

Design of cooperative catalysts for nucleophilic addition of *O*-nucleophiles toward alkynes

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Nucleophilic addition of *O*-nucleophiles toward alkynes is one of the most effective methods for preparing synthetically important enol derivatives due to its 100% atom-efficiency, in which soft Lewis acids such as silver and gold serve as the efficient catalysts in terms of their high affinity toward alkyne π -systems. Among them, nucleophilic addition of weak *O*-nucleophiles such as carboxylic acids toward non-activated alkynes has been developed in this decade.¹ We envisioned that acid-base cooperative catalysts are one of the most effective systems to the nucleophilic addition, since the cooperative action of acid site and base site can realize the dual activation of electrophiles and nucleophiles as in enzymatic reactions. In this context, we report our recent developments of novel acid-base cooperative systems as highly effective catalysts for the nucleophilic additions (Figure 1). Cationic silver(I) catalysts bearing imidazole moiety as the basic site at the vicinity of metal center showed high activity toward cyclization of alkyne-tethered carboxylic acids through intramolecular *O*-nucleophilic addition.² Additionally, NHC-gold(I) complex bearing coordinative *N*-heteroaromatic moiety were prepared as templates for constructing heterobimetallic complexes through the coordination of the *N*-heteroaromatics to basic Zn(acac)₂ salt to achieve highly effective intermolecular nucleophilic addition of carboxylic acids toward non-activated alkynes.³

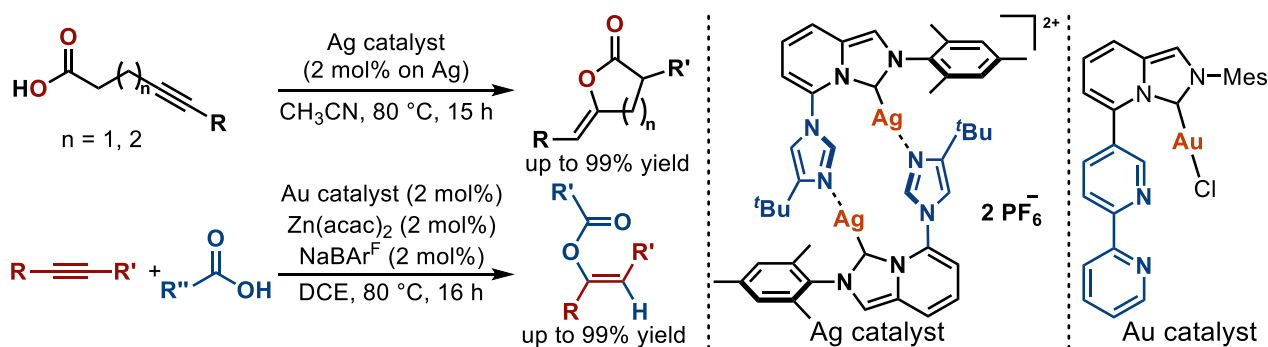


Figure 1. Acid-base cooperative catalysts for *O*-nucleophilic addition to alkynes.

References

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Kosuke Higashida was born in Nara in 1992. He completed his Ph.D. Sci. in 2019 at the Graduate School of Engineering Science, Osaka University, under the supervision of Prof. Kazushi Mashima. He started his academic career as a Specially Appointed Assistant Professor at the Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, in 2019. His current research topic is designing cooperative catalysts and heterobimetallic catalysts by using DFT calculations.