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SYNFACTS Highlights in Chemical Synthesis

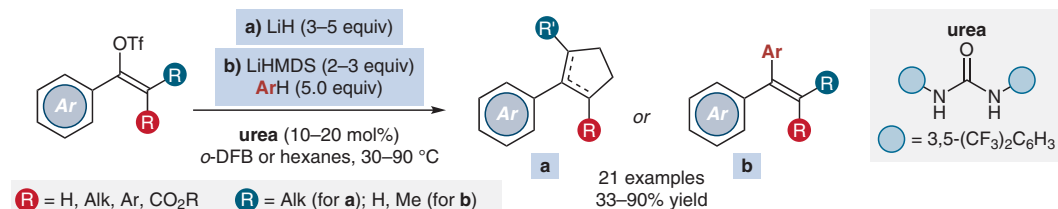
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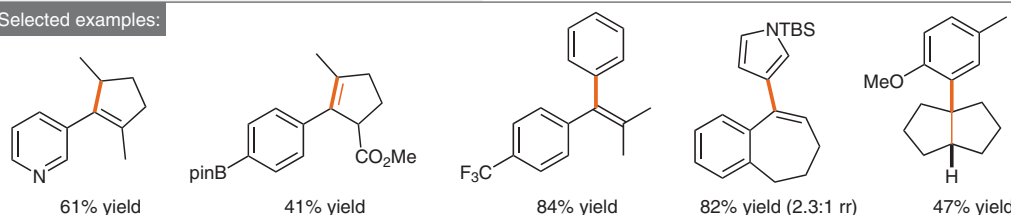
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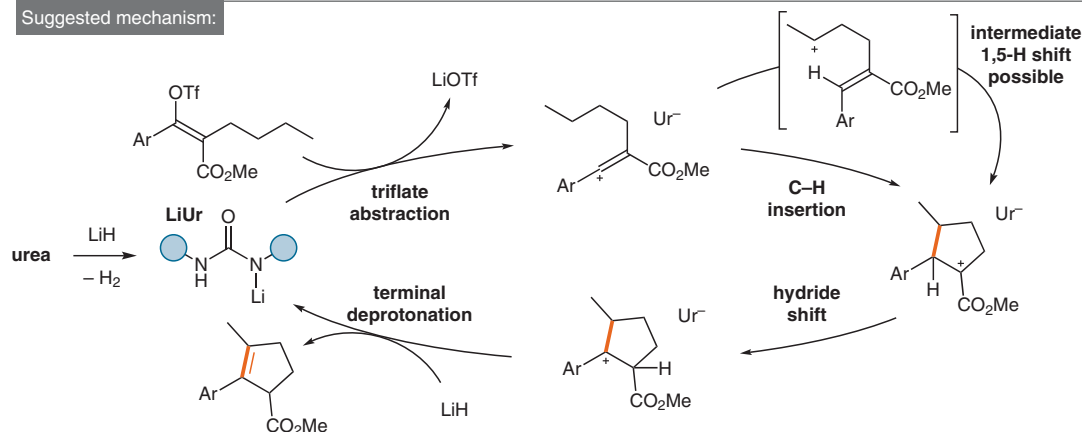
Mild Generation of Highly Reactive Vinyl Carbocations Under Anion Binding Catalysis



Selected examples:



Suggested mechanism:



Significance: Nelson and co-workers disclose a reaction of styrenyl or vinyl triflates with intra- or intermolecular C–H nucleophiles to form five-membered rings and carbon–arene bonds, respectively. The reaction is thought to proceed by mild triflate abstraction to form a highly reactive vinyl cation intermediate that is captured either by a proximate C–H bond or by an electron-neutral arene. The products are generally formed in good yields under relatively mild conditions, considering the high bond-dissociation energy of the functionalized σ -bonds.

Comment: The generation of vinyl carbocations and their ability to engage in C–H insertion reactions has been studied by the authors (*J. Am. Chem. Soc.* **2019**, *141*, 9140). Whereas those reactions relied on the application of sensitive weakly coordinating anion salts as catalysts, the authors now demonstrate that widely established modular lithiated ureas are competent anion-binding catalysts for the generation of vinyl cations. This advance will allow this reactivity to find broader application in the toolbox of synthetic organic chemists. Deeper insights into the mechanism, especially with regard to the composition of the counteranion, are desirable.