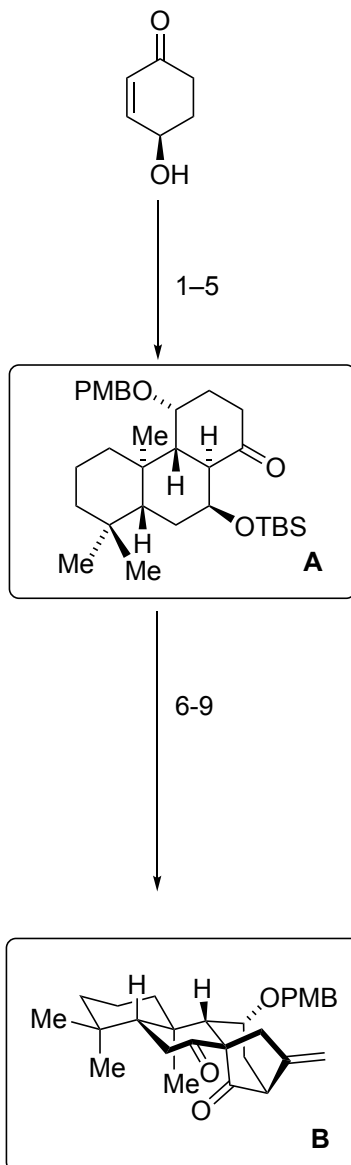


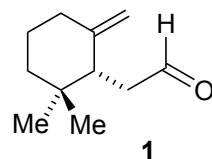
Divergent Asymmetric Synthesis of Glutinosasins A–E

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

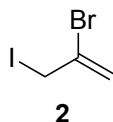
J. Am. Chem. Soc. **2026**, *148* (28), 30456-30465



- 1) PMBTCA, CSA, CH_2Cl_2 , rt, *then*
- I_2 , pyridine, $0\text{ }^\circ\text{C}$ to rt
- 2) *p*-TsOH· H_2O , $(\text{CH}_2\text{OH})_2$, $\text{CH}(\text{OEt})_3$, toluene, $36\text{ }^\circ\text{C}$
- 3) *n*-BuLi, THF, $-78\text{ }^\circ\text{C}$, *then* **1**, $0\text{ }^\circ\text{C}$
- 4) PPTS, acetone, H_2O , $50\text{ }^\circ\text{C}$, *then*
- TBSCl, imidazole, DMAP, CH_2Cl_2 , $0\text{ }^\circ\text{C}$ to rt
- 5) $\text{Fe}(\text{acac})_3$, PhSiH_3 , EtOAc, $(\text{CH}_2\text{OH})_2$, $60\text{ }^\circ\text{C}$



- 6) HF, CH_3CN , $0\text{ }^\circ\text{C}$ to rt
- 7) DMP, NaHCO_3 , CH_2Cl_2 , $0\text{ }^\circ\text{C}$
- 8), Cs_2CO_3 , **2**, acetone, $28\text{ }^\circ\text{C}$
- 9) $\text{Pd}(\text{OAc})_2$, (*S*)-BINAP, Cs_2CO_3 , toluene, $85\text{ }^\circ\text{C}$



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

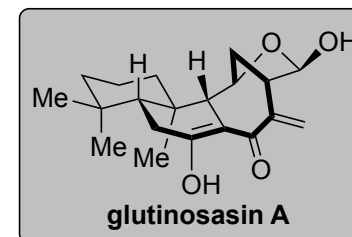
Derived from (*R*)- γ -coronal

5) Hint: Tricyclic ring system formed.

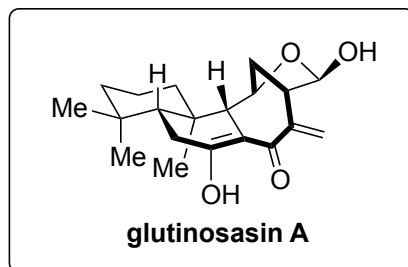
8) Hint: Consider most acidic proton. What would you estimate the pK_a to be?

$\text{pK}_\text{a} \sim 9$ for 1,3-diketone

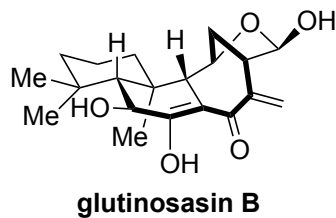
9) Hint: Imagine enol tautomer.



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?

Retro-Claisen condensation

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

Rubottom oxidation, followed by same series of redox manipulations

