SUPPORTING INFORMATION:

A standard set of pericyclic reactions of hydrocarbons for the benchmarking of computational methods: The performance of ab initio, density functional, CASSCF, CASPT2, and CBS-QB3 methods for the prediction of activation barriers, reaction energetics, and transition state geometries.

Vildan Guner, Kelli S. Khuong, Andrew G. Leach, Patrick S. Lee, Michael D. Bartberger, and K. N. Houk*

Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90095-1569
Department of Chemistry, Hacettepe University, 06532, Beytepe, Ankara, Turkey

CONTENTS

SECTION I.

Table 1. B3LYP/6-31G* optimized geometries and energies for reactants.

R1: Cyclobutene E(RB+HF-LYP) = -155.97326

H	0.000000	-1.420641	1.601473
C	0.000000	0.670170	0.814819
C	0.000000	-0.670170	0.814819
C	0.000000	0.786311	-0.699697
C	0.000000	-0.786311	-0.699697
H	0.890109	-1.246599	-1.146101
H	-0.890109	-1.246599	-1.146101
H	0.000000	1.420641	1.601473
H	-0.890109	1.246599	-1.146101
H	0.890109	1.246599	-1.146101

R2: *cis*-1,3,5-Hexatriene E(RB+HF-LYP) = -233.39551

C	-0.318884	0.000066	2.894521
H	0.641335	0.000179	3.405963
H	-1.205045	0.000070	3.521831
C	-0.400823	-0.000062	1.553914
H	-1.386558	-0.000136	1.092276
C	0.757542	-0.000064	0.677687
H	1.723262	0.000044	1.182403
C	0.757542	-0.000037	-0.677687
H	1.723262	0.000084	-1.182403
C	-0.400823	0.000002	-1.553914
H	-1.386558	-0.000050	-1.092276
C	-0.318884	0.000046	-2.894521
H	0.641335	0.000081	-3.405963
H	-1.205045	0.000024	-3.521831

R3: ortho-xylylene E(RB+HF-LYP) = -309.60604

H	-0.144883	1.244000	2.790787
C	-0.079370	0.721429	1.840229

C	-0.128693	1.408985	0.677482
C	0.079370	-0.721429	1.840229
C	0.128693	-1.408985	0.677482
H	0.144883	-1.244000	2.790787
H	-0.221218	2.492345	0.677508
C	-0.006727	0.748467	-0.621344
C	0.006727	-0.748467	-0.621344
H	0.221218	-2.492345	0.677508
C	0.128693	1.497447	-1.739509
C	-0.128693	-1.497447	-1.739509
H	0.089546	2.581730	-1.689010
H	0.294457	1.064480	-2.720427
H	-0.294457	-1.064480	-2.720427
H	-0.089546	-2.581730	-1.689010

R4: 1,3-Pentadiene E(RB+HF-LYP) = -195.30981

C	-0.907602	0.000000	-1.959333
C	0.448390	0.000000	-1.314843
C	0.737123	0.000000	0.000000
C	-0.208361	0.000000	1.108435
C	0.156236	0.000000	2.399613
H	1.288112	0.000000	-2.009782
H	1.788622	0.000000	0.288446
H	-1.269802	0.000000	0.866648
H	-0.576276	0.000000	3.201222
H	1.203097	0.000000	2.696162
H	-1.726378	0.000000	-1.235084
H	-1.031048	0.879920	-2.605421
H	-1.031048	-0.879920	-2.605421

R5, R8, R9: 1,3-Cyclopentadiene E(RB+HF-LYP) = -194.10106

H	-1.880936	0.878816	0.000098
C	-1.218209	0.000144	-0.000003
C	-0.283259	0.000058	-1.181349
C	0.993103	-0.000300	-0.734692
C	0.993099	0.000400	0.734696
C	-0.283264	-0.000375	1.181348
H	-1.881417	-0.878142	-0.000107
H	-0.610081	-0.000604	2.214541
H	-0.610071	0.000119	-2.214544
H	1.886846	-0.000395	-1.349345
H	1.886834	0.000643	1.349358

R6: 1,5-Hexadiene E(RB+HF-LYP) = -234.61171

C	0.212008	-0.489628	0.560189
C	-0.213065	0.490150	-0.560496
C	0.440942	0.181256	-1.879436
C	-0.202486	-0.151173	-2.999141
C	-0.440948	-0.179996	1.879477
C	0.203556	0.149567	2.999410
H	-0.053029	-1.508938	0.243769
H	1.303948	-0.469025	0.673099
H	-1.304918	0.468734	-0.674089
H	0.051048	1.509570	-0.243686
H	1.531747	0.228282	-1.890037
H	-1.288609	-0.212599	-3.036997
H	0.327672	-0.370274	-3.922273
H	-1.531880	-0.224031	1.890204
H	-0.325868	0.369191	3.922838
H	1.289844	0.208031	3.037154

R7 and P1: 1,3-Butadiene E(RB+HF-LYP) = -155.99214

C	-0.109085	-0.000069	1.848679
C	0.400562	-0.000032	0.608786
C	-0.400562	-0.000025	-0.608786
H	1.482677	0.000010	0.474076
H	-1.482677	-0.000059	-0.474076
C	0.109084	0.000021	-1.848679
H	1.183013	0.000282	-2.022593
H	0.526435	0.000053	2.729085
H	-1.183013	0.000495	2.022594
H	-0.526435	-0.000149	-2.729085

R7 and R8: Ethylene E(RB+HF-LYP) = -78.58746

C	0.000000	0.665524	0.000000
C	0.000000	-0.665524	0.000000
H	0.923558	1.239453	0.000000
H	-0.923558	1.239453	0.000000
H	0.923558	-1.239453	0.000000
H	-0.923558	-1.239453	0.000000

R10: Cis-triscyclopropacyclohexane E(RB+HF-LYP) = -350.08083

H	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.087522
C	1.211746	0.000000	4.333340
C	-0.065187	1.363516	1.732037
H	1.994644	0.978297	1.044957
H	-0.608089	1.472137	2.666650
H	-0.149889	2.230695	1.081860
C	1.242524	0.609410	1.738458
C	1.843474	-0.032288	2.962682
H	0.007429	-2.980676	2.902031
C	-0.013773	-1.893411	2.912480
H	1.869531	0.074348	5.195719
C	-1.390168	-1.276139	2.970246
H	-0.971476	-1.935396	0.907856
H	-1.522300	-0.349174	3.520990
H	-2.245294	-1.943816	3.040038
C	-0.623562	-1.242275	1.670248
H	2.930891	-0.021434	2.952233
H	0.272971	0.531337	4.461499
C	1.210739	-1.292834	3.553979
H	1.915152	-2.045011	3.901452

R11: Cis-triscyclobutacyclohexane E(RB+HF-LYP) = -468.02745

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.551632
H	0.973426	0.000000	2.052989
H	-1.653336	-1.377602	2.204550
H	-0.600061	0.818639	1.962804
H	0.929232	-0.407196	-0.409279
H	-0.203099	0.950622	-0.505158
C	-1.165397	-1.035030	0.042758
C	-0.787125	-1.343935	1.532932
C	0.053502	-2.609292	1.760307
H	-2.100665	-0.461419	0.047635
H	2.036737	-4.384032	0.146625
C	0.562030	-2.967838	-1.743354
C	-0.541882	-2.028937	-2.297795
H	-0.241631	-1.014889	-2.581472
H	-2.392072	-2.403460	-1.075448
H	-1.079006	-2.478184	-3.139808
H	1.400560	-2.407781	-1.319097
H	0.970587	-3.723660	-2.423011

C	-0.457652	-3.464122	-0.673206
C	-1.323068	-2.188150	-0.959709
C	-0.076750	-3.819659	0.771782
H	-0.979942	-4.326136	-1.106707
H	-0.758033	-4.601777	1.127690
C	1.433629	-4.109575	1.018320
C	1.600244	-2.669994	1.572762
H	2.211447	-2.542971	2.472992
H	-0.159433	-2.979186	2.771057
H	1.974025	-1.978928	0.811508
H	1.582180	-4.868565	1.793675

Table S2. B3LYP/6-31G* optimized geometries and energies for transition structures

TS1 E(RB+HF-LYP) = -155.91655

H	1.881849	-1.100924	-0.435440
C	1.064845	-0.626082	0.119166
C	-1.065620	-0.625274	-0.119189
C	0.683760	0.732882	-0.083831
C	-0.682927	0.733403	0.083647
H	-1.882719	-1.099377	0.435915
H	-1.338688	1.542124	0.403314
H	0.870699	-1.086421	1.080648
H	-0.871987	-1.086153	-1.080502
H	1.340495	1.541172	-0.402694

TS2 E(RB+HF-LYP) = -233.34730

C	-1.203716	1.140653	-0.106083
C	0.119843	1.482489	0.188734
C	1.242319	0.702964	-0.106083
C	1.242319	-0.702964	-0.106083
C	0.119843	-1.482489	0.188734
C	-1.203716	-1.140653	-0.106083
H	0.296276	2.340488	0.841280
H	2.220000	1.175106	-0.016579
H	2.220000	-1.175106	-0.016579
H	0.296276	-2.340488	0.841280
H	-1.999204	-1.641147	0.447050
H	-1.467749	-0.936255	-1.131155
H	-1.999204	1.641147	0.447050
H	-1.467749	0.936255	-1.131155

TS3 E(RB+HF-LYP) = -309.56144

H	0.696138	2.508565	0.264710
C	0.687715	1.425476	0.168400
C	0.687709	-1.425477	-0.168399
C	-0.516000	0.709437	-0.014178
C	1.867142	0.702428	0.105773
C	1.867138	-0.702434	-0.105775
C	-0.516002	-0.709434	0.014188
C	-1.855138	1.105047	-0.302705
H	2.820250	1.219913	0.179461
H	2.820245	-1.219922	-0.179473
H	-2.323464	-0.714596	1.196424
H	0.696128	-2.508565	-0.264714
H	-2.323460	0.714584	-1.196421
H	-2.295179	2.031077	0.075446
H	-2.295185	-2.031066	-0.075465
C	-1.855143	-1.105042	0.302701

TS4 E(RB+HF-LYP) = -195.24816

C	-0.906955	1.309420	0.015864
C	-0.906955	-1.309420	0.015864
C	0.507865	1.211640	0.015864
C	0.507865	-1.211640	0.015864
C	1.185505	0.000000	-0.142456
H	-1.206145	0.000000	0.498374
H	-1.333655	2.181680	0.515504
H	-1.333655	-2.181680	0.515504
H	-1.451815	1.068700	-0.896696
H	-1.451815	-1.068700	-0.896696
H	1.091195	2.046030	0.405514
H	1.091195	-2.046030	0.405514
H	2.270755	0.000000	-0.073006

TS5 E(RB+HF-LYP) = -194.05497

C	0.745102	-0.040400	-0.937637
C	-0.745573	-0.040390	-0.937240
C	1.149270	-0.018772	0.412626
C	-1.149046	-0.018741	0.413240
C	0.000315	-0.008670	1.215464
H	-0.000331	1.017963	-1.168788
H	1.353558	-0.191751	-1.821052

H	-1.354605	-0.191775	-1.820266
H	2.174927	0.032335	0.756061
H	-2.174548	0.032221	0.757150
H	0.000593	0.062844	2.298174

TS6 E(RB+HF-LYP) = -234.61171

C	-0.003155	-0.259864	1.431103
C	0.002591	0.260010	-1.431105
C	-1.220424	0.254898	0.946470
C	1.220515	-0.253526	-0.946841
C	1.216780	0.253454	0.951796
C	-1.216584	-0.254976	-0.951603
H	-2.148156	-0.189265	1.306919
H	2.147543	0.193044	-1.306082
H	-1.300374	1.331981	0.810063
H	1.302403	-1.330624	-0.811832
H	1.299585	1.330509	0.817030
H	-1.296918	-1.332081	-0.815640
H	2.142225	-0.193424	1.314724
H	-2.142946	0.189153	-1.315595
H	-0.004566	-1.277561	1.822935
H	0.002856	1.278291	-1.821448
H	-2.148156	-0.189265	1.306919
H	2.147543	0.193044	-1.306082
H	-1.300374	1.331981	0.810063
H	1.302403	-1.330624	-0.811832
H	1.299585	1.330509	0.817030
H	-1.296918	-1.332081	-0.815640
H	2.142225	-0.193424	1.314724
H	-2.142946	0.189153	-1.315595
H	-0.004566	-1.277561	1.822935
H	0.002856	1.278291	-1.821448

TS7 E(RB+HF-LYP) = -234.54390

C	-0.436584	1.437291	0.499253
C	-0.436584	-1.437291	0.499253
C	-1.328804	0.703590	-0.261329
C	-1.328804	-0.703590	-0.261329
C	1.571834	0.692999	-0.261329
C	1.571834	-0.692999	-0.261329
H	-0.386519	2.517676	0.387554
H	-0.095393	1.068674	1.459891

H	-0.386519	-2.517676	0.387554
H	-0.095393	-1.068674	1.459891
H	-1.893469	1.213289	-1.040733
H	-1.893469	-1.213289	-1.040733
H	2.088050	1.235813	0.525348
H	1.448651	1.235917	-1.191624
H	2.088050	-1.235813	0.525348
H	1.448651	-1.235917	-1.191624
H	-0.386519	2.517676	0.387554
H	-0.095393	1.068674	1.459891
H	-0.386519	-2.517676	0.387554
H	-0.095393	-1.068674	1.459891
H	-1.893469	1.213289	-1.040733
H	-1.893469	-1.213289	-1.040733
H	2.088050	1.235813	0.525348
H	1.448651	1.235917	-1.191624
H	2.088050	-1.235813	0.525348
H	1.448651	-1.235917	-1.191624

TS8 E(RB+HF-LYP) = -272.65677

H	-1.328818	-1.543634	-1.574115
C	-0.702911	-0.744238	-1.189919
H	0.000000	2.002461	0.480633
C	-1.157427	0.358447	-0.460333
C	0.702911	-0.744238	-1.189919
H	0.000000	1.942119	-1.293139
C	0.000000	1.326385	-0.376846
C	-0.693970	-0.332112	1.629129
H	-2.195444	0.671846	-0.407232
C	0.693970	-0.332112	1.629129
H	1.328818	-1.543634	-1.574115
C	1.157427	0.358447	-0.460333
H	2.195444	0.671846	-0.407232
H	1.241173	0.492420	2.077388
H	-1.243940	-1.264662	1.567484
H	-1.241173	0.492420	2.077388
H	1.243940	-1.264662	1.567484
C	0.000000	1.326385	-0.376846
C	-0.693970	-0.332112	1.629129
H	-2.195444	0.671846	-0.407232
C	0.693970	-0.332112	1.629129
H	1.328818	-1.543634	-1.574115
C	1.157427	0.358447	-0.460333
H	2.195444	0.671846	-0.407232

H	1.241173	0.492420	2.077388
H	-1.243940	-1.264662	1.567484
H	-1.241173	0.492420	2.077388
H	1.243940	-1.264662	1.567484

TS9 E(RB+HF-LYP) = -350.04253

H	2.076944	-1.137875	1.181589
C	1.486502	-0.360667	0.707184
C	-1.858680	0.685712	0.000000
C	0.929340	0.685712	1.609664
H	-0.015186	-1.137875	2.389481
H	0.658144	1.631867	1.139939
H	1.468246	0.857609	2.543077
C	-0.130812	-0.360667	1.640941
C	-1.355690	-0.360667	0.933756
H	-0.015186	-1.137875	-2.389481
C	-0.130812	-0.360667	-1.640941
H	-2.936492	0.857609	0.000000
C	0.929340	0.685712	-1.609664
H	2.076944	-1.137875	-1.181589
H	0.658144	1.631867	-1.139939
H	1.468246	0.857609	-2.543077
C	1.486502	-0.360667	-0.707184
H	-2.061758	-1.137875	1.207892
H	-1.316288	1.631867	0.000000
C	-1.355690	-0.360667	-0.933756
H	-2.061758	-1.137875	-1.207892

TS10 E(RB+HF-LYP) = -467.94154

C	1.804707	-0.757478	-1.129797
C	2.523036	-0.422644	0.181626
H	2.614943	-1.254379	0.889487
H	3.535610	-0.043379	0.000000
H	1.073183	-1.558180	-0.973470
H	2.443599	-1.063528	-1.970959
C	1.097301	0.580973	-1.318664
C	1.629699	0.733203	0.669199
H	2.101596	1.714392	0.674492
C	0.593346	0.580973	1.609622
H	1.766555	1.400750	-1.574983
C	-0.235306	0.733203	-1.745960
C	-1.104225	-0.422644	-2.275826

C	-1.880787	-0.757478	-0.998023
H	-0.537153	-1.254379	-2.709351
H	-0.466670	1.714392	-2.157281
H	-1.767805	-0.043379	-3.061928
H	-1.379641	-1.558180	-0.442669
H	-2.928700	-1.063528	-1.130740
C	-1.690647	0.580973	-0.290959
C	-1.394392	0.733203	1.076761
H	-2.247253	1.400750	-0.742390
H	-1.634925	1.714392	1.482789
C	-1.418810	-0.422644	2.094200
H	-2.077790	-1.254379	1.819864
C	0.076080	-0.757478	2.127821
H	0.485101	-1.063528	3.101698
H	0.480698	1.400750	2.317373
H	0.306458	-1.558180	1.416139
H	-1.767805	-0.043379	3.061928

TS11 E(RB+HF-LYP) = -388.17124

H	-0.601715	-1.961067	-1.564867
C	-0.604649	-1.964045	-0.470569
C	0.755468	-1.980192	0.174084
C	0.707026	-1.237074	1.323199
C	-0.517893	-0.514977	1.383811
C	-1.227891	-0.730056	0.175459
H	-1.173747	-2.854214	-0.151236
C	0.719778	0.520877	-1.287993
H	1.571944	-2.619789	-0.142109
H	1.506536	-1.154993	2.053292
H	-0.842957	0.102313	2.211861
C	-0.674082	0.674385	-1.078093
H	-2.305453	-0.584770	0.128984
H	-1.383291	0.476803	-1.879586
H	1.185090	-0.092305	-2.049487
C	1.411566	1.299081	-0.317758
C	0.517091	2.017448	0.429837
H	2.485339	1.271828	-0.158829
H	0.757148	2.687974	1.247433
C	-0.839714	1.921773	-0.214898
H	-1.684854	1.894142	0.479711
H	-0.994238	2.790758	-0.877644

Table S3. B3LYP/6-31G* optimized geometries and energies for products

P2: 1,3-Cyclohexadiene E(RB+HF-LYP) = -233.41894

C	1.425072	0.064404	-0.113709
H	2.506315	0.184407	-0.115975
C	0.726228	0.103966	-1.260241
H	1.227292	0.271791	-2.211014
C	-0.726221	-0.103965	-1.260245
H	-1.227280	-0.271792	-2.211021
C	-1.425071	-0.064406	-0.113717
H	-2.506314	-0.184410	-0.115991
C	-0.731802	0.239418	1.195328
H	-0.763329	1.329969	1.361867
H	-1.272110	-0.209868	2.036877
C	0.731794	-0.239418	1.195333
H	0.763319	-1.329969	1.361873
H	1.272099	0.209869	2.036884

P3: Benzocyclobutane E(RB+HF-LYP) = -309.63086

H	0.000000	2.526222	-0.737147
C	0.000000	1.439157	-0.719642
C	0.000000	-1.439157	-0.719642
C	0.000000	0.697807	0.453266
C	0.000000	0.701083	-1.914717
C	0.000000	-0.701083	-1.914717
C	0.000000	-0.697807	0.453266
C	0.000000	0.790511	1.973735
H	0.000000	1.227787	-2.865796
H	0.000000	-1.227787	-2.865796
H	0.888881	-1.247376	2.423545
H	0.000000	-2.526222	-0.737147
H	-0.888881	1.247376	2.423545
H	0.888881	1.247376	2.423545
H	-0.888881	-1.247376	2.423545
C	0.000000	-0.790511	1.973735

P7: Cyclohexene E(RB+HF-LYP) = -234.64829

C	-1.192312	-0.318563	-0.698255
C	-1.192311	0.318563	0.698256
C	0.047937	-0.110725	1.498944
C	0.047936	0.110725	-1.498944

C	1.306095	-0.056999	0.666078
C	1.306095	0.056999	-0.666079
H	-1.192983	-1.412587	-0.593439
H	-1.192983	1.412587	0.593439
H	-2.105884	-0.053601	-1.244612
H	-2.105883	0.053601	1.244614
H	0.163847	0.526617	2.386746
H	0.163845	-0.526617	-2.386746
H	-0.089974	-1.132133	1.888891
H	-0.089976	1.132133	-1.888892
H	2.254680	-0.112069	1.199545
H	2.254680	0.112069	-1.199547

P8: Norbornene E(RB+HF-LYP) = -272.72738

C	0.249942	1.128504	0.221544
C	0.791597	0.000000	1.132010
H	1.883548	0.000000	1.207345
C	0.249942	-1.128504	0.221544
H	0.351766	0.000000	2.137499
C	0.792001	-0.670298	-1.125762
H	0.477305	-2.157748	0.510542
H	-1.761738	1.177749	1.122286
H	1.012169	-1.328726	-1.960780
C	0.792001	0.670298	-1.125762
H	-1.761738	-1.177749	1.122286
C	-1.279495	-0.780534	0.221544
H	-1.794869	1.206609	-0.644462
H	0.477305	2.157748	0.510542
H	1.012169	1.328726	-1.960780
H	-1.794869	-1.206609	-0.644462
C	-1.279495	0.780534	0.221544

P10: Cyclonona-1,4,7-triene E(RB+HF-LYP) = -350.11250

H	2.522255	-0.956120	1.181673
C	1.833155	-0.284678	0.669299
C	-1.806194	0.514195	0.000000
C	0.903097	0.514195	1.564210
H	-0.237769	-0.956120	2.775174
H	0.621787	1.453060	1.076966
H	1.434144	0.790149	2.484011
C	-0.336948	-0.284678	1.922208
C	-1.496208	-0.284678	1.252909

H	-0.237769	-0.956120	-2.775174
C	-0.336948	-0.284678	-1.922208
H	-2.868289	0.790149	0.000000
C	0.903097	0.514195	-1.564210
H	2.522255	-0.956120	-1.181673
H	0.621787	1.453060	-1.076966
H	1.434144	0.790149	-2.484011
C	1.833155	-0.284678	-0.669299
H	-2.284486	-0.956120	1.593501
H	-1.243574	1.453060	0.000000
C	-1.496208	-0.284678	-1.252909
H	-2.284486	-0.956120	-1.593501

P11: Cyclododeca-1,5,9-triene E(RB+HF-LYP) = -468.04533

C	1.807243	-0.690798	-1.010302
C	2.586625	-0.347739	0.289531
H	2.780511	-1.287408	0.824124
H	2.466384	1.626679	1.283168
H	3.572440	0.036909	0.000000
H	0.983689	-1.374577	-0.786891
H	2.495817	-1.252036	-1.661995
C	1.288578	0.518974	-1.739541
C	1.951099	0.668237	1.223119
C	0.862198	0.518974	1.985712
H	1.983374	1.358380	-1.801822
H	-2.103967	-1.287408	1.995931
C	-1.778568	-0.690798	-1.059967
C	-1.042572	-0.347739	-2.384849
H	-0.676543	-1.287408	-2.820055
H	-0.121936	1.626679	-2.777536
H	-1.786220	0.036909	-3.093824
H	-1.173312	-1.374577	-0.458454
H	-2.687238	-1.252036	-1.330444
C	-2.150776	0.518974	-0.246170
C	0.083702	0.668237	-2.301260
C	-2.034801	0.668237	1.078142
H	-2.552110	1.358380	-0.816741
H	-2.344448	1.626679	1.494368
C	-1.544054	-0.347739	2.095318
C	-0.028674	-0.690798	2.070269
H	0.191421	-1.252036	2.992438
H	0.568736	1.358380	2.618563
H	0.189623	-1.374577	1.245345
H	-1.786220	0.036909	3.093824

SECTION II.
Table S4. Reaction 1.

R1: CYCLOBUTENE (C_{2v})

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-154.89962	0.09324	0.9135	-154.81445	63.33
B3LYP/6-31G(d)	-155.97326	0.08694	0.9804	-155.88803	63.90
B3LYP/6-31+G(d,p)	-155.98861	0.08637	1.0000	-155.90225	63.97
KMLYP/6-31G(d)	-155.67276	0.09102	1.0000	-155.58174	63.51
KMLYP/6-311G	-155.65066	0.09080	1.0000	-155.55986	62.07
MP2/6-31G(d)	-155.41018	0.08838	0.9646	-155.32493	63.97
CASSCF/6-31G(d,p)	-154.95565 [1]				
CASMP2/6-311+G(d,p)	-155.56180 [1]				
CAS(4,4)/6-31G(d)	-154.94545	0.09158	1.0000	-154.85391	62.39
CASPT2/6-31G(d) [b]	-155.41747	0.08694	0.9804	-155.33224	
CASPT2/6-31G(d) [c]	-155.41676	0.09158	1.0000	-155.32519	
BPW91/6-31G(d)	-155.94861	0.08471	1.0000	-155.86390	64.15
MPW1K/6-31+G(d,p)	-155.94524	0.08922	0.9515	-155.86034	62.33
CBS-QB3				-155.64680	

[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.
[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

TS1: TRANSITION STRUCTURE (C_2)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-154.82483	0.09033	0.9135	-154.74231	63.24
B3LYP/6-31G(d)	-155.91655	0.08422	0.9804	-155.83398	63.89
B3LYP/6-31+G(d,p)	-155.93486	0.08373	1.0000	-155.85113	63.96
KMLYP/6-31G(d)	-155.60267	0.08822	1.0000	-155.51447	62.04
KMLYP/6-311G	-155.58729	0.08798	1.0000	-155.49930	63.34
MP2/6-31G(d)	-155.35056	0.08562	0.9646	-155.26797	63.77
CASSCF/6-31G(d,p)	-154.89789 [1]				
CASMP2/6-311+G(d,p)	-155.49953 [1]				
CAS(4,4)/6-31G(d)	-155.88719	0.08754	1.0000	-154.79965	64.34
CASPT2/6-31G(d) [b]	-155.36072	0.08422	0.9804	-155.27816	
CASPT2/6-31G(d) [c]	-155.35903	0.08754	1.0000	-155.27149	
BPW91/6-31G(d)	-155.89464	0.08205	1.0000	-155.81259	64.146
MPW1K/6-31+G(d,p)	-155.88091	0.08648	0.9515	-155.79862	62.632
CBS-QB3				-155.59578	

1) Sakai, S. *J. Mol. Struct.* **1999**, *461-462*, 283-295.

P1: 1,3-BUTADIENE (C2h)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-154.91965	0.09154	0.9135	-154.83603	65.54

B3LYP/6-31G(d)	-155.99214	0.08548	0.9804	-155.90833	66.06
B3LYP/6-31+G(d,p)	-156.01065	0.08504	1.0000	-155.92560	66.13
KMLYP/6-31G(d)	-155.68023	0.08925	1.0000	-155.59101	65.70
KMLYP/6-311G	-155.67022	0.08916	1.0000	-155.58105	65.54
MP2/6-31G(d)	-155.42266	0.08636	0.9646	-155.33935	66.27
CASSCF/6-31G(d,p) [a]	-154.98165 [1]				
CASMP2/6-311+G(d,p) [a]	-155.49953 [1]				
CAS(4,4)/6-31G(d)	-154.97547	0.08930	1.0000	-154.88644	67.49
CASPT2/6-31G(d) [b]	-155.43396	0.08548	0.9804	-155.35019	
CASPT2/6-31G(d) [c]	-155.43361	0.08903	1.0000	-155.34466	
BPW91/6-31G(d)	-155.96280	0.08328	1.0000	-155.87952	66.37
MPW1K/6-31+G(d,p)	-155.95592	0.08760	0.9515	-155.87257	65.94
CBS-QB3				-155.66691	

[a] for s-cis-butadiene (C_2)

Table S5. Reaction 2.

R2: t-Z-t-1,3,5-HEXATRIENE (C2v)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-231.80590	0.12802	0.9135	-231.68896	78.93
B3LYP/6-31G(d)	-233.39551	0.11937	0.9804	-233.27847	79.75
B3LYP/6-31+G(d,p)	-233.42064	0.11876	1.0000	-233.30160	79.94
KMLYP/6-31G(d)	-232.92935	0.12449	1.0000	-232.80486	77.57
KMLYP/6-311G	-232.91021	0.12476	1.0000	-232.78545	78.83
MP2/6-31G(d)	-232.55979	0.12026	0.9646	-232.4438	80.30
	-232.55979 [1]	0.11187	0.93		
CASSCF/6-31G(d,p) [a]	-231.89056 [2]				
CASMP2/6-311+G(d,p)[a]	-231.77348 [2]				
CAS(6,6)/6-31G(d)	-231.88841	0.12447	1.0000	-231.76393	79.80
CASPT2/6-31G(d) [b]	-232.57568	0.11937	0.9804	-232.45864	
CASPT2/6-31G(d) [c]	-232.57501	0.12447	1.0000	-232.45054	
BPW91/6-31G(d)	-233.35486	0.11621	1.0000	-233.23865	80.31
MPW1K/6-31+G(d,p)	-233.34039	0.12237	0.9515	-233.22395	79.72
CBS-QB3				-232.91658	

[a] for c-Z-c-1,3,5-hexatriene

[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.

[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

TS2: TRANSITION STRUCTURE (C_s)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-231.73188	0.12870	0.9135	-231.6142	73.17
B3LYP/6-31G(d)	-233.34730	0.11943	0.9804	-233.2305	74.12
B3LYP/6-31+G(d,p)	-233.37158	0.11883	1.0000	-233.2527	74.25

KMLYP/6-31G(d)	-232.87654	0.12482	1.0000	-232.75173	74.02
KMLYP/6-311G	-232.85911	0.12483	1.0000	-232.73428	73.62
MP2/6-31G(d)	-232.51703 -232.51703 [1]	0.12081 0.11235	0.9646 0.93	-232.40050	74.67
CASSCF/6-31G(d,p) CASMP2/6-311+G(d,p) CAS(6,6)/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-231.83200 [2] -232.71414 [2] -231.81804 -232.52735 -232.52608	 0.12489 0.11943 0.12489	 1.0000 0.9804 1.0000	 -231.69314 -232.41026 -232.40119	 74.05
BPW91/6-31G(d,p)	-233.31321	0.11631	1.0000	-233.19690	74.66
MPW1K/6-31+G(d,p)	-233.29189	0.12243	0.9515	-233.17540	74.13
CBS-QB3				-232.87079	

P2: 1,3-CYCLOHEXADIENE (C2)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-231.83189	0.13165	0.9135	-231.71163	71.32
B3LYP/6-31G(d)	-233.41894	0.12283	0.9804	-233.29852	72.33
B3LYP/6-31+G(d,p)	-233.44062	0.12216	1.0000	-233.28404	72.32
KMLYP/6-31G(d)	-232.96816	0.12849	1.0000	-232.83967	70.22
KMLYP/6-311G	-232.94576	0.12854	1.0000	-232.81722	70.01
MP2/6-31G(d)	-232.59362 -233.59362 [1]	0.12459	0.9646	-232.47344	72.08
CASSCF/6-31G(d,p) CASMP2/6-311+G(d,p) CAS(6,6)/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-231.91710 [2] -231.81102 [2] -231.90383 -232.60522 -232.60430	 0.12913 0.12283 0.12913	 1.0000 0.9804 1.0000	 -231.77470 -232.48479 -232.47517	
BPW91/6-31G(d,p)	-233.37797	0.11966	1.0000	-233.25831	72.80
MPW1K/6-31+G(d,p)	-233.37522	0.12602	0.9515	-233.25531	71.88
CBS-QB3				-232.94026	

1) Jia, H.; Schleyer, P.R. *J. Am Chem. Soc*. **1995**, *117*, 11529-11535.
2) Sakai, S.; Takane, S. *J. Phys. Chem. A* **1999**, *103*, 2878-2882.

Table 6. Reaction 3

R3: ORTHO-XYLYLENE (C2)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-307.53983	0.14250	0.9135	-307.40965	79.63
B3LYP/6-31G(d)	-309.60604	0.13261	0.9804	-309.47603	80.15
B3LYP/6-31+G(d,p)	-309.63169	0.13205	1.0000	-309.49965	81.24
KMLYP/6-31G(d)	-308.97768	0.13894	1.0000	-308.83874	78.75
KMLYP/6-311G	-308.90096	0.13903	1.0000	-308.81229	79.83
MP2/6-31G(d)	-308.54584	0.13267	0.9646	-308.41787	81.09

CASSCF/6-31G(d,p)	-307.66678 [1]				
CASMP2/6-311+G(d,p)	-308.79569 [1]				
CAS(8,8)/6-31G(d)	-307.65259	0.13806	1.0000	-307.51452	81.56
CASPT2/6-31G(d) [b]	-308.56507	0.13261	0.9804	-308.43506	
CASPT2/6-31G(d) [c]	-308.56416	0.13806	1.0000	-308.42611	
BPW91/6-31G(d)	-309.56044	0.12904	1.0000	-309.43139	82.09
MPW1K/6-31+G(d,p)	-309.53261	0.13623	0.9515	-309.40298	80.44
CBS-QB3				-308.99908	

[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.
[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

TS3: TRANSITION STRUCTURE (C2)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-307.47336	0.14101	0.9135	-307.34455	75.86
B3LYP/6-31G(d)	-309.56144	0.13145	0.9804	-309.43257	77.39
B3LYP/6-31+G(d,p)	-309.58764	0.13080	1.0000	-309.45684	77.54
KMLYP/6-31G(d)	-308.92935	0.13782	1.0000	-308.79153	75.01
KMLYP/6-311G	-308.90096	0.13783	1.0000	-308.76312	76.08
MP2/6-31G(d)	-308.50891	0.13217	0.9646	-308.38142	77.65
CASSCF/6-31G(d,p)	-307.60814 [1]				
CASMP2/6-311+G(d,p)	-308.74003 [1]				
CAS(8,8)/6-31G(d)	-307.59388	0.13639	1.0000	-307.45749	77.79
CASPT2/6-31G(d) [b]	-308.52456	0.13145	0.9804	-308.39568	
CASPT2/6-31G(d) [c]	-308.52209	0.13639	1.0000	-308.38570	
BPW91/6-31G(d)	-309.52302	0.12801	1.0000	-309.39501	78.09
MPW1K/6-31+G(d,p)	-309.48811	0.13507	0.9515	-309.35959	76.89
CBS-QB3				-308.95898	

1) Sakai, S. *J. Phys. Chem. A* **2000**, *104*, 11615-11621.

P3: BENZOCYCLOBUTENE (C2v)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-307.56543	0.14442	0.9135	-307.43350	74.51
B3LYP/6-31G(d)	-309.63086	0.13501	0.9804	-309.49850	75.89
B3LYP/6-31+G(d,p)	-309.65344	0.13432	1.0000	-309.51911	76.01
KMLYP/6-31G(d)	-309.01622	0.14140	1.0000	-308.87481	75.00
KMLYP/6-311G	-308.98125	0.14155	1.0000	-308.83975	74.68
MP2/6-31G(d)	-308.58075	0.13562	0.9646	-308.44993	78.22
CASSCF/6-31G(d,p)	- 307.66966 [1]				
CASMP2/6-311+G(d,p)	-308.80836 [1]				
CAS(8,8)/6-31G(d)	-307.65618	0.14189	1.0000	-307.51487	75.27
CASPT2/6-31G(d) [a]	-308.58895	0.13501	0.9804	-308.45659	
CASPT2/6-31G(d) [b]	-308.58810	0.14189	1.0000	-308.44321	
BPW91/6-31G(d)	-309.58866	0.13159	1.0000	-309.45707	76.54

MPW1K/6-31+G(d,p)	-309.56768	0.13869	0.9515	-309.43572	75.46
CBS-QB3				-309.01949	

Table S7. Reaction 4

R4: Z-s-E-1,3-PENTADIENE (Cs)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-193.956368	0.12195	0.9135	-193.84496	75.25
B3LYP/6-31G(d)	-195.30981 -195.30980[3,4]	0.11406 0.11405	0.9804	-195.19799	75.82
B3LYP/6-31+G(d,p)	-195.33132	0.11371	1.0000	-195.21794	76.06
KMLYP/6-31G(d)	-194.92976	0.11902	1.0000	-194.81074	75.19
KMLYP/6-311G	-194.91471	0.11894	1.0000	-194.79576	75.21
MP2/6-31G(d)	-194.59137	0.11556	0.9646	-194.47990	76.58
CAS(6,6)/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-194.02027 -194.60372 -194.60325	0.11983 0.11405 0.11983	1.0000 0.9804 1.0000	-193.90045 -194.49191 -194.48342	76.20
BPW91/6-31G(d)	-195.27248	0.11161	1.0000	-195.16087	76.21
MPW1K/6-31+G(d,p)	-195.26815	0.11673	0.9515	-195.15707	75.46
CBS-QB3				-194.89508	

[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.
[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

TS 4: TRANSITION STRUCTURE (Cs)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-193.86279 -193.75908 [1,5]	0.11838	0.9135	-193.75465	68.26
B3LYP/6-31G(d)	-195.24815 -195.24815 [3,4,6]	0.11065	0.9804	-195.13244	69.13
B3LYP/6-31+G(d,p)	-195.27093	0.10991	1.0000	-195.16102	69.24
KMLYP/6-31G(d)	-194.86398	0.11575	1.0000	-194.74823	68.51
KMLYP/6-311G	-194.84898	0.11578	1.0000	-194.73321	68.36
MP2/6-31G(d)	-194.53128 -195.55527 [4,6]	0.11255 0.11018	0.9646	-194.42271	68.95
CAS(6,6)/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-193.93994 -194.54036 -194.53914	0.11587 0.11065 0.11587	1.0000 0.9804 1.0000	-193.82408 -194.43188 -194.42328	68.96
BPW91/6-31G(d,p)	-195.22039	0.10783	1.0000	-195.11255	69.53
MPW1K/6-31+G(d,p)	-195.20555	0.11335	0.9515	-195.09770	68.83
CBS-QB3				-194.83642	

1) Hess, B.A.; Schaad, L.J. Pancir, J. *J. Am. Chem. Soc*. **1985**, *107*, 149-154.
2) Hess, B.A., Schaad, L.J. *J. Am. Chem. Soc.* **1983**, *105*, 7185-7186.
3) Jursic, B.S., *J. Mol. Struct.* **1998**, *423*, 189-194.

4) Wiest, O.; Saettel, N. J. *J. Org. Chem*. **2000**, *65*, 2331-2336.
5) Jensen, F.; Houk, K.N. *J. Am. Chem. Soc*. **1987**, *109*, 3139-3140.
6) Jiao, H.; Schleyer, P.R. *J. Chem. Soc. Faraday Trans* **1994**, *90*, 1559-1567.

Table S8: Reaction 5

R5: CYCLOPENTADIENE (C2v)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-192.79172 -192.79172 [1]	0.09973	0.9135 0.89	-192.70062	65.91
B3LYP/6-31G(d)	-194.10106	0.09288	0.9804	-194.01000	66.68
B3LYP/6-31+G(d,p)	-194.11982	0.09243	1.0000	-194.02739	69.76
KMLYP/6-31G(d)	-193.71768	0.09727	1.0000	-193.62041	64.81
KMLYP/6-311G	-193.69860	0.09732	1.0000	-193.60123	65.98
MP2/6-31G(d)	-193.42538 -193.44967 [1,2]	0.09382	0.9646	-193.33488	66.80
CAS(6,6)/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-192.86289 -193.43645 -193.43653	0.09692 0.09288 0.09692	1.0000 0.9804 1.0000	-192.76597 -193.34542 -193.3396	66.55
BPW91/6-31G(d)	-194.07189	0.09049	1.0000	-193.98140	67.04
MPW1K/6-31+G(d,p)	-194.06308	0.09538	0.9515	-193.97233	66.43
CBS-QB3				-193.71274	

[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.
[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

TS5: TRANSITION STRUCTURE (Cs)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-192.72992 -192.72992 [1]	0.09601	0.9135 0.89	-192.64221	64.80
B3LYP/6-31G(d)	-194.05497	0.08916	0.9804	-193.96758	65.50
B3LYP/6-31+G(d,p)	-194.07614	0.08915	1.0000	-193.98669	65.56
KMLYP/6-31G(d)	-193.67103	0.09402	1.0000	-193.57701	65.01
KMLYP/6-311G	-193.64692	0.09382	1.0000	-193.55310	64.89
MP2/6-31G(d)	-194.07614 -193.40407[1,2]	0.0904	0.9646	-193.98894	65.60
CAS(6,6)/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-192.79457 -193.38698 -193.38624	0.09349 0.08916 0.09349	1.0000 0.9804 1.0000	-192.70108 -193.29956	65.21
BPW91/6-31G(d)	-194.03160	0.08738	1.0000	-193.94422	65.81
MPW1K/6-31+G(d,p)	-194.02036	0.09215	0.9515	-193.93269	65.24
CBS-QB3				-193.67155	

1) Alkorta, I.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2497-2503.
2) Jiao, H.; Schleyer, V.R. *J. Chem. Soc., Faraday Trans. 2* **1994,** *90*, 1559-1567.

Table S9. Reaction 6

R6: 1,5-HEXADIENE (C2)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-232.98332	0.15246	0.9135	-232.84404	82.53
B3LYP/6-31G(d)	-234.61171	0.14251	0.9804	-234.47199	83.89
B3LYP/6-31+G(d,p)	-234.63812	0.14169	1.0000	-234.49643	84.01
KMLYP/6-31G(d)	-234.16483	0.14873	1.0000	-234.01609	81.55
KMLYP/6-311G	-234.14488	0.14853	1.0000	-233.99635	82.99
MP2/6-31G(d)	-233.74810	0.14485	0.9646	-233.60838	83.72
CAS(6,6)/6-31G(d) [a]	-233.05479	0.14949	1.0000	-232.90529	83.72
CASPT2/6-31G(d) [b]	-233.76106	0.14251	0.9804	-233.62134	
CASPT2/6-31G(d) [c]	-233.76036	0.14949	1.0000	-233.61087	
BPW91/6-31G(d)	-234.56450	0.13889	1.0000	-234.42562	84.52
MPW1K/6-31+G(d,p)	-234.56748	0.14597	0.9515	-234.42859	83.42
CBS-QB3				-234.11262	

[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.
[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

TS6: TRANSITION STRUCTURE (C2h)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-232.89314	0.15131	0.9135	-232.75492	74.12
B3LYP/6-31G(d)	-234.55698	0.14207	0.9804	-234.41769	75.23
B3LYP/6-31+G(d,p)	-234.58224	0.14105	1.0000	-234.44119	75.69
KMLYP/6-31G(d)	-234.10340	0.14846	1.0000	-233.95495	72.37
KMLYP/6-311G	-234.08298	0.14778	1.0000	-233.93520	73.92
MP2/6-31G(d)	-233.70273	0.14504	0.9646	-233.56282	72.46
CASSCF/6-31G(d)	-232.9771 [1]				
CAS(6,6)/6-31G(d)	-232.97713	0.14772	1.0000	-232.82941	76.71
CASPT2/6-31G(d) [b]	-233.70776	0.14207	0.9804	-233.56848	
CASPT2/6-31G(d) [c]	-233.70129	0.14772	1.0000	-233.55356	
BPW91/6-31G(d)	-234.52050	0.13892	1.0000	-234.38158	75.29
MPW1K/6-31+G(d,p)	-234.50867	0.14567	0.9515	-234.37006	74.28
CBS-QB3				-234.06000	

Table S10. Reaction 7

R7: s-trans 1,3-BUTADIENE (C2h)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-154.91965	0.09154	0.9135	-154.83603	65.54
B3LYP/6-31G(d)	-155.99214	0.08548	0.9804	-155.90833	66.06
B3LYP/6-31+G(d,p)	-156.01065	0.08504	1.0000	-155.92560	67.49

KMLYP/6-31G(d)	-155.68026	0.08925	1.0000	-155.59101	65.70
KMLYP/6-311G	-155.67021	0.08916	1.0000	-155.58105	
MP2/6-31G(d)	-155.42266	0.08636	0.9646	-155.33935	66.27
CAS(4,4)/6-31G(d)	-154.97457	0.08903	1.0000	-154.88644	67.49
CASPT2/6-31G(d) [a]	-155.43396	0.08548	0.9804	-155.35015	
CASPT2/6-31G(d) [b]	-155.43362	0.08903	1.0000	-155.34458	
BPW91/6-31G(d)	-155.96280	0.08328	1.0000	-155.87952	67.73
MPW1K/6-31+G(d,p)	-155.95592	0.08760	0.9515	-155.87257	67.30
CBS-QB3/6-31G(d)				-155.66691	

[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.
[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

R7: ETHYLENE (D2h)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-78.03172	0.05478	0.9135	-77.98168	52.1
B3LYP/6-31G(d)	-78.58746	0.05151	0.9804	-78.53723	52.36
	-78.58746 [1]	0.05122			52.30
B3LYP/6-31+G(d,p)	-78.59964	0.05099	1.0000	-78.54865	52.34
KMLYP/6-31G(d)	-78.43252	0.05342	1.0000	-78.37909	52.17
KMLYP/6-311G	-74.33957	0.05332	1.0000	-78.37581	52.11
MP2/6-31G(d)	-78.28503	0.05204	0.9646	-78.23483	52.37
CAS(2,2)/6-31G(d)	-78.06025	0.05336	1.0000	-78.00689	52.32
CASPT2/6-31G(d) [b]	-78.29085	0.05151	0.9804	-78.24035	
CASPT2/6-31G(d) [c]	-78.29076	0.05336	1.0000	-78.23739	
BPW91/6-31G(d)	-78.56985	0.04996	1.0000	-78.51989	52.44
MPW1K/6-31+G(d,p)	-78.57002	0.05250	0.9515	-78.52007	52.23
CBS-QB3				-78.41663	

1) Goldstein, E.; Beno, B.; Houk, K.N. *J. Am. Chem. Soc*. **1996**, *118*, 6036-6043.
2) Brodley, A. Z.; Kociolek, M.G.; Johnson, R.P. *J. Org. Chem*. **2000**, *65*, 7134-7138.

TS7: TRANSITION STRUCTURE (Cs)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-232.87961	0.15067	0.9135	-232.74197	75.41
B3LYP/6-31G(d)	-234.51563 [2]	0.14603			75.60
	-234.54389 [3]				
	-234.54389	0.14057	0.9804	-234.40608	77.74
B3LYP/6-31+G(d,p)	-234.57061	0.13982	1.0000	-234.43079	77.93
KMLYP/6-31G(d)	-234.08321	0.14666	1.0000	-233.93655	76.69
KMLYP/6-311G	-234.06756	0.14643	1.0000	-233.92113	76.36
MP2/6-31G(d)	-233.65352 [2,4]	0.14286			75.2
	-233.67910	0.14221	0.9646	-233.54193	77.6
CASSCF/6-31G(d)	-232.96590 [6]				
CASSCF/6-31G(d, p)	-232.98315 [6]				
CASMP2/6-311+G(d,p)	-234.03469 [5]				

CAS(6,6)/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-232.96590 -233.69007 -233.68959	0.14750 0.14603 0.14750	1.0000 0.9804 1.0000	-232.81840 -233.54689 -233.54209	77.30
BPW91/6-31G(d)	-234.50434	0.13678	1.0000	-234.36757	79.05
MPW1K/6-31+G(d,p)	-234.49062	0.1439	0.9515	-234.35370	77.34
CBS-QB3				-234.04711	

3) Goldstein, E., Beno, B., Houk, K.N. *J. Am. Chem. Soc.* **1996**, *118*, 6036-6043.
4) Huei, C.; Tsai, L.C.; Hu, W.P. *J. Phys. Chem. A*, **2001**, *105*, 9945-9953.
5) Sakai, S. *J. Phys. Chem. A.* **2000**, *104*, 922-927.
6) Li, Y.; Houk, K.N. *J. Am. Chem. Soc.* **1993**, 115, 7478-7485.

P7: CYCLOHEXENE (C2)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-234.6489 [3] -233.01966	0.15707	0.9135	-232.87612	72.4 72.69
B3LYP/6-31G(d)	-234.64829 [3] -234.64829	0.14698	0.9804	-234.50419	73.82
B3LYP/6-31+G(d,p)	-234.67001	0.14599	1.0000	-234.52402	73.90
KMLYP/6-31G(d)	-234.21822	0.15352	1.0000	-234.06469	71.59
KMLYP/6-311G	-234.19192				
MP2/6-31G(d)	-233.79141	0.14991	0.9646	-233.64681	73.49
CASSCF/6-31G(d,p) CASMP2/6-311+G(d,p) CAS(6,6)/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-233.09454 [6] -234.03469 [5] -233.07876 -233.80146 -233.80031	0.15513 0.14698 0.15513	1.0000 0.9804 1.0000	-232.92363 -233.65736 -233.64518	73.38
BPW91/6-31G(d)	-234.60358	0.14337	1.0000	-234.46021	72.49
MPW1K/6-31+G(d,p)	-234.61285	0.15052	0.9515	-234.46963	73.42
CBS-QB3				-234.14460	

Table S11. Reaction 8

R8: CYCLOPENTADIENE (C2v)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-192.79172 -192.79172 [1]	0.09973	0.9135 0.89	-192.70062	65.92
B3LYP/6-31G(d)	-194.10106	0.09288	0.9804	-194.00994	66.68
B3LYP/6-31+G(d,p)	-194.11980	0.09243	1.0000	-194.02737	69.76
KMLYP/6-31G(d)	-193.71768	0.09727	1.0000	-193.62041	64.81
KMLYP/6-311G	-193.69860	0.09732	1.0000	-193.60128	65.98
MP2/6-31G(d)	-193.42538 -193.44967 [1]	0.09382	0.9646	-193.33488	66.80
CAS(4,4)/6-31G(d) CASPT2/6-31G(d) [b]	-192.84662 -193.43465	0.09768 0.09288	1.0000 0.9804	-192.74894 -193.34359	66.54

CASPT2/6-31G(d) [c]	-193.43410	0.09768	1.0000	-193.33642	
BPW91/6-31G(d)	-194.07189	0.09049	1.0000	-193.98140	67.04
MPW1K/6-31+G(d,p)	-194.06308	0.09538	0.9515	-193.97233	66.43
CBS-QB3				-193.71274	

1) Alkorta, I.; Elguero, J. *J. Chem. Soc., Perkin Tran.s 2*, **1998**, 2497-2503.
[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.
[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

R8: ETHYLENE (D2h)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-78.03172	0.05478	0.9135	-77.98168	52.1
B3LYP/6-31G(d)	-78.58746	0.05151	0.9804	-78.53723	52.36
B3LYP/6-31+G(d,p)	-78.59964	0.05099	1.0000	-78.54865	52.34
KMLYP/6-31G(d)	-78.43252	0.05342	1.0000	-78.37909	52.17
KMLYP/6-311G	-78.42913	0.05332	1.0000	-78.37581	52.14
MP2/6-31G(d)	-78.28503	0.05204	0.9646	-78.23483	52.37
CAS(2,2)/6-31G(d)	-78.06026	0.05336	1.0000	-78.00689	52.32
CASPT2/6-31G(d) [b]	-78.29085	0.05151	0.9804	-78.24035	
CASPT2/6-31G(d) [c]	-78.29076	0.05336	1.0000	-78.23739	
BPW91/6-31G(d)	-78.56985	0.04996	1.0000	-78.51989	52.44
MPW1K/6-31+G(d,p)	-78.57002	0.05250	0.9515	-78.52007	52.23
CBS-QB3				-78.41663	

TS8: TRANSITION STRUCTURE (Cs)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-270.76023	0.15864	0.9135	-270.61531	74.85
B3LYP/6-31G(d)	-272.65678	0.14795	0.9804	-272.51173	76.93
B3LYP/6-31+G(d,p)	-272.68381	0.14721	1.0000	-272.53660	77.06
KMLYP/6-31G(d)	-272.12665	0.15462	1.0000	-271.97203	75.92
KMLYP/6-311G	-272.10094	0.15435	1.0000	-271.94659	75.59
MP2/6-31G(d)	-271.69160	0.14986	0.9646	-271.54705	76.86
CASSCF/6-31G(d)	-270.86769 [2]				
CAS(6,6)/6-31G(d)	-270.84294	0.15594	1.0000	-270.68701	76.35
CASPT2/6-31G(d) [b]	-271.70094	0.14795	0.9804	-271.55589	
CASPT2/6-31G(d) [c]	-271.70018	0.15594	1.0000	-271.54424	
BPW91/6-31G(d)	-275.61735	0.14401	1.0000	-272.47334	78.02
MPW1K/6-31+G(d,p)	-272.60380	0.15168	0.9515	-272.45947	76.46
CBS-QB3				-272.10180	

2) Beno, B.R.; Wilsey, S.; Houk, K.N. *J. Am. Chem. Soc*. **1999**, *121*, 4816-4826.

P8: NORBORNENE (Cs)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-270.86184	0.16451	0.9135	-270.71156	71.76

B3LYP/6-31G(d)	-272.72738	0.15363	0.9804	-272.57676	72.98
B3LYP/6-31+G(d,p)	-272.75012	0.15265	1.0000	-272.59747	73.07
KMLYP/6-31G(d)	-272.2238	0.16081	1.0000	-272.06299	72.15
KMLYP/6-311G	-272.18975	0.16039	1.0000	-272.02936	72.02
MP2/6-31G(d)	-271.76898	0.15626	0.9646	-271.61825	72.77
CASSCF/6-31G(d)	-270.94952 [2]				
CAS(6,6)/6-31G(d)	-270.92312	0.16256	1.0000	-270.76056	72.37
CASPT2/6-31G(d) [b]	-271.77918	0.15363	0.9804	-271.62856	
CASPT2/6-31G(d) [c]	-271.77816	0.16256	1.0000	-271.61560	
BPW91/6-31G(d)	-272.68427	0.14977	1.0000	-272.53450	73.51
MPW1K/6-31+G(d,p)	-272.69059	0.15765	0.9515	-272.54058	72.53
CBS-QB3				-272.16858	

Table S12. Reaction 9

R9: CYCLOPENTADIENE (C2v)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-192.79172 -192.79172 [1]	0.09973	0.9135 0.89	-192.70062	65.92
B3LYP/6-31G(d)	-194.10106	0.09288	0.9804	-194.00994	66.68
B3LYP/6-31+G(d,p)	-194.11982	0.09243	1.0000	-194.02737	69.76
KMLYP/6-31G(d)	-193.71768	0.09727	1.0000	-193.62041	64.81
KMLYP/6-311G	-193.69860	0.09732	1.0000	-193.60128	65.98
MP2/6-31G(d)	-193.42538 -193.44967 [1]	0.09382	0.9646	-193.33488	66.80
CAS(4,4)/6-31G(d)	-192.84662	0.09768	1.0000	-192.74894	66.53
CASPT2/6-31G(d) [b]	-193.43380	0.09288	0.9804	-193.34275	
CASPT2/6-31G(d) [c]	-193.43410	0.09768	1.0000	-193.33642	
BPW91/6-31G(d)	-194.07189	0.09049	1.0000	-193.98140	67.05
MPW1K/6-31+G(d,p)	-194.06308	0.09538	0.9515	-193.97233	66.43
CBS-QB3				-193.71274	

1)Alkorta, I.; Elguero, J. *J. Chem. Soc.Perkin Trans 2*, 1998, 2497-2503.

[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.

[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

TS9: TRANSITION STRUCTURE (C2)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-385.51844	0.20280	0.9135	-385.33318	84.37
B3LYP/6-31G(d)	-388.17124 -388.17124 [2]	0.18866	0.9804	-387.98628	87.69
B3LYP/6-31+G(d,p)	-388.20554	0.18779	1.0000	-388.01774	87.63
KMLYP/6-31G(d)	-387.41439	0.19768	1.0000	-387.21671	84.79
KMLYP/6-311G	-387.37372	0.19748	1.0000	-387.17622	85.79
MP2/6-31G(d)	-386.84180	0.19063	0.9646	-386.65792	87.28

CAS(6,6)/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-385.63127 -386.85123 -386.85079	0.19816 0.18866 0.19816	1.0000 0.9804 1.0000	-385.43311 -386.66627 -386.65262	87.79
BPW91/6-31G(d)	-388.12020	0.18359	1.0000	-387.93661	88.89
MPW1K/6-31+G(d,p)	-388.09877	0.19378	0.9515	-387.91439	86.85
CBS-QB3				-387.40701	

2) Caramella, P.; Quadrelli, P.; Toma, L. *J. Am. Chem. Soc.* **2002**, *124,* 1130-1131

P9: CYCLOPENTADIENE-DIMER PRODUCT (C1)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-385.61277	0.20855	0.9135	-385.42226	80.63
B3LYP/6-31G(d)	-388.22802 -388.22802 [2]	0.19421	0.9804	-388.03762	82.56
B3LYP/6-31+G(d,p)	-388.25758	0.19313	1.0000	-388.06445	82.69
KMLYP/6-31G(d)	-387.49832	0.20369	1.0000	-387.29463	81.18
KMLYP/6-311G	-387.45133	0.20334	1.0000	-387.24798	80.87
MP2/6-31G(d)	-386.90366	0.19707	0.9646	-386.71357	82.21
CAS(6,6)/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-385.70197 -386.91819 -386.91696	0.20559 0.19421 0.20559	1.0000 0.9804 1.0000	-385.49638 -386.72779 -386.71137	81.65
BPW91/6-31G(d,p)	-388.17159	0.18914	1.0000	-387.98244	83.39
MPW1K/6-31+G(d,p)	-388.17214	0.19962	0.9515	-387.98220	81.78
CBS-QB3				-387.46083	

Table S13. Reaction 10

R10: CIS-TRISCYCLOPROPACYCLOHEXANE (C3v)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-375.69547	0.20125	0.9135	-374.51163	77.08
B3LYP/6-31G(d)	-350.08083 -349.89323 [1,2]	0.18753	0.9804	-349.89698	78.87
B3LYP/6-31+G(d,p)	-350.10899	0.18635	1.0000	-349.92264	79.07
KMLYP/6-31G(d)	-349.43489	0.19653	1.0000	-349.23836	77.58
KMLYP/6-311G	-349.38121	0.19681	1.0000	-349.18440	77.23
MP2/6-31G(d)	-348.86180	0.19145	0.9646	-347.50911	80.47
CASSCF/6-31G(d) CASPT2/6-31G(d) [b] CASPT2/6-31G(d) [c]	-347.74738 -348.87288 -348.87157	0.20003 0.18753 0.20003	1.0000 0.9804 1.0000	-347.54735 -348.68903 -348.67153	79.54
BPW91/6-31G(d)	-350.03170	0.18275	1.0000	-349.84895	79.63
MPW1K/6-31+G(d,p)	-350.03839	0.19267	0.9515	-349.85506	78.13
CBS-QB3				-349.36755	

1) Sawicka, D.; Li, Y.; Houk, K.N. *J Chem. Soc., Perkin Trans. 2*, **1999,** 2349-2355.

2) Sawicka, D.; Wilsey, S.; Houk, K.N. *J. Am. Chem. Soc.*, **1999**, *121*, 864-865.

[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.

[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

TS10: TRANSITION STRUCTURE (C3v)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-347.62335	0.19729	0.9135	-347.44312	78.36
B3LYP/6-31G(d)	-350.04255 -349.48862 [1,2]	0.18421	0.9804	-349.86196	80.42
B3LYP/6-31+G(d,p)	-350.07261	0.18315	1.0000	-349.88947	80.66
KMLYP/6-31G(d)	-349.37241	0.19266	1.0000	-349.17974	78.99
KMLYP/6-311G	-349.32645	0.19277	1.0000	-349.13367	80.87
MP2/6-31G(d)	-348.82356	0.18699	0.9646	-348.64332	80.33
CASSCF/6-31G(d)	-347.70046 [1,2]	0.19471	1.0000	-347.50575	82.49
CASPT2/6-31G(d) [b]	-348.82879	0.18421	0.9804	-348.64819	
CASPT2/6-31G(d) [c]	-348.82757	0.19471	1.0000	-348.63286	
BPW91/6-31G(d)	-349.99831	0.17959	1.0000	-349.81872	81.33
MPW1K/6-31+G(d,p)	-349.98361	0.18910	0.9515	-349.80368	79.61
CBS-QB3				-349.33328	

P10: CYCLONONA-1,4,7-TRIENE

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-347.73012	0.19976	0.9135	-347.54764	82.15
B3LYP/6-31G(d)	-350.11250 -349.92644 [1,2]	0.18609	0.9804	-349.93005	84.32 84.31
B3LYP/6-31+G(d,p)	-350.14432	0.18506	1.0000	-349.95927	84.53
KMLYP/6-31G(d)	-349.44060	0.19480	1.0000	-349.24580	82.83
KMLYP/6-311G	-349.40766	0.19488	1.0000	-349.21277	84.64
MP2/6-31G(d)	-348.87888	0.18874	0.9646	-348.6968	83.83
CASSCF/6-31G(d)	-347.81431				85.46
CASPT2/6-31G(d) [b]	-348.89515	0.18609	0.9804	-348.71271	
CASPT2/6-31G(d) [c]	-348.89424	0.19649	1.0000	-348.69775	
BPW91/6-31G(d)	-350.05131	0.18109	1.0000	-349.87022	85.34
MPW1K/6-31+G(d,p)	-350.04719	0.19086	0.9515	-349.86556	83.66
CBS-QB3				-349.39910	

Table S14. Reaction 11

R11: CIS-TRISCYCLOBUTACYCLOHEXANE (C1)

	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-464.80491	0.29588	0.9135	-464.53462	89.38
B3LYP/6-31G(d)	-468.02745 -467.75102 [1,2]	0.27649	0.9804	-467.75639	91.81
B3LYP/6-31+G(d,p)	-468.06286	0.27460	1.0000	-467.78826	92.06
KMLYP/6-31G(d)	-467.18654	0.28919	1.0000	-466.89734	89.65

KMLYP/6-311G	-467.11966	0.12887	1.0000	-466.83091	89.21
MP2/6-31G(d)	-466.37220	0.28182	0.9646	-466.10035	90.37
CASSCF/6-31G(d)	-464.85695 [1,2]	0.29469	1.0000	-464.56223	91.97
CASPT2/6-31G(d) [b]	-466.38568	0.27649	0.9804	-466.11461	
CASPT2/6-31G(d) [c]	-466.38360	0.2949	1.0000	-466.08891	
BPW91/6-31G(d)	-467.95160 [1,2]	0.26948	1.0000	-467.68212	92.95
MPW1K/6-31+G(d,p)	-467.97297	0.28334	0.9515	-467.70337	90.77
CBS-QB3				NA	

1) Sawicka, D.; Li, Y.; Houk, K.N. *J Chem. Soc., Perkin Trans. 2*, **1999,** 2349-2355.
2) Sawicka, D.; Wilsey, S.; Houk, K.N. *J. Am. Chem. Soc.*, **1999**, *121*, 864-865.
[b] Single point calculation with B3LYP/6-31G* optimized geometry, includes scaled B3LYP ZPE correction.
[c] Single point calculation with CASSCF/6-31G* optimized geometry, includes unscaled CAS ZPE correction.

TS11: TRANSITION STRUCTURE(C1)

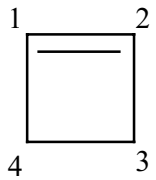
	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-464.67250	0.29044	0.9135	-464.40718	95.05
B3LYP/6-31G(d)	-467.94154 -467.67063 [1,2]	0.27072	0.9804	-467.67613	97.14
B3LYP/6-31+G(d,p)	-467.98014	0.26897	1.0000	-467.71116	97.29
KMLYP/6-31G(d)	-467.06623	0.28339	1.0000	-466.78284	93.91
KMLYP/6-311G	-467.01095	0.28292	1.0000	-466.72803	93.72
MP2/6-31G(d)	-466.28298	0.27606	0.9646	-466.01668	96.33
CAS(6,6)/6-31G(d)	-464.76254 [1,2]	0.28782	1.0000	-464.47473	96.91
CASPT2/6-31G(d) [b]	-466.29208	0.27072	0.9804	-466.02667	
CASPT2/6-31G(d) [c]	-466.29023	0.28782	1.0000	-466.00241	
BPW91/6-31G(d,p)	-467.87271	0.26371	1.0000	-467.60901	98.76
MPW1K/6-31+G(d,p)	-467.86389	0.27769	0.9515	-467.59967	95.25
CBS-QB3				NA	

P11: CYCLODODECA-1,5,9-TRIENE(C1)

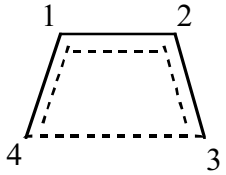
	E_0 (au)	ZPE (au)	Scale factor	E_0 + scaled ZPE (au)	S (eu)
HF/6-31G(d)	-464.82517	0.29139	0.9135	-464.55899	101.06
B3LYP/6-31G(d)	-468.04533 -467.77323 [1,2]	0.27216	0.9804	-467.77851	103.92 103.90
B3LYP/6-31+G(d,p)	-468.08759	0.27052	1.0000	-467.81736	104.03
KMLYP/6-31G(d)	-467.17164	0.28427	1.0000	-466.88737	101.95
KMLYP/6-311G	-467.12402	0.28409	1.0000	-466.83991	101.43
MP2/6-31G(d)	-466.37045	0.27669	0.9646	-466.10354	102.86
CASSCF/6-31G(d)	-464.90886 [1,2]	0.28815	1.0000	-464.62071	91.97
CASPT2/6-31G(d) [b]	-466.38940	0.27216	0.9804	-466.12258	
CASPT2/6-31G(d) [c]	-466.38857	0.28815	1.0000	-466.10042	
BPW91/6-31G(d)	-467.95672	0.25089	1.0000	-467.69163	105.35
MPW1K/6-31+G(d,p)	-467.96582	0.27877	0.9515	-467.70057	102.87
CBS-QB3				NA	

SECTION III.

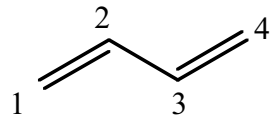
Table S15. Reaction 1. Distances and angles are given in Å and degrees, respectively.



	C1-C2	C2-C3	C3-C4
HF/6-31G(d)	1.323	1.515	1.562
B3LYP/6-31G(d)	1.340	1.519	1.573
B3LYP/6-31+G(d,p)	1.344	1.520	1.573
KMLYP/6-31G(d)	1.322	1.497	1.546
KMLYP/6-311G(d)	1.326	1.506	1.555
MP2/6-31G(d)	1.347	1.514	1.566
CAS(4,4)/6-31G(d)	1.342	1.515	1.600
CAS-MP2/6-311+G(d,p)	1.360	1.516	1.561
BPW91/6-31G(d)	1.350	1.521	1.576
MPW1K/6-31+G(d,p)	1.333	1.506	1.555
CBS-QB3	1.338	1.519	1.572

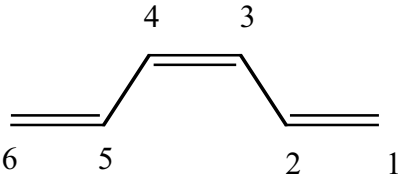


	C1-C2	C2-C3	C3-C4
HF/6-31G(d)	1.413	1.368	2.130
B3LYP/6-31G(d)	1.426	1.377	2.144
B3LYP/6-31+G(d,p)	1.430	1.378	2.143
KMLYP/6-31G(d)	1.365	1.401	2.113
KMLYP/6-311G	1.363	1.411	2.115
MP2/6-31G(d)	1.425	1.381	2.135
CAS(4,4)/6-31G(d)	1.443	1.363	2.234
CAS-MP2/6-311+G(d,p)	1.443	1.362	2.234
BPW91/6-31G(d)	1.431	1.385	2.156
MPW1K/6-31+G(d,p)	1.412	1.373	2.216
CBS-QB3	1.373	1.427	2.138

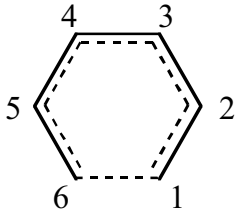


	C1-C2	C2-C3	C1-C2-C3-C4
HF/6-31G(d)	1.322	1.468	180.0
B3LYP/6-31G(d)	1.341	1.458	180.0
B3LYP/6-31+G(d,p)	1.343	1.459	180.0
KMLYP/6-31G(d)	1.321	1.445	180.0
KMLYP/6-311G	1.322	1.444	180.0
MP2/6-31G(d)	1.344	1.514	180.0
CAS(4,4)/6-31G(d)	1.344	1.465	180.0
BPW91/6-31G(d)	1.351	1.457	180.0
MPW1K/6-31+G(d,p)	1.332	1.452	180.0
CBS-QB3	1.337	1.456	180.0

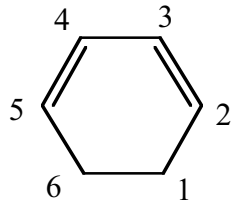
Table S16. Reaction 2. Distances and angles are given in Å and degrees, respectively.



	C1-C2	C2-C3	C3-C4	C1-C2-C3	C2-C3-C4
HF/6-31G(d)	1.324	1.466	1.331	123.3	127.2
B3LYP/6-31G(d)	1.343	1.452	1.355	122.8	126.7
B3LYP/6-31+G(d,p)	1.346	1.453	1.357	122.6	127.0
KMLYP/6-31G(d)	1.323	1.439	1.329	124.1	123.9
KMLYP/6-311G	1.323	1.441	1.333	123.5	126.6
MP2/6-31G(d)	1.346 [1, 2,, 3]	1.454	1.356	122.8	126.7
CAS(6,6)/6-31G(d)	1.346	1.463	1.354	123.3	127.1
BPW91/6-31G(d)	1.354	1.451	1.368	123.7	127.2
MPW1K/6-31+G(d,p)	1.334	1.448	1.344	123.3	126.8
CBS-QB3	1.340	1.451	1.352	123.7	127.1



	C1-C2	C2-C3	C3-C4	C1-C6	C2C3C4	C1C2C3	C1C6C2
HF/6-31G(d)	1.390	1.387	1.396	2.243	123.9	124.9	104.6
B3LYP/6-31G(d)	1.398	1.398	1.406	2.281	123.9	125.4	104.2
B3LYP/6-31+G(d,p)	1.402	1.398	1.409	2.270	123.8	125.4	104.3
KMLYP/6-31G(d)	1.375	1.385	1.383	2.251	123.6	125.1	103.9
KMLYP/6-311G	1.378	1.383	1386	2.248	123.6	125.2	104.0
MP2/6-31G(d)	1.396	1.403	1.404	2.259	123.4	124.6	104.3
CAS(6,6)/6-31G(d)	1.412	1.395	1.410	2.293	124.7	125.1	104.5
BPW91/6-31G(d)	1.402	1.407	1.411	2.313	123.8	125.6	103.7
MPW1K/6-31+G(d,p)	1.385	1.392	1.393	2.261	123.5	125.2	103.9
CBS-QB3	1.398	1.393	1.406	2.261	123.8	125.4	104.4

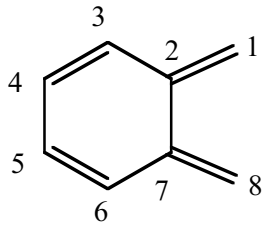


	C1-C2	C2-C3	C3-C4	C1-C6	C2C3C4	C1C2C3	C2C3C4C5
HF/6-31G(d)	1.511 [1]	1.324	1.475	1.533	120.6	120.7	14.1
B3LYP/6-31G(d)	1.512	1.343	1.467	1.540	120.7	116.6	13.7
B3LYP/6-31+G(d,p)	1.512	1.346	1.467	1.539	120.6	120.3	14.3
KMLYP/6-31G(d)	1.491	1.324	1.453	1.513	120.4	120.2	15.1
KMLYP/6-311G	1.492	1.325	1.452	1.516	120.5	115.7	15.2
MP2/6-31G(d)	1.507 [1]	1.349	1.464	1.529	120.2	119.6	16.2
CAS(6,6)/6-31G(d)	1.511	1.345	1.473	1.563	120.7	120.8	13.0
BPW91/6-31G(d)	1.514	1.353	1.467	1.543	120.7	120.2	13.8
MPW1K/6-31+G(d,p)	1.498	1.335	1.459	1.523	120.4	120.2	15.2
CBS-QB3	1.511	1.340	1.466	1.538	120.7	120.5	14.4
Experimental	1.523 [4]	1.350	1.468	1.534	120.1	120.1	18.3
	1.494 [5]	1.339	1.468	1.510	121.6	118.2	17.0
	1.518 [6]	1.348	1.464	1.538	120.3	120.3	18.0
	1.500 [7]	1.350	1.470	1.500	120.2	120.2	17.5

1) Evanseck, J.D.; Thomas, B.E.; Spellmeyer, D.C.; Houk, K.N. *J. Org. Chem*. **1995**, 60, 7134-41.
2) Jiao, H.; Schleyer, P.R. *J. Am. Chem. Soc*. **1995,** 117, 11529-535.
3) Liu, R.; Zhou, X. *J. Phys. Chem*. **1993**, 97, 1850-55.
4) Oberhammer, H.; Bauer, S.H. *J. Am. Chem. Soc*. **1969,** 91, 10.
5) Dalling, G.; Toneman, L.H. *J. Mol. Struct*. **1968**, 1, 11.
6) Traetteberg, M. *Acta Chem. Scand*. **1968**, 22, 2305.
7) Butcher, S.S. *J. Chem. Phys*. **1965,** 42, 1830

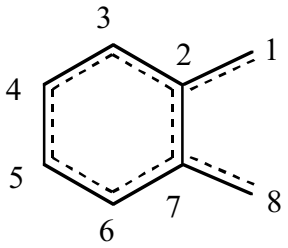
Table S17. Reaction 3. Distances and angles are given in Å and degrees, respectively.

.



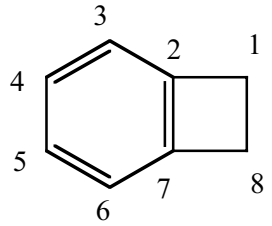
	C1-C2	C2-C3	C3-C4	C4-C5	C1-C8	C2-C7	C1C2C7C8
HF/6-31G(d)	1.330	1.473	1.329	1.465	2.994	1.496	-21
B3LYP/6-31G(d)	1.353	1.462	1.352	1.452	3.006	1.500	-14
B3LYP/6-31+G(d,p)	1.355	1.463	1.354	1.452	3.010	1.497	-19
KMLYP/6-31G(d)	1.330	1.449	1.330	1.442	2.954	1.475	-19
KMLYP/6-311G	1.331	1.449	1.331	1.440	2.954	1.476	-19
MP2/6-31G(d)	1.356	1.458	1.357	1.451	2.989	1.484	-27
CAS(8,8)/6-31G(d)	1.356	1.468	1.351	1.459	3.000	1.491	+0
CAS-MP2/6-311+G(d,p)	1.356 [1]	1.468	1.351	1.459		1.491	+0
BPW91/6-31G(d)	1.364	1.462	1.364	1.450	3.022	1.500	-16
MPW1K/6-31+G(d,p)	1.342	1.455	1.341	1.447	2.980	1.483	-23
CBS-QB3	1.349	1.461	1.348	1.451	3.001	1.495	-20

1) Sakai, S. *J. Phys. Chem*. **2000**, *104*, 1161.



	C1-C2	C2-C3	C3-C4	C4-C5	C1-C8	C2-C7
HF/6-31G(d)	1.412	1.418	1.361	1.428	2.261	1.401
B3LYP/6-31G(d)	1.426	1.412	1.385	1.421	2.292	1.419
B3LYP/6-31+G(d,p)	1.430	1.412	1.388	1.421	2.292	1.419
KMLYP/6-31G(d)	1.400	1.400	1.361	1.409	2.257	1.400
KMLYP/6-311G	1.407	1.390	1.360	1.400	2.260	1.400
MP2/6-31G(d) [8,11]	1.424	1.408	1.390	1.416	2.307	1.421
CAS(8,8)/6-31G(d)	1.456	1.409	1.387	1.414	2.396	1.395
CAS-MP2/6-311+G(d,p)	1.456 [1]	1.409	1.387	1.413	2.396	1.395
BPW91/6-31G(d)	1.432	1.416	1.394	1.424	2.306	1.429
MPW1K/6-31+G(d,p)	1.412	1.406	1.373	1.415	2.275	1.409
CBS-QB3	1.426	1.409	1.383	1.417	2.284	1.416

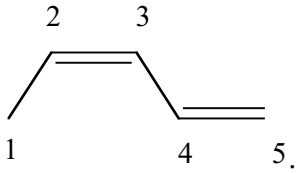
1) Sakai, S. *J. Phys. Chem*. **2000**, *104*, 1161.



	C1-C2	C2-C3	C3-C4	C4-C5	C1-C8	C2-C7
HF/6-31G(d)	1.519	1.378	1.394	1.392	1.572	1.381
B3LYP/6-31G(d)	1.523	1.388	1.405	1.402	1.581	1.396
B3LYP/6-31+G(d,p)	1.523	1.389	1.407	1.404	1.583	1.397
KMLYP/6-31G(d)	1.501	1.370	1.385	1.384	1.555	1.376
KMLYP/6-311G	1.506	1.368	1.388	1.384	1.562	1.380
MP2/6-31G(d) [8,11]	1.519	1.389	1.403	1.405	1.574	1.396
CAS(8,8)/6-31G(d)	1.518	1.388	1.404	1.402	1.611	1.388
CAS-MP2/6-311+G(d,p)	1.518 [1]	1.388	1.403	1.402	1.612	1.388
BPW91/6-31G(d)	1.526	1.395	1.411	1.409	1.585	1.404
MPW1K/6-31+G(d,p)	1.509	1.379	1.395	1.393	1.564	1.385
CBS-QB3	1.523	1.385	1.402	1.400	1.582	1.393

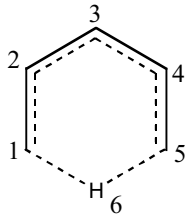
1) Sakai, S. *J. Phys. Chem*. **2000**, *104*, 1161.

Table S18. Reaction 4. Distances and angles are given in Å and degrees, respectively.



	C1-C2	C2-C3	C3-C4	C4-C5	C5C1C2	C1C2C3	C2C3C4C5
HF/6-31G(d)	1.503	1.324	1.468	1.323	50.5	128.2	180.0
B3LYP/6-31G(d)	1.501 [1]	1.346	1.457	1.342	50.0	127.1	180.0
B3LYP/6-31+G(d,p)	1.502	1.349	1.458	1.345	50.9	127.8	180.0
KMLYP/6-31G(d)	1.482	1.326	1.445	1.322	51.4	127.4	180.0
KMLYP/6-311G	1.481	1.326	1.444	1.323	51.6	127.3	180.0
MP2/6-31G(d)	1.503	1.357	1.456	1.352	50.8	127.4	180.0
CAS(6,6)/6-31G(d)	1.504	1.349	1.466	1.345	50.7	127.9	180.0
BPW91/6-31G(d)	1.503	1.357	1.456	1.352	50.8	127.8	180.0
MPW1K/6-31+G(d,p)	1.489	1.337	1.452	1.333	51.2	127.7	180.0
CBS-QB3	1.500	1.342	1.455	1.338	60.0	127.8	180.0

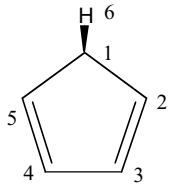
1) Alkorta, I.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2*, **1998**, 2497-503.



	C1-C2	C2-C3	C3-C4	H6-C5	C1H6C5	C4C5H6	C3C4C5	C3C4 C5H6	C4C5 H6C1
HF/6-31G(d)	1.407	1.387	1.387	1.444	130.8	97.6	123.4	29.6	-61.2
B3LYP/6-31G(d)	1.418 [1]	1.397	1.397	1.427	133.1	98.4	122.9	27.7	-58.9
	1.418 [2]	1.397	1.397	1.427	133.3	98.3	122.9	27.6	
B3LYP/6-31+G(d,p)	1.419	1.399	1.399	1.424	133.8	98.2	122.9	27.5	-58.9
KMLYP/6-31G(d)	1.397	1.379	1.379	1.411	132.2	97.9	123.1	28.9	-60.8
KMLYP/6-311G	1.397	1.379	1.379	1.414	131.9	98.2	123.0	28.9	-60.1
MP2/6-31G(d)	1.419	1.398	1.398	1.409	132.7	98.7	122.4	28.5	-60.5
CAS(6,6)/6-31G(d)	1.422	1.397	1.397	1.473	128.6	98.8	123.0	29.2	-60.0
BPW91/6-31G(d)	1.425	1.404	1.404	1.423	134.3	98.4	122.8	27.2	-58.4
MPW1K/6-31+G(d,p)	1.407	1.388	1.388	1.409	135.6	97.8	122.9	28.3	-60.4
CBS-QB3	1.415	1.394	1.394	1.426	133.6	98.1	123.1	27.7	-58.9

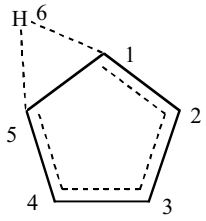
2) Jursic, B.S. *J. Mol. Struct.* **1998**, *423*, 18.

Table S19. Reaction 5. Distances and angles are given in Å and degrees, respectively.



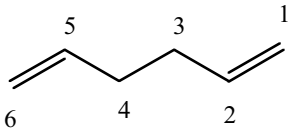
	C1-C2	C2-C3	C3-C4	C5-H6	C5C1C2	C1C2C3
HF/6-31G(d)	1.506 [1]	1.328	1.477		102.5	109.6
	1.506	1.329	1.477	2.164	102.5	109.6
B3LYP/6-31G(d)	1.507 [2]	1.349	1.470	2.174	103.3	109.1
	1.507	1.349	1.470	2.174	103.2	109.1
B3LYP/6-31+G(d,p)	1.507	1.352	1.469	2.173	103.3	109.1
KMLYP6-31G(d)	1.485	1.329	1.545	2.146	103.2	109.2
KMLYP/6-311G	1.489	1.332	1.456	2.146	103.0	109.3
MP2/6-31G(d)	1.499 [1]	1.352	1.463		103.4	109.1
	1.501	1.354	1.465	2.165	103.4	109.1
CAS(6,6)/6-31G(d)	1.510	1.348	1.478	2.180	102.5	109.7
BPW91/6-31G(d)	1.508	1.359	1.470	2.181	103.6	108.9
MPW1K/6-31+G(d,p)	1.493	1.341	1.460	2.154	103.3	109.2
CBS-QB3	1.505	1.346	1.469	2.170	103.2	109.1
Exp.	1.506	1.352			103.2	109.3

1) Alkorta, I.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2*, **1998**, 2497-2503.
2) Bachrach, S.M. *J. Org. Chem*. **1993**, *58*, 5414-5421.

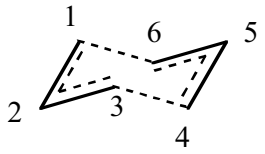


	C1-C2	C2-C3	C1-C5	C5-H6	C1H6C5	H6C1C2C3
HF/6-31G(d)	1.400 [1]	1.390	1.470	1.304	68.7	
	1.400	1.390	1.470	1.304	68.6	58.7
B3LYP/6-31G(d)	1.409 [2]	1.402	1.489	1.316	68.9	58.5
	1.409	1.402	1.491	1.315	69.1	58.5
B3LYP/6-31+G(d,p)	1.412	1.404	1.490	1.313	69.3	58.5
KMLYP/6-31G(d)	1.392	1.383	1.463	1.293	68.9	58.5
KMLYP/6-311G	1.393	1.387	1.474	1.312	68.4	58.9
MP2/6-31G(d)	1.499	1.353		1.300	69.8	
	1.408	1.402	1.489	1.301	69.8	57.9
CAS(6,6)/6-31G(d)	1.407	1.400	1.481	1.346	66.9	59.6
BPW91/6-31G(d)	1.416	1.408	1.498	1.320	69.1	58.1
MPW1K/6-31+G(d,p)	1.401	1.392	1.472	1.298	69.1	58.4
CBS-QB3	1.408	1.400	1.490	1.314	69.1	58.5

Table S20. Reaction 6. Distances and angles are given in Å and degrees, respectively.

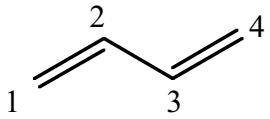


	C1-C2	C2-C3	C3-C4	C1C2C3	C2C3C4	C1C2C3C4
HF/6-31G(d)	1.319	1.505	1.539	125.3	112.4	118.8
B3LYP/6-31G(d)	1.334	1.504	1.548	125.3	112.7	118.5
B3LYP/6-31+G(d,p)	1.337	1.504	1.548	125.4	112.8	119.8
KMLYP/6-31G(d)	1.316	1.483	1.519	124.9	112.3	119.6
KMLYP/6-311G	1.316	1.483	1.522	125.2	112.4	119.5
MP2/6-31G(d)	1.339	1.499	1.538	124.6	112.0	116.5
CAS(6,6)/6-31G(d)	1.339	1.505	1.566	125.0	112.3	118.1
BPW91/6-31G(d)	1.342	1.507	1.554	125.3	112.7	118.6
MPW1K/6-31+G(d,p)	1.326	1.492	1.530	125.2	112.5	119.7
CBS-QB3	1.330	1.502	1.546	125.3	112.7	119.1

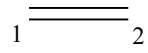


	C1-C2	C2-C3	C3-C4	C1C2C3	C2C3C4	C2C1C6	C1C2C3C4
HF/6-31G(d)	1.390	1.390	2.046	120.8	102.1	102.1	-67.9
B3LYP/6-31G(d)	1.408	1.408	1.965	119.9	103.6	103.6	-65.2
B3LYP/6-31+G(d,p)	1.407	1.407	2.001	120.5	103.0	103.0	-66.3
KMLYP/6-31G(d)	1.393	1.393	1.862	118.7	104.2	104.2	-64.6
KMLYP/6-311G	1.389	1.389	1.928	120.1	103.1	103.1	-66.1
MP2/6-31G(d)	1.423	1.4309	1.784	116.9	106.4	105.7	-62.4
CAS(6,6)/6-31G(d)	1.398	1.398	2.192	121.7	101.1	101.1	-69.5
BPW91/6-31G(d)	1.423	1.423	1.878	118.7	105.1	105.1	-62.9
MPW1K/6-31+G(d,p)	1.403	1.403	1.877	119.0	104.1	104.1	-64.7
CBS-QB3	1.399	1.399	2.039	120.9	102.4	102.4	-67.2

Table S21. Reaction 7. Distances and angles are given in Å and degrees, respectively.

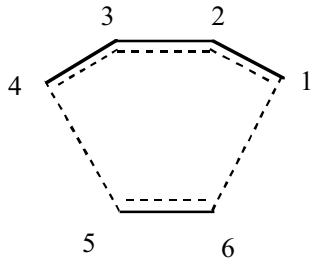


	C1-C2	C2-C3	C1-C2-C3-C4
HF/6-31G(d)	1.322	1.468	180.0
B3LYP/6-31G(d)	1.341	1.458	180.0
B3LYP/6-31+G(d,p)	1.343	1.459	180.0
KMLYP/6-31G(d)	1.321	1.445	180.0
KMLYP/6-311G	1.322	1.444	180.0
MP2/6-31G(d)	1.344	1.514	180.0
CAS(4,4)/6-31G(d)	1.344	1.465	179.9
BPW91/6-31G(d)	1.351	1.457	180.0
MPW1K/6-31+G(d,p)	1.332	1.452	180.0
CBS-QB3	1.337	1.456	180.0



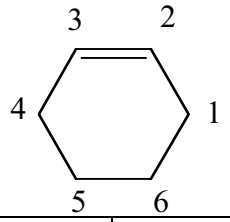
	C1-C2
HF/6-31G(d)	1.317 [1]
B3LYP/6-31G(d)	1.331
B3LYP/6-31+G(d,p)	1.334
KMLYP/6-31G(d)	1.314
KMLYP/6-311G	1.315
MP2/6-31G(d)	1.336
CAS(2,2)/6-31G(d)	1.385
BPW91/6-31G(d)	1.339
MPW1K/6-31+G(d,p)	1.324
CBS-QB3	1.327

1) Huei, C.; Tsai, L.C.; Hu, W.P. *J. Phys. Chem. A,* **2001,** *105*, 9945-9953.



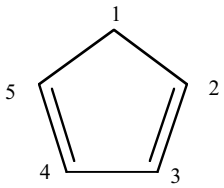
	C1-C2	C2-C3	C1-C6	C6-C5	C1C6C5	C2C3C4C5
HF/6-31G(d)	1.377 [2,3,4]	1.393	2.201	1.383	109.2	
B3LYP/6-31G(d)	1.383 [2,4]	1.407	2.273	1.386	109.1	57.9
B3LYP/6-31+G(d,p)	1.387	1.407	2.259	1.391	109.2	57.9
KMLYP/6-31G(d)	1.359	1.395	2.250	1.362	108.9	58.9
KMLYP/6-311G	1.362	1.392	2.238	1.366	108.9	58.8
MP2/6-31G(d)	1.380 1.378 [2] 1.380 [5]	1.412 1.410 1.412	2.285 2.286 2.286	1.382	108.9	58.8
CAS(6,6)/6-31G(d)	1.398	1.397	2.222	1.404	109.1	57.5
CAS-MP2/6-311+G(d,p)	1.399 [6]	1.396	2.2213	1.404	109.1	
BPW91/6-31G(d)	1.386	1.418	2.331	1.387	109.0	58.2
MPW1K/6-31+G(d,p)	1.370	1.403	2.264	1.373	108.9	58.7
CBS-QB3	1.383	1.402	2.250	1.387	109.2	57.7

2) Goldstein, E.; Beno, B.; Houk, K,.N. *J. Am. Chem. Soc.* **1996**, *118*, 6036-43.
3) Wiest, O.; Montiel, D.C.; Houk, K.N. *J. Phys. Chem.* **1997**, *101*, 8378-88.
4) Barone, V.; Arnaud, R. *Chem. Phys. Lett.* **1996**, *251*, 393-99.
5) Froese, R.D.; Caxon, J.M.; West, C.S., Mamkuma, K. *J. Org. Chem.* **1997**, *62*, 6991-96.
6) Sakai, S. J. *Phys. Chem. A* **2000**, *104*, 922-27.



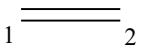
	C1-C2	C2-C3	C1C6	C5C6	C6C1C2	C1C2C3
HF/6-31G(d)	1.500 [1,5] 1.509	1.321 1.321	1.529 1.531	1.520 1.529	111.8	123.6
B3LYP/6-31G(d)	1.509	1.337	1.537	1.535	111.02	123.5
B3LYP/6-31+G(d,p)	1.510	1.339	1.538	1.536	112.1	123.5
KMLYP/6-31G(d)	1.489	1.319	1.512	1.511	111.7	1234.
KMLYP/6-311G	1.489	1.320	1.515	1.514	111.8	123.5
MP2/6-31G(d)	1.505 [1] 1.505	1.342 1.342	1.531 1.529	1.527 1.527	111.5	123.3
CAS(6,6)/6-31G(d)	1.509	1.341	1.559	1.527	111.7	123.7
CAS-MP2/6-311+G(d,p)	1.569 [6]	1.340	1.508	1.547	111.1	113.8
BPW91/6-31G(d)	1.512	1.346	1.541	1.539	112.0	123.5
MPW1K/6-31+G(d,p)	1.497	1.329	1.522	1.521	111.8	123.4
CBS-QB3	1.508	1.332	1.536	1.534	112.1	123.6

Table S22. Reaction 8. Distances and angles are given in Å and degrees, respectively.



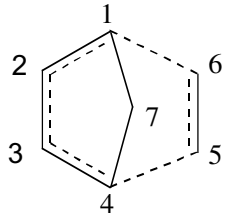
	C1-C2	C2-C3	C3-C4	C5-H6	C5C1C2	C1C2C3
HF/6-31G(d)	1.506 [1]	1.328	1.477		102.5	109.6
	1.506	1.329	1.477	2.164	102.5	109.6
B3LYP/6-31G(d)	1.507 [2]	1.349	1.470	2.174	103.3	109.1
	1.507	1.349	1.470	2.174	103.2	109.1
B3LYP/6-31+G(d,p)	1.507	1.352	1.469	2.173	103.3	109.1
KMLYP6-31G(d)	1.485	1.329	1.545	2.146	103.2	109.2
KMLYP/6-311G	1.489	1.332	1.456	2.146	103.0	109.3
MP2/6-31G(d)	1.499 [1]	1.352	1.463		103.4	109.1
	1.501	1.354	1.465	2.165	103.4	109.1
CAS(6,6)/6-31G(d)	1.510	1.348	1.478	2.180	102.5	109.7
BPW91/6-31G(d)	1.508	1.359	1.470	2.181	103.6	108.9
MPW1K/6-31+G(d,p)	1.493	1.341	1.460	2.154	103.3	109.2
CBS-QB3	1.505	1.346	1.469	2.170	103.2	109.1
Exp.	1.506	1.352			103.2	109.3

1) Alkorta, I.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2*, **1998**, 2497-2503.
2) Bachrach, S.M. *J. Org. Chem*. **1993**, *58*, 5414-21.



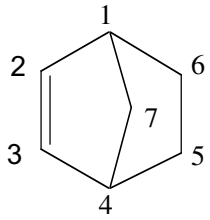
	C1-C2
HF/6-31G(d)	1.317 [1]
B3LYP/6-31G(d)	1.331
B3LYP/6-31+G(d,p)	1.334
KMLYP/6-31G(d)	1.314
KMLYP/6-311G	1.315
MP2/6-31G(d)	1.336
CAS(2,2)/6-31G(d)	1.385
BPW91/6-31G(d)	1.339
MPW1K/6-31+G(d,p)	1.324
CBS-QB3	1.327

1) Huei, C.; Tsai, L.C.; Hu, W.P. *J. Phys. Chem. A,* **2001,** *105*, 9945-9953.



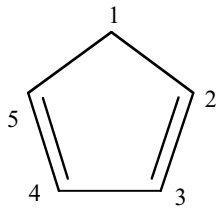
	C1-C2	C2-C3	C4-C5	C5-C6	C1C2C3	C3C4C5	C4C5C6
HF/6-31G(d)	1.389	1.392	2.193	1.382	108.9	100.7	102.1
B3LYP/6-31G(d)	1.398 [4,5]	1.406	2.248 2.250 [6]	1.388	108.9	100.1	101.9
B3LYP/6-31+G(d,p)	1.403	1.405	2.233	1.393	108.9	100.1	101.9
KMLYP/6-31G(d)	1.373	1.393	2.234	1.362	108.9	99.4	101.9
KMLYP/6-311G	1.380	1.392	2.217	1.367	108.9	99.2	102.0
MP2/6-31G(d)	1.393	1.410	2.217 [6]	1.381	108.9	99.9	101.9
CAS(6,6)/6-31G(d)	1.407	1.398	2.211	1.403	108.8	101.3	101.8
BPW91/6-31G(d)	1.401	1.416	2.304	1.389	108.9	99.4	101.8
MPW1K/6-31+G(d,p)	1.385	1.400	2.246	1.374	108.9	99.4	101.8
CBS-QB3	1.400	1.400	2.223	1.390	109.0	100.0	102.0

4) Beno, B.R.; Wilsey, S.; Houk, K.N. *J. Am. Chem. Soc*. **1999**, *121*, 4816-4826.
5) Froose, R.D.; Caxon, J.M.; West, S.C.; Marokuma, K. *J. Org. Chem*, **1997**, *62*, 6991-6996.
6) Branchadell, V. *Int. Quantum Chem*. **1997**, 381-388.



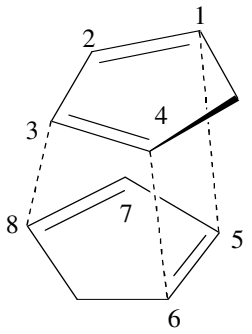
	C1-C2	C2-C3	C4-C5	C5-C6	C1C2C3	C3C4C5	C4C5C6
HF/6-31G(d)	1.522	1.323	1.557	1.557	107.6	106.5	102.7
B3LYP/6-31G(d)	1.523	1.341	1.569	1.561	107.5	106.3	102.8
B3LYP/6-31+G(d,p)	1.523	1.343	1.569	1.562	107.5	106.3	102.8
KMLYP/6-31G(d)	1.540	1.537	1.502	1.322	102.9	106.0	107.4
KMLYP/6-311G	1.546	1.539	1.507	1.324	102.9	106.0	107.5
MP2/6-31G(d)	1.513	1.348	1.558	1.553	107.3	106.1	102.8
CAS(6,6)/6-31G(d)	1.520	1.344	1.587	1.553	107.4	106.4	102.7
BPW91/6-31G(d,p)	1.525	1.350	1.573	1.563	107.4	106.1	102.8
MPW1K/6-31+G(d,p)	1.509	1.333	1.551	1.545	107.4	106.1	102.9
CBS-QB3	1.522	1.337	1.522	1.561	107.6	106.2	102.8

Table S23. Reaction 9. Distances and angles are given in Å and degrees, respectively.

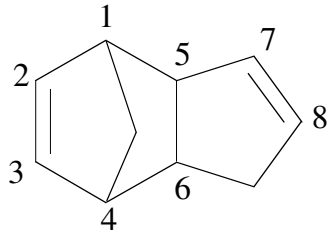


	C1-C2	C2-C3	C3-C4	C5-H6	C5C1C2	C1C2C3
HF/6-31G(d)	1.506 [1]	1.328	1.477		102.5	109.6
	1.506	1.329	1.477	2.164	102.5	109.6
B3LYP/6-31G(d)	1.507 [2]	1.349	1.470	2.174	103.3	109.1
	1.507	1.349	1.470	2.174	103.2	109.1
B3LYP/6-31+G(d,p)	1.507	1.352	1.469	2.173	103.3	109.1
KMLYP6-31G(d)	1.485	1.329	1.545	2.146	103.2	109.2
KMLYP/6-311G	1.489	1.332	1.456	2.146	103.0	109.3
MP2/6-31G(d)	1.499 [1]	1.352	1.463		103.4	109.1
	1.501	1.354	1.465	2.165	103.4	109.1
CAS(4,4)/6-31G(d)	1.510	1.348	1.478	2.180	102.5	109.7
BPW91/6-31G(d)	1.508	1.359	1.470	2.181	103.6	108.9
MPW1K/6-31+G(d,p)	1.493	1.341	1.460	2.154	103.3	109.2
CBS-QB3	1.505	1.346	1.469	2.170	103.2	109.1
Exp.	1.506	1.352			103.2	109.3

1) Alkorta, I.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2497-503.
2) Bachrach, S.M. *J. Org. Chem*. **1993**, *58*, 5414-5421.

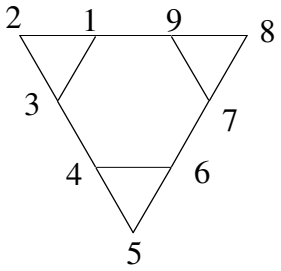


	C1-C2	C4-C6	C1-C5	C3-C8	C2-C7	C4C6C5	C1C5C6C4
HF/6-31G(d)	1.377	2.031	3.267	2.392	3.050	104.4	5.4
B3LYP/6-31G(d)		1.96 [1]	2.90				
	1.369	1.962	2.897	2.897	3.102	107.1	8.0
B3LYP/6-31+G(d,p)	1.372	1.938	2.926	2.926	3.139	107.6	8.2
KMLYP/6-31G(d)	1.348	1.977	2.762	2.762	2.941	105.6	9.0
KMLYP/6-311G	1.351	1.956	2.774	2.771	2.955	105.7	9.0
MP2/6-31G(d)	1.369	2.093	2.805	2.80	2.954	104.5	9.1
CAS(6,6)/6-31G(d)	1.368	1.927	3.055	3.055	2.290	109.1	6.1
BPW91/6-31G(d)	1.376	2.064	2.951	2.951	3.126	105.9	8.5
MPW1K/6-31+G(d,p)	1.358	1.987	2.837	2.837	3.019	106.0	8.8
CBS-QB3	1.368	1.926	2.891	2.891	3.101	107.4	8.1



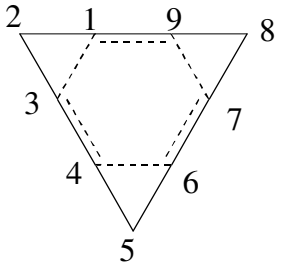
	C1-C2	C2-C3	C1-C5	C5-C7	C4C6C5	C2C1C5C7	C1C5C6C4
HF/6-31G(d)	1.519	1.322	1.565	1.505	102.4	47.7	-0.4
B3LYP/6-31G(d)	1.520	1.340	1.581	1.505	102.4	47.2	-0.2
B3LYP/6-31+G(d,p)	1.521	1.343	1.583	1.506	102.4	47.4	-0.2
KMLYP/6-31G(d)	1.500	1.322	1.549	1.486	102.5	47.0	-0.5
KMLYP/6-311G	1.520	1.340	1.581	1.505	102.4	47.2	-0.2
MP2/6-31G(d)	1.510	1.349	1.569	1.498	102.5	46.0	-0.0
CAS(6,6)/6-31G(d)	1.518	1.344	1.596	1.505	102.4	48.9	0.1
BPW91/6-31G(d)	1.522	1.350	1.588	1.507	102.5	46.9	-0.1
MPW1K/6-31+G(d,p)	1.508	1.332	1.561	1.494	102.5	47.1	-0.3
CBS-QB3	1.520	1.337	1.581	1.504	102.4	47.2	-0.1

Table S24. Reaction 10. Distances and angles are given in Å and degrees, respectively.

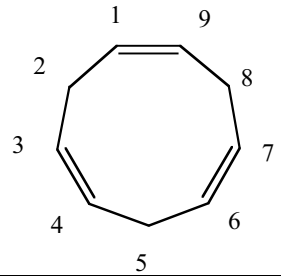


	C1-C3	C2-C3	C3-C4	C1C2C3	C2C3C4C6	C2C3C4C5
HF/6-31G(d)	1.509	1.499	1.509	60.5	-71.9	0.0
B3LYP/6-31G(d)	1.529	1.511	1.508	60.9	-71.6	0.0
	1.529 [1,2]	1.509	1.507	60.9	-71.6	0.0
B3LYP/6-31+G(d,p)	1.531	1.511	1.508	60.9	-71.6	0.0
KMLYP/6-31G(d)	1.485	1.485	1.488	60.7	-71.6	0.0
KMLYP/6-311G	1.493	1.493	1.482	60.8	-71.5	0.0
MP2/6-31G(d)	1.524	1.505	1.499	59.6	-71.5	0.0
CAS(6,6)/6-31G(d)	1.542	1.498	1.507	61.9	-71.0	0.0
BPW91/6-31G(d)	1.539	1.515	1.508	61.0	-71.6	0.0
MPW1K/6-31+G(d,p)	1.512	1.496	1.495	59.6	-71.6	0.0
CBS-QB3	1.529	1.509	1.505	59.6	-71.6	0.0

1) Sawicka, D.; Li, Y.; Houk. K.N. *J. Chem. Soc., Perkin Trans. 2,* **1999**, 2349-55.
2) Sawicka, D.; Wilsey, S.; Houk, K.N. *J. Am. Chem. Soc.* **1999**, *121*, 864-65.

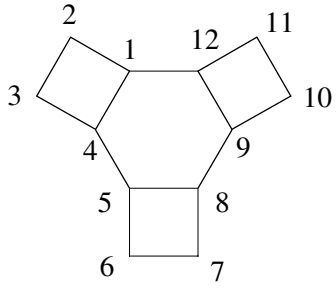


	C1-C3	C2-C3	C3-C4	C1C2C3	C2C3C4C6	C2C3C4C5
HF/6-31G(d)	1.877	1.481	1.399	78.6	-61.4	0.0
B3LYP/6-31G(d)	1.867 [1,2]	1.489	1.414	77.6	-61.9	0.0
B3LYP/6-31+G(d,p)	1.864	1.491	1.418	77.4	-62.1	0.0
KMLYP/6-31G(d)	1.874	1.468	1.385	79.3	-60.8	0.0
KMLYP/6-311G	1.865	1.474	1.386	78.5	-61.3	0.1
MP2/6-31G(d)	1.856	1.486	1.409	77.3	-62.1	0.0
CAS(6,6)/6-31G(d)	1.878	1.484	1.419	78.5	-61.4	0.0
BPW91/6-31G(d)	1.879	1.495	1.418	77.9	-61.8	0.0
MPW1K/6-31+G(d,p)	1.882	1.477	1.396	79.1	-61.0	0.0
CBS-QB3	1.859	1.489	1.413	77.2	-62.2	0.0



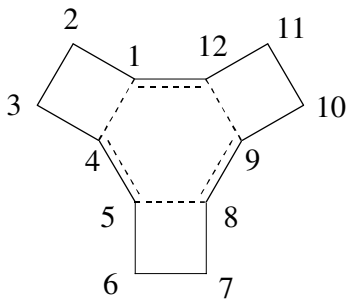
	C1-C3	C2-C3	C3-C4	C1C2C3	C2C3C4C6	C2C3C4C5
HF/6-31G(d)	2.508	1.481	1.399	78.6	-61.4	0.0
B3LYP/6-31G(d)	2.508 2.506[1,2]	1.518 1.518	1.344 1.339	111.4 111.3	-40.6 -40.7	0.0 0.0
B3LYP/6-31+G(d,p)	2.508	1.518	1.344	111.4	-40.6	0.0
KMLYP/6-31G(d)	2.461	1.495	1.320	110.8	-40.9	0.0
KMLYP/6-311G	2.472	1.498	1.320	113.4	-40.5	0.0
MP2/6-31G(d)	2.468	1.509	1.345	109.7	-41.6	0.0
CAS(6,6)/6-31G(d)	2.512	1.516	1.343	111.9	-40.3	0.0
BPW91/6-31G(d)	2.503	1.520	1.348	110.8	-40.9	0.0
MPW1K/6-31+G(d,p)	2.478	1.504	1.331	110.9	-40.8	0.0
CBS-QB3	2.505	1.516	1.335	111.4	-40.6	0.0

Table S25. Reaction 11. Distances and angles are given in Å and degrees, respectively.



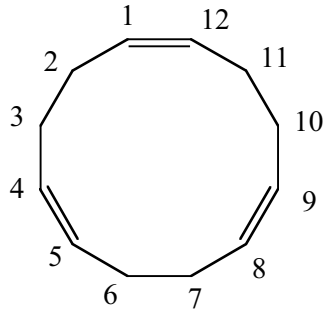
	C1-C2	C2-C3	C1-C4	C2C1C4	C1C2C3	C2C3C4	C3C2C4C5
HF/6-31G(d)	1.551	1.544	1.555	88.7	88.2	89.2	99.5
B3LYP/6-31G(d)	1.559 [1,2]	1.552	1.568	88.6	88.4	89.3	99.8
B3LYP/6-31+G(d,p)	1.560	1.553	1.568	88.6	88.4	88.3	99.7
KMLYP/6-31G(d)	1.533	1.528	1.539	88.7	88.2	88.9	98.5
KMLYP/6-311G	1.539	1.533	1.547	88.6	88.4	88.2	98.9
MP2/6-31G(d)	1.552	1.546	1.557	88.5	87.9	89.0	96.9
CAS(6,6)/6-31G(d)	1.549	1.543	1.590	88.1	88.9	88.8	99.4
BPW91/6-31(d)	1.563	1.555	1.573	88.6	88.4	88.3	99.5
MPW1K/6-31+G(d,p)	1.543	1.537	1.549	88.7	88.3	88.2	99.2
CBS-QB3	NA						

1) Sawicka, D.; Li, Y.; Houk. K.N. *J. Chem. Soc., Perkin Trans. 2*, **1999**, 2349-55.
2) Sawicka, D.; Wilsey, S.; Houk, K.N. *J. Am. Chem. Soc.* **1999**, *121*, 864-65.



	C1-C2	C2-C3	C1C4	C3C4	C2C1C4	C1C2C3	C2C3C4C5
HF/6-31G(d)	1.519	1.525	2.054	1.534	80.0	97.4	97.6
B3LYP/6-31G(d)	1.526 [1,2]	1.532	2.063	1.540	79.9	97.6	97.9
B3LYP/6-31+G(d,p)	1.527	1.533	2.058	1.541	80.1	97.4	97.5
KMLYP/6-31G(d)	1.501	1.508	2.050	1.515	79.6	97.5	95.6
KMLYP/6-311G	1.505	1.511	2.041	1.519	79.8	97.4	96.1
MP2/6-31G(d)	1.518	1.526	2.053	1.532	79.8	96.8	93.9
CAS(6,6)/6-31G(d)	1.521	1.526	2.070	1.534	79.5	97.8	97.0
BPW91/6-31G(d)	1.528	1.536	2.080	1.543	79.8	97.7	97.4
MPW1K/6-31+G(d,p)	1.510	1.517	2.069	1.524	79.6	97.5	95.9
CBS-QB3	NA						

1) Sawicka, D.; Li, Y.; Houk. K. N. *J. Chem. Soc., Perkin Trans. 2*, **1999**, 2349-55.
2) Sawicka, D.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 864-65.



	C1-C2	C2-C3	C1-C4	C3-C4	C2C3C4	C3C4C5C6
HF/6-31G(d0	1.505	1.545	3.025	1.519	116.9	-2.0
B3LYP/6-31G(d)	1.505 [1,2]	1.554	3.040	1.519	116.9	-2.1
B3LYP/6-31+G(d,p)	1.505	1.554	3.055	1.519	117.1	-1.9
KMLYP/6-31G(d)	1.484	1.526	2.944	1.498	115.9	-1.6
KMLYP/6-311G	1.484	1.528	2.952	1.497	115.8	-1.4
MP2/6-31G(d)	1.499	1.545	2.931	1.512	115.2	-2.4
CAS(6,6)/6-31G(d)	1.506	1.544	3.015	1.519	116.7	-2.1
BPW91/6-31G(d)	1.507	1.559	3.046	1.521	113.7	-2.0
MPW1K/6-31+G(d,p)	1.506	1.536	2.989	1.506	113.3	-1.7
CBS-QB3	NA					