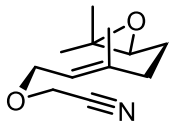


# Total Synthesis of (±)-Leonuketal

Grant, P. S.; Furkert, D. P.; Brimble, M. A. *Org. Lett.* **2020**, *22*, 8735-8740.



↓ 1 - 5

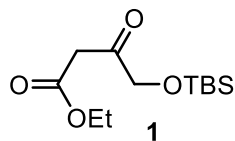


↓ 6 - 13

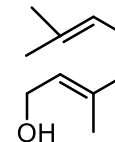


- 1)  $\text{Cp}_2\text{TiCl}_2$ , Zn then aq.  $\text{KH}_2\text{PO}_4$
- 2) ethylene glycol, TsOH
- 3) DMP, pyridine
- 4) L-selectride
- 5) aq. HCl

- 6)  $\text{TsNHNH}_2$ , PPTS
- 7) MeLi
- 8) TIPSOTf, DIPEA
- 9) MeLi,  $\text{CH}_2\text{O}$
- 10) MsCl,  $\text{Et}_3\text{N}$
- 11) NaI
- 12) NaH, **1**
- 13) TsOH then  $\text{K}_2\text{CO}_3$

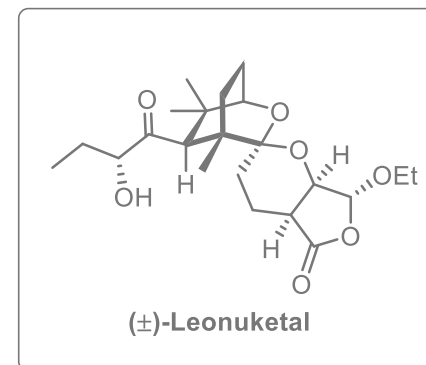


How would you synthesize the starting material from geraniol?

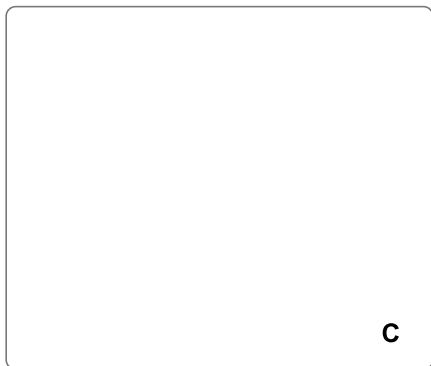


*Hint: steps 2-5 overall epimerization sequence*

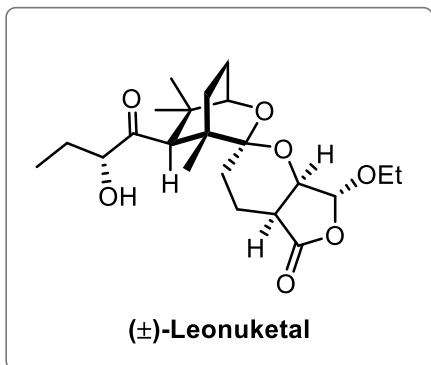
Step 7: Name of the reaction



↓  
14 - 18



↓  
19 - 23



- 14) AuCl•DMS, PPTS
- 15) H<sub>2</sub>, Rh-Al<sub>2</sub>O<sub>3</sub>
- 16) LiOH
- 17) DMP
- 18) PPTS, EtOH

- 19) TBAF
- 20) DMP
- 21) *n*PrMgBr
- 22) DMP
- 23) O<sub>2</sub>, LiHMDS *then* P(OEt)<sub>3</sub>

Step 14: Suggest possible mechanism

Step 15: *proceeds with epimerization*