H. MIYABE, K. YOSHIDA, M. YAMAUCHI, Y. TAKEMOTO* (KYOTO UNIVERSITY, JAPAN)
Hydroxylamines as Oxygen Atom Nucleophiles in Transition-Metal-Catalyzed Allylic Substitution
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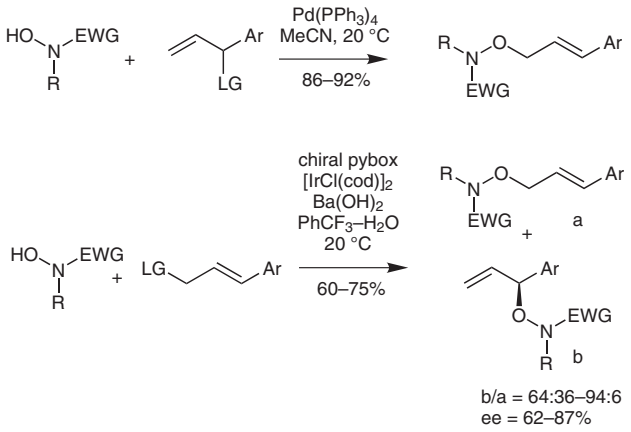
Hydroxylamines as Oxygen-Based Nucleophiles in Allylic Substitution Reaction



Significance: Transition-metal-catalyzed allylation with oxygen-based nucleophiles are not well developed due to their low nucleophilicity and poor regioselectivity. Hydroxylamines were shown to give better yields and regioselectivity in both Pd- and Ir-catalyzed *O*-allylic substitution reactions due to their higher nucleophilicity. In the case of Ir-catalyzed reactions, good enantiomeric excess was obtained using a chiral Ph-pybox ligand.

Comments: The typical behavior of Pd- and Ir-catalyzed allylation reactions is that the former catalyst resulted in predominantly linear products and the latter gave mostly branched products. The regioselectivity for Ir is not as high. It is important to notice that the EWG is attached on the hydroxylamine nitrogen so that the nucleophilicity of oxygen atom is greatly increased. When BnNHOH is reacted using Ir, *N*-allylation was observed, but with BzN(OH)Ph, *O*-allylation took place.

SYNFACTS Contributors: Mark Lautens, Y. Eric Fang
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asymmetric allylic substitution
palladium
iridium
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