

Supporting Information

norbornene 1
(8,8) active space
-270.94952

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 1.130305 | 1.332818 | 1.897490 |
| 2 | 6 | 0.539962 | 0.680307 | 1.280780 |
| 3 | 6 | 0.540072 | -0.680276 | 1.280774 |
| 4 | 6 | -0.331595 | 1.126137 | 0.118811 |
| 5 | 1 | 1.130683 | -1.332698 | 1.897321 |
| 6 | 6 | -0.331582 | -1.126147 | 0.118871 |
| 7 | 1 | -2.001687 | -0.000105 | -0.783952 |
| 8 | 1 | -0.698050 | 2.143859 | 0.159014 |
| 9 | 1 | 1.469153 | 1.199186 | -1.191022 |
| 10 | 1 | -0.698069 | -2.143859 | 0.159063 |
| 11 | 6 | 0.471551 | 0.776336 | -1.204953 |
| 12 | 6 | -1.378508 | -0.000016 | 0.106082 |
| 13 | 1 | 1.468940 | -1.199314 | -1.191168 |
| 14 | 1 | -0.044671 | 1.173434 | -2.072890 |
| 15 | 1 | -2.010430 | 0.000051 | 0.986895 |
| 16 | 6 | 0.471383 | -0.776360 | -1.205030 |
| 17 | 1 | -0.044918 | -1.173352 | -2.072967 |

(6,6) active space
-270.93272

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 1.120319 | 1.333288 | 1.898313 |
| 2 | 6 | 0.539285 | 0.678195 | 1.275509 |
| 3 | 6 | 0.545624 | -0.682108 | 1.274270 |
| 4 | 6 | -0.324933 | 1.123984 | 0.105331 |
| 5 | 1 | 1.131366 | -1.332389 | 1.897629 |
| 6 | 6 | -0.313806 | -1.134550 | 0.105423 |
| 7 | 1 | -2.012373 | 0.009709 | -0.785160 |
| 8 | 1 | -0.684917 | 2.144167 | 0.148258 |
| 9 | 1 | 1.461764 | 1.196668 | -1.182027 |
| 10 | 1 | -0.680701 | -2.152011 | 0.149254 |
| 11 | 6 | 0.462551 | 0.776683 | -1.188874 |
| 12 | 6 | -1.386477 | 0.011564 | 0.102812 |
| 13 | 1 | 1.465944 | -1.197214 | -1.189186 |
| 14 | 1 | -0.048580 | 1.167356 | -2.063121 |
| 15 | 1 | -2.009689 | 0.008973 | 0.989355 |
| 16 | 6 | 0.465114 | -0.780988 | -1.190733 |
| 17 | 1 | -0.047952 | -1.171326 | -2.063935 |

bicyclo[3.2.0]hept-2-ene 2
(8,8) active space
-270.93439

| | | | | |
|---|---|-----------|-----------|----------|
| 1 | 1 | -2.157410 | -0.801659 | 0.413944 |
| 2 | 6 | -1.265569 | -0.479045 | 0.945481 |
| 3 | 6 | -0.167010 | -1.520005 | 0.916338 |
| 4 | 6 | 1.016129 | -1.019182 | 0.534002 |
| 5 | 6 | 0.922143 | 0.478576 | 0.211148 |
| 6 | 6 | -0.606248 | 0.736406 | 0.275431 |
| 7 | 1 | -1.570739 | -0.267353 | 1.968365 |

| | | | | |
|----|---|-----------|-----------|-----------|
| 8 | 1 | -0.334943 | -2.544716 | 1.197293 |
| 9 | 1 | -1.024571 | -0.139823 | -1.733294 |
| 10 | 1 | 1.290968 | 1.838141 | -1.508704 |
| 11 | 1 | 1.930642 | -1.581292 | 0.458920 |
| 12 | 1 | 1.579550 | 1.076971 | 0.833165 |
| 13 | 6 | 0.913273 | 0.837959 | -1.327411 |
| 14 | 1 | -0.897748 | 1.682057 | 0.715991 |
| 15 | 6 | -0.628714 | 0.775168 | -1.306860 |
| 16 | 1 | 1.423241 | 0.147080 | -1.989159 |
| 17 | 1 | -1.147484 | 1.615635 | -1.753474 |

bicyclo[4.1.0]hept-2-ene 3a

(6,6) active space

-270.91745

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | .404153 | -.677494 | -2.264657 |
| 2 | 6 | .062472 | -.322571 | -1.307629 |
| 3 | 6 | .392520 | 1.120193 | -.987009 |
| 4 | 6 | .050245 | -1.287584 | -.160248 |
| 5 | 1 | .572994 | 1.786409 | -1.813509 |
| 6 | 6 | .431437 | 1.575398 | .274267 |
| 7 | 6 | -1.258918 | -.914464 | -.779041 |
| 8 | 6 | .489125 | -.783021 | 1.202456 |
| 9 | 1 | .395887 | -2.284527 | -.381328 |
| 10 | 1 | .634603 | 2.616152 | .461680 |
| 11 | 6 | .143259 | .690763 | 1.464624 |
| 12 | 1 | -1.921061 | -.249599 | -.252973 |
| 13 | 1 | -.905881 | .783079 | 1.737990 |
| 14 | 1 | 1.568254 | -.900890 | 1.264594 |
| 15 | 1 | .061972 | -1.402190 | 1.986684 |
| 16 | 1 | .703573 | 1.037706 | 2.327965 |
| 17 | 1 | -1.758586 | -1.650990 | -1.384271 |

tricyclo[3.2.1.0^{3,7}]heptane 4a

(8,8) active space

-270.90406

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | 1.419720 | .367352 | .402141 |
| 2 | 1 | 1.412564 | .428458 | 1.487546 |
| 3 | 1 | 2.442290 | .464471 | .055152 |
| 4 | 6 | .487395 | 1.289762 | -.373722 |
| 5 | 6 | .710743 | -.852666 | -.247944 |
| 6 | 6 | -.933926 | .806385 | -.293925 |
| 7 | 6 | .028644 | .103937 | -1.246712 |
| 8 | 6 | -1.339495 | -.141521 | .870907 |
| 9 | 6 | -.435502 | -1.377055 | .671311 |
| 10 | 1 | .715608 | 2.299488 | -.668824 |
| 11 | 1 | 1.358009 | -1.627937 | -.636156 |
| 12 | 1 | -1.675219 | 1.467090 | -.710158 |
| 13 | 1 | -.086577 | .001044 | -2.309987 |
| 14 | 1 | -2.392134 | -.394638 | .805422 |
| 15 | 1 | -.975736 | -2.169200 | .160447 |
| 16 | 1 | -1.179481 | .331515 | 1.834362 |
| 17 | 1 | -.056961 | -1.780390 | 1.605526 |

(6,6) active space

-270.88871

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 1.656147 | -0.030195 | -1.619470 |
| 2 | 6 | 0.812924 | 0.031961 | -0.956539 |
| 3 | 6 | -0.509570 | 0.817946 | -1.064565 |
| 4 | 6 | 0.054993 | -1.109233 | -0.245036 |
| 5 | 1 | -0.811989 | 1.533637 | -1.809247 |
| 6 | 6 | 0.487939 | 1.170961 | 0.004371 |
| 7 | 6 | -1.292150 | -0.466124 | -0.670348 |
| 8 | 6 | 0.313547 | -0.898341 | 1.249688 |
| 9 | 1 | 0.220313 | -2.122163 | -0.588258 |
| 10 | 1 | 0.992977 | 2.112303 | -0.130872 |
| 11 | 6 | 0.279023 | 0.639873 | 1.420061 |
| 12 | 1 | -2.066036 | -0.378971 | 0.087453 |
| 13 | 1 | -0.663053 | 0.979233 | 1.839699 |
| 14 | 1 | 1.294647 | -1.284828 | 1.512413 |
| 15 | 1 | -0.417068 | -1.406713 | 1.871856 |
| 16 | 1 | 1.064818 | 0.985457 | 2.083654 |
| 17 | 1 | -1.708547 | -0.944201 | -1.549291 |

Concerted Diels-Alder transition state 5

(8,8) active space

-270.86769

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 1.608907 | 1.332258 | 1.503519 |
| 2 | 6 | .802355 | .709433 | 1.163175 |
| 3 | 6 | .802468 | -.708579 | 1.162707 |
| 4 | 6 | -.334011 | 1.155527 | .464490 |
| 5 | 1 | 1.609288 | -1.331266 | 1.502527 |
| 6 | 6 | -.333753 | -1.154950 | .463509 |
| 7 | 1 | -2.018468 | .000162 | -.360089 |
| 8 | 1 | -.656595 | 2.180949 | .451458 |
| 9 | 1 | 1.175919 | 1.233114 | -1.646549 |
| 10 | 1 | -.656482 | -2.180383 | .450812 |
| 11 | 6 | .244067 | .699841 | -1.633301 |
| 12 | 6 | -1.307758 | .000116 | .454605 |
| 13 | 1 | 1.174875 | -1.234530 | -1.646643 |
| 14 | 1 | -.584614 | 1.229406 | -2.068629 |
| 15 | 1 | -1.865708 | -.000603 | 1.391438 |
| 16 | 6 | .243280 | -.700804 | -1.632379 |
| 17 | 1 | -.585635 | -1.229690 | -2.068242 |

Norbornene to anti intermediate transition state 6

(8,8) active space

-270.85645

| | | | | |
|----|---|-----------|-----------|----------|
| 1 | 6 | -1.260596 | -.735544 | -.016902 |
| 2 | 1 | -1.856537 | -.023757 | -.571275 |
| 3 | 1 | -.929398 | -1.489378 | -.729887 |
| 4 | 6 | -2.015901 | -1.406103 | 1.107561 |
| 5 | 6 | -.021271 | -.111385 | .679063 |
| 6 | 6 | -1.182154 | -1.527143 | 2.217841 |
| 7 | 6 | .038687 | -.865047 | 1.978704 |
| 8 | 6 | -1.255229 | 2.228343 | .401354 |
| 9 | 6 | -.089242 | 1.493825 | .965593 |
| 10 | 1 | -2.992009 | -1.838820 | 1.003217 |

| | | | | |
|----|---|-----------|-----------|----------|
| 11 | 1 | .867207 | -.269639 | .079160 |
| 12 | 1 | -1.431716 | -2.048767 | 3.123685 |
| 13 | 1 | .846675 | -.774350 | 2.680656 |
| 14 | 1 | -2.183897 | 2.260741 | .942529 |
| 15 | 1 | -.065259 | 1.636344 | 2.039297 |
| 16 | 1 | -1.317315 | 2.405511 | -.657981 |
| 17 | 1 | .829083 | 1.918610 | .572879 |

Anti biradical intermediate 7

(8,8) active space

-270.86520

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -.554186 | .429797 | -.003480 |
| 2 | 1 | -1.137317 | .832267 | .819896 |
| 3 | 1 | .486440 | .471769 | .309035 |
| 4 | 6 | -.774041 | 1.215141 | -1.274678 |
| 5 | 6 | -.980222 | -1.024907 | -.360420 |
| 6 | 6 | -1.193550 | .366913 | -2.301343 |
| 7 | 6 | -1.300358 | -.951545 | -1.832043 |
| 8 | 6 | -1.926875 | -1.727251 | 1.937304 |
| 9 | 6 | -2.221180 | -1.538641 | .483276 |
| 10 | 1 | -.613681 | 2.272450 | -1.359381 |
| 11 | 1 | -.165348 | -1.719846 | -.177932 |
| 12 | 1 | -1.401673 | .679377 | -3.308375 |
| 13 | 1 | -1.609253 | -1.799901 | -2.413753 |
| 14 | 1 | -1.338240 | -2.571401 | 2.251621 |
| 15 | 1 | -3.033998 | -.830615 | .349185 |
| 16 | 1 | -1.943808 | -.886245 | 2.606951 |
| 17 | 1 | -2.544219 | -2.482179 | .051397 |

Anti fragmentation transition state 8

(8,8) active space

-270.85562

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -0.445662 | 0.397282 | -0.016848 |
| 2 | 1 | -0.845103 | 0.685269 | 0.947987 |
| 3 | 1 | 0.632397 | 0.544510 | 0.029465 |
| 4 | 6 | -1.023485 | 1.194314 | -1.164162 |
| 5 | 6 | -0.753770 | -1.056163 | -0.404826 |
| 6 | 6 | -1.329919 | 0.356477 | -2.202475 |
| 7 | 6 | -1.056070 | -1.010567 | -1.814124 |
| 8 | 6 | -2.108223 | -1.786197 | 1.874910 |
| 9 | 6 | -2.324948 | -1.562349 | 0.482706 |
| 10 | 1 | -1.122724 | 2.262741 | -1.160991 |
| 11 | 1 | -0.058348 | -1.805680 | -0.066396 |
| 12 | 1 | -1.705532 | 0.659614 | -3.162404 |
| 13 | 1 | -1.206900 | -1.871501 | -2.437678 |
| 14 | 1 | -1.996613 | -0.958451 | 2.552973 |
| 15 | 1 | -2.949147 | -0.714053 | 0.243423 |
| 16 | 1 | -1.726503 | -2.731251 | 2.219795 |
| 17 | 1 | -2.620614 | -2.441850 | -0.068336 |

Norbornene to gauche-out intermediate transition state 9

(8,8) active space

-270.85668

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | 1.465480 | -.385429 | .092055 |
| 2 | 1 | 1.951966 | .498002 | -.315549 |
| 3 | 1 | 2.159240 | -.812885 | .810817 |
| 4 | 6 | 1.116999 | -1.357038 | -1.008848 |
| 5 | 6 | .097226 | -.021658 | .746367 |
| 6 | 6 | -.270126 | -1.468538 | -1.136145 |
| 7 | 6 | -.915279 | -.695053 | -.161187 |
| 8 | 6 | -1.382757 | 2.073640 | .297532 |
| 9 | 6 | -.135719 | 1.540461 | .944100 |
| 10 | 1 | 1.845094 | -1.848384 | -1.624857 |
| 11 | 1 | .042518 | -.485778 | 1.728398 |
| 12 | 1 | -.770916 | -2.074790 | -1.868795 |
| 13 | 1 | -1.974910 | -.657198 | .000169 |
| 14 | 1 | -2.338250 | 1.937435 | .771466 |
| 15 | 1 | -.162727 | 1.756849 | 2.007881 |
| 16 | 1 | -1.394222 | 2.279614 | -.757167 |
| 17 | 1 | .720820 | 2.074338 | .545079 |

Gauche-out biradical intermediate 10

(8,8) active space

-270.86502

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | 1.340493 | 0.594216 | 0.416814 |
| 2 | 1 | 1.176816 | 1.116445 | 1.356502 |
| 3 | 1 | 2.337741 | 0.165066 | 0.474049 |
| 4 | 6 | 1.209504 | 1.523492 | -0.765187 |
| 5 | 6 | 0.265128 | -0.506893 | 0.177705 |
| 6 | 6 | 0.235088 | 1.048448 | -1.647025 |
| 7 | 6 | -0.334921 | -0.135467 | -1.156817 |
| 8 | 6 | -1.813758 | -1.655627 | 1.196404 |
| 9 | 6 | -0.799823 | -0.566287 | 1.347008 |
| 10 | 1 | 1.783819 | 2.421186 | -0.887750 |
| 11 | 1 | 0.731978 | -1.487068 | 0.127315 |
| 12 | 1 | -0.041060 | 1.525914 | -2.569467 |
| 13 | 1 | -1.106728 | -0.702387 | -1.641595 |
| 14 | 1 | -2.672610 | -1.514404 | 0.565670 |
| 15 | 1 | -1.290925 | 0.401163 | 1.403885 |
| 16 | 1 | -1.537857 | -2.673122 | 1.409667 |
| 17 | 1 | -0.254193 | -0.704686 | 2.276939 |

Gauche-out fragmentation transition state 11

(8,8) active space

-270.85341

| | | | | |
|---|---|-----------|-----------|-----------|
| 1 | 6 | 1.416143 | .501374 | .346015 |
| 2 | 1 | 1.387270 | .828560 | 1.379587 |
| 3 | 1 | 2.425341 | .139357 | .157424 |
| 4 | 6 | 1.068356 | 1.596874 | -.631029 |
| 5 | 6 | .405829 | -.612320 | .018212 |
| 6 | 6 | .207540 | 1.110958 | -1.581263 |
| 7 | 6 | -.130109 | -.257214 | -1.273246 |
| 8 | 6 | -1.891919 | -1.565671 | 1.296574 |
| 9 | 6 | -.927220 | -.519932 | 1.349011 |

| | | | | |
|----|---|-----------|-----------|-----------|
| 10 | 1 | 1.463397 | 2.593140 | -.581397 |
| 11 | 1 | .752228 | -1.622641 | .158901 |
| 12 | 1 | -.166508 | 1.659653 | -2.425989 |
| 13 | 1 | -.791052 | -.873467 | -1.852623 |
| 14 | 1 | -2.709795 | -1.528878 | .599303 |
| 15 | 1 | -1.303209 | .475328 | 1.165557 |
| 16 | 1 | -1.682002 | -2.525086 | 1.734794 |
| 17 | 1 | -.295599 | -.550045 | 2.224286 |

Gauche-in biradical 12

(8,8) active space

-270.86340

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -.558542 | .298142 | .490075 |
| 2 | 1 | -.747126 | .401371 | 1.555819 |
| 3 | 1 | .519105 | .218070 | .375749 |
| 4 | 6 | -1.120615 | 1.472417 | -.274182 |
| 5 | 6 | -1.290385 | -.942722 | -.100242 |
| 6 | 6 | -2.111792 | 1.042451 | -1.164530 |
| 7 | 6 | -2.258892 | -.348195 | -1.097912 |
| 8 | 6 | -3.034668 | -1.209169 | 1.807193 |
| 9 | 6 | -1.972887 | -1.868197 | .978775 |
| 10 | 1 | -.816530 | 2.489281 | -.118308 |
| 11 | 1 | -.575048 | -1.572789 | -.625274 |
| 12 | 1 | -2.675430 | 1.690216 | -1.810953 |
| 13 | 1 | -2.942479 | -.935312 | -1.682666 |
| 14 | 1 | -3.972102 | -.938497 | 1.356835 |
| 15 | 1 | -2.400768 | -2.718956 | .452647 |
| 16 | 1 | -2.780914 | -.710402 | 2.724334 |
| 17 | 1 | -1.192484 | -2.261493 | 1.624663 |

Transition state leading to bicyclo[3.2.0]hept-2-ene 13

(8,8) active space

-270.86353

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -.605024 | -1.102153 | -1.342234 |
| 2 | 6 | .237873 | -.146138 | -1.884641 |
| 3 | 1 | .167136 | 1.962044 | -1.397843 |
| 4 | 1 | .732054 | -.215721 | -2.834879 |
| 5 | 1 | -.614055 | .662863 | 2.421039 |
| 6 | 6 | -1.062325 | -.691086 | -.065852 |
| 7 | 1 | 1.648416 | -.890068 | 1.003561 |
| 8 | 6 | -.534737 | .693157 | .258305 |
| 9 | 1 | 1.451765 | 1.098070 | -.605439 |
| 10 | 1 | -1.788632 | -1.203867 | .534942 |
| 11 | 1 | .787064 | 1.514368 | 1.821323 |
| 12 | 1 | 1.098259 | -1.088112 | 2.728531 |
| 13 | 1 | -.865859 | -2.030703 | -1.816379 |
| 14 | 6 | .923852 | -.649928 | 1.761056 |
| 15 | 6 | .155548 | .639615 | 1.654448 |
| 16 | 1 | -1.340597 | 1.423313 | .283211 |
| 17 | 6 | .417420 | 1.013076 | -.931721 |

Gauche-in biradical with methylene twisted by 120° clockwise **14**

(8,8) active space

-270.86409

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -1.031654 | -1.200176 | -1.171081 |
| 2 | 6 | .020885 | -.516652 | -1.783666 |
| 3 | 1 | .297046 | 1.609382 | -1.532575 |
| 4 | 1 | .494275 | -.792168 | -2.706200 |
| 5 | 1 | -.564785 | .753036 | 2.428595 |
| 6 | 6 | -1.401311 | -.563334 | .023955 |
| 7 | 1 | 1.332102 | -1.221767 | 1.061095 |
| 8 | 6 | -.547253 | .662695 | .263112 |
| 9 | 1 | 1.456039 | .648431 | -.661941 |
| 10 | 1 | -2.185869 | -.877235 | .686253 |
| 11 | 1 | .859820 | 1.462306 | 1.725193 |
| 12 | 1 | 1.337435 | -.866089 | 2.852973 |
| 13 | 1 | -1.490026 | -2.091644 | -1.558695 |
| 14 | 6 | .906237 | -.679780 | 1.885207 |
| 15 | 6 | .179274 | .611961 | 1.647448 |
| 16 | 1 | -1.165149 | 1.557597 | .261508 |
| 17 | 6 | .412662 | .690023 | -.964240 |

Anti biradical with methylene twisted 120° clockwise **15**

(8,8) active space

-270.86491

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -0.606799 | 0.433849 | 0.007066 |
| 2 | 1 | -1.264317 | 0.851095 | 0.765637 |
| 3 | 1 | 0.397290 | 0.468762 | 0.420965 |
| 4 | 6 | -0.704660 | 1.204483 | -1.287644 |
| 5 | 6 | -1.026380 | -1.019130 | -0.366091 |
| 6 | 6 | -1.163610 | 0.372918 | -2.314847 |
| 7 | 6 | -1.370341 | -0.926832 | -1.835534 |
| 8 | 6 | -1.854483 | -1.734723 | 1.945611 |
| 9 | 6 | -2.209888 | -1.570626 | 0.498205 |
| 10 | 1 | -0.477639 | 2.248807 | -1.380653 |
| 11 | 1 | -0.186212 | -1.697164 | -0.226243 |
| 12 | 1 | -1.332027 | 0.688085 | -3.328463 |
| 13 | 1 | -1.715578 | -1.761778 | -2.416292 |
| 14 | 1 | -2.632890 | -1.780906 | 2.685559 |
| 15 | 1 | -3.062219 | -0.903700 | 0.395316 |
| 16 | 1 | -0.912247 | -2.181334 | 2.211722 |
| 17 | 1 | -2.519165 | -2.529657 | 0.078703 |

Gauche-out biradical with methylene twisted 120° clockwise **16**

(8,8) active space

-270.86448

| | | | | |
|---|---|-----------|-----------|-----------|
| 1 | 6 | 1.364734 | 0.574092 | 0.395983 |
| 2 | 1 | 1.264648 | 1.023749 | 1.380403 |
| 3 | 1 | 2.374168 | 0.172457 | 0.342428 |
| 4 | 6 | 1.124826 | 1.570242 | -0.712147 |
| 5 | 6 | 0.306007 | -0.542164 | 0.158503 |
| 6 | 6 | 0.175926 | 1.072061 | -1.609590 |
| 7 | 6 | -0.304903 | -0.171154 | -1.174066 |
| 8 | 6 | -1.806803 | -1.644621 | 1.133934 |
| 9 | 6 | -0.752658 | -0.596515 | 1.321512 |

| | | | | |
|----|---|-----------|-----------|-----------|
| 10 | 1 | 1.649375 | 2.501311 | -0.805419 |
| 11 | 1 | 0.780097 | -1.517980 | 0.109644 |
| 12 | 1 | -0.139102 | 1.571399 | -2.507671 |
| 13 | 1 | -1.029829 | -0.771477 | -1.689318 |
| 14 | 1 | -2.261680 | -2.102857 | 1.993094 |
| 15 | 1 | -1.205255 | 0.392290 | 1.404720 |
| 16 | 1 | -2.367998 | -1.686043 | 0.218074 |
| 17 | 1 | -0.225157 | -0.775785 | 2.254673 |

Gauche-in biradical with methylene twisted by 120° anticlockwise 17

(8,8) active space

-270.86485

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | 0.010669 | -0.030342 | -0.018027 |
| 2 | 1 | 0.116482 | -0.077810 | 1.060023 |
| 3 | 1 | 1.014772 | 0.045172 | -0.432631 |
| 4 | 6 | -0.829305 | 1.134176 | -0.482924 |
| 5 | 6 | -0.719820 | -1.267755 | -0.600307 |
| 6 | 6 | -1.684162 | 0.715818 | -1.512177 |
| 7 | 6 | -1.609990 | -0.675128 | -1.664400 |
| 8 | 6 | -2.551648 | -1.199781 | 1.214486 |
| 9 | 6 | -1.547533 | -2.046007 | 0.497858 |
| 10 | 1 | -0.682036 | 2.148167 | -0.165187 |
| 11 | 1 | -0.014952 | -1.979087 | -1.019923 |
| 12 | 1 | -2.313459 | 1.367418 | -2.090686 |
| 13 | 1 | -2.179111 | -1.261467 | -2.361554 |
| 14 | 1 | -3.245387 | -0.599916 | 0.657342 |
| 15 | 1 | -2.034603 | -2.887543 | 0.004647 |
| 16 | 1 | -2.818859 | -1.436913 | 2.228064 |
| 17 | 1 | -0.848600 | -2.472673 | 1.212867 |

Anti biradical with methylene twisted 120° anticlockwise 18

(8,8) active space

-270.86437

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -0.595127 | 0.440819 | 0.000204 |
| 2 | 1 | -1.240918 | 0.864709 | 0.766141 |
| 3 | 1 | 0.416097 | 0.479389 | 0.396445 |
| 4 | 6 | -0.714158 | 1.206326 | -1.295490 |
| 5 | 6 | -1.018920 | -1.015200 | -0.360248 |
| 6 | 6 | -1.168649 | 0.365080 | -2.317522 |
| 7 | 6 | -1.360529 | -0.933465 | -1.831477 |
| 8 | 6 | -1.859773 | -1.752590 | 1.946773 |
| 9 | 6 | -2.211153 | -1.551476 | 0.502213 |
| 10 | 1 | -0.495694 | 2.251943 | -1.393955 |
| 11 | 1 | -0.183783 | -1.695536 | -0.210809 |
| 12 | 1 | -1.342285 | 0.673871 | -3.332185 |
| 13 | 1 | -1.696988 | -1.775334 | -2.407301 |
| 14 | 1 | -1.238854 | -1.037202 | 2.455802 |
| 15 | 1 | -3.045775 | -0.855566 | 0.402162 |
| 16 | 1 | -2.498739 | -2.355752 | 2.566434 |
| 17 | 1 | -2.551250 | -2.494468 | 0.080504 |

Gauche-out biradical with methylene twisted 120° anticlockwise **19**

(8,8) active space

-270.86475

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | 1.323828 | .613099 | .410958 |
| 2 | 1 | 1.107862 | 1.174241 | 1.318266 |
| 3 | 1 | 2.310717 | .179126 | .546740 |
| 4 | 6 | 1.259725 | 1.506098 | -.804254 |
| 5 | 6 | .243368 | -.478507 | .156907 |
| 6 | 6 | .225434 | 1.094383 | -1.652144 |
| 7 | 6 | -.407482 | -.043782 | -1.137525 |
| 8 | 6 | -1.741245 | -1.751540 | 1.156210 |
| 9 | 6 | -.762788 | -.631023 | 1.346615 |
| 10 | 1 | 1.893923 | 2.357991 | -.955277 |
| 11 | 1 | .722936 | -1.446182 | .018664 |
| 12 | 1 | -.045148 | 1.585105 | -2.569290 |
| 13 | 1 | -1.231059 | -.561715 | -1.590516 |
| 14 | 1 | -1.388788 | -2.707231 | .808592 |
| 15 | 1 | -1.292731 | .308278 | 1.482644 |
| 16 | 1 | -2.663406 | -1.754061 | 1.708756 |
| 17 | 1 | -.184902 | -.794460 | 2.258207 |

Transition state for forming twisted biradical (120° clock) with HA-C6-C5-HB frozen) **20**

(8,8) active space

-270.86348

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -.502598 | .248745 | .468177 |
| 2 | 1 | -.493605 | .249828 | 1.553627 |
| 3 | 1 | .537504 | .261854 | .148995 |
| 4 | 6 | -1.245288 | 1.431873 | -.105623 |
| 5 | 6 | -1.239991 | -.991636 | -.113380 |
| 6 | 6 | -2.163855 | 1.001846 | -1.068608 |
| 7 | 6 | -2.176824 | -.399020 | -1.138728 |
| 8 | 6 | -3.041158 | -1.088501 | 1.741631 |
| 9 | 6 | -1.996621 | -1.843239 | .973191 |
| 10 | 1 | -1.031420 | 2.452967 | .144487 |
| 11 | 1 | -.531393 | -1.666433 | -.585770 |
| 12 | 1 | -2.776586 | 1.653168 | -1.664880 |
| 13 | 1 | -2.798008 | -.988808 | -1.786512 |
| 14 | 1 | -3.423524 | -.155712 | 1.374569 |
| 15 | 1 | -2.449298 | -2.691990 | .460281 |
| 16 | 1 | -3.182746 | -1.288203 | 2.787900 |
| 17 | 1 | -1.261603 | -2.264839 | 1.655760 |

Transition state for forming twisted biradical (120° anticlock) with HA-C6-C5-HB frozen) **21**

(8,8) active space

-270.86236

| | | | | |
|---|---|-----------|-----------|-----------|
| 1 | 6 | -.533193 | .286672 | .481004 |
| 2 | 1 | -.691650 | .388400 | 1.552282 |
| 3 | 1 | .540569 | .198010 | .340038 |
| 4 | 6 | -1.103137 | 1.465991 | -.270021 |
| 5 | 6 | -1.286385 | -.949227 | -.095203 |
| 6 | 6 | -2.126287 | 1.047352 | -1.127274 |
| 7 | 6 | -2.290150 | -.342427 | -1.052408 |
| 8 | 6 | -3.074770 | -1.205147 | 1.740389 |
| 9 | 6 | -1.949937 | -1.864278 | .990321 |

| | | | | |
|----|---|-----------|-----------|-----------|
| 10 | 1 | -.779982 | 2.479039 | -.127880 |
| 11 | 1 | -.585095 | -1.573437 | -.645391 |
| 12 | 1 | -2.705148 | 1.701532 | -1.753436 |
| 13 | 1 | -2.999269 | -.921825 | -1.613432 |
| 14 | 1 | -4.033081 | -1.684523 | 1.811590 |
| 15 | 1 | -2.316241 | -2.763248 | .502120 |
| 16 | 1 | -3.053788 | -.148442 | 1.932051 |
| 17 | 1 | -1.171993 | -2.191545 | 1.680890 |

Transition state between two twisted biradicals (with HA-C6-C5-HB frozen) **22**
(8,8) active space

-270.86218

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -1.122514 | -1.175383 | -1.229556 |
| 2 | 6 | -.113755 | -.454905 | -1.880509 |
| 3 | 1 | .510511 | 1.577546 | -1.431028 |
| 4 | 1 | .284355 | -.673478 | -2.852468 |
| 5 | 1 | -.584137 | .764830 | 2.413449 |
| 6 | 6 | -1.369512 | -.631711 | .037394 |
| 7 | 1 | 2.063765 | -.583301 | 1.753254 |
| 8 | 6 | -.526239 | .607246 | .255536 |
| 9 | 1 | 1.453278 | .336828 | -.647756 |
| 10 | 1 | -2.107316 | -.979277 | .736306 |
| 11 | 1 | .802395 | 1.541732 | 1.695314 |
| 12 | 1 | .644137 | -1.320209 | 2.631573 |
| 13 | 1 | -1.634497 | -2.023796 | -1.645710 |
| 14 | 6 | 1.007324 | -.576088 | 1.947745 |
| 15 | 6 | .183429 | .648205 | 1.652495 |
| 16 | 1 | -1.165153 | 1.487889 | .198141 |
| 17 | 6 | .444098 | .601742 | -.958751 |

Transition state for CH₂ inversion from gauche-in to gauche-in 120° clock twisted biradical **23**
(8,8) active space

-270.86264

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -1.056280 | -1.195082 | -1.197741 |
| 2 | 6 | -.053789 | -.464772 | -1.844726 |
| 3 | 1 | .430693 | 1.613242 | -1.454377 |
| 4 | 1 | .367047 | -.693076 | -2.804809 |
| 5 | 1 | -.574296 | .816858 | 2.426171 |
| 6 | 6 | -1.346568 | -.627354 | .050377 |
| 7 | 1 | 1.774352 | -.899447 | 1.352275 |
| 8 | 6 | -.528950 | .629102 | .266677 |
| 9 | 1 | 1.466624 | .472181 | -.646130 |
| 10 | 1 | -2.088120 | -.979316 | .742792 |
| 11 | 1 | .833890 | 1.537203 | 1.694654 |
| 12 | 1 | .682440 | -1.222490 | 2.790474 |
| 13 | 1 | -1.534514 | -2.068446 | -1.602255 |
| 14 | 6 | .957845 | -.584335 | 1.973646 |
| 15 | 6 | .182880 | .663771 | 1.662610 |
| 16 | 1 | -1.180723 | 1.500129 | .218673 |
| 17 | 6 | .437637 | .649701 | -.952880 |

Transition state for CH₂ inversion from gauche-in to gauche-in 120° anticlock twisted biradical **24**
(8,8) active space
-270.86371

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -1.071252 | -1.190592 | -1.141513 |
| 2 | 6 | .045066 | -.577480 | -1.719807 |
| 3 | 1 | .308793 | 1.555402 | -1.551378 |
| 4 | 1 | .552678 | -.907318 | -2.605445 |
| 5 | 1 | -.611913 | .611726 | 2.431426 |
| 6 | 6 | -1.474034 | -.490669 | .003822 |
| 7 | 1 | 2.093006 | -.497179 | 2.075111 |
| 8 | 6 | -.554368 | .677417 | .267792 |
| 9 | 1 | 1.460550 | .634627 | -.624175 |
| 10 | 1 | -2.301619 | -.748903 | .638114 |
| 11 | 1 | .746855 | 1.505737 | 1.806097 |
| 12 | 1 | .657814 | -1.591689 | 1.735692 |
| 13 | 1 | -1.551538 | -2.072764 | -1.524069 |
| 14 | 6 | 1.047515 | -.599335 | 1.858042 |
| 15 | 6 | .167821 | .596936 | 1.670279 |
| 16 | 1 | -1.123942 | 1.603439 | .279112 |
| 17 | 6 | .423005 | .661134 | -.943197 |

Transition state for CH₂ inversion between twisted biradicals **25**
(8,8) active space
-270.86386

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -.501615 | .272092 | .458630 |
| 2 | 1 | -.549794 | .320764 | 1.542707 |
| 3 | 1 | .553743 | .238881 | .198675 |
| 4 | 6 | -1.181736 | 1.453952 | -.190775 |
| 5 | 6 | -1.254087 | -.971824 | -.101360 |
| 6 | 6 | -2.157216 | 1.017927 | -1.091893 |
| 7 | 6 | -2.234965 | -.382739 | -1.089757 |
| 8 | 6 | -3.029088 | -1.117587 | 1.755795 |
| 9 | 6 | -1.956233 | -1.840486 | .998209 |
| 10 | 1 | -.918273 | 2.476037 | .001326 |
| 11 | 1 | -.554240 | -1.628548 | -.611957 |
| 12 | 1 | -2.764450 | 1.665879 | -1.697368 |
| 13 | 1 | -2.902238 | -.975100 | -1.687260 |
| 14 | 1 | -3.273672 | -.094639 | 1.548759 |
| 15 | 1 | -2.376987 | -2.719787 | .510647 |
| 16 | 1 | -3.479100 | -1.574706 | 2.617224 |
| 17 | 1 | -1.197063 | -2.218216 | 1.683514 |

Transition state leading to tricyclo[3.2.1.0^{3,7}]heptane **26**
(8,8) active space
-270.79924

| | | | | |
|---|---|-----------|-----------|-----------|
| 1 | 6 | 1.475999 | .376160 | .238148 |
| 2 | 1 | 1.886554 | .210300 | 1.228599 |
| 3 | 1 | 2.300084 | .634258 | -.429641 |
| 4 | 6 | .427630 | 1.464900 | .169935 |
| 5 | 6 | .729033 | -.843196 | -.327801 |
| 6 | 6 | -.602988 | .957927 | -.804192 |
| 7 | 6 | -.105518 | -.217264 | -1.431783 |
| 8 | 6 | -1.316199 | -.056776 | .786233 |
| 9 | 6 | -.365812 | -1.248234 | .736529 |

| | | | | |
|----|---|-----------|-----------|-----------|
| 10 | 1 | .191021 | 2.120950 | .984903 |
| 11 | 1 | 1.377457 | -1.663644 | -.609231 |
| 12 | 1 | -1.359577 | 1.600750 | -1.218693 |
| 13 | 1 | -.669695 | -.794885 | -2.141491 |
| 14 | 1 | -2.307364 | -.226996 | .400898 |
| 15 | 1 | -.886472 | -2.142533 | .409407 |
| 16 | 1 | -1.348915 | .500412 | 1.707008 |
| 17 | 1 | .074703 | -1.456036 | 1.706554 |

Metastable biradical with Hs flipped up (C1-C3 bondlength constrained to 2.3 Å) 27

(8,8) active space

-270.84269

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | 1.508334 | .368493 | .249489 |
| 2 | 1 | 1.801804 | .217595 | 1.286853 |
| 3 | 1 | 2.418915 | .550008 | -.314894 |
| 4 | 6 | .500241 | 1.487889 | .070860 |
| 5 | 6 | .734450 | -.842603 | -.333339 |
| 6 | 6 | -.779781 | .859145 | -.450284 |
| 7 | 6 | -1.105429 | -.177009 | -1.395868 |
| 8 | 6 | -1.392254 | -.079843 | .664806 |
| 9 | 6 | -.378083 | -1.254968 | .718864 |
| 10 | 1 | .555720 | 2.441310 | .562658 |
| 11 | 1 | 1.364477 | -1.667465 | -.639906 |
| 12 | 1 | -1.485303 | 1.548628 | -.894779 |
| 13 | 1 | -.580139 | -.662489 | -2.229384 |
| 14 | 1 | -2.381025 | -.420883 | .373700 |
| 15 | 1 | -.841092 | -2.188715 | .417800 |
| 16 | 1 | -1.486350 | .440537 | 1.612437 |
| 17 | 1 | .045456 | -1.403532 | 1.706372 |

Metastable biradical with Hs flipped down (C1-C3 bondlength constrained to 2.3 Å) 28

(8,8) active space

-270.85456

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | 1.451616 | .324669 | .259823 |
| 2 | 1 | 1.813971 | .202546 | 1.278892 |
| 3 | 1 | 2.319584 | .506896 | -.365919 |
| 4 | 6 | .412840 | 1.455683 | .122134 |
| 5 | 6 | .661129 | -.885958 | -.286525 |
| 6 | 6 | -.885576 | .809847 | -.349516 |
| 7 | 6 | -.222923 | -.206134 | -1.335319 |
| 8 | 6 | -1.433503 | -.148789 | .763917 |
| 9 | 6 | -.407623 | -1.312572 | .784342 |
| 10 | 1 | .716422 | 2.420068 | -.251047 |
| 11 | 1 | 1.281748 | -1.704062 | -.629060 |
| 12 | 1 | -1.614547 | 1.497833 | -.753629 |
| 13 | 1 | .165733 | .101861 | -2.293476 |
| 14 | 1 | -2.422421 | -.501435 | .490673 |
| 15 | 1 | -.871296 | -2.249010 | .493882 |
| 16 | 1 | -1.510064 | .362562 | 1.716912 |
| 17 | 1 | .044849 | -1.457911 | 1.759298 |

Transition state for cleaving methylene bridge **29**

(6,6) active space

-270.84568

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | .609094 | 1.248886 | 2.118464 |
| 2 | 6 | .401225 | .607737 | 1.281563 |
| 3 | 6 | .652049 | -.745399 | 1.285142 |
| 4 | 6 | -.331339 | 1.109065 | .058590 |
| 5 | 1 | 1.027689 | -1.254776 | 2.156171 |
| 6 | 6 | .293282 | -1.485465 | .104139 |
| 7 | 1 | -2.415696 | .824392 | -.699673 |
| 8 | 1 | -.399162 | 2.195986 | .072941 |
| 9 | 1 | 1.426633 | 1.085308 | -1.180568 |
| 10 | 1 | .233530 | -2.559105 | .157950 |
| 11 | 6 | .425373 | .666421 | -1.207288 |
| 12 | 6 | -1.717907 | .503655 | .058916 |
| 13 | 1 | 1.445045 | -1.187546 | -1.668634 |
| 14 | 1 | -.058438 | 1.058750 | -2.097485 |
| 15 | 1 | -2.151211 | .185039 | .989042 |
| 16 | 6 | .483495 | -.872021 | -1.264507 |
| 17 | 1 | -.267960 | -1.263230 | -1.941750 |

Transition state for methylene torsion leading to inversion of stereochemistry at C7 **30**

(6,6) active space

-270.85507

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 0.061465 | 0.878908 | 2.292681 |
| 2 | 6 | 0.180864 | 0.390426 | 1.341702 |
| 3 | 6 | 0.802707 | -0.859739 | 1.269378 |
| 4 | 6 | -0.382895 | 1.063920 | 0.109272 |
| 5 | 1 | 1.180997 | -1.307233 | 2.173014 |
| 6 | 6 | 0.938498 | -1.553084 | 0.057214 |
| 7 | 1 | -2.415670 | 1.471067 | -0.729734 |
| 8 | 1 | -0.179406 | 2.132555 | 0.192319 |
| 9 | 1 | 1.362685 | 0.951266 | -1.137633 |
| 10 | 1 | 1.381217 | -2.532291 | 0.043223 |
| 11 | 6 | 0.348091 | 0.562182 | -1.152298 |
| 12 | 6 | -1.879080 | 0.894060 | 0.003559 |
| 13 | 1 | 1.034790 | -1.269722 | -2.060513 |
| 14 | 1 | -0.132988 | 0.960670 | -2.040985 |
| 15 | 1 | -2.447629 | 0.504754 | 0.827535 |
| 16 | 6 | 0.408830 | -0.967713 | -1.225060 |
| 17 | 1 | -0.583404 | -1.367481 | -1.429943 |

Biradical leading to bicyclo[4.1.0]hept-2-ene (C1-C7 bondlength constrained to 2.5 Å) **31**

(6,6) active space

-270.86227

| | | | | |
|---|---|-----------|-----------|-----------|
| 1 | 1 | -0.055989 | 0.989180 | 2.258079 |
| 2 | 6 | 0.124649 | 0.492949 | 1.321570 |
| 3 | 6 | 0.654937 | -0.827617 | 1.307198 |
| 4 | 6 | -0.380753 | 1.146775 | 0.036383 |
| 5 | 1 | 0.940969 | -1.276891 | 2.243303 |
| 6 | 6 | 0.831125 | -1.533675 | 0.133688 |
| 7 | 1 | -2.279292 | -0.028214 | -0.274680 |
| 8 | 1 | -0.183904 | 2.213566 | 0.085335 |
| 9 | 1 | 1.405780 | 0.943997 | -1.122564 |

| | | | | |
|----|---|-----------|-----------|-----------|
| 10 | 1 | 1.223315 | -2.534609 | 0.161607 |
| 11 | 6 | 0.383429 | 0.578362 | -1.169438 |
| 12 | 6 | -1.897078 | 0.958674 | -0.073321 |
| 13 | 1 | 1.107227 | -1.285365 | -1.970773 |
| 14 | 1 | -0.048636 | 0.956041 | -2.091268 |
| 15 | 1 | -2.529835 | 1.579172 | 0.539431 |
| 16 | 6 | 0.420352 | -0.955888 | -1.195774 |
| 17 | 1 | -0.554048 | -1.353239 | -1.477019 |

Transition state for interconversion of bicyclo[4.1.0]hept-2-ene and tricyclo[3.2.1.0^{3,7}]heptane 32
(6,6) active space

-270.78599

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 0.609206 | -0.671818 | -2.267416 |
| 2 | 6 | 0.620358 | -0.322240 | -1.246226 |
| 3 | 6 | -0.194751 | 0.969013 | -0.973982 |
| 4 | 6 | -0.053398 | -1.220417 | -0.224131 |
| 5 | 1 | -0.540765 | 1.581642 | -1.789753 |
| 6 | 6 | -0.042435 | 1.527331 | 0.309823 |
| 7 | 6 | -1.309501 | -0.555767 | -0.706684 |
| 8 | 6 | 0.288740 | -0.833401 | 1.219519 |
| 9 | 1 | 0.022957 | -2.283737 | -0.406845 |
| 10 | 1 | -0.623208 | 2.376737 | 0.619989 |
| 11 | 6 | 0.679696 | 0.664105 | 1.311423 |
| 12 | 1 | -2.061818 | -0.201976 | -0.024535 |
| 13 | 1 | 0.556952 | 1.028737 | 2.325579 |
| 14 | 1 | 1.113853 | -1.439589 | 1.582403 |
| 15 | 1 | -0.565163 | -1.050117 | 1.856967 |
| 16 | 1 | 1.744048 | 0.724662 | 1.077011 |
| 17 | 1 | -1.721794 | -0.946845 | -1.621728 |

Biradical with Hs flipped up 33

(6,6) active space

-270.80127

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 1.059557 | -0.665760 | -2.175815 |
| 2 | 6 | 0.785224 | -0.310472 | -1.195754 |
| 3 | 6 | -0.268784 | 0.831675 | -1.052181 |
| 4 | 6 | -0.051260 | -1.174604 | -0.261013 |
| 5 | 1 | -0.465624 | 1.485614 | -1.892146 |
| 6 | 6 | -0.120686 | 1.532673 | 0.265371 |
| 7 | 6 | -1.272790 | -0.397349 | -0.798051 |
| 8 | 6 | 0.213554 | -0.799055 | 1.206125 |
| 9 | 1 | -0.040881 | -2.247466 | -0.412099 |
| 10 | 1 | -0.915657 | 2.200567 | 0.556658 |
| 11 | 6 | 0.567865 | 0.706171 | 1.324674 |
| 12 | 1 | -2.101686 | -0.212961 | -0.122343 |
| 13 | 1 | 0.356615 | 1.075869 | 2.322248 |
| 14 | 1 | 1.030251 | -1.393175 | 1.606023 |
| 15 | 1 | -0.667832 | -1.035408 | 1.797296 |
| 16 | 1 | 1.641840 | 0.803525 | 1.173155 |
| 17 | 1 | -1.644298 | -0.809751 | -1.728375 |

Transition state for closure of biradical **34**

(6,6) active space

-270.79855

| | | | | |
|----|---|----------|-----------|-----------|
| 1 | 1 | 1.392196 | -0.576701 | -2.217449 |
| 2 | 6 | 1.638330 | -0.975722 | -1.248389 |
| 3 | 6 | 1.996346 | -2.469481 | -0.998012 |
| 4 | 6 | 2.871985 | -0.585932 | -0.451950 |
| 5 | 1 | 1.766331 | -3.206156 | -1.757027 |
| 6 | 1 | 1.292275 | -3.853574 | 0.619864 |
| 7 | 6 | 3.491556 | -1.941815 | -0.870957 |
| 8 | 6 | 2.552408 | -0.591763 | 1.050848 |
| 9 | 1 | 3.401763 | 0.317467 | -0.732714 |
| 10 | 6 | 1.478920 | -2.824818 | 0.366785 |
| 11 | 6 | 1.708874 | -1.828191 | 1.482547 |
| 12 | 1 | 4.140188 | -2.443399 | -0.158116 |
| 13 | 1 | 2.191606 | -2.324295 | 2.320661 |
| 14 | 1 | 2.021374 | 0.320341 | 1.303777 |
| 15 | 1 | 3.487428 | -0.569618 | 1.603827 |
| 16 | 1 | 0.746913 | -1.491844 | 1.862865 |
| 17 | 1 | 3.978320 | -1.890376 | -1.838493 |

Biradical with Hs flipped down (C2-C7 bondlength constrained) **35**

(6,6) active space

-270.81481

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 1.779055 | -0.427938 | -1.427818 |
| 2 | 6 | 0.701985 | -0.444694 | -1.331972 |
| 3 | 6 | -0.267202 | 0.804114 | -1.094792 |
| 4 | 6 | -0.097255 | -1.178149 | -0.261038 |
| 5 | 1 | -0.513595 | 1.460208 | -1.918490 |
| 6 | 1 | 1.012585 | 2.288983 | 0.000642 |
| 7 | 6 | -1.308418 | -0.295473 | -0.642992 |
| 8 | 6 | 0.410081 | -0.819563 | 1.146892 |
| 9 | 1 | -0.199352 | -2.252705 | -0.376364 |
| 10 | 6 | 0.263617 | 1.526881 | 0.141359 |
| 11 | 6 | 0.284761 | 0.708536 | 1.417721 |
| 12 | 1 | -2.016631 | -0.029535 | 0.134135 |
| 13 | 1 | -0.641896 | 0.887982 | 1.958981 |
| 14 | 1 | 1.450581 | -1.121750 | 1.235522 |
| 15 | 1 | -0.142491 | -1.375864 | 1.900568 |
| 16 | 1 | 1.080863 | 1.038327 | 2.077067 |
| 17 | 1 | -1.838974 | -0.692717 | -1.499787 |

 $^1(\pi\pi^*)/S_0$ conical intersection **36**

(8,8) active space

-270.78265/-270.78271

| | | | | |
|---|---|-----------|-----------|-----------|
| 1 | 6 | 1.482195 | 0.381789 | 0.265697 |
| 2 | 1 | 1.764966 | 0.231095 | 1.303711 |
| 3 | 1 | 2.397561 | 0.566244 | -0.293972 |
| 4 | 6 | 0.498828 | 1.510847 | 0.077103 |
| 5 | 6 | 0.717013 | -0.821002 | -0.329087 |
| 6 | 6 | -0.572515 | 1.040402 | -0.764202 |
| 7 | 6 | -0.088273 | -0.187703 | -1.434530 |
| 8 | 6 | -1.437948 | -0.192914 | 0.836103 |
| 9 | 6 | -0.391717 | -1.284601 | 0.721701 |

| | | | | |
|----|---|-----------|-----------|-----------|
| 10 | 1 | 0.464022 | 2.394041 | 0.681142 |
| 11 | 1 | 1.358432 | -1.647763 | -0.609292 |
| 12 | 1 | -1.352358 | 1.678825 | -1.136970 |
| 13 | 1 | -0.699563 | -0.764092 | -2.108363 |
| 14 | 1 | -2.408254 | -0.379160 | 0.407647 |
| 15 | 1 | -0.836656 | -2.209355 | 0.368344 |
| 16 | 1 | -1.469430 | 0.393386 | 1.739872 |
| 17 | 1 | 0.073636 | -1.493941 | 1.680481 |

 $I(\pi\pi^*)/S_0$ conical intersection 37

(6,6) active space

-270.75242/-270.75246

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 1.262001 | -0.719697 | -2.066064 |
| 2 | 6 | 0.927167 | -0.338098 | -1.121430 |
| 3 | 6 | 0.233001 | 0.949968 | -1.069029 |
| 4 | 6 | 0.061870 | -1.193105 | -0.217754 |
| 5 | 1 | 0.195358 | 1.614594 | -1.921624 |
| 6 | 6 | -0.112688 | 1.451850 | 0.255921 |
| 7 | 6 | -1.253114 | -0.614532 | -0.714558 |
| 8 | 6 | 0.308456 | -0.845732 | 1.255581 |
| 9 | 1 | 0.164348 | -2.259916 | -0.384992 |
| 10 | 1 | -0.765379 | 2.288485 | 0.387284 |
| 11 | 6 | 0.443085 | 0.693173 | 1.428786 |
| 12 | 1 | -2.062539 | -0.375311 | -0.036253 |
| 13 | 1 | -0.000429 | 1.023853 | 2.360018 |
| 14 | 1 | 1.220256 | -1.328883 | 1.593572 |
| 15 | 1 | -0.502056 | -1.234071 | 1.864613 |
| 16 | 1 | 1.506549 | 0.925203 | 1.487055 |
| 17 | 1 | -1.559838 | -0.901411 | -1.711532 |

Second-order saddle point on S_1 38

(8,8) active space

-270.64979

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 1.059583 | 1.413217 | 1.969880 |
| 2 | 6 | .536725 | .777730 | 1.287941 |
| 3 | 6 | .534711 | -.777115 | 1.288950 |
| 4 | 6 | -.289637 | 1.144212 | .134217 |
| 5 | 1 | 1.070198 | -1.413397 | 1.960391 |
| 6 | 6 | -.292841 | -1.143169 | .136723 |
| 7 | 1 | -1.943461 | .001242 | -.785689 |
| 8 | 1 | -.647375 | 2.166548 | .139750 |
| 9 | 1 | 1.461042 | 1.196471 | -1.253276 |
| 10 | 1 | -.652441 | -2.164867 | .142362 |
| 11 | 6 | .464809 | .774124 | -1.232766 |
| 12 | 6 | -1.351609 | .001712 | .124405 |
| 13 | 1 | 1.458769 | -1.200812 | -1.250836 |
| 14 | 1 | -.094597 | 1.182765 | -2.070158 |
| 15 | 1 | -1.998020 | .003615 | .990438 |
| 16 | 6 | .463420 | -.776375 | -1.231377 |
| 17 | 1 | -.096735 | -1.185900 | -2.067835 |

(6,6) active space

-270.63283

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 1 | 1.064560 | 1.410198 | 1.955543 |
| 2 | 6 | .527019 | .772874 | 1.286819 |
| 3 | 6 | .536201 | -.780622 | 1.284132 |
| 4 | 6 | -.285353 | 1.141429 | .117164 |
| 5 | 1 | 1.077005 | -1.414708 | 1.953685 |
| 6 | 6 | -.272319 | -1.154519 | .122913 |
| 7 | 1 | -1.955283 | .003688 | -.791538 |
| 8 | 1 | -.634966 | 2.167022 | .132491 |
| 9 | 1 | 1.453152 | 1.195242 | -1.238422 |
| 10 | 1 | -.630718 | -2.176763 | .132493 |
| 11 | 6 | .455011 | .776695 | -1.211693 |
| 12 | 6 | -1.365957 | .020836 | .119753 |
| 13 | 1 | 1.456046 | -1.195985 | -1.245512 |
| 14 | 1 | -.094966 | 1.174629 | -2.061232 |
| 15 | 1 | -2.005189 | .020855 | .990337 |
| 16 | 6 | .457260 | -.779238 | -1.210449 |
| 17 | 1 | -.098964 | -1.181631 | -2.053366 |

Third-order saddle point for cleaving C1-C6 bond 39

(8,8) active space

-270.64122

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -1.347239 | .002520 | .129238 |
| 2 | 1 | -1.938582 | .093038 | -.774701 |
| 3 | 1 | -1.996854 | -.024136 | .994169 |
| 4 | 6 | -.295237 | 1.126947 | .265581 |
| 5 | 6 | -.332279 | -1.162882 | .116237 |
| 6 | 6 | .578450 | .754848 | 1.320038 |
| 7 | 6 | .611235 | -.764370 | 1.192259 |
| 8 | 6 | .581092 | .586963 | -1.304834 |
| 9 | 6 | .333017 | -.926019 | -1.301235 |
| 10 | 1 | -.563078 | 2.159711 | .103857 |
| 11 | 1 | -.751988 | -2.160186 | .208756 |
| 12 | 1 | .919374 | 1.356957 | 2.140682 |
| 13 | 1 | 1.249234 | -1.423879 | 1.743521 |
| 14 | 1 | 1.601494 | .911411 | -1.198557 |
| 15 | 1 | 1.263779 | -1.472962 | -1.391992 |
| 16 | 1 | .057061 | 1.160715 | -2.055744 |
| 17 | 1 | -.327501 | -1.228214 | -2.113676 |

Transition state for the anti addition of S₁ cyclopentadiene to ethylene 40

(8,8) active space

-270.73389

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -.415927 | .351252 | -.025062 |
| 2 | 1 | -.825732 | .534521 | .966675 |
| 3 | 1 | .660741 | .508911 | .060326 |
| 4 | 6 | -1.016664 | 1.237457 | -1.084179 |
| 5 | 6 | -.729475 | -1.056967 | -.534668 |
| 6 | 6 | -1.377472 | .423633 | -2.249237 |
| 7 | 6 | -1.125743 | -.942836 | -1.913060 |
| 8 | 6 | -2.070081 | -1.713633 | 1.955766 |
| 9 | 6 | -2.356901 | -1.681019 | .528031 |
| 10 | 1 | -.924066 | 2.306152 | -1.091769 |

| | | | | |
|----|---|-----------|-----------|-----------|
| 11 | 1 | -.079375 | -1.863157 | -.238424 |
| 12 | 1 | -1.765131 | .793647 | -3.176666 |
| 13 | 1 | -1.288033 | -1.778257 | -2.567832 |
| 14 | 1 | -2.251370 | -.855734 | 2.574747 |
| 15 | 1 | -3.082572 | -.950074 | .211162 |
| 16 | 1 | -1.487996 | -2.511139 | 2.378726 |
| 17 | 1 | -2.505366 | -2.640608 | .058481 |

Anti biradical on S₁ 41

(8,8) active space

-270.74949

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -.760105 | .480677 | -.003103 |
| 2 | 1 | -1.599100 | .971896 | .492653 |
| 3 | 1 | .072943 | .509524 | .691917 |
| 4 | 6 | -.454816 | 1.167284 | -1.309150 |
| 5 | 6 | -1.154505 | -.966298 | -.394002 |
| 6 | 6 | -1.114625 | .436892 | -2.401513 |
| 7 | 6 | -1.636653 | -.844382 | -1.817882 |
| 8 | 6 | -1.722617 | -1.786538 | 1.975122 |
| 9 | 6 | -2.208447 | -1.627111 | .566598 |
| 10 | 1 | -.171336 | 2.201053 | -1.372119 |
| 11 | 1 | -.259343 | -1.589686 | -.372875 |
| 12 | 1 | -.933886 | .605387 | -3.445190 |
| 13 | 1 | -1.944041 | -1.687708 | -2.407546 |
| 14 | 1 | -.997328 | -2.547443 | 2.203815 |
| 15 | 1 | -3.111319 | -1.023245 | .547538 |
| 16 | 1 | -1.787475 | -.964831 | 2.665262 |
| 17 | 1 | -2.468857 | -2.600289 | .157736 |

Transition state for the gauche-out addition of S₁ cyclopentadiene to ethylene 42

(8,8) active space

-270.73307

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | 1.425573 | .572056 | .363848 |
| 2 | 1 | 1.375704 | .864738 | 1.409190 |
| 3 | 1 | 2.464811 | .301375 | .169687 |
| 4 | 6 | .968500 | 1.668420 | -.570961 |
| 5 | 6 | .488491 | -.596497 | .027912 |
| 6 | 6 | .100538 | 1.077529 | -1.598417 |
| 7 | 6 | -.104881 | -.317114 | -1.250256 |
| 8 | 6 | -1.933223 | -1.547224 | 1.201873 |
| 9 | 6 | -.901605 | -.556829 | 1.427634 |
| 10 | 1 | 1.520041 | 2.579082 | -.711714 |
| 11 | 1 | .849130 | -1.594097 | .218254 |
| 12 | 1 | -.292264 | 1.585337 | -2.455605 |
| 13 | 1 | -.705313 | -1.009376 | -1.807950 |
| 14 | 1 | -2.760596 | -1.336675 | .550066 |
| 15 | 1 | -1.223444 | .470300 | 1.361021 |
| 16 | 1 | -1.768230 | -2.577139 | 1.460833 |
| 17 | 1 | -.274543 | -.733896 | 2.288703 |

Gauche-out biradical on S₁ 43

(8,8) active space

-270.74952

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | 1.225164 | 0.700586 | 0.444216 |
| 2 | 1 | 0.836438 | 1.429020 | 1.157740 |
| 3 | 1 | 2.132167 | 0.291181 | 0.878656 |
| 4 | 6 | 1.457538 | 1.355337 | -0.892477 |
| 5 | 6 | 0.158285 | -0.391057 | 0.176884 |
| 6 | 6 | 0.285337 | 1.115146 | -1.746537 |
| 7 | 6 | -0.573485 | 0.101270 | -1.046738 |
| 8 | 6 | -1.735330 | -1.788399 | 1.217719 |
| 9 | 6 | -0.759580 | -0.670336 | 1.421994 |
| 10 | 1 | 2.134006 | 2.177823 | -1.029923 |
| 11 | 1 | 0.668350 | -1.324432 | -0.065764 |
| 12 | 1 | 0.211982 | 1.377731 | -2.783125 |
| 13 | 1 | -1.349265 | -0.457371 | -1.534858 |
| 14 | 1 | -2.671992 | -1.605200 | 0.723489 |
| 15 | 1 | -1.288879 | 0.246286 | 1.666267 |
| 16 | 1 | -1.389571 | -2.806771 | 1.231428 |
| 17 | 1 | -0.112476 | -0.900825 | 2.265146 |

Gauche-in biradical on S₁ 44

(8,8) active space

-270.74815

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | -.684001 | .363700 | .536930 |
| 2 | 1 | -1.145242 | .634365 | 1.486491 |
| 3 | 1 | .363792 | .164747 | .741475 |
| 4 | 6 | -.886992 | 1.469240 | -.467849 |
| 5 | 6 | -1.402158 | -.864473 | -.074867 |
| 6 | 6 | -2.061972 | 1.147291 | -1.289879 |
| 7 | 6 | -2.457551 | -.267146 | -.972619 |
| 8 | 6 | -2.964970 | -1.390861 | 1.930494 |
| 9 | 6 | -1.936621 | -1.910759 | .972026 |
| 10 | 1 | -.535203 | 2.471396 | -.308151 |
| 11 | 1 | -.684538 | -1.400147 | -.699168 |
| 12 | 1 | -2.395728 | 1.708862 | -2.139535 |
| 13 | 1 | -3.086158 | -.862307 | -1.609231 |
| 14 | 1 | -3.944973 | -1.131361 | 1.574189 |
| 15 | 1 | -2.353396 | -2.744478 | .411092 |
| 16 | 1 | -2.671691 | -.981022 | 2.879209 |
| 17 | 1 | -1.084155 | -2.300831 | 1.521416 |

Transition state from gauche-in biradical to conical intersection 45

(8,8) active space

-270.74722

| | | | | |
|---|---|-----------|-----------|-----------|
| 1 | 6 | 1.083230 | 0.482415 | 0.423974 |
| 2 | 1 | 0.808463 | 0.263754 | 1.453683 |
| 3 | 1 | 1.816760 | 1.284003 | 0.471052 |
| 4 | 6 | -0.122292 | 0.885925 | -0.381086 |
| 5 | 6 | 1.669334 | -0.777033 | -0.275424 |
| 6 | 6 | -0.423118 | -0.106332 | -1.421030 |
| 7 | 6 | 0.748004 | -1.046899 | -1.432458 |
| 8 | 6 | 0.562748 | -2.500339 | 1.326693 |
| 9 | 6 | 1.832377 | -2.017814 | 0.693969 |

| | | | | |
|----|---|-----------|-----------|-----------|
| 10 | 1 | -0.800504 | 1.656948 | -0.069624 |
| 11 | 1 | 2.670079 | -0.560934 | -0.644348 |
| 12 | 1 | -1.025074 | 0.100488 | -2.285933 |
| 13 | 1 | 0.842054 | -1.897776 | -2.079785 |
| 14 | 1 | -0.207975 | -2.936073 | 0.717707 |
| 15 | 1 | 2.280283 | -2.821617 | 0.113658 |
| 16 | 1 | 0.272505 | -2.160949 | 2.303485 |
| 17 | 1 | 2.550998 | -1.749226 | 1.463242 |

Transition state between gauche-in and anti biradicals on S₁ 46
(8,8) active space

-270.74071

| | | | | |
|----|---|-----------|-----------|----------|
| 1 | 6 | -1.223985 | -.741562 | -.041296 |
| 2 | 1 | -1.754564 | -.031304 | -.664623 |
| 3 | 1 | -.896733 | -1.547767 | -.698233 |
| 4 | 6 | -2.078509 | -1.301951 | 1.067174 |
| 5 | 6 | .013988 | -.127642 | .665923 |
| 6 | 6 | -1.229885 | -1.529903 | 2.245933 |
| 7 | 6 | .101172 | -.905557 | 1.950706 |
| 8 | 6 | -1.310985 | 2.169143 | .503758 |
| 9 | 6 | -.064492 | 1.468153 | .940867 |
| 10 | 1 | -2.987813 | -1.842293 | .879937 |
| 11 | 1 | .900600 | -.282878 | .060759 |
| 12 | 1 | -1.578818 | -1.822218 | 3.216177 |
| 13 | 1 | .864932 | -.742918 | 2.687549 |
| 14 | 1 | -2.220939 | 2.044939 | 1.062720 |
| 15 | 1 | .075499 | 1.626168 | 2.005124 |
| 16 | 1 | -1.417038 | 2.499404 | -.513958 |
| 17 | 1 | .788698 | 1.921627 | .446974 |

Transition state between gauche-in and gauche-out biradicals on S₁ 47
(8,8) active space

-270.74204

| | | | | |
|----|---|-----------|-----------|-----------|
| 1 | 6 | 1.421865 | -0.317835 | -0.010446 |
| 2 | 1 | 1.719677 | 0.509887 | -0.655888 |
| 3 | 1 | 2.207452 | -0.438506 | 0.729263 |
| 4 | 6 | 1.191198 | -1.554146 | -0.841584 |
| 5 | 6 | 0.047731 | -0.007454 | 0.634727 |
| 6 | 6 | -0.240899 | -1.622875 | -1.164658 |
| 7 | 6 | -0.946718 | -0.577256 | -0.350376 |
| 8 | 6 | -1.336001 | 2.200842 | 0.419543 |
| 9 | 6 | -0.145814 | 1.523298 | 1.030778 |
| 10 | 1 | 1.954217 | -1.980865 | -1.466245 |
| 11 | 1 | -0.025764 | -0.592556 | 1.552272 |
| 12 | 1 | -0.716862 | -2.398993 | -1.729467 |
| 13 | 1 | -2.002831 | -0.606664 | -0.159162 |
| 14 | 1 | -2.316926 | 2.030485 | 0.826337 |
| 15 | 1 | -0.212836 | 1.590502 | 2.112109 |
| 16 | 1 | -1.295294 | 2.532669 | -0.602143 |
| 17 | 1 | 0.752240 | 2.063055 | 0.746256 |

Transition state for cleaving C4-C7 bond on S₁ 48

(6,6) single point, geometry optimized in (4,4) active space

-270.62764

| | | | | |
|----|---|-----------|----------|-----------|
| 1 | 1 | 0.995057 | 1.354836 | 1.973100 |
| 2 | 6 | 0.413583 | 1.935555 | 1.292570 |
| 3 | 6 | -1.093697 | 2.132711 | 1.307439 |
| 4 | 6 | 0.893364 | 2.699583 | 0.085193 |
| 5 | 1 | -1.808994 | 1.615929 | 1.921119 |
| 6 | 6 | -1.424838 | 2.910209 | 0.173229 |
| 7 | 6 | 0.001828 | 3.925011 | 0.145525 |
| 8 | 6 | 0.477634 | 2.056725 | -1.245368 |
| 9 | 1 | 1.957479 | 2.890764 | 0.188520 |
| 10 | 1 | -2.424194 | 3.324955 | 0.154087 |
| 11 | 6 | -1.066658 | 2.199923 | -1.197427 |
| 12 | 1 | -0.148575 | 4.505675 | -0.757921 |
| 13 | 1 | -1.447012 | 2.835967 | -1.989182 |
| 14 | 1 | 0.787413 | 1.021262 | -1.297246 |
| 15 | 1 | 0.889606 | 2.581613 | -2.105595 |
| 16 | 1 | -1.587131 | 1.252427 | -1.263807 |
| 17 | 1 | 0.112936 | 4.541288 | 1.021343 |

¹(ππ^{*})/S₀ conical intersection 49

(6,6) active space

-270.75074/-270.75081

| | | | | |
|----|---|-----------|----------|-----------|
| 1 | 1 | .906914 | 1.748619 | 2.111855 |
| 2 | 6 | .360548 | 1.850580 | 1.195184 |
| 3 | 6 | -1.013781 | 2.326540 | 1.236541 |
| 4 | 6 | .923486 | 2.656485 | .050670 |
| 5 | 1 | -1.560229 | 2.361699 | 2.170325 |
| 6 | 6 | -1.781825 | 2.412896 | -.012146 |
| 7 | 6 | .200364 | 3.936503 | .442900 |
| 8 | 6 | .413974 | 2.075343 | -1.274806 |
| 9 | 1 | 2.005329 | 2.733289 | .046876 |
| 10 | 1 | -2.743723 | 2.883362 | -.006437 |
| 11 | 6 | -1.137193 | 2.110582 | -1.340750 |
| 12 | 1 | -.256826 | 4.584854 | -.295600 |
| 13 | 1 | -1.464841 | 2.843800 | -2.071062 |
| 14 | 1 | .767832 | 1.051754 | -1.346429 |
| 15 | 1 | .833940 | 2.612727 | -2.118769 |
| 16 | 1 | -1.502438 | 1.152168 | -1.705478 |
| 17 | 1 | .576271 | 4.443230 | 1.322707 |