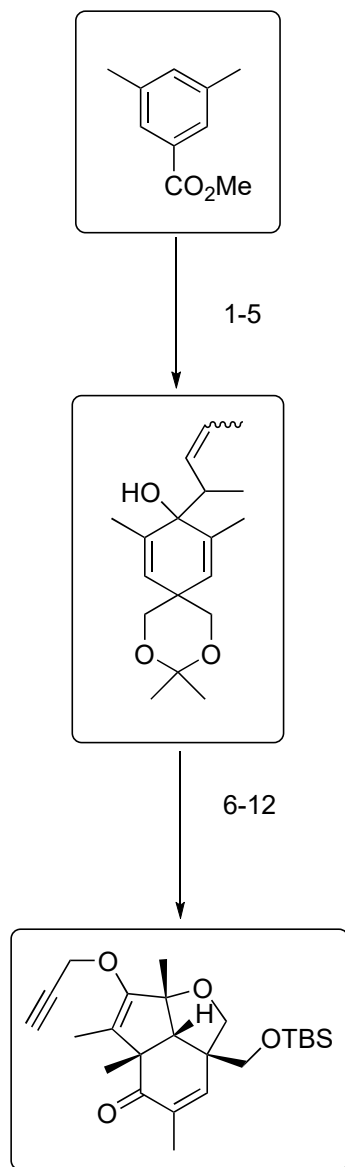


# Total Synthesis and Stereochemical Reassignment of (±)-Indoxamycin B

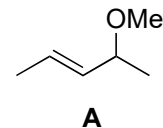
Oliver F. Jeker, Erick M. Carreira

Angew. Chem. Int. Ed. 2012, 51, 3474-3477

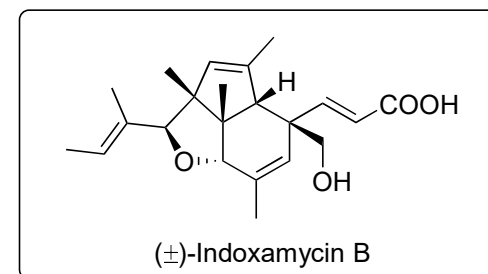
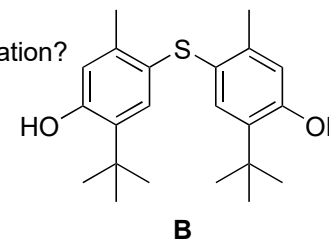


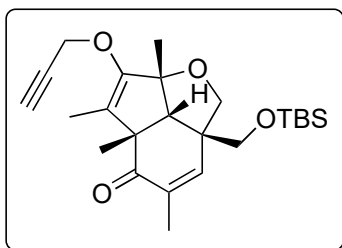
- 1) Li (2.2 equiv), *t*-BuOH (1.05 equiv), NH<sub>3</sub> then ICH<sub>2</sub>OCOt-Bu (1 equiv)
- 2) LiAlH<sub>4</sub> (1.5 equiv)
- 3) TsOH, Me<sub>2</sub>C(OMe)<sub>2</sub>
- 4) Pd/C, *t*-BuOOH, K<sub>2</sub>CO<sub>3</sub>
- 5) [Cp<sub>2</sub>TiCl<sub>2</sub>], *n*-BuLi, **A** then product from step 4)

- 6) *t*-BuOK, 18-crown-6 then TESCl
- 7) Pd(OAc)<sub>2</sub>, O<sub>2</sub>
- 8) HCl (aq)
- 9) [VO(acac)<sub>2</sub>], *t*-BuOOH, **B**
- 10) TBSCl, NEt<sub>3</sub>, DMAP
- 11) DMP
- 12) KH, 18-crown-6, propargyl bromide

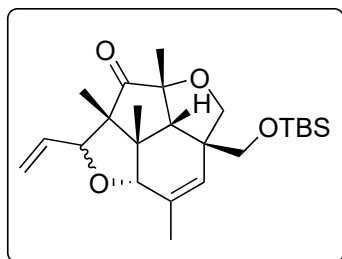


- 6) name reaction and classification?  
oxy-Cope, [3,3] sigmatropic

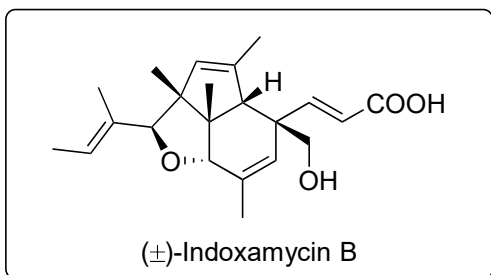




13-15

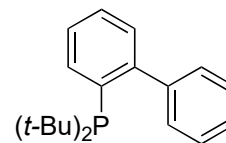


16-23



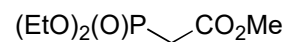
- 13)  $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$   
 14)  $\text{LiBHET}_3$   
 15) **C**,  $\text{AuCl}$ ,  $\text{AgOTs}$

- 16)  $[\text{Mn}(\text{dpm})_3]$ ,  $\text{PhSiH}_3$ ,  $\text{O}_2$   
 17) DMP  
 18)  $\text{Ph}_3\text{PEtBr}$ ,  $\text{KHMDS}$   
 19)  $\text{SmI}_2$   
 20) DMP  
 21) **D**,  $\text{NaH}$   
 22)  $\text{BH}_3 \cdot t\text{-BuNH}_2$   
 23) Burgess' reagent  
 24)  $\text{LiOH}$ , then  $\text{HCl}$  (aq)



**C**

- 13) name reaction and classification?  
 Saucy-Marlet, propargylic Claisen, [3,3] sigmatropic  
 15) hint: new diastereomeric center formed, separation after step 16



**D**

- 16) name reaction, provide a mechanism  
 Mukaiyama hydration  
 18) hint: proceeding with (*E*)-isomer

- 22) structure of Burgess' reagent and possible preparation

