Supplementary Information for:
"Hydrogen abstraction by photoexcited benzophenone: consequences for DNA photosensitization"

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Computational Details

The three lowest-lying singlet and triplet electronic states were considered for all CAS-PT2 and RAS-PT2 calculations, including averaging with equal weights. In order to avoid singularities (*i.e.* intruder states), an imaginary shift was added in the energy denominator (0.2 a.u.). The net effect ensures that the energy is almost unaffected except in the vicinity of the weak singularity, which is removed.[1] The so called IPEA shift, that introduces a modified zero-th order Hamiltonian,[2] was set to 0.00, *i.e.* it was not considered.
The complete active space self-consistent field (CAS-SCF) natural orbitals of the BP/S and BP/Thy systems in their reactant conformation can be seen in Figure S1 and S2, respectively.

The basis set superposition error (BSSE) was taken into account at the DFT, CASP-T2, and RAS-PT2 level of theory, in order to properly describe the binding energies between BP and Thy/S. Especially, the counterpoise (CP) method was employed, hence the BSSE was calculated and then subtracted a posteriori from the uncorrected energy.[3] The BSSE calculation was performed by introducing so called "ghost orbitals", basis set functions which have no electrons or protons.

(1) Forsberg, N., and Malmqvist, P.-Å. (1997) Multiconfiguration perturbation theory with imaginary level shift. *Chem. Phys. Lett. 274*, 196–204.
(2) Ghigo, G., Roos, B. O., and Malmqvist, P.-Å. (2004) A modified definition of the zeroth-order Hamiltonian in multiconfigurational perturbation theory (CASPT2). *Chem. Phys. Lett. 396*, 142–149.
(3) van Duijneveldt, F. B., van Duijneveldt-van de Rijdt, J. G. C. M., and van Lenthe, J. H. (1994) State of the Art in Counterpoise Theory. *Chem. Rev. 94*, 1873–1885.

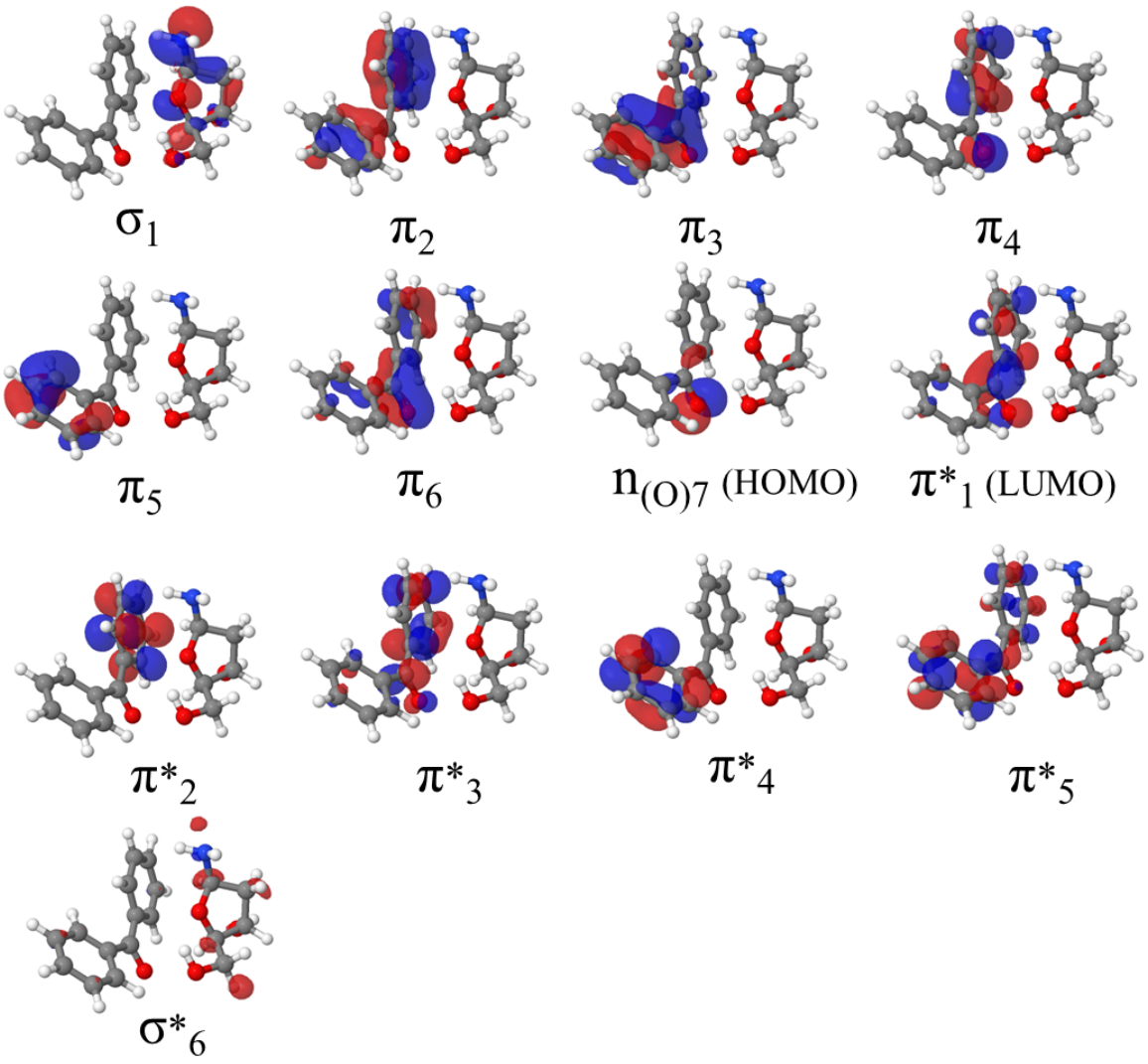

Figure S1. CAS-SCF natural orbitals of the BP/S system.

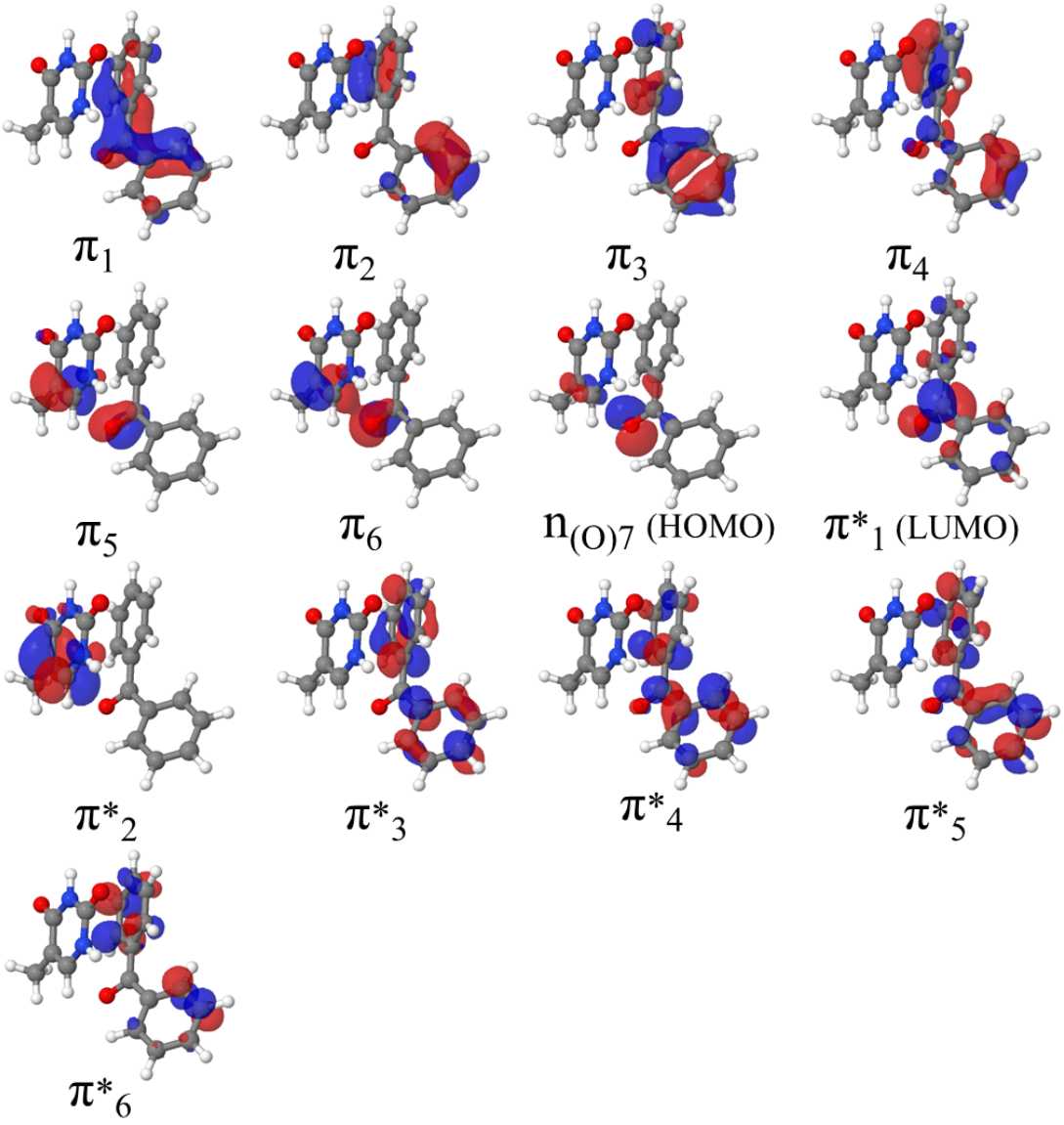

Figure S2. CAS-SCF natural orbitals of the BP/Thy system.

Table S1. Hydrogen abstraction from thymine (T) by ^{3}BP. The relative energies (eV) of the isolated molecules, reactant, transition state, and product computed at three different levels of theory. The values in parentheses are computed in the solvent (water) phase. Counterpoise (CP) corrected energy values are also given for DFT and CAS/RAS-PT2 to take into account the effects of the BSSE

Level of theory		**Relative energy (eV)**				
		^{3}BP + ^{1}T	**R**	**TS**	**P**	**^{2}[BP-OH]$^{\cdot}$ + ^{2}[T-CH$_2$]$^{\cdot}$**
M06-2X/6-31+G(d)	BSSE Uncorrected	0.46 (0.38)	0.00 (0.00)	0.49 (0.44)	-0.77 (-0.78)	-0.23 (-0.38)
	CP Corrected	0.40	0.00	0.50	-0.77	-0.29
M06-2X/6-311++G(d,p)	BSSE Uncorrected	0.49 (0.39)	0.00 (0.00)	0.50 (0.45)	-0.80 (-0.80)	-0.23 (-0.38)
	CP Corrected	0.40	0.00	0.41	-0.80	-0.31
CASPT2(14,13)	BSSE Uncorrected	1.59	0.00	0.59	-0.71	0.72
	CP Corrected	0.56	0.00	0.59	-0.71	-0.22
RASPT2(26,2,2;10,5,8)	BSSE Uncorrected	1.43	0.00	0.60	-0.84	0.58
	CP Corrected	0.37	0.00	0.60	-0.84	-0.48

Table S2. Hydrogen abstraction from sugar (S) by ^{3}BP. Relative energy (eV) of the isolated molecules, reactants, transition state, and products computed at different levels of theory. The values in parentheses are computed in the solvent (water) phase. Counterpoise (CP) corrected energy values are also given for DFT and CAS-PT2 to take into account the effects of the BSSE

Level of theory		**Relative energy (eV)**				
		^{3}BP + ^{1}S	**R**	**TS**	**P**	**^{2}[BP-OH]$^{\cdot}$ + ^{2}[S]$^{\cdot}$**
M06-2X/6-31+G(d)	BSSE Uncorrected	0.34 (0.25)	0.00 (0.00)	0.40 (0.32)	-0.97 (-0.98)	-0.22 (-0.34)
	CP Corrected	0.30	0.00	0.43	-0.94	-0.29
M06-2X/6-311++G(d,p)	BSSE Uncorrected	0.38 (0.25)	0.00 (0.00)	0.42 (0.35)	-0.98 (-1.00)	-0.21 (-0.34)
	CP Corrected	0.31	0.00	0.46	-0.95	-0.29
CASPT2(14,13) Ano-S-VDZP	BSSE Uncorrected	1.08	0.00	0.13	-1.32	0.16
	CP Corrected	0.12	0.00	0.13	-1.32	-0.83

Details of the QM/MM partition

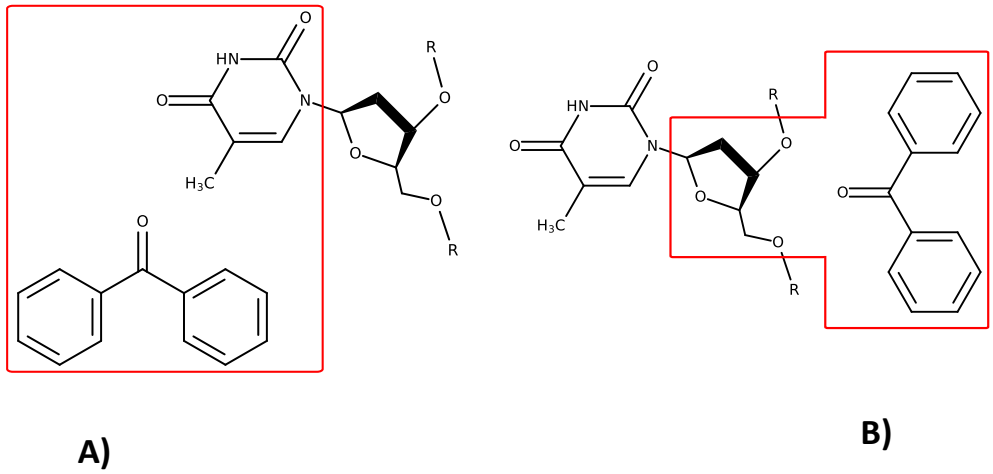

Figure S3. Scheme of the QM/MM partition for the study of H_abst from Thy (A) and Sugar (B). The atoms inside the red squares have been treated at QM level. The covalent bonds intersecting the red squares represent the QM/MM frontier and have been saturated with link atoms.

Triplet triplet energy transfer from benzophenone to thymine computed at the RAS-PT2(26,2,2;l0,5,8) level

In our previous work on the triplet triplet energy transfer (TTET) process from benzophenone to thymine,[4] we employed the RAS-PT2(20,2,2;7,5,11) level of theory to characterize the potential energy surfaces of the two lowest-lying triplet states along the TTET path. At this level of theory, the most relevant orbitals (π HOMO, π* LUMO, and n_O, for BP, and π HOMO and π* LUMO for T) were included in the RAS2 space, and 7 π and 11 π* orbitals constituted the RAS1 and RAS3 spaces, respectively. This distribution of orbitals allows a high flexibility of the unoccupied π* space and a less flexible occupied π space, since three extra π* orbitals are added in the RAS3 while three valence π orbitals are kept inactive. The more balanced RAS-PT2(26,2,2;l0,5,8) level, which include only the valence orbitals in the active space (10 π and 8 π* orbitals are included in the RAS1 and RAS3 spaces, respectively), provides the same results for the TTET mechanism, within the errors of the RAS-PT2 method (see Figure S3), and it is therefore used in the present work for the study of the H abstraction.

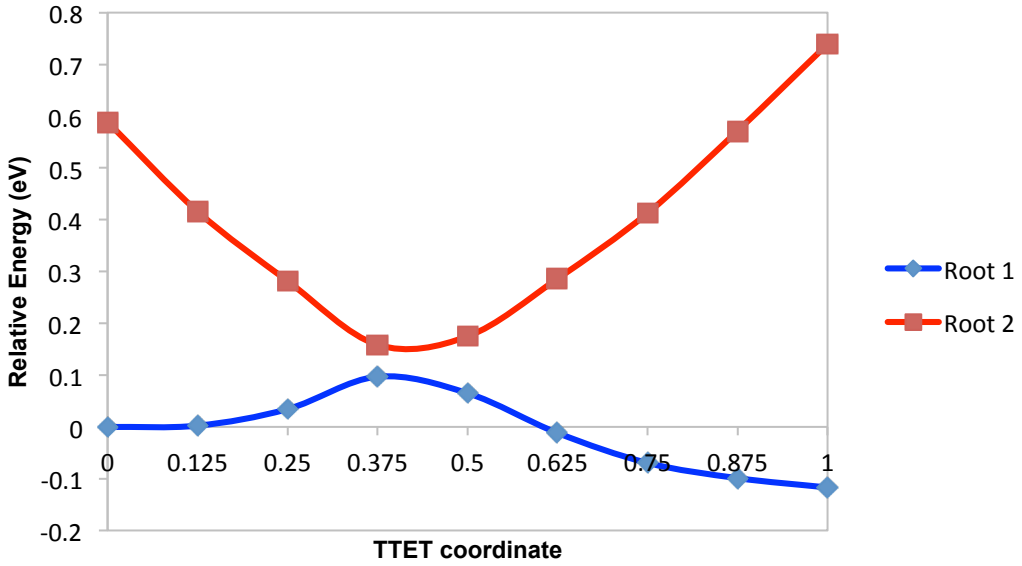

Figure S4. Potential energy surfaces of the two lowest-lying triplet states computed at the RASPT2(26,2,2;l0,5,8) level for the ^{3}BP → ^{3}T transfer in B-DNA for the double insertion mode. Geometries are taken from the previous work.[4] The TTET process is expected to be an efficient process in which the energy barrier is 0.1 eV and the stabilization energy is 0.12 eV at the RASPT2(26,2,2;l0,5,8) level and 0.07 and 0.20 eV, respectively, at the RASPT2(20,2,2;7,5,11) level.[4] Similar findings were obtained with the CASPT2 and TD-DFT methods.[4]

(4) Dumont, E., Wibowo, M., Roca-Sanjuán, D., Garavelli, M., Assfeld, X., and Monari, A. (2015) Resolving the benzophenone DNA-photosensitization mechanism at QM/MM level. *J. Phys. Chem. Lett. 6*, 576–580.

Cartesian Coordinates of the Optimized Structures

The Cartesian Coordinates of the optimized reactant, transition state, and product are given in Ångström, for BP/S and BP/Thy systems.

BP/S reactant

O	14.572963	3.196782	-14.539370
H	15.049726	2.913485	-15.323881
H	11.076457	5.155914	-14.649116
C	11.693513	5.200666	-13.739550
O	10.885638	5.393837	-12.599017
H	12.362364	6.060719	-13.814919
C	12.497629	3.920279	-13.621184
H	13.229032	4.002290	-12.810041
O	11.572458	2.874595	-13.335366
C	11.961584	1.702087	-14.078573
H	12.779587	1.209469	-13.544172
N	10.888746	0.779036	-14.228200
H	10.071432	1.240859	-14.614110
C	13.240211	3.522088	-14.910046
H	13.240464	4.339411	-15.640625
C	12.460392	2.300068	-15.388861
H	11.597041	2.604871	-15.989578
H	13.068811	1.606304	-15.970409
O	13.202433	4.198246	-10.401456
C	12.422194	3.149564	-10.177880
C	12.863788	1.880091	-10.681824
C	11.985317	0.778316	-10.790779
C	12.441418	-0.435547	-11.274779
C	13.765626	-0.586787	-11.695041
C	14.627506	0.505917	-11.634727
C	14.191227	1.725132	-11.139098
H	10.944414	0.894497	-10.515625
H	11.756250	-1.273652	-11.341131
H	14.112750	-1.539521	-12.075252
H	15.651664	0.408432	-11.975096
H	14.876868	2.562763	-11.086827
C	11.238364	3.462442	-9.392526
C	10.693079	2.533522	-8.486172
C	9.571849	2.862867	-7.742272
C	8.988280	4.124584	-7.859989
C	9.543846	5.060878	-8.727478
C	10.660127	4.743262	-9.487990
H	11.169825	1.570221	-8.352898
H	9.159132	2.137612	-7.050510
H	8.113350	4.376215	-7.272748
H	9.099649	6.044861	-8.822052
H	11.070286	5.460293	-10.189364
H	10.639942	0.377914	-13.331332
H	10.451736	4.550229	-12.420793

BP/S transition state

O	14.427366	3.411812	-14.612927
H	14.690814	3.932562	-15.372337
H	11.051836	5.058663	-14.622951
C	11.691037	5.095474	-13.728124
O	10.950806	5.524756	-12.605771
H	12.483234	5.829872	-13.893490
C	12.290372	3.725359	-13.491386
H	12.984596	3.767539	-12.645902
O	11.227443	2.822309	-13.183958

C	11.310041	1.639361	-14.005184
H	11.091891	0.796434	-13.350162
N	10.356559	1.618179	-15.085007
H	10.504586	2.390755	-15.726314
C	13.042523	3.124328	-14.681649
H	12.626829	3.500831	-15.625824
C	12.746754	1.636676	-14.511968
H	12.867661	1.051090	-15.421901
H	13.415312	1.252871	-13.735908
O	13.340411	4.255797	-10.229784
C	12.571707	3.180636	-10.107739
C	13.111231	1.944407	-10.605655
C	12.288578	0.829263	-10.874252
C	12.839288	-0.346162	-11.355324
C	14.208091	-0.441596	-11.615143
C	15.022438	0.667989	-11.397556
C	14.489680	1.847176	-10.901388
H	11.218042	0.908940	-10.733554
H	12.192592	-1.194497	-11.550553
H	14.628592	-1.364376	-11.995613
H	16.083084	0.613335	-11.612441
H	15.135619	2.698024	-10.718767
C	11.298941	3.432907	-9.456735
C	10.658354	2.444743	-8.685601
C	9.450674	2.719431	-8.065128
C	8.868336	3.982496	-8.172083
C	9.514250	4.976576	-8.902364
C	10.719088	4.714864	-9.538205
H	11.127100	1.477440	-8.553885
H	8.966591	1.948033	-7.477556
H	7.925383	4.190029	-7.681072
H	9.073724	5.963326	-8.985355
H	11.202617	5.481372	-10.132132
H	9.412424	1.698157	-14.723946
H	10.382475	4.787931	-12.350063

BP/S product

O	14.082601	3.818110	-13.561456
H	14.850738	4.171453	-14.020542
H	10.261069	4.307205	-12.337767
C	10.826512	4.660342	-13.211865
O	11.580419	5.820723	-12.923120
H	10.094092	4.956708	-13.974463
C	11.707320	3.563366	-13.702839
H	13.603365	3.931580	-11.804818
O	11.167775	2.331275	-13.855364
C	12.201908	1.465502	-14.421204
H	12.801230	1.105242	-13.582414
N	11.657931	0.357023	-15.115346
H	11.002672	0.651038	-15.831393
C	12.967620	3.728635	-14.485053
H	12.962736	4.633629	-15.099304
C	13.004339	2.428954	-15.291220
H	12.488571	2.565340	-16.246979
H	14.014767	2.067788	-15.479065
O	13.147390	4.205634	-10.984470
C	12.369540	3.200069	-10.505278
C	12.698344	1.839508	-10.882480
C	11.706596	0.847907	-11.025501
C	12.041862	-0.440546	-11.410789
C	13.369371	-0.781176	-11.674777
C	14.358278	0.192937	-11.558096
C	14.030732	1.486097	-11.174940

H	10.667549	1.112824	-10.873414
H	11.260582	-1.185046	-11.518087
H	13.627306	-1.789805	-11.973935
H	15.392918	-0.057716	-11.761889
H	14.814083	2.228101	-11.071029
C	11.314987	3.598879	-9.613131
C	10.709980	2.689959	-8.716816
C	9.701706	3.100637	-7.861324
C	9.266639	4.425468	-7.858908
C	9.872832	5.341406	-8.716296
C	10.884595	4.943529	-9.574836
H	11.063220	1.667667	-8.670719
H	9.260794	2.384692	-7.177162
H	8.476205	4.741602	-7.189306
H	9.553061	6.377116	-8.716510
H	11.342446	5.670708	-10.232546
H	11.192712	-0.282055	-14.481902
H	12.200461	5.589867	-12.220410

BP/Thy reactant

C	-2.621803	1.667335	-1.104631
C	-1.785376	2.212954	-2.079316
C	-2.273308	0.492110	-0.451843
C	-1.065042	-0.168546	-0.767871
C	-0.209961	0.409618	-1.731862
C	-0.578164	1.576868	-2.383444
C	-0.692732	-1.374795	-0.065615
C	0.218958	-2.419108	-0.477789
C	0.459838	-2.686317	-1.843297
C	0.844261	-3.233713	0.491946
C	1.705012	-4.252270	0.103981
C	1.962131	-4.487378	-1.247233
C	1.330947	-3.699756	-2.214383
O	-1.257653	-1.545850	1.127645
H	-3.558657	2.157192	-0.857503
H	-2.065089	3.127608	-2.591461
H	-2.939501	0.059724	0.288130
H	0.751025	-0.048770	-1.940206
H	0.090049	2.006297	-3.123583
H	-0.060295	-2.112152	-2.602954
H	0.666876	-3.039138	1.544936
H	2.186534	-4.861693	0.862533
H	2.639340	-5.280609	-1.546198
H	1.507903	-3.890260	-3.268529
C	-1.042216	0.698142	3.316796
H	-0.758396	-0.265814	3.745070
H	-1.015453	1.457533	4.103396
H	-2.076251	0.639941	2.965618
C	-0.126988	1.074752	2.192807
C	-0.383539	2.348218	1.507584
C	0.911455	0.327983	1.770816
H	0.350106	3.518538	-0.024811
O	-1.283297	3.116335	1.788980
N	0.502564	2.644211	0.465052

N	1.731526	0.711923	0.730114
C	1.571239	1.888861	0.022588
O	2.297895	2.217760	-0.892688
H	1.161996	-0.623332	2.228874
H	2.504011	0.134606	0.431089

BP/Thy transition state

C	-2.809236	1.701683	-0.878376
C	-1.916997	2.193637	-1.832586
C	-2.532556	0.529216	-0.186265
C	-1.347026	-0.196533	-0.440648
C	-0.438882	0.331410	-1.390980
C	-0.726698	1.500201	-2.079724
C	-1.060955	-1.416640	0.281639
C	-0.247256	-2.512977	-0.207958
C	-0.049415	-2.750359	-1.587986
C	0.337411	-3.412145	0.714210
C	1.127366	-4.465464	0.272803
C	1.347268	-4.663530	-1.091360
C	0.746770	-3.802021	-2.015430
O	-1.625403	-1.648708	1.471241
H	-3.725583	2.241821	-0.661619
H	-2.138637	3.109757	-2.370621
H	-3.238332	0.150746	0.547123
H	0.507959	-0.172765	-1.561605
H	-0.006421	1.890730	-2.792449
H	-0.547028	-2.118797	-2.316675
H	0.166716	-3.257394	1.774371
H	1.578269	-5.136764	0.997565
H	1.966619	-5.486444	-1.433129
H	0.886856	-3.966131	-3.079638
C	-1.273651	0.454102	2.971934
H	-0.785278	-0.114687	3.766343
H	-2.150528	0.998855	3.322643
H	-1.663430	-0.414701	2.263345
C	-0.367871	1.289124	2.178388
C	-0.860149	2.571636	1.648770
C	0.863535	0.863197	1.788128
H	-0.328687	4.051525	0.320900
O	-1.922526	3.084334	1.938795
N	0.014556	3.204830	0.760615
N	1.646034	1.574745	0.925980
C	1.232711	2.749721	0.306993
O	1.903287	3.315062	-0.530369
H	1.271007	-0.087138	2.121458
H	2.535816	1.216352	0.607212

BP/Thy product

C	-2.066170	1.800356	-1.863582
C	-2.119884	2.717737	-0.814997
C	-1.034044	0.871936	-1.935193
C	-0.017756	0.837560	-0.954102
C	-0.094586	1.766686	0.107754
C	-1.127494	2.690526	0.168629
C	1.014384	-0.173463	-1.012078
C	2.354191	-0.078473	-0.495817
C	2.970419	1.165064	-0.227544
C	3.111570	-1.253511	-0.289926
C	4.408240	-1.183555	0.200293
C	4.994301	0.050588	0.488151
C	4.267538	1.221827	0.261995
O	0.724788	-1.350125	-1.635371
H	-2.825818	1.815860	-2.639403
H	-2.925857	3.442080	-0.760428
H	-0.982798	0.199825	-2.788019
H	0.641495	1.726614	0.903861
H	-1.171116	3.386027	1.001264
H	2.437610	2.085942	-0.440091
H	2.659142	-2.213585	-0.511316
H	4.967444	-2.100178	0.362332
H	6.008181	0.101013	0.871608
H	4.722829	2.188841	0.453537
H	-0.232892	-1.467439	-1.678619
C	-1.916080	-2.919845	-0.947393
H	-1.170539	-3.682042	-1.137456
H	-2.822506	-2.902207	-1.536991
C	-1.725425	-1.964941	0.044894
C	-2.794350	-0.949090	0.250043
C	-0.608563	-1.885806	0.862501
H	-3.248701	0.682028	1.417560
O	-3.824982	-0.896898	-0.385855
N	-2.534962	-0.019862	1.256878
N	-0.480835	-0.913798	1.826830
C	-1.421938	0.064855	2.076629
O	-1.284203	0.915103	2.932401
H	0.214918	-2.584131	0.781185
H	0.341380	-0.867245	2.412053