



E0001

Place student sticker here

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
Examiner: Prof. Dr. Thorsten Bach

Date: Thursday 11th April, 2024
Time: 14:00 – 15:30

	P 1	P 2	P 3	P 4	P 5
I					

Working instructions

- This exam consists of **18 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 in red or green nor use pencils.
- Every correctly 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) In a Jablonski diagram, a horizontal transition is called. . .

- ☐ intersystem crossing.
- ☐ internal conversion.
- ☐ phosphorescence.
- ☐ fluorescence.

b) The S_1 is rapidly populated due to. . .

- ☐ the molar extinction coefficient of the molecule.
- ☐ the instantaneous transition of an electron to the excited state.
- ☐ the relatively slower "spin-forbidden" phosphorescent radiation.
- ☐ fast vibrational relaxation of excited electronic states within the same spin multiplicity.

c) Photoexcited alkene isomerization will selectively form one isomer if. . .

- ☐ the molar extinction coefficient of the major product is lower than that of the minor product.
- ☐ the maximum absorbance of the major product is higher than that of the minor product.
- ☐ there is no energy difference between the two radical transition states.
- ☐ the transition state does not allow for free rotation of the C-C bond.

d) The high difference in energy levels between the S_1 state and the T_1 state in aliphatic alkenes is due to...

- ☐ the involvement of non-bonding orbitals in the T_1 state vs. the S_1 state.
- ☐ the high electron-electron repulsion in the S_1 state.
- ☐ a combination of high electron-electron repulsion in the S_1 state and a low electron-electron repulsion in the T_1 state.
- ☐ the lack of electron-electron repulsion in the T_1 state.

e) Suprafacial [1,3]-sigmatropic hydrogen shifts are. . .

- ☐ thermally forbidden and photochemically allowed.
- ☐ thermally allowed and photochemically forbidden.
- ☐ thermally and photochemically forbidden.
- ☐ thermally and photochemically allowed.

f) Enantioselective photoreactions catalyzed by chiral Lewis acids can be accomplished because of the. . .

- ☐ the bathochromic shift of the substrate-Lewis acid complex.
- ☐ the hydrogen bonding of the substrate-Lewis acid complex.
- ☐ the hypsochromic shift of the substrate-Lewis acid complex.
- ☐ the extinction coefficient of the Lewis acid catalyst.





g) Which technique should be used to detect the formation of an EDA complex in a photoredox reaction?

- ☐ Laser flash photolysis.
- ☐ Cyclic voltammetry.
- ☐ Absorption spectroscopy.
- ☐ Emission spectroscopy.

h) Phthalimide precursors are often used to photochemically generate...

- ☐ aryl radicals in a reductive manner.
- ☐ alkyl radicals in an oxidative manner.
- ☐ alkyl radicals in a reductive manner.
- ☐ aryl radicals in an oxidative manner.

i) What is the advantage of proton coupled electron transfer (PCET)?

- ☐ Lowering the reduction potential of the starting material.
- ☐ Lowering the oxidation potential of the starting material.
- ☐ Increasing the oxidation potential of the starting material.
- ☐ Increasing the reduction potential of the starting material.

j) Tertiary amines (e.g. NBu_3) are commonly employed into various photoredox reactions...

- ☐ to accept electrons from the photocatalytic cycle.
- ☐ to generate an alpha amino radical as a radical initiator.
- ☐ as proton scavengers.
- ☐ to donate electrons into the photocatalytic cycle.





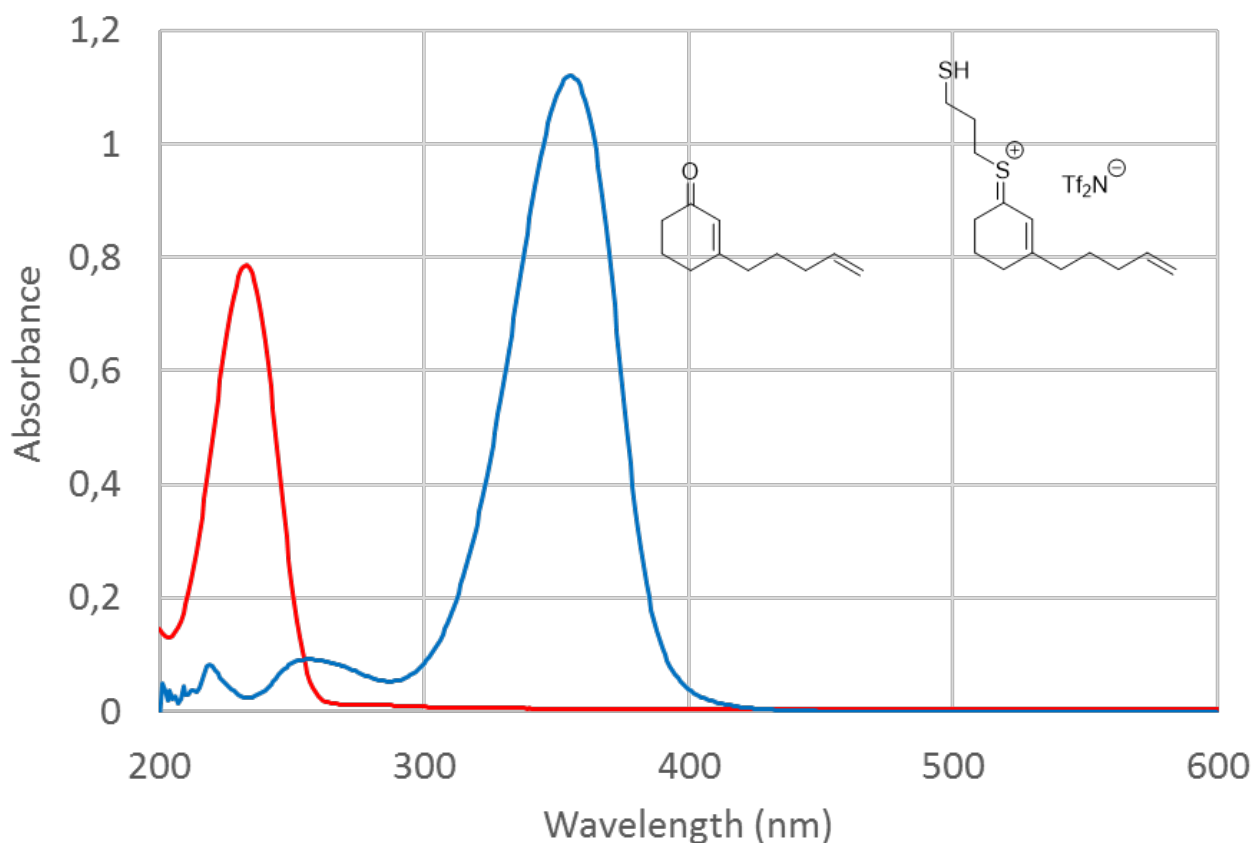
Problem 2 Fundamentals of Photochemistry (12 credits)

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

Constants: Avogadro constant = 6.0221×10^{23} /mol, Planck constant = 6.6261×10^{-34} J s, speed of light = 299.79×10^6 m/s.

Important: Provide equations for all your calculations and all numbers with three significant digits.

- 0 ☐
- 1 ☐
- 2 ☐
- 3 ☐
- 4 ☐
- a) The UV/Vis spectra of the enone and sulfonium ion are shown below in red and blue, respectively. Assuming the spectra were recorded using a 1 mm quartz cuvette and 0.5 mM concentration for both samples, calculate the absorption coefficient ϵ_{enone} for the enone at 235 nm and the absorption coefficient $\epsilon_{\text{sulfonium}}$ of the sulfonium ion at 357 nm. The absorbance A_{enone} for the enone at 235 nm is 0.77 and the absorbance $A_{\text{sulfonium}}$ of the sulfonium ion at 357 nm is 1.11. What is the name of the equation that you have to use for this calculation?





b) Describe in words El Sayed's rule.

0
1

c) What type of organic molecules are usually used as triplet photosensitizers? Give one example.

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) Non-conjugated alkenes normally absorb weakly over 200 nm, which would make their excitation hard to achieve using direct irradiation. Triplet energy transfer from a photosensitizer can be a solution for this problem. What are the requirements regarding triplet energies for the *E/Z* isomers of the alkene [$E_T(E)$ and $E_T(Z)$] and the sensitizer [$E_T(sens)$] to achieve a successful energy transfer and enrich the *Z* isomer?

0
1
2





Problem 3 Direct Excitation (30 credits)

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

a) Irradiation of the compound shown below results in the formation of a fused tetracyclic compound. Give the structures for the two short-lived intermediates and the final product of the reaction. What is the name of the reaction?

0 ☐

1 ☐

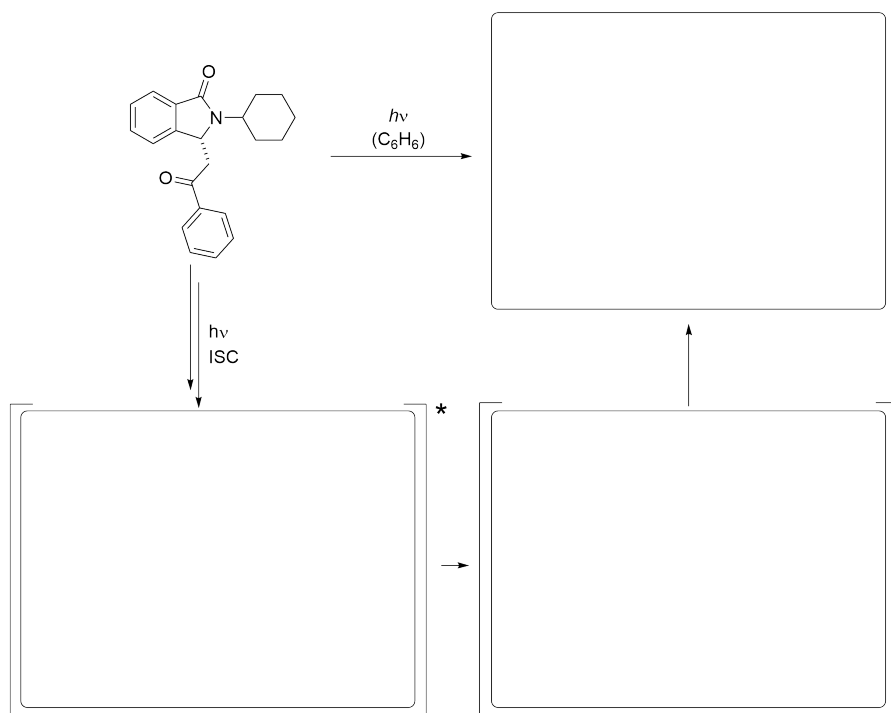
2 ☐

3 ☐

4 ☐

5 ☐

6 ☐

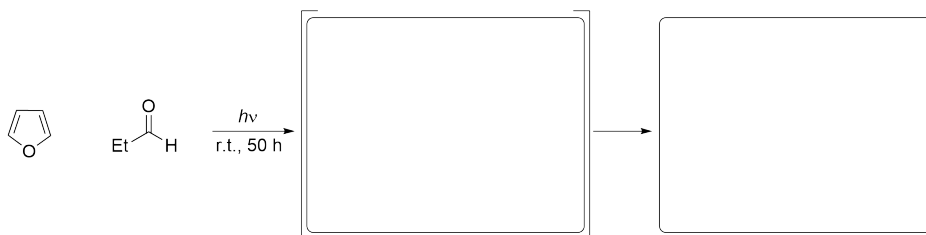


Name of the reaction:





b) Give the structures of the reactive intermediate and for the product of the reaction. What is the reason for the observed regioselectivity? What is the name of the reaction?



☐	0
☐	1
☐	2
☐	3
☐	4
☐	5
☐	6

Reason for regioselectivity:

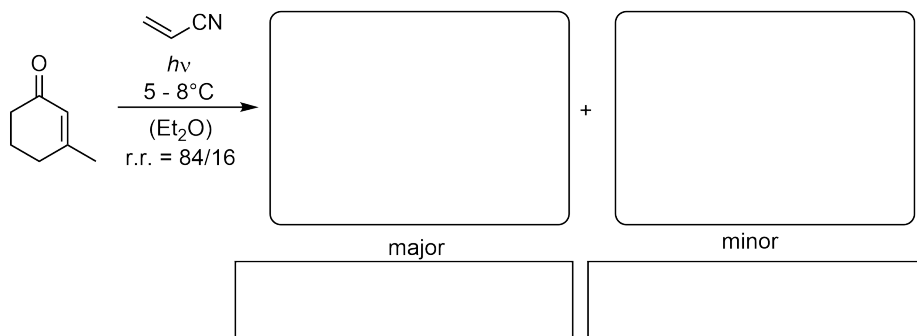
Name of the reaction:





- 0 ☐
- 1 ☐
- 2 ☐
- 3 ☐
- 4 ☐
- 5 ☐
- 6 ☐
- 7 ☐
- 8 ☐
- 9 ☐
- 10 ☐
- 11 ☐
- 12 ☐
- 13 ☐

c) Fill in the major and the minor product of the following photoreaction. Give the mechanism and explain the observed regioselectivity by considering the polarization of the reactive center of the substrate. Classify the major and the minor product in terms of regioselectivity. What is the spin multiplicity of the photoexcited substrate in the reaction?



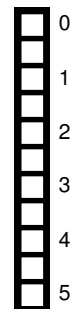
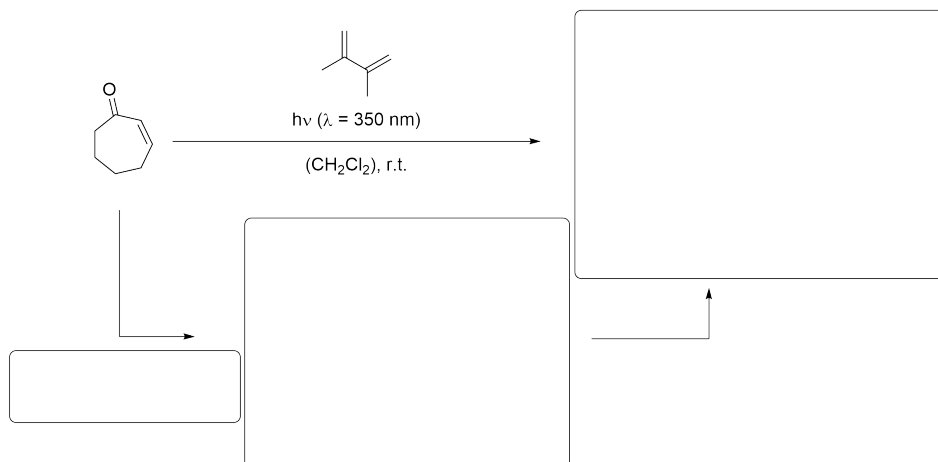
Explanation of regioselectivity:

Spin multiplicity:





d) The Bach group published an example of a [4+2] cycloaddition reaction (Diels-Alder reaction) of 2-cyclohepten-1-one with 2,3-dimethylbutadiene under direct irradiation. This reaction only occurs after photochemical activation of the cycloheptenone. State what transformation is required for this activation and give the correct structure of the reactive intermediate. Why is this intermediate more reactive towards cycloaddition reactions than the starting material? Give the correct structure of the obtained product.



Reason for higher reactivity of the intermediate:

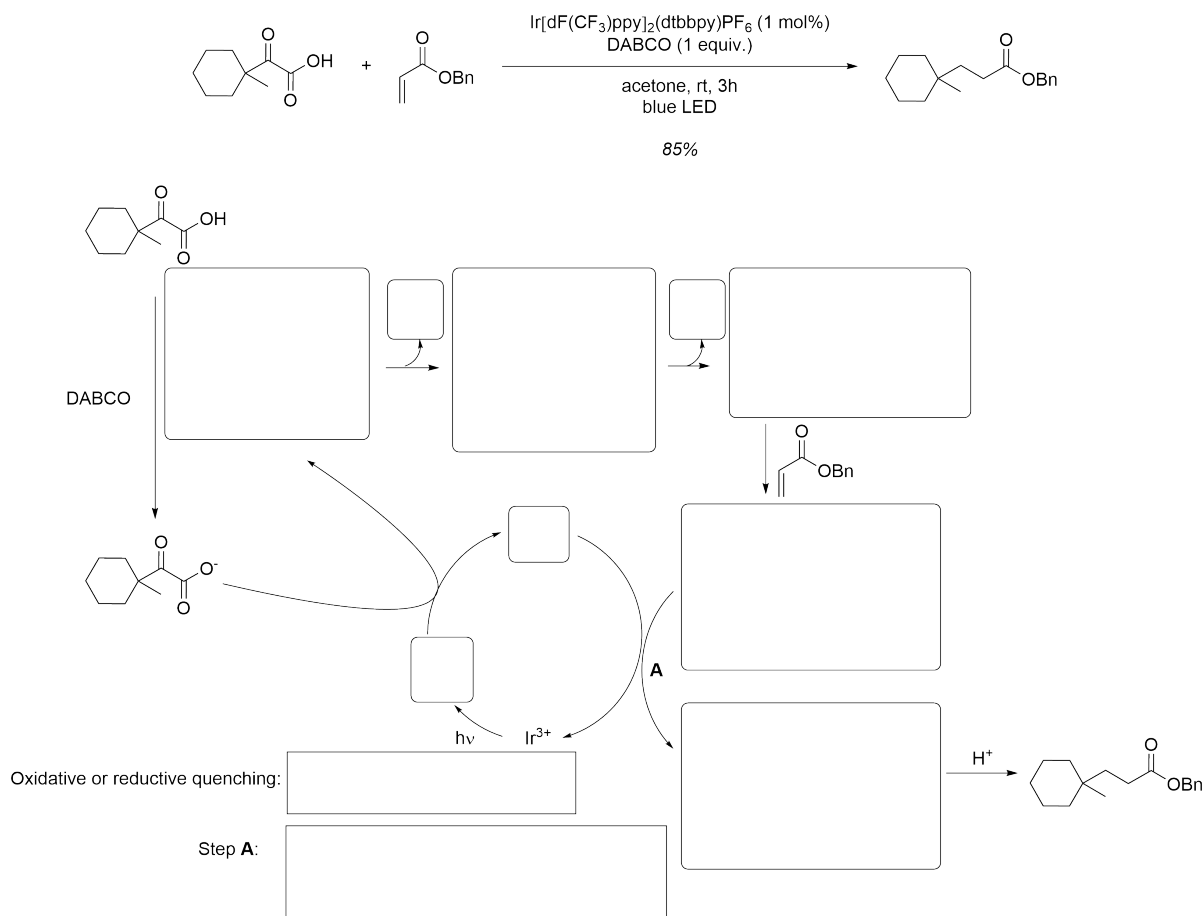




Problem 4 Photoredox Chemistry (21 credits)

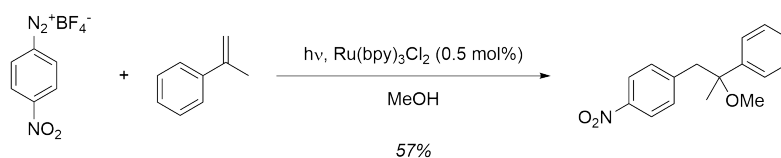
In recent years, the field of photoredox chemistry has experienced a rapid gain in importance and attention.

a) The following light-mediated alkylation was developed by Xu and coworkers in 2018. Complete the catalytic cycle. Is this reaction going through an oxidative or a reductive quench of the catalyst?

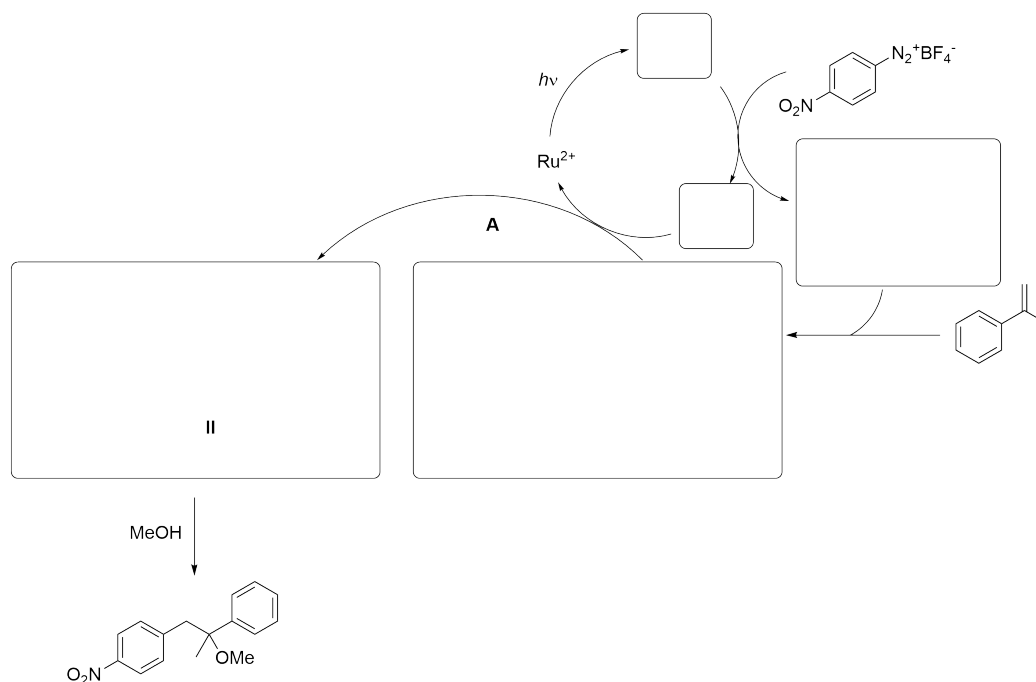




b) The following scheme shows the light-mediated reaction between a diazonium salt and an alkene.



Fill in the missing intermediates and products.



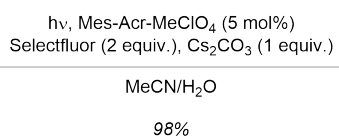
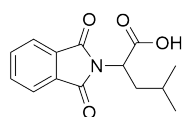
In addition to step A, another propagation of the catalytic cycle was observed. What is the name of this alternative mechanism? Suggest an experiment to determine whether this alternative mechanism is taking place. Which result would indicate that?





0 ☐
1 ☐
2 ☐

c) Selectfluor is a strong fluorinating reagent that can donate an electrophilic fluorine atom. What is the product of the reaction below? A side product of this reaction is a gas.



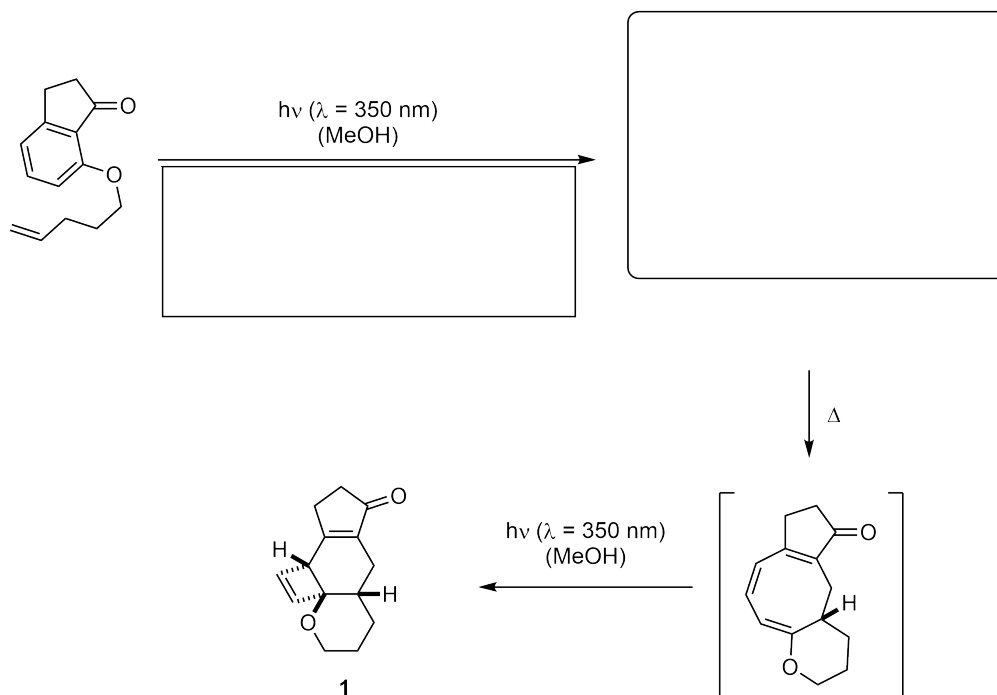


Problem 5 Diverse Reactivity (27 credits)

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

a) In 2020, the Bach group reported a remarkable synthesis of complex carbocyclic skeletons from aryl ketones. The product is formed in three different, consecutive photoreactions.

The first step consists of a well known photoreaction of aromatic compounds which is followed by a thermal ring opening reaction to a cyclooctatriene. Give the correct structure of the formed intermediate and the name of the reaction. The formed cyclooctatriene then engages in the second photochemical reaction leading to compound **1**. Give the name of the reaction and classify it as con- or disrotatory.



Type of reaction:

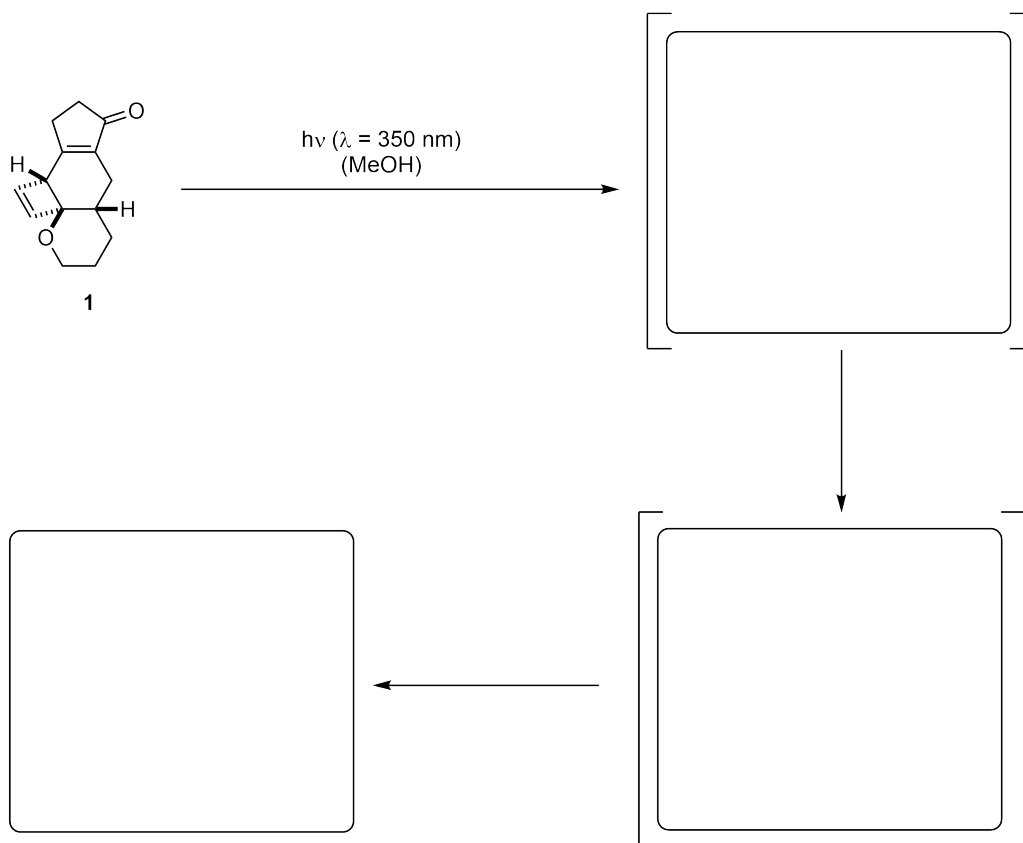
Woodward-Hoffmann classification:

- 0
- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10
- 11
- 12
- 13
- 14





Once compound **1** is formed, a photoinduced rearrangement reaction takes place to deliver the final product. Give the structures of the relevant intermediates and of the product. Ignore any stereogenic centers other than the ones already present in **1**. What is the name of this reaction and on which hypersurface does it occur?



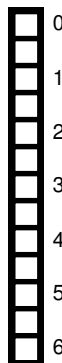
Type of reaction:

Hypersurface (Spin multiplicity):



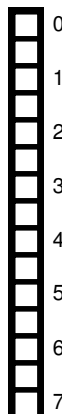


b) Copper catalyzed reactions also play a significant role in photochemistry. The example below shows a Cu(I)-catalyzed diastereoselective photoreaction. Draw the transition state and give the structure of the product. Explain the function of the catalyst.



Function of the catalyst:

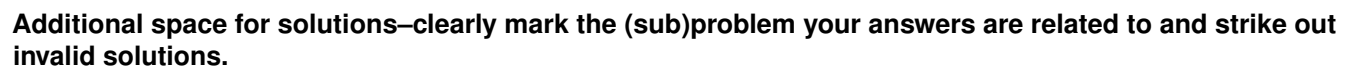
c) Fill in the missing structures of the product and the short lived intermediate of the reaction below and give an explanation on the diastereoselectivity of the reaction. What is the name of the reaction? *Hint:* The carbonyl starting material behaves like an aromatic aldehyde and a CPh group has a smaller steric bulk than a Ph group.



Reason for observed diastereoselectivity:

Name of the reaction:



This image shows a full page of blank graph paper. The grid consists of small, equal-sized squares formed by thin gray lines. There are 20 columns and 20 rows of squares, creating a total of 400 square units. The grid covers the entire area of the page, leaving no margins or other markings.