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Supporting Information: Photochemical mechanism of 1,5-benzodiazepin-2-one: electronic structure calculations and nonadiabatic surface-hopping dynamics simulations

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1. OM2/MRCI Active Space

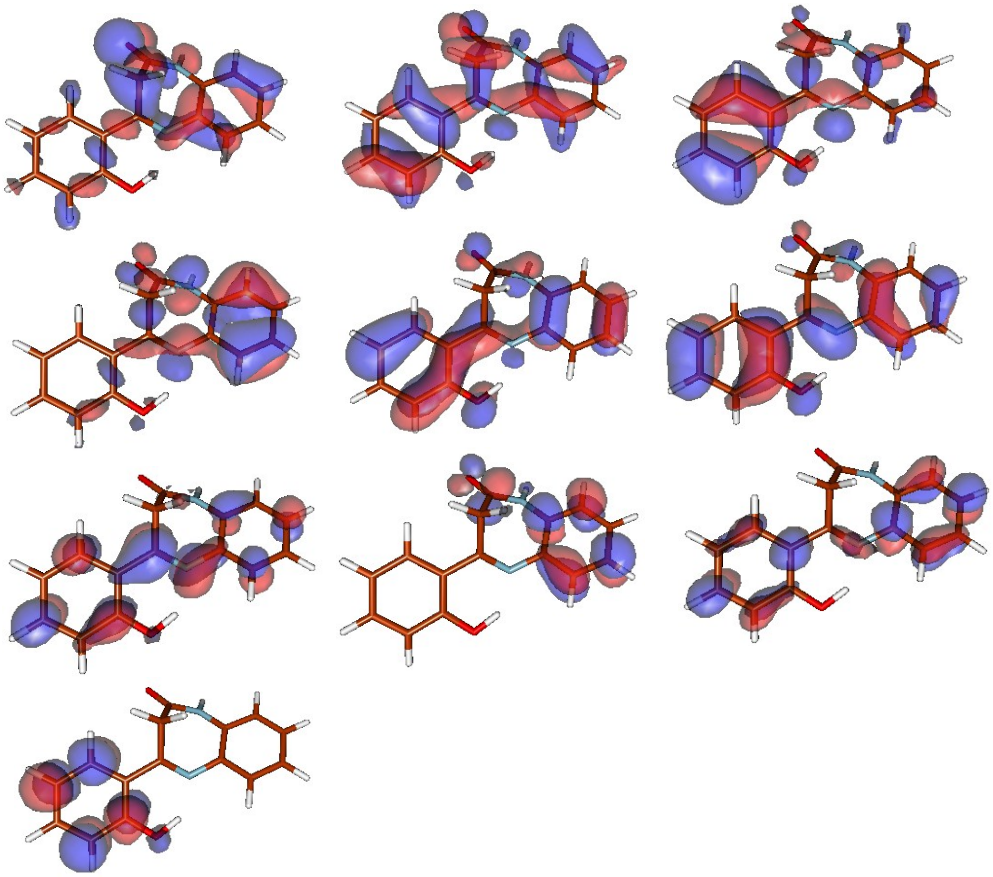

Fig. S1: The active space (12e,10o) of 1,5-benzodiazepin-2-one (enol form) used in the OM2/MRCI calculations. See text for simulation details.

2. Optimized Structures of S0-ENOL-1 and S0-KETO-1

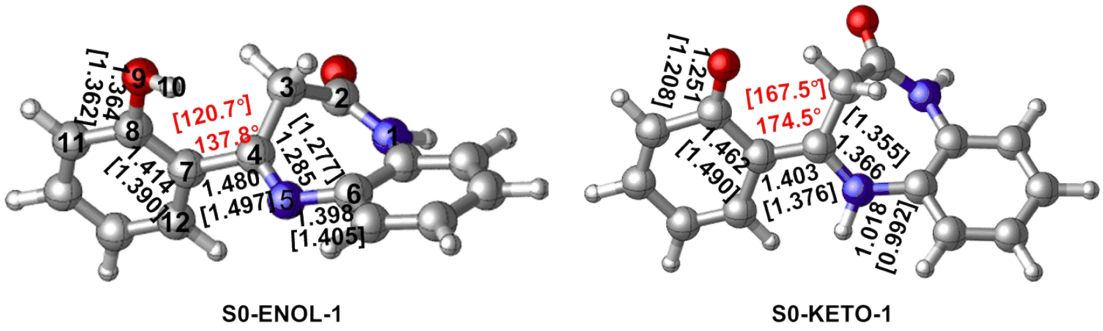

Fig. S2. Stationary points with atom labellings (blue represents nitrogen atom, red represents oxygen atom, grey represents carbon atom and light grey represents hydrogen atom) and selected geometric parameters obtained from OM2/MRCI and CASSCF (in brackets) methods.

3. Optimization Path

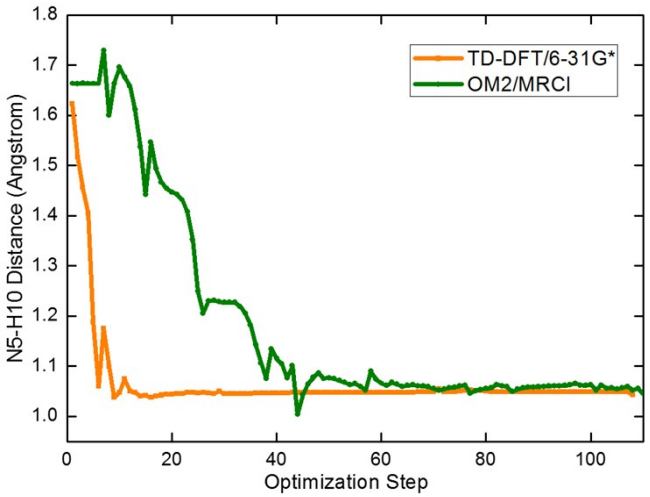

Fig. S3. TD-DFT/6-31G* and OM2/MRCI optimization paths starting from the corresponding S_0 enol minimum, which lead directly to keto species.

4. Typical Trajectory of Type I

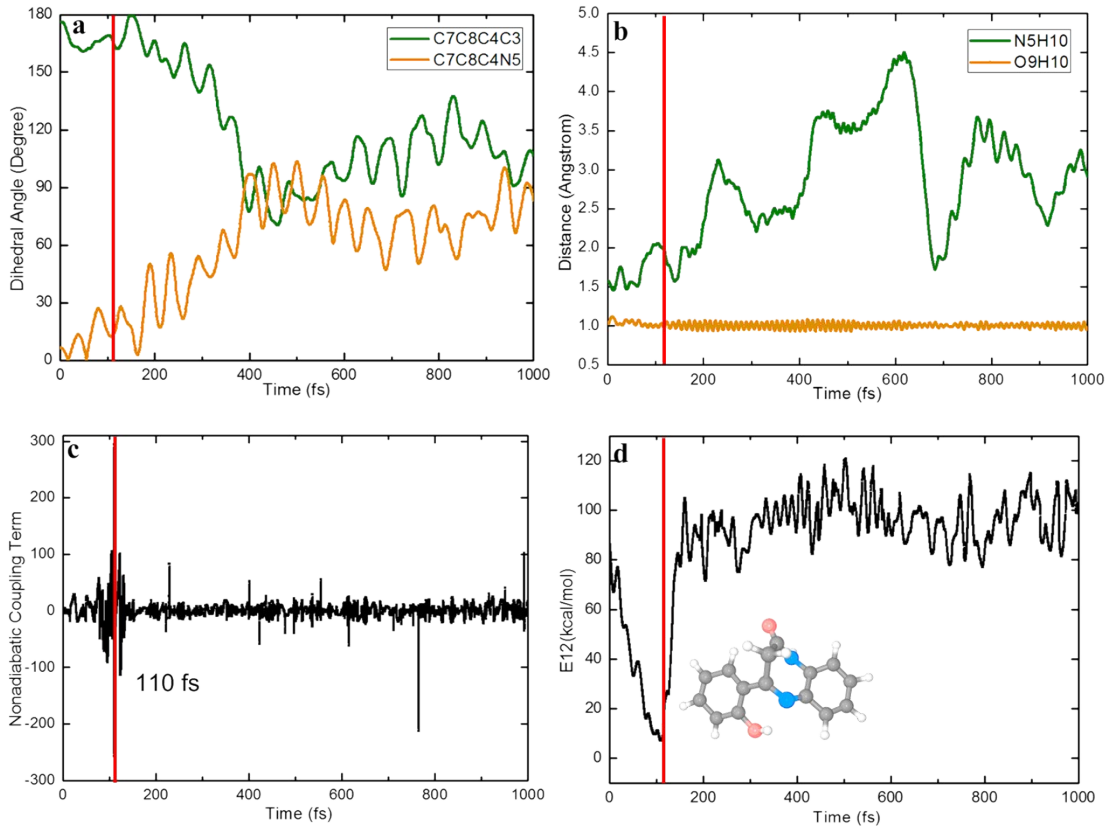

Fig. S4 Time evolution of several key geometric parameters and energy gap from a typical OM2/MRCI trajectory of type (II): (a) two key dihedral angles; (b) two important bond lengths; (c) nonadiabatic coupling term; and (d) S_1-S_0 energy gap.

As shows in Fig. S4, this typical trajectory hops to the ground state at 110 fs, and after the hopping point, the dihedrals of C7C8C4C3 and C7C8C4N5 rotate a little until the end of the simulation.

5. Cartesian Coordinates of All Optimized CASSCF Structures

S0-ENOL

C	4.322026	3.637048	0.182493
C	5.105226	3.794036	-0.974016
H	5.014105	4.705122	-1.538343
C	5.981430	2.806024	-1.380595
H	6.571234	2.944452	-2.268143
C	6.097345	1.632566	-0.624742
H	6.776082	0.855851	-0.925997
C	5.321358	1.473691	0.506504
H	5.376350	0.572269	1.088074
C	4.423881	2.473598	0.929667
C	3.287334	3.019767	2.915402
C	2.373797	2.628303	4.013064
C	2.137161	1.289951	4.319587
C	1.303672	0.951963	5.404659
H	1.166811	-0.090597	5.621896
C	0.680379	1.934229	6.135819
H	0.037605	1.662861	6.953902
C	0.866957	3.289169	5.805051
H	0.357805	4.058826	6.354885
C	1.696960	3.614046	4.774876
H	1.811147	4.648635	4.513597
C	3.831184	4.436058	2.865110
H	3.680025	4.980880	3.779422
H	4.897896	4.376027	2.673583
C	3.162509	5.185661	1.735175
N	3.623333	2.166448	2.037771
N	3.419254	4.669571	0.502743
H	3.026385	5.191325	-0.251182
O	2.665511	0.268229	3.653334
H	3.104573	0.599860	2.868556
O	2.449955	6.131842	1.900855

S0-ENOL-1

C	2.178673	1.233457	1.206117
C	3.515301	1.600099	1.288423
H	4.008150	1.543049	2.243218
C	4.216020	2.027474	0.175210
H	5.250235	2.303279	0.271115

C	3.575563	2.098425	-1.062881
H	4.108720	2.432690	-1.933793
C	2.235374	1.751541	-1.155033
H	1.705506	1.830651	-2.085813
C	1.522018	1.303520	-0.033924
C	-0.445758	0.079465	0.364228
C	-1.919806	-0.074704	0.150356
C	-2.447878	-1.248373	-0.375791
C	-3.816181	-1.408705	-0.513810
H	-4.189162	-2.328197	-0.924713
C	-4.667703	-0.388122	-0.132876
H	-5.729929	-0.517033	-0.239220
C	-4.158345	0.799612	0.368587
H	-4.818678	1.597295	0.655579
C	-2.790194	0.949742	0.502210
H	-2.383115	1.863628	0.894511
C	0.242241	-0.886239	1.320858
H	-0.411689	-1.696504	1.597404
H	1.130756	-1.296842	0.848570
C	0.650894	-0.164851	2.585559
N	0.159365	1.030245	-0.237033
N	1.511235	0.876175	2.394250
H	1.830991	1.295207	3.240826
O	-1.649473	-2.285475	-0.754109
H	-0.863933	-1.968973	-1.178316
O	0.251247	-0.458934	3.672628

S0-KETO

C	4.338237	3.626903	0.152801
C	5.143502	3.751254	-0.977318
H	5.053824	4.640644	-1.575730
C	6.027705	2.761438	-1.340965
H	6.628889	2.880127	-2.223521
C	6.143607	1.612434	-0.557761
H	6.833577	0.834969	-0.828620
C	5.367534	1.481484	0.581557
H	5.445535	0.604796	1.198737
C	4.454526	2.480329	0.949661
C	3.210014	3.108654	2.984243
C	2.365381	2.700317	4.025168
C	2.035407	1.280215	4.183231
C	1.187457	0.925977	5.315324
H	0.965481	-0.118519	5.430127
C	0.713799	1.856534	6.145801

H	0.085387	1.566945	6.970638
C	1.015241	3.263271	5.968029
H	0.590757	3.981289	6.645076
C	1.800404	3.650997	4.964103
H	1.988753	4.698325	4.832103
C	3.714455	4.523890	2.820189
H	3.508597	5.133833	3.678593
H	4.791316	4.485198	2.686742
C	3.082706	5.194804	1.618012
N	3.650071	2.236895	2.070237
N	3.390275	4.633534	0.415870
H	3.008610	5.118819	-0.367655
O	2.446545	0.404822	3.424606
H	3.370834	1.283541	2.255546
O	2.359930	6.140982	1.709470

S0-KETO-1

C	2.519740	0.357805	-0.345553
C	3.915034	0.408065	-0.251146
H	4.421836	1.310131	-0.544179
C	4.637088	-0.687554	0.199824
H	5.708886	-0.638566	0.253916
C	3.960859	-1.839039	0.595750
H	4.506912	-2.689546	0.960991
C	2.588332	-1.884655	0.532938
H	2.063226	-2.768370	0.851034
C	1.849945	-0.802045	0.048777
C	-0.516887	-0.059383	0.232249
C	-1.848992	-0.346727	0.038177
C	-2.944997	0.480154	0.616242
C	-4.318181	0.014135	0.346917
H	-5.090979	0.626455	0.772609
C	-4.585513	-1.084681	-0.360295
H	-5.603346	-1.389781	-0.528588
C	-3.513972	-1.874029	-0.929287
H	-3.755145	-2.727043	-1.536943
C	-2.240520	-1.523762	-0.731637
H	-1.482752	-2.101862	-1.227109
C	0.003293	1.255424	0.764231
H	-0.800533	1.857458	1.135787
H	0.712901	1.059035	1.562984
C	0.691709	2.032218	-0.347770
N	0.452762	-0.951083	-0.084734
N	1.824051	1.465260	-0.861039

H	2.291220	2.034363	-1.533702
O	-2.787095	1.456213	1.310928
H	0.164733	-1.880233	-0.280494
O	0.278288	3.071898	-0.761515

S1S0-ENOL

C	4.338720	3.891059	0.429873
C	3.951282	3.613887	-0.877197
H	3.689598	4.428947	-1.531740
C	3.896991	2.309206	-1.334349
H	3.601087	2.111361	-2.350315
C	4.203046	1.258735	-0.477597
H	4.151768	0.242697	-0.828899
C	4.568604	1.507821	0.853698
H	4.786623	0.690070	1.515831
C	4.648144	2.819050	1.307478
C	3.642856	3.588120	3.097021
C	2.808551	2.655391	3.895287
C	3.262547	1.427246	4.366914
C	2.402572	0.589449	5.078982
H	2.796510	-0.341958	5.435854
C	1.099311	0.951973	5.315533
H	0.455388	0.287603	5.859271
C	0.622732	2.178215	4.864020
H	-0.391741	2.473886	5.047970
C	1.470934	3.006043	4.178161
H	1.096602	3.941839	3.822290
C	3.386453	5.057226	3.109106
H	2.322813	5.245481	3.058748
H	3.725751	5.509210	4.032426
C	3.996022	5.863630	1.977360
N	4.955864	3.204536	2.656014
N	4.433854	5.241298	0.845051
H	4.678691	5.904548	0.138506
O	4.509530	0.957223	4.197472
H	5.129748	1.656555	4.028127
O	4.045230	7.058297	2.070279

S1S0-ENOL-1

C	4.497048	3.569225	0.360223
C	4.778977	2.805355	-0.754466
H	4.409747	3.120847	-1.716059
C	5.534069	1.634996	-0.652415
H	5.742913	1.059112	-1.537089

C	6.002089	1.220518	0.584862
H	6.588283	0.322765	0.672591
C	5.709907	1.974010	1.733917
H	6.075413	1.663435	2.695946
C	4.955987	3.131921	1.627846
C	3.175403	3.818773	2.843481
C	2.620323	2.917195	3.883848
C	1.269412	2.501969	3.882036
C	0.789716	1.657959	4.862824
H	-0.241442	1.350442	4.838709
C	1.629840	1.201259	5.865994
H	1.244078	0.549530	6.627618
C	2.952808	1.583793	5.879194
H	3.610771	1.243301	6.656926
C	3.435928	2.435822	4.889868
H	4.456326	2.757280	4.932002
C	2.434343	4.992522	2.292804
H	1.376919	4.793561	2.237419
H	2.557869	5.849258	2.947534
C	2.855934	5.456537	0.911371
N	4.581604	3.919536	2.747764
N	3.799385	4.783711	0.180900
H	3.867284	5.176825	-0.734775
O	0.472105	2.911119	2.869464
H	-0.386823	2.520956	2.946282
O	2.330860	6.424733	0.435396

S1S0-KETO

C	4.375884	3.416122	0.023774
C	5.404925	3.658543	-0.874063
H	5.252284	4.385609	-1.648307
C	6.598675	2.967062	-0.785892
H	7.376000	3.160749	-1.499115
C	6.799482	2.042863	0.227508
H	7.728949	1.515025	0.312600
C	5.791712	1.816493	1.136493
H	5.916150	1.121509	1.943808
C	4.582643	2.486371	1.039746
C	3.002872	3.065833	2.800585
C	2.217022	2.635604	3.957541
C	0.786897	2.298389	3.905075
C	0.160905	2.011616	5.219001
H	-0.894931	1.781996	5.206468
C	0.882075	2.040045	6.387944

H	0.381283	1.825833	7.322288
C	2.288366	2.349344	6.398332
H	2.839410	2.367962	7.330068
C	2.913073	2.638847	5.186659
H	3.966775	2.902424	5.150725
C	3.017143	4.452023	2.257896
H	2.514716	5.125673	2.916669
H	4.046810	4.764966	2.144866
C	2.325708	4.474999	0.908528
N	3.537390	2.154097	1.924878
N	3.136147	4.061588	-0.122299
H	2.708061	4.053427	-1.020113
O	0.164159	2.252452	2.867895
H	3.531138	1.219156	2.216334
O	1.217566	4.861090	0.737122

S1S0-KETO-1

C	2.420061	0.343709	-0.015526
C	3.793852	0.368178	-0.126177
H	4.294952	1.313942	-0.151463
C	4.521181	-0.817053	-0.262288
H	5.583445	-0.768262	-0.382079
C	3.882163	-2.027722	-0.203663
H	4.432114	-2.943908	-0.264555
C	2.499981	-2.059025	-0.082870
H	1.966929	-2.985768	-0.037664
C	1.765036	-0.902944	-0.014149
C	-0.516866	-0.415941	0.788541
C	-1.937706	-0.344187	0.384155
C	-2.937358	-1.289206	0.895500
C	-4.317941	-1.075624	0.381275
H	-5.086391	-1.747105	0.745484
C	-4.600082	-0.065779	-0.500590
H	-5.620457	0.063628	-0.843236
C	-3.562535	0.839278	-0.991704
H	-3.809141	1.612883	-1.718317
C	-2.292550	0.679829	-0.544468
H	-1.487727	1.308916	-0.911811
C	0.148122	0.631986	1.609470
H	-0.496085	0.982105	2.381143
H	1.018739	0.170951	2.051760
C	0.547617	1.785154	0.726782
N	0.366776	-0.981617	-0.106667
N	1.675542	1.540069	-0.007737

H	1.965321	2.273930	-0.610747
O	-2.666158	-2.155638	1.704986
H	0.053226	-1.776801	-0.571125
O	-0.056625	2.806820	0.645390

6. Cartesian Coordinates of All Optimized OM2/MRCI Structures

S0-ENOL

C	4.306366	3.622233	0.147513
C	5.107826	3.780534	-0.992940
H	4.998664	4.672000	-1.617027
C	6.021046	2.789809	-1.353469
H	6.592354	2.898609	-2.278766
C	6.153300	1.656805	-0.553327
H	6.900329	0.898840	-0.825125
C	5.367441	1.458914	0.562054
H	5.454017	0.566749	1.184299
C	4.428966	2.451244	0.943586
C	3.289525	3.078415	2.926885
C	2.385759	2.696083	4.024910
C	2.118120	1.326085	4.264930
C	1.279388	0.924037	5.323058
H	1.114092	-0.138562	5.489981
C	0.701342	1.897199	6.127768
H	0.073094	1.597007	6.974701
C	0.913483	3.256569	5.867787
H	0.399532	4.010382	6.469902
C	1.757101	3.657064	4.836903
H	1.892960	4.724310	4.635746
C	3.854232	4.485477	2.856168
H	3.671860	5.056410	3.777777
H	4.937948	4.423213	2.653755
C	3.121106	5.135987	1.705378
N	3.634192	2.181612	2.058724
N	3.358023	4.613976	0.444561
H	2.953348	5.118511	-0.337474
O	2.624843	0.313904	3.533083
H	3.077787	0.675484	2.707372
O	2.317014	6.064668	1.861590

S0-ENOL-1

C	2.185132	1.211885	1.243515
C	3.553180	1.545505	1.323171
H	4.078031	1.438623	2.277428

C	4.220185	2.011482	0.198037
H	5.286738	2.253400	0.260588
C	3.538570	2.185396	-1.007106
H	4.073197	2.563664	-1.884335
C	2.184628	1.885430	-1.100671
H	1.638100	2.027418	-2.036191
C	1.485775	1.390618	0.020784
C	-0.438886	0.093549	0.353694
C	-1.897591	-0.076263	0.173933
C	-2.470987	-1.330085	-0.140758
C	-3.858887	-1.493772	-0.264208
H	-4.265055	-2.479206	-0.484793
C	-4.676508	-0.385416	-0.069348
H	-5.763645	-0.493572	-0.149132
C	-4.121736	0.872385	0.200987
H	-4.781244	1.735633	0.329766
C	-2.744412	1.033960	0.309246
H	-2.310478	2.016271	0.513077
C	0.273937	-0.927162	1.204938
H	-0.357249	-1.795457	1.440094
H	1.212276	-1.245688	0.708109
C	0.603188	-0.201830	2.500830
N	0.123353	1.130230	-0.155798
N	1.516066	0.831693	2.416560
H	1.805997	1.263852	3.288196
O	-1.725352	-2.460316	-0.301405
H	-0.907417	-2.233973	-0.817872
O	0.063926	-0.481553	3.576421

S0-KETO

C	4.210531	3.254293	0.336359
C	5.047005	3.426287	-0.769548
H	4.963332	4.332291	-1.376609
C	5.945968	2.418091	-1.135685
H	6.559265	2.551695	-2.033038
C	6.033641	1.250828	-0.386267
H	6.735577	0.464533	-0.679627
C	5.241063	1.069863	0.732490
H	5.310942	0.160748	1.334419
C	4.309268	2.072769	1.114215
C	3.147013	2.743100	3.163179
C	2.280571	2.372115	4.214046
C	1.908587	0.966541	4.348750
C	1.056131	0.589991	5.458022

H	0.794041	-0.465463	5.539171
C	0.622157	1.526462	6.342914
H	-0.033004	1.248889	7.179651
C	0.986390	2.897676	6.203612
H	0.583607	3.623648	6.914801
C	1.809517	3.306022	5.183518
H	2.081183	4.366921	5.099953
C	3.737836	4.122656	3.029443
H	3.587124	4.727702	3.936904
H	4.814394	4.037196	2.803415
C	3.012549	4.785405	1.865705
N	3.535536	1.820859	2.247124
N	3.254481	4.255092	0.614718
H	2.853551	4.744512	-0.178759
O	2.320650	0.109032	3.521561
H	3.226271	0.831289	2.434274
O	2.300224	5.786295	2.015554

S0-KETO-1

C	5.622189	4.453738	1.484214
C	6.383602	5.098822	0.487728
H	7.350563	4.677939	0.197574
C	5.925035	6.274100	-0.096440
H	6.529672	6.773214	-0.859005
C	4.693659	6.812007	0.280903
H	4.334572	7.733659	-0.187348
C	3.914766	6.183644	1.247834
H	2.954707	6.613062	1.550405
C	4.373215	5.007782	1.870901
C	3.257351	3.128597	3.030276
C	2.399081	2.681247	4.045497
C	1.977800	1.281431	4.085710
C	1.067459	0.884285	5.160301
H	0.781017	-0.169214	5.181093
C	0.626363	1.777262	6.074880
H	-0.056778	1.476213	6.881914
C	1.035560	3.144892	6.022035
H	0.659516	3.837426	6.779129
C	1.889374	3.578251	5.038810
H	2.185128	4.641836	5.031692
C	3.866418	2.190844	2.023775
H	3.434053	1.184544	2.140653
H	3.718137	2.589405	1.000436
C	5.354147	2.145642	2.337843

N	3.583595	4.448515	2.895669
N	6.112538	3.280505	2.060886
H	7.118501	3.195019	2.162911
O	2.330470	0.446779	3.223590
H	3.121469	5.124604	3.500699
O	5.925609	1.145274	2.775610

S1S0-ENOL

C	3.764501	3.465315	0.617328
C	3.464215	3.088232	-0.711760
H	2.721226	3.663404	-1.277142
C	4.087894	2.002468	-1.302716
H	3.828652	1.719014	-2.328390
C	5.072677	1.281927	-0.613303
H	5.583121	0.452179	-1.109096
C	5.374402	1.606998	0.690372
H	6.122646	1.043838	1.256090
C	4.703006	2.670638	1.367629
C	4.069569	3.572310	3.377784
C	2.914409	2.885695	3.932044
C	2.973250	1.486356	4.171867
C	1.907527	0.802460	4.790859
H	2.000229	-0.265504	4.975946
C	0.770232	1.519280	5.142364
H	-0.076728	0.999490	5.605886
C	0.691435	2.900248	4.912042
H	-0.214971	3.444513	5.191679
C	1.745264	3.579137	4.311051
H	1.657088	4.652885	4.119230
C	4.177287	5.050383	3.381027
H	3.740376	5.534715	4.271807
H	5.227345	5.376791	3.255604
C	3.394646	5.495453	2.155101
N	4.998418	2.881660	2.666775
N	3.219571	4.683101	1.034777
H	2.621167	5.128484	0.334156
O	4.030979	0.706898	3.852196
H	4.818051	1.273274	3.606460
O	2.886269	6.623248	2.100581

S1S0-ENOL-1

C	3.975727	3.190771	0.890875
C	4.287342	2.573249	-0.332543
H	3.573317	2.623432	-1.163200

C	5.485042	1.888112	-0.505755
H	5.694889	1.384479	-1.455901
C	6.440642	1.855522	0.521922
H	7.396800	1.354403	0.351284
C	6.157246	2.431705	1.738024
H	6.872701	2.401613	2.565129
C	4.907382	3.078179	1.978208
C	3.371936	3.770423	3.544870
C	2.566820	2.676342	4.052162
C	1.157181	2.759956	4.214652
C	0.399823	1.688152	4.708741
H	-0.684672	1.782418	4.806899
C	1.047961	0.507683	5.061800
H	0.470834	-0.330629	5.463994
C	2.435567	0.398241	4.909136
H	2.932889	-0.535179	5.187917
C	3.183632	1.465272	4.421810
H	4.268836	1.373370	4.329842
C	2.812706	5.113715	3.224687
H	1.941582	5.398757	3.833544
H	3.594203	5.896444	3.281602
C	2.360329	4.993905	1.774849
N	4.665297	3.559245	3.218663
N	2.845592	4.024208	0.893144
H	2.366907	4.060435	-0.010467
O	0.572120	3.932656	3.860213
H	-0.415671	3.862744	3.960684
O	1.561293	5.818716	1.305318

S1S0-KETO

C	4.192258	3.168250	0.188366
C	4.858445	3.270235	-1.049280
H	4.351703	3.765857	-1.883474
C	6.120287	2.722567	-1.222022
H	6.614109	2.792211	-2.196143
C	6.762718	2.085258	-0.157730
H	7.761017	1.659528	-0.298842
C	6.137642	1.983437	1.075708
H	6.634727	1.481325	1.911978
C	4.842602	2.502230	1.261274
C	3.500440	3.272704	3.171557
C	2.500276	2.813358	4.139086
C	1.211979	2.363122	3.610753
C	0.204168	1.971224	4.578243

H	-0.778430	1.694511	4.195635
C	0.485783	2.000568	5.923639
H	-0.283669	1.726282	6.656072
C	1.754986	2.395760	6.393561
H	1.950653	2.399952	7.472109
C	2.755521	2.796211	5.509381
H	3.739890	3.088197	5.889519
C	3.375341	4.631481	2.579751
H	2.906765	5.325333	3.298873
H	4.367058	5.013597	2.261410
C	2.465904	4.512227	1.358989
N	4.230200	2.329329	2.514433
N	2.917873	3.729733	0.306782
H	2.292259	3.640111	-0.488153
O	1.039931	2.271613	2.379451
H	4.270809	1.394079	2.914663
O	1.386047	5.107420	1.277428

S1S0-KETO-1

C	2.516080	0.340631	0.000012
C	3.911441	0.226659	0.138627
H	4.505890	1.134162	0.287963
C	4.535059	-1.009038	0.055425
H	5.621906	-1.081697	0.162090
C	3.777710	-2.165639	-0.153389
H	4.274799	-3.138825	-0.211105
C	2.400005	-2.085613	-0.279885
H	1.804271	-2.990476	-0.438182
C	1.750688	-0.836868	-0.218770
C	-0.489654	-0.005093	0.308396
C	-1.924257	-0.132297	0.077989
C	-2.667856	-1.151681	0.815031
C	-4.103078	-1.204487	0.600188
H	-4.671697	-1.953503	1.152782
C	-4.710302	-0.322856	-0.272607
H	-5.797081	-0.354919	-0.418815
C	-3.957990	0.636010	-0.978342
H	-4.471676	1.325087	-1.656434
C	-2.579463	0.727471	-0.817405
H	-2.006085	1.481725	-1.362976
C	0.034183	0.800717	1.442674
H	-0.787041	1.210385	2.054515
H	0.721368	0.195746	2.070940
C	0.788240	1.940973	0.782701

N	0.360173	-0.800862	-0.405589
N	1.928532	1.609173	0.051508
H	2.493257	2.386394	-0.276641
O	-2.080523	-1.955730	1.564186
H	-0.047109	-1.580108	-0.924361
O	0.417651	3.119356	0.817120