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

Han, X. and Floreancig, P. E.
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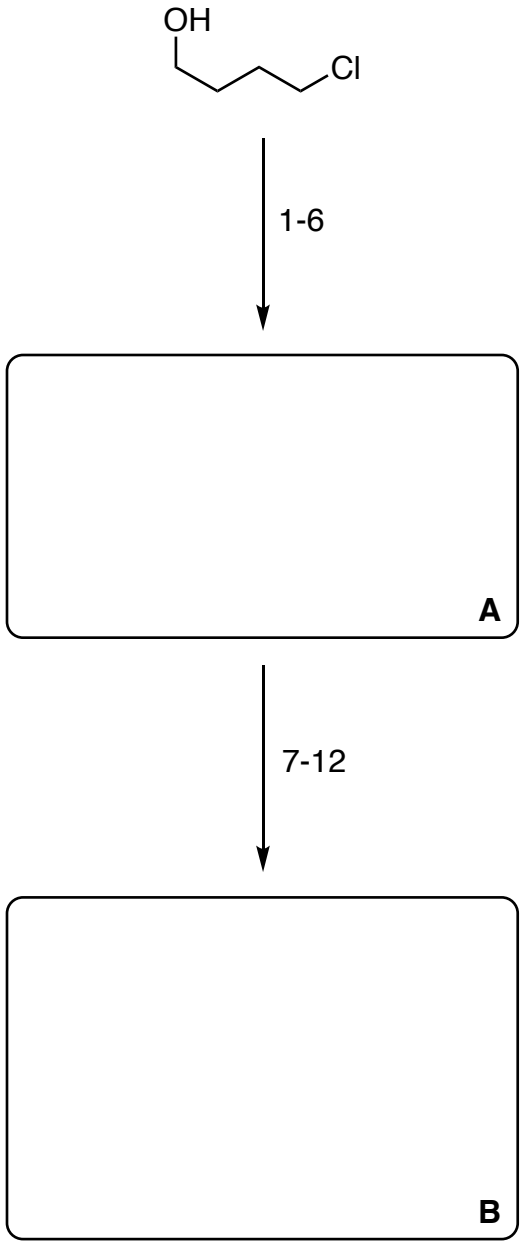
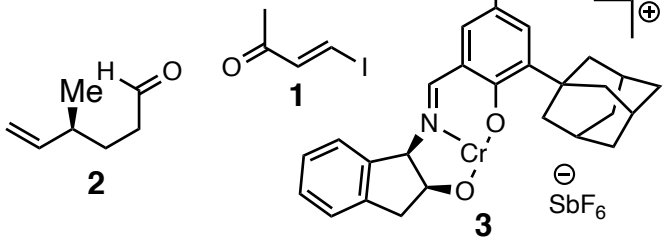
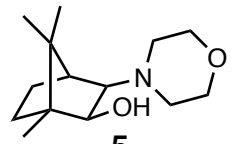
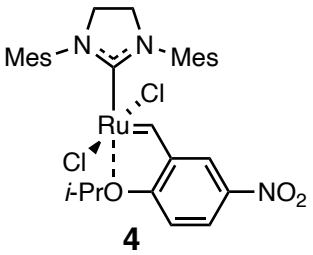


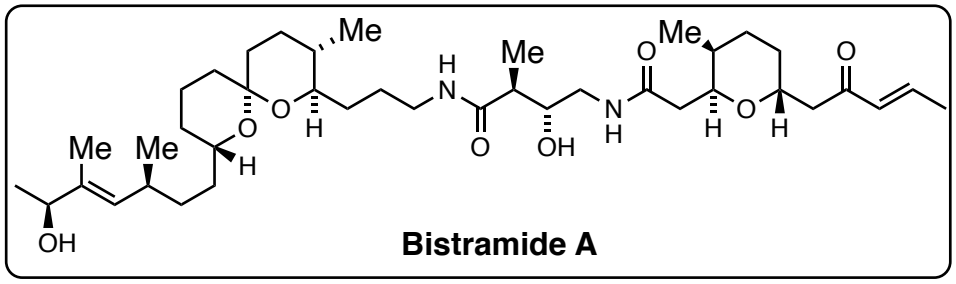
1. $(COCl)_2$, DMSO, Et_3N
2. *trans*-2-butene, *n*-BuLi, *t*-BuOK
   (–)-$(Ipc)_2BOMe$
   then BF_3 OEt_2 *then* product of step 1
   then NaOH, H_2O_2
3. TESCl, imidazole
4. $(9\text{-BBN})_2$, *then* **1**, $[Pd(dppf)Cl_2]$, K_3PO_4
5. TESOTf, Et_3N
6. **2**, **3** (cat.), 4 Å MS *then* DDQ
   then *p*-TsOH H_2O



7. *p*-$TsNHNH_2$, MeOH
8. $NaBH_3CN$, MeOH pH > 4
9. NaOAc, EtOH, 75 °C
10. methacrolein, **4**
11. Me_2Zn, **5**
12. NaN_3, DMF, 60 °C







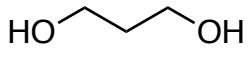
1. Name of the reaction?

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.

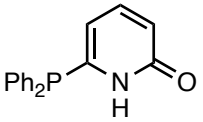


13-21

13. TBSCl, Imidazole
14. SO_3·Py, DMSO, Et_3N
15. *cis*-2-butene, *n*-BuLi, *t*-BuOK,
    (+)-$(Ipc)_2BOMe$
    then BF_3·OEt_2 *then* product of step 14
    then NaOH, H_2O_2
16. $[Rh(CO)_2acac]$, **6**, H_2/CO
    then Ac_2O DMAP, Et_3N
17. (*E*)-3-penten-2-one, TMSOTf, Et_3N
    then TMSOTf (1.25 equiv.)
18. H_5IO_6, CrO_3
19. *N*-hydroxysuccinimide, DCC
20. **7**, *i*-Pr_2NEt
21. *N*-hydroxysuccinimide, DCC

13. *Hint*: Excess of diol
14. Please name the reaction.

15. *Hint*: 3*S*,4*S* product obtained in 90%*ee*



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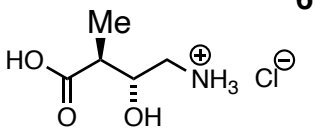


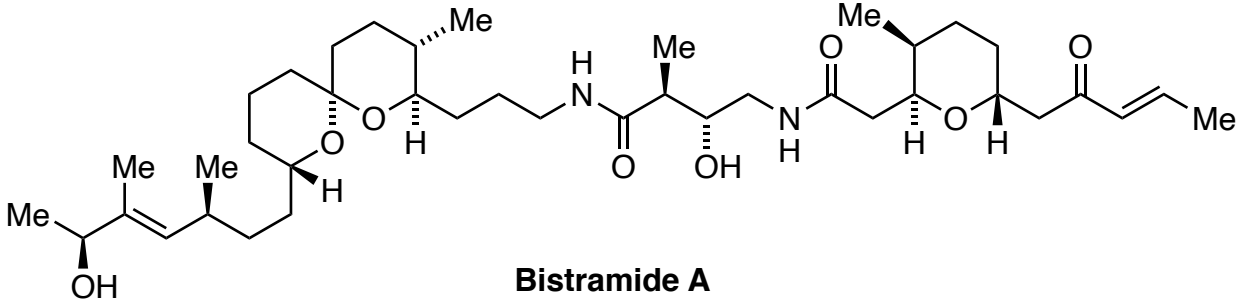
7

C

22

22) PMe_3, H_2O
then **B**

22. Please name the reaction?



Bistramide A