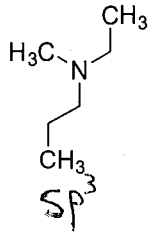
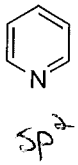
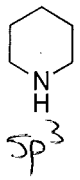
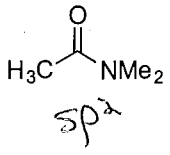
Worksheet 8, Chem 51C, Jarvo

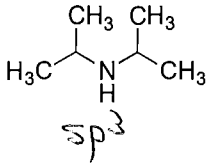
1. a. Label the hybridization of each nitrogen.

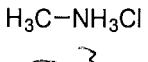




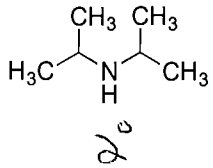


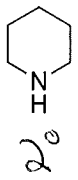


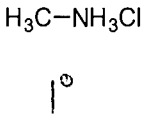


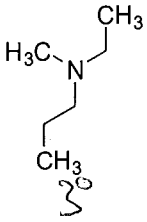


b. Label each amine as 1°, 2°, or 3°

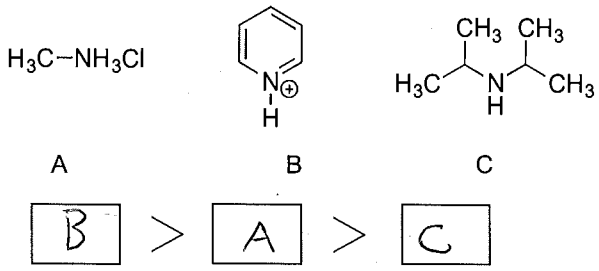




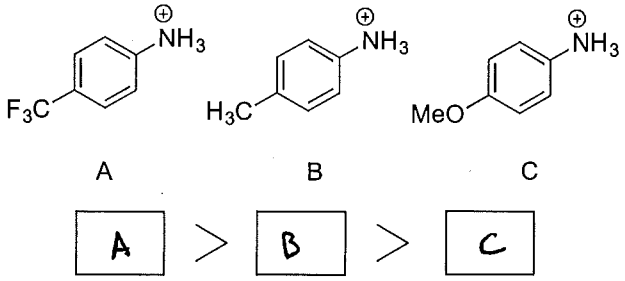




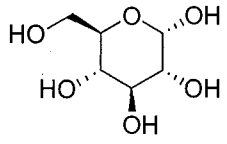
c. Rank from most to least acidic. For each compound, label with the pK_a and draw the conjugate base.

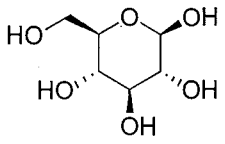


d. Rank from most to least acidic. For each compound, label with the pK_a and draw the conjugate base..

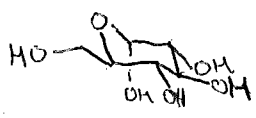


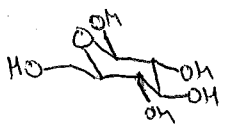
e. Draw the three-dimensional chair represenations of the following carbohydrates:



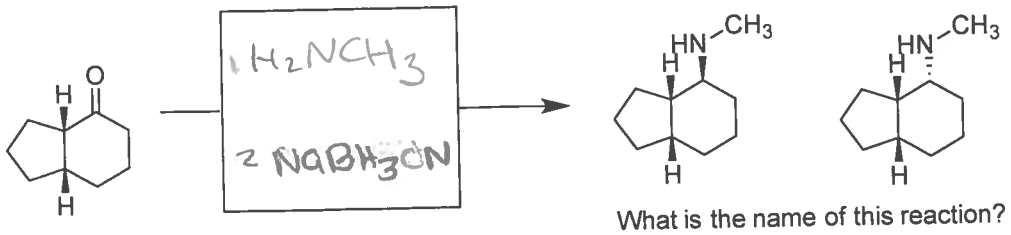


What are the names of these compounds?
What is the relationship between them?

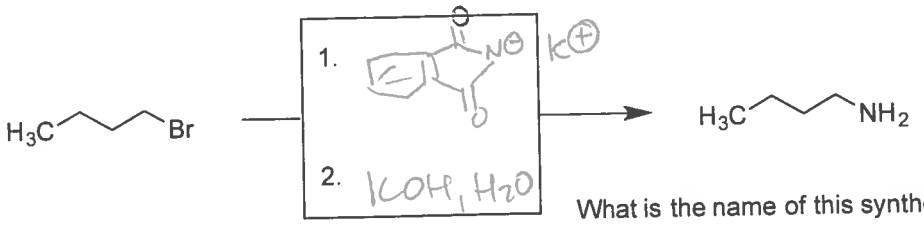




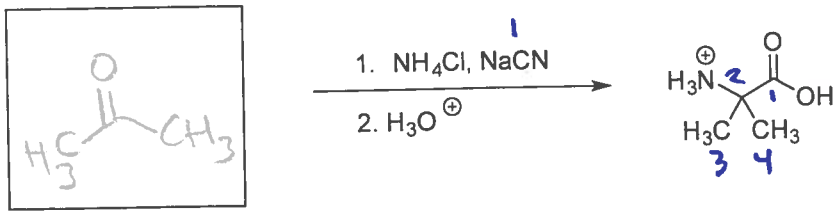
2. Fill in the boxes with the appropriate starting material, reagent or major product.
Show stereochemistry where appropriate

a. 

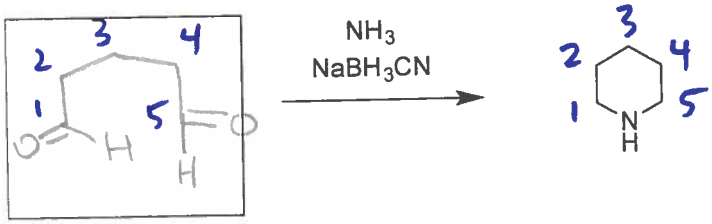
What is the name of this reaction? Reductive amination

b. 

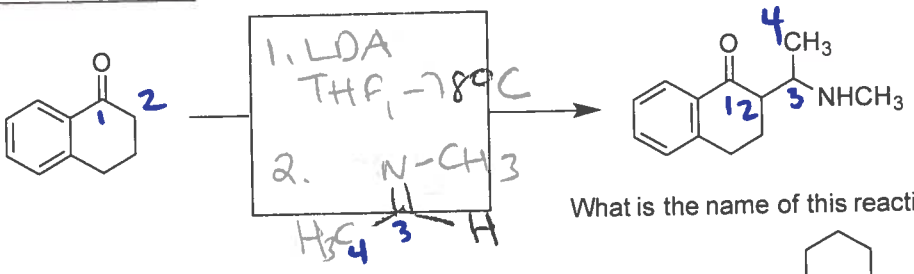
What is the name of this synthesis? Gabriel Synthesis

c. 

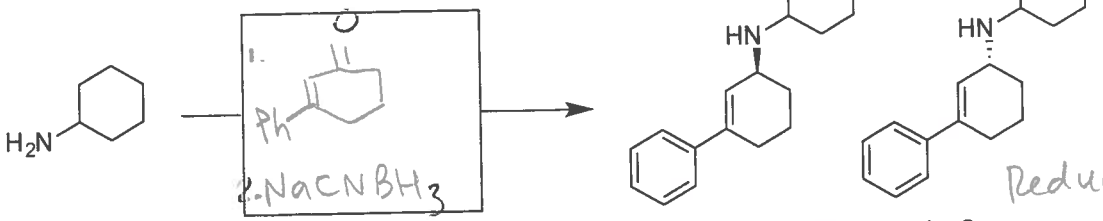
Strecker

d. 

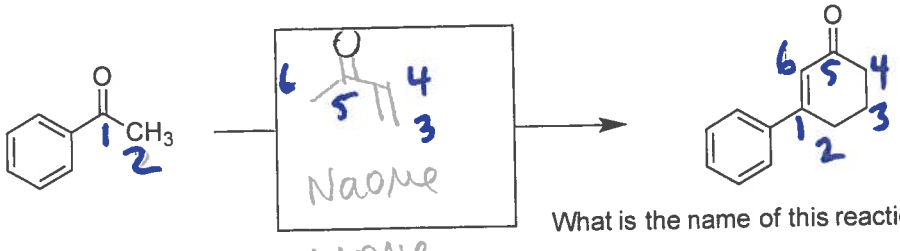
reductive amination

e. 

What is the name of this reaction? mannich

f. 

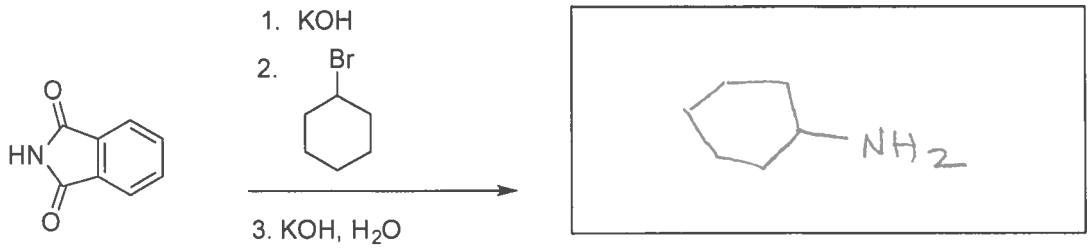
What is the name of this reaction? Reductive amination

g. 

What is the name of this reaction? Robinson annulation

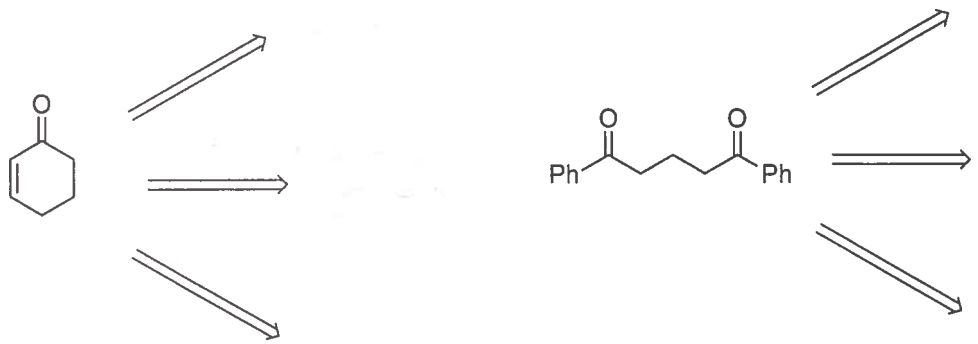
3. Fill in the blank and provide an arrow-pushing mechanism.

a.

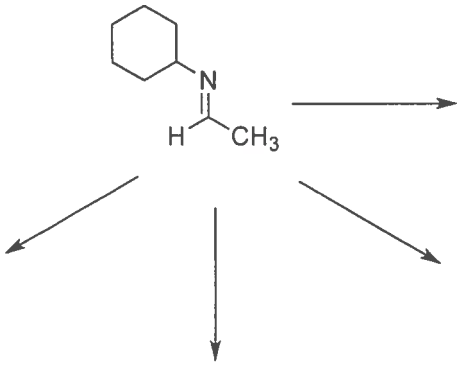


Gabriel synthesis

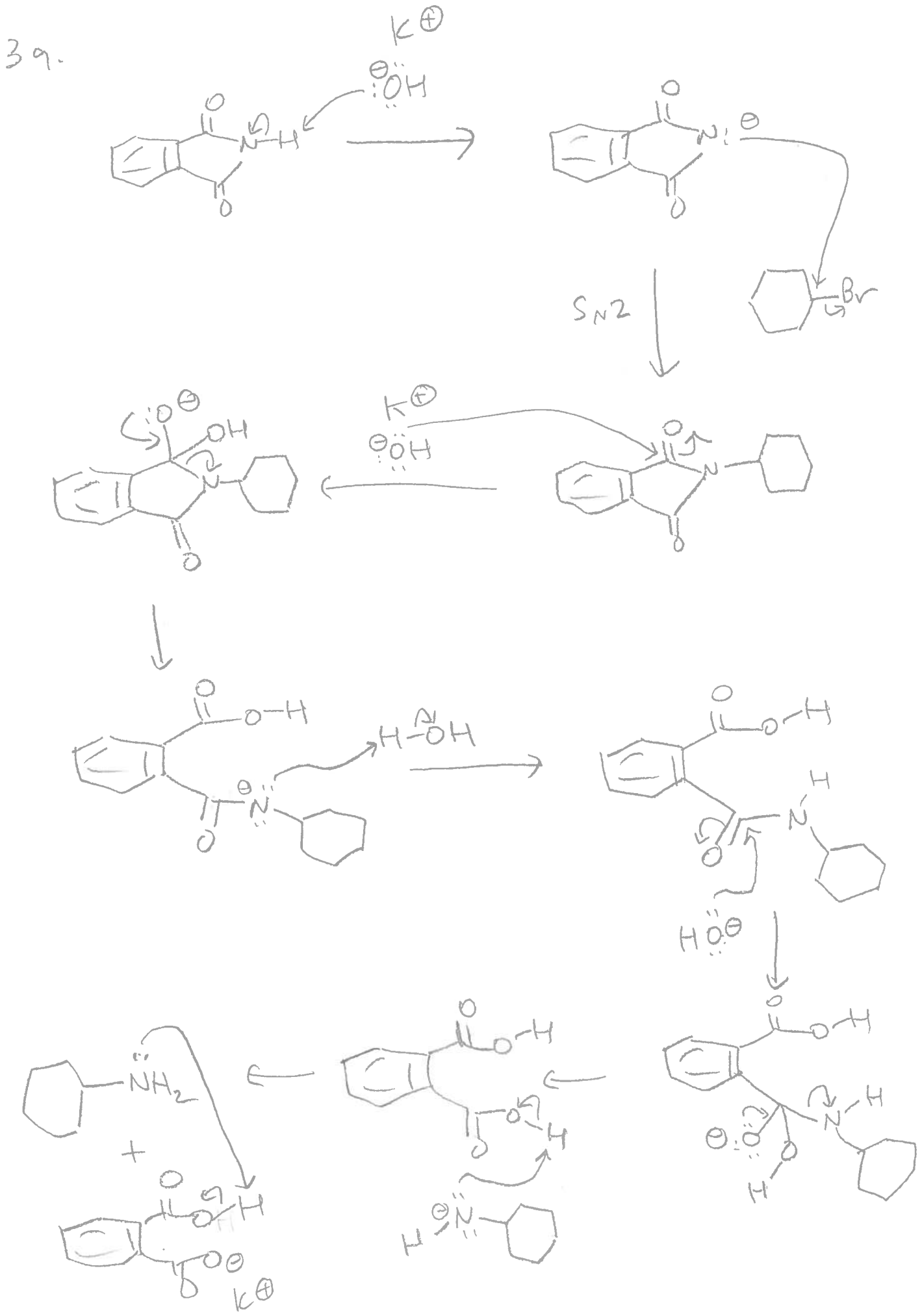
b. Propose 3 different syntheses, each starting from different starting materials



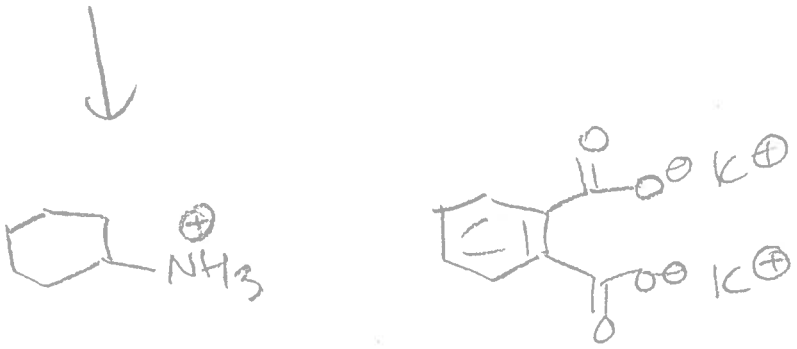
c. Propose 4 different reactions of the imine below, each leading to different products



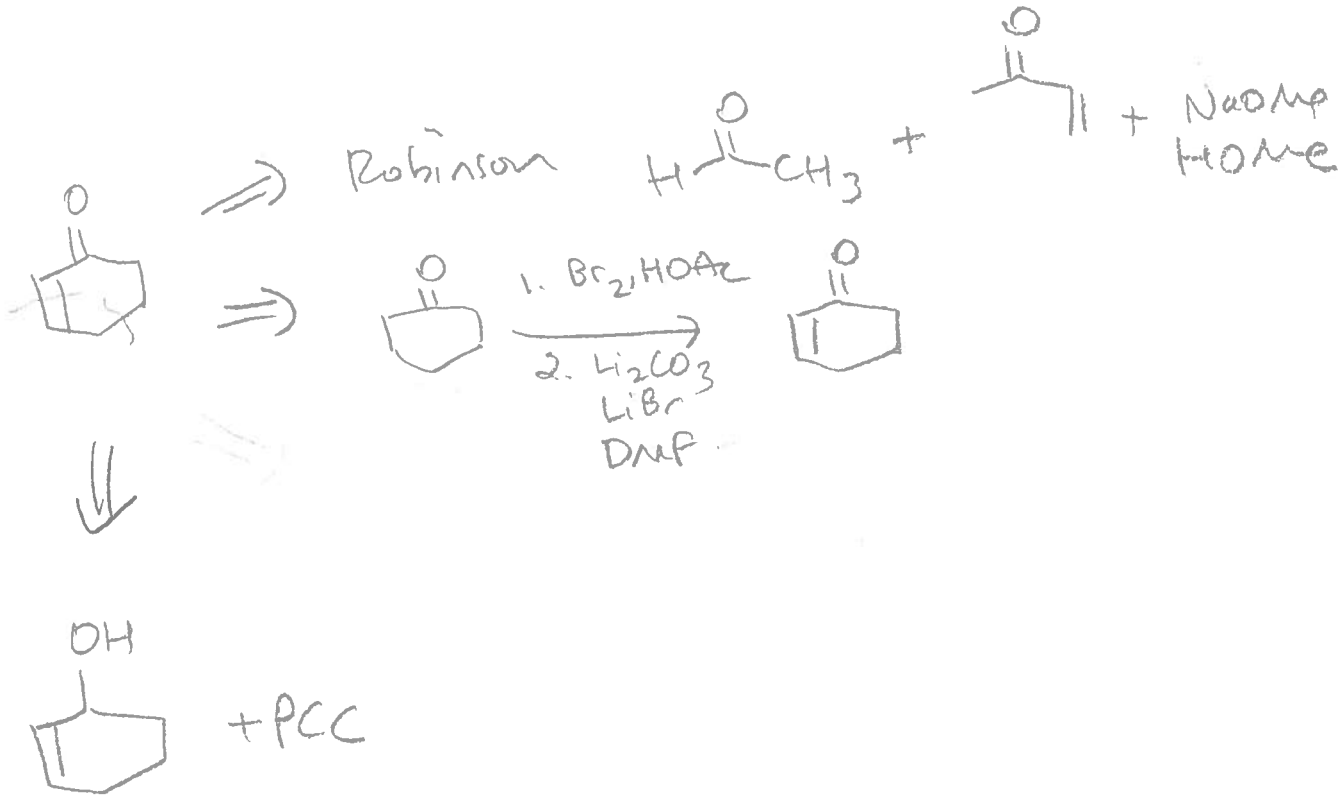
39.

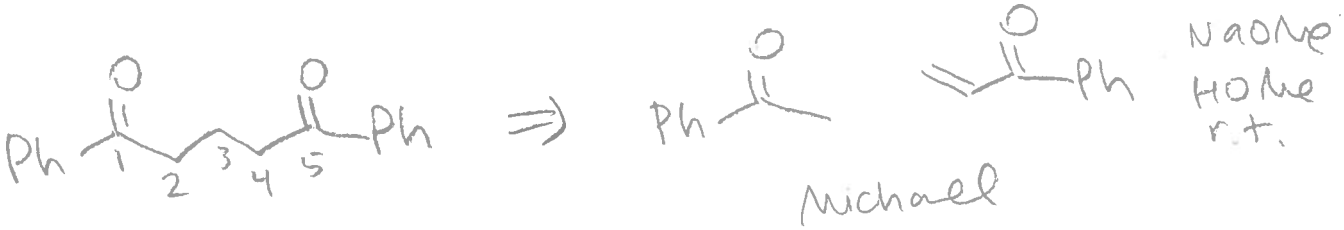


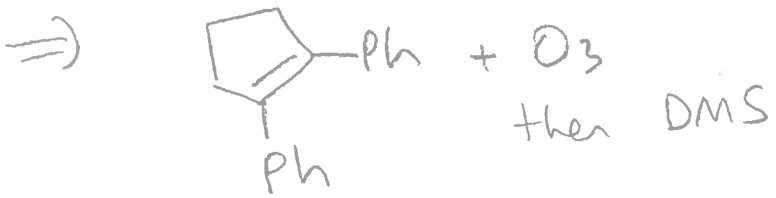
3a continued



36.

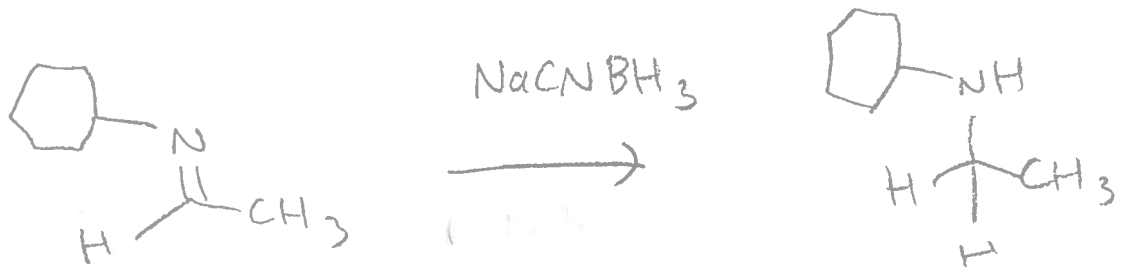

Robinson
+
NaOMe
HOMe
1. Br_2, HOAc
2. Li_2CO_3
LiBr
DMF
OH
+PCC

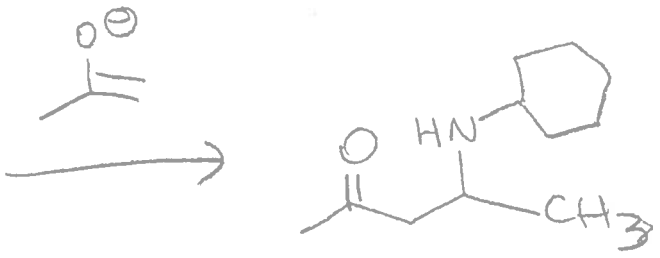

Ph
Ph
1
2
3
4
5
Ph
Michael
NaOMe
HOMe
r.t.


Ph
Ph
+ O_3
then DMS

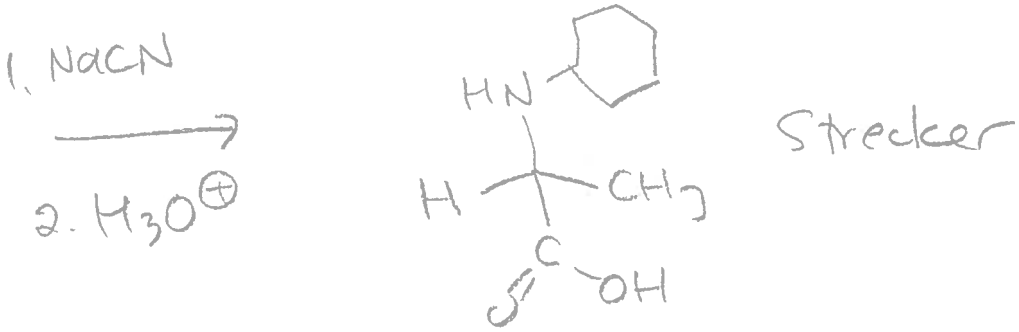

Cl
Cl
+ Ph_2CuLi

3c.

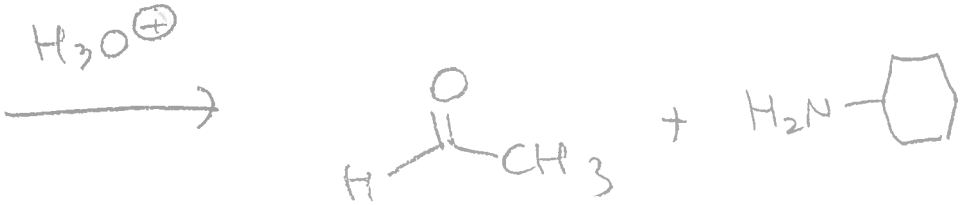




Mannich

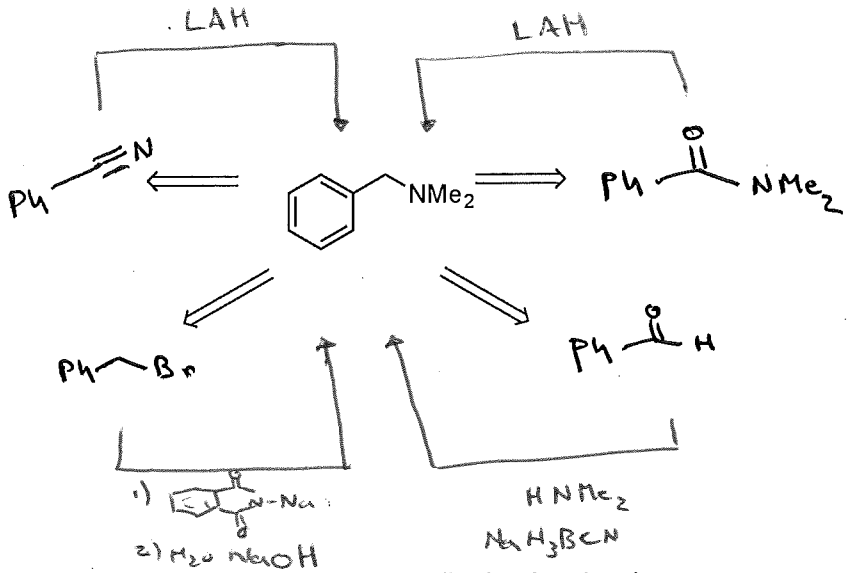


Strecker

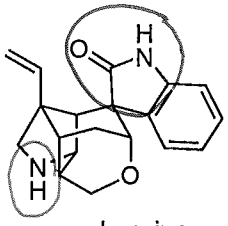


hydrolysis

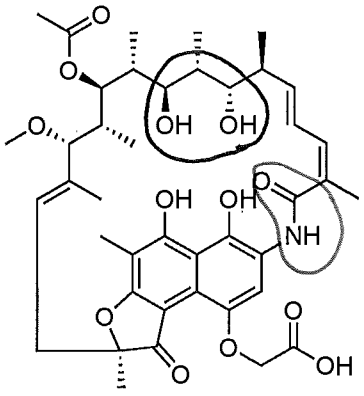
4. a. Show at least four different methods for synthesis of the amine below, each one from a different starting material.



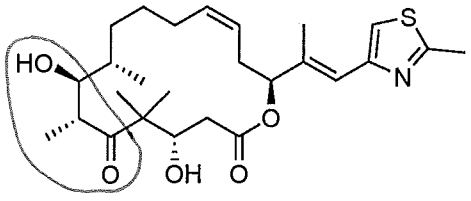
b. In the following natural products, circle and label the following functional groups:
lactam, amide, amine, β-hydroxyketone, 1,3-diol



gelsemine

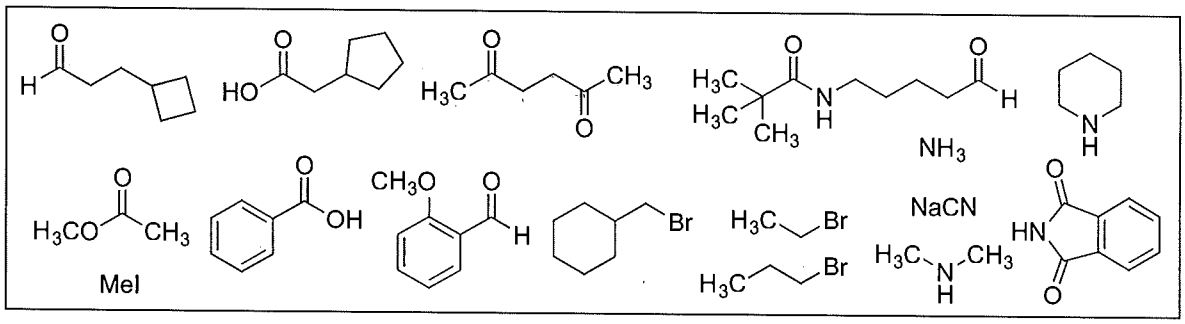


Rifamycin B

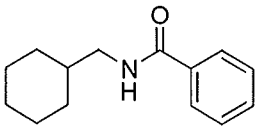


Epothilone C

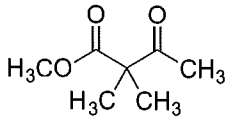
5. Propose syntheses of the targets shown below.
All carbons in the product must come from the starting materials provided, you can use any reagent you wish.



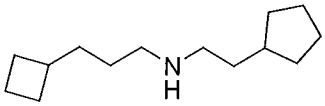
Target A.



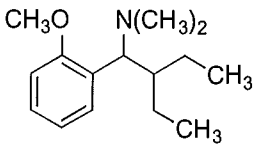
Target B.



Target C.

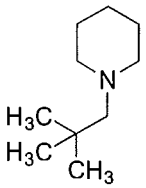


Target E.

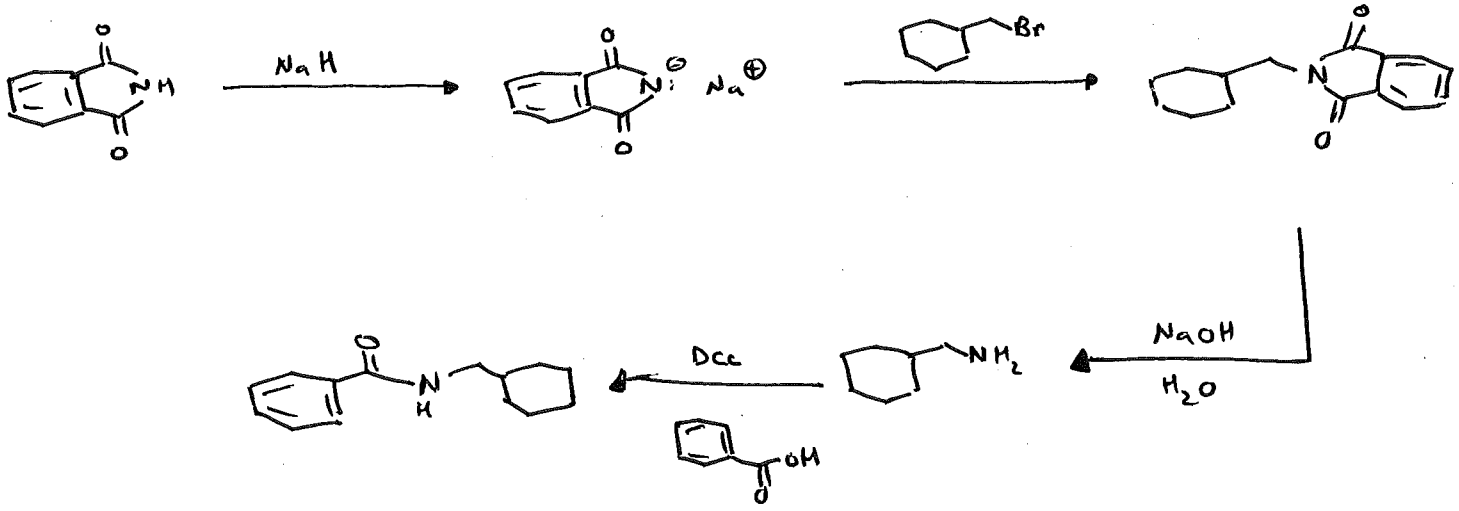


(racemic)

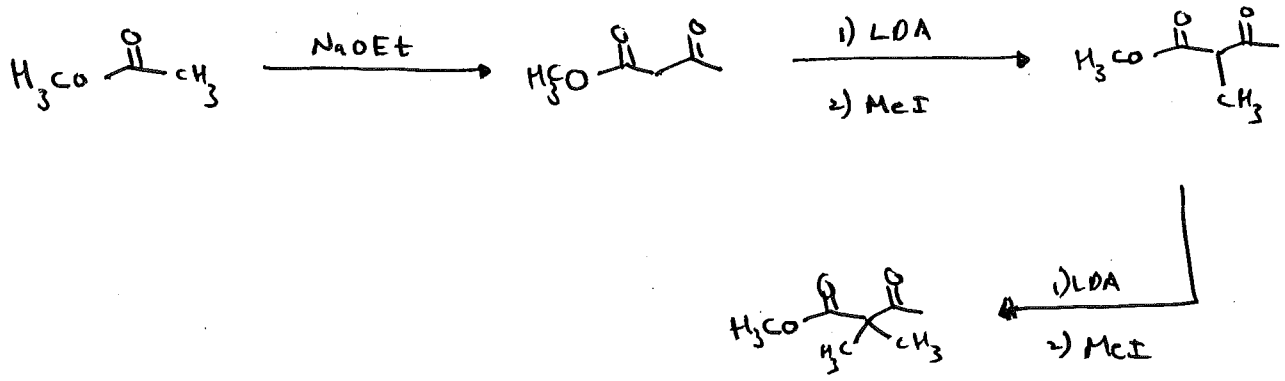
Target F.



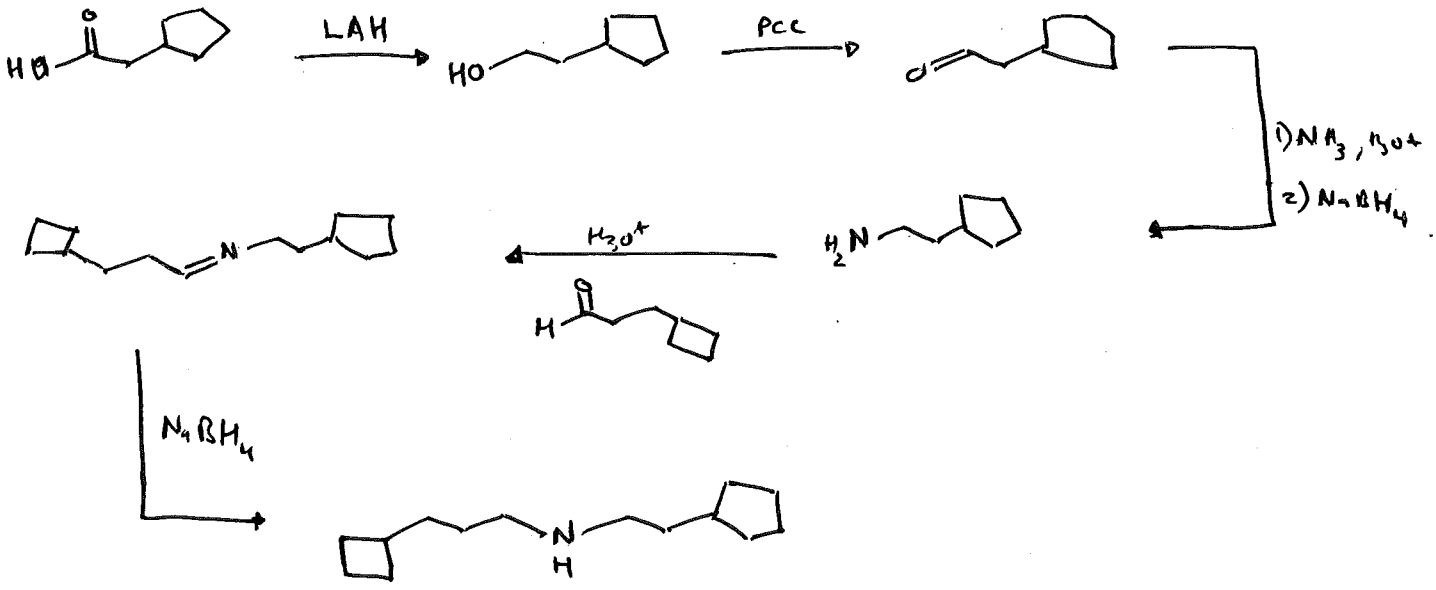
5. A)


NaH
Br
NaOH
H2O
DCC
OH

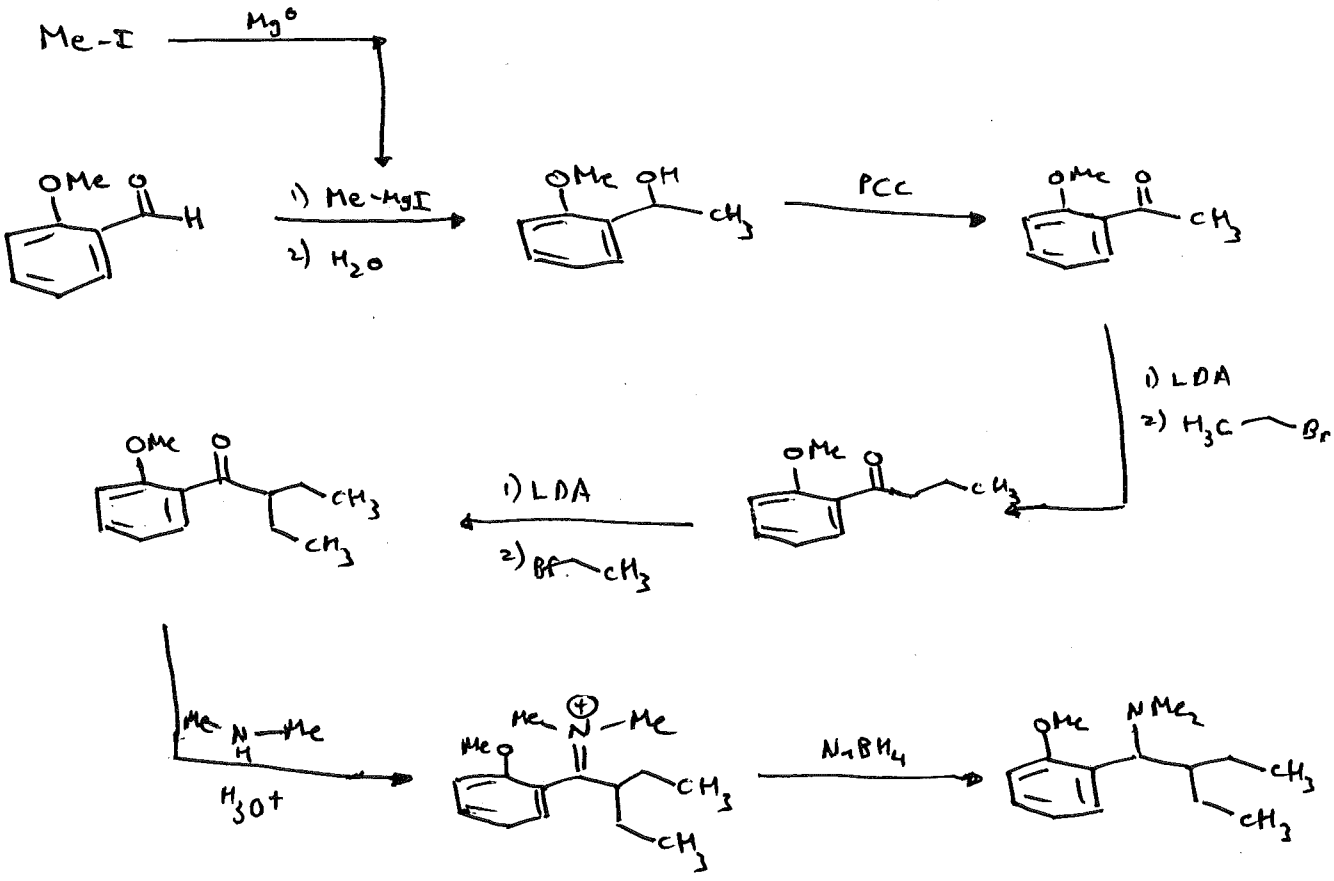
5. B)


NaOEt
1) LDA
2) MeI
1) LDA
2) MeI

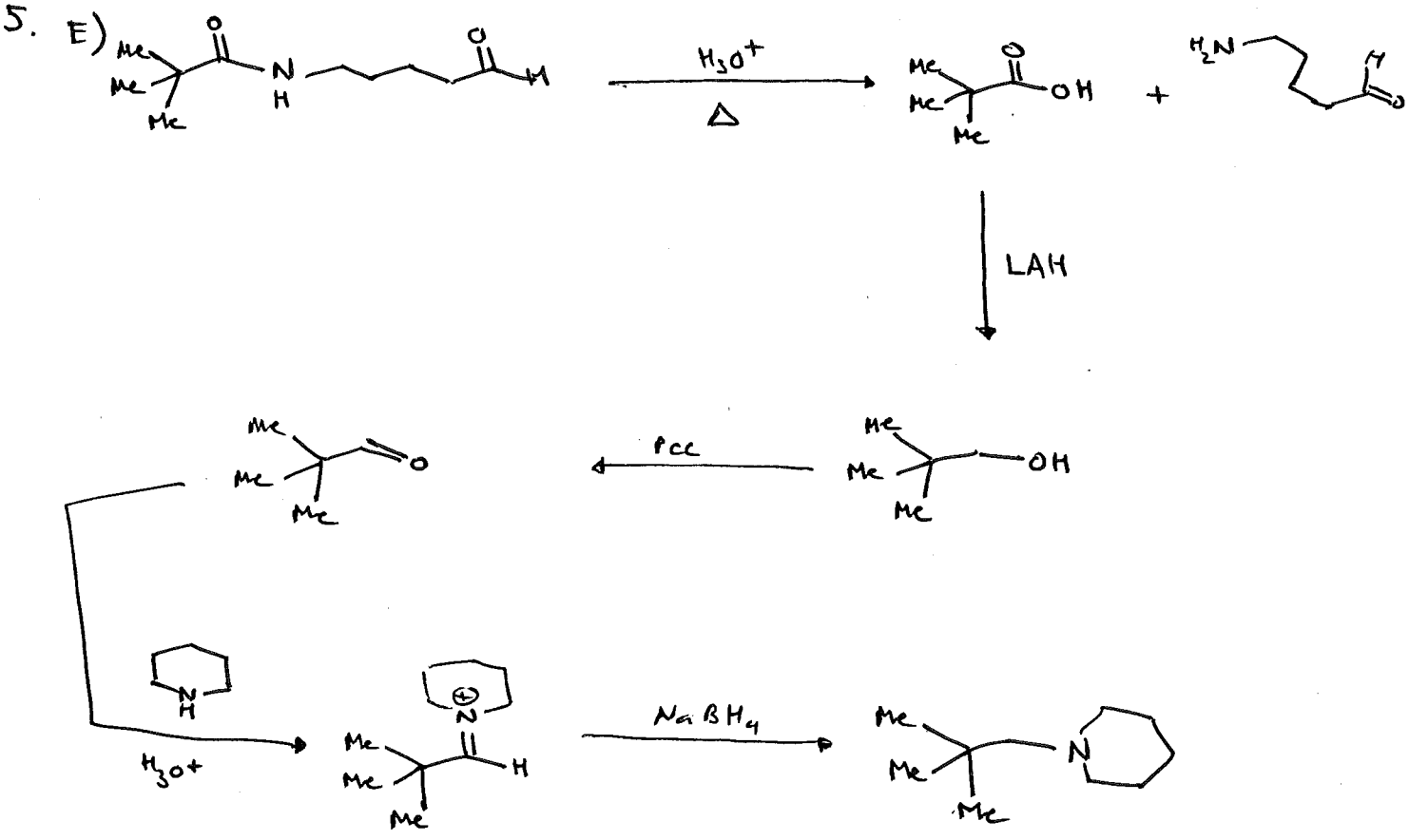
5. C)


LAH
PCC
1) NH3, H3O+
2) NaBH4
H3O+
NaBH4

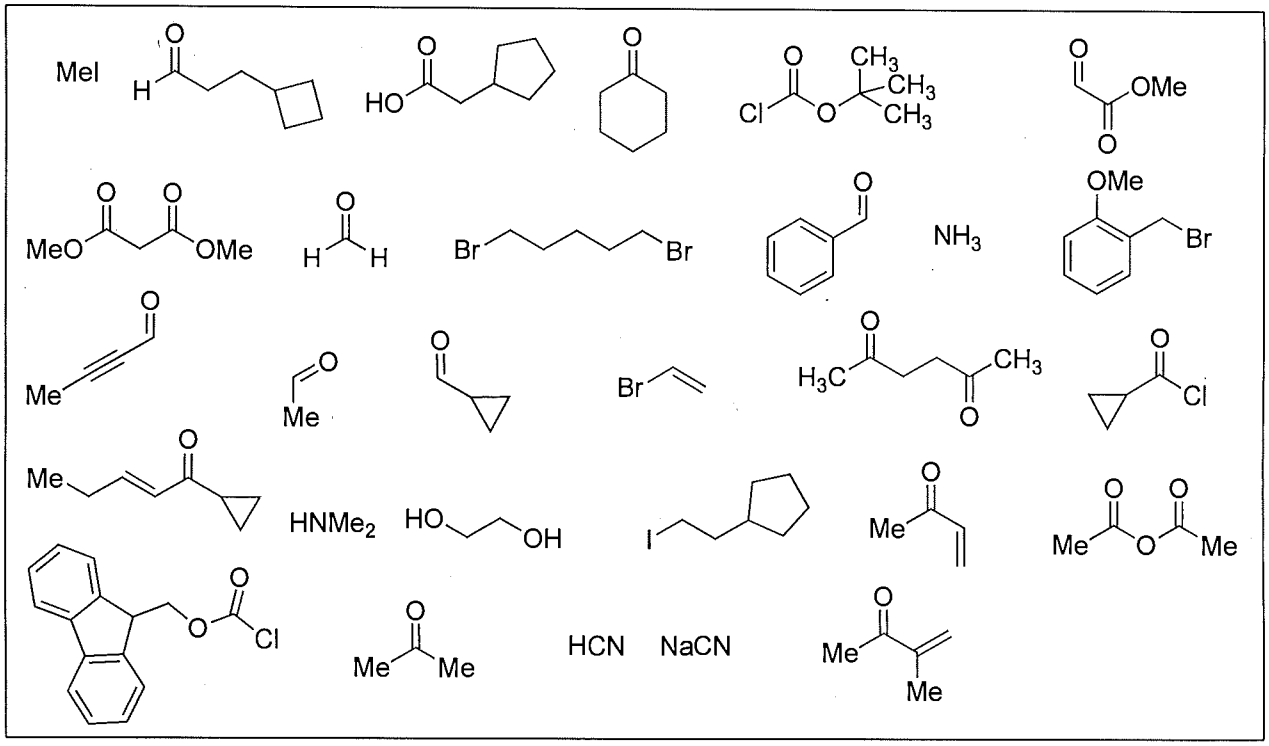
5. D)


Me-I
Mg°
1) Me-MgI
2) H2O
PCC
1) LDA
2) H3C—Br
1) LDA
2) Br—CH3
H3O+
NaBH4

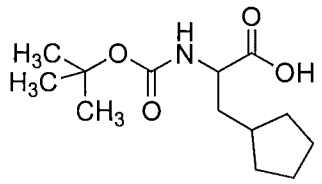
5. E)


H3O+
Δ
LAH
PCC
H3O+
NaBH4

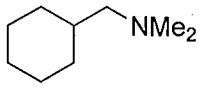
4. Propose syntheses of the targets shown below.
All carbons in the product must come from the starting materials provided, you can use any reagent you wish.



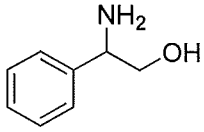
Target A.



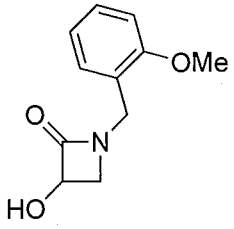
Target B.



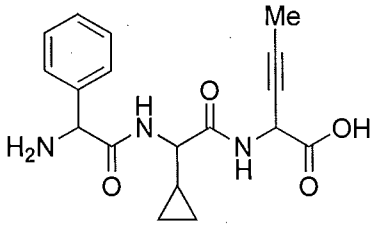
Target C.



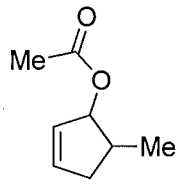
Target D.



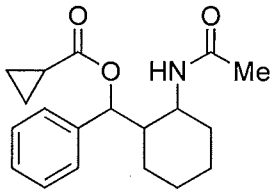
Target E.



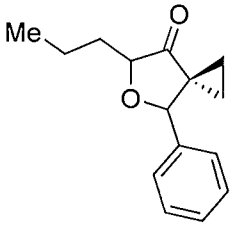
Target F.



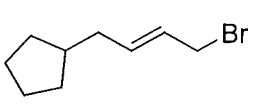
Target G.



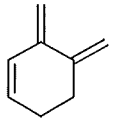
Target H.



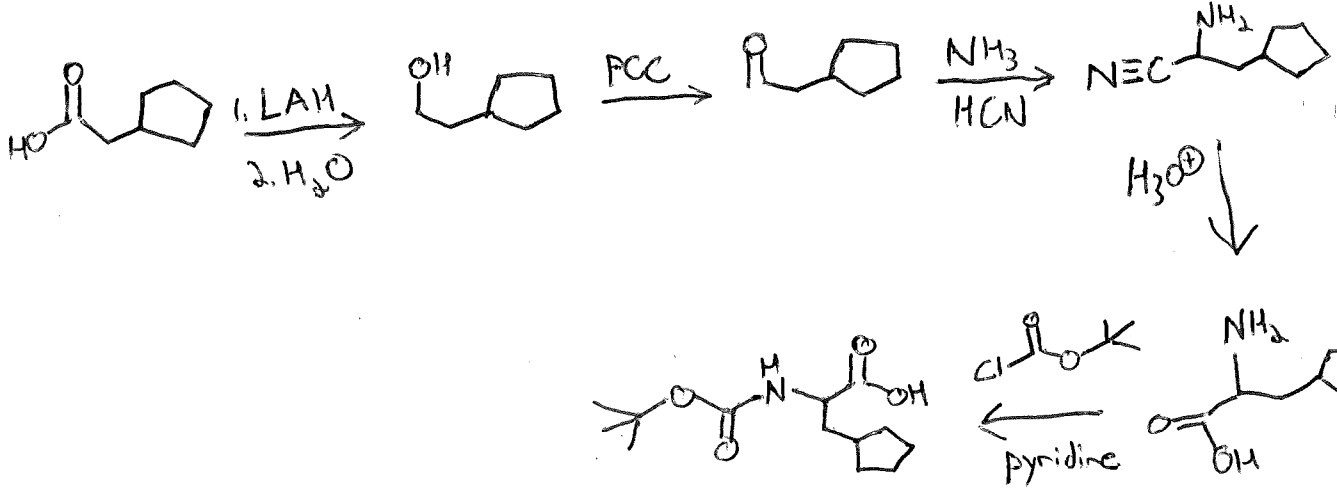
Target I.



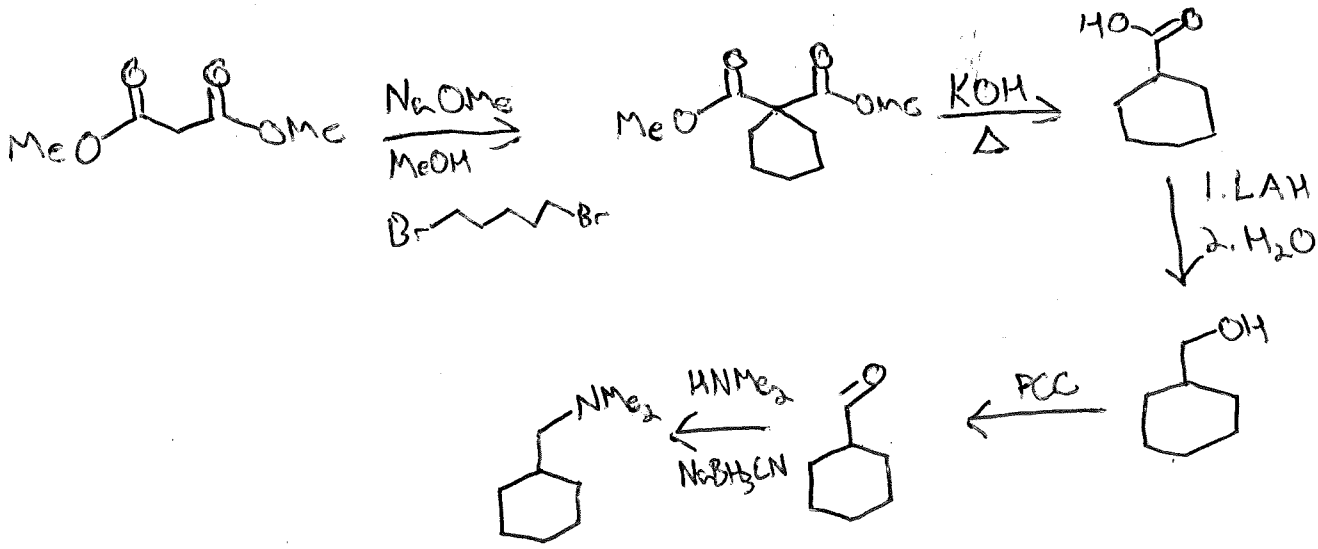
Target J.



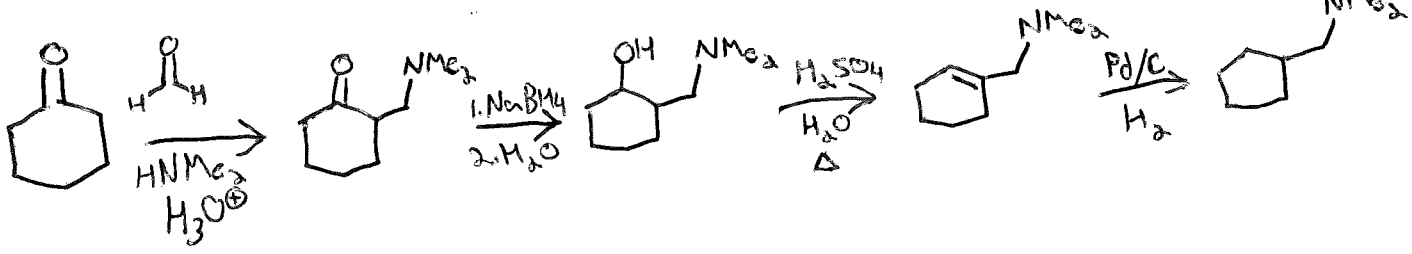
4a


1. LAH
2. H_2O
PCC
NH_3
HCN
$H_3O^{\oplus}$
pyridine

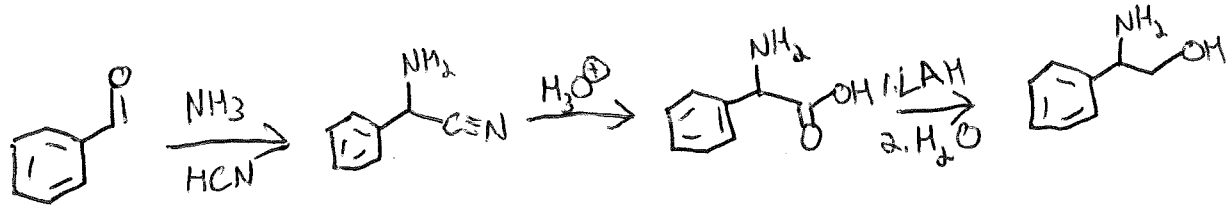
4b


NaOMe
MeOH
KOH
1. LAH
2. H_2O
PCC
$HNMe_2$
$NaBH_3CN$

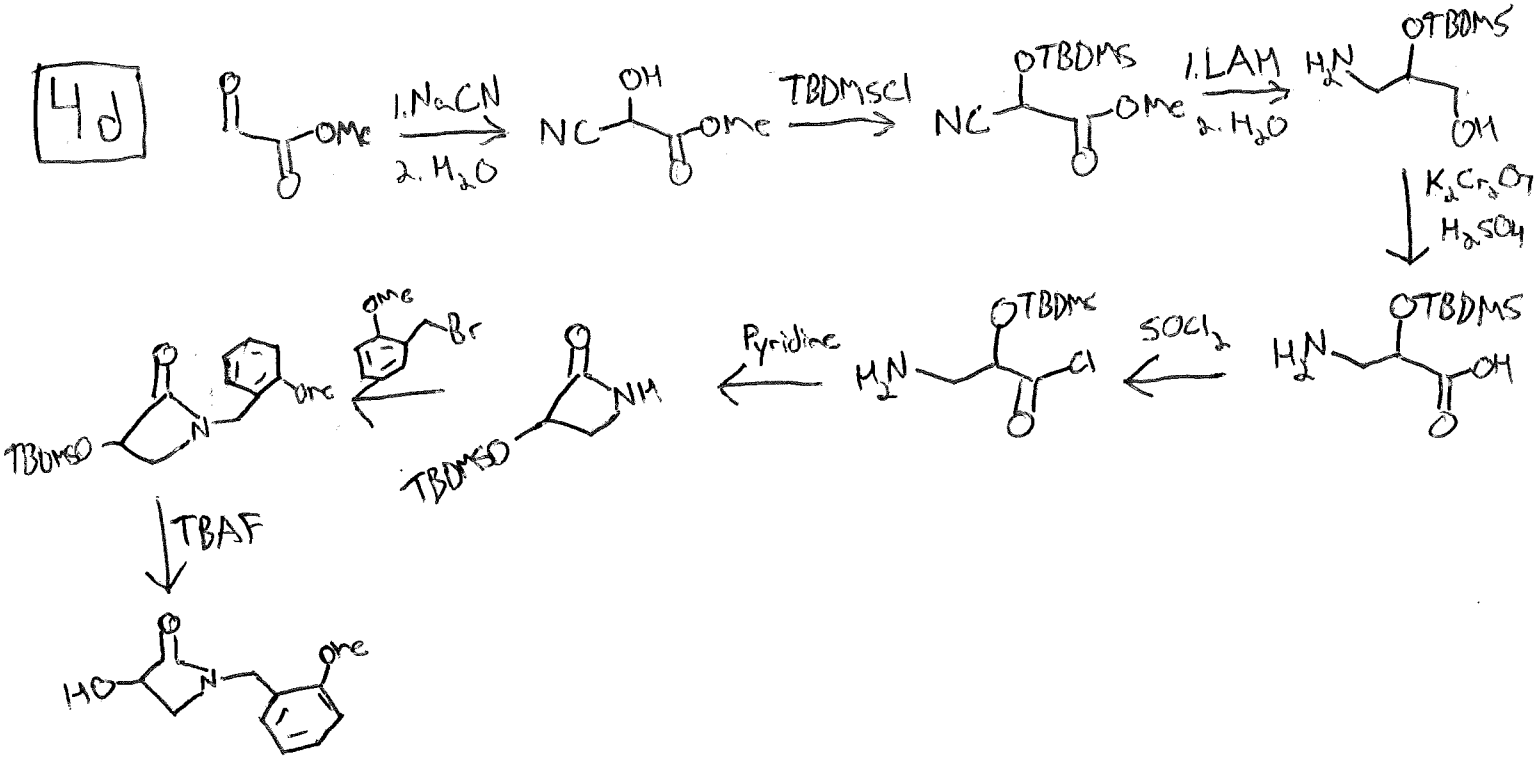
OR


$HNMe_2$
$H_3O^{\oplus}$
1. $NaBH_4$
2. H_2O
H_2SO_4
H_2O
Pd/C
H_2

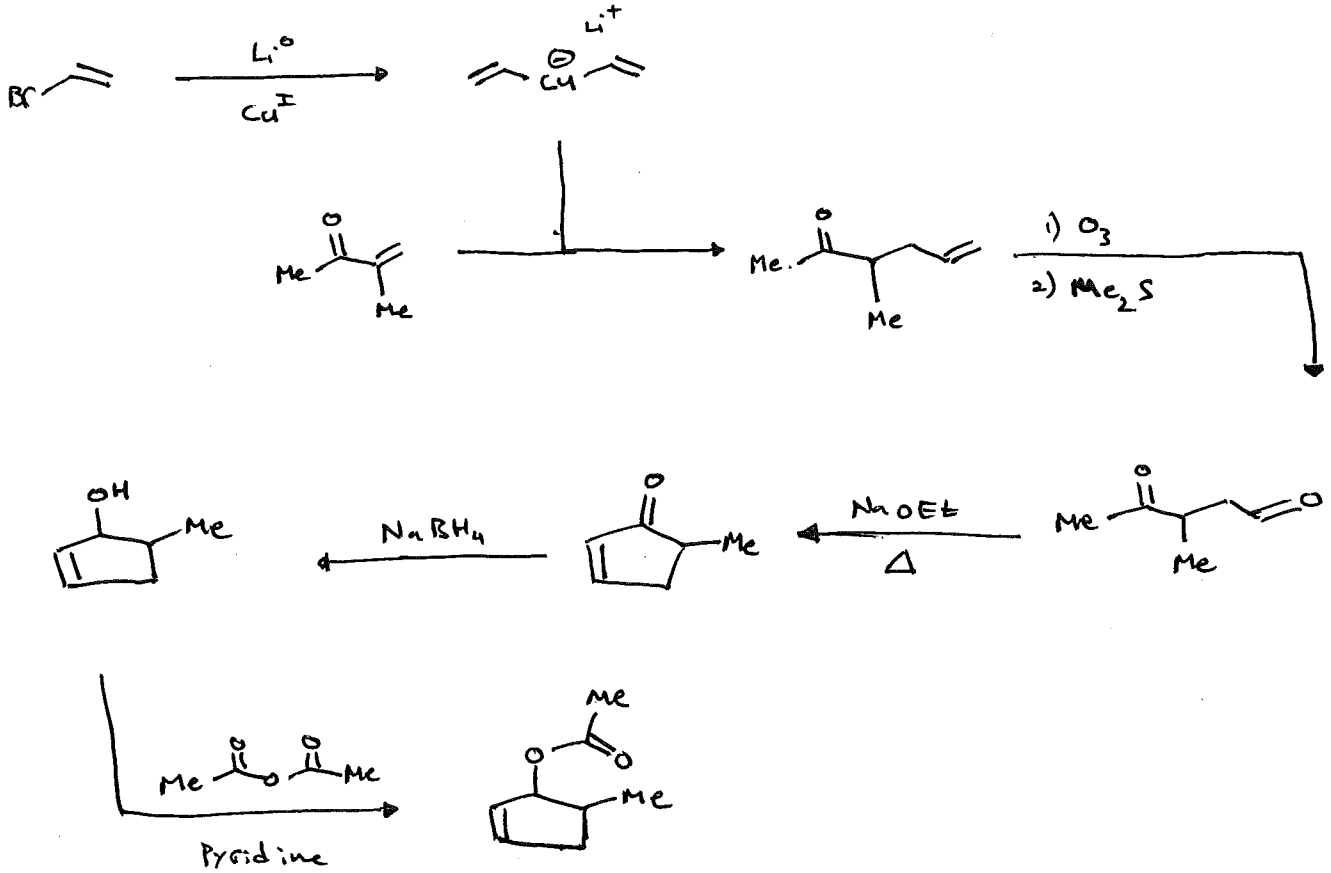
4c


NH3
HCN
NH2
C≡N
H3O⊕
NH2
OH
1. LAH
2. H2O
NH2
OH

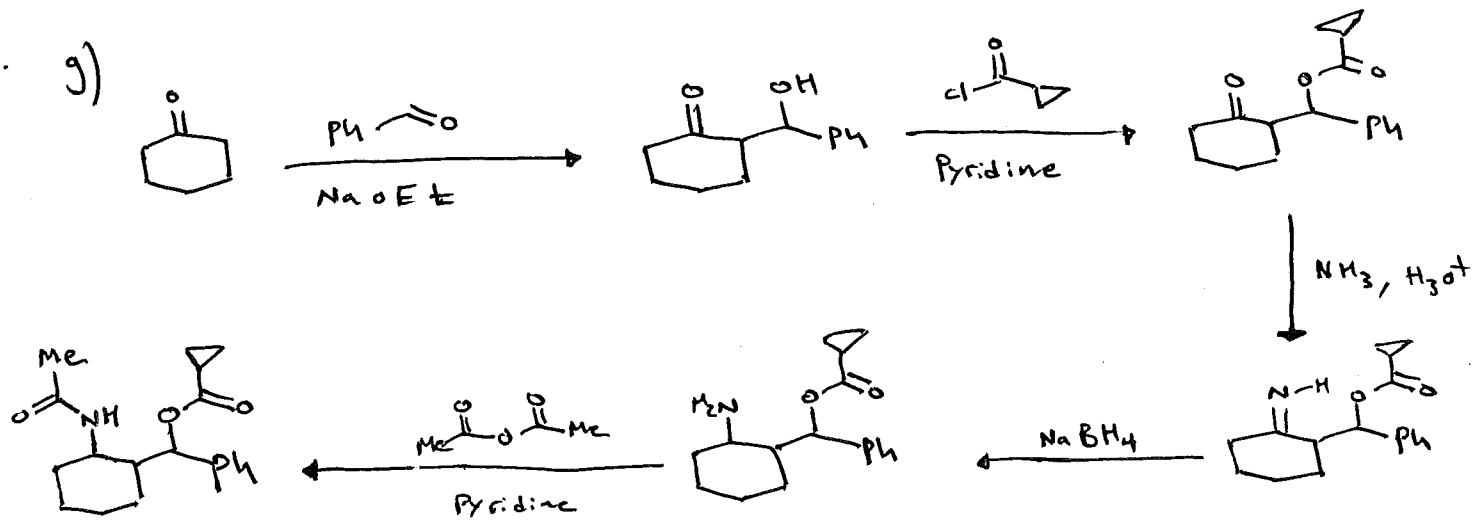
4d


OMe
1. NaCN
2. H2O
NC
OH
OMe
TBDMSCl
NC
OTBDMS
OMe
1. LAH
2. H2O
H2N
OTBDMS
OH
K2Cr2O7
H2SO4
H2N
OTBDMS
OH
SOCl2
H2N
OTBDMS
Cl
Pyridine
TBDMSO
NH
OMe
Br
TBDMSO
N
OMe
TBAF
HO
N
OMe

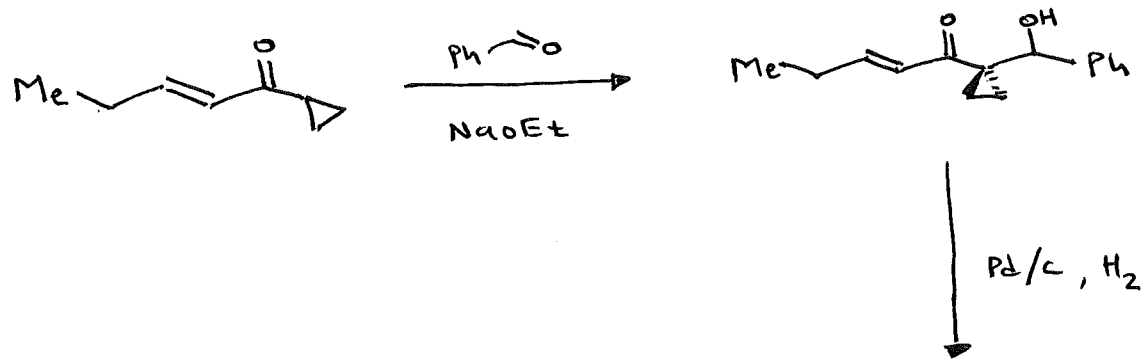
4. f)


Li°
Cu^I
Li+
Me
Me
Me
Me
1) O3
2) Me2S
OH
Me
NaBH4
Me
NaOEt
Δ
Me
Me
Me
Me
Me
Me
Me
Pyridine

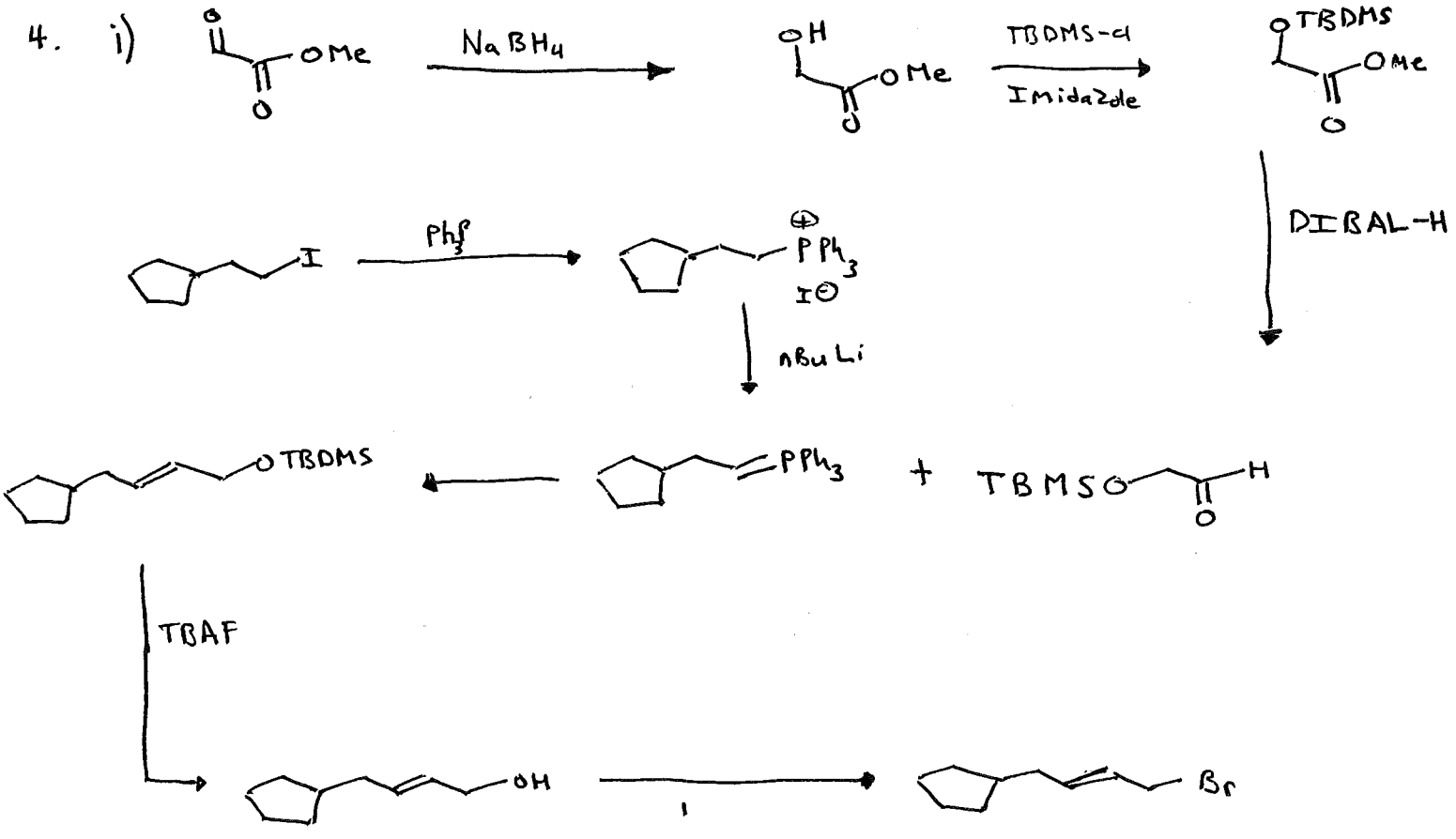
4. g)


Ph
NaOEt
OH
Ph
Cl
Pyridine
Ph
NH3, H3O+
N-H
Ph
NaBH4
H2N
Ph
Me
Me
Pyridine
Me
NH
Ph

4. h)


Me
Ph
NaOEt
OH
Ph
Pd/C , H_2
Me
OH
Ph
Me
OH
Br_2
Me
OH
Ph
Br
NaH
Me

4. i)


OMe
$NaBH_4$
OH
OMe
TBDMS-Cl
Imidazole
OTBDMS
OMe
DIBAL-H
I
PPh_3
$I^\ominus$
nBuLi
OTBDMS
PPh_3
+
TBMSO
H
TBAF
OH
Br

[4J]