Supporting Information for:

# An Investigation of the Enolization and Isomeric Products Distribution in the Water Promoted Aldol Reaction of Tropinone and Granatanone

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## Contents:

Tables S2-S129 contains geometries (Å) for reactants, products and transition states in the gas phase calculated at the B3LYP/6-31g(d) level of theory for all reactions investigated in the paper.

| | Piperidinone ring | | | |
|---|---|---|---|---|
| Atoms | N9-C1-C2-C3-C4-C5 | | N19-C11-C12-C13-C14-C15 | |
| Compound | I | II | I | II |
| Q [Å] | 0.5092(11) | 0.506(2) | 0.5090(11) | 0.502(2) |
| θ [°] | 163.22(12) | 163.0(2) | 163.72(12) | 163.7(2) |
| φ [°] | 181.3(4) | 183.1(8) | 179.0(5) | 180.6(8) |
| | | | | |
| | Piperidine ring | | | |
| Atoms | N9-C1-C2-C3-C4-C5 | | N19-C11-C12-C13-C14-C15 | |
| Compound | I | II | I | II |
| Q [Å] | 0.5866(11) | 0.591(2) | 0.5814(11) | 0.587(2) |
| θ [°] | 8.97(12) | 9.14(19) | 9.16(11) | 9.3(2) |
| φ [°] | 355.3(7) | 358(13) | 4.0(7) | 354.7(12) |

**Table S1.** Puckering parameters of piperidinone and piperidine rings in crystal structures of 9-methyl-9-azabicyclo[3.3.1]nonan-3-one (compound I) and its hemihydrate (compound II).

| **Atom** | **x** | **y** | **z** |
|---|---|---|---|
| O | -0.98917 | 1.797876 | -0.18109 |
| C | -1.72136 | 0.666573 | 0.033364 |
| C | -2.96075 | 0.609176 | -0.82304 |
| C | -2.3343 | -1.51898 | 1.011187 |
| N | -2.96297 | -1.76191 | -0.307 |
| C | -3.67347 | -3.03213 | -0.40052 |
| C | -3.84476 | -0.58228 | -0.41399 |
| C | -4.47587 | -0.39255 | 1.009504 |
| C | -3.52786 | -1.18142 | 1.954928 |
| C | -1.41201 | -0.32181 | 0.886523 |
| H | -2.66828 | 0.521957 | -1.87857 |
| H | -3.51251 | 1.554214 | -0.72539 |
| H | -1.77622 | -2.40679 | 1.328135 |
| H | -4.09239 | -3.13238 | -1.40841 |
| H | -4.50081 | -3.16803 | 0.320595 |
| H | -2.96296 | -3.8532 | -0.25221 |
| H | -4.60743 | -0.75421 | -1.18072 |
| H | -5.49361 | -0.79508 | 1.042633 |
| H | -4.54182 | 0.66638 | 1.278691 |
| H | -4.00819 | -2.09474 | 2.327182 |
| H | -3.21324 | -0.59769 | 2.82476 |
| H | -0.53684 | -0.26167 | 1.528979 |
| H | -0.17029 | 1.765439 | 0.361172 |
| C | 2.111094 | 1.022833 | -0.22946 |
| O | 1.620304 | 1.486776 | 0.793226 |

| | | | |
|---|---|---|---|
| C | 3.518364 | 0.617505 | -0.36382 |
| C | 4.407097 | 0.750571 | 0.715963 |
| C | 3.970632 | 0.093524 | -1.58345 |
| C | 5.733657 | 0.361645 | 0.571299 |
| C | 5.300945 | -0.29581 | -1.72602 |
| C | 6.180124 | -0.16114 | -0.64884 |
| H | 1.482681 | 0.886456 | -1.1308 |
| H | 4.034723 | 1.158567 | 1.650495 |
| H | 3.276016 | -0.00719 | -2.41444 |
| H | 6.424526 | 0.462459 | 1.403513 |
| H | 5.65234 | -0.70226 | -2.66992 |
| H | 7.217927 | -0.46443 | -0.75824 |

**Table S2.** Geometry (Å) for reactant (anti) of the reaction tropinone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.29822 | 2.82804 | 0.081098 |
| C | -1.53115 | 1.554424 | 0.098917 |
| C | -2.75835 | 1.054979 | -0.63158 |
| C | -0.94081 | -0.83109 | 0.584056 |
| N | -1.64887 | -1.09896 | -0.6878 |
| C | -1.75236 | -2.51988 | -1.01159 |
| C | -2.95605 | -0.457 | -0.4322 |
| C | -3.32805 | -0.81707 | 1.044679 |
| C | -1.96906 | -1.1865 | 1.701234 |
| C | -0.60059 | 0.645327 | 0.622975 |
| H | -2.64021 | 1.290049 | -1.69827 |
| H | -3.62762 | 1.626462 | -0.28134 |
| H | -0.02894 | -1.43351 | 0.641241 |
| H | -2.27977 | -2.6317 | -1.96513 |
| H | -2.281 | -3.13131 | -0.25883 |
| H | -0.74617 | -2.93493 | -1.13368 |
| H | -3.69872 | -0.82646 | -1.14613 |
| H | -4.02423 | -1.6611 | 1.076241 |
| H | -3.82126 | 0.020124 | 1.549187 |
| H | -1.92256 | -2.25414 | 1.9439 |
| H | -1.77955 | -0.63593 | 2.627437 |
| H | 0.033204 | 0.989386 | 1.434606 |
| H | -0.15222 | 2.900458 | -0.17121 |
| C | 0.925944 | 1.277712 | -0.75855 |
| O | 0.995926 | 2.541281 | -0.5031 |
| C | 2.044813 | 0.388776 | -0.35736 |
| C | 3.001067 | 0.823564 | 0.572725 |
| C | 2.176115 | -0.88174 | -0.93728 |
| C | 4.062674 | -0.00597 | 0.923754 |
| C | 3.24142 | -1.71045 | -0.5849 |
| C | 4.184963 | -1.27509 | 0.348142 |
| H | 0.379932 | 0.942064 | -1.6516 |
| H | 2.900891 | 1.818539 | 0.994666 |
| H | 1.44193 | -1.21053 | -1.66919 |
| H | 4.802606 | 0.337407 | 1.641983 |
| H | 3.339045 | -2.69166 | -1.04188 |
| H | 5.017294 | -1.91849 | 0.620798 |

**Table S3.** Geometry (Å) for transition state (anti) of the reaction tropinone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.5767 | 2.9468 | 0.2367 |
| C | -1.6353 | 1.7289 | 0.1190 |
| C | -2.8556 | 1.0701 | -0.5124 |
| C | -0.8455 | -0.6218 | 0.6541 |
| N | -1.6366 | -1.0223 | -0.5290 |
| C | -1.6728 | -2.4682 | -0.7422 |
| C | -2.9578 | -0.4362 | -0.2265 |
| C | -3.2167 | -0.7246 | 1.2805 |
| C | -1.7890 | -0.8203 | 1.8827 |
| C | -0.4381 | 0.8551 | 0.4898 |
| C | 0.6855 | 1.1352 | -0.5792 |
| O | 1.1038 | 2.4864 | -0.4826 |
| C | 1.8990 | 0.2448 | -0.3870 |
| C | 2.8641 | 0.5590 | 0.5780 |
| C | 2.0681 | -0.9072 | -1.1641 |
| C | 3.9686 | -0.2709 | 0.7693 |
| C | 3.1721 | -1.7406 | -0.9722 |
| C | 4.1247 | -1.4252 | -0.0023 |
| H | -2.7504 | 1.2198 | -1.5961 |
| H | -3.7484 | 1.6229 | -0.1995 |
| H | 0.0529 | -1.2381 | 0.7257 |
| H | -2.2819 | -2.6858 | -1.6261 |
| H | -2.0817 | -3.0492 | 0.1036 |
| H | -0.6567 | -2.8261 | -0.9363 |
| H | -3.7213 | -0.8788 | -0.8741 |
| H | -3.7598 | -1.6668 | 1.4040 |
| H | -3.8251 | 0.0564 | 1.7484 |
| H | -1.6202 | -1.7999 | 2.3405 |
| H | -1.6077 | -0.0723 | 2.6613 |
| H | -0.0367 | 1.2350 | 1.4376 |
| H | 0.2603 | 0.9267 | -1.5729 |
| H | 0.3183 | 3.0232 | -0.2606 |
| H | 2.7531 | 1.4718 | 1.1545 |
| H | 1.3329 | -1.1466 | -1.9292 |
| H | 4.7140 | -0.0124 | 1.5172 |
| H | 3.2924 | -2.6287 | -1.5874 |
| H | 4.9881 | -2.0686 | 0.1453 |

**Table S4.** Geometry (Å) for product (HBO anti) of the reaction tropinone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.8849 | 2.8820 | -8.5712 |
| C | -0.1388 | 3.3607 | -7.3797 |
| C | 0.9828 | 2.3445 | -7.0856 |
| C | 0.4393 | 0.9277 | -6.9129 |
| C | -0.7343 | 0.5459 | -7.8216 |
| C | -1.6780 | 1.7618 | -7.9953 |
| C | -2.2067 | 2.2910 | -6.6288 |
| C | -1.1885 | 3.3974 | -6.2328 |
| C | -0.2487 | -0.0016 | -9.2097 |
| O | 0.9031 | 0.1536 | -6.0992 |
| O | 0.5858 | 0.9273 | -9.8751 |
| C | 0.4623 | -1.3386 | -9.0933 |
| C | 1.8529 | -1.4326 | -9.2008 |
| C | 2.4878 | -2.6704 | -9.0833 |
| C | 1.7421 | -3.8276 | -8.8570 |
| C | 0.3518 | -3.7421 | -8.7547 |
| C | -0.2806 | -2.5059 | -8.8769 |
| C | -1.7095 | 3.9188 | -9.1994 |
| H | 0.2959 | 4.3432 | -7.5882 |
| H | 1.5473 | 2.6137 | -6.1875 |
| H | 1.6773 | 2.3212 | -7.9350 |
| H | -1.2758 | -0.2642 | -7.3214 |
| H | -2.4867 | 1.4953 | -8.6846 |
| H | -3.2151 | 2.7026 | -6.7350 |
| H | -2.2652 | 1.4893 | -5.8861 |
| H | -1.6731 | 4.3774 | -6.1804 |
| H | -0.7265 | 3.2160 | -5.2576 |
| H | -1.1742 | -0.1663 | -9.7934 |
| H | 0.1792 | 1.8096 | -9.7032 |
| H | 2.4276 | -0.5334 | -9.3918 |
| H | 3.5698 | -2.7294 | -9.1708 |
| H | 2.2383 | -4.7903 | -8.7664 |
| H | -0.2401 | -4.6384 | -8.5877 |
| H | -1.3660 | -2.4491 | -8.8100 |
| H | -2.2384 | 3.4864 | -10.0545 |
| H | -2.4556 | 4.3703 | -8.5260 |
| H | -1.0587 | 4.7160 | -9.5722 |

**Table S5.** Geometry (Å) for product (HBN anti) of the reaction tropinone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.212553 | 1.117647 | 0.60333 |
| C | 1.242475 | 0.252628 | 0.358831 |
| C | 1.945091 | -0.18186 | 1.619088 |
| C | 2.797632 | -1.14386 | -0.95635 |
| N | 2.832283 | -1.9859 | 0.260278 |
| C | 3.755918 | -3.11139 | 0.174032 |
| C | 3.212521 | -0.98576 | 1.278311 |
| C | 4.317556 | -0.09717 | 0.609018 |
| C | 4.13436 | -0.34269 | -0.9144 |
| C | 1.619343 | -0.19478 | -0.84748 |
| H | 1.260233 | -0.79152 | 2.22473 |
| H | 2.196176 | 0.703498 | 2.219421 |
| H | 2.704917 | -1.77599 | -1.84608 |
| H | 3.710905 | -3.68197 | 1.108685 |
| H | 4.813758 | -2.84361 | -0.00497 |
| H | 3.437539 | -3.77552 | -0.63746 |
| H | 3.580363 | -1.49001 | 2.178036 |
| H | 5.316176 | -0.39888 | 0.94188 |
| H | 4.197044 | 0.957556 | 0.875986 |
| H | 4.962775 | -0.93345 | -1.32418 |
| H | 4.076833 | 0.585707 | -1.48981 |
| H | 1.130229 | 0.147944 | -1.75621 |
| H | -0.25598 | 1.317648 | -0.23502 |
| C | -2.60731 | 1.330177 | -1.84686 |
| O | -1.41709 | 1.556649 | -1.67959 |
| C | -3.54071 | 0.771684 | -0.85494 |
| C | -3.11862 | 0.402751 | 0.435123 |
| C | -4.88528 | 0.609426 | -1.22492 |
| C | -4.04185 | -0.11854 | 1.335549 |
| C | -5.80539 | 0.088056 | -0.31904 |
| C | -5.3815 | -0.27536 | 0.961591 |
| H | -3.06439 | 1.557728 | -2.83216 |
| H | -2.07734 | 0.523296 | 0.719148 |
| H | -5.20321 | 0.895856 | -2.22519 |
| H | -3.71996 | -0.4058 | 2.33241 |
| H | -6.84547 | -0.03557 | -0.60659 |
| H | -6.09625 | -0.68348 | 1.671329 |

**Table S6.** Geometry (Å) for reactant (syn) of the reaction tropinone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.723318 | 2.63769 | 0.718959 |
| C | 1.073468 | 1.421013 | 0.453976 |
| C | 1.326798 | 0.485063 | 1.610296 |
| C | 1.532117 | -0.48652 | -1.10232 |
| N | 1.068619 | -1.31845 | 0.023285 |
| C | 1.151401 | -2.75324 | -0.22386 |
| C | 1.931648 | -0.84258 | 1.120414 |
| C | 3.355972 | -0.65809 | 0.494959 |
| C | 3.0901 | -0.5535 | -1.03305 |
| C | 1.069252 | 0.940979 | -0.86715 |
| H | 0.368941 | 0.300338 | 2.11582 |
| H | 1.979343 | 0.991427 | 2.332848 |
| H | 1.134344 | -0.87359 | -2.04723 |
| H | 0.793733 | -3.28816 | 0.66227 |
| H | 2.162566 | -3.13067 | -0.46264 |
| H | 0.489057 | -3.01183 | -1.05683 |
| H | 1.930319 | -1.56878 | 1.938678 |
| H | 3.99675 | -1.51485 | 0.725558 |
| H | 3.858455 | 0.230084 | 0.89208 |
| H | 3.461464 | -1.4391 | -1.56096 |
| H | 3.566039 | 0.319492 | -1.48983 |
| H | 1.321162 | 1.662497 | -1.63985 |
| H | -0.10073 | 2.872471 | -0.06374 |
| C | -0.95558 | 1.404754 | -1.23253 |
| O | -0.98694 | 2.6631 | -0.92921 |
| C | -1.82333 | 0.439085 | -0.50308 |
| C | -2.39938 | 0.796556 | 0.724694 |
| C | -2.12201 | -0.81094 | -1.06131 |
| C | -3.24251 | -0.09215 | 1.389142 |
| C | -2.97103 | -1.69646 | -0.40089 |
| C | -3.52967 | -1.34017 | 0.829205 |
| H | -0.79695 | 1.144207 | -2.2886 |
| H | -2.19051 | 1.780159 | 1.133304 |
| H | -1.69452 | -1.08284 | -2.02425 |
| H | -3.68792 | 0.192578 | 2.338893 |
| H | -3.20326 | -2.66043 | -0.84605 |
| H | -4.19527 | -2.02805 | 1.344106 |

**Table S7.** Geometry (Å) for transition state (syn) of the reaction tropinone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.5557 | 2.5293 | 1.0009 |
| C | 0.9057 | 1.3918 | 0.7050 |
| C | 1.3519 | 0.4164 | 1.7820 |
| C | 1.5182 | -0.4375 | -0.9784 |
| N | 1.1877 | -1.3393 | 0.1395 |
| C | 1.3760 | -2.7542 | -0.1631 |
| C | 2.0534 | -0.8279 | 1.2171 |
| C | 3.4246 | -0.4879 | 0.5522 |
| C | 3.0718 | -0.3077 | -0.9489 |
| C | 0.8368 | 0.9298 | -0.7501 |
| C | -0.6364 | 1.0547 | -1.2868 |
| O | -1.0114 | 2.4214 | -1.3041 |
| C | -1.6672 | 0.1791 | -0.5818 |
| C | -2.3294 | 0.6225 | 0.5701 |
| C | -1.9972 | -1.0782 | -1.1004 |
| C | -3.2720 | -0.1875 | 1.2045 |
| C | -2.9411 | -1.8903 | -0.4710 |
| C | -3.5784 | -1.4485 | 0.6893 |
| H | 0.4332 | 0.1033 | 2.2963 |
| H | 1.9632 | 0.9595 | 2.5121 |
| H | 1.1625 | -0.8659 | -1.9215 |
| H | 1.1369 | -3.3447 | 0.7274 |
| H | 2.3957 | -3.0284 | -0.4899 |
| H | 0.6764 | -3.0472 | -0.9527 |
| H | 2.1510 | -1.5790 | 2.0068 |
| H | 4.1407 | -1.3029 | 0.6954 |
| H | 3.8745 | 0.4102 | 0.9891 |
| H | 3.5265 | -1.1000 | -1.5523 |
| H | 3.4204 | 0.6448 | -1.3601 |
| H | 1.3744 | 1.6918 | -1.3301 |
| H | -0.5930 | 0.7362 | -2.3367 |
| H | -0.6282 | 2.8319 | -0.5040 |
| H | -2.1210 | 1.6137 | 0.9603 |
| H | -1.5185 | -1.4219 | -2.0154 |
| H | -3.7781 | 0.1736 | 2.0963 |
| H | -3.1870 | -2.8614 | -0.8932 |
| H | -4.3191 | -2.0750 | 1.1794 |

**Table S8.** Geometry (Å) for product (HBO syn) of the reaction tropinone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.4927 | -1.1581 | -0.8113 |
| C | -5.7999 | -2.3653 | -1.3292 |
| C | -4.8070 | -2.8361 | -0.2504 |
| C | -3.8627 | -1.7251 | 0.2015 |
| C | -4.4276 | -0.2990 | 0.1899 |
| C | -5.4384 | -0.1172 | -0.9639 |
| C | -4.7903 | -0.3865 | -2.3541 |
| C | -5.0676 | -1.8934 | -2.6167 |
| C | -5.0353 | 0.0190 | 1.5978 |
| O | -2.7315 | -1.9536 | 0.5842 |
| O | -6.0705 | -0.8912 | 1.9256 |
| C | -7.7313 | -0.8404 | -1.5287 |
| C | -5.4722 | 1.4812 | 1.7064 |
| C | -6.8111 | 1.8166 | 1.9303 |
| C | -7.2037 | 3.1540 | 2.0289 |
| C | -6.2606 | 4.1747 | 1.9106 |
| C | -4.9181 | 3.8492 | 1.7004 |
| C | -4.5291 | 2.5140 | 1.6007 |
| H | -6.5329 | -3.1539 | -1.5260 |
| H | -4.2099 | -3.6887 | -0.5892 |
| H | -5.3658 | -3.1480 | 0.6416 |
| H | -3.5769 | 0.3735 | 0.0381 |
| H | -5.8912 | 0.8758 | -0.8963 |
| H | -5.2508 | 0.2393 | -3.1249 |
| H | -3.7215 | -0.1509 | -2.3502 |
| H | -5.7042 | -2.0286 | -3.4967 |
| H | -4.1527 | -2.4673 | -2.7940 |
| H | -4.2310 | -0.1502 | 2.3258 |
| H | -6.5409 | -1.0777 | 1.0779 |
| H | -8.1665 | 0.0686 | -1.1021 |
| H | -7.5971 | -0.6822 | -2.6109 |
| H | -8.4455 | -1.6581 | -1.3890 |
| H | -7.5346 | 1.0176 | 2.0531 |
| H | -8.2487 | 3.3961 | 2.2068 |
| H | -6.5649 | 5.2150 | 1.9903 |
| H | -4.1723 | 4.6360 | 1.6200 |
| H | -3.4781 | 2.2738 | 1.4512 |

**Table S9.** Geometry (Å) for product (HBN syn) of the reaction tropinone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.96756 | 2.2114 | -0.52716 |
| C | -2.68207 | 1.095959 | -0.19085 |
| C | -3.84909 | 0.858457 | -1.11444 |
| C | -3.30004 | -0.94015 | 1.064653 |
| N | -3.81349 | -1.40623 | -0.24279 |
| C | -4.47237 | -2.70687 | -0.19077 |
| C | -4.72277 | -0.29687 | -0.5939 |
| C | -5.47203 | 0.074489 | 0.732191 |
| C | -4.57246 | -0.5109 | 1.855932 |
| C | -2.40652 | 0.261827 | 0.823202 |
| H | -3.47355 | 0.628197 | -2.12103 |
| H | -4.43709 | 1.782382 | -1.20085 |
| H | -2.74189 | -1.74475 | 1.555547 |
| H | -4.80839 | -2.97607 | -1.19859 |
| H | -5.3479 | -2.76931 | 0.481765 |
| H | -3.74859 | -3.4637 | 0.132082 |
| H | -5.41449 | -0.61542 | -1.38051 |
| H | -6.47186 | -0.37113 | 0.753018 |
| H | -5.6028 | 1.15706 | 0.827634 |
| H | -5.04797 | -1.37354 | 2.338206 |
| H | -4.34385 | 0.217455 | 2.639154 |
| H | -1.58902 | 0.456961 | 1.513206 |
| H | -1.18885 | 2.28905 | 0.063185 |
| C | 1.058901 | 1.305404 | -0.34396 |
| O | 0.636924 | 2.019803 | 0.553718 |
| C | 2.438814 | 0.776878 | -0.39116 |
| C | 3.355883 | 1.098476 | 0.622549 |
| C | 2.823649 | -0.05107 | -1.4549 |
| C | 4.64977 | 0.596586 | 0.57515 |
| C | 4.11706 | -0.56223 | -1.51419 |
| C | 5.005388 | -0.22648 | -0.49517 |
| N | 6.380929 | -0.76452 | -0.54953 |
| O | 7.147408 | -0.45377 | 0.359607 |
| O | 6.669851 | -1.48811 | -1.50022 |
| H | 0.399855 | 1.015943 | -1.18369 |
| H | 3.034276 | 1.741041 | 1.435554 |
| H | 2.107474 | -0.29676 | -2.23476 |
| H | 5.382263 | 0.824937 | 1.339304 |
| H | 4.444901 | -1.20557 | -2.32098 |

**Table S10.** Geometry (Å) for reactant (anti) of the reaction tropinone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.214 | 3.136693 | -0.04099 |
| C | -2.43576 | 1.860517 | -0.03179 |
| C | -3.67128 | 1.360536 | -0.74183 |
| C | -1.82442 | -0.52066 | 0.435866 |
| N | -2.54851 | -0.78596 | -0.82653 |
| C | -2.64909 | -2.20696 | -1.15564 |
| C | -3.85674 | -0.15395 | -0.54927 |
| C | -4.20686 | -0.52529 | 0.928936 |
| C | -2.83522 | -0.87588 | 1.569273 |
| C | -1.48247 | 0.957043 | 0.470855 |
| H | -3.57066 | 1.604026 | -1.80846 |
| H | -4.53667 | 1.926805 | -0.37432 |
| H | -0.91319 | -1.12455 | 0.482133 |
| H | -3.18835 | -2.3167 | -2.10241 |
| H | -3.16447 | -2.82279 | -0.39807 |
| H | -1.64302 | -2.6172 | -1.29306 |
| H | -4.60599 | -0.52198 | -1.25651 |
| H | -4.88778 | -1.38127 | 0.963419 |
| H | -4.70958 | 0.3003 | 1.442999 |
| H | -2.77377 | -1.94072 | 1.818892 |
| H | -2.63876 | -0.31716 | 2.489095 |
| H | -0.86224 | 1.302586 | 1.292934 |
| H | -1.09944 | 3.232231 | -0.27234 |
| C | 0.004387 | 1.607813 | -0.89468 |
| O | 0.082973 | 2.868908 | -0.64398 |
| C | 1.129509 | 0.719138 | -0.48878 |
| C | 2.085155 | 1.169354 | 0.435818 |
| C | 1.26603 | -0.55533 | -1.06105 |
| C | 3.150566 | 0.355398 | 0.799814 |
| C | 2.328757 | -1.38074 | -0.70688 |
| C | 3.254812 | -0.91224 | 0.22402 |
| N | 4.379815 | -1.77893 | 0.60537 |
| O | 5.186693 | -1.34139 | 1.425602 |
| O | 4.44665 | -2.89258 | 0.083952 |
| H | -0.52458 | 1.269671 | -1.79805 |
| H | 1.982068 | 2.168445 | 0.845596 |
| H | 0.5357 | -0.89393 | -1.79109 |
| H | 3.901157 | 0.680771 | 1.509643 |
| H | 2.455781 | -2.36659 | -1.13672 |

**Table S11.** Geometry (Å) for transition state (anti) of the reaction tropinone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.5480 | 3.2092 | -0.0560 |
| C | -2.5683 | 1.9904 | -0.1685 |
| C | -3.7032 | 1.2937 | -0.9067 |
| C | -1.7749 | -0.3348 | 0.4702 |
| N | -2.4384 | -0.7715 | -0.7763 |
| C | -2.4277 | -2.2226 | -0.9633 |
| C | -3.7957 | -0.2113 | -0.6117 |
| C | -4.1923 | -0.4858 | 0.8674 |
| C | -2.8279 | -0.5324 | 1.6069 |
| C | -1.3870 | 1.1493 | 0.3202 |
| H | -3.4958 | 1.4356 | -1.9768 |
| H | -4.6359 | 1.8262 | -0.6905 |
| H | -0.8761 | -0.9313 | 0.6422 |
| H | -2.9474 | -2.4677 | -1.8955 |
| H | -2.9026 | -2.7955 | -0.1478 |
| H | -1.3922 | -2.5654 | -1.0556 |
| H | -4.4824 | -0.6798 | -1.3235 |
| H | -4.7191 | -1.4411 | 0.9537 |
| H | -4.8638 | 0.2843 | 1.2608 |
| H | -2.6803 | -1.4975 | 2.1009 |
| H | -2.7406 | 0.2357 | 2.3821 |
| H | -1.0801 | 1.5504 | 1.2942 |
| H | -0.6187 | 3.3363 | -0.3673 |
| C | -0.1888 | 1.4576 | -0.6542 |
| O | 0.1930 | 2.8145 | -0.5232 |
| C | 1.0268 | 0.5971 | -0.3660 |
| C | 1.9348 | 0.9667 | 0.6358 |
| C | 1.2553 | -0.5773 | -1.0965 |
| C | 3.0420 | 0.1729 | 0.9184 |
| C | 2.3571 | -1.3845 | -0.8263 |
| C | 3.2349 | -0.9967 | 0.1839 |
| N | 4.4018 | -1.8418 | 0.4771 |
| O | 5.1647 | -1.4755 | 1.3711 |
| O | 4.5463 | -2.8691 | -0.1867 |
| H | -0.5239 | 1.2398 | -1.6796 |
| H | 1.7771 | 1.8959 | 1.1721 |
| H | 0.5655 | -0.8560 | -1.8886 |
| H | 3.7562 | 0.4437 | 1.6864 |
| H | 2.5506 | -2.2924 | -1.3841 |

**Table S12.** Geometry (Å) for product (anti HBO) of the reaction tropinone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.94033 | 2.849669 | -8.93296 |
| C | -0.12448 | 3.58549 | -7.933 |
| C | 1.07768 | 2.695586 | -7.55961 |
| C | 0.651406 | 1.30657 | -7.09142 |
| C | -0.58808 | 0.713898 | -7.77534 |
| C | -1.61283 | 1.832951 | -8.07885 |
| C | -2.04385 | 2.592489 | -6.78892 |
| C | -1.07201 | 3.804352 | -6.72104 |
| C | -0.19963 | -0.07199 | -9.07573 |
| O | 1.260068 | 0.697602 | -6.2345 |
| O | 0.505271 | 0.742652 | -9.98914 |
| C | 0.61328 | -1.31884 | -8.7741 |
| C | -0.01137 | -2.44082 | -8.21026 |
| C | 0.711212 | -3.59084 | -7.9163 |
| C | 2.075981 | -3.61101 | -8.20267 |
| C | 2.72241 | -2.51693 | -8.77254 |
| C | 1.982861 | -1.3718 | -9.05663 |
| C | -1.8785 | 3.705328 | -9.66787 |
| N | 2.848781 | -4.82377 | -7.90239 |
| O | 4.049856 | -4.8217 | -8.17399 |
| O | 2.250761 | -5.7744 | -7.39601 |
| H | 0.231346 | 4.52432 | -8.36805 |
| H | 1.693436 | 3.15332 | -6.77933 |
| H | 1.706119 | 2.551193 | -8.44811 |
| H | -1.02908 | -0.00224 | -7.07361 |
| H | -2.46451 | 1.407274 | -8.62066 |
| H | -3.08418 | 2.923503 | -6.86165 |
| H | -1.97569 | 1.950043 | -5.90552 |
| H | -1.61532 | 4.749234 | -6.81932 |
| H | -0.51838 | 3.849726 | -5.77841 |
| H | -1.15822 | -0.40284 | -9.51766 |
| H | 0.069997 | 1.628431 | -9.93773 |
| H | -1.07877 | -2.41885 | -8.00258 |
| H | 0.242794 | -4.46465 | -7.48086 |
| H | 3.782778 | -2.575 | -8.98512 |
| H | 2.458735 | -0.51222 | -9.51286 |
| H | -2.44423 | 3.091307 | -10.3755 |
| H | -2.596 | 4.23935 | -9.02521 |
| H | -1.31265 | 4.446754 | -10.2402 |

**Table S13.** Geometry (Å) for product (anti HBN) of the reaction tropinone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.099044 | 1.73828 | 0.614595 |
| C | 2.046513 | 0.813739 | 0.261497 |
| C | 2.720077 | 0.188662 | 1.454843 |
| C | 3.44244 | -0.57652 | -1.22521 |
| N | 3.408835 | -1.53986 | -0.10262 |
| C | 4.215104 | -2.73538 | -0.32448 |
| C | 3.898677 | -0.69377 | 1.003928 |
| C | 5.077753 | 0.148822 | 0.404877 |
| C | 4.850539 | 0.085636 | -1.13142 |
| C | 2.363285 | 0.463253 | -0.99246 |
| H | 1.988323 | -0.41188 | 2.01284 |
| H | 3.064253 | 0.980021 | 2.134773 |
| H | 3.277367 | -1.10039 | -2.17278 |
| H | 4.125532 | -3.39217 | 0.548157 |
| H | 5.291782 | -2.55466 | -0.49933 |
| H | 3.821829 | -3.27813 | -1.19135 |
| H | 4.225383 | -1.32216 | 1.838742 |
| H | 6.045124 | -0.28391 | 0.679801 |
| H | 5.067613 | 1.176031 | 0.782808 |
| H | 5.611299 | -0.53403 | -1.62124 |
| H | 4.875028 | 1.07125 | -1.60499 |
| H | 1.899643 | 0.94488 | -1.85035 |
| H | 0.654332 | 2.069549 | -0.19216 |
| C | -1.68886 | 2.047579 | -1.89304 |
| O | -0.56553 | 2.435788 | -1.61792 |
| C | -2.54129 | 1.186742 | -1.0438 |
| C | -2.09968 | 0.719318 | 0.206378 |
| C | -3.81584 | 0.839132 | -1.51763 |
| C | -2.93105 | -0.08872 | 0.973384 |
| C | -4.65539 | 0.03124 | -0.75799 |
| C | -4.19307 | -0.4173 | 0.477193 |
| N | -5.07734 | -1.27563 | 1.293605 |
| O | -4.65054 | -1.65904 | 2.38017 |
| O | -6.18378 | -1.5503 | 0.832914 |
| H | -2.14814 | 2.346587 | -2.85708 |
| H | -1.11146 | 0.986249 | 0.56944 |
| H | -4.14899 | 1.204078 | -2.48599 |
| H | -2.62219 | -0.46714 | 1.939811 |
| H | -5.64329 | -0.25323 | -1.09766 |

**Table S14.** Geometry (Å) for reactant (syn) of the reaction tropinone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.490762 | 2.994101 | 0.506526 |
| C | 1.831464 | 1.77489 | 0.235129 |
| C | 2.087518 | 0.837477 | 1.386525 |
| C | 2.267243 | -0.12619 | -1.33281 |
| N | 1.796101 | -0.95545 | -0.20817 |
| C | 1.862948 | -2.39173 | -0.46092 |
| C | 2.671362 | -0.49645 | 0.887765 |
| C | 4.094823 | -0.32923 | 0.257692 |
| C | 3.824388 | -0.2074 | -1.26821 |
| C | 1.817195 | 1.305546 | -1.09269 |
| H | 1.134215 | 0.664805 | 1.905045 |
| H | 2.753059 | 1.336911 | 2.10196 |
| H | 1.864456 | -0.50553 | -2.27852 |
| H | 1.499907 | -2.92601 | 0.423062 |
| H | 2.87017 | -2.77669 | -0.70089 |
| H | 1.198612 | -2.64068 | -1.29506 |
| H | 2.662323 | -1.22503 | 1.703373 |
| H | 4.721876 | -1.19845 | 0.477967 |
| H | 4.61412 | 0.546559 | 0.660468 |
| H | 4.184638 | -1.09111 | -1.8061 |
| H | 4.307537 | 0.664829 | -1.71878 |
| H | 2.098805 | 2.029856 | -1.85283 |
| H | 0.710665 | 3.25505 | -0.26663 |
| C | -0.1651 | 1.795899 | -1.47968 |
| O | -0.21562 | 3.04484 | -1.15647 |
| C | -1.04187 | 0.814897 | -0.76836 |
| C | -1.63357 | 1.165467 | 0.454715 |
| C | -1.3291 | -0.433 | -1.33964 |
| C | -2.47484 | 0.275378 | 1.112935 |
| C | -2.1742 | -1.33139 | -0.6994 |
| C | -2.73043 | -0.96415 | 0.525908 |
| N | -3.62162 | -1.90907 | 1.21355 |
| O | -4.1012 | -1.56282 | 2.29348 |
| O | -3.83429 | -2.99455 | 0.671478 |
| H | -0.00751 | 1.546931 | -2.53957 |
| H | -1.43676 | 2.148824 | 0.868105 |
| H | -0.89449 | -0.69731 | -2.30035 |
| H | -2.94222 | 0.524277 | 2.057775 |
| H | -2.41361 | -2.29749 | -1.126 |

**Table S15.** Geometry (Å) for transition state (syn) of the reaction tropinone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.5480 | 3.2092 | -0.0560 |
| C | -2.5683 | 1.9904 | -0.1685 |
| C | -3.7032 | 1.2937 | -0.9067 |
| C | -1.7749 | -0.3348 | 0.4702 |
| N | -2.4384 | -0.7715 | -0.7763 |
| C | -2.4277 | -2.2226 | -0.9633 |
| C | -3.7957 | -0.2113 | -0.6117 |
| C | -4.1923 | -0.4858 | 0.8674 |
| C | -2.8279 | -0.5324 | 1.6069 |
| C | -1.3870 | 1.1493 | 0.3202 |
| H | -3.4958 | 1.4356 | -1.9768 |
| H | -4.6359 | 1.8262 | -0.6905 |
| H | -0.8761 | -0.9313 | 0.6422 |
| H | -2.9474 | -2.4677 | -1.8955 |
| H | -2.9026 | -2.7955 | -0.1478 |
| H | -1.3922 | -2.5654 | -1.0556 |
| H | -4.4824 | -0.6798 | -1.3235 |
| H | -4.7191 | -1.4411 | 0.9537 |
| H | -4.8638 | 0.2843 | 1.2608 |
| H | -2.6803 | -1.4975 | 2.1009 |
| H | -2.7406 | 0.2357 | 2.3821 |
| H | -1.0801 | 1.5504 | 1.2942 |
| H | -0.6187 | 3.3363 | -0.3673 |
| C | -0.1888 | 1.4576 | -0.6542 |
| O | 0.1930 | 2.8145 | -0.5232 |
| C | 1.0268 | 0.5971 | -0.3660 |
| C | 1.9348 | 0.9667 | 0.6358 |
| C | 1.2553 | -0.5773 | -1.0965 |
| C | 3.0420 | 0.1729 | 0.9184 |
| C | 2.3571 | -1.3845 | -0.8263 |
| C | 3.2349 | -0.9967 | 0.1839 |
| N | 4.4018 | -1.8418 | 0.4771 |
| O | 5.1647 | -1.4755 | 1.3711 |
| O | 4.5463 | -2.8691 | -0.1867 |
| H | -0.5239 | 1.2398 | -1.6796 |
| H | 1.7771 | 1.8959 | 1.1721 |
| H | 0.5655 | -0.8560 | -1.8886 |
| H | 3.7562 | 0.4437 | 1.6864 |
| H | 2.5506 | -2.2924 | -1.3841 |

**Table S16.** Geometry (Å) for product (syn HBO) of the reaction tropinone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.3465 | -1.2747 | -0.8220 |
| C | -5.5826 | -2.4839 | -1.2230 |
| C | -4.6472 | -2.8550 | -0.0569 |
| C | -3.7770 | -1.6856 | 0.3941 |
| C | -4.3853 | -0.2815 | 0.2569 |
| C | -5.3205 | -0.2056 | -0.9709 |
| C | -4.5674 | -0.5329 | -2.2943 |
| C | -4.7852 | -2.0598 | -2.4876 |
| C | -5.0973 | 0.0913 | 1.6004 |
| O | -2.6711 | -1.8455 | 0.8717 |
| O | -6.1471 | -0.8073 | 1.8982 |
| C | -7.5474 | -1.0451 | -1.6334 |
| C | -5.5524 | 1.5513 | 1.6071 |
| C | -6.9104 | 1.8773 | 1.7044 |
| C | -7.3288 | 3.2062 | 1.7063 |
| C | -6.3696 | 4.2118 | 1.6165 |
| C | -5.0074 | 3.9215 | 1.5369 |
| C | -4.6092 | 2.5896 | 1.5343 |
| N | -6.8020 | 5.6162 | 1.6132 |
| O | -5.9311 | 6.4836 | 1.5382 |
| O | -8.0100 | 5.8444 | 1.6824 |
| H | -6.2751 | -3.3085 | -1.4171 |
| H | -3.9980 | -3.7001 | -0.3066 |
| H | -5.2532 | -3.1421 | 0.8126 |
| H | -3.5465 | 0.4092 | 0.1222 |
| H | -5.8117 | 0.7712 | -0.9993 |
| H | -4.9868 | 0.0351 | -3.1301 |
| H | -3.5083 | -0.2648 | -2.2288 |
| H | -5.3621 | -2.2621 | -3.3952 |
| H | -3.8454 | -2.6131 | -2.5760 |
| H | -4.3449 | -0.0240 | 2.3923 |
| H | -6.5248 | -1.0818 | 1.0260 |
| H | -8.0421 | -0.1320 | -1.2883 |
| H | -7.3474 | -0.9411 | -2.7116 |
| H | -8.2393 | -1.8812 | -1.4923 |
| H | -7.6327 | 1.0750 | 1.8039 |
| H | -8.3760 | 3.4728 | 1.7815 |
| H | -4.2905 | 4.7316 | 1.4831 |
| H | -3.5484 | 2.3563 | 1.4855 |

**Table S17.** Geometry (Å) for product (syn HBN) of the reaction tropinone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -0.97672 | 1.867294 | -0.31101 |
| C | -1.68831 | 0.739894 | -0.0183 |
| C | -2.88816 | 0.565194 | -0.91413 |
| C | -2.28349 | -1.36299 | 1.134552 |
| N | -2.8451 | -1.74788 | -0.17985 |
| C | -3.51497 | -3.04352 | -0.18169 |
| C | -3.75477 | -0.6127 | -0.43453 |
| C | -4.4568 | -0.31585 | 0.935631 |
| C | -3.52594 | -0.974 | 1.991782 |
| C | -1.38771 | -0.15566 | 0.934641 |
| H | -0.17231 | 1.901389 | 0.251969 |
| H | -2.54769 | 0.392161 | -1.9444 |
| H | -3.47065 | 1.496676 | -0.92679 |
| H | -1.71717 | -2.19955 | 1.558139 |
| H | -3.88475 | -3.25182 | -1.19225 |
| H | -4.37016 | -3.13734 | 0.51323 |
| H | -2.7892 | -3.82358 | 0.074788 |
| H | -4.47483 | -0.87949 | -1.2151 |
| H | -5.45972 | -0.75435 | 0.963425 |
| H | -4.57355 | 0.760088 | 1.09964 |
| H | -3.99348 | -1.86093 | 2.436764 |
| H | -3.26586 | -0.29545 | 2.809188 |
| H | -0.54187 | -0.01061 | 1.60223 |
| C | 2.101399 | 1.096341 | -0.26324 |
| O | 1.625602 | 1.669209 | 0.710504 |
| C | 3.502073 | 0.668526 | -0.36827 |
| C | 4.404838 | 0.908808 | 0.682715 |
| C | 3.941577 | 0.012898 | -1.52863 |
| C | 5.727 | 0.50067 | 0.577163 |
| C | 5.264098 | -0.40223 | -1.64844 |
| C | 6.132162 | -0.14888 | -0.58985 |
| F | 7.411158 | -0.54495 | -0.6948 |
| H | 1.462224 | 0.870923 | -1.13844 |
| H | 4.046144 | 1.417144 | 1.57204 |
| H | 3.240817 | -0.17264 | -2.33907 |
| H | 6.447512 | 0.671299 | 1.370031 |
| H | 5.630909 | -0.91156 | -2.53297 |

**Table S18.** Geometry (Å) for reactant (anti) of the reaction tropinone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.32138 | 2.824383 | 0.106088 |
| C | -1.55175 | 1.550484 | 0.119163 |
| C | -2.77657 | 1.051204 | -0.61497 |
| C | -0.95635 | -0.83563 | 0.595759 |
| N | -1.66059 | -1.09993 | -0.67902 |
| C | -1.76147 | -2.5201 | -1.00806 |
| C | -2.97024 | -0.46224 | -0.4232 |
| C | -3.34435 | -0.82974 | 1.051233 |
| C | -1.98589 | -1.19839 | 1.709222 |
| C | -0.61899 | 0.641384 | 0.640592 |
| H | -2.65804 | 1.29242 | -1.68026 |
| H | -3.64781 | 1.618416 | -0.26274 |
| H | -0.04353 | -1.43685 | 0.653007 |
| H | -2.28449 | -2.62912 | -1.96427 |
| H | -2.2929 | -3.13416 | -0.25964 |
| H | -0.75458 | -2.93448 | -1.127 |
| H | -3.71021 | -0.83048 | -1.14047 |
| H | -4.03851 | -1.67554 | 1.077957 |
| H | -3.84063 | 0.004119 | 1.558186 |
| H | -1.93701 | -2.26692 | 1.947232 |
| H | -1.79981 | -0.65145 | 2.638249 |
| H | 0.010113 | 0.983794 | 1.456668 |
| H | -0.17434 | 2.90016 | -0.13746 |
| C | 0.906518 | 1.28215 | -0.73317 |
| O | 0.976786 | 2.544048 | -0.46722 |
| C | 2.02926 | 0.394953 | -0.34408 |
| C | 2.992182 | 0.829865 | 0.580283 |
| C | 2.162514 | -0.87443 | -0.92703 |
| C | 4.06105 | 0.010329 | 0.927802 |
| C | 3.229014 | -1.7058 | -0.58919 |
| C | 4.159906 | -1.24722 | 0.336858 |
| F | 5.196103 | -2.04337 | 0.668245 |
| H | 0.361305 | 0.953478 | -1.6292 |
| H | 2.893189 | 1.823201 | 1.005576 |
| H | 1.425851 | -1.2069 | -1.6541 |
| H | 4.818925 | 0.328302 | 1.636415 |
| H | 3.352811 | -2.68833 | -1.03261 |

**Table S19.** Geometry (Å) for transition state (anti) of the reaction tropinone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.9444 | 2.8354 | -8.9325 |
| C | -0.1159 | 3.5756 | -7.9472 |
| C | 1.0909 | 2.6870 | -7.5842 |
| C | 0.6635 | 1.3070 | -7.0892 |
| C | -0.5724 | 0.7047 | -7.7670 |
| C | -1.6029 | 1.8208 | -8.0652 |
| C | -2.0218 | 2.5884 | -6.7757 |
| C | -1.0479 | 3.7997 | -6.7236 |
| C | -0.1937 | -0.0887 | -9.0671 |
| O | 1.2654 | 0.7218 | -6.2108 |
| O | 0.5068 | 0.7239 | -9.9894 |
| C | 0.6171 | -1.3384 | -8.7728 |
| C | -0.0123 | -2.4752 | -8.2505 |
| C | 0.7104 | -3.6303 | -7.9582 |
| C | 2.0786 | -3.6365 | -8.2053 |
| C | 2.7333 | -2.5317 | -8.7335 |
| C | 1.9939 | -1.3823 | -9.0148 |
| C | -1.8935 | 3.6868 | -9.6569 |
| F | 2.7876 | -4.7545 | -7.9323 |
| H | 0.2340 | 4.5127 | -8.3911 |
| H | 1.7200 | 3.1529 | -6.8195 |
| H | 1.7021 | 2.5290 | -8.4821 |
| H | -1.0073 | -0.0113 | -7.0613 |
| H | -2.4594 | 1.3895 | -8.5949 |
| H | -3.0624 | 2.9207 | -6.8407 |
| H | -1.9459 | 1.9509 | -5.8893 |
| H | -1.5914 | 4.7451 | -6.8178 |
| H | -0.4821 | 3.8470 | -5.7883 |
| H | -1.1592 | -0.4109 | -9.5007 |
| H | 0.0652 | 1.6054 | -9.9460 |
| H | -1.0859 | -2.4652 | -8.0721 |
| H | 0.2328 | -4.5170 | -7.5544 |
| H | 3.8015 | -2.5798 | -8.9191 |
| H | 2.4808 | -0.5128 | -9.4409 |
| H | -2.4705 | 3.0689 | -10.3520 |
| H | -2.6012 | 4.2255 | -9.0068 |
| H | -1.3368 | 4.4249 | -10.2428 |

**Table S20.** Geometry (Å) for product (anti HBO) of the reaction tropinone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.9444 | 2.8354 | -8.9325 |
| C | -0.1159 | 3.5756 | -7.9472 |
| C | 1.0909 | 2.6870 | -7.5842 |
| C | 0.6635 | 1.3070 | -7.0892 |
| C | -0.5724 | 0.7047 | -7.7670 |
| C | -1.6029 | 1.8208 | -8.0652 |
| C | -2.0218 | 2.5884 | -6.7757 |
| C | -1.0479 | 3.7997 | -6.7236 |
| C | -0.1937 | -0.0887 | -9.0671 |
| O | 1.2654 | 0.7218 | -6.2108 |
| O | 0.5068 | 0.7239 | -9.9894 |
| C | 0.6171 | -1.3384 | -8.7728 |
| C | -0.0123 | -2.4752 | -8.2505 |
| C | 0.7104 | -3.6303 | -7.9582 |
| C | 2.0786 | -3.6365 | -8.2053 |
| C | 2.7333 | -2.5317 | -8.7335 |
| C | 1.9939 | -1.3823 | -9.0148 |
| C | -1.8935 | 3.6868 | -9.6569 |
| F | 2.7876 | -4.7545 | -7.9323 |
| H | 0.2340 | 4.5127 | -8.3911 |
| H | 1.7200 | 3.1529 | -6.8195 |
| H | 1.7021 | 2.5290 | -8.4821 |
| H | -1.0073 | -0.0113 | -7.0613 |
| H | -2.4594 | 1.3895 | -8.5949 |
| H | -3.0624 | 2.9207 | -6.8407 |
| H | -1.9459 | 1.9509 | -5.8893 |
| H | -1.5914 | 4.7451 | -6.8178 |
| H | -0.4821 | 3.8470 | -5.7883 |
| H | -1.1592 | -0.4109 | -9.5007 |
| H | 0.0652 | 1.6054 | -9.9460 |
| H | -1.0859 | -2.4652 | -8.0721 |
| H | 0.2328 | -4.5170 | -7.5544 |
| H | 3.8015 | -2.5798 | -8.9191 |
| H | 2.4808 | -0.5128 | -9.4409 |
| H | -2.4705 | 3.0689 | -10.3520 |
| H | -2.6012 | 4.2255 | -9.0068 |
| H | -1.3368 | 4.4249 | -10.2428 |

**Table S21.** Geometry (Å) for product (anti HBN) of the reaction tropinone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.271986 | 1.310208 | 0.739604 |
| C | 1.248757 | 0.409284 | 0.414055 |
| C | 1.998791 | -0.09442 | 1.619812 |
| C | 2.658822 | -1.01631 | -1.02642 |
| N | 2.719082 | -1.89615 | 0.162533 |
| C | 3.579565 | -3.06169 | -0.00759 |
| C | 3.204102 | -0.94789 | 1.184828 |
| C | 4.31277 | -0.09175 | 0.479191 |
| C | 4.033776 | -0.28168 | -1.03781 |
| C | 1.536835 | -0.0166 | -0.82381 |
| H | -0.22908 | 1.554231 | -0.06779 |
| H | 1.320096 | -0.68753 | 2.248465 |
| H | 2.327349 | 0.760078 | 2.22735 |
| H | 2.485994 | -1.61583 | -1.92664 |
| H | 3.559487 | -3.65682 | 0.912533 |
| H | 4.637429 | -2.83927 | -0.24024 |
| H | 3.183428 | -3.68581 | -0.81658 |
| H | 3.595867 | -1.4965 | 2.047608 |
| H | 5.312314 | -0.45009 | 0.746318 |
| H | 4.257672 | 0.958949 | 0.781037 |
| H | 4.807758 | -0.8989 | -1.51006 |
| H | 3.990961 | 0.665548 | -1.58305 |
| H | 1.014979 | 0.376399 | -1.69307 |
| C | -2.61346 | 1.442646 | -1.6344 |
| O | -1.4571 | 1.80383 | -1.46278 |
| C | -3.45313 | 0.714833 | -0.67295 |
| C | -2.97045 | 0.332233 | 0.593537 |
| C | -4.77109 | 0.396553 | -1.04099 |
| C | -3.79649 | -0.35491 | 1.472983 |
| C | -5.60724 | -0.29061 | -0.16806 |
| C | -5.10009 | -0.65358 | 1.076828 |
| F | -5.89748 | -1.31771 | 1.929315 |
| H | -3.11098 | 1.67129 | -2.59956 |
| H | -1.95058 | 0.572425 | 0.879464 |
| H | -5.14055 | 0.691774 | -2.02035 |
| H | -3.45315 | -0.6644 | 2.454381 |
| H | -6.62832 | -0.54764 | -0.42831 |

**Table S22.** Geometry (Å) for reactant (syn) of the reaction tropinone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.722716 | 2.581542 | 0.747112 |
| C | 1.094761 | 1.372953 | 0.475847 |
| C | 1.371245 | 0.437599 | 1.627218 |
| C | 1.580718 | -0.5202 | -1.08955 |
| N | 1.137582 | -1.3664 | 0.0342 |
| C | 1.253427 | -2.79842 | -0.21948 |
| C | 1.996435 | -0.87785 | 1.13001 |
| C | 3.414321 | -0.66565 | 0.49943 |
| C | 3.139902 | -0.55591 | -1.02671 |
| C | 1.08947 | 0.896661 | -0.84669 |
| H | 0.420125 | 0.235192 | 2.138723 |
| H | 2.019278 | 0.952397 | 2.347774 |
| H | 1.187973 | -0.91121 | -2.03505 |
| H | 0.904619 | -3.34579 | 0.662534 |
| H | 2.273575 | -3.15158 | -0.45604 |
| H | 0.601072 | -3.06828 | -1.05684 |
| H | 2.011381 | -1.60656 | 1.945857 |
| H | 4.070367 | -1.51294 | 0.721667 |
| H | 3.903643 | 0.228223 | 0.900073 |
| H | 3.527124 | -1.42973 | -1.56263 |
| H | 3.595758 | 0.329877 | -1.47926 |
| H | 1.320408 | 1.625213 | -1.61944 |
| H | -0.10907 | 2.803559 | -0.03214 |
| C | -0.94625 | 1.318217 | -1.18906 |
| O | -0.9981 | 2.577398 | -0.88979 |
| C | -1.79092 | 0.34424 | -0.4463 |
| C | -2.37231 | 0.706573 | 0.778247 |
| C | -2.06249 | -0.92247 | -0.98164 |
| C | -3.19135 | -0.18445 | 1.46722 |
| C | -2.88525 | -1.82231 | -0.30995 |
| C | -3.43185 | -1.43658 | 0.909999 |
| F | -4.23183 | -2.30206 | 1.568036 |
| H | -0.79391 | 1.055758 | -2.24531 |
| H | -2.18647 | 1.700661 | 1.171408 |
| H | -1.63274 | -1.20312 | -1.94036 |
| H | -3.65374 | 0.078032 | 2.41327 |
| H | -3.11306 | -2.80361 | -0.7131 |

**Table S23.** Geometry (Å) for transition state (syn) of the reaction tropinone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.69008 | 2.497998 | 1.018669 |
| C | 1.004881 | 1.356053 | 0.701362 |
| C | 1.483669 | 0.367578 | 1.753024 |
| C | 1.483293 | -0.48464 | -1.01439 |
| N | 1.175528 | -1.37648 | 0.118373 |
| C | 1.300393 | -2.79674 | -0.19362 |
| C | 2.111992 | -0.89843 | 1.151685 |
| C | 3.459222 | -0.60325 | 0.419472 |
| C | 3.039532 | -0.4116 | -1.06261 |
| C | 0.861492 | 0.904766 | -0.7523 |
| H | 0.589293 | 0.085281 | 2.324758 |
| H | 2.154357 | 0.892236 | 2.44352 |
| H | 1.066792 | -0.89842 | -1.93919 |
| H | 1.081877 | -3.3808 | 0.706322 |
| H | 2.293927 | -3.10474 | -0.56668 |
| H | 0.555948 | -3.06372 | -0.95083 |
| H | 2.22335 | -1.65489 | 1.934311 |
| H | 4.155602 | -1.44023 | 0.529092 |
| H | 3.957913 | 0.280021 | 0.832559 |
| H | 3.434058 | -1.2208 | -1.68554 |
| H | 3.402023 | 0.526889 | -1.49356 |
| H | 1.402585 | 1.650644 | -1.3498 |
| C | -0.62606 | 1.083293 | -1.22925 |
| O | -0.95485 | 2.461704 | -1.22801 |
| C | -1.65881 | 0.243015 | -0.48573 |
| C | -2.27109 | 0.713998 | 0.683217 |
| C | -2.04505 | -1.00741 | -0.98207 |
| C | -3.21711 | -0.05514 | 1.360544 |
| C | -2.99089 | -1.79153 | -0.32202 |
| C | -3.55808 | -1.30082 | 0.847338 |
| F | -4.47882 | -2.0491 | 1.494705 |
| H | -0.6362 | 0.76687 | -2.28072 |
| H | -0.52586 | 2.855599 | -0.44274 |
| H | -2.02168 | 1.70038 | 1.060252 |
| H | -1.60877 | -1.3756 | -1.90801 |
| H | -3.69967 | 0.302817 | 2.264375 |
| H | -3.29922 | -2.75924 | -0.70435 |

**Table S24.** Geometry (Å) for product (syn HBO) of the reaction tropinone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.3623 | -1.1957 | -0.8382 |
| C | -5.5933 | -2.3757 | -1.3119 |
| C | -4.6260 | -2.7818 | -0.1852 |
| C | -3.7856 | -1.6198 | 0.3281 |
| C | -4.3971 | -0.2177 | 0.2369 |
| C | -5.3544 | -0.1064 | -0.9703 |
| C | -4.6274 | -0.3685 | -2.3210 |
| C | -4.8346 | -1.8877 | -2.5752 |
| C | -5.0914 | 0.1099 | 1.6032 |
| O | -2.6908 | -1.7941 | 0.8393 |
| O | -6.1412 | -0.8055 | 1.8748 |
| C | -7.5893 | -0.9509 | -1.6086 |
| C | -5.5457 | 1.5675 | 1.6714 |
| C | -6.9028 | 1.9078 | 1.6630 |
| C | -7.3120 | 3.2425 | 1.7217 |
| C | -6.3414 | 4.2325 | 1.7939 |
| C | -4.9829 | 3.9343 | 1.8150 |
| C | -4.5953 | 2.5963 | 1.7551 |
| F | -6.7276 | 5.5301 | 1.8541 |
| H | -6.2770 | -3.2026 | -1.5219 |
| H | -3.9594 | -3.5936 | -0.4929 |
| H | -5.2090 | -3.1410 | 0.6738 |
| H | -3.5663 | 0.4853 | 0.1161 |
| H | -5.8576 | 0.8635 | -0.9479 |
| H | -5.0730 | 0.2298 | -3.1208 |
| H | -3.5702 | -0.0910 | -2.2661 |
| H | -5.4364 | -2.0564 | -3.4730 |
| H | -3.8927 | -2.4272 | -2.7135 |
| H | -4.3284 | -0.0389 | 2.3793 |
| H | -6.5094 | -1.0613 | 0.9878 |
| H | -8.0867 | -0.0610 | -1.2118 |
| H | -7.4155 | -0.7989 | -2.6844 |
| H | -8.2624 | -1.8045 | -1.4860 |
| H | -7.6450 | 1.1176 | 1.6280 |
| H | -8.3626 | 3.5147 | 1.7171 |
| H | -4.2541 | 4.7354 | 1.8832 |
| H | -3.5352 | 2.3547 | 1.7814 |

**Table S25.** Geometry (Å) for product (syn HBN) of the reaction tropinone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -0.80552 | 1.802266 | -0.05473 |
| C | -1.63258 | 0.724117 | 0.079493 |
| C | -2.80763 | 0.778559 | -0.86258 |
| C | -2.47655 | -1.42461 | 0.958796 |
| N | -3.0264 | -1.59486 | -0.4049 |
| C | -3.82386 | -2.80455 | -0.57361 |
| C | -3.80666 | -0.34904 | -0.54594 |
| C | -4.52273 | -0.13789 | 0.832962 |
| C | -3.7035 | -1.00861 | 1.825812 |
| C | -1.4573 | -0.30166 | 0.926008 |
| H | -0.03322 | 1.699562 | 0.542833 |
| H | -2.44764 | 0.68868 | -1.89682 |
| H | -3.29227 | 1.761164 | -0.78126 |
| H | -2.01321 | -2.35883 | 1.294098 |
| H | -4.70383 | -2.88857 | 0.090509 |
| H | -3.18908 | -3.6807 | -0.39941 |
| H | -4.1825 | -2.85346 | -1.60809 |
| H | -4.52186 | -0.44734 | -1.36923 |
| H | -5.56603 | -0.46683 | 0.785546 |
| H | -4.53314 | 0.918494 | 1.119437 |
| H | -4.27547 | -1.88676 | 2.150137 |
| H | -3.40541 | -0.46088 | 2.724354 |
| H | -0.62751 | -0.32161 | 1.628555 |
| C | 2.235119 | 0.915687 | -0.02787 |
| O | 1.741841 | 1.325648 | 1.015842 |
| C | 3.638393 | 0.499199 | -0.16945 |
| C | 4.518417 | 0.566892 | 0.923031 |
| C | 4.102086 | 0.031579 | -1.40692 |
| C | 5.842585 | 0.174013 | 0.782034 |
| C | 5.42686 | -0.36673 | -1.56178 |
| C | 6.284177 | -0.2902 | -0.4625 |
| Cl | 7.953881 | -0.78667 | -0.64434 |
| H | 1.615522 | 0.843022 | -0.94214 |
| H | 4.144052 | 0.931398 | 1.874464 |
| H | 3.420757 | -0.02172 | -2.25278 |
| H | 6.532595 | 0.222274 | 1.617383 |
| H | 5.794746 | -0.73083 | -2.51462 |

**Table S26.** Geometry (Å) for reactant (anti) of the reaction tropinone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.2888 | 2.837784 | 0.056313 |
| C | -1.53469 | 1.566497 | 0.066762 |
| C | -2.74562 | 1.080094 | -0.69704 |
| C | -0.98406 | -0.82352 | 0.572247 |
| N | -1.65917 | -1.08711 | -0.71806 |
| C | -1.77166 | -2.50838 | -1.03938 |
| C | -2.96575 | -0.42923 | -0.50094 |
| C | -3.38331 | -0.78083 | 0.965497 |
| C | -2.0473 | -1.16 | 1.66233 |
| C | -0.62482 | 0.648791 | 0.614855 |
| H | -2.59361 | 1.312195 | -1.7601 |
| H | -3.61787 | 1.662351 | -0.3731 |
| H | -0.08318 | -1.43883 | 0.658633 |
| H | -2.32826 | -3.10958 | -0.29895 |
| H | -0.76804 | -2.93698 | -1.1322 |
| H | -2.27399 | -2.61739 | -2.00656 |
| H | -3.69191 | -0.79142 | -1.2351 |
| H | -4.08726 | -1.61876 | 0.979466 |
| H | -3.88383 | 0.062151 | 1.452772 |
| H | -2.01864 | -2.22629 | 1.912952 |
| H | -1.87796 | -0.60535 | 2.58996 |
| H | -0.01658 | 0.98793 | 1.448065 |
| H | -0.1433 | 2.901599 | -0.15196 |
| C | 0.93566 | 1.263565 | -0.71708 |
| O | 1.019621 | 2.525324 | -0.45853 |
| C | 2.035252 | 0.36166 | -0.28972 |
| C | 2.977945 | 0.789054 | 0.656754 |
| C | 2.168167 | -0.91285 | -0.85864 |
| C | 4.025146 | -0.04281 | 1.040079 |
| C | 3.213482 | -1.75596 | -0.48503 |
| C | 4.13208 | -1.31194 | 0.465986 |
| Cl | 5.455809 | -2.36536 | 0.943585 |
| H | 0.415348 | 0.936427 | -1.62866 |
| H | 2.883796 | 1.786977 | 1.072637 |
| H | 1.449017 | -1.24292 | -1.60424 |
| H | 4.758293 | 0.285485 | 1.769288 |
| H | 3.320937 | -2.74065 | -0.92738 |

**Table S27.** Geometry (Å) for transition state (anti) of the reaction tropinone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.7317 | 2.8967 | 0.1118 |
| C | -1.7402 | 1.6794 | -0.0196 |
| C | -2.8736 | 0.9849 | -0.7631 |
| C | -0.9225 | -0.6486 | 0.5750 |
| N | -1.5900 | -1.0696 | -0.6749 |
| C | -1.5650 | -2.5163 | -0.8884 |
| C | -2.9511 | -0.5256 | -0.4926 |
| C | -3.3362 | -0.8286 | 0.9842 |
| C | -1.9665 | -0.8790 | 1.7138 |
| C | -0.5503 | 0.8416 | 0.4500 |
| H | -2.6739 | 1.1459 | -1.8318 |
| H | -3.8097 | 1.5053 | -0.5323 |
| H | -0.0160 | -1.2378 | 0.7294 |
| H | -2.0881 | -2.7504 | -1.8216 |
| H | -2.0287 | -3.1093 | -0.0804 |
| H | -0.5263 | -2.8454 | -0.9930 |
| H | -3.6382 | -0.9885 | -1.2078 |
| H | -3.8562 | -1.7889 | 1.0572 |
| H | -4.0101 | -0.0700 | 1.3955 |
| H | -1.8080 | -1.8532 | 2.1864 |
| H | -1.8804 | -0.1266 | 2.5044 |
| H | -0.2440 | 1.2283 | 1.4300 |
| C | 0.6450 | 1.1730 | -0.5206 |
| O | 1.0153 | 2.5320 | -0.3691 |
| C | 1.8666 | 0.3165 | -0.2457 |
| C | 2.7556 | 0.6568 | 0.7812 |
| C | 2.1231 | -0.8261 | -1.0127 |
| C | 3.8675 | -0.1380 | 1.0476 |
| C | 3.2334 | -1.6270 | -0.7506 |
| C | 4.1070 | -1.2847 | 0.2840 |
| C | 5.2747 | -2.1746 | 0.6085 |
| F | 4.9481 | -3.1119 | 1.5322 |
| F | 6.3173 | -1.4783 | 1.1137 |
| F | 5.7211 | -2.8414 | -0.4798 |
| H | 0.3096 | 0.9692 | -1.5488 |
| H | 0.1990 | 3.0439 | -0.2061 |
| H | 2.5827 | 1.5653 | 1.3479 |
| H | 1.4517 | -1.0839 | -1.8279 |
| H | 4.5589 | 0.1375 | 1.8375 |
| H | 3.431087 | -2.50422 | -1.35796 |

**Table S28.** Geometry (Å) for product (anti HBO) of the reaction tropinone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.94343 | 2.848181 | -8.929 |
| C | -0.12037 | 3.586097 | -7.93721 |
| C | 1.084883 | 2.697088 | -7.57055 |
| C | 0.657305 | 1.313709 | -7.08545 |
| C | -0.57774 | 0.714308 | -7.76863 |
| C | -1.60662 | 1.831315 | -8.0679 |
| C | -2.03118 | 2.594384 | -6.77764 |
| C | -1.05891 | 3.806548 | -6.71808 |
| C | -0.19385 | -0.07373 | -9.06983 |
| O | 1.258939 | 0.721619 | -6.21166 |
| O | 0.512182 | 0.740989 | -9.98526 |
| C | 0.614432 | -1.325 | -8.77551 |
| C | -0.01444 | -2.45773 | -8.24546 |
| C | 0.705368 | -3.61519 | -7.9571 |
| C | 2.075776 | -3.6379 | -8.21304 |
| C | 2.724439 | -2.52858 | -8.74958 |
| C | 1.987987 | -1.3765 | -9.02779 |
| C | -1.88883 | 3.70131 | -9.65653 |
| Cl | 2.996028 | -5.09888 | -7.86242 |
| H | 0.231485 | 4.524518 | -8.37669 |
| H | 1.708678 | 3.15993 | -6.79969 |
| H | 1.702508 | 2.544361 | -8.465 |
| H | -1.01516 | -0.0034 | -7.06619 |
| H | -2.46084 | 1.402091 | -8.603 |
| H | -3.07189 | 2.925632 | -6.8456 |
| H | -1.958 | 1.954228 | -5.89302 |
| H | -1.60293 | 4.751473 | -6.81313 |
| H | -0.49804 | 3.852536 | -5.77973 |
| H | -1.15663 | -0.39523 | -9.50984 |
| H | 0.071565 | 1.62325 | -9.94049 |
| H | -1.08638 | -2.4447 | -8.05755 |
| H | 0.212066 | -4.49003 | -7.54716 |
| H | 3.790316 | -2.56531 | -8.94872 |
| H | 2.477273 | -0.51091 | -9.45928 |
| H | -2.46078 | 3.085284 | -10.3574 |
| H | -2.60115 | 4.236702 | -9.00887 |
| H | -1.32917 | 4.442035 | -10.2361 |

**Table S29.** Geometry (Å) for product (anti HBN) of the reaction tropinone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.293552 | 1.391283 | 0.766502 |
| C | 1.23462 | 0.460441 | 0.418911 |
| C | 1.954111 | -0.11071 | 1.612963 |
| C | 2.59263 | -0.97973 | -1.05607 |
| N | 2.605404 | -1.89715 | 0.105289 |
| C | 3.414035 | -3.09464 | -0.09471 |
| C | 3.123925 | -1.00309 | 1.159239 |
| C | 4.275085 | -0.17624 | 0.487271 |
| C | 3.99778 | -0.305 | -1.03656 |
| C | 1.51301 | 0.060737 | -0.82973 |
| H | 1.246127 | -0.69178 | 2.220175 |
| H | 2.315566 | 0.710365 | 2.247291 |
| H | 2.40087 | -1.54337 | -1.97541 |
| H | 3.360564 | -3.71513 | 0.807112 |
| H | 4.482581 | -2.91391 | -0.31444 |
| H | 2.995897 | -3.67619 | -0.92405 |
| H | 3.484388 | -1.59427 | 2.007377 |
| H | 5.25523 | -0.58895 | 0.747647 |
| H | 4.266762 | 0.865702 | 0.822537 |
| H | 4.747464 | -0.93921 | -1.52506 |
| H | 3.998537 | 0.660245 | -1.551 |
| H | 1.01464 | 0.50168 | -1.68975 |
| H | -0.18982 | 1.681008 | -0.03595 |
| C | -2.56662 | 1.670953 | -1.63457 |
| O | -1.40886 | 2.009484 | -1.43426 |
| C | -3.42553 | 0.91277 | -0.71084 |
| C | -2.96269 | 0.477015 | 0.54372 |
| C | -4.74034 | 0.620779 | -1.10517 |
| C | -3.80574 | -0.23716 | 1.386169 |
| C | -5.59245 | -0.09315 | -0.26893 |
| C | -5.11283 | -0.51516 | 0.972617 |
| Cl | -6.17392 | -1.4143 | 2.037313 |
| H | -3.05088 | 1.945171 | -2.59439 |
| H | -1.94469 | 0.695874 | 0.853184 |
| H | -5.09787 | 0.956447 | -2.07602 |
| H | -3.46018 | -0.5801 | 2.355251 |
| H | -6.60963 | -0.32193 | -0.5671 |

**Table S30.** Geometry (Å) for reactant (syn) of the reaction tropinone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.780479 | 2.631645 | 0.75791 |

| | | | |
|---|---|---|---|
| C | 1.115066 | 1.415217 | 0.470778 |
| C | 1.378511 | 0.462343 | 1.609761 |
| C | 1.524907 | -0.47447 | -1.11998 |
| N | 1.066823 | -1.31499 | 0.001788 |
| C | 1.128394 | -2.74798 | -0.26557 |
| C | 1.955184 | -0.86706 | 1.091146 |
| C | 3.371498 | -0.69469 | 0.444733 |
| C | 3.082311 | -0.56387 | -1.07711 |
| C | 1.084358 | 0.955659 | -0.858 |
| H | 0.42927 | 0.284604 | 2.133726 |
| H | 2.052127 | 0.951086 | 2.325091 |
| H | 1.106849 | -0.84247 | -2.06375 |
| H | 0.774622 | -3.29025 | 0.617491 |
| H | 2.131971 | -3.13348 | -0.52127 |
| H | 0.453637 | -2.98759 | -1.09423 |
| H | 1.956208 | -1.60427 | 1.899292 |
| H | 4.002956 | -1.56398 | 0.652519 |
| H | 3.893572 | 0.180142 | 0.846058 |
| H | 3.432075 | -1.44666 | -1.62385 |
| H | 3.563444 | 0.308771 | -1.52909 |
| H | 1.340948 | 1.685604 | -1.62131 |
| H | -0.03961 | 2.889817 | -0.00705 |
| C | -0.92762 | 1.445949 | -1.19563 |
| O | -0.95299 | 2.697269 | -0.86686 |
| C | -1.79822 | 0.473684 | -0.47622 |
| C | -2.36762 | 0.817036 | 0.757881 |
| C | -2.10703 | -0.76868 | -1.04429 |
| C | -3.20927 | -0.07003 | 1.424567 |
| C | -2.95277 | -1.66385 | -0.39484 |
| C | -3.49195 | -1.30598 | 0.841267 |
| Cl | -4.56091 | -2.42879 | 1.671856 |
| H | -0.78495 | 1.203469 | -2.25853 |
| H | -2.15593 | 1.794626 | 1.178796 |
| H | -1.6899 | -1.03618 | -2.01246 |
| H | -3.65314 | 0.194211 | 2.378686 |
| H | -3.19819 | -2.62301 | -0.83823 |

**Table S31.** Geometry (Å) for transition state (syn) of the reaction tropinone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.7052 | 2.5481 | 1.0489 |
| C | 1.0232 | 1.4086 | 0.7107 |
| C | 1.5451 | 0.4218 | 1.7389 |
| C | 1.4107 | -0.4358 | -1.0253 |

| | | | |
|---|---|---|---|
| N | 1.0985 | -1.3124 | 0.1216 |
| C | 1.1766 | -2.7383 | -0.1977 |
| C | 2.0935 | -0.8733 | 1.1214 |
| C | 3.4254 | -0.6469 | 0.3430 |
| C | 2.9653 | -0.4220 | -1.1218 |
| C | 0.8488 | 0.9763 | -0.7451 |
| H | 0.6874 | 0.1806 | 2.3820 |
| H | 2.2788 | 0.9341 | 2.3722 |
| H | 0.9510 | -0.8329 | -1.9356 |
| H | 0.9695 | -3.3188 | 0.7072 |
| H | 2.1524 | -3.0656 | -0.5951 |
| H | 0.4088 | -2.9826 | -0.9389 |
| H | 2.1957 | -1.6289 | 1.9051 |
| H | 4.0736 | -1.5246 | 0.4228 |
| H | 3.9872 | 0.2030 | 0.7437 |
| H | 3.3061 | -1.2375 | -1.7670 |
| H | 3.3469 | 0.5082 | -1.5534 |
| H | 1.4188 | 1.7056 | -1.3363 |
| C | -0.6286 | 1.2077 | -1.2197 |
| O | -0.9394 | 2.5960 | -1.1587 |
| C | -1.6848 | 0.3624 | -0.5155 |
| C | -2.2708 | 0.7824 | 0.6861 |
| C | -2.1212 | -0.8401 | -1.0842 |
| C | -3.2424 | 0.0106 | 1.3238 |
| C | -3.0927 | -1.6270 | -0.4640 |
| C | -3.6397 | -1.1917 | 0.7411 |
| Cl | -4.8748 | -2.1734 | 1.5368 |
| H | -0.6417 | 0.9353 | -2.2820 |
| H | -0.4843 | 2.9456 | -0.3652 |
| H | -1.9790 | 1.7289 | 1.1294 |
| H | -1.7048 | -1.1722 | -2.0318 |
| H | -3.6892 | 0.3439 | 2.2546 |
| H | -3.4240 | -2.5559 | -0.9158 |

**Table S32.** Geometry (Å) for product (syn HBO) of the reaction tropinone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.30179 | -1.25908 | -0.90747 |
| C | -5.49577 | -2.42616 | -1.34739 |
| C | -4.57526 | -2.82701 | -0.17933 |
| C | -3.74714 | -1.65698 | 0.345375 |
| C | -4.3909 | -0.26633 | 0.261562 |
| C | -5.30248 | -0.15727 | -0.9807 |
| C | -4.51496 | -0.39887 | -2.30265 |

| | | | |
|---|---|---|---|
| C | -4.68247 | -1.9207 | -2.57156 |
| C | -5.14058 | 0.027344 | 1.604249 |
| O | -2.64678 | -1.81267 | 0.838142 |
| O | -6.15561 | -0.92988 | 1.845438 |
| C | -7.48886 | -1.02128 | -1.73582 |
| C | -5.66136 | 1.464773 | 1.657656 |
| C | -7.03042 | 1.729147 | 1.756204 |
| C | -7.51134 | 3.039192 | 1.805032 |
| C | -6.60676 | 4.096784 | 1.760401 |
| C | -5.2338 | 3.863126 | 1.6786 |
| C | -4.77276 | 2.548989 | 1.629641 |
| Cl | -7.20093 | 5.753543 | 1.818156 |
| H | -6.16034 | -3.25922 | -1.59632 |
| H | -3.89743 | -3.64116 | -0.45458 |
| H | -5.19062 | -3.17123 | 0.662278 |
| H | -3.56968 | 0.453032 | 0.175856 |
| H | -5.81947 | 0.806236 | -0.97043 |
| H | -4.93557 | 0.195243 | -3.11963 |
| H | -3.46583 | -0.10343 | -2.20297 |
| H | -5.23156 | -2.09738 | -3.50164 |
| H | -3.72451 | -2.44188 | -2.66181 |
| H | -4.39922 | -0.09346 | 2.405253 |
| H | -6.52326 | -1.16108 | 0.95802 |
| H | -8.0181 | -0.14188 | -1.35616 |
| H | -7.26682 | -0.85482 | -2.80195 |
| H | -8.15925 | -1.88283 | -1.65628 |
| H | -7.7198 | 0.894197 | 1.820788 |
| H | -8.57552 | 3.236195 | 1.884329 |
| H | -4.53956 | 4.696725 | 1.659114 |
| H | -3.70037 | 2.372562 | 1.5801 |

**Table S33.** Geometry (Å) for product (syn HBN) of the reaction tropinone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -0.92899 | 1.804583 | -0.07503 |
| C | -1.78447 | 0.753228 | 0.096962 |
| C | -2.92578 | 0.771397 | -0.88677 |
| C | -2.70171 | -1.32012 | 1.078363 |
| N | -3.2095 | -1.56339 | -0.29013 |
| C | -4.02332 | -2.76744 | -0.4142 |
| C | -3.95855 | -0.31444 | -0.53381 |
| C | -4.71297 | -0.00282 | 0.805247 |
| C | -3.94766 | -0.8293 | 1.875889 |
| C | -1.65987 | -0.21954 | 1.011969 |

| | | | |
|---|---|---|---|
| H | -0.17811 | 1.719285 | 0.550701 |
| H | -2.53402 | 0.60886 | -1.90041 |
| H | -3.39147 | 1.766433 | -0.88392 |
| H | -2.26789 | -2.24005 | 1.48509 |
| H | -4.34613 | -2.87345 | -1.45616 |
| H | -4.92776 | -2.79711 | 0.221419 |
| H | -3.41139 | -3.64162 | -0.1645 |
| H | -4.64918 | -0.45049 | -1.37249 |
| H | -5.76218 | -0.30983 | 0.743303 |
| H | -4.70616 | 1.069072 | 1.026914 |
| H | -4.54936 | -1.67538 | 2.230091 |
| H | -3.66906 | -0.23568 | 2.751283 |
| H | -0.85518 | -0.21053 | 1.743406 |
| C | 2.069494 | 0.812567 | 0.056011 |
| O | 1.585437 | 1.289193 | 1.073688 |
| C | 3.447321 | 0.293992 | -0.03684 |
| C | 4.299277 | 0.329914 | 1.078159 |
| C | 3.904858 | -0.23552 | -1.25056 |
| C | 5.593867 | -0.16219 | 0.977665 |
| C | 5.202443 | -0.72945 | -1.35414 |
| C | 6.04342 | -0.69227 | -0.23892 |
| C | 7.430147 | -1.27984 | -0.32802 |
| F | 7.431275 | -2.58483 | 0.024814 |
| F | 8.294409 | -0.64594 | 0.492311 |
| F | 7.925817 | -1.20595 | -1.58131 |
| H | 1.466169 | 0.750989 | -0.8696 |
| H | 3.927351 | 0.748266 | 2.007887 |
| H | 3.242829 | -0.25853 | -2.11269 |
| H | 6.261754 | -0.13228 | 1.831966 |
| H | 5.564852 | -1.13498 | -2.29242 |

**Table S34.** Geometry (Å) for reactant (anti) of the reaction tropinone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.36846 | 2.828769 | 0.123908 |
| C | -1.58681 | 1.551939 | 0.117737 |
| C | -2.81658 | 1.055405 | -0.60666 |
| C | -0.96659 | -0.83355 | 0.554117 |
| N | -1.68363 | -1.08425 | -0.71572 |
| C | -1.77538 | -2.50033 | -1.06571 |
| C | -2.99591 | -0.46238 | -0.43544 |
| C | -3.35044 | -0.85623 | 1.036269 |
| C | -1.98048 | -1.21433 | 1.676096 |
| C | -0.63566 | 0.645305 | 0.614058 |
| H | -2.71225 | 1.313313 | -1.66952 |
| H | -3.68697 | 1.611833 | -0.23575 |

| | | | |
|---|---|---|---|
| H | -0.0506 | -1.43084 | 0.594068 |
| H | -2.31067 | -2.59942 | -2.01605 |
| H | -2.29027 | -3.13035 | -0.31927 |
| H | -0.76643 | -2.90286 | -1.2052 |
| H | -3.74061 | -0.82475 | -1.15059 |
| H | -4.03063 | -1.71339 | 1.05597 |
| H | -3.85573 | -0.03865 | 1.560608 |
| H | -1.91687 | -2.28358 | 1.906265 |
| H | -1.78986 | -0.67199 | 2.606902 |
| H | -0.01397 | 0.981539 | 1.438664 |
| H | -0.24453 | 2.925265 | -0.11576 |
| C | 0.862786 | 1.315224 | -0.74326 |
| O | 0.927707 | 2.57554 | -0.47911 |
| C | 1.992634 | 0.43211 | -0.34324 |
| C | 2.938436 | 0.872851 | 0.593845 |
| C | 2.146515 | -0.8307 | -0.93246 |
| C | 4.00637 | 0.05704 | 0.949874 |
| C | 3.21645 | -1.64978 | -0.57922 |
| C | 4.14565 | -1.20783 | 0.36624 |
| C | 5.266664 | -2.11367 | 0.798461 |
| F | 4.911365 | -2.87005 | 1.86512 |
| F | 6.36615 | -1.41783 | 1.162862 |
| F | 5.63262 | -2.96936 | -0.18198 |
| H | 0.334459 | 0.982233 | -1.64863 |
| H | 2.827612 | 1.865335 | 1.018034 |
| H | 1.427164 | -1.16436 | -1.67606 |
| H | 4.742249 | 0.401922 | 1.669039 |
| H | 3.338663 | -2.62286 | -1.04338 |

**Table S35.** Geometry (Å) for transition state (anti) of the reaction tropinone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.73168 | 2.896714 | 0.111849 |
| C | -1.74021 | 1.679384 | -0.0196 |
| C | -2.87364 | 0.984892 | -0.76308 |
| C | -0.92255 | -0.6486 | 0.574976 |
| N | -1.59 | -1.06961 | -0.67492 |
| C | -1.56503 | -2.51631 | -0.88838 |
| C | -2.95115 | -0.52556 | -0.49256 |
| C | -3.33618 | -0.82865 | 0.984238 |
| C | -1.96647 | -0.879 | 1.713796 |
| C | -0.55026 | 0.841563 | 0.449969 |
| H | -2.6739 | 1.145852 | -1.83185 |
| H | -3.80975 | 1.505316 | -0.5323 |
| H | -0.01599 | -1.23776 | 0.729389 |
| H | -2.08806 | -2.75044 | -1.82163 |

| | | | |
|---|---|---|---|
| H | -2.02873 | -3.10926 | -0.08041 |
| H | -0.52627 | -2.84543 | -0.99303 |
| H | -3.63816 | -0.98846 | -1.20783 |
| H | -3.85618 | -1.7889 | 1.057223 |
| H | -4.0101 | -0.07004 | 1.395503 |
| H | -1.80799 | -1.85321 | 2.186368 |
| H | -1.88036 | -0.12665 | 2.504412 |
| H | -0.24399 | 1.22825 | 1.430027 |
| C | 0.645008 | 1.173032 | -0.52059 |
| O | 1.015287 | 2.532026 | -0.36912 |
| C | 1.866619 | 0.316459 | -0.24573 |
| C | 2.755642 | 0.656752 | 0.781165 |
| C | 2.12308 | -0.82613 | -1.01266 |
| C | 3.867509 | -0.13799 | 1.047577 |
| C | 3.233428 | -1.627 | -0.75058 |
| C | 4.106977 | -1.28466 | 0.284017 |
| C | 5.274669 | -2.17465 | 0.608513 |
| F | 4.948148 | -3.1119 | 1.532224 |
| F | 6.317253 | -1.47832 | 1.113693 |
| F | 5.721121 | -2.84142 | -0.4798 |
| H | 0.309639 | 0.969218 | -1.54882 |
| H | 0.198997 | 3.043949 | -0.20614 |
| H | 2.582653 | 1.565309 | 1.347942 |
| H | 1.451747 | -1.0839 | -1.8279 |
| H | 4.558876 | 0.13748 | 1.8375 |
| H | 3.431087 | -2.50422 | -1.35796 |

**Table S36.** Geometry (Å) for product (anti HBO) of the reaction tropinone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.87638 | 2.911021 | -8.94883 |
| C | -0.13622 | 3.644154 | -7.89079 |
| C | 1.051995 | 2.764113 | -7.45344 |
| C | 0.609015 | 1.368263 | -7.02082 |
| C | -0.57146 | 0.765772 | -7.79388 |
| C | -1.58904 | 1.875467 | -8.15157 |
| C | -2.11464 | 2.614364 | -6.88539 |
| C | -1.16077 | 3.833228 | -6.73703 |
| C | -0.09024 | -0.00183 | -9.07394 |
| O | 1.157935 | 0.766851 | -6.11923 |
| O | 0.673996 | 0.827993 | -9.92582 |
| C | 0.701584 | -1.25229 | -8.73398 |
| C | 0.039791 | -2.38427 | -8.2404 |
| C | 0.745147 | -3.53563 | -7.90784 |
| C | 2.133084 | -3.57185 | -8.0756 |
| C | 2.800907 | -2.45394 | -8.57744 |

| | | | |
|---|---|---|---|
| C | 2.087673 | -1.30103 | -8.9036 |
| C | -1.77646 | 3.763477 | -9.73278 |
| C | 2.884176 | -4.83749 | -7.77162 |
| F | 2.367434 | -5.48382 | -6.70053 |
| F | 4.190362 | -4.60625 | -7.51321 |
| F | 2.839394 | -5.71207 | -8.80699 |
| H | 0.2329 | 4.593725 | -8.29013 |
| H | 1.614521 | 3.221325 | -6.63365 |
| H | 1.732849 | 2.632469 | -8.30433 |
| H | -1.04865 | 0.036205 | -7.13073 |
| H | -2.3972 | 1.445456 | -8.75351 |
| H | -3.15066 | 2.937754 | -7.02472 |
| H | -2.10044 | 1.961039 | -6.00752 |
| H | -1.70577 | 4.775127 | -6.8529 |
| H | -0.66754 | 3.86679 | -5.76089 |
| H | -1.01586 | -0.32519 | -9.58609 |
| H | 0.224629 | 1.706647 | -9.90326 |
| H | -1.04098 | -2.36732 | -8.11527 |
| H | 0.223736 | -4.4041 | -7.5181 |
| H | 3.877814 | -2.48222 | -8.70661 |
| H | 2.600001 | -0.43324 | -9.30209 |
| H | -2.28215 | 3.152102 | -10.4867 |
| H | -2.54565 | 4.275883 | -9.13329 |
| H | -1.18539 | 4.523098 | -10.2537 |

**Table S37.** Geometry (Å) for product (anti HBN) of the reaction tropinone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.256003 | 1.175187 | 0.53758 |
| C | 1.322014 | 0.355662 | 0.282055 |
| C | 2.071331 | -0.02617 | 1.531989 |
| C | 2.910909 | -0.98548 | -1.04908 |
| N | 3.013516 | -1.80561 | 0.178318 |
| C | 3.987784 | -2.88704 | 0.086246 |
| C | 3.368527 | -0.77294 | 1.172711 |
| C | 4.413403 | 0.157496 | 0.464697 |
| C | 4.207934 | -0.1204 | -1.05046 |
| C | 1.691652 | -0.09134 | -0.92618 |
| H | -0.22156 | 1.363114 | -0.29713 |
| H | 1.430835 | -0.65948 | 2.16139 |
| H | 2.292136 | 0.879001 | 2.114231 |
| H | 2.827813 | -1.63492 | -1.92713 |
| H | 3.993064 | -3.44341 | 1.030381 |
| H | 5.026326 | -2.57112 | -0.12335 |

| | | | |
|---|---|---|---|
| H | 3.682227 | -3.57901 | -0.70661 |
| H | 3.780368 | -1.245 | 2.070691 |
| H | 5.43268 | -0.09098 | 0.778208 |
| H | 4.248724 | 1.209327 | 0.71911 |
| H | 5.053948 | -0.67806 | -1.4705 |
| H | 4.092766 | 0.79472 | -1.63828 |
| H | 1.16825 | 0.215821 | -1.82871 |
| C | -2.62168 | 1.262777 | -1.8662 |
| O | -1.45174 | 1.577496 | -1.71325 |
| C | -3.47127 | 0.562391 | -0.88277 |
| C | -2.97716 | 0.164811 | 0.371607 |
| C | -4.80412 | 0.293364 | -1.22681 |
| C | -3.81476 | -0.49649 | 1.261912 |
| C | -5.64236 | -0.36766 | -0.33451 |
| C | -5.1435 | -0.76323 | 0.909245 |
| C | -6.0257 | -1.53674 | 1.857686 |
| F | -5.88694 | -2.8689 | 1.675683 |
| F | -7.33183 | -1.24495 | 1.678276 |
| F | -5.72164 | -1.27834 | 3.14668 |
| H | -3.12837 | 1.508818 | -2.82177 |
| H | -1.94664 | 0.375322 | 0.642327 |
| H | -5.18318 | 0.60632 | -2.19685 |
| H | -3.44339 | -0.80216 | 2.234302 |
| H | -6.67535 | -0.57128 | -0.59437 |

**Table S38.** Geometry (Å) for reactant (syn) of the reaction tropinone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.786573 | 2.643796 | 0.754637 |
| C | 1.119271 | 1.424715 | 0.474138 |
| C | 1.358643 | 0.472795 | 1.618297 |
| C | 1.547779 | -0.46666 | -1.10856 |
| N | 1.065106 | -1.30279 | 0.005878 |
| C | 1.120348 | -2.73664 | -0.25919 |
| C | 1.937103 | -0.85995 | 1.110337 |
| C | 3.365236 | -0.69568 | 0.488999 |
| C | 3.103781 | -0.5635 | -1.03761 |
| C | 1.10985 | 0.966418 | -0.85625 |
| H | 0.399613 | 0.300628 | 2.126171 |
| H | 2.02211 | 0.959499 | 2.344415 |
| H | 1.144816 | -0.83339 | -2.05927 |
| H | 0.747536 | -3.27528 | 0.618151 |
| H | 2.125269 | -3.12938 | -0.49761 |
| H | 0.457835 | -2.97167 | -1.09888 |

| | | | |
|---|---|---|---|
| H | 1.919521 | -1.59654 | 1.918716 |
| H | 3.987702 | -1.56867 | 0.707877 |
| H | 3.885633 | 0.175933 | 0.899488 |
| H | 3.458392 | -1.44818 | -1.57798 |
| H | 3.597456 | 0.306488 | -1.48112 |
| H | 1.393539 | 1.695057 | -1.61133 |
| H | -0.0035 | 2.910954 | -0.02217 |
| C | -0.87929 | 1.470952 | -1.24094 |
| O | -0.91422 | 2.719373 | -0.90798 |
| C | -1.76729 | 0.493663 | -0.54259 |
| C | -2.35516 | 0.830977 | 0.6842 |
| C | -2.07355 | -0.74035 | -1.13033 |
| C | -3.20978 | -0.06159 | 1.324389 |
| C | -2.93379 | -1.63308 | -0.49948 |
| C | -3.4987 | -1.29627 | 0.734553 |
| C | -4.37947 | -2.28447 | 1.447915 |
| F | -3.65691 | -3.12808 | 2.225073 |
| F | -5.07704 | -3.05593 | 0.583359 |
| F | -5.27191 | -1.67533 | 2.259461 |
| H | -0.71753 | 1.23115 | -2.30213 |
| H | -2.14812 | 1.805664 | 1.113513 |
| H | -1.64526 | -0.99642 | -2.09655 |
| H | -3.66966 | 0.20412 | 2.270658 |
| H | -3.1791 | -2.5822 | -0.96486 |

**Table S39.** Geometry (Å) for transition state (syn) of the reaction tropinone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.6905 | 2.5090 | 1.0804 |
| C | 0.9927 | 1.3758 | 0.7229 |
| C | 1.4304 | 0.3336 | 1.7393 |
| C | 1.4855 | -0.3930 | -1.0626 |
| N | 1.1398 | -1.3325 | 0.0195 |
| C | 1.2614 | -2.7384 | -0.3547 |
| C | 2.0556 | -0.9138 | 1.0967 |
| C | 3.4243 | -0.6072 | 0.4119 |
| C | 3.0433 | -0.3308 | -1.0675 |
| C | 0.8687 | 0.9881 | -0.7514 |
| H | 0.5173 | 0.0392 | 2.2742 |
| H | 2.0901 | 0.8153 | 2.4703 |
| H | 1.0902 | -0.7595 | -2.0162 |
| H | 1.0101 | -3.3612 | 0.5099 |
| H | 2.2632 | -3.0380 | -0.7114 |
| H | 0.5388 | -2.9628 | -1.1461 |
| H | 2.1360 | -1.7056 | 1.8473 |
| H | 4.1016 | -1.4628 | 0.4929 |

| | | | |
|---|---|---|---|
| H | 3.9301 | 0.2430 | 0.8817 |
| H | 3.4482 | -1.1069 | -1.7248 |
| H | 3.4229 | 0.6273 | -1.4361 |
| H | 1.4220 | 1.7547 | -1.3099 |
| C | -0.6106 | 1.2008 | -1.2379 |
| O | -0.9273 | 2.5800 | -1.1876 |
| C | -1.6584 | 0.3459 | -0.5307 |
| C | -2.2909 | 0.7969 | 0.6345 |
| C | -2.0388 | -0.8928 | -1.0603 |
| C | -3.2482 | 0.0133 | 1.2752 |
| C | -2.9977 | -1.6812 | -0.4301 |
| C | -3.6011 | -1.2308 | 0.7468 |
| C | -4.5927 | -2.1034 | 1.4637 |
| F | -3.9821 | -2.9507 | 2.3288 |
| F | -5.3027 | -2.8724 | 0.6066 |
| F | -5.4766 | -1.3806 | 2.1874 |
| H | -0.6170 | 0.9219 | -2.2999 |
| H | -0.4979 | 2.9426 | -0.3872 |
| H | -2.0482 | 1.7765 | 1.0322 |
| H | -1.5888 | -1.2418 | -1.9868 |
| H | -3.7362 | 0.3757 | 2.1741 |
| H | -3.29071 | -2.63464 | -0.85778 |

**Table S40.** Geometry (Å) for product (syn HBO) of the reaction tropinone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.5254 | -1.33436 | -0.61608 |
| C | -5.82577 | -2.57018 | -1.05233 |
| C | -4.73434 | -2.88654 | -0.01214 |
| C | -3.80295 | -1.70423 | 0.235916 |
| C | -4.42535 | -0.30603 | 0.120837 |
| C | -5.52682 | -0.2848 | -0.96266 |
| C | -4.97141 | -0.68781 | -2.36099 |
| C | -5.21194 | -2.22186 | -2.43723 |
| C | -4.93511 | 0.137823 | 1.532812 |
| O | -2.63571 | -1.85062 | 0.542104 |
| O | -5.92368 | -0.74633 | 2.026071 |
| C | -7.8235 | -1.13611 | -1.26994 |
| C | -5.39526 | 1.596641 | 1.534597 |
| C | -6.72605 | 1.928118 | 1.806789 |
| C | -7.14453 | 3.258558 | 1.808292 |
| C | -6.23025 | 4.278697 | 1.540643 |
| C | -4.89308 | 3.961686 | 1.280455 |
| C | -4.48353 | 2.631694 | 1.279582 |
| C | -6.66277 | 5.717152 | 1.599147 |
| F | -6.49756 | 6.243771 | 2.835905 |

| | | | |
|---|---|---|---|
| F | -7.9698 | 5.865099 | 1.283906 |
| F | -5.95101 | 6.492671 | 0.74901 |
| H | -6.53935 | -3.39828 | -1.10177 |
| H | -4.13254 | -3.75315 | -0.30328 |
| H | -5.20997 | -3.11376 | 0.951006 |
| H | -3.61617 | 0.372399 | -0.16885 |
| H | -6.01343 | 0.694592 | -0.97126 |
| H | -5.50829 | -0.16392 | -3.15757 |
| H | -3.91445 | -0.42265 | -2.46322 |
| H | -5.90837 | -2.47066 | -3.24395 |
| H | -4.29255 | -2.78519 | -2.62415 |
| H | -4.07493 | 0.058382 | 2.210916 |
| H | -6.43672 | -1.04566 | 1.236131 |
| H | -8.26736 | -0.20413 | -0.90664 |
| H | -7.76872 | -1.08502 | -2.36884 |
| H | -8.49079 | -1.95983 | -0.99789 |
| H | -7.42431 | 1.131973 | 2.040305 |
| H | -8.18096 | 3.503727 | 2.017154 |
| H | -4.17922 | 4.753639 | 1.077654 |
| H | -3.43865 | 2.399362 | 1.086166 |

**Table S41.** Geometry (Å) for product (syn HBN) of the reaction tropinone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -0.98751 | 1.762303 | -0.04279 |
| C | -1.81248 | 0.689845 | 0.133385 |
| C | -3.01674 | 0.734852 | -0.77189 |
| C | -2.63445 | -1.44446 | 1.06726 |
| N | -3.22614 | -1.63176 | -0.27666 |
| C | -4.02993 | -2.8417 | -0.40633 |
| C | -4.00777 | -0.38615 | -0.41073 |
| C | -4.6819 | -0.15553 | 0.986141 |
| C | -3.83424 | -1.01461 | 1.965204 |
| C | -1.61428 | -0.32494 | 0.988301 |
| H | -0.19151 | 1.661988 | 0.524735 |
| H | -2.6888 | 0.630921 | -1.81545 |
| H | -3.49675 | 1.719605 | -0.68853 |
| H | -2.16326 | -2.37539 | 1.400889 |
| H | -4.41711 | -2.9042 | -1.42983 |
| H | -4.89204 | -2.91582 | 0.282531 |
| H | -3.39199 | -3.7167 | -0.23775 |
| H | -4.74779 | -0.49384 | -1.21071 |
| H | -5.72671 | -0.48318 | 0.974516 |
| H | -4.68227 | 0.90459 | 1.258749 |
| H | -4.39784 | -1.8871 | 2.318286 |
| H | -3.50812 | -0.4555 | 2.846841 |

| | | | |
|---|---|---|---|
| H | -0.76158 | -0.33901 | 1.66289 |
| C | 2.067101 | 0.873909 | -0.07053 |
| O | 1.578856 | 1.297757 | 0.970014 |
| C | 3.472444 | 0.462728 | -0.22472 |
| C | 4.354431 | 0.554759 | 0.855632 |
| C | 3.913434 | -0.01897 | -1.46826 |
| C | 5.68826 | 0.166093 | 0.702271 |
| C | 5.240836 | -0.40546 | -1.61456 |
| C | 6.13134 | -0.31639 | -0.54019 |
| O | 6.474322 | 0.291116 | 1.80678 |
| C | 7.841628 | -0.08153 | 1.713099 |
| H | 1.439135 | 0.782526 | -0.97767 |
| H | 4.005726 | 0.928306 | 1.812444 |
| H | 3.219101 | -0.08714 | -2.30147 |
| H | 5.598451 | -0.78119 | -2.56897 |
| H | 7.161903 | -0.62301 | -0.67843 |
| H | 8.267694 | 0.102246 | 2.7006 |
| H | 8.37496 | 0.525258 | 0.96966 |
| H | 7.953775 | -1.14441 | 1.46203 |

**Table S42.** Geometry (Å) for reactant (anti) of the reaction tropinone + *m*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.30151 | 2.818545 | 0.084948 |
| C | -1.53456 | 1.544856 | 0.1048 |
| C | -2.76932 | 1.046526 | -0.61352 |
| C | -0.94089 | -0.84049 | 0.584231 |
| N | -1.66192 | -1.10754 | -0.68045 |
| C | -1.76809 | -2.52801 | -1.00439 |
| C | -2.96611 | -0.46528 | -0.4119 |
| C | -3.32366 | -0.82504 | 1.068618 |
| C | -1.95832 | -1.19546 | 1.711343 |
| C | -0.59921 | 0.635833 | 0.620345 |
| H | -2.66168 | 1.281286 | -1.68138 |
| H | -3.63458 | 1.618761 | -0.25462 |
| H | -0.02869 | -1.443 | 0.631541 |
| H | -2.30467 | -2.63934 | -1.95289 |
| H | -2.28929 | -3.1404 | -0.24708 |
| H | -0.76284 | -2.94221 | -1.13645 |
| H | -3.71608 | -0.83434 | -1.11842 |
| H | -4.02018 | -1.66853 | 1.107228 |
| H | -3.8111 | 0.012536 | 1.578124 |
| H | -1.91027 | -2.26328 | 1.953101 |
| H | -1.75922 | -0.64547 | 2.635894 |
| H | 0.040758 | 0.979309 | 1.427268 |
| H | -0.15923 | 2.891202 | -0.17333 |

| | | | |
|---|---|---|---|
| C | 0.918153 | 1.267661 | -0.76653 |
| O | 0.98858 | 2.531317 | -0.51473 |
| C | 2.038109 | 0.37655 | -0.36677 |
| C | 2.983854 | 0.814169 | 0.561816 |
| C | 2.166382 | -0.8945 | -0.95313 |
| C | 4.054043 | -0.01253 | 0.921061 |
| C | 3.234833 | -1.71008 | -0.59445 |
| C | 4.182254 | -1.2833 | 0.341458 |
| O | 4.919937 | 0.508156 | 1.838893 |
| C | 6.033238 | -0.27564 | 2.235899 |
| H | 0.371721 | 0.929715 | -1.6585 |
| H | 2.900521 | 1.804558 | 0.995771 |
| H | 1.435819 | -1.22507 | -1.68643 |
| H | 3.344472 | -2.69199 | -1.04738 |
| H | 5.007912 | -1.93555 | 0.601966 |
| H | 6.579997 | 0.328389 | 2.96223 |
| H | 6.691207 | -0.50409 | 1.386852 |
| H | 5.718665 | -1.21497 | 2.710213 |

**Table S43.** Geometry (Å) for transition state (anti) of the reaction tropinone + *m*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.6758 | 2.8907 | 0.0947 |
| C | -1.6884 | 1.6712 | -0.0196 |
| C | -2.8523 | 0.9704 | -0.7095 |
| C | -0.8526 | -0.6502 | 0.5706 |
| N | -1.5693 | -1.0827 | -0.6481 |
| C | -1.5488 | -2.5299 | -0.8526 |
| C | -2.9215 | -0.5367 | -0.4184 |
| C | -3.2487 | -0.8231 | 1.0757 |
| C | -1.8512 | -0.8717 | 1.7508 |
| C | -0.4845 | 0.8381 | 0.4166 |
| H | -2.6954 | 1.1179 | -1.7873 |
| H | -3.7774 | 1.4958 | -0.4472 |
| H | 0.0605 | -1.2364 | 0.6922 |
| H | -2.1066 | -2.7719 | -1.7637 |
| H | -1.9800 | -3.1194 | -0.0237 |
| H | -0.5134 | -2.8555 | -0.9945 |
| H | -3.6367 | -1.0070 | -1.1008 |
| H | -3.7694 | -1.7804 | 1.1790 |
| H | -3.9031 | -0.0576 | 1.5056 |
| H | -1.6763 | -1.8436 | 2.2226 |
| H | -1.7328 | -0.1148 | 2.5329 |
| H | -0.1433 | 1.2351 | 1.3808 |
| C | 0.6829 | 1.1481 | -0.5951 |
| O | 1.0532 | 2.5118 | -0.4864 |

| | | | |
|---|---|---|---|
| C | 1.9102 | 0.2936 | -0.3344 |
| C | 2.7988 | 0.6413 | 0.6806 |
| C | 2.1536 | -0.8563 | -1.1013 |
| C | 3.9237 | -0.1513 | 0.9447 |
| C | 3.2713 | -1.6429 | -0.8352 |
| C | 4.1636 | -1.3038 | 0.1861 |
| O | 4.7252 | 0.2870 | 1.9612 |
| C | 5.8957 | -0.4540 | 2.2610 |
| H | 0.3178 | 0.9209 | -1.6083 |
| H | 0.2419 | 3.0246 | -0.3042 |
| H | 2.6468 | 1.5470 | 1.2571 |
| H | 1.4733 | -1.1207 | -1.9065 |
| H | 3.4641 | -2.5299 | -1.4333 |
| H | 5.0307 | -1.9276 | 0.3711 |
| H | 6.3815 | 0.0732 | 3.0843 |
| H | 6.58048 | -0.49459 | 1.403309 |
| H | 5.657636 | -1.47834 | 2.578632 |

**Table S44.** Geometry (Å) for product (anti HBO) of the reaction tropinone + *m*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -1.0080 | 2.8205 | -8.6097 |
| C | -0.1434 | 3.3946 | -7.5478 |
| C | 1.0486 | 2.4380 | -7.3432 |
| C | 0.5877 | 1.0179 | -7.0221 |
| C | -0.6692 | 0.5396 | -7.7582 |
| C | -1.6778 | 1.7092 | -7.8812 |
| C | -2.0608 | 2.2996 | -6.4920 |
| C | -1.0448 | 3.4579 | -6.2816 |
| C | -0.3328 | -0.0748 | -9.1619 |
| O | 1.1739 | 0.3150 | -6.2228 |
| O | 0.3702 | 0.8411 | -9.9804 |
| C | 0.4513 | -1.3717 | -9.0552 |
| C | 1.8284 | -1.4098 | -9.3075 |
| C | 2.5169 | -2.6135 | -9.1853 |
| C | 1.8619 | -3.7907 | -8.8134 |
| C | 0.4850 | -3.7518 | -8.5665 |
| C | -0.2115 | -2.5441 | -8.6945 |
| C | -1.9452 | 3.7881 | -9.1884 |
| O | -0.2724 | -4.8333 | -8.2057 |
| C | 0.3781 | -6.0832 | -8.0559 |
| H | 0.2191 | 4.3788 | -7.8603 |
| H | 1.7089 | 2.7805 | -6.5405 |
| H | 1.6311 | 2.3870 | -8.2719 |
| H | -1.1111 | -0.2570 | -7.1502 |
| H | -2.5512 | 1.3741 | -8.4514 |

| | | | |
|---|---|---|---|
| H | -3.0892 | 2.6741 | -6.4994 |
| H | -2.0026 | 1.5413 | -5.7052 |
| H | -1.5567 | 4.4231 | -6.2161 |
| H | -0.4589 | 3.3433 | -5.3646 |
| H | -1.3131 | -0.3139 | -9.6148 |
| H | -0.0480 | 1.7173 | -9.8065 |
| H | 2.3385 | -0.5031 | -9.6099 |
| H | 3.5855 | -2.6448 | -9.3828 |
| H | 2.4223 | -4.7146 | -8.7256 |
| H | -1.2829 | -2.5511 | -8.5091 |
| H | -2.5512 | 3.2874 | -9.9500 |
| H | -2.6269 | 4.2502 | -8.4562 |
| H | -1.3779 | 4.5861 | -9.6775 |
| H | -0.3984 | -6.7927 | -7.7627 |
| H | 0.836511 | -6.41789 | -8.99636 |
| H | 1.149185 | -6.04798 | -7.27453 |

**Table S45.** Geometry (Å) for product (anti HBN) of the reaction tropinone + *m*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.115044 | 1.122725 | 0.489509 |
| C | 1.179844 | 0.300869 | 0.251616 |
| C | 1.946824 | -0.03053 | 1.505654 |
| C | 2.766301 | -1.07594 | -1.04732 |
| N | 2.892332 | -1.85022 | 0.207644 |
| C | 3.878354 | -2.92256 | 0.14343 |
| C | 3.24668 | -0.77846 | 1.159624 |
| C | 4.275263 | 0.135151 | 0.406294 |
| C | 4.05515 | -0.19938 | -1.09541 |
| C | 1.540329 | -0.1891 | -0.94335 |
| H | -0.38661 | 1.262182 | -0.3416 |
| H | 1.317471 | -0.64539 | 2.16369 |
| H | 2.166266 | 0.896598 | 2.05292 |
| H | 2.680476 | -1.75805 | -1.90011 |
| H | 3.900483 | -3.44494 | 1.106706 |
| H | 4.911172 | -2.60279 | -0.0886 |
| H | 3.573 | -3.64604 | -0.62097 |
| H | 3.67329 | -1.21347 | 2.069543 |
| H | 5.300449 | -0.09258 | 0.716701 |
| H | 4.103129 | 1.193946 | 0.62414 |
| H | 4.90231 | -0.76302 | -1.50551 |
| H | 3.922853 | 0.692731 | -1.71415 |
| H | 1.003893 | 0.079228 | -1.85036 |
| C | -2.76106 | 1.169969 | -1.91181 |
| O | -1.57151 | 1.415003 | -1.77251 |
| C | -3.67672 | 0.643059 | -0.88431 |

| | | | |
|---|---|---|---|
| C | -3.22781 | 0.334079 | 0.404498 |
| C | -5.02559 | 0.455418 | -1.23518 |
| C | -4.13045 | -0.16349 | 1.350928 |
| C | -5.91511 | -0.03782 | -0.28893 |
| C | -5.47795 | -0.34895 | 1.002184 |
| O | -3.60862 | -0.43733 | 2.576936 |
| C | -4.46858 | -0.94806 | 3.584497 |
| H | -3.23517 | 1.351665 | -2.89831 |
| H | -2.18816 | 0.469516 | 0.687037 |
| H | -5.36273 | 0.697475 | -2.23974 |
| H | -6.96017 | -0.1865 | -0.54547 |
| H | -6.18854 | -0.73371 | 1.724827 |
| H | -3.84117 | -1.08944 | 4.465828 |
| H | -4.90512 | -1.9122 | 3.292186 |
| H | -5.2749 | -0.24201 | 3.823126 |

**Table S46.** Geometry (Å) for reactant (syn) of the reaction tropinone + *m*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.772179 | 2.628925 | 0.712208 |
| C | 1.122161 | 1.414141 | 0.444354 |
| C | 1.359009 | 0.468885 | 1.598625 |
| C | 1.590836 | -0.49104 | -1.11455 |
| N | 1.112011 | -1.32876 | 0.00096 |
| C | 1.199051 | -2.76231 | -0.25235 |
| C | 1.963371 | -0.85937 | 1.110346 |
| C | 3.39558 | -0.67807 | 0.502127 |
| C | 3.147961 | -0.56422 | -1.02817 |
| C | 1.129828 | 0.935792 | -0.87613 |
| H | 0.394852 | 0.28635 | 2.092906 |
| H | 2.006516 | 0.967587 | 2.330957 |
| H | 1.202885 | -0.87193 | -2.06623 |
| H | 0.827577 | -3.30221 | 0.625101 |
| H | 2.213876 | -3.13844 | -0.4773 |
| H | 0.550213 | -3.01721 | -1.09712 |
| H | 1.950236 | -1.58927 | 1.925419 |
| H | 4.029895 | -1.53899 | 0.735492 |
| H | 3.897195 | 0.205796 | 0.909768 |
| H | 3.523015 | -1.44799 | -1.55677 |
| H | 3.631205 | 0.310234 | -1.47427 |
| H | 1.369883 | 1.658443 | -1.65133 |
| H | -0.07134 | 2.861975 | -0.08577 |
| C | -0.92133 | 1.399234 | -1.23212 |
| O | -0.93072 | 2.663876 | -0.94043 |
| C | -1.79022 | 0.455987 | -0.49132 |
| C | -2.38079 | 0.83495 | 0.719932 |

| | | | |
|---|---|---|---|
| C | -2.0839 | -0.81603 | -1.01119 |
| C | -3.22941 | -0.0295 | 1.410939 |
| C | -2.93072 | -1.68367 | -0.34083 |
| C | -3.50671 | -1.29705 | 0.880721 |
| O | -4.32505 | -2.21898 | 1.46308 |
| C | -4.9505 | -1.88453 | 2.69248 |
| H | -0.76075 | 1.128709 | -2.28443 |
| H | -2.18073 | 1.827867 | 1.109986 |
| H | -1.64787 | -1.12043 | -1.96018 |
| H | -3.67669 | 0.29455 | 2.343792 |
| H | -3.17094 | -2.66466 | -0.73871 |
| H | -5.54759 | -2.7549 | 2.970491 |
| H | -4.21175 | -1.68472 | 3.479733 |
| H | -5.60845 | -1.01218 | 2.58595 |

**Table S47.** Geometry (Å) for transition state (syn) of the reaction tropinone + *m*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.6100 | 2.4609 | 1.1402 |
| C | 0.9316 | 1.3373 | 0.7696 |
| C | 1.4068 | 0.2997 | 1.7745 |
| C | 1.4495 | -0.4067 | -1.0325 |
| N | 1.1427 | -1.3602 | 0.0486 |
| C | 1.2852 | -2.7601 | -0.3361 |
| C | 2.0602 | -0.9248 | 1.1161 |
| C | 3.4115 | -0.5742 | 0.4165 |
| C | 3.0053 | -0.3094 | -1.0582 |
| C | 0.8051 | 0.9585 | -0.7064 |
| H | 0.5064 | -0.0240 | 2.3137 |
| H | 2.0598 | 0.7944 | 2.5030 |
| H | 1.0489 | -0.7781 | -1.9818 |
| H | 1.0699 | -3.3927 | 0.5313 |
| H | 2.2838 | -3.0376 | -0.7201 |
| H | 0.5460 | -2.9946 | -1.1089 |
| H | 2.1733 | -1.7195 | 1.8598 |
| H | 4.1175 | -1.4072 | 0.4896 |
| H | 3.8943 | 0.2922 | 0.8813 |
| H | 3.4191 | -1.0782 | -1.7189 |
| H | 3.3585 | 0.6561 | -1.4338 |
| H | 1.3403 | 1.7418 | -1.2596 |
| C | -0.6799 | 1.1392 | -1.1895 |
| O | -1.0323 | 2.5094 | -1.1142 |
| C | -1.7037 | 0.2342 | -0.5102 |
| C | -2.3129 | 0.6161 | 0.6835 |
| C | -2.0713 | -0.9827 | -1.1036 |
| C | -3.2577 | -0.2140 | 1.3025 |

| | | | |
|---|---|---|---|
| C | -3.0113 | -1.8047 | -0.4905 |
| C | -3.6106 | -1.4352 | 0.7173 |
| O | -3.7814 | 0.2657 | 2.4711 |
| C | -4.7655 | -0.5092 | 3.1337 |
| H | -0.6737 | 0.8845 | -2.2576 |
| H | -0.6272 | 2.8640 | -0.2983 |
| H | -2.0882 | 1.5705 | 1.1469 |
| H | -1.6298 | -1.2768 | -2.0529 |
| H | -3.2973 | -2.7439 | -0.9574 |
| H | -4.3465 | -2.0862 | 1.1751 |
| H | -5.0454 | 0.0585 | 4.0232 |
| H | -4.37322 | -1.48894 | 3.439113 |
| H | -5.65421 | -0.65941 | 2.506008 |

**Table S48.** Geometry (Å) for product (syn HBO) of the reaction tropinone + *m*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.5458 | -1.2289 | -0.6717 |
| C | -5.8530 | -2.4460 | -1.1661 |
| C | -4.7806 | -2.8314 | -0.1294 |
| C | -3.8379 | -1.6756 | 0.1901 |
| C | -4.4430 | -0.2679 | 0.1460 |
| C | -5.5324 | -0.1728 | -0.9459 |
| C | -4.9666 | -0.5020 | -2.3591 |
| C | -5.2155 | -2.0281 | -2.5215 |
| C | -4.9629 | 0.1089 | 1.5756 |
| O | -2.6747 | -1.8543 | 0.4974 |
| O | -5.9686 | -0.7881 | 2.0099 |
| C | -7.8328 | -0.9807 | -1.3292 |
| C | -5.3978 | 1.5735 | 1.6435 |
| C | -6.7350 | 1.9210 | 1.8299 |
| C | -7.1037 | 3.2711 | 1.8785 |
| C | -6.1525 | 4.2739 | 1.7488 |
| C | -4.8026 | 3.9288 | 1.5750 |
| C | -4.4289 | 2.5835 | 1.5214 |
| O | -3.9342 | 4.9791 | 1.4723 |
| C | -2.5518 | 4.6973 | 1.3298 |
| H | -6.5742 | -3.2622 | -1.2722 |
| H | -4.1864 | -3.6903 | -0.4570 |
| H | -5.2733 | -3.1000 | 0.8142 |
| H | -3.6247 | 0.4176 | -0.0974 |
| H | -6.0073 | 0.8110 | -0.9004 |
| H | -5.4933 | 0.0679 | -3.1306 |
| H | -3.9072 | -0.2386 | -2.4379 |
| H | -5.9009 | -2.2287 | -3.3509 |
| H | -4.2967 | -2.5870 | -2.7247 |

| | | | |
|---|---|---|---|
| H | -4.1113 | -0.0224 | 2.2563 |
| H | -6.4810 | -1.0322 | 1.2024 |
| H | -8.2678 | -0.0618 | -0.9242 |
| H | -7.7650 | -0.8755 | -2.4238 |
| H | -8.5144 | -1.8077 | -1.1064 |
| H | -7.4711 | 1.1371 | 1.9683 |
| H | -8.1462 | 3.5404 | 2.0283 |
| H | -6.4196 | 5.3252 | 1.7902 |
| H | -3.3862 | 2.3066 | 1.4017 |
| H | -2.3451 | 4.1351 | 0.4091 |
| H | -2.16294 | 4.134041 | 2.188488 |
| H | -2.05214 | 5.666582 | 1.278749 |

**Table S49.** Geometry (Å) for product (syn HBN) of the reaction tropinone + *m*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.75089 | 1.815746 | -0.61133 |
| C | -2.52855 | 0.756242 | -0.24751 |
| C | -3.71169 | 0.566094 | -1.16263 |
| C | -3.2701 | -1.20397 | 1.061755 |
| N | -3.81842 | -1.67301 | -0.23147 |
| C | -4.5609 | -2.92479 | -0.13854 |
| C | -4.6552 | -0.51736 | -0.61134 |
| C | -5.37539 | -0.06352 | 0.705914 |
| C | -4.51207 | -0.67653 | 1.843375 |
| C | -2.30425 | -0.06785 | 0.787573 |
| H | -3.35314 | 0.285541 | -2.16268 |
| H | -4.24171 | 1.522014 | -1.27435 |
| H | -2.76247 | -2.02943 | 1.572747 |
| H | -4.92682 | -3.19717 | -1.13517 |
| H | -5.42982 | -2.91104 | 0.545452 |
| H | -3.8848 | -3.7195 | 0.196779 |
| H | -5.36885 | -0.81226 | -1.3878 |
| H | -6.40219 | -0.44264 | 0.739846 |
| H | -5.43497 | 1.027435 | 0.772969 |
| H | -5.04058 | -1.4955 | 2.346707 |
| H | -4.23571 | 0.055269 | 2.607746 |
| H | -1.46851 | 0.088963 | 1.464958 |
| H | -0.96022 | 1.858318 | -0.02711 |
| C | 1.317808 | 1.00847 | -0.36172 |
| O | 0.776054 | 1.625468 | 0.552228 |
| C | 2.70759 | 0.554507 | -0.34817 |
| C | 3.538039 | 0.804097 | 0.755311 |
| C | 3.229344 | -0.14568 | -1.45154 |
| C | 4.856972 | 0.36978 | 0.767774 |
| C | 4.542074 | -0.58419 | -1.45376 |

| | | | |
|---|---|---|---|
| C | 5.365696 | -0.32931 | -0.34223 |
| O | 6.633198 | -0.79782 | -0.43659 |
| C | 7.527775 | -0.58618 | 0.650438 |
| H | 0.741655 | 0.761904 | -1.27481 |
| H | 3.127031 | 1.344777 | 1.602396 |
| H | 2.591806 | -0.34426 | -2.31012 |
| H | 5.480964 | 0.572265 | 1.630336 |
| H | 4.961639 | -1.12602 | -2.29497 |
| H | 8.470512 | -1.0456 | 0.3503 |
| H | 7.1634 | -1.06648 | 1.5668 |
| H | 7.686013 | 0.483351 | 0.835579 |

**Table S50.** Geometry (Å) for reactant (anti) of the reaction tropinone + *p*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.04295 | 2.952626 | -0.09804 |
| C | -2.2403 | 1.67422 | -0.06411 |
| C | -3.42056 | 1.123606 | -0.83746 |
| C | -1.60245 | -0.68736 | 0.48556 |
| N | -2.24717 | -0.99904 | -0.81016 |
| C | -2.29837 | -2.42817 | -1.10936 |
| C | -3.58181 | -0.39052 | -0.62126 |
| C | -4.00552 | -0.73751 | 0.84522 |
| C | -2.66608 | -1.05872 | 1.563932 |
| C | -1.31114 | 0.798652 | 0.512742 |
| H | -3.26542 | 1.345312 | -1.90233 |
| H | -4.32144 | 1.672192 | -0.53345 |
| H | -0.6751 | -1.25929 | 0.591317 |
| H | -2.78241 | -2.57283 | -2.08142 |
| H | -2.84125 | -3.04024 | -0.36723 |
| H | -1.27719 | -2.81764 | -1.18182 |
| H | -4.28258 | -0.79412 | -1.35886 |
| H | -4.67992 | -1.59957 | 0.862556 |
| H | -4.54119 | 0.094242 | 1.314111 |
| H | -2.59969 | -2.12146 | 1.823845 |
| H | -2.53191 | -0.48989 | 2.488721 |
| H | -0.70079 | 1.174752 | 1.327839 |
| H | -0.86585 | 3.04884 | -0.32239 |
| C | 0.252612 | 1.461098 | -0.85886 |
| O | 0.279771 | 2.726248 | -0.59086 |
| C | 1.382268 | 0.603342 | -0.45303 |
| C | 2.335706 | 1.056131 | 0.467553 |
| C | 1.542373 | -0.67635 | -1.01486 |
| C | 3.418652 | 0.259671 | 0.832033 |
| C | 2.616204 | -1.47964 | -0.66096 |
| C | 3.562854 | -1.01712 | 0.267812 |

| | | | |
|---|---|---|---|
| O | 4.581381 | -1.87646 | 0.54835 |
| C | 5.57864 | -1.46552 | 1.47226 |
| H | -0.28539 | 1.117037 | -1.75231 |
| H | 2.223503 | 2.051898 | 0.88466 |
| H | 0.813984 | -1.034 | -1.73868 |
| H | 4.144091 | 0.639375 | 1.542441 |
| H | 2.753182 | -2.46631 | -1.09222 |
| H | 6.282515 | -2.29678 | 1.540057 |
| H | 5.15196 | -1.26912 | 2.46441 |
| H | 6.107247 | -0.56962 | 1.121935 |

**Table S51.** Geometry (Å) for transition state (anti) of the reaction tropinone + *p*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.38159 | 3.00679 | -0.11912 |
| C | -2.35854 | 1.785808 | -0.21544 |
| C | -3.46772 | 1.04544 | -0.95252 |
| C | -1.50055 | -0.50393 | 0.458794 |
| N | -2.1476 | -0.97891 | -0.78251 |
| C | -2.089 | -2.4298 | -0.95119 |
| C | -3.52004 | -0.45625 | -0.6318 |
| C | -3.91439 | -0.71628 | 0.851313 |
| C | -2.55074 | -0.72333 | 1.593955 |
| C | -1.15804 | 0.988806 | 0.28996 |
| H | -3.25491 | 1.173417 | -2.02318 |
| H | -4.4169 | 1.554991 | -0.75266 |
| H | -0.58111 | -1.06537 | 0.637904 |
| H | -2.59533 | -2.70384 | -1.88297 |
| H | -2.54983 | -3.00897 | -0.13113 |
| H | -1.04184 | -2.73786 | -1.0334 |
| H | -4.19138 | -0.95637 | -1.33708 |
| H | -4.42216 | -1.68082 | 0.951078 |
| H | -4.6025 | 0.046077 | 1.23129 |
| H | -2.38017 | -1.68251 | 2.092826 |
| H | -2.48525 | 0.050635 | 2.36548 |
| H | -0.86763 | 1.411993 | 1.259708 |
| H | -0.44411 | 3.177323 | -0.43584 |
| C | 0.04549 | 1.304819 | -0.67831 |
| O | 0.384779 | 2.678402 | -0.57043 |
| C | 1.278338 | 0.481919 | -0.36445 |
| C | 2.143336 | 0.852959 | 0.667245 |
| C | 1.580074 | -0.67409 | -1.09922 |
| C | 3.275019 | 0.094667 | 0.97544 |
| C | 2.699872 | -1.44301 | -0.80383 |
| C | 3.556281 | -1.06286 | 0.239183 |
| O | 4.633125 | -1.87718 | 0.450423 |

| | | | |
|---|---|---|---|
| C | 5.548345 | -1.5251 | 1.474765 |
| H | -0.27798 | 1.060874 | -1.70199 |
| H | 1.942989 | 1.765615 | 1.219645 |
| H | 0.929791 | -0.96961 | -1.91947 |
| H | 3.929281 | 0.418934 | 1.776857 |
| H | 2.940706 | -2.33418 | -1.37528 |
| H | 6.322026 | -2.29521 | 1.462987 |
| H | 5.06637 | -1.51154 | 2.461572 |
| H | 6.008842 | -0.54602 | 1.286994 |

**Table S52.** Geometry (Å) for product (anti HBO) of the reaction tropinone + *p*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.93872 | 2.868308 | -8.94739 |
| C | -0.10271 | 3.598975 | -7.96151 |
| C | 1.090938 | 2.69448 | -7.59322 |
| C | 0.63871 | 1.326319 | -7.08707 |
| C | -0.59681 | 0.735567 | -7.77385 |
| C | -1.61202 | 1.863831 | -8.07964 |
| C | -2.02625 | 2.641086 | -6.79417 |
| C | -1.03456 | 3.837937 | -6.74025 |
| C | -0.22158 | -0.06795 | -9.06999 |
| O | 1.218733 | 0.746343 | -6.19042 |
| O | 0.494986 | 0.732942 | -9.99185 |
| C | 0.56794 | -1.3281 | -8.76943 |
| C | -0.0792 | -2.46679 | -8.28675 |
| C | 0.622035 | -3.63556 | -7.98141 |
| C | 2.007976 | -3.67431 | -8.17201 |
| C | 2.667914 | -2.54231 | -8.66904 |
| C | 1.954914 | -1.38643 | -8.96129 |
| C | -1.87486 | 3.731064 | -9.67446 |
| O | 2.798511 | -4.76046 | -7.91462 |
| C | 2.181666 | -5.92877 | -7.40315 |
| H | 0.261065 | 4.530464 | -8.40627 |
| H | 1.726749 | 3.156176 | -6.83149 |
| H | 1.698381 | 2.520443 | -8.49053 |
| H | -1.0453 | 0.025814 | -7.07033 |
| H | -2.47174 | 1.441334 | -8.61139 |
| H | -3.06142 | 2.988987 | -6.8653 |
| H | -1.96415 | 2.004797 | -5.90595 |
| H | -1.56365 | 4.791319 | -6.83605 |
| H | -0.47035 | 3.876872 | -5.80357 |
| H | -1.19097 | -0.3745 | -9.50671 |
| H | 0.062992 | 1.618766 | -9.95626 |
| H | -1.15888 | -2.45478 | -8.14553 |
| H | 0.082816 | -4.4992 | -7.60893 |

| | | | |
|---|---|---|---|
| H | 3.742124 | -2.59336 | -8.81848 |
| H | 2.468487 | -0.51812 | -9.35862 |
| H | -2.45924 | 3.119851 | -10.3694 |
| H | -2.57639 | 4.280496 | -9.02649 |
| H | -1.3075 | 4.460683 | -10.2608 |
| H | 2.983972 | -6.65609 | -7.26378 |
| H | 1.693103 | -5.73959 | -6.43767 |
| H | 1.441576 | -6.33741 | -8.10478 |

**Table S53.** Geometry (Å) for product (anti HBN) of the reaction tropinone + *p*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.230034 | 1.103033 | 0.585144 |
| C | 1.290764 | 0.299355 | 0.275466 |
| C | 2.104797 | -0.07822 | 1.486227 |
| C | 2.835442 | -1.01268 | -1.13559 |
| N | 3.011921 | -1.83686 | 0.081417 |
| C | 4.00134 | -2.89824 | -0.06298 |
| C | 3.395435 | -0.80191 | 1.062631 |
| C | 4.3899 | 0.149164 | 0.309922 |
| C | 4.117174 | -0.12681 | -1.19499 |
| C | 1.609637 | -0.13917 | -0.95079 |
| H | 1.504526 | -0.72524 | 2.141014 |
| H | 2.338622 | 0.826961 | 2.063496 |
| H | 2.721524 | -1.66013 | -2.01178 |
| H | 4.061131 | -3.4604 | 0.876032 |
| H | 5.023139 | -2.56123 | -0.31777 |
| H | 3.673156 | -3.59128 | -0.84586 |
| H | 3.858091 | -1.27033 | 1.937719 |
| H | 5.42713 | -0.08268 | 0.573709 |
| H | 4.219145 | 1.197017 | 0.57645 |
| H | 4.951647 | -0.6688 | -1.65699 |
| H | 3.958654 | 0.788207 | -1.7727 |
| H | 1.038589 | 0.163104 | -1.82527 |
| H | -0.29223 | 1.288954 | -0.22621 |
| C | -2.68225 | 1.272119 | -1.72818 |
| O | -1.48878 | 1.529029 | -1.61208 |
| C | -3.54684 | 0.650702 | -0.72452 |
| C | -3.06299 | 0.24249 | 0.530617 |
| C | -4.90799 | 0.452484 | -1.02806 |
| C | -3.91245 | -0.34578 | 1.459088 |
| C | -5.76347 | -0.13081 | -0.11076 |
| C | -5.26947 | -0.53518 | 1.142847 |
| O | -6.17913 | -1.09662 | 1.974337 |
| C | -5.75564 | -1.53484 | 3.261441 |
| H | -3.19209 | 1.524752 | -2.68115 |

| | | | |
|---|---|---|---|
| H | -2.01504 | 0.385704 | 0.77756 |
| H | -5.29013 | 0.764109 | -1.99781 |
| H | -3.51749 | -0.65416 | 2.419927 |
| H | -6.81443 | -0.28902 | -0.32934 |
| H | -6.64558 | -1.94519 | 3.74056 |
| H | -4.98902 | -2.31547 | 3.185172 |
| H | -5.37021 | -0.70077 | 3.860357 |

**Table S54.** Geometry (Å) for reactant (syn) of the reaction tropinone + *p*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.772179 | 2.628925 | 0.712208 |
| C | 1.122161 | 1.414141 | 0.444354 |
| C | 1.359009 | 0.468885 | 1.598625 |
| C | 1.590836 | -0.49104 | -1.11455 |
| N | 1.112011 | -1.32876 | 0.00096 |
| C | 1.199051 | -2.76231 | -0.25235 |
| C | 1.963371 | -0.85937 | 1.110346 |
| C | 3.39558 | -0.67807 | 0.502127 |
| C | 3.147961 | -0.56422 | -1.02817 |
| C | 1.129828 | 0.935792 | -0.87613 |
| H | 0.394852 | 0.28635 | 2.092906 |
| H | 2.006516 | 0.967587 | 2.330957 |
| H | 1.202885 | -0.87193 | -2.06623 |
| H | 0.827577 | -3.30221 | 0.625101 |
| H | 2.213876 | -3.13844 | -0.4773 |
| H | 0.550213 | -3.01721 | -1.09712 |
| H | 1.950236 | -1.58927 | 1.925419 |
| H | 4.029895 | -1.53899 | 0.735492 |
| H | 3.897195 | 0.205796 | 0.909768 |
| H | 3.523015 | -1.44799 | -1.55677 |
| H | 3.631205 | 0.310234 | -1.47427 |
| H | 1.369883 | 1.658443 | -1.65133 |
| H | -0.07134 | 2.861975 | -0.08577 |
| C | -0.92133 | 1.399234 | -1.23212 |
| O | -0.93072 | 2.663876 | -0.94043 |
| C | -1.79022 | 0.455987 | -0.49132 |
| C | -2.38079 | 0.83495 | 0.719932 |
| C | -2.0839 | -0.81603 | -1.01119 |
| C | -3.22941 | -0.0295 | 1.410939 |
| C | -2.93072 | -1.68367 | -0.34083 |
| C | -3.50671 | -1.29705 | 0.880721 |
| O | -4.32505 | -2.21898 | 1.46308 |
| C | -4.9505 | -1.88453 | 2.69248 |
| H | -0.76075 | 1.128709 | -2.28443 |
| H | -2.18073 | 1.827867 | 1.109986 |

| | | | |
|---|---|---|---|
| H | -1.64787 | -1.12043 | -1.96018 |
| H | -3.67669 | 0.29455 | 2.343792 |
| H | -3.17094 | -2.66466 | -0.73871 |
| H | -5.54759 | -2.7549 | 2.970491 |
| H | -4.21175 | -1.68472 | 3.479733 |
| H | -5.60845 | -1.01218 | 2.58595 |

**Table S55.** Geometry (Å) for transition state (syn) of the reaction tropinone + *p*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.722768 | 2.483764 | 1.06021 |
| C | 1.019538 | 1.348803 | 0.703166 |
| C | 1.500088 | 0.321537 | 1.716314 |
| C | 1.468056 | -0.43661 | -1.07744 |
| N | 1.179801 | -1.36806 | 0.028002 |
| C | 1.306525 | -2.77606 | -0.33323 |
| C | 2.126519 | -0.92052 | 1.064732 |
| C | 3.462918 | -0.59244 | 0.325669 |
| C | 3.02357 | -0.35861 | -1.14463 |
| C | 0.849687 | 0.942867 | -0.76032 |
| H | 0.606148 | 0.016779 | 2.277091 |
| H | 2.172784 | 0.819208 | 2.424561 |
| H | 1.038298 | -0.81931 | -2.0095 |
| H | 1.100014 | -3.39126 | 0.548675 |
| H | 2.297154 | -3.0675 | -0.72724 |
| H | 0.554637 | -3.0204 | -1.09064 |
| H | 2.251928 | -1.70244 | 1.819839 |
| H | 4.167473 | -1.42641 | 0.401399 |
| H | 3.95947 | 0.28215 | 0.759561 |
| H | 3.411332 | -1.14866 | -1.79589 |
| H | 3.37858 | 0.592909 | -1.55262 |
| H | 1.37924 | 1.70637 | -1.34563 |
| H | -0.52372 | 2.891297 | -0.37751 |
| C | -0.64816 | 1.136946 | -1.19988 |
| O | -0.96093 | 2.520202 | -1.16895 |
| C | -1.67093 | 0.293992 | -0.44828 |
| C | -2.28197 | 0.757648 | 0.71866 |
| C | -2.05739 | -0.96372 | -0.93358 |
| C | -3.22572 | -0.01137 | 1.405734 |
| C | -2.99492 | -1.7422 | -0.26763 |
| C | -3.58374 | -1.27127 | 0.914395 |
| O | -4.4975 | -2.10508 | 1.497313 |
| C | -5.14775 | -1.66287 | 2.676734 |
| H | -0.6837 | 0.840306 | -2.25685 |
| H | -2.03808 | 1.745973 | 1.09531 |
| H | -1.6245 | -1.33767 | -1.85931 |

| | | | |
|---|---|---|---|
| H | -3.68134 | 0.387849 | 2.30489 |
| H | -3.29866 | -2.71235 | -0.64895 |
| H | -5.82785 | -2.46705 | 2.964321 |
| H | -4.43287 | -1.48499 | 3.491546 |
| H | -5.72562 | -0.74555 | 2.500955 |

**Table S56.** Geometry (Å) for product (syn HBO) of the reaction tropinone + *p*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.34016 | -1.22663 | -0.83032 |
| C | -5.63473 | -2.46738 | -1.23786 |
| C | -4.7414 | -2.90789 | -0.06256 |
| C | -3.81521 | -1.7947 | 0.421717 |
| C | -4.34821 | -0.36186 | 0.306317 |
| C | -5.25335 | -0.21336 | -0.93599 |
| C | -4.49525 | -0.5565 | -2.25299 |
| C | -4.79108 | -2.0656 | -2.48011 |
| C | -5.06683 | 0.028668 | 1.642626 |
| O | -2.72397 | -2.02718 | 0.905609 |
| O | -6.14177 | -0.8528 | 1.920651 |
| C | -7.50696 | -0.91485 | -1.66161 |
| C | -5.49019 | 1.497921 | 1.646826 |
| C | -6.84072 | 1.8641 | 1.724601 |
| C | -7.2256 | 3.200378 | 1.724013 |
| C | -6.26051 | 4.213356 | 1.651658 |
| C | -4.90496 | 3.867625 | 1.588735 |
| C | -4.53753 | 2.519828 | 1.588581 |
| O | -6.73812 | 5.494313 | 1.65543 |
| C | -5.80212 | 6.55777 | 1.607893 |
| H | -6.36582 | -3.25114 | -1.45962 |
| H | -4.13537 | -3.78334 | -0.31667 |
| H | -5.37711 | -3.17304 | 0.792265 |
| H | -3.47471 | 0.290208 | 0.200052 |
| H | -5.68828 | 0.789595 | -0.94964 |
| H | -4.86808 | 0.048254 | -3.08541 |
| H | -3.42445 | -0.34814 | -2.1637 |
| H | -5.36133 | -2.21956 | -3.40168 |
| H | -3.88131 | -2.66823 | -2.56214 |
| H | -4.32993 | -0.12043 | 2.442725 |
| H | -6.5437 | -1.06743 | 1.045206 |
| H | -7.95825 | 0.016473 | -1.30593 |
| H | -7.27812 | -0.79871 | -2.73322 |
| H | -8.24666 | -1.71468 | -1.55474 |
| H | -7.58895 | 1.0835 | 1.812729 |
| H | -8.27149 | 3.485098 | 1.789217 |
| H | -4.13447 | 4.629355 | 1.546705 |

| | | | |
|---|---|---|---|
| H | -3.47833 | 2.271645 | 1.551911 |
| H | -5.20335 | 6.530354 | 0.687323 |
| H | -5.12769 | 6.542899 | 2.47457 |
| H | -6.3909 | 7.476932 | 1.626135 |

**Table S57.** Geometry (Å) for product (syn HBN) of the reaction tropinone + *p*-MeO-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -0.74209 | 1.649857 | -0.06471 |
| C | -1.72188 | 0.786363 | 0.331771 |
| C | -2.99504 | 0.95559 | -0.45736 |
| C | -2.79734 | -1.02941 | 1.617106 |
| N | -3.56132 | -1.25435 | 0.369054 |
| C | -4.57451 | -2.29793 | 0.474088 |
| C | -4.12072 | 0.093006 | 0.140762 |
| C | -4.57811 | 0.607749 | 1.549642 |
| C | -3.79356 | -0.28135 | 2.554093 |
| C | -1.6121 | -0.13935 | 1.296606 |
| H | 0.08625 | 1.455001 | 0.428324 |
| H | -2.81302 | 0.671587 | -1.50314 |
| H | -3.27994 | 2.016702 | -0.46393 |
| H | -2.46199 | -1.98813 | 2.027439 |
| H | -5.07913 | -2.40325 | -0.49321 |
| H | -5.35344 | -2.12938 | 1.241111 |
| H | -4.08496 | -3.25207 | 0.69996 |
| H | -4.95505 | 0.036173 | -0.56618 |
| H | -5.65937 | 0.49024 | 1.676876 |
| H | -4.35507 | 1.671782 | 1.67716 |
| H | -4.46056 | -0.98596 | 3.065923 |
| H | -3.27805 | 0.300971 | 3.323131 |
| H | -0.70357 | -0.23813 | 1.885684 |
| C | 2.010106 | 0.125328 | -0.29724 |
| O | 1.777984 | 0.755456 | 0.731971 |
| C | 3.254751 | -0.62467 | -0.53211 |
| C | 4.21864 | -0.59532 | 0.467685 |
| C | 3.489611 | -1.36299 | -1.74444 |
| C | 5.439605 | -1.27664 | 0.325488 |
| C | 4.742176 | -2.05414 | -1.8791 |
| C | 5.692577 | -1.98984 | -0.82727 |
| C | 2.561461 | -1.45553 | -2.81808 |
| C | 2.855659 | -2.18194 | -3.95144 |
| C | 4.090958 | -2.85829 | -4.08018 |
| C | 5.012496 | -2.79362 | -3.06211 |
| H | 1.25027 | 0.120422 | -1.09504 |
| H | 4.002107 | -0.02668 | 1.366523 |
| H | 6.177604 | -1.23811 | 1.121207 |

| | | | |
|---|---|---|---|
| H | 6.634533 | -2.51981 | -0.9482 |
| H | 1.602244 | -0.95434 | -2.75657 |
| H | 2.127621 | -2.23622 | -4.75602 |
| H | 4.305711 | -3.42625 | -4.98081 |
| H | 5.965903 | -3.30956 | -3.14547 |

**Table S58.** Geometry (Å) for reactant (anti) of the reaction tropinone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.24468 | 2.723648 | 0.032146 |
| C | -1.55794 | 1.468985 | 0.056813 |
| C | -2.83805 | 1.05718 | -0.63697 |
| C | -1.15129 | -0.94903 | 0.574041 |
| N | -1.93149 | -1.18947 | -0.66126 |
| C | -2.18124 | -2.606 | -0.92488 |
| C | -3.16382 | -0.42247 | -0.38092 |
| C | -3.50894 | -0.70339 | 1.119629 |
| C | -2.16517 | -1.18043 | 1.737253 |
| C | -0.68521 | 0.49499 | 0.569375 |
| H | -0.08192 | 2.725524 | -0.18927 |
| H | -2.72238 | 1.243952 | -1.71349 |
| H | -3.64477 | 1.715896 | -0.29091 |
| H | -0.29537 | -1.62921 | 0.617743 |
| H | -2.76638 | -2.69834 | -1.84649 |
| H | -2.72685 | -3.13692 | -0.12511 |
| H | -1.2249 | -3.11491 | -1.07967 |
| H | -3.96378 | -0.74401 | -1.05502 |
| H | -4.27826 | -1.47727 | 1.20373 |
| H | -3.90217 | 0.190459 | 1.614664 |
| H | -2.20758 | -2.24135 | 2.008576 |
| H | -1.8911 | -0.62663 | 2.640034 |
| H | -0.01905 | 0.795632 | 1.371776 |
| C | 0.916388 | 1.063114 | -0.79075 |
| O | 1.045168 | 2.311994 | -0.48101 |
| C | 1.99832 | 0.119584 | -0.40771 |
| C | 2.929982 | 0.54923 | 0.525332 |
| C | 2.146581 | -1.17285 | -1.02052 |
| C | 4.023392 | -0.25651 | 0.897725 |
| C | 3.279984 | -1.97635 | -0.65146 |
| C | 4.197419 | -1.49323 | 0.317735 |
| C | 1.244019 | -1.69888 | -1.98779 |
| C | 1.459744 | -2.93158 | -2.56638 |
| C | 2.582899 | -3.71354 | -2.20861 |
| C | 3.467293 | -3.24419 | -1.26627 |
| H | 0.361398 | 0.816759 | -1.70195 |
| H | 2.808354 | 1.540832 | 0.948287 |
| H | 4.734821 | 0.10985 | 1.632679 |
| H | 5.046285 | -2.11679 | 0.588324 |

| | | | |
|---|---|---|---|
| H | 0.35107 | -1.14415 | -2.25241 |
| H | 0.756879 | -3.3072 | -3.30536 |
| H | 2.740175 | -4.68204 | -2.67536 |
| H | 4.331325 | -3.83757 | -0.97637 |

**Table S59**. Geometry (Å) for transition state (anti) of the reaction tropinone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.5379 | 2.8332 | -0.0548 |
| C | -1.6789 | 1.6172 | -0.1083 |
| C | -2.9337 | 1.0158 | -0.7255 |
| C | -1.0567 | -0.7596 | 0.5457 |
| N | -1.8682 | -1.1539 | -0.6270 |
| C | -2.0165 | -2.6035 | -0.7653 |
| C | -3.1452 | -0.4608 | -0.3633 |
| C | -3.4316 | -0.6523 | 1.1555 |
| C | -2.0207 | -0.8562 | 1.7704 |
| C | -0.5542 | 0.6854 | 0.3459 |
| H | -2.8042 | 1.1008 | -1.8136 |
| H | -3.7880 | 1.6469 | -0.4560 |
| H | -0.2003 | -1.4295 | 0.6472 |
| H | -2.6560 | -2.8154 | -1.6290 |
| H | -2.4571 | -3.1048 | 0.1142 |
| H | -1.0349 | -3.0467 | -0.9558 |
| H | -3.9357 | -0.8808 | -0.9931 |
| H | -4.0645 | -1.5296 | 1.3214 |
| H | -3.9610 | 0.2064 | 1.5816 |
| H | -1.9377 | -1.8397 | 2.2433 |
| H | -1.7823 | -0.1151 | 2.5398 |
| H | -0.1862 | 1.0738 | 1.3039 |
| C | 0.6552 | 0.8743 | -0.6478 |
| O | 1.1291 | 2.2095 | -0.5552 |
| C | 1.8224 | -0.0512 | -0.3252 |
| C | 2.6786 | 0.3199 | 0.6945 |
| C | 2.0726 | -1.2653 | -1.0476 |
| C | 3.7927 | -0.4698 | 1.0531 |
| C | 3.2186 | -2.0577 | -0.6881 |
| C | 4.0591 | -1.6352 | 0.3743 |
| C | 1.2548 | -1.7329 | -2.1175 |
| C | 1.5540 | -2.8963 | -2.7929 |
| C | 2.6861 | -3.6669 | -2.4383 |
| C | 3.4944 | -3.2531 | -1.4058 |
| H | 0.2965 | 0.6772 | -1.6657 |
| H | 0.3519 | 2.7864 | -0.4183 |

| | | | |
|---|---|---|---|
| H | 2.5007 | 1.2617 | 1.2026 |
| H | 4.4431 | -0.1429 | 1.8601 |
| H | 4.9197 | -2.2467 | 0.6353 |
| H | 0.363989 | -1.18048 | -2.39409 |
| H | 0.913635 | -3.2247 | -3.60745 |
| H | 2.911691 | -4.58123 | -2.98041 |
| H | 4.366382 | -3.83738 | -1.12054 |

**Table S60.** Geometry (Å) for product (anti HBO) of the reaction tropinone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.6099 | 2.8763 | 0.7362 |
| C | -1.6216 | 1.7318 | 0.3290 |
| C | -2.8461 | 1.1310 | -0.3592 |
| C | -0.8803 | -0.6413 | 0.7559 |
| N | -1.7641 | -1.0620 | -0.3653 |
| C | -1.9114 | -2.5165 | -0.4765 |
| C | -3.0293 | -0.3625 | -0.0248 |
| C | -3.2167 | -0.5845 | 1.5025 |
| C | -1.7640 | -0.7303 | 2.0358 |
| C | -0.4076 | 0.8060 | 0.4762 |
| C | 0.5218 | 0.8704 | -0.7886 |
| O | -0.2020 | 0.5788 | -1.9717 |
| C | 1.2168 | 2.2142 | -0.9354 |
| C | 0.7653 | 3.1124 | -1.8804 |
| C | 2.3336 | 2.5656 | -0.1055 |
| C | 1.3658 | 4.3825 | -2.0394 |
| C | 2.9352 | 3.8600 | -0.2669 |
| C | 2.4241 | 4.7526 | -1.2462 |
| C | 2.8934 | 1.6952 | 0.8730 |
| C | 3.9658 | 2.0780 | 1.6494 |
| C | 4.5439 | 3.3585 | 1.4937 |
| C | 4.0373 | 4.2242 | 0.5520 |
| H | -2.6890 | 1.2408 | -1.4398 |
| H | -3.7264 | 1.7186 | -0.0805 |
| H | -0.0095 | -1.3048 | 0.8008 |
| H | -2.5977 | -2.7448 | -1.2980 |
| H | -2.2934 | -3.0017 | 0.4361 |
| H | -0.9385 | -2.9573 | -0.7155 |
| H | -3.8504 | -0.7776 | -0.6174 |
| H | -3.7984 | -1.4916 | 1.6942 |
| H | -3.7563 | 0.2463 | 1.9672 |
| H | -1.6237 | -1.6914 | 2.5402 |
| H | -1.5010 | 0.0496 | 2.7569 |
| H | 0.1665 | 1.1724 | 1.3331 |
| H | 1.2925 | 0.0951 | -0.6324 |
| H | -0.7990 | -0.1677 | -1.7277 |
| H | -0.0628 | 2.8236 | -2.5170 |

| | | | |
|---|---|---|---|
| H | 0.9799 | 5.0639 | -2.7929 |
| H | 2.8891 | 5.7294 | -1.3573 |
| H | 2.47933 | 0.701832 | 1.011199 |
| H | 4.372278 | 1.389251 | 2.385479 |
| H | 5.387342 | 3.651965 | 2.11277 |
| H | 4.47718 | 5.209904 | 0.417665 |

**Table S61.** Geometry (Å) for product (anti HBN) of the reaction tropinone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.528368 | 1.1768 | 0.537435 |
| C | 1.690148 | 0.458023 | 0.486499 |
| C | 2.349835 | 0.329422 | 1.835214 |
| C | 3.526561 | -0.86136 | -0.50526 |
| N | 3.588969 | -1.49867 | 0.829185 |
| C | 4.669408 | -2.46794 | 0.971047 |
| C | 3.741823 | -0.31224 | 1.695039 |
| C | 4.75744 | 0.625649 | 0.95473 |
| C | 4.726306 | 0.134315 | -0.51927 |
| C | 2.21894 | -0.10032 | -0.6117 |
| H | 0.107103 | 1.184473 | -0.34831 |
| H | 1.715228 | -0.28023 | 2.493322 |
| H | 2.424797 | 1.322459 | 2.299401 |
| H | 3.594669 | -1.62508 | -1.28756 |
| H | 4.637211 | -2.89241 | 1.981006 |
| H | 5.687864 | -2.06985 | 0.806772 |
| H | 4.512455 | -3.28716 | 0.2603 |
| H | 4.107345 | -0.61474 | 2.681953 |
| H | 5.760655 | 0.529881 | 1.383024 |
| H | 4.470042 | 1.677859 | 1.047144 |
| H | 5.660151 | -0.37406 | -0.78888 |
| H | 4.577047 | 0.948024 | -1.23471 |
| H | 1.75679 | 0.023546 | -1.5881 |
| C | -1.9775 | 0.474143 | -2.21673 |
| O | -0.92625 | 1.016374 | -1.89349 |
| C | -2.8672 | -0.27836 | -1.31527 |
| C | -2.48126 | -0.43012 | 0.012096 |
| C | -4.10177 | -0.85841 | -1.78135 |
| C | -3.27471 | -1.1491 | 0.923542 |
| C | -4.90007 | -1.59198 | -0.83839 |
| C | -4.45728 | -1.71815 | 0.503931 |
| C | -4.58836 | -0.75203 | -3.11398 |
| C | -5.77982 | -1.3351 | -3.4881 |
| C | -6.55851 | -2.05845 | -2.55601 |
| C | -6.12318 | -2.18096 | -1.25783 |
| H | -2.28966 | 0.548144 | -3.27271 |

| | | | |
|---|---|---|---|
| H | -1.54852 | 0.012298 | 0.347065 |
| H | -2.94811 | -1.25375 | 1.953742 |
| H | -5.07551 | -2.27769 | 1.202167 |
| H | -4.02533 | -0.2042 | -3.86075 |
| H | -6.12486 | -1.23615 | -4.51364 |
| H | -7.49504 | -2.5117 | -2.86787 |
| H | -6.71034 | -2.73196 | -0.52723 |

**Table S62.** Geometry (Å) for reactant (syn) of the reaction tropinone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.730528 | 2.599837 | 0.820057 |
| C | 1.1062 | 1.39971 | 0.521058 |
| C | 1.33199 | 0.426254 | 1.652025 |
| C | 1.659628 | -0.44237 | -1.07949 |
| N | 1.168204 | -1.32466 | -0.00492 |
| C | 1.293441 | -2.74758 | -0.30391 |
| C | 1.976749 | -0.87446 | 1.143137 |
| C | 3.42181 | -0.6454 | 0.585809 |
| C | 3.215718 | -0.47552 | -0.94516 |
| C | 1.152383 | 0.965989 | -0.81548 |
| H | 0.357432 | 0.210028 | 2.111723 |
| H | 1.946591 | 0.916826 | 2.417359 |
| H | 1.315043 | -0.80726 | -2.05194 |
| H | 0.914368 | -3.32405 | 0.546584 |
| H | 2.322903 | -3.09142 | -0.51386 |
| H | 0.669621 | -2.98505 | -1.17122 |
| H | 1.953527 | -1.62878 | 1.935295 |
| H | 4.063314 | -1.50515 | 0.803078 |
| H | 3.897312 | 0.228828 | 1.04286 |
| H | 3.630328 | -1.32661 | -1.49709 |
| H | 3.68772 | 0.428662 | -1.34148 |
| H | 1.407282 | 1.719619 | -1.55599 |
| H | -0.08907 | 2.849235 | 0.024316 |
| C | -0.89673 | 1.422098 | -1.22028 |
| O | -0.95098 | 2.663337 | -0.84849 |
| C | -1.76072 | 0.4123 | -0.54651 |
| C | -2.30792 | 0.748652 | 0.681616 |
| C | -2.08076 | -0.85557 | -1.14315 |
| C | -3.14468 | -0.14208 | 1.384743 |
| C | -2.9394 | -1.75385 | -0.4224 |
| C | -3.44901 | -1.37125 | 0.846711 |
| C | -1.62123 | -1.2684 | -2.42517 |
| C | -1.97358 | -2.49071 | -2.95653 |
| C | -2.80584 | -3.37684 | -2.23419 |
| C | -3.27674 | -3.0098 | -0.9952 |

| | | | |
|---|---|---|---|
| H | -0.69956 | 1.244819 | -2.28167 |
| H | -2.08659 | 1.728131 | 1.091862 |
| H | -3.55291 | 0.152008 | 2.347866 |
| H | -4.09614 | -2.06438 | 1.379184 |
| H | -0.98871 | -0.61022 | -3.0102 |
| H | -1.61342 | -2.77314 | -3.94233 |
| H | -3.07597 | -4.33806 | -2.66268 |
| H | -3.92521 | -3.67746 | -0.4325 |

**Table S63.** Geometry (Å) for transition state (syn) of the reaction tropinone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.7065 | 2.5041 | 1.1451 |
| C | 0.9954 | 1.3731 | 0.7697 |
| C | 1.3871 | 0.3004 | 1.7720 |
| C | 1.5780 | -0.3330 | -1.0385 |
| N | 1.2162 | -1.3218 | -0.0069 |
| C | 1.4062 | -2.7088 | -0.4246 |
| C | 2.0683 | -0.9147 | 1.1244 |
| C | 3.4588 | -0.5584 | 0.5143 |
| C | 3.1332 | -0.2114 | -0.9633 |
| C | 0.8997 | 1.0161 | -0.7142 |
| H | 0.4459 | -0.0273 | 2.2343 |
| H | 1.9933 | 0.7628 | 2.5593 |
| H | 1.2468 | -0.6826 | -2.0206 |
| H | 1.1366 | -3.3704 | 0.4052 |
| H | 2.4359 | -2.9592 | -0.7383 |
| H | 0.7303 | -2.9262 | -1.2567 |
| H | 2.1312 | -1.7267 | 1.8552 |
| H | 4.1411 | -1.4116 | 0.5784 |
| H | 3.9365 | 0.2706 | 1.0474 |
| H | 3.6008 | -0.9297 | -1.6443 |
| H | 3.4882 | 0.7814 | -1.2571 |
| H | 1.4357 | 1.8124 | -1.2472 |
| C | -0.5825 | 1.2001 | -1.2153 |
| O | -0.9278 | 2.5737 | -1.1196 |
| C | -1.6239 | 0.3033 | -0.5404 |
| C | -2.2015 | 0.7310 | 0.6406 |
| C | -2.0481 | -0.9448 | -1.1092 |
| C | -3.1520 | -0.0510 | 1.3341 |
| C | -3.0169 | -1.7373 | -0.4004 |
| C | -3.5443 | -1.2673 | 0.8305 |
| C | -1.5865 | -1.4448 | -2.3616 |
| C | -2.0306 | -2.6462 | -2.8705 |
| C | -2.9645 | -3.4296 | -2.1538 |
| C | -3.4454 | -2.9768 | -0.9477 |

| | | | |
|---|---|---|---|
| H | -0.5622 | 0.9814 | -2.2873 |
| H | -0.5033 | 2.9235 | -0.3118 |
| H | -1.9292 | 1.7008 | 1.0424 |
| H | -3.5732 | 0.3217 | 2.2641 |
| H | -4.2747 | -1.8786 | 1.3555 |
| H | -0.88009 | -0.86661 | -2.94664 |
| H | -1.66531 | -2.99092 | -3.83442 |
| H | -3.30545 | -4.37715 | -2.56188 |
| H | -4.17423 | -3.5617 | -0.39109 |

**Table S64.** Geometry (Å) for product (syn HBO) of the reaction tropinone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.1404 | 2.5809 | 1.1800 |
| C | 1.1420 | 1.4588 | 0.7095 |
| C | 1.3254 | 0.2150 | 1.5738 |
| C | 1.6294 | -0.0374 | -1.2822 |
| N | 1.2015 | -1.1801 | -0.4282 |
| C | 1.4520 | -2.4890 | -1.0402 |
| C | 1.9895 | -0.9445 | 0.8077 |
| C | 3.4154 | -0.5661 | 0.3160 |
| C | 3.1697 | 0.0710 | -1.0808 |
| C | 0.8983 | 1.2287 | -0.7849 |
| C | -0.6513 | 1.2017 | -1.0357 |
| O | -1.2538 | 0.1076 | -0.3663 |
| C | -0.9812 | 1.2402 | -2.5277 |
| C | -1.4637 | 0.1069 | -3.1501 |
| C | -0.8035 | 2.4419 | -3.2941 |
| C | -1.7558 | 0.0876 | -4.5344 |
| C | -1.0961 | 2.4161 | -4.7004 |
| C | -1.5670 | 1.2151 | -5.2961 |
| C | -0.3681 | 3.6751 | -2.7278 |
| C | -0.2143 | 4.8038 | -3.5037 |
| C | -0.4856 | 4.7665 | -4.8907 |
| C | -0.9202 | 3.5969 | -5.4705 |
| H | 0.3188 | -0.0927 | 1.8872 |
| H | 1.8881 | 0.4880 | 2.4722 |
| H | 1.3537 | -0.2332 | -2.3221 |
| H | 1.1364 | -3.2747 | -0.3466 |
| H | 2.5064 | -2.6671 | -1.3056 |
| H | 0.8515 | -2.5778 | -1.9507 |
| H | 1.9822 | -1.8471 | 1.4266 |
| H | 4.0475 | -1.4561 | 0.2362 |
| H | 3.9127 | 0.1175 | 1.0110 |
| H | 3.7023 | -0.4780 | -1.8634 |
| H | 3.5087 | 1.1101 | -1.1354 |

| | | | |
|---|---|---|---|
| H | 1.3030 | 2.0997 | -1.3080 |
| H | -1.0576 | 2.1079 | -0.5692 |
| H | -0.5774 | -0.6109 | -0.3414 |
| H | -1.6469 | -0.7757 | -2.5464 |
| H | -2.1339 | -0.8247 | -4.9884 |
| H | -1.7859 | 1.2101 | -6.3614 |
| H | -0.16051 | 3.741177 | -1.66486 |
| H | 0.114352 | 5.731847 | -3.04377 |
| H | -0.35775 | 5.66251 | -5.49212 |
| H | -1.1426 | 3.558923 | -6.53456 |

**Table S65.** Geometry (Å) for product (syn HBN) of the reaction tropinone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -0.71955 | 1.787146 | -0.30101 |
| C | -1.46542 | 0.664192 | -0.08226 |
| C | -2.72329 | 0.654883 | -0.90898 |
| C | -2.04579 | -1.54185 | 0.897495 |
| N | -2.84013 | -1.71092 | -0.33487 |
| C | -3.55374 | -2.97325 | -0.42959 |
| C | -3.6688 | -0.51552 | -0.55928 |
| C | -4.62326 | -0.23038 | 0.629326 |
| C | -2.94836 | -1.38812 | 2.15384 |
| C | -1.13622 | -0.34347 | 0.737873 |
| C | -3.90125 | -0.19157 | 1.989799 |
| H | 0.108687 | 1.738295 | 0.225351 |
| H | -2.43706 | 0.590774 | -1.96789 |
| H | -3.23692 | 1.618237 | -0.78861 |
| H | -1.43208 | -2.44632 | 1.010496 |
| H | -4.01801 | -3.04729 | -1.42049 |
| H | -4.34841 | -3.13719 | 0.321419 |
| H | -2.8372 | -3.79803 | -0.33468 |
| H | -4.28955 | -0.71236 | -1.44299 |
| H | -5.38452 | -1.0225 | 0.650777 |
| H | -5.16484 | 0.708882 | 0.4553 |
| H | -2.3235 | -1.2592 | 3.047089 |
| H | -3.52511 | -2.31118 | 2.306761 |
| H | -0.23389 | -0.29944 | 1.343867 |
| H | -4.63973 | -0.18137 | 2.801892 |
| H | -3.32776 | 0.738251 | 2.076702 |
| C | 2.395922 | 0.997481 | -0.37605 |
| O | 1.900973 | 1.457722 | 0.646175 |
| C | 3.80502 | 0.597436 | -0.50705 |
| C | 4.690199 | 0.735159 | 0.575103 |
| C | 4.262584 | 0.073382 | -1.72467 |
| C | 6.018533 | 0.350797 | 0.434778 |

| | | | |
|---|---|---|---|
| C | 5.594596 | -0.31175 | -1.86274 |
| C | 6.470229 | -0.17238 | -0.78324 |
| H | 1.770387 | 0.860046 | -1.27943 |
| H | 4.313656 | 1.143163 | 1.507953 |
| H | 3.570818 | -0.03087 | -2.55761 |
| H | 6.706665 | 0.455429 | 1.26878 |
| H | 5.950124 | -0.71853 | -2.80494 |
| H | 7.509363 | -0.4723 | -0.88921 |

**Table S66.** Geometry (Å) for reactant (anti) of the reaction granatanone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.28239 | 2.792676 | 0.165285 |
| C | -1.52891 | 1.520782 | 0.163534 |
| C | -2.7623 | 1.061012 | -0.57793 |
| C | -0.92753 | -0.87723 | 0.640692 |
| N | -1.75964 | -1.15333 | -0.54727 |
| C | -1.87155 | -2.56399 | -0.89033 |
| C | -3.05004 | -0.44759 | -0.43821 |
| C | -3.8302 | -0.81925 | 0.846635 |
| C | -1.61228 | -1.31351 | 1.96544 |
| C | -0.59671 | 0.600514 | 0.660792 |
| C | -2.98699 | -0.64518 | 2.122059 |
| H | -0.14446 | 2.855417 | -0.13455 |
| H | -2.61108 | 1.310278 | -1.63734 |
| H | -3.61146 | 1.669741 | -0.24231 |
| H | 0.002953 | -1.44772 | 0.527007 |
| H | -2.40106 | -2.65898 | -1.84544 |
| H | -2.40089 | -3.19172 | -0.15172 |
| H | -0.86717 | -2.98276 | -1.02019 |
| H | -3.65741 | -0.74968 | -1.30036 |
| H | -4.14822 | -1.86756 | 0.766753 |
| H | -4.75007 | -0.22315 | 0.905979 |
| H | -0.96332 | -1.0689 | 2.8158 |
| H | -1.72653 | -2.40614 | 1.965328 |
| H | 0.056379 | 0.944857 | 1.457454 |
| H | -3.51929 | -1.06717 | 2.983503 |
| H | -2.85259 | 0.422628 | 2.337884 |
| C | 0.905416 | 1.22334 | -0.75354 |
| O | 0.979772 | 2.490769 | -0.51584 |
| C | 2.035846 | 0.344787 | -0.36294 |
| C | 2.996969 | 0.790944 | 0.557073 |
| C | 2.174947 | -0.92536 | -0.94157 |
| C | 4.069727 | -0.02703 | 0.900045 |
| C | 3.252127 | -1.74273 | -0.59766 |
| C | 4.199416 | -1.29626 | 0.325812 |

| | | | |
|---|---|---|---|
| H | 0.34568 | 0.876897 | -1.6345 |
| H | 2.89104 | 1.785985 | 0.977418 |
| H | 1.440335 | -1.26299 | -1.66914 |
| H | 4.812666 | 0.325242 | 1.610815 |
| H | 3.355406 | -2.7236 | -1.054 |
| H | 5.040571 | -1.93072 | 0.592209 |

**Table S67.** Geometry (Å) for transition state (TS anti) of the reaction granatanone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.41465 | 2.979962 | 0.476696 |
| C | -1.49056 | 1.774424 | 0.266505 |
| C | -2.69908 | 1.185778 | -0.44155 |
| C | -0.71793 | -0.61673 | 0.754031 |
| N | -1.64137 | -0.99373 | -0.33275 |
| C | -1.73758 | -2.42879 | -0.56717 |
| C | -2.9382 | -0.31269 | -0.17669 |
| C | -3.60965 | -0.57629 | 1.191324 |
| C | -1.30221 | -0.88842 | 2.163175 |
| C | -0.30841 | 0.863168 | 0.57465 |
| C | 0.762211 | 1.133712 | -0.55402 |
| O | 1.200689 | 2.479749 | -0.47576 |
| C | 1.975744 | 0.230661 | -0.43681 |
| C | 2.992247 | 0.523284 | 0.481039 |
| C | 2.094197 | -0.91105 | -1.23786 |
| C | 4.097815 | -0.31804 | 0.602862 |
| C | 3.19975 | -1.75562 | -1.1161 |
| C | 4.203892 | -1.46175 | -0.19274 |
| C | -2.67484 | -0.22637 | 2.359848 |
| H | -2.49677 | 1.312413 | -1.51467 |
| H | -3.57243 | 1.803685 | -0.20721 |
| H | 0.180881 | -1.2292 | 0.638618 |
| H | -2.35706 | -2.607 | -1.45361 |
| H | -2.16792 | -3.01346 | 0.265129 |
| H | -0.73706 | -2.82594 | -0.77 |
| H | -3.60057 | -0.69068 | -0.96502 |
| H | -3.88303 | -1.63824 | 1.251204 |
| H | -4.54758 | -0.01026 | 1.258028 |
| H | -0.59219 | -0.5514 | 2.928778 |
| H | -1.40401 | -1.97416 | 2.294225 |
| H | 0.151911 | 1.232023 | 1.499269 |
| H | 0.280856 | 0.936673 | -1.52475 |
| H | 0.450841 | 3.022971 | -0.16498 |
| H | 2.919154 | 1.428453 | 1.075518 |
| H | 1.317451 | -1.13481 | -1.96582 |
| H | 4.883015 | -0.07675 | 1.314888 |

| | | | |
|---|---|---|---|
| H | 3.280258 | -2.63564 | -1.74908 |
| H | 5.068461 | -2.11376 | -0.09958 |
| H | -3.11887 | -0.54767 | 3.309938 |
| H | -2.56143 | 0.864127 | 2.438359 |

**Table S68.** Geometry (Å) for product (HBO anti) of the reaction granatanone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.8885 | 2.702077 | -8.50454 |
| C | 0.003852 | 3.200279 | -7.42935 |
| C | 1.083689 | 2.125955 | -7.16858 |
| C | 0.521133 | 0.72418 | -6.968 |
| C | -0.6629 | 0.340783 | -7.85651 |
| C | -1.65615 | 1.522179 | -8.02792 |
| C | -2.48737 | 1.82464 | -6.76028 |
| C | -0.77267 | 3.591035 | -6.15159 |
| C | -0.18547 | -0.17447 | -9.26385 |
| O | 1.001158 | -0.05537 | -6.16693 |
| O | 0.558788 | 0.808459 | -9.95861 |
| C | 0.614739 | -1.46233 | -9.17973 |
| C | 2.003789 | -1.46672 | -9.33717 |
| C | 2.720396 | -2.66181 | -9.25109 |
| C | 2.058276 | -3.86529 | -9.00739 |
| C | 0.66983 | -3.8695 | -8.85565 |
| C | -0.04412 | -2.67585 | -8.94606 |
| C | -1.71 | 3.738936 | -9.12938 |
| C | -1.64205 | 2.434908 | -5.62854 |
| H | 0.503613 | 4.094686 | -7.82051 |
| H | 1.706341 | 2.380628 | -6.3055 |
| H | 1.731867 | 2.068672 | -8.05238 |
| H | -1.17174 | -0.49554 | -7.36549 |
| H | -2.34955 | 1.25126 | -8.83524 |
| H | -3.29064 | 2.523612 | -7.02959 |
| H | -2.98095 | 0.90542 | -6.42132 |
| H | -1.40915 | 4.458126 | -6.37344 |
| H | -0.06342 | 3.918537 | -5.3815 |
| H | -1.11857 | -0.3986 | -9.81394 |
| H | 0.133802 | 1.669723 | -9.7337 |
| H | 2.512421 | -0.53166 | -9.54347 |
| H | 3.800078 | -2.65118 | -9.37745 |
| H | 2.617672 | -4.79487 | -8.94195 |
| H | 0.142667 | -4.80274 | -8.67477 |
| H | -1.12772 | -2.68859 | -8.84037 |
| H | -2.25958 | 3.301433 | -9.96955 |
| H | -2.44011 | 4.213882 | -8.45599 |
| H | -1.05512 | 4.522721 | -9.52439 |

| | | | |
|---|---|---|---|
| H | -1.00708 | 1.664147 | -5.176 |
| H | -2.29803 | 2.792602 | -4.82566 |

**Table S69.** Geometry (Å) for product (HBN anti) of the reaction granatanone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -0.00904 | 1.04494 | 0.700054 |
| C | 1.004505 | 0.176003 | 0.398593 |
| C | 1.755655 | -0.26527 | 1.625342 |
| C | 2.460086 | -1.21688 | -1.04874 |
| N | 2.686619 | -1.99523 | 0.184298 |
| C | 3.585823 | -3.12649 | 0.032154 |
| C | 3.020831 | -1.08636 | 1.291983 |
| C | 4.276753 | -0.22741 | 0.989273 |
| C | 3.733769 | -0.4411 | -1.48754 |
| C | 1.304297 | -0.26612 | -0.82925 |
| C | 4.20112 | 0.502986 | -0.36583 |
| H | 1.079238 | -0.8715 | 2.243841 |
| H | 2.012542 | 0.617843 | 2.225796 |
| H | 2.191726 | -1.93387 | -1.8368 |
| H | 3.598214 | -3.70077 | 0.966484 |
| H | 4.63384 | -2.87986 | -0.2192 |
| H | 3.204282 | -3.78389 | -0.7583 |
| H | 3.248791 | -1.70989 | 2.166118 |
| H | 4.442577 | 0.490922 | 1.803148 |
| H | 5.150272 | -0.89401 | 0.987998 |
| H | 3.526217 | 0.127504 | -2.40327 |
| H | 4.531093 | -1.15506 | -1.73717 |
| H | 0.758137 | 0.090095 | -1.70006 |
| H | 5.181907 | 0.929618 | -0.61276 |
| H | 3.502584 | 1.344019 | -0.29193 |
| H | -0.50512 | 1.263675 | -0.11734 |
| C | -2.876 | 1.311947 | -1.70771 |
| O | -1.68334 | 1.530251 | -1.54724 |
| C | -3.8065 | 0.762217 | -0.70842 |
| C | -3.37639 | 0.389528 | 0.577843 |
| C | -5.15585 | 0.61354 | -1.06627 |
| C | -4.29676 | -0.12087 | 1.487343 |
| C | -6.07309 | 0.102899 | -0.15145 |
| C | -5.64144 | -0.26334 | 1.125795 |
| H | -3.33731 | 1.5412 | -2.69059 |
| H | -2.33086 | 0.497366 | 0.851229 |
| H | -5.47964 | 0.90221 | -2.06402 |
| H | -3.96889 | -0.41068 | 2.481497 |

| | | | |
|---|---|---|---|
| H | -7.11699 | -0.01011 | -0.42936 |
| H | -6.35412 | -0.6626 | 1.842587 |

**Table S70.** Geometry (Å) for reactant (syn) of the reaction granatanone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.526302 | 2.643084 | 0.676454 |
| C | 0.878133 | 1.422822 | 0.423879 |
| C | 1.121258 | 0.508274 | 1.595911 |
| C | 1.319395 | -0.48621 | -1.15972 |
| N | 1.005649 | -1.32214 | 0.008844 |
| C | 1.077174 | -2.75451 | -0.22741 |
| C | 1.735947 | -0.84853 | 1.194901 |
| C | 3.269159 | -0.8137 | 0.975796 |
| C | 2.83442 | -0.50148 | -1.50636 |
| C | 0.853349 | 0.933162 | -0.8916 |
| C | 3.673729 | -0.05049 | -0.2988 |
| H | 0.146431 | 0.334996 | 2.072924 |
| H | 1.73942 | 1.039777 | 2.3301 |
| H | 0.75972 | -0.89518 | -2.01257 |
| H | 0.716183 | -3.28132 | 0.66312 |
| H | 2.081668 | -3.14922 | -0.46572 |
| H | 0.412021 | -3.0139 | -1.05885 |
| H | 1.527251 | -1.55542 | 2.006904 |
| H | 3.763392 | -0.38246 | 1.856035 |
| H | 3.62594 | -1.84983 | 0.900138 |
| H | 3.028949 | 0.142015 | -2.37392 |
| H | 3.122033 | -1.51943 | -1.8019 |
| H | 1.077264 | 1.659665 | -1.66875 |
| H | 4.740982 | -0.2031 | -0.50162 |
| H | 3.544257 | 1.028647 | -0.14506 |
| H | -0.32262 | 2.853885 | -0.08434 |
| C | -1.1783 | 1.353408 | -1.2118 |
| O | -1.2364 | 2.612762 | -0.91537 |
| C | -2.00501 | 0.370775 | -0.45619 |
| C | -2.57007 | 0.726655 | 0.777417 |
| C | -2.27399 | -0.89601 | -0.99183 |
| C | -3.37243 | -0.1789 | 1.469314 |
| C | -3.08026 | -1.79949 | -0.30248 |
| C | -3.62805 | -1.44386 | 0.932597 |
| H | -1.03928 | 1.089654 | -2.26999 |
| H | -2.38604 | 1.722698 | 1.167524 |
| H | -1.85881 | -1.16679 | -1.9603 |
| H | -3.81047 | 0.105415 | 2.422599 |

| | | | |
|---|---|---|---|
| H | -3.28882 | -2.77678 | -0.72996 |
| H | -4.26148 | -2.14547 | 1.469075 |

**Table S71.** Geometry (Å) for transition state (TS syn) of the reaction granatanone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.592183 | 2.643751 | 0.714869 |
| C | 0.88085 | 1.473737 | 0.48084 |
| C | 1.257988 | 0.532685 | 1.606498 |
| C | 1.464841 | -0.41612 | -1.17456 |
| N | 1.29379 | -1.28055 | 0.002823 |
| C | 1.517114 | -2.69603 | -0.24751 |
| C | 2.009869 | -0.73813 | 1.166723 |
| C | 3.516521 | -0.50243 | 0.902124 |
| C | 2.956047 | -0.21141 | -1.54404 |
| C | 0.757981 | 0.941456 | -0.94166 |
| C | -0.75242 | 1.004419 | -1.38669 |
| O | -1.16094 | 2.359603 | -1.44754 |
| C | -1.70997 | 0.149352 | -0.5631 |
| C | -2.35771 | 0.673675 | 0.562708 |
| C | -1.98155 | -1.17226 | -0.93593 |
| C | -3.22954 | -0.11593 | 1.314185 |
| C | -2.85489 | -1.96375 | -0.18983 |
| C | -3.47862 | -1.43854 | 0.943182 |
| C | 3.753001 | 0.350187 | -0.3553 |
| H | 0.29951 | 0.222487 | 2.045505 |
| H | 1.793984 | 1.103663 | 2.3728 |
| H | 0.969216 | -0.91741 | -2.01559 |
| H | 1.269924 | -3.26296 | 0.656852 |
| H | 2.546843 | -2.96625 | -0.54289 |
| H | 0.843121 | -3.03074 | -1.04402 |
| H | 1.916072 | -1.47263 | 1.975492 |
| H | 3.981035 | -0.03773 | 1.78132 |
| H | 4.004311 | -1.47805 | 0.77256 |
| H | 3.039258 | 0.448282 | -2.41706 |
| H | 3.383671 | -1.17777 | -1.84277 |
| H | 1.229739 | 1.696673 | -1.58318 |
| H | -0.77096 | 0.629391 | -2.41853 |
| H | -0.70603 | 2.830947 | -0.72155 |
| H | -2.19485 | 1.711141 | 0.837218 |
| H | -1.51369 | -1.58442 | -1.82766 |
| H | -3.72592 | 0.308552 | 2.183249 |
| H | -3.05644 | -2.98621 | -0.4993 |
| H | -4.16465 | -2.05008 | 1.523398 |
| H | 4.822743 | 0.382681 | -0.59516 |
| H | 3.458719 | 1.392167 | -0.16457 |

**Table S72.** Geometry (Å) for product (HBO syn) of the reaction granatanone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.36035 | -1.14271 | -0.90367 |
| C | -5.65618 | -2.39406 | -1.27534 |
| C | -4.6381 | -2.71728 | -0.15961 |
| C | -3.76251 | -1.53938 | 0.243957 |
| C | -4.41904 | -0.15742 | 0.228497 |
| C | -5.42141 | 0.01018 | -0.94107 |
| C | -4.73562 | 0.178276 | -2.3154 |
| C | -5.00236 | -2.31356 | -2.6732 |
| C | -5.09405 | 0.092523 | 1.623947 |
| O | -2.61453 | -1.68687 | 0.621923 |
| O | -6.14134 | -0.8315 | 1.863344 |
| C | -7.61009 | -0.91969 | -1.63116 |
| C | -5.54391 | 1.54635 | 1.776714 |
| C | -6.89795 | 1.87334 | 1.898818 |
| C | -7.29962 | 3.204822 | 2.033928 |
| C | -6.3509 | 4.226928 | 2.056351 |
| C | -4.99434 | 3.908647 | 1.950454 |
| C | -4.59628 | 2.579584 | 1.813205 |
| C | -4.0495 | -1.11239 | -2.79343 |
| H | -6.40907 | -3.19127 | -1.28765 |
| H | -3.99371 | -3.56013 | -0.42822 |
| H | -5.19414 | -2.9936 | 0.745676 |
| H | -3.60872 | 0.571171 | 0.125135 |
| H | -6.01561 | 0.909209 | -0.74154 |
| H | -4.01558 | 1.004174 | -2.26258 |
| H | -5.49396 | 0.47945 | -3.05045 |
| H | -4.47137 | -3.25107 | -2.88013 |
| H | -5.79165 | -2.23222 | -3.43237 |
| H | -4.32243 | -0.10189 | 2.380926 |
| H | -6.53137 | -1.0373 | 0.980107 |
| H | -8.10224 | -0.02854 | -1.22789 |
| H | -7.49136 | -0.77979 | -2.71714 |
| H | -8.27335 | -1.77655 | -1.47197 |
| H | -7.62831 | 1.071119 | 1.913834 |
| H | -8.35658 | 3.440858 | 2.130002 |
| H | -6.6625 | 5.262439 | 2.164941 |
| H | -4.24546 | 4.696022 | 1.981037 |
| H | -3.53595 | 2.343003 | 1.74587 |
| H | -3.71739 | -0.99832 | -3.83241 |
| H | -3.14035 | -1.29551 | -2.20698 |

**Table S73.** Geometry (Å) for product (HBN syn) of the reaction granatanone + Ph-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.5723177 | 1.8573459 | -0.6020341 |
| C | -2.3902871 | 0.820112 | -0.2445234 |
| C | -3.5723341 | 0.6906029 | -1.1669112 |
| C | -3.1624294 | -1.1255836 | 1.0884166 |
| N | -3.8639153 | -1.5054375 | -0.152843 |
| C | -4.6370816 | -2.7330287 | -0.0603195 |
| C | -4.6061416 | -0.3478133 | -0.6779426 |
| C | -5.6315995 | 0.2072536 | 0.3442309 |
| C | -4.1506628 | -0.6902536 | 2.2067553 |
| C | -2.1804779 | -0.0163664 | 0.7804904 |
| C | -5.0181839 | 0.4870255 | 1.729578 |
| H | -3.2036856 | 0.4001457 | -2.1604431 |
| H | -4.040001 | 1.6767714 | -1.2892556 |
| H | -2.6089177 | -2.0115716 | 1.4288164 |
| H | -5.0270246 | -2.9846977 | -1.0538892 |
| H | -5.4943507 | -2.711531 | 0.6371228 |
| H | -3.9765415 | -3.5494346 | 0.2555235 |
| H | -5.1665973 | -0.6928224 | -1.5562561 |
| H | -6.4362825 | -0.5332037 | 0.4517503 |
| H | -6.1032793 | 1.1141265 | -0.0566661 |
| H | -4.7882617 | -1.5412196 | 2.4840471 |
| H | -3.5915788 | -0.4122818 | 3.1095899 |
| H | -1.3309145 | 0.1164416 | 1.4474285 |
| H | -5.8165489 | 0.688 | 2.4554244 |
| H | -4.4017669 | 1.3920342 | 1.6837808 |
| H | -0.8075056 | 1.8919156 | 0.0100302 |
| C | 1.5085189 | 1.1272072 | -0.4580162 |
| O | 1.0061055 | 1.6419923 | 0.5301442 |
| C | 2.9275191 | 0.7208838 | -0.5394044 |
| C | 3.783459 | 0.9136384 | 0.5571358 |
| C | 3.4125838 | 0.1422594 | -1.7205562 |
| C | 5.11576 | 0.5307925 | 0.4756455 |
| C | 4.7461096 | -0.245259 | -1.8162499 |
| C | 5.5719044 | -0.0423277 | -0.7130164 |
| N | 6.9895034 | -0.4506627 | -0.8053653 |
| O | 7.6981806 | -0.264597 | 0.1813639 |
| O | 7.3682224 | -0.949661 | -1.8629153 |
| H | 0.8971576 | 0.9414557 | -1.3612176 |
| H | 3.3849939 | 1.3636689 | 1.4604747 |
| H | 2.7439279 | -0.0042348 | -2.5648963 |
| H | 5.8027457 | 0.6642861 | 1.3019817 |
| H | 5.1516117 | -0.6942147 | -2.7141995 |

**Table S74.** Geometry (Å) for reactant (anti) of the reaction granatanone + p-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.98609 | 3.1526723 | -0.1261859 |
| C | -2.228111 | 1.8792923 | -0.1183329 |
| C | -3.47007 | 1.4140633 | -0.8358619 |
| C | -1.61789 | -0.5098577 | 0.3805021 |
| N | -2.463403 | -0.7978417 | -0.7940569 |
| C | -2.578898 | -2.2129677 | -1.1216379 |
| C | -3.75419 | -0.0931547 | -0.6765969 |
| C | -4.518222 | -0.4489967 | 0.6215681 |
| C | -2.287118 | -0.9214057 | 1.7210081 |
| C | -1.278979 | 0.9680973 | 0.3741721 |
| C | -3.660294 | -0.2516487 | 1.8832961 |
| H | -3.331431 | 1.6531093 | -1.8993899 |
| H | -4.313675 | 2.0279823 | -0.4960319 |
| H | -0.692899 | -1.0885497 | 0.2666451 |
| H | -3.119793 | -2.3173467 | -2.0690119 |
| H | -3.098816 | -2.8316427 | -0.3696329 |
| H | -1.576476 | -2.6335577 | -1.2596229 |
| H | -4.37061 | -0.4042787 | -1.5285549 |
| H | -4.832443 | -1.4994737 | 0.5610821 |
| H | -5.439768 | 0.1440633 | 0.6824261 |
| H | -2.400977 | -2.0135747 | 1.7387861 |
| H | -1.627757 | -0.6643307 | 2.5594941 |
| H | -0.640649 | 1.3242933 | 1.1781951 |
| H | -4.180673 | -0.6601017 | 2.7580961 |
| H | -3.526551 | 0.8200133 | 2.0813591 |
| H | -0.87805 | 3.2284933 | -0.4021949 |
| C | 0.190939 | 1.5787313 | -1.0281969 |
| O | 0.276194 | 2.8477833 | -0.8198409 |
| C | 1.325067 | 0.7064453 | -0.6118499 |
| C | 2.278302 | 1.1812873 | 0.3032121 |
| C | 1.474684 | -0.5751167 | -1.1641519 |
| C | 3.352506 | 0.3847013 | 0.6784421 |
| C | 2.547234 | -1.3836227 | -0.7992019 |
| C | 3.469283 | -0.8908987 | 0.1225651 |
| N | 4.604314 | -1.7393307 | 0.5155761 |
| O | 5.406881 | -1.2804827 | 1.3283141 |
| O | 4.683132 | -2.8597387 | 0.0107321 |
| H | -0.348825 | 1.2135463 | -1.9150689 |
| H | 2.16601 | 2.1860493 | 0.6963431 |
| H | 0.750377 | -0.9329877 | -1.8910959 |
| H | 4.100641 | 0.7293173 | 1.3817401 |
| H | 2.684213 | -2.3744597 | -1.2142359 |

**Table S75.** Geometry (Å) for transition state (TS anti) of the reaction granatanone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.37161 | 3.185916 | 0.046092 |
| C | -2.37275 | 1.97811 | -0.16056 |
| C | -3.46281 | 1.329065 | -0.99454 |
| C | -1.5556 | -0.37193 | 0.444406 |
| N | -2.32836 | -0.80247 | -0.73525 |
| C | -2.34019 | -2.24506 | -0.9494 |
| C | -3.66332 | -0.17726 | -0.74039 |
| C | -4.47774 | -0.4586 | 0.543734 |
| C | -2.28557 | -0.65056 | 1.78149 |
| C | -1.19056 | 1.122104 | 0.285618 |
| C | -3.70223 | -0.05397 | 1.807523 |
| H | -3.14451 | 1.458522 | -2.03899 |
| H | -4.38458 | 1.906948 | -0.86983 |
| H | -0.62605 | -0.94884 | 0.446898 |
| H | -2.84316 | -2.46254 | -1.89829 |
| H | -2.84202 | -2.83261 | -0.16107 |
| H | -1.30845 | -2.60524 | -1.02555 |
| H | -4.21159 | -0.59042 | -1.59549 |
| H | -4.71057 | -1.5308 | 0.586863 |
| H | -5.44068 | 0.065278 | 0.492838 |
| H | -2.3512 | -1.73795 | 1.919478 |
| H | -1.68563 | -0.27011 | 2.617685 |
| H | -0.84519 | 1.521256 | 1.247059 |
| H | -4.23734 | -0.38849 | 2.70438 |
| H | -3.65143 | 1.04138 | 1.883999 |
| H | -0.45431 | 3.311374 | -0.38827 |
| C | -0.02794 | 1.436851 | -0.7339 |
| O | 0.342842 | 2.798868 | -0.62642 |
| C | 1.209108 | 0.593013 | -0.48939 |
| C | 2.150394 | 0.977526 | 0.475376 |
| C | 1.424566 | -0.58093 | -1.22473 |
| C | 3.27722 | 0.198176 | 0.717929 |
| C | 2.545491 | -1.37386 | -0.99437 |
| C | 3.456283 | -0.97167 | -0.01971 |
| N | 4.643524 | -1.80195 | 0.231833 |
| O | 5.435685 | -1.42277 | 1.094428 |
| O | 4.774475 | -2.83032 | -0.43294 |
| H | -0.39742 | 1.210237 | -1.7458 |
| H | 2.001952 | 1.906579 | 1.014429 |
| H | 0.708545 | -0.87161 | -1.98904 |
| H | 4.016545 | 0.480357 | 1.457462 |
| H | 2.728237 | -2.28177 | -1.55573 |

**Table S76.** Geometry (Å) for product (HBO anti) of the reaction granatanone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -1.00709 | 2.758781 | -8.37029 |
| C | 0.005921 | 3.463751 | -7.54411 |
| C | 1.165535 | 2.480945 | -7.26845 |
| C | 0.713947 | 1.122303 | -6.75187 |
| C | -0.57361 | 0.561202 | -7.36076 |
| C | -1.63973 | 1.667267 | -7.58448 |
| C | -2.29139 | 2.17114 | -6.2771 |
| C | -0.59669 | 4.056738 | -6.25117 |
| C | -0.27793 | -0.18858 | -8.70955 |
| O | 1.354439 | 0.495169 | -5.92988 |
| O | 0.265208 | 0.674521 | -9.68637 |
| C | 0.638009 | -1.38635 | -8.52074 |
| C | 0.162785 | -2.53566 | -7.87241 |
| C | 0.98335 | -3.64041 | -7.67978 |
| C | 2.293925 | -3.58768 | -8.15397 |
| C | 2.791088 | -2.4659 | -8.81234 |
| C | 1.955048 | -1.36708 | -8.99372 |
| C | -1.96086 | 3.649528 | -9.03389 |
| N | 3.169063 | -4.75175 | -7.96154 |
| O | 4.320475 | -4.6823 | -8.39271 |
| O | 2.700809 | -5.73186 | -7.38043 |
| C | -1.32127 | 2.992362 | -5.40961 |
| H | 0.397175 | 4.285249 | -8.15575 |
| H | 1.892879 | 2.899648 | -6.5663 |
| H | 1.68334 | 2.286403 | -8.21673 |
| H | -0.96054 | -0.18131 | -6.65486 |
| H | -2.42854 | 1.24021 | -8.21818 |
| H | -3.15854 | 2.792022 | -6.5386 |
| H | -2.68514 | 1.316142 | -5.71374 |
| H | 0.19852 | 4.534974 | -5.66641 |
| H | -1.30207 | 4.853503 | -6.52165 |
| H | -1.25829 | -0.57396 | -9.04693 |
| H | -0.15516 | 1.555768 | -9.53073 |
| H | -0.86401 | -2.57082 | -7.51594 |
| H | 0.63077 | -4.53388 | -7.17986 |
| H | 3.812659 | -2.46746 | -9.17205 |
| H | 2.312496 | -0.48868 | -9.5174 |
| H | -2.61037 | 3.056169 | -9.68591 |
| H | -2.60061 | 4.22612 | -8.34885 |
| H | -1.40932 | 4.358659 | -9.65971 |
| H | -1.87071 | 3.472225 | -4.59097 |
| H | -0.59028 | 2.329794 | -4.93054 |

**Table S77.** Geometry (Å) for product (HBN anti) of the reaction granatanone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.798162 | 1.527421 | 0.572306 |
| C | 1.769756 | 0.636119 | 0.19445 |
| C | 2.469987 | 0.027123 | 1.378169 |
| C | 3.166796 | -0.68337 | -1.37249 |
| N | 3.318364 | -1.59857 | -0.22555 |
| C | 4.144144 | -2.76622 | -0.48513 |
| C | 3.688434 | -0.83399 | 0.975848 |
| C | 5.00029 | -0.02968 | 0.782702 |
| C | 4.493695 | 0.05339 | -1.70871 |
| C | 2.065395 | 0.30897 | -1.06928 |
| C | 4.995049 | 0.842973 | -0.48716 |
| H | 1.747286 | -0.5952 | 1.924041 |
| H | 2.770076 | 0.826819 | 2.06855 |
| H | 2.870892 | -1.29509 | -2.23573 |
| H | 4.104854 | -3.4313 | 0.385876 |
| H | 5.209291 | -2.56543 | -0.70176 |
| H | 3.731723 | -3.3135 | -1.34119 |
| H | 3.858933 | -1.5588 | 1.782052 |
| H | 5.831002 | -0.74616 | 0.721255 |
| H | 5.194014 | 0.586426 | 1.670697 |
| H | 5.249917 | -0.68047 | -2.02004 |
| H | 4.341191 | 0.72577 | -2.56284 |
| H | 1.55843 | 0.786661 | -1.90524 |
| H | 6.004364 | 1.231153 | -0.67496 |
| H | 4.348407 | 1.714282 | -0.33325 |
| H | 0.337608 | 1.860501 | -0.22462 |
| C | -2.06918 | 1.932325 | -1.83339 |
| O | -0.91019 | 2.247469 | -1.62016 |
| C | -2.93597 | 1.150026 | -0.92468 |
| C | -2.46376 | 0.669734 | 0.309449 |
| C | -4.2563 | 0.891921 | -1.32451 |
| C | -3.31096 | -0.06083 | 1.134638 |
| C | -5.11192 | 0.161834 | -0.50627 |
| C | -4.6189 | -0.30054 | 0.711753 |
| N | -5.51994 | -1.07673 | 1.589794 |
| O | -5.06594 | -1.47303 | 2.660587 |
| O | -6.66627 | -1.27551 | 1.19203 |
| H | -2.553 | 2.242447 | -2.78175 |
| H | -1.43981 | 0.865345 | 0.61459 |
| H | -4.61269 | 1.265723 | -2.28117 |
| H | -2.97997 | -0.4459 | 2.091087 |
| H | -6.13498 | -0.05283 | -0.78817 |

**Table S78.** Geometry (Å) for reactant (syn) of the reaction granatanone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.235503 | 3.014895 | 0.485102 |
| C | 1.576222 | 1.792722 | 0.220811 |
| C | 1.800156 | 0.865704 | 1.383858 |
| C | 2.015982 | -0.09661 | -1.38415 |
| N | 1.672917 | -0.94138 | -0.22989 |
| C | 1.729993 | -2.37301 | -0.4842 |
| C | 2.398045 | -0.49531 | 0.971424 |
| C | 3.933563 | -0.47839 | 0.771755 |
| C | 3.535309 | -0.1227 | -1.70938 |
| C | 1.560246 | 1.325431 | -1.10592 |
| C | 4.363072 | 0.300873 | -0.48446 |
| H | 0.821256 | 0.703104 | 1.85655 |
| H | 2.420921 | 1.382423 | 2.126299 |
| H | 1.465862 | -0.48833 | -2.25092 |
| H | 1.349641 | -2.90692 | 0.393598 |
| H | 2.73307 | -2.77487 | -0.71278 |
| H | 1.074811 | -2.61353 | -1.32897 |
| H | 2.168391 | -1.20893 | 1.771256 |
| H | 4.277309 | -1.5176 | 0.683259 |
| H | 4.422059 | -0.06901 | 1.6653 |
| H | 3.814712 | -1.13947 | -2.01567 |
| H | 3.748501 | 0.530104 | -2.56541 |
| H | 1.827363 | 2.061352 | -1.86058 |
| H | 5.430906 | 0.140138 | -0.67609 |
| H | 4.244484 | 1.379316 | -0.31544 |
| H | 0.443684 | 3.263598 | -0.2802 |
| C | -0.42339 | 1.785249 | -1.47522 |
| O | -0.49545 | 3.033855 | -1.1529 |
| C | -1.27686 | 0.789653 | -0.75468 |
| C | -1.87261 | 1.136737 | 0.467776 |
| C | -1.53713 | -0.46991 | -1.31374 |
| C | -2.69145 | 0.233469 | 1.136451 |
| C | -2.35796 | -1.38247 | -0.66168 |
| C | -2.91931 | -1.0172 | 0.561747 |
| N | -3.7868 | -1.97623 | 1.260361 |
| O | -4.2712 | -1.63125 | 2.338487 |
| O | -3.97587 | -3.07101 | 0.72848 |
| H | -0.27234 | 1.537905 | -2.53649 |
| H | -1.69775 | 2.128582 | 0.87073 |
| H | -1.10248 | -0.73191 | -2.27492 |
| H | -3.16232 | 0.480345 | 2.080098 |
| H | -2.57572 | -2.35781 | -1.07878 |

**Table S79.** Geometry (Å) for transition state (TS syn) of the reaction granatanone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.238773 | 2.878412 | 0.751116 |
| C | 1.474195 | 1.719159 | 0.423907 |
| C | 1.791595 | 0.669985 | 1.46916 |
| C | 1.969971 | -0.05712 | -1.38346 |
| N | 1.726366 | -1.00263 | -0.28288 |
| C | 1.867265 | -2.40532 | -0.64832 |
| C | 2.464424 | -0.60546 | 0.927748 |
| C | 3.984704 | -0.4438 | 0.692339 |
| C | 3.475432 | 0.087101 | -1.7224 |
| C | 1.342538 | 1.316615 | -1.04152 |
| C | 4.28746 | 0.497863 | -0.48402 |
| H | 0.816921 | 0.387511 | 1.89089 |
| H | 2.3618 | 1.144381 | 2.275496 |
| H | 1.457624 | -0.45453 | -2.26897 |
| H | 1.569508 | -3.02843 | 0.201941 |
| H | 2.883428 | -2.71312 | -0.95183 |
| H | 1.189547 | -2.63055 | -1.47939 |
| H | 2.315528 | -1.39768 | 1.670659 |
| H | 4.412937 | -1.4327 | 0.481476 |
| H | 4.466744 | -0.08746 | 1.611594 |
| H | 3.847592 | -0.87464 | -2.09948 |
| H | 3.608117 | 0.811426 | -2.53603 |
| H | 1.866602 | 2.094105 | -1.61177 |
| H | 5.360133 | 0.487958 | -0.71128 |
| H | 4.051096 | 1.535469 | -0.20746 |
| H | 0.002707 | 3.273486 | -0.6832 |
| C | -0.15346 | 1.512216 | -1.4914 |
| O | -0.48538 | 2.885894 | -1.4377 |
| C | -1.16969 | 0.654362 | -0.74254 |
| C | -1.82325 | 1.149483 | 0.394833 |
| C | -1.49182 | -0.63111 | -1.19963 |
| C | -2.74966 | 0.371002 | 1.08306 |
| C | -2.41878 | -1.42258 | -0.5303 |
| C | -3.03184 | -0.90968 | 0.61165 |
| N | -4.0111 | -1.73729 | 1.328777 |
| O | -4.53875 | -1.26063 | 2.334089 |
| O | -4.24503 | -2.86245 | 0.885233 |
| H | -0.18933 | 1.223216 | -2.55002 |
| H | -1.61806 | 2.159902 | 0.730525 |
| H | -1.01936 | -1.01615 | -2.09935 |
| H | -3.26063 | 0.740983 | 1.963511 |
| H | -2.67858 | -2.41533 | -0.87633 |

**Table S80.** Geometry (Å) for product (HBO syn) of the reaction granatanone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.27121 | -1.31769 | -0.94678 |
| C | -5.54594 | -2.59028 | -1.18568 |
| C | -4.61031 | -2.83673 | 0.017983 |
| C | -3.76236 | -1.63376 | 0.402573 |
| C | -4.41021 | -0.25392 | 0.244582 |
| C | -5.3302 | -0.16702 | -0.99984 |
| C | -4.55048 | -0.09052 | -2.33151 |
| C | -4.79588 | -2.60047 | -2.53634 |
| C | -5.17556 | 0.085472 | 1.571085 |
| O | -2.64694 | -1.74951 | 0.874879 |
| O | -6.26848 | -0.78684 | 1.780935 |
| C | -7.46999 | -1.14801 | -1.77045 |
| C | -5.58823 | 1.556853 | 1.620203 |
| C | -6.93949 | 1.922083 | 1.643948 |
| C | -7.31699 | 3.262422 | 1.689742 |
| C | -6.32429 | 4.23849 | 1.720173 |
| C | -4.96895 | 3.907518 | 1.716105 |
| C | -4.61164 | 2.564955 | 1.66733 |
| N | -6.7134 | 5.654643 | 1.766906 |
| O | -5.81402 | 6.495319 | 1.797556 |
| O | -7.91606 | 5.919118 | 1.770017 |
| C | -3.83343 | -1.40843 | -2.66875 |
| H | -6.29868 | -3.38723 | -1.1971 |
| H | -3.95136 | -3.6947 | -0.14667 |
| H | -5.22995 | -3.0541 | 0.898059 |
| H | -3.58886 | 0.462975 | 0.147115 |
| H | -5.93719 | 0.741254 | -0.9061 |
| H | -3.83637 | 0.740975 | -2.28709 |
| H | -5.25676 | 0.154393 | -3.13563 |
| H | -4.25485 | -3.5487 | -2.64351 |
| H | -5.52983 | -2.57051 | -3.35245 |
| H | -4.46551 | -0.0815 | 2.392959 |
| H | -6.56962 | -1.07588 | 0.883851 |
| H | -7.98724 | -0.23293 | -1.46363 |
| H | -7.27717 | -1.08252 | -2.85224 |
| H | -8.14385 | -1.99354 | -1.59753 |
| H | -7.69025 | 1.140017 | 1.651932 |
| H | -8.3584 | 3.559789 | 1.708625 |
| H | -4.22608 | 4.694628 | 1.755211 |
| H | -3.55748 | 2.298343 | 1.677695 |
| H | -3.42734 | -1.36407 | -3.68627 |
| H | -2.96904 | -1.54793 | -2.00743 |

**Table S81.** Geometry (Å) for product (HBN syn) of the reaction granatanone + *p*-$NO_2$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.04464 | 1.824256 | -0.31292 |
| C | -1.79356 | 0.70325 | -0.08946 |
| C | -2.96202 | 0.611378 | -1.0333 |
| C | -2.43429 | -1.44394 | 0.978234 |
| N | -3.09442 | -1.71367 | -0.31367 |
| C | -3.77154 | -2.99689 | -0.39454 |
| C | -3.91683 | -0.55716 | -0.70199 |
| C | -4.99327 | -0.21619 | 0.361671 |
| C | -3.46321 | -1.23028 | 2.123305 |
| C | -1.53318 | -0.23763 | 0.828214 |
| C | -4.41561 | -0.07077 | 1.782946 |
| H | -2.56996 | 0.486721 | -2.05224 |
| H | -3.50217 | 1.567722 | -1.02857 |
| H | -1.81955 | -2.32343 | 1.214797 |
| H | -4.1255 | -3.14956 | -1.42133 |
| H | -4.63909 | -3.12854 | 0.277906 |
| H | -3.05498 | -3.79512 | -0.16641 |
| H | -4.44034 | -0.82788 | -1.62798 |
| H | -5.52865 | 0.697096 | 0.07 |
| H | -5.74065 | -1.0217 | 0.359482 |
| H | -2.93582 | -1.02811 | 3.064556 |
| H | -4.03584 | -2.15555 | 2.278486 |
| H | -0.6938 | -0.13398 | 1.512667 |
| H | -5.23383 | -0.02495 | 2.513288 |
| H | -3.87025 | 0.876402 | 1.864708 |
| C | 2.044228 | 1.166097 | -0.32136 |
| O | 1.547565 | 1.582812 | 0.718922 |
| C | 3.463956 | 0.828162 | -0.48349 |
| C | 4.362765 | 0.977724 | 0.587485 |
| C | 3.926255 | 0.35291 | -1.72033 |
| C | 5.703524 | 0.657861 | 0.426243 |
| C | 5.267513 | 0.027769 | -1.89658 |
| C | 6.13113 | 0.187586 | -0.8163 |
| F | 7.428013 | -0.12312 | -0.97507 |
| H | 1.410251 | 1.025333 | -1.21792 |
| H | 3.986398 | 1.34683 | 1.536218 |
| H | 3.228658 | 0.237822 | -2.54643 |
| H | 6.421591 | 0.762521 | 1.232664 |
| H | 5.652152 | -0.34207 | -2.84084 |
| H | -0.25522 | 1.812972 | 0.271515 |

**Table S82.** Geometry (Å) for reactant (anti) of the reaction granatanone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.54598 | 2.921772 | -0.13801 |
| C | -1.76084 | 1.644874 | -0.10318 |
| C | -2.95135 | 1.126246 | -0.8753 |
| C | -1.1195 | -0.7185 | 0.482917 |
| N | -1.89574 | -1.05958 | -0.72534 |
| C | -1.96016 | -2.48499 | -1.01719 |
| C | -3.20644 | -0.38386 | -0.69306 |
| C | -4.02907 | -0.72952 | 0.572796 |
| C | -1.84459 | -1.12589 | 1.794618 |
| C | -0.82528 | 0.766541 | 0.460009 |
| C | -3.24223 | -0.4909 | 1.873836 |
| H | -2.76326 | 1.342162 | -1.93616 |
| H | -3.82862 | 1.723473 | -0.59629 |
| H | -0.17157 | -1.26885 | 0.42724 |
| H | -2.45185 | -2.63028 | -1.98605 |
| H | -2.49973 | -3.09782 | -0.2737 |
| H | -0.94165 | -2.88206 | -1.09505 |
| H | -3.77081 | -0.73171 | -1.56696 |
| H | -4.96367 | -0.15373 | 0.574708 |
| H | -4.32051 | -1.78704 | 0.517712 |
| H | -1.23675 | -0.83355 | 2.660202 |
| H | -1.9294 | -2.22054 | 1.830005 |
| H | -0.20984 | 1.155857 | 1.265957 |
| H | -3.79744 | -0.89906 | 2.727385 |
| H | -3.1447 | 0.586678 | 2.059097 |
| C | 0.702677 | 1.379836 | -0.92742 |
| O | 0.751388 | 2.652681 | -0.71 |
| C | 1.838581 | 0.52914 | -0.49962 |
| C | 2.7799 | 1.011278 | 0.423947 |
| C | 2.007944 | -0.75268 | -1.04468 |
| C | 3.86186 | 0.226169 | 0.807575 |
| C | 3.088717 | -1.54994 | -0.67101 |
| C | 3.996622 | -1.04485 | 0.253238 |
| F | 5.04632 | -1.80752 | 0.619805 |
| H | 0.171037 | 1.009617 | -1.81587 |
| H | 2.653795 | 2.013783 | 0.819459 |
| H | 1.290663 | -1.12231 | -1.77325 |
| H | 4.603113 | 0.580649 | 1.516439 |
| H | 3.240083 | -2.54118 | -1.08543 |
| H | -0.39588 | 3.003459 | -0.38827 |

**Table S83.** Geometry (Å) for transition state (TS anti) of the reaction granatanone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.92256 | 2.942879 | 0.049231 |
| C | -1.8975 | 1.733033 | -0.14677 |
| C | -2.9708 | 1.058763 | -0.98413 |
| C | -1.0452 | -0.59635 | 0.481706 |
| N | -1.80355 | -1.04968 | -0.69898 |
| C | -1.78466 | -2.49222 | -0.90625 |
| C | -3.14826 | -0.44845 | -0.71842 |
| C | -3.96661 | -0.73389 | 0.562657 |
| C | -1.77898 | -0.88168 | 1.815202 |
| C | -0.706 | 0.902429 | 0.314875 |
| C | -3.20578 | -0.3092 | 1.828911 |
| H | -2.64618 | 1.183768 | -2.02711 |
| H | -3.90298 | 1.622398 | -0.87138 |
| H | -0.10344 | -1.15275 | 0.491673 |
| H | -2.27786 | -2.72475 | -1.85692 |
| H | -2.27887 | -3.08724 | -0.11813 |
| H | -0.74499 | -2.83048 | -0.97492 |
| H | -3.68423 | -0.87816 | -1.57345 |
| H | -4.93763 | -0.22588 | 0.502492 |
| H | -4.18238 | -1.80957 | 0.611359 |
| H | -1.19139 | -0.4862 | 2.653215 |
| H | -1.82723 | -1.96944 | 1.95899 |
| H | -0.37581 | 1.314689 | 1.276204 |
| H | -3.7415 | -0.64706 | 2.724386 |
| H | -3.17332 | 0.787252 | 1.898388 |
| C | 0.466153 | 1.218112 | -0.69456 |
| O | 0.810988 | 2.590337 | -0.60249 |
| C | 1.713247 | 0.398389 | -0.42455 |
| C | 2.608095 | 0.77718 | 0.584637 |
| C | 1.990149 | -0.75 | -1.17593 |
| C | 3.747553 | 0.020262 | 0.851554 |
| C | 3.124969 | -1.52205 | -0.92131 |
| C | 3.984895 | -1.1217 | 0.093689 |
| F | 5.088847 | -1.85815 | 0.345773 |
| H | 0.10958 | 0.972268 | -1.70687 |
| H | 2.41808 | 1.688197 | 1.14243 |
| H | 1.312864 | -1.04188 | -1.97501 |
| H | 4.453325 | 0.305223 | 1.625199 |
| H | 3.353492 | -2.41083 | -1.50049 |
| H | 0.001783 | 3.091295 | -0.38302 |

**Table S84.** Geometry (Å) for product (HBO anti) of the reaction granatanone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.96187 | 2.69486 | -8.83776 |
| C | -0.00598 | 3.430677 | -7.97274 |
| C | 1.154979 | 2.473704 | -7.62142 |
| C | 0.697884 | 1.117781 | -7.09955 |
| C | -0.53769 | 0.519219 | -7.77337 |
| C | -1.61112 | 1.601276 | -8.06821 |
| C | -2.34074 | 2.113877 | -6.80517 |
| C | -0.68379 | 4.031411 | -6.72112 |
| C | -0.15266 | -0.24434 | -9.09368 |
| O | 1.296685 | 0.528929 | -6.21943 |
| O | 0.453281 | 0.615187 | -10.0401 |
| C | 0.747729 | -1.44015 | -8.83839 |
| C | 0.212174 | -2.61557 | -8.29705 |
| C | 1.017311 | -3.72252 | -8.03616 |
| C | 2.373006 | -3.64091 | -8.33355 |
| C | 2.935649 | -2.49639 | -8.88276 |
| C | 2.114223 | -1.39654 | -9.13287 |
| C | -1.89852 | 3.55573 | -9.5607 |
| F | 3.161767 | -4.71123 | -8.0902 |
| C | -1.43272 | 2.966612 | -5.90154 |
| H | 0.401688 | 4.250461 | -8.57631 |
| H | 1.837283 | 2.918704 | -6.89076 |
| H | 1.722715 | 2.270461 | -8.53842 |
| H | -0.94858 | -0.22429 | -7.08197 |
| H | -2.3584 | 1.149466 | -8.73455 |
| H | -3.2036 | 2.714618 | -7.12264 |
| H | -2.74809 | 1.260445 | -6.24905 |
| H | -1.38741 | 4.812596 | -7.038 |
| H | 0.072372 | 4.531488 | -6.1036 |
| H | -1.11168 | -0.62628 | -9.49071 |
| H | -8.4E-05 | 1.485808 | -9.93696 |
| H | -0.85223 | -2.67354 | -8.07796 |
| H | 0.612644 | -4.63819 | -7.61756 |
| H | 3.997012 | -2.47625 | -9.10836 |
| H | 2.528889 | -0.49847 | -9.57607 |
| H | -2.49848 | 2.940409 | -10.2395 |
| H | -2.58804 | 4.124471 | -8.91773 |
| H | -1.33123 | 4.271516 | -10.1648 |
| H | -0.71643 | 2.324107 | -5.37595 |
| H | -2.0328 | 3.448613 | -5.12039 |

**Table S85.** Geometry (Å) for product (HBN anti) of the reaction granatanone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.27555 | 1.31691 | 0.790907 |
| C | 1.256877 | 0.422971 | 0.454164 |
| C | 1.937963 | -0.15279 | 1.666071 |
| C | 2.692441 | -0.92861 | -1.05117 |
| N | 2.82982 | -1.81215 | 0.122432 |
| C | 3.668419 | -2.97989 | -0.0897 |
| C | 3.170817 | -1.01283 | 1.309532 |
| C | 4.47974 | -0.20263 | 1.119123 |
| C | 4.021179 | -0.19303 | -1.38274 |
| C | 1.580339 | 0.064551 | -0.79474 |
| C | 4.493235 | 0.634373 | -0.17459 |
| C | -2.42916 | 1.779388 | -1.76393 |
| O | -1.27376 | 2.061478 | -1.47679 |
| C | -3.37261 | 1.016504 | -0.93511 |
| C | -3.00554 | 0.501615 | 0.323255 |
| C | -4.6719 | 0.801407 | -1.42397 |
| C | -3.92679 | -0.21408 | 1.07621 |
| C | -5.60271 | 0.086566 | -0.6784 |
| C | -5.20888 | -0.40835 | 0.56202 |
| F | -6.09864 | -1.1005 | 1.291934 |
| H | 1.209064 | -0.76789 | 2.211991 |
| H | 2.217553 | 0.665552 | 2.343218 |
| H | 2.416507 | -1.56551 | -1.90285 |
| H | 3.616202 | -3.62241 | 0.797612 |
| H | 4.736783 | -2.77801 | -0.2903 |
| H | 3.27712 | -3.55255 | -0.93916 |
| H | 3.33314 | -1.7147 | 2.137647 |
| H | 4.651241 | 0.439419 | 1.993286 |
| H | 5.317217 | -0.91353 | 1.093637 |
| H | 3.880658 | 0.454101 | -2.25815 |
| H | 4.788639 | -0.92961 | -1.65842 |
| H | 1.087173 | 0.517881 | -1.65189 |
| H | 5.503525 | 1.024503 | -0.35354 |
| H | 3.837527 | 1.504563 | -0.05816 |
| H | -2.83974 | 2.117432 | -2.73778 |
| H | -0.16794 | 1.635991 | -0.02377 |
| H | -2.0003 | 0.663143 | 0.701375 |
| H | -4.95164 | 1.199276 | -2.39669 |
| H | -3.67416 | -0.62412 | 2.048238 |
| H | -6.61181 | -0.09308 | -1.03311 |

**Table S86.** Geometry (Å) for reactant (syn) of the reaction granatanone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.764972 | 2.758694 | 0.748831 |
| C | 1.13765 | 1.554807 | 0.452599 |
| C | 1.326379 | 0.581842 | 1.586861 |
| C | 1.670064 | -0.26863 | -1.20257 |
| N | 1.299403 | -1.16536 | -0.09687 |
| C | 1.395198 | -2.58354 | -0.40284 |
| C | 1.96543 | -0.75197 | 1.148779 |
| C | 3.507741 | -0.70327 | 1.01236 |
| C | 3.201029 | -0.26137 | -1.46968 |
| C | 1.18197 | 1.133468 | -0.88597 |
| C | 3.974618 | 0.126419 | -0.19786 |
| C | -0.83272 | 1.558956 | -1.28415 |
| O | -0.91365 | 2.802705 | -0.93052 |
| C | -1.69332 | 0.542826 | -0.61838 |
| C | -2.32663 | 0.843817 | 0.597196 |
| C | -1.92604 | -0.70332 | -1.21687 |
| C | -3.15769 | -0.08699 | 1.215661 |
| C | -2.75855 | -1.6432 | -0.61498 |
| C | -3.35683 | -1.31802 | 0.598214 |
| F | -4.16676 | -2.22168 | 1.188411 |
| H | 0.330676 | 0.383823 | 2.007917 |
| H | 1.906179 | 1.075813 | 2.376468 |
| H | 1.159052 | -0.63469 | -2.10419 |
| H | 0.988416 | -3.15807 | 0.436941 |
| H | 2.414556 | -2.95992 | -0.60353 |
| H | 0.780866 | -2.8024 | -1.28367 |
| H | 1.717872 | -1.50008 | 1.911387 |
| H | 3.95317 | -0.31763 | 1.938535 |
| H | 3.872575 | -1.73333 | 0.902021 |
| H | 3.436436 | 0.42854 | -2.29017 |
| H | 3.509358 | -1.26082 | -1.8049 |
| H | 1.44042 | 1.899948 | -1.61241 |
| H | 5.051519 | -0.01364 | -0.3528 |
| H | 3.832988 | 1.195875 | 0.005162 |
| H | -0.64108 | 1.346461 | -2.34551 |
| H | -0.0436 | 3.006007 | -0.0456 |
| H | -2.1723 | 1.823328 | 1.037922 |
| H | -1.45991 | -0.93607 | -2.17141 |
| H | -3.66031 | 0.128971 | 2.152923 |
| H | -2.95559 | -2.60926 | -1.06804 |

**Table S87.** Geometry (Å) for transition state (TS syn) of the reaction granatanone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.786392 | 2.636823 | 1.002221 |
| C | 1.033745 | 1.486153 | 0.65313 |
| C | 1.326011 | 0.414869 | 1.684148 |
| C | 1.586788 | -0.24847 | -1.17564 |
| N | 1.322272 | -1.21864 | -0.10208 |
| C | 1.472232 | -2.612 | -0.49364 |
| C | 2.024102 | -0.84366 | 1.135062 |
| C | 3.549353 | -0.66805 | 0.943877 |
| C | 3.100058 | -0.0947 | -1.47365 |
| C | 0.947618 | 1.117323 | -0.82299 |
| C | 3.877701 | 0.296502 | -0.207 |
| C | -0.53377 | 1.318114 | -1.31889 |
| O | -0.86261 | 2.694634 | -1.25341 |
| C | -1.5766 | 0.446417 | -0.6268 |
| C | -2.24058 | 0.893356 | 0.523096 |
| C | -1.91438 | -0.80926 | -1.14556 |
| C | -3.19194 | 0.097039 | 1.161122 |
| C | -2.86513 | -1.61947 | -0.52564 |
| C | -3.48545 | -1.15152 | 0.626245 |
| F | -4.41099 | -1.92624 | 1.234125 |
| H | 0.340253 | 0.11577 | 2.066596 |
| H | 1.86747 | 0.874578 | 2.518491 |
| H | 1.095911 | -0.62917 | -2.08037 |
| H | 1.156933 | -3.25325 | 0.336825 |
| H | 2.494925 | -2.91444 | -0.78239 |
| H | 0.811455 | -2.81891 | -1.34298 |
| H | 1.861433 | -1.65271 | 1.85697 |
| H | 4.004945 | -0.32581 | 1.881959 |
| H | 3.989102 | -1.65059 | 0.726095 |
| H | 3.251858 | 0.644854 | -2.27013 |
| H | 3.485779 | -1.04857 | -1.85748 |
| H | 1.490661 | 1.906959 | -1.358 |
| H | 4.956228 | 0.296349 | -0.40575 |
| H | 3.627582 | 1.327222 | 0.08245 |
| H | -0.52754 | 1.051915 | -2.3842 |
| H | -0.4138 | 3.061294 | -0.46568 |
| H | -2.0264 | 1.882931 | 0.913021 |
| H | -1.43627 | -1.16046 | -2.05706 |
| H | -3.7144 | 0.43648 | 2.049775 |
| H | -3.13653 | -2.59122 | -0.9253 |

**Table S88.** Geometry (Å) for product (HBO syn) of the reaction granatanone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.22118 | -1.14221 | -0.95281 |
| C | -5.46736 | -2.38398 | -1.25229 |
| C | -4.52709 | -2.66735 | -0.06037 |
| C | -3.70688 | -1.46472 | 0.384325 |
| C | -4.38477 | -0.09557 | 0.292846 |
| C | -5.30642 | 0.030419 | -0.94591 |
| C | -4.53038 | 0.190351 | -2.27248 |
| C | -4.7152 | -2.31163 | -2.60023 |
| C | -5.15695 | 0.169441 | 1.633095 |
| O | -2.58855 | -1.58169 | 0.851036 |
| O | -6.21064 | -0.76066 | 1.813813 |
| C | -7.42263 | -0.95822 | -1.76797 |
| C | -5.63395 | 1.619237 | 1.733783 |
| C | -6.99739 | 1.927805 | 1.779862 |
| C | -7.43446 | 3.250809 | 1.875237 |
| C | -6.48755 | 4.264459 | 1.9317 |
| C | -5.123 | 3.9953 | 1.90403 |
| C | -4.70638 | 2.668996 | 1.806755 |
| F | -6.89985 | 5.547822 | 2.025278 |
| C | -3.7815 | -1.09183 | -2.67265 |
| H | -6.20147 | -3.1968 | -1.30513 |
| H | -3.84804 | -3.50046 | -0.26642 |
| H | -5.14169 | -2.9411 | 0.807165 |
| H | -3.58083 | 0.644676 | 0.22955 |
| H | -5.93228 | 0.919209 | -0.80516 |
| H | -3.83659 | 1.035853 | -2.188 |
| H | -5.24295 | 0.455906 | -3.06466 |
| H | -4.15129 | -3.2405 | -2.75125 |
| H | -5.44852 | -2.26006 | -3.41598 |
| H | -4.4381 | -0.00472 | 2.445051 |
| H | -6.52578 | -0.99915 | 0.908712 |
| H | -7.96151 | -0.07326 | -1.41368 |
| H | -7.23246 | -0.83064 | -2.84515 |
| H | -8.07634 | -1.82773 | -1.64136 |
| H | -7.71604 | 1.115525 | 1.767454 |
| H | -8.49008 | 3.500126 | 1.915469 |
| H | -4.41297 | 4.813736 | 1.965204 |
| H | -3.64027 | 2.45222 | 1.799746 |
| H | -3.37506 | -0.98867 | -3.68596 |
| H | -2.91532 | -1.24288 | -2.01626 |

**Table S89.** Geometry (Å) for product (HBN syn) of the reaction granatanone + *p*-F-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.31735 | 1.93492 | -0.5862 |
| C | -2.0914 | 0.846462 | -0.29606 |
| C | -3.23675 | 0.698196 | -1.26125 |
| C | -2.79954 | -1.19759 | 0.921396 |
| N | -3.43245 | -1.55817 | -0.3617 |
| C | -4.13101 | -2.83239 | -0.3588 |
| C | -4.22269 | -0.42216 | -0.86219 |
| C | -5.3177 | 0.020742 | 0.14214 |
| C | -3.85184 | -0.87355 | 2.019026 |
| C | -1.87194 | -0.02269 | 0.699844 |
| C | -4.77274 | 0.270532 | 1.56162 |
| C | 1.765998 | 1.239734 | -0.41273 |
| O | 1.235112 | 1.753107 | 0.564598 |
| C | 3.187485 | 0.869088 | -0.48089 |
| C | 4.040548 | 1.100055 | 0.610698 |
| C | 3.695718 | 0.280538 | -1.64725 |
| C | 5.381887 | 0.748788 | 0.538824 |
| C | 5.038275 | -0.07701 | -1.73252 |
| C | 5.868108 | 0.162335 | -0.63552 |
| Cl | 7.559517 | -0.28184 | -0.73042 |
| H | -2.82137 | 0.483583 | -2.25565 |
| H | -3.75783 | 1.661138 | -1.34878 |
| H | -2.20803 | -2.06592 | 1.243074 |
| H | -5.01699 | -2.89713 | 0.299548 |
| H | -3.4348 | -3.62183 | -0.05096 |
| H | -4.46288 | -3.0596 | -1.37914 |
| H | -4.72815 | -0.75704 | -1.77717 |
| H | -5.829 | 0.916082 | -0.23554 |
| H | -6.07904 | -0.77049 | 0.184852 |
| H | -3.34348 | -0.6043 | 2.953911 |
| H | -4.44578 | -1.77281 | 2.234524 |
| H | -1.04997 | 0.122007 | 1.397885 |
| H | -5.60771 | 0.388992 | 2.264208 |
| H | -4.21153 | 1.211632 | 1.581265 |
| H | 1.168282 | 1.029007 | -1.32022 |
| H | 3.631891 | 1.556779 | 1.506607 |
| H | 3.03534 | 0.100946 | -2.49236 |
| H | 6.051358 | 0.921993 | 1.374357 |
| H | 5.440724 | -0.53348 | -2.63002 |
| H | -0.55126 | 1.964593 | 0.027171 |

**Table S90.** Geometry (Å) for reactant (anti) of the reaction granatanone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.80138 | 3.085538 | -0.3093 |
| C | -2.0313 | 1.811794 | -0.25176 |
| C | -3.18592 | 1.283556 | -1.06965 |
| C | -1.44908 | -0.53978 | 0.432913 |
| N | -2.16683 | -0.91052 | -0.80225 |
| C | -2.23716 | -2.34426 | -1.05007 |
| C | -3.4683 | -0.21819 | -0.85954 |
| C | -4.36003 | -0.51656 | 0.370644 |
| C | -2.24652 | -0.89208 | 1.718412 |
| C | -1.13101 | 0.939454 | 0.375788 |
| C | -3.64016 | -0.24216 | 1.702542 |
| C | 0.442727 | 1.500374 | -0.97211 |
| O | 0.516705 | 2.773391 | -0.76782 |
| C | 1.544351 | 0.625154 | -0.5019 |
| C | 2.475668 | 1.093153 | 0.436859 |
| C | 1.692173 | -0.6675 | -1.02459 |
| C | 3.526229 | 0.283785 | 0.856918 |
| C | 2.741494 | -1.48828 | -0.61413 |
| C | 3.648556 | -1.00357 | 0.32778 |
| Cl | 4.977445 | -2.02796 | 0.851315 |
| H | -2.93872 | 1.467395 | -2.12451 |
| H | -4.06975 | 1.897597 | -0.85554 |
| H | -0.50828 | -1.10442 | 0.444362 |
| H | -2.82096 | -2.92478 | -0.31426 |
| H | -1.22189 | -2.75648 | -1.06467 |
| H | -2.68295 | -2.51544 | -2.03668 |
| H | -3.99026 | -0.58473 | -1.75184 |
| H | -5.28784 | 0.066444 | 0.30558 |
| H | -4.65852 | -1.57282 | 0.333757 |
| H | -1.68106 | -0.57571 | 2.603951 |
| H | -2.34579 | -1.98387 | 1.786913 |
| H | -0.54453 | 1.345382 | 1.195173 |
| H | -4.24319 | -0.61762 | 2.538459 |
| H | -3.54249 | 0.840159 | 1.858829 |
| H | -0.0673 | 1.132591 | -1.87433 |
| H | 2.370525 | 2.10414 | 0.816951 |
| H | 0.982652 | -1.02947 | -1.76463 |
| H | 4.250718 | 0.643121 | 1.580105 |
| H | 2.860389 | -2.48674 | -1.02123 |
| H | -0.64529 | 3.152393 | -0.50193 |

**Table S91.** Geometry (Å) for transition state (TS anti) of the reaction granatanone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.17084 | 3.112752 | -0.14119 |
| C | -2.16405 | 1.898448 | -0.30823 |
| C | -3.22184 | 1.225337 | -1.16575 |
| C | -1.379 | -0.43159 | 0.403082 |
| N | -2.10415 | -0.89752 | -0.79351 |
| C | -2.10744 | -2.34485 | -0.96704 |
| C | -3.43572 | -0.27212 | -0.87414 |
| C | -4.30336 | -0.5131 | 0.383312 |
| C | -2.16506 | -0.67066 | 1.716262 |
| C | -1.00494 | 1.056365 | 0.213475 |
| C | -3.57919 | -0.07062 | 1.66468 |
| C | 0.205865 | 1.327849 | -0.76238 |
| O | 0.574221 | 2.694533 | -0.69034 |
| C | 1.427275 | 0.492901 | -0.42873 |
| C | 2.298113 | 0.885206 | 0.59482 |
| C | 1.704767 | -0.68325 | -1.13403 |
| C | 3.412657 | 0.114722 | 0.921281 |
| C | 2.81498 | -1.46854 | -0.81932 |
| C | 3.658608 | -1.06086 | 0.211723 |
| Cl | 5.065057 | -2.03918 | 0.617769 |
| H | -2.86248 | 1.323203 | -2.20016 |
| H | -4.14676 | 1.807328 | -1.09411 |
| H | -0.44992 | -1.00624 | 0.459533 |
| H | -2.64329 | -2.91079 | -0.18491 |
| H | -1.07333 | -2.70552 | -0.98854 |
| H | -2.56959 | -2.58962 | -1.93013 |
| H | -3.94913 | -0.7115 | -1.738 |
| H | -5.26271 | 0.00931 | 0.276999 |
| H | -4.53919 | -1.58356 | 0.449922 |
| H | -1.59962 | -0.26637 | 2.565224 |
| H | -2.23993 | -1.75349 | 1.883462 |
| H | -0.70007 | 1.485361 | 1.175842 |
| H | -4.15267 | -0.37455 | 2.548841 |
| H | -3.52653 | 1.026316 | 1.707842 |
| H | -0.11982 | 1.063914 | -1.78048 |
| H | 2.111378 | 1.81694 | 1.118562 |
| H | 1.048451 | -0.98903 | -1.94535 |
| H | 4.089211 | 0.423799 | 1.711152 |
| H | 3.028362 | -2.37734 | -1.37213 |
| H | -0.23183 | 3.215997 | -0.51026 |

**Table S92.** Geometry (Å) for product (HBO anti) of the reaction granatanone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.84703 | 2.482913 | -8.54299 |
| C | 0.154535 | 3.157466 | -7.67994 |
| C | 1.334575 | 2.182213 | -7.46626 |
| C | 0.911248 | 0.785466 | -7.03079 |
| C | -0.36041 | 0.234543 | -7.67764 |
| C | -1.45051 | 1.330549 | -7.82494 |
| C | -2.10489 | 1.736753 | -6.48473 |
| C | -0.45595 | 3.65884 | -6.3518 |
| C | -0.05479 | -0.42027 | -9.07379 |
| O | 1.561085 | 0.13087 | -6.23783 |
| O | 0.484294 | 0.51456 | -9.98759 |
| C | 0.868278 | -1.62227 | -8.97154 |
| C | 0.39192 | -2.8308 | -8.44975 |
| C | 1.219705 | -3.94566 | -8.33805 |
| C | 2.54372 | -3.84778 | -8.76438 |
| C | 3.040156 | -2.66121 | -9.29767 |
| C | 2.197268 | -1.55369 | -9.39834 |
| C | -1.82081 | 3.389066 | -9.15257 |
| Cl | 3.599537 | -5.25226 | -8.63621 |
| C | -1.1494 | 2.527915 | -5.57394 |
| H | 0.527119 | 4.021983 | -8.24218 |
| H | 2.054637 | 2.572561 | -6.74056 |
| H | 1.852935 | 2.055779 | -8.42557 |
| H | -0.73026 | -0.56165 | -7.02289 |
| H | -2.23411 | 0.92712 | -8.48018 |
| H | -2.99026 | 2.349523 | -6.70072 |
| H | -2.47176 | 0.838696 | -5.97254 |
| H | -1.18161 | 4.453261 | -6.5714 |
| H | 0.330466 | 4.119923 | -5.74167 |
| H | -1.03402 | -0.78297 | -9.43882 |
| H | 0.040223 | 1.372785 | -9.78449 |
| H | -0.64446 | -2.91111 | -8.12762 |
| H | 0.844404 | -4.87945 | -7.93307 |
| H | 4.070774 | -2.60426 | -9.632 |
| H | 2.566318 | -0.62912 | -9.82729 |
| H | -2.45444 | 2.821226 | -9.84199 |
| H | -2.477 | 3.907765 | -8.43687 |
| H | -1.28623 | 4.148871 | -9.73222 |
| H | -0.39814 | 1.856387 | -5.14174 |
| H | -1.7047 | 2.942762 | -4.72418 |

**Table S93.** Geometry (Å) for product (HBN anti) of the reaction granatanone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.512424 | 1.495568 | 0.559617 |
| C | 1.507983 | 0.647025 | 0.153132 |
| C | 2.278824 | 0.084002 | 1.315878 |
| C | 2.902769 | -0.63163 | -1.44956 |
| N | 3.134805 | -1.52618 | -0.29917 |
| C | 4.001086 | -2.65948 | -0.57712 |
| C | 3.516047 | -0.73192 | 0.879094 |
| C | 4.785209 | 0.123784 | 0.628558 |
| C | 4.185101 | 0.154207 | -1.84278 |
| C | 1.771655 | 0.31697 | -1.11724 |
| C | 4.696461 | 0.979862 | -0.64956 |
| C | -2.46653 | 1.784334 | -1.69079 |
| O | -1.29782 | 2.115502 | -1.55163 |
| C | -3.273 | 1.010139 | -0.73343 |
| C | -2.7372 | 0.542812 | 0.480135 |
| C | -4.6119 | 0.736008 | -1.05231 |
| C | -3.53263 | -0.18462 | 1.35681 |
| C | -5.41689 | 0.009459 | -0.18098 |
| C | -4.86502 | -0.44406 | 1.018783 |
| Cl | -5.86543 | -1.36022 | 2.126778 |
| H | 1.603354 | -0.55977 | 1.896394 |
| H | 2.570887 | 0.904843 | 1.984639 |
| H | 2.60216 | -1.26616 | -2.29454 |
| H | 4.019734 | -3.31777 | 0.299828 |
| H | 5.048808 | -2.41483 | -0.83087 |
| H | 3.584701 | -3.23161 | -1.41485 |
| H | 3.746438 | -1.43858 | 1.686605 |
| H | 4.985013 | 0.758323 | 1.502189 |
| H | 5.642774 | -0.55801 | 0.544122 |
| H | 3.973183 | 0.808766 | -2.69804 |
| H | 4.96001 | -0.55144 | -2.17345 |
| H | 1.211255 | 0.758969 | -1.93833 |
| H | 5.680711 | 1.40845 | -0.87843 |
| H | 4.018264 | 1.824258 | -0.48185 |
| H | -3.00486 | 2.079213 | -2.61498 |
| H | -0.00876 | 1.784744 | -0.21891 |
| H | -1.70043 | 0.748109 | 0.731259 |
| H | -5.02577 | 1.096009 | -1.99154 |
| H | -3.13121 | -0.55159 | 2.2951 |
| H | -6.4525 | -0.20528 | -0.4205 |

**Table S94.** Geometry (Å) for reactant (syn) of the reaction granatanone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.970154 | 2.955625 | 0.554173 |
| C | 1.351591 | 1.762522 | 0.225145 |
| C | 1.675706 | 0.801921 | 1.337402 |
| C | 1.787264 | -0.04702 | -1.47167 |
| N | 1.551457 | -0.95144 | -0.33573 |
| C | 1.667713 | -2.36697 | -0.64897 |
| C | 2.316 | -0.51149 | 0.842742 |
| C | 3.83637 | -0.41022 | 0.563418 |
| C | 3.285667 | 0.01307 | -1.87934 |
| C | 1.281527 | 1.338797 | -1.11196 |
| C | 4.160333 | 0.430885 | -0.68496 |
| C | -0.76705 | 1.694421 | -1.31627 |
| O | -0.86423 | 2.934159 | -0.9561 |
| C | -1.51852 | 0.646272 | -0.56805 |
| C | -2.04572 | 0.927964 | 0.700356 |
| C | -1.75223 | -0.61312 | -1.13508 |
| C | -2.77027 | -0.03418 | 1.400124 |
| C | -2.47884 | -1.58416 | -0.45123 |
| C | -2.97682 | -1.28518 | 0.817314 |
| Cl | -3.89687 | -2.50393 | 1.690882 |
| H | 0.729353 | 0.572729 | 1.847149 |
| H | 2.30813 | 1.317866 | 2.070441 |
| H | 1.209125 | -0.43389 | -2.32246 |
| H | 1.364758 | -2.95226 | 0.226343 |
| H | 2.675574 | -2.70691 | -0.94739 |
| H | 0.979709 | -2.61129 | -1.46633 |
| H | 2.165701 | -1.26463 | 1.625311 |
| H | 4.352022 | -0.00625 | 1.444254 |
| H | 4.225166 | -1.42734 | 0.420126 |
| H | 3.41993 | 0.707708 | -2.71841 |
| H | 3.596048 | -0.97625 | -2.24148 |
| H | 1.44797 | 2.111429 | -1.85858 |
| H | 5.222158 | 0.326149 | -0.93952 |
| H | 4.003367 | 1.495742 | -0.46968 |
| H | -0.67469 | 1.484558 | -2.39159 |
| H | 0.089571 | 3.176184 | -0.15514 |
| H | -1.89566 | 1.916653 | 1.121959 |
| H | -1.37119 | -0.83482 | -2.12916 |
| H | -3.18166 | 0.182934 | 2.380348 |
| H | -2.66506 | -2.55719 | -0.89325 |

**Table S95.** Geometry (Å) for transition state (TS syn) of the reaction granatanone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.016797 | 2.811053 | 0.819548 |
| C | 1.266331 | 1.671183 | 0.438805 |
| C | 1.675052 | 0.596679 | 1.425155 |
| C | 1.720084 | -0.02265 | -1.45585 |
| N | 1.589023 | -1.01692 | -0.38021 |
| C | 1.773867 | -2.39718 | -0.80343 |
| C | 2.374609 | -0.62496 | 0.800305 |
| C | 3.87036 | -0.38124 | 0.487026 |
| C | 3.194637 | 0.200153 | -1.87771 |
| C | 1.057735 | 1.309821 | -1.02718 |
| C | 4.061846 | 0.606885 | -0.67509 |
| C | -0.47272 | 1.454231 | -1.37139 |
| O | -0.84 | 2.818583 | -1.27581 |
| C | -1.40823 | 0.553741 | -0.57018 |
| C | -2.01916 | 1.014226 | 0.601983 |
| C | -1.69814 | -0.7448 | -1.0044 |
| C | -2.87175 | 0.193703 | 1.341514 |
| C | -2.55086 | -1.57854 | -0.28294 |
| C | -3.127 | -1.10035 | 0.892734 |
| Cl | -4.20877 | -2.14173 | 1.813519 |
| H | 0.732443 | 0.254551 | 1.874742 |
| H | 2.261978 | 1.061899 | 2.224782 |
| H | 1.170537 | -0.4111 | -2.32281 |
| H | 1.549632 | -3.06218 | 0.037874 |
| H | 2.78564 | -2.64787 | -1.16933 |
| H | 1.064352 | -2.62595 | -1.60655 |
| H | 2.306149 | -1.44804 | 1.52136 |
| H | 4.385661 | -0.02634 | 1.388734 |
| H | 4.333303 | -1.34165 | 0.223624 |
| H | 3.247914 | 0.956356 | -2.67112 |
| H | 3.584689 | -0.73085 | -2.30989 |
| H | 1.511227 | 2.125634 | -1.60421 |
| H | 5.118624 | 0.650394 | -0.96496 |
| H | 3.79957 | 1.624402 | -0.35164 |
| H | -0.56825 | 1.180885 | -2.43064 |
| H | -0.32955 | 3.202672 | -0.53508 |
| H | -1.84421 | 2.033031 | 0.931057 |
| H | -1.26143 | -1.11409 | -1.92912 |
| H | -3.34351 | 0.559105 | 2.247665 |
| H | -2.77378 | -2.5818 | -0.63045 |

**Table S96.** Geometry (Å) for product (HBO syn) of the reaction granatanone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -5.71304 | -1.23968 | -0.69221 |
| C | -4.95501 | -2.51519 | -0.68288 |
| C | -4.51575 | -2.79833 | 0.770012 |
| C | -3.86131 | -1.61322 | 1.465297 |
| C | -4.40559 | -0.22476 | 1.11832 |
| C | -4.81164 | -0.10039 | -0.3717 |
| C | -3.60295 | -0.00613 | -1.33061 |
| C | -3.76939 | -2.5078 | -1.67295 |
| C | -5.59853 | 0.097695 | 2.085204 |
| O | -2.99116 | -1.75458 | 2.304645 |
| O | -6.68373 | -0.78947 | 1.882595 |
| C | -6.52749 | -1.03634 | -1.89117 |
| C | -6.01985 | 1.56497 | 1.991334 |
| C | -7.29326 | 1.920705 | 1.538045 |
| C | -7.68088 | 3.2595 | 1.45207 |
| C | -6.78192 | 4.252425 | 1.832416 |
| C | -5.5103 | 3.926204 | 2.304551 |
| C | -5.14059 | 2.584924 | 2.381248 |
| Cl | -7.25801 | 5.944518 | 1.727165 |
| C | -2.81868 | -1.32556 | -1.42098 |
| H | -5.65595 | -3.30304 | -0.98353 |
| H | -3.84199 | -3.65851 | 0.831224 |
| H | -5.41013 | -3.03044 | 1.362988 |
| H | -3.60429 | 0.486817 | 1.341729 |
| H | -5.40655 | 0.814021 | -0.47911 |
| H | -2.94868 | 0.814084 | -1.01032 |
| H | -3.97017 | 0.26656 | -2.32893 |
| H | -3.23052 | -3.46059 | -1.60068 |
| H | -4.15986 | -2.45103 | -2.6977 |
| H | -5.22925 | -0.0791 | 3.104471 |
| H | -6.65916 | -1.04129 | 0.927429 |
| H | -7.12195 | -0.12504 | -1.76798 |
| H | -5.95241 | -0.94247 | -2.82527 |
| H | -7.21669 | -1.88009 | -2.00186 |
| H | -7.99227 | 1.133967 | 1.275536 |
| H | -8.67206 | 3.527987 | 1.101349 |
| H | -4.82553 | 4.70984 | 2.611359 |
| H | -4.15278 | 2.334728 | 2.762578 |
| H | -2.07348 | -1.26448 | -2.22317 |
| H | -2.25048 | -1.49013 | -0.49672 |

**Table S97.** Geometry (Å) for product (HBN syn) of the reaction granatanone + *p*-Cl-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.95788 | 2.105534 | -0.56292 |

| | | | |
|---|---|---|---|
| C | -2.77408 | 1.072337 | -0.19376 |
| C | -3.98978 | 0.972406 | -1.07557 |
| C | -3.52044 | -0.89134 | 1.128274 |
| N | -4.26709 | -1.24102 | -0.09563 |
| C | -5.04819 | -2.46329 | -0.00049 |
| C | -5.01585 | -0.06684 | -0.57257 |
| C | -6.00138 | 0.476329 | 0.4943 |
| C | -4.46692 | -0.46984 | 2.287361 |
| C | -2.53853 | 0.214434 | 0.808119 |
| C | -5.33861 | 0.724267 | 1.862719 |
| C | 1.102225 | 1.246003 | -0.50235 |
| O | 0.637335 | 1.798304 | 0.485512 |
| C | 2.490749 | 0.757408 | -0.59636 |
| C | 3.372887 | 0.90604 | 0.48564 |
| C | 2.927901 | 0.141796 | -1.77634 |
| C | 4.676584 | 0.439216 | 0.38595 |
| C | 4.235152 | -0.32694 | -1.87914 |
| C | 5.105625 | -0.17816 | -0.79668 |
| C | 6.504767 | -0.73739 | -0.87385 |
| F | 6.950544 | -0.80514 | -2.14581 |
| F | 6.558141 | -1.98841 | -0.36457 |
| F | 7.379809 | 0.013682 | -0.17202 |
| H | -3.65886 | 0.700117 | -2.08737 |
| H | -4.452 | 1.965068 | -1.16099 |
| H | -2.96417 | -1.78867 | 1.432782 |
| H | -5.47602 | -2.69069 | -0.98431 |
| H | -5.87967 | -2.44927 | 0.727873 |
| H | -4.38461 | -3.292 | 0.274365 |
| H | -5.60877 | -0.38973 | -1.43795 |
| H | -6.80824 | -0.25969 | 0.615402 |
| H | -6.47845 | 1.394518 | 0.126919 |
| H | -3.87558 | -0.21484 | 3.176313 |
| H | -5.10321 | -1.32052 | 2.568768 |
| H | -1.66441 | 0.324919 | 1.44645 |
| H | -6.10986 | 0.918699 | 2.619142 |
| H | -4.71507 | 1.624156 | 1.812935 |
| H | 0.471139 | 1.086038 | -1.39737 |
| H | -1.16255 | 2.112375 | 0.011554 |
| H | 3.016376 | 1.389645 | 1.389383 |
| H | 2.242716 | 0.032148 | -2.61337 |
| H | 5.367304 | 0.554952 | 1.214516 |
| H | 4.581459 | -0.79917 | -2.79187 |

**Table S98.** Geometry (Å) for reactant (anti) of the reaction granatanone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.33334 | 3.320678 | -0.14907 |
| C | -2.57829 | 2.048828 | -0.10212 |

| | | | |
|---|---|---|---|
| C | -3.83937 | 1.567977 | -0.77754 |
| C | -1.95907 | -0.33074 | 0.433436 |
| N | -2.83537 | -0.64546 | -0.71183 |
| C | -2.96126 | -2.06753 | -1.00152 |
| C | -4.12125 | 0.065118 | -0.57778 |
| C | -4.8523 | -0.26109 | 0.746963 |
| C | -2.59388 | -0.71315 | 1.799311 |
| C | -1.62118 | 1.145809 | 0.384913 |
| C | -3.96242 | -0.039 | 1.982185 |
| C | -0.1938 | 1.718353 | -1.0922 |
| O | -0.096 | 2.990788 | -0.9033 |
| C | 0.949947 | 0.844297 | -0.71496 |
| C | 1.950157 | 1.320429 | 0.146024 |
| C | 1.064872 | -0.44441 | -1.2539 |
| C | 3.034344 | 0.515671 | 0.474532 |
| C | 2.15125 | -1.25377 | -0.927 |
| C | 3.135683 | -0.77506 | -0.05964 |
| C | 4.284891 | -1.65835 | 0.344017 |
| F | 4.5318 | -2.62071 | -0.57192 |
| F | 4.040828 | -2.28747 | 1.518811 |
| F | 5.425661 | -0.95283 | 0.510661 |
| H | -3.72849 | 1.782951 | -1.84944 |
| H | -4.67413 | 2.189552 | -0.4298 |
| H | -1.0365 | -0.91097 | 0.307395 |
| H | -3.52803 | -2.19418 | -1.93102 |
| H | -3.46089 | -2.66778 | -0.22105 |
| H | -1.96319 | -2.49267 | -1.15644 |
| H | -4.76006 | -0.26399 | -1.40636 |
| H | -5.17012 | -1.3119 | 0.717022 |
| H | -5.77089 | 0.335478 | 0.818743 |
| H | -1.91317 | -0.43773 | 2.614607 |
| H | -2.70733 | -1.80472 | 1.844491 |
| H | -0.94788 | 1.517345 | 1.152443 |
| H | -4.46081 | -0.42878 | 2.878164 |
| H | -3.82277 | 1.036284 | 2.154041 |
| H | -0.778 | 1.346108 | -1.94699 |
| H | -1.2235 | 3.380591 | -0.47306 |
| H | 1.867691 | 2.331726 | 0.530282 |
| H | 0.304959 | -0.80662 | -1.94181 |
| H | 3.812762 | 0.888592 | 1.1326 |
| H | 2.242616 | -2.2473 | -1.35281 |

**Table S99.** Geometry (Å) for transition state (TS anti) of the reaction granatanone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.69218 | 3.356301 | -0.01771 |

| | | | |
|---|---|---|---|
| C | -2.72282 | 2.141701 | -0.1808 |
| C | -3.87831 | 1.486513 | -0.91633 |
| C | -1.89486 | -0.20378 | 0.433478 |
| N | -2.75212 | -0.64736 | -0.68174 |
| C | -2.78865 | -2.09229 | -0.87119 |
| C | -4.07816 | -0.00916 | -0.60706 |
| C | -4.80149 | -0.24884 | 0.738694 |
| C | -2.53309 | -0.45062 | 1.822764 |
| C | -1.52784 | 1.283922 | 0.224432 |
| C | -3.93339 | 0.171814 | 1.935209 |
| C | -0.40336 | 1.555371 | -0.84834 |
| O | -0.02837 | 2.920742 | -0.81311 |
| C | 0.841064 | 0.720708 | -0.60621 |
| C | 1.77976 | 1.112361 | 0.356255 |
| C | 1.070137 | -0.45088 | -1.3371 |
| C | 2.911426 | 0.338424 | 0.5987 |
| C | 2.200792 | -1.23092 | -1.09973 |
| C | 3.122392 | -0.83831 | -0.12659 |
| C | 4.312174 | -1.7074 | 0.173765 |
| F | 4.732296 | -2.38441 | -0.91885 |
| F | 4.027662 | -2.63546 | 1.120268 |
| F | 5.360795 | -0.99016 | 0.634845 |
| H | -3.63399 | 1.58283 | -1.98393 |
| H | -4.78094 | 2.081859 | -0.7423 |
| H | -0.97259 | -0.78967 | 0.381212 |
| H | -3.35969 | -2.32088 | -1.7782 |
| H | -3.2368 | -2.66401 | -0.03962 |
| H | -1.76726 | -2.46123 | -1.01495 |
| H | -4.69047 | -0.43809 | -1.40939 |
| H | -5.04322 | -1.31666 | 0.82364 |
| H | -5.75932 | 0.286869 | 0.743502 |
| H | -1.86965 | -0.0673 | 2.60811 |
| H | -2.60699 | -1.53442 | 1.9836 |
| H | -1.13678 | 1.701465 | 1.160342 |
| H | -4.41008 | -0.1323 | 2.874895 |
| H | -3.85883 | 1.267669 | 1.980881 |
| H | -0.80956 | 1.285601 | -1.83553 |
| H | -0.81321 | 3.443543 | -0.55732 |
| H | 1.628188 | 2.043534 | 0.891757 |
| H | 0.361517 | -0.74936 | -2.10588 |
| H | 3.639279 | 0.652504 | 1.339812 |
| H | 2.375655 | -2.13172 | -1.67904 |

**Table S100.** Geometry (Å) for product (HBO anti) of the reaction granatanone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|

| | | | |
|---|---|---|---|
| N | -0.80459 | 2.696845 | -8.69401 |
| C | 0.142048 | 3.390854 | -7.78471 |
| C | 1.282561 | 2.40704 | -7.44183 |
| C | 0.798723 | 1.038899 | -6.97981 |
| C | -0.43785 | 0.48295 | -7.69089 |
| C | -1.48776 | 1.590355 | -7.97367 |
| C | -2.23559 | 2.072314 | -6.70938 |
| C | -0.55403 | 3.959496 | -6.52805 |
| C | -0.04064 | -0.2453 | -9.02578 |
| O | 1.377503 | 0.405524 | -6.11772 |
| O | 0.597507 | 0.631008 | -9.93307 |
| C | 0.835355 | -1.46285 | -8.78573 |
| C | 0.276576 | -2.62902 | -8.24719 |
| C | 1.061965 | -3.75046 | -8.00242 |
| C | 2.426992 | -3.72092 | -8.30396 |
| C | 2.991875 | -2.56827 | -8.85208 |
| C | 2.199059 | -1.44665 | -9.09092 |
| C | -1.71302 | 3.595062 | -9.4082 |
| C | 3.264111 | -4.95157 | -8.09608 |
| F | 2.844169 | -5.67289 | -7.03101 |
| F | 4.566825 | -4.6524 | -7.89414 |
| F | 3.216653 | -5.78157 | -9.16747 |
| C | -1.33236 | 2.878347 | -5.75958 |
| H | 0.573165 | 4.224015 | -8.35242 |
| H | 1.953625 | 2.816072 | -6.68035 |
| H | 1.870158 | 2.230034 | -8.35183 |
| H | -0.87276 | -0.2724 | -7.02773 |
| H | -2.22769 | 1.172251 | -8.66957 |
| H | -3.0816 | 2.697913 | -7.02403 |
| H | -2.66873 | 1.207533 | -6.19162 |
| H | 0.195563 | 4.429353 | -5.87962 |
| H | -1.24155 | 4.759419 | -6.83307 |
| H | -0.99552 | -0.60337 | -9.45354 |
| H | 0.159208 | 1.507223 | -9.80928 |
| H | -0.78605 | -2.66272 | -8.01583 |
| H | 0.620665 | -4.64576 | -7.57658 |
| H | 4.051394 | -2.54518 | -9.08542 |
| H | 2.630622 | -0.553 | -9.52631 |
| H | -2.30285 | 3.012198 | -10.1235 |
| H | -2.4115 | 4.147863 | -8.76134 |
| H | -1.12258 | 4.325307 | -9.97131 |
| H | -0.63504 | 2.207081 | -5.24421 |
| H | -1.93945 | 3.341401 | -4.97252 |

**Table S101.** Geometry (Å) for product (HBN anti) of the reaction granatanone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.909828 | 1.619896 | 0.490153 |
| C | 2.014379 | 0.887812 | 0.141163 |
| C | 2.674386 | 0.259034 | 1.337481 |
| C | 3.697568 | -0.1186 | -1.3761 |
| N | 3.850598 | -1.11262 | -0.29705 |
| C | 4.829168 | -2.15338 | -0.56374 |
| C | 4.015996 | -0.42556 | 0.993454 |
| C | 5.23766 | 0.529161 | 1.000175 |
| C | 4.95402 | 0.786605 | -1.51544 |
| C | 2.46206 | 0.712963 | -1.10822 |
| C | 5.2479 | 1.509164 | -0.1892 |
| C | -1.87556 | 1.912264 | -1.99813 |
| O | -0.73913 | 2.280627 | -1.74523 |
| C | -2.72177 | 1.051084 | -1.14816 |
| C | -2.25892 | 0.535862 | 0.074901 |
| C | -4.01979 | 0.751591 | -1.58713 |
| C | -3.09399 | -0.268 | 0.841682 |
| C | -4.8556 | -0.05242 | -0.81829 |
| C | -4.38884 | -0.5613 | 0.396443 |
| C | -5.26611 | -1.47903 | 1.21157 |
| F | -5.0262 | -1.35325 | 2.533565 |
| F | -5.05233 | -2.77442 | 0.889937 |
| F | -6.57745 | -1.23033 | 1.007743 |
| H | 1.98351 | -0.48348 | 1.760454 |
| H | 2.815839 | 1.023848 | 2.113056 |
| H | 3.557648 | -0.67747 | -2.3115 |
| H | 4.785624 | -2.89807 | 0.240097 |
| H | 5.879175 | -1.81831 | -0.64909 |
| H | 4.568202 | -2.65897 | -1.50115 |
| H | 4.194629 | -1.19861 | 1.75177 |
| H | 5.276579 | 1.078417 | 1.950191 |
| H | 6.147964 | -0.08517 | 0.965406 |
| H | 5.816725 | 0.17225 | -1.80901 |
| H | 4.800915 | 1.515371 | -2.32191 |
| H | 1.975719 | 1.200477 | -1.9507 |
| H | 4.494817 | 2.289769 | -0.0314 |
| H | 6.219093 | 2.017872 | -0.24236 |
| H | -2.35203 | 2.235825 | -2.94619 |
| H | 0.46019 | 1.939509 | -0.31943 |
| H | -1.25382 | 0.765551 | 0.416586 |
| H | -4.37428 | 1.154811 | -2.53283 |
| H | -2.74819 | -0.66459 | 1.790327 |
| H | -5.86268 | -0.27927 | -1.15068 |

**Table S102.** Geometry (Å) for reactant (syn) of the reaction granatanone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.333604 | 3.238341 | 0.694674 |
| C | 1.744698 | 2.061902 | 0.340425 |
| C | 1.97387 | 1.04747 | 1.427559 |
| C | 2.328737 | 0.339791 | -1.40145 |
| N | 1.991969 | -0.61755 | -0.33658 |
| C | 2.128502 | -2.01694 | -0.70943 |
| C | 2.652793 | -0.24317 | 0.924211 |
| C | 4.191789 | -0.13712 | 0.784178 |
| C | 3.857126 | 0.409936 | -1.67274 |
| C | 1.795827 | 1.709482 | -1.01897 |
| C | 4.62443 | 0.763502 | -0.38735 |
| C | -0.21307 | 2.092884 | -1.40814 |
| O | -0.3592 | 3.302109 | -0.97424 |
| C | -1.02777 | 0.990312 | -0.81435 |
| C | -1.65931 | 1.170623 | 0.424553 |
| C | -1.21812 | -0.2112 | -1.50843 |
| C | -2.44073 | 0.157106 | 0.970852 |
| C | -2.00373 | -1.22573 | -0.97009 |
| C | -2.61159 | -1.04468 | 0.275659 |
| C | -3.41096 | -2.16013 | 0.890889 |
| F | -4.41007 | -1.69484 | 1.673228 |
| F | -2.6402 | -2.95377 | 1.674311 |
| F | -3.96754 | -2.96091 | -0.04565 |
| H | 0.988654 | 0.797676 | 1.845815 |
| H | 2.54261 | 1.525187 | 2.235034 |
| H | 1.825737 | -0.00084 | -2.31707 |
| H | 1.750192 | -2.64216 | 0.106879 |
| H | 3.156908 | -2.34948 | -0.93815 |
| H | 1.510752 | -2.2142 | -1.59281 |
| H | 2.433518 | -1.03373 | 1.651434 |
| H | 4.629349 | 0.218968 | 1.725757 |
| H | 4.589477 | -1.1482 | 0.624017 |
| H | 4.195268 | -0.56299 | -2.05371 |
| H | 4.06648 | 1.143094 | -2.46218 |
| H | 2.039889 | 2.519472 | -1.7021 |
| H | 4.450026 | 1.817285 | -0.13372 |
| H | 5.704333 | 0.666372 | -0.55319 |
| H | -0.01464 | 1.957549 | -2.48147 |
| H | 0.531037 | 3.50158 | -0.07298 |
| H | -1.54473 | 2.120271 | 0.937 |
| H | -0.75949 | -0.3463 | -2.48511 |
| H | -2.93482 | 0.302037 | 1.926212 |
| H | -2.15827 | -2.14976 | -1.51737 |

**Table S103.** Geometry (Å) for transition state (TS syn) of the reaction granatanone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.316261 | 3.056823 | 0.975096 |
| C | 1.634834 | 1.94962 | 0.551598 |
| C | 2.000049 | 0.8343 | 1.510003 |
| C | 2.279717 | 0.373932 | -1.39025 |
| N | 2.07194 | -0.67552 | -0.381 |
| C | 2.29376 | -2.03176 | -0.86055 |
| C | 2.760948 | -0.34528 | 0.876277 |
| C | 4.273074 | -0.075 | 0.692431 |
| C | 3.780262 | 0.630436 | -1.68042 |
| C | 1.567812 | 1.675829 | -0.9474 |
| C | 4.54152 | 0.980319 | -0.39214 |
| C | 0.078551 | 1.829266 | -1.43473 |
| O | -0.33462 | 3.17227 | -1.26638 |
| C | -0.90849 | 0.845574 | -0.81294 |
| C | -1.61827 | 1.177145 | 0.347709 |
| C | -1.15113 | -0.39628 | -1.41213 |
| C | -2.51739 | 0.276792 | 0.915941 |
| C | -2.05118 | -1.30044 | -0.85491 |
| C | -2.73339 | -0.96703 | 0.318027 |
| C | -3.66073 | -1.96304 | 0.955803 |
| F | -4.63447 | -1.36265 | 1.675911 |
| F | -3.0015 | -2.78944 | 1.80532 |
| F | -4.26306 | -2.75341 | 0.038037 |
| H | 1.037984 | 0.456513 | 1.883125 |
| H | 2.524697 | 1.271352 | 2.366953 |
| H | 1.806212 | 0.02678 | -2.31728 |
| H | 2.00662 | -2.74022 | -0.07579 |
| H | 3.331978 | -2.26318 | -1.15864 |
| H | 1.649355 | -2.2163 | -1.72732 |
| H | 2.646649 | -1.20768 | 1.543392 |
| H | 4.715534 | 0.228404 | 1.649861 |
| H | 4.763941 | -1.01557 | 0.408547 |
| H | 4.215535 | -0.2737 | -2.12621 |
| H | 3.886877 | 1.427351 | -2.42731 |
| H | 2.065744 | 2.529023 | -1.42571 |
| H | 4.235971 | 1.974058 | -0.03452 |
| H | 5.617228 | 1.053717 | -0.59214 |
| H | 0.098554 | 1.643146 | -2.51671 |
| H | 0.098019 | 3.508696 | -0.45596 |
| H | -1.48376 | 2.156178 | 0.795139 |
| H | -0.64159 | -0.65688 | -2.33672 |
| H | -3.06599 | 0.547859 | 1.812139 |
| H | -2.23711 | -2.25509 | -1.33639 |

**Table S104.** Geometry (Å) for product (HBO syn) of the reaction granatanone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.50799 | -1.4252 | -0.70405 |
| C | -5.85916 | -2.73526 | -0.95693 |
| C | -4.77947 | -2.94745 | 0.125785 |
| C | -3.85219 | -1.75669 | 0.322438 |
| C | -4.47117 | -0.36515 | 0.16048 |
| C | -5.5483 | -0.31616 | -0.95234 |
| C | -4.95528 | -0.34542 | -2.37898 |
| C | -5.29721 | -2.85282 | -2.39139 |
| C | -5.03851 | 0.090882 | 1.549887 |
| O | -2.68877 | -1.88931 | 0.654317 |
| O | -6.10728 | -0.73654 | 1.970463 |
| C | -7.7975 | -1.25653 | -1.37584 |
| C | -5.4157 | 1.573052 | 1.541615 |
| C | -6.74301 | 1.978606 | 1.711843 |
| C | -7.08371 | 3.331087 | 1.695033 |
| C | -6.09411 | 4.298394 | 1.51307 |
| C | -4.76044 | 3.906636 | 1.358187 |
| C | -4.42875 | 2.555386 | 1.374173 |
| C | -6.44613 | 5.759337 | 1.550771 |
| F | -6.35517 | 6.268143 | 2.802672 |
| F | -7.71101 | 5.98613 | 1.128877 |
| F | -5.62106 | 6.496219 | 0.771507 |
| C | -4.32911 | -1.70611 | -2.72647 |
| H | -6.62993 | -3.50309 | -0.82034 |
| H | -4.17339 | -3.83699 | -0.07154 |
| H | -5.28184 | -3.0914 | 1.091439 |
| H | -3.64815 | 0.310406 | -0.09321 |
| H | -6.10851 | 0.618567 | -0.83405 |
| H | -4.21819 | 0.460351 | -2.48236 |
| H | -5.75683 | -0.12187 | -3.09554 |
| H | -4.80143 | -3.82444 | -2.50795 |
| H | -6.13318 | -2.84591 | -3.10338 |
| H | -4.22623 | -0.04045 | 2.277598 |
| H | -6.5496 | -1.0584 | 1.147523 |
| H | -8.24539 | -0.31027 | -1.05507 |
| H | -7.74331 | -1.25113 | -2.47532 |
| H | -8.46626 | -2.06931 | -1.07381 |
| H | -7.50221 | 1.222397 | 1.878869 |
| H | -8.11814 | 3.634182 | 1.822016 |
| H | -3.98886 | 4.657646 | 1.222702 |
| H | -3.38685 | 2.263753 | 1.261583 |
| H | -4.06444 | -1.73637 | -3.7902 |
| H | -3.38655 | -1.83856 | -2.18029 |

**Table S105.** Geometry (Å) for product (HBN syn) of the reaction granatanone + *p*-$CF_3$-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.35317 | 1.667052 | -0.44488 |
| C | -2.18253 | 0.600317 | -0.24528 |
| C | -3.37188 | 0.634642 | -1.16682 |
| C | -2.97351 | -1.52512 | 0.763284 |
| N | -3.68082 | -1.69451 | -0.52066 |
| C | -4.46103 | -2.91527 | -0.62998 |
| C | -4.41309 | -0.46205 | -0.85151 |
| C | -5.43509 | -0.07135 | 0.24806 |
| C | -3.95789 | -1.26875 | 1.938674 |
| C | -1.9807 | -0.3908 | 0.633695 |
| C | -4.81817 | -0.02396 | 1.659347 |
| H | -3.01058 | 0.511476 | -2.19721 |
| H | -3.83132 | 1.631162 | -1.12046 |
| H | -2.42811 | -2.45951 | 0.955411 |
| H | -4.84973 | -2.99982 | -1.6521 |
| H | -5.32107 | -3.00403 | 0.059348 |
| H | -3.80631 | -3.77643 | -0.44994 |
| H | -4.97642 | -0.65685 | -1.77324 |
| H | -5.89956 | 0.892193 | -0.00026 |
| H | -6.24578 | -0.81301 | 0.237196 |
| H | -3.39642 | -1.14248 | 2.873389 |
| H | -4.60178 | -2.14885 | 2.077212 |
| H | -1.12354 | -0.37807 | 1.303559 |
| H | -4.19491 | 0.871841 | 1.75974 |
| H | -5.61475 | 0.062878 | 2.409703 |
| H | -0.56441 | 1.583517 | 0.135133 |
| C | 1.719319 | 0.816492 | -0.40258 |
| O | 1.201789 | 1.247222 | 0.620792 |
| C | 3.131235 | 0.415042 | -0.51702 |
| C | 3.984303 | 0.524885 | 0.584677 |
| C | 3.607611 | -0.07639 | -1.7436 |
| C | 5.324304 | 0.144166 | 0.470041 |
| C | 4.941028 | -0.45473 | -1.85142 |
| C | 5.802717 | -0.34809 | -0.75537 |
| O | 6.080554 | 0.286425 | 1.593023 |
| C | 7.451654 | -0.08054 | 1.539774 |
| H | 1.114822 | 0.710247 | -1.32406 |
| H | 3.608239 | 0.905844 | 1.528109 |
| H | 2.935707 | -0.15826 | -2.59379 |
| H | 5.325913 | -0.83772 | -2.79224 |
| H | 6.838609 | -0.64874 | -0.86356 |
| H | 7.850403 | 0.11609 | 2.536158 |
| H | 8.001765 | 0.520704 | 0.804106 |
| H | 7.57523 | -1.14553 | 1.303515 |

**Table S106.** Geometry (Å) for reactant (anti) of the reaction granatanone + *m*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.68114 | 2.818908 | -0.24079 |
| C | -1.9435 | 1.550202 | -0.22048 |
| C | -3.18184 | 1.093258 | -0.95519 |
| C | -1.37319 | -0.84601 | 0.300396 |
| N | -2.20884 | -1.1327 | -0.88246 |
| C | -2.33791 | -2.54743 | -1.20106 |
| C | -3.4897 | -0.40841 | -0.7872 |
| C | -4.27524 | -0.74652 | 0.503698 |
| C | -2.06371 | -1.25042 | 1.631896 |
| C | -1.02345 | 0.627722 | 0.294877 |
| C | -3.43029 | -0.56264 | 1.776799 |
| H | -3.02544 | 1.319446 | -2.019 |
| H | -4.02323 | 1.719839 | -0.63309 |
| H | -0.45005 | -1.42984 | 0.196835 |
| H | -2.86919 | -2.65261 | -2.15416 |
| H | -2.87424 | -3.15621 | -0.45153 |
| H | -1.33859 | -2.98007 | -1.32415 |
| H | -4.10092 | -0.71829 | -1.6439 |
| H | -5.18695 | -0.13698 | 0.552477 |
| H | -4.60756 | -1.79159 | 0.441329 |
| H | -1.41202 | -0.99939 | 2.478282 |
| H | -2.19173 | -2.34141 | 1.650417 |
| H | -0.36871 | 0.977682 | 1.087627 |
| H | -3.28316 | 0.506747 | 1.975906 |
| H | -3.96834 | -0.96426 | 2.644415 |
| H | -0.54356 | 2.862313 | -0.53601 |
| C | 0.492368 | 1.205209 | -1.11866 |
| O | 0.578909 | 2.476198 | -0.90932 |
| C | 1.60964 | 0.320186 | -0.69874 |
| C | 2.553544 | 0.776694 | 0.222937 |
| C | 1.739149 | -0.96299 | -1.25741 |
| C | 3.621345 | -0.04293 | 0.603734 |
| C | 2.805991 | -1.77183 | -0.8779 |
| C | 3.750113 | -1.32623 | 0.052053 |
| O | 4.484482 | 0.496652 | 1.513 |
| C | 5.595089 | -0.27949 | 1.932158 |
| H | -0.06145 | 0.844913 | -1.99783 |
| H | 2.470259 | 1.776517 | 0.634647 |
| H | 1.013845 | -1.30861 | -1.98909 |
| H | 2.916183 | -2.76311 | -1.30967 |
| H | 4.573926 | -1.97368 | 0.329813 |
| H | 6.139766 | 0.340298 | 2.646694 |
| H | 6.25616 | -0.52802 | 1.091218 |
| H | 5.277254 | -1.20726 | 2.426583 |

**Table S107.** Geometry (Å) for transition state (TS anti) of the reaction granatanone + *m*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.08264 | 2.861058 | -0.12586 |
| C | -2.09631 | 1.648058 | -0.30473 |
| C | -3.2291 | 0.99335 | -1.07701 |
| C | -1.26559 | -0.69782 | 0.298257 |
| N | -2.09297 | -1.1337 | -0.84226 |
| C | -2.10794 | -2.57479 | -1.05572 |
| C | -3.42483 | -0.5078 | -0.79202 |
| C | -4.17922 | -0.77127 | 0.532451 |
| C | -1.93522 | -0.971 | 1.667492 |
| C | -0.90626 | 0.79513 | 0.118575 |
| C | -3.34322 | -0.36174 | 1.755573 |
| H | -2.95961 | 1.104828 | -2.13699 |
| H | -4.14034 | 1.579699 | -0.91725 |
| H | -0.33629 | -1.27297 | 0.258508 |
| H | -2.65675 | -2.79562 | -1.97847 |
| H | -2.56679 | -3.16622 | -0.24342 |
| H | -1.07877 | -2.92757 | -1.1835 |
| H | -4.01447 | -0.9309 | -1.61445 |
| H | -5.14088 | -0.24229 | 0.521758 |
| H | -4.41507 | -1.84203 | 0.596465 |
| H | -1.29423 | -0.59392 | 2.474188 |
| H | -2.00437 | -2.05785 | 1.810654 |
| H | -0.541 | 1.202324 | 1.06925 |
| H | -3.27854 | 0.733801 | 1.818219 |
| H | -3.84012 | -0.68308 | 2.679139 |
| H | -0.18097 | 2.966091 | -0.61344 |
| C | 0.247595 | 1.084544 | -0.91885 |
| O | 0.614306 | 2.451702 | -0.85205 |
| C | 1.483787 | 0.243435 | -0.65513 |
| C | 2.363792 | 0.599921 | 0.364495 |
| C | 1.742724 | -0.90347 | -1.42077 |
| C | 3.493207 | -0.18311 | 0.636774 |
| C | 2.866366 | -1.67978 | -1.14824 |
| C | 3.748382 | -1.33314 | -0.12102 |
| O | 4.282914 | 0.260339 | 1.660133 |
| C | 5.451627 | -0.47726 | 1.975198 |
| H | -0.13092 | 0.830236 | -1.92115 |
| H | 2.200486 | 1.504063 | 0.940656 |
| H | 1.069657 | -1.17543 | -2.22974 |
| H | 3.070799 | -2.56503 | -1.74512 |
| H | 4.619332 | -1.94971 | 0.069959 |
| H | 5.924658 | 0.051086 | 2.80518 |
| H | 6.148128 | -0.51533 | 1.126899 |
| H | 5.212269 | -1.50238 | 2.289149 |

**Table S108.** Geometry (Å) for product (HBO anti) of the reaction granatanone + *m*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -1.01337 | 2.830478 | -8.49252 |
| C | 0.033424 | 3.443621 | -7.63909 |
| C | 1.164283 | 2.406395 | -7.4519 |
| C | 0.675224 | 1.027131 | -7.02606 |
| C | -0.63044 | 0.548579 | -7.66269 |
| C | -1.66352 | 1.702516 | -7.77722 |
| C | -2.27498 | 2.127337 | -6.42222 |
| C | -0.52917 | 3.962061 | -6.29678 |
| C | -0.38266 | -0.09848 | -9.07494 |
| O | 1.300281 | 0.335601 | -6.24436 |
| O | 0.230021 | 0.810991 | -9.97001 |
| C | 0.433493 | -1.37712 | -9.00344 |
| C | 1.797231 | -1.39107 | -9.32299 |
| C | 2.51155 | -2.58266 | -9.23673 |
| C | 1.89539 | -3.77213 | -8.8379 |
| C | 0.531428 | -3.75769 | -8.52539 |
| C | -0.19035 | -2.56138 | -8.61398 |
| C | -1.94763 | 3.789187 | -9.08177 |
| O | -0.19047 | -4.85351 | -8.13665 |
| C | 0.48182 | -6.09743 | -8.04445 |
| C | -1.26752 | 2.860364 | -5.51893 |
| H | 0.442217 | 4.293822 | -8.19833 |
| H | 1.911319 | 2.750775 | -6.73013 |
| H | 1.664219 | 2.264645 | -8.41854 |
| H | -1.03156 | -0.23869 | -7.01576 |
| H | -2.47839 | 1.348685 | -8.42265 |
| H | -2.67857 | 1.243494 | -5.91292 |
| H | -3.13173 | 2.786206 | -6.61799 |
| H | 0.289483 | 4.375753 | -5.69489 |
| H | -1.21627 | 4.79537 | -6.49611 |
| H | -1.38927 | -0.36913 | -9.44325 |
| H | -0.17122 | 1.688537 | -9.76668 |
| H | 2.277008 | -0.4769 | -9.6517 |
| H | 3.569611 | -2.59526 | -9.48604 |
| H | 2.47481 | -4.68662 | -8.78159 |
| H | -1.25162 | -2.58713 | -8.37896 |
| H | -2.61507 | 3.259793 | -9.76992 |
| H | -2.57158 | 4.332191 | -8.35492 |
| H | -1.38276 | 4.528276 | -9.65975 |
| H | -0.2701 | -6.82239 | -7.72617 |
| H | 0.895404 | -6.40786 | -9.01364 |
| H | 1.291416 | -6.06732 | -7.30286 |
| H | -1.78847 | 3.294489 | -4.65693 |
| H | -0.54536 | 2.147075 | -5.10443 |

**Table S109.** Geometry (Å) for product (HBN anti) of the reaction granatanone + *m*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.369359 | 1.101145 | 0.252358 |
| C | 1.424749 | 0.260007 | 0.031293 |
| C | 2.157983 | -0.07263 | 1.302438 |
| C | 2.977424 | -1.15728 | -1.28613 |
| N | 3.198512 | -1.84866 | -0.00186 |
| C | 4.145584 | -2.94902 | -0.0595 |
| C | 3.463446 | -0.86068 | 1.055684 |
| C | 4.693967 | 0.027988 | 0.734908 |
| C | 4.231715 | -0.35827 | -1.73814 |
| C | 1.777887 | -0.24438 | -1.15811 |
| C | 4.631309 | 0.669676 | -0.66498 |
| H | 1.487584 | -0.66519 | 1.940161 |
| H | 2.363023 | 0.85603 | 1.85196 |
| H | 2.761454 | -1.93168 | -2.03514 |
| H | 4.156648 | -3.46137 | 0.910155 |
| H | 5.189296 | -2.67642 | -0.30241 |
| H | 3.810745 | -3.67071 | -0.81432 |
| H | 3.688862 | -1.41978 | 1.973109 |
| H | 4.806401 | 0.801636 | 1.506138 |
| H | 5.592637 | -0.60104 | 0.800576 |
| H | 4.028051 | 0.14556 | -2.69189 |
| H | 5.062874 | -1.05328 | -1.92347 |
| H | 1.242813 | 0.03259 | -2.06385 |
| H | 5.602657 | 1.117633 | -0.91172 |
| H | 3.900967 | 1.486631 | -0.66227 |
| H | -0.12037 | 1.240192 | -0.58576 |
| C | -2.45437 | 1.106108 | -2.22103 |
| O | -1.27314 | 1.370055 | -2.04933 |
| C | -3.39748 | 0.598851 | -1.20868 |
| C | -2.98719 | 0.333058 | 0.102392 |
| C | -4.73266 | 0.38731 | -1.59623 |
| C | -3.91521 | -0.14402 | 1.034646 |
| C | -5.64749 | -0.08615 | -0.66408 |
| C | -5.24916 | -0.35342 | 0.649228 |
| O | -3.4307 | -0.37463 | 2.284646 |
| C | -4.32005 | -0.85526 | 3.281514 |
| H | -2.8974 | 1.253062 | -3.22757 |
| H | -1.95795 | 0.485696 | 0.412978 |
| H | -5.03971 | 0.595855 | -2.61781 |
| H | -6.68234 | -0.25317 | -0.94911 |
| H | -5.97891 | -0.72338 | 1.360439 |
| H | -3.72118 | -0.9598 | 4.187487 |
| H | -4.74048 | -1.83266 | 3.010434 |
| H | -5.13836 | -0.14717 | 3.467492 |

**Table S110.** Geometry (Å) for reactant (syn) of the reaction granatanone + *m*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.978475 | 2.695275 | 0.441778 |
| C | 1.329695 | 1.47558 | 0.18544 |
| C | 1.553595 | 0.552955 | 1.354661 |
| C | 1.784157 | -0.42296 | -1.40578 |
| N | 1.447666 | -1.26346 | -0.24692 |
| C | 1.505734 | -2.69451 | -0.49263 |
| C | 2.165262 | -0.80466 | 0.952193 |
| C | 3.701592 | -0.77914 | 0.754752 |
| C | 3.303811 | -0.44859 | -1.7309 |
| C | 1.325414 | 0.99849 | -1.13492 |
| C | 4.129233 | -0.01075 | -0.50914 |
| H | 0.572418 | 0.382924 | 1.819581 |
| H | 2.165996 | 1.077166 | 2.098967 |
| H | 1.232784 | -0.82249 | -2.26815 |
| H | 1.134446 | -3.22356 | 0.392376 |
| H | 2.507576 | -3.09817 | -0.72783 |
| H | 0.841734 | -2.94062 | -1.32886 |
| H | 1.940721 | -1.51627 | 1.755849 |
| H | 4.18662 | -0.35712 | 1.644563 |
| H | 4.052011 | -1.81735 | 0.677102 |
| H | 3.515933 | 0.197962 | -2.59214 |
| H | 3.587846 | -1.46717 | -2.02793 |
| H | 1.57537 | 1.730946 | -1.89852 |
| H | 5.198289 | -0.16923 | -0.69798 |
| H | 4.004533 | 1.068286 | -0.35061 |
| H | 0.139456 | 2.912147 | -0.32147 |
| C | -0.69435 | 1.433874 | -1.50604 |
| O | -0.77434 | 2.677879 | -1.1593 |
| C | -1.53613 | 0.408677 | -0.82484 |
| C | -2.11877 | 0.694547 | 0.410644 |
| C | -1.79352 | -0.823 | -1.44829 |
| C | -2.94002 | -0.24903 | 1.039853 |
| C | -2.6152 | -1.75371 | -0.82362 |
| C | -3.19095 | -1.48152 | 0.42193 |
| O | -3.45541 | 0.129153 | 2.247135 |
| C | -4.31709 | -0.77132 | 2.92277 |
| H | -0.52061 | 1.215874 | -2.5698 |
| H | -1.95707 | 1.659 | 0.879927 |
| H | -1.36356 | -1.0368 | -2.42361 |
| H | -2.82433 | -2.70513 | -1.30587 |
| H | -3.83256 | -2.22051 | 0.888092 |
| H | -4.61143 | -0.26825 | 3.845737 |
| H | -3.80693 | -1.71204 | 3.170636 |
| H | -5.21468 | -0.995 | 2.330709 |

**Table S111.** Geometry (Å) for transition state (TS syn) of the reaction granatanone + *m*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.945482 | 2.490844 | 0.790521 |
| C | 1.199063 | 1.34407 | 0.434137 |
| C | 1.543424 | 0.278187 | 1.45476 |
| C | 1.733163 | -0.37828 | -1.4116 |
| N | 1.525198 | -1.35408 | -0.33141 |
| C | 1.690523 | -2.74329 | -0.72881 |
| C | 2.254334 | -0.96323 | 0.883898 |
| C | 3.76889 | -0.75234 | 0.647219 |
| C | 3.23301 | -0.18901 | -1.7553 |
| C | 1.073785 | 0.972247 | -1.03885 |
| C | 4.039834 | 0.21946 | -0.51247 |
| H | 0.574594 | -0.04325 | 1.86127 |
| H | 2.096603 | 0.748695 | 2.275272 |
| H | 1.2239 | -0.77042 | -2.30088 |
| H | 1.423336 | -3.39085 | 0.113659 |
| H | 2.707645 | -3.02338 | -1.05816 |
| H | 1.000232 | -2.96523 | -1.55031 |
| H | 2.132566 | -1.77617 | 1.609668 |
| H | 4.24465 | -0.39923 | 1.571247 |
| H | 4.22431 | -1.72464 | 0.41563 |
| H | 3.343258 | 0.554764 | -2.55472 |
| H | 3.629387 | -1.13311 | -2.1525 |
| H | 1.581997 | 1.774179 | -1.5895 |
| H | 5.11162 | 0.244093 | -0.74399 |
| H | 3.774958 | 1.243991 | -0.21449 |
| H | -0.333 | 2.879466 | -0.6268 |
| C | -0.42549 | 1.140472 | -1.49143 |
| O | -0.78225 | 2.508796 | -1.41217 |
| C | -1.42697 | 0.236994 | -0.77736 |
| C | -2.05352 | 0.660499 | 0.393185 |
| C | -1.75292 | -1.02025 | -1.30823 |
| C | -2.97638 | -0.16496 | 1.051011 |
| C | -2.67117 | -1.83722 | -0.65686 |
| C | -3.28857 | -1.42465 | 0.527917 |
| O | -3.52097 | 0.358634 | 2.190524 |
| C | -4.48717 | -0.40913 | 2.887194 |
| H | -0.44373 | 0.879374 | -2.55778 |
| H | -1.86068 | 1.645485 | 0.803882 |
| H | -1.29783 | -1.34996 | -2.23889 |
| H | -2.92532 | -2.80787 | -1.07535 |
| H | -4.00726 | -2.0734 | 1.015308 |
| H | -4.78924 | 0.195577 | 3.744502 |
| H | -4.06935 | -1.36003 | 3.245132 |
| H | -5.36684 | -0.61696 | 2.263181 |

**Table S112.** Geometry (Å) for product (HBO syn) of the reaction granatanone + *m*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -6.52345 | -1.29814 | -0.75746 |
| C | -5.88511 | -2.60294 | -1.0568 |
| C | -4.81174 | -2.86588 | 0.021687 |
| C | -3.87271 | -1.69271 | 0.262602 |
| C | -4.48 | -0.29285 | 0.158033 |
| C | -5.55225 | -0.18933 | -0.95566 |
| C | -4.95288 | -0.16771 | -2.37999 |
| C | -5.31845 | -2.67045 | -2.49295 |
| C | -5.0484 | 0.112891 | 1.564675 |
| O | -2.70903 | -1.85106 | 0.584808 |
| O | -6.1209 | -0.72827 | 1.949818 |
| C | -7.80646 | -1.09165 | -1.42994 |
| C | -5.41437 | 1.597163 | 1.610667 |
| C | -6.74092 | 2.010191 | 1.72652 |
| C | -7.04473 | 3.37699 | 1.754049 |
| C | -6.0399 | 4.331341 | 1.673766 |
| C | -4.70126 | 3.919943 | 1.572204 |
| C | -4.39177 | 2.557874 | 1.539969 |
| O | -3.77823 | 4.92622 | 1.51485 |
| C | -2.4064 | 4.57665 | 1.436451 |
| C | -4.33956 | -1.51984 | -2.78083 |
| H | -6.66299 | -3.36892 | -0.95287 |
| H | -4.21513 | -3.75496 | -0.20494 |
| H | -5.32039 | -3.0363 | 0.979611 |
| H | -3.65301 | 0.388501 | -0.06509 |
| H | -6.10276 | 0.745369 | -0.79993 |
| H | -4.20596 | 0.632956 | -2.44668 |
| H | -5.74785 | 0.094567 | -3.09102 |
| H | -4.83037 | -3.64113 | -2.64541 |
| H | -6.15167 | -2.62856 | -3.20702 |
| H | -4.23827 | -0.05529 | 2.286975 |
| H | -6.57212 | -1.00067 | 1.115357 |
| H | -8.2471 | -0.15402 | -1.07562 |
| H | -7.74518 | -1.04461 | -2.5283 |
| H | -8.485 | -1.90902 | -1.16373 |
| H | -7.52081 | 1.263487 | 1.825484 |
| H | -8.07932 | 3.697733 | 1.847072 |
| H | -6.25699 | 5.394589 | 1.699097 |
| H | -3.35922 | 2.228905 | 1.475636 |
| H | -2.18608 | 4.000694 | 0.527495 |
| H | -2.08517 | 3.998805 | 2.31327 |
| H | -1.85789 | 5.520031 | 1.406111 |
| H | -4.07355 | -1.51063 | -3.84479 |
| H | -3.39918 | -1.68316 | -2.23938 |

**Table S113.** Geometry (Å) for product (HBN syn) of the reaction granatanone + *m*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.39676 | 1.89838 | -0.39571 |
| C | -2.20046 | 0.814332 | -0.18828 |
| C | -3.32619 | 0.751543 | -1.18528 |
| C | -2.97807 | -1.28553 | 0.882315 |
| N | -3.58313 | -1.55478 | -0.43708 |
| C | -4.30545 | -2.81229 | -0.52915 |
| C | -4.34014 | -0.37521 | -0.88618 |
| C | -5.45524 | 0.022947 | 0.115081 |
| C | -4.05465 | -1.0094 | 1.969523 |
| C | -2.02305 | -0.11904 | 0.75698 |
| C | -4.94217 | 0.178169 | 1.559548 |
| H | -2.89073 | 0.597757 | -2.18235 |
| H | -3.82935 | 1.727383 | -1.21923 |
| H | -2.41208 | -2.18394 | 1.165169 |
| H | -4.61661 | -2.97 | -1.56901 |
| H | -5.20817 | -2.89901 | 0.103461 |
| H | -3.63198 | -3.63306 | -0.25425 |
| H | -4.8252 | -0.64271 | -1.83389 |
| H | -5.94439 | 0.947067 | -0.22029 |
| H | -6.22761 | -0.75825 | 0.091673 |
| H | -4.67039 | -1.90867 | 2.113068 |
| H | -3.56743 | -0.80786 | 2.93233 |
| H | -1.21256 | -0.03673 | 1.477779 |
| H | -5.79224 | 0.271988 | 2.247793 |
| H | -4.3637 | 1.104798 | 1.648412 |
| H | -0.62507 | 1.856907 | 0.213107 |
| C | 1.643867 | 1.027081 | -0.2137 |
| O | 1.10817 | 1.528299 | 0.77175 |
| C | 3.029697 | 0.562941 | -0.26084 |
| C | 3.866035 | 0.669959 | 0.860968 |
| C | 3.54189 | -0.0016 | -1.44358 |
| C | 5.181522 | 0.227391 | 0.814589 |
| C | 4.850767 | -0.44721 | -1.50484 |
| C | 5.680492 | -0.33554 | -0.37442 |
| O | 6.94376 | -0.79875 | -0.53123 |
| C | 7.844983 | -0.72586 | 0.568257 |
| H | 1.065013 | 0.90386 | -1.14975 |
| H | 3.462513 | 1.107191 | 1.769172 |
| H | 2.900003 | -0.08892 | -2.3173 |
| H | 5.810196 | 0.319326 | 1.692493 |
| H | 5.262922 | -0.886 | -2.40755 |
| H | 8.782202 | -1.15412 | 0.210323 |
| H | 7.480454 | -1.30889 | 1.422865 |
| H | 8.01373 | 0.3126 | 0.878752 |

**Table S114.** Geometry (Å) for reactant (anti) of the reaction granatanone + *p*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.82733 | 2.998863 | -0.19234 |
| C | -2.0311 | 1.720893 | -0.15815 |
| C | -3.17691 | 1.182893 | -0.98685 |
| C | -1.39617 | -0.6368 | 0.46647 |
| N | -2.10843 | -0.99455 | -0.77626 |
| C | -2.14688 | -2.42276 | -1.05783 |
| C | -3.42473 | -0.3298 | -0.81354 |
| C | -4.3062 | -0.68047 | 0.410776 |
| C | -2.18056 | -1.04795 | 1.74295 |
| C | -1.11979 | 0.850099 | 0.449266 |
| C | -3.58868 | -0.42988 | 1.748955 |
| H | -2.93954 | 1.39779 | -2.03809 |
| H | -4.07495 | 1.769084 | -0.75434 |
| H | -0.43949 | -1.17494 | 0.458953 |
| H | -2.59068 | -2.58084 | -2.04771 |
| H | -2.71611 | -3.03448 | -0.33566 |
| H | -1.12236 | -2.81112 | -1.08343 |
| H | -3.94147 | -0.68648 | -1.71319 |
| H | -5.24541 | -0.11395 | 0.364544 |
| H | -4.58454 | -1.74098 | 0.344848 |
| H | -2.25352 | -2.14356 | 1.780996 |
| H | -1.62034 | -0.74265 | 2.635831 |
| H | -0.51417 | 1.24771 | 1.258313 |
| H | -4.18156 | -0.84266 | 2.574724 |
| H | -3.51249 | 0.649149 | 1.935007 |
| H | -0.64008 | 3.085816 | -0.41434 |
| C | 0.452635 | 1.484603 | -0.93633 |
| O | 0.494539 | 2.751307 | -0.67424 |
| C | 1.575353 | 0.617561 | -0.53691 |
| C | 2.543757 | 1.063373 | 0.371738 |
| C | 1.716437 | -0.66538 | -1.09688 |
| C | 3.623832 | 0.257934 | 0.724221 |
| C | 2.787326 | -1.47753 | -0.75471 |
| C | 3.749989 | -1.02114 | 0.160367 |
| O | 4.765041 | -1.88817 | 0.428289 |
| C | 5.782152 | -1.48209 | 1.33264 |
| H | -0.09297 | 1.144558 | -1.82703 |
| H | 2.446015 | 2.061025 | 0.787899 |
| H | 0.976604 | -1.01806 | -1.81155 |
| H | 4.361492 | 0.632353 | 1.424755 |
| H | 2.909819 | -2.46633 | -1.18535 |
| H | 6.480927 | -2.31842 | 1.38977 |
| H | 5.375399 | -1.2799 | 2.331946 |
| H | 6.3107 | -0.59115 | 0.969848 |

**Table S115.** Geometry (Å) for transition state (TS anti) of the reaction granatanone + *p*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -2.20956 | 3.012233 | -0.03241 |
| C | -2.16875 | 1.802573 | -0.22848 |
| C | -3.2203 | 1.119314 | -1.08674 |
| C | -1.31103 | -0.51846 | 0.417683 |
| N | -2.04466 | -0.98086 | -0.77512 |
| C | -2.01077 | -2.42333 | -0.97887 |
| C | -3.39223 | -0.38879 | -0.82205 |
| C | -4.2332 | -0.67776 | 0.443643 |
| C | -2.06797 | -0.80642 | 1.737738 |
| C | -0.9795 | 0.981887 | 0.252378 |
| C | -3.49948 | -0.2456 | 1.723332 |
| H | -2.87564 | 1.24482 | -2.12316 |
| H | -4.15879 | 1.676039 | -0.99333 |
| H | -0.36485 | -1.06646 | 0.445984 |
| H | -2.48412 | -2.66161 | -1.93826 |
| H | -2.51558 | -3.02081 | -0.1991 |
| H | -0.96732 | -2.75318 | -1.02696 |
| H | -3.90894 | -0.8237 | -1.68641 |
| H | -5.20657 | -0.17677 | 0.364262 |
| H | -4.4421 | -1.75494 | 0.490129 |
| H | -2.11016 | -1.89422 | 1.8837 |
| H | -1.49977 | -0.4038 | 2.585708 |
| H | -0.66455 | 1.398136 | 1.21706 |
| H | -4.04951 | -0.58638 | 2.609114 |
| H | -3.47693 | 0.851116 | 1.791558 |
| H | -0.27217 | 3.172138 | -0.4373 |
| C | 0.20704 | 1.301178 | -0.7412 |
| O | 0.543836 | 2.675925 | -0.64066 |
| C | 1.450835 | 0.48345 | -0.45873 |
| C | 2.338496 | 0.854886 | 0.553385 |
| C | 1.740282 | -0.66868 | -1.20458 |
| C | 3.479499 | 0.09965 | 0.833083 |
| C | 2.869114 | -1.43459 | -0.93752 |
| C | 3.747529 | -1.05498 | 0.087206 |
| O | 4.830901 | -1.8669 | 0.271567 |
| C | 5.765586 | -1.51879 | 1.279659 |
| H | -0.13716 | 1.05809 | -1.75863 |
| H | 2.147668 | 1.765215 | 1.112899 |
| H | 1.072389 | -0.96441 | -2.01069 |
| H | 4.150926 | 0.423573 | 1.620284 |
| H | 3.099563 | -2.32337 | -1.51689 |
| H | 6.539315 | -2.28833 | 1.249434 |
| H | 5.302617 | -1.51004 | 2.275562 |
| H | 6.221817 | -0.5386 | 1.087424 |

**Table S116.** Geometry (Å) for product (HBO anti) of the reaction granatanone + *p*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -0.89264 | 2.502727 | -8.52617 |
| C | 0.126184 | 3.183994 | -7.69009 |
| C | 1.323939 | 2.221904 | -7.51958 |
| C | 0.929728 | 0.818672 | -7.07553 |
| C | -0.35021 | 0.25449 | -7.6906 |
| C | -1.45791 | 1.337082 | -7.79819 |
| C | -2.07865 | 1.728211 | -6.43745 |
| C | -0.44934 | 3.669321 | -6.34043 |
| C | -0.07688 | -0.39023 | -9.10019 |
| O | 1.608752 | 0.174199 | -6.29847 |
| O | 0.434726 | 0.556554 | -10.0203 |
| C | 0.848698 | -1.59008 | -9.03288 |
| C | 0.375903 | -2.81933 | -8.54911 |
| C | 1.205817 | -3.92832 | -8.46538 |
| C | 2.543824 | -3.83457 | -8.87637 |
| C | 3.027758 | -2.6206 | -9.37275 |
| C | 2.178132 | -1.51255 | -9.44552 |
| C | -1.89644 | 3.398865 | -9.09928 |
| O | 3.281036 | -4.98067 | -8.76113 |
| C | -1.10657 | 2.525191 | -5.54981 |
| C | 4.643123 | -4.93916 | -9.15007 |
| H | 0.470653 | 4.057105 | -8.25734 |
| H | 2.062431 | 2.61819 | -6.81587 |
| H | 1.810775 | 2.10437 | -8.49621 |
| H | -0.69148 | -0.55154 | -7.03227 |
| H | -2.25516 | 0.926974 | -8.43251 |
| H | -2.97672 | 2.332104 | -6.62428 |
| H | -2.41991 | 0.823047 | -5.92008 |
| H | -1.19044 | 4.456767 | -6.53252 |
| H | 0.349744 | 4.135571 | -5.75082 |
| H | -1.06656 | -0.74864 | -9.4412 |
| H | -0.01937 | 1.406018 | -9.80806 |
| H | -0.66272 | -2.91303 | -8.23639 |
| H | 0.84189 | -4.88069 | -8.09241 |
| H | 4.054923 | -2.52316 | -9.70584 |
| H | 2.551301 | -0.57642 | -9.84598 |
| H | -2.54138 | 2.827142 | -9.77502 |
| H | -2.54001 | 3.902512 | -8.36117 |
| H | -1.39029 | 4.171393 | -9.68781 |
| H | -0.33472 | 1.859999 | -5.14526 |
| H | -1.64121 | 2.928363 | -4.68124 |
| H | 5.038017 | -5.9409 | -8.96908 |
| H | 5.212328 | -4.21256 | -8.55486 |
| H | 4.753413 | -4.69417 | -10.2152 |

**Table S117.** Geometry (Å) for product (HBN anti) of the reaction granatanone + *p*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.569283 | 1.275976 | 0.547861 |
| C | 1.564252 | 0.40637 | 0.193931 |
| C | 2.319002 | -0.1071 | 1.390447 |
| C | 2.980546 | -0.94269 | -1.33201 |
| N | 3.203132 | -1.78363 | -0.1396 |
| C | 4.07892 | -2.92297 | -0.35491 |
| C | 3.565294 | -0.93479 | 1.006009 |
| C | 4.833811 | -0.08479 | 0.731956 |
| C | 4.26539 | -0.17145 | -1.74583 |
| C | 1.844894 | 0.017876 | -1.05659 |
| C | 4.758758 | 0.710814 | -0.58588 |
| H | 1.637008 | -0.72962 | 1.986446 |
| H | 2.598321 | 0.741308 | 2.029672 |
| H | 2.691773 | -1.61626 | -2.15058 |
| H | 4.087995 | -3.54246 | 0.550232 |
| H | 5.12943 | -2.68449 | -0.60365 |
| H | 3.678051 | -3.53358 | -1.17288 |
| H | 3.790025 | -1.60313 | 1.847305 |
| H | 5.019666 | 0.590659 | 1.577619 |
| H | 5.695313 | -0.76566 | 0.690253 |
| H | 4.061391 | 0.442317 | -2.63269 |
| H | 5.047246 | -0.88784 | -2.03439 |
| H | 1.297036 | 0.424668 | -1.90362 |
| H | 5.744539 | 1.132274 | -0.82166 |
| H | 4.075103 | 1.558701 | -0.46596 |
| H | 0.07057 | 1.547486 | -0.25397 |
| C | -2.25922 | 1.654635 | -1.85843 |
| O | -1.07531 | 1.908141 | -1.66336 |
| C | -3.17499 | 0.984925 | -0.93456 |
| C | -2.75885 | 0.5214 | 0.32555 |
| C | -4.51657 | 0.798534 | -1.32116 |
| C | -3.65577 | -0.10814 | 1.179242 |
| C | -5.41878 | 0.173765 | -0.47902 |
| C | -4.99294 | -0.28422 | 0.781126 |
| O | -5.94504 | -0.88169 | 1.536481 |
| C | -5.59259 | -1.37159 | 2.82642 |
| H | -2.71668 | 1.951673 | -2.82509 |
| H | -1.7257 | 0.652797 | 0.633847 |
| H | -4.84608 | 1.152838 | -2.29554 |
| H | -3.3132 | -0.45886 | 2.14554 |
| H | -6.45552 | 0.023742 | -0.76183 |
| H | -6.50733 | -1.79925 | 3.23909 |
| H | -4.82259 | -2.14995 | 2.761501 |
| H | -5.24119 | -0.56266 | 3.478425 |

**Table S118.** Geometry (Å) for reactant (syn) of the reaction granatanone + *p*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.091432 | 2.838813 | 0.474957 |
| C | 1.417001 | 1.616741 | 0.202217 |
| C | 1.634204 | 0.674859 | 1.359222 |
| C | 1.816782 | -0.27886 | -1.41079 |
| N | 1.48115 | -1.12764 | -0.25719 |
| C | 1.523212 | -2.55711 | -0.51683 |
| C | 2.218434 | -0.68905 | 0.938211 |
| C | 3.752723 | -0.6856 | 0.723262 |
| C | 3.331826 | -0.32577 | -1.75531 |
| C | 1.384642 | 1.14599 | -1.1187 |
| C | 4.178615 | 0.086493 | -0.53922 |
| H | 0.653654 | 0.516915 | 1.829845 |
| H | 2.262499 | 1.178057 | 2.104659 |
| H | 1.249202 | -0.65999 | -2.27147 |
| H | 1.144939 | -3.09072 | 0.362465 |
| H | 2.520242 | -2.96993 | -0.75584 |
| H | 0.858009 | -2.78845 | -1.35656 |
| H | 1.99208 | -1.4044 | 1.738198 |
| H | 4.253612 | -0.27759 | 1.610869 |
| H | 4.087128 | -1.72819 | 0.634387 |
| H | 3.543492 | 0.32676 | -2.61206 |
| H | 3.595973 | -1.34547 | -2.06679 |
| H | 1.608976 | 1.878688 | -1.88972 |
| H | 5.242562 | -0.08842 | -0.74176 |
| H | 4.073484 | 1.165793 | -0.36988 |
| H | 0.222581 | 3.073394 | -0.28876 |
| C | -0.66277 | 1.609898 | -1.4142 |
| O | -0.67809 | 2.870597 | -1.10564 |
| C | -1.50732 | 0.649277 | -0.6651 |
| C | -2.07798 | 1.01097 | 0.561031 |
| C | -1.79802 | -0.62134 | -1.1903 |
| C | -2.90429 | 0.131674 | 1.260612 |
| C | -2.62056 | -1.50475 | -0.50986 |
| C | -3.17758 | -1.13468 | 0.725415 |
| O | -3.97484 | -2.07032 | 1.315027 |
| C | -4.5866 | -1.75051 | 2.555169 |
| H | -0.52951 | 1.354289 | -2.47434 |
| H | -1.88165 | 2.003423 | 0.954346 |
| H | -1.38144 | -0.91157 | -2.15225 |
| H | -3.33767 | 0.443466 | 2.20415 |
| H | -2.85797 | -2.48479 | -0.91176 |
| H | -5.16994 | -2.62925 | 2.835944 |
| H | -3.83924 | -1.54735 | 3.333389 |
| H | -5.25568 | -0.88498 | 2.463312 |

**Table S119.** Geometry (Å) for transition state (TS syn) of the reaction granatanone + *p*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.079823 | 2.64137 | 0.808931 |
| C | 1.29308 | 1.488627 | 0.445214 |
| C | 1.614232 | 0.404822 | 1.453995 |
| C | 1.761745 | -0.23432 | -1.41693 |
| N | 1.557511 | -1.21863 | -0.34332 |
| C | 1.71746 | -2.6056 | -0.75266 |
| C | 2.302714 | -0.84218 | 0.867445 |
| C | 3.816975 | -0.64611 | 0.615586 |
| C | 3.259328 | -0.06064 | -1.77852 |
| C | 1.126034 | 1.121911 | -1.02343 |
| C | 4.087036 | 0.32808 | -0.54277 |
| H | 0.638341 | 0.096032 | 1.853863 |
| H | 2.176266 | 0.852794 | 2.280918 |
| H | 1.235817 | -0.6107 | -2.30357 |
| H | 1.440351 | -3.25933 | 0.081765 |
| H | 2.73488 | -2.88871 | -1.07787 |
| H | 1.033161 | -2.81699 | -1.58205 |
| H | 2.179125 | -1.65787 | 1.589828 |
| H | 4.305727 | -0.30161 | 1.536097 |
| H | 4.260421 | -1.62191 | 0.376064 |
| H | 3.368861 | 0.68827 | -2.57315 |
| H | 3.638736 | -1.00621 | -2.18838 |
| H | 1.626395 | 1.916618 | -1.59099 |
| H | 5.156156 | 0.338081 | -0.7874 |
| H | 3.841446 | 1.354849 | -0.23622 |
| H | -0.21347 | 3.069549 | -0.60748 |
| C | -0.38755 | 1.312911 | -1.41982 |
| O | -0.69595 | 2.696456 | -1.37159 |
| C | -1.38497 | 0.473653 | -0.6294 |
| C | -2.03422 | 0.990253 | 0.493449 |
| C | -1.70209 | -0.83467 | -1.02469 |
| C | -2.9509 | 0.228596 | 1.225156 |
| C | -2.61279 | -1.60541 | -0.31474 |
| C | -3.24188 | -1.07883 | 0.822895 |
| O | -4.12312 | -1.91177 | 1.454535 |
| C | -4.80845 | -1.41863 | 2.593414 |
| H | -0.45841 | 1.019556 | -2.47585 |
| H | -1.84219 | 2.014587 | 0.795811 |
| H | -1.23669 | -1.25584 | -1.91299 |
| H | -3.43744 | 0.670249 | 2.087499 |
| H | -2.86325 | -2.61493 | -0.62614 |
| H | -5.45265 | -2.23242 | 2.932033 |
| H | -4.11287 | -1.14854 | 3.399486 |
| H | -5.42735 | -0.54543 | 2.347032 |

**Table S120.** Geometry (Å) for product (HBO syn) of the reaction granatanone + *p*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| N | -5.71437 | -1.23901 | -0.69288 |
| C | -4.97812 | -2.52662 | -0.69158 |
| C | -4.53947 | -2.82354 | 0.758779 |
| C | -3.86136 | -1.65266 | 1.4564 |
| C | -4.38471 | -0.25533 | 1.120006 |
| C | -4.79364 | -0.11663 | -0.36756 |
| C | -3.58748 | -0.03714 | -1.33102 |
| C | -3.79517 | -2.53427 | -1.68534 |
| C | -5.56959 | 0.084822 | 2.093084 |
| O | -2.98829 | -1.81514 | 2.289635 |
| O | -6.66445 | -0.79498 | 1.89819 |
| C | -6.52805 | -1.0153 | -1.88807 |
| C | -5.97477 | 1.555371 | 1.996207 |
| C | -7.23653 | 1.933903 | 1.518614 |
| C | -7.60097 | 3.273167 | 1.43113 |
| C | -6.70725 | 4.275647 | 1.830175 |
| C | -5.44717 | 3.915975 | 2.324139 |
| C | -5.09797 | 2.56587 | 2.402133 |
| C | -2.82482 | -1.36845 | -1.43145 |
| H | -5.69263 | -3.30167 | -0.99412 |
| H | -3.88117 | -3.69608 | 0.814391 |
| H | -5.43637 | -3.04059 | 1.353459 |
| H | -3.5729 | 0.444039 | 1.34442 |
| H | -5.37357 | 0.808121 | -0.46601 |
| H | -2.91858 | 0.770427 | -1.00873 |
| H | -3.95373 | 0.246759 | -2.32673 |
| H | -3.27133 | -3.49593 | -1.61882 |
| H | -4.18795 | -2.4667 | -2.70866 |
| H | -5.1961 | -0.09865 | 3.109415 |
| H | -6.65762 | -1.03306 | 0.940373 |
| H | -7.10615 | -0.09448 | -1.75799 |
| H | -5.95441 | -0.92628 | -2.82387 |
| H | -7.23228 | -1.84636 | -2.00163 |
| H | -7.94324 | 1.159031 | 1.240471 |
| H | -8.5802 | 3.567521 | 1.065546 |
| H | -4.73985 | 4.668383 | 2.65457 |
| H | -4.11936 | 2.304943 | 2.801166 |
| H | -2.08173 | -1.31566 | -2.23638 |
| H | -2.25612 | -1.54679 | -0.51008 |
| O | -7.15739 | 5.560628 | 1.706944 |
| C | -6.30155 | 6.612178 | 2.120981 |
| H | -6.85378 | 7.536756 | 1.942015 |
| H | -5.36969 | 6.629483 | 1.539617 |
| H | -6.05648 | 6.538129 | 3.189013 |

**Table S121.** Geometry (Å) for product (HBN syn) of the reaction granatanone + *p*-OMe-$C_6H_4CHO$ in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.23466 | 2.829648 | 0.065777 |
| C | -1.82018 | 1.639064 | 0.38377 |
| C | -3.00726 | 1.347829 | -0.49557 |
| C | -2.10021 | -0.53527 | 1.549849 |
| N | -2.7475 | -0.94777 | 0.28735 |
| C | -3.22372 | -2.32213 | 0.273269 |
| C | -3.75533 | 0.054876 | -0.10113 |
| C | -4.83702 | 0.257856 | 0.989461 |
| C | -3.11477 | -0.43428 | 2.722793 |
| C | -1.39289 | 0.782912 | 1.324872 |
| C | -4.2422 | 0.553347 | 2.378868 |
| C | 1.584461 | 1.517973 | -0.1011 |
| O | 1.504 | 2.496208 | 0.638211 |
| C | 2.80591 | 0.717851 | -0.28473 |
| C | 4.006461 | 1.244544 | 0.170872 |
| C | 2.774768 | -0.55592 | -0.95082 |
| C | 5.222207 | 0.568864 | -0.03794 |
| C | 4.023372 | -1.23127 | -1.16829 |
| C | 5.226844 | -0.63884 | -0.70367 |
| C | 1.579897 | -1.20056 | -1.37766 |
| C | 1.62699 | -2.42204 | -2.0143 |
| C | 2.86099 | -3.07101 | -2.25303 |
| C | 4.032784 | -2.48811 | -1.8313 |
| H | -0.35348 | 2.895139 | 0.496813 |
| H | -2.64969 | 1.265796 | -1.53111 |
| H | -3.68632 | 2.210985 | -0.47697 |
| H | -1.35444 | -1.30403 | 1.79427 |
| H | -3.59183 | -2.56197 | -0.73155 |
| H | -4.03262 | -2.5595 | 0.987733 |
| H | -2.38508 | -2.99408 | 0.491661 |
| H | -4.25712 | -0.32258 | -1.00129 |
| H | -5.52315 | 1.059526 | 0.686201 |
| H | -5.44198 | -0.65767 | 1.045268 |
| H | -3.53495 | -1.42845 | 2.930159 |
| H | -2.59418 | -0.11873 | 3.636014 |
| H | -0.55758 | 1.03555 | 1.973368 |
| H | -5.03193 | 0.507752 | 3.139617 |
| H | -3.84444 | 1.574589 | 2.401184 |
| H | 0.702152 | 1.215762 | -0.68456 |
| H | 3.984325 | 2.20476 | 0.676986 |
| H | 6.151929 | 1.004458 | 0.316072 |
| H | 6.163199 | -1.16335 | -0.87972 |
| H | 0.611409 | -0.75354 | -1.17898 |
| H | 0.701486 | -2.89618 | -2.32884 |
| H | 2.8774 | -4.03276 | -2.7579 |
| H | 4.986846 | -2.98429 | -1.99223 |

**Table S122.** Geometry (Å) for reactant (anti) of the reaction granatanone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.35495 | 3.317978 | 0.207758 |
| C | -1.6684 | 2.065336 | 0.297374 |
| C | -2.96026 | 1.635687 | -0.35854 |
| C | -1.21201 | -0.32629 | 0.943855 |
| N | -2.13496 | -0.64229 | -0.16554 |
| C | -2.38142 | -2.06688 | -0.35002 |
| C | -3.35654 | 0.176929 | -0.05893 |
| C | -4.08555 | -0.0075 | 1.294994 |
| C | -1.84821 | -0.58794 | 2.337284 |
| C | -0.77428 | 1.11964 | 0.820748 |
| C | -3.15676 | 0.201909 | 2.504434 |
| C | 0.746545 | 1.609491 | -0.65355 |
| O | 0.901665 | 2.870555 | -0.40971 |
| C | 1.842588 | 0.673999 | -0.29368 |
| C | 2.834874 | 1.135878 | 0.557863 |
| C | 1.940145 | -0.64755 | -0.85218 |
| C | 3.943122 | 0.336002 | 0.897513 |
| C | 3.088515 | -1.44541 | -0.51917 |
| C | 4.07012 | -0.92784 | 0.365604 |
| C | 0.970873 | -1.20955 | -1.73081 |
| C | 1.137535 | -2.47089 | -2.26168 |
| C | 2.276069 | -3.24692 | -1.94154 |
| C | 3.22472 | -2.74302 | -1.08329 |
| H | -0.20194 | 3.304645 | -0.07583 |
| H | -2.83123 | 1.765502 | -1.44218 |
| H | -3.74637 | 2.340484 | -0.06034 |
| H | -0.33685 | -0.97766 | 0.834183 |
| H | -2.99558 | -2.20855 | -1.24702 |
| H | -2.89521 | -2.56964 | 0.487834 |
| H | -1.42563 | -2.5763 | -0.51178 |
| H | -4.03666 | -0.15156 | -0.85454 |
| H | -4.94654 | 0.671616 | 1.347116 |
| H | -4.49635 | -1.02552 | 1.3292 |
| H | -2.04493 | -1.66316 | 2.445284 |
| H | -1.13291 | -0.32284 | 3.126055 |
| H | -0.069 | 1.472533 | 1.567031 |
| H | -3.66891 | -0.10166 | 3.425897 |
| H | -2.92844 | 1.269452 | 2.618756 |
| H | 0.14115 | 1.329064 | -1.52224 |
| H | 2.748427 | 2.147382 | 0.940382 |
| H | 4.702781 | 0.727839 | 1.568233 |
| H | 4.929493 | -1.54755 | 0.610641 |

| | | | |
|---|---|---|---|
| H | 0.065677 | -0.65914 | -1.961 |
| H | 0.383216 | -2.87443 | -2.93193 |
| H | 2.394142 | -4.2385 | -2.36977 |
| H | 4.100844 | -3.33187 | -0.82185 |

**Table S123.** Geometry (Å) for transition state (TS anti) of the reaction granatanone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.67065 | 3.393398 | 0.343962 |
| C | -1.79571 | 2.178481 | 0.23233 |
| C | -3.02662 | 1.588862 | -0.43151 |
| C | -1.12418 | -0.20205 | 0.908632 |
| N | -2.07023 | -0.61975 | -0.14529 |
| C | -2.2425 | -2.06457 | -0.25281 |
| C | -3.33349 | 0.131842 | -0.04209 |
| C | -4.00899 | 0.00948 | 1.343651 |
| C | -1.71448 | -0.35002 | 2.333267 |
| C | -0.65588 | 1.248099 | 0.636347 |
| C | -3.05089 | 0.394285 | 2.482297 |
| C | 0.481384 | 1.414341 | -0.44731 |
| O | 0.941835 | 2.757251 | -0.43717 |
| C | 1.682099 | 0.513708 | -0.18041 |
| C | 2.621935 | 0.942259 | 0.738023 |
| C | 1.879093 | -0.73565 | -0.85821 |
| C | 3.77122 | 0.178075 | 1.03622 |
| C | 3.060002 | -1.50218 | -0.56158 |
| C | 3.98777 | -1.01988 | 0.397718 |
| C | 0.971879 | -1.26482 | -1.82216 |
| C | 1.219868 | -2.46181 | -2.45859 |
| C | 2.386957 | -3.20627 | -2.1677 |
| C | 3.281343 | -2.73329 | -1.23657 |
| H | 0.186077 | 3.331555 | -0.20552 |
| H | -2.81583 | 1.613989 | -1.51028 |
| H | -3.87101 | 2.263823 | -0.25574 |
| H | -0.2524 | -0.85818 | 0.835783 |
| H | -2.89124 | -2.28312 | -1.10877 |
| H | -2.68499 | -2.54975 | 0.634469 |
| H | -1.26896 | -2.52758 | -0.44167 |
| H | -4.01716 | -0.27835 | -0.7953 |
| H | -4.91528 | 0.62812 | 1.369824 |
| H | -4.33859 | -1.02867 | 1.482969 |
| H | -1.87061 | -1.41735 | 2.53857 |
| H | -0.98579 | 0.002455 | 3.073797 |
| H | -0.22043 | 1.663547 | 1.553259 |
| H | -3.5068 | 0.167585 | 3.453792 |

| | | | |
|---|---|---|---|
| H | -2.88036 | 1.480202 | 2.480254 |
| H | 0.055959 | 1.178225 | -1.4313 |
| H | 2.480108 | 1.908368 | 1.210259 |
| H | 4.487367 | 0.55031 | 1.763947 |
| H | 4.874038 | -1.61252 | 0.612217 |
| H | 0.052629 | -0.73381 | -2.04249 |
| H | 0.510887 | -2.83766 | -3.19173 |
| H | 2.571265 | -4.14778 | -2.67797 |
| H | 4.180667 | -3.29757 | -1.00027 |

**Table S124.** Geometry (Å) for product (HBO anti) of the reaction granatanone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -0.74461 | 3.886766 | 0.068106 |
| C | -0.96281 | 2.704035 | -0.11345 |
| C | -2.24259 | 2.213675 | -0.77966 |
| C | -0.64259 | 0.354781 | 0.833545 |
| N | -1.66109 | -0.08176 | -0.15704 |
| C | -2.07957 | -1.47598 | -0.0114 |
| C | -2.78286 | 0.888761 | -0.1986 |
| C | -3.46057 | 1.068393 | 1.178075 |
| C | -1.22946 | 0.535505 | 2.252197 |
| C | 0.052233 | 1.628913 | 0.281529 |
| C | 0.985094 | 1.260451 | -0.93179 |
| O | 0.231372 | 0.776013 | -2.02972 |
| C | 1.856847 | 2.422033 | -1.38197 |
| C | 1.542574 | 3.099113 | -2.54241 |
| C | 3.003687 | 2.825587 | -0.61905 |
| C | 2.312293 | 4.197856 | -2.98915 |
| C | 3.776716 | 3.94795 | -1.07333 |
| C | 3.401883 | 4.619202 | -2.26737 |
| C | 3.43281 | 2.166769 | 0.568297 |
| C | 4.539184 | 2.593701 | 1.270295 |
| C | 5.285178 | 3.708914 | 0.82565 |
| C | 4.909318 | 4.364627 | -0.32397 |
| C | -2.4533 | 1.466809 | 2.270156 |
| H | -1.98837 | 2.04674 | -1.83423 |
| H | -2.99027 | 3.011339 | -0.73218 |
| H | 0.11398 | -0.44034 | 0.876136 |
| H | -2.76277 | -1.73019 | -0.82864 |
| H | -2.58594 | -1.70738 | 0.938753 |
| H | -1.19974 | -2.12325 | -0.0916 |
| H | -3.52299 | 0.487401 | -0.90136 |
| H | -3.9499 | 0.125985 | 1.457963 |
| H | -4.25803 | 1.817194 | 1.095514 |

| | | | |
|---|---|---|---|
| H | -1.51849 | -0.45116 | 2.638569 |
| H | -0.44764 | 0.911324 | 2.923726 |
| H | 0.684279 | 2.067395 | 1.059776 |
| H | 1.644078 | 0.455608 | -0.56179 |
| H | -0.50109 | 0.248092 | -1.63228 |
| H | 0.691125 | 2.765593 | -3.12405 |
| H | 2.031318 | 4.707258 | -3.90708 |
| H | 3.996093 | 5.467245 | -2.59957 |
| H | 2.888885 | 1.30084 | 0.930863 |
| H | 4.842536 | 2.067303 | 2.17155 |
| H | 6.153775 | 4.040197 | 1.38829 |
| H | 5.478868 | 5.219646 | -0.68136 |
| H | -2.13645 | 2.506789 | 2.127419 |
| H | -2.93443 | 1.43176 | 3.255029 |

**Table S125.** Geometry (Å) for product (HBN anti) of the reaction granatanone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.663955 | 1.487793 | 1.04793 |
| C | 1.809913 | 0.756376 | 0.890122 |
| C | 2.497142 | 0.49592 | 2.203236 |
| C | 3.560803 | -0.51057 | -0.32836 |
| N | 3.764144 | -1.17984 | 0.970832 |
| C | 4.802259 | -2.19655 | 0.976231 |
| C | 3.879933 | -0.17246 | 2.036685 |
| C | 5.041756 | 0.823214 | 1.783173 |
| C | 4.764094 | 0.39775 | -0.70844 |
| C | 2.278465 | 0.290907 | -0.27493 |
| C | 5.000595 | 1.458574 | 0.38007 |
| C | -1.89706 | 0.990288 | -1.70744 |
| O | -0.86197 | 1.541077 | -1.3484 |
| C | -2.74867 | 0.132994 | -0.86473 |
| C | -2.34683 | -0.10599 | 0.444893 |
| C | -3.9637 | -0.45655 | -1.36863 |
| C | -3.10676 | -0.9207 | 1.302692 |
| C | -4.72818 | -1.28779 | -0.48028 |
| C | -4.27167 | -1.49831 | 0.846767 |
| C | -4.46112 | -0.27105 | -2.6885 |
| C | -5.632 | -0.86948 | -3.10131 |
| C | -6.37816 | -1.68779 | -2.22269 |
| C | -5.93116 | -1.88933 | -0.93841 |
| H | 0.212967 | 1.581094 | 0.182025 |
| H | 1.848146 | -0.15204 | 2.808661 |
| H | 2.586589 | 1.441514 | 2.754953 |
| H | 3.459003 | -1.30101 | -1.08469 |

| | | | |
|---|---|---|---|
| H | 4.79479 | -2.70878 | 1.946037 |
| H | 5.832753 | -1.83672 | 0.799651 |
| H | 4.57785 | -2.94188 | 0.203741 |
| H | 4.100701 | -0.70964 | 2.96811 |
| H | 5.040131 | 1.601803 | 2.557485 |
| H | 5.988234 | 0.277436 | 1.900876 |
| H | 4.576134 | 0.879077 | -1.67693 |
| H | 5.66458 | -0.21952 | -0.8356 |
| H | 1.772757 | 0.517752 | -1.21097 |
| H | 5.937917 | 1.996856 | 0.188559 |
| H | 4.197174 | 2.202368 | 0.33541 |
| H | -2.22529 | 1.143527 | -2.74993 |
| H | -1.42743 | 0.34283 | 0.807112 |
| H | -2.76883 | -1.09162 | 2.320298 |
| H | -4.86436 | -2.13102 | 1.503438 |
| H | -3.92237 | 0.34995 | -3.39485 |
| H | -5.98583 | -0.70897 | -4.11601 |
| H | -7.29885 | -2.15185 | -2.56438 |
| H | -6.493 | -2.51487 | -0.24907 |

**Table S126.** Geometry (Å) for reactant (syn) of the reaction granatanone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | -1.35495 | 3.317978 | 0.207758 |
| C | -1.6684 | 2.065336 | 0.297374 |
| C | -2.96026 | 1.635687 | -0.35854 |
| C | -1.21201 | -0.32629 | 0.943855 |
| N | -2.13496 | -0.64229 | -0.16554 |
| C | -2.38142 | -2.06688 | -0.35002 |
| C | -3.35654 | 0.176929 | -0.05893 |
| C | -4.08555 | -0.0075 | 1.294994 |
| C | -1.84821 | -0.58794 | 2.337284 |
| C | -0.77428 | 1.11964 | 0.820748 |
| C | -3.15676 | 0.201909 | 2.504434 |
| C | 0.746545 | 1.609491 | -0.65355 |
| O | 0.901665 | 2.870555 | -0.40971 |
| C | 1.842588 | 0.673999 | -0.29368 |
| C | 2.834874 | 1.135878 | 0.557863 |
| C | 1.940145 | -0.64755 | -0.85218 |
| C | 3.943122 | 0.336002 | 0.897513 |
| C | 3.088515 | -1.44541 | -0.51917 |
| C | 4.07012 | -0.92784 | 0.365604 |
| C | 0.970873 | -1.20955 | -1.73081 |
| C | 1.137535 | -2.47089 | -2.26168 |
| C | 2.276069 | -3.24692 | -1.94154 |
| C | 3.22472 | -2.74302 | -1.08329 |
| H | -0.20194 | 3.304645 | -0.07583 |
| H | -2.83123 | 1.765502 | -1.44218 |
| H | -3.74637 | 2.340484 | -0.06034 |
| H | -0.33685 | -0.97766 | 0.834183 |
| H | -2.99558 | -2.20855 | -1.24702 |
| H | -2.89521 | -2.56964 | 0.487834 |
| H | -1.42563 | -2.5763 | -0.51178 |
| H | -4.03666 | -0.15156 | -0.85454 |
| H | -4.94654 | 0.671616 | 1.347116 |
| H | -4.49635 | -1.02552 | 1.3292 |
| H | -2.04493 | -1.66316 | 2.445284 |
| H | -1.13291 | -0.32284 | 3.126055 |
| H | -0.069 | 1.472533 | 1.567031 |
| H | -3.66891 | -0.10166 | 3.425897 |
| H | -2.92844 | 1.269452 | 2.618756 |
| H | 0.14115 | 1.329064 | -1.52224 |
| H | 2.748427 | 2.147382 | 0.940382 |
| H | 4.702781 | 0.727839 | 1.568233 |
| H | 4.929493 | -1.54755 | 0.610641 |
| H | 0.065677 | -0.65914 | -1.961 |
| H | 0.383216 | -2.87443 | -2.93193 |
| H | 2.394142 | -4.2385 | -2.36977 |

| | | | |
|---|---|---|---|
| H | 4.100844 | -3.33187 | -0.82185 |

**Table S127.** Geometry (Å) for transition state (TS syn) of the reaction granatanone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 0.939532 | 2.86654 | 1.532511 |
| C | 1.184146 | 1.735699 | 1.121401 |
| C | 1.51425 | 0.619839 | 2.091784 |
| C | 1.739254 | 0.112027 | -0.80046 |
| N | 1.514355 | -0.91895 | 0.223906 |
| C | 1.688162 | -2.28705 | -0.24351 |
| C | 2.228017 | -0.59371 | 1.46743 |
| C | 3.745667 | -0.37123 | 1.265191 |
| C | 3.244227 | 0.326678 | -1.10636 |
| C | 1.063454 | 1.437405 | -0.36974 |
| C | 4.030791 | 0.667378 | 0.168923 |
| C | -0.43675 | 1.629342 | -0.82063 |
| O | -0.79294 | 2.992402 | -0.65117 |
| C | -1.44807 | 0.692699 | -0.1538 |
| C | -1.99809 | 1.069713 | 1.05756 |
| C | -1.87063 | -0.54106 | -0.75486 |
| C | -2.91444 | 0.24805 | 1.750992 |
| C | -2.80278 | -1.37549 | -0.0443 |
| C | -3.29984 | -0.9579 | 1.217691 |
| C | -1.44772 | -0.98471 | -2.04175 |
| C | -1.88828 | -2.1748 | -2.57916 |
| C | -2.78079 | -3.00222 | -1.85933 |
| C | -3.22772 | -2.60248 | -0.62198 |
| H | -0.3231 | 3.320668 | 0.140967 |
| H | 0.540624 | 0.281157 | 2.47195 |
| H | 2.060121 | 1.047976 | 2.939898 |
| H | 1.25396 | -0.23787 | -1.71756 |
| H | 1.403289 | -2.97683 | 0.55869 |
| H | 2.713532 | -2.54868 | -0.56206 |
| H | 1.014545 | -2.46353 | -1.0883 |
| H | 2.094511 | -1.44258 | 2.148457 |
| H | 4.207428 | -0.07282 | 2.215248 |
| H | 4.205577 | -1.32805 | 0.983671 |
| H | 3.36446 | 1.112941 | -1.86259 |
| H | 3.650027 | -0.59358 | -1.54721 |
| H | 1.571187 | 2.268371 | -0.87621 |
| H | 5.105752 | 0.709484 | -0.04457 |
| H | 3.756772 | 1.672045 | 0.521593 |
| H | -0.44669 | 1.458304 | -1.90159 |
| H | -1.72938 | 2.030752 | 1.482571 |

| | | | |
|---|---|---|---|
| H | -3.31475 | 0.581431 | 2.704785 |
| H | -4.00306 | -1.60019 | 1.742621 |
| H | -0.7784 | -0.36893 | -2.63181 |
| H | -1.55358 | -2.47539 | -3.56861 |
| H | -3.11886 | -3.9407 | -2.29017 |
| H | -3.92718 | -3.22025 | -0.06326 |

**Table S128.** Geometry (Å) for product (HBO syn) of the reaction granatanone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| Atom | x | y | z |
|---|---|---|---|
| O | 1.13534 | 2.684214 | 1.015835 |
| C | 1.128324 | 1.542663 | 0.589575 |
| C | 1.270077 | 0.3358 | 1.505163 |
| C | 1.616305 | -0.00044 | -1.40134 |
| N | 1.322878 | -1.11694 | -0.46408 |
| C | 1.575882 | -2.44645 | -1.02007 |
| C | 1.968785 | -0.87425 | 0.848296 |
| C | 3.498891 | -0.68989 | 0.731765 |
| C | 3.131582 | 0.226216 | -1.59986 |
| C | 0.877314 | 1.260736 | -0.89052 |
| C | -0.6786 | 1.176372 | -1.11072 |
| O | -1.21926 | 0.021559 | -0.49096 |
| C | -1.04266 | 1.27325 | -2.59164 |
| C | -1.49844 | 0.154535 | -3.25872 |
| C | -0.92925 | 2.518283 | -3.29915 |
| C | -1.82581 | 0.193518 | -4.63472 |
| C | -1.2596 | 2.551825 | -4.69683 |
| C | -1.70087 | 1.364679 | -5.3414 |
| C | -0.52144 | 3.736513 | -2.6818 |
| C | -0.43159 | 4.907692 | -3.40311 |
| C | -0.7423 | 4.93048 | -4.78206 |
| C | -1.1497 | 3.775708 | -5.40957 |
| C | 3.871578 | 0.420233 | -0.26551 |
| H | 0.24381 | 0.041969 | 1.763296 |
| H | 1.771188 | 0.646105 | 2.427327 |
| H | 1.178282 | -0.27395 | -2.3683 |
| H | 1.246635 | -3.20305 | -0.29997 |
| H | 2.630038 | -2.64816 | -1.26676 |
| H | 0.986096 | -2.56828 | -1.93456 |
| H | 1.769898 | -1.75626 | 1.46877 |
| H | 3.915401 | -0.47531 | 1.723818 |
| H | 3.947901 | -1.63807 | 0.407274 |
| H | 3.551078 | -0.64215 | -2.12518 |
| H | 3.286905 | 1.088634 | -2.25951 |
| H | 1.237867 | 2.133925 | -1.44057 |

| | | | |
|---|---|---|---|
| H | -1.11684 | 2.040667 | -0.59565 |
| H | -0.49042 | -0.64239 | -0.43886 |
| H | -1.63199 | -0.76299 | -2.69538 |
| H | -2.18053 | -0.70894 | -5.1258 |
| H | -1.94835 | 1.405073 | -6.39964 |
| H | -0.27997 | 3.756847 | -1.62402 |
| H | -0.12188 | 5.822723 | -2.90545 |
| H | -0.66495 | 5.859897 | -5.33975 |
| H | -1.40056 | 3.782788 | -6.46797 |
| H | 3.629136 | 1.403093 | 0.158388 |
| H | 4.955308 | 0.426033 | -0.43346 |

**Table S129.** Geometry (Å) for product (HBN syn) of the reaction granatanone + α-Naphth-CHO in the gas phase calculated at the B3LYP/6-31g(d) level of theory.

| **GasTropinone + p-$NO_2$-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
|---|---|---|---|---|
| | 25 °C | | | |
| $\varepsilon_0$ | -992.69788 | -992.67319 | -992.71842 | -992.72231 |
| $G_{corr}$ | 0.26632 | 0.267474 | 0.273498 | 0.274787 |
| $G(\varepsilon_0 + G_{corr})$ | -992.43156 | -992.4057116 | -992.44492 | -992.44753 |
| **$H_2O$ Tropinone + p-$NO_2$-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -992.69788 | -992.67319 | -992.71842 | -992.72231 |
| $G_{corr}$ | 0.26632 | 0.267474 | 0.273498 | 0.274787 |
| $G(\varepsilon_0 + G_{corr})$ | -992.43156 | -992.4057116 | -992.44492 | -992.44753 |
| **Gas Tropinone + p-$NO_2$-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -992.69788 | -992.67088 | -992.71491 | -992.72346 |
| $G_{corr}$ | 0.26632 | 0.267683 | 0.27363 | 0.274488 |
| $G(\varepsilon_0 + G_{corr})$ | -992.43156 | -992.4031961 | -992.44128 | -992.44897 |
| **$H_2O$ Tropinone + p-$NO_2$-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -992.71122 | -992.68448 | -992.72943 | -992.73870 |
| $G_{corr}$ | 0.265651 | 0.267861 | 0.273591 | 0.274259 |
| $G(\varepsilon_0 + G_{corr})$ | -992.44557 | -992.4166179 | -992.45584 | -992.46444 |
| **Gas Tropinone + p-F-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -887.43506 | -887.40556 | -887.44952 | -887.45244 |
| $G_{corr}$ | 0.258171 | 0.25935 | 0.26541 | 0.266769 |

| | | | | |
|---|---|---|---|---|
| $G(\varepsilon_0 + G_{corr})$ | -887.17689 | -887.1462075 | -887.18411 | -887.18567 |
| **$H_2O$ Tropinone + p-F-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -887.44475 | -887.41416 | -887.45922 | -887.46530 |
| $G_{corr}$ | 0.257458 | 0.258856 | 0.265081 | 0.266684 |
| $G(\varepsilon_0 + G_{corr})$ | -887.18729 | -887.1553065 | -887.19414 | -887.19862 |
| **Gas Tropinone + p-F-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -887.43506 | -887.40250 | -887.44522 | -887.45418 |
| $G_{corr}$ | 0.258171 | 0.259541 | 0.265621 | 0.266576 |
| $G(\varepsilon_0 + G_{corr})$ | -887.17689 | -887.1429578 | -887.17960 | -887.18760 |
| **$H_2O$ Tropinone + p-F-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -887.44475 | -887.41233 | -887.45618 | -887.46543 |
| $G_{corr}$ | 0.257458 | 0.259571 | 0.265747 | 0.266372 |
| $G(\varepsilon_0 + G_{corr})$ | -887.18729 | -887.1527567 | -887.19043 | -887.19905 |
| **Gas Tropinone + p-Cl-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -1247.79641 | -1247.76804 | -1247.81244 | -1247.81548 |
| $G_{corr}$ | 0.256207 | 0.256982 | 0.263258 | 0.264445 |
| $G(\varepsilon_0 + G_{corr})$ | -1247.54021 | -1247.51106 | -1247.54918 | -1247.55103 |
| **$H_2O$ Tropinone + p-Cl-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -1247.80626 | -1247.77690 | -1247.82240 | -1247.82871 |
| $G_{corr}$ | 0.254484 | 0.256735 | 0.262697 | 0.264326 |
| $G(\varepsilon_0 + G_{corr})$ | -1247.55177 | -1247.520169 | -1247.55970 | -1247.56438 |
| **Gas Tropinone + p-Cl-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -1247.79641 | -1247.76511 | -1247.80824 | -1247.81722 |
| $G_{corr}$ | 0.256207 | 0.256937 | 0.262802 | 0.264115 |
| $G(\varepsilon_0 + G_{corr})$ | -1247.54021 | -1247.508173 | -1247.54544 | -1247.55311 |
| **$H_2O$ Tropinone + p-Cl-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -1247.80626 | -1247.77527 | -1247.81950 | -1247.82880 |
| $G_{corr}$ | 0.254484 | 0.257653 | 0.263332 | 0.263956 |
| $G(\varepsilon_0 + G_{corr})$ | -1247.55177 | -1247.517617 | -1247.55616 | -1247.56484 |
| **Gas Tropinone + p-$CF_3$-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -1125.23601 | -1125.20924 | -1125.25417 | -1125.25749 |

| | | | | |
|---|---|---|---|---|
| $G_{corr}$ | 0.266968 | 0.26675 | 0.273801 | 0.275247 |
| $G(\varepsilon_0 + G_{corr})$ | -1124.96905 | -1124.942488 | -1124.98037 | -1124.98224 |
| **$H_2O$ Tropinone + p-$CF_3$-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -1125.24590 | -1125.21816 | -1125.26404 | -1125.27055 |
| $G_{corr}$ | 0.264683 | 0.265905 | 0.273092 | 0.273952 |
| $G(\varepsilon_0 + G_{corr})$ | -1124.98122 | -1124.952259 | -1124.99095 | -1124.99659 |
| **Gas Tropinone + p-$CF_3$-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -1125.23601 | -1125.20654 | -1125.25025 | -1125.25918 |
| $G_{corr}$ | 0.266968 | 0.267537 | 0.273025 | 0.275324 |
| $G(\varepsilon_0 + G_{corr})$ | -1124.96905 | -1124.939001 | -1124.97722 | -1124.98386 |
| **$H_2O$ Tropinone + p-$CF_3$-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -1125.24590 | -1125.21667 | -1125.26135 | -1125.27075 |
| $G_{corr}$ | 0.264683 | 0.268008 | 0.273376 | 0.27479 |
| $G(\varepsilon_0 + G_{corr})$ | -1124.98122 | -1124.948665 | -1124.98797 | -1124.99596 |
| **Gas Tropinone + m-MeO-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -902.72284 | -902.69431 | -902.73846 | -902.74115 |
| $G_{corr}$ | 0.297844 | 0.298104 | 0.304438 | 0.305319 |
| $G(\varepsilon_0 + G_{corr})$ | -902.42499 | -902.3962013 | -902.43403 | -902.43583 |
| **$H_2O$ Tropinone + m-MeO-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -902.73508 | -902.70497 | -902.75016 | -902.75595 |
| $G_{corr}$ | 0.297651 | 0.297911 | 0.303995 | 0.305246 |
| $G(\varepsilon_0 + G_{corr})$ | -902.43743 | -902.4070587 | -902.44617 | -902.45070 |
| **Gas Tropinone + m-MeO-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -902.72284 | -902.69084 | -902.73404 | -902.74356 |
| $G_{corr}$ | 0.297844 | 0.298252 | 0.304211 | 0.305836 |
| $G(\varepsilon_0 + G_{corr})$ | -902.42499 | -902.3925833 | -902.42983 | -902.43773 |
| **$H_2O$ Tropinone + m-MeO-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -902.73508 | -902.70293 | -902.74712 | -902.75640 |
| $G_{corr}$ | 0.297651 | 0.298282 | 0.304421 | 0.30559 |
| $G(\varepsilon_0 + G_{corr})$ | -902.43743 | -902.4046434 | -902.44270 | -902.45081 |
| **Gas Tropinone + p-MeO-** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |

| $C_6H_4CHO$ (ANTI) | 25 °C | | | |
|---|---|---|---|---|
| $\varepsilon_0$ | -902.72762 | -902.69587 | -902.73872 | -902.74093 |
| $G_{corr}$ | 0.298342 | 0.298144 | 0.304487 | 0.305501 |
| $G(\varepsilon_0 + G_{corr})$ | -902.42928 | -902.3977274 | -902.43423 | -902.43543 |
| **$H_2O$ Tropinone + p-MeO-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -902.73919 | -902.70624 | -902.75013 | -902.75587 |
| $G_{corr}$ | 0.297889 | 0.297113 | 0.303583 | 0.305378 |
| $G(\varepsilon_0 + G_{corr})$ | -902.44130 | -902.409129 | -902.44655 | -902.45049 |
| **Gas Tropinone + p-MeO-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -902.72762 | -902.69235 | -902.7341412 | -902.74312 |
| $G_{corr}$ | 0.298342 | 0.298002 | 0.304219 | 0.305726 |
| $G(\varepsilon_0 + G_{corr})$ | -902.42928 | -902.3943528 | -902.42992 | -902.43739 |
| **$H_2O$ Tropinone + p-MeO-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -902.73919 | -902.70403 | -902.74687 | -902.75605 |
| $G_{corr}$ | 0.297889 | 0.298445 | 0.304279 | 0.305528 |
| $G(\varepsilon_0 + G_{corr})$ | -902.44130 | -902.40558 | -902.44260 | -902.45053 |
| **Gas Tropinone + p-Napth-CHO (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -941.84044 | -941.81214 | -941.85618 | -941.85949 |
| $G_{corr}$ | 0.311242 | 0.313605 | 0.320025 | 0.320654 |
| $G(\varepsilon_0 + G_{corr})$ | -941.52920 | -941.4985374 | -941.53615 | -941.53883 |
| **$H_2O$ Tropinone + p-Napth-CHO (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -941.85140 | -941.82105 | -941.86646 | -941.87346 |
| $G_{corr}$ | 0.310663 | 0.31297 | 0.319651 | 0.320743 |
| $G(\varepsilon_0 + G_{corr})$ | -941.54074 | -941.5080786 | -941.54681 | -941.55272 |
| **Gas Tropinone + p-Napth-CHO (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -941.84044 | -941.80868 | -941.85109 | -941.86213 |
| $G_{corr}$ | 0.311242 | 0.313585 | 0.320306 | 0.321103 |
| $G(\varepsilon_0 + G_{corr})$ | -941.52920 | -941.4950987 | -941.53078 | -941.54103 |
| **$H_2O$ Tropinone + p-Napth-CHO (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -941.85140 | -941.81909 | -941.86255 | -941.87409 |
| $G_{corr}$ | 0.310663 | 0.313003 | 0.319879 | 0.320685 |
| $G(\varepsilon_0 + G_{corr})$ | -941.54074 | -941.5060833 | -941.54267 | -941.55340 |

Table **S130.** Energies and free energies (at T=25°C) in the gas phase and in water of reactants, transition states and products (both HBO and HBN) involved in aldol reactions of tropinone investigated in this study.

| Gas Granatanone + p-$NO_2$-$C_6H_4CHO$ (ANTI) | REACT | TS | PROD HBO | PROD HBN |
|---|---|---|---|---|
| | 25 °C | | | |
| $\varepsilon_0$ | -1032.01758 | -1031.99205 | -1032.03542 | -1032.03970 |
| $G_{corr}$ | 0.294941 | 0.296629 | 0.301606 | 0.304407 |
| $G(\varepsilon_0 + G_{corr})$ | -1031.72264 | -1031.695424 | -1031.73381 | -1031.73529 |
| $H_2O$ Granatanone + p-$NO_2$-$C_6H_4CHO$ (ANTI) | REACT | TS | PROD HBO | PROD HBN |
| | 25 °C | | | |
| $\varepsilon_0$ | -1032.03035 | -1032.00430 | -1032.04848 | -1032.05588 |
| $G_{corr}$ | 0.294356 | 0.296461 | 0.301457 | 0.303956 |
| $G(\varepsilon_0 + G_{corr})$ | -1031.73599 | -1031.70784 | -1031.74702 | -1031.75193 |
| Gas Granatanone + p-$NO_2$-$C_6H_4CHO$ (SYN) | React | TS | Prod SYN HBO | Prod Syn HBN |
| | 25 °C | | | |
| $\varepsilon_0$ | -1032.01758 | -1031.99070 | -1032.03292 | -1032.04080 |
| $G_{corr}$ | 0.294941 | 0.296861 | 0.301946 | 0.303855 |
| $G(\varepsilon_0 + G_{corr})$ | -1031.72264 | -1031.693842 | -1031.73097 | -1031.73694 |
| $H_2O$ Granatanone + p-$NO_2$-$C_6H_4CHO$ (SYN) | React | TS | Prod SYN HBO | Prod Syn HBN |
| | **25 °C** | | | |
| $\varepsilon_0$ | -1032.03035 | -1032.00392 | -1032.04677 | -1032.05566 |
| $G_{corr}$ | 0.294356 | 0.297104 | 0.301973 | 0.30338 |
| $G(\varepsilon_0 + G_{corr})$ | -1031.73599 | -1031.706818 | -1031.74480 | -1031.75228 |
| Gas Granatanone + p-F-$C_6H_4CHO$ (ANTI) | REACT | TS | PROD HBO | PROD HBN |
| | 25 °C | | | |
| $\varepsilon_0$ | -926.75483 | -926.72447 | -926.76665 | -926.76977 |
| $G_{corr}$ | 0.287449 | 0.287433 | 0.294086 | 0.295846 |
| $G(\varepsilon_0 + G_{corr})$ | -926.46738 | -926.4370402 | -926.47256 | -926.47392 |
| $H_2O$ Granatanone + p-F-$C_6H_4CHO$ (ANTI) | REACT | TS | PROD HBO | PROD HBN |
| | 25 °C | | | |
| $\varepsilon_0$ | -926.76402 | -926.73290 | -926.77606 | -926.78240 |
| $G_{corr}$ | 0.287143 | 0.287571 | 0.293483 | 0.295596 |
| $G(\varepsilon_0 + G_{corr})$ | -926.47688 | -926.445325 | -926.48258 | -926.48680 |
| Gas Granatanone + p-F-$C_6H_4CHO$ (SYN) | React | TS | Prod SYN HBO | Prod Syn HBN |
| | **25 °C** | | | |
| $\varepsilon_0$ | -926.76402 | -926.73185 | -926.77368 | -926.78237 |
| $G_{corr}$ | 0.287143 | 0.288339 | 0.294365 | 0.295094 |
| $G(\varepsilon_0 + G_{corr})$ | -926.47688 | -926.4435092 | -926.47932 | -926.48727 |
| $H_2O$ Granatanone + p-F-$C_6H_4CHO$ (SYN) | React | TS | Prod SYN HBO | Prod Syn HBN |
| | **25 °C** | | | |

| | | | | |
|---|---|---|---|---|
| $\varepsilon_0$ | -1287.11621 | -1287.08502 | -1287.12656 | -1287.13459 |
| $G_{corr}$ | 0.285783 | 0.286311 | 0.292756 | 0.293651 |
| $G(\varepsilon_0 + G_{corr})$ | -1286.83042 | -1286.798704 | -1286.83381 | -1286.84094 |
| **Gas Granatanone + p-Cl-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -1287.11621 | -1287.08696 | -1287.12955 | -1287.13274 |
| $G_{corr}$ | 0.285783 | 0.286049 | 0.292079 | 0.292955 |
| $G(\varepsilon_0 + G_{corr})$ | -1286.83042 | -1286.800912 | -1286.83747 | -1286.83978 |
| **$H_2O$ Granatanone + p-Cl-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -1287.12547 | -1287.09558 | -1287.13922 | -1287.14576 |
| $G_{corr}$ | 0.284331 | 0.28746 | 0.291559 | 0.292958 |
| $G(\varepsilon_0 + G_{corr})$ | -1286.84114 | -1286.808122 | -1286.84766 | -1286.85280 |
| **Gas Granatanone + p-Cl-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -1287.12547 | -1287.09476 | -1287.13703 | -1287.14582 |
| $G_{corr}$ | 0.284331 | 0.286267 | 0.291939 | 0.293185 |
| $G(\varepsilon_0 + G_{corr})$ | -1286.84114 | -1286.808494 | -1286.84509 | -1286.85263 |
| **$H_2O$ Granatanone + p-Cl-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -1164.55576 | -1164.52639 | -1164.56847 | -1164.57644 |
| $G_{corr}$ | 0.295449 | 0.296236 | 0.302787 | 0.303972 |
| $G(\varepsilon_0 + G_{corr})$ | -1164.26031 | -1164.230152 | -1164.26568 | -1164.27246 |
| **Gas Granatanone + p-$CF_3$-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -1164.55576 | -1164.52818 | -1164.57126 | -1164.57476 |
| $G_{corr}$ | 0.295449 | 0.296568 | 0.302758 | 0.303995 |
| $G(\varepsilon_0 + G_{corr})$ | -1164.26031 | -1164.231609 | -1164.26850 | -1164.27076 |
| **$H_2O$ Granatanone + p-$CF_3$-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -1164.56529 | -1164.53689 | -1164.58092 | -1164.58761 |
| $G_{corr}$ | 0.29477 | 0.296069 | 0.302413 | 0.303413 |
| $G(\varepsilon_0 + G_{corr})$ | -1164.27052 | -1164.240817 | -1164.27851 | -1164.28420 |
| **Gas Granatanone + p-$CF_3$-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -1164.56529 | -1164.53615 | -1164.57891 | -1164.58767 |
| $G_{corr}$ | 0.29477 | 0.296307 | 0.302693 | 0.302532 |
| $G(\varepsilon_0 + G_{corr})$ | -1164.27052 | -1164.239846 | -1164.27621 | -1164.28513 |
| **$H_2O$ Granatanone + p-$CF_3$-** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |

| $C_6H_4CHO$ (SYN) | 25 °C | | | |
|---|---|---|---|---|
| $\varepsilon_0$ | -942.04257 | -942.01084 | -942.05228 | -942.06095 |
| $G_{corr}$ | 0.325979 | 0.327415 | 0.333577 | 0.335039 |
| $G(\varepsilon_0 + G_{corr})$ | -941.71659 | -941.6834239 | -941.71870 | -941.72591 |
| **Gas Granatanone + m-MeO-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -942.04257 | -942.01327 | -942.05561 | -942.05842 |
| $G_{corr}$ | 0.325979 | 0.327101 | 0.333022 | 0.334367 |
| $G(\varepsilon_0 + G_{corr})$ | -941.71659 | -941.6861671 | -941.72259 | -941.72405 |
| **$H_2O$ Granatanone + m-MeO-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -942.05414 | -942.02375 | -942.06706 | -942.07299 |
| $G_{corr}$ | 0.325453 | 0.326892 | 0.332945 | 0.33407 |
| $G(\varepsilon_0 + G_{corr})$ | -941.72869 | -941.6968547 | -941.73412 | -941.73892 |
| **Gas Granatanone + m-MeO-$C_6H_4CHO$ (SYN)** | | | | |
| | **25 °C** | | | |
| $\varepsilon_0$ | -942.05414 | -942.02255 | -942.06463 | -942.07342 |
| $G_{corr}$ | 0.325453 | 0.32744 | 0.333049 | 0.334505 |
| $G(\varepsilon_0 + G_{corr})$ | -941.72869 | -941.6951064 | -941.73158 | -941.73891 |
| **$H_2O$ Granatanone + m-MeO-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -827.52094 | -827.48868 | -827.52987 | -827.53815 |
| $G_{corr}$ | 0.297089 | 0.298326 | 0.303912 | 0.305518 |
| $G(\varepsilon_0 + G_{corr})$ | -827.22385 | -827.1903566 | -827.22596 | -827.23264 |
| **Gas Granatanone + p-MeO-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -942.04738 | -942.01481 | -942.05585 | -942.05854 |
| $G_{corr}$ | 0.327053 | 0.32683 | 0.333096 | 0.333984 |
| $G(\varepsilon_0 + G_{corr})$ | -941.72033 | -941.6879823 | -941.72276 | -941.72455 |
| **$H_2O$ Granatanone + p-MeO-$C_6H_4CHO$ (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -942.05837 | -942.02501 | -942.06700 | -942.07303 |
| $G_{corr}$ | 0.32598 | 0.326072 | 0.332163 | 0.333968 |
| $G(\varepsilon_0 + G_{corr})$ | -941.73239 | -941.6989401 | -941.73484 | -941.73906 |
| **Gas Granatanone + p-MeO-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -942.04738 | -942.01232 | -942.0524403 | -942.06048 |
| $G_{corr}$ | 0.327053 | 0.327398 | 0.33332 | 0.334737 |

| | | | | |
|---|---|---|---|---|
| $G(\varepsilon_0 + G_{corr})$ | -941.72033 | -941.6849178 | -941.71912 | -941.72574 |
| **$H_2O$ Granatanone + p-MeO-$C_6H_4CHO$ (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -942.05837 | -942.02360 | -942.06442 | -942.07309 |
| $G_{corr}$ | 0.32598 | 0.327189 | 0.332667 | 0.334423 |
| $G(\varepsilon_0 + G_{corr})$ | -941.73239 | -941.6964148 | -941.73175 | -941.73867 |
| **Gas Granatanone + p-Napth-CHO (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -981.15989 | -981.13113 | -981.17348 | -981.17669 |
| $G_{corr}$ | 0.338941 | 0.342582 | 0.34913 | 0.349714 |
| $G(\varepsilon_0 + G_{corr})$ | -980.82095 | -980.7885516 | -980.82435 | -980.82697 |
| **$H_2O$ Granatanone + p-Napth-CHO (ANTI)** | **REACT** | **TS** | **PROD HBO** | **PROD HBN** |
| | 25 °C | | | |
| $\varepsilon_0$ | -981.17005 | -981.13988 | -981.18346 | -981.19043 |
| $G_{corr}$ | 0.33962 | 0.341948 | 0.348184 | 0.349526 |
| $G(\varepsilon_0 + G_{corr})$ | -980.83043 | -980.7979316 | -980.83527 | -980.84091 |
| **Gas Granatanone + p-Napth-CHO (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -981.15989 | -981.12825 | -981.16903 | -981.17960 |
| $G_{corr}$ | 0.338941 | 0.342207 | 0.349315 | 0.349584 |
| $G(\varepsilon_0 + G_{corr})$ | -980.82095 | -980.7860464 | -980.81971 | -980.83002 |
| **$H_2O$ Granatanone + p-Napth-CHO (SYN)** | **React** | **TS** | **Prod SYN HBO** | **Prod Syn HBN** |
| | **25 °C** | | | |
| $\varepsilon_0$ | -981.17005 | -981.13836 | -981.17997 | -981.19115 |
| $G_{corr}$ | 0.33962 | 0.341581 | 0.348859 | 0.349197 |
| $G(\varepsilon_0 + G_{corr})$ | -980.83043 | -980.7967777 | -980.83112 | -980.84195 |

Table **S131**. Energies and free energies (at T=25°C) in the gas phase and in water of reactants, transition states and products (both HBO and HBN) involved in aldol reactions of granatanone investigated in this study.

| | time | Integration of ax-H at C2 | Integration of eq-H at C2 | % deuteration ax-H at C2 | % deuteration eq-H at C2 |
|---|---|---|---|---|---|
| Tropinone in $D_2O$ | 0h | 1.983 | 2.053 | 0.0 | 0.0 |
| | 1h | 1.806 | 2.046 | 8.9 | 0.3 |
| | 2h | 1.64 | 2.006 | 17.3 | 2.3 |
| | 4h | 1.39 | 1.979 | 29.9 | 3.6 |
| | 6h | 1.154 | 1.973 | 41.8 | 3.9 |
| | 24h | 0.65 | 1.669 | 67.2 | 18.7 |
| Granatanone in $D_2O$ | 0 h | 1.66 | 2.03 | 0 | 0 |
| | 1h | 0.91 | 2 | 69.9 | 1.5 |
| | 2h | 0.5 | 1.95 | 91.6 | 3.9 |
| | 4h | 0.14 | 1.86 | 97.0 | 8.4 |
| | 6h | 0.05 | 1.75 | 98.8 | 13.8 |
| | 24h | 0.02 | 1.43 | 100.0 | 29.6 |

Table **S132**. Spontaneous protium-deuterium exchange in $D_2O$ solution monitored by $^1$H-NMR

| pH of aqueous solution of amines | |
|---|---|
| **Tropinone** | |
| 0.1 M | 10.02 |
| 0.5 M | 10.34 |
| **Granatanone (Pseudopelletierine)** | |
| 0.1 M | 9.20 |
| 0.5 M | 9.50 |
| **Triethylamine** | |
| 0.1 M | 11.85 |
| 0.5 M | 12.22 |
| **3-Tropine** | |
| 0.1 M | 11.62 |
| 0.5 M | 11.98 |

Table **S133**. Experimentally measured pH of aqueous solutions of amines related to the current study

| Adjusted pH of reaction mixture in 2.5 mL of $H_2O$ | Result in 24 h at rt |
|---|---|
| 5 | no rxn |
| 6 | trace of product |
| 7 | very low conversion ca 20% |
| 8 | conversion 50-75% |
| 9 | conversion 90-98% |
| 10 | conversion 92-98% |

Table **S134**. Observed dependence of reactions of tropinone with benzaldehyde in water (2.5 mL/mmol) on pH of the reaction mixture

| Additive (0.1 molar equiv) | Result in 24 h at rt |
|---|---|
| no additive | conversion 96% , precipitate, 75 % isolated yield |
| benzyl alcohol | conversion 95% |
| triethylamine | conversion 77% lower stereoselctivity ca 2:1 |
| benzoic acid | conversion 92% |
| p-toluenesulfonic acid | conversion 72%, forming elimination products |
| tartaric acid | conversion 50 %, some elimination products |

Table **S135.** Effect of additives on aldol reaction of tropinone with benzaldehyde in water (2.5 mL/mmol)

| Electrophilic reagent | Result in 24 h at rt |
|---|---|
| Trimethylsilyl chloride TMS-Cl | no rxn |
| acetic anhydride $Ac_2O$ | no rxn |
| 2.2.2-trichloroethyl chloroformate Troc-Cl | no rxn |
| Benzyl chloroformate Cbz-Cl | no rxn |
| cinnamoyl cyanide | no rxn |
| methyl cyanoformate MeOCOCN | no rxn |

Table **S136**. Attempted reactions of tropinone with other electrophiles in water under the aqueous aldol reaction conditions