

Swiss Science Concentrates

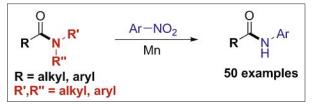
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Manganese-Mediated Reductive Transamidation of Tertiary Amides with Nitroarenes

Chi Wai Cheung, Jun-An Ma, and Xile Hu*, *J. Am. Chem. Soc.* **2018**, *140*, 6789. EPFL

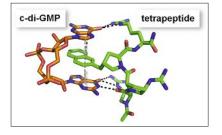
An efficient and broad-scope method for transamidation of tertiary amides utilizing elemental manganese as the sole catalyst has been introduced by Cheung, Ma and Hu. At the heart of this simple approach is reductive transamidation of tertiary amides with nitroarenes as the nitrogen source. By using nitroarenes instead of a tertiary amine, the previous problem of obtaining a product mixture under thermodynamic control has been avoided. Moreover, as compared to anilines, nitroarenes are generally more accessible, more stable, and less costly. Although the mechanism of this manganese-mediated reductive transamidation is not still clear, the researchers found azoarene as an active intermediate in the pathway. This new method can be used for the efficient preparation of tertiary amides with far-reaching applications in medicinal and materials chemistry.



Functionalized Proline-rich Peptides Bind the Bacterial Second Messenger c-di-GMP

Carlotta Foletti, Rolf A. Kramer, Harald Mauser, Urs Jenal, Konrad H. Bleicher, and Helma Wennemers*, *Angew. Chem. Int. Ed.* **2018**, *57*, 7729. ETH Zurich

The rapidly emerging resistance of pathogenic bacteria towards common antibiotics demands identification and exploitation of new drug targets. Bis-(3',5')-cyclic dimeric guanosine monophosphate (c-di-GMP) is a second messenger of bacterial biofilm formation, cell cycle progression, and virulence of several known pathogens. Since higher eukaryotes lack c-di-GMP, it is a potentially attractive drug target. The Wennemers group and collaborators identified short, proline-rich peptides bearing cationic and aromatic groups that selectively bind to c-di-GMP with micromolar affinities. These same peptides inhibited biofilm forma-

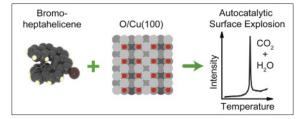


tion by the opportunistic pathogen *P. aeruginosa*. In the future, such compounds could be used in both therapeutic and analytical capacities to tackle the emerging problem of antibiotic drug resistance.

Stereospecific Autocatalytic Surface Explosion Chemistry of Polycyclic Aromatic Hydrocarbons

Anaïs Mairena, Martin Wienke, Kévin Martin, Narcis Avarvari, Andreas Terfort, Karl-Heinz Ernst*, and Christian Wäckerlin*, J. *Am. Chem. Soc.* **2018**, *140*, 7705. Empa Dübendorf

Coal has been used to reduce CuO since the bronze age. Despite being studied for a very long time, the combustion chemistry of polycyclic hydrocarbons (PAHs) still bears surprises. Wäckerlin and coworkers studied the combustion of monolayers of PAHs adsorbed on an atomic layer of oxygen on Cu(100) using temperature programmed reaction spectroscopy. Molecules like bromo-heptahelicene combust autocatalytically into CO₂ and H₂O, but others, such as bromo-pyrene, for example, undergo regular combustion. This surprising result is explained by the steric overcrowding of bromo-heptahelicene which allows facile dehydrogenation. These results may have implications for the better understanding of heterogeneous catalysis.



Molecular Dynamic Staircases: All-carbon Axial Chiral 'Geländer' Structures

Rajesh Mannancherry, Michel Rickhaus, Daniel Häussinger, Alessandro Prescimone, and Marcel Mayor*, *Chem. Sci.* **2018**, *9*, 5758. University of Basel

Molecules with helical structures are inherently beautiful to chemists and non-chemists alike. Mayor and co-workers opened a new molecular window in the design and synthesis of polycyclic aromatic compounds with helical structures. Geländer (in German: "banister of a spiral staircase") molecules with axial chirality were prepared from terphenylenes containing two, all-carbon bridges between the ortho positions of the benzene units in the terphenylene core. The researchers demonstrated that a compact arrangement of these short bridges resulted in a higher racemization barrier to give the most tightly packed Geländer oligomers reported to date.

