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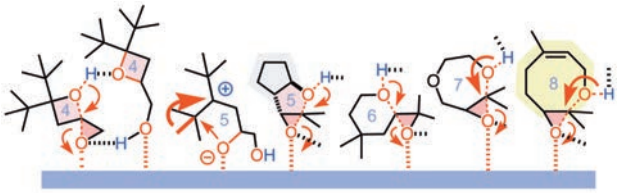
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Primary Anion–π Catalysis of Epoxide-Opening Ether Cyclization into Rings of Different Sizes: Access to New Reactivity

M. Paraja and S. Matile,* *Angew. Chem. Int. Ed.* **2020**, *59*, 6273. University of Geneva

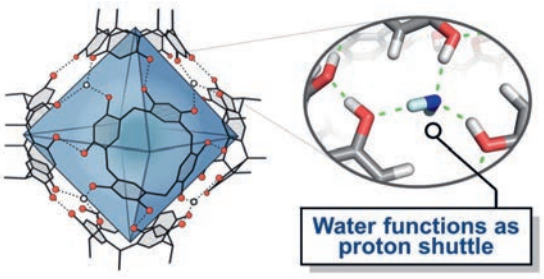
Anion–π catalysis was introduced explicitly only seven years ago and since then a library of catalysts and reactions has been created and constantly updated. Epoxide-opening ether cyclizations have served as model reactions in this context. The authors report epoxide-opening cyclizations on π-acidic aromatic surfaces providing access to ring sizes that are beyond reach for Brønsted acids. The reaction outcome of a range of substrates was interpreted by the following rationale: i) small rings arise from SN1-type behavior from epoxide opening induced by alcoholate-π interactions ii) large rings are formed due to ground state destabilization derived from anion-π autocatalysis.



Requirements for Terpene Cyclizations inside the Supramolecular Resorcinarene Capsule: Bound Water and Its Protonation Determine the Catalytic Activity

S. Merget, L. Catti, G. Piccini, and K. Tiefenbacher,* *J. Am. Chem. Soc.* **2020**, *142*, 4400. University of Basel

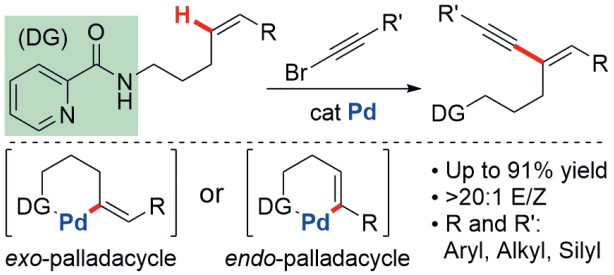
Natural enzymes exhibit unique catalytic effciency and selectivity, which inspired chemists to design new catalytic systems based on self-assembled supramolecular host systems. However, elucidating the requirements for catalytic activity within supramolecular hosts is essential to design more efficient catalysts. The authors synthesized a number of resorcinarene-based capsules containing resorcinol and pyrogallol units, and studied their catalytic activity in the monoterpene cyclization. The results, supported by molecular dynamics simulations, indicate the critical role of water incorporated in the supramolecular self-assembly by hydrogen-bonding, which acts as a proton shuttle to activate the encapsulated substrate.



Palladium-Catalyzed C–H Alkynylation of Unactivated Alkenes

B. S. Schreib, M. Fadel, and E. M. Carreira, *Angew. Chem. Int. Ed.,* doi: 10.1002/anie.202000935. ETH Zurich

Conjugated 1,3-enynes are abundantly found in natural products, bioactive molecules and organic materials. While a number of methods have already been reported to generate this motif, the *E*/*Z* stereoselectivity still remains an issue, especially for tri- and tetrasubstituted olefins. Carreira and co-workers report an interesting solution to this problem by developing the Pd-catalyzed directed C–H alkynylation of alkenes with bromoalkynes. This method can proceed through *exo*- or *endo*-alkenylpalladacycles and produces a variety of 1,3-enynes with tri- or tetrasubstituted alkenes in a stereospecific manner. It shows a broad scope and a high degree of tolerance towards functional groups.



A Releasable Disulfide-linked Peptide Tag Facilitates the Synthesis and Purification of Short Peptides

Y. Wu, A. Zorzi, J. Williams, and C. Heinis,* *Chem. Commun.* **2020**, *56*, 2917. EPFL Lausanne

Combinatorial cyclization of random linear peptides by structurally diverse chemical linkers offers access to large macrocyclic peptide libraries. However, the preparation of large numbers of short random linear peptides remains a challenge. The authors established an approach for the efficient generation of large numbers of short peptides without chromatographic purification. They synthesized peptides conjugates containing a precipitable tag and a disulfide linker allowing purification to a high degree and determination of the concentrations by absorption. The tag was easily cleaved by reduction of the disulfide bridge, hence generating a thiol that was directly used for peptide macrocyclization with diverse bis-electrophiles.

Prepared by Shu-Min Guo, Anton Kudashev, Takeru Miyakoshi, Marco Zuccarello, and Olivier Baudoin*

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