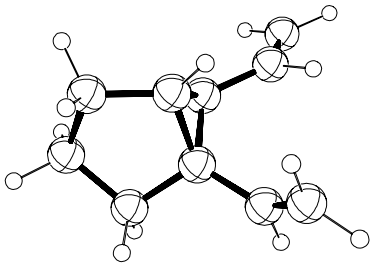
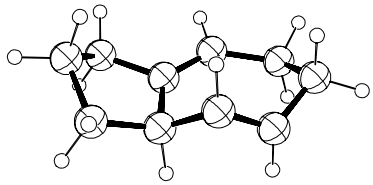
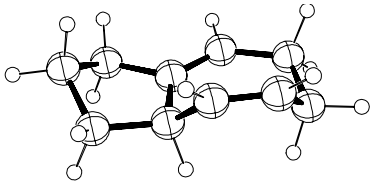
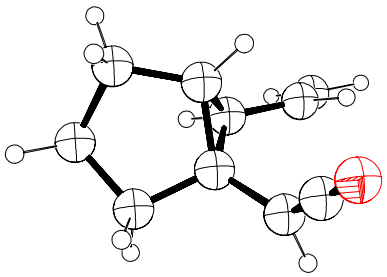
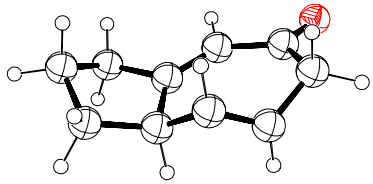
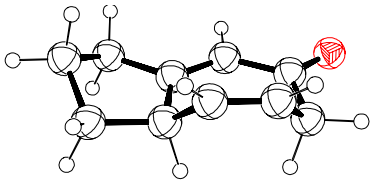
#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)
4		**Divinylcyclopropane starting substrate** **B3LYP/6-31G**//HF=-389.433829, G=-21.8649** C 0.000000 0.000000 0.000000 H -0.722510 0.748520 -0.317400 C 4.940150 0.000000 0.000000 H -0.365490 -0.784990 0.654860 C 4.131750 1.062430 0.000000 H 1.124350 1.839630 -1.587690 C 3.302580 1.530830 -1.143950 C 2.981710 1.518000 -3.589890 C 1.839990 1.074070 -1.291840 H 3.929990 1.299120 -4.097460 C 1.275210 0.041860 -0.397210 H 2.175830 1.307790 -4.302920 C 2.895280 0.679930 -2.320590 C 2.958820 2.984420 -3.093090 H 3.162750 -0.372210 -2.370800 H 1.927260 3.347980 -3.040550 H 5.519970 -0.272240 0.877090 H 3.494520 3.661960 -3.764750 H 5.050490 -0.633670 -0.876410 C 3.585790 2.943210 -1.679460 H 4.064370 1.673130 0.902360 H 3.199790 3.734190 -1.025150 H 1.967160 -0.724620 -0.051410 H 4.673710 3.072720 -1.739250
5		**Divinylcyclopropane trans product** **B3LYP/6-31G**//HF=-389.422687, G=-20.7224** C 0.000000 0.000000 0.000000 H -1.648590 0.427770 -1.368750 C 1.575660 0.000000 0.000000 C 0.637110 3.128300 -1.249870 C 1.872220 1.465060 0.000000 H 0.551850 3.661050 -0.294130 C 1.747850 2.117900 -1.165540 C -1.465850 2.796040 -2.501140 C -0.569630 2.170630 -1.447290 H -2.098740 2.067490 -3.017190 C -0.744120 0.907900 -0.990880 H -2.130240 3.540620 -2.035630 H -0.361210 -1.025120 -0.154100 C -0.465440 3.516950 -3.426500 H -0.314370 0.271580 1.017790 H -0.933660 4.272930 -4.064950 H 1.943590 -0.484980 -0.911100 H 0.012870 2.780880 -4.084480 H 1.937150 -0.566600 0.866610 C 0.572830 4.112800 -2.449680 H 1.573950 1.992710 0.910140 H 0.233160 5.095550 -2.102830 H 1.960050 1.582190 -2.092930 H 1.554740 4.257480 -2.910840
6		**Divinylcyclopropane cis product** **B3LYP/6-31G**//HF=-389.468748, G=-20.7467** C 0.000000 0.000000 0.000000 H -0.331300 2.764960 -0.684830 C 1.542690 0.000000 0.000000 C 0.191060 2.923630 0.270600 C 2.222370 1.349840 0.000000 H -0.900750 2.555820 2.192110 C 1.680140 2.569250 0.094810 C 2.482690 3.856340 0.159930 C -0.489210 2.058130 1.314690 H 3.503390 3.701150 0.523470 C -0.588940 0.732150 1.183940 H 2.557250 4.311720 -0.839990 H 1.900800 -0.563960 0.875550 C 1.625650 4.761240 1.062690 H 1.895330 -0.569880 -0.872690 H 1.757880 4.465370 2.111090 H -0.351490 -1.037300 -0.020730 H 1.877800 5.823410 0.981740 H -0.349520 0.463900 -0.933580 C 0.190940 4.444470 0.600200 H -1.080700 0.147150 1.959010 H -0.034790 5.019830 -0.305500 H 3.311060 1.296070 -0.061480 H -0.569550 4.706790 1.343060
7		**Ketene-substituted substrate** **B3LYP/6-31G**//HF=-463.437375, G=-22.9534** H 1.596420 -0.607930 0.247180 H -0.167490 0.194100 3.399390 C -0.634820 -0.746250 0.199750 H 1.203710 -0.333560 2.439380 H -1.374090 -1.178710 -0.470110 H -1.739790 -1.034410 2.019150 C -0.210850 0.698950 0.052990 C 0.982940 -0.684730 -1.825340 H -0.341590 -2.106620 1.900850 C -2.053110 1.582610 -1.322130 C -0.784820 1.633800 -0.966840 H -0.177220 2.418370 -1.409230 C 0.731970 -0.431660 -0.390900 O -3.179350 1.506050 -1.643210 C 0.043210 1.240690 1.467410 C 2.147430 -1.104420 -2.328210 H -0.823180 1.848020 1.756160 H 0.143950 -0.509340 -2.497080 H 0.926500 1.888130 1.523570 H 3.011510 -1.287360 -1.693480 C 0.160680 -0.006250 2.375090 H 2.275900 -1.281100 -3.391590 C -0.697170 -1.093220 1.681680
8		**Ketene-substituted trans product** **B3LYP/6-31G**//HF=-463.437328, G=-21.6821** C 0.000000 0.000000 0.000000 C -0.665940 0.692950 -1.149950 C 1.341520 0.000000 0.000000 H -0.121370 0.476650 -2.079040 C 0.555720 2.711810 0.000000 C -2.201180 0.582710 -1.370440 C -0.422450 2.172310 -0.774720 H -2.410720 0.310890 -2.409880 C 1.768770 2.226650 0.766710 H -2.640160 -0.198430 -0.742630 C 2.016790 0.728060 1.115160 C -2.782920 1.983320 -1.047080 H 1.538450 0.538660 2.085360 H -3.078350 2.033500 0.007430 H 3.094790 0.584810 1.226610 H -3.666200 2.225820 -1.645120 O 2.563620 3.071080 1.148540 C -1.609120 2.958050 -1.286970 H -0.527920 0.059950 0.954260 H -1.492260 3.136560 -2.366720 H 0.506980 3.794620 0.118710 H -1.731070 3.929320 -0.799820 H 1.857410 0.025350 -0.962070

#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)

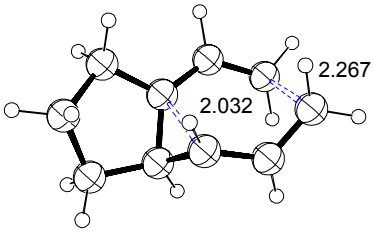
9



Ketene-substituted cis product
B3LYP/6-31G//HF=-463.48486, G=-21.5273**

H	-1.328720	0.850920	0.602720	H	2.204150	-1.084900	1.540110
C	-0.802470	-0.074530	0.319600	H	1.078170	-0.248650	2.614910
C	-1.141380	-0.355010	-1.134820	C	-0.912110	0.544930	-2.092730
C	-1.181470	-1.214120	1.304820	H	-1.585510	-1.319470	-1.372930
C	0.700140	0.136720	0.536160	H	2.580910	0.962290	0.072540
H	-1.947650	-1.877840	0.892550	O	2.035140	2.496190	-1.840250
H	-1.589570	-0.785190	2.227450	C	-0.281240	1.889200	-1.803550
C	0.144810	-1.933270	1.614220	H	-1.161220	0.319700	-3.126650
H	0.401240	-2.621680	0.799490	C	1.169270	1.816150	-1.305870
H	0.114220	-2.512440	2.541730	H	-0.276700	2.535670	-2.683080
C	1.160560	-0.776910	1.652630	H	-0.862780	2.403610	-1.020600
C	1.520200	0.936610	-0.170590				

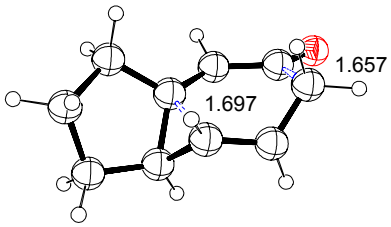
10



Divinylcyclopropane trans transition state (UB3LYP->closed shell)
B3LYP/6-31G//HF=-389.38608, G=-20.555; λ=-409.73, 137.01**

C	0.000000	0.000000	0.000000	H	-0.632020	-0.102250	-2.016040
C	2.267350	0.000000	0.000000	C	0.767420	3.027140	-1.070650
C	2.272660	1.387890	0.000000	H	0.486360	3.248310	-0.037200
C	1.985260	2.151710	-1.135680	C	-0.178140	2.212200	-3.188880
C	0.064180	1.848680	-1.723120	H	0.118150	1.421130	-3.887080
C	-0.277700	0.580160	-1.241710	H	-1.259490	2.359540	-3.324040
H	-0.310450	-1.030330	0.157560	C	0.571210	3.539380	-3.434050
H	0.041160	0.592340	0.904580	H	0.077750	4.171050	-4.178770
H	2.412530	-0.546360	-0.928060	H	1.582300	3.339940	-3.806060
H	2.468410	-0.562730	0.908730	C	0.641940	4.203160	-2.043140
H	2.060320	1.864010	0.961210	H	-0.289870	4.743650	-1.833920
H	2.410490	1.910070	-2.104950	H	1.468680	4.914770	-1.949210

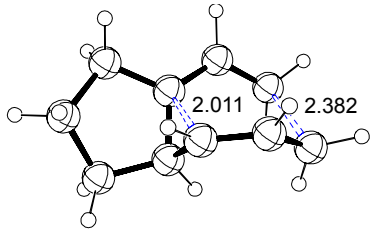
11



Ketene-substituted trans transition state (UB3LYP->closed shell)
B3LYP/6-31G//HF=-463.407608, G=-20.9727; λ=-242.2, 94.81**

C	0.000000	0.000000	0.000000	C	-0.719670	0.492520	-1.191820
C	1.419670	0.000000	0.000000	H	-0.115360	0.577540	-2.093440
C	0.575170	2.508830	0.000000	C	-2.214350	0.249610	-1.340600
C	-0.520690	1.609100	-0.142330	H	-2.577730	0.819040	-2.204100
C	1.909170	2.211010	0.415420	H	-2.460270	-0.803240	-1.515870
C	2.082960	0.698180	1.069220	C	-2.839330	0.794380	-0.034220
H	1.575790	0.664570	2.035750	H	-2.852870	0.012140	0.733230
H	3.158580	0.566770	1.169180	H	-3.875650	1.115090	-0.173290
O	2.913360	2.906430	0.377870	C	-1.911590	1.946540	0.403650
H	-0.539130	-0.410710	0.850490	H	-2.223430	2.892910	-0.059070
H	0.331250	3.568440	0.071710	H	-1.911450	2.106920	1.486700
H	1.952730	-0.135740	-0.939250				

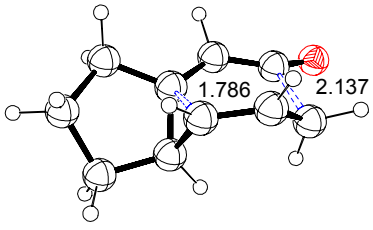
12



Divinylcyclopropane cis transition state (UB3LYP->closed shell)
B3LYP/6-31G//HF=-389.4037, G=-20.5746; λ=-423.56, 144.24**

C	0.000000	0.000000	0.000000	H	1.111740	1.006110	-2.385590
C	2.381940	0.000000	0.000000	C	1.173660	2.011570	-1.964000
C	2.723180	1.343100	0.000000	H	-0.074590	3.337890	-0.710970
C	2.224580	2.273610	-0.917350	C	2.750060	3.692150	-1.085170
C	0.215130	2.300440	-0.845640	H	2.742130	4.275260	-0.157040
C	-0.287400	1.354570	0.051280	H	3.799760	3.630590	-1.404720
H	2.710070	-0.639630	0.814100	C	1.889300	4.329700	-2.202340
H	2.194510	-0.509330	-0.935300	H	1.074940	4.917490	-1.766160
H	-0.339710	-0.654570	0.797210	H	2.464400	5.013380	-2.833710
H	0.161120	-0.487260	-0.952560	C	1.320310	3.132140	-3.000270
H	-0.771450	1.745040	0.946290	H	2.036530	2.814290	-3.767660
H	3.265940	1.743370	0.857430	H	0.377360	3.369110	-3.504810

13

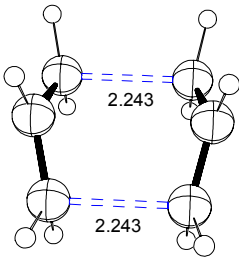


Ketene-substituted cis transition state (UB3LYP->closed shell)
B3LYP/6-31G//HF=-463.410916, G=-21.4128; λ=-571.85, 78.58**

O	0.000000	0.000000	0.000000	C	4.828670	-1.302170	-0.167600
C	1.191140	0.000000	0.000000	H	4.564270	-2.230830	-0.689620
C	1.802110	2.048210	0.000000	H	4.982990	-1.560970	0.885730
H	0.970410	2.544260	0.487970	C	6.066140	-0.653070	-0.824280
H	1.688850	1.922600	-1.076100	H	6.640430	-0.089230	-0.081870
C	3.063880	2.076400	0.555670	H	6.747870	-1.394580	-1.250220
H	3.184870	2.494340	1.553960	C	5.488390	0.300650	-1.897270
C	4.160160	1.357610	0.026730	H	6.147730	1.150770	-2.105010
H	5.113930	1.422290	0.539270	H	5.332390	-0.234750	-2.841530
C	3.680300	-0.315720	-0.374460	C	4.129650	0.726150	-1.341810
C	2.345940	-0.735350	-0.055030	H	3.419630	1.145690	-2.053980
H	2.251200	-1.671760	0.494130				

#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)

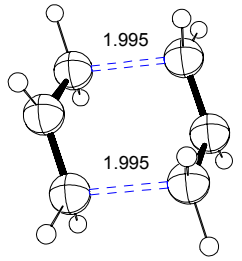
14-boat



Generic Cope boat transition state (UB3LYP->closed shell)
B3LYP/6-31G//HF=-234.553443, G=-18.0793; λ=-512.3, 135.39**
GVB energies (hartrees): -232.933904, -232.926145, -232.933904

C	0.000000	0.000000	0.000000	H	2.236200	-0.075180	-1.083410
C	2.242310	0.000000	0.000000	H	2.460580	-0.927380	0.520970
C	2.243930	2.441030	0.000000	H	0.006250	-0.078010	-1.083320
C	0.000640	2.440890	-0.005520	H	-0.218190	-0.926540	0.523010
C	2.556970	1.220280	0.592320	H	0.008500	2.513360	-1.089050
C	-0.314370	1.221900	0.589280	H	-0.217820	3.370160	0.512550
H	2.747590	1.220370	1.666130	H	2.239530	2.516660	-1.083350
H	-0.506230	1.224240	1.662870	H	2.461270	3.368380	0.521900

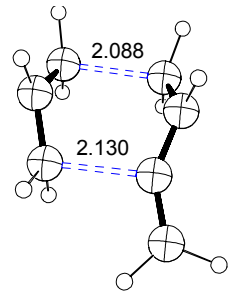
14-chair



Generic Cope chair transition state (UB3LYP->closed shell)
B3LYP/6-31G//HF=-234.567254, G=-17.7522; λ=-573.97, 194.93**
GVB energies (hartrees): -232.948406, -232.922181, -232.948406

C	0.000000	0.000000	0.000000	H	-0.228660	-0.926500	0.524540
C	1.994800	0.000000	0.000000	H	-0.134490	-0.078540	-1.076290
C	1.994680	2.440020	0.000000	H	2.224070	-0.926270	-0.524400
C	-0.000100	2.439830	0.000010	H	2.128810	-0.078260	1.076470
C	-0.322750	1.219900	0.621320	H	2.128660	2.518270	1.076400
C	2.317750	1.220050	-0.621360	H	2.223910	3.366300	-0.524410
H	2.437760	1.220110	-1.704770	H	-0.228780	3.366340	0.524500
H	-0.442070	1.219850	1.704740	H	-0.134550	2.518380	-1.076400

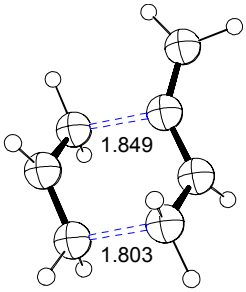
15-boat



Allene-substituted Cope boat transition state (UB3LYP->closed sh)
B3LYP/6-31G//HF=-272.621244, G=-19.451; λ=-603.46, 87.46**
GVB energies (hartrees): -270.77432, -270.739081, -270.738088

C	0.000000	0.000000	0.000000	C	-0.045770	-2.227790	0.957140
C	2.129750	0.000000	0.000000	H	-0.141510	-1.873910	1.979960
C	2.515390	1.262860	0.000000	H	-0.279260	-3.282660	0.836580
H	3.550730	1.531750	0.198540	C	2.039790	-2.193860	1.054740
H	1.824820	2.082410	-0.180140	H	2.303840	-3.244990	0.974410
H	0.011020	0.479230	0.975150	H	2.021290	-1.819850	2.073850
H	-0.202260	0.666780	-0.833250	C	2.505170	-1.324760	0.052910
C	-0.371070	-1.337730	-0.075870	H	2.789870	-1.772690	-0.902320
H	-0.555490	-1.757270	-1.064830				

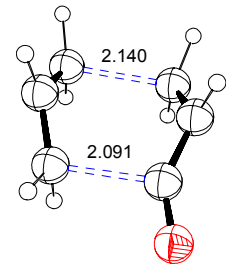
15-chair



Allene-substituted Cope chair transition state (UB3LYP->closed sh)
B3LYP/6-31G//HF=-272.638304, G=-19.124; λ=-493.97, 100.73**
GVB energies (hartrees): -270.804085, -270.750585, -270.736274

C	0.000000	0.000000	0.000000	C	0.012250	-2.302060	0.805860
C	1.849480	0.000000	0.000000	H	-0.285850	-3.002510	1.586820
C	2.365530	1.226960	0.000000	H	-0.160640	-2.721850	-0.185050
H	1.753440	2.115520	-0.119260	C	1.812900	-2.285450	0.893350
H	3.433730	1.380440	0.123250	H	2.125580	-3.314200	0.704790
H	-0.262900	1.039240	0.186770	H	1.943120	-2.030680	1.944240
H	-0.178540	-0.283670	-1.036890	C	2.290980	-1.323700	-0.052970
C	-0.365850	-0.942030	0.989440	H	2.648810	-1.687790	-1.016560
H	-0.515280	-0.585550	2.007070				

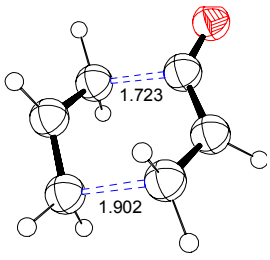
16-boat



Ketene-substituted Cope boat transition state (UB3LYP->closed sh)
B3LYP/6-31G//HF=-308.554856, G=-19.491; λ=-615.74, 73.26**
GVB energies (hartrees): -306.624116, -306.591312, -306.585994

H	0.000000	0.000000	0.000000	H	1.200730	-2.111620	0.431360
C	1.090210	0.000000	0.000000	H	2.804280	-1.255930	0.245730
C	1.738540	1.235520	0.000000	O	2.440580	-2.065170	2.869110
C	2.278290	1.427440	2.062300	H	2.783040	1.273460	-0.294430
C	1.731630	-1.164740	0.418660	H	1.174690	2.133600	-0.236100
C	2.103090	-1.000180	2.470230	H	3.326410	1.457030	1.783070
C	1.827210	0.333650	2.808160	H	1.858640	2.396780	2.312510
H	0.862530	0.409470	3.314610				

16-chair

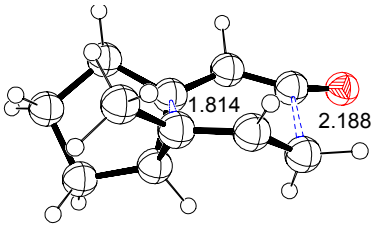


Ketene-substituted Cope chair transition state (UB3LYP->closed sh)
B3LYP/6-31G//HF=-308.571242, G=-18.947; λ=-536.62, 105.58**
GVB energies (hartrees): -306.621082, -306.62092, -306.602494

H	0.000000	0.000000	0.000000	H	1.195740	-2.099820	-0.416230
C	1.088520	0.000000	0.000000	H	2.772470	-1.329240	-0.053880
C	1.757230	1.232430	0.000000	O	2.141390	-2.052810	-2.729820
C	1.769500	-1.175830	-0.457930	H	1.221550	2.115190	0.342440
C	2.103510	-0.995190	-2.138210	H	2.813350	1.238360	0.260680
C	1.879880	1.497130	-1.880350	H	0.818370	1.686680	-2.022820
C	2.447440	0.340970	-2.475240	H	2.458280	2.415180	-2.003970
H	3.408750	0.425320	-2.977410				

#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)

17a-cis

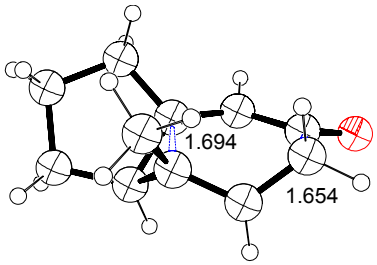


1-substituted ketene cis transition state

B3LYP/6-31G//HF=-502.721747, G=-22.5035; λ=-560.93, 68.67**

O	0.000000	0.000000	0.000000	H	4.477680	-2.199270	-0.662690
C	1.189140	0.000000	0.000000	H	5.115550	-1.416850	0.774400
C	1.793240	2.102450	0.000000	C	6.009360	-0.699340	-1.121380
H	0.956390	2.590240	0.487140	H	6.800200	-0.303700	-0.480310
H	1.671270	1.944790	-1.069950	H	6.464200	-1.489710	-1.725490
C	3.043020	2.129050	0.569040	C	5.411650	0.423320	-2.007970
H	3.135330	2.556710	1.567140	H	6.110250	1.253290	-2.161660
C	4.190510	1.445160	0.073770	H	5.156380	0.033750	-3.000150
C	5.499920	1.645270	0.817500	C	4.115380	0.852810	-1.322580
C	3.688460	-0.233010	-0.398800	H	3.380610	1.318110	-1.980040
C	2.365610	-0.687600	-0.066780	H	6.290170	2.031730	0.164410
H	2.299760	-1.639490	0.459790	H	5.878980	0.730060	1.286050
C	4.831960	-1.239330	-0.270640	H	5.358000	2.375080	1.619860

17a-trans

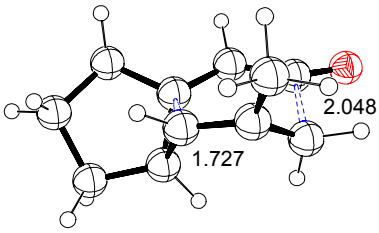


1-substituted ketene trans transition state

B3LYP/6-31G//HF=-502.718422, G=-22.2046; λ=-200.9, 94.51**

C	0.000000	0.000000	0.000000	H	3.184530	1.266040	0.190250
C	1.435040	0.000000	0.000000	H	1.969950	-0.865810	-0.386770
C	2.113210	1.267610	0.000000	H	0.464250	1.853510	-3.051870
C	1.985080	1.517510	-1.630420	H	-3.274520	0.471360	-0.191820
O	3.004100	1.866550	-2.210250	H	-3.722980	0.165490	-1.855260
C	-0.440690	0.687460	-1.484910	H	-1.973700	1.539480	-2.690210
C	0.676810	1.287970	-2.145120	H	-1.946590	2.229520	-1.077880
C	-1.841750	1.288500	-1.630300	H	-0.074800	1.199810	1.792000
C	-2.867710	0.221200	-1.175440	H	-0.999190	-0.299110	1.888330
C	-0.730520	0.532420	1.226980	H	-1.643160	1.083400	0.996440
C	-0.621090	-0.792990	-1.092460	H	-2.304180	-1.724700	-2.016180
C	-2.104440	-1.131890	-1.116940	H	-2.415600	-1.740160	-0.260170
H	1.608960	2.078540	0.528930	H	0.056020	-1.488980	-1.586750

17b-cis

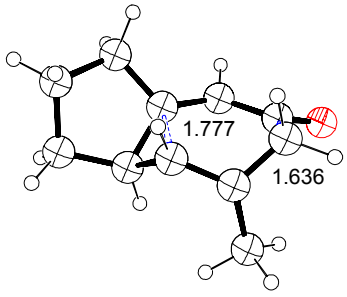


2-substituted ketene cis transition state

B3LYP/6-31G//HF=-502.732968, G=-22.8127; λ=-560.34, 82.57**

O	0.000000	0.000000	0.000000	H	4.546870	-2.292720	-0.585880
C	1.197020	0.000000	0.000000	H	4.893490	-1.669930	1.026290
C	1.821350	1.950390	0.000000	C	6.092460	-0.750970	-0.597640
H	0.961970	2.463440	0.418960	H	6.634830	-0.215030	0.188360
H	1.814120	1.871280	-1.085670	H	6.782010	-1.499560	-0.997950
C	3.032080	1.968890	0.675010	C	5.601870	0.237200	-1.683820
C	3.095310	2.471570	2.095200	H	6.286870	1.081010	-1.824920
C	4.149480	1.235430	0.182520	H	5.503700	-0.272280	-2.649970
H	5.071900	1.285980	0.752890	C	4.214200	0.667880	-1.215480
C	3.691180	-0.365280	-0.274120	H	3.554110	1.113540	-1.957580
C	2.322550	-0.778020	-0.062780	H	4.078290	2.890590	2.331240
H	2.172510	-1.769240	0.360410	H	2.921090	1.638820	2.791100
C	4.804780	-1.383760	-0.027520	H	2.334190	3.231250	2.289000

17b-trans



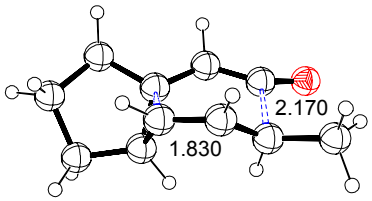
2-substituted ketene trans transition state

B3LYP/6-31G//HF=-502.726707, G=-22.1006; λ=-358.99, 87.29**

C	0.000000	0.000000	0.000000	H	3.082490	1.390690	0.208480
C	1.415160	0.000000	0.000000	H	2.879110	-1.475300	0.505380
C	2.015150	1.322140	0.000000	H	2.966940	-0.952910	-1.172900
C	2.267170	-1.187280	-0.360950	H	1.674330	-2.058940	-0.647600
C	-0.568390	0.784690	-1.490170	H	0.316160	2.082300	-2.941440
C	0.538200	1.409130	-2.113490	H	-2.287000	1.519630	-2.518000
C	1.875840	1.547230	-1.614430	H	-1.949810	2.440360	-1.054200
O	2.901850	1.818590	-2.227010	H	-0.530730	0.582130	0.749750
C	-1.957650	1.429290	-1.473280	H	-0.182410	-1.410810	-1.644170
C	-0.754310	-0.684400	-1.070940	H	-2.626340	-1.375820	-1.853360
C	-2.250150	-0.937890	-0.921260	H	-2.483430	-1.638200	-0.112380
C	-2.872520	0.459920	-0.697370	H	-2.865170	0.711960	0.369120
H	1.447850	2.088210	0.533200	H	-3.915010	0.507230	-1.024860

#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)

17c-cis

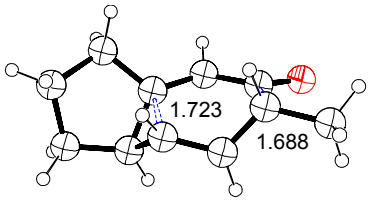


3-substituted ketene cis transition state

B3LYP/6-31G//HF=-502.731804, G=-22.4902; λ=-567.42, 79.76**

O	0.000000	0.000000	0.000000	H	4.554270	-2.266090	-0.736970
C	1.192350	0.000000	0.000000	H	4.956700	-1.627320	0.854920
C	1.799820	2.082740	0.000000	C	6.055310	-0.684760	-0.826910
C	0.648720	2.854080	0.584360	H	6.621290	-0.134690	-0.067920
H	1.733150	1.905120	-1.076310	H	6.741960	-1.416970	-1.261030
C	3.066750	2.071450	0.558210	C	5.485500	0.288710	-1.885780
H	3.191500	2.503380	1.551320	H	6.146720	1.141680	-2.074850
C	4.158010	1.352440	0.032700	H	5.333200	-0.229740	-2.840000
H	5.108150	1.400140	0.553590	C	4.125050	0.708920	-1.328110
C	3.666810	-0.357920	-0.394050	H	3.421740	1.136290	-2.043480
C	2.336660	-0.754800	-0.061280	H	0.838140	3.122460	1.628610
H	2.233110	-1.684580	0.498300	H	-0.268760	2.256060	0.544200
C	4.812370	-1.347060	-0.194360	H	0.463210	3.779620	0.025060

17c-trans

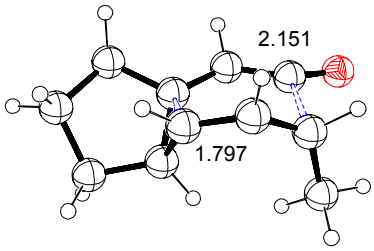


3-substituted ketene trans transition state

B3LYP/6-31G//HF=-502.726983, G=-22.1001; λ=-310.6, 88.48**

C	0.000000	0.000000	0.000000	H	4.114690	0.490740	-0.080810
C	1.414340	0.000000	0.000000	H	3.697620	1.308830	1.440130
C	2.094550	1.269370	0.000000	H	4.018150	2.249260	-0.041370
C	3.570890	1.334870	0.353090	H	1.951660	-0.868660	-0.379590
C	-0.529420	0.729730	-1.467860	H	0.342220	1.974180	-2.980940
C	0.573600	1.330070	-2.132820	H	-2.235100	1.470170	-2.515400
C	1.913390	1.482130	-1.664220	H	-1.917810	2.380280	-1.040300
O	2.925580	1.779640	-2.281530	H	-0.540220	0.528490	0.781370
C	-1.919440	1.372370	-1.467620	H	-0.118300	-1.468630	-1.596230
C	-0.721640	-0.741960	-1.054160	H	-2.579580	-1.443090	-1.857370
C	-2.216150	-1.000010	-0.922690	H	-2.458410	-1.697290	-0.113520
C	-2.844240	0.397730	-0.709040	H	-2.856360	0.647340	0.357960
H	1.513110	2.063090	0.479010	H	-3.881170	0.443370	-1.053710

17d-cis

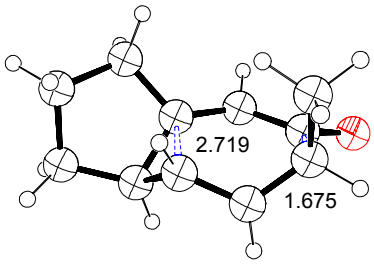


4-substituted ketene cis transition state

B3LYP/6-31G//HF=-502.718759, G=-22.7657; λ=-582.61, 55.1**

O	0.000000	0.000000	0.000000	H	4.550540	-2.340670	-0.529720
C	1.193670	0.000000	0.000000	H	4.884700	-1.602190	1.034760
C	1.767180	2.072780	0.000000	C	6.086440	-0.794960	-0.645870
H	1.040940	2.480300	0.701580	H	6.625470	-0.206060	0.103520
C	1.339840	2.298800	-1.444880	H	6.778980	-1.566360	-0.994520
C	3.061630	1.998970	0.502060	C	5.592110	0.114150	-1.796130
H	3.181310	2.292750	1.545480	H	6.277470	0.943760	-2.002840
C	4.165970	1.299660	-0.028400	H	5.486740	-0.464570	-2.721620
H	5.093340	1.351930	0.532910	C	4.206370	0.587260	-1.353870
C	3.683580	-0.399640	-0.359770	H	3.555380	0.957440	-2.139780
C	2.327590	-0.770630	-0.075800	H	1.797290	1.624050	-2.172090
H	2.191370	-1.718790	0.444020	H	1.585120	3.322860	-1.751870
C	4.799910	-1.391590	-0.037020	H	0.257540	2.171050	-1.524760

17d-trans



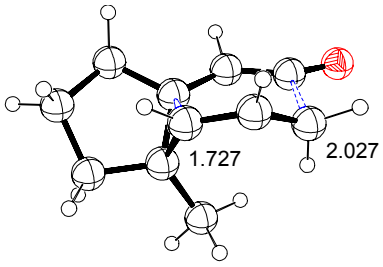
4-substituted ketene trans transition state

B3LYP/6-31G//HF=-502.724126, G=-22.0505; λ=-287.56, 91.74**

C	0.000000	0.000000	0.000000	H	1.783400	2.256570	1.894690
C	1.415940	0.000000	0.000000	H	0.542460	2.606290	0.676430
C	2.122270	1.257710	0.000000	H	3.205280	1.156390	0.079380
C	1.611080	2.433260	0.826320	H	1.934920	-0.862150	-0.416060
C	-0.519310	0.757790	-1.452550	H	0.340580	2.044030	-2.935900
C	0.580600	1.377400	-2.108050	H	-2.218970	1.513530	-2.497830
C	1.922650	1.522810	-1.642140	H	-1.922750	2.391060	-0.999340
O	2.931240	1.851460	-2.250340	H	-0.552410	0.496720	0.792630
C	-1.913310	1.393050	-1.449470	H	-0.097690	-1.436590	-1.628870
C	-0.708930	-0.725170	-1.075320	H	-2.555650	-1.415680	-1.911960
C	-2.203260	-0.992820	-0.963760	H	-2.450230	-1.709990	-0.173570
C	-2.840710	0.396440	-0.723760	H	-2.866280	0.620770	0.348600
H	2.143070	3.345930	0.543390	H	-3.873960	0.445100	-1.079030

#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)

17e-cis

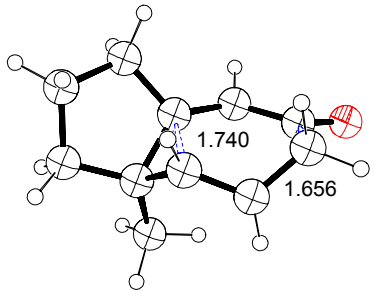


5-substituted ketene cis transition state

B3LYP/6-31G//HF=-502.723235, G=-22.3437; λ=-563.16, 84.83**

O	0.000000	0.000000	0.000000	H	4.528110	-2.434490	-0.224790
C	1.197690	0.000000	0.000000	H	4.675210	-1.672630	1.358520
C	1.819150	1.929360	0.000000	C	6.110400	-0.933290	-0.161370
H	1.012400	2.468890	0.485230	H	6.561970	-0.339440	0.639990
H	1.715150	1.843550	-1.077560	H	6.822620	-1.729210	-0.397420
C	3.081670	1.938490	0.566770	C	5.795060	-0.052050	-1.389810
H	3.188500	2.389580	1.553090	H	6.510830	0.768550	-1.519150
C	4.183600	1.157940	0.139020	H	5.824610	-0.656210	-2.304980
H	5.075010	1.229330	0.754040	C	4.353130	0.450740	-1.200610
C	3.706270	-0.466550	-0.199610	C	3.660240	0.939030	-2.464710
C	2.308980	-0.804230	-0.065350	H	3.750510	2.022600	-2.590710
H	2.102110	-1.793290	0.340520	H	4.118440	0.464020	-3.338360
C	4.740010	-1.483600	0.281570	H	2.600530	0.671760	-2.480820

17e-trans

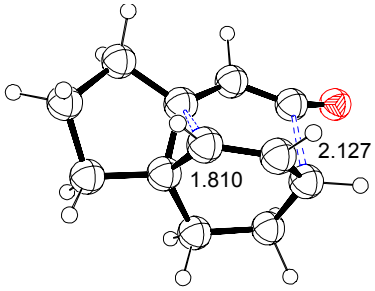


5-substituted ketene trans transition state

B3LYP/6-31G//HF=-502.725639, G=-21.8695; λ=-282.81, 86.12**

C	0.000000	0.000000	0.000000	H	3.146250	1.299450	0.175370
C	1.411760	0.000000	0.000000	H	1.957330	-0.851050	-0.397910
C	2.071820	1.284870	0.000000	H	0.323170	2.091930	-2.909050
C	-0.545880	0.800030	-1.445830	H	-2.274420	1.583190	-2.426040
C	0.559230	1.408730	-2.092940	H	-1.851060	2.505520	-0.984850
C	1.902950	1.567480	-1.612240	H	-0.525390	0.535460	0.787890
O	2.903180	1.914840	-2.222580	H	0.894490	-1.490730	-2.206790
C	-1.910310	1.491580	-1.393090	H	-0.700990	-2.007810	-2.762090
C	-0.770560	-0.694570	-1.059610	H	-0.011440	-2.706950	-1.285360
C	-0.102230	-1.785810	-1.873100	H	-2.720460	-1.273730	-1.739380
C	-2.276550	-0.854250	-0.828360	H	-2.498950	-1.548590	-0.010590
C	-2.829380	0.563960	-0.575440	H	-2.769200	0.818250	0.488760
H	1.560290	2.070740	0.561000	H	-3.881780	0.653140	-0.859660

18

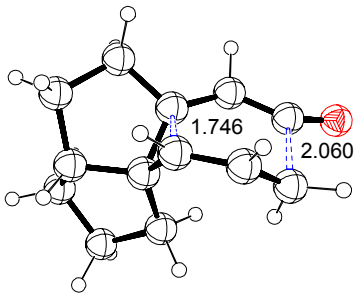


Cyclic cis-enforced transition state I

B3LYP/6-31G//HF=-540.837096, G=-22.1795; λ=-595.71, 81.12**

O	0.000000	0.000000	0.000000	H	4.857940	-1.732930	0.867520
C	1.192770	0.000000	0.000000	C	6.101710	-0.578300	-0.562810
C	1.833460	2.028380	0.000000	H	6.587810	-0.130000	0.310000
H	0.933460	2.486150	0.401810	H	6.833710	-1.250290	-1.019720
C	1.960810	2.072100	-1.526490	C	5.619210	0.518850	-1.535070
C	2.959860	1.981360	0.808800	H	6.284970	1.389470	-1.559710
H	2.879870	2.274080	1.853870	H	5.555870	0.124640	-2.557770
C	4.126350	1.318050	0.379840	C	4.206530	0.881520	-1.064940
H	5.007670	1.296670	1.010620	H	3.939210	2.629700	-2.228550
C	3.682520	-0.297050	-0.306020	C	3.371310	1.710330	-2.038530
C	2.336170	-0.748720	-0.110250	H	1.710740	3.092630	-1.846740
H	2.217600	-1.742140	0.322030	H	1.204160	1.434480	-1.994860
C	4.811330	-1.310980	-0.142710	H	3.301670	1.181810	-2.996690
H	4.607530	-2.145490	-0.826720				

19



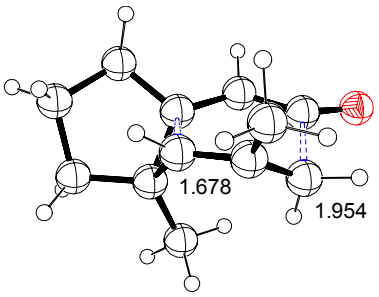
Cyclic cis-enforced transition state II

B3LYP/6-31G//HF=-580.144263, G=-23.2069; λ=-567.85, 68.93**

O	0.000000	0.000000	0.000000	C	6.098370	-0.927550	-0.462960
C	1.195480	0.000000	0.000000	H	6.665170	-0.393590	0.307200
C	1.816330	1.964350	0.000000	H	6.743240	-1.737490	-0.818910
H	0.997630	2.487470	0.482520	C	5.696830	0.040550	-1.595170
H	1.713800	1.858170	-1.076710	H	6.403820	0.878330	-1.671880
C	3.076770	1.981600	0.566580	C	5.478560	-0.559910	-2.994920
H	3.187580	2.420480	1.557600	C	4.282290	0.544350	-1.247330
C	4.177560	1.223470	0.098860	C	3.589200	0.956130	-2.553310
H	5.096510	1.291210	0.674200	H	6.413130	-0.721820	-3.541970
C	3.703420	-0.419560	-0.253410	H	5.143250	1.302840	-4.050830
C	2.321070	-0.782230	-0.065140	H	4.974780	-1.531830	-2.907070
H	2.144890	-1.760830	0.379060	H	3.427480	2.036600	-2.616720
C	4.766940	-1.452260	0.118560	H	2.610570	0.469200	-2.629690
H	4.484760	-2.399600	-0.357650	C	4.547490	0.461950	-3.675920
H	4.814440	-1.643710	1.196270	H	4.008040	0.044040	-4.531350

#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)

20-cis

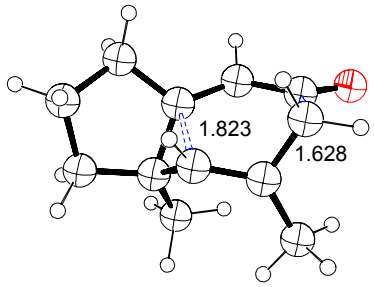


2,5 CH3-substituted ketene cis transition state

B3LYP/6-31G//HF=-542.045399, G=-23.8314; λ=-521.31, 56.98**

O	0.000000	0.000000	0.000000	H	4.108710	-3.141880	-1.915380
C	1.203510	0.000000	0.000000	H	3.102810	-1.879840	-2.625300
C	2.289410	0.839790	0.000000	H	2.340910	-3.329790	-1.949720
C	3.701320	0.516250	0.101300	H	5.044570	-1.198410	-0.748410
C	4.164970	-1.081280	-0.121960	H	4.495270	2.490780	-0.044430
C	3.060370	-1.912670	-0.478650	H	4.623230	1.609590	-1.566340
C	1.830420	-1.842920	0.168660	H	6.542880	0.361200	-0.787630
C	3.154980	-2.615220	-1.810480	H	6.804420	1.829880	0.133220
C	4.711350	1.506190	-0.479310	H	6.550780	-0.584560	1.443690
C	6.098730	1.009150	-0.024800	H	5.878900	0.891160	2.142040
C	4.380970	-0.296760	1.171840	H	3.766420	-1.757020	2.679020
C	5.825020	0.220460	1.275620	H	4.226500	-0.173850	3.311200
C	3.717410	-0.680640	2.485060	H	2.670900	-0.363910	2.515950
H	1.004750	-2.434000	-0.215340	H	2.052110	1.830590	-0.379780
H	1.807560	-1.697330	1.243700				

20-trans

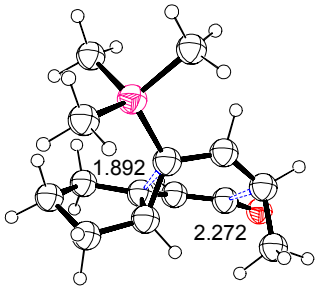


2,5 CH3-substituted ketene trans transition state

B3LYP/6-31G//HF=-542.040651, G=-22.8283; λ=-353.92, 80.54**

C	0.000000	0.000000	0.000000	H	2.947420	-1.353120	0.588570
C	1.411110	0.000000	0.000000	H	2.988800	-0.970570	-1.127310
C	2.001960	1.331030	0.000000	H	1.761650	-2.094270	-0.485070
C	1.859240	1.555260	-1.605920	H	0.289570	2.224780	-2.859620
O	2.882900	1.788510	-2.236560	H	-2.729880	0.983180	0.569730
C	2.309880	-1.173440	-0.288200	H	-3.919580	0.826810	-0.713100
C	-0.616190	0.893660	-1.464960	H	-2.375100	1.688980	-2.380830
C	0.500950	1.490610	-2.081530	H	-1.867660	2.635270	-0.982410
C	-1.961970	1.614160	-1.364490	H	0.692120	-1.414970	-2.369600
C	-2.855160	0.717580	-0.485880	H	-0.966680	-1.736190	-2.878520
C	-0.847160	-0.590340	-1.069790	H	-0.279040	-2.637940	-1.519750
C	-0.307150	-1.657240	-2.008090	H	-2.849670	-1.127350	-1.636690
C	-2.346500	-0.713920	-0.754490	H	-2.538150	-1.398330	0.078670
H	1.428750	2.092710	0.533710	H	-0.500780	0.610960	0.749430
H	3.067970	1.403150	0.216670				

21-cis



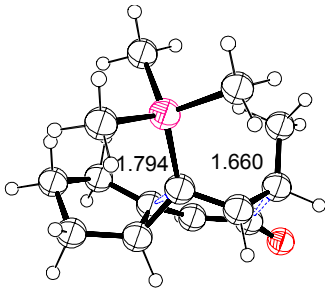
1-(Si(CH3)3),4-(CH3) substituted ketene cis transition state

B3LYP/6-31G//HF=-911.389283, G=-28.4075; λ=-536.77, 40.82**

O	0.000000	0.000000	0.000000	H	5.032060	1.504620	-0.854880
C	1.186880	0.000000	0.000000	H	1.582490	-1.329960	2.312160
C	2.367120	0.686130	0.000000	H	1.679590	-3.087430	2.241310
C	3.685080	0.296080	0.398900	H	0.191940	-2.250990	1.774130
C	4.800270	1.321050	0.199300	H	0.963910	-2.638340	-0.382010
C	6.009980	0.817460	1.014360	H	2.995850	-2.529990	-1.318340
C	4.126000	-0.701810	1.413290	H	6.182040	-4.085660	-2.248020
C	4.185100	-1.507110	0.119910	H	4.539810	-3.534080	-2.574660
C	2.979190	-2.154550	-0.296160	H	4.886420	-4.440270	-1.096350
C	1.716140	-2.193420	0.266880	H	7.015540	-1.316640	-2.856770
C	1.282820	-2.203550	1.726370	H	6.692410	0.079790	-1.826610
Si	5.718180	-2.070600	-0.870030	H	5.411530	-0.575980	-2.852900
C	5.278100	-3.679050	-1.779210	H	7.962680	-3.000730	-0.367520
C	6.260800	-0.846490	-2.215380	H	6.894010	-3.226270	1.019390
C	7.192050	-2.513740	0.242160	H	7.659480	-1.657520	0.735120
C	5.415620	-0.168900	2.044640	H	5.141110	0.367900	2.961070
H	6.728900	0.314170	0.364640	H	6.113630	-0.960090	2.333380
H	6.550580	1.638080	1.495640	H	3.411750	-1.061550	2.147250
H	4.437290	2.271530	0.611470	H	2.294500	1.583610	-0.615210

#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)

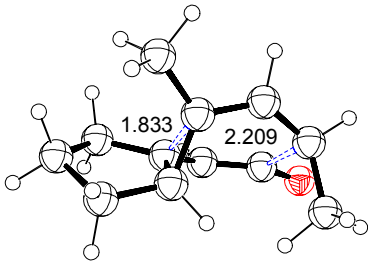
21-trans



1-(Si(CH3)3),4-(CH3) substituted ketene trans transition state
B3LYP/6-31G//HF=-911.395532, G=-27.3264; λ=-331.92, 62.37**

C	0.000000	0.000000	0.000000	H	3.290330	1.012580	0.066600
C	1.425630	0.000000	0.000000	H	1.926610	-0.863910	-0.443760
C	2.219490	1.212720	0.000000	H	0.479980	2.195780	-2.885130
C	2.031820	1.528820	-1.619000	H	-3.165990	0.405280	-0.300740
O	3.052390	1.846520	-2.217100	H	-3.716740	0.194080	-1.949930
C	1.859280	2.464790	0.792260	H	-1.947610	1.554310	-2.829840
C	-0.432940	0.808100	-1.541780	H	-2.024660	2.294830	-1.237800
C	0.687580	1.478510	-2.091960	H	1.077660	1.018360	3.069820
C	-1.847640	1.347690	-1.756110	H	0.863710	-0.734810	3.059700
C	-2.820680	0.230470	-1.323120	H	-0.204860	0.283320	4.035720
Si	-0.916680	0.333650	1.663280	H	-1.663610	-2.055820	1.865160
C	0.331490	0.221660	3.080910	H	-3.035520	-1.056000	1.362280
C	-2.141490	-1.078270	1.989950	H	-2.472940	-1.008700	3.033040
C	-1.836490	1.985040	1.805350	H	-1.164590	2.844110	1.719880
C	-0.544930	-0.683790	-1.221080	H	-2.306070	2.037280	2.795160
C	-2.006180	-1.083800	-1.403570	H	-2.629450	2.105200	1.062400
H	2.428720	3.310630	0.395420	H	-2.103300	-1.522150	-2.403980
H	2.119390	2.358690	1.850220	H	-2.347720	-1.838510	-0.689940
H	0.797830	2.707470	0.714600	H	0.183910	-1.315030	-1.734350

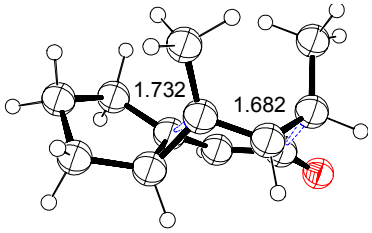
22-cis



1,4 CH3-substituted ketene cis transition state
B3LYP/6-31G//HF=-542.028588, G=-23.8935; λ=-576.64, 50.61**

O	0.000000	0.000000	0.000000	H	5.032060	1.504620	-0.854880
C	1.186880	0.000000	0.000000	H	1.582490	-1.329960	2.312160
C	2.367120	0.686130	0.000000	H	1.679590	-3.087430	2.241310
C	3.685080	0.296080	0.398900	H	0.191940	-2.250990	1.774130
C	4.800270	1.321050	0.199300	H	0.963910	-2.638340	-0.382010
C	6.009980	0.817460	1.014360	H	2.995850	-2.529990	-1.318340
C	4.126000	-0.701810	1.413290	H	6.182040	-4.085660	-2.248020
C	4.185100	-1.507110	0.119910	H	4.539810	-3.534080	-2.574660
C	2.979190	-2.154550	-0.296160	H	4.886420	-4.440270	-1.096350
C	1.716140	-2.193420	0.266880	H	7.015540	-1.316640	-2.856770
C	1.282820	-2.203550	1.726370	H	6.692410	0.079790	-1.826610
Si	5.718180	-2.070600	-0.870030	H	5.411530	-0.575980	-2.852900
C	5.278100	-3.679050	-1.779210	H	7.962680	-3.000730	-0.367520
C	6.260800	-0.846490	-2.215380	H	6.894010	-3.226270	1.019390
C	7.192050	-2.513740	0.242160	H	7.659480	-1.657520	0.735120
C	5.415620	-0.168900	2.044640	H	5.141110	0.367900	2.961070
H	6.728900	0.314170	0.364640	H	6.113630	-0.960090	2.333380
H	6.550580	1.638080	1.495640	H	3.411750	-1.061550	2.147250
H	4.437290	2.271530	0.611470	H	2.294500	1.583610	-0.615210

22-trans

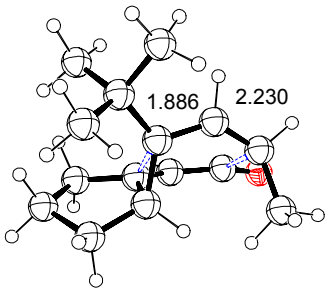


1,4 CH3-substituted ketene trans transition state
B3LYP/6-31G//HF=-542.032401, G=-23.074; λ=-296.59, 86.32**

C	0.000000	0.000000	0.000000	H	0.690060	2.711430	0.613460
C	1.429610	0.000000	0.000000	H	3.255010	1.078780	0.080330
C	2.177990	1.231400	0.000000	H	1.938760	-0.860920	-0.433200
C	2.004930	1.488100	-1.652860	H	0.459370	1.987590	-2.993890
O	3.031270	1.803970	-2.239250	H	-3.201400	0.480810	-0.142910
C	1.741790	2.468850	0.778180	H	-3.743430	0.214980	-1.787670
C	-0.441570	0.723860	-1.510010	H	-1.997880	1.565540	-2.692500
C	0.675370	1.349160	-2.137990	H	-1.944120	2.266670	-1.084540
C	-1.844240	1.322750	-1.633390	H	-0.092440	0.824270	1.994510
C	-2.852950	0.251360	-1.153360	H	-1.353870	-0.350540	1.643020
C	-0.780160	0.482340	1.220900	H	-1.479470	1.297090	1.015100
C	-0.608190	-0.753580	-1.131950	H	-2.291770	-1.648960	-2.091810
C	-2.089680	-1.101030	-1.164800	H	-2.394330	-1.752050	-0.337260
H	2.340170	3.325030	0.453260	H	0.073720	-1.441050	-1.632570
H	1.903140	2.335880	1.854440				

#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)

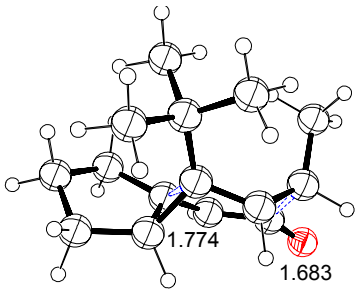
23-cis



1-(t-Bu),4-(CH3) substituted ketene cis transition state
B3LYP/6-31G//HF=-659.950186, G=-26.3236; λ=-572.96, 48.29**

O	0.000000	0.000000	0.000000	H	5.043940	1.571860	-0.823620
C	1.189330	0.000000	0.000000	H	1.615810	-1.268380	2.335100
C	2.365980	0.686010	0.000000	H	1.735000	-3.026450	2.275500
C	3.697590	0.292140	0.372770	H	0.233570	-2.211110	1.813890
C	4.764320	1.382840	0.217460	H	0.981970	-2.581300	-0.346920
C	5.955350	0.983110	1.112980	H	2.987230	-2.481340	-1.308620
C	4.166600	-0.690370	1.397170	H	6.161050	-3.748250	-1.773360
C	4.227730	-1.497250	0.099610	H	4.535760	-3.259730	-2.224270
C	2.998390	-2.119750	-0.284830	H	4.807980	-4.086880	-0.680610
C	1.742460	-2.139790	0.293710	H	6.747210	-1.471130	-2.393110
C	1.323390	-2.150930	1.758450	H	6.330540	-0.073730	-1.406070
C	5.503980	-1.990310	-0.677860	H	5.111790	-0.794230	-2.464250
C	5.220790	-3.350710	-1.377360	H	7.489230	-2.778750	-0.280130
C	5.948320	-1.018360	-1.794490	H	6.382000	-2.950390	1.087370
C	6.687750	-2.280840	0.276420	H	7.119400	-1.384690	0.718790
C	5.377970	-0.058760	2.095460	H	6.116830	-0.778300	2.455340
H	6.765220	0.556610	0.517000	H	4.985260	0.456300	2.981230
H	6.377750	1.845940	1.637060	H	3.452740	-1.082330	2.114690
H	4.315540	2.311570	0.590160	H	2.282670	1.605740	-0.579270

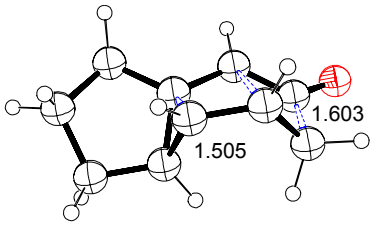
23-trans



1-(t-Bu),4-(CH3) substituted ketene trans transition state
B3LYP/6-31G//HF=-659.953015, G=-25.2406; λ=-374.96, 67.5**

C	0.000000	0.000000	0.000000	H	3.340420	0.909900	0.049730
C	1.441620	0.000000	0.000000	H	1.922630	-0.867420	-0.456410
C	2.282430	1.172360	0.000000	H	0.597090	2.072920	-2.974090
C	2.112860	1.472330	-1.646970	H	-3.253670	0.353170	-0.621500
O	3.155850	1.762900	-2.219520	H	-3.563550	0.141540	-2.332220
C	2.027900	2.474530	0.748800	H	-1.746090	1.546100	-2.957130
C	-0.355500	0.771950	-1.557410	H	-1.986660	2.250190	-1.369650
C	0.784070	1.414830	-2.126760	H	0.746010	-0.722560	2.556710
C	-1.753230	1.313800	-1.884310	H	-0.355930	0.323420	3.469030
C	-2.765110	0.186270	-1.585200	H	0.932350	1.033700	2.498440
C	-0.790100	0.271170	1.341220	H	-1.297520	-1.858730	1.508510
C	0.202720	0.226630	2.531110	H	-2.651070	-0.865800	0.940700
C	-1.786800	-0.884620	1.604420	H	-2.166010	-0.801130	2.628700
C	-1.553300	1.610270	1.419680	H	-0.894300	2.467050	1.261520
C	-0.499550	-0.712300	-1.233130	H	-1.996150	1.715220	2.416770
C	-1.934900	-1.120430	-1.557900	H	-2.368120	1.673420	0.697780
H	2.661530	3.251750	0.310540	H	-1.909770	-1.559730	-2.562680
H	2.294660	2.393080	1.808140	H	-2.353580	-1.881030	-0.894330
H	0.990160	2.801340	0.672100	H	0.263690	-1.348740	-1.685420

S1

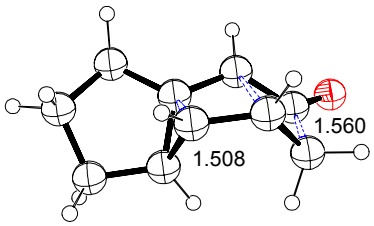


Diradical ts, restricted (only case UB3LYP->different geometry)
B3LYP/6-31G//HF=-463.368345, G=-20.8842; λ=-479.07, 106.14**

C	0.000000	0.000000	0.000000	C	-0.697510	0.610280	-1.213810
C	1.500860	0.000000	0.000000	H	-0.518260	-0.691150	0.660820
C	1.074020	2.211810	0.000000	C	-2.221580	0.555490	-1.191540
C	-0.264520	1.480220	-0.057810	H	-2.621290	-0.445780	-1.390940
C	2.221280	1.941100	-0.797040	H	-2.600360	1.218600	-1.978700
C	2.259030	0.385750	-1.183950	C	-2.630150	1.085880	0.206980
H	1.802600	0.154560	-2.146700	H	-2.694490	0.256430	0.919730
H	3.305560	0.085400	-1.174110	H	-3.610200	1.571040	0.199300
O	3.222970	2.637140	-0.931260	C	-1.494800	2.046520	0.624540
H	-0.200370	0.627070	-2.178950	H	-1.668800	3.062250	0.241860
H	1.071240	3.176660	0.507500	H	-1.385350	2.123540	1.712800
H	2.016710	-0.362060	0.884210

#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)

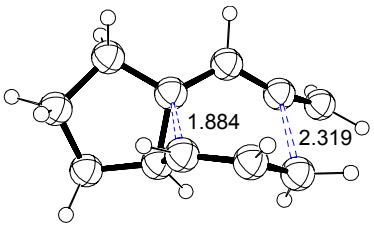
S2



Diradical transition state, unrestricted
UB3LYP/6-31G//HF=-463.369972, G=-20.9642; λ=-627.18, 93.38**

C	0.000000	0.000000	0.000000	C	-0.685780	0.599990	-1.214590
C	1.509910	0.000000	0.000000	H	-0.523680	-0.697740	0.650180
C	1.079630	2.173260	0.000000	C	-2.210830	0.553340	-1.215900
C	-0.273740	1.482350	-0.052390	H	-2.610930	-0.448690	-1.410280
C	2.194660	1.935340	-0.898360	H	-2.574670	1.208780	-2.016420
C	2.268840	0.408980	-1.212590	C	-2.641950	1.101080	0.168700
H	1.830750	0.106250	-2.166830	H	-2.713810	0.280710	0.891190
H	3.318590	0.110640	-1.194770	H	-3.623190	1.583130	0.139670
O	3.118140	2.715900	-1.095740	C	-1.514450	2.069100	0.591680
H	-0.178370	0.629270	-2.173930	H	-1.682370	3.077150	0.186860
H	1.141230	3.088450	0.589750	H	-1.430530	2.165290	1.680810
H	2.031200	-0.405280	0.861440				

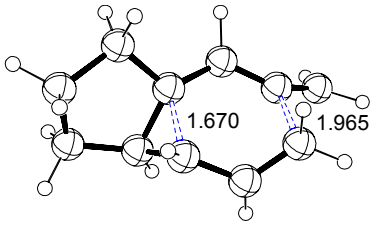
S3



Allyl-substituted cis transition state
B3LYP/6-31G//HF=-427.472647, G=-21.539; λ=-506.88, 87.77**

C	0.000000	0.000000	0.000000	H	-0.136140	-3.305240	0.796960
C	2.318620	0.000000	0.000000	C	1.035530	-1.926130	2.070300
C	2.647040	1.277660	0.000000	H	0.962670	-0.903720	2.439970
H	1.987380	2.055570	-0.374770	C	1.167880	-3.014000	3.137430
H	3.601290	1.608460	0.408860	H	1.872880	-2.671130	3.903970
H	0.202850	0.488710	0.943470	H	0.219740	-3.238050	3.637880
H	-0.305560	0.659100	-0.806820	C	1.746940	-4.234630	2.383770
C	-0.322220	-1.337700	-0.035620	H	2.330950	-4.886850	3.039150
H	-0.786540	-1.744510	-0.932410	H	0.937540	-4.847710	1.974810
C	2.669800	-1.307670	0.135700	C	2.600050	-3.635040	1.240950
H	3.307480	-1.732850	-0.642530	H	2.591160	-4.253470	0.336410
C	2.055860	-2.229630	1.014720	H	3.648670	-3.549300	1.553530
C	0.176600	-2.270800	0.893020				

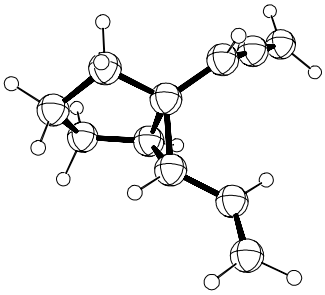
S4



Allyl-substituted trans transition state
B3LYP/6-31G//HF=-427.458735, G=-21.479; λ=-497.79, 93.03**

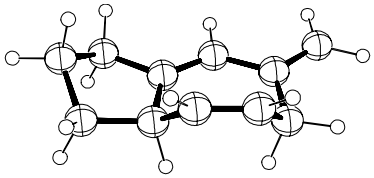
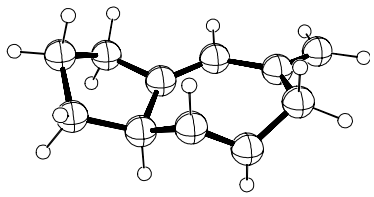
C	0.000000	0.000000	0.000000	C	1.264310	-2.584510	2.109910
C	1.965350	0.000000	0.000000	H	1.614300	-1.838010	2.821180
C	2.467530	1.234170	0.000000	H	-0.465280	-2.837620	0.707060
H	3.475290	1.431540	0.355620	C	1.371920	-4.052680	2.490080
H	1.889860	2.093390	-0.328510	H	0.584540	-4.375590	3.179960
C	-0.129010	-0.718850	1.185950	H	2.333890	-4.218090	2.990020
H	0.003060	-0.168050	2.116910	C	1.325720	-4.809150	1.143200
H	-0.198430	-0.504810	-0.943120	H	0.287320	-5.024620	0.869620
H	-0.224770	1.063250	-0.009750	H	1.843080	-5.771660	1.189560
C	2.358680	-1.322500	-0.008310	C	1.959370	-3.845720	0.116740
H	3.050860	-1.597740	-0.805220	H	1.550070	-3.981780	-0.890560
C	1.738020	-2.428610	0.658550	H	3.041260	-4.016200	0.046870
C	0.187710	-2.120260	1.197400				

S5



Allyl-substituted starting structure
B3LYP/6-31G//HF=-427.497237, G=-22.917**

C	0.000000	0.000000	0.000000	C	2.896290	-0.692620	2.319690
C	4.841130	0.000000	0.000000	H	3.202420	0.349400	2.349430
C	5.538960	1.105810	0.000000	H	1.103230	-1.827340	1.608400
H	6.569710	1.130010	0.348130	C	2.978120	-1.521730	3.593950
H	5.118110	2.046290	-0.350610	H	2.180870	-1.294030	4.310870
C	1.273300	-0.045560	0.400980	H	3.932970	-1.312910	4.092550
H	1.968320	0.716200	0.053100	C	2.930090	-2.990720	3.109130
H	-0.726960	-0.742440	0.320520	H	1.893070	-3.338750	3.063840
H	-0.360600	0.782360	-0.660720	H	3.458390	-3.671170	3.783310
C	4.124790	-1.097040	0.008460	C	3.550810	-2.969400	1.693100
H	4.139620	-1.737490	-0.875190	H	3.152760	-3.760880	1.046930
C	3.281380	-1.560180	1.151450	H	4.637140	-3.111120	1.749270
C	1.828310	-1.074790	1.302750				

#	Ball-and-stick figure	Level of theory/basis//HF (hartree), ΔG correction (kcal/mol) from calc. real frequencies; λ_1, λ_2 (two lowest eigenvalues, transition structures)
S6		**Allyl-substituted cis product** **B3LYP/6-31G**//HF=-427.559298, G=-21.524** C 0.000000 0.000000 0.000000 C 1.728810 -2.521300 -0.044070 C 1.520760 0.000000 0.000000 C 0.249710 -2.918820 -0.163400 C 2.206560 1.156470 0.000000 H -0.252510 -2.724130 0.796680 H 3.292720 1.170060 0.019060 C 0.280090 -4.450600 -0.423380 H 1.704670 2.118950 -0.013830 H -0.500950 -4.766800 -1.121910 H -0.344770 -0.436940 0.950200 H 0.107750 -4.988970 0.515670 H -0.359270 1.032540 -0.015780 C 1.703230 -4.746800 -0.929630 C 2.239430 -1.278040 0.004660 H 1.785830 -4.492900 -1.993540 H 3.325350 -1.186110 0.028350 H 1.990320 -5.796320 -0.814050 C -0.594740 -0.789330 -1.147770 C 2.567530 -3.780990 -0.100880 H -1.105580 -0.237840 -1.933450 H 2.700590 -4.193280 0.911590 C -0.474680 -2.115770 -1.226990 H 3.566080 -3.606850 -0.512990 H -0.891280 -2.658620 -2.073760
S7		**Allyl-substituted trans product** **B3LYP/6-31G**//HF=-427.510661, G=-21.654** C 0.000000 0.000000 0.000000 C 0.898990 -3.281670 0.808840 C 1.546000 0.000000 0.000000 H 0.864850 -3.227600 1.905350 C 2.203430 1.173330 0.000000 H -0.285810 -2.467470 -0.855900 H 3.288730 1.221490 -0.004470 C 1.054060 -4.753000 0.332690 H 1.673650 2.121020 0.012070 H 0.179930 -5.087060 -0.234480 C -0.331570 -1.207490 0.819970 H 1.144870 -5.417950 1.197980 H -0.111930 -1.126170 1.886380 C 2.350090 -4.792370 -0.513090 H -0.355470 -0.120740 -1.031740 H 2.118080 -4.590230 -1.565390 H -0.372960 0.956620 0.379330 H 2.857420 -5.760960 -0.469930 C 2.359130 -1.254270 -0.018170 C 3.204750 -3.634970 0.044130 H 3.373390 -1.040250 -0.358920 H 4.004150 -3.314430 -0.630270 C 2.172470 -2.559910 0.309770 H 3.673130 -3.949530 0.989680 C -0.160970 -2.397610 0.226850

Note on restricted/unrestricted calculations: All transition states were calculated using closed shell methods, then reoptimized with unrestricted DFT with appropriate combinations of orbitals taken to break spin symmetry. In all transition states but one (**S1**), the energy and geometry remain unchanged and this is indicated with the notation (UB3LYP→closed shell) in the table above. In structure **S1**, the energy and geometry does change, and this is indicated with the note (UB3LYP→different geometry) in the table above. In that case the unrestricted energy and geometry is shown in addition to the restricted energy and geometry.