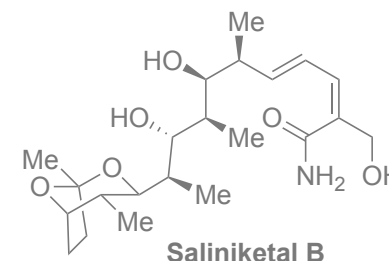


A Concise Total Synthesis of Salinketal B

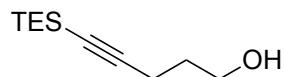
Jun Liu and Jef K. De Brabander

JACS **2009**, 131, 12562

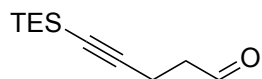


Name of this reaction?

Swern oxidation

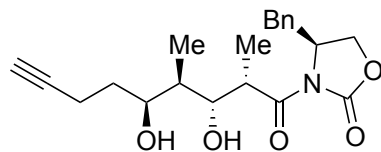


↓ 1



A

↓ 2-4



B

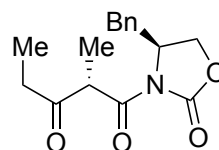
↓ 5

1) $(\text{COCl})_2$, DMSO, Et_3N , CH_2Cl_2 , -78°C , 2 h

2) **1**, $\text{Sn}(\text{OTf})_2$, Et_3N , CH_2Cl_2 , -20°C , then -78°C , **A**

3) $\text{Na}(\text{AcO})_3\text{BH}$, HOAc , 0°C to rt

4) TBAF, THF, 3 min



1

5) $[\text{PtCl}_2(\text{CH}_2\text{CH}_2)]_2$ (5 mol%), THF, 5 min

What is the name of the heterocycle in **1** and what role does it play?

Oxazolidinone - Chiral auxiliary

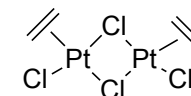
$\text{Sn}(\text{OTf})_2$ is required to obtain the desired anti:syn stereochemistry, however with TiCl_4 , a syn:syn relationship is observed. Draw the 2 transitions that would lead to these two products.

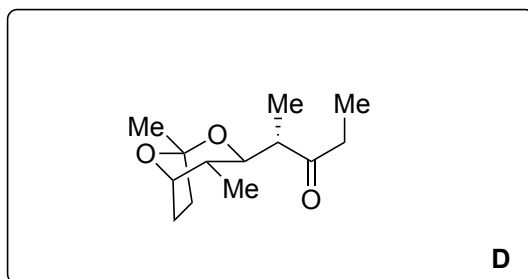
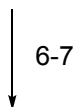
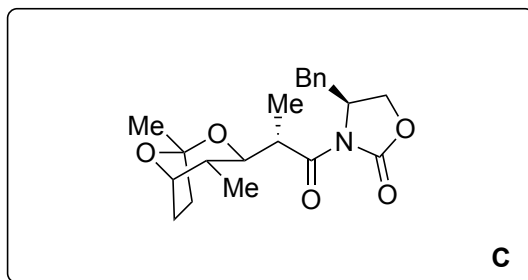
Diastomeric chairs on last page - Evan's himself did not have a reason for the different selectivities, but I was curious about what we would come up with.

Name of this catalyst and structure?

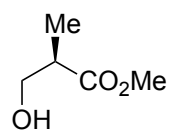
Zeise's Dimer

What is the mechanism of this reaction?

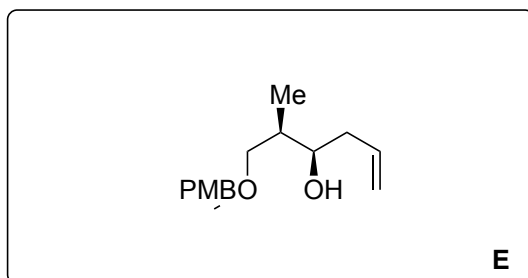




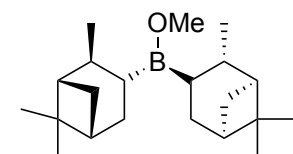
6) MeONHMe•HCl, AlMe₃, THF,
7) EtMgBr, THF, 0°C to rt, 2 h



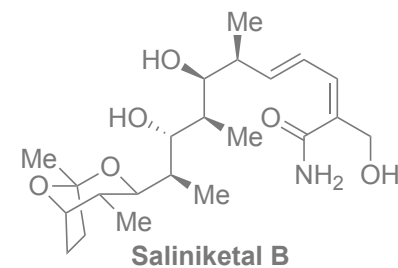
8-10

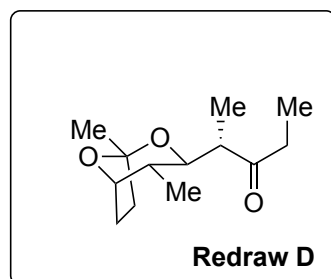
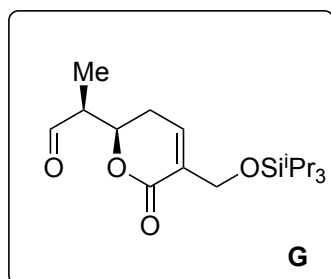
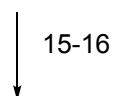
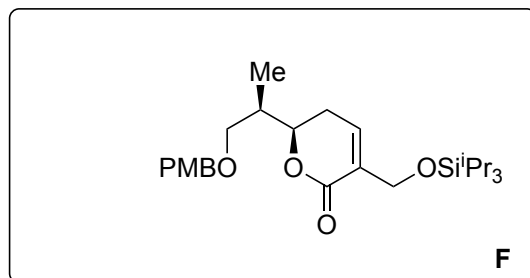
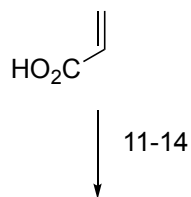


8) 4-MeOBnOC(NH)CCl₃, PPTS,
CH₂Cl₂, rt, 18 h
9) DIBAL-H, CH₂Cl₂, -78 °C, 2 h
10) Brown's reagent, allylMgBr,
0 °C, *then* substrate, - 98°C,
then NaOH, 30% H₂O₂, Et₂O,
reflux

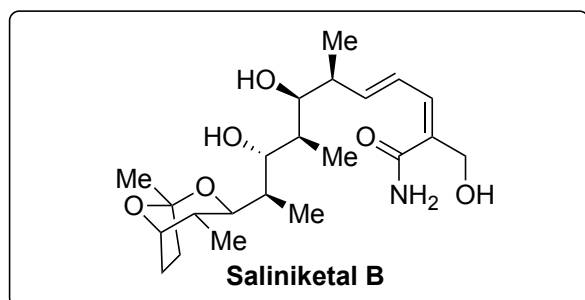


Diisopinocampheylborane
Brown's Reagent





17-19

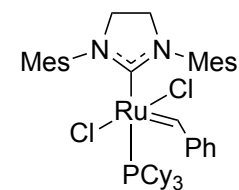


- 11) paraformaldehyde, DABCO, dioxane/H₂O (1:1), 72 h.
- 12) TIPS, imidazole, DMAP, CH₂Cl₂, 0 °C, to rt, 1 h
- 13) **E**, DCC, DMAP, CH₂Cl₂, 0 °C to rt, 12 h
- 14) Grubbs-II, (10 mol %)

- 15) DDQ, CH₂Cl₂/H₂O (20/1), rt, 1 h
- 16) DMP, NaHCO₃, CH₂Cl₂, 30 min, rt

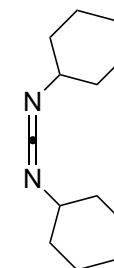
- 17) **D**, LiHMDS, -78 °C, 1 h, *then* **G**, THF
- 18) NMe₄, Na(AcO)₃BH, MeCN/AcOH (1:1), -20 °C
- 19) TBAF, THF, 48 h, *then* NH₃(g) HOBT, EDC, rt

Name of step 11?
 Structure of DCC?
 Name of step 13?
 Structure of Grubbs-II?



Baylis-Hillman

Steglich Esterification



N,N'-dicyclohexylcarbodiimide

Diastereomeric Chairs

J. Am. Chem. Soc. **1990**, *112*, 866-868

