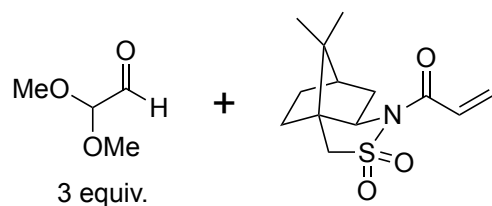


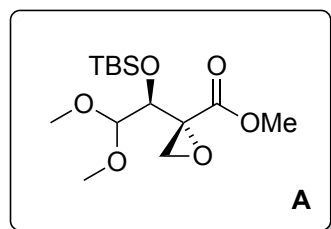
Component-based Synthesis of Trioxacarin A

Jakub Švenda, Nicholas Hill, and Andrew G. Myers, *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 6709–6714.

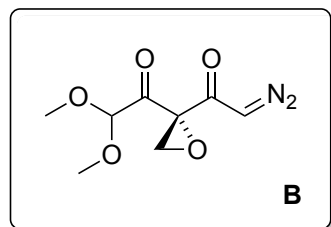
Thomas Magauer, Daniel J. Smaltz, and Andrew G. Myers, *Nat. Chem.* **2013**, *5*, 886–893.



1–4



5–8



- 1) DABCO
 - 2) Et₃N, MeOH
 - 3) TBSOTf, DIPEA
 - 4) *t*-BuOOH, *t*-BuOK
- anti:syn = 13:1

- 5) LiOH (aq)
- 6) ClCO₂*i*-Bu, Et₃N, then CH₂N₂
- 7) Et₃N • 3HF
- 8) DMP, aq. NaHCO₃

Name the reaction of step 1?

Oppolzer sultam auxiliary-controlled Morita–Baylis–Hillman

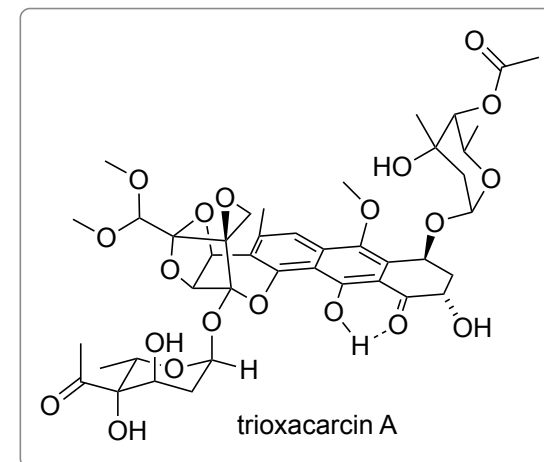
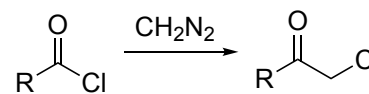
Hint: The (*S*)-enantiomer is obtained after step 2

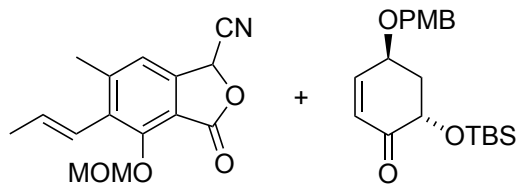
James W. Leahy et al - UC Berkeley

J. Am. Chem. Soc. **1997**, *119*, 18, 4317–4318.

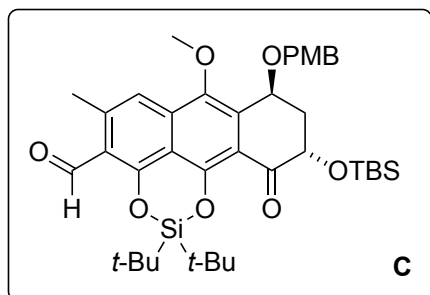
Step 6: Why is it important to form the mixed anhydride as the activated species over an acid chloride?

avoiding the Nierenstein reaction

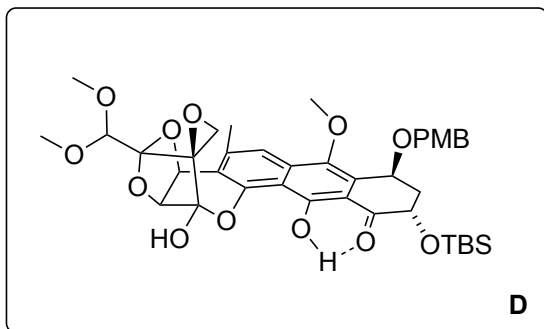




9-12



13, 14

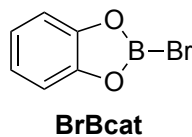


9) *t*-BuOLi (3 equiv.), then (MeO)₂SO₂

10) K₂OsO₄, NaIO₄

11) BrBcat

12) *t*-Bu₂SiCl₂, Et₃N, HOBT

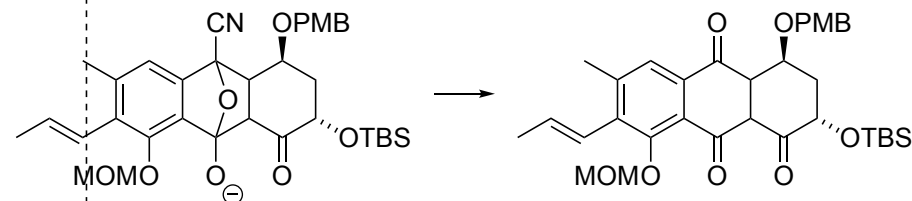
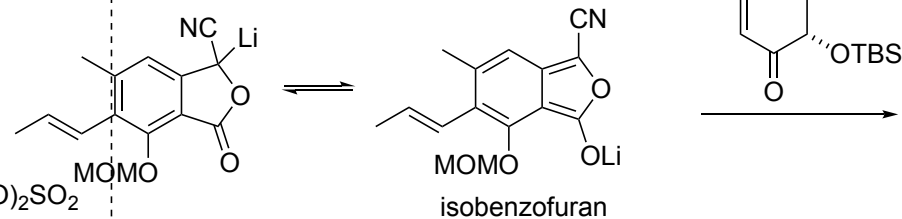


13) **B**, Rh₂(OAc)₄

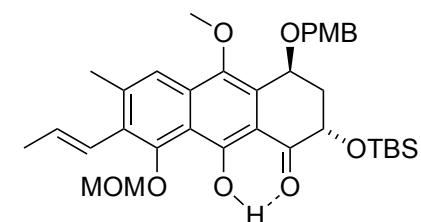
14) Et₃N · 3HF

Please provide a mechanism and the name reaction of step 9.

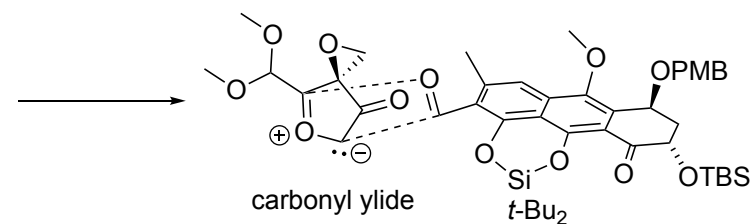
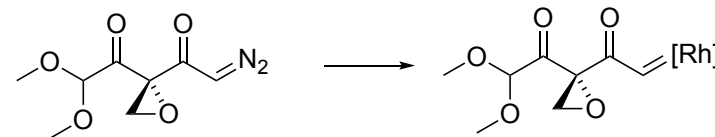
Kraus Sugimoto annulation
also: *Hauser Kraus annulation*

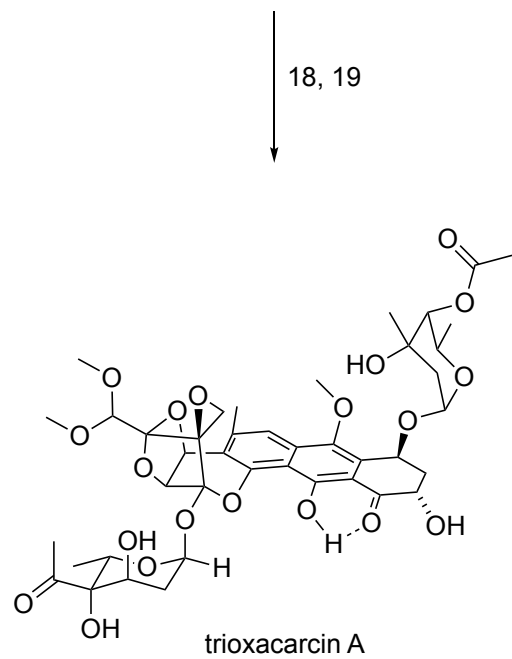
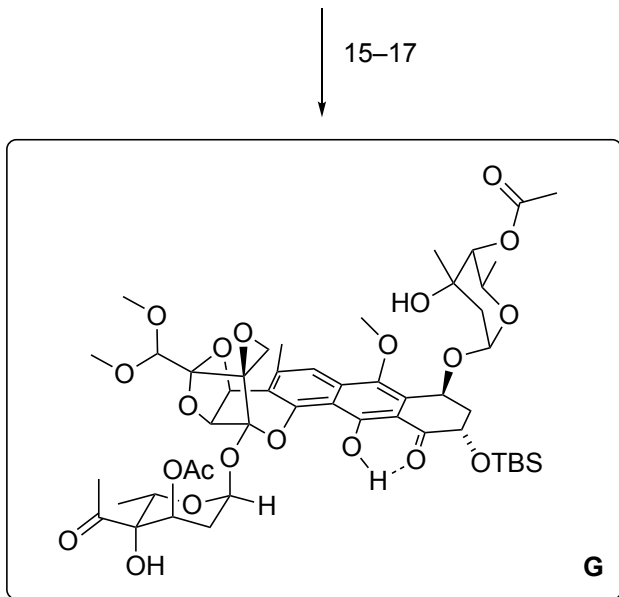


(MeO)₂SO₂

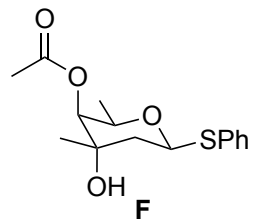
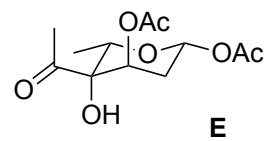


Please provide a mechanism for the key step happening in step 13.
Hint: It's a 1,3-dipolar cycloaddition reaction.





- 15) **E**, TMSNTf₂
 16) DDQ
 17) **F**, AgPF₆



- 18) K₂CO₃, MeOH
 19) Et₃N • 3HF

