Table S1: Specific wavenumber range for peaks tracked in Figure 2. All numbers are in units of cm^{-1}.

Precursor Alkene		POZ (red)		POZ decomposition product (blue)
Cyclohexene	*	783-819	x	951-1184
	□	954-990	+	1669-1823
Methyl-Cyclohexene	*	850-860	x	1657-1785
	□	1149-1164	+	2700-2760
Methylene-Cyclohexane	*	779-785	x	1630-1675
	□	916-943		-
	◊	1216-1233		-
	o	766-815		-

Table S2: Experimentally corrected pre-exponential factors for 1-methyl-cyclohexene POZ decomposition as a function of temperature.

MECYHE POZ Decomposition A-Factor * 10^-14 [1/s]											
Temp [K]	100	125	150	175	200	225	250	275	298	300	325
TS1	0.10	0.17	0.27	0.39	0.53	0.68	0.85	1.01	1.15	1.17	1.32
TS2	0.04	0.07	0.10	0.15	0.20	0.26	0.33	0.39	0.45	0.45	0.51
TS3	0.04	0.06	0.10	0.14	0.20	0.25	0.31	0.38	0.43	0.44	0.49
TS4	0.04	0.06	0.09	0.14	0.19	0.25	0.31	0.38	0.44	0.44	0.50

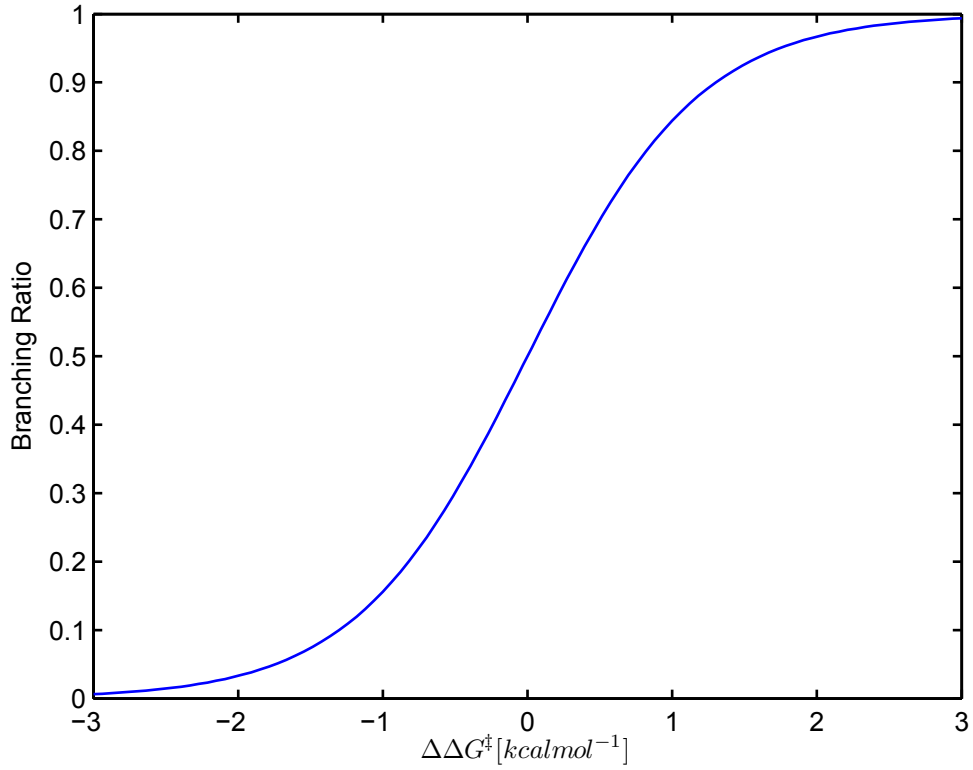

Figure S1: Branching ratio (selectivity) as a function of the difference in Gibbs free energy of activation for a two pathway POZ decomposition. $\Delta\Delta G^{\ddagger}$, defined as $\Delta G^{\ddagger}_{p} - \Delta G^{\ddagger}_{n}$ yields the branching ratio or selectivity of path "n".

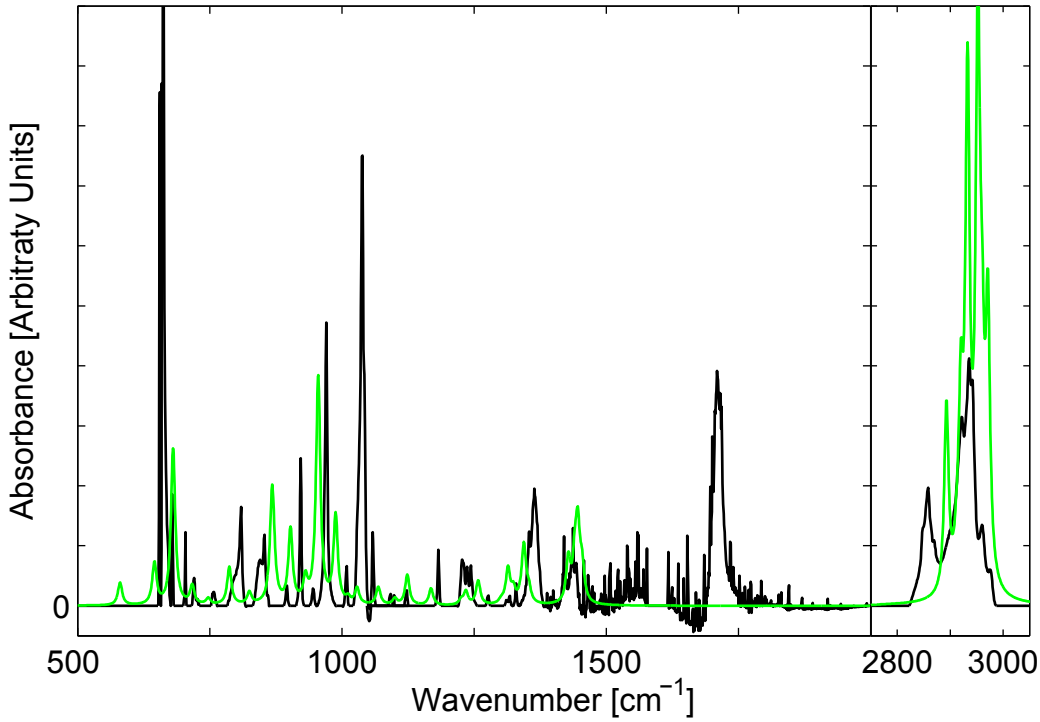

Figure S2: The experimental cyclohexene POZ spectrum at 110 K (black). The green spectrum is computationally predicted with DFT B3LYP 6-311G++(2d,2p) at 298K. A piecewise linear baseline was used between the absorption peaks to create a baseline for the spectrum.

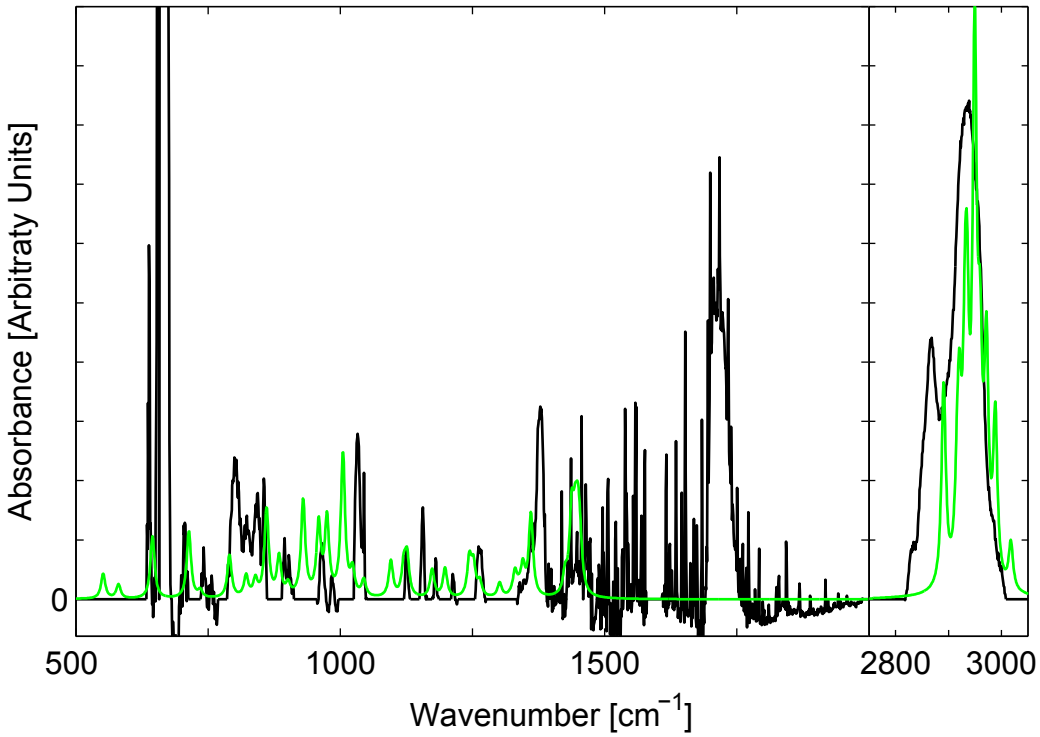

Figure S3: The experimental 1-methyl-cyclohexene POZ spectrum at 120 K (black). The green spectrum is computationally predicted with DFT B3LYP 6-311G++(2d,2p) at 298K. A piecewise linear baseline was used between the absorption peaks to create a baseline for the spectrum.

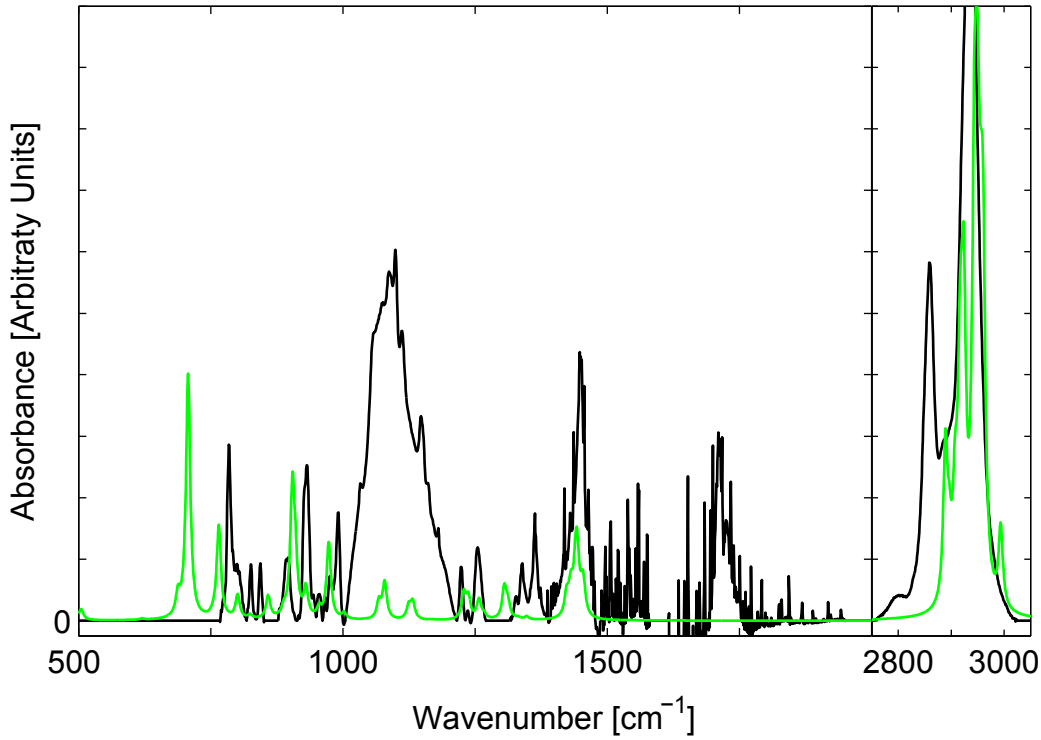

Figure S4: The experimental methylene-cyclohexane POZ spectrum at 160 K (black). The green spectrum is computationally predicted with DFT B3LYP 6-311G++(2d,2p) at 298K. A piecewise linear baseline was used between the absorption peaks to create a baseline for the spectrum.

Derivation of Equation 3

We define a system of competing unimolecular decompositions with rate constants k_1 through k_4:

POZ→ A; rate constant k_1
POZ → B; rate constant k_2
POZ → C; rate constant k_3
POZ → D; rate constant k_4

In line with the definition of differential selectivity of "A" from Butt[1*]:

S_A = rate of production of A / rate of consumption of POZ EQS1

Assuming decomposition reactions are first order[2]:

$$S_A = \frac{k_1[POZ]}{k_1[POZ] + k_2[POZ] + k_3[POZ] + k_4[POZ]} \quad \text{EQS2}$$

$$S_A = \frac{k_1}{k_1 + k_2 + k_3 + k_4} \quad \text{EQS3}$$

Generalizing for a system with "p" possible paths where "n" is the path of interest:

$$S_n = \frac{k_n}{\sum_{p=1}^{\#paths} k_p} \quad \text{EQS4}$$

Defining the rate constant in terms of the Gibbs free energy of activation ($\Delta G^{\ddagger}$)[3,4]:

$$k_n = \frac{k_B \cdot T}{h} \exp\left(\frac{-\Delta G_n^{\mp}}{RT}\right) \quad \text{EQS5}$$

where k_B is the Boltzmann constant, T is the temperature, h is Planck's constant, and R is the universal gas constant. Plugging EQS5 into EQS4 yields:

[*] Starting with the definition of Overall Selectivity introduced in Butt 2000 yields the same result, but is not as conceptually straight-forward

$$S_n = \frac{\exp\left(\frac{-\Delta G_n^{\mp}}{RT}\right)}{\sum_{p=1}^{\#paths} \exp\left(\frac{-\Delta G_p^{\mp}}{RT}\right)} \qquad \text{EQS6}$$

which is algebraically equivalent to the following expression:

$$\frac{1-S_n}{S_n} = \left(\sum_{p=1}^{\#paths} e^{\left(\frac{-\Delta G_n^{\mp}+\Delta G_p^{\mp}}{RT}\right)}\right) - 1 \qquad \text{EQS7}$$

Since $\Delta G_p^{\ddagger} = G_p^{TS} - G^{POZ}$ and $\Delta G_n^{\ddagger} = G_n^{TS} - G^{POZ}$, ($G_p^{TS}$ is the Gibbs free energy of the transition state and G_p^{POZ} is the Gibbs free energy of the POZ) EQS7 simplifies to the following:

$$\frac{1-S_n}{S_n} = \left(\sum_{p=1}^{\#paths} e^{\left(\frac{G_p^{TS}-G_n^{TS}}{RT}\right)}\right) - 1$$

Supporting Information References

(1) Butt, J. B. *Reaction kinetics and reactor design*, 2nd ed.; Marcel Dekker, Inc: New York, NY, 2000.

(2) Epstein, S. A.; Donahue, N. M. *The Journal of Physical Chemistry A* 2008, *112*, 13535.

(3) Wynne-Jones, W. F. K.; Eyring, H. *The Journal of Chemical Physics* 1935, *3*, 492.

(4) Laidler, K. J. *Chemical Kinetics*; McGraw-Hill Book Co., Inc: New York, NY, 1965.

1-Methylene-Cyclohexane Computational Calculations

All calculations were completed using DFT B3LYP 6-31G(d). Values presented here are at 1 atm and 298 K and have not been scaled by 0.9613.

Lowest Energy POZ

```
SCF Done:  E(RB+HF-LYP) =  -499.473078063     A.U. after    1 cycles
             Convg  =    0.2893D-08             -V/T =  2.0091
             S**2   =   0.0000

Rotational temperatures (Kelvin)      0.08975     0.06579     0.05423
Rotational constants (GHZ):           1.87001     1.37089     1.13006
Zero-point vibrational energy     494899.3 (Joules/Mol)
                                  118.28377 (Kcal/Mol)
Vibrational temperatures:     134.55   219.97   268.05   323.46   378.32
          (Kelvin)            403.49   518.48   540.68   613.17   649.58
                              715.14   847.64   889.77   991.55  1057.71
                             1091.93  1174.06  1237.28  1276.44  1290.91
                             1315.27  1348.64  1426.40  1445.33  1457.25
                             1511.68  1528.71  1579.98  1675.63  1693.63
                             1708.54  1787.57  1835.46  1871.15  1907.40
                             1970.68  1973.58  1994.35  2006.36  2026.06
                             2048.79  2067.01  2168.18  2175.65  2179.46
                             2187.21  2203.46  2207.64  4347.63  4351.93
                             4372.46  4392.16  4402.69  4410.72  4431.52
                             4444.42  4454.46  4480.79  4512.26  4520.99

Zero-point correction=                           0.188497
(Hartree/Particle)
Thermal correction to Energy=                    0.197538
Thermal correction to Enthalpy=                  0.198482
Thermal correction to Gibbs Free Energy=         0.154989
Sum of electronic and zero-point Energies=          -499.284581
Sum of electronic and thermal Energies=             -499.275541
Sum of electronic and thermal Enthalpies=           -499.274596
Sum of electronic and thermal Free Energies=        -499.318089

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                 123.957             36.043            91.537

Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -1.336854   -0.850860    1.048854
    2          1             0       -1.649607   -0.179690    1.861818
    3          1             0       -1.521293   -1.871688    1.402927
    4          6             0        0.170364   -0.658784    0.857943
    5          1             0        0.686100   -0.696506    1.827977
    6          6             0        0.589273    0.643911    0.128623
    7          6             0       -0.318735    0.978672   -1.069743
    8          1             0       -0.077148    1.987642   -1.425182
    9          1             0       -0.068067    0.282712   -1.876702
```

10	6	0	-1.817097	0.853177	-0.750287
11	1	0	-2.398113	1.065332	-1.655870
12	1	0	-2.116170	1.608358	-0.008316
13	6	0	-2.145198	-0.547747	-0.217582
14	1	0	-3.216213	-0.636849	0.000317
15	1	0	-1.910081	-1.295638	-0.985068
16	8	0	1.899891	0.238886	-0.319118
17	8	0	0.687611	-1.701983	0.029318
18	8	0	1.657102	-1.040591	-0.898500
19	6	0	0.811924	1.817707	1.074914
20	1	0	1.493721	1.544139	1.885626
21	1	0	1.237972	2.666844	0.531629
22	1	0	-0.139993	2.138401	1.510897

TS1

```
SCF Done:  E(RB+HF-LYP) =  -499.441603688     A.U. after    1 cycles
             Convg  =    0.2679D-08             -V/T =  2.0092
             S**2   =   0.0000

Rotational temperatures (Kelvin)      0.09244     0.06249     0.04909
Rotational constants (GHZ):           1.92623     1.30218     1.02297
    1 imaginary frequencies ignored.
Zero-point vibrational energy     487609.2 (Joules/Mol)
                                  116.54139 (Kcal/Mol)
Vibrational temperatures:      67.67   160.43   268.92   365.94   393.02
          (Kelvin)            418.02   479.62   532.84   576.50   634.57
                              694.72   721.54   809.92   879.59   943.81
                             1074.35  1186.31  1224.26  1272.40  1357.04
                             1365.57  1424.92  1462.36  1501.79  1563.47
                             1595.71  1613.81  1645.51  1661.75  1753.92
                             1819.59  1824.36  1850.23  1902.10  1945.54
                             1969.24  1985.71  2000.59  2029.05  2050.42
                             2111.13  2162.94  2165.73  2169.37  2196.78
                             2197.17  2206.51  4222.16  4360.72  4371.11
                             4382.11  4391.96  4398.67  4440.06  4442.24
                             4462.05  4480.57  4501.44  4601.82

Zero-point correction=                           0.185721
(Hartree/Particle)
Thermal correction to Energy=                    0.195024
Thermal correction to Enthalpy=                  0.195968
Thermal correction to Gibbs Free Energy=         0.151365
Sum of electronic and zero-point Energies=           -499.255883
Sum of electronic and thermal Energies=              -499.246580
Sum of electronic and thermal Enthalpies=            -499.245635
Sum of electronic and thermal Free Energies=         -499.290238

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                 122.379             36.170            93.874
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.157186	-1.533249	-0.213971
2	1	0	1.650857	-2.018733	-1.068029
3	1	0	0.872522	-2.328457	0.481712
4	6	0	-0.149073	-0.932938	-0.763478
5	1	0	-0.060642	-0.521628	-1.787370
6	6	0	-0.465013	0.768730	-0.028038
7	6	0	0.811291	1.572831	0.198459
8	1	0	0.735880	2.521437	-0.345087
9	1	0	0.855251	1.818106	1.266837
10	6	0	2.109409	0.837028	-0.181955
11	1	0	2.958193	1.441285	0.158908
12	1	0	2.199912	0.761422	-1.274440
13	6	0	2.149064	-0.557766	0.451197
14	1	0	3.161413	-0.973978	0.391750
15	1	0	1.916439	-0.462887	1.520106
16	8	0	-0.917962	0.268980	1.159705
17	8	0	-1.252236	-1.552973	-0.526005
18	8	0	-2.020121	-0.453223	0.990182
19	6	0	-1.519719	1.360925	-0.940024
20	1	0	-2.280675	0.624536	-1.193376
21	1	0	-1.997795	2.203914	-0.424025
22	1	0	-1.047670	1.739341	-1.851177

TS2

```
SCF Done:  E(RB+HF-LYP) =  -499.447384019     A.U. after    2 cycles
             Convg  =    0.8754D-08             -V/T =  2.0092
             S**2   =   0.0000
Rotational temperatures (Kelvin)      0.08697     0.06230     0.05292
Rotational constants (GHZ):           1.81213     1.29815     1.10269
    1 imaginary frequencies ignored.
Zero-point vibrational energy     487911.9 (Joules/Mol)
                                  116.61373 (Kcal/Mol)

Vibrational temperatures:     160.81   206.94   251.28   325.68   396.60
          (Kelvin)            453.71   460.44   513.46   562.53   623.53
                              698.01   755.97   763.33   919.04   948.16
                             1065.67  1184.19  1208.64  1304.10  1316.89
                             1380.67  1413.88  1460.31  1486.82  1519.50
                             1577.58  1626.88  1658.66  1688.12  1738.70
                             1809.17  1848.77  1870.62  1910.37  1952.65
                             1982.59  1996.28  2003.48  2027.44  2071.42
                             2130.40  2159.55  2169.34  2176.87  2186.29
                             2194.11  2202.54  4203.45  4349.96  4364.39
                             4375.21  4397.05  4401.27  4429.52  4435.20
                             4462.45  4501.50  4538.43  4544.06
```

```
Zero-point correction=                           0.185836
(Hartree/Particle)
Thermal correction to Energy=                    0.195017
Thermal correction to Enthalpy=                  0.195961
Thermal correction to Gibbs Free Energy=         0.152243
Sum of electronic and zero-point Energies=           -499.261548
Sum of electronic and thermal Energies=              -499.252367
Sum of electronic and thermal Enthalpies=            -499.251423
Sum of electronic and thermal Free Energies=         -499.295142

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                 122.375             36.183             92.014

Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -1.526701   -0.754628    0.939071
    2          1             0       -1.776243   -0.112444    1.796114
    3          1             0       -1.874597   -1.761737    1.196317
    4          6             0       -0.067864   -0.937672    0.894181
    5          1             0        0.390690   -1.126986    1.875130
    6          6             0        0.727380    0.651579    0.152676
    7          6             0       -0.152197    1.055181   -0.978259
    8          1             0        0.250282    2.042224   -1.236093
    9          1             0        0.034379    0.396473   -1.832467
   10          6             0       -1.666591    1.134606   -0.724328
   11          1             0       -2.164629    1.504219   -1.628769
   12          1             0       -1.887514    1.864385    0.068691
   13          6             0       -2.221079   -0.238670   -0.326120
   14          1             0       -3.302949   -0.185882   -0.155055
   15          1             0       -2.060147   -0.949681   -1.146010
   16          8             0        1.987821    0.092105   -0.280505
   17          8             0        0.361566   -1.956090    0.021488
   18          8             0        1.644588   -1.037617   -1.032016
   19          6             0        1.070262    1.697509    1.206859
   20          1             0        1.663013    1.259743    2.015530
   21          1             0        1.642343    2.515079    0.757402
   22          1             0        0.154302    2.120002    1.632990
 ---------------------------------------------------------------------
```

TS3

```
SCF Done:  E(RB+HF-LYP) =  -499.440889059     A.U. after    1 cycles
             Convg  =    0.2844D-08             -V/T =  2.0092
             S**2   =   0.0000

Rotational temperatures (Kelvin)      0.08324     0.07172     0.05235
 Rotational constants (GHZ):           1.73448     1.49447     1.09073
    1 imaginary frequencies ignored.
 Zero-point vibrational energy     488296.0 (Joules/Mol)
```

116.70555 (Kcal/Mol)

Vibrational temperatures: (Kelvin)					
	152.63	253.65	290.43	330.71	352.08
	404.19	419.97	469.01	570.07	616.02
	697.87	776.88	815.95	884.33	1022.33
	1118.32	1157.48	1214.93	1260.10	1331.68
	1384.80	1423.73	1444.91	1468.16	1553.51
	1576.42	1610.87	1623.75	1688.57	1717.51
	1734.05	1797.68	1840.20	1876.30	1938.39
	1989.91	2000.81	2020.52	2043.96	2053.82
	2084.63	2142.10	2172.14	2177.38	2185.83
	2200.53	2207.27	4366.07	4374.68	4389.52
	4392.43	4415.00	4417.10	4437.53	4466.04
	4481.69	4532.65	4535.09	4552.71	

Zero-point correction= (Hartree/Particle)	0.185982
Thermal correction to Energy=	0.195189
Thermal correction to Enthalpy=	0.196133
Thermal correction to Gibbs Free Energy=	0.152457
Sum of electronic and zero-point Energies=	-499.254907
Sum of electronic and thermal Energies=	-499.245700
Sum of electronic and thermal Enthalpies=	-499.244756
Sum of electronic and thermal Free Energies=	-499.288432

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	122.483	36.275	91.925

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.914879	-1.432431	0.724076
2	1	0	-1.383100	-1.406268	1.716434
3	1	0	-0.679560	-2.481937	0.500852
4	6	0	0.439821	-0.687102	0.864798
5	1	0	0.729596	-0.477073	1.894551
6	6	0	0.475273	0.950835	-0.098966
7	6	0	-0.962175	1.403372	-0.564499
8	1	0	-1.087622	2.470952	-0.334580
9	1	0	-0.951115	1.309214	-1.655659
10	6	0	-2.157290	0.606557	-0.037807
11	1	0	-3.061137	0.952395	-0.553937
12	1	0	-2.325082	0.787918	1.034289
13	6	0	-1.930439	-0.887190	-0.281351
14	1	0	-2.861487	-1.455171	-0.164842
15	1	0	-1.573278	-1.049684	-1.304769
16	8	0	1.271673	0.588157	-1.129363
17	8	0	1.525619	-1.307220	0.318376
18	8	0	1.336891	-1.217607	-1.013275
19	6	0	1.104240	1.825296	1.005277
20	1	0	2.078801	1.426314	1.298239
21	1	0	1.254605	2.836275	0.607451
22	1	0	0.458611	1.904397	1.886898

TS4

```
SCF Done:  E(RB+HF-LYP) =  -499.445323469     A.U. after    1 cycles
             Convg  =    0.3411D-08             -V/T =  2.0091
             S**2   =   0.0000
Rotational temperatures (Kelvin)      0.08459     0.06393     0.04945
Rotational constants (GHZ):           1.76248     1.33210     1.03038
    1 imaginary frequencies ignored.
Zero-point vibrational energy     487841.6 (Joules/Mol)
                                  116.59694 (Kcal/Mol)
Vibrational temperatures:     155.00   220.25   290.99   334.12   373.71
          (Kelvin)            434.57   490.13   521.07   545.10   642.33
                              671.57   734.80   782.49   831.99   936.06
                             1058.15  1173.87  1224.52  1282.59  1331.71
                             1373.26  1417.92  1435.98  1500.63  1528.35
                             1569.22  1597.18  1655.84  1709.55  1723.00
                             1749.16  1835.18  1856.43  1875.18  1971.93
                             1987.34  2013.54  2022.31  2035.63  2043.36
                             2078.89  2157.92  2161.22  2173.86  2187.78
                             2196.88  2200.18  4359.83  4371.14  4374.47
                             4392.64  4395.84  4426.15  4437.65  4457.07
                             4464.47  4486.93  4533.83  4554.80

Zero-point correction=                           0.185809
(Hartree/Particle)
Thermal correction to Energy=                    0.195000
Thermal correction to Enthalpy=                  0.195944
Thermal correction to Gibbs Free Energy=         0.152247
Sum of electronic and zero-point Energies=           -499.259514
Sum of electronic and thermal Energies=              -499.250324
Sum of electronic and thermal Enthalpies=            -499.249379
Sum of electronic and thermal Free Energies=         -499.293077

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                 122.364             36.400             91.969

Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0       -1.101707   -1.178841    0.976965
    2          1             0       -1.420563   -0.614809    1.861437
    3          1             0       -1.150341   -2.240435    1.257350
    4          6             0        0.337183   -0.815406    0.707862
    5          1             0        1.014510   -0.679092    1.549742
    6          6             0        0.531948    0.952607   -0.023172
    7          6             0       -0.610117    1.056694   -1.059183
    8          1             0       -0.654350    2.108208   -1.376790
    9          1             0       -0.288709    0.480384   -1.933831
   10          6             0       -2.004285    0.597710   -0.606644
```

11	1	0	-2.714068	0.766443	-1.425921
12	1	0	-2.356412	1.215487	0.231924
13	6	0	-2.041486	-0.881778	-0.202734
14	1	0	-3.060593	-1.172756	0.078222
15	1	0	-1.758682	-1.505443	-1.060124
16	8	0	1.720349	0.893490	-0.507632
17	8	0	0.899461	-1.478172	-0.310363
18	8	0	2.173256	-1.121937	-0.452586
19	6	0	0.382687	1.801401	1.256414
20	1	0	1.253610	1.651107	1.899388
21	1	0	0.357307	2.858467	0.965345
22	1	0	-0.531575	1.591073	1.820857