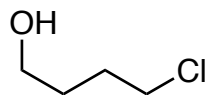


## Spiroacetal Formation through Telescoped Cycloaddition and Carbon–Hydrogen Bond Functionalization: Total Synthesis of Bistramide A

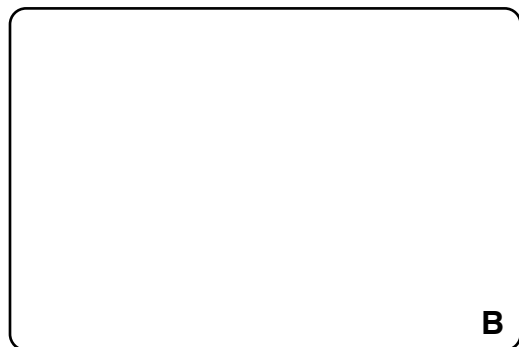
Han, X. and Floreancig, P. E.  
*Angew. Chem. Int. Ed.* **2014**, *53*, 11075–11078.



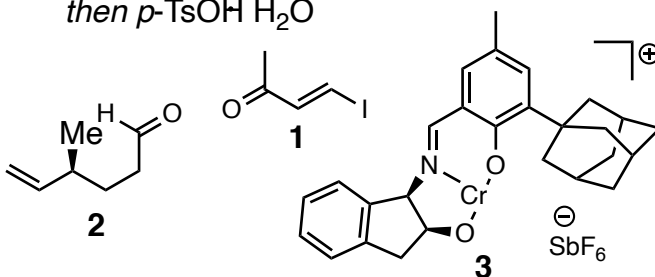
1-6



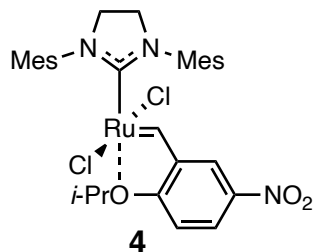
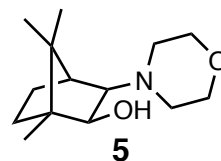
7-12



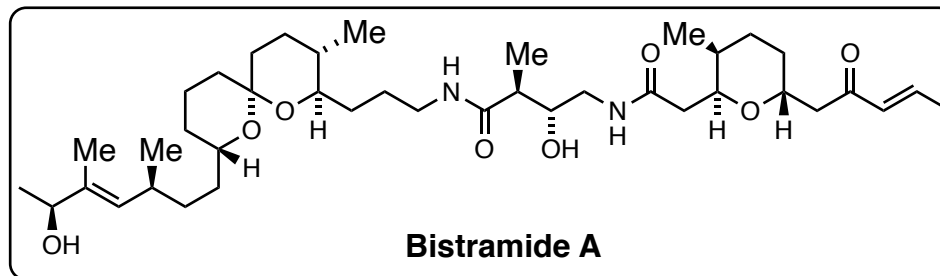
1. (COCl)<sub>2</sub>, DMSO, Et<sub>3</sub>N
2. *trans*-2-butene, *n*-BuLi, *t*-BuOK  
 (–)-(Ipc)<sub>2</sub>BOMe  
 then BF<sub>3</sub> OEt<sub>2</sub> then product of step 1  
 then NaOH, H<sub>2</sub>O<sub>2</sub>
3. TESCl, imidazole
4. (9-BBN)<sub>2</sub>, then **1**, [Pd(dppf)Cl<sub>2</sub>], K<sub>3</sub>PO<sub>4</sub>
5. TESOTf, Et<sub>3</sub>N
6. **2**, **3** (cat.), 4 Å MS then DDQ  
 then *p*-TsOH H<sub>2</sub>O

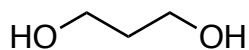


7. *p*-TsNHNH<sub>2</sub>, MeOH
8. NaBH<sub>3</sub>CN, MeOH pH > 4
9. NaOAc, EtOH, 75 °C
10. methacrolein, **4**
11. Me<sub>2</sub>Zn, **5**
12. NaN<sub>3</sub>, DMF, 60 °C



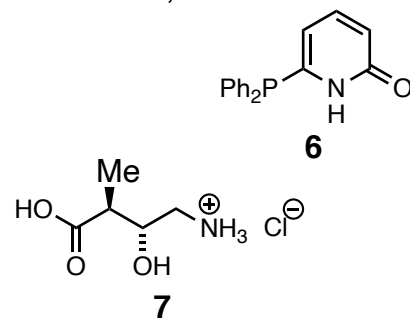
1. Name of the reaction?
2. Please name the reaction and explain the stereoselectivity of 90% *ee*.  
*Hint: 3*S*,4*R* product obtained.*
6. What type of catalyst is this?
7. Step 7-9 is one sequence, propose a mechanism and name the reaction.





13-21

13. TBSCl, Imidazole
14.  $\text{SO}_3 \cdot \text{Py}$ , DMSO,  $\text{Et}_3\text{N}$
15. *cis*-2-butene, *n*-BuLi, *t*-BuOK, (+)-(lpc)<sub>2</sub>BOMe then  $\text{BF}_3 \cdot \text{OEt}_2$  then product of step 14 then NaOH,  $\text{H}_2\text{O}_2$
16.  $[\text{Rh}(\text{CO})_2\text{acac}]$ , **6**,  $\text{H}_2/\text{CO}$  then  $\text{Ac}_2\text{O}$  DMAP,  $\text{Et}_3\text{N}$
17. (*E*)-3-penten-2-one, TMSOTf,  $\text{Et}_3\text{N}$  then TMSOTf (1.25 equiv.)
18.  $\text{H}_5\text{IO}_6$ ,  $\text{CrO}_3$
19. *N*-hydroxysuccinimide, DCC
20. **7**, *i*-Pr<sub>2</sub>NEt
21. *N*-hydroxysuccinimide, DCC



**C**

22

- 22)  $\text{PMe}_3$ ,  $\text{H}_2\text{O}$  then **B**

13. *Hint*: Excess of diol
14. Please name the reaction.
15. *Hint*: 3*S*,4*S* product obtained in 90%*ee*

22. Please name the reaction?

