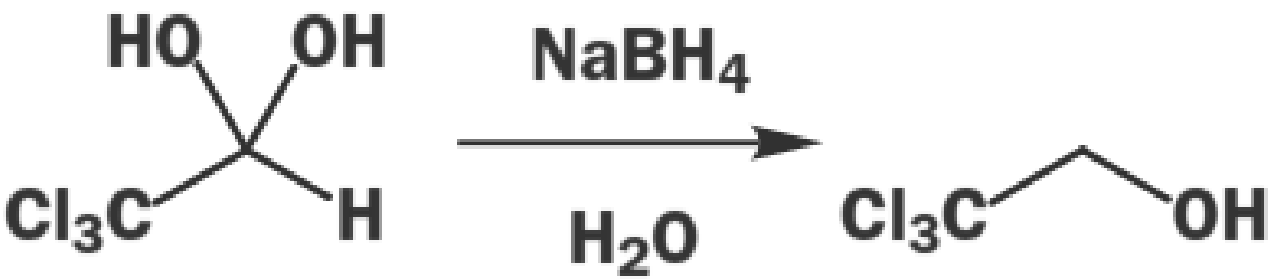
نمونه سوالات مکانیسم

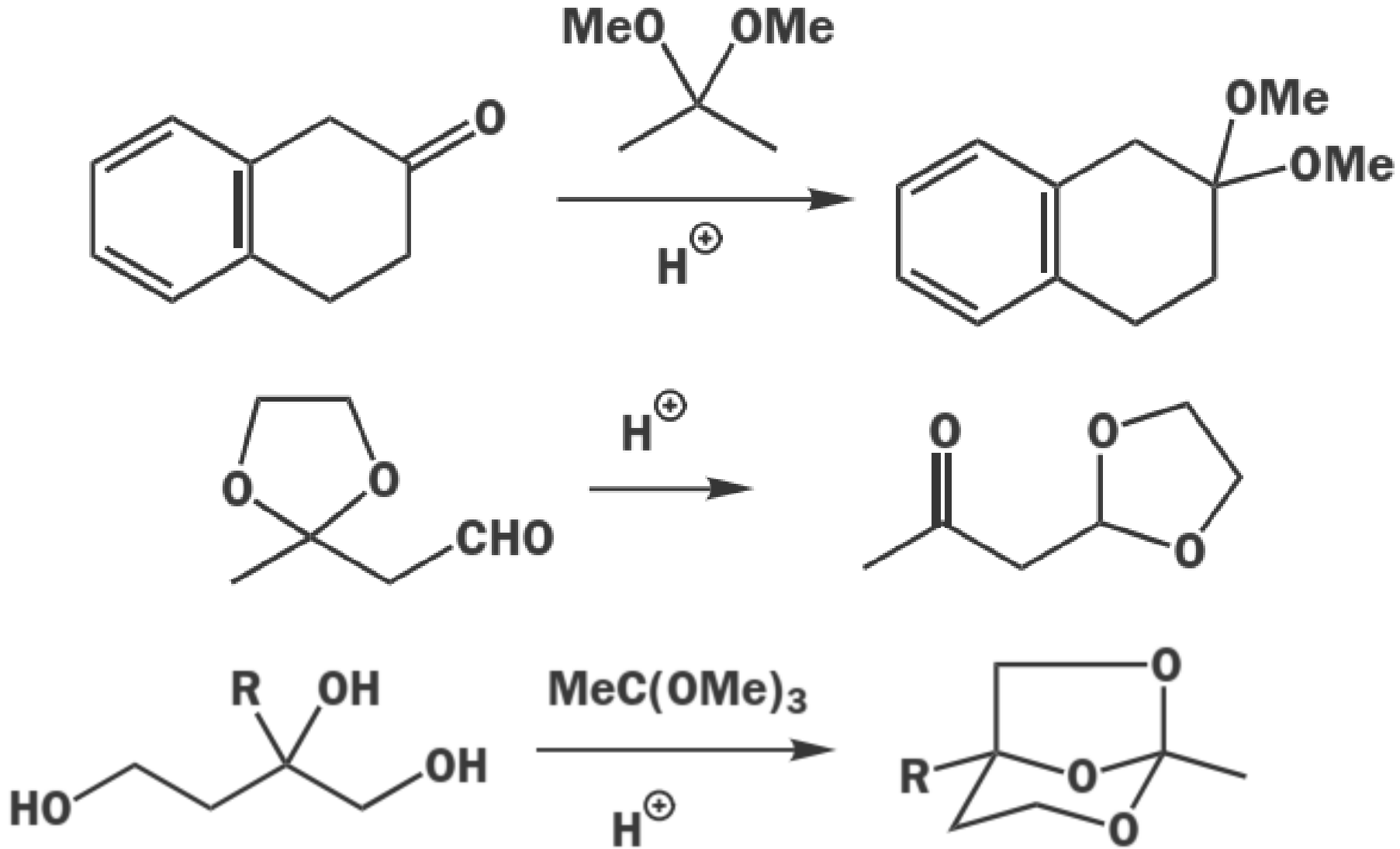
ایمان فروغمند

Clayden

Clayden-Chap. 5-Problem 7



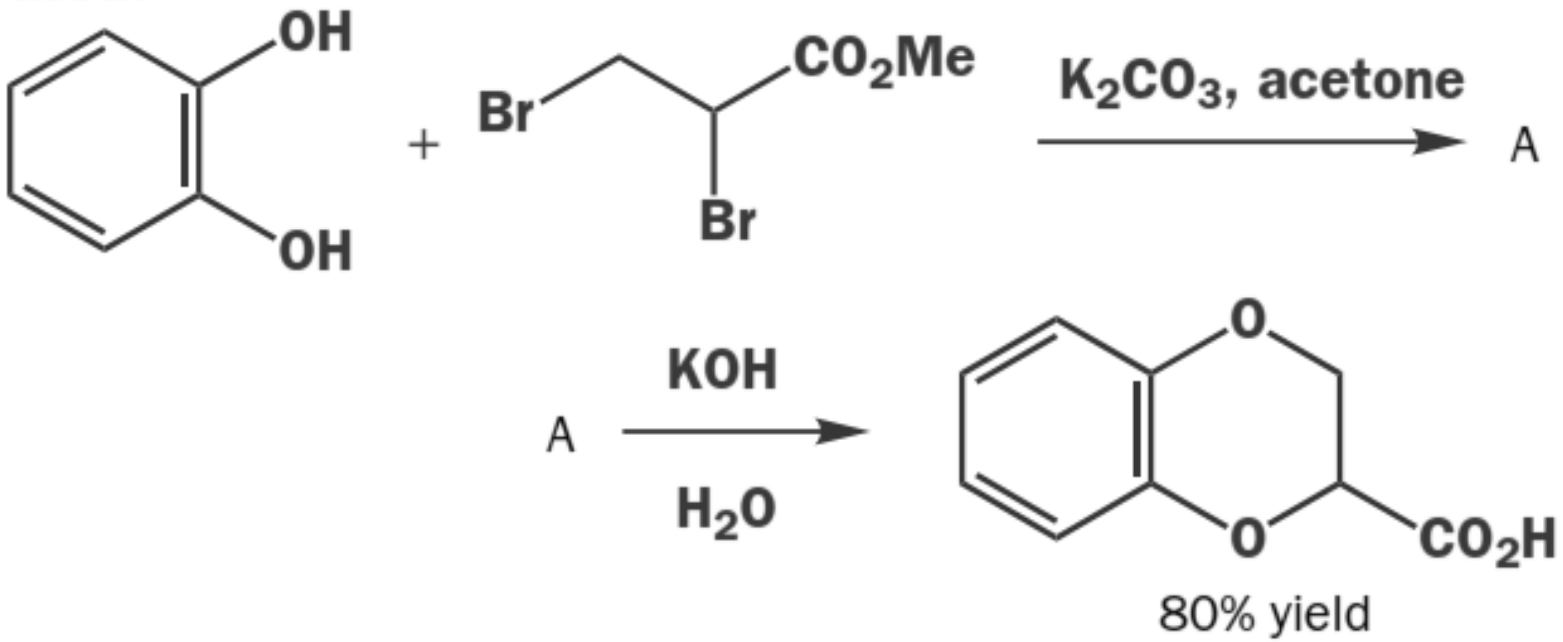
Clayden-Chap. 6-Problem 8



Clayden-Chap. 14-Problem 4

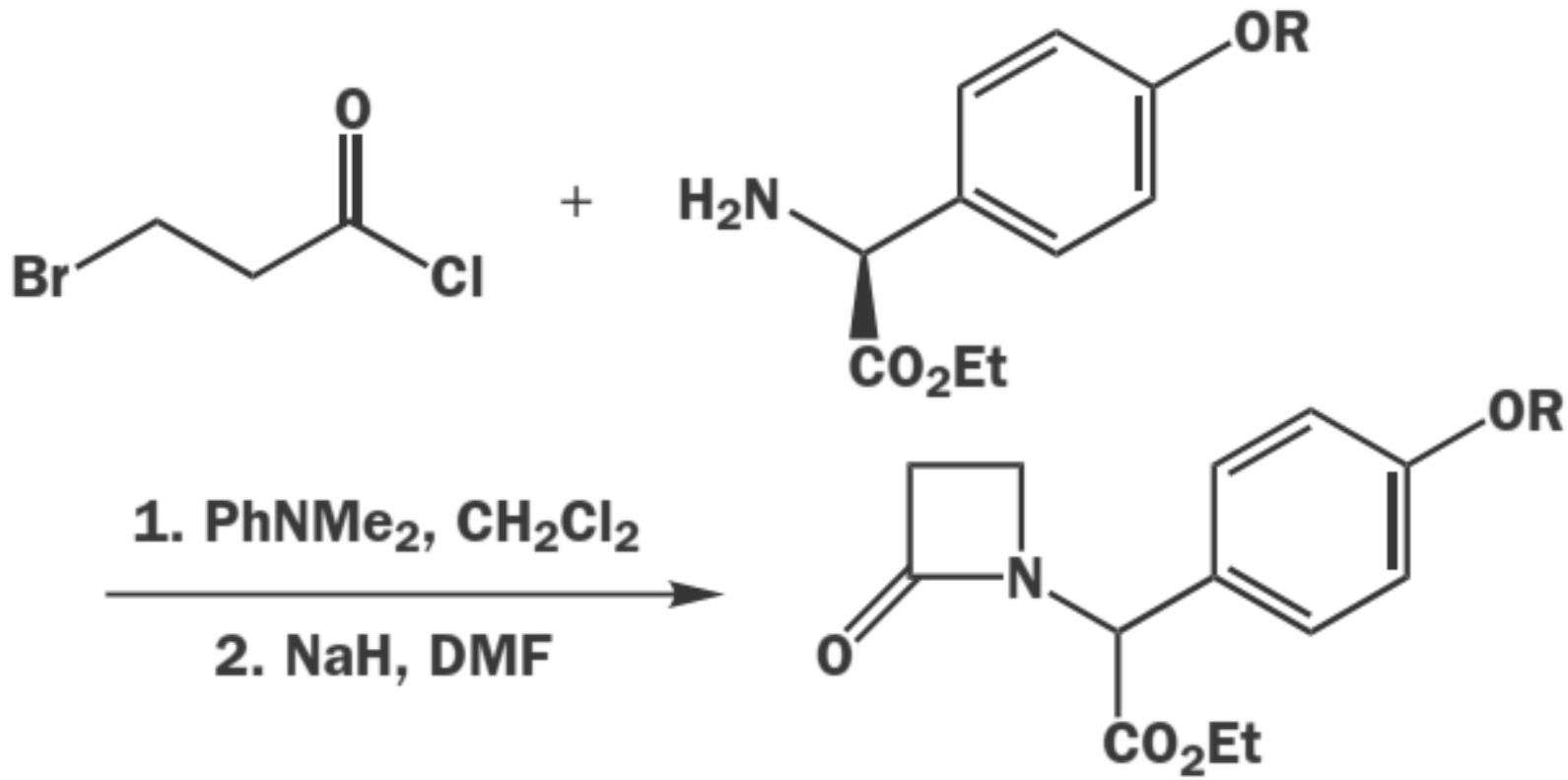
Clayden-Chap. 17-Problem 7

4. The chemistry shown here is the first step in the manufacture of Pfizer's doxasolin (Cardura), a drug for hypertension. Draw mechanisms for the reactions involved and comment on the bases used.



Clayden-Chap. 17

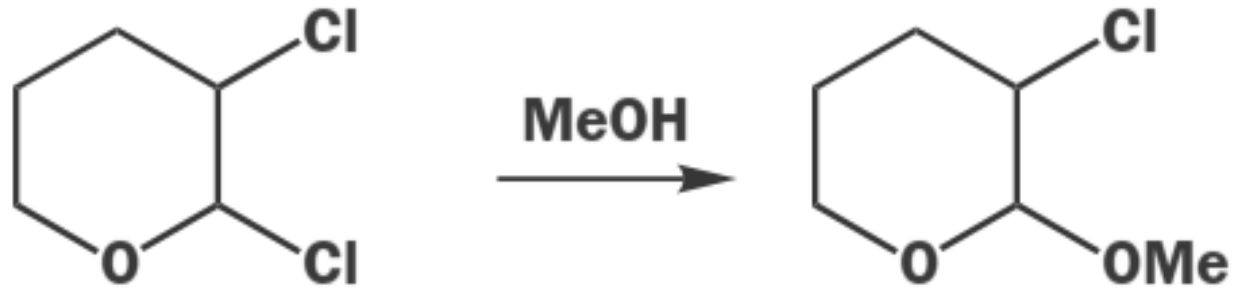
6. Draw mechanisms for these reactions and describe the stereochemistry of the product.



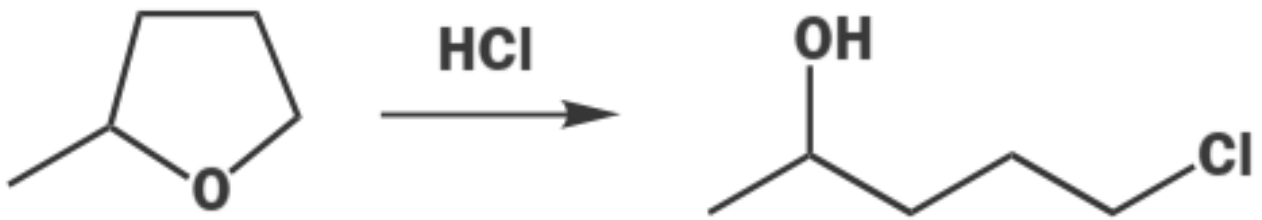
Clayden-Chap. 17

3. Draw mechanisms for these reactions, explaining why these particular products are formed.

(a)

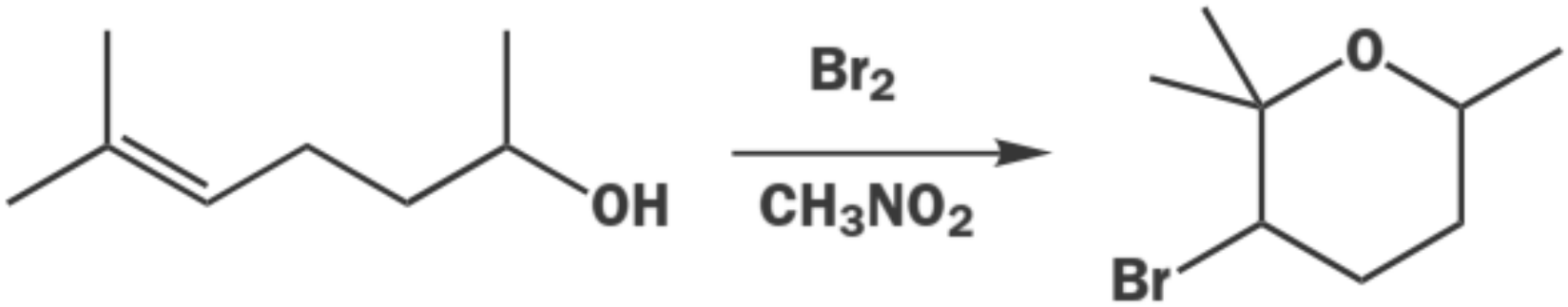


(b)



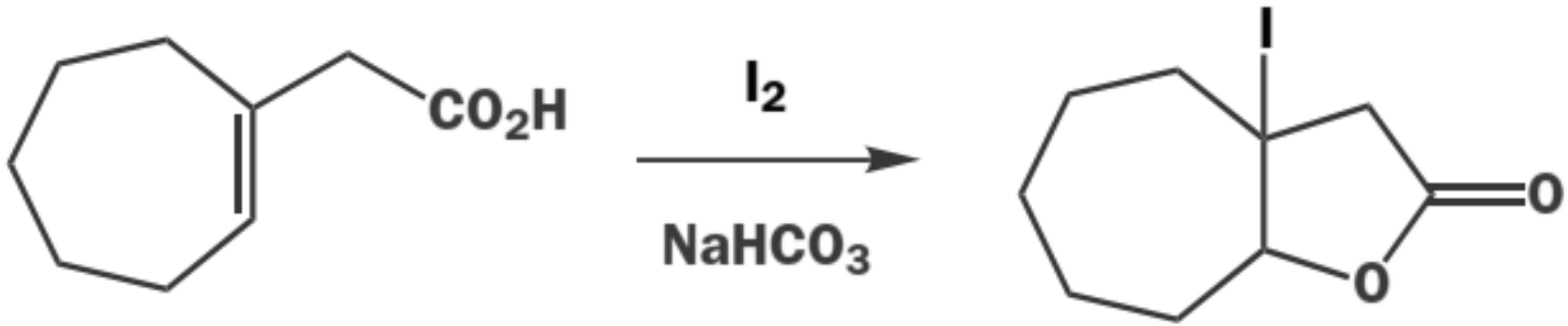
Clayden-Chap. 17

12. Suggest a mechanism for the following reaction. What is the stereochemistry and conformation of the product?



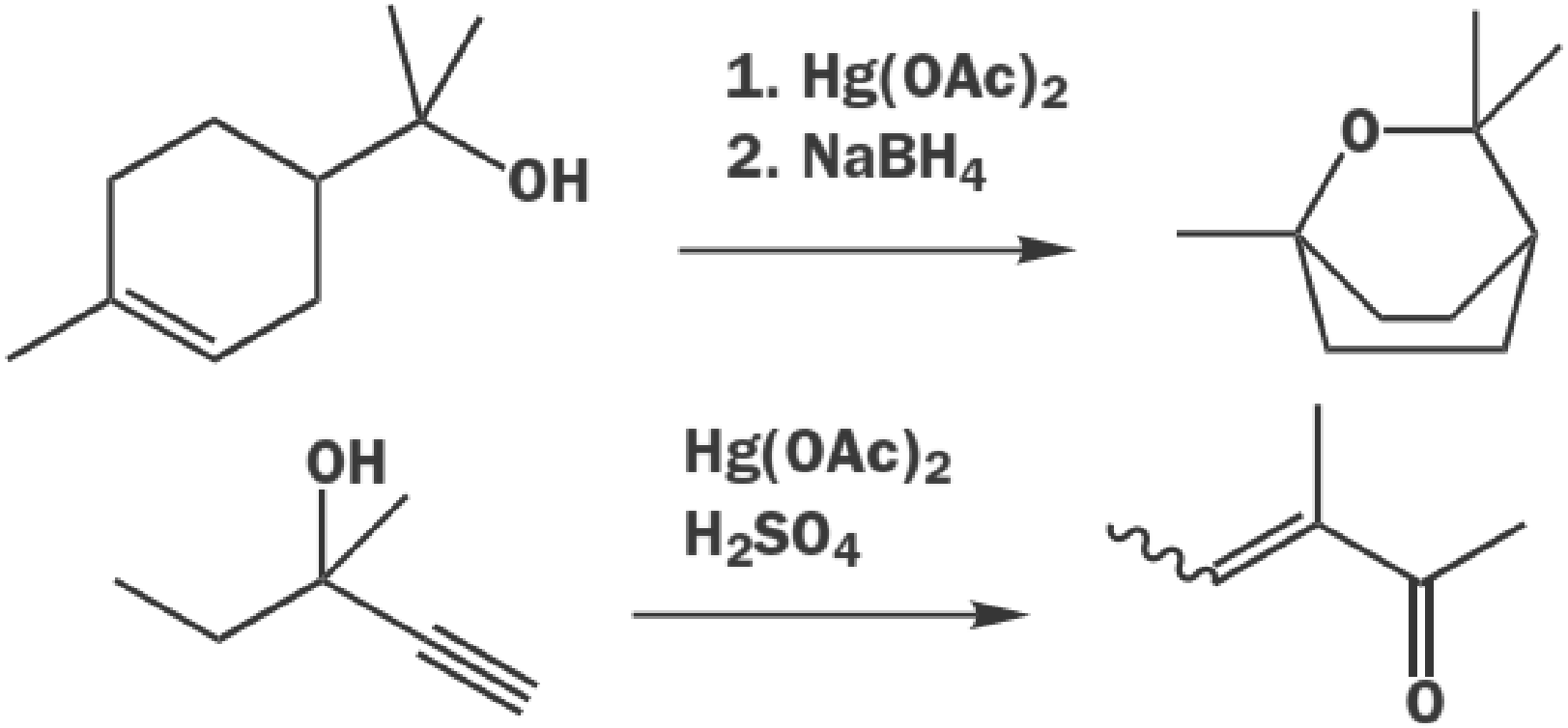
Clayden-Chap. 20

13. Give a mechanism for this reaction and show clearly the stereochemistry of the product.



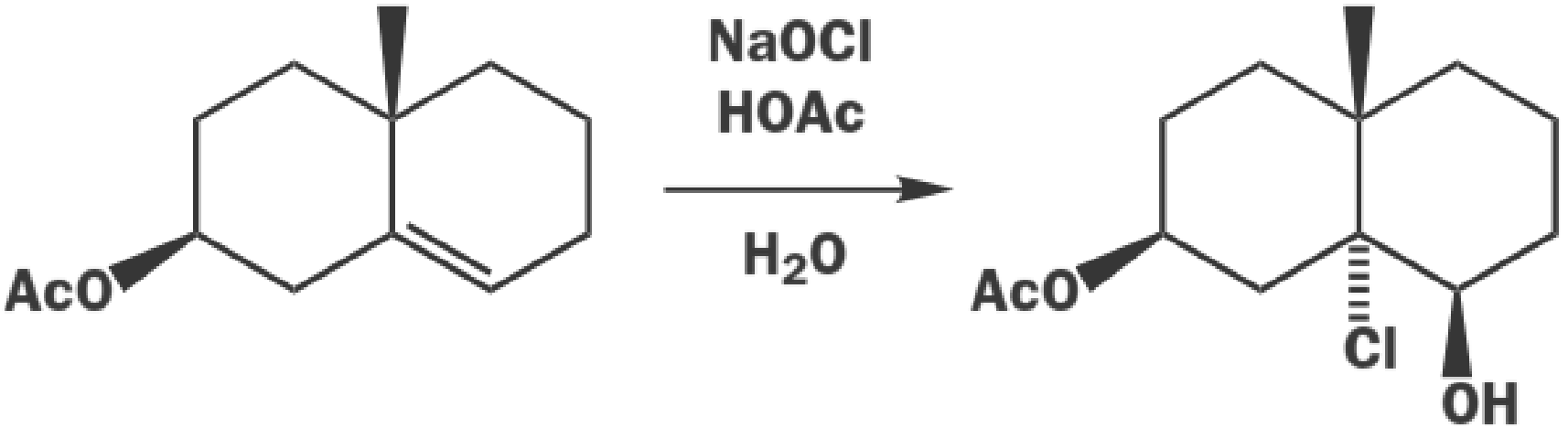
Clayden-Chap. 20

8. Suggest mechanisms for these reactions.



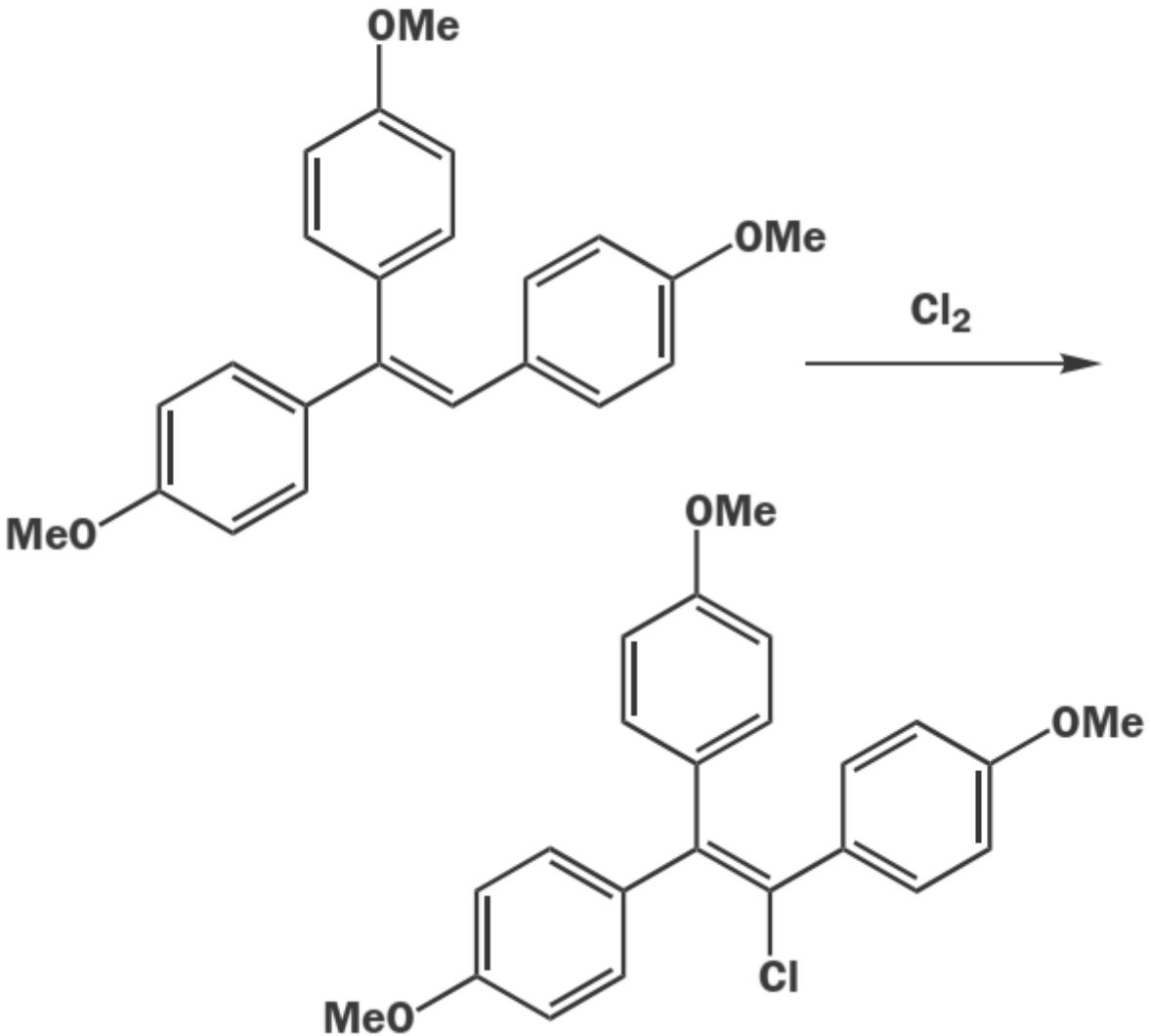
Clayden-Chap. 20

9. Comment on the formation of a single diastereoisomer in this reaction.

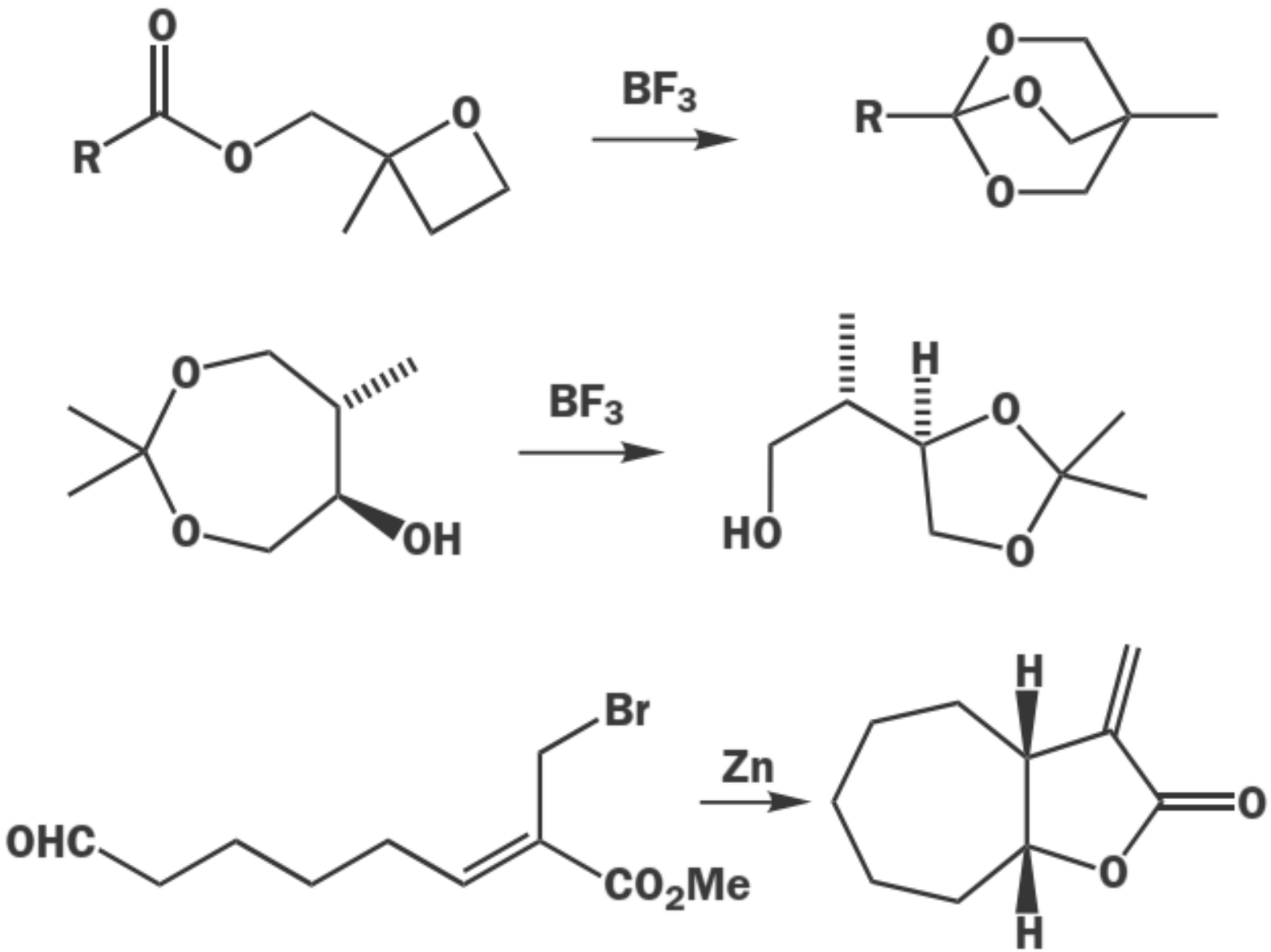


Clayden-Chap. 20

10. Chlorination of this triarylethylene leads to a chloro-alkene rather than a dichloroalkane. Suggest a mechanism and an explanation.

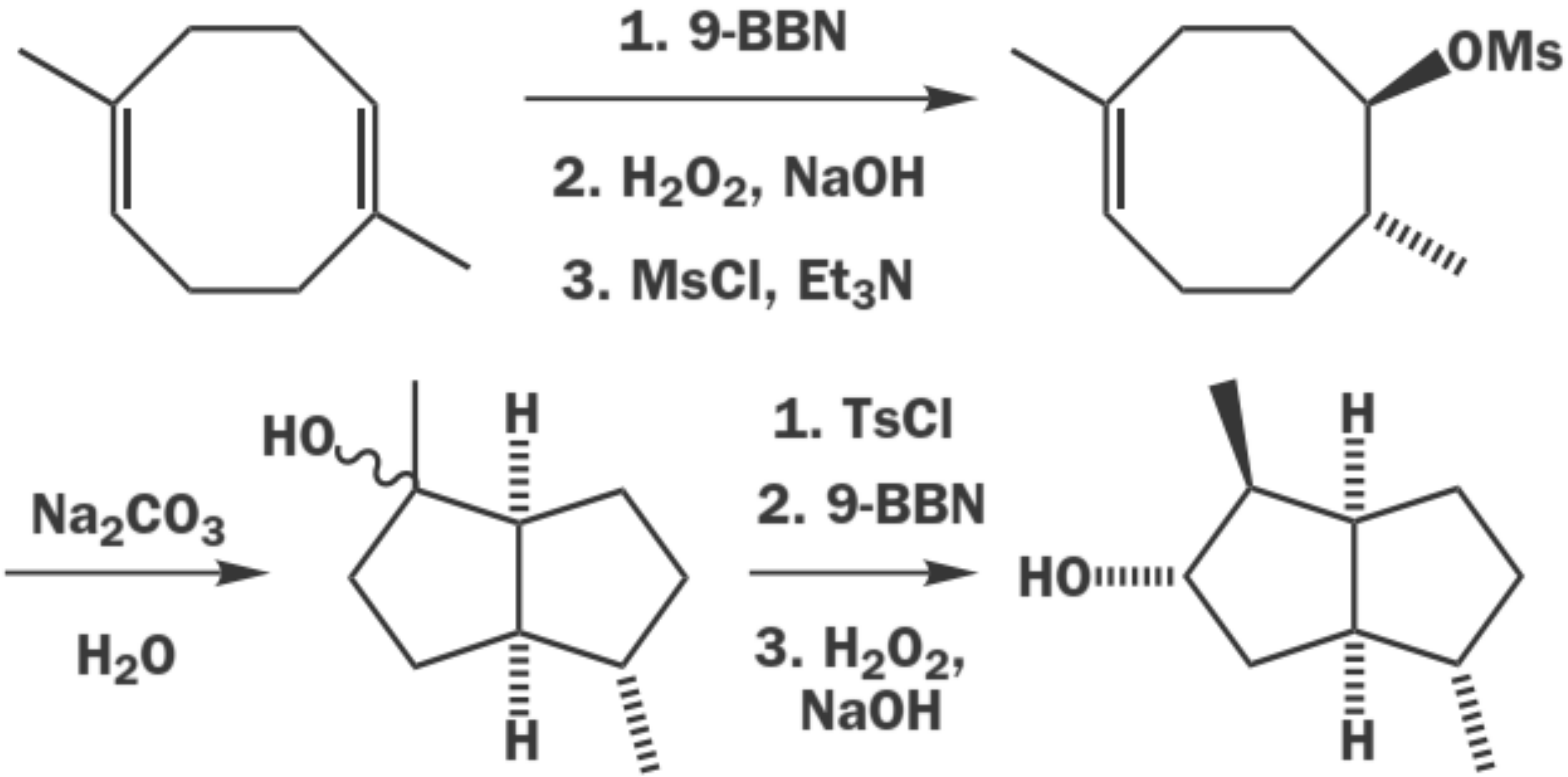


Clayden-Chap. 20



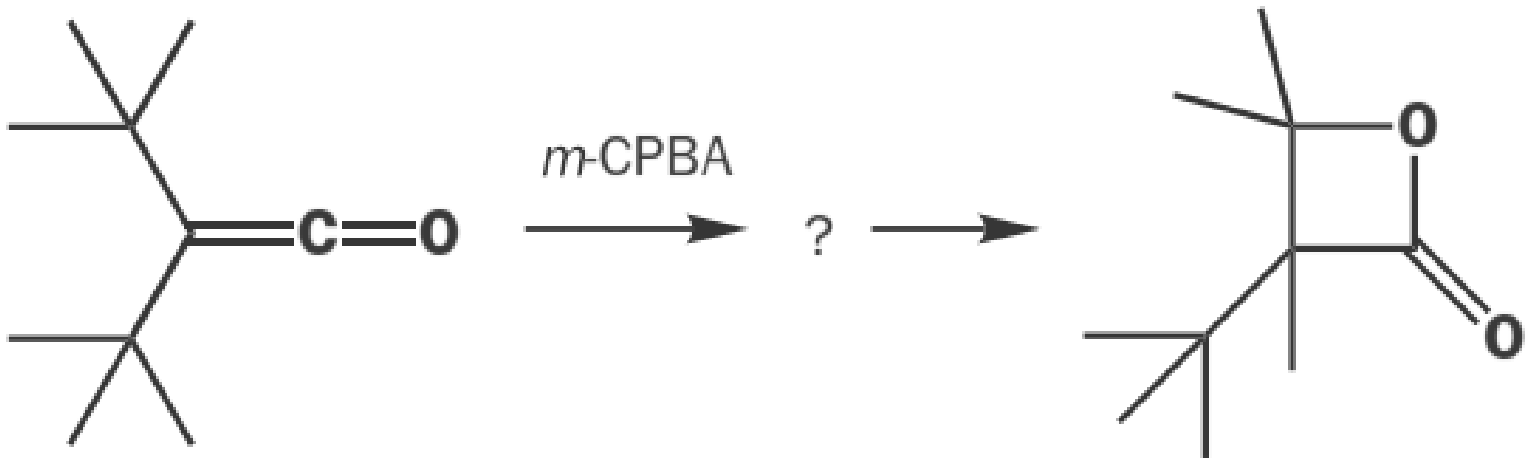
Clayden-Chap. 37-Problem 1

3. Draw mechanisms for the reactions and structures for the intermediates. Explain the stereochemistry, especially of the reactions involving boron. Why was 9-BBN chosen as the hydroborating agent?



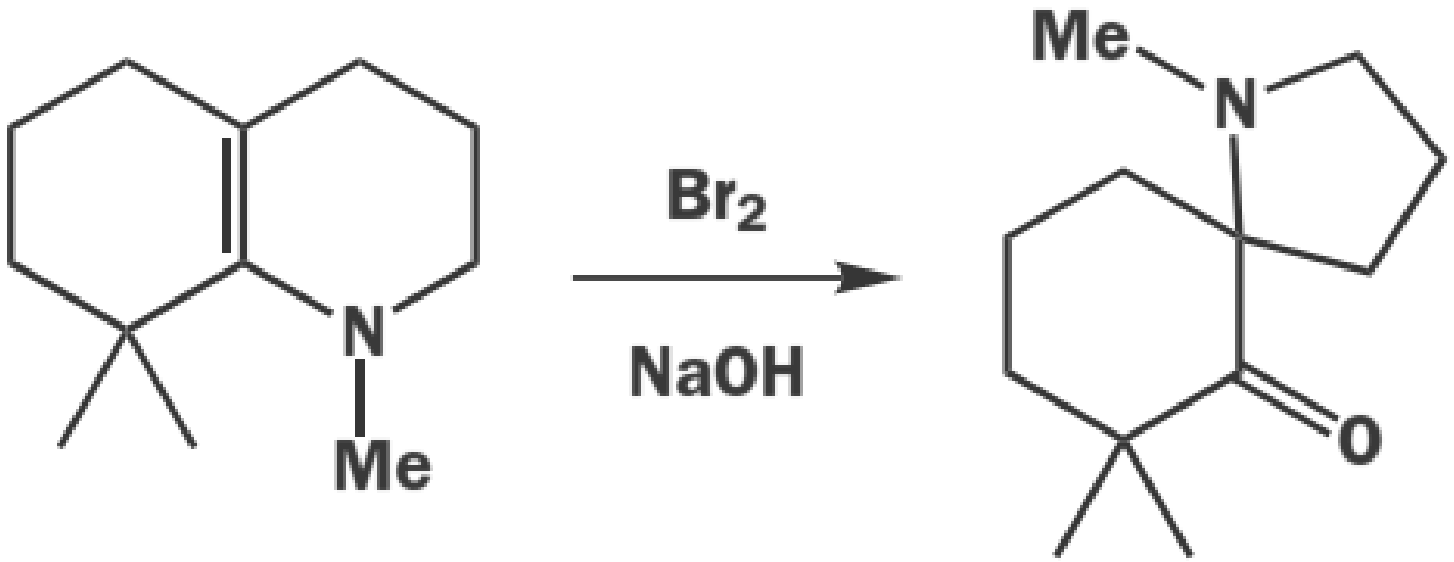
Clayden-Chap. 37

4. It is very difficult to prepare three-membered ring lactones. One attempted preparation, by the epoxidation of di-*t*-butyl ketene, gave an unstable compound with an IR stretch at 1900 cm^{-1} that decomposed rapidly to the four-membered lactone shown. Do you think they made the three-membered ring?



Clayden-Chap. 37

5. Suggest a mechanism for this rearrangement.

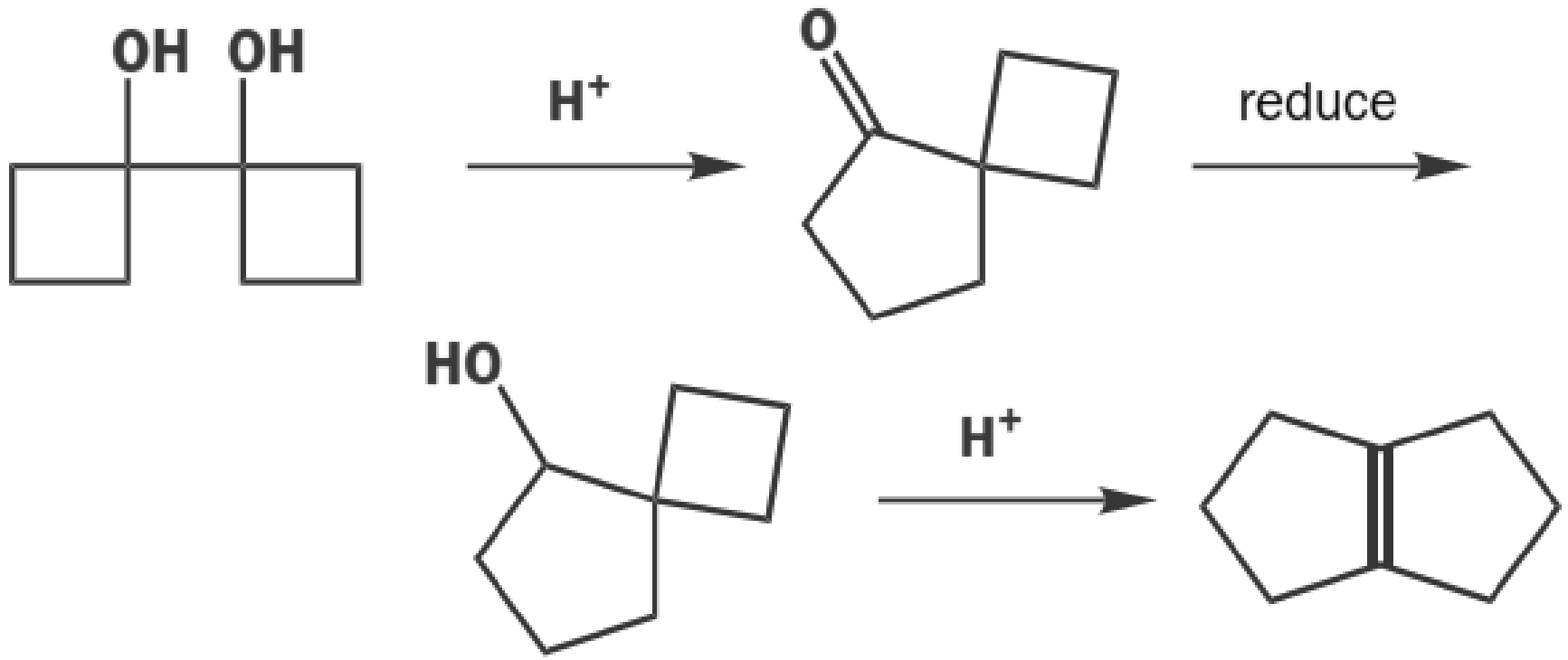


Clayden-Chap. 37

6. A single enantiomer of the epoxide below rearranges with Lewis acid catalysis to give a single enantiomer of product. Suggest a mechanism and comment on the stereochemistry.

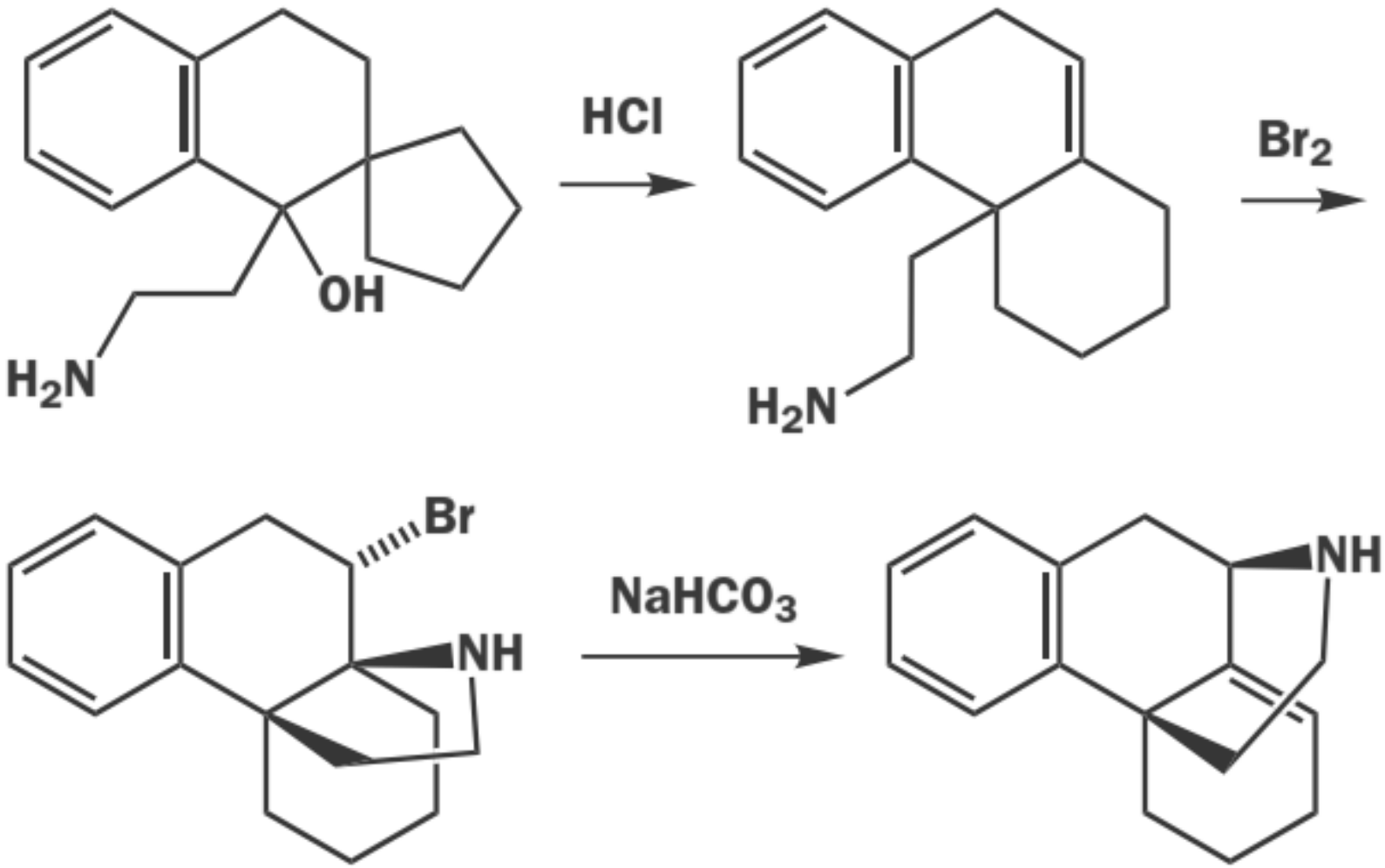
(+) (–)

Clayden-Chap. 37



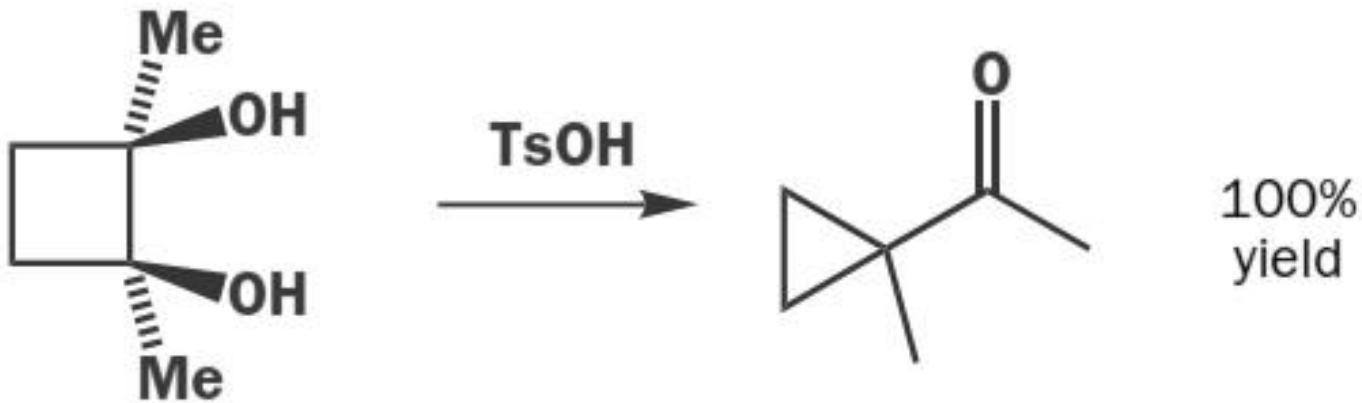
Clayden-Chap. 37

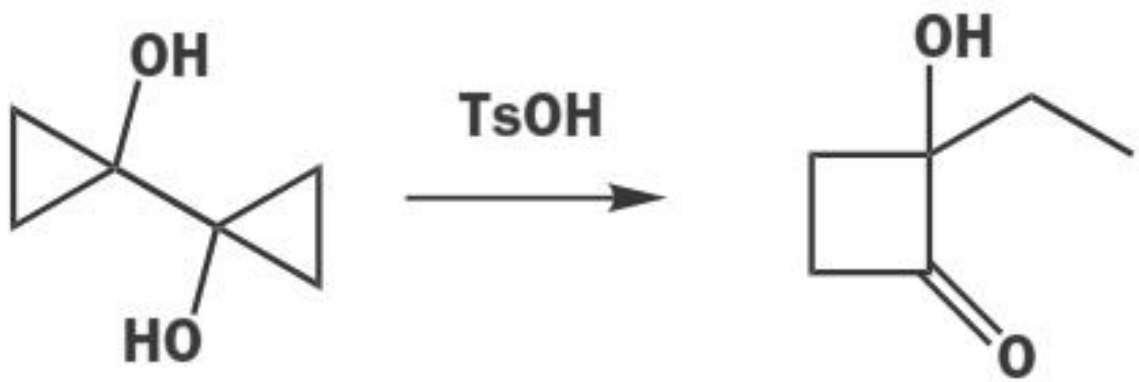
9. Suggest mechanisms for these rearrangements explaining the stereochemistry in the second example.



Clayden-Chap. 37

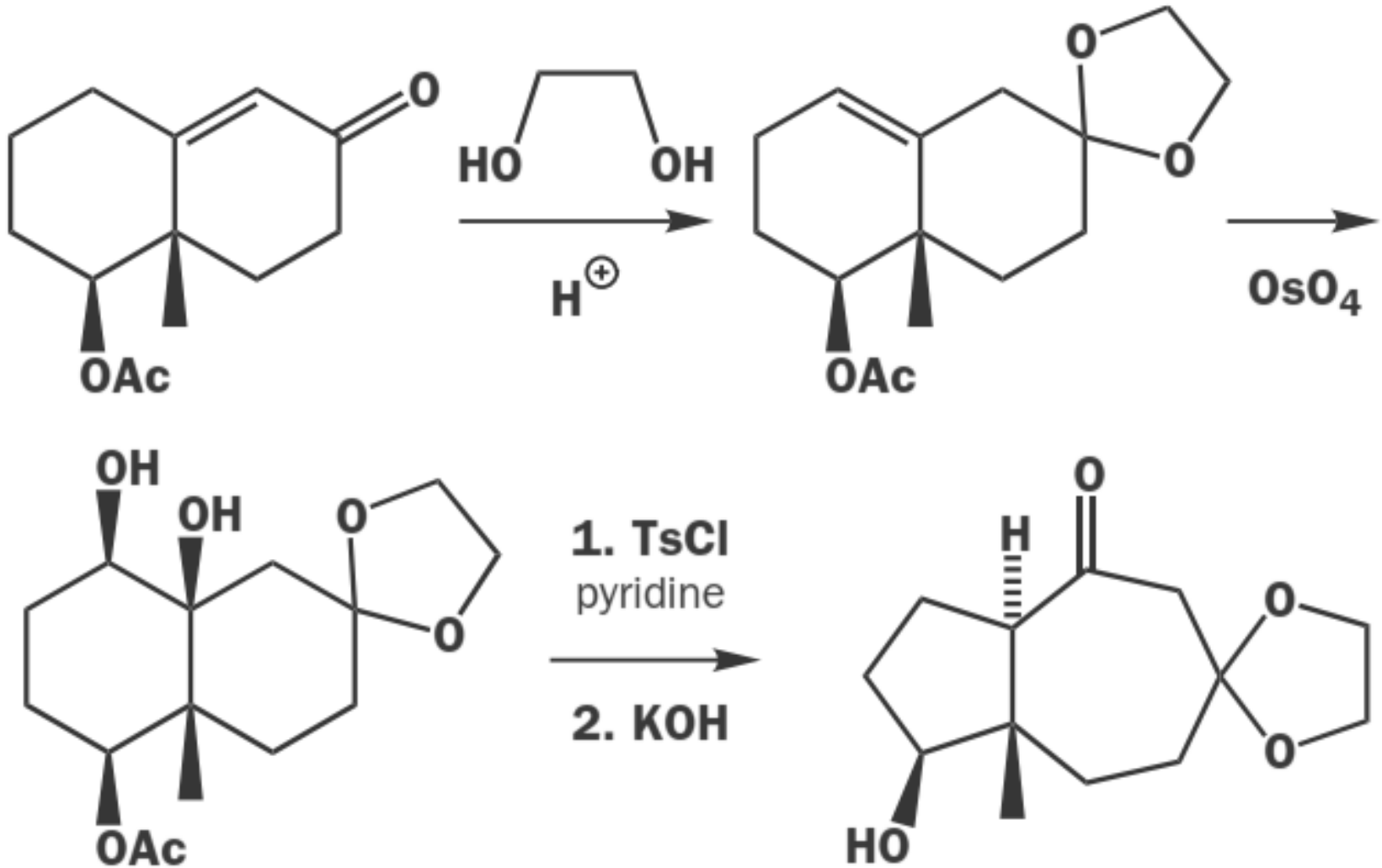
11. Suggest mechanisms for these reactions that explain any selectivity in the migration.





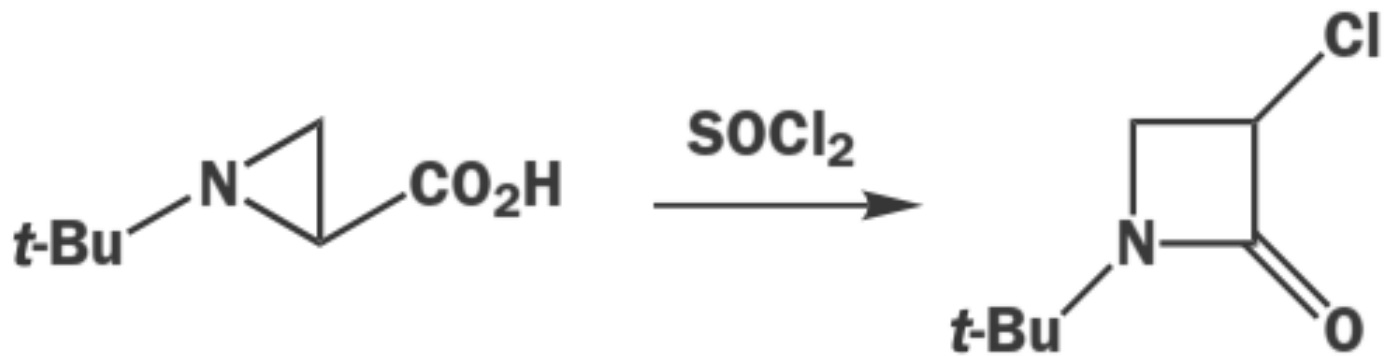
Clayden-Chap. 37

10. Give mechanisms for these reactions, commenting on any regio- and stereoselectivity. What controls the rearrangement?



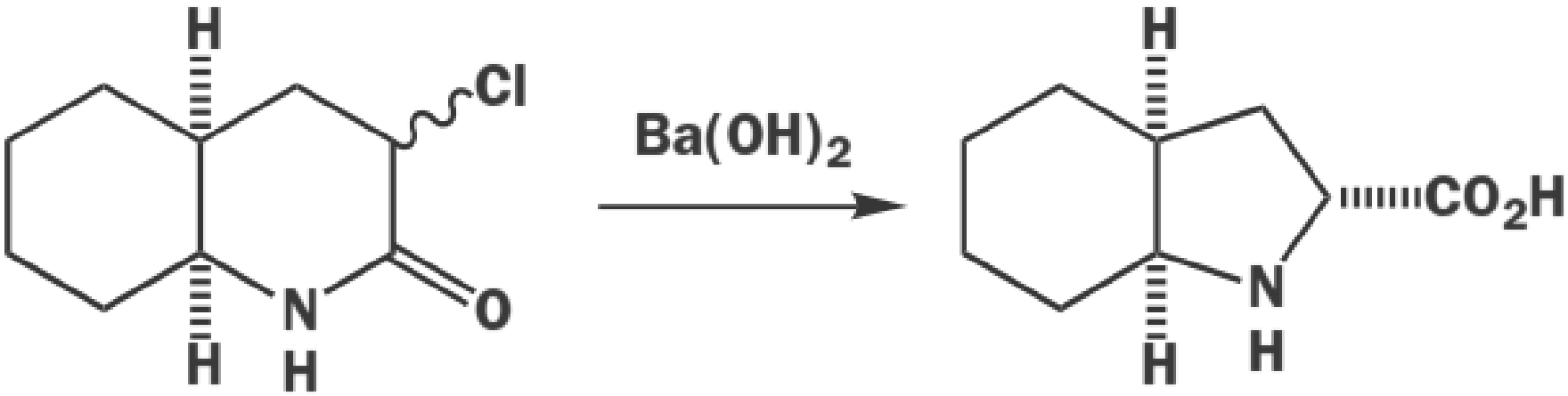
Clayden-Chap. 37

12. Attempts to produce the acid chloride from this unusual amino acid by treatment with $SOCl_2$ gave instead a β-lactam. What has happened?



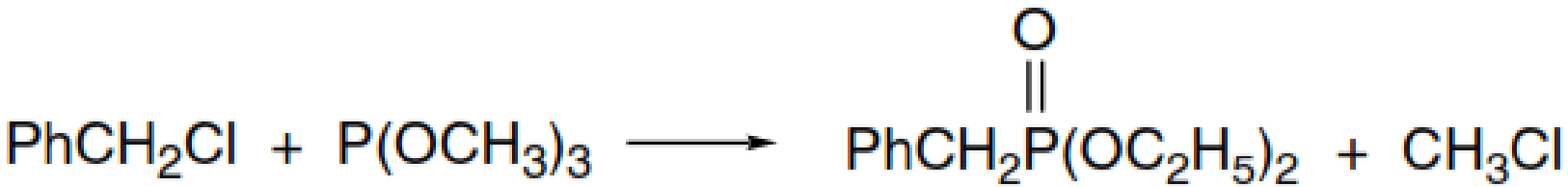
Clayden-Chap. 37

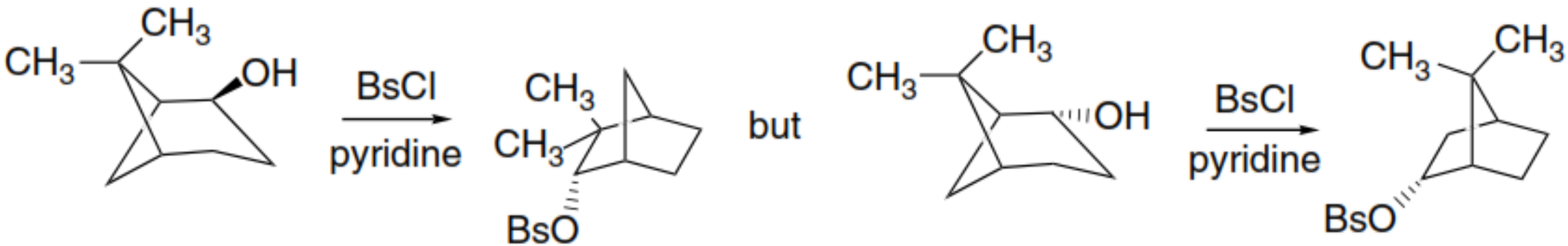
14. Suggest a mechanism for this rearrangement, comparing it with a reaction discussed in the chapter. What controls the stereochemistry?

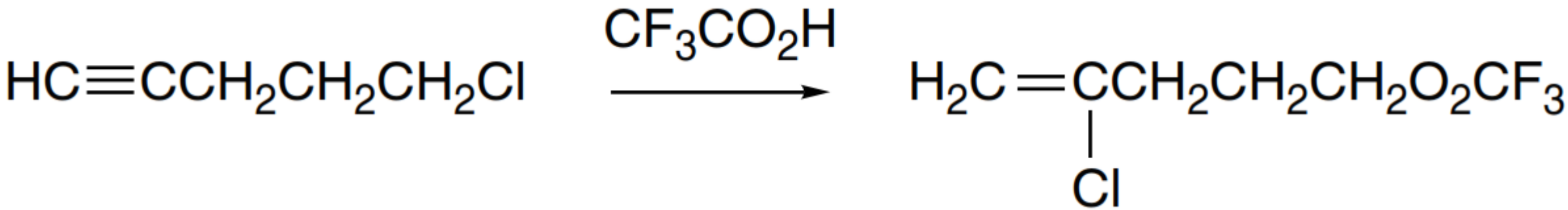


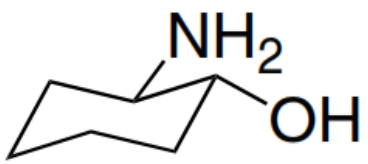
Clayden-Chap. 37

Adv. Carey

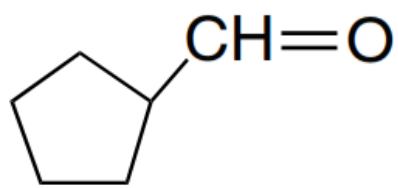

PhCH2Cl + P(OCH3)3
O
PhCH2P(OC2H5)2 + CH3Cl


CH3
CH3
OH
BsCl
pyridine
CH3
CH3
BsO
but
CH3
CH3
OH
BsCl
pyridine
CH3
CH3
BsO

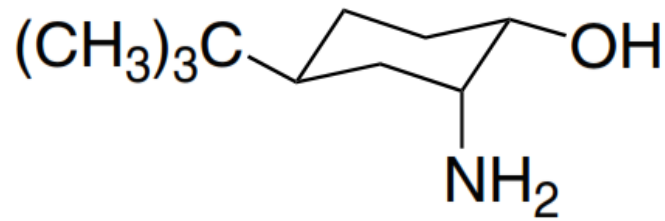

CF3CO2H
HC≡CCH2CH2CH2Cl
H2C=CCH2CH2CH2O2CF3
Cl



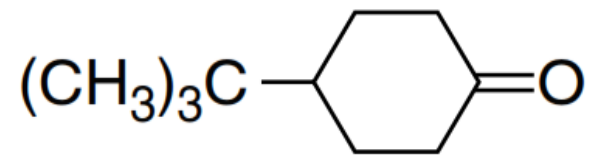
$\xrightarrow[HClO_4]{NaNO_2,\ H_2O}$

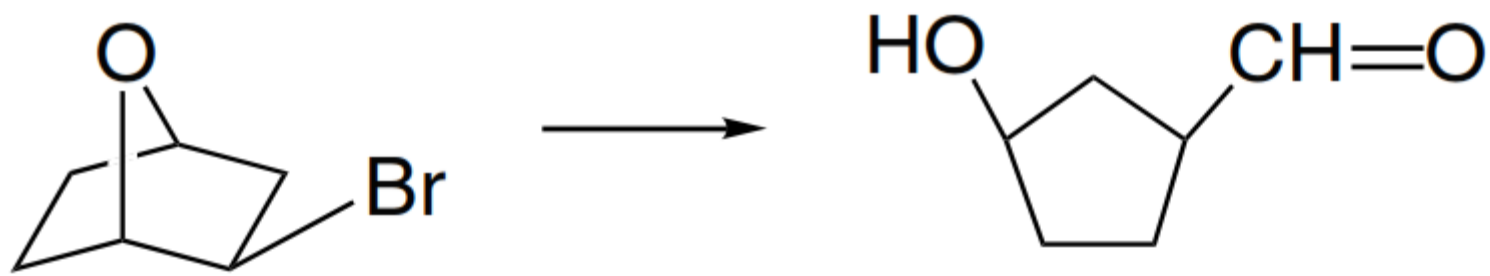


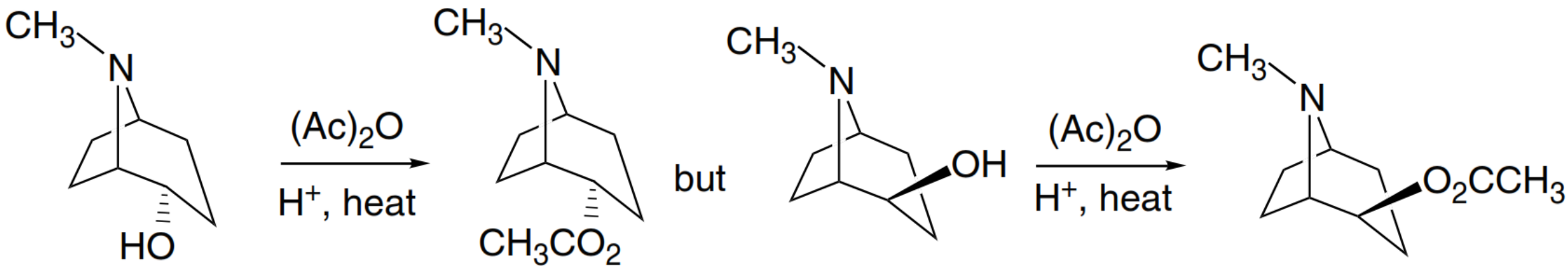
but



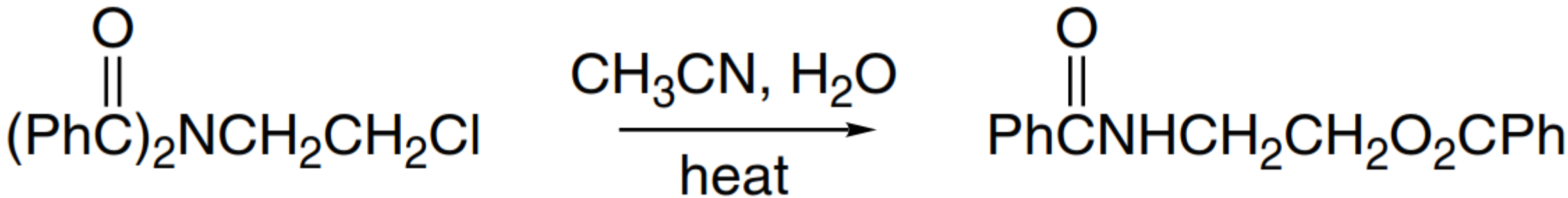
$\xrightarrow[HClO_4]{NaNO_2,\ H_2O}$

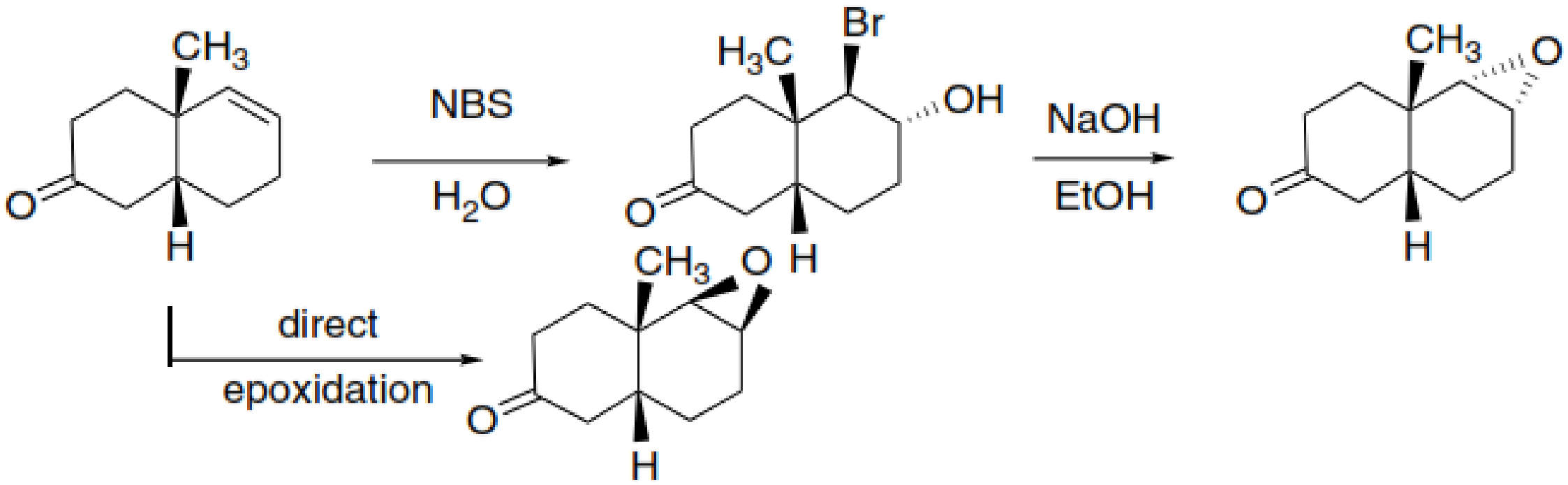


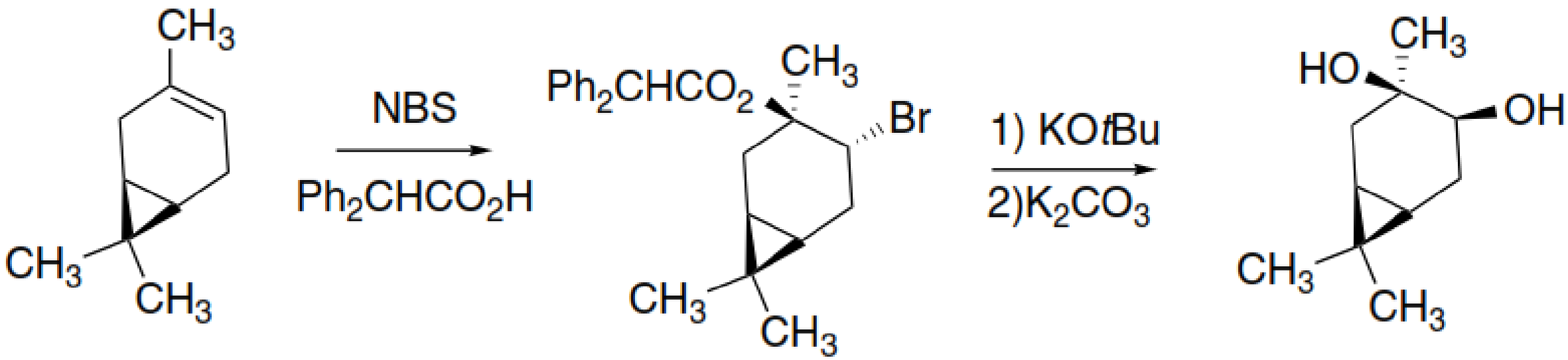

O
Br
HO
CH=O

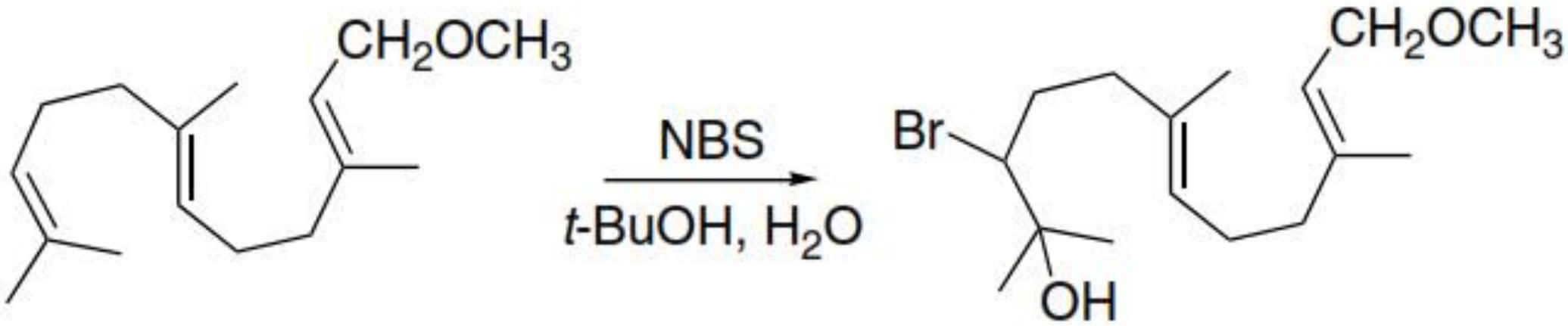


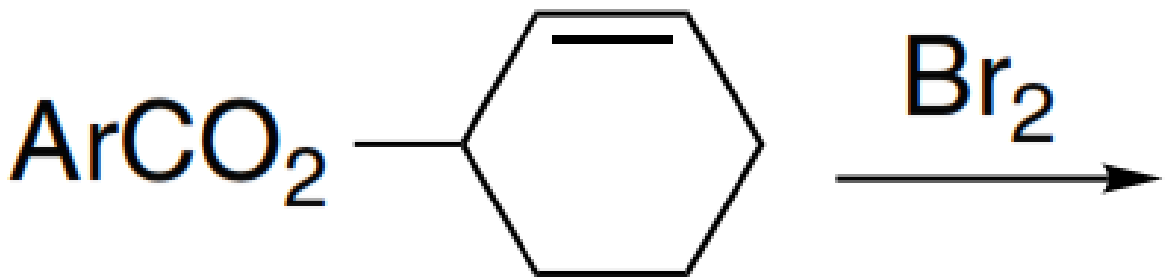
non-racemic racemic non-racemic no racemization

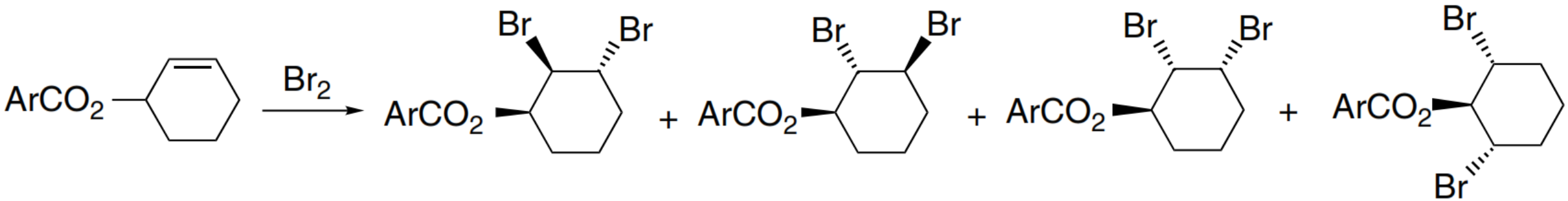

O
(PhC)2NCH2CH2Cl
CH3CN, H2O
heat
O
PhCNHCH2CH2O2CPh

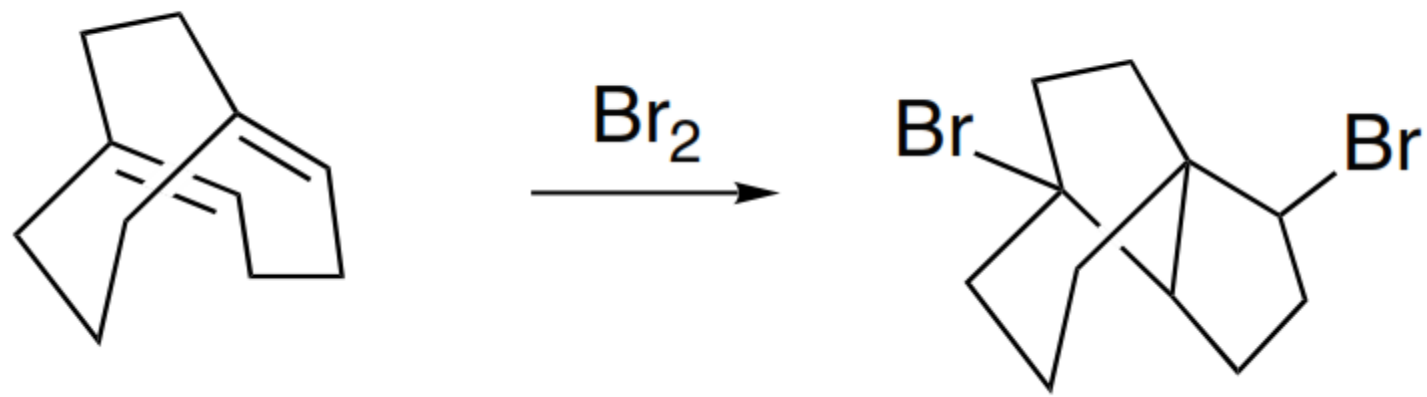

CH3
O
H
NBS
H2O
H3C
Br
OH
O
NaOH
EtOH
CH3
O
O
H
direct
epoxidation
CH3
O
H
O

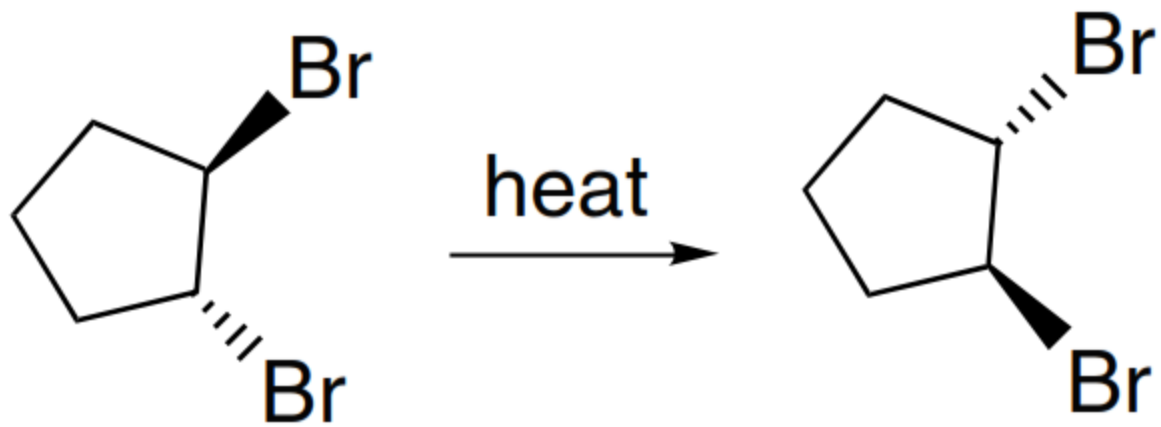

CH3
CH3
CH3
NBS
Ph2CHCO2H
Ph2CHCO2
CH3
Br
CH3
CH3
1) KOtBu
2)K2CO3
HO
CH3
OH
CH3
CH3


CH2OCH3
NBS
t-BuOH, H2O
Br
CH2OCH3
OH


ArCO2
Br2


ArCO2
Br2
Br
Br
ArCO2
+
Br
Br
ArCO2
+
Br
Br
ArCO2
+
Br
ArCO2
Br


Br2
Br
Br

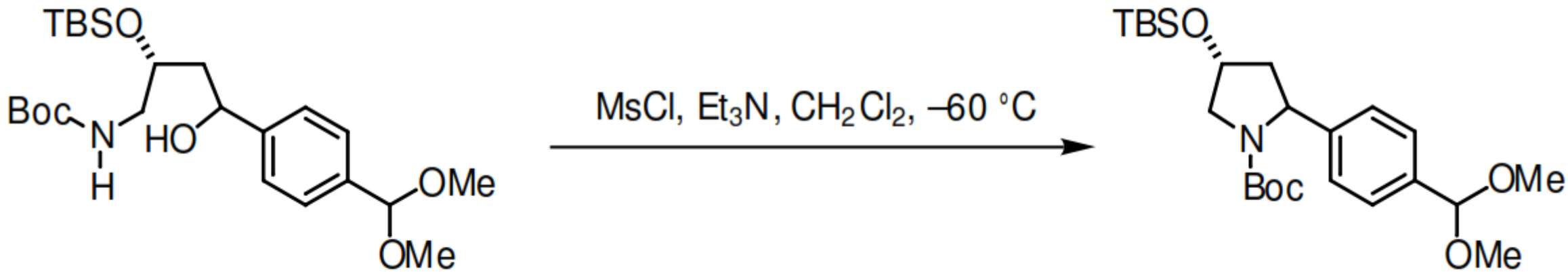


optically active

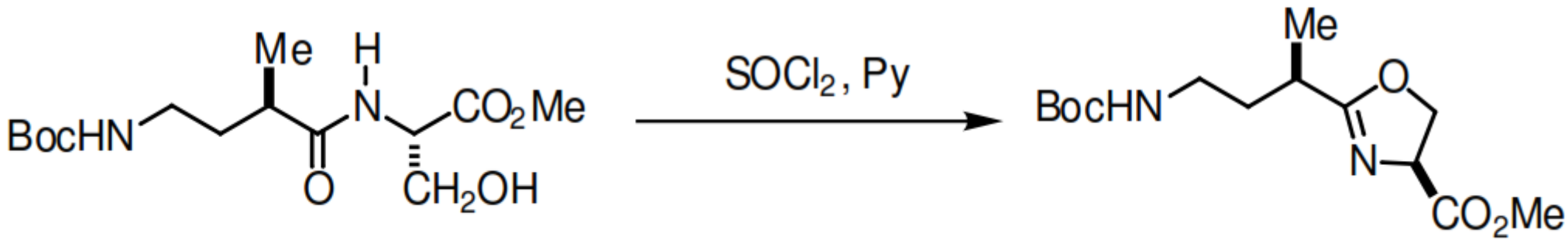
racemic

Suarez

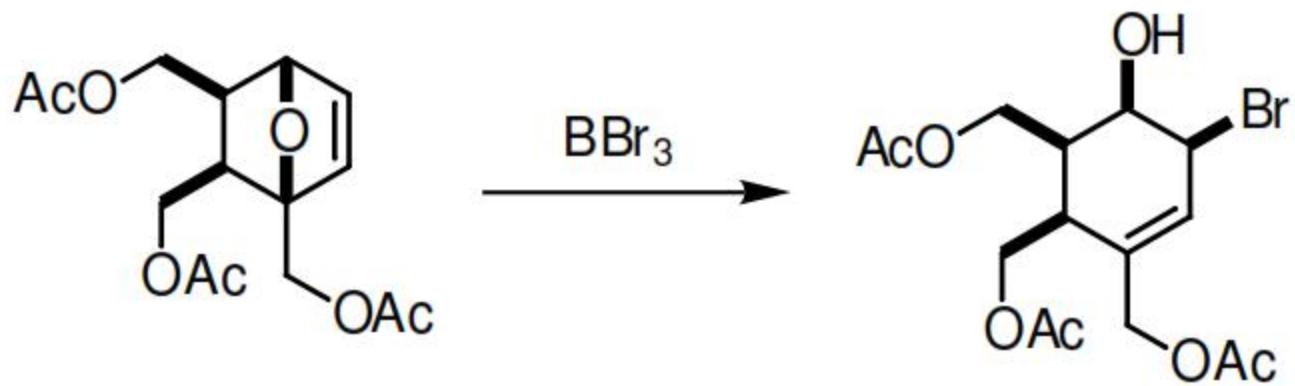
Exercise 1



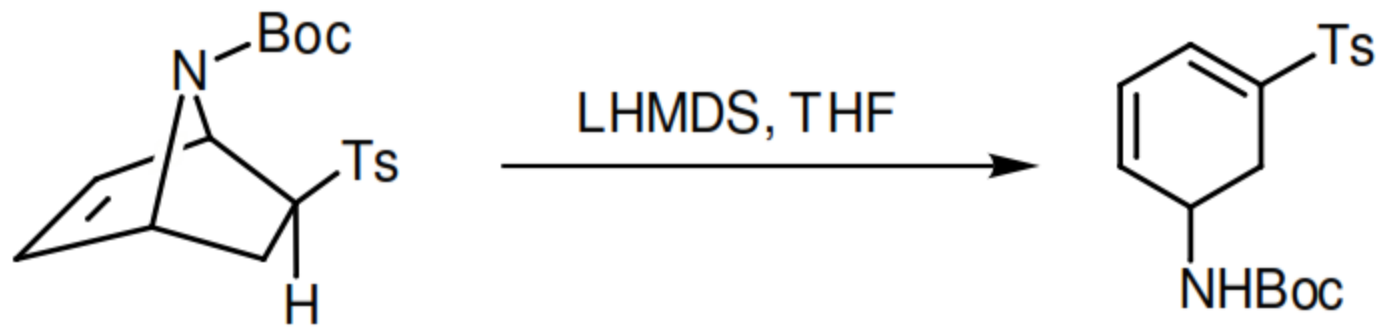
Exercise 2



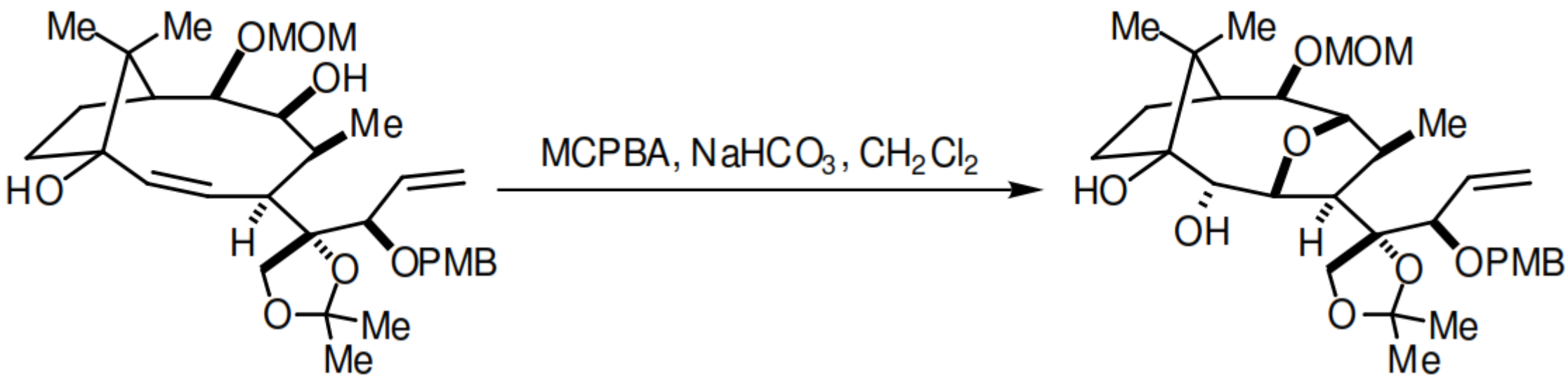
Exercise 3



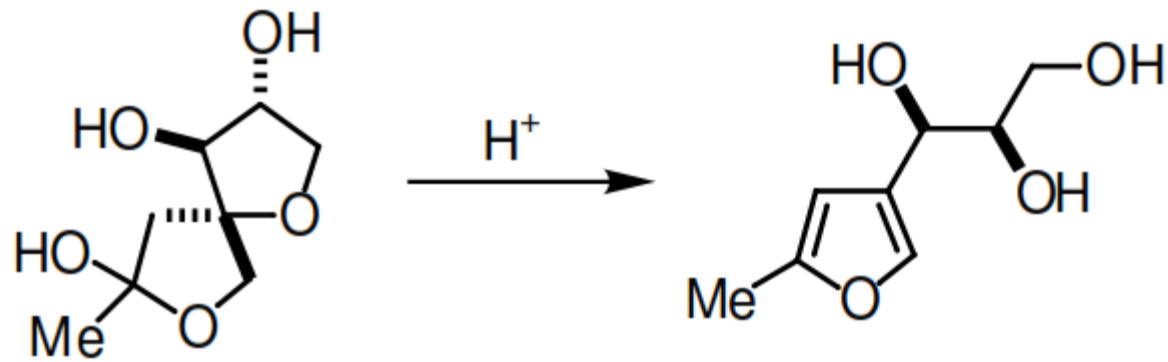
Exercise 4



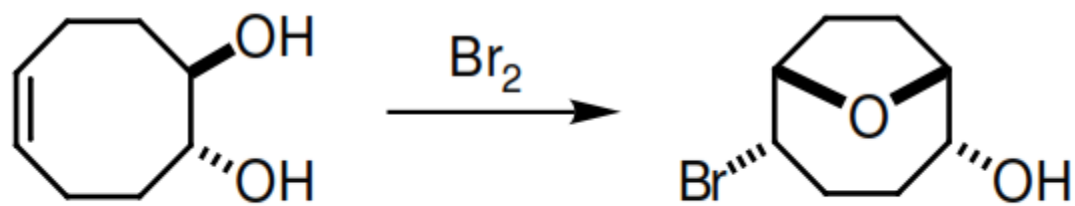
Exercise 5


Me
Me
OMOM
OH
Me
HO
H
O
OPMB
O
Me
Me
MCPBA, NaHCO3, CH2Cl2
Me
Me
OMOM
Me
O
HO
OH
H
O
OPMB
O
Me
Me

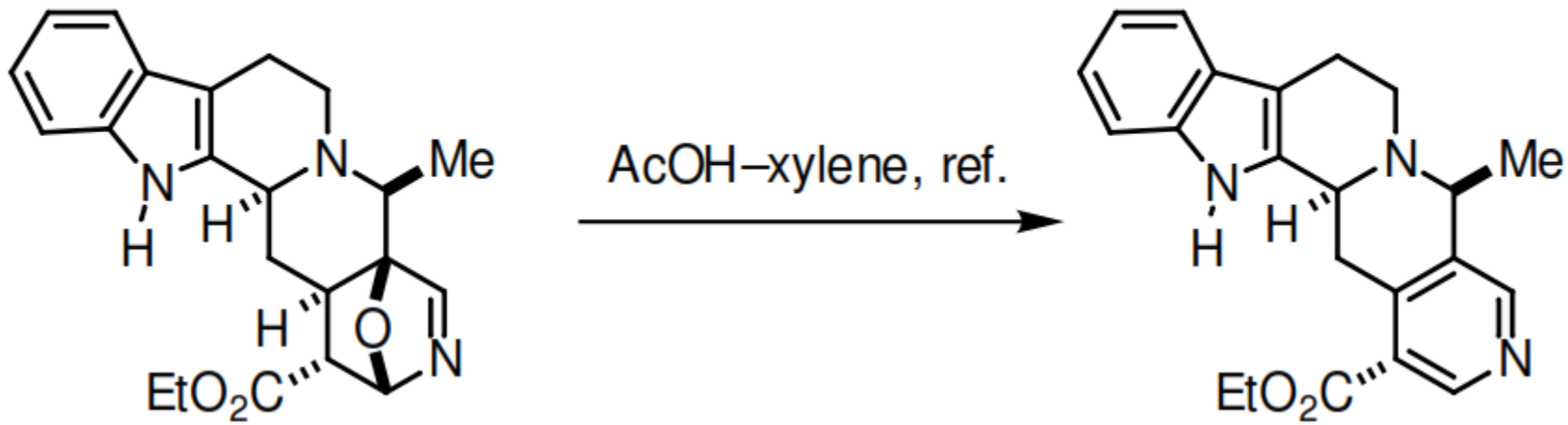
Exercise 6



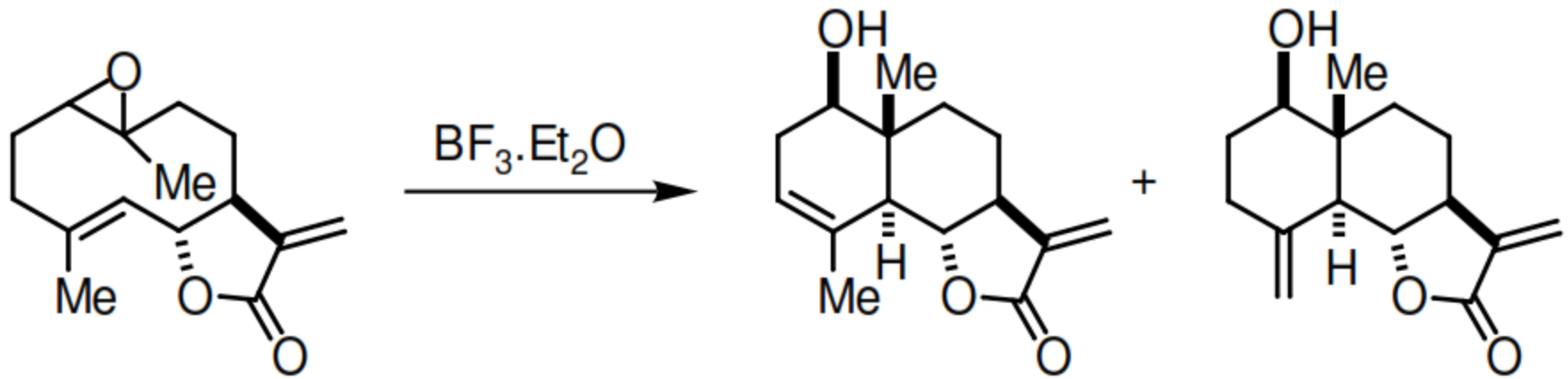
Exercise 7



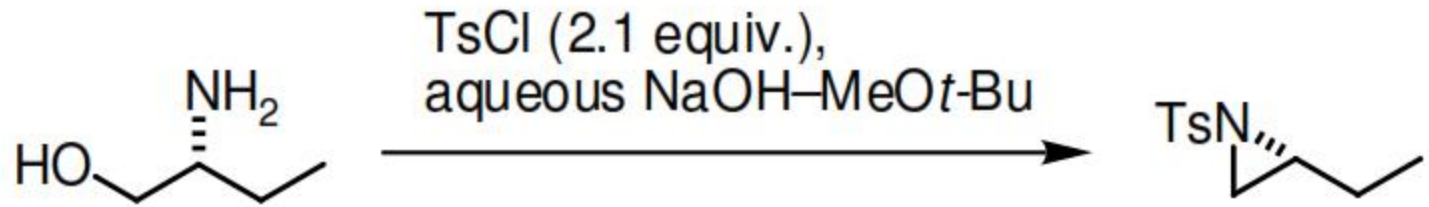
Exercise 8



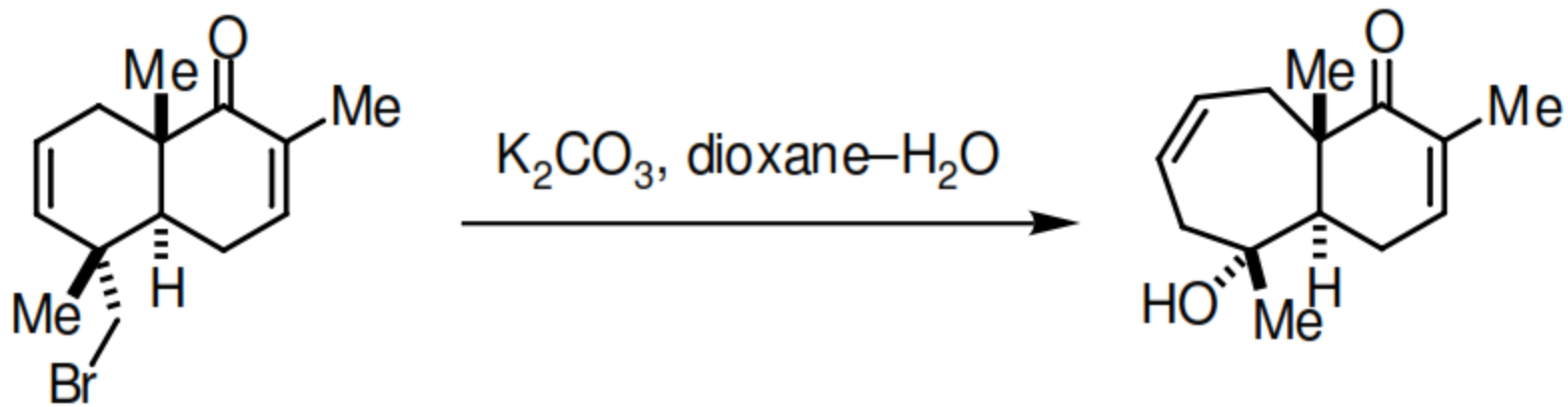
Exercise 9



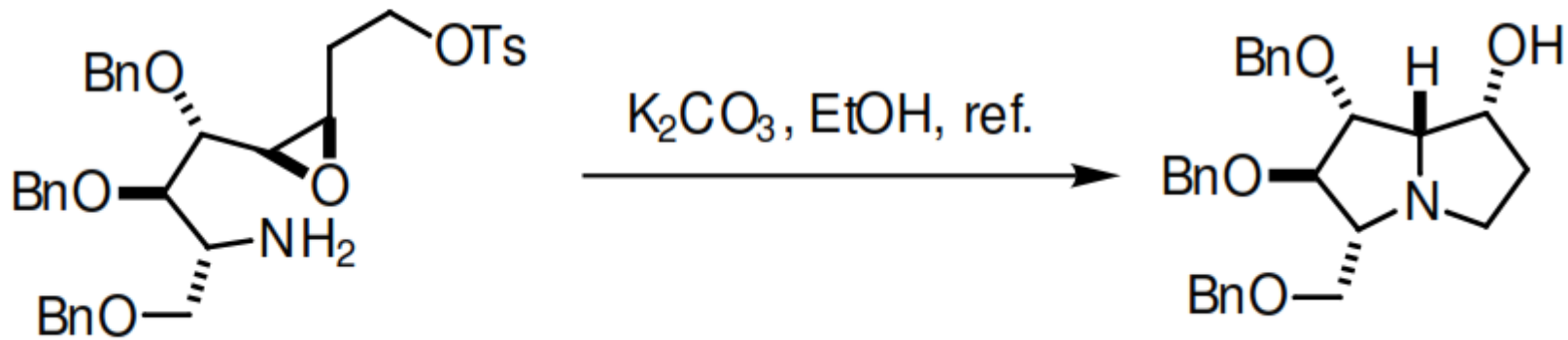
Exercise 10



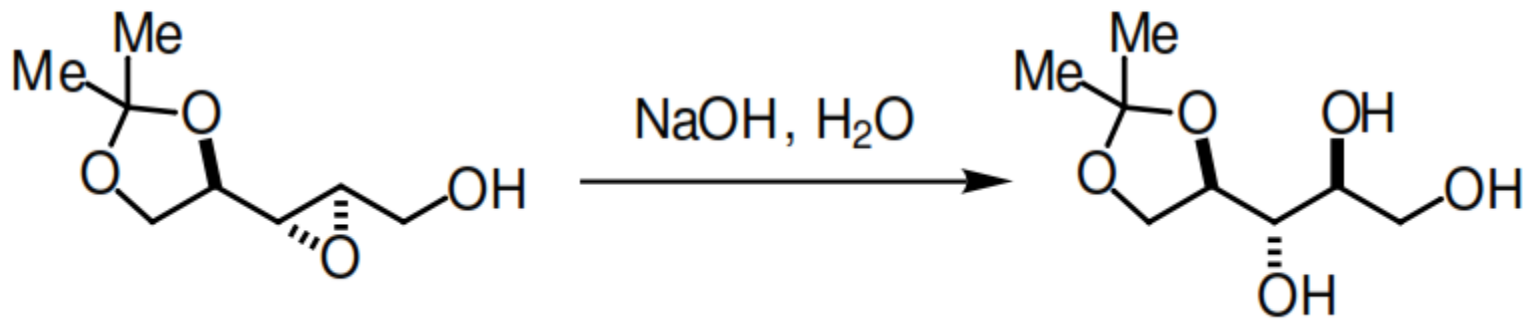
Exercise 11



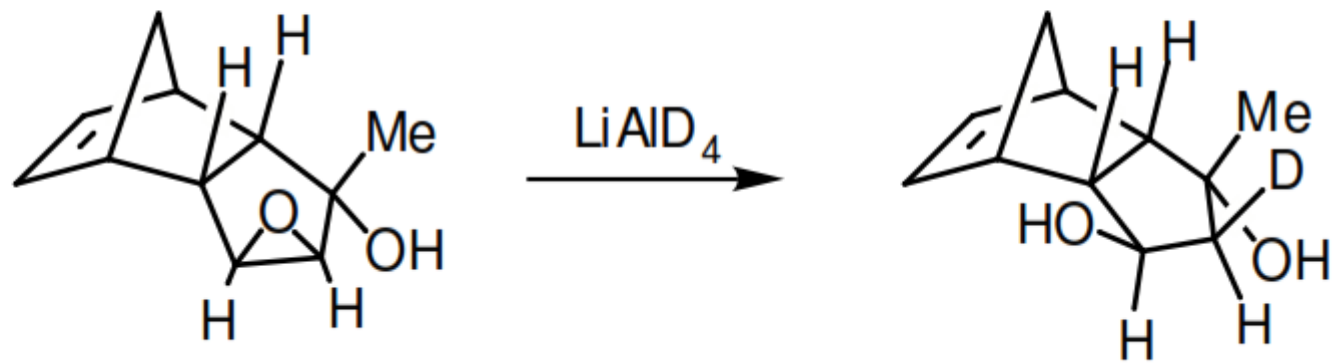
Exercise 12



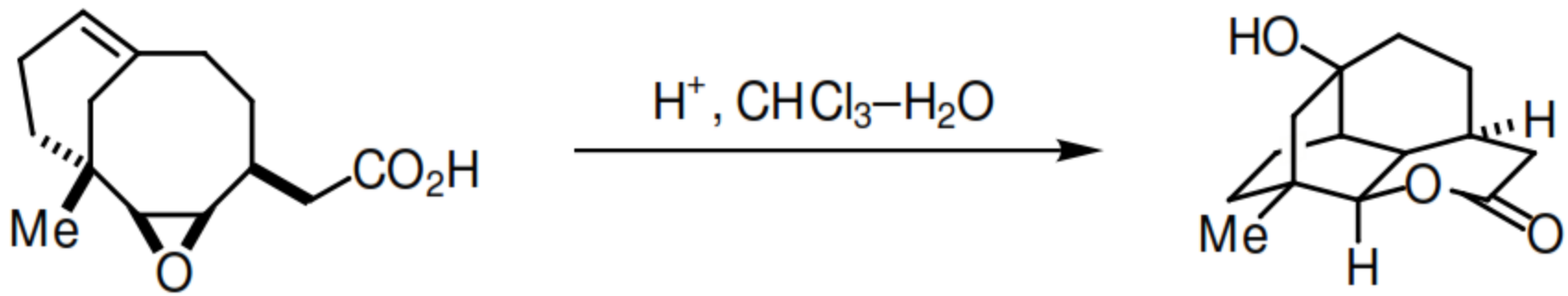
Exercise 13



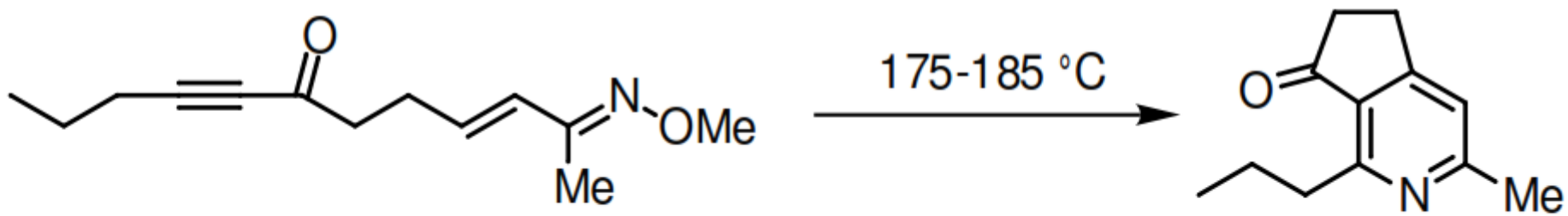
Exercise 14



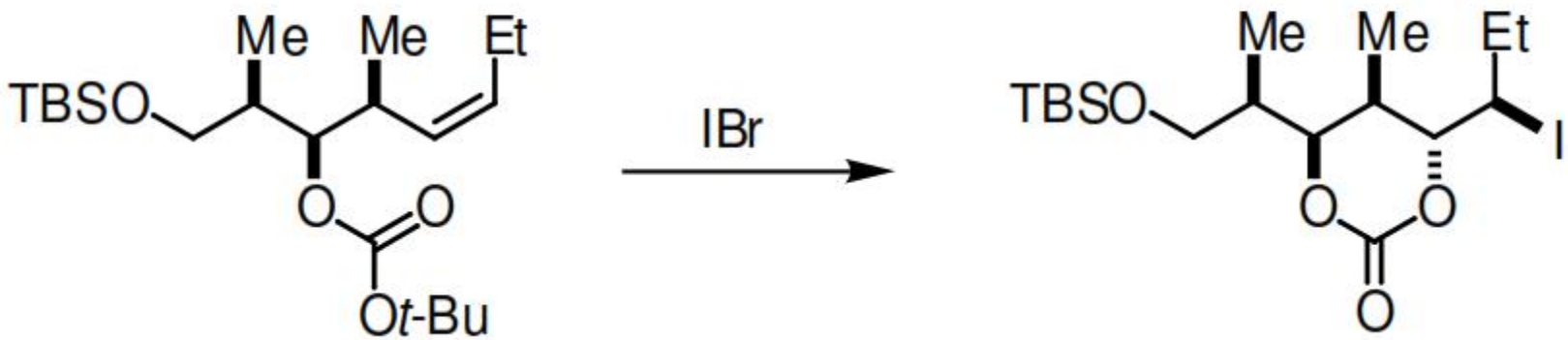
Exercise 15



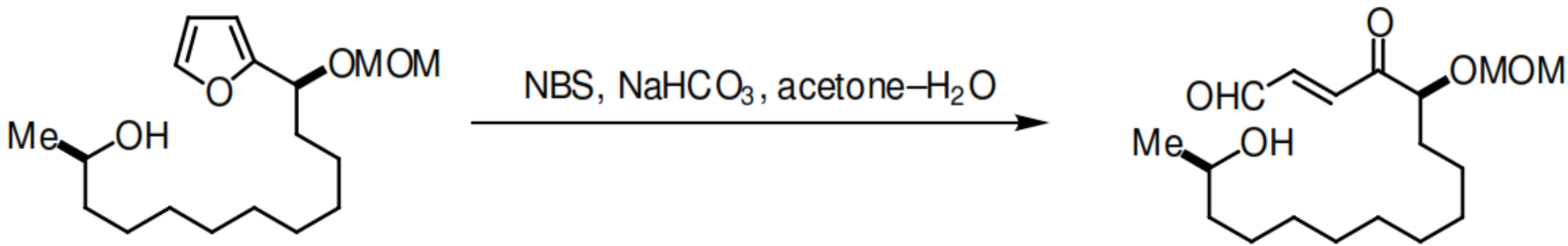
Exercise 16



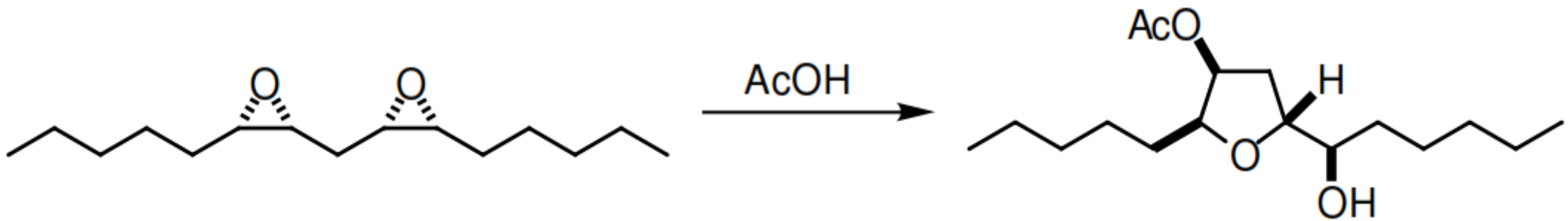
Exercise 17



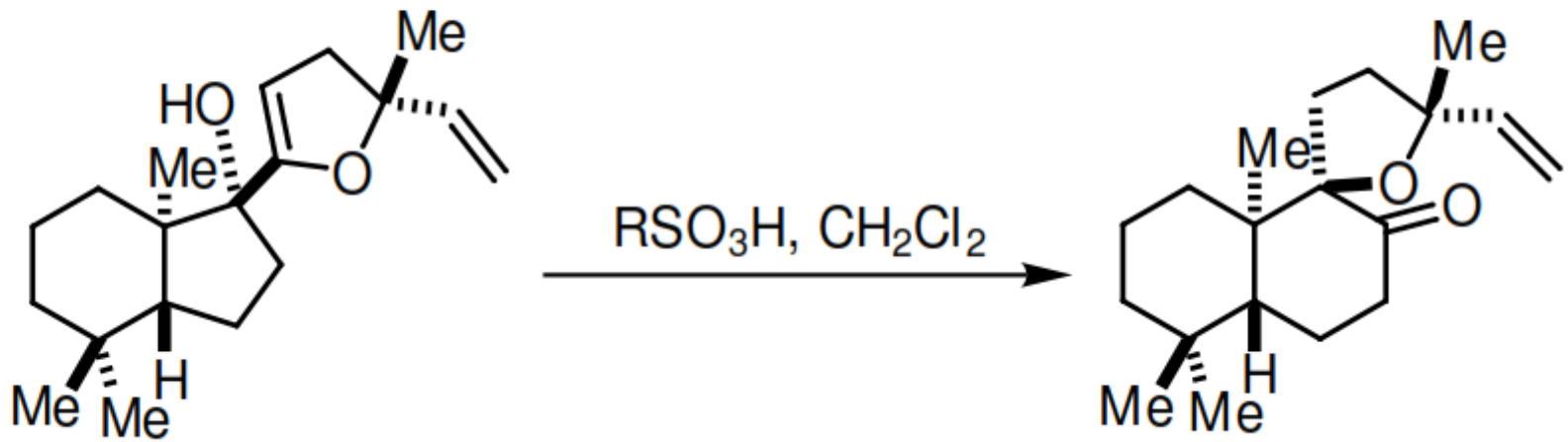
Exercise 18



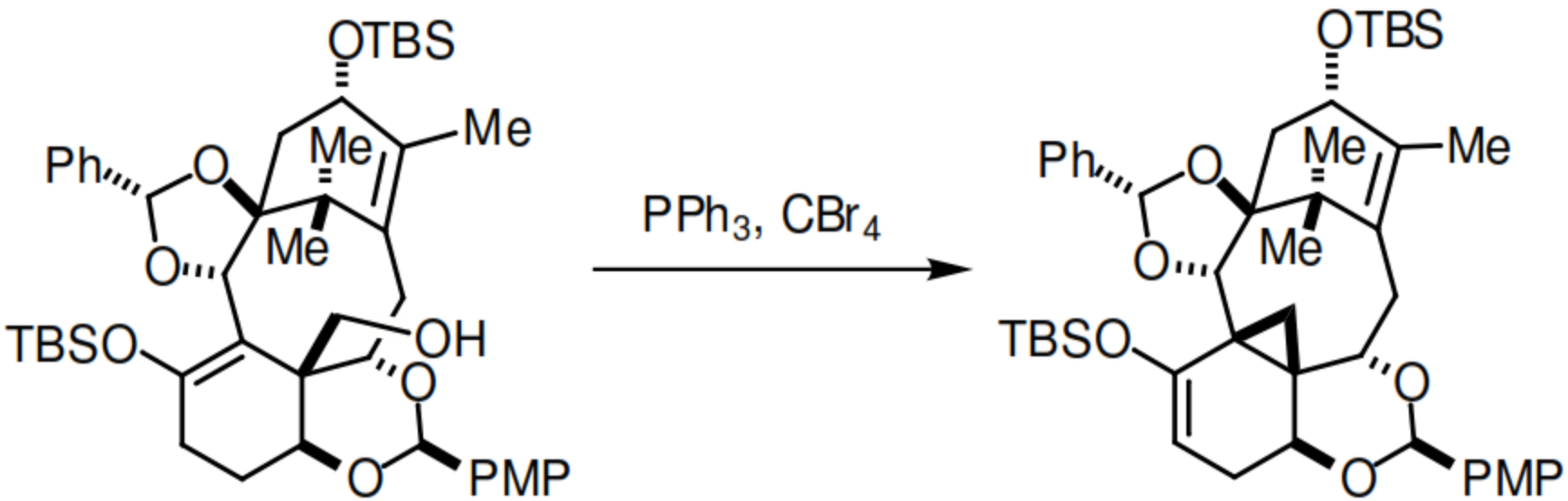
Exercise 19



Exercise 20



Exercise 21


OTBS
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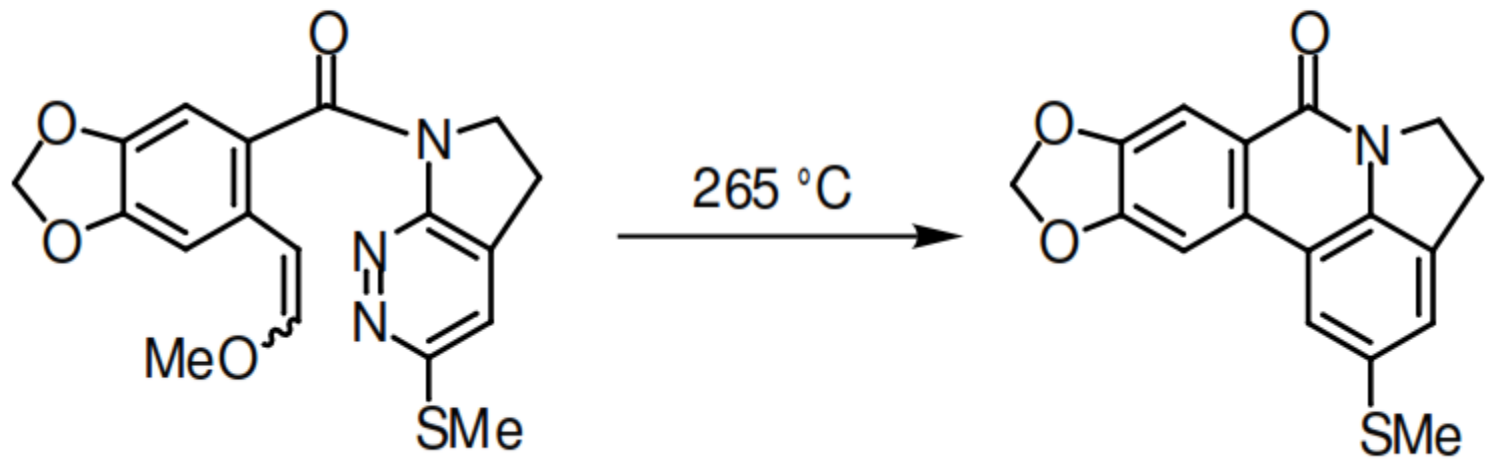
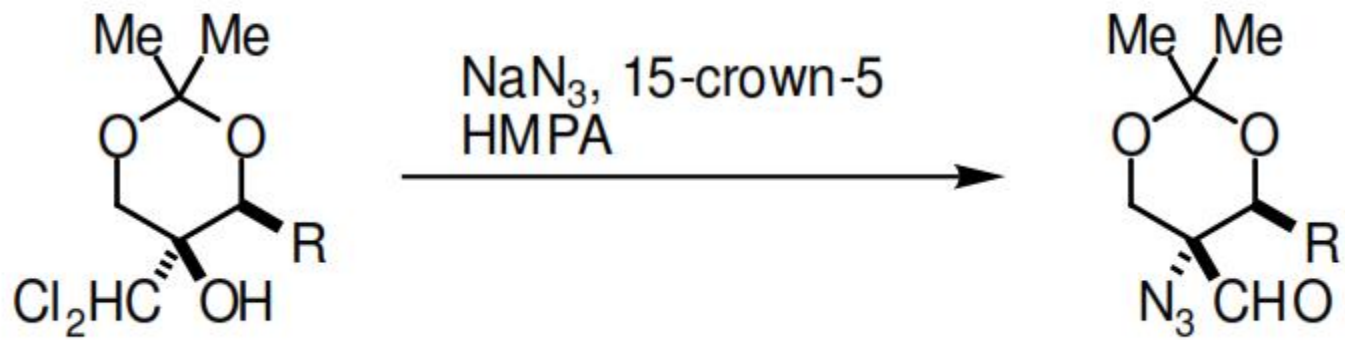
Ph
O
Me
O
TBSO
OH
O
O
PMP
PPh3, CBr4
OTBS
Me
Me
Ph
O
Me
O
TBSO
O
O
PMP

Exercise 22



Exercise 23



Exercise 24