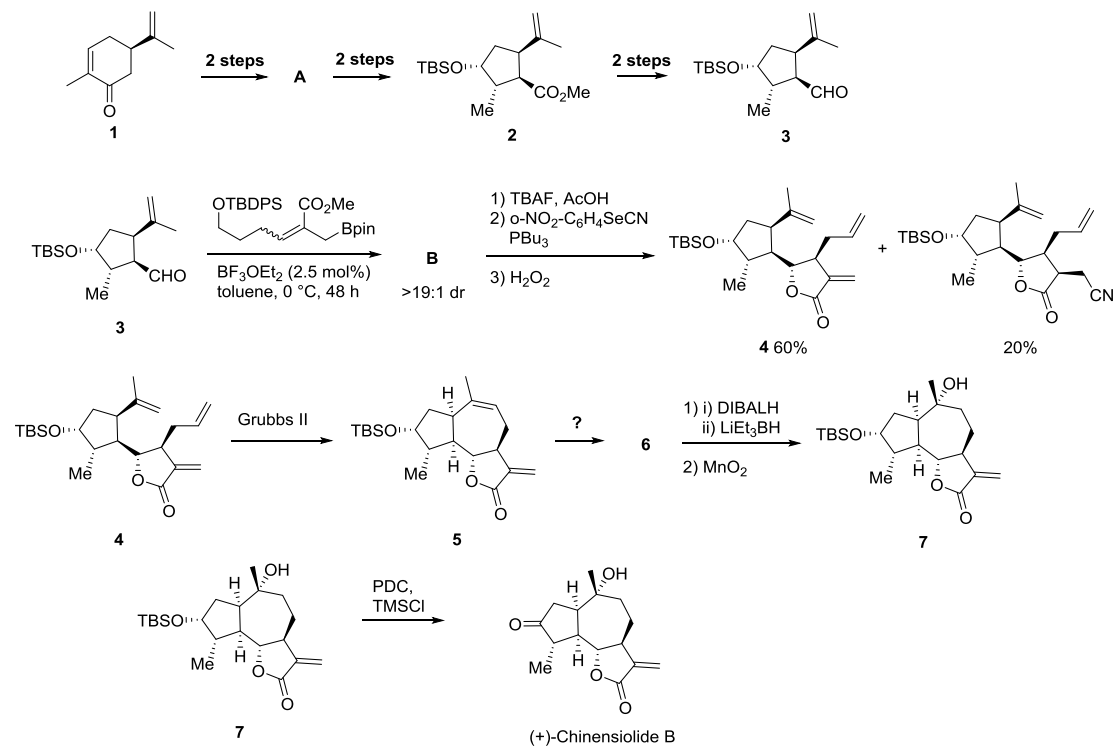


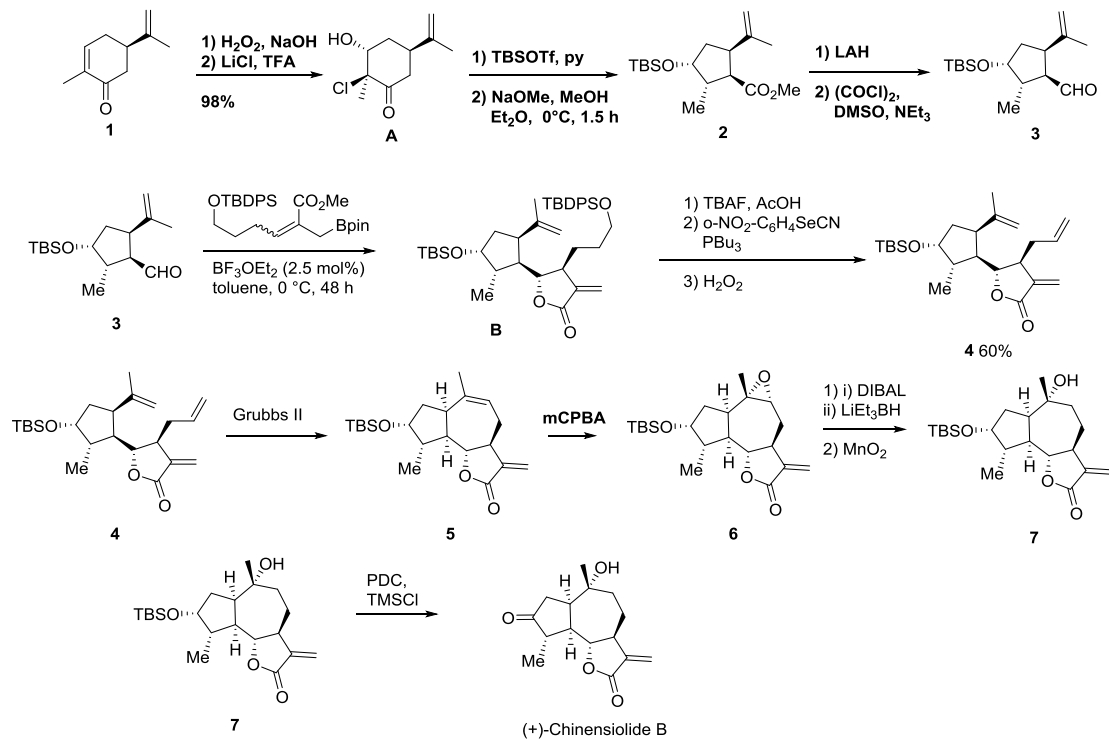
Total Synthesis of (+)-Chinensiolide B

Problem:

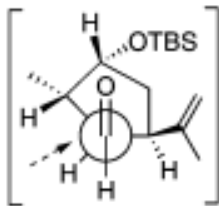


- 1) Give the reagents for the transformation **1** to **3**
- 2) What is the product **A**?
- 3) Give the product **B** and give a rationale for the stereochemical outcome.
- 4) Explain the byproduct in the reaction from **B** to **4**. (Mechanism)
- 5) Give the reagent for the transformation of **5** to **6** as well as product **6**.
- 6) Explain the reagents for the transformation of **6** to **7**

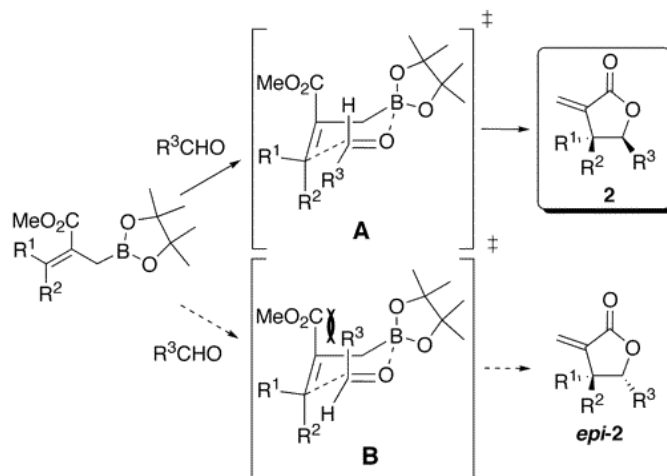
Solution:



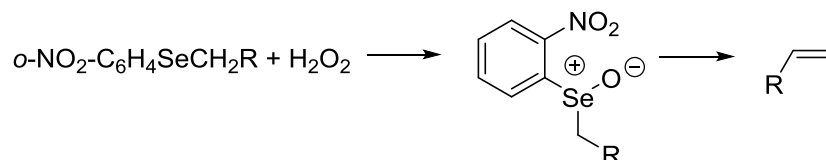
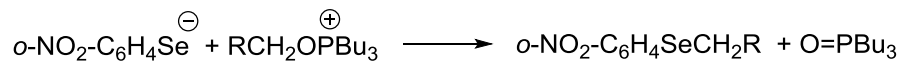
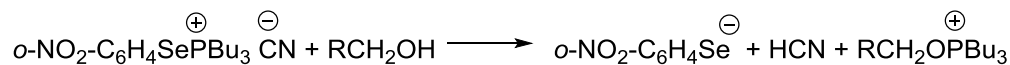
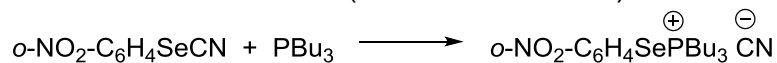
Rational for stereochemical outcome of reaction 3 to B:



The Felkin-Ahn model explains the remarkable diastereofacial selectivity on the aldehyde whereas the Zimmerman-Traxler model explains the *trans* diastereoselectivity of the allylboronation step.



Mechanism from **B** to **4** (Grieco Elimination):



Byproduct is formed by conjugate addition of the cyanide anion to the enolate.

Choice of reagents for the transformation of **6** to **7**:

By the use of LAH, the lactone was over-reduced to give the fully saturated triol and the LiEt_3BH underwent preferentially conjugate addition on the α -methylene group then opening the epoxide.

Therefore, the lactone was reduced by DIBALH to the diol, followed by region- and chemoselective epoxide opening with LiEt_3BH . Re-oxidation with MnO_2 reformed the α -methylene γ -lactone.

References:

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trans-selectivity: J. W. J. Kennedy; D. G. Hall, *J. Org. Chem.* **2004**, 69, 4412

Grieco Elimination: P.A. Grieco, S. Gilman, M. Nishizawa, *J. Org. Chem.* **1976**, 41, 1485-1486

Keywords: Favorskii rearrangement, Tandem Allylboration/Lactonization, Grieco Elimination