α-Hydroxyacids accelerate the Diels-Alder reaction of dibutyl vinylboronate with cyclopentadiene: experimental results and mechanistic insights

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Supporting Information

List of contents:

General experimental procedures

All reagents and solvents were used directly as purchased or purified according to standard procedures. Microwave heating was performed in a CEM Discover® System using septum-sealed 10 mL vials for high-pressure reaction conditions with stirring and IR-monitored temperature control. Analytical thin layer chromatography was carried out using commercial silica gel plates (Merck, Silica Gel 60 F254) and visualization was effected with a *p*-anysaldehyde solution (2.5 mL *p*-anysaldehyde + 2.5 mL H_2SO4 + 0.25 mL AcOH + 95 mL EtOH). Column chromatography was performed with silica gel 60 H (Merck), slurry packed, run under low pressure of nitrogen. The Diels-Alder reactions were monitored using ^{11}B NMR analysis in $CDCl_3$. NMR spectra were recorded at 300 MHz for ^{1}H, 75 MHz for ^{13}C and 96 MHz for ^{11}B on a Bruker Avance-300 DPX spectrometer with $CDCl_3$ as solvent and $(CH_3)_4Si$ (^{1}H) and $CDCl_3$ (^{13}C, 76.9 ppm) as internal standards. ^{11}B NMR spectra were externally referenced to $BF_3 \cdot Et_2O$. Isomeric ratios were determined by ^{1}H NMR integration. Due to the volatility of the 5-norbornen-2-ol (**8**), yields were determined by ^{1}H NMR using α-naphthol as internal standard.

^{11}B NMR spectra

We performed a^{11}B NMR study to compare the spectra of **1** after 2 h of MW irradiation at 70 ºC in DCM (Figure S1, blue spectrum) with the spectrum of a mixture of **1** and **5** (Figure S1, red spectrum) and the spectrum of a mixture of **1**, **2** and **5** both under the same conditions (Figure S1, green spectra). Initialy, we observed that the addition of the α-hydroxyacid gave rise to a new peak at δ = 30.29 ppm, which suggested the formation of a new boron species (Figure S1, red spectrum). When comparing the mixture that also contained the diene, we found the presence of a new peak at a higher chemical shift, δ = 35.81 ppm (Figure S1, green spectrum), which indicated the formation of a new species, probably the product of the Diels-Alder reaction.

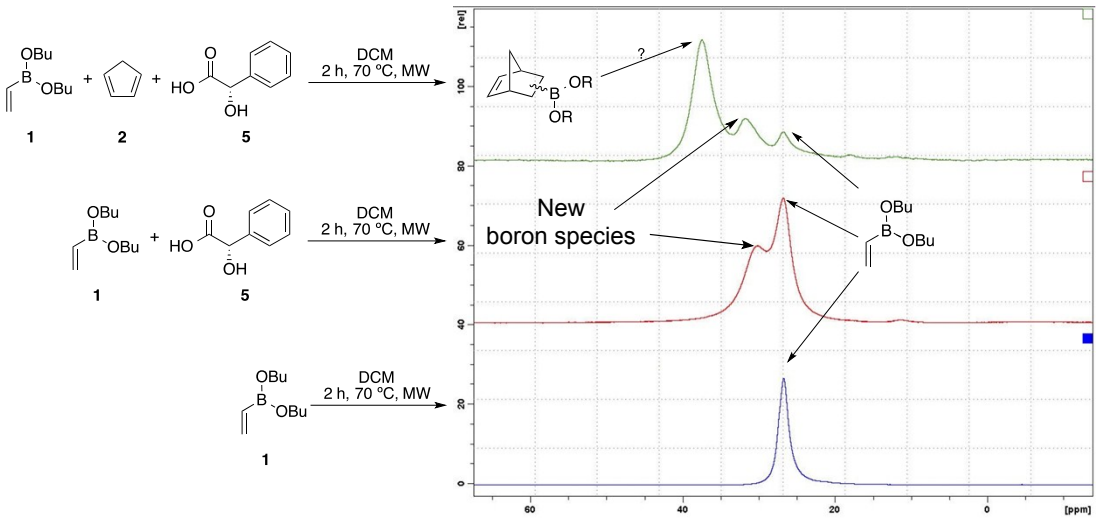

Figure S1. ^{11}B NMR spectra.

Computational methods

Conformational searches for the reactants and the transition structures (TSs) were run to locate the global minima at the B3LYP/6-311++G** level of theory. Initially, a large number of geometries were generated using the conformational search module of Hyperchem with the MM+ method.[1] Selected structures were then successively reoptimized at the RHF/3-21G, B3LYP/6-31G* and B3LYP/6-311++G** levels of theory.[2] Geometries for all structures were fully optimized and normal mode analysis was used to confirm the nature of the stationary points and to evaluate the thermochemical properties. Reported thermochemical properties include zero-point energies (ZPEs) without scaling and were calculated at 1 atm and 298.15 K. The molecular orbitals of the reactants were calculated to analyse the frontier orbital interactions. Intrinsic reaction coordinate (IRCs) calculations were run to verify the connectivity between reactants, TSs and products. To examine the more important interactions in the TSs, we performed natural bond orbital calculations and Wiberg bond indexes (WBIs) were analysed. *Endo/exo* and *Re*/*Si* ratios were computed using Boltzmann factors based on $\Delta G^{\neq}$.

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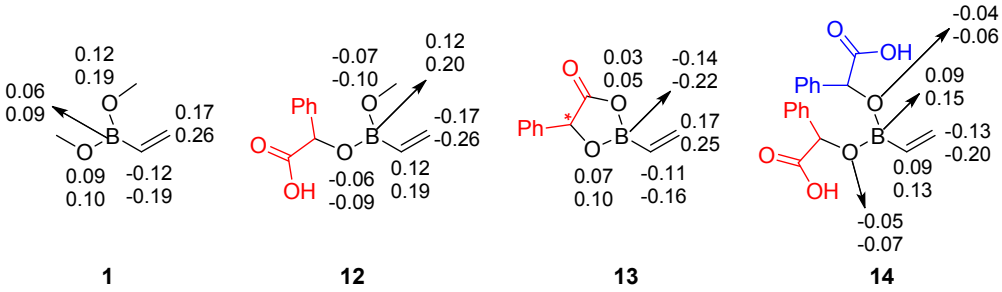
1 Hyperchem Professional Release 7.52, Hypercube, Inc., 2005.

2 Gaussian 09, Revision D.01: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.



1 **12** **13** **14**

Figure S2. Coefficients of FMOs of reactants.

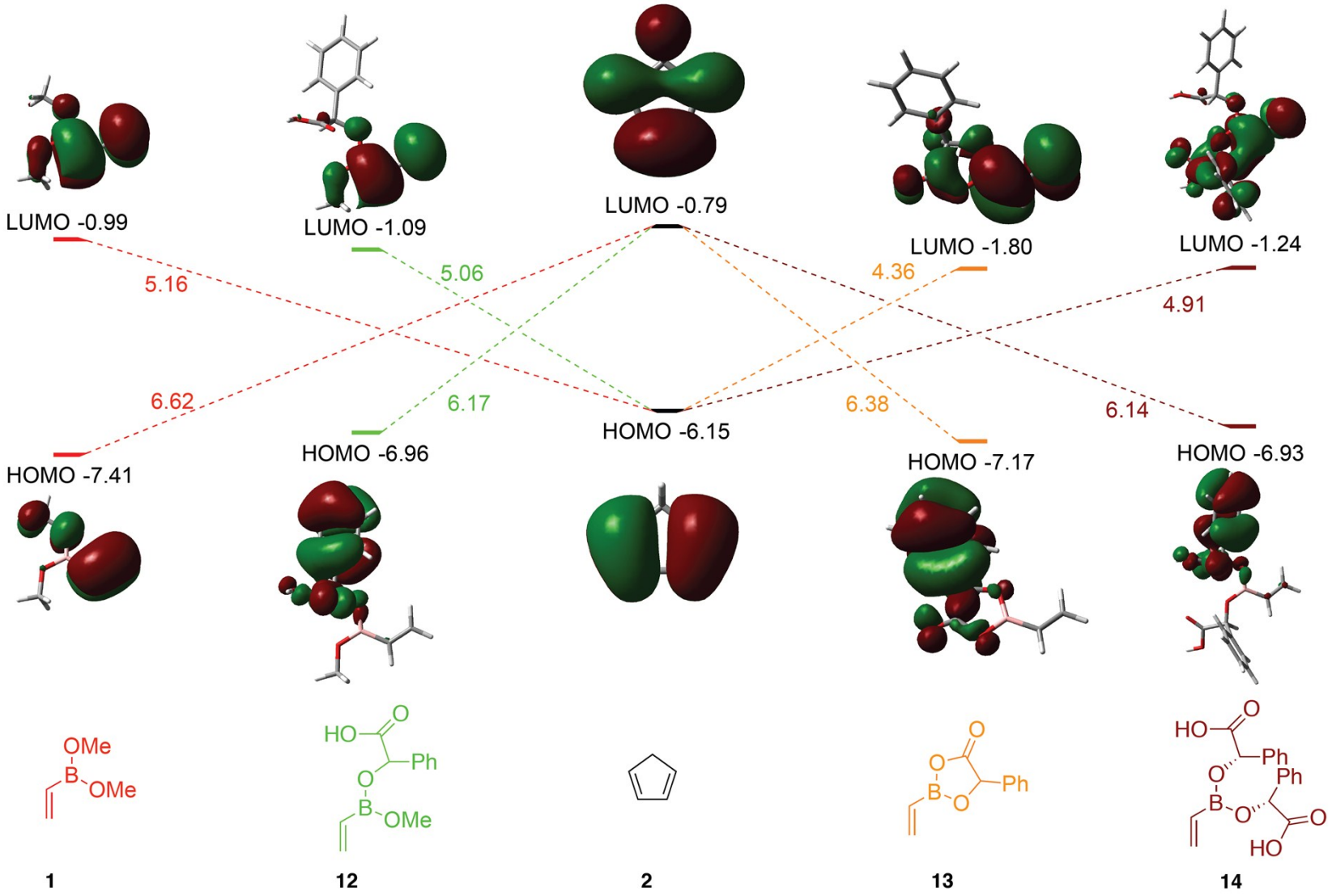


Figure S3. Shapes and energies (in ev) of FMOs of reactants (top: LUMOs, bottom: HOMOs).

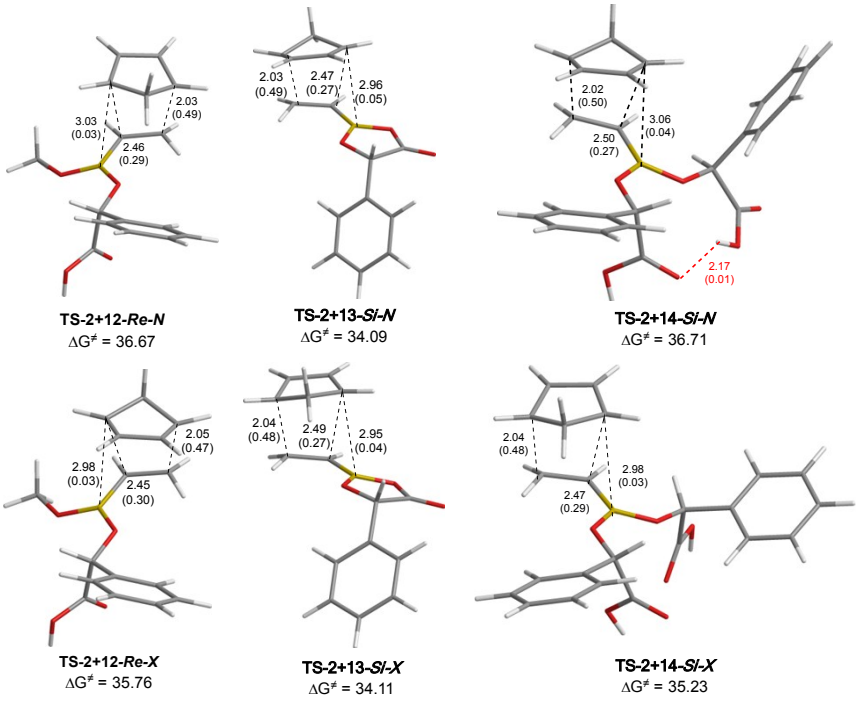
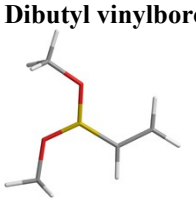


Figure S4. B3LYP/6-311++G** Optimized geometries of selected transition structures of the Diels-Alder reactions of cyclopentadiene (**2**) with **12**, **13** and **14** with interatomic distances in Å and, in parentheses, Wiberg bond indexes. Free activation energies in the gas phase and, in parentheses, relative to the most stable attack, in Kcal/mol.

Reactants

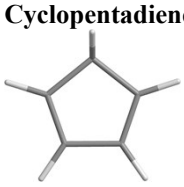
Dibutyl vinylboronate (1)



C	2.484161	-0.788544	-0.000030
C	1.593352	0.209679	0.000027
B	0.048239	-0.029870	0.000000
O	-0.408328	-1.316162	-0.000083
O	-0.885390	0.974572	0.000053
C	-0.550978	2.357689	0.000138
C	-1.803647	-1.610414	-0.000113
H	3.556077	-0.611288	-0.000012
H	2.162291	-1.825304	-0.000098
H	1.983470	1.226264	0.000093
H	-1.486128	2.918763	0.000213
H	0.022309	2.629315	0.891468
H	0.022241	2.629438	-0.891197
H	-2.292299	-1.199790	0.887449
H	-2.292302	-1.199605	-0.887587
H	-1.904441	-2.696185	-0.000226

Energy + ZPE = -333.180105
Free energy = -333.215113
Number of imaginary frequencies = 0

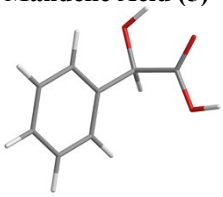
Cyclopentadiene (2)



C	0.734105	0.990239	-0.000022
C	-0.734106	0.990238	-0.000024
C	-1.179407	-0.281699	0.000005
C	1.179407	-0.281698	0.000008
C	0.000000	-1.216057	0.000028
H	1.347623	1.882188	-0.000042
H	-1.347625	1.882187	-0.000045
H	-2.210522	-0.607820	0.000011
H	2.210523	-0.607818	0.000017
H	0.000000	-1.877421	0.877192
H	0.000002	-1.877460	-0.877106

Energy + ZPE = -194.064204
Free energy = -194.090803
Number of imaginary frequencies = 0

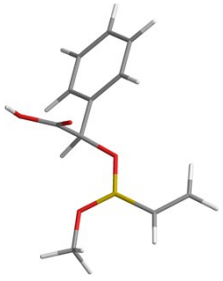
Mandelic Acid (5)



C	-2.318279	-1.038080	-0.752495
C	-3.063165	0.086210	-0.400544
C	-0.983051	-1.144672	-0.367868
C	-2.467775	1.103420	0.344053
C	-0.382125	-0.124760	0.371944
C	-1.133666	0.996610	0.730100
C	1.085204	-0.230928	0.779565
O	1.483270	-1.564458	1.001886
C	1.993562	0.386974	-0.285933
O	2.793035	-0.256055	-0.923128
O	1.820891	1.710275	-0.424669
H	-2.778020	-1.837428	-1.322936
H	-4.102998	0.165711	-0.696962
H	-0.409703	-2.028152	-0.619856
H	-3.043497	1.975981	0.631785
H	-0.675861	1.789460	1.312152
H	1.233280	0.351475	1.697417
H	2.197850	-1.760041	0.378021
H	2.417154	2.016258	-1.125266

Energy + ZPE = -535.36105
Free energy = -535.397692
Number of imaginary frequencies = 0

2-((butoxy(vinyl)boranyl)oxy)-2-phenylacetic acid (12)

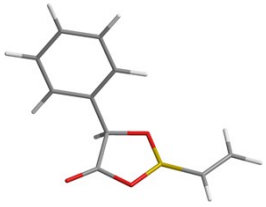


C	3.999777	-1.129943	-0.033602
O	2.613726	-0.800519	-0.027113
O	0.775614	0.641454	0.047776
B	2.140243	0.481988	0.024733
C	3.035267	1.759113	0.024733

C	2.533967	2.999416	0.024733
C	-0.094554	-0.473053	0.082196
C	-0.018699	-1.161389	1.453508
C	-1.519048	-0.015471	-0.184373
C	-2.345259	-0.739885	-1.044652
C	-3.657445	-0.329019	-1.274558
C	-4.151633	0.811370	-0.645058
C	-3.328583	1.538760	0.214974
C	-2.018936	1.127017	0.447371
O	0.414563	-0.677073	2.463883
O	-0.537296	-2.409377	1.386879
H	4.075252	-2.215532	-0.099754
H	4.509300	-0.686816	-0.893906
H	4.487152	-0.796934	0.886805
H	4.119112	1.657211	0.023593
H	3.167468	3.881862	0.023596
H	1.462185	3.170959	0.025417
H	0.196316	-1.217206	-0.663719
H	-1.962917	-1.626894	-1.538582
H	-4.289279	-0.896134	-1.948934
H	-5.170767	1.134382	-0.825754
H	-3.707781	2.428091	0.706009
H	-1.375721	1.693124	1.110362
H	-0.512015	-2.780384	2.281752

Energy + ZPE = -752.822995
Free energy = -752.869815
Number of imaginary frequencies = 0

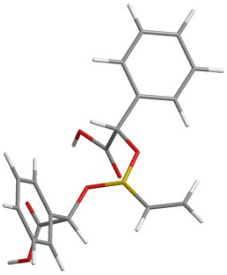
5-phenyl-2-vinyl-1,3,2-dioxaborolan-4-one (13)



C	-1.463102	-1.413259	-3.477971
C	-2.729014	-0.834511	-3.510868
C	-0.623124	-1.207797	-2.383396
C	-3.157178	-0.049115	-2.440529
C	-1.050013	-0.420878	-1.313550
C	-2.324005	0.155601	-1.344763
C	-0.154843	-0.169684	-0.115270
O	1.040134	-0.956283	-0.133741
C	0.355295	1.283112	-0.032116
O	-0.278798	2.288325	0.048152
O	1.726065	1.229818	-0.042935
B	2.120512	-0.113617	-0.091629
C	3.593610	-0.556259	-0.091629
C	3.960666	-1.843353	-0.091629
H	-1.124917	-2.029240	-4.303636
H	-3.380241	-0.995697	-4.362393
H	0.356635	-1.666731	-2.354363
H	-4.141636	0.404461	-2.457760
H	-2.658184	0.774749	-0.519983
H	-0.700301	-0.387193	0.808928
H	4.364852	0.210231	-0.085179
H	5.002663	-2.148272	-0.087026
H	3.224231	-2.641396	-0.093573

Energy + ZPE = -637.100172
Free energy = -637.139956
Number of imaginary frequencies = 0

2,2'-((vinylboranediyl)bis(oxy))bis(2-phenylacetic acid) (14)



O	-1.255771	0.164784	2.029006
O	0.861983	1.098781	2.322992
B	0.089703	-0.032047	2.197845
C	0.637452	-1.490564	2.197845
C	-0.161926	-2.563080	2.197845
C	2.236051	1.103167	2.649645
C	2.487679	2.321722	3.548876
C	3.123458	1.186646	1.414366
C	2.764854	2.014838	0.346969
C	3.584538	2.103372	-0.775284
C	4.769717	1.370906	-0.838723
C	5.131946	0.547123	0.225124
C	4.310972	0.455562	1.347694
O	1.800586	3.302744	3.622080
O	3.632315	2.153183	4.251388
C	-1.832919	1.456232	2.113090
C	-3.297522	1.384621	1.716598
C	-1.697688	2.003789	3.543512
C	-3.855636	2.365466	0.895481
C	-5.205372	2.312272	0.551109
C	-6.006116	1.275280	1.024997
C	-5.451802	0.292283	1.844857
C	-4.104547	0.347139	2.192206
O	-1.435947	1.354229	4.520575

O	-1.934668	3.330627	3.564170
H	1.711396	-1.667099	2.186153
H	0.227207	-3.577138	2.191623
H	-1.242024	-2.457343	2.202166
H	2.507762	0.216946	3.229004
H	1.843245	2.582120	0.397375
H	3.298345	2.745408	-1.600758
H	5.405886	1.440272	-1.713844
H	6.049809	-0.028141	0.180622
H	4.596910	-0.185496	2.174951
H	3.781624	2.962685	4.762973
H	-1.310107	2.156550	1.456888
H	-3.234786	3.173902	0.524227
H	-5.628095	3.077176	-0.090637
H	-7.055197	1.230678	0.754717
H	-6.070159	-0.517952	2.214944
H	-3.670870	-0.417397	2.825379
H	-1.823420	3.632902	4.478047

Energy + ZPE = -1172.463832
Free energy = -1172.522431
Number of imaginary frequencies = 0

Diels-Alder reaction with dibutyl vinylboronate (1)

TS-2+1-*N*

C	2.099344	1.233718	-0.502105
C	1.294263	0.556912	-1.424665
C	1.290380	-0.801635	-1.116336
C	2.573219	0.312422	0.456036
C	2.452372	-1.053081	-0.193463
H	2.208687	2.308519	-0.440123
H	0.684748	1.028643	-2.184061
H	0.808872	-1.572467	-1.703446
H	3.380035	0.549972	1.140381
H	2.351793	-1.897457	0.486348
H	3.351662	-1.216072	-0.808423
C	0.014533	-0.661426	0.979308
C	0.977297	0.071695	1.694384
B	-1.237968	-0.009247	0.358724
O	-2.297270	-0.698623	-0.192831
O	-1.327280	1.361536	0.359550
C	-2.446004	2.030039	-0.212919
C	-2.356662	-2.115731	-0.225172
H	0.054466	-1.742729	1.073820
H	1.553591	-0.435260	2.463490
H	0.764331	1.110119	1.918385
H	-3.380531	1.717579	0.261212
H	-2.301134	3.100050	-0.055634
H	-2.521856	1.830327	-1.286159
H	-2.351686	-2.540114	0.784128
H	-3.289245	-2.395734	-0.717786
H	-1.519947	-2.539922	-0.789916

Energy + ZPE = -527.206835
Free energy = -527.246854
Number of imaginary frequencies = 1 (-466.67)

TS-2+1-*X*

C	-2.308812	1.161934	-0.687720
C	-3.060907	0.330617	0.150358
C	-2.413335	-0.918292	0.254032
C	-1.219600	0.444540	-1.183609
C	-1.495706	-1.013684	-0.947086
H	-2.486422	2.218560	-0.844309
H	-3.911566	0.643775	0.742490
H	-2.889444	-1.792071	0.684300
H	-0.515357	0.812466	-1.918524
H	-0.619394	-1.646843	-0.828857
H	-2.089324	-1.391883	-1.794869
C	-0.890568	-0.525810	1.583446
C	-0.036495	0.388261	0.945056
B	1.314826	-0.001801	0.308134
O	2.281995	0.897856	-0.083403
O	1.600759	-1.333409	0.112040
C	2.137770	2.301695	0.074039
C	2.842647	-1.747658	-0.450783
H	-1.508073	-0.189004	2.408180
H	-0.558145	-1.555319	1.672854
H	-0.222879	1.438826	1.143210
H	3.033735	2.771857	-0.334251
H	1.263841	2.677792	-0.467665
H	2.045042	2.577668	1.129211
H	2.980815	-1.337964	-1.455466
H	3.683188	-1.426733	0.170611
H	2.827848	-2.837313	-0.503080

Energy + ZPE = -527.207892
Free energy = -527.247557
Number of imaginary frequencies = 1 (-468.14)

Diels-Alder reaction with 2-((butoxy(vinyl)boranyl)oxy)-2-phenylacetic acid (12)

TS-2+12-*Re-N*

C	-2.112776	-2.468852	-0.224415
C	-2.143251	-1.579237	-1.303230
C	-3.257854	-0.752478	-1.180948
C	-3.186650	-2.175794	0.643208
C	-4.187869	-1.399684	-0.190850
H	-1.308746	-3.160499	-0.009995
H	-1.365979	-1.478604	-2.049003
H	-3.570671	-0.016152	-1.909546
H	-3.500980	-2.854773	1.427905
H	-4.847888	-0.729460	0.357031
H	-4.813526	-2.127009	-0.732013
C	-2.510908	0.524185	0.780554
C	-2.515114	-0.558190	1.678042
B	-1.228002	1.069866	0.132215
O	-0.055479	0.352178	0.287155
O	-1.135186	2.221691	-0.615524
C	1.158154	0.806320	-0.272856
C	1.671531	2.038657	0.487681
C	2.197982	-0.300579	-0.200411
O	1.360817	2.362965	1.601888
C	3.002710	-0.592022	-1.302693
C	3.964708	-1.598870	-1.228226
C	4.127732	-2.321672	-0.048467
C	3.325572	-2.033390	1.056204
C	2.366495	-1.026734	0.982546
O	2.570643	2.719603	-0.262201
C	-2.233832	3.098889	-0.818063
H	-3.414321	1.125147	0.734621
H	-3.302664	-0.610383	2.424566
H	-1.562351	-0.942949	2.021223
H	1.022286	1.110868	-1.313987
H	2.878265	-0.030931	-2.222928
H	4.581796	-1.819834	-2.092013
H	4.873703	-3.106410	0.010409
H	3.448994	-2.592908	1.976927
H	1.738988	-0.802543	1.836771
H	2.899950	3.452101	0.280028
H	-3.072343	2.585526	-1.299368
H	-1.894909	3.905992	-1.469021
H	-2.575746	3.528704	0.128340

Energy + ZPE = -946.850511
Free energy = -946.902176
Number of imaginary frequencies = 1 (-462.58)

TS-2+12-*Re-X*

C	-4.329787	-0.912740	-0.900264
C	-4.431474	-1.752890	0.215050
C	-2.987226	-0.789092	-1.257018
C	-3.134112	-2.119428	0.630147
C	-2.233665	-1.890085	-0.565867
H	-5.150312	-0.368426	-1.350730
H	-5.343409	-1.960736	0.760413
H	-2.620791	-0.261933	-2.128358
H	-2.949985	-2.915287	1.342846
H	-1.188318	-1.685569	-0.347342
H	-2.285115	-2.789019	-1.201071
C	-2.410955	0.581986	0.694633
C	-2.495249	-0.450596	1.642451
B	-1.091247	1.083748	0.083612
O	0.057345	0.325219	0.243642
O	-0.946141	2.242134	-0.643744
C	1.300978	0.767975	-0.260311
C	1.832088	1.935931	0.584589
C	2.300214	-0.377318	-0.231952
O	1.485901	2.216941	1.700072
C	2.417942	-1.177687	0.908503
C	3.117959	-0.631762	-1.333913
C	3.339826	-2.220736	0.940371
C	4.042897	-1.674669	-1.300918
C	4.155209	-2.471460	-0.163665
O	2.788149	2.615269	-0.092083
C	-2.015599	3.151059	-0.869105
H	-3.289552	1.209726	0.586788
H	-3.285705	-0.425609	2.383519
H	-1.569198	-0.887772	2.002262
H	1.200622	1.138257	-1.283740
H	1.780804	-0.982416	1.762815
H	3.032553	-0.013189	-2.221128
H	3.423603	-2.838150	1.827909
H	4.670547	-1.865913	-2.164158
H	4.871917	-3.284684	-0.137560
H	3.122731	3.306238	0.499263
H	-1.630738	3.963484	-1.486897
H	-2.384928	3.567151	0.072821
H	-2.844801	2.667665	-1.395190

Energy + ZPE = -946.851493
Free energy = -946.903632
Number of imaginary frequencies = 1 (-463.40)

TS-2+12-*Si-N*

C	-2.282906	-0.901769	1.523880
C	-2.229306	-2.174373	0.943527

C	-3.340231	-0.194444	0.957320
C	-3.213918	-2.268637	-0.062564
C	-4.227856	-1.186993	0.256674
H	-1.547692	-0.488151	2.199815
H	-1.457885	-2.911336	1.127100
H	-3.658932	0.794628	1.258658
H	-3.507605	-3.215547	-0.501925
H	-4.936319	-1.596562	0.993876
H	-4.802839	-0.806040	-0.585738
C	-2.378823	0.089659	-1.295034
C	-2.360013	-1.278043	-1.621528
B	-1.134651	0.875274	-0.853693
O	0.029355	0.183154	-0.561084
O	-1.050681	2.246818	-0.760480
C	1.217296	0.867889	-0.226774
C	1.126378	1.469525	1.183939
C	2.398072	-0.090127	-0.282187
O	0.404906	1.097454	2.071613
C	3.632274	0.337840	-0.774958
C	2.262735	-1.401324	0.181839
C	4.720451	-0.532810	-0.804395
C	3.349397	-2.271776	0.149317
C	4.581310	-1.839822	-0.341807
C	-2.141405	3.109466	-1.049459
O	2.013253	2.481031	1.328266
H	-3.258867	0.649455	-1.598502
H	-1.401884	-1.782625	-1.662072
H	-3.078934	-1.648389	-2.347027
H	1.392668	1.700427	-0.912804
H	3.743933	1.354212	-1.137414
H	1.301828	-1.733662	0.554387
H	5.673118	-0.191537	-1.193881
H	3.234999	-3.288953	0.507527
H	5.425915	-2.519289	-0.367669
H	-2.472375	2.999091	-2.086777
H	-1.799797	4.134028	-0.895809
H	-2.988360	2.916653	-0.383625
H	1.956881	2.784009	2.247088

Energy + ZPE = -946.851302
Free energy = -946.902584
Number of imaginary frequencies = 1 (-463.69)

TS-2+12-*Si-X*

C	-4.388969	-1.740854	0.183914
C	-4.372131	-0.435209	0.688902
C	-3.067471	-0.103988	1.053762
C	-3.066320	-2.233141	0.145942
C	-2.278192	-1.378297	1.116937
H	-5.250988	-2.233266	-0.248492
H	-5.218496	0.240078	0.705300
H	-2.759822	0.810968	1.541766
H	-2.839434	-3.281677	-0.012020
H	-2.405355	-1.805512	2.124421
H	-1.213930	-1.276043	0.924342
C	-2.277163	0.033029	-1.280986
C	-2.300633	-1.350311	-1.528158
B	-1.014554	0.820921	-0.901318
O	0.145099	0.130699	-0.578647
O	-0.915437	2.193713	-0.877725
C	1.313219	0.821082	-0.188983
C	1.148377	1.377063	1.233738
C	2.510825	-0.115088	-0.237351
C	2.404871	-1.423920	0.241319
C	3.507674	-2.273738	0.210898
C	4.727688	-1.823357	-0.293248
C	4.838254	-0.519032	-0.770439
C	3.733460	0.330524	-0.742665
O	0.333849	1.016869	2.042379
C	-2.007096	3.049886	-1.185924
O	2.070058	2.334110	1.485142
H	-3.147746	0.595224	-1.603223
H	-1.355475	-1.884472	-1.513833
H	-3.015197	-1.746741	-2.240477
H	1.496565	1.677941	-0.842214
H	1.455353	-1.775070	0.626084
H	3.414997	-3.288839	0.580903
H	5.585068	-2.486641	-0.317550
H	5.781494	-0.163327	-1.169766
H	3.822920	1.344876	-1.116673
H	-1.667248	4.077356	-1.049080
H	-2.856047	2.865110	-0.520702
H	-2.332584	2.919995	-2.222569
H	1.951776	2.614412	2.405224

Energy + ZPE = -946.852384
Free energy = -946.903927
Number of imaginary frequencies = 1 (-456.27)

Diels-Alder reaction with 5-phenyl-2-vinyl-1,3,2-dioxaborolan-4-one (13)

TS-2+13-*Re-N*

C	-4.100591	1.063236	-0.319205
C	-3.342478	1.064516	0.856878

C	-3.298097	-0.229487	1.370455
C	-4.498111	-0.259972	-0.610939
C	-4.389357	-1.016682	0.699366
H	-4.230863	1.912244	-0.977498
H	-2.795947	1.914381	1.244024
H	-2.820215	-0.523332	2.295414
H	-5.272450	-0.482956	-1.336249
H	-4.230263	-2.090416	0.622725
H	-5.322296	-0.850534	1.260662
C	-1.916995	-1.269710	-0.410086
C	-2.840296	-1.052130	-1.450185
B	-0.731545	-0.372454	-0.132448
O	0.287312	-0.633526	0.762619
O	-0.512983	0.862149	-0.788604
C	1.224540	0.440496	0.721825
C	0.627785	1.425173	-0.304170
C	2.631562	-0.010407	0.372351
O	1.043581	2.498770	-0.624199
C	3.671299	0.925716	0.366436
C	2.903813	-1.343291	0.063100
C	4.966715	0.530097	0.046399
C	5.237510	-0.802488	-0.265244
C	4.204358	-1.735826	-0.254505
H	-1.943080	-2.227306	0.100924
H	-3.358218	-1.912323	-1.864403
H	-2.618081	-0.287621	-2.185313
H	1.231416	0.940185	1.697289
H	3.463491	1.964532	0.595644
H	2.101142	-2.068985	0.080428
H	5.765200	1.263485	0.039718
H	6.247486	-1.109444	-0.512578
H	4.407195	-2.774246	-0.491918

Energy + ZPE = -831.131199
Free energy = -831.176659
Number of imaginary frequencies = 1 (-452.54)

TS-2+13-*Re-X*

C	-4.259946	-0.860976	1.260371
C	-4.980001	-0.815394	0.060500
C	-3.289575	0.138265	1.246391
C	-4.416073	0.171246	-0.776028
C	-3.634746	1.092000	0.139275
H	-4.375171	-1.609813	2.033334
H	-5.746739	-1.519942	-0.235764
H	-2.628560	0.373700	2.069987
H	-4.916284	0.537481	-1.665304
H	-2.802268	1.625935	-0.313510
H	-4.339242	1.837536	0.540726
C	-1.915746	-1.032406	-0.460188
C	-2.780231	-0.772355	-1.538634
B	-0.688969	-0.209697	-0.132805
O	0.309675	-0.571560	0.748916
O	-0.405097	1.052218	-0.711215
C	1.305494	0.449474	0.768009
C	0.764743	1.524291	-0.195537
C	2.684883	-0.057135	0.385424
O	1.236276	2.591181	-0.452761
C	2.882911	-1.382258	-0.003297
C	3.774448	0.819380	0.429917
C	5.045536	0.373255	0.080316
C	5.242224	-0.951287	-0.310975
C	4.159437	-1.825681	-0.350142
H	-1.998912	-1.995777	0.032069
H	-3.291437	-1.602960	-2.011215
H	-2.512644	0.021703	-2.229266
H	1.341393	0.888762	1.771381
H	2.042119	-2.063340	-0.024719
H	3.624859	1.852453	0.721904
H	5.883039	1.060983	0.113264
H	6.233359	-1.297752	-0.581185
H	4.304349	-2.857711	-0.649609

Energy + ZPE = -831.131383
Free energy = -831.176881
Number of imaginary frequencies = 1 (-448.71)

TS-2+13-*Si-N*

C	3.342478	1.064516	0.856878
C	4.100591	1.063236	-0.319205
C	3.298097	-0.229487	1.370455
C	4.498111	-0.259972	-0.610939
C	4.389357	-1.016682	0.699366
H	2.795946	1.914381	1.244024
H	4.230863	1.912244	-0.977498
H	2.820215	-0.523332	2.295414
H	5.272450	-0.482956	-1.336249
H	5.322296	-0.850534	1.260662
H	4.230263	-2.090416	0.622726
C	1.916995	-1.269710	-0.410086
C	2.840296	-1.052130	-1.450185
B	0.731545	-0.372454	-0.132448
O	-0.287312	-0.633526	0.762619
O	0.512983	0.862149	-0.788604
C	-1.224540	0.440496	0.721825
C	-0.627785	1.425173	-0.304170

C	-2.631562	-0.010407	0.372351
O	-1.043581	2.498770	-0.624199
C	-3.671299	0.925716	0.366436
C	-2.903813	-1.343291	0.063100
C	-4.966715	0.530097	0.046399
C	-4.204358	-1.735826	-0.254505
C	-5.237510	-0.802488	-0.265244
H	1.943080	-2.227306	0.100924
H	2.618081	-0.287621	-2.185313
H	3.358218	-1.912323	-1.864403
H	-1.231416	0.940185	1.697289
H	-3.463491	1.964532	0.595645
H	-2.101142	-2.068985	0.080428
H	-5.765200	1.263485	0.039718
H	-4.407195	-2.774246	-0.491918
H	-6.247486	-1.109444	-0.512578

Energy + ZPE = -831.131016
Free energy = -831.176428
Number of imaginary frequencies = 1 (-449.76)

TS-2+13-*Si-X*

C	-4.933062	-0.634227	-0.077159
C	-4.568540	0.717537	-0.052375
C	-3.374113	0.854070	0.650776
C	-3.920033	-1.394429	0.544414
C	-3.144314	-0.421057	1.409500
H	-5.778446	-1.044030	-0.615086
H	-5.081038	1.515303	-0.574197
H	-2.891562	1.795451	0.877901
H	-4.061059	-2.429954	0.832522
H	-3.668404	-0.342981	2.375103
H	-2.105856	-0.677732	1.608409
C	-2.033413	-0.221068	-1.146446
C	-2.497471	-1.526525	-0.912771
B	-0.747934	0.346682	-0.584431
O	0.063864	-0.252453	0.361895
O	-0.209837	1.592107	-0.981297
C	1.185529	0.594465	0.612670
C	0.940089	1.821207	-0.289569
C	2.515684	-0.086860	0.349571
O	1.598514	2.814117	-0.374479
C	3.702467	0.579525	0.672787
C	4.932397	-0.026730	0.434399
C	4.989557	-1.304082	-0.123513
C	3.808923	-1.969802	-0.441998
C	2.574089	-1.364268	-0.208033
H	-2.511251	0.351078	-1.934535
H	-1.854463	-2.210548	-0.366808
H	-3.101715	-2.012108	-1.670156
H	1.147039	0.933672	1.653884
H	3.663725	1.576828	1.095852
H	5.846910	0.499084	0.684629
H	5.948359	-1.776072	-0.305982
H	3.844505	-2.964218	-0.872848
H	1.655869	-1.883892	-0.449014

Energy + ZPE = -831.131123
Free energy = -831.176404
Number of imaginary frequencies = 1 (-448.33)

Diels-Alder with 2,2'-((vinylboranediyl)bis(oxy))bis(2-phenylacetic acid) (14)

TS-2+14-*Re-N*

C	0.055863	3.491270	0.582175
C	1.725068	4.109128	-0.908903
C	2.295705	3.426767	0.184100
C	1.277348	3.016657	1.056325
C	0.350035	4.554680	-0.437337
H	-0.896902	3.386016	1.081238
H	2.322614	4.701371	-1.594367
H	3.337057	3.141223	0.259943
H	1.401281	2.349989	1.896925
H	0.485862	5.507114	0.098751
H	-0.405188	4.700794	-1.214378
O	1.256273	0.092189	-0.553401
O	-1.049002	-0.026847	-0.184163
B	0.019303	0.695070	-0.703418
C	-0.072180	2.042585	-1.426690
C	1.037037	2.606235	-2.081201
C	-2.406200	0.389060	-0.214696
C	-2.801571	1.096114	1.107874
C	-3.321422	-0.802358	-0.455110
C	-4.594730	-0.595997	-0.992113
C	-5.461264	-1.669455	-1.182160
C	-5.063358	-2.960620	-0.838625
C	-3.794619	-3.170703	-0.302548
C	-2.927478	-2.096638	-0.108548
O	-3.820946	1.726489	1.196687
O	-1.958384	0.958355	2.141675
C	1.422331	-1.210589	-0.034903
C	2.866837	-1.649401	-0.219449
C	1.033931	-1.287131	1.448668
C	3.162677	-2.896399	-0.769818

C	4.487391	-3.306037	-0.915223
C	5.524545	-2.468614	-0.511124
C	5.232889	-1.218867	0.036116
C	3.910075	-0.810583	0.182878
O	0.760091	-0.355629	2.164680
O	1.016569	-2.563623	1.874995
H	-1.052066	2.467350	-1.650275
H	0.838514	3.259349	-2.930507
H	1.947725	2.031514	-2.196218
H	-2.574300	1.126029	-1.001922
H	-4.911169	0.406926	-1.255162
H	-6.445620	-1.497101	-1.602498
H	-5.736551	-3.796810	-0.990018
H	-3.477254	-4.172181	-0.033808
H	-1.939797	-2.264809	0.301505
H	-1.151379	0.478293	1.879720
H	0.765750	-1.918246	-0.551941
H	2.357301	-3.549749	-1.088290
H	4.707180	-4.275037	-1.348894
H	6.555168	-2.784799	-0.626037
H	6.037226	-0.562208	0.348353
H	3.681832	0.164769	0.596033
H	0.785931	-2.557223	2.817003

Energy + ZPE = -1366.494766
Free energy = -1366.556178
Number of imaginary frequencies = 1 (-446.88)

TS-2+14-*Re-X*

C	1.730753	4.098265	-0.782908
C	0.268299	3.330822	0.844282
C	-0.247008	4.503216	0.299328
C	0.657603	5.005568	-0.644759
C	1.719874	3.253945	0.476122
H	2.654271	4.364625	-1.285029
H	-0.188474	2.758742	1.639916
H	-1.226958	4.910999	0.511307
H	0.488589	5.870388	-1.274074
H	2.294993	3.792648	1.245872
H	2.128386	2.250827	0.384110
O	-1.005690	-0.135403	-0.222576
O	1.305703	0.088389	-0.505851
B	0.050845	0.656733	-0.660039
C	-0.077794	2.038732	-1.300392
C	0.966792	2.674944	-1.997188
C	1.497095	-1.230121	-0.042658
C	1.059819	-1.373646	1.422058
C	2.959314	-1.619083	-0.196691
C	3.966157	-0.767879	0.267626
C	5.304565	-1.127214	0.134132
C	5.648966	-2.340888	-0.461110
C	4.648550	-3.192013	-0.924854
C	3.308474	-2.830965	-0.793148
O	0.733257	-0.473046	2.156822
O	1.071682	-2.663456	1.804616
C	-2.367438	0.259868	-0.251480
C	-3.272373	-0.948400	-0.461146
C	-2.758486	0.989689	1.055746
C	-4.609762	-0.747453	-0.818996
C	-5.459354	-1.834299	-1.003499
C	-4.983564	-3.134631	-0.835505
C	-3.653061	-3.338608	-0.479575
C	-2.800442	-2.250749	-0.290919
O	-3.751962	1.662742	1.124902
O	-1.943638	0.819018	2.107087
H	-1.068766	2.458823	-1.434410
H	0.721145	3.318101	-2.834355
H	1.892978	2.124057	-2.130994
H	0.881232	-1.933507	-0.612886
H	3.700895	0.178574	0.723865
H	6.079554	-0.460167	0.494692
H	6.691611	-2.618956	-0.565513
H	4.908994	-4.134003	-1.394025
H	2.532515	-3.495063	-1.158857
H	0.804409	-2.698615	2.736244
H	-2.545543	0.976919	-1.055489
H	-4.986997	0.261463	-0.939281
H	-6.493619	-1.665104	-1.281224
H	-5.645256	-3.980714	-0.982777
H	-3.273812	-4.345938	-0.347380
H	-1.766315	-2.415103	-0.018757
H	-1.154745	0.296791	1.872435

Energy + ZPE = -1366.494963
Free energy = -1366.557227
Number of imaginary frequencies = 1 (-446.02)

TS-2+14-*Si-N*

C	1.331767	2.893043	0.505699
C	-0.105237	4.354672	-0.589273
C	-0.729480	3.861049	0.568435
C	0.129573	2.942327	1.196932
C	1.371457	4.087338	-0.410298
H	2.198467	2.307751	0.782398
H	-0.467499	5.228151	-1.117619
H	-1.759451	4.042070	0.847167

H	-0.142903	2.303897	2.027042
H	1.792676	4.929235	0.161801
H	1.958679	3.969383	-1.320650
O	0.796787	-0.561322	-0.608008
O	-1.342011	0.368567	-0.583374
B	-0.012188	0.524205	-0.931281
C	0.429603	1.811662	-1.627874
C	-0.454228	2.854962	-1.929567
C	-1.777268	-0.796779	0.093754
C	-1.598765	-2.052829	-0.770857
C	-3.233460	-0.662960	0.509906
C	-4.107103	0.174619	-0.186093
C	-5.443534	0.264318	0.198755
C	-5.918549	-0.486199	1.273026
C	-5.049535	-1.327250	1.966440
C	-3.711992	-1.414093	1.587183
O	-1.191574	-3.107891	-0.343941
O	-1.954169	-1.862248	-2.051562
C	2.191898	-0.634232	-0.848559
C	2.988224	-0.642275	0.452250
C	2.502194	-1.914682	-1.655410
C	2.369001	-0.836268	1.687834
C	3.127803	-0.860315	2.858131
C	4.508957	-0.690985	2.802959
C	5.131422	-0.498959	1.569501
C	4.376556	-0.475720	0.400199
O	3.421031	-1.968171	-2.427359
O	1.705718	-2.971657	-1.429681
H	1.415651	1.866933	-2.069193
H	-0.239987	3.503437	-2.774544
H	-1.511108	2.689705	-1.760184
H	-3.733639	0.755389	-1.019433
H	-6.115373	0.920250	-0.343604
H	-6.958937	-0.415223	1.569491
H	-5.410429	-1.912000	2.804942
H	-3.038605	-2.069093	2.130354
H	-1.827718	-2.702501	-2.519181
H	1.295599	-0.966486	1.733905
H	2.636447	-1.012300	3.812668
H	5.097493	-0.708864	3.713147
H	6.206165	-0.366689	1.517327
H	4.865817	-0.337356	-0.557631
H	0.969139	-2.746397	-0.837672
H	-1.163712	-0.974645	0.980022
H	2.532087	0.193448	-1.471202

Energy + ZPE = -1366.492148
Free energy = -1366.554728
Number of imaginary frequencies = 1 (-451.84)

TS-2+14-*Si-X*

C	1.314180	4.349233	-0.379643
C	-0.251787	3.071036	-1.506261
C	-0.835271	4.289182	-1.159371
C	0.119281	5.087651	-0.518633
C	1.237265	3.238335	-1.406821
H	2.255979	4.809739	-0.103450
H	-0.735480	2.288245	-2.076009
H	-1.881530	4.539835	-1.281159
H	-0.073072	6.053854	-0.069567
H	1.599064	3.643484	-2.365304
H	1.803263	2.337696	-1.181469
O	-0.898601	-0.120469	0.211336
O	1.384092	0.352755	0.189729
B	0.101512	0.815356	0.412449
C	-0.116145	2.277093	0.828246
C	0.919502	3.142264	1.219984
C	1.627039	-1.004085	-0.155396
C	1.072655	-1.984096	0.891955
C	3.118262	-1.233001	-0.335294
C	4.049473	-0.546742	0.448227
C	5.412020	-0.789383	0.289455
C	5.855921	-1.724065	-0.645501
C	4.929677	-2.414194	-1.425131
C	3.566690	-2.167948	-1.271374
O	0.634131	-3.072117	0.612060
O	1.159311	-1.505386	2.142309
C	-2.264321	0.086615	0.486081
C	-3.118610	-0.801875	-0.408228
C	-2.553539	-0.247888	1.958746
C	-4.326566	-0.325356	-0.921695
C	-5.121410	-1.141791	-1.724239
C	-4.711022	-2.440454	-2.019277
C	-3.504754	-2.918343	-1.507960
C	-2.709599	-2.106315	-0.702090
O	-1.883866	-0.946773	2.671329
O	-3.703322	0.340737	2.361024
H	-1.124356	2.605241	1.059812
H	0.709516	3.922674	1.942133
H	1.921471	2.732193	1.297167
H	3.701157	0.177826	1.173341
H	6.128539	-0.249746	0.898946
H	6.916958	-1.911446	-0.766919
H	5.266525	-3.140259	-2.156541
H	2.847829	-2.706792	-1.879474
H	0.669472	-2.107490	2.723270
H	-4.648789	0.685495	-0.694539

H	-6.055557	-0.761403	-2.122105
H	-5.326314	-3.075764	-2.646563
H	-3.179670	-3.927429	-1.735045
H	-1.771104	-2.480432	-0.310614
H	-3.874903	0.053542	3.270837
H	1.106903	-1.260348	-1.081380
H	-2.551073	1.129299	0.325414

Energy + ZPE = -1366.493656
Free energy = -1366.557092
Number of imaginary frequencies = 1 (-456.50)