



Swiss Science Concentrates

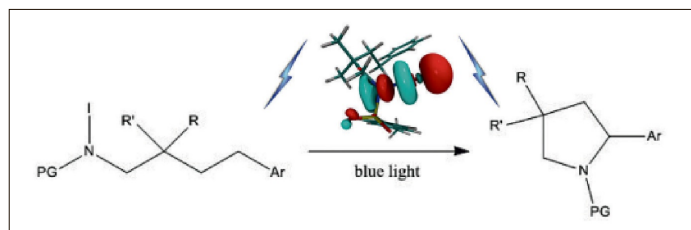
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Cooperative Light-Activated Iodine and Photoredox Catalysis for the Amination of C_{sp³}-H Bonds

P. Becker, T. Duhamel, C. J. Stein, M. Reiher*, and K. Muñiz*, *Angew. Chem. Int. Ed.* **2017**, *56*, 8004. ETH Zurich

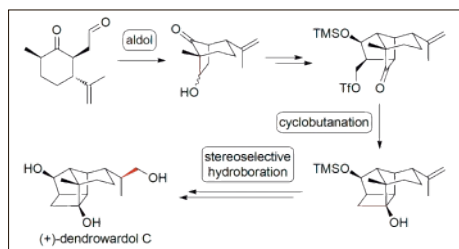
The development of effective and ecologically benign catalytic processes is a fundamental goal of contemporary research and development. A new field in catalysis describes the activation of small organic molecules by photoredox catalysis under visible-light irradiation. Reiher, Muñiz and coworkers introduce a new method for dual light-activated intramolecular amination of remote benzylic positions. The process is based on the cooperative interplay between molecular iodine and photoredox catalysis. Iodine activates a C_{sp³}-H bond by visible-light irradiation for the formation of a new C–N bond, while an organic photoredox catalyst induces the re-oxidation of iodine catalyst. The key N–I bond activation was elucidated by computational methods.



Total Synthesis of (+)-Dendrowardol C

H. Wolleb and E. M. Carreira*, *Angew. Chem. Int. Ed.* **2017**, *56*, 10890. ETH Zurich

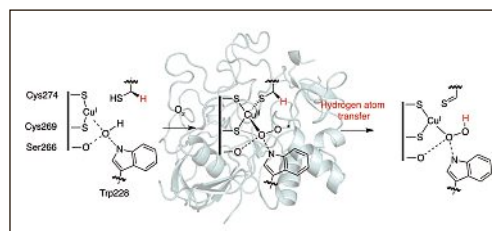
Dendrobium species have been applied in traditional Chinese medicine for various beneficial purposes. In 2013, the sesquiterpenoid (+)-dendrowardol C was isolated from *Dendrobium wardianum* Warner. Its structure is based on an unprecedented tetracyclic ring system with nine stereogenic centers. Carreira and Wolleb describe now the first total synthesis of the tetracyclic sesquiterpenoid (+)-dendrowardol C. It features an intramolecular aldol reaction to construct the central bicyclic scaffold, followed by cyclization of a γ -triflyloxy ketone to form the cyclobutane. The generation of a carbocycle from a triflated ketone instead of the corresponding halide may prove to be of general use in cyclization reactions. The last chiral center is set by diastereoselective hydroboration of a 1,1-disubstituted double bond in the presence of a chiral Co(I) catalyst.



Structural Basis for Copper–Oxygen Mediated C–H Bond Activation by the Formylglycine-Generating Enzyme

M. Meury, M. Knop, and F. P. Seebeck*, *Angew. Chem. Int. Ed.* **2017**, *56*, 8115. University of Basel

Copper is a powerful catalyst for the transfer of electrons from organic matter to molecular oxygen. Understanding the nature of the catalytic species involved in the process is a major scientific objective. Formylglycine-generating enzyme (FGE) catalyzes oxygen-dependent C–H activation. Seebeck and coworkers now present crystal structures of FGE in complex with either Ag^I or Cd^{II} providing evidence for a high-affinity metal-binding site in this enzyme. The structures reveal a bis-cysteine linear coordination of the monovalent metal, and tetrahedral coordination of the bivalent metal. Such complexation of copper atoms is unprecedented for redox-active copper enzymes or synthetic copper catalysts. Comparison of these structures with published ones of homologous apo-enzymes provides a model for substrate-binding, oxygen-activation and stereoselective hydrogen-atom abstraction.



Terpene Cyclizations inside a Supramolecular Catalyst: Leaving-Group-Controlled Product Selectivity and Mechanistic Studies

Q. Zhang, L. Catti, J. Pleiss, and K. Tiefenbacher*, *J. Am. Chem. Soc.* **2017**, *139*, 11482. University of Basel and ETH Zurich

Terpenes constitute one of the largest classes of natural products and, arguably, one of the most complex reactions found in nature is the tail-to-head terpene cyclization. Tiefenbacher and collaborators describe the first man-made enzyme-like catalyst, a hydrogen-bond-based resorcinarene capsule that is capable of catalyzing this reaction. The noncovalent interactions between the capsule and the substrate enable product selectivity by using different leaving groups. Mechanistic investigations revealed that the cleavage of the leaving group is the rate determining step in the cyclization of geranyl acetate. The studies also showed that trace amounts of acids are required as co-catalyst for the activation of the substrate.

