SUPPORTING INFORMATION

Observation, Prediction, and Origin of an Isotope Effect on Recrossing. Entropic Intermediates and Hidden Rate-Limiting Steps in Seemingly Concerted Cycloadditions

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Experimental Procedures

Oven-dried glassware was cooled under a stream of nitrogen prior to use, and reactions were carried out under a positive pressure of nitrogen. Standard syringe-and-septa techniques were employed. THF was dried by distilling from benzophenone / sodium prior to use.

Reaction Procedures

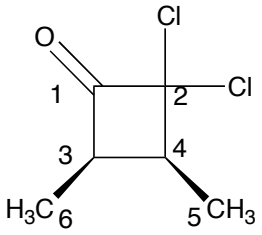
cis-2,2-Dichloro-3,4-dimethylcyclobutanone (**3**). Example Procedure. To 100 mL of dry tetrahydrofuran (THF) at 25 °C in a flask equipped with a dry ice / acetone condenser was added 5 g (76 mmol) of activated zinc-copper complex. While stirring the solution, approximately 3.4 g (60 mmol) of cis-2-butene was added to the reaction mixture using a balloon. Using an addition

funnel, 7 mL (11.3 g, 62 mmol) of trichloroacetyl chloride in 100 mL of THF was added to the solution over a 4 h period while the temperature was maintained at 25 °C. The reaction was allowed to stir at 25 °C for an additional 16 h. Aliquots of 0.5 mL of the reaction mixture were analyzed directly by ^{1}H NMR to insure completion of the reaction. The reaction mixture was then filtered through celite, and 200 mL of pentane was added to precipitate salts from the solution. The resulting solution was filtered and the filtrate was concentrated under reduced pressure. The residue was mixed with 50 mL of pentane, the resulting mixture was filtered, and the filtrate was again concentrated under reduced pressure. The residue was rapidly chromatographed through a 3 inch x 2 inch plug of silica gel, eluting with 1% ethyl acetate in hexanes. Concentration of the eluted material under vacuum was followed by two successive vacuum distillations to afford 600 mg of **3** as a clear viscous oil with no observable impurities in the ^{1}H NMR: bp 35 - 45 °C (0.1 mm). Closely analogous procedures were used to obtain two additional samples of **3** for analysis.

NMR Measurements

All NMR samples consisted of 200 mg of **3** in 5 mm NMR tubes filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, 160 s delays between calibrated $\pi/2$ pulses, and a 5 s acquisition time to collect 347 224 points. Integrations were numerically determined using a constant integration region for each peak that was a constant multiple of the peak widths at half height. In accord with the methodology we have previously published (ref 7a in main text), for the integration of the methine carbons the transmitter was set half way in between the two carbons. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. Six spectra were recorded for each sample.

The assignment of the peaks in the ^{13}C spectrum of **3** was based on mapping the ^{13}C-^{13}C coupling constants that could be observed in the very high signal-to-noise ^{13}C spectra of **3**. The coupling constants in Hz were J(1-2)=30.6, J(1,3)=33.6, J(2,4)=31.7, J(2,3)=20, J(3,4)=29.7, J(3,6)=35.5, J(4,5)=36.8. The unusual two-bond coupling between carbons 2 and 3 or 20 Hz should be noted and it affects the analysis as described below.



NMR Results and Calculation of KIEs

For the integrations of the peaks for carbon 3 versus carbon 4, the integration of carbon 4 was set to 1000 and the integration of carbon 3 was recorded. For the integrations of the peaks for carbon 5 versus carbon 6, the integration of carbon 6 was set to 1000 and the integration of carbon 5 was recorded. The raw results are shown in the first section of the tables below.

A complication in the raw results for carbon 3 versus carbon 4 is that carbon 4 is subject to three ^{13}C-^{13}C couplings leading to satellites not included in the integration range, while carbon 3 is subject to four such couplings (due to the 20 Hz C2-C4 coupling discussed above). As a result, the integration of carbon 3 is diminished by the natural abundance of ^{13}C at carbon 2. To

allow for this, the integrations at carbon 3 were adjusted by the 0.0107(8) natural abundance of ^{13}C. The second section of the first table below shows the adjusted results.

The isotope effects were then calculated as 1000 divided by the integration, the results were averaged, and 95% confidence ranges were calculated in a standard way. (See: http://www.iupac.org/publications/analytical_compendium/Cha02sec3.pdf.)

Table of Results for Carbon 3 versus Carbon 4

Raw Integration Results					
992.2	992.7	998.2	998.1	996.4	998.1
992.4	991.8	996.0	998.9	995.9	1000.5
992.9	996.1	997.9	1000.1	992.0	995.7
991.9	997.5	995.6	997.6	997.2	997.9
Adjusted for Satellites					
1002.9	1003.3	1008.9	1008.8	1007.1	1008.8
1003.0	1002.4	1006.7	1009.5	1006.6	1011.2
1003.5	1006.7	1008.6	1010.8	1002.6	1006.4
1002.5	1008.1	1006.2	1008.3	1007.8	1008.6
Isotope Effect					
0.9971	0.9967	0.9912	0.9913	0.9930	0.9913
0.9970	0.9976	0.9934	0.9906	0.9934	0.9889
0.9965	0.9933	0.9915	0.9893	0.9974	0.9936
0.9975	0.9919	0.9938	0.9918	0.9922	0.9915
average	standard deviation		95% confidence		
0.993	0.0027		0.0012		

Table of Results for Carbon 5 versus Carbon 6

1003.8	1003.6	1001.3	1002.1	999.3	990.1
1004.7	1005.2	999.3	999.8	1001.1	995.6
1003.6	1001.1	1000.9	997.3	995.8	999.5
1003.3	1001.7	1000.2	1001.0	996.4	994.2
0.9962	0.9964	0.9987	0.9979	1.0007	1.0100
0.9953	0.9948	1.0007	1.0002	0.9989	1.0045
0.9964	0.9989	0.9991	1.0027	1.0042	1.0005
0.9967	0.9983	0.9998	0.9990	1.0037	1.0058
average	standard deviation		95% confidence		
1.0000	0.0036		0.0015		

Computational Procedures and Supporting Computational Results

General

Calculations of structures, energies, and frequencies employed standard procedures in Gaussian09 (S1) unless otherwise noted. Most structures were optimized with tight convergence criteria (opt=tight in Gaussian09) instead of the default criteria. Complete structures and energetics are provided in a section below.

The program suite PROGDYN used for dynamics is a series of component programs as either Unix shell scripts or awk programs. Gaussian09 was used to calculate the forces at each point in trajectories. A full description of PROGDYN including either listings or the

subprograms used or references to the exact subprograms used can be found at the end of the Supporting Information. The latest version of this program can be obtained by emailing Daniel Singleton at singleton@mail.chem.tamu.edu. The original version of this program was published in the Supporting Information of a previous paper (S2).

RRKM calculations were carried out using an available program (S3) and employing the Beyer-Swinehart direct count algorithm (S4). An example input file showing all of the options employed is shown in a later section.

GAUSSRATE Calculations

A number of the calculations in the manuscript made use of the programs GAUSSRATE (reference 17a in the main text) and POLYRATE (reference 17b in the main text, see the last section for the complete reference) (S5). These programs were modified in minor ways. In particular, the subroutine *mepout* was modified to output frequencies with higher precision, and the utility program *shuttle* was modified to save copies of all frequency calculations so that data could be extracted from them later. Simple *awk* programs were used to automate the use of data output from GAUSSRATE in subsequent RRKM calculations.

To show the complete set of options selected for these calculations, a sample set of input files for GAUSSRATE / POLYRATE are given in a later section. For the sake of simplicity, the starting material in these calculations was generally taken to be a minimized loose complex of reactants. Such complexes are not kinetically significant but this does not matter for the purpose at hand.

Exploration of DFT and ab initio Methods

A variety of computational method / basis set combinations were explored for the study of the reaction of **1** with **2**. In general terms, we considered whether the energy surfaces predicted by these method / basis set combinations were consistent with the experimentally observed intramolecular KIE and consistent with CCSD(T)/6-311++G**/PCM(CH_2Cl_2) single-point energies on a grid of M06-2X/6-31+G** geometries. Some were consistent with both while some were consistent with neither.

For the various transition structures, conventional TST isotope effects were predicted by the method of Bigeleisen and Mayer (S6). A one-dimensional infinite parabola tunneling correction was also applied (S7). Such KIE predictions have proven highly accurate in reactions not involving hydrogen transfer, so long as the calculation accurately depicts the mechanism and transition state geometry (S8).

For the intramolecular KIE, surfaces for which the transition structure has C_s-symmetry provide no prediction from conventional transition state theory. As explored in detail for the main text with MPW1K/6-31+G** calculations, such structures can be consistent with the experimental isotope effects. This includes M06/6-31+G**, MP2/6-31+G**, MPW1K/6-31+G**, MPW1K/6-31+G**/PCM(CH_2Cl_2), and MPW1K/6-31G* surfaces. Other surfaces lead to asymmetric transition structures with isotope effects that are clearly inconsistent with experiment – the predicted isotope effects for HF/6-31+G*, HF/6-31+G*/PCM(CH_2Cl_2), B3LYP/6-31+G**, B3LYP/6-31+G**/PCM(CH_2Cl_2), and MPW3LYP/6-31+G** transition structures were 1.001, 1.016, 1.019, 1.014, and 1.018, respectively. For a third class of structures, it is not obvious that the structures are inconsistent with the observed KIE due to the complexity of the energy surface. On the M062X/6-31+G**/PCM(CH_2Cl_2) there is an early

slightly asymmetric transition structure that leads to an asymmetric intermediate that leads to a highly unsymmetrical rate-limiting transition structure. The isotope effect predicted for this reaction from conventional TST is 1.001, but it seems plausible that a likely later variational transition state could lead to isotope effects nearer that observed. However, the M06-2X surfaces did not fit well with the CCSD(T)/6-311++G**/PCM(CH_2Cl_2) surface and so they were not considered further.

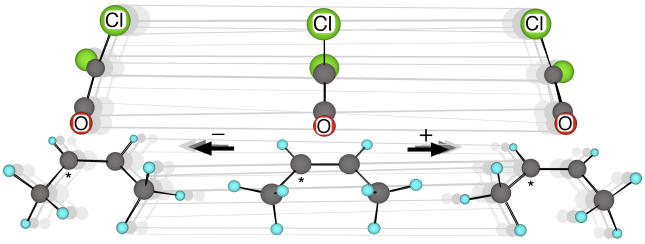
The table below shows the grid of CCSD(T)/6-311++G**/PCM(CH_2Cl_2) single-point energies on M06-2X/6-31+G** geometries, along with relative energies in the lower part of the table. The geometries were obtained by fixing the distances between the olefinic carbons and carbonyl carbon of the ketene; these fixed distances are shown across the top row and in the left column of the table. The key observation is that the CCSD(T) calculations suggest a symmetrical potential energy saddle point with C-C distances between 2.2 and 2.1 Å. This is exactly what is observed in the MPW1K/6-31+G** calculations, supporting the choice of the later for the focal studies in the main text. M06/6-31+G** calculations are similar in the area of the saddle point but their energy drops more rapidly in the area after the saddle point than seen in the CCSD(T) calculations.

	2.3	2.2	2.1	2	1.9	1.8	1.7	1.6
2.3	-1227.189256	-1227.188867	-1227.188196	-1227.187307	-1227.186382	-1227.185609	-1227.185262	-1227.264464
2.2	-1227.188867	-1227.188622	-1227.188591	-1227.188374	-1227.188070	-1227.188026	-1227.188824	-1227.269317
2.1	-1227.188196	-1227.188591	-1227.188616	-1227.188792	-1227.189034	-1227.189469	-1227.190846	-1227.268318
2	-1227.187307	-1227.188374	-1227.188792	-1227.188871	-1227.189236	-1227.189928	-1227.191246	-1227.261752
1.9	-1227.186382	-1227.188070	-1227.189034	-1227.189236	-1227.189225	-1227.189650	-1227.190494	-1227.250039
1.8	-1227.185609	-1227.188026	-1227.189469	-1227.189928	-1227.189650	-1227.189407	-1227.189132	-1227.233294
1.7	-1227.185262	-1227.188824	-1227.190846	-1227.191246	-1227.190494	-1227.189132	-1227.187508	-1227.185256
1.6	-1227.264464	-1227.269317	-1227.268318	-1227.261752	-1227.250039	-1227.233294	-1227.185256	-1227.180864

	2.3	2.2	2.1	2	1.9	1.8	1.7	1.6
2.3	**0.00**	0.24	0.67	1.22	1.80	2.29	2.51	-47.19
2.2	0.24	**0.40**	0.42	0.55	0.74	0.77	0.27	-50.24
2.1	0.67	0.42	**0.40**	0.29	0.14	-0.13	-1.00	-49.61
2	1.22	0.55	0.29	**0.24**	0.01	-0.42	-1.25	-45.49
1.9	1.80	0.74	0.14	0.01	**0.02**	-0.25	-0.78	-38.14
1.8	2.29	0.77	-0.13	-0.42	-0.25	-0.09	0.08	-27.63
1.7	2.51	0.27	-1.00	-1.25	-0.78	0.08	1.10	2.51
1.6	-47.19	-50.24	-49.61	-45.49	-38.14	-27.63	2.51	5.27

The stationary points **5**‡ and **6**‡, as well as the VRI, are all spin-unrestricted stable in UMPW1K/6-31+G** calculations.

Mode 3.



As discussed in the main text, "mode 3" desymmetrizes the transition structure in such a way that the combination of motion in this mode and motion along the transition vector morphs the transition structure toward the product geometries. This is a simplification – naturally motion toward the products involves some combination of motion in all of the normal modes of the transition structure – but the combination of the two modes accounts for the largest geometry changes needed to get the molecule to a point where it is committed to form a particular product.

Mode 3 itself is well separated in energy from other modes (74.1 cm^{-1} with nearest neighbors at 33.5 and 116.1 cm^{-1}. As a result, the nature of this mode changes little with isotopic mass in the olefinic carbons. The frequency also changes little (to 72.6 cm^{-1}) with a change in the olefinic carbon mass to 140, since most of the motion associated with the mode is in the dichloroketene moiety.

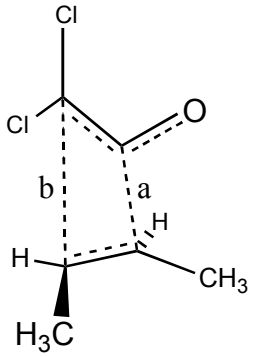
The frequencies above are for the MPW1K/6-31G* calculations since those are the calculations that are relevant to the trajectories. However, the frequencies in the MPW1K/6-31+G** calculations are similar: 77.3 cm^{-1} for mode 3 and 43.1 cm^{-1} and 97.4 cm^{-1} for the nearest neighbors.

Initialization of Trajectories and Additional Details on Trajectories

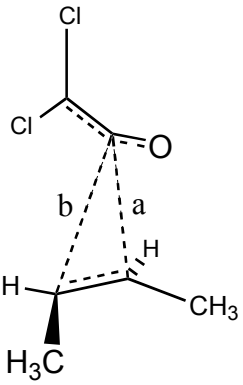
Most of the trajectories employed in the manuscript are quasiclassical, i. e. including zero-point energy plus a Boltzmann distribution of quantized vibrational energies for each mode. As mentioned in the main text, some trajectories started from **5**‡ were carried out in fully classical mode, i. e. including only a classical Boltzmann distribution of energy. For the trajectories, the desired energy in each of the normal modes was mapped from a random number generator to a Boltzmann distribution set at 25 °C. The phase of each of the normal modes was mapped from Gaussian distribution of random numbers. This distribution is not correct for a classical oscillator but would be approximately correct for a quantum oscillator in its ground state (only ignoring mode displacements outside of the classical limit), and has the advantage that a larger portion of the trajectories start with an energy approximating the initially desired energy. The sign on the velocity of the normal modes was randomized, except that for trajectories started from **5**‡ the "controlphase" option in PROGDYN was used to obtain an equal number of trajectories with positive versus negative velocities in mode 3. After an energy/force calculation on the initial geometry, the total initial energy was calculated and the trajectory was thrown out if the energy did not agree satisfactorily (within 1 kcal/mol) with the desired energy. (This is a variation of the conventional practice of scaling energies. (S9)) The mode corresponding to the transition vector was treated classically. For most trajectories, the sign on the transition vector was set so as to start the trajectory in the direction of the cycloadduct product, but a portion of the trajectories were integrated both forward and backward in time as a check for anomalies.

After exploratory study of over 1000 trajectories started from **5**‡, the stopping criteria for

trajectories were set as shown in the diagram below. These distances were set in such a way that the trajectory was fully committed to product formation or recrossing; in other words the stopping criteria made no mistakes in over 1000 test cases of trajectories continued for longer times. A 500 fs time limit was set for the trajectories to minimize the effect of nonphysical intramolecular redistribution of the zero-point energy. A small proportion of trajectories did not complete within this time limit, depending logically on the isotopologue under study (0.2% for the parent isotopologue, 2.5% when both olefinic carbons were mass 140). These trajectories were ignored.



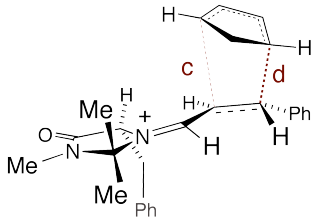
assigned as forming product when a>1.8 and b>2.3



assigned as recrossing when a>2.2 and b>2.2

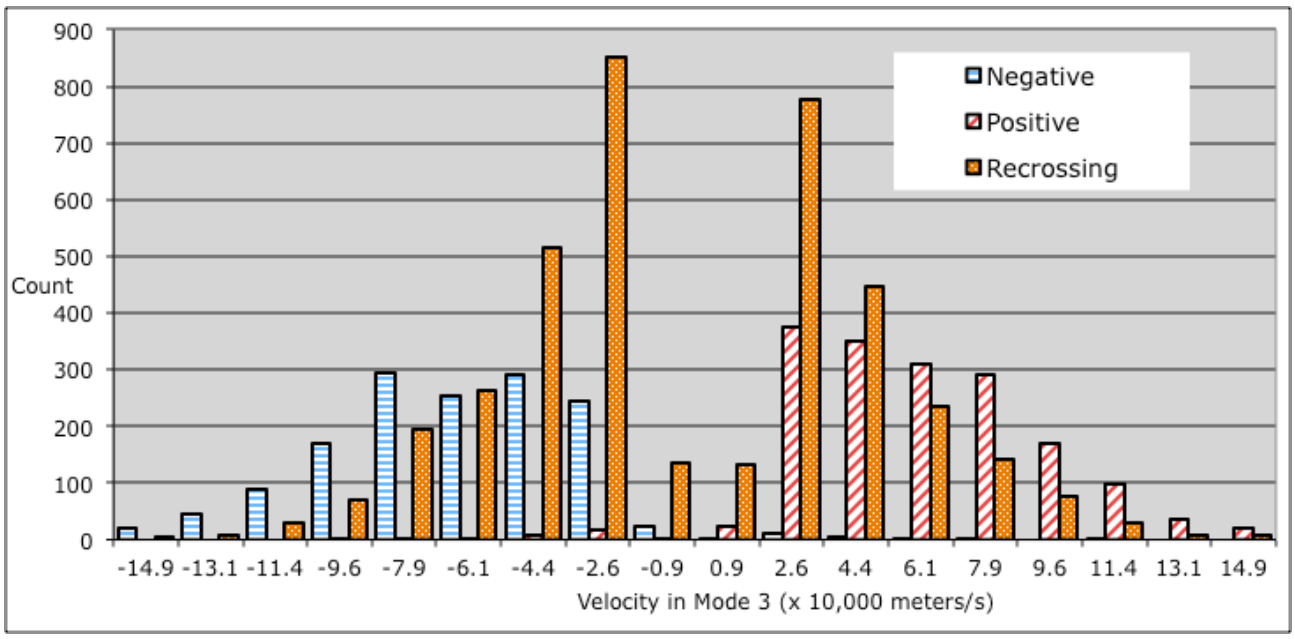
We performed a limited set of trajectories started from **5**‡ with M06/6-31G* calculations. The M06 surface is qualitatively similar to the MPW1K surface, but as described above the M06 surface does not fit quite as well with the CCSD(T) surface, so we focused on the MPW1K calculations. In 36 trajectories without isotopic labeling, 19 M06 trajectories recrossed and 17 formed product. The average times for recrossing and product formation were 243 and 191 fs. This is in the ballpark of what is seen with MPW1K but the uncertainties derived from this limited set of numbers is very large. The important observation is that there is no qualitative difference.

For the Diels-Alder reactions of **7**, the trajectories were assigned as product forming when distance c in the drawing below was < 2.0 Å and distance d was < 1.8 Å. The trajectories were assigned as recrossing when c > 2.5 and d > 2.3. No Diels-Alder trajectories reached the 500 fs time limit.



A reviewer asked whether the energy in mode 3 of **5**‡ influenced the outcome of trajectories. It does. The graph below shows a histogram of the outcome of trajectories versus the velocity in mode 3. It can be seen that the recrossing trajectories are center-weighted, that is, as the reviewer expected, the greater the velocity in mode 3 the greater the chance that a product is formed instead of recrossing to the starting material. This is qualitatively understandable from

the expectation that trajectories proceeding down the middle of the potential energy surface in Figure 1 of the main text would be positioned well to bounce back to the starting materials. We have previously described this phenomenon for a Diels-Alder reaction in reference 6b from the main text.



Uncertainties in the Trajectory Ratios, and Extrapolation of the Trajectory-Predicted KIE

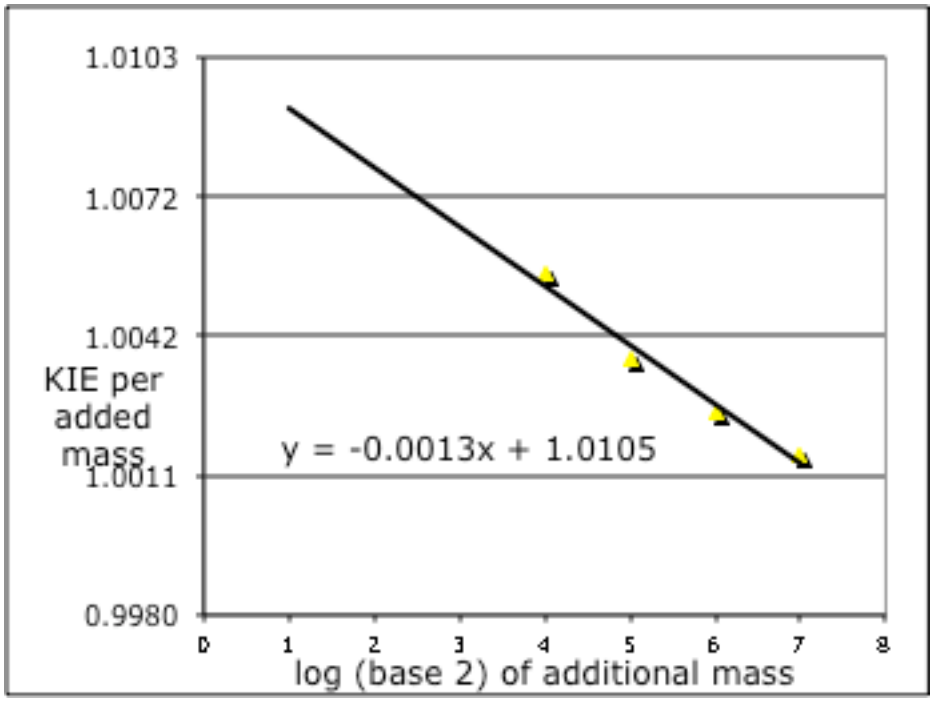
To calculate the uncertainties in the trajectory ratios, we set up an Excel spreadsheet that would repeatedly simulate the complete set of trajectory runs with each choice of superheavy carbon. In the simulations, the outcome each individual trajectory depended on a random number and on a weighting that corresponded to the ratio of outcomes actually observed in the set of trajectories. Because of the weighting, the average outcome of an infinite number of Excel simulations would be equal to the outcome observed in the trajectories. Each individual simulation, however, departs from the observed outcome in a way that reflects the role of random chance on the results in a set of trajectories. From the results of 204 simulations, standard deviations was calculated: mass-140: 0.018; mass 76 0.022; mass 44 0.025; mass 28 0.018. The 95% confidence ranges would be twice these standard deviations. (A common mistake in handling experimental data is to set the 95% confidence range to twice the standard deviation, but in this case, because of the nature of the simulation, it is actually correct.)

The main text notes that when the trajectories have an initial positive sign for the mode-3 velocity (defining positive as in Figure 2), then ≈98% of the product formed is **3'**, while when mode 3 is negative, ≈98% of the product formed is **3**. The actual percentages calculated for the eight individual cases (counting each mass and each mode-3 sign) in Table 1 are 97-99%, and the uncertainties on these percentages, calculated as above, are between 0.5% and 0.8%.

To extrapolate the isotope effect to ^{13}C, the procedure in reference 9 of the main text was employed. The extrapolation assumes that the additional isotope effect per additional mass unit decreases as the mass grows. For example, the effect of going from ^{13}C to ^{14}C would be larger than the effect of going from ^{140}C to ^{141}C. We further assumed that this decrease with mass is

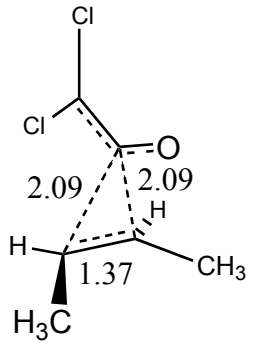
nonlinear with a decreasing slope, that is, that a plot of the additional isotope effect per additional mass versus mass would have a greater slope at low masses (e.g., ^{13}C to ^{14}C) than at high masses (e.g. ^{140}C to ^{141}C). These simple assumptions exclude some extrapolation processes that would lead to physically unreasonable isotope effects at both high masses and at ^{13}C.

The "isotope effect per mass" is defined as the geometric average isotope effect, i. e., as in the equation below where the "additional mass" is defined as the mass beyond 12 amu. The extrapolation was then carried out by assuming a linear relationship between the log of the additional mass (the base is arbitrary but set most conveniently as 2) versus the isotope effect per mass. The extrapolation process used the Regression tool in Microsoft Excel 2004 for Mac, Version 11.3.3. The reported confidence limit in the main text is based on that analysis and the fit of the points to the regression line. The graph associated with the extrapolation is shown below.

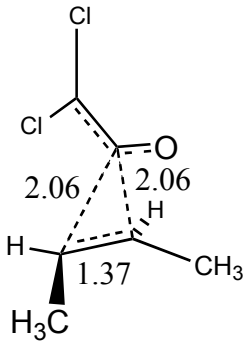


The Canonical Variational TS near 5‡. Geometry and Discussion

The figure below shows the geometry of the canonical variational TS near **5**‡ at the MPW1K/6-31+G** and MPW1K/6-31G* levels. These TS's are near each other (interestingly more so than are the potential energy saddle points). While they are displaced somewhat from the potential energy saddle point (as is typical for bimolecular reactions), they are still fairly closely associated with the saddle points. This can be understood because the potential energy saddle point is straddled by areas of higher entropy. Going backward, then entropy increases due to the dissociation into two components. Going forward, the entropy increases as the structure approaches a valley-ridge inflection point and one of the transverse frequencies approaches 0.



MPW1K/6-31+G**
first variational TS



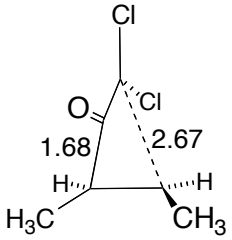
MPW1K/6-31+G**
first variational TS

These structures are geometrically far from the average turning points seen in the recrossing trajectories, where the average closest approach of the carbonyl carbon to the olefinic carbons was 1.69 Å.

It should be noted that a standard GAUSSRATE/POLYRATE calculation on these reactions cannot locate the later dynamical bottlenecks. This is because the MEP going forward from the potential energy saddle point remains symmetrical all the way to **6**‡. Only when the path is redefined as in the Lluch procedure (see the next section) can the asymmetric second variational TS / dynamical bottleneck be located.

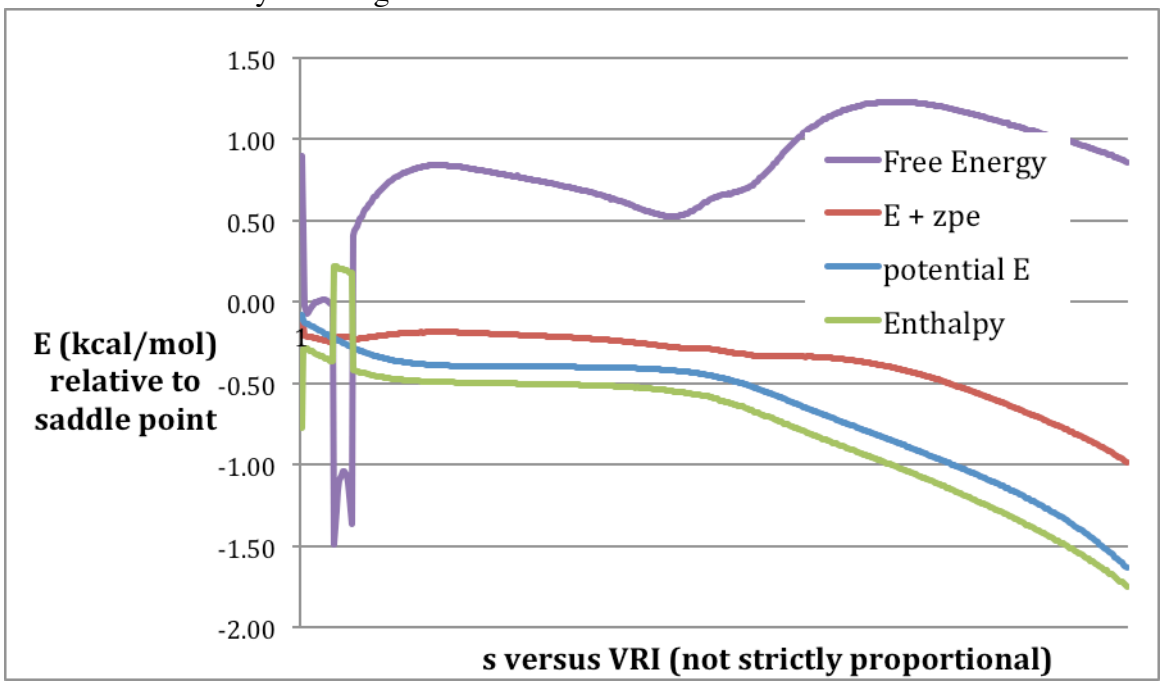
The Second Variational TS / Dynamical Bottleneck

In going forward from **5**‡ along the IRC, the path reaches a C_s-symmetric valley-ridge inflection point, defined by having a force constant of 0 in an orthogonal mode. To continue along two separate paths to the products **3** and **3'**, we followed the procedure of Lluch (reference 14 in the main text). For the ^{13}C-substituted molecule, we created the starting point for two paths by stepping away from the VRI along the orthogonal mode in each direction by 0.05 au. These points were then followed downward using the Page-McIver algorithm in POLYRATE, treating the starting points as the initial point in the path using the NOSADDLE algorithm in POLYRATE. After some distance, these paths encounter dynamical bottlenecks at positions that depend on the temperature (for the canonical variational TS, treating the energy distribution as a canonical Boltzmann distribution) or the energy (for the microcanonical RRKM procedure described in the main text). The canonical variational TSs for formation of **3** or **3'** at 25 °C were determined using POLYRATE, and they have the approximate geometry shown below. The energy-dependent bottlenecks for the variational RRKM procedure in the main text were roughly in the area of the structure below; more details will be provided in a later section.



The graph below shows the potential energy as one proceeds along the Lluch path after the VRI, along with the "raw" E+zpe, Enthalpy (298), and Free energy (298) that one gets from a Gaussian calculation. These raw numbers arise from harmonic frequencies in Cartesian coordinates without factoring out motion along the reaction coordinate. (As an aside, we do not

use these raw numbers for anything in the main text; rather we use the free energies and frequencies from Polyrate. However, Polyrate uses a strange vibrational partition function of 1 x 10^{10} for extra imaginary frequencies and it does not calculate enthalpy, making it less useful for the discussion here.) A problem is that there are too many imaginary frequencies (or bad near-zero frequencies) in the area of the VRI. As a result, the free energy takes wild jumps in this area and is not really meaningful.



Microcanonical Variational Prediction of the KIE

The two complete paths from **5**‡ to **3** and **3'** consist of two parts – a part passing through **5**‡ up to the area of the VRI, which was treated as being identical for the two paths, and the part after the step away from the VRI, which was different for the two paths due to the presence of a ^{13}C. The POLYRATE calculations provided frequency calculations at regular intervals (0.023813 Å amu$^{1/2}$) along each path, having factored out motion along the reaction coordinate and having calculated the frequencies at these non-stationary points in redundant curvilinear coordinates. The POLYRATE frequencies (with extra digits added due to the modifications described in a previous section) and the rotational constants from the saved frequency calculation files were used to construct input files for the RRKM program.

In a short area of the surface past the VRI, the points on the path have an extra imaginary frequency, i. e., one that is not associated with the reaction coordinate. Although POLYRATE makes estimates, the free-energy in these areas is not well defined, but it is largely sufficient for our purposes here to note that an area of the surface with an extra imaginary frequency should not have a dynamical bottleneck along the path. Accordingly, no RRKM rate constants were calculated for these points.

The RRKM rate constants were calculated at each point along the paths at a series of energies up to 18 kcal/mol above the threshold energy, in 0.1 kcal/mol increments. At each energy, three points were located: 1. the minimum rate constant in the area of **5**‡ (referred to below as k_1), 2. the minimum rate constant in the area of the second dynamical bottleneck (referred to below as k_2), and 3. the maximum rate constant in between the two areas (referred to

below as k_c). The calculated k_1, which is exactly the same for the two paths, was divided by 2 to allow for the division of trajectories passing **5**‡ between the two channels. The unified statistical rate constant (k_{US}) at each energy was then calculated from the equation: $(1/k_{US}) = 1/k_1 - 1/k_c + 1/k_2$. The k_2 passes below k_1 at 1.0 kcal/mol above the threshold energy, and at most energies the k_{US} was within 25% of the k_2 value.

Our inability to calculate realistic rate constants in the area of the surface past the VRI, as described above, could lead to an underestimation of k_c values. However, the predicted KIE is not very sensitive to the k_c values and it remains at 0.992 when all of the values are increased by a factor of 10.

Because of numerical noise in the calculated k_2 values and because of their non-continuous nature, the k_2 values at each point were calculated by least-squares fitting of the point and the surrounding 20 points (10 in each direction) to a quadratic function. The reported k_2 values and corresponding s values (see below) were for the minimum of the derived quadratic function.

The energy distribution in **5**‡ was calculated using the subprogram *proggenHP* of PROGDYN. In a repeated process, each normal mode in **5**‡ was given its zero-point energy plus a Boltzmann sampling of additional energy appropriate for 25 °C, and the transition vector was given a classical Boltzmann sampling of energy. The total energy was recorded, and the process was repeated 23,559 times. Using the histogram function in an Excel spreadsheet, the resulting energies were divided into bins separated by 0.1 kcal/mol.

The overall rate constant along each path was found by taking the count in each bin, multiplying by k_{US}, adding up the results, and dividing by 23,559. The KIE was then calculated from the ratio of the overall rate constants for the two paths.

A total k_1 rate constant was calculated by taking the count in each bin, multiplying by k_1, adding up the results, and dividing by 23,559. The recrossing percentage was calculated as $100 \times (1 - k_{US}/k_1)$ (using the total k_1 and k_{US} values instead of the energy-specific values).

The table below gives:

Ebin - the energy of the bins starting at the threshold energy. The energies were calculated versus a prereactive complex. The complex is not kinetically significant and its energetics cancel out in the calculations of isotope effects. Its choice as the formal starting material for RRKM calculations was solely to make the calculations convenient. An Ebin of 8.1 kcal/mol refers to energies between 8.05 and 8.15 kcal/mol.

count – the number of molecules out of 23,559 that have an energy in the bin

k_1 – the minimum rate constant in the area of **5**‡ at the Ebin energy in s^{-1}. k_1 is the same for both paths.

s1 - the distance along on the path corresponding to k_1, relative to **5**‡, in Å $amu^{1/2}$.

k_2-**3** - the minimum rate constant in the area of the second dynamical bottleneck along the path leading to product **3** (the major product, having the ^{13}C next to the carbonyl).

s2-**3** – a measure of the distance along the path corresponding to k_2-**3**. The 0 for these numbers is arbitrary, but each unit is equal to 0.023813 Å $amu^{1/2}$.

k_c-**3** - the maximum rate constant in between the two bottleneck areas along the path leading to product **3**

k_{US}-**3** – the unified statistical rate constant at that energy along the path leading to product **3**, calculated as described above

Ebin	count	s1	k_1	s2-**3**	k_2-**3**	k_c-**3**	k_{US}-**3**
8	0	--	0.00	36.95	0.0826	0.7045	0
8.1	1	0.143	0.06	36.67	0.4441	2.338	0.0566
8.2	2	0.143	0.23	38.10	0.7948	5.192	0.1864
8.3	5	0.191	0.53	38.60	1.4077	9.528	0.4012
8.4	9	0.238	1.02	38.78	2.2515	16.56	0.7338
8.5	12	0.238	1.81	38.86	3.8240	26.95	1.289
8.6	9	0.238	3.10	71.44	4.6811	39.98	1.9578
8.7	12	0.238	4.51	72.77	6.0656	57.04	2.7083
8.8	22	0.238	6.55	74.29	8.4506	78.94	3.8709
8.9	27	0.238	9.21	73.35	10.4754	106	5.1386
9	47	0.238	12.41	73.97	12.2528	139.5	6.4505
9.1	40	0.238	16.54	75.61	15.1093	180.1	8.257
9.2	51	0.238	21.53	76.65	18.3504	228.8	10.3551
9.3	76	0.286	27.44	76.76	21.8377	285.7	12.6997
9.4	77	0.286	34.56	77.17	25.4763	353.4	15.3004
9.5	94	0.286	42.99	77.98	29.7680	431.5	18.3353
9.6	103	0.286	52.60	78.15	34.3911	521.3	21.6589
9.7	111	0.286	63.85	78.63	39.7148	623.4	25.4861
9.8	124	0.286	76.70	78.95	45.4784	739.4	29.6966
9.9	141	0.286	91.20	79.90	51.4920	870.2	34.2041
10	128	0.286	107.85	80.33	58.2072	1017	39.2636
10.1	169	0.286	126.50	80.70	65.5521	1180	44.8175
10.2	170	0.286	147.15	81.31	73.4593	1361	50.8284
10.3	208	0.286	170.50	81.54	81.8091	1562	57.3116
10.4	221	0.286	196.10	81.95	90.5689	1782	64.1866
10.5	201	0.286	224.35	82.58	100.2562	2023	71.7491
10.6	211	0.286	255.50	82.96	110.4411	2286	79.8018
10.7	254	0.286	289.50	83.47	121.2954	2571	88.4204
10.8	293	0.286	326.55	83.75	132.6864	2881	97.544
10.9	263	0.286	366.90	84.40	144.7484	3216	107.2601
11	284	0.286	410.50	84.79	157.3762	3576	117.5003
11.1	280	0.286	457.55	85.25	170.8226	3963	128.4151
11.2	297	0.286	508.50	85.55	184.8795	4378	139.9173
11.3	322	0.286	563.00	85.85	199.5456	4821	151.972
11.4	310	0.286	621.00	86.35	215.0659	5294	164.7134
11.5	345	0.286	683.50	86.73	231.0400	5797	177.9737
11.6	370	0.286	750.00	87.14	247.7975	6331	191.9042
11.7	374	0.333	820.50	87.44	265.2180	6897	206.4298
11.8	424	0.333	895.50	87.72	283.2987	7495	221.5764
11.9	386	0.333	974.50	88.33	302.3433	8128	237.4939
12	371	0.333	1058.50	88.68	321.7724	8794	253.884
12.1	367	0.333	1147.00	89.00	341.9725	9496	270.9481
12.2	422	0.333	1240.50	89.43	363.0067	10230	288.7549
12.3	431	0.333	1339.00	89.76	384.6075	11010	307.1204

12.4	421	0.333	1442.50	90.06	406.9683	11820	326.1757
12.5	435	0.333	1551.00	90.37	429.9620	12670	345.8286
12.6	382	0.333	1664.50	90.65	453.6826	13550	366.1442
12.7	419	0.333	1784.00	90.95	478.1732	14480	387.1813
12.8	380	0.333	1908.50	91.23	503.5276	15450	408.9586
12.9	401	0.333	2038.50	91.51	529.4057	16450	431.2804
13	452	0.333	2174.00	91.79	555.9918	17500	454.251
13.1	366	0.333	2315.50	92.37	583.3671	18590	477.9507
13.2	400	0.333	2463.00	92.66	611.4113	19720	502.2957
13.3	379	0.333	2616.00	92.92	640.1487	20890	527.2787
13.4	387	0.333	2775.00	93.75	669.9270	22110	553.1488
13.5	388	0.333	2940.00	94.05	700.0433	23370	579.4316
13.6	381	0.333	3111.50	94.34	730.8651	24670	606.3932
13.7	401	0.333	3289.00	94.63	762.4160	26020	634.0223
13.8	348	0.333	3472.50	94.91	794.6596	27410	662.298
13.9	374	0.333	3662.50	95.45	827.6976	28850	691.3018
14	347	0.333	3859.50	95.73	861.3375	30340	720.915
14.1	328	0.333	4062.50	96.00	895.6581	31870	751.1602
14.2	375	0.333	4272.00	96.27	930.6869	33450	782.0673
14.3	322	0.333	4488.00	96.53	966.3645	35070	813.598
14.4	304	0.333	4711.00	96.78	1002.6461	36740	845.7291
14.5	329	0.333	4941.00	97.42	1040.2409	38460	878.9641
14.6	322	0.333	5175.00	97.56	1077.8597	40230	912.2888
14.7	305	0.333	5420.00	97.95	1116.5592	42050	946.6745
14.8	277	0.333	5670.00	98.34	1155.8330	43910	981.5759
14.9	304	0.333	5930.00	98.55	1195.4444	45830	1016.9595
15	282	0.333	6195.00	98.87	1236.0679	47790	1053.1719
15.1	244	0.333	6465.00	99.22	1278.2421	49800	1090.6039
15.2	267	0.333	6745.00	99.58	1319.9752	51870	1127.9438
15.3	241	0.333	7030.00	99.91	1362.4845	53980	1165.9422
15.4	229	0.333	7320.00	100.15	1405.7416	56140	1204.5759
15.5	242	0.333	7620.00	100.50	1449.5646	58360	1243.8416
15.6	244	0.333	7930.00	100.75	1493.9125	60630	1283.7083
15.7	208	0.333	8245.00	101.22	1538.8823	62940	1324.1179
15.8	208	0.333	8565.00	101.52	1584.6583	65310	1365.1998
15.9	200	0.333	8895.00	101.83	1630.9179	67730	1406.846
16	182	0.333	9235.00	102.19	1678.2831	70200	1449.5154
16.1	195	0.333	9580.00	102.48	1725.7431	72730	1492.3253
16.2	180	0.333	9930.00	102.81	1773.8749	75300	1535.7154
16.3	172	0.333	10290.00	103.05	1822.7561	77930	1579.8551
16.4	139	0.333	10660.00	103.34	1872.3077	80610	1624.6862
16.5	152	0.333	11035.00	103.56	1922.1743	83350	1669.8189
16.6	146	0.333	11420.00	103.89	1973.0308	86130	1715.8846
16.7	131	0.333	11810.00	104.16	2024.2218	88970	1762.2659
16.8	130	0.333	12205.00	104.42	2076.0031	91870	1809.1573
16.9	124	0.333	12615.00	104.68	2128.3555	94810	1856.7702

17	127	0.333	13025.00	104.92	2181.5236	97810	1904.9551
17.1	114	0.333	13450.00	105.14	2234.8499	100900	1953.5219
17.2	113	0.333	13880.00	105.38	2289.0471	104000	2002.829
17.3	80	0.333	14315.00	105.66	2344.0195	107100	2052.8092
17.4	95	0.333	14760.00	105.91	2399.2353	110300	2103.1203
17.5	110	0.333	15215.00	106.61	2455.1077	113600	2154.0773
17.6	90	0.333	15675.00	106.81	2511.5391	116900	2205.5397
17.7	83	0.333	16145.00	107.50	2568.7387	120300	2257.7326
17.8	66	0.333	16620.00	107.81	2626.3621	123700	2310.3267
17.9	74	0.333	17105.00	108.78	2684.3837	127200	2363.3634
18	66	0.333	17600.00	109.05	2742.7697	130800	2416.814
18.1	60	0.333	18100.00	109.56	2801.8092	134300	2470.8755
18.2	71	0.333	18610.00	109.87	2861.1477	138000	2525.2636
18.3	67	0.333	19125.00	110.17	2921.0199	141700	2580.1352
18.4	49	0.333	19650.00	110.10	2980.7123	145400	2635.0233
18.5	53	0.333	20185.00	110.36	3041.8956	149200	2691.1981
18.6	40	0.333	20725.00	110.59	3103.5344	153100	2747.7623
18.7	54	0.333	21275.00	111.13	3164.7244	157000	2804.1258
18.8	47	0.333	21830.00	111.35	3226.8902	161000	2861.2858
18.9	37	0.333	22395.00	111.58	3290.1426	165000	2919.4488
19	31	0.333	22970.00	111.78	3353.6444	169100	2977.9235
19.1	44	0.333	23550.00	112.04	3417.3402	173200	3036.6117
19.2	36	0.333	24140.00	112.25	3481.7078	177400	3095.9425
19.3	40	0.333	24735.00	112.48	3546.7491	181700	3155.8355
19.4	36	0.333	25340.00	112.67	3612.0089	185900	3216.072
19.5	23	0.333	25955.00	112.87	3678.0132	190300	3276.9772
19.6	28	0.333	26575.00	113.10	3744.3019	194700	3338.1656
19.7	23	0.333	27205.00	113.30	3811.2114	199200	3399.9539
19.8	23	0.333	27845.00	113.47	3878.4707	203700	3462.1544
19.9	16	0.333	28490.00	113.68	3946.1849	208200	3524.7722
20	20	0.333	29145.00	113.89	4014.3313	212800	3587.8372
20.1	18	0.333	29805.00	114.08	4082.9700	217500	3651.3212
20.2	13	0.333	30475.00	114.26	4152.2344	222200	3715.4346
20.3	16	0.333	31155.00	114.44	4221.7502	227000	3779.8484
20.4	12	0.333	31840.00	114.65	4291.9114	231900	3844.8044
20.5	15	0.333	32535.00	114.83	4362.0499	236700	3909.8943
20.6	15	0.333	33235.00	115.42	4433.0102	241700	3975.6412
20.7	9	0.333	33945.00	115.57	4504.2294	246700	4041.7191
20.8	11	0.333	34665.00	115.75	4575.8894	251700	4108.2725
20.9	11	0.333	35390.00	115.94	4647.9349	256800	4175.1596
21	10	0.333	36125.00	116.12	4720.5350	262000	4242.5867
21.1	7	0.333	36865.00	116.29	4793.2223	267200	4310.1329
21.2	6	0.333	37615.00	116.46	4866.6418	272400	4378.3878
21.3	3	0.333	38375.00	116.64	4940.3481	277700	4446.9642
21.4	7	0.333	39140.00	117.58	5014.4268	283100	4515.8638
21.5	7	0.333	39915.00	117.74	5088.7722	288500	4585.0928

21.6	4	0.333	40695.00	117.92	5163.3571	294000	4654.5372
21.7	8	0.333	41485.00	118.10	5238.4798	299500	4724.5298
21.8	1	0.333	42285.00	118.27	5314.1096	305100	4795.0198
21.9	5	0.333	43090.00	118.41	5389.9527	310700	4865.7282
22	5	0.333	43900.00	118.59	5466.2704	316400	4936.8435
22.1	9	0.333	44725.00	118.73	5542.7173	322100	5008.2346
22.2	4	0.333	45550.00	118.92	5619.7578	327900	5080.067
22.3	5	0.333	46390.00	119.05	5697.1842	333700	5152.3824
22.4	0	0.333	47235.00	119.22	5774.8126	339600	5224.8817
22.5	6	0.333	48085.00	119.36	5852.8846	345500	5297.7867
22.6	0	0.333	48950.00	119.52	5931.3636	351500	5371.1648
22.7	5	0.333	49815.00	119.67	6010.2459	357600	5444.8319
22.8	1	0.333	50700.00	119.82	6089.5473	363700	5519.0633
22.9	2	0.333	51600.00	119.96	6169.1627	369800	5593.7099
23	5	0.333	52450.00	120.13	6248.7098	376000	5667.6735
23.1	0	0.333	53350.00	120.26	6328.8210	382200	5742.6701
23.2	1	0.333	54250.00	120.42	6409.5770	388500	5818.1577
23.3	2	0.333	55200.00	120.56	6490.4932	394900	5894.3097
23.4	0	0.333	56100.00	120.70	6571.5810	401300	5970.014
23.5	0	0.333	57050.00	120.86	6653.1384	407700	6046.6546
23.6	3	0.333	58000.00	120.98	6734.9267	414200	6123.4437
23.7	0	0.333	58900.00	122.30	6818.4882	420700	6201.1268
23.8	0	0.333	59900.00	122.21	6900.8935	427300	6278.9229
23.9	2	0.333	60850.00	122.69	6983.4289	434000	6356.2351
24	1	0.333	61800.00	122.83	7066.2282	440700	6433.7509
24.1	2	0.333	62800.00	122.73	7149.6569	447400	6512.3126
24.2	1	0.333	63750.00	122.91	7233.3442	454200	6590.5137
24.3	0	0.333	64750.00	123.08	7316.9282	461000	6669.1479
24.4	0	0.333	65750.00	123.23	7401.1014	467900	6748.2329
24.5	1	0.333	66750.00	123.40	7485.6179	474800	6827.587
24.6	0	0.333	67750.00	123.59	7570.2008	481800	6906.9603
24.7	1	0.333	68800.00	123.75	7655.2297	488800	6987.2066
24.8	0	0.333	69800.00	123.92	7740.3623	495900	7066.9865
24.9	0	0.333	70850.00	124.09	7825.9739	503100	7147.6424
25	0	0.333	71900.00	124.24	7911.6216	510200	7228.3307
25.1	0	0.333	72950.00	124.40	7997.8532	517500	7309.4497
25.2	0	0.333	74000.00	124.58	8084.2752	524700	7390.7323
25.3	0	0.333	75050.00	124.73	8170.7985	532000	7472.0651
25.4	0	0.333	76150.00	124.90	8257.6793	539400	7554.1559
25.5	0	0.333	77200.00	125.99	8347.5614	546800	7638.2517
25.6	0	0.333	78300.00	124.36	8436.1049	554300	7721.6837
25.7	0	0.333	79400.00	124.61	8523.6874	561800	7804.2944
25.8	1	0.333	80500.00	125.08	8610.6263	569300	7886.349
25.9	1	0.333	163200.00	125.28	8698.8400	576900	8378.5844

The table below gives:

Ebin - the energy of the bins starting at the threshold energy. The energies were calculated versus a prereactive complex. The complex is not kinetically significant and its energetics cancel out in the calculations of isotope effects. Its choice as the formal starting material for RRKM calculations was solely to make the calculations convenient. An Ebin of 8.1 kcal/mol refers to energies between 8.05 and 8.15 kcal/mol.

k_2-**3'** - the minimum rate constant in the area of the second dynamical bottleneck along the path leading to product **3'** (the minor product, having the ^{13}C distal to the carbonyl).

s2-**3'** – a measure of the distance along the path corresponding to k_2-**3'**. The 0 for these numbers is arbitrary, but each unit is equal to 0.023813 Å amu$^{1/2}$.

k_c-**3'** - the maximum rate constant in between the two bottleneck areas along the path leading to product **3'**

k_{US}-**3'** – the unified statistical rate constant at that energy along the path leading to product **3'**, calculated as described above

KIE-E – The isotope effect at that energy, from the ratio of k_{US}-**3'** and k_{US}-**3**.

Ebin	s2-**3'**	k_2-**3'**	k_c-**3'**	k_{US}-**3'**	KIE-E
8	37.64	0.0832	1.285	0	
8.1	37.82	0.4392	3.077	0.0562	0.9929
8.2	38.81	0.7785	5.747	0.1848	0.9914
8.3	39.28	1.388	9.82	0.3991	0.9948
8.4	39.35	2.2047	16.42	0.7291	0.9936
8.5	39.50	3.779	26.79	1.2842	0.9963
8.6	71.94	4.6357	39.75	1.9504	0.9962
8.7	73.19	5.9946	56.81	2.6946	0.9949
8.8	74.33	8.3406	78.63	3.8484	0.9942
8.9	73.89	10.41	105.6	5.1238	0.9971
9	74.33	12.1426	139	6.4209	0.9954
9.1	75.86	14.9395	179.5	8.2073	0.9940
9.2	77.22	18.1754	228.1	10.3006	0.9947
9.3	77.29	21.6772	285	12.6466	0.9958
9.4	77.57	25.2432	352.6	15.2175	0.9946
9.5	78.41	29.4964	430.6	18.2335	0.9944
9.6	78.75	34.0601	520.4	21.5287	0.9940
9.7	79.34	39.4005	622.5	25.3577	0.9950
9.8	79.67	45.1112	738.5	29.5411	0.9948
9.9	80.44	51.034	869.2	34.003	0.9941
10	80.64	57.5939	1016	38.9851	0.9929
10.1	80.99	64.8852	1179	44.5061	0.9931
10.2	81.59	72.7374	1361	50.4818	0.9932
10.3	81.83	81.0185	1561	56.9238	0.9932
10.4	82.39	89.704	1781	63.7522	0.9932
10.5	82.72	99.2447	2022	71.2308	0.9928
10.6	83.35	109.483	2285	79.3015	0.9937
10.7	83.62	120.1483	2571	87.8092	0.9931

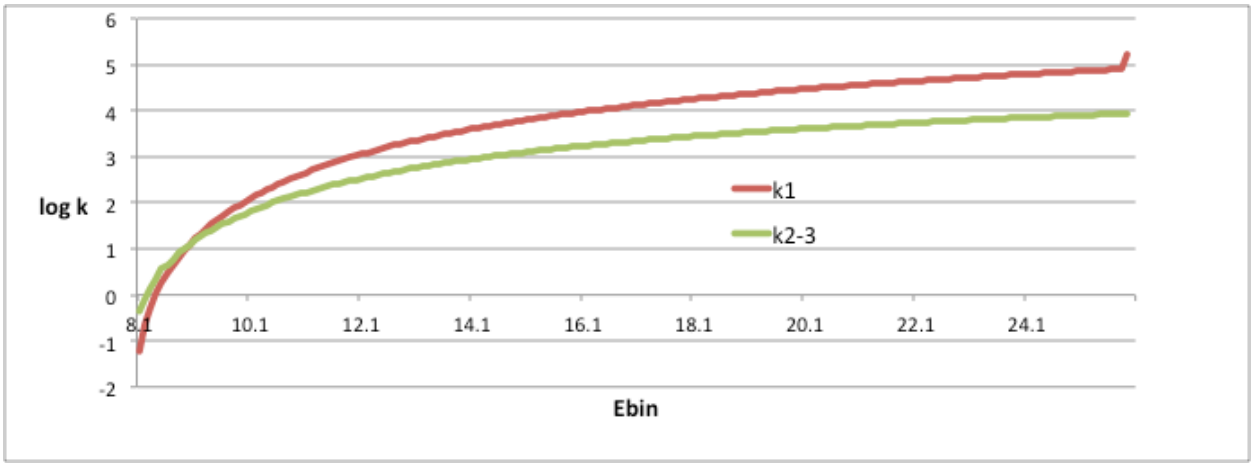
10.8	83.88	131.379	2881	96.8356	0.9927
10.9	84.39	143.3843	3216	106.5092	0.9930
11	84.75	155.9243	3577	116.6881	0.9931
11.1	85.21	169.2155	3965	127.5027	0.9929
11.2	85.46	183.0904	4380	138.8881	0.9926
11.3	85.73	197.6864	4824	150.8883	0.9929
11.4	86.31	212.994	5297	163.4925	0.9926
11.5	86.60	228.874	5801	176.6819	0.9927
11.6	86.86	245.4763	6336	190.5046	0.9927
11.7	87.39	262.97	6903	205.0601	0.9934
11.8	87.68	280.8918	7503	220.0944	0.9933
11.9	87.94	299.5057	8137	235.7319	0.9926
12	88.55	319.0192	8804	252.1587	0.9932
12.1	88.84	339.0975	9507	269.1313	0.9933
12.2	89.31	360.0783	10250	286.8832	0.9935
12.3	89.61	381.5009	11020	305.1285	0.9935
12.4	89.90	403.6925	11830	324.0606	0.9935
12.5	90.64	426.7786	12690	343.7515	0.9940
12.6	90.96	450.3719	13580	363.9632	0.9940
12.7	91.27	474.6777	14500	384.8722	0.9940
12.8	91.57	499.6355	15470	406.3737	0.9937
12.9	91.85	525.3309	16480	428.552	0.9937
13	92.27	551.947	17530	451.5274	0.9940
13.1	92.57	579.0749	18620	475.0461	0.9939
13.2	92.86	606.9181	19760	499.2336	0.9939
13.3	93.13	635.4383	20930	524.0537	0.9939
13.4	93.40	664.6776	22150	549.5404	0.9935
13.5	93.66	694.6432	23420	575.6968	0.9936
13.6	93.91	725.3235	24720	602.5438	0.9937
13.7	94.47	757.0487	26080	630.271	0.9941
13.8	94.74	789.1141	27470	658.407	0.9941
13.9	95.00	821.8723	28920	687.1938	0.9941
14	95.71	855.9859	30410	717.1232	0.9947
14.1	96.61	890.5272	31940	747.5096	0.9951
14.2	96.98	925.3282	33520	778.2421	0.9951
14.3	97.63	960.9162	35150	809.6901	0.9952
14.4	97.96	996.9879	36830	841.6527	0.9952
14.5	98.61	1033.6957	38560	874.2349	0.9946
14.6	99.02	1071.6672	40330	907.7979	0.9951
14.7	99.36	1109.7925	42150	941.7558	0.9948
14.8	99.72	1148.2845	44020	976.0723	0.9944
14.9	100.16	1187.867	45940	1011.4172	0.9946
15	100.54	1227.8932	47910	1047.174	0.9943
15.1	100.91	1268.673	49930	1083.569	0.9935
15.2	101.29	1310.1946	52000	1120.7338	0.9936
15.3	102.11	1352.1161	54120	1158.2768	0.9934

15.4	102.15	1394.449	56300	1196.2021	0.9930
15.5	102.58	1437.8361	58520	1235.1245	0.9930
15.6	102.92	1481.489	60790	1274.4538	0.9928
15.7	103.23	1526.1136	63120	1314.5752	0.9928
15.8	104.01	1570.7469	65490	1354.785	0.9924
15.9	104.33	1616.3164	67920	1395.8872	0.9922
16	104.68	1662.5444	70400	1437.6763	0.9918
16.1	105.04	1709.3801	72940	1479.987	0.9917
16.2	106.15	1756.3339	75520	1522.4611	0.9914
16.3	106.36	1804.1501	78160	1565.7659	0.9911
16.4	106.61	1852.7943	80850	1609.8772	0.9909
16.5	107.00	1901.9108	83590	1654.4113	0.9908
16.6	107.19	1951.5934	86390	1699.547	0.9905
16.7	107.41	2001.764	89240	1745.1165	0.9903
16.8	107.63	2052.6922	92140	1791.326	0.9901
16.9	107.81	2104.118	95100	1838.1881	0.9900
17	108.01	2156.1853	98110	1885.4946	0.9898
17.1	108.20	2208.5771	101200	1933.3077	0.9897
17.2	108.42	2261.754	104300	1981.7948	0.9895
17.3	108.59	2315.5804	107500	2030.8212	0.9893
17.4	108.78	2369.8771	110700	2080.3858	0.9892
17.5	108.96	2424.5698	114000	2130.3929	0.9890
17.6	109.13	2479.9958	117300	2181.0385	0.9889
17.7	109.31	2536.1055	120700	2232.347	0.9888
17.8	109.48	2592.6888	124100	2284.0937	0.9886
17.9	109.66	2649.6686	127600	2336.2786	0.9885
18	109.84	2707.2952	131200	2389.0947	0.9885
18.1	110.01	2765.3305	134800	2442.2967	0.9884
18.2	110.17	2824.1153	138400	2496.2412	0.9885
18.3	110.35	2883.3737	142200	2550.5572	0.9885
18.4	110.49	2942.7224	145900	2605.1303	0.9887
18.5	110.65	3003.1045	149700	2660.6326	0.9886
18.6	110.81	3063.7321	153600	2716.3595	0.9886
18.7	110.97	3125.0708	157600	2772.763	0.9888
18.8	111.35	3187.034	161500	2829.7514	0.9890
18.9	111.48	3249.133	165600	2886.9311	0.9889
19	111.65	3311.815	169700	2944.7143	0.9888
19.1	111.80	3375.2163	173800	3003.1255	0.9890
19.2	111.94	3438.8552	178000	3061.8353	0.9890
19.3	112.09	3503.2186	182300	3121.1487	0.9890
19.4	112.24	3567.9055	186600	3180.8566	0.9891
19.5	112.37	3633.0031	191000	3240.9974	0.9890
19.6	112.54	3698.6182	195400	3301.6061	0.9890
19.7	112.66	3764.7967	199900	3362.7684	0.9891
19.8	112.82	3831.4426	204400	3424.4345	0.9891
19.9	112.93	3898.6157	209000	3486.5479	0.9892

20	113.07	3966.0117	213600	3548.9683	0.9892
20.1	113.22	4034.1787	218300	3612.0317	0.9892
20.2	113.34	4102.5532	223000	3675.3879	0.9892
20.3	113.46	4171.3472	227800	3739.1779	0.9892
20.4	113.61	4240.8031	232700	3803.5244	0.9893
20.5	113.73	4310.6059	237600	3868.2726	0.9894
20.6	113.84	4380.992	242600	3933.5149	0.9894
20.7	113.99	4451.7881	247600	3999.2084	0.9895
20.8	114.13	4524.1128	252600	4066.2551	0.9898
20.9	114.27	4595.9436	257800	4132.9014	0.9899
21	114.41	4667.7019	262900	4199.6316	0.9899
21.1	114.54	4740.4931	268200	4267.1954	0.9900
21.2	114.66	4813.1928	273400	4334.8255	0.9901
21.3	114.79	4886.3742	278800	4402.9093	0.9901
21.4	114.91	4960.2469	284200	4471.6014	0.9902
21.5	115.06	5034.9975	289600	4541.1192	0.9904
21.6	115.18	5109.4417	295100	4610.4097	0.9905
21.7	115.30	5184.6381	300600	4680.4228	0.9907
21.8	115.42	5259.9798	306200	4750.6388	0.9907
21.9	115.53	5335.6735	311900	4821.1626	0.9908
22	115.67	5411.8242	317600	4892.1045	0.9909
22.1	115.78	5488.4045	323300	4963.5657	0.9911
22.2	115.89	5565.4402	329200	5035.3346	0.9912
22.3	116.90	5642.9427	335000	5107.6749	0.9913
22.4	117.04	5720.3656	340900	5179.9695	0.9914
22.5	117.19	5798.3539	346900	5252.7472	0.9915
22.6	117.32	5876.5554	352900	5325.8613	0.9916
22.7	117.45	5955.1609	359000	5399.2667	0.9916
22.8	117.59	6034.1613	365100	5473.214	0.9917
22.9	117.73	6113.5492	371200	5547.6353	0.9918
23	117.84	6193.2757	377500	5621.6975	0.9919
23.1	118.00	6273.3959	383700	5696.6671	0.9920
23.2	118.52	6354.3649	390100	5772.2765	0.9921
23.3	118.67	6435.0011	396400	5848.1801	0.9922
23.4	118.80	6516.0928	402800	5923.8586	0.9923
23.5	118.95	6597.5062	409300	6000.3225	0.9923
23.6	118.91	6679.5815	415800	6077.3148	0.9925
23.7	119.07	6761.7752	422400	6153.8211	0.9924
23.8	119.18	6843.9954	429000	6231.4237	0.9924
23.9	119.31	6926.8366	435700	6308.9595	0.9926
24	119.46	7009.8227	442400	6386.6017	0.9927
24.1	119.59	7093.0975	449200	6464.98	0.9927
24.2	119.71	7176.9051	456000	6543.2557	0.9928
24.3	119.85	7260.9776	462900	6622.2436	0.9930
24.4	119.98	7345.1784	469800	6701.3218	0.9930
24.5	119.87	7431.4381	476800	6782.0789	0.9933

24.6	120.02	7516.3424	483800	6861.6938	0.9934
24.7	120.15	7601.6112	490800	6942.1086	0.9935
24.8	120.27	7687.2465	498000	7022.2645	0.9937
24.9	120.39	7772.8929	505100	7102.9412	0.9937
25	120.53	7859.1588	512300	7184.0987	0.9939
25.1	120.66	7945.5483	519600	7265.3245	0.9940
25.2	120.79	8032.5047	526900	7347.0101	0.9941
25.3	120.89	8119.3555	534200	7428.5939	0.9942
25.4	121.32	8208.4225	541600	7512.4886	0.9945
25.5	121.46	8296.0144	549100	7594.6282	0.9943
25.6	121.59	8383.6612	556600	7677.2839	0.9942
25.7	121.72	8471.7726	564100	7760.3134	0.9944
25.8	121.87	8560.2576	571700	7843.6229	0.9946
25.9	122.00	8648.8424	579300	8331.692	0.9944

The graph below shows a plot of log k_1 and log k_2-**3** versus Ebin. The graph shows how at low energies k_1 is dominant (lower) while at high energies k_2-**3** is dominant (lower). In crude thermodynamic parlance, the change may be understood as resulting from a dominance of "enthalpy" at low energies and "entropy" at high energies. On this log scale, a plot of k_2-**3'** appears identical to that of k_2-**3**.



On the Nature of 6‡, and Trajectory Studies

Structure **6**‡ is a potential energy saddle point, and the IRC passing through **6**‡ leads from **3** to **3'**. The normal interpretation of this would be that **6**‡ is the transition structure for a concerted isomerization of **3** to **3'**. This is misleading. Because the dynamical bottlenecks between **6**‡ and **3** or **3'** (for a qualitative picture, see Figure 1 in the main text) are much tighter at 298 than the bottleneck for dissociation into **1** + **2**, trajectories that pass into through the hypersurface perpendicular to the IRC through **6**‡ would statistically not be expected to pass on to **3** or **3'**.

This idea was supported by trajectory studies. A series of trajectories were started statistically in the area of **6**‡ on the MPW1K/6-31G* surface. Each normal mode in **6**‡ was given

its zero-point energy (ZPE) plus a Boltzmann sampling of additional energy appropriate for 25 °C, with a random phase and sign for its initial velocity. The transition vector was given a Boltzmann sampling of energy in a random direction from the col, and the trajectories were integrated both forward and backward in time until the products **3** / **3'** were formed, separate starting materials **1** + **2** were formed, or a 500 fs time limit was reached. The results were as follows:

trajectories passing between **3** and **3'**:	14
trajectories passing between **3** or **3'** and **1** + **2**:	86
trajectories passing between **1** + **2** and **1** + **2**:	206
trajectories reaching the time limit:	4
trajectories starting at **3** and finishing at **3**:	0
trajectories starting at **3'** and finishing at **3'**:	0

The "normal interpretation" described above would have assumed that all of the trajectories started from **6**‡ pass between **3** and **3'**. Instead, only 5% do. Two-thirds of the trajectories passing through the area of **6**‡ are not reactive trajectories and have nothing to do with **3** / **3'**. A smaller portion of trajectories passing through the area of **6**‡ are doing a different reaction, passing from **1** + **2** to **3** / **3'**.

Overall, while **6**‡ is the potential energy saddle point on IRC passing from **3** to **3'**, at 25 °C **6**‡ is irrelevant as a transition state.

The trajectory results with **6**‡ fit with statistical expectations. If we assume that the outcome of the trajectories would be canonical-statistically governed by the dynamical bottlenecks governing either formation of **3** and **3'** or passage through **5**‡, then the energy difference of 1.2 kcal/mol between the pathways would lead to 21% formation of **3** or **3'** (allowing for the factor of 2 for the two pathways) and 79% formation of **1** + **2**. The trajectories predict 19% formation of **3** or **3'** [(28 + 86)/(28 + 86 + 86 + 412)]. In the main text it was noted that the amount of recrossing observed in the trajectories started from **5**‡ was much less than statistical expectations. The agreement of statistical and trajectory results with **6**‡ suggests that the disagreement with **5**‡ is not simply the result of inaccuracy in the trajectories.

It should perhaps be noted that the situation with **6**‡ is quite different from that observed in the reaction of diphenylketene with cyclopentadiene (reference 6a in the main text). In that case, trajectories started statistically from the area of the transition structure isomerizing the products did in fact pass between the two products. The distinction is important because in reference 6a the recrossing was described as "non-statistical", while the results in the current case could be described (with some reservations as suggested in the main text) as statistical. The differing results of trajectories started from the rearrangement transition structures in the two cases support the different descriptions.

Microcanonical Variational RRKM Study of the Reaction of 7

In the main text, a canonical variational TS model was used to locate a variational TS near **8**‡ and a second variational TS **9**‡. This model assumed that the energy distribution at each point along the IRC is canonical for 25 °C. This assumption is surely inexact, because the time scale for the reaction coordinate is not sufficient to allow energy equilibration with solution. To allow for a non-canonical distribution of energy in the area past **8**‡, we employed the microcanonical variational RRKM model that we had used to calculate the isotope effects for the

reaction of **1** with **2**. The key assumptions in our model are that the total molecular energy is conserved over the time course of the reaction coordinate past the initial TS **8**‡, and that the energy is statistically distributed. For each energy slice out of a canonical energy distribution for 25 °C in **8**‡, the RRKM rate constant was calculated at each point along the path leading to the cycloadduct product. At each energy, two RRKM TSs (one near **8**‡, the other near **9**‡) were defined by points at which the RRKM rate constant was a minimum.

Based on the rate constants at these TSs, 92% of the energy distribution passing through **8**‡ faces its tightest bottleneck (lowest k) at the second TS in the area of **9**‡. This supports the idea that the second TS is mainly rate-limiting in this reaction.

Calculated Structures and Energies

Transition Structures for the reaction of 1 with 2.

These are listed by method and basis set. When the surface involves two saddle points, these are described as "First saddle point" and "Second saddle point", and the intermediate in between is labeled as "intermediate".

HF/3-21G

E(RHF) = -1219.46491561

Zero-point correction= 0.134983 (Hartree/Particle)
Thermal correction to Energy= 0.144478
Thermal correction to Enthalpy= 0.145422
Thermal correction to Gibbs Free Energy= 0.100127
Sum of electronic and ZPE= -1219.329933
Sum of electronic and thermal Energies= -1219.320438
Sum of electronic and thermal Enthalpies= -1219.319493
Sum of electronic and thermal Free Energies= -1219.364789

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	90.661	33.866	95.332

C,0,1.114422697,0.8480132725,-0.4777908159
C,0,2.1250896529,1.5987056039,0.3756541851
H,0,2.7199206826,0.9781736657,1.0179524174
C,0,1.7896442668,2.8725927478,0.9225796818
C,0,3.1479786743,2.4694242106,-0.663033419
O,0,2.7254325074,2.682020573,-1.7958196838
C,0,4.2127977297,2.9837522363,0.0155397703
Cl,0,5.4498355737,3.9016364238,-0.9077421381
Cl,0,4.8267429185,2.4071637258,1.6192606426
C,0,0.7738072676,3.7456829226,0.2804733624
H,0,2.2976757022,3.2106030307,1.8019053746
H,0,0.7603544521,4.7366975081,0.7070011566
H,0,0.9961306784,3.7975300062,-0.7842653225
H,0,-0.2097554809,3.2931596619,0.3832811699
H,0,0.8235572111,1.4357271594,-1.3333592307
H,0,1.5666182929,-0.0649764017,-0.8424119335
H,0,0.2420011738,0.5846356535,0.1097807829

HF/6-31+G**

E(RHF) = -1225.57421853

Zero-point correction= 0.134332 (Hartree/Particle)
Thermal correction to Energy= 0.143933
Thermal correction to Enthalpy= 0.144877
Thermal correction to Gibbs Free Energy= 0.099283
Sum of electronic and ZPE= -1225.439887
Sum of electronic and thermal Energies= -1225.430286
Sum of electronic and thermal Enthalpies= -1225.429342
Sum of electronic and thermal Free Energies= -1225.474935

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	90.319	33.979	95.960

C,0,1.1475514087,0.8155940104,-0.5042789061
C,0,2.091167291,1.6166295812,0.3700926397
H,0,2.6728425021,1.0164574056,1.0484148678
C,0,1.7647163572,2.896074932,0.8643082078
C,0,3.1489179038,2.5156056869,-0.6025643875
O,0,2.759639288,2.7268858913,-1.7356076394
C,0,4.2917250341,2.9270011461,0.0333679188
Cl,0,5.5199943376,3.6956952658,-0.8966589851
Cl,0,4.8043225338,2.4535181766,1.6219625702
C,0,0.7330279018,3.7879580555,0.2698951548
H,0,2.2781963641,3.237800894,1.7426438464
H,0,0.8140555336,4.7950548734,0.6541734757
H,0,0.8267038978,3.7940971658,-0.8102725023
H,0,-0.2499779791,3.3923462884,0.5201738544
H,0,0.6555873634,1.4284016529,-1.2430544765
H,0,1.7012198794,0.046427298,-1.0271058731
H,0,0.4025643828,0.3349936763,0.1235162346

HF/6-31+G pcm(THF)**

E(RHF) = -1225.58910344

Zero-point correction= 0.133870 (Hartree/Particle)
Thermal correction to Energy= 0.143900
Thermal correction to Enthalpy= 0.144845
Thermal correction to Gibbs Free Energy= 0.097967
Sum of electronic and ZPE= -1225.455234
Sum of electronic and thermal Energies= -1225.445203
Sum of electronic and thermal Enthalpies= -1225.444259
Sum of electronic and thermal Free Energies= -1225.491137

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	90.299	34.540	98.663

C,0,1.2101330558,0.7665712028,-0.5730874694
C,0,1.9479867551,1.5379388215,0.4630471472
H,0,2.6299457769,0.9777674174,1.0757708874
C,0,1.7996658718,2.8851774117,0.7517177817

C,0,3.1221509301,2.9423129567,-0.4888120588
O,0,2.7207859066,3.2010663243,-1.6079173083
C,0,4.3642518682,2.8570480926,0.03984831
Cl,0,5.7117620546,3.2844586958,-0.9630677592
Cl,0,4.7845243471,2.4903212526,1.6771829761
C,0,0.6598540383,3.7499293965,0.2719747352
H,0,2.2536549573,3.2129659649,1.6690803473
H,0,0.9638064224,4.788604474,0.2609663219
H,0,0.3166626422,3.4810811761,-0.7140605822
H,0,-0.1611517632,3.6443642471,0.9746473578
H,0,0.7856071045,1.3943336254,-1.3397907832
H,0,1.8495675696,0.0164415456,-1.0192721983
H,0,0.4036024625,0.2501573951,-0.0544557049

B3LYP/6-31+G*

E(RB3LYP) = -1228.98459450

Zero-point correction= 0.125363 (Hartree/Particle)
Thermal correction to Energy= 0.135862
Thermal correction to Enthalpy= 0.136806
Thermal correction to Gibbs Free Energy= 0.089062
Sum of electronic and ZPE= -1228.859232
Sum of electronic and thermal Energies= -1228.848733
Sum of electronic and thermal Enthalpies= -1228.847789
Sum of electronic and thermal Free Energies= -1228.895533

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	85.254	36.452	100.486

C,0,1.2004139497,0.7760880428,-0.5529996217
C,0,1.9748968331,1.4941274801,0.4966153352
H,0,2.7018188676,0.9343776372,1.0778839835
C,0,1.8227433054,2.8578969667,0.7819933165
C,0,3.1175811984,2.9780585752,-0.5297093121
O,0,2.6715322459,3.2181761653,-1.6422282032
C,0,4.3931801457,2.8788284465,-0.0122385829
Cl,0,5.7150582037,3.4076774439,-1.0094538112
Cl,0,4.8217613092,2.5399214759,1.6460011699
C,0,0.6418461911,3.6800358931,0.322744234
H,0,2.3103845032,3.2133435767,1.6866013254
H,0,0.880498355,4.746973622,0.3554168804
H,0,0.3396937125,3.4320770591,-0.6962334623
H,0,-0.2041440217,3.4988602045,0.9989461374
H,0,1.3026194914,1.3111249475,-1.5105701288
H,0,1.5440563963,-0.2531486707,-0.6795042035
H,0,0.1288693133,0.7661211343,-0.3094930564

B3LYP/6-31+G* pcm(THF)

E(RB3LYP) = -1228.99274784

Zero-point correction= 0.125094 (Hartree/Particle)
Thermal correction to Energy= 0.135909

Thermal correction to Enthalpy= 0.136853
Thermal correction to Gibbs Free Energy= 0.088039
Sum of electronic and ZPE= -1228.867653
Sum of electronic and thermal Energies= -1228.856839
Sum of electronic and thermal Enthalpies= -1228.855895
Sum of electronic and thermal Free Energies= -1228.904709

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	85.284	36.793	102.737

C,0,1.1854767605,0.7750667098,-0.5560158449
C,0,1.9670023991,1.5250519307,0.4727138695
H,0,2.683896841,0.96184393,1.0632671828
C,0,1.7612255975,2.8544195395,0.8172912443
C,0,3.1813177794,2.8985283566,-0.5747576173
O,0,2.7321072073,3.1492819011,-1.6824374602
C,0,4.4178317821,2.8944613148,0.007530147
Cl,0,5.7666655118,3.4514387939,-0.9597251055
Cl,0,4.8197510363,2.489993639,1.6530609262
C,0,0.6383078405,3.7126574845,0.3115500682
H,0,2.2786429185,3.2202036097,1.7000373458
H,0,0.9149014587,4.7706072563,0.3329134073
H,0,0.3304150024,3.447264524,-0.7014177354
H,0,-0.2237427966,3.5786656358,0.9794145699
H,0,1.0328755172,1.3786606832,-1.4573315406
H,0,1.6833151213,-0.1581734205,-0.8300171285
H,0,0.1928200229,0.5305681117,-0.1523043284

MPW1K/6-31+G**

E(RmPW+HF-PW91) = -1228.91125508

Zero-point correction= 0.128793 (Hartree/Particle)
Thermal correction to Energy= 0.139476
Thermal correction to Enthalpy= 0.140420
Thermal correction to Gibbs Free Energy= 0.091187
Sum of electronic and ZPE= -1228.782462
Sum of electronic and thermal Energies= -1228.771779
Sum of electronic and thermal Enthalpies= -1228.770835
Sum of electronic and thermal Free Energies= -1228.820068

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	87.522	35.977	103.621

C,0,-2.4913065465,-0.191493205,1.5059266627
C,0,-1.5965828733,0.6628401978,0.6817917688
C,0,-1.5965828733,0.6628401978,-0.6817917688
C,0,-2.4913065465,-0.191493205,-1.5059266627
C,0,-0.0573081075,-0.6984962799,0.
C,0,1.0971247845,-0.0072929876,0.
Cl,0,1.3131292915,1.6942645086,0.
O,0,-0.505957456,-1.8002023592,0.
H,0,-0.9986390729,1.4082719702,1.1857346672

H,0,-0.9986390729,1.4082719702,-1.1857346672
H,0,-2.2422555148,-0.1269471884,-2.5600104499
H,0,-2.4177047308,-1.2330694007,-1.1941619709
H,0,-3.5288971499,0.1186567285,-1.3773523453
H,0,-2.4177047308,-1.2330694007,1.1941619709
H,0,-2.2422555148,-0.1269471884,2.5600104499
H,0,-3.5288971499,0.1186567285,1.3773523453
Cl,0,2.5476168057,-0.934706976,0.

MPW1K/6-31G* (with grid=ultrafine)

E(RmPW+HF-PW91) = -1228.89194855

Zero-point correction= 0.129716 (Hartree/Particle)
Thermal correction to Energy= 0.140249
Thermal correction to Enthalpy= 0.141193
Thermal correction to Gibbs Free Energy= 0.092038
Sum of electronic and ZPE= -1228.762233
Sum of electronic and thermal Energies= -1228.751700
Sum of electronic and thermal Enthalpies= -1228.750756
Sum of electronic and thermal Free Energies= -1228.799910

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	88.007	35.579	103.455

C,0,-2.4691518551,-0.2023792042,1.5101504411
C,0,-1.5564630465,0.6343072299,0.6871160442
C,0,-1.5564630465,0.6343072299,-0.6871160442
C,0,-2.4691518551,-0.2023792042,-1.5101504411
C,0,-0.1527530228,-0.635276163,0.
C,0,1.0347913188,0.0182005348,0.
Cl,0,1.2981190995,1.7154001556,0.
O,0,-0.5444505618,-1.7703803327,0.
H,0,-0.9754866211,1.3948112104,1.1875306613
H,0,-0.9754866211,1.3948112104,-1.1875306613
H,0,-2.225115742,-0.1313653656,-2.5655991152
H,0,-2.3977134658,-1.2456415322,-1.2039478488
H,0,-3.5014731174,0.1212198037,-1.3705120649
H,0,-2.3977134658,-1.2456415322,1.2039478488
H,0,-2.225115742,-0.1313653656,2.5655991152
H,0,-3.5014731174,0.1212198037,1.3705120649
Cl,0,2.4589349785,-0.9397674844,0.

m05/6-31+G**

E(RM05) = -1228.78963476

Zero-point correction= 0.125769 (Hartree/Particle)
Thermal correction to Energy= 0.136676
Thermal correction to Enthalpy= 0.137620
Thermal correction to Gibbs Free Energy= 0.088470

Sum of electronic and ZPE= -1228.663866
Sum of electronic and thermal Energies= -1228.652959
Sum of electronic and thermal Enthalpies= -1228.652015
Sum of electronic and thermal Free Energies= -1228.701164

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	85.765	36.963	103.444

C,0,-2.5118877928,-0.1016030547,1.5139944176
C,0,-1.5747253432,0.682906591,0.6595567022
C,0,-1.5917966283,0.6977165524,-0.7116435143
C,0,-2.5180117316,-0.1082858471,-1.555159572
C,0,-0.0700494854,-0.7904141661,0.0310473127
O,0,-0.6012287449,-1.8638564353,0.0246343833
C,0,1.1340159714,-0.1620002445,0.0280248639
Cl,0,2.5275627468,-1.1886536068,0.0662714571
Cl,0,1.4532416179,1.53236218,0.0169523548
H,0,-0.9339314564,1.4033941771,1.1591810613
H,0,-0.9378549095,1.4062151533,-1.2113158601
H,0,-2.3043726835,0.0175680863,-2.6167330272
H,0,-2.4356275826,-1.1722204284,-1.3082375968
H,0,-3.5576830881,0.1851547909,-1.3740628653
H,0,-2.115470079,-0.2298019758,2.5224494929
H,0,-3.4665352135,0.4314571179,1.5946410496
H,0,-2.7144755972,-1.0890498901,1.0943703405

m052x/6-31+G**

E(RM052X) = -1228.89726124

Zero-point correction= 0.126801 (Hartree/Particle)
Thermal correction to Energy= 0.137792
Thermal correction to Enthalpy= 0.138737
Thermal correction to Gibbs Free Energy= 0.088894
Sum of electronic and ZPE= -1228.770460
Sum of electronic and thermal Energies= -1228.759469
Sum of electronic and thermal Enthalpies= -1228.758525
Sum of electronic and thermal Free Energies= -1228.808368

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	86.466	36.788	104.903

C,0,-2.4418762643,-0.2941429554,1.5309030294
C,0,-1.6431327611,0.6749384914,0.7149818717
C,0,-1.7135302661,0.7826999908,-0.6348406962
C,0,-2.5921354497,-0.0696763257,-1.5015848254
C,0,0.0675752582,-0.7858216408,-0.0822836682
O,0,-0.4811604515,-1.8317732752,-0.1295971672
C,0,1.1799680269,-0.0410239742,-0.0683497507
Cl,0,2.6665767419,-0.9418603103,-0.1388643885
Cl,0,1.3407171723,1.6707085028,0.0093583383
H,0,-1.0356199715,1.3914154442,1.2566936129
H,0,-1.1440267849,1.5717395183,-1.1126226179

H,0,-2.3837972547,-1.1302683478,-1.3355805643
H,0,-3.6459068242,0.100079631,-1.2657801198
H,0,-2.434903515,0.1516923668,-2.5555070119
H,0,-1.8632008885,-0.6517765704,2.3831829339
H,0,-3.3332018455,0.2071344818,1.9207827352
H,0,-2.7611749221,-1.1531760273,0.9430792888

m06/6-31+G**

E(RM06) = -1228.71870471

Zero-point correction= 0.124760 (Hartree/Particle)
Thermal correction to Energy= 0.135312
Thermal correction to Enthalpy= 0.136256
Thermal correction to Gibbs Free Energy= 0.088322
Sum of electronic and ZPE= -1228.593945
Sum of electronic and thermal Energies= -1228.583393
Sum of electronic and thermal Enthalpies= -1228.582449
Sum of electronic and thermal Free Energies= -1228.630383

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	84.909	36.785	100.886

C,0,-2.498318952,-0.1817629434,1.5057652643
C,0,-1.5857921754,0.6604436095,0.6866805897
C,0,-1.5857029484,0.6606227715,-0.6864575449
C,0,-2.4981863632,-0.1813065929,-1.5058891765
C,0,-0.0742203952,-0.6890759998,-0.0001042179
C,0,1.0997640638,-0.0101199649,0.0001020747
Cl,0,1.3509372601,1.7037704804,0.0003604192
O,0,-0.5159600879,-1.8065048738,-0.0002977879
H,0,-0.9723340919,1.4017941116,1.1955341759
H,0,-0.9722301146,1.4021513563,-1.1950313776
H,0,-2.3344384979,-0.0338385431,-2.5754379629
H,0,-2.3438563135,-1.2443667128,-1.2735568414
H,0,-3.5474349297,0.0492424513,-1.2792105945
H,0,-2.3438646103,-1.2447507801,1.2731644471
H,0,-2.3347380106,-0.0345652892,2.5753761515
H,0,-3.5475557423,0.0487474936,1.2789915383
Cl,0,2.5477654508,-0.9703964637,0.0000108428

m062x/6-31+G**

E(RM062X) = -1228.78286075

Zero-point correction= 0.126920 (Hartree/Particle)
Thermal correction to Energy= 0.136733
Thermal correction to Enthalpy= 0.137677
Thermal correction to Gibbs Free Energy= 0.091784
Sum of electronic and ZPE= -1228.655941
Sum of electronic and thermal Energies= -1228.646128
Sum of electronic and thermal Enthalpies= -1228.645184
Sum of electronic and thermal Free Energies= -1228.691077

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	85.801	35.363	96.590

C,0,-2.3660334487,-0.2604962812,1.5418154825
C,0,-1.5153954304,0.6325166436,0.7125561586
C,0,-1.4660221164,0.5418116354,-0.7032448945
C,0,-2.5190550494,-0.1971057559,-1.4926946437
C,0,-0.2489662477,-0.5461297262,-0.248602563
C,0,0.9547690947,0.0701698243,0.0790985783
Cl,0,1.2954576034,1.7615089963,-0.0492268983
O,0,-0.5353914171,-1.7418333123,-0.2645401846
H,0,-0.9656891078,1.4332469836,1.1971352942
H,0,-1.0060203199,1.3857645841,-1.2122013671
H,0,-2.1431924909,-0.4334726785,-2.4898411677
H,0,-2.7925577515,-1.1339795771,-1.0074771713
H,0,-3.40572907,0.4367036249,-1.5928535286
H,0,-2.1653663969,-1.305109038,1.2640468499
H,0,-2.1802959016,-0.1210817958,2.6062756201
H,0,-3.4249476742,-0.0663214821,1.3303657051
Cl,0,2.3282692662,-0.9261085348,0.32938873

m062x/6-31+G pcm(THF) first saddle point**

E(RM062X) = -1228.79017767

Zero-point correction= 0.125995 (Hartree/Particle)
Thermal correction to Energy= 0.136927
Thermal correction to Enthalpy= 0.137871
Thermal correction to Gibbs Free Energy= 0.088325
Sum of electronic and ZPE= -1228.664183
Sum of electronic and thermal Energies= -1228.653251
Sum of electronic and thermal Enthalpies= -1228.652307
Sum of electronic and thermal Free Energies= -1228.701852

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	85.923	36.913	104.277

C,0,-2.4407243628,-0.2966633486,1.5324064606
C,0,-1.658174269,0.6862189988,0.7182506564
C,0,-1.7294803399,0.7956057806,-0.6307919893
C,0,-2.597355956,-0.0631637221,-1.5016891931
C,0,0.0945357975,-0.8037869865,-0.0869366192
O,0,-0.4676718499,-1.8405571025,-0.1317283119
C,0,1.2003388925,-0.0510673051,-0.071613917
Cl,0,2.6935147772,-0.9508779221,-0.1360626808
Cl,0,1.3491832308,1.660648038,-0.0021486359
H,0,-1.0543640573,1.407586755,1.2643462929
H,0,-1.1687811182,1.5940250483,-1.1106325325
H,0,-2.4185363284,-1.1268360247,-1.307075704
H,0,-3.6565071958,0.1284226189,-1.2974264849
H,0,-2.4110521256,0.1312062277,-2.5584437549
H,0,-1.8597290962,-0.6449711247,2.3901299958
H,0,-3.3444840295,0.1867559821,1.9217995041

H,0,-2.7495419694,-1.1616569131,0.9415879138

m062x/6-31+G pcm(THF) second saddle point**

E(RM062X) = -1228.79238063

Zero-point correction= 0.126980 (Hartree/Particle)
Thermal correction to Energy= 0.136735
Thermal correction to Enthalpy= 0.137680
Thermal correction to Gibbs Free Energy= 0.091810
Sum of electronic and ZPE= -1228.665401
Sum of electronic and thermal Energies= -1228.655645
Sum of electronic and thermal Enthalpies= -1228.654701
Sum of electronic and thermal Free Energies= -1228.700570

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	85.803	35.242	96.540

C,0,-2.3697835451,-0.2652900743,1.5473744676
C,0,-1.5165181857,0.6173162961,0.7137407515
C,0,-1.4611802938,0.5247942163,-0.7042089706
C,0,-2.5166780782,-0.2077694138,-1.4961892194
C,0,-0.2443040886,-0.5303062943,-0.2501204071
C,0,0.9580007799,0.086146729,0.0683353303
Cl,0,1.2948473501,1.7759054352,-0.0351737274
O,0,-0.501868249,-1.7444296271,-0.271471994
H,0,-0.974089326,1.4237905943,1.1974655049
H,0,-1.0136237866,1.3775916819,-1.2097304252
H,0,-2.129973239,-0.4724550392,-2.4818986719
H,0,-2.834766215,-1.1211013432,-0.9944622946
H,0,-3.3795202699,0.4521058559,-1.6250522775
H,0,-2.2370258888,-1.309280091,1.2381699737
H,0,-2.145211177,-0.1586053523,2.6076059
H,0,-3.4222365121,-0.006994658,1.3730324294
Cl,0,2.3377642666,-0.911334805,0.3225836301

m062x/6-31+G pcm(THF) intermediate**

E(RM062X) = -1228.79257705

Zero-point correction= 0.127140 (Hartree/Particle)
Thermal correction to Energy= 0.138035
Thermal correction to Enthalpy= 0.138979
Thermal correction to Gibbs Free Energy= 0.090250
Sum of electronic and ZPE= -1228.665437
Sum of electronic and thermal Energies= -1228.654543
Sum of electronic and thermal Enthalpies= -1228.653598
Sum of electronic and thermal Free Energies= -1228.702327

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	86.618	37.739	102.559

C,0,1.2309646668,0.8274518535,-0.5851982959
C,0,2.0929891493,1.5704872776,0.3881001792
C,0,1.7961627042,2.842839392,0.8754178938
C,0,0.6270539942,3.6543980838,0.4235525168
C,0,3.0765160747,2.8182588596,-0.5769688198
C,0,4.3327583924,2.9578870015,-0.0478847085
Cl,0,4.8528055333,2.497118926,1.5326563445
O,0,2.6002631586,3.0976276266,-1.67560093
Cl,0,5.5680639614,3.604890003,-1.0665802721
H,0,2.8271851359,0.9854049465,0.9350423556
H,0,2.3508473576,3.1922950849,1.7413820678
H,0,0.7052042268,4.6829655556,0.7751526679
H,0,0.5527326637,3.6477428319,-0.667045467
H,0,-0.2884331419,3.2095600522,0.83000306
H,0,1.8282118727,0.1329208644,-1.1781234012
H,0,0.4983501044,0.2491043167,-0.0115110949
H,0,0.6999091459,1.5034803243,-1.2546330961

MP2/6-31+G**

-0.1311210389D+01 EUMP2

Zero-point correction= 0.127845 (Hartree/Particle)
Thermal correction to Energy= 0.138482
Thermal correction to Enthalpy= 0.139426
Thermal correction to Gibbs Free Energy= 0.090312
Sum of electronic and ZPE= -1226.757128
Sum of electronic and thermal Energies= -1226.746491
Sum of electronic and thermal Enthalpies= -1226.745547
Sum of electronic and thermal Free Energies= -1226.794661

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	86.899	36.130	103.370

C,0,-2.4764475718,-0.203927326,1.5116305209
C,0,-1.5475474464,0.6322024601,0.6928273883
C,0,-1.5469489883,0.6300239192,-0.6950339328
C,0,-2.475202851,-0.208603199,-1.5120179231
C,0,-0.148710285,-0.641073443,0.0013872797
C,0,1.0481513826,0.0310373296,0.0008645133
Cl,0,1.2914958052,1.7383151157,-0.0016693061
O,0,-0.5348141111,-1.8033448274,0.0030300217
H,0,-0.9725461314,1.3992860605,1.1960562598
H,0,-0.9715435537,1.3955495857,-1.2001706231
H,0,-2.2211157913,-0.1552111973,-2.5680625812
H,0,-2.4264057144,-1.2500584399,-1.1888833935
H,0,-3.5017975986,0.1413490724,-1.3803400026
H,0,-2.427019552,-1.2464442752,1.1920200649
H,0,-2.2234924365,-0.1469398412,2.5677579178
H,0,-3.5030037482,0.1452766428,1.3776930799
Cl,0,2.4807821338,-0.9273535266,0.002910716

mpwlyp/6-31+G**
E(RmPW+HF-LYP) = -1229.00679093

Zero-point correction= 0.124886 (Hartree/Particle)
Thermal correction to Energy= 0.135410
Thermal correction to Enthalpy= 0.136355
Thermal correction to Gibbs Free Energy= 0.088512
Sum of electronic and ZPE= -1228.881905
Sum of electronic and thermal Energies= -1228.871381
Sum of electronic and thermal Enthalpies= -1228.870436
Sum of electronic and thermal Free Energies= -1228.918279

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	84.971	36.531	100.693

C,0,-2.4642386658,-0.2284077586,1.5716288721
C,0,-1.6062265281,0.6629795695,0.7462127847
C,0,-1.5059744181,0.5703374108,-0.6479124174
C,0,-2.485156373,-0.1960591211,-1.5025223372
C,0,-0.1616547682,-0.6058953531,-0.1693776042
C,0,1.048658403,0.0331565958,-0.0011212201
Cl,0,1.3335104299,1.7539460311,-0.0601301128
O,0,-0.5100367877,-1.7775155583,-0.165655058
H,0,-1.0223652693,1.4306466435,1.2445115238
H,0,-0.9919826934,1.3885926594,-1.1450360937
H,0,-2.0607519738,-0.39235175,-2.4899378699
H,0,-2.7552443926,-1.152689278,-1.0537540088
H,0,-3.3927395408,0.4054039565,-1.6343282211
H,0,-2.2159488874,-1.2771483436,1.3456047553
H,0,-2.32882166,-0.049200264,2.6393094083
H,0,-3.5235959997,-0.093856209,1.3178463714
Cl,0,2.4864026668,-0.9418551204,0.0046612275

VRI for the reaction of 1 with 2.

This is the valley-ridge inflection point for the reaction of **1** with **2**, obtained by following the IRC forward from the symmetrical transition structure in the MPW1K calculations until an orthogonal frequency most closely approached 0.
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1228.91144852

Zero-point correction= 0.128809 (Hartree/Particle)
Thermal correction to Energy= 0.139440
Thermal correction to Enthalpy= 0.140385
Thermal correction to Gibbs Free Energy= 0.089352
Sum of electronic and ZPE= -1228.782639
Sum of electronic and thermal Energies= -1228.772008
Sum of electronic and thermal Enthalpies= -1228.771064
Sum of electronic and thermal Free Energies= -1228.822096

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	87.500	35.766	107.407

6 1.495821 1.968062 1.507230
6 1.495821 0.728605 0.687076
6 1.495821 0.728605 -0.687076
6 1.495821 1.968062 -1.507230
6 -0.400428 0.528032 0.000000
6 -0.708653 -0.791996 0.000000
17 0.385391 -2.115450 0.000000
8 -0.978501 1.581307 0.000000
1 1.666476 -0.213384 1.187583
1 1.666476 -0.213384 -1.187583
1 1.381976 1.743830 -2.562575
1 0.682482 2.623800 -1.198599
1 2.433385 2.506476 -1.365462
1 0.682482 2.623800 1.198599
1 1.381976 1.743830 2.562575
1 2.433385 2.506476 1.365462
17 -2.370441 -1.222675 0.000000

Structure 6‡

MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1228.91188370

Zero-point correction= 0.129296 (Hartree/Particle)
Thermal correction to Energy= 0.139492
Thermal correction to Enthalpy= 0.140436
Thermal correction to Gibbs Free Energy= 0.093179
Sum of electronic and ZPE= -1228.782588
Sum of electronic and thermal Energies= -1228.772392
Sum of electronic and thermal Enthalpies= -1228.771448
Sum of electronic and thermal Free Energies= -1228.818705

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	87.532	35.364	99.461

C,0,-2.4510110458,-0.2183519891,1.5236051265
C,0,-1.5185346745,0.5904561429,0.6934656135
C,0,-1.517993897,0.5872171105,-0.6967837836
C,0,-2.4496189849,-0.2257061951,-1.5238334044
C,0,-0.228402671,-0.5664875811,0.0018486346
C,0,0.9907530229,0.0574154575,0.000873033
Cl,0,1.2767431353,1.7502383918,-0.0031893639
O,0,-0.5526843276,-1.7411036679,0.0045748902
H,0,-0.9711475082,1.3828128921,1.1827279819
H,0,-0.970087507,1.3771826217,-1.1893198761
H,0,-2.1559345667,-0.2123745985,-2.5683966213
H,0,-2.462402618,-1.2563062107,-1.1768822267
H,0,-3.4574688861,0.1820478028,-1.4408764508
H,0,-2.4636179065,-1.2506308589,1.1816853218
H,0,-2.1582805048,-0.1999585307,2.5683590773
H,0,-3.4587248672,0.189130799,1.4377402019
Cl,0,2.3922473488,-0.915497476,0.0044018459

Cyclobutanone Product 3 / 3'

MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1228.99719575

Zero-point correction= 0.133228 (Hartree/Particle)
Thermal correction to Energy= 0.142798
Thermal correction to Enthalpy= 0.143742
Thermal correction to Gibbs Free Energy= 0.098011
Sum of electronic and ZPE= -1228.863968
Sum of electronic and thermal Energies= -1228.854397
Sum of electronic and thermal Enthalpies= -1228.853453
Sum of electronic and thermal Free Energies= -1228.899185

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	89.607	34.113	96.251

6	-0.986648	1.917236	-0.726862
6	-0.561453	0.488427	-0.979065
1	-0.351552	0.333893	-2.033432
6	-1.488129	-0.595374	-0.345881
6	-0.483423	-0.707117	0.782053
8	-0.525977	-1.030171	1.922800
6	0.593828	-0.011158	-0.071098
17	1.618060	1.158242	0.734716
17	1.574892	-1.245093	-0.892378
6	-2.926818	-0.301691	0.005906
1	-1.421687	-1.507861	-0.940862
1	-3.348105	-1.133835	0.564548
1	-3.018867	0.589390	0.621320
1	-3.523738	-0.161671	-0.892822
1	-1.160298	2.118252	0.328464
1	-0.224523	2.610325	-1.073183
1	-1.907748	2.127391	-1.266501

Cis-2-butene (1) Starting Material

Structures for cis-2-butene were calculated at all of the levels used for the transition structures. We provide here a single example.
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -157.198685414

Zero-point correction= 0.110986 (Hartree/Particle)
Thermal correction to Energy= 0.116456
Thermal correction to Enthalpy= 0.117400
Thermal correction to Gibbs Free Energy= 0.083138
Sum of electronic and ZPE= -157.087700
Sum of electronic and thermal Energies= -157.082229
Sum of electronic and thermal Enthalpies= -157.081285
Sum of electronic and thermal Free Energies= -157.115548

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	73.077	17.826	72.112

C,0,1.0924978651,0.7779415164,-0.3096367879
C,0,2.070746273,1.4842343855,0.567810653
C,0,2.2065271902,2.796016635,0.7451247217
C,0,1.4146078889,3.8898552359,0.1109993694
H,0,2.7439842145,0.8388327899,1.1199191464
H,0,2.9805777756,3.1245589336,1.4288803414
H,0,0.9222016216,4.4982231061,0.8701666947
H,0,2.0653103818,4.5587533265,-0.4529792886
H,0,0.6501927309,3.5205153655,-0.5662987634
H,0,0.4672752857,0.103495103,0.2761357595
H,0,0.4367556843,1.4582061364,-0.8450969859
H,0,1.6104140885,0.1639494662,-1.0469878601

Dichloroketene (2) Starting Material

Structures for **2** were calculated at all of the levels used for the transition structures. We provide here a single example.
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1071.72174242

Zero-point correction= 0.016271 (Hartree/Particle)
Thermal correction to Energy= 0.021228
Thermal correction to Enthalpy= 0.022173
Thermal correction to Gibbs Free Energy= -0.013388
Sum of electronic and ZPE= -1071.705471
Sum of electronic and thermal Energies= -1071.700514
Sum of electronic and thermal Enthalpies= -1071.699570
Sum of electronic and thermal Free Energies= -1071.735130

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	13.321	15.071	74.843

Cl,0,1.1394989217,1.1790502808,-0.4430569264
Cl,0,2.7524527893,1.732220456,1.9813664815
C,0,2.0273643984,0.6130482833,0.9072787553
C,0,2.1521448582,-0.6774992247,1.1185386062
O,0,2.2618600324,-1.8131217954,1.3042120834

Starting Material Complex Used for RRKM Calculations on 1 + 2

This loose reactant complex is not kinetically significant and its energetics cancel out in the relevant RRKM calculations used in the main text. Its choice as the formal starting material for RRKM calculations was solely to make the calculations convenient.
MPW1K/6-31+G**
E(RmPW+HF-PW91) = -1228.92152325

Zero-point correction= 0.127628 (Hartree/Particle)
Thermal correction to Energy= 0.140548
Thermal correction to Enthalpy= 0.141492
Thermal correction to Gibbs Free Energy= 0.079397
Sum of electronic and ZPE= -1228.793896
Sum of electronic and thermal Energies= -1228.780975
Sum of electronic and thermal Enthalpies= -1228.780031

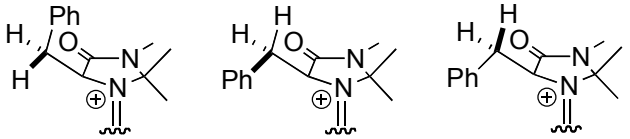
Sum of electronic and thermal Free Energies= -1228.842126

	E KCal/Mol	CV Cal/Mol-K	S Cal/Mol-K
Total	88.195	38.827	130.689

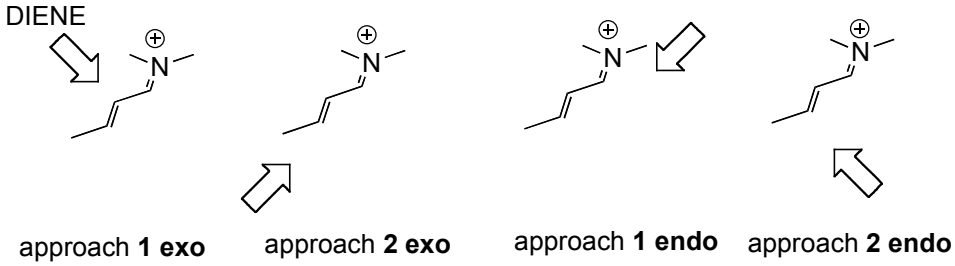
6 -2.061176 1.754334 -0.924882
6 -2.075067 0.280315 -1.155289
6 -2.689991 -0.651480 -0.430065
6 -3.518573 -0.457274 0.794994
6 0.677639 -0.162809 1.251337
6 1.525954 -0.171891 0.248048
17 1.560046 -1.486605 -0.846536
8 -0.062304 -0.141973 2.138626
1 -1.518697 -0.056009 -2.022449
1 -2.589530 -1.678949 -0.760700
1 -3.099715 -1.010756 1.635572
1 -3.597645 0.584359 1.091284
1 -4.528200 -0.838058 0.638593
1 -2.593294 2.046946 -0.024580
1 -1.037806 2.122016 -0.844305
1 -2.514601 2.279016 -1.766452
17 2.606143 1.141902 0.037075

Transition Structures for the Reaction of 7 with Cyclopentadiene

A total of 16 transition states were searched. Following the convention of Gordillio and Houk (*J. Am. Chem. Soc.* **2006**, *128*, 3543-3553)**,** they are named as follows:



conformer **a** conformer **b** conformer **c**



approach **1 exo** approach **2 exo** approach **1 endo** approach **2 endo**

Structure: E_a1_endo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00386564

1 imaginary frequency.

Zero-point correction= 0.522204 (Hartree/Particle)
Thermal correction to Energy= 0.549723
Thermal correction to Enthalpy= 0.550667

Thermal correction to Gibbs Free Energy= 0.462372
Sum of electronic and ZPE= -1231.481661
Sum of electronic and thermal Energies= -1231.454143
Sum of electronic and thermal Enthalpies= -1231.453199
Sum of electronic and thermal Free Energies= -1231.541493

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.956	107.950	185.831

C	-3.3498016277	2.2367800477	0.6639257443
C	-1.9744597634	1.9600954715	0.6197727954
C	-1.1962489576	2.5714543440	-0.3729503568
C	-1.7769526536	3.4277478031	-1.3104296117
C	-3.1481996199	3.6851446597	-1.2663774192
C	-3.9317599231	3.0903006492	-0.2746041465
C	-1.3395277944	1.0191984673	1.6208689205
C	-1.5097070824	-0.4946106157	1.3080546896
N	-1.1362735536	-0.9353368677	-0.0408693942
C	-2.2983599704	-1.4948225438	-0.8148275219
N	-3.3476151285	-1.4511204838	0.2043734460
C	-2.9772364249	-0.9076840016	1.4001540766
C	0.1058655265	-0.9495874423	-0.5205818050
O	-3.6806952545	-0.7452634644	2.3805930417
C	-4.7166516273	-1.8795657694	-0.0440218199
C	-2.6297397385	-0.6059325137	-2.0234118879
C	-2.0179134463	-2.9456093951	-1.2420315599
C	1.2696079263	-0.5736050019	0.1369660972
C	2.5261462356	-0.3900229210	-0.5700104484
C	3.5974245868	-1.8673694264	-0.2964737620
C	3.0888978701	-2.8719699402	-1.1844177564
C	2.0673088312	-3.5924266360	-0.5557662731
C	1.9941194997	-3.1819027967	0.7706516360
C	3.1935497081	-2.3547950455	1.0940609437
H	1.4193948872	-4.3209240011	-1.0297614693
H	3.3803022142	-2.9778287758	-2.2248741659
H	4.6003573271	-1.4824263051	-0.4594910572
H	1.2811185216	-3.5409384067	1.5050990585
H	3.0570315440	-1.5915126155	1.8596639222
H	3.9856663539	-3.0332785439	1.4531131374
H	2.3997475661	-0.4081543226	-1.6521552562
H	1.2053571268	-0.2518008982	1.1684337051
H	-4.7599015289	-2.9396640279	-0.3134289371
H	-5.1812091689	-1.2852295034	-0.8374465762
H	-5.2674136821	-1.7258237019	0.8850854252
H	-1.7916080820	-0.5850726408	-2.7278615588
H	-3.4945035660	-1.0081688245	-2.5595253762
H	-2.8493271016	0.4154102340	-1.7058177430
H	-2.9063284183	-3.3725816627	-1.7155605713
H	-1.2092042683	-2.9964373935	-1.9776591793
H	-1.7579611627	-3.5602605216	-0.3749581502
H	-0.9389231114	-1.0688555551	2.0511105167
H	-0.2751449735	1.2507188754	1.7237750734
H	-1.7907574210	1.1450643650	2.6115801111
H	-0.1239032259	2.3894739995	-0.4032102542
H	-1.1574308035	3.9015209229	-2.0669968305

H	-3.6011588230	4.3566742527	-1.9901374761
H	-4.9961306548	3.3017204076	-0.2219703018
H	-3.9624829220	1.7884175554	1.4414521073
H	0.1887650883	-1.2790940795	-1.5540124672
C	3.4035194602	0.7711406575	-0.1768506156
C	4.1341759781	1.4256603096	-1.1806393183
C	3.5353814750	1.2162418640	1.1477576218
C	4.9666777044	2.5010768804	-0.8734865052
H	4.0446074414	1.0951853827	-2.2132267964
C	4.3698342431	2.2898913952	1.4556880074
H	2.9836616813	0.7385742769	1.9530213661
C	5.0883697033	2.9355831167	0.4470899099
H	5.5168070587	2.9995476358	-1.6660813442
H	4.4554672456	2.6247808793	2.4852300972
H	5.7363586756	3.7723621922	0.6896422627

Structure: E_a1_exo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00508896

1 imaginary frequency.

Zero-point correction= 0.521904 (Hartree/Particle)
Thermal correction to Energy= 0.549529
Thermal correction to Enthalpy= 0.550473
Thermal correction to Gibbs Free Energy= 0.461603
Sum of electronic and ZPE= -1231.483185
Sum of electronic and thermal Energies= -1231.455560
Sum of electronic and thermal Enthalpies= -1231.454616
Sum of electronic and thermal Free Energies= -1231.543486

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.835	108.149	187.043

C	-3.4495911772	2.0936265036	0.9422177187
C	-2.0733444875	1.8538752332	0.8079908440
C	-1.3479829861	2.6000305191	-0.1313784513
C	-1.9818822607	3.5542365776	-0.9293571842
C	-3.3538936557	3.7755983486	-0.7970208519
C	-4.0848067304	3.0451562962	0.1429508746
C	-1.3808163788	0.8130163698	1.6607417177
C	-1.5094349909	-0.6543307328	1.1607117792
N	-1.1420002021	-0.9150718526	-0.2348015993
C	-2.3011120594	-1.3934064368	-1.0646172293
N	-3.3381153325	-1.5075223639	-0.0382749824
C	-2.9635254347	-1.1185360149	1.2151128799
C	0.1027002945	-0.8718202211	-0.7104675807
O	-3.6565906843	-1.1061920310	2.2163186541
C	-4.7025852308	-1.9236439926	-0.3283334199
C	-2.6648939163	-0.3604859298	-2.1422893931
C	-1.9994410422	-2.7691423754	-1.6837948837
C	1.2582632451	-0.5454369267	-0.0161134766

C	2.5224220979	-0.3810289966	-0.6894883894
C	3.5639046764	-1.9599759875	-0.4591734303
C	2.5753938061	-3.0767412323	-0.7756256610
C	1.9572808654	-3.3235417151	0.5612367007
C	2.7850206963	-2.8246097225	1.5482838566
C	3.8080211511	-2.0725972195	0.9373323253
H	-5.1781061577	-1.2482280651	-1.0467272878
H	-4.7347736805	-2.9465244340	-0.7167726807
H	-5.2499219002	-1.8845111880	0.6145696228
H	-2.9047850660	0.6039363982	-1.6900783274
H	-3.5245816270	-0.7079066910	-2.7233062012
H	-1.8324949725	-0.2252982101	-2.8409366340
H	-2.8883276058	-3.1506504117	-2.1940200431
H	-1.2061399219	-2.7071014374	-2.4353761612
H	-0.9080853779	-1.2975780151	1.8184007180
H	-1.8081447257	0.7939210286	2.6695782403
H	-0.3222193471	1.0680238008	1.7676319675
H	-4.0209651924	1.5381260280	1.6810533487
H	-5.1492448428	3.2254722015	0.2644833348
H	-3.8479074255	4.5224593716	-1.4119230264
H	-1.4032830254	4.1310223680	-1.6457285605
H	-0.2753770727	2.4444964423	-0.2290285419
H	-1.7103891815	-3.4875366587	-0.9105669317
H	2.6554534293	-2.9613454015	2.6158265742
H	4.6103860593	-1.5683782011	1.4642960582
H	2.4330284131	-0.4747557622	-1.7737106798
H	4.3901234114	-1.7489024752	-1.1334258678
H	1.1888721592	-0.2926251307	1.0341714488
H	1.0642748334	-3.9174478639	0.7228776494
H	3.1624915357	-3.9683927978	-1.0526551878
H	1.8738242588	-2.8935077728	-1.5911242802
H	0.1892915995	-1.0975332988	-1.7710448828
C	3.4296095419	0.7554900394	-0.3248367912
C	4.1817671174	1.3651600483	-1.3400466472
C	3.5542909435	1.2383670304	0.9874314251
C	5.0307072968	2.4355945905	-1.0563782468
H	4.0966148658	1.0054595623	-2.3633417727
C	4.4028561930	2.3060152451	1.2718174026
H	2.9894098427	0.7845403502	1.7978043020
C	5.1437712755	2.9086906581	0.2506290195
H	5.6003888467	2.8980445050	-1.8568851792
H	4.4844817749	2.6713926780	2.2913259804
H	5.8038914614	3.7409623717	0.4754000212

Structure: E_a2_endo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00090185

1 imaginary frequency.

Zero-point correction= 0.522480 (Hartree/Particle)
Thermal correction to Energy= 0.549884
Thermal correction to Enthalpy= 0.550828

Thermal correction to Gibbs Free Energy= 0.463256
Sum of electronic and ZPE= -1231.478422
Sum of electronic and thermal Energies= -1231.451018
Sum of electronic and thermal Enthalpies= -1231.450074
Sum of electronic and thermal Free Energies= -1231.537646

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	345.057	107.877	184.311

C	-1.2710508871	2.8639350291	1.7055625144
C	-2.5422456591	2.3898709151	2.0452829926
C	-3.2331747541	1.9392778040	0.8677454085
C	-2.7941269359	0.1948907314	0.6750515895
C	-1.4523749297	0.0564396139	0.1143412887
C	-1.1707245379	2.8873592924	0.3197611474
C	-2.5142077777	2.6497573738	-0.2797590873
C	-0.3919866933	-0.3701917447	0.8996318851
N	0.7920074328	-0.8369679556	0.4914254549
C	1.1525611957	-1.0355397788	-0.9173183544
C	2.3504485069	-1.9765517042	-0.8344616568
N	2.6536609637	-2.1644176177	0.4832225263
C	1.7472482595	-1.5201065285	1.4354806920
O	2.9379325361	-2.4372334524	-1.7961072217
C	3.7990248547	-2.9639394259	0.8927266274
C	1.5036957784	0.2415746256	-1.7286049078
C	2.7434476411	0.9951470020	-1.2910845949
C	2.6706588440	2.0189478495	-0.3363522702
C	3.8114482918	2.7237317241	0.0530135246
C	5.0490011512	2.4116764000	-0.5123270706
C	5.1354403176	1.3948917521	-1.4650254469
C	3.9930890825	0.6930494292	-1.8522064070
C	1.0181856844	-2.5768578944	2.2849373200
C	2.4713441268	-0.4953173508	2.3201275929
H	0.3277758563	-1.5507559244	-1.4269801825
H	1.6297503534	-0.1069760994	-2.7590246572
H	0.6346477242	0.9085260411	-1.7237513970
H	1.7103553437	2.2668712286	0.1102565149
H	3.7334904639	3.5202553963	0.7882209127
H	5.9376413027	2.9626308928	-0.2182545108
H	6.0934904732	1.1505407613	-1.9148417402
H	4.0684809040	-0.0990043957	-2.5913413784
H	4.5115416649	-2.3662073546	1.4701131091
H	4.2821552698	-3.3111209813	-0.0217518970
H	3.4913191798	-3.8323856514	1.4839187017
H	1.7470936828	-3.1528591473	2.8616188727
H	0.4558873729	-3.2659801093	1.6481630861
H	0.3368729160	-2.1161286635	3.0064093931
H	3.0126596916	0.2303993857	1.7094540368
H	3.1769788577	-1.0018510287	2.9854594104
H	1.7526644536	0.0369407962	2.9528221518
H	-2.8430485466	-0.1671079177	1.7024162708
H	-2.9154532881	2.2724428272	3.0581631904
H	-4.3200683501	1.9296556061	0.8839540832
H	-2.9988335644	3.6300156203	-0.4249379038
H	-2.5204764628	2.1483128632	-1.2474865972

H	-0.2940194077	3.1836608155	-0.2453694362
H	-0.4878263335	3.1403970109	2.4021303666
H	-1.3401012440	0.0580049202	-0.9631407577
H	-0.5327090677	-0.3836193888	1.9781123518
C	-3.9420764131	-0.3909142257	-0.1147106454
C	-4.9958755427	-0.9947983697	0.5879152068
C	-4.0100646926	-0.3426629364	-1.5152151345
C	-6.0843024809	-1.5446089818	-0.0883886560
H	-4.9609993192	-1.0424122972	1.6742293821
C	-5.0994173704	-0.8898393383	-2.1920200217
H	-3.2109023595	0.1098485272	-2.0960326574
C	-6.1401080261	-1.4920398707	-1.4817169844
H	-6.8853388613	-2.0154619413	0.4737243036
H	-5.1323551477	-0.8493094732	-3.2768083115
H	-6.9863235244	-1.9189036854	-2.0114660227

Structure: E_a2_exo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00220134

1 imaginary frequency.

Zero-point correction= 0.522166 (Hartree/Particle)
Thermal correction to Energy= 0.549739
Thermal correction to Enthalpy= 0.550683
Thermal correction to Gibbs Free Energy= 0.462370
Sum of electronic and ZPE= -1231.480036
Sum of electronic and thermal Energies= -1231.452463
Sum of electronic and thermal Enthalpies= -1231.451519
Sum of electronic and thermal Free Energies= -1231.539831

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.966	108.107	185.869

C	3.4570845527	3.0543271823	-0.1651212399
C	2.4074749017	2.2539618442	-0.6200113465
C	2.6522218460	1.0516382127	-1.2957500889
C	3.9847972365	0.6754529383	-1.5278752143
C	5.0365598826	1.4706807488	-1.0703702982
C	4.7775477261	2.6589947543	-0.3836172572
C	1.4988719491	0.2000639135	-1.7860366861
C	1.1797049182	-1.0763391653	-0.9606353311
N	0.8630775194	-0.9074622447	0.4648904010
C	1.8922663326	-1.5418254500	1.3628996102
N	2.7356256503	-2.2166064525	0.3741037175
C	2.3815748537	-2.0172019166	-0.9278427628
C	-0.3287860397	-0.5152389066	0.9249465401
O	2.9333510669	-2.4692039958	-1.9153340706
C	3.9083432482	-3.0022718547	0.7296527041
C	2.6622624526	-0.4631290335	2.1408198171
C	1.2563074749	-2.5703878065	2.3137186207
C	-1.4092002865	-0.0553774462	0.1884714719

C	-1.0708322831	2.7810396974	1.0919623865
C	-1.9457566730	2.1679237152	2.1321551454
C	-3.1631559632	1.7506278358	1.3127751822
C	-2.7370706750	0.0037424437	0.7580685025
C	-3.1221140767	2.5768650035	0.1542348593
C	-1.8309029057	3.1155280791	-0.0118099142
H	-0.0246756417	3.0214790110	1.2420121248
H	-1.2953340373	0.0979215460	-0.8782728486
H	-2.2686446339	2.9651739392	2.8225065668
H	-1.4746518685	1.3960067070	2.7434307058
H	-4.1164178968	1.5717700040	1.8041855328
H	-1.4887985886	3.6774691309	-0.8733717813
H	-3.9413652647	2.6933751907	-0.5465095566
H	-2.7768673194	-0.4276069874	1.7600638554
H	0.3412560154	-1.5917905052	-1.4466669837
H	4.3482575094	-3.3504458326	-0.2060098864
H	4.6432087171	-2.3941857820	1.2671337385
H	3.6400349802	-3.8702411345	1.3402718265
H	3.4326681689	-0.9221952685	2.7677694011
H	3.1346273517	0.2464333150	1.4580568820
H	1.9816032893	0.0813144422	2.8043114686
H	2.0441615371	-3.1146579907	2.8414624237
H	0.6483265951	-3.2908580816	1.7587961353
H	0.6409113512	-2.0925755074	3.0817483086
H	1.3795221512	2.5769855636	-0.4737980397
H	0.5932318664	0.8115368758	-1.8582578994
H	1.7087282273	-0.1761107933	-2.7940113896
H	3.2463181500	3.9897696286	0.3464972606
H	5.5982535665	3.2802420693	-0.0368997579
H	6.0615780226	1.1678045937	-1.2648515764
H	4.1969553244	-0.2373363435	-2.0767708612
H	-0.4568690839	-0.6338612801	1.9977279567
C	-3.9049576534	-0.4577513236	-0.0645975901
C	-4.9248087959	-1.1851374252	0.5663157929
C	-4.0165096889	-0.1946781847	-1.4387302466
C	-6.0237231121	-1.6499480029	-0.1574112556
H	-4.8550204896	-1.3991263289	1.6307388856
C	-5.1142207508	-0.6562415988	-2.1616913894
H	-3.2462521233	0.3730546815	-1.9551655422
C	-6.1211950474	-1.3867424044	-1.5233874394
H	-6.8001007270	-2.2171229205	0.3473006204
H	-5.1839462949	-0.4483816858	-3.2254046124
H	-6.9752495145	-1.7459734137	-2.0895175775

Structure: E_c1_endo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00255200

1 imaginary frequency.

Zero-point correction= 0.522362 (Hartree/Particle)
Thermal correction to Energy= 0.549861
Thermal correction to Enthalpy= 0.550805

Thermal correction to Gibbs Free Energy= 0.462558
Sum of electronic and ZPE= -1231.480190
Sum of electronic and thermal Energies= -1231.452691
Sum of electronic and thermal Enthalpies= -1231.451747
Sum of electronic and thermal Free Energies= -1231.539994

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	345.043	107.860	185.730

C	1.8656730163	-1.3060823513	2.4693746808
C	0.4739709515	-1.8221124177	2.6185201612
C	0.4414813550	-3.1650511175	2.2575405230
C	1.6545626127	-3.4832081655	1.6390004262
C	2.4377415531	-2.2937054228	1.4515295112
C	1.9217439440	-1.6176247071	-0.1674138679
C	0.6564438265	-0.9122268303	-0.0131453824
C	-0.5439059295	-1.4743475153	-0.4212450942
N	-1.7315520843	-0.8679105026	-0.4796094371
C	-2.9905679397	-1.5623585149	-0.9019087838
N	-3.9904394325	-0.5737162511	-0.4938873296
C	-3.4844436470	0.5912635551	0.0107923912
C	-1.9607821854	0.5104265286	-0.0364278772
C	-2.9906582683	-1.7839895388	-2.4237382650
C	-3.1848763410	-2.8833431009	-0.1407075920
C	-1.3473988565	1.6096998850	-0.9643550775
C	-0.6707490915	2.7349338782	-0.2051534268
C	0.6515466252	3.0912929032	-0.5021989640
C	1.2804833006	4.1336822448	0.1839057394
C	0.5942467523	4.8283034286	1.1802230842
C	-0.7255402060	4.4817558176	1.4799597910
C	-1.3572155254	3.4457817512	0.7914482750
O	-4.1236271735	1.5521026241	0.4003082275
C	-5.4235248705	-0.7734539146	-0.6584985104
H	-0.3948252364	-3.8395849690	2.4016396632
H	2.3911271534	-1.4698029877	3.4253352801
H	1.9223114312	-4.4621190577	1.2531966378
H	3.5155627306	-2.3930030723	1.3544512926
H	1.8171407999	-2.5202837032	-0.7697978856
H	-0.3345066021	-1.2752755887	3.0918869600
H	1.9583111690	-0.2467019825	2.2317681104
H	0.6730880778	0.1317559121	0.2780641898
H	-3.1490938011	-2.7154928218	0.9397623865
H	1.1889343170	2.5631270787	-1.2870266823
H	-1.2701790007	5.0272785564	2.2455943239
H	1.0798446544	5.6407270470	1.7132873169
H	2.3016388077	4.4073012485	-0.0680924587
H	-2.3912500372	3.1932538236	1.0133239493
H	-1.5637133528	0.6288896642	0.9796945630
H	-2.1480503165	2.0130255554	-1.5958968594
H	-0.6277321509	1.1340357962	-1.6381544388
H	-5.9089095076	0.1507830727	-0.3415659267
H	-5.7876506572	-1.5975598945	-0.0364428270
H	-5.6777488275	-0.9709383238	-1.7047930051
H	-4.1569254053	-3.3164039342	-0.3923599298
H	-2.4271665900	-3.6226385265	-0.4176414269

H	-3.9286279659	-2.2461771841	-2.7454490464
H	-2.1755505309	-2.4544729705	-2.7151003850
H	-2.8694076825	-0.8335704543	-2.9509940616
H	-0.5425305988	-2.5091795207	-0.7558615520
C	3.1257000223	-0.8365770670	-0.6327179187
C	4.0373310608	-1.4671198766	-1.4933551125
C	3.3852870129	0.4811754492	-0.2258629772
C	5.1738246467	-0.7981261606	-1.9461653240
H	3.8519818124	-2.4884821672	-1.8189815201
C	4.5236724815	1.1486768384	-0.6768868878
H	2.6986225363	1.0096181525	0.4291166129
C	5.4217053026	0.5127772347	-1.5369027643
H	5.8623403671	-1.3007794868	-2.6189360359
H	4.7077608463	2.1698754943	-0.3559208843
H	6.3066886472	1.0362295598	-1.8859395790

Structure: E_c1_exo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00398961

1 imaginary frequency.

Zero-point correction= 0.521957 (Hartree/Particle)
Thermal correction to Energy= 0.549616
Thermal correction to Enthalpy= 0.550560
Thermal correction to Gibbs Free Energy= 0.461882
Sum of electronic and ZPE= -1231.482032
Sum of electronic and thermal Energies= -1231.454374
Sum of electronic and thermal Enthalpies= -1231.453430
Sum of electronic and thermal Free Energies= -1231.542107

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.889	108.154	186.638

C	-2.9918821881	-1.7145624418	-0.8659795771
N	-1.7446336527	-0.9836611994	-0.4742335178
C	-1.9995440049	0.4016885475	-0.0707402878
C	-3.5227497091	0.4422075693	0.0181066974
N	-4.0091066621	-0.7489237246	-0.4429681424
C	-0.5412669807	-1.5587761920	-0.4035977496
C	-1.4435762607	1.4853009832	-1.0518854945
C	-0.7723659997	2.6505157515	-0.3504150786
C	-1.4454529855	3.3743102495	0.6458025228
C	-0.8202143058	4.4471659003	1.2818710116
C	0.4798990329	4.8176707981	0.9294026128
C	1.1527616987	4.1097756059	-0.0668516709
C	0.5302718371	3.0307633592	-0.7003029688
O	-4.1776125978	1.3946176093	0.4028583386
C	-5.4397172502	-0.9909739854	-0.5665451209
C	-3.0177108790	-1.9459134332	-2.3865012484
C	-3.1369525167	-3.0352274655	-0.0942338764
C	0.6477860509	-0.9425726489	-0.0461364024

C	1.9056747581	-1.6460033590	-0.1117311230
C	2.3845325473	-2.2272918543	1.6388590344
C	1.0954365329	-2.8408762496	2.1741608697
C	0.4252015487	-1.6550971454	2.7872118268
C	1.3610270374	-0.6666076859	3.0194870367
C	2.5719837956	-1.0443206903	2.4056331789
H	1.3727200866	-3.5367084740	2.9837547614
H	0.4901299976	-3.4069234337	1.4640368673
H	1.8005730178	-2.6506526189	-0.5270237903
H	3.2391836912	-2.8578435353	1.4070772092
H	3.4886700078	-0.4657317975	2.4291397498
H	1.1882387431	0.2603641258	3.5540064383
H	0.6466454646	0.1179147639	0.1779050026
H	-0.6105886717	-1.6353599413	3.1083464016
H	-1.5748559129	0.5626571008	0.9281497067
H	-2.2728548584	1.8488868535	-1.6704477691
H	-1.3551457743	5.0026785972	2.0472084308
H	-2.4650252844	3.1022756924	0.9080933667
H	1.0554056685	2.4930077944	-1.4872148018
H	2.1577236361	4.4018088819	-0.3598910825
H	0.9601787738	5.6589788533	1.4208910759
H	-5.9426674007	-0.0763646591	-0.2490344327
H	-5.7162863777	-1.2102578311	-1.6028696893
H	-5.7633189216	-1.8162080976	0.0759692120
H	-2.1934693270	-2.5997289886	-2.6899578545
H	-2.9283153289	-0.9965249992	-2.9219802146
H	-3.9515042987	-2.4305108589	-2.6868590384
H	-4.1040349128	-3.4926182701	-0.3208366348
H	-2.3702073398	-3.7594013206	-0.3858279875
H	-3.0801736709	-2.8617160396	0.9844674322
H	-0.7333316764	1.0058467111	-1.7329920292
H	-0.5179935001	-2.6080587121	-0.6887668791
C	3.1278259663	-0.9697488389	-0.6550499520
C	4.0487018649	-1.7375823298	-1.3834347871
C	3.3885538691	0.3971242504	-0.4670438494
C	5.1984274150	-1.1570285158	-1.9200987382
H	3.8611448105	-2.7978460808	-1.5400289948
C	4.5379058511	0.9760307487	-1.0015274623
H	2.6951577644	1.0222191008	0.0893818020
C	5.4467462901	0.2018969244	-1.7293421011
H	5.8962697018	-1.7668158144	-2.4861201107
H	4.7250175029	2.0354226830	-0.8515237541
H	6.3411542863	0.6573947774	-2.1436073742

Structure: E_c2_endo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00111226

1 imaginary frequency.

Zero-point correction= 0.522360 (Hartree/Particle)
Thermal correction to Energy= 0.549879
Thermal correction to Enthalpy= 0.550823

Thermal correction to Gibbs Free Energy= 0.462536
Sum of electronic and ZPE= -1231.478752
Sum of electronic and thermal Energies= -1231.451233
Sum of electronic and thermal Enthalpies= -1231.450289
Sum of electronic and thermal Free Energies= -1231.538577

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	345.054	107.872	185.817

C	-0.1629446729	2.7276837100	1.7053344547
C	0.9508576796	2.5082433124	0.8840185957
C	1.3148774607	3.4993638107	-0.0400117117
C	0.5707080132	4.6747616830	-0.1425230163
C	-0.5417630794	4.8819318861	0.6768506971
C	-0.9056419661	3.9073320826	1.6062472041
C	1.7571268929	1.2291141210	1.0035850973
C	1.9297579962	0.4722569718	-0.3529774210
N	1.7168517935	-0.9785204540	-0.2856771392
C	2.9655588471	-1.7636201539	-0.5564002569
N	3.8787538315	-0.6888418198	-0.9494087895
C	3.3606717233	0.5729278886	-0.8722669954
C	0.5126850903	-1.5417881050	-0.1567972839
C	3.4367499755	-2.4718848072	0.7249023186
C	2.7641057392	-2.7601582182	-1.7091632301
C	5.2551031665	-0.9223211977	-1.3639508677
O	3.9374509271	1.6142343322	-1.1303366117
C	-0.6937972416	-0.8799550043	0.0138355260
C	-1.9769545068	-1.5458986823	-0.1903858008
C	-2.7133992643	-1.9678072768	1.4060532922
C	-2.2050972060	-0.8848001528	2.3594090810
C	-0.8764230751	-1.4440031067	2.7430113157
C	-0.8896596693	-2.8240786942	2.5646469643
C	-2.0369850594	-3.1610160565	1.8423059384
H	-0.1226558146	-3.5134377987	2.8991218570
H	-2.3194241712	-4.1679012716	1.5501003103
H	-0.0948338494	-0.8820285029	3.2426202600
H	-2.8492483295	-0.8972693745	3.2548269783
H	-2.2003747009	0.1373800667	1.9814516276
H	-3.7779164263	-2.0292833246	1.1948540678
H	-1.8629537172	-2.5247443245	-0.6563454644
H	-0.6840633206	0.1993674061	0.1147476538
H	-0.4357962657	1.9838952214	2.4525014878
H	-1.7588782766	4.0668401282	2.2599969086
H	-1.1146570252	5.8012955438	0.5975485958
H	0.8666229893	5.4355491993	-0.8592563371
H	2.1908952280	3.3502583265	-0.6667121118
H	2.7529056497	1.4526273275	1.4042927271
H	1.2762250603	0.5560188079	1.7204935588
H	1.2469079048	0.8967408263	-1.0983178665
H	3.7165354212	-3.2380635859	-1.9548321936
H	2.0700926133	-3.5603179608	-1.4351960998
H	2.3893528477	-2.2493493882	-2.6006670995
H	3.5944417237	-1.7484888549	1.5301348758
H	4.3747622888	-3.0062787051	0.5475590774
H	2.6950816792	-3.2091518664	1.0504017302

H	5.8202642505	-1.4451440868	-0.5855550285
H	5.3009163001	-1.4990924838	-2.2933027821
H	5.7035112323	0.0578171341	-1.5329122118
H	0.5032685903	-2.6261421019	-0.2347331211
C	-3.0541541598	-0.7690114135	-0.9106433273
C	-3.9149720726	-1.4669151729	-1.7714403082
C	-3.2436826464	0.6112300883	-0.7420485728
C	-4.9339862019	-0.8049438625	-2.4550112501
H	-3.7813843082	-2.5370905252	-1.9149774855
C	-4.2646327118	1.2721861261	-1.4243747343
H	-2.5919543057	1.1920744765	-0.0949657019
C	-5.1129709309	0.5681150031	-2.2815445798
H	-5.5838290831	-1.3614480007	-3.1238818288
H	-4.3924758203	2.3422101746	-1.2895561569
H	-5.9052440369	1.0871976804	-2.8125138154

Structure: E_c2_exo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00184563

1 imaginary frequency.

Zero-point correction= 0.522025 (Hartree/Particle)
Thermal correction to Energy= 0.549684
Thermal correction to Enthalpy= 0.550628
Thermal correction to Gibbs Free Energy= 0.461928
Sum of electronic and ZPE= -1231.479821
Sum of electronic and thermal Energies= -1231.452162
Sum of electronic and thermal Enthalpies= -1231.451218
Sum of electronic and thermal Free Energies= -1231.539918

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.932	108.118	186.685

C	1.5891254193	3.4268240810	-0.2072759101
C	1.0900460286	2.5028914017	0.7234585618
C	-0.0656877223	2.8301530831	1.4441935040
C	-0.7158579709	4.0503257552	1.2425772784
C	-0.2162446118	4.9587153003	0.3094747610
C	0.9375027487	4.6430174494	-0.4122478843
C	1.7902450478	1.1765485799	0.9543412234
C	1.9781639191	0.3413853568	-0.3528513917
N	1.7050074030	-1.0956637314	-0.2235572756
C	2.9222629189	-1.9440114003	-0.4393312255
N	3.8927594918	-0.9255595362	-0.8421416762
C	3.4285212764	0.3591734438	-0.8294297152
C	0.4756602115	-1.6089121484	-0.1078829652
O	4.0615649900	1.3616007953	-1.1094524017
C	5.2697587562	-1.2335372509	-1.2016610130
C	2.7043168789	-2.9689705988	-1.5644627089
C	3.3302586376	-2.6297363854	0.8755824442
C	-0.7096590146	-0.9047480785	0.0234907321

C	-1.9945180795	-1.5484772557	-0.1548102805
C	-0.9661062480	-1.5167872527	2.9308831992
C	-1.8539241330	-0.4592011449	2.9892931694
C	-2.9733939555	-0.7693206398	2.1950570488
C	-2.7529044836	-1.9895200287	1.4907617963
C	-1.6169532134	-2.6728534638	2.2483343638
H	-1.8947194520	-2.5793843902	-0.5012724827
H	-3.6128321816	-2.5701670801	1.1649944374
H	-2.0737316383	-3.3131410916	3.0215393543
H	-0.6745743758	0.1756905430	0.1090327761
H	0.0052466907	-1.5564968053	3.4117150763
H	-1.7057515860	0.4649831482	3.5354044379
H	-3.8377127438	-0.1290487842	2.0580707437
H	-0.9509421148	-3.3107977190	1.6648142755
H	3.5014444401	-1.8866295357	1.6598598077
H	2.3706158482	-2.4728487254	-2.4802552188
H	1.9719417681	-3.7309502525	-1.2814446056
H	3.6407962942	-3.4937596216	-1.7727749340
H	4.2466170517	-3.2117365001	0.7397424010
H	2.5484194678	-3.3216984501	1.2065960737
H	5.3192571659	-1.8529186311	-2.1029467722
H	5.7884807136	-1.7436297237	-0.3834818482
H	5.7642472064	-0.2812604667	-1.3988216817
H	1.3364277143	0.7525993235	-1.1413242502
H	2.7762134827	1.3465641414	1.4027920958
H	-0.4484490291	2.1332313746	2.1871448425
H	1.2187130023	0.5793449496	1.6720720828
H	2.4943879492	3.1913088209	-0.7610745018
H	1.3378024513	5.3502924126	-1.1331329265
H	-0.7169861592	5.9094496185	0.1507916672
H	-1.6045561574	4.2929311475	1.8192082399
H	0.4306225208	-2.6933762474	-0.1723449410
C	-3.0667443290	-0.8328972640	-0.9262361014
C	-3.9177254140	-1.5872168483	-1.7474011498
C	-3.2519677000	0.5569190542	-0.8574225980
C	-4.9257306243	-0.9712114906	-2.4899483035
H	-3.7859252895	-2.6652651637	-1.8142609655
C	-4.2598546668	1.1716141627	-1.5976820653
H	-2.6085126899	1.1726884946	-0.2339369458
C	-5.0999220103	0.4104680245	-2.4159828604
H	-5.5705712147	-1.5712279779	-3.1250901366
H	-4.3868193688	2.2487006934	-1.5401568936
H	-5.8831863176	0.8938955294	-2.9920597633

Structure: Z_a1_endo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1231.99945351

1 imaginary frequency.

Zero-point correction= 0.522562 (Hartree/Particle)
Thermal correction to Energy= 0.549978
Thermal correction to Enthalpy= 0.550922
Thermal correction to Gibbs Free Energy= 0.463407
Sum of electronic and ZPE= -1231.476891

Sum of electronic and thermal Energies= -1231.449476
Sum of electronic and thermal Enthalpies= -1231.448532
Sum of electronic and thermal Free Energies= -1231.536046

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	345.116	107.876	184.190

C	-2.0066078276	-3.1109382640	-1.7922888742
C	-2.0794780525	-3.2227105504	-0.4073100718
C	-3.3158743906	-2.5394659317	0.0739118736
C	-3.5629047928	-1.5495549157	-1.0646768004
C	-2.9563311723	-2.1731991790	-2.2076700201
C	-2.4785357322	-0.1297828464	-0.6565363286
C	-1.3073340795	-0.6049809604	0.0677525788
C	-0.0887029089	-0.7837083981	-0.5753561418
N	1.1385311778	-0.9797573771	-0.0906431890
C	2.2854894729	-1.1627949445	-1.0037454332
C	3.4486782152	-1.3933955446	-0.0481594233
N	2.9766755122	-1.3138771486	1.2287826556
C	1.5402904588	-1.0419467144	1.3549443048
C	2.5677678854	0.0076483262	-1.9806542885
C	2.7361268668	1.3661807919	-1.3338145149
C	1.6824121639	2.2901765281	-1.3300978778
C	1.8245993628	3.5386948044	-0.7217947323
C	3.0303416042	3.8821931908	-0.1087337814
C	4.0922596081	2.9746102196	-0.1160507184
C	3.9488513708	1.7276703394	-0.7259328175
C	1.2937706323	0.3045546983	2.0544278982
C	0.8526535723	-2.2156156261	2.0751239693
C	3.8669023471	-1.4466738934	2.3733391191
O	4.5986033005	-1.5971678044	-0.3940361915
H	2.1410603420	-2.0775018897	-1.5935139974
H	3.8904057009	-0.5282525129	2.9684141267
H	3.5747495591	-2.2855372799	3.0130061741
H	4.8638272032	-1.6371377543	1.9731033903
H	1.0464896918	-3.1534672935	1.5455521545
H	1.2497343136	-2.3064767373	3.0899108614
H	-0.2259386346	-2.0710656556	2.1639963928
H	1.8357657508	1.1026094907	1.5417343163
H	0.2313564940	0.5592272096	2.0714700040
H	1.6364239634	0.2507803765	3.0918846077
H	3.4812061836	-0.2862419621	-2.5102167645
H	1.7699487636	0.0432871491	-2.7323046672
H	0.7454850621	2.0404384596	-1.8243233143
H	5.0402648312	3.2424345546	0.3420091620
H	3.1472867768	4.8557933262	0.3584874434
H	0.9991979920	4.2450701897	-0.7366862315
H	4.7836154839	1.0324583951	-0.7392083520
H	-2.2281477282	0.2468106979	-1.6478439312
H	-4.5453171508	-1.0985732304	-1.1768621862
H	-3.1302596036	-1.8725841335	-3.2363327739
H	-1.3057944241	-3.6330480739	-2.4339473297
H	-1.3600051241	-0.6461522153	1.1465760975
H	-1.4453123535	-3.8498930402	0.2095757775
H	-4.1371561345	-3.2754964376	0.0602829431

H	-3.2739310501	-2.1255519409	1.0810483459
H	-0.1055926737	-0.7374069072	-1.6627866033
C	-3.3911970844	0.8481341921	0.0407006182
C	-3.9816181817	1.8688963066	-0.7197699682
C	-3.6906874373	0.7727376141	1.4095920907
C	-4.8387346927	2.7967473216	-0.1291877622
H	-3.7623333784	1.9432490659	-1.7826994901
C	-4.5497044955	1.6985771067	2.0003563411
H	-3.2524884369	-0.0022640809	2.0329579702
C	-5.1265129504	2.7134087708	1.2337000734
H	-5.2786403627	3.5842378262	-0.7338797956
H	-4.7664467261	1.6283147765	3.0622633581
H	-5.7943300832	3.4336805160	1.6964967237

Structure: Z_a1_exo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00048365

1 imaginary frequency.

Zero-point correction= 0.522084 (Hartree/Particle)
Thermal correction to Energy= 0.549676
Thermal correction to Enthalpy= 0.550620
Thermal correction to Gibbs Free Energy= 0.462199
Sum of electronic and ZPE= -1231.478400
Sum of electronic and thermal Energies= -1231.450807
Sum of electronic and thermal Enthalpies= -1231.449863
Sum of electronic and thermal Free Energies= -1231.538285

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.927	108.150	186.099

C	-3.1077217422	-3.1380700467	0.2706656293
C	-2.1733371206	-3.2797029398	-0.7379471336
C	-2.5911365841	-2.4668707131	-1.9176889099
C	-3.5581984476	-1.4731416911	-1.2817015184
C	-4.0016872909	-2.1111201414	-0.0885749279
C	-1.2703888361	-0.5805934086	-0.0537429639
C	-2.4283182630	-0.0585730683	-0.7429641881
C	-0.0565681339	-0.7173346316	-0.7127661038
N	1.1677948716	-0.9843554233	-0.2514824835
C	2.3145051718	-1.0745575818	-1.1785165581
C	3.4741429213	-1.4224535135	-0.2536988056
N	2.9976806683	-1.4941392170	1.0218794125
C	1.5640493085	-1.2236362307	1.1766621958
C	2.6101334521	0.1945624027	-2.0173546751
C	2.7893643037	1.4711004286	-1.2231991614
C	4.0123745560	1.7638552430	-0.5994640560
C	4.1674032788	2.9357067669	0.1423658964
C	3.1068364255	3.8359799995	0.2685921087
C	1.8901181732	3.5611755826	-0.3573996527
C	1.7362081415	2.3874569600	-1.0974489307

C	1.3345200036	0.0320101000	2.0340747093
C	0.8585056132	-2.4660318193	1.7475845877
C	3.8832970044	-1.7615666716	2.1462011120
O	4.6243336308	-1.5897575458	-0.6177917663
H	-1.7776675066	-2.0493741726	-2.5132164895
H	-3.1782659736	-3.1148797279	-2.5899154905
H	-4.2750815807	-0.9355201648	-1.8974367061
H	-1.3363252220	-3.9691825141	-0.7349580107
H	-4.8478006450	-1.7843211085	0.5055557722
H	-3.1349333230	-3.7020364702	1.1960520573
H	-2.1931980213	0.2729971991	-1.7564099929
H	-1.3265649714	-0.7159465638	1.0174869488
H	3.5817933603	-2.6640097197	2.6874827111
H	3.9118129720	-0.9155868184	2.8402101264
H	4.8799871577	-1.9141372212	1.7295049320
H	0.2763405852	0.2993113876	2.0820236586
H	1.6737752944	-0.1518602283	3.0577432518
H	1.0599001830	-3.3389399249	1.1191635389
H	-0.2215114952	-2.3269515459	1.8254799118
H	1.2343668310	-2.6721997117	2.7536623452
H	2.1630082107	-1.9158519692	-1.8676874717
H	1.8149576995	0.3221433096	-2.7620135185
H	3.5219178001	-0.0468135117	-2.5754132097
H	1.8901771913	0.8780733034	1.6230222683
H	4.8458948272	1.0747758642	-0.7034931299
H	5.1234160477	3.1519984682	0.6109344173
H	3.2330065331	4.7519177051	0.8387077908
H	1.0650852621	4.2638864933	-0.2796639570
H	0.7896189273	2.1926829920	-1.5980637717
H	-0.0656388081	-0.5503839738	-1.7885846623
C	-3.3185766091	0.9334087350	-0.0534653790
C	-3.8723770520	1.9766330757	-0.8098763596
C	-3.6200408855	0.8615009099	1.3154538821
C	-4.6987714168	2.9308368980	-0.2148461363
H	-3.6497203485	2.0486332762	-1.8723938696
C	-4.4462137897	1.8126782488	1.9103219690
H	-3.2130737749	0.0603535801	1.9275938119
C	-4.9879893619	2.8512312839	1.1470174467
H	-5.1140815262	3.7338949076	-0.8163518045
H	-4.6670500340	1.7454031898	2.9716236945
H	-5.6318296433	3.5908946794	1.6132146079

Structure: Z_a2_endo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1231.99825704

1 imaginary frequency.

Zero-point correction= 0.522489 (Hartree/Particle)
Thermal correction to Energy= 0.549991
Thermal correction to Enthalpy= 0.550935
Thermal correction to Gibbs Free Energy= 0.463215
Sum of electronic and ZPE= -1231.475768

Sum of electronic and thermal Energies= -1231.448266
Sum of electronic and thermal Enthalpies= -1231.447322
Sum of electronic and thermal Free Energies= -1231.535042

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	345.125	107.989	184.623

C	-2.2342473472	2.4302296631	1.1356805672
C	-0.8518480952	2.7051680361	0.6432476891
C	-0.9177995772	3.1749406613	-0.6597858989
C	-2.2252006640	2.9899051851	-1.1337913054
C	-2.9914532390	2.2562847521	-0.1780617057
C	-1.4315360625	0.0211371521	-0.0680495016
C	-2.6892989383	0.4637289381	-0.6400408309
C	-0.2977961185	-0.1516357996	-0.8514949291
N	0.8217265206	-0.8391839218	-0.6062403739
C	1.8970387417	-0.9081351842	-1.6167971373
C	2.8096850555	-1.9993524606	-1.0737681137
N	2.3190323461	-2.4067639901	0.1305391278
C	1.0655421416	-1.7690109842	0.5508019568
C	2.6764634549	0.4044234993	-1.8825202074
C	3.3445641833	1.0412557220	-0.6800684968
C	4.5187839510	0.5042502371	-0.1284335557
C	5.1198079647	1.1013778175	0.9808906244
C	4.5686026754	2.2506894009	1.5515992845
C	3.4147991611	2.8075780313	0.9982328194
C	2.8123523376	2.2036699607	-0.1073758782
C	1.2603991496	-0.9858146279	1.8589449944
C	-0.0419732932	-2.8330517956	0.6581755844
C	3.0070313245	-3.4151558858	0.9245454699
O	3.8188972258	-2.3975402678	-1.6283715272
H	0.0398731292	2.6755488911	1.2595704339
H	-0.0941625354	3.5876136499	-1.2306432638
H	-2.5765320016	3.2672030495	-2.1229063364
H	-4.0746989496	2.3304716475	-0.1935359858
H	-2.6125181949	3.3487978849	1.6152700398
H	-2.3291449310	1.6294205876	1.8689162016
H	-1.4420374959	-0.3582495700	0.9441278559
H	-2.6580321381	0.5243419500	-1.7268821197
H	0.2230848387	-3.5533883036	1.4369666368
H	-0.1454825356	-3.3698027740	-0.2892165764
H	-1.0099015760	-2.4068741643	0.9260167556
H	0.3499509013	-0.4506848514	2.1415662534
H	1.4977326437	-1.6755527286	2.6742511425
H	2.0761825958	-0.2662175544	1.7555171123
H	2.3861427415	-4.3044094819	1.0715723261
H	3.3056000314	-3.0162166491	1.8991490191
H	3.9003254037	-3.6964871170	0.3649612750
H	1.4755508049	-1.2519220565	-2.5700040673
H	2.9971740106	3.7208244360	1.4144852511
H	1.9308272981	2.6564480981	-0.5542753453
H	1.9978878184	1.1232163023	-2.3579779608
H	3.4243349891	0.1345125808	-2.6373963112
H	5.0459238362	2.7194168866	2.4072541871
H	6.0319400777	0.6757544326	1.3896281099

H	4.9700003813	-0.3761206225	-0.5764953303
H	-0.3075604240	0.3020010566	-1.8424695063
C	-3.9547977131	-0.2197166080	-0.1967222385
C	-4.9594689297	-0.4507807052	-1.1489709888
C	-4.1794201971	-0.6235673136	1.1289325173
C	-6.1513501380	-1.0801181532	-0.7915787191
H	-4.8037074672	-0.1440419076	-2.1808563743
C	-5.3724208179	-1.2488934548	1.4872522614
H	-3.4255405961	-0.4593873475	1.8944143176
C	-6.3621068231	-1.4798029257	0.5286807186
H	-6.9126359688	-1.2586516923	-1.5451214531
H	-5.5285648666	-1.5586525687	2.5164216944
H	-7.2899641001	-1.9684640428	0.8101248116

Structure: Z_a2_exo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00099134

1 imaginary frequency.

Zero-point correction= 0.522056 (Hartree/Particle)
Thermal correction to Energy= 0.549672
Thermal correction to Enthalpy= 0.550616
Thermal correction to Gibbs Free Energy= 0.462536
Sum of electronic and ZPE= -1231.478935
Sum of electronic and thermal Energies= -1231.451320
Sum of electronic and thermal Enthalpies= -1231.450375
Sum of electronic and thermal Free Energies= -1231.538456

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.924	108.228	185.380

C	-1.6098959615	2.3253129434	1.8926134534
C	-0.6320957190	2.5211409750	0.9385526227
C	-1.2762835348	2.8015954353	-0.3785019642
C	-2.6864522572	2.2692066946	-0.1608624359
C	-2.8626733462	2.2560599781	1.2462268475
C	-1.3519335215	-0.1552632266	-0.0721033478
C	-2.5220058834	0.4179999810	-0.6864848166
C	-0.1876739765	-0.3473823249	-0.8019304084
N	0.9200583255	-1.0354513051	-0.5049582050
C	1.9957817445	-1.2064786897	-1.5042691008
C	2.9875236571	-2.1136591103	-0.7853657252
N	2.4685013498	-2.4375517263	0.4317515847
C	1.1561669663	-1.8544407109	0.7320505562
C	2.6627159843	0.0807237656	-2.0435811060
C	3.1639442022	1.0728234202	-1.0126967379
C	4.2426076973	0.7697438390	-0.1660851496
C	4.6974266292	1.7020049895	0.7679789144
C	4.0972323973	2.9597947181	0.8622090636
C	3.0434198576	3.2839000008	0.0066948974
C	2.5817207945	2.3438290840	-0.9189133303

C	1.2396856997	-0.9580461283	1.9780870630
C	0.1078451814	-2.9732982546	0.8708428088
C	3.1891975070	-3.3000118361	1.3575074207
O	4.0605992736	-2.4662676405	-1.2424005808
H	0.4372343891	2.5724667103	1.1115670168
H	-2.3771056247	0.6404468940	-1.7451638493
H	-3.5037022115	2.5744805230	-0.8088436690
H	-3.8149843805	2.1171116554	1.7460949850
H	-1.4457417379	2.2138998453	2.9583914622
H	-0.7373792709	2.4250170485	-1.2493672978
H	-1.4447067094	-0.5731981697	0.9201381614
H	-1.3516399938	3.8954815856	-0.4988947576
H	3.4930474619	-0.2845738337	-2.6605200480
H	1.9687306382	0.5813528965	-2.7289584786
H	1.7821661490	2.6158031726	-1.6058819984
H	2.5965189227	4.2742296805	0.0429426618
H	4.4649112996	3.6889734727	1.5783390127
H	4.7479951575	-0.1867826746	-0.2594167324
H	5.5390329882	1.4525838858	1.4080964396
H	1.6048853859	-1.7644982823	-2.3660675003
H	3.4306530078	-2.7737150133	2.2865612415
H	2.6163648059	-4.2027676847	1.5918494868
H	4.1164794073	-3.5873888176	0.8596897014
H	0.3660984313	-3.6140672331	1.7186105759
H	-0.8958230231	-2.5839210436	1.0498473582
H	0.0875377077	-3.5879324194	-0.0336941436
H	0.2982715763	-0.4358216388	2.1625913385
H	2.0357831243	-0.2183971311	1.8556000673
H	1.4558753227	-1.5662704179	2.8611635930
H	-0.1553789039	0.0855418424	-1.8005794696
C	-3.8731081151	-0.1787546503	-0.4426506596
C	-4.7999146207	-0.1888745875	-1.4960766893
C	-4.2500794467	-0.7356988243	0.7900028408
C	-6.0665951338	-0.7495280925	-1.3291807704
H	-4.5249762080	0.2368457012	-2.4587532098
C	-5.5152193731	-1.2936017864	0.9581652319
H	-3.5587674277	-0.7362438617	1.6290612882
C	-6.4279140351	-1.3030581301	-0.1012313942
H	-6.7674733694	-0.7534833600	-2.1585706112
H	-5.7904954325	-1.7238767594	1.9166722450
H	-7.4133158249	-1.7388433730	0.0330632470

Structure: Z_b2_endo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1231.99876913

1 imaginary frequency.

Zero-point correction= 0.522190 (Hartree/Particle)
Thermal correction to Energy= 0.549862
Thermal correction to Enthalpy= 0.550807
Thermal correction to Gibbs Free Energy= 0.462264
Sum of electronic and ZPE= -1231.476579

Sum of electronic and thermal Energies= -1231.448907
Sum of electronic and thermal Enthalpies= -1231.447963
Sum of electronic and thermal Free Energies= -1231.536505

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	345.044	108.202	186.353

C	2.3267397607	2.4099862353	-1.6706637663
C	2.7328667817	1.9885152584	-0.3949716784
C	2.6873444612	2.9176412348	0.6544853620
C	2.2453209706	4.2257897401	0.4418575821
C	1.8270726521	4.6254114250	-0.8285363243
C	1.8718414116	3.7127179675	-1.8845301271
C	3.2998224204	0.6024254080	-0.1453061211
C	2.5719040835	-0.5956914257	-0.7879793275
N	1.3062405879	-1.0291081529	-0.1564243124
C	1.3424016091	-2.4740562063	0.2538260712
N	2.7275674332	-2.8242431098	-0.0749073138
C	3.4498473345	-1.8400519080	-0.6835354542
C	0.2255100739	-0.2370599717	-0.1664704211
C	1.0962854359	-2.6255649925	1.7639734266
C	0.3721881991	-3.3207001391	-0.5909668634
C	3.2956592371	-4.1438503336	0.1637190126
O	4.6034778148	-1.9059745775	-1.0644282533
C	-1.0700633304	-0.4758167209	0.2694782128
C	-2.1567248619	0.4085845608	-0.1195083936
C	-2.6295958652	1.4899486166	1.3116285001
C	-1.6242220368	2.5073219464	1.3464066846
C	-0.5441866073	2.0898389349	2.1362900779
C	-0.8840085919	0.8891411399	2.7401938543
C	-2.3382886059	0.6247516845	2.5363497420
H	2.3963685545	-0.3959732137	-1.8521511534
H	3.3867683577	0.4228252970	0.9327515060
H	4.3200823162	0.5471832359	-0.5481016044
H	3.0320291843	2.6208641792	1.6432026315
H	2.2409852974	4.9346138175	1.2657193657
H	1.4883161333	5.6431711527	-0.9992129168
H	2.3855637275	1.7292022923	-2.5169346313
H	1.5702885743	4.0190014009	-2.8823328685
H	-0.6710023383	-3.0428948012	-0.4307862599
H	0.4764074926	-4.3762961788	-0.3242369078
H	0.6025470474	-3.2085283751	-1.6543620138
H	0.0913202556	-2.3024446296	2.0441640983
H	1.1955333528	-3.6749605421	2.0554443430
H	1.8269824677	-2.0378790091	2.3272597762
H	2.7641482408	-4.9179673555	-0.3992318912
H	3.2800455740	-4.3964263292	1.2285465788
H	4.3309939191	-4.1051100551	-0.1781996708
H	-1.8451760160	1.1504194176	-0.8538913197
H	-3.6542105697	1.7670015589	1.0800328529
H	-1.6434995344	3.4156705355	0.7522493235
H	-2.6282662296	-0.4243569741	2.4749903708
H	-2.8872331807	1.0574384201	3.3895382744
H	-1.3223890305	-1.4150674213	0.7410898580
H	0.4104216266	2.5948481341	2.2100160801

H	-0.2392593210	0.3012312104	3.3845955133
H	0.4227915204	0.7316943564	-0.6205402504
C	-3.4656242208	-0.2093710215	-0.5378469555
C	-4.1955212329	0.4058296281	-1.5668352038
C	-3.9947526219	-1.3629890188	0.0615307719
C	-5.4140800836	-0.1202309735	-1.9936760478
H	-3.8016077237	1.3002300375	-2.0445369603
C	-5.2147357294	-1.8878460876	-0.3625767229
H	-3.4591140330	-1.8703671430	0.8595200978
C	-5.9286974132	-1.2689352624	-1.3911321755
H	-5.9584110720	0.3662528901	-2.7976388672
H	-5.6067185152	-2.7839832570	0.1095427231
H	-6.8779321437	-1.6806955295	-1.7203059141

Structure: Z_b2_exo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1232.00129194

1 imaginary frequency.

Zero-point correction= 0.521819 (Hartree/Particle)
Thermal correction to Energy= 0.549601
Thermal correction to Enthalpy= 0.550545
Thermal correction to Gibbs Free Energy= 0.461423
Sum of electronic and ZPE= -1231.479473
Sum of electronic and thermal Energies= -1231.451691
Sum of electronic and thermal Enthalpies= -1231.450747
Sum of electronic and thermal Free Energies= -1231.539869

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.880	108.371	187.574

C	2.3035555310	2.9142114590	0.8203083342
C	2.6630538578	2.1288885031	-0.2835172543
C	2.4522661180	2.6517121210	-1.5696670744
C	1.8878523308	3.9155525357	-1.7447879527
C	1.5326556745	4.6874044906	-0.6354272711
C	1.7483663922	4.1857887340	0.6486492674
C	3.3218441182	0.7782236574	-0.0839900867
C	2.6663844749	-0.4219587221	-0.8023207595
N	1.4082608743	-0.9326910817	-0.2188616549
C	1.5089352709	-2.3791088991	0.1748744821
N	2.9079504407	-2.6626864378	-0.1588817273
C	3.5935930549	-1.6309990095	-0.7310920882
C	0.2940116500	-0.1882082318	-0.2359098867
C	1.2675457712	-2.5568780734	1.6830120588
C	0.5782391222	-3.2588034952	-0.6801356254
C	3.5336186619	-3.9599049706	0.0566736227
O	4.7524718822	-1.6368922437	-1.1016675016
C	-0.9945708955	-0.4870937845	0.1816382464
C	-2.0935424091	0.3777350696	-0.1729478354
C	-2.5803343075	1.4532369639	1.3316364973

C	-1.2378947472	1.9734753195	1.8294801115
C	-0.8280293680	0.8999655858	2.7800245285
C	-1.9337095994	0.1566439893	3.1429027101
C	-3.0196359193	0.5449289587	2.3314875729
H	0.1675232407	0.8032356790	3.1989366649
H	-1.2160699159	-1.4412966301	0.6390411416
H	-1.9609401793	-0.6149225209	3.9039688203
H	-1.4387896560	2.8874988056	2.4142117104
H	-4.0226226251	0.1378854599	2.3962721831
H	-0.4930449402	2.2436458886	1.0794096136
H	-3.2940621162	2.1245463602	0.8612131257
H	-1.7778490025	1.2187494203	-0.7928751555
H	0.7510542671	-4.3126866119	-0.4443919405
H	-0.4773580541	-3.0515748167	-0.4964667291
H	0.7843089412	-3.1040961891	-1.7431118271
H	0.2579077387	-2.2527472603	1.9679445346
H	1.3864867278	-3.6078688936	1.9615262969
H	1.9877722043	-1.9628008429	2.2531293164
H	3.0522147866	-4.7429660917	-0.5381152219
H	3.5080086254	-4.2421276629	1.1139345098
H	4.5726496652	-3.8623937352	-0.2615295687
H	2.5046996930	-0.1739966295	-1.8584625002
H	2.4898839411	2.5395909965	1.8249105712
H	1.4987196053	4.7876827785	1.5184253175
H	1.1074837397	5.6774092277	-0.7723151100
H	1.7423221895	4.3053954887	-2.7482710178
H	2.7526177646	2.0792688119	-2.4447865175
H	4.3480646058	0.8038486205	-0.4724286374
H	3.4007494041	0.5493454264	0.9851674964
H	0.4546712736	0.7898056216	-0.6841862433
C	-3.3792211097	-0.2051204808	-0.6758962749
C	-4.0817562861	0.4861378077	-1.6743375764
C	-3.9070231411	-1.4149928353	-0.1976726156
C	-5.2754869403	-0.0197148130	-2.1903056321
H	-3.6866945199	1.4242460699	-2.0583598352
C	-5.0998381047	-1.9197951098	-0.7105000028
H	-3.3909632511	-1.9721076842	0.5803635933
C	-5.7880049981	-1.2241779195	-1.7093035108
H	-5.8013318663	0.5274774206	-2.9670027073
H	-5.4933257168	-2.8590595307	-0.3327834338
H	-6.7172839701	-1.6205750638	-2.1071855516

Structure: Z_c2_endo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1231.99543896

1 imaginary frequency.

Zero-point correction= 0.522117 (Hartree/Particle)
Thermal correction to Energy= 0.549828
Thermal correction to Enthalpy= 0.550773
Thermal correction to Gibbs Free Energy= 0.461175
Sum of electronic and ZPE= -1231.473322

Sum of electronic and thermal Energies= -1231.445611
Sum of electronic and thermal Enthalpies= -1231.444666
Sum of electronic and thermal Free Energies= -1231.534263

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	345.022	108.107	188.573

C	1.7277548118	-2.8306788398	1.4192209841
C	2.8667958394	-1.9707391950	1.2758914672
C	2.7712751853	-1.0198031607	2.4688268087
C	1.3043553037	-1.0455946470	2.7412985664
C	0.7650466841	-2.2204455950	2.2317941045
C	1.5853512607	0.1630525201	0.2258311549
C	2.4874662804	-0.9066846741	-0.1764857588
C	0.2285310479	0.1039150113	-0.0594922301
N	-0.7125878769	1.0520727013	-0.0205596129
C	-2.1154482113	0.7177768502	-0.3528296995
C	-2.7936332661	2.0833212874	-0.3473321285
N	-1.8610079472	3.0246361520	-0.0164559515
C	-0.5069901311	2.5172688087	0.2213195498
C	-2.7868605533	-0.2848937364	0.6358027164
C	-3.7129357153	-1.2820843531	-0.0356047225
C	-3.4129384050	-2.6496366189	0.0005326172
C	-4.2509708459	-3.5839561233	-0.6106719960
C	-5.4021877413	-3.1567387206	-1.2724034016
C	-5.7090327163	-1.7948470648	-1.3158858976
C	-4.8737872582	-0.8616583412	-0.7014047593
C	0.4743372068	3.1169242860	-0.8007027896
C	-0.0804509924	2.7848981797	1.6752587959
C	-2.2130168343	4.4349236981	0.0791707042
O	-3.9734984642	2.2859633159	-0.5721309124
H	2.0184498636	1.0811450052	0.5983985604
H	2.0114465157	-1.6173129530	-0.8511190526
H	3.8254966885	-2.4131702333	1.0192544990
H	3.2822800839	-1.5005112562	3.3200234659
H	-0.2413682398	-2.5837227317	2.4064145608
H	0.7852148849	-0.3369300782	3.3773792974
H	3.2178433709	-0.0332926037	2.3465856263
H	1.5927449697	-3.7658326435	0.8844271592
H	-0.0212732646	3.8619858613	1.8556795191
H	0.9045881755	2.3648232804	1.8928123682
H	-0.8104959372	2.3573484071	2.3689444773
H	-1.6567918169	5.0357730650	-0.6472241952
H	-2.0319154188	4.8242898845	1.0859880797
H	-3.2787209973	4.5063334366	-0.1427421579
H	1.4781630180	2.6992724443	-0.7026630577
H	0.1176256661	2.9337470465	-1.8181813582
H	0.5511774608	4.1971201378	-0.6483238777
H	-2.1561549045	0.3053119909	-1.3677584268
H	-1.9923375902	-0.8318811090	1.1563646964
H	-3.3251802746	0.2859297918	1.4018569426
H	-5.1143388220	0.1966750724	-0.7403241767
H	-6.6057096842	-1.4558267793	-1.8269960335
H	-6.0578575123	-3.8800760648	-1.7485491382
H	-4.0062922936	-4.6416854495	-0.5668261497

H	-2.5202349977	-2.9924754041	0.5222017380
H	-0.1595639070	-0.8563925997	-0.3972169286
C	3.8431591649	-0.5243374665	-0.7140870547
C	4.3817850645	-1.2809269192	-1.7660397948
C	4.5962830195	0.5422933437	-0.1994859527
C	5.6333509334	-0.9746230352	-2.2989502379
H	3.8125838932	-2.1113759237	-2.1778538739
C	5.8491113778	0.8469690757	-0.7297146477
H	4.2124450219	1.1511331250	0.6147373294
C	6.3717769765	0.0900720372	-1.7808072525
H	6.0285428821	-1.5662520744	-3.1193263880
H	6.4168102873	1.6786516468	-0.3228454661
H	7.3471606810	0.3303139318	-2.1929267077

Structure: Z_c2_exo

B3LYP/6-31(g), gas phase
E(RB3LYP) = -1231.99662786

1 imaginary frequency.

Zero-point correction= 0.521744 (Hartree/Particle)
Thermal correction to Energy= 0.549568
Thermal correction to Enthalpy= 0.550512
Thermal correction to Gibbs Free Energy= 0.460504
Sum of electronic and ZPE= -1231.474884
Sum of electronic and thermal Energies= -1231.447060
Sum of electronic and thermal Enthalpies= -1231.446116
Sum of electronic and thermal Free Energies= -1231.536124

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.859	108.324	189.439

C	1.4317056999	-2.0515938972	2.0941520572
C	1.3093534654	-0.8079463116	2.9104556120
C	2.5640527256	-0.2673870076	3.1138795376
C	3.4865918977	-0.9583398683	2.3026718730
C	2.8023017092	-1.8684327017	1.4514148704
C	2.4064184641	-0.9072727890	-0.1425680328
C	1.5210998387	0.1933573525	0.1576379985
C	0.1607518729	0.0936707641	-0.0924376611
N	-0.7992863890	1.0246053352	-0.0927406503
C	-2.1974449938	0.6426939407	-0.3874327044
C	-2.9056646331	1.9907987545	-0.4507010330
N	-1.9925387419	2.9684493791	-0.1757277659
C	-0.6241491994	2.5040110356	0.0696845889
C	-2.8388222543	-0.3138284475	0.6661582340
C	-3.7040788314	-1.4018447538	0.0592506836
C	-4.8326279671	-1.0825520301	-0.7104815191
C	-5.6164066706	-2.0956853482	-1.2628963296
C	-5.2898042066	-3.4373870306	-1.0523226413
C	-4.1713387006	-3.7634764872	-0.2852538628
C	-3.3839083596	-2.7496692607	0.2636571821

C	-0.1827369152	2.8526154427	1.5015996512
C	0.3286722807	3.0728560626	-0.9962540738
C	-2.3743559401	4.3736974981	-0.1463703474
O	-4.0916150593	2.1526159398	-0.6770602532
H	1.9539575245	1.1412425488	0.4466612554
H	0.3883693402	-0.4648729922	3.3689474050
H	2.7994969560	0.5660374536	3.7658777521
H	4.5516381651	-0.7589790845	2.2609230456
H	3.3348885777	-2.7209433829	1.0376260349
H	1.8888724391	-1.7364906750	-0.6286063058
H	1.5037549680	-2.9087478003	2.7846447927
H	0.5967394402	-2.2585146390	1.4224920196
H	0.3660689161	4.1626238699	-0.9124006337
H	1.3483216829	2.7005546779	-0.8807924985
H	-0.0270141625	2.8133404726	-1.9973539654
H	-0.1100253048	3.9375777990	1.6194876033
H	-0.9114231874	2.4737294068	2.2243763604
H	0.7975670267	2.4299269956	1.7346588036
H	-2.1604497303	4.8234113713	0.8282875889
H	-1.8633974289	4.9445415369	-0.9283645637
H	-3.4496492821	4.4093960072	-0.3270826214
H	-2.2425404783	0.1722961593	-1.3765921008
H	-3.4214095309	0.2875756313	1.3742947616
H	-2.5192467904	-3.0133510483	0.8711740196
H	-3.9124546737	-4.8042538133	-0.1111169355
H	-5.9054553025	-4.2231730038	-1.4805265468
H	-6.4888644487	-1.8351180680	-1.8554807048
H	-5.0918410103	-0.0398639873	-0.8727252401
H	-2.0316299092	-0.7783930952	1.2445107178
H	-0.2175312616	-0.8900579564	-0.3684531840
C	3.7289041191	-0.6463958091	-0.7981315561
C	4.2003206341	-1.5673614297	-1.7455570904
C	4.5121610825	0.4822288449	-0.5091275841
C	5.4175760023	-1.3635729398	-2.3966853816
H	3.6056637472	-2.4467299905	-1.9836309322
C	5.7285414111	0.6853814739	-1.1569965923
H	4.1791587666	1.2114000482	0.2254507123
C	6.1851098073	-0.2366720165	-2.1038078799
H	5.7623928607	-2.0846556197	-3.1317078473
H	6.3213099964	1.5655444284	-0.9255164480
H	7.1333439454	-0.0753689454	-2.6075766739

Listing of Subprograms for Program Suite PROGDYN

A full description and listing of most of the subprograms of PROGDYN can be found in the Supporting Information of a recent publication (S10). We describe here only the differences versus the programs in S19, and this description is facilitated by a description of the overall structure of PROGDYN.

The master control program for dynamics, in the form of a Unix Shell Script, is called *progdynstarterHP*. *progdynstarterHP* takes as necessary input files:

freqinHP - This is the standard output from a Gaussian 98, 03, or 09 frequency calculation using freq=hpmodes. For isotopically labeled compounds, use freq=(hpmodes,readisotopes).

progdyn.conf – This is a file giving a variety of configuration options, called on by many of the subprograms. progdyn.conf contains explanations of many of the program options.

progdynstarterHP takes as optional input files:
isomernumber - A number in file isomernumber provides a start for numbering runs.
detour – A signal file that, by existing, signals the program to do a side calculations
nogo – A signal file that, by existing, signals the program to stop between points
methodfile – A file that contains lines to be added to the end of each g09.com input file, such as lines that call for an NMR calculation

progdynstarterHP calls the following programs:
proggenHP - An awk program that starts a trajectory, giving each mode its zero point energy (if a quasiclassical calculation) plus random additional excitations depending on the temperature.
prog1stpoint – Awk program that creates the first Gaussian input file for each run
prog2ndpoint – Awk program that creates the second Gaussian input file for each run. prog2ndpoint also checks the energy of the first point to see if it fits with the desired energy, and aborts the run if it does not by creating appropriate output in file Echeck
progdynb – Creates subsequent Gaussian input files until run is completed, used the awk
proganal – A program to analyze the latest point and see if a run is done. This program must be redone for each new system. Elaborate changes are often programmed into proganal, such as the automatic changing of configuration variables. proganal creates the output to dynfollowfile and NMRlist or NMRlistdis
randgen – A program that generates random numbers between 0 and 1. These are generated all at once and stored in a file for use by proggenHP.

progdynstarterHP has the following output files:
isomernumber – A running tab of the trajectory number
runpointnumber – a running tab of the point in the trajectory
Echeck – output form where prog2ndpoint checks the energy of the trajectory to see if it fits with the desired energy
geoRecord – A record of all of the geoPlusVel files.
geoPlusVel – Created by proggen, this gives the starting positions, velocities, isotopic masses, excitations of the normal modes, and initial displacements of the normal modes for current run.
g09.com – Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest input file for Gaussian09 for current run and latest point.
olddynrun and *olderdynrun* – files containing the last two outputs from Gaussian, for creation of the next point
traj, traj1, traj2, traj3, etc. – files containing the geometries and energies for each trajectory, numbered by the isomernumber, in a format suitable for reading by Molden.
dyn - A record of the Gaussian outputs.
dynfollowfile – A short record of the runs and their results.
NMRlist or *NMRlistdis* – output of NMR predictions at each point in a trajectory
skipstart - A signal file that, by existing, tells progdynstarterHP that we are in the middle of a run. For trajectories that are propagated forward and backward in time, skipstart keeps track of whether one is in the forward or reverse part.
diagnostics – optional output that follows which subprograms are running and configuration variables, decided by variable in progdyn.conf
vellist – optional output that list the velocities of each atom, decided by variable in progdyn.conf
A number of files starting with *'temp'* are created then later erased.

The control program *progdynstarterHP* and the subprograms *proggenHP*, *prog1stpoint*, *prog2ndpoint*, *progdynb*, and *randgen* are algorithmically identical to those listed in S19. The only differences are in lines that contain paths to input and output files in progdynstarterHP, and these are lines that are routinely modified in changing computer systems.

The awk program *proganal* differed for the current study. An example listing of *proganal*is given below, along with a description of how *proganal* was varied for the various studies.

The configuration file named *progdyn.conf* also differed for the current study. An example listing of *progdyn.conf* is given below, along with a description of how *progdyn.conf* was varied for the various studies.

Program proganal

The version of proganal shown below was used for the trajectories for the reaction of **1** with **2**. For the reactions of **7**, proganal was modified to keep track of the interatomic distances in the forming bonds (using lines "short=Distance(1,11)" and "long=Distance(6,10)"), and the stopping criteria for recrossing and for product formation were "if ((short>2.3) && (long>2.5)) {" and "if ((short<1.8) && (long<2.0)) {", respectively

```
BEGIN {
firsttitle=1
getline < "isomernumber"
isomer=$1
}
/ dichloroket/ {
  if (firsttitle==1) {
    printf("%s %s %s %s %s %s %s  ",$1,$2,$3,$4,$6,$7,$8)
    runpoint=$6
    }
  firsttitle++
  }
/Standard orientation/,/Rotational constants/ {
  if (($1>.5) && ($1<30)) {
    A[$1]=$4;B[$1]=$5;C[$1]=$6
    }
  }

END {
  C2C5=Distance(2,5)
  C4C5=Distance(4,5)
  C2C7=Distance(2,7)
  C4C7=Distance(4,7)
  printf("%s %.3f  %s %.3f  %s %.3f  %s %.3f
","C2C5",C2C5,"C2C7",C2C7,"C4C5",C4C5,"C4C7",C4C7)
  if (runpoint>500) {
    print "Too many points.  XXXX"
    }
  if ((C2C5>2.2) && (C4C5>2.2) && (C2C5<3.0)) {
    print "Recrossed XXXX"
    }
  if ((C2C5>3.0) || (C2C5<1.2) || (C4C5<1.2)) {
    print "Probably bad trajectory XXXX"
    }
  if ((C2C5<1.8) && (C4C7<2.3)) {
    print "Formed light cyclobutanone product XXXX"
    }
  if ((C4C5<1.8) && (C2C7<2.3)) {
    print "Formed heavy cyclobutanone product XXXX"
```

```
    }
  system("date '+%b:%d:%Y %T'")
  system("tail -1 Echeck | grep XXXX")
  }

function Distance(Atom1,Atom2) {
 return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2*Distanc
e(Atom1,Atom2)*Distance(Atom2,Atom3)))
  return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
  B1x=A[Atom2]-A[Atom1]
  B1y=B[Atom2]-B[Atom1]
  B1z=C[Atom2]-C[Atom1]
  B2x=A[Atom3]-A[Atom2]
  B2y=B[Atom3]-B[Atom2]
  B2z=C[Atom3]-C[Atom2]
  B3x=A[Atom4]-A[Atom3]
  B3y=B[Atom4]-B[Atom3]
  B3z=C[Atom4]-C[Atom3]
  modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
  yAx=modB2*(B1x)
  yAy=modB2*(B1y)
  yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
  CP2x=(B2y*B3z)-(B2z*B3y)
  CP2y=(B2z*B3x)-(B2x*B3z)
  CP2z=(B2x*B3y)-(B2y*B3x)
  termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
  CPx=(B1y*B2z)-(B1z*B2y)
  CPy=(B1z*B2x)-(B1x*B2z)
  CPz=(B1x*B2y)-(B1y*B2x)
```

```
  termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
 dihed4=(180/3.141592)*atan2(termY,termX)
 return dihed4
}

function killdyn(isomer) {
  system("rm -f dyn")
}
```

progdyn.conf

The progdyn.conf below is the one used for quasiclassical trajectories for the reaction of **1** with **2** with a ^{44}C in an olefinic carbon of **1**. Other calculations would differ in obvious ways in the lines labeled title and charge. The line labeled method was changed to "method B3LYP/6-31G*" and the lines labeled method3 and controlphase were commented out for reactions of **8**‡. The line labeled classical was changed from "classical 0" to "classical 1" for fully classical simulations.

```
#This is the configuration file for PROGDYN.  This file is read by progdynstarterHP and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running jobs
#***The keywords are case sensitive.  The following keywords should always be defined:***
#***method, charge, multiplicity, memory, processors, title
#*** method --The following word is copied exactly to the gaussian input file.
method mpwpw91/6-31G*
#*** method2 --The options here are restricted, unrestricted, and read. restricted is the default
#If the method is U..., put unrestricted here and the .com files will have in them guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword checkpoint.
method2 restricted
charge 0
multiplicity 1
processors 2
#*** memory --The following "word" is copied exactly to the gaussian input file after %mem=.
memory 200mw
#*** killcheck and checkpoint -- You can use a specifically defined checkpoint file name by putting
#the name after the keyword checkpoint.  This is necessary if you use the read option with method2.
#Defined checkpoint names are an unnecessary modest hastle and if you do not want to bother, use killcheck 1
killcheck 1
#checkpoint dyn20.chk
#*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical calculations
diagnostics 0
#*** title -- the title keyword must be followed by exactly four words
title dichloroketene cis-but mpw1k 298dis2qc44
#*** initialdis -- 0 (default) turns off displacement of the normal modes, so that all trajectories start from the same place
# and only the energies and signs of the motion in the modes are randomized
# 1 gives a flat distribution of displacements where all of the possible values are equally likely
# 2 (recommended) gives a QM-like gaussian distribution of displacements, so that displacements in the middle are more likely
            that
# those at the end by 1/e
```

```
initialdis 2
#*** timestep -- this is the time between points in the trajectory.  Typical values would be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
#*** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 298.15
#*** method3, method4, method5, and method6 -- These keywords let you add extra lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line.  Here are some examples to uncomment if needed
method3 IOp(3/76=0572004280)
#method3 scrf=(pcm,Solvent=water)
#add the line below with big structures to get it to put out the distance matrix and the input orientation
#method3 iop(2/9=2000)
#method4 scrf=(pcm,solvent=dmso,read)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian input files
#such as a gen basis set.  Put after the keyword the number of lines in a file you create called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
#*** numimag --This tells the program the number of imaginary frequencies in the starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in random direction
numimag 1
#*** searchdir -- This keyword says what direction to follow the mode associated with the imaginary frequency.
#The choices are "negative" and "positive".  Positive moves in the direction defined in the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction.  The correct choice can be made either
#by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.
searchdir negative
#*** classical --  for quassiclassical dynamics, the default, use 0.  for classical dynamics, use 1
#if there are no normal modes and the velocities are to be generated from scratch, use classical 2
classical 0
#*** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line below, otherwise leave it at 0 or comment it
        out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
#*** cannonball -- The program can "fire" a trajectory from a starting position toward a particular target, such as toward
#a ts.  To use this, make a file cannontraj with numAtom lines and three numbers per line that defines the vector
#for firing the trajectory, relative to the starting geometry's standard orientation.  The number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
#*** keepevery --This tells the program how often to write the gaussian output file to file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or molden loading time.
keepevery 10
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,
#which must come before the medium level atoms.  Use some high value such as 999 if not using ONIOM
highlevel 999
#*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is, initialdis=0
#fixedatom1 2
#fixedatom2 3
#fixedatom3 19
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the edge
#are reflected back toward the middle.  Useful for dynamics with solvent molecules.  This is a crude
```

```
#implementation that is ok for a few thousand femtoseconds but will not conserve energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15 x 15 angstroms
boxon 0
boxsize 7.5
#*** displacements -- This keyword lets you set the initialdis of particular modes by using a series of lines of the format
# displacements NumberOfMode InitialDisForThatMode, as in the example below. You should be able to do as many of these as
        you like
# you might consider this for rotations where a straight-line displacement goes wrong at large displacements
# The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same thing as 0 but is maintained for now
        because
# a previous version of the program had a bug that made 0 not work.
displacements 2 0
#*** etolerance --This sets the allowable difference between the desired energy in a trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial velocities.
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems.  For very large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 1
#*** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
controlphase 3 positive
#*** damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the
        velocities
#by the damping factor.  A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values
        range
#from 0.95 to 1.05.  The use of damping lets one do simulated annealing - you add energy until the structure is moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1
#*** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.
#reversetraj true


#updated Aug 9, 2007 to include the possibility of classical dynamics by the keyword classical
#updated Jan 2008 to include fixed atoms, ONIOM jobs, keepevery, and box size
#update Feb 2008 to include methodfile parameter
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# update Aug 2010 to include etolerance, damping controlphase and reversetraj
```

Sample Input Files

Gaussrate

p.dat

```
*General

 TITLE
MacMillan Diels-Alder phenyl exo full
ultrafine, sstep 0.01, pm
END

 ATOMS
 1  C
 2  C
 3  H
 4  C
 5  H
```

6 C
7 C
8 H
9 H
10 C
11 C
12 C
13 H
14 C
15 H
16 N
17 H
18 C
19 C
20 C
21 H
22 C
23 N
24 C
25 C
26 C
27 O
28 H
29 H
30 C
31 C
32 C
33 C
34 C
35 H
36 H
37 H
38 H
39 H
40 H
41 C
42 H
43 H
44 H
45 H
46 H
47 H
48 H
49 H
50 H
51 H
52 C
53 C
54 C
55 C
56 C

```
 57  H
 58  H
 59  H
 60  H
 61  H
  END

  NOSUPERMOL

  INPUNIT AU

  MDMOVIE ON

*OPTIMIZATION

  OPTMIN  OHOOK
  OPTTS   OHOOK

*SECOND

  HESSCAL HHOOK

*REACT1
  INITGEO  HOOKS
  SPECIES   NONLINRP
  GEOM
    1
    2
    3
    4
    5
    6
    7
    8
    9
   10
   11
   12
   13
   14
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   25
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  56
  57
  58
  59
  60
  61
 END
# end of react1 section

*PROD1
 INITGEO  HOOKS
 SPECIES   NONLINRP
 GEOM
  1
  2
  3
  4
  5
  6
  7
  8
```

```
 60
 61
END

# end of prod1 section

*START
 SPECIES NONLINTS
 INITGEO  HOOKS
 GEOM
  1
  2
  3
  4
  5
  6
  7
  8
  9
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  57
  58
  59
  60
  61
 END
# end of start section

*PATH

 SCALEMASS  1.00

 INTMU   3
 SSTEP   0.01
 INH     9

 SRANGE
  SLP   3.59
  SLM  -1.5
 END

 RPM       pagem

 SIGN    REACTANT

 IDIRECT   1

 COORD CURV3

 INTDEF
7-6 10-6 11-1 4-1-2 7-6-4 10-6-7 11-1-2 12-10-11 14-11-1
2-1 3-1 4-1 5-2 6-4 7-2 8-6 9-7 10-1 11-10 12-10 13-11 14-11
15-10 16-12 17-12 18-16 19-16 20-18 21-18 22-18 23-19 24-19
25-19 26-23 27-20 28-4 29-4 30-14 31-30 32-31 33-32 34-14 35-30
36-31 37-32 38-33 39-34 40-22 41-22 42-22 43-24 44-24 45-24
46-25 47-25 48-25 49-26 50-26 51-26 52-41 53-52 54-53 55-54
```

```
56-41 57-52 58-53 59-54 60-55 61-56 3-1-2 4-1-3 5-2-1 6-4-1
7-2-1 8-6-4 9-7-2 10-1-2 11-10-1 12-10-1 13-11-10 14-11-10
15-10-11 16-12-10 17-12-10 18-16-12 19-16-12 20-18-16 21-18-16
22-18-16 23-19-16 24-19-16 25-19-16 26-23-19 27-20-18 28-4-1
29-4-1 30-14-11 31-30-14 32-31-30 33-32-31 34-14-11 35-30-14
36-31-30 37-32-31 38-33-32 39-34-14 40-22-18 41-22-18 42-22-18
43-24-19 44-24-19 45-24-19 46-25-19 47-25-19 48-25-19 49-26-23
50-26-23 51-26-23 52-41-22 53-52-41 54-53-52 55-54-53 56-41-22
57-52-41 58-53-52 59-54-53 60-55-54 61-56-41 4-1-3-2 5-2-1-4
6-4-1-2 7-2-1-4 8-6-4-1 9-7-2-1 10-1-2-7 11-10-1-2 12-10-1-2
13-11-10-12 14-11-10-12 15-10-11-14 16-12-10-11 17-12-10-11
18-16-12-10 19-16-12-10 20-18-16-12 21-18-16-12 22-18-16-12
23-19-16-12 24-19-16-12 25-19-16-12 26-23-19-16 27-20-18-16
28-4-1-2 29-4-1-2 30-14-11-10 31-30-14-11 32-31-30-14
33-32-31-30 34-14-11-10 35-30-14-11 36-31-30-14 37-32-31-30
38-33-32-31 39-34-14-11 40-22-18-16 41-22-18-16 42-22-18-16
43-24-19-16 44-24-19-16 45-24-19-16 46-25-19-16 47-25-19-16
48-25-19-16 49-26-23-19 50-26-23-19 51-26-23-19 52-41-22-18
53-52-41-22 54-53-52-41 55-54-53-52 56-41-22-18 57-52-41-22
58-53-52-41 59-54-53-52 60-55-54-53 61-56-41-22
 END

 PRPATH
  COORD 1 11
  INTERVAL 1
  XMOL
 END

 SPECSTOP
  CURVE vag
  POINT savegrid
  PERCENTDOWN 95.
 END

*TUNNEL

 QUAD
  NQE   40
  NQTH  40
 END

  SCT

*RATE


 FORWARDK

 SIGMAF       1
 CVT
 CUS 2
```

```
 PRDELG ON
 PRGIGT ON
 ICVT ON
# MUVT ON
# MUVTOPT
#    prenergy 4
#    niter 30
# END

 TEMP
#  200.
   298.15
   398.15
 END
```

p.70

```
*GRGENERAL

 GRRESTART
 RSTTOL 0.000001

*GRSTART

 CHARGE       1
 MULTIPLICITY  1

*GRREACT1

 CHARGE       1
 MULTIPLICITY  1

*GRPROD1

 CHARGE       1
 MULTIPLICITY  1

*GRCOMMON

 GRENER
    #p B3LYP/6-31G* UNITS=AU FCHK NOSYMM
    scf=tight integral(grid=ultrafinegrid) guess=tcheck
 END

 GRFIRST
    #p B3LYP/6-31G* FORCE UNITS=AU FCHK NOSYMM
    scf=tight integral(grid=ultrafinegrid) guess=tcheck
 END
```

```
 GRSEC
    #p B3LYP/6-31G* FREQ=NORAMAN UNITS=AU FCHK NOSYMM
    scf=tight integral(grid=ultrafinegrid) guess=tcheck
 END

 GRLINK0
   %chk=g09.chk
   %nproc=8
   %mem=4gb
 END
```

p.71

```
%nproc=8
%mem=4gb
%chk=g09.chk
#p B3LYP/6-31G* opt fchk NOSYMM
scf=tight integral(grid=ultrafine)

sm for macmillan da phenyl full exo

1 1
 C,0,4.1866583914,-0.7146486672,-0.0912112322
 C,0,3.2767651126,-1.6820165193,-0.3447593687
 H,0,4.9342286506,-0.3273038582,-0.7742773043
 C,0,4.0616808997,-0.281046592,1.3454191089
 H,0,3.1502016242,-2.2209443893,-1.2781278696
 C,0,2.9282301433,-1.1273159591,1.864281676
 C,0,2.4943985494,-1.9404067045,0.8735286935
 H,0,2.5912061349,-1.1197680648,2.8948838982
 H,0,1.7279581113,-2.705005966,0.9551912327
 C,0,-0.0892002348,1.5832606645,-0.8770843488
 C,0,1.0327064819,1.2689123132,-1.6040787498
 C,0,-0.2753587311,0.9955637948,0.3959215055
 H,0,1.7473665331,0.5833017863,-1.1464014555
 C,0,1.3904443742,1.7356555462,-2.9188836632
 H,0,-0.8413838096,2.2555644484,-1.2717359388
 N,0,-1.2908969627,1.1921181903,1.2030612032
 H,0,0.4806018786,0.2926471686,0.7438261935
 C,0,-2.4249863725,2.1027972819,0.9492195913
 C,0,-1.4602659881,0.4027180512,2.4854303625
 C,0,-3.3895583281,1.7592382256,2.0829989478
 H,0,-2.8926941835,1.8317205409,-0.0047824737
 C,0,-2.1004598297,3.6225805547,0.9382360717
 N,0,-2.8007935818,0.8268391395,2.8859212931
```

C,0,-1.4236351022,-1.1038782645,2.1852858625
C,0,-0.3908251382,0.8077844201,3.5096855813
C,0,-3.4566073895,0.3407367351,4.0926891043
O,0,-4.4825038293,2.2726036193,2.2310607027
H,0,3.884331103,0.7995834314,1.4554457631
H,0,4.9901043055,-0.4832415778,1.9018005324
C,0,2.6057110032,1.2751658134,-3.476475391
C,0,3.0069437263,1.6858703563,-4.7417084482
C,0,2.201488737,2.563669797,-5.4726100088
C,0,0.9932516004,3.0312565902,-4.9364606384
C,0,0.5889271479,2.6243723316,-3.6742277157
H,0,3.2252602157,0.5934524092,-2.9000928167
H,0,3.9415775858,1.3261093971,-5.1602389319
H,0,2.5120483174,2.8863010405,-6.4620129422
H,0,0.3732653692,3.7125513529,-5.5106903604
H,0,-0.3493715053,2.9937602694,-3.2722514473
H,0,-3.0815595231,4.1030144393,0.8521448485
C,0,-1.3567403639,4.1406040259,2.150544153
H,0,-1.5453823623,3.8682102313,0.0279515651
H,0,-1.6456544027,-1.6641379275,3.0977427995
H,0,-2.1660607989,-1.3675796085,1.4264173146
H,0,-0.4320580763,-1.4184733295,1.8472455457
H,0,-0.5466349961,0.2561452976,4.4415271485
H,0,0.6080118874,0.5526646624,3.1414951578
H,0,-0.4337475636,1.8786017215,3.7188916298
H,0,-4.4286725417,0.8333499854,4.1417741184
H,0,-3.607085444,-0.7425840366,4.0548057772
H,0,-2.8795547314,0.5970254672,4.98686353
C,0,0.0303935549,4.3369853769,2.1020362303
C,0,0.7253664371,4.8073959532,3.2178540243
C,0,0.0386138604,5.0888197247,4.4001441895
C,0,-1.3452948721,4.9065512654,4.456722201
C,0,-2.0395494408,4.4391921864,3.3398866693
H,0,0.5701035555,4.1379491322,1.1782047723
H,0,1.7987086137,4.965718826,3.1598272792
H,0,0.5754901532,5.4627628423,5.2671486731
H,0,-1.8886052343,5.142690553,5.3673034089
H,0,-3.1180307211,4.3143705045,3.3857077449

p.73

%nproc=8
%mem=4gb
%chk=g09.chk
#p B3LYP/6-31G* opt fchk NOSYMM
scf=tight integral(grid=ultrafine)

product from MacMillan Diels-Alder phenyl

1 1
C,0,3.7748530952,-0.6214694319,-0.3931442934
C,0,3.2627974771,-1.8511038795,-1.1183403821
H,0,4.524787828,-0.0263490212,-0.9163017745
C,0,4.1689589188,-1.2399338475,0.9652109956
H,0,3.2945708895,-1.9958423195,-2.1920761065
C,0,2.8229704896,-1.9722951354,1.1390539254
C,0,2.6962853004,-2.6576017174,-0.2063701696
H,0,2.6823635733,-2.5987405293,2.0222847894
H,0,2.15571235,-3.5822801621,-0.376883685
C,0,1.7778692492,-0.7344344053,1.0410071621
C,0,2.5293385902,0.2519057683,0.0578485322
C,0,1.5802082212,-0.1599949454,2.3812703371
H,0,2.9428186246,1.0815579192,0.6448816174
C,0,1.6904397936,0.8618322345,-1.0468393101
H,0,0.8355946219,-1.0817753427,0.6220630704
N,0,0.4918348484,-0.1461305197,3.0814571499
H,0,2.4613501809,0.2343257491,2.8842272442
C,0,-0.8375672207,-0.6416404,2.6408818014
C,0,0.4778148984,0.2969399054,4.5458324669
C,0,-1.6251926613,-0.6827710074,3.9480821732
H,0,-0.7198307185,-1.6621795866,2.2634757256
C,0,-1.5658319516,0.2169431366,1.5689535511
N,0,-0.8587541352,-0.1397781014,4.939239277
C,0,1.5585721763,-0.4612899958,5.3312703096
C,0,0.6592732201,1.8170830251,4.6420007416
C,0,-1.3796825475,0.0356681047,6.2901104471
O,0,-2.7599569811,-1.1065950387,4.0462693145
H,0,4.3954111941,-0.4974243756,1.7411017187
H,0,5.0038971777,-1.9407517149,0.8891162298
C,0,1.8721578837,2.218054847,-1.3590097961
C,0,1.1600196682,2.8200982108,-2.3972116397
C,0,0.2449915148,2.0741732934,-3.1411042913
C,0,0.0528429713,0.7243416685,-2.8422435838
C,0,0.7691394736,0.1225144305,-1.806223913
H,0,2.5865206898,2.8081996473,-0.7883227835
H,0,1.3205196069,3.8704117379,-2.6227277062
H,0,-0.3135127744,2.5399987579,-3.9474468466
H,0,-0.6540263036,0.1345091795,-3.4187770852
H,0,0.6188108878,-0.934753163,-1.6081097221
H,0,-2.5217696824,-0.3006317686,1.4278357218
C,0,-1.7973727672,1.6704669131,1.9270145701
H,0,-1.0201507084,0.1463226451,0.623030282

H,0,1.4609399302,-0.2267619775,6.3945218594
H,0,1.4500005155,-1.542530111,5.2052897646
H,0,2.5667822028,-0.1586504024,5.033571687
H,0,0.6134063461,2.1221024321,5.6914082573
H,0,1.6418338336,2.1135382368,4.2602792515
H,0,-0.1158855189,2.345022882,4.0839111729
H,0,-2.3970193341,-0.3578263985,6.2864710472
H,0,-0.7858213146,-0.5202774342,7.0219161147
H,0,-1.4052695938,1.0940147268,6.5675688543
C,0,-2.8455270748,2.0444952463,2.7831871532
C,0,-3.0462828917,3.3855999044,3.1122805524
C,0,-2.2099792863,4.3727926506,2.5850735861
C,0,-1.1772389607,4.0125853347,1.7179574507
C,0,-0.9738886587,2.6702488379,1.3903437883
H,0,-3.5120836651,1.2851984375,3.1827403972
H,0,-3.8669705341,3.6608344943,3.768641986
H,0,-2.374217492,5.4170838961,2.8346009181
H,0,-0.5377030877,4.7764887107,1.2845180812
H,0,-0.1851693785,2.4030607681,0.6908750126

p.75

%nproc=8
%mem=4gb
%chk=g09.chk
#p B3LYP/6-31G* opt=(ts,calcfc,noeigentest) fchk NOSYMM
scf=tight integral(grid=ultrafine)

ts for MacMillan Diels-Alder phenyl full exo

1 1
C,0,3.3130182665,-0.3020391629,-0.1878881601
C,0,2.7867002209,-1.5262546654,-0.6836548044
H,0,4.2107885258,0.1181386902,-0.6340725628
C,0,3.1755429771,-0.4009300381,1.3270601076
H,0,2.9086020053,-1.8815595294,-1.7008203996
C,0,2.0854873421,-1.4122072248,1.4673889727
C,0,1.9814188381,-2.1388104757,0.2971253068
H,0,1.5585810571,-1.6202401507,2.3922011747
H,0,1.3613575653,-3.0149934572,0.1457338028
C,0,0.7968724772,0.7702697425,0.0312671039
C,0,2.039014933,1.0433167118,-0.647150594
C,0,0.4360862963,1.4538075449,1.183489942
H,0,2.5928001216,1.8654391423,-0.1893320035
C,0,2.0774355803,1.1403738394,-2.142385719
H,0,0.0773193159,0.1118173907,-0.4383305431

N,0,-0.7369120152,1.4142770931,1.8151226342
H,0,1.1658925878,2.1265789767,1.6287102169
C,0,-1.8802158787,0.5919488212,1.4046976612
C,0,-0.9658371548,2.1224678525,3.1219684613
C,0,-2.826998275,0.7184406779,2.5967057167
H,0,-1.5603090645,-0.4558610178,1.3183431198
C,0,-2.5990077404,0.9957160569,0.0860575586
N,0,-2.2686562444,1.5744826653,3.5009294189
C,0,0.1075661061,1.7272877695,4.1508533713
C,0,-1.0159605225,3.6445185668,2.9186136994
C,0,-2.9717735252,1.9620278276,4.7152300468
O,0,-3.9051673062,0.159440402,2.6855563586
H,0,3.0224918681,0.5342389514,1.8683207795
H,0,4.1078003505,-0.8452812934,1.7142747101
C,0,2.9503724401,2.0674224382,-2.7312872416
C,0,3.0151266867,2.2078626868,-4.1180037255
C,0,2.2098200589,1.4171866901,-4.9373254795
C,0,1.3392836564,0.4863367519,-4.3623098415
C,0,1.2741245682,0.3478231816,-2.9775740085
H,0,3.5791650908,2.6913386803,-2.0995422727
H,0,3.6931653378,2.9349886909,-4.5547431
H,0,2.2578744996,1.5229848783,-6.0168844004
H,0,0.7077495872,-0.1306356538,-4.9948101019
H,0,0.5911844682,-0.383805956,-2.553304949
H,0,-3.4754973725,0.3394481346,0.0426176311
C,0,-3.0144896001,2.4478184127,-0.0075855202
H,0,-1.9645924439,0.7368745322,-0.7668785805
H,0,-0.1304213259,2.165227356,5.1242058795
H,0,0.1541948721,0.6398100346,4.2631826852
H,0,1.0948370705,2.104629898,3.8666377663
H,0,-1.207920195,4.1458375554,3.8720566946
H,0,-0.0554865602,4.0140651886,2.5442908797
H,0,-1.7990231934,3.9157302547,2.2076712327
H,0,-3.9137175478,1.411681137,4.7220667376
H,0,-2.3986249503,1.6989374409,5.6100115559
H,0,-3.1844930345,3.0359117735,4.7244991203
C,0,-2.2198704113,3.3703092196,-0.7022899998
C,0,-2.5901316811,4.7139334592,-0.7841368307
C,0,-3.7645740308,5.1534088651,-0.1705861628
C,0,-4.5692271144,4.2410850447,0.5161206641
C,0,-4.199547164,2.8975253604,0.5949090604
H,0,-1.3112322585,3.0319889577,-1.1962520959
H,0,-1.9679764915,5.4139180311,-1.3351250707
H,0,-4.0586532561,6.1968508512,-0.2390330544
H,0,-5.4940465951,4.5724683704,0.9800425689
H,0,-4.8364958184,2.1901730269,1.1192425817

RRKM Sample Input File

Simple awk scripts were used to generate the hundreds of RRKM input files used in this work, including the example below.

dapt10

```
run on pt 10 s= -0.333 macmillian dielsalder phenyl exo full
from polyrate frequencies b3lyp/6-31g* calcs
19,0.1,300,
0,
-1,0,1,298,
0,
-1,
-1,
1.0
177,0
14.8754,16.5583,21.1123,22.5714,34.3062,41.9799,43.7295
47.5948,53.1679,61.1288,67.1768,68.8582,70.6149,106.4053
111.2375,121.5096,155.5549,170.1545,185.5917,198.0251,217.3203
221.4924,253.9969,270.7334,280.7489,306.6553,332.1782,354.6935
363.2389,364.7175,373.7847,379.4320,401.6893,409.2540,420.6435
452.7855,488.7365,495.7100,513.4032,526.0209,551.6511,562.2371
584.8953,607.9175,622.6353,628.2837,636.6359,649.6340,684.5251
689.3031,697.4594,719.9825,727.2585,760.8800,772.2429,780.4511
809.4499,813.3764,815.3061,844.6500,850.7130,871.7100,884.0497
893.3195,919.2069,926.6159,934.9138,940.3829,945.1099,952.4235
953.8428,958.2967,960.3438,974.4850,981.2243,983.2186,983.5009
993.6633,1012.2418,1014.4024,1016.7713,1019.5128,1021.4125,1023.4728
1030.2939,1053.5208,1059.5363,1062.6248,1067.2679,1117.0829,1121.4867
1122.8607,1134.7823,1140.0631,1142.5004,1161.8172,1175.0561,1197.1812
1203.1679,1208.2792,1214.7795,1219.5007,1219.9576,1221.8848,1233.5116
1243.6078,1279.8219,1284.2138,1286.8713,1318.0518,1322.7090,1332.3488
1340.2829,1355.7057,1365.1470,1378.2124,1381.8610,1387.0985,1398.1270
1416.9222,1427.2858,1432.6841,1442.8771,1446.4500,1459.6428,1473.6125
1500.1737,1501.4190,1505.1545,1508.6865,1513.2342,1523.7549,1531.4612
1536.7315,1540.8290,1541.7734,1547.0235,1562.2111,1620.8994,1640.2101
1642.2255,1647.2778,1649.0292,1663.1743,1674.9400,1826.8485,3033.0534
3056.6608,3066.6691,3069.3334,3071.5954,3076.4008,3079.7393,3120.3539
3130.1312,3140.6437,3149.1263,3152.9716,3155.0661,3171.7506,3173.8948
3176.7422,3180.0931,3193.3986,3199.5997,3200.1406,3203.9791,3208.2384
3210.8231,3211.4170,3218.0777,3221.3598,3222.3636,3228.2588,3238.4037
3238.9669,3245.2529
3978.9,3978.9,6052.2
0,
19.35
```

176,0
3257.4900,3247.9700,3246.5000,3236.0900,3224.0900,3218.9800,3216.7700
3213.1200,3206.8800,3204.7400,3198.9000,3191.8000,3189.6500,3186.3700
3180.2800,3178.4000,3174.1400,3173.4800,3151.4600,3142.2300,3140.9000
3137.5600,3135.4100,3126.1500,3119.5300,3077.4300,3073.5400,3067.3400
3064.3300,3042.6800,3020.9600,1822.8800,1663.7300,1658.0700,1646.8800
1642.2700,1639.3300,1560.5900,1549.2400,1547.2200,1542.4200,1537.3100
1532.5200,1530.4800,1522.5800,1512.1100,1509.9300,1504.5100,1500.9300
1493.8100,1473.4700,1472.4400,1457.5900,1450.2200,1440.6700,1437.4500
1430.5900,1417.7400,1399.7700,1380.3700,1373.5000,1369.6400,1362.5500
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1206.7000,1199.9100,1196.6300,1175.6600,1162.3100,1153.9200,1144.8800
1135.1400,1118.0000,1117.5800,1115.0800,1103.6000,1084.9600,1082.9400
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1010.9200,1008.4500,991.0600,985.1500,983.1200,977.4600,975.8900
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824.4200,816.7300,808.0700,779.5900,772.5400,761.1100,720.6800
719.4900,707.6300,684.1100,648.8500,636.8200,633.3200,625.5200
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496.7700,451.3400,436.2300,420.3400,411.9100,397.7600,396.1700
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16.7300
3380.30,3380.30,5738.95
0,

References, and Complete Reference 17b:

S1. Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.;

Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

S2. Singleton, D. A.; Hang, C.; Szymanski, M. J.; Greenwald, E. E. *J. Am. Chem. Soc.* **2003**, 125, 1176-1177.

S3. Zhu, L. Hase, W. L. A General RRKM Program. *Quantum Chemistry Program Exchange*, Indiana University: Bloomington, IN, 1994, Program No. QCPE 644.

S4. Beyer, T. Swinehart, D. F. *Commun. Assoc. Comput. Machin.* **16**, 379 (1973).

S5. Reference 17b: J. Zheng, S. Zhang, B. J. Lynch, J. C. Corchado, Y.-Y. Chuang, P. L. Fast, W.-P. Hu, Y.-P. Liu, G. C. Lynch, K. A. Nguyen, C. F. Jackels, A. Fernandez Ramos, B. A. Ellingson, V. S. Melissas, J. Villà, I. Rossi, E. L. Coitiño, J. Pu, T. V. Albu, R. Steckler, B. C. Garrett, A. D. Isaacson, and D. G. Truhlar, POLYRATE–version 2010, University of Minnesota, Minneapolis, 2010.

S6. Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261-267. Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225-233. Bigeleisen, J. *J. Chem. Phys.* **1949**, *17*, 675-678.

S7. Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman & Hall: London, 1980; pp 60-63.

S8. (a) Meyer, M. P.; DelMonte, A. J.; Singleton, D. A. *J. Am. Chem. Soc.* **1999**, *121*, 10865-10874. (b) DelMonte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Strassner, T.; Thomas, A. A. *J. Am. Chem. Soc.* **1997**, *119*, 9907-9908. (c) Singleton, D. A.; Merrigan, S. R.; Liu, J.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 3385-3386. (d) Beno, B. R.; Houk, K. N.; Singleton, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 9984-9985.

S9. Chapman, S.; Bunker, D.L. *J. Chem. Phys.* **1975,** *62,* 2890-2899.

S10. L. M. M. Quijano and D. A. Singleton, *J. Am. Chem. Soc.* **2011**, *133*, 13824-13827.