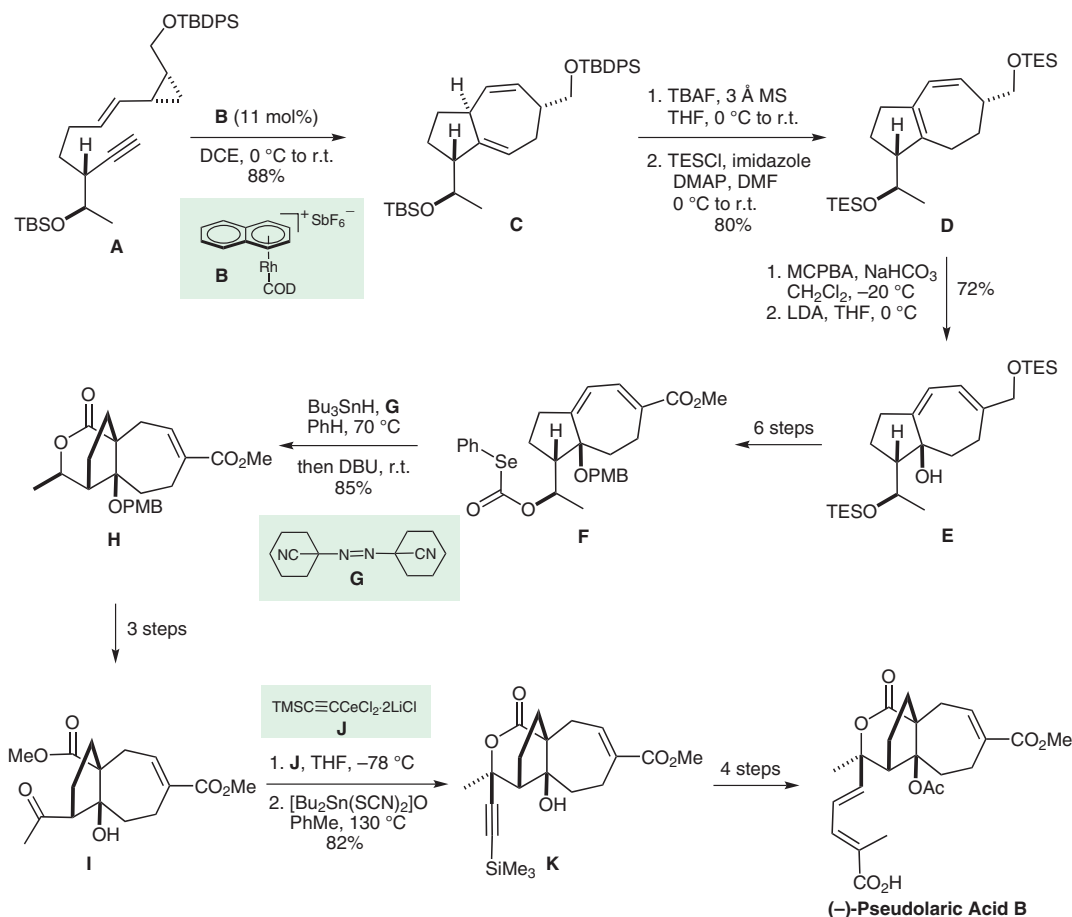


Synthesis of (-)-Pseudolaric Acid B



Significance: Pseudolaric acid B was isolated from the root bark of *Pseudolarix kaempferi* Gordon, which has been used as an antifungal remedy in traditional Chinese medicine. It showed some antifungal, antifertility and cytotoxic properties along with activity against certain tumor cell lines that are resistant to many drugs. The key to the synthesis is a rhodium-mediated cycloaddition to form the hydroazulene ring system (**A**→**C**).

Comment: Treatment of **A** with rhodium catalyst **B** afforded hexahydroazulene **C**, which was converted into **D** via a TBAF-mediated isomerization and subsequent TES protection. Epoxidation of the tetrasubstituted double bond in **D** followed by eliminative opening of the epoxide gave **E**. Compound **H** was formed in a good yield by an intramolecular alkoxy carbonyl radical cyclization, followed by treatment with DBU.