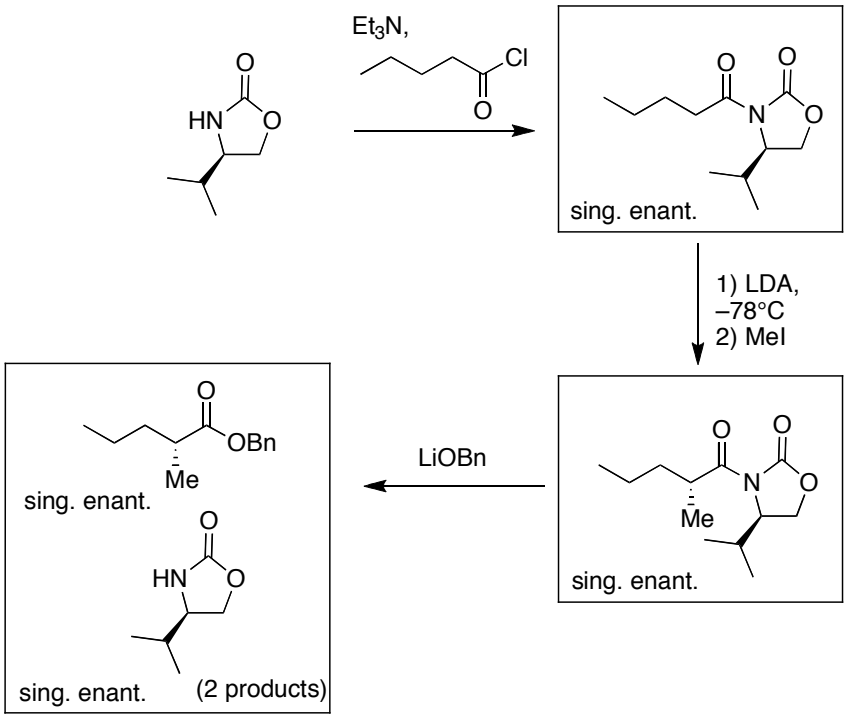
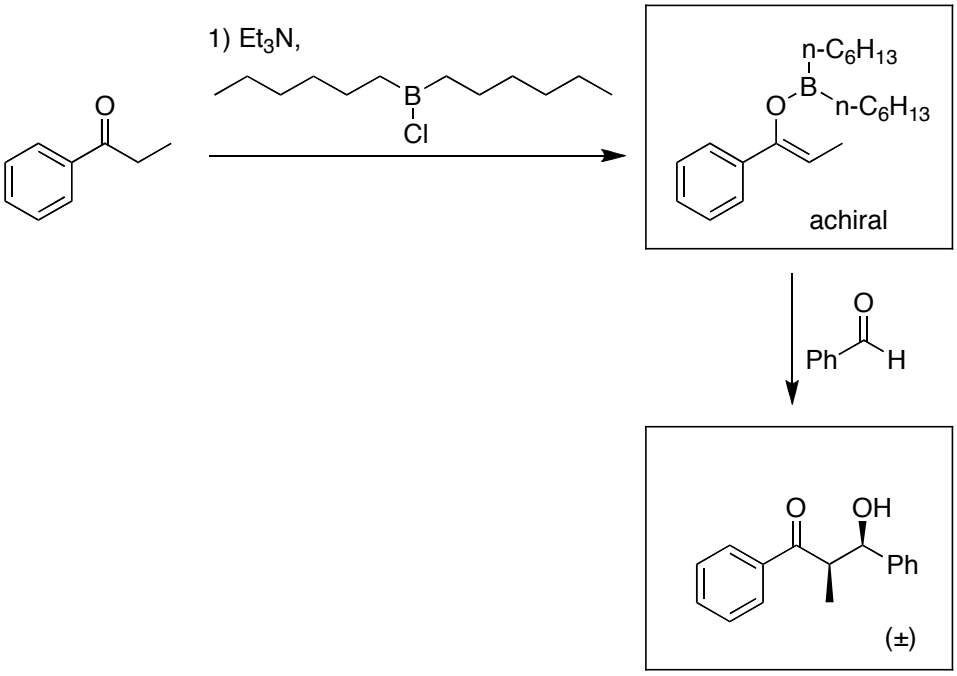
Problem set 7 — ANSWER KEY
Chapter 45.

1. Fill in the boxes with the reagents required to produce the stereoisomer shown, or with the MAJOR stereoisomer produced by the reaction conditions given. If an empty box contains a name instead of a compound, give the structure of the compound. For **all structures**, indicate whether the structure is achiral, a single enantiomer, or racemic.

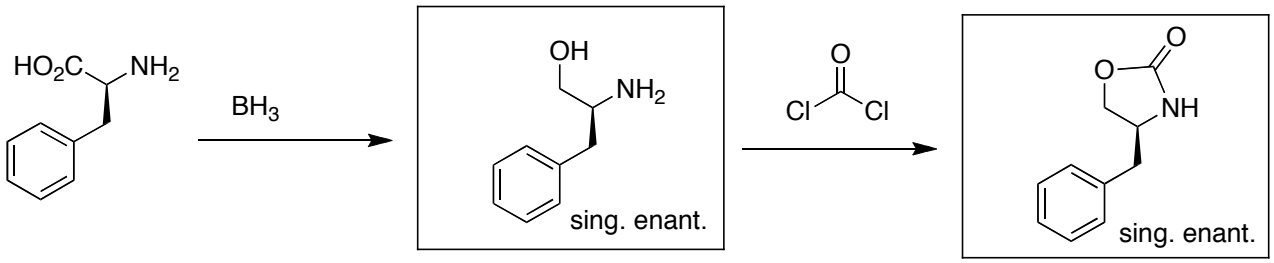
a)



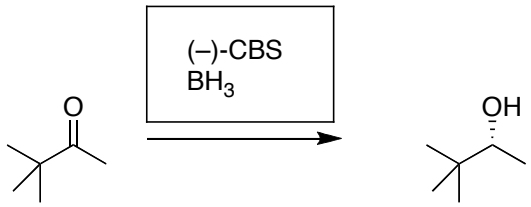
b)



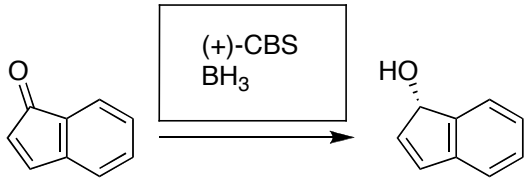
c)


HO2C
NH2
BH3
OH
NH2
sing. enant.
O
Cl
Cl
O
O
NH
sing. enant.

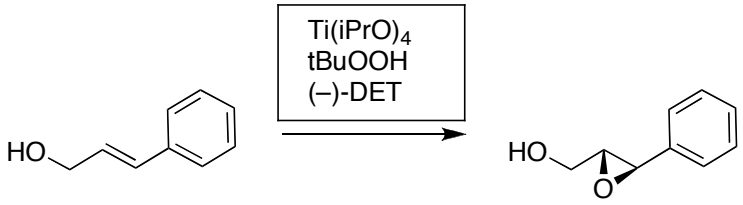
d)


(–)-CBS
BH3
O
OH

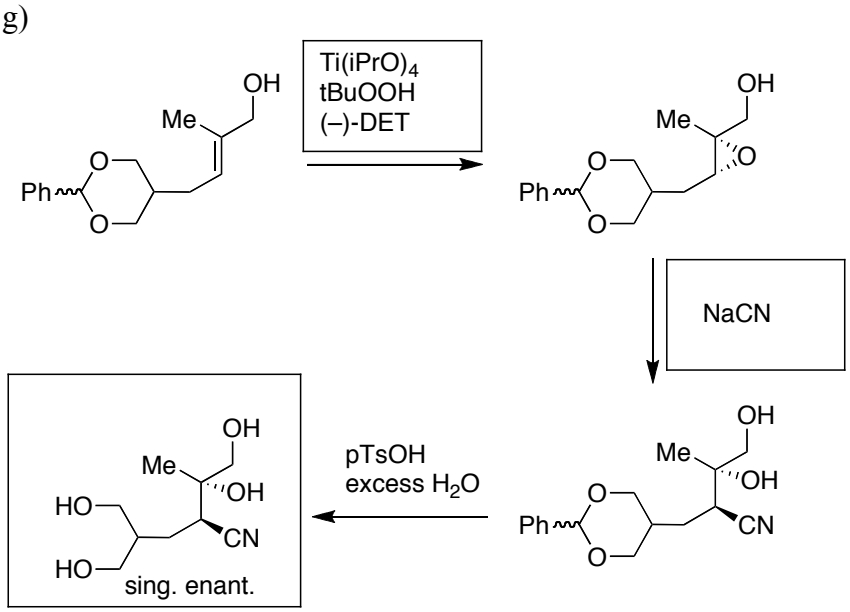
e)


(+)-CBS
BH3
O
HO

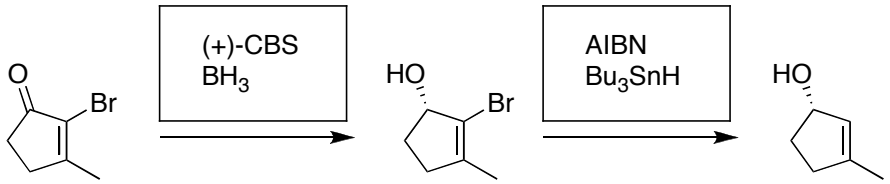
f)


Ti(iPrO)4
tBuOOH
(–)-DET
HO
HO
O

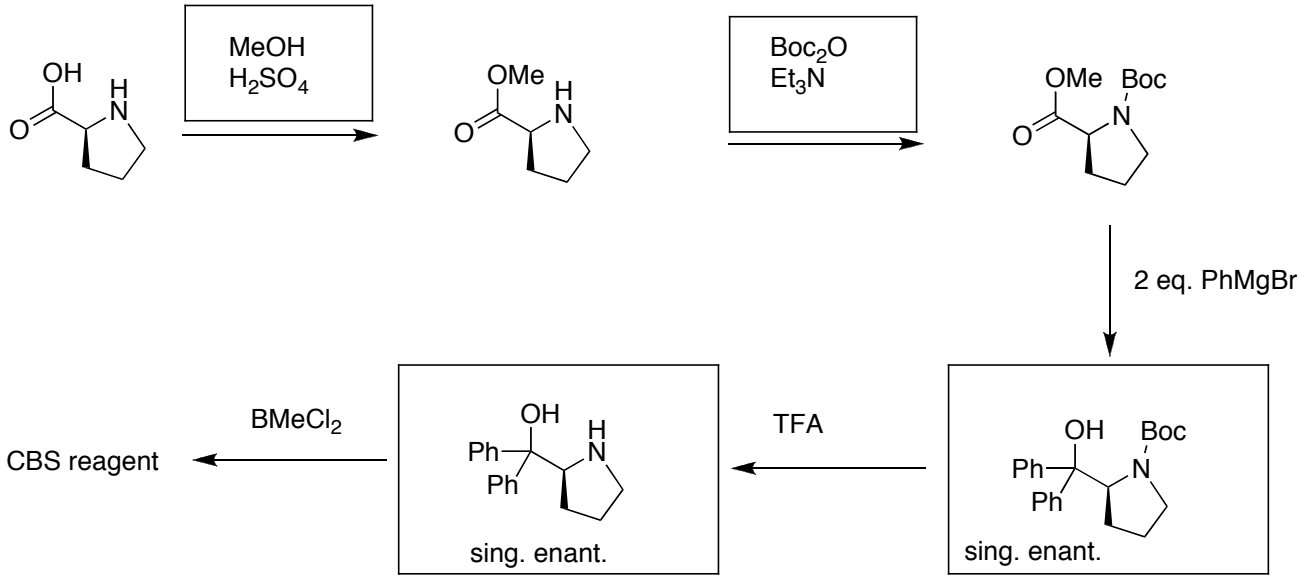
g)


Ti(iPrO)4
tBuOOH
(–)-DET
OH
Me
O
Ph
O
Me
OH
O
Ph
O
NaCN
OH
Me
OH
HO
CN
HO
sing. enant.
pTsOH
excess H2O
OH
Me
OH
O
Ph
CN
O

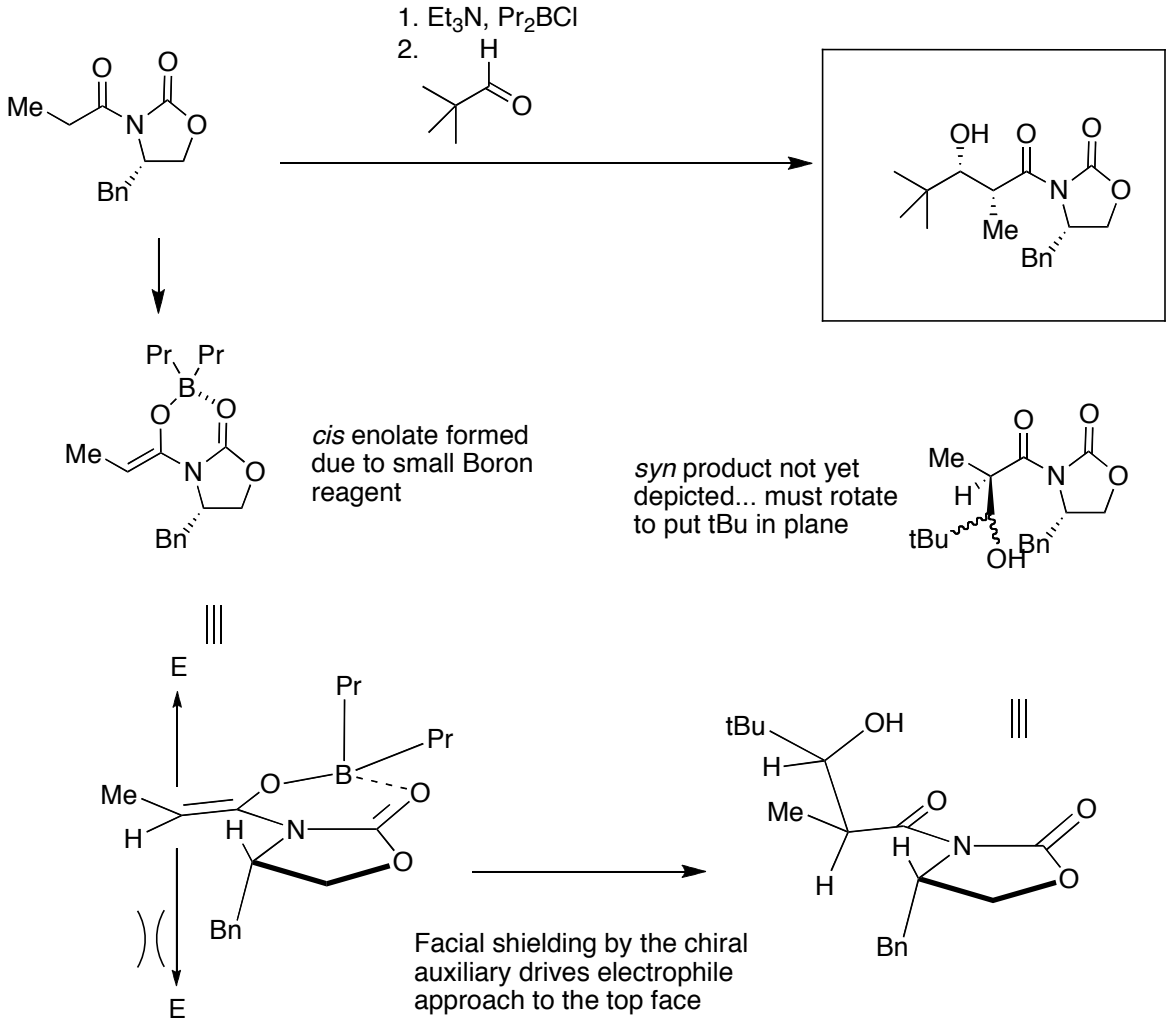
h)


(+)-CBS
BH_3
AIBN
Bu_3SnH
O
Br
HO
Br
HO

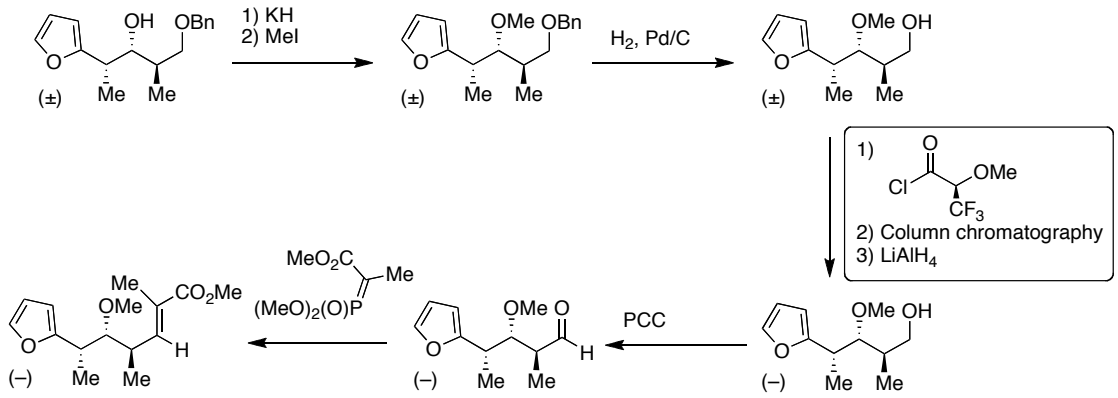
i)


MeOH
H_2SO_4
Boc_2O
Et_3N
OH
H
N
O
OMe
H
N
O
OMe
Boc
N
O
2 eq. PhMgBr
OH
Boc
Ph
N
Ph
sing. enant.
TFA
OH
H
Ph
N
Ph
sing. enant.
$BMeCl_2$
CBS reagent

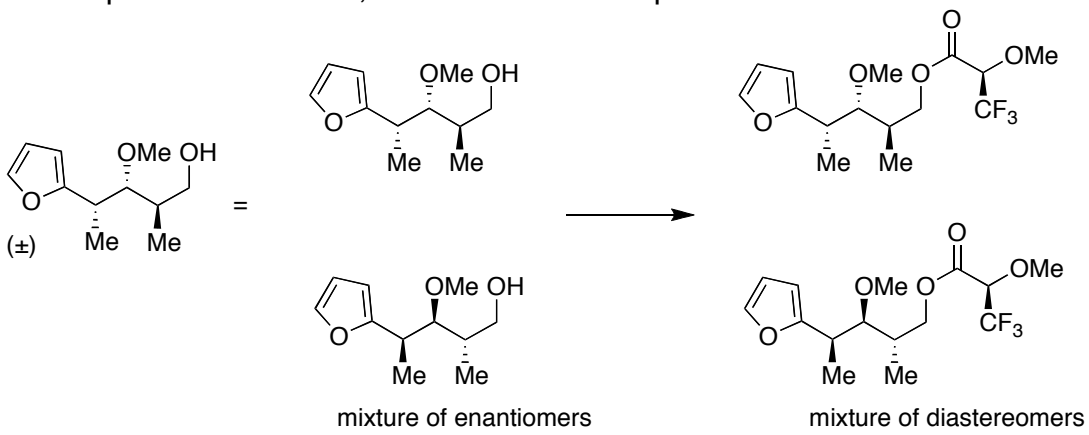
2. Give the product of the following reaction. Predict the stereochemistry at all new stereocenters, and explain the origin of the observed stereoselectivity at each center.



3. The following reaction sequence was used in the synthesis of Monensin. The steps highlighted in the box are especially interesting. Give the structure of the product of each of these three steps, and explain in detail why these steps were carried out.



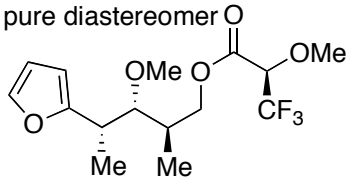
STEP 1: The racemic starting alcohol is actually two enantiomers. Upon reaction with the enantiopure acid chloride, two diastereomeric products result:



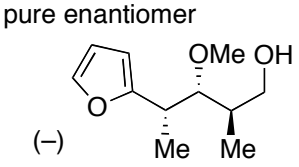
mixture of enantiomers

mixture of diastereomers

STEP 2: Column chromatography can separate these two compounds *because they are diastereomers*. As the beginning enantiomers, they would have been inseparable using normal chromatography. The diastereomer with the desired stereochemistry is isolated.



STEP 3: treatment with $LiAlH_4$ (the hammer) reduces (crushes) the ester back down to the alcohol, which is now a single enantiomer.



4. Give a definition and an example of chiral induction. Include the structures of starting materials and products, and make the source of the induction clear using a 3D diagram.

Chiral induction is the use of an existing stereocenter to set the stereochemistry of a new, neighbouring stereocenter. There are many, many examples of this throughout the course — check out Assignments 4 and 5 for several good examples of chiral induction and the 3D diagrams that help to explain it.

END