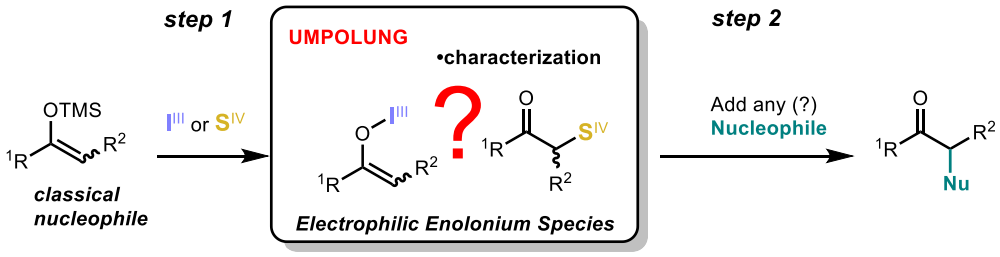
Enolonium Species: From Structure to New Reactivity

Our group has developed a unique synthetic strategy involving the umpolung of enolates, which are classically used as nucleophiles, through the action of hypervalent iodine to form electrophilic enolonium species.[1] These species, whose structures were controversial for over 40 years, have been characterized using in situ NMR and IR spectroscopy.[1a] We have applied this strategy to a plethora of new ketone α-functionalization reactions, including allylation,[1a] arylation,[1b] azidation,[1c] N-heteroarylation,[1c] and cross-coupling with TMS enol ethers to give 1,4-dicarbonyl compounds.[1d] This chemistry has also led us to develop new reactive intermediates such as azido-enolonium species.[1e]

As an aside, this chemistry also led to the serendipitous discovery of the nitro-cyclopropanation of enones[1f] and the synthesis of indoline-3-ones.[1g] We have developed the first *umpolung* Morita–Baylis–Hillman reaction, in which the key nucleophilic enolate intermediate of the classical Morita–Baylis–Hillman reaction is inverted into an electrophilic enolonium species that can react with nucleophiles.[2]



In the last year, we have achieved an important breakthrough, finally allowing this method to be broadly applicable to different carbonyl classes, including ketones, esters, and imides.[3] A new element, sulfur, is showing considerable promise as a novel concept for enolate *umpolung*.[4] The key points in the development of the discrete enolonium species strategy will be detailed, and the mechanistic underpinnings, including both experimental and computational support,[5] will be discussed.

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