Supporting information for

Support for a dioxyallyl cation in the mechanism leading to (-)-levoglucosenone

Ben W. Greatrex,[a,*] Jan Meisner,[b] Stephen A. Glover[a] and Warwick Raverty[c]

[a] *School of Science and Technology, University of New England, Armidale, New South Wales, 2351, Australia*

[b] *Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

[c] *Circa Group, Bio-21 Institute, Melbourne, Victoria, 3052, Australia*

ben.greatrex@une.edu.au

Cartesian coordinates (Å), energies, and the number of imaginary frequencies (N_{imag}) for computed structures at the M06-2X/def2-TZVP level in THF using Turbomole v. 7.0.1.

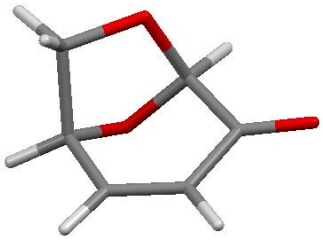
Water

E = -76.43626529 hartrees
ZPE = 56263.48657 J.mol^{-1}
Enthalpy correction = 7.5186 J.mol^{-1}
S = 56263.5 J.mol^{-1}.K^{-1}
G = -47951 kcal.mol^{-1}

Hydronium

E = -76.82043657 hartrees
ZPE = 92963.31781 J.mol^{-1}
Enthalpy correction = 101.84414 J.mol^{-1}
S = 92963.3 J.mol^{-1}.K^{-1}
G = -48183.3 kcal.mol^{-1}

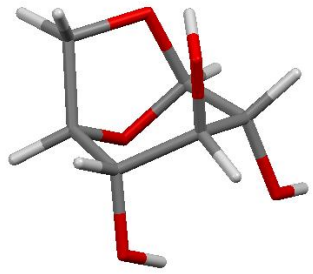
Compound 1 - Levoglucosenone



E = -457.885023 hartrees
ZPE = 306811.86932 J.mol^{-1}
Enthalpy correction = 9569.90525 J.mol^{-1}
S = 306811.9 J.mol^{-1}.K^{-1}
G = -287255.2 kcal.mol^{-1}
N_{imag} = 0

C -4.152788 1.889899 0.528900
C -2.889385 2.671645 0.300015
O -2.197201 2.143971 -0.835159
H -3.065532 3.731088 0.142793
C -1.864310 2.362901 1.402473
C -1.766356 0.899223 -0.365909
C -2.966541 -0.051012 -0.290173
H -0.965894 0.505487 -0.989104
C -4.188151 0.588811 0.236927
O -2.879846 -1.218359 -0.594288
H -5.002393 2.400428 0.965728
H -5.067341 -0.026067 0.378257
O -1.315428 1.117170 0.964577
H -2.305702 2.238688 2.389015
H -1.081580 3.121162 1.423441

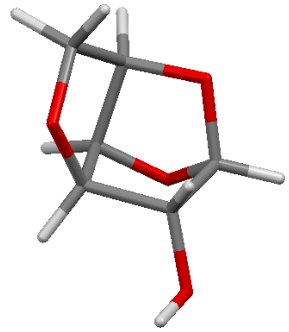
Compound 2 – Levoglucosan



E = -610.7808206 hartrees
ZPE = 457109.26853 J.mol^{-1}
Enthalpy correction = 17026.55494 J.mol^{-1}
S = 457109.3 J.mol^{-1}.K^{-1}
G = -383163.9 kcal.mol^{-1}
N_{imag} = 0

C -4.373551 2.015004 -0.357976
C -3.106762 2.799044 -0.015953
O -1.981480 2.055345 -0.499759
H -3.110348 3.771774 -0.501648
C -2.782254 2.850888 1.470148
C -1.891678 1.003591 0.420797
C -2.973269 -0.040611 0.120964
H -0.884088 0.587718 0.389738
C -4.358843 0.602815 0.264047
H -2.890464 -0.869008 0.831599
O -2.859828 -0.493203 -1.214530
O -4.500929 1.926342 -1.764016
H -5.250931 2.546690 0.013243
O -4.787860 0.608638 1.612982
H -5.074097 -0.003026 -0.294202
O -2.145980 1.580746 1.699097
H -3.659874 2.941131 2.108252
H -2.076875 3.651072 1.691573
H -3.774682 1.374335 -2.087945
H -4.021169 0.754003 2.181504
H -1.980113 -0.861373 -1.359768

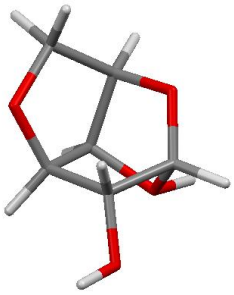
Compound 12 – 1,4:3,6-dianhydroglucopyranose



E = -534.3289428 hartrees
ZPE = 385359.94829 J.mol^{-1}
Enthalpy correction = 11249.21344 J.mol^{-1}
S = 385359.9 J.mol^{-1}.K^{-1}
G = -335205.9 kcal.mol^{-1}
N_{imag} = 0

C -0.247352 1.045182 -0.159821
O -0.450948 -0.702742 1.302566
C 1.550223 -0.507659 0.007899
C 0.819075 -0.067198 1.274490
C 0.633576 0.146144 -1.060122
C -1.240095 -0.036376 0.300908
H 1.336452 -0.191576 2.220313
H 1.210091 0.672670 -1.818248
H -2.164146 0.324887 0.746492
O -0.231609 -0.780807 -1.686408
C -1.439834 -0.898345 -0.924046
H -1.608217 -1.943094 -0.662359
H -2.278621 -0.532842 -1.520891
O 2.843123 0.048538 0.043311
H 3.325802 -0.231987 -0.741895
H -0.650020 1.959562 -0.578422
O 0.525025 1.283795 1.004642
H 1.566409 -1.593214 -0.102626

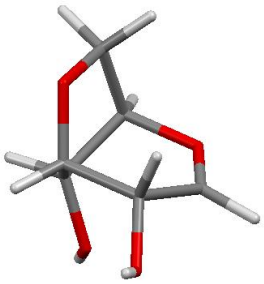
Compound 22



E = -534.7091097 hartrees
ZPE = 417388.42263 J.mol^{-1}
Enthalpy correction = 12284.81811 J.mol^{-1}
S = 417388.4 J.mol^{-1}.K^{-1}
G = -335437 kcal.mol^{-1}
N_{imag} = 0

C -0.279094 1.045346 -0.198280
O -0.452819 -0.675854 1.328233
C 1.555051 -0.507183 -0.005769
C 0.821148 -0.181213 1.279849
C 0.627220 0.156821 -1.067930
C -1.248214 -0.031088 0.298913
H 1.350698 -0.266144 2.222535
H 1.207241 0.685994 -1.819320
H -2.170243 0.313785 0.756260
O -0.232041 -0.769912 -1.680341
C -1.436657 -0.906823 -0.916891
H -1.588946 -1.948525 -0.638514
H -2.281425 -0.556551 -1.511189
O 2.817070 0.086458 0.072724
H 3.388104 -0.274926 -0.615846
H -0.667419 1.976956 -0.589449
O 0.577207 1.296153 0.972817
H 0.127683 1.777437 1.696106
H 1.585806 -1.587287 -0.156286

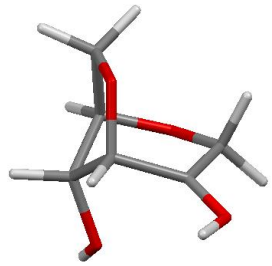
Compound 23



E = -534.7094959 hartrees
ZPE = 410778.59655 J.mol^{-1}
Enthalpy correction = 15187.04557 J.mol^{-1}
S = 410778.6 J.mol^{-1}.K^{-1}
G = -335439.5 kcal.mol^{-1}
N_{imag} = 0

C -0.343787 1.179730 -0.467856
O -0.397803 -0.362953 1.377668
C 1.540482 -0.394995 -0.062585
C 0.838270 -0.467839 1.246325
C 0.609378 0.203787 -1.148226
C -1.217386 0.144184 0.247696
H 1.393798 -0.670184 2.161274
H 1.208536 0.626961 -1.950145
H -2.125942 0.489584 0.726274
O -0.235044 -0.809580 -1.648776
C -1.388251 -0.926200 -0.803805
H -1.448252 -1.926734 -0.375596
H -2.289777 -0.725980 -1.382617
O 2.748741 0.268096 0.135537
H 3.439541 -0.154767 -0.387015
H -0.954259 1.709256 -1.201012
O 0.369023 2.020429 0.384728
H -0.203717 2.716471 0.727576
H 1.680649 -1.456394 -0.327150

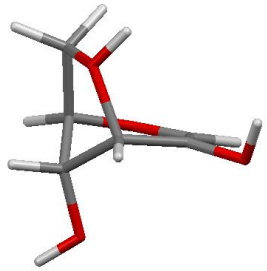
Compound 24



E = -534.7106627 hartrees
ZPE = 412501.83117 J.mol^{-1}
Enthalpy correction = 14751.81796 J.mol^{-1}
S = 412501.8 J.mol^{-1}.K^{-1}
G = -335439.8 kcal.mol^{-1}
N_{imag} = 0

C -0.412837 1.221016 -0.477817
O -0.472849 -0.268576 1.412764
C 1.498061 -0.074906 0.010846
C 0.846008 -0.698319 1.190436
C 0.614281 0.304296 -1.147526
C -1.208675 0.140223 0.269638
H 1.438191 -0.505087 2.084252
H 1.169454 0.726195 -1.984293
H -2.175007 0.476178 0.635844
O -0.061381 -0.867164 -1.521632
C -1.305324 -0.950092 -0.781510
H -1.385496 -1.942888 -0.342473
H -2.132794 -0.779468 -1.469803
O 2.747997 0.014575 0.011995
H 3.129263 0.366052 -0.818468
H -1.031163 1.735764 -1.213987
O 0.317121 2.090713 0.343341
H -0.267068 2.545169 0.962991
H 0.891783 -1.780864 0.983433

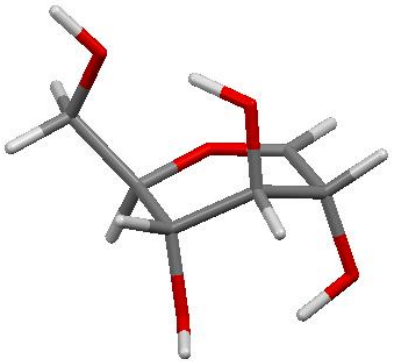
Compound 25



E = -534.6983817 hartrees
ZPE = 411222.13045 J.mol^{-1}
Enthalpy correction = 16049.55478 J.mol^{-1}
S = 411222.1 J.mol^{-1}.K^{-1}
G = -335432.6 kcal.mol^{-1}
N_{imag} = 0

C -0.445505 1.207574 -0.464940
O -0.431405 -0.313186 1.429609
C 1.518766 -0.183630 0.084509
C 0.903074 -0.456496 1.235531
C 0.700014 0.371890 -1.031017
C -1.188418 0.103883 0.298753
H 1.424225 -0.801735 2.117582
H 1.270795 0.823361 -1.835915
H -2.163730 0.404560 0.669897
O -0.138297 -0.712086 -1.659060
C -1.291843 -1.004185 -0.729531
H -1.141329 -1.996691 -0.316760
H -2.179336 -0.949586 -1.350260
O 2.882741 -0.229449 -0.028058
H 3.155185 -0.874521 -0.692935
H -1.072021 1.577161 -1.278775
O 0.066421 2.221727 0.332523
H -0.588718 2.922571 0.424523
H 0.369465 -1.510426 -1.892463

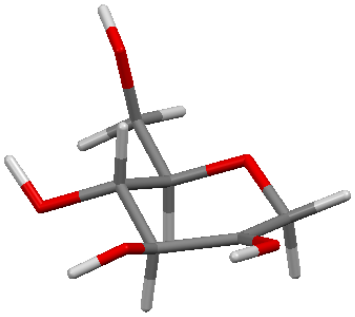
Compound 26



E = -611.154539 hartrees
ZPE = 482431.0604 J.mol^{-1}
Enthalpy correction = 21595.61844 J.mol^{-1}
S = 482431.1 J.mol^{-1}.K^{-1}
G = -383394.3 kcal.mol^{-1}
N_{imag} = 0

C -4.354810 2.114292 -0.072279
C -3.068974 2.883113 -0.364511
O -1.834085 2.131045 -0.000833
H -2.957713 2.986980 -1.443051
C -2.944706 4.246187 0.264979
C -1.812047 0.992016 0.492748
C -3.036839 0.173985 0.789377
H -0.812344 0.578003 0.624304
C -4.219482 1.094344 1.066324
H -2.833937 -0.425840 1.676048
O -3.141787 -0.686432 -0.318824
O -4.682865 1.426808 -1.268806
H -5.124163 2.847378 0.183179
O -4.010714 1.667965 2.327355
H -5.130403 0.490441 1.077852
O -3.167692 4.137566 1.654371
H -3.696042 4.878901 -0.213848
H -1.953606 4.652001 0.052908
H -3.225611 5.011783 2.056862
H -5.614872 1.173226 -1.252903
H -3.815745 2.620316 2.253202
H -3.614116 -0.216351 -1.026053

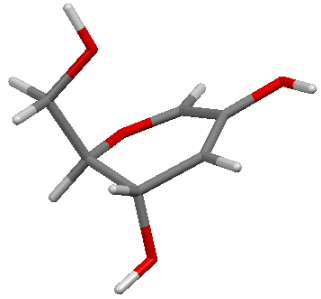
Compound 27



E = -611.1678202 hartrees
ZPE = 478943.85399 J.mol^{-1}
Enthalpy correction = 22731.79422 J.mol^{-1}
S = 478943.9 J.mol^{-1}.K^{-1}
G = -383403.5 kcal.mol^{-1}
N_{imag} = 0

C	-4.218196	2.073629	-0.008227
C	-2.925144	2.776007	-0.436247
O	-1.838855	2.168567	0.256570
H	-2.781569	2.665480	-1.518651
C	-2.957632	4.249600	-0.102917
C	-1.581399	0.849062	-0.144515
C	-2.823636	0.043313	0.016402
H	-1.285068	0.782165	-1.201892
C	-4.129326	0.596799	-0.407031
H	-0.786881	0.437205	0.474191
O	-2.772074	-1.095996	0.528843
O	-5.347256	2.585353	-0.660928
H	-4.312856	2.139131	1.077867
O	-5.119328	-0.224272	0.126971
H	-4.104130	0.558304	-1.509568
O	-3.431830	4.399216	1.221897
H	-3.618917	4.747016	-0.817429
H	-1.949694	4.654408	-0.219359
H	-3.384823	5.329016	1.467373
H	-5.711072	3.313573	-0.142488
H	-5.948318	-0.107361	-0.353414
H	-3.678152	-1.489799	0.592268

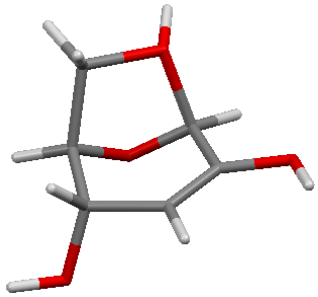
Compound 28



E = -534.7146108 hartrees
ZPE = 405002.58851 J.mol^{-1}
Enthalpy correction = 18905.5099 J.mol^{-1}
S = 405002.6 J.mol^{-1}.K^{-1}
G = -335445.1 kcal.mol^{-1}
N_{imag} = 0

C -0.521449 1.188598 -0.455543
O -0.340056 -0.411198 1.429939
C 1.487998 -0.188572 -0.088335
C 0.852933 -0.645507 1.114716
C 0.850658 0.723856 -0.831912
C -1.250843 0.212988 0.463402
H 1.423106 -1.196609 1.859293
H 1.337459 1.215024 -1.666378
H -1.954991 0.757923 1.088311
O -1.019081 -1.663994 -0.966105
C -1.967279 -0.924588 -0.232887
H -2.465334 -1.541825 0.517936
H -2.728251 -0.474322 -0.878249
O 2.727584 -0.683742 -0.244172
H 3.166075 -0.289735 -1.010455
H -1.125192 1.270237 -1.364033
O -0.345083 2.452149 0.148973
H -1.120742 3.002782 -0.013708
H -1.418063 -2.492101 -1.255147

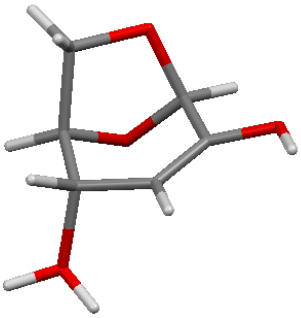
Compound 29



E = -534.7129752 hartrees
ZPE = 413764.93118 J.mol^{-1}
Enthalpy correction = 14895.42405 J.mol^{-1}
S = 413764.9 J.mol^{-1}.K^{-1}
G = -335440.7 kcal.mol^{-1}
N_{imag} = 0

C -0.514306 1.395364 -0.420638
O -0.477318 -0.247142 1.365881
C 1.308853 -0.234675 -0.237912
C 0.430034 -1.002977 0.703694
C 0.866336 0.905500 -0.753020
C -1.293728 0.315857 0.331141
H 0.948604 -1.708164 1.346112
H 1.483194 1.512425 -1.403813
H -2.182826 0.729570 0.797726
O -0.483642 -1.828591 -0.232747
C -1.620209 -0.919709 -0.526262
H -2.523651 -1.426463 -0.207506
H -1.609476 -0.744243 -1.596363
O 2.481169 -0.860796 -0.442407
H 3.029461 -0.369632 -1.069404
H -1.055948 1.608264 -1.348081
O -0.392166 2.565677 0.361028
H -1.199580 3.087814 0.288044
H -0.782541 -2.652740 0.194862

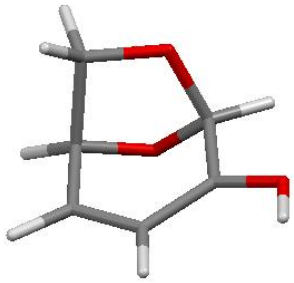
Compound 30



E = -534.7172044 hartrees
ZPE = 412582.73709 J.mol^{-1}
Enthalpy correction = 15457.251 J.mol^{-1}
S = 412582.7 J.mol^{-1}.K^{-1}
G = -335444.1 kcal.mol^{-1}l
N_{imag} = 0

C -0.497314 1.326004 -0.522876
O -0.477319 -0.151529 1.344828
C 1.294855 -0.261570 -0.244981
C 0.365833 -1.043727 0.670448
C 0.876535 0.877964 -0.813075
C -1.295870 0.323214 0.288397
H 0.908447 -1.670080 1.373755
H 1.478904 1.423745 -1.528288
H -2.199658 0.762442 0.701806
O -0.489003 -1.826008 -0.130506
C -1.548748 -0.955597 -0.538007
H -2.497115 -1.415894 -0.272083
H -1.508162 -0.778075 -1.613022
O 2.450820 -0.880390 -0.451683
H 2.995558 -0.415797 -1.104044
H -1.039191 1.683517 -1.395012
O -0.405210 2.584889 0.386566
H -1.160289 3.196921 0.301425
H 0.424529 3.080156 0.253265

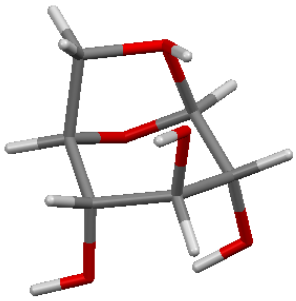
Compound 31



E = -458.278483 hartrees
ZPE = 340434.39347 J.mol^{-1}
Enthalpy correction = 9926.85749 J.mol^{-1}
S = 340434.4 J.mol^{-1}.K^{-1}
G = -287494.1 kcal.mol^{-1}l
N_{imag} = 0

C -0.452054 1.224893 -0.527314
O -0.466236 -0.220257 1.370788
C 1.317469 -0.270600 -0.182592
C 0.359932 -1.081326 0.673138
C 0.849369 0.939803 -0.749074
C -1.279217 0.334867 0.338474
H 0.861137 -1.786969 1.330619
H 1.490402 1.537912 -1.383219
H -2.135524 0.834436 0.777604
O -0.444319 -1.734388 -0.293549
C -1.628419 -0.951853 -0.451730
H -2.463504 -1.455617 0.032242
H -1.824387 -0.792343 -1.509247
O 2.441714 -0.813808 -0.425332
H 2.996089 -0.321442 -1.059431
H -0.931386 2.060605 -1.023711

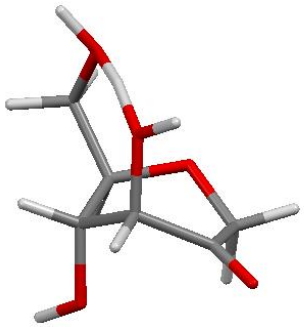
Compound 32



E = -611.1709007 hartrees
ZPE = 488629.1743 J.mol^{-1}
Enthalpy correction = 17857.11305 J.mol^{-1}
S = 488629.2 J.mol^{-1}.K^{-1}
G = -383401.4 kcal.mol^{-1}
N_{imag} = 0

C	-4.438235	1.928168	-0.142559
C	-3.163985	2.778511	-0.063131
O	-2.045149	2.027004	-0.551986
H	-3.251996	3.678784	-0.666467
C	-2.681035	3.068389	1.346750
C	-1.843442	1.035269	0.366462
C	-2.922138	-0.048894	0.272611
H	-0.819318	0.678844	0.350768
C	-4.283811	0.581795	0.587273
H	-2.722021	-0.839788	0.995916
O	-2.857130	-0.607070	-1.006187
O	-4.693050	1.578277	-1.484716
H	-5.269123	2.488965	0.297363
O	-4.296502	0.737956	2.003182
H	-5.078593	-0.088996	0.262088
O	-2.042407	1.777580	1.699034
H	-3.449088	3.263408	2.088520
H	-1.894787	3.813747	1.368539
H	-2.737094	1.284130	2.229621
H	-4.880938	2.365827	-2.009672
H	-5.169503	0.988841	2.329606
H	-3.201053	0.035293	-1.645754

Compound 33

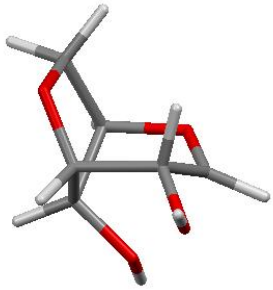


E = -611.170948 hartrees
ZPE = 477218.83244 J.mol^{-1}
Enthalpy correction = 20535.6267 J.mol^{-1}
S = 477218.8 J.mol^{-1}.K^{-1}
G = -383405 kcal.mol^{-1}
N_{imag} = 0

C	-4.176417	2.083218	-0.159085
C	-2.858711	2.894933	-0.086246
O	-1.755208	2.109967	0.327783
H	-2.681473	3.311913	-1.084926
C	-2.910845	4.062425	0.871827
C	-1.712155	0.801951	-0.206492
C	-2.920414	0.003105	0.229491
H	-0.804579	0.327844	0.162499
C	-4.097572	0.849318	0.731095
H	-3.760148	0.563890	2.698818
O	-2.986334	-1.192338	0.154270
O	-4.378467	1.544147	-1.443885
H	-5.019004	2.709954	0.147421
O	-3.903656	1.289979	2.076486
H	-5.014653	0.266578	0.667302
O	-3.017992	3.534912	2.233665
H	-3.767501	4.701405	0.673218
H	-1.985927	4.630697	0.841160
H	-3.461999	4.141343	2.846630
H	-4.631692	2.240969	-2.060004
H	-3.396502	2.519347	2.275040
H	-1.686281	0.810936	-1.302221

Transition states

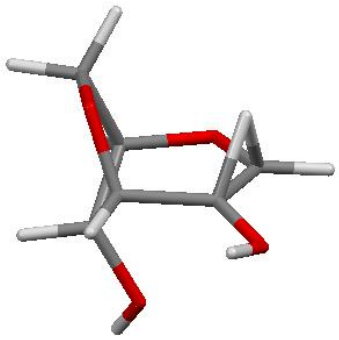
TS1



E = -534.7026988 hartrees
ZPE = 411071.4483 J.mol^{-1}
Enthalpy correction = 12550.87193 J.mol^{-1}
S = 411071.4 J.mol^{-1}.K^{-1}
G = -335434.6 kcal.mol^{-1}l
N_{imag} = 1

C -0.273907 1.088785 -0.175932
O -0.434570 -0.631455 1.406449
C 1.520614 -0.527819 -0.016601
C 0.827516 -0.422395 1.303975
C 0.623977 0.215749 -1.052042
C -1.217991 -0.021388 0.322799
H 1.393161 -0.471427 2.230822
H 1.246080 0.747616 -1.766813
H -2.147115 0.279917 0.792872
O -0.244673 -0.659217 -1.720441
C -1.374665 -0.924457 -0.880871
H -1.401978 -1.975567 -0.592452
H -2.286351 -0.673351 -1.421535
O 2.794197 0.016630 0.130970
H 3.394747 -0.388382 -0.505436
H -0.782890 1.906120 -0.678123
O 0.560939 1.522009 0.885011
H 0.068698 2.018396 1.558318
H 1.535861 -1.595461 -0.270885

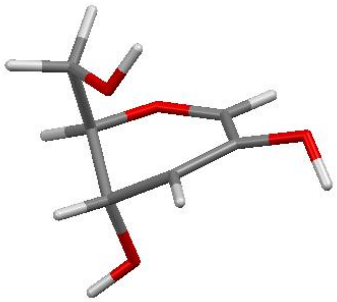
TS2



E = -534.683494 hartrees
ZPE = 402575.73132 J.mol^{-1}
Enthalpy correction = 13792.06286 J.mol^{-1}
S = 402575.7 J.mol^{-1}.K^{-1}
G = -335424.8kcal.mol^{-1}
N_{imag} = 1

C -0.351062 1.183933 -0.455196
O -0.392927 -0.461030 1.349455
C 1.574067 -0.167055 0.034680
C 0.916526 -0.534697 1.213213
C 0.662524 0.245505 -1.124025
C -1.170794 0.111989 0.262236
H 1.471328 -0.805023 2.105381
H 1.244169 0.680746 -1.934074
H -2.095635 0.450385 0.716866
O -0.091452 -0.848340 -1.577012
C -1.334394 -0.912027 -0.837070
H -1.470343 -1.921921 -0.455712
H -2.162265 -0.649695 -1.495630
O 2.872677 0.026834 0.052487
H 3.246129 0.034012 -0.842886
H -0.972639 1.661889 -1.213727
O 0.313828 2.091426 0.369329
H -0.293814 2.779094 0.665697
H 1.272997 -1.464301 0.301047

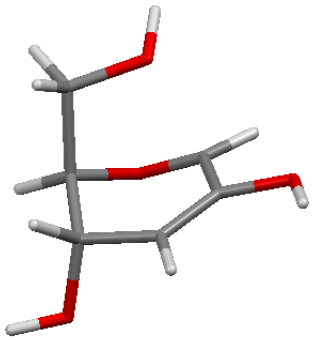
TS3



E = -534.6886483 hartrees
ZPE = 404494.06161 J.mol^{-1}
Enthalpy correction = 16319.46411 J.mol^{-1}
S = 404494.1 J.mol^{-1}.K^{-1}
G = -335428.1 kcal.mol^{-1}
N_{imag} = 1

C -0.371837 1.187088 -0.474140
O -0.395955 -0.385194 1.379639
C 1.582485 -0.198838 0.087513
C 0.898244 -0.504318 1.236641
C 0.877690 0.458560 -0.925683
C -1.158536 0.101559 0.237229
H 1.396326 -0.922167 2.104715
H 1.391907 0.789020 -1.820316
H -2.092774 0.453553 0.663807
O -0.299786 -0.849640 -1.773441
C -1.365384 -0.996555 -0.789650
H -1.333809 -1.985715 -0.338718
H -2.310397 -0.857564 -1.310017
O 2.877208 -0.620744 -0.045936
H 3.465222 0.132081 -0.186232
H -0.935712 1.531025 -1.341091
O 0.037311 2.240938 0.350804
H -0.633189 2.934619 0.342432
H 0.151435 -1.691309 -1.931595

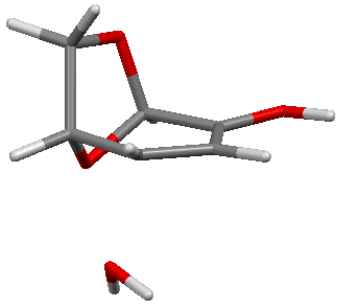
TS4



E = -534.7067995 hartrees
ZPE = 407618.35636 J.mol^{-1}
Enthalpy correction = 15365.60792 J.mol^{-1}
S = 407618.4 J.mol^{-1}.K^{-1}
G = -335438.6 kcal.mol^{-1}
N_{imag} = 1

C -0.547522 1.379425 -0.404675
O -0.411373 -0.253473 1.415977
C 1.307855 -0.211689 -0.257337
C 0.590701 -0.827659 0.857012
C 0.803315 0.883142 -0.823385
C -1.282383 0.329609 0.428568
H 1.090503 -1.585941 1.453373
H 1.351003 1.446188 -1.568819
H -2.104287 0.785205 0.972050
O -0.670237 -1.854868 -0.382990
C -1.751431 -0.923089 -0.361469
H -2.610631 -1.361629 0.137106
H -2.006917 -0.650334 -1.383485
O 2.455415 -0.856408 -0.526135
H 2.918422 -0.444395 -1.268061
H -1.157397 1.550063 -1.297234
O -0.359395 2.579164 0.310710
H -1.146781 3.131394 0.235941
H -0.945939 -2.699941 -0.000707

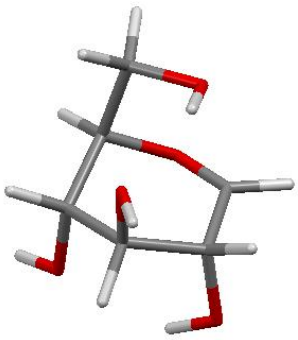
TS5



E = -534.7135868 hartrees
ZPE = 406755.04614 J.mol^{-1}
Enthalpy correction = 15472.72677 J.mol^{-1}
S = 406755 J.mol^{-1}.K^{-1}
G = -335443.2 kcal.mol^{-1}
N_{imag} = 1

C -0.607355 1.326872 -0.916213
O -1.566571 0.884116 1.204278
C 0.695935 0.309712 0.758247
C -0.609245 -0.107909 1.417263
C 0.665584 1.034534 -0.401780
C -1.797933 0.769735 -0.195324
H -0.490865 -0.322654 2.475991
H 1.568764 1.297522 -0.935281
H -2.719427 1.275839 -0.459876
O -1.063336 -1.244416 0.717286
C -1.845498 -0.763840 -0.378961
H -2.866341 -1.123147 -0.269049
H -1.423328 -1.101669 -1.324291
O 1.752566 -0.180388 1.338000
H 2.573130 0.020383 0.858517
H -0.722816 1.529680 -1.973156
O -1.023234 3.208454 -0.513715
H -0.348679 3.795169 -0.886128
H -0.973639 3.313767 0.449098

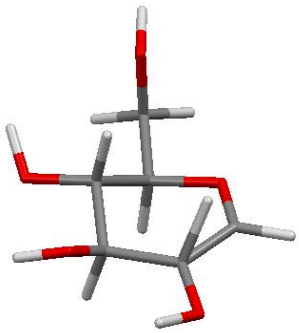
TS6



E = -611.1576129 hartrees
ZPE = 484871.07873 J.mol^{-1}
Enthalpy correction = 17958.34183 J.mol^{-1}
S = 484871.1 J.mol^{-1}.K^{-1}
G = -383393.9 kcal.mol^{-1}
N_{imag} = 1

C	-4.466175	1.907279	-0.032954
C	-3.247556	2.810638	0.113304
O	-2.101119	2.206321	-0.553677
H	-3.407741	3.759664	-0.390859
C	-2.695630	3.008676	1.537580
C	-1.837385	1.028989	-0.181845
C	-2.888832	-0.021572	0.081949
H	-0.820119	0.701951	-0.383396
C	-4.234343	0.526773	0.576047
H	-2.492349	-0.754233	0.783382
O	-2.974340	-0.634717	-1.185964
O	-4.707465	1.654957	-1.401973
H	-5.314734	2.387869	0.459251
O	-4.279227	0.632193	1.983436
H	-5.015438	-0.140987	0.210612
O	-1.949396	1.861191	1.902872
H	-3.517672	3.185792	2.230223
H	-2.020543	3.860133	1.539902
H	-2.545446	1.266254	2.389953
H	-4.934680	2.469973	-1.866255
H	-4.589770	-0.197446	2.364560
H	-3.517349	-0.075155	-1.765055

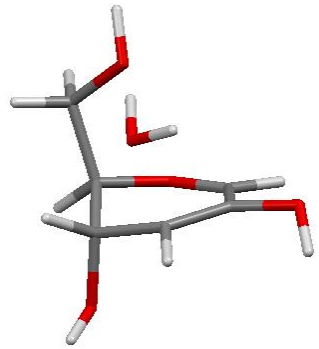
TS7



E = -611.1369508 hartrees
ZPE = 470342.19156 J.mol^{-1}
Enthalpy correction = 21585.10481 J.mol^{-1}
S = 470342.2 J.mol^{-1}.K^{-1}
G = -383385.7 kcal.mol^{-1}
N_{imag} = 1

C	-4.240684	2.043009	0.041994
C	-3.001090	2.761674	-0.490940
O	-1.814855	2.242254	0.182530
H	-2.873568	2.563244	-1.558044
C	-3.032313	4.248749	-0.252714
C	-1.725719	0.948675	0.352641
C	-2.782164	0.053330	0.125693
H	-0.751906	0.573270	0.652613
C	-4.134253	0.564323	-0.293022
H	-2.550200	0.519915	1.349092
O	-2.550978	-1.246796	0.129467
O	-5.400007	2.523914	-0.582420
H	-4.292829	2.161161	1.128255
O	-5.069988	-0.243024	0.364405
H	-4.192596	0.440896	-1.381449
O	-3.420085	4.468202	1.087108
H	-3.745531	4.687405	-0.955539
H	-2.041546	4.659038	-0.462438
H	-3.356459	5.408752	1.283908
H	-5.742781	3.278070	-0.087891
H	-5.933878	-0.139984	-0.054140
H	-3.394824	-1.720666	0.240850

TS8



E = -611.1477751 hartrees
ZPE = 473661.60368 J.mol^{-1}
Enthalpy correction = 22854.82581 J.mol^{-1}
S = 473661.6 J.mol^{-1}.K^{-1}
G = -383392.3 kcal.mol^{-1}
N_{imag} = 1

C 1.520369 -0.811504 0.383981
C -0.006111 1.079812 -0.095508
O -0.350207 -0.434813 1.814767
C -1.003924 0.382775 0.820259
C 0.774479 -1.010895 1.524154
C 1.150560 0.195924 -0.488294
H -0.537571 1.411338 -0.989115
H -1.513700 1.159999 1.388216
H 1.135302 -1.671479 2.305896
H 1.889626 0.637670 -1.144997
O 0.335238 -0.642628 -2.163361
H -0.367301 -1.191435 -1.746889
H 0.985542 -1.250427 -2.540971
O 0.534888 2.170547 0.619784
H 0.877333 2.830202 0.004296
O 2.623631 -1.600403 0.207873
H 3.404654 -1.060403 0.030038
C -2.066576 -0.463929 0.147702
H -2.598703 0.162147 -0.573579
H -2.769050 -0.797705 0.911691
O -1.465023 -1.584725 -0.481407
H -2.135839 -2.253404 -0.661900