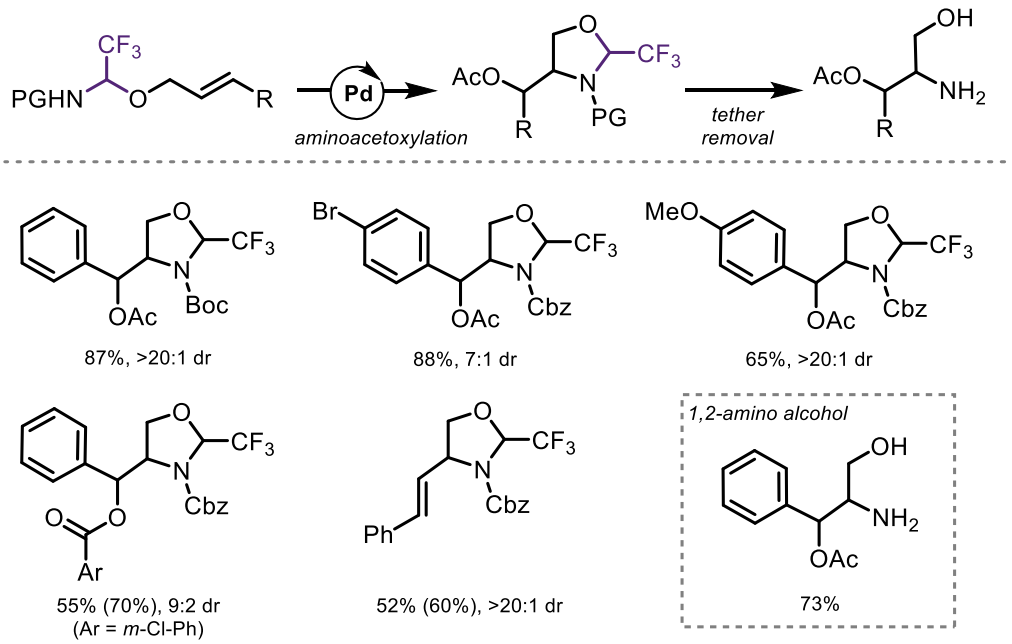
Pd(II)-Catalyzed Aminoacetoxylation of Alkenes *via* Tether Formation

Thomas Rossolini, Ashis Das, Nicolai Stefano, Jérôme Waser

Laboratory of Catalysis and Organic Synthesis, EPFL, 1015 Lausanne, Switzerland
thomas.rossolini@epfl.ch

In the field of alkene derivatization strategies, palladium-catalyzed processes constitute a major synthetic approach.[1,2] Owing to their broad accessibility and unparalleled reactivity, olefin components play a key role in the synthesis of valuable building blocks, generating molecular complexity from simple precursors.[3,4] Despite significant advances in palladium catalysis towards alkene multifunctionalization, reactivity and selectivity challenges commonly encountered in intermolecular transition-metal catalyzed reactions limit broad application of these transformations.[4]

To this end, a novel catalytic tethering approach involving a high-valent palladium center for olefin difunctionalization is reported.[5] Pivoting on an easily introduced trifluoroacetaldehyde-derived tether, simultaneous introduction of oxygen and nitrogen heteroatoms across an unsaturated carbon-carbon bond under oxidative conditions is accomplished. While good reaction efficiency and high diastereoselectivity is demonstrated with a range of unactivated alkenes, non-terminal aliphatic-derived olefin substrates give access to aza-Heck cyclization products. Tether cleavage under mild conditions gives access to functionalized β-amino alcohols, which represent important building blocks frequently found in ligands and bioactive molecules.[6,7]



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