



Swiss Science Concentrates

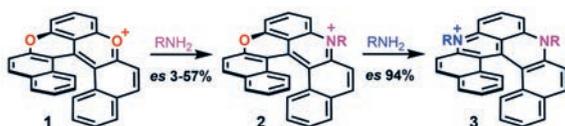
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Stereochemical Significance of O to N Atom Interchanges within Cationic Helicenes: Experimental and Computational Evidence of Near Racemization to Remarkable Enantiospecificity

G. M. Labrador, C. Besnard, T. Bürgi, A. I. Poblador-Bahamonde*, J. Bosson*, and J. Lacour*, *Chem. Sci.* **2019**, *10*, 7059. University of Geneva

The formation of pyridinium ions by treatment of pyrylium salts with primary amines is a method of choice for the construction of cationic aza aromatics. Lacour and co-workers successfully extended this methodology to cationic helicenes. They report the direct transformation of enantioenriched dioxa helicene **1** to azaxoxa **2** and diaza **3** helicenes, with low to high enantiospecificity (*es*). Stereoretention was confirmed by in depth experimental and theoretical studies which also helped improve the chirality transfer. The mild reaction conditions are compatible with functional groups which were not previously tolerated. This late-stage functionalization strategy could stimulate future developments and applications of these original chromophores and fluorophores.



Catalytic Synthesis of Potassium Acyltrifluoroborates (KATs) by Chemoselective Cross-Coupling with a Bifunctional Reagent

D. Wu, N. A. Fohn, and J. W. Bode*, *Angew. Chem. Int. Ed.* **2019**, *58*, 11058. ETH Zürich

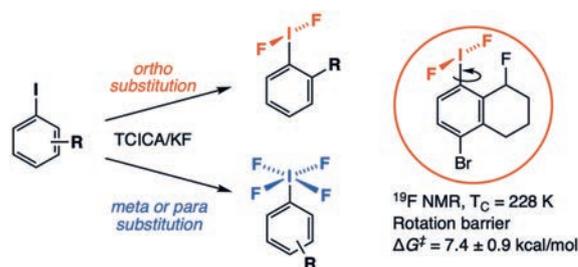
The interest in potassium acyltrifluoroborates (KATs) has recently increased due to their use in different research fields including bioconjugation and material chemistry. However, their broader application is limited by the scarcity of reported synthetic approaches. In this work, Wu, Fohn and Bode report a new synthesis of KATs *via* Stille cross-coupling of aryl- and vinyl (pseudo) halides with a new bench-stable stannyl iminium trifluoroborate reagent, prepared in only one step from commercially available precursors. The reaction occurs under mild conditions and shows a high functional group tolerance, hence allowing the synthesis of previously inaccessible KATs including precursors of amino acids.



Substituent-controlled, Mild Oxidative Fluorination of Iodoarenes: Synthesis and Structural Study of Aryl I(III)- and I(V)-Fluorides

J. Häfliger, C. R. Pitts, D. Bornemann, R. Käser, N. Santschi, J. Charpentier, E. Otth, N. Trapp, R. Verel, H. P. Lüthi, A. Togni*, *Chem. Sci.* **2019**, *10*, 7251. ETH Zürich

Studying the structure and reactivity of difluoro(aryl)- λ^3 -iodanes and tetrafluoro(aryl)- λ^5 -iodanes has been so far limited by the harsh conditions required for oxidative fluorination. In this study, Togni and co-workers report a mild, safe and inexpensive oxidative fluorination of aryl iodides using trichloroisocyanuric acid (TCICA) and potassium fluoride. They discovered that the selectivity of aryl-IF₂ vs. aryl-IF₄ formation is controlled by the substitution pattern of the arene. In addition, they performed detailed mechanistic investigations revealing the role of the *ortho*-substituent in inhibiting further oxidative fluorination. This study should stimulate further work in fluorination chemistry.



Molecular Complex of Tb in the +4 Oxidation State

C. T. Palumbo, I. Zivkovic, R. Scopelliti, and M. Mazzanti*, *J. Am. Chem. Soc.* **2019**, *141*, 9827. EPFL

Whereas rare earth metals chemistry has been limited mostly to the +3 oxidation state, the +2 oxidation state has recently been shown to be accessible for most lanthanides. However, the only example of an isolated Ln⁴⁺ molecular complex remained Ce⁴⁺, which found numerous applications in various fields thanks to its high oxidation power. In this work, the authors report the first example of a molecular Tb⁴⁺ complex. [Tb(OSi(O^tBu)₃)₄] was prepared by oxidation of its Tb³⁺ ate complex with [N(C₆H₄Br)₃][SbCl₆]. Cyclic voltammetry measurements revealed that the redox events of the Tb⁴⁺ complex are about 1 V more positive than the Ce⁴⁺ analogue.

