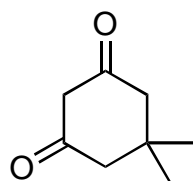


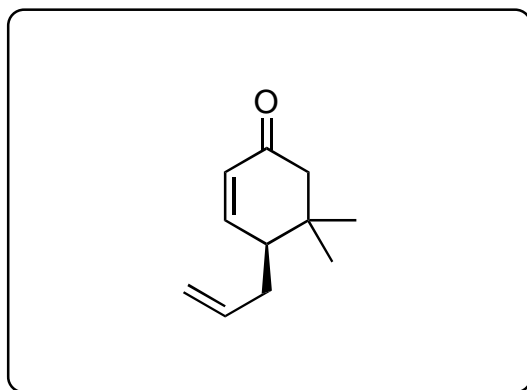
Enantioselective Total synthesis of (+)-Garsubellin A

Dongseok Jang, Minchul Choi, Jinglong Chen, and Chulbom Lee

D. Jang, M. Choi, J. Chen, C. Lee, *Angew. Chemie Int. Ed.* 2021, DOI 10.1002/anie.202109193.



1-4



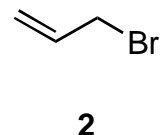
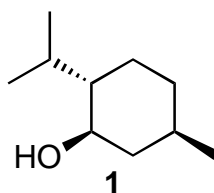
4-8

1) **1**, (+) CSA

2) LDA, **2**

3) *t*-BuOK

4) LiAlH₄
then, aq HCl

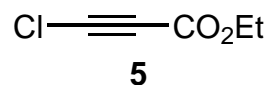
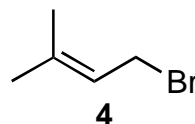
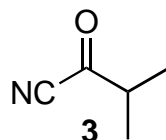


5) LiHMDS, **3**

6) L-selectride,
then, cat TBAI, **4**

7) *t*-BuOK, **5**

8) Dibal-H



1) Name of compound **1**

(-)-menthol

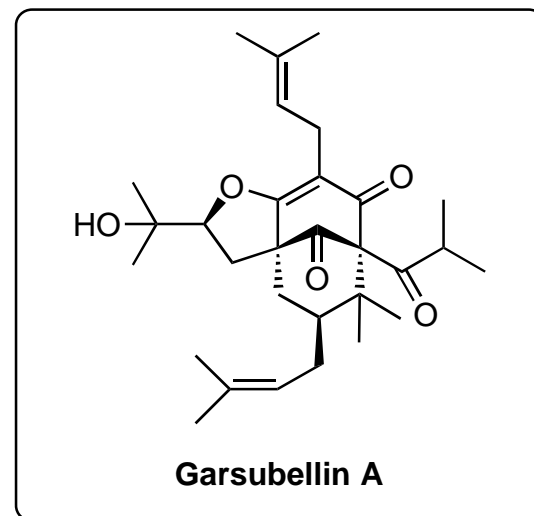
3) tip: epimerization to β -allylated enone

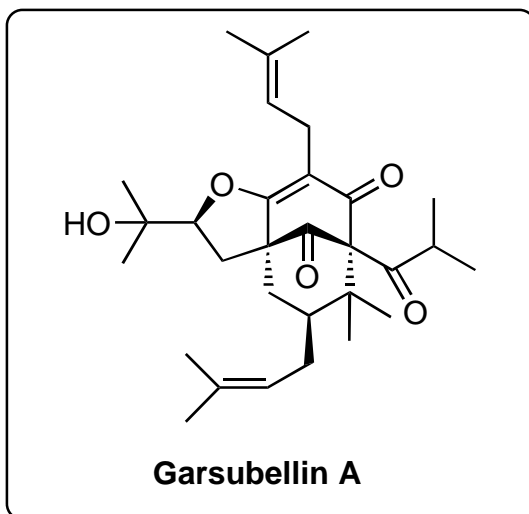
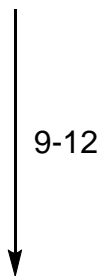
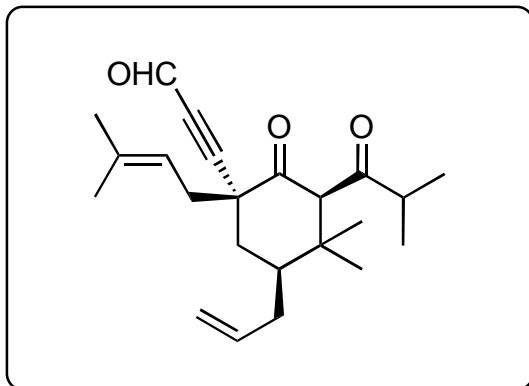
4) Name reaction?

Stork–Danheiser transposition

5-7) tip: a-facial preference.

Please rationalize the diastereoselectivity in reaction 5



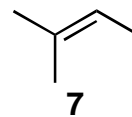
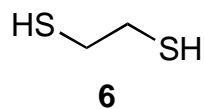


9) TMG, **6**
then, DMP

10) m-CPBA (4.5 eq)

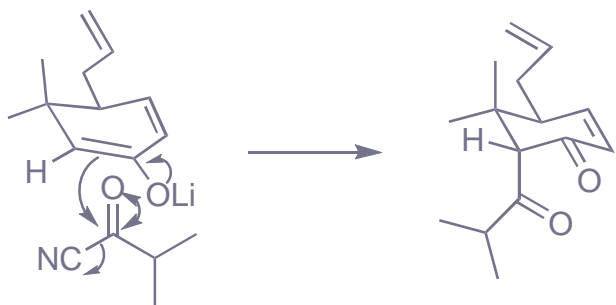
11) MeLi, Et₂Zn
then, LDA, **2**
(2-Th)Cu(CN)Li

12) Grubbs' 2nd, **7**



10) Please suggest a mechanism for the tricyclic ketone formation.

5) Rationale for the diastereoselectivity.



10) Possible reaction pathway in the dithiolane oxidative removal step.

Thioethers can be converted to THF upon formation and hydrolysis of the prenyl epoxide likely due to the intermediacy of a β -sulfinyl enone.

