

Enzymatic Nitrene Transfer/Sigmatropic Rearrangement to Access Allylic Amines

Category

Organo- and Biocatalysis

Key words

sigmatropic rearrangement

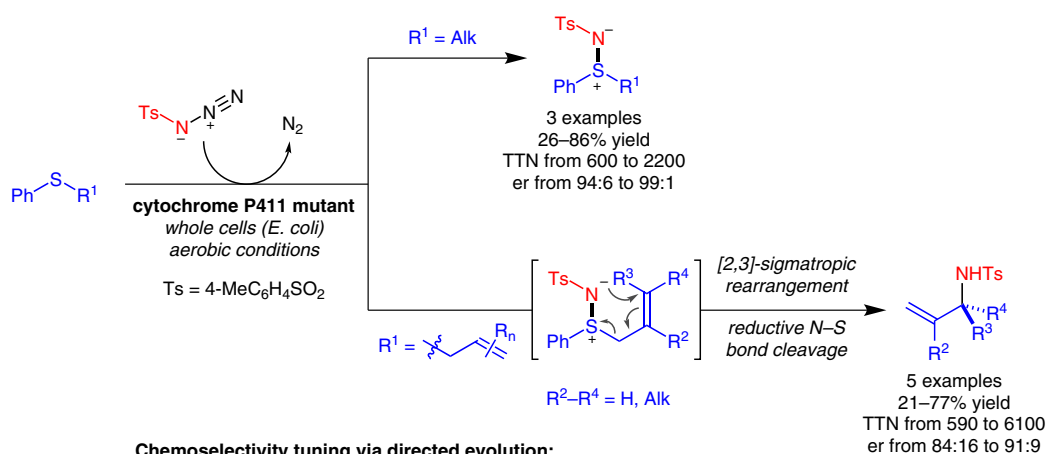
nitrene

directed evolution

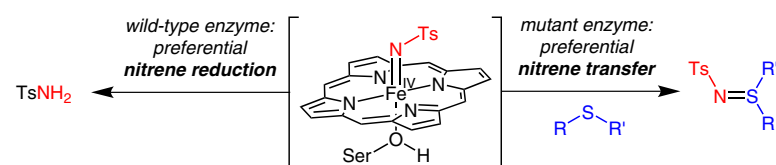
allylic amines

enzymes

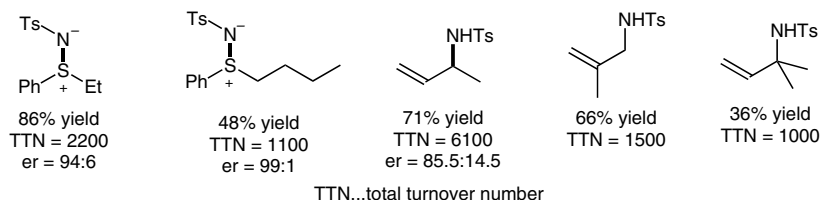
Synfact
of the month



Chemoselectivity tuning via directed evolution:



Selected examples:



Significance: Arnold and co-workers report an enzymatic synthesis of allylic amines through a sulfimidation/[2,3]-sigmatropic rearrangement of phenyl allyl sulfides with tosyl azide. A mutant variant of cytochrome P411 from *Bacillus megaterium* efficiently catalyzes a highly enantioselective nitrene transfer to the sulfides, and permits a subsequent rearrangement with partial retention of the stereochemical information. In a scale-up experiment with reduced catalyst loading, 0.1 mmol of substrate was converted into the corresponding allylic amine in 71% yield and a remarkable total turnover number of 6100.

Comment: The authors have successfully employed directed evolution to achieve a chemoselective nitrene transfer over the competing reduction. Furthermore, they achieved a sigmatropic rearrangement of the intermediate allylic sulfimides, a process unknown in wild-type biological systems.

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