Supporting information

Density Functional Theory and Time-Resolved Resonance Raman Investigation of the Photocyclization of 2-Pyridyl Phenyl Ketone in Acid Solution

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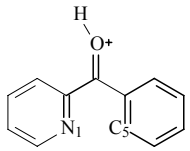
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Cartesian coordinates of the triplet stationary points

1



Reactant **1**

C	-2.359291	1.063896	-0.366544
C	-1.218760	0.493887	0.195040
C	-1.300834	-0.849822	0.692784
C	-2.437377	-1.649703	0.425864
C	-3.540061	-1.089519	-0.196319
C	-3.507476	0.274011	-0.564010
N	1.101218	-0.891670	-0.052224
C	1.262044	0.444538	0.125214
C	0.052740	1.192160	0.219240
C	2.101969	-1.723068	-0.278979
C	3.421291	-1.252136	-0.331802
C	3.646127	0.115009	-0.119130
C	2.579932	0.970843	0.114459
O	-0.008782	2.534946	0.189881
H	-2.464090	-2.673526	0.785324
H	-4.435349	-1.676436	-0.372391

H	-4.374614	0.717768	-1.044951
H	-2.341160	2.093019	-0.707189
H	4.658415	0.507061	-0.134624
H	4.236629	-1.947883	-0.494996
H	1.861528	-2.777094	-0.391202
H	2.757513	2.030369	0.276280
H	-0.592988	-1.189521	1.439550
H	0.854021	2.937784	-0.004183

E(UB+HF-LYP) = -592.943514697

Transition State **1**

C	2.531145	0.916512	-0.141113
C	1.186851	0.563415	0.125804
N	0.852970	-0.763057	0.163175
C	1.727388	-1.737725	-0.050920
C	3.065350	-1.440214	-0.318536
C	3.458385	-0.091367	-0.357328
C	0.052656	1.405063	0.291394
O	0.021288	2.739488	0.211902
C	-1.197470	0.664204	0.293218
C	-1.045906	-0.695839	0.788208
C	-2.013428	-1.677343	0.395708
C	-3.136853	-1.289872	-0.322325
C	-3.339043	0.060871	-0.646860
C	-2.350947	1.039792	-0.358249
H	-1.915641	-2.695649	0.759309
H	-3.891080	-2.024945	-0.584151
H	-4.241910	0.359986	-1.170111
H	-2.469173	2.056585	-0.718510
H	4.492942	0.164411	-0.563466
H	3.776838	-2.243325	-0.472298
H	1.357382	-2.757243	0.006424
H	2.831522	1.958705	-0.196624
H	-0.620437	-0.823165	1.783064
H	0.909696	3.125152	0.124904

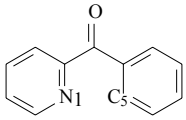
E(UB+HF-LYP) = -592.940251823

Product **1**

C	-2.475914	0.979474	-0.042674
C	-1.181398	0.701945	0.277253
C	-0.729077	-0.704845	0.584569
C	-1.595013	-1.748683	-0.046952
C	-2.905873	-1.423609	-0.352592

C	-3.392350	-0.109592	-0.263589
N	0.721820	-0.650400	0.198990
C	1.132673	0.674492	0.052065
C	0.000167	1.513187	0.151949
C	1.585562	-1.682400	0.136052
C	2.922500	-1.454303	-0.122043
C	3.378718	-0.123763	-0.295630
C	2.497035	0.933685	-0.206424
O	-0.069038	2.833651	0.009128
H	-1.247057	-2.775117	-0.105696
H	-3.577272	-2.211237	-0.681676
H	-4.434062	0.103396	-0.474523
H	-2.791172	2.001537	-0.229909
H	4.428220	0.062475	-0.498110
H	3.605320	-2.293254	-0.178685
H	1.174871	-2.672974	0.293868
H	2.841794	1.954666	-0.336838
H	-0.721089	-0.856411	1.684257
H	0.797834	3.236985	-0.170543

E(UB+HF-LYP) = -592.957258523

2 

Reactant **2**

N	1.405470	-1.015424	-0.297580
C	1.332266	0.298955	0.002770
C	2.496619	1.077792	0.232584
C	3.735785	0.466825	0.151526
C	3.807555	-0.900223	-0.147729
C	2.606859	-1.586062	-0.357907
C	0.031201	0.929869	0.056364
O	-0.025483	2.237983	0.204441
C	-1.280383	0.295870	0.026530
C	-2.403098	1.072268	-0.369863
C	-3.675715	0.516708	-0.381276
C	-3.867838	-0.813880	0.002354
C	-2.767087	-1.584899	0.406948
C	-1.491428	-1.041379	0.444489
H	-2.913333	-2.619353	0.706423
H	-4.862888	-1.249610	-0.011222

H	-4.521249	1.119187	-0.702121
H	-2.246070	2.094445	-0.696130
H	4.641129	1.042750	0.325110
H	4.758578	-1.417560	-0.223084
H	2.616427	-2.648211	-0.599362
H	2.390907	2.128843	0.484750
H	-0.646350	-1.637442	0.762442

E(UB+HF-LYP) = -592.571731817

Transition State **2**

N	0.882531	-0.739265	0.212498
C	1.177723	0.591912	0.157781
C	2.508044	0.971520	-0.159989
C	3.450549	-0.004652	-0.391337
C	3.091716	-1.379425	-0.327859
C	1.776537	-1.699885	-0.025736
C	0.044883	1.479799	0.288953
O	0.070391	2.731637	0.225199
C	-1.195899	0.674147	0.309027
C	-2.374348	1.062249	-0.320127
C	-3.322156	0.091960	-0.663813
C	-3.115456	-1.274145	-0.358617
C	-2.008733	-1.665404	0.374792
C	-1.048421	-0.689134	0.785396
H	-1.918329	-2.686691	0.734934
H	-3.861637	-2.007556	-0.650267
H	-4.210311	0.384321	-1.217757
H	-2.482441	2.096265	-0.632440
H	4.473135	0.272095	-0.632858
H	3.818776	-2.165984	-0.496455
H	1.424603	-2.726659	0.039296
H	2.731168	2.031782	-0.222660
H	-0.622441	-0.829477	1.778302

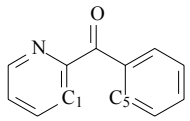
E(UB+HF-LYP) = -592.549745640

Product **2**

C	-0.717101	-0.668331	0.562239
C	-1.180058	0.733856	0.256881
C	-2.488790	1.000127	-0.037500
C	-3.386133	-0.076242	-0.257256
C	-2.898826	-1.410212	-0.326662
C	-1.598743	-1.727226	-0.029828
C	0.005702	1.612141	0.122735

O	0.013798	2.850908	0.017112
C	1.133220	0.712923	0.032234
N	0.709420	-0.622031	0.155679
C	1.598199	-1.656773	0.133400
C	2.924538	-1.422677	-0.099513
C	3.389067	-0.075637	-0.284015
C	2.492903	0.967628	-0.209030
H	-1.243229	-2.752312	-0.085020
H	-3.576245	-2.195535	-0.652879
H	-4.426160	0.124965	-0.494515
H	-2.798755	2.028253	-0.203956
H	4.441400	0.110740	-0.471275
H	3.613015	-2.259180	-0.136159
H	1.189681	-2.648832	0.291877
H	2.796199	2.003247	-0.326422
H	-0.716100	-0.801860	1.669597

E(UB+HF-LYP) = -592.575110308

3 

Reactant **3**

C	2.359847	1.079233	0.431232
C	1.308972	0.269643	-0.060600
C	1.618129	-1.030153	-0.521356
C	2.920647	-1.511869	-0.445108
C	3.948547	-0.708435	0.060655
C	3.660032	0.590364	0.489607
C	-0.039803	0.813958	-0.130403
O	-0.113133	2.130556	-0.293617
C	-1.310547	0.175039	-0.033116
N	-2.325230	1.072889	-0.234126
C	-3.580372	0.655054	-0.139005
C	-3.931801	-0.668944	0.151200
C	-2.898416	-1.587120	0.382106
C	-1.577446	-1.173014	0.301796
H	3.139549	-2.516205	-0.798250
H	4.964353	-1.089734	0.112676
H	4.452688	1.222961	0.879921
H	2.133859	2.080356	0.783467
H	-4.349358	1.408241	-0.306179

H	-4.975186	-0.962487	0.203248
H	-3.127867	-2.618516	0.636729
H	0.843003	-1.644243	-0.967212
H	-0.766094	-1.857580	0.521372

E(UB+HF-LYP) = -592.567745771

Transition State **3**

C	-1.016208	-0.606708	0.952271
C	-1.145266	0.735915	0.362422
C	-2.209119	1.039999	-0.478356
C	-3.078581	0.030672	-0.901112
C	-2.855625	-1.323611	-0.510154
C	-1.862207	-1.651689	0.372750
C	0.071082	1.578598	0.396319
O	0.109366	2.796438	0.241058
C	1.242576	0.655798	0.401816
C	0.995386	-0.714558	0.919815
C	1.697151	-1.757750	0.165552
C	2.704800	-1.399581	-0.680901
C	3.061217	-0.016523	-0.804261
N	2.310530	0.973511	-0.327101
H	-1.751221	-2.674444	0.724471
H	-3.505040	-2.100029	-0.906541
H	-3.888162	0.262611	-1.586791
H	-2.283840	2.048135	-0.877904
H	3.956214	0.270785	-1.352250
H	3.275810	-2.146284	-1.225525
H	1.466874	-2.803589	0.354735
H	-1.039504	-0.624226	2.048940
H	1.088988	-0.842404	2.005155

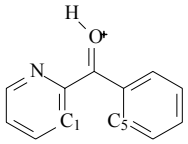
E(UB+HF-LYP) = -592.515114407

Product **3**

N	2.438661	0.944706	-0.122311
C	1.235889	0.681644	0.345399
C	0.776988	-0.698094	0.776746
C	1.466457	-1.732480	-0.076534
C	2.684683	-1.426182	-0.598864
C	3.210246	-0.096858	-0.464831
C	-0.799990	-0.585739	0.824057
C	-1.111784	0.774155	0.253958

C	0.089316	1.621502	0.208875
C	-2.322021	1.052879	-0.344863
C	-3.228437	0.010410	-0.601315
C	-2.852773	-1.346003	-0.350989
C	-1.677668	-1.667748	0.264513
O	0.141579	2.828095	-0.024741
H	-1.423014	-2.706582	0.460509
H	-3.520719	-2.138503	-0.679864
H	-4.176775	0.220530	-1.086275
H	-2.515926	2.062091	-0.700090
H	4.232691	0.126445	-0.759346
H	3.265860	-2.167442	-1.140678
H	1.038380	-2.726462	-0.175940
H	-1.045145	-0.546825	1.905553
H	1.115950	-0.885873	1.813332

E(UB+HF-LYP) = -592.545536143

4 

Reactant **4**

C	2.353049	0.988107	0.561878
C	1.305688	0.279682	-0.069858
C	1.580187	-0.976396	-0.654499
C	2.863385	-1.508791	-0.593335
C	3.889435	-0.803555	0.043513
C	3.631544	0.445094	0.618037
C	-0.010227	0.894348	-0.147501
O	-0.133756	2.227225	-0.312439
C	-1.254314	0.238591	-0.003466
N	-2.403695	0.916674	-0.208309
C	-3.665241	0.551083	-0.191490
C	-3.911552	-0.781440	0.149908
C	-2.800335	-1.602026	0.450579
C	-1.510807	-1.119586	0.392861
H	3.069722	-2.467631	-1.058491
H	4.889101	-1.224319	0.088440
H	4.425586	0.989469	1.119318
H	2.150983	1.938823	1.048922
H	-4.434961	1.291662	-0.393846
H	-4.936288	-1.129584	0.212621

H	-2.967245	-2.634695	0.741456
H	0.804503	-1.504497	-1.200494
H	-0.652074	-1.737259	0.634338
H	0.721714	2.612849	-0.574351

E(UB+HF-LYP) = -592.935467531

Transition State **4**

N	2.323806	0.944107	-0.217161
C	1.240867	0.539133	0.456129
C	1.057869	-0.863736	0.862199
C	1.802823	-1.812715	0.085794
C	2.769154	-1.369334	-0.785449
C	3.091580	0.023587	-0.781104
C	0.093751	1.400432	0.484322
O	0.254457	2.698162	0.263394
C	-1.138780	0.674661	0.372291
C	-1.145392	-0.660106	0.946543
C	-2.070863	-1.615210	0.434336
C	-2.995108	-1.248986	-0.525723
C	-3.061988	0.092281	-0.973530
C	-2.145818	1.045449	-0.531295
H	-2.099050	-2.609664	0.869803
H	-3.711049	-1.973674	-0.900061
H	-3.811795	0.375027	-1.705979
H	-2.151282	2.035270	-0.979637
H	3.999949	0.378626	-1.262576
H	3.375820	-2.060438	-1.360722
H	1.680577	-2.874284	0.281884
H	-0.932809	-0.751318	2.005662
H	0.954090	-1.119151	1.912243
H	-0.595311	3.172822	0.285267

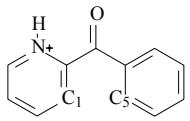
E(UB+HF-LYP) = -592.892341181

Product **4**

C	-2.332315	1.040144	-0.302017
C	-1.112480	0.737747	0.279386
C	-0.807778	-0.647965	0.804896
C	-1.695698	-1.697747	0.224019
C	-2.879924	-1.349967	-0.382798
C	-3.247429	0.004354	-0.582540
C	0.780485	-0.764317	0.772652
C	1.220673	0.623997	0.375753
C	0.089263	1.499045	0.236118
C	1.514644	-1.767895	-0.078937

C	2.707815	-1.417930	-0.630148
C	3.208340	-0.079007	-0.467821
N	2.420679	0.925050	-0.090740
O	0.252669	2.771580	-0.047654
H	-1.456586	-2.743134	0.397770
H	-3.554613	-2.129405	-0.724216
H	-4.201670	0.242397	-1.039733
H	-2.564782	2.048411	-0.639680
H	4.233212	0.169557	-0.729263
H	3.309350	-2.140110	-1.172823
H	1.154257	-2.791543	-0.129215
H	-1.054355	-0.645522	1.884437
H	1.091252	-0.985898	1.808781
H	-0.595747	3.244500	-0.131020

E(UB+HF-LYP) = -592.910608225

5 

Reactant **5**

C	-2.342254	0.969740	-0.656394
C	-1.320453	0.258781	0.043239
C	-1.645502	-0.914436	0.766208
C	-2.931426	-1.418319	0.695625
C	-3.930899	-0.730258	-0.032523
C	-3.631742	0.460448	-0.702641
C	1.508949	-1.108771	-0.437150
C	1.278784	0.219398	-0.002718
C	0.020936	0.862165	0.089789
C	2.795364	-1.595891	-0.524704
C	3.900963	-0.772700	-0.191705
C	3.663587	0.516805	0.217729
N	2.391766	0.981686	0.305504
O	-0.081843	2.122404	0.362904
H	-3.181255	-2.341420	1.209435
H	-4.941205	-1.127330	-0.056637
H	-4.404528	0.987645	-1.252327
H	-2.086304	1.891591	-1.165780
H	4.446253	1.215909	0.488005
H	4.918179	-1.137846	-0.261872
H	2.964229	-2.613515	-0.861458

H	-0.887441	-1.417116	1.357721
H	0.659872	-1.721694	-0.716151
H	2.226727	1.930970	0.628770

E(UB+HF-LYP) = -592.965933529

Transition State **5**

N	2.268550	0.907084	-0.233109
C	1.171248	0.551961	0.498058
C	1.003503	-0.843756	0.889074
C	1.803365	-1.783058	0.166211
C	2.783488	-1.361117	-0.722795
C	3.056329	0.007515	-0.847403
C	0.049680	1.492808	0.483043
O	0.191276	2.697159	0.252669
C	-1.185168	0.698150	0.414193
C	-1.133554	-0.678930	0.909741
C	-2.007457	-1.654437	0.289927
C	-2.976288	-1.239377	-0.585223
C	-3.126367	0.145853	-0.902603
C	-2.234701	1.099450	-0.410820
H	-1.964094	-2.688169	0.619750
H	-3.672159	-1.957379	-1.008085
H	-3.916203	0.450710	-1.582448
H	-2.279037	2.133526	-0.739617
H	3.880220	0.398899	-1.433102
H	3.409014	-2.071032	-1.250691
H	1.704386	-2.842665	0.387542
H	-1.066598	-0.796124	1.991966
H	0.904398	-1.074194	1.949834
H	2.365543	1.909201	-0.413164

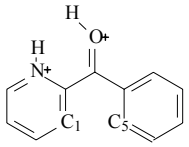
E(UB+HF-LYP) = -592.904784775

Product **5**

C	-2.393813	1.074435	-0.256729
C	-1.154959	0.763411	0.293021
C	-0.844635	-0.631236	0.780637
C	-1.710531	-1.684951	0.155182
C	-2.893086	-1.332281	-0.420625
C	-3.277040	0.041264	-0.569957
C	0.029131	1.594458	0.235025
O	0.186985	2.788610	-0.040163

C	1.149286	0.635187	0.347654
N	2.358518	0.888038	-0.124743
C	3.221871	-0.118498	-0.500483
C	2.740193	-1.440290	-0.523782
C	1.507026	-1.767339	-0.009174
C	0.741288	-0.733876	0.773392
H	-1.455085	-2.731126	0.299315
H	-3.565659	-2.101806	-0.787260
H	-4.238096	0.273587	-1.017782
H	-2.616829	2.101733	-0.530942
H	4.196536	0.184142	-0.859352
H	3.366526	-2.198387	-0.982078
H	1.131342	-2.783609	-0.070468
H	-1.125316	-0.667540	1.852140
H	1.052995	-0.867146	1.828943
H	2.559700	1.863308	-0.362982

E(UB+HF-LYP) = -592.927757275

6 

Reactant **6**

C	-1.622009	-0.976051	0.616511
C	-1.298926	0.279001	0.061631
C	0.027163	0.869711	0.118089
C	1.287267	0.183455	0.014897
C	1.493587	-1.153272	-0.368520
N	2.409369	0.938964	0.264259
C	3.668984	0.467494	0.185282
C	3.891892	-0.856292	-0.162384
C	2.785652	-1.667627	-0.448279
C	-2.968116	-1.510365	0.551767
C	-4.012583	-0.789726	-0.025500
C	-3.721672	0.462796	-0.551670
C	-2.376347	1.000329	-0.511276
O	0.163260	2.215681	0.159920
H	-3.147468	-2.493225	0.981003
H	-5.018473	-1.194296	-0.063031
H	-4.498761	1.064401	-1.016417
H	-2.207110	1.974470	-0.963202
H	4.463206	1.173303	0.402774

H	4.906305	-1.233808	-0.223033
H	2.933685	-2.699432	-0.751956
H	-0.874284	-1.558146	1.146612
H	0.650445	-1.774023	-0.645821
H	-0.569820	2.667431	0.616031
H	2.261266	1.918408	0.504573

E(UB+HF-LYP) = -593.189106293

Transition State **6**

C	0.989847	-0.819573	0.854119
C	1.153593	0.562240	0.418299
N	2.256477	0.914189	-0.294755
C	3.114760	0.001000	-0.807180
C	2.874292	-1.366345	-0.629215
C	1.850328	-1.778812	0.210566
C	-0.000901	1.414930	0.447421
O	0.191570	2.698360	0.204268
C	-1.204224	0.655625	0.406209
C	-2.336268	1.036587	-0.324892
C	-3.212054	0.050252	-0.808363
C	-2.959078	-1.327342	-0.596206
C	-1.912200	-1.732990	0.212078
C	-1.062934	-0.748813	0.848630
H	-1.809747	-2.778360	0.490352
H	-3.632496	-2.065059	-1.022285
H	-4.067624	0.351109	-1.406097
H	-2.492412	2.068259	-0.629738
H	3.962376	0.391343	-1.360590
H	3.553224	-2.081099	-1.081975
H	1.758079	-2.829776	0.472369
H	-1.058616	-0.887239	1.932195
H	0.914024	-0.984662	1.930481
H	-0.616037	3.246799	0.236670
H	2.390362	1.901923	-0.521040

E(UB+HF-LYP) = -593.131150623

Product **6**

C	-0.830609	-0.697535	0.732621
C	-1.166773	0.714389	0.297164
C	-2.452185	1.022430	-0.182340
C	-3.330567	-0.021582	-0.507922
C	-2.913923	-1.377445	-0.446788

C	-1.689824	-1.731610	0.084312
C	-0.005831	1.496644	0.225958
O	0.206095	2.763451	-0.056394
C	1.143200	0.618731	0.317397
C	0.761780	-0.761933	0.746148
C	1.582572	-1.791017	0.017204
C	2.812744	-1.438684	-0.483522
C	3.249728	-0.098998	-0.478189
N	2.365392	0.890930	-0.141064
H	-1.417732	-2.780497	0.169782
H	-3.579381	-2.149245	-0.822811
H	-4.318834	0.215917	-0.890331
H	-2.749438	2.045867	-0.399489
H	4.230976	0.219905	-0.808632
H	3.475947	-2.187703	-0.904654
H	1.256979	-2.826959	0.003348
H	-1.126398	-0.782774	1.797983
H	1.044481	-0.878278	1.812577
H	-0.597904	3.317110	-0.104985
H	2.612919	1.862199	-0.346451

E(UB+HF-LYP) = -593.147896329

Reactant **7**

C	2.520261	1.063784	0.300322
C	1.312623	0.362080	0.042858
N	1.426296	-0.956289	-0.361614
C	2.619845	-1.590616	-0.504861
C	3.794048	-0.925943	-0.250665
C	3.734382	0.431159	0.158358
C	0.038518	0.961613	0.145508
O	-0.131481	2.216105	0.405569
C	-1.291678	0.313793	0.071265
C	-1.608789	-0.812847	0.864921
C	-2.873517	-1.373808	0.771893
C	-3.851043	-0.789029	-0.058699
C	-3.558092	0.356151	-0.804589
C	-2.291351	0.922998	-0.733102
H	-3.116850	-2.259116	1.351266
H	-4.843545	-1.226793	-0.105441
H	-4.318631	0.808677	-1.432535
H	-2.046853	1.815602	-1.298004
H	4.651850	0.972929	0.364365
H	4.739978	-1.440465	-0.367078

H	2.571946	-2.624047	-0.827213
H	-0.870001	-1.231159	1.542471
H	0.574842	-1.464036	-0.580488
H	2.453792	2.097585	0.620141

E(UB+HF-LYP) = -592.961718058

Transition State **7**

C	-2.244238	1.044658	-0.490967
C	-1.168885	0.783300	0.333363
C	-0.987571	-0.543310	0.934690
C	-1.789076	-1.636530	0.391310
C	-2.821296	-1.343117	-0.464865
C	-3.095416	-0.008055	-0.874561
C	0.052408	1.627185	0.354140
O	0.119790	2.830297	0.169261
C	1.212035	0.704506	0.370702
C	2.406490	0.913961	-0.281708
C	3.179668	-0.172242	-0.718136
C	2.648940	-1.492065	-0.596309
C	1.506863	-1.736931	0.095350
N	0.849783	-0.645649	0.796022
H	-1.662693	-2.640338	0.785519
H	-3.471426	-2.142265	-0.808385
H	-3.927090	0.185750	-1.543913
H	-2.359368	2.040040	-0.910433
H	4.115835	-0.009015	-1.239444
H	3.155619	-2.326651	-1.070597
H	1.070600	-2.714704	0.255803
H	-0.961950	-0.550698	2.031010
H	1.068975	-0.750230	1.795822
H	2.665165	1.937105	-0.539686

E(UB+HF-LYP) = -592.895128951

Product **7**

N	0.769149	-0.629565	0.734973
C	1.208433	0.735986	0.341768
C	2.465759	0.902936	-0.176271

C	3.241400	-0.211074	-0.550174
C	2.628464	-1.500598	-0.566340
C	1.403123	-1.722379	-0.029302
C	0.047903	1.653823	0.254237
O	0.126879	2.850755	0.024977
C	-1.149975	0.801174	0.277591
C	-2.320425	1.043395	-0.405329
C	-3.186169	-0.026557	-0.701959
C	-2.811773	-1.364510	-0.377373
C	-1.671703	-1.657066	0.319853
C	-0.857309	-0.538076	0.862238
H	-1.458799	-2.674682	0.633301
H	-3.464046	-2.176764	-0.684602
H	-4.103037	0.153512	-1.252685
H	-2.511652	2.041463	-0.789544
H	4.238189	-0.078664	-0.954328
H	3.131659	-2.330779	-1.052458
H	0.875073	-2.665247	-0.010921
H	-0.957699	-0.520854	1.960579
H	1.078466	-0.767071	1.708113
H	2.786401	1.917683	-0.395723

E(UB+HF-LYP) = -592.896413108

Reactant **8**

C	2.490212	1.002110	0.412223
C	1.326130	0.318183	0.018109
N	1.484364	-0.958957	-0.466970
C	2.682168	-1.584759	-0.556002
C	3.834460	-0.936146	-0.149201
C	3.732100	0.377877	0.331437
C	0.025226	0.941231	0.066856
O	0.094729	2.285167	0.058053
C	-1.273215	0.287890	0.037695
C	-1.541051	-0.949668	0.640151
C	-2.874814	-1.514960	0.637889
C	-3.962982	-0.843971	0.060278
C	-3.726095	0.386937	-0.525823
C	-2.398147	0.957631	-0.543413
H	-3.020315	-2.482250	1.113507
H	-4.955513	-1.281792	0.076078
H	-4.531559	0.947600	-0.993113
H	-2.262090	1.918307	-1.034104
H	4.622739	0.913126	0.646616

H	4.789708	-1.444090	-0.221044
H	2.671670	-2.587390	-0.968613
H	-0.765594	-1.496141	1.170333
H	0.679333	-1.439796	-0.857565
H	2.397345	2.013340	0.788101
H	-0.658046	2.716328	0.502965

E(UB+HF-LYP) = -593.179141128

Transition State **8**

C	-2.319786	1.023102	-0.387315
C	-1.172766	0.734139	0.340151
C	-0.954206	-0.633300	0.870544
C	-1.765580	-1.703966	0.282985
C	-2.867367	-1.372797	-0.477518
C	-3.192991	-0.023429	-0.762485
C	0.034184	1.503927	0.331021
O	0.191943	2.779444	0.098237
C	1.192094	0.669055	0.354984
C	2.417301	0.927101	-0.238884
C	3.227338	-0.138047	-0.668649
C	2.733840	-1.469887	-0.582590
C	1.578810	-1.760395	0.079821
N	0.845084	-0.696913	0.753890
H	-1.593673	-2.732844	0.586313
H	-3.522166	-2.161350	-0.837103
H	-4.083416	0.207228	-1.338914
H	-2.512154	2.025052	-0.763566
H	4.183060	0.060846	-1.142315
H	3.289459	-2.287268	-1.033213
H	1.199948	-2.760194	0.256226
H	-0.975643	-0.690179	1.965934
H	1.048285	-0.807847	1.758018
H	2.685576	1.956601	-0.461108
H	-0.635627	3.299792	0.094214

E(UB+HF-LYP) = -593.113473864

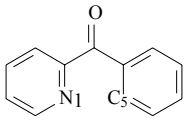
Product **8**

N	0.777171	-0.669625	0.712372
C	1.181783	0.706658	0.316634
C	2.449792	0.930416	-0.167862
C	3.283640	-0.158722	-0.509723
C	2.732576	-1.470294	-0.520377
C	1.502348	-1.745917	-0.006798

C	0.015427	1.534074	0.236099
O	0.173048	2.801418	-0.032449
C	-1.161908	0.746707	0.293248
C	-2.401682	1.006978	-0.279691
C	-3.266564	-0.064570	-0.583193
C	-2.836976	-1.409615	-0.417448
C	-1.637421	-1.726028	0.174821
C	-0.835801	-0.632331	0.793700
H	-1.368406	-2.762473	0.356406
H	-3.481815	-2.211327	-0.765914
H	-4.233561	0.139974	-1.031410
H	-2.681526	2.011395	-0.588913
H	4.289912	0.016874	-0.874168
H	3.292301	-2.289008	-0.964391
H	1.044674	-2.724910	0.048585
H	-0.996227	-0.689519	1.883272
H	1.060510	-0.787721	1.698105
H	2.754571	1.952099	-0.380859
H	-0.656297	3.316502	-0.084184

E(UB+HF-LYP) = -593.114871379

Cartesian coordinates of the ground state stationary points

2 

Reactant **2** (0,1)

C	-1.471937	-1.051968	0.348518
C	-1.300648	0.300964	0.009640
C	-2.436275	1.075019	-0.291914
C	-3.706949	0.511195	-0.273794
C	-3.867166	-0.835933	0.064274
C	-2.749903	-1.610309	0.378958
C	0.012259	1.021413	0.008642
O	0.035001	2.248837	0.014741
C	1.345751	0.301876	-0.003511
N	1.405361	-0.994139	-0.350030
C	2.607904	-1.575378	-0.397939
C	3.798927	-0.910648	-0.101007
C	3.732458	0.434523	0.261706
C	2.488086	1.054665	0.306025
H	-2.871231	-2.656214	0.647826

H	-4.859864	-1.278484	0.083382
H	-4.573502	1.119704	-0.518187
H	-2.294169	2.122356	-0.535974
H	4.634836	0.990362	0.501540
H	4.747759	-1.436100	-0.154407
H	2.619225	-2.624314	-0.689399
H	2.373297	2.100857	0.563748
H	-0.608931	-1.662400	0.576179

E(UB+HF-LYP) = -592.669373111

Transition State **2** (0,1)

C	-0.810946	-0.706439	0.657646
C	-1.186136	0.697116	0.356421
C	-2.482688	1.011361	-0.103131
C	-3.383775	0.018839	-0.418496
C	-2.967885	-1.345660	-0.322299
C	-1.742193	-1.722543	0.153284
C	-0.050362	1.554392	0.173835
O	0.058225	2.777593	0.026586
C	1.132846	0.634116	0.036959
N	0.783079	-0.667403	0.092614
C	1.679983	-1.659748	0.014384
C	3.017964	-1.366943	-0.202713
C	3.416782	-0.019025	-0.267743
C	2.472866	0.990270	-0.134171
H	-1.499585	-2.774964	0.281408
H	-3.668173	-2.124644	-0.619157
H	-4.374167	0.257195	-0.792139
H	-2.708857	2.059672	-0.282134
H	4.464758	0.225999	-0.415422
H	3.733124	-2.172121	-0.331985
H	1.295469	-2.672525	0.092502
H	2.723788	2.045506	-0.152808
H	-0.492449	-0.907449	1.694886

E(UB+HF-LYP) = -592.596129240

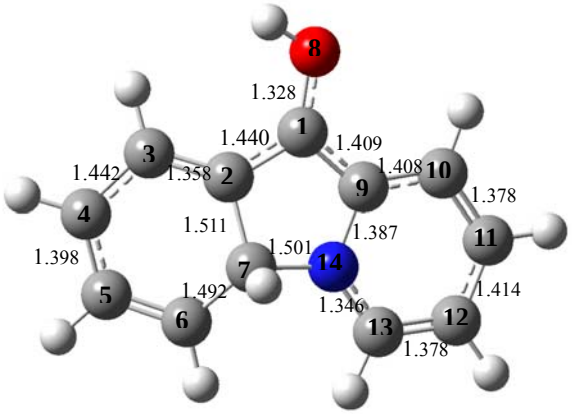
Product **2** (0,1)

C	2.454839	0.996019	-0.200835
C	1.109588	0.676459	0.013820
N	0.754449	-0.624068	0.188500
C	1.642687	-1.635198	0.165818
C	2.976566	-1.367268	-0.075251

C	3.385512	-0.027592	-0.254061
C	-0.717157	-0.701568	0.541750
C	-1.172068	0.710008	0.297312
C	-0.072094	1.588907	0.085350
C	-2.545751	0.966162	0.085746
C	-3.408621	-0.067971	-0.185470
C	-2.876246	-1.396322	-0.381163
C	-1.578566	-1.717702	-0.148020
O	0.023122	2.815839	-0.082391
H	-1.206531	-2.726848	-0.308892
H	-3.541996	-2.164970	-0.769397
H	-4.460854	0.115858	-0.377037
H	-2.873785	2.001974	0.047998
H	4.434661	0.193443	-0.428552
H	3.686279	-2.184760	-0.126893
H	1.250952	-2.633068	0.328680
H	2.710494	2.043401	-0.319430
H	-0.657475	-0.946869	1.623174

E(UB+HF-LYP) = -592.598772672

Comparison of the experimental vibrational frequencies with those calculated from the DFT calculations for PR1.



Expt frequency	Vibrational mode	Calculated frequency	Assignment or description
726	ν_{21}	731	ring deformation (i.p. ring)
935	ν_{28}	922	ring deformation (i.p. ring)
994	ν_{31}	980	C-H bending (i.p. ring without N14)
1027	ν_{34}	1017	C-H bending (major i.p. ring with N14)
1149	ν_{39}	1148	C-H bending (i.p. ring)
1181	ν_{40}	1166	C-H bending (i.p. ring with N14)
1225	ν_{41}	1227	C-H bending (i.p. ring) +O-H bending
1487	ν_{52}	1467	C-C stretching (ring)
1564	ν_{54}	1566	C1-C9 + C10-C11 stretching
1593	ν_{56}	1590	C2-C3 + C9-C10 stretching

Table 1S. Comparison of the vibrational frequencies of the 70 ns TR^3 spectrum shown in Figure 4 and 1S to the vibrational frequencies calculated for the PR1 species Scaling factor for the calculated frequencies is 0.978 for the 2PPK triplet cation species.

Comparison of the calculated Raman spectrum of the possible species in Scheme 2 with the experimental spectrum

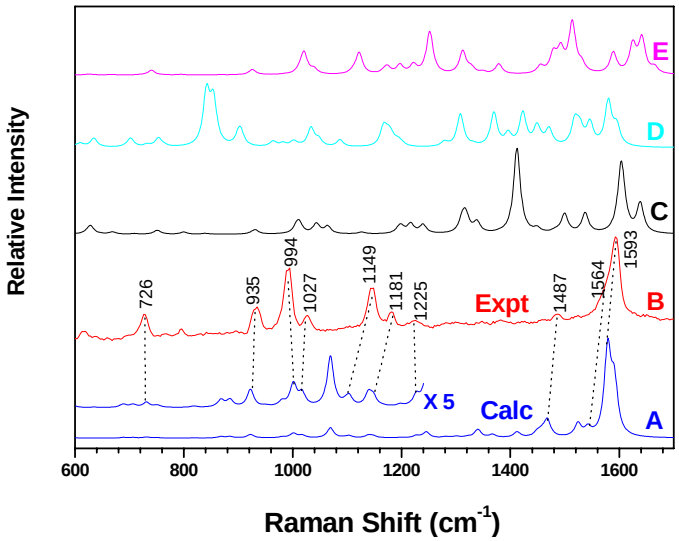
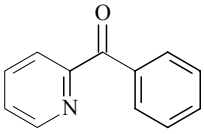
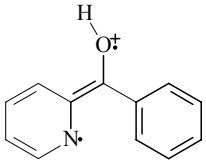
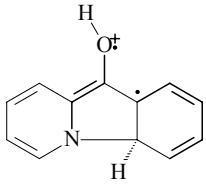
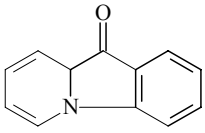


Figure 1S. Comparison of the experimental resonance Raman spectra (70 ns time delay) of excitation of 2-PPK obtained in acid solution (B) with the DFT calculated spectra for the PR1 (A) (see Scheme 1) and ground state 2-PPK (C), the carbonyl protonated triplet 2-PPK (D), the cyclization product of 2-PPK (E).
(See Scheme 2 in the text and note that the ground state 2-PPK is denoted **1**, the carbonyl protonated triplet 2-PPK is denoted **2**, the PR1 species is denoted **3** and the cyclization product of 2-PPK is denoted **4** in Scheme 2).

Table 2S. The TD-DFT calculated absorption band of the possible species in Scheme 2 (the top 3 oscillator strength transitions in 230-500 nm region)

(266 nm pump, 355 nm probe in the experiments)

TD//B3LYP/6-31G*			
 **1** ground state	 **2** triplet state	 **3** PR1	 **4** final product
286.88 nm f=0.0550 278.93 nm f=0.1641 253.96 nm f=0.1010	474.87 nm f=0.0859 307.76 nm f=0.3886 269.02 nm f=0.1270	432.04 nm f=0.1361 286.34 nm f=0.1008 251.45 nm f=0.0664	567.66 nm f=0.1238 341.01 nm f=0.0517 298.48 nm f=0.0168