Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Theoretical investigation of the Diels-Alder reactions of unsaturated boronates

Nicolás Grimblat and Silvina C. Pellegrinet*

Instituto de Química Rosario (CONICET), Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531. Rosario (2000), Argentina

Supporting Information

List of contents:

Computational methods

Conformational searches for the reactants, the transition structures (TSs) and the products were run to locate the global minima at the B3LYP/6-31G* 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/AM1, RHF/3-21G and B3LYP/6-31G* 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 (C1-C6, C2-C3 and C6-B) we performed natural bond orbital calculations and Wiberg bond indexes (WBIs) were analysed. Free energies in solution were computed on the structures optimized in the gas phase at the B3LYP/6-31G* level of theory with the polarisable continuum model (PCM) using toluene and dichloromethane as solvents (ε_{DCM}= 8.93, $\varepsilon_{Toluene}$= 2.38).[3] All the calculations were run with Gaussian 03.[4]

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

2 In the case of vinylboronate **5**, we observed that the optimizations with the semiempirical method AM1 generated flat geometries for the borolane ring. Therefore, for these systems optimizations at this level of theory were avoided.

3 (a) Miertš, S.; Scrocco, E.; Tomasi, *J. Chem. Phys.* 1981, **55**, 117-129. (b) B. Mennucci and J. Tomasi, *J. Chem. Phys.* 1997, **106**, 5151-5158. (c) J. Tomasi, B., Mennucci and R. Cammi, *Chem. Rev.* 2005, **105**, 2999-3094.

4 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr., Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y. Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

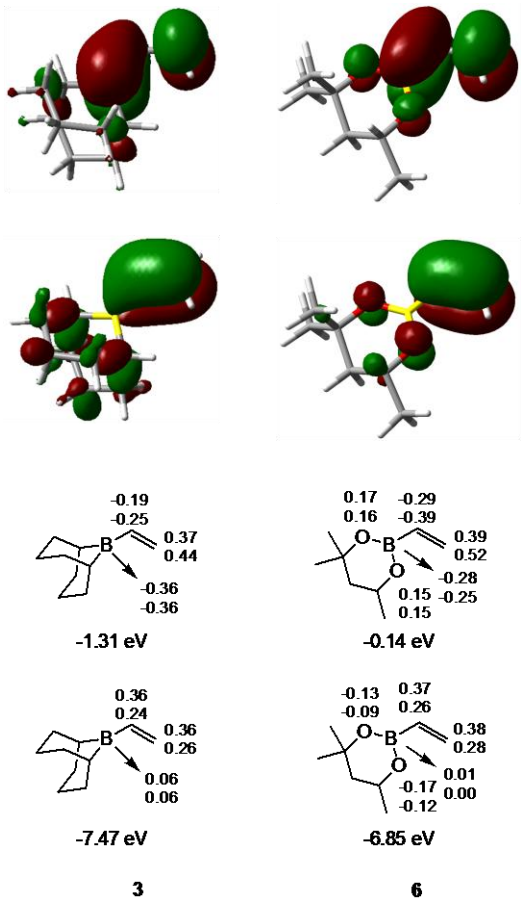

Figure S1. FMO shapes, energies and coefficients of dienophiles **3** and **6** (top: LUMOs, bottom: HOMOs).

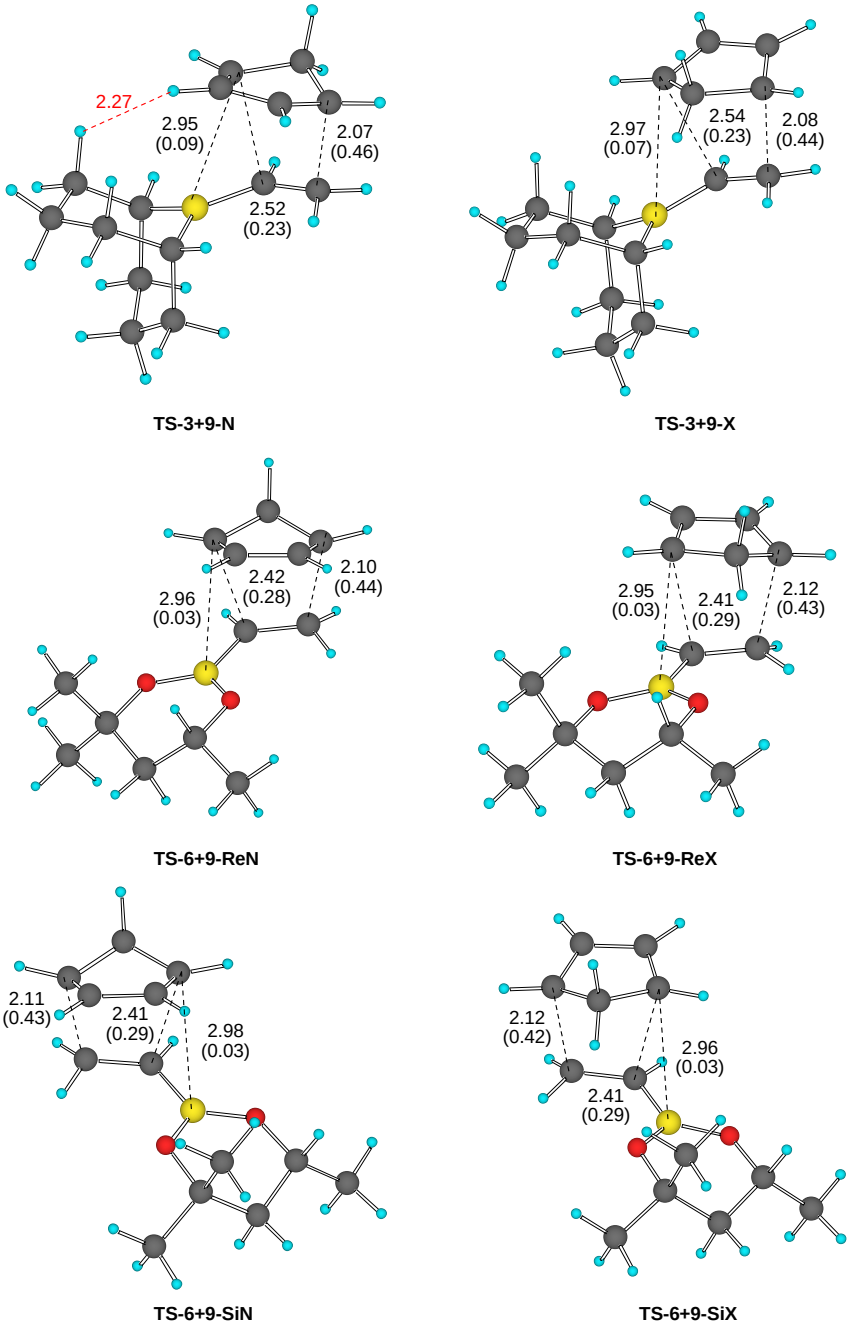

Figure S2. B3LYP/6-31G* optimized geometries for the transition structures of the Diels-Alder reaction of dienophiles **3** and **6** with cyclopentadiene (**9**) with selected distances in Å and Wiberg bond indexes in parentheses.

Calculations in the gas phase

Dienophiles

Dichlorovinylborane (1)
B3LYP/6-31G* Geometry

C	0	-0.945970	-1.696989	0.000035
C	0	-0.964730	-0.353439	-0.000061
B	0	0.299728	0.526306	-0.000012
Cl	0	1.931975	-0.160505	0.000181
Cl	0	0.143711	2.288487	-0.000151
H	0	-1.859171	-2.288487	-0.000004
H	0	-0.012255	-2.254198	0.000155
H	0	-1.931975	0.149199	-0.000181

B3LYP/6-31G* Energy + ZPE = -1023.283218
B3LYP/6-31G* Free energy = -1023.313692
B3LYP/6-31G* Free energy in DCM = -1023.330142
B3LYP/6-31G* Free energy in Tol = -1023.328706
Number of imaginary frequencies = 0

Dimethylvinylborane (2)
B3LYP/6-31G* Geometry

C	0	-0.766204	-1.962554	-0.103560
C	0	-1.026683	-0.644830	-0.122725
B	0	0.059994	0.478804	-0.076319
C	0	1.607808	0.167763	-0.014308
C	0	-0.425127	1.984914	-0.072027
H	0	-1.548491	-2.719987	-0.141047
H	0	0.251532	-2.344200	-0.050007
H	0	-2.080528	-0.356609	-0.178834
H	0	2.080528	0.541932	-0.935929
H	0	2.080370	0.738562	0.798151
H	0	1.892560	-0.883476	0.099151
H	0	-0.808995	2.216864	0.935929
H	0	0.358118	2.719987	-0.289511
H	0	-1.270355	2.159781	-0.751344

B3LYP/6-31G* Energy + ZPE = -182.569104
B3LYP/6-31G* Free energy = -182.600715
B3LYP/6-31G* Free energy in DCM = -182.680994
B3LYP/6-31G* Free energy in Tol = -182.680319
Number of imaginary frequencies = 0

Vinyl-9-BBN (3)
B3LYP/6-31G* Geometry

C	0	-1.001434	-2.358410	0.000090
C	0	0.077483	-1.556813	0.000028
B	0	0.011668	-0.001384	0.000020
C	0	1.295299	0.918483	-0.000048
C	0	1.274479	1.761597	1.310284
C	0	-0.036655	2.531531	1.575715
C	0	-1.315818	1.709644	1.310991
C	0	-1.308991	0.866793	0.000077
C	0	1.274353	1.761584	-1.310386
C	0	-0.036810	2.531506	-1.575710
C	0	-1.315945	1.709618	-1.310852
H	0	-2.011952	-1.953961	0.000139
H	0	-0.930841	-3.445726	0.000094
H	0	1.055448	-2.047163	-0.000020
H	0	2.232148	0.342249	-0.000090
H	0	2.118928	2.467043	1.316487
H	0	1.453612	1.075253	2.151391
H	0	-0.043570	2.870868	2.620546
H	0	-0.055174	3.445726	0.975208
H	0	-2.187365	2.381234	1.319210
H	0	-1.465696	1.015218	2.151030
H	0	-2.232148	0.270083	0.000129
H	0	1.453414	1.075231	-2.151502
H	0	2.118797	2.467035	-1.316675
H	0	-0.055280	3.445711	-0.975217
H	0	-0.043823	2.870824	-2.620546
H	0	-1.465898	1.015175	-2.150864
H	0	-2.187495	2.381204	-1.319003

B3LYP/6-31G* Energy + ZPE = -415.886370
B3LYP/6-31G* Free energy = -415.923045
B3LYP/6-31G* Free energy in DCM = -416.135276
B3LYP/6-31G* Free energy in Tol = -416.134863
Number of imaginary frequencies = 0

Methanol vinylboronate (4)
B3LYP/6-31G* Geometry

C	0	-1.803715	-2.410623	0.083735
C	0	-1.791334	-1.071166	0.043828
B	0	-0.465325	-0.237653	0.036286
O	0	0.720575	-0.915344	0.072208
O	0	-0.413676	1.132855	-0.004138
C	0	-1.573694	1.948173	-0.043837
C	0	1.961975	-0.222454	0.067788
H	0	-2.725384	-2.990822	0.088995
H	0	-0.877154	-2.979653	0.112917
H	0	-2.756487	-0.561844	0.015924
H	0	-1.244432	2.990822	-0.071002
H	0	-2.177470	1.748724	-0.937758
H	0	-2.200661	1.802492	0.844484
H	0	2.076076	0.384682	-0.837576
H	0	2.052611	0.438040	0.937758
H	0	2.756487	-0.973157	0.100852

B3LYP/6-31G* Energy + ZPE = -333.075379
B3LYP/6-31G* Free energy = -333.110447
B3LYP/6-31G* Free energy in DCM = -333.200457
B3LYP/6-31G* Free energy in Tol = -333.199068
Number of imaginary frequencies = 0

Pinacol vinylboronate (5)
B3LYP/6-31G* Geometry

C	0	-2.758796	2.160393	0.060400

C	0	-1.422339	2.219035	-0.016395
B	0	-0.525834	0.951883	-0.013646
O	0	0.848038	0.999743	-0.031609
O	0	-1.018235	-0.333316	0.008159
C	0	0.104306	-1.228625	0.240382
C	0	1.333149	-0.357294	-0.234402
C	0	-0.129983	-2.512635	-0.553524
C	0	0.118615	-1.535495	1.744289
C	0	1.635637	-0.493699	-1.732879
C	0	2.614216	-0.538850	0.577795
H	0	-3.388850	3.048499	0.055367
H	0	-3.277515	1.206423	0.131488
H	0	-0.945785	3.197894	-0.084644
H	0	-0.285911	-2.308674	-1.615149
H	0	0.719172	-3.197894	-0.449214
H	0	-1.022545	-3.020311	-0.173760
H	0	-0.851383	-1.954758	2.029026
H	0	0.896790	-2.261350	2.003092
H	0	0.279493	-0.628054	2.334895
H	0	2.350780	0.282698	-2.021843
H	0	2.071354	-1.469643	-1.972114
H	0	0.731396	-0.359747	-2.334895
H	0	3.388850	0.133503	0.195114
H	0	2.459994	-0.306550	1.633930
H	0	2.987148	-1.566400	0.496062

B3LYP/6-31G* Energy + ZPE = -489.054300
B3LYP/6-31G* Free energy = -489.091254
B3LYP/6-31G* Free energy in DCM = -489.271474
B3LYP/6-31G* Free energy in Tol = -489.269220
Number of imaginary frequencies = 0

2-Methyl-2,4-pentanediol vinylboronate (6)
B3LYP/6-31G* Geometry

C	0	-0.235014	-2.830211	0.116901
C	0	-1.069203	-1.782647	0.089603
B	0	-0.588433	-0.297195	0.100918
O	0	0.756754	-0.030778	0.149108
O	0	-1.541924	0.687018	0.067856
C	0	1.241506	1.318554	0.157909
C	0	0.187948	2.257196	0.750488
C	0	-1.194271	2.088729	0.090420
C	0	-2.277985	2.782525	0.920131
C	0	-1.219550	2.600780	-1.356735
C	0	2.556024	1.338600	0.928805
H	0	0.843589	-2.689457	0.148626
H	0	-0.583526	-3.861995	0.109181
H	0	-2.143163	-1.974413	0.057708
H	0	1.441779	1.601334	-0.885473
H	0	0.522072	3.297905	0.658299
H	0	0.093892	2.040555	1.823475
H	0	-2.097408	3.861995	0.975632
H	0	-3.261934	2.617105	0.469276
H	0	-2.296765	2.379632	1.938094
H	0	-1.032857	3.680303	-1.392615
H	0	-0.466580	2.100909	-1.974792
H	0	-2.200485	2.404348	-1.800966
H	0	3.006752	2.337238	0.902572
H	0	2.391496	1.056821	1.974792
H	0	3.261934	0.626640	0.489749

B3LYP/6-31G* Energy + ZPE = -489.057657
B3LYP/6-31G* Free energy = -489.095078
B3LYP/6-31G* Free energy in DCM = -489.275637
B3LYP/6-31G* Free energy in Tol = -489.273623
Number of imaginary frequencies = 0

(-)-Dimethyl tartrate vinylboronate (7)
B3LYP/6-31G* Geometry

C	0	1.657181	2.702209	-0.369293
C	0	0.470932	2.078751	-0.369278
B	0	0.340179	0.537231	-0.369278
O	0	-0.871231	-0.119324	-0.409317
O	0	1.415604	-0.325806	-0.331436
C	0	0.918579	-1.659500	-0.442123
C	0	-0.619141	-1.523376	-0.314667
C	0	1.330170	-2.325012	-1.757004
C	0	-1.145813	-2.102539	1.001740
O	0	0.643829	-3.145172	-2.330017
O	0	2.545547	-1.934967	-2.159088
O	0	-0.563828	-2.949020	1.646957
O	0	-2.342285	-1.593445	1.318924
C	0	3.023926	-2.557358	-3.366196
C	0	-2.932953	-2.109985	2.526108
H	0	1.749588	3.786942	-0.368362
H	0	2.590088	2.142273	-0.369751
H	0	-0.438477	2.679993	-0.369781
H	0	1.319931	-2.270721	0.373734
H	0	-1.128174	-2.044556	-1.132492
H	0	2.352295	-2.337891	-4.199951
H	0	3.090790	-3.640579	-3.236450
H	0	4.009811	-2.127594	-3.541946
H	0	-2.288940	-1.901962	3.384277
H	0	-3.084137	-3.189500	2.445419
H	0	-3.886749	-1.592392	2.625732

B3LYP/6-31G* Energy + ZPE = -787.551827
B3LYP/6-31G* Free energy = -787.599387
B3LYP/6-31G* Free energy in DCM = -787.746983
B3LYP/6-31G* Free energy in Tol = -787.741738
Number of imaginary frequencies = 0

Methanol alkynylboronate (8)
B3LYP/6-31G* Geometry

C	0	-0.402175	-0.925731	0.622965
B	0	-0.408937	0.602691	0.428218
O	0	0.704153	1.312993	0.087706
O	0	-1.586530	1.258382	0.607790
C	0	-1.661870	2.671866	0.443137
C	0	1.987241	0.739612	-0.126241
C	0	-0.374824	-2.129206	0.771372
H	0	-1.382988	2.967253	-0.574355
H	0	-2.696858	2.965295	0.635651
H	0	-1.000169	3.188118	1.147392

H	0	2.696858	1.190508	0.575620
H	0	1.976604	-0.345494	0.016030
H	0	2.310353	0.968371	-1.147392
H	0	-0.370414	-3.188118	0.906356

B3LYP/6-31G* Energy + ZPE = -331.854222
B3LYP/6-31G* Free energy = -331.888262
B3LYP/6-31G* Free energy in DCM = -331.958281
B3LYP/6-31G* Free energy in Tol = -331.955467
Number of imaginary frequencies = 0

Dienes

Cyclopentadiene (9)
B3LYP/6-31G* Geometry

C	0	-0.875080	-0.858199	0.000065
C	0	-0.990265	0.607114	0.000067
C	0	0.243773	1.151557	0.000038
C	0	0.428870	-1.203137	0.000035
C	0	1.269201	0.047542	0.000015
H	0	-1.720357	-1.539055	0.000085
H	0	-1.931543	1.147533	0.000088
H	0	0.490909	2.207116	0.000032
H	0	0.837901	-2.207116	0.000027
H	0	1.931503	0.099605	-0.878154
H	0	1.931543	0.099606	0.878154

B3LYP/6-31G* Energy + ZPE = -194.008161
B3LYP/6-31G* Free energy = -194.034758
B3LYP/6-31G* Free energy in DCM = -194.101477
B3LYP/6-31G* Free energy in Tol = -194.100015
Number of imaginary frequencies = 0

1,3-Cyclohexadiene (10)
B3LYP/6-31G* Geometry

C	0	-1.222455	-0.768632	0.261496
C	0	-1.248185	0.768708	0.175562
C	0	0.140913	1.361515	0.250137
C	0	1.198862	0.675676	-0.213340
C	0	1.034645	-0.675742	-0.760665
C	0	-0.103774	-1.361515	-0.565316
H	0	-1.081376	-1.077208	1.311684
H	0	-2.192908	-1.176499	-0.044881
H	0	-1.889766	1.176623	0.965487
H	0	-1.708405	1.077293	-0.778896
H	0	0.255619	2.376431	0.624709
H	0	2.192908	1.117337	-0.208665
H	0	1.861978	-1.117459	-1.311684
H	0	-0.214226	-2.376431	-0.941165

B3LYP/6-31G* Energy + ZPE = -233.296105
B3LYP/6-31G* Free energy = -233.324356
B3LYP/6-31G* Free energy in DCM = -233.418978
B3LYP/6-31G* Free energy in Tol = -233.417787
Number of imaginary frequencies = 0

Piperylene (11)

***s-trans* conformation**
B3LYP/6-31G* Geometry

C	0	1.204657	0.876912	0.000081
C	0	1.219376	2.217893	0.000137
C	0	-0.002296	0.062649	0.000083
C	0	-0.008601	-1.280516	0.000027
C	0	-1.236814	-2.139933	0.000028
H	0	2.151042	0.334538	0.000030
H	0	2.148487	2.779758	0.000132
H	0	0.298807	2.797696	0.000189
H	0	-0.952468	0.599629	0.000134
H	0	0.948285	-1.805756	-0.000024
H	0	-1.263313	-2.797617	-0.879964
H	0	-1.263256	-2.797696	0.879964
H	0	-2.151042	-1.536891	0.000085

B3LYP/6-31G* Energy + ZPE = -195.198432
B3LYP/6-31G* Free energy = -195.227223
B3LYP/6-31G* Free energy in DCM = -195.308284
B3LYP/6-31G* Free energy in Tol = -195.307003
Number of imaginary frequencies = 0

***s-cis* conformation**
B3LYP/6-31G* Geometry

C	0	1.678136	0.294304	-0.058761
C	0	1.691284	1.608576	0.201647
C	0	0.523213	-0.605018	0.062071
C	0	-0.763885	-0.257852	-0.090905
C	0	-1.929545	-1.188921	0.063495
H	0	2.608458	-0.178666	-0.376040
H	0	2.588159	2.204758	0.060625
H	0	0.811973	2.130121	0.571894
H	0	0.755022	-1.650343	0.273757
H	0	-1.001202	0.772544	-0.358386
H	0	-2.608458	-0.846488	0.856999
H	0	-2.527496	-1.237332	-0.856999
H	0	-1.604728	-2.204758	0.312841

B3LYP/6-31G* Energy + ZPE = -195.192898
B3LYP/6-31G* Free energy = -195.221944
B3LYP/6-31G* Free energy in DCM = -195.302507
B3LYP/6-31G* Free energy in Tol = -195.301298
Number of imaginary frequencies = 0

Isoprene (12)

***s-trans* conformation**
B3LYP/6-31G* Geometry

C	0	-1.182075	-1.822806	-0.000116
C	0	-1.189859	-0.482597	-0.000319
C	0	-0.008643	0.389377	-0.000338
C	0	-0.164254	1.724386	-0.000551
C	0	1.360748	-0.245893	-0.000111

H	0	-2.107865	-2.390491	-0.000119
H	0	-0.262249	-2.400928	0.000059
H	0	-2.149100	0.035282	-0.000488
H	0	0.685846	2.400928	-0.000571
H	0	-1.150453	2.182218	-0.000713
H	0	2.149100	0.512200	-0.000152
H	0	1.501511	-0.884259	0.881363
H	0	1.501679	-0.884529	-0.881363

B3LYP/6-31G* Energy + ZPE = -195.196338
B3LYP/6-31G* Free energy = -195.224814
B3LYP/6-31G* Free energy in DCM = -195.305442
B3LYP/6-31G* Free energy in Tol = -195.304482
Number of imaginary frequencies = 0

***s-cis* conformation**
B3LYP/6-31G* Geometry

C	0	-1.212920	-1.823065	-0.004189
C	0	-1.163660	-0.552709	0.412964
C	0	-0.007285	0.359471	0.283677
C	0	1.259735	-0.069614	0.382226
C	0	-0.341527	1.816355	0.056566
H	0	-2.100152	-2.432998	0.140965
H	0	-0.373545	-2.292303	-0.511259
H	0	-2.057109	-0.118320	0.865545
H	0	2.100152	0.609377	0.264035
H	0	1.495973	-1.108092	0.595961
H	0	0.560190	2.432998	-0.002623
H	0	-0.912744	1.953013	-0.871081
H	0	-0.967266	2.206283	0.871081

B3LYP/6-31G* Energy + ZPE = -195.191876
B3LYP/6-31G* Free energy = -195.220743
B3LYP/6-31G* Free energy in DCM = -195.300142
B3LYP/6-31G* Free energy in Tol = -195.299201
Number of imaginary frequencies = 0

Diels-Alder reaction of dichlorovinylborane (1) with cyclopentadiene (9)

***Endo* transition structure (TS-1+9-N)**
B3LYP/6-31G* Geometry

C	0	1.162758	-0.353825	-0.988472
C	0	1.162758	1.053056	-0.988472
C	0	-0.148609	-0.804799	-0.988472
C	0	-0.164690	1.520256	-0.905264
C	0	-1.038002	0.355117	-1.340549
H	0	2.044375	-0.978730	-0.904687
H	0	2.048547	1.675704	-0.921052
H	0	-0.463076	-1.841710	-1.003309
H	0	-0.429743	2.548179	-1.137329
H	0	-2.048547	0.328495	-0.931358
H	0	-1.125281	0.395131	-2.439941
C	0	-0.568319	1.421379	1.083161
C	0	-0.791439	0.069368	1.398555
B	0	0.221623	-0.871642	1.997701
Cl	0	-0.218639	-2.548179	2.439941
Cl	0	1.895792	-0.355621	2.370537
H	0	-1.429698	2.084127	1.016795
H	0	0.321290	1.904706	1.475584
H	0	-1.803908	-0.310206	1.271015

B3LYP/6-31G* Energy + ZPE = -1217.268010
B3LYP/6-31G* Free energy = -1217.304244
B3LYP/6-31G* Free energy in DCM = -1217.415888
B3LYP/6-31G* Free energy in Tol = -1217.412347
Number of imaginary frequencies = 1 (-398.81)

***Exo* transition structure (TS-1+9-X)**
B3LYP/6-31G* Geometry

C	0	1.785309	-0.342190	-0.958059
C	0	1.785309	1.065476	-0.958059
C	0	0.473531	-0.794783	-0.958059
C	0	0.458624	1.528715	-0.852289
C	0	-0.421126	0.366432	-1.273124
H	0	2.667502	-0.969809	-0.890787
H	0	2.671507	1.689970	-0.907805
H	0	0.161466	-1.832142	-0.988128
H	0	0.182284	2.559068	-1.058523
H	0	-1.419169	0.331172	-0.836652
H	0	-0.538636	0.419725	-2.369199
C	0	0.079764	1.401444	1.154569
C	0	0.183015	0.048518	1.519101
B	0	-0.955667	-0.914417	1.735525
Cl	0	-0.657336	-2.559068	2.369199
Cl	0	-2.671507	-0.478359	1.442630
H	0	-0.911352	1.848312	1.108902
H	0	0.854030	2.092370	1.476995
H	0	1.173706	-0.309795	1.791974

B3LYP/6-31G* Energy + ZPE = -1217.267566
B3LYP/6-31G* Free energy = -1217.303828
B3LYP/6-31G* Free energy in DCM = -1217.414637
B3LYP/6-31G* Free energy in Tol = -1217.411318
Number of imaginary frequencies = 1 (-399.24)

***Endo* product (P-1+9-N)**
B3LYP/6-31G* Geometry

C	0	-1.228500	0.369872	-0.938726
C	0	-0.083463	0.536486	-1.616027
C	0	0.904991	1.225411	-0.686492
C	0	1.307045	0.162356	0.395922
C	0	-0.005942	-0.023190	1.223665
C	0	-1.022380	0.947597	0.453246
C	0	-0.061751	2.114174	0.128755
B	0	-0.596595	-1.454890	1.435915
Cl	0	-1.917476	-1.682333	2.601575
Cl	0	-0.048322	-2.890932	0.562997
H	0	-2.111273	-0.174452	-1.259690
H	0	0.158372	0.151096	-2.601575
H	0	1.755867	1.716856	-1.164323

H	0	2.111273	0.546632	1.033458
H	0	1.661914	-0.764271	-0.061782
H	0	0.121777	0.411971	2.225018
H	0	-1.921094	1.174763	1.029447
H	0	0.395438	2.565424	1.017677
H	0	-0.538476	2.890932	-0.477368

B3LYP/6-31G* Energy + ZPE = -1217.310176
B3LYP/6-31G* Free energy = -1217.346200
B3LYP/6-31G* Free energy in DCM = -1217.459283
B3LYP/6-31G* Free energy in Tol = -1217.457541
Number of imaginary frequencies = 0

***Exo* product (P-1+9-X)**
B3LYP/6-31G* Geometry

C	0	-2.120503	0.148224	0.233751
C	0	-1.973307	1.269305	-0.487322
C	0	-0.586165	1.820930	-0.199470
C	0	0.442582	0.847200	-0.876224
C	0	0.258604	-0.489413	-0.087438
C	0	-0.836218	-0.061189	1.018032
C	0	-0.424404	1.403791	1.280368
B	0	1.505023	-1.138089	0.597208
Cl	0	1.494892	-2.873384	0.968508
Cl	0	2.938616	-0.227958	1.105052
H	0	-2.938616	-0.564081	0.193015
H	0	-2.655589	1.664365	-1.233618
H	0	-0.422759	2.873384	-0.443137
H	0	1.455986	1.246410	-0.769221
H	0	0.247820	0.716574	-1.944805
H	0	-0.198829	-1.258680	-0.718456
H	0	-0.898373	-0.733484	1.876405
H	0	0.596506	1.519734	1.659877
H	0	-1.126032	1.917078	1.944805

B3LYP/6-31G* Energy + ZPE = -1217.309954
B3LYP/6-31G* Free energy = -1217.345529
B3LYP/6-31G* Free energy in DCM = -1217.459154
B3LYP/6-31G* Free energy in Tol = -1217.457538
Number of imaginary frequencies = 0

Diels-Alder reaction of dimethylvinylborane (2) with cyclopentadiene (9)

***Endo* transition structure (TS-2+9-N)**
B3LYP/6-31G* Geometry

C	0	-1.419765	0.393517	0.918765
C	0	-1.066448	1.749761	1.000113
C	0	0.244587	1.856260	1.506067
C	0	-0.376337	-0.380429	1.422898
C	0	0.519162	0.541422	2.211390
H	0	-2.316107	0.007943	0.445275
H	0	-1.650792	2.572636	0.601233
H	0	0.657880	2.795147	1.864033
H	0	-0.397578	-1.456400	1.551421
H	0	0.108720	0.617588	3.233505
H	0	1.565973	0.247930	2.293216
C	0	1.419300	1.456799	-0.155737
C	0	1.363113	0.065344	-0.329700
B	0	0.429759	-0.714646	-1.270214
C	0	-0.585459	0.022569	-2.248801
C	0	0.560294	-2.296932	-1.385535
H	0	2.316107	1.903129	0.273079
H	0	0.918375	2.102440	-0.871697
H	0	2.108319	-0.505335	0.229295
H	0	-0.099261	0.118695	-3.233505
H	0	-1.504158	-0.552104	-2.425845
H	0	-0.870998	1.036221	-1.944411
H	0	1.275150	-2.748884	-0.686484
H	0	-0.410150	-2.795147	-1.245640
H	0	0.879123	-2.572560	-2.402788

B3LYP/6-31G* Energy + ZPE = -376.548622
B3LYP/6-31G* Free energy = -376.584761
B3LYP/6-31G* Free energy in DCM = -376.76047
B3LYP/6-31G* Free energy in Tol = -376.758879
Number of imaginary frequencies = 1 (-423.05)

***Exo* transition structure (TS-2+9-X)**
B3LYP/6-31G* Geometry

C	0	-2.101248	-1.313502	0.719139
C	0	-1.823942	-0.006135	1.152453
C	0	-0.444189	0.177514	1.199064
C	0	-0.890245	-1.957542	0.400504
C	0	0.193974	-1.181998	1.122569
H	0	-3.092075	-1.710856	0.523750
H	0	-2.565842	0.764451	1.334841
H	0	0.056593	1.062393	1.574733
H	0	-0.817736	-3.029459	0.238180
H	0	1.187367	-1.218177	0.677562
H	0	0.266501	-1.584841	2.147705
C	0	-0.284471	0.181820	-1.320990
C	0	-0.425334	-1.203964	-1.484707
B	0	1.016406	0.986252	-1.168858
C	0	0.952086	2.576599	-1.171316
C	0	2.458884	0.315651	-1.097904
H	0	-1.208274	0.753833	-1.424541
H	0	0.467018	-1.812775	-1.621785
H	0	-1.299702	-1.599742	-1.996036
H	0	-0.053003	2.987168	-1.014618
H	0	1.626892	3.029459	-0.431208
H	0	1.300507	2.950002	-2.147705
H	0	2.974225	0.587541	-0.164499
H	0	2.488434	-0.776895	-1.187897
H	0	3.092075	0.721905	-1.901093

B3LYP/6-31G* Energy + ZPE = -376.547981
B3LYP/6-31G* Free energy = -376.584188
B3LYP/6-31G* Free energy in DCM = -376.75911
B3LYP/6-31G* Free energy in Tol = -376.75764
Number of imaginary frequencies = 1 (-425.23)

***Endo* product (P-2+9-N)**
B3LYP/6-31G* Geometry

C	0	-1.316774	0.468045	1.089214
C	0	-1.041364	1.780145	1.055353
C	0	0.448844	1.942539	1.320808
C	0	1.183781	1.404505	0.042450
C	0	0.892726	-0.131899	0.069212
C	0	-0.013418	-0.264882	1.376976
C	0	0.679190	0.766459	2.297633
B	0	0.255045	-0.859905	-1.184732
C	0	-0.203438	-0.062685	-2.469773
C	0	0.074260	-2.431767	-1.149644
H	0	-2.260048	-0.012781	0.846254
H	0	-1.712759	2.586355	0.775185
H	0	0.775065	2.934281	1.644664
H	0	2.260048	1.603967	0.111497
H	0	0.819194	1.899039	-0.862905
H	0	1.825144	-0.672198	0.303140
H	0	-0.104819	-1.287992	1.748342
H	0	0.158932	0.899953	3.252052
H	0	1.738090	0.545798	2.479793
H	0	0.653176	0.465096	-2.916116
H	0	-0.663180	-0.677495	-3.252052
H	0	-0.913758	0.730268	-2.192958
H	0	0.570728	-2.885251	-2.021037
H	0	0.443863	-2.934281	-0.248482
H	0	-0.989728	-2.687963	-1.269372

B3LYP/6-31G* Energy + ZPE = -376.594905
B3LYP/6-31G* Free energy = -376.631145
B3LYP/6-31G* Free energy in DCM = -376.809358
B3LYP/6-31G* Free energy in Tol = -376.808477
Number of imaginary frequencies = 0

***Exo* product (P-2+9-X)**
B3LYP/6-31G* Geometry

C	0	-2.051144	-1.498214	0.943357
C	0	-2.166381	-0.165910	0.847475
C	0	-0.764071	0.423991	0.920313
C	0	-0.062252	0.046778	-0.440176
C	0	0.099071	-1.519986	-0.295571
C	0	-0.570446	-1.816548	1.089455
C	0	-0.099547	-0.580863	1.891014
B	0	1.302573	0.754101	-0.822551
C	0	1.997048	1.833253	0.101090
C	0	1.980043	0.405221	-2.210765
H	0	-2.835033	-2.239350	0.819930
H	0	-3.065944	0.402069	0.628441
H	0	-0.702451	1.482573	1.184590
H	0	-0.754989	0.244386	-1.273058
H	0	1.152234	-1.828123	-0.265141
H	0	-0.374511	-2.068602	-1.114929
H	0	-0.323886	-2.800361	1.497830
H	0	0.992210	-0.487857	1.944270
H	0	-0.520343	-0.542050	2.900739
H	0	1.515347	2.800361	-0.126212
H	0	1.856452	1.678033	1.176755
H	0	3.065944	1.971077	-0.101314
H	0	2.896428	-0.175262	-2.016338
H	0	1.362874	-0.181289	-2.900739
H	0	2.323487	1.310099	-2.731990

B3LYP/6-31G* Energy + ZPE = -376.594387
B3LYP/6-31G* Free energy = -376.630555
B3LYP/6-31G* Free energy in DCM = -376.809036
B3LYP/6-31G* Free energy in Tol = -376.808125
Number of imaginary frequencies = 0

Diels-Alder reaction of vinyl-9-BBN (3) with cyclopentadiene (9)

***Endo* transition structure (TS-3+9-N)**
B3LYP/6-31G* Geometry

C	0	0.147015	-2.746973	-1.286033
C	0	1.084916	-1.707177	-1.181555
C	0	-0.918215	-2.326982	-2.106439
C	0	0.672582	-0.638527	-1.973482
C	0	-0.377649	-1.164779	-2.917978
H	0	0.169209	-3.668634	-0.713675
H	0	1.943787	-1.703415	-0.520077
H	0	-1.648209	-3.019971	-2.515428
H	0	1.233377	0.273654	-2.141672
H	0	-1.112103	-0.444024	-3.278370
H	0	0.141553	-1.584531	-3.797348
C	0	-2.061500	-1.175688	-0.822837
C	0	-1.393204	0.053001	-0.702619
B	0	-0.512001	0.510397	0.466202
C	0	-0.241025	-0.308722	1.798751
C	0	-0.015112	2.008771	0.626772
C	0	1.238904	-0.216304	2.254066
C	0	1.480816	2.057049	1.029293
C	0	-1.250608	0.314172	2.816663
C	0	-0.986706	2.636315	1.677237
C	0	1.854977	1.200094	2.256174
C	0	-1.136527	1.844979	2.997622
H	0	-2.949014	-1.238184	-1.451799
H	0	-2.091733	-1.846674	0.031551
H	0	-1.630927	0.792087	-1.471791
H	0	-0.493823	-1.376452	1.719881
H	0	-0.129607	2.595286	-0.297536
H	0	1.834419	-0.850611	1.582175
H	0	1.356156	-0.657800	3.255902
H	0	1.797910	3.095976	1.208404
H	0	2.070593	1.710874	0.166299
H	0	-1.140763	-0.173607	3.797348
H	0	-2.267262	0.075311	2.472059
H	0	-1.976727	2.714214	1.204841
H	0	-0.680753	3.668634	1.906837
H	0	2.949014	1.111535	2.310533
H	0	1.564559	1.727728	3.169595
H	0	-2.028915	2.206404	3.527060
H	0	-0.296575	2.072165	3.660874

B3LYP/6-31G* Energy + ZPE = -609.865319
B3LYP/6-31G* Free energy = -609.906712
B3LYP/6-31G* Free energy in DCM = -610.212064
B3LYP/6-31G* Free energy in Tol = -610.210854
Number of imaginary frequencies = 1 (-428.14)

***Exo* transition structure (TS-3+9-X)**
B3LYP/6-31G* Geometry

C	0	3.223093	0.705014	-0.735474
C	0	3.164581	1.753025	-1.670833
C	0	2.143755	-0.149299	-0.938490
C	0	1.987673	1.623655	-2.431874
C	0	1.552053	0.179524	-2.281240
H	0	3.944696	0.624073	0.070850
H	0	3.841683	2.600557	-1.703812
H	0	1.979542	-1.084283	-0.415657
H	0	1.813426	2.183022	-3.346894
H	0	0.485335	-0.012073	-2.392866
H	0	2.085225	-0.411983	-3.045588
C	0	0.511364	1.570909	-0.035766
C	0	0.521075	2.391053	-1.174240
B	0	-0.488929	0.455101	0.284378
C	0	-0.596516	-0.218036	1.718631
C	0	-1.681153	-0.038326	-0.643176
C	0	-0.591869	-1.764779	1.593327
C	0	-1.680357	-1.587088	-0.754421
C	0	-1.891656	0.369050	2.359875
C	0	-2.971382	0.555209	0.005862
C	0	-1.605607	-2.348658	0.586349
C	0	-3.169754	0.229025	1.502979
H	0	1.201567	1.866029	0.756786
H	0	-0.290035	2.297434	-1.895152
H	0	0.927977	3.397492	-1.110573
H	0	0.239104	0.061133	2.377866
H	0	-1.643449	0.361303	-1.668117
H	0	-0.756378	-2.229356	2.577760
H	0	0.420499	-2.071844	1.288336
H	0	-2.566125	-1.928962	-1.311524
H	0	-0.814644	-1.878869	-1.368699
H	0	-2.066320	-0.086146	3.346894
H	0	-1.713208	1.437757	2.549249
H	0	-2.928800	1.647874	-0.111342
H	0	-3.858724	0.225559	-0.555996
H	0	-1.346186	-3.397492	0.385845
H	0	-2.598495	-2.380832	1.044730
H	0	-3.573845	-0.782326	1.607846
H	0	-3.944696	0.893465	1.909546

B3LYP/6-31G* Energy + ZPE = -609.865808
B3LYP/6-31G* Free energy = -609.906901
B3LYP/6-31G* Free energy in DCM = -610.212290
B3LYP/6-31G* Free energy in Tol = -610.211082
Number of imaginary frequencies = 1 (-420.73)

Products

***Endo* product (P-3+9-N)**
B3LYP/6-31G* Geometry

C	0	0.923354	-1.999844	-2.026143
C	0	0.923354	-0.658941	-2.026143
C	0	-0.529356	-2.456421	-2.026143
C	0	-0.530694	-0.201521	-2.022072
C	0	-1.096639	-2.118914	-0.604917
C	0	-1.169363	-1.327843	-2.869412
C	0	-1.106879	-0.543003	-0.595582
B	0	-0.497008	0.164825	0.673733
C	0	-0.821959	-0.299620	2.151983
C	0	0.423118	1.451133	0.683509
C	0	0.528139	-0.680089	2.830950
C	0	1.766765	1.063789	1.371637
C	0	-1.598523	0.851089	2.857307
C	0	-0.359020	2.594004	1.397824
C	0	1.630330	0.398383	2.757379
C	0	-0.928408	2.239108	2.788169
H	0	1.780518	-2.659294	-1.930666
H	0	1.783384	-0.002300	-1.941878
H	0	-0.711687	-3.485609	-2.345872
H	0	-0.711720	0.826911	-2.343959
H	0	-2.105286	-2.530062	-0.484361
H	0	-0.473478	-2.550974	0.184688
H	0	-2.266230	-1.327263	-2.840487
H	0	-0.828135	-1.330801	-3.909505
H	0	-2.167144	-0.223265	-0.579440
H	0	-1.462397	-1.192305	2.189699
H	0	0.670365	1.815121	-0.323018
H	0	0.901553	-1.594216	2.344990
H	0	0.354810	-0.952413	3.882584
H	0	2.411779	1.951073	1.455596
H	0	2.294810	0.369599	0.701783
H	0	-1.783729	0.588285	3.909505
H	0	-2.592061	0.918197	2.388808
H	0	-1.192923	2.888295	0.742961
H	0	0.279686	3.485609	1.483363
H	0	2.592061	-0.058189	3.027541
H	0	1.449042	1.163493	3.517489
H	0	-1.663016	3.003354	3.075755
H	0	-0.135705	2.303410	3.539168

B3LYP/6-31G* Energy + ZPE = -609.911733
B3LYP/6-31G* Free energy = -609.953307
B3LYP/6-31G* Free energy in DCM = -610.262035
B3LYP/6-31G* Free energy in Tol = -610.261406
Number of imaginary frequencies = 0

***Exo* product (P-3+9-X)**
B3LYP/6-31G* Geometry

C	0	3.163376	0.647858	-1.481842
C	0	3.163376	1.988785	-1.481842
C	0	1.711716	0.188339	-1.481842
C	0	1.711853	2.443207	-1.492859
C	0	1.152542	0.526352	-0.045349
C	0	1.072922	1.312042	-2.330917
C	0	1.118622	2.109833	-0.081192
B	0	-0.261597	-0.033508	0.370026
C	0	-0.770477	0.008316	1.868378

C	0	-1.314621	-0.759430	-0.560028
C	0	-0.813065	-1.477829	2.344635
C	0	-1.348358	-2.243103	-0.070038
C	0	-2.137161	0.745026	1.935898
C	0	-2.682541	-0.024185	-0.477020
C	0	-1.614990	-2.435272	1.437820
C	0	-3.209976	0.239212	0.949188
H	0	4.020966	-0.009262	-1.370468
H	0	4.018524	2.648834	-1.372513
H	0	1.532898	-0.839844	-1.807068
H	0	1.527222	3.470978	-1.816757
H	0	1.883224	0.217285	0.715912
H	0	-0.023500	1.317000	-2.305573
H	0	1.415176	1.307251	-3.370575
H	0	0.098190	2.510956	-0.013200
H	0	1.694595	2.555389	0.734970
H	0	-0.077637	0.537827	2.538422
H	0	-1.020569	-0.783981	-1.617996
H	0	-1.207031	-1.529465	3.370575
H	0	0.224319	-1.840286	2.405869
H	0	-2.096176	-2.805527	-0.648621
H	0	-0.377777	-2.700302	-0.315613
H	0	-2.537949	0.703812	2.959839
H	0	-1.950317	1.810425	1.733551
H	0	-2.572235	0.941833	-0.992630
H	0	-3.442551	-0.578964	-1.047440
H	0	-1.371811	-3.470993	1.711441
H	0	-2.684448	-2.326447	1.639633
H	0	-3.674026	-0.669693	1.343323
H	0	-4.020981	0.978241	0.896454

B3LYP/6-31G* Energy + ZPE = -609.911675
B3LYP/6-31G* Free energy = -609.952682
B3LYP/6-31G* Free energy in DCM = -610.262270
B3LYP/6-31G* Free energy in Tol = -610.261600
Number of imaginary frequencies = 0

Diels-Alder reaction of methanol vinylboronate (4) with cyclopentadiene (9)

***Endo* transition structure (TS-4+9-N)**
B3LYP/6-31G* Geometry

C	0	-2.726357	0.198277	-0.544932
C	0	-1.854985	0.867151	-1.418551
C	0	-1.334618	1.986993	-0.774733
C	0	-2.724840	0.859200	0.698511
C	0	-2.208165	2.258940	0.422921
H	0	-3.197296	-0.758548	-0.744161
H	0	-1.551048	0.505669	-2.395162
H	0	-0.697067	2.732894	-1.236690
H	0	-3.467021	0.663788	1.467906
H	0	-1.729892	2.765913	1.262856
H	0	-3.061433	2.878505	0.096280
C	0	0.078071	0.813220	0.878849
C	0	-0.971486	0.199684	1.577640
B	0	0.902468	0.074820	-0.200689
O	0	2.039883	0.567359	-0.805639
O	0	0.484874	-1.176325	-0.587554
C	0	1.176808	-1.896610	-1.595312
C	0	2.583387	1.829778	-0.471687
H	0	0.429569	1.769710	1.263133
H	0	-1.243463	0.572752	2.564101
H	0	-1.118346	-0.868798	1.454376
H	0	2.234707	-2.030383	-1.341061
H	0	0.702016	-2.878505	-1.685088
H	0	1.122939	-1.384153	-2.564101
H	0	2.888859	1.874728	0.581859
H	0	3.467021	1.990524	-1.097056
H	0	1.868952	2.641817	-0.660478

B3LYP/6-31G* Energy + ZPE = -527.051557
B3LYP/6-31G* Free energy = -527.091530
B3LYP/6-31G* Free energy in DCM = -527.274337
B3LYP/6-31G* Free energy in Tol = -527.272106
Number of imaginary frequencies = 1 (-454.11)

***Exo transition structure* (TS-4+9-X)**
B3LYP/6-31G* Geometry

C	0	-2.830548	0.520998	-0.252063
C	0	-2.775836	1.672149	-1.054236
C	0	-1.658581	2.439528	-0.673687
C	0	-1.800494	0.569912	0.686158
C	0	-1.292133	1.985946	0.725046
H	0	-3.502570	-0.317836	-0.404730
H	0	-3.399045	1.860311	-1.922808
H	0	-1.500701	3.461316	-1.007844
H	0	-1.654560	-0.142901	1.490867
H	0	-0.245882	2.104126	1.007559
H	0	-1.911623	2.556151	1.439205
C	0	-0.072838	1.416387	-1.574874
C	0	-0.014882	0.164131	-0.948267
B	0	1.009553	-0.197580	0.153258
O	0	1.222019	-1.469003	0.640006
O	0	1.776003	0.807904	0.699375
C	0	0.501844	-2.590982	0.163275
C	0	2.734419	0.526126	1.709476
H	0	-0.434260	1.492376	-2.596795
H	0	0.680083	2.157396	-1.315584
H	0	-0.564525	-0.641332	-1.430779
H	0	0.813814	-3.461316	0.748597
H	0	-0.580983	-2.456743	0.281788
H	0	0.714360	-2.787097	-0.895481
H	0	2.266716	0.082985	2.596795
H	0	3.502570	-0.167230	1.347678
H	0	3.207802	1.472485	1.987425

B3LYP/6-31G* Energy + ZPE = -527.052932
B3LYP/6-31G* Free energy = -527.092773
B3LYP/6-31G* Free energy in DCM = -527.275223
B3LYP/6-31G* Free energy in Tol = -527.273319
Number of imaginary frequencies = 1 (-452.87)

***Endo* product (P-4+9-N)**
B3LYP/6-31G* Geometry

C	0	-0.978996	-1.722488	1.905495
C	0	-0.926994	-0.385483	1.821495
C	0	0.530983	0.002487	1.620491
C	0	0.442986	-2.245483	1.761498
C	0	0.936989	-0.451492	0.149498
C	0	0.845986	-2.011490	0.263497
C	0	1.223992	-1.103485	2.450493
B	0	0.077004	0.221497	-1.001487
O	0	0.185982	1.535492	-1.387489
O	0	-0.840995	-0.538498	-1.669487
C	0	-1.653999	0.020493	-2.694496
C	0	1.080986	2.467500	-0.809486
H	0	-1.868003	-2.344498	1.938500
H	0	-1.765998	0.303497	1.774498
H	0	0.791985	1.037491	1.857491
H	0	0.621987	-3.261490	2.121498
H	0	1.990990	-0.167511	0.016503
H	0	1.815987	-2.477493	0.052513
H	0	0.112984	-2.438492	-0.423484
H	0	2.307991	-1.153488	2.291497
H	0	1.010994	-1.026489	3.522499
H	0	-1.043998	0.400497	-3.522499
H	0	-2.307991	-0.774490	-3.063484
H	0	-2.266990	0.844498	-2.313484
H	0	2.042992	2.013489	-0.544487
H	0	1.258980	3.261490	-1.541496
H	0	0.646981	2.918488	0.091515

B3LYP/6-31G* Energy + ZPE = -527.103407
B3LYP/6-31G* Free energy = -527.142881
B3LYP/6-31G* Free energy in DCM = -527.330490
B3LYP/6-31G* Free energy in Tol = -527.328878
Number of imaginary frequencies = 0

***Exo* product (P-4+9-X)**
B3LYP/6-31G* Geometry

C	0	-2.664682	-0.080773	1.483891
C	0	-2.668704	1.260088	1.511290
C	0	-1.219046	1.717302	1.569132
C	0	-1.213078	-0.537146	1.519756
C	0	-0.591962	1.407413	0.165066
C	0	-0.607576	-0.169934	0.107375
C	0	-0.599433	0.572983	2.404006
B	0	0.818118	-0.796168	-0.193660
O	0	1.393469	-0.837302	-1.439594
O	0	1.540474	-1.326147	0.838678
C	0	0.755599	-0.334778	-2.602933
C	0	2.830450	-1.888767	0.623494
H	0	-3.517505	-0.737174	1.335825
H	0	-3.522795	1.919963	1.390869
H	0	-1.046997	2.740820	1.913135
H	0	-1.032309	-1.568448	1.828234
H	0	-1.162086	1.864662	-0.650067
H	0	0.426411	1.814766	0.120855
H	0	-1.306272	-0.492326	-0.676450
H	0	0.495363	0.566721	2.406569
H	0	-0.973957	0.550162	3.432435
H	0	1.463142	-0.423336	-3.432435
H	0	-0.144668	-0.912030	-2.847993
H	0	0.475452	0.719191	-2.490222
H	0	3.522795	-1.149399	0.205560
H	0	3.205167	-2.227721	1.593233
H	0	2.782034	-2.740820	-0.063762

B3LYP/6-31G* Energy + ZPE = -527.104225
B3LYP/6-31G* Free energy = -527.144148
B3LYP/6-31G* Free energy in DCM = -527.331516
B3LYP/6-31G* Free energy in Tol = -527.329978
Number of imaginary frequencies = 0

Diels-Alder reaction of pinacol vinylboronate (5) with cyclopentadiene (9)

***Endo* transition structure (TS-5+9-N)**
B3LYP/6-31G* Geometry

C	0	-2.713363	0.969580	-1.993332
C	0	-1.409565	0.557421	-2.310723
C	0	-0.548789	1.648889	-2.208986
C	0	-2.688654	2.329375	-1.634265
C	0	-1.405181	2.889669	-2.215709
H	0	-3.568896	0.310251	-1.889763
H	0	-1.106920	-0.468827	-2.488812
H	0	0.505131	1.642345	-2.463740
H	0	-3.588033	2.931101	-1.536145
H	0	-0.990954	3.763623	-1.710372
H	0	-1.600969	3.167865	-3.265942
C	0	-0.581975	1.946925	0.200446
C	0	-1.941391	2.263912	0.320910
B	0	-0.008656	0.557304	0.513749
O	0	-0.782931	-0.570714	0.721473
O	0	1.342602	0.298537	0.651983
C	0	0.082362	-1.606911	1.252906
C	0	1.510488	-1.137185	0.769351
C	0	2.652659	-1.412127	1.747219
C	0	1.882055	-1.658427	-0.626619
C	0	-0.380338	-2.956760	0.705464
C	0	-0.080753	-1.578963	2.779833
H	0	0.122897	2.772558	0.116149
H	0	-2.235323	3.290899	0.531073
H	0	-2.616694	1.519639	0.732182
H	0	3.588033	-1.016616	1.337956
H	0	2.479830	-0.932240	2.713073
H	0	2.782435	-2.488660	1.908752
H	0	2.780140	-1.136383	-0.971692
H	0	2.090378	-2.733762	-0.618654
H	0	1.081814	-1.465867	-1.348137
H	0	-0.410457	-2.961881	-0.386635
H	0	0.281771	-3.763623	1.040604
H	0	-1.389489	-3.174137	1.070555
H	0	0.489232	-2.378059	3.265942
H	0	0.242152	-0.619111	3.195090
H	0	-1.139136	-1.712512	3.024649

B3LYP/6-31G* Energy + ZPE = -683.030070
B3LYP/6-31G* Free energy = -683.072457
B3LYP/6-31G* Free energy in DCM = -683.343933
B3LYP/6-31G* Free energy in Tol = -683.341167
Number of imaginary frequencies = 1 (-460.34)

***Exo* transition structure (TS-5+9-X)**
B3LYP/6-31G* Geometry

C	0	3.285655	-2.196402	-1.509981
C	0	3.261140	-0.792254	-1.547340
C	0	1.963810	-2.675422	-1.522481
C	0	1.939283	-0.362557	-1.648316
C	0	1.111276	-1.548318	-2.068782
H	0	4.170294	-2.802899	-1.343129
H	0	4.122180	-0.145989	-1.409689
H	0	1.711014	-3.720210	-1.680318
H	0	1.628162	0.668788	-1.772971
H	0	1.131057	-1.612335	-3.170747
H	0	0.069819	-1.537505	-1.746111
C	0	1.344404	-0.949269	0.631364
C	0	1.350181	-2.340397	0.467128
B	0	0.067452	-0.096092	0.612254
O	0	-1.178159	-0.572507	0.234690
O	0	0.024370	1.233873	0.985964
C	0	-2.088069	0.557730	0.171831
C	0	-1.369863	1.618830	1.094871
C	0	-1.507154	3.073026	0.645460
C	0	-1.750725	1.491318	2.577129
C	0	-2.171117	0.988645	-1.299519
C	0	-3.462482	0.096992	0.656190
H	0	2.238501	-0.490946	1.047608
H	0	0.398493	-2.855824	0.355534
H	0	2.122561	-2.938238	0.942562
H	0	-1.115260	3.223377	-0.363115
H	0	-2.555212	3.393866	0.665324
H	0	-0.942778	3.720210	1.324661
H	0	-1.652628	0.457894	2.924266
H	0	-1.071786	2.111329	3.170747
H	0	-2.776610	1.825948	2.764954
H	0	-1.197628	1.320361	-1.674309
H	0	-2.492866	0.133627	-1.902649
H	0	-2.891695	1.800606	-1.444934
H	0	-4.170294	0.933632	0.684313
H	0	-3.859385	-0.658409	-0.029930
H	0	-3.409729	-0.349040	1.651846

B3LYP/6-31G* Energy + ZPE = -683.031328
B3LYP/6-31G* Free energy = -683.073860
B3LYP/6-31G* Free energy in DCM = -683.345491
B3LYP/6-31G* Free energy in Tol = -683.342818
Number of imaginary frequencies = 1 (-451.44)

***Endo* product (P-5+9-N)**
B3LYP/6-31G* Geometry

C	0	0.596967	-2.032385	-2.396346
C	0	0.596967	-0.691085	-2.396346
C	0	-0.855200	-2.490931	-2.396346
C	0	-0.856736	-0.235351	-2.391408
C	0	-1.423865	-2.153622	-0.974278
C	0	-1.497477	-1.360858	-3.235706
C	0	-1.430000	-0.585442	-0.960092
B	0	-0.659441	0.103355	0.224957
O	0	-0.459263	-0.474949	1.456410
O	0	-0.130744	1.372022	0.143625
C	0	0.447292	0.378215	2.210116
C	0	0.286257	1.768938	1.479842
C	0	-0.845695	2.632231	2.053979
C	0	1.565550	2.595519	1.361085
C	0	1.847745	-0.232535	2.061020
C	0	0,021281	0,358365	3,677224
H	0	1,454075	-2,691483	-2,294222
H	0	1,451275	-0,028944	-2,296647
H	0	-1,036160	-3,519571	-2,719225
H	0	-1,038543	0,796181	-2,700052
H	0	-2,437424	-2,556208	-0,862989
H	0	-0,810920	-2,583114	-0,176977
H	0	-2,594247	-1,361130	-3,203335
H	0	-1,158998	-1,360092	-4,277047
H	0	-2,472712	-0,232468	-0,926188
H	0	-1,024453	3,475985	1,380240
H	0	-1,777196	2,063179	2,135875
H	0	-0,592751	3.028287	3.043198
H	0	1.355476	3.519571	0.812827
H	0	1.948995	2.868914	2.350887
H	0	2.346849	2.055249	0.821776
H	0	2.165324	-0.248459	1.013729
H	0	2.594247	0.316955	2.644343
H	0	1.823122	-1.266235	2.419701
H	0	0.649903	1.026669	4.277047
H	0	-1.022192	0.657277	3.800383
H	0	0.129846	-0.655490	4.075672

B3LYP/6-31G* Energy + ZPE = -683.083644
B3LYP/6-31G* Free energy = -683.125764
B3LYP/6-31G* Free energy in DCM = -683.401734
B3LYP/6-31G* Free energy in Tol = -683.399421
Number of imaginary frequencies = 0

***Exo* product (P-5+9-X)**
B3LYP/6-31G* Geometry

C	0	-3.378376	-2.040059	1.197079
C	0	-3.378376	-0.699121	1.197079
C	0	-1.928263	-0.241996	1.197079
C	0	-1.361190	-0.585220	-0.253556
C	0	-1.352559	-2.151396	-0.226460
C	0	-1.927539	-2.496310	1.192547
C	0	-1.279781	-1.370112	2.031975
B	0	0.036612	0.091309	-0.496375
O	0	0.184778	1.315266	-1.107058
O	0	1.238680	-0.442861	-0.087517
C	0	1.561590	1.746541	-0.919403
C	0	2.305922	0.383915	-0.631800
C	0	2.801330	-0.322403	-1.901131
C	0	3.431990	0.459525	0.397772

C	0	2.012908	2.483452	-2.179434
C	0	1.560972	2.706221	0.278563
H	0	-4.235834	-2.697541	1.088304
H	0	-4.233560	-0.038961	1.086278
H	0	-1.749432	0.787638	1.518397
H	0	-2.063775	-0.202525	-1.002225
H	0	-0.335703	-2.547251	-0.321259
H	0	-1.956976	-2.585898	-1.029087
H	0	-1.742704	-3.525876	1.510044
H	0	-1.616588	-1.370437	3.073686
H	0	-0.184835	-1.369640	1.991645
H	0	2.007487	-0.397529	-2.650939
H	0	3.653915	0.198979	-2.348857
H	0	3.116461	-1.337774	-1.641407
H	0	4.235834	1.119027	0.050849
H	0	3.074137	0.824144	1.363271
H	0	3.856029	-0.538101	0.551045
H	0	1.890741	1.868281	-3.073686
H	0	1.410798	3.388530	-2.308878
H	0	3.064101	2.784541	-2.102392
H	0	2.553393	3.133300	0.457838
H	0	0.864812	3.525876	0.075466
H	0	1.230593	2.201719	1.192136

B3LYP/6-31G* Energy + ZPE = -683.083786
B3LYP/6-31G* Free energy = -683.125973
B3LYP/6-31G* Free energy in DCM = -683.402092
B3LYP/6-31G* Free energy in Tol = -683.399949
Number of imaginary frequencies = 0

Diels-Alder reaction of 2-methyl-2,4-pentanediol vinylboronate (6) with cyclopentadiene (9)

***Re endo* transition structure (TS-6+9-ReN)**
B3LYP/6-31G* Geometry

C	0	-1.843233	-0.739515	-2.252258
C	0	-0.605723	-0.077536	-2.214754
C	0	-0.824973	1.292877	-2.085450
C	0	-2.872055	0.206876	-2.098215
C	0	-2.262672	1.546751	-2.462991
H	0	-1.976501	-1.816370	-2.241665
H	0	0.362310	-0.566175	-2.173213
H	0	-0.053810	2.054949	-2.100256
H	0	-3.918185	-0.020476	-2.284205
H	0	-2.730644	2.424049	-2.013153
H	0	-2.317890	1.658739	-3.560010
C	0	-1.659154	1.339838	0.183554
C	0	-2.827153	0.599065	-0.034701
B	0	-0.369260	0.744946	0.789612
O	0	-0.285229	-0.619323	0.971294
O	0	0.649914	1.600078	1.148355
C	0	0.902326	-1.215605	1.500452
C	0	1.620003	-0.232095	2.427425
C	0	1.868724	1.134021	1.758727
C	0	2.251290	2.184250	2.806272
C	0	2.944639	1.059766	0.664940
C	0	0.505066	-2.509461	2.201949
H	0	-1.735947	2.425443	0.140036
H	0	-3.790050	1.107204	-0.046749
H	0	-2.872245	-0.424601	0.324551
H	0	1.558183	-1.465225	0.652673
H	0	2.570919	-0.661891	2.766022
H	0	0.996133	-0.080023	3.318839
H	0	3.186247	1.914451	3.310602
H	0	2.382114	3.161612	2.330127
H	0	1.462270	2.275402	3.560010
H	0	2.686659	0.324108	-0.104010
H	0	3.041623	2.034552	0.176195
H	0	3.918185	0.786667	1.088543
H	0	-0.038102	-3.161612	1.510634
H	0	1.390305	-3.044960	2.563794
H	0	-0.148286	-2.297251	3.055652

B3LYP/6-31G* Energy + ZPE = -683.033027
B3LYP/6-31G* Free energy = -683.076256
B3LYP/6-31G* Free energy in DCM = -683.346328
B3LYP/6-31G* Free energy in Tol = -683.343923
Number of imaginary frequencies = 1 (-459.03)

***Si endo* transition structure (TS-6+9-SiN)**
B3LYP/6-31G* Geometry

C	0	-1.297656	2.119057	0.754067
C	0	-2.534820	1.582808	1.145663
C	0	-3.351827	1.442424	0.010007
C	0	-1.322564	2.369529	-0.616832
C	0	-2.770634	2.371379	-1.038148
H	0	-0.426615	2.209651	1.394231
H	0	-2.763812	1.195408	2.133141
H	0	-4.416158	1.231838	0.068290
H	0	-0.530298	2.849749	-1.180305
H	0	-3.180441	3.381594	-0.863381
H	0	-2.968994	2.104949	-2.077674
C	0	-2.569692	-0.284218	-0.906417
C	0	-1.329581	0.097205	-1.431946
B	0	0.024777	-0.284616	-0.793128
O	0	1.181415	-0.035296	-1.501417
O	0	0.036041	-0.883488	0.447340
C	0	2.460583	-0.378653	-0.960341
C	0	2.332183	-1.556682	0.008169
C	0	1.252271	-1.322186	1.082324
C	0	0.911766	-2.632682	1.798865
C	0	1.670445	-0.254206	2.103897
C	0	3.398952	-0.671161	-2.125922
H	0	-3.426279	-0.389120	-1.570139
H	0	-2.590876	-0.948323	-0.047630
H	0	-1.308186	0.465434	-2.456792
H	0	2.840066	0.501034	-0.419186
H	0	3.299619	-1.754801	0.485756
H	0	2.065408	-2.452050	-0.569948
H	0	0.113481	-2.466379	2.529818
H	0	0.564481	-3.381594	1.079521
H	0	1.786892	-3.032333	2.323874
H	0	0.852002	-0.078032	2.809227
H	0	2.551872	-0.577454	2.669937
H	0	1.905526	0.698166	1.617520

H	0	3.050436	-1.545175	-2.687535
H	0	3.429056	0.183423	-2.809227
H	0	4.416158	-0.868210	-1.768386

B3LYP/6-31G* Energy + ZPE = -683.032867
B3LYP/6-31G* Free energy = -683.076002
B3LYP/6-31G* Free energy in DCM = -683.346965
B3LYP/6-31G* Free energy in Tol = -683.344644
Number of imaginary frequencies = 1 (-460.73)

***Re exo* transition structure (TS-6+9-*Re*X)**
B3LYP/6-31G* Geometry

C	0	2.086354	2.354449	-1.809048
C	0	2.946974	2.608782	-0.728577
C	0	0.805308	2.099721	-1.321021
C	0	2.228147	2.456914	0.470341
C	0	0.763686	2.586093	0.104049
H	0	2.392616	2.260441	-2.846167
H	0	4.021479	2.744199	-0.802370
H	0	-0.075815	1.953752	-1.936266
H	0	2.611703	2.767177	1.438394
H	0	0.509556	3.660578	0.097287
H	0	0.060824	2.071314	0.759560
C	0	1.330953	-0.077008	-0.419866
C	0	2.116839	0.351861	0.656271
B	0	-0.152954	-0.493222	-0.296852
O	0	-0.839014	-0.216901	0.869986
O	0	-0.744713	-1.143358	-1.356286
C	0	-2.212976	-0.589548	1.027919
C	0	-2.109899	-1.601684	-1.314449
C	0	-2.537419	-1.801772	0.152593
C	0	-2.978809	-0.562814	-2.038915
C	0	-2.136963	-2.934163	-2.069329
C	0	-2.461779	-0.844964	2.510009
H	0	1.849440	-0.389122	-1.323787
H	0	1.672856	0.369838	1.649367
H	0	3.187887	0.170186	0.653144
H	0	-2.827996	0.265965	0.711922
H	0	-2.006845	-2.674391	0.557627
H	0	-3.610755	-2.022210	0.204156
H	0	-4.021479	-0.895957	-2.099234
H	0	-2.957290	0.405779	-1.528582
H	0	-2.603919	-0.413658	-3.056535
H	0	-3.151076	-3.348853	-2.098595
H	0	-1.789160	-2.792044	-3.097806
H	0	-1.477037	-3.660578	-1.583783
H	0	-3.519596	-1.064044	2.695052
H	0	-1.862792	-1.693985	2.857852
H	0	-2.180997	0.034792	3.097806

B3LYP/6-31G* Energy + ZPE = -683.033963
B3LYP/6-31G* Free energy = -683.077260
B3LYP/6-31G* Free energy in DCM = -683.347381
B3LYP/6-31G* Free energy in Tol = -683.345089
Number of imaginary frequencies = 1 (-457.42)

***Si exo* transition structure (TS-6+9-SiX)**
B3LYP/6-31G* Geometry

C	0	-3.707973	-0.801415	-1.763645
C	0	-3.089095	0.352618	-2.272254
C	0	-2.280331	0.909599	-1.282427
C	0	-3.247922	-1.024220	-0.453924
C	0	-2.695675	0.300371	0.030920
H	0	-4.316851	-1.490730	-2.340267
H	0	-3.143610	0.691495	-3.302026
H	0	-1.751441	1.852365	-1.371031
H	0	-3.699396	-1.745242	0.221906
H	0	-1.917333	0.243095	0.792002
H	0	-3.536161	0.890199	0.436991
C	0	-0.582112	-0.803034	-1.385148
C	0	-1.319508	-1.833093	-0.790140
B	0	0.474611	0.049985	-0.645498
O	0	0.540889	0.011250	0.732662
O	0	1.336992	0.816997	-1.398225
C	0	1.529827	0.752196	1.475992
C	0	2.750406	1.012632	0.572701
C	0	2.359716	1.606303	-0.782683
C	0	1.916925	-0.129177	2.666933
C	0	0.879826	2.054537	1.966328
C	0	3.533493	1.691726	-1.751907
H	0	-0.543385	-0.781974	-2.472133
H	0	-1.133300	-2.069628	0.255383
H	0	-1.645693	-2.681560	-1.384947
H	0	3.268236	0.059435	0.398687
H	0	3.458133	1.678222	1.082063
H	0	1.954829	2.618702	-0.635421
H	0	2.339959	-1.077149	2.318664
H	0	2.657038	0.370844	3.302026
H	0	1.033014	-0.352528	3.273583
H	0	-0.002178	1.824423	2.572844
H	0	1.578550	2.634377	2.580497
H	0	0.556407	2.681560	1.129146
H	0	3.198096	2.086845	-2.715934
H	0	4.316851	2.349713	-1.358429
H	0	3.963632	0.698226	-1.920969

B3LYP/6-31G* Energy + ZPE = -683.033873
B3LYP/6-31G* Free energy = -683.077194
B3LYP/6-31G* Free energy in DCM = -683.348160
B3LYP/6-31G* Free energy in Tol = -683.345650
Number of imaginary frequencies = 1 (-456.70)

***Re endo* product (P-6+9-*Re*N)**
B3LYP/6-31G* Geometry

C	0	-0.266770	-1.576179	-2.324435
C	0	0.851032	-1.227331	-1.670676
C	0	1.126211	0.237181	-1.986554
C	0	0.009972	1.072743	-1.241827
C	0	-1.286999	0.656614	-2.016869
C	0	-0.750128	-0.352030	-3.090763
C	0	0.607616	0.301812	-3.441953
B	0	-0.008665	0.882125	0.328855
O	0	-1.210384	0.847891	0.988809

O	0	1.193388	0.790008	0.984135
C	0	-1.274737	0.713809	2.416328
C	0	0.007900	1.244691	3.059918
C	0	1.278289	0.652813	2.420020
C	0	2.518102	1.440793	2.850896
C	0	1.454987	-0.838504	2.738309
C	0	-2.526105	1.438504	2.897369
H	0	-0.812913	-2.511511	-2.243628
H	0	1.406580	-1.819898	-0.950397
H	0	2.142258	0.587678	-1.794510
H	0	0.214453	2.137442	-1.438026
H	0	-1.753905	1.519864	-2.505956
H	0	-2.040042	0.201053	-1.368165
H	0	-1.442678	-0.541971	-3.915233
H	0	0.513595	1.325067	-3.827087
H	0	1.202707	-0.300438	-4.136667
H	0	-1.381838	-0.357336	2.638068
H	0	-0.002045	1.035953	4.136667
H	0	0.031355	2.336846	2.942120
H	0	2.666276	1.376000	3.934803
H	0	3.409302	1.043936	2.353823
H	0	2.415248	2.495754	2.576093
H	0	0.592863	-1.425520	2.405466
H	0	2.340525	-1.223859	2.222897
H	0	1.585111	-0.996453	3.815226
H	0	-3.409302	1.049158	2.381400
H	0	-2.664145	1.302203	3.976077
H	0	-2.452809	2.511511	2.687765

B3LYP/6-31G* Energy + ZPE = -683.086442
B3LYP/6-31G* Free energy = -683.129379
B3LYP/6-31G* Free energy in DCM = -683.404941
B3LYP/6-31G* Free energy in Tol = -683.403234
Number of imaginary frequencies = 0

***Si endo* product (P-6+9-SiN)**
B3LYP/6-31G* Geometry

C	0	0.485022	0.147508	2.661609
C	0	0.001357	1.309668	3.124421
C	0	1.019682	2.392776	2.794831
C	0	0.959906	2.594429	1.240230
C	0	1.521850	1.241303	0.685223
C	0	1.831549	0.439717	2.012283
C	0	2.331030	1.582408	2.926260
B	0	0.613105	0.460057	-0.347679
O	0	0.848291	-0.881635	-0.524299
O	0	-0.347205	1.136404	-1.053175
C	0	0.088708	-1.652846	-1.466105
C	0	-0.442262	-0.753673	-2.584222
C	0	-1.175769	0.489180	-2.044982
C	0	-1.387434	1.517763	-3.158970
C	0	-2.513566	0.138456	-1.379444
C	0	0.982371	-2.775271	-1.980385
H	0	-0.019741	-0.813335	2.632689
H	0	-0.982070	1.492426	3.547646
H	0	0.942518	3.318500	3.371484
H	0	1.590682	3.440534	0.942464
H	0	-0.055636	2.805467	0.894334
H	0	2.486211	1.433583	0.188363
H	0	2.491324	-0.417873	1.866585
H	0	2.528249	1.255498	3.952778
H	0	3.210009	2.106217	2.529867
H	0	-0.754578	-2.098301	-0.919493
H	0	-1.109828	-1.327396	-3.238700
H	0	0.407195	-0.422783	-3.197661
H	0	-1.866323	2.416619	-2.757087
H	0	-0.427566	1.809799	-3.597519
H	0	-2.023297	1.109668	-3.952778
H	0	-2.967148	1.043038	-0.962234
H	0	-3.210009	-0.295150	-2.106474
H	0	-2.380622	-0.576102	-0.560793
H	0	1.836971	-2.364160	-2.529331
H	0	1.366260	-3.366009	-1.142795
H	0	0.424924	-3.440534	-2.649614

B3LYP/6-31G* Energy + ZPE = -683.086461
B3LYP/6-31G* Free energy = -683.128909
B3LYP/6-31G* Free energy in DCM = -683.404725
B3LYP/6-31G* Free energy in Tol = -683.402930
Number of imaginary frequencies = 0

***Re exo* product (P-6+9-*Re*X)**
B3LYP/6-31G* Geometry

C	0	3.520262	0.813325	-1.410824
C	0	3.520262	2.154297	-1.410824
C	0	2.069933	0.356291	-1.410824
C	0	2.069637	2.609958	-1.409005
C	0	1.503453	0.699256	0.040612
C	0	1.423192	1.483092	-2.248367
C	0	1.489141	2.263736	0.008439
B	0	0.110621	-0.003742	0.300780
O	0	-1.048947	0.609246	-0.107172
O	0	0.115221	-1.235374	0.904201
C	0	-2.327303	-0.021297	0.063680
C	0	-1.099279	-1.977512	1.153560
C	0	-2.283749	-0.996176	1.241888
C	0	-1.265824	-2.997490	0.018652
C	0	-0.891671	-2.695879	2.489520
C	0	-3.369893	1.076323	0.237251
H	0	4.375496	0.153642	-1.296657
H	0	4.377379	2.811984	-1.299739
H	0	1.892045	-0.673692	-1.731919
H	0	1.884939	3.639479	-1.727316
H	0	2.214892	0.324877	0.785109
H	0	1.761050	1.482055	-3.289903
H	0	0.328693	1.483845	-2.207053
H	0	0.470270	2.655717	0.095747
H	0	2.087573	2.703359	0.813020
H	0	-2.546511	-0.571293	-0.862523
H	0	-2.192305	-0.416335	2.170550
H	0	-3.227362	-1.552421	1.298864
H	0	-2.136830	-3.639479	0.193767
H	0	-1.391507	-2.504238	-0.950715
H	0	-0.375444	-3.631311	-0.041842
H	0	-1.770299	-3.295878	2.752185
H	0	-0.022584	-3.359157	2.430475

H	0	-0.713366	-1.970291	3.289903
H	0	-4.377379	0.649221	0.297755
H	0	-3.177084	1.646937	1.152573
H	0	-3.335354	1.767513	-0.610681

B3LYP/6-31G* Energy + ZPE = -683.086745
B3LYP/6-31G* Free energy = -683.129320
B3LYP/6-31G* Free energy in DCM = -683.405649
B3LYP/6-31G* Free energy in Tol = -683.403696
Number of imaginary frequencies = 0

***Si exo* product (P-6+9-SiX)**
B3LYP/6-31G* Geometry

C	0	-3.338043	-2.248444	1.363663
C	0	-2.763855	-1.415268	2.243607
C	0	-1.291763	-1.306564	1.877182
C	0	-1.237045	-0.466873	0.522446
C	0	-1.890945	-1.463440	-0.490540
C	0	-2.256851	-2.705826	0.396942
C	0	-1.033463	-2.734039	1.342728
B	0	0.237061	-0.000412	0.187622
O	0	1.059418	-0.806839	-0.558212
O	0	0.654633	1.205292	0.694153
C	0	2.422318	-0.443481	-0.875610
C	0	2.562897	1.089203	-0.812256
C	0	1.992615	1.677734	0.479874
C	0	2.677689	-0.953384	-2.296280
C	0	3.343200	-1.158310	0.122757
C	0	1.954895	3.201218	0.472748
H	0	-4.396606	-2.467728	1.259735
H	0	-3.257126	-0.813980	3.001785
H	0	-0.628113	-0.936310	2.663284
H	0	-1.852203	0.431030	0.650223
H	0	-1.181396	-1.761292	-1.269577
H	0	-2.772583	-1.040695	-0.983246
H	0	-2.469650	-3.614456	-0.172607
H	0	-0.078552	-2.837463	0.815689
H	0	-1.116882	-3.498459	2.122253
H	0	2.022644	1.528076	-1.662292
H	0	3.617294	1.372452	-0.917419
H	0	2.598465	1.345383	1.334839
H	0	1.984787	-0.483215	-3.001800
H	0	3.702637	-0.730865	-2.613708
H	0	2.527252	-2.037003	-2.340988
H	0	3.167511	-2.237961	0.081772
H	0	4.396591	-0.969910	-0.114487
H	0	3.157608	-0.827591	1.149734
H	0	1.508209	3.572113	1.400467
H	0	2.965973	3.614471	0.382767
H	0	1.352585	3.565918	-0.366776

B3LYP/6-31G* Energy + ZPE = -683.086654
B3LYP/6-31G* Free energy = -683.129374
B3LYP/6-31G* Free energy in DCM = -683.406098
B3LYP/6-31G* Free energy in Tol = -683.403930
Number of imaginary frequencies = 0

Diels-Alder reaction of (-)-dimethyl tartrate vinylboronate (7) with cyclopentadiene (9)

***Re endo* transition structure (TS-7+9-ReN)**
B3LYP/6-31G* Geometry

C	0	-0.146744	-2.888453	-2.866637
C	0	0.013133	-1.503112	-3.029096
C	0	-1.515465	-3.207109	-2.952389
C	0	-1.230407	-0.928596	-3.281237
C	0	-2.165501	-2.042098	-3.676125
H	0	0.636685	-3.577538	-2.567855
H	0	0.929713	-0.946929	-2.871273
H	0	-1.876048	-4.226276	-3.063032
H	0	-1.396942	0.120937	-3.492266
H	0	-3.224671	-1.879338	-3.470401
H	0	-2.055458	-2.215415	-4.760697
C	0	-2.252135	-1.255847	-1.071489
C	0	-2.227211	-2.657193	-1.074930
B	0	-1.186667	-0.387892	-0.415744
O	0	-1.270058	0.997493	-0.302943
O	0	-0.011596	-0.872244	0.152263
C	0	-0.047273	1.481227	0.205735
C	0	0.663678	0.197280	0.774333
C	0	0.504506	0.121519	2.293717
C	0	0.790589	2.096414	-0.915796
O	0	1.440066	0.893374	2.888207
O	0	-0.348987	-0.498371	2.880375
O	0	0.709619	1.810725	-2.088616
O	0	1.679153	2.971007	-0.403662
C	0	2.581639	3.565817	-1.354233
C	0	1.359635	0.963218	4.323223
H	0	-3.162839	-0.762931	-1.406356
H	0	-3.161665	-3.203696	-1.189784
H	0	-1.494496	-3.169382	-0.458687
H	0	-0.219961	2.235402	0.978579
H	0	1.730117	0.175199	0.529340
H	0	3.224671	4.226276	-0.772524
H	0	2.024121	4.132136	-2.104499
H	0	3.172329	2.794709	-1.855623
H	0	2.164649	1.631576	4.629211
H	0	1.495249	-0.029238	4.760697
H	0	0.389361	1.359544	4.633713

B3LYP/6-31G* Energy + ZPE = -981.531381
B3LYP/6-31G* Free energy = -981.582304
B3LYP/6-31G* Free energy in DCM = -981.823968
B3LYP/6-31G* Free energy in Tol = -981.817314
Number of imaginary frequencies = 1 (-445.70)

***Si endo* transition structure (TS-7+9-SiN)**
B3LYP/6-31G* Geometry

C	0	2.142366	0.989971	0.432244
C	0	2.089568	2.356950	0.737514
B	0	0.919213	0.082473	0.367281
O	0	-0.370374	0.465272	0.724477
O	0	0.948274	-1.228113	-0.095592

C	0	-1.248828	-0.620732	0.531451
C	0	-0.371835	-1.708605	-0.204436
C	0	-0.781373	-1.811820	-1.673338
C	0	-1.772265	-1.159026	1.861571
O	0	-0.316158	-1.156449	-2.574549
O	0	-1.784148	-2.704830	-1.809878
O	0	-2.934258	-1.812603	1.659262
O	0	-1.221418	-1.065734	2.934028
C	0	-3.504285	-2.438774	2.822889
C	0	-2.316224	-2.834443	-3.140653
H	0	3.066727	0.602849	0.007750
H	0	2.862825	3.016351	0.347514
H	0	1.119826	2.834422	0.840907
H	0	-2.104111	-0.310677	-0.076926
H	0	-0.460344	-2.694289	0.262499
H	0	-2.812255	-3.175350	3.239309
H	0	-4.417955	-2.921627	2.476276
H	0	-3.729382	-1.689279	3.585838
H	0	-2.705431	-1.875446	-3.492533
H	0	-3.116525	-3.570751	-3.065207
H	0	-1.539796	-3.177814	-3.829071
C	0	1.650693	2.031882	3.428947
C	0	1.661086	0.628628	3.369964
C	0	2.748186	2.534836	2.706358
C	0	2.792860	0.217529	2.669679
C	0	3.737765	1.389563	2.606794
H	0	0.839266	2.631305	3.829071
H	0	0.851156	-0.015292	3.690582
H	0	3.070918	3.570751	2.767291
H	0	3.096365	-0.812176	2.516787
H	0	4.417955	1.414845	1.753808
H	0	4.349730	1.389905	3.525368

B3LYP/6-31G* Energy + ZPE = -981.531152
B3LYP/6-31G* Free energy = -981.583027
B3LYP/6-31G* Free energy in DCM = -981.823637
B3LYP/6-31G* Free energy in Tol = -981.817120
Number of imaginary frequencies = 1 (-447.82)

***Re exo* transition structure (TS-7+9-ReX)**
B3LYP/6-31G* Geometry

C	0	3.172743	-2.592774	2.455007
C	0	3.052871	-1.217951	2.717270
C	0	1.898102	-3.116289	2.167195
C	0	1.706857	-0.859662	2.678830
C	0	0.902878	-2.130135	2.746235
H	0	4.109734	-3.129479	2.343292
H	0	3.881897	-0.526781	2.831071
H	0	1.694039	-4.182654	2.120259
H	0	1.302921	0.122875	2.895137
H	0	0.756079	-2.385762	3.809909
H	0	-0.077355	-2.096415	2.269873
C	0	1.550150	-1.098650	0.229921
C	0	1.587832	-2.499059	0.194237
B	0	0.273645	-0.267632	0.222525
O	0	0.243307	1.111477	0.045657
O	0	-1.013816	-0.785425	0.374217
C	0	-1.077388	1.562547	0.273517
C	0	-1.940665	0.262153	0.161732
C	0	-2.646826	0.198006	-1.196910
C	0	-1.191529	2.168462	1.673511
O	0	-2.374105	-0.918512	-1.882241
O	0	-3.382409	1.083814	-1.578328
O	0	-2.259268	2.985403	1.738125
O	0	-0.461431	1.922166	2.606977
C	0	-2.519190	3.569480	3.027834
C	0	-3.023569	-1.024316	-3.162840
H	0	2.481822	-0.565663	0.055987
H	0	0.653342	-3.042124	0.068657
H	0	2.447704	-3.001485	-0.239978
H	0	-1.375378	2.306232	-0.468814
H	0	-2.728398	0.227553	0.922797
H	0	-1.671787	4.182559	3.344776
H	0	-2.693966	2.789156	3.773172
H	0	-3.410429	4.182654	2.895346
H	0	-2.727249	-0.194872	-3.809909
H	0	-4.109734	-1.012007	-3.041431
H	0	-2.691548	-1.975745	-3.577834

B3LYP/6-31G* Energy + ZPE = -981.532296
B3LYP/6-31G* Free energy = -981.583439
B3LYP/6-31G* Free energy in DCM = -981.823936
B3LYP/6-31G* Free energy in Tol = -981.817888
Number of imaginary frequencies = 1 (-440.72)

***Si exo* transition structure (TS-7+9-SiX)**
B3LYP/6-31G* Geometry

C	0	3.169304	-2.236794	-2.722004
C	0	3.214635	-0.850699	-2.498803
C	0	1.832542	-2.621028	-2.940647
C	0	1.932723	-0.324590	-2.644790
C	0	1.093004	-1.360024	-3.339041
H	0	4.004832	-2.918468	-2.596743
H	0	4.087555	-0.296898	-2.168085
H	0	1.554763	-3.599751	-3.322662
H	0	1.669133	0.725488	-2.600079
H	0	1.217799	-1.223576	-4.427134
H	0	0.026814	-1.323356	-3.120373
C	0	1.117892	-1.326819	-0.540781
C	0	1.047275	-2.646723	-1.008325
B	0	-0.059445	-0.361031	-0.506265
O	0	-0.030005	0.882165	0.120433
O	0	-1.308899	-0.611206	-1.071921
C	0	-1.336521	1.422667	0.095086
C	0	-2.083225	0.570116	-0.981947
C	0	-2.099964	1.293221	-2.328912
C	0	-2.062144	1.352863	1.443859
O	0	-3.129317	2.159874	-2.374618
O	0	-1.287125	1.147172	-3.213553
O	0	-1.256854	1.012884	2.456750
O	0	-3.243329	1.606984	1.552323
C	0	-3.220805	2.955003	-3.570920
C	0	-1.888274	0.956587	3.749271
H	0	2.003158	-1.041575	0.022685
H	0	0.078194	-3.042460	-1.305279
H	0	1.718827	-3.396105	-0.598670

H	0	-1.297529	2.483310	-0.179552
H	0	-3.107698	0.347661	-0.675300
H	0	-2.313954	3.550266	-3.705552
H	0	-4.087555	3.599751	-3.426265
H	0	-3.359063	2.312591	-4.444296
H	0	-2.303220	1.932561	4.013891
H	0	-1.099092	0.670570	4.444296
H	0	-2.691554	0.215452	3.748982

B3LYP/6-31G* Energy + ZPE = -981.532162
B3LYP/6-31G* Free energy = -981.583868
B3LYP/6-31G* Free energy in DCM = -981.824608
B3LYP/6-31G* Free energy in Tol = -981.818552
Number of imaginary frequencies = 1 (-441.15)

Diels-Alder reaction of methanol alkynylboronate (8) with cyclopentadiene (9)

Transition structure (TS-8+9)
B3LYP/6-31G* Geometry

C	0	1.062245	-1.760220	-0.368855
C	0	1.062245	-0.507822	-0.368855
B	0	1.108792	1.012855	-0.368855
O	0	1.270462	1.768817	0.766172
O	0	1.011534	1.667754	-1.570213
C	0	1.073995	3.086585	-1.621202
C	0	1.379329	1.214384	2.066380
H	0	1.707493	-2.621564	-0.330250
H	0	2.033757	3.459246	-1.244399
H	0	0.961223	3.380600	-2.668801
H	0	0.273569	3.546732	-1.029368
H	0	0.519202	1.530372	2.668801
H	0	1.415507	0.120295	2.042506
H	0	2.292071	1.595137	2.538522
C	0	-1.554817	-0.369759	-0.439204
C	0	-0.754306	-2.545018	-0.546503
C	0	-1.307329	-2.310126	0.729745
C	0	-1.733397	-0.968350	0.797659
C	0	-1.313791	-1.457634	-1.450030
H	0	-1.826114	0.646732	-0.699663
H	0	-0.558065	-3.546732	-0.920845
H	0	-1.262258	-2.997027	1.568355
H	0	-2.065396	-0.463584	1.699334
H	0	-2.292071	-1.804509	-1.827499
H	0	-0.693939	-1.183493	-2.302783

B3LYP/6-31G* Energy + ZPE = -525.829897
B3LYP/6-31G* Free energy = -525.871607
B3LYP/6-31G* Free energy in DCM = -526.028934
B3LYP/6-31G* Free energy in Tol = -526.02588
Number of imaginary frequencies = 1 (-427.58)

Product (P-8+9)
B3LYP/6-31G* Geometry

C	0	0.411950	-2.033125	0.392427
C	0	0.332667	-0.690952	0.295110
C	0	1.809337	-0.216148	0.118924
C	0	1.890491	-2.451260	0.288793
C	0	2.365611	-2.086728	-1.133290
C	0	2.315355	-0.754935	-1.230931
C	0	2.509543	-1.243271	1.056321
B	0	-0.877110	0.286819	0.239172
O	0	-2.173111	0.023729	0.603247
O	0	-0.602486	1.552229	-0.209276
C	0	-1.625480	2.535411	-0.299288
C	0	-2.623867	-1.206994	1.137693
H	0	-0.401686	-2.746216	0.466382
H	0	1.976153	0.845590	0.301218
H	0	2.128417	-3.459939	0.633282
H	0	2.618249	-2.810462	-1.900321
H	0	2.521022	-0.138837	-2.099240
H	0	3.602659	-1.212532	0.998569
H	0	2.180523	-1.176351	2.099240
H	0	-1.161103	3.459939	-0.653812
H	0	-2.408620	2.231754	-1.003511
H	0	-2.092577	2.715169	0.675785
H	0	-2.737694	-1.960872	0.348247
H	0	-1.936685	-1.593849	1.898774
H	0	-3.602659	-1.033583	1.595179

B3LYP/6-31G* Energy + ZPE = -525.891828
B3LYP/6-31G* Free energy = -525.93063
B3LYP/6-31G* Free energy in DCM = -526.095613
B3LYP/6-31G* Free energy in Tol = -526.093705
Number of imaginary frequencies = 0

Diels-Alder reaction of vinylboronate de pinacol (5) with 1,3-cyclohexadiene (10)

***Endo* transition structure (TS-5+10-N)**
B3LYP/6-31G* Geometry

C	0	0.451511	-2.651123	-1.860780
C	0	1.042613	-1.381928	-1.740829
C	0	-0.859499	-2.731445	-2.330881
C	0	0.337448	-0.274798	-2.173710
C	0	-1.309091	-1.780293	-3.430534
C	0	-0.600635	-0.395349	-3.355306
H	0	0.900750	-3.503181	-1.355571
H	0	1.935258	-1.261422	-1.132187
H	0	-1.342371	-3.707710	-2.341747
H	0	0.702154	0.723936	-1.945361
H	0	-2.399185	-1.664966	-3.407430
H	0	-1.076241	-2.251646	-4.394134
H	0	0.006291	-0.253607	-4.261838
H	0	-1.327400	0.423005	-3.356013
C	0	-1.918717	-1.850612	-0.718192
C	0	-1.591428	-0.495824	-0.622191
B	0	-0.728039	0.086654	0.507105
O	0	-0.108970	-0.678526	1.478561
O	0	-0.524354	1.442330	0.700015
C	0	0.716453	0.202380	2.283564
C	0	0.065097	1.615902	2.013777

C	0	-1.085548	1.947041	2.975649
C	0	1.046366	2.786116	1.955377
C	0	0.656583	-0.275687	3.734355
C	0	2.153709	0.083946	1.756771
H	0	-2.858331	-2.141225	-1.184500
H	0	-1.584814	-2.523353	0.066741
H	0	-2.168895	0.201723	-1.226513
H	0	-1.807254	1.125711	3.027158
H	0	-0.723711	2.156331	3.988098
H	0	-1.610648	2.833759	2.607011
H	0	0.503085	3.707710	1.722260
H	0	1.550543	2.925405	2.918828
H	0	1.805080	2.640102	1.183073
H	0	-0.372649	-0.342387	4.094215
H	0	1.104413	-1.271952	3.810882
H	0	1.215415	0.398263	4.394134
H	0	2.228809	0.427729	0.720642
H	0	2.858331	0.662077	2.364370
H	0	2.456071	-0.967656	1.787576

B3LYP/6-31G* Energy + ZPE = -722.311779
B3LYP/6-31G* Free energy = -722.355824
B3LYP/6-31G* Free energy in DCM = -722.654772
B3LYP/6-31G* Free energy in Tol = -722.652348
Number of imaginary frequencies = 1 (-469.22)

***Exo* transition structure (TS-5+10-X)**
B3LYP/6-31G* Geometry

C	0	3.360734	-1.762389	-0.887289
C	0	3.290328	-0.359083	-0.945367
C	0	2.169720	-2.487613	-0.925997
C	0	2.060178	0.237814	-1.147100
C	0	1.037134	-2.008075	-1.821046
C	0	1.022467	-0.462553	-1.996821
H	0	4.278361	-2.240921	-0.551190
H	0	4.143966	0.236777	-0.628473
H	0	2.216448	-3.565866	-0.778571
H	0	1.961196	1.316030	-1.042285
H	0	1.168039	-2.481352	-2.803194
H	0	0.073831	-2.359122	-1.436928
H	0	1.248267	-0.214371	-3.044376
H	0	0.022904	-0.067892	-1.799650
C	0	1.323034	-1.926609	0.957453
C	0	1.170202	-0.537665	1.023908
B	0	-0.191176	0.165216	0.897096
O	0	-1.316285	-0.399645	0.319745
O	0	-0.436355	1.433037	1.386339
C	0	-2.453892	0.438746	0.656687
C	0	-1.769670	1.827679	0.972086
C	0	-2.411180	2.624239	2.108291
C	0	-1.604900	2.724279	-0.263668
C	0	-3.421637	0.442008	-0.525552
C	0	-3.125611	-0.201122	1.880230
H	0	0.440068	-2.541964	0.798803
H	0	2.100432	-2.407250	1.544625
H	0	1.961197	0.022895	1.516374
H	0	-3.443793	2.898320	1.862791
H	0	-2.412223	2.061275	3.044376
H	0	-1.845918	3.547391	2.272214
H	0	-0.954609	3.565866	-0.005152
H	0	-1.139150	2.182278	-1.092936
H	0	-2.565038	3.123983	-0.607260
H	0	-2.935549	0.771851	-1.446583
H	0	-3.802412	-0.571301	-0.689873
H	0	-4.278361	1.097049	-0.329236
H	0	-4.033557	0.336421	2.173729
H	0	-3.399915	-1.231909	1.634759
H	0	-2.445477	-0.228862	2.737273

B3LYP/6-31G* Energy + ZPE = -722.310849
B3LYP/6-31G* Free energy = -722.354971
B3LYP/6-31G* Free energy in DCM = -722.653574
B3LYP/6-31G* Free energy in Tol = -722.651144
Number of imaginary frequencies = 1 (-473.20)

***Endo* product (P-5+10-N)**
B3LYP/6-31G* Geometry

C	0	0.597336	-2.000229	-2.267715
C	0	0.684006	-0.663696	-2.245377
C	0	-0.816559	-2.532242	-2.202011
C	0	-0.650146	0.044098	-2.158203
C	0	-1.472168	-2.004166	-0.895020
C	0	-1.610062	-1.945511	-3.403458
C	0	-1.373642	-0.445053	-0.857010
C	0	-1.504715	-0.394882	-3.379227
B	0	-0.690750	0.121155	0.445328
O	0	-0.161880	1.389420	0.530807
O	0	-0.579193	-0.577530	1.624435
C	0	0.550171	1.492477	1.795059
C	0	-0.117111	0.345093	2.650452
C	0	0.829269	-0.406982	3.584671
C	0	-1.363037	0.803100	3.420700
C	0	2.032394	1.240067	1.486800
C	0	0.362961	2.906921	2.341537
H	0	1.456116	-2.664688	-2.330765
H	0	1.620682	-0.113129	-2.291580
H	0	-0.845947	-3.627090	-2.224365
H	0	-0.536255	1.131546	-2.138107
H	0	-2.519669	-2.330063	-0.860657
H	0	-0.974777	-2.450714	-0.028244
H	0	-2.656479	-2.269211	-3.336166
H	0	-1.211365	-2.349030	-4.340622
H	0	-2.392288	-0.023773	-0.883636
H	0	-1.045959	-0.021606	-4.301712
H	0	-2.498886	0.064636	-3.309631
H	0	1.650833	-0.873459	3.036484
H	0	1.250351	0.265869	4.340622
H	0	0.279404	-1.198135	4.104630
H	0	-1.879761	-0.077576	3.814468
H	0	-1.103348	1.455215	4.261307
H	0	-2.059600	1.338943	2.768082
H	0	2.367828	1.966782	0.740234
H	0	2.656494	1.350754	2.379883
H	0	2.187622	0.238144	1.074600
H	0	0.821167	3.627106	1.656036
H	0	-0.693420	3.165482	2.443069

H	0	0.845779	3.016663	3.319534

B3LYP/6-31G* Energy + ZPE = -722.382553
B3LYP/6-31G* Free energy = -722.425960
B3LYP/6-31G* Free energy in DCM = -722.730500
B3LYP/6-31G* Free energy in Tol = -722.728556
Number of imaginary frequencies = 0

***Exo* product (P-5+10-X)**
B3LYP/6-31G* Geometry

C	0	3.471815	-1.878015	-0.663121
C	0	3.444332	-0.539592	-0.641474
C	0	2.108438	-2.524806	-0.748445
C	0	2.056387	0.055774	-0.700833
C	0	1.256463	-2.053571	0.465032
C	0	1.406171	-2.003573	-2.033243
C	0	1.248181	-0.495668	0.535153
C	0	1.376830	-0.449131	-2.005057
B	0	-0.179417	0.164987	0.625344
O	0	-1.354522	-0.445881	0.252307
O	0	-0.372983	1.451909	1.073537
C	0	-2.456851	0.412187	0.662607
C	0	-1.754252	1.819774	0.802699
C	0	-2.257493	2.686910	1.955770
C	0	-1.747410	2.634183	-0.498412
C	0	-3.552410	0.331395	-0.398961
C	0	-2.973935	-0.147831	1.994811
H	0	4.384583	-2.467897	-0.621726
H	0	4.330859	0.087548	-0.578976
H	0	2.169676	-3.618338	-0.765875
H	0	2.074966	1.150031	-0.677321
H	0	0.239318	-2.447892	0.354674
H	0	1.665308	-2.475725	1.390012
H	0	1.937788	-2.367348	-2.919332
H	0	0.388309	-2.410310	-2.076776
H	0	1.801638	-0.169354	1.425671
H	0	1.903692	-0.033223	-2.870691
H	0	0.344127	-0.082513	-2.053653
H	0	-3.313988	2.945519	1.819769
H	0	-2.142372	2.185449	2.919332
H	0	-1.683350	3.618338	1.990739
H	0	-1.079046	3.492030	-0.375043
H	0	-1.380517	2.041011	-1.342078
H	0	-2.745965	3.009047	-0.747167
H	0	-3.175124	0.591606	-1.390482
H	0	-3.943273	-0.690178	-0.444890
H	0	-4.384583	1.001608	-0.154392
H	0	-3.850161	0.402781	2.353163
H	0	-3.259110	-1.194816	1.852604
H	0	-2.200755	-0.111145	2.768727

B3LYP/6-31G* Energy + ZPE = -722.381966
B3LYP/6-31G* Free energy = -722.425769
B3LYP/6-31G* Free energy in DCM = -722.729723
B3LYP/6-31G* Free energy in Tol = -722.727700
Number of imaginary frequencies = 0

Diels-Alder reaction of pinacol vinylboronate (2) with *trans*-piperylene (11)

***Ortho endo* transition structure (TS-5+11-ON)**
B3LYP/6-31G* Geometry

C	0	-0.911817	-1.391038	3.158740
C	0	-0.692019	-0.014802	2.985724
C	0	0.562821	0.558678	2.929269
C	0	0.135782	-2.312408	3.245514
C	0	0.798999	2.016794	2.657440
H	0	-1.920598	-1.765621	2.994505
H	0	-1.550654	0.612081	2.746402
H	0	1.403453	0.020735	3.352787
H	0	-0.116977	-3.365154	3.356544
H	0	1.035519	-2.032409	3.786948
H	0	1.222989	2.514164	3.541337
H	0	-0.132719	2.531266	2.396154
H	0	1.503236	2.162235	1.830397
C	0	1.556647	-1.015510	1.115982
C	0	1.072276	-2.288333	1.455873
B	0	0.896038	-0.144859	0.042439
O	0	-0.275460	-0.489675	-0.609950
O	0	1.431091	1.041032	-0.436918
C	0	-0.662258	0.622822	-1.454719
C	0	0.701305	1.399293	-1.639242
C	0	1.534206	0.893450	-2.826300
C	0	0.580141	2.921631	-1.700016
C	0	-1.269143	0.063150	-2.741499
C	0	-1.722446	1.424944	-0.686998
H	0	2.549995	-0.742858	1.470980
H	0	1.787341	-3.043728	1.780018
H	0	0.257815	-2.690117	0.858633
H	0	1.091529	1.178006	-3.786948
H	0	2.536131	1.329869	-2.765846
H	0	1.639824	-0.195726	-2.800655
H	0	-0.007217	3.234584	-2.571117
H	0	0.110718	3.326118	-0.800311
H	0	1.577330	3.365154	-1.788311
H	0	-0.586755	-0.627335	-3.242250
H	0	-2.187490	-0.483994	-2.504696
H	0	-1.525637	0.869294	-3.438825
H	0	-2.549995	0.757218	-0.427477
H	0	-1.314993	1.832914	0.242597
H	0	-2.120524	2.251073	-1.285990

B3LYP/6-31G* Energy + ZPE = -684.215974
B3LYP/6-31G* Free energy = -684.260149
B3LYP/6-31G* Free energy in DCM = -684.548377
B3LYP/6-31G* Free energy in Tol = -684.545949
Number of imaginary frequencies = 1 (-472.17)

***Meta endo* transition structure (TS-5+11-MN)**
B3LYP/6-31G* Geometry

C	0	0.505965	-1.734464	-2.673159
C	0	0.548205	-0.332836	-2.696181
C	0	-0.687757	-2.455776	-2.628104

C	0	-0.592138	0.447718	-2.700405
C	0	-0.679195	-3.965561	-2.560934
H	0	1.433435	-2.267580	-2.464326
H	0	1.506252	0.146627	-2.503982
H	0	-1.543876	-2.035709	-3.151664
H	0	-1.512147	0.094121	-3.148885
H	0	-0.526533	1.525621	-2.583331
H	0	-0.605971	-4.401782	-3.566748
H	0	-1.595426	-4.358262	-2.106053
H	0	0.170979	-4.334776	-1.976543
C	0	-1.741636	-0.398819	-0.770921
C	0	-1.566376	-1.786670	-0.798492
B	0	-0.880794	0.532718	0.100115
O	0	0.242445	0.113543	0.787705
O	0	-1.170277	1.865813	0.328323
C	0	0.871890	1.284872	1.368198
C	0	-0.319653	2.321333	1.412211
C	0	-1.153909	2.231761	2.698235
C	0	0.069185	3.774750	1.144027
C	0	2.008214	1.702155	0.423558
C	0	1.447212	0.895384	2.729706
H	0	-2.686439	-0.009755	-1.148970
H	0	-2.429749	-2.422497	-0.982398
H	0	-0.814145	-2.228720	-0.151214
H	0	-2.062219	2.829515	2.573323
H	0	-1.455495	1.199666	2.902782
H	0	-0.606350	2.613225	3.566748
H	0	-0.828301	4.401782	1.155958
H	0	0.752895	4.148166	1.915309
H	0	0.546692	3.891945	0.168471
H	0	2.583308	2.543039	0.825959
H	0	2.686439	0.853425	0.290508
H	0	1.624981	1.985410	-0.561571
H	0	2.236616	0.148899	2.593544
H	0	1.886150	1.763748	3.234642
H	0	0.684386	0.461873	3.380365

B3LYP/6-31G* Energy + ZPE = -684.214226
B3LYP/6-31G* Free energy = -684.258840
B3LYP/6-31G* Free energy in DCM = -684.545817
B3LYP/6-31G* Free energy in Tol = -684.543161
Number of imaginary frequencies = 1 (-487.65)

***Ortho exo* transition structure (TS-5+11-OX)**
B3LYP/6-31G* Geometry

C	0	3.457883	-1.737386	0.829766
C	0	3.445753	-0.332526	0.834291
C	0	2.284825	-2.493235	0.859343
C	0	2.299210	0.425087	0.966843
C	0	2.283375	1.920826	0.830660
H	0	4.388182	-2.233471	0.557520
H	0	4.368731	0.183976	0.569183
H	0	1.443858	-2.151751	1.455701
H	0	2.367118	-3.577406	0.811882
H	0	1.436254	-0.016159	1.455606
H	0	1.417690	2.256195	0.248522
H	0	3.191853	2.289182	0.341741
H	0	2.213841	2.403839	1.817054
C	0	1.083410	-0.662721	-1.012608
C	0	1.308066	-2.041572	-0.878628
B	0	-0.238983	-0.012404	-0.592615
O	0	-0.605998	1.286226	-0.901556
O	0	-1.207169	-0.664803	0.152989
C	0	-2.007474	1.442514	-0.554569
C	0	-2.219370	0.307576	0.523159
C	0	-3.584990	-0.377340	0.484856
C	0	-1.903352	0.759831	1.956243
C	0	-2.809324	1.212654	-1.843919
C	0	-2.228367	2.868948	-0.052917
H	0	1.771133	-0.095660	-1.634583
H	0	0.457631	-2.668520	-0.617170
H	0	2.017757	-2.524792	-1.545785
H	0	-4.388182	0.336639	0.701152
H	0	-3.621394	-1.166571	1.242968
H	0	-3.778167	-0.836656	-0.487071
H	0	-2.664530	1.445668	2.343448
H	0	-0.930045	1.257588	2.013522
H	0	-1.872228	-0.120436	2.606142
H	0	-2.659305	0.199294	-2.229261
H	0	-2.462832	1.917429	-2.606142
H	0	-3.881967	1.370997	-1.689508
H	0	-3.268714	3.018334	0.258541
H	0	-2.012163	3.577406	-0.859122
H	0	-1.575197	3.108788	0.789147

B3LYP/6-31G* Energy + ZPE = -684.216450
B3LYP/6-31G* Free energy = -684.260908
B3LYP/6-31G* Free energy in DCM = -684.547675
B3LYP/6-31G* Free energy in Tol = -684.545348
Number of imaginary frequencies = 1 (-475.75)

***Meta exo* transition structure (TS-5+11-MX)**
B3LYP/6-31G* Geometry

C	0	3.301593	-1.394152	0.835062
C	0	3.289189	0.008721	0.859538
C	0	2.132990	-2.154464	0.825176
C	0	2.118780	0.741593	0.924629
C	0	2.177247	-3.661482	0.741427
H	0	4.241514	-1.893136	0.598291
H	0	4.215543	0.528944	0.619665
H	0	1.273481	-1.759363	1.361075
H	0	2.141572	1.821374	0.805178
H	0	1.244667	0.354613	1.435107
H	0	1.276166	-4.067388	0.267657
H	0	2.242199	-4.108356	1.743244
H	0	3.044609	-4.006675	0.167304
C	0	1.077046	-0.089413	-1.043519
C	0	1.161739	-1.485018	-0.975857
B	0	-0.214618	0.661957	-0.673601
O	0	-0.529609	1.933666	-1.104276
O	0	-1.191186	0.125195	0.147027
C	0	-1.712332	2.368768	-0.381773
C	0	-2.348859	1.000275	0.083244
C	0	-3.306695	0.392893	-0.951654
C	0	-3.013577	1.022410	1.459093
C	0	-2.576197	3.201180	-1.328621

C	0	-1.225672	3.242692	0.783112
H	0	1.815687	0.429263	-1.649260
H	0	0.265876	-2.045095	-0.719098
H	0	1.850532	-2.013532	-1.629554
H	0	-2.847020	0.355528	-1.944280
H	0	-4.241514	0.959124	-1.022521
H	0	-3.546817	-0.632350	-0.653005
H	0	-3.382266	0.020789	1.703220
H	0	-3.867786	1.709256	1.472435
H	0	-2.313044	1.322018	2.241997
H	0	-2.818400	2.653165	-2.241997
H	0	-2.034553	4.108356	-1.615617
H	0	-3.511084	3.504569	-0.843281
H	0	-2.061564	3.675329	1.343317
H	0	-0.620554	4.061569	0.381587
H	0	-0.601701	2.672488	1.478544

B3LYP/6-31G* Energy + ZPE = -684.214518
B3LYP/6-31G* Free energy = -684.259612
B3LYP/6-31G* Free energy in DCM = -684.545197
B3LYP/6-31G* Free energy in Tol = -684.542929
Number of imaginary frequencies = 1 (-490.71)

Diels-Alder reaction of pinacol vinylboronate (2) with isoprene (12)

***Meta endo* transition structure (TS-5+12-MN)**
B3LYP/6-31G* Geometry

C	0	-0.543174	-2.004785	3.049021
C	0	-0.598243	-0.594438	3.070459
C	0	0.568244	0.143935	3.091796
C	0	0.650771	-2.715190	2.971351
C	0	-1.935536	0.077038	2.829749
H	0	-1.471353	-2.537772	2.843493
H	0	0.542938	1.226238	2.998368
H	0	1.487504	-0.258743	3.495794
H	0	0.605413	-3.799587	2.895152
H	0	1.529556	-2.354328	3.496998
H	0	-2.234736	-0.020622	1.778758
H	0	-1.904710	1.143265	3.076128
H	0	-2.721092	-0.383231	3.440530
C	0	1.762147	-0.787976	1.108569
C	0	1.493298	-2.159682	1.139037
B	0	0.968627	0.218088	0.259317
O	0	1.442932	1.475755	-0.064754
O	0	-0.251474	-0.052579	-0.339929
C	0	0.400191	2.174316	-0.791417
C	0	-0.494032	0.986750	-1.324247
C	0	-1.994448	1.271949	-1.375631
C	0	-0.022983	0.432659	-2.677130
C	0	-0.324483	3.077183	0.216942
C	0	1.058264	3.029154	-1.874554
H	0	2.721092	-0.460338	1.509695
H	0	2.316126	-2.854335	1.298266
H	0	0.703463	-2.545364	0.500540
H	0	-2.525821	0.376989	-1.715690
H	0	-2.389782	1.545567	-0.394717
H	0	-2.215422	2.083288	-2.078964
H	0	1.049568	0.214464	-2.664855
H	0	-0.554266	-0.502459	-2.880478
H	0	-0.226480	1.129917	-3.496998
H	0	-0.806792	2.487520	1.002335
H	0	0.408095	3.738660	0.690298
H	0	-1.085955	3.697927	-0.267421
H	0	1.679273	3.799587	-1.405860
H	0	1.700415	2.430957	-2.524844
H	0	0.304202	3.531274	-2.491888

B3LYP/6-31G* Energy + ZPE = -684.214571
B3LYP/6-31G* Free energy = -684.258783
B3LYP/6-31G* Free energy in DCM = -684.546372
B3LYP/6-31G* Free energy in Tol = -684.543969
Number of imaginary frequencies = 1 (-487.36)

***Para endo* transition structure (TS-5+12-PN)**
B3LYP/6-31G* Geometry

C	0	-0.472510	-2.075083	2.936810
C	0	-0.534093	-0.663713	2.958481
C	0	0.577244	0.147137	2.947983
C	0	0.769510	-2.709273	2.913336
C	0	-1.731593	-2.848110	2.612544
H	0	-1.506373	-0.204663	2.781964
H	0	0.478019	1.221841	2.826144
H	0	1.532052	-0.184922	3.334011
H	0	0.801218	-3.796027	2.863468
H	0	1.602507	-2.274249	3.456045
H	0	-2.601939	-2.413523	3.117618
H	0	-1.656630	-3.898239	2.912504
H	0	-1.941601	-2.823433	1.533320
C	0	1.783300	-0.788277	0.964976
C	0	1.622867	-2.172674	1.079527
B	0	0.867080	0.088906	0.099250
O	0	1.119113	1.415689	-0.202868
O	0	-0.274900	-0.383034	-0.525503
C	0	0.228067	1.798345	-1.280531
C	0	-0.942773	0.745814	-1.145155
C	0	-2.056618	1.196138	-0.189308
C	0	-1.552356	0.278602	-2.466611
C	0	1.024303	1.655180	-2.586150
C	0	-0.180085	3.257394	-1.078936
H	0	2.720183	-0.360771	1.320634
H	0	2.496788	-2.789181	1.282688
H	0	0.873183	-2.656800	0.459225
H	0	-2.720183	0.347787	0.006642
H	0	-1.647988	1.533920	0.767844
H	0	-2.654283	2.008603	-0.616512
H	0	-0.801824	-0.172545	-3.119462
H	0	-2.322398	-0.474575	-2.269237
H	0	-2.024001	1.112882	-2.998887
H	0	0.445908	1.984642	-3.456045
H	0	1.926487	2.271179	-2.518763
H	0	1.336184	0.618595	-2.748445
H	0	0.704597	3.898239	-1.153444
H	0	-0.894249	3.575855	-1.847400
H	0	-0.629726	3.419696	-0.096603

B3LYP/6-31G* Energy + ZPE = -684.215501
B3LYP/6-31G* Free energy = -684.260445
B3LYP/6-31G* Free energy in DCM = -684.545076
B3LYP/6-31G* Free energy in Tol = -684.542787
Number of imaginary frequencies = 1 (-476.66)

***Meta exo* transition structure (TS-5+12-MX)**
B3LYP/6-31G* Geometry

C	0	-2.766703	-1.815026	0.944705
C	0	-2.787439	-0.403860	0.988708
C	0	-1.599593	0.300354	1.047396
C	0	-1.585575	-2.544291	0.868165
C	0	-4.101484	0.319347	0.769337
H	0	-3.703258	-2.325436	0.719945
H	0	-1.597994	1.383743	0.959207
H	0	-0.711174	-0.128218	1.493350
H	0	-1.643307	-3.625162	0.758689
H	0	-0.700548	-2.204573	1.396061
H	0	-3.944492	1.385815	0.579358
H	0	-4.746522	0.236241	1.654102
H	0	-4.663306	-0.096398	-0.076176
C	0	-0.577579	-0.538744	-1.009738
C	0	-0.685152	-1.932756	-0.947438
B	0	0.724498	0.195196	-0.647024
O	0	1.706001	-0.362591	0.154416
O	0	1.051491	1.466495	-1.071124
C	0	2.875776	0.494676	0.076718
C	0	2.251673	1.877203	-0.363513
C	0	1.796054	2.744074	0.819143
C	0	3.113155	2.705997	-1.315625
C	0	3.804455	-0.117398	-0.981812
C	0	3.566924	0.494592	1.439408
H	0	-1.333472	-0.000007	-1.575529
H	0	0.211741	-2.510478	-0.736145
H	0	-1.405288	-2.440888	-1.582992
H	0	1.197443	3.576937	0.437047
H	0	1.174404	2.173166	1.516028
H	0	2.646687	3.156892	1.372018
H	0	3.330441	2.163005	-2.238169
H	0	2.582323	3.625162	-1.584038
H	0	4.061308	2.987945	-0.843188
H	0	3.325873	-0.138237	-1.965985
H	0	4.746522	0.435020	-1.064930
H	0	4.034229	-1.149007	-0.697181
H	0	2.885545	0.796247	2.238169
H	0	3.926637	-0.514139	1.667138
H	0	4.430416	1.169914	1.442723

B3LYP/6-31G* Energy + ZPE = -684.214524
B3LYP/6-31G* Free energy = -684.260662
B3LYP/6-31G* Free energy in DCM = -684.543873
B3LYP/6-31G* Free energy in Tol = -684.541585
Number of imaginary frequencies = 1 (-494.05)

***Para exo* transition structure (TS-5+12-PX)**
B3LYP/6-31G* Geometry

C	0	0.928520	0.523708	-0.464114
C	0	0.979724	1.921322	-0.449627
B	0	-0.400428	-0.246689	-0.437403
O	0	-1.586808	0.309511	0.012209
O	0	-0.557062	-1.554558	-0.849340
C	0	-2.660206	-0.603718	-0.337373
C	0	-1.897777	-1.978547	-0.488744
C	0	-1.779558	-2.758511	0.828672
C	0	-2.425871	-2.897320	-1.590068
C	0	-3.713136	-0.559675	0.769347
C	0	-3.263600	-0.094647	-1.654423
H	0	1.833459	-0.011606	-0.739846
H	0	0.045721	2.471349	-0.539300
H	0	1.838884	2.427179	-0.884017
H	0	-1.397794	-2.124677	1.635255
H	0	-2.742894	-3.175167	1.141839
H	0	-1.076092	-3.585175	0.688105
H	0	-3.460164	-3.198977	-1.387587
H	0	-2.388104	-2.415891	-2.569846
H	0	-1.812373	-3.802907	-1.636895
H	0	-3.280914	-0.782350	1.747605
H	0	-4.153109	0.441822	0.816131
H	0	-4.520359	-1.274767	0.572734
H	0	-4.127418	-0.692333	-1.964697
H	0	-3.592562	0.940116	-1.516191
H	0	-2.524043	-0.107889	-2.461225
C	0	2.461236	2.041020	1.938458
C	0	2.452170	0.638340	2.114354
C	0	1.343394	-0.147508	1.901539
C	0	1.306590	2.680885	1.492281
C	0	3.786656	2.771119	1.932471
H	0	3.415278	0.144617	2.246037
H	0	1.426263	-1.230596	1.919829
H	0	0.338891	0.243185	2.005461
H	0	1.334142	3.754921	1.317084
H	0	0.332725	2.311942	1.794782
H	0	4.520359	2.265769	2.569846
H	0	3.686151	3.802907	2.285752
H	0	4.216523	2.815195	0.920401

B3LYP/6-31G* Energy + ZPE = -684.215046
B3LYP/6-31G* Free energy = -684.261140
B3LYP/6-31G* Free energy in DCM = -684.544840
B3LYP/6-31G* Free energy in Tol = -684.542467
Number of imaginary frequencies = 1 (-475.74)

Calculations in toluene

Dienophiles

Dichlorovinylborane (1)
B3LYP/6-31G* Geometry in Toluene

C	0	2.342707	-0.876190	0.000062
C	0	1.031930	-1.175428	0.000062
B	0	-0.089568	-0.123603	0.000062
Cl	0	0.235301	1.619471	-0.000398
Cl	0	-1.785222	-0.640097	0.000324
H	0	3.110995	-1.647115	0.000062
H	0	2.695193	0.152886	0.000062
H	0	0.742484	-2.227396	0.000062

B3LYP/6-31G* Energy + ZPE = -1023.284946
B3LYP/6-31G* Free energy = -1023.315449
Number of imaginary frequencies = 0

Dimethylvinylborane (2)
B3LYP/6-31G* Geometry in Toluene

C	0	2.126876	-0.082601	0.009141
C	0	0.943735	-0.719490	-0.011340
B	0	-0.449950	-0.009842	-0.011309
C	0	-0.607959	1.562335	-0.000940
C	0	-1.748068	-0.914708	-0.000736
H	0	3.081131	-0.609131	0.004473
H	0	2.192859	1.003743	0.030665
H	0	0.978793	-1.813413	-0.033441
H	0	-1.084473	1.874938	-0.943464
H	0	-1.309388	1.871272	0.787702
H	0	0.311511	2.146031	0.113699
H	0	-1.881398	-1.304635	1.022821
H	0	-2.674249	-0.390178	-0.262470
H	0	-1.652538	-1.802642	-0.640186

B3LYP/6-31G* Energy + ZPE = -182.569868
B3LYP/6-31G* Free energy = -182.601454
Number of imaginary frequencies = 0

Vinyl-9-BBN (3)
B3LYP/6-31G* Geometry in Toluene

C	0	3.436593	-0.000019	0.153911
C	0	2.419785	-0.001095	-0.725848
B	0	0.915504	-0.000535	-0.324181
C	0	-0.260719	-0.000603	-1.378211
C	0	-1.078829	1.310187	-1.175741
C	0	-1.546858	1.576198	0.270906
C	0	-0.467411	1.311465	1.341814
C	0	0.353782	0.000228	1.153211
C	0	-1.079723	-1.310669	-1.174694
C	0	-1.547874	-1.575231	0.272180
C	0	-0.468208	-1.310364	1.342828
H	0	3.261225	0.001182	1.228504
H	0	4.482973	-0.000225	-0.151280
H	0	2.686630	-0.002212	-1.787619
H	0	0.099185	-0.001146	-2.417997
H	0	-1.950606	1.316391	-1.847490
H	0	-0.446710	2.151038	-1.498789
H	0	-1.875774	2.621544	0.350648
H	0	-2.435612	0.975897	0.487072
H	0	-0.934670	1.319873	2.338187
H	0	0.243230	2.151506	1.336996
H	0	1.136315	0.000302	1.925548
H	0	-0.448209	-2.152216	-1.497121
H	0	-1.951528	-1.316797	-1.846407
H	0	-2.436218	-0.974165	0.487904
H	0	-1.877480	-2.620294	0.352770
H	0	0.241920	-2.150845	1.338606
H	0	-0.935414	-1.317740	2.339236

B3LYP/6-31G* Energy + ZPE = -415.887615
B3LYP/6-31G* Free energy = -415.924346
Number of imaginary frequencies = 0

Methanol vinylboronate (4)
B3LYP/6-31G* Geometry in Toluene

C	0	2.492048	-0.766017	-0.000316
C	0	1.591431	0.226868	-0.000316
B	0	0.045360	-0.027543	-0.000316
O	0	-0.394794	-1.322583	-0.001359
O	0	-0.900404	0.965123	0.000741
C	0	-0.570164	2.346848	0.002025
C	0	-1.786509	-1.621102	-0.000937
H	0	3.566441	-0.585899	-0.000242
H	0	2.180559	-1.808687	-0.000400
H	0	1.974911	1.249292	-0.000219
H	0	-1.507489	2.910275	0.003820
H	0	0.006151	2.622428	0.893477
H	0	0.003982	2.624538	-0.890177
H	0	-2.280525	-1.213502	0.888395
H	0	-2.281702	-1.210702	-0.888317
H	0	-1.888385	-2.709926	-0.002566

B3LYP/6-31G* Energy + ZPE = -333.076978
B3LYP/6-31G* Free energy = -333.112074
Number of imaginary frequencies = 0

Pinacol vinylboronate (5)
B3LYP/6-31G* Geometry in Toluene

C	0	-3.695430	0.285857	0.110789
C	0	-2.759657	-0.643026	-0.129829
B	0	-1.237575	-0.342656	-0.064126
O	0	-0.275148	-1.271836	-0.383265
O	0	-0.709838	0.870770	0.313525
C	0	0.716988	0.837466	0.019882

C	0	1.017976	-0.711941	-0.008500
C	0	1.453165	1.622617	1.103630
C	0	0.901545	1.520187	-1.342185
C	0	1.362266	-1.292778	1.369422
C	0	2.054465	-1.155226	-1.039084
H	0	-4.762571	0.072521	0.065398
H	0	-3.423340	1.308600	0.365901
H	0	-3.082991	-1.654384	-0.384345
H	0	1.224550	1.245080	2.102844
H	0	2.537485	1.575398	0.950984
H	0	1.152131	2.674591	1.063067
H	0	0.482316	2.530001	-1.291890
H	0	1.959201	1.600487	-1.614385
H	0	0.378807	0.976826	-2.135867
H	0	1.353860	-2.385456	1.305917
H	0	2.355121	-0.975803	1.705613
H	0	0.627751	-0.992483	2.123476
H	0	2.165114	-2.243975	-1.003336
H	0	1.759954	-0.879605	-2.054325
H	0	3.032453	-0.708928	-0.825247

B3LYP/6-31G* Energy + ZPE = -489.056706
B3LYP/6-31G* Free energy = -489.092211
Number of imaginary frequencies = 0

Dienes

Cyclopentadiene (9)
B3LYP/6-31G* Geometry in Toluene

C	0	0.735238	0.991763	-0.000018
C	0	-0.735273	0.991737	-0.000028
C	0	-1.181435	-0.282037	-0.000013
C	0	1.181444	-0.281996	0.000026
C	0	0.000021	-1.217399	0.000028
H	0	1.347804	1.889010	-0.000057
H	0	-1.347870	1.888963	-0.000030
H	0	-2.215083	-0.612247	0.000022
H	0	2.215105	-0.612170	0.000007
H	0	0.000012	-1.882963	0.877727
H	0	0.000055	-1.883003	-0.877641

B3LYP/6-31G* Energy + ZPE = -194.01018
B3LYP/6-31G* Free energy = -194.036781
Number of imaginary frequencies = 0

Piperylene (11)
***s-cis* conformation**
B3LYP/6-31G* Geometry in Toluene

C	0	1.465457	0.519627	0.079684
C	0	2.178513	-0.602985	-0.088397
C	0	0.009901	0.658227	-0.065207
C	0	-0.898318	-0.309326	0.137484
C	0	-2.378907	-0.147961	-0.041520
H	0	1.999222	1.437899	0.331820
H	0	3.254312	-0.617912	0.063570
H	0	1.715249	-1.539899	-0.389805
H	0	-0.346243	1.653074	-0.341390
H	0	-0.557432	-1.292169	0.467735
H	0	-2.764971	-0.846097	-0.797551
H	0	-2.920259	-0.368883	0.888823
H	0	-2.639756	0.868499	-0.355464

B3LYP/6-31G* Energy + ZPE = -195.194421
B3LYP/6-31G* Free energy = -195.223488
Number of imaginary frequencies = 0

Isoprene (12)
***s-cis* conformation**
B3LYP/6-31G* Geometry in Toluene

C	0	-2.040879	-0.109355	0.183245
C	0	-0.854026	-0.570607	-0.230796
C	0	0.449203	0.104710	-0.058705
C	0	0.568721	1.441203	-0.089342
C	0	1.662764	-0.792394	0.135589
H	0	-2.957841	-0.663288	0.000670
H	0	-2.134546	0.828690	0.725527
H	0	-0.817230	-1.546852	-0.719136
H	0	1.528535	1.930763	0.060454
H	0	-0.284502	2.086757	-0.277808
H	0	2.399711	-0.653251	-0.664297
H	0	2.166566	-0.573196	1.084143
H	0	1.384612	-1.850964	0.150499

B3LYP/6-31G* Energy + ZPE = -195.193026
B3LYP/6-31G* Free energy = -195.221906
Number of imaginary frequencies = 0

Diels-Alder reaction of dichlorovinylborane (1) with cyclopentadiene (9)

***Endo* transition structure (TS-1+9-N)**
B3LYP/6-31G* Geometry in Toluene

C	0	-1.304886	0.225091	-1.519634
C	0	-2.115107	0.981406	-0.651042
C	0	-1.219239	-1.071959	-1.040015
C	0	-2.488901	0.187386	0.452887
C	0	-2.272153	-1.252206	0.016135
H	0	-0.767983	0.618592	-2.376595
H	0	-2.311212	2.045148	-0.749100
H	0	-0.672412	-1.886842	-1.502675
H	0	-3.309515	0.465762	1.109904
H	0	-2.044202	-1.970210	0.804902
H	0	-3.196722	-1.591457	-0.482670
C	0	-0.904203	0.354463	1.693355
C	0	0.121062	-0.472527	1.196415
B	0	1.273507	-0.025232	0.347793
Cl	0	2.564695	-1.168900	-0.158029

Cl	0	1.503187	1.687183	-0.145591
H	0	-1.460414	0.013400	2.565349
H	0	-0.760265	1.430759	1.668180
H	0	0.101753	-1.519731	1.496687

B3LYP/6-31G* Energy + ZPE = -1217.272914
B3LYP/6-31G* Free energy = -1217.309243
Number of imaginary frequencies = 1 (-384.25)

***Exo* transition structure (TS-1+9-X)**
B3LYP/6-31G* Geometry in Toluene

C	0	-2.218424	1.418526	-0.389032
C	0	-2.938047	0.464132	0.357263
C	0	-1.266480	0.766537	-1.157292
C	0	-2.373163	-0.810564	0.151613
C	0	-1.559297	-0.702401	-1.124496
H	0	-2.344328	2.494798	-0.319994
H	0	-3.719043	0.693152	1.076917
H	0	-0.579531	1.237800	-1.852337
H	0	-2.889577	-1.727675	0.424992
H	0	-0.695478	-1.362130	-1.206423
H	0	-2.233365	-0.935274	-1.967197
C	0	-0.813352	-0.840158	1.458787
C	0	0.081177	0.182654	1.095649
B	0	1.349957	0.029951	0.311516
Cl	0	2.463557	1.418774	0.072586
Cl	0	1.905907	-1.536456	-0.378509
H	0	-0.526338	-1.870916	1.258925
H	0	-1.401678	-0.722689	2.365211
H	0	-0.115811	1.171400	1.508048

B3LYP/6-31G* Energy + ZPE = -1217.272132
B3LYP/6-31G* Free energy = -1217.308453
Number of imaginary frequencies = 1 (-385.97)

Diels-Alder reaction of dimethylvinylborane (2) with cyclopentadiene (9)

***Endo* transition structure (TS-2+9-N)**
B3LYP/6-31G* Geometry in Toluene

C	0	-0.834437	0.319079	-1.495395
C	0	-1.709323	1.040189	-0.667082
C	0	-2.070681	0.237565	0.434780
C	0	-0.671507	-0.964852	-0.978256
C	0	-1.786598	-1.191278	0.010539
H	0	-0.296080	0.728387	-2.344615
H	0	-1.952131	2.092987	-0.779614
H	0	-2.902381	0.485758	1.089776
H	0	-0.107995	-1.764995	-1.446299
H	0	-2.665619	-1.554577	-0.550705
H	0	-1.587216	-1.902246	0.812896
C	0	-0.447216	0.424026	1.696029
C	0	0.552976	-0.399607	1.153980
B	0	1.698264	0.022839	0.222880
C	0	1.932592	1.542387	-0.190799
C	0	2.782093	-1.048132	-0.242561
H	0	-0.993614	0.085612	2.576252
H	0	-0.326018	1.503221	1.655646
H	0	0.522259	-1.443338	1.476803
H	0	2.684769	1.970655	0.492127
H	0	2.350865	1.651151	-1.200398
H	0	1.046355	2.183526	-0.118836
H	0	2.572410	-2.077024	0.076386
H	0	2.902778	-1.052284	-1.335830
H	0	3.772901	-0.777282	0.154603

B3LYP/6-31G* Energy + ZPE = -376.550977
B3LYP/6-31G* Free energy = -376.587106
Number of imaginary frequencies = 1 (-420.71)

***Exo* transition structure (TS-2+9-X)**
B3LYP/6-31G* Geometry in Toluene

C	0	-2.473225	0.363124	-0.389498
C	0	-1.699392	1.420761	0.117757
C	0	-0.699691	0.903729	0.938322
C	0	-1.916721	-0.859039	0.037095
C	0	-1.057990	-0.524626	1.241121
H	0	-3.280008	0.466709	-1.109514
H	0	-1.809435	2.466165	-0.155683
H	0	-0.005718	1.493856	1.527259
H	0	-2.442436	-1.807208	-0.047323
H	0	-0.222277	-1.195463	1.435565
H	0	-1.712098	-0.533092	2.130573
C	0	0.536926	-0.049482	-1.065754
C	0	-0.324473	-1.140469	-1.260280
B	0	1.811469	0.005978	-0.212382
C	0	2.729196	1.306978	-0.264185
C	0	2.333331	-1.214841	0.668200
H	0	0.313667	0.827390	-1.677243
H	0	-0.039886	-2.114061	-0.863504
H	0	-0.915010	-1.203734	-2.171641
H	0	2.245981	2.180331	-0.719625
H	0	3.100631	1.600451	0.728100
H	0	3.631168	1.092391	-0.859748
H	0	2.418155	-0.928131	1.727223
H	0	1.735483	-2.132972	0.619766
H	0	3.356671	-1.479331	0.361033

B3LYP/6-31G* Energy + ZPE = -376.55022
B3LYP/6-31G* Free energy = -376.586469
Number of imaginary frequencies = 1 (-422.94)

Diels-Alder reaction of vinyl-9-BBN (3) with cyclopentadiene (9)

***Endo* transition structure (TS-3+9-N)**

B3LYP/6-31G* Geometry in Toluene

C	0	2.996452	0.553744	1.179078
C	0	2.213232	1.420973	0.399888
C	0	3.460286	-0.502976	0.369623
C	0	2.214065	0.976370	-0.919837
C	0	3.350014	-0.003925	-1.059022
H	0	3.108813	0.610861	2.257961
H	0	1.633187	2.254414	0.781924
H	0	4.260756	-1.168969	0.682691
H	0	1.749121	1.485225	-1.757568
H	0	3.242249	-0.766624	-1.830953
H	0	4.264964	0.572854	-1.282558
C	0	1.839228	-1.767819	0.287569
C	0	0.934918	-1.195065	-0.622530
B	0	-0.330332	-0.401736	-0.283077
C	0	-0.895171	-0.136040	1.177692
C	0	-1.418380	-0.014653	-1.373033
C	0	-1.417912	1.314302	1.348279
C	0	-1.874972	1.456457	-1.200830
C	0	-2.002831	-1.225753	1.344246
C	0	-2.556802	-1.068654	-1.191224
C	0	-2.337484	1.834863	0.221518
C	0	-3.095277	-1.220957	0.250685
H	0	2.439643	-2.620826	-0.028074
H	0	1.580732	-1.792427	1.343194
H	0	1.106819	-1.445422	-1.672832
H	0	-0.157281	-0.314287	1.974144
H	0	-1.045459	-0.128026	-2.402820
H	0	-0.543536	1.977201	1.413572
H	0	-1.940901	1.419287	2.311901
H	0	-2.679349	1.696392	-1.913739
H	0	-1.028064	2.103229	-1.477871
H	0	-2.481475	-1.125570	2.330834
H	0	-1.510336	-2.209217	1.344980
H	0	-2.160392	-2.041276	-1.517909
H	0	-3.395671	-0.842447	-1.867912
H	0	-2.405839	2.929413	0.295993
H	0	-3.357684	1.472206	0.380023
H	0	-3.667733	-2.156739	0.317509
H	0	-3.817111	-0.425776	0.460284

B3LYP/6-31G* Energy + ZPE = -609.867927
B3LYP/6-31G* Free energy = -609.909333
Number of imaginary frequencies = 1 (-426.56)

***Exo* transition structure (TS-3+9-X)**
B3LYP/6-31G* Geometry in Toluene

C	0	3.200910	0.951451	-1.003329
C	0	3.953633	-0.109103	-0.468271
C	0	2.146065	1.241962	-0.143603
C	0	3.328601	-0.569343	0.706913
C	0	2.426035	0.558986	1.166060
H	0	3.366913	1.412208	-1.972788
H	0	4.797965	-0.586804	-0.957176
H	0	1.451443	2.065918	-0.262715
H	0	3.819457	-1.234869	1.413011
H	0	1.553089	0.265459	1.748294
H	0	3.033037	1.241192	1.786688
C	0	0.957451	-0.931912	-0.760967
C	0	1.798803	-1.765419	-0.006460
B	0	-0.378271	-0.330564	-0.317637
C	0	-1.391806	0.356598	-1.330513
C	0	-1.055425	-0.482719	1.112790
C	0	-1.846673	1.737593	-0.788486
C	0	-1.519669	0.900197	1.644744
C	0	-2.550900	-0.668637	-1.524879
C	0	-2.213241	-1.509837	0.908385
C	0	-2.368677	1.737735	0.664279
C	0	-3.211648	-1.167118	-0.220010
H	0	1.230269	-0.824948	-1.813171
H	0	1.463128	-2.097386	0.975391
H	0	2.433550	-2.489768	-0.512084
H	0	-0.945231	0.523793	-2.322739
H	0	-0.391290	-0.918121	1.875281
H	0	-2.615830	2.173205	-1.445299
H	0	-0.984745	2.419779	-0.849901
H	0	-2.077078	0.778521	2.586532
H	0	-0.619806	1.477875	1.906065
H	0	-3.325851	-0.246337	-2.183489
H	0	-2.140040	-1.536550	-2.061798
H	0	-1.755671	-2.484960	0.685616
H	0	-2.766862	-1.643882	1.850700
H	0	-2.412806	2.774130	1.027582
H	0	-3.403584	1.382726	0.680748
H	0	-3.927618	-0.420881	0.137660
H	0	-3.811853	-2.060073	-0.444151

B3LYP/6-31G* Energy + ZPE = -609.86831
B3LYP/6-31G* Free energy = -609.909451
Number of imaginary frequencies = 1 (-419.29)

Diels-Alder reaction of methanol vinylboronate (4) with cyclopentadiene (9)

***Endo* transition structure (TS-4+9-N)**
B3LYP/6-31G* Geometry in Toluene

C	0	2.079233	1.235512	-0.506191
C	0	1.245841	0.571765	-1.420159
C	0	1.241410	-0.790292	-1.127653
C	0	2.572221	0.301351	0.426661
C	0	2.422202	-1.058169	-0.230532
H	0	2.196344	2.312804	-0.434767
H	0	0.622121	1.057337	-2.164473
H	0	0.747642	-1.555268	-1.718343
H	0	3.396302	0.524058	1.100535
H	0	2.329934	-1.909357	0.446554
H	0	3.308823	-1.228249	-0.866393
C	0	0.010281	-0.677634	1.019497

C	0	0.986131	0.048664	1.718867
B	0	-1.230299	-0.012570	0.382586
O	0	-2.286248	-0.688770	-0.193026
O	0	-1.307950	1.361440	0.397987
C	0	-2.394203	2.035699	-0.218842
C	0	-2.332569	-2.103199	-0.244340
H	0	0.054652	-1.762758	1.103053
H	0	1.589007	-0.459729	2.470379
H	0	0.789716	1.092230	1.945957
H	0	-3.357156	1.710625	0.192237
H	0	-2.268222	3.106796	-0.032542
H	0	-2.411284	1.862314	-1.302183
H	0	-2.342278	-2.545239	0.760379
H	0	-3.254592	-2.389959	-0.759541
H	0	-1.479213	-2.516285	-0.797321

B3LYP/6-31G* Energy + ZPE = -527.054205
B3LYP/6-31G* Free energy = -527.094065
Number of imaginary frequencies = 1 (-454.37)

Exo transition structure **(TS-4+9-X)**
B3LYP/6-31G* Geometry in Toluene

C	0	-2.294653	1.178886	-0.643881
C	0	-3.056262	0.293616	0.136185
C	0	-2.399504	-0.951679	0.184577
C	0	-1.189766	0.499954	-1.156705
C	0	-1.451432	-0.973512	-0.997868
H	0	-2.482036	2.244146	-0.747513
H	0	-3.923658	0.568534	0.729796
H	0	-2.871718	-1.855892	0.561334
H	0	-0.477009	0.911420	-1.864730
H	0	-0.566447	-1.600877	-0.888976
H	0	-2.017011	-1.322475	-1.879801
C	0	-0.889156	-0.617153	1.580468
C	0	-0.034052	0.337163	1.010761
B	0	1.316265	-0.006677	0.340189
O	0	2.249324	0.922151	-0.067279
O	0	1.632475	-1.331848	0.128960
C	0	2.043003	2.315872	0.088826
C	0	2.855245	-1.696813	-0.497334
H	0	-1.535874	-0.336216	2.407608
H	0	-0.557148	-1.652860	1.612788
H	0	-0.240244	1.376540	1.258381
H	0	2.889691	2.832563	-0.373311
H	0	1.118510	2.644430	-0.402299
H	0	1.995321	2.599964	1.147760
H	0	2.934443	-1.271959	-1.505124
H	0	3.719133	-1.355800	0.085130
H	0	2.877793	-2.788556	-0.565610

B3LYP/6-31G* Energy + ZPE = -527.055468
B3LYP/6-31G* Free energy = -527.09534
Number of imaginary frequencies = 1 (-452.84)

Diels-Alder reaction of pinacol vinylboronate (5) with *trans*-piperylene (11)

Ortho endo **transition structure (TS-5+11-ON)**
B3LYP/6-31G* Geometry in Toluene

C	0	3.320426	-0.404668	1.112451
C	0	2.568069	0.780317	1.055885
C	0	2.267505	1.441917	-0.118482
C	0	3.796402	-1.046804	-0.035173
C	0	1.390711	2.659641	-0.182753
H	0	3.336692	-0.947912	2.056641
H	0	2.084245	1.120067	1.972023
H	0	2.878371	1.259261	-0.995963
H	0	4.354572	-1.972692	0.092398
H	0	4.161170	-0.441001	-0.860830
H	0	1.970614	3.541573	-0.490186
H	0	0.935408	2.877426	0.790059
H	0	0.580273	2.532276	-0.909576
C	0	1.322591	-0.616281	-1.415507
C	0	2.178828	-1.670413	-1.058216
B	0	-0.029795	-0.381983	-0.735887
O	0	-0.489678	-1.123225	0.339848
O	0	-0.965196	0.547109	-1.168022
C	0	-1.734347	-0.531753	0.793257
C	0	-2.214863	0.270010	-0.480710
C	0	-3.069691	-0.568330	-1.442426
C	0	-2.914526	1.596598	-0.186032
C	0	-2.668659	-1.656306	1.240005
C	0	-1.396206	0.368051	1.990052
H	0	1.538512	-0.086957	-2.343939
H	0	2.801265	-2.114822	-1.834469
H	0	1.810267	-2.392417	-0.333544
H	0	-4.064285	-0.772163	-1.031551
H	0	-3.191583	-0.016007	-2.379687
H	0	-2.586732	-1.523018	-1.674296
H	0	-3.839914	1.434238	0.378633
H	0	-2.273882	2.273992	0.383376
H	0	-3.176135	2.090621	-1.127680
H	0	-2.818108	-2.395213	0.449344
H	0	-2.235441	-2.170239	2.104510
H	0	-3.646457	-1.259941	1.537519
H	0	-0.892451	-0.234148	2.752857
H	0	-0.720252	1.177512	1.699572
H	0	-2.295612	0.806533	2.435514

B3LYP/6-31G* Energy + ZPE = -684.218757
B3LYP/6-31G* Free energy = -684.262907
Number of imaginary frequencies = 1 (-470.99)

Meta endo **transition structure (TS-5+11-MN)**
B3LYP/6-31G* Geometry in Toluene

C	0	3.087305	1.168460	0.025362
C	0	2.056226	1.503723	-0.864483
C	0	3.727670	-0.072386	0.009253

C	0	1.609960	0.641630	-1.848393
C	0	4.809617	-0.395183	1.014442
H	0	3.242459	1.813263	0.891256
H	0	1.464900	2.390528	-0.641739
H	0	3.856044	-0.554848	-0.957819
H	0	2.272104	-0.087132	-2.300135
H	0	0.723987	0.877216	-2.431298
H	0	5.785642	-0.027399	0.668791
H	0	4.910369	-1.474737	1.172440
H	0	4.604411	0.070115	1.985185
C	0	1.110833	-1.327277	-0.548655
C	0	2.131611	-1.420483	0.404604
B	0	-0.266611	-0.710943	-0.250442
O	0	-0.579512	-0.065747	0.931273
O	0	-1.349866	-0.788697	-1.109436
C	0	-1.903346	0.513082	0.785103
C	0	-2.527106	-0.358927	-0.374382
C	0	-3.223916	-1.631490	0.128790
C	0	-3.450466	0.395315	-1.330314
C	0	-1.711645	1.987198	0.401491
C	0	-2.622804	0.416756	2.130063
H	0	1.204326	-1.953137	-1.436563
H	0	2.828508	-2.254047	0.347093
H	0	1.933394	-1.072281	1.414790
H	0	-3.445233	-2.275937	-0.727982
H	0	-2.581083	-2.192112	0.815003
H	0	-4.165359	-1.405405	0.640788
H	0	-3.807699	-0.285789	-2.109910
H	0	-4.324920	0.789032	-0.799508
H	0	-2.936666	1.226111	-1.819830
H	0	-2.667938	2.517086	0.336834
H	0	-1.099117	2.475405	1.166186
H	0	-1.195070	2.085400	-0.558199
H	0	-2.097657	1.028509	2.871139
H	0	-3.651150	0.788458	2.052971
H	0	-2.649806	-0.610540	2.500744

B3LYP/6-31G* Energy + ZPE = -684.217201
B3LYP/6-31G* Free energy =-684.261797
Number of imaginary frequencies = 1 (-486.94)

***Ortho exo* transition structure (TS-5+11-OX)**
B3LYP/6-31G* Geometry in Toluene

C	0	4.095245	-0.391719	0.280910
C	0	3.559906	0.904629	0.192989
C	0	3.301473	-1.510022	0.544675
C	0	2.237858	1.208283	0.451719
C	0	1.648116	2.570316	0.221488
H	0	5.103956	-0.548877	-0.100174
H	0	4.185130	1.683487	-0.246402
H	0	2.473151	-1.424288	1.242169
H	0	3.776723	-2.489254	0.558581
H	0	1.666348	0.546531	1.095020
H	0	0.656671	2.498924	-0.239834
H	0	2.287660	3.181029	-0.425181
H	0	1.520466	3.108352	1.173001
C	0	1.290744	-0.479078	-1.239266
C	0	2.030839	-1.656172	-1.043318
B	0	-0.121272	-0.301314	-0.670613
O	0	-0.975632	0.733633	-1.012287
O	0	-0.687478	-1.162445	0.254973
C	0	-2.285893	0.423957	-0.462715
C	0	-1.935094	-0.572546	0.710590
C	0	-2.949470	-1.693415	0.933242
C	0	-1.637009	0.131983	2.041917
C	0	-3.095059	-0.229046	-1.592511
C	0	-2.954573	1.728442	-0.031545
H	0	1.640935	0.217992	-1.997187
H	0	1.514247	-2.511507	-0.611023
H	0	2.785613	-1.929132	-1.777219
H	0	-3.925817	-1.286024	1.220022
H	0	-2.605065	-2.345526	1.742817
H	0	-3.076228	-2.306542	0.038123
H	0	-2.544650	0.546158	2.493778
H	0	-0.914883	0.944578	1.912753
H	0	-1.208027	-0.595122	2.738822
H	0	-2.630801	-1.162527	-1.926113
H	0	-3.127947	0.455536	-2.445978
H	0	-4.123509	-0.443344	-1.283250
H	0	-3.930088	1.533984	0.428927
H	0	-3.115995	2.364228	-0.908291
H	0	-2.339140	2.284741	0.679161

B3LYP/6-31G* Energy + ZPE = -684.219004
B3LYP/6-31G* Free energy = -684.263454
Number of imaginary frequencies = 1 (-475.54)

***Meta exo* transition structure (TS-5+11-MX)**
B3LYP/6-31G* Geometry in Toluene

C	0	-3.874484	-0.765786	0.282755
C	0	-2.996718	-1.858227	0.359793
C	0	-3.442257	0.554226	0.408628
C	0	-1.644871	-1.710876	0.611198
C	0	-4.401409	1.711467	0.262456
H	0	-4.879931	-0.944018	-0.101204
H	0	-3.358854	-2.826323	0.013733
H	0	-2.604770	0.745926	1.075295
H	0	-0.977422	-2.564826	0.529946
H	0	-1.274441	-0.894874	1.220776
H	0	-3.893993	2.615221	-0.093900
H	0	-4.863018	1.962253	1.227715
H	0	-5.208470	1.477486	-0.441100
C	0	-1.103407	-0.303386	-1.225662
C	0	-2.039434	0.737844	-1.212255
B	0	0.320450	-0.124594	-0.667587
O	0	1.399105	-0.909314	-1.022741
O	0	0.655614	0.846648	0.258107
C	0	2.503413	-0.573770	-0.136592
C	0	2.105374	0.867798	0.368833
C	0	2.603353	1.992794	-0.549430

C	0	2.475419	1.175472	1.818999
C	0	3.803968	-0.647675	-0.935404
C	0	2.515664	-1.629431	0.977946
H	0	-1.284173	-1.129980	-1.909433
H	0	-1.722873	1.713385	-0.850813
H	0	-2.816809	0.770530	-1.971262
H	0	2.340791	1.798980	-1.594335
H	0	3.688840	2.121390	-0.481929
H	0	2.126515	2.931546	-0.250133
H	0	2.124044	2.178788	2.081562
H	0	3.562118	1.150807	1.960291
H	0	2.017442	0.466491	2.512723
H	0	3.769439	-0.014104	-1.824772
H	0	3.975003	-1.678505	-1.262901
H	0	4.658730	-0.342373	-0.320944
H	0	3.365620	-1.493728	1.655192
H	0	2.593825	-2.622489	0.524064
H	0	1.594712	-1.599975	1.568842

B3LYP/6-31G* Energy + ZPE = -684.217255
B3LYP/6-31G* Free energy = -684.262361
Number of imaginary frequencies = 1 (-491.67)

Diels-Alder reaction of pinacol vinylboronate (5) with isoprene (12)

***Meta endo* transition structure (TS-5+12-MN)**
B3LYP/6-31G* Geometry in Toluene

C	0	3.425167	0.430935	0.610231
C	0	2.534449	1.175006	-0.193806
C	0	2.105912	0.668113	-1.404710
C	0	3.852196	-0.852122	0.279442
C	0	1.886080	2.408871	0.402017
H	0	3.587553	0.778490	1.631158
H	0	1.339573	1.179711	-1.981052
H	0	2.695120	-0.049052	-1.960970
H	0	4.489739	-1.383744	0.983186
H	0	4.044722	-1.107459	-0.758438
H	0	1.130865	2.128416	1.146838
H	0	1.396700	3.020330	-0.362967
H	0	2.628880	3.037559	0.907090
C	0	1.218697	-1.561274	-0.700571
C	0	2.119390	-2.013989	0.268881
B	0	-0.098270	-0.839972	-0.373163
O	0	-1.141031	-0.722352	-1.275818
O	0	-0.419239	-0.315784	0.868843
C	0	-2.172699	0.096051	-0.662924
C	0	-1.847575	-0.048444	0.874940
C	0	-2.109104	1.200306	1.715807
C	0	-2.522641	-1.264944	1.525342
C	0	-1.988359	1.524996	-1.192553
C	0	-3.536441	-0.445023	-1.091828
H	0	1.343909	-1.947367	-1.712864
H	0	2.710702	-2.904658	0.062827
H	0	1.858610	-1.886912	1.316118
H	0	-1.816085	1.011090	2.753852
H	0	-1.538542	2.059510	1.355738
H	0	-3.173782	1.461205	1.708129
H	0	-2.347080	-2.175338	0.943315
H	0	-2.096711	-1.414817	2.522566
H	0	-3.603523	-1.122928	1.630787
H	0	-1.018950	1.936622	-0.896011
H	0	-2.029485	1.506246	-2.286431
H	0	-2.775054	2.195728	-0.830882
H	0	-3.654178	-0.326429	-2.174122
H	0	-3.641560	-1.506627	-0.856434
H	0	-4.348337	0.104482	-0.601424

B3LYP/6-31G* Energy + ZPE = -684.217234
B3LYP/6-31G* Free energy = -684.261401
Number of imaginary frequencies = 1 (-486.70)

***Para endo* transition structure (TS-5+12-PN)**
B3LYP/6-31G* Geometry in Toluene

C	0	-3.173744	0.491686	0.472760
C	0	-2.263588	-0.042000	1.412365
C	0	-1.828709	-1.347138	1.391066
C	0	-3.684489	-0.330578	-0.533182
C	0	-3.313883	1.994458	0.377474
H	0	-1.742947	0.664060	2.059816
H	0	-1.030892	-1.674688	2.051706
H	0	-2.418398	-2.142101	0.953169
H	0	-4.363662	0.102437	-1.265523
H	0	-3.887777	-1.374715	-0.316873
H	0	-4.211412	2.288541	-0.175948
H	0	-2.445235	2.436055	-0.132033
H	0	-3.365185	2.450167	1.373333
C	0	-1.054489	-1.488516	-0.996765
C	0	-2.055147	-0.828269	-1.720061
B	0	0.228661	-0.782927	-0.536305
O	0	1.366350	-1.439819	-0.098925
O	0	0.399727	0.591209	-0.575563
C	0	2.297753	-0.436043	0.386031
C	0	1.807220	0.867880	-0.357907
C	0	1.929639	2.161428	0.446679
C	0	2.444351	1.051039	-1.742905
C	0	2.127132	-0.365786	1.910155
C	0	3.717054	-0.885631	0.041674
H	0	-1.101457	-2.576437	-0.948702
H	0	-2.687494	-1.406969	-2.391747
H	0	-1.854044	0.183429	-2.063185
H	0	1.531399	2.996283	-0.139584
H	0	1.367968	2.110019	1.382343
H	0	2.977856	2.381875	0.679733
H	0	2.363728	0.137074	-2.339987
H	0	1.914503	1.848441	-2.273728
H	0	3.501505	1.328539	-1.671721
H	0	2.294438	-1.362167	2.331867
H	0	2.842802	0.325638	2.367655

H	0	1.115779	-0.047488	2.181538
H	0	4.451627	-0.128348	0.339212
H	0	3.949925	-1.811040	0.579105
H	0	3.830441	-1.080266	-1.027331

B3LYP/6-31G* Energy + ZPE = -684.217877
B3LYP/6-31G* Free energy = -684.262794
Number of imaginary frequencies = 1 (-479.70)

***Meta exo* transition structure (TS-5+12-MX)**
B3LYP/6-31G* Geometry in Toluene

C	0	-3.873993	-0.603272	0.419433
C	0	-3.366657	0.714406	0.391064
C	0	-2.021900	0.939760	0.618265
C	0	-3.056169	-1.716506	0.581370
C	0	-4.265793	1.837718	-0.086625
H	0	-4.892545	-0.759324	0.061873
H	0	-1.599897	1.931892	0.479393
H	0	-1.432048	0.267540	1.228390
H	0	-3.501318	-2.707341	0.516510
H	0	-2.192747	-1.666760	1.237006
H	0	-3.695329	2.751010	-0.283176
H	0	-5.023631	2.081179	0.669880
H	0	-4.804769	1.569976	-1.003870
C	0	-1.116086	-0.437904	-1.192974
C	0	-1.751897	-1.680053	-1.078833
B	0	0.303078	-0.193651	-0.652625
O	0	0.887067	-0.982633	0.322707
O	0	1.135860	0.823102	-1.075939
C	0	2.292263	-0.617651	0.400104
C	0	2.293576	0.844590	-0.194840
C	0	2.031291	1.930462	0.858264
C	0	3.525186	1.207954	-1.023014
C	0	3.060985	-1.626067	-0.465390
C	0	2.742419	-0.729276	1.855721
H	0	-1.528112	0.274913	-1.903993
H	0	-1.178880	-2.519319	-0.690727
H	0	-2.515216	-1.956348	-1.801495
H	0	1.843841	2.880838	0.348408
H	0	1.152505	1.693545	1.466303
H	0	2.889098	2.062384	1.526260
H	0	3.651826	0.534736	-1.874006
H	0	3.419264	2.226268	-1.411483
H	0	4.433440	1.172472	-0.410424
H	0	2.748292	-1.571359	-1.513060
H	0	4.142598	-1.461328	-0.416472
H	0	2.850502	-2.637219	-0.102699
H	0	2.119448	-0.124913	2.519140
H	0	2.670250	-1.771944	2.182395
H	0	3.785267	-0.411364	1.969560

B3LYP/6-31G* Energy + ZPE = -684.216946
B3LYP/6-31G* Free energy = -684.262921
Number of imaginary frequencies = 1 (-494.85)

***Para exo* transition structure (TS-5+12-PX)**
B3LYP/6-31G* Geometry in Toluene

C	0	-1.063188	-0.177784	-1.184689
C	0	-1.864528	-1.308777	-0.995740
B	0	0.374877	-0.091341	-0.651490
O	0	0.854505	-0.893176	0.370294
O	0	1.333001	0.782997	-1.127026
C	0	2.295033	-0.710004	0.434054
C	0	2.486107	0.702270	-0.244808
C	0	2.375139	1.873145	0.741950
C	0	3.751841	0.851850	-1.087879
C	0	2.730087	-0.793933	1.896460
C	0	2.923966	-1.859480	-0.366215
H	0	-1.388257	0.552394	-1.922599
H	0	-1.409334	-2.195380	-0.559612
H	0	-2.662427	-1.520156	-1.704178
H	0	1.473408	1.793510	1.357289
H	0	3.244302	1.926551	1.406156
H	0	2.316526	2.808619	0.176469
H	0	4.649721	0.737646	-0.469578
H	0	3.788867	0.116950	-1.895378
H	0	3.776863	1.849523	-1.538545
H	0	2.191186	-0.077238	2.520554
H	0	2.525061	-1.797988	2.282291
H	0	3.805326	-0.606377	1.997357
H	0	4.017955	-1.835956	-0.319897
H	0	2.582476	-2.811171	0.053285
H	0	2.619910	-1.825625	-1.417293
C	0	-3.858878	0.087241	0.407464
C	0	-3.153260	1.312191	0.369667
C	0	-1.800247	1.417686	0.595100
C	0	-3.162479	-1.095579	0.649815
C	0	-5.277431	0.039448	-0.117266
H	0	-3.676651	2.179446	-0.035385
H	0	-1.286996	2.359680	0.421819
H	0	-1.265435	0.702555	1.207649
H	0	-3.705713	-2.039022	0.634336
H	0	-2.309561	-1.092573	1.319863
H	0	-5.771103	1.012010	-0.016090
H	0	-5.883285	-0.704890	0.410802
H	0	-5.300256	-0.224016	-1.185474

B3LYP/6-31G* Energy + ZPE = -684.217578
B3LYP/6-31G* Free energy = -684.263382
Number of imaginary frequencies = 1 (-474.31)