| Model species | DLPNO-CCSDT/cc-pvdz |
|---|---|
| $[B_{10}H_8O_2CCH_3(H^{fac})]+CH_3CN$ | 0.0 |
| **Formation of Tris_$B_1$** | |
| $TS_{migr}$_$B_1$+$CH_3CN$ | 61.0 |
| $H_2$_$B_1$+$CH_3CN$ | 45.1 |
| $TS_{elim}$_$B_1$ | 163.5 |
| Tris_$B_1$ +$H_2$ | -86.7 |
| **Formation of Tris_$B_3$** | |
| $Ts_{migr}$_$B_3$+$CH_3CN$ | 50.9 |
| $H_2$_$B_3$+$CH_3CN$ | 37.0 |
| Tselim_$B_3$ | 124.4 |
| Tris_$B_3$+$H_2$ | -89.9 |
| **Formation of Tris_$B_4$** | |
| $TS_{migr}$_$B_4$+$CH_3CN$ | 47.6 |
| $H_2$_$B_4$+$CH_3CN$ | 29.7 |
| $TS_{elim}$_$B_4$ | 120.2 |
| Tris_$B_4$+$H_2$ | -95.9 |
| | |
| $[B_{10}H_{11}]^-$+$CH_3CN$ | 0.0 |
| **Formation of [1-$B_{10}H_9NCCH_3$]$^-$** | |
| $B_{10}$_$TS_{migr}$_ap + $CH_3CN$ | 67.7 |
| $B_{10}$_$H_2$_ap+$CH_3CN$ | 52.9 |
| $B_{10}$_$TS_{elim}$_ap | 174.9 |
| [1-$B_{10}H_9NCCH_3$]$^-$ +$H_2$ | -62.2 |
| **Formation of [2-$B_{10}H_9NCCH_3$]$^-$** | |
| $B_{10}$_$TS_{migr}$_eq + $CH_3CN$ | 78.8 |
| $B_{10}$_$H_2$_eq + $CH_3CN$ | 41.8 |
| $B_{10}$_$TS_{elim}$_eq | 119.6 |
| [2-$B_{10}H_9NCCH_3$]$^-$+$H_2$ | -64.2 |

**Table S1.** Relative electronic energies (DLPNO-CCSDT/cc-pvdz level of theory) of main molecular species in kJ/mol.

| Model species | $\rho(r)$ (e Å$^{-3}$) | $\nabla^2\rho(r)$ (e Å$^{-5}$) | $H_b$ (h e$^{-1}$) | δ |
|---|---|---|---|---|
| **$B_1$-$H_2$** | | | | |
| B-$H_2$ | 0.132 | 0.353 | -0.104 | 0.359 |
| H-H | 0.217 | -0.721 | -0.200 | 0.633 |
| **$B_3$-$H_2$** | | | | |
| B-$H_2$ | 0.128 | 0.314 | -0.100 | 0.332 |
| H-H | 0.220 | -0.746 | -0.205 | 0.637 |
| **$B_4$-$H_2$** | | | | |
| B-$H_2$ | 0.126 | 0.329 | -0.098 | 0.330 |
| H-H | 0.222 | -0.762 | -0.209 | 0.641 |

**Table S2.** Main topological parameters of electron density for interactions in B-$H_2$ fragments. *ρ(r)* – electron density at the bcp, $\nabla^2\rho(r)$ – Laplacian of electron density at the bcp, $H_b$ – total energy at the bcp, δ – delocalization index.

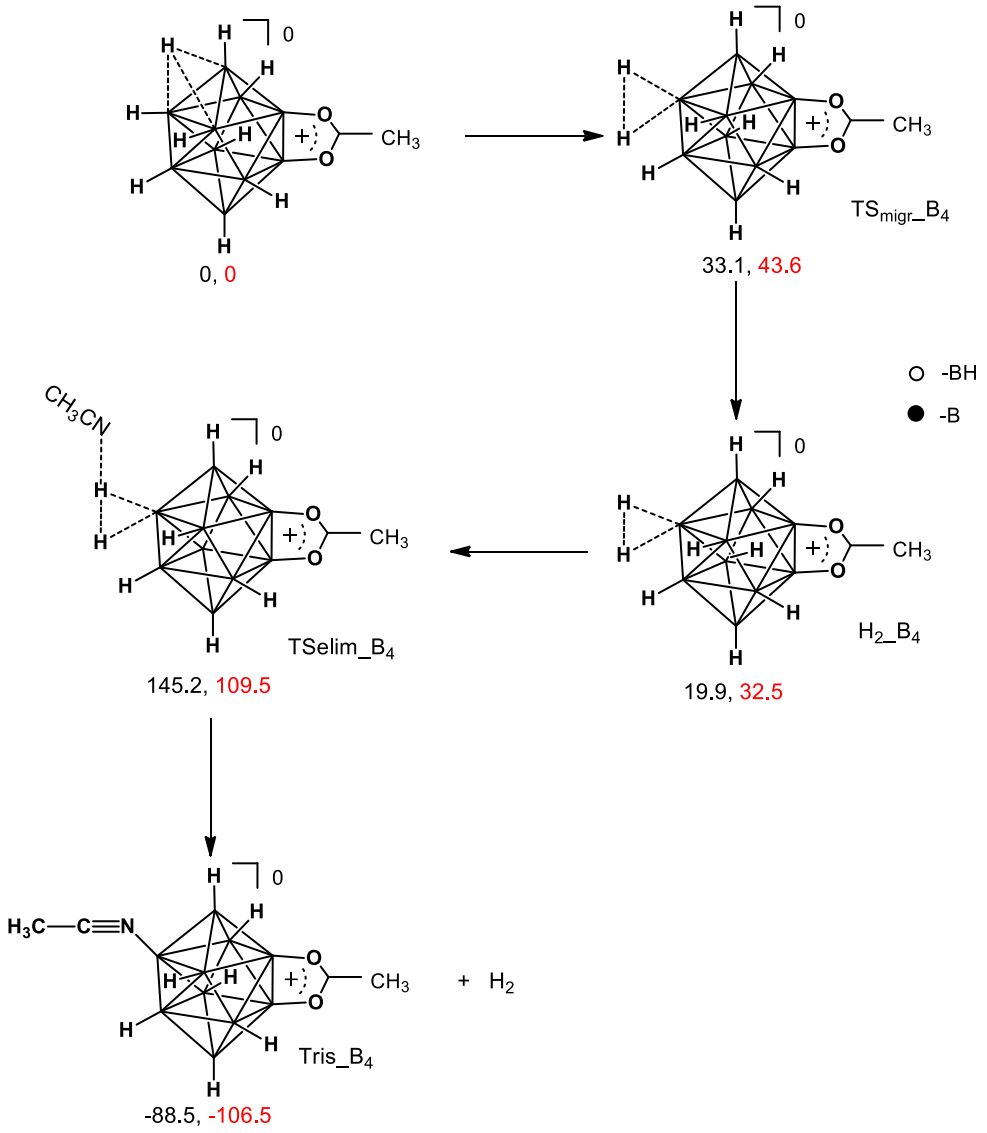


**Figure S1.** Expanded general scheme for the formation of trisubstituted derivative Tris_$B_4$. Relative Gibbs energy (wB97X-D3 level of theory; kJ/mol) is marked in black and relative electronic energy (DLPNO-CCSDT level of theory + ZPE corrections; kJ/mol) is marked in red. All hydrogen atoms are shown in an explicit form on the scheme.

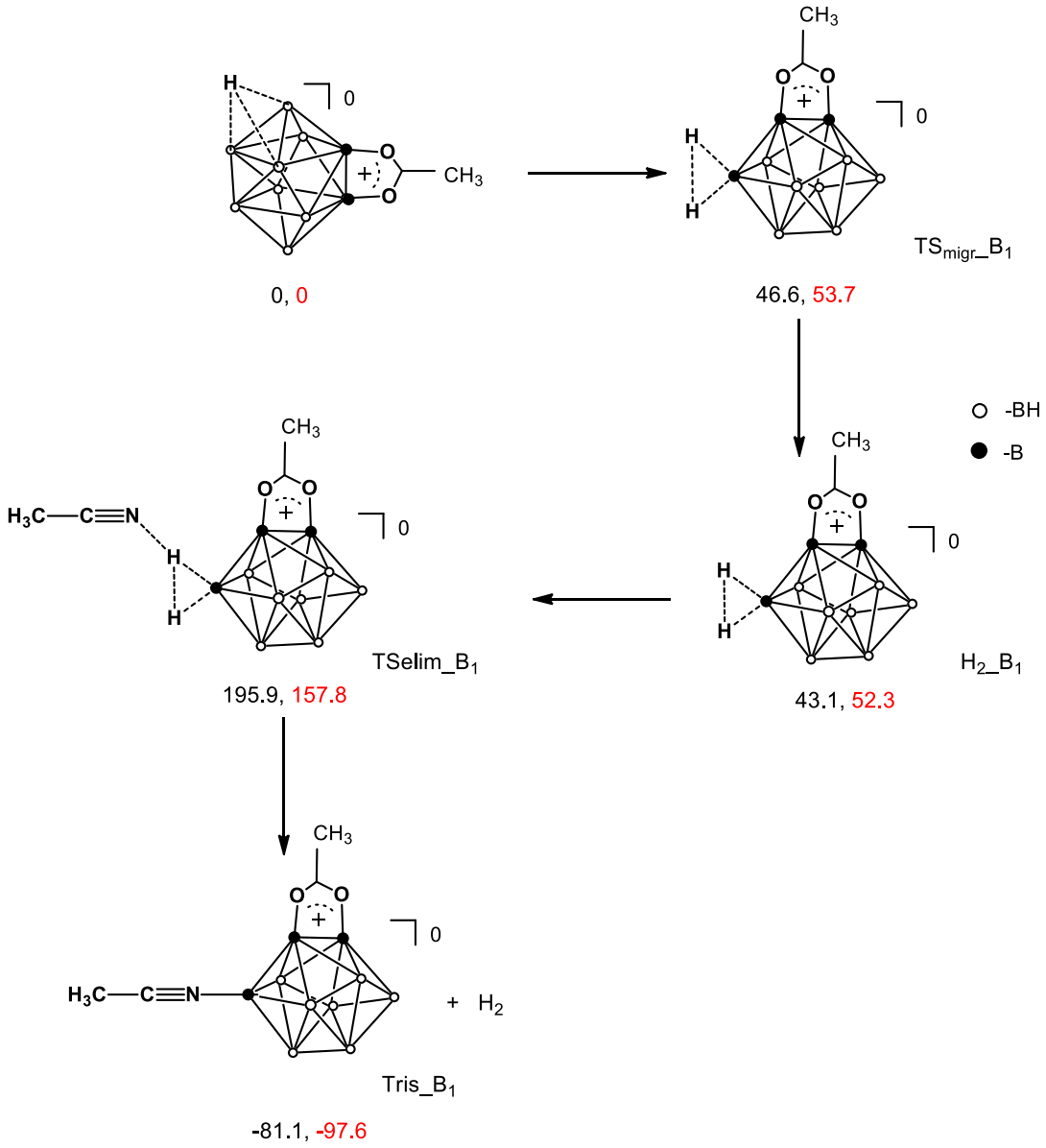


**Figure S2.** General scheme for the formation of trisubstituted derivative Tris_$B_1$. Relative Gibbs energy (wB97X-D3 level; kJ/mol) is marked in black and relative electronic energy (DLPNO-CCSDT level + ZPE corrections; kJ/mol) is marked in red.

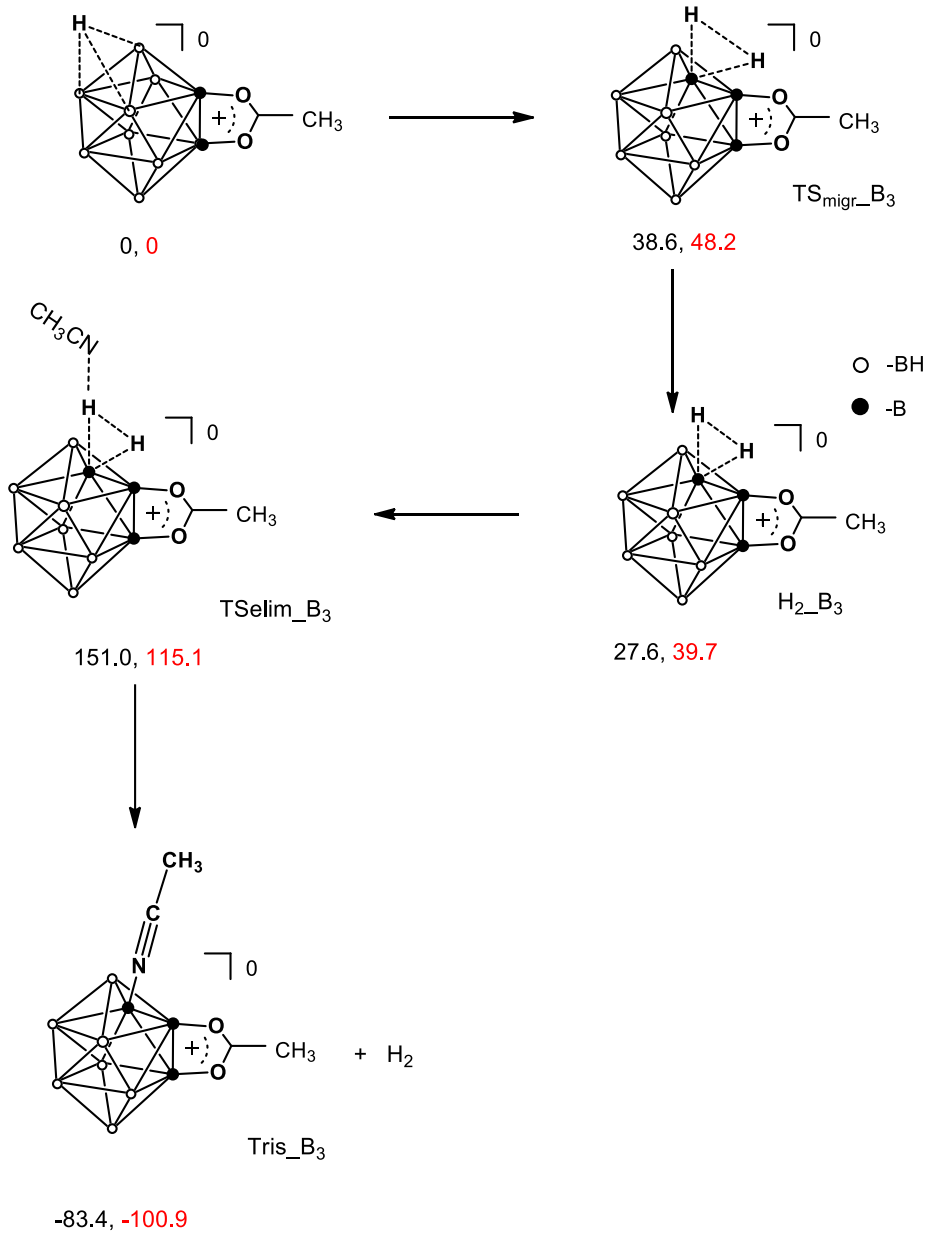


**Figure S3.** General scheme for the formation of trisubstituted derivative Tris_$B_3$. Relative Gibbs energy (wB97X-D3 level; kJ/mol) is marked in black and relative electronic energy (DLPNO-CCSDT level + ZPE corrections; kJ/mol) is marked in red.

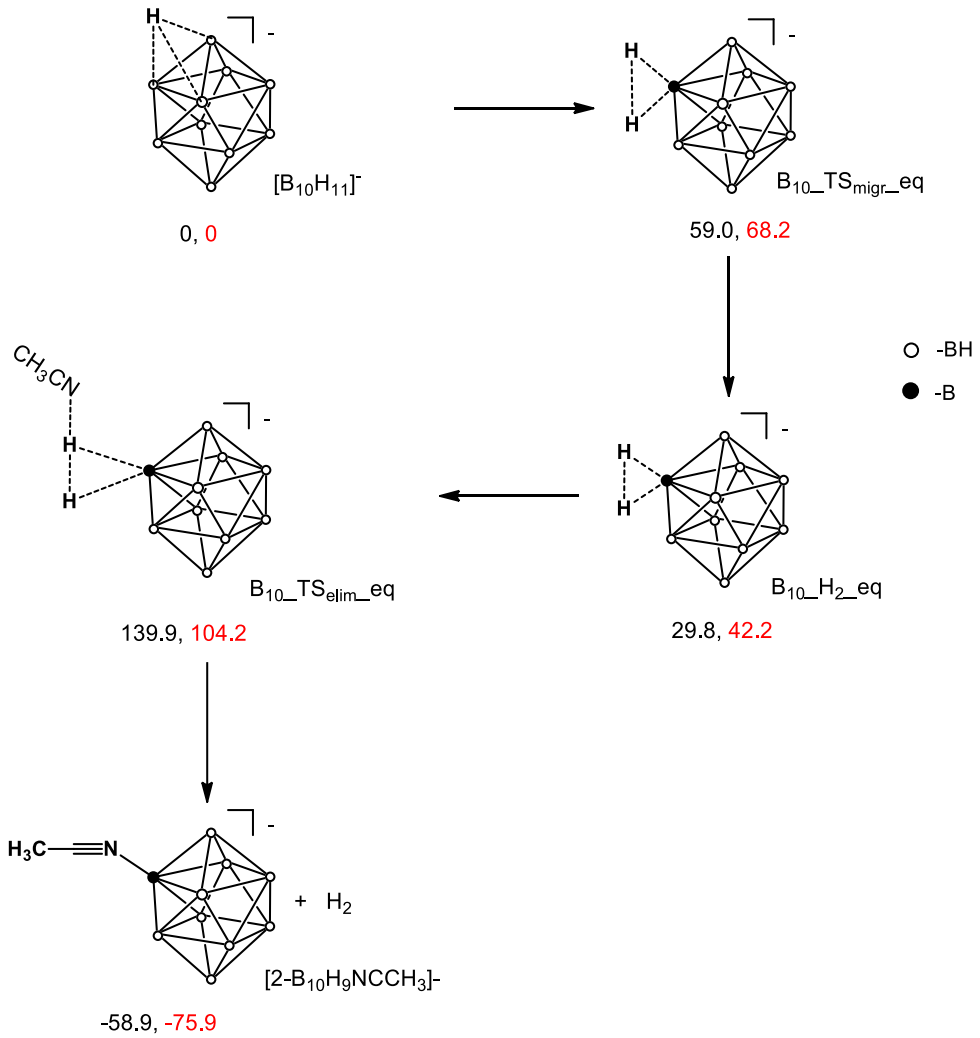


**Figure S4.** General scheme for the formation of $[2\text{-}B_{10}H_9NCCH_3]^-$. Relative Gibbs energy (wB97X-D3 level of theory; kJ/mol) is marked in black and relative electronic energy (DLPNO-CCSDT level of theory + ZPE corrections; kJ/mol) is marked in red.

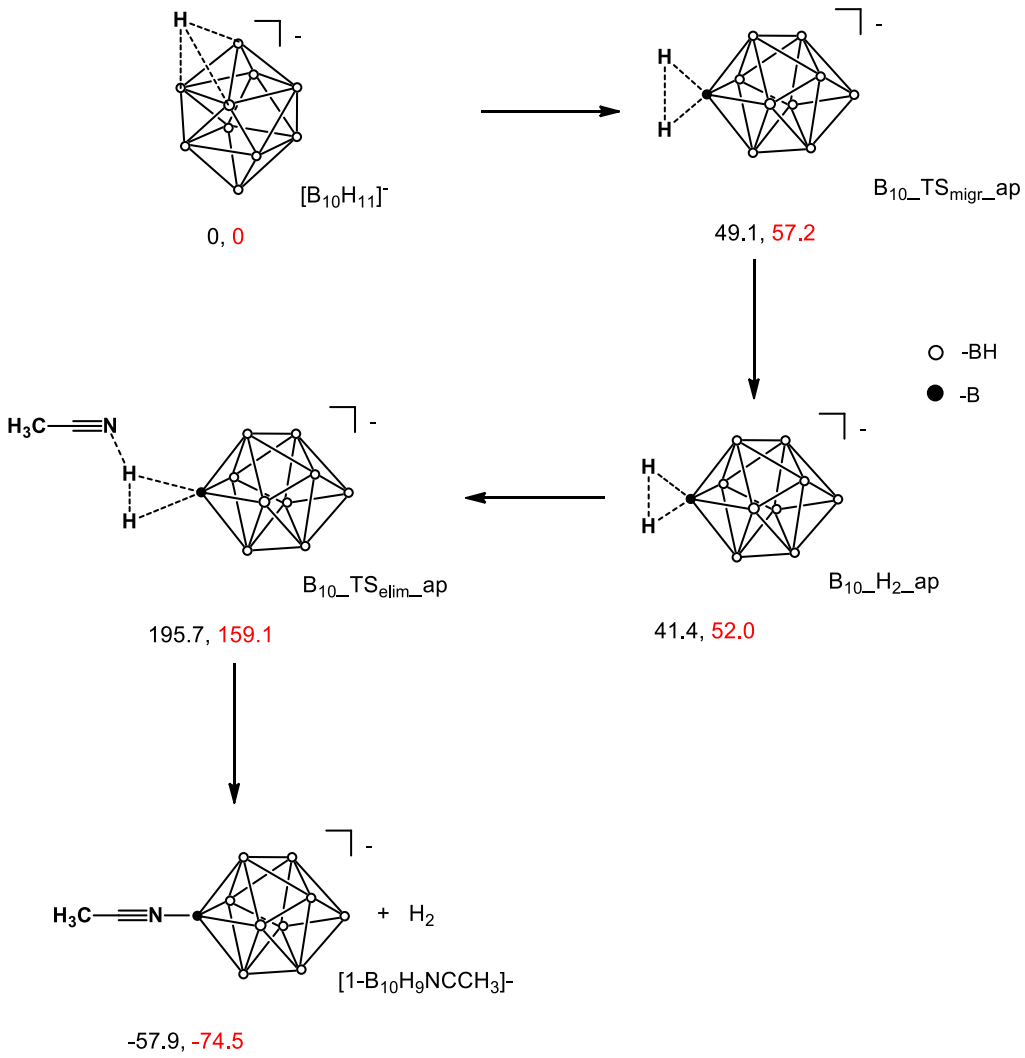


**Figure S5.** General scheme for the formation of $[1\text{-}B_{10}H_9NCCH_3]^-$. Relative Gibbs energy (wB97X-D3 level of theory; kJ/mol) is marked in black and relative electronic energy (DLPNO-CCSDT level of theory + ZPE corrections; kJ/mol) is marked in red.

| Model species | Atom | x | y | z |
|---|---|---|---|---|
| **$[B_{10}H_8O_2CCH_3(H^{fac})]^0$** | | | | |
| ΔG | O | 7.262623 | 6.722111 | 11.198505 |
| -482.46148622 | O | 6.553767 | 5.125584 | 9.844496 |
| Electronic energy | C | 7.309035 | 5.504208 | 10.804796 |
| -481.103131538571 | C | 8.232902 | 4.549637 | 11.434990 |
| Electronic energy+ZPE | H | 7.685947 | 3.648724 | 11.709650 |
| -480.918349828571 | H | 8.712885 | 4.991293 | 12.301937 |
| | H | 8.984759 | 4.272232 | 10.693848 |
| | B | 5.568584 | 6.829003 | 7.713112 |
| | H | 5.766450 | 6.377785 | 6.635151 |
| | B | 5.772746 | 6.269678 | 9.285359 |
| | B | 4.171334 | 6.815492 | 8.674765 |
| | H | 3.168743 | 6.295097 | 8.302959 |
| | B | 4.993088 | 8.378871 | 8.155920 |
| | H | 4.742628 | 9.142351 | 7.276917 |
| | B | 6.606671 | 7.719226 | 8.699578 |
| | H | 7.735809 | 7.944448 | 8.398822 |
| | B | 6.249054 | 7.491439 | 10.427749 |
| | B | 4.524376 | 6.905347 | 10.426617 |
| | H | 4.036437 | 6.152054 | 11.206706 |
| | B | 3.948052 | 8.345098 | 9.623757 |
| | H | 2.933328 | 8.958987 | 9.638799 |
| | B | 5.858145 | 9.054748 | 9.665576 |
| | H | 6.339998 | 10.135649 | 9.569779 |
| | B | 5.000663 | 8.401195 | 11.107467 |
| | H | 4.847665 | 8.714699 | 12.237722 |
| | H | 4.790613 | 9.509129 | 10.477487 |

| | | | | |
|---|---|---|---|---|
| **$TS_{migr}\_B_1$** | | | | |
| ΔG | O | 7.285140 | 6.724169 | 11.193005 |
| -482.44374631 | O | 6.512019 | 5.122878 | 9.881325 |
| Electronic energy | C | 7.300888 | 5.499849 | 10.811169 |
| -481.079882204925 | C | 8.244162 | 4.549683 | 11.419332 |
| Electronic energy+ZPE | H | 7.845379 | 3.540421 | 11.372229 |
| -480.897899574925 | H | 8.469905 | 4.841592 | 12.440858 |
| | H | 9.165732 | 4.588761 | 10.832721 |
| | B | 5.545498 | 6.795846 | 7.740142 |
| | H | 5.737136 | 6.275815 | 6.691375 |
| | B | 5.739682 | 6.282552 | 9.331265 |
| | B | 4.139112 | 6.859173 | 8.692793 |
| | H | 3.140368 | 6.322565 | 8.330525 |
| | B | 5.006163 | 8.372959 | 8.134911 |
| | H | 4.764590 | 9.121774 | 7.239805 |
| | B | 6.603710 | 7.707740 | 8.690792 |
| | H | 7.740406 | 7.867427 | 8.370344 |
| | B | 6.274326 | 7.506641 | 10.434441 |
| | B | 4.489238 | 6.935142 | 10.463109 |
| | H | 3.984631 | 6.172064 | 11.222844 |
| | B | 4.002264 | 8.402219 | 9.617912 |
| | H | 2.997827 | 9.037041 | 9.652108 |
| | B | 5.824490 | 9.049971 | 9.631323 |
| | H | 6.281099 | 10.145550 | 9.581068 |
| | B | 5.022473 | 8.437272 | 11.015382 |
| | H | 4.863655 | 8.834053 | 12.155311 |
| | H | 4.850002 | 9.621620 | 11.242140 |
| **$TS_{migr}\_B_3$** | | | | |

| | | | | |
|---|---|---|---|---|
| ΔG | O | 7.133186 | 6.683334 | 11.442373 |
| -482.44678374 | O | 6.479090 | 5.102115 | 10.044200 |
| Electronic energy | C | 7.216308 | 5.476894 | 11.016078 |
| -481.083751630950 | C | 8.155073 | 4.542446 | 11.656647 |
| Electronic energy+ZPE | H | 7.855262 | 4.413643 | 12.697429 |
| -480.899996730950 | H | 9.150809 | 4.985090 | 11.648776 |
| | H | 8.156905 | 3.586528 | 11.143912 |
| | B | 5.504362 | 6.813444 | 7.940972 |
| | H | 5.764021 | 6.346219 | 6.881837 |
| | B | 5.664302 | 6.244825 | 9.511355 |
| | B | 4.058985 | 6.789982 | 8.867534 |
| | H | 3.091779 | 6.220015 | 8.472160 |
| | B | 4.857181 | 8.334004 | 8.323863 |
| | H | 4.623254 | 9.103670 | 7.446939 |
| | B | 6.502873 | 7.722051 | 8.964001 |
| | H | 7.644354 | 7.936941 | 8.705462 |
| | B | 6.081379 | 7.430401 | 10.699098 |
| | B | 4.393826 | 6.838234 | 10.639140 |
| | H | 3.862652 | 6.070443 | 11.378267 |
| | B | 3.849764 | 8.307433 | 9.812100 |
| | H | 2.822792 | 8.906884 | 9.821844 |
| | B | 5.571296 | 8.952381 | 9.868088 |
| | H | 6.054182 | 10.084672 | 9.743683 |
| | B | 4.805621 | 8.385380 | 11.270780 |
| | H | 4.564465 | 8.846403 | 12.334953 |
| | H | 5.481364 | 9.866478 | 10.697474 |
| **$TS_{migr}\_B_4$** | | | | |
| ΔG | O | 7.123149 | 6.708116 | 11.274444 |

| | | | | |
|---|---|---|---|---|
| -482.44888864 | O | 6.539319 | 5.079224 | 9.894909 |
| Electronic energy | C | 7.238258 | 5.493895 | 10.880922 |
| -481.084989764549 | C | 8.195925 | 4.591812 | 11.539921 |
| Electronic energy+ZPE | H | 7.829914 | 3.569226 | 11.508060 |
| -480.901725424549 | H | 8.381616 | 4.915017 | 12.559820 |
| | H | 9.131427 | 4.642483 | 10.977226 |
| | B | 5.523848 | 6.731279 | 7.742941 |
| | H | 5.738859 | 6.240895 | 6.684039 |
| | B | 5.711793 | 6.188069 | 9.317155 |
| | B | 4.101859 | 6.674597 | 8.684010 |
| | H | 3.126901 | 6.121951 | 8.288261 |
| | B | 4.979756 | 8.296093 | 8.106504 |
| | H | 4.702352 | 9.045061 | 7.225052 |
| | B | 6.523532 | 7.690881 | 8.748259 |
| | H | 7.672287 | 7.873219 | 8.488238 |
| | B | 6.092350 | 7.425105 | 10.472996 |
| | B | 4.436120 | 6.753696 | 10.436604 |
| | H | 3.887457 | 5.973596 | 11.147511 |
| | B | 3.958690 | 8.254692 | 9.589742 |
| | H | 3.361204 | 8.918312 | 10.451772 |
| | B | 5.658364 | 8.956007 | 9.653583 |
| | B | 4.793418 | 8.341061 | 11.046863 |
| | H | 4.603569 | 8.803641 | 12.120914 |
| | H | 6.030612 | 10.083996 | 9.684061 |
| | H | 2.861229 | 8.787264 | 9.411612 |
| **$H_2$_$B_1$** | | | | |
| ΔG | O | 7.283555 | 6.749118 | 11.176227 |
| -482.44506627 | O | 6.505648 | 5.129710 | 9.888358 |

| | | | | |
|---|---|---|---|---|
| Electronic energy | C | 7.294683 | 5.519101 | 10.811275 |
| -481.085969180365 | C | 8.236763 | 4.577475 | 11.436188 |
| Electronic energy+ZPE | H | 7.848405 | 3.564520 | 11.385301 |
| -480.898418620365 | H | 8.441906 | 4.873524 | 12.461090 |
| | H | 9.168666 | 4.625008 | 10.867028 |
| | B | 5.535700 | 6.765990 | 7.729488 |
| | H | 5.721607 | 6.208878 | 6.697923 |
| | B | 5.731765 | 6.285443 | 9.318726 |
| | B | 4.131463 | 6.878645 | 8.689561 |
| | H | 3.125219 | 6.340450 | 8.347304 |
| | B | 5.022919 | 8.354980 | 8.069104 |
| | H | 4.780639 | 9.084527 | 7.157207 |
| | B | 6.601938 | 7.710517 | 8.653898 |
| | H | 7.742502 | 7.838361 | 8.328504 |
| | B | 6.270734 | 7.521245 | 10.408611 |
| | B | 4.504064 | 6.973835 | 10.454799 |
| | H | 3.978107 | 6.226271 | 11.217851 |
| | B | 4.035014 | 8.461310 | 9.572656 |
| | H | 3.019884 | 9.083268 | 9.589581 |
| | B | 5.820931 | 9.067440 | 9.548591 |
| | H | 6.281754 | 10.163158 | 9.510296 |
| | B | 5.037863 | 8.490756 | 10.921228 |
| | H | 4.898798 | 8.681269 | 12.186227 |
| | H | 4.809367 | 9.439977 | 11.76121 |
| **$H_2$_$B_3$** | | | | |
| ΔG | O | 7.248962 | 6.667726 | 11.218812 |
| -482.45097085 | O | 6.556928 | 5.066903 | 9.860619 |
| Electronic energy | C | 7.316252 | 5.454951 | 10.810308 |

| | | | | |
|---|---|---|---|---|
| -481.089037456508 | C | 8.271323 | 4.515172 | 11.419749 |
| Electronic energy+ZPE | H | 7.741494 | 3.610978 | 11.717090 |
| -480.903238296508 | H | 8.769146 | 4.967652 | 12.270952 |
| | H | 9.005301 | 4.238260 | 10.661243 |
| | B | 5.553427 | 6.732620 | 7.743397 |
| | H | 5.786924 | 6.224402 | 6.696393 |
| | B | 5.738377 | 6.204595 | 9.320117 |
| | B | 4.129350 | 6.758263 | 8.696755 |
| | H | 3.144449 | 6.198356 | 8.329513 |
| | B | 4.954591 | 8.275478 | 8.105122 |
| | H | 4.709927 | 9.048329 | 7.232399 |
| | B | 6.569345 | 7.675580 | 8.721819 |
| | H | 7.711143 | 7.882425 | 8.452184 |
| | B | 6.181213 | 7.409107 | 10.492145 |
| | B | 4.488804 | 6.824200 | 10.466263 |
| | H | 3.957628 | 6.046626 | 11.196875 |
| | B | 3.959172 | 8.308834 | 9.629470 |
| | H | 2.930831 | 8.906800 | 9.627449 |
| | B | 5.659178 | 8.886954 | 9.643607 |
| | H | 6.256134 | 9.998752 | 9.280845 |
| | B | 4.917318 | 8.363769 | 11.061626 |
| | H | 4.719836 | 8.898598 | 12.100280 |
| | H | 5.909725 | 10.094689 | 10.066703 |
| **$H_2$_$B_4$** | | | | |
| ΔG | O | 7.161960 | 6.663260 | 11.170002 |
| -482.45391083 | O | 6.540951 | 5.060284 | 9.778365 |
| Electronic energy | C | 7.263743 | 5.457583 | 10.755189 |
| -481.091812032097 | C | 8.214509 | 4.527409 | 11.386985 |

| | | | | |
|---|---|---|---|---|
| Electronic energy+ZPE | H | 7.680205 | 3.629040 | 11.694887 |
| -480.905980872097 | H | 8.703186 | 4.992518 | 12.236648 |
| | H | 8.954787 | 4.236126 | 10.640604 |
| | B | 5.525567 | 6.731306 | 7.661564 |
| | H | 5.757671 | 6.244257 | 6.604161 |
| | B | 5.713280 | 6.183257 | 9.228697 |
| | B | 4.100773 | 6.696035 | 8.597915 |
| | H | 3.111284 | 6.152565 | 8.221628 |
| | B | 4.941802 | 8.277198 | 8.043510 |
| | H | 4.656489 | 9.046123 | 7.180232 |
| | B | 6.509273 | 7.694457 | 8.671190 |
| | H | 7.652079 | 7.904405 | 8.402582 |
| | B | 6.108066 | 7.401586 | 10.408489 |
| | B | 4.439454 | 6.745333 | 10.378312 |
| | H | 3.887786 | 5.947087 | 11.066400 |
| | B | 3.993534 | 8.229189 | 9.549989 |
| | H | 2.961445 | 8.896918 | 9.999430 |
| | B | 5.639255 | 8.952205 | 9.611503 |
| | B | 4.830221 | 8.305734 | 10.996498 |
| | H | 4.573947 | 8.790745 | 12.046584 |
| | H | 6.021125 | 10.077656 | 9.626257 |
| | H | 2.835548 | 8.720647 | 9.169111 |
| **$TS_{elim}$_$B_1$** | | | | |
| ΔG | O | 7.528916 | 6.704845 | 10.417115 |
| -615.14065826 | O | 5.768923 | 5.451097 | 9.952665 |
| Electronic energy | C | 6.866682 | 5.618440 | 10.577967 |
| -613.446674737330 | C | 7.377939 | 4.590417 | 11.499706 |
| Electronic energy+ZPE | H | 6.784669 | 3.684462 | 11.434837 |

| | | | | |
|---|---|---|---|---|
| -613.218437647330 | H | 7.332497 | 4.993136 | 12.512960 |
| | H | 8.422227 | 4.388249 | 11.266329 |
| | B | 5.071037 | 6.670291 | 7.435101 |
| | H | 4.663688 | 5.840551 | 6.688991 |
| | B | 5.475648 | 6.624950 | 9.053536 |
| | B | 4.224436 | 7.783848 | 8.406427 |
| | H | 3.032232 | 7.805363 | 8.410194 |
| | B | 5.472176 | 8.306280 | 7.173708 |
| | H | 5.340863 | 8.761048 | 6.077912 |
| | B | 6.664550 | 7.110998 | 7.802485 |
| | H | 7.598796 | 6.520355 | 7.351471 |
| | B | 6.795418 | 7.635617 | 9.512290 |
| | B | 5.099398 | 8.154586 | 9.954347 |
| | H | 4.520780 | 8.051164 | 10.991296 |
| | B | 5.127740 | 9.343745 | 8.601152 |
| | H | 4.557502 | 10.380184 | 8.469157 |
| | B | 6.885687 | 8.873550 | 8.182181 |
| | H | 7.781417 | 9.475725 | 7.677543 |
| | B | 6.364058 | 9.227131 | 9.742762 |
| | H | 7.842772 | 9.970054 | 10.240656 |
| | H | 7.640667 | 9.589184 | 10.874832 |
| | C | 5.136842 | 11.657295 | 11.608563 |
| | N | 5.738605 | 10.919584 | 10.972706 |
| | C | 4.36978 | 12.587304 | 12.409183 |
| | H | 4.317381 | 12.222752 | 13.433695 |
| | H | 3.364525 | 12.670068 | 11.999181 |
| | H | 4.851587 | 13.563498 | 12.394042 |
| **$TS_{elim}$_$B_3$** | | | | |

| | | | | |
|---|---|---|---|---|
| ΔG | O | 6.659471 | 5.282354 | 11.023339 |
| -615.15774023 | O | 5.961648 | 3.974424 | 9.385231 |
| Electronic energy | C | 6.610450 | 4.125092 | 10.473194 |
| -613.461565219376 | C | 7.293357 | 2.975626 | 11.087553 |
| Electronic energy+ZPE | H | 6.542834 | 2.228256 | 11.347716 |
| -613.234698049376 | H | 7.842023 | 3.281376 | 11.972207 |
| | H | 7.964548 | 2.531370 | 10.352981 |
| | B | 5.554076 | 5.974312 | 7.376590 |
| | H | 5.849869 | 5.514861 | 6.322545 |
| | B | 5.414753 | 5.282278 | 8.891185 |
| | B | 4.025227 | 6.168141 | 8.119087 |
| | H | 3.033932 | 5.837427 | 7.547022 |
| | B | 5.178476 | 7.560785 | 7.838076 |
| | H | 5.183217 | 8.455595 | 7.051756 |
| | B | 6.545909 | 6.643831 | 8.584301 |
| | H | 7.733995 | 6.669686 | 8.527018 |
| | B | 5.845226 | 6.260534 | 10.262631 |
| | B | 4.110950 | 6.006437 | 9.930861 |
| | H | 3.351056 | 5.271472 | 10.482264 |
| | B | 3.953204 | 7.624974 | 9.210646 |
| | H | 3.035819 | 8.376666 | 9.125379 |
| | B | 5.698314 | 7.857923 | 9.521528 |
| | H | 5.915697 | 9.744328 | 8.935616 |
| | B | 4.691053 | 7.388531 | 10.750104 |
| | H | 4.422235 | 7.846474 | 11.810050 |
| | H | 5.722175 | 9.813722 | 9.663057 |
| | C | 8.583385 | 8.767888 | 11.308391 |
| | N | 7.661139 | 8.690502 | 10.633015 |

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|---|---|---|---|---|
| | C | 9.751233 | 8.863629 | 12.160582 |
| | H | 10.62606 | 9.088753 | 11.552983 |
| | H | 9.903302 | 7.917629 | 12.67774 |
| | H | 9.603367 | 9.656569 | 12.891825 |
| **$TS_{elim}$_$B_4$** | | | | |
| ΔG | O | 8.182478 | 6.415632 | 10.880133 |
| -615.15994785 | O | 7.711011 | 4.669199 | 9.602994 |
| Electronic energy | C | 8.520291 | 5.289706 | 10.376052 |
| -613.463158395253 | C | 9.839927 | 4.708277 | 10.670325 |
| Electronic energy+ZPE | H | 9.704119 | 3.698281 | 11.056511 |
| -613.236807125253 | H | 10.37998 | 5.321689 | 11.383564 |
| | H | 10.39788 | 4.636185 | 9.735937 |
| | B | 5.762144 | 5.910082 | 7.897676 |
| | H | 5.885005 | 5.485013 | 6.796637 |
| | B | 6.483986 | 5.488089 | 9.342495 |
| | B | 4.676411 | 5.500827 | 9.148455 |
| | H | 3.820521 | 4.683535 | 9.046998 |
| | B | 4.849373 | 7.216913 | 8.485067 |
| | H | 4.151339 | 7.872216 | 7.779653 |
| | B | 6.639351 | 7.154039 | 8.676939 |
| | H | 7.548555 | 7.692050 | 8.123702 |
| | B | 6.798743 | 6.797162 | 10.459027 |
| | B | 5.44033 | 5.681675 | 10.819915 |
| | H | 5.35076 | 4.758313 | 11.559998 |
| | B | 4.473859 | 6.943604 | 10.156671 |
| | H | 2.577611 | 7.974321 | 10.518490 |
| | B | 5.742478 | 8.136725 | 9.880140 |
| | B | 5.506825 | 7.310299 | 11.386261 |

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|---|---|---|---|---|
| | H | 5.372447 | 7.736754 | 12.482953 |
| | H | 5.789387 | 9.321610 | 9.840259 |
| | H | 2.899989 | 8.491314 | 10.078140 |
| | C | 1.537543 | 5.216803 | 11.966316 |
| | N | 2.250663 | 5.892448 | 11.375097 |
| | C | 0.636771 | 4.36155 | 12.713908 |
| | H | 0.597398 | 3.378493 | 12.247615 |
| | H | -0.3599 | 4.799767 | 12.719403 |
| | H | 0.994437 | 4.263444 | 13.737443 |
| **Tris_$B_1$** | | | | |
| ΔG | O | 7.288963 | 6.661453 | 11.32483 |
| -614.06980779 | O | 6.559572 | 5.134051 | 9.902519 |
| Electronic energy | C | 7.331063 | 5.467729 | 10.860539 |
| -612.377989431539 | C | 8.269938 | 4.495609 | 11.447219 |
| Electronic energy+ZPE | H | 7.996965 | 4.339214 | 12.491496 |
| -612.161834151539 | H | 9.273965 | 4.918128 | 11.423711 |
| | H | 8.238892 | 3.555597 | 10.906613 |
| | B | 5.548475 | 6.915545 | 7.884472 |
| | H | 5.748825 | 6.447037 | 6.810862 |
| | B | 5.749543 | 6.312102 | 9.423699 |
| | B | 4.139565 | 6.925931 | 8.854087 |
| | H | 3.139110 | 6.400547 | 8.471858 |
| | B | 5.004534 | 8.459021 | 8.340854 |
| | H | 4.748230 | 9.255345 | 7.488737 |
| | B | 6.585666 | 7.813148 | 8.892971 |
| | H | 7.729509 | 7.988308 | 8.596523 |
| | B | 6.239296 | 7.464585 | 10.627293 |
| | B | 4.521703 | 6.883973 | 10.614102 |

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|---|---|---|---|---|
| | H | 3.993113 | 6.075694 | 11.315393 |
| | B | 4.025141 | 8.440451 | 9.858307 |
| | H | 2.990924 | 9.031871 | 9.926906 |
| | B | 5.760464 | 9.068838 | 9.883378 |
| | H | 6.205815 | 10.172866 | 9.946515 |
| | B | 4.998602 | 8.379347 | 11.232448 |
| | C | 4.568910 | 9.337762 | 13.627627 |
| | N | 4.757443 | 8.933183 | 12.579516 |
| | C | 4.332028 | 9.836175 | 14.954558 |
| | H | 5.285155 | 9.921055 | 15.474724 |
| | H | 3.681778 | 9.13809 | 15.48052 |
| | H | 3.8537 | 10.812644 | 14.8893 |
| **Tris_$B_3$** | | | | |
| ΔG | O | 7.403607 | 7.137458 | 10.998226 |
| -614.07071892 | O | 6.696895 | 5.500419 | 9.691687 |
| Electronic energy | C | 7.520366 | 5.940292 | 10.560750 |
| -612.379217697753 | C | 8.585829 | 5.067334 | 11.082543 |
| Electronic energy+ZPE | H | 8.179262 | 4.527110 | 11.941009 |
| -612.163072117753 | H | 9.432626 | 5.661840 | 11.413847 |
| | H | 8.882216 | 4.344588 | 10.327476 |
| | B | 5.305474 | 7.090087 | 7.746843 |
| | H | 5.443876 | 6.605957 | 6.670452 |
| | B | 5.724201 | 6.571672 | 9.275574 |
| | B | 4.010101 | 7.002823 | 8.860903 |
| | H | 3.032464 | 6.371428 | 8.599539 |
| | B | 4.652237 | 8.582817 | 8.217030 |
| | H | 4.240508 | 9.349120 | 7.399648 |
| | B | 6.341282 | 8.115708 | 8.618725 |

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|---|---|---|---|---|
| | H | 7.423924 | 8.430169 | 8.225340 |
| | B | 6.198668 | 7.801235 | 10.412743 |
| | B | 4.57178 | 7.067777 | 10.580559 |
| | H | 4.195813 | 6.219595 | 11.331823 |
| | B | 3.838135 | 8.525793 | 9.848878 |
| | B | 5.476898 | 9.272571 | 9.673295 |
| | B | 4.941288 | 8.621559 | 11.149269 |
| | H | 4.835189 | 9.134541 | 12.215099 |
| | C | 6.20692 | 11.802078 | 9.578093 |
| | N | 5.899644 | 10.706313 | 9.620970 |
| | C | 6.596061 | 13.184054 | 9.517816 |
| | H | 7.147868 | 13.437595 | 10.422021 |
| | H | 5.697271 | 13.796084 | 9.449550 |
| | H | 7.221325 | 13.339846 | 8.639792 |
| | H | 2.761867 | 9.023511 | 9.975126 |
| **Tris_$B_4$** | | | | |
| ΔG | O | 7.488075 | 6.577946 | 11.128956 |
| -614.07266191 | O | 6.534092 | 5.098624 | 9.784611 |
| Electronic energy | C | 7.417253 | 5.401111 | 10.647566 |
| -612.381505939589 | C | 8.362437 | 4.360069 | 11.117561 |
| Electronic energy+ZPE | H | 7.873418 | 3.788193 | 11.908063 |
| -612.165223249589 | H | 9.259065 | 4.821856 | 11.519538 |
| | H | 8.599797 | 3.681274 | 10.302832 |
| | B | 5.383873 | 6.945225 | 7.898707 |
| | H | 5.439247 | 6.482181 | 6.808669 |
| | B | 5.721681 | 6.320137 | 9.406233 |
| | B | 4.099463 | 6.985634 | 9.023938 |
| | H | 3.020729 | 6.539996 | 8.781262 |

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|---|---|---|---|---|
| | B | 4.971904 | 8.502354 | 8.427681 |
| | H | 4.625686 | 9.340654 | 7.653449 |
| | B | 6.563145 | 7.786868 | 8.802426 |
| | H | 7.675341 | 7.919008 | 8.392414 |
| | B | 6.382344 | 7.442121 | 10.569788 |
| | B | 4.675501 | 6.914699 | 10.753419 |
| | H | 4.162912 | 6.117242 | 11.475885 |
| | B | 4.226061 | 8.471554 | 10.057186 |
| | B | 5.925411 | 9.059191 | 9.908499 |
| | H | 6.398608 | 10.150121 | 9.909363 |
| | B | 5.285681 | 8.397805 | 11.367706 |
| | H | 5.195355 | 8.859876 | 12.456875 |
| | C | 2.008217 | 9.876911 | 10.330070 |
| | N | 2.963386 | 9.266581 | 10.233190 |
| | C | 0.793893 | 10.654031 | 10.447483 |
| | H | 0.884643 | 11.350919 | 11.279137 |
| | H | -0.044955 | 9.982455 | 10.624698 |
| | H | 0.627075 | 11.205263 | 9.523292 |
| **$B_{10}$_$TS_{migr}$_ap** | | | | |
| ΔG | B | -0.01643 | 1.835419 | 0.004942 |
| -255.25441176 | B | -0.48912 | 0.767313 | -1.204436 |
| Electronic energy | B | 1.189317 | 0.727683 | -0.494505 |
| -254.437216652525 | B | 0.493234 | 0.756457 | 1.189584 |
| Electronic energy+ZPE | B | -1.19987 | 0.696580 | 0.485271 |
| -254.292823612525 | H | -0.03757 | 3.026174 | 0.018855 |
| | H | -0.9249 | 1.186240 | -2.236752 |
| | H | 2.232648 | 1.129476 | -0.921186 |
| | H | 0.909252 | 1.165982 | 2.233797 |

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|---|---|---|---|---|
| | H | -2.24542 | 1.087743 | 0.916690 |
| | B | 0.472038 | -0.743874 | -1.241866 |
| | B | 0.035148 | -1.833228 | -0.033037 |
| | B | -1.18581 | -0.760790 | -0.566408 |
| | B | -0.4567 | -0.768871 | 1.212580 |
| | B | 1.198522 | -0.752051 | 0.530612 |
| | H | 0.931189 | -1.153510 | -2.264650 |
| | H | -2.2244 | -1.183089 | -0.974752 |
| | H | -0.91223 | -1.194654 | 2.229753 |
| | H | 2.241557 | -1.167711 | 0.935653 |
| | H | 0.243704 | -3.028864 | -0.127696 |
| | H | -0.81451 | -2.629144 | 0.313176 |
| **$B_{10}$_$TS_{migr}$_eq** | | | | |
| ΔG | B | 0.169786 | 1.816468 | -0.009962 |
| -255.25061666 | B | -0.281408 | 0.717409 | -1.239031 |
| Electronic energy | B | 1.379083 | 0.723732 | -0.510328 |
| -254.432966757142 | B | 0.704755 | 0.755780 | 1.165540 |
| Electronic energy+ZPE | B | -1.070970 | 0.729126 | 0.409180 |
| -254.288636937142 | H | 0.125903 | 3.006721 | -0.002170 |
| | H | -0.713530 | 1.119180 | -2.279237 |
| | H | 2.430408 | 1.119247 | -0.920193 |
| | H | 1.064690 | 1.113738 | 2.245401 |
| | H | -2.113611 | 1.175846 | 0.784607 |
| | B | 0.700800 | -0.770493 | -1.208858 |
| | B | 0.152849 | -1.902689 | -0.058288 |
| | B | -1.008858 | -0.795727 | -0.603588 |
| | B | -0.360462 | -0.795404 | 1.097213 |
| | B | 1.347165 | -0.769364 | 0.489201 |

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|---|---|---|---|---|
| | H | 1.173834 | -1.224905 | -2.208082 |
| | H | -2.045611 | -1.187193 | -1.049738 |
| | H | -0.777222 | -1.438833 | 2.037108 |
| | H | 2.342350 | -1.201646 | 0.988634 |
| | H | 0.161191 | -3.088714 | -0.011350 |
| | H | -1.058556 | -0.130118 | 1.866234 |
| **$B_{10}$_$H_2$_ap** | | | | |
| ΔG | B | 0.006498 | 1.849499 | -0.00433 |
| -255.25732679 | B | -0.502339 | 0.769611 | -1.19842 |
| Electronic energy | B | 1.183257 | 0.723405 | -0.49245 |
| -254.442841042443 | B | 0.479123 | 0.758464 | 1.194559 |
| Electronic energy+ZPE | B | -1.207021 | 0.76592 | 0.488832 |
| -254.294815752443 | H | 0.026203 | 3.041333 | -0.00696 |
| | H | -0.922767 | 1.18478 | -2.24011 |
| | H | 2.232593 | 1.110347 | -0.92143 |
| | H | 0.913178 | 1.163822 | 2.234537 |
| | H | -2.242892 | 1.189053 | 0.91626 |
| | B | 0.452546 | -0.7543 | -1.21437 |
| | B | -0.054665 | -1.77619 | 0.003227 |
| | B | -1.238750 | -0.72488 | -0.52069 |
| | B | -0.526307 | -0.73235 | 1.21672 |
| | B | 1.164436 | -0.76318 | 0.523537 |
| | H | 0.886308 | -1.18624 | -2.24071 |
| | H | -2.280585 | -1.13136 | -0.9421 |
| | H | -0.974637 | -1.14591 | 2.244416 |
| | H | 2.191366 | -1.20279 | 0.948233 |
| | H | 0.331901 | -2.99464 | -0.15302 |
| | H | -0.477816 | -2.98112 | 0.169874 |

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| **$B_{10}$_$H_2$_eq** | | | | |
| ΔG | B | 0.089384 | 1.815822 | -0.33539 |
| -255.26175990 | B | -0.343618 | 0.742494 | -1.57959 |
| Electronic energy | B | 1.309173 | 0.731729 | -0.8088 |
| -254.447069435971 | B | 0.562875 | 0.704296 | 0.846037 |
| Electronic energy+ZPE | B | -1.131956 | 0.715179 | 0.056116 |
| -254.298544945971 | H | 0.079264 | 3.007132 | -0.29951 |
| | H | -0.734036 | 1.163142 | -2.63021 |
| | H | 2.369165 | 1.142701 | -1.18399 |
| | H | 0.930972 | 1.052517 | 1.92912 |
| | H | -2.194029 | 1.074158 | 0.472204 |
| | B | 0.646676 | -0.764999 | -1.56462 |
| | B | 0.108409 | -1.906631 | -0.42873 |
| | B | -1.069926 | -0.782414 | -0.97122 |
| | B | -0.406286 | -0.779907 | 0.68773 |
| | B | 1.292464 | -0.797132 | 0.13279 |
| | H | 1.122338 | -1.169558 | -2.58537 |
| | H | -2.098973 | -1.187712 | -1.42179 |
| | H | -0.811804 | -1.656620 | 1.557343 |
| | H | 2.292464 | -1.216427 | 0.633155 |
| | H | 0.099316 | -3.095458 | -0.4243 |
| | H | -0.966248 | -0.861047 | 1.86869 |
| **$B_{10}$_$TS_{elim}$_ap** | | | | |
| ΔG | B | -0.499951 | 2.017721 | 0.248538 |
| -387.95234186 | B | -0.975891 | 0.969136 | -0.989322 |
| Electronic energy | B | 0.704032 | 0.940204 | -0.243303 |
| -386.802169127510 | B | -0.040801 | 0.905170 | 1.436509 |
| Electronic energy+ZPE | B | -1.720889 | 0.938369 | 0.690369 |

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|---|---|---|---|---|
| -386.614190847510 | H | -0.490419 | 3.208436 | 0.275660 |
| | H | -1.376428 | 1.411969 | -2.026319 |
| | H | 1.755528 | 1.352901 | -0.637869 |
| | H | 0.363948 | 1.293117 | 2.493704 |
| | H | -2.767996 | 1.344657 | 1.104695 |
| | B | 0.021539 | -0.535634 | -1.029969 |
| | B | -0.531242 | -1.498402 | 0.166782 |
| | B | -1.741048 | -0.533689 | -0.354658 |
| | B | -1.059431 | -0.581711 | 1.409442 |
| | B | 0.698370 | -0.581346 | 0.730084 |
| | H | 0.470940 | -0.952344 | -2.053531 |
| | H | -2.761656 | -0.947079 | -0.815195 |
| | H | -1.512801 | -1.031529 | 2.417892 |
| | H | 1.708592 | -1.037807 | 1.170961 |
| | H | 0.962913 | -3.349159 | -0.336590 |
| | H | 0.353005 | -3.771196 | -0.231043 |
| | C | -2.885568 | -3.452033 | 0.981875 |
| | N | -1.965435 | -3.937036 | 0.495565 |
| | C | -4.026801 | -2.799944 | 1.589246 |
| | H | -4.145072 | -3.144865 | 2.614877 |
| | H | -4.926894 | -3.023762 | 1.019270 |
| | H | -3.857953 | -1.723158 | 1.587630 |
| **$B_{10}$_$TS_{elim}$_eq** | | | | |
| ΔG | B | 5.909372 | 6.059835 | 7.530827 |
| -387.97361420 | H | 6.314172 | 5.612215 | 6.504263 |
| Electronic energy | B | 5.824369 | 5.342796 | 9.069167 |
| -386.823236004072 | B | 4.348092 | 6.007537 | 8.197003 |
| Electronic energy+ZPE | H | 3.464167 | 5.479967 | 7.588053 |

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|---|---|---|---|---|
| -386.635098724072 | B | 5.231775 | 7.570446 | 7.883762 |
| | H | 5.096011 | 8.454377 | 7.094032 |
| | B | 6.714799 | 6.904852 | 8.758643 |
| | H | 7.869010 | 7.208486 | 8.728654 |
| | B | 6.029278 | 6.485910 | 10.446312 |
| | B | 4.369562 | 5.910515 | 10.022236 |
| | H | 3.676947 | 5.116080 | 10.586359 |
| | B | 3.907268 | 7.448470 | 9.190813 |
| | H | 2.875822 | 8.007805 | 8.997343 |
| | B | 5.544344 | 7.893304 | 9.557007 |
| | H | 5.352447 | 10.469136 | 8.763558 |
| | B | 4.604306 | 7.419763 | 10.782626 |
| | H | 4.204736 | 7.866704 | 11.806689 |
| | H | 5.760327 | 10.552233 | 9.384496 |
| | C | 8.318592 | 9.047040 | 11.321308 |
| | N | 7.487388 | 9.798085 | 11.071116 |
| | C | 9.360895 | 8.089091 | 11.635906 |
| | H | 9.532677 | 7.443072 | 10.776277 |
| | H | 9.055334 | 7.482244 | 12.486633 |
| | H | 10.280936 | 8.617412 | 11.881550 |
| | H | 6.798668 | 6.231168 | 11.317056 |
| | H | 6.236804 | 4.230953 | 9.225541 |
| **[1-$B_{10}H_9NCCH_3$]$^-$** | | | | |
| ΔG | B | -0.029688 | 1.572347 | 0.020214 |
| -386.87263146 | B | -0.493994 | 0.511393 | -1.21547 |
| Electronic energy | B | 1.183056 | 0.507722 | -0.49389 |
| -385.728507273240 | B | 0.461677 | 0.442203 | 1.182178 |
| Electronic energy+ZPE | B | -1.215190 | 0.445434 | 0.460319 |

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|---|---|---|---|---|
| -385.549298683240 | H | -0.044282 | 2.765031 | 0.059101 |
| | H | -0.917753 | 0.944434 | -2.25056 |
| | H | 2.227058 | 0.937679 | -0.89862 |
| | H | 0.875074 | 0.814052 | 2.244922 |
| | H | -2.269966 | 0.819768 | 0.89182 |
| | B | 0.517039 | -0.97783 | -1.26037 |
| | B | 0.017038 | -2.0846 | -0.10335 |
| | B | -1.189947 | -1.0222 | -0.5819 |
| | B | -0.510922 | -1.07154 | 1.124891 |
| | B | 1.196819 | -1.02722 | 0.446686 |
| | H | 0.965531 | -1.36557 | -2.30167 |
| | H | -2.211662 | -1.4498 | -1.03917 |
| | H | -0.949722 | -1.54051 | 2.136488 |
| | H | 2.229741 | -1.45664 | 0.876039 |
| | C | 0.026978 | -4.70252 | -0.20617 |
| | N | 0.027959 | -3.56412 | -0.15772 |
| | C | 0.005766 | -6.14044 | -0.26699 |
| | H | -0.512825 | -6.44811 | -1.17408 |
| | H | -0.518984 | -6.52401 | 0.60703 |
| | H | 1.028100 | -6.51569 | -0.27935 |
| **[2-$B_{10}H_9NCCH_3$]$^-$** | | | | |
| ΔG | B | -0.224136 | 1.815875 | -0.462928 |
| -386.87301506 | B | -0.113241 | 0.613043 | -1.662453 |
| Electronic energy | B | 1.209363 | 0.927662 | -0.450768 |
| -385.729271167470 | B | 0.008869 | 0.845963 | 0.916121 |
| Electronic energy+ZPE | B | -1.278983 | 0.515260 | -0.295784 |
| -385.549833157470 | H | 2.259062 | 1.497368 | -0.550604 |
| | H | -0.027806 | 1.339702 | 2.006147 |

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|---|---|---|---|---|
| | B | 1.031848 | -0.702639 | -1.212458 |
| | B | 0.357115 | -1.847756 | -0.160323 |
| | B | -0.754077 | -0.992818 | -1.105634 |
| | B | -0.667957 | -0.828064 | 0.717170 |
| | B | 1.118056 | -0.539613 | 0.602671 |
| | H | -1.544516 | -1.548617 | -1.814965 |
| | H | -1.382813 | -1.242679 | 1.585390 |
| | H | 2.005173 | -0.734926 | 1.384918 |
| | H | 0.546022 | -3.022191 | -0.065182 |
| | H | 1.843198 | -1.041936 | -2.027214 |
| | H | -0.258160 | 0.901847 | -2.815313 |
| | H | -0.458784 | 2.980962 | -0.555896 |
| | C | -3.880937 | 0.967667 | -0.241810 |
| | N | -2.757944 | 0.779146 | -0.257480 |
| | C | -5.301328 | 1.200381 | -0.227944 |
| | H | -5.642560 | 1.242034 | 0.805652 |
| | H | -5.798449 | 0.382760 | -0.748176 |
| | H | -5.514388 | 2.144674 | -0.726591 |

**Table S3.** Cartesian atomic coordinates of the calculated optimized equilibrium model structures. All calculations were performed in dichlromethane $CH_2Cl_2$ phase. Solvent molecules were not taken into account explicitly**. S**olvent effects were considered using the Solvation Model based on Density (SMD). Atomic coordinates are given in Angstrom units. Gibbs energy (wB97X-D3 level of theory; kJ/mol), electronic energy (DLPNO-CCSDT level of theory; kJ/mol), electronic energy + ZPE corrections (DLPNO-CCSDT level of theory; kJ/mol). All coordinates are given in Angstrom units, Å.