

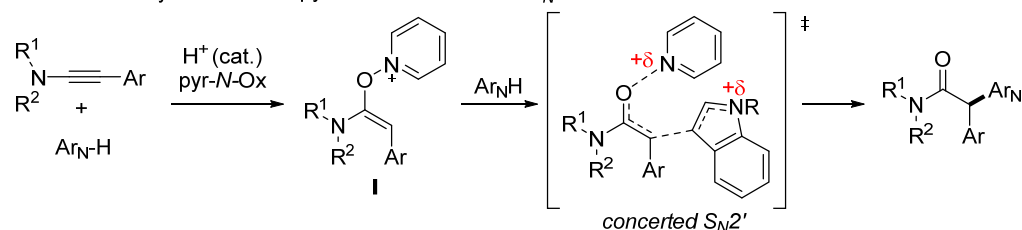
UMPOLUNG ALKYLATION BASED ON THE OXIDATION OF YNAMIDES

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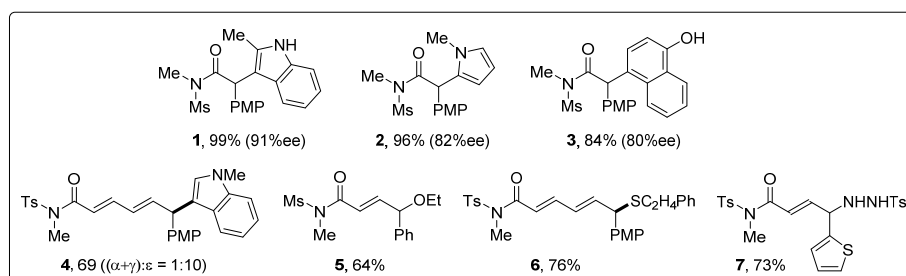
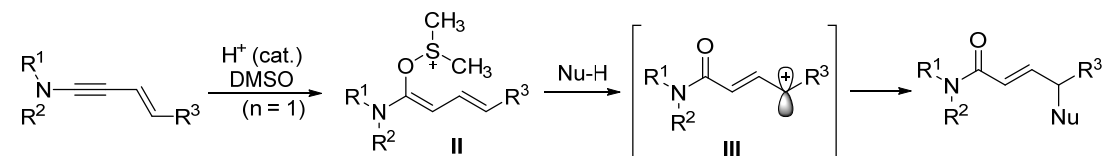
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Inverting natural polarity, *i.e.* umpolung, provides outstanding opportunities for streamlining redox-efficient processes and enables novel disconnections with complementary selectivity to traditional methods. Recently, we reported that Brønsted acid can catalyze the oxidation of ynamides and subsequent alkylation occurred with electron-rich arenes, such as indoles, pyrroles, phenols as well as silyl enol ethers [1]. The mechanism was unambiguously determined to be a concerted S_N2' and by using optically active *N*-oxides, enantioselective α -aryl imides were achieved as in **1-3**. The mild oxidizing conditions of enynamides also allowed the use of unmodified heteroatom donors, such as alcohols/thiols as in **5-7**, an hallmark of umpolung chemistry, for which the kinetic analysis elucidated a carbocationic mechanism.

A. Oxidation of ynamides with pyr-*N*-oxide: Concerted S_N2'



B. Dienolonium carbocation



[1] (a) Patil, D. V.; Kim, S. W.; Nguyen, Q. H.; Kim, H.; Wang, S. Hoang, T.; Shin, S. *Angew. Chem. Int. Ed.* **2017**, *56*, 3670-3674. (b) Patil, D. V.; Shin, S. *Asian J. Org. Chem.* **2019**, *8*, 63-73.