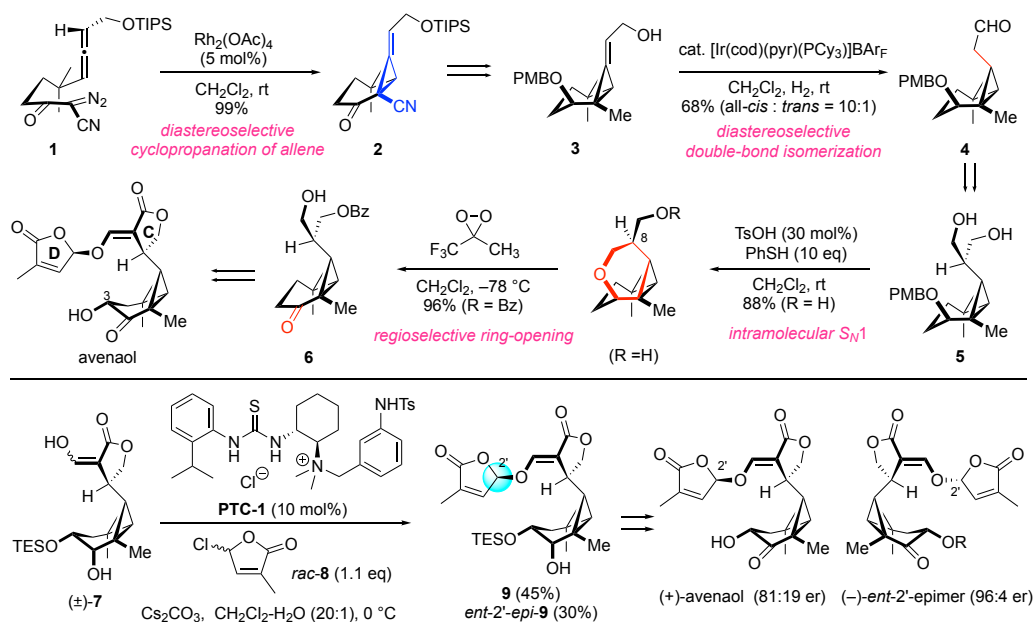


TOTAL SYNTHESIS OF AVENAOL VIA ASYMMETRIC *O*-ALKYLATION USING CHIRAL AMMONIUM SALT

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Strigolactones (SLs) constitute a new class of plant hormones of increasing importance in plant science. Avenaol, isolated from the allelopathic plant black oat, is the first C20 germination stimulant related to SLs, and consists of a bicyclo[4.1.0]heptanone skeleton containing a cyclopropane ring bearing three main chains projecting in the same direction. We have completed the first total synthesis of (\pm)-avenaol using a robust strategy involving the formation of an all-cis-substituted cyclopropane via an alkylidenecyclopropane [1]. The key factors in the success of the synthesis include the Rh-catalysed intramolecular cyclopropanation of allene (**1** \rightarrow **2**), an Ir-catalysed stereoselective double-bond isomerization (**3** \rightarrow **4**), and the differentiation of two prochiral hydroxymethyl groups (**5** \rightarrow **6**). Furthermore, we have explored the enantioselective *O*-alkylation of enols with racemic chloro butenolide **8** using chiral **PTC-1**. The application of this method to racemic synthetic intermediate **7** successfully provides optically active avenaol via 2'-acetal **9** [2]. This study confirms the proposed structure of avenaol, including its unique all-cis-substituted cyclopropane moiety.



[1] Total synthesis of avenaol, Motohiro Yasui, Rina Ota, Chihiro Tsukano, Yoshiji Takemoto, *Nat. Commun.* **2017**, *8*, 674.

[2] Manuscript under preparation.