



Swiss Science Concentrates

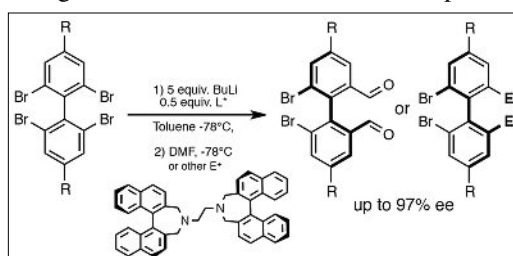
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Asymmetric Bromine–Lithium Exchange: on the Importance of Both the Diamine Ligand and the Organolithium Reagent

J. Praz, J. Graff, L. Egger, L. Guénée, S. Wagschal, E. P. Kündig, and A. Alexakis*, *Chem. Commun.* **2015**, 51, 16912. University of Geneva

Halogen–lithium exchange is widely used for the preparation of organolithium compounds and has found many applications in total synthesis and in the elaboration of key intermediates in organic chemistry. Alexakis and coworkers investigated the formation of axially chiral biaryls by desymmetrization of prochiral substrates *via* asymmetric bromine–lithium exchange. As in many asymmetric organolithium reactions, the chiral ligand (here a diamine) was expected to be the enantio-controlling element. While the authors indeed found new and more efficient diamines, they also identified the nature of the RLi reagent as the most important factor. Using *s*-BuLi, enantiomeric excesses of up to 97% were obtained

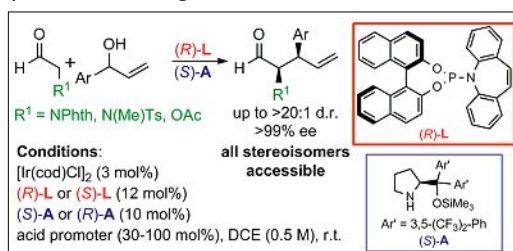


rendering the findings interesting for the synthesis of natural products and new atropisomeric phosphorus ligands.

Stereodivergent Dual Catalytic α -Allylation of Protected α -Amino- and α -Hydroxyacetaldehydes

T. Sandmeier, S. Krautwald, H. F. Zipfel, and E. M. Carreira*, *Angew. Chem. Int. Ed.* **2015**, 54, 14363. ETH Zürich

Formation of multiple stereogenic centers in a single chemical transformation with complete control of absolute and relative configuration represents a significant challenge in asymmetric synthesis. Carreira and co-workers achieved the fully stereodivergent dual-catalytic α -allylation of protected α -amino- and α -hydroxyacetaldehydes through iridium- and amine-catalyzed substitution of racemic allylic alcohols with chiral enamines generated *in situ*. The operationally simple method furnishes useful aldehyde building blocks in good yields, more than 99% *ee*, and with d.r. values greater than 20:1 in some cases. Additionally, the γ,δ -unsaturated products can be further functionalized in a stereodivergent fashion with high selectivity and with preservation of stereochemical integrity at the C α position.

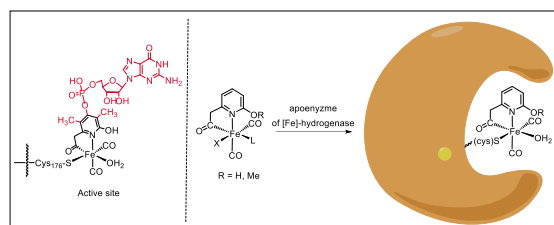


reodivergent fashion with high selectivity and with preservation of stereochemical integrity at the C α position.

Reconstitution of [Fe]-Hydrogenase Using Model Complexes

S. Shima*, D. Chen, T. Xu, M. D. Wodrich, T. Fujishiro, K. M. Schultz, J. Kahnt, K. Ataka, and X. L. Hu*, *Nat. Chem.* **2015**, 7, 995. EPF Lausanne

[Fe]-Hydrogenase catalyzes the reversible hydrogenation of a tetrahydromethanopterin substrate in the methanogenesis from CO $_2$ and H $_2$. Although the structure and properties of [Fe]-hydrogenase have been studied thoroughly, the mechanism of H $_2$ activation remains speculative. In an elegant study, Shima, Hu and collaborators now describe the reconstitution of semisynthetic [Fe]-hydrogenase using two types of small molecule mimics of iron-guanylylpyridinol (FeGP) cofactor. They show that a mimic containing a 2-hydroxypyridine group restores activity, whereas the analogous enzyme with a 2-methoxypyridine complex is essentially inactive. These findings, together with DFT computations, support a mechanism in which the 2-hydroxy group is deprotonated before it serves as an internal base for heterolytic H $_2$ cleavage.



Measurement and Laser Control of Attosecond Charge Migration in Ionized Iodoacetylene

P. M. Kraus, B. Mignolet, D. Baykusheva, A. Rupenyan, L. Horný, E. F. Penka, G. Grassi, O. I. Tolstikhin, J. Schneider, F. Jensen, L. B. Madsen, A. D. Bandrauk, F. Remacle, and H. J. Wörner*, *Science* **2015**, 350, 790. ETH Zürich

The ultrafast motion of electrons and holes after light–matter interaction is fundamental to a broad range of chemical and biophysical processes. The measurement of charge migration is a key goal of attosecond science. Using advanced *high-harmonic spectroscopy*, Wörner and collaborators reconstructed the full quantum dynamics of charge migration in spatially oriented polar molecules at a resolution of \sim 100 attoseconds. The migration of an electron hole after ionization of iodoacetylene was resolved in a spatial and temporal manner. This multidimensional approach enables the reconstruction of both quantum amplitudes and phases of the involved electronic states and, at the same time, opens the prospect of controlling electronic primary processes.

