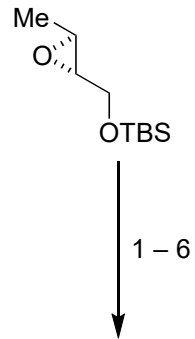
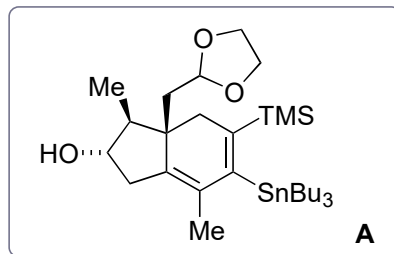


# Total Synthesis of (–)-Jiadifenin

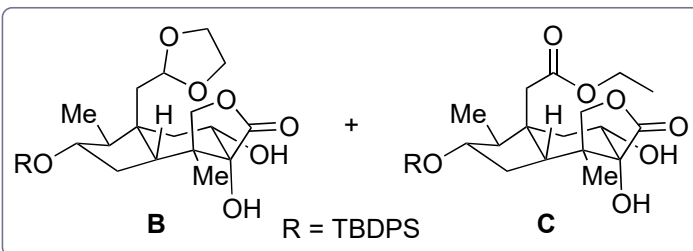
X. Cheng, G. C. Micalizio, *J. Am. Chem. Soc.* **2016**, *138*, 1150



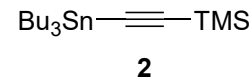
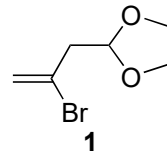
1 – 6



7 – 12



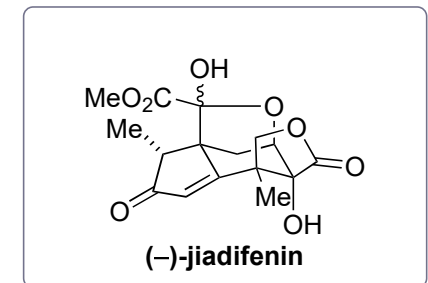
- 1) **1**, Mg, CuI
- 2) TBAF
- 3) TsCl (1.2 equiv), Et<sub>3</sub>N, DMAP
- 4) NaH
- 5) Propyne, *n*-BuLi, BF<sub>3</sub>•OEt<sub>2</sub>
- 6) Ti(O*i*-Pr)<sub>4</sub>, *n*-BuLi, then **2**, then *n*-BuLi and substrate, then PhCHO

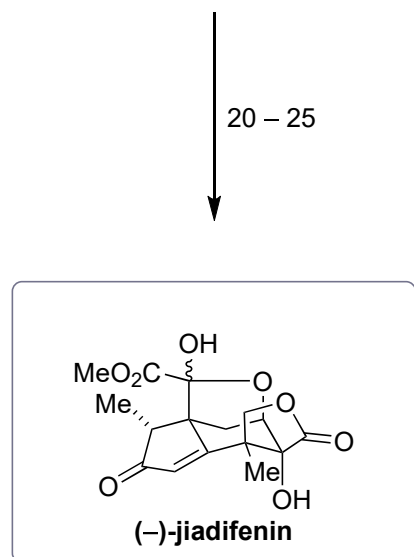
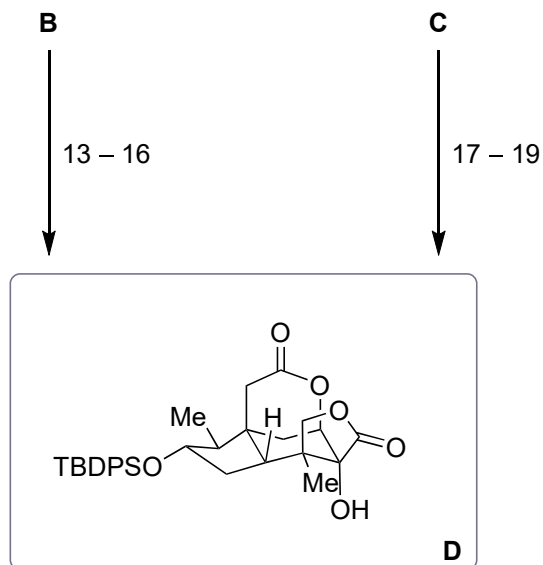


- 6) Mechanism? See below.

- 7) TBAF
- 8) TBDPSCI, imH
- 9) MeLi, then CO<sub>2</sub>
- 10) PhSeCH<sub>2</sub>Cl, *i*-Pr<sub>2</sub>NEt, NaI
- 11) OsO<sub>4</sub>
- 12) *n*-Bu<sub>3</sub>SnH, AIBN

- 12) Hint: An additional unexpected HAT gives rise to the second product. Propose a mechanism how both products are formed. See below.

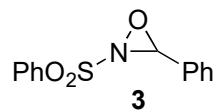




- 13)  $(\text{COCl})_2$ , DMSO,  $\text{Et}_3\text{N}$   
 14) HCl, THF/ $\text{H}_2\text{O}$   
 15)  $\text{NaClO}_2$ , 2-methylbut-2-ene,  $\text{NaH}_2\text{PO}_4$   
 16)  $\text{NaBH}_4$ , *then* TsOH

- 17)  $(\text{COCl})_2$ , DMSO,  $\text{Et}_3\text{N}$   
 18)  $\text{NaBH}_4$   
 19) TsOH

- 20) TBAF  
 21) IBX  
 22) LDA, TMSCl, *then*  $\text{Pd}(\text{OAc})_2$   
 23) TBAF  
 24) NaHMDS, **3**  
 25)  $\text{CrO}_3$ ,  $\text{H}_2\text{SO}_4$ , *then* MeOH



- 13) Name of the reaction? Swern oxidation  
 15) Name of the reaction? Pinnick–Lindgren–Kraus oxidation

- 22) Name of the reaction? Saegusa–Ito oxidation  
 24) Hint: Additionally, an epimerization takes place.  
 25) Name of the oxidation reaction? Jones oxidation

