Marchetti, B., Karsili, T. N. V., & Ashfold, M. N. R. (2019). Exploring Norrish type I and type II reactions: an ab initio mechanistic study highlighting singlet-state mediated chemistry. *Physical Chemistry Chemical Physics*, *21*, 14418-14428. https://doi.org/10.1039/C8CP07292B, https://doi.org/10.5523/bris.1shnooapazkr528t0hgrffg82v

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


*Electronic Supplementary Information for:*

# Exploring Norrish Type I and Type II Reactions: An *ab initio* Mechanistic Study Highlighting Singlet-State Mediated Chemistry.

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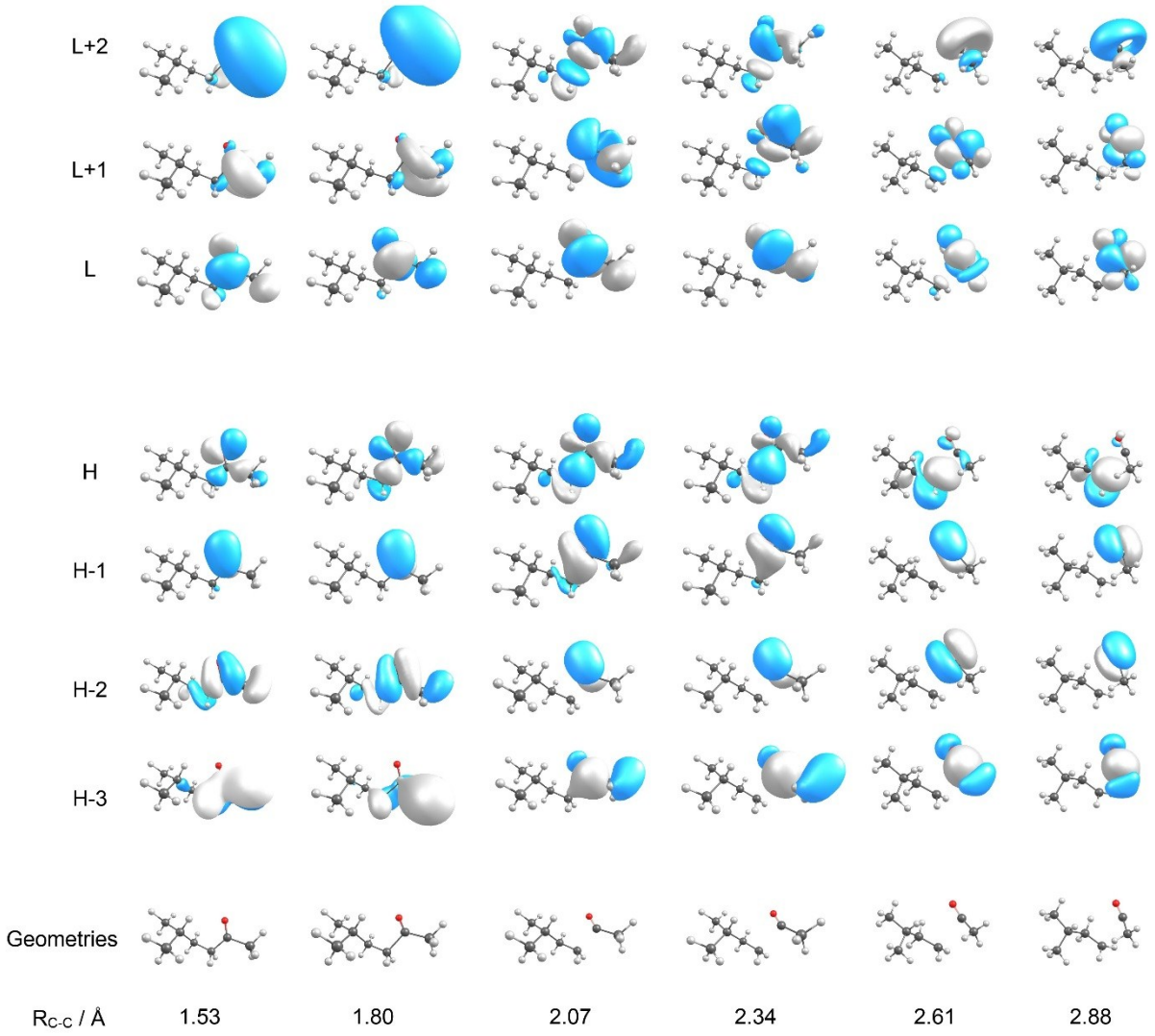
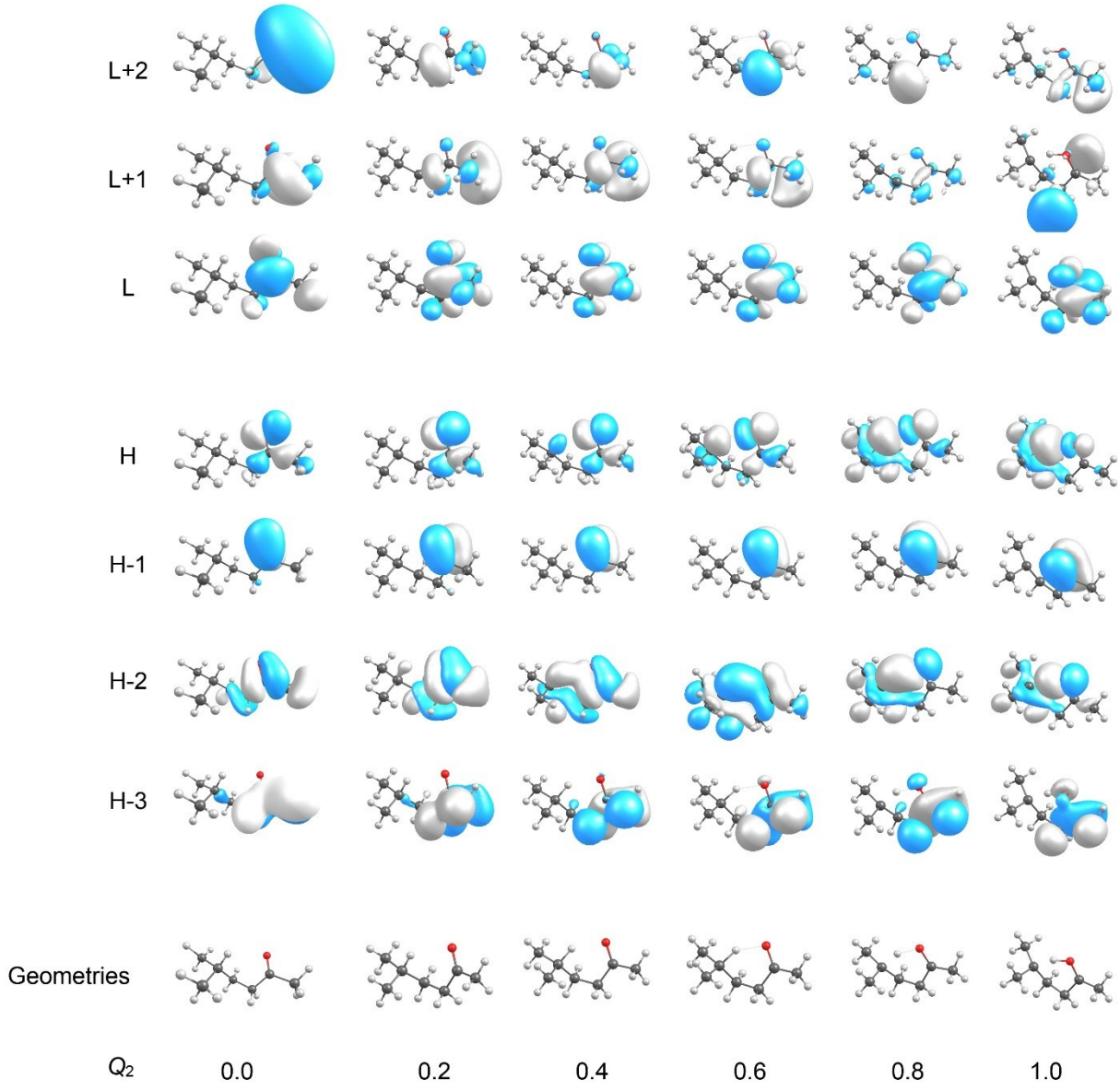
Figure S1: Full set of orbitals included in thw CASSCF/CASPT2 active space (10 electrons in 8 orbitals) of 5-MHONE for various points of the LIIC along $R_{C\text{-}C}$. The corresponding geometries are also depicted. The predominant electronic excitations contributing to each excited singlet and triplet states are tabulated below.




| | Excited State | | | | | |
|---|---|---|---|---|---|---|
| $R_{C\text{-}C}$ / Å | $S_1$ | $S_2$ | $S_3$ | $T_1$ | $T_2$ | $T_3$ |
| 1.53 ($S_0$ min) | H → L | H → L+1 | H → L+2 | H → L | H- → L | H → L+1 |
| 1.80 | | | | | | |
| 2.07 | H → L | H → L+1 | H-1 → L | H → L | H → L+1 | H → L+2 |
| 2.34 | | | | H → L | H → L+2 | H → L+1 |
| 2.61 | H → L<br>H → L+1 | H → L+2 | H | H → L<br>H → L+1 | H → L+1<br>H → L | H → L+2 |
| 2.88 ($CI_{C\text{-}C}$) | H → L<br>H → L+1 | H → L+2 | H | H → L<br>H → L+1 | H → L+1<br>H → L | |

Figure S2: Full set of orbitals included in thw CASSCF/CASPT2 active space (10 electrons in 8 orbitals) of 5-MHONE for various points of the LIIC along $Q_2$ (PT coordinate). The corresponding geometries are also depicted. The predominant electronic excitations contributing to each excited singlet and triplet states are tabulated below.




| | Excited State | | | | | |
|---|---|---|---|---|---|---|
| $Q_2$ | $S_1$ | $S_2$ | $S_3$ | $T_1$ | $T_2$ | $T_3$ |
| 0.0 ($S_0$ min) | H → L | H → L+1 | H → L+2 | H → L | H-1 → L | H → L+1 |
| 0.2 | | | | | | |
| 0.4 | | | | | | |
| 0.6 | | | | | | |
| 0.8 | | | | | | |
| 1.0 ($CI_{O\text{-}H}$) | H | H → L+2 | H → L+1 | H → L | H → L+2 | H → L+1 |

Table S1: Cartesian coordinates of the optimised critical structures of 5-MHONE.

- Ground state parent

| Atom | x | y | z |
|---|---|---|---|
| C | -2.62504 | -0.17205 | 0.195945 |
| C | -1.94423 | -1.50435 | -0.12494 |
| H | -2.70886 | -2.21138 | -0.48622 |
| H | -1.58112 | -1.92381 | 0.831562 |
| C | -0.77227 | -1.38742 | -1.1247 |
| H | -0.07688 | -0.61873 | -0.75391 |
| H | -0.22261 | -2.34499 | -1.14492 |
| C | -1.17947 | -1.02354 | -2.57921 |
| H | -1.75762 | -0.0862 | -2.53888 |
| O | -2.12107 | 0.934593 | -0.15194 |
| C | -3.93273 | -0.23067 | 0.975905 |
| H | -3.80889 | -0.81941 | 1.896555 |
| H | -4.24873 | 0.787525 | 1.228581 |
| H | -4.71427 | -0.71602 | 0.372301 |
| C | 0.086768 | -0.76219 | -3.4311 |
| H | -0.18344 | -0.4736 | -4.45742 |
| H | 0.690727 | 0.045923 | -2.99395 |
| H | 0.708836 | -1.66982 | -3.48332 |
| C | -2.05666 | -2.11719 | -3.2362 |
| H | -1.5141 | -3.07554 | -3.26671 |
| H | -2.99914 | -2.27385 | -2.69246 |
| H | -2.31085 | -1.83647 | -4.26889 |

- $Cl_{C\text{-}C}$

| Atom | x | y | z |
|---|---|---|---|
| C | -2.65292 | 0.784557 | 0.752372 |
| C | -1.8263 | -1.85256 | -0.0785 |
| H | -2.72079 | -2.37487 | -0.37133 |
| H | -1.46746 | -2.0809 | 0.911383 |
| C | -0.8134 | -1.45831 | -1.114 |
| H | -0.25136 | -0.61246 | -0.72794 |
| H | -0.08688 | -2.26321 | -1.25044 |
| C | -1.39812 | -1.08296 | -2.48539 |
| H | -2.19119 | -0.35605 | -2.31973 |
| O | -1.60458 | 1.297616 | 0.422714 |
| C | -4.00718 | 0.21077 | 0.887942 |
| H | -3.96197 | -0.60236 | 1.600048 |
| H | -4.70087 | 0.955724 | 1.266638 |
| H | -4.38949 | -0.17807 | -0.0479 |
| C | -0.32903 | -0.41723 | -3.35653 |
| H | -0.73185 | -0.13191 | -4.32407 |
| H | 0.062213 | 0.47709 | -2.88191 |

| | | | |
|---|---|---|---|
| H | 0.504793 | -1.09268 | -3.53306 |
| C | -1.99934 | -2.29074 | -3.21211 |
| H | -1.2373 | -3.04142 | -3.40723 |
| H | -2.78882 | -2.76507 | -2.63853 |
| H | -2.42363 | -1.99612 | -4.16758 |

- TS 1

| Atom | x | y | z |
|---|---|---|---|
| C | -1.83075 | 0.824508 | 0.066375 |
| C | -2.37832 | -1.84421 | -0.22241 |
| H | -3.3815 | -1.95441 | -0.62746 |
| H | -2.14908 | -2.48579 | 0.623182 |
| C | -1.32813 | -1.41688 | -1.0667 |
| H | -1.15875 | -0.22778 | -0.57697 |
| H | -0.34265 | -1.84777 | -0.85947 |
| C | -1.60664 | -1.16386 | -2.54239 |
| H | -2.57359 | -0.64242 | -2.60792 |
| O | -2.10285 | 1.925149 | -0.23684 |
| C | -3.24073 | -0.21371 | 1.050926 |
| H | -3.51337 | -1.13867 | 1.558961 |
| H | -3.03476 | 0.51133 | 1.843067 |
| H | -4.08807 | 0.137727 | 0.460105 |
| C | -0.53745 | -0.26653 | -3.16426 |
| H | -0.7403 | -0.08916 | -4.22527 |
| H | -0.49168 | 0.704548 | -2.6612 |
| H | 0.448552 | -0.73779 | -3.08498 |
| C | -1.72368 | -2.4839 | -3.30607 |
| H | -0.78194 | -3.04047 | -3.24524 |
| H | -2.51437 | -3.11204 | -2.8861 |
| H | -1.94545 | -2.30903 | -4.36447 |

- TS 2

| Atom | x | y | z |
|---|---|---|---|
| C | -2.33175 | 0.899019 | 2.474947 |
| C | -2.79521 | -1.46321 | -0.75249 |
| H | -3.84036 | -1.40473 | -1.06271 |
| H | -2.52332 | -2.37671 | -0.22203 |
| C | -1.77118 | -0.77875 | -1.60008 |
| H | -2.0435 | 0.278292 | -1.7383 |
| H | -0.79463 | -0.7831 | -1.09332 |
| C | -1.58451 | -1.40369 | -3.00153 |
| H | -2.56233 | -1.38213 | -3.50338 |
| O | -1.16305 | 0.798391 | 2.718534 |
| C | -3.25935 | 0.331616 | 1.48073 |
| H | -2.7939 | -0.37634 | 0.74943 |

| | | | |
|---|---|---|---|
| H | -4.0641 | -0.18068 | 2.022252 |
| H | -3.71972 | 1.163889 | 0.93398 |
| C | -0.60144 | -0.57338 | -3.82536 |
| H | -0.48611 | -0.98354 | -4.83409 |
| H | -0.93742 | 0.464622 | -3.91748 |
| H | 0.385759 | -0.56791 | -3.34966 |
| C | -1.12513 | -2.85593 | -2.90692 |
| H | -0.16421 | -2.91732 | -2.38238 |
| H | -1.84851 | -3.46862 | -2.36234 |
| H | -0.99153 | -3.29095 | -3.90292 |

- TS 3

| Atom | x | y | z |
|---|---|---|---|
| C | 1.84186 | 1.411355 | 0.045379 |
| C | 2.54339 | -2.40756 | -0.54303 |
| H | -3.5845 | -2.17483 | -0.78226 |
| H | 2.37355 | -2.91696 | 0.406107 |
| C | 1.48055 | -1.53979 | -1.11248 |
| H | 1.39513 | -0.55737 | -0.59951 |
| H | 0.49815 | -2.01698 | -0.97552 |
| C | 1.67642 | -1.227 | -2.60212 |
| H | -2.6738 | -0.77262 | -2.71373 |
| O | 1.40355 | 2.495951 | -0.18054 |
| C | 2.99585 | 0.892969 | 0.843895 |
| H | 2.73247 | 0.979713 | 1.903041 |
| H | 3.88159 | 1.502126 | 0.644091 |
| H | 3.18711 | -0.16141 | 0.606865 |
| C | 0.63713 | -0.21803 | -3.08849 |
| H | 0.79276 | 0.035726 | -4.14232 |
| H | 0.67654 | 0.709714 | -2.50643 |
| H | 0.37154 | -0.6348 | -2.98933 |
| C | 1.63755 | -2.50223 | -3.43861 |
| H | 0.65368 | -2.97812 | -3.351 |
| H | 2.38761 | -3.2172 | -3.09047 |
| H | 1.81497 | -2.28829 | -4.49842 |

- Product 1

| Atom | x | y | z |
|---|---|---|---|
| C | -0.76517 | 2.29228 | -0.34617 |
| C | -2.2151 | -1.93655 | 0.035893 |
| H | -2.76803 | -2.7586 | -0.43306 |
| H | -1.7842 | -2.35133 | 0.955518 |
| C | -1.06523 | -1.49236 | -0.87198 |
| H | -0.44738 | -0.76857 | -0.32304 |
| H | -0.4172 | -2.35623 | -1.08014 |

| | | | |
|---|---|---|---|
| C | -1.47211 | -0.86439 | -2.20899 |
| H | -2.05573 | 0.041842 | -1.99996 |
| O | -0.00704 | 3.066421 | -0.73443 |
| C | -3.179 | -0.80888 | 0.399646 |
| H | -3.90963 | -1.14292 | 1.142692 |
| H | -2.6373 | 0.046332 | 0.814937 |
| H | -3.73469 | -0.45675 | -0.47384 |
| C | -0.22697 | -0.44423 | -2.98985 |
| H | -0.49562 | 0.046399 | -3.9312 |
| H | 0.38958 | 0.250426 | -2.40998 |
| H | 0.388323 | -1.31865 | -3.23011 |
| C | -2.33427 | -1.80607 | -3.04782 |
| H | -1.80105 | -2.7453 | -3.23594 |
| H | -3.27911 | -2.04801 | -2.5533 |
| H | -2.57205 | -1.35581 | -4.01715 |

- Product 2

| Atom | x | y | z |
|---|---|---|---|
| C | -2.5427 | 0.291878 | 0.750647 |
| C | -0.96446 | 1.151424 | -2.79686 |
| H | -0.88539 | 2.242199 | -2.73761 |
| H | -0.89493 | 0.866808 | -3.84999 |
| C | 0.120811 | 0.4852 | -1.95359 |
| H | -0.06944 | 0.698319 | -0.89467 |
| H | 0.05575 | -0.60643 | -2.06508 |
| C | 1.549667 | 0.924359 | -2.28727 |
| H | 1.596783 | 2.017442 | -2.17275 |
| O | -1.60631 | 0.695353 | 1.347317 |
| C | -3.58946 | -0.15857 | 0.083756 |
| H | -1.95786 | 0.866447 | -2.43871 |
| H | -3.66066 | -1.21125 | -0.14957 |
| H | -4.36856 | 0.528636 | -0.21362 |
| C | 2.538991 | 0.302607 | -1.30251 |
| H | 3.561384 | 0.641166 | -1.49932 |
| H | 2.286738 | 0.564386 | -0.26991 |
| H | 2.525154 | -0.79002 | -1.38633 |
| C | 1.940522 | 0.579839 | -3.72367 |
| H | 1.861373 | -0.50088 | -3.88997 |
| H | 1.302599 | 1.082371 | -4.45549 |
| H | 2.975156 | 0.874831 | -3.92653 |

- Product 3

| Atom | x | y | z |
|---|---|---|---|
| C | -1.38007 | 0.837178 | 1.004612 |
| C | -2.8017 | -2.8578 | -0.6253 |

| | | | |
|---|---|---|---|
| H | -3.61728 | -3.31756 | -1.17744 |
| H | -2.72804 | -3.10417 | 0.429723 |
| H | -1.92529 | -2.0402 | -1.22434 |
| H | -1.09131 | 0.486138 | 2.016373 |
| H | -1.11465 | -1.59974 | -0.64144 |
| C | -1.95421 | -1.66081 | -2.67679 |
| H | -2.75587 | -2.2325 | -3.16459 |
| O | -0.51967 | 1.016547 | 0.150539 |
| C | -2.85181 | 1.028704 | 0.778437 |
| H | -3.31343 | 1.526655 | 1.636094 |
| H | -3.01633 | 1.602443 | -0.13412 |
| H | -3.318 | 0.042771 | 0.668141 |
| C | -2.25322 | -0.16618 | -2.83379 |
| H | -2.22399 | 0.127415 | -3.88851 |
| H | -3.24581 | 0.07253 | -2.43965 |
| H | -1.51709 | 0.430848 | -2.28628 |
| C | -0.62366 | -2.02128 | -3.34316 |
| H | 0.197481 | -1.46478 | -2.87864 |
| H | -0.41083 | -3.08979 | -3.24473 |
| H | -0.64154 | -1.76969 | -4.40856 |

- $Cl_{O\text{-}H}$

| Atom | x | y | z |
|---|---|---|---|
| C | -2.61154 | -0.28663 | -0.05348 |
| C | -1.96952 | -1.64959 | -0.10964 |
| H | -2.71713 | -2.39407 | -0.39093 |
| H | -1.64045 | -1.92509 | 0.88809 |
| C | -0.78253 | -1.70182 | -1.07989 |
| H | 0.02248 | -1.09704 | -0.67275 |
| H | -0.40709 | -2.72462 | -1.13861 |
| C | -1.13903 | -1.18823 | -2.46815 |
| H | -2.03995 | -0.09140 | -1.92436 |
| O | -2.68689 | 0.45193 | -1.19997 |
| C | -3.69473 | 0.01266 | 0.93579 |
| H | -3.40121 | -0.29587 | 1.93396 |
| H | -3.90753 | 1.07509 | 0.95242 |
| H | -4.61971 | -0.50855 | 0.68760 |
| C | -0.00536 | -0.54802 | -3.23680 |
| H | -0.35849 | -0.08935 | -4.15490 |
| H | 0.49366 | 0.21613 | -2.64964 |
| H | 0.74554 | -1.29086 | -3.51264 |
| C | -2.03366 | -2.08580 | -3.29617 |
| H | -1.49102 | -2.97592 | -3.61957 |
| H | -2.90642 | -2.41983 | -2.74611 |
| H | -2.38226 | -1.57651 | -4.18887 |

- TS($S_1$)

| Atom | x | y | z |
|---|---|---|---|
| C | -2.40900 | -0.28921 | 0.58580 |
| C | -1.55984 | -1.52005 | 0.21084 |
| H | -2.23860 | -2.35864 | 0.09839 |
| H | -0.92292 | -1.75380 | 1.06004 |
| C | -0.65977 | -1.35508 | -1.02653 |
| H | 0.02677 | -0.53514 | -0.83856 |
| H | -0.04566 | -2.24975 | -1.11461 |
| C | -1.36363 | -1.10795 | -2.36955 |
| H | -2.03666 | -0.23343 | -2.25199 |
| O | -1.67321 | 0.86254 | 0.66133 |
| C | -3.81946 | -0.06563 | 0.09661 |
| H | -4.05050 | -0.68248 | -0.76477 |
| H | -4.54099 | -0.30063 | 0.87336 |
| H | -3.96797 | 0.97080 | -0.18671 |
| C | -0.33392 | -0.74655 | -3.44465 |
| H | -0.81537 | -0.54409 | -4.39677 |
| H | 0.23354 | 0.13586 | -3.16556 |
| H | 0.37082 | -1.56021 | -3.59764 |
| C | -2.20642 | -2.30448 | -2.82312 |
| H | -1.58280 | -3.18453 | -2.95978 |
| H | -2.98218 | -2.56012 | -2.10915 |
| H | -2.69390 | -2.09662 | -3.77091 |

- TS 4

| Atom | x | y | z |
|---|---|---|---|
| C | -1.57310 | 0.19790 | 0.37012 |
| C | -1.23766 | 1.38487 | -0.25396 |
| H | -0.70740 | 2.12904 | 0.329786 |
| H | -1.83514 | 1.76101 | -1.08006 |
| C | 0.58320 | 0.67168 | -1.12663 |
| H | 0.13023 | 0.15463 | -1.97082 |
| H | 0.86178 | 1.70292 | -1.33078 |
| C | 1.30671 | -0.06967 | -0.18009 |
| H | 0.27171 | -0.18667 | 0.806427 |
| O | -0.75844 | -0.22226 | 1.321987 |
| C | -2.52358 | -0.80849 | -0.21276 |
| H | -3.07966 | -1.29996 | 0.590041 |
| H | -3.23243 | -0.34091 | -0.90095 |
| H | -1.96937 | -1.58795 | -0.75086 |
| C | 1.53596 | -1.55013 | -0.42907 |
| H | 1.68882 | -2.09550 | 0.507608 |
| H | 0.68183 | -1.99937 | -0.94425 |
| H | 2.42605 | -1.70416 | -1.05227 |
| C | 2.38199 | 0.63761 | 0.621253 |

| | | | |
|---|---|---|---|
| H | 2.09226 | 1.66962 | 0.843064 |
| H | 2.56700 | 0.12962 | 1.573317 |
| H | 3.33072 | 0.66322 | 0.070698 |

- TS 5

| Atom | x | y | z |
|---|---|---|---|
| C | -3.26594 | -0.34602 | 0.25725 |
| C | -2.60459 | -0.40791 | -1.1288 |
| H | -2.28423 | 0.61310 | -1.38347 |
| H | -3.37108 | -0.69889 | -1.8526 |
| C | -1.38492 | -1.34499 | -1.23795 |
| H | -0.62344 | -1.04457 | -0.51272 |
| H | -1.69368 | -2.36360 | -0.97607 |
| C | -0.70153 | -1.42347 | -2.62632 |
| H | -4.10293 | 1.31917 | -0.25294 |
| O | -4.32036 | 0.56672 | 0.330475 |
| C | -3.61575 | -1.61481 | 0.972916 |
| H | -2.71970 | -2.21491 | 1.160822 |
| H | -4.07912 | -1.37776 | 1.934702 |
| H | -4.32111 | -2.22532 | 0.393943 |
| C | 0.42730 | -2.40878 | -2.74708 |
| H | 0.80322 | -2.71631 | -1.76298 |
| H | 0.11545 | -3.32307 | -3.27092 |
| H | 1.27187 | -1.99039 | -3.308 |
| C | -0.75749 | -0.25607 | -3.56711 |
| H | -0.11234 | 0.57077 | -3.23482 |
| H | -0.41955 | -0.55077 | -4.56655 |
| H | -1.77292 | 0.14448 | -3.66638 |

- Product 4

| Atom | x | y | z |
|---|---|---|---|
| C | -2.37534 | -0.69941 | -0.31820 |
| C | -2.37652 | -2.02849 | -0.06151 |
| H | -1.54294 | -2.67486 | -0.33410 |
| H | -3.22181 | -2.49354 | 0.43838 |
| C | 1.05512 | -2.167141 | -2.41263 |
| H | 1.98441 | -1.72656 | -2.04867 |
| H | 0.82127 | -3.17196 | -2.05735 |
| C | 0.25354 | -1.51737 | -3.29646 |
| H | -0.59417 | -0.65294 | -1.22209 |
| O | -1.30914 | -0.02649 | -0.96505 |
| C | -3.47016 | 0.27591 | 0.03054 |
| H | -4.29902 | -0.24106 | 0.52956 |
| H | -3.08218 | 1.05813 | 0.69677 |
| H | -3.84708 | 0.76548 | -0.87760 |

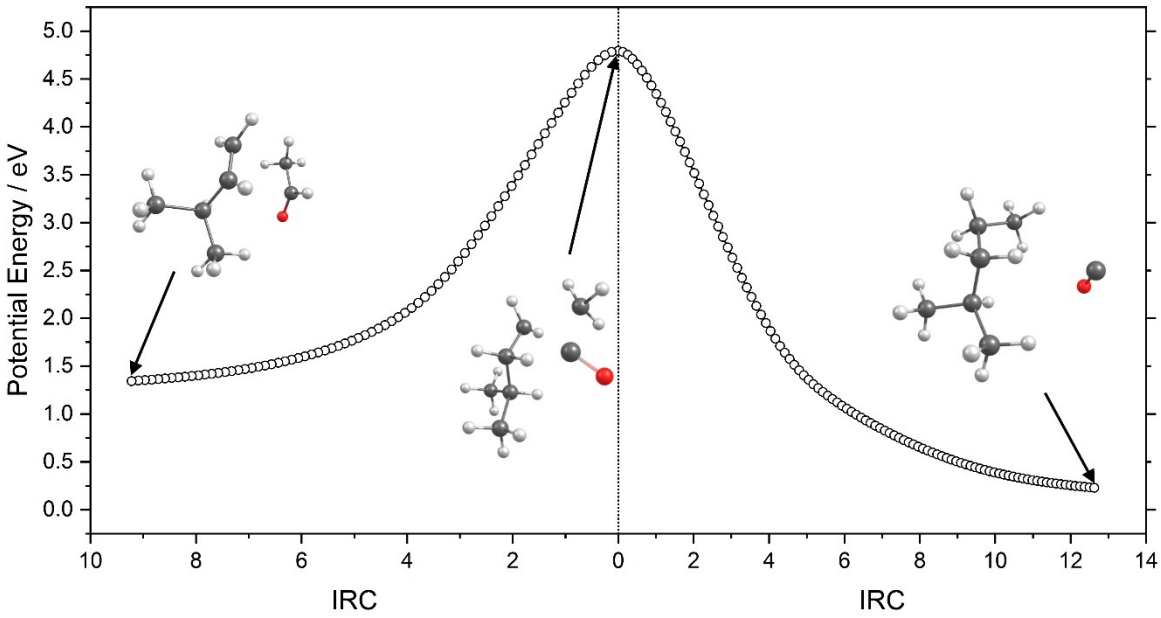
| | | | |
|---|---|---|---|
| C | 0.57874 | -0.12178 | -3.80926 |
| H | -0.20537 | 0.58845 | -3.50707 |
| H | 1.54008 | 0.23233 | -3.41226 |
| H | 0.63399 | -0.11571 | -4.90850 |
| C | -1.03642 | -2.13104 | -3.82087 |
| H | -1.01528 | -2.19666 | -4.91937 |
| H | -1.19072 | -3.14033 | -3.41518 |
| H | -1.89936 | -1.50871 | -3.53961 |

- Product 5

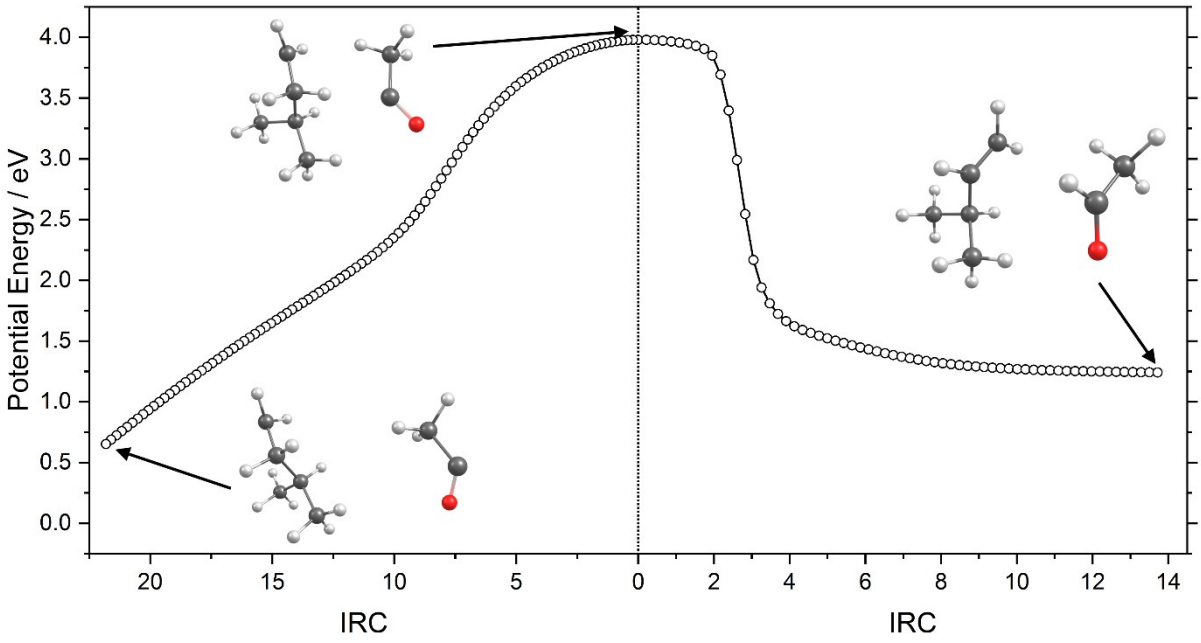
| Atom | x | y | z |
|---|---|---|---|
| C | -2.75068 | -0.76943 | -0.71474 |
| C | -2.60841 | -2.17650 | -0.06871 |
| H | -3.28361 | -2.88498 | -0.56397 |
| H | -2.74944 | -2.24157 | 1.018184 |
| C | -1.14517 | -2.24762 | -0.63299 |
| H | -0.40288 | -1.89842 | 0.100135 |
| H | -0.80664 | -3.20495 | -1.0512 |
| C | -1.51849 | -1.11610 | -1.6672 |
| H | -4.14588 | 0.29409 | -1.72886 |
| O | -4.06260 | -0.61303 | -1.36087 |
| C | -2.51240 | 0.38344 | 0.269321 |
| H | -1.58998 | 0.23354 | 0.846631 |
| H | -2.43072 | 1.34627 | -0.25902 |
| H | -3.35896 | 0.43411 | 0.967719 |
| C | -0.46419 | -0.02817 | -1.9244 |
| H | -0.88420 | 0.79757 | -2.52114 |
| H | -0.07298 | 0.38786 | -0.9855 |
| H | 0.38285 | -0.45155 | -2.48594 |
| C | -2.00300 | -1.72371 | -3.00072 |
| H | -1.14686 | -2.15848 | -3.53931 |
| H | -2.75359 | -2.50705 | -2.83779 |
| H | -2.45932 | -0.95212 | -3.63768 |

Figure S3: Intrinsic reaction paths associated with the various transition states.

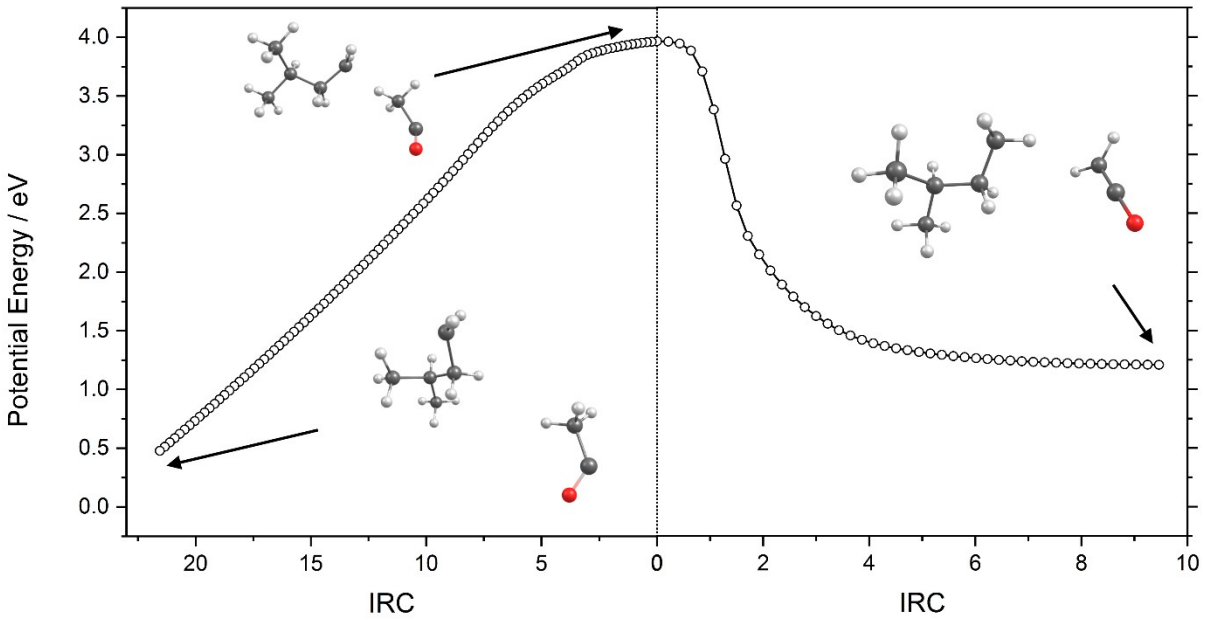
Reaction 1




Reaction 2



Reaction 3




Reaction 4