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Swiss Science Concentrates

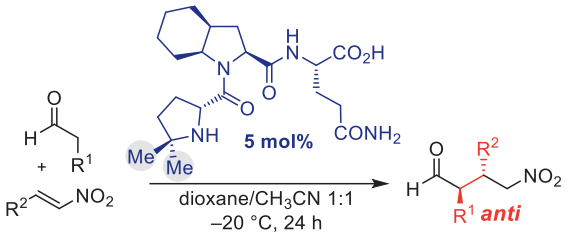
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Organocatalysed Conjugate Addition Reactions of Aldehydes to Nitroolefins with *Anti* Selectivity

T. Schnitzer, A. Budinská, and H. Wennemers,* *Nat. Catal.* **2020**, *3*, 143. ETH Zurich

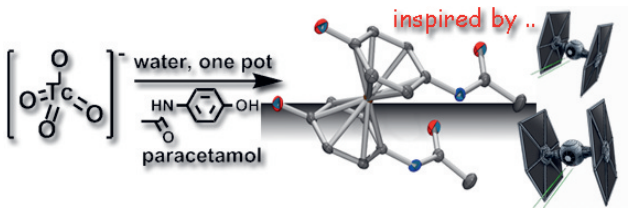
In the past two decades, the organocatalyzed asymmetric conjugate addition between aldehydes and nitroolefins has been an intense research focus due to the variety of structures accessible from the resulting γ-nitroaldehydes. The authors designed a tripeptide catalyst enabling the synthesis of the more challenging *anti* products instead of the usually obtained *syn* diastereoisomers. The introduction of substituents at Cδ of the reactive pyrrolidine was key to favour the formation of s-*cis* enamine intermediates, while maintaining the *Si*-facial selectivity. A range of γ-nitroaldehydes were obtained with d.r. in the range of 2:1 to 20:1 and excellent enantioselectivities (96–98% *ee*).



To Sandwich Technetium: Highly Functionalized Bis-Arene Complexes $[^{99m}Tc(\eta^6\text{-arene})_2]^+$ Directly from Water and $[^{99m}TcO_4]^-$

Q. Nadeem, G. Meola, H. Braband, R. Bolliger, O. Blacque, D. Hernández-Valdés, and R. Alberto,* *Angew. Chem. Int. Ed.* **2020**, *59*, 1197. Department of Chemistry, University of Zurich

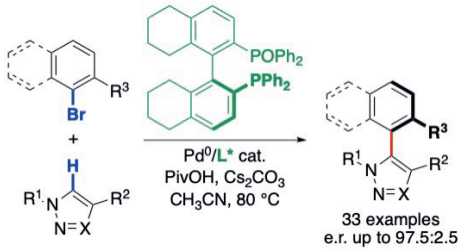
Molecular imaging, as a technique for non-invasive detection of abnormal physiological issues, typically relies on ^{18}F and ^{123}I labeling. In contrast, metallic radionuclides such as ^{99m}Tc usually employ multidentate ligands to prevent transmetalation with competing ligand sites present in the organism. Phenyl groups are ubiquitously present in drug candidates, and therefore are attractive ligands for such radionuclides. In this paper, Alberto and co-workers report a new method to label such motifs by forming $[^{99m}Tc(\eta^6\text{-arene})_2]^+$ complexes under mild, aqueous conditions from $[^{99m}TcO_4]^-$. This method shows a high degree of functional group tolerance, not reachable by classic Fischer-Hafner synthesis.



Intermolecular Palladium(0)-Catalyzed Atropo-enantioselective C–H Arylation of Heteroarenes

Q.-H. Nguyen, S.-M. Guo, T. Royal, O. Baudoin,* and N. Cramer,* *J. Am. Chem. Soc.* **2020**, *142*, 2161. University of Basel, EPFL

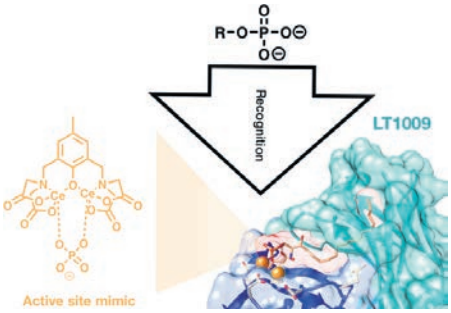
Axially chiral molecules are important structural motifs in asymmetric catalysis as well as in natural products and bioactive molecules. However, the straightforward and efficient construction of the stereogenic axis by C–H functionalization methods is rare and challenging. The authors report a highly enantioselective intermolecular C–H arylation providing an efficient access to atropisomeric (hetero)biaryls using Pd(0) catalysis and H_8-BINAPO as a chiral ligand. The method allows the synthesis of a broad range of arylated triazoles and pyrazoles in high yields and excellent atropo-enantioselectivities. Furthermore, a double atroposelective C–H arylation was performed with over 99.5:0.5 e.r.



A Biomimetic Cerium-Based Biosensor for the Direct Visual Detection of Phosphate under Physiological Conditions

T. Rossel,* and M. Creus, *Chem. Commun.* **2019**, *55*, 14894. Gymnase français de Bienne, University of Basel

Phosphates are fundamental anions that play key roles in living systems. The authors reported an indicator displacement assay for phosphate anions based on the dinuclear complex $[Ce_2(HXTA)]^{3+}$ and employing pyrocatechol violet (PCV) as the chromogenic indicator. The addition of phosphate anions to the violet solution of the $[Ce_2(HXTA)(PCV)]^+$ complex resulted in a change of color to pale yellow. This cerium-based sensor shows the best affinity constant of similar known systems, an excellent selectivity towards phosphate over other anions in various types of aqueous solutions and mimics the active site of LT1009 (a clinical monoclonal antibody).



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

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