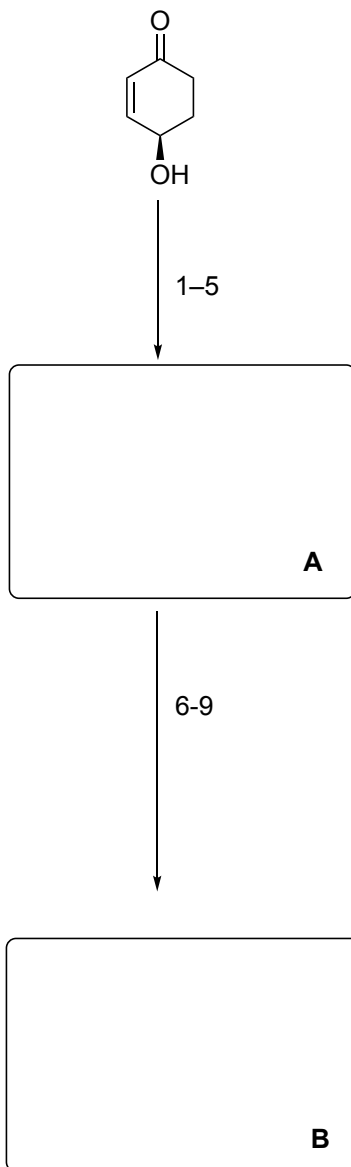


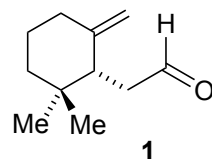
Divergent Asymmetric Synthesis of Glutinosasins A–E

Lim X.; Fang, W.; Hu, Q.; Tang, J.; Jiang, H.; Chen, K.; Ma, Z.

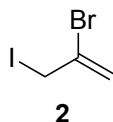
J. Am. Chem. Soc. **2026**, *148* (28), 30456-30465



- 1) PMBTCA, CSA, CH₂Cl₂, rt, *then*
I₂, pyridine, 0 °C to rt
- 2) *p*-TsOH·H₂O, (CH₂OH)₂, CH(OEt)₃, toluene, 36 °C
- 3) *n*-BuLi, THF, -78 °C, *then* **1**, 0 °C
- 4) PPTS, acetone, H₂O, 50 °C, *then*
TBSCl, imidazole, DMAP, CH₂Cl₂, 0 °C to rt
- 5) Fe(acac)₃, PhSiH₃, EtOAc, (CH₂OH)₂, 60 °C



- 6) HF, CH₃CN, 0 °C to rt
- 7) DMP, NaHCO₃, CH₂Cl₂, 0 °C
- 8), Cs₂CO₃, **2**, acetone, 28 °C
- 9) Pd(OAc)₂, (*S*)-BINAP, Cs₂CO₃, toluene, 85 °C

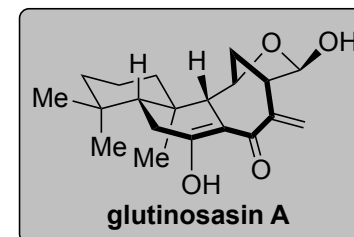


3) How would you make **1**?

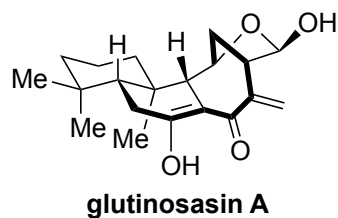
5) Hint: Tricyclic ring system formed.

8) Hint: Consider most acidic proton. What would you estimate the pK_a to be?

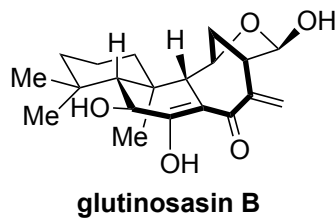
9) Hint: Imagine enol tautomer.



10-13



- 10) $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , CH_3OH , 0°C
- 11) L-Selectride, THF, -78°C
- 12) SeO_2 , $t\text{-BuOOH}$, CH_2Cl_2 , rt
- 13) DMP, NaHCO_3 , CH_2Cl_2 , 0°C



10) Hint: Skeletal reorganization occurs. Start with PMB deprotection and look at structure of natural product. Name of reaction?

Bonus: How would you make glutinosasin B from the intermediate obtained after step 10?

