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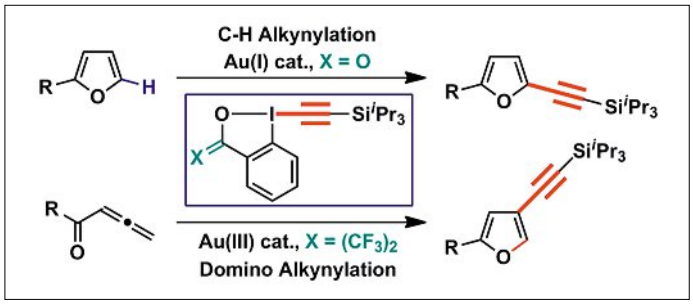
Short Abstracts of Interesting Recent Publications of Swiss Origin

Gold-Catalyzed Regioselective Synthesis of 2- and 3-Alkynyl Furans

Y. Li, J. P. Brand, and J. Waser*, *Angew. Chem. Int. Ed.* **2013**, *52*, 6743. EPF Lausanne

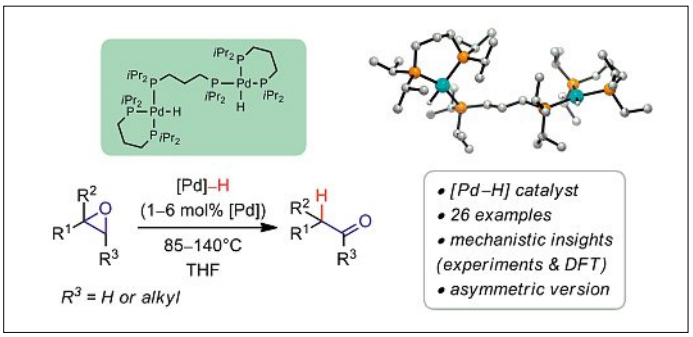
Furan rings are a common structural motif found in many functional organic materials, bioactive compounds and natural products. In this communication, Waser and co-workers outline a selective and efficient access to C(2)- or C(3)-alkynylated furans using gold catalysis. Direct C–H alkynylation at C(2) was achieved using hypervalent TIPS-ethynylbenziodoxolone in combination with a Au^{I} catalyst. For the C(3)-selective variation, a modification of the ethynyl reagent was required. Replacement of the carbonyl- by two trifluoromethyl groups enabled a domino cyclization/alkynylation process, relying on allenes as starting material in combination with a Au^{III} precursor. The broad substrate scope, good yields and mild conditions open fascinating perspectives for this novel methodology.



Isomerization of Terminal Epoxides by a [Pd–H] Catalyst: A Combined Experimental and Theoretical Mechanistic Study

D. J. Vyas, E. Larionov, C. Besnard, L. Guénée, and C. Mazet*, *J. Am. Chem. Soc.* **2013**, *135*, 6177. University of Geneva

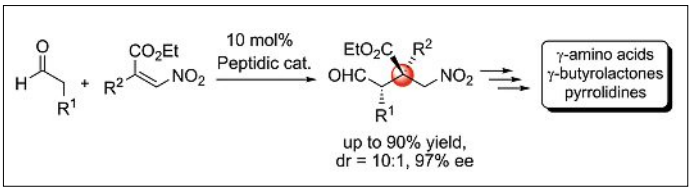
Mazet and coworkers report on an original method for the preparation of carbonyl compounds by isomerization of epoxides. For this purpose, a well-defined palladium hydride catalyst was developed. A broad variety of epoxides, including several non-terminal ones, were isomerized to the corresponding ketones and aldehydes in fair to good yields. Mechanistic insight provided by experimental- and computational studies suggests that the reaction proceeds *via* two distinct enantiodetermining steps: opening of the epoxide and hydride transfer to the cationic intermediate. This strategy shows promise for the development of an asymmetric variant of this reaction.



Peptide-Catalyzed Stereoselective Conjugate Addition Reactions Generating All-Carbon Quaternary Stereogenic Centers

R. Kastl and H. Wennemers*, *Angew. Chem. Int. Ed.* **2013**, *28*, 7228. ETH Zürich

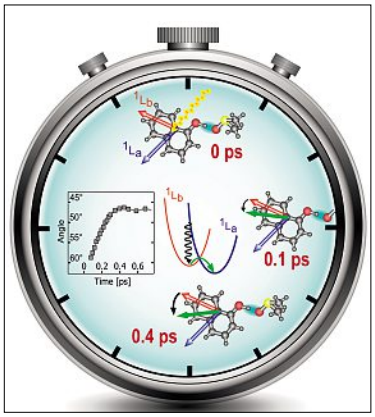
All carbon, enantiopure quaternary stereocenters remain a synthetic challenge. To address this, Wennemers and co-workers report on a new method for conjugate addition reactions of aldehydes to β,β-disubstituted nitroolefins. The procedure, which relies on a peptide-based organocatalyst, gives a straightforward access to γ-nitroaldehydes bearing a quarternary all-carbon center. These synthetically versatile intermediates can be further elaborated into high-added value products including pyrrolidines, γ-amino acids and γ-butyrolactones.



Ultrafast Solvent-Assisted Electronic Level Crossing in 1-Naphthol

F. Messina, M. Prémont-Schwarz, O. Braem, D. Xiao, V. S. Batista, E. T. J. Nibbering, and M. Chergui*, *Angew. Chem. Int. Ed.* **2013**, *52*, 6871. EPF Lausanne

Photoabsorption by large molecules can trigger a sequence of events where electronic excited states change *via* so-called, non-adiabatic transitions, en route to either the ground state or to photoproduct states. Using ultrafast anisotropy fluorescence measurements, Chergui and co-workers determined the time scale for ultrafast electronic excited state level crossing in a classical case: the solvent-driven level crossing in 1-naphthol. This level crossing has been postulated as the mechanism for the much higher photoacidity of 1-naphthol compared to other photoacids. They found that the level crossing is mediated by H-bonds between one of the excited states and the solvent molecules.



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