Ruthenium-Catalyzed Enantioselective Propargylic Reduction of Propargylic Alcohols with Hantzsch Esters

(*School of Engineering, The University of Tokyo*) ○Haowei Ding, Shogo Kuriyama, Ken Sakata, Yoshiaki Nishibayashi

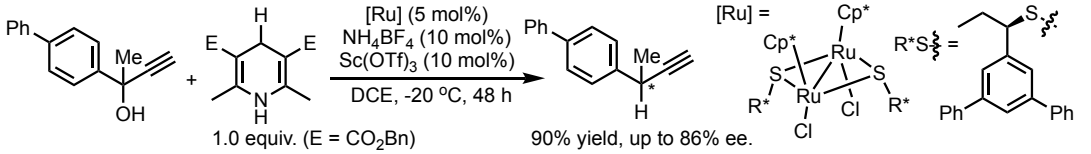
Keywords: Hantzsch ester; Diruthenium complex; Propargylic substitution

Deoxygenation reactions, removal of oxygen functional groups from organic skeletons, are attractive molecular transformations because of their broad utility. As one of the most useful protocols, transition metal-catalyzed enantioselective allylic reduction of allylic alcohol derivatives with reductant has been extensively studied to date since the first successful example of the enantioselective allylic reduction of allylic alcohol derivatives with formic acid reported by Hayashi and co-workers in 1994.[1] In sharp contrast to the allylic reduction, the enantioselective propargylic reduction of propargylic alcohols has been severely limited. To our knowledge, only one protocol was reported by Sun and co-workers in 2017 by applying optically active phosphoric acids as chiral catalysts and Hantzsch esters as reductants.[2]

Previously, our group reported non-enantioselective propargylic reduction of propargylic alcohols with some hydride sources such as triethylsiliane,[3] isopropyl alcohol[4] and Hantzsch ester[5] by using thiolate-bridged diruthenium complexes as catalysts. As an extensive study, we have now investigated the ruthenium-catalyzed enantioselective propargylic reduction of propargylic alcohols with Hantzsch esters as formal hydride donors.

Reactions of tertiary propargylic alcohols with Hantzsch ester in the presence of catalytic amounts of a chiral thiolate-bridged diruthenium complex, ammonium tetrafluoroborate and a Lewis acid gave the corresponding propargylic reduction products in good yields with a high enantioselectivity (up to 86% ee) (Scheme 1). Details of the present reaction system will be shown in this presentation.

Scheme 1.



1) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775.

2) Chen, M.; Sun, J. *Angew. Chem. Int. Ed.* **2017**, *56*, 11966.

3) Nishibayashi, Y.; Shinoda, A.; Miyake, Y.; Matsuzawa, H.; Sato, M. *Angew. Chem. Int. Ed.* **2006**, *45*, 4835.

4) Yuki, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2010**, *29*, 5994.

5) Ding, H.; Sakata, K.; Kuriyama, S.; Nishibayashi, Y. *Organometallics* **2020**, *39*, 2130.