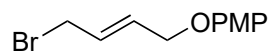


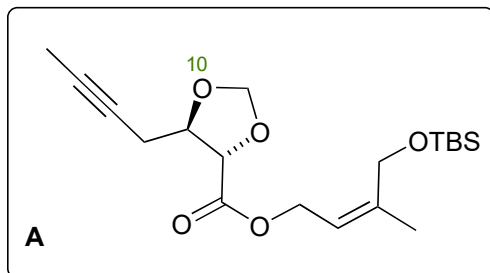
Total Synthesis of (-)-Jiadifenin

Dr. Yang Yang Dr. Xingnian Fu Dr. Jianwei Chen Prof. Dr. Hongbin Zhai

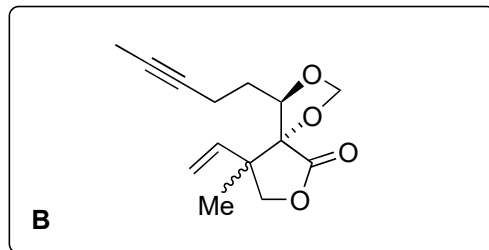
Angew. Chem. Int. Ed. **2012**, *51*, 9825–9828



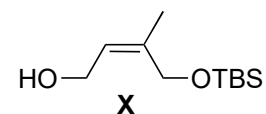
1-6



7-8



- 1) 1-bromo-1-propene, *n*BuLi, CuI, -78 °C
- 2) AD-mix-β, MeSO₂NH₂, *t*BuOH/H₂O, 0 °C
- 3) KOH, CH₂I₂, 18-c-6
- 4) CAN, MeCN/H₂O
- 5) Jones reagent
- 6) DCC, DMAP, **X**

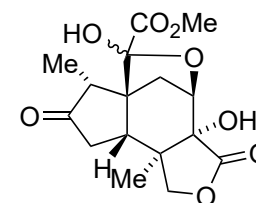


what's jones reagent?
CrO₃•H₂SO₄

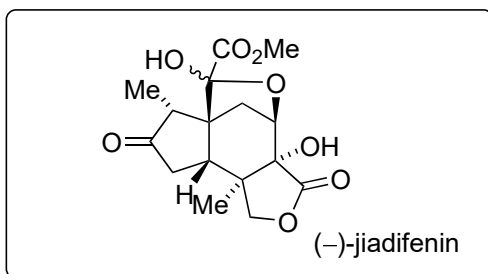
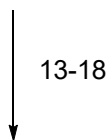
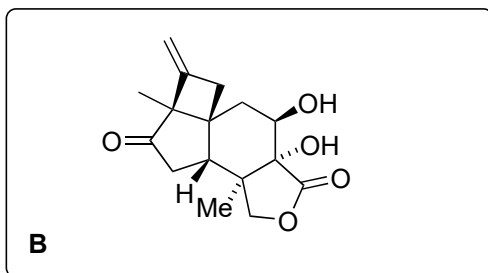
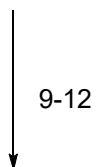
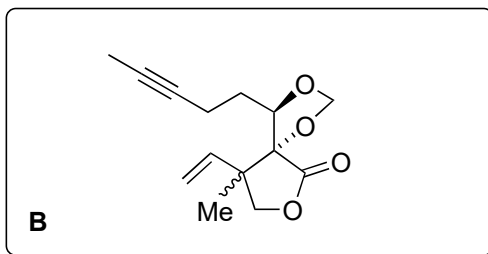
- 7) LDA, TMSCl, THF -78 °C to reflux
- 8) TsOH•H₂O, MeOH, Δ

name the reaction in 7) and draw the transition state

Ireland - Claisen rearrangement

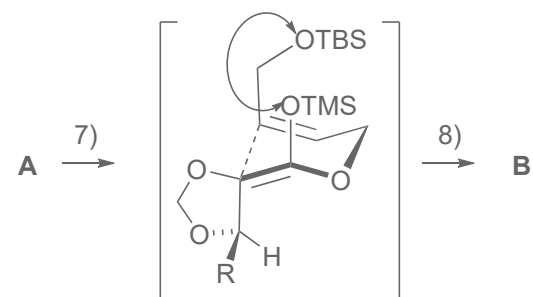


(-)-jiadifenin



- 9) $\text{Ph}_3\text{C BF}_4$, CH_2Cl_2 , Δ
- 10) TBSOTf, Et_3N , CH_2Cl_2 , r.t.
- 11) $[\text{Co}_2(\text{CO})_8]$, Bu_3PS , toluene, Δ
- 12) $h\nu$, allene, THF -78°C

- 13) O_3 , MeOH, then Me_2S -78°C
- 14) NaOMe, MeOH
- 15) LDA, TMSCl, Et_3N
- 16) $\text{Pd}(\text{OAc})_2$, O_2 ,
- 17) TBAF
- 18) NaHMDS, -78°C
- (-)-trans-(phenylsulfonyl)-3-phenyloxaziridine
- 19) Jones reagent, then MeOH



name reaction 15+16
Saegusa-Ito