

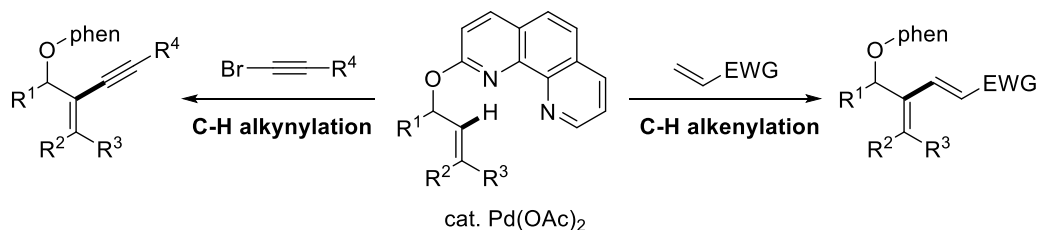
Palladium-Catalyzed Regioselective C-H Alkenylation and Alkynylation of Allylic Alcohols by Phenanthroline-Type Bidentate Auxiliary

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Allylic alcohols are important structural motifs and frequently occurring in natural products and bioactive molecules. Accordingly, the development of efficient and general access to multiply substituted allylic alcohol derivatives is of great meaning. As an attractive strategy, manipulation of relatively simple allylic alcohols *via* metal-mediated alkenyl C-H functionalizations has recently received much attentions from synthetic chemists. However, despite certain advances,^[1] a significant limitation in scope should be noticed: only terminal or *cis*-allylic alcohols could be employed.

In this study, we developed a phenanthroline-directed,^[2] Pd-catalyzed regioselective C-H alkenylation of allylic alcohols: a bidentate coordinating nature of phenanthroline auxiliary enables the C-H activation selectively at the proximal position over the conceivable allylic C-O activation.^[3] The Pd catalysis accommodates *cis*-, *trans*-, and even more challenging trisubstituted substrates. Additionally, a related C-H alkynylation of allylic alcohols was also demonstrated under the Pd/phenanthroline catalytic system. Mechanistic studies with the putative 6-membered palladacycle intermediate and further transformations of the products will also be included in this presentation.



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