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


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 AuI 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 AuIII 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


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


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 quaternary 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


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.