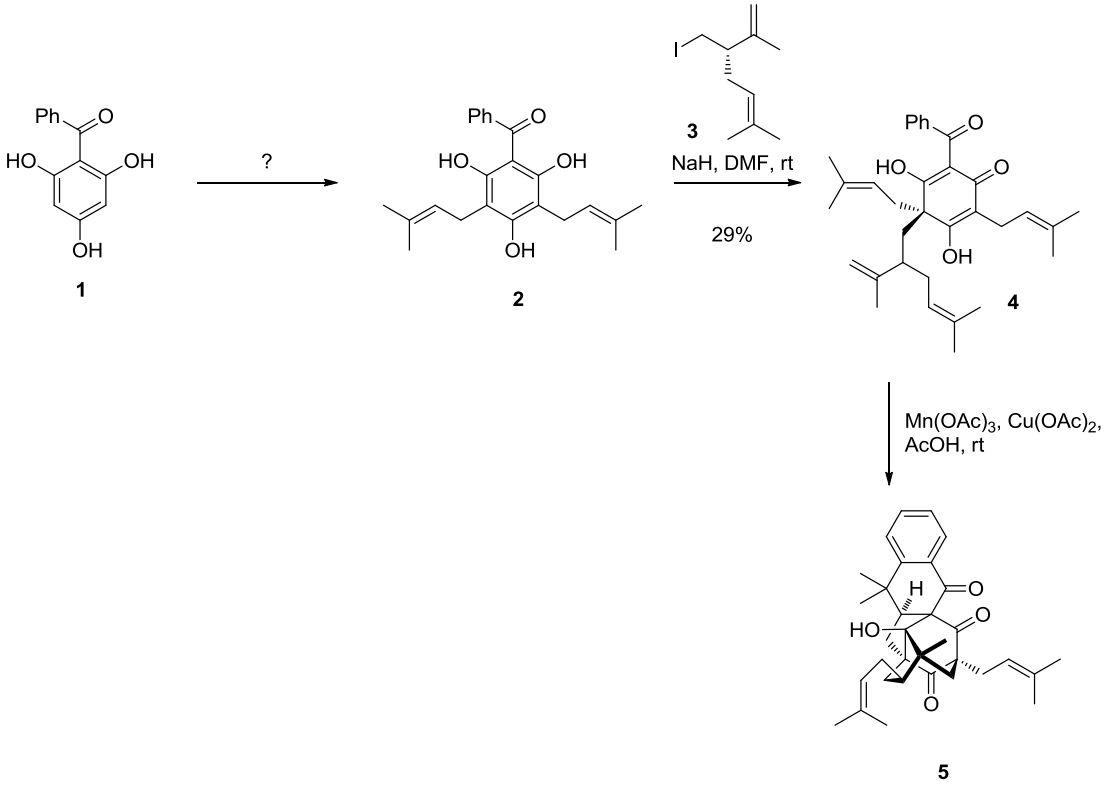
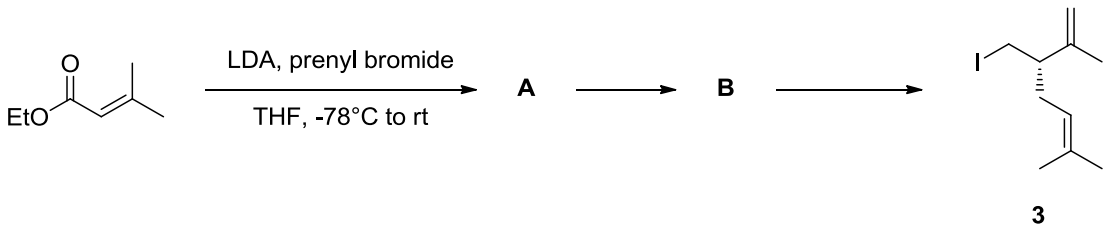
Submitted by Christian Gloor

Biomimetic Total Synthesis of (±)-and (+)-Garcibracteatone

Problem:

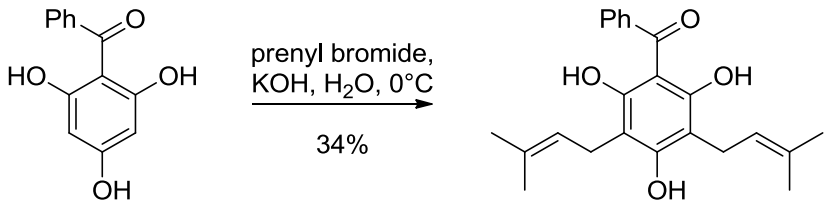


1) Give the reagents for the synthesis of **2**.
2) Give a mechanism for the transformation from **4** to **5**.



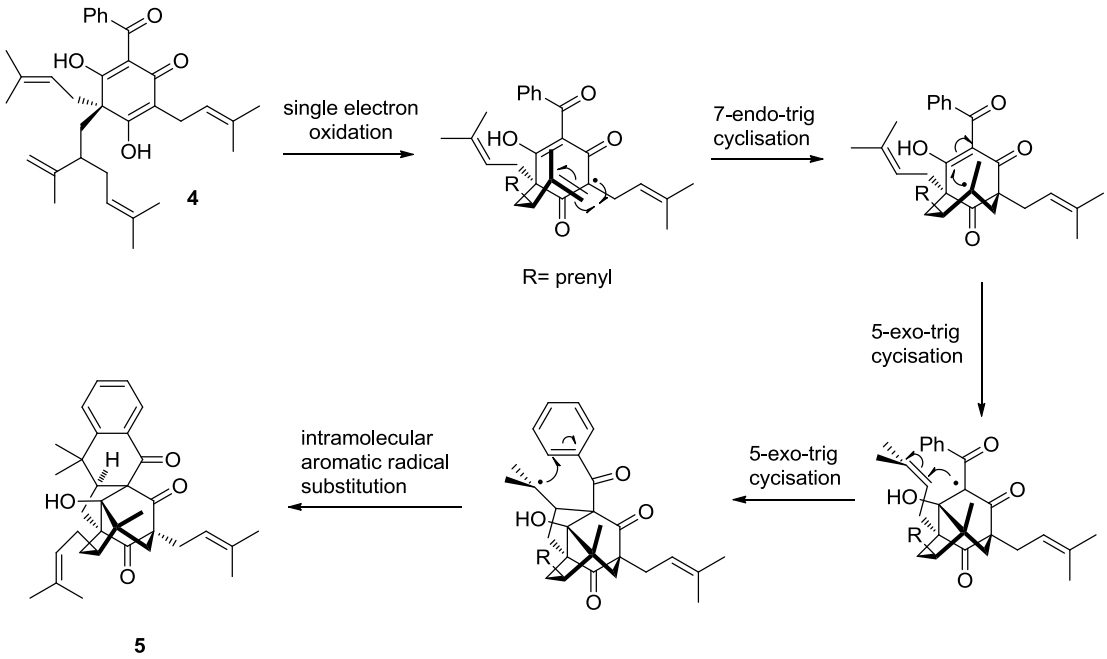
3) Give the Products A and B, as well as the reaction conditions leading to racemic **3**.
4) How would you synthesize **3** enantioselective?

Solution:

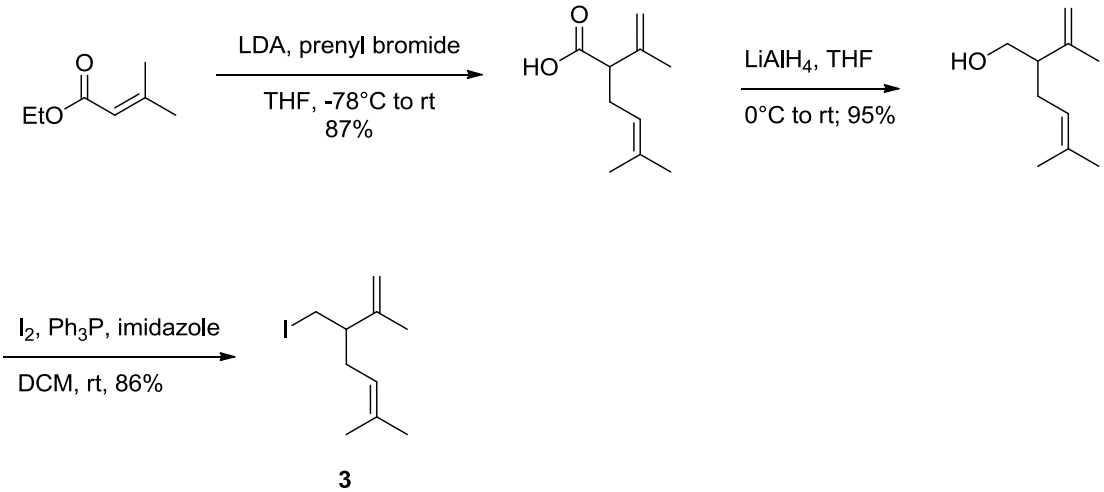


1 **2**

The mechanism of **4** to **5** goes *via* a cascade of 7-endo-trig / 5-exo-trig / 5-exo-trig and an intramolecular aromatic radical substitution.

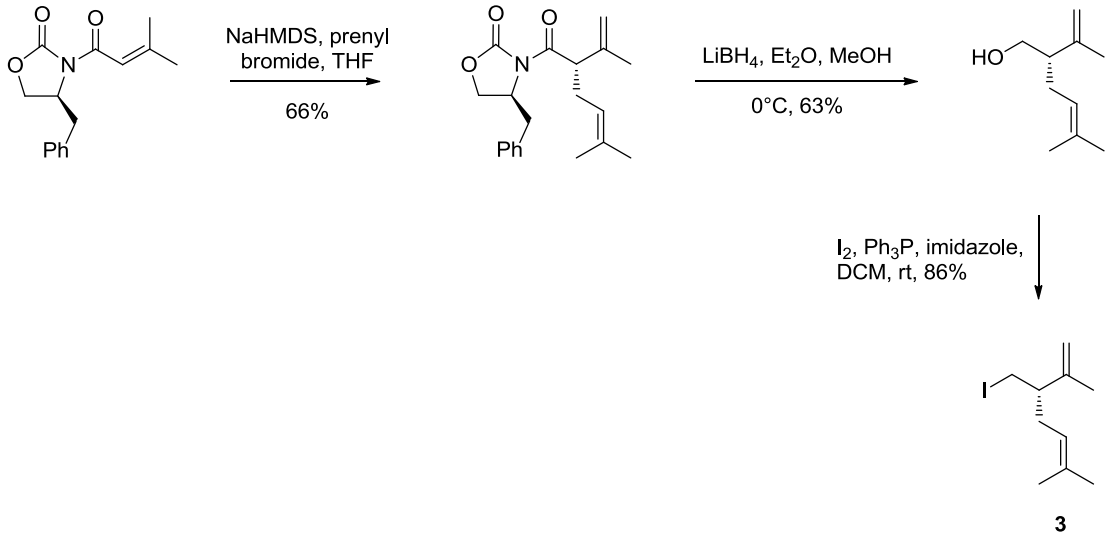


Molecule **3** is prepared *via* alkylation, reduction and Appel-reaction.



3

The enantioselektive synthesis of **3** is carried out with an Evans auxiliary:



References:
H. P. Pepper, S. J. Tulip, Y. Nakano, J. H. George, *J. Org. Chem.,* **2014**, *79*, 2564-2573

Keywords: radical cyclisation cascade