Swiss Science Concentrates

A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

## Spatial Anion Control on Palladium for Mild C–H Arylation of Arenes

J. Dhankhar, E. González-Fernández, C.-C. Dong, T. K. Mukhopadhyay, A. Linden, and I. Čorić,* *J. Am. Chem. Soc.* **2020**, *142*, 19040–19046.
University of Zurich

Transition-metal-catalyzed C–H bond activation is a transformative methodology offering access to organic intermediates from more accessible and sustainable precursors. Among other transition-metals, Pd was shown to catalyze C–H bond functionalization without recourse to a directing group. However, previous methods required an excess of coupling partners, high temperatures and different additives, and were limited to specific substrates. In this work, the authors designed a structurally constrained dicarboxylate ligand which allows a dramatic enhancement of the reactivity in the non-directed intermolecular C–H arylation of arenes. Using this catalytic system, reactions could be performed at room temperature and with the arene as limiting reactant, thereby demonstrating suitability for late-stage structural diversification. The observed site-selectivity was found to be complementary to other C–H functionalization methods. DFT studies indicated that the spatially controlled carboxylates function as cooperative ligands. This work provides a new approach to enhance reactivity in challenging catalytic transformations.

Authors' comments:
"Our work shows that precise positioning of coordinated anions on a transition metal can facilitate difficult bond activation processes. This spatial anion control concept might find broad use in catalysis."
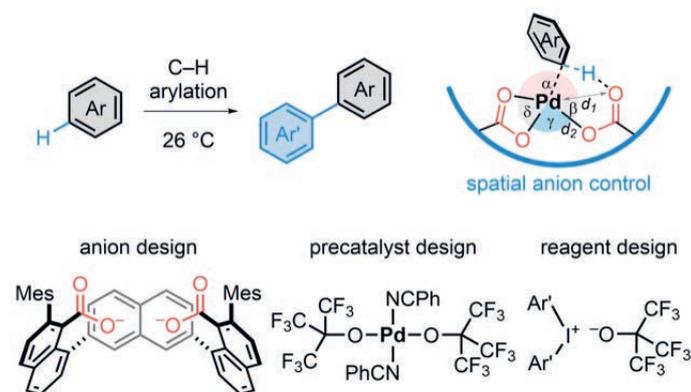
A Strategic Ser/Cys Exchange in the Catalytic Triad Unlocks an Acyltransferase-Mediated Synthesis of Thioesters and Tertiary Amides
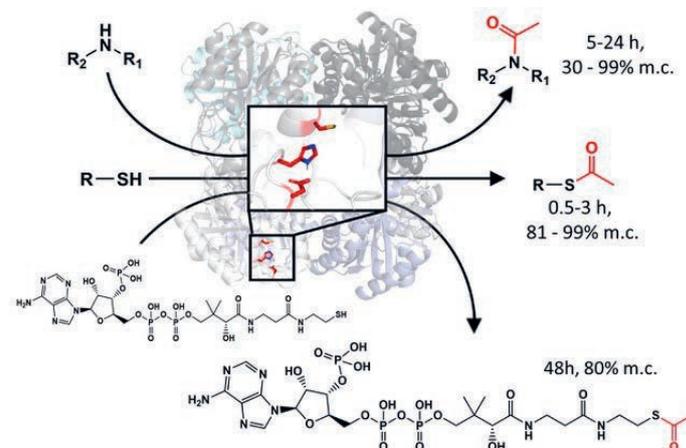
M. L. Contente, D. Roura-Padrosa, F. Molinari,* and F. Paradisi,* *Nat. Catal.* **2020**, *3*, 1020–1026.
University of Bern, University of Nottingham, University of Milan

Enzymatic catalysis is a powerful tool in asymmetric synthesis, which has dramatically expanded in the last years. In particular, the acylation of a range of nucleophiles such as alcohols and amines has been achieved using wild-type enzymes. However, most of the existing methods are not compatible with thiol and secondary amine nucleophiles. In this work, the authors report the preparation of thioesters and tertiary amides using a mutant of the acyltransferase from *Mycobacterium smegmatis* and vinyl esters as acylating agents. This reactivity was unlocked from the wild-type enzyme by a strategic Ser/Cys exchange in the catalytic triad. A broad scope of thioesters and tertiary amides was achieved, including examples on a preparative scale demonstrating the robustness and synthetic utility of the method. Additionally, acetyl-CoA, which plays an essential role in many biological processes, was readily obtained from CoA. Finally, computational studies provided insights into the binding mode of the substrate inside the enzymatic pocket. This work further demonstrates the power of enzyme evolution to expand the toolbox of available transformations.

Authors' comments:
"Changing one of the catalytic amino acids in an enzyme is rarely performed when the aim is to shift the substrate scope. However, in this case it worked surprisingly well!"


Prepared by Shu-Min Guo, Anton Kudashev, Takeru Miyakoshi, Marco Zuccarello, and Olivier Baudoin*
Do you want your article to appear in the SWISS SCIENCE CONCENTRATES highlight?
Please contact olivier.baudoin@unibas.ch

Data-Powered Augmented Volcano Plots for Homogeneous Catalysis

M. D. Wodrich, A. Fabrizio, B. Meyer and C. Corminboeuf*
Chem. Sci. **2020**, *11*, 12070–12080.
Ecole Polytechnique Fédérale de Lausanne

Identifying the relationships between molecular structure, reactivity and other experimental observables helps chemists to properly understand and predict the behavior and activity of catalysts. Traditional volcano plots, built upon linear scaling relationships between the free energies of intermediates and transition-states, are generally constructed from small data sets of catalysts. These plots measure 'activity' based on a single numeric value associated with the largest energy barrier encountered in the catalytic cycle. In this work, the authors introduced a big data-inspired variant, the 'augmented volcano plot', that provides a one-dimensional similarity measure of the entire catalytic cycle free energy profile against that of an ideal reference without relying upon linear scaling relationships. They applied this method to a model and industrially important hydroformylation reaction catalyzed by group 9 metal complexes. The results indicate that iridium catalysts match more closely the ideal thermodynamic reference profile than cobalt and rhodium catalysts. This novel computational tool could reveal hidden trends in catalysis that are not accessible using models based on smaller data sets.

Authors' comments:
"The latest addition to our molecular volcano tool kit provides a means of rapidly assessing the similarity of the entire catalytic cycle energy profile to that of a reference species".
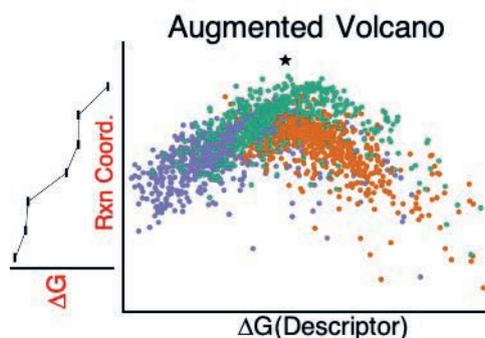
4 V Room-Temperature All-Solid-State Sodium Battery Enabled by a Passivating Cathode/Hydroborate Solid Electrolyte Interface

R. Asakura, D. Reber, L. Duchêne, S. Payandeh, A. Remhof*, H. Hagemann, and C. Battaglia. *Energy Environ. Sci.* **2020**, *13*, 5048-5058.
Empa, Swiss Federal Laboratories for Materials Science and Technology, Université de Genève, Ecole Polytechnique Fédérale de Lausanne

Various options are considered for the next-generation battery technology. All-solid-state batteries are promising candidates due to their operational safety, higher energy and power density compared to the latest lithium-ion battery technologies. The key challenge for the development of all-solid-state batteries is to design a solid electrolyte that combines high ionic conductivity with interfacial stability to the electrodes. In this work, Asakura and co-workers developed a 4 V all-solid-state sodium battery employing a hydroborate solid electrolyte with liquid-like ionic conductivity and high electrochemical stability. The highest cell discharge voltage and specific energy per cathode active material among all-solid-state sodium batteries were achieved. The high operating voltage was enabled by a self-passivation of the cathode/solid electrolyte interface, making the use of artificial protective layers redundant. This work showcases the high potential of hydroborate solid electrolytes for the design of competitive all-solid-state batteries.

Authors' comments:
"We believe that our work represents not only a breakthrough for hydroborate-based all-solid-state batteries, but also for the future development of a competitive all-solid-state battery technology."