

Regiodivergent and Stereoselective Intermolecular [2 + 2] Cycloaddition of Amino-functionalized Alkenes and Allenes by Rare-Earth Catalysts

(¹*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science,*
²*Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology*)○

Wenxuan Xu^{1,2}, Xuefeng Cong¹, Kun An¹, Shaojie Lou¹, Zhenghua Li¹, Masayoshi Nishiura¹,
 Tetsuro Murahashi^{1,2}, Zhaomin Hou^{1,2}

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The catalytic [2 + 2] cycloaddition of allenenes and alkenes is, in principle, the most atom-efficient and straightforward route for the construction of cyclobutane or cyclobutene skeletons, which are important structural motifs in many natural products and bioactive compounds as well as useful building blocks in organic synthesis. However, most of the [2 + 2] cycloaddition reactions of allenenes and alkenes reported previously were intramolecular reactions, while the analogous intermolecular reactions were limited to electronically biased allenenes or alkenes. The involvement of allene C–H activation in the cycloaddition reactions has not been reported previously. Here we report the unprecedented regio- and stereoselective intermolecular [2 + 2] cycloaddition reactions of amino-functionalized alkenes with a wide range of allenenes via rare-earth-catalyzed allene C–H activation.

The reaction of amino-functionalized alkenes with monosubstituted allenenes in the presence of a half-sandwich scandium catalyst afforded the methylenecyclobutane products in high yields with excellent regio- and stereoselectivity (see scheme shown below). In contrast, the reaction with 1,3-disubstituted allenenes exclusively yielded the cyclobutene products. In these transformations, an allenyl rare earth species like **A** formed by allene C–H activation acted as a true catalyst species. Both steric and electronic factors played an important role in determining the regio- and stereoselectivity.

