

KETONE ACTIVATION ENABLES METAL-FREE ALPHA-ARYLATION AND ALPHA-OXYAMINATION OF ACETOPHENONES

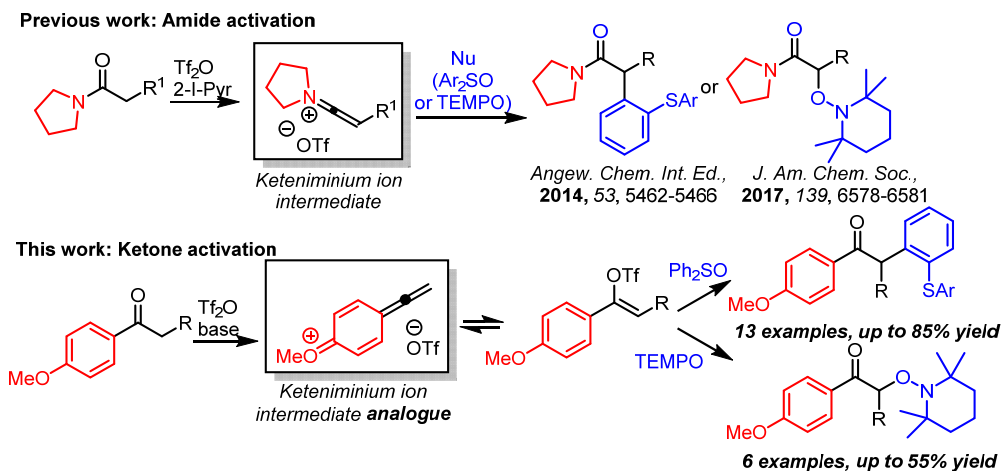
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The Maulide group has a long-standing interest in the chemoselective activation of amides inspired by pioneering early work of Ghosez and more recently Charette, Movassaghi, Huang and others. Treatment of a carboxamide with triflic anhydride and a base leads to a highly electrophilic keteniminium intermediate, which can be attacked by nucleophilic species. This led to transformations such as α -arylation of amides when using diaryl sulfoxides [1], and more recently to α -oxygenation when TEMPO was applied [2].

We envisaged that the triflic-anhydride-mediated activation of carbonyl functionalities can also occur when the nitrogen atom of the carboxamide moiety is replaced with other groups, such as electron-rich aromatic rings. In this poster, we will present the extension of the concept of metal-free amide activation to ketones. Upon treatment of the resulting vinyl triflate intermediates with diaryl sulfoxides and TEMPO, α -arylation and α -oxygenation of acetophenones was achieved. The concept of ketone activation was verified by computational studies of the intermediates present during the reaction.



[1] B. Peng, D. Geerdink, C. Fares and N. Maulide, *Angew. Chem. Int. Ed.*, **2014**, 53, 5462-5466.

[2] A. de la Torre, D. Kaiser and N. Maulide, *J. Am. Chem. Soc.*, **2017**, 139, 6578-6581.