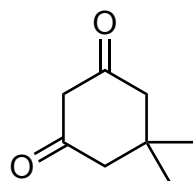


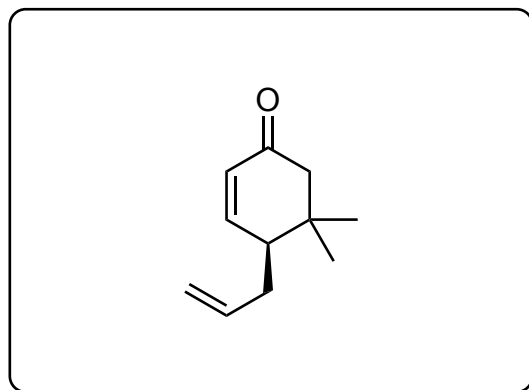
Enantioselective Total synthesis of (+)-Garsubellin A

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

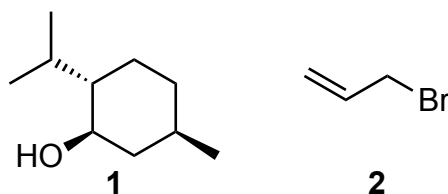
Angew. Chemie Int. Ed. 2021, DOI 10.1002/anie.202109193.



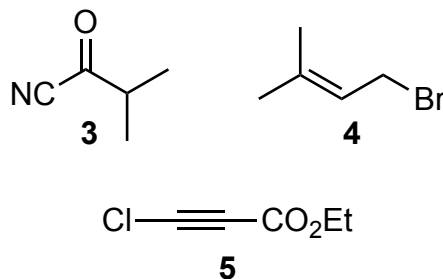
1-4



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

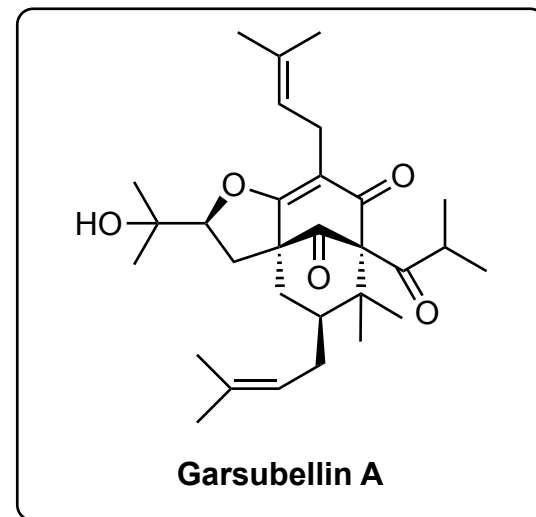
4) Named reaction?

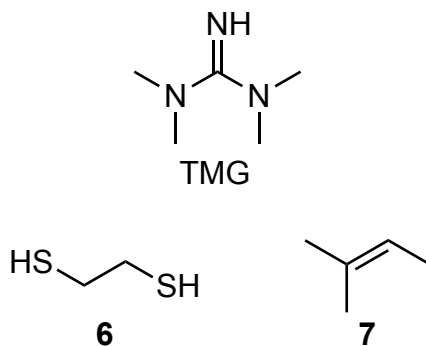
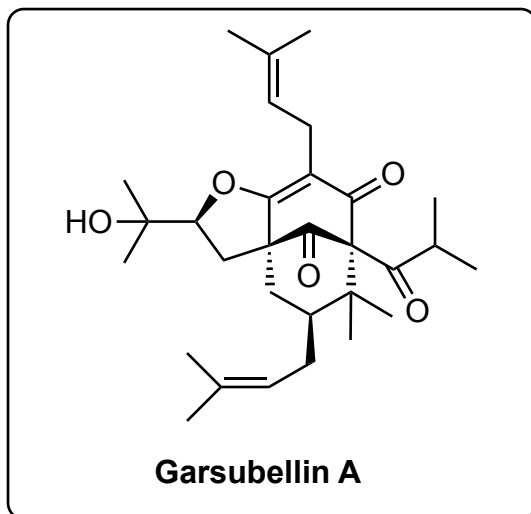
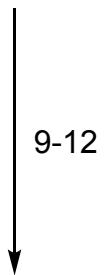
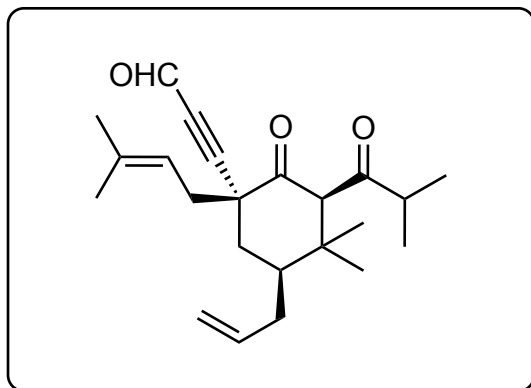
Stork–Danheiser transposition

5-7) tip: α -facial preference.

t-BuOK is a bulky base.

8) aldehyde formed

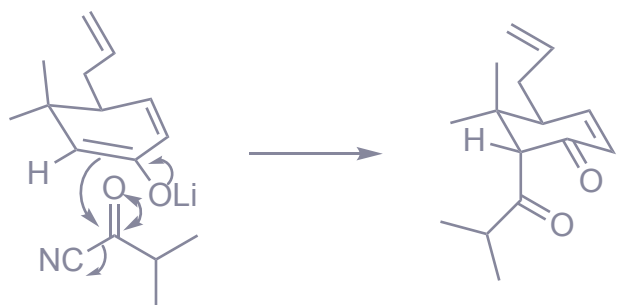




- 9) TMG, **6**
then, DMP
 10) m-CPBA (4.5 eq), H₂O
 11) MeLi, Et₂Zn, *then*, LDA,
 (2-thiophene)Cu(CN)Li, **2**
 12) Grubbs' 2nd, **7**

9) **6** will do double 1,4-addition, one ring was formed.
 10) The final THF-ring formed in this step, please suggest a mechanism.

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.

