

**Note:**

- During the attendance check a sticker containing a unique code will be put on this exam.
- This code contains a unique number that associates this exam with your registration number.
- This number is printed both next to the code and to the signature field in the attendance check list.

## Organic Photochemistry

**Exam:** CH3038 / Retake      **Date:** Tuesday 4<sup>th</sup> April, 2023  
**Examiner:** Prof. Thorsten Bach      **Time:** 08:30 – 10:00

	P 1	P 2	P 3	P 4	P 5
I					

### Working instructions

- This exam consists of **16 pages** with a total of **5 problems**.  
Please make sure now that you received a complete copy of the exam.
- The total amount of achievable credits in this exam is 100 credits.
- Detaching pages from the exam is prohibited. You may only use the distributed paper to give your answers; no additional sheets are allowed. There is additional space at the end of the exam but make sure to clearly indicate which question you are answering. **Short answers please!**
- Allowed resources:
  - one **non-programmable pocket calculator**
  - one **analog dictionary** English ↔ native language

No other resources are allowed (also no molecule models). Cheating and cheating attempts will result in the candidate failing the exam.

- Do not write with red or green colors nor use pencils.
- Every correct and fully answered problem will be awarded the number of credits shown. It is possible to obtain only a fraction of the credits if the answer is not completely satisfactory.
- Consider the relative and absolute configuration of molecules, unless otherwise noted.
- Physically turn off all electronic devices, put them into your bag and close the bag.

Left room from \_\_\_\_\_ to \_\_\_\_\_ / Early submission at \_\_\_\_\_

## Problem 1 Multiple Choice Questions (10 credits)

There is only **one** correct answer option. Please answer multiple choice questions in the following way:

Mark correct answers with a cross



To undo a cross, completely fill out the answer option



To re-mark an option, use a human-readable marking



a) Which wavelength is typically chosen to directly excite a substrate for a reaction?

- The wavelength exactly between the absorption and the emission maximum of the substrate.
- The exact wavelength of the absorption maximum of the substrate.
- The shortest possible wavelength within the absorption of the substrate.
- The longest possible wavelength within the absorption of the substrate.

b) The formation of dienols upon irradiation of  $\alpha,\beta$ -unsaturated carbonyl derivatives...

- typically occurs in the singlet state.
- is disfavored in the presence of esters or amides.
- usually leads to decomposition of starting material.
- often competes with intermolecular protonation.

c) Which of these statements regarding the photoreactivity of *ortho*-substituted aromatic ketones is **incorrect**?

- Upon excitation, *ortho*-substituted aromatic ketones undergo rapid ISC.
- After hydrogen abstraction, the *Z*-isomer tautomerizes rapidly.
- Hydrogen abstraction of *ortho*-substituted aromatic ketones typically occurs on the singlet hypersurface.
- After hydrogen abstraction, the *E*-isomer can be trapped by a dienophile.

d) Under which conditions is a  $E \rightarrow Z$  isomerization favored?

- $\lambda_{\max}(Z) > \lambda_{\max}(E)$  and/or  $\epsilon_{\max}(Z) > \epsilon_{\max}(E)$
- $\lambda_{\max}(E) > \lambda_{\max}(Z)$  and/or  $\epsilon_{\max}(E) > \epsilon_{\max}(Z)$
- A  $E \rightarrow Z$  isomerization is favored irregardless of any properties or conditions.
- A  $E \rightarrow Z$  isomerization can never be favored.

e) Which statement about photochemical triplet sensitization of alkenes is **wrong**?

- There is high electron-electron repulsion in  $S_1$ .
- The ISC rate  $S_1 \rightarrow T_1$  for alkenes is high.
- Energy transfer from photosensitizers with low  $T_1$  states is facile.
- There is almost no electron-electron repulsion in  $T_1$ .

f) How does the use of an  $\alpha,\beta$ -unsaturated ester change the regioselectivity of a [2+2] photocycloaddition compared to an  $\alpha,\beta$ -unsaturated ketone?

- There is no change in regioselectivity for the reaction with both donor- and acceptor-substituted olefins.
- The reaction with an acceptor-substituted olefin leads to the head-to-tail product.
- The reaction with a donor-substituted olefin leads to the head-to-head product.
- For either donor- and acceptor-substituted olefins, only the head-to-head product is formed.

g) The transition state of a conrotatory ring closure has what kind of symmetry?

- $\sigma$
- $S_2$
- $C_2$
- $\pi$

h) *Ortho*-photocycloaddition is favored over *meta*-photocycloaddition if...

- the alkene is acceptor-substituted; substitution on the arene does not matter.
- the alkene and the arene are both donor-substituted.
- one reaction partner (alkene or arene) is acceptor- and the other one is donor-substituted.
- the alkene and the arene are both acceptor-substituted.
- the arene is donor-substituted; substitution on the alkene does not matter.

i) Eosin Y can act as...

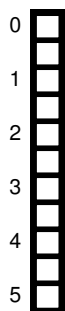
- a triplet sensitizer.
- all of the other choices.
- a hydrogen atom transfer agent.
- a photoredox catalyst.

j) Why are electron-rich amines usually protected in photoredox chemistry?

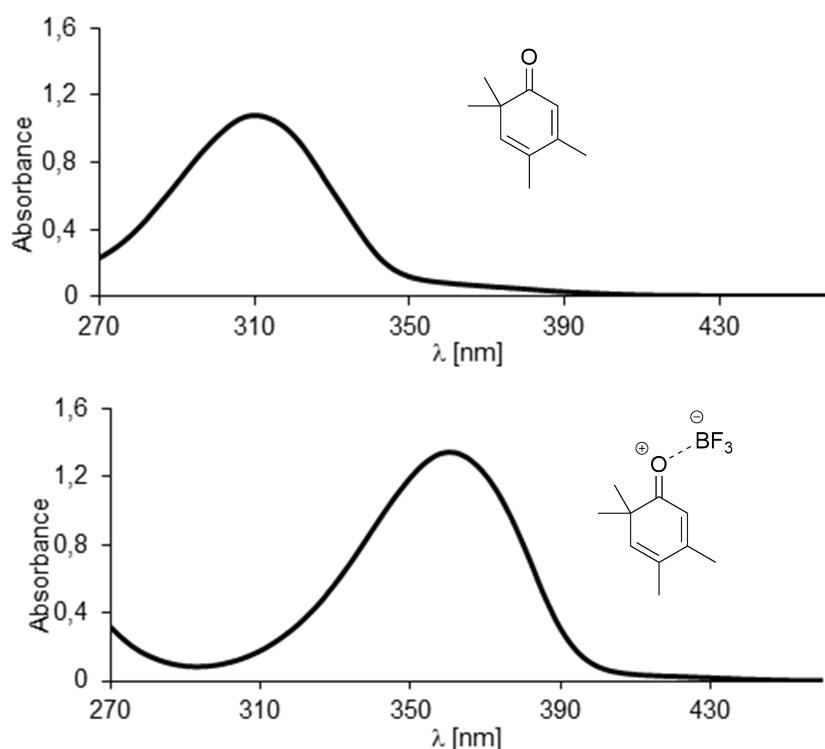
- They easily undergo oxidation.
- They act as good electrophiles.
- They quench the triplet state of the catalysts and hinder any further reactivity.
- All of the other choices.

## Problem 2 Fundamentals of Photochemistry (14 credits)

To successfully conduct photochemical reactions, fundamental processes and properties of organic and organometallic compounds upon irradiation need to be studied and understood.



a) The UV-vis spectra of 2,4-cyclohexadienone and its complex with the Lewis acid  $\text{BF}_3$  are shown below. The spectra were recorded using 1.0 mm quartz cuvettes with concentrations of 2.0 mM.



Give the formula to calculate the extinction coefficients. What is the name of this formula? Specify the meaning of each parameter. Calculate the extinction coefficient for the uncomplexed compound at  $\lambda = 310$  nm. The absorbance for the compound at this wavelength is 1.07.

In the case of the Lewis acid complex, the UV-vis spectrum shows a significant shift of  $\lambda_{\text{max}}$  compared to the uncomplexed compound. What is this name of this shift?

b) What does Kasha's rule say?

0
1
2

c) Explain why intersystem crossing is generally very fast for carbonyl compounds.

0
1
2

d) Explain why photoexcited transition metal complexes are both stronger oxidants and stronger reductants than their corresponding ground state species.

0
1
2
3

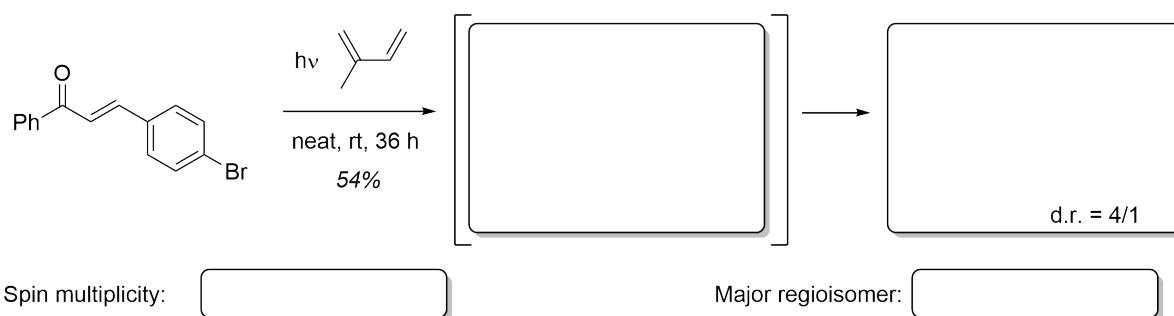
e) Give two reasons why organic photoredox catalysts are often preferred over transition metal complexes.

0
1
2

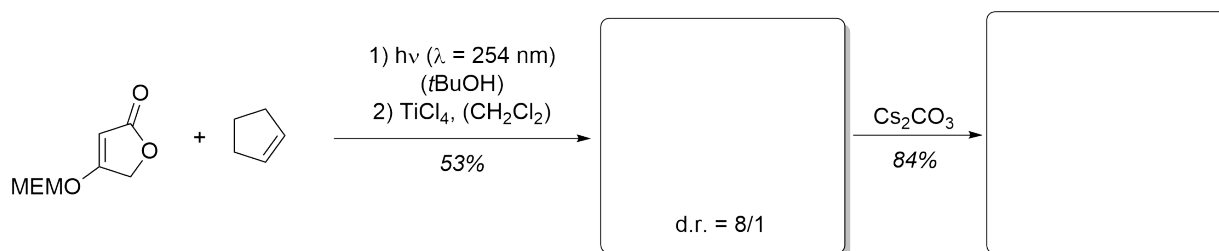
### Problem 3 Direct Excitation (33 credits)

Many photochemical processes are induced upon absorption of light by an organic substrate.

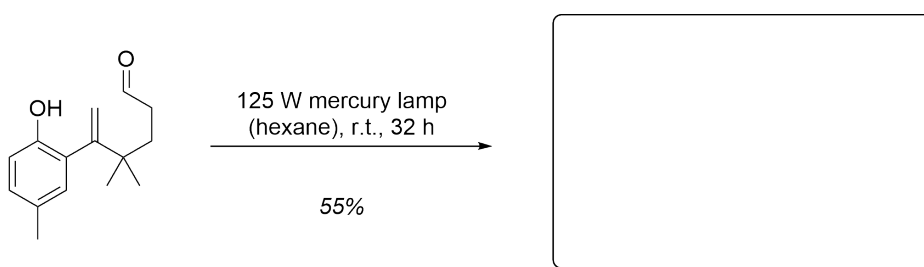
a) Fill the following boxes with the diradical intermediate and final product of the following photocycloaddition reaction. Consider regio- and diastereoselectivity. Name the type of regioisomer that is predominantly formed.



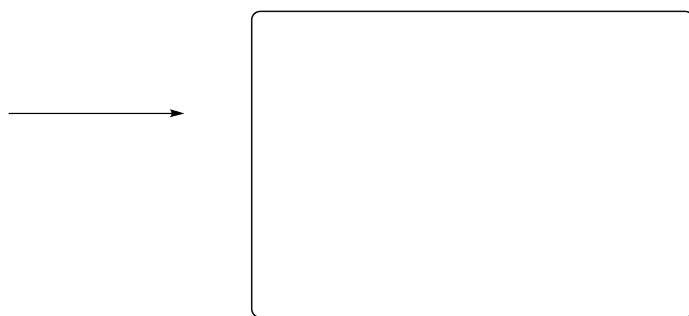
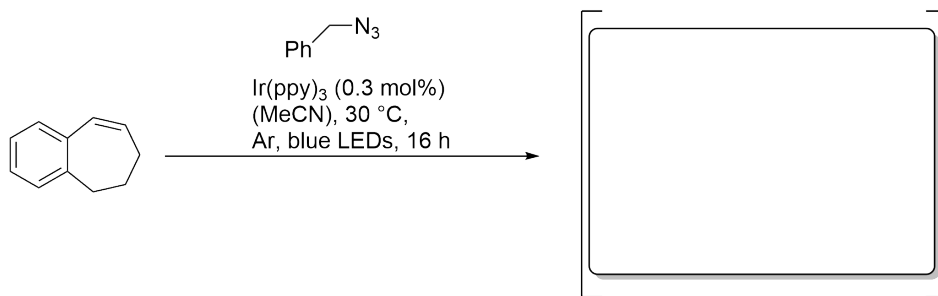
b) Upon photocycloaddition with cyclopentene, followed by a MEM-deprotection (MEM = 2-methoxyethoxy-methyl) with  $\text{TiCl}_4$ , the photoproduct was obtained with a 53% yield and an 8/1 diastereoisomeric ratio. Further treatment with  $\text{Cs}_2\text{CO}_3$  led to a consecutive reaction. Fill in the following boxes with the photoproduct and the final product. Show only the major diastereoisomer. What is the name of this reaction sequence?



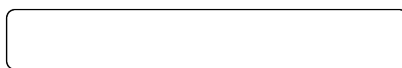
c) *Boxall et al.* utilize a named reaction for the total synthesis of 1,13-herbetenediol. What is the name of this reaction? Please draw the structure of the product with the correct relative configuration.



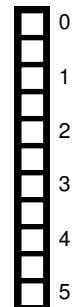
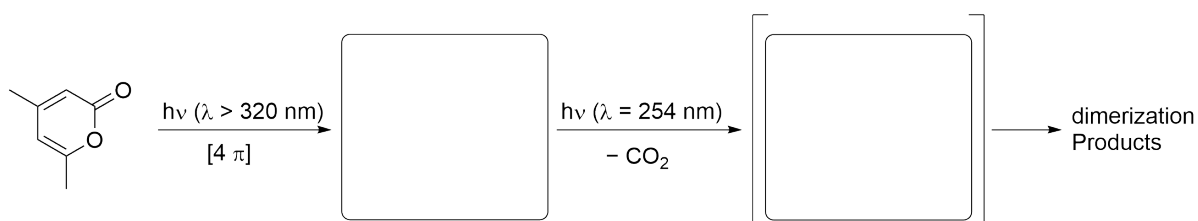
d) In 2022, the Nobel Prize in chemistry was awarded to scientists *Carolyn R. Bertozzi*, *Morten Meldal* and *K. Barry Sharpless* for their contributions to what is known as click chemistry. In the example below, a cycloaddition of an alkene with an azide is depicted. Please fill in the missing intermediate and product. Explain which process is necessary to transform the starting material into its strained, reactive intermediate.



type of reaction in first step:



e) The photochemistry of 4,6-dimethyl-2-pyrone is full of surprises: Upon irradiation at  $\lambda > 320$  nm, a clean  $[4\pi]$ -cyclization to a bicyclic lactone is observed. If the thereby formed compound is further irradiated at  $\lambda = 254$  nm,  $\text{CO}_2$  loss occurs and a  $[4\pi]$ -ring opening leads to a highly strained diene, which thermally dimerizes. Please provide the missing structures.



- 0
- 1
- 2
- 3
- 4
- 5
- 6

f) Upon irradiation of 3-(2-benzylphenoxy)-1-phenylpropan-1-one with UV light, a 7-membered ring is formed. Fill in the boxes with the biradical intermediate and the major diastereomer of the product, and give the name of the reaction.



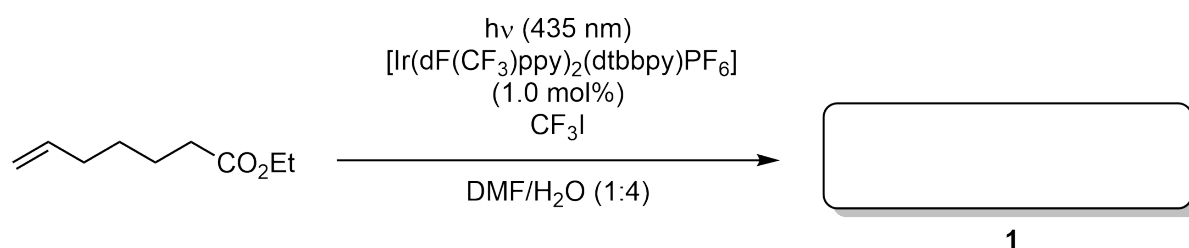
Name of the reaction:



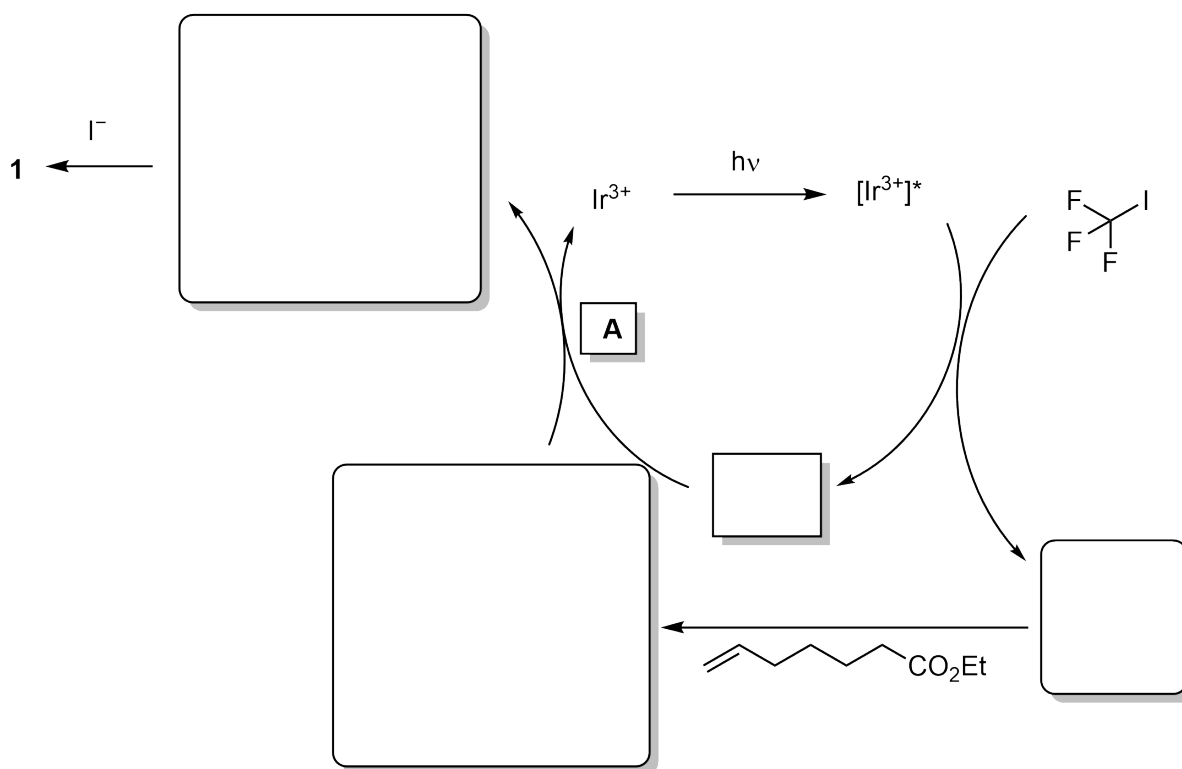
## Problem 4 Photoredox Chemistry (18 credits)

In recent years, the field of photoredox chemistry has experienced a steep gain in importance and attention.

a) The following scheme shows a photochemical conversion of an alkene with  $\text{CF}_3\text{I}$  utilizing an iridium(III) catalyst.



Fill in the missing intermediates and products. Which term describes what happens in step **A**?



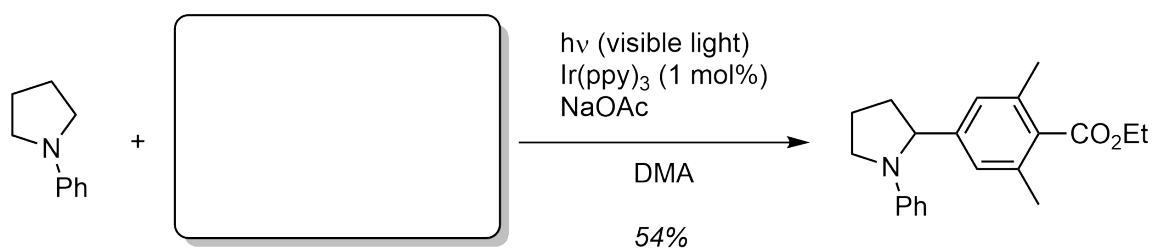
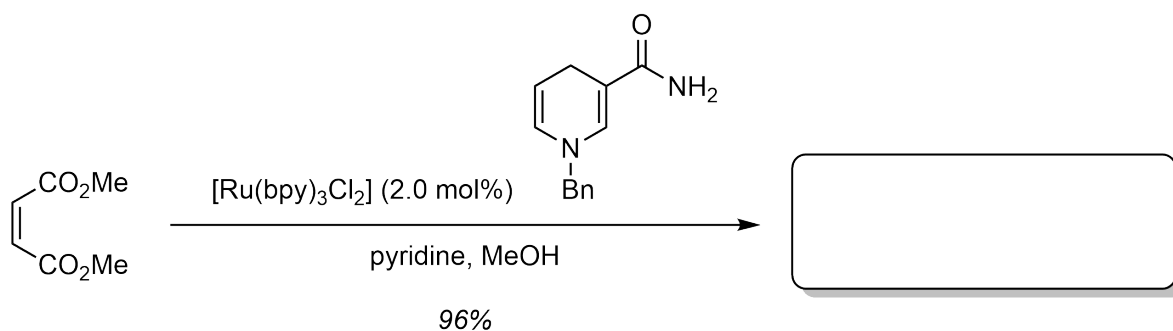
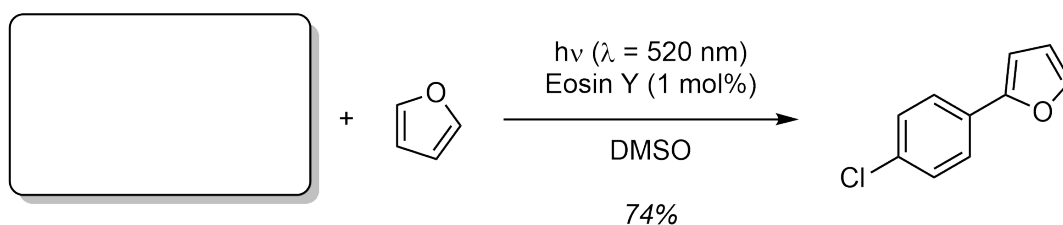
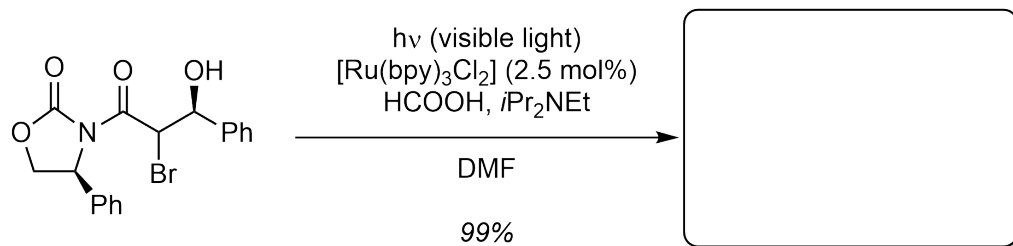
Step **A**:



In addition to step **A** another propagation of the mechanism was also observed. What is the name of this alternative mechanism? Suggest an experiment to determine whether this alternative mechanism is taking place. Which results would indicate that?

- 0
- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8

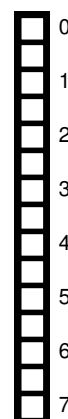
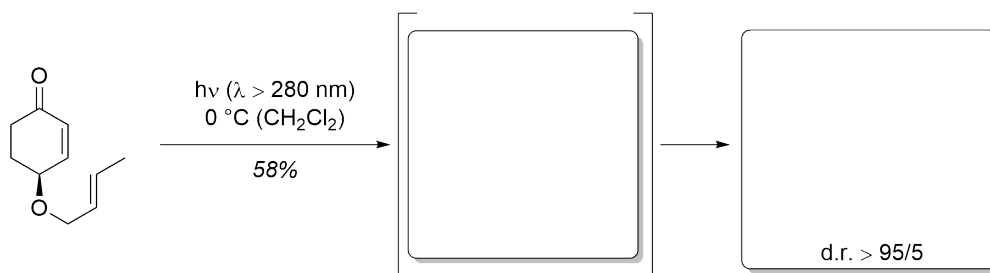
b) Fill in the missing products and starting materials for the following reactions.



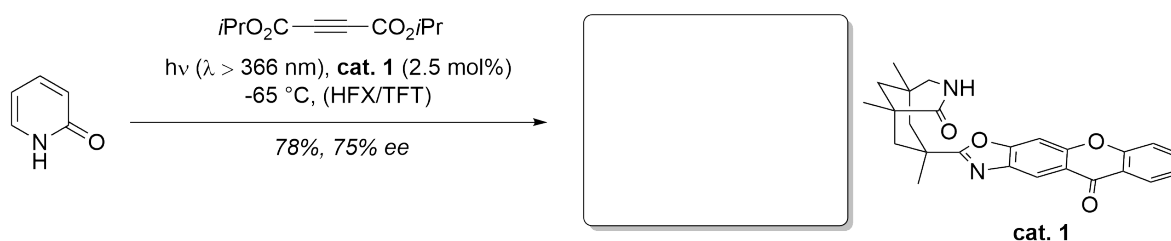
## Problem 5 Diverse Reactivity (25 credits)

Organic photochemistry gives rise to a diverse set of chemical reactions.

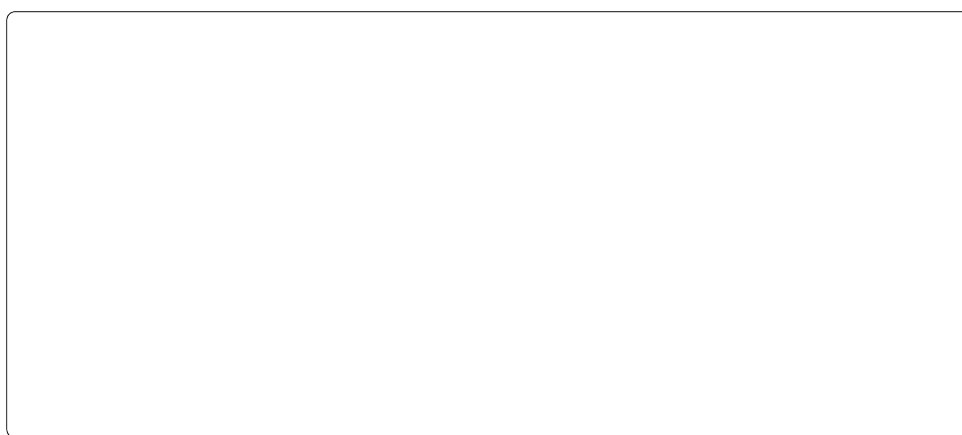
a) Fill the following boxes with the biradical intermediate and final product of the following intramolecular photoreaction. Consider regio- and diastereoselectivity.



b) Introducing enantioselectivity into photochemistry has been accomplished in a variety of ways. The following photocycloaddition has been performed in the presence of the chiral catalyst **cat. 1** with high enantioselectivity. Draw the final compound with the correct absolute configuration.

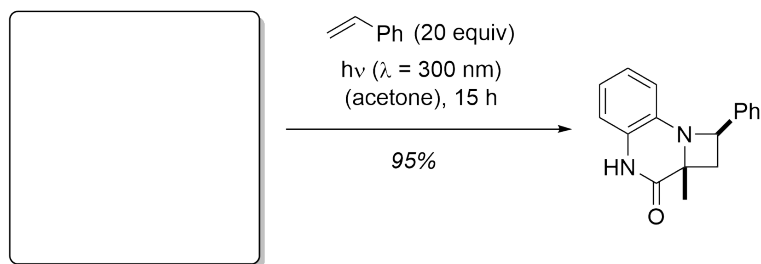


Draw the substrate-catalyst complex which indicates the enantioselectivity of the reaction.



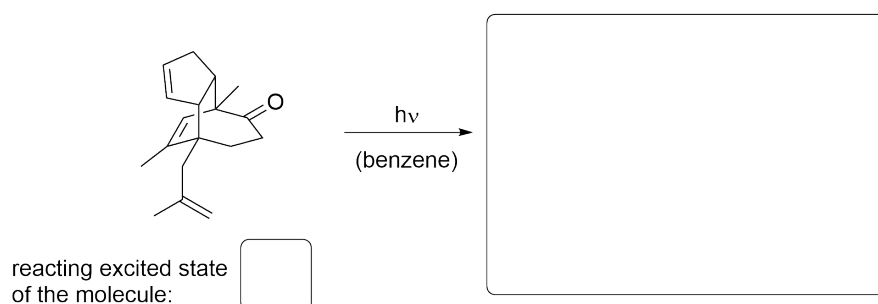
0  
1  
2

c) Shown below is a variant of a known photochemical reaction. Please fill in the structure of the starting material.



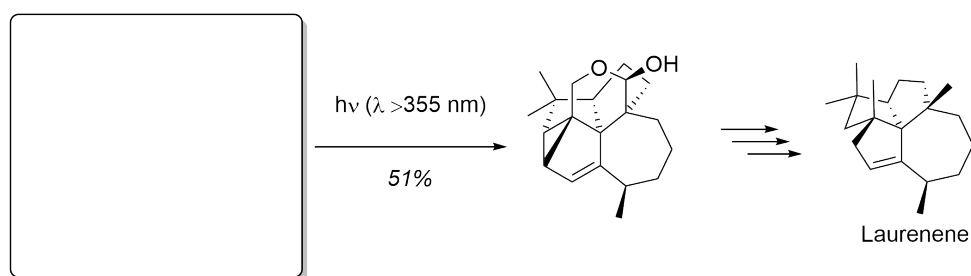
0  
1  
2  
3  
4  
5

d) A stereoselective synthetic route to simple *cis*-hydrindanes involves a photochemical rearrangement reaction. Please provide the missing structures and the involved excited state of the substrate.



0  
1  
2  
3  
4  
5

e) In 1988, *Wender* and coworkers were able to complete the total synthesis of the diterpene laurenene. The group utilized a photoreaction to access a key intermediate, which was further derivatized to lead to the desired natural product. Please give the structure of the corresponding photosubstrate, briefly explain the observed stereoselectivity and give the name of the photoreaction.



Name of the photoreaction:

Reason for stereoselectivity:

**Additional space for solutions—clearly mark the (sub)problem your answers are related to and strike out invalid solutions.**

