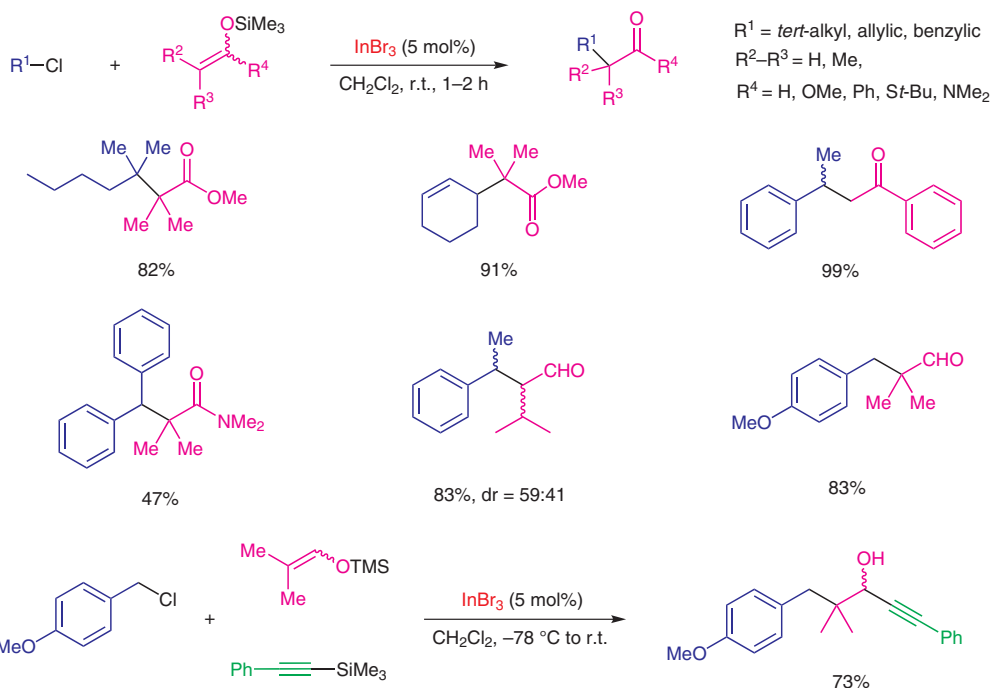


Indium(III)-Catalyzed Coupling of Alkyl Chlorides with Silyl Enolates



Significance: The alkylation of metal enolates is one of the synthetically most useful methods for a new C–C bond formation. The authors describe herein a very simple and elegant protocol for the alkylation of the silyl enolates of ketones, some aldehydes, amines and esters with tertiary, allylic, and benzylic alkyl chlorides. Excellent yields and very practical reaction conditions make this method useful for a large variety of synthetic targets, especially for those possessing neighboring sterically hindered quaternary carbon atoms.

Comment: $InBr_3$ is a very specific catalyst for this reaction, and most other common Lewis acids are completely inefficient (only $ZnBr_2$ shows some activity). The combination of $InBr_3$ and Me_3SiCl , formed in the reaction, probably gives a stronger Lewis acidic catalyst. Interestingly, sterically hindered aldehyde enolates, despite their lower nucleophilicity, are sufficiently reactive toward alkylation. Addition of a nucleophile like allylsilane or TMS-acetylene in the case of aldehyde enolates affords secondary alcohols in a one-pot sequence.