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Swiss Science Concentrates

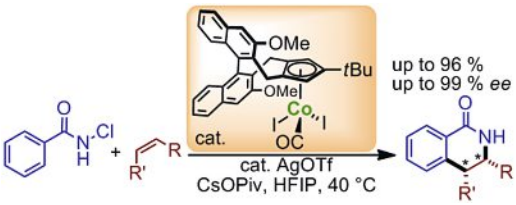
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Chiral Cyclopentadienyl Cobalt(III) Complexes Enable Highly Enantioselective 3d-Metal-Catalyzed C–H Functionalizations

K. Ozols, Y.-S. Jang, and N. Cramer*, *J. Am. Chem. Soc.* **2019**, *141*, 5675. EPFL

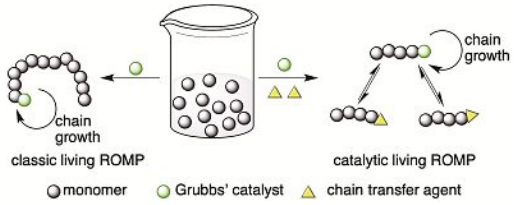
The use of abundant 3d-metal catalysts for C–H functionalization is a current hot topic of research. However, enantioselective methods remain underdeveloped. In this work, the authors disclose the preparation of cobalt(III) complexes bearing chiral cyclopentadienyl ligands. To demonstrate their utility as C–H functionalization catalysts, the synthesis of dihydroisoquinolones from *N*-chlorobenzamides was chosen as a benchmark transformation. The excellent enantio- and regioselectivities observed with a large variety of alkenes outperform the best rhodium(III) based methods for this reaction. Moreover, the regioselectivity towards alkyl alkenes was shown to be complementary to the one observed with rhodium.



Catalytic Living Ring-opening Metathesis Polymerization with Grubbs' Second- and Third-generation Catalysts

M. Yasir, P. Liu, I. K. Tennie, and A. F. M. Kilbinger,* *Nat. Chem.* **2019**, *11*, 488. University of Fribourg

Conventional living ring-opening metathesis polymerization (ROMP) requires an equal number of ruthenium complexes to the number of polymer chains synthesized, leading to high loadings of ruthenium. Kilbinger and co-workers developed a reversible chain-transfer agent to produce living ROMP polymers from norbornene derivatives using catalytic amounts of Grubbs' ruthenium complexes. The polymers obtained by this method showed all of the characteristics of a living polymerization and monomers bearing various functional moieties could also be catalytically polymerized in a living fashion. This more economical and environmentally friendly method could lead to new applications in materials science, biology or medicine.



C-Terminal Bioconjugation of Peptides through Photoredox Catalyzed Decarboxylative Alkynylation

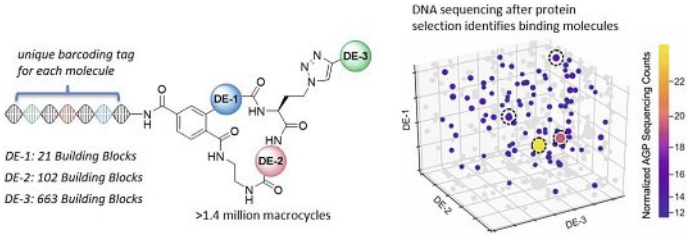
M. Garreau, F. Le Vaillant, and J. Waser*, *Angew. Chem. Int. Ed.* **2019**, doi: 10.1002/anie.201901922. EPFL

Late-stage modification of peptides at the C-terminus is an underexplored field in organic chemistry. Waser and co-workers report the efficient decarboxylative alkynylation of peptides at the terminal carboxylic acid using organic dyes and hypervalent iodine reagents (EBX) at room temperature under blue LED irradiation. A broad range of EBX-reagents was used to successfully install a variety of functional groups. Fine-tuning of the organic dye allowed C-terminal selectivity in the presence of other carboxylic acids thanks to their different oxidation potentials. Most other amino acid side-chains were tolerated, making this methodology broadly applicable for the late-stage functionalization of peptides.

A DNA-encoded Chemical Library Incorporating Elements of Natural Macrocycles

C. J. Stress, B. Sauter, L. A. Schneider, T. Sharpe, and D. Gillingham*, *Angew. Chem. Int. Ed.* **2019**, doi: 10.1002/anie.201902513. University of Basel

The development of novel macrocycle drugs is challenging as they violate Lipinski's rules for oral bioavailability. Recent work based on approved drugs suggest that the backbone plays a crucial role in the binding of macrocycles to their target. To better understand the unusual properties of macrocycle drugs, Gillingham and co-workers expand the available DNA-encoded macrocycle libraries (DEML) sets by incorporating diverse hydrophobic components in the backbone. This diversity comes at the cost of custom synthesis of bifunctional building block libraries, and stresses the need for new DNA-compatible synthetic methods.



Prepared by Yann Baumgartner, Nadja Niggli, David Savary, Pierre Thesmar and Olivier Baudoin*

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