

A Concise Total Synthesis of Salinketal B

Jun Liu and Jef K. De Brabander

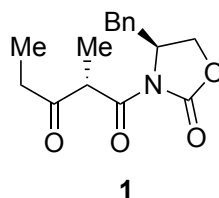
JACS **2009**, *131*, 12562

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

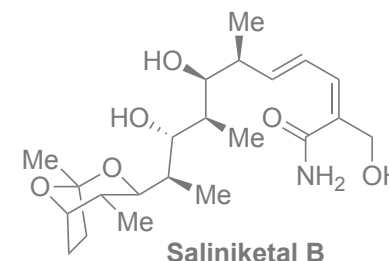
2) **1**, $\text{Sn}(\text{OTf})_2$, Et_3N , CH_2Cl_2 , -20°C , then -78°C , **A**

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

4) TBAF, THF, 3 min



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



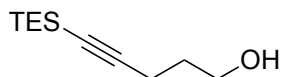
Name of this reaction?

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

$\text{Sn}(\text{OTf})_2$ 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 and hypothesize a reason for the altered selectivity.

Name of this catalyst?
Structure of this catalyst?

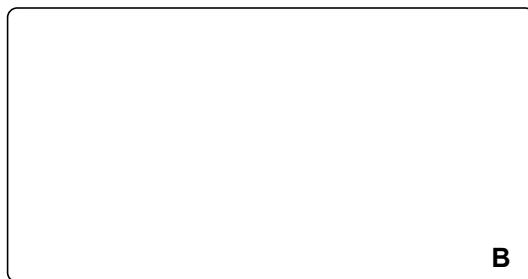
What is the mechanism of this reaction?



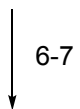
↓
1



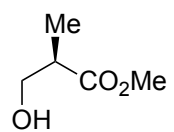
↓
2-4



↓
5



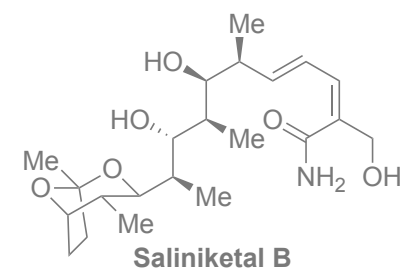
6) MeONHMe•HCl, AlMe₃, THF,
7) EtMgBr, THF, 0°C to rt, 2 h

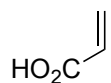


↓ 8-10

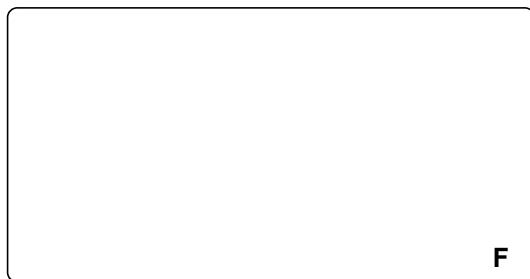


8) 4-MeOBnOC(NH)CCl₃, PPTS,
CH₂Cl₂, rt, 18 h
9) DIBAL-H, CH₂Cl₂, -78 °C, 2 h
10) Brown's reagent, allylMgBr,
0 °C, *then* substrate, -98 °C,
then NaOH, 30% H₂O₂, Et₂O,
refulx

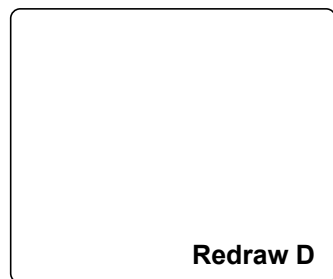




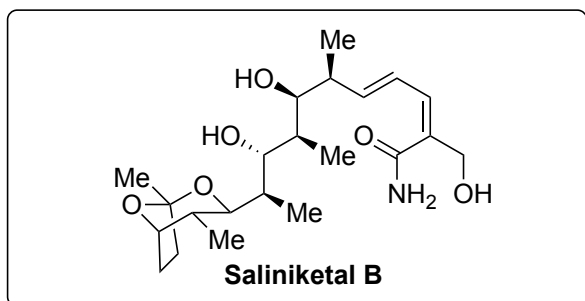
11-14



15-16



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(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?