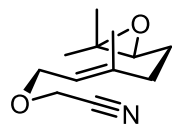
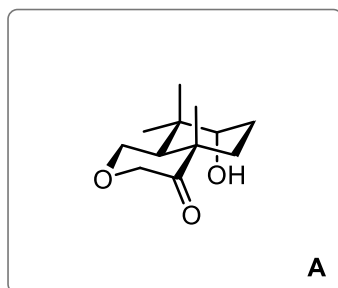


Total Synthesis of (±)-Leonuketal

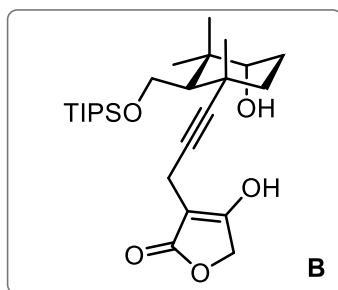
Grant, P. S.; Furkert, D. P.; Brimble, M. A. *Org. Lett.* **2020**, *22*, 8735-8740.



↓ 1 - 5

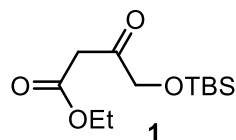


↓ 6 - 13

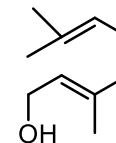


- 1) Cp_2TiCl_2 , Zn then aq. KH_2PO_4
- 2) ethylene glycol, TsOH
- 3) DMP, pyridine
- 4) L-selectride
- 5) aq. HCl

- 6) TsNHNH_2 , PPTS
- 7) MeLi
- 8) TIPSOTf, DIPEA
- 9) MeLi, CH_2O
- 10) MsCl, Et_3N
- 11) NaI
- 12) NaH, **1**
- 13) TsOH then K_2CO_3



How would you synthesize the starting material from geraniol?

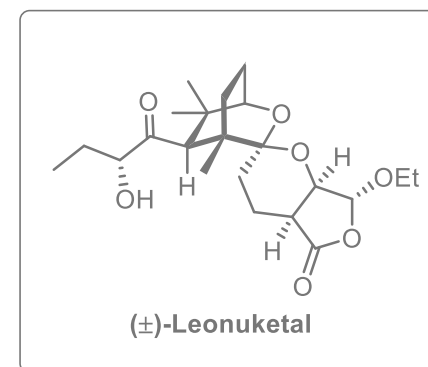


- 1) NaH, NCCH_2Br , THF
- 2) NBS, THF/ H_2O
- 3) K_2CO_3 , MeOH

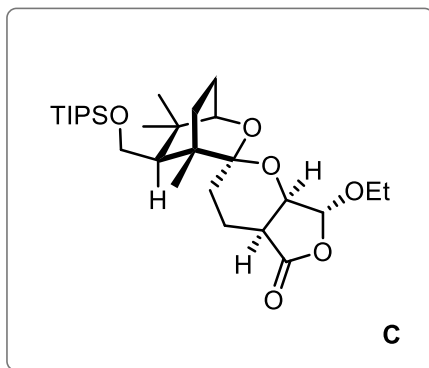
Hint: steps 2-5 overall epimerization sequence

Step 7: Name of the reaction

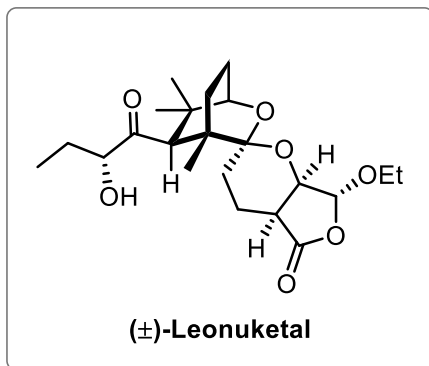
Shapiro-type Fragmentation



14 - 18



19 - 23



- 14) AuCl•DMS, PPTS
- 15) H₂, Rh-Al₂O₃
- 16) LiOH
- 17) DMP
- 18) PPTS, EtOH

- 19) TBAF
- 20) DMP
- 21) *n*PrMgBr
- 22) DMP
- 23) O₂, LiHMDS then P(OEt)₃

Step 14: Suggest possible mechanism

Step 15: proceeds with epimerization

