Copper-Catalysed Hydrosilylation and Aminosilylation of Heterobicyclic Alkenes under Mild Conditions

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There has been a growing interest in copper catalysis based on boronation[1] and aminoboronation[2,3] processes over the past decade. Advancements in catalytic systems have enabled the hydroamination[4,5] of alkenes utilizing tris(trimethylsilyl)silane (TMS_3SiH) as a hydrogen source. Significant efforts have also been directed toward developing modifications of boron-mediated amination reactions, such as boroalkylation,[6] borylacylation,[7] and alkynylboration.[8] Recently, new approaches have emerged for copper-catalysed transformations, including hydrosilylation[9,10] and initial attempts towards aminosilylations.[11] For instance, Hirano et al. 2022[12] demonstrated that the aminosilylation is feasible for *α*,*β*-unsaturated esters; however, this method presents notable limitations. Specifically, the reaction typically yields diastereomeric mixtures with diastereomer ratios ranging from 1:1 to 4:1. To improve the diastereoselectivity, the authors employed an excess of cyano reagents, necessitating additional reagents. Moreover, pivaloylhydroxylamines were used as limiting agents only with *α*,*β*-unsaturated esters as starting materials.

Here, we aimed to develop a mild, copper-catalysed protocol applicable to hydrosilylations and aminosilylations across a broad spectrum of substrates, including heterobicyclic alkenes and various open-chain alkenes. The presented approach is summarized in Figure 1, which illustrates the optimized conditions for the copper-catalysed transformation.

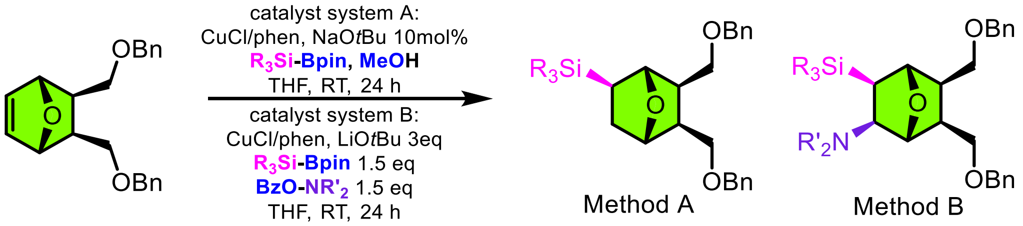

Figure 1. Copper-Catalysed Protocol for the Hydrosilylation and Aminosilylation.

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