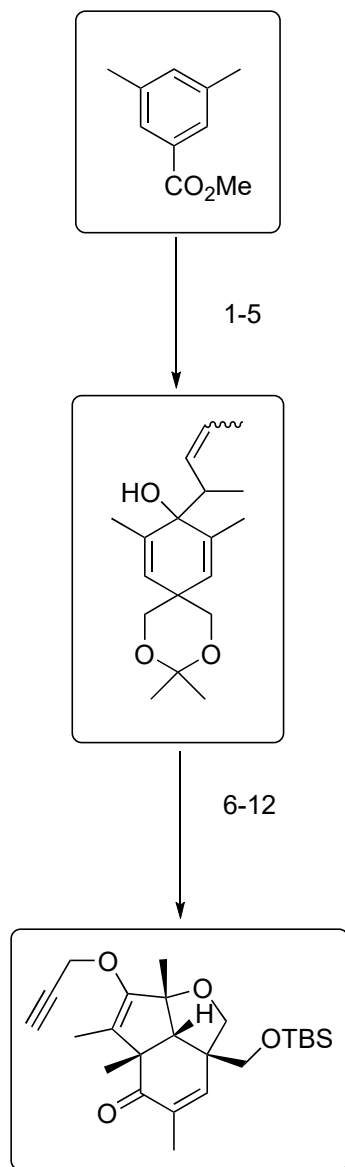


Total Synthesis and Stereochemical Reassignment of (±)-Indoxamycin B

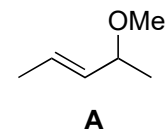
Oliver F. Jeker, Erick M. Carreira

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

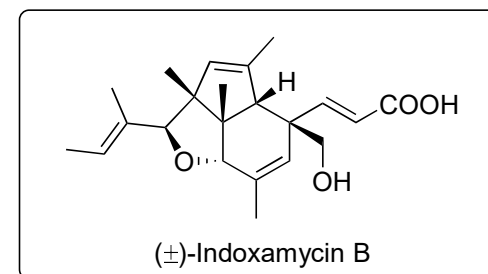
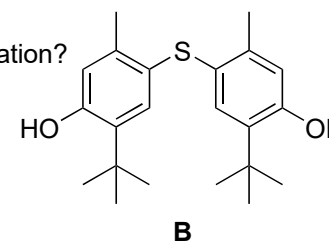


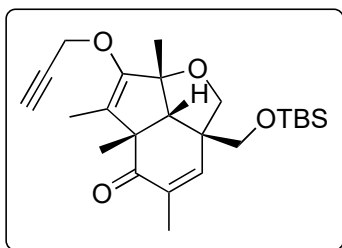
- 1) Li (2.2 equiv), *t*-BuOH (1.05 equiv), NH₃ then ICH₂OCOt-Bu (1 equiv)
- 2) LiAlH₄ (1.5 equiv)
- 3) TsOH, Me₂C(OMe)₂
- 4) Pd/C, *t*-BuOOH, K₂CO₃
- 5) [Cp₂TiCl₂], *n*-BuLi, **A** then product from step 4)

- 6) *t*-BuOK, 18-crown-6 then TESCl
- 7) Pd(OAc)₂, O₂
- 8) HCl (aq)
- 9) [VO(acac)₂], *t*-BuOOH, **B**
- 10) TBSCl, NEt₃, DMAP
- 11) DMP
- 12) KH, 18-crown-6, propargyl bromide

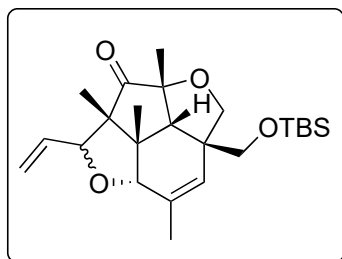


- 6) name reaction and classification?
oxy-Cope, [3,3] sigmatropic

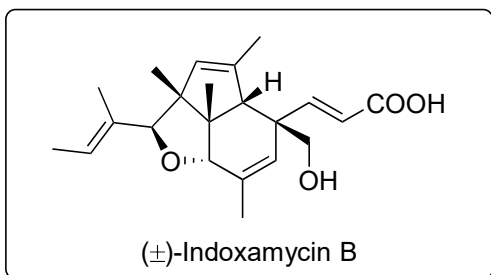




13-15

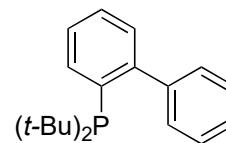


16-23



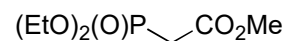
- 13) $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$
 14) LiBHET_3
 15) **C**, AuCl , AgOTs

- 16) $[\text{Mn}(\text{dpm})_3]$, PhSiH_3 , O_2
 17) DMP
 18) Ph_3PEtBr , KHMDS
 19) SmI_2
 20) DMP
 21) **D**, NaH
 22) $\text{BH}_3 \cdot t\text{-BuNH}_2$
 22) Burgess' reagent
 23) LiOH , then 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

