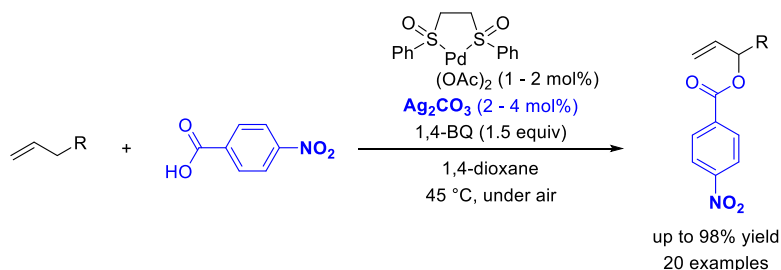


Significant Effects of Silver Carbonate and *p*-Nitrobenzoic Acid in Bidentate Sulfoxide-Ligated Palladium-Catalyzed Allylic C-H Acyloxylation

Transformation of Thioesters to Ketone Using Organocuprates (¹*Graduate School of Engineering Science, Osaka University*, ²*Tokuyama Corporation*) ○Skhiri Aymen,¹ Haruki Nagae,¹ Hayato Tsurugi,¹ Masahiko Seki,² Kazushi Mashima¹

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Allylic C(sp³)-H bond functionalization of simple alkenes with carboxylic acids under oxidative conditions, *i.e.*, oxidative allylic C(sp³)-H acyloxylation, is a powerful method to prepare synthetically valuable allyl esters. Various oxidants have been applied for oxidizing the allylic C(sp³)-H bond using peracids and high-valent metal complexes; however, due to the high reactivity of those oxidants, the functional group tolerance is narrow, and over stoichiometric amounts of wastes are produced as by-products after the reaction. As a pioneering work to overcome the issue, White *et al.* developed a new catalyst system of a bidentate sulfoxide-ligated palladium catalyst, *i.e.*, the White catalyst, in combination with 1,4-benzoquinone (1,4-BQ) for branch-selective allylic acyloxylation of terminal alkenes with acetic acid, though high catalyst loading (generally, more than 5 mol%) and longer reaction time are still required.¹⁾ Herein, we report a significant positive effect for the catalytic activity by using *p*-nitrobenzoic acid as a carboxylate source and Ag₂CO₃ as a co-catalyst in the branch-selective allylic C(sp³)-H acyloxylation of terminal alkenes with low loadings (1-2 mol%) of the palladium catalyst.²⁾ This system was applicable to terminal alkylalkenes having various functional groups on the aliphatic chain. In addition, cyclic alkenes were converted to the corresponding C-H acyloxylation products. One of the C-H acyloxylation product, ethyl 6-acyloxy-7-octenoate, was a useful starting material for synthesizing ethyl 6,8-dihydroxyoctanoate, a key synthetic intermediate of (*R*)- α -lipoic acid.



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