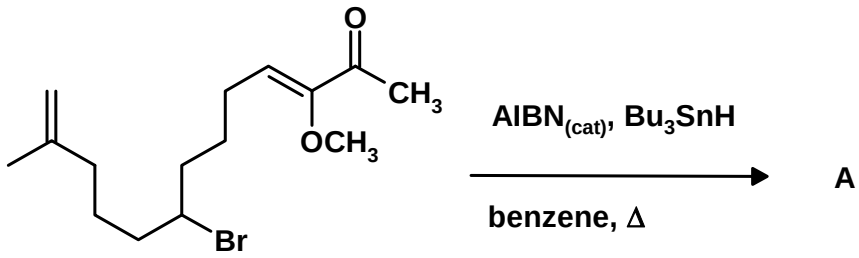
UNIVERSITY OF WINDSOR
CHEMISTRY AND BIOCHEMISTRY

Chemistry 59-531/431 **Apr. 7, 2009**
Final Examination **Time:3 hours**

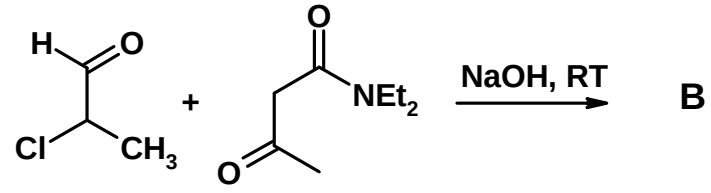
Answer all questions in the exam booklet.

1. Do any nine (9) 'letters'. (45 marks) Provide the major reaction product in each of the following transformations. Include stereochemical (relative and or absolute) information where it is relevant. I do wish you to show any intermediates that could be isolated. Mechanisms are not necessary, but showing your work may be a help. A warning, though…if you do the 1st letter of a series, you must do them all (i.e. you *can't* do **C** but not **D** / **E** or **I** but not **J).**

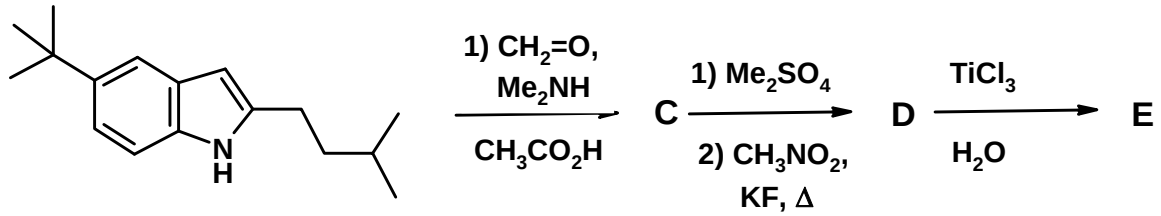
a)



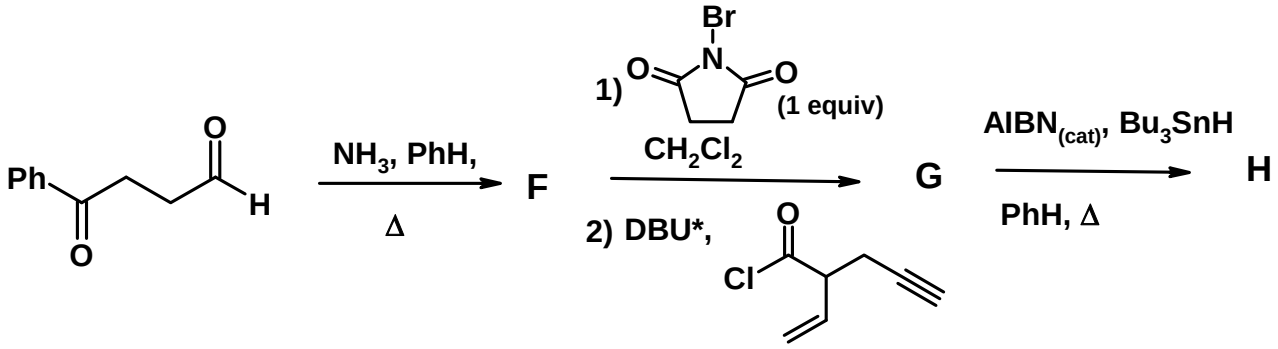
b)



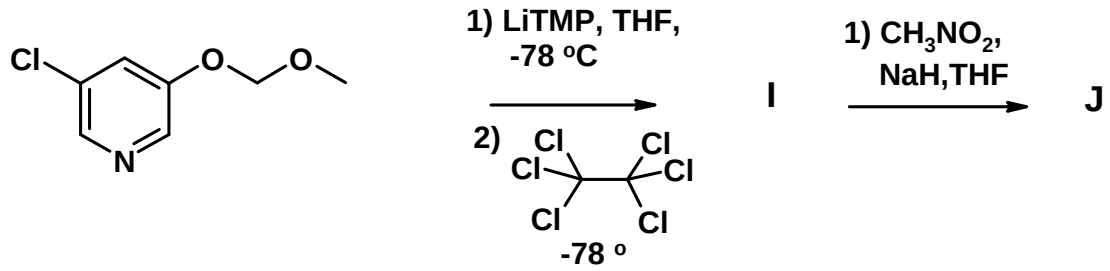
c)



d) For G → H, also classify any ring closings according to Baldwin's rules



e)



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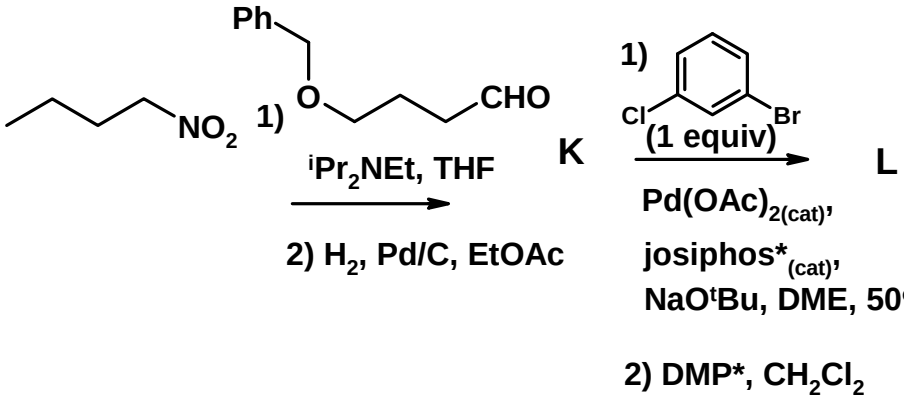
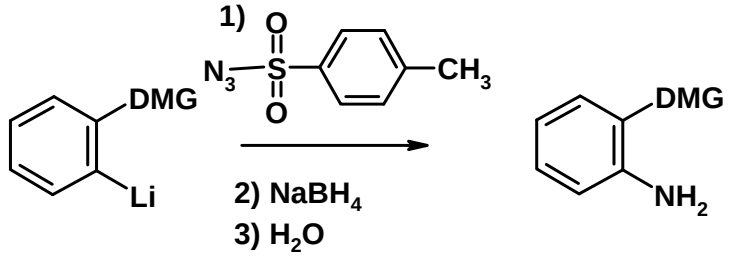


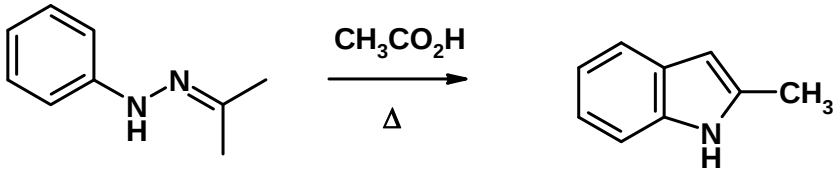
2. (**Total 30 marks**)

a) The most common method of introducing an amine function by way of directed metal(l)ation is by way azidation (using tosyl azide), and subsequent reduction to the amine. Show by way of mechanism these two steps. I do want to see at least one valid valence bond (resonance) structure in your answer.

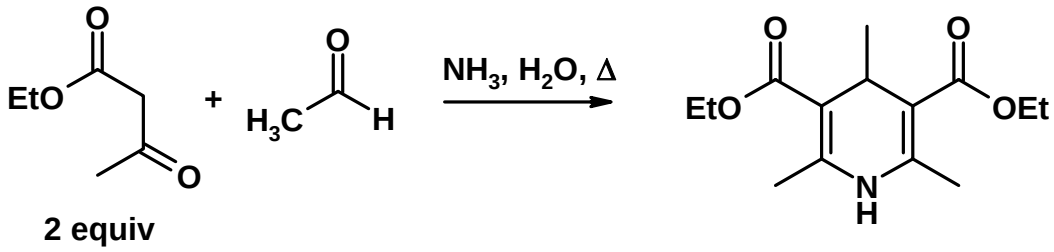


b) **Do *either* i) *or* ii) (but not both) and iii) (10 marks each).**

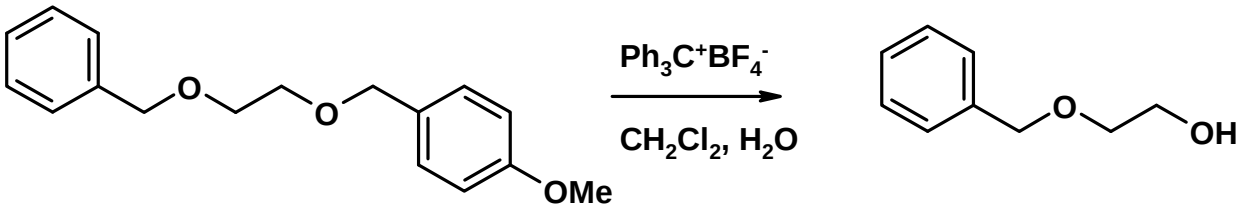
i) The most well known of the indole syntheses is the Fischer indole synthesis. Give the complete mechanism of this transformation



ii) The Hantsch synthesis is one of the most common syntheses of pyridines, although it actually gives a dihydropyridine (which must be oxidized later). Give the complete mechanism of this ring preparation.



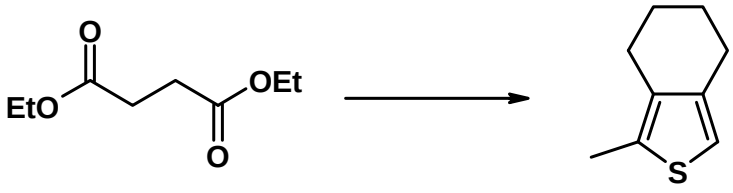
iii) The PMB protecting group is useful in that it is cleavable under oxidative conditions (admittedly an odd type of oxidation) whereas the other common groups are pretty much inert. Show by way of mechanism why PMB 'deprotects' in preference to a simple benzyl. Take the mechanism as far towards completion as you can.



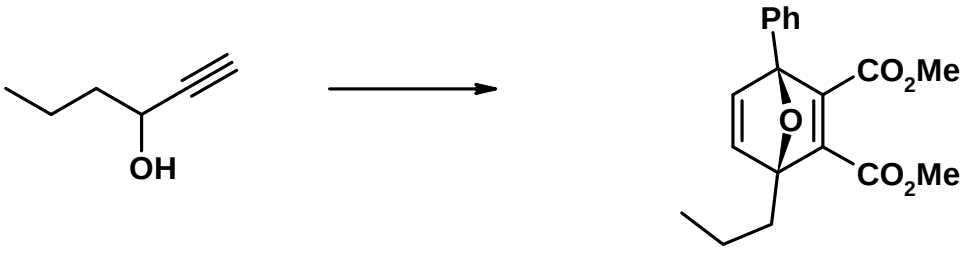
3. Do any five (5) of the following.

Show by equation how you would prepare the illustrated below from the given starting material. You may use any other reagents which you deem fit. Show all reagents, conditions, and isolable intermediates; show the structures of all acronyms used (at least once), other than for solvents. Mechanisms are not necessary, but may be a help. (**Total 50 marks**)

a)



b)



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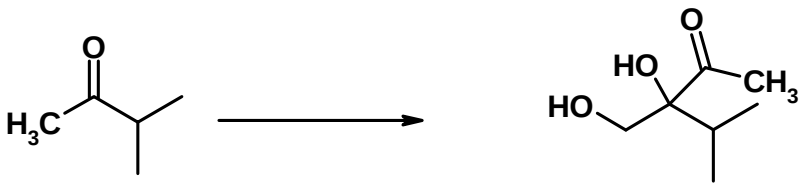

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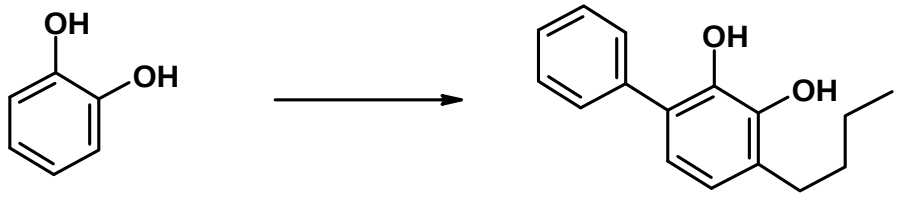

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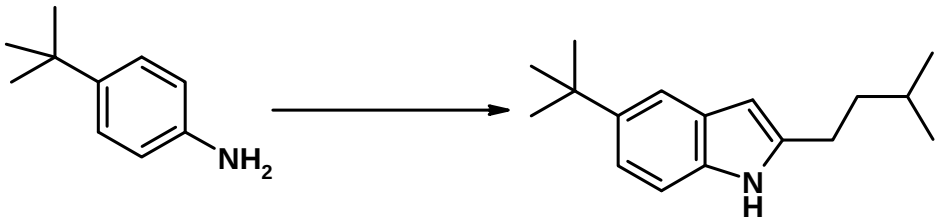

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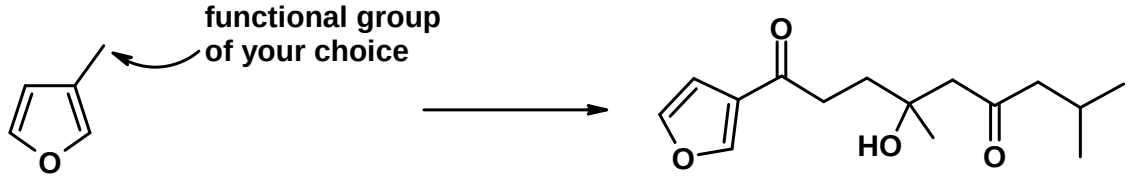
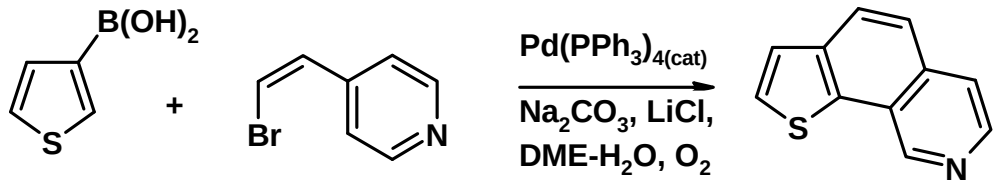


hydroxymyoporone

Bonus: In an attempt to make a 3-vinyl substituted thiophene, the following cross coupling reaction was attempted. On a small amount of the intended material was observed, with the majr product being the indicated tricyclic system. The person carrying out the reaction was a bit sloppy and got some air into the reaction mixture. Can you propose by mechanism what happened here??



Assorted Cheat-sheet info

Baldwin's Rules for Ring Closure

For tetrahedral substrates:

a) 3- to 7- exo-tet favoured
b) 5- to 6- endo-tet disfavoured

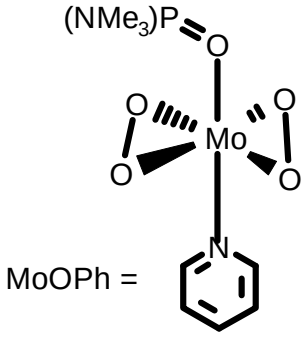
For trigonal substrates

a) 3- to 7- exo-trig favoured
b) 3- to 5- endo-trig disfavoured
c) 6- to 7- endo-trig favoured

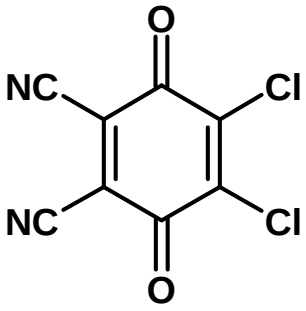
For digonal substrates

a) 3- to 4- exo-dig disfavoured
b) 5- to 7- exo-dig favoured
c) 3- to 7- endo-dig favoured

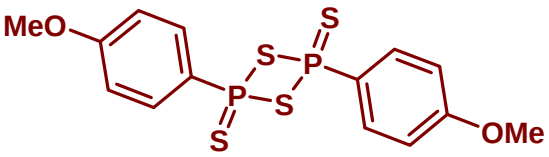
The structure of MoOPh is:



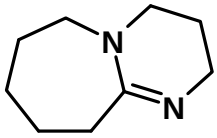
The structure of DDQ is



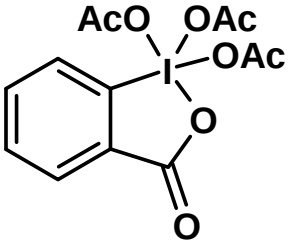
The structure of Laweson's reagent is



DBU (diazabicycloundecane) is



DMP (Dess-Martin periodinane) is



The structure of josiphos is