Palladium-catalyzed 1,2-*anti*-Markovnikov hydroamidation of 1,3-dienes

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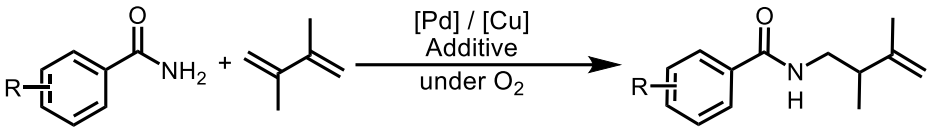
C-N Bond forming reactions are important to synthesize nitrogen-containing medicines and natural compounds. Especially, hydroaminations and hydroamidations of unsaturated hydrocarbons which are abundant feedstocks are widely recognized as atom-economical reactions. Functionalized alkenes synthesized by hydrofunctionalizations of 1,3-dienes are important for useful building blocks. Therefore, a regioselective transition metal-catalyzed hydrofunctionalization of 1,3-dienes is highly desirable. 1,4-Addition and 1,2-Markovnikov hydrofunctionalization of 1,3-dienes have been reported extensively because the reactions often proceed through stabilized π-allyl intermediates.[1] In contrast, 1,2-*anti*-Markovnikov hydrofunctionalization of 1,3-dienes remains poorly developed despite the importance of homoallylic compounds because the reaction proceeds through instability intermediates.[2] Therefore, 1,4-addition hydroamidation of 1,3-dienes has been reported, and 1,2-*anti*-Markovnikov hydroamidation of 1,3-dienes has not been reported to date.[3]

In this study, we developed palladium-catalyzed 1,2-*anti*-Markovnikov hydroamidation of 1,3-dienes by employing an additive under oxygen atmosphere to generate homoallylic amides. This protocol provided only 1,2-*anti*-Markovnikov product and did not give 1,4-addition and 1,2-Markovnikov hydroamidation products.

In this presentation, we report that the details of reactions conditions and a plausible reaction mechanism based on experimental results.



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