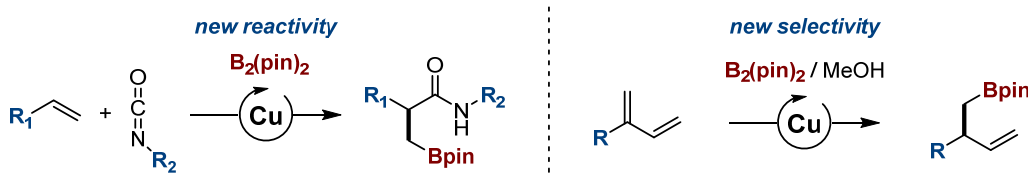


# COPPER-CATALYZED BORYLATION OF OLEFINS: A QUEST FOR REACTIVITY AND SELECTIVITY

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Copper-catalyzed borylation of olefins represents a cutting-edge methodology for the introduction of boron in organic molecules. Migratory insertion of alkenes across a copper-boron bond generates nucleophilic alkyl copper intermediates, which display broad reactivity towards electrophiles.<sup>[1]</sup> Proton is the simplest electrophile that can be employed and the resulting protoboration of olefins complements hydroboration approaches.<sup>[2]</sup> Furthermore, the use of carbon based electrophiles offers new strategies for the construction of C–C bonds.<sup>[3]</sup> Herein we describe our results in the identification of two novel reactions in the context of copper-borylation of olefins. As a continuation of our efforts in the carbofunctionalization of alkenes,<sup>[4]</sup> we developed a Cu-catalyzed borylative carboxamidation of olefins using isocyanates as electrophiles. The method allows expedient access to chiral secondary amides bearing a boronate handle starting from commodity chemicals and a readily accessible [(NHC)Cu] precatalyst. Preliminary results for the enantioselective version of the reaction will be disclosed.<sup>[5]</sup> Amongst conjugated alkenes, 1,3-dienes represent an underexplored class of substrates for selective transition metal catalysis. This is due to the numerous coordination and insertion modes conceivable for a transient organometallic species. In this context, we devised a Cu-catalyzed 1,2-protoboration of 2-substituted 1,3-dienes with exquisite anti-Markovnikov selectivity. The use of a chiral phosphanamine ligand is essential in achieving high chemo-, regio- and enantioselectivity, providing rapid access to a variety of synthetically relevant homoallylic boronates.<sup>[6]</sup>



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