

Palladium-Catalyzed Reactions Using Lewis Acidic Organoboronic Reagents

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Palladium-Catalyzed cross-coupling of aryl- and allyl halides with organoboronic reagents (Suzuki-Miyaura cross-coupling) is one of the most useful carbon-carbon bond forming reactions in organic synthesis due to the functional group compatibility, availability, stability, and nontoxicity of the organoboron reagents. Although the cross-coupling reaction is highly mild and efficient, the use of these halides adding to Pd(0) oxidatively requires not only their preparation but also addition of a base for neutralization of the generating acid, which cause formation of a stoichiometric amount of their salt as a byproduct. Therefore, Suzuki-Miyaura cross-coupling should not be satisfied with environmental benignity and atom-economy significantly demanded for recent organic synthesis.

To solve the above problem, we attempted to utilize oxygen-containing functional groups, activated by Lewis acidity and oxophilicity of the boron reagents, as oxidizing agents for Pd(0). Our investigation revealed that allylic alcohols could oxidize Pd(0) and be directly coupled with aryl- and alkenylboronic acids. Prior to the cross-coupling, an intramolecular alkyne in allylic alcohols could also be inserted. Furthermore, alkynyl enals and enones oxidized Pd(0) in the presence of the organoboronic acids and brought about *cis*-selective alkylative cyclization to provide five-membered cyclized compounds with *exo*- tri- or tetrasubstituted olefin groups. In contrast, oxidative addition of alkynals and alkynones to Pd(0) resulted in *trans*-selective alkylative cyclization to provide six-membered allylic alcohols with *endo*- tri- or tetrasubstituted olefin as major products. Since these carbon-carbon bond formations require neither introduction of the leaving group nor addition of a base, they would be environmentally benign and atom-economical.