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Supporting Information

Quantum Mechanics/Molecular Mechanics Study on the Photoreactions of Dark- and Light-Adapted States of a Blue-Light YtvA LOV Photoreceptor

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1. Computational Methods

1.1 System Setup

The initial geometry was constructed from an X-ray structure of YtvA LOV domains (PDB ID: 2PR5, chain A). [1] In this structure, there are two main conformations with different orientations of the Cys62 residue, which are labeled as conf-A and conf-B in Fig. S1. Both are used in our work in order to study possible conformation-dependent spectroscopic properties and excited-state reactions.

The constructed system consisted of 102 amino acids, 252 crystal waters, and a flavin mononucleotide (FMN) cofactor. It was first solvated in an equilibrated water box with a radius of 35 Å (with its origin at the center of mass of the FMN cofactor). The protonation states of ionizable groups were determined using the PDB2PQR web server. [2] The system was then neutralized by adding nine sodium ions on the protein surface near negatively charged residues. A spherical quartic boundary potential was applied to the outer water molecules to prevent them from diffusing away. [3]

To maintain the proper protein structure in the initial MM minimizations, all non-hydrogen atoms of the protein and cofactor were restrained with harmonic potentials and only their hydrogen atoms and the water molecules were allowed to move. The solvated system was first relaxed by performing energy minimizations of 500 steps. Then, successive MD simulations of 15 ps were carried out to heat the system gradually to 300 K, while the force constants of the harmonic restraints to the protein were gradually reduced from 90 to 20 kcal • mol^{-1} • $Å^{-2}$. Finally, all restraints were removed and a production NVT MD of 2 ns was run with a 1 fs time step (T=300K). [3]

In MM minimizations and MD simulations, the protein residues and the FMN cofactor were described with the CHARMM22 all-atom force field [4], and the water molecules were represented by the TIP3P [5] model.

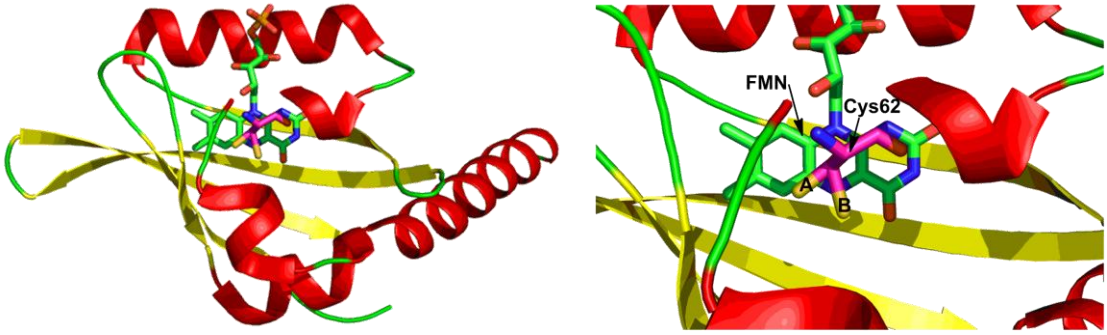


Figure S1. Overview (left) and view (right) into the FMN binding pocket of the YtvA LOV domain (PDB code 2PR5). Shown are the two conformations of the cysteine residue, conf-A and conf-B.

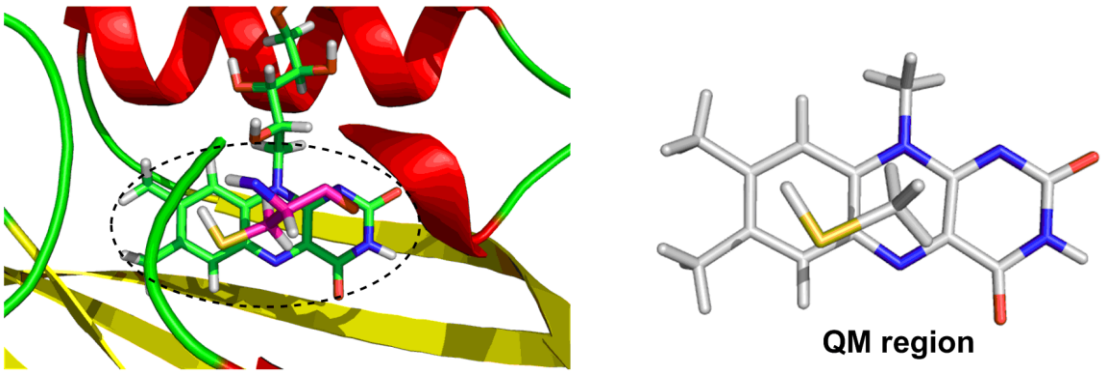


Figure S2. Illustration of binding pocket (left) and selected QM region (right) employed in the QM/MM geometry optimizations.

1.2 QM/MM Method

The QM region in our QM/MM calculations consisted of lumiflavin and the thiol group of the Cys62 residue. The remaining atoms made up the MM region (see Fig. S2). The QM/MM partitioning involved cuts through two covalent bonds between the QM and the MM subsystems. To explore possible conformation-dependent effects, photochemical reactions were

initiated from both conformations (conf-A and conf-B) considering two different orientations of the H atom of the thiol group. Hence, a total of four conformers were studied (AU, AD, BU, and BD).

The QM region was described using the complete-active-space self-consistent field (CASSCF) method. Two-state averaged and state-specific CASSCF calculations were carried out for singlet state (S_1) and for the singlet state (S_0) and triplet state (T_1), respectively. All CASSCF computations made use of an active space of 10 electrons distributed over 8 molecular orbitals (see Fig. S3). Since the CASSCF approach does not treat dynamic correlation, the complete-active-space second-order perturbation (CASPT2) approach [6, 7] was applied to re-evaluate the energies of all optimized structures and paths. The MS-CASPT2 computations employed a larger active space of 12 electrons in 9 molecular orbitals (see Fig. S3). In addition, we used the Cholesky decomposition technique with unbiased auxiliary basis sets for accurate two-electron integral approximations [8] and the imaginary shift technique (0.2 au) to avoid intruder-state issues. [9] The ionization potential electron affinity shift was set to zero. [10, 11] According to our experience, the CASPT2 method without IPEA correction performs better for organic systems, as also shown by González and coworkers. [11]

The MM region was described by the all-atom CHARMM22 force field (protein residues and FMN cofactor) and the TIP3P model (water molecules). [5, 12, 13] The electrostatic embedding scheme [14] was adopted in QM/MM calculations. No cutoffs were imposed for nonbonding QM/MM interactions. Hydrogen link atoms were used at the QM/MM boundary in combination with the charge shift model. [15, 16]

In all QM/MM geometry optimizations, the QM atoms and all MM atoms within 12 Å from the center of mass of the FMN core chromophore were allowed to move. The other atoms were frozen after the 2 ns MD simulations (see above). To obtain detailed mechanistic information, minimum-energy reaction pathways in ground and excited states were computed using constrained geometry optimizations along selected reaction coordinates.

In addition, we employed the QM(UB3LYP)/MM method [17, 18] to study inter-conversion paths of the four conformers in the T_1 state (AU, AD, BD, and BU). Specifically, we optimized T_1 minimum-energy paths (MEPs) that connect either AU and AD or BU and BD, while the conversion between AU and BD was studied with the nudged elastic band (NEB) method. [19-21]

The QM(MS-CASPT2)/MM method was used to calculate vertical excitation energies and oscillator strengths at optimized QM/MM geometries.

The 6-31G* basis set [22, 23] was chosen for all QM(CASSCF)/MM and QM(UB3LYP)/MM calculations. The larger cc-pVTZ basis set [24] was employed for all QM(MS-CASPT2)/MM single-point calculations.

The following codes were used: QM/MM calculations, ChemShell3.5 package; [25] QM(CASSCF), GAUSSIAN09 package; [26] QM(MS-CASPT2), MOLCAS8.0 [27, 28]; MM DL_POLY module [29] as implemented in the ChemShell3.5. [25]

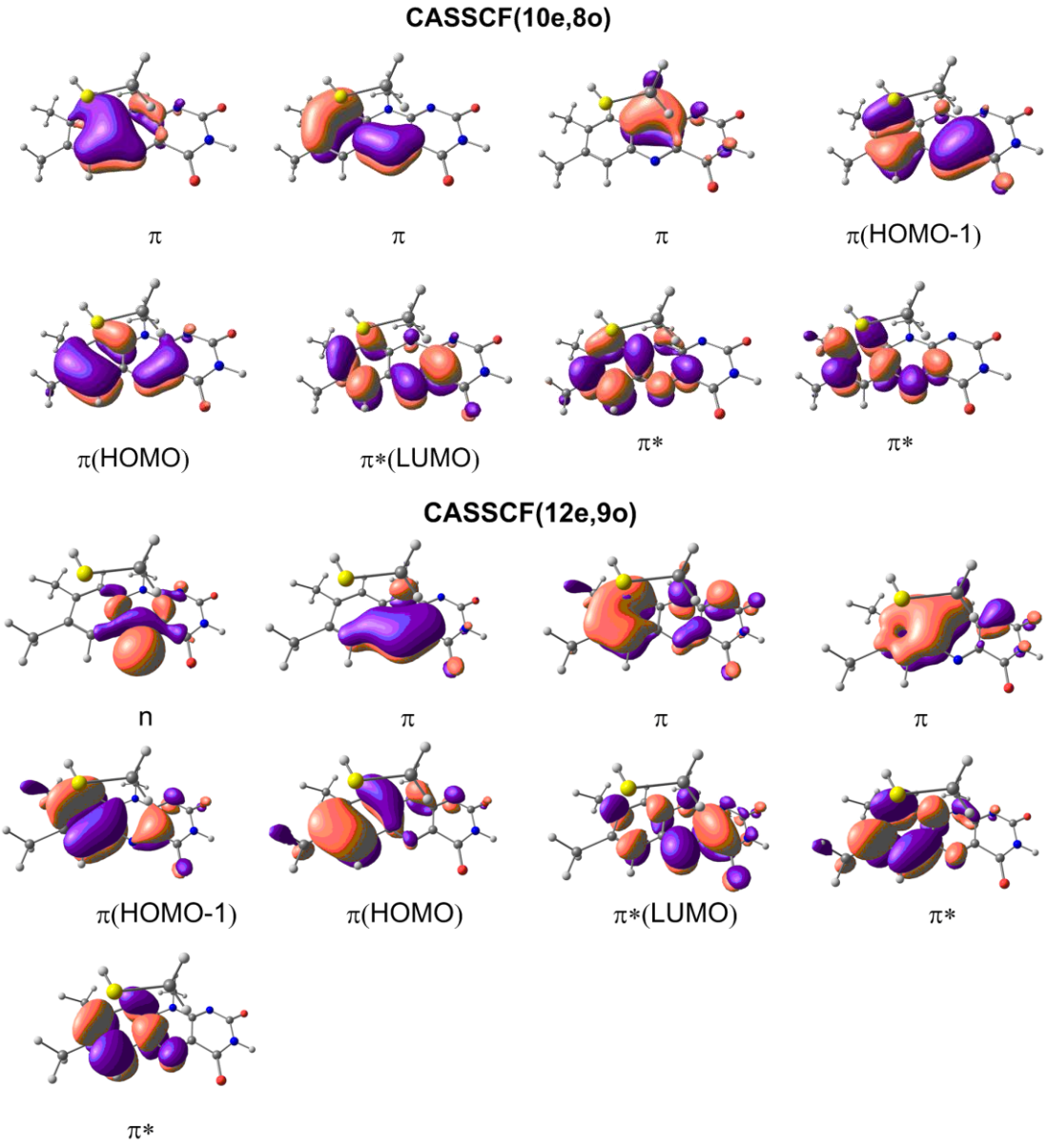
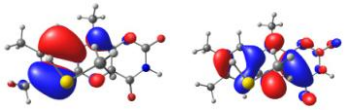
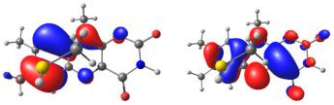
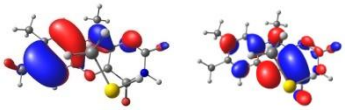
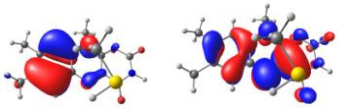
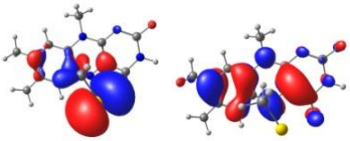
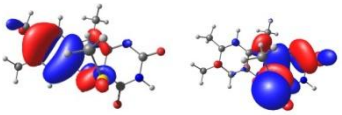


Figure S3. Active spaces used to obtain the CASSCF (top) and MS-CASPT2 (bottom) results (see text). Shown are the natural orbitals from CASSCF calculations.

1.2.1 Vertical Excitation Energies

Table S1. Vertical Excitation Energies ($E_{\perp}$, kcal/mol), Oscillator Strengths (f), and Singly Occupied Orbitals Involved in the $S_0 \rightarrow S_1$ ($^1\pi\pi^*$) Electronic Transition; Computed with the 5-Root State-Averaged QM(MS-CASPT2)/MM Method at the QM(CASSCF)/MM Optimized S_0 Minima.

	$E_{\perp}$	f	singly occupied orbitals
AU	63.7 (448.8 nm)	0.2879	
AD	63.5 (450.2 nm)	0.2839	
BU	63.7(448.8 nm)	0.3112	
BD	63.5 (450.2 nm)	0.3037	
INT	13.2 (2162.5 nm)	_	
P	70.4 (406 nm)	0.2555	

1.2.2 Geometric Parameters of Key Minima

Table S2. Selected Key Geometric Parameters of Stationary Structures Optimized by the QM(CASSCF)/MM Method (Distances in Å and Angles in °).

	Distance		Angle		Dihedral Angle
	N5-H	C4a-S	N5-H-S	H-N5-C4a	S-H-N5-C4a
AU-S0	4.569	4.601	60.5	104.8	-96.5
AU-S1	4.706	4.606	52.3	105.5	-99.3
AU-T1	4.520	4.546	57.7	104.3	-98.1
AD-S0	4.910	4.561	40.1	105.7	104.4

AD-S1	4.900	4.589	41.0	105.8	102.5
AD-T1	4.897	4.607	41.1	106.1	102.3
BU-S0	3.799	3.647	71.3	61.4	175.3
BU-S1	3.779	3.677	72.9	61.5	174.6
BU-T1	3.886	3.569	65.9	59.4	177.3
BD-S0	3.291	3.675	91.6	105.4	8.4
BD-S1	3.260	3.703	93.3	105.7	8.6
BD-T1	3.264	3.669	92.6	104.3	8.8
INT-S0	1.030	3.372	115.4	116.9	72.3
INT-S1	0.997	3.727	83.3	118.3	82.2
INT-T1	1.000	3.720	85.8	118.5	75.4
P-S0	0.997	1.928	67.8	114.1	33.9
P-S1	1.003	1.939	69.6	115.9	37.5
P-T1	0.998	1.906	70.7	114.4	33.3

2. Inter-Conversion Paths

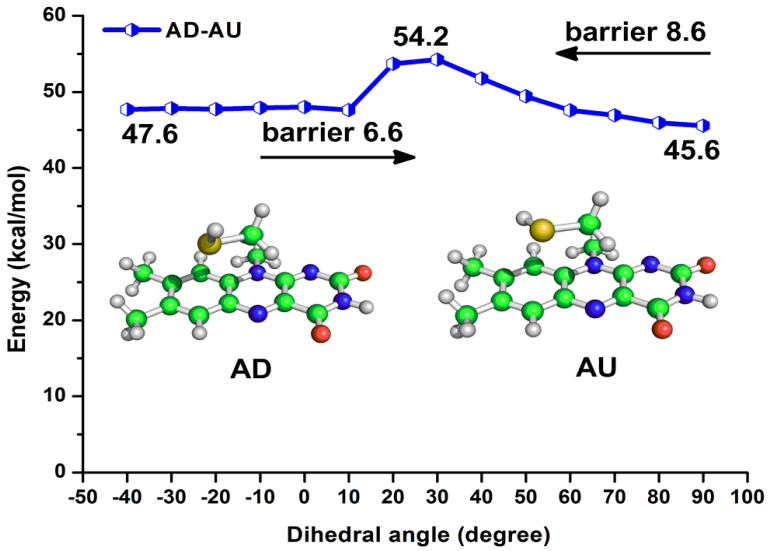


Figure S4. QM(UB3LYP)/MM computed T_1 inter-conversion path with respect to the rotation along the H-C-S-H dihedral angle, which connects the AD and AU conformers.

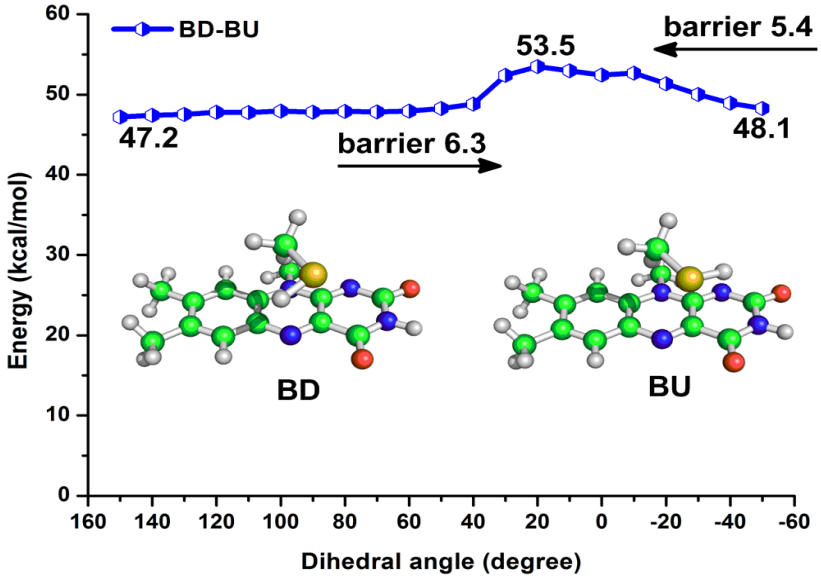


Figure S5. QM(UB3LYP)/MM computed T_1 inter-conversion path with respect to the rotation along the H-C-S-H dihedral angle, which connects the BD and BU conformers.

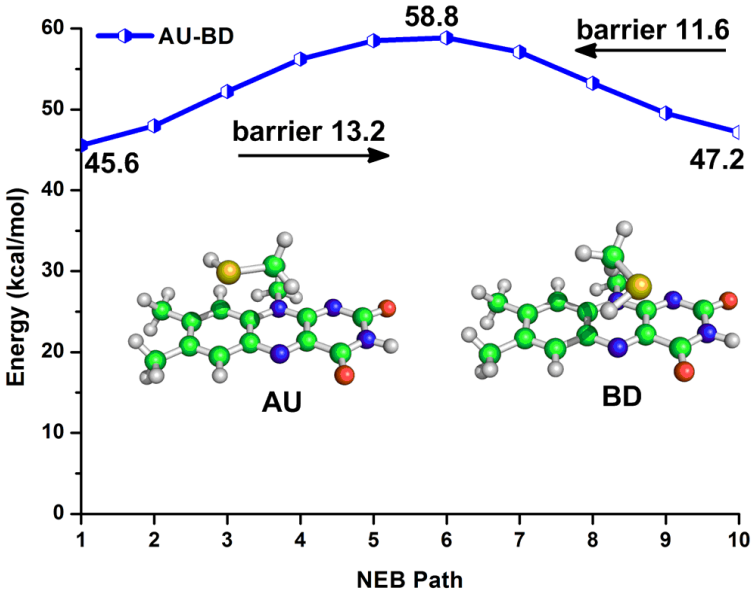


Figure S6. QM(UB3LYP)/MM computed T_1 NEB path connecting AU and BD.

3. Minimum-Energy Paths from AU, AD, and BU

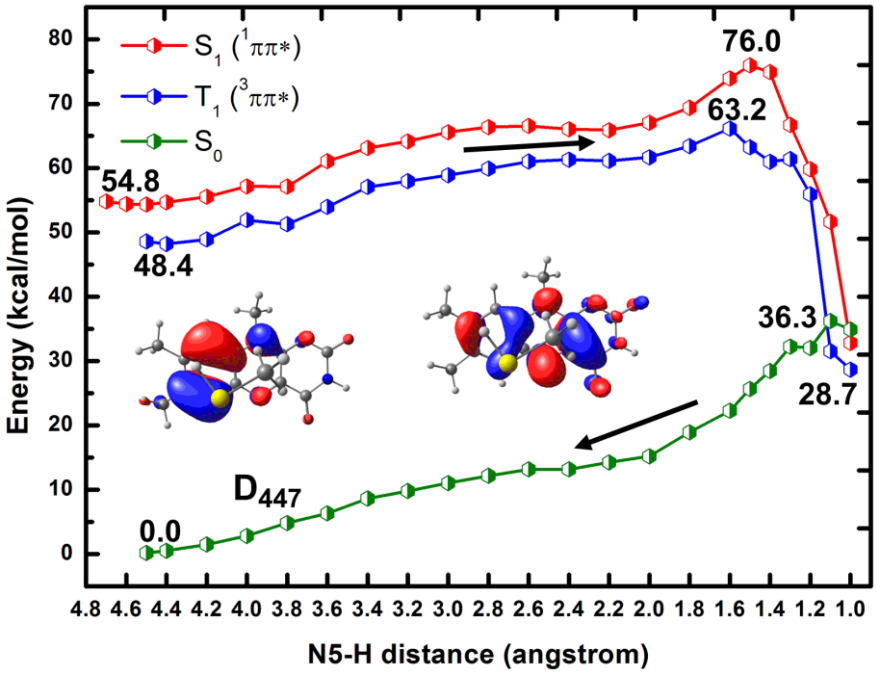


Figure S7. QM(MS-CASPT2//CASSCF)/MM computed minimum-energy reaction paths from AU along the N5-H distance in the S_0, S_1, and T_1 states.

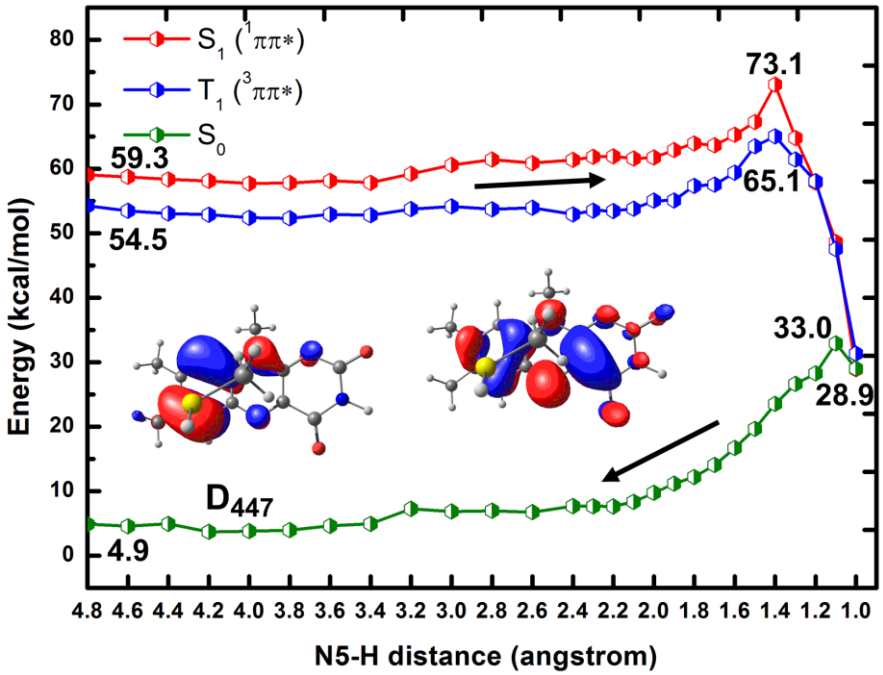


Figure S8. QM(MS-CASPT2//CASSCF)/MM computed minimum-energy reaction paths of AD along the N5-H distance in the S_0, S_1, and T_1 states.

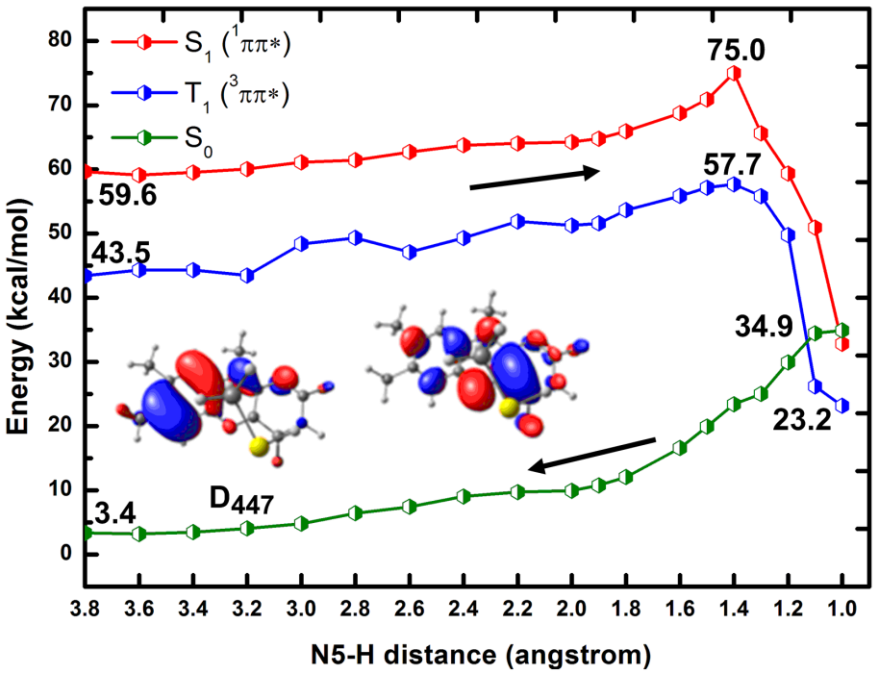


Figure S9. QM(MS-CASPT2//CASSCF)/MM computed minimum-energy reaction paths of BU along the N5-H distance in the S_0, S_1, and T_1 states.

4. Tables

Tables S3-S17 document the energies obtained in the reaction path calculations. The total QM/MM energy can be decomposed into a QM contribution that contains the electrostatic QM-MM interaction energy (denoted as CASSCF A.E. or MS-CASPT2 A.E.) and an MM contribution that contains the van-der-Waals QM-MM interaction energy (denoted as MM). These quantities are given as absolute energies (in Hartree). Also listed are the relative energies at the MS-CASPT2 level (ΔE, in kcal/mol) with respect to the lowest ground-state conformer AU-S0.

Table S3. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from AU-S1 (Reaction Coordinate: N5-H Distance). The Total QM/MM Energy Profiles are Plotted in Figure S7 (Red Line).

(N5-H)	CASSCF A.E.	MS-CASPT2 A.E.	MM	MS-CASPT2 ∆E
S_1-min (4.706)				
Root1 (S_0)	-3091.10440	-1308.65920	-105.503029	3.6
Root2 (S_1)	-3091.00480	-1308.58177		52.2
Root3		-1308.55160		71.2
S_1 (4.70)				
Root1 (S_0)	-3091.10440	-1308.65916	-105.50302	3.7
Root2 (S_1)	-3091.00480	-1308.58175		52.2
Root3		-1308.55157		71.2
S_1 (4.60)				
Root1 (S_0)	-3091.10500	-1308.65914	-105.50391	3.7
Root2 (S_1)	-3091.00400	-1308.58149		52.4
Root3		-1308.55070		71.7
S_1 (4.40)				
Root1 (S_0)	-3091.10400	-1308.65820	-105.50462	4.3
Root2 (S_1)	-3091.00220	-1308.58035		53.1
Root3		-1308.54992		72.2
S_1 (4.20)				
Root1 (S_0)	-3091.10060	-1308.65594	-105.50489	5.7
Root2 (S_1)	-3090.99940	-1308.57871		54.2
Root3		-1308.54875		73.0
S_1 (3.80)				
Root1 (S_0)	-3091.09740	-1308.65263	-105.50364	7.8
Root2 (S_1)	-3090.99480	-1308.57743		55.0
Root3		-1308.55019		72.1
S_1 (3.40)				
Root1 (S_0)	-3091.09810	-1308.64859	-105.50070	10.3
Root2 (S_1)	-3090.99430	-1308.57080		59.1
Root3		-1308.53988		78.5
S_1 (3.00)				
Root1 (S_0)	-3091.09770	-1308.64609	-105.49868	11.9
Root2 (S_1)	-3090.99390	-1308.56891		60.3
Root3		-1308.53740		80.1
S_1 (2.60)				
Root1 (S_0)	-3091.09730	-1308.64540	-105.49678	12.3
Root2 (S_1)	-3090.99610	-1308.56927		60.1
Root3		-1308.53655		80.6

S_1 (2.20)				
Root1 (S_0)	-3091.09040	-1308.64363	-105.49695	13.4
Root2 (S_1)	-3090.99360	-1308.57015		59.5
Root3		-1308.53808		79.7
S_1 (1.80)				
Root1 (S_0)	-3091.07500	-1308.63660	-105.49611	17.8
Root2 (S_1)	-3090.98200	-1308.56545		62.5
Root3		-1308.53405		82.2
S_1 (1.60)				
Root1 (S_0)	-3091.06880	-1308.63580	-105.50117	18.3
Root2 (S_1)	-3090.97490	-1308.56056		65.5
Root3		-1308.53692		80.4
S_1 (1.50)				
Root1 (S_0)	-3091.05730	-1308.62959	-105.50131	22.2
Root2 (S_1)	-3090.96710	-1308.55684		67.9
Root3		-1308.53719		80.2
S_1 (1.40)				
Root1 (S_0)	-3091.04500	-1308.62191	-105.50140	27.0
Root2 (S_1)	-3090.95850	-1308.55135		71.3
Root3		-1308.54639		74.4
S_1 (1.30)				
Root1 (S_0)	-3091.03120	-1308.61578	-105.50117	30.9
Root2 (S_1)	-3090.95110	-1308.56463		63.0
Root3		-1308.54800		73.4
S_1 (1.20)				
Root1 (S_0)	-3091.01710	-1308.60902	-105.50027	35.1
Root2 (S_1)	-3090.94710	-1308.57653		55.5
Root3		-1308.53833		79.5
S_1 (1.10)				
Root1 (S_0)	-3091.00720	-1308.60194	-105.49857	39.6
Root2 (S_1)	-3090.94770	-1308.59124		46.3
Root3		-1308.54742		73.8
S_1 (1.00)				
Root1 (S_0)	-3091.06940	-1308.62198	-105.50200	27.0
Root2 (S_1)	-3091.06540	-1308.61778		29.6
Root3		-1308.55220		70.8

Table S4. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from AU-T1 (Reaction Coordinate: N5-H Distance).The Corresponding Energy Profiles are Plotted in Figure S7 (Blue Line).

(N5-H)	CASSCF A.E.	MS-CASPT2 A.E.	MM	MS-CASPT2 ∆E
T_1-min (4.520)				
Root1 (T_1)	-3091.04080	-1308.58753	-105.50746	48.6
Root2		-1308.56233		64.4
Root3		-1308.54523		75.2
T_1 (4.50)				
Root1 (T_1)	-3091.04090	-1308.58722	-105.50746	48.8
Root2		-1308.56206		64.6
Root3		-1308.54506		75.3
T_1 (4.40)				
Root1 (T_1)	-3091.04000	-1308.58735	-105.50796	48.7
Root2		-1308.56180		64.8
Root3		-1308.54458		75.6
T_1 (4.20)				
Root1 (T_1)	-3091.03740	-1308.58589	-105.50830	49.6
Root2		-1308.56006		65.9
Root3		-1308.54288		76.6
T_1 (3.80)				
Root1 (T_1)	-3091.03360	-1308.58403	-105.50637	50.8
Root2		-1308.57084		59.1
Root3		-1308.52407		88.4
T_1 (3.40)				
Root1 (T_1)	-3091.03210	-1308.57722	-105.50395	55.1
Root2		-1308.55166		71.1
Root3		-1308.53503		81.6
T_1 (3.00)				
Root1 (T_1)	-3091.03050	-1308.57546	-105.50281	56.2
Root2		-1308.54952		72.5
Root3		-1308.53239		83.2
T_1 (2.60)				
Root1 (T_1)	-3091.03120	-1308.57402	-105.50084	57.1
Root2		-1308.54806		73.4
Root3		-1308.52975		84.9
T_1 (2.20)				
Root1 (T_1)	-3091.02660	-1308.57428	-105.50043	56.9
Root2		-1308.54933		72.6
Root3		-1308.52990		84.8

T_1 (1.80)				
Root1 (T_1)	-3091.02000	-1308.57222	-105.49881	58.2
Root2		-1308.54798		73.4
Root3		-1308.52735		86.4
T_1 (1.60)				
Root1 (T_1)	-3091.00730	-1308.56784	-105.49885	61.0
Root2		-1308.54434		75.7
Root3		-1308.53202		83.5
T_1 (1.50)				
Root1 (T_1)	-3090.99850	-1308.56201	-105.49880	64.6
Root2		-1308.53920		78.9
Root3		-1308.53188		83.5
T_1 (1.40)				
Root1 (T_1)	-3090.99330	-1308.56969	-105.50522	59.8
Root2		-1308.54328		76.4
Root3		-1308.53386		82.3
T_1 (1.30)				
Root1 (T_1)	-3090.98700	-1308.57112	-105.50315	58.9
Root2		-1308.55354		69.9
Root3		-1308.53778		79.8
T_1 (1.20)				
Root1 (T_1)	-3090.98190	-1308.58039	-105.50260	53.1
Root2		-1308.56137		65.0
Root3		-1308.54954		72.5
T_1 (1.10)				
Root1 (T_1)	-3091.06580	-1308.62072	-105.50109	27.8
Root2		-1308.61423		31.9
Root3		-1308.52486		87.9
T_1 (1.00)				
Root1 (T_1)	-3091.07250	-1308.62498	-105.50141	25.1
Root2		-1308.61834		29.3
Root3		-1308.53120		84.0

Table S5. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from AU-S0 (Reaction Coordinate: N5-H Distance). The Corresponding Energy Profiles are Plotted in Figure S7 (Green Line).

(N5-H)	CASSCF A.E.	MS-CASPT2 A.E.	MM	MS-CASPT2 ∆E
S_0-min (4.569)				
Root1 (S_0)	-3091.13640	-1308.66500	-105.50711	0.0
Root2 (S_1)		-1308.56356		63.7
Root3		-1308.53980		78.6
S_0 (4.50)				
Root1 (S_0)	-3091.13570	-1308.66443	-105.50739	0.4
Root2 (S_1)		-1308.56291		64.1
Root3		-1308.53952		78.7
S_0 (4.40)				
Root1 (S_0)	-3091.13480	-1308.66374	-105.50754	0.8
Root2 (S_1)		-1308.56222		64.5
Root3		-1308.53898		79.1
S_0 (4.20)				
Root1 (S_0)	-3091.13270	-1308.66211	-105.50760	1.8
Root2 (S_1)		-1308.56079		65.4
Root3		-1308.53783		79.8
S_0 (3.80)				
Root1 (S_0)	-3091.12900	-1308.65797	-105.50643	4.4
Root2 (S_1)		-1308.55658		68.0
Root3		-1308.53360		82.5
S_0 (3.40)				
Root1 (S_0)	-3091.12740	-1308.65407	-105.50426	6.9
Root2 (S_1)		-1308.55247		70.6
Root3		-1308.52875		85.5
S_0 (3.00)				
Root1 (S_0)	-3091.12550	-1308.65089	-105.50362	8.9
Root2 (S_1)		-1308.54982		72.3
Root3		-1308.52562		87.5
S_0 (2.60)				
Root1 (S_0)	-3091.12620	-1308.64934	-105.50179	9.8
Root2 (S_1)		-1308.54865		73.0
Root3		-1308.52349		88.8
S_0 (2.20)				
Root1 (S_0)	-3091.12200	-1308.64842	-105.50098	10.4
Root2 (S_1)		-1308.54949		72.5
Root3		-1308.52503		87.8

S_0 (1.80)				
Root1 (S_0)	-3091.10950	-1308.64182	-105.50012	14.5
Root2 (S_1)		-1308.53210		83.4
Root3		-1308.52375		88.6
S_0 (1.60)				
Root1 (S_0)	-3091.09900	-1308.63812	-105.49849	16.9
Root2 (S_1)		-1308.53005		84.7
Root3		-1308.52558		87.5
S_0 (1.50)				
Root1 (S_0)	-3091.08920	-1308.63237	-105.49883	20.5
Root2 (S_1)		-1308.53290		82.9
Root3		-1308.52688		86.7
S_0 (1.40)				
Root1 (S_0)	-3091.07710	-1308.62796	-105.49879	23.2
Root2 (S_1)		-1308.54729		73.9
Root3		-1308.53636		80.7
S_0 (1.30)				
Root1 (S_0)	-3091.06370	-1308.62194	-105.49875	27.0
Root2 (S_1)		-1308.55415		69.6
Root3		-1308.53254		83.1
S_0 (1.20)				
Root1 (S_0)	-3091.05520	-1308.61768	-105.50334	29.7
Root2 (S_1)		-1308.56700		61.5
Root3		-1308.53889		79.1
S_0 (1.10)				
Root1 (S_0)	-3091.05150	-1308.61623	-105.49812	30.6
Root2 (S_1)		-1308.59343		44.9
Root3		-1308.56599		62.1
S_0 (1.00)				
Root1 (S_0)	-3091.04240	-1308.61612	-105.50033	30.7
Root2 (S_1)		-1308.60072		40.3
Root3		-1308.55969		66.1

Table S6. Absolute Energies (A.E., Hartree), Relative Energies (ΔE, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from AD-S1 (Reaction Coordinate: N5-H Distance). The Corresponding Energy Profiles are Plotted in Figure S8 (Red Line).

(N5-H)	CASSCF A.E.	MS-CASPT2 A.E.	MM	MS-CASPT2 ΔE
S_1-min (4.900)				
Root1 (S_0)	-3091.10810	-1308.65130	-105.50419	8.6
Root2 (S_1)	-3091.00480	-1308.57346		57.4
Root3		-1308.54162		77.4
S_1 (4.80)				
Root1 (S_0)	-3091.10760	-1308.65157	-105.50405	8.4
Root2 (S_1)	-3091.00460	-1308.57398		57.1
Root3		-1308.54228		77.0
S_1 (4.60)				
Root1 (S_0)	-3091.10660	-1308.65317	-105.50246	7.4
Root2 (S_1)	-3091.00500	-1308.57599		55.9
Root3		-1308.54442		75.7
S_1 (4.40)				
Root1 (S_0)	-3091.10530	-1308.65336	-105.50244	7.3
Root2 (S_1)	-3091.00430	-1308.57664		55.5
Root3		-1308.54564		74.9
S_1 (4.20)				
Root1 (S_0)	-3091.10490	-1308.65393	-105.50225	7.0
Root2 (S_1)	-3091.00430	-1308.57724		55.1
Root3		-1308.54651		74.4
S_1 (3.80)				
Root1 (S_0)	-3091.10240	-1308.65346	-105.50276	7.2
Root2 (S_1)	-3091.00260	-1308.57722		55.1
Root3		-1308.54635		74.5
S_1 (3.40)				
Root1 (S_0)	-3091.10220	-1308.65279	-105.50320	7.7
Root2 (S_1)	-3091.00260	-1308.57676		55.4
Root3		-1308.54509		75.2
S_1 (3.00)				
Root1 (S_0)	-3091.10380	-1308.65212	-105.50339	8.1
Root2 (S_1)	-3091.00370	-1308.57213		58.3
Root3		-1308.54373		76.1
S_1 (2.60)				
Root1 (S_0)	-3091.10290	-1308.65085	-105.50369	8.9
Root2 (S_1)	-3091.00260	-1308.57136		58.8
Root3		-1308.54272		76.7

S_1 (2.20)				
Root1 (S_0)	-3091.09660	-1308.64866	-105.50319	10.3
Root2 (S_1)	-3090.99790	-1308.57019		59.5
Root3		-1308.54217		77.1
S_1 (1.80)				
Root1 (S_0)	-3091.08240	-1308.64402	-105.50203	13.2
Root2 (S_1)	-3090.98840	-1308.56818		60.8
Root3		-1308.54067		78.0
S_1 (1.60)				
Root1 (S_0)	-3091.07220	-1308.63673	-105.50067	17.7
Root2 (S_1)	-3090.98070	-1308.56740		61.2
Root3		-1308.53459		81.8
S_1 (1.50)				
Root1 (S_0)	-3091.06160	-1308.63125	-105.50075	21.2
Root2 (S_1)	-3090.97330	-1308.55436		69.4
Root3		-1308.54138		77.6
S_1 (1.40)				
Root1 (S_0)	-3091.04760	-1308.62273	-105.50323	26.5
Root2 (S_1)	-3090.96260	-1308.55244		70.6
Root3		-1308.54795		73.5
S_1 (1.30)				
Root1 (S_0)	-3091.03410	-1308.61714	-105.50321	30.0
Root2 (S_1)	-3090.95530	-1308.56564		62.4
Root3		-1308.55125		71.4
S_1 (1.20)				
Root1 (S_0)	-3091.02460	-1308.61207	-105.50448	33.2
Root2 (S_1)	-3090.95100	-1308.57542		56.2
Root3		-1308.53836		79.5
S_1 (1.10)				
Root1 (S_0)	-3091.01630	-1308.61256	-105.50082	32.9
Root2 (S_1)	-3090.95320	-1308.59377		44.7
Root3		-1308.55410		69.6
S_1 (1.00)				
Root1 (S_0)	-3091.07030	-1308.62333	-105.50725	26.2
Root2 (S_1)	-3091.06580	-1308.61877		29.0
Root3		-1308.55534		68.8

Table S7. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from AD-T1 (Reaction Coordinate: N5-H Distance).The Corresponding Energy Profiles are Plotted in Figure S8 (Blue Line).

(N5-H)	CASSCF A.E.	MS-CASPT2 A.E.	MM	MS-CASPT2 ∆E
T_1-min (4.897)				
Root1 (T_1)	-3091.03690	-1308.58297	-105.50232	51.5
Root2		-1308.56861		60.5
Root3		-1308.54294		76.6
T_1 (4.80)				
Root1 (T_1)	-3091.03650	-1308.58371	-105.50194	51.0
Root2		-1308.56914		60.2
Root3		-1308.54313		76.5
T_1 (4.60)				
Root1 (T_1)	-3091.03650	-1308.58523	-105.50164	50.1
Root2		-1308.57090		59.1
Root3		-1308.54421		75.8
T_1 (4.40)				
Root1 (T_1)	-3091.03680	-1308.58684	-105.50071	49.1
Root2		-1308.57230		58.2
Root3		-1308.54554		75.0
T_1 (4.20)				
Root1 (T_1)	-3091.03480	-1308.58714	-105.50067	48.9
Root2		-1308.57255		58.0
Root3		-1308.54545		75.0
T_1 (3.80)				
Root1 (T_1)	-3091.03520	-1308.58798	-105.50070	48.3
Root2		-1308.57301		57.7
Root3		-1308.54538		75.1
T_1 (3.40)				
Root1 (T_1)	-3091.03520	-1308.58688	-105.50108	49.0
Root2		-1308.57104		59.0
Root3		-1308.54383		76.0
T_1 (3.00)				
Root1 (T_1)	-3091.03680	-1308.58499	-105.50080	50.2
Root2		-1308.56885		60.3
Root3		-1308.54212		77.1
T_1 (2.60)				
Root1 (T_1)	-3091.03540	-1308.58502	-105.50109	50.2
Root2		-1308.56886		60.3
Root3		-1308.54122		77.7

T_1 (2.20)				
Root1 (T_1)	-3091.03110	-1308.58612	-105.50077	49.5
Root2		-1308.57029		59.4
Root3		-1308.54211		77.1
T_1 (1.80)				
Root1 (T_1)	-3091.01570	-1308.57979	-105.50091	53.5
Root2		-1308.56204		64.6
Root3		-1308.53094		84.1
T_1 (1.60)				
Root1 (T_1)	-3091.01180	-1308.57903	-105.49840	53.9
Root2		-1308.55829		67.0
Root3		-1308.53135		83.9
T_1 (1.50)				
Root1 (T_1)	-3091.00400	-1308.57232	-105.49860	58.2
Root2		-1308.55677		67.9
Root3		-1308.54306		76.5
T_1 (1.40)				
Root1 (T_1)	-3090.99610	-1308.56989	-105.49855	59.7
Root2		-1308.56131		65.1
Root3		-1308.54418		75.8
T_1 (1.30)				
Root1 (T_1)	-3090.99010	-1308.57537	-105.49880	56.2
Root2		-1308.56774		61.0
Root3		-1308.54805		73.4
T_1 (1.20)				
Root1 (T_1)	-3090.98730	-1308.58098	-105.49856	52.7
Root2		-1308.56826		60.7
Root3		-1308.56132		65.1
T_1 (1.10)				
Root1 (T_1)	-3090.98760	-1308.59838	-105.49799	41.8
Root2		-1308.58395		50.9
Root3		-1308.55184		71.0
T_1 (1.00)				
Root1 (T_1)	-3090.98680	-1308.62518	-105.49699	25.0
Root2		-1308.61738		29.9
Root3		-1308.53195		83.5

Table S8. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from AD-S0 (Reaction Coordinate: N5-H Distance).The Corresponding Energy Profiles are Plotted in Figure S8 (Green Line).

(N5-H)	CASSCF A.E.	MS-CASPT2 A.E.	MM	MS-CASPT2 ∆E
S_0-min (4.910)				
Root1 (S_0)	-3091.13820	-1308.65770	-105.50662	4.6
Root2 (S_1)		-1308.55653		68.1
Root3		-1308.53173		83.6
S_0 (4.80)				
Root1 (S_0)	-3091.13750	-1308.65754	-105.50675	4.7
Root2 (S_1)		-1308.55679		67.9
Root3		-1308.53223		83.3
S_0 (4.60)				
Root1 (S_0)	-3091.13760	-1308.65843	-105.50637	4.1
Root2 (S_1)		-1308.55796		67.2
Root3		-1308.53396		82.2
S_0 (4.40)				
Root1 (S_0)	-3091.13470	-1308.65798	-105.50625	4.4
Root2 (S_1)		-1308.55787		67.2
Root3		-1308.53424		82.1
S_0 (4.20)				
Root1 (S_0)	-3091.13560	-1308.65965	-105.50653	3.4
Root2 (S_1)		-1308.55897		66.5
Root3		-1308.53480		81.7
S_0 (3.80)				
Root1 (S_0)	-3091.13460	-1308.65915	-105.50664	3.7
Root2 (S_1)		-1308.55893		66.6
Root3		-1308.53497		81.6
S_0 (3.40)				
Root1 (S_0)	-3091.13330	-1308.65722	-105.50701	4.9
Root2 (S_1)		-1308.55732		67.6
Root3		-1308.53282		83.0
S_0 (3.00)				
Root1 (S_0)	-3091.13660	-1308.65451	-105.50664	6.6
Root2 (S_1)		-1308.55433		69.5
Root3		-1308.52804		86.0
S_0 (2.60)				
Root1 (S_0)	-3091.13300	-1308.65368	-105.50764	7.1
Root2 (S_1)		-1308.55444		69.4
Root3		-1308.52818		85.9

S_0 (2.20)				
Root1 (S_0)	-3091.12890	-1308.65327	-105.50667	7.4
Root2 (S_1)		-1308.55502		69.0
Root3		-1308.52891		85.4
S_0 (1.80)				
Root1 (S_0)	-3091.11680	-1308.64744	-105.50525	11.0
Root2 (S_1)		-1308.53767		79.9
Root3		-1308.52591		87.3
S_0 (1.60)				
Root1 (S_0)	-3091.10300	-1308.63999	-105.50552	15.7
Root2 (S_1)		-1308.53306		82.8
Root3		-1308.52659		86.9
S_0 (1.50)				
Root1 (S_0)	-3091.09300	-1308.63517	-105.50558	18.7
Root2 (S_1)		-1308.54033		78.2
Root3		-1308.53942		78.8
S_0 (1.40)				
Root1 (S_0)	-3091.08070	-1308.62903	-105.50554	22.6
Root2 (S_1)		-1308.54767		73.6
Root3		-1308.53862		79.3
S_0 (1.30)				
Root1 (S_0)	-3091.06770	-1308.62480	-105.50483	25.2
Root2 (S_1)		-1308.55530		68.8
Root3		-1308.52791		86.0
S_0 (1.20)				
Root1 (S_0)	-3091.05880	-1308.61889	-105.50813	28.9
Root2 (S_1)		-1308.56866		60.5
Root3		-1308.54042		78.2
S_0 (1.10)				
Root1 (S_0)	-3091.05200	-1308.61497	-105.50463	31.4
Root2 (S_1)		-1308.59183		45.9
Root3		-1308.56488		62.8
S_0 (1.00)				
Root1 (S_0)	-3091.05150	-1308.62264	-105.50319	26.6
Root2 (S_1)		-1308.59981		40.9
Root3		-1308.56417		63.3

Table S9. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from BU-S1 (Reaction Coordinate: N5-H Distance). The Corresponding Energy Profiles are Plotted in Figure S9 (Red Line).

(N5-H)	CASSCF A.E.	MS-CASPT2 A.E.	MM	MS-CASPT2 ∆E
S_1-min (3.779)				
Root1 (S_0)	-3091.10120	-1308.64901	-105.50836	10.0
Root2 (S_1)	-3090.99420	-1308.57422		57.0
Root3		-1308.54378		76.1
S_1 (3.60)				
Root1 (S_0)	-3091.10090	-1308.65203	-105.50829	8.1
Root2 (S_1)	-3090.99400	-1308.56964		59.8
Root3		-1308.53937		78.8
S_1 (3.40)				
Root1 (S_0)	-3091.09930	-1308.65167	-105.50754	8.4
Root2 (S_1)	-3090.99360	-1308.56973		59.8
Root3		-1308.53924		78.9
S_1 (3.00)				
Root1 (S_0)	-3091.09650	-1308.65059	-105.50570	9.0
Root2 (S_1)	-3090.99210	-1308.56904		60.2
Root3		-1308.53896		79.1
S_1 (2.60)				
Root1 (S_0)	-3091.09140	-1308.64705	-105.50528	11.3
Root2 (S_1)	-3090.98920	-1308.56689		61.6
Root3		-1308.53652		80.6
S_1 (2.20)				
Root1 (S_0)	-3091.08770	-1308.64560	-105.50387	12.2
Root2 (S_1)	-3090.98630	-1308.56617		62.0
Root3		-1308.53559		81.2
S_1 (1.80)				
Root1 (S_0)	-3091.07640	-1308.64061	-105.50368	15.3
Root2 (S_1)	-3090.97790	-1308.56333		63.8
Root3		-1308.53503		81.6
S_1 (1.60)				
Root1 (S_0)	-3091.06120	-1308.63307	-105.50413	20.0
Root2 (S_1)	-3090.96620	-1308.55840		66.9
Root3		-1308.53287		82.9
S_1 (1.50)				
Root1 (S_0)	-3091.05000	-1308.62510	-105.50412	25.0
Root2 (S_1)	-3090.95900	-1308.54754		73.7
Root3		-1308.53721		80.2

S_1 (1.40)				
Root1 (S_0)	-3091.04400	-1308.62523	-105.50173	25.0
Root2 (S_1)	-3090.95450	-1308.55087		71.6
Root3		-1308.54781		73.5
S_1 (1.30)				
Root1 (S_0)	-3091.03070	-1308.61867	-105.50194	29.1
Root2 (S_1)	-3090.94760	-1308.56559		62.4
Root3		-1308.55081		71.7
S_1 (1.20)				
Root1 (S_0)	-3091.01720	-1308.61269	-105.50131	32.8
Root2 (S_1)	-3090.94370	-1308.57621		55.7
Root3		-1308.53925		78.9
S_1 (1.10)				
Root1 (S_0)	-3091.01080	-1308.61485	-105.49579	31.5
Root2 (S_1)	-3090.94790	-1308.59514		43.8
Root3		-1308.55641		68.1

Table S10. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from BU-T1 (Reaction Coordinate: N5-H Distance). The Corresponding Energy Profiles are Plotted in Figure S9 (Blue Line).

(N5-H)	**CASSCF A.E.**	**MS-CASPT2 A.E.**	**MM**	**MS-CASPT2 ∆E**
T_1-min (3.886)				
Root1 (T_1)	-3091.04450	-1308.58701	-105.51578	48.9
Root2		-1308.56492		62.8
Root3		-1308.54274		76.7
T_1 (3.60)				
Root1 (T_1)	-3091.04420	-1308.58603	-105.51542	49.6
Root2		-1308.56425		63.2
Root3		-1308.54097		77.8
T_1 (3.40)				
Root1 (T_1)	-3091.04230	-1308.58607	-105.51544	49.5
Root2		-1308.56568		62.3
Root3		-1308.54273		76.7
T_1 (3.00)				
Root1 (T_1)	-3091.04020	-1308.58066	-105.51435	52.9
Root2		-1308.55477		69.2
Root3		-1308.54076		78.0
T_1 (2.60)				

Root1 (T_1)	-3091.03870	-1308.58484		50.3
Root2		-1308.56402	-105.51224	63.4
Root3		-1308.52003		91.0
T_1 (2.20)				
Root1 (T_1)	-3091.03690	-1308.57857		54.2
Root2		-1308.55491	-105.51086	69.1
Root3		-1308.54275		76.7
T_1 (1.80)				
Root1 (T_1)	-3091.02780	-1308.57537		56.2
Root2		-1308.55165	-105.51124	71.1
Root3		-1308.49741		105.2
T_1 (1.60)				
Root1 (T_1)	-3091.01640	-1308.57141		58.7
Root2		-1308.54618	-105.51165	74.6
Root3		-1308.51292		95.4
T_1 (1.50)				
Root1 (T_1)	-3091.00900	-1308.56926		60.1
Root2		-1308.53707	-105.51175	80.3
Root3		-1308.53389		82.3
T_1 (1.40)				
Root1 (T_1)	-3091.00050	-1308.56850		60.6
Root2		-1308.54393	-105.51169	76.0
Root3		-1308.53194		83.5
T_1 (1.30)				
Root1 (T_1)	-3090.99180	-1308.57149		58.7
Root2		-1308.55506	-105.51164	69.0
Root3		-1308.53823		79.6
T_1 (1.20)				
Root1 (T_1)	-3090.98730	-1308.58243		51.8
Root2		-1308.56305	-105.51038	64.0
Root3		-1308.54998		72.2
T_1 (1.10)				
Root1 (T_1)	-3091.06640	-1308.62293		26.4
Root2		-1308.61589	-105.50740	30.8
Root3		-1308.52889		85.4

Table S11. Absolute Energies (A.E., Hartree), Relative Energies (ΔE, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from BU-S0 (Reaction Coordinate: N5-H Distance). The Corresponding Energy Profiles are Plotted in Figure S9 (Green Line).

(N5-H)	CASSCF A.E.	MS-CASPT2 A.E.	MM	MS-CASPT2 ΔE
S_0-min (3.799)				
Root1 (S_0)	-3091.13080	-1308.65591	-105.51084	5.7
Root2 (S_1)		-1308.55442		69.4
Root3		-1308.52690		86.7
S_0 (3.60)				
Root1 (S_0)	-3091.12970	-1308.65604	-105.51096	5.6
Root2 (S_1)		-1308.55481		69.1
Root3		-1308.52823		85.8
S_0 (3.40)				
Root1 (S_0)	-3091.12850	-1308.65563	-105.51088	5.9
Root2 (S_1)		-1308.55485		69.1
Root3		-1308.52832		85.8
S_0 (3.00)				
Root1 (S_0)	-3091.12530	-1308.65419	-105.51026	6.8
Root2 (S_1)		-1308.55388		69.7
Root3		-1308.52722		86.5
S_0 (2.60)				
Root1 (S_0)	-3091.12250	-1308.65163	-105.50858	8.4
Root2 (S_1)		-1308.55198		70.9
Root3		-1308.52501		87.9
S_0 (2.20)				
Root1 (S_0)	-3091.11850	-1308.64934	-105.50727	9.8
Root2 (S_1)		-1308.55035		71.9
Root3		-1308.52258		89.4
S_0 (1.80)				
Root1 (S_0)	-3091.10790	-1308.64591	-105.50696	12.0
Root2 (S_1)		-1308.54931		72.6
Root3		-1308.52072		90.5
S_0 (1.60)				
Root1 (S_0)	-3091.09480	-1308.63868	-105.50699	16.5
Root2 (S_1)		-1308.53015		84.6
Root3		-1308.52118		90.3
S_0 (1.50)				
Root1 (S_0)	-3091.08530	-1308.63330	-105.50702	19.9
Root2 (S_1)		-1308.53207		83.4
Root3		-1308.52525		87.7

S_0 (1.40)				
Root1 (S_0)	-3091.07270	-1308.62768	-105.50711	23.4
Root2 (S_1)		-1308.54736		73.8
Root3		-1308.52818		85.9
S_0 (1.30)				
Root1 (S_0)	-3091.06580	-1308.62778	-105.50445	23.4
Root2 (S_1)		-1308.55527		68.9
Root3		-1308.52514		87.8
S_0 (1.20)				
Root1 (S_0)	-3091.05110	-1308.61975	-105.50463	28.4
Root2 (S_1)		-1308.56851		60.6
Root3		-1308.54016		78.3
S_0 (1.10)				
Root1 (S_0)	-3091.04790	-1308.61694	-105.50026	30.2
Root2 (S_1)		-1308.59297		45.2
Root3		-1308.56664		61.7

Table S12. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from BD-S1 (Reaction Coordinate: N5-H Distance). The Corresponding Energy Profiles are Plotted in Figure S10 (Red Line).

(N5-H)	**CASSCF A.E.**	**MS-CASPT2 A.E.**	**MM**	**MS-CASPT2 ∆E**
S_1-min (3.260)				
Root1 (S_0)	-3091.10440	-1308.64520	-105.51260	12.4
Root2 (S_1)	-3090.99350	-1308.56290		64.1
Root3		-1308.53104		84.1
S_1 (3.10)				
Root1 (S_0)	-3091.10300	-1308.64576	-105.51199	12.1
Root2 (S_1)	-3090.99370	-1308.56398		63.4
Root3		-1308.53203		83.4
S_1 (2.90)				
Root1 (S_0)	-3091.10130	-1308.64527	-105.51176	12.4
Root2 (S_1)	-3090.99340	-1308.56429		63.2
Root3		-1308.53214		83.4
S_1 (2.70)				
Root1 (S_0)	-3091.10040	-1308.64596	-105.51144	12.0
Root2 (S_1)	-3090.99300	-1308.56540		62.5

Root3		-1308.53308		82.8
S_1 (2.50)				
Root1 (S_0)	-3091.10000	-1308.64679		11.4
Root2 (S_1)	-3090.99410	-1308.56652	-105.51040	61.8
Root3		-1308.53464		81.8
S_1 (2.30)				
Root1 (S_0)	-3091.09910	-1308.64722		11.2
Root2 (S_1)	-3090.99510	-1308.56768	-105.50977	61.1
Root3		-1308.53637		80.7
S_1 (2.10)				
Root1 (S_0)	-3091.09370	-1308.64518		12.4
Root2 (S_1)	-3090.99170	-1308.56686	-105.51026	61.6
Root3		-1308.53562		81.2
S_1 (1.90)				
Root1 (S_0)	-3091.08620	-1308.64167		14.6
Root2 (S_1)	-3090.98660	-1308.56458	-105.51076	63.0
Root3		-1308.53525		81.4
S_1 (1.70)				
Root1 (S_0)	-3091.07450	-1308.63614		18.1
Root2 (S_1)	-3090.97800	-1308.56087	-105.51107	65.3
Root3		-1308.53330		82.7
S_1 (1.60)				
Root1 (S_0)	-3091.06510	-1308.63069		21.5
Root2 (S_1)	-3090.97210	-1308.55768	-105.51107	67.3
Root3		-1308.53175		83.6
S_1 (1.50)				
Root1 (S_0)	-3091.05920	-1308.62819		23.1
Root2 (S_1)	-3090.96700	-1308.55572	-105.51076	68.6
Root3		-1308.53566		81.2
S_1 (1.40)				
Root1 (S_0)	-3091.04590	-1308.61924		28.7
Root2 (S_1)	-3090.95890	-1308.54933	-105.51081	72.6
Root3		-1308.54426		75.8
S_1 (1.30)				
Root1 (S_0)	-3091.03180	-1308.61323		32.5
Root2 (S_1)	-3090.95130	-1308.55927	-105.51076	66.4
Root3		-1308.54120		77.7
S_1 (1.20)				
Root1 (S_0)	-3091.01840	-1308.60670		36.6
Root2 (S_1)	-3090.94840	-1308.57421	-105.50993	57.0
Root3		-1308.53610		80.9
S_1 (1.10)				
Root1 (S_0)	-3091.00880	-1308.60117		40.1
Root2 (S_1)	-3090.94960	-1308.58936	-105.50858	47.5
Root3		-1308.54741		73.8

Table S13. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from BD-T1 (Reaction Coordinate: N5-H Distance). The Corresponding Energy Profiles are Plotted in Figure S10 (Blue Line).

(N5-H)	CASSCF A.E.	MS-CASPT2 A.E.	MM	MS-CASPT2 ∆E
T_1-min (3.264)				
Root1 (T_1)	-3091.04220	-1308.57619	-105.51359	55.7
Root2		-1308.55114		71.5
Root3		-1308.54145		77.5
T_1 (3.10)				
Root1 (T_1)	-3091.04190	-1308.57650	-105.51372	55.5
Root2		-1308.55182		71.0
Root3		-1308.54056		78.1
T_1 (2.90)				
Root1 (T_1)	-3091.04110	-1308.57664	-105.51376	55.5
Root2		-1308.55197		70.9
Root3		-1308.54008		78.4
T_1 (2.70)				
Root1 (T_1)	-3091.04160	-1308.57714	-105.51340	55.1
Root2		-1308.55219		70.8
Root3		-1308.54033		78.2
T_1 (2.50)				
Root1 (T_1)	-3091.04060	-1308.57702	-105.51320	55.2
Root2		-1308.54925		72.6
Root3		-1308.53111		84.0
T_1 (2.30)				
Root1 (T_1)	-3091.03930	-1308.57744	-105.51303	55.0
Root2		-1308.54977		72.3
Root3		-1308.53077		84.2
T_1 (2.10)				
Root1 (T_1)	-3091.03600	-1308.57663	-105.51331	55.5
Root2		-1308.54905		72.8
Root3		-1308.52903		85.3
T_1 (1.90)				
Root1 (T_1)	-3091.03090	-1308.57369	105.51371	57.3
Root2		-1308.55041		71.9
Root3		-1308.49560		106.3
T_1 (1.70)				
Root1 (T_1)	-3091.02290	-1308.57149	-105.51387	58.7
Root2		-1308.54739		73.8
Root3		-1308.50031		103.4

T_1 (1.60)				
Root1 (T_1)	-3091.01660	-1308.56966	-105.51394	59.8
Root2		-1308.54510		75.2
Root3		-1308.52329		88.9
T_1 (1.50)				
Root1 (T_1)	-3091.00840	-1308.56738	-105.51405	61.3
Root2		-1308.53960		78.7
Root3		-1308.53197		83.5
T_1 (1.40)				
Root1 (T_1)	-3091.00080	-1308.56786	-105.51387	61.0
Root2		-1308.54329		76.4
Root3		-1308.53008		84.7
T_1 (1.30)				
Root1 (T_1)	-3090.99160	-1308.57188	-105.51384	58.4
Root2		-1308.55267		70.5
Root3		-1308.53737		80.1
T_1 (1.20)				
Root1 (T_1)	-3090.98690	-1308.58128	-105.51244	52.5
Root2		-1308.56103		65.2
Root3		-1308.54776		73.6
T_1 (1.10)				
Root1 (T_1)	-3091.06850	-1308.62097	-105.50906	27.6
Root2		-1308.61441		31.8
Root3		-1308.52694		86.6

Table S14. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for N5-H Bond Formation from BD-S0 (Reaction Coordinate: N5-H Distance). The Corresponding Energy Profiles are Plotted in Figure S10 (Green Line).

(N5-H)	**CASSCF A.E.**	**MS-CASPT2 A.E.**	**MM**	**MS-CASPT2 ∆E**
S_0-min (3.291)				
Root1 (S_0)	-3091.13630	-1308.65013	-105.51498	9.3
Root2 (S_1)		-1308.54893		72.8
Root3		-1308.52006		91.0
S_0 (3.10)				
Root1 (S_0)	-3091.13570	-1308.65021	-105.51497	9.3
Root2 (S_1)		-1308.54932		72.6
Root3		-1308.52085		90.5
S_0 (2.90)				

Root1 (S_0)	-3091.13590	-1308.65058		9.1
Root2 (S_1)		-1308.54988	-105.51462	72.2
Root3		-1308.52104		90.3
S_0 (2.70)				
Root1 (S_0)	-3091.13420	-1308.65042		9.2
Root2 (S_1)		-1308.54999	-105.51463	72.2
Root3		-1308.52111		90.3
S_0 (2.50)				
Root1 (S_0)	-3091.13400	-1308.65074		9.0
Root2 (S_1)		-1308.55073	-105.51422	71.7
Root3		-1308.52141		90.1
S_0 (2.30)				
Root1 (S_0)	-3091.13070	-1308.64971		9.6
Root2 (S_1)		-1308.55049	-105.51443	71.9
Root3		-1308.52127		90.2
S_0 (2.10)				
Root1 (S_0)	-3091.12840	-1308.64875		10.2
Root2 (S_1)		-1308.53632	-105.51422	80.8
Root3		-1308.52004		91.0
S_0 (1.90)				
Root1 (S_0)	-3091.12140	-1308.64606		11.9
Root2 (S_1)		-1308.53485	-105.51458	81.7
Root3		-1308.52001		91.0
S_0 (1.70)				
Root1 (S_0)	-3091.11170	-1308.64173		14.6
Root2 (S_1)		-1308.53256	-105.51453	83.1
Root3		-1308.52081		90.5
S_0 (1.60)				
Root1 (S_0)	-3091.10320	-1308.63697		17.6
Root2 (S_1)		-1308.52985	-105.51466	84.8
Root3		-1308.52275		89.3
S_0 (1.50)				
Root1 (S_0)	-3091.09340	-1308.63163		20.9
Root2 (S_1)		-1308.53501	-105.51476	81.6
Root3		-1308.52518		87.7
S_0 (1.40)				
Root1 (S_0)	-3091.08100	-1308.62617		24.4
Root2 (S_1)		-1308.54803	-105.51480	73.4
Root3		-1308.52561		87.5
S_0 (1.30)				
Root1 (S_0)	-3091.07370	-1308.62697		23.9
Root2 (S_1)		-1308.55708	-105.51064	67.7
Root3		-1308.52466		88.1
S_0 (1.20)				
Root1 (S_0)	-3091.06130	-1308.62124		27.5
Root2 (S_1)		-1308.57157	-105.51066	58.6
Root3		-1308.54206		77.1

S_0 (1.10)				
Root1 (S_0)	-3091.05310	-1308.61464	-105.50960	31.6
Root2 (S_1)		-1308.59067		46.6
Root3		-1308.55920		66.4

Table S15. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM energies (Hartree) of Optimized Structures for C4a-S Bond Formation from INT-S1 (Reaction Coordinate: C4a-S Distance). The Corresponding Energy Profiles are Plotted in Figure 3 (Red Line).

(C4a-S)	**CASSCF A.E.**	**MS-CASPT2 A.E.**	**MM**	**MS-CASPT2 ∆E**
S_1-min (3.727)				
Root1 (S_0)	-3091.06960	-1308.62204	-105.50212	27.0
Root2 (S_1)	-3091.06560	-1308.61784		29.6
Root3		-1308.55210		70.8
S_1 (3.70)				
Root1 (S_0)	-3091.06980	-1308.62239	-105.50233	26.7
Root2 (S_1)	-3091.06590	-1308.61814		29.4
Root3		-1308.55296		70.3
S_1 (3.50)				
Root1 (S_0)	-3091.06810	-1308.62297	-105.50358	26.4
Root2 (S_1)	-3091.06500	-1308.61839		29.3
Root3		-1308.55594		68.4
S_1 (3.30)				
Root1 (S_0)	-3091.06570	-1308.62388	-105.50401	25.8
Root2 (S_1)	-3091.06290	-1308.61842		29.2
Root3		-1308.55912		66.4
S_1 (3.10)				
Root1 (S_0)	-3091.06200	-1308.62536	-105.50420	24.9
Root2 (S_1)	-3091.05890	-1308.61744		29.9
Root3		-1308.56080		65.4
S_1 (2.90)				
Root1 (S_0)	-3091.06010	-1308.62854	-105.50352	22.9
Root2 (S_1)	-3091.05340	-1308.61673		30.3
Root3		-1308.56177		64.8
S_1 (2.70)				
Root1 (S_0)	-3091.05930	-1308.62827	-105.50336	23.1
Root2 (S_1)	-3091.04240	-1308.60975		34.7
Root3		-1308.55685		67.9
S_1 (2.50)				
Root1 (S_0)	-3091.05980	-1308.62571	-105.50378	24.7
Root2 (S_1)	-3091.02200	-1308.59464		44.2

Root3		-1308.53768		79.9
S_1 (2.30)				
Root1 (S_0)	-3091.06630	-1308.63122	-105.50313	21.2
Root2 (S_1)	-3090.99640	-1308.57892		54.0
Root3		-1308.53869		79.3
S_1 (2.10)				
Root1 (S_0)	-3091.05250	-1308.62154	-105.50342	27.3
Root2 (S_1)	-3090.96300	-1308.57245		58.1
Root3		-1308.52678		86.7
S_1 (1.90)				
Root1 (S_0)	-3091.03290	-1308.61128	-105.50374	33.7
Root2 (S_1)	-3090.93200	-1308.56566		62.3
Root3		-1308.51041		97.0

Table S16. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for C4a-S Bond Formation from INT-T1 (Reaction Coordinate: C4a-S Distance). The Corresponding Energy Profiles are Plotted in Figure 3 (Blue Line).

(C4a-S)	**CASSCF A.E.**	**MS-CASPT2 A.E.**	**MM**	**MS-CASPT2 ∆E**
	QM+QM-MM (ele)	QM+QM-MM (ele)	MM + QM-MM (vdw)	
T_1-min (3.720)				
Root1 (T_1)	-3091.07250	-1308.62499	-105.50141	25.1
Root2		-1308.61834		29.3
Root3		-1308.53120		84.0
T_1 (3.70)				
Root1 (T_1)	-3091.07240	1308.62499	-105.50143	25.1
Root2		-1308.61838		29.3
Root3		-1308.53126		83.9
T_1 (3.50)				
Root1 (T_1)	-3091.07030	-1308.62527	-105.50260	24.9
Root2		-1308.61792		29.5
Root3		-1308.53170		83.6
T_1 (3.30)				
Root1 (T_1)	-3091.06770	-1308.62482	-105.50308	25.2
Root2		-1308.61782		29.6
Root3		-1308.53246		83.2
T_1 (3.10)				
Root1 (T_1)	-3091.06410	-1308.62493	-105.50363	25.2

Root2		-1308.61766		29.7
Root3		-1308.53534		81.4
T_1 (2.90)				
Root1 (T_1)	-3091.05850	-1308.62062	-105.50344	27.9
Root2		-1308.61201		33.3
Root3		-1308.53109		84.0
T_1 (2.70)				
Root1 (T_1)	-3091.05170	-1308.61862	-105.50328	29.1
Root2		-1308.60563		37.3
Root3		-1308.53094		84.1
T_1 (2.50)				
Root1 (T_1)	-3091.03880	-1308.61386	-105.50327	32.1
Root2		-1308.59239		45.6
Root3		-1308.52552		87.5
T_1 (2.30)				
Root1 (T_1)	-3091.01810	-1308.60428	-105.50312	38.1
Root2		-1308.57093		59.0
Root3		-1308.53936		78.8
T_1 (2.10)				
Root1 (T_1)	-3090.99190	-1308.59626	-105.50176	43.1
Root2		-1308.55462		69.3
Root3		-1308.53567		81.2
T_1 (1.90)				
Root1 (T_1)	-3090.99630	-1308.58099	-105.49963	52.7
Root2		-1308.53455		81.9
Root3		-1308.52322		89.0

Table S17. Absolute Energies (A.E., Hartree), Relative Energies (∆E, kcal/mol), and MM Energies (Hartree) of Optimized Structures for C4a-S Bond Formation from INT-S0 (Reaction Coordinate: C4a-S Distance). The Corresponding Energy Profiles are Plotted in Figure 3 (Green Line).

(C4a-S)	**CASSCF A.E.**	**MS-CASPT2 A.E.**	**MM**	**MS-CASPT2 ∆E**
S_0-min (3.372)				
Root1 (S_0)	-3091.04460	-1308.61977	-105.50016	28.4
Root2 (S_1)		-1308.59870		41.6
Root3		-1308.56020		65.8
S_0 (3.10)				
Root1 (S_0)	-3091.04090	-1308.61996	-105.50173	28.3
Root2 (S_1)		-1308.59628		43.1
Root3		-1308.55773		67.3

S_0 (2.90)				
Root1 (S_0)	-3091.04760	-1308.62686	-105.49963	23.9
Root2 (S_1)		-1308.60095		40.2
Root3		-1308.55873		66.7
S_0 (2.70)				
Root1 (S_0)	-3091.07400	-1308.62980	-105.50264	22.1
Root2 (S_1)		-1308.59564		43.5
Root3		-1308.54615		74.6
S_0 (2.50)				
Root1 (S_0)	-3091.08080	-1308.63161	-105.50288	21.0
Root2 (S_1)		-1308.57746		54.9
Root3		-1308.53143		83.8
S_0 (2.30)				
Root1 (S_0)	-3091.09170	-1308.63893	-105.50294	16.4
Root2 (S_1)		-1308.55375		69.8
Root3		-1308.53809		79.6
S_0 (2.10)				
Root1 (S_0)	-3091.10640	-1308.65158	-105.50411	8.4
Root2 (S_1)		-1308.54295		76.6
Root3		-1308.52785		86.1
S_0 (1.90)				
Root1 (S_0)	-3091.10990	-1308.65142	-105.50470	8.5
Root2 (S_1)		-1308.53769		79.9
Root3		-1308.51004		97.2

5. Comparison with Previous Theoretical Work

On the computational side, early TD-DFT and MCQDPT2 calculations addressed model systems of a photo-LOV1 domain from *Chlamydomonas reinhardtii*. [30, 31] The formation of the C4a-S covalent adduct in this photo-LOV1 domain was explored in the T_1 state at the QM/MM level using the restricted open-shell Hartree-Fock method. [32] This process was later re-investigated in the S_0 and T_1 states using high-level CASSCF and MCQDPT2 calculations on a model system consisting of lumiflavin and thiomethanol, without considering the protein environment. [33] The photophysics and photochemistry of structurally modified deaza flavin derivatives in the YtvA LOV domain were investigated both experimentally and at the QM/MM level. [34] Recent QM/MM studies also addressed the photophysical properties of a LOV-based fluorescent protein (iLOV-Q489K). [35, 36] In the realm of the

YtvA photoreceptors, the spectroscopic properties of the YtvA LOV domain from *Bacillus subtilis* were explored at the TD-DFT and DFT/MRCI levels. [37]

At the QM(CASSCF)/MM level, we optimized four S_0 conformers of the dark-adapted state, which are referred to as AU, AD, BU, and BD in Fig. 2. In AU and AD, the cysteine residue is oriented toward the dimethyl substituted part of the flavin core, while it points toward the two carbonyl groups of the flavin in BU and BD. At the QM(MS-CASPT2)/MM level, AU is predicted to be most stable (Table S18), in agreement with previous work. [37] We also optimized the corresponding S_1 and T_1 conformers at the QM(CASSCF)/MM level. In the S_1 state, AU is still the most stable conformer, about 5 kcal/mol lower than the others at the QM(MS-CASPT2)/MM level, while BU is the lowest minimum in the T_1 state, 4.9 kcal/mol lower than AU (see Table S18). One should note that only the BD conformer was considered in previous theoretical calculations of photo-LOV1 domains, [30–33] although it is obviously not the most stable in our YtvA photoreceptor.

Table S18. QM(MS-CASPT2(12,9)/cc-pVTZ//CASSCF(10,8)/6-31G*)/MM Calculated Relative Energies (kcal/mol) of Reactants, Intermediates, Products, and Transition States in the S_0, T_1, and S_1 Electronic States.

	AU	AD	BU	BD	INT	P
S_0	0.0	4.9	3.4	4.4	32.7	10.0
S_0(TS)	36.3	33.0	34.9	36.3	-	-
T_1	48.4	54.5	43.5	51.7	28.7	57.3
T_1(TS)	63.2	65.1	57.7	56.9	-	-
S_1	54.8	59.3	59.6	60.6	32.7	62.9
S_1(TS)	76.0	73.1	75.0	70.3	-	-

Only one intermediate and one adduct product could be located in the S_0 state at the QM(CASSCF)/MM level. In photo-LOV1 domains, the S_0 adduct product was previously estimated to be 8.7 kcal/mol higher in energy than the BD conformer at the QM(RHF)/MM level [32] which is close to our QM(MS-CASPT2)/MM value of 5.6 kcal/mol. In MCQDPT2//CASSCF (2,2) model calculations, this S_0 adduct was computed to be 12.8 kcal/mol lower than BD; [33] this qualitative discrepancy might be caused by the neglect of polarization effects from the surroundings. The energy of the T_1 intermediate was previously found to be 17.6 kcal/mol relative to BD at the QM(ROHF)/MM

level [32] which is smaller than our QM(MS-CASPT2)/MM value of 24.3 kcal/mol (see Table S18).

The computed $S_0 \rightarrow S_1$ vertical excitation energies at the four S_0 reactant minima are nearly the same, 63.5 kcal/mol for AD and BD, and 63.7 kcal/mol for AU and BU. They are very close to the experimentally measured absorption band maximum of 447 nm [63.7 kcal/mol] [38] and previous QM/MM results. [37] Model calculations on the isolated chromophore gave higher $S_0 \rightarrow S_1$ vertical excitation energies of 75.9 and 77.6 kcal/mol [33] at the MCQDPT2//CASSCF(2,2) and MCQDPT2//CASSCF(4,4) levels, respectively.

The computed $S_0 \rightarrow S_1$ vertical excitation energy of 70.4 kcal/mol [406 nm] at the S_0 product minimum is slightly lower than the experimentally measured absorption band maximum of 390 nm [73.3 kcal/mol]. [38] Model calculations on the isolated chromophore again gave higher values of 86.3 and 77.7 kcal/mol at the MCQDPT2//CASSCF(2,2) and MCQDPT2//CASSCF(4,4) levels, respectively. [33]

The photochemical reaction from the dark-adapted starts with an excited-state hydrogen transfer that produces a diradical intermediate. We computed the corresponding minimum-energy pathways for all four conformers in the S_1 and T_1 states. The energies of the computed transition states range between 70.3-76.0 kcal/mol in the S_1 case and between 56.9-65.1 kcal/mol in the T_1 case at the QM(MS-CASPT2)/MM level (see Table S18). We note that previous theoretical calculations for photo-LOV1 domains at the QM(ROHF)/MM and MCQDPT2//CASSCF(2,2) levels predicted the T_1 energy of the BD transition state to be 81.0 and 61.4 kcal/mol, respectively, relative to the S_0 BD minimum. [32, 33]

6. References

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7. Cartesian Coordinates of All Optimized Structures (QM part)

In xyz format (unit: angström)

CASSCF method

AU-S0

C	27.218967000	29.283184000	14.934504000
H	26.495216000	29.531513000	14.173592000
H	26.930215000	29.714652000	15.880403000
S	27.277966000	27.473730000	15.121077000
H	27.585032000	27.439508000	16.429275000
C	25.263589000	31.490006000	18.404716000
H	24.737887000	32.428127000	18.423713000
H	24.996779000	30.919691000	19.270745000
N	23.787415000	32.630794000	13.795081000
H	23.585704000	33.153534000	12.959366000
C	23.534110000	31.301306000	13.764931000
O	23.042362000	30.741244000	12.819936000
C	23.904081000	30.600155000	15.020986000
C	24.484981000	31.404136000	16.101965000
N	24.664100000	32.694649000	16.006100000
C	24.333722000	33.337442000	14.858754000
O	24.489162000	34.535473000	14.729164000
N	23.654346000	29.342940000	15.088052000
C	23.987855000	28.688385000	16.249703000
C	24.583133000	29.353751000	17.308961000
N	24.799750000	30.740549000	17.223465000
C	23.738871000	27.306997000	16.310773000
H	23.305071000	26.842529000	15.452029000
C	24.082110000	26.568237000	17.416777000
C	23.808001000	25.088591000	17.467613000
H	23.565907000	24.698704000	16.488263000
H	22.970741000	24.875392000	18.122160000
H	24.660604000	24.538129000	17.847342000
C	24.719455000	27.238440000	18.496451000
C	25.132479000	26.469719000	19.723457000
H	25.816108000	25.670879000	19.465766000
H	24.271502000	26.023196000	20.209507000
H	25.624839000	27.123216000	20.430076000
C	24.975912000	28.596658000	18.427731000
H	25.560252000	29.047930000	19.205865000
H	28.190045000	29.690653000	14.653357000
H	26.337905000	31.668205000	18.451153000

AD-S0

C	27.163528000	29.239908000	14.843303000
H	26.445381000	29.607878000	14.127365000
H	26.901678000	29.557458000	15.843235000
S	27.137819000	27.420454000	14.883802000
H	27.863191000	27.157854000	13.806531000
C	25.212915000	31.521205000	18.367324000

H	24.692574000	32.461470000	18.367527000
H	24.914321000	30.955032000	19.223691000
N	23.753919000	32.634492000	13.746702000
H	23.554223000	33.150497000	12.907047000
C	23.500700000	31.305980000	13.726955000
O	23.005193000	30.736882000	12.789502000
C	23.880885000	30.611535000	14.982823000
C	24.454164000	31.424789000	16.060055000
N	24.626110000	32.716075000	15.959230000
C	24.297653000	33.349982000	14.807806000
O	24.452622000	34.546689000	14.670021000
N	23.650029000	29.350985000	15.051447000
C	23.989579000	28.702679000	16.213653000
C	24.573915000	29.377962000	17.271118000
N	24.770212000	30.765621000	17.181964000
C	23.758005000	27.315759000	16.279607000
H	23.320291000	26.851334000	15.420556000
C	24.104280000	26.585130000	17.390422000
C	23.834217000	25.102502000	17.457336000
H	23.586853000	24.697748000	16.484435000
H	22.998880000	24.894747000	18.117735000
H	24.685661000	24.553409000	17.841930000
C	24.736815000	27.268807000	18.468074000
C	25.170685000	26.505342000	19.691086000
H	25.846898000	25.702005000	19.429015000
H	24.316686000	26.061227000	20.192303000
H	25.674317000	27.158283000	20.390710000
C	24.974742000	28.629562000	18.393932000
H	25.540217000	29.099305000	19.176286000
H	28.146598000	29.656120000	14.623282000
H	26.287932000	31.688965000	18.432601000

BU-S0

C	27.384291000	29.004891000	14.412936000
H	26.789000000	29.301820000	15.263872000
H	27.633609000	27.959704000	14.535632000
S	26.506488000	29.179709000	12.824939000
H	26.514675000	30.512158000	12.819496000
C	25.307522000	31.477378000	18.377619000
H	24.796654000	32.423018000	18.368902000
H	25.007413000	30.922617000	19.243295000
N	23.802632000	32.608264000	13.777327000
H	23.594464000	33.128912000	12.942496000
C	23.538643000	31.279832000	13.756367000
O	23.022896000	30.727134000	12.820954000
C	23.937304000	30.577908000	15.003667000
C	24.533962000	31.384410000	16.074150000
N	24.693603000	32.677133000	15.981402000
C	24.356088000	33.316886000	14.835119000
O	24.505344000	34.515682000	14.702857000

N	23.699274000	29.319724000	15.074980000
C	24.077144000	28.663374000	16.222724000
C	24.677845000	29.334495000	17.273957000
N	24.866211000	30.722439000	17.191602000
C	23.841428000	27.277462000	16.293458000
H	23.380483000	26.809381000	15.446970000
C	24.193876000	26.550107000	17.406599000
C	23.887301000	25.076369000	17.491627000
H	23.634284000	24.672964000	16.520238000
H	23.041538000	24.899688000	18.147356000
H	24.720239000	24.506225000	17.886285000
C	24.837539000	27.232465000	18.476719000
C	25.268536000	26.483875000	19.707509000
H	25.916134000	25.656629000	19.450361000
H	24.409588000	26.071716000	20.226294000
H	25.797843000	27.135586000	20.390279000
C	25.083036000	28.589900000	18.395886000
H	25.635950000	29.059765000	19.185207000
H	28.323065000	29.558705000	14.420695000
H	26.383249000	31.637682000	18.449596000

BD-S0

C	27.364676000	29.032000000	14.463423000
H	26.741278000	29.438701000	15.244612000
H	27.640117000	28.024155000	14.745610000
S	26.548646000	29.001926000	12.830092000
H	25.904776000	27.857433000	13.002935000
C	25.277580000	31.457056000	18.323386000
H	24.773074000	32.405932000	18.299325000
H	24.945179000	30.907466000	19.179515000
N	23.824300000	32.569607000	13.707013000
H	23.606127000	33.094518000	12.877730000
C	23.552506000	31.243198000	13.689146000
O	23.010315000	30.690051000	12.769502000
C	23.957339000	30.539627000	14.934510000
C	24.549040000	31.350407000	16.006808000
N	24.723933000	32.638397000	15.907356000
C	24.394458000	33.276342000	14.757006000
O	24.558352000	34.472738000	14.623168000
N	23.717833000	29.281295000	15.007282000
C	24.082609000	28.630096000	16.166900000
C	24.664884000	29.306682000	17.223391000
N	24.860840000	30.694562000	17.134638000
C	23.846151000	27.243294000	16.247306000
H	23.395836000	26.768983000	15.399454000
C	24.174415000	26.522061000	17.373338000
C	23.866758000	25.046258000	17.462310000
H	23.635057000	24.632835000	16.489259000
H	23.007750000	24.870280000	18.101354000
H	24.691746000	24.478613000	17.877655000

C	24.789109000	27.213186000	18.453426000
C	25.169428000	26.479301000	19.710894000
H	25.832181000	25.650961000	19.496201000
H	24.287881000	26.068773000	20.192704000
H	25.657153000	27.140164000	20.415274000
C	25.041370000	28.569848000	18.361814000
H	25.565684000	29.051784000	19.161042000
H	28.297145000	29.594930000	14.422449000
H	26.352684000	31.610271000	18.416903000

AU-S1

C	27.196998000	29.244799000	14.973527000
H	26.491985000	29.528697000	14.205481000
H	26.891892000	29.659927000	15.920102000
S	27.206839000	27.430922000	15.093864000
H	27.716784000	27.337233000	16.331821000
C	25.245715000	31.499440000	18.378046000
H	24.733411000	32.444023000	18.377540000
H	24.969875000	30.955265000	19.260911000
N	23.778819000	32.648841000	13.779369000
H	23.580747000	33.152723000	12.935475000
C	23.516319000	31.302603000	13.766812000
O	23.002533000	30.779110000	12.798919000
C	23.883618000	30.618475000	14.977475000
C	24.441573000	31.399221000	16.025108000
N	24.645696000	32.685282000	15.970340000
C	24.324462000	33.349206000	14.820488000
O	24.500346000	34.552195000	14.711483000
N	23.642477000	29.303803000	15.036430000
C	23.984674000	28.709727000	16.199862000
C	24.572933000	29.388096000	17.287824000
N	24.779995000	30.741338000	17.211876000
C	23.780389000	27.352097000	16.326923000
H	23.358446000	26.853433000	15.475590000
C	24.118111000	26.559839000	17.489281000
C	23.815477000	25.085917000	17.481376000
H	23.624848000	24.727899000	16.478511000
H	22.935287000	24.873546000	18.079725000
H	24.638073000	24.512696000	17.896162000
C	24.727075000	27.213356000	18.548053000
C	25.133532000	26.484952000	19.797668000
H	25.799307000	25.664553000	19.561271000
H	24.267620000	26.076468000	20.308267000
H	25.647581000	27.153072000	20.474413000
C	24.991189000	28.603502000	18.415180000
H	25.623805000	29.063363000	19.150922000
H	28.184714000	29.638627000	14.733977000
H	26.320988000	31.671101000	18.426905000

AD-S1

C	27.162833000	29.240582000	14.843008000
H	26.434336000	29.606870000	14.136138000
H	26.904247000	29.561849000	15.841776000
S	27.146467000	27.420256000	14.886197000
H	27.862048000	27.152792000	13.803400000
C	25.207423000	31.520533000	18.363630000
H	24.691728000	32.462509000	18.363365000
H	24.909671000	30.967965000	19.230865000
N	23.754753000	32.656015000	13.745854000
H	23.554659000	33.153929000	12.900020000
C	23.501531000	31.309771000	13.735329000
O	22.997486000	30.772806000	12.767712000
C	23.868687000	30.631435000	14.947682000
C	24.419866000	31.411049000	16.004929000
N	24.617068000	32.694119000	15.944615000
C	24.296068000	33.357974000	14.792906000
O	24.469370000	34.557519000	14.691525000
N	23.633780000	29.319813000	15.002126000
C	23.974677000	28.724409000	16.161033000
C	24.564509000	29.401071000	17.256749000
N	24.758447000	30.756139000	17.187935000
C	23.764647000	27.366424000	16.279318000
H	23.315905000	26.892598000	15.425435000
C	24.125911000	26.575545000	17.438751000
C	23.835763000	25.097695000	17.458708000
H	23.594314000	24.714009000	16.476448000
H	22.992310000	24.886409000	18.109224000
H	24.677511000	24.533234000	17.846394000
C	24.744098000	27.226938000	18.499865000
C	25.182109000	26.482352000	19.729586000
H	25.863964000	25.681868000	19.475764000
H	24.334226000	26.039872000	20.241416000
H	25.685372000	27.145759000	20.418909000
C	24.976645000	28.622690000	18.390056000
H	25.556064000	29.106406000	19.158123000
H	28.146154000	29.656127000	14.622852000
H	26.282748000	31.685422000	18.431120000

BU-S1

C	27.389226000	29.002509000	14.404651000
H	26.780443000	29.308601000	15.242533000
H	27.641969000	27.959063000	14.534844000
S	26.528020000	29.168153000	12.808258000
H	26.494276000	30.499021000	12.823994000
C	25.301446000	31.475593000	18.372866000
H	24.793804000	32.422382000	18.364060000
H	25.004175000	30.934383000	19.249393000
N	23.802137000	32.628883000	13.774861000
H	23.590650000	33.130172000	12.930823000
C	23.540090000	31.281937000	13.763174000

O	23.020167000	30.759392000	12.799353000
C	23.921975000	30.599019000	14.971917000
C	24.497243000	31.373686000	16.019200000
N	24.686890000	32.657306000	15.967571000
C	24.352499000	33.324698000	14.818862000
O	24.518885000	34.528593000	14.723743000
N	23.677748000	29.289646000	15.033651000
C	24.060802000	28.685922000	16.172004000
C	24.671819000	29.358317000	17.260296000
N	24.854322000	30.714725000	17.197624000
C	23.848705000	27.330128000	16.293924000
H	23.379828000	26.861745000	15.448376000
C	24.215652000	26.539388000	17.452548000
C	23.886604000	25.071215000	17.490328000
H	23.639600000	24.679139000	16.513339000
H	23.034578000	24.891990000	18.137974000
H	24.709361000	24.488666000	17.889520000
C	24.846545000	27.191241000	18.506927000
C	25.278977000	26.457633000	19.746685000
H	25.934088000	25.632282000	19.503687000
H	24.427769000	26.046918000	20.279300000
H	25.807922000	27.117510000	20.419573000
C	25.084595000	28.583124000	18.390489000
H	25.648405000	29.068906000	19.164337000
H	28.326261000	29.559143000	14.418514000
H	26.377326000	31.633584000	18.447622000

BD-S1

C	27.365924000	29.031261000	14.454294000
H	26.730484000	29.443463000	15.222713000
H	27.646259000	28.026215000	14.740921000
S	26.564337000	28.993686000	12.814628000
H	25.900827000	27.862041000	12.998049000
C	25.273351000	31.454236000	18.317518000
H	24.771970000	32.403791000	18.289427000
H	24.943563000	30.918757000	19.183955000
N	23.823603000	32.587625000	13.703508000
H	23.603362000	33.091332000	12.863160000
C	23.552174000	31.242877000	13.697438000
O	23.005639000	30.721727000	12.748064000
C	23.939507000	30.558111000	14.905592000
C	24.512927000	31.337572000	15.954754000
N	24.714494000	32.616045000	15.894640000
C	24.388691000	33.281204000	14.740839000
O	24.569704000	34.482592000	14.645643000
N	23.705737000	29.248308000	14.970152000
C	24.066320000	28.649924000	16.117257000
C	24.658144000	29.329915000	17.214951000
N	24.850678000	30.684190000	17.139496000
C	23.848937000	27.294130000	16.245436000

H	23.392248000	26.814852000	15.399316000
C	24.193777000	26.513082000	17.420890000
C	23.867582000	25.044708000	17.460960000
H	23.641831000	24.644949000	16.481727000
H	23.002622000	24.867244000	18.091565000
H	24.683902000	24.467174000	17.879956000
C	24.795617000	27.173761000	18.484773000
C	25.179401000	26.453254000	19.747780000
H	25.847747000	25.627798000	19.545365000
H	24.307415000	26.042613000	20.244511000
H	25.668073000	27.123071000	20.440289000
C	25.040597000	28.566137000	18.361572000
H	25.578630000	29.064783000	19.147086000
H	28.297749000	29.595729000	14.420453000
H	26.348217000	31.606644000	18.414996000

AU-T1

C	27.196777000	29.302872000	14.945315000
H	26.473851000	29.550362000	14.182419000
H	26.911620000	29.746374000	15.887155000
S	27.228424000	27.494247000	15.142680000
H	27.588728000	27.460644000	16.437410000
C	25.273977000	31.498838000	18.402613000
H	24.750793000	32.438594000	18.432797000
H	25.004380000	30.922377000	19.266012000
N	23.788009000	32.645063000	13.785827000
H	23.581561000	33.158713000	12.945074000
C	23.545211000	31.303716000	13.774012000
O	23.045797000	30.738732000	12.831186000
C	23.929455000	30.619202000	15.007382000
C	24.491446000	31.419016000	16.095103000
N	24.652689000	32.707113000	15.998916000
C	24.319740000	33.354301000	14.845522000
O	24.471290000	34.555360000	14.730352000
N	23.678284000	29.265166000	15.066980000
C	23.985132000	28.681699000	16.189665000
C	24.596837000	29.357259000	17.317961000
N	24.816678000	30.762970000	17.221037000
C	23.738800000	27.256805000	16.306709000
H	23.316757000	26.794078000	15.443662000
C	24.084062000	26.527204000	17.411981000
C	23.808030000	25.046950000	17.482588000
H	23.568713000	24.649358000	16.506712000
H	22.968053000	24.844086000	18.137767000
H	24.662067000	24.503132000	17.870007000
C	24.719463000	27.203604000	18.491987000
C	25.127894000	26.462591000	19.732106000
H	25.811693000	25.660498000	19.481149000
H	24.270005000	26.012931000	20.222818000
H	25.621039000	27.118236000	20.435221000

C	24.979450000	28.615791000	18.375256000
H	25.547730000	29.064598000	19.164515000
H	28.172763000	29.695863000	14.660576000
H	26.348712000	31.672508000	18.455996000

AD-T1

C	27.165581000	29.239861000	14.841431000
H	26.437026000	29.606470000	14.136863000
H	26.910910000	29.558196000	15.842421000
S	27.155238000	27.418925000	14.887352000
H	27.862334000	27.150818000	13.799647000
C	25.199674000	31.512321000	18.356825000
H	24.679742000	32.451100000	18.328651000
H	24.894849000	30.967319000	19.225879000
N	23.762030000	32.667702000	13.759231000
H	23.563614000	33.178170000	12.917547000
C	23.503737000	31.327247000	13.742087000
O	22.997345000	30.780232000	12.781237000
C	23.877241000	30.654787000	14.959270000
C	24.411288000	31.420436000	15.986104000
N	24.617656000	32.717134000	15.952169000
C	24.303459000	33.373394000	14.809222000
O	24.472342000	34.578565000	14.680971000
N	23.643187000	29.319345000	15.013029000
C	23.967540000	28.709079000	16.151829000
C	24.565568000	29.410367000	17.254853000
N	24.752247000	30.733427000	17.181699000
C	23.749690000	27.333939000	16.282761000
H	23.307440000	26.828723000	15.451980000
C	24.132067000	26.567558000	17.457155000
C	23.841835000	25.090550000	17.471553000
H	23.612753000	24.723309000	16.480882000
H	22.983642000	24.878719000	18.101088000
H	24.673213000	24.515315000	17.862964000
C	24.742517000	27.223862000	18.495907000
C	25.187595000	26.495295000	19.737216000
H	25.870519000	25.695032000	19.484695000
H	24.339988000	26.056712000	20.252589000
H	25.691744000	27.163312000	20.421724000
C	24.981959000	28.632714000	18.379609000
H	25.567916000	29.108771000	19.143527000
H	28.148834000	29.655815000	14.621741000
H	26.274724000	31.679168000	18.423880000

BU-T1

C	27.351091000	29.027517000	14.475619000
H	26.780381000	29.369397000	15.327295000
H	27.567106000	27.977382000	14.619066000
S	26.464786000	29.202263000	12.891579000
H	26.560197000	30.530816000	12.842153000

C	25.254806000	31.504533000	18.317407000
H	24.734218000	32.445110000	18.322536000
H	24.953759000	30.940467000	19.176844000
N	23.761716000	32.589428000	13.700729000
H	23.559151000	33.092940000	12.854181000
C	23.490820000	31.250440000	13.710817000
O	22.961823000	30.697845000	12.778715000
C	23.887540000	30.574920000	14.944436000
C	24.478244000	31.390405000	16.005608000
N	24.636625000	32.672835000	15.902803000
C	24.302618000	33.309713000	14.743981000
O	24.461568000	34.507193000	14.623981000
N	23.633401000	29.232075000	15.044749000
C	24.013653000	28.659227000	16.131980000
C	24.660819000	29.353376000	17.239966000
N	24.821497000	30.752958000	17.139582000
C	23.806600000	27.227525000	16.270027000
H	23.339368000	26.741860000	15.439501000
C	24.183175000	26.534247000	17.379294000
C	23.885178000	25.064154000	17.500765000
H	23.650492000	24.636297000	16.535876000
H	23.029696000	24.912601000	18.150667000
H	24.716612000	24.515865000	17.926713000
C	24.852583000	27.237738000	18.454719000
C	25.300081000	26.512300000	19.693289000
H	25.939221000	25.670710000	19.452741000
H	24.449547000	26.115867000	20.243216000
H	25.842152000	27.175623000	20.355668000
C	25.084131000	28.628564000	18.333572000
H	25.637769000	29.116431000	19.113756000
H	28.308629000	29.548068000	14.460995000
H	26.330218000	31.668522000	18.385703000

BD-T1

C	27.364403000	29.032352000	14.459428000
H	26.740442000	29.438036000	15.240880000
H	27.644307000	28.024997000	14.738789000
S	26.545550000	29.004046000	12.828155000
H	25.902132000	27.858995000	12.999395000
C	25.279250000	31.475083000	18.326324000
H	24.780276000	32.428718000	18.317845000
H	24.947543000	30.924663000	19.182855000
N	23.824443000	32.580421000	13.704600000
H	23.603340000	33.087699000	12.866036000
C	23.562092000	31.242418000	13.708439000
O	23.012014000	30.689656000	12.785873000
C	23.970552000	30.557695000	14.930200000
C	24.548045000	31.364620000	16.000611000
N	24.719221000	32.645135000	15.897643000
C	24.389085000	33.290648000	14.739159000

O	24.559012000	34.485996000	14.621027000
N	23.718865000	29.212566000	15.013499000
C	24.054413000	28.636946000	16.113820000
C	24.669570000	29.324567000	17.243227000
N	24.864276000	30.721674000	17.141940000
C	23.826778000	27.208159000	16.238120000
H	23.378601000	26.736064000	15.389556000
C	24.162611000	26.504785000	17.354486000
C	23.861859000	25.031721000	17.453893000
H	23.626937000	24.610733000	16.485607000
H	23.006087000	24.865500000	18.099374000
H	24.691593000	24.474412000	17.872925000
C	24.791937000	27.202478000	18.458301000
C	25.170544000	26.473175000	19.716131000
H	25.837095000	25.645311000	19.509569000
H	24.295315000	26.059080000	20.208072000
H	25.658933000	27.137970000	20.415699000
C	25.043824000	28.592160000	18.349601000
H	25.573662000	29.075580000	19.149473000
H	28.296976000	29.595351000	14.421921000
H	26.355388000	31.619862000	18.421364000

INT-S0

C	27.185379000	29.116203000	14.596639000
H	26.670164000	29.653137000	15.392389000
H	27.467350000	28.157720000	15.023104000
S	26.161606000	28.856240000	13.094511000
H	24.041086000	28.874753000	14.167948000
C	25.205316000	31.533860000	18.468693000
H	24.679527000	32.470217000	18.474043000
H	24.924452000	30.971498000	19.333466000
N	23.841562000	32.672493000	13.807726000
H	23.635247000	33.191590000	12.971262000
C	23.670048000	31.338885000	13.752298000
O	23.176313000	30.736539000	12.838711000
C	24.063621000	30.668454000	15.013561000
C	24.474755000	31.466223000	16.154907000
N	24.560400000	32.759550000	16.084257000
C	24.282030000	33.397468000	14.910496000
O	24.377164000	34.598146000	14.802885000
N	24.004567000	29.378940000	15.065534000
C	24.249175000	28.682060000	16.218492000
C	24.653964000	29.392754000	17.334619000
N	24.761071000	30.781487000	17.281347000
C	24.056152000	27.285873000	16.227097000
H	23.745961000	26.809519000	15.320783000
C	24.262010000	26.567049000	17.373520000
C	23.945364000	25.092790000	17.426291000
H	23.768746000	24.694303000	16.436798000
H	23.045806000	24.925201000	18.008776000

H	24.741120000	24.516963000	17.883811000
C	24.764064000	27.267199000	18.518287000
C	25.103613000	26.502988000	19.768777000
H	25.796213000	25.701592000	19.547753000
H	24.215389000	26.055868000	20.200821000
H	25.555213000	27.151343000	20.506238000
C	24.960555000	28.633265000	18.482746000
H	25.434484000	29.105554000	19.319083000
H	28.126893000	29.643483000	14.443037000
H	26.283241000	31.692487000	18.500045000

INT-S1

C	27.313305000	29.122815000	14.507267000
H	26.685371000	29.651911000	15.208715000
H	27.522869000	28.142536000	14.915342000
S	26.487080000	28.974724000	12.894496000
H	23.288339000	28.873967000	14.323515000
C	25.236465000	31.498928000	18.384516000
H	24.714415000	32.438415000	18.401655000
H	24.958086000	30.933587000	19.251342000
N	23.755545000	32.664882000	13.794356000
H	23.561844000	33.171738000	12.949388000
C	23.549396000	31.328649000	13.769150000
O	23.084800000	30.737505000	12.806508000
C	23.914789000	30.668863000	14.992290000
C	24.452837000	31.425833000	16.076956000
N	24.597635000	32.729501000	16.005841000
C	24.266370000	33.379088000	14.868713000
O	24.390226000	34.586204000	14.746758000
N	23.739433000	29.341699000	15.079498000
C	24.081911000	28.649172000	16.225380000
C	24.626971000	29.347309000	17.280700000
N	24.786660000	30.754696000	17.202535000
C	23.889695000	27.264086000	16.279464000
H	23.486011000	26.766562000	15.416294000
C	24.218433000	26.535149000	17.405639000
C	23.935019000	25.051938000	17.457486000
H	23.828190000	24.629391000	16.464723000
H	23.010815000	24.858252000	17.992425000
H	24.721493000	24.503925000	17.962376000
C	24.797115000	27.229783000	18.496548000
C	25.185767000	26.498025000	19.754558000
H	25.853435000	25.674399000	19.539559000
H	24.312929000	26.088623000	20.252605000
H	25.686352000	27.167085000	20.440368000
C	25.010923000	28.598347000	18.409218000
H	25.538734000	29.074775000	19.212101000
H	28.268318000	29.642608000	14.430891000
H	26.311813000	31.670989000	18.430226000

INT-T1

C	27.331405000	29.107201000	14.433619000
H	26.710982000	29.509771000	15.220459000
H	27.567902000	28.083901000	14.710018000
S	26.473113000	29.021318000	12.840944000
H	23.234419000	28.869041000	14.326701000
C	25.245043000	31.488213000	18.375481000
H	24.717033000	32.424742000	18.401915000
H	24.977082000	30.915114000	19.240449000
N	23.817914000	32.651615000	13.773556000
H	23.625494000	33.159408000	12.929523000
C	23.571627000	31.321156000	13.757798000
O	23.094941000	30.751327000	12.788146000
C	23.910137000	30.658179000	14.983640000
C	24.473767000	31.409403000	16.057356000
N	24.661123000	32.707646000	15.979019000
C	24.339963000	33.360561000	14.842003000
O	24.478908000	34.566864000	14.713959000
N	23.647901000	29.345183000	15.102926000
C	24.004952000	28.650555000	16.238759000
C	24.601620000	29.343029000	17.275212000
N	24.792581000	30.743998000	17.190155000
C	23.788017000	27.271358000	16.315761000
H	23.340183000	26.782205000	15.474249000
C	24.151092000	26.546643000	17.436064000
C	23.879344000	25.062210000	17.504360000
H	23.695602000	24.648429000	16.520930000
H	23.005179000	24.854612000	18.112466000
H	24.709491000	24.520380000	17.942210000
C	24.779702000	27.237619000	18.499459000
C	25.211185000	26.509739000	19.748284000
H	25.890014000	25.699312000	19.514626000
H	24.357802000	26.083491000	20.266484000
H	25.715321000	27.186210000	20.425463000
C	25.012012000	28.602140000	18.389903000
H	25.580621000	29.078012000	19.166284000
H	28.279868000	29.642824000	14.393718000
H	26.319453000	31.665260000	18.424116000

P-S0

C	27.163696000	29.335128000	14.929015000
H	26.934122000	29.690245000	15.920576000
H	27.297753000	28.265134000	15.000750000
S	25.829094000	29.650035000	13.731532000
H	22.977660000	28.933854000	14.486198000
C	25.305896000	31.449332000	18.281309000
H	24.768907000	32.381582000	18.258239000
H	24.992909000	30.881819000	19.134931000
N	23.915859000	32.537614000	13.674364000
H	23.597642000	33.075223000	12.885674000

C	23.701120000	31.214521000	13.646091000
O	23.059282000	30.669351000	12.781134000
C	24.366592000	30.401791000	14.738164000
C	24.784965000	31.282034000	15.912653000
N	24.943487000	32.568456000	15.809637000
C	24.569687000	33.225991000	14.687781000
O	24.719967000	34.421411000	14.561363000
N	23.443972000	29.438639000	15.208788000
C	23.929620000	28.648790000	16.258966000
C	24.675778000	29.274268000	17.225335000
N	24.949224000	30.671303000	17.081617000
C	23.685245000	27.282845000	16.333348000
H	23.163028000	26.813390000	15.522995000
C	24.113812000	26.529223000	17.419259000
C	23.813988000	25.049630000	17.476953000
H	23.603534000	24.649955000	16.492634000
H	22.946297000	24.851282000	18.097142000
H	24.640208000	24.485066000	17.893622000
C	24.825696000	27.182109000	18.447130000
C	25.264502000	26.449596000	19.690053000
H	25.934607000	25.633486000	19.455562000
H	24.412060000	26.032572000	20.216854000
H	25.776853000	27.124684000	20.363759000
C	25.130566000	28.531504000	18.315840000
H	25.750850000	28.997793000	19.057500000
H	28.125539000	29.758231000	14.639347000
H	26.374745000	31.633898000	18.388843000

P-S1

C	27.142780000	29.343263000	14.849761000
H	26.902685000	29.713432000	15.835719000
H	27.265121000	28.270341000	14.921091000
S	25.827786000	29.728036000	13.654645000
H	23.213468000	28.778076000	14.339258000
C	25.295728000	31.460705000	18.298057000
H	24.783504000	32.406525000	18.254847000
H	24.983339000	30.934315000	19.176693000
N	23.839382000	32.588358000	13.736914000
H	23.494578000	33.128790000	12.963925000
C	23.678870000	31.263826000	13.676897000
O	23.056411000	30.695195000	12.802934000
C	24.394117000	30.460361000	14.734830000
C	24.697865000	31.305619000	15.887160000
N	24.925631000	32.615557000	15.813876000
C	24.501676000	33.291042000	14.756737000
O	24.607047000	34.505977000	14.614961000
N	23.606512000	29.298477000	15.101550000
C	23.991397000	28.614933000	16.205194000
C	24.652161000	29.332316000	17.260207000
N	24.905414000	30.667719000	17.141270000

C	23.756482000	27.227092000	16.311527000
H	23.314518000	26.732011000	15.468197000
C	24.116082000	26.507028000	17.424144000
C	23.840953000	25.029902000	17.507655000
H	23.620064000	24.621787000	16.529599000
H	22.982504000	24.833850000	18.141476000
H	24.679400000	24.477148000	17.916719000
C	24.766063000	27.219227000	18.483800000
C	25.207307000	26.489381000	19.719498000
H	25.882851000	25.683314000	19.457559000
H	24.359434000	26.044212000	20.233417000
H	25.717464000	27.157175000	20.400186000
C	25.026353000	28.578357000	18.373849000
H	25.588234000	29.055709000	19.153957000
H	28.119904000	29.747529000	14.585442000
H	26.368548000	31.629727000	18.390557000

P-T1

C	27.149897000	29.339709000	14.836175000
H	26.909571000	29.700100000	15.823435000
H	27.278367000	28.266325000	14.908238000
S	25.839226000	29.723156000	13.634978000
H	23.173500000	28.813707000	14.356326000
C	25.294659000	31.438114000	18.304085000
H	24.763615000	32.367839000	18.228130000
H	24.983310000	30.912515000	19.184595000
N	23.831119000	32.579425000	13.744628000
H	23.482648000	33.126436000	12.976241000
C	23.689334000	31.256789000	13.648430000
O	23.063128000	30.712083000	12.763481000
C	24.416158000	30.423347000	14.691173000
C	24.757173000	31.275973000	15.854940000
N	24.923667000	32.608594000	15.822632000
C	24.493039000	33.280540000	14.773420000
O	24.591052000	34.497585000	14.631339000
N	23.553668000	29.350391000	15.106381000
C	23.994041000	28.619210000	16.185422000
C	24.644881000	29.331535000	17.263504000
N	24.906894000	30.622289000	17.135765000
C	23.771951000	27.251350000	16.293617000
H	23.313273000	26.744251000	15.467917000
C	24.129371000	26.531344000	17.425468000
C	23.848404000	25.055063000	17.504950000
H	23.626578000	24.649278000	16.526836000
H	22.989575000	24.862750000	18.140298000
H	24.683737000	24.501843000	17.918610000
C	24.773995000	27.242421000	18.516264000
C	25.215835000	26.483689000	19.735433000
H	25.886463000	25.680724000	19.459020000
H	24.365576000	26.039567000	20.242814000

H	25.731014000	27.137483000	20.424882000
C	25.012492000	28.567536000	18.425806000
H	25.581686000	29.047841000	19.196986000
H	28.127540000	29.746615000	14.577893000
H	26.365789000	31.621710000	18.387985000

B3LYP method

AU-S0

C	27.213907000	29.284835000	14.930188000
H	26.476119000	29.538421000	14.168742000
H	26.919492000	29.713505000	15.888143000
S	27.253437000	27.456076000	15.118998000
H	27.593956000	27.438059000	16.445979000
C	25.268769000	31.486510000	18.410561000
H	24.735245000	32.434547000	18.416918000
H	25.001792000	30.912197000	19.291142000
N	23.788815000	32.646333000	13.785792000
H	23.582618000	33.163428000	12.932200000
C	23.532562000	31.299630000	13.761116000
O	23.024790000	30.734640000	12.790821000
C	23.905272000	30.610210000	15.015034000
C	24.478243000	31.414536000	16.079121000
N	24.669978000	32.726203000	16.008345000
C	24.334305000	33.372380000	14.853329000
O	24.484791000	34.599732000	14.719324000
N	23.656832000	29.329022000	15.079499000
C	23.986618000	28.681390000	16.228706000
C	24.593363000	29.358337000	17.322039000
N	24.803358000	30.734201000	17.230907000
C	23.737434000	27.294175000	16.307059000
H	23.297307000	26.829070000	15.435211000
C	24.077975000	26.556494000	17.420229000
C	23.807552000	25.076439000	17.472831000
H	23.561726000	24.683296000	16.484633000
H	22.962863000	24.850827000	18.133497000
H	24.665608000	24.515231000	17.860164000
C	24.718150000	27.233813000	18.505199000
C	25.133502000	26.469724000	19.728237000
H	25.819368000	25.658962000	19.462752000
H	24.267955000	26.009213000	20.219208000
H	25.634861000	27.125714000	20.442311000
C	24.977832000	28.598475000	18.437680000
H	25.570313000	29.048909000	19.226929000
H	28.186063000	29.690781000	14.650570000
H	26.342503000	31.668142000	18.457160000

AD-S0

C	27.159424000	29.244078000	14.843541000
H	26.426355000	29.617103000	14.128179000
H	26.895223000	29.559191000	15.856501000

S	27.124647000	27.405902000	14.887624000
H	27.875272000	27.148983000	13.796453000
C	25.217327000	31.520281000	18.373452000
H	24.691266000	32.471549000	18.365266000
H	24.918166000	30.948059000	19.242786000
N	23.754578000	32.651084000	13.739670000
H	23.550470000	33.162329000	12.883652000
C	23.499600000	31.305090000	13.721654000
O	22.987927000	30.732819000	12.758578000
C	23.881751000	30.618321000	14.974372000
C	24.447429000	31.432615000	16.036995000
N	24.632306000	32.743605000	15.960896000
C	24.300605000	33.383339000	14.804271000
O	24.454340000	34.610342000	14.663631000
N	23.648827000	29.335834000	15.040155000
C	23.983016000	28.694691000	16.194159000
C	24.580217000	29.380626000	17.284921000
N	24.772070000	30.759902000	17.190400000
C	23.754412000	27.302409000	16.275498000
H	23.308790000	26.830082000	15.409550000
C	24.101546000	26.574667000	17.393140000
C	23.835153000	25.094193000	17.458802000
H	23.583040000	24.689200000	16.476500000
H	22.992440000	24.877910000	18.125764000
H	24.690448000	24.534830000	17.853520000
C	24.737878000	27.262535000	18.476341000
C	25.173135000	26.503393000	19.696067000
H	25.851767000	25.686937000	19.432120000
H	24.313942000	26.047775000	20.203425000
H	25.682909000	27.162921000	20.401025000
C	24.977500000	28.630558000	18.406178000
H	25.553818000	29.101114000	19.198800000
H	28.143524000	29.658172000	14.624130000
H	26.292023000	31.690302000	18.438164000

BU-S0

C	27.382517000	29.006184000	14.414218000
H	26.777362000	29.301696000	15.274475000
H	27.640521000	27.951686000	14.538278000
S	26.494574000	29.170904000	12.809987000
H	26.509971000	30.526292000	12.826175000
C	25.311724000	31.476091000	18.382903000
H	24.792837000	32.431003000	18.363053000
H	25.012975000	30.914193000	19.261297000
N	23.800366000	32.624398000	13.768274000
H	23.588546000	33.139385000	12.916700000
C	23.537915000	31.277871000	13.749742000
O	23.009583000	30.718403000	12.789038000
C	23.938581000	30.584828000	14.995247000
C	24.527075000	31.396660000	16.050467000

N	24.699586000	32.709775000	15.981959000
C	24.355810000	33.351453000	14.829427000
O	24.500294000	34.581681000	14.691915000
N	23.705674000	29.305348000	15.062742000
C	24.076529000	28.656047000	16.202950000
C	24.686021000	29.339724000	17.287721000
N	24.869502000	30.719200000	17.197706000
C	23.840345000	27.265979000	16.291699000
H	23.372820000	26.794589000	15.436307000
C	24.188869000	26.537774000	17.409203000
C	23.885334000	25.065238000	17.490838000
H	23.627382000	24.653919000	16.512167000
H	23.032983000	24.881358000	18.154982000
H	24.723760000	24.488755000	17.896213000
C	24.836723000	27.225063000	18.485727000
C	25.270201000	26.477693000	19.713834000
H	25.921608000	25.637548000	19.457486000
H	24.406705000	26.054572000	20.241569000
H	25.804984000	27.136418000	20.401635000
C	25.082992000	28.589737000	18.408981000
H	25.649201000	29.063791000	19.206018000
H	28.321904000	29.558967000	14.421229000
H	26.387152000	31.638532000	18.454558000

BD-S0

C	27.359783000	29.039659000	14.461423000
H	26.727919000	29.442717000	15.255077000
H	27.644678000	28.021468000	14.738094000
S	26.535766000	29.008994000	12.811480000
H	25.898047000	27.836876000	13.002666000
C	25.282685000	31.454105000	18.327144000
H	24.771169000	32.412361000	18.289305000
H	24.950755000	30.898847000	19.196163000
N	23.824585000	32.584339000	13.698464000
H	23.600989000	33.101451000	12.850254000
C	23.551637000	31.240735000	13.684944000
O	22.995772000	30.683538000	12.739903000
C	23.959547000	30.545673000	14.928131000
C	24.542522000	31.358827000	15.983941000
N	24.729808000	32.667995000	15.908704000
C	24.394802000	33.309797000	14.752376000
O	24.554058000	34.535921000	14.615851000
N	23.725762000	29.264842000	14.999159000
C	24.081297000	28.621744000	16.149248000
C	24.671586000	29.311482000	17.239413000
N	24.863651000	30.688116000	17.140637000
C	23.843197000	27.232445000	16.244401000
H	23.386570000	26.752761000	15.388025000
C	24.168872000	26.512011000	17.375086000
C	23.866301000	25.039233000	17.461040000

H	23.629342000	24.619423000	16.480711000
H	23.001107000	24.857064000	18.108907000
H	24.698013000	24.467114000	17.886648000
C	24.786954000	27.208084000	18.462399000
C	25.171407000	26.472522000	19.714502000
H	25.837085000	25.631649000	19.498804000
H	24.286275000	26.050522000	20.206351000
H	25.665085000	27.142636000	20.421239000
C	25.039971000	28.571987000	18.378445000
H	25.578177000	29.058939000	19.187729000
H	28.294831000	29.598508000	14.423485000
H	26.357151000	31.611133000	18.421649000

AU-T1

C	27.209577000	29.289770000	14.931403000
H	26.466077000	29.537511000	14.173843000
H	26.917057000	29.721390000	15.888820000
S	27.245818000	27.460893000	15.121670000
H	27.596197000	27.441302000	16.445214000
C	25.270542000	31.482492000	18.411231000
H	24.739105000	32.431687000	18.427176000
H	25.004747000	30.917112000	19.298017000
N	23.790934000	32.665819000	13.777683000
H	23.582174000	33.169654000	12.917356000
C	23.535225000	31.301825000	13.760729000
O	23.019326000	30.758236000	12.775609000
C	23.900136000	30.608873000	14.986431000
C	24.452137000	31.387407000	16.040877000
N	24.648933000	32.702632000	15.994961000
C	24.322076000	33.374504000	14.830248000
O	24.489537000	34.608053000	14.748419000
N	23.647954000	29.284664000	15.017158000
C	23.982418000	28.672388000	16.190717000
C	24.594928000	29.350867000	17.313599000
N	24.804518000	30.719796000	17.241695000
C	23.729296000	27.305754000	16.305714000
H	23.293631000	26.823275000	15.443075000
C	24.079774000	26.562507000	17.433481000
C	23.812608000	25.089111000	17.471964000
H	23.564787000	24.694159000	16.485425000
H	22.968122000	24.866412000	18.136862000
H	24.667876000	24.529795000	17.870729000
C	24.723477000	27.227144000	18.529321000
C	25.138370000	26.457030000	19.748022000
H	25.827547000	25.649662000	19.482370000
H	24.277343000	25.995656000	20.245955000
H	25.642019000	27.111156000	20.461588000
C	24.979191000	28.584703000	18.437594000
H	25.567866000	29.047996000	19.220828000
H	28.182588000	29.692601000	14.650256000

H	26.344004000	31.665245000	18.459692000

AD-T1

C	27.156711000	29.244758000	14.844598000
H	26.415526000	29.616807000	14.136713000
H	26.895871000	29.554754000	15.859747000
S	27.124740000	27.405286000	14.887912000
H	27.878211000	27.149750000	13.798065000
C	25.218005000	31.515905000	18.374523000
H	24.694072000	32.468764000	18.375537000
H	24.920400000	30.953700000	19.251242000
N	23.755992000	32.672556000	13.733393000
H	23.549215000	33.170297000	12.869766000
C	23.501842000	31.308403000	13.723013000
O	22.983780000	30.757693000	12.743795000
C	23.873869000	30.619921000	14.947582000
C	24.420052000	31.404120000	15.998482000
N	24.614532000	32.719533000	15.948177000
C	24.290734000	33.386533000	14.781183000
O	24.463227000	34.618552000	14.693993000
N	23.635290000	29.292817000	14.981772000
C	23.974799000	28.688477000	16.158043000
C	24.580791000	29.374370000	17.276801000
N	24.770586000	30.745338000	17.202365000
C	23.750392000	27.316970000	16.274137000
H	23.306413000	26.828673000	15.419074000
C	24.108085000	26.581162000	17.408827000
C	23.841771000	25.108142000	17.456826000
H	23.587775000	24.703595000	16.475434000
H	22.997577000	24.894684000	18.126070000
H	24.691633000	24.546626000	17.863077000
C	24.745925000	27.255419000	18.500282000
C	25.179369000	26.491036000	19.717103000
H	25.861837000	25.677390000	19.454296000
H	24.323754000	26.035293000	20.231172000
H	25.691512000	27.148116000	20.422513000
C	24.979400000	28.617373000	18.405280000
H	25.551861000	29.099813000	19.191643000
H	28.140739000	29.658740000	14.624655000
H	26.292408000	31.687209000	18.440701000

BU-T1

C	27.382717000	29.005814000	14.412027000
H	26.772755000	29.299672000	15.269803000
H	27.639177000	27.950457000	14.534561000
S	26.500030000	29.171145000	12.805377000
H	26.499013000	30.527023000	12.835664000
C	25.311835000	31.473078000	18.384020000
H	24.796063000	32.430426000	18.375331000
H	25.014175000	30.921169000	19.269659000

N	23.801290000	32.643599000	13.760822000
H	23.582658000	33.145179000	12.902077000
C	23.545565000	31.277893000	13.749504000
O	23.009533000	30.739531000	12.773973000
C	23.934915000	30.585761000	14.968517000
C	24.502067000	31.366917000	16.012269000
N	24.681765000	32.685344000	15.968385000
C	24.344243000	33.354027000	14.805335000
O	24.505776000	34.588306000	14.721471000
N	23.678410000	29.262252000	15.014209000
C	24.064855000	28.650665000	16.167986000
C	24.689564000	29.333808000	17.280316000
N	24.867477000	30.705709000	17.210591000
C	23.840497000	27.276357000	16.286945000
H	23.372443000	26.791375000	15.442674000
C	24.195898000	26.543307000	17.421039000
C	23.890594000	25.078439000	17.488766000
H	23.630493000	24.668410000	16.511062000
H	23.036955000	24.897696000	18.155342000
H	24.724152000	24.500404000	17.904904000
C	24.845465000	27.218349000	18.507320000
C	25.274122000	26.466627000	19.733490000
H	25.929401000	25.629190000	19.477778000
H	24.414110000	26.041687000	20.266790000
H	25.810981000	27.121933000	20.423012000
C	25.087117000	28.578037000	18.407109000
H	25.646826000	29.061537000	19.200677000
H	28.321609000	29.559416000	14.420692000
H	26.387048000	31.636225000	18.457289000

BD-T1

C	27.358763000	29.039163000	14.458318000
H	26.721660000	29.441002000	15.248442000
H	27.642432000	28.019809000	14.735499000
S	26.536841000	29.010978000	12.806967000
H	25.893199000	27.843299000	13.004566000
C	25.283797000	31.453066000	18.327832000
H	24.774233000	32.413058000	18.300649000
H	24.952319000	30.906470000	19.202675000
N	23.826541000	32.602460000	13.689792000
H	23.598050000	33.106474000	12.834669000
C	23.558659000	31.239862000	13.686503000
O	22.993864000	30.703026000	12.726649000
C	23.956712000	30.546105000	14.901713000
C	24.516973000	31.329026000	15.946403000
N	24.710310000	32.645287000	15.895007000
C	24.382155000	33.311615000	14.727287000
O	24.558459000	34.543502000	14.644808000
N	23.707031000	29.218895000	14.948006000
C	24.069518000	28.616218000	16.114275000

C	24.673499000	29.306544000	17.233668000
N	24.863336000	30.676541000	17.152167000
C	23.842401000	27.241443000	16.242067000
H	23.386138000	26.747491000	15.395694000
C	24.173718000	26.517732000	17.387189000
C	23.871817000	25.051395000	17.460104000
H	23.632633000	24.633284000	16.480165000
H	23.005941000	24.871383000	18.110920000
H	24.700024000	24.478620000	17.894322000
C	24.794315000	27.202142000	18.484298000
C	25.176396000	26.461343000	19.733131000
H	25.844769000	25.623314000	19.515823000
H	24.295408000	26.037045000	20.231106000
H	25.673384000	27.126379000	20.442337000
C	25.041026000	28.561009000	18.377570000
H	25.573347000	29.058626000	19.182737000
H	28.293296000	29.598983000	14.422028000
H	26.358128000	31.609981000	18.424041000