

Supporting Information (SI) for

Tunable Photochemical 6π Heterocyclization Reaction Mediated by a Boron Lewis Acid

Lishuang Ma,^{*a} Wenxu Feng,^a Hongyan Shang,^{ab} Xufeng Lin,^{*ab} Yanyan Xi^{bc}

^a Department of Chemistry, College of Science, China University of Petroleum (East China), Qingdao, 266580, P. R. China

^b State Key Laboratory of Heavy Oil Processing China University of Petroleum (East China), Qingdao, 266580, P. R. China

^c State Key Laboratory of Heavy Oil Processing China University of Petroleum (East China), Qingdao, P. R. China, 266580

Contents

| | |
|---|-----|
| 1. Selected Orbitals in Active Space..... | S2 |
| 2. Geometric Parameters of Critical Structures..... | S5 |
| 3. Charge Translocation Calculations..... | S9 |
| 4. Intersystem Crossing Rate Constant Calculations..... | S10 |
| 5. References..... | S10 |
| 6. MEPs for the Disrotatory 6π Photocyclization..... | S11 |
| 7. MEPs for the Stepwise Pathway via Two Consecutive [1,2]-H Shift..... | S12 |
| 8. MEPs for the 6π cyclization pathways in in the ground state..... | S13 |
| 9. Tables for the Absolute and Relative Energies..... | S14 |
| 10. Cartesian Coordinates..... | S49 |

1. Selected Orbitals in Active Space

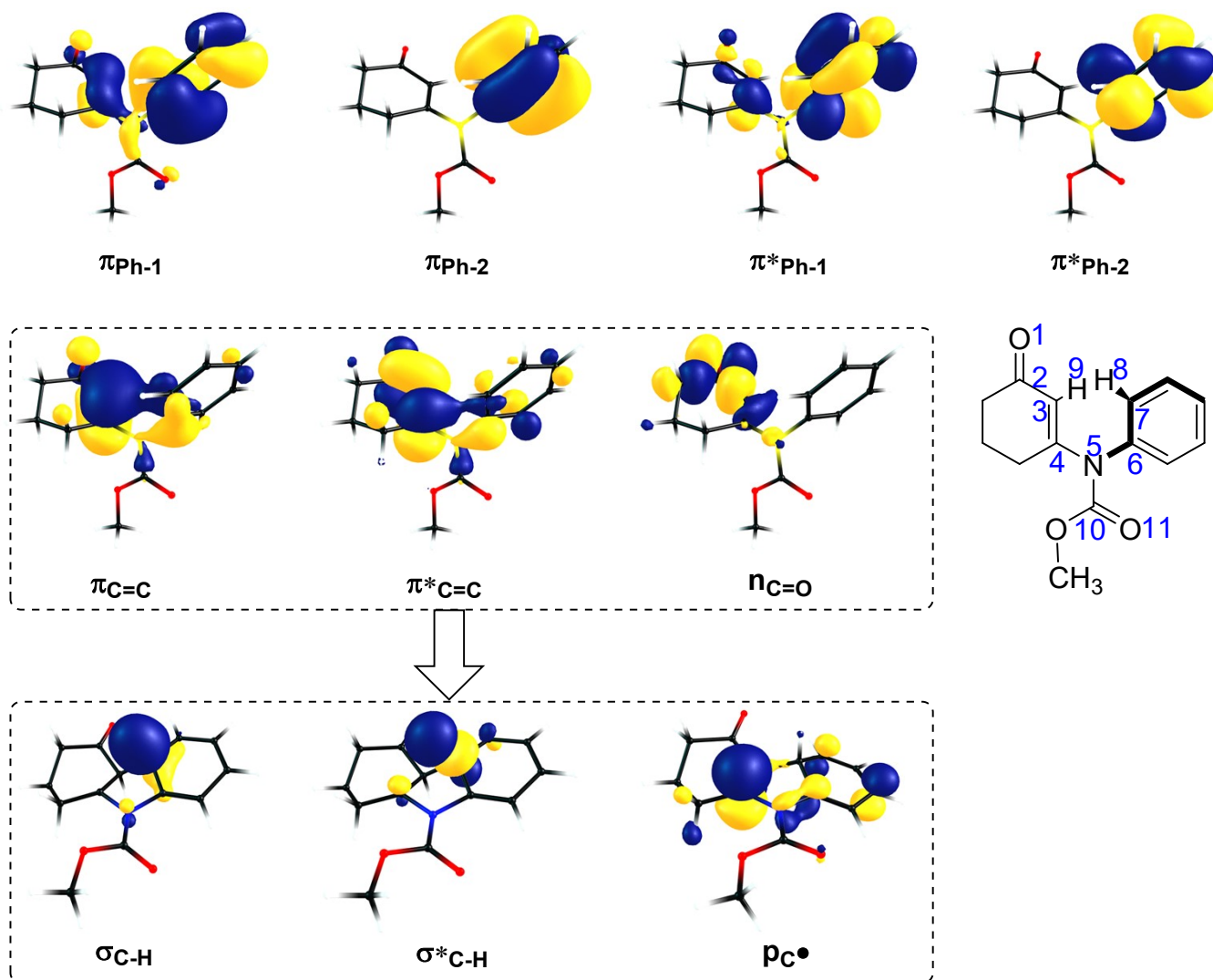


Figure S1. Molecular orbitals of the enaminone substrate **2** used in defining the active spaces for the CASPT2// CASSCF(8e/7o) calculations. The π/π^* orbitals of C3=C4 double bond and the n orbital of C2=O1 carbonyl group were included for the 6 π photocyclization reaction, which subsequently were replaced by the σ/σ^* orbitals of C-H bond and the p orbital of the carbon atom for describing the 1,4-H shift process, as shown in the dashed boxes.

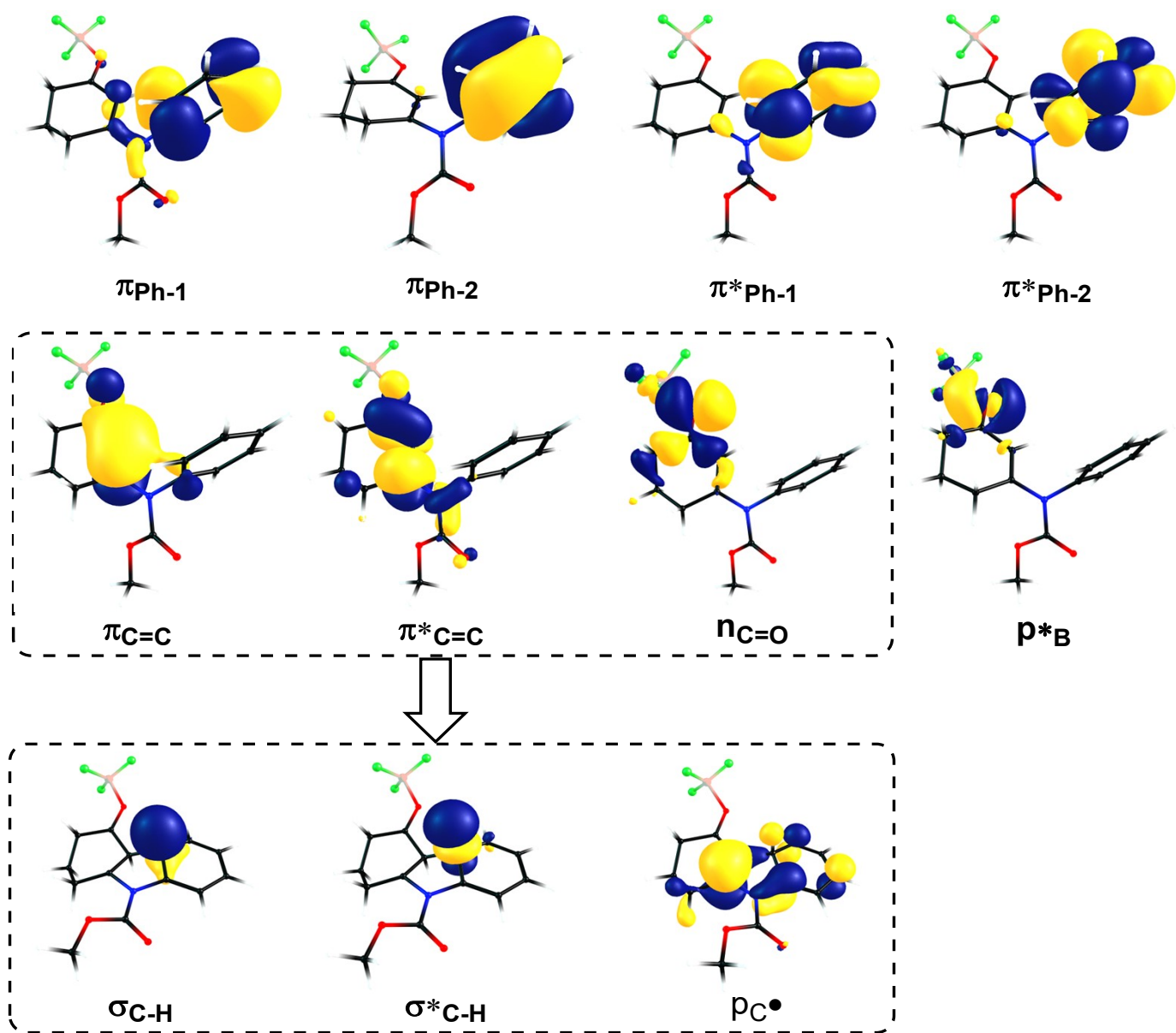


Figure S2. Molecular orbitals of 2- BF_3 complex used in defining the active space for the CASPT2//CASSCF(8e/8o) calculations. The π/π^* orbitals of C3=C4 double bond and the n orbital of C2=O1 carbonyl group were included for the 6π photocyclization reaction, which subsequently were replaced by the σ/σ^* orbitals of C-H bond and the p orbital of the carbon atom for describing the 1,4-H shift process as shown in the dashed boxes.

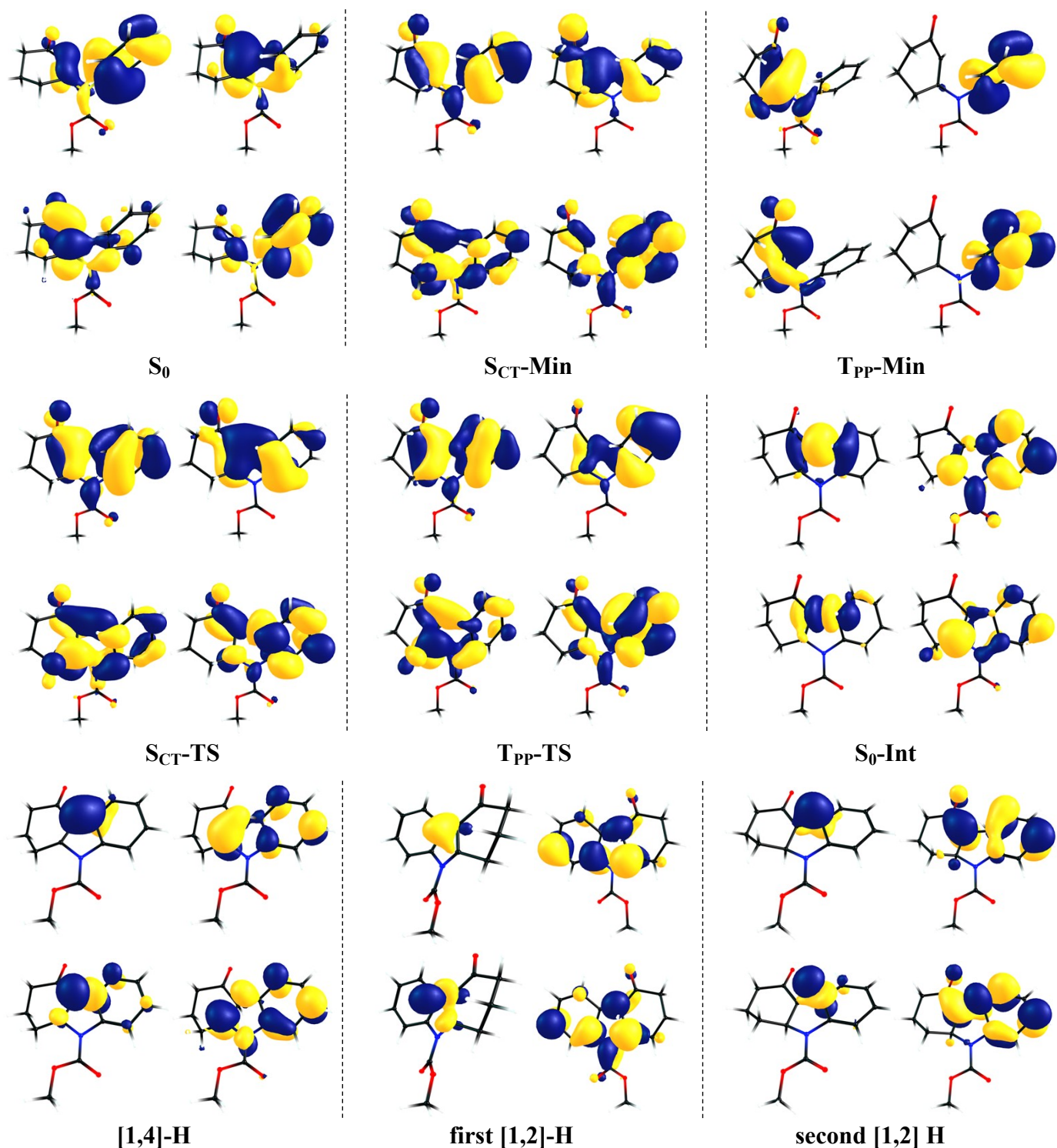


Figure S3. Schematic orbitals evolution in the active space of **2** is shown to account for the possible orbitals participating in the 6π photocyclization reaction. Only the most relevant four orbitals are shown for clarity. As illustrated in the figure, one pair of π/π^* orbitals are gradually evolved to be the pair of σ/σ^* orbitals of C3-C7 bond along the photoinduced ring-closure process, which are further replaced by the σ/σ^* orbitals of different C-H bonds for the subsequent [1,4]-H shift process or the stepwise [1,2]-H shift processes.

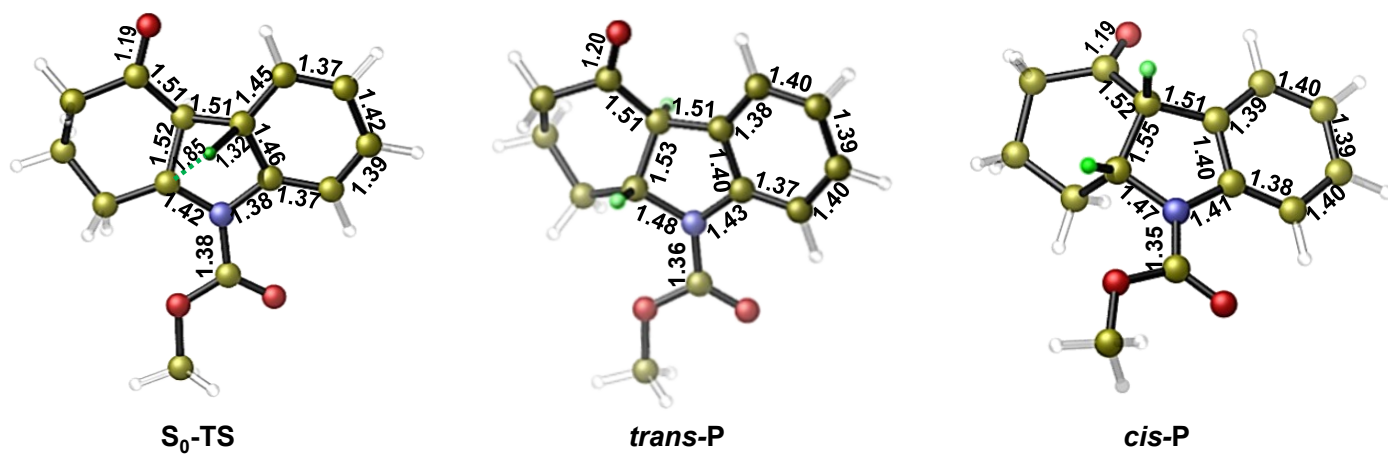
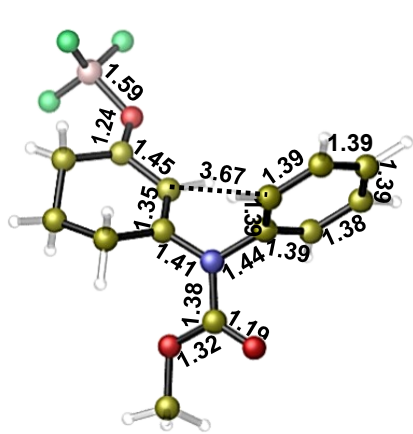
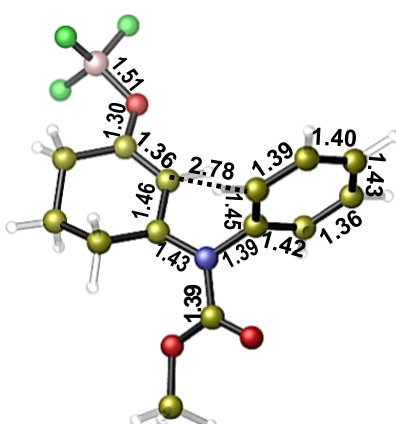


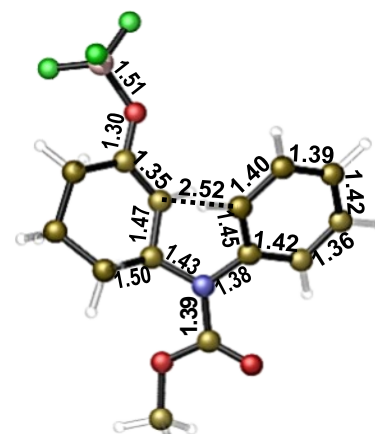
Figure S4. The critical structures for the free **2** along the 6π photocyclization reaction pathways. Selected key bond lengths are given in Å. All the Hydrogen atoms are set to be transparent for clarity, except that involved in the [1,4]-H shift reaction are highlighted in green.



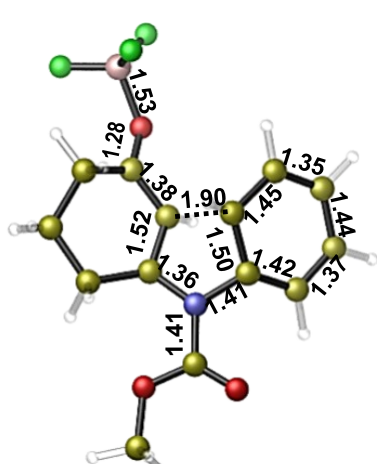
S_0 -Min



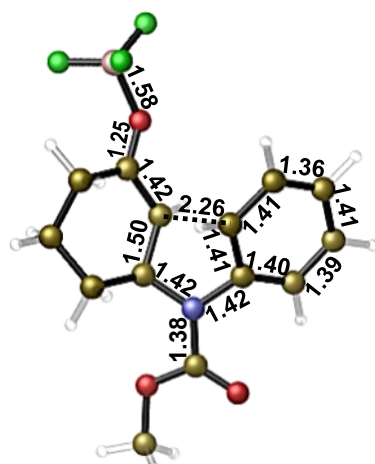
S_{CT} -Min



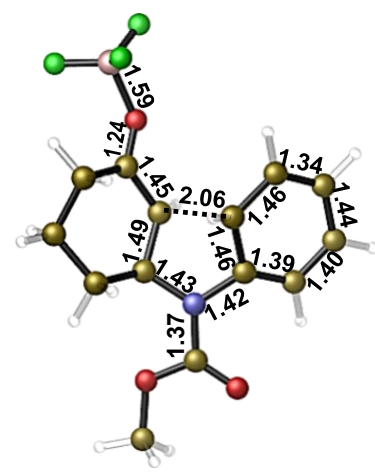
S_{CT} -TS



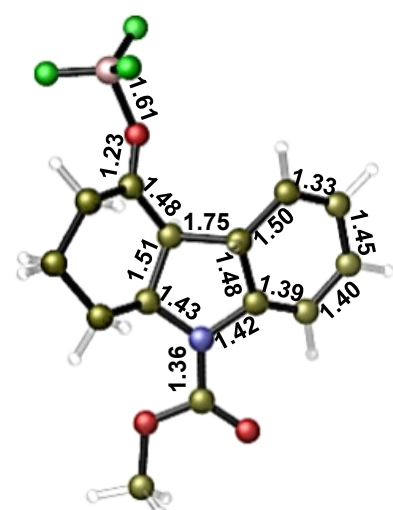
CI(S_{CT}/S_0)



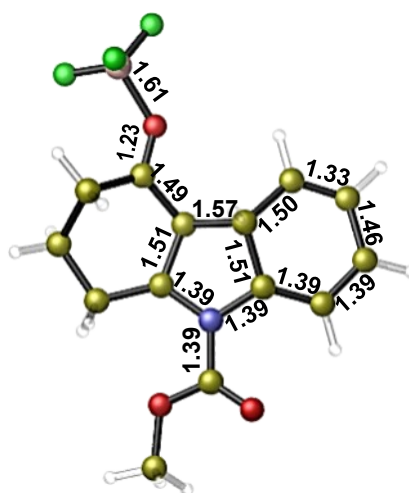
T_{pp} -Min



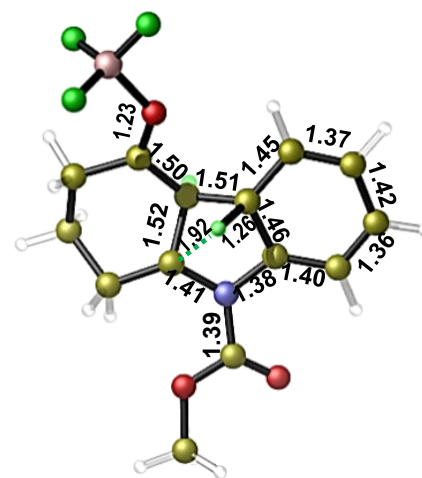
T_{pp} -TS



STC(T_{pp}/S_0)



S_0 -Int



S_0 -TS

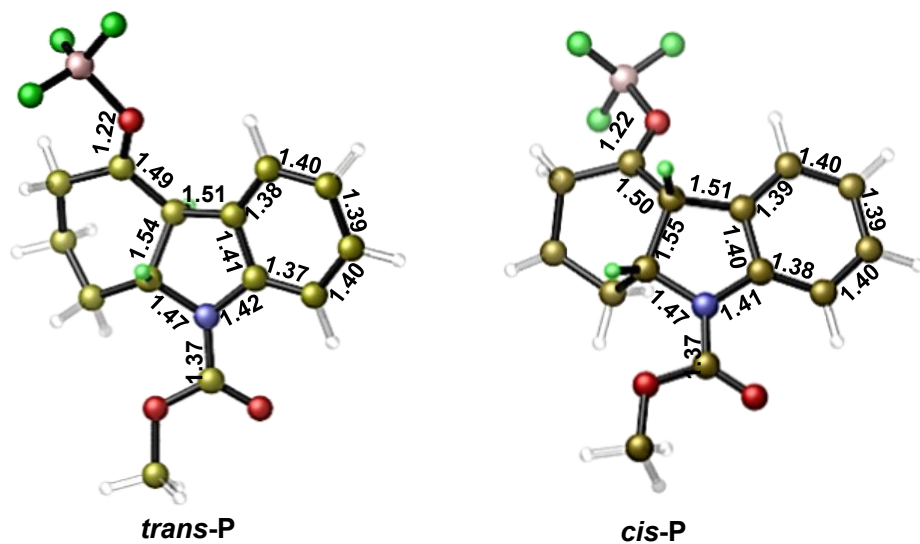


Figure S5. The critical structures for the **2-BF₃** along the 6π photocyclization reaction pathways. Selected key bond lengths are given in Å. All the Hydrogen atoms are set to be transparent for clarity, except that involved in the [1,4]-H shift process are highlighted in green.

3. Charge Translocation Calculations

To further explore the excited-state properties of different transitions for the enaminone **2** and the **2-BF₃** complex, charge translocation calculations were performed based on the CASPT2 computations and an appropriate fragment partitioning strategy. As shown in Figure S6, the β -enaminone moiety, the phenyl group and the N-alkoxycarbonyl moiety are defined as part I, II and III, respectively, and the BF₃ Lewis acid is referred as part IV in **2-BF₃** complex. Table S1 summarizes the Mulliken charge populations of the four parts in the S₀, S_{CT}(¹ $\pi\pi^*$) and S_{NP}(¹ $n\pi^*$) states upon the photoexcitation of **2** and **2-BF₃**.

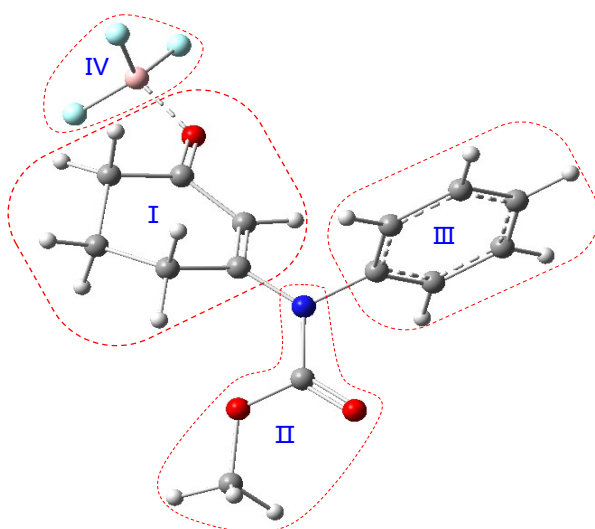


Figure S6. The scheme of fragment partition for **2** and **2-BF₃**.

Table S1. Charge populations (*e*) of **2** and **2-BF₃** in part I, II, III and IV in the S₀, S_{CT}(¹ $\pi\pi^*$) and S_{NP}(¹ $n\pi^*$) states upon the photoexcitation.

| Complexes | Part | S ₀ | S _{CT} | S _{NP} |
|-------------------------|------|----------------|-----------------|-----------------|
| 2 | I | 0.310 | -0.052 | 0.310 |
| | II | -0.642 | -0.586 | -0.641 |
| | III | 0.333 | 0.637 | 0.330 |
| 2-BF₃ | I | 0.548 | 0.150 | 0.414 |
| | II | -0.615 | -0.586 | -0.616 |
| | III | 0.340 | 0.722 | 0.398 |
| | IV | -0.273 | -0.286 | -0.195 |

4. Intersystem Crossing Rate Constant Calculations

The intersystem crossing (ISC) rates between singlet and triplet states in this work were estimated in the Condon approximation as^{S1,S2}

$$k_{\text{ISC}} = \frac{2\pi}{\hbar} \cdot \left| \langle {}^1\psi_0 | \hat{H}_{\text{SO}} | {}^3\psi_0 \rangle \right|^2 \cdot \left| \langle \chi_0 | \chi_n \rangle \right|^2 \cdot \rho \quad (1)$$

where the electronic coupling between the singlet state ${}^1\psi_0$ and the triplet state ${}^3\psi_0$ can be calculated as the SOC, the Franck–Condon factor of $\langle \chi_0 | \chi_n \rangle$ is taken equal to 1 at the STC point, and $\rho = 1/\Delta E_{\text{S/T}}$ is the reciprocal of the energy difference between the singlet and triplet states.

Table S2. The computed spin–orbit coupling values (SOC, cm^{-1}) and the singlet–triplet energy gaps ($\Delta E_{\text{S/T}}$, kcal/mol) of the involved singlet–triplet crossings (STCs) between S_{NP} and T_{PP} states or the minima of S_{CT} state. The rate of intersystem crossing (k_{ISC} , s^{-1}) is estimated in the Condon approximation.

| species | Critical points | $\Delta E_{\text{S/T}}$ | SOC | k_{ISC} |
|-------------------------|--|-------------------------|------|----------------------|
| 2 | STC($\text{S}_{\text{NP}}/\text{T}_{\text{PP}}$) | 0.6 | 36.5 | 7.5×10^{12} |
| 2-BF₃ | S_{CT} .Min | 7.2 | 0.29 | 3.9×10^7 |

5. References

(S1) Marian, C. M. *WIREs Comput. Mol. Sci.* **2002**, 2, 187–203.

(S2) Emelina, T. B.; Freidzon, A. Y.; Bagaturyants, A. A.; Karasev, V. E. *J. Phys. Chem. A* **2016**, 120, 7529–7537.

7. MEPs for the Stepwise Pathway via Two Consecutive [1,2]-H Shift

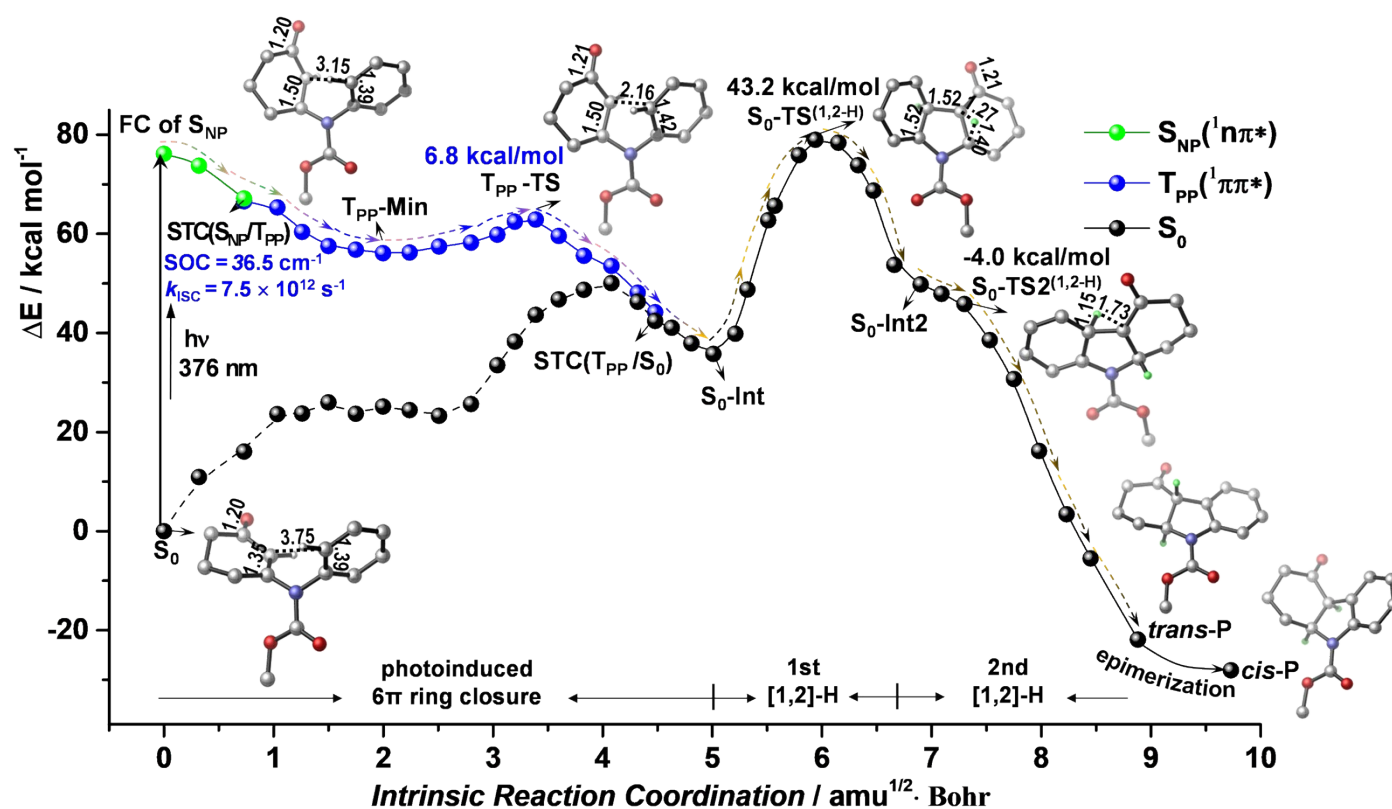


Figure S8. MEPs of the 6π photocyclization reaction for free **2** in triplet state followed by two consecutive [1,2]-H shift reactions at the CASPT2//CASSCF(8e/7o)/PCM level of theory.

8. MEPs for the 6π cyclization pathways in the ground state

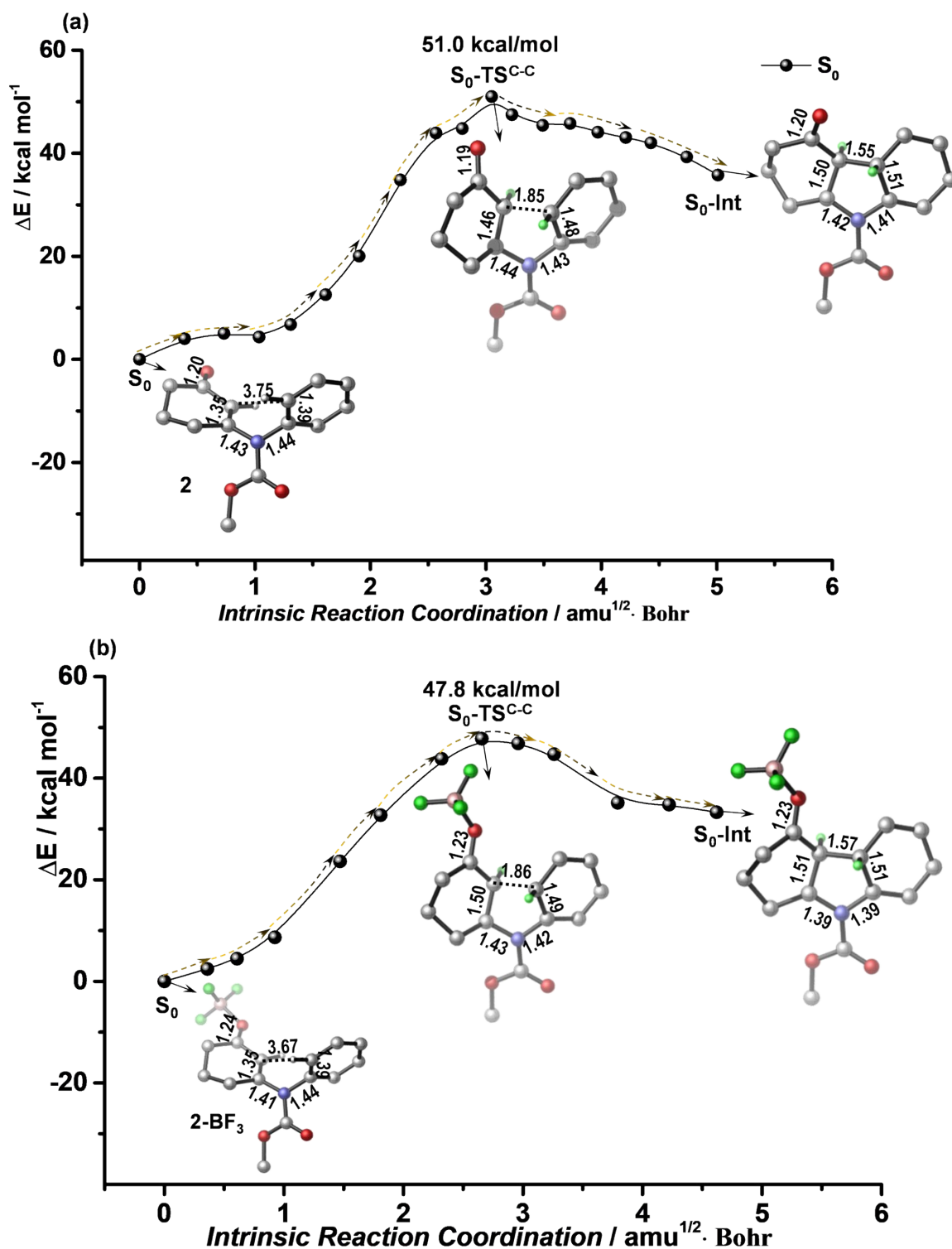


Figure S9. MEPs of the 6π cyclization reaction pathways for free **2** (a) and **2-BF₃** complex (b) in the singlet S_0 ground state at the CASPT2//CASSCF/PCM level of theory.

9. Tables for the Absolute and Relative Energies

Table S3. Absolute energies (A.E., Hartree), relative energies (R.E., kcal/mol) for the optimized structures of free enaminone **2** along the 6π photocyclization reaction pathway in the singlet excited state and subsequent [1,4]-H shift in ground state obtained by CASPT2//CASSCF(8e/7o)/PCM/6-31G** calculations. The corresponding energy profiles are plotted in Figure 1a of the main article.

| 2 | | CASSCF | RASSCF | CASPT2 | |
|------------------------------|--|---------------|---------------|---------------|-------------|
| | | A.E. | A.E. | A.E. | R.E. |
| S₀-Min | Root1(S ₀) | -818.05468 | -818.02669 | -820.51544 | 0.0 |
| | Root2[S _{NP} (¹ nπ*)] | | -817.83347 | -820.39409 | 76.1 |
| | Root3 | | -817.79469 | | |
| | Root4[S _{CT} (¹ ππ*)] | | -817.75482 | -820.35083 | 103.3 |
| | Root5 | | -817.72963 | | |
| | Root1[T _{PP} (³ ππ*)] | | -817.89165 | -820.39841 | 73.4 |
| | Root2 | | -817.86938 | | |
| | Root3 | | -817.82737 | | |
| | Root4 | | -817.82276 | | |
| | Root5 | | -817.82189 | | |
| Path S_{CT}-1 | Root1(S ₀) | | -818.01331 | -820.51528 | 0.1 |
| | Root2 | | -817.83690 | | |
| | Root3 | | -817.79100 | | |
| | Root4[S _{CT} (¹ ππ*)] | -817.83616 | -817.77659 | -820.35173 | 102.7 |
| | Root5 | | -817.74380 | | |
| Path S_{CT}-2 | Root1 | | -818.00799 | -820.51154 | 2.4 |
| | Root2 | | -817.83365 | | |
| | Root3 | | -817.78724 | | |
| | Root4[S _{CT} (¹ ππ*)] | -817.84137 | -817.77942 | -820.35586 | 100.1 |
| | Root5 | | -817.74185 | | |
| Path S_{CT}-3 | Root1(S ₀) | | -818.00721 | -820.51145 | 2.5 |
| | Root2 | | -817.83408 | | |
| | Root3 | | -817.78685 | | |
| | Root4[S _{CT} (¹ ππ*)] | -817.85094 | -817.78089 | -820.35884 | 98.3 |
| | Root5 | | -817.74206 | | |
| Path S_{CT}-4 | Root1(S ₀) | | -818.00694 | -820.51230 | 2.0 |
| | Root2 | | -817.83511 | | |
| | Root3 | | -817.78708 | | |
| | Root4[S _{CT} (¹ ππ*)] | -817.84715 | -817.78016 | -820.36076 | 97.1 |
| | Root5 | | -817.74144 | | |

| | | | | | |
|-------------------------------|--|------------|------------|------------|------|
| Path S_{CT}-5 | Root1(S ₀) | | -818.00642 | -820.51302 | 1.5 |
| | Root2 | | -817.83610 | | |
| | Root3 | | -817.78606 | | |
| | Root4[S _{CT} (¹ ππ*)] | -817.85205 | -817.78141 | -820.36508 | 94.4 |
| | Root5 | | -817.74020 | | |
| Path S_{CT}-6 | Root1(S ₀) | | -817.98874 | -820.49808 | 10.9 |
| | Root2 | | -817.82698 | | |
| | Root3[S _{CT} (¹ ππ*)] | -817.85259 | -817.78615 | -820.37179 | 90.1 |
| | Root4 | | -817.77580 | | |
| | Root5 | | -817.76071 | | |
| Path S_{CT}-7 | Root1(S ₀) | | -817.98755 | -820.49851 | 10.6 |
| | Root2 | | -817.82659 | | |
| | Root3[S _{CT} (¹ ππ*)] | -817.85473 | -817.78698 | -820.37648 | 87.2 |
| | Root4 | | -817.77479 | | |
| | Root5 | | -817.76208 | | |
| Path S_{CT}-8 | Root1(S ₀) | | -817.98418 | -820.49646 | 11.9 |
| | Root2 | | -817.82427 | | |
| | Root3[S _{CT} (¹ ππ*)] | -817.85483 | -817.78564 | -820.37807 | 86.2 |
| | Root4 | | -817.77213 | | |
| | Root5 | | -817.76401 | | |
| Path S_{CT}-9 | Root1(S ₀) | | -817.98026 | -820.49293 | 14.1 |
| | Root2 | | -817.82047 | | |
| | Root3[S _{CT} (¹ ππ*)] | -817.84318 | -817.79112 | -820.37593 | 87.5 |
| | Root4 | | -817.77356 | | |
| | Root5 | | -817.76702 | | |
| Path S_{CT}-10 | Root1(S ₀) | | -817.97071 | -820.48248 | 20.7 |
| | Root2 | | -817.80809 | | |
| | Root3[S _{CT} (¹ ππ*)] | -817.82950 | -817.79727 | -820.37225 | 89.9 |
| | Root4 | | -817.77116 | | |
| | Root5 | | -817.76628 | | |
| Path S_{CT}-11 | Root1(S ₀) | | -817.96031 | -820.47179 | 27.4 |
| | Root2[S _{CT} (¹ ππ*)] | -817.82747 | -817.80660 | -820.36593 | 93.8 |
| | Root3 | | -817.78934 | | |
| | Root4 | | -817.77090 | | |
| | Root5 | | -817.76368 | | |
| Path S_{CT}-12 | Root1(S ₀) | | -817.95215 | -820.46397 | 32.3 |
| | Root2[S _{CT} (¹ ππ*)] | -817.82697 | -817.80952 | -820.35950 | 97.9 |
| | Root3 | | -817.77825 | | |

| | | | | | |
|-------------------------------|--|------------|------------|------------|-------|
| | Root4 | | -817.77000 | | |
| | Root5 | | -817.76060 | | |
| | | | | | |
| Path S_{CT}-13 | Root1(S ₀) | | -817.94333 | -820.45618 | 37.2 |
| | Root2[S _{CT} (¹ ππ*)] | -817.82735 | -817.81225 | -820.35591 | 100.1 |
| | Root3 | | -817.77030 | | |
| | Root4 | | -817.76615 | | |
| | Root5 | | -817.75641 | | |
| | | | | | |
| Path S_{CT}-14 | Root1(S ₀) | | -817.94524 | -820.44829 | 42.1 |
| | Root2[S _{CT} (¹ ππ*)] | -817.82823 | -817.82682 | -820.36199 | 96.3 |
| | Root3 | | -817.78704 | | |
| | Root4 | | -817.77218 | | |
| | Root5 | | -817.72152 | | |
| | | | | | |
| Path S_{CT}-15 | Root1(S ₀) | | -817.93210 | -820.43745 | 48.9 |
| | Root2[S _{CT} (¹ ππ*)] | -817.83273 | -817.83095 | -820.36549 | 94.1 |
| | Root3 | | -817.78422 | | |
| | Root4 | | -817.77057 | | |
| | Root5 | | -817.71246 | | |
| | | | | | |
| Path S_{CT}-16 | Root1(S ₀) | | -817.92373 | -820.43216 | 52.3 |
| | Root2[S _{CT} (¹ ππ*)] | -817.83903 | -817.83675 | -820.37343 | 89.1 |
| | Root3 | | -817.78210 | | |
| | Root4 | | -817.77109 | | |
| | Root5 | | -817.70613 | | |
| | | | | | |
| Path S_{CT}-17 | Root1(S ₀) | | -817.92052 | -820.43037 | 53.4 |
| | Root2[S _{CT} (¹ ππ*)] | -817.84249 | -817.84009 | -820.37768 | 86.4 |
| | Root3 | | -817.78262 | | |
| | Root4 | | -817.77130 | | |
| | Root5 | | -817.70482 | | |
| | | | | | |
| Path S_{CT}-18 | Root1(S ₀) | | -817.91073 | -820.42546 | 56.5 |
| | Root2[S _{CT} (¹ ππ*)] | -817.84381 | -817.84237 | -820.38592 | 81.3 |
| | Root3 | | -817.77773 | | |
| | Root4 | | -817.77061 | | |
| | Root5 | | -817.69694 | | |
| | | | | | |
| Path S_{CT}-19 | Root1(S ₀) | | -817.87868 | -820.41739 | 61.5 |
| | Root2[S _{CT} (¹ ππ*)] | -817.85395 | -817.82698 | -820.39477 | 75.7 |
| | Root3 | | -817.76070 | | |
| | Root4 | | -817.73365 | | |
| | Root5 | | -817.67649 | | |
| | | | | | |
| Path S_{CT}-20 | Root1(S ₀) | | -817.89622 | -820.41696 | 61.8 |

| | | | | | |
|--|--|------------|------------|------------|------|
| | Root2[S _{CT} (¹ $\pi\pi^*$)] | -817.85351 | -817.85345 | -820.40376 | 70.1 |
| | Root3 | | -817.77696 | | |
| | Root4 | | -817.75609 | | |
| | Root5 | | -817.69476 | | |
| | | | | | |
| CI(S_{CT}/S₀) | Root1(S ₀) | | -817.85948 | -820.40682 | 68.2 |
| | Root2[S _{CT} (¹ $\pi\pi^*$)] | -817.85969 | -817.82467 | -820.40455 | 69.6 |
| | Root3 | | -817.75115 | | |
| | Root4 | | -817.69552 | | |
| | Root5 | | -817.66156 | | |
| | | | | | |
| Path S₀[*]-1 | Root1(S ₀) | -817.89176 | -817.88561 | -820.41657 | 62.0 |
| | Root2 | | -817.84754 | | |
| | Root3 | | -817.77286 | | |
| | Root4 | | -817.69418 | | |
| | Root5 | | -817.66735 | | |
| | | | | | |
| Path S₀[*]-2 | Root1(S ₀) | -817.91630 | -817.90613 | -820.42979 | 53.7 |
| | Root2 | | -817.82654 | | |
| | Root3 | | -817.79080 | | |
| | Root4 | | -817.70272 | | |
| | Root5 | | -817.67229 | | |
| | | | | | |
| Path S₀[*]-3 | Root1(S ₀) | -817.92964 | -817.91978 | -820.44136 | 46.5 |
| | Root2 | | -817.82425 | | |
| | Root3 | | -817.78576 | | |
| | Root4 | | -817.72222 | | |
| | Root5 | | -817.68165 | | |
| | | | | | |
| Path S₀[*]-4 | Root1(S ₀) | -817.94296 | -817.93266 | -820.45526 | 37.8 |
| | Root2 | | -817.82728 | | |
| | Root3 | | -817.77714 | | |
| | Root4 | | -817.74307 | | |
| | Root5 | | -817.69720 | | |
| | | | | | |
| Path S₀[*]-5/ S₀-Int | Root1(S ₀) | -817.94828 | -817.93773 | -820.45846 | 35.8 |
| | Root2 | | -817.82684 | | |
| | Root3 | | -817.76558 | | |
| | Root4 | | -817.74886 | | |
| | Root5 | | -817.70261 | | |
| | | | | | |
| Path S₀[*]-6 | Root1(S ₀) | -817.92909 | -817.92932 | -820.45303 | 39.2 |
| | Root2 | | -817.81440 | | |
| | Root3 | | -817.74794 | | |
| | Root4 | | -817.74011 | | |
| | Root5 | | -817.69320 | | |

| | | | | | |
|-----------------------------------|----------------|------------|------------|------------|------|
| Path S_0^*-7 | Root1(S_0) | -817.92224 | -817.92190 | -820.44715 | 42.9 |
| | Root2 | | -817.80353 | | |
| | Root3 | | -817.73695 | | |
| | Root4 | | -817.73265 | | |
| | Root5 | | -817.68415 | | |
| Path S_0^*-8 | Root1(S_0) | -817.90888 | -817.91706 | -820.44430 | 44.6 |
| | Root2 | | -817.78847 | | |
| | Root3 | | -817.73797 | | |
| | Root4 | | -817.72012 | | |
| | Root5 | | -817.67846 | | |
| Path S_0^*-9 | Root1(S_0) | -817.90884 | -817.91769 | -820.44348 | 45.2 |
| | Root2 | | -817.77963 | | |
| | Root3 | | -817.74340 | | |
| | Root4 | | -817.71139 | | |
| | Root5 | | -817.67549 | | |
| Path S_0^*-10 | Root1(S_0) | -817.90739 | -817.92603 | -820.44895 | 41.7 |
| | Root2 | | -817.76968 | | |
| | Root3 | | -817.75160 | | |
| | Root4 | | -817.70444 | | |
| | Root5 | | -817.67351 | | |
| Path S_0^*-11 | Root1(S_0) | -817.93214 | -817.92942 | -820.45220 | 39.7 |
| | Root2 | | -817.77451 | | |
| | Root3 | | -817.75739 | | |
| | Root4 | | -817.70913 | | |
| | Root5 | | -817.67882 | | |
| Path S_0^*-12 | Root1(S_0) | -817.95928 | -817.96791 | -820.47445 | 25.7 |
| | Root2 | | -817.75968 | | |
| | Root3 | | -817.69893 | | |
| | Root4 | | -817.66017 | | |
| | Root5 | | -817.64412 | | |
| Path S_0^*-13 | Root1(S_0) | -817.98707 | -817.99262 | -820.49609 | 12.1 |
| | Root2 | | -817.78151 | | |
| | Root3 | | -817.72091 | | |
| | Root4 | | -817.68047 | | |
| | Root5 | | -817.66393 | | |
| Path S_0^*-14 | Root1(S_0) | -818.01017 | -818.01412 | -820.51616 | -0.5 |
| | Root2 | | -817.80219 | | |
| | Root3 | | -817.74233 | | |
| | Root4 | | -817.70110 | | |

| | | | | | |
|----------------|------------------------|------------|------------|------------|-------|
| | Root5 | | -817.68390 | | |
| trans-P | Root1(S ₀) | -818.04608 | -818.05362 | -820.55105 | -22.3 |
| | Root2 | | -817.84200 | | |
| | Root3 | | -817.78109 | | |
| | Root4 | | -817.74345 | | |
| | Root5 | | -817.72135 | | |
| cis-P | Root1(S ₀) | -818.05619 | -818.06370 | -820.56019 | -28.1 |
| | Root2 | | -817.85358 | | |
| | Root3 | | -817.79208 | | |
| | Root4 | | -817.75694 | | |
| | Root5 | | -817.73287 | | |

Table S4. Absolute energies (A.E., Hartree), relative energies (R.E., kcal/mol) for the optimized structures of free enaminone **2** along reaction pathway of the ¹nπ* decay, and the 6π photocyclization reaction pathway in the triplet excited state, as well as the subsequent [1,4]-H shift in ground state obtained by CASPT2//CASSCF(8e/7o)/PCM/6-31G** calculations. The corresponding energy profiles are plotted in Figure 1b of the main article.

| 2 | | CASSCF | RASSCF | CASPT2 | |
|-------------------------------|--|---------------|---------------|---------------|-------------|
| | | A.E. | A.E. | A.E. | R.E. |
| S₀-Min | Root1(S ₀) | -818.05468 | -818.02669 | -820.51544 | 0.0 |
| | Root2[S _{NP} (¹ nπ*)] | | -817.83347 | -820.39409 | 76.1 |
| | Root3 | | -817.79469 | | |
| | Root4[S _{CT} (¹ ππ*)] | | -817.75482 | -820.35083 | 103.3 |
| | Root5 | | -817.72963 | | |
| | Root1[T _{PP} (³ ππ*)] | | -817.89165 | -820.39841 | 73.4 |
| | Root2 | | -817.86938 | | |
| | Root3 | | -817.82737 | | |
| | Root4 | | -817.82276 | | |
| | Root5 | | -817.82189 | | |
| Path S_{NP}-1 | Root1(S ₀) | | -818.00811 | | |
| | Root2[S _{NP} (¹ nπ*)] | -817.91816 | -817.91314 | -820.39789 | 73.8 |
| | Root3 | | -817.78017 | | |
| | Root4 | | -817.76186 | | |
| | Root5 | | -817.73825 | | |
| Path S_{NP}-2/ | Root1(S ₀) | | -817.98415 | -820.48987 | 16.0 |
| | Root2[S _{NP} (¹ nπ*)] | -817.92099 | -817.91659 | -820.40842 | 67.2 |

| | | | | | |
|---|--|------------|------------|------------|------|
| STC(S_{NP}/T_{PP}) | Root3 | | -817.76293 | | |
| | Root4 | | -817.75773 | | |
| | Root5 | | -817.75369 | | |
| | | | | | |
| | Root1 | | -817.91702 | | |
| | Root2[T _{PP} (¹ ππ*)] | | -817.90353 | -820.40937 | 66.6 |
| | Root3 | | -817.82184 | | |
| | Root4 | | -817.77871 | | |
| | | | | | |
| | | | | | |
| Path T_{PP}-1 | Root1[T _{PP} (¹ ππ*)] | -817.93034 | -817.91747 | -820.41132 | 65.3 |
| | Root2 | | -817.91326 | | |
| | Root3 | | -817.81042 | | |
| | Root4 | | -817.76749 | | |
| | Root5 | | -817.76180 | | |
| | | | | | |
| | Root1(S ₀) | | -817.97327 | -820.47776 | 23.6 |
| | Root2 | | -817.91705 | | |
| | Root3 | | -817.76381 | | |
| | Root4 | | -817.76279 | | |
| Root5 | | -817.74525 | | | |
| | | | | | |
| Path T_{PP}-2 | Root1[T _{PP} (¹ ππ*)] | -817.93458 | -817.91602 | -820.41913 | 60.4 |
| | Root2 | | -817.82178 | | |
| | Root3 | | -817.78870 | | |
| | Root4 | | -817.78684 | | |
| | Root5 | | -817.75179 | | |
| | | | | | |
| | Root1(S ₀) | | -817.98559 | -820.47769 | 23.7 |
| | Root2 | | -817.77319 | | |
| | Root3 | | -817.77101 | | |
| | Root4 | | -817.74798 | | |
| Root5 | | -817.72854 | | | |
| | | | | | |
| Path T_{PP}-3 | Root1[T _{PP} (¹ ππ*)] | -817.94516 | -817.93329 | -820.42375 | 57.5 |
| | Root2 | | -817.81666 | | |
| | Root3 | | -817.79487 | | |
| | Root4 | | -817.77536 | | |
| | Root5 | | -817.76484 | | |
| | | | | | |
| | Root1(S ₀) | | -817.97387 | -820.47402 | 26.0 |
| | Root2 | | -817.81527 | | |
| | Root3 | | -817.77629 | | |
| | Root4 | | -817.75532 | | |
| Root5 | | -817.74512 | | | |
| | | | | | |

| | | | | | |
|------------------------------|--|------------|------------|------------|------|
| Path T_{PP-4} | Root1[T _{PP} (¹ ππ*)] | -817.94376 | -817.93238 | -820.42488 | 56.8 |
| | Root2 | | -817.82653 | | |
| | Root3 | | -817.79475 | | |
| | Root4 | | -817.78112 | | |
| | Root5 | | -817.77113 | | |
| | Root1(S ₀) | | -817.97658 | -820.47768 | 23.7 |
| | Root2 | | -817.81443 | | |
| | Root3 | | -817.77813 | | |
| | Root4 | | -817.75946 | | |
| | Root5 | | -817.75020 | | |
| Path T_{PP-5} | Root1[T _{PP} (¹ ππ*)] | -817.94325 | -817.93204 | -820.42601 | 56.1 |
| | Root2 | | -817.82327 | | |
| | Root3 | | -817.79196 | | |
| | Root4 | | -817.78073 | | |
| | Root5 | | -817.76782 | | |
| | Root1(S ₀) | | -817.97276 | -820.47535 | 25.2 |
| | Root2 | | -817.81561 | | |
| | Root3 | | -817.77791 | | |
| | Root4 | | -817.76034 | | |
| | Root5 | | -817.74757 | | |
| Path T_{PP-6} | Root1[T _{PP} (¹ ππ*)] | -817.94215 | -817.93093 | -820.42582 | 56.2 |
| | Root2 | | -817.82533 | | |
| | Root3 | | -817.79138 | | |
| | Root4 | | -817.78046 | | |
| | Root5 | | -817.76936 | | |
| | Root1(S ₀) | | -817.97354 | -820.47652 | 24.4 |
| | Root2 | | -817.81346 | | |
| | Root3 | | -817.77820 | | |
| | Root4 | | -817.76190 | | |
| | Root5 | | -817.74960 | | |
| Path T_{PP-7} | Root1[T _{PP} (¹ ππ*)] | -817.93628 | -817.92569 | -820.42386 | 57.5 |
| | Root2 | | -817.83037 | | |
| | Root3 | | -817.78758 | | |
| | Root4 | | -817.77841 | | |
| | Root5 | | -817.77255 | | |
| | Root1(S ₀) | | -817.97387 | -820.47833 | 23.3 |
| | Root2 | | -817.80499 | | |
| | Root3 | | -817.77674 | | |
| | Root4 | | -817.76889 | | |

| | | | | | |
|--|--|------------|------------|------------|------|
| | Root5 | | -817.75512 | | |
| | | | | | |
| Path T_{PP}-8 | Root1[T _{PP} (¹ ππ*)] | -817.92725 | -817.91492 | -820.42264 | 58.2 |
| | Root2 | | -817.80907 | | |
| | Root3 | | -817.78335 | | |
| | Root4 | | -817.78150 | | |
| | Root5 | | -817.77028 | | |
| | | | | | |
| | Root1(S ₀) | | -817.96528 | -820.47454 | 25.7 |
| | Root2 | | -817.79683 | | |
| | Root3 | | -817.77591 | | |
| | Root4 | | -817.76789 | | |
| | | | | | |
| Path T_{PP}-9 | Root1[T _{PP} (¹ ππ*)] | -817.91818 | -817.91717 | -820.42007 | 59.8 |
| | Root2 | | -817.81987 | | |
| | Root3 | | -817.78935 | | |
| | Root4 | | -817.77524 | | |
| | Root5 | | -817.75632 | | |
| | | | | | |
| | Root1(S ₀) | | -817.95671 | -820.46206 | 33.5 |
| | Root2 | | -817.81154 | | |
| | Root3 | | -817.78038 | | |
| | Root4 | | -817.77356 | | |
| | | | | | |
| Path T_{PP}-10 | Root1[T _{PP} (¹ ππ*)] | -817.91530 | -817.90575 | -820.41590 | 62.5 |
| | Root2 | | -817.80790 | | |
| | Root3 | | -817.77093 | | |
| | Root4 | | -817.76160 | | |
| | Root5 | | -817.75778 | | |
| | | | | | |
| | Root1(S ₀) | | -817.94083 | -820.45449 | 38.2 |
| | Root2 | | -817.80464 | | |
| | Root3 | | -817.77095 | | |
| | Root4 | | -817.76250 | | |
| | | | | | |
| Path T_{PP}-11/ T_{PP}-TS | Root1[T _{PP} (¹ ππ*)] | -817.91238 | -817.90231 | -820.41522 | 62.9 |
| | Root2 | | -817.80020 | | |
| | Root3 | | -817.77008 | | |
| | Root4 | | -817.75832 | | |
| | Root5 | | -817.74496 | | |
| | | | | | |
| | Root1(S ₀) | | -817.93012 | -820.44584 | 43.7 |
| Root2 | | -817.80015 | | | |

| | | | | | | |
|-------------------------------|--|------------|------------|------------|------|--|
| | Root3 | | -817.77344 | | | |
| | Root4 | | -817.76435 | | | |
| | Root5 | | -817.73963 | | | |
| | | | | | | |
| Path T_{pp}-12 | Root1[T _{pp} (¹ ππ*)] | -817.91353 | -817.90900 | -820.42050 | 59.6 | |
| | Root2 | | -817.80288 | | | |
| | Root3 | | -817.79491 | | | |
| | Root4 | | -817.75450 | | | |
| | Root5 | | -817.74149 | | | |
| | | | | | | |
| | Root1(S ₀) | | -817.92841 | -820.44092 | 46.8 | |
| | Root2 | | -817.82162 | | | |
| | Root3 | | -817.79099 | | | |
| | Root4 | | -817.77343 | | | |
| Root5 | | -817.71441 | | | | |
| | | | | | | |
| Path T_{pp}-13 | Root1[T _{pp} (¹ ππ*)] | -817.92022 | -817.91639 | -820.42685 | 55.6 | |
| | Root2 | | -817.80964 | | | |
| | Root3 | | -817.76698 | | | |
| | Root4 | | -817.75477 | | | |
| | Root5 | | -817.72971 | | | |
| | | | | | | |
| | Root1(S ₀) | | -817.92462 | -820.43782 | 48.7 | |
| | Root2 | | -817.82821 | | | |
| | Root3 | | -817.78337 | | | |
| | Root4 | | -817.77528 | | | |
| Root5 | | -817.74965 | | | | |
| | | | | | | |
| Path T_{pp}-14 | Root1[T _{pp} (¹ ππ*)] | -817.92473 | -817.91860 | -820.43016 | 53.5 | |
| | Root2 | | -817.81129 | | | |
| | Root3 | | -817.75447 | | | |
| | Root4 | | -817.75017 | | | |
| | Root5 | | -817.72636 | | | |
| | | | | | | |
| | Root1(S ₀) | | -817.92845 | -820.43565 | 50.1 | |
| | Root2 | | -817.83445 | | | |
| | Root3 | | -817.77762 | | | |
| | Root4 | | -817.77462 | | | |
| Root5 | | -817.75050 | | | | |
| | | | | | | |
| Path T_{pp}-15 | Root1[T _{pp} (¹ ππ*)] | -817.93250 | -817.92659 | -820.43469 | 50.7 | |
| | Root2 | | -817.82441 | | | |
| | Root3 | | -817.76140 | | | |
| | Root4 | | -817.73421 | | | |
| | Root5 | | -817.71269 | | | |
| | | | | | | |

| | | | | | | |
|--|--|------------|------------|------------|------|--|
| | Root1(S ₀) | | -817.92553 | -820.43924 | 47.8 | |
| | Root2 | | -817.82526 | | | |
| | Root3 | | -817.77730 | | | |
| | Root4 | | -817.75191 | | | |
| | Root5 | | -817.72225 | | | |
| | | | | | | |
| Path T_{PP}-16 | Root1[T _{PP} (¹ ππ*)] | -817.93714 | -817.93051 | -820.43875 | 48.1 | |
| | Root2 | | -817.82811 | | | |
| | Root3 | | -817.76387 | | | |
| | Root4 | | -817.73656 | | | |
| | Root5 | | -817.71229 | | | |
| | | | | | | |
| | Root1(S ₀) | | -817.94603 | -820.44163 | 46.3 | |
| | Root2 | | -817.85283 | | | |
| | Root3 | | -817.79049 | | | |
| | Root4 | | -817.77150 | | | |
| | Root5 | | -817.73766 | | | |
| | | | | | | |
| Path T_{PP}-17 | Root1[T _{PP} (¹ ππ*)] | -817.94170 | -817.93477 | -820.44323 | 45.3 | |
| | Root2 | | -817.83037 | | | |
| | Root3 | | -817.76461 | | | |
| | Root4 | | -817.73914 | | | |
| | Root5 | | -817.71245 | | | |
| | | | | | | |
| | Root1(S ₀) | | -817.95192 | -820.44614 | 43.5 | |
| | Root2 | | -817.85674 | | | |
| | Root3 | | -817.79533 | | | |
| | Root4 | | -817.77360 | | | |
| | Root5 | | -817.74113 | | | |
| | | | | | | |
| STC(T_{PP}/S₀) | Root1[T _{PP} (¹ ππ*)] | -817.94359 | -817.93646 | -820.44503 | 44.2 | |
| | Root2 | | -817.83136 | | | |
| | Root3 | | -817.76491 | | | |
| | Root4 | | -817.74028 | | | |
| | Root5 | | -817.71281 | | | |
| | | | | | | |
| | Root1(S ₀) | | -817.95400 | -820.44781 | 42.4 | |
| | Root2 | | -817.85801 | | | |
| | Root3 | | -817.79714 | | | |
| | Root4 | | -817.77424 | | | |
| | Root5 | | -817.74222 | | | |
| | | | | | | |
| Path S₀*-1 | Root1(S ₀) | -817.94480 | -817.93242 | -820.45004 | 41.0 | |
| | Root2 | | -817.83101 | | | |
| | Root3 | | -817.77353 | | | |
| | Root4 | | -817.74835 | | | |

| | | | | | |
|--|------------------------|------------|------------|------------|------|
| | Root5 | | -817.70185 | | |
| Path S₀[*]-2 | Root1(S ₀) | -817.94872 | -817.93763 | -820.45503 | 37.9 |
| | Root2 | | -817.83234 | | |
| | Root3 | | -817.77273 | | |
| | Root4 | | -817.75546 | | |
| | Root5 | | -817.70379 | | |
| Path S₀[*]-3/ S₀[*]-Int | Root1(S ₀) | -817.94828 | -817.93773 | -820.45846 | 35.8 |
| | Root2 | | -817.82684 | | |
| | Root3 | | -817.76558 | | |
| | Root4 | | -817.74886 | | |
| | Root5 | | -817.70261 | | |
| Path S₀[*]-4 | Root1(S ₀) | -817.92909 | -817.92932 | -820.45303 | 39.2 |
| | Root2 | | -817.81440 | | |
| | Root3 | | -817.74794 | | |
| | Root4 | | -817.74011 | | |
| | Root5 | | -817.69320 | | |
| Path S₀[*]-5 | Root1(S ₀) | -817.92224 | -817.92190 | -820.44715 | 42.9 |
| | Root2 | | -817.80353 | | |
| | Root3 | | -817.73695 | | |
| | Root4 | | -817.73265 | | |
| | Root5 | | -817.68415 | | |
| Path S₀[*]-6 | Root1(S ₀) | -817.90888 | -817.91706 | -820.44430 | 44.6 |
| | Root2 | | -817.78847 | | |
| | Root3 | | -817.73797 | | |
| | Root4 | | -817.72012 | | |
| | Root5 | | -817.67846 | | |
| Path S₀[*]-7 | Root1(S ₀) | -817.90884 | -817.91769 | -820.44348 | 45.2 |
| | Root2 | | -817.77963 | | |
| | Root3 | | -817.74340 | | |
| | Root4 | | -817.71139 | | |
| | Root5 | | -817.67549 | | |
| Path S₀[*]-8 | Root1(S ₀) | -817.90739 | -817.92603 | -820.44895 | 41.7 |
| | Root2 | | -817.76968 | | |
| | Root3 | | -817.75160 | | |
| | Root4 | | -817.70444 | | |
| | Root5 | | -817.67351 | | |
| Path S₀[*]-9 | Root1(S ₀) | -817.93214 | -817.92942 | -820.45220 | 39.7 |
| | Root2 | | -817.77451 | | |
| | Root3 | | -817.75739 | | |

| | | | | | |
|-------------------------------|------------------------|------------|------------|------------|-------|
| | Root4 | | -817.70913 | | |
| | Root5 | | -817.67882 | | |
| Path S₀*-10 | Root1(S ₀) | -817.95928 | -817.96791 | -820.47445 | 25.7 |
| | Root2 | | -817.75968 | | |
| | Root3 | | -817.69893 | | |
| | Root4 | | -817.66017 | | |
| | Root5 | | -817.64412 | | |
| Path S₀*-11 | Root1(S ₀) | -817.98707 | -817.99262 | -820.49609 | 12.1 |
| | Root2 | | -817.78151 | | |
| | Root3 | | -817.72091 | | |
| | Root4 | | -817.68047 | | |
| | Root5 | | -817.66393 | | |
| Path S₀*-12 | Root1(S ₀) | -818.01017 | -818.01412 | -820.51616 | -0.5 |
| | Root2 | | -817.80219 | | |
| | Root3 | | -817.74233 | | |
| | Root4 | | -817.70110 | | |
| | Root5 | | -817.68390 | | |
| trans-P | Root1(S ₀) | -818.04608 | -818.05362 | -820.55105 | -22.3 |
| | Root2 | | -817.84200 | | |
| | Root3 | | -817.78109 | | |
| | Root4 | | -817.74345 | | |
| | Root5 | | -817.72135 | | |
| cis-P | Root1(S ₀) | -818.05619 | -818.06370 | -820.56019 | -28.1 |
| | Root2 | | -817.85358 | | |
| | Root3 | | -817.79208 | | |
| | Root4 | | -817.75694 | | |
| | Root5 | | -817.73287 | | |

Table S5. Absolute energies (A.E., Hartree), relative energies (R.E., kcal/mol) for the optimized structures of free enaminone **2** along reaction pathway of the ¹nπ* decay, and the 6π photocyclization reaction pathway in the triplet excited state, as well as the stepwise [1,2]-H shift processes in ground state by CASPT2//CASSCF(8e/7o)/PCM/6-31G** calculations. The corresponding energy profiles are plotted in Figure S8.

| 2 | | CASSCF | RASSCF | CASPT2 | |
|--------------------------|------------------------|---------------|---------------|---------------|-------------|
| | | A.E. | A.E. | A.E. | R.E. |
| S₀-Min | Root1(S ₀) | -818.05468 | -818.02669 | -820.51544 | 0.0 |

| | | | | | |
|--|--|------------|------------|------------|-------|
| | Root2[S _{NP} (¹ nπ*)] | | -817.83347 | -820.39409 | 76.1 |
| | Root3 | | -817.79469 | | |
| | Root4[S _{CT} (¹ ππ*)] | | -817.75482 | -820.35083 | 103.3 |
| | Root5 | | -817.72963 | | |
| | | | | | |
| | Root1[T _{PP} (³ ππ*)] | | -817.89165 | -820.39841 | 73.4 |
| | Root2 | | -817.86938 | | |
| | Root3 | | -817.82737 | | |
| | Root4 | | -817.82276 | | |
| | Root5 | | -817.82189 | | |
| | | | | | |
| Path S_{NP}-1 | Root1(S ₀) | | -818.00811 | | |
| | Root2[S _{NP} (¹ nπ*)] | -817.91816 | -817.91314 | -820.39789 | 73.8 |
| | Root3 | | -817.78017 | | |
| | Root4 | | -817.76186 | | |
| | Root5 | | -817.73825 | | |
| | | | | | |
| Path S_{NP}-2/ STC(S_{NP}/T_{PP}) | Root1(S ₀) | | -817.98415 | -820.48987 | 16.0 |
| | Root2[S _{NP} (¹ nπ*)] | -817.92099 | -817.91659 | -820.40842 | 67.2 |
| | Root3 | | -817.76293 | | |
| | Root4 | | -817.75773 | | |
| | Root5 | | -817.75369 | | |
| | | | | | |
| | Root1 | | -817.91702 | | |
| | Root2[T _{PP} (¹ ππ*)] | | -817.90353 | -820.40937 | 66.6 |
| | Root3 | | -817.82184 | | |
| | Root4 | | -817.77871 | | |
| Root5 | | -817.77605 | | | |
| | | | | | |
| Path T_{PP}-1 | Root1[T _{PP} (¹ ππ*)] | -817.93034 | -817.91747 | -820.41132 | 65.3 |
| | Root2 | | -817.91326 | | |
| | Root3 | | -817.81042 | | |
| | Root4 | | -817.76749 | | |
| | Root5 | | -817.76180 | | |
| | | | | | |
| | Root1(S ₀) | | -817.97327 | -820.47776 | 23.6 |
| | Root2 | | -817.91705 | | |
| | Root3 | | -817.76381 | | |
| | Root4 | | -817.76279 | | |
| Root5 | | -817.74525 | | | |
| | | | | | |
| Path T_{PP}-2 | Root1[T _{PP} (¹ ππ*)] | -817.93458 | -817.91602 | -820.41913 | 60.4 |
| | Root2 | | -817.82178 | | |
| | Root3 | | -817.78870 | | |
| | Root4 | | -817.78684 | | |
| | Root5 | | -817.75179 | | |

| | | | | | |
|------------------------------|--|------------|------------|------------|------|
| | Root1(S ₀) | | -817.98559 | -820.47769 | 23.7 |
| | Root2 | | -817.77319 | | |
| | Root3 | | -817.77101 | | |
| | Root4 | | -817.74798 | | |
| | Root5 | | -817.72854 | | |
| Path T_{PP-3} | Root1[T _{PP} (¹ ππ*)] | -817.94516 | -817.93329 | -820.42375 | 57.5 |
| | Root2 | | -817.81666 | | |
| | Root3 | | -817.79487 | | |
| | Root4 | | -817.77536 | | |
| | Root5 | | -817.76484 | | |
| | Root1(S ₀) | | -817.97387 | -820.47402 | 26.0 |
| | Root2 | | -817.81527 | | |
| | Root3 | | -817.77629 | | |
| | Root4 | | -817.75532 | | |
| | Root5 | | -817.74512 | | |
| Path T_{PP-4} | Root1[T _{PP} (¹ ππ*)] | -817.94376 | -817.93238 | -820.42488 | 56.8 |
| | Root2 | | -817.82653 | | |
| | Root3 | | -817.79475 | | |
| | Root4 | | -817.78112 | | |
| | Root5 | | -817.77113 | | |
| | Root1(S ₀) | | -817.97658 | -820.47768 | 23.7 |
| | Root2 | | -817.81443 | | |
| | Root3 | | -817.77813 | | |
| | Root4 | | -817.75946 | | |
| | Root5 | | -817.75020 | | |
| Path T_{PP-5} | Root1[T _{PP} (¹ ππ*)] | -817.94325 | -817.93204 | -820.42601 | 56.1 |
| | Root2 | | -817.82327 | | |
| | Root3 | | -817.79196 | | |
| | Root4 | | -817.78073 | | |
| | Root5 | | -817.76782 | | |
| | Root1(S ₀) | | -817.97276 | -820.47535 | 25.2 |
| | Root2 | | -817.81561 | | |
| | Root3 | | -817.77791 | | |
| | Root4 | | -817.76034 | | |
| | Root5 | | -817.74757 | | |
| Path T_{PP-6} | Root1[T _{PP} (¹ ππ*)] | -817.94215 | -817.93093 | -820.42582 | 56.2 |
| | Root2 | | -817.82533 | | |
| | Root3 | | -817.79138 | | |

| | | | | | |
|-------------------------------|--|------------|------------|------------|------|
| | Root4 | | -817.78046 | | |
| | Root5 | | -817.76936 | | |
| | Root1(S ₀) | | -817.97354 | -820.47652 | 24.4 |
| | Root2 | | -817.81346 | | |
| | Root3 | | -817.77820 | | |
| | Root4 | | -817.76190 | | |
| | Root5 | | -817.74960 | | |
| | | | | | |
| Path T_{pp}-7 | Root1[T _{pp} (¹ ππ*)] | -817.93628 | -817.92569 | -820.42386 | 57.5 |
| | Root2 | | -817.83037 | | |
| | Root3 | | -817.78758 | | |
| | Root4 | | -817.77841 | | |
| | Root5 | | -817.77255 | | |
| | Root1(S ₀) | | -817.97387 | -820.47833 | 23.3 |
| | Root2 | | -817.80499 | | |
| | Root3 | | -817.77674 | | |
| | Root4 | | -817.76889 | | |
| | Root5 | | -817.75512 | | |
| | | | | | |
| Path T_{pp}-8 | Root1[T _{pp} (¹ ππ*)] | -817.92725 | -817.91492 | -820.42264 | 58.2 |
| | Root2 | | -817.80907 | | |
| | Root3 | | -817.78335 | | |
| | Root4 | | -817.78150 | | |
| | Root5 | | -817.77028 | | |
| | Root1(S ₀) | | -817.96528 | -820.47454 | 25.7 |
| | Root2 | | -817.79683 | | |
| | Root3 | | -817.77591 | | |
| | Root4 | | -817.76789 | | |
| | Root5 | | -817.75795 | | |
| | | | | | |
| Path T_{pp}-9 | Root1[T _{pp} (¹ ππ*)] | -817.91818 | -817.91717 | -820.42007 | 59.8 |
| | Root2 | | -817.81987 | | |
| | Root3 | | -817.78935 | | |
| | Root4 | | -817.77524 | | |
| | Root5 | | -817.75632 | | |
| | Root1(S ₀) | | -817.95671 | -820.46206 | 33.5 |
| | Root2 | | -817.81154 | | |
| | Root3 | | -817.78038 | | |
| | Root4 | | -817.77356 | | |
| | Root5 | | -817.73683 | | |
| | | | | | |
| Path T_{pp}-10 | Root1[T _{pp} (¹ ππ*)] | -817.91530 | -817.90575 | -820.41590 | 62.5 |

| | | | | | |
|--|--|------------|------------|------------|------|
| | Root2 | | -817.80790 | | |
| | Root3 | | -817.77093 | | |
| | Root4 | | -817.76160 | | |
| | Root5 | | -817.75778 | | |
| | | | | | |
| | Root1(S ₀) | | -817.94083 | -820.45449 | 38.2 |
| | Root2 | | -817.80464 | | |
| | Root3 | | -817.77095 | | |
| | Root4 | | -817.76250 | | |
| | Root5 | | -817.75149 | | |
| | | | | | |
| Path T_{PP-11}/ T_{PP-TS} | Root1[T _{PP} (¹ ππ*)] | -817.91238 | -817.90231 | -820.41522 | 62.9 |
| | Root2 | | -817.80020 | | |
| | Root3 | | -817.77008 | | |
| | Root4 | | -817.75832 | | |
| | Root5 | | -817.74496 | | |
| | | | | | |
| | Root1(S ₀) | | -817.93012 | -820.44584 | 43.7 |
| | Root2 | | -817.80015 | | |
| | Root3 | | -817.77344 | | |
| | Root4 | | -817.76435 | | |
| | Root5 | | -817.73963 | | |
| | | | | | |
| Path T_{PP-12} | Root1[T _{PP} (¹ ππ*)] | -817.91353 | -817.90900 | -820.42050 | 59.6 |
| | Root2 | | -817.80288 | | |
| | Root3 | | -817.79491 | | |
| | Root4 | | -817.75450 | | |
| | Root5 | | -817.74149 | | |
| | | | | | |
| | Root1(S ₀) | | -817.92841 | -820.44092 | 46.8 |
| | Root2 | | -817.82162 | | |
| | Root3 | | -817.79099 | | |
| | Root4 | | -817.77343 | | |
| | Root5 | | -817.71441 | | |
| | | | | | |
| Path T_{PP-13} | Root1[T _{PP} (¹ ππ*)] | -817.92022 | -817.91639 | -820.42685 | 55.6 |
| | Root2 | | -817.80964 | | |
| | Root3 | | -817.76698 | | |
| | Root4 | | -817.75477 | | |
| | Root5 | | -817.72971 | | |
| | | | | | |
| | Root1(S ₀) | | -817.92462 | -820.43782 | 48.7 |
| | Root2 | | -817.82821 | | |
| | Root3 | | -817.78337 | | |
| | Root4 | | -817.77528 | | |
| | Root5 | | -817.74965 | | |

| | | | | | |
|-------------------------------|--|--|------------|------------|------------|
| Path T_{pp}-14 | Root1[T _{pp} (¹ ππ*)] | -817.92473 | -817.91860 | -820.43016 | 53.5 |
| | Root2 | | -817.81129 | | |
| | Root3 | | -817.75447 | | |
| | Root4 | | -817.75017 | | |
| | Root5 | | -817.72636 | | |
| | Root1(S ₀) | | -817.92845 | -820.43565 | 50.1 |
| | Root2 | | -817.83445 | | |
| | Root3 | | -817.77762 | | |
| | Root4 | | -817.77462 | | |
| | Root5 | | -817.75050 | | |
| | Path T_{pp}-15 | Root1[T _{pp} (¹ ππ*)] | -817.93250 | -817.92659 | -820.43469 |
| Root2 | | | -817.82441 | | |
| Root3 | | | -817.76140 | | |
| Root4 | | | -817.73421 | | |
| Root5 | | | -817.71269 | | |
| Root1(S ₀) | | | -817.92553 | -820.43924 | 47.8 |
| Root2 | | | -817.82526 | | |
| Root3 | | | -817.77730 | | |
| Root4 | | | -817.75191 | | |
| Root5 | | | -817.72225 | | |
| Path T_{pp}-16 | | Root1[T _{pp} (¹ ππ*)] | -817.93714 | -817.93051 | -820.43875 |
| | Root2 | | -817.82811 | | |
| | Root3 | | -817.76387 | | |
| | Root4 | | -817.73656 | | |
| | Root5 | | -817.71229 | | |
| | Root1(S ₀) | | -817.94603 | -820.44163 | 46.3 |
| | Root2 | | -817.85283 | | |
| | Root3 | | -817.79049 | | |
| | Root4 | | -817.77150 | | |
| | Root5 | | -817.73766 | | |
| | Path T_{pp}-17 | Root1[T _{pp} (¹ ππ*)] | -817.94170 | -817.93477 | -820.44323 |
| Root2 | | | -817.83037 | | |
| Root3 | | | -817.76461 | | |
| Root4 | | | -817.73914 | | |
| Root5 | | | -817.71245 | | |
| Root1(S ₀) | | | -817.95192 | -820.44614 | 43.5 |
| Root2 | | | -817.85674 | | |
| Root3 | | | -817.79533 | | |

| | | | | | |
|--|--|------------|------------|------------|------|
| | Root4 | | -817.77360 | | |
| | Root5 | | -817.74113 | | |
| | | | | | |
| STC(T_{PP}/S₀) | Root1[T _{PP} (¹ ππ*)] | -817.94359 | -817.93646 | -820.44503 | 44.2 |
| | Root2 | | -817.83136 | | |
| | Root3 | | -817.76491 | | |
| | Root4 | | -817.74028 | | |
| | Root5 | | -817.71281 | | |
| | | | | | |
| | Root1(S ₀) | | -817.95400 | -820.44781 | 42.4 |
| | Root2 | | -817.85801 | | |
| | Root3 | | -817.79714 | | |
| | Root4 | | -817.77424 | | |
| Root5 | | -817.74222 | | | |
| | | | | | |
| Path S₀[*]-1 | Root1(S ₀) | -817.94480 | -817.93242 | -820.45004 | 41.0 |
| | Root2 | | -817.83101 | | |
| | Root3 | | -817.77353 | | |
| | Root4 | | -817.74835 | | |
| | Root5 | | -817.70185 | | |
| | | | | | |
| Path S₀[*]-2 | Root1(S ₀) | -817.94872 | -817.93763 | -820.45503 | 37.9 |
| | Root2 | | -817.83234 | | |
| | Root3 | | -817.77273 | | |
| | Root4 | | -817.75546 | | |
| | Root5 | | -817.70379 | | |
| | | | | | |
| Path S₀[*]-3/ S₀-Int | Root1(S ₀) | -817.94828 | -817.93773 | -820.45846 | 35.8 |
| | Root2 | | -817.82684 | | |
| | Root3 | | -817.76558 | | |
| | Root4 | | -817.74886 | | |
| | Root5 | | -817.70261 | | |
| | | | | | |
| Path S₀[*]-4 | Root1(S ₀) | -817.93246 | -817.92407 | -820.45196 | 39.8 |
| | Root2 | | -817.81563 | | |
| | Root3 | | -817.76912 | | |
| | Root4 | | -817.71878 | | |
| | Root5 | | -817.69012 | | |
| | | | | | |
| Path S₀[*]-5 | Root1(S ₀) | -817.91600 | -817.90743 | -820.43771 | 48.8 |
| | Root2 | | -817.80054 | | |
| | Root3 | | -817.75884 | | |
| | Root4 | | -817.68771 | | |
| | Root5 | | -817.67445 | | |
| | | | | | |
| Path S₀[*]-6 | Root1(S ₀) | -817.91077 | -817.90191 | -820.41543 | 62.8 |

| | | | | | |
|--|------------------------|------------|------------|------------|------|
| | Root2 | | -817.79476 | | |
| | Root3 | | -817.73415 | | |
| | Root4 | | -817.69693 | | |
| | Root5 | | -817.66504 | | |
| | | | | | |
| Path S₀[*]-7 | Root1(S ₀) | -817.90490 | -817.89646 | -820.41078 | 65.7 |
| | Root2 | | -817.78924 | | |
| | Root3 | | -817.73050 | | |
| | Root4 | | -817.69164 | | |
| | Root5 | | -817.65807 | | |
| | | | | | |
| Path S₀[*]-8 | Root1(S ₀) | -817.88343 | -817.87428 | -820.39447 | 75.9 |
| | Root2 | | -817.76716 | | |
| | Root3 | | -817.71470 | | |
| | Root4 | | -817.67177 | | |
| | Root5 | | -817.64428 | | |
| | | | | | |
| Path S₀[*]-9/ S₀-TS1^(1,2-H) | Root1(S ₀) | -817.86202 | -817.85871 | -820.38955 | 79.0 |
| | Root2 | | -817.74792 | | |
| | Root3 | | -817.72248 | | |
| | Root4 | | -817.68948 | | |
| | Root5 | | -817.66995 | | |
| | | | | | |
| Path S₀[*]-10 | Root1(S ₀) | -817.88436 | -817.87874 | -820.39051 | 78.4 |
| | Root2 | | -817.76804 | | |
| | Root3 | | -817.73869 | | |
| | Root4 | | -817.72249 | | |
| | Root5 | | -817.68745 | | |
| | | | | | |
| Path S₀[*]-11 | Root1(S ₀) | -817.89275 | -817.88962 | -820.39776 | 73.8 |
| | Root2 | | -817.77913 | | |
| | Root3 | | -817.75244 | | |
| | Root4 | | -817.73547 | | |
| | Root5 | | -817.69263 | | |
| | | | | | |
| Path S₀[*]-12 | Root1(S ₀) | -817.90682 | -817.90099 | -820.40592 | 68.7 |
| | Root2 | | -817.79076 | | |
| | Root3 | | -817.76872 | | |
| | Root4 | | -817.75234 | | |
| | Root5 | | -817.69189 | | |
| | | | | | |
| Path S₀[*]-13 | Root1(S ₀) | -817.93719 | -817.92544 | -820.42982 | 53.7 |
| | Root2 | | -817.81447 | | |
| | Root3 | | -817.80636 | | |
| | Root4 | | -817.78714 | | |
| | Root5 | | -817.69273 | | |
| | | | | | |

| | | | | | |
|---|----------------|------------|------------|------------|------|
| Path S_0^*-14/ S_0-Int2 | Root1(S_0) | -817.93755 | -817.93738 | -820.43610 | 49.8 |
| | Root2 | | -817.82776 | | |
| | Root3 | | -817.82270 | | |
| | Root4 | | -817.75327 | | |
| | Root5 | | -817.71202 | | |
| Path S_0^*-15 | Root1(S_0) | -817.94774 | -817.94774 | -817.84234 | 47.9 |
| | Root2 | | -817.84234 | | |
| | Root3 | | -817.82156 | | |
| | Root4 | | -817.78459 | | |
| | Root5 | | -817.72217 | | |
| Path S_0^*-16/ S_0-TS1^(1,2-H) | Root1(S_0) | -817.92811 | -817.94645 | -820.44242 | 45.8 |
| | Root2 | | -817.83796 | | |
| | Root3 | | -817.81902 | | |
| | Root4 | | -817.77981 | | |
| | Root5 | | -817.72063 | | |
| Path S_0^*-17 | Root1(S_0) | -817.92637 | -817.94391 | -820.45400 | 38.6 |
| | Root2 | | -817.81278 | | |
| | Root3 | | -817.78314 | | |
| | Root4 | | -817.75572 | | |
| | Root5 | | -817.70125 | | |
| Path S_0^*-18 | Root1(S_0) | -817.94490 | -817.95647 | -820.46651 | 30.7 |
| | Root2 | | -817.79923 | | |
| | Root3 | | -817.74839 | | |
| | Root4 | | -817.72396 | | |
| | Root5 | | -817.68184 | | |
| Path S_0^*-19 | Root1(S_0) | -817.97556 | -817.97995 | -820.48966 | 16.2 |
| | Root2 | | -817.77742 | | |
| | Root3 | | -817.72970 | | |
| | Root4 | | -817.67859 | | |
| | Root5 | | -817.67201 | | |
| Path S_0^*-20 | Root1(S_0) | -818.00249 | -818.00576 | -820.51002 | 3.4 |
| | Root2 | | -817.79697 | | |
| | Root3 | | -817.74271 | | |
| | Root4 | | -817.69808 | | |
| | Root5 | | -817.68592 | | |
| Path S_0^*-21 | Root1(S_0) | -818.05348 | -818.03827 | -820.52421 | -5.5 |
| | Root2 | | -817.84440 | | |
| | Root3 | | -817.82680 | | |
| | Root4 | | -817.76402 | | |
| | Root5 | | -817.74449 | | |

| | | | | | |
|-------------------------------|------------------------|------------|------------|------------|-------|
| Path S₀*-22 | Root1(S ₀) | -818.04882 | -818.05270 | -820.55030 | -21.9 |
| | Root2 | | -817.84266 | | |
| | Root3 | | -817.78160 | | |
| | Root4 | | -817.74481 | | |
| | Root5 | | -817.72311 | | |
| cis-P | Root1(S ₀) | -818.05619 | -818.06370 | -820.56019 | -28.1 |
| | Root2 | | -817.85358 | | |
| | Root3 | | -817.79208 | | |
| | Root4 | | -817.75694 | | |
| | Root5 | | -817.73287 | | |

Table S6. Absolute energies (A.E., Hartree), relative energies (R.E., kcal/mol) for the optimized structures of **2-BF₃** along the 6 π photocyclization reaction pathway in the singlet excited state, and the subsequent [1,4]-H shift in ground state obtained by CASPT2//CASSCF(8e/8o)/PCM/6-31G** calculations. The corresponding energy profiles are plotted in Figure 2a of the main article.

| 2-BF₃ | | CASSCF | RASSCF | CASPT2 | |
|------------------------------|--|---------------|---------------|---------------|-------------|
| | | A.E. | A.E. | A.E. | R.E. |
| S₀-Min | Root1(S ₀) | -1141.28066 | -1141.25925 | -1144.31818 | 0.0 |
| | Root2 | | -1141.03046 | -1144.16427 | |
| | Root3[S _{CT} (¹ $\pi\pi^*$)] | | -1141.02668 | -1144.18463 | 83.8 |
| | Root4[S _{NP} (¹ $n\pi^*$)] | | -1141.01514 | -1144.14237 | 110.3 |
| | Root5 | | -1140.99914 | -1144.16713 | |
| | Root1[T _{PP} (³ $\pi\pi^*$)] | | -1141.13320 | -1144.21331 | 65.8 |
| | Root2 | | -1141.09912 | | |
| | Root3 | | -1141.05639 | | |
| | Root4 | | -1141.04943 | | |
| | Root5 | | -1141.01332 | | |
| Path S_{CT}-1 | Root1(S ₀) | | -1141.25658 | -1144.31183 | 4.0 |
| | Root2 | | -1141.03922 | | |
| | Root3[S _{CT} (¹ $\pi\pi^*$)] | -1141.05923 | -1141.02845 | -1144.19088 | 79.9 |
| | Root4 | | -1141.01372 | | |
| | Root5 | | -1140.99821 | | |
| Path S_{CT}-2 | Root1(S ₀) | | -1141.24461 | -1144.31223 | 3.7 |
| | Root2[S _{CT} (¹ $\pi\pi^*$)] | -1141.06900 | -1141.04653 | -1144.20074 | 73.7 |
| | Root3 | | -1141.02402 | | |
| | Root4 | | -1141.01030 | | |

| | | | | | |
|-------------------------------|--|-------------|-------------|-------------|------|
| | Root5 | | -1141.00201 | | |
| Path S_{CT}-3 | Root1(S ₀) | | -1141.24830 | -1144.30930 | 5.6 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.07392 | -1141.05857 | -1144.20600 | 70.4 |
| | Root3 | | -1141.02896 | | |
| | Root4 | | -1141.01720 | | |
| | Root5 | | -1141.00559 | | |
| Path S_{CT}-4 | Root1(S ₀) | | -1141.23879 | -1144.30482 | 8.4 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.07842 | -1141.06210 | -1144.20676 | 69.9 |
| | Root3 | | -1141.02394 | | |
| | Root4 | | -1141.01351 | | |
| | Root5 | | -1141.00211 | | |
| Path S_{CT}-5 | Root1(S ₀) | | -1141.23845 | -1144.30606 | 7.6 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.08347 | -1141.06722 | -1144.20667 | 70.0 |
| | Root3 | | -1141.02769 | | |
| | Root4 | | -1141.00947 | | |
| | Root5 | | -1140.99890 | | |
| Path S_{CT}-6 | Root1(S ₀) | | -1141.23628 | -1144.30431 | 8.7 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.08598 | -1141.07106 | -1144.21004 | 67.9 |
| | Root3 | | -1141.02823 | | |
| | Root4 | | -1141.01002 | | |
| | Root5 | | -1140.99950 | | |
| Path S_{CT}-7 | Root1(S ₀) | | -1141.23483 | -1144.30400 | 8.9 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.08837 | -1141.07469 | -1144.21360 | 65.6 |
| | Root3 | | -1141.02974 | | |
| | Root4 | | -1141.01112 | | |
| | Root5 | | -1140.99971 | | |
| Path S_{CT}-8 | Root1(S ₀) | | -1141.22401 | -1144.30468 | 8.5 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09562 | -1141.08192 | -1144.21789 | 62.9 |
| | Root3 | | -1141.02760 | | |
| | Root4 | | -1141.00657 | | |
| | Root5 | | -1140.99125 | | |
| Path S_{CT}-9 | Root1(S ₀) | | -1141.22007 | -1144.29998 | 11.4 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09774 | -1141.08594 | -1144.22014 | 61.5 |
| | Root3 | | -1141.03180 | | |
| | Root4 | | -1141.01125 | | |
| | Root5 | | -1140.99084 | | |
| Path S_{CT}-10 | Root1(S ₀) | | -1141.20500 | -1144.29040 | 17.4 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09738 | -1141.08954 | -1144.21946 | 61.9 |

| | | | | | |
|-------------------------------|--|-------------|-------------|-------------|------|
| | Root3 | | -1141.02828 | | |
| | Root4 | | -1141.00897 | | |
| | Root5 | | -1140.97974 | | |
| | | | | | |
| Path S_{CT}-11 | Root1(S ₀) | | -1141.20400 | -1144.28984 | 17.8 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09789 | -1141.08774 | -1144.21814 | 62.8 |
| | Root3 | | -1141.02633 | | |
| | Root4 | | -1141.00626 | | |
| | Root5 | | -1140.97688 | | |
| | | | | | |
| Path S_{CT}-12 | Root1(S ₀) | | -1141.20259 | -1144.28887 | 18.4 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09562 | -1141.08645 | -1144.21730 | 63.3 |
| | Root3 | | -1141.02414 | | |
| | Root4 | | -1141.00535 | | |
| | Root5 | | -1140.97466 | | |
| | | | | | |
| Path S_{CT}-13 | Root1(S ₀) | | -1141.19437 | -1144.28167 | 22.9 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09537 | -1141.09139 | -1144.21999 | 61.6 |
| | Root3 | | -1141.02605 | | |
| | Root4 | | -1141.01151 | | |
| | Root5 | | -1140.97240 | | |
| | | | | | |
| Path S_{CT}-14 | Root1(S ₀) | | -1141.17556 | -1144.26772 | 31.7 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09537 | -1141.09618 | -1144.22244 | 60.1 |
| | Root3 | | -1141.01728 | | |
| | Root4 | | -1141.00608 | | |
| | Root5 | | -1140.96059 | | |
| | | | | | |
| Path S_{CT}-15 | Root1(S ₀) | | -1141.16019 | -1144.25542 | 39.4 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09674 | -1141.10021 | -1144.22339 | 59.5 |
| | Root3 | | -1141.01409 | | |
| | Root4 | | -1141.00205 | | |
| | Root5 | | -1140.95276 | | |
| | | | | | |
| Path S_{CT}-16 | Root1(S ₀) | | -1141.14511 | -1144.24332 | 47.0 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09809 | -1141.10238 | -1144.22503 | 58.5 |
| | Root3 | | -1141.01185 | | |
| | Root4 | | -1140.99607 | | |
| | Root5 | | -1140.94660 | | |
| | | | | | |
| Path S_{CT}-17 | Root1(S ₀) | | -1141.14211 | -1144.24124 | 48.3 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09857 | -1141.10282 | -1144.22589 | 57.9 |
| | Root3 | | -1141.01107 | | |
| | Root4 | | -1140.99479 | | |
| | Root5 | | -1140.94594 | | |
| | | | | | |

| | | | | | |
|--|--|-------------|-------------|-------------|------|
| Path S_{CT}-18 | Root1(S ₀) | | -1141.13875 | -1144.23883 | 49.8 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09845 | -1141.10312 | -1144.22700 | 57.2 |
| | Root3 | | -1141.00968 | | |
| | Root4 | | -1140.99403 | | |
| | Root5 | | -1140.94445 | | |
| Path S_{CT}-19 | Root1(S ₀) | | -1141.13808 | -1144.23839 | 50.1 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09877 | -1141.10322 | -1144.22741 | 57.0 |
| | Root3 | | -1141.00938 | | |
| | Root4 | | -1140.99407 | | |
| | Root5 | | -1140.94400 | | |
| Path S_{CT}-20 | Root1(S ₀) | | -1141.13192 | -1144.23489 | 52.3 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09787 | -1141.09984 | -1144.23031 | 55.1 |
| | Root3 | | -1141.00883 | | |
| | Root4 | | -1140.99170 | | |
| | Root5 | | -1140.93787 | | |
| CI(S_{CT}/S₀) | Root1(S ₀) | | -1141.12840 | -1144.23948 | 49.4 |
| | Root2[S _{CT} (¹ ππ*)] | -1141.09705 | -1141.10753 | -1144.23569 | 51.8 |
| | Root3 | | -1141.01302 | | |
| | Root4 | | -1140.98971 | | |
| | Root5 | | -1140.95138 | | |
| Path S₀[*]-1 | Root1(S ₀) | -1141.16074 | -1141.14610 | -1144.24194 | 47.8 |
| | Root2 | | -1141.04185 | | |
| | Root3 | | -1141.01675 | | |
| | Root4 | | -1141.00192 | | |
| | Root5 | | -1140.96243 | | |
| Path S₀[*]-2 | Root1(S ₀) | -1141.16913 | -1141.15129 | -1144.25226 | 41.4 |
| | Root2 | | -1141.04709 | | |
| | Root3 | | -1141.01337 | | |
| | Root4 | | -1141.00452 | | |
| | Root5 | | -1140.95291 | | |
| Path S₀[*]-3 | Root1(S ₀) | -1141.17040 | -1141.15919 | -1144.26300 | 34.6 |
| | Root2 | | -1141.05610 | | |
| | Root3 | | -1140.99456 | | |
| | Root4 | | -1140.97052 | | |
| | Root5 | | -1140.92458 | | |
| Path S₀[*]-4/ S₀-Int | Root1(S ₀) | -1141.16979 | -1141.15503 | -1144.26518 | 33.3 |
| | Root2 | | -1141.04217 | | |
| | Root3 | | -1140.99228 | | |
| | Root4 | | -1140.95668 | | |

| | | | | | |
|--|------------------------|---------------------|-------------|-------------|------|
| | Root5 | | -1140.93579 | | |
| Path S₀[*]-5 | Root1(S ₀) | -1141.15916 | -1141.15438 | -1144.26130 | 35.7 |
| | Root2 | | -1141.03430 | | |
| | Root3 | | -1140.96994 | | |
| | Root4 | | -1140.93972 | | |
| | Root5 | | -1140.91749 | | |
| Path S₀[*]-6 | Root1(S ₀) | -1141.15648 | -1141.15192 | -1144.25830 | 37.6 |
| | Root2 | | -1141.02932 | | |
| | Root3 | | -1140.96565 | | |
| | Root4 | | -1140.93597 | | |
| | Root5 | | -1140.91226 | | |
| Path S₀[*]-7 | Root1(S ₀) | -1141.15256 | -1141.14892 | -1144.25396 | 40.3 |
| | Root2 | | -1141.02388 | | |
| | Root3 | | -1140.96038 | | |
| | Root4 | | -1140.93189 | | |
| | Root5 | | -1140.90505 | | |
| Path S₀[*]-8 | Root1(S ₀) | -1141.14727 | -1141.14565 | -1144.24861 | 43.7 |
| | Root2 | | -1141.01516 | | |
| | Root3 | | -1140.95403 | | |
| | Root4 | | -1140.92719 | | |
| | Root5 | | -1140.89512 | | |
| Path S₀[*]-9 | Root1(S ₀) | - 1141.1408 3 | -1141.14408 | -1144.24774 | 44.2 |
| | Root2 | | -1141.01026 | | |
| | Root3 | | -1140.95522 | | |
| | Root4 | | -1140.92730 | | |
| | Root5 | | -1140.88724 | | |
| Path S₀[*]-10 | Root1(S ₀) | -1141.13870 | -1141.14625 | -1144.25188 | 41.6 |
| | Root2 | | -1141.00571 | | |
| | Root3 | | -1140.96280 | | |
| | Root4 | | -1140.92333 | | |
| | Root5 | | -1140.88612 | | |
| Path S₀[*]-11 | Root1(S ₀) | -1141.13873 | -1141.16048 | -1144.25939 | 36.9 |
| | Root2 | | -1140.98804 | | |
| | Root3 | | -1140.96456 | | |
| | Root4 | | -1140.90219 | | |
| | Root5 | | -1140.89971 | | |

| | | | | | |
|-------------------------------|------------------------|-------------|-------------|-------------|-------|
| Path S₀*-12 | Root1(S ₀) | -1141.14361 | -1141.16819 | -1144.26466 | 33.6 |
| | Root2 | | -1140.98686 | | |
| | Root3 | | -1140.96043 | | |
| | Root4 | | -1140.90399 | | |
| | Root5 | | -1140.89879 | | |
| Path S₀*-13 | Root1(S ₀) | -1141.20249 | -1141.20670 | -1144.29262 | 16.0 |
| | Root2 | | -1140.97395 | | |
| | Root3 | | -1140.93018 | | |
| | Root4 | | -1140.87744 | | |
| | Root5 | | -1140.87294 | | |
| Path S₀*-14 | Root1(S ₀) | -1141.22824 | -1141.22958 | -1144.31411 | 2.5 |
| | Root2 | | -1140.99519 | | |
| | Root3 | | -1140.95396 | | |
| | Root4 | | -1140.89800 | | |
| | Root5 | | -1140.89383 | | |
| <i>trans</i>-P | Root1(S ₀) | -1141.27636 | -1141.27636 | -1144.34301 | -15.6 |
| | Root2 | | -1141.27636 | | |
| | Root3 | | -1141.27636 | | |
| | Root4 | | -1141.27636 | | |
| | Root5 | | -1141.27636 | | |
| <i>cis</i>-P | Root1(S ₀) | -1141.28699 | -1141.28781 | -1144.36527 | -29.5 |
| | Root2 | | -1141.05282 | | |
| | Root3 | | -1141.01118 | | |
| | Root4 | | -1140.95315 | | |
| | Root5 | | -1140.94985 | | |

Table S7. Absolute energies (A.E., Hartree), relative energies (R.E., kcal/mol) for the optimized structures of **2-BF₃** along the 6π photocyclization reaction pathway in the triplet excited state, and the subsequent [1,4]-H shift in ground state obtained by CASPT2//CASSCF(8e/8o)/PCM/6-31G** calculations. The corresponding energy profiles are plotted in Figure 2b of the main article.

| 2 | | CASSCF | RASSCF | CASPT2 | |
|--------------------------|--|---------------|---------------|---------------|-------------|
| | | A.E. | A.E. | A.E. | R.E. |
| S₀-Min | Root1(S ₀) | -1141.28066 | -1141.25925 | -1144.31818 | 0.0 |
| | Root2 | | -1141.03046 | -1144.16427 | |
| | Root3[S _{CT} (¹ $\pi\pi^*$)] | | -1141.02668 | -1144.18463 | 83.8 |
| | Root4[S _{NP} (¹ $n\pi^*$)] | | -1141.01514 | -1144.14237 | 110.3 |
| | Root5 | | -1140.99914 | -1144.16713 | |

| | | | | | | |
|-----------------------------------|-------------------------------|-------------|-------------|-------------|------|--|
| | Root1[$T_{pp}(^3\pi\pi^*)$] | | -1141.13320 | -1144.21331 | 65.8 | |
| | Root2 | | -1141.09912 | | | |
| | Root3 | | -1141.05639 | | | |
| | Root4 | | -1141.04943 | | | |
| | Root5 | | -1141.01332 | | | |
| | | | | | | |
| Path T_{pp-1} | Root1[$T_{pp}(^1\pi\pi^*)$] | -1141.15411 | -1141.15823 | -1144.21806 | 62.8 | |
| | Root2 | | -1141.11876 | | | |
| | Root3 | | -1141.07225 | | | |
| | Root4 | | -1141.05985 | | | |
| | Root5 | | -1141.00505 | | | |
| | | | | | | |
| | Root1(S_0) | | -1141.26372 | -1144.31750 | 0.4 | |
| | Root2 | | -1141.04607 | | | |
| | Root3 | | -1141.03454 | | | |
| | Root4 | | -1141.01119 | | | |
| | Root5 | | | | | |
| | | | | | | |
| Path T_{pp-2} | Root1[$T_{pp}(^1\pi\pi^*)$] | -1141.16229 | -1141.16715 | -1144.22620 | 57.7 | |
| | Root2 | | -1141.11006 | | | |
| | Root3 | | -1141.06401 | | | |
| | Root4 | | -1141.05145 | | | |
| | Root5 | | -1141.01038 | | | |
| | | | | | | |
| | Root1(S_0) | | -1141.25906 | -1144.31782 | 0.2 | |
| | Root2 | | -1141.04964 | | | |
| | Root3 | | -1141.03130 | | | |
| | Root4 | | -1141.01369 | | | |
| | Root5 | | -1140.99829 | | | |
| | | | | | | |
| Path T_{pp-3} | Root1[$T_{pp}(^1\pi\pi^*)$] | -1141.16708 | -1141.17365 | -1144.22983 | 55.4 | |
| | Root2 | | -1141.10119 | | | |
| | Root3 | | -1141.05488 | | | |
| | Root4 | | -1141.04216 | | | |
| | Root5 | | -1141.01528 | | | |
| | | | | | | |
| | Root1(S_0) | | -1141.25472 | -1144.31556 | 1.6 | |
| | Root2 | | -1141.04517 | | | |
| | Root3 | | -1141.02864 | | | |
| | Root4 | | -1141.01063 | | | |
| | Root5 | | -1140.99284 | | | |
| | | | | | | |
| Path T_{pp-4} | Root1[$T_{pp}(^1\pi\pi^*)$] | -1141.16783 | -1141.17432 | -1144.22974 | 55.5 | |
| | Root2 | | -1141.09904 | | | |
| | Root3 | | -1141.05278 | | | |
| | Root4 | | -1141.03988 | | | |
| | | | | | | |

| | | | | | |
|------------------------------|--|-------------|-------------|-------------|------|
| | Root5 | | -1141.01588 | | |
| | Root1(S ₀) | | -1141.25197 | -1144.31247 | 3.6 |
| | Root2 | | -1141.04360 | | |
| | Root3 | | -1141.02672 | | |
| | Root4 | | -1141.00930 | | |
| | Root5 | | -1140.99295 | | |
| Path T_{PP}-5 | Root1[T _{PP} (¹ ππ*)] | -1141.16877 | -1141.17547 | -1144.23017 | 55.2 |
| | Root2 | | -1141.09653 | | |
| | Root3 | | -1141.05015 | | |
| | Root4 | | -1141.03745 | | |
| | Root5 | | -1141.01718 | | |
| | Root1(S ₀) | | -1141.24860 | -1144.30871 | 5.9 |
| | Root2 | | -1141.04554 | | |
| | Root3 | | -1141.02495 | | |
| | Root4 | | -1141.00797 | | |
| | Root5 | | -1140.99405 | | |
| Path T_{PP}-6 | Root1[T _{PP} (¹ ππ*)] | -1141.16884 | -1141.17560 | -1144.23122 | 54.6 |
| | Root2 | | -1141.09447 | | |
| | Root3 | | -1141.04827 | | |
| | Root4 | | -1141.03505 | | |
| | Root5 | | -1141.01747 | | |
| | Root1(S ₀) | | -1141.24579 | -1144.30562 | 7.9 |
| | Root2 | | -1141.05031 | | |
| | Root3 | | -1141.02374 | | |
| | Root4 | | -1141.00868 | | |
| | Root5 | | -1140.99420 | | |
| Path T_{PP}-7 | Root1[T _{PP} (¹ ππ*)] | -1141.16923 | -1141.17565 | -1144.23166 | 54.3 |
| | Root2 | | -1141.09277 | | |
| | Root3 | | -1141.04609 | | |
| | Root4 | | -1141.03303 | | |
| | Root5 | | -1141.01836 | | |
| | Root1(S ₀) | | -1141.24282 | -1144.30592 | 7.7 |
| | Root2 | | -1141.05304 | | |
| | Root3 | | -1141.02392 | | |
| | Root4 | | -1141.00755 | | |
| | Root5 | | -1140.99557 | | |
| Path T_{PP}-8 | Root1[T _{PP} (¹ ππ*)] | -1141.16927 | -1141.17537 | -1144.23244 | 53.8 |
| | Root2 | | -1141.09233 | | |

| | | | | | |
|-------------------------------|--|-------------|-------------|-------------|------|
| | Root3 | | -1141.04547 | | |
| | Root4 | | -1141.03273 | | |
| | Root5 | | -1141.01820 | | |
| | Root1(S ₀) | | -1141.24164 | -1144.30592 | 7.7 |
| | Root2 | | -1141.05585 | | |
| | Root3 | | -1141.02525 | | |
| | Root4 | | -1141.00805 | | |
| | Root5 | | -1140.99544 | | |
| | | | | | |
| Path T_{pp}-9 | Root1[T _{pp} (¹ ππ*)] | -1141.16901 | -1141.17453 | -1144.23329 | 53.3 |
| | Root2 | | -1141.08288 | | |
| | Root3 | | -1141.03928 | | |
| | Root4 | | -1141.02959 | | |
| | Root5 | | -1141.01437 | | |
| | Root1(S ₀) | | -1141.23095 | -1144.30151 | 10.5 |
| | Root2 | | -1141.05886 | | |
| | Root3 | | -1141.02387 | | |
| | Root4 | | -1141.00906 | | |
| | Root5 | | -1140.99369 | | |
| | | | | | |
| Path T_{pp}-10 | Root1[T _{pp} (¹ ππ*)] | -1141.15764 | -1141.16303 | -1144.23539 | 52.0 |
| | Root2 | | -1141.07130 | | |
| | Root3 | | -1141.02870 | | |
| | Root4 | | -1141.01829 | | |
| | Root5 | | -1141.00797 | | |
| | Root1(S ₀) | | -1141.20998 | -1144.28973 | 17.8 |
| | Root2 | | -1141.06669 | | |
| | Root3 | | -1141.02419 | | |
| | Root4 | | -1141.00642 | | |
| | Root5 | | -1140.97610 | | |
| | | | | | |
| Path T_{pp}-11 | Root1[T _{pp} (¹ ππ*)] | -1141.15345 | -1141.15957 | -1144.23770 | 50.5 |
| | Root2 | | -1141.06842 | | |
| | Root3 | | -1141.02839 | | |
| | Root4 | | -1141.01690 | | |
| | Root5 | | -1141.00015 | | |
| | Root1(S ₀) | | -1141.20084 | -1144.28308 | 22.0 |
| | Root2 | | -1141.07273 | | |
| | Root3 | | -1141.02587 | | |
| | Root4 | | -1141.00853 | | |
| | Root5 | | -1140.97067 | | |

| | | | | | |
|-------------------------------|--|-------------|-------------|-------------|------|
| Path T_{pp}-12 | Root1[T _{pp} (¹ ππ*)] | -1141.15125 | -1141.15791 | -1144.23859 | 49.9 |
| | Root2 | | -1141.06680 | | |
| | Root3 | | -1141.02865 | | |
| | Root4 | | -1141.01660 | | |
| | Root5 | | -1140.99528 | | |
| | Root1(S ₀) | | -1141.19559 | -1144.27893 | 24.6 |
| | Root2 | | -1141.07488 | | |
| | Root3 | | -1141.02681 | | |
| | Root4 | | -1141.00983 | | |
| | Root5 | | -1140.96725 | | |
| Path T_{pp}-13 | Root1[T _{pp} (¹ ππ*)] | -1141.14871 | -1141.15598 | -1144.23927 | 49.5 |
| | Root2 | | -1141.06419 | | |
| | Root3 | | -1141.02906 | | |
| | Root4 | | -1141.01594 | | |
| | Root5 | | -1140.98948 | | |
| | Root1(S ₀) | | -1141.18875 | -1144.27352 | 28.0 |
| | Root2 | | -1141.07715 | | |
| | Root3 | | -1141.02795 | | |
| | Root4 | | -1141.01081 | | |
| | Root5 | | -1140.96235 | | |
| Path T_{pp}-14 | Root1[T _{pp} (¹ ππ*)] | -1141.14642 | -1141.15380 | -1144.23902 | 49.7 |
| | Root2 | | -1141.06172 | | |
| | Root3 | | -1141.02925 | | |
| | Root4 | | -1141.01507 | | |
| | Root5 | | -1140.98293 | | |
| | Root1(S ₀) | | -1141.18100 | -1144.26681 | 32.2 |
| | Root2 | | -1141.07824 | | |
| | Root3 | | -1141.02928 | | |
| | Root4 | | -1141.01223 | | |
| | Root5 | | -1140.95544 | | |
| Path T_{pp}-15 | Root1[T _{pp} (¹ ππ*)] | -1141.14504 | -1141.15156 | -1144.23787 | 50.4 |
| | Root2 | | -1141.05615 | | |
| | Root3 | | -1141.02900 | | |
| | Root4 | | -1141.01098 | | |
| | Root5 | | -1140.97706 | | |
| | Root1(S ₀) | | -1141.17254 | -1144.25958 | 36.8 |
| | Root2 | | -1141.07726 | | |
| | Root3 | | -1141.02987 | | |
| | Root4 | | -1141.01209 | | |

| | | | | | |
|--|--|-------------|-------------|-------------|------|
| | Root5 | | -1140.94581 | | |
| Path T_{pp}-16/ T_{pp}-TS | Root1[T _{pp} (¹ ππ*)] | -1141.14503 | -1141.15015 | -1144.23575 | 51.7 |
| | Root2 | | -1141.05036 | | |
| | Root3 | | -1141.03083 | | |
| | Root4 | | -1141.01018 | | |
| | Root5 | | -1140.97247 | | |
| | Root1(S ₀) | | -1141.16120 | -1144.24954 | 43.1 |
| | Root2 | | -1141.07680 | | |
| | Root3 | | -1141.03290 | | |
| | Root4 | | -1141.01101 | | |
| | Root5 | | -1140.93400 | | |
| Path T_{pp}-17 | Root1[T _{pp} (¹ ππ*)] | -1141.14506 | -1141.15040 | -1144.23788 | 50.4 |
| | Root2 | | -1141.04695 | | |
| | Root3 | | -1141.02996 | | |
| | Root4 | | -1141.00384 | | |
| | Root5 | | -1140.97354 | | |
| | Root1(S ₀) | | -1141.16234 | -1144.25177 | 41.7 |
| | Root2 | | -1141.07529 | | |
| | Root3 | | -1141.03153 | | |
| | Root4 | | -1141.01087 | | |
| | Root5 | | -1140.93163 | | |
| Path T_{pp}-18 | Root1[T _{pp} (¹ ππ*)] | -1141.14777 | -1141.15509 | -1144.24049 | 48.7 |
| | Root2 | | -1141.04691 | | |
| | Root3 | | -1141.03234 | | |
| | Root4 | | -1141.00559 | | |
| | Root5 | | -1140.97639 | | |
| | Root1(S ₀) | | -1141.15941 | -1144.24883 | 43.5 |
| | Root2 | | -1141.07419 | | |
| | Root3 | | -1141.03828 | | |
| | Root4 | | -1141.01247 | | |
| | Root5 | | -1140.92270 | | |
| Path T_{pp}-19 | Root1[T _{pp} (¹ ππ*)] | -1141.15120 | -1141.15306 | -1144.24233 | 47.6 |
| | Root2 | | -1141.04264 | | |
| | Root3 | | -1141.02683 | | |
| | Root4 | | -1140.99811 | | |
| | Root5 | | -1140.97426 | | |
| | Root1(S ₀) | | -1141.14553 | -1144.24673 | 44.8 |
| | Root2 | | -1141.05896 | | |

| | | | | | |
|-------------------------------------|-------------------------------|-------------|-------------|-------------|------|
| | Root3 | | -1141.02862 | | |
| | Root4 | | -1141.00868 | | |
| | Root5 | | -1140.95560 | | |
| | | | | | |
| Path T_{PP-20} | Root1[$T_{PP}(^1\pi\pi^*)$] | -1141.14858 | -1141.15410 | -1144.24309 | 47.1 |
| | Root2 | | -1141.04448 | | |
| | Root3 | | -1141.03155 | | |
| | Root4 | | -1141.00050 | | |
| | Root5 | | -1140.97607 | | |
| | | | | | |
| | Root1(S_0) | | -1141.15561 | -1144.25158 | 41.8 |
| | Root2 | | -1141.06793 | | |
| | Root3 | | -1141.03423 | | |
| | Root4 | | -1141.01357 | | |
| Root5 | | -1140.93523 | | | |
| | | | | | |
| Path T_{PP-21} | Root1[$T_{PP}(^1\pi\pi^*)$] | -1141.15292 | -1141.14905 | -1144.24365 | 46.8 |
| | Root2 | | -1141.03908 | | |
| | Root3 | | -1141.02579 | | |
| | Root4 | | -1140.99333 | | |
| | Root5 | | -1140.97217 | | |
| | | | | | |
| | Root1(S_0) | | -1141.14479 | -1144.24617 | 45.2 |
| | Root2 | | -1141.05235 | | |
| | Root3 | | -1141.02797 | | |
| | Root4 | | -1141.00507 | | |
| Root5 | | -1140.95973 | | | |
| | | | | | |
| STC(T_{PP}/S_0) | Root1[$T_{PP}(^1\pi\pi^*)$] | -1141.15744 | -1141.14843 | -1144.24442 | 46.3 |
| | Root2 | | -1141.03921 | | |
| | Root3 | | -1141.01959 | | |
| | Root4 | | -1140.98801 | | |
| | Root5 | | -1140.97287 | | |
| | | | | | |
| | Root1(S_0) | | -1141.14570 | -1144.24414 | 46.5 |
| | Root2 | | -1141.04422 | | |
| | Root3 | | -1141.02249 | | |
| | Root4 | | -1141.00044 | | |
| Root5 | | -1140.96136 | | | |
| | | | | | |
| Path S_0^*-1 | Root1(S_0) | -1141.16813 | -1141.15247 | -1144.25307 | 40.9 |
| | Root2 | | -1141.04884 | | |
| | Root3 | | -1141.00717 | | |
| | Root4 | | -1141.00480 | | |
| | Root5 | | -1140.95087 | | |
| | | | | | |

| | | | | | |
|---|------------------------|-------------|-------------|-------------|------|
| Path S₀[*]-2 | Root1(S ₀) | -1141.17139 | -1141.15459 | -1144.25624 | 38.9 |
| | Root2 | | -1141.04944 | | |
| | Root3 | | -1141.00886 | | |
| | Root4 | | -1140.99832 | | |
| | Root5 | | -1140.94942 | | |
| | | | | | |
| Path S₀[*]-3 | Root1(S ₀) | -1141.17296 | -1141.15959 | -1144.26201 | 35.2 |
| | Root2 | | -1141.05699 | | |
| | Root3 | | -1140.99057 | | |
| | Root4 | | -1140.95880 | | |
| | Root5 | | -1140.91672 | | |
| | | | | | |
| S₀[*]-Int | Root1(S ₀) | -1141.16979 | -1141.15503 | -1144.26518 | 33.3 |
| | Root2 | | -1141.04217 | | |
| | Root3 | | -1140.99228 | | |
| | Root4 | | -1140.95668 | | |
| | Root5 | | -1140.93579 | | |
| | | | | | |
| Path S₀[*]-5 | Root1(S ₀) | -1141.15916 | -1141.15438 | -1144.26130 | 35.7 |
| | Root2 | | -1141.03430 | | |
| | Root3 | | -1140.96994 | | |
| | Root4 | | -1140.93972 | | |
| | Root5 | | -1140.91749 | | |
| | | | | | |
| Path S₀[*]-6 | Root1(S ₀) | -1141.15648 | -1141.15192 | -1144.25830 | 37.6 |
| | Root2 | | -1141.02932 | | |
| | Root3 | | -1140.96565 | | |
| | Root4 | | -1140.93597 | | |
| | Root5 | | -1140.91226 | | |
| | | | | | |
| Path S₀[*]-7 | Root1(S ₀) | -1141.15256 | -1141.14892 | -1144.25396 | 40.3 |
| | Root2 | | -1141.02388 | | |
| | Root3 | | -1140.96038 | | |
| | Root4 | | -1140.93189 | | |
| | Root5 | | -1140.90505 | | |
| | | | | | |
| Path S₀[*]-8 | Root1(S ₀) | -1141.14727 | -1141.14565 | -1144.24861 | 43.7 |
| | Root2 | | -1141.01516 | | |
| | Root3 | | -1140.95403 | | |
| | Root4 | | -1140.92719 | | |
| | Root5 | | -1140.89512 | | |
| | | | | | |
| Path S₀[*]-9 | Root1(S ₀) | -1141.14083 | -1141.14408 | -1144.24774 | 44.2 |
| | Root2 | | -1141.01026 | | |
| | Root3 | | -1140.95522 | | |
| | Root4 | | -1140.92730 | | |
| | Root5 | | -1140.88724 | | |

| | | | | | |
|--|------------------------|-------------|-------------|-------------|-------|
| Path S₀[*]-10 | Root1(S ₀) | -1141.13870 | -1141.14625 | -1144.25188 | 41.6 |
| | Root2 | | -1141.00571 | | |
| | Root3 | | -1140.96280 | | |
| | Root4 | | -1140.92333 | | |
| | Root5 | | -1140.88612 | | |
| Path S₀[*]-11 | Root1(S ₀) | -1141.13873 | -1141.16048 | -1144.25939 | 36.9 |
| | Root2 | | -1140.98804 | | |
| | Root3 | | -1140.96456 | | |
| | Root4 | | -1140.90219 | | |
| | Root5 | | -1140.89971 | | |
| Path S₀[*]-12 | Root1(S ₀) | -1141.14361 | -1141.16819 | -1144.26466 | 33.6 |
| | Root2 | | -1140.98686 | | |
| | Root3 | | -1140.96043 | | |
| | Root4 | | -1140.90399 | | |
| | Root5 | | -1140.89879 | | |
| Path S₀[*]-13 | Root1(S ₀) | -1141.20249 | -1141.20670 | -1144.29262 | 16.0 |
| | Root2 | | -1140.97395 | | |
| | Root3 | | -1140.93018 | | |
| | Root4 | | -1140.87744 | | |
| | Root5 | | -1140.87294 | | |
| Path S₀[*]-14 | Root1(S ₀) | -1141.22824 | -1141.22958 | -1144.31411 | 2.5 |
| | Root2 | | -1140.99519 | | |
| | Root3 | | -1140.95396 | | |
| | Root4 | | -1140.89800 | | |
| | Root5 | | -1140.89383 | | |
| trans-P | Root1(S ₀) | -1141.27636 | -1141.27636 | -1144.34301 | -15.6 |
| | Root2 | | -1141.27636 | | |
| | Root3 | | -1141.27636 | | |
| | Root4 | | -1141.27636 | | |
| | Root5 | | -1141.27636 | | |
| cis-P | Root1(S ₀) | -1141.28699 | -1141.28781 | -1144.36527 | -29.5 |
| | Root2 | | -1141.05282 | | |
| | Root3 | | -1141.01118 | | |
| | Root4 | | -1140.95315 | | |
| | Root5 | | -1140.94985 | | |

10. Cartesian Coordinates

10.1 Critical Structures of Free 2 in Figure 1, Figure S7, Figure S8 and Figure S9.

S₀-Min (2)

| | | | |
|---|-------------|-------------|-------------|
| C | -3.87121616 | -1.71859881 | 0.15124013 |
| C | -3.50882094 | -1.04792546 | -1.01065094 |
| C | -2.35261141 | -0.27107411 | -1.03972018 |
| C | -1.56891331 | -0.15830530 | 0.10853601 |
| C | -1.93690190 | -0.82419089 | 1.27571991 |
| C | -3.08935429 | -1.60958663 | 1.28831927 |
| C | 1.18380243 | -1.01738285 | -0.79788651 |
| C | 0.90018453 | -0.07179273 | 0.11815568 |
| C | 1.80156435 | 0.20193479 | 1.30059799 |
| C | 3.24337485 | -0.21168726 | 1.00952821 |
| C | 3.30891203 | -1.64403682 | 0.47777188 |
| C | 2.41001101 | -1.84790837 | -0.72210843 |
| H | -3.37067841 | -2.12612326 | 2.19160356 |
| H | -4.76355652 | -2.32343764 | 0.16670468 |
| H | -4.11611428 | -1.13102424 | -1.89717228 |
| H | -2.06403312 | 0.24445088 | -1.94083417 |
| H | -1.33316640 | -0.72867570 | 2.16285404 |
| H | 1.41377997 | -0.35622686 | 2.15252940 |
| H | 1.75654703 | 1.25025998 | 1.56527466 |
| H | 3.84215707 | -0.11929436 | 1.90997618 |
| H | 3.66749446 | 0.46660527 | 0.27283622 |
| H | 4.31574012 | -1.93324190 | 0.19956456 |
| H | 2.97006331 | -2.34040268 | 1.24539474 |
| H | 0.52207128 | -1.22573755 | -1.62108400 |
| O | 2.65146626 | -2.66325720 | -1.57303609 |
| N | -0.35505776 | 0.60990315 | 0.08469220 |
| C | -0.43343161 | 1.96754399 | -0.05622285 |
| O | -1.45426447 | 2.59661470 | -0.00325083 |
| O | 0.74733495 | 2.49140506 | -0.32875383 |
| C | 0.82893068 | 3.90403309 | -0.47373249 |
| H | 1.86765487 | 4.11649055 | -0.67483362 |
| H | 0.51503220 | 4.39806461 | 0.43516956 |
| H | 0.21293728 | 4.23473468 | -1.29778909 |

S_{CT}-Min (2)

| | | | |
|---|-------------|-------------|-------------|
| C | 3.47475561 | 1.95340478 | 0.20487009 |
| C | 3.66446387 | 0.75096959 | -0.52402601 |
| C | 2.65481519 | -0.16948588 | -0.62131114 |
| C | 1.38756533 | 0.09701906 | 0.01623614 |
| C | 1.21830611 | 1.33809506 | 0.73356402 |
| C | 2.25542676 | 2.22455493 | 0.82821914 |
| C | -1.08292337 | 1.11119958 | -0.73204736 |
| C | -1.00410309 | -0.19246075 | -0.12436351 |
| C | -1.89333826 | -0.53508084 | 1.03518756 |
| C | -3.24590346 | 0.15480044 | 0.87002448 |
| C | -3.06838730 | 1.66098558 | 0.68742997 |
| C | -2.09430627 | 2.02587475 | -0.42908283 |
| H | 2.12155474 | 3.13987854 | 1.38260490 |
| H | 4.28389014 | 2.66978650 | 0.27359071 |
| H | 4.60181205 | 0.57132425 | -1.02683565 |
| H | 2.78313511 | -1.06393760 | -1.20200466 |
| H | 0.27931947 | 1.54062453 | 1.20983540 |
| H | -1.44042832 | -0.19778368 | 1.96922894 |
| H | -2.02088643 | -1.60788640 | 1.12309132 |
| H | -3.87532297 | -0.05045443 | 1.73047077 |
| H | -3.74764892 | -0.25553412 | -0.00214849 |
| H | -4.01339455 | 2.13967926 | 0.45809419 |
| H | -2.70559366 | 2.11271921 | 1.60965649 |
| H | -0.46599969 | 1.33335923 | -1.57390372 |
| O | -2.22732689 | 3.13319565 | -0.96395033 |
| N | 0.32483257 | -0.75536934 | -0.09365374 |
| C | 0.52632378 | -2.13930481 | -0.19559964 |
| O | 1.58312720 | -2.65644117 | 0.00796205 |
| O | -0.56482492 | -2.76130699 | -0.53036018 |
| C | -0.51508812 | -4.18284072 | -0.63942746 |
| H | -1.51996876 | -4.48172246 | -0.89059513 |
| H | -0.21214188 | -4.61999605 | 0.30042333 |

| | | | |
|------------------------------|-------------|-------------|-------------|
| H | 0.17154066 | -4.47056272 | -1.42195966 |
| S_{CT}-TS (2) | | | |
| C | 3.32433509 | 2.04589301 | 0.09165674 |
| C | 3.57895196 | 0.81520810 | -0.62922004 |
| C | 2.63181338 | -0.17765352 | -0.63401743 |
| C | 1.44324794 | -0.00920387 | 0.10478124 |
| C | 1.10598972 | 1.28852266 | 0.73437930 |
| C | 2.16242036 | 2.28080303 | 0.73735060 |
| C | -0.86482736 | 1.20324167 | -0.62047330 |
| C | -0.90272711 | -0.20051887 | -0.06210780 |
| C | -1.95973020 | -0.56896081 | 0.94794094 |
| C | -3.25363191 | 0.21605706 | 0.75303699 |
| C | -2.98717047 | 1.72113810 | 0.67590870 |
| C | -1.95832961 | 2.10619082 | -0.37820090 |
| H | 2.02814168 | 3.18280670 | 1.30903968 |
| H | 4.11228807 | 2.78630593 | 0.11163103 |
| H | 4.50767515 | 0.68372164 | -1.15369270 |
| H | 2.79491169 | -1.08906830 | -1.17691587 |
| H | 0.39147411 | 1.31141577 | 1.53713779 |
| H | -1.54630150 | -0.32263007 | 1.92948681 |
| H | -2.14837822 | -1.63503285 | 0.95587084 |
| H | -3.92702918 | 0.00345321 | 1.57874020 |
| H | -3.75325252 | -0.11617511 | -0.15306975 |
| H | -3.89554764 | 2.26586130 | 0.44917436 |
| H | -2.62664575 | 2.08689787 | 1.63673672 |
| H | -0.35393837 | 1.32639480 | -1.55776445 |
| O | -2.07968399 | 3.16423800 | -0.96659562 |
| N | 0.33828374 | -0.83643736 | 0.03153598 |
| C | 0.51391162 | -2.20763005 | -0.05991250 |
| O | 1.54380142 | -2.74874378 | 0.20383936 |
| O | -0.55967591 | -2.81636426 | -0.49205061 |
| C | -0.49782358 | -4.23467448 | -0.60230802 |
| H | -1.47718486 | -4.53579164 | -0.93625733 |
| H | -0.26983019 | -4.67327030 | 0.35788774 |
| H | 0.25350410 | -4.51878843 | -1.32495970 |

| | | | |
|---|-------------|-------------|-------------|
| CI(S_{CT}/S₀) (2) | | | |
| C | 2.41825185 | -2.82543274 | -0.16858100 |
| C | 1.20401229 | -3.25033920 | -0.79123469 |
| C | 0.06527565 | -2.51851945 | -0.54441715 |
| C | 0.07123532 | -1.46006725 | 0.35388268 |
| C | 1.32436159 | -0.84992294 | 0.82424490 |
| C | 2.49748907 | -1.71612389 | 0.62354337 |
| C | 1.22762506 | 0.55924495 | -0.29559191 |
| C | -0.23511795 | 0.77079445 | -0.17773450 |
| C | -0.87090831 | 2.14701932 | -0.25277835 |
| C | 0.18480645 | 3.26799894 | -0.29843693 |
| C | 1.43638314 | 2.95050746 | 0.53278763 |
| C | 2.10983520 | 1.73219733 | -0.06161679 |
| H | 3.43156111 | -1.44675695 | 1.07593467 |
| H | 3.30496735 | -3.42549695 | -0.28923582 |
| H | 1.17651029 | -4.12914911 | -1.39794022 |
| H | -0.85819677 | -2.78131325 | -1.03591267 |
| H | 1.27682596 | -0.35502555 | 1.79141503 |
| H | -1.54142444 | 2.28681980 | 0.58883299 |
| H | -1.48594880 | 2.18339429 | -1.14736884 |
| H | -0.27322367 | 4.19299886 | 0.03545278 |
| H | 0.49477188 | 3.43216728 | -1.32735329 |
| H | 2.13849389 | 3.77397608 | 0.52345882 |
| H | 1.16570691 | 2.74325610 | 1.56746967 |
| H | 1.49378440 | 0.00862456 | -1.19091382 |
| O | 3.26899991 | 1.71843003 | -0.36145691 |
| N | -0.85034198 | -0.35016523 | 0.12544894 |
| C | -2.26145769 | -0.56593978 | 0.30171360 |
| O | -2.67590917 | -1.44947424 | 0.96041688 |
| O | -2.95936202 | 0.31354744 | -0.35856713 |
| C | -4.38327319 | 0.21124426 | -0.25714628 |
| H | -4.77209260 | 1.01023022 | -0.86695139 |
| H | -4.69200458 | 0.32980297 | 0.77123583 |
| H | -4.70827777 | -0.74836627 | -0.63121651 |

| | | | |
|---|-------------|------------|------------|
| STC(S_{NP}/T_{PP}) (2) | | | |
| C | -1.58622525 | 3.67346183 | 0.72559066 |

| | | | |
|---|-------------|-------------|-------------|
| C | -0.86818234 | 3.53392145 | -0.45167227 |
| C | -0.09471123 | 2.40222132 | -0.67087827 |
| C | -0.03143278 | 1.40569230 | 0.30637138 |
| C | -0.74484891 | 1.54619159 | 1.49081766 |
| C | -1.52841945 | 2.68460864 | 1.69481226 |
| C | -0.93056390 | -1.04881574 | -1.17554010 |
| C | 0.05747560 | -1.01171846 | -0.16429544 |
| C | 0.16854991 | -2.11457062 | 0.85663176 |
| C | -0.52657640 | -3.39568224 | 0.38902793 |
| C | -1.92349383 | -3.11477637 | -0.16440042 |
| C | -1.83228605 | -2.03334062 | -1.20505022 |
| H | -2.08079375 | 2.78805484 | 2.61386596 |
| H | -2.18690241 | 4.55382745 | 0.88375101 |
| H | -0.91466566 | 4.30573657 | -1.20193395 |
| H | 0.46386805 | 2.28280623 | -1.58389590 |
| H | -0.69184590 | 0.78248082 | 2.24807849 |
| H | -0.25412817 | -1.77040000 | 1.80082576 |
| H | 1.21270934 | -2.33016883 | 1.04824348 |
| H | -0.58308205 | -4.10240129 | 1.21064432 |
| H | 0.07052684 | -3.85733531 | -0.39276553 |
| H | -2.35812640 | -4.01163067 | -0.59421458 |
| H | -2.58654541 | -2.78300550 | 0.63395201 |
| H | -0.93631649 | -0.28241184 | -1.92880069 |
| O | -2.76547430 | -2.14402054 | -2.18288682 |
| N | 0.74053684 | 0.21725354 | 0.07251579 |
| C | 2.09835551 | 0.32230188 | 0.08472374 |
| O | 2.69385685 | 1.32975009 | 0.35117043 |
| O | 2.69609852 | -0.79493354 | -0.28549798 |
| C | 4.11655766 | -0.79520721 | -0.29340156 |
| H | 4.40378092 | -1.78615287 | -0.60879870 |
| H | 4.50003124 | -0.59016941 | 0.69591688 |
| H | 4.49076004 | -0.05693742 | -0.98780271 |

T_{PP}-Min (2)

| | | | |
|---|-------------|------------|-------------|
| C | -1.81689785 | 3.42393023 | 0.40136660 |
| C | -0.71414638 | 3.50494306 | -0.44422565 |
| C | 0.16019227 | 2.44609719 | -0.55960502 |

| | | | |
|---|-------------|-------------|-------------|
| C | -0.03819573 | 1.28946128 | 0.19861392 |
| C | -1.11987488 | 1.21311137 | 1.07125995 |
| C | -2.02021200 | 2.27628640 | 1.15974046 |
| C | -1.02902679 | -0.96611979 | -1.20759782 |
| C | 0.25730758 | -1.08246325 | -0.45115096 |
| C | 0.46862480 | -2.34346092 | 0.36782215 |
| C | -0.72480790 | -3.30335396 | 0.27201332 |
| C | -2.06219429 | -2.56910475 | 0.43387786 |
| C | -2.25772045 | -1.58506084 | -0.70241894 |
| H | -2.87058724 | 2.20182363 | 1.81695951 |
| H | -2.50939972 | 4.24685430 | 0.46753054 |
| H | -0.54657017 | 4.39662873 | -1.02620232 |
| H | 1.00261418 | 2.50858836 | -1.22605445 |
| H | -1.26101874 | 0.33616284 | 1.67812817 |
| H | 0.60674184 | -2.04713577 | 1.40590391 |
| H | 1.37829086 | -2.85098818 | 0.06810542 |
| H | -0.62859591 | -4.07186944 | 1.03186261 |
| H | -0.71412215 | -3.81265045 | -0.68898441 |
| H | -2.90377865 | -3.25201594 | 0.43409153 |
| H | -2.08160810 | -2.02792135 | 1.37907287 |
| H | -1.04365076 | -0.54891425 | -2.20142436 |
| O | -3.32877891 | -1.38330932 | -1.21306036 |
| N | 0.81204845 | 0.14858755 | 0.02379154 |
| C | 2.16196368 | 0.30283072 | 0.16535183 |
| O | 2.69129281 | 1.28887377 | 0.59499017 |
| O | 2.82646449 | -0.76386527 | -0.23516233 |
| C | 4.24408475 | -0.72133251 | -0.14976224 |
| H | 4.58314608 | -1.67876027 | -0.51395237 |
| H | 4.55908518 | -0.57435477 | 0.87302731 |
| H | 4.63487678 | 0.07318654 | -0.76943944 |

T_{PP}-TS (2)

| | | | |
|---|-------------|------------|-------------|
| C | -2.04573472 | 3.14145008 | 0.13905093 |
| C | -0.78590398 | 3.49322496 | -0.35514136 |
| C | 0.26824231 | 2.57733050 | -0.33733819 |
| C | 0.07551064 | 1.33523001 | 0.20855473 |
| C | -1.18730586 | 0.95294703 | 0.73319154 |

| | | | |
|---|-------------|-------------|-------------|
| C | -2.24142563 | 1.88850161 | 0.70545273 |
| C | -1.15596660 | -0.59287744 | -0.73838548 |
| C | 0.24411118 | -0.95307097 | -0.31972054 |
| C | 0.48060822 | -2.24400793 | 0.43308204 |
| C | -0.65699333 | -3.24607597 | 0.22016561 |
| C | -2.02342144 | -2.61772898 | 0.51311095 |
| C | -2.29259504 | -1.46543769 | -0.42929939 |
| H | -3.19096571 | 1.62488889 | 1.14022449 |
| H | -2.85230515 | 3.85509727 | 0.11161746 |
| H | -0.62583243 | 4.47097342 | -0.77726411 |
| H | 1.21374443 | 2.84239653 | -0.77178849 |
| H | -1.22725569 | 0.16234045 | 1.45866021 |
| H | 0.56383330 | -2.01510142 | 1.49619446 |
| H | 1.42314721 | -2.68644229 | 0.13695911 |
| H | -0.50157487 | -4.10647039 | 0.86256175 |
| H | -0.64125623 | -3.61260450 | -0.80405538 |
| H | -2.83186041 | -3.33194182 | 0.41261192 |
| H | -2.04409554 | -2.24139349 | 1.53624140 |
| H | -1.26837661 | -0.01025792 | -1.63864222 |
| O | -3.38192562 | -1.26713484 | -0.90748270 |
| N | 0.94864821 | 0.23100120 | 0.06531808 |
| C | 2.30928731 | 0.35104124 | 0.08966225 |
| O | 2.89398809 | 1.33492259 | 0.44541541 |
| O | 2.91046493 | -0.74647702 | -0.31936180 |
| C | 4.33224744 | -0.75652688 | -0.28352673 |
| H | 4.62290637 | -1.73130677 | -0.64277504 |
| H | 4.68523257 | -0.60707612 | 0.72682323 |
| H | 4.72993909 | 0.01540644 | -0.92631709 |

T_{PP}-TS^{dis} (2 in Figure S7a)

| | | | |
|---|------------|-------------|-------------|
| C | 2.66311452 | -2.36872074 | 0.20743786 |
| C | 2.36291229 | -1.73004480 | -0.93823985 |
| C | 1.05775863 | -1.12383120 | -1.12302751 |
| C | 0.11086714 | -1.26559135 | -0.05302663 |
| C | 0.46050694 | -1.87294338 | 1.15023962 |
| C | 1.71352400 | -2.46962793 | 1.27580647 |
| C | 0.88183633 | 0.95494682 | -1.08358786 |

| | | | |
|---|-------------|-------------|-------------|
| C | -0.50271271 | 0.98696574 | -0.49299789 |
| C | -0.87674726 | 2.11418320 | 0.45843861 |
| C | 0.32479858 | 3.00406565 | 0.81346980 |
| C | 1.59236489 | 2.16682003 | 1.03666637 |
| C | 2.00208016 | 1.55161013 | -0.28524273 |
| H | 1.97870669 | -2.98024794 | 2.18306614 |
| H | 3.63023037 | -2.82514403 | 0.33094053 |
| H | 3.07829142 | -1.66957276 | -1.73869600 |
| H | 0.65848385 | -1.10436995 | -2.12246848 |
| H | -0.23942017 | -1.88739058 | 1.96567216 |
| H | -1.27814675 | 1.67234162 | 1.36452530 |
| H | -1.67049594 | 2.71812935 | 0.03014121 |
| H | 0.09390917 | 3.58565771 | 1.69950495 |
| H | 0.51248437 | 3.71777055 | 0.01461068 |
| H | 2.41766083 | 2.75990578 | 1.40986845 |
| H | 1.39169382 | 1.37389355 | 1.75519945 |
| H | 0.95578566 | 1.20026877 | -2.13285664 |
| O | 3.12703397 | 1.55947966 | -0.69273347 |
| N | -0.96040211 | -0.34067197 | -0.18214169 |
| C | -2.26426548 | -0.71562366 | -0.08356323 |
| O | -2.62863281 | -1.82501351 | 0.19110741 |
| O | -3.08127364 | 0.29157195 | -0.32989206 |
| C | -4.47240746 | 0.04034930 | -0.24222764 |
| H | -4.95523141 | 0.97819377 | -0.46905580 |
| H | -4.74030505 | -0.28483015 | 0.75332117 |
| H | -4.76963584 | -0.71355358 | -0.95750862 |

S₀-TS^{C-C} (2 in Figure S9a)

| | | | |
|---|-------------|-------------|-------------|
| C | 1.96374383 | 3.21169598 | -0.08632902 |
| C | 0.65487028 | 3.60707793 | 0.10247289 |
| C | -0.42829082 | 2.62302336 | 0.05429136 |
| C | -0.15480305 | 1.36334819 | -0.26006996 |
| C | 1.21634789 | 0.89882081 | -0.58575036 |
| C | 2.26415497 | 1.88956007 | -0.46693759 |
| C | 1.12190674 | -0.48883256 | 0.63559286 |
| C | -0.18733005 | -0.95557563 | 0.19722322 |
| C | -0.28698514 | -2.11948503 | -0.75750010 |

| | | | |
|---|-------------|-------------|-------------|
| C | 0.76993516 | -3.17768518 | -0.44184065 |
| C | 2.17569117 | -2.57321210 | -0.44436577 |
| C | 2.29529617 | -1.42583064 | 0.53387527 |
| H | 3.27091854 | 1.60950446 | -0.71377676 |
| H | 2.75947626 | 3.93005099 | -0.00633443 |
| H | 0.41665720 | 4.62063156 | 0.36232265 |
| H | -1.41518594 | 2.92252456 | 0.34122747 |
| H | 1.27778214 | 0.31586419 | -1.49577592 |
| H | -0.16003278 | -1.75861241 | -1.77838877 |
| H | -1.27613081 | -2.55152038 | -0.69597337 |
| H | 0.71635576 | -3.97808768 | -1.17077074 |
| H | 0.56417530 | -3.62112585 | 0.52871819 |
| H | 2.93851989 | -3.30243297 | -0.20570933 |
| H | 2.39774215 | -2.17835995 | -1.43462323 |
| H | 1.12822364 | 0.05029516 | 1.57039602 |
| O | 3.27175431 | -1.24761162 | 1.19822638 |
| N | -0.98481315 | 0.21190917 | -0.08560632 |
| C | -2.34152233 | 0.26451729 | -0.00686765 |
| O | -3.00092336 | 1.23805136 | -0.22717672 |
| O | -2.85475945 | -0.89883073 | 0.34292527 |
| C | -4.26545875 | -0.98537921 | 0.42953833 |
| H | -4.47781459 | -2.00047447 | 0.72330647 |
| H | -4.71826742 | -0.77141296 | -0.52622332 |
| H | -4.64263567 | -0.29534012 | 1.16905273 |

STC(T_{PP}/S₀) (2)

| | | | |
|---|-------------|-------------|-------------|
| C | -2.00428015 | 3.18238481 | 0.10014612 |
| C | -0.69851456 | 3.58525324 | -0.24168956 |
| C | 0.38359297 | 2.61396058 | -0.25445213 |
| C | 0.14038429 | 1.36284395 | 0.11475253 |
| C | -1.21553273 | 0.83828711 | 0.49183207 |
| C | -2.29572393 | 1.87455772 | 0.42547366 |
| C | -1.22728714 | -0.41095473 | -0.50764405 |
| C | 0.18435723 | -0.93670314 | -0.30485965 |
| C | 0.42974417 | -2.21674726 | 0.45696402 |
| C | -0.70089541 | -3.22441768 | 0.24770641 |
| C | -2.06939113 | -2.61106562 | 0.56309857 |

| | | | |
|---|-------------|-------------|-------------|
| C | -2.34345564 | -1.41676930 | -0.31579464 |
| H | -3.28619703 | 1.60005504 | 0.74624654 |
| H | -2.79041143 | 3.91969267 | 0.11519083 |
| H | -0.49779191 | 4.59562421 | -0.54866116 |
| H | 1.35671441 | 2.91184687 | -0.59582958 |
| H | -1.16941950 | 0.42939071 | 1.50479085 |
| H | 0.51429069 | -1.98342146 | 1.51978406 |
| H | 1.37281162 | -2.65333494 | 0.15814227 |
| H | -0.53678081 | -4.08595480 | 0.88599859 |
| H | -0.69065703 | -3.58748187 | -0.77773633 |
| H | -2.87494386 | -3.32341467 | 0.43062379 |
| H | -2.08673801 | -2.27285493 | 1.59932724 |
| H | -1.33746268 | -0.00651997 | -1.51104328 |
| O | -3.39629176 | -1.25383681 | -0.86527865 |
| N | 0.97655397 | 0.22422741 | -0.00897245 |
| C | 2.33505895 | 0.29222273 | 0.02732128 |
| O | 2.95409965 | 1.26672478 | 0.35302365 |
| O | 2.90290065 | -0.83983574 | -0.33505199 |
| C | 4.32330089 | -0.88292800 | -0.29414793 |
| H | 4.59302488 | -1.86843104 | -0.63940693 |
| H | 4.67591590 | -0.72702747 | 0.71542940 |
| H | 4.73977853 | -0.12782343 | -0.94479252 |

S₀-Int (2)

| | | | |
|---|-------------|-------------|-------------|
| C | -2.02373937 | 3.24978074 | -0.33964276 |
| C | -0.66381041 | 3.66108448 | -0.41925477 |
| C | 0.40136128 | 2.70005540 | -0.30680990 |
| C | 0.10563270 | 1.44265797 | 0.03624123 |
| C | -1.28314759 | 1.01909708 | 0.45067194 |
| C | -2.35279879 | 1.96267691 | -0.01293621 |
| C | -1.32126326 | -0.45133334 | -0.03529242 |
| C | 0.10806823 | -0.88086942 | 0.15599712 |
| C | 0.51795935 | -2.29877025 | -0.12465590 |
| C | -0.74573634 | -3.15177574 | -0.32674927 |
| C | -1.83535448 | -2.84309343 | 0.70399153 |
| C | -2.25238921 | -1.38545587 | 0.70384457 |
| H | -3.37697122 | 1.64030412 | 0.04870397 |

| | | | |
|---|-------------|-------------|-------------|
| H | -2.79726639 | 3.96184900 | -0.57541827 |
| H | -0.42806587 | 4.67690660 | -0.68082786 |
| H | 1.40161978 | 2.99486270 | -0.54563509 |
| H | -1.29072025 | 0.98529598 | 1.54584899 |
| H | 1.09473796 | -2.69066331 | 0.70632607 |
| H | 1.15166215 | -2.37681041 | -1.00245385 |
| H | -0.48141216 | -4.20174837 | -0.27194511 |
| H | -1.14217599 | -2.98545335 | -1.32471236 |
| H | -2.72170078 | -3.44727831 | 0.54395188 |
| H | -1.48207428 | -3.06351402 | 1.71018285 |
| H | -1.60702759 | -0.49265991 | -1.09580761 |
| O | -3.22985321 | -1.00159216 | 1.27697267 |
| N | 0.90887915 | 0.28583510 | 0.07176629 |
| C | 2.28211100 | 0.33260568 | 0.09209467 |
| O | 2.92038246 | 1.33478607 | -0.03001896 |
| O | 2.81756315 | -0.85445706 | 0.25771905 |
| C | 4.23936552 | -0.93652920 | 0.27053059 |
| H | 4.46488112 | -1.98158681 | 0.40707353 |
| H | 4.63975248 | -0.35430673 | 1.08617619 |
| H | 4.64348385 | -0.58235320 | -0.66544280 |

S₀-TS (2)

| | | | |
|---|-------------|-------------|-------------|
| C | 1.89657517 | 3.21605583 | -0.23630869 |
| C | 0.54860715 | 3.62387836 | -0.06013642 |
| C | -0.46738725 | 2.70300699 | 0.15000567 |
| C | -0.13870260 | 1.36985660 | 0.16078614 |
| C | 1.20378622 | 0.88814172 | -0.13487452 |
| C | 2.24952036 | 1.89140863 | -0.20570942 |
| C | 1.27347887 | -0.47875843 | 0.50644043 |
| C | -0.07280983 | -0.89458355 | -0.05370392 |
| C | -0.51140357 | -2.33056288 | 0.04319276 |
| C | 0.69502237 | -3.21915472 | 0.38497390 |
| C | 1.97121402 | -2.79276044 | -0.34330850 |
| C | 2.38370168 | -1.38362417 | 0.01720727 |
| H | 3.27106745 | 1.57685127 | -0.28169876 |
| H | 2.65482839 | 3.96978090 | -0.35654293 |
| H | 0.30935018 | 4.67087707 | -0.07285284 |

| | | | |
|---|-------------|-------------|-------------|
| H | -1.47551612 | 3.02359498 | 0.30570594 |
| H | 0.82109944 | 0.23362108 | -1.21097358 |
| H | -0.95060098 | -2.64368673 | -0.89775953 |
| H | -1.27669562 | -2.46215432 | 0.79754407 |
| H | 0.46433724 | -4.24917527 | 0.13928493 |
| H | 0.87424393 | -3.18952714 | 1.45708702 |
| H | 2.80123057 | -3.45696250 | -0.13360085 |
| H | 1.81471143 | -2.80578115 | -1.42117109 |
| H | 1.30637141 | -0.47037098 | 1.60660484 |
| O | 3.51519362 | -1.00826587 | -0.06464823 |
| N | -0.91265194 | 0.22250748 | 0.18660741 |
| C | -2.29263802 | 0.26583488 | 0.11425999 |
| O | -2.93453903 | 1.21712199 | 0.43064217 |
| O | -2.80765487 | -0.85031357 | -0.33645100 |
| C | -4.23014539 | -0.90590691 | -0.40521078 |
| H | -4.45819565 | -1.89035161 | -0.77910064 |
| H | -4.59663373 | -0.14605301 | -1.07899347 |
| H | -4.65428892 | -0.76147658 | 0.57728562 |

S₀-TS' (2 in Figure S7a)

| | | | |
|---|-------------|-------------|-------------|
| C | 3.08325803 | 2.30845190 | 0.75653524 |
| C | 1.89004160 | 2.55836845 | 0.14591814 |
| C | 0.99977079 | 1.44663489 | -0.15001073 |
| C | 1.33838182 | 0.17208771 | 0.44503273 |
| C | 2.56478908 | -0.05976934 | 1.06888915 |
| C | 3.41824714 | 0.99430978 | 1.21603351 |
| C | -0.51050761 | 1.46871202 | -0.23892497 |
| C | -0.59245740 | 0.04999060 | -0.78814180 |
| C | -1.97950561 | -0.49782137 | -1.05671167 |
| C | -3.03844988 | 0.52618090 | -0.61844372 |
| C | -2.77992824 | 1.02118915 | 0.80783861 |
| C | -1.38439137 | 1.59623889 | 0.99264796 |
| H | 4.36127770 | 0.84066611 | 1.70694464 |
| H | 3.77960073 | 3.10941087 | 0.93015941 |
| H | 1.61606492 | 3.55125936 | -0.15920263 |
| H | 0.92451881 | 0.96993757 | -1.36685287 |
| H | 2.81552651 | -1.03125059 | 1.43872803 |

| | | | |
|---|-------------|-------------|-------------|
| H | -2.14037685 | -1.41932968 | -0.51639213 |
| H | -2.10194699 | -0.73455437 | -2.10890350 |
| H | -4.02373670 | 0.07703147 | -0.67523357 |
| H | -3.04656953 | 1.36997300 | -1.30321944 |
| H | -3.50076236 | 1.77640463 | 1.10538490 |
| H | -2.87647917 | 0.20468123 | 1.52008256 |
| H | -0.84447608 | 2.19222796 | -0.97735536 |
| O | -1.03110323 | 2.08336349 | 2.02426050 |
| N | 0.34112599 | -0.67717860 | 0.01239539 |
| C | 0.52509008 | -2.05304737 | 0.01291353 |
| O | 1.19324202 | -2.62144788 | 0.81634956 |
| O | -0.10164062 | -2.64604220 | -0.97260469 |
| C | -0.00111976 | -4.06821551 | -1.01934231 |
| H | -0.59409898 | -4.36693857 | -1.86788709 |
| H | -0.39127914 | -4.49769806 | -0.10866466 |
| H | 1.02987326 | -4.36038346 | -1.15059571 |

S₀-TS1^(1,2-H) (2 in Figure S8)

| | | | |
|---|-------------|-------------|-------------|
| C | 3.04151123 | 2.29234417 | -0.74273006 |
| C | 3.67189428 | 0.97131607 | -0.69873805 |
| C | 2.92805523 | -0.15115701 | -0.35234403 |
| C | 1.63797013 | 0.02968300 | 0.14903401 |
| C | 1.11081908 | 1.40751411 | 0.50269604 |
| C | 1.83215614 | 2.50317520 | -0.24340702 |
| C | -0.36948403 | 1.23836309 | 0.25576902 |
| C | -0.68040305 | -0.20174302 | 0.08324001 |
| C | -2.01898216 | -0.70793905 | 0.54778104 |
| C | -3.08977724 | 0.32809003 | 0.18188201 |
| C | -2.81139321 | 1.70552913 | 0.78832106 |
| C | -1.38627311 | 2.20510817 | 0.63553805 |
| H | 1.35430410 | 3.46299226 | -0.29507402 |
| H | 3.57476127 | 3.09169124 | -1.22721710 |
| H | 4.68051536 | 0.85773607 | -1.04840008 |
| H | 3.32770925 | -1.13386309 | -0.49411704 |
| H | 1.25441710 | 1.58465012 | 1.57327212 |
| H | -1.99608515 | -0.84555706 | 1.62887513 |
| H | -2.25847817 | -1.65829013 | 0.10040801 |

| | | | |
|---|-------------|-------------|-------------|
| H | -4.05645731 | -0.02273000 | 0.52335304 |
| H | -3.15306224 | 0.40481803 | -0.90011707 |
| H | -3.47663927 | 2.45832919 | 0.38314103 |
| H | -2.99244023 | 1.67803913 | 1.86059314 |
| H | -0.68010005 | 0.64602105 | -0.90160107 |
| O | -1.10524208 | 3.34889926 | 0.89099507 |
| N | 0.56414704 | -0.88015707 | 0.14167701 |
| C | 0.74984406 | -2.22681117 | -0.07031401 |
| O | 1.78806914 | -2.78262421 | 0.10761401 |
| O | -0.34012303 | -2.82288622 | -0.49651704 |
| C | -0.27898302 | -4.23441133 | -0.68307205 |
| H | -1.26323410 | -4.52345335 | -1.01245808 |
| H | -0.03190300 | -4.72417136 | 0.24600702 |
| H | 0.45754804 | -4.47861534 | -1.43213211 |

S₀-TS2^(1,2-H) (2 in Figure S8)

| | | | |
|---|-------------|-------------|-------------|
| C | 3.19932781 | 2.38818312 | -0.34126207 |
| C | 3.73361717 | 1.09965159 | -0.38998762 |
| C | 2.88665722 | -0.06199931 | -0.32403868 |
| C | 1.56754258 | 0.10521555 | -0.16967620 |
| C | 0.96940328 | 1.44083749 | 0.02290858 |
| C | 1.83260963 | 2.59801905 | -0.21891984 |
| C | -0.49060316 | 1.28353495 | -0.09137575 |
| C | -0.81688122 | -0.18253226 | -0.22859456 |
| C | -1.90022805 | -0.57892895 | 0.77330813 |
| C | -3.11882389 | 0.31134513 | 0.49294013 |
| C | -2.84338376 | 1.80765569 | 0.69888873 |
| C | -1.44553618 | 2.27831232 | 0.34165638 |
| H | 1.39971633 | 3.57535627 | -0.16931847 |
| H | 3.85759339 | 3.23425114 | -0.42699365 |
| H | 4.79157267 | 0.96070501 | -0.50586057 |
| H | 3.31378203 | -1.03741310 | -0.40661135 |
| H | 0.70976296 | 1.44477662 | 1.14813806 |
| H | -1.53684193 | -0.43614071 | 1.78845931 |
| H | -2.17676257 | -1.61611154 | 0.65960799 |
| H | -3.94667896 | 0.01267525 | 1.12596326 |
| H | -3.43996079 | 0.13575851 | -0.53054918 |

| | | | |
|---|-------------|-------------|-------------|
| H | -3.55348083 | 2.41583660 | 0.14897665 |
| H | -2.96597029 | 2.07202126 | 1.74550864 |
| H | -1.19979598 | -0.36852512 | -1.23085313 |
| O | -1.13851402 | 3.43966792 | 0.47630651 |
| N | 0.51440594 | -0.83042539 | -0.11952617 |
| C | 0.71703421 | -2.16542743 | -0.30686241 |
| O | 1.78495892 | -2.70314878 | -0.28511412 |
| O | -0.41330997 | -2.80412472 | -0.54293108 |
| C | -0.33455240 | -4.20794629 | -0.75087666 |
| H | -1.34931757 | -4.53229484 | -0.91789763 |
| H | 0.07769970 | -4.69555146 | 0.11964119 |
| H | 0.27691170 | -4.42777056 | -1.61313440 |

trans-P (2)

| | | | |
|---|-------------|-------------|-------------|
| C | 1.93558026 | 3.30813600 | -0.00886269 |
| C | 0.60282655 | 3.68966942 | -0.04138731 |
| C | -0.43048972 | 2.74303104 | 0.02336043 |
| C | -0.08789921 | 1.41868903 | 0.11827056 |
| C | 1.25936995 | 1.01889182 | 0.17300487 |
| C | 2.27487897 | 1.95202987 | 0.10880109 |
| C | 1.27929166 | -0.47659799 | 0.36472834 |
| C | -0.07312831 | -0.89858808 | -0.22294590 |
| C | -0.47639404 | -2.31041068 | 0.20205822 |
| C | 0.78381174 | -3.17531585 | 0.41986893 |
| C | 1.96002736 | -2.76368964 | -0.47823134 |
| C | 2.38941596 | -1.33355227 | -0.19669931 |
| H | 3.30055422 | 1.63832097 | 0.14402444 |
| H | 2.71128286 | 4.05100533 | -0.06823764 |
| H | 0.34591355 | 4.73133919 | -0.12190359 |
| H | -1.45439871 | 3.05186414 | -0.00005800 |
| H | 0.03823060 | -0.87537752 | -1.32742007 |
| H | -1.09426741 | -2.74694441 | -0.57168137 |
| H | -1.07034127 | -2.29462113 | 1.10658976 |
| H | 0.54172567 | -4.21935602 | 0.25740812 |
| H | 1.10354013 | -3.09509330 | 1.45536897 |
| H | 2.81922271 | -3.40899944 | -0.33886750 |
| H | 1.68310906 | -2.82249831 | -1.53018897 |

| | | | |
|---|-------------|-------------|-------------|
| H | 1.25842061 | -0.66694398 | 1.44178045 |
| O | 3.50412359 | -0.94150400 | -0.37220981 |
| N | -0.92082578 | 0.26190993 | 0.13124792 |
| C | -2.27511152 | 0.32362194 | 0.02748718 |
| O | -2.93584463 | 1.29218468 | 0.27441547 |
| O | -2.79805180 | -0.82509494 | -0.36110913 |
| C | -4.21484497 | -0.89851627 | -0.43402324 |
| H | -4.43812158 | -1.90510120 | -0.75147549 |
| H | -4.59277767 | -0.18554367 | -1.15207418 |
| H | -4.65435285 | -0.70387470 | 0.53354277 |

cis-P (2)

| | | | |
|---|-------------|-------------|-------------|
| C | -1.95583146 | 3.18920896 | -0.38782307 |
| C | -0.65631027 | 3.51531129 | -0.75940415 |
| C | 0.39374168 | 2.61030679 | -0.59168121 |
| C | 0.10622163 | 1.37891061 | -0.04649952 |
| C | -1.19324532 | 1.03209596 | 0.32710604 |
| C | -2.23214139 | 1.93600707 | 0.16643754 |
| C | -1.19035373 | -0.34629950 | 0.94711869 |
| C | 0.20444226 | -0.90844625 | 0.56681922 |
| C | 0.09241490 | -1.87545659 | -0.60944383 |
| C | -0.73542579 | -3.11004721 | -0.23440307 |
| C | -1.99223793 | -2.75384189 | 0.59765101 |
| C | -2.32831331 | -1.28065159 | 0.55902133 |
| H | -3.22959409 | 1.66939471 | 0.45557773 |
| H | -2.74965145 | 3.90137267 | -0.52533248 |
| H | -0.44874298 | 4.48144851 | -1.18424225 |
| H | 1.39299525 | 2.86675444 | -0.87346058 |
| H | 0.67986830 | -1.41028337 | 1.42483506 |
| H | 1.07763958 | -2.17545420 | -0.94188026 |
| H | -0.37942400 | -1.34905283 | -1.43712028 |
| H | -0.12019328 | -3.80552849 | 0.32578456 |
| H | -1.03377948 | -3.62195534 | -1.14170579 |
| H | -2.86218852 | -3.31128130 | 0.27828943 |
| H | -1.81968465 | -2.99365204 | 1.64538236 |
| H | -1.26446213 | -0.25710003 | 2.03394586 |
| O | -3.41160861 | -0.87561414 | 0.26092018 |

| | | | | | | | |
|---|------------|-------------|-------------|---|------------|-------------|-------------|
| N | 0.97529121 | 0.29720035 | 0.22148837 | H | 4.52795650 | -1.90478423 | 0.76155924 |
| C | 2.32529520 | 0.34900698 | 0.16956060 | H | 4.71010999 | -0.19647253 | 1.19409730 |
| O | 2.97089443 | 1.31378952 | -0.12852448 | H | 4.67003477 | -0.67271914 | -0.50380174 |
| O | 2.86954789 | -0.81619559 | 0.49536888 | | | | |
| C | 4.28859283 | -0.89073063 | 0.48248333 | | | | |

10.2 Critical Structures of 2-BF₃ complex in Figure 2, Figure S7, and Figure S9.

| | | | | | | | |
|---|-------------|-------------|-------------|--|-------------|-------------|-------------|
| S₀-Min (2-BF₃) | | | | O | -0.82203000 | -2.33390801 | 0.54098000 |
| C | 3.98974202 | 1.32353901 | -1.00250101 | C | -0.90617901 | -3.69282302 | 0.96091101 |
| C | 3.41396402 | 0.35634800 | -1.81866601 | H | -1.95526701 | -3.93968402 | 0.92829900 |
| C | 2.22391201 | -0.23861200 | -1.45767301 | H | -0.52264900 | -3.79958002 | 1.96493401 |
| C | 1.59972301 | 0.12672700 | -0.26891900 | H | -0.34705700 | -4.32473302 | 0.28724200 |
| C | 2.17139801 | 1.08300500 | 0.55969700 | B | -3.39451902 | 3.56504502 | -2.74396101 |
| C | 3.37117102 | 1.68790901 | 0.18775800 | F | -4.58680302 | 2.90007802 | -2.80043901 |
| C | -1.07119601 | 0.97309500 | -1.16239501 | F | -3.37513601 | 4.51798402 | -1.76583701 |
| C | -0.84729700 | 0.27334200 | -0.02774400 | F | -2.98404001 | 4.02731702 | -3.95004602 |
| C | -1.74866601 | 0.42364300 | 1.17780201 | C | -3.08935429 | -1.60958663 | 1.28831927 |
| C | -3.16026201 | 0.82632200 | 0.76843600 | C | 1.18380243 | -1.01738285 | -0.79788651 |
| C | -3.14920302 | 2.05007701 | -0.14343600 | C | 0.90018453 | -0.07179273 | 0.11815568 |
| C | -2.19754601 | 1.87402001 | -1.28682300 | C | 1.80156435 | 0.20193479 | 1.30059799 |
| H | 3.81660702 | 2.43047601 | 0.82594100 | C | 3.24337485 | -0.21168726 | 1.00952821 |
| H | 4.91947902 | 1.78626401 | -1.28996701 | | | | |
| H | 3.89399502 | 0.07048900 | -2.73767601 | S_{CT}-Min (2-BF₃) | | | |
| H | 1.77673401 | -0.98824000 | -2.08683401 | C | 3.44796283 | 1.62987137 | -1.18379032 |
| H | 1.68753201 | 1.34919501 | 1.48270401 | C | 3.40878394 | 0.24511053 | -1.55171654 |
| H | -1.30317900 | 1.19107301 | 1.81091301 | C | 2.39838867 | -0.56558034 | -1.14478838 |
| H | -1.76931801 | -0.48542600 | 1.75438101 | C | 1.34421960 | -0.01332920 | -0.37036896 |
| H | -3.75221702 | 1.04293501 | 1.64971501 | C | 1.36306073 | 1.39066986 | -0.02150162 |
| H | -3.63816202 | -0.00401500 | 0.25594800 | C | 2.42200670 | 2.19084433 | -0.42178487 |
| H | -4.12931502 | 2.27810401 | -0.53116500 | C | -1.07690290 | 0.83200038 | -1.23701592 |
| H | -2.80328302 | 2.93236601 | 0.39330800 | C | -1.03862811 | -0.13709142 | -0.14130764 |
| H | -0.41254400 | 0.91419800 | -2.00614501 | C | -1.84366800 | 0.15239170 | 1.08976203 |
| O | -2.29110301 | 2.49282901 | -2.35369601 | C | -3.14313201 | 0.85416736 | 0.70193853 |
| N | 0.34625300 | -0.47353800 | 0.10677700 | C | -2.88237144 | 2.12579145 | -0.10647480 |
| C | 0.37802500 | -1.79219501 | 0.51031500 | C | -1.92342443 | 1.89001658 | -1.24547130 |
| O | 1.38282401 | -2.37566801 | 0.77019900 | H | 2.44427295 | 3.23235564 | -0.15307369 |

| | | | | | | | |
|---|-------------|-------------|-------------|---|-------------|-------------|-------------|
| H | 4.27559044 | 2.23958278 | -1.51150663 | C | -1.79877618 | 1.94954957 | -1.09346736 |
| H | 4.18938096 | -0.14756447 | -2.18431789 | H | 2.09300423 | 3.31711140 | -0.45001891 |
| H | 2.35896158 | -1.59899590 | -1.43040915 | H | 3.90943217 | 2.39539063 | -1.86645374 |
| H | 0.54715306 | 1.78898793 | 0.55642418 | H | 4.08394674 | -0.04659712 | -2.25706395 |
| H | -1.27501941 | 0.81546435 | 1.74169712 | H | 2.46864209 | -1.59773937 | -1.26677664 |
| H | -2.03876502 | -0.75040622 | 1.64997217 | H | 0.50194407 | 1.75908057 | 0.63064898 |
| H | -3.71192987 | 1.10008861 | 1.59125466 | H | -1.27530401 | 0.64321027 | 1.87824080 |
| H | -3.74784566 | 0.17427910 | 0.10952093 | H | -2.12704451 | -0.85694634 | 1.62642977 |
| H | -3.80499072 | 2.50356928 | -0.51860057 | H | -3.67942783 | 1.09774562 | 1.66694535 |
| H | -2.47798541 | 2.91702075 | 0.51703014 | H | -3.72951013 | 0.27965141 | 0.12375078 |
| H | -0.51390854 | 0.65553649 | -2.12475726 | H | -3.63078741 | 2.65365688 | -0.32448425 |
| O | -1.87871299 | 2.71783165 | -2.24212951 | H | -2.28494971 | 2.89688220 | 0.73988583 |
| N | 0.23935809 | -0.75965884 | 0.01316258 | H | -0.47355705 | 0.66962592 | -2.03425364 |
| C | 0.42076278 | -2.05619794 | 0.48017579 | O | -1.71483965 | 2.81421415 | -2.05541137 |
| O | 1.50245858 | -2.51542407 | 0.68603176 | N | 0.26023329 | -0.78871057 | 0.10000646 |
| O | -0.71233268 | -2.66423303 | 0.68762064 | C | 0.42717756 | -2.10030844 | 0.53937915 |
| C | -0.66228117 | -3.98372999 | 1.22764663 | O | 1.49877333 | -2.56152924 | 0.77851281 |
| H | -1.68832132 | -4.31085495 | 1.27040687 | O | -0.71836408 | -2.69175511 | 0.72390726 |
| H | -0.22951729 | -3.96308833 | 2.21708416 | C | -0.69909657 | -4.02257856 | 1.23908166 |
| H | -0.08415168 | -4.62826735 | 0.58342072 | H | -1.73294007 | -4.32400074 | 1.28129893 |
| B | -2.77627158 | 3.90908085 | -2.45187131 | H | -0.25968495 | -4.03308388 | 2.22559164 |
| F | -4.08992151 | 3.49406681 | -2.59229216 | H | -0.14126992 | -4.66755787 | 0.57741124 |
| F | -2.66317636 | 4.77742792 | -1.37989389 | B | -2.51238325 | 4.08649339 | -2.18019809 |
| F | -2.32915252 | 4.50623064 | -3.60774947 | F | -3.85935101 | 3.79396199 | -2.30830983 |
| | | | | F | -2.30014631 | 4.87791892 | -1.06423754 |
| | | | | F | -2.03987173 | 4.70720882 | -3.31279947 |

S_{CT}-TS (2-BF₃)

| | | | |
|---|-------------|-------------|-------------|
| C | 3.17863561 | 1.73843192 | -1.42161961 |
| C | 3.29138312 | 0.32596341 | -1.62791944 |
| C | 2.40382020 | -0.54425931 | -1.08039302 |
| C | 1.32801820 | -0.02765822 | -0.31328594 |
| C | 1.22307024 | 1.39435291 | -0.07158743 |
| C | 2.15965922 | 2.26013618 | -0.63680411 |
| C | -1.00114312 | 0.85762200 | -1.12747202 |
| C | -1.01351782 | -0.16147900 | -0.06549586 |
| C | -1.85807596 | 0.07582275 | 1.15192980 |
| C | -3.10150344 | 0.87817543 | 0.77658324 |
| C | -2.74117244 | 2.18170355 | 0.06153110 |

CI(S_{CT}/S₀) (2-BF₃)

| | | | |
|---|-------------|------------|-------------|
| C | 1.61878663 | 4.47370386 | 2.25534193 |
| C | 2.64825254 | 3.71808584 | 1.59646256 |
| C | 2.36122301 | 2.47909368 | 1.08914987 |
| C | 1.07038587 | 1.93128877 | 1.29701178 |
| C | -0.00394313 | 2.71608798 | 1.86303494 |
| C | 0.36055029 | 4.01248515 | 2.39828881 |
| C | -0.97604812 | 2.84031809 | 0.23143158 |
| C | -0.74863840 | 1.39834660 | 0.00269832 |
| C | -1.87665324 | 0.47529434 | -0.40149760 |

| | | | | | | | |
|--|-------------|-------------|-------------|---|-------------|-------------|-------------|
| C | -3.24278403 | 1.18136201 | -0.37770825 | C | -0.85389976 | 1.23877200 | -0.08721852 |
| C | -3.33733315 | 2.29121518 | 0.67748887 | C | -1.98784539 | 0.32296875 | 0.30275163 |
| C | -2.26882267 | 3.30423587 | 0.38155845 | C | -3.34538114 | 0.99839663 | 0.10807592 |
| H | -0.39020845 | 4.59235613 | 2.90204994 | C | -3.41782167 | 2.35929973 | 0.81058261 |
| H | 1.87306289 | 5.43984849 | 2.65781923 | C | -2.35247945 | 3.27362284 | 0.27575540 |
| H | 3.62977191 | 4.13728995 | 1.49501759 | H | -0.20869180 | 4.69584903 | 2.79203780 |
| H | 3.10216540 | 1.91242222 | 0.56012177 | H | 2.05840841 | 5.52836232 | 2.39378307 |
| H | -0.74651557 | 2.16004437 | 2.40766219 | H | 3.70043368 | 4.14413467 | 1.16404531 |
| H | -1.87256896 | -0.37479799 | 0.27390532 | H | 3.06074638 | 1.94393792 | 0.25409635 |
| H | -1.68371340 | 0.08528986 | -1.39506756 | H | -0.69825775 | 2.32359550 | 2.22898623 |
| H | -4.01678553 | 0.44203191 | -0.20395941 | H | -1.86679055 | 0.03939629 | 1.34876929 |
| H | -3.44152196 | 1.62218786 | -1.34940251 | H | -1.93908672 | -0.59016907 | -0.27509655 |
| H | -4.30984724 | 2.75158050 | 0.66218779 | H | -4.12914126 | 0.35775884 | 0.49477518 |
| H | -3.17671274 | 1.89096768 | 1.67811829 | H | -3.54270417 | 1.13335324 | -0.95237971 |
| H | -0.27389330 | 3.49968944 | -0.24986735 | H | -4.38193916 | 2.82383271 | 0.68120918 |
| O | -2.48381460 | 4.55991907 | 0.31545050 | H | -3.25207802 | 2.25068152 | 1.88121788 |
| N | 0.45901287 | 0.97883833 | 0.46321516 | H | -0.46145196 | 3.34049847 | -0.69578686 |
| C | 1.11485831 | -0.23016136 | 0.13971564 | O | -2.50195085 | 4.50692461 | 0.13215068 |
| O | 2.13446770 | -0.54533610 | 0.65260783 | N | 0.46897763 | 0.96073870 | 0.35878866 |
| O | 0.46746774 | -0.91312259 | -0.76202958 | C | 1.18031580 | -0.16663646 | 0.02227099 |
| C | 1.02090296 | -2.17795382 | -1.13781130 | O | 2.28474748 | -0.39451940 | 0.41401289 |
| H | 0.32336084 | -2.59676951 | -1.84449827 | O | 0.50162415 | -0.95400815 | -0.78266130 |
| H | 1.11316517 | -2.81329249 | -0.26966395 | C | 1.13762562 | -2.16197122 | -1.19079839 |
| H | 1.98818073 | -2.03386086 | -1.59538226 | H | 0.43233205 | -2.65302212 | -1.84217711 |
| B | -3.72845773 | 5.25273712 | 0.87560338 | H | 1.35315675 | -2.78059404 | -0.33207406 |
| F | -4.81944630 | 4.91659532 | 0.10297622 | H | 2.05269377 | -1.94376530 | -1.72165611 |
| F | -3.89868465 | 4.82208631 | 2.17543092 | B | -3.75614128 | 5.34921213 | 0.58298225 |
| F | -3.46134404 | 6.59108864 | 0.81013142 | F | -4.81560618 | 4.94791666 | -0.18499278 |
| T_{PP}-Min (2-BF₃) | | | | F | -3.95031276 | 5.07802045 | 1.91040769 |
| C | 1.76505449 | 4.56622904 | 2.01522449 | F | -3.39181470 | 6.63540798 | 0.34921792 |
| C | 2.70350096 | 3.77221754 | 1.32033268 | T_{PP}-TS (2-BF₃) | | | |
| C | 2.35529374 | 2.52966773 | 0.81045330 | C | 1.77438025 | 4.59576931 | 1.99906266 |
| C | 1.06115760 | 2.04886326 | 1.04609312 | C | 2.76430438 | 3.74076090 | 1.39273485 |
| C | 0.13710284 | 2.82575275 | 1.77601609 | C | 2.40769236 | 2.49185296 | 0.88672749 |
| C | 0.50304322 | 4.10683905 | 2.24004755 | C | 1.10261359 | 2.03982472 | 1.04965333 |
| C | -1.10774610 | 2.71310977 | -0.11102068 | C | 0.09187900 | 2.87244898 | 1.69048860 |

| | | | | | | | |
|---|-------------|-------------|-------------|--|-------------|-------------|-------------|
| C | 0.50358741 | 4.20038382 | 2.13823093 | C | 1.65077560 | -0.83478041 | 0.41336436 |
| C | -1.05259496 | 2.73473210 | -0.02015196 | C | 1.95587685 | -0.98457374 | 1.74846839 |
| C | -0.83828472 | 1.26527885 | -0.08978708 | C | 2.42268584 | 0.12699353 | 2.48488404 |
| C | -1.96500816 | 0.32865704 | 0.27701715 | C | -0.06947194 | 0.37098671 | -1.06154724 |
| C | -3.32807111 | 0.99427089 | 0.09023358 | C | -0.26668554 | -1.11230010 | -0.97323130 |
| C | -3.41448337 | 2.33940988 | 0.82344179 | C | -1.63638163 | -1.55305486 | -0.52098510 |
| C | -2.36077511 | 3.27129145 | 0.30645123 | C | -1.94352894 | -0.87765643 | 0.82397522 |
| H | -0.22928621 | 4.83230028 | 2.60605851 | C | -1.91641852 | 0.65409642 | 0.71977584 |
| H | 2.07806656 | 5.56487560 | 2.35401994 | C | -0.95341498 | 1.21632542 | -0.28615577 |
| H | 3.77624613 | 4.08660968 | 1.29719165 | H | 2.68852893 | 0.00425036 | 3.51681956 |
| H | 3.13049049 | 1.88521954 | 0.38051592 | H | 2.83462809 | 2.25040022 | 2.47275399 |
| H | -0.60674497 | 2.34972175 | 2.32731525 | H | 2.28327032 | 2.56611995 | 0.09934161 |
| H | -1.84701171 | 0.02353542 | 1.31697245 | H | 2.19966603 | 0.42908228 | -1.23885290 |
| H | -1.90941255 | -0.57170612 | -0.32004495 | H | 1.83730557 | -1.93908550 | 2.22055336 |
| H | -4.10792577 | 0.34136426 | 0.46493033 | H | -1.70027843 | -2.62709159 | -0.43497277 |
| H | -3.52760485 | 1.14791005 | -0.96726392 | H | -2.36517459 | -1.24065003 | -1.26335037 |
| H | -4.38671043 | 2.79345218 | 0.72395890 | H | -1.22808735 | -1.21415670 | 1.56433556 |
| H | -3.22309145 | 2.20164873 | 1.88697771 | H | -2.92141765 | -1.17876560 | 1.17933334 |
| H | -0.47634380 | 3.35672090 | -0.68663823 | H | -2.88350458 | 1.03815572 | 0.41551531 |
| O | -2.52337196 | 4.49042803 | 0.16065185 | H | -1.70693133 | 1.12448407 | 1.67261016 |
| N | 0.49320830 | 0.96902592 | 0.34718212 | H | 0.12331131 | 0.77840645 | -2.04142362 |
| C | 1.18268921 | -0.16390404 | 0.00310769 | O | -0.88465190 | 2.44008593 | -0.49963205 |
| O | 2.27901847 | -0.42751853 | 0.39862971 | N | 0.88798388 | -1.73434212 | -0.37564795 |
| O | 0.48772457 | -0.93393091 | -0.80786475 | C | 1.19194175 | -3.05841991 | -0.46381797 |
| C | 1.09101710 | -2.16021883 | -1.20438331 | O | 2.07470491 | -3.58285754 | 0.14288964 |
| H | 0.37555967 | -2.63553762 | -1.85644370 | O | 0.37798370 | -3.68891007 | -1.28319723 |
| H | 1.28514765 | -2.78007226 | -0.34121130 | C | 0.57916478 | -5.08770143 | -1.44673229 |
| H | 2.01435157 | -1.97042504 | -1.73133550 | H | -0.18056646 | -5.40794217 | -2.13993687 |
| B | -3.79607175 | 5.32882489 | 0.59877109 | H | 0.46673467 | -5.59595434 | -0.50211189 |
| F | -4.83934995 | 4.89482293 | -0.16872036 | H | 1.56140676 | -5.27879701 | -1.84842675 |
| F | -3.98215242 | 5.06917816 | 1.92764667 | B | -1.66485608 | 3.57869321 | 0.24361220 |
| F | -3.44363189 | 6.61306447 | 0.34697152 | F | -2.99636532 | 3.39445642 | -0.01460687 |
| | | | | F | -1.38033415 | 3.46236299 | 1.57681930 |
| | | | | F | -1.17782573 | 4.72248004 | -0.30290768 |
| T_{PP}-TS^{dis} (2-BF₃ in Figure S7b) | | | | | | | |
| C | 2.49664887 | 1.41781551 | 1.88533273 | | | | |
| C | 2.17987547 | 1.60632476 | 0.56558320 | | | | |
| C | 1.76602683 | 0.46524249 | -0.25277914 | | | | |
| | | | | S₀-TS^{C-C} (2-BF₃ in Figure S9b) | | | |
| C | 1.78952949 | 4.61282055 | 1.91766673 | | | | |

| | | | |
|---|-------------|-------------|-------------|
| C | 2.80967419 | 3.66336494 | 1.48702173 |
| C | 2.44267494 | 2.40861141 | 0.99743998 |
| C | 1.11286183 | 2.01296719 | 1.06528093 |
| C | 0.05813668 | 2.91120960 | 1.61831348 |
| C | 0.50017397 | 4.29217197 | 1.94595874 |
| C | -1.06890961 | 2.71295074 | 0.14820149 |
| C | -0.83928913 | 1.24313841 | -0.06053312 |
| C | -1.95398511 | 0.26943768 | 0.25371532 |
| C | -3.32167624 | 0.91191609 | 0.03296866 |
| C | -3.48209764 | 2.20000439 | 0.84853772 |
| C | -2.42483436 | 3.19070921 | 0.46683416 |
| H | -0.24563683 | 5.00242501 | 2.25478813 |
| H | 2.10448872 | 5.60007435 | 2.20878593 |
| H | 3.84033912 | 3.96291612 | 1.48460633 |
| H | 3.17973037 | 1.75217666 | 0.58247887 |
| H | -0.48959535 | 2.43907334 | 2.43226309 |
| H | -1.86436958 | -0.04744710 | 1.29308739 |
| H | -1.86049591 | -0.61877519 | -0.35524471 |
| H | -4.10580627 | 0.21952327 | 0.31664388 |
| H | -3.46436700 | 1.13297216 | -1.02222195 |
| H | -4.45854163 | 2.64113875 | 0.72839292 |
| H | -3.34354141 | 1.99429058 | 1.90987332 |
| H | -0.59322533 | 3.35105787 | -0.58928474 |
| O | -2.60028618 | 4.40827286 | 0.43494775 |
| N | 0.49465929 | 0.95314369 | 0.35602488 |
| C | 1.18284190 | -0.17475027 | -0.01484915 |
| O | 2.28874267 | -0.43675661 | 0.35346394 |
| O | 0.48754462 | -0.92831430 | -0.84039217 |
| C | 1.09806926 | -2.13493200 | -1.27833522 |
| H | 0.37832226 | -2.60275337 | -1.93142731 |
| H | 1.31473724 | -2.77577711 | -0.43583150 |
| H | 2.01059492 | -1.92105206 | -1.81553732 |
| B | -3.92776343 | 5.21606122 | 0.86110053 |
| F | -4.91186014 | 4.78377406 | 0.02645403 |
| F | -4.15627652 | 4.89487093 | 2.16522213 |
| F | -3.58007075 | 6.50783102 | 0.67230874 |

STC(T_{pp}/S₀) (2-BF₃)

| | | | |
|---|-------------|-------------|-------------|
| C | 1.72294566 | 4.56365462 | 2.01852571 |
| C | 2.70959261 | 3.76825552 | 1.31227187 |
| C | 2.35832708 | 2.51246739 | 0.81412967 |
| C | 1.08304771 | 2.01876397 | 1.03515582 |
| C | -0.01690154 | 2.85536858 | 1.57730914 |
| C | 0.46285890 | 4.14963011 | 2.16777723 |
| C | -0.97352919 | 2.75096532 | 0.11158082 |
| C | -0.84700226 | 1.25916592 | -0.08660895 |
| C | -1.98117765 | 0.33353872 | 0.29942681 |
| C | -3.34053250 | 1.00199273 | 0.10293025 |
| C | -3.42059069 | 2.36284645 | 0.80699351 |
| C | -2.34363540 | 3.28305085 | 0.31947945 |
| H | -0.22729565 | 4.72064689 | 2.76319239 |
| H | 2.04164338 | 5.51002760 | 2.42486072 |
| H | 3.70286586 | 4.14860847 | 1.16708933 |
| H | 3.06863340 | 1.93123248 | 0.26227087 |
| H | -0.63775098 | 2.30618540 | 2.28616858 |
| H | -1.86341617 | 0.04756815 | 1.34587917 |
| H | -1.93256202 | -0.58212601 | -0.27621426 |
| H | -4.12557657 | 0.36377604 | 0.49394527 |
| H | -3.54270588 | 1.13460156 | -0.95635526 |
| H | -4.38570931 | 2.82434428 | 0.68071966 |
| H | -3.25030197 | 2.24814438 | 1.87766412 |
| H | -0.46992134 | 3.32546135 | -0.66793230 |
| O | -2.49571401 | 4.49036440 | 0.14152214 |
| N | 0.48321823 | 0.94097726 | 0.33467705 |
| C | 1.18216672 | -0.17801665 | 0.01108861 |
| O | 2.28746556 | -0.41287170 | 0.40380748 |
| O | 0.49751134 | -0.96734578 | -0.78974631 |
| C | 1.13633725 | -2.16881630 | -1.19343428 |
| H | 0.43320284 | -2.66133559 | -1.84517073 |
| H | 1.35408881 | -2.78558211 | -0.33378751 |
| H | 2.05167438 | -1.94666235 | -1.72230240 |
| B | -3.77330058 | 5.36073226 | 0.58575355 |
| F | -4.81390808 | 4.94759023 | -0.18848894 |
| F | -3.95047626 | 5.08025045 | 1.90785934 |

| | | | |
|---|-------------|-------------|-------------|
| F | -3.38849779 | 6.63321946 | 0.34618447 |
| S₀-Int (2-BF₃) | | | |
| C | 1.83058899 | 4.59024373 | 2.01384047 |
| C | 2.81224681 | 3.51755688 | 1.88563832 |
| C | 2.44762814 | 2.27597587 | 1.37850452 |
| C | 1.10056190 | 2.03228694 | 1.12456084 |
| C | 0.02266179 | 3.00929229 | 1.52588457 |
| C | 0.53934990 | 4.39280569 | 1.79395894 |
| C | -1.01159730 | 2.81300549 | 0.35862626 |
| C | -0.82667646 | 1.35101262 | 0.03771280 |
| C | -1.92252058 | 0.44618176 | -0.44056885 |
| C | -3.27358072 | 1.17395018 | -0.36594411 |
| C | -3.39149669 | 2.06256058 | 0.88912132 |
| C | -2.41104536 | 3.17486386 | 0.73423542 |
| H | -0.16614131 | 5.19960107 | 1.86498382 |
| H | 2.18199022 | 5.57524266 | 2.26569445 |
| H | 3.84217693 | 3.72094464 | 2.10696846 |
| H | 3.18813306 | 1.53437709 | 1.16821032 |
| H | -0.44097629 | 2.60536517 | 2.43752401 |
| H | -1.96297872 | -0.44704527 | 0.17617374 |
| H | -1.75773217 | 0.10510673 | -1.45594472 |
| H | -4.07916682 | 0.45153713 | -0.34999298 |
| H | -3.42474177 | 1.78565229 | -1.25073303 |
| H | -4.39038456 | 2.42846398 | 1.04087689 |
| H | -3.08826239 | 1.49307078 | 1.76500235 |
| H | -0.72672657 | 3.45308379 | -0.48509271 |
| O | -2.66413644 | 4.37122599 | 0.84143799 |
| N | 0.47633864 | 1.01671051 | 0.40278638 |
| C | 1.13323698 | -0.16454315 | 0.07604959 |
| O | 2.15146076 | -0.50526268 | 0.57889922 |
| O | 0.46961899 | -0.86606377 | -0.80371913 |
| C | 1.02526983 | -2.13163293 | -1.16715152 |
| H | 0.33125163 | -2.55209212 | -1.87470990 |
| H | 1.11211206 | -2.76039926 | -0.29549149 |
| H | 1.99374261 | -1.98928843 | -1.61917093 |
| B | -4.07862427 | 5.00576885 | 1.27869572 |

| | | | |
|---|-------------|------------|------------|
| F | -4.95898378 | 4.66644073 | 0.29748394 |
| F | -4.38614779 | 4.44706278 | 2.48111545 |
| F | -3.82143535 | 6.32987291 | 1.34562468 |

S₀-TS (2-BF₃)

| | | | |
|---|-------------|-------------|-------------|
| C | 0.36314133 | 3.72021148 | -0.00789592 |
| C | 1.78291602 | 3.63298411 | 0.00068803 |
| C | 2.42181279 | 2.43773627 | -0.11399267 |
| C | 1.64842031 | 1.27813199 | -0.22623449 |
| C | 0.19436278 | 1.28374288 | -0.07026153 |
| C | -0.43430521 | 2.61269495 | -0.11635330 |
| C | -0.25147483 | 0.02583385 | -0.77631870 |
| C | 0.81081766 | -0.83629746 | -0.10635128 |
| C | 0.73847065 | -2.32919662 | -0.23928643 |
| C | -0.55399915 | -2.71582292 | -0.97078960 |
| C | -1.79398359 | -1.98206718 | -0.45518990 |
| C | -1.60387530 | -0.49732068 | -0.41236803 |
| H | -1.50547357 | 2.68204185 | -0.15756235 |
| H | -0.11122312 | 4.69111420 | 0.04641903 |
| H | 2.35029032 | 4.53944918 | 0.07823711 |
| H | 3.48840456 | 2.38605715 | -0.13524652 |
| H | 0.16852368 | 0.60486346 | 0.99352692 |
| H | 0.76950770 | -2.78912169 | 0.74402163 |
| H | 1.58486278 | -2.70929762 | -0.79010774 |
| H | -0.71802094 | -3.78148345 | -0.87292396 |
| H | -0.43795163 | -2.51321162 | -2.03113258 |
| H | -2.66729840 | -2.18715480 | -1.06347804 |
| H | -2.05383290 | -2.28065910 | 0.55661674 |
| H | -0.17699853 | 0.02082652 | -1.87601026 |
| O | -2.48231752 | 0.28898950 | -0.07975699 |
| N | 1.98259158 | -0.05976448 | -0.18942291 |
| C | 3.28126805 | -0.48943151 | 0.06991700 |
| O | 4.24291482 | 0.16823887 | -0.16570487 |
| O | 3.30338459 | -1.68475930 | 0.59819234 |
| C | 4.58272326 | -2.24684548 | 0.87864169 |
| H | 4.38151531 | -3.22224726 | 1.29039107 |
| H | 5.10770457 | -1.63266930 | 1.59452675 |

| | | | |
|---|-------------|-------------|-------------|
| H | 5.16088017 | -2.32881993 | -0.02959700 |
| B | -4.00138795 | -0.07679240 | 0.35322126 |
| F | -4.55401113 | -0.68401487 | -0.73090359 |
| F | -3.88669432 | -0.89974781 | 1.42940620 |
| F | -4.53340560 | 1.13027120 | 0.63719786 |

trans-P (2-BF₃)

| | | | |
|---|-------------|-------------|-------------|
| C | 0.35923173 | 3.77350586 | -0.03443931 |
| C | 1.74142600 | 3.67717727 | 0.00298954 |
| C | 2.39528771 | 2.43994951 | -0.08366111 |
| C | 1.62108333 | 1.32215052 | -0.22936222 |
| C | 0.21995039 | 1.41966620 | -0.37529565 |
| C | -0.42470337 | 2.62778208 | -0.22775000 |
| C | -0.26251006 | 0.03815913 | -0.75373987 |
| C | 0.75255462 | -0.78413101 | 0.06801580 |
| C | 0.70413848 | -2.30074930 | -0.20214306 |
| C | -0.57713283 | -2.69119201 | -0.96031678 |
| C | -1.81639111 | -1.96421040 | -0.44207431 |
| C | -1.62170690 | -0.47212583 | -0.39833767 |
| H | -1.49571357 | 2.68817426 | -0.26507597 |
| H | -0.11777266 | 4.73306144 | 0.03151437 |
| H | 2.33656076 | 4.56504228 | 0.10602923 |
| H | 3.46330394 | 2.37832636 | -0.04945828 |
| H | 0.43872373 | -0.38514737 | 1.10457820 |
| H | 0.77501916 | -2.84579058 | 0.72990840 |
| H | 1.55149963 | -2.61381887 | -0.79726223 |
| H | -0.73498837 | -3.76195279 | -0.88430511 |
| H | -0.46030054 | -2.48100814 | -2.01986536 |
| H | -2.69274171 | -2.16502712 | -1.04683918 |
| H | -2.06873879 | -2.27129610 | 0.56956892 |
| H | -0.14837769 | -0.07339742 | -1.83785448 |
| O | -2.49827172 | 0.31472543 | -0.06607903 |
| N | 1.99479335 | -0.05268545 | -0.21217640 |
| C | 3.26992213 | -0.46174081 | 0.07109674 |
| O | 4.24022978 | 0.20044588 | -0.14309790 |
| O | 3.31486487 | -1.67147331 | 0.59660771 |
| C | 4.60487637 | -2.20881301 | 0.87124193 |

| | | | |
|---|-------------|-------------|-------------|
| H | 4.42653941 | -3.19123928 | 1.28019316 |
| H | 5.12445670 | -1.59137661 | 1.58916768 |
| H | 5.18629467 | -2.27931595 | -0.03658219 |
| B | -4.02078929 | -0.03622592 | 0.35700186 |
| F | -4.57352378 | -0.63829945 | -0.73016353 |
| F | -3.92567601 | -0.85898060 | 1.43572554 |
| F | -4.53882527 | 1.17829708 | 0.63635353 |

cis-P (2-BF₃)

| | | | |
|---|-------------|-------------|-------------|
| C | 2.20793520 | 3.86839069 | 0.01791538 |
| C | 2.54002811 | 2.74573555 | -0.73268642 |
| C | 1.73500133 | 1.60688905 | -0.73011030 |
| C | 0.59199029 | 1.62347263 | 0.03809845 |
| C | 0.23849864 | 2.74560762 | 0.78980668 |
| C | 1.04781826 | 3.87213843 | 0.79604287 |
| C | -1.01787152 | 2.43481299 | 1.57327217 |
| C | -1.55936102 | 1.14190899 | 0.90529637 |
| C | -2.68480034 | 1.48583200 | -0.07075858 |
| C | -3.88919923 | 2.10252050 | 0.65286801 |
| C | -3.47782068 | 3.01125042 | 1.84088793 |
| C | -2.07605602 | 3.49939748 | 1.66989787 |
| H | 0.78644187 | 4.73285735 | 1.37961004 |
| H | 2.84417673 | 4.73444882 | 0.00229529 |
| H | 3.43527668 | 2.74874405 | -1.32830035 |
| H | 1.99926605 | 0.74315694 | -1.30219447 |
| H | -1.89852852 | 0.43083586 | 1.64386792 |
| H | -2.99011609 | 0.60031449 | -0.61103215 |
| H | -2.29310925 | 2.18819250 | -0.80386883 |
| H | -4.53831029 | 1.32434257 | 1.03446734 |
| H | -4.46962406 | 2.68627756 | -0.04995826 |
| H | -4.16704730 | 3.82365319 | 1.98512351 |
| H | -3.45305470 | 2.42414115 | 2.75665375 |
| H | -0.76214215 | 2.22967511 | 2.64226516 |
| O | -1.73323946 | 4.67387671 | 1.65130141 |
| N | -0.37822083 | 0.61199947 | 0.21346368 |
| C | -0.25476446 | -0.67312921 | -0.19831389 |
| O | 0.69127458 | -1.12329587 | -0.77703439 |

| | | | | | | | |
|---|-------------|-------------|-------------|---|-------------|------------|------------|
| O | -1.32366958 | -1.38660749 | 0.12248536 | B | -2.69927842 | 5.97456264 | 1.78325023 |
| C | -1.31894525 | -2.76034314 | -0.24766627 | F | -3.58616565 | 5.86650904 | 0.76000415 |
| H | -2.26135387 | -3.15551085 | 0.09648079 | F | -3.27628600 | 5.87321832 | 3.00875883 |
| H | -0.49853781 | -3.27556074 | 0.22851638 | F | -1.83447125 | 7.00259478 | 1.66228160 |
| H | -1.23738521 | -2.86110927 | -1.31934716 | | | | |