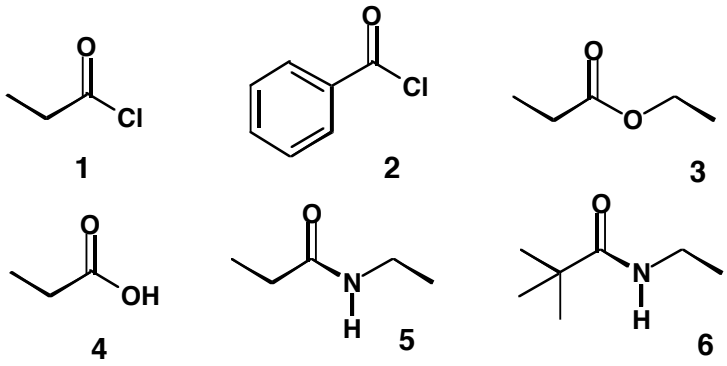
Answer Guide

1.

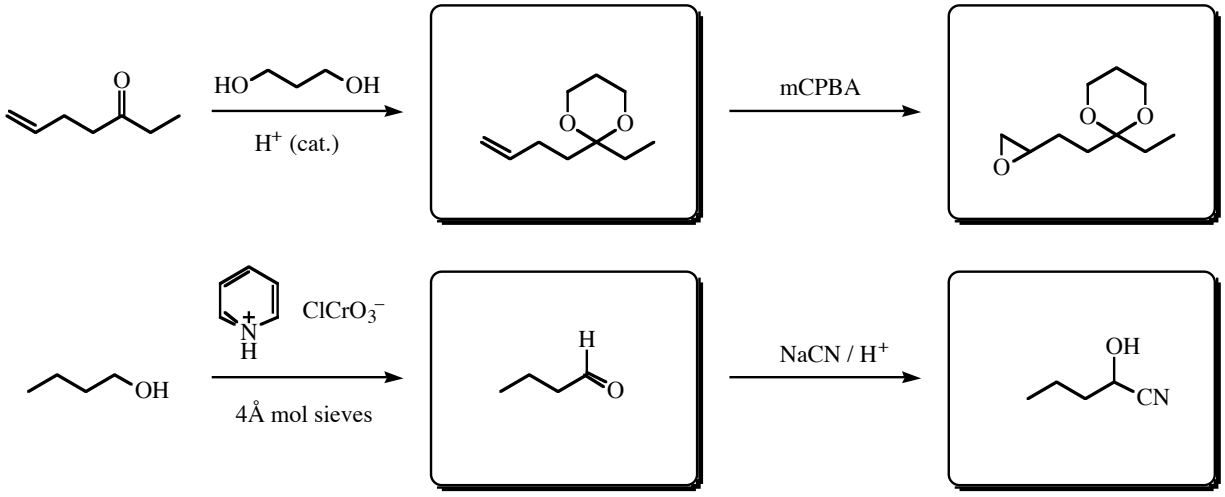


difference between 1 and 2 = resonance stabilization
difference between 5 and 6 = steric effects

2.

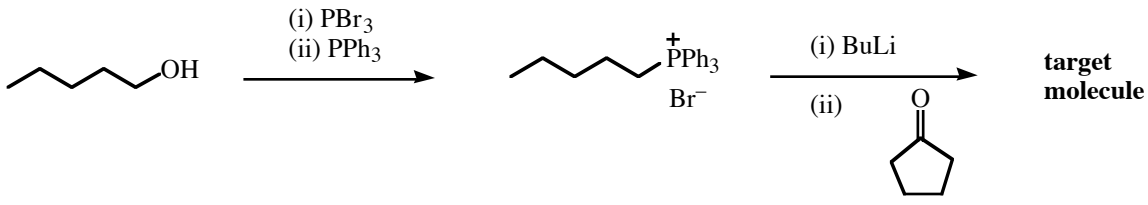
(i) SOCl2
(ii) HNC_5H_{10} / base (e.g. pyridine)
(iii) $LiAlH_4$

3.

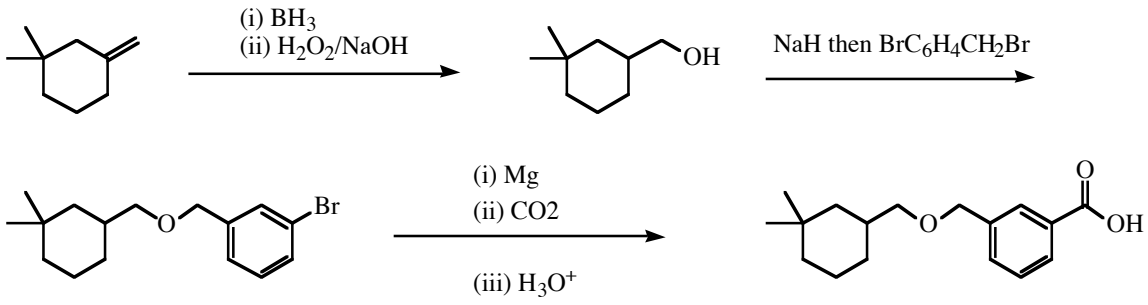


4. see notes on imine formation

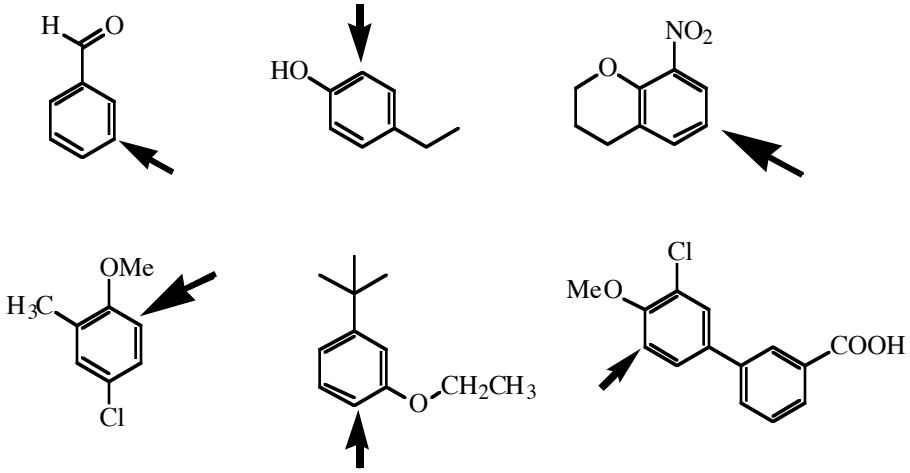
5. use a Wittig based strategy



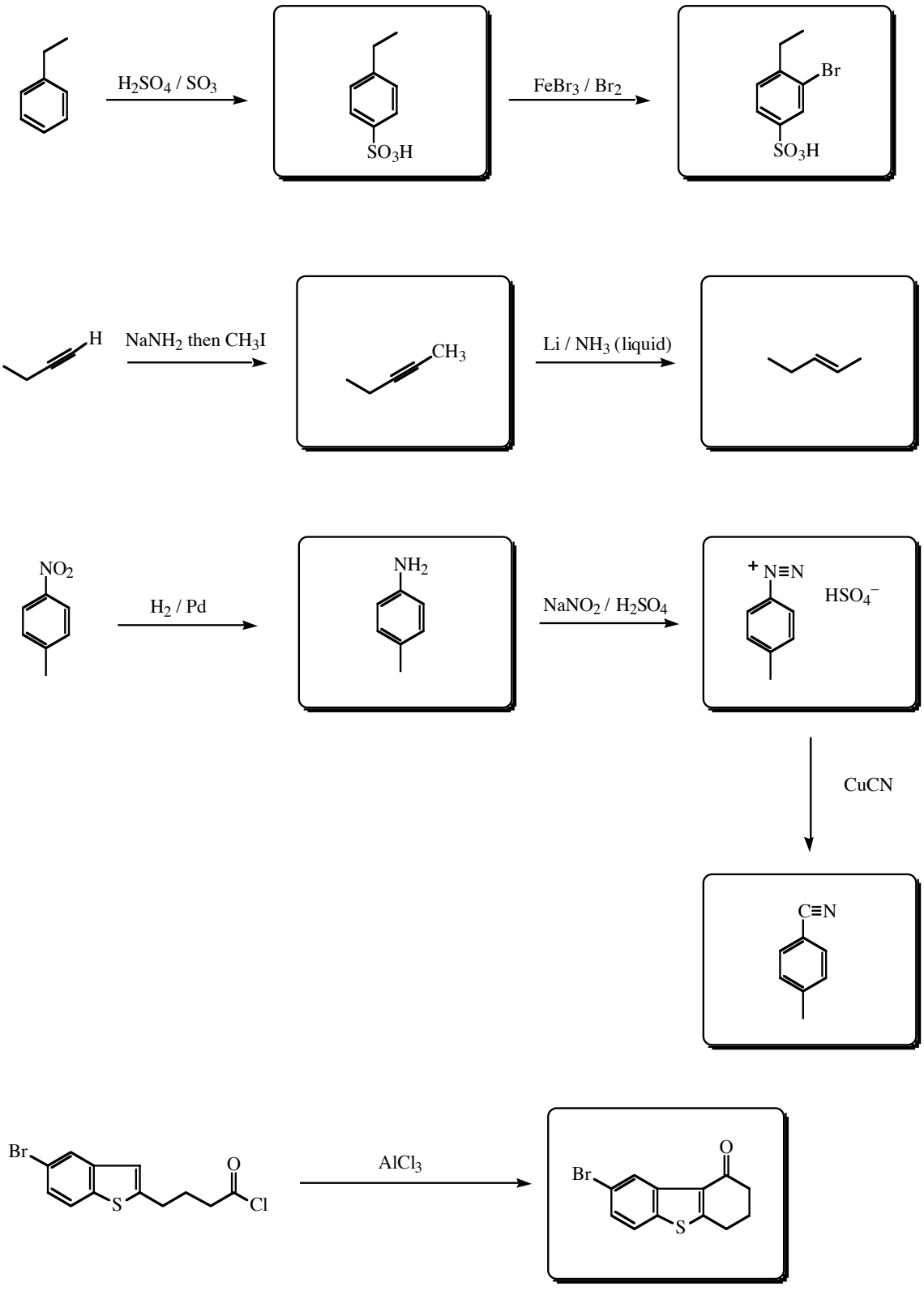
6.


(i) BH_3
(ii) H_2O_2/NaOH
OH
NaH then $BrC_6H_4CH_2Br$
Br
O
(i) Mg
(ii) CO2
(iii) H_3O^+
O
OH

7.


H
O
HO
NO_2
O
OMe
H_3C
Cl
O
CH_2CH_3
Cl
MeO
COOH

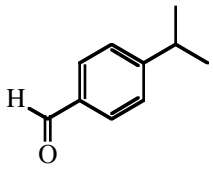
8.


H2SO4 / SO3
SO3H
FeBr3 / Br2
Br
SO3H
H
NaNH2 then CH3I
CH3
Li / NH3 (liquid)
NO2
H2 / Pd
NH2
NaNO2 / H2SO4
+ N≡N
HSO4−
CuCN
C≡N
Br
O
Cl
S
AlCl3
Br
O
S

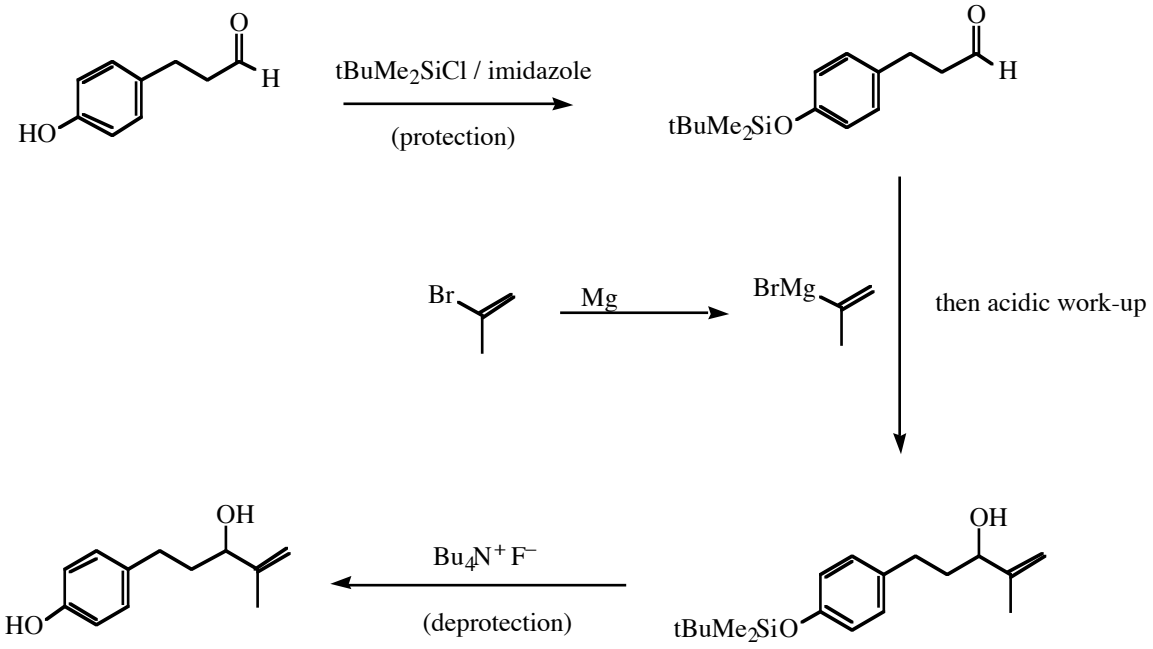
9. (a) **Nucelophilic aromatic substitution mechanism** – the NaH base initially deprotonates the thiol to make the more reactive CH_3S^- anion.

(b) the para position C–F relative to the nitro group is the most electron deficient position through resonance effects – hence the transition state for attack at this position is lower in energy than the transition state corresponding to attack at the meta C–F position.

10.

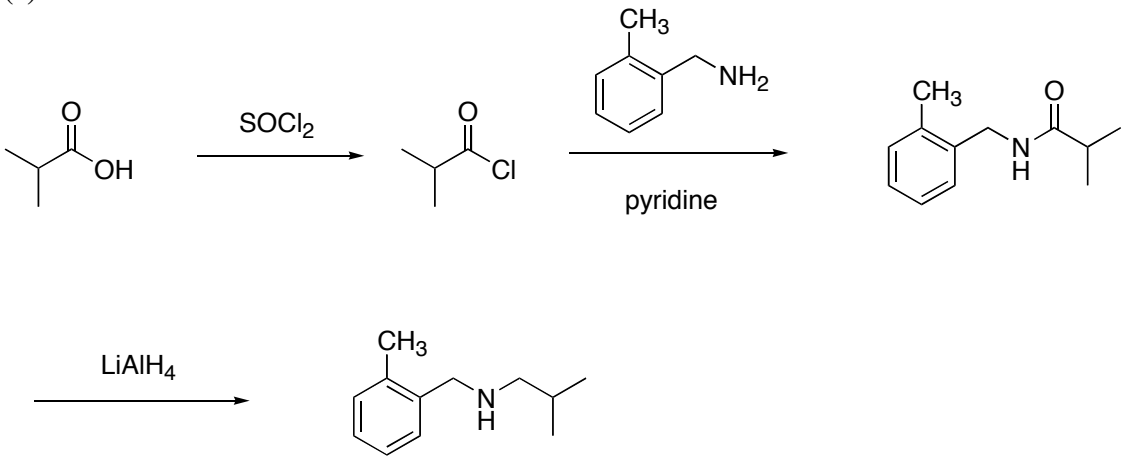


11.

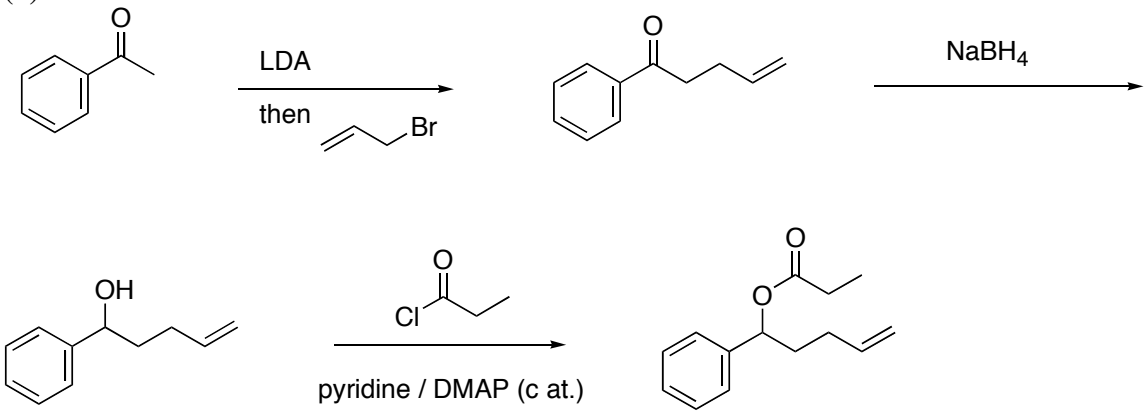


12.

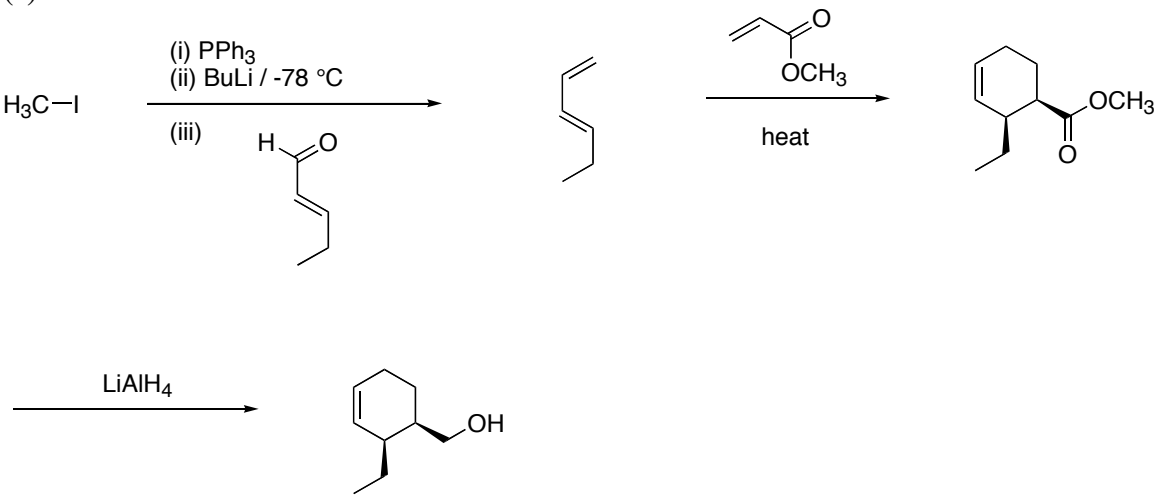
(a)


O
OH
SOCl2
O
Cl
CH3
NH2
pyridine
CH3
O
N
H
LiAlH4
CH3
N
H

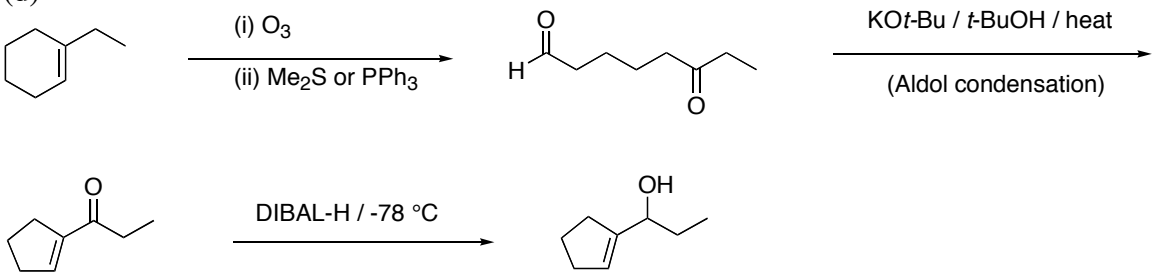
(b)


O
LDA
then
Br
O
NaBH4
OH
O
Cl
pyridine / DMAP (c at.)
O
O

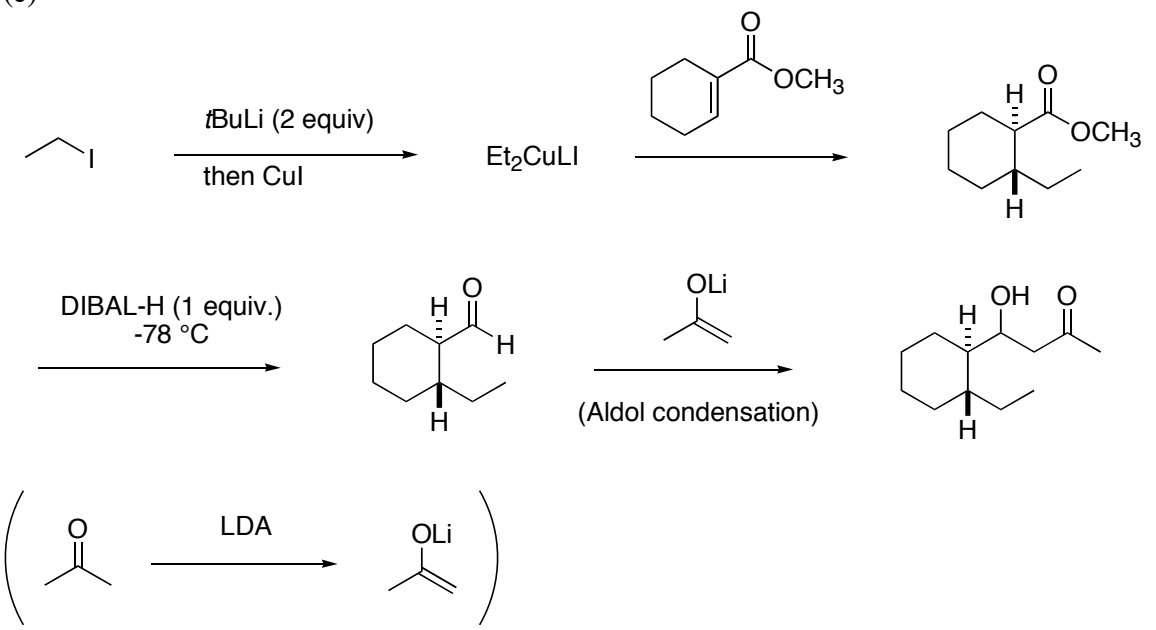
(c)


H3C—I
(i) PPh3
(ii) BuLi / -78 °C
(iii)
H
O
O
OCH3
heat
OCH3
O
LiAlH4
OH

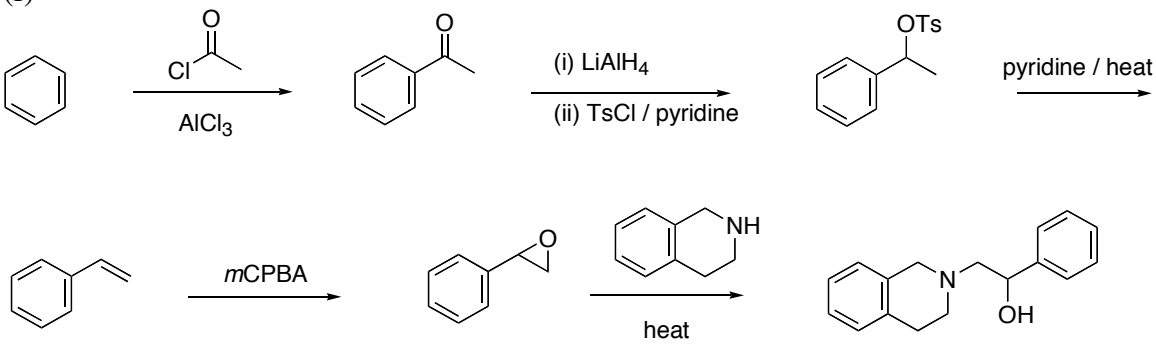
(d)


(i) O_3
(ii) Me_2S or PPh_3
KO*t*-Bu / *t*-BuOH / heat
(Aldol condensation)
DIBAL-H / -78 °C

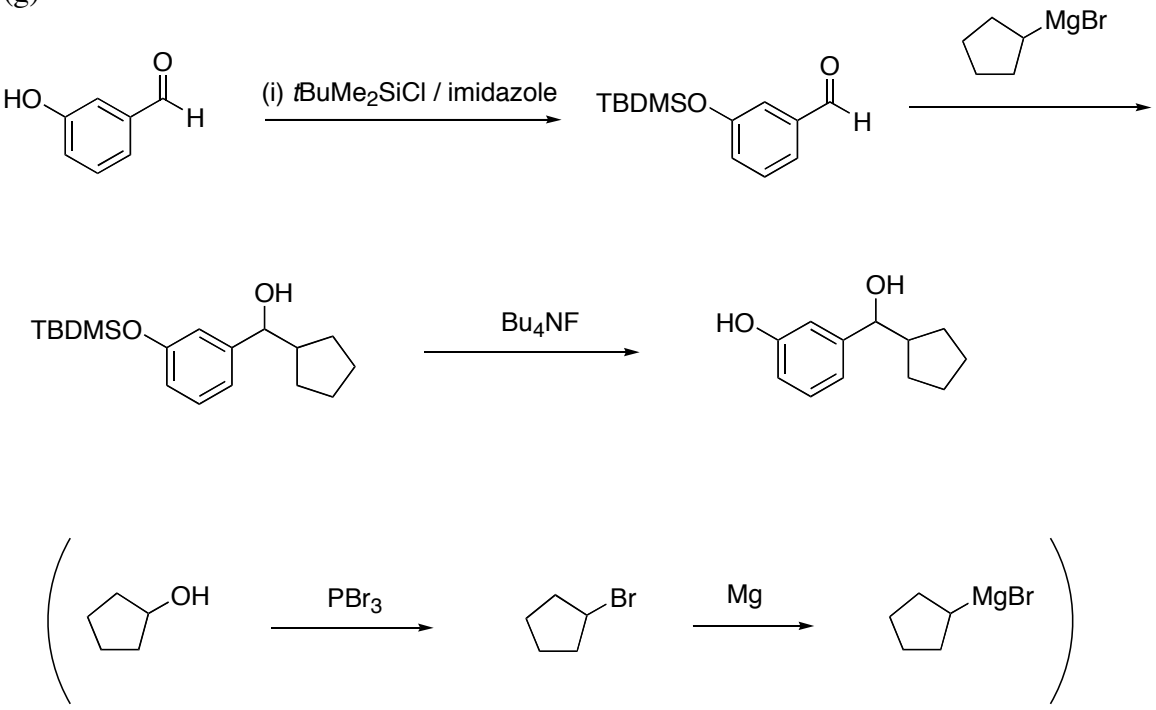
(e)


*t*BuLi (2 equiv)
then CuI
Et_2CuLI
DIBAL-H (1 equiv.)
-78 °C
(Aldol condensation)
LDA

(f)


$AlCl_3$
(i) $LiAlH_4$
(ii) TsCl / pyridine
pyridine / heat
*m*CPBA
heat

(g)


HO
O
H
(i) tBuMe2SiCl / imidazole
TBDMSO
O
H
MgBr
TBDMSO
OH
Bu4NF
HO
OH
OH
PBr3
Br
Mg
MgBr