

EXAM Fonctions et Réactions Organiques III / CH-234

June 27, 2019

Duration of the exam: 120 Minutes

Answer the Questions only on the associated sheet of the question!

NO loose sheets are accepted!

NO PENCIL or RED pen is allowed!

Allowed aids: **NONE**

Name: _____

First Name: _____

Stud. ID No. _____

Place Number _____

Signature _____

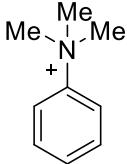
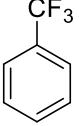
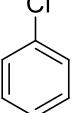
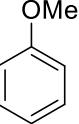
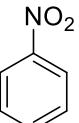
Exercise 1	10 Points	
Exercise 2	10 Points	
Exercise 3	10 Points	
Exercise 4	10 Points	
Exercise 5	10 Points	
Exercise 6	10 Points	
Exercise 7	10 Points	
Exercise 8	10 Points	
Exercise 9	10 Points	
Exercise 10	10 Points	
Total Points	100 Points	
GRADE		

GOOD LUCK!

1. Characterize the properties of the substituents by ticking the appropriate answers! (10P)

CAUTION: Wrong answers lead to a deduction of points. There is a minimum of 0 points for each subpart of the question. (2P max. for each subpart)

0.5 points for each box

	σ -donor	σ -acceptor	π -donor	π -acceptor	
a)		<input type="checkbox"/> yes <input checked="" type="checkbox"/> no	<input checked="" type="checkbox"/> yes <input type="checkbox"/> no	<input type="checkbox"/> yes <input checked="" type="checkbox"/> no	<input type="checkbox"/> yes <input checked="" type="checkbox"/> no
b)		<input type="checkbox"/> yes <input checked="" type="checkbox"/> no	<input checked="" type="checkbox"/> yes <input type="checkbox"/> no	<input type="checkbox"/> yes <input checked="" type="checkbox"/> no	<input type="checkbox"/> yes <input checked="" type="checkbox"/> no
c)		<input type="checkbox"/> yes <input checked="" type="checkbox"/> no	<input checked="" type="checkbox"/> yes <input type="checkbox"/> no	<input checked="" type="checkbox"/> yes <input type="checkbox"/> no	<input type="checkbox"/> yes <input checked="" type="checkbox"/> no
d)		<input type="checkbox"/> yes <input checked="" type="checkbox"/> no	<input checked="" type="checkbox"/> yes <input type="checkbox"/> no	<input checked="" type="checkbox"/> yes <input type="checkbox"/> no	<input type="checkbox"/> yes <input checked="" type="checkbox"/> no
e)		<input checked="" type="checkbox"/> yes <input type="checkbox"/> no	<input checked="" type="checkbox"/> yes <input type="checkbox"/> no	<input type="checkbox"/> yes <input checked="" type="checkbox"/> no	<input checked="" type="checkbox"/> yes <input type="checkbox"/> no

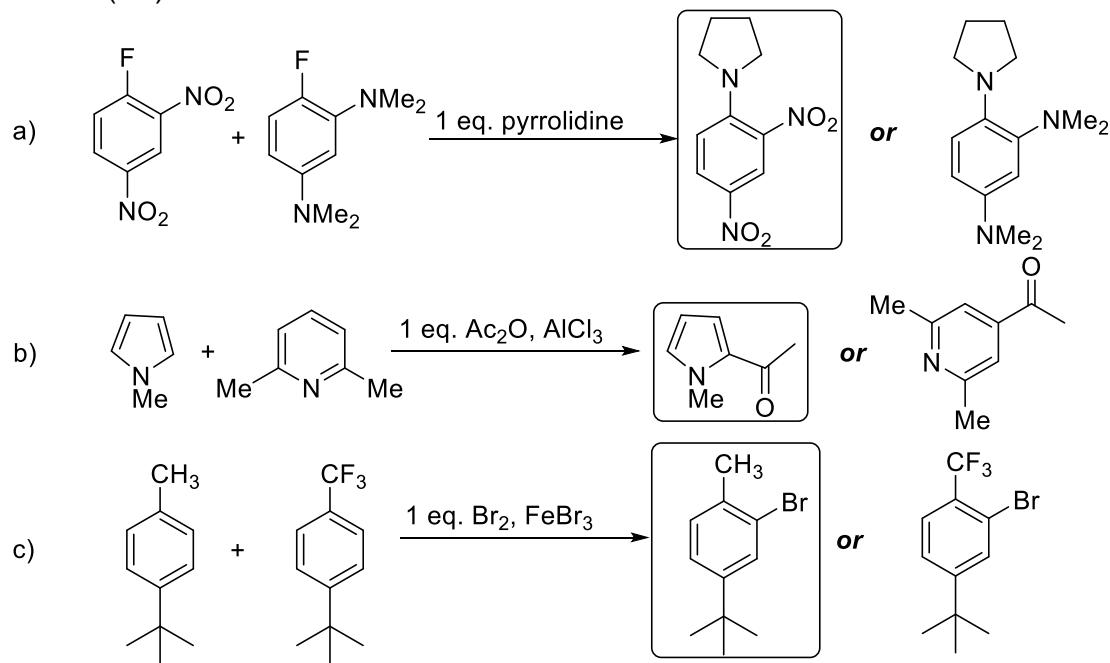
2a. Characterize the following molecules according to *Hückel* criteria by ticking the appropriate answer! (5P)

	aromatic	anti-aromatic	non-aromatic		
a)		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	1P
b)		<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	1P
c)		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	1P
d)		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	1P
e)		<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	1P

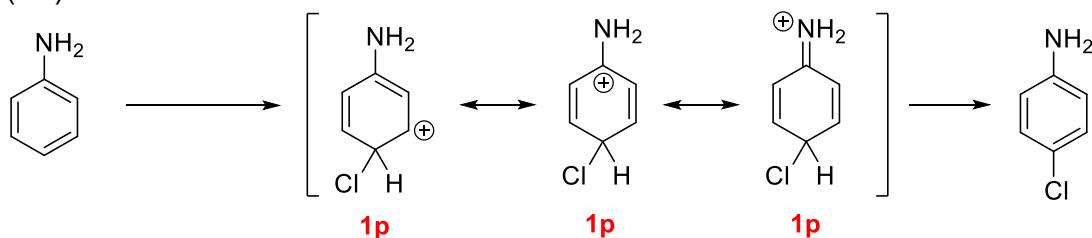
2b. Name the asked molecule according to the Hantzsch-Widman system (2P)

a)	b)
Name: 1,2-oxazepine	Name: 1,3-oxathiolane

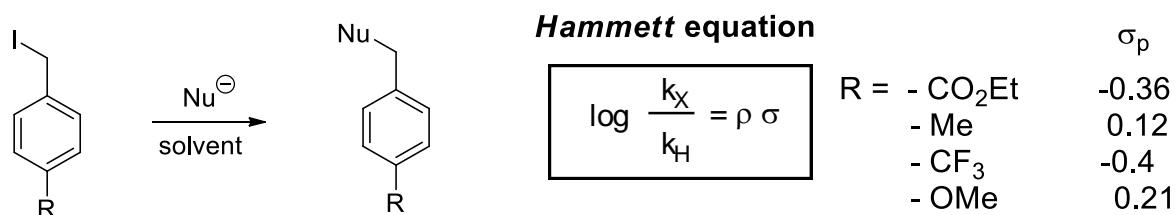
2c. Competing Reactants: An **equimolar** (1:1) mixture of two starting materials is reacted with just **1 equivalent** of the indicated reagent. **Encircle** the major product that is formed. (3P)



3a. Aniline is chlorinated in an electrophilic aromatic substitution reaction. Draw the reasonable mesomeric structures of the transition state of the para-chlorination. (3P)



3b. The Hammett-Equation provides reaction mechanism insights. The shown values were measured for this substitution reaction. (3P)



These results indicate that the reaction proceeds **faster** with substrates having **donating substituents**. Please answer the following questions:

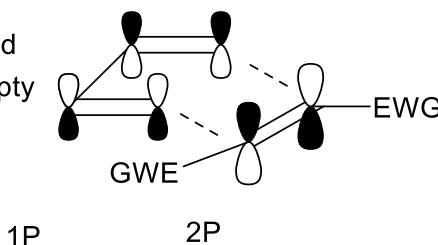
- What (partial) charge is present in the transition state
 positive **1p** neutral negative
- What sign has then the value "rho" in the equation?
 plus minus **1p**
- With which of the three given substituents R, the reaction proceeds fastest? **1p**
 $R =$ CN NMe₂ Et

3c. The "unassigned" frontier orbitals for a model Diels-Alder reaction is shown. Color the correct orbital lobes that are involved in the Diels-Alder process and name them. (4P)

Tick:

orbital is filled
 orbital is empty

Orbital Name
HOMO



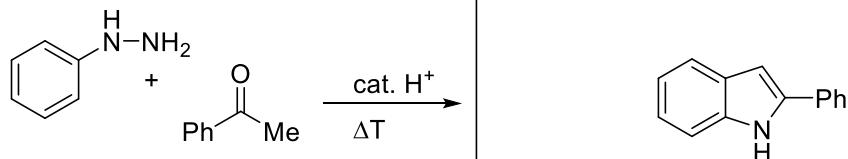
Tick:

orbital is filled
 orbital is empty

Orbital Name
LUMO

1P

4. Complete the following scheme by adding the missing structures and reaction names! (10P)

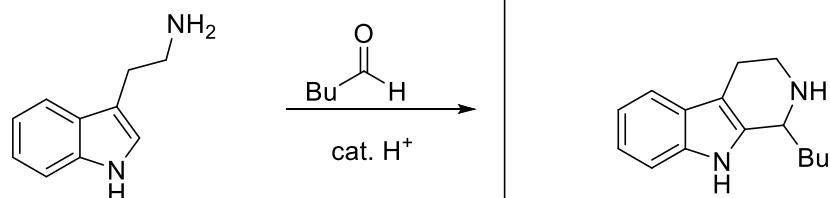


2P

Fischer-Indole Synthesis

Reaction Name

1P

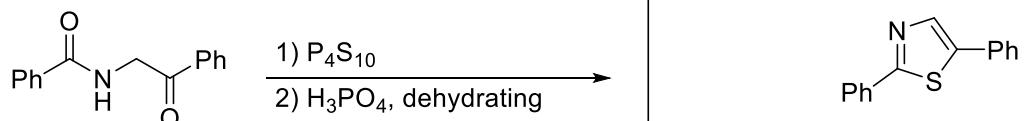


2P

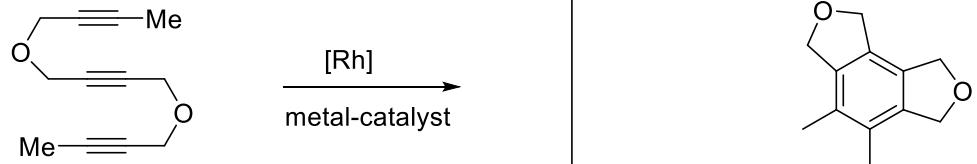
Pictet-Spengler Reaction

Reaction Name

1P

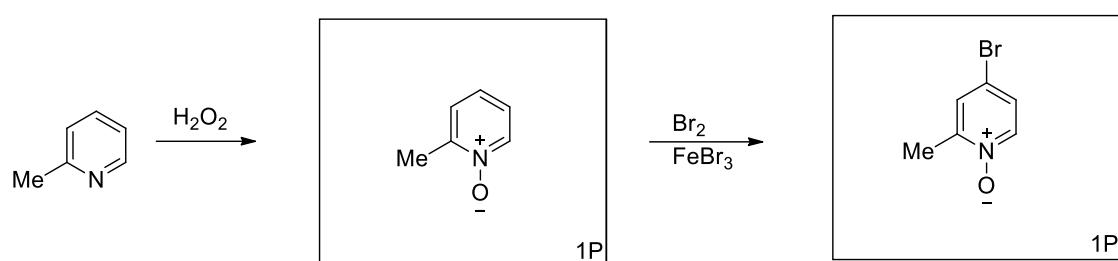
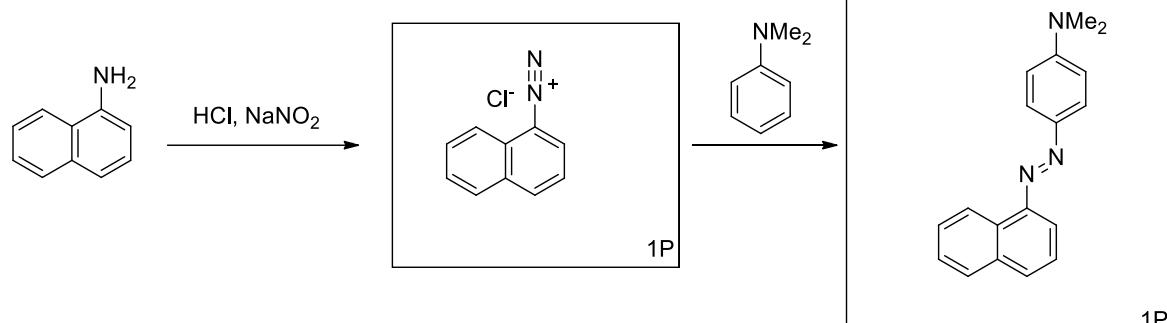
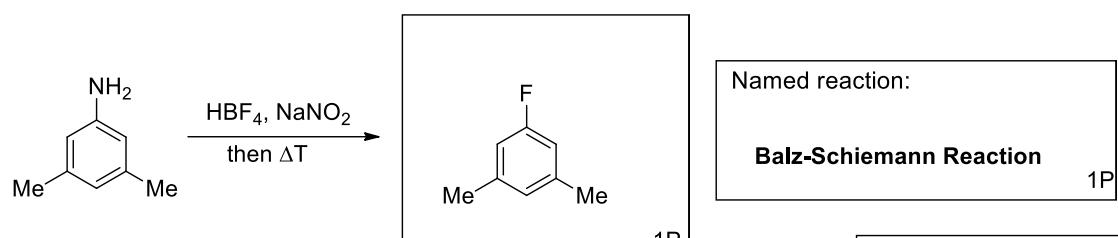
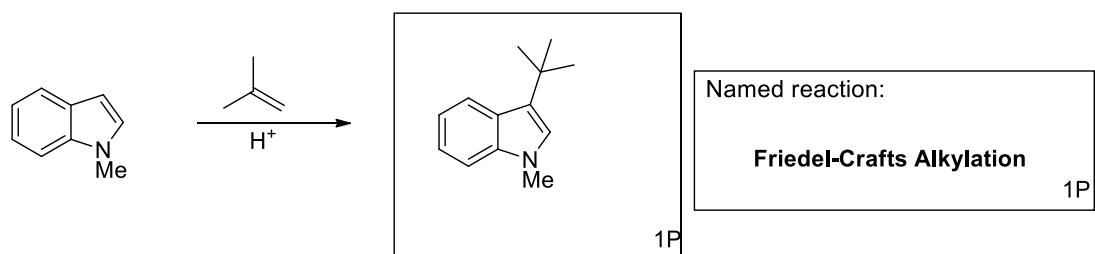
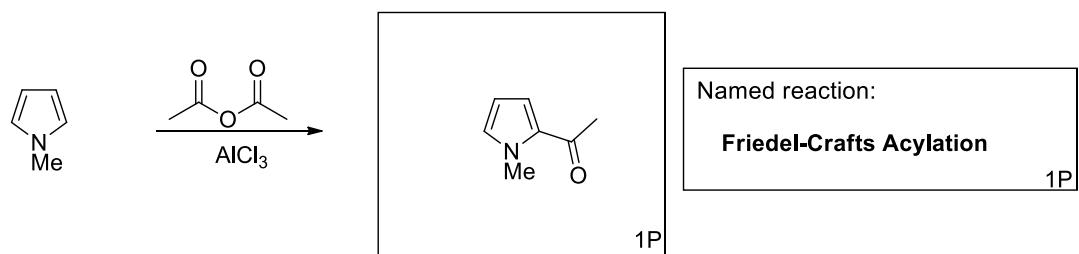


2P

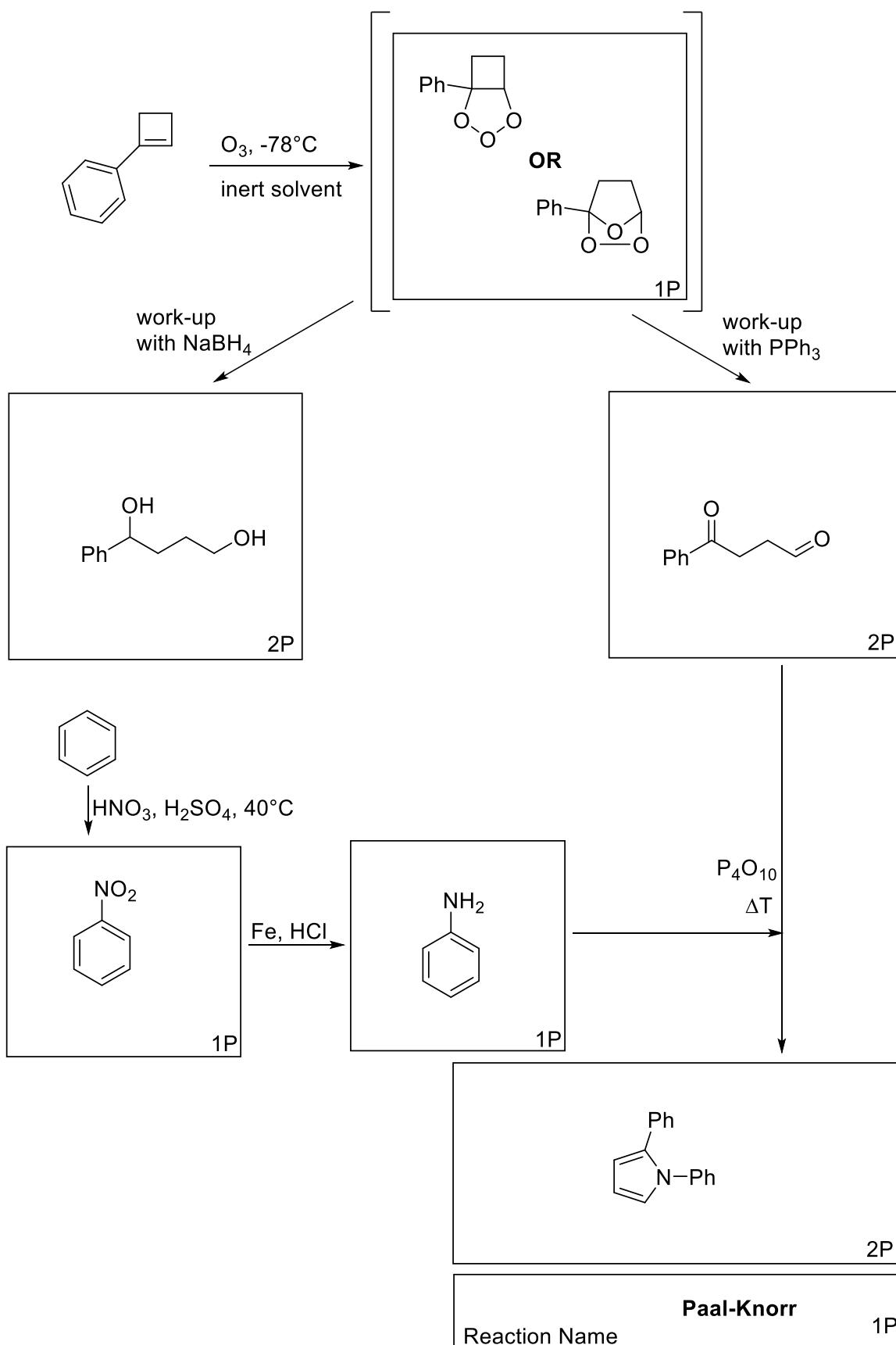


2P

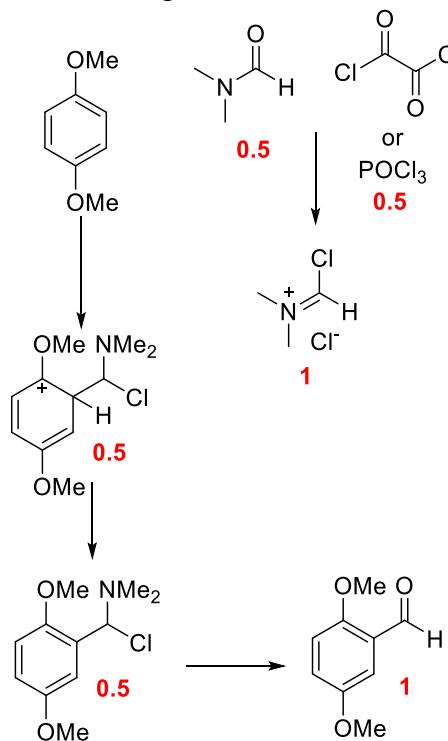
5. Complete the following schemes by adding the major product! If asked, give the name of the reaction. (10P)



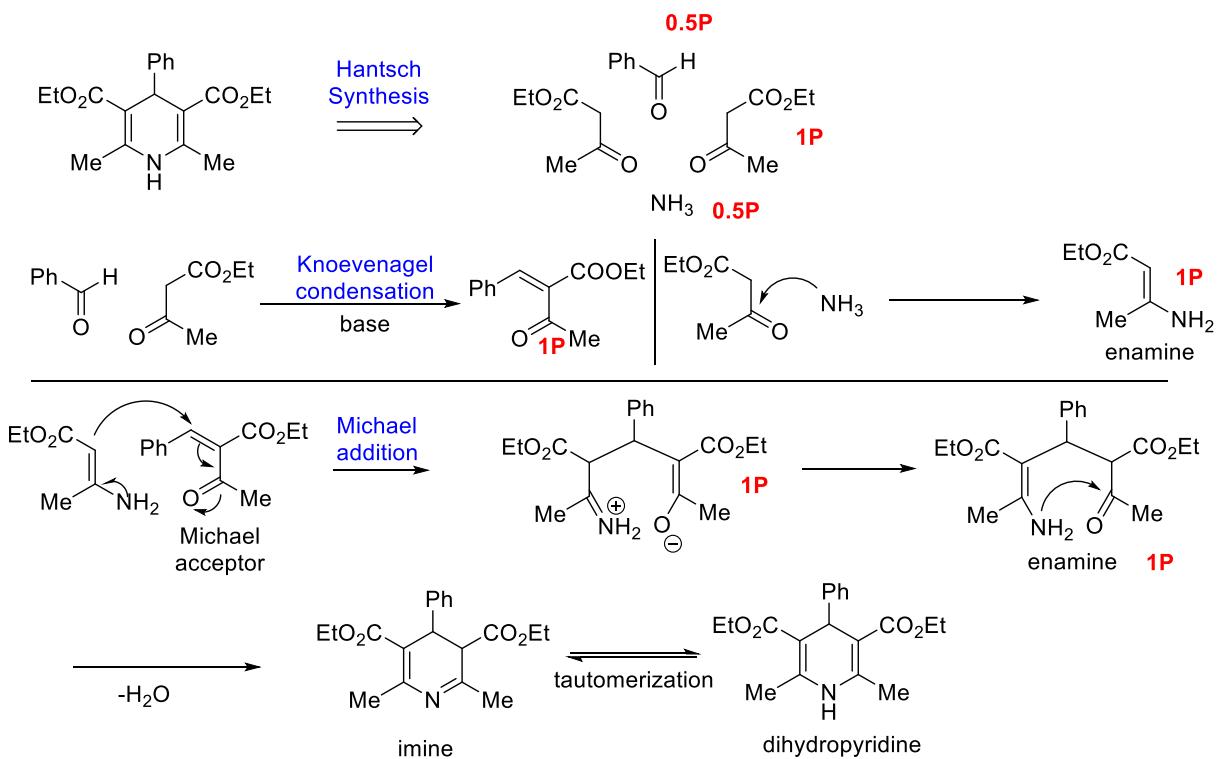
6. Complete the blanks by filling in the missing compounds and the reaction name.
(10P)



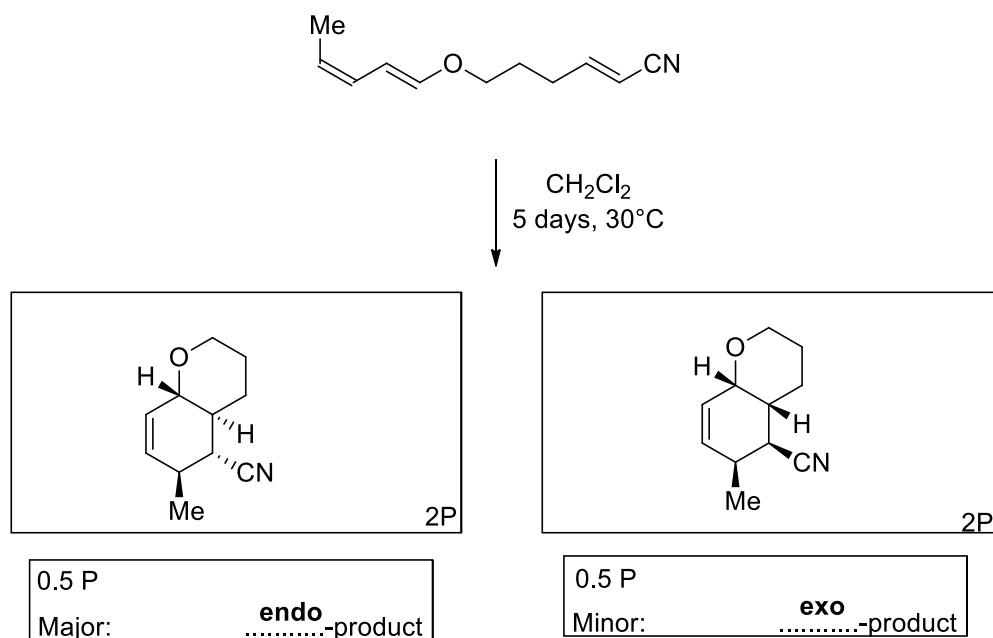
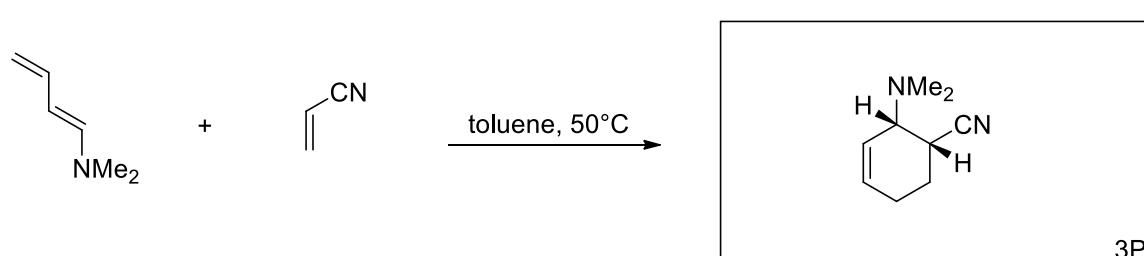
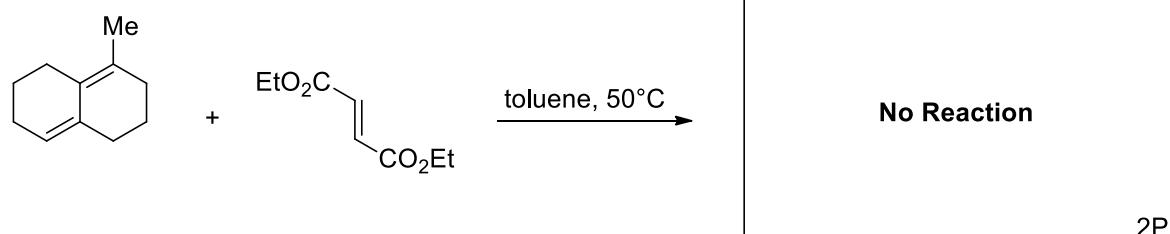
7a. 1,4-Dimethoxy benzene is submitted to a Vilsmeye-Haack formylation. Draw the required reagents and the product. Provide the appropriate details on the reaction mechanism by drawing the active reagent and relevant intermediates (4P).



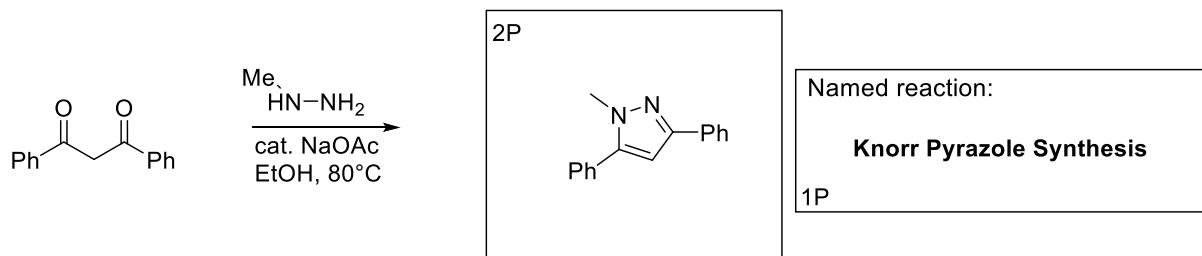
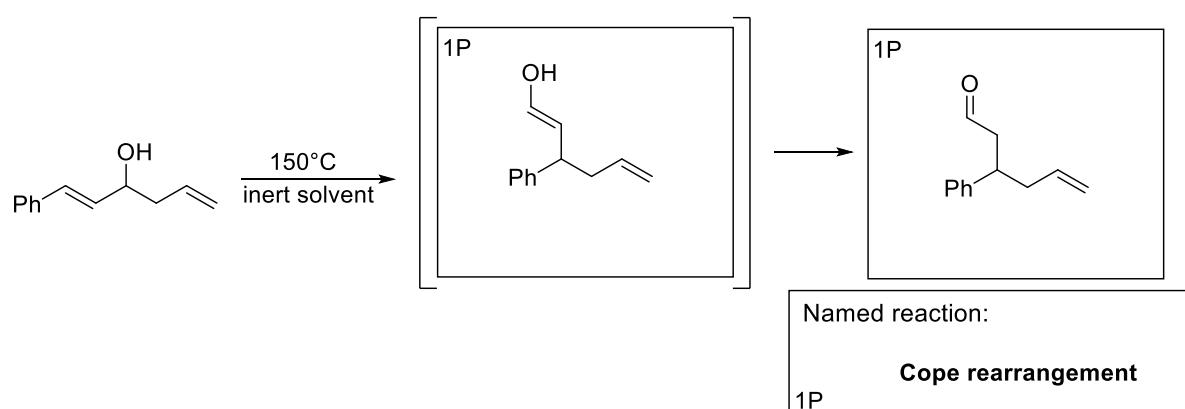
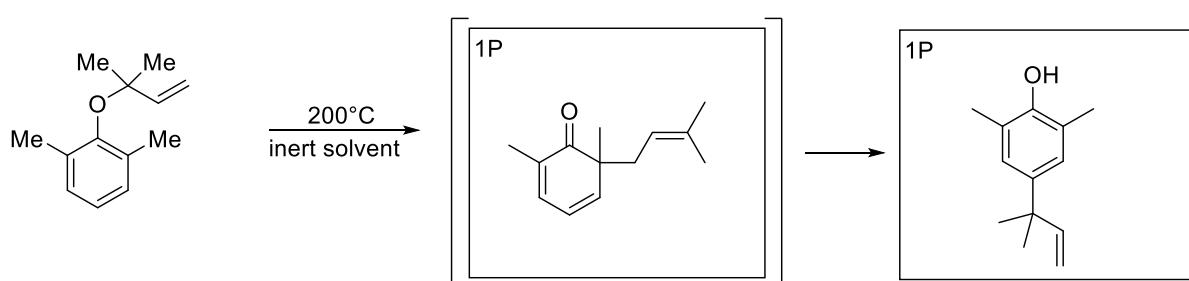
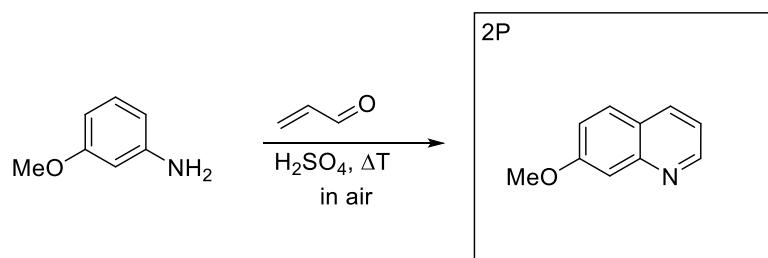
7b. The Hantzsch-dihydropyridine synthesis gives access to the shown dihydropyridine. Draw the required starting materials and illustrate the reaction mechanism in appropriate detail by drawing the relevant intermediates and condensation steps! (6P)



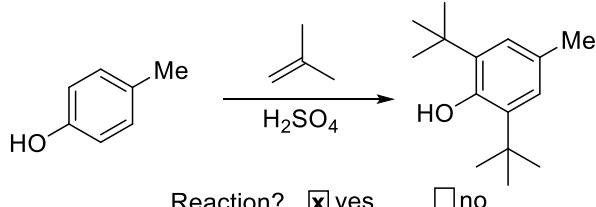
8. Fill in the blanks! Pay especially attention to the regio- and stereochemistry of your products. Clearly mark the stereochemistry in your answers. (10P)



9. Draw the main product of the shown reactions and provide their reaction name.
(10P)



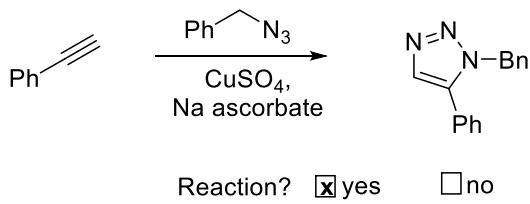
10. 1) Do the starting materials **react** with each other under the given conditions?
 2) Are the shown products the **expected main products**?
If not: draw the correct product in the box **or** explain in very **FEW** words why no reaction is taking place(10P total)



Reaction? yes no

if yes,
correct main product? yes no

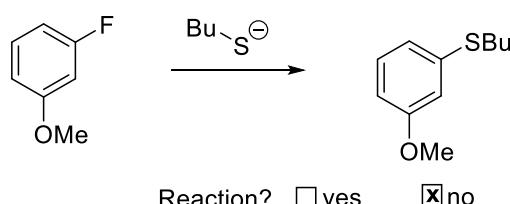
Fill out **only** when one **NO** before:
 Give a reason why there is no reaction
 or draw the correct reaction product



Reaction? yes no

if yes,
correct main product? yes no

Fill out **only** when one **NO** before:
 Give a reason why there is no reaction
 or draw the correct reaction product

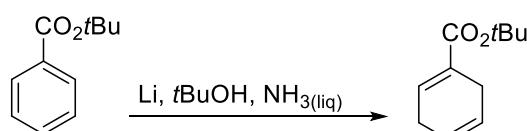


Reaction? yes no

if yes,
correct main product? yes no

Fill out **only** when one **NO** before:
 Give a reason why there is no reaction
 or draw the correct reaction product

Aryl ring is not activated for nucleophilic attack



Reaction? yes no

if yes,
correct main product? yes no

Fill out **only** when one **NO** before:
 Give a reason why there is no reaction
 or draw the correct reaction product