Reverse Biomimetics:
Teaching Enzymes the Art of Modern Organic Synthesis

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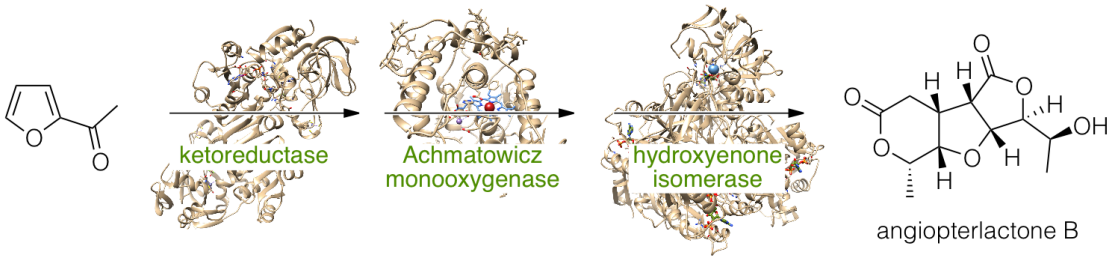
Thanks to unrivalled selectivities and good availability of stable and optimized enzyme preparations, biocatalysis is increasingly gaining ground as module in the organic chemist's toolbox for the synthesis of well-defined building blocks. However, with regard to an even broader application of enzyme catalysts in classical synthetic chemistry, the lack of biosynthetic precedence for numerous synthetically relevant reactions and the consequent lack of biocatalysts to promote those reactions needs to be considered a major drawback. Since many years, catalytic promiscuity, the enzymes' capability to catalyze fundamentally different chemical interconversions, has been in the scientific focus,[1] however, just recently entirely abiotic transformations came within reach by means of specialized, evolved proteins.[2-4]

In our search of biological catalysts with abilities to address synthetically important reactions beyond the biosynthetic repertoire, a set of wild-type metalloenzymes was identified to be effective promoters in a range of transformations for the preparation of *O*-heterocyclic compounds.[5,6] This talk will present the development of biocatalytic versions of the Achmatowicz-type ring expansion of furfuryl alcohols and the Doyle-Kirmse-type rearrangements of oxonium ylides,[7] as well as their implementation in the construction of short *ex vivo* metabolisms and natural product synthesis.[8]



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