Electronic Supplementary Material (ESI) for Chemical Science.
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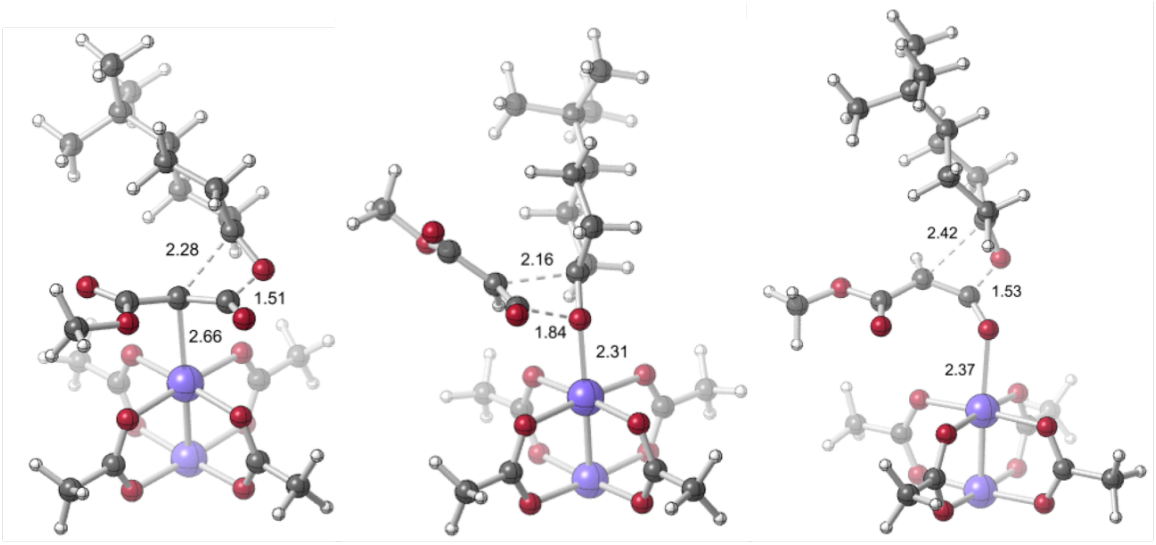
Supplementary Information

[2+2]-Cycloaddition Transition State Structure ($\beta$-TS2$_{cat}$) Configurations




Configuration 1
$\Delta G_{rel,reactant}$= 3.3 kcal/mol
$\Delta G_{rel,fragment}$= 52.3 kcal/mol

Configuration 2
$\Delta G_{rel,reactant}$= -3.0 kcal/mol
$\Delta G_{rel,fragment}$= 46.0 kcal/mol

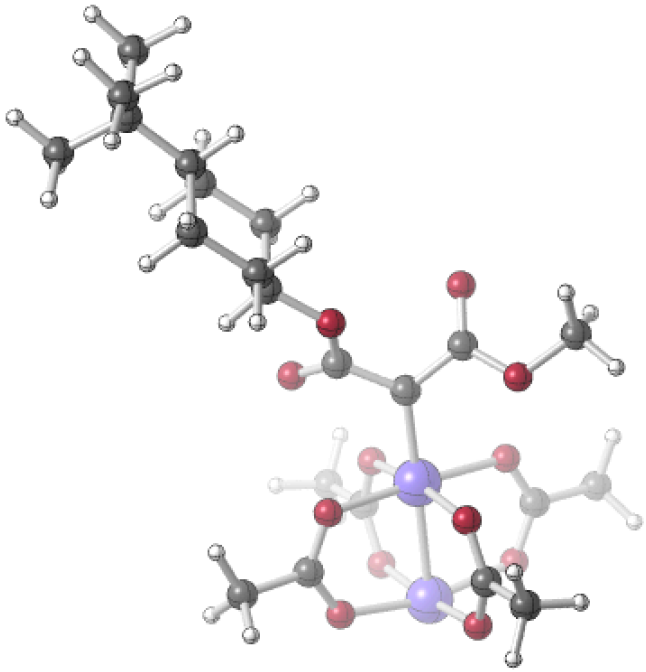
Configuration 3
$\Delta G_{rel,reactant}$= 1.0 kcal/mol
$\Delta G_{rel,fragment}$= 50.1 kcal/mol

**Figure S1**: Three configurations of $\beta$-TS2$_{cat}$ investigated. Configuration 1 has the carbenoid carbon coordinated to the Rh catalyst, configuration 2 has the oxygen of the ketone fragment coordinated to Rh, and configuration 3 has the oxygen of the ketene fragment coordinated to the Rh. Relative free energies reported above are relative to the reactant Rh-carbenoid (top) and relative to the fragmented product (bottom) to illustrate the barrier to formation of the $\beta$-lactone product if the fragmented product was an intermediate along the $\beta$-lactone formation pathway.

**Cartesian Coordinates of and Energies of Triplet Structures (including energies relative to singlet counterparts)**

*B3LYP/6-31G(d) for C, H, O and LANL2DZ for Rh*

Rh-carbenoid "reactant"



E(UB3LYP) = -1980.67683214 hartrees
Sum of electronic and thermal Free Energies= -1980.201675 hartrees
$E_{triplet} - E_{singlet}$= +12.2 kcal/mol
$G_{triplet} - G_{singlet}$= +12.4 kcal/mol

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -6.743823 | 0.110228 | 0.063894 |
| 2 | 6 | -5.881890 | -0.247741 | -1.168516 |
| 3 | 6 | -4.476036 | 0.373060 | -1.096716 |
| 4 | 6 | -3.758428 | -0.045768 | 0.185697 |
| 5 | 6 | -4.580417 | 0.308854 | 1.420024 |
| 6 | 6 | -5.985418 | -0.313593 | 1.342513 |
| 7 | 1 | -3.880989 | 0.071118 | -1.965134 |
| 8 | 1 | -5.784307 | -1.339866 | -1.246440 |
| 9 | 1 | -6.364730 | 0.087749 | -2.092072 |
| 10 | 1 | -6.818757 | 1.210357 | 0.089374 |
| 11 | 1 | -3.549469 | -1.120842 | 0.158620 |
| 12 | 1 | -4.059243 | -0.030142 | 2.323704 |
| 13 | 1 | -4.659092 | 1.402449 | 1.487064 |
| 14 | 1 | -5.892702 | -1.408702 | 1.369285 |

| | | | | |
|---|---|---|---|---|
| 15 | 1 | -6.543750 | -0.027143 | 2.239911 |
| 16 | 1 | -4.542487 | 1.469041 | -1.113659 |
| 17 | 6 | -8.223341 | -0.409289 | -0.007187 |
| 18 | 6 | -8.913681 | 0.154183 | -1.269250 |
| 19 | 1 | -8.486550 | -0.250532 | -2.192598 |
| 20 | 1 | -9.980745 | -0.099565 | -1.265749 |
| 21 | 1 | -8.832587 | 1.247918 | -1.311705 |
| 22 | 6 | -8.306573 | -1.949336 | -0.044502 |
| 23 | 1 | -7.872688 | -2.404693 | 0.852821 |
| 24 | 1 | -9.354282 | -2.270193 | -0.098879 |
| 25 | 1 | -7.791501 | -2.365731 | -0.917297 |
| 26 | 6 | -9.015297 | 0.098757 | 1.218198 |
| 27 | 1 | -8.940353 | 1.189316 | 1.316874 |
| 28 | 1 | -10.077996 | -0.152651 | 1.115842 |
| 29 | 1 | -8.666341 | -0.348774 | 2.154560 |
| 30 | 8 | -2.492212 | 0.650267 | 0.302533 |
| 31 | 6 | -1.428707 | 0.119019 | -0.351631 |
| 32 | 8 | -1.455850 | -0.948244 | -0.937809 |
| 33 | 6 | -0.242305 | 0.990020 | -0.219989 |
| 34 | 6 | -0.414731 | 2.442695 | -0.352466 |
| 35 | 8 | -1.260740 | 2.949430 | -1.073880 |
| 36 | 8 | 0.459785 | 3.168577 | 0.378320 |
| 37 | 6 | 0.361127 | 4.586316 | 0.203487 |
| 38 | 1 | 1.120817 | 5.015320 | 0.858313 |
| 39 | 1 | 0.552306 | 4.861765 | -0.838239 |
| 40 | 1 | -0.633116 | 4.944942 | 0.484705 |
| 41 | 45 | 1.555235 | 0.132238 | -0.054365 |
| 42 | 45 | 3.845514 | -1.017256 | 0.153762 |
| 43 | 8 | 4.476790 | 0.652228 | -0.809782 |
| 44 | 6 | 3.738309 | 1.609453 | -1.228621 |
| 45 | 6 | 4.431410 | 2.712928 | -1.990068 |
| 46 | 8 | 2.489359 | 1.687425 | -1.057933 |
| 47 | 1 | 4.796238 | 2.315146 | -2.943301 |
| 48 | 1 | 3.741459 | 3.536210 | -2.178566 |
| 49 | 1 | 5.299370 | 3.063633 | -1.424265 |
| 50 | 8 | 4.026164 | -0.027857 | 1.962116 |
| 51 | 6 | 3.088093 | 0.735719 | 2.375731 |
| 52 | 8 | 1.986182 | 0.986280 | 1.795998 |
| 53 | 6 | 3.336866 | 1.441038 | 3.692044 |
| 54 | 1 | 3.944352 | 2.333887 | 3.502930 |
| 55 | 1 | 2.392377 | 1.750277 | 4.142646 |
| 56 | 1 | 3.895943 | 0.790453 | 4.368552 |
| 57 | 8 | 3.445043 | -1.899811 | -1.668537 |
| 58 | 6 | 2.345581 | -1.636740 | -2.268032 |
| 59 | 6 | 2.102172 | -2.357030 | -3.576155 |
| 60 | 8 | 1.423986 | -0.856151 | -1.877541 |
| 61 | 1 | 1.568830 | -1.702670 | -4.269205 |
| 62 | 1 | 3.044446 | -2.698149 | -4.008671 |
| 63 | 1 | 1.465191 | -3.227543 | -3.381205 |
| 64 | 8 | 0.730912 | -1.470932 | 0.956833 |

| | | | | |
|---|---|---|---|---|
| 65 | 6 | 1.493120 | -2.420300 | 1.290761 |
| 66 | 8 | 2.751469 | -2.463491 | 1.061035 |
| 67 | 6 | 0.896392 | -3.597529 | 2.021561 |
| 68 | 1 | 1.174501 | -4.524273 | 1.510926 |
| 69 | 1 | 1.309492 | -3.640754 | 3.035028 |
| 70 | 1 | -0.188987 | -3.502971 | 2.067476 |

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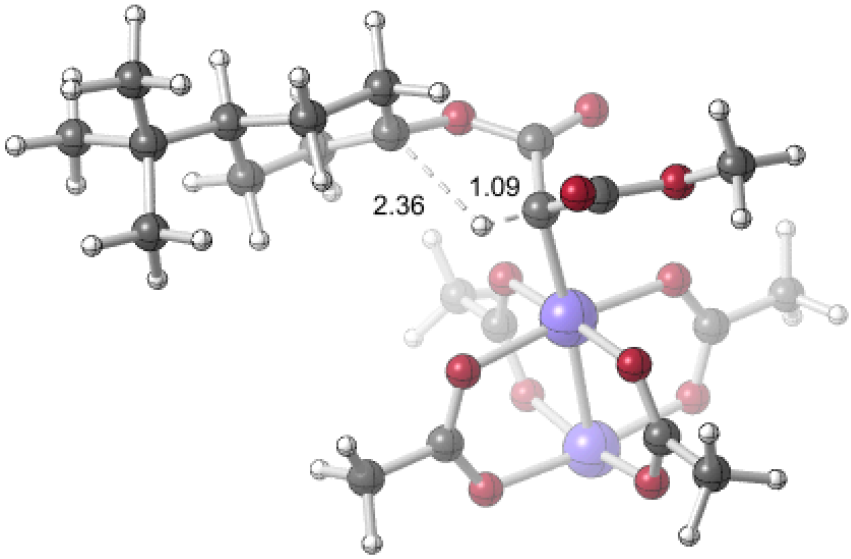
β-TS1$_{cat}$




E(UB3LYP) = -1980.66496003 hartrees
Sum of electronic and thermal Free Energies= -1980.191569 hartrees
$E_{triplet} - E_{singlet}$= +8.1 kcal/mol
$G_{triplet} - G_{singlet}$= +10.8 kcal/mol

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -5.508683 | -0.052273 | -0.295861 |
| 2 | 6 | -4.496502 | -1.103715 | -0.805211 |
| 3 | 6 | -3.515077 | -0.513852 | -1.834689 |
| 4 | 6 | -2.880244 | 0.739315 | -1.328442 |
| 5 | 6 | -3.736744 | 1.766739 | -0.650501 |
| 6 | 6 | -4.723611 | 1.117617 | 0.338778 |
| 7 | 1 | -2.736368 | -1.242800 | -2.092180 |
| 8 | 1 | -3.920102 | -1.495681 | 0.043159 |
| 9 | 1 | -5.010579 | -1.955592 | -1.262069 |
| 10 | 1 | -6.026826 | 0.351909 | -1.182544 |
| 11 | 1 | -1.225965 | 1.038273 | 0.322490 |
| 12 | 1 | -3.121124 | 2.509124 | -0.127245 |

| | | | | |
|---|---|---|---|---|
| 13 | 1 | -4.305014 | 2.325151 | -1.419611 |
| 14 | 1 | -4.160579 | 0.754142 | 1.208578 |
| 15 | 1 | -5.403107 | 1.893418 | 0.704337 |
| 16 | 1 | -4.060150 | -0.303371 | -2.775588 |
| 17 | 6 | -6.640364 | -0.641848 | 0.618421 |
| 18 | 6 | -7.632997 | 0.475430 | 1.010138 |
| 19 | 1 | -8.012807 | 0.998851 | 0.123314 |
| 20 | 1 | -8.494881 | 0.051187 | 1.539226 |
| 21 | 1 | -7.181440 | 1.221087 | 1.672640 |
| 22 | 6 | -7.437170 | -1.711286 | -0.161531 |
| 23 | 1 | -6.836263 | -2.598262 | -0.387117 |
| 24 | 1 | -8.300751 | -2.046257 | 0.425696 |
| 25 | 1 | -7.816363 | -1.310460 | -1.110265 |
| 26 | 6 | -6.081251 | -1.281221 | 1.906136 |
| 27 | 1 | -5.534891 | -0.555458 | 2.518678 |
| 28 | 1 | -6.900587 | -1.676177 | 2.519457 |
| 29 | 1 | -5.405180 | -2.115480 | 1.687215 |
| 30 | 8 | -1.844466 | 1.193795 | -2.133375 |
| 31 | 6 | -0.720661 | 1.820775 | -1.633923 |
| 32 | 8 | -0.044022 | 2.470076 | -2.391935 |
| 33 | 6 | -0.423448 | 1.579839 | -0.175528 |
| 34 | 6 | -0.136370 | 2.825356 | 0.618035 |
| 35 | 8 | -0.816648 | 3.165506 | 1.569498 |
| 36 | 8 | 0.916308 | 3.527250 | 0.171130 |
| 37 | 6 | 1.201599 | 4.729622 | 0.895946 |
| 38 | 1 | 2.061307 | 5.174387 | 0.393952 |
| 39 | 1 | 0.346647 | 5.410932 | 0.868259 |
| 40 | 1 | 1.439056 | 4.501937 | 1.939280 |
| 41 | 45 | 1.143716 | 0.175881 | -0.017658 |
| 42 | 45 | 2.913724 | -1.618669 | 0.260726 |
| 43 | 8 | 3.385205 | -0.573277 | 1.938431 |
| 44 | 6 | 2.800638 | 0.495056 | 2.328709 |
| 45 | 6 | 3.319156 | 1.129171 | 3.595744 |
| 46 | 8 | 1.836981 | 1.050370 | 1.727330 |
| 47 | 1 | 4.321484 | 1.531128 | 3.411316 |
| 48 | 1 | 2.655659 | 1.933002 | 3.917102 |
| 49 | 1 | 3.406052 | 0.370835 | 4.379090 |
| 50 | 8 | 1.499471 | -2.667632 | 1.358201 |
| 51 | 6 | 0.334917 | -2.177676 | 1.538438 |
| 52 | 8 | -0.099704 | -1.061055 | 1.112105 |
| 53 | 6 | -0.637876 | -3.034549 | 2.319793 |
| 54 | 1 | -1.083814 | -3.770558 | 1.640475 |
| 55 | 1 | -0.111469 | -3.579389 | 3.106815 |
| 56 | 1 | -1.434646 | -2.419569 | 2.741612 |
| 57 | 8 | 4.152205 | -0.409983 | -0.862152 |
| 58 | 6 | 3.719197 | 0.715300 | -1.294322 |
| 59 | 6 | 4.702494 | 1.549498 | -2.085486 |
| 60 | 8 | 2.567464 | 1.212194 | -1.111210 |
| 61 | 1 | 5.345535 | 2.095759 | -1.385400 |
| 62 | 1 | 5.339720 | 0.903937 | -2.694458 |

| | | | | |
|---|---|---|---|---|
| 63 | 1 | 4.169098 | 2.269754 | -2.707808 |
| 64 | 8 | 0.518654 | -0.783458 | -1.736115 |
| 65 | 6 | 1.135075 | -1.827807 | -2.095568 |
| 66 | 8 | 2.102400 | -2.360924 | -1.450977 |
| 67 | 6 | 0.714493 | -2.503071 | -3.376959 |
| 68 | 1 | 1.532152 | -2.433561 | -4.102374 |
| 69 | 1 | 0.527648 | -3.564923 | -3.190711 |
| 70 | 1 | -0.176456 | -2.023225 | -3.783512 |

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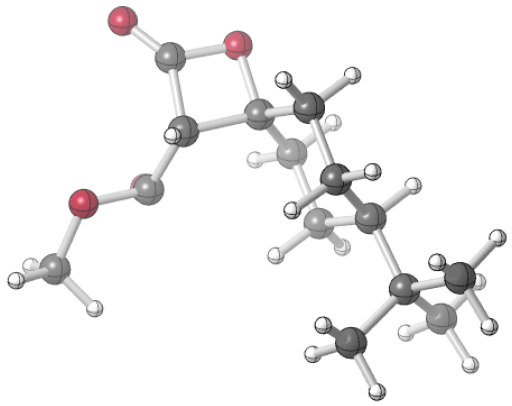
β-lactone



E(UB3LYP) = -847.497014312 hartrees
Sum of electronic and thermal Free Energies= -847.202044 hartrees
$E_{triplet} - E_{singlet}$= +92.3 kcal/mol
$G_{triplet} - G_{singlet}$= +95.9 kcal/mol

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 2.121589 | -0.500670 | 0.169944 |
| 2 | 6 | 1.406502 | -0.919210 | -1.134022 |
| 3 | 6 | 0.234204 | -1.877097 | -0.862665 |
| 4 | 6 | -0.776370 | -1.270266 | 0.102215 |
| 5 | 6 | -0.105270 | -0.825451 | 1.394359 |
| 6 | 6 | 1.080130 | 0.118856 | 1.127933 |
| 7 | 1 | -0.265790 | -2.156548 | -1.798253 |
| 8 | 1 | 1.029916 | -0.026977 | -1.654063 |
| 9 | 1 | 2.101205 | -1.409939 | -1.822797 |
| 10 | 1 | 2.483383 | -1.428501 | 0.644551 |
| 11 | 1 | -1.736304 | -0.197114 | -1.616981 |
| 12 | 1 | -0.840321 | -0.340712 | 2.052257 |
| 13 | 1 | 0.238494 | -1.727338 | 1.918648 |
| 14 | 1 | 0.692864 | 1.053833 | 0.702560 |
| 15 | 1 | 1.537176 | 0.375965 | 2.088376 |

| | | | | |
|---|---|---|---|---|
| 16 | 1 | 0.610038 | -2.807169 | -0.415515 |
| 17 | 6 | 3.398450 | 0.385354 | -0.047841 |
| 18 | 6 | 3.067590 | 1.744710 | -0.697918 |
| 19 | 1 | 2.395157 | 2.345058 | -0.075061 |
| 20 | 1 | 3.985719 | 2.327348 | -0.840967 |
| 21 | 1 | 2.600422 | 1.625833 | -1.682086 |
| 22 | 6 | 4.091160 | 0.639670 | 1.309175 |
| 23 | 1 | 4.305531 | -0.302715 | 1.829173 |
| 24 | 1 | 5.044878 | 1.158967 | 1.158100 |
| 25 | 1 | 3.486012 | 1.262275 | 1.976234 |
| 26 | 6 | 4.405023 | -0.363169 | -0.948870 |
| 27 | 1 | 4.039770 | -0.479437 | -1.974428 |
| 28 | 1 | 5.350835 | 0.188908 | -1.003007 |
| 29 | 1 | 4.627009 | -1.362721 | -0.553911 |
| 30 | 8 | -1.860150 | -2.248050 | 0.386155 |
| 31 | 6 | -2.822964 | -1.436774 | -0.150027 |
| 32 | 8 | -3.997830 | -1.637564 | -0.228209 |
| 33 | 6 | -1.830502 | -0.312853 | -0.532571 |
| 34 | 6 | -2.042320 | 1.053386 | 0.046843 |
| 35 | 8 | -2.410824 | 1.154687 | 1.338880 |
| 36 | 8 | -2.893083 | 1.844399 | -0.710350 |
| 37 | 6 | -2.861458 | 3.256840 | -0.446487 |
| 38 | 1 | -3.517506 | 3.516106 | 0.388773 |
| 39 | 1 | -1.838456 | 3.585006 | -0.235293 |
| 40 | 1 | -3.229525 | 3.732143 | -1.358518 |

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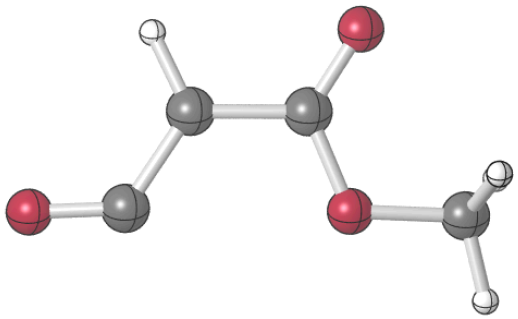
fragmentation product, ketene



E(UB3LYP) = -380.395085383 hartrees
Sum of electronic and thermal Free Energies= -380.353943 hartrees
$E_{triplet} - E_{singlet}$= +51.3 kcal/mol
$G_{triplet} - G_{singlet}$= +53.7 kcal/mol

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|

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| | | | | |
|---|---|---|---|---|
| 1 | 6 | -0.952938 | 0.656818 | -0.000076 |
| 2 | 6 | -1.861055 | -0.478132 | 0.000132 |
| 3 | 8 | -3.061002 | -0.424290 | 0.000061 |
| 4 | 1 | -1.343690 | 1.673855 | 0.000777 |
| 5 | 6 | 0.509713 | 0.529777 | -0.000584 |
| 6 | 8 | 0.927457 | -0.750654 | -0.000227 |
| 7 | 8 | 1.251004 | 1.498137 | 0.000181 |
| 8 | 6 | 2.354390 | -0.927240 | 0.000215 |
| 9 | 1 | 2.795735 | -0.470680 | -0.889813 |
| 10 | 1 | 2.795183 | -0.470666 | 0.890513 |
| 11 | 1 | 2.512440 | -2.005394 | 0.000287 |

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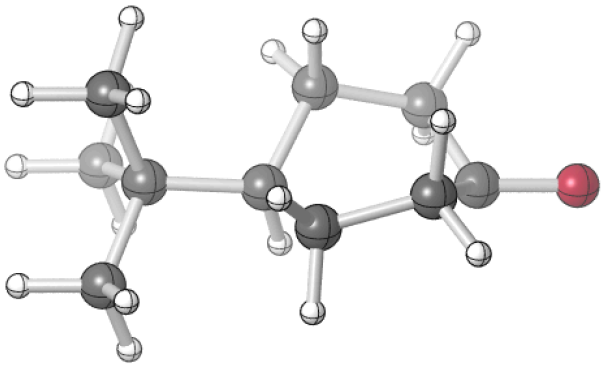
fragmentation product, ketone



E(UB3LYP) = -467.016829249 hartrees
Sum of electronic and thermal Free Energies= -466.793204 hartrees
$E_{triplet} - E_{singlet}$= +72.0 kcal/mol
$G_{triplet} - G_{singlet}$= +74.1 kcal/mol

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 8 | 3.770483 | -0.015902 | -0.403228 |
| 2 | 6 | 2.459967 | -0.018840 | -0.329017 |
| 3 | 6 | 1.828092 | 1.341145 | 0.011036 |
| 4 | 6 | 1.849483 | -1.212293 | 0.409728 |
| 5 | 1 | 1.996230 | -1.083476 | 1.496526 |
| 6 | 1 | 1.834883 | 1.965728 | -0.892571 |
| 7 | 1 | 2.440539 | 1.863766 | 0.762315 |
| 8 | 1 | 2.382783 | -2.126869 | 0.133028 |
| 9 | 6 | 0.390192 | 1.145365 | 0.523236 |
| 10 | 1 | -0.137190 | 2.101695 | 0.436714 |
| 11 | 1 | 0.411012 | 0.897716 | 1.592148 |
| 12 | 6 | 0.346032 | -1.330911 | 0.066564 |

| | | | | |
|---|---|---|---|---|
| 13 | 1 | -0.150243 | -1.813166 | 0.918346 |
| 14 | 1 | 0.226960 | -2.003518 | -0.788491 |
| 15 | 6 | -0.334116 | 0.028670 | -0.255512 |
| 16 | 1 | -0.154771 | 0.226171 | -1.323424 |
| 17 | 6 | -1.890226 | 0.012948 | -0.081702 |
| 18 | 6 | -2.494567 | 1.285417 | -0.714053 |
| 19 | 1 | -3.589291 | 1.259052 | -0.654851 |
| 20 | 1 | -2.165027 | 2.199293 | -0.208207 |
| 21 | 1 | -2.220892 | 1.369791 | -1.773073 |
| 22 | 6 | -2.483509 | -1.202982 | -0.825398 |
| 23 | 1 | -2.181926 | -1.208407 | -1.880619 |
| 24 | 1 | -2.169368 | -2.153252 | -0.381278 |
| 25 | 1 | -3.579350 | -1.172619 | -0.794010 |
| 26 | 6 | -2.308989 | -0.048835 | 1.401080 |
| 27 | 1 | -1.909405 | -0.935426 | 1.906904 |
| 28 | 1 | -1.971353 | 0.834036 | 1.955325 |
| 29 | 1 | -3.401609 | -0.091395 | 1.485268 |

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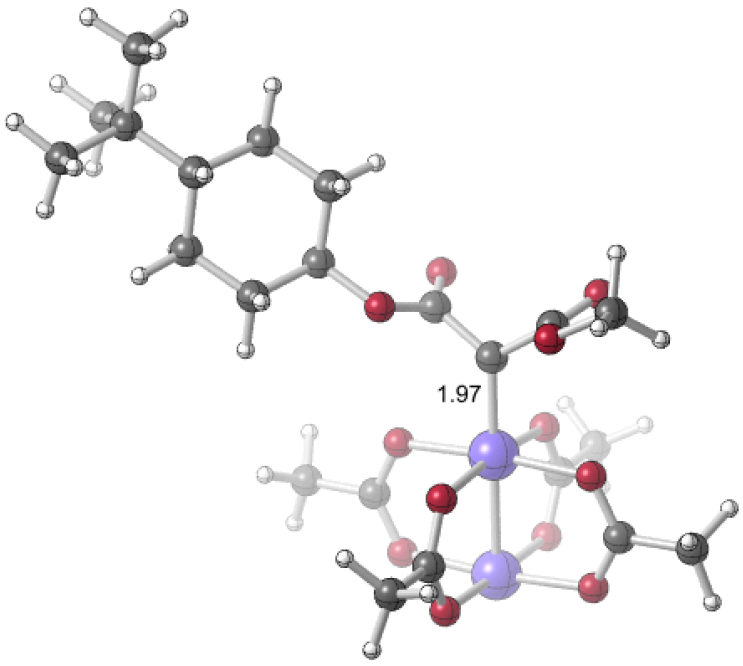
**Cartesian Coordinates and Energies of Singlet Structures**

*Lee System*

*B3LYP/6-31+G(d,p) for C, H, O and SDD for Rh*

Rh-carbenoid "reactant"




E(UB3LYP) = -1982.9523595 hartrees

Sum of electronic and thermal Free Energies = -1982.482377 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -6.364451 | -0.034821 | 0.314028 |
| 2 | 6 | -5.833742 | 0.814338 | -0.863113 |
| 3 | 6 | -4.411834 | 1.346082 | -0.605052 |
| 4 | 6 | -3.452880 | 0.195919 | -0.308801 |
| 5 | 6 | -3.937798 | -0.652947 | 0.858531 |
| 6 | 6 | -5.361316 | -1.177269 | 0.596339 |
| 7 | 1 | -4.056277 | 1.914831 | -1.470265 |
| 8 | 1 | -5.828108 | 0.212493 | -1.782027 |
| 9 | 1 | -6.490395 | 1.667758 | -1.055264 |
| 10 | 1 | -6.360481 | 0.618133 | 1.202638 |
| 11 | 1 | -3.313442 | -0.417748 | -1.204658 |
| 12 | 1 | -3.244413 | -1.484918 | 1.023733 |
| 13 | 1 | -3.925945 | -0.038752 | 1.768555 |
| 14 | 1 | -5.337319 | -1.865468 | -0.259731 |
| 15 | 1 | -5.675551 | -1.768524 | 1.461677 |
| 16 | 1 | -4.418193 | 2.025124 | 0.258352 |
| 17 | 6 | -7.852389 | -0.508632 | 0.151033 |
| 18 | 6 | -8.773175 | 0.718802 | -0.038181 |
| 19 | 1 | -8.598921 | 1.229108 | -0.990420 |
| 20 | 1 | -9.824512 | 0.409238 | -0.025186 |
| 21 | 1 | -8.633068 | 1.449536 | 0.768136 |
| 22 | 6 | -8.041732 | -1.458078 | -1.051431 |
| 23 | 1 | -7.451951 | -2.374993 | -0.947260 |
| 24 | 1 | -9.093577 | -1.756007 | -1.133381 |
| 25 | 1 | -7.763545 | -0.982348 | -1.997781 |
| 26 | 6 | -8.312452 | -1.235936 | 1.434779 |
| 27 | 1 | -8.157166 | -0.610750 | 2.322776 |
| 28 | 1 | -9.381934 | -1.468273 | 1.376169 |
| 29 | 1 | -7.784886 | -2.181907 | 1.591280 |
| 30 | 8 | -2.133708 | 0.718675 | 0.068004 |
| 31 | 6 | -1.281885 | 1.015351 | -0.912761 |
| 32 | 8 | -1.482971 | 0.942359 | -2.109503 |
| 33 | 6 | 0.042258 | 1.461514 | -0.406396 |
| 34 | 6 | 0.247305 | 2.929538 | -0.323406 |
| 35 | 8 | 0.525191 | 3.576146 | -1.313850 |
| 36 | 8 | 0.110803 | 3.405731 | 0.917540 |
| 37 | 6 | 0.369421 | 4.819297 | 1.080505 |
| 38 | 1 | 0.203306 | 5.018069 | 2.138355 |
| 39 | 1 | 1.400556 | 5.043168 | 0.799082 |
| 40 | 1 | -0.315531 | 5.404457 | 0.462652 |
| 41 | 45 | 1.521402 | 0.195167 | -0.107806 |

| | | | | |
|---|---|---|---|---|
| 42 | 45 | 3.368530 | -1.384644 | 0.250826 |
| 43 | 8 | 4.552926 | 0.252938 | 0.699647 |
| 44 | 6 | 4.056001 | 1.417839 | 0.664078 |
| 45 | 6 | 4.962211 | 2.584147 | 0.988113 |
| 46 | 8 | 2.842963 | 1.712612 | 0.377096 |
| 47 | 1 | 4.984168 | 3.274921 | 0.139896 |
| 48 | 1 | 4.561912 | 3.129719 | 1.848098 |
| 49 | 1 | 5.970003 | 2.231402 | 1.208750 |
| 50 | 8 | 2.812152 | -1.532564 | 2.228887 |
| 51 | 6 | 1.819780 | -0.853489 | 2.627868 |
| 52 | 8 | 1.104352 | -0.076100 | 1.907177 |
| 53 | 6 | 1.439036 | -0.942226 | 4.087984 |
| 54 | 1 | 1.717865 | -0.007480 | 4.585895 |
| 55 | 1 | 0.356906 | -1.058969 | 4.186118 |
| 56 | 1 | 1.960346 | -1.773366 | 4.564299 |
| 57 | 8 | 3.868170 | -1.189714 | -1.734274 |
| 58 | 6 | 3.171552 | -0.417104 | -2.458729 |
| 59 | 6 | 3.545059 | -0.270557 | -3.914781 |
| 60 | 8 | 2.165968 | 0.268488 | -2.067321 |
| 61 | 1 | 3.844060 | 0.764344 | -4.107942 |
| 62 | 1 | 4.363589 | -0.946304 | -4.164636 |
| 63 | 1 | 2.672817 | -0.480793 | -4.539952 |
| 64 | 8 | 0.329273 | -1.434195 | -0.561108 |
| 65 | 6 | 0.841702 | -2.607610 | -0.534911 |
| 66 | 8 | 2.040868 | -2.892131 | -0.241501 |
| 67 | 6 | -0.091044 | -3.746794 | -0.878927 |
| 68 | 1 | 0.465692 | -4.680952 | -0.958691 |
| 69 | 1 | -0.849723 | -3.840125 | -0.094945 |
| 70 | 1 | -0.608891 | -3.530257 | -1.817214 |

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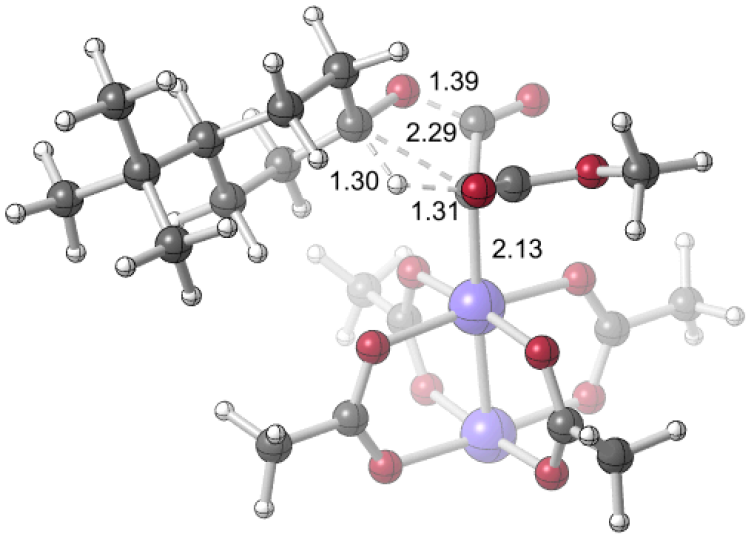
β-TS1$_{cat}$, Conformation 1




E(UB3LYP) = -1982.9349837 hartrees
Sum of electronic and thermal Free Energies = -1982.461740 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -4.846178 | -0.257559 | -0.428879 |
| 2 | 6 | -3.563686 | -1.056025 | -0.750916 |
| 3 | 6 | -2.691303 | -0.367298 | -1.813095 |
| 4 | 6 | -2.420054 | 1.083309 | -1.499605 |
| 5 | 6 | -3.599307 | 1.895390 | -1.021645 |
| 6 | 6 | -4.438269 | 1.158665 | 0.034663 |
| 7 | 1 | -1.741362 | -0.886712 | -1.967035 |
| 8 | 1 | -2.961454 | -1.186535 | 0.155193 |
| 9 | 1 | -3.805980 | -2.056674 | -1.119619 |
| 10 | 1 | -5.404083 | -0.144125 | -1.374033 |
| 11 | 1 | -1.575909 | 0.988711 | -0.517492 |
| 12 | 1 | -3.270449 | 2.872685 | -0.656480 |
| 13 | 1 | -4.199696 | 2.082994 | -1.925959 |
| 14 | 1 | -3.856083 | 1.104116 | 0.960976 |
| 15 | 1 | -5.317941 | 1.772130 | 0.248439 |
| 16 | 1 | -3.208666 | -0.351349 | -2.786352 |
| 17 | 6 | -5.832834 | -0.988543 | 0.549582 |
| 18 | 6 | -7.141223 | -0.174484 | 0.669700 |
| 19 | 1 | -7.589132 | 0.006052 | -0.315414 |
| 20 | 1 | -7.874548 | -0.723316 | 1.271244 |
| 21 | 1 | -6.987478 | 0.794240 | 1.154466 |
| 22 | 6 | -6.202434 | -2.376626 | -0.021126 |
| 23 | 1 | -5.354313 | -3.068259 | -0.017289 |

| | | | | |
|---|---|---|---|---|
| 24 | 1 | -6.994972 | -2.834739 | 0.581208 |
| 25 | 1 | -6.572065 | -2.299292 | -1.051262 |
| 26 | 6 | -5.231829 | -1.174461 | 1.959244 |
| 27 | 1 | -5.009352 | -0.216789 | 2.440726 |
| 28 | 1 | -5.942331 | -1.706496 | 2.602464 |
| 29 | 1 | -4.307773 | -1.761550 | 1.936692 |
| 30 | 8 | -1.640711 | 1.721855 | -2.477417 |
| 31 | 6 | -0.514933 | 2.238265 | -1.853607 |
| 32 | 8 | 0.258391 | 2.975172 | -2.392887 |
| 33 | 6 | -0.462998 | 1.683191 | -0.462802 |
| 34 | 6 | -0.690389 | 2.609187 | 0.686741 |
| 35 | 8 | -1.579554 | 2.454562 | 1.507093 |
| 36 | 8 | 0.210048 | 3.596752 | 0.704701 |
| 37 | 6 | 0.165667 | 4.471275 | 1.850631 |
| 38 | 1 | 0.975748 | 5.182753 | 1.695046 |
| 39 | 1 | -0.797086 | 4.985603 | 1.901168 |
| 40 | 1 | 0.322438 | 3.895260 | 2.765138 |
| 41 | 45 | 0.978653 | 0.156655 | -0.080820 |
| 42 | 45 | 2.723252 | -1.504793 | 0.333992 |
| 43 | 8 | 2.951563 | -0.688980 | 2.215898 |
| 44 | 6 | 2.228697 | 0.296580 | 2.557316 |
| 45 | 6 | 2.445859 | 0.878610 | 3.936410 |
| 46 | 8 | 1.337239 | 0.860736 | 1.836076 |
| 47 | 1 | 2.992988 | 1.822980 | 3.841754 |
| 48 | 1 | 1.484112 | 1.094586 | 4.408318 |
| 49 | 1 | 3.028618 | 0.191245 | 4.550806 |
| 50 | 8 | 1.245888 | -2.751217 | 1.069243 |
| 51 | 6 | 0.044169 | -2.352495 | 1.099195 |
| 52 | 8 | -0.380847 | -1.217747 | 0.685882 |
| 53 | 6 | -0.993354 | -3.297423 | 1.664667 |
| 54 | 1 | -1.584785 | -2.784414 | 2.428225 |
| 55 | 1 | -1.676531 | -3.608277 | 0.867599 |
| 56 | 1 | -0.510676 | -4.177448 | 2.090704 |
| 57 | 8 | 4.108665 | -0.178344 | -0.409452 |
| 58 | 6 | 3.700048 | 0.955420 | -0.813465 |
| 59 | 6 | 4.734534 | 1.929876 | -1.328127 |
| 60 | 8 | 2.491210 | 1.362111 | -0.807037 |
| 61 | 1 | 4.294609 | 2.583845 | -2.083137 |
| 62 | 1 | 5.076002 | 2.552370 | -0.493384 |
| 63 | 1 | 5.594395 | 1.390314 | -1.729089 |
| 64 | 8 | 0.739312 | -0.689372 | -1.960236 |
| 65 | 6 | 1.504941 | -1.654955 | -2.309651 |
| 66 | 8 | 2.387316 | -2.204002 | -1.584599 |
| 67 | 6 | 1.343735 | -2.162168 | -3.724907 |
| 68 | 1 | 1.823914 | -1.453617 | -4.408646 |
| 69 | 1 | 1.817091 | -3.138652 | -3.834800 |

| | | | | |
|---|---|---|---|---|
| 70 | 1 | 0.285728 | -2.214052 | -3.992970 |

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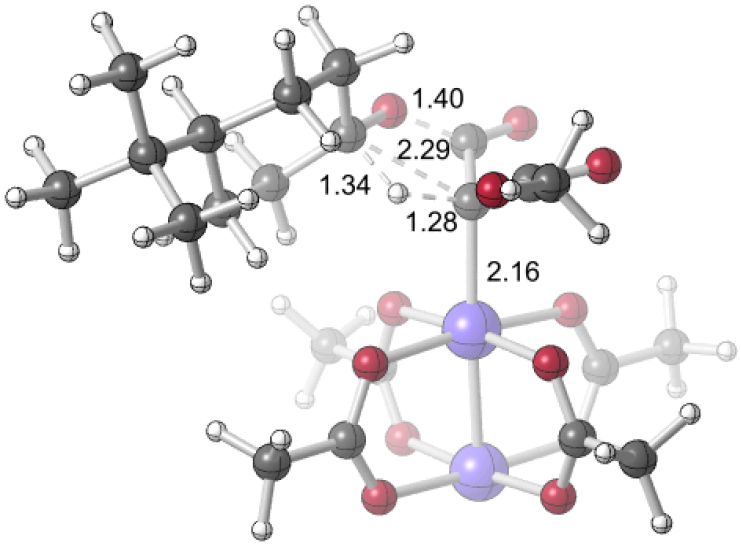
β-TS1$_{cat}$, Conformation 2




E(UB3LYP) = -1982.9329626 hartrees
Sum of electronic and thermal Free Energies = -1982.459613 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -4.782443 | -0.348321 | -0.538003 |
| 2 | 6 | -3.467318 | -1.115106 | -0.797615 |
| 3 | 6 | -2.583332 | -0.432303 | -1.853099 |
| 4 | 6 | -2.374896 | 1.036567 | -1.592712 |
| 5 | 6 | -3.584353 | 1.824960 | -1.155032 |
| 6 | 6 | -4.430671 | 1.091771 | -0.101898 |
| 7 | 1 | -1.610516 | -0.920589 | -1.958281 |
| 8 | 1 | -2.888228 | -1.201981 | 0.128489 |
| 9 | 1 | -3.668734 | -2.133023 | -1.142481 |
| 10 | 1 | -5.313341 | -0.274688 | -1.502274 |
| 11 | 1 | -1.524917 | 1.000870 | -0.555105 |
| 12 | 1 | -3.289107 | 2.823064 | -0.816686 |
| 13 | 1 | -4.169955 | 1.972948 | -2.076457 |
| 14 | 1 | -3.875137 | 1.072562 | 0.842563 |
| 15 | 1 | -5.333760 | 1.683533 | 0.071775 |
| 16 | 1 | -3.065614 | -0.469245 | -2.844150 |
| 17 | 6 | -5.778016 | -1.083782 | 0.427961 |

| | | | | |
|---|---|---|---|---|
| 18 | 6 | -7.103713 | -0.293299 | 0.508516 |
| 19 | 1 | -7.526219 | -0.122274 | -0.489296 |
| 20 | 1 | -7.844213 | -0.854345 | 1.089478 |
| 21 | 1 | -6.982301 | 0.678872 | 0.995957 |
| 22 | 6 | -6.108953 | -2.485258 | -0.133865 |
| 23 | 1 | -5.246313 | -3.158228 | -0.113135 |
| 24 | 1 | -6.899074 | -2.955150 | 0.462404 |
| 25 | 1 | -6.466859 | -2.425029 | -1.169160 |
| 26 | 6 | -5.205584 | -1.242238 | 1.852718 |
| 27 | 1 | -5.004596 | -0.274662 | 2.324429 |
| 28 | 1 | -5.924150 | -1.771596 | 2.488939 |
| 29 | 1 | -4.275412 | -1.819829 | 1.859381 |
| 30 | 8 | -1.588834 | 1.667377 | -2.554516 |
| 31 | 6 | -0.491342 | 2.243639 | -1.907242 |
| 32 | 8 | 0.265518 | 2.987752 | -2.453948 |
| 33 | 6 | -0.472003 | 1.719077 | -0.507555 |
| 34 | 6 | -0.615181 | 2.707128 | 0.596031 |
| 35 | 8 | 0.054494 | 3.714974 | 0.675959 |
| 36 | 8 | -1.539324 | 2.325055 | 1.505670 |
| 37 | 6 | -1.617024 | 3.149190 | 2.686912 |
| 38 | 1 | -2.402066 | 2.704441 | 3.298192 |
| 39 | 1 | -0.660534 | 3.131863 | 3.213338 |
| 40 | 1 | -1.868936 | 4.178937 | 2.421816 |
| 41 | 45 | 1.014814 | 0.213328 | -0.083286 |
| 42 | 45 | 2.797582 | -1.395590 | 0.365296 |
| 43 | 8 | 2.993131 | -0.552245 | 2.237669 |
| 44 | 6 | 2.229438 | 0.406089 | 2.568518 |
| 45 | 6 | 2.400470 | 0.993523 | 3.951884 |
| 46 | 8 | 1.314952 | 0.924183 | 1.841813 |
| 47 | 1 | 2.519498 | 2.078195 | 3.878115 |
| 48 | 1 | 1.499884 | 0.797069 | 4.542864 |
| 49 | 1 | 3.265061 | 0.552033 | 4.448444 |
| 50 | 8 | 1.343908 | -2.674834 | 1.095250 |
| 51 | 6 | 0.129804 | -2.314899 | 1.096932 |
| 52 | 8 | -0.324226 | -1.197837 | 0.666478 |
| 53 | 6 | -0.887000 | -3.291437 | 1.647983 |
| 54 | 1 | -1.518053 | -2.792769 | 2.389029 |
| 55 | 1 | -1.535893 | -3.638119 | 0.837031 |
| 56 | 1 | -0.383755 | -4.147772 | 2.097887 |
| 57 | 8 | 4.154200 | -0.038090 | -0.372557 |
| 58 | 6 | 3.719260 | 1.087028 | -0.776090 |
| 59 | 6 | 4.730239 | 2.094831 | -1.270943 |
| 60 | 8 | 2.499311 | 1.457929 | -0.784534 |
| 61 | 1 | 4.291941 | 2.712494 | -2.057031 |
| 62 | 1 | 5.005327 | 2.751976 | -0.438380 |
| 63 | 1 | 5.628938 | 1.586854 | -1.624852 |

| | | | | |
|---|---|---|---|---|
| 64 | 8 | 0.832968 | -0.641034 | -1.965795 |
| 65 | 6 | 1.624216 | -1.592780 | -2.295534 |
| 66 | 8 | 2.502078 | -2.121937 | -1.550404 |
| 67 | 6 | 1.503002 | -2.108426 | -3.711811 |
| 68 | 1 | 1.996646 | -1.399956 | -4.386033 |
| 69 | 1 | 1.986583 | -3.081727 | -3.804473 |
| 70 | 1 | 0.452979 | -2.169033 | -4.007806 |

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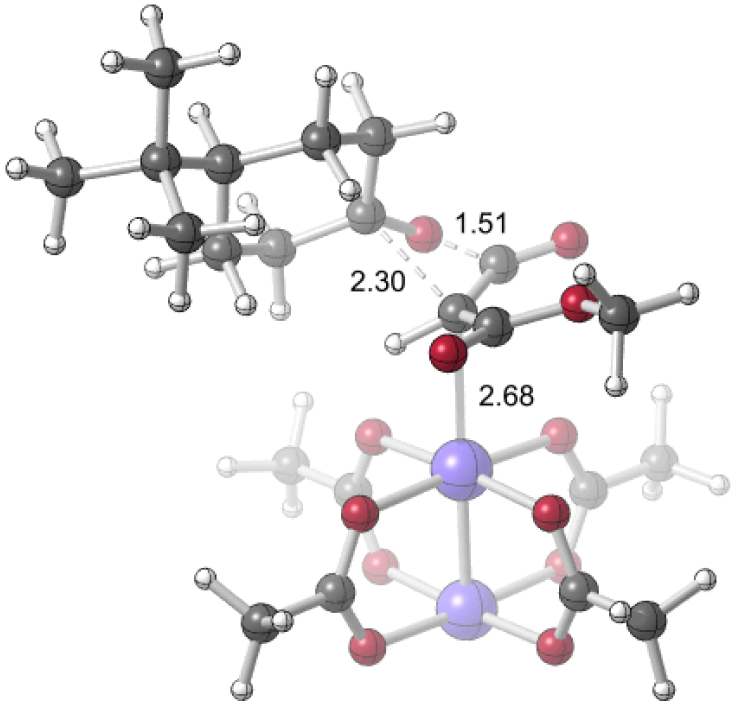
β-TS2$_{cat}$, Configuration 1




E(UB3LYP) = -1982.944116 hartrees
Sum of electronic and thermal Free Energies =
-1982.472090 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -5.129690 | -0.657173 | -0.444916 |
| 2 | 6 | -3.813204 | -1.460632 | -0.367877 |
| 3 | 6 | -2.902565 | -1.230670 | -1.591906 |
| 4 | 6 | -2.704654 | 0.214864 | -1.905235 |
| 5 | 6 | -3.910476 | 1.102641 | -1.849259 |
| 6 | 6 | -4.792905 | 0.841517 | -0.614611 |
| 7 | 1 | -1.926841 | -1.714305 | -1.488996 |

| | | | | |
|---|---|---|---|---|
| 8 | 1 | -3.255711 | -1.180120 | 0.533267 |
| 9 | 1 | -4.012213 | -2.533123 | -0.297303 |
| 10 | 1 | -5.653036 | -0.977089 | -1.362215 |
| 11 | 1 | -1.274234 | 0.216233 | -0.247753 |
| 12 | 1 | -3.632246 | 2.155072 | -1.947238 |
| 13 | 1 | -4.479100 | 0.845782 | -2.762406 |
| 14 | 1 | -4.267510 | 1.210702 | 0.273131 |
| 15 | 1 | -5.703361 | 1.436855 | -0.723087 |
| 16 | 1 | -3.375516 | -1.660914 | -2.492688 |
| 17 | 6 | -6.126985 | -0.958891 | 0.730284 |
| 18 | 6 | -5.536517 | -0.596393 | 2.109876 |
| 19 | 1 | -5.268264 | 0.462328 | 2.179583 |
| 20 | 1 | -6.272794 | -0.801092 | 2.895754 |
| 21 | 1 | -4.640866 | -1.180801 | 2.343102 |
| 22 | 6 | -7.432834 | -0.158954 | 0.521798 |
| 23 | 1 | -7.855587 | -0.335489 | -0.475274 |
| 24 | 1 | -8.184128 | -0.464973 | 1.258307 |
| 25 | 1 | -7.284938 | 0.918519 | 0.642140 |
| 26 | 6 | -6.497268 | -2.459687 | 0.722543 |
| 27 | 1 | -5.644945 | -3.101987 | 0.964894 |
| 28 | 1 | -7.273966 | -2.660939 | 1.468699 |
| 29 | 1 | -6.888929 | -2.768987 | -0.254657 |
| 30 | 8 | -1.643891 | 0.544155 | -2.630599 |
| 31 | 6 | -1.072856 | 1.699054 | -1.843114 |
| 32 | 8 | -0.712120 | 2.683181 | -2.410543 |
| 33 | 6 | -1.253518 | 1.277138 | -0.477513 |
| 34 | 6 | -1.413029 | 2.173880 | 0.673738 |
| 35 | 8 | -1.846018 | 1.796307 | 1.753997 |
| 36 | 8 | -1.107495 | 3.459552 | 0.403139 |
| 37 | 6 | -1.253645 | 4.378308 | 1.497628 |
| 38 | 1 | -2.289986 | 4.404886 | 1.845540 |
| 39 | 1 | -0.605072 | 4.085821 | 2.327166 |
| 40 | 1 | -0.956793 | 5.348750 | 1.099714 |
| 41 | 45 | 1.111061 | 0.078463 | -0.063407 |
| 42 | 45 | 3.239421 | -0.956335 | 0.376760 |
| 43 | 8 | 3.661804 | 0.590599 | 1.666390 |
| 44 | 6 | 2.795297 | 1.509946 | 1.826752 |
| 45 | 6 | 3.137795 | 2.634533 | 2.776174 |
| 46 | 8 | 1.658276 | 1.569028 | 1.253694 |
| 47 | 1 | 3.139771 | 3.582222 | 2.228867 |
| 48 | 1 | 2.369529 | 2.702721 | 3.552094 |
| 49 | 1 | 4.114676 | 2.467300 | 3.230777 |
| 50 | 8 | 2.345442 | -1.989539 | 1.922317 |
| 51 | 6 | 1.105062 | -1.813586 | 2.149198 |
| 52 | 8 | 0.330207 | -1.041805 | 1.493284 |
| 53 | 6 | 0.490616 | -2.575228 | 3.300986 |

| | | | | |
|---|---|---|---|---|
| 54 | 1 | 1.215718 | -3.264142 | 3.735300 |
| 55 | 1 | 0.154101 | -1.863369 | 4.061324 |
| 56 | 1 | -0.389830 | -3.122944 | 2.953051 |
| 57 | 8 | 4.024227 | 0.132584 | -1.185637 |
| 58 | 6 | 3.258135 | 0.923599 | -1.828247 |
| 59 | 6 | 3.878634 | 1.734721 | -2.941040 |
| 60 | 8 | 2.017961 | 1.104402 | -1.600286 |
| 61 | 1 | 4.616532 | 1.133829 | -3.477208 |
| 62 | 1 | 3.107186 | 2.102481 | -3.618797 |
| 63 | 1 | 4.398952 | 2.593065 | -2.501687 |
| 64 | 8 | 0.696808 | -1.498539 | -1.347898 |
| 65 | 6 | 1.577478 | -2.408774 | -1.510267 |
| 66 | 8 | 2.713571 | -2.452044 | -0.942030 |
| 67 | 6 | 1.224213 | -3.543184 | -2.445044 |
| 68 | 1 | 0.553233 | -4.236393 | -1.925438 |
| 69 | 1 | 0.698344 | -3.157359 | -3.321508 |
| 70 | 1 | 2.123436 | -4.083499 | -2.743649 |

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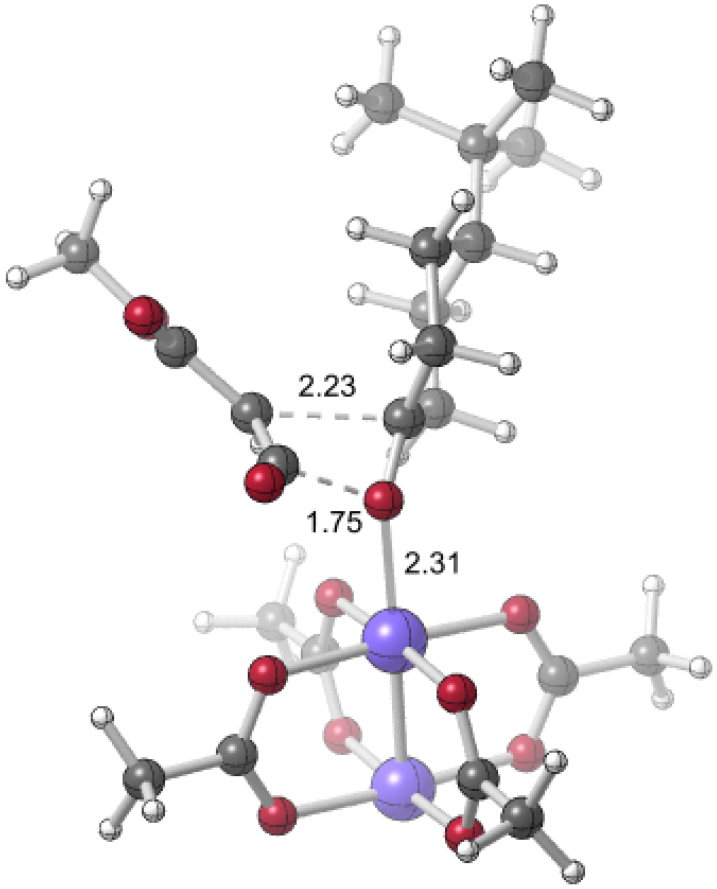
β-TS2$_{cat}$, Configuration 2



E(UB3LYP) = -1982.9532316 hartrees
Sum of electronic and thermal Free Energies = -1982.482018 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -4.513985 | -1.622541 | -0.376455 |
| 2 | 6 | -3.548595 | -1.261464 | 0.773559 |
| 3 | 6 | -2.094177 | -1.090273 | 0.299267 |
| 4 | 6 | -1.955688 | -0.186738 | -0.886358 |
| 5 | 6 | -2.976067 | -0.356661 | -1.981009 |
| 6 | 6 | -4.412609 | -0.533376 | -1.466299 |
| 7 | 1 | -1.432760 | -0.759637 | 1.102734 |
| 8 | 1 | -3.871284 | -0.328726 | 1.252142 |
| 9 | 1 | -3.557216 | -2.033949 | 1.547175 |
| 10 | 1 | -4.145243 | -2.561648 | -0.822263 |
| 11 | 1 | -1.704796 | 1.509825 | 0.710436 |
| 12 | 1 | -2.899548 | 0.449101 | -2.716021 |
| 13 | 1 | -2.654198 | -1.274738 | -2.502720 |
| 14 | 1 | -4.760591 | 0.428034 | -1.070850 |
| 15 | 1 | -5.050563 | -0.772104 | -2.321541 |
| 16 | 1 | -1.685942 | -2.057416 | -0.039654 |
| 17 | 6 | -5.982506 | -1.930700 | 0.085840 |
| 18 | 6 | -6.677217 | -0.697139 | 0.700957 |
| 19 | 1 | -6.771633 | 0.122408 | -0.019023 |
| 20 | 1 | -7.689589 | -0.961030 | 1.028025 |
| 21 | 1 | -6.139427 | -0.319239 | 1.576824 |
| 22 | 6 | -6.814594 | -2.420356 | -1.121525 |
| 23 | 1 | -6.337216 | -3.277541 | -1.612321 |
| 24 | 1 | -7.808954 | -2.740365 | -0.790435 |
| 25 | 1 | -6.961839 | -1.639141 | -1.873554 |
| 26 | 6 | -5.972257 | -3.068583 | 1.132051 |
| 27 | 1 | -5.514809 | -2.761770 | 2.077661 |
| 28 | 1 | -6.997076 | -3.385225 | 1.356378 |
| 29 | 1 | -5.428658 | -3.946222 | 0.760684 |
| 30 | 8 | -0.772031 | 0.306408 | -1.201329 |
| 31 | 6 | -1.362036 | 1.943524 | -1.344288 |
| 32 | 8 | -1.126818 | 2.492613 | -2.352265 |
| 33 | 6 | -2.159759 | 1.920499 | -0.179910 |
| 34 | 6 | -3.181536 | 2.963169 | 0.009208 |
| 35 | 8 | -3.636051 | 3.700588 | -0.848062 |
| 36 | 8 | -3.623634 | 2.959435 | 1.297784 |
| 37 | 6 | -4.674712 | 3.895611 | 1.594313 |
| 38 | 1 | -4.342638 | 4.918136 | 1.397589 |
| 39 | 1 | -5.559264 | 3.685864 | 0.987049 |

| | | | | |
|---|---|---|---|---|
| 40 | 1 | -4.894232 | 3.759717 | 2.653373 |
| 41 | 45 | 1.298861 | -0.073178 | -0.247431 |
| 42 | 45 | 3.526443 | -0.377101 | 0.615337 |
| 43 | 8 | 2.754628 | -0.114745 | 2.512766 |
| 44 | 6 | 1.512723 | 0.106415 | 2.658305 |
| 45 | 6 | 1.009025 | 0.343726 | 4.063766 |
| 46 | 8 | 0.651554 | 0.168185 | 1.715494 |
| 47 | 1 | 0.951427 | 1.423916 | 4.238838 |
| 48 | 1 | 0.005549 | -0.070149 | 4.184877 |
| 49 | 1 | 1.696053 | -0.090260 | 4.791703 |
| 50 | 8 | 3.132532 | -2.400977 | 0.731018 |
| 51 | 6 | 2.000478 | -2.836380 | 0.351095 |
| 52 | 8 | 1.035001 | -2.124469 | -0.087714 |
| 53 | 6 | 1.783415 | -4.332108 | 0.397895 |
| 54 | 1 | 0.746684 | -4.559506 | 0.655348 |
| 55 | 1 | 1.983865 | -4.747436 | -0.596125 |
| 56 | 1 | 2.468028 | -4.793206 | 1.111369 |
| 57 | 8 | 3.793764 | 1.659247 | 0.444792 |
| 58 | 6 | 2.837398 | 2.376572 | 0.007718 |
| 59 | 6 | 3.091226 | 3.858656 | -0.137190 |
| 60 | 8 | 1.687096 | 1.948467 | -0.341521 |
| 61 | 1 | 2.157593 | 4.416447 | -0.046240 |
| 62 | 1 | 3.819370 | 4.192140 | 0.604476 |
| 63 | 1 | 3.505756 | 4.046620 | -1.133966 |
| 64 | 8 | 2.077776 | -0.327502 | -2.137364 |
| 65 | 6 | 3.328304 | -0.533899 | -2.272399 |
| 66 | 8 | 4.175332 | -0.617793 | -1.324829 |
| 67 | 6 | 3.856415 | -0.665802 | -3.682063 |
| 68 | 1 | 3.057564 | -0.962431 | -4.363380 |
| 69 | 1 | 4.245202 | 0.306931 | -4.003354 |
| 70 | 1 | 4.679050 | -1.383423 | -3.710023 |

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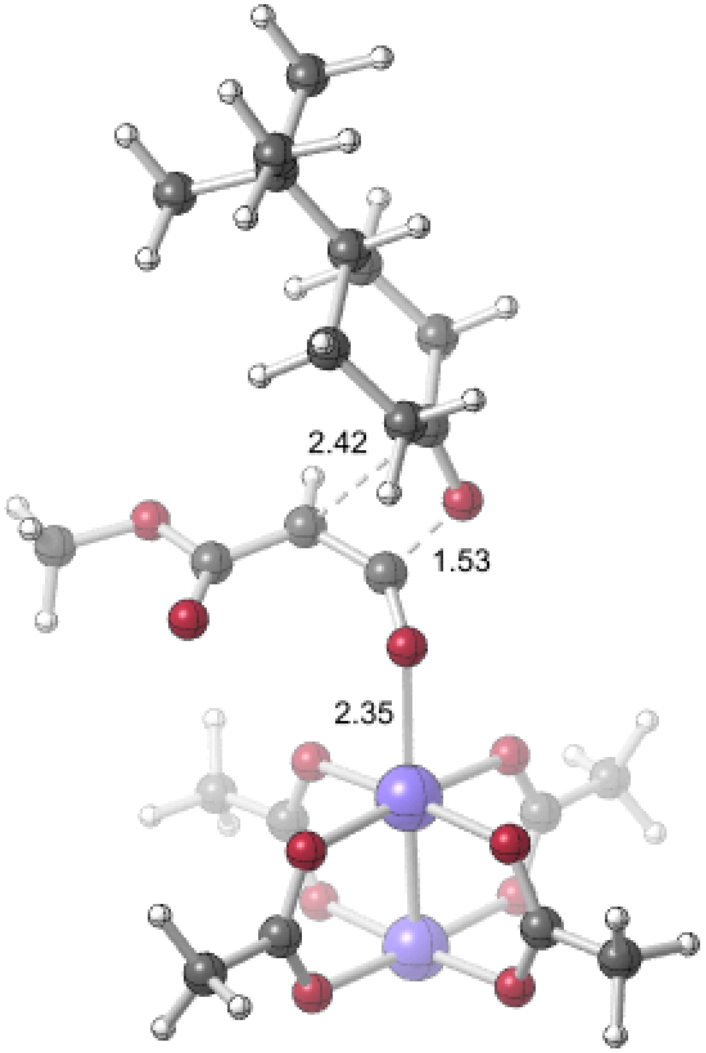
β-TS2$_{cat}$, Configuration 3




E(UB3LYP) = -1982.947074 hartrees
Sum of electronic and thermal Free Energies = -1982.476223 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 6.353749 | -1.007312 | 0.216052 |
| 2 | 6 | 5.846370 | -0.900761 | -1.238972 |
| 3 | 6 | 4.580582 | -1.749411 | -1.487327 |
| 4 | 6 | 3.515627 | -1.507518 | -0.470666 |
| 5 | 6 | 3.940088 | -1.432115 | 0.964271 |
| 6 | 6 | 5.214577 | -0.594917 | 1.174363 |
| 7 | 1 | 4.170761 | -1.600032 | -2.490362 |
| 8 | 1 | 5.614310 | 0.143347 | -1.478616 |
| 9 | 1 | 6.610451 | -1.228423 | -1.948386 |
| 10 | 1 | 6.565045 | -2.073164 | 0.405525 |

| | | | | |
|---|---|---|---|---|
| 11 | 1 | 2.781636 | 0.485654 | -1.660892 |
| 12 | 1 | 3.120787 | -1.106468 | 1.608782 |
| 13 | 1 | 4.153897 | -2.483076 | 1.234737 |
| 14 | 1 | 4.957076 | 0.460322 | 1.028636 |
| 15 | 1 | 5.520094 | -0.708624 | 2.217363 |
| 16 | 1 | 4.836579 | -2.820222 | -1.409164 |
| 17 | 6 | 7.711538 | -0.262067 | 0.475272 |
| 18 | 6 | 7.593466 | 1.263821 | 0.273097 |
| 19 | 1 | 6.868406 | 1.714514 | 0.958484 |
| 20 | 1 | 8.561052 | 1.741863 | 0.463357 |
| 21 | 1 | 7.299463 | 1.522841 | -0.749502 |
| 22 | 6 | 8.183694 | -0.538301 | 1.921054 |
| 23 | 1 | 8.238580 | -1.615040 | 2.123867 |
| 24 | 1 | 9.184755 | -0.121365 | 2.077404 |
| 25 | 1 | 7.526157 | -0.085624 | 2.669440 |
| 26 | 6 | 8.796276 | -0.809092 | -0.480350 |
| 27 | 1 | 8.604773 | -0.544787 | -1.525015 |
| 28 | 1 | 9.775125 | -0.393066 | -0.217857 |
| 29 | 1 | 8.872805 | -1.901468 | -0.413856 |
| 30 | 8 | 2.273042 | -1.737440 | -0.821560 |
| 31 | 6 | 1.539666 | -0.526180 | -0.245494 |
| 32 | 8 | 0.604641 | -0.731036 | 0.488024 |
| 33 | 6 | 2.303622 | 0.570193 | -0.694335 |
| 34 | 6 | 2.131679 | 1.918181 | -0.148321 |
| 35 | 8 | 1.626245 | 2.215248 | 0.918678 |
| 36 | 8 | 2.705559 | 2.841650 | -0.978836 |
| 37 | 6 | 2.664002 | 4.198280 | -0.508838 |
| 38 | 1 | 1.629999 | 4.525227 | -0.371474 |
| 39 | 1 | 3.193634 | 4.293942 | 0.443327 |
| 40 | 1 | 3.154792 | 4.790509 | -1.281768 |
| 41 | 45 | -1.680028 | -0.272874 | 0.204190 |
| 42 | 45 | -4.023214 | 0.130077 | -0.170916 |
| 43 | 8 | -3.984237 | 1.466337 | 1.396975 |
| 44 | 6 | -2.889838 | 1.633046 | 2.030819 |
| 45 | 6 | -2.915568 | 2.571732 | 3.215627 |
| 46 | 8 | -1.782995 | 1.063595 | 1.770011 |
| 47 | 1 | -1.924503 | 2.997990 | 3.380558 |
| 48 | 1 | -3.658359 | 3.356856 | 3.061044 |
| 49 | 1 | -3.200370 | 2.002571 | 4.107803 |
| 50 | 8 | -3.487183 | 1.636399 | -1.476934 |
| 51 | 6 | -2.252230 | 1.884607 | -1.661100 |
| 52 | 8 | -1.278119 | 1.266521 | -1.120766 |
| 53 | 6 | -1.913678 | 3.034409 | -2.583531 |
| 54 | 1 | -1.948950 | 3.966469 | -2.008267 |
| 55 | 1 | -0.908194 | 2.915135 | -2.990717 |
| 56 | 1 | -2.651615 | 3.105093 | -3.385358 |

| | | | | |
|---|---|---|---|---|
| 57 | 8 | -4.431481 | -1.397713 | 1.152027 |
| 58 | 6 | -3.460404 | -2.028344 | 1.684064 |
| 59 | 6 | -3.809578 | -3.178884 | 2.601246 |
| 60 | 8 | -2.223778 | -1.792607 | 1.494528 |
| 61 | 1 | -3.936155 | -4.083763 | 1.996118 |
| 62 | 1 | -3.004789 | -3.352449 | 3.317676 |
| 63 | 1 | -4.751988 | -2.979931 | 3.115386 |
| 64 | 8 | -1.727333 | -1.593132 | -1.393517 |
| 65 | 6 | -2.828999 | -1.780320 | -2.004647 |
| 66 | 8 | -3.942190 | -1.230133 | -1.722045 |
| 67 | 6 | -2.808277 | -2.719135 | -3.190516 |
| 68 | 1 | -2.625039 | -2.133581 | -4.098634 |
| 69 | 1 | -2.005160 | -3.450499 | -3.083648 |
| 70 | 1 | -3.774697 | -3.215879 | -3.296651 |

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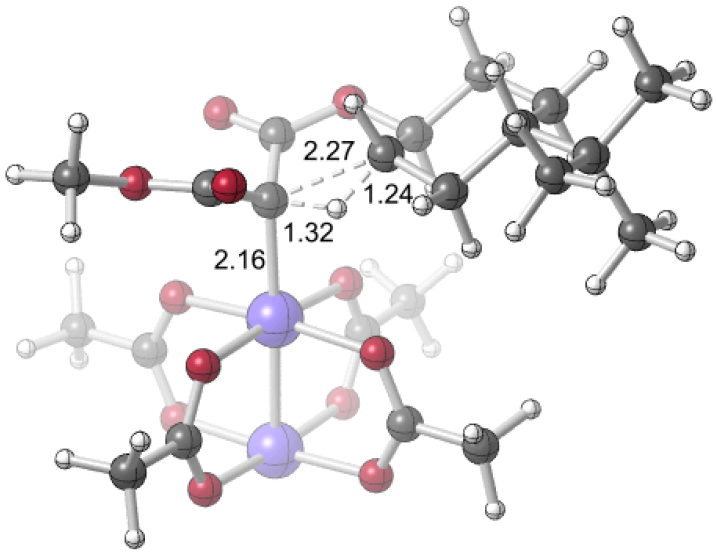
γ-TS1-eq-*half-chair*




E(UB3LYP) = -1982.9315398 hartrees
Sum of electronic and thermal Free Energies = -1982.455862 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 45 | 0.984005 | 0.141169 | 0.049246 |
| 2 | 45 | 2.676912 | -1.599058 | -0.222970 |
| 3 | 6 | -0.447927 | 1.738600 | 0.300726 |
| 4 | 6 | -0.635684 | 2.199464 | 1.717194 |

| | | | | |
|---|---|---|---|---|
| 5 | 6 | -0.440087 | 2.794199 | -0.773991 |
| 6 | 8 | -1.249653 | 2.844496 | -1.685050 |
| 7 | 6 | -2.629604 | 1.116538 | 0.306790 |
| 8 | 1 | -1.474283 | 1.015503 | -0.119522 |
| 9 | 1 | -2.938102 | 2.155459 | 0.185910 |
| 10 | 6 | 2.363891 | 0.156619 | -2.521320 |
| 11 | 6 | 1.321029 | -1.621681 | 2.354973 |
| 12 | 6 | 0.000703 | -2.370020 | -1.089122 |
| 13 | 6 | 3.688004 | 0.859689 | 0.900237 |
| 14 | 8 | 1.462393 | 0.778237 | -1.862552 |
| 15 | 8 | 0.611864 | -0.642361 | 1.935746 |
| 16 | 8 | 3.022265 | -0.850281 | -2.117529 |
| 17 | 8 | 2.223210 | -2.222563 | 1.697120 |
| 18 | 8 | -0.396498 | -1.202204 | -0.743185 |
| 19 | 8 | 2.499276 | 1.312550 | 0.819017 |
| 20 | 8 | 1.181620 | -2.812289 | -0.987374 |
| 21 | 8 | 4.072546 | -0.300120 | 0.547483 |
| 22 | 8 | 0.118556 | 2.994001 | 2.226486 |
| 23 | 8 | -1.676803 | 1.679865 | 2.426604 |
| 24 | 6 | -2.492097 | 0.708990 | 1.749609 |
| 25 | 1 | -1.985181 | -0.261444 | 1.818223 |
| 26 | 6 | -3.444902 | 0.164486 | -0.547023 |
| 27 | 1 | -3.468905 | 0.534384 | -1.573102 |
| 28 | 1 | -2.977420 | -0.823214 | -0.552051 |
| 29 | 6 | -3.879537 | 0.632712 | 2.382444 |
| 30 | 1 | -3.792640 | 0.284642 | 3.417092 |
| 31 | 1 | -4.310390 | 1.641449 | 2.414666 |
| 32 | 6 | -4.877390 | 0.097684 | 0.069670 |
| 33 | 1 | -5.283480 | 1.121305 | 0.043612 |
| 34 | 6 | -4.777239 | -0.312558 | 1.559567 |
| 35 | 1 | -5.770330 | -0.328747 | 2.016710 |
| 36 | 1 | -4.382156 | -1.334010 | 1.634747 |
| 37 | 6 | -5.875207 | -0.770170 | -0.779308 |
| 38 | 6 | -7.298386 | -0.630890 | -0.191408 |
| 39 | 1 | -8.020785 | -1.152036 | -0.829325 |
| 40 | 1 | -7.381755 | -1.062819 | 0.810431 |
| 41 | 1 | -7.604485 | 0.420768 | -0.135180 |
| 42 | 6 | -5.919452 | -0.248145 | -2.232986 |
| 43 | 1 | -6.119318 | 0.829758 | -2.264867 |
| 44 | 1 | -4.986388 | -0.434657 | -2.773133 |
| 45 | 1 | -6.719484 | -0.749738 | -2.788540 |
| 46 | 6 | -5.487245 | -2.263594 | -0.797566 |
| 47 | 1 | -5.510281 | -2.707661 | 0.203056 |
| 48 | 1 | -6.194082 | -2.825660 | -1.418434 |
| 49 | 1 | -4.488513 | -2.423125 | -1.217531 |
| 50 | 8 | 0.587269 | 3.627398 | -0.616817 |

| | | | | |
|---|---|---|---|---|
| 51 | 6 | 0.759313 | 4.617812 | -1.649981 |
| 52 | 1 | -0.121535 | 5.261414 | -1.711619 |
| 53 | 1 | 1.635817 | 5.190099 | -1.348554 |
| 54 | 1 | 0.924069 | 4.128760 | -2.612712 |
| 55 | 6 | 4.734866 | 1.804778 | 1.444449 |
| 56 | 1 | 5.214755 | 2.319135 | 0.604186 |
| 57 | 1 | 4.271304 | 2.552819 | 2.089502 |
| 58 | 1 | 5.502584 | 1.245115 | 1.982494 |
| 59 | 6 | 2.686170 | 0.692692 | -3.898419 |
| 60 | 1 | 1.788418 | 1.100040 | -4.368002 |
| 61 | 1 | 3.416953 | 1.503206 | -3.798406 |
| 62 | 1 | 3.124674 | -0.092524 | -4.516359 |
| 63 | 6 | -1.048610 | -3.299062 | -1.660459 |
| 64 | 1 | -1.773965 | -3.553391 | -0.880404 |
| 65 | 1 | -1.588693 | -2.798314 | -2.468994 |
| 66 | 1 | -0.583323 | -4.213145 | -2.030443 |
| 67 | 6 | 1.064439 | -2.079805 | 3.773053 |
| 68 | 1 | 1.521837 | -1.361640 | 4.462290 |
| 69 | 1 | -0.008587 | -2.096542 | 3.978872 |
| 70 | 1 | 1.503706 | -3.064023 | 3.940578 |

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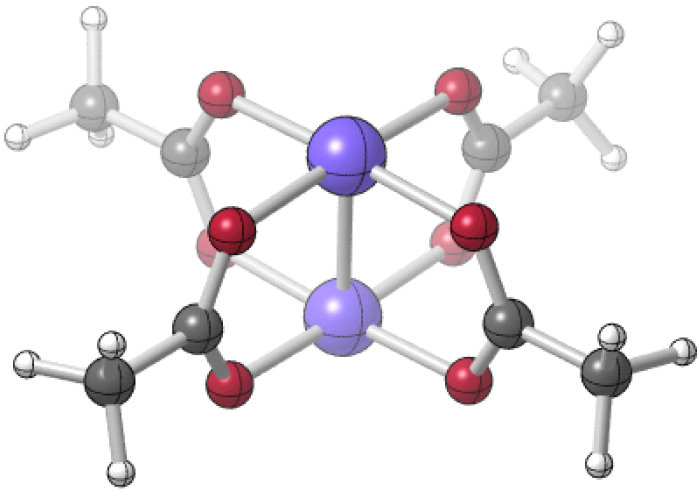
$Rh_2(OAc)_4$

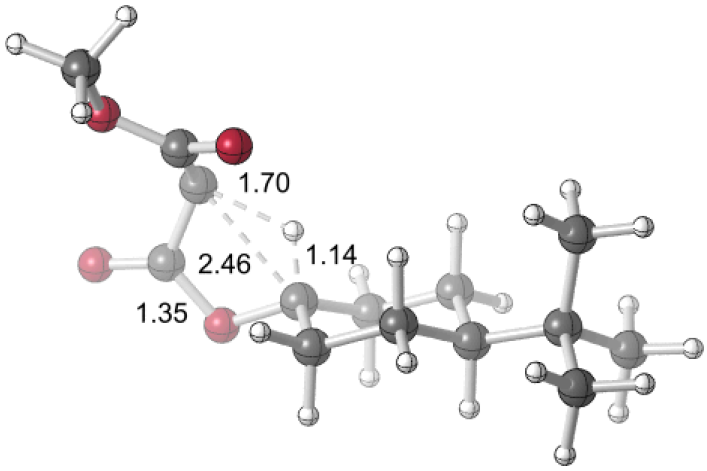


E(UB3LYP) = -1135.3095845 hartrees
Sum of electronic and thermal Free Energies = -1135.152714 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| 1 | 45 | 0.003545 | -0.003642 | -1.194711 |
| 2 | 45 | 0.002986 | -0.002994 | 1.195447 |
| 3 | 8 | 1.455185 | -1.460466 | 1.134872 |
| 4 | 6 | 1.870561 | -1.871341 | 0.001391 |
| 5 | 8 | 1.454025 | -1.462830 | -1.132683 |
| 6 | 6 | 2.966505 | -2.909819 | -0.000046 |
| 7 | 1 | 2.859447 | -3.570299 | -0.862683 |
| 8 | 1 | 3.932929 | -2.399618 | -0.080442 |
| 9 | 1 | 2.952003 | -3.479413 | 0.930474 |
| 10 | 8 | -1.447588 | 1.456342 | -1.133468 |
| 11 | 6 | -1.864444 | 1.865471 | 0.000197 |
| 12 | 8 | -1.449639 | 1.455032 | 1.134052 |
| 13 | 6 | -2.960145 | 2.904405 | -0.002180 |
| 14 | 1 | -2.849274 | 3.567859 | -0.862093 |
| 15 | 1 | -3.926477 | 2.395074 | -0.088958 |
| 16 | 1 | -2.949633 | 3.470726 | 0.930373 |
| 17 | 8 | 1.460744 | 1.449407 | 1.134439 |
| 18 | 6 | 1.870969 | 1.864883 | 0.000761 |
| 19 | 8 | 1.463079 | 1.447220 | -1.133094 |
| 20 | 6 | 2.908140 | 2.962145 | -0.001336 |
| 21 | 1 | 2.397166 | 3.927370 | -0.090621 |
| 22 | 1 | 3.472793 | 2.953968 | 0.932243 |
| 23 | 1 | 3.573331 | 2.851051 | -0.859894 |
| 24 | 8 | -1.453181 | -1.456995 | 1.134557 |
| 25 | 6 | -1.869162 | -1.866826 | 0.000931 |
| 26 | 8 | -1.454081 | -1.456435 | -1.132970 |
| 27 | 6 | -2.963938 | -2.906680 | -0.001152 |
| 28 | 1 | -3.930354 | -2.398973 | -0.096033 |
| 29 | 1 | -2.847774 | -3.574679 | -0.856871 |
| 30 | 1 | -2.957312 | -3.468089 | 0.934353 |

$\beta$-TS1$_{uncat}$




E(UB3LYP) = -847.5936815 hartrees
Sum of electronic and thermal Free Energies = -847.301141 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 2.453899 | -0.296140 | 0.235319 |
| 2 | 6 | 1.857916 | -0.969736 | -1.021671 |
| 3 | 6 | 0.681421 | -1.900772 | -0.681207 |
| 4 | 6 | -0.388525 | -1.178416 | 0.120329 |
| 5 | 6 | 0.149421 | -0.457636 | 1.344665 |
| 6 | 6 | 1.327784 | 0.460497 | 0.976210 |
| 7 | 1 | 0.238862 | -2.324019 | -1.589311 |
| 8 | 1 | 1.512883 | -0.201423 | -1.726313 |
| 9 | 1 | 2.615209 | -1.557490 | -1.547765 |
| 10 | 1 | 2.789000 | -1.108136 | 0.902219 |
| 11 | 1 | -0.864744 | -0.409000 | -0.580913 |
| 12 | 1 | -0.648900 | 0.118942 | 1.822793 |
| 13 | 1 | 0.471468 | -1.225862 | 2.061290 |
| 14 | 1 | 0.950748 | 1.279537 | 0.351587 |
| 15 | 1 | 1.703712 | 0.915792 | 1.896549 |
| 16 | 1 | 1.028240 | -2.745849 | -0.069956 |
| 17 | 6 | 3.734080 | 0.569470 | -0.042490 |
| 18 | 6 | 4.315423 | 1.080760 | 1.295181 |
| 19 | 1 | 4.506027 | 0.252500 | 1.988628 |
| 20 | 1 | 5.268090 | 1.593719 | 1.121723 |
| 21 | 1 | 3.651433 | 1.793499 | 1.793325 |
| 22 | 6 | 4.818380 | -0.303216 | -0.714546 |
| 23 | 1 | 4.540805 | -0.604872 | -1.729005 |
| 24 | 1 | 5.759205 | 0.253440 | -0.789435 |
| 25 | 1 | 5.016273 | -1.211799 | -0.132539 |

| | | | | |
|---|---|---|---|---|
| 26 | 6 | 3.440842 | 1.782405 | -0.950704 |
| 27 | 1 | 2.716922 | 2.468688 | -0.499647 |
| 28 | 1 | 4.361718 | 2.350310 | -1.126198 |
| 29 | 1 | 3.054771 | 1.479911 | -1.929664 |
| 30 | 8 | -1.449475 | -2.098118 | 0.466236 |
| 31 | 6 | -2.636224 | -1.599013 | 0.061197 |
| 32 | 8 | -3.718959 | -2.123212 | 0.239131 |
| 33 | 6 | -2.559419 | -0.410149 | -0.753356 |
| 34 | 6 | -2.923763 | 0.926822 | -0.340956 |
| 35 | 8 | -2.065861 | 1.782321 | -0.147931 |
| 36 | 8 | -4.247257 | 1.122079 | -0.279766 |
| 37 | 6 | -4.676890 | 2.470669 | 0.020226 |
| 38 | 1 | -5.764575 | 2.429641 | -0.008845 |
| 39 | 1 | -4.327217 | 2.768957 | 1.010770 |
| 40 | 1 | -4.293597 | 3.165691 | -0.729820 |

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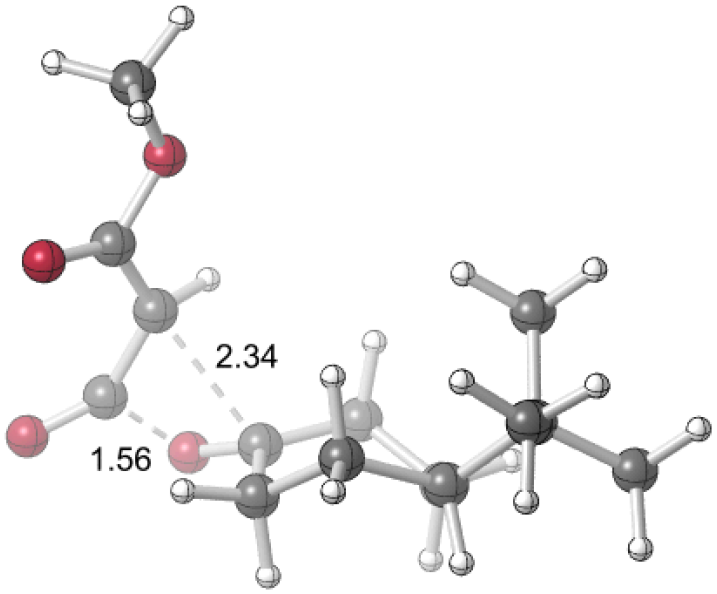
β-TS2$_{uncat}$




E(UB3LYP) = -847.6330644 hartrees
Sum of electronic and thermal Free Energies = -847.339784 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 8 | -1.338557 | -2.411657 | -0.574335 |
| 2 | 6 | -0.337016 | -1.610987 | -0.281199 |
| 3 | 6 | 0.073537 | -1.327832 | 1.136036 |

| | | | | |
|---|---|---|---|---|
| 4 | 6 | 0.713778 | -1.384892 | -1.328771 |
| 5 | 1 | 0.548010 | -0.390218 | -1.761809 |
| 6 | 1 | 0.566123 | -2.254834 | 1.481670 |
| 7 | 1 | -0.786269 | -1.177621 | 1.791563 |
| 8 | 1 | 0.558768 | -2.107447 | -2.137148 |
| 9 | 6 | 1.073354 | -0.164517 | 1.185346 |
| 10 | 1 | 1.272771 | 0.091212 | 2.229006 |
| 11 | 1 | 0.592397 | 0.713589 | 0.737533 |
| 12 | 6 | 2.140578 | -1.464634 | -0.746392 |
| 13 | 1 | 2.848367 | -1.278530 | -1.558025 |
| 14 | 1 | 2.320498 | -2.498987 | -0.431900 |
| 15 | 6 | 2.402447 | -0.507061 | 0.459390 |
| 16 | 1 | 3.005448 | -1.078498 | 1.178960 |
| 17 | 6 | 3.269830 | 0.752033 | 0.110154 |
| 18 | 6 | 3.397163 | 1.656467 | 1.356006 |
| 19 | 1 | 4.096259 | 2.476849 | 1.158911 |
| 20 | 1 | 2.440855 | 2.105004 | 1.641899 |
| 21 | 1 | 3.779684 | 1.095676 | 2.217489 |
| 22 | 6 | 4.692939 | 0.300733 | -0.286563 |
| 23 | 1 | 5.167180 | -0.265256 | 0.524004 |
| 24 | 1 | 4.699630 | -0.328581 | -1.182416 |
| 25 | 1 | 5.324109 | 1.171254 | -0.497535 |
| 26 | 6 | 2.665950 | 1.578520 | -1.045063 |
| 27 | 1 | 2.627410 | 1.009267 | -1.980602 |
| 28 | 1 | 1.653443 | 1.928695 | -0.817169 |
| 29 | 1 | 3.279948 | 2.466116 | -1.234370 |
| 30 | 6 | -2.534675 | -1.587102 | 0.001349 |
| 31 | 6 | -2.249576 | -0.292004 | -0.515319 |
| 32 | 8 | -3.288622 | -2.114744 | 0.756621 |
| 33 | 6 | -2.915569 | 0.902156 | 0.000776 |
| 34 | 1 | -1.864515 | -0.236600 | -1.523840 |
| 35 | 8 | -2.693826 | 1.965974 | -0.832745 |
| 36 | 8 | -3.536098 | 1.005118 | 1.045544 |
| 37 | 6 | -3.248040 | 3.217041 | -0.395786 |
| 38 | 1 | -4.334142 | 3.142783 | -0.297307 |
| 39 | 1 | -2.825309 | 3.511822 | 0.568640 |
| 40 | 1 | -2.982035 | 3.939226 | -1.168031 |

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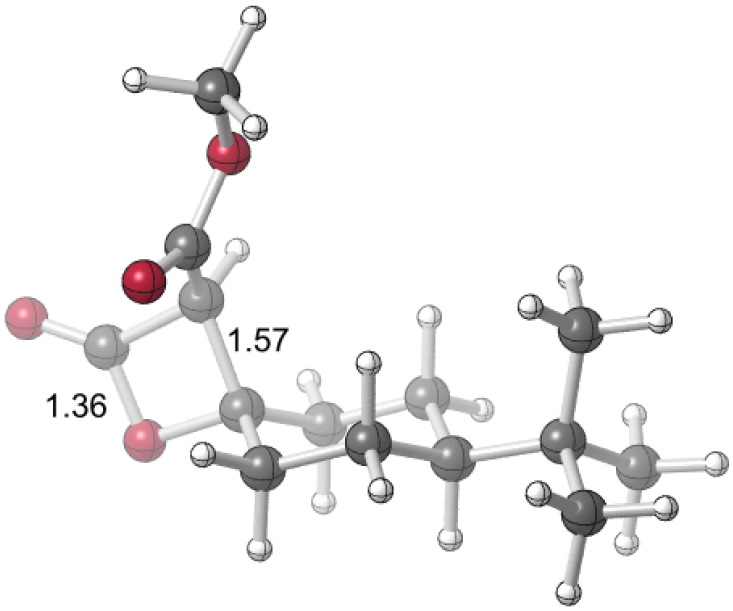
β-lactone




E(UB3LYP) = -847.7077667 hartrees
Sum of electronic and thermal Free Energies = -847.409224 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 2.040830 | -0.579743 | 0.169124 |
| 2 | 6 | 1.301853 | -0.927431 | -1.142294 |
| 3 | 6 | 0.104649 | -1.861922 | -0.894883 |
| 4 | 6 | -0.877508 | -1.261514 | 0.101563 |
| 5 | 6 | -0.187207 | -0.890485 | 1.404526 |
| 6 | 6 | 1.026311 | 0.026801 | 1.163325 |
| 7 | 1 | -0.408756 | -2.095451 | -1.835067 |
| 8 | 1 | 0.948791 | -0.005272 | -1.624724 |
| 9 | 1 | 1.973863 | -1.412193 | -1.856320 |
| 10 | 1 | 2.380444 | -1.534403 | 0.604079 |
| 11 | 1 | -1.811123 | -0.168751 | -1.608411 |
| 12 | 1 | -0.895508 | -0.420948 | 2.090695 |
| 13 | 1 | 0.143843 | -1.829909 | 1.866514 |
| 14 | 1 | 0.675749 | 0.997930 | 0.789129 |
| 15 | 1 | 1.497857 | 0.224761 | 2.129804 |
| 16 | 1 | 0.456079 | -2.815752 | -0.480519 |
| 17 | 6 | 3.342936 | 0.275000 | -0.028506 |
| 18 | 6 | 3.051666 | 1.658882 | -0.647338 |
| 19 | 1 | 2.390404 | 2.260208 | -0.014584 |
| 20 | 1 | 3.985197 | 2.220584 | -0.767729 |
| 21 | 1 | 2.591457 | 1.577729 | -1.637775 |
| 22 | 6 | 4.042557 | 0.479531 | 1.334206 |

| | | | | |
|---|---|---|---|---|
| 23 | 1 | 4.223588 | -0.478875 | 1.835965 |
| 24 | 1 | 5.013268 | 0.967607 | 1.192442 |
| 25 | 1 | 3.458971 | 1.110607 | 2.011335 |
| 26 | 6 | 4.328384 | -0.481594 | -0.947397 |
| 27 | 1 | 3.956631 | -0.572711 | -1.972469 |
| 28 | 1 | 5.285265 | 0.050129 | -0.996965 |
| 29 | 1 | 4.529403 | -1.491252 | -0.568869 |
| 30 | 8 | -1.995408 | -2.221902 | 0.356510 |
| 31 | 6 | -2.925374 | -1.371432 | -0.154111 |
| 32 | 8 | -4.107466 | -1.529728 | -0.255588 |
| 33 | 6 | -1.917677 | -0.271182 | -0.526560 |
| 34 | 6 | -2.179164 | 1.081603 | 0.095377 |
| 35 | 8 | -2.406347 | 1.281062 | 1.270697 |
| 36 | 8 | -2.143991 | 2.055205 | -0.837836 |
| 37 | 6 | -2.431043 | 3.389384 | -0.366017 |
| 38 | 1 | -3.428288 | 3.424718 | 0.077743 |
| 39 | 1 | -1.692407 | 3.694472 | 0.378641 |
| 40 | 1 | -2.376313 | 4.024294 | -1.249253 |

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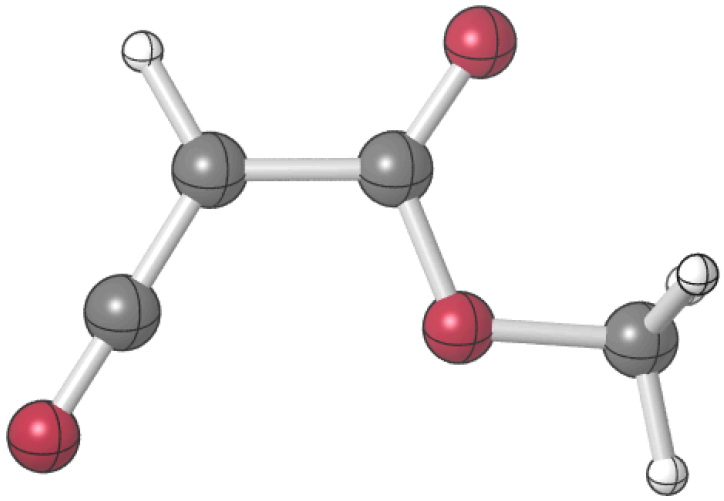
fragmented product, ketene



E(UB3LYP) = -380.5039936 hartrees
Sum of electronic and thermal Free Energies = -380.459471 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|

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| | | | | |
|---|---|---|---|---|
| 1 | 6 | -0.922665 | 0.951263 | 0.000059 |
| 2 | 6 | -1.865294 | 0.014387 | -0.000111 |
| 3 | 8 | -2.702088 | -0.793302 | -0.000242 |
| 4 | 1 | -1.221104 | 1.991973 | 0.000117 |
| 5 | 6 | 0.504840 | 0.616180 | 0.000172 |
| 6 | 8 | 0.703691 | -0.727591 | -0.000010 |
| 7 | 8 | 1.402249 | 1.435282 | 0.000226 |
| 8 | 6 | 2.078046 | -1.160222 | -0.000066 |
| 9 | 1 | 2.592689 | -0.793396 | -0.891094 |
| 10 | 1 | 2.592411 | -0.794442 | 0.891558 |
| 11 | 1 | 2.035626 | -2.248888 | -0.000699 |

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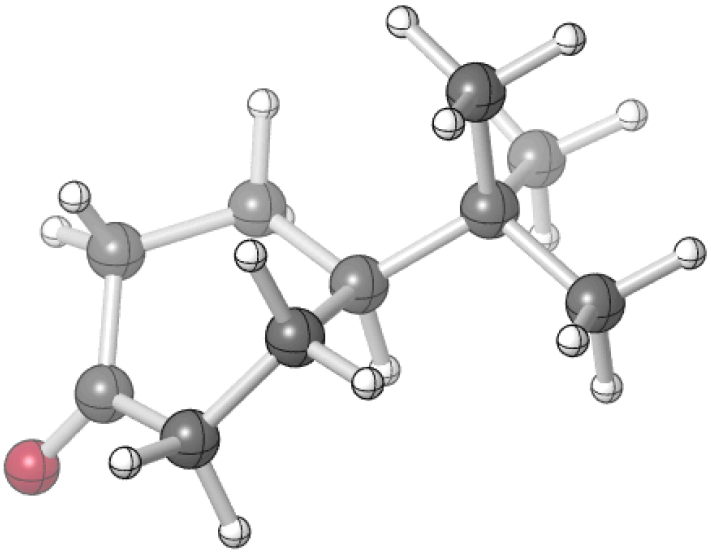
fragmented product, ketone



E(UB3LYP) = -467.175509 hartrees
Sum of electronic and thermal Free Energies = -466.950367 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 8 | 3.622956 | -0.066207 | -0.678677 |
| 2 | 6 | 2.553317 | 0.014406 | -0.098279 |
| 3 | 6 | 1.822081 | 1.342990 | 0.068737 |
| 4 | 6 | 1.859210 | -1.178054 | 0.529544 |
| 5 | 1 | 1.903538 | -1.016493 | 1.616714 |
| 6 | 1 | 1.851666 | 1.855074 | -0.900659 |
| 7 | 1 | 2.414177 | 1.960520 | 0.757612 |

| | | | | |
|---|---|---|---|---|
| 8 | 1 | 2.430491 | -2.083590 | 0.311673 |
| 9 | 6 | 0.375439 | 1.172069 | 0.562765 |
| 10 | 1 | -0.155048 | 2.122581 | 0.454296 |
| 11 | 1 | 0.370129 | 0.936111 | 1.634703 |
| 12 | 6 | 0.373770 | -1.313349 | 0.095732 |
| 13 | 1 | -0.163718 | -1.830937 | 0.897549 |
| 14 | 1 | 0.321626 | -1.966493 | -0.780658 |
| 15 | 6 | -0.316197 | 0.042594 | -0.230697 |
| 16 | 1 | -0.118052 | 0.252952 | -1.294008 |
| 17 | 6 | -1.877410 | 0.002828 | -0.103165 |
| 18 | 6 | -2.481249 | 1.282059 | -0.724539 |
| 19 | 1 | -3.575941 | 1.233267 | -0.707281 |
| 20 | 1 | -2.189007 | 2.186595 | -0.182115 |
| 21 | 1 | -2.170380 | 1.399595 | -1.769533 |
| 22 | 6 | -2.431319 | -1.204863 | -0.891253 |
| 23 | 1 | -2.096399 | -1.183182 | -1.935591 |
| 24 | 1 | -2.121177 | -2.160643 | -0.457774 |
| 25 | 1 | -3.527122 | -1.187156 | -0.894477 |
| 26 | 6 | -2.337249 | -0.097382 | 1.366207 |
| 27 | 1 | -1.942443 | -0.990365 | 1.862848 |
| 28 | 1 | -2.027762 | 0.776805 | 1.948661 |
| 29 | 1 | -3.430591 | -0.154784 | 1.417140 |

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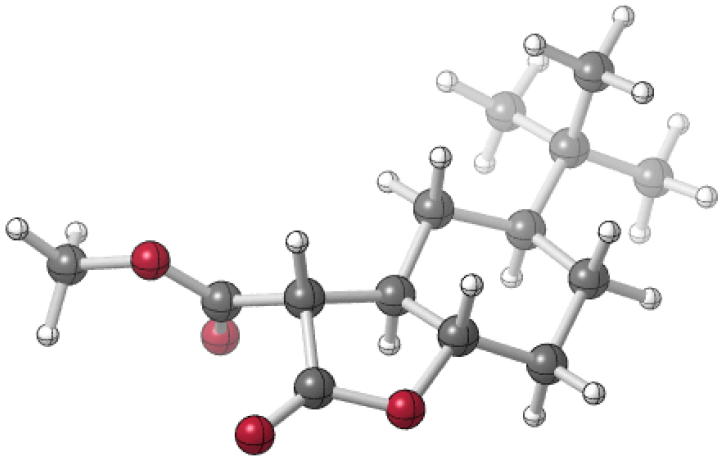
γ-lactone-eq-*trans*

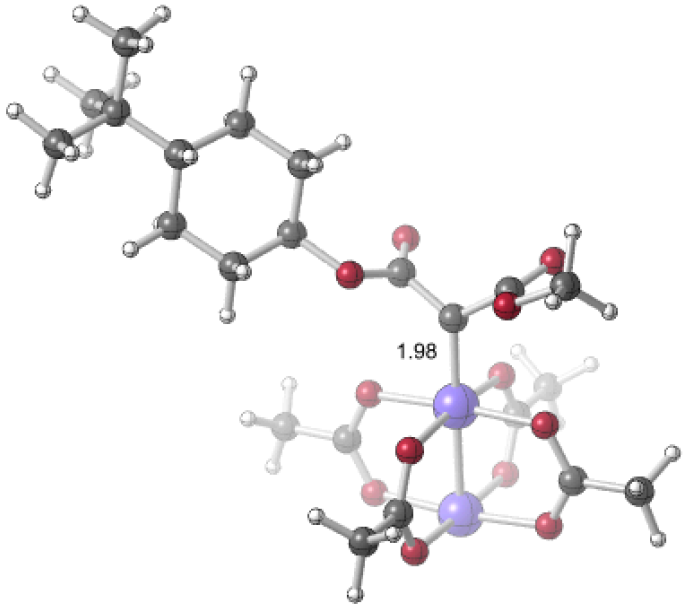


E(UB3LYP) = -847.7246137 hartrees
Sum of electronic and thermal Free Energies = -847.424489 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 1.792611 | 0.162568 | 0.445318 |
| 2 | 6 | 2.412891 | 1.555427 | 0.152697 |
| 3 | 6 | 2.591524 | -0.944669 | -0.215168 |
| 4 | 8 | 2.459142 | -1.291565 | -1.371037 |
| 5 | 6 | 0.371519 | 0.361251 | -0.086334 |
| 6 | 1 | 1.813724 | 0.021147 | 1.533643 |
| 7 | 1 | 0.439053 | 0.294848 | -1.181054 |
| 8 | 8 | 3.578524 | 1.839662 | 0.063808 |
| 9 | 8 | 1.409995 | 2.464883 | -0.000249 |
| 10 | 6 | 0.137058 | 1.821785 | 0.276230 |
| 11 | 1 | -0.034407 | 1.919998 | 1.359270 |
| 12 | 6 | -0.800632 | -0.501806 | 0.374886 |
| 13 | 1 | -0.616836 | -1.547453 | 0.112826 |
| 14 | 1 | -0.893437 | -0.452517 | 1.468531 |
| 15 | 6 | -1.052633 | 2.388128 | -0.466750 |
| 16 | 1 | -1.223900 | 3.438127 | -0.205869 |
| 17 | 1 | -0.870501 | 2.340575 | -1.547466 |
| 18 | 6 | -2.100394 | 0.008715 | -0.310155 |
| 19 | 1 | -1.944259 | -0.125421 | -1.392557 |
| 20 | 6 | -2.284182 | 1.533816 | -0.076881 |
| 21 | 1 | -3.145672 | 1.897362 | -0.642920 |
| 22 | 1 | -2.509645 | 1.718270 | 0.982022 |
| 23 | 6 | -3.375932 | -0.842158 | 0.031231 |
| 24 | 6 | -4.579197 | -0.336756 | -0.797017 |
| 25 | 1 | -5.435553 | -1.007838 | -0.667096 |
| 26 | 1 | -4.904401 | 0.663069 | -0.494198 |
| 27 | 1 | -4.341394 | -0.306772 | -1.867328 |
| 28 | 6 | -3.134361 | -2.318630 | -0.357362 |
| 29 | 1 | -2.816838 | -2.409079 | -1.403159 |
| 30 | 1 | -2.374487 | -2.795825 | 0.268787 |
| 31 | 1 | -4.058407 | -2.895528 | -0.239649 |
| 32 | 6 | -3.745946 | -0.780607 | 1.528814 |
| 33 | 1 | -3.975983 | 0.239041 | 1.855173 |
| 34 | 1 | -4.635835 | -1.391008 | 1.720295 |
| 35 | 1 | -2.944100 | -1.168264 | 2.166017 |
| 36 | 8 | 3.468372 | -1.493028 | 0.643089 |
| 37 | 6 | 4.344394 | -2.500758 | 0.094888 |
| 38 | 1 | 4.943926 | -2.075599 | -0.712803 |
| 39 | 1 | 4.978177 | -2.812433 | 0.924014 |
| 40 | 1 | 3.762194 | -3.342163 | -0.287740 |

*B3LYP/6-31G(d) for C, H, O and LANL2DZ for Rh*

Rh-carbenoid “reactant”




E(UB3LYP) = -1980.48211620 hartrees
Sum of electronic and thermal Free Energies = -1980.010361 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -6.419085 | -0.010690 | 0.315644 |
| 2 | 6 | -5.878452 | 0.784282 | -0.905178 |
| 3 | 6 | -4.446186 | 1.320776 | -0.662240 |
| 4 | 6 | -3.499937 | 0.165208 | -0.312134 |
| 5 | 6 | -3.989665 | -0.632325 | 0.896048 |
| 6 | 6 | -5.424813 | -1.158650 | 0.648093 |
| 7 | 1 | -4.083449 | 1.848349 | -1.552436 |
| 8 | 1 | -5.873468 | 0.138857 | -1.796378 |
| 9 | 1 | -6.529794 | 1.635189 | -1.134934 |
| 10 | 1 | -6.410372 | 0.681077 | 1.178160 |
| 11 | 1 | -3.351076 | -0.482987 | -1.185433 |
| 12 | 1 | -3.300938 | -1.462751 | 1.095877 |
| 13 | 1 | -3.976697 | 0.021907 | 1.778988 |
| 14 | 1 | -5.406666 | -1.882103 | -0.180991 |
| 15 | 1 | -5.749087 | -1.706606 | 1.540310 |
| 16 | 1 | -4.452179 | 2.034780 | 0.173920 |
| 17 | 6 | -7.914236 | -0.484149 | 0.159760 |
| 18 | 6 | -8.832735 | 0.748204 | -0.073513 |
| 19 | 1 | -8.650610 | 1.224281 | -1.044393 |
| 20 | 1 | -9.888010 | 0.444228 | -0.052096 |

| | | | | |
|---|---|---|---|---|
| 21 | 1 | -8.686787 | 1.505753 | 0.709728 |
| 22 | 6 | -8.100245 | -1.474622 | -1.020785 |
| 23 | 1 | -7.504297 | -2.386329 | -0.887011 |
| 24 | 1 | -9.153383 | -1.778301 | -1.094776 |
| 25 | 1 | -7.820295 | -1.023108 | -1.980912 |
| 26 | 6 | -8.385779 | -1.173778 | 1.470476 |
| 27 | 1 | -8.217027 | -0.525561 | 2.342232 |
| 28 | 1 | -9.461118 | -1.391334 | 1.418901 |
| 29 | 1 | -7.869323 | -2.124463 | 1.649752 |
| 30 | 8 | -2.148608 | 0.710581 | 0.067204 |
| 31 | 6 | -1.275986 | 1.019927 | -0.927788 |
| 32 | 8 | -1.488032 | 0.934786 | -2.150895 |
| 33 | 6 | 0.043446 | 1.474313 | -0.398763 |
| 34 | 6 | 0.282289 | 2.944182 | -0.326651 |
| 35 | 8 | 0.597393 | 3.614868 | -1.324510 |
| 36 | 8 | 0.142034 | 3.429048 | 0.942234 |
| 37 | 6 | 0.471899 | 4.856918 | 1.149171 |
| 38 | 1 | 0.282277 | 5.031329 | 2.208277 |
| 39 | 1 | 1.522879 | 5.027898 | 0.898938 |
| 40 | 1 | -0.167363 | 5.485692 | 0.521948 |
| 41 | 45 | 1.522208 | 0.197670 | -0.094948 |
| 42 | 45 | 3.398659 | -1.403776 | 0.237410 |
| 43 | 8 | 4.582580 | 0.242744 | 0.689993 |
| 44 | 6 | 4.087862 | 1.436789 | 0.670477 |
| 45 | 6 | 4.995887 | 2.601889 | 0.992581 |
| 46 | 8 | 2.841335 | 1.722565 | 0.390136 |
| 47 | 1 | 5.012318 | 3.298761 | 0.146845 |
| 48 | 1 | 4.605800 | 3.143338 | 1.862193 |
| 49 | 1 | 6.005486 | 2.242733 | 1.200463 |
| 50 | 8 | 2.856412 | -1.568217 | 2.224885 |
| 51 | 6 | 1.846360 | -0.887324 | 2.660235 |
| 52 | 8 | 1.120475 | -0.089162 | 1.923541 |
| 53 | 6 | 1.461567 | -1.004115 | 4.116977 |
| 54 | 1 | 1.545056 | -0.022481 | 4.597596 |
| 55 | 1 | 0.415912 | -1.321313 | 4.197459 |
| 56 | 1 | 2.112979 | -1.721753 | 4.619475 |
| 57 | 8 | 3.880094 | -1.188025 | -1.757665 |
| 58 | 6 | 3.170112 | -0.399015 | -2.497066 |
| 59 | 6 | 3.521976 | -0.247501 | -3.957570 |
| 60 | 8 | 2.149140 | 0.291786 | -2.065169 |
| 61 | 1 | 3.740527 | 0.804082 | -4.174866 |
| 62 | 1 | 4.385540 | -0.869678 | -4.200636 |
| 63 | 1 | 2.662549 | -0.536417 | -4.572983 |
| 64 | 8 | 0.316196 | -1.425585 | -0.555315 |
| 65 | 6 | 0.826847 | -2.630773 | -0.548144 |
| 66 | 8 | 2.055940 | -2.907011 | -0.258561 |
| 67 | 6 | -0.105540 | -3.766150 | -0.904205 |
| 68 | 1 | 0.438283 | -4.712593 | -0.897747 |
| 69 | 1 | -0.929361 | -3.805374 | -0.181887 |
| 70 | 1 | -0.540531 | -3.587745 | -1.893961 |

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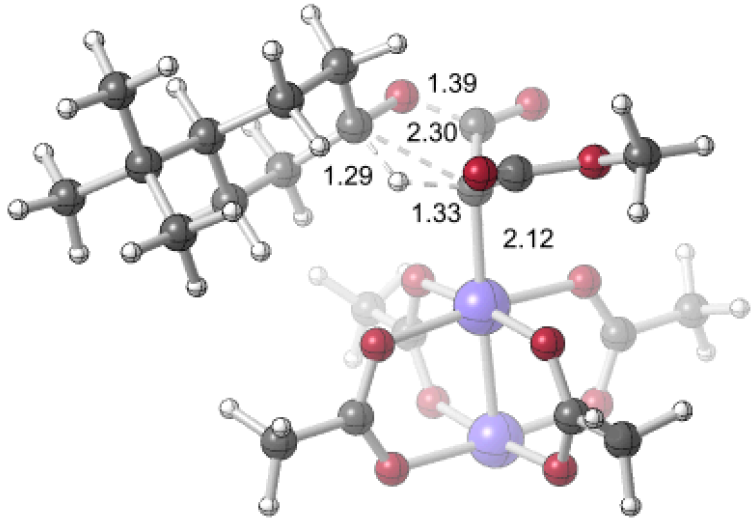
β-TS1$_{cat}$, Conformation 1




E(RB3LYP) = -1980.68215784 hartrees
Sum of electronic and thermal Free Energies = -1980.204522 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -4.832742 | -0.247578 | -0.433058 |
| 2 | 6 | -3.555034 | -1.056243 | -0.748472 |
| 3 | 6 | -2.678667 | -0.385977 | -1.818746 |
| 4 | 6 | -2.398518 | 1.066523 | -1.517458 |
| 5 | 6 | -3.576881 | 1.892201 | -1.056923 |
| 6 | 6 | -4.419416 | 1.173936 | 0.008561 |
| 7 | 1 | -1.730602 | -0.912686 | -1.961332 |
| 8 | 1 | -2.950748 | -1.178926 | 0.157653 |
| 9 | 1 | -3.804109 | -2.060590 | -1.104427 |
| 10 | 1 | -5.393944 | -0.145502 | -1.377777 |
| 11 | 1 | -1.574410 | 0.987376 | -0.531559 |
| 12 | 1 | -3.240860 | 2.870816 | -0.700680 |
| 13 | 1 | -4.175084 | 2.073209 | -1.964071 |
| 14 | 1 | -3.836110 | 1.132513 | 0.935335 |
| 15 | 1 | -5.297655 | 1.793350 | 0.213820 |
| 16 | 1 | -3.194341 | -0.380439 | -2.793249 |
| 17 | 6 | -5.813879 | -0.960962 | 0.562719 |
| 18 | 6 | -7.115374 | -0.138222 | 0.687737 |
| 19 | 1 | -7.572231 | 0.036942 | -0.294789 |
| 20 | 1 | -7.846885 | -0.676842 | 1.301627 |
| 21 | 1 | -6.950871 | 0.834628 | 1.162067 |

| | | | | |
|---|---|---|---|---|
| 22 | 6 | -6.197624 | -2.352171 | 0.011572 |
| 23 | 1 | -5.353225 | -3.049355 | 0.014104 |
| 24 | 1 | -6.987053 | -2.799481 | 0.626982 |
| 25 | 1 | -6.577175 | -2.284633 | -1.016144 |
| 26 | 6 | -5.200108 | -1.135204 | 1.967519 |
| 27 | 1 | -4.961830 | -0.173265 | 2.434266 |
| 28 | 1 | -5.908868 | -1.651503 | 2.626221 |
| 29 | 1 | -4.281856 | -1.732715 | 1.942995 |
| 30 | 8 | -1.611463 | 1.690412 | -2.497006 |
| 31 | 6 | -0.493031 | 2.216452 | -1.871958 |
| 32 | 8 | 0.288682 | 2.944769 | -2.408221 |
| 33 | 6 | -0.447407 | 1.683461 | -0.474616 |
| 34 | 6 | -0.676801 | 2.616280 | 0.665762 |
| 35 | 8 | -1.584766 | 2.488436 | 1.466731 |
| 36 | 8 | 0.250991 | 3.578431 | 0.697230 |
| 37 | 6 | 0.206033 | 4.442960 | 1.847240 |
| 38 | 1 | 1.014234 | 5.158295 | 1.698013 |
| 39 | 1 | -0.757937 | 4.954370 | 1.906598 |
| 40 | 1 | 0.367234 | 3.859540 | 2.756785 |
| 41 | 45 | 0.976487 | 0.160787 | -0.081927 |
| 42 | 45 | 2.704239 | -1.514003 | 0.347127 |
| 43 | 8 | 2.925303 | -0.691518 | 2.234661 |
| 44 | 6 | 2.205008 | 0.296269 | 2.565875 |
| 45 | 6 | 2.412462 | 0.880316 | 3.947853 |
| 46 | 8 | 1.321925 | 0.868522 | 1.842018 |
| 47 | 1 | 2.915323 | 1.849833 | 3.856245 |
| 48 | 1 | 1.445476 | 1.050927 | 4.429605 |
| 49 | 1 | 3.027416 | 0.214427 | 4.555188 |
| 50 | 8 | 1.204600 | -2.753872 | 1.071141 |
| 51 | 6 | 0.008923 | -2.343788 | 1.085702 |
| 52 | 8 | -0.406804 | -1.206763 | 0.671709 |
| 53 | 6 | -1.045443 | -3.281128 | 1.637864 |
| 54 | 1 | -1.618017 | -2.772798 | 2.420051 |
| 55 | 1 | -1.744928 | -3.555850 | 0.840901 |
| 56 | 1 | -0.580445 | -4.182136 | 2.040293 |
| 57 | 8 | 4.107106 | -0.191350 | -0.387452 |
| 58 | 6 | 3.707655 | 0.942203 | -0.792793 |
| 59 | 6 | 4.750514 | 1.911801 | -1.305505 |
| 60 | 8 | 2.504357 | 1.363759 | -0.795542 |
| 61 | 1 | 4.368041 | 2.442378 | -2.180935 |
| 62 | 1 | 4.956797 | 2.656533 | -0.528089 |
| 63 | 1 | 5.675327 | 1.384355 | -1.545735 |
| 64 | 8 | 0.744625 | -0.680748 | -1.970336 |
| 65 | 6 | 1.502238 | -1.656127 | -2.307523 |
| 66 | 8 | 2.372780 | -2.214548 | -1.579786 |
| 67 | 6 | 1.340415 | -2.164330 | -3.724530 |
| 68 | 1 | 1.770993 | -1.431373 | -4.416193 |
| 69 | 1 | 1.853168 | -3.119415 | -3.848385 |
| 70 | 1 | 0.279867 | -2.265525 | -3.971476 |

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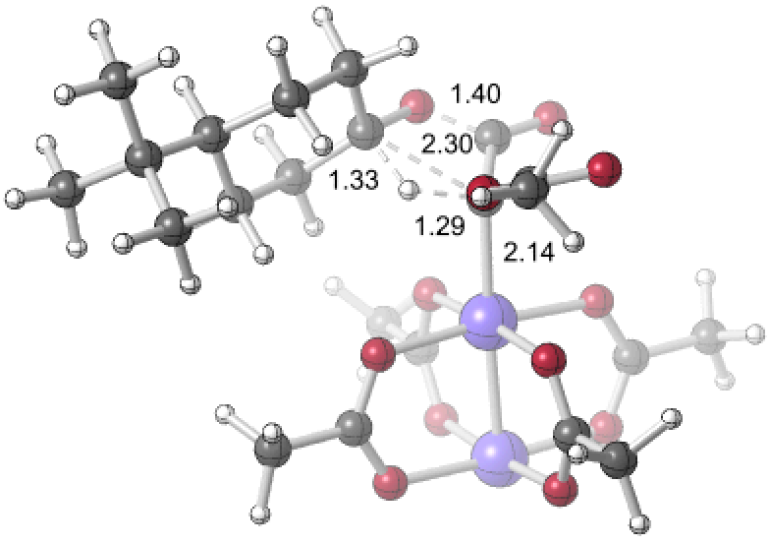
β-TS1$_{cat}$, Conformation 2




E(RB3LYP) = -1980.68039168 hartrees
Sum of electronic and thermal Free Energies = -1980.202716 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -4.767345 | -0.344092 | -0.539483 |
| 2 | 6 | -3.457687 | -1.121922 | -0.793945 |
| 3 | 6 | -2.569207 | -0.458889 | -1.857949 |
| 4 | 6 | -2.349956 | 1.011921 | -1.610346 |
| 5 | 6 | -3.560283 | 1.813373 | -1.193528 |
| 6 | 6 | -4.408495 | 1.101435 | -0.128142 |
| 7 | 1 | -1.599157 | -0.955349 | -1.951920 |
| 8 | 1 | -2.875981 | -1.201328 | 0.131390 |
| 9 | 1 | -3.667587 | -2.143175 | -1.125912 |
| 10 | 1 | -5.303213 | -0.283203 | -1.502131 |
| 11 | 1 | -1.524226 | 0.996351 | -0.572694 |
| 12 | 1 | -3.260156 | 2.815108 | -0.868654 |
| 13 | 1 | -4.144684 | 1.949293 | -2.117585 |
| 14 | 1 | -3.850225 | 1.096980 | 0.815524 |
| 15 | 1 | -5.309483 | 1.699529 | 0.038078 |
| 16 | 1 | -3.050630 | -0.506550 | -2.849162 |
| 17 | 6 | -5.756579 | -1.059610 | 0.446709 |
| 18 | 6 | -7.076417 | -0.261323 | 0.530468 |
| 19 | 1 | -7.509305 | -0.101010 | -0.465224 |
| 20 | 1 | -7.814239 | -0.810051 | 1.127457 |
| 21 | 1 | -6.944347 | 0.717560 | 1.002950 |
| 22 | 6 | -6.101079 | -2.466342 | -0.091029 |
| 23 | 1 | -5.241566 | -3.144331 | -0.069658 |

| | | | | |
|---|---|---|---|---|
| 24 | 1 | -6.888021 | -2.923729 | 0.520032 |
| 25 | 1 | -6.469099 | -2.419668 | -1.123993 |
| 26 | 6 | -5.170235 | -1.200886 | 1.866778 |
| 27 | 1 | -4.954466 | -0.227358 | 2.321018 |
| 28 | 1 | -5.886243 | -1.713629 | 2.520204 |
| 29 | 1 | -4.244515 | -1.787074 | 1.872750 |
| 30 | 8 | -1.556639 | 1.627377 | -2.575447 |
| 31 | 6 | -0.468773 | 2.216999 | -1.929091 |
| 32 | 8 | 0.294071 | 2.954973 | -2.473800 |
| 33 | 6 | -0.455069 | 1.715938 | -0.522511 |
| 34 | 6 | -0.590953 | 2.714220 | 0.568691 |
| 35 | 8 | 0.103010 | 3.703688 | 0.643084 |
| 36 | 8 | -1.533608 | 2.362631 | 1.470076 |
| 37 | 6 | -1.596113 | 3.202897 | 2.637424 |
| 38 | 1 | -2.407584 | 2.798550 | 3.242676 |
| 39 | 1 | -0.649122 | 3.153836 | 3.179258 |
| 40 | 1 | -1.801630 | 4.239150 | 2.357121 |
| 41 | 45 | 1.011923 | 0.216273 | -0.084523 |
| 42 | 45 | 2.777221 | -1.406350 | 0.382646 |
| 43 | 8 | 2.959238 | -0.557784 | 2.261893 |
| 44 | 6 | 2.198802 | 0.404429 | 2.579492 |
| 45 | 6 | 2.359109 | 0.996407 | 3.964408 |
| 46 | 8 | 1.294805 | 0.931263 | 1.847386 |
| 47 | 1 | 2.521180 | 2.075884 | 3.884542 |
| 48 | 1 | 1.437483 | 0.841091 | 4.535781 |
| 49 | 1 | 3.195756 | 0.529496 | 4.486006 |
| 50 | 8 | 1.299737 | -2.681144 | 1.095816 |
| 51 | 6 | 0.091960 | -2.308624 | 1.081794 |
| 52 | 8 | -0.351603 | -1.188377 | 0.651346 |
| 53 | 6 | -0.942781 | -3.277311 | 1.618694 |
| 54 | 1 | -1.547903 | -2.784374 | 2.386215 |
| 55 | 1 | -1.616259 | -3.579668 | 0.809367 |
| 56 | 1 | -0.457273 | -4.160423 | 2.036267 |
| 57 | 8 | 4.153226 | -0.051106 | -0.341004 |
| 58 | 6 | 3.728038 | 1.073425 | -0.747869 |
| 59 | 6 | 4.748927 | 2.077095 | -1.236768 |
| 60 | 8 | 2.512916 | 1.458137 | -0.770786 |
| 61 | 1 | 4.372664 | 2.587059 | -2.127097 |
| 62 | 1 | 4.901037 | 2.835287 | -0.460036 |
| 63 | 1 | 5.699750 | 1.583552 | -1.445341 |
| 64 | 8 | 0.840087 | -0.634650 | -1.975352 |
| 65 | 6 | 1.624269 | -1.596059 | -2.291274 |
| 66 | 8 | 2.489721 | -2.133829 | -1.542176 |
| 67 | 6 | 1.504564 | -2.113632 | -3.709151 |
| 68 | 1 | 1.949565 | -1.381488 | -4.392568 |
| 69 | 1 | 2.027918 | -3.065327 | -3.813521 |
| 70 | 1 | 0.452162 | -2.223661 | -3.985216 |

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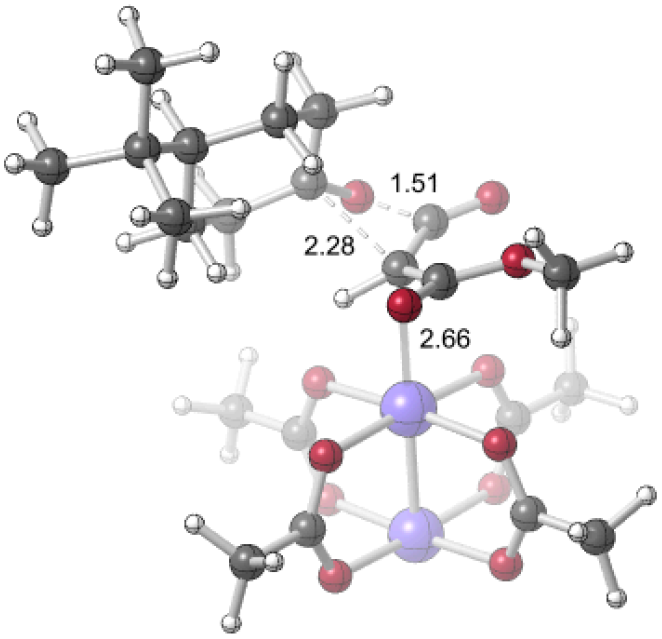
β-TS2$_{cat}$, Configuration 1




E(RB3LYP) = -1980.69180725 hartrees
Sum of electronic and thermal Free Energies = -1980.215832 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 5.116948 | -0.637103 | 0.440992 |
| 2 | 6 | 3.810555 | -1.457562 | 0.367081 |
| 3 | 6 | 2.920688 | -1.273170 | 1.614243 |
| 4 | 6 | 2.697586 | 0.166219 | 1.949448 |
| 5 | 6 | 3.895119 | 1.068373 | 1.910363 |
| 6 | 6 | 4.763535 | 0.852141 | 0.656494 |
| 7 | 1 | 1.952838 | -1.774674 | 1.517861 |
| 8 | 1 | 3.232168 | -1.159236 | -0.515502 |
| 9 | 1 | 4.022924 | -2.525314 | 0.262167 |
| 10 | 1 | 5.661946 | -0.972956 | 1.339917 |
| 11 | 1 | 1.304935 | 0.152799 | 0.283291 |
| 12 | 1 | 3.603941 | 2.114628 | 2.038851 |
| 13 | 1 | 4.480624 | 0.794845 | 2.808072 |
| 14 | 1 | 4.219762 | 1.237929 | -0.213158 |
| 15 | 1 | 5.668595 | 1.456022 | 0.768438 |
| 16 | 1 | 3.422840 | -1.711916 | 2.494687 |
| 17 | 6 | 6.090934 | -0.893267 | -0.763359 |
| 18 | 6 | 5.452756 | -0.533503 | -2.121490 |
| 19 | 1 | 5.124943 | 0.510555 | -2.162707 |
| 20 | 1 | 6.181077 | -0.682024 | -2.927955 |

| | | | | |
|---|---|---|---|---|
| 21 | 1 | 4.584479 | -1.161420 | -2.348311 |
| 22 | 6 | 7.376590 | -0.056874 | -0.580137 |
| 23 | 1 | 7.827738 | -0.224597 | 0.406571 |
| 24 | 1 | 8.120115 | -0.336996 | -1.335432 |
| 25 | 1 | 7.193832 | 1.016897 | -0.690950 |
| 26 | 6 | 6.506217 | -2.381255 | -0.785031 |
| 27 | 1 | 5.664435 | -3.047208 | -1.001771 |
| 28 | 1 | 7.260011 | -2.552618 | -1.562355 |
| 29 | 1 | 6.943528 | -2.688627 | 0.173744 |
| 30 | 8 | 1.628233 | 0.471195 | 2.669887 |
| 31 | 6 | 1.053892 | 1.626706 | 1.880275 |
| 32 | 8 | 0.674177 | 2.603970 | 2.443151 |
| 33 | 6 | 1.265962 | 1.211300 | 0.517298 |
| 34 | 6 | 1.423544 | 2.114201 | -0.630668 |
| 35 | 8 | 1.916162 | 1.756583 | -1.689367 |
| 36 | 8 | 1.033805 | 3.379123 | -0.376034 |
| 37 | 6 | 1.163333 | 4.288945 | -1.475353 |
| 38 | 1 | 2.202067 | 4.347823 | -1.812976 |
| 39 | 1 | 0.534981 | 3.965915 | -2.309754 |
| 40 | 1 | 0.827918 | 5.254009 | -1.094341 |
| 41 | 45 | -1.096948 | 0.079469 | 0.066378 |
| 42 | 45 | -3.227307 | -0.938821 | -0.398058 |
| 43 | 8 | -3.643094 | 0.636792 | -1.663085 |
| 44 | 6 | -2.771170 | 1.551447 | -1.803407 |
| 45 | 6 | -3.105213 | 2.695548 | -2.735402 |
| 46 | 8 | -1.635170 | 1.599996 | -1.229802 |
| 47 | 1 | -3.089006 | 3.636198 | -2.175251 |
| 48 | 1 | -2.341403 | 2.763678 | -3.516747 |
| 49 | 1 | -4.087495 | 2.550137 | -3.187082 |
| 50 | 8 | -2.331370 | -1.947110 | -1.967343 |
| 51 | 6 | -1.092192 | -1.766341 | -2.185391 |
| 52 | 8 | -0.314238 | -1.012224 | -1.515245 |
| 53 | 6 | -0.475746 | -2.500325 | -3.356316 |
| 54 | 1 | -1.189780 | -3.200902 | -3.791675 |
| 55 | 1 | -0.167059 | -1.770978 | -4.112976 |
| 56 | 1 | 0.422947 | -3.031105 | -3.028038 |
| 57 | 8 | -4.014499 | 0.123603 | 1.187280 |
| 58 | 6 | -3.245837 | 0.898142 | 1.842960 |
| 59 | 6 | -3.867682 | 1.692459 | 2.969474 |
| 60 | 8 | -2.006183 | 1.083498 | 1.623598 |
| 61 | 1 | -4.606685 | 1.082817 | 3.495290 |
| 62 | 1 | -3.096881 | 2.046596 | 3.655956 |
| 63 | 1 | -4.387127 | 2.559852 | 2.545603 |
| 64 | 8 | -0.684566 | -1.525400 | 1.323094 |
| 65 | 6 | -1.570765 | -2.432007 | 1.466496 |
| 66 | 8 | -2.705356 | -2.463855 | 0.899384 |
| 67 | 6 | -1.222425 | -3.577415 | 2.392673 |
| 68 | 1 | -0.406172 | -4.162303 | 1.954148 |
| 69 | 1 | -0.870498 | -3.182888 | 3.350525 |
| 70 | 1 | -2.088020 | -4.223386 | 2.545860 |

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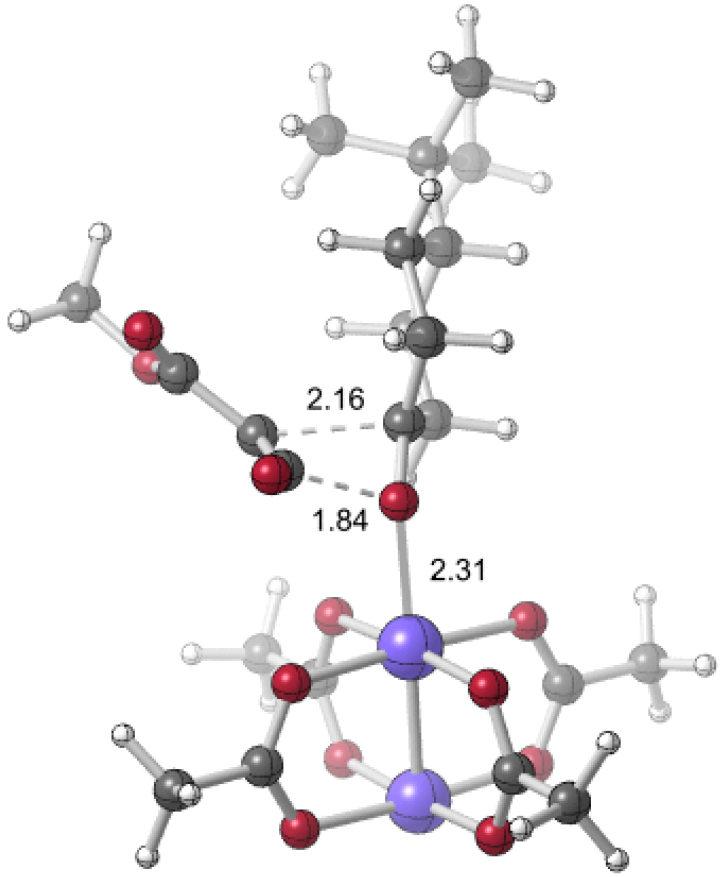
β-TS2$_{cat}$, Configuration 2




E(UB3LYP) = -1980.70044045 hartrees
Sum of electronic and thermal Free Energies = -1980.225855 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -4.546245 | -1.537707 | -0.439842 |
| 2 | 6 | -3.516236 | -1.249596 | 0.674270 |
| 3 | 6 | -2.070648 | -1.197245 | 0.148346 |
| 4 | 6 | -1.903899 | -0.268602 | -1.023206 |
| 5 | 6 | -2.965024 | -0.388899 | -2.094141 |
| 6 | 6 | -4.397764 | -0.470539 | -1.546206 |
| 7 | 1 | -1.358674 | -0.942255 | 0.935289 |
| 8 | 1 | -3.744949 | -0.292387 | 1.159899 |
| 9 | 1 | -3.561126 | -2.017816 | 1.451992 |
| 10 | 1 | -4.267540 | -2.506328 | -0.888534 |
| 11 | 1 | -1.498149 | 1.334844 | 0.611102 |
| 12 | 1 | -2.860238 | 0.409110 | -2.835199 |
| 13 | 1 | -2.713331 | -1.325865 | -2.619709 |

| | | | | |
|---|---|---|---|---|
| 14 | 1 | -4.678720 | 0.517355 | -1.162038 |
| 15 | 1 | -5.068729 | -0.681430 | -2.384490 |
| 16 | 1 | -1.767878 | -2.188886 | -0.226436 |
| 17 | 6 | -6.017046 | -1.722807 | 0.075701 |
| 18 | 6 | -6.585675 | -0.433666 | 0.704975 |
| 19 | 1 | -6.639600 | 0.386438 | -0.019690 |
| 20 | 1 | -7.603650 | -0.611006 | 1.072617 |
| 21 | 1 | -5.985446 | -0.094795 | 1.556956 |
| 22 | 6 | -6.929385 | -2.148353 | -1.095934 |
| 23 | 1 | -6.540943 | -3.044029 | -1.597207 |
| 24 | 1 | -7.934551 | -2.384844 | -0.727396 |
| 25 | 1 | -7.038364 | -1.360565 | -1.848438 |
| 26 | 6 | -6.061444 | -2.850525 | 1.130946 |
| 27 | 1 | -5.549877 | -2.573479 | 2.058486 |
| 28 | 1 | -7.100227 | -3.085046 | 1.391983 |
| 29 | 1 | -5.599603 | -3.771116 | 0.751531 |
| 30 | 8 | -0.707968 | 0.145656 | -1.388959 |
| 31 | 6 | -1.325016 | 1.876938 | -1.432872 |
| 32 | 8 | -1.147201 | 2.441486 | -2.436109 |
| 33 | 6 | -2.046286 | 1.734366 | -0.231921 |
| 34 | 6 | -3.114777 | 2.713231 | 0.053747 |
| 35 | 8 | -3.658886 | 3.443107 | -0.751943 |
| 36 | 8 | -3.478857 | 2.631701 | 1.361117 |
| 37 | 6 | -4.580014 | 3.471982 | 1.737964 |
| 38 | 1 | -4.348853 | 4.521817 | 1.539488 |
| 39 | 1 | -5.482185 | 3.197607 | 1.183736 |
| 40 | 1 | -4.722375 | 3.305526 | 2.806290 |
| 41 | 45 | 1.315071 | -0.114142 | -0.312056 |
| 42 | 45 | 3.483030 | -0.284053 | 0.723690 |
| 43 | 8 | 2.571453 | 0.099496 | 2.546193 |
| 44 | 6 | 1.321589 | 0.301835 | 2.584700 |
| 45 | 6 | 0.711104 | 0.632996 | 3.929526 |
| 46 | 8 | 0.526760 | 0.276304 | 1.584186 |
| 47 | 1 | 0.583847 | 1.719404 | 4.004127 |
| 48 | 1 | -0.276185 | 0.173481 | 4.022440 |
| 49 | 1 | 1.365957 | 0.301259 | 4.737093 |
| 50 | 8 | 3.132576 | -2.307640 | 0.975959 |
| 51 | 6 | 2.036942 | -2.797326 | 0.561052 |
| 52 | 8 | 1.087322 | -2.154230 | 0.003809 |
| 53 | 6 | 1.846284 | -4.291388 | 0.713717 |
| 54 | 1 | 0.807270 | -4.516869 | 0.966927 |
| 55 | 1 | 2.071646 | -4.777028 | -0.243000 |
| 56 | 1 | 2.521020 | -4.686878 | 1.474919 |
| 57 | 8 | 3.713053 | 1.748309 | 0.410410 |
| 58 | 6 | 2.777360 | 2.393902 | -0.156071 |
| 59 | 6 | 2.996064 | 3.870933 | -0.400227 |
| 60 | 8 | 1.668489 | 1.909115 | -0.559035 |
| 61 | 1 | 2.097283 | 4.431904 | -0.129711 |
| 62 | 1 | 3.856048 | 4.230217 | 0.167114 |
| 63 | 1 | 3.175881 | 4.032779 | -1.469076 |

| | | | | |
|---|---|---|---|---|
| 64 | 8 | 2.229687 | -0.503286 | -2.119673 |
| 65 | 6 | 3.490913 | -0.675409 | -2.148668 |
| 66 | 8 | 4.274607 | -0.651047 | -1.147298 |
| 67 | 6 | 4.117887 | -0.898902 | -3.507394 |
| 68 | 1 | 3.394133 | -1.344981 | -4.192421 |
| 69 | 1 | 4.428696 | 0.069588 | -3.916809 |
| 70 | 1 | 5.004511 | -1.530018 | -3.415365 |

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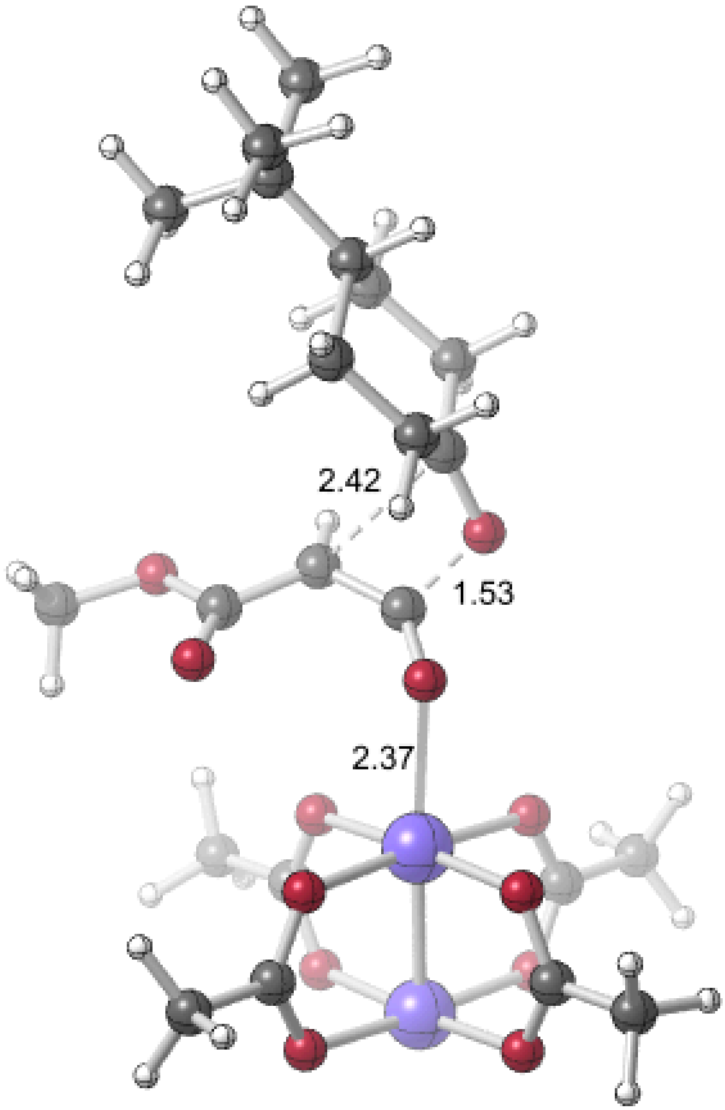
β-TS2$_{cat}$, Configuration 3




E(UB3LYP) = -1980.69379882 hartrees
Sum of electronic and thermal Free Energies = -1980.219436 hartrees

| Center | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| Number | Number | X | Y | Z |

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| | | | | |
|---|---|---|---|---|
| 1 | 6 | 6.328320 | -0.953922 | 0.228511 |
| 2 | 6 | 5.822721 | -0.862245 | -1.228129 |
| 3 | 6 | 4.603985 | -1.774865 | -1.485889 |
| 4 | 6 | 3.521198 | -1.577429 | -0.475778 |
| 5 | 6 | 3.935340 | -1.492074 | 0.963095 |
| 6 | 6 | 5.167127 | -0.596375 | 1.182303 |
| 7 | 1 | 4.194942 | -1.647176 | -2.492695 |
| 8 | 1 | 5.536463 | 0.170334 | -1.461203 |
| 9 | 1 | 6.606096 | -1.144012 | -1.936953 |
| 10 | 1 | 6.583656 | -2.011187 | 0.412908 |
| 11 | 1 | 2.707673 | 0.395520 | -1.685107 |
| 12 | 1 | 3.097687 | -1.207237 | 1.604174 |
| 13 | 1 | 4.197564 | -2.532291 | 1.232585 |
| 14 | 1 | 4.858944 | 0.445446 | 1.035131 |
| 15 | 1 | 5.472518 | -0.696330 | 2.227305 |
| 16 | 1 | 4.915629 | -2.830555 | -1.403601 |
| 17 | 6 | 7.649576 | -0.151187 | 0.498389 |
| 18 | 6 | 7.464879 | 1.368083 | 0.303587 |
| 19 | 1 | 6.717448 | 1.782588 | 0.988910 |
| 20 | 1 | 8.409838 | 1.888628 | 0.499161 |
| 21 | 1 | 7.162112 | 1.619221 | -0.719179 |
| 22 | 6 | 8.126103 | -0.413801 | 1.944401 |
| 23 | 1 | 8.225660 | -1.488578 | 2.143247 |
| 24 | 1 | 9.108311 | 0.044533 | 2.108140 |
| 25 | 1 | 7.445776 | 0.006794 | 2.692028 |
| 26 | 6 | 8.762375 | -0.644420 | -0.452998 |
| 27 | 1 | 8.564642 | -0.385249 | -1.498437 |
| 28 | 1 | 9.720490 | -0.185230 | -0.183577 |
| 29 | 1 | 8.888456 | -1.732990 | -0.390916 |
| 30 | 8 | 2.290661 | -1.841944 | -0.835782 |
| 31 | 6 | 1.530187 | -0.653378 | -0.241466 |
| 32 | 8 | 0.626894 | -0.889709 | 0.522846 |
| 33 | 6 | 2.240942 | 0.466188 | -0.711872 |
| 34 | 6 | 1.987362 | 1.810854 | -0.183875 |
| 35 | 8 | 1.483355 | 2.088068 | 0.886431 |
| 36 | 8 | 2.479632 | 2.753502 | -1.041333 |
| 37 | 6 | 2.351847 | 4.103752 | -0.581009 |
| 38 | 1 | 1.299965 | 4.363100 | -0.431447 |
| 39 | 1 | 2.883405 | 4.245341 | 0.365006 |
| 40 | 1 | 2.791886 | 4.725090 | -1.362649 |
| 41 | 45 | -1.645101 | -0.297419 | 0.222985 |
| 42 | 45 | -3.966840 | 0.182019 | -0.182028 |
| 43 | 8 | -3.906727 | 1.524772 | 1.385637 |
| 44 | 6 | -2.815714 | 1.652110 | 2.030641 |
| 45 | 6 | -2.823146 | 2.591627 | 3.217245 |
| 46 | 8 | -1.725573 | 1.045928 | 1.790006 |
| 47 | 1 | -1.837364 | 3.044424 | 3.343822 |
| 48 | 1 | -3.589994 | 3.358793 | 3.091325 |
| 49 | 1 | -3.053614 | 2.016672 | 4.122036 |

| | | | | |
|---|---|---|---|---|
| 50 | 8 | -3.364359 | 1.673021 | -1.487137 |
| 51 | 6 | -2.119808 | 1.877918 | -1.649646 |
| 52 | 8 | -1.172820 | 1.231410 | -1.098828 |
| 53 | 6 | -1.732758 | 3.008586 | -2.580131 |
| 54 | 1 | -2.060973 | 3.959018 | -2.145229 |
| 55 | 1 | -0.652337 | 3.029487 | -2.732558 |
| 56 | 1 | -2.248542 | 2.891863 | -3.538023 |
| 57 | 8 | -4.443826 | -1.332632 | 1.139645 |
| 58 | 6 | -3.499096 | -1.992464 | 1.679704 |
| 59 | 6 | -3.896502 | -3.137727 | 2.586419 |
| 60 | 8 | -2.253745 | -1.799614 | 1.509265 |
| 61 | 1 | -4.010130 | -4.044707 | 1.980678 |
| 62 | 1 | -3.120966 | -3.318564 | 3.333540 |
| 63 | 1 | -4.854423 | -2.926157 | 3.066502 |
| 64 | 8 | -1.714402 | -1.619064 | -1.379555 |
| 65 | 6 | -2.814616 | -1.768691 | -2.000176 |
| 66 | 8 | -3.913792 | -1.187848 | -1.732589 |
| 67 | 6 | -2.807005 | -2.703340 | -3.191780 |
| 68 | 1 | -2.567433 | -2.126109 | -4.092876 |
| 69 | 1 | -2.045046 | -3.475413 | -3.065702 |
| 70 | 1 | -3.793257 | -3.152430 | -3.327560 |

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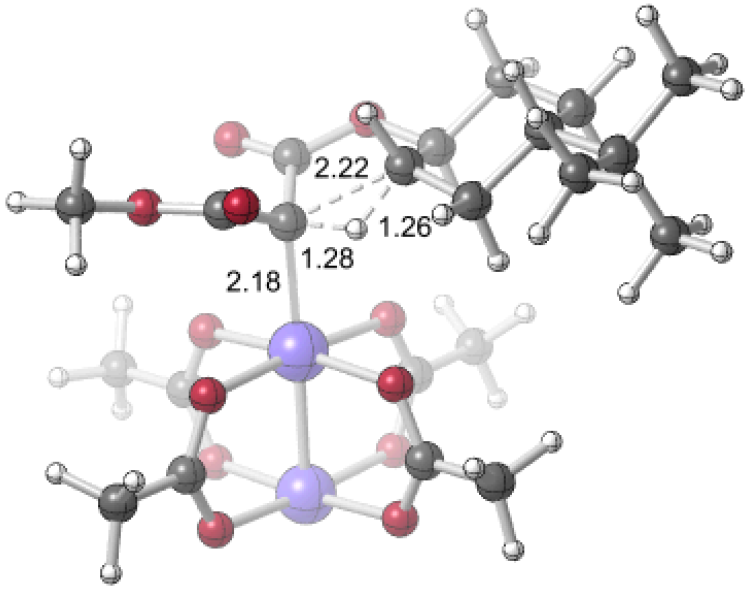
γ-TS1-eq-*half-chair*




E(UB3LYP) = -1980.67769548 hartrees
Sum of electronic and thermal Free Energies = -1980.197336 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|

---

| | | | | |
|---|---|---|---|---|
| 1 | 45 | 0.981994 | 0.145084 | 0.055966 |
| 2 | 45 | 2.663952 | -1.603643 | -0.210094 |
| 3 | 6 | -0.475308 | 1.751237 | 0.292313 |
| 4 | 6 | -0.633231 | 2.235336 | 1.700291 |
| 5 | 6 | -0.451716 | 2.769848 | -0.811104 |
| 6 | 8 | -1.231857 | 2.773810 | -1.746042 |
| 7 | 6 | -2.606983 | 1.137471 | 0.314965 |
| 8 | 1 | -1.430989 | 0.992006 | -0.103985 |
| 9 | 1 | -2.907658 | 2.173255 | 0.159786 |
| 10 | 6 | 2.615790 | 0.355231 | -2.355782 |
| 11 | 6 | 1.046462 | -1.834450 | 2.205403 |
| 12 | 6 | 0.074129 | -2.218389 | -1.413668 |
| 13 | 6 | 3.584019 | 0.719696 | 1.245161 |
| 14 | 8 | 1.660109 | 0.937315 | -1.741454 |
| 15 | 8 | 0.416388 | -0.785643 | 1.832620 |
| 16 | 8 | 3.226431 | -0.689151 | -1.979769 |
| 17 | 8 | 1.984676 | -2.407804 | 1.579752 |
| 18 | 8 | -0.346011 | -1.088342 | -0.985614 |
| 19 | 8 | 2.424361 | 1.217944 | 1.072614 |
| 20 | 8 | 1.233314 | -2.695269 | -1.253419 |
| 21 | 8 | 3.982994 | -0.417442 | 0.845375 |
| 22 | 8 | 0.127084 | 3.035378 | 2.185645 |
| 23 | 8 | -1.670356 | 1.729687 | 2.430820 |
| 24 | 6 | -2.488666 | 0.759344 | 1.767629 |
| 25 | 1 | -1.996355 | -0.216228 | 1.856203 |
| 26 | 6 | -3.400822 | 0.163317 | -0.531540 |
| 27 | 1 | -3.406764 | 0.510347 | -1.566168 |
| 28 | 1 | -2.928895 | -0.822450 | -0.505925 |
| 29 | 6 | -3.888154 | 0.709681 | 2.376744 |
| 30 | 1 | -3.822278 | 0.394783 | 3.423948 |
| 31 | 1 | -4.315265 | 1.720876 | 2.368160 |
| 32 | 6 | -4.843716 | 0.105393 | 0.062721 |
| 33 | 1 | -5.254414 | 1.125644 | -0.001550 |
| 34 | 6 | -4.771441 | -0.258886 | 1.566360 |
| 35 | 1 | -5.773897 | -0.261130 | 2.003900 |
| 36 | 1 | -4.378255 | -1.277931 | 1.680977 |
| 37 | 6 | -5.816389 | -0.796165 | -0.778595 |
| 38 | 6 | -7.247898 | -0.668574 | -0.210692 |
| 39 | 1 | -7.956146 | -1.206343 | -0.851570 |
| 40 | 1 | -7.338518 | -1.090284 | 0.795540 |
| 41 | 1 | -7.568712 | 0.379956 | -0.169659 |
| 42 | 6 | -5.851419 | -0.305367 | -2.242456 |
| 43 | 1 | -6.077543 | 0.766848 | -2.300033 |
| 44 | 1 | -4.905345 | -0.479129 | -2.765304 |
| 45 | 1 | -6.630512 | -0.838109 | -2.799807 |
| 46 | 6 | -5.403853 | -2.282153 | -0.760286 |
| 47 | 1 | -5.420471 | -2.702053 | 0.251488 |
| 48 | 1 | -6.100033 | -2.871679 | -1.368417 |
| 49 | 1 | -4.401050 | -2.435795 | -1.175138 |

| | | | | |
|---|---|---|---|---|
| 50 | 8 | 0.555733 | 3.628648 | -0.648009 |
| 51 | 6 | 0.757089 | 4.553289 | -1.730721 |
| 52 | 1 | -0.139713 | 5.156053 | -1.894620 |
| 53 | 1 | 1.592014 | 5.179896 | -1.418333 |
| 54 | 1 | 1.002257 | 4.007916 | -2.645365 |
| 55 | 6 | 4.582435 | 1.591638 | 1.975465 |
| 56 | 1 | 5.041448 | 2.281390 | 1.257366 |
| 57 | 1 | 4.074893 | 2.187319 | 2.737388 |
| 58 | 1 | 5.368464 | 0.978071 | 2.420043 |
| 59 | 6 | 3.060915 | 0.995625 | -3.654279 |
| 60 | 1 | 2.191071 | 1.192731 | -4.287910 |
| 61 | 1 | 3.538224 | 1.957706 | -3.437048 |
| 62 | 1 | 3.769735 | 0.350406 | -4.175409 |
| 63 | 6 | -0.928160 | -3.055934 | -2.182358 |
| 64 | 1 | -1.771741 | -3.310020 | -1.530887 |
| 65 | 1 | -1.322379 | -2.477453 | -3.023927 |
| 66 | 1 | -0.461347 | -3.972212 | -2.546275 |
| 67 | 6 | 0.623268 | -2.427075 | 3.533460 |
| 68 | 1 | 0.861600 | -1.718935 | 4.334500 |
| 69 | 1 | -0.459935 | -2.583237 | 3.545612 |
| 70 | 1 | 1.139891 | -3.370819 | 3.713827 |

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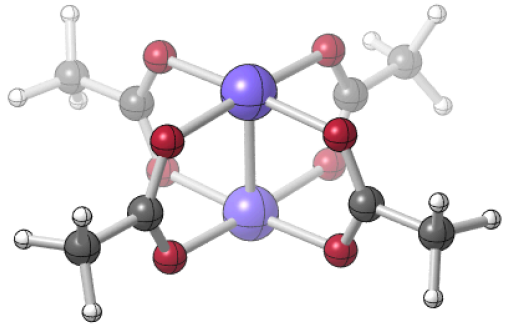
$Rh_2(OAc)_4$



E(UB3LYP) = -1133.11303849 hartrees
Sum of electronic and thermal Free Energies = -1132.955659 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 45 | 0.003598 | -0.003850 | -1.192808 |
| 2 | 45 | 0.002777 | -0.002929 | 1.193686 |
| 3 | 8 | 1.456673 | -1.465780 | 1.134990 |
| 4 | 6 | 1.868255 | -1.874791 | 0.001286 |
| 5 | 8 | 1.455192 | -1.468700 | -1.133117 |
| 6 | 6 | 2.966384 | -2.913402 | -0.000257 |

| | | | | |
|---|---|---|---|---|
| 7 | 1 | 2.858254 | -3.575888 | -0.861930 |
| 8 | 1 | 3.934217 | -2.404722 | -0.082179 |
| 9 | 1 | 2.952649 | -3.483856 | 0.930363 |
| 10 | 8 | -1.448865 | 1.462197 | -1.133447 |
| 11 | 6 | -1.862045 | 1.869125 | 0.000462 |
| 12 | 8 | -1.451094 | 1.460567 | 1.134607 |
| 13 | 6 | -2.959213 | 2.909078 | -0.001986 |
| 14 | 1 | -2.846540 | 3.574500 | -0.860844 |
| 15 | 1 | -3.927263 | 2.401952 | -0.090498 |
| 16 | 1 | -2.949030 | 3.476065 | 0.930764 |
| 17 | 8 | 1.466200 | 1.450941 | 1.134729 |
| 18 | 6 | 1.874583 | 1.862351 | 0.000722 |
| 19 | 8 | 1.468750 | 1.448372 | -1.133370 |
| 20 | 6 | 2.912698 | 2.961088 | -0.001673 |
| 21 | 1 | 2.404028 | 3.928039 | -0.093354 |
| 22 | 1 | 3.477800 | 2.953812 | 0.932251 |
| 23 | 1 | 3.580167 | 2.847848 | -0.858896 |
| 24 | 8 | -1.458724 | -1.458739 | 1.134820 |
| 25 | 6 | -1.871365 | -1.865988 | 0.000861 |
| 26 | 8 | -1.459630 | -1.457987 | -1.133266 |
| 27 | 6 | -2.969913 | -2.904402 | -0.001512 |
| 28 | 1 | -3.936895 | -2.396762 | -0.097491 |
| 29 | 1 | -2.853849 | -3.574191 | -0.856609 |
| 30 | 1 | -2.964738 | -3.467044 | 0.933959 |

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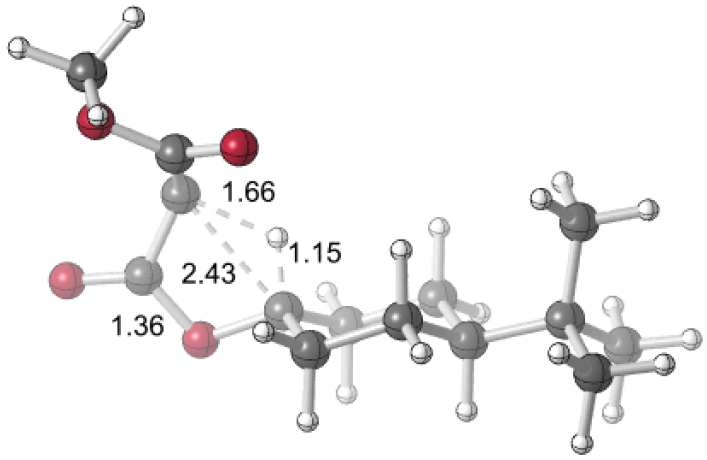
β-TS1$_{uncat}$

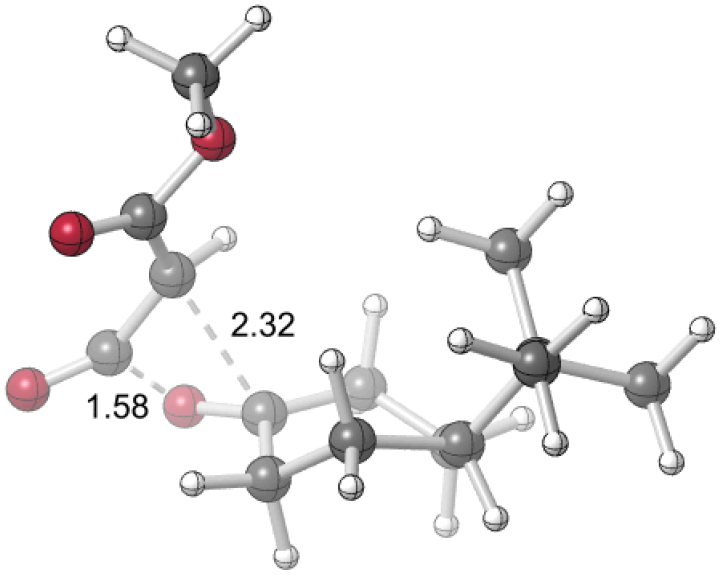



E(UB3LYP) = -847.534404247 hartrees
Sum of electronic and thermal Free Energies = -847.239513 hartrees

| Center | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| Number | Number | X | Y | Z |

| | | | | |
|---|---|---|---|---|
| 1 | 6 | 2.419448 | -0.304840 | 0.251873 |
| 2 | 6 | 1.850993 | -1.029014 | -0.989778 |
| 3 | 6 | 0.675259 | -1.955593 | -0.637578 |
| 4 | 6 | -0.411700 | -1.215344 | 0.123343 |
| 5 | 6 | 0.100725 | -0.451841 | 1.332307 |
| 6 | 6 | 1.275109 | 0.464466 | 0.950318 |
| 7 | 1 | 0.248100 | -2.411640 | -1.537687 |
| 8 | 1 | 1.513262 | -0.289780 | -1.728893 |
| 9 | 1 | 2.622908 | -1.629260 | -1.480759 |
| 10 | 1 | 2.752852 | -1.089726 | 0.951779 |
| 11 | 1 | -0.871840 | -0.461233 | -0.616118 |
| 12 | 1 | -0.710463 | 0.134307 | 1.776299 |
| 13 | 1 | 0.416350 | -1.193338 | 2.079989 |
| 14 | 1 | 0.894019 | 1.257322 | 0.294293 |
| 15 | 1 | 1.634083 | 0.955747 | 1.859608 |
| 16 | 1 | 1.017044 | -2.778782 | 0.006497 |
| 17 | 6 | 3.691201 | 0.567071 | -0.039493 |
| 18 | 6 | 4.248205 | 1.132510 | 1.285817 |
| 19 | 1 | 4.438356 | 0.332254 | 2.012352 |
| 20 | 1 | 5.198309 | 1.649876 | 1.107332 |
| 21 | 1 | 3.569496 | 1.855547 | 1.749555 |
| 22 | 6 | 4.795385 | -0.312243 | -0.666795 |
| 23 | 1 | 4.532529 | -0.657740 | -1.671878 |
| 24 | 1 | 5.728843 | 0.256035 | -0.754630 |
| 25 | 1 | 5.002174 | -1.195411 | -0.048806 |
| 26 | 6 | 3.393400 | 1.743112 | -0.992421 |
| 27 | 1 | 2.649535 | 2.431653 | -0.577000 |
| 28 | 1 | 4.307466 | 2.321527 | -1.172878 |
| 29 | 1 | 3.028325 | 1.401141 | -1.967265 |
| 30 | 8 | -1.479698 | -2.117763 | 0.464604 |
| 31 | 6 | -2.655434 | -1.584874 | 0.051294 |
| 32 | 8 | -3.751735 | -2.068204 | 0.236837 |
| 33 | 6 | -2.521462 | -0.408367 | -0.775984 |
| 34 | 6 | -2.839477 | 0.939546 | -0.358077 |
| 35 | 8 | -1.966817 | 1.777772 | -0.170497 |
| 36 | 8 | -4.160815 | 1.159868 | -0.283998 |
| 37 | 6 | -4.544909 | 2.513227 | 0.033897 |
| 38 | 1 | -5.634156 | 2.512111 | 0.006160 |
| 39 | 1 | -4.185653 | 2.789565 | 1.028289 |
| 40 | 1 | -4.139471 | 3.209551 | -0.704139 |

β-TS2$_{uncat}$




E(RB3LYP) = -847.573265352 hartrees
Sum of electronic and thermal Free Energies = -847.276090 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 8 | -1.537541 | -2.426253 | -0.596541 |
| 2 | 6 | -0.437533 | -1.816738 | -0.225466 |
| 3 | 6 | -0.085313 | -1.565684 | 1.211966 |
| 4 | 6 | 0.703904 | -1.786764 | -1.203672 |
| 5 | 1 | 0.563413 | -0.924127 | -1.866125 |
| 6 | 1 | 0.398257 | -2.494190 | 1.566776 |
| 7 | 1 | -0.977800 | -1.423732 | 1.825516 |
| 8 | 1 | 0.610549 | -2.671089 | -1.848137 |
| 9 | 6 | 0.895894 | -0.389029 | 1.324527 |
| 10 | 1 | 1.087934 | -0.184659 | 2.381963 |
| 11 | 1 | 0.381857 | 0.491851 | 0.924850 |
| 12 | 6 | 2.080487 | -1.731184 | -0.517252 |
| 13 | 1 | 2.849745 | -1.631501 | -1.288123 |
| 14 | 1 | 2.260060 | -2.708162 | -0.051940 |
| 15 | 6 | 2.239892 | -0.630392 | 0.574856 |
| 16 | 1 | 2.941093 | -1.046583 | 1.311455 |
| 17 | 6 | 2.914289 | 0.696918 | 0.079670 |
| 18 | 6 | 2.973637 | 1.706848 | 1.246844 |
| 19 | 1 | 3.529907 | 2.602440 | 0.945727 |
| 20 | 1 | 1.978710 | 2.032957 | 1.566114 |
| 21 | 1 | 3.484578 | 1.277645 | 2.118203 |
| 22 | 6 | 4.367725 | 0.409518 | -0.354965 |
| 23 | 1 | 4.946513 | -0.033631 | 0.464939 |
| 24 | 1 | 4.425176 | -0.271120 | -1.211516 |
| 25 | 1 | 4.868006 | 1.339598 | -0.649309 |
| 26 | 6 | 2.159684 | 1.338805 | -1.102943 |

| | | | | |
|---|---|---|---|---|
| 27 | 1 | 2.189725 | 0.701966 | -1.995156 |
| 28 | 1 | 1.109419 | 1.550342 | -0.870898 |
| 29 | 1 | 2.629593 | 2.291332 | -1.375524 |
| 30 | 6 | -2.607720 | -1.382954 | -0.091373 |
| 31 | 6 | -2.040180 | -0.169530 | -0.566572 |
| 32 | 8 | -3.492524 | -1.759113 | 0.606434 |
| 33 | 6 | -2.505134 | 1.127782 | -0.079843 |
| 34 | 1 | -1.565305 | -0.184034 | -1.536697 |
| 35 | 8 | -1.886215 | 2.133496 | -0.778170 |
| 36 | 8 | -3.267793 | 1.341662 | 0.843140 |
| 37 | 6 | -2.218773 | 3.457167 | -0.342720 |
| 38 | 1 | -3.291699 | 3.641943 | -0.447476 |
| 39 | 1 | -1.940832 | 3.605160 | 0.705076 |
| 40 | 1 | -1.651483 | 4.130689 | -0.986970 |

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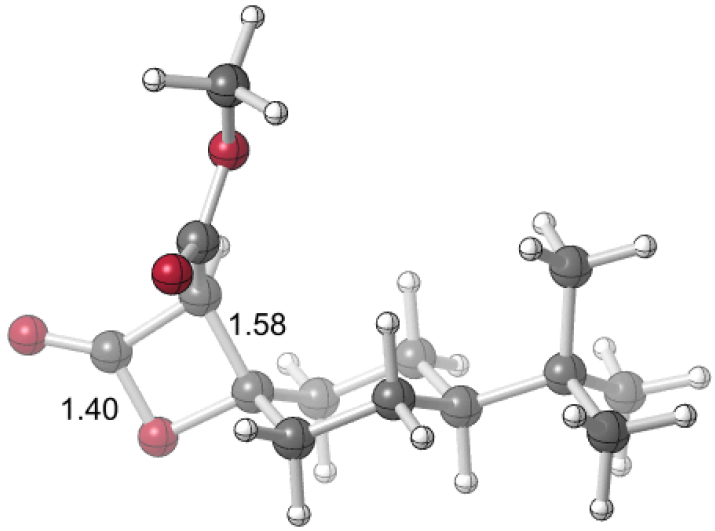
β-lactone




E(RB3LYP) = -847.510193566 hartrees
Sum of electronic and thermal Free Energies = -847.211543 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 2.034404 | -0.611862 | 0.169424 |
| 2 | 6 | 1.292101 | -0.934198 | -1.156464 |
| 3 | 6 | 0.082626 | -1.870932 | -0.918893 |
| 4 | 6 | -0.891383 | -1.267985 | 0.090551 |
| 5 | 6 | -0.207037 | -0.912991 | 1.406594 |
| 6 | 6 | 1.021648 | 0.002199 | 1.173861 |
| 7 | 1 | -0.433165 | -2.088665 | -1.863692 |
| 8 | 1 | 0.947121 | -0.000343 | -1.625808 |

| | | | | |
|---|---|---|---|---|
| 9 | 1 | 1.964763 | -1.418326 | -1.873308 |
| 10 | 1 | 2.364130 | -1.577685 | 0.595075 |
| 11 | 1 | -1.835764 | -0.141292 | -1.603829 |
| 12 | 1 | -0.914267 | -0.438612 | 2.094226 |
| 13 | 1 | 0.117902 | -1.856620 | 1.867328 |
| 14 | 1 | 0.683190 | 0.982699 | 0.807360 |
| 15 | 1 | 1.497466 | 0.180201 | 2.144367 |
| 16 | 1 | 0.433443 | -2.831664 | -0.516003 |
| 17 | 6 | 3.345513 | 0.242171 | -0.021053 |
| 18 | 6 | 3.055103 | 1.639197 | -0.632351 |
| 19 | 1 | 2.390928 | 2.234670 | 0.006952 |
| 20 | 1 | 3.991714 | 2.201617 | -0.746885 |
| 21 | 1 | 2.593892 | 1.563994 | -1.625328 |
| 22 | 6 | 4.048633 | 0.434306 | 1.351653 |
| 23 | 1 | 4.216695 | -0.530871 | 1.850196 |
| 24 | 1 | 5.026908 | 0.913627 | 1.213175 |
| 25 | 1 | 3.466674 | 1.069743 | 2.029945 |
| 26 | 6 | 4.332972 | -0.515501 | -0.951815 |
| 27 | 1 | 3.958583 | -0.592278 | -1.979631 |
| 28 | 1 | 5.295554 | 0.011552 | -0.993933 |
| 29 | 1 | 4.524583 | -1.533024 | -0.582562 |
| 30 | 8 | -2.054038 | -2.253752 | 0.344798 |
| 31 | 6 | -2.992968 | -1.344723 | -0.162604 |
| 32 | 8 | -4.201937 | -1.470416 | -0.260320 |
| 33 | 6 | -1.942941 | -0.263144 | -0.523697 |
| 34 | 6 | -2.160980 | 1.092882 | 0.106560 |
| 35 | 8 | -2.422156 | 1.315741 | 1.299151 |
| 36 | 8 | -2.040160 | 2.090811 | -0.838550 |
| 37 | 6 | -2.276613 | 3.475764 | -0.381535 |
| 38 | 1 | -3.288142 | 3.565189 | 0.025663 |
| 39 | 1 | -1.548261 | 3.746504 | 0.389112 |
| 40 | 1 | -2.154092 | 4.089416 | -1.274437 |

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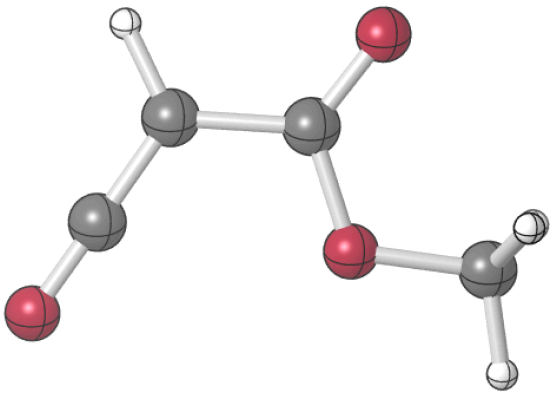
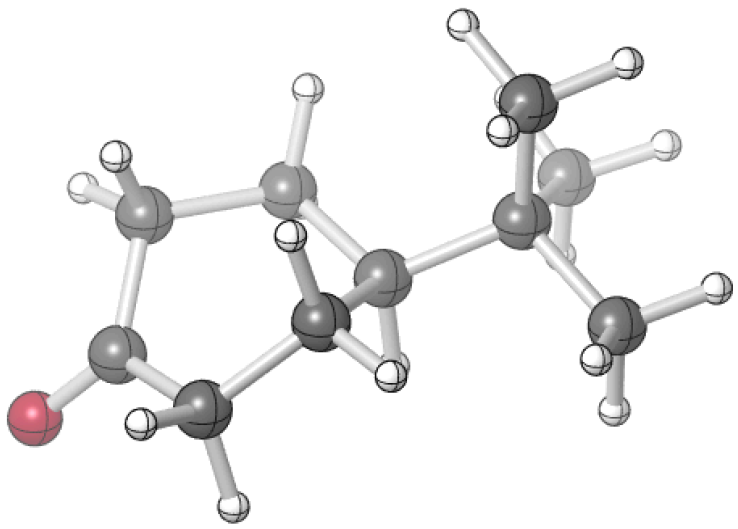
fragmented product, ketene



E(UB3LYP) = -380.480709519 hartrees
Sum of electronic and thermal Free Energies = -380.435648 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -0.919005 | 0.959782 | -0.000023 |
| 2 | 6 | -1.858706 | 0.021932 | -0.000016 |
| 3 | 8 | -2.689146 | -0.792737 | 0.000018 |
| 4 | 1 | -1.213017 | 2.001655 | -0.000065 |
| 5 | 6 | 0.508140 | 0.617574 | 0.000009 |
| 6 | 8 | 0.690343 | -0.729501 | 0.000022 |
| 7 | 8 | 1.410869 | 1.426266 | 0.000022 |
| 8 | 6 | 2.059626 | -1.163235 | -0.000029 |
| 9 | 1 | 2.579094 | -0.797793 | -0.889754 |
| 10 | 1 | 2.578591 | -0.799602 | 0.890762 |
| 11 | 1 | 2.018469 | -2.252795 | -0.001084 |

fragmented product, ketone



E(UB3LYP) = -467.134866997 hartrees
Sum of electronic and thermal Free Energies = -466.907942 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 8 | 3.614167 | -0.069496 | -0.689311 |
| 2 | 6 | 2.553636 | 0.013439 | -0.100224 |
| 3 | 6 | 1.822107 | 1.344757 | 0.073124 |

| | | | | |
|---|---|---|---|---|
| 4 | 6 | 1.857126 | -1.175662 | 0.537490 |
| 5 | 1 | 1.895885 | -1.009995 | 1.624703 |
| 6 | 1 | 1.853065 | 1.862590 | -0.893648 |
| 7 | 1 | 2.410455 | 1.961778 | 0.766664 |
| 8 | 1 | 2.429339 | -2.082919 | 0.326534 |
| 9 | 6 | 0.374774 | 1.172921 | 0.564064 |
| 10 | 1 | -0.157475 | 2.123301 | 0.456296 |
| 11 | 1 | 0.368170 | 0.936240 | 1.636267 |
| 12 | 6 | 0.373995 | -1.313316 | 0.098959 |
| 13 | 1 | -0.166829 | -1.831686 | 0.898792 |
| 14 | 1 | 0.323353 | -1.966614 | -0.778045 |
| 15 | 6 | -0.314667 | 0.042753 | -0.230199 |
| 16 | 1 | -0.112595 | 0.251977 | -1.293330 |
| 17 | 6 | -1.875005 | 0.002613 | -0.104416 |
| 18 | 6 | -2.478941 | 1.280446 | -0.726354 |
| 19 | 1 | -3.574281 | 1.230945 | -0.711671 |
| 20 | 1 | -2.188530 | 2.185979 | -0.183215 |
| 21 | 1 | -2.165935 | 1.399359 | -1.771144 |
| 22 | 6 | -2.427463 | -1.204864 | -0.892211 |
| 23 | 1 | -2.096104 | -1.180678 | -1.938249 |
| 24 | 1 | -2.111389 | -2.160694 | -0.461565 |
| 25 | 1 | -3.523992 | -1.191972 | -0.892082 |
| 26 | 6 | -2.335676 | -0.097149 | 1.363863 |
| 27 | 1 | -1.943401 | -0.992031 | 1.860654 |
| 28 | 1 | -2.022595 | 0.775772 | 1.947530 |
| 29 | 1 | -3.429784 | -0.151012 | 1.415416 |

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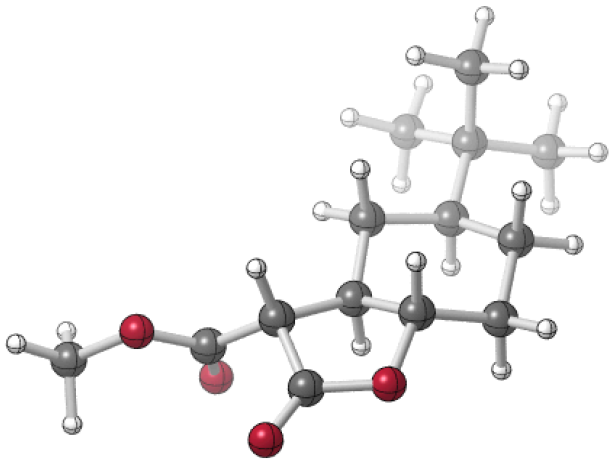
γ-lactone-eq-*trans*

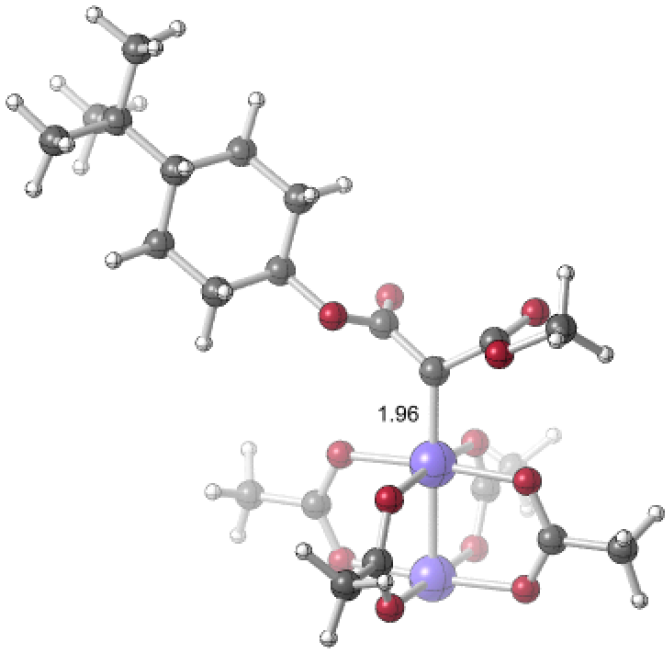


E(UB3LYP) = -847.666400230 hartrees
Sum of electronic and thermal Free Energies = -847.364313 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 1.785534 | 0.150859 | 0.461644 |
| 2 | 6 | 2.412372 | 1.538061 | 0.152693 |
| 3 | 6 | 2.579304 | -0.961363 | -0.196712 |
| 4 | 8 | 2.385122 | -1.371064 | -1.320945 |
| 5 | 6 | 0.368517 | 0.349765 | -0.075055 |
| 6 | 1 | 1.807893 | 0.015909 | 1.551034 |
| 7 | 1 | 0.442693 | 0.270423 | -1.168615 |
| 8 | 8 | 3.576925 | 1.813695 | 0.052744 |
| 9 | 8 | 1.412185 | 2.450204 | -0.012974 |
| 10 | 6 | 0.139805 | 1.816645 | 0.266959 |
| 11 | 1 | -0.040426 | 1.927376 | 1.347637 |
| 12 | 6 | -0.809560 | -0.504228 | 0.385870 |
| 13 | 1 | -0.625805 | -1.552622 | 0.132695 |
| 14 | 1 | -0.908901 | -0.447486 | 1.478992 |
| 15 | 6 | -1.044335 | 2.375794 | -0.491815 |
| 16 | 1 | -1.213078 | 3.431442 | -0.250226 |
| 17 | 1 | -0.854781 | 2.310203 | -1.570725 |
| 18 | 6 | -2.103454 | 0.004121 | -0.311201 |
| 19 | 1 | -1.942166 | -0.143475 | -1.391450 |
| 20 | 6 | -2.281266 | 1.532787 | -0.097722 |
| 21 | 1 | -3.139781 | 1.893371 | -0.671516 |
| 22 | 1 | -2.510191 | 1.731478 | 0.958317 |
| 23 | 6 | -3.383829 | -0.834741 | 0.036965 |
| 24 | 6 | -4.579100 | -0.340652 | -0.808038 |
| 25 | 1 | -5.441177 | -1.003677 | -0.669189 |
| 26 | 1 | -4.899795 | 0.668116 | -0.528467 |
| 27 | 1 | -4.335584 | -0.334137 | -1.878051 |
| 28 | 6 | -3.145783 | -2.318431 | -0.321703 |
| 29 | 1 | -2.820790 | -2.430569 | -1.363731 |
| 30 | 1 | -2.391127 | -2.786657 | 0.318563 |
| 31 | 1 | -4.073015 | -2.890654 | -0.199988 |
| 32 | 6 | -3.763563 | -0.743387 | 1.529784 |
| 33 | 1 | -3.996456 | 0.283142 | 1.834204 |
| 34 | 1 | -4.654551 | -1.350860 | 1.728928 |
| 35 | 1 | -2.964840 | -1.116319 | 2.180755 |
| 36 | 8 | 3.533043 | -1.427255 | 0.626980 |
| 37 | 6 | 4.400140 | -2.428821 | 0.064773 |
| 38 | 1 | 4.920936 | -2.031044 | -0.809550 |
| 39 | 1 | 5.108767 | -2.676292 | 0.855091 |
| 40 | 1 | 3.825290 | -3.310764 | -0.229796 |

*BP86/6-31G(d) for C, H, O and LANL2DZ for Rh*

Rh-carbenoid "reactant"




E(RB-P86) = -1980.87641175 hartrees
Sum of electronic and thermal Free Energies = -1980.417602 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -6.447153 | -0.020458 | 0.327956 |
| 2 | 6 | -5.865016 | 0.824208 | -0.832888 |
| 3 | 6 | -4.433388 | 1.318011 | -0.533719 |
| 4 | 6 | -3.508486 | 0.137793 | -0.220361 |
| 5 | 6 | -4.047113 | -0.708064 | 0.931774 |
| 6 | 6 | -5.479431 | -1.194791 | 0.623863 |
| 7 | 1 | -4.033187 | 1.886847 | -1.391475 |
| 8 | 1 | -5.851355 | 0.220769 | -1.762676 |
| 9 | 1 | -6.501597 | 1.702368 | -1.039923 |
| 10 | 1 | -6.447214 | 0.631169 | 1.230525 |
| 11 | 1 | -3.362465 | -0.476700 | -1.127190 |
| 12 | 1 | -3.373208 | -1.564612 | 1.115382 |
| 13 | 1 | -4.047926 | -0.092811 | 1.852976 |
| 14 | 1 | -5.449305 | -1.877347 | -0.249246 |
| 15 | 1 | -5.837400 | -1.795265 | 1.478809 |
| 16 | 1 | -4.444427 | 1.996893 | 0.341958 |
| 17 | 6 | -7.944829 | -0.456353 | 0.120815 |
| 18 | 6 | -8.830286 | 0.798101 | -0.083565 |
| 19 | 1 | -8.615451 | 1.315723 | -1.035037 |

| | | | | |
|---|---|---|---|---|
| 20 | 1 | -9.898598 | 0.513734 | -0.101785 |
| 21 | 1 | -8.692564 | 1.525846 | 0.738674 |
| 22 | 6 | -8.121836 | -1.393302 | -1.097172 |
| 23 | 1 | -7.553657 | -2.333930 | -0.981568 |
| 24 | 1 | -9.186730 | -1.666336 | -1.216728 |
| 25 | 1 | -7.798082 | -0.913168 | -2.038199 |
| 26 | 6 | -8.458421 | -1.182769 | 1.388528 |
| 27 | 1 | -8.317192 | -0.560368 | 2.292499 |
| 28 | 1 | -9.539319 | -1.396508 | 1.296126 |
| 29 | 1 | -7.949681 | -2.148169 | 1.557647 |
| 30 | 8 | -2.182273 | 0.631101 | 0.194761 |
| 31 | 6 | -1.317707 | 0.923301 | -0.799421 |
| 32 | 8 | -1.526883 | 0.823373 | -2.005861 |
| 33 | 6 | -0.003167 | 1.400285 | -0.303921 |
| 34 | 6 | 0.203384 | 2.867353 | -0.269526 |
| 35 | 8 | 0.337215 | 3.512345 | -1.306332 |
| 36 | 8 | 0.252398 | 3.373011 | 0.982996 |
| 37 | 6 | 0.519993 | 4.797968 | 1.040664 |
| 38 | 1 | 0.480877 | 5.053483 | 2.108306 |
| 39 | 1 | 1.516656 | 5.012444 | 0.622589 |
| 40 | 1 | -0.241105 | 5.359893 | 0.475023 |
| 41 | 45 | 1.515453 | 0.180689 | -0.076217 |
| 42 | 45 | 3.428466 | -1.328320 | 0.175545 |
| 43 | 8 | 4.616008 | 0.336072 | 0.500195 |
| 44 | 6 | 4.074213 | 1.494288 | 0.469030 |
| 45 | 6 | 4.978771 | 2.693729 | 0.691623 |
| 46 | 8 | 2.829164 | 1.764603 | 0.266762 |
| 47 | 1 | 4.939242 | 3.355624 | -0.190428 |
| 48 | 1 | 4.620721 | 3.274407 | 1.558840 |
| 49 | 1 | 6.013551 | 2.364614 | 0.864778 |
| 50 | 8 | 3.050411 | -1.464909 | 2.193235 |
| 51 | 6 | 2.058953 | -0.800112 | 2.655990 |
| 52 | 8 | 1.250019 | -0.055591 | 1.985105 |
| 53 | 6 | 1.803420 | -0.868661 | 4.150506 |
| 54 | 1 | 2.085204 | 0.094083 | 4.612453 |
| 55 | 1 | 0.730099 | -1.027700 | 4.343526 |
| 56 | 1 | 2.398896 | -1.675587 | 4.602169 |
| 57 | 8 | 3.790860 | -1.177441 | -1.841520 |
| 58 | 6 | 3.000868 | -0.448353 | -2.536726 |
| 59 | 6 | 3.241079 | -0.371705 | -4.031856 |
| 60 | 8 | 1.997803 | 0.229476 | -2.097454 |
| 61 | 1 | 3.216695 | 0.679133 | -4.363220 |
| 62 | 1 | 4.206477 | -0.833433 | -4.285934 |
| 63 | 1 | 2.429048 | -0.903527 | -4.558010 |
| 64 | 8 | 0.327056 | -1.502184 | -0.399549 |
| 65 | 6 | 0.896556 | -2.659568 | -0.376925 |
| 66 | 8 | 2.135683 | -2.905406 | -0.175807 |
| 67 | 6 | -0.022846 | -3.848602 | -0.594387 |
| 68 | 1 | 0.567571 | -4.760309 | -0.766781 |
| 69 | 1 | -0.653860 | -3.990132 | 0.300981 |

| | | | | |
|---|---|---|---|---|
| 70 | 1 | -0.692157 | -3.657108 | -1.448744 |

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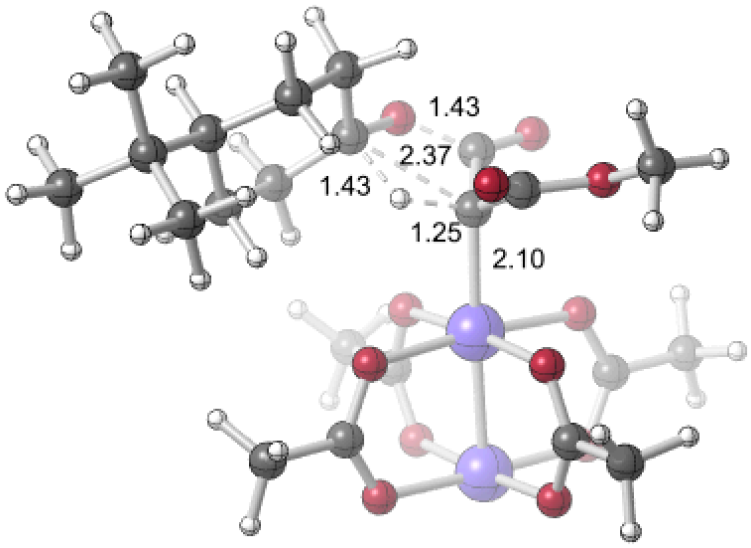
β-TS1$_{cat}$, Conformation 1




E(RB-P86) = -1980.86106051 hartrees
Sum of electronic and thermal Free Energies = -1980.402644 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -4.854073 | -0.256814 | -0.436038 |
| 2 | 6 | -3.584529 | -1.087601 | -0.746353 |
| 3 | 6 | -2.715218 | -0.452823 | -1.851659 |
| 4 | 6 | -2.449303 | 1.010668 | -1.615236 |
| 5 | 6 | -3.595165 | 1.865723 | -1.133414 |
| 6 | 6 | -4.421543 | 1.173860 | -0.031228 |
| 7 | 1 | -1.752568 | -0.978854 | -1.978336 |
| 8 | 1 | -2.961047 | -1.184220 | 0.162617 |
| 9 | 1 | -3.848348 | -2.110084 | -1.067784 |
| 10 | 1 | -5.431977 | -0.172968 | -1.384755 |
| 11 | 1 | -1.530348 | 0.955654 | -0.522683 |
| 12 | 1 | -3.223688 | 2.850543 | -0.799291 |
| 13 | 1 | -4.227793 | 2.056378 | -2.029007 |
| 14 | 1 | -3.807635 | 1.145145 | 0.887948 |
| 15 | 1 | -5.298536 | 1.807219 | 0.187485 |
| 16 | 1 | -3.239458 | -0.506671 | -2.832772 |
| 17 | 6 | -5.831915 | -0.938336 | 0.592303 |
| 18 | 6 | -7.132056 | -0.104050 | 0.704712 |
| 19 | 1 | -7.607088 | 0.035353 | -0.284998 |
| 20 | 1 | -7.861800 | -0.619502 | 1.355815 |
| 21 | 1 | -6.955642 | 0.894332 | 1.141605 |

| | | | | |
|---|---|---|---|---|
| 22 | 6 | -6.227352 | -2.347168 | 0.084465 |
| 23 | 1 | -5.379543 | -3.054481 | 0.101708 |
| 24 | 1 | -7.020476 | -2.775402 | 0.724472 |
| 25 | 1 | -6.618135 | -2.308312 | -0.950218 |
| 26 | 6 | -5.201544 | -1.072273 | 1.998504 |
| 27 | 1 | -4.957365 | -0.089093 | 2.438395 |
| 28 | 1 | -5.907809 | -1.574940 | 2.684968 |
| 29 | 1 | -4.274719 | -1.673299 | 1.980263 |
| 30 | 8 | -1.599851 | 1.604253 | -2.543793 |
| 31 | 6 | -0.484893 | 2.166318 | -1.854385 |
| 32 | 8 | 0.294247 | 2.909479 | -2.398114 |
| 33 | 6 | -0.481154 | 1.632845 | -0.454608 |
| 34 | 6 | -0.677786 | 2.584915 | 0.679540 |
| 35 | 8 | -1.570240 | 2.461159 | 1.518460 |
| 36 | 8 | 0.242084 | 3.579915 | 0.679073 |
| 37 | 6 | 0.146529 | 4.479998 | 1.807860 |
| 38 | 1 | 0.938957 | 5.224163 | 1.647599 |
| 39 | 1 | -0.843565 | 4.964068 | 1.839642 |
| 40 | 1 | 0.311180 | 3.928567 | 2.747640 |
| 41 | 45 | 0.961092 | 0.158178 | -0.074760 |
| 42 | 45 | 2.725699 | -1.480703 | 0.340008 |
| 43 | 8 | 2.953820 | -0.686315 | 2.232391 |
| 44 | 6 | 2.206220 | 0.296263 | 2.573784 |
| 45 | 6 | 2.414269 | 0.873653 | 3.963264 |
| 46 | 8 | 1.300148 | 0.865746 | 1.857363 |
| 47 | 1 | 2.929160 | 1.847414 | 3.880640 |
| 48 | 1 | 1.440698 | 1.049325 | 4.449162 |
| 49 | 1 | 3.028759 | 0.194060 | 4.571799 |
| 50 | 8 | 1.275106 | -2.767072 | 1.056351 |
| 51 | 6 | 0.057330 | -2.378636 | 1.080711 |
| 52 | 8 | -0.394759 | -1.239173 | 0.677190 |
| 53 | 6 | -0.968780 | -3.343058 | 1.648855 |
| 54 | 1 | -1.427967 | -2.903195 | 2.551246 |
| 55 | 1 | -1.774825 | -3.512454 | 0.914953 |
| 56 | 1 | -0.491727 | -4.299597 | 1.907011 |
| 57 | 8 | 4.119245 | -0.149138 | -0.378283 |
| 58 | 6 | 3.689809 | 0.989136 | -0.784503 |
| 59 | 6 | 4.719520 | 1.982785 | -1.289757 |
| 60 | 8 | 2.469299 | 1.393887 | -0.792953 |
| 61 | 1 | 4.317922 | 2.536055 | -2.153126 |
| 62 | 1 | 4.937365 | 2.715597 | -0.492212 |
| 63 | 1 | 5.651300 | 1.463273 | -1.558907 |
| 64 | 8 | 0.733364 | -0.681284 | -1.972126 |
| 65 | 6 | 1.523111 | -1.645678 | -2.309791 |
| 66 | 8 | 2.421630 | -2.191194 | -1.581862 |
| 67 | 6 | 1.372018 | -2.159744 | -3.730639 |
| 68 | 1 | 1.800271 | -1.419700 | -4.429927 |
| 69 | 1 | 1.901178 | -3.116494 | -3.850166 |
| 70 | 1 | 0.305949 | -2.276267 | -3.984850 |

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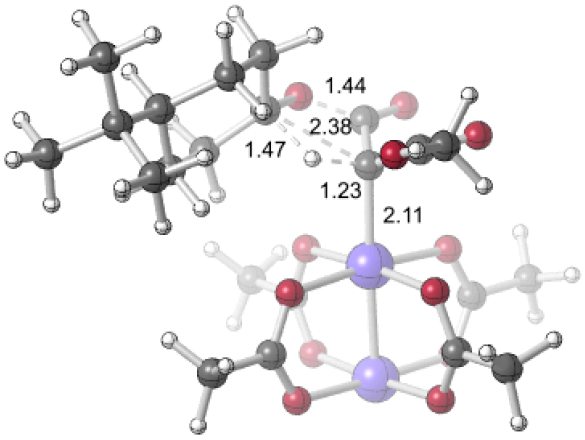
β-TS1$_{cat}$, Conformation 2




E(RB-P86) = -1980.85988511 hartrees
Sum of electronic and thermal Free Energies = -1980.400847 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -4.808425 | -0.352580 | -0.526820 |
| 2 | 6 | -3.504367 | -1.160055 | -0.741079 |
| 3 | 6 | -2.615093 | -0.573110 | -1.855879 |
| 4 | 6 | -2.405725 | 0.909856 | -1.716678 |
| 5 | 6 | -3.588195 | 1.758454 | -1.320569 |
| 6 | 6 | -4.434133 | 1.115331 | -0.203074 |
| 7 | 1 | -1.631551 | -1.072004 | -1.910424 |
| 8 | 1 | -2.908861 | -1.179078 | 0.191023 |
| 9 | 1 | -3.728004 | -2.209147 | -1.001434 |
| 10 | 1 | -5.354762 | -0.345175 | -1.497465 |
| 11 | 1 | -1.499633 | 0.973277 | -0.561452 |
| 12 | 1 | -3.252991 | 2.775601 | -1.048317 |
| 13 | 1 | -4.199302 | 1.872224 | -2.243925 |
| 14 | 1 | -3.856855 | 1.160664 | 0.739641 |
| 15 | 1 | -5.337119 | 1.732980 | -0.057502 |
| 16 | 1 | -3.097662 | -0.714956 | -2.849894 |
| 17 | 6 | -5.800068 | -1.001751 | 0.508922 |
| 18 | 6 | -7.111261 | -0.179028 | 0.563251 |
| 19 | 1 | -7.557731 | -0.067226 | -0.442966 |
| 20 | 1 | -7.855218 | -0.687018 | 1.203894 |
| 21 | 1 | -6.958230 | 0.830948 | 0.982431 |
| 22 | 6 | -6.170598 | -2.433768 | 0.048889 |
| 23 | 1 | -5.313288 | -3.127953 | 0.095371 |
| 24 | 1 | -6.961510 | -2.851054 | 0.698708 |
| 25 | 1 | -6.555584 | -2.436142 | -0.988558 |

| | | | | |
|---|---|---|---|---|
| 26 | 6 | -5.196196 | -1.073886 | 1.931076 |
| 27 | 1 | -4.956313 | -0.072042 | 2.330037 |
| 28 | 1 | -5.917019 | -1.541544 | 2.626907 |
| 29 | 1 | -4.272270 | -1.678775 | 1.957863 |
| 30 | 8 | -1.544485 | 1.470533 | -2.643865 |
| 31 | 6 | -0.455314 | 2.108244 | -1.960902 |
| 32 | 8 | 0.312362 | 2.831692 | -2.541805 |
| 33 | 6 | -0.473476 | 1.657116 | -0.535192 |
| 34 | 6 | -0.554003 | 2.712454 | 0.512456 |
| 35 | 8 | 0.134831 | 3.724006 | 0.534995 |
| 36 | 8 | -1.481051 | 2.392986 | 1.469598 |
| 37 | 6 | -1.516898 | 3.318946 | 2.580610 |
| 38 | 1 | -2.309707 | 2.945886 | 3.244442 |
| 39 | 1 | -0.544874 | 3.324087 | 3.099098 |
| 40 | 1 | -1.746268 | 4.340143 | 2.233390 |
| 41 | 45 | 0.996686 | 0.211731 | -0.081813 |
| 42 | 45 | 2.787473 | -1.379419 | 0.395816 |
| 43 | 8 | 2.992306 | -0.522065 | 2.261801 |
| 44 | 6 | 2.217916 | 0.450491 | 2.571819 |
| 45 | 6 | 2.408714 | 1.077975 | 3.941906 |
| 46 | 8 | 1.291564 | 0.966971 | 1.841235 |
| 47 | 1 | 2.758431 | 2.118349 | 3.822582 |
| 48 | 1 | 1.445059 | 1.110508 | 4.477466 |
| 49 | 1 | 3.145236 | 0.507593 | 4.526307 |
| 50 | 8 | 1.355323 | -2.673483 | 1.135730 |
| 51 | 6 | 0.128887 | -2.312520 | 1.131846 |
| 52 | 8 | -0.343943 | -1.195793 | 0.690456 |
| 53 | 6 | -0.881874 | -3.285533 | 1.714018 |
| 54 | 1 | -1.349809 | -2.839818 | 2.609186 |
| 55 | 1 | -1.683640 | -3.480455 | 0.981884 |
| 56 | 1 | -0.389064 | -4.229312 | 1.988999 |
| 57 | 8 | 4.159562 | -0.039169 | -0.346609 |
| 58 | 6 | 3.711525 | 1.084375 | -0.775114 |
| 59 | 6 | 4.723147 | 2.093356 | -1.284164 |
| 60 | 8 | 2.482449 | 1.461222 | -0.803948 |
| 61 | 1 | 4.331100 | 2.599898 | -2.180154 |
| 62 | 1 | 4.885737 | 2.863852 | -0.509477 |
| 63 | 1 | 5.680561 | 1.597806 | -1.503653 |
| 64 | 8 | 0.815774 | -0.673653 | -1.961990 |
| 65 | 6 | 1.621560 | -1.637254 | -2.262339 |
| 66 | 8 | 2.513559 | -2.154575 | -1.506132 |
| 67 | 6 | 1.500600 | -2.187613 | -3.672370 |
| 68 | 1 | 1.943978 | -1.465051 | -4.380503 |
| 69 | 1 | 2.033246 | -3.146241 | -3.756291 |
| 70 | 1 | 0.440427 | -2.311228 | -3.946775 |

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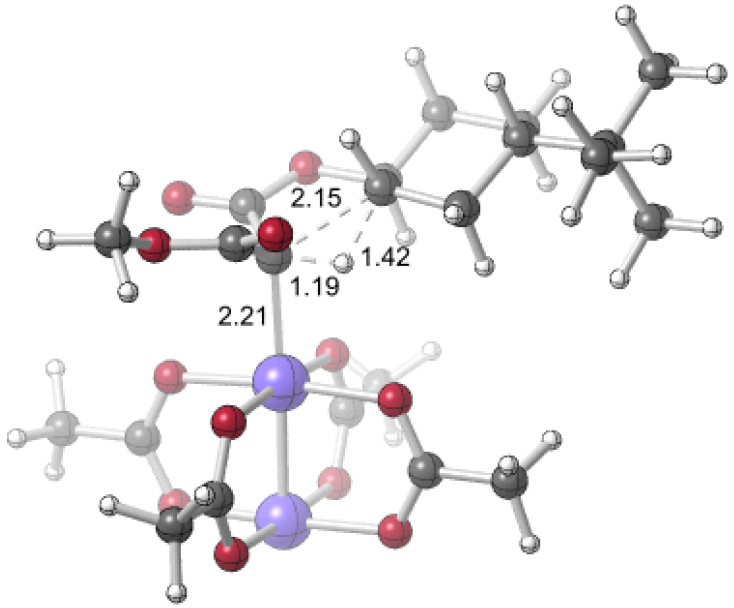
γ-TS1-eq-*half-chair*




E(UB-P86) = -1980.85032679 hartrees
Sum of electronic and thermal Free Energies = -1980.388914 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 45 | 0.963118 | 0.135120 | 0.042308 |
| 2 | 45 | 2.714685 | -1.539696 | -0.215331 |
| 3 | 6 | -0.572895 | 1.709526 | 0.295703 |
| 4 | 6 | -0.638904 | 2.164839 | 1.724781 |
| 5 | 6 | -0.552993 | 2.729842 | -0.806375 |
| 6 | 8 | -1.297902 | 2.691741 | -1.784774 |
| 7 | 6 | -2.639197 | 1.133040 | 0.379526 |
| 8 | 1 | -1.316660 | 0.855477 | -0.063198 |
| 9 | 1 | -2.931887 | 2.186011 | 0.268037 |
| 10 | 6 | 2.645251 | 0.435468 | -2.334799 |
| 11 | 6 | 1.073375 | -1.880391 | 2.163715 |
| 12 | 6 | 0.180223 | -2.240915 | -1.483461 |
| 13 | 6 | 3.531656 | 0.782894 | 1.287062 |
| 14 | 8 | 1.644886 | 0.979607 | -1.734697 |
| 15 | 8 | 0.401172 | -0.840813 | 1.801808 |
| 16 | 8 | 3.297479 | -0.601316 | -1.958120 |
| 17 | 8 | 2.055853 | -2.411591 | 1.540311 |
| 18 | 8 | -0.304830 | -1.127646 | -1.046514 |
| 19 | 8 | 2.349624 | 1.250943 | 1.100487 |
| 20 | 8 | 1.367201 | -2.679651 | -1.304362 |
| 21 | 8 | 3.987529 | -0.346134 | 0.879034 |
| 22 | 8 | 0.119117 | 2.981364 | 2.212229 |

| | | | | |
|---|---|---|---|---|
| 23 | 8 | -1.648648 | 1.612534 | 2.504875 |
| 24 | 6 | -2.486617 | 0.675271 | 1.806297 |
| 25 | 1 | -1.989669 | -0.314935 | 1.828598 |
| 26 | 6 | -3.411593 | 0.194889 | -0.519752 |
| 27 | 1 | -3.437660 | 0.604524 | -1.540963 |
| 28 | 1 | -2.926100 | -0.795916 | -0.554791 |
| 29 | 6 | -3.884193 | 0.577250 | 2.433036 |
| 30 | 1 | -3.801540 | 0.206053 | 3.470438 |
| 31 | 1 | -4.329735 | 1.589346 | 2.480386 |
| 32 | 6 | -4.854042 | 0.077640 | 0.090789 |
| 33 | 1 | -5.287825 | 1.101207 | 0.082619 |
| 34 | 6 | -4.757587 | -0.366500 | 1.575306 |
| 35 | 1 | -5.764834 | -0.419535 | 2.022830 |
| 36 | 1 | -4.335078 | -1.389102 | 1.627571 |
| 37 | 6 | -5.819407 | -0.802273 | -0.790025 |
| 38 | 6 | -7.256265 | -0.703863 | -0.218285 |
| 39 | 1 | -7.963341 | -1.241145 | -0.876246 |
| 40 | 1 | -7.342708 | -1.151765 | 0.787105 |
| 41 | 1 | -7.592565 | 0.348097 | -0.155011 |
| 42 | 6 | -5.853144 | -0.257474 | -2.238700 |
| 43 | 1 | -6.082269 | 0.824612 | -2.258112 |
| 44 | 1 | -4.898180 | -0.413070 | -2.770236 |
| 45 | 1 | -6.637412 | -0.774853 | -2.820692 |
| 46 | 6 | -5.393063 | -2.288264 | -0.821835 |
| 47 | 1 | -5.424171 | -2.751999 | 0.180320 |
| 48 | 1 | -6.078820 | -2.864088 | -1.469912 |
| 49 | 1 | -4.373605 | -2.418344 | -1.228033 |
| 50 | 8 | 0.397474 | 3.667247 | -0.600119 |
| 51 | 6 | 0.531302 | 4.624101 | -1.676152 |
| 52 | 1 | -0.418840 | 5.157375 | -1.844852 |
| 53 | 1 | 1.315035 | 5.318470 | -1.343184 |
| 54 | 1 | 0.829858 | 4.111742 | -2.605007 |
| 55 | 6 | 4.489759 | 1.681514 | 2.047266 |
| 56 | 1 | 5.289725 | 1.082809 | 2.508557 |
| 57 | 1 | 4.949106 | 2.397288 | 1.341807 |
| 58 | 1 | 3.943724 | 2.259416 | 2.808688 |
| 59 | 6 | 3.102513 | 1.112827 | -3.615271 |
| 60 | 1 | 2.232466 | 1.339948 | -4.253001 |
| 61 | 1 | 3.594879 | 2.069864 | -3.367127 |
| 62 | 1 | 3.814200 | 0.471366 | -4.155409 |
| 63 | 6 | -0.766940 | -3.109554 | -2.294293 |
| 64 | 1 | -1.145503 | -2.539220 | -3.159739 |
| 65 | 1 | -0.252501 | -4.017065 | -2.641966 |
| 66 | 1 | -1.636928 | -3.393545 | -1.676557 |
| 67 | 6 | 0.652600 | -2.522744 | 3.474164 |
| 68 | 1 | 0.832880 | -1.815298 | 4.302270 |
| 69 | 1 | -0.428093 | -2.743851 | 3.458458 |
| 70 | 1 | 1.222237 | -3.446992 | 3.648930 |

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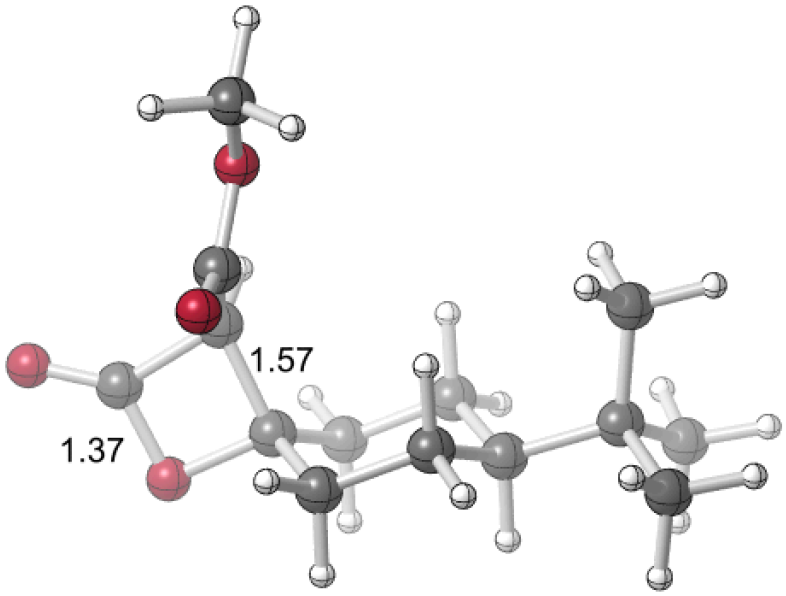
β-lactone




E(RB-P86) = -847.640757406 hartrees
Sum of electronic and thermal Free Energies = -847.352261 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 2.063431 | -0.565786 | 0.164939 |
| 2 | 6 | 1.321519 | -0.918427 | -1.147820 |
| 3 | 6 | 0.133063 | -1.869733 | -0.895744 |
| 4 | 6 | -0.853062 | -1.272728 | 0.105514 |
| 5 | 6 | -0.163465 | -0.896676 | 1.412207 |
| 6 | 6 | 1.045268 | 0.032357 | 1.165780 |
| 7 | 1 | -0.386860 | -2.113378 | -1.841456 |
| 8 | 1 | 0.950002 | 0.010494 | -1.626943 |
| 9 | 1 | 2.002744 | -1.393577 | -1.875344 |
| 10 | 1 | 2.418126 | -1.526778 | 0.601234 |
| 11 | 1 | -1.789159 | -0.176310 | -1.614741 |
| 12 | 1 | -0.883639 | -0.422242 | 2.097950 |
| 13 | 1 | 0.177153 | -1.840790 | 1.881292 |
| 14 | 1 | 0.677393 | 1.007395 | 0.788985 |
| 15 | 1 | 1.524517 | 0.239818 | 2.138167 |
| 16 | 1 | 0.501414 | -2.826851 | -0.477057 |
| 17 | 6 | 3.356190 | 0.308504 | -0.038977 |
| 18 | 6 | 3.038366 | 1.691648 | -0.654125 |
| 19 | 1 | 2.366900 | 2.286616 | -0.009202 |
| 20 | 1 | 3.969436 | 2.273964 | -0.783101 |
| 21 | 1 | 2.565909 | 1.603670 | -1.649171 |
| 22 | 6 | 4.060934 | 0.519573 | 1.323718 |
| 23 | 1 | 4.262997 | -0.445918 | 1.824884 |

| | | | | |
|---|---|---|---|---|
| 24 | 1 | 5.030660 | 1.030150 | 1.179225 |
| 25 | 1 | 3.463983 | 1.142143 | 2.013106 |
| 26 | 6 | 4.347669 | -0.434850 | -0.967355 |
| 27 | 1 | 3.965778 | -0.532219 | -1.998748 |
| 28 | 1 | 5.305050 | 0.114944 | -1.025387 |
| 29 | 1 | 4.568192 | -1.450666 | -0.588346 |
| 30 | 8 | -1.969512 | -2.253139 | 0.366721 |
| 31 | 6 | -2.909247 | -1.394179 | -0.149638 |
| 32 | 8 | -4.100519 | -1.555462 | -0.244304 |
| 33 | 6 | -1.894342 | -0.282972 | -0.522867 |
| 34 | 6 | -2.167131 | 1.068794 | 0.106286 |
| 35 | 8 | -2.301556 | 1.291559 | 1.302350 |
| 36 | 8 | -2.279316 | 2.022617 | -0.861619 |
| 37 | 6 | -2.612727 | 3.342865 | -0.364455 |
| 38 | 1 | -3.570694 | 3.317040 | 0.179572 |
| 39 | 1 | -1.824708 | 3.709756 | 0.313253 |
| 40 | 1 | -2.686760 | 3.977789 | -1.258134 |

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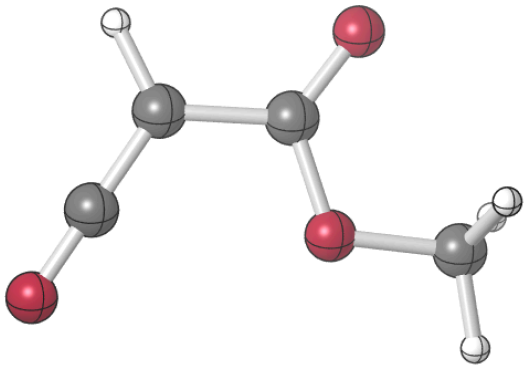
fragmented product, ketene



E(RB-P86) = -380.488508776 hartrees
Sum of electronic and thermal Free Energies = -380.446224 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -0.918109 | 0.972542 | 0.000054 |
| 2 | 6 | -1.867498 | 0.033336 | -0.000075 |
| 3 | 8 | -2.702557 | -0.795267 | -0.000180 |
| 4 | 1 | -1.205235 | 2.025330 | 0.000141 |
| 5 | 6 | 0.513840 | 0.621027 | 0.000087 |
| 6 | 8 | 0.681363 | -0.741460 | -0.000016 |
| 7 | 8 | 1.431753 | 1.429540 | 0.000177 |
| 8 | 6 | 2.060742 | -1.174135 | -0.000041 |
| 9 | 1 | 2.584752 | -0.805372 | -0.897227 |

| | | | | |
|---|---|---|---|---|
| 10 | 1 | 2.584389 | -0.806583 | 0.897861 |
| 11 | 1 | 2.017773 | -2.272492 | -0.000768 |

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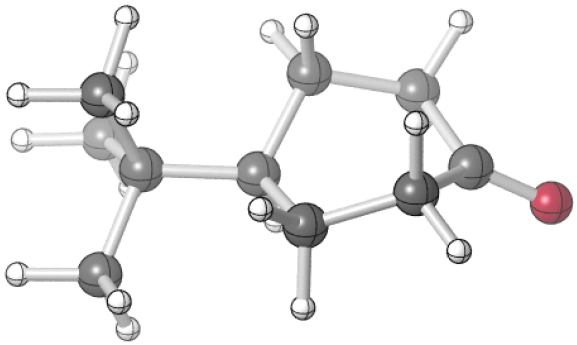
fragmented product, ketone



E(RB-P86) = -467.114277707 hartrees
Sum of electronic and thermal Free Energies = -466.895738 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 8 | 3.636598 | -0.071597 | -0.687373 |
| 2 | 6 | 2.562861 | 0.012943 | -0.099420 |
| 3 | 6 | 1.823154 | 1.348341 | 0.068658 |
| 4 | 6 | 1.857414 | -1.175997 | 0.543307 |
| 5 | 1 | 1.883475 | -0.996108 | 1.638321 |
| 6 | 1 | 1.850700 | 1.865683 | -0.909147 |
| 7 | 1 | 2.418237 | 1.977664 | 0.760226 |
| 8 | 1 | 2.436030 | -2.093587 | 0.348150 |
| 9 | 6 | 0.374189 | 1.174585 | 0.566767 |
| 10 | 1 | -0.165988 | 2.132627 | 0.466644 |
| 11 | 1 | 0.371754 | 0.928454 | 1.646651 |
| 12 | 6 | 0.373278 | -1.315709 | 0.091308 |
| 13 | 1 | -0.178122 | -1.842994 | 0.891829 |
| 14 | 1 | 0.330342 | -1.970486 | -0.796501 |
| 15 | 6 | -0.317254 | 0.044752 | -0.234134 |
| 16 | 1 | -0.115592 | 0.261658 | -1.306432 |
| 17 | 6 | -1.881719 | 0.002483 | -0.104896 |
| 18 | 6 | -2.488470 | 1.289836 | -0.714137 |
| 19 | 1 | -3.592789 | 1.240081 | -0.697577 |
| 20 | 1 | -2.194411 | 2.197107 | -0.157236 |
| 21 | 1 | -2.174694 | 1.420729 | -1.766728 |
| 22 | 6 | -2.434188 | -1.201674 | -0.905519 |
| 23 | 1 | -2.106693 | -1.162838 | -1.961792 |
| 24 | 1 | -2.106761 | -2.168432 | -0.484293 |

| | | | | |
|---|---|---|---|---|
| 25 | 1 | -3.539817 | -1.195396 | -0.898507 |
| 26 | 6 | -2.337510 | -0.112271 | 1.367952 |
| 27 | 1 | -1.942283 | -1.021334 | 1.857094 |
| 28 | 1 | -2.016300 | 0.760692 | 1.964126 |
| 29 | 1 | -3.440400 | -0.164476 | 1.424842 |

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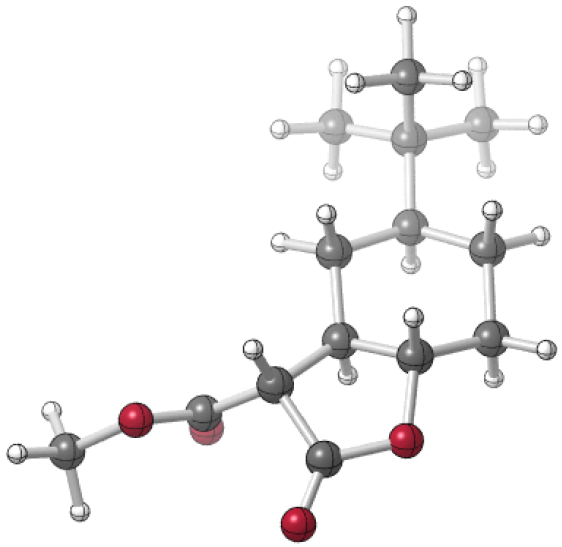
γ-lactone-eq-*trans*



E(UB-P86) = -847.655509516 hartrees
Sum of electronic and thermal Free Energies = -847.365346 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 1.792292 | 0.154413 | 0.464688 |
| 2 | 6 | 2.426604 | 1.548012 | 0.154207 |
| 3 | 6 | 2.581042 | -0.964690 | -0.199948 |
| 4 | 8 | 2.393598 | -1.370115 | -1.338854 |
| 5 | 6 | 0.370991 | 0.353977 | -0.073389 |
| 6 | 1 | 1.816640 | 0.019448 | 1.563831 |
| 7 | 1 | 0.448025 | 0.271202 | -1.177048 |
| 8 | 8 | 3.600720 | 1.830911 | 0.059134 |
| 9 | 8 | 1.417506 | 2.471137 | -0.018634 |
| 10 | 6 | 0.138808 | 1.826490 | 0.265898 |
| 11 | 1 | -0.041165 | 1.939633 | 1.357007 |
| 12 | 6 | -0.810895 | -0.501905 | 0.390334 |
| 13 | 1 | -0.625213 | -1.560531 | 0.139853 |
| 14 | 1 | -0.913332 | -0.439635 | 1.492586 |
| 15 | 6 | -1.050905 | 2.383487 | -0.495958 |
| 16 | 1 | -1.222550 | 3.448888 | -0.257910 |

| | | | | |
|---|---|---|---|---|
| 17 | 1 | -0.861741 | 2.310759 | -1.583914 |
| 18 | 6 | -2.107032 | 0.005310 | -0.310918 |
| 19 | 1 | -1.943149 | -0.142819 | -1.401305 |
| 20 | 6 | -2.288050 | 1.536178 | -0.094097 |
| 21 | 1 | -3.159087 | 1.899206 | -0.665858 |
| 22 | 1 | -2.512199 | 1.732879 | 0.973426 |
| 23 | 6 | -3.389821 | -0.838299 | 0.036909 |
| 24 | 6 | -4.588148 | -0.342217 | -0.810034 |
| 25 | 1 | -5.457602 | -1.010416 | -0.670047 |
| 26 | 1 | -4.911376 | 0.674975 | -0.527550 |
| 27 | 1 | -4.342872 | -0.335559 | -1.888880 |
| 28 | 6 | -3.147724 | -2.324715 | -0.324934 |
| 29 | 1 | -2.824011 | -2.435904 | -1.376935 |
| 30 | 1 | -2.382725 | -2.794928 | 0.317420 |
| 31 | 1 | -4.080239 | -2.904776 | -0.198705 |
| 32 | 6 | -3.768618 | -0.747554 | 1.534212 |
| 33 | 1 | -4.002765 | 0.287526 | 1.841891 |
| 34 | 1 | -4.666700 | -1.359795 | 1.736382 |
| 35 | 1 | -2.962183 | -1.124249 | 2.188899 |
| 36 | 8 | 3.532029 | -1.445863 | 0.641371 |
| 37 | 6 | 4.388484 | -2.461561 | 0.062335 |
| 38 | 1 | 4.922351 | -2.057536 | -0.812752 |
| 39 | 1 | 5.094865 | -2.732529 | 0.859141 |
| 40 | 1 | 3.794031 | -3.335956 | -0.249508 |

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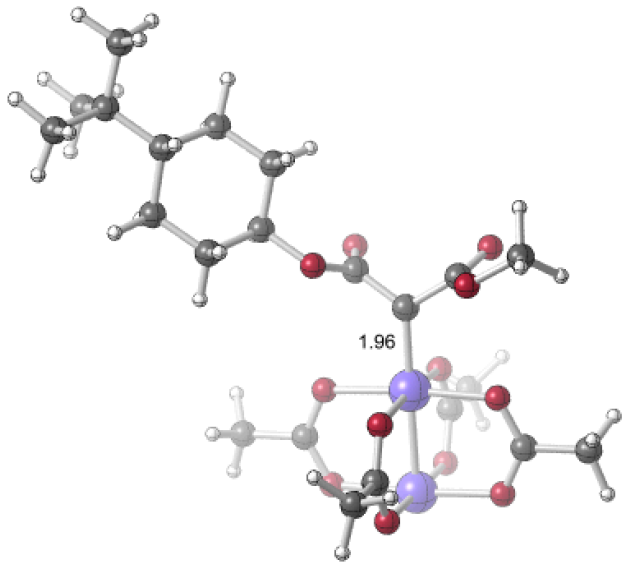
*BPW91/6-31G(d) for C, H, O and LANL2DZ for Rh*

Rh-carbenoid “reactant”



E(RB-PW91) = -1980.63310137 hartrees
Sum of electronic and thermal Free Energies = -1980.171982 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -6.450990 | -0.029291 | 0.323230 |
| 2 | 6 | -5.872612 | 0.813318 | -0.839775 |
| 3 | 6 | -4.442611 | 1.311138 | -0.544888 |
| 4 | 6 | -3.513897 | 0.135348 | -0.230870 |
| 5 | 6 | -4.048901 | -0.709549 | 0.922609 |
| 6 | 6 | -5.479901 | -1.199594 | 0.619291 |
| 7 | 1 | -4.048330 | 1.877717 | -1.404058 |
| 8 | 1 | -5.859042 | 0.210502 | -1.766922 |
| 9 | 1 | -6.508821 | 1.688803 | -1.046691 |
| 10 | 1 | -6.448968 | 0.623087 | 1.221945 |
| 11 | 1 | -3.368422 | -0.479849 | -1.134246 |
| 12 | 1 | -3.375154 | -1.563734 | 1.104668 |
| 13 | 1 | -4.048119 | -0.095852 | 1.841963 |
| 14 | 1 | -5.449722 | -1.883839 | -0.249237 |
| 15 | 1 | -5.832032 | -1.797005 | 1.475759 |
| 16 | 1 | -4.453520 | 1.992231 | 0.326016 |
| 17 | 6 | -7.949688 | -0.466450 | 0.124013 |
| 18 | 6 | -8.836621 | 0.786848 | -0.078915 |
| 19 | 1 | -8.629114 | 1.300340 | -1.031563 |
| 20 | 1 | -9.902807 | 0.502884 | -0.089735 |
| 21 | 1 | -8.695085 | 1.516229 | 0.738068 |
| 22 | 6 | -8.134625 | -1.406492 | -1.089710 |
| 23 | 1 | -7.567543 | -2.345204 | -0.975873 |
| 24 | 1 | -9.198098 | -1.679320 | -1.201426 |
| 25 | 1 | -7.818297 | -0.930534 | -2.032600 |
| 26 | 6 | -8.457357 | -1.188914 | 1.396006 |
| 27 | 1 | -8.310500 | -0.566775 | 2.296398 |
| 28 | 1 | -9.536972 | -1.400338 | 1.310630 |
| 29 | 1 | -7.951483 | -2.153353 | 1.564062 |
| 30 | 8 | -2.188997 | 0.632865 | 0.180263 |
| 31 | 6 | -1.316959 | 0.907925 | -0.810738 |
| 32 | 8 | -1.516054 | 0.792322 | -2.016196 |
| 33 | 6 | -0.006512 | 1.392257 | -0.311812 |
| 34 | 6 | 0.181592 | 2.861464 | -0.276668 |
| 35 | 8 | 0.324119 | 3.505074 | -1.311662 |
| 36 | 8 | 0.197289 | 3.369907 | 0.974707 |
| 37 | 6 | 0.429933 | 4.799176 | 1.040132 |
| 38 | 1 | 0.378386 | 5.048474 | 2.106643 |
| 39 | 1 | 1.421267 | 5.041248 | 0.630404 |
| 40 | 1 | -0.340729 | 5.344233 | 0.474996 |
| 41 | 45 | 1.519997 | 0.181099 | -0.076644 |
| 42 | 45 | 3.439887 | -1.317221 | 0.180562 |
| 43 | 8 | 4.623237 | 0.355594 | 0.493263 |
| 44 | 6 | 4.076554 | 1.509939 | 0.457961 |

| | | | | |
|---|---|---|---|---|
| 45 | 6 | 4.975158 | 2.714238 | 0.673535 |
| 46 | 8 | 2.831401 | 1.772857 | 0.256837 |
| 47 | 1 | 4.929470 | 3.371843 | -0.208734 |
| 48 | 1 | 4.617828 | 3.294765 | 1.538435 |
| 49 | 1 | 6.010448 | 2.392491 | 0.844169 |
| 50 | 8 | 3.064820 | -1.442431 | 2.202537 |
| 51 | 6 | 2.071929 | -0.780572 | 2.662641 |
| 52 | 8 | 1.259423 | -0.044760 | 1.989228 |
| 53 | 6 | 1.818840 | -0.841846 | 4.157151 |
| 54 | 1 | 2.096754 | 0.122706 | 4.612474 |
| 55 | 1 | 0.748634 | -1.004278 | 4.352506 |
| 56 | 1 | 2.416830 | -1.642041 | 4.612371 |
| 57 | 8 | 3.799218 | -1.177994 | -1.840459 |
| 58 | 6 | 3.006016 | -0.456837 | -2.537871 |
| 59 | 6 | 3.243780 | -0.387396 | -4.033038 |
| 60 | 8 | 2.001945 | 0.218407 | -2.101451 |
| 61 | 1 | 3.215063 | 0.659441 | -4.369605 |
| 62 | 1 | 4.208714 | -0.845532 | -4.286282 |
| 63 | 1 | 2.434803 | -0.924338 | -4.554167 |
| 64 | 8 | 0.340295 | -1.514508 | -0.386514 |
| 65 | 6 | 0.914431 | -2.667682 | -0.358076 |
| 66 | 8 | 2.153856 | -2.906111 | -0.158336 |
| 67 | 6 | 0.000578 | -3.861800 | -0.566159 |
| 68 | 1 | 0.593101 | -4.770077 | -0.736073 |
| 69 | 1 | -0.624934 | -4.001920 | 0.330652 |
| 70 | 1 | -0.671668 | -3.678669 | -1.417293 |

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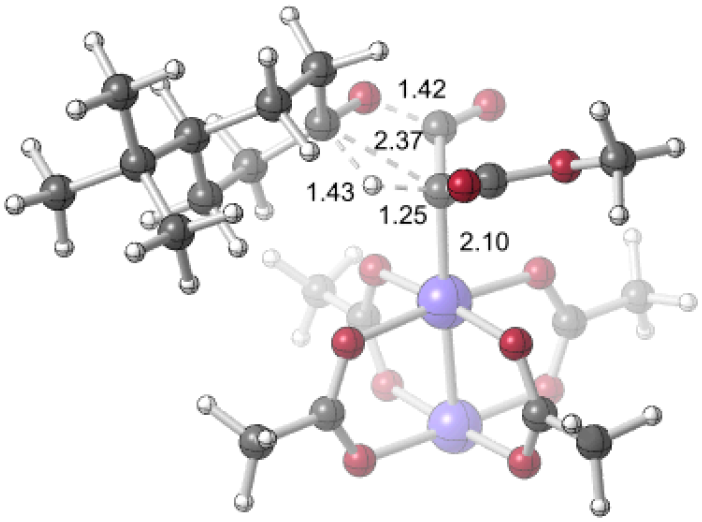
β-TS1$_{cat}$, Conformation 1




E(RB-PW91) = -1980.61555424 hartrees
Sum of electronic and thermal Free Energies = -1980.155034 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -4.909397 | -0.260865 | -0.428486 |
| 2 | 6 | -3.646309 | -1.102826 | -0.730161 |
| 3 | 6 | -2.761194 | -0.474114 | -1.824281 |
| 4 | 6 | -2.477057 | 0.984607 | -1.583781 |
| 5 | 6 | -3.616977 | 1.847326 | -1.102687 |
| 6 | 6 | -4.462443 | 1.161182 | -0.013200 |
| 7 | 1 | -1.809488 | -1.014513 | -1.947691 |
| 8 | 1 | -3.035616 | -1.210546 | 0.182628 |
| 9 | 1 | -3.916064 | -2.118912 | -1.058523 |
| 10 | 1 | -5.473860 | -0.165233 | -1.380963 |
| 11 | 1 | -1.542774 | 0.929028 | -0.505047 |
| 12 | 1 | -3.240725 | 2.824936 | -0.760899 |
| 13 | 1 | -4.238161 | 2.049786 | -2.000815 |
| 14 | 1 | -3.861633 | 1.119924 | 0.910805 |
| 15 | 1 | -5.330857 | 1.804733 | 0.197977 |
| 16 | 1 | -3.277815 | -0.517265 | -2.807257 |
| 17 | 6 | -5.908519 | -0.936516 | 0.583592 |
| 18 | 6 | -7.201657 | -0.089940 | 0.679990 |
| 19 | 1 | -7.660524 | 0.057091 | -0.313626 |
| 20 | 1 | -7.944397 | -0.598956 | 1.317461 |
| 21 | 1 | -7.022926 | 0.903191 | 1.122057 |
| 22 | 6 | -6.311561 | -2.338810 | 0.064609 |
| 23 | 1 | -5.475063 | -3.055408 | 0.095537 |
| 24 | 1 | -7.119494 | -2.758481 | 0.687655 |
| 25 | 1 | -6.682794 | -2.293344 | -0.974491 |
| 26 | 6 | -5.302199 | -1.083416 | 1.998442 |
| 27 | 1 | -5.057409 | -0.107170 | 2.447515 |
| 28 | 1 | -6.022149 | -1.582296 | 2.669607 |
| 29 | 1 | -4.382814 | -1.691529 | 1.992676 |
| 30 | 8 | -1.634508 | 1.570805 | -2.521978 |
| 31 | 6 | -0.515223 | 2.136516 | -1.847945 |
| 32 | 8 | 0.254742 | 2.878941 | -2.403523 |
| 33 | 6 | -0.494575 | 1.610166 | -0.446019 |
| 34 | 6 | -0.690011 | 2.570625 | 0.681308 |
| 35 | 8 | -1.569088 | 2.442314 | 1.531485 |
| 36 | 8 | 0.211690 | 3.580958 | 0.657220 |
| 37 | 6 | 0.109629 | 4.502934 | 1.765498 |
| 38 | 1 | 0.892485 | 5.250298 | 1.587740 |
| 39 | 1 | -0.882760 | 4.978118 | 1.788218 |
| 40 | 1 | 0.281223 | 3.977194 | 2.716033 |
| 41 | 45 | 0.972498 | 0.150459 | -0.069952 |
| 42 | 45 | 2.767269 | -1.458205 | 0.329977 |
| 43 | 8 | 2.990837 | -0.670465 | 2.228198 |
| 44 | 6 | 2.226108 | 0.294155 | 2.578389 |
| 45 | 6 | 2.428461 | 0.865955 | 3.970315 |
| 46 | 8 | 1.307724 | 0.849626 | 1.869794 |
| 47 | 1 | 2.935609 | 1.841817 | 3.892980 |

| | | | | |
|---|---|---|---|---|
| 48 | 1 | 1.455487 | 1.031743 | 4.455857 |
| 49 | 1 | 3.046731 | 0.189918 | 4.575232 |
| 50 | 8 | 1.343102 | -2.773899 | 1.048283 |
| 51 | 6 | 0.119481 | -2.408593 | 1.079987 |
| 52 | 8 | -0.355129 | -1.278153 | 0.682303 |
| 53 | 6 | -0.884379 | -3.395942 | 1.646781 |
| 54 | 1 | -1.384656 | -2.952739 | 2.522303 |
| 55 | 1 | -1.660062 | -3.615983 | 0.896979 |
| 56 | 1 | -0.380226 | -4.325415 | 1.940785 |
| 57 | 8 | 4.139887 | -0.100949 | -0.387491 |
| 58 | 6 | 3.689782 | 1.032331 | -0.781431 |
| 59 | 6 | 4.701016 | 2.048042 | -1.278027 |
| 60 | 8 | 2.463944 | 1.415114 | -0.781937 |
| 61 | 1 | 4.266669 | 2.649556 | -2.088527 |
| 62 | 1 | 4.962187 | 2.730172 | -0.451806 |
| 63 | 1 | 5.615075 | 1.541455 | -1.616026 |
| 64 | 8 | 0.757736 | -0.683228 | -1.974107 |
| 65 | 6 | 1.562057 | -1.630192 | -2.319230 |
| 66 | 8 | 2.469268 | -2.166044 | -1.596799 |
| 67 | 6 | 1.420472 | -2.134785 | -3.743768 |
| 68 | 1 | 0.358679 | -2.248785 | -4.006846 |
| 69 | 1 | 1.854632 | -1.392057 | -4.433222 |
| 70 | 1 | 1.949316 | -3.088967 | -3.866359 |

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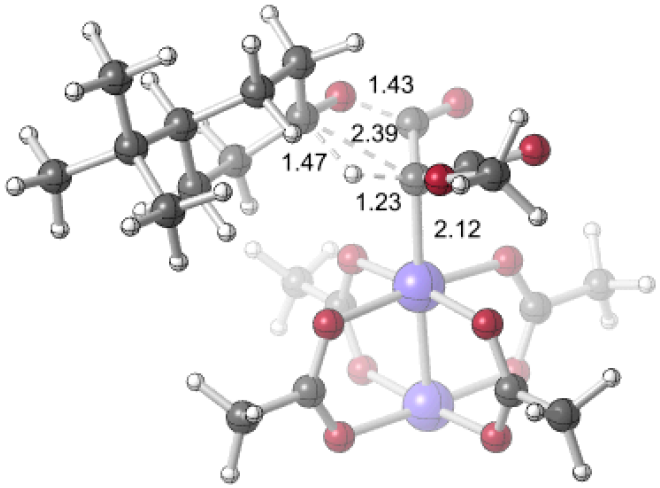
β-TS1$_{cat}$, Conformation 2




E(RB-PW91) = -1980.61438320 hartrees
Sum of electronic and thermal Free Energies = -1980.153514 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|

---

| | | | | |
|---|---|---|---|---|
| 1 | 6 | -4.863938 | -0.358616 | -0.517910 |
| 2 | 6 | -3.565381 | -1.177141 | -0.717076 |
| 3 | 6 | -2.660967 | -0.601158 | -1.823369 |
| 4 | 6 | -2.434893 | 0.879047 | -1.688309 |
| 5 | 6 | -3.611422 | 1.737437 | -1.297476 |
| 6 | 6 | -4.476923 | 1.104168 | -0.191222 |
| 7 | 1 | -1.687163 | -1.113421 | -1.870090 |
| 8 | 1 | -2.982921 | -1.200951 | 0.219697 |
| 9 | 1 | -3.793795 | -2.222376 | -0.978415 |
| 10 | 1 | -5.395919 | -0.346009 | -1.493332 |
| 11 | 1 | -1.511253 | 0.945630 | -0.547167 |
| 12 | 1 | -3.271103 | 2.749174 | -1.021311 |
| 13 | 1 | -4.210627 | 1.859298 | -2.224777 |
| 14 | 1 | -3.913904 | 1.143558 | 0.756982 |
| 15 | 1 | -5.372220 | 1.731625 | -0.058763 |
| 16 | 1 | -3.135648 | -0.739383 | -2.818997 |
| 17 | 6 | -5.877006 | -0.997776 | 0.503532 |
| 18 | 6 | -7.180895 | -0.162900 | 0.537380 |
| 19 | 1 | -7.610246 | -0.046803 | -0.473223 |
| 20 | 1 | -7.938156 | -0.662745 | 1.164789 |
| 21 | 1 | -7.026127 | 0.843400 | 0.958738 |
| 22 | 6 | -6.255107 | -2.425808 | 0.038196 |
| 23 | 1 | -5.408840 | -3.128480 | 0.100981 |
| 24 | 1 | -7.060365 | -2.832905 | 0.672866 |
| 25 | 1 | -6.621246 | -2.425797 | -1.003583 |
| 26 | 6 | -5.297780 | -1.076548 | 1.934958 |
| 27 | 1 | -5.057199 | -0.079684 | 2.339464 |
| 28 | 1 | -6.032279 | -1.538156 | 2.616789 |
| 29 | 1 | -4.381806 | -1.688182 | 1.976983 |
| 30 | 8 | -1.579737 | 1.426511 | -2.627673 |
| 31 | 6 | -0.485258 | 2.069235 | -1.963359 |
| 32 | 8 | 0.273301 | 2.788444 | -2.559285 |
| 33 | 6 | -0.486777 | 1.631787 | -0.533467 |
| 34 | 6 | -0.568665 | 2.702142 | 0.499076 |
| 35 | 8 | 0.111397 | 3.718503 | 0.500338 |
| 36 | 8 | -1.489084 | 2.393367 | 1.464489 |
| 37 | 6 | -1.546135 | 3.345622 | 2.550156 |
| 38 | 1 | -2.326207 | 2.970467 | 3.224479 |
| 39 | 1 | -0.576834 | 3.391394 | 3.066724 |
| 40 | 1 | -1.803971 | 4.348991 | 2.178263 |
| 41 | 45 | 1.008829 | 0.203774 | -0.078274 |
| 42 | 45 | 2.830484 | -1.353764 | 0.390014 |
| 43 | 8 | 3.034881 | -0.490600 | 2.255784 |
| 44 | 6 | 2.243960 | 0.465249 | 2.570892 |
| 45 | 6 | 2.416951 | 1.081597 | 3.947742 |
| 46 | 8 | 1.307163 | 0.965813 | 1.845578 |
| 47 | 1 | 2.596295 | 2.163502 | 3.848601 |
| 48 | 1 | 1.491986 | 0.950320 | 4.531400 |
| 49 | 1 | 3.256098 | 0.611224 | 4.476120 |

| | | | | |
|---|---|---|---|---|
| 50 | 8 | 1.426986 | -2.672305 | 1.144978 |
| 51 | 6 | 0.195183 | -2.334198 | 1.149870 |
| 52 | 8 | -0.300815 | -1.229143 | 0.709516 |
| 53 | 6 | -0.791795 | -3.325945 | 1.739572 |
| 54 | 1 | -1.292723 | -2.875296 | 2.611163 |
| 55 | 1 | -1.568991 | -3.569204 | 0.998731 |
| 56 | 1 | -0.273233 | -4.242943 | 2.047363 |
| 57 | 8 | 4.178439 | 0.007016 | -0.365389 |
| 58 | 6 | 3.708551 | 1.122084 | -0.789007 |
| 59 | 6 | 4.698691 | 2.148470 | -1.303301 |
| 60 | 8 | 2.474531 | 1.476964 | -0.808741 |
| 61 | 1 | 4.289456 | 2.655357 | -2.188677 |
| 62 | 1 | 4.860582 | 2.913406 | -0.525982 |
| 63 | 1 | 5.658539 | 1.669640 | -1.538360 |
| 64 | 8 | 0.835708 | -0.689898 | -1.958216 |
| 65 | 6 | 1.655447 | -1.637819 | -2.262053 |
| 66 | 8 | 2.558520 | -2.139968 | -1.510509 |
| 67 | 6 | 1.540245 | -2.188547 | -3.671750 |
| 68 | 1 | 1.989383 | -1.468893 | -4.375974 |
| 69 | 1 | 2.070757 | -3.146244 | -3.753099 |
| 70 | 1 | 0.483787 | -2.309938 | -3.952097 |

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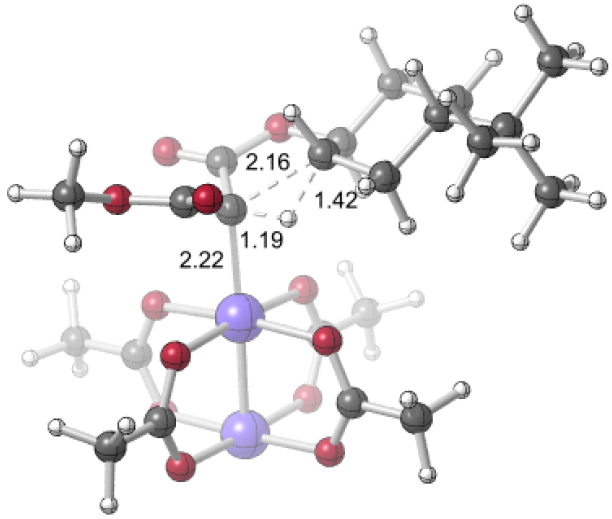
γ-TS1-eq-*half-chair*




E(UB-PW91) = -1980.60497764 hartrees
Sum of electronic and thermal Free Energies = -1980.140986 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 45 | 0.971876 | 0.133868 | 0.038297 |

| | | | | |
|---|---|---|---|---|
| 2 | 45 | 2.742110 | -1.522951 | -0.200883 |
| 3 | 6 | -0.587794 | 1.698782 | 0.285811 |
| 4 | 6 | -0.664408 | 2.161696 | 1.711467 |
| 5 | 6 | -0.579117 | 2.718179 | -0.817636 |
| 6 | 8 | -1.319888 | 2.668917 | -1.797143 |
| 7 | 6 | -2.659808 | 1.111512 | 0.368711 |
| 8 | 1 | -1.331872 | 0.841697 | -0.065058 |
| 9 | 1 | -2.950875 | 2.161033 | 0.244551 |
| 10 | 6 | 2.681214 | 0.449449 | -2.322327 |
| 11 | 6 | 1.077545 | -1.884775 | 2.160299 |
| 12 | 6 | 0.230613 | -2.248749 | -1.501800 |
| 13 | 6 | 3.525655 | 0.805732 | 1.309379 |
| 14 | 8 | 1.667163 | 0.979936 | -1.736868 |
| 15 | 8 | 0.405305 | -0.848234 | 1.795995 |
| 16 | 8 | 3.340987 | -0.577827 | -1.936727 |
| 17 | 8 | 2.071056 | -2.405221 | 1.548174 |
| 18 | 8 | -0.271231 | -1.144466 | -1.065951 |
| 19 | 8 | 2.343774 | 1.263247 | 1.107739 |
| 20 | 8 | 1.419378 | -2.674960 | -1.311309 |
| 21 | 8 | 3.994722 | -0.319682 | 0.909962 |
| 22 | 8 | 0.085952 | 2.983405 | 2.199397 |
| 23 | 8 | -1.675523 | 1.612760 | 2.490069 |
| 24 | 6 | -2.512139 | 0.671413 | 1.799493 |
| 25 | 1 | -2.021311 | -0.318092 | 1.836481 |
| 26 | 6 | -3.430450 | 0.165035 | -0.520492 |
| 27 | 1 | -3.450471 | 0.559637 | -1.545088 |
| 28 | 1 | -2.952135 | -0.826549 | -0.538736 |
| 29 | 6 | -3.911852 | 0.584611 | 2.421979 |
| 30 | 1 | -3.833266 | 0.223650 | 3.461026 |
| 31 | 1 | -4.352713 | 1.596585 | 2.459028 |
| 32 | 6 | -4.875958 | 0.062849 | 0.084169 |
| 33 | 1 | -5.301506 | 1.086824 | 0.063274 |
| 34 | 6 | -4.786975 | -0.363484 | 1.573356 |
| 35 | 1 | -5.793440 | -0.402954 | 2.018219 |
| 36 | 1 | -4.373148 | -1.386047 | 1.641289 |
| 37 | 6 | -5.846073 | -0.818107 | -0.790968 |
| 38 | 6 | -7.282408 | -0.706852 | -0.220992 |
| 39 | 1 | -7.991582 | -1.238906 | -0.877147 |
| 40 | 1 | -7.374015 | -1.151578 | 0.782801 |
| 41 | 1 | -7.610771 | 0.345314 | -0.160209 |
| 42 | 6 | -5.877130 | -0.283005 | -2.242969 |
| 43 | 1 | -6.100402 | 0.797747 | -2.270472 |
| 44 | 1 | -4.925573 | -0.446972 | -2.773336 |
| 45 | 1 | -6.662410 | -0.799139 | -2.820384 |
| 46 | 6 | -5.430990 | -2.306829 | -0.813676 |
| 47 | 1 | -5.461847 | -2.762572 | 0.189595 |
| 48 | 1 | -6.122419 | -2.881045 | -1.453293 |
| 49 | 1 | -4.416800 | -2.448224 | -1.222190 |
| 50 | 8 | 0.353725 | 3.671200 | -0.608120 |
| 51 | 6 | 0.466547 | 4.642491 | -1.671402 |

| | | | | |
|---|---|---|---|---|
| 52 | 1 | -0.488804 | 5.167474 | -1.822475 |
| 53 | 1 | 1.243885 | 5.340190 | -1.337067 |
| 54 | 1 | 0.761345 | 4.149595 | -2.609205 |
| 55 | 6 | 4.469904 | 1.711403 | 2.077187 |
| 56 | 1 | 5.052624 | 2.313651 | 1.360157 |
| 57 | 1 | 3.902171 | 2.394312 | 2.723076 |
| 58 | 1 | 5.174308 | 1.110014 | 2.668830 |
| 59 | 6 | 3.147937 | 1.132313 | -3.595650 |
| 60 | 1 | 2.285238 | 1.359672 | -4.239430 |
| 61 | 1 | 3.635323 | 2.087405 | -3.339703 |
| 62 | 1 | 3.864855 | 0.496416 | -4.131203 |
| 63 | 6 | -0.699840 | -3.134031 | -2.312947 |
| 64 | 1 | -1.462635 | -3.574535 | -1.649825 |
| 65 | 1 | -1.222301 | -2.534988 | -3.073918 |
| 66 | 1 | -0.134634 | -3.943538 | -2.792618 |
| 67 | 6 | 0.623554 | -2.556450 | 3.444227 |
| 68 | 1 | 0.488981 | -1.802159 | 4.234006 |
| 69 | 1 | -0.350471 | -3.046604 | 3.281300 |
| 70 | 1 | 1.355830 | -3.310276 | 3.761048 |

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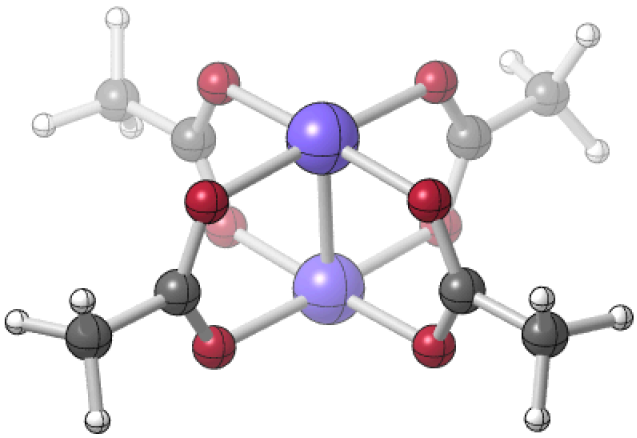
$Rh_2(OAc)_4$



E(RB-PW91) = -1133.14988965 hartrees
Sum of electronic and thermal Free Energies = -1132.999017 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 45 | 0.003601 | -0.003788 | -1.192847 |
| 2 | 45 | 0.003102 | -0.003205 | 1.193515 |
| 3 | 8 | 1.460782 | -1.468022 | 1.147780 |
| 4 | 6 | 1.873628 | -1.876024 | 0.001350 |
| 5 | 8 | 1.459772 | -1.470092 | -1.145526 |

| | | | | |
|---|---|---|---|---|
| 6 | 6 | 2.976266 | -2.915437 | -0.000052 |
| 7 | 1 | 2.869010 | -3.583071 | -0.866288 |
| 8 | 1 | 3.951298 | -2.406432 | -0.080985 |
| 9 | 1 | 2.962012 | -3.491061 | 0.935211 |
| 10 | 8 | -1.453209 | 1.463471 | -1.146374 |
| 11 | 6 | -1.867235 | 1.870127 | 0.000149 |
| 12 | 8 | -1.455050 | 1.462393 | 1.146900 |
| 13 | 6 | -2.969168 | 2.910529 | -0.002139 |
| 14 | 1 | -2.857809 | 3.581129 | -0.865608 |
| 15 | 1 | -3.944399 | 2.402957 | -0.089437 |
| 16 | 1 | -2.958595 | 3.482813 | 0.935210 |
| 17 | 8 | 1.468122 | 1.454907 | 1.147310 |
| 18 | 6 | 1.875732 | 1.867630 | 0.000706 |
| 19 | 8 | 1.470165 | 1.452929 | -1.145983 |
| 20 | 6 | 2.914702 | 2.970787 | -0.001307 |
| 21 | 1 | 2.405668 | 3.945084 | -0.090387 |
| 22 | 1 | 3.485751 | 2.961961 | 0.936804 |
| 23 | 1 | 3.586596 | 2.859406 | -0.863777 |
| 24 | 8 | -1.460045 | -1.463177 | 1.147461 |
| 25 | 6 | -1.873117 | -1.870559 | 0.000907 |
| 26 | 8 | -1.460664 | -1.462834 | -1.145824 |
| 27 | 6 | -2.974724 | -2.911233 | -0.001109 |
| 28 | 1 | -3.949611 | -2.404625 | -0.097360 |
| 29 | 1 | -2.858082 | -3.586924 | -0.859926 |
| 30 | 1 | -2.968962 | -3.478050 | 0.939539 |

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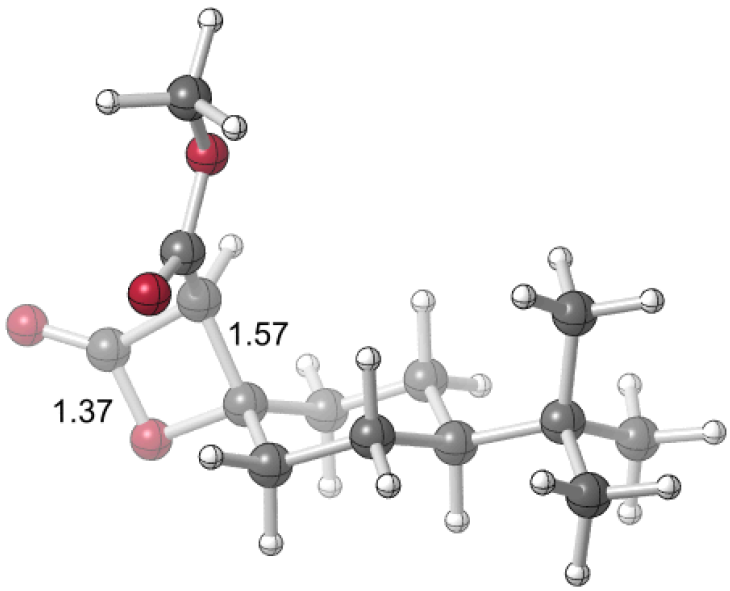
β-lactone

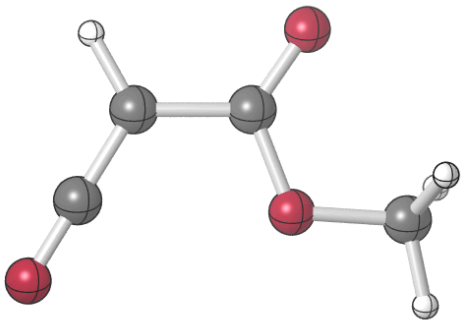



E(RB-PW91) = -847.536258721 hartrees

Sum of electronic and thermal Free Energies = -847.245894 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 2.072471 | -0.554121 | 0.159087 |
| 2 | 6 | 1.327889 | -0.898311 | -1.153336 |
| 3 | 6 | 0.142213 | -1.852292 | -0.904919 |
| 4 | 6 | -0.844608 | -1.267289 | 0.102170 |
| 5 | 6 | -0.150878 | -0.895045 | 1.407039 |
| 6 | 6 | 1.055613 | 0.036146 | 1.164462 |
| 7 | 1 | -0.376481 | -2.090792 | -1.849947 |
| 8 | 1 | 0.955521 | 0.030297 | -1.626107 |
| 9 | 1 | 2.005486 | -1.369063 | -1.883569 |
| 10 | 1 | 2.425493 | -1.516230 | 0.587330 |
| 11 | 1 | -1.799726 | -0.177779 | -1.606435 |
| 12 | 1 | -0.867160 | -0.427301 | 2.097729 |
| 13 | 1 | 0.191676 | -1.838916 | 1.869678 |
| 14 | 1 | 0.687566 | 1.011592 | 0.797260 |
| 15 | 1 | 1.534088 | 0.235048 | 2.136362 |
| 16 | 1 | 0.512862 | -2.809552 | -0.494887 |
| 17 | 6 | 3.367851 | 0.318153 | -0.038964 |
| 18 | 6 | 3.057143 | 1.706362 | -0.645000 |
| 19 | 1 | 2.387360 | 2.298475 | 0.000279 |
| 20 | 1 | 3.988692 | 2.285265 | -0.766472 |
| 21 | 1 | 2.589311 | 1.628406 | -1.640439 |
| 22 | 6 | 4.073093 | 0.518245 | 1.324870 |
| 23 | 1 | 4.269693 | -0.448379 | 1.820818 |
| 24 | 1 | 5.043766 | 1.023063 | 1.183841 |
| 25 | 1 | 3.481311 | 1.139900 | 2.015827 |
| 26 | 6 | 4.357944 | -0.422156 | -0.970830 |
| 27 | 1 | 3.978486 | -0.511484 | -2.001359 |
| 28 | 1 | 5.315086 | 0.123940 | -1.024450 |
| 29 | 1 | 4.575319 | -1.438887 | -0.599334 |
| 30 | 8 | -1.949053 | -2.259225 | 0.363573 |
| 31 | 6 | -2.898460 | -1.409170 | -0.144842 |
| 32 | 8 | -4.087282 | -1.582957 | -0.236728 |
| 33 | 6 | -1.898511 | -0.286797 | -0.516551 |
| 34 | 6 | -2.186751 | 1.061597 | 0.112363 |
| 35 | 8 | -2.316152 | 1.285255 | 1.307328 |
| 36 | 8 | -2.322298 | 2.009178 | -0.857694 |
| 37 | 6 | -2.676669 | 3.325317 | -0.369027 |
| 38 | 1 | -3.627482 | 3.286467 | 0.182382 |
| 39 | 1 | -1.891269 | 3.714007 | 0.296006 |
| 40 | 1 | -2.771355 | 3.950080 | -1.265468 |

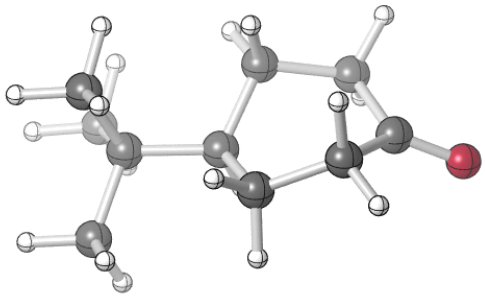
fragmented product, ketene



E(RB-PW91) = -380.450068394 hartrees
Sum of electronic and thermal Free Energies = -380.407439 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -0.918553 | 0.968122 | 0.000055 |
| 2 | 6 | -1.868335 | 0.031335 | -0.000079 |
| 3 | 8 | -2.704227 | -0.794822 | -0.000189 |
| 4 | 1 | -1.205891 | 2.018860 | 0.000140 |
| 5 | 6 | 0.513726 | 0.620561 | 0.000095 |
| 6 | 8 | 0.685802 | -0.740163 | -0.000014 |
| 7 | 8 | 1.427053 | 1.432582 | 0.000183 |
| 8 | 6 | 2.063595 | -1.172841 | -0.000043 |
| 9 | 1 | 2.587045 | -0.806172 | -0.895770 |
| 10 | 1 | 2.586694 | -0.807358 | 0.896381 |
| 11 | 1 | 2.020529 | -2.269169 | -0.000756 |

fragmented product, ketone

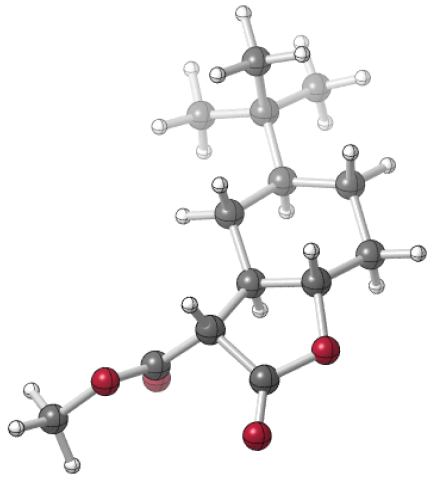


E(RB-PW91) = -467.051994855 hartrees
Sum of electronic and thermal Free Energies = -466.832109 hartrees

| Center | Atomic | Coordinates (Angstroms) |
|---|---|---|

| Number | Number | X | Y | Z |
|---|---|---|---|---|
| 1 | 8 | 3.634767 | -0.070616 | -0.689030 |
| 2 | 6 | 2.562678 | 0.013040 | -0.100148 |
| 3 | 6 | 1.823457 | 1.346912 | 0.070203 |
| 4 | 6 | 1.858909 | -1.175595 | 0.542158 |
| 5 | 1 | 1.888991 | -0.998827 | 1.635193 |
| 6 | 1 | 1.851288 | 1.865938 | -0.904103 |
| 7 | 1 | 2.417113 | 1.973327 | 0.762111 |
| 8 | 1 | 2.434718 | -2.091771 | 0.344051 |
| 9 | 6 | 0.375602 | 1.173628 | 0.568130 |
| 10 | 1 | -0.161780 | 2.130353 | 0.466922 |
| 11 | 1 | 0.373571 | 0.930348 | 1.646114 |
| 12 | 6 | 0.374858 | -1.314901 | 0.094607 |
| 13 | 1 | -0.172333 | -1.841801 | 0.894835 |
| 14 | 1 | 0.331179 | -1.968709 | -0.791080 |
| 15 | 6 | -0.316706 | 0.043904 | -0.230716 |
| 16 | 1 | -0.114790 | 0.258896 | -1.300589 |
| 17 | 6 | -1.881750 | 0.002444 | -0.104636 |
| 18 | 6 | -2.486624 | 1.288394 | -0.718213 |
| 19 | 1 | -3.588721 | 1.238470 | -0.705698 |
| 20 | 1 | -2.196413 | 2.195148 | -0.163126 |
| 21 | 1 | -2.170314 | 1.418016 | -1.767769 |
| 22 | 6 | -2.433500 | -1.202171 | -0.904571 |
| 23 | 1 | -2.103199 | -1.167131 | -1.957638 |
| 24 | 1 | -2.111261 | -2.166966 | -0.480916 |
| 25 | 1 | -3.536857 | -1.193730 | -0.901867 |
| 26 | 6 | -2.343273 | -0.109403 | 1.366152 |
| 27 | 1 | -1.950872 | -1.015209 | 1.858136 |
| 28 | 1 | -2.026265 | 0.763002 | 1.961042 |
| 29 | 1 | -3.444103 | -0.161929 | 1.418838 |

γ-lactone-eq-*trans*



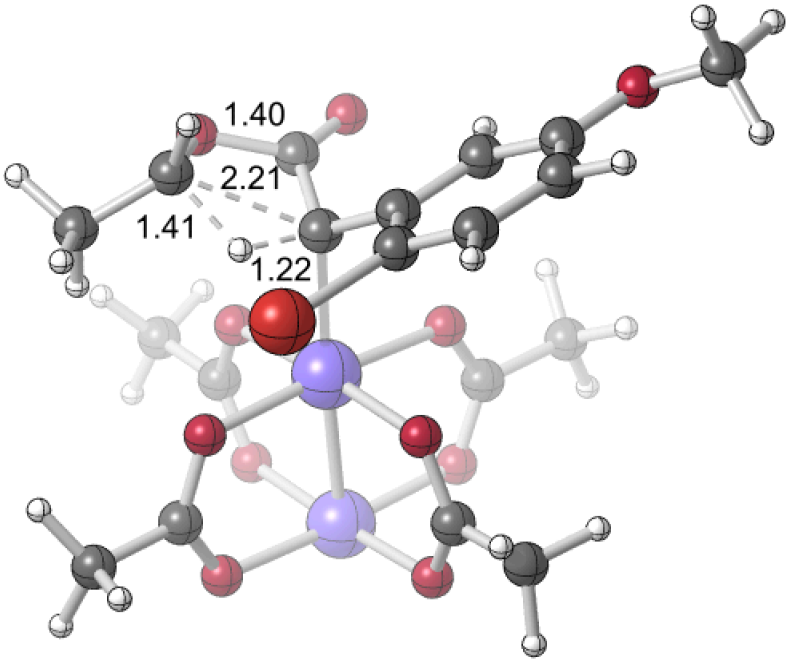
E(UB-PW91) = -847.550962084 hartrees
Sum of electronic and thermal Free Energies = -847.258984 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 1.794371 | 0.156758 | 0.459701 |
| 2 | 6 | 2.426523 | 1.550396 | 0.151056 |
| 3 | 6 | 2.581921 | -0.962606 | -0.205139 |
| 4 | 8 | 2.404700 | -1.357128 | -1.348122 |
| 5 | 6 | 0.372084 | 0.356997 | -0.073856 |
| 6 | 1 | 1.820256 | 0.021676 | 1.556361 |
| 7 | 1 | 0.445524 | 0.277070 | -1.175383 |
| 8 | 8 | 3.599249 | 1.834871 | 0.055963 |
| 9 | 8 | 1.417755 | 2.472183 | -0.017200 |
| 10 | 6 | 0.141229 | 1.827500 | 0.269151 |
| 11 | 1 | -0.034509 | 1.938985 | 1.358516 |
| 12 | 6 | -0.808292 | -0.499102 | 0.391141 |
| 13 | 1 | -0.622700 | -1.554791 | 0.138949 |
| 14 | 1 | -0.907549 | -0.439054 | 1.491151 |
| 15 | 6 | -1.050521 | 2.385582 | -0.486926 |
| 16 | 1 | -1.221834 | 3.447808 | -0.244457 |
| 17 | 1 | -0.865524 | 2.318319 | -1.573550 |
| 18 | 6 | -2.105190 | 0.008310 | -0.306671 |
| 19 | 1 | -1.941390 | -0.134984 | -1.395027 |
| 20 | 6 | -2.285724 | 1.537599 | -0.085120 |
| 21 | 1 | -3.154914 | 1.902331 | -0.654055 |
| 22 | 1 | -2.507892 | 1.732224 | 0.980551 |
| 23 | 6 | -3.387753 | -0.838804 | 0.035036 |
| 24 | 6 | -4.585138 | -0.339958 | -0.811132 |
| 25 | 1 | -5.451477 | -1.009956 | -0.678577 |
| 26 | 1 | -4.912012 | 0.671853 | -0.522646 |
| 27 | 1 | -4.338603 | -0.324643 | -1.887190 |
| 28 | 6 | -3.144040 | -2.322600 | -0.335315 |
| 29 | 1 | -2.818059 | -2.427799 | -1.384757 |
| 30 | 1 | -2.382908 | -2.796142 | 0.305184 |
| 31 | 1 | -4.074661 | -2.902729 | -0.215558 |
| 32 | 6 | -3.770730 | -0.758562 | 1.531300 |
| 33 | 1 | -4.006601 | 0.271717 | 1.845081 |
| 34 | 1 | -4.667068 | -1.371561 | 1.726460 |
| 35 | 1 | -2.968187 | -1.138517 | 2.184878 |
| 36 | 8 | 3.518056 | -1.458028 | 0.643605 |
| 37 | 6 | 4.374716 | -2.475776 | 0.072602 |
| 38 | 1 | 4.925325 | -2.072015 | -0.789455 |
| 39 | 1 | 5.065345 | -2.756511 | 0.877032 |
| 40 | 1 | 3.780626 | -3.342878 | -0.252435 |

*Davies Systems*

*B3LYP/6-31G(d) for C, H, O, Br and LANL2DZ for Rh*

Figure 5, Entries 3-5, *trans*-β-$TS1_{cat}$




E(RB3LYP) = -4355.87845714 hartrees
Sum of electronic and thermal Free Energies = -4355.545222 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -1.232577 | 0.531693 | 1.211178 |
| 2 | 6 | -1.118175 | 0.245434 | 2.666951 |
| 3 | 8 | -0.813698 | 1.467588 | 3.284085 |
| 4 | 6 | -1.142942 | 2.424313 | 2.350343 |
| 5 | 1 | -0.932206 | 1.713179 | 1.153619 |
| 6 | 8 | -1.224520 | -0.781993 | 3.272589 |
| 7 | 45 | 0.649057 | -0.048198 | 0.192289 |
| 8 | 45 | 2.695558 | -0.842396 | -0.868326 |
| 9 | 8 | 3.097069 | 1.134301 | -1.361587 |
| 10 | 8 | 1.625286 | -1.057306 | -2.626654 |
| 11 | 8 | 2.173803 | -2.764988 | -0.315014 |
| 12 | 8 | 3.641890 | -0.582412 | 0.959713 |
| 13 | 8 | -0.287172 | -0.330720 | -1.639235 |
| 14 | 8 | 1.210600 | 1.884476 | -0.346411 |
| 15 | 8 | 0.259054 | -2.029592 | 0.659906 |
| 16 | 8 | 1.746454 | 0.188194 | 1.943332 |
| 17 | 6 | 1.088696 | -2.936416 | 0.319667 |
| 18 | 6 | 2.979779 | -0.144741 | 1.947060 |
| 19 | 6 | 2.290008 | 2.043977 | -1.011714 |

| | | | | |
|---|---|---|---|---|
| 20 | 6 | 0.389767 | -0.768856 | -2.627043 |
| 21 | 6 | 3.700042 | -0.024800 | 3.273464 |
| 22 | 1 | 3.375356 | 0.875686 | 3.800978 |
| 23 | 1 | 3.437605 | -0.887522 | 3.896824 |
| 24 | 1 | 4.780828 | -0.014050 | 3.121996 |
| 25 | 6 | 2.611485 | 3.458686 | -1.447827 |
| 26 | 1 | 3.682255 | 3.564757 | -1.631628 |
| 27 | 1 | 2.075557 | 3.671265 | -2.380470 |
| 28 | 1 | 2.278242 | 4.178406 | -0.696126 |
| 29 | 6 | -0.373772 | -0.984509 | -3.917193 |
| 30 | 1 | 0.316213 | -1.101335 | -4.754573 |
| 31 | 1 | -0.979862 | -1.893132 | -3.824648 |
| 32 | 1 | -1.054376 | -0.147492 | -4.093822 |
| 33 | 6 | 0.720964 | -4.351512 | 0.712794 |
| 34 | 1 | 1.532649 | -5.039764 | 0.472346 |
| 35 | 1 | 0.496872 | -4.387637 | 1.783110 |
| 36 | 1 | -0.186503 | -4.651403 | 0.177614 |
| 37 | 6 | -2.485918 | 0.200123 | 0.518546 |
| 38 | 6 | -3.171088 | -0.969361 | 0.888496 |
| 39 | 6 | -3.022974 | 0.964570 | -0.541421 |
| 40 | 6 | -4.324326 | -1.383849 | 0.213969 |
| 41 | 1 | -2.786617 | -1.586070 | 1.691679 |
| 42 | 6 | -4.186349 | 0.572817 | -1.187970 |
| 43 | 6 | -4.842189 | -0.606394 | -0.828494 |
| 44 | 1 | -4.586769 | 1.189744 | -1.985004 |
| 45 | 1 | -5.739574 | -0.896631 | -1.361582 |
| 46 | 35 | -2.215042 | 2.610404 | -1.090868 |
| 47 | 1 | -2.206000 | 2.666505 | 2.300372 |
| 48 | 8 | -4.874085 | -2.547829 | 0.658197 |
| 49 | 6 | -6.064558 | -3.009197 | 0.039329 |
| 50 | 1 | -5.911002 | -3.214940 | -1.028357 |
| 51 | 1 | -6.326588 | -3.936820 | 0.550848 |
| 52 | 1 | -6.884600 | -2.287764 | 0.154153 |
| 53 | 6 | -0.157387 | 3.538790 | 2.211693 |
| 54 | 1 | -0.453248 | 4.222184 | 1.412809 |
| 55 | 1 | -0.139162 | 4.089952 | 3.163890 |
| 56 | 1 | 0.841367 | 3.143108 | 2.015695 |

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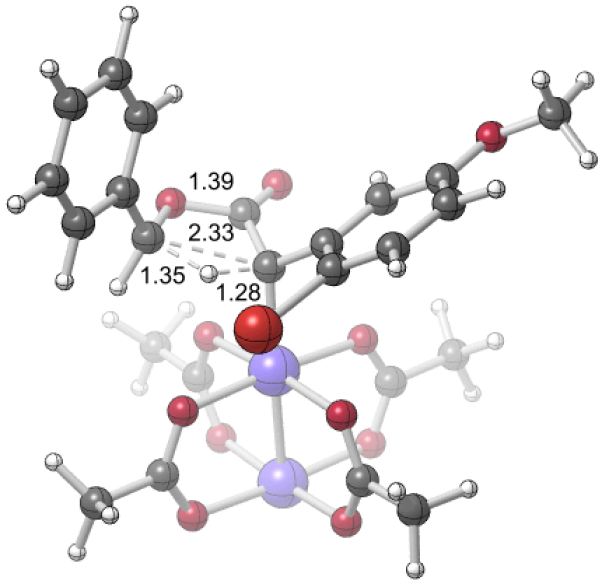
Figure 5, Entries 1 and 2, *cis*-β-$TS1_{cat}$




E(UB3LYP) = -4547.61331514 hartrees
Sum of electronic and thermal Free Energies = -4547.233464 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 1.049473 | 0.113761 | 0.750668 |
| 2 | 6 | 1.195017 | -0.148101 | 2.217560 |
| 3 | 8 | 1.589341 | -1.471464 | 2.400110 |
| 4 | 6 | 1.881778 | -2.023990 | 1.161422 |
| 5 | 1 | 1.461247 | -1.031414 | 0.344016 |
| 6 | 8 | 1.003387 | 0.588021 | 3.143394 |
| 7 | 45 | -1.005190 | -0.082019 | 0.177573 |
| 8 | 45 | -3.396785 | -0.222260 | -0.327943 |
| 9 | 8 | -2.992141 | -2.035171 | -1.264088 |
| 10 | 8 | -3.008613 | 0.772391 | -2.102500 |
| 11 | 8 | -3.647218 | 1.589972 | 0.635525 |
| 12 | 8 | -3.636363 | -1.205471 | 1.485119 |
| 13 | 8 | -0.799443 | 0.963466 | -1.606185 |
| 14 | 8 | -0.774247 | -1.910041 | -0.792564 |
| 15 | 8 | -1.431508 | 1.712060 | 1.122949 |
| 16 | 8 | -1.408808 | -1.148214 | 1.918103 |
| 17 | 6 | -2.630482 | 2.149154 | 1.145884 |
| 18 | 6 | -2.618870 | -1.450405 | 2.196641 |
| 19 | 6 | -1.806412 | -2.471424 | -1.300277 |
| 20 | 6 | -1.822976 | 1.152729 | -2.342851 |
| 21 | 6 | -2.839634 | -2.151560 | 3.520458 |
| 22 | 1 | -2.085703 | -2.930525 | 3.663344 |
| 23 | 1 | -2.719986 | -1.424766 | 4.331922 |
| 24 | 1 | -3.843372 | -2.577421 | 3.564464 |

| | | | | |
|---|---|---|---|---|
| 25 | 6 | -1.562248 | -3.774765 | -2.033976 |
| 26 | 1 | -0.911706 | -4.425859 | -1.442688 |
| 27 | 1 | -2.507671 | -4.276964 | -2.244512 |
| 28 | 1 | -1.049833 | -3.562376 | -2.979309 |
| 29 | 6 | -1.586130 | 1.933542 | -3.619403 |
| 30 | 1 | -1.514886 | 3.000147 | -3.376321 |
| 31 | 1 | -0.638954 | 1.630078 | -4.072641 |
| 32 | 1 | -2.412453 | 1.785292 | -4.316900 |
| 33 | 6 | -2.837716 | 3.469661 | 1.857491 |
| 34 | 1 | -2.238081 | 4.244945 | 1.369422 |
| 35 | 1 | -3.891741 | 3.750915 | 1.842738 |
| 36 | 1 | -2.485751 | 3.385887 | 2.890581 |
| 37 | 6 | 1.854345 | 1.193677 | 0.160290 |
| 38 | 6 | 2.086122 | 2.355187 | 0.919678 |
| 39 | 6 | 2.356470 | 1.169048 | -1.162127 |
| 40 | 6 | 2.750020 | 3.462050 | 0.382144 |
| 41 | 1 | 1.710537 | 2.417644 | 1.933316 |
| 42 | 6 | 3.047426 | 2.253574 | -1.682664 |
| 43 | 6 | 3.241380 | 3.412676 | -0.926909 |
| 44 | 1 | 3.439805 | 2.199329 | -2.692227 |
| 45 | 1 | 3.769790 | 4.249762 | -1.367567 |
| 46 | 35 | 2.181955 | -0.378893 | -2.269406 |
| 47 | 1 | 1.116418 | -2.717106 | 0.804403 |
| 48 | 8 | 2.877814 | 4.528960 | 1.220190 |
| 49 | 6 | 3.562779 | 5.677813 | 0.748426 |
| 50 | 1 | 3.059728 | 6.119547 | -0.122090 |
| 51 | 1 | 3.549124 | 6.392803 | 1.572860 |
| 52 | 1 | 4.604229 | 5.448334 | 0.485531 |
| 53 | 6 | 3.276777 | -2.362415 | 0.893400 |
| 54 | 6 | 4.324595 | -1.812378 | 1.655531 |
| 55 | 6 | 3.573188 | -3.262373 | -0.148350 |
| 56 | 6 | 5.642233 | -2.160961 | 1.376440 |
| 57 | 1 | 4.094336 | -1.134478 | 2.470452 |
| 58 | 6 | 4.892435 | -3.605726 | -0.421704 |
| 59 | 1 | 2.763117 | -3.683396 | -0.737701 |
| 60 | 6 | 5.928896 | -3.054495 | 0.339113 |
| 61 | 1 | 6.448437 | -1.740822 | 1.970640 |
| 62 | 1 | 5.115959 | -4.302683 | -1.223992 |
| 63 | 1 | 6.959444 | -3.324821 | 0.126399 |

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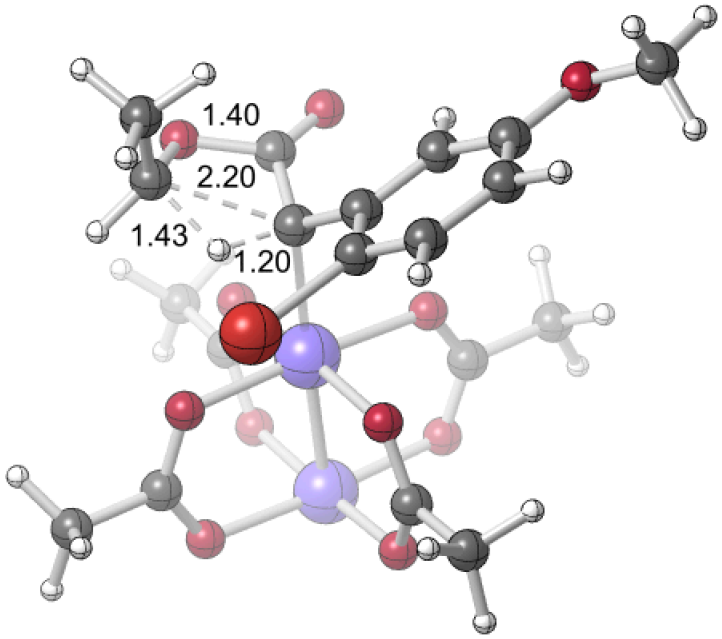
Figure 5, Entries 3-5, *cis*-β-TS1$_{cat}$




E(RB3LYP) = -4355.87586581 hartrees
Sum of electronic and thermal Free Energies = -4355.542611 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 1.264024 | -0.387947 | 1.205183 |
| 2 | 6 | 1.146114 | 0.015508 | 2.629735 |
| 3 | 8 | 0.839051 | -1.155105 | 3.339735 |
| 4 | 6 | 1.203369 | -2.172365 | 2.482286 |
| 5 | 1 | 0.973757 | -1.556925 | 1.211727 |
| 6 | 8 | 1.251742 | 1.087932 | 3.151056 |
| 7 | 45 | -0.693832 | 0.044363 | 0.214351 |
| 8 | 45 | -2.817041 | 0.607951 | -0.832374 |
| 9 | 8 | -3.160514 | -1.434082 | -1.013596 |
| 10 | 8 | -1.846665 | 0.597945 | -2.658730 |
| 11 | 8 | -2.344967 | 2.603963 | -0.580255 |
| 12 | 8 | -3.671963 | 0.590530 | 1.055874 |
| 13 | 8 | 0.140366 | 0.084147 | -1.686898 |
| 14 | 8 | -1.207268 | -1.962710 | 0.015070 |
| 15 | 8 | -0.348372 | 2.080729 | 0.368921 |
| 16 | 8 | -1.694348 | 0.058079 | 2.034715 |
| 17 | 6 | -1.232365 | 2.900849 | -0.046217 |
| 18 | 6 | -2.939102 | 0.339777 | 2.059470 |
| 19 | 6 | -2.312441 | -2.255354 | -0.558043 |
| 20 | 6 | -0.603938 | 0.344502 | -2.688734 |
| 21 | 6 | -3.582457 | 0.395751 | 3.428774 |
| 22 | 1 | -3.239434 | 1.299403 | 3.945256 |

| | | | | |
|---|---|---|---|---|
| 23 | 1 | -4.669748 | 0.422426 | 3.340650 |
| 24 | 1 | -3.267141 | -0.463735 | 4.026754 |
| 25 | 6 | -2.611931 | -3.731671 | -0.717950 |
| 26 | 1 | -2.426215 | -4.256554 | 0.223759 |
| 27 | 1 | -3.645311 | -3.880040 | -1.034767 |
| 28 | 1 | -1.938814 | -4.155086 | -1.472067 |
| 29 | 6 | 0.079624 | 0.354492 | -4.040264 |
| 30 | 1 | 0.828431 | 1.153510 | -4.061214 |
| 31 | 1 | 0.606418 | -0.592970 | -4.190512 |
| 32 | 1 | -0.647846 | 0.511579 | -4.837982 |
| 33 | 6 | -0.903021 | 4.369692 | 0.115828 |
| 34 | 1 | -1.743415 | 4.988744 | -0.201652 |
| 35 | 1 | -0.655117 | 4.575824 | 1.161553 |
| 36 | 1 | -0.018987 | 4.610867 | -0.484050 |
| 37 | 6 | 2.478433 | -0.072536 | 0.445276 |
| 38 | 6 | 3.170398 | 1.115915 | 0.736826 |
| 39 | 6 | 2.971743 | -0.872947 | -0.611667 |
| 40 | 6 | 4.283079 | 1.516619 | -0.010495 |
| 41 | 1 | 2.817278 | 1.761181 | 1.532079 |
| 42 | 6 | 4.096499 | -0.493424 | -1.329467 |
| 43 | 6 | 4.755896 | 0.705121 | -1.048158 |
| 44 | 1 | 4.463578 | -1.135135 | -2.122942 |
| 45 | 1 | 5.620444 | 0.983724 | -1.638607 |
| 46 | 35 | 2.158884 | -2.544989 | -1.067568 |
| 47 | 8 | 4.840916 | 2.701993 | 0.360233 |
| 48 | 6 | 5.980709 | 3.160621 | -0.349875 |
| 49 | 1 | 5.755813 | 3.322177 | -1.412441 |
| 50 | 1 | 6.255105 | 4.111864 | 0.109009 |
| 51 | 1 | 6.821196 | 2.459373 | -0.260707 |
| 52 | 1 | 0.390372 | -2.877949 | 2.293939 |
| 53 | 6 | 2.585333 | -2.726265 | 2.620243 |
| 54 | 1 | 2.806854 | -3.421917 | 1.807595 |
| 55 | 1 | 3.338848 | -1.933699 | 2.641224 |
| 56 | 1 | 2.638654 | -3.271560 | 3.573806 |

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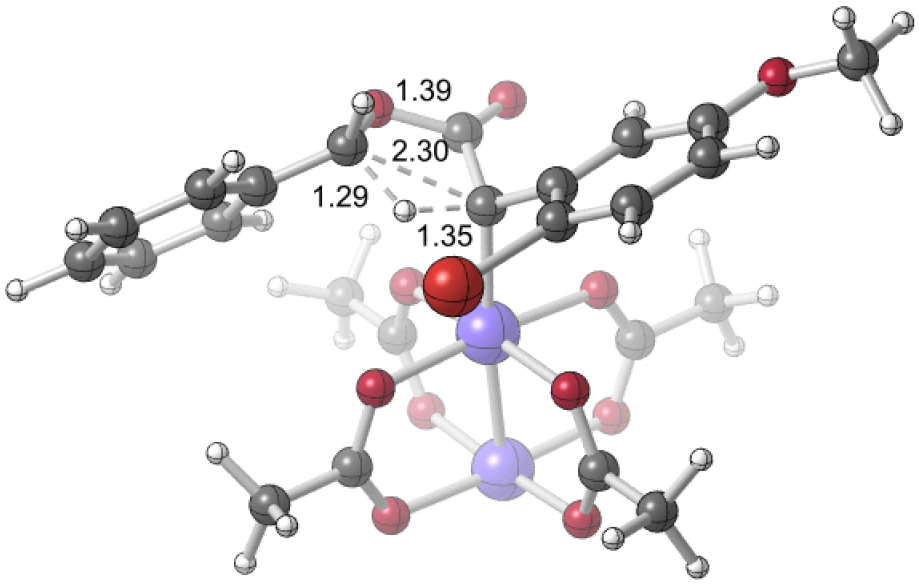
Figure 5, Entries 1 and 2, *trans*-β-$TS1_{cat}$ , low energy conformation



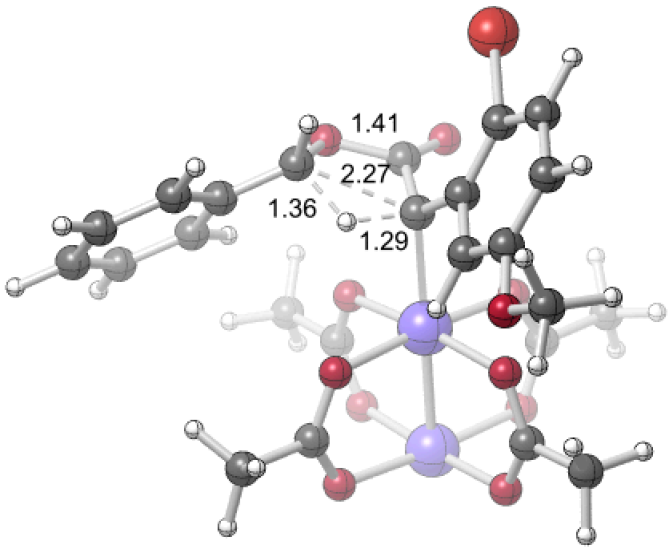

E(UB3LYP) = -4547.61635107 hartrees
Sum of electronic and thermal Free Energies = -4547.233615 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -0.871917 | 0.957603 | 0.936132 |
| 2 | 6 | -0.653139 | 1.124674 | 2.408579 |
| 3 | 8 | 0.180642 | 2.212879 | 2.608063 |
| 4 | 6 | 0.239459 | 2.918834 | 1.402580 |
| 5 | 1 | -0.093904 | 1.990020 | 0.564041 |
| 6 | 8 | -1.069966 | 0.453496 | 3.311988 |
| 7 | 45 | 0.288234 | -0.638861 | 0.130356 |
| 8 | 45 | 1.477071 | -2.628050 | -0.655262 |
| 9 | 8 | 2.722990 | -1.352127 | -1.719166 |
| 10 | 8 | 0.171510 | -2.686640 | -2.260950 |
| 11 | 8 | 0.171606 | -3.788393 | 0.450863 |
| 12 | 8 | 2.694171 | -2.454285 | 1.019100 |
| 13 | 8 | -0.948611 | -0.854293 | -1.521265 |
| 14 | 8 | 1.621222 | 0.492668 | -0.985465 |
| 15 | 8 | -0.939017 | -1.946594 | 1.180078 |
| 16 | 8 | 1.628186 | -0.579113 | 1.728347 |
| 17 | 6 | -0.736545 | -3.204586 | 1.115127 |
| 18 | 6 | 2.506969 | -1.502665 | 1.831316 |
| 19 | 6 | 2.530455 | -0.101869 | -1.657529 |
| 20 | 6 | -0.736502 | -1.806180 | -2.343772 |
| 21 | 6 | 3.408265 | -1.428322 | 3.046752 |
| 22 | 1 | 2.798618 | -1.350169 | 3.951977 |
| 23 | 1 | 4.051793 | -2.307648 | 3.099556 |

| | | | | |
|---|---|---|---|---|
| 24 | 1 | 4.028327 | -0.526698 | 2.989310 |
| 25 | 6 | 3.444873 | 0.789095 | -2.472533 |
| 26 | 1 | 2.904144 | 1.139825 | -3.359166 |
| 27 | 1 | 3.730901 | 1.667614 | -1.887997 |
| 28 | 1 | 4.329344 | 0.235504 | -2.792393 |
| 29 | 6 | -1.649743 | -1.861416 | -3.550965 |
| 30 | 1 | -2.662821 | -1.561202 | -3.272724 |
| 31 | 1 | -1.283852 | -1.154626 | -4.305025 |
| 32 | 1 | -1.649205 | -2.864283 | -3.982021 |
| 33 | 6 | -1.692394 | -4.069574 | 1.909211 |
| 34 | 1 | -1.751989 | -3.702831 | 2.938099 |
| 35 | 1 | -2.694812 | -3.993010 | 1.473993 |
| 36 | 1 | -1.366943 | -5.110893 | 1.895267 |
| 37 | 6 | -2.243567 | 1.123960 | 0.433005 |
| 38 | 6 | -3.301716 | 0.593048 | 1.191968 |
| 39 | 6 | -2.560834 | 1.712244 | -0.813236 |
| 40 | 6 | -4.616274 | 0.597155 | 0.713790 |
| 41 | 1 | -3.096298 | 0.128053 | 2.148399 |
| 42 | 6 | -3.871028 | 1.755523 | -1.266979 |
| 43 | 6 | -4.907023 | 1.187751 | -0.521325 |
| 44 | 1 | -4.090499 | 2.231768 | -2.216298 |
| 45 | 1 | -5.917342 | 1.218826 | -0.911673 |
| 46 | 35 | -1.218710 | 2.543500 | -1.889915 |
| 47 | 8 | -5.537502 | 0.015133 | 1.530556 |
| 48 | 6 | -6.891130 | -0.012657 | 1.106227 |
| 49 | 1 | -7.007542 | -0.568481 | 0.166338 |
| 50 | 1 | -7.441364 | -0.524009 | 1.897791 |
| 51 | 1 | -7.296327 | 1.000216 | 0.979785 |
| 52 | 1 | -0.575830 | 3.637026 | 1.285412 |
| 53 | 6 | 1.571568 | 3.397792 | 1.014527 |
| 54 | 6 | 2.729607 | 2.712264 | 1.421131 |
| 55 | 6 | 1.683453 | 4.553805 | 0.222415 |
| 56 | 6 | 3.981688 | 3.197139 | 1.054192 |
| 57 | 1 | 2.628220 | 1.804761 | 2.005838 |
| 58 | 6 | 2.938727 | 5.028977 | -0.145609 |
| 59 | 1 | 0.785368 | 5.076529 | -0.096576 |
| 60 | 6 | 4.089406 | 4.352873 | 0.272494 |
| 61 | 1 | 4.878103 | 2.673595 | 1.374306 |
| 62 | 1 | 3.022502 | 5.927163 | -0.750536 |
| 63 | 1 | 5.069740 | 4.726826 | -0.010099 |

---

Figure 5, Entries 1 and 2, *trans*-β-TS1$_{cat}$ , high energy conformation




E(RB3LYP) = -4547.60580770 hartrees
Sum of electronic and thermal Free Energies = -4547.221026 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 1.353324 | 0.347044 | -0.515805 |
| 2 | 6 | 1.345455 | 1.042565 | -1.836236 |
| 3 | 8 | 1.332635 | 2.427765 | -1.581043 |
| 4 | 6 | 1.647498 | 2.584037 | -0.245714 |
| 5 | 1 | 1.190697 | 1.390640 | 0.219617 |
| 6 | 8 | 1.236159 | 0.600092 | -2.941540 |
| 7 | 45 | -0.742707 | -0.356493 | -0.193697 |
| 8 | 45 | -3.058495 | -1.096401 | 0.090464 |
| 9 | 8 | -3.110629 | 0.088387 | 1.807354 |
| 10 | 8 | -2.373800 | -2.692347 | 1.209020 |
| 11 | 8 | -2.856178 | -2.207957 | -1.637632 |
| 12 | 8 | -3.637949 | 0.522312 | -1.063071 |
| 13 | 8 | -0.218286 | -2.083691 | 0.846847 |
| 14 | 8 | -0.930799 | 0.687026 | 1.595956 |
| 15 | 8 | -0.724693 | -1.477159 | -1.934176 |
| 16 | 8 | -1.505706 | 1.277192 | -1.246769 |
| 17 | 6 | -1.752438 | -2.152944 | -2.264542 |
| 18 | 6 | -2.760060 | 1.330909 | -1.482873 |
| 19 | 6 | -2.067374 | 0.696798 | 2.183228 |
| 20 | 6 | -1.121833 | -2.844719 | 1.328064 |
| 21 | 6 | -3.238179 | 2.497034 | -2.324418 |
| 22 | 1 | -2.494191 | 2.745934 | -3.084879 |
| 23 | 1 | -4.196478 | 2.257797 | -2.789267 |
| 24 | 1 | -3.378366 | 3.373710 | -1.680149 |
| 25 | 6 | -2.150988 | 1.527457 | 3.447455 |

| | | | | |
|---|---|---|---|---|
| 26 | 1 | -1.409395 | 1.170749 | 4.169795 |
| 27 | 1 | -1.907227 | 2.569344 | 3.214500 |
| 28 | 1 | -3.150110 | 1.466240 | 3.881251 |
| 29 | 6 | -0.630758 | -4.056315 | 2.093065 |
| 30 | 1 | 0.255285 | -3.794669 | 2.677542 |
| 31 | 1 | -1.420244 | -4.445509 | 2.738670 |
| 32 | 1 | -0.344627 | -4.836320 | 1.377710 |
| 33 | 6 | -1.622808 | -2.987462 | -3.521146 |
| 34 | 1 | -1.026193 | -3.879225 | -3.296624 |
| 35 | 1 | -2.606778 | -3.297988 | -3.876877 |
| 36 | 1 | -1.094229 | -2.419874 | -4.291165 |
| 37 | 6 | 2.487408 | -0.415882 | 0.028616 |
| 38 | 6 | 2.306773 | -0.934548 | 1.327796 |
| 39 | 6 | 3.762183 | -0.632598 | -0.568614 |
| 40 | 6 | 3.287690 | -1.672423 | 1.990782 |
| 41 | 1 | 1.362555 | -0.777242 | 1.829643 |
| 42 | 6 | 4.727008 | -1.397446 | 0.077931 |
| 43 | 6 | 4.504511 | -1.926929 | 1.350273 |
| 44 | 1 | 5.680820 | -1.564499 | -0.409557 |
| 45 | 1 | 5.285487 | -2.512343 | 1.821560 |
| 46 | 35 | 4.301285 | 0.134933 | -2.230993 |
| 47 | 8 | 2.955054 | -2.112662 | 3.238310 |
| 48 | 6 | 3.914240 | -2.871852 | 3.958586 |
| 49 | 1 | 4.833434 | -2.297365 | 4.135079 |
| 50 | 1 | 3.449025 | -3.109675 | 4.916573 |
| 51 | 1 | 4.165549 | -3.804720 | 3.436729 |
| 52 | 1 | 2.713631 | 2.497591 | -0.019521 |
| 53 | 6 | 0.923742 | 3.618634 | 0.494347 |
| 54 | 6 | 1.520620 | 4.185688 | 1.635575 |
| 55 | 6 | -0.350923 | 4.049468 | 0.085534 |
| 56 | 6 | 0.856037 | 5.174826 | 2.353866 |
| 57 | 1 | 2.508191 | 3.854746 | 1.948050 |
| 58 | 6 | -1.006149 | 5.044410 | 0.804857 |
| 59 | 1 | -0.806267 | 3.583625 | -0.779874 |
| 60 | 6 | -0.407880 | 5.606572 | 1.938209 |
| 61 | 1 | 1.322554 | 5.615176 | 3.230244 |
| 62 | 1 | -1.987735 | 5.383594 | 0.486033 |
| 63 | 1 | -0.925333 | 6.382262 | 2.496079 |

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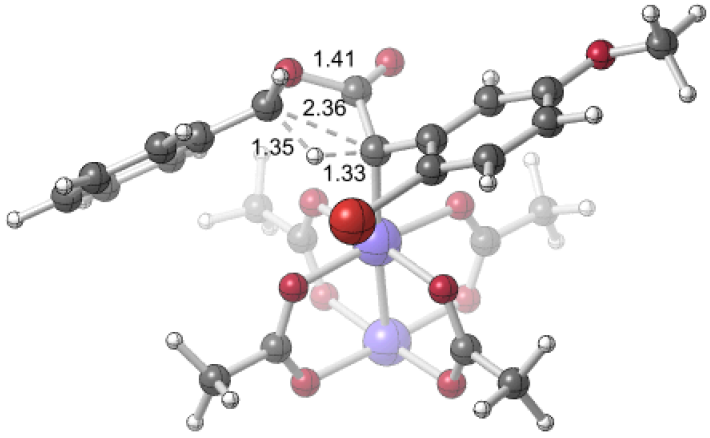
*BP86/6-31G(d) for C, H, O, Br and LANL2DZ for Rh*

Figure 5, Entries 1 and 2, *trans*-β-$TS1_{cat}$, high energy conformation




E(RB-P86) = -4548.05960587 hartrees
Sum of electronic and thermal Free Energies = -4547.692329 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 0.800368 | 0.973592 | -0.934043 |
| 2 | 6 | 0.567134 | 1.147087 | -2.408015 |
| 3 | 8 | -0.329862 | 2.210644 | -2.616889 |
| 4 | 6 | -0.444384 | 2.924260 | -1.412103 |
| 5 | 1 | -0.007185 | 1.967106 | -0.568392 |
| 6 | 8 | 1.014926 | 0.499104 | -3.330259 |
| 7 | 45 | -0.232493 | -0.645963 | -0.138778 |
| 8 | 45 | -1.314960 | -2.682908 | 0.676435 |
| 9 | 8 | -2.569856 | -1.483913 | 1.800843 |
| 10 | 8 | 0.040289 | -2.723287 | 2.232633 |
| 11 | 8 | -0.036959 | -3.812899 | -0.476248 |
| 12 | 8 | -2.617643 | -2.564097 | -0.930219 |
| 13 | 8 | 1.068656 | -0.809567 | 1.478856 |
| 14 | 8 | -1.580341 | 0.428736 | 1.009957 |
| 15 | 8 | 1.017687 | -1.914688 | -1.225827 |
| 16 | 8 | -1.612482 | -0.649768 | -1.710788 |
| 17 | 6 | 0.845440 | -3.188231 | -1.165282 |
| 18 | 6 | -2.480578 | -1.602220 | -1.763093 |
| 19 | 6 | -2.440492 | -0.212844 | 1.724303 |
| 20 | 6 | 0.919424 | -1.793246 | 2.296699 |
| 21 | 6 | -3.456820 | -1.552329 | -2.926359 |
| 22 | 1 | -3.794867 | -2.568708 | -3.179742 |
| 23 | 1 | -4.342596 | -0.959244 | -2.634381 |
| 24 | 1 | -2.989566 | -1.072061 | -3.799783 |
| 25 | 6 | -3.370020 | 0.637320 | 2.570732 |
| 26 | 1 | -2.824912 | 0.994042 | 3.462944 |

| | | | | |
|---|---|---|---|---|
| 27 | 1 | -3.698969 | 1.521190 | 2.001382 |
| 28 | 1 | -4.236261 | 0.043119 | 2.897786 |
| 29 | 6 | 1.875254 | -1.828936 | 3.476312 |
| 30 | 1 | 1.485153 | -1.174851 | 4.276852 |
| 31 | 1 | 1.955959 | -2.853541 | 3.869580 |
| 32 | 1 | 2.864239 | -1.447717 | 3.178416 |
| 33 | 6 | 1.802845 | -4.023805 | -1.995549 |
| 34 | 1 | 1.488493 | -5.077752 | -1.996911 |
| 35 | 1 | 1.841146 | -3.633651 | -3.025913 |
| 36 | 1 | 2.819774 | -3.944290 | -1.572879 |
| 37 | 6 | 2.175057 | 1.200276 | -0.441879 |
| 38 | 6 | 3.265419 | 0.711466 | -1.198345 |
| 39 | 6 | 2.470946 | 1.842114 | 0.792042 |
| 40 | 6 | 4.588874 | 0.816376 | -0.732895 |
| 41 | 1 | 3.074514 | 0.209054 | -2.149992 |
| 42 | 6 | 3.786441 | 1.979644 | 1.238934 |
| 43 | 6 | 4.856210 | 1.459624 | 0.492176 |
| 44 | 1 | 3.981245 | 2.495697 | 2.183546 |
| 45 | 1 | 5.874795 | 1.566461 | 0.873843 |
| 46 | 35 | 1.081103 | 2.611153 | 1.863449 |
| 47 | 8 | 5.543828 | 0.269326 | -1.550997 |
| 48 | 6 | 6.903445 | 0.359190 | -1.124345 |
| 49 | 1 | 7.064272 | -0.163706 | -0.160969 |
| 50 | 1 | 7.494807 | -0.134769 | -1.909689 |
| 51 | 1 | 7.232906 | 1.412369 | -1.026116 |
| 52 | 1 | 0.340797 | 3.687158 | -1.279438 |
| 53 | 6 | -1.801797 | 3.313972 | -1.020419 |
| 54 | 6 | -1.982312 | 4.427611 | -0.164063 |
| 55 | 6 | -2.931410 | 2.594053 | -1.478498 |
| 56 | 6 | -3.269642 | 4.820876 | 0.217409 |
| 57 | 1 | -1.105822 | 4.979026 | 0.195969 |
| 58 | 6 | -4.215683 | 2.999082 | -1.098362 |
| 59 | 1 | -2.778212 | 1.721714 | -2.119913 |
| 60 | 6 | -4.389986 | 4.109857 | -0.251144 |
| 61 | 1 | -3.403380 | 5.687309 | 0.874229 |
| 62 | 1 | -5.089543 | 2.447085 | -1.461743 |
| 63 | 1 | -5.398388 | 4.422326 | 0.042283 |

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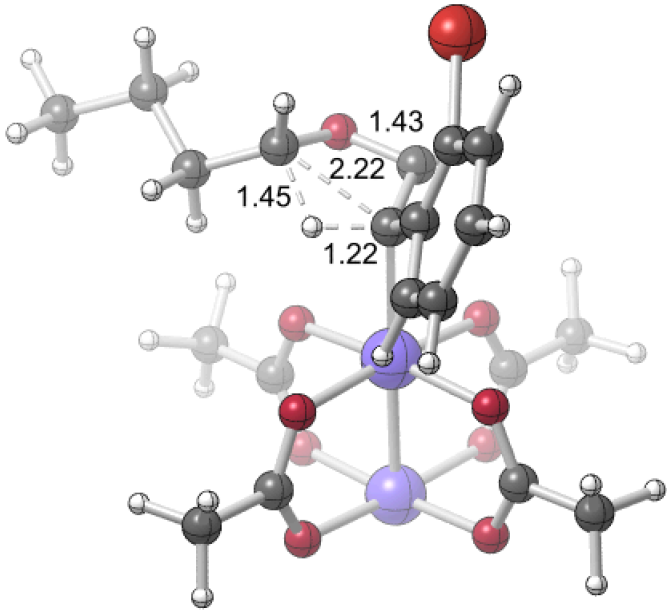
*Bach Systems*

*B3LYP/6-31G(d) for C, H, O, Br and LANL2DZ for Rh*

Figure 5, Entry 6, *trans*-β-$TS1_{cat}$




E(UB3LYP) = -4319.97626948 hartrees
Sum of electronic and thermal Free Energies = -4319.618362 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | -1.614881 | -0.035129 | 0.031073 |
| 2 | 6 | -1.965655 | 0.598980 | 1.323078 |
| 3 | 8 | -2.147317 | 1.983704 | 1.036675 |
| 4 | 6 | -2.394089 | 2.015954 | -0.305334 |
| 5 | 1 | -1.536790 | 0.923919 | -0.712159 |
| 6 | 6 | -1.837220 | 3.180167 | -1.064158 |
| 7 | 1 | -0.771853 | 3.269394 | -0.840545 |
| 8 | 8 | -2.013178 | 0.156717 | 2.431610 |
| 9 | 45 | 0.715231 | -0.109416 | 0.043735 |
| 10 | 45 | 3.154337 | -0.242230 | 0.065055 |
| 11 | 8 | 3.092024 | -0.164399 | -2.012756 |
| 12 | 8 | 2.992808 | -2.297594 | -0.000712 |
| 13 | 8 | 3.080243 | -0.313127 | 2.124635 |
| 14 | 8 | 3.191699 | 1.831318 | 0.148672 |
| 15 | 8 | 0.725270 | -2.192694 | 0.022053 |
| 16 | 8 | 0.825109 | -0.047460 | -2.047297 |
| 17 | 8 | 0.815317 | -0.158332 | 2.106898 |
| 18 | 8 | 0.926591 | 1.963743 | 0.095857 |
| 19 | 6 | 1.942981 | -0.258625 | 2.689152 |
| 20 | 6 | 2.099503 | 2.469025 | 0.153580 |
| 21 | 6 | 1.976448 | -0.083407 | -2.603380 |
| 22 | 6 | 1.836223 | -2.818098 | 0.014501 |
| 23 | 6 | 2.176509 | 3.981015 | 0.218585 |
| 24 | 1 | 3.196563 | 4.301083 | 0.436078 |

| | | | | |
|---|---|---|---|---|
| 25 | 1 | 1.866469 | 4.403582 | -0.744326 |
| 26 | 1 | 1.491288 | 4.355686 | 0.984639 |
| 27 | 6 | 1.996659 | 0.011050 | -4.115536 |
| 28 | 1 | 2.934576 | -0.385582 | -4.508345 |
| 29 | 1 | 1.144655 | -0.523866 | -4.542610 |
| 30 | 1 | 1.913476 | 1.064488 | -4.408198 |
| 31 | 6 | 1.756824 | -4.329614 | 0.056666 |
| 32 | 1 | 1.663214 | -4.648839 | 1.101368 |
| 33 | 1 | 0.872890 | -4.678890 | -0.482011 |
| 34 | 1 | 2.664298 | -4.770404 | -0.360584 |
| 35 | 6 | 1.914515 | -0.350941 | 4.199311 |
| 36 | 1 | 1.934707 | -1.408382 | 4.488478 |
| 37 | 1 | 2.797525 | 0.133122 | 4.623061 |
| 38 | 1 | 0.998678 | 0.096427 | 4.589555 |
| 39 | 6 | -2.371724 | -1.154714 | -0.561674 |
| 40 | 6 | -1.743444 | -1.910317 | -1.580318 |
| 41 | 6 | -3.706059 | -1.523961 | -0.247635 |
| 42 | 6 | -2.366165 | -2.986049 | -2.202463 |
| 43 | 1 | -0.742643 | -1.625489 | -1.873552 |
| 44 | 6 | -4.323980 | -2.622636 | -0.841671 |
| 45 | 6 | -3.652121 | -3.360976 | -1.815144 |
| 46 | 1 | -1.842792 | -3.536959 | -2.978393 |
| 47 | 1 | -5.338680 | -2.878907 | -0.559246 |
| 48 | 1 | -4.146312 | -4.211169 | -2.277196 |
| 49 | 35 | -4.817703 | -0.508764 | 0.935329 |
| 50 | 1 | -3.384681 | 1.656804 | -0.593679 |
| 51 | 6 | -2.582705 | 4.483944 | -0.679453 |
| 52 | 1 | -3.655512 | 4.368909 | -0.882098 |
| 53 | 1 | -2.479325 | 4.644450 | 0.399463 |
| 54 | 1 | -1.955699 | 2.993380 | -2.138955 |
| 55 | 6 | -2.034880 | 5.691395 | -1.447268 |
| 56 | 1 | -2.146671 | 5.560704 | -2.530214 |
| 57 | 1 | -2.567296 | 6.605605 | -1.163030 |
| 58 | 1 | -0.970039 | 5.844371 | -1.236161 |

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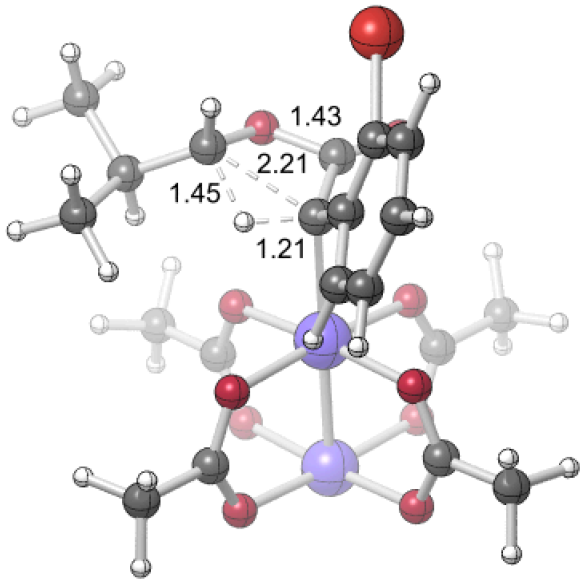
Figure 5, Entry 7, *trans*-β-TS1$_{cat}$




E(UB3LYP) = -4319.97756656 hartrees
Sum of electronic and thermal Free Energies = -4319.619501 hartrees

| Center Number | Atomic Number | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | 6 | 1.616662 | 0.109055 | -0.083193 |
| 2 | 6 | 1.929517 | 0.767228 | -1.372793 |
| 3 | 8 | 2.069508 | 2.153424 | -1.071705 |
| 4 | 6 | 2.298576 | 2.177430 | 0.273146 |
| 5 | 1 | 1.473826 | 1.046164 | 0.664098 |
| 6 | 6 | 1.680284 | 3.303567 | 1.053849 |
| 7 | 1 | 0.651515 | 3.408764 | 0.700072 |
| 8 | 8 | 1.979038 | 0.340895 | -2.487342 |
| 9 | 45 | -0.708376 | -0.073061 | -0.075905 |
| 10 | 45 | -3.140711 | -0.290560 | -0.058150 |
| 11 | 8 | -3.053823 | -0.071550 | 2.008278 |
| 12 | 8 | -2.908395 | -2.329687 | 0.143655 |
| 13 | 8 | -3.083522 | -0.495203 | -2.109273 |
| 14 | 8 | -3.251748 | 1.768728 | -0.276907 |
| 15 | 8 | -0.646772 | -2.151072 | 0.065417 |
| 16 | 8 | -0.791769 | 0.116384 | 2.012020 |
| 17 | 8 | -0.825222 | -0.260173 | -2.126953 |
| 18 | 8 | -0.992521 | 1.983529 | -0.249789 |
| 19 | 6 | -1.954166 | -0.437413 | -2.688890 |
| 20 | 6 | -2.182787 | 2.443365 | -0.329194 |
| 21 | 6 | -1.937406 | 0.079613 | 2.581817 |
| 22 | 6 | -1.734996 | -2.811651 | 0.134427 |
| 23 | 6 | -2.313373 | 3.945129 | -0.481739 |
| 24 | 1 | -2.046115 | 4.430983 | 0.464024 |

| | | | | |
|---|---|---|---|---|
| 25 | 1 | -1.621328 | 4.303701 | -1.248997 |
| 26 | 1 | -3.338634 | 4.213377 | -0.741063 |
| 27 | 6 | -1.946192 | 0.263177 | 4.085897 |
| 28 | 1 | -2.886246 | -0.096400 | 4.507711 |
| 29 | 1 | -1.099096 | -0.260031 | 4.537280 |
| 30 | 1 | -1.842611 | 1.329921 | 4.317241 |
| 31 | 6 | -1.606297 | -4.319727 | 0.179564 |
| 32 | 1 | -1.576996 | -4.701483 | -0.847852 |
| 33 | 1 | -0.676558 | -4.608768 | 0.674590 |
| 34 | 1 | -2.468350 | -4.759681 | 0.685191 |
| 35 | 6 | -1.931865 | -0.626190 | -4.190014 |
| 36 | 1 | -1.750286 | -1.684891 | -4.409866 |
| 37 | 1 | -2.892940 | -0.341687 | -4.623144 |
| 38 | 1 | -1.117829 | -0.046341 | -4.630108 |
| 39 | 6 | 2.422959 | -0.975446 | 0.509953 |
| 40 | 6 | 1.842705 | -1.728421 | 1.558573 |
| 41 | 6 | 3.760575 | -1.308146 | 0.172695 |
| 42 | 6 | 2.512597 | -2.771628 | 2.186538 |
| 43 | 1 | 0.840624 | -1.468256 | 1.870082 |
| 44 | 6 | 4.424757 | -2.377751 | 0.770953 |
| 45 | 6 | 3.799233 | -3.116926 | 1.773726 |
| 46 | 1 | 2.025196 | -3.321759 | 2.986101 |
| 47 | 1 | 5.439897 | -2.608522 | 0.468671 |
| 48 | 1 | 4.329375 | -3.943438 | 2.238834 |
| 49 | 35 | 4.814730 | -0.276838 | -1.047340 |
| 50 | 1 | 3.299624 | 1.857140 | 0.575439 |
| 51 | 6 | 1.683088 | 3.004544 | 2.560373 |
| 52 | 1 | 1.285040 | 3.862553 | 3.112266 |
| 53 | 1 | 1.058535 | 2.134344 | 2.790730 |
| 54 | 1 | 2.698387 | 2.814667 | 2.931325 |
| 55 | 6 | 2.466314 | 4.594454 | 0.717723 |
| 56 | 1 | 2.005070 | 5.442340 | 1.236356 |
| 57 | 1 | 3.509591 | 4.523286 | 1.047547 |
| 58 | 1 | 2.454392 | 4.798551 | -0.356847 |

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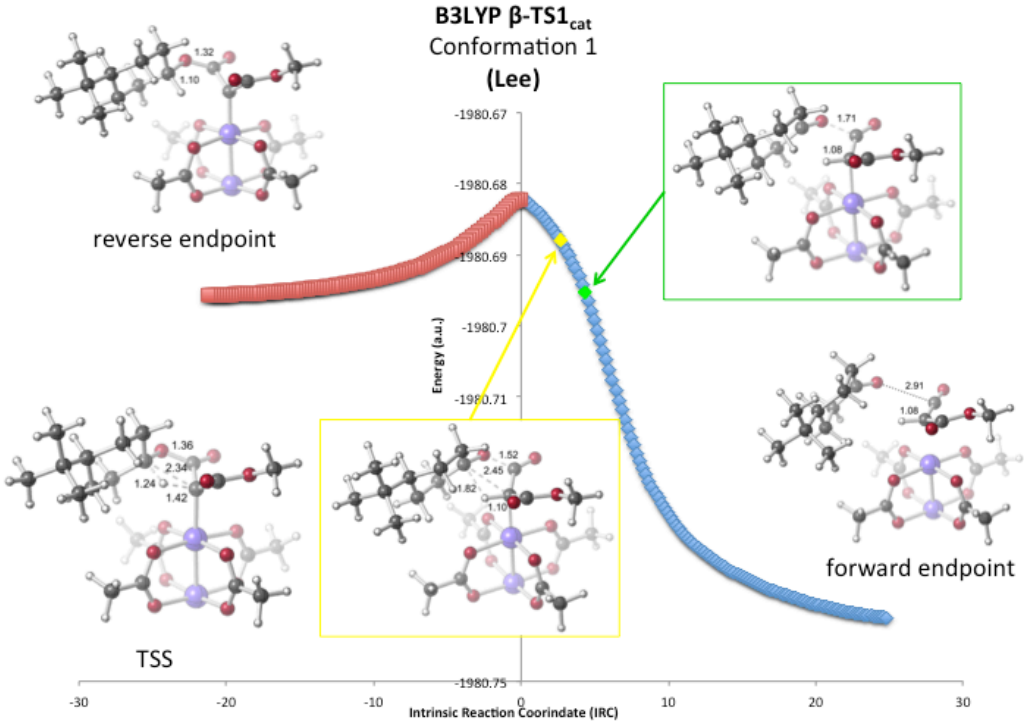
**Intrinsic Reaction Coordinates (IRCs)**

In the following graphs that correspond to β-TS1 IRCs, the yellow dot and corresponding picture represent the point along the IRC at which the forming C–H bond first reaches below 1.11 Å. The green dot and corresponding picture represent either (1) the point at which the forming C–C bond reaches below 1.57 Å in the case of the IRC going to the β-lactone product or (2) the point at which the breaking C–O bond reaches greater than 1.7 Å in the case of the IRC forming the fragmented product.

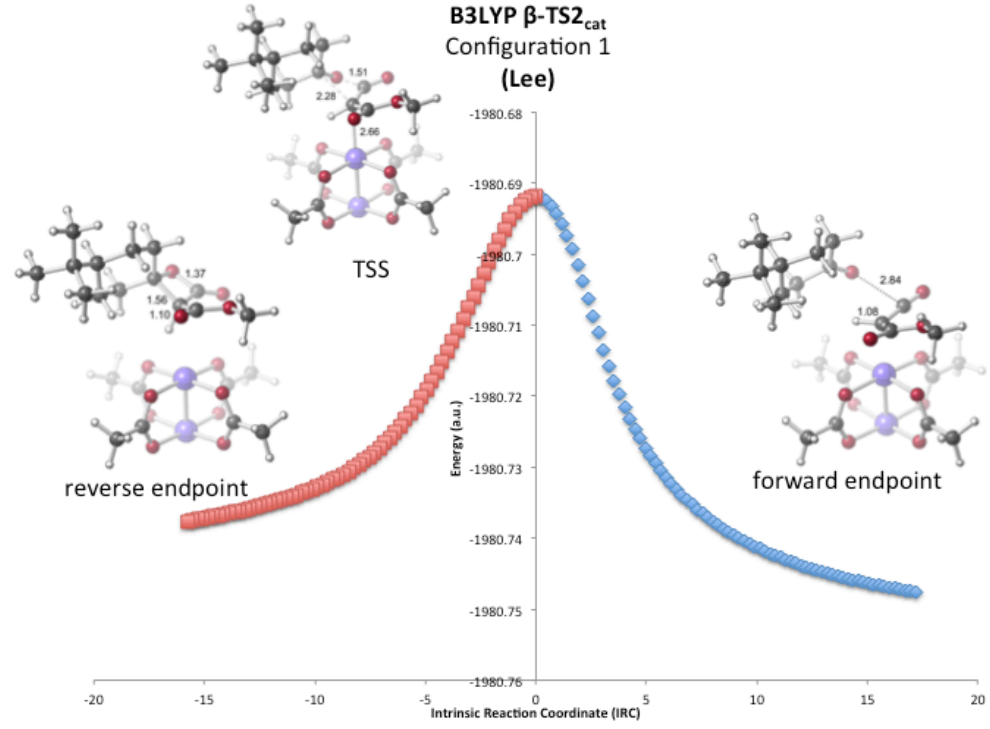
*Lee Systems*

*B3LYP/6-31G(d) for C, H, O and LANL2DZ for Rh*

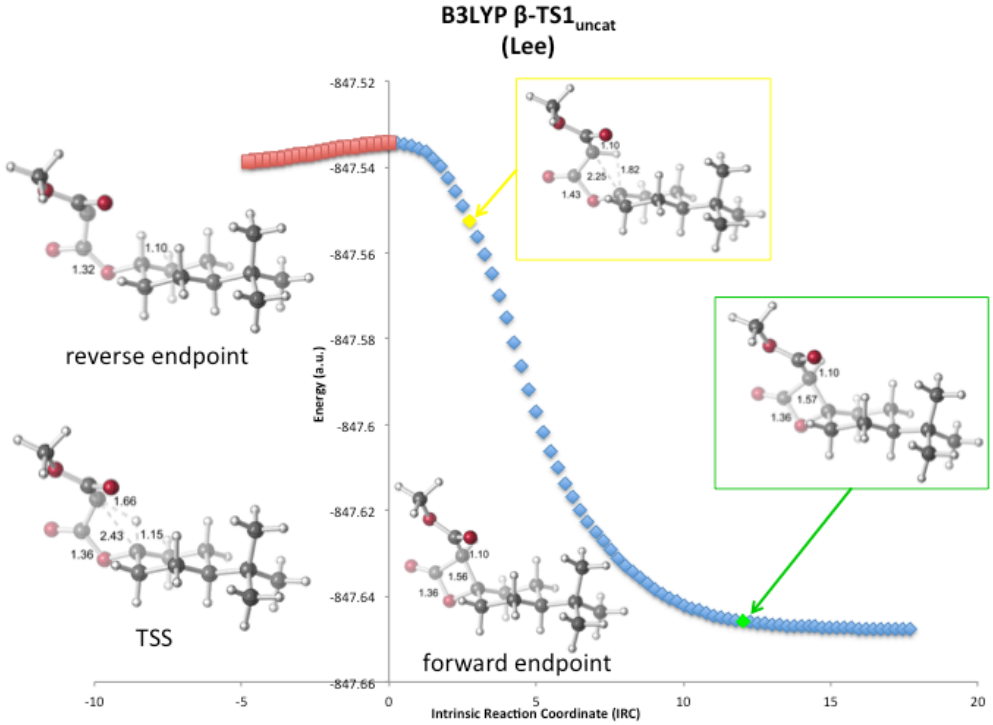
β-TS1$_{cat}$, Conformation 1



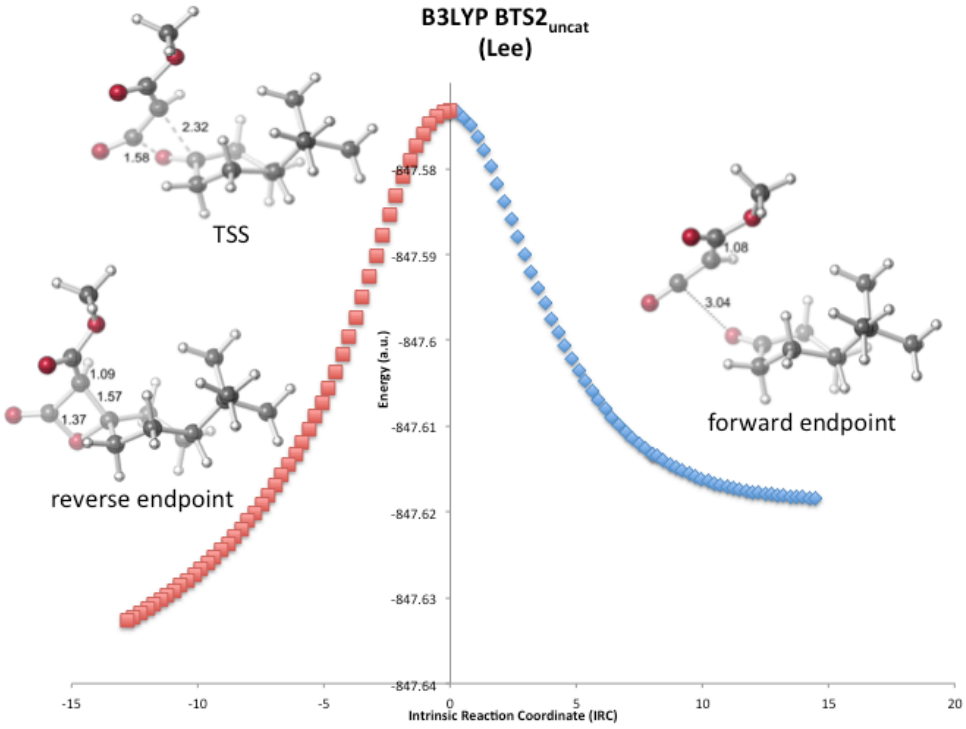

β-TS2$_{cat}$, Configuration 1



β-TS1$_{uncat}$

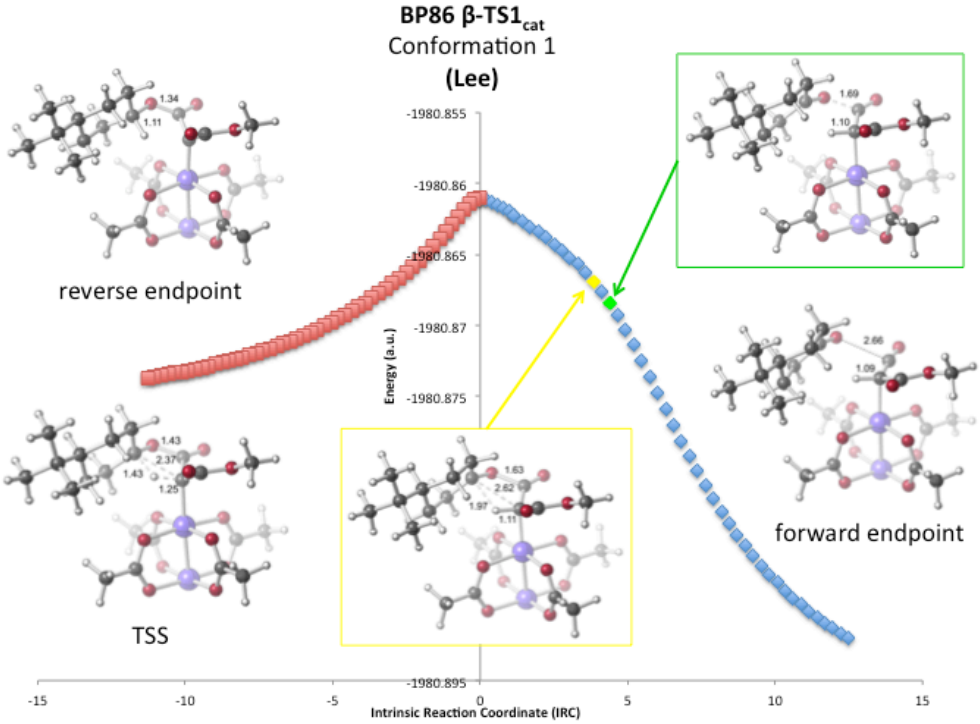



β-TS2$_{uncat}$



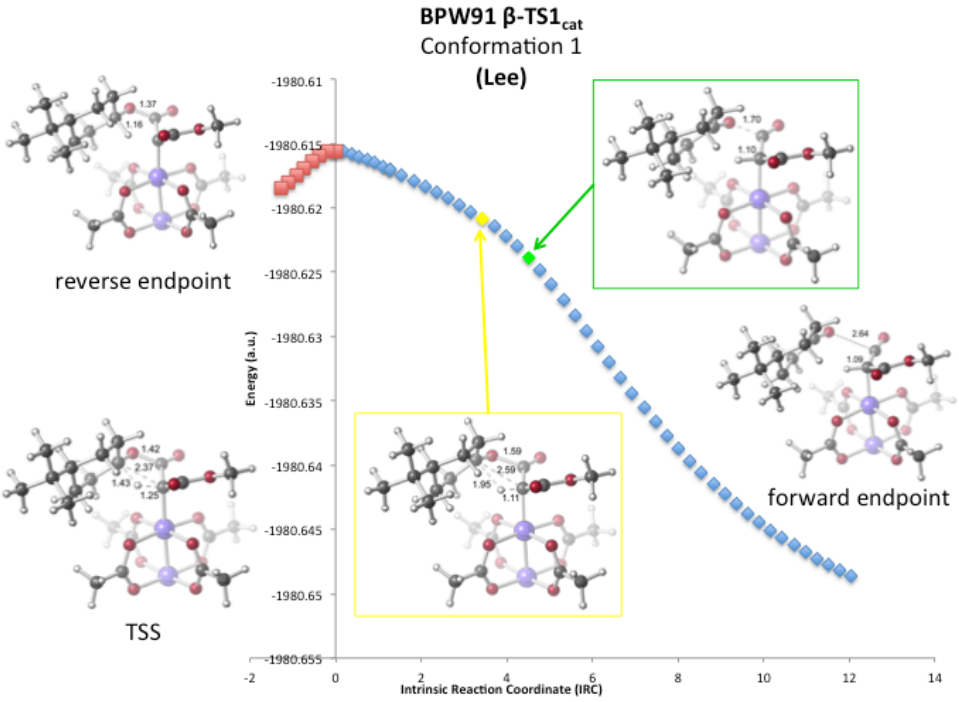
*BP86/6-31G(d) for C, H, O and LANL2DZ for Rh*

β-TS1$_{cat}$




BPW91/6-31G(d) for C, H, O and LANL2DZ for Rh

β-TS1$_{cat}$



*Davies Systems*

*B3LYP/6-31G(d) for C, H, O, Br and LANL2DZ for Rh*

Figure 5, Entries 1 and 2 *trans*-β-TS1$_{cat,}$ low energy conformation

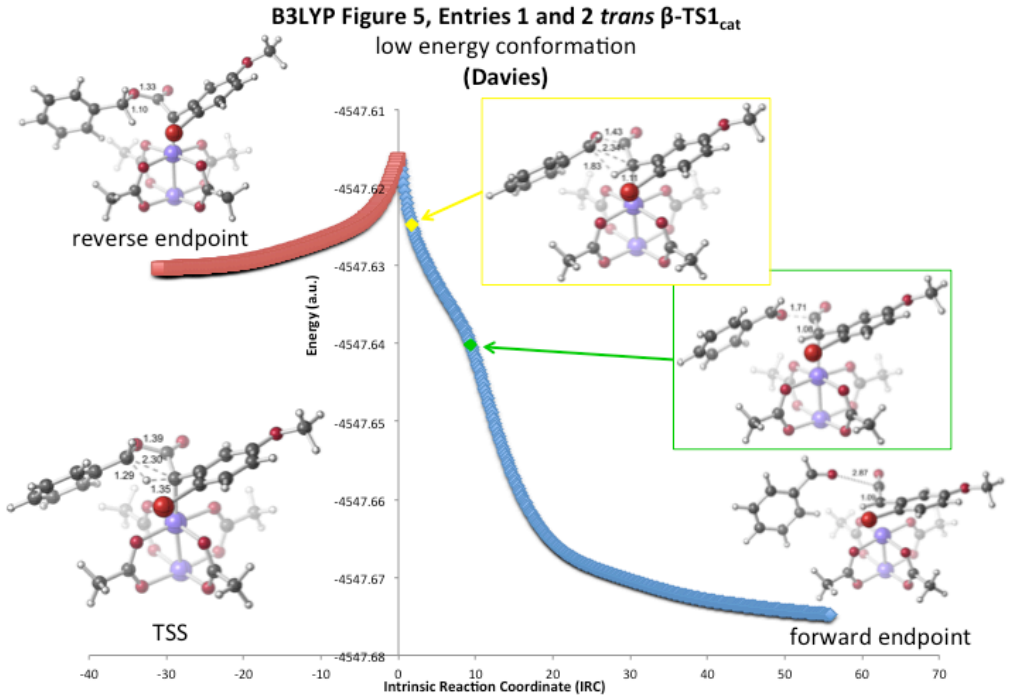



Figure 5, Entries 1 and 2 *trans*-β-TS1$_{cat}$, high energy conformation

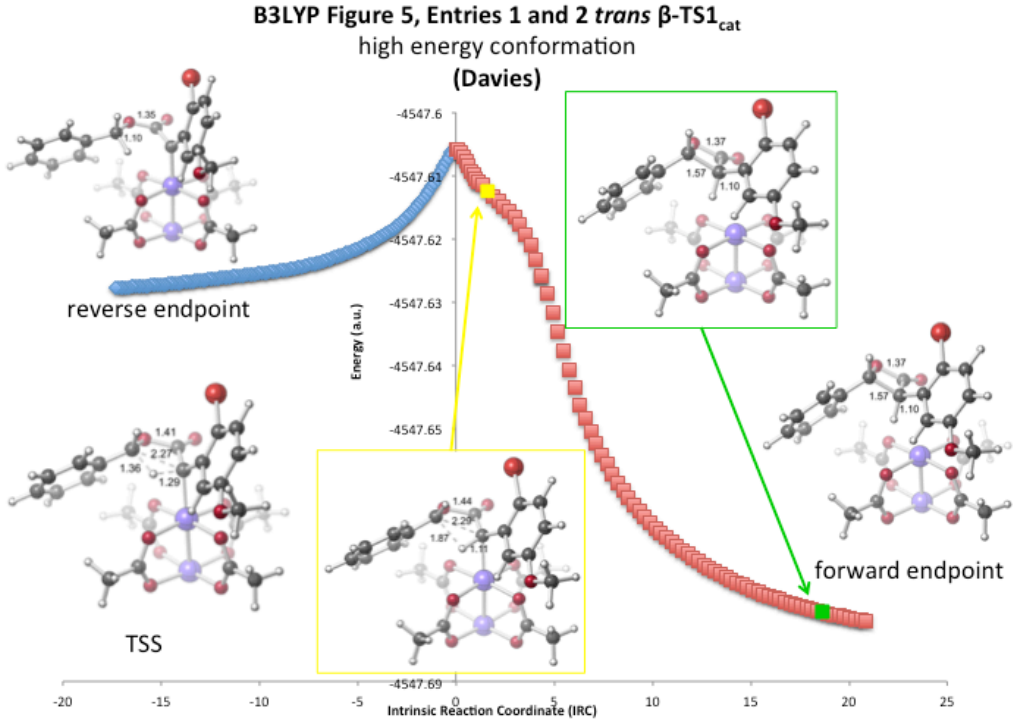


Figure 5, Entries 1 and 2 *cis*-β-TS1$_{cat,}$ low energy conformation

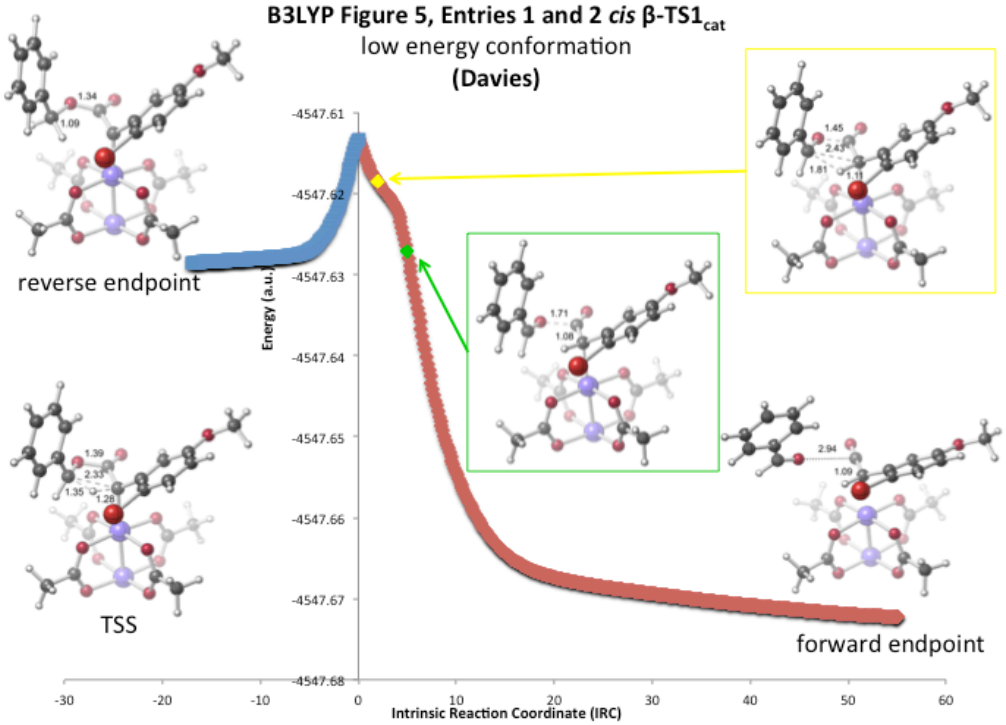



Figure 5, Entries 3-5 *trans*-β-TS1$_{cat}$

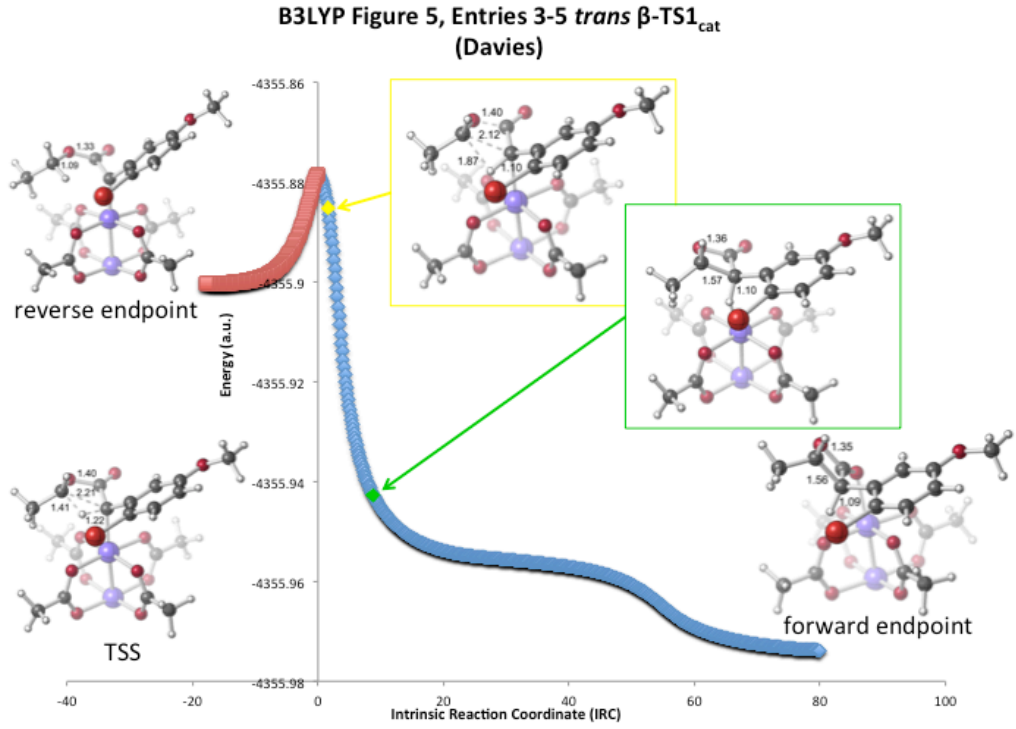
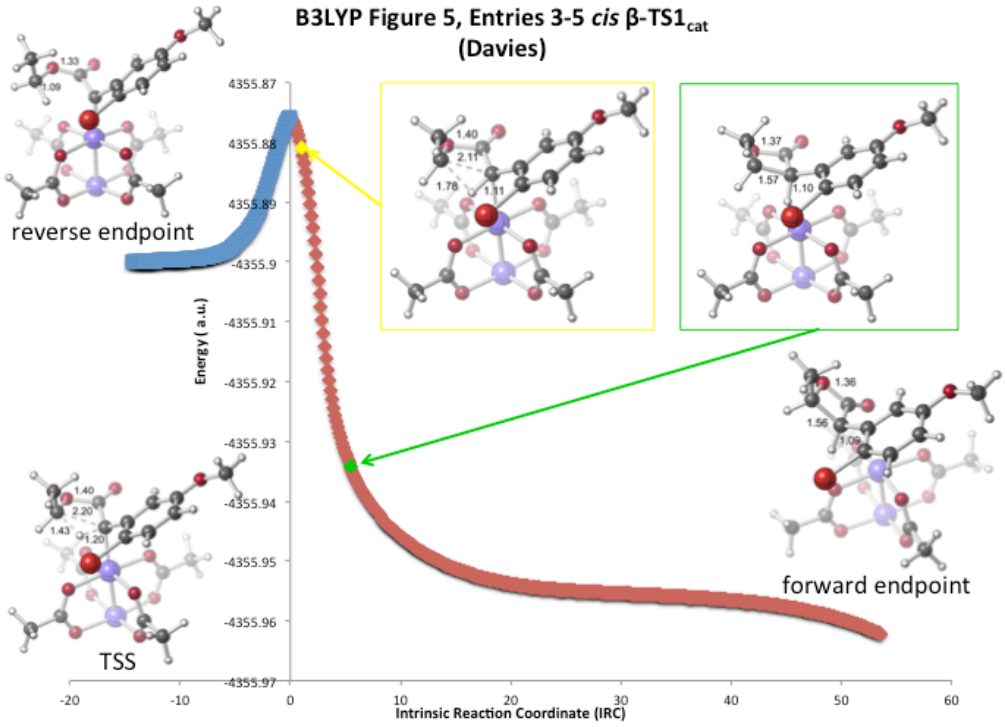
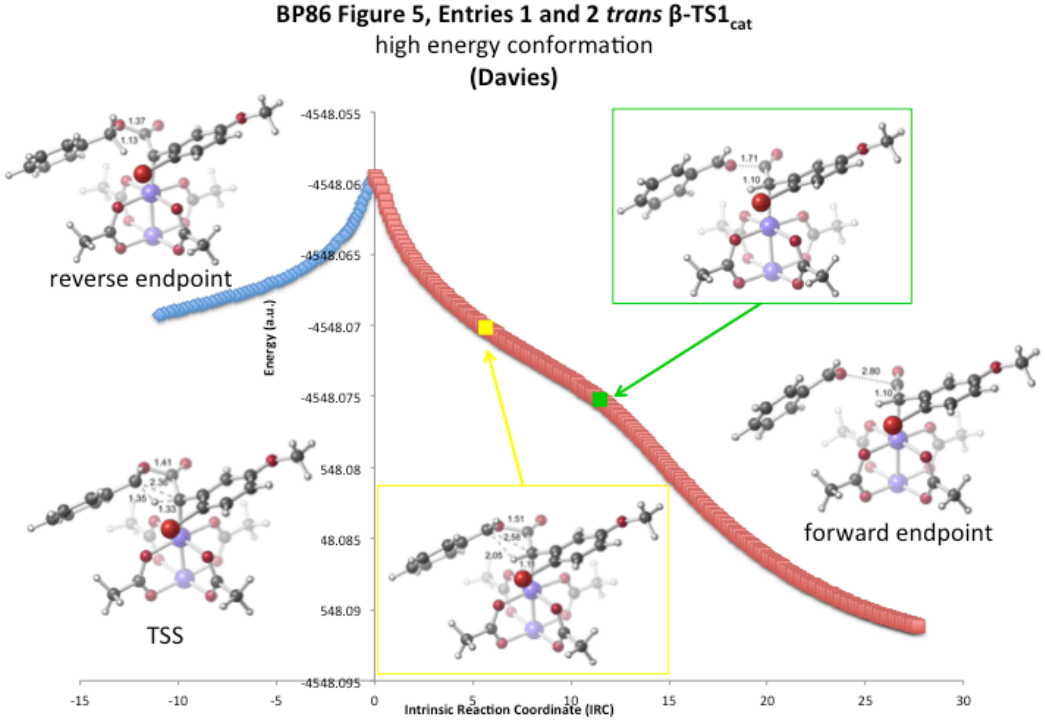


Figure 5, Entries 3-5 cis-β-TS1cat




*BP86/6-31G(d) for C, H, O, Br and LANL2DZ for Rh*

Figure 5, Entries 1 and 2 *trans*-β-TS1$_{cat,}$ high energy conformation



*Bach Systems*

*B3LYP/6-31G(d) for C, H, O, Br and LANL2DZ for Rh*

Figure 5, Entry 6 *trans*-β-TS1$_{cat}$

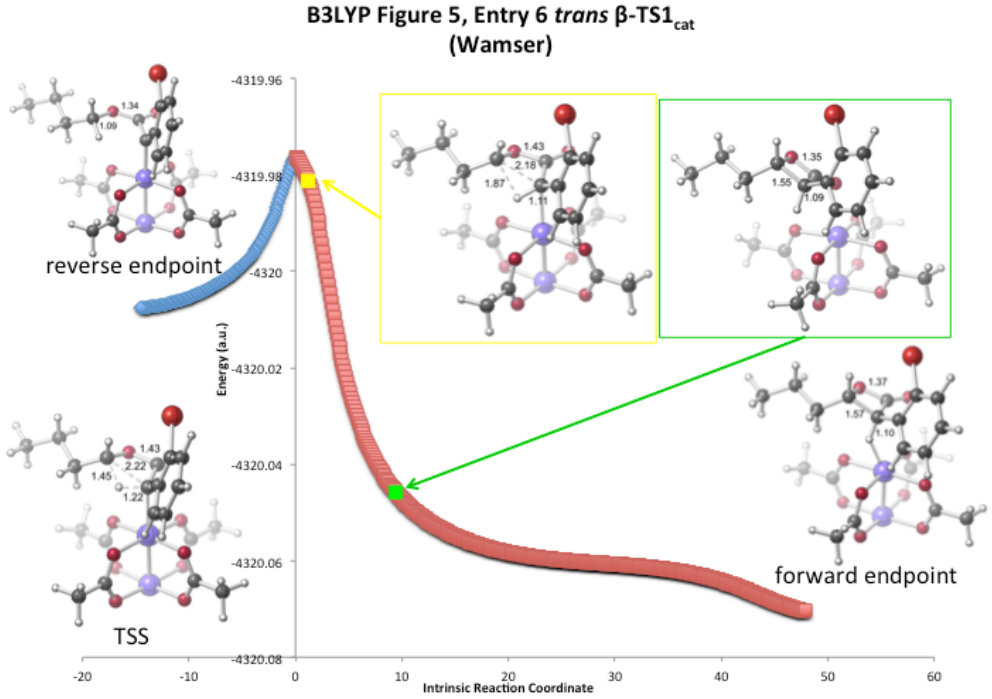
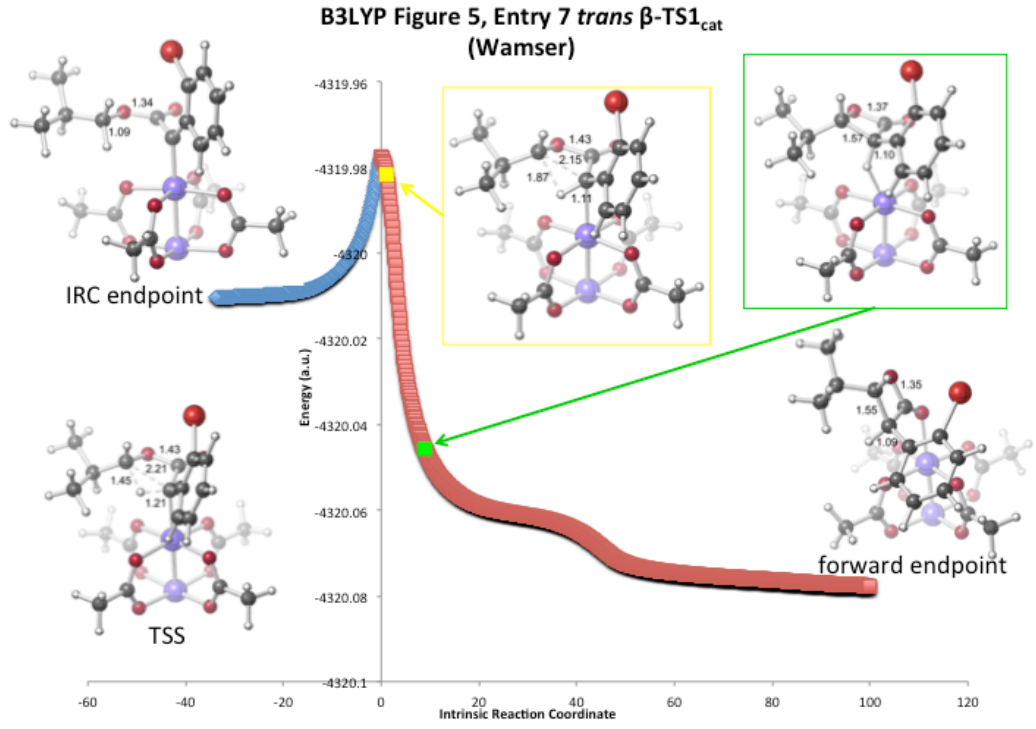



Figure 5, Entry 7 *trans*-β-TS1$_{cat}$



**Configuration File for Molecular Dynamics**

Shown below are example contents of progdyn.conf, the configuration file for molecular dynamics. The only keyword that was changed for use of different functionals was line 11, the "method" line. In the case of the uncatalyzed β-TS1 dynamics trajectories, lines 125-134, where the initial displacements can be specified as 0 for specific modes, were commented out.

```
#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 b3lyp/gen
#To do a nonstandard route, make nonstandard 1.  For normal
calcs, use nonstandard 0 or else leave it out.
#Then make a file called "nonstandard" containing the nonstandard
route with no extra lines.
#nonstandard 0
# NMRoptions NMRtype 1 will add a section for an NMR calc at
every NMRevery intervals.  The NMRmethod is the calculation used
#for the NMR calculation.  The awk program progNMRm might be
useful as a starting point for pulling out the data from files
named
#NMRlist
#NMRtype 1
#NMRmethod B3LYP/6-31G*
#NMRevery 4
#Use geometry linear to get the program to recognize 3N-5 normal
modes instead of 3N-6 when reading from freqinHP
#geometry linear
#Rotationmode controls whether molecular rotations are turned on.
They should be turned on with rotationmode 1 but this can be set
#at 0 to reproduce older calculations.
rotationmode 1
#*** 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 24
#*** memory --The following "word" is copied exactly to the
gaussian input file after %mem=.
memory 2GB
#*** 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 g09.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 1
#*** title -- the title keyword must be followed by exactly four
words
title Rh Lee Rxn8 beta
#*** 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 pseudo=read
#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
method4 iop(2/9=2000)
#method4 scrf=(pcm,solvent=dmso,read)
#method4
IOp(3/76=1000001970)IOp(3/77=0800008000)IOp(3/78=0700010000)
#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 10
#*** 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 1
#*** 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
#linkatoms 1
#*** 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
displacements 3 0
displacements 4 0
displacements 5 0
displacements 6 0
displacements 7 0
displacements 8 0
displacements 9 0
displacements 10 0
displacements 11 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 1.0
#*** 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
```