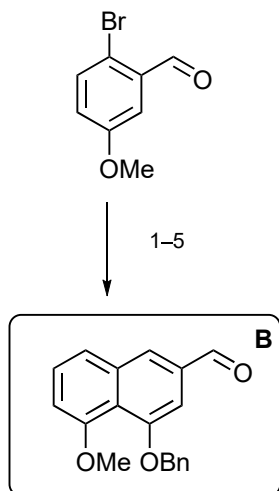
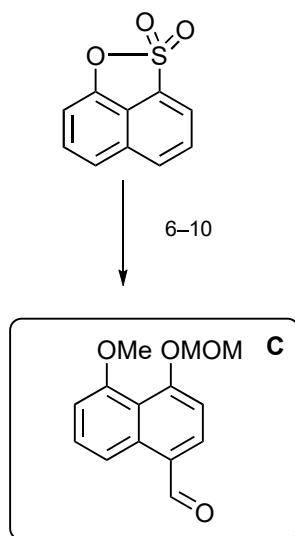


## Total Syntheses of Dalesconol A and B

S. Snyder, T. Sherwood, A. Ross, *Angew. Chem. Int. Ed.* **2010**, *49*, 5146–5150.



- 1) DBU, LiCl, **A**
- 2) TFA/ H<sub>2</sub>O, Ac<sub>2</sub>O, NaOAc
- 3) H<sub>2</sub>, Pd/C, NaOMe
- 4) NaH, BnBr
- 5) PDBBA

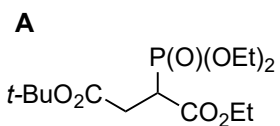


- 6) NaOH, KOH, 210 °C
- 7) NaH, Me<sub>2</sub>SO<sub>4</sub>
- 8) NBS
- 9) NaH, MOMCl
- 10) *n*-BuLi, DMF

Which variant of the HWE reaction represents step 5? What is the role of LiCl?

Masamune–Roush-modified HWE reaction

LiCl coordinates to the carbonyl groups of the ketophosphonate and makes the CH<sub>2</sub>-group more acidic → weaker bases can be employed; ideal for base sensitive substrates



Hint step 5: PDBBA can be prepared by admixing DIBAL-H with KOt-Bu

What is the advantage over DIBAL-H?

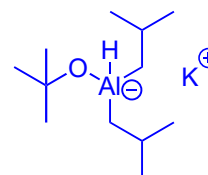
A.R. Jeon et al., *Tetrahedron* **2014**, *70*, 4420-4424.

high product yields,

mild reaction conditions (0 °C)

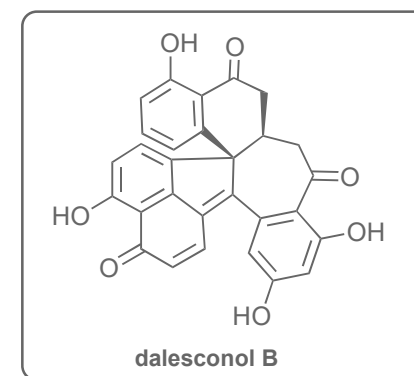
process simplicity

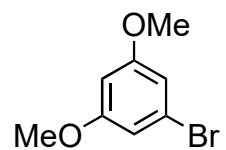
potassium diisobutyl-tert-butoxyaluminum hydride: PDBBA



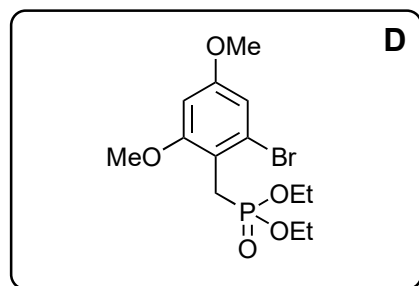
Name the reaction in step 6?

alkali fusion

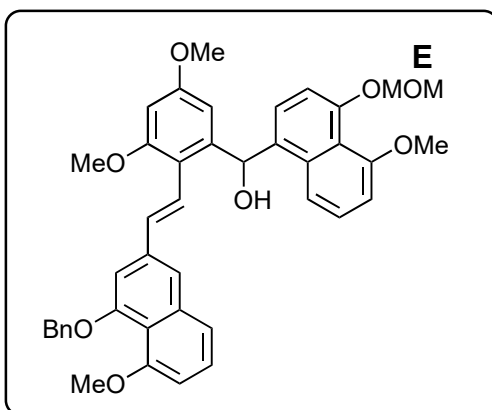




12–14



15–16



- 12)  $\text{POCl}_3$ , DMF
- 12)  $\text{NaBH}_4$
- 13)  $\text{PBr}_3$
- 14) KHMDS,  $\text{HP(O)(OEt)}_2$

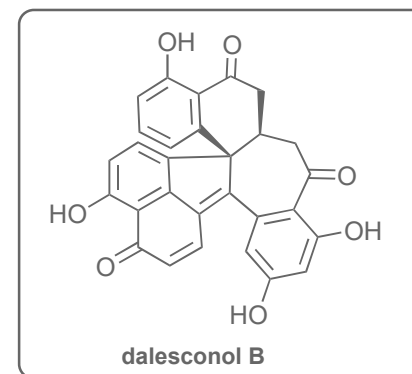
- 15)  $\text{KO}^t\text{-Bu}$ , then **B**
- 16)  $n\text{-BuLi}$ , then **C**

Name the reaction in step 12?

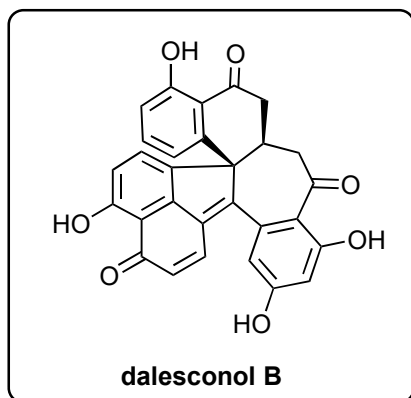
Vilsmeier–Haack reaction

Name the reaction in step 15?

Horner–Wadsworth–Emmons olefination



17-24

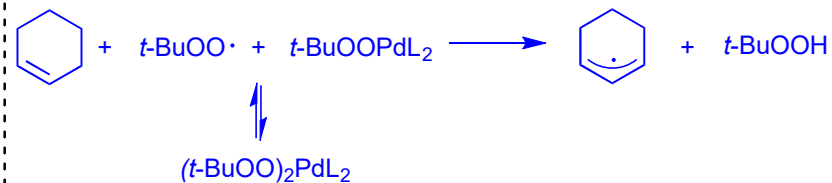


- 17) H<sub>2</sub>, Pd/C; TFA; PhI(OAc)<sub>2</sub>
- 18) Pd/C, H<sub>2</sub>
- 19) HCl, THF
- 20) DDQ; BBr<sub>3</sub>
- 21) KHMDS, MOMCl
- 22) Pd(OAc)<sub>2</sub>, *t*-BuOOH
- 23) DMP
- 24) BBr<sub>3</sub>

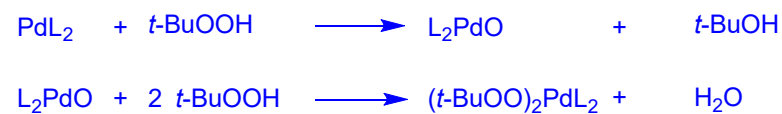
Provide a mechanism for step 17

Step 22: Under these conditions usually hydroperoxides or ketones are formed: please come up with a mechanism

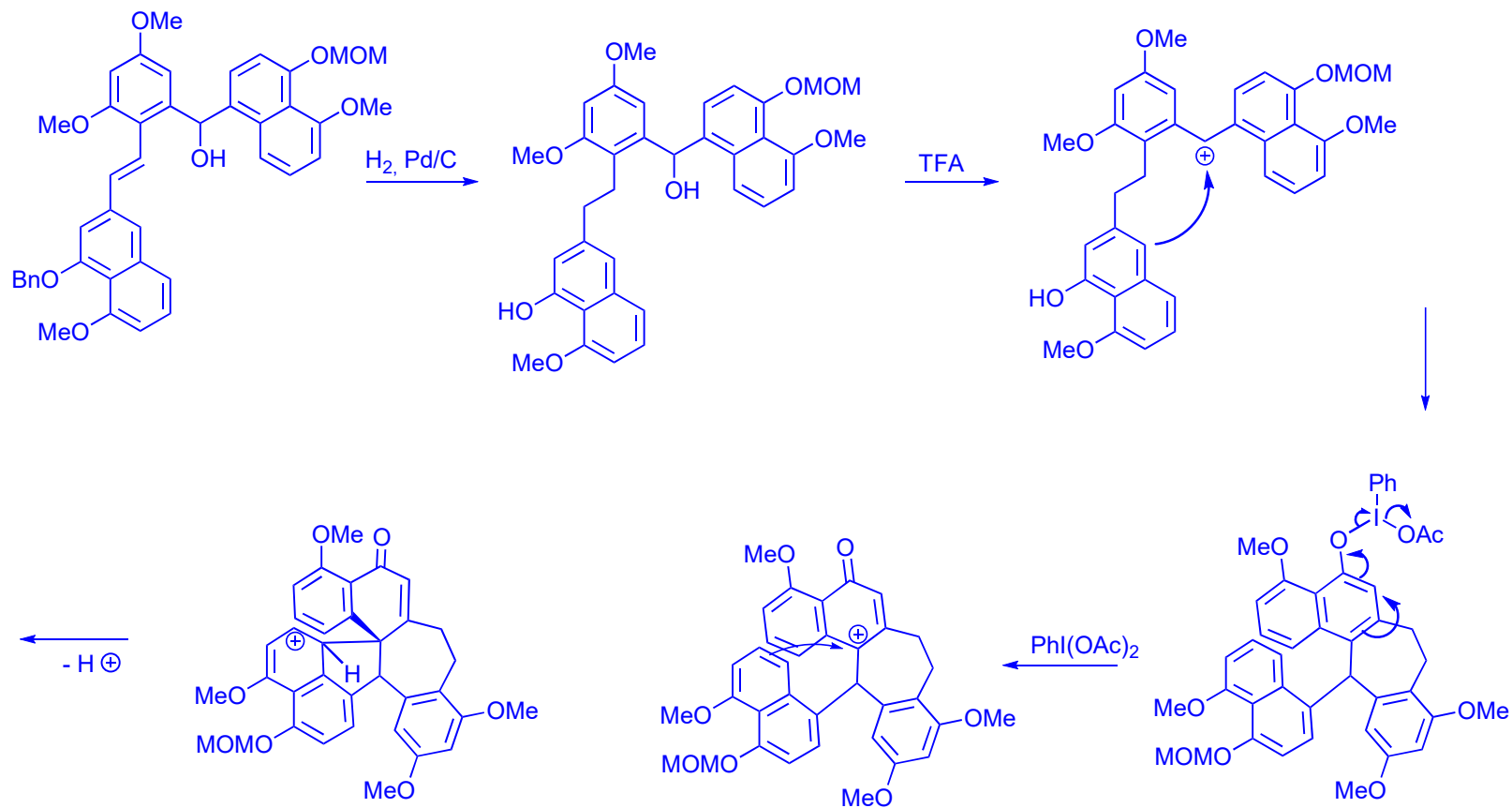
J. Yu, E. Corey, *Org. Lett.* **2002**, *4*, 2717-2730.



catalyst regeneration:



Step 17:



S. Snyder, A. Zografos, Y. Lin, *Angew. Chem. Int. Ed.* **2007**, *46*, 8186–8191.  
L. Pouysegou, D. Deffieux, S. Quideau, *Tetrahedron* **2010**, *66*, 2235–2261.