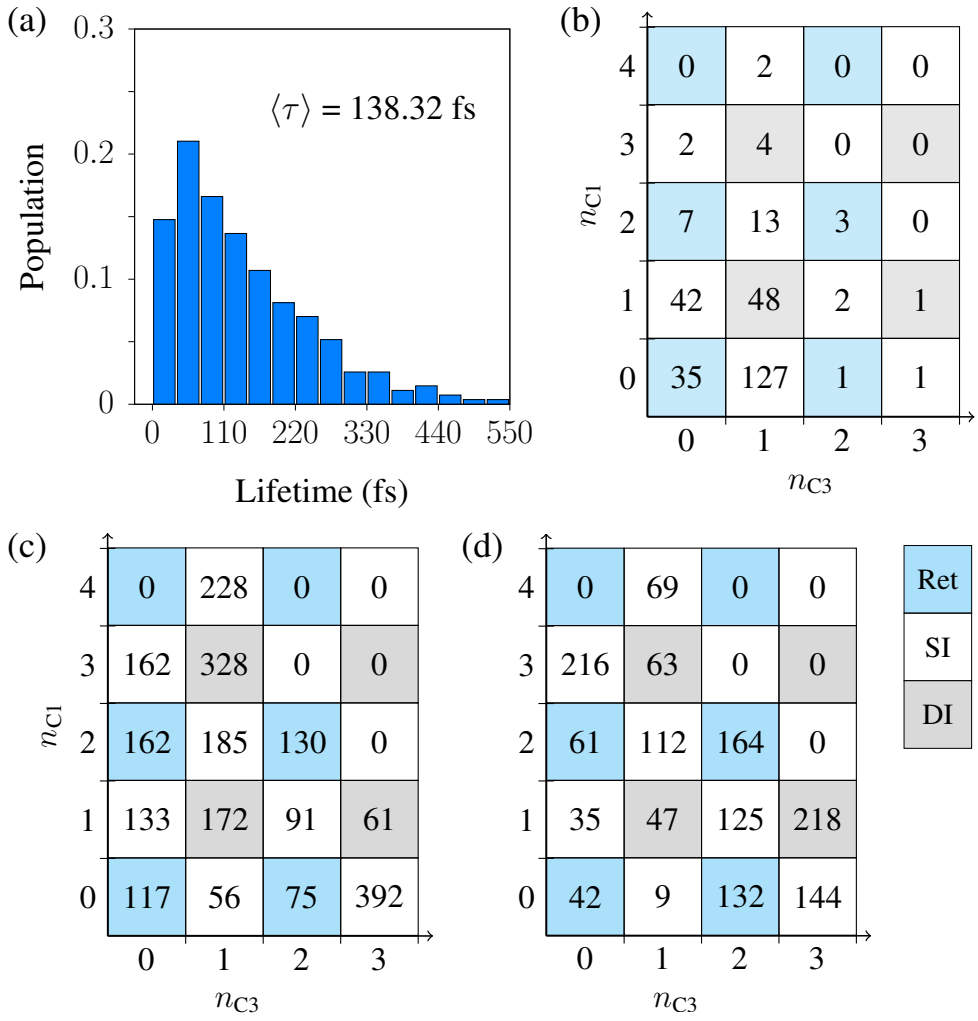

Fig. S23: (a) The lifetime distribution of diradicals obtained for the **TS5** trajectories. Matrix representing (b) the number of trajectories showing (n_{C1}, n_{C3}) inversions at the C1 and C3 atoms, (c) average lifetimes (fs) of **DZ**, and (d) average lifetimes (fs) of **TMD** for each (n_{C1}, n_{C3}) inversions for the **TS5** trajectories.

References

[1] R. Pradhan and U. Lourderaj, *Phys. Chem. Chem. Phys.*, 2019, **21**, 12837–12842.

[2] R. Pradhan and U. Lourderaj, *Phys. Chem. Chem. Phys.*, 2017, **19**, 27468–27477.