

exploration of transition states involving monomeric B–N species resulted in high overall energy barriers (>30.0 kcal mol $^{-1}$). Hence, pathfinder explorations of the potential energy surfaces were then carried out for the different putative B–X–B-mediated catalytic cycles, organised around five possible routes based on the number of amines involved (Fig. 9–13), in order to explore the mechanistic diversity of these systems. Key transition state structures in each cycle are shown together in Fig. 14. To enable a high quality basis set to be employed (Def2-TZVPP), substituents were all modelled at this stage using methyl groups. Each cycle included the reaction free energies of the pre-step involving species used to assemble the reactant used as the start point in the cycle, and the energies of all subsequent steps in the cycle, ending in the final products. A final reaction free energy is included to re-generate the starting reactant ready for a second catalytic cycle.

The cycle involving one amine is illustrated in Fig. 9. The pre-assembly condensation step (blue) indicates a modestly endoenergetic step ($\Delta\Delta G_{298} +9.4$ kcal mol $^{-1}$) producing water, which agrees with the need for water removal using molecular sieves for the reaction to proceed. With the reactant in the cycle set to a relative energy of 0.0, the high point is reached with C–O cleavage (TS3) corresponding to $\Delta G_{298} +23.4$ kcal mol $^{-1}$, corresponding to a relatively slow ambient temperature reaction. The product in this cycle is $+0.3$ kcal mol $^{-1}$ relative to the reactant, but -4.2 kcal mol $^{-1}$ is recovered in the next regeneration step (red). Such a computational exploration can only demonstrate the viability of a single pathway to product; it does not preclude, of course, that lower energy pathways might not be discovered upon a more complete exploration of the potential energy

surface. These variants might include lower energy conformations of the various species explored. Rather more certain is that the free energy barrier surmounted during the cycle is probably an upper calculated bound to any true value. It should also be noted that the model used for the substituents (methyl) may introduce further uncertainty, but since the purpose here was a broad exploration of various mechanistic alternatives, we did not undertake the much more computationally resource-intensive recalculation using larger substituents.

A cycle involving two amine species is illustrated in Fig. 10. The pre-assembly step (blue) is rather more endoenergetic ($\Delta G_{298} +25.4$ kcal mol $^{-1}$) than the previous cycle, but the energetic maximum in the cycle (TS3, $\Delta G_{298} +24.8$ kcal mol $^{-1}$) relative to the assembled reactants is very similar. The product of the first cycle is exoenergetic by $\Delta G_{298} 22.3$ kcal mol $^{-1}$, offset in part by the regeneration step for the second cycle being $\Delta G_{298} +16.5$ endoenergetic.

The three-amine cycle (Fig. 11) again shows similar overall behavior. The condensation reaction resulting in the initial cycle reactant is endoenergetic by $\Delta G_{298} +24.4$ kcal mol $^{-1}$, matched by the exoenergetic products ($\Delta G_{298} -24.8$ kcal mol $^{-1}$), and with a regenerative step for the start of the second cycle being endoenergetic by $\Delta G_{298} +14.1$ kcal mol $^{-1}$. The rate limiting TS3 has $\Delta G_{298} 21.1$ kcal mol $^{-1}$, slightly more favourable than the previous two cycles.

The four-amine cycle (Fig. 12) has a highly endoenergetic condensation step ($\Delta G_{298} +37.9$ kcal mol $^{-1}$), again offset by the products being exoenergetic by 32.4 kcal mol $^{-1}$. The regeneration step for the second cycle is endoenergetic by $+24.9$ kcal mol $^{-1}$ and the overall barrier originating from TS1 is 25.4 kcal mol $^{-1}$. This makes this model cycle less favourable.

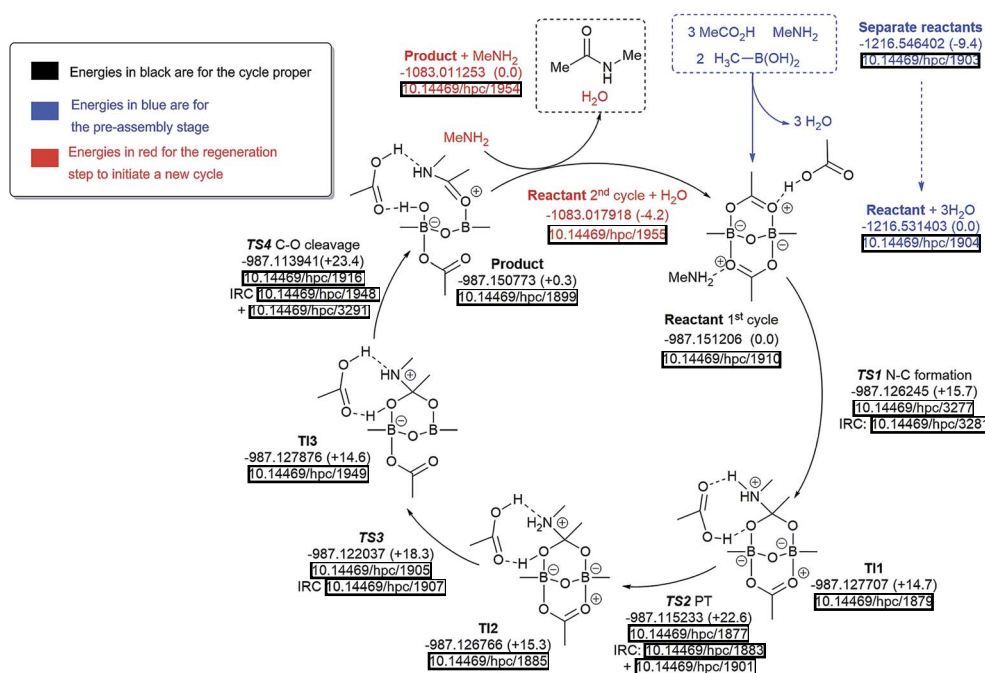


Fig. 9 Catalytic cycle involving one amine (data²⁹ sub-collection DOI: [10.14469/hpc/1854](https://doi.org/10.14469/hpc/1854)). The total computed free energy for each stationary point is shown in Hartree, with the relative energies shown in parentheses in kcal mol $^{-1}$. The DOI for data repository entries for individual species are shown in the form e.g. [10.14469/hpc/1885](https://doi.org/10.14469/hpc/1885). Energies in blue are for the pre-assembly stage, in black for the cycle proper and in red for the regeneration step to initiate a new cycle. All DOIs in this figure are available as clickable links (final paginated PDF only).

