THE HUNT FOR ARTIFICIAL REACTIVITIES IN BIOCATALYSIS: FUNGAL COPPER-DEPENDENT METALLOPROTEINS AS MEDIATORS FOR PERICYCLIC REACTIONS

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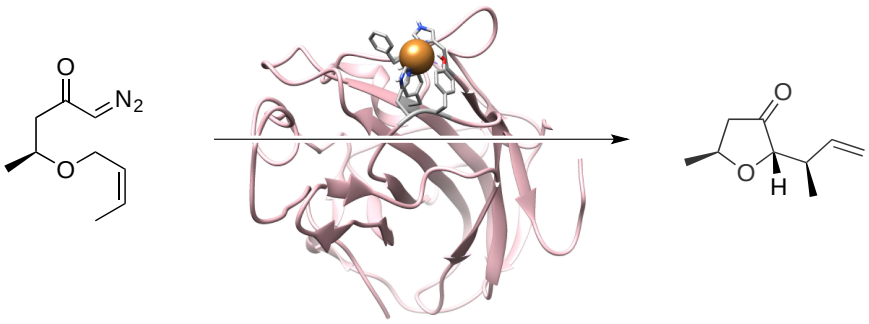
Biocatalysis is increasingly gaining ground as powerful module in the organic chemist's toolbox for the synthesis of well-defined building blocks, thanks to unrivalled selectivities and good availability of stable and optimized enzyme preparations. The lack of biosynthetic precedence for numerous synthetically relevant reactions and the consequent lack of biocatalysts to promote those reactions need to be considered a major drawback, since this prevents an even broader application of enzyme catalysts in classical synthetic chemistry. For 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, various wild-type metalloenzymes were identified as effective promoters in a range of unnatural transformations for the synthesis of *O*-heterocyclic compounds.[5-7] In this presentation, our most recent discoveries exploiting copper-proteins will be disclosed that emerged as versatile biocatalysts in pericyclic reactions. On one side, copper-dependent oligosaccharide-degrading oxidoreductases are introduced as powerful mediators in sigmatropic rearrangements enabling the preparation of complex tetrahydrofurans in high stereoselectivities.[8] Moreover, the synthesis of stereodefined *N*-heterocycles by means of blue multicopper enzymes through ene-type rearrangements will be discussed.



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