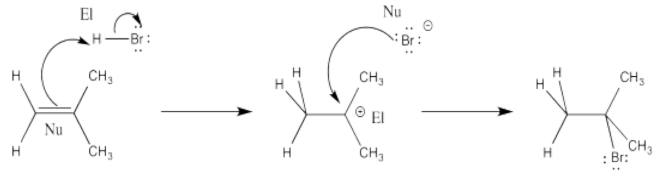
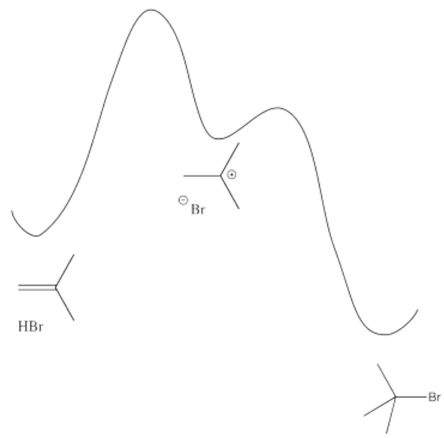
6.14: Solutions for Selected Problems.

Exercise 6.1.1:

El = electrophile; Nu = nucleophile



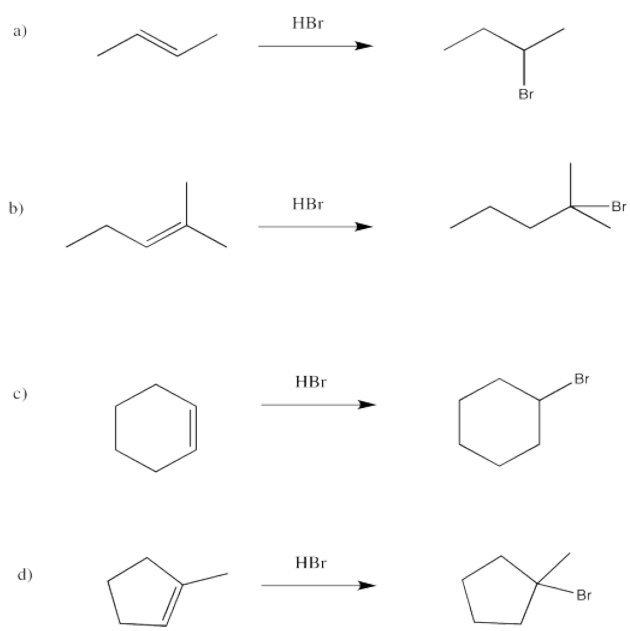
Exercise 6.1.2:



Exercise 6.1.3:

$$Rate = \frac{d[alkyl\ bromide]}{dt} = k[alkene][HBr]$$

Exercise 6.1.4:



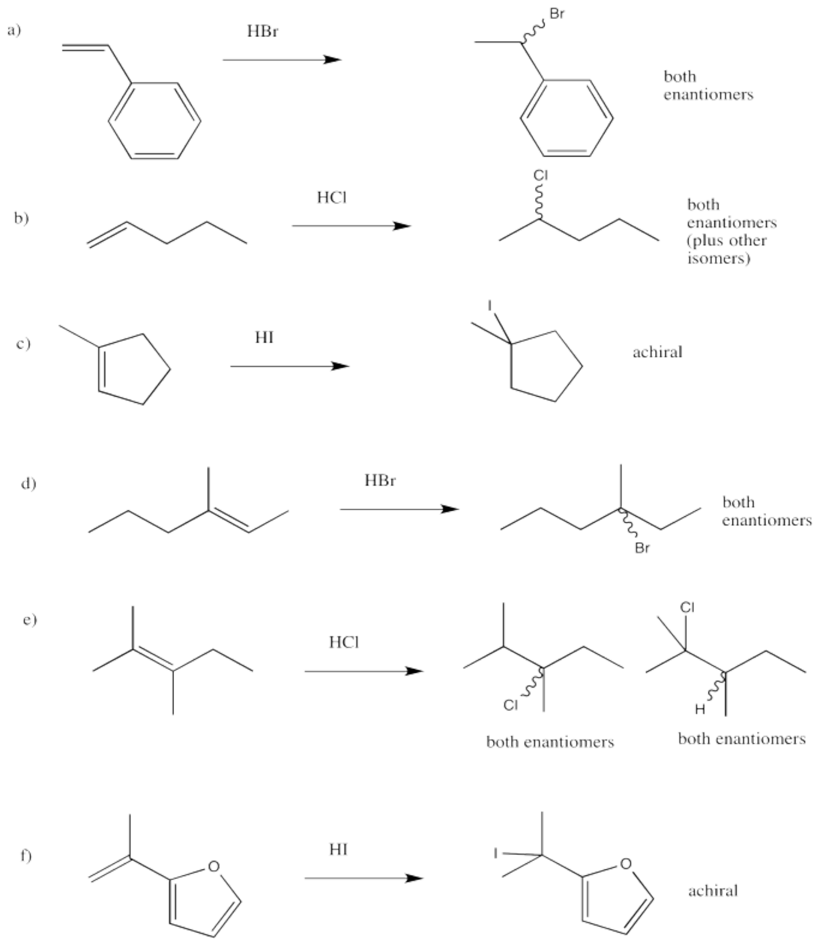
Exercise 6.2.1:

a, e, f, g are prochiral.

Exercise 6.2.2:

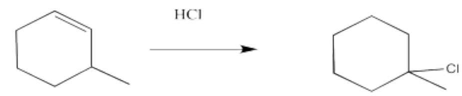
a) re b) si c) re d) si e) either; if the Br adds on one end of the double dond it is re, but at the other it is si f) re

Exercise 6.2.3:

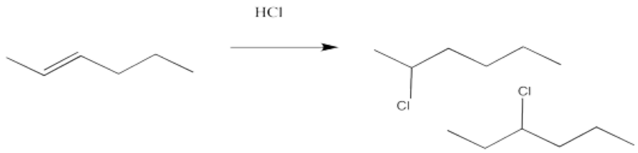


Exercise 6.2.4:

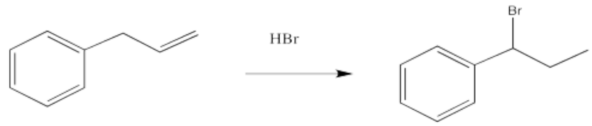
a)



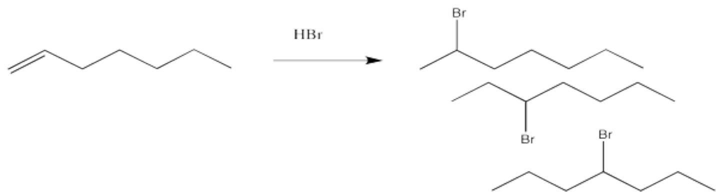
b)



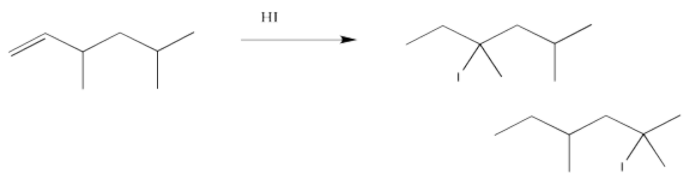
c)



d)



e)

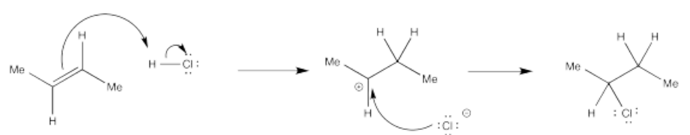


Exercise 6.3.1:

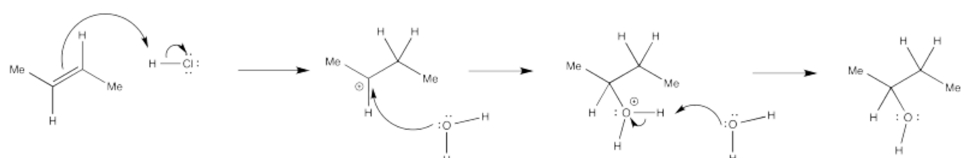
If the acid is regenerated at the end of the reaction, it isn't a reagent. It is a catalyst. It makes addition of water to the double bond occur much more quickly than if water acted alone, since water would never manage to protonate the alkene.

Exercise 6.3.2:

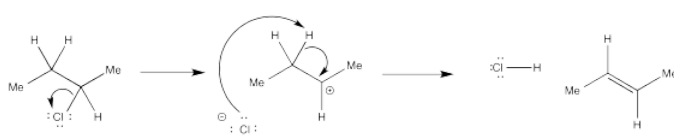
a)



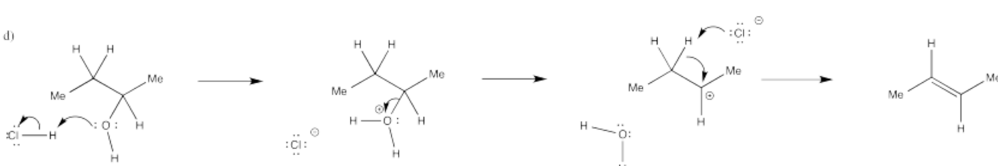
b)



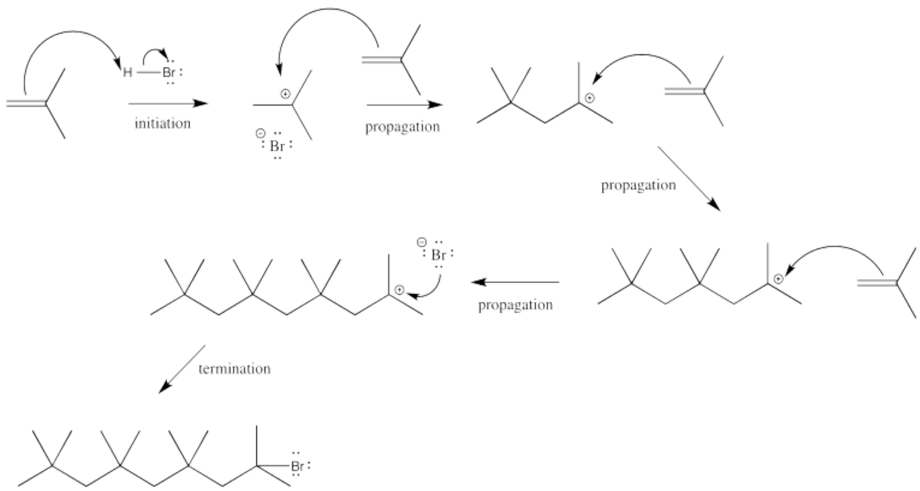
c)



d)

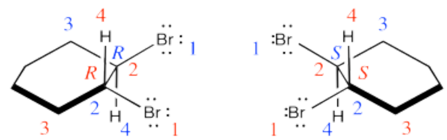


Exercise 6.3.3:



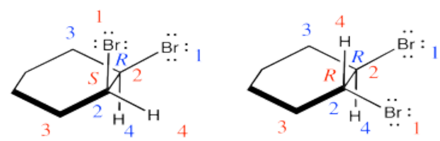
Exercise 6.4.1:

Two products are formed and they are enantiomers.



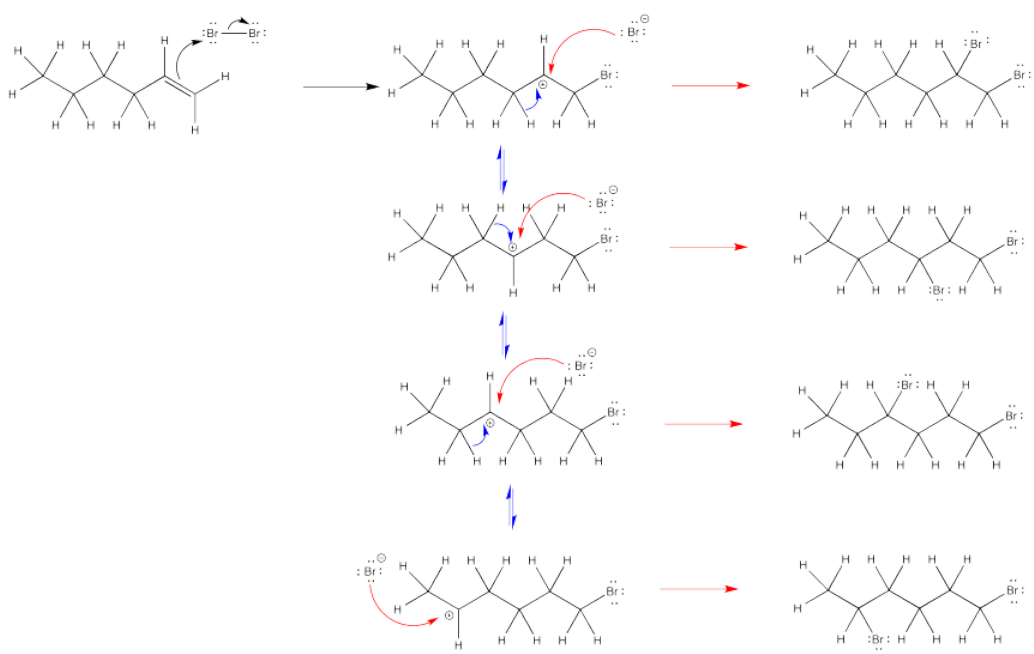
Exercise 6.4.2:

They are diastereomers. One chiral center has the same configuration in both compounds but the others are opposite.



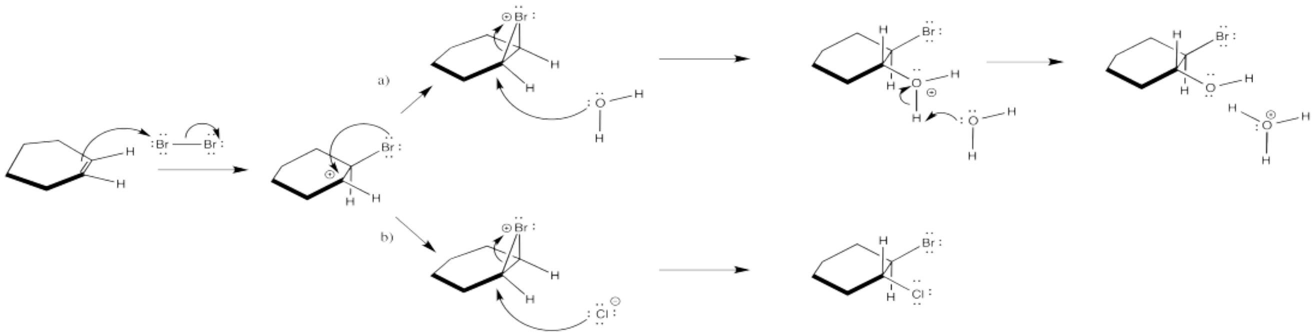
Exercise 6.4.3:

The second bromine could occupy any of the secondary positions if there were a true carbocation. That doesn't happen; the second bromine occupies only the position next to the other bromine.

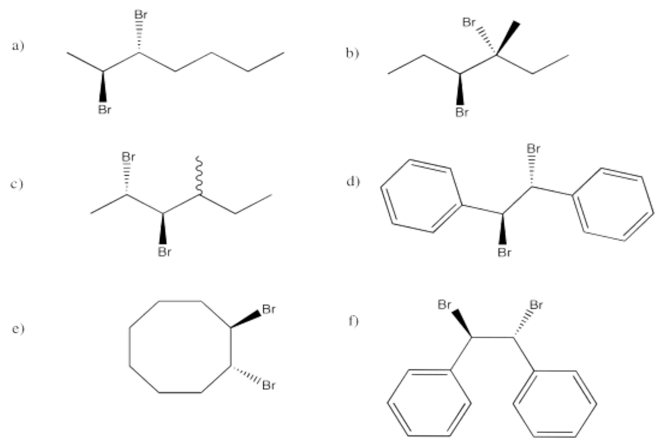


Exercise 6.4.5:

The nucleophile in the second step changes under different conditions.

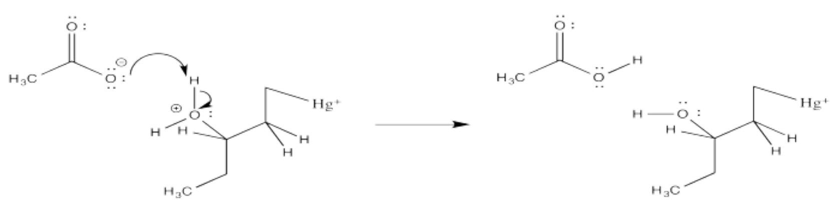


Exercise 6.4.6:

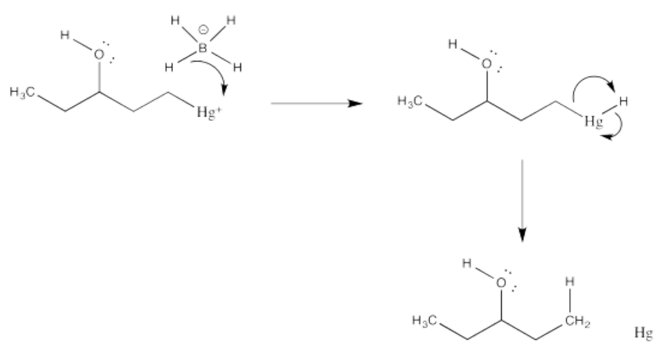


& enantiomer in each case

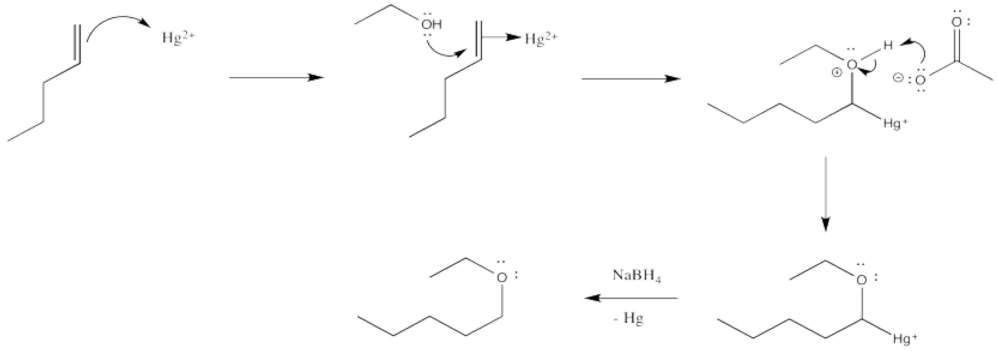
Exercise 6.5.2:



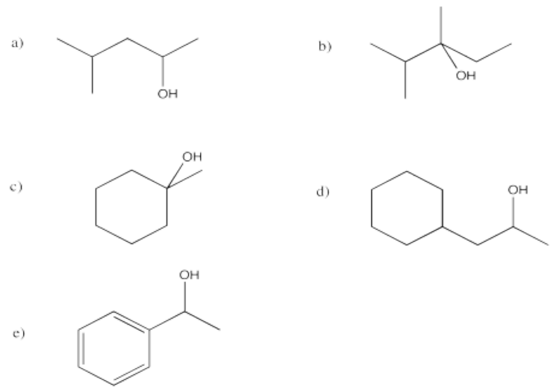
Exercise 6.5.3:



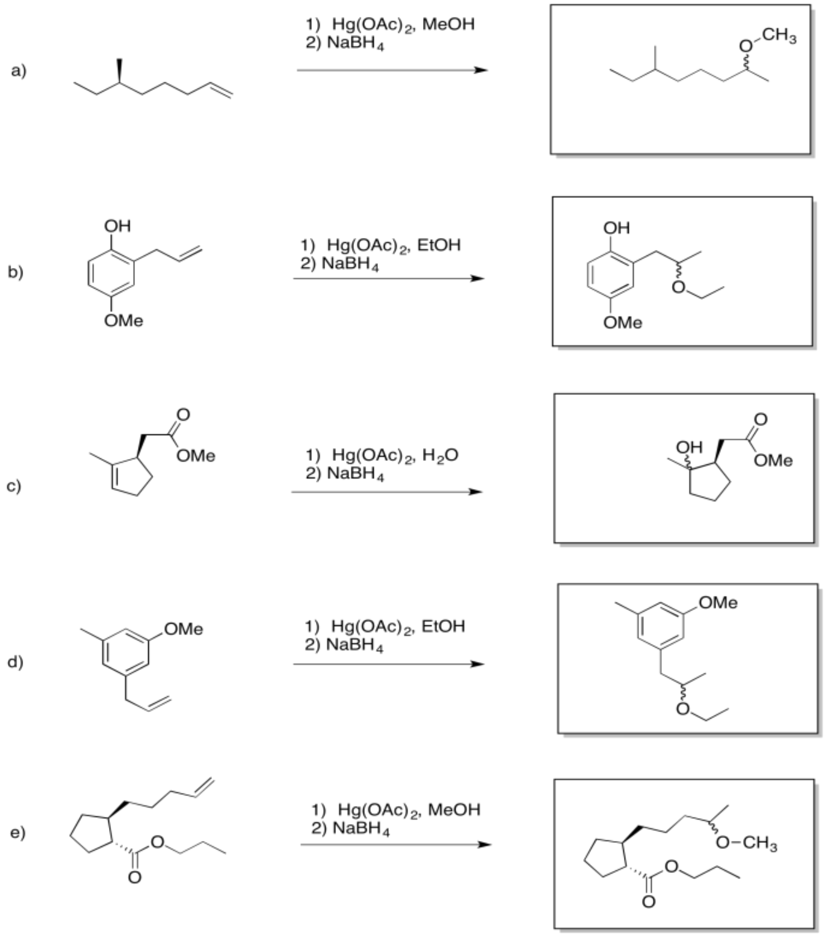
Exercise 6.5.4:



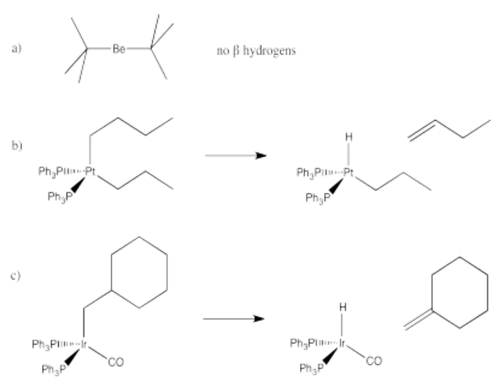
Exercise 6.5.5:



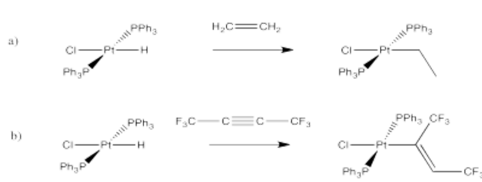
Exercise 6.5.6:



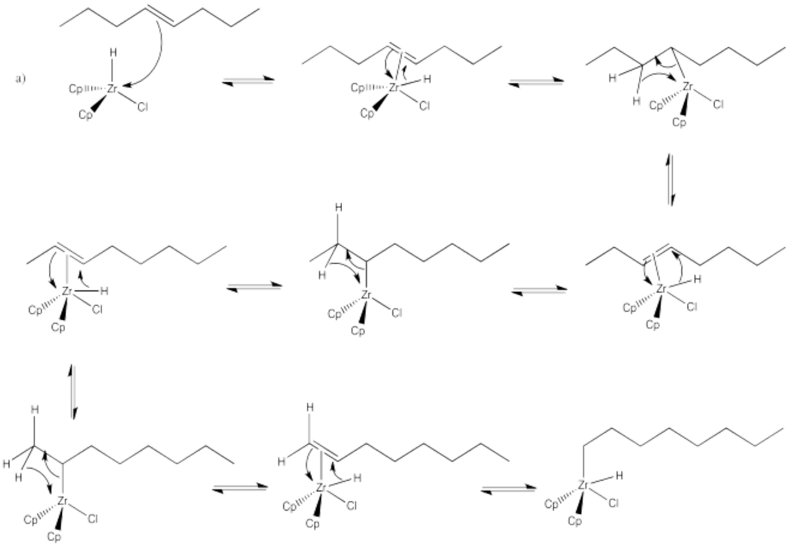
Exercise 6.6.1:



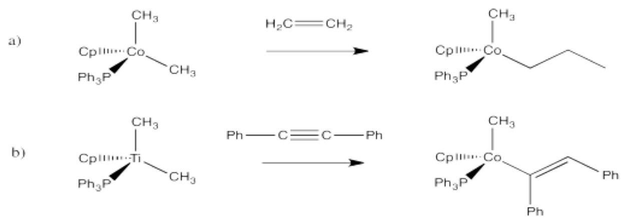
Exercise 6.6.2:



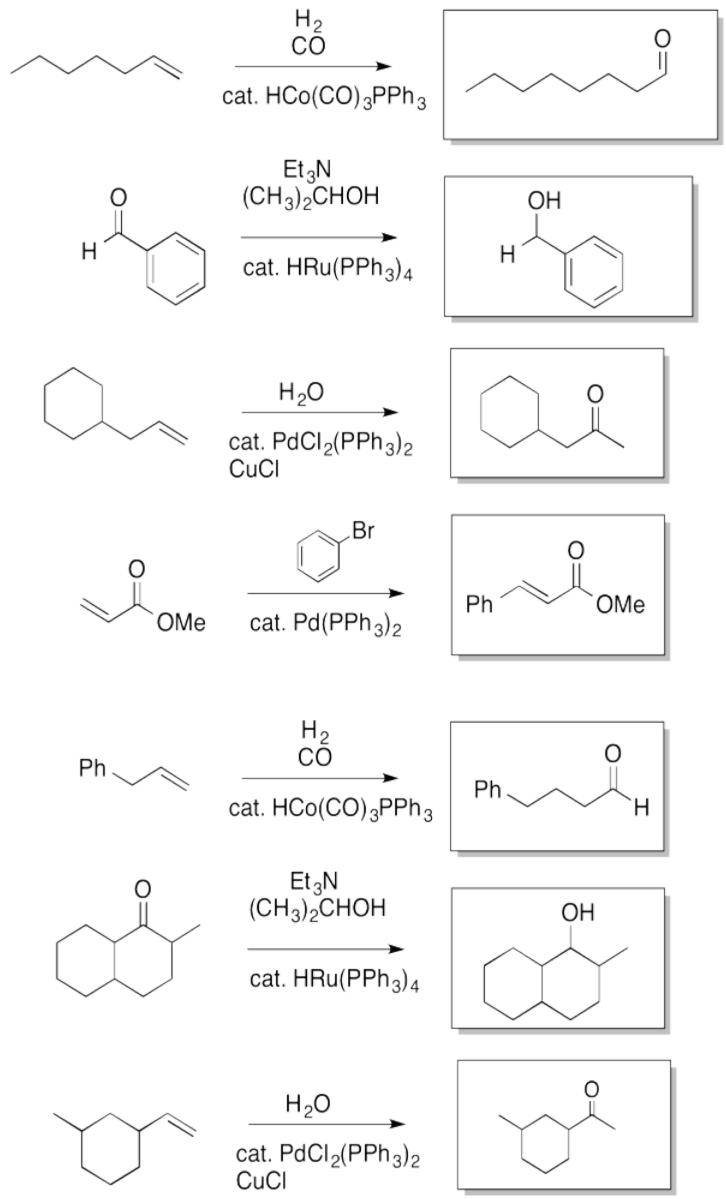
Exercise 6.6.3:



Exercise 6.6.4:

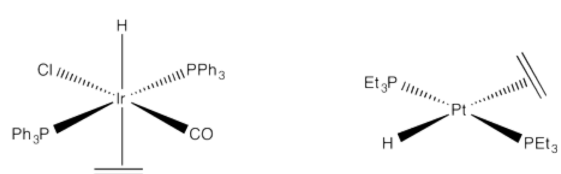


Exercise 6.6.5:



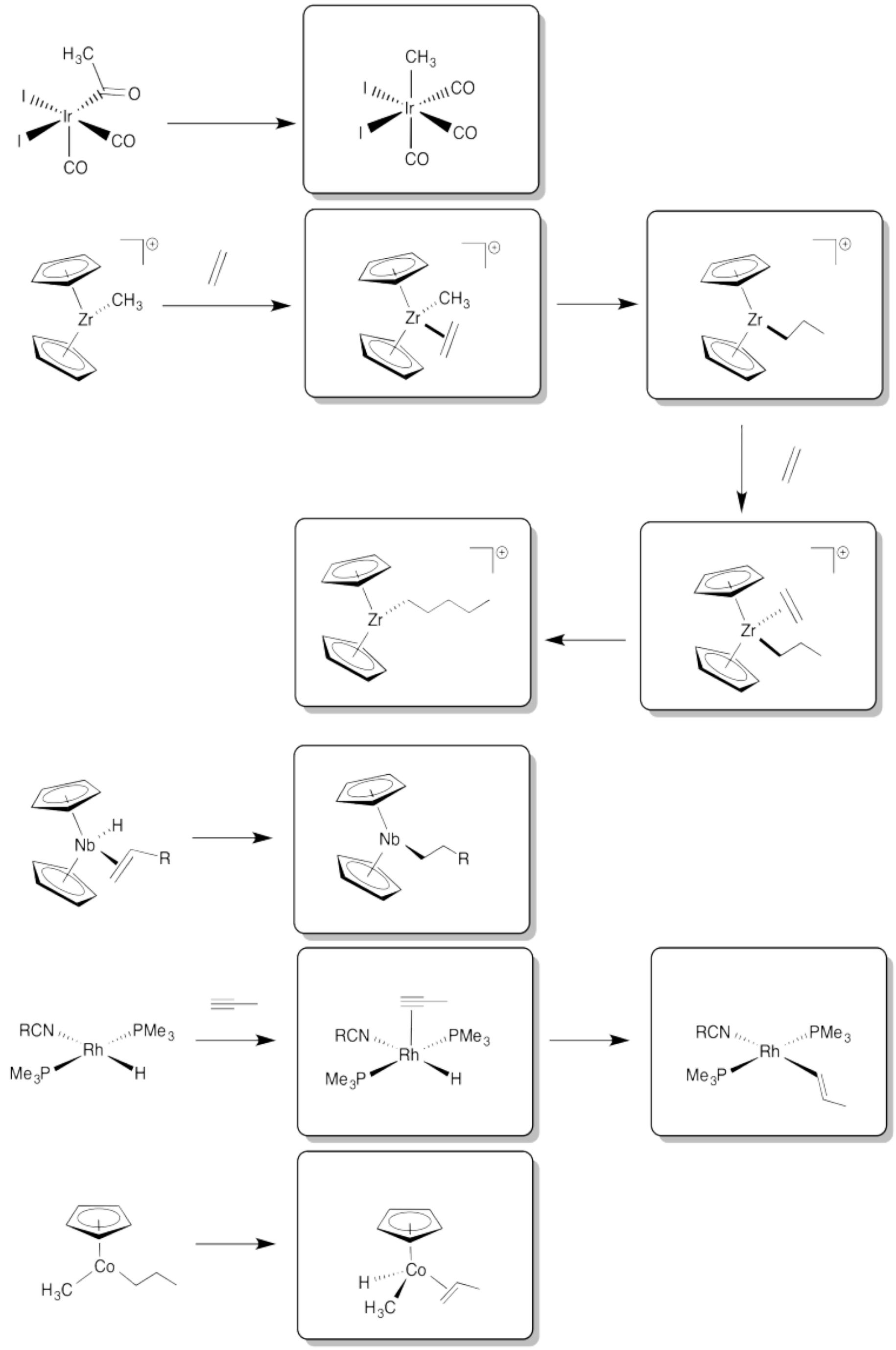
<u>Exercise 6.6.6:</u>

Why don't either of these complexes undergo hydride insertions at room temperature?



The hydride and the alkene group are trans to each other in this complex. In order for ar insertion reaction, the two ligands need to be closer.

<u>Exercise 6.6.7:</u>



Exercise 6.6.8:

Scorpionate Ligands: A Ligand with a Greater Propensity to Sting?
Dyson, Zech, Rawe, Haddow, Hamilton and Owen, *Organometallics*, **2011**, *30*, 5844-5850.

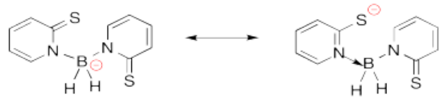
1. A ligand that we have seen before, **COD**.

COD

a. What will the denticity of this ligand be? ____2_____
b. Circle the sites that bind to the metal.

2. Show a molecular orbital cartoon showing how the orbitals of COD that bind to the M.

3. New Ligand, **Bmp**.
   a. Add formal charges to these two resonance structures.



When rhodium is complexed with Bmp and the COD, the following complex is formed.

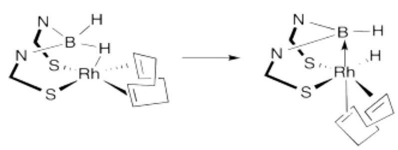
4. What is the geometry of the rhodium in this complex?

Geometry: **distorted square pyramidal**

5. What is the valence electron count on Rh in this complex?

Valence electrons on Metal:	___9____
Charge on the ligands:	___-1____
Charge on the Metal:	___+1____
Revised Count on the Metal (accounting for charge):	___8____
Number of electrons donated from the ligands:	___10____
Total electrons in this complex:	___18____

6. Upon formation, the hydride quickly moves to the metal.

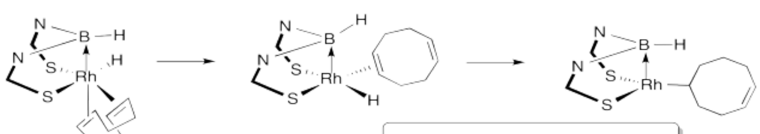


a. Why did this occur?

b. Why is there an arrow toward the B in the product?

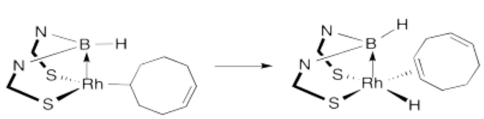
For the rhodium complex, a novel "chain-walking mechanism" is observed.

7. In this reaction, the COD partially dissociates and then the first step of the "chain-walking" occurs. Provide a name for the mechanism type.



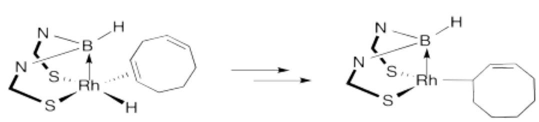
Mechanism Type: **1,2 insertion**

8. The second step of the "chain-walking" occurs. Provide a name for the mechanism type.



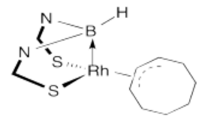
Mechanism Type: **beta elimination**

9. Eventually the hydride "walks" to the final position. Show the rest of the mechanism.



Chain walking is a series of 1,2 insertions and beta eliminations

10. The final product can also be represented in the following way. Show how this structure is equivalent to the one above.



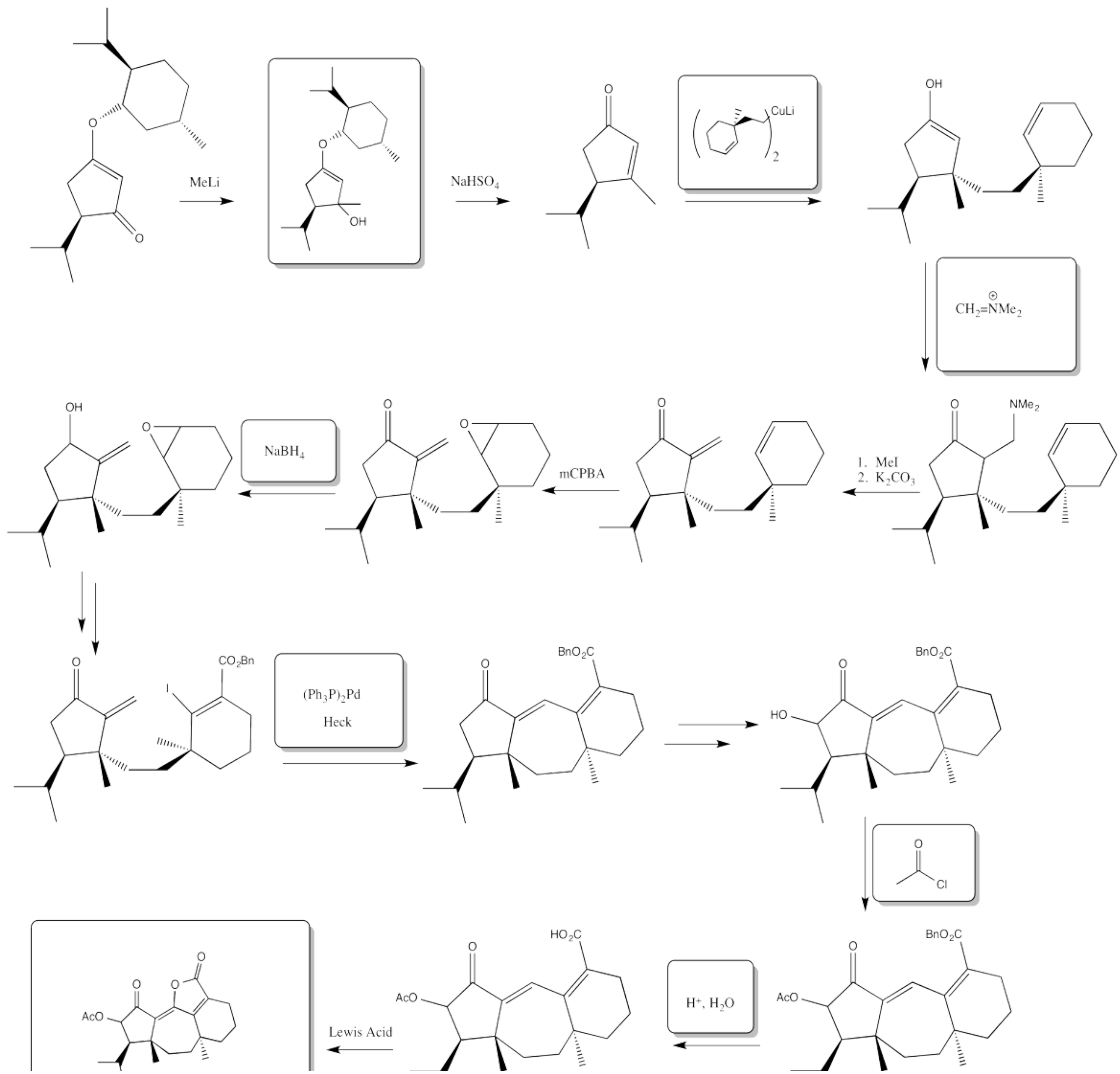
11. Considering structure and thermodynamics, why is this the final product?

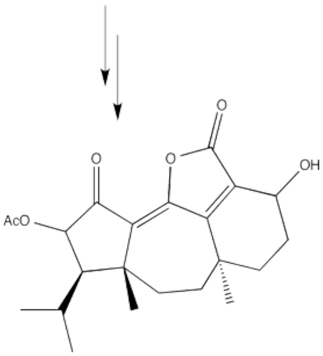
resonance stabilized

<u>Exercise 6.6.9:</u>

Guanacastepene N

Iimura, Overman, Paulini, Zakarian, *J. Am. Chem. Soc.* **2006,** *128*, 13095.



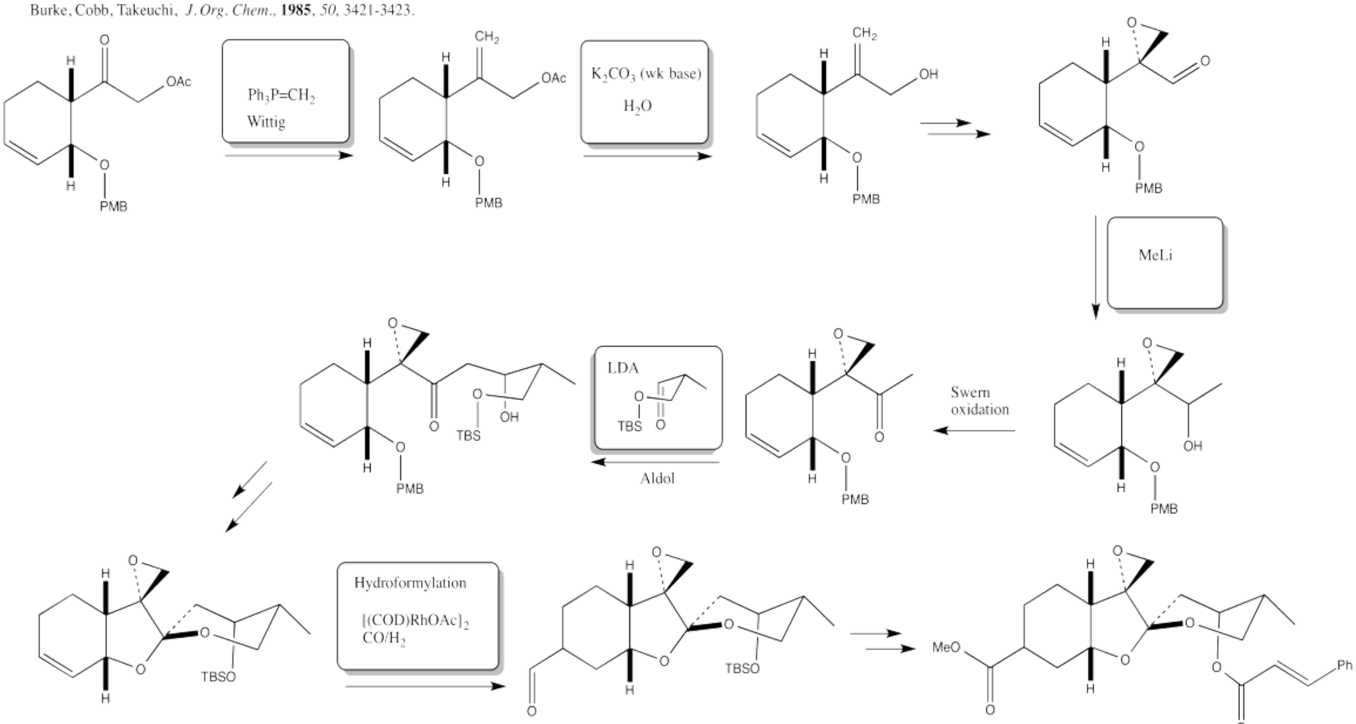


Guanacastepene N

Exercise 6.6.10:

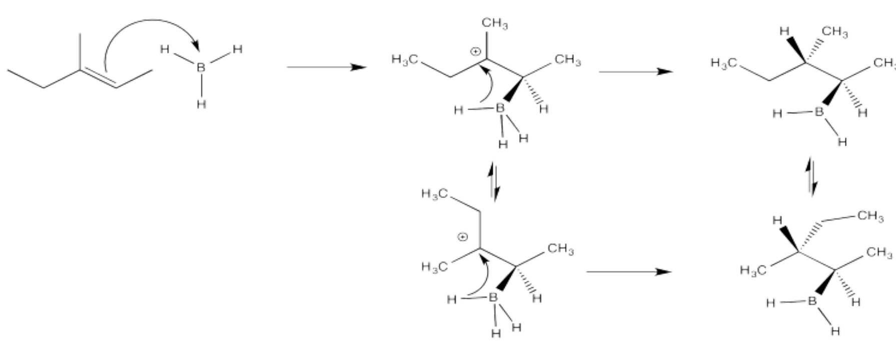
Phyllanthocin

Burke, Cobb, Takeuchi, *J. Org. Chem.*, **1985**, *50*, 3421-3423.



phyllanthoside: antineoplastic against myeloma and melanoma

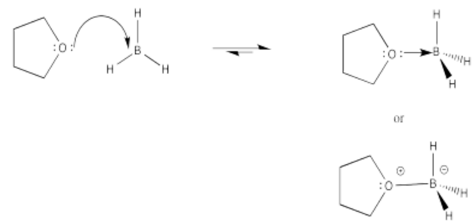
Exercise 6.7.2:



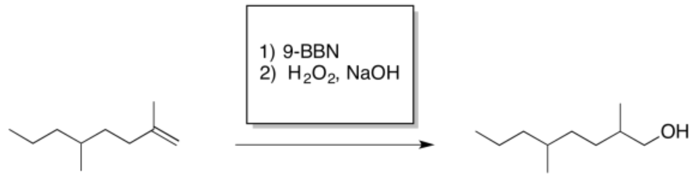
Exercise 6.7.3:

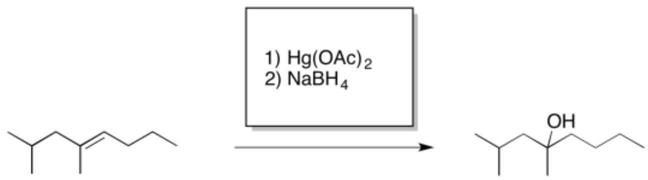
Crowding is more severe in the structure on the left than in the structure on the right. The structure on the right, representing an approach to the transition state of the reaction, is more favorable than the other one.

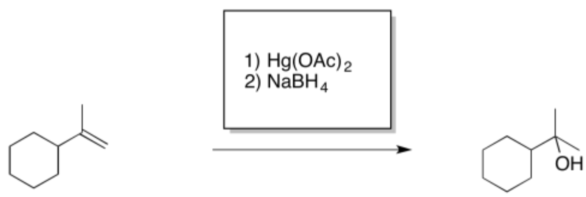
Exercise 6.7.4:

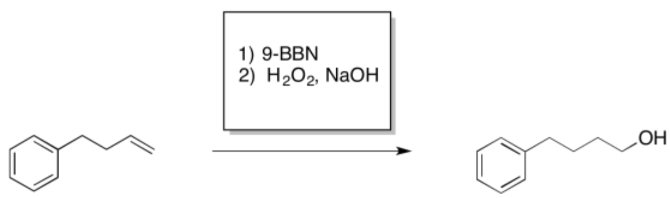


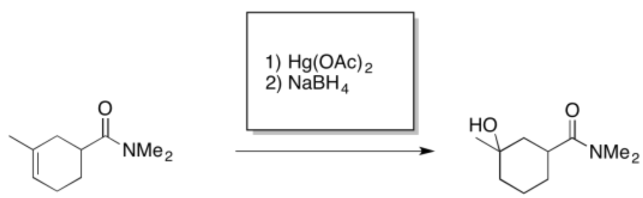
Exercise 6.7.5:

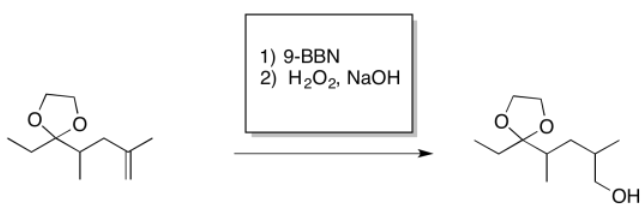
a) 

b) 

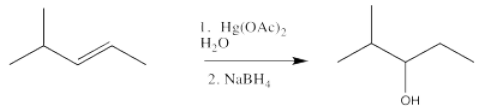
c) 

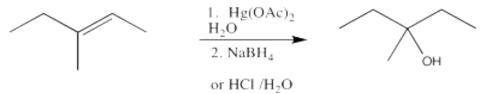
d) 

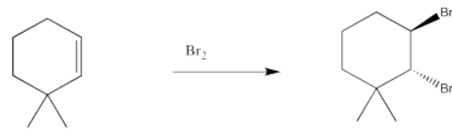
e) 

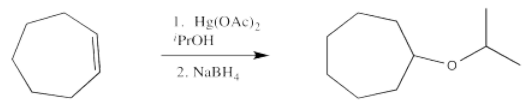
f) 

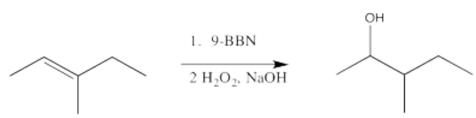
<u>Exercise 6.7.6:</u>

a) 

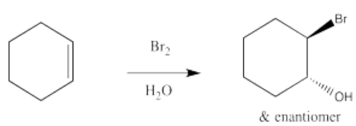
b) 

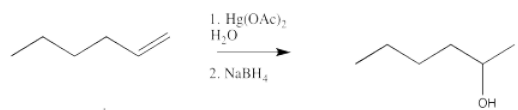
c) 

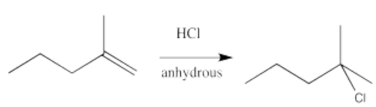
d) 

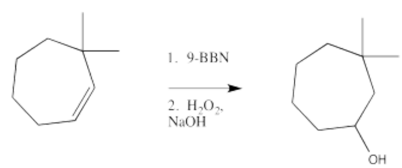
e) 

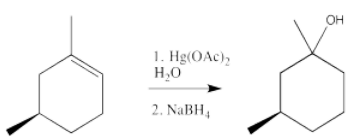
Exercise 6.7.7:

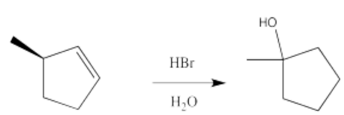
a) 

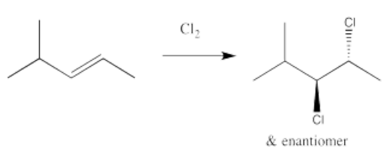
b) 

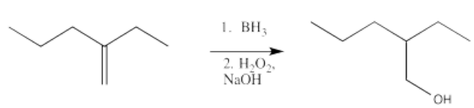
c) 

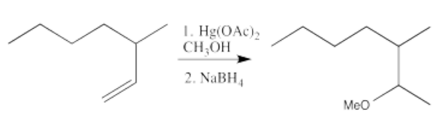
d) 

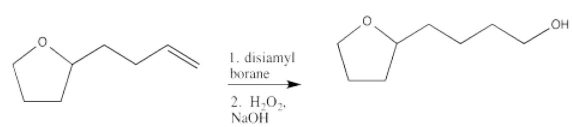
e) 

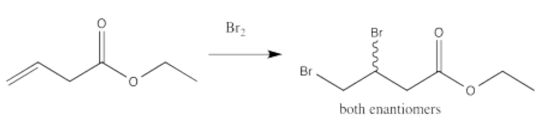
f) 

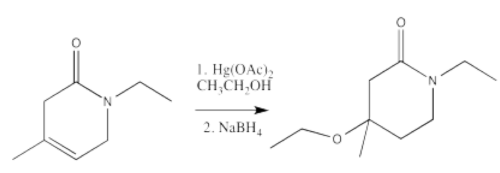
g) 

h) 

i) 

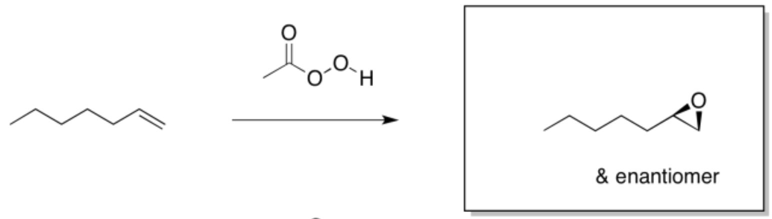
j) 

k) 

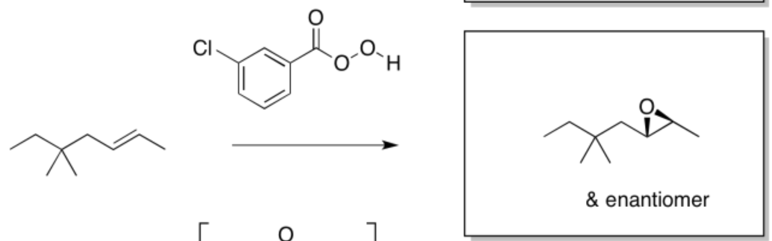
l) 

Exercise 6.8.1:

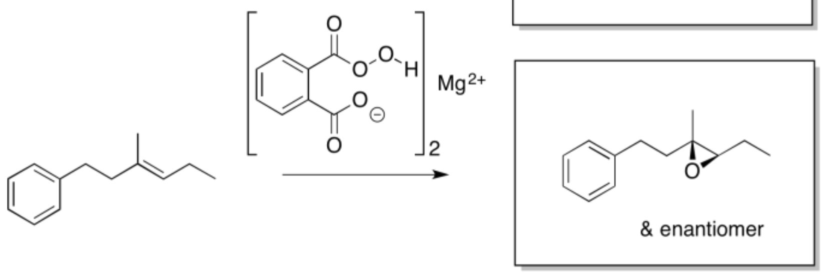
a)



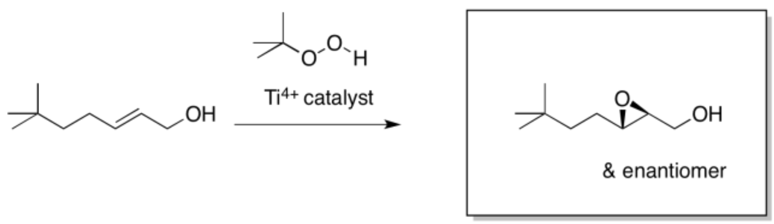
b)



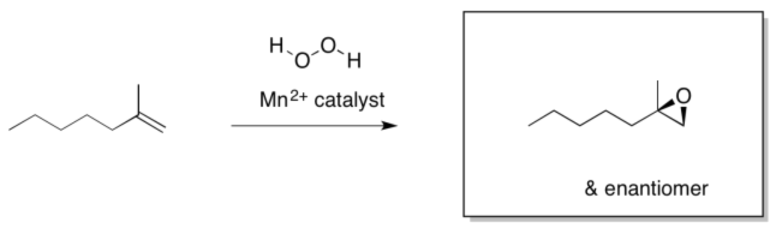
c)



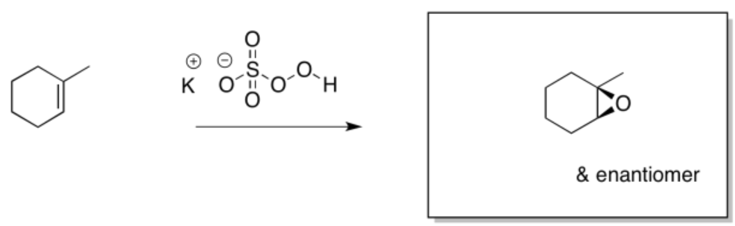
d)



e)

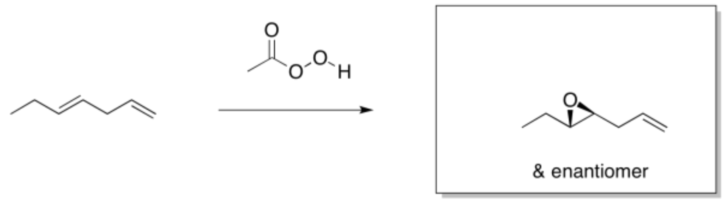


f)

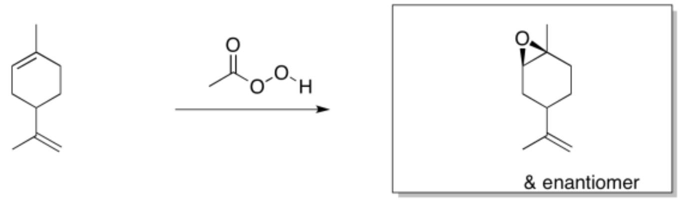


Exercise 6.8.2:

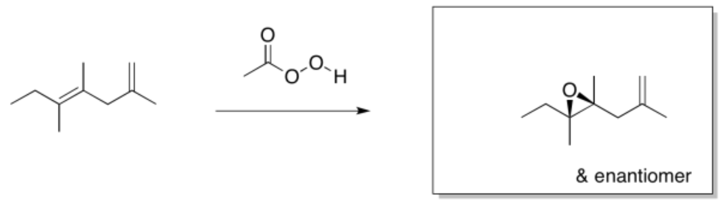
a)



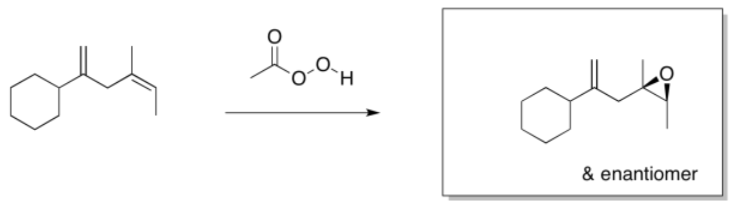
b)



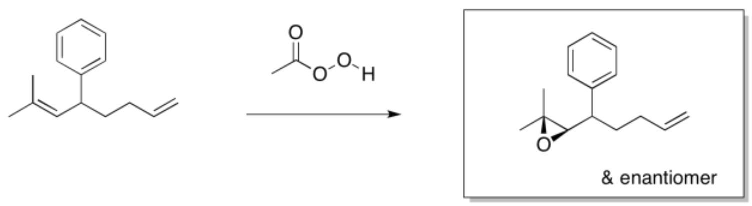
c)



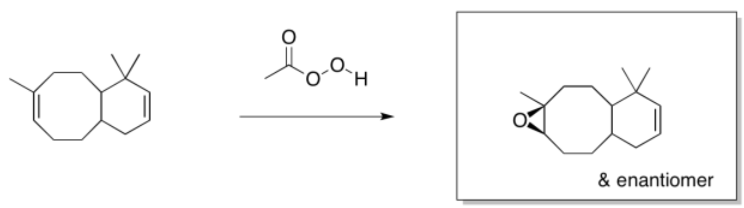
d)



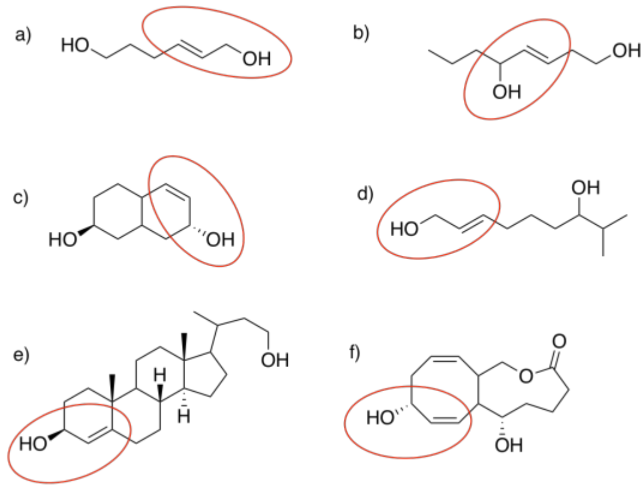
e)



f)



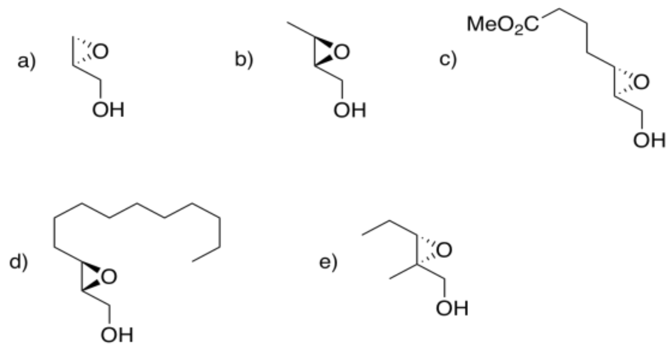
<u>Exercise 6.8.3:</u>



Exercise 6.8.4:

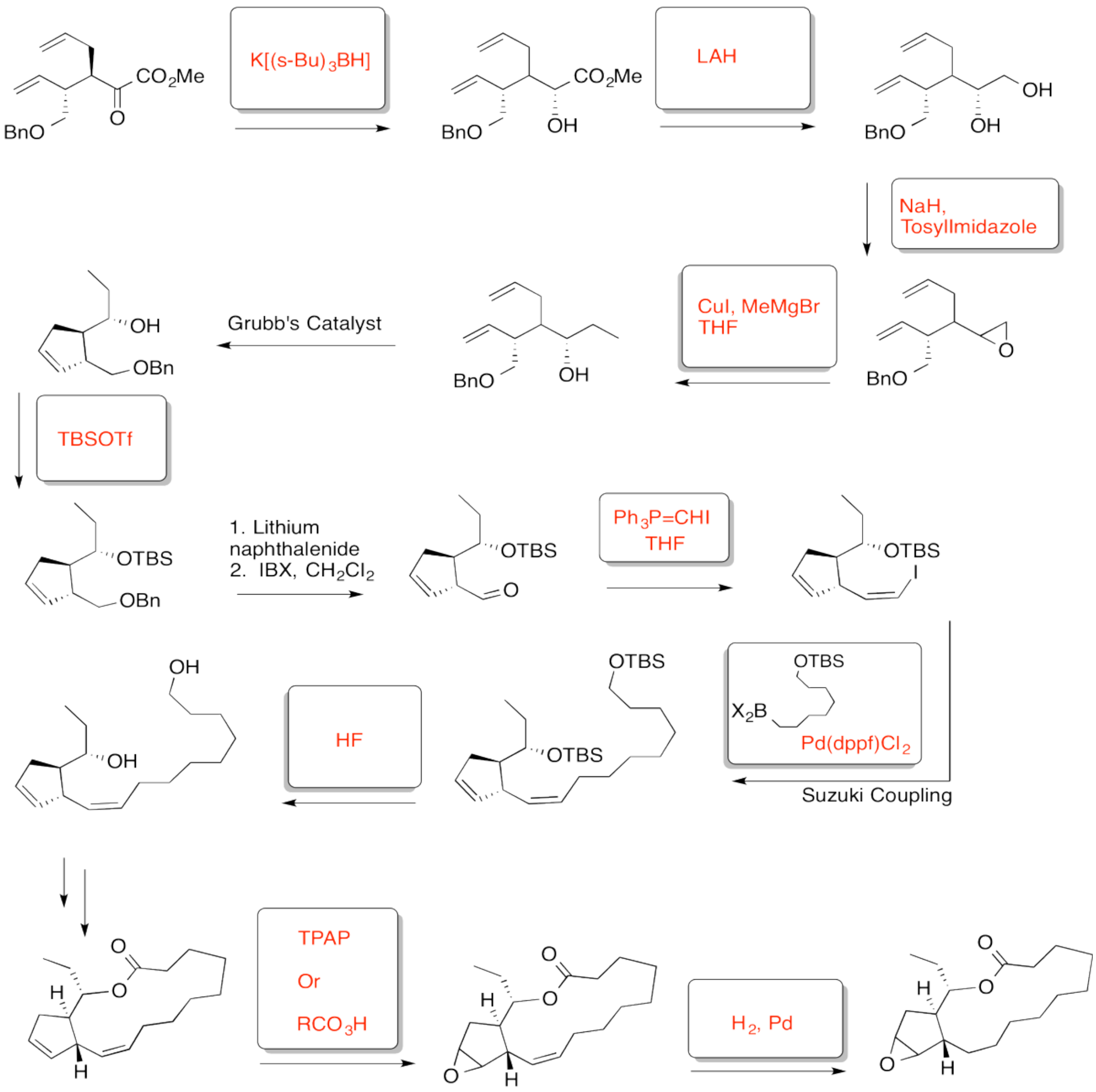
D-(-)-tartrate is the (*2S,3S*)-isomer. L-(+)-tartrate is the (*2R,3R*)-isomer. Each chiral center is configured opposite to the corresponding one in the other molecule, so the molecules are enantiomers.

Exercise 6.8.5:



Exercise 6.8.6:

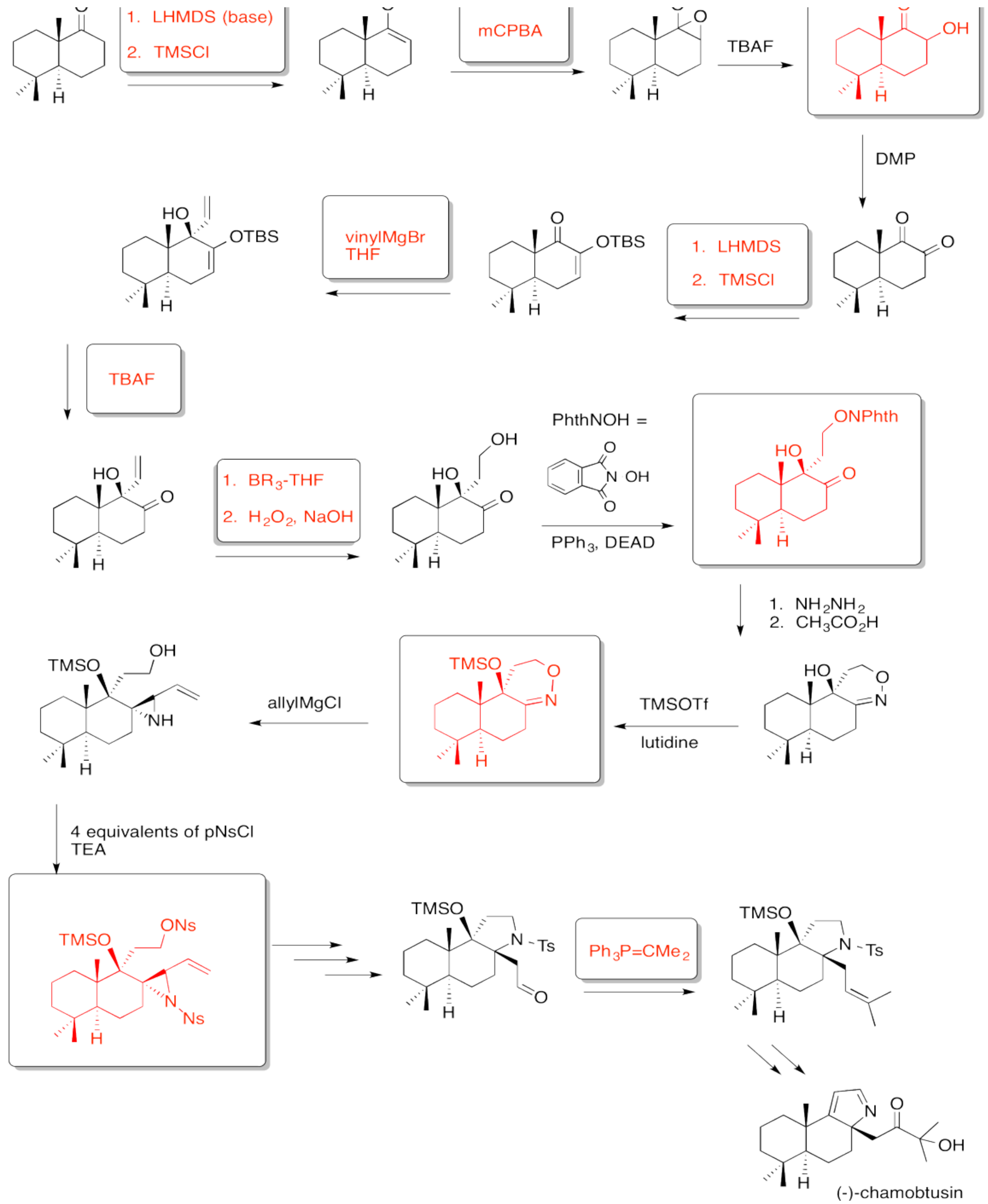
Becker, Butt, Kiedrowski, Mieschler, Quentin and Hiersemann, Total Synthesis of (-)-Ecklonialactone B, *Org. Lett.*, **2013**, *15* (23), 5982-5985.



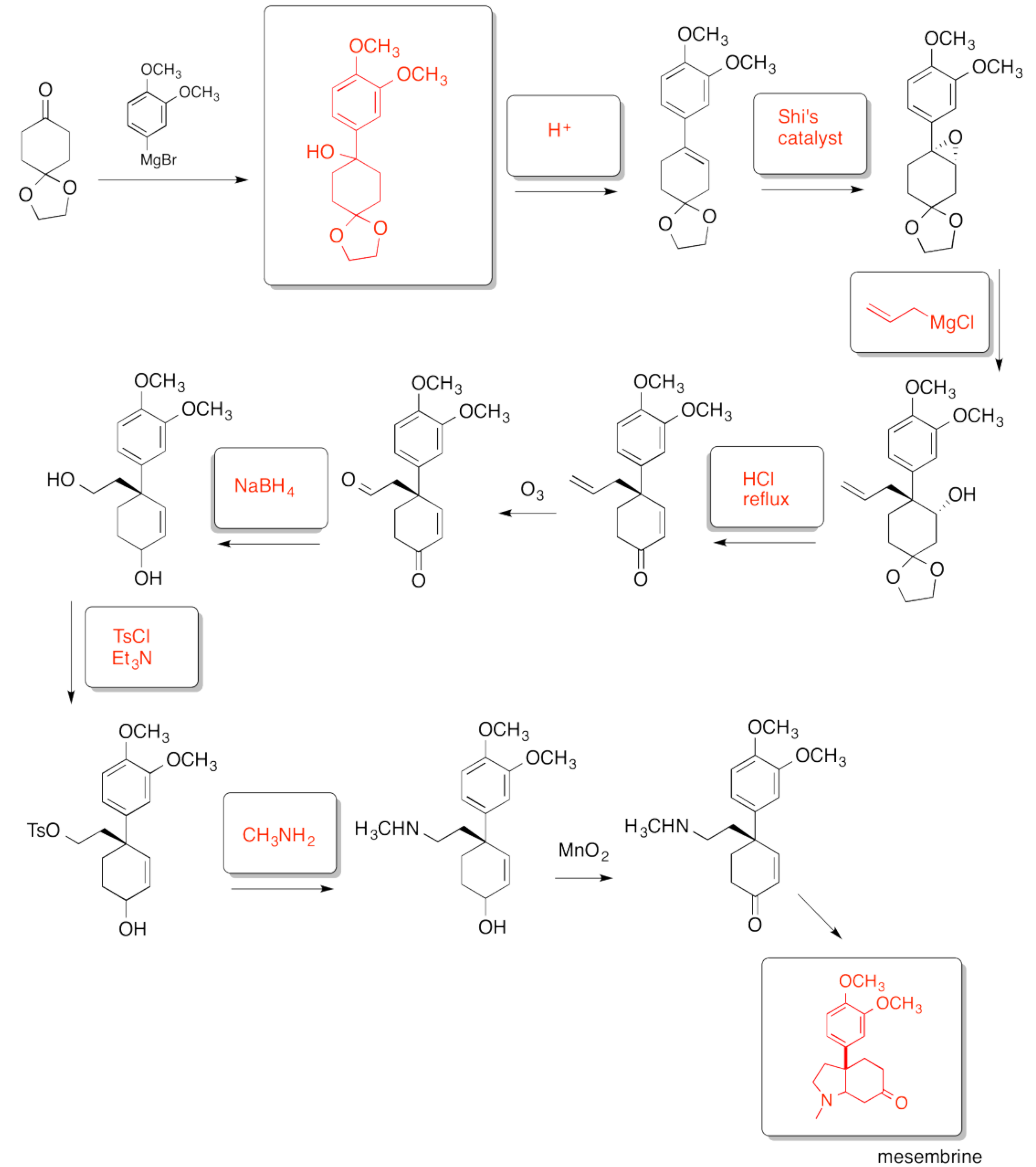
Ecklonialactone

Exercise 6.8.7:

Suzuki and Aoyagi, Total Synthesis of (-)-Chamobtusin A, *Org. Lett.*, **2012**, *14* (24), 6374-6376.



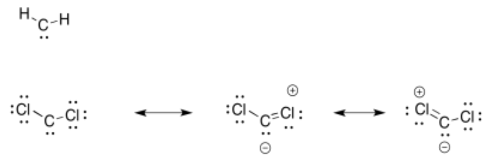
Exercise 6.8.8:



Taber and He, Opening of Aryl-Substituted Epoxides To Form Quaternary Stereogenic Centers: Synthesis of (-)-Mesembrine, *J. Org. Chem.*, **2005**, *70*, 7711-7714.

Exercise 6.9.1:

The chlorines can (weakly) share their electrons to fill the octet on carbon.

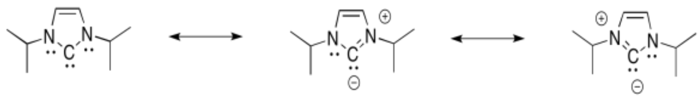


Exercise 6.9.2:

The oxygen can π-donate to help fill the octet on the carbon.

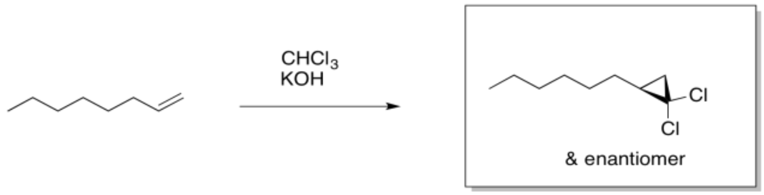
Exercise 6.9.3:

Not only can the nitrogens π-donate to help fill the octet on carbon, but this is an aromatic system. It is planar, cyclic, fully conjugated, with an odd number of electron pairs in the π-system.

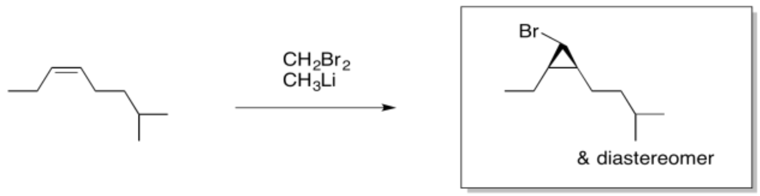


Exercise 6.9.4:

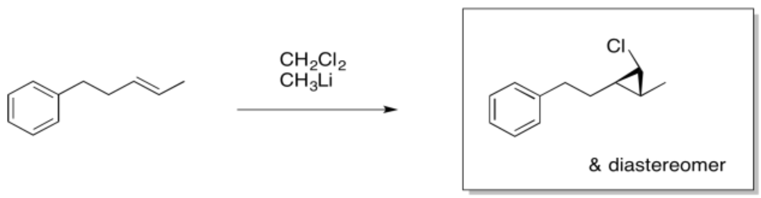
a)



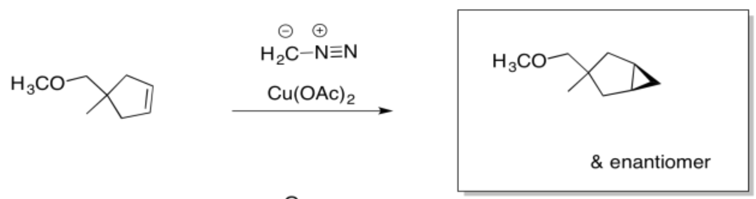
b)



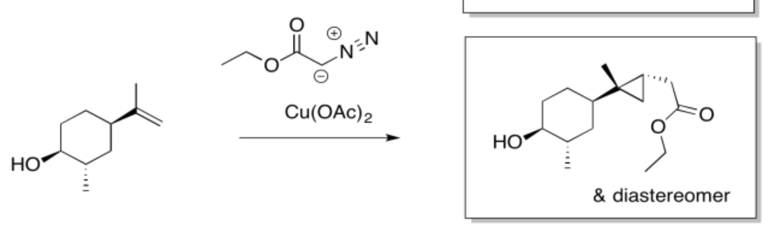
c)



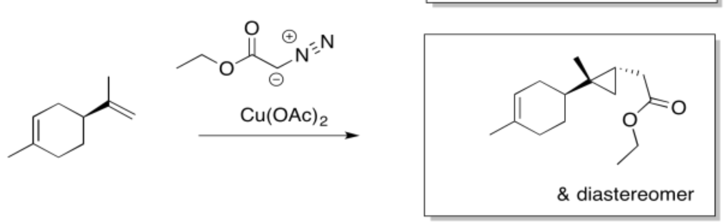
d)



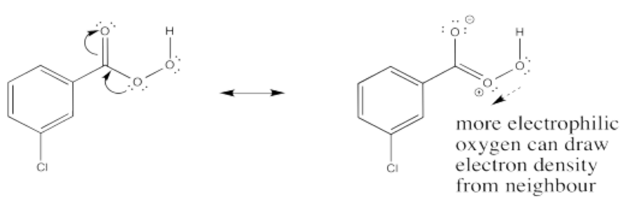
e)



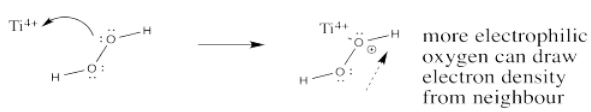
f)



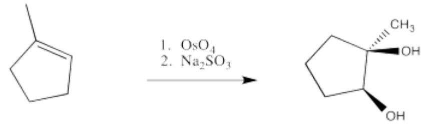
Exercise 6.10.1:



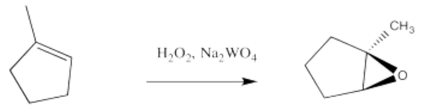
Exercise 6.10.2:



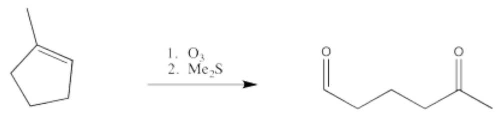
Exercise 6.10.3:

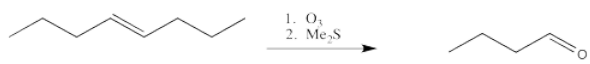


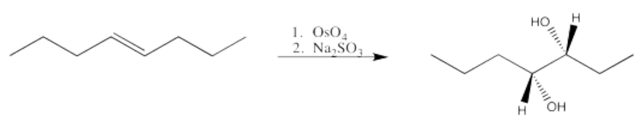
& enantiomer

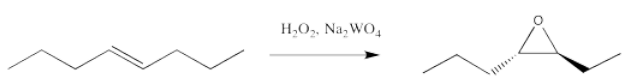


& enantiomer

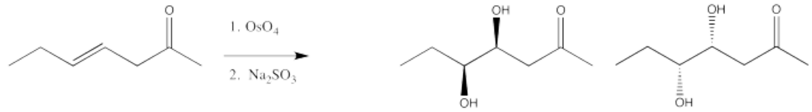


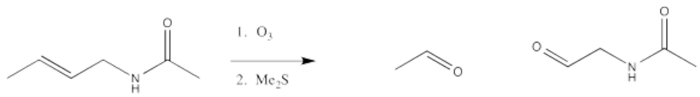


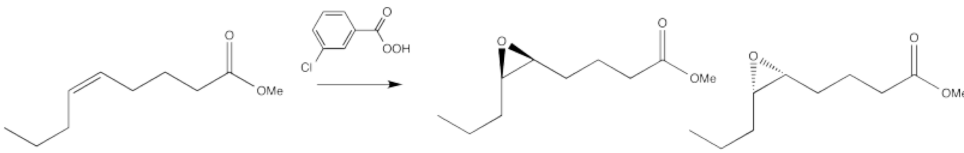


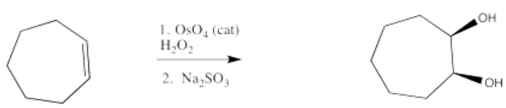


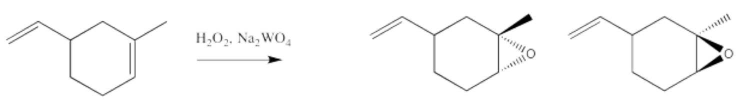
Exercise 6.10.4:

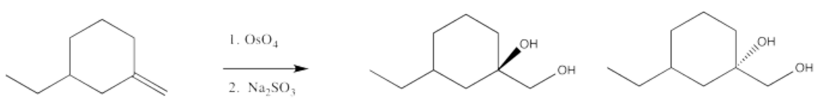


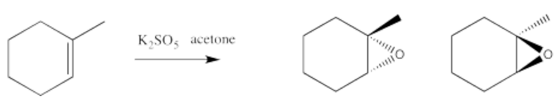












Exercise 6.10.5:

iso-Aloperine

Brosius, Overman, *J. Org. Chem.* **1997**, *62*, 440.