

Construction of a Helical Exocyclic Diene Scaffold via Rh-Catalyzed Cycloisomerization of 1,6-Diynes Bearing a Cyclopropanol Moiety

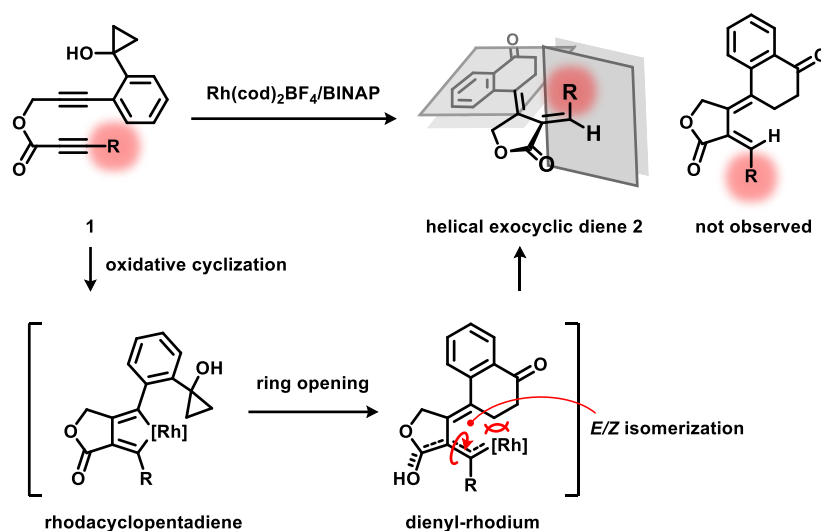
(¹Graduate School of Pharmaceutical Sciences, Nagoya University)

○Tomohiro Kikuchi,¹ Takeshi Yasui,¹ Yoshihiko Yamamoto¹

Keywords: Rh Catalysis; Cycloisomerization; Exocyclic Dienes; Helical Scaffold; Cyclopropanol

Exocyclic dienes possessing terminal substituents oriented inside the diene moiety can create a helical motif.¹ Such helical exocyclic dienes have been used as photochromic molecules, ligands, organocatalysts.² However, the synthetic method for them has been limited due to the steric hindrance between the substituents inside the diene moiety.

Herein, we report the rhodium-catalyzed cycloisomerization of ester-tethered 1,6-diynes **1** bearing a cyclopropanol moiety.³ This reaction gave helical exocyclic dienes **2** with excellent stereoselectivity. Control experiments and density functional theory calculations indicated that oxidative cyclization of the diyne afforded a rhodacyclopentadiene species, followed by the ring-opening of the cyclopropanol moiety. We also found that the construction of thermodynamically unfavorable geometry of the diene moiety is enabled by *E/Z* isomerization in a dienyl-rhodium intermediate.



1) T. V. RajanBabu *et al.*, *J. Am. Chem. Soc.* **2010**, 132, 13078. 2) a) Y. Yokoyama, *Chem. Rev.* **2000**, 100, 1717. b) M. Ogasawara *et al.*, *Angew. Chem., Int. Ed.* **2013**, 52, 13798. c) M. Ogasawara *et al.*, *Org. Lett.* **2017**, 19, 4102. 3) Y. Yamamoto *et al.*, *Chem. Commun.* **2020**, 56, 12865.