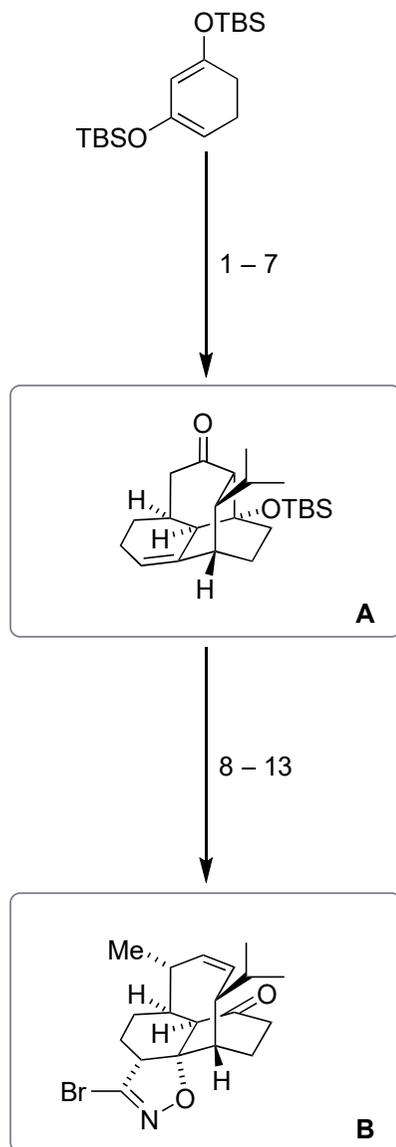
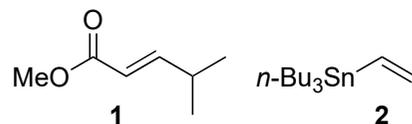


Total Synthesis of Vinigrol

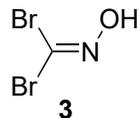
T. J. Maimone, J. Shi, S. Ashida, P. S. Baran, *J. Am. Chem. Soc.* **2009**, *131*, 17066.



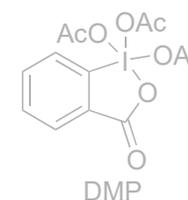
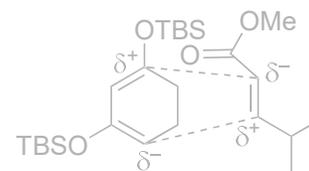
- 1) AlCl_3 , **1**
- 2) LDA, Tf_2O
- 3) $\text{Pd}(\text{PPh}_3)_4$, LiCl, **2**
- 4) DIBAL (2.5 equiv)
- 5) DMP
- 6) Allyl-MgCl, then Δ
- 7) DMP



- 8) LDA (1.3 equiv), MeI (1.6 equiv)
- 9) TBAF
- 10) $\text{Me}_4\text{NBH}(\text{OAc})_3$
- 11) MsCl, py
- 12) KHMDS
- 13) KHCO_3 , **3**



- 1) Explain the regioselectivity. see below
- 3) Name of the reaction? Stille coupling
- 5) Structure of DMP?

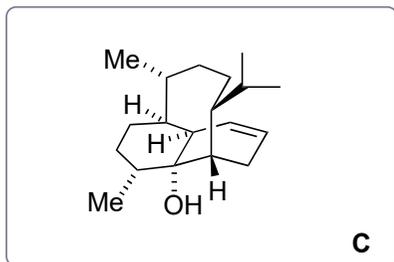


Resonance structures explain the partial charges, which can be used to predict the regioselectivity.

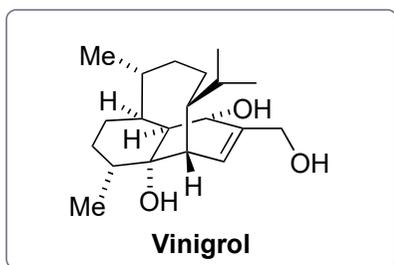
- 12) Name of the reaction? Grob fragmentation
- 13) Classify the reaction. 1,3-dipolar cycloaddition

B

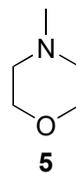
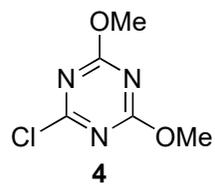
14 – 21



22 – 25

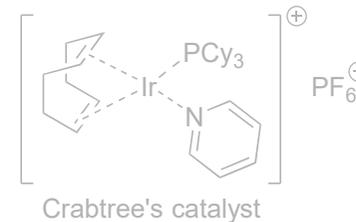


- 14) DIBAL (1.2 equiv)
- 15) Crabtree cat., H₂, B(O-*i*Pr)₃
- 16) NaH, CS₂, MeI
- 17) 180 °C
- 18) LiAlH₄ (20 equiv)
- 19) HCO₂H, **4**, **5**, DMAP
- 20) COCl₂, NEt₃
- 21) AIBN, *n*-Bu₃SnH



- 22) OsO₄, NMO
- 23) TEMPO, NaOCl
- 24) TrisNHNH₂
- 25) *n*-BuLi, TMEDA, then (CH₂O)_n

- 15) Structure of Crabtree cat.?
- 16) Name of the new functional group? Xanthate
- 17) Name of the reaction? Chugaev elimination
- 19–21) Name of the sequence? Saegusa deamination sequence



- 25) Name of the reaction? Shapiro reaction