Electronic Supplementary Information

Computational Investigation on the Mechanism and the Stereoselectivity of Morita–Baylis–Hillman Reaction and the Effect of the Bifunctional Catalyst N-methylprolinol

*Liang Dong, Song Qin, Zhishan Su, Huaqing Yang, Changwei Hu**

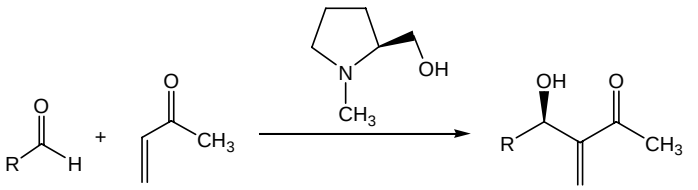
Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan, 610064, China.

AUTHOR EMAIL ADDRESS: chwehu@mail.sc.cninfo.net, gchem@scu.edu.cn

CONTENTS:

A. Computational methods.

The N-methylprolinol-catalyzed MBH reaction used in present simulation.



(R=H, or Ph) R=Ph: Yield=80%, ee=78%

All the stationary points such as the transition states, reactants and products were optimized in the gas-phase at the 6-311++G(d,p) basis set. Zero-point vibrational energies (ZPVE) and basis-set superposition error (BSSE) corrections were also applied in relative energies. All the transition states were characterized by one and only one imaginary frequency pertaining to the desired reaction coordinate. Considering the effect of the solvent, single-point B3LYP (PCM)/6-311++G(d,p) calculations were performed in 1,4-dioxane and water, respectively. The energies of solvation were obtained from PCM total electronic energies including ZPVE.

B. Energies and geometries

Table 1. The relative energies (in kJ/mol) for all the species along the MBH reaction between MVK and aldehyde catalyzed by N-methylprolinol.

(a) Imaginary frequencies at B3LYP/6-311++G(d,p) are shown.

(b) Single-point B3LYP (PCM, 1,4-dioxane)/[6-311++G(d,p)] calculations are shown.

(c) Single-point B3LYP (PCM, H_2O)/[6-311++G(d,p)] calculations are shown.

Species	E (Hartree)	$E_{BSSE+ZPVE}$ (Hartree)	E_{PCM}[(b)] (Hartree)	E_{PCM}[(c)] (Hartree)	i[(a)] (cm^{-1})	ΔE	ΔE_{PCM}[(b)]	ΔE_{PCM}[(c)]
HCHO	-114.515332	-	-114.544076	-114.547156	-	-	-	-
PhCHO	-345.559831	-	-345.672877	-345.678333	-	-	-	-
MVK	-231.218370	-	-231.310862	-231.315793	-	-	-	-
N-methylprolinol	-366.345918	-	-366.540088	-366.547070	-	-	-	-
product	-345.752896	-	-345.880930	-345.888815	-	-50.4	-49.0	-48.7
syn-IM1	-597.554000	-597.553700	-597.840663	-597.852328	-	27.8	28.6	29.3
anti-IM1	-597.553887	-597.553677	-597.841098	-597.854009	-	27.9	26.2	23.5
syn-TSa1	-712.018266	-	-712.351563	-712.378958	-198	161.1	140.1	107.5
syn-IMa2	-712.026167	-	-712.362517	-712.394060	-	140.3	114.6	71.2
syn-TSa2	-711.982828	-	-712.316015	-712.346188	-1569	254.1	226.7	186.9
syn-TSb1	-712.026075	-	-712.356350	-712.379642	-111	140.6	126.6	104.8
syn-IMb2	-712.042389	-	-712.375055	-712.401804	-	97.7	82.2	51.4
syn-TSb2	-711.989839	-	-712.320249	-712.348151	-1562	235.7	216.6	182.7
anti-TSc1	-712.021880	-	-712.355914	-712.385500	-175	151.6	127.7	89.4
anti-IMc2	-712.023144	-	-712.357470	-712.385938	-	148.3	129.3	93.9
anti-TSc2	-711.986765	-	-712.317610	-712.345376	-1610	243.8	224.2	190.6
anti-TSd1	-712.017653	-	-712.350982	-712.37974	-135	162.7	140.3	104.1
anti-IMd2	-712.021667	-	-712.356062	-712.386273	-	152.2	132.8	92.8
anti-TSd2	-711.979393	-	-712.310485	-712.339072	-1576	263.1	242.2	206.5
syn-a-H_2O	-788.483915	-	-788.844753	-788.875489	-	86.5	74.6	51.2
syn-TSa-H_2O	-788.474299	-	-788.830805	-788.856164	-893	120.1	105.7	96.4
syn-b-H_2O	-788.496285	-	-788.855284	-788.882897	-	45.5	49.9	34.8
syn-TSb-H_2O	-788.484681	-	-788.837949	-788.858027	-1050	84.5	89.1	93.7
anti-c-H_2O	-788.492202	-	-788.851383	-788.878513	-	64.9	60.5	46.6
anti-TSc-H_2O	-788.469236	-	-788.824771	-788.847967	-1150	125.0	125.5	121.9
anti-d-H_2O	-788.492182	-	-788.849263	-788.873049	-	64.8	66.6	61.5
anti-TSd-H_2O	-788.479057	-	-788.833552	-788.855725	-1105	99.3	101.9	101.0
re-syn-OH-TS1	-943.059930	-	-943.471709	-943.498040	-242	168.5	157.3	133.8
si-syn-OH-TS2	-943.065465	-	-943.476726	-943.501280	-220	154.0	145.7	126.8
re-anti-OH-TS3	-943.063543	-	-943.474656	-943.498349	-231	159.0	152.4	135.8
si-anti-OH-TS4	-943.063164	-	-943.474463	-943.497715	-193	160.0	153.0	137.6
si-syn-CH_3-TS1	-943.054652	-	-943.467120	-943.494488	-155	182.4	170.9	144.6
re-syn-CH_3-TS2	-943.056658	-	-943.473080	-943.505107	-155	177.1	155.5	117.0
si-anti-CH_3-TS3	-943.042906	-	-943.457272	-943.487352	-220	213.2	196.8	163.4

re-anti-CH_3-TS4	-943.051831	-	-943.465990	-943.497296	-153	189.8	172.4	135.8
IM-OH-TS2	-943.071095	-	-943.483904	-943.511003	-	139.2	129.0	103.5
TS2-OH-TS2	-943.022870	-	-943.431093	-943.457248	-1599	265.8	256.8	233.7
pro-OH-TS2	-576.779367	-	-576.988319	-576.998673	-	-3.1	1.3	1.4
com-H_2O-OH-TS2	-1019.508920	-	-1019.94983	-1019.983509	-	137.7	131.5	106.6
TS-H_2O-OH-TS2	-1019.502771	-	-1019.93576	-1019.958423	-886	153.8	164.5	168.6
IM-OH-TS3	-943.065517	-	-943.478968	-943.507280	-	153.9	142.0	113.3
TS2-OH-TS3	-943.021617	-	-943.430579	-943.457481	-1624	269.1	259.5	234.5
pro-OH-TS3	-576.779367	-	-576.988304	-576.998813	-	-3.1	1.3	1.0
com-H_2O-OH-TS3	-1019.512491	-	-1019.951899	-1019.981151	-	128.3	128.6	115.4
TS-H_2O-OH-TS3	-1019.496944	-	-1019.931708	-1019.957483	-719	169.1	174.0	169.9

HCHO:

Zero-point Energy: B3LYP/6-311++G(d,p) = -114.515332 (a.u.) Zero-point Correction = 0.026517 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -114.544076 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -114.547156 (a.u.)

PhCHO:

Zero-point Energy: B3LYP/6-311++G(d,p) = -345.559831 (a.u.) Zero-point Correction = 0.109356 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -345.672877 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -345.678333 (a.u.)

MVK:

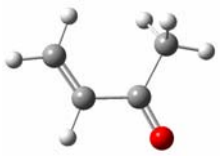
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.885999	-0.620944	0.000000
2	6	0	0.471463	-1.889496	0.000000
3	6	0	0.000000	0.575703	0.000000
4	1	0	1.944808	-0.379765	0.000000
5	6	0	-1.505615	0.389437	0.000000
6	8	0	0.498048	1.686606	0.000000
7	1	0	-0.579602	-2.156270	0.000000
8	1	0	1.177851	-2.711930	0.000000
9	1	0	-1.981555	1.368629	0.000000
10	1	0	-1.828485	-0.170856	0.882213
11	1	0	-1.828485	-0.170856	-0.882213

Zero-point Energy: B3LYP/6-311++G(d,p) = -231.218370 (a.u.) Zero-point Correction = 0.089024 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -231.310862 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -231.315793 (a.u.)



N-methylprolinol:

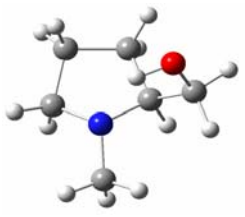
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.436402	0.744224	-0.200135
2	6	0	-1.746288	0.104013	-0.333798
3	6	0	-1.406119	-1.384722	-0.368669
4	6	0	-0.233118	-1.501799	0.629705
5	6	0	0.357182	-0.069557	0.745688
6	6	0	-0.497314	2.162859	0.114674
7	6	0	1.842773	0.022328	0.381648
8	8	0	2.065797	-0.333872	-0.974025
9	1	0	-2.255891	0.458921	-1.234060
10	1	0	-2.395588	0.334324	0.532159
11	1	0	-1.081174	-1.665665	-1.373379
12	1	0	-2.256712	-2.015116	-0.102234
13	1	0	0.518809	-2.212971	0.285152
14	1	0	-0.584834	-1.838214	1.607695
15	1	0	0.232132	0.304602	1.776969
16	1	0	-0.993622	2.358763	1.082494
17	1	0	0.507399	2.588957	0.155728
18	1	0	-1.050141	2.691311	-0.665921
19	1	0	2.215932	1.037674	0.580151
20	1	0	2.423824	-0.666654	1.000206
21	1	0	1.345608	0.086743	-1.467300

Zero-point Energy: B3LYP/6-311++G(d,p) = -366.345918 (a.u.) Zero-point Correction = 0.189978 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -366.540088 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -366.547070 (a.u.)



product:

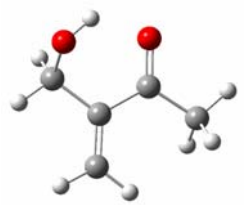
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.211982	1.942947	-0.095343
2	6	0	-0.144435	0.670890	0.113222
3	1	0	1.235829	2.237964	-0.291772
4	1	0	-0.523453	2.740364	-0.076026
5	6	0	0.847192	-0.450810	0.075559
6	8	0	0.455599	-1.599051	0.221162
7	6	0	2.318098	-0.163871	-0.145535
8	1	0	2.864457	-1.105150	-0.116948
9	1	0	2.708548	0.507858	0.623555
10	1	0	2.477008	0.315477	-1.115585
11	1	0	-1.604696	-1.449782	-0.461905
12	6	0	-1.574872	0.270499	0.414740
13	8	0	-2.114444	-0.633025	-0.541183
14	1	0	-1.621665	-0.163474	1.422584
15	1	0	-2.213052	1.155428	0.400407

Zero-point Energy: B3LYP/6-311++G(d,p) = -345.752896 (a.u.) Zero-point Correction = 0.122856 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -345.880930 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -345.888815 (a.u.)



***syn*-IM1:**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.528337	-2.272066	1.149646
2	6	0	-3.251796	-1.949592	-0.229327
3	6	0	-1.795495	-1.699750	0.259940
4	6	0	-3.709021	-0.569091	-0.770313
5	1	0	-3.892007	-2.282742	0.590563
6	1	0	-3.287148	-2.728009	-0.994484
7	6	0	-2.449740	0.322877	-0.614708
8	7	0	-1.677758	-0.252460	0.516316

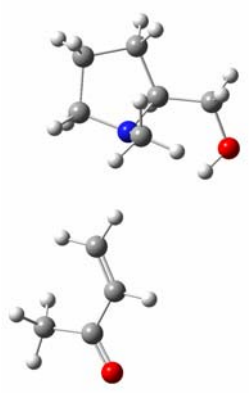
9	1	0	-1.088921	-1.964474	-0.533246
10	1	0	-4.539528	-0.172863	-0.178853
11	1	0	-4.042985	-0.612176	-1.808838
12	6	0	-2.716390	1.814025	-0.491130
13	6	0	-2.175589	0.102061	1.852666
14	8	0	-1.512200	2.575138	-0.441090
15	1	0	-3.265378	2.157425	-1.371085
16	1	0	-3.341423	2.020770	0.388146
17	1	0	-1.579179	-0.433361	2.593881
18	1	0	-2.044385	1.169448	2.039800
19	1	0	-0.891887	2.084776	0.110480
20	1	0	-3.235320	-0.143978	2.025636
21	1	0	-1.816418	0.180550	-1.499359
22	6	0	3.168862	0.426525	0.177513
23	6	0	4.610888	0.092458	0.025301
24	8	0	5.453129	0.881324	0.414892
25	6	0	5.008015	-1.227338	-0.610538
26	1	0	4.609424	-2.068481	-0.036087
27	1	0	6.094660	-1.290240	-0.637236
28	1	0	4.611901	-1.305207	-1.626982
29	6	0	2.149901	-0.353935	-0.190867
30	1	0	2.307737	-1.328922	-0.639711
31	1	0	1.118697	-0.043066	-0.055410
32	1	0	2.989558	1.398699	0.627293

Zero-point Energy: B3LYP/6-311++G(d,p) = -597.554000 (a.u.) Zero-point Correction = 0.279614 (a.u.)

BSSE Correction = -597.833314 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -597.840663 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -597.852328 (a.u.)



***anti*-IM1:**

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

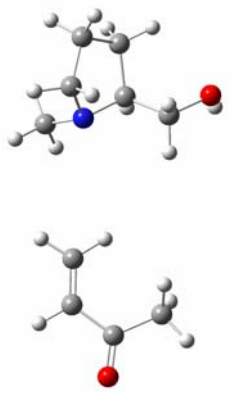
Number	Number	Type	X	Y	Z
1	1	0	2.017313	-0.720775	-1.947239
2	6	0	2.390902	-1.265216	-1.075030
3	6	0	3.888358	-0.940262	-0.838395
4	7	0	1.658398	-0.809766	0.122600
5	1	0	2.199397	-2.324935	-1.254145
6	6	0	3.870067	0.210016	0.202255
7	1	0	4.386781	-0.654701	-1.767029
8	1	0	4.418859	-1.810786	-0.445759
9	6	0	2.366623	0.416972	0.544838
10	6	0	-2.541508	-1.087515	-0.074742
11	6	0	1.621455	-1.826360	1.176419
12	1	0	4.307113	1.134657	-0.178429
13	1	0	4.435273	-0.064853	1.095233
14	6	0	1.760109	1.633654	-0.170018
15	1	0	2.217046	0.557423	1.621020
16	6	0	-3.873938	-1.097656	0.006834
17	1	0	-1.967201	-0.178402	-0.209919
18	1	0	-1.967900	-2.005148	-0.011308
19	1	0	2.617353	-2.140142	1.533473
20	1	0	1.062179	-1.444274	2.033479
21	1	0	1.102423	-2.714290	0.808318
22	8	0	2.402559	2.859098	0.182839
23	1	0	1.883298	1.546066	-1.251764
24	1	0	0.685319	1.676622	0.040908
25	6	0	-4.752036	0.101980	-0.059734
26	8	0	-5.957226	-0.032555	0.055524
27	6	0	-4.133009	1.474238	-0.250419
28	1	0	-3.397764	1.481989	-1.058136
29	1	0	-3.621016	1.779911	0.667847
30	1	0	-4.924977	2.190525	-0.463629
31	1	0	-4.418069	-2.027605	0.144179
32	1	0	2.210984	3.055633	1.105743

Zero-point Energy: B3LYP/6-311++G(d,p) = -597.553887 (a.u.) Zero-point Correction = 0.279112 (a.u.)

BSSE Correction = -597.832789 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -597.841098 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -597.854009 (a.u.)



***syn*-TSa1:**

Standard orientation:

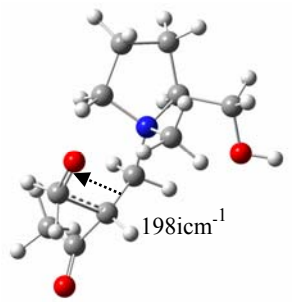
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.242769	1.603552	-0.587117
2	8	0	1.354944	2.350951	-1.098447
3	1	0	3.111467	1.289421	-1.182452
4	1	0	0.023053	2.077780	0.314080
5	6	0	-2.110325	1.962683	0.938939
6	6	0	-0.695175	1.410556	0.801481
7	6	0	-3.033066	0.722622	0.876524
8	1	0	-2.333642	2.659323	0.128892
9	1	0	-2.218293	2.515764	1.872633
10	6	0	-2.130311	-0.467120	0.481888
11	7	0	-0.838132	0.166045	-0.060979
12	1	0	-0.308579	1.069827	1.763499
13	1	0	-3.834855	0.862354	0.146669
14	1	0	-3.510758	0.515855	1.835518
15	6	0	-2.854429	-1.438612	-0.438141
16	6	0	-0.955061	0.545039	-1.511406
17	8	0	-2.053598	-2.587815	-0.681114
18	1	0	-3.782944	-1.712141	0.079960
19	1	0	-3.134023	-0.942367	-1.374731
20	1	0	-0.103014	1.185976	-1.753088
21	1	0	-0.952194	-0.365020	-2.108173
22	1	0	-2.544220	-3.210860	-1.226595
23	1	0	-1.885178	1.091295	-1.667706
24	1	0	-1.807930	-1.011749	1.371743
25	6	0	1.689593	-0.385232	-0.457183
26	6	0	2.890013	-0.846382	0.224460
27	8	0	3.957412	-0.987453	-0.374188

28	6	0	2.876888	-1.055656	1.742831
29	1	0	2.313823	-0.283227	2.275407
30	1	0	3.907981	-1.053018	2.095083
31	1	0	2.434768	-2.027071	1.993148
32	6	0	0.369236	-0.803785	0.131660
33	1	0	0.423207	-0.935997	1.212413
34	1	0	0.001614	-1.735083	-0.300907
35	1	0	1.754303	-0.585294	-1.524690
36	1	0	2.501479	1.740452	0.482527

Zero-point Energy: B3LYP/6-311++G(d,p) = -712.018266 (a.u.) Zero-point Correction = 0.315419 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.351563 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.378958 (a.u.)



***syn*-IMa2:**

Standard orientation:

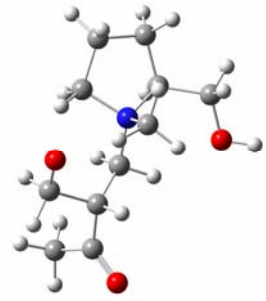
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.952948	-1.655867	-0.294419
2	8	0	-1.084112	-2.352245	-1.049738
3	1	0	-3.019578	-1.807988	-0.578230
4	1	0	0.373418	-2.256917	0.097523
5	6	0	2.541671	-1.821401	0.588792
6	6	0	1.041990	-1.556757	0.635053
7	6	0	3.200072	-0.419987	0.646966
8	1	0	2.818698	-2.347828	-0.326459
9	1	0	2.842583	-2.455529	1.423471
10	6	0	2.049130	0.601825	0.516223
11	7	0	0.869330	-0.202345	-0.052501
12	1	0	0.702956	-1.413591	1.662777
13	1	0	3.929264	-0.290330	-0.157344
14	1	0	3.730446	-0.251071	1.585520
15	6	0	2.468383	1.836742	-0.265643
16	6	0	0.961702	-0.380540	-1.548993

17	8	0	1.438688	2.817429	-0.226475
18	1	0	3.381047	2.210878	0.216793
19	1	0	2.725148	1.568597	-1.296540
20	1	0	0.222536	-1.161922	-1.793923
21	1	0	0.725397	0.568046	-2.027859
22	1	0	1.714053	3.595008	-0.722177
23	1	0	1.973526	-0.689754	-1.807995
24	1	0	1.709323	0.918537	1.504813
25	6	0	-1.722689	-0.082021	-0.385606
26	6	0	-2.931812	0.699839	0.118946
27	8	0	-3.507168	1.495120	-0.599687
28	6	0	-3.443901	0.407964	1.517506
29	1	0	-3.686955	-0.654979	1.610721
30	1	0	-4.329745	1.011249	1.713422
31	1	0	-2.683048	0.625699	2.273845
32	6	0	-0.468434	0.449724	0.325163
33	1	0	-0.542218	0.321989	1.407620
34	1	0	-0.337707	1.509351	0.112019
35	1	0	-1.657976	0.162301	-1.448384
36	1	0	-1.914733	-1.904872	0.801166

Zero-point Energy: B3LYP/6-311++G(d,p) = -712.026167 (a.u.) Zero-point Correction = 0.316672 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.362517 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.394060 (a.u.)



***syn*-TSa2:**

Standard orientation:

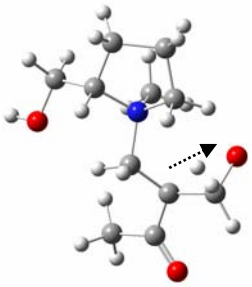
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.960127	-1.806472	-0.415489
2	8	0	1.470414	-2.297628	0.838599
3	1	0	3.020629	-2.025364	-0.574777
4	1	0	-0.454254	-2.320160	0.151871
5	6	0	-2.650057	-1.861268	-0.098085

6	6	0	-1.164060	-1.671244	-0.376838
7	6	0	-3.276188	-0.467889	-0.351583
8	1	0	-2.819857	-2.187988	0.929621
9	1	0	-3.067541	-2.630042	-0.749152
10	6	0	-2.091107	0.515844	-0.498417
11	7	0	-0.869838	-0.238609	0.043676
12	1	0	-0.963348	-1.714227	-1.448507
13	1	0	-3.931919	-0.171178	0.471247
14	1	0	-3.879912	-0.449443	-1.260346
15	6	0	-2.391097	1.865781	0.135411
16	6	0	-0.784220	-0.156756	1.540471
17	8	0	-1.327658	2.776240	-0.112503
18	1	0	-3.323511	2.218004	-0.324925
19	1	0	-2.577195	1.754911	1.210107
20	1	0	-0.094577	-0.928789	1.873714
21	1	0	-0.416034	0.828253	1.819121
22	1	0	-1.554435	3.640624	0.244799
23	1	0	-1.771875	-0.322947	1.968647
24	1	0	-1.858989	0.676140	-1.553210
25	6	0	1.742218	-0.312910	-0.154267
26	6	0	2.910280	0.589156	-0.149152
27	8	0	4.044098	0.210839	-0.418226
28	6	0	2.716993	2.045380	0.291355
29	1	0	2.509462	2.674867	-0.581452
30	1	0	3.651504	2.391160	0.733794
31	1	0	1.903201	2.181240	1.007757
32	6	0	0.453359	0.293687	-0.630594
33	1	0	0.261689	0.104026	-1.693240
34	1	0	0.410280	1.366082	-0.464838
35	1	0	1.402595	-2.200742	-1.284011
36	1	0	1.590629	-0.929637	0.998227

Zero-point Energy: B3LYP/6-311++G(d,p) = -711.982828 (a.u.) Zero-point Correction = 0.312867 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.316015 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.346188 (a.u.)



1569icm^{-1}

***syn*-TSb1:**

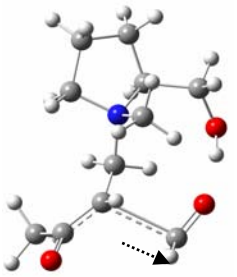
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.336715	-2.492726	0.863019
2	6	0	-2.493083	-2.260567	0.342723
3	6	0	-0.994775	-2.017682	0.138112
4	6	0	-3.176972	-0.976026	-0.195558
5	1	0	-2.725783	-2.416701	1.397449
6	1	0	-2.811462	-3.157289	-0.189935
7	6	0	-2.042420	-0.001517	-0.573066
8	7	0	-0.824048	-0.521472	0.208785
9	1	0	-0.679988	-2.319055	-0.861642
10	1	0	-3.830889	-0.534300	0.560754
11	1	0	-3.797353	-1.174883	-1.070452
12	6	0	-2.415645	1.478929	-0.365617
13	6	0	-0.862156	-0.059963	1.635219
14	8	0	-1.576738	2.418568	-0.985603
15	1	0	-3.400277	1.587660	-0.833078
16	1	0	-2.556125	1.688641	0.702084
17	1	0	-0.142154	-0.642794	2.203058
18	1	0	-0.582672	0.992103	1.673327
19	1	0	-0.778020	2.604068	-0.447904
20	1	0	-1.860946	-0.209658	2.041716
21	1	0	-1.760563	-0.131408	-1.620520
22	6	0	1.736333	-0.103408	0.324466
23	6	0	2.923352	-0.806349	-0.065497
24	8	0	3.876561	-0.975705	0.707675
25	6	0	3.061380	-1.313375	-1.509009
26	1	0	2.393679	-2.162573	-1.697005
27	1	0	4.087386	-1.649144	-1.655211
28	1	0	2.830556	-0.539467	-2.247812
29	6	0	0.507176	-0.030246	-0.487549
30	1	0	0.566109	-0.614930	-1.405958
31	1	0	0.227368	0.988185	-0.748574
32	1	0	1.673713	0.079309	1.387175
33	6	0	1.977648	2.229110	0.392005
34	8	0	0.800442	2.623384	0.527878
35	1	0	2.644157	2.124340	1.255851
36	1	0	2.481156	2.267524	-0.584817

Zero-point Energy: B3LYP/6-311++G(d,p) = -712.026075 (a.u.) Zero-point Correction = 0.315072 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.356350 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.379642 (a.u.)



111icm^{-1}

***syn*-IMb2:**

Standard orientation:

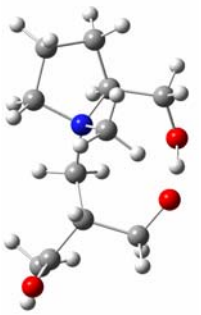
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.843094	-2.620938	-0.685327
2	6	0	2.897907	-1.936094	-0.168274
3	6	0	1.379767	-1.984077	0.017245
4	6	0	3.302508	-0.517587	0.314913
5	1	0	3.174222	-2.094108	-1.211524
6	1	0	3.373683	-2.727382	0.412291
7	6	0	1.995331	0.216658	0.655836
8	7	0	0.909748	-0.552861	-0.141274
9	1	0	1.127044	-2.290720	1.032711
10	1	0	3.858976	0.018627	-0.457495
11	1	0	3.941936	-0.553887	1.197689
12	6	0	2.025818	1.739682	0.434724
13	6	0	0.952392	-0.176815	-1.605586
14	8	0	0.897404	2.410300	0.880658
15	1	0	2.904136	2.081459	1.002362
16	1	0	2.246339	1.944300	-0.624619
17	1	0	0.439799	-0.951238	-2.173282
18	1	0	0.440028	0.791600	-1.711414
19	1	0	0.166781	2.366559	0.112126
20	1	0	1.992223	-0.128987	-1.921594
21	1	0	1.721489	0.032608	1.697834
22	6	0	-1.678763	-0.121050	-0.420321
23	6	0	-2.964853	-0.735094	0.103597
24	8	0	-3.756625	-1.251585	-0.660947
25	6	0	-3.282193	-0.622743	1.587046
26	1	0	-2.755896	-1.409290	2.140043
27	1	0	-4.352171	-0.762801	1.737244
28	1	0	-2.967563	0.338263	2.001132

29	6	0	-0.479965	-0.340242	0.517797
30	1	0	-0.617943	-1.221011	1.144612
31	1	0	-0.354997	0.529489	1.158718
32	1	0	-1.518002	-0.578806	-1.395836
33	6	0	-1.883385	1.451460	-0.646546
34	8	0	-0.719337	2.075430	-0.979819
35	1	0	-2.662606	1.545749	-1.421842
36	1	0	-2.327737	1.842797	0.293355

Zero-point Energy: B3LYP/6-311++G(d,p) = -712.042389 (a.u.) Zero-point Correction = 0.316869 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.375055 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.401804 (a.u.)



***syn*-TSb2:**

Standard orientation:

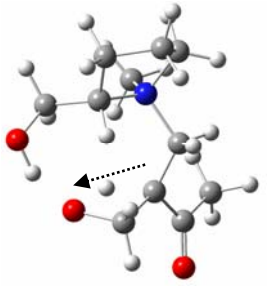
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-2.240226	-2.483931	0.635767
2	6	0	-2.680052	-1.474016	-1.220026
3	6	0	-1.702920	-2.090010	-0.228384
4	6	0	-2.999172	-0.138410	-0.549544
5	1	0	-3.552975	-2.113209	-1.362848
6	1	0	-2.211736	-1.323694	-2.196382
7	6	0	-1.644520	0.367742	-0.049885
8	7	0	-0.825361	-0.941317	0.264658
9	1	0	-1.061085	-2.874417	-0.627852
10	1	0	-3.687463	-0.289369	0.289842
11	1	0	-3.451476	0.596346	-1.216366
12	6	0	-1.720456	1.453591	1.054253
13	6	0	-0.520372	-1.139195	1.712308
14	8	0	-1.660749	2.716900	0.457169
15	1	0	-2.674242	1.370770	1.586777
16	1	0	-0.913893	1.331982	1.782874
17	1	0	-0.150368	-2.156068	1.847631

18	1	0	0.242597	-0.429924	2.020478
19	1	0	-1.426166	-0.997882	2.300121
20	1	0	-1.103291	0.817924	-0.875625
21	6	0	1.515768	0.128972	-0.332612
22	6	0	2.918293	-0.304049	-0.103553
23	8	0	3.878969	0.320979	-0.524797
24	6	0	3.183127	-1.547846	0.753648
25	1	0	3.234064	-2.438074	0.116045
26	1	0	2.429381	-1.722595	1.524937
27	1	0	4.158061	-1.428769	1.225860
28	6	0	0.522486	-0.977929	-0.556833
29	1	0	0.928399	-1.958027	-0.302998
30	1	0	0.179614	-1.014123	-1.593615
31	1	0	-0.697365	2.790549	0.176439
32	6	0	1.317438	1.447752	-1.096679
33	8	0	0.858331	2.253946	-0.007699
34	1	0	2.256934	1.816241	-1.518129
35	1	0	0.586165	1.366390	-1.922008
36	1	0	1.182467	1.034895	0.562898

Zero-point Energy: B3LYP/6-311++G(d,p) = -711.989839 (a.u.) Zero-point Correction = 0.313246 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.320249 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.348151 (a.u.)



1562icm^{-1}

***anti*-TSc1:**

Standard orientation:

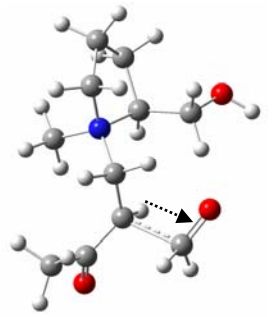
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.208382	0.656854	-1.381511
2	1	0	1.615296	-0.533010	-2.065259
3	6	0	1.652453	-1.297794	-1.290751
4	6	0	3.043938	-1.396170	-0.639683
5	7	0	0.709813	-0.850190	-0.195103
6	1	0	1.281477	-2.232198	-1.710503
7	6	0	2.938138	-0.608583	0.694955

8	1	0	3.796207	-0.969799	-1.303911
9	1	0	3.326568	-2.434998	-0.463114
10	6	0	1.575093	0.102471	0.648520
11	6	0	0.307400	-2.027474	0.643044
12	1	0	3.727228	0.132550	0.811729
13	1	0	3.005267	-1.280292	1.552248
14	6	0	1.689732	1.509668	0.043251
15	1	0	1.107067	0.188259	1.627853
16	1	0	1.190815	-2.524096	1.038689
17	1	0	-0.329360	-1.677020	1.451640
18	1	0	-0.253562	-2.718278	0.015187
19	8	0	2.528478	2.235907	0.946779
20	1	0	2.165355	1.470509	-0.946232
21	1	0	0.716156	1.992941	-0.076508
22	1	0	2.217906	3.145601	0.973650
23	6	0	-0.571380	-0.196750	-0.794533
24	6	0	-1.564785	0.261289	0.211402
25	1	0	-0.967796	-0.951924	-1.475663
26	6	0	-2.756278	-0.506029	0.528308
27	1	0	-1.132814	0.713864	1.100918
28	8	0	-3.328094	-0.403370	1.615675
29	6	0	-3.389326	-1.389644	-0.551255
30	1	0	-4.453777	-1.482848	-0.335971
31	1	0	-2.957605	-2.397248	-0.521149
32	1	0	-3.258291	-0.994859	-1.562107
33	6	0	-2.114632	2.001348	-0.584943
34	8	0	-1.070691	2.558449	-1.046243
35	1	0	-2.885626	1.637693	-1.294210
36	1	0	-2.570493	2.367751	0.350362

Zero-point Energy: B3LYP/6-311++G(d,p) = -712.021880 (a.u.) Zero-point Correction = 0.315040 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.355914 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.385500 (a.u.)



175icm^{-1}

***anti*-IMc2:**

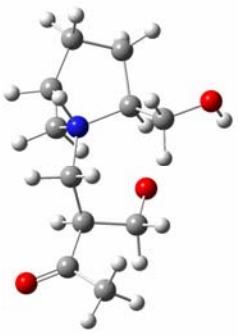
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.853528	-0.926531	1.272381
2	1	0	1.344709	-1.382317	-1.893083
3	6	0	1.589358	-1.707310	-0.881177
4	6	0	3.058633	-1.430610	-0.537899
5	7	0	0.771531	-0.851599	0.063784
6	1	0	1.282299	-2.746930	-0.768254
7	6	0	3.056898	-0.071518	0.215958
8	1	0	3.654325	-1.395657	-1.450984
9	1	0	3.474623	-2.226586	0.081579
10	6	0	1.611284	0.445399	0.188017
11	6	0	0.710003	-1.493357	1.430106
12	1	0	3.710602	0.665724	-0.249822
13	1	0	3.407298	-0.197905	1.241340
14	6	0	1.376843	1.456718	-0.943534
15	1	0	1.221903	0.914724	1.102745
16	1	0	1.718459	-1.754758	1.743743
17	1	0	0.261800	-0.745317	2.094266
18	1	0	0.101928	-2.395425	1.359727
19	8	0	2.119974	2.632670	-0.648993
20	1	0	1.748469	1.105039	-1.911680
21	1	0	0.316872	1.697958	-1.040632
22	1	0	1.720443	3.044014	0.128110
23	1	0	-0.572901	-0.113172	-1.391957
24	6	0	-0.650284	-0.723120	-0.492256
25	6	0	-1.755149	-0.213374	0.449946
26	1	0	-0.904092	-1.739279	-0.806745
27	6	0	-3.071992	-0.349494	-0.326875
28	8	0	-3.719826	-1.376475	-0.260999
29	6	0	-3.546587	0.821072	-1.162097
30	1	0	-3.681712	1.702265	-0.528133
31	1	0	-4.485995	0.563650	-1.650224
32	1	0	-2.800879	1.091979	-1.916238
33	6	0	-1.509537	1.202685	1.094696
34	8	0	-0.444856	1.217287	1.920849
35	1	0	-1.449268	1.934096	0.244441
36	1	0	-2.475234	1.455225	1.596766

Zero-point Energy: B3LYP/6-311++G(d,p) = -712.023144 (a.u.) Zero-point Correction = 0.317200 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.357470 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.385938 (a.u.)



***anti*-TSc2:**

Standard orientation:

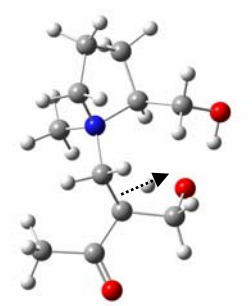
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.202181	-0.103823	-1.798293
2	1	0	1.779300	-1.071164	-1.917867
3	6	0	1.788502	-1.583036	-0.955170
4	6	0	3.150242	-1.438810	-0.251777
5	7	0	0.790781	-0.862922	-0.077319
6	1	0	1.460649	-2.611145	-1.107468
7	6	0	2.970074	-0.270732	0.758248
8	1	0	3.927055	-1.227906	-0.987471
9	1	0	3.435511	-2.361439	0.255702
10	6	0	1.608018	0.356024	0.421553
11	6	0	0.434245	-1.719930	1.100110
12	1	0	3.750284	0.484611	0.670472
13	1	0	3.005875	-0.635914	1.785841
14	6	0	1.727598	1.521701	-0.601203
15	1	0	1.076586	0.750520	1.282523
16	1	0	1.322575	-1.954187	1.679820
17	1	0	-0.279574	-1.174365	1.713096
18	1	0	-0.017526	-2.641176	0.735633
19	8	0	1.582664	2.744885	0.059093
20	1	0	2.719331	1.507297	-1.064984
21	1	0	0.997058	1.412435	-1.410166
22	1	0	0.639766	2.724281	0.416800
23	6	0	-0.536971	-0.580441	-0.878033
24	6	0	-1.608179	0.223583	-0.181472
25	1	0	-0.862538	-1.590293	-1.134281
26	6	0	-2.944946	-0.403287	-0.028753
27	8	0	-3.975017	0.254367	0.001222
28	6	0	-3.057617	-1.921609	0.157205

29	1	0	-2.912810	-2.442918	-0.796073
30	1	0	-4.064508	-2.141754	0.509234
31	1	0	-2.334933	-2.321912	0.871784
32	6	0	-1.575113	1.743184	-0.396607
33	8	0	-0.845910	2.112349	0.785892
34	1	0	-1.070704	2.056532	-1.324957
35	1	0	-2.587385	2.154024	-0.404114
36	1	0	-1.146320	0.776067	0.931740

Zero-point Energy: B3LYP/6-311++G(d,p) = -711.986765 (a.u.) Zero-point Correction = 0.313489 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.317610 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.345376 (a.u.)



1610icm^{-1}

***anti*-TSd1:**

Standard orientation:

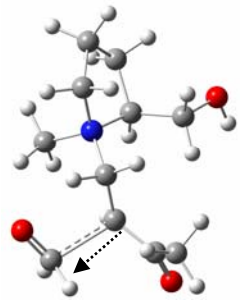
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.577146	-0.655864	2.024530
2	6	0	-1.770419	-1.252917	1.134165
3	6	0	-3.197127	-1.045785	0.600850
4	7	0	-0.844623	-0.740329	0.048257
5	1	0	-1.505337	-2.285998	1.351617
6	6	0	-3.065579	-0.028239	-0.565501
7	1	0	-3.841705	-0.670972	1.396619
8	1	0	-3.633171	-1.984201	0.256081
9	6	0	-1.603824	0.448095	-0.547114
10	6	0	0.537994	-0.423675	0.641122
11	6	0	-0.680112	-1.823514	-0.995880
12	1	0	-3.729082	0.828821	-0.456715
13	1	0	-3.307773	-0.498747	-1.519466
14	6	0	-1.420589	1.745678	0.261583
15	1	0	-1.203523	0.616725	-1.545913
16	6	0	1.522484	0.073217	-0.367503
17	1	0	0.365522	0.263056	1.470858

18	1	0	0.861382	-1.399351	1.046282
19	1	0	-1.646412	-2.281953	-1.195640
20	1	0	-0.289003	-1.378395	-1.906841
21	1	0	0.047919	-2.545010	-0.616144
22	8	0	-2.195155	2.777896	-0.338428
23	1	0	-1.795847	1.631273	1.282372
24	1	0	-0.366373	2.021347	0.306249
25	6	0	2.766331	-1.632641	-0.479890
26	6	0	2.412015	1.169213	-0.070912
27	8	0	2.165762	-2.581296	0.095246
28	8	0	2.966767	1.831782	-0.954436
29	6	0	2.751740	1.454963	1.395538
30	1	0	2.804028	-1.580313	-1.581330
31	1	0	3.654908	2.063311	1.432859
32	1	0	2.904820	0.538520	1.973418
33	1	0	1.944639	2.020883	1.877707
34	1	0	3.652375	-1.174402	-0.008421
35	1	0	1.207357	0.071731	-1.405230
36	1	0	-1.651694	3.248425	-0.978493

Zero-point Energy: B3LYP/6-311++G(d,p) = -712.017653 (a.u.) Zero-point Correction = 0.314904 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.350982 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.379737 (a.u.)



135icm^{-1}

***anti*-IMd2:**

Standard orientation:

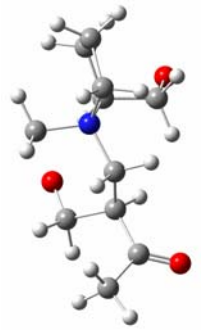
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.468971	-0.697764	-2.216125
2	6	0	1.669926	-1.307717	-1.335583
3	6	0	3.107872	-1.109910	-0.821555
4	7	0	0.773171	-0.807589	-0.220602
5	1	0	1.407439	-2.340466	-1.562659
6	6	0	2.996048	-0.108001	0.364202

7	1	0	3.735882	-0.721514	-1.624342
8	1	0	3.549094	-2.055002	-0.502297
9	6	0	1.550572	0.404148	0.337696
10	6	0	-0.630659	-0.506689	-0.751432
11	6	0	0.692950	-1.873717	0.857649
12	1	0	3.681086	0.733402	0.265197
13	1	0	3.224580	-0.595223	1.312506
14	6	0	1.438872	1.664934	-0.538896
15	1	0	1.076980	0.593463	1.311181
16	6	0	-1.595841	0.309729	0.126310
17	1	0	-0.479827	0.014327	-1.699246
18	1	0	-1.048798	-1.489014	-0.983532
19	1	0	1.696976	-2.232824	1.070315
20	1	0	0.243618	-1.377072	1.738238
21	1	0	0.089511	-2.693042	0.468912
22	8	0	2.105683	2.734403	0.118695
23	1	0	1.956058	1.544840	-1.495214
24	1	0	0.401382	1.930609	-0.747137
25	6	0	-2.940827	0.348571	-0.599780
26	8	0	-3.275622	1.330610	-1.234755
27	6	0	-3.868239	-0.842750	-0.459003
28	1	0	-4.759002	-0.685676	-1.066260
29	1	0	-4.152381	-0.959357	0.591679
30	1	0	-3.379422	-1.775790	-0.755029
31	1	0	-1.259348	1.347628	0.147810
32	1	0	1.594596	2.977346	0.900143
33	6	0	-1.713838	-0.118669	1.648127
34	8	0	-0.589498	0.155300	2.334674
35	1	0	-2.616908	0.414095	2.024611
36	1	0	-2.008196	-1.201927	1.650135

Zero-point Energy: B3LYP/6-311++G(d,p) = -712.021667 (a.u.) Zero-point Correction = 0.317138 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.356062 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.386273 (a.u.)



***anti*-TSd2:**

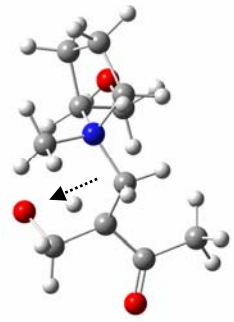
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.582088	0.366038	-2.186623
2	6	0	1.895790	-0.509746	-1.618880
3	6	0	3.263241	-0.292960	-0.953537
4	7	0	0.909198	-0.689376	-0.484849
5	1	0	1.842596	-1.378839	-2.273497
6	6	0	2.950693	0.143568	0.504253
7	1	0	3.825541	0.467008	-1.497392
8	1	0	3.861900	-1.204586	-0.972672
9	6	0	1.420828	0.286567	0.590939
10	6	0	-0.544356	-0.456511	-1.016552
11	6	0	1.036026	-2.093180	0.060697
12	1	0	3.415909	1.092850	0.767147
13	1	0	3.313870	-0.595815	1.218796
14	6	0	0.975664	1.741269	0.358628
15	1	0	0.993228	-0.065094	1.529848
16	6	0	-1.657339	-0.370498	-0.003378
17	1	0	-0.472260	0.459958	-1.600596
18	1	0	-0.667304	-1.285179	-1.724496
19	1	0	2.085405	-2.306400	0.251811
20	1	0	0.448336	-2.128588	0.986047
21	1	0	0.654741	-2.782393	-0.691220
22	8	0	1.522047	2.565663	1.381268
23	1	0	1.368052	2.137563	-0.582328
24	1	0	-0.111384	1.813315	0.343383
25	6	0	-2.835069	0.423960	-0.414477
26	8	0	-3.971425	0.149034	-0.049029
27	6	0	-2.646712	1.676576	-1.279248
28	1	0	-3.502322	2.331243	-1.114842
29	1	0	-2.639674	1.398903	-2.339778
30	1	0	-1.727469	2.230657	-1.071093
31	1	0	0.998149	2.453258	2.182319
32	6	0	-1.886666	-1.579238	0.908807
33	8	0	-1.020256	-1.182621	1.979428
34	1	0	-2.936779	-1.636945	1.208397
35	1	0	-1.613234	-2.551763	0.463829
36	1	0	-1.159304	-0.064996	1.180064

Zero-point Energy: B3LYP/6-311++G(d,p) = -711.979393 (a.u.) Zero-point Correction = 0.313238 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -712.310485 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -712.339072 (a.u.)



1576icm^{-1}

***syn*-a-H_2O:**

Standard orientation:

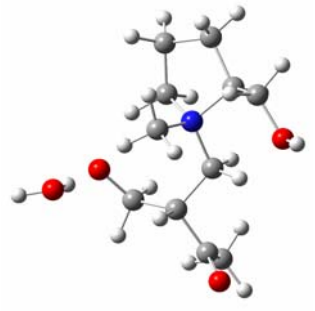
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.060855	1.086646	-0.750898
2	8	0	-1.350854	2.191409	-0.393609
3	1	0	-3.153378	1.200466	-0.582035
4	1	0	0.298519	1.830411	-1.151263
5	6	0	2.541662	1.505919	-1.286472
6	6	0	1.082844	1.067773	-1.306407
7	6	0	3.320126	0.275114	-0.756790
8	1	0	2.682931	2.370881	-0.636217
9	1	0	2.864003	1.802117	-2.285244
10	6	0	2.253177	-0.746158	-0.304404
11	7	0	0.962950	0.078608	-0.147956
12	1	0	0.865886	0.489987	-2.207577
13	1	0	3.975994	0.547132	0.074297
14	1	0	3.951432	-0.176462	-1.523696
15	6	0	2.701850	-1.546824	0.907983
16	6	0	0.929548	0.818772	1.164492
17	8	0	1.772226	-2.588748	1.177041
18	1	0	3.687288	-1.959596	0.654370
19	1	0	2.832100	-0.892377	1.776754
20	1	0	0.150394	1.575484	1.098226
21	1	0	0.711123	0.111557	1.962211
22	1	0	2.043944	-3.070849	1.964458
23	1	0	1.897331	1.286702	1.335277
24	1	0	2.029175	-1.444714	-1.113645
25	6	0	-1.642344	-0.199035	0.053279
26	6	0	-2.659689	-1.343160	-0.068163
27	8	0	-3.002924	-1.974286	0.910651
28	6	0	-3.235583	-1.651009	-1.437047

29	1	0	-3.778142	-0.780608	-1.817297
30	1	0	-3.909049	-2.504363	-1.365381
31	1	0	-2.442905	-1.866643	-2.160413
32	6	0	-0.274616	-0.814026	-0.297212
33	1	0	-0.250731	-1.149892	-1.337204
34	1	0	-0.084562	-1.671414	0.345760
35	1	0	-1.963134	0.842309	-1.835899
36	1	0	-1.647998	0.064660	1.113801
37	1	0	-1.501924	2.790951	1.082707
38	8	0	-1.405689	3.050029	2.054386
39	1	0	-1.837748	3.902706	2.145794

Zero-point Energy: B3LYP/6-311++G(d,p) = -788.483915 (a.u.) Zero-point Correction = 0.341541 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -788.844753 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -788.875489 (a.u.)



***syn*-TSa-H_2O:**

Standard orientation:

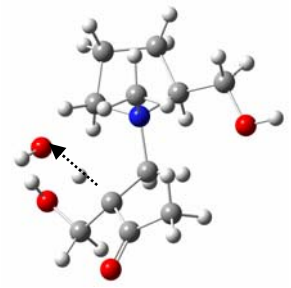
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.310602	-1.012106	-1.246250
2	8	0	1.736471	-2.314778	-1.108529
3	1	0	3.383741	-1.034191	-1.047922
4	1	0	-0.317858	-2.128454	0.677165
5	6	0	-2.504746	-2.030253	0.293357
6	6	0	-1.046773	-1.694017	-0.005164
7	6	0	-3.312234	-0.801185	-0.184621
8	1	0	-2.656846	-2.205916	1.359968
9	1	0	-2.795834	-2.945127	-0.223784
10	6	0	-2.274245	0.285208	-0.539559
11	7	0	-0.954534	-0.177021	0.102134
12	1	0	-0.759638	-1.950425	-1.023853
13	1	0	-3.994548	-0.449382	0.593873
14	1	0	-3.921020	-1.023792	-1.062318

15	6	0	-2.765495	1.673405	-0.157931
16	6	0	-0.861987	0.218213	1.546609
17	8	0	-1.845928	2.668179	-0.591344
18	1	0	-3.737260	1.798492	-0.653012
19	1	0	-2.937335	1.735402	0.923109
20	1	0	0.003898	-0.295001	1.971103
21	1	0	-0.759424	1.298749	1.610689
22	1	0	-2.202788	3.540443	-0.396163
23	1	0	-1.766666	-0.099979	2.064216
24	1	0	-2.068125	0.275018	-1.611224
25	6	0	1.665474	0.014825	-0.297236
26	6	0	2.572448	1.134979	0.062742
27	8	0	3.789941	1.050066	-0.049142
28	6	0	1.997433	2.416895	0.672565
29	1	0	1.482183	3.018449	-0.083539
30	1	0	2.827094	3.000272	1.069738
31	1	0	1.285063	2.212022	1.475156
32	6	0	0.259539	0.401717	-0.714393
33	1	0	0.051215	0.048909	-1.727702
34	1	0	0.078241	1.471909	-0.686768
35	1	0	2.171629	-0.733105	-2.298331
36	1	0	1.759214	-2.502701	-0.147500
37	8	0	1.495437	-1.760583	1.618641
38	1	0	2.263362	-1.860976	2.190929
39	1	0	1.645984	-0.720633	0.773523

Zero-point Energy: B3LYP/6-311++G(d,p) = -788.474299 (a.u.) Zero-point Correction = 0.339432 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -788.830805 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -788.856164 (a.u.)



893icm^{-1}

***syn*-b-H_2O:**

Standard orientation:

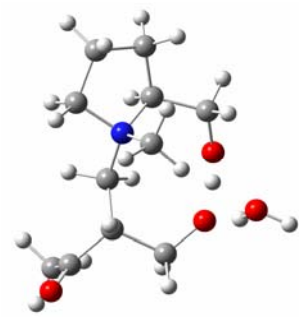
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.727476	-1.089916	1.625530

2	1	0	0.798120	-2.292336	-1.714476
3	6	0	2.863936	-1.965936	-0.950172
4	6	0	1.344165	-2.069739	-0.798209
5	6	0	3.292820	-0.936334	0.129376
6	1	0	3.139486	-1.629529	-1.950300
7	1	0	3.324733	-2.943222	-0.801921
8	6	0	1.998782	-0.436761	0.792125
9	7	0	0.899474	-0.723411	-0.263122
10	1	0	1.082565	-2.812444	-0.043957
11	1	0	3.847262	-0.106554	-0.314819
12	1	0	3.940642	-1.381217	0.885584
13	6	0	2.055402	1.005571	1.321008
14	6	0	0.955912	0.290611	-1.381673
15	8	0	0.959652	1.374750	2.098004
16	1	0	2.959392	1.038250	1.944534
17	1	0	2.225589	1.699346	0.486243
18	1	0	0.409575	-0.102726	-2.236069
19	1	0	0.500835	1.214659	-1.029574
20	1	0	1.994750	0.447450	-1.660098
21	6	0	-1.685263	-0.171458	-0.289661
22	6	0	-2.965220	-0.984164	-0.151927
23	8	0	-3.731202	-1.090440	-1.088279
24	6	0	-3.300043	-1.605595	1.195871
25	1	0	-4.379410	-1.734365	1.272859
26	1	0	-2.932588	-1.008479	2.033273
27	1	0	-2.839753	-2.598015	1.264410
28	1	0	-1.516051	-0.083227	-1.361787
29	6	0	-0.487966	-0.823698	0.425889
30	1	0	-0.643190	-1.893570	0.562952
31	1	0	-0.351781	-0.366679	1.403047
32	6	0	-1.918770	1.292440	0.289014
33	1	0	-2.378754	1.170871	1.290164
34	1	0	-2.684905	1.757738	-0.352381
35	8	0	-0.757137	2.016431	0.343029
36	1	0	0.223400	1.716603	1.463996
37	8	0	0.109250	3.560949	-1.617857
38	1	0	0.005013	4.500734	-1.449514
39	1	0	-0.315760	3.097356	-0.844866

Zero-point Energy: B3LYP/6-311++G(d,p) = -788.496285 (a.u.) Zero-point Correction = 0.342681 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -788.855284 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -788.882897 (a.u.)



***syn*-TSb-H_2O:**

Standard orientation:

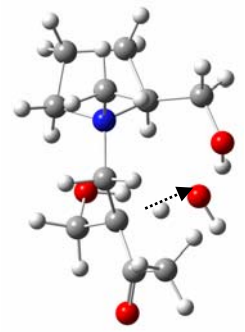
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.012629	0.560517	2.172617
2	1	0	-1.825432	0.655165	2.681084
3	1	0	1.758753	-1.748570	-1.913524
4	6	0	3.108970	-1.296478	-0.204635
5	6	0	1.738914	-1.403770	-0.879553
6	6	0	2.977551	-0.092614	0.763022
7	1	0	3.908470	-1.136026	-0.930872
8	1	0	3.333880	-2.224629	0.321103
9	6	0	1.553798	0.459963	0.576695
10	7	0	1.150795	-0.003968	-0.841638
11	1	0	1.075725	-2.026545	-0.284121
12	1	0	3.728515	0.672260	0.544654
13	1	0	3.115725	-0.386340	1.803772
14	6	0	1.433638	1.957166	0.851641
15	6	0	1.806490	0.839942	-1.891654
16	8	0	0.129999	2.459007	0.724818
17	1	0	1.824985	2.094514	1.871513
18	1	0	2.087130	2.534838	0.189570
19	1	0	1.574180	0.416920	-2.868439
20	1	0	1.415347	1.852322	-1.830163
21	1	0	2.884857	0.850622	-1.747522
22	1	0	0.866614	-0.067815	1.231045
23	1	0	-0.579123	1.007300	-1.474456
24	6	0	-0.375353	-0.022305	-1.199155
25	6	0	-1.406142	-0.499801	-0.198241
26	1	0	-0.373573	-0.629496	-2.115485
27	6	0	-2.773984	0.004130	-0.493748
28	8	0	-3.779572	-0.611451	-0.155279
29	6	0	-2.946813	1.378739	-1.138525

30	1	0	-3.973891	1.701298	-0.971589
31	1	0	-2.782883	1.319521	-2.220842
32	1	0	-2.256204	2.121759	-0.731387
33	1	0	-0.425037	1.935540	1.367634
34	6	0	-1.367843	-1.970351	0.191033
35	1	0	-1.068637	-2.622269	-0.639978
36	1	0	-2.366814	-2.275681	0.504280
37	8	0	-0.413181	-2.240646	1.244595
38	1	0	-0.596388	-1.597276	1.948869
39	1	0	-1.274060	0.113221	1.001021

Zero-point Energy: B3LYP/6-311++G(d,p) = -788.484681 (a.u.) Zero-point Correction = 0.340264 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -788.837948 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -788.858027 (a.u.)



1050icm^{-1}

***anti*-c-H_2O:**

Standard orientation:

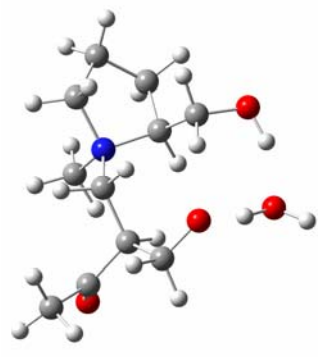
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.080215	0.522043	0.924790
2	1	0	1.585218	-1.245880	-2.048532
3	6	0	1.539934	-1.856409	-1.147859
4	6	0	2.907159	-1.949422	-0.442216
5	7	0	0.626534	-1.136096	-0.175621
6	1	0	1.094030	-2.817988	-1.401239
7	6	0	2.846987	-0.930215	0.730443
8	1	0	3.701843	-1.706450	-1.147817
9	1	0	3.099794	-2.960729	-0.081315
10	6	0	1.585941	-0.099230	0.467686
11	6	0	0.152729	-2.110665	0.868010
12	1	0	3.706207	-0.261207	0.755626
13	1	0	2.811757	-1.440291	1.694633
14	6	0	1.911431	1.108574	-0.442739

15	1	0	1.104367	0.272850	1.369974
16	1	0	1.005504	-2.611526	1.317635
17	1	0	-0.420551	-1.583241	1.626316
18	1	0	-0.487553	-2.846846	0.382478
19	8	0	2.592993	2.055227	0.349398
20	1	0	2.578232	0.796444	-1.256320
21	1	0	1.004623	1.542041	-0.870143
22	1	0	1.893275	2.686551	0.648375
23	1	0	-0.211170	0.191932	-1.602028
24	6	0	-0.588343	-0.542842	-0.891090
25	6	0	-1.590770	0.166517	0.027226
26	1	0	-1.036678	-1.378413	-1.434798
27	6	0	-2.738692	-0.709368	0.495255
28	8	0	-2.833637	-1.062223	1.658489
29	6	0	-3.813318	-1.071812	-0.510730
30	1	0	-4.425354	-0.182829	-0.698578
31	1	0	-4.447720	-1.860423	-0.107169
32	1	0	-3.399862	-1.372334	-1.477053
33	6	0	-2.063233	1.498232	-0.722977
34	8	0	-1.000029	2.270731	-1.033644
35	1	0	-2.641497	1.184769	-1.618570
36	1	0	-2.795753	1.971194	-0.035454
37	1	0	-0.320294	2.965900	0.086754
38	8	0	0.275560	3.334553	0.863157
39	1	0	0.118011	4.280641	0.916534

Zero-point Energy: B3LYP/6-311++G(d,p) = -788.492202 (a.u.) Zero-point Correction = 0.342786 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -788.851383 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -788.878513 (a.u.)



***anti*-TSc-H_2O:**

Standard orientation:

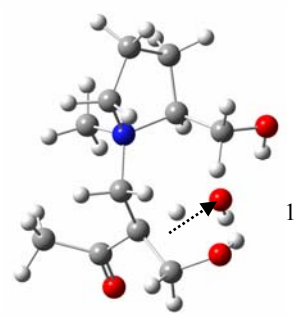
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	1	0	-0.936693	2.641058	-1.083631
2	1	0	-1.977929	-0.812417	2.029729
3	6	0	-1.997092	-1.448703	1.144899
4	6	0	-3.316761	-1.300572	0.365970
5	7	0	-0.912466	-0.936812	0.222844
6	1	0	-1.759823	-2.468309	1.448146
7	6	0	-3.009921	-0.303912	-0.787095
8	1	0	-4.098405	-0.930421	1.030065
9	1	0	-3.658466	-2.261817	-0.020948
10	6	0	-1.606224	0.245038	-0.494134
11	6	0	-0.593970	-1.975323	-0.808881
12	1	0	-3.714455	0.526275	-0.826199
13	1	0	-3.061465	-0.801314	-1.756941
14	6	0	-1.667092	1.559299	0.313765
15	1	0	-1.011079	0.456262	-1.378892
16	1	0	-1.493792	-2.246555	-1.354435
17	1	0	0.140109	-1.560065	-1.494581
18	1	0	-0.189215	-2.854631	-0.312541
19	8	0	-1.800908	2.615483	-0.614711
20	1	0	-2.551387	1.581385	0.959001
21	1	0	-0.783090	1.700466	0.936320
22	1	0	0.054450	0.047386	1.823270
23	6	0	0.387647	-0.624665	1.034184
24	6	0	1.549735	0.007982	0.291766
25	1	0	0.611551	-1.591571	1.497872
26	6	0	2.616298	-0.842395	-0.297546
27	8	0	3.586423	-0.329983	-0.847959
28	6	0	2.589136	-2.376806	-0.262758
29	1	0	3.621576	-2.709541	-0.151266
30	1	0	2.230408	-2.770687	-1.218608
31	1	0	1.988923	-2.812224	0.538693
32	6	0	2.184744	1.135825	1.155170
33	8	0	1.361538	2.290423	1.275233
34	1	0	2.363154	0.798218	2.184000
35	1	0	3.148371	1.385179	0.707497
36	1	0	1.178052	2.573107	0.358662
37	8	0	0.722596	1.840236	-1.392344
38	1	0	1.380636	2.043216	-2.065255
39	1	0	1.129638	0.840803	-0.703676

Zero-point Energy: B3LYP/6-311++G(d,p) = -788.469236 (a.u.) Zero-point Correction = 0.340935 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -788.824771 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -788.847967 (a.u.)



1150icm^{-1}

***anti*-d-H_2O:**

Standard orientation:

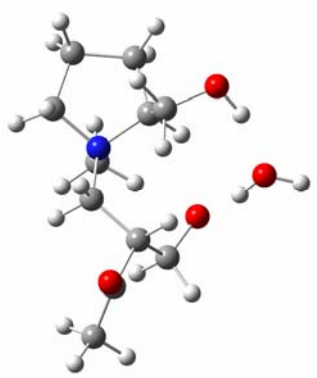
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.407499	-2.069201	-1.510313
2	6	0	1.622024	-2.116545	-0.443002
3	6	0	3.080396	-1.733753	-0.143793
4	7	0	0.774220	-1.053327	0.229450
5	1	0	1.322240	-3.096237	-0.071282
6	6	0	3.042939	-0.234237	0.264302
7	1	0	3.694192	-1.902486	-1.029335
8	1	0	3.496522	-2.351453	0.653390
9	6	0	1.603047	0.235913	0.015811
10	6	0	-0.636548	-1.073816	-0.358179
11	6	0	0.705659	-1.335126	1.715662
12	1	0	3.722621	0.380901	-0.324535
13	1	0	3.327375	-0.107788	1.309674
14	6	0	1.458081	0.874420	-1.381255
15	1	0	1.223042	0.935175	0.756313
16	6	0	-1.614295	0.091954	-0.084823
17	1	0	-0.510802	-1.160843	-1.437649
18	1	0	-1.058570	-2.017879	-0.001349
19	1	0	1.711707	-1.509585	2.089404
20	1	0	0.259693	-0.445406	2.181978
21	1	0	0.103593	-2.231658	1.861793
22	8	0	2.034689	2.157204	-1.328876
23	1	0	2.007601	0.302161	-2.136959
24	1	0	0.413462	0.927152	-1.697370
25	6	0	-2.917841	-0.356130	-0.774708
26	8	0	-3.040922	-0.232977	-1.976298
27	6	0	-4.016503	-0.968171	0.068217
28	1	0	-4.831894	-1.294721	-0.576049
29	1	0	-4.386174	-0.236152	0.792065

30	1	0	-3.637081	-1.814748	0.648903
31	1	0	-1.280217	0.959938	-0.656489
32	1	0	1.443853	2.698284	-0.754050
33	6	0	-1.774884	0.583053	1.388124
34	8	0	-0.652720	1.221032	1.843884
35	1	0	-2.670370	1.237821	1.389905
36	1	0	-2.054705	-0.287003	2.022471
37	1	0	-0.244997	2.415117	1.045160
38	8	0	0.133380	3.134897	0.391239
39	1	0	0.014024	3.995291	0.800436

Zero-point Energy: B3LYP/6-311++G(d,p) = -788.492182 (a.u.) Zero-point Correction = 0.343001 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -788.849263 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -788.873049 (a.u.)



***anti*-TSd-H_2O:**

Standard orientation:

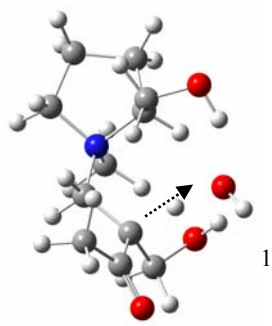
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.847616	-0.285901	2.239597
2	6	0	-2.161508	-0.936170	1.423688
3	6	0	-3.468773	-0.440579	0.775246
4	7	0	-1.106827	-0.832522	0.339559
5	1	0	-2.195774	-1.961344	1.791223
6	6	0	-3.032455	0.337869	-0.499249
7	1	0	-4.009250	0.195878	1.476707
8	1	0	-4.130276	-1.271437	0.526401
9	6	0	-1.507958	0.462744	-0.389670
10	6	0	0.319948	-0.856256	0.951761
11	6	0	-1.263046	-2.003965	-0.598493
12	1	0	-3.470664	1.333875	-0.557071
13	1	0	-3.332196	-0.191870	-1.404386

14	6	0	-1.110143	1.760744	0.354401
15	1	0	-0.990789	0.457373	-1.344658
16	6	0	1.492188	-0.435557	0.079077
17	1	0	0.248072	-0.223892	1.832130
18	1	0	0.411780	-1.892139	1.304243
19	1	0	-2.300776	-2.082126	-0.911620
20	1	0	-0.611640	-1.846625	-1.459409
21	1	0	-0.980165	-2.907331	-0.059090
22	8	0	-1.068481	2.805246	-0.581569
23	1	0	-1.858916	2.018458	1.111091
24	1	0	-0.145901	1.649110	0.855345
25	6	0	2.674207	0.021394	0.858463
26	8	0	3.811132	-0.031302	0.404115
27	6	0	2.481049	0.670738	2.230944
28	1	0	3.415445	1.157705	2.506371
29	1	0	2.249867	-0.082833	2.992239
30	1	0	1.677274	1.412848	2.236607
31	1	0	-0.260123	2.600134	-1.121875
32	6	0	1.854446	-1.381518	-1.069975
33	8	0	1.096253	-1.126319	-2.268030
34	1	0	2.921130	-1.279355	-1.273647
35	1	0	1.663683	-2.432474	-0.817260
36	1	0	1.124954	-0.156604	-2.403762
37	1	0	1.280048	0.689637	-0.638356
38	8	0	1.075661	1.565601	-1.579786
39	1	0	1.905355	2.024090	-1.752728

Zero-point Energy: B3LYP/6-311++G(d,p) = -788.479057 (a.u.) Zero-point Correction = 0.340746 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -788.833552 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -788.855725 (a.u.)



1105icm^{-1}

***re-syn*-OH-TS1:**

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

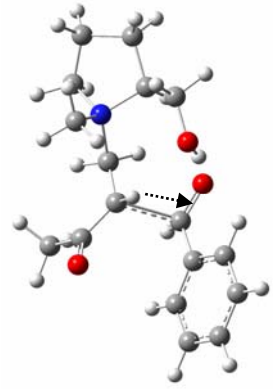
Number	Number	Type	X	Y	Z
1	1	0	3.703896	2.071071	-0.053950
2	6	0	4.834776	0.163397	-0.153249
3	6	0	3.644470	1.062580	-0.463017
4	6	0	4.248838	-1.266070	-0.209439
5	1	0	5.247111	0.382984	0.833302
6	1	0	5.636431	0.319378	-0.876380
7	6	0	2.710041	-1.118060	-0.235016
8	7	0	2.429290	0.368572	0.111265
9	1	0	3.477224	1.130971	-1.539595
10	1	0	4.568374	-1.856271	0.652599
11	1	0	4.579132	-1.800740	-1.101046
12	6	0	2.019424	-2.173148	0.634435
13	6	0	2.339166	0.609466	1.584526
14	8	0	0.632159	-2.088680	0.724404
15	1	0	2.351598	-3.135500	0.208399
16	1	0	2.422750	-2.137833	1.653464
17	1	0	2.177644	1.673447	1.750513
18	1	0	1.497302	0.053410	1.985129
19	1	0	0.219378	-1.914011	-0.171990
20	1	0	3.264965	0.292632	2.063344
21	1	0	2.330453	-1.212561	-1.252755
22	6	0	-1.195993	-0.252112	-1.331416
23	8	0	-0.392454	-1.225580	-1.542707
24	6	0	-0.149270	0.885010	0.064796
25	6	0	-0.795248	2.118078	0.490400
26	8	0	-1.596239	2.149572	1.424179
27	6	0	-0.547808	3.410495	-0.300666
28	1	0	-0.459203	3.242877	-1.378261
29	1	0	0.371653	3.902499	0.038933
30	1	0	-1.375509	4.092571	-0.107510
31	6	0	1.155825	0.941900	-0.645941
32	1	0	1.435330	1.967766	-0.883737
33	1	0	1.157217	0.337678	-1.558045
34	6	0	-2.514842	-0.463131	-0.653375
35	1	0	-0.270459	0.086840	0.784473
36	1	0	-1.249350	0.536298	-2.102102
37	6	0	-2.804741	-1.665588	0.001357
38	6	0	-3.498539	0.529876	-0.707599
39	6	0	-4.045970	-1.860213	0.600181
40	6	0	-5.018308	-0.860935	0.546948
41	6	0	-4.741717	0.335379	-0.112928
42	1	0	-3.287784	1.463800	-1.218952

43	1	0	-5.491346	1.117680	-0.158632
44	1	0	-5.985134	-1.015024	1.013642
45	1	0	-4.258904	-2.796417	1.105258
46	1	0	-2.056157	-2.447593	0.028041

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.059930 (a.u.) Zero-point Correction = 0.396157 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.471709 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.498040 (a.u.)



242icm^{-1}

***si-syn*-OH-TS2:**

Standard orientation:

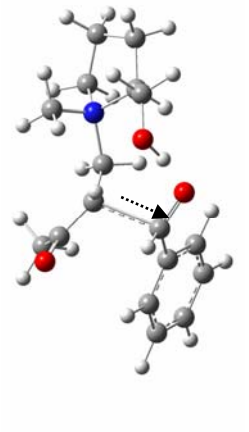
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	2.531546	0.654948	-2.672290
2	6	0	4.023336	-0.737619	-1.801066
3	6	0	2.615153	-0.190249	-1.989210
4	6	0	3.982236	-1.397555	-0.405150
5	1	0	4.764165	0.063520	-1.838302
6	1	0	4.275260	-1.442672	-2.594372
7	6	0	2.696051	-0.896227	0.292970
8	7	0	2.141589	0.237026	-0.617046
9	1	0	1.931302	-0.974827	-2.318773
10	1	0	4.868123	-1.139237	0.179758
11	1	0	3.956240	-2.485715	-0.478635
12	6	0	2.949623	-0.543607	1.762828
13	6	0	2.700297	1.579451	-0.269755
14	8	0	1.855515	-0.069789	2.482716
15	1	0	3.359016	-1.472904	2.195122
16	1	0	3.750515	0.201852	1.835489
17	1	0	2.296579	2.311470	-0.967764
18	1	0	2.397852	1.840470	0.739546
19	1	0	1.041719	-0.620702	2.280462

20	1	0	3.786804	1.553349	-0.342928
21	1	0	1.911319	-1.651753	0.255384
22	6	0	-1.191368	-0.364310	1.397468
23	8	0	-0.304553	-1.267631	1.575566
24	6	0	-0.130879	1.107557	0.351449
25	6	0	-0.963955	2.232531	-0.033939
26	8	0	-1.315037	3.081530	0.789457
27	6	0	-1.507993	2.320950	-1.461639
28	1	0	-1.945185	1.373189	-1.788930
29	1	0	-0.717368	2.591570	-2.171949
30	1	0	-2.271405	3.097362	-1.492131
31	6	0	0.559695	0.270578	-0.659420
32	1	0	0.327662	0.590199	-1.674797
33	1	0	0.315908	-0.792880	-0.553789
34	6	0	-2.395009	-0.678613	0.561944
35	1	0	0.401612	1.283793	1.275281
36	6	0	-3.511357	0.168986	0.564907
37	6	0	-2.436408	-1.850309	-0.202608
38	6	0	-4.633324	-0.137476	-0.199578
39	6	0	-4.659146	-1.298393	-0.975376
40	6	0	-3.558399	-2.154620	-0.971734
41	1	0	-1.591236	-2.527137	-0.155079
42	1	0	-3.581990	-3.068645	-1.556141
43	1	0	-5.535895	-1.539055	-1.566714
44	1	0	-5.491635	0.525602	-0.187095
45	1	0	-3.492246	1.073016	1.164780
46	1	0	-1.398502	0.356668	2.198731

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.065465 (a.u.) Zero-point Correction = 0.396734 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.476726 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.501280 (a.u.)



220icm^{-1}

***re-anti*-OH-TS3:**

Standard orientation:

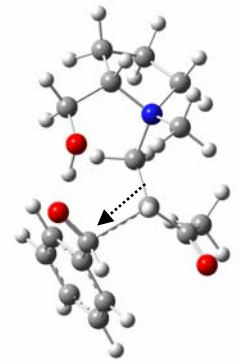
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	2.136008	1.691556	1.997516
2	6	0	2.878024	-0.363866	2.405303
3	6	0	2.811426	0.932689	1.604134
4	6	0	3.309959	-1.430348	1.368577
5	1	0	1.903163	-0.609687	2.829378
6	1	0	3.578654	-0.271252	3.235917
7	6	0	3.154540	-0.776174	-0.020994
8	7	0	2.344837	0.519229	0.227995
9	1	0	3.804778	1.372689	1.492323
10	1	0	2.689717	-2.325480	1.446326
11	1	0	4.344751	-1.741421	1.519717
12	6	0	2.580480	-1.723927	-1.092912
13	8	0	2.140897	-1.069972	-2.251523
14	1	0	3.398938	-2.415643	-1.337541
15	1	0	1.775067	-2.327102	-0.662731
16	1	0	1.140805	-1.138674	-2.253306
17	1	0	4.121255	-0.403355	-0.367053
18	6	0	-1.223723	-0.372335	-1.492611
19	8	0	-0.411877	-1.337399	-1.729535
20	6	0	-0.068766	1.049782	-0.663351
21	6	0	-0.834893	2.204636	-0.205548
22	8	0	-1.217046	3.068185	-0.995768
23	6	0	-1.250507	2.305692	1.262191
24	1	0	-0.408693	2.640757	1.880230
25	1	0	-1.605058	1.350657	1.658732
26	1	0	-2.044555	3.046681	1.346450
27	6	0	0.770090	0.250991	0.267848
28	1	0	0.670119	-0.807440	0.022804
29	1	0	0.487140	0.401599	1.306464
30	6	0	-2.364991	-0.619102	-0.539553
31	1	0	-1.514944	0.293429	-2.318334
32	6	0	2.725178	1.565086	-0.777330
33	1	0	3.792550	1.759861	-0.669070
34	1	0	2.155245	2.471794	-0.587717
35	1	0	2.519663	1.180996	-1.771489
36	6	0	-2.350347	-1.735974	0.302705
37	6	0	-3.475156	0.234072	-0.510747
38	6	0	-4.534439	-0.009847	0.360358
39	6	0	-3.407705	-1.979003	1.177533

40	6	0	-4.502152	-1.114606	1.212546
41	1	0	-3.505208	1.093114	-1.173327
42	1	0	-5.389496	0.657619	0.369696
43	1	0	-3.387672	-2.852685	1.820945
44	1	0	-1.514280	-2.422195	0.232976
45	1	0	-5.329616	-1.307822	1.886522
46	1	0	0.369901	1.234305	-1.635666

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.063543 (a.u.) Zero-point Correction = 0.397231 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.474656 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.498349 (a.u.)



231icm^{-1}

***si-anti*-OH-TS4:**

Standard orientation:

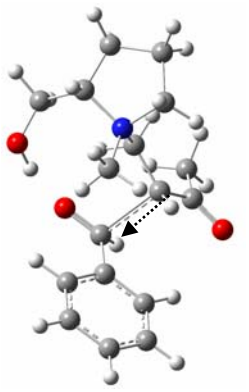
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.859150	1.074847	-2.277020
2	6	0	3.855123	0.518857	-1.463685
3	6	0	2.431312	0.209570	-1.945050
4	6	0	4.090682	-0.417247	-0.248818
5	1	0	3.957110	1.566150	-1.177883
6	1	0	4.568843	0.337297	-2.268138
7	6	0	2.821038	-1.270308	-0.114063
8	7	0	1.715780	-0.406793	-0.762265
9	1	0	2.433197	-0.538857	-2.738978
10	1	0	4.260617	0.161944	0.661603
11	1	0	4.960693	-1.060315	-0.386406
12	6	0	2.539571	-1.770790	1.312709
13	8	0	1.347620	-2.497767	1.449733
14	1	0	3.374873	-2.440815	1.549956
15	1	0	2.594163	-0.939501	2.024104
16	1	0	0.615645	-1.878930	1.682542
17	1	0	2.885306	-2.139802	-0.772948

18	6	0	-1.279551	0.286668	1.315949
19	8	0	-0.497626	-0.524336	1.914944
20	6	0	-0.063627	1.331409	-0.122105
21	6	0	-0.279927	2.725110	0.216810
22	8	0	-1.178685	3.397133	-0.295787
23	6	0	0.572475	3.345328	1.324584
24	1	0	0.101610	4.270434	1.655226
25	1	0	1.574413	3.587960	0.950466
26	1	0	0.692052	2.669069	2.177015
27	6	0	1.252915	0.694750	0.207528
28	1	0	1.148831	0.196709	1.177447
29	1	0	2.083259	1.400682	0.262151
30	6	0	-2.399913	-0.231582	0.453824
31	6	0	0.576748	-1.262002	-1.245056
32	1	0	0.998383	-2.122553	-1.762409
33	1	0	-0.035783	-0.683411	-1.930040
34	1	0	-0.014614	-1.590167	-0.399218
35	6	0	-3.260011	0.647663	-0.220928
36	6	0	-2.638846	-1.607787	0.369812
37	6	0	-3.699788	-2.100301	-0.390523
38	6	0	-4.316635	0.154853	-0.980234
39	6	0	-4.540295	-1.221341	-1.070822
40	1	0	-2.002424	-2.282717	0.930673
41	1	0	-3.878810	-3.169442	-0.437952
42	1	0	-4.970971	0.845699	-1.501112
43	1	0	-3.081105	1.716340	-0.166569
44	1	0	-5.369614	-1.601723	-1.657244
45	1	0	-0.550577	1.056919	-1.048110
46	1	0	-1.552807	1.214377	1.837988

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.063164 (a.u.) Zero-point Correction = 0.397276 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.474463 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.497715 (a.u.)



193icm^{-1}

***si-syn*-CH_3-TS1:**

Standard orientation:

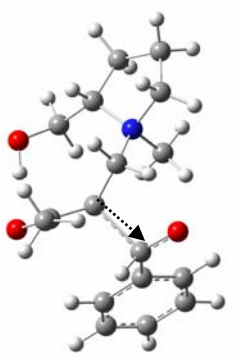
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-2.541337	-1.800531	-2.028366
2	6	0	-3.978293	-1.863692	-0.322482
3	6	0	-2.989754	-1.162976	-1.268663
4	6	0	-3.680025	-1.272380	1.078100
5	1	0	-3.846232	-2.946317	-0.335520
6	1	0	-5.002231	-1.663589	-0.639819
7	6	0	-2.687758	-0.126676	0.840182
8	7	0	-1.885153	-0.616562	-0.383913
9	1	0	-3.444325	-0.304208	-1.762751
10	1	0	-3.247256	-2.025043	1.742391
11	1	0	-4.573669	-0.889404	1.571998
12	6	0	-1.928387	0.343753	2.097029
13	6	0	-0.934329	-1.746648	-0.074652
14	8	0	-1.712568	1.733703	2.133084
15	1	0	-2.586214	0.111159	2.941445
16	1	0	-1.009591	-0.229112	2.255301
17	1	0	-0.319107	-1.896449	-0.965228
18	1	0	-0.286037	-1.476544	0.751938
19	1	0	-1.503959	-2.637493	0.181061
20	1	0	-3.223064	0.747811	0.461863
21	1	0	-0.823449	1.986032	1.824457
22	1	0	-0.836366	0.005382	-2.093263
23	6	0	-1.143818	0.482322	-1.145128
24	6	0	0.105127	0.960124	-0.451467
25	1	0	-1.883013	1.265973	-1.321751
26	6	0	0.246037	2.408170	-0.297341
27	8	0	0.585675	2.914160	0.777833
28	6	0	0.007981	3.304881	-1.501025
29	1	0	-0.956442	3.811231	-1.383356
30	1	0	0.010489	2.761495	-2.447792
31	1	0	0.775021	4.081038	-1.521790
32	1	0	0.288254	0.487160	0.506774
33	6	0	1.504411	0.222425	-1.545425
34	8	0	0.963449	-0.591944	-2.383228
35	6	0	2.472397	-0.350014	-0.514112
36	6	0	2.738614	-1.722228	-0.511167
37	6	0	3.143519	0.465307	0.406423
38	6	0	3.635098	-2.273683	0.404926

39	1	0	2.249967	-2.335422	-1.259792
40	6	0	4.039026	-0.082649	1.321982
41	1	0	2.957503	1.534098	0.416624
42	6	0	4.285854	-1.456865	1.328252
43	1	0	3.838407	-3.339809	0.387371
44	1	0	4.547565	0.563167	2.030082
45	1	0	4.987673	-1.882452	2.037364
46	1	0	1.916833	1.165383	-1.955972

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.054652 (a.u.) Zero-point Correction = 0.396744 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.467120 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.494488 (a.u.)



155icm^{-1}

***re-syn*-CH_3-TS2:**

Standard orientation:

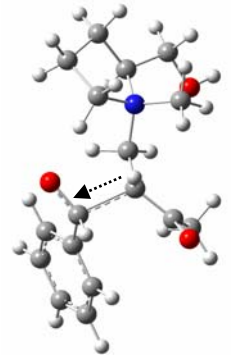
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	2.851788	-0.354817	-2.274283
2	6	0	3.031667	-2.093663	-0.971362
3	6	0	2.278039	-0.881448	-1.511963
4	6	0	3.869165	-1.532139	0.179042
5	1	0	3.632487	-2.564102	-1.750914
6	1	0	2.321777	-2.838528	-0.603257
7	6	0	2.907672	-0.551099	0.847982
8	7	0	2.116098	0.090102	-0.318088
9	1	0	1.273345	-1.141150	-1.872966
10	1	0	4.758039	-1.012050	-0.195969
11	1	0	4.203515	-2.295780	0.884055
12	6	0	3.574405	0.416691	1.811228
13	6	0	2.629178	1.445101	-0.689764
14	1	0	4.101314	-0.200557	2.549256
15	1	0	4.324663	1.032996	1.301609
16	1	0	2.072667	1.795024	-1.555214

17	1	0	2.473462	2.128232	0.141986
18	1	0	3.687506	1.374954	-0.941017
19	1	0	2.154297	-1.112572	1.403643
20	1	0	0.347735	-0.877945	0.228374
21	6	0	0.615069	0.174379	0.083428
22	6	0	-0.265357	0.773469	-0.975490
23	1	0	0.600775	0.707458	1.031467
24	6	0	-0.931140	2.063391	-0.721938
25	8	0	-1.257994	2.796139	-1.652960
26	6	0	-1.288873	2.458965	0.707216
27	1	0	-2.048796	3.239146	0.675093
28	1	0	-0.406756	2.861581	1.218853
29	1	0	-1.658212	1.612260	1.290260
30	1	0	0.197298	0.805708	-1.958985
31	8	0	2.582663	1.224584	2.436228
32	6	0	-1.400296	-0.632381	-1.449063
33	8	0	-0.626684	-1.660920	-1.579473
34	1	0	-1.792525	-0.158226	-2.367228
35	6	0	-2.504199	-0.717810	-0.404468
36	6	0	-2.456019	-1.707146	0.581848
37	6	0	-3.603391	0.149401	-0.431278
38	6	0	-3.461752	-1.805348	1.543315
39	1	0	-1.635786	-2.415542	0.551655
40	6	0	-4.613072	0.050518	0.523509
41	1	0	-3.667518	0.904196	-1.209381
42	6	0	-4.542337	-0.924092	1.520748
43	1	0	-3.413207	-2.581625	2.300533
44	1	0	-5.460296	0.727492	0.486116
45	1	0	-5.330843	-1.005332	2.261275
46	1	0	2.984146	1.739308	3.143355

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.056658 (a.u.) Zero-point Correction = 0.396823 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.473080 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.505107 (a.u.)



155icm^{-1}

***si-anti*-CH_3-TS3:**

Standard orientation:

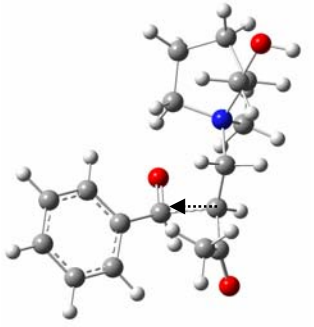
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.086361	-1.448511	0.641366
2	6	0	-1.466218	-1.332426	-0.373602
3	6	0	-2.773999	-2.099776	-0.585772
4	7	0	-1.842979	0.134288	-0.526758
5	1	0	-0.658634	-1.527519	-1.086238
6	6	0	-3.914464	-1.096426	-0.258324
7	1	0	-2.805399	-2.978020	0.060122
8	1	0	-2.852202	-2.459146	-1.612886
9	6	0	-3.217522	0.212675	0.158640
10	6	0	-2.011503	0.456282	-1.992412
11	1	0	-4.556529	-1.435707	0.553533
12	1	0	-4.560664	-0.938636	-1.122634
13	6	0	-3.141412	0.340224	1.695178
14	1	0	-3.714409	1.101510	-0.237381
15	1	0	-2.850085	-0.113920	-2.385305
16	1	0	-2.214436	1.522214	-2.089956
17	1	0	-1.082936	0.172380	-2.495229
18	8	0	-4.457657	0.341423	2.236043
19	1	0	-2.637609	-0.524713	2.131483
20	1	0	-2.599802	1.237223	2.001027
21	1	0	-4.823824	1.230220	2.188328
22	6	0	-0.819514	1.097889	0.100214
23	6	0	0.404398	1.458119	-0.720632
24	1	0	-1.414963	1.995929	0.310491
25	1	0	-0.546452	0.649424	1.055224
26	6	0	1.350323	2.339939	-0.030194
27	8	0	2.089366	3.094375	-0.661882
28	6	0	1.477457	2.271697	1.489830
29	1	0	1.553060	1.241281	1.847970
30	1	0	0.605356	2.734679	1.968437
31	1	0	2.366586	2.823081	1.793402
32	1	0	0.139540	1.910620	-1.673187
33	6	0	1.494904	0.006811	-1.558376
34	8	0	0.715999	-0.765430	-2.220276
35	1	0	2.058350	0.777580	-2.110323
36	6	0	2.368074	-0.603250	-0.472536
37	6	0	3.534278	0.045623	-0.043845
38	6	0	2.083532	-1.868392	0.052825

39	6	0	4.363592	-0.532500	0.914847
40	1	0	3.793267	1.008539	-0.470242
41	6	0	2.908408	-2.448427	1.015696
42	1	0	1.234034	-2.414295	-0.338086
43	6	0	4.049292	-1.778975	1.457091
44	1	0	5.263610	-0.015192	1.230114
45	1	0	2.673949	-3.433689	1.406022
46	1	0	4.697991	-2.232826	2.198412

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.042906 (a.u.) Zero-point Correction = 0.396758 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.457272 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.487352 (a.u.)



220icm^{-1}

***re-anti*-CH_3-TS4:**

Standard orientation:

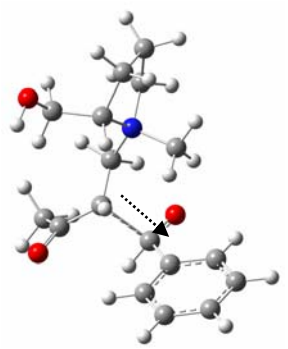
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.256886	-0.227235	-1.753415
2	6	0	2.719380	-1.126818	-1.456426
3	6	0	3.598288	-2.075869	-0.624813
4	7	0	1.592691	-0.690462	-0.539938
5	1	0	2.280132	-1.570495	-2.348077
6	6	0	3.187291	-1.842469	0.854496
7	1	0	4.651886	-1.850489	-0.793079
8	1	0	3.445704	-3.115966	-0.915036
9	6	0	2.250892	-0.624052	0.843019
10	6	0	0.984343	0.616022	-1.051138
11	6	0	0.523446	-1.760350	-0.544322
12	1	0	4.037336	-1.643553	1.505817
13	1	0	2.675162	-2.717581	1.256578
14	6	0	3.006595	0.695175	1.091828
15	1	0	1.453923	-0.702672	1.581506
16	6	0	-0.164025	1.121834	-0.217121
17	1	0	1.814318	1.315969	-1.149435

18	1	0	0.583272	0.364523	-2.050219
19	1	0	0.992443	-2.737213	-0.447055
20	1	0	-0.157265	-1.588457	0.285042
21	1	0	-0.037486	-1.658971	-1.474979
22	8	0	3.629196	0.639523	2.370098
23	1	0	3.810516	0.832328	0.363136
24	1	0	2.328823	1.547226	1.024653
25	6	0	-0.239575	2.574320	-0.007017
26	8	0	-0.700044	3.065444	1.021148
27	6	0	0.182824	3.483782	-1.156689
28	1	0	1.266788	3.648307	-1.129383
29	1	0	-0.302905	4.452370	-1.041082
30	1	0	-0.065562	3.054115	-2.131107
31	1	0	-0.309558	0.604540	0.727160
32	1	0	3.029433	1.001363	3.030295
33	6	0	-1.702709	0.650085	-1.284038
34	8	0	-1.293117	0.047327	-2.345347
35	6	0	-2.591522	-0.125731	-0.312804
36	6	0	-3.062896	0.441479	0.879597
37	6	0	-3.001149	-1.419771	-0.646322
38	6	0	-3.901988	-0.280151	1.725531
39	1	0	-2.763155	1.448930	1.149658
40	6	0	-3.842430	-2.144032	0.200027
41	1	0	-2.667031	-1.830133	-1.592623
42	6	0	-4.292835	-1.578957	1.391691
43	1	0	-4.256901	0.173007	2.645425
44	1	0	-4.158926	-3.144183	-0.079030
45	1	0	-4.951655	-2.137021	2.048333
46	1	0	-2.116878	1.669199	-1.413706

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.051831 (a.u.) Zero-point Correction = 0.396177 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.465990 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.497296 (a.u.)



153icm^{-1}

IM-OH-TS2:

Standard orientation:

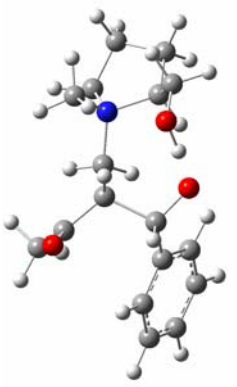
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	2.655702	0.556537	-2.661742
2	6	0	3.888134	-0.994018	-1.660470
3	6	0	2.581781	-0.287143	-1.975238
4	6	0	3.567765	-1.742934	-0.355996
5	1	0	4.701024	-0.277373	-1.520434
6	1	0	4.181426	-1.659625	-2.473779
7	6	0	2.473851	-0.925774	0.366995
8	7	0	2.052356	0.210372	-0.640283
9	1	0	1.846069	-0.993840	-2.363058
10	1	0	4.452135	-1.853199	0.275189
11	1	0	3.199674	-2.747669	-0.574284
12	6	0	2.919521	-0.422239	1.748168
13	6	0	2.687652	1.535886	-0.327830
14	8	0	1.972460	0.344421	2.409890
15	1	0	3.175809	-1.345837	2.297707
16	1	0	3.858582	0.144211	1.661035
17	1	0	2.291696	2.276109	-1.022838
18	1	0	2.454723	1.809299	0.697229
19	1	0	1.037162	-0.129686	2.264648
20	1	0	3.765350	1.453490	-0.452541
21	1	0	1.549774	-1.482884	0.515748
22	6	0	-1.031935	0.114478	1.268575
23	8	0	-0.135443	-0.787122	1.728285
24	6	0	-0.231697	1.151297	0.281094
25	6	0	-1.108810	2.271203	-0.243039
26	8	0	-1.382506	3.209236	0.483055
27	6	0	-1.691133	2.202756	-1.648795
28	1	0	-1.970460	1.186544	-1.934900
29	1	0	-0.956359	2.574067	-2.373433
30	1	0	-2.564399	2.852198	-1.698784
31	6	0	0.522626	0.362215	-0.792649
32	1	0	0.411349	0.828986	-1.772143
33	1	0	0.148602	-0.659654	-0.857069
34	6	0	-2.231044	-0.531282	0.568084
35	1	0	0.453636	1.614755	0.987479
36	6	0	-3.446450	0.149645	0.421309
37	6	0	-2.145967	-1.845407	0.099171
38	6	0	-4.532517	-0.451614	-0.211901
39	6	0	-4.424709	-1.752611	-0.705262

40	6	0	-3.228880	-2.449520	-0.540935
41	1	0	-1.232630	-2.395349	0.294170
42	1	0	-3.146650	-3.473172	-0.892205
43	1	0	-5.271810	-2.224385	-1.191306
44	1	0	-5.468198	0.089251	-0.307733
45	1	0	-3.549424	1.153628	0.821817
46	1	0	-1.434493	0.789101	2.045681

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.071095 (a.u.) Zero-point Correction = 0.397584 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.483904 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.511003 (a.u.)



TS2-OH-TS2:

Standard orientation:

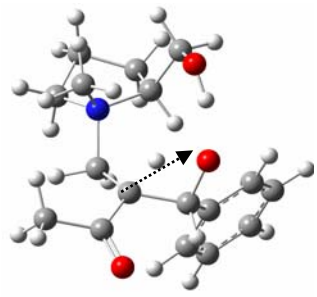
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.234757	-0.738492	-2.008523
2	6	0	2.240896	-2.658263	-1.513012
3	6	0	2.259584	-1.162496	-1.773716
4	6	0	0.926038	-2.823117	-0.745847
5	1	0	3.096639	-2.967501	-0.906380
6	1	0	2.272093	-3.225850	-2.444645
7	6	0	0.883753	-1.622089	0.216019
8	7	0	1.730056	-0.508222	-0.499435
9	1	0	1.566177	-0.912116	-2.577891
10	1	0	0.866798	-3.764141	-0.196800
11	1	0	0.079177	-2.793804	-1.436387
12	6	0	1.341030	-2.030373	1.629084
13	6	0	2.897778	-0.014394	0.303319
14	8	0	1.373504	-1.017868	2.585327
15	1	0	0.632716	-2.829048	1.906496
16	1	0	2.332115	-2.500922	1.597069

17	1	0	3.408714	0.747374	-0.283805
18	1	0	2.553211	0.387342	1.248482
19	1	0	0.583853	-0.411619	2.463309
20	1	0	3.574531	-0.845679	0.494133
21	1	0	-0.115308	-1.206894	0.296401
22	6	0	-1.011140	1.293909	0.873261
23	8	0	-0.385155	0.835575	2.077860
24	6	0	0.282370	1.647958	0.085904
25	6	0	0.493319	3.089313	-0.188061
26	8	0	-0.321063	3.949465	0.118735
27	6	0	1.812811	3.543169	-0.822630
28	1	0	1.729733	3.533076	-1.915606
29	1	0	2.669713	2.928862	-0.538477
30	1	0	1.993446	4.573473	-0.517546
31	6	0	0.820686	0.705382	-0.949051
32	1	0	1.462058	1.220748	-1.664790
33	1	0	0.024045	0.208605	-1.509457
34	6	0	-2.031731	0.352593	0.268056
35	1	0	0.622528	1.368775	1.336546
36	6	0	-2.582447	0.604052	-0.997479
37	6	0	-2.508909	-0.743551	0.994790
38	6	0	-3.562650	-0.230940	-1.530267
39	6	0	-4.020087	-1.330322	-0.801749
40	6	0	-3.493962	-1.578447	0.464767
41	1	0	-2.106703	-0.913327	1.986810
42	1	0	-3.859761	-2.416818	1.048559
43	1	0	-4.788586	-1.975988	-1.212251
44	1	0	-3.978998	-0.017534	-2.509209
45	1	0	-2.256002	1.475532	-1.557526
46	1	0	-1.529660	2.241825	1.061824

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.022870 (a.u.) Zero-point Correction = 0.393426 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.431093 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.457248 (a.u.)



1599icm^{-1}

pro-OH-TS2:

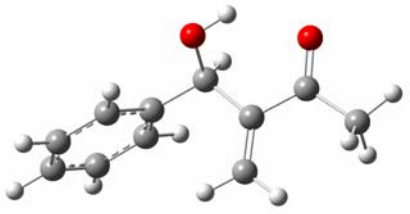
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.349385	-0.383008	-0.167119
2	6	0	-2.797080	-0.098139	0.097537
3	8	0	-3.116579	0.929112	0.678773
4	6	0	-3.862141	-1.078179	-0.352269
5	1	0	-3.685763	-2.073776	0.062456
6	1	0	-3.867266	-1.169249	-1.442112
7	1	0	-4.832078	-0.710810	-0.021180
8	6	0	-0.973166	-1.432024	-0.906475
9	1	0	-1.693794	-2.114879	-1.339978
10	1	0	0.071598	-1.638322	-1.103684
11	6	0	-0.374721	0.620963	0.462017
12	8	0	-0.612763	1.928961	-0.058708
13	1	0	-0.574020	0.622796	1.542491
14	6	0	1.084088	0.271776	0.255894
15	6	0	1.723319	-0.607384	1.134803
16	6	0	1.806865	0.806029	-0.813753
17	6	0	3.143614	0.458198	-1.003713
18	6	0	3.771811	-0.428029	-0.130064
19	6	0	3.057809	-0.959762	0.942942
20	1	0	1.175864	-1.016147	1.978716
21	1	0	3.541612	-1.639636	1.635491
22	1	0	4.812275	-0.694982	-0.277892
23	1	0	3.696670	0.884806	-1.833358
24	1	0	1.319979	1.506510	-1.480306
25	1	0	-1.516412	2.156470	0.200039

Zero-point Energy: B3LYP/6-311++G(d,p) = -576.779367 (a.u.) Zero-point Correction = 0.203445 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -576.988319 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -576.998673 (a.u.)



com-H_2O-OH-TS2:

Standard orientation:

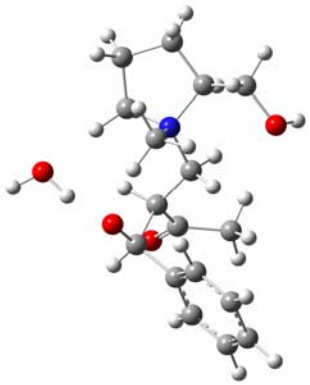
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.291575	-3.177626	-1.810450
2	1	0	1.000243	-4.034186	-2.131893
3	1	0	2.176691	-1.936098	-0.459641
4	6	0	4.085736	-0.867106	-0.132142
5	6	0	2.612702	-1.153958	0.163203
6	6	0	4.272728	0.646494	0.132734
7	1	0	4.330535	-1.122408	-1.163518
8	1	0	4.721223	-1.480997	0.506875
9	6	0	2.885428	1.174559	0.536239
10	7	0	1.887895	0.166580	-0.071966
11	1	0	2.463701	-1.399409	1.216230
12	1	0	4.636512	1.162379	-0.759459
13	1	0	4.989790	0.846265	0.930546
14	6	0	2.689289	2.641133	0.160084
15	6	0	1.699028	0.396184	-1.552141
16	8	0	1.423815	3.186162	0.499744
17	1	0	3.506365	3.198644	0.635070
18	1	0	2.802686	2.774728	-0.916466
19	1	0	0.937722	-0.327825	-1.882186
20	1	0	1.320005	1.405647	-1.696254
21	1	0	2.653058	0.270037	-2.060652
22	1	0	2.751920	1.059786	1.615414
23	1	0	0.779654	0.558207	1.656986
24	6	0	0.525495	0.229664	0.649761
25	6	0	-0.307323	-1.064959	0.728105
26	1	0	-0.022375	1.041304	0.173304
27	6	0	-1.069309	-1.179362	2.040053
28	8	0	-1.378154	-2.278030	2.461938
29	6	0	-1.483781	0.072042	2.803208
30	1	0	-2.335633	-0.168273	3.438606
31	1	0	-1.737978	0.902015	2.141234
32	1	0	-0.661394	0.390385	3.455376
33	1	0	1.410742	3.438183	1.428238
34	6	0	-1.286226	-1.315412	-0.554411
35	6	0	-2.394451	-0.255481	-0.626638
36	1	0	-1.778456	-2.267730	-0.278598
37	8	0	-0.546348	-1.393242	-1.681044
38	1	0	0.474835	-2.565111	-1.810778
39	6	0	-2.289338	0.812626	-1.521921
40	6	0	-3.552869	-0.353353	0.154905
41	6	0	-4.558952	0.608108	0.071757

42	6	0	-4.426430	1.686951	-0.802881
43	6	0	-3.289335	1.781845	-1.603978
44	1	0	-5.453269	0.507417	0.678019
45	1	0	-5.211087	2.432446	-0.874043
46	1	0	-3.190430	2.602045	-2.307818
47	1	0	-1.432747	0.837547	-2.184804
48	1	0	-3.678491	-1.201895	0.820892
49	1	0	0.329470	-1.947132	0.695961

Zero-point Energy: B3LYP/6-311++G(d,p) = -1019.508920 (a.u.) Zero-point Correction = 0.422308 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -1019.949826 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -1019.983509 (a.u.)



TS-H_2O-OH-TS2:

Standard orientation:

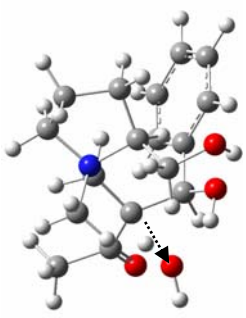
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.326284	2.001113	2.018295
2	1	0	1.182971	2.822838	2.499399
3	1	0	2.535643	0.298275	-2.902567
4	6	0	2.935406	-1.668719	-1.950687
5	6	0	2.068182	-0.465828	-2.283115
6	6	0	2.195771	-2.259445	-0.746858
7	1	0	3.952115	-1.362809	-1.687081
8	1	0	3.006150	-2.355457	-2.795890
9	6	0	1.765873	-1.038068	0.081877
10	7	0	1.692398	0.149843	-0.937258
11	1	0	1.142140	-0.788709	-2.761092
12	1	0	2.801925	-2.932786	-0.140681
13	1	0	1.321287	-2.820916	-1.087222
14	6	0	2.661048	-0.803410	1.311996
15	6	0	2.655638	1.265709	-0.637716

16	8	0	2.348341	-1.822235	2.255497
17	1	0	3.719524	-0.929736	1.066326
18	1	0	2.504027	0.186471	1.742313
19	1	0	2.552976	2.009979	-1.427301
20	1	0	2.424325	1.711022	0.331691
21	1	0	3.669969	0.868450	-0.647970
22	1	0	0.757898	-1.142340	0.467506
23	1	0	1.497342	-1.586664	2.649934
24	1	0	0.285152	1.333128	-1.939579
25	6	0	0.234243	0.699863	-1.054192
26	6	0	-0.387936	1.429874	0.120727
27	1	0	-0.343823	-0.189277	-1.317944
28	6	0	-1.058141	2.710084	-0.242891
29	8	0	-2.037084	3.136300	0.355920
30	6	0	-0.447855	3.590478	-1.336622
31	1	0	-0.790766	4.611345	-1.172669
32	1	0	-0.801275	3.274739	-2.324647
33	1	0	0.644302	3.572228	-1.342787
34	6	0	-1.210783	0.562881	1.124220
35	6	0	-2.089017	-0.501565	0.487747
36	1	0	-1.874508	1.270999	1.628545
37	8	0	-0.354786	-0.047242	2.102822
38	1	0	0.260182	0.676530	2.385483
39	6	0	-1.947668	-1.859714	0.786952
40	6	0	-3.091348	-0.118874	-0.416252
41	6	0	-3.910892	-1.069460	-1.018156
42	6	0	-3.749310	-2.425314	-0.726467
43	6	0	-2.769120	-2.814344	0.181860
44	1	0	-4.686210	-0.751344	-1.707000
45	1	0	-4.390997	-3.165358	-1.191762
46	1	0	-2.646913	-3.862730	0.433120
47	1	0	-1.208901	-2.163409	1.517019
48	1	0	-3.241085	0.933908	-0.628942
49	1	0	0.493190	1.884329	0.959797

Zero-point Energy: B3LYP/6-311++G(d,p) = -1019.502771 (a.u.) Zero-point Correction = 0.420832 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -1019.935762 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -1019.958423 (a.u.)



886icm^{-1}

IM-OH-TS3:

Standard orientation:

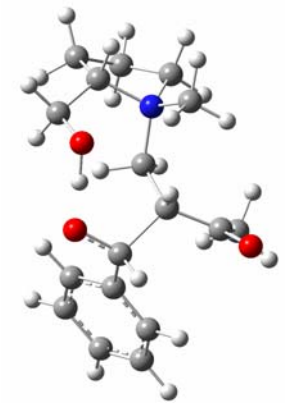
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	2.038972	1.154183	2.384209
2	6	0	2.766125	-0.944503	2.281241
3	6	0	2.714187	0.507648	1.824775
4	6	0	3.295834	-1.700658	1.040045
5	1	0	1.771999	-1.299342	2.558712
6	1	0	3.408564	-1.057178	3.155345
7	6	0	3.102441	-0.754860	-0.165106
8	7	0	2.265392	0.442509	0.379779
9	1	0	3.711624	0.951599	1.831885
10	1	0	2.756582	-2.637351	0.886959
11	1	0	4.352527	-1.949851	1.150590
12	6	0	2.515362	-1.434300	-1.417635
13	8	0	2.024720	-0.536980	-2.359049
14	1	0	3.340871	-2.036467	-1.829652
15	1	0	1.733975	-2.142504	-1.113526
16	1	0	0.977539	-0.652793	-2.335259
17	1	0	4.050873	-0.284266	-0.431940
18	6	0	-1.140559	0.033952	-1.440983
19	8	0	-0.399677	-0.949413	-1.966180
20	6	0	-0.113184	1.044504	-0.579263
21	6	0	-0.797986	2.232532	0.040996
22	8	0	-1.016678	3.227084	-0.631472
23	6	0	-1.259024	2.184625	1.492179
24	1	0	-0.418810	2.420242	2.156991
25	1	0	-1.653316	1.206069	1.773011
26	1	0	-2.025053	2.944766	1.641492
27	6	0	0.721502	0.168070	0.340544
28	1	0	0.610499	-0.860859	0.002821
29	1	0	0.391957	0.238066	1.373787

30	6	0	-2.296993	-0.463478	-0.569845
31	1	0	-1.559635	0.744846	-2.176896
32	6	0	2.662266	1.700344	-0.338582
33	1	0	3.718382	1.879361	-0.137658
34	1	0	2.068682	2.535276	0.028904
35	1	0	2.510012	1.548657	-1.403207
36	6	0	-2.252490	-1.742334	-0.007520
37	6	0	-3.433183	0.323738	-0.348851
38	6	0	-4.481691	-0.139147	0.444809
39	6	0	-3.296127	-2.207393	0.792624
40	6	0	-4.412522	-1.405115	1.027351
41	1	0	-3.503145	1.302876	-0.813802
42	1	0	-5.358230	0.481654	0.598105
43	1	0	-3.249240	-3.205582	1.216293
44	1	0	-1.406757	-2.375421	-0.249776
45	1	0	-5.230233	-1.770138	1.639342
46	1	0	0.472962	1.419319	-1.412247

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.065517 (a.u.) Zero-point Correction = 0.397590 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.478968 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.507280 (a.u.)



TS2-OH-TS3:

Standard orientation:

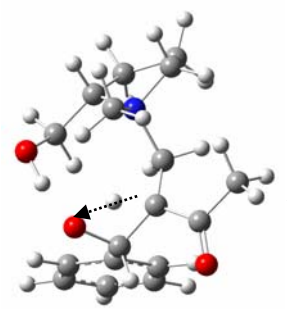
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.405345	0.356654	-1.371611
2	6	0	-2.623621	-1.624260	-2.015682
3	6	0	-3.155552	-0.629654	-0.982868
4	6	0	-1.689055	-2.556201	-1.203682
5	1	0	-2.073534	-1.112511	-2.806842
6	1	0	-3.447356	-2.159843	-2.488942

7	6	0	-1.640293	-1.982437	0.223484
8	7	0	-2.057655	-0.501484	0.052120
9	1	0	-4.030344	-1.032477	-0.469473
10	1	0	-0.688482	-2.585753	-1.641035
11	1	0	-2.055054	-3.583305	-1.174596
12	6	0	-0.322420	-2.252548	0.956954
13	8	0	-0.290066	-1.791992	2.273572
14	1	0	-0.224508	-3.347274	0.956112
15	1	0	0.519359	-1.869369	0.368511
16	1	0	0.154637	-0.882155	2.275201
17	1	0	-2.450737	-2.401769	0.825653
18	6	0	-2.625191	0.048419	1.324820
19	1	0	-3.487780	-0.561295	1.594173
20	1	0	-2.931426	1.079394	1.165646
21	1	0	-1.883399	-0.011028	2.113216
22	6	0	1.106993	1.206675	0.918456
23	8	0	0.629232	0.632112	2.148884
24	6	0	-0.271929	1.493595	0.270402
25	6	0	-0.565209	2.892906	-0.096914
26	8	0	0.206189	3.815941	0.131090
27	6	0	-1.910237	3.230561	-0.753713
28	1	0	-2.744782	2.618075	-0.402763
29	1	0	-1.835385	3.106404	-1.840466
30	1	0	-2.130241	4.279280	-0.556309
31	6	0	-0.884624	0.411477	-0.575923
32	1	0	-0.134787	-0.309196	-0.892162
33	1	0	-1.355149	0.812649	-1.470556
34	6	0	2.135218	0.385230	0.169527
35	1	0	1.559680	2.184541	1.120527
36	6	0	2.854195	-0.622118	0.821614
37	6	0	2.445262	0.668469	-1.168024
38	6	0	3.432669	-0.048212	-1.841676
39	6	0	3.846510	-1.337221	0.150257
40	6	0	4.136220	-1.058075	-1.184202
41	1	0	1.920492	1.470235	-1.678967
42	1	0	3.659312	0.187019	-2.876300
43	1	0	4.397703	-2.111106	0.674103
44	1	0	2.629774	-0.830284	1.860839
45	1	0	4.908012	-1.614231	-1.704911
46	1	0	-0.443539	1.219613	1.550760

Zero-point Energy: B3LYP/6-311++G(d,p) = -943.021617 (a.u.) Zero-point Correction = 0.393951 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -943.430579 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -943.457481 (a.u.)



1624icm^{-1}

pro-OH-TS3:

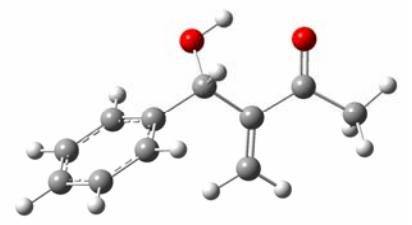
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.374708	0.620806	0.462127
2	8	0	0.612687	1.928926	-0.058420
3	6	0	1.349426	-0.382983	-0.167112
4	6	0	2.797096	-0.098166	0.097617
5	8	0	3.116601	0.929082	0.678875
6	6	0	3.862199	-1.078053	-0.352375
7	1	0	3.868739	-1.166951	-1.442408
8	1	0	3.684864	-2.074394	0.060095
9	1	0	4.831905	-0.711774	-0.019398
10	6	0	0.973285	-1.431761	-0.906859
11	1	0	-0.071452	-1.637975	-1.104299
12	1	0	1.693959	-2.114479	-1.340509
13	6	0	-1.084096	0.271624	0.255930
14	1	0	0.573982	0.622557	1.542604
15	6	0	-1.807008	0.806462	-0.813335
16	6	0	-1.723216	-0.608045	1.134409
17	6	0	-3.057734	-0.960311	0.942529
18	6	0	-3.143782	0.458738	-1.003313
19	6	0	-3.771882	-0.427960	-0.130073
20	1	0	-1.175651	-1.017306	1.978013
21	1	0	-3.541415	-1.640594	1.634761
22	1	0	-3.696940	0.885812	-1.832651
23	1	0	-1.320193	1.507291	-1.479567
24	1	0	-4.812370	-0.694804	-0.277920
25	1	0	1.516303	2.156451	0.200368

Zero-point Energy: B3LYP/6-311++G(d,p) = -576.779367 (a.u.) Zero-point Correction = 0.203444 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -576.988304 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -576.998813 (a.u.)



com-H_2O-OH-TS3:

Standard orientation:

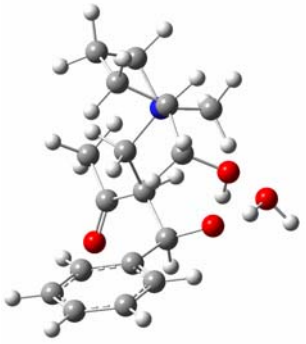
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.319714	0.657157	-1.494365
2	6	0	-2.896912	-1.430596	-2.144020
3	6	0	-3.217072	-0.354349	-1.103383
4	6	0	-2.031260	-2.465256	-1.380785
5	1	0	-2.352689	-1.013547	-2.992903
6	1	0	-3.819053	-1.861302	-2.535999
7	6	0	-1.879968	-1.927909	0.049730
8	7	0	-2.071855	-0.390805	-0.108676
9	1	0	-4.120399	-0.602437	-0.544680
10	1	0	-1.053566	-2.583593	-1.853701
11	1	0	-2.493946	-3.452458	-1.354878
12	6	0	-0.618873	-2.398413	0.784349
13	8	0	-0.527598	-1.961226	2.099031
14	1	0	-0.689954	-3.495689	0.771190
15	1	0	0.276052	-2.146406	0.198905
16	1	0	-0.042725	-1.058443	2.097634
17	1	0	-2.742931	-2.217116	0.654261
18	6	0	-2.513906	0.245318	1.182004
19	1	0	-3.330402	-0.354170	1.581203
20	1	0	-2.863103	1.256408	0.978447
21	1	0	-1.682506	0.268602	1.878262
22	6	0	1.059152	0.980304	0.906077
23	8	0	0.527887	0.364376	2.025262
24	6	0	-0.131414	1.444233	-0.012118
25	6	0	0.128550	2.645743	-0.935265
26	8	0	1.195265	3.213051	-0.983460
27	6	0	-1.051741	3.186222	-1.741167
28	1	0	-2.015987	2.994826	-1.264427
29	1	0	-1.062365	2.728357	-2.736325
30	1	0	-0.916311	4.259262	-1.875742
31	6	0	-0.823791	0.284973	-0.757312

32	1	0	-0.095921	-0.506403	-0.914882
33	1	0	-1.165090	0.605635	-1.738674
34	6	0	2.118476	0.110495	0.198708
35	1	0	1.574790	1.916082	1.181647
36	6	0	2.670273	-0.967095	0.902730
37	6	0	2.599606	0.362226	-1.094850
38	6	0	3.575152	-0.451705	-1.671720
39	6	0	3.652734	-1.775866	0.332053
40	6	0	4.105393	-1.528120	-0.962462
41	1	0	2.242293	1.218552	-1.651151
42	1	0	3.930483	-0.233258	-2.673607
43	1	0	4.066053	-2.600609	0.903438
44	1	0	2.314409	-1.153630	1.907753
45	1	0	4.868272	-2.156817	-1.408867
46	1	0	-0.275429	1.495686	2.892376
47	1	0	-0.829279	1.891116	0.705756
48	8	0	-0.923631	2.199394	3.202321
49	1	0	-0.539781	2.593847	3.989406

Zero-point Energy: B3LYP/6-311++G(d,p) = -1019.512491 (a.u.) Zero-point Correction = 0.423309 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -1019.951899 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -1019.981151 (a.u.)



TS-H_2O-OH-TS3:

Standard orientation:

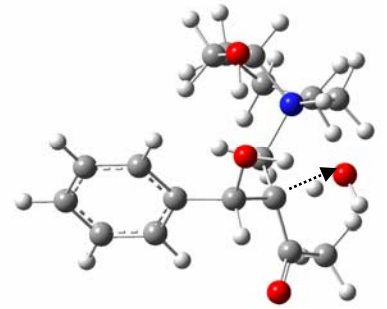
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.198638	0.547729	-1.675639
2	6	0	-2.676577	-1.556068	-2.181488
3	6	0	-3.122244	-0.443608	-1.231772
4	6	0	-1.930173	-2.562680	-1.270024
5	1	0	-2.016070	-1.170933	-2.959962
6	1	0	-3.539147	-1.998760	-2.680839

7	6	0	-1.897885	-1.930244	0.133738
8	7	0	-2.091030	-0.416195	-0.121749
9	1	0	-4.077711	-0.688341	-0.765227
10	1	0	-0.916691	-2.744463	-1.635085
11	1	0	-2.431733	-3.530275	-1.225621
12	6	0	-0.685619	-2.355913	0.966034
13	8	0	-0.686815	-1.871825	2.279938
14	1	0	-0.741280	-3.451844	0.999582
15	1	0	0.246035	-2.111205	0.444225
16	1	0	-0.125852	-1.059716	2.307734
17	1	0	-2.797003	-2.205146	0.690686
18	6	0	-2.680381	0.272057	1.074057
19	1	0	-3.595532	-0.256758	1.340585
20	1	0	-2.895673	1.307284	0.823881
21	1	0	-1.987796	0.261020	1.903841
22	6	0	1.150163	1.013703	0.901163
23	8	0	0.738620	0.434705	2.147405
24	6	0	-0.107830	1.415759	0.077751
25	6	0	0.058375	2.660692	-0.730164
26	8	0	1.012704	3.411003	-0.595555
27	6	0	-1.069161	3.077550	-1.678171
28	1	0	-2.060090	2.802785	-1.307947
29	1	0	-0.930621	2.620776	-2.664672
30	1	0	-1.019691	4.158389	-1.805164
31	6	0	-0.775038	0.274807	-0.678763
32	1	0	-0.072530	-0.545415	-0.807308
33	1	0	-1.067981	0.594482	-1.674540
34	6	0	2.156275	0.102638	0.215592
35	1	0	1.666187	1.955972	1.112463
36	6	0	2.715010	-0.992210	0.884331
37	6	0	2.594279	0.379270	-1.087723
38	6	0	3.543966	-0.427643	-1.709918
39	6	0	3.666784	-1.801088	0.260828
40	6	0	4.081793	-1.526912	-1.039773
41	1	0	2.212249	1.249789	-1.608196
42	1	0	3.873806	-0.190063	-2.715708
43	1	0	4.089053	-2.642444	0.799991
44	1	0	2.410227	-1.196185	1.902503
45	1	0	4.824317	-2.152670	-1.522494
46	1	0	0.100811	1.132003	2.527829
47	1	0	-0.741507	1.910867	1.051376
48	8	0	-1.054262	2.226217	2.406337
49	1	0	-0.782304	3.115043	2.656761

Zero-point Energy: B3LYP/6-311++G(d,p) = -1019.496944 (a.u.) Zero-point Correction = 0.420392 (a.u.)

SCF Energy: B3LYP (PCM, 1,4-dioxane)/6-311++G(d,p) = -1019.931708 (a.u.)

B3LYP (PCM, H_2O)/6-311++G(d,p) = -1019.957483 (a.u.)



719icm^{-1}

C. AIM analysis.

The bonding properties of *syn*-TSb1, *anti*-TSc1, *re-syn*-OH-TS1, *si-syn*-OH-TS2, *re-anti*-OH-TS3 and *si-anti*-OH-TS4 have been investigated using the topological methodology AIM, which might be used to assess the chemical bonding situation in a given molecule. The gradient paths of the gradient vector field $\nabla\rho(r)$, which originate at a bond critical point and terminate at the nuclei, might be used to define a chemical bond. A bond can be characterized by the positive-negative of $\nabla^2\rho(r)$. If $\nabla^2\rho(r) > 0$, the bond is defined as a closed-shell interaction (ionic bonds, hydrogen bonds, and van der Waals interactions). If $\nabla^2\rho(r) < 0$, the bond is defined as a shared interaction (covalent bond).

Table 2. The bonding properties of *syn*-TSb1, *anti*-TSc1, *re-syn*-OH-TS1, *si-syn*-OH-TS2, *re-anti*-OH-TS3 and *si-anti*-OH-TS4.

	syn-TSb1	*anti*-TSc1	*re-syn*-OH-TS1
$L(r)$	-0.026	-0.017	-0.035
$\nabla^2\rho(r)$	0.026	0.017	0.035
Bonding property	hydrogen-bond	hydrogen-bond	hydrogen-bond
	si-syn-OH-TS2	*re-anti*-OH-TS3	*si-anti*-OH-TS4
$L(r)$	-0.034	-0.035	-0.031
$\nabla^2\rho(r)$	0.034	0.035	0.031
Bonding property	hydrogen-bond	hydrogen-bond	hydrogen-bond

D. The geometry evolution and charge transfer in C−C bond formation.

As proposed by Hammond, the formation of the intermediates involves remarkable structural changes and significant electronic reorganizations.[1] To understand the details of electronic evolution and to check these structural changes along the reaction paths, IRC analysis was carried out for the kinetically favored *syn*-TSb1 transition structure. We constructed PES as a function of the formed N−C and C−C bond by the geometry optimizations starting from the reactants with gradual reducing of the N−C and C−C distances. Fig. 1 presents the evolutions of the relative energies, the N−C1 and C2−C3 bond distances, the electronic populations and the total charge on N atom as the reaction proceeds along the intrinsic reaction coordinate.

The following features are observed during the evolution of the species along the reaction coordinate. The highest energy point on the potential energy curve represents the structure of the transition state *syn*-TSb1. From *syn*-TSb1 to *syn*-IMb2, the bond distance of C2−C3 shortens from 2.346 Å to 1.602 Å; namely, the interaction between two atoms is gradually strengthened and then leads to the formation of *syn*-IMb2 on PES. From *syn*-TSb1 to the reaction entrance, the C2−C3 distance elongates and the bond strength becomes weakened, which is followed by the elongation of N−C1 bond along the reaction coordinate. Finally, the structure is stabilized in the separated formaldehyde and enamine intermediate *syn*-IM1.

Along the structural evolution, a considerable amount of charge is reorganized among N, C1 and C2 atoms. NBO analysis illustrates that, accompanied by the cleavage of N−C1 bond, the electronic populations on 2p orbital of N atom increase and reach the maximum point of 4.24 at IRC=150 bohr$^{1/2}$, which are very close to those in the free catalyst N-methylprolinol (4.27). From the total charge distribution of N atom, it is found that the charge accumulates gradually during the cleavage of the N−C1 bond and stabilizes at −0.553*e* finally. In the reverse direction, the populations on N atom decrease gradually and stabilize at 4.08 in *syn*-IMb2 and the charge on N atom decreases gradually along the bond formation path and stabilizes at −0.374*e*, which indicates that the charge transfers from N atom toward MVK during the formation of *syn*-TSb1. Meanwhile, the charge accumulated on C2 atom stabilizes at −0.536*e* finally. Combining with the curve of the populations on N atom, we conclude that the charge transfers from N-2p orbital to C2 atom.

The electrophilicity index ω is powerful tool for correctly explaining the electronic motion. Table 3 shows the electronic chemical potential μ, chemical hardness η and electrophilicity index ω of *syn*-IM1, *syn*-TSb1 and *syn*-IMb2. According to electrophilicity index ω, it is clear that from *syn*-IM1 to *syn*-TSb1, the electrophilicity of alkene moiety becomes stronger, suggesting that the charge transfers from N-2p orbital to MVK. On the other hand, the index ω indicates that from *syn*-TSb1 to *syn*-IMb2, the electrophilicity decreases, suggesting that *syn*-TSb1 is more reactive with higher electrophilicity index. The trend of the

variation of electrophilicity index is in agreement with the pronounced charge transfer character in NBO analysis.

Consequently, after the *syn*-enamine attacks formaldehyde, the charge transfers from N atom of N-methylprolinol to MVK. The increasing charge on MVK makes the interaction between MVK and N-methylprolinol greater and the structure of *syn*-TSb1 becomes more compact, as compared to the structure in *syn*-enamine. On the other hand, the charge accumulated on C2 atom makes MVK more nucleophilic and then enhances the interaction between MVK and formaldehyde.

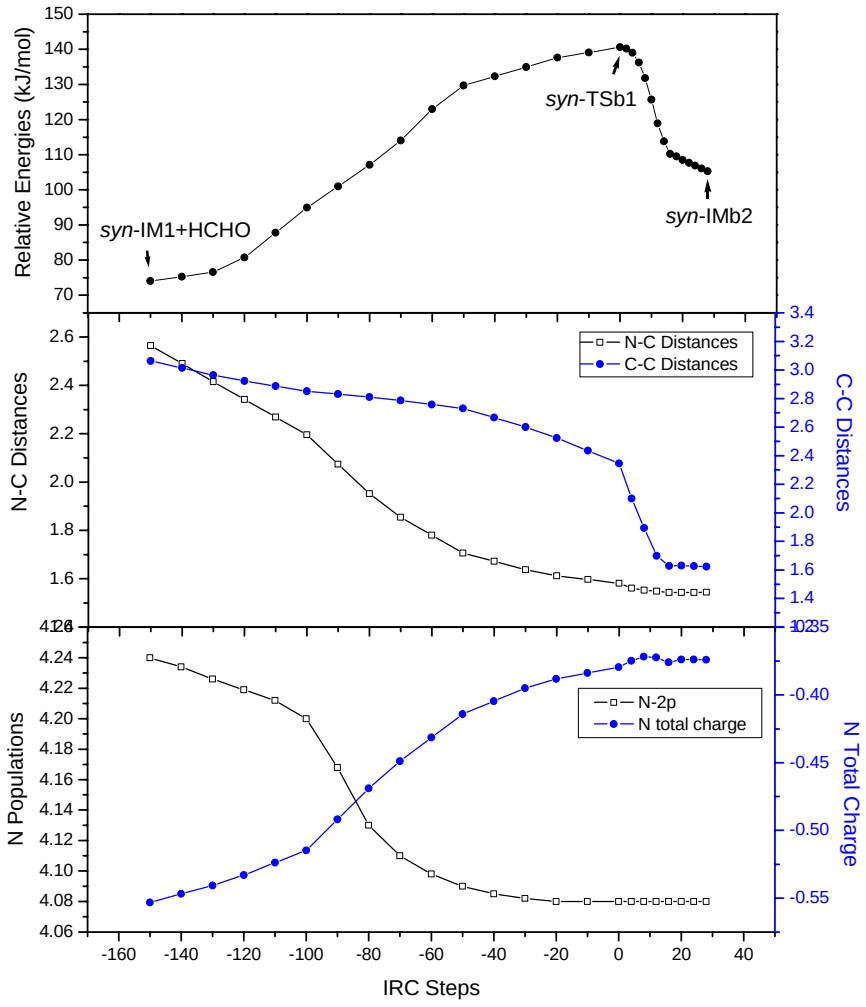


Fig. 1 The variations of the computed potential energies, the bond distances, the electronic populations and the distribution of the total charge on N atom along the intrinsic reaction coordinate.

Table 3 Electronic chemical potential μ, chemical hardness η and electrophilicity index ω calculated in the process of the attack of enamine to formaldehyde.

	Chemical Potential μ (a.u.)	Chemical Hardness η (a.u.)	Electrophilicity Index ω (eV)
syn-IM1	−0.15	0.17	1.14
syn-TSb1	−0.11	0.14	1.18
syn-IMb2	−0.12	0.16	1.08

E. The energy profiles along different paths in the presence of water.

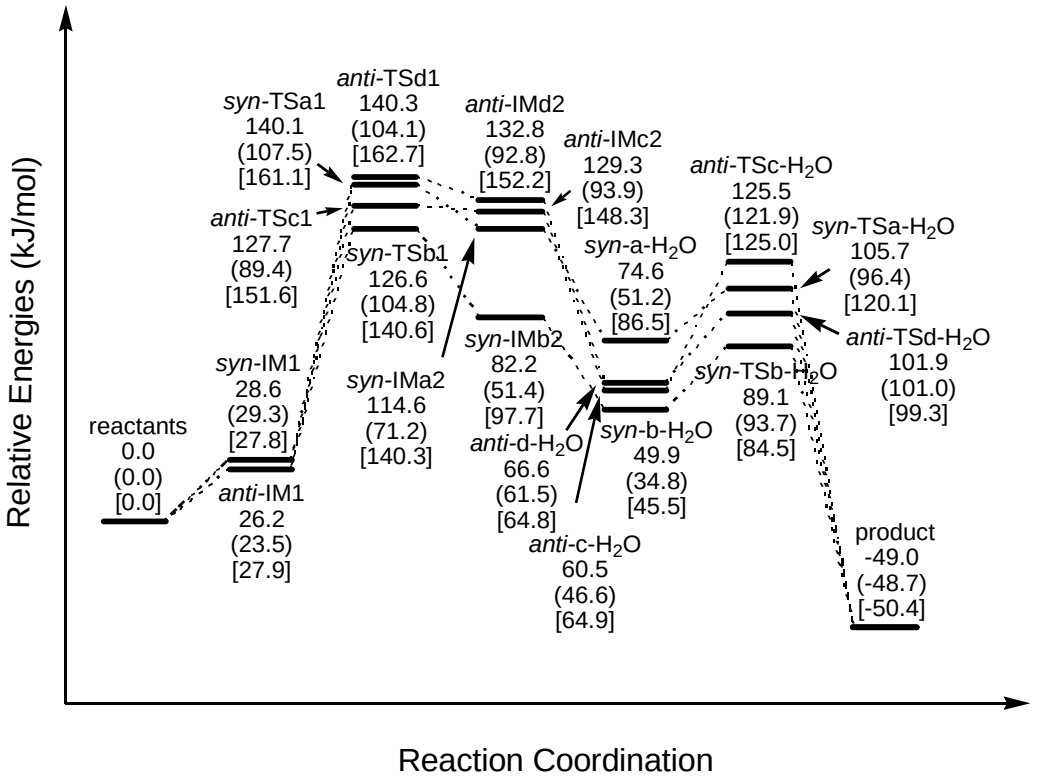


Fig. 2 PCM energies (in kJ/mol) in 1,4-dioxane for various intermediates and transition states calculated at the B3LYP/6-311++G(d,p) level. PCM energies (in kJ/mol) in water are listed in parentheses. The relative energies (in kJ/mol) in the gas-phase are listed in square brackets.

F. The complete paths via *si-syn*-OH-TS2, *re-anti*-OH-TS3.

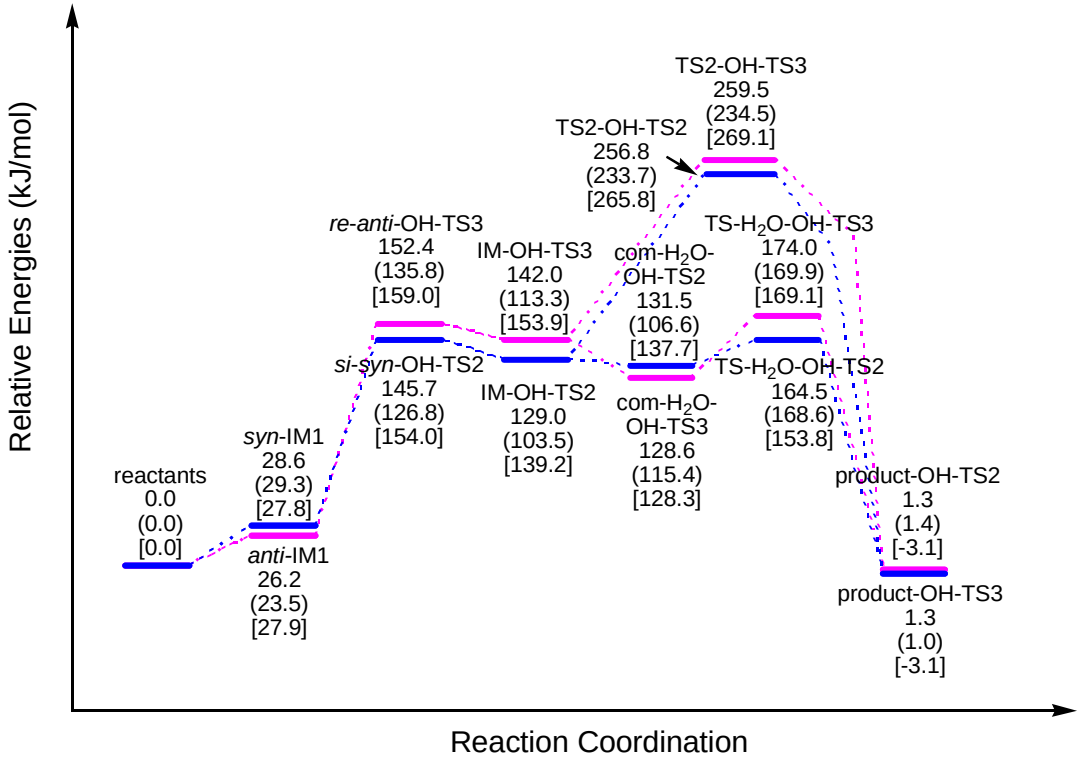


Fig. 3 The complete paths via *si-syn*-OH-TS2, *re-anti*-OH-TS3 concerning the direct proton transfer mechanism and a water-assisted proton transfer mechanism. PCM energies (in kJ/mol) in 1,4-dioxane for various intermediates and transition states calculated at the B3LYP/6-311++G(d,p) level. PCM energies (in kJ/mol) in water are listed in parentheses. The relative energies (in kJ/mol) in the gas-phase are listed in square brackets. (The blue curve represents the path via *si-syn*-OH-TS2, the red one represents the path via *re-anti*-OH-TS3.)