

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:** Thursday 14th April, 2022
Examiner: Prof. Thorsten Bach **Time:** 08:30 – 10:00

	P 1	P 2	P 3	P 4	P 5	P 6	P 7	P 8
I								

Working instructions

- This exam consists of **16 pages** with a total of **8 problems**. Please make sure now that you received a complete copy of the exam. Detaching pages from the exam is prohibited.
- The total amount of achievable credits in this exam is 100 credits.
- Allowed resources:
 - one **non-programmable pocket calculator**
 - one **analog dictionary** English ↔ native language

No molecule models are allowed.

Cheating and cheating attempts will result in the candidate failing the exam.

- Do not write with red or green colors nor use pencils.
- Physically turn off all electronic devices, put them into your bag and close the bag.
- 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!**
- 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.

Left room from _____ to _____ / Early submission at _____

Problem 1 Multiple Choice Questions (14 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) The El-Sayed rules...

- are the basis to measure transient absorption signals.
- were published by Mostafa El-Sayed in the 19th century.
- state that thermal reactions are always feasible.
- describe whether a radiationless electronic transition is allowed.

b) What is the correct order of steps for ab initio molecular dynamics, considering the following options:

1. Via quantum chemistry, calculate the energy gradient of a state
2. Estimate the MOs of the current molecular geometry
3. Advance the nuclei from the current state to the next one

- 3, 1, 2
- 1, 2, 3
- 2, 3, 1
- 1, 3, 2
- 2, 1, 3
- 3, 2, 1

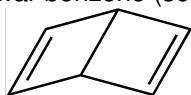
c) Which structures are obtained in an intramolecular *meta*-photocycloaddition of an arene bearing a chain with an alkene at the 4-position?

- Cyclobutadienes and bicyclobutanes
- Hexadienes and octatrienes
- Fulvenes and benzvalenes
- Linear and angular triquinanes

d) Which compounds are obtained upon reaction of singlet oxygen with dienes?

- dicarbonyl compounds
- dioxetanes
- endoperoxides
- hydroperoxides

e) Dewar benzene (see below) is kinetically stable under thermal conditions, because...



- the ring opening process in the mechanism of the 4π electrocyclic ring opening occurs in conrotatory fashion, which leads to a *cis*-configured double bond in the benzene ring.
- the ring opening process in the mechanism of the 4π electrocyclic ring opening occurs in disrotatory fashion, which would lead to a *cis*-configured double bond in the benzene ring.
- the ring opening process in the mechanism of the 4π electrocyclic ring opening occurs in disrotatory fashion, which leads to a *trans*-configured double bond in the benzene ring.
- none of the other options.
- the ring opening process in the mechanism of the 4π electrocyclic ring opening occurs in conrotatory fashion, which would lead to a *trans*-configured double bond in the benzene ring.

f) Why is EPR spectroscopy a useful tool in addition to NMR spectroscopy to detect radicals in the flavin-catalyzed photooxidation of benzylic alcohols?

- Since EPR spectroscopy is a method for unpaired electron spins it is the obvious tool for radicals.
- Radicals are usually paramagnetic compounds and therefore it's difficult to measure NMR spectra with them.
- Both methods (EPR and NMR spectroscopy) work with spins that are excited in a magnetic field.
- All of the other options.

g) What is/are the possible electronic transition(s) of $[\text{Ru}(\text{bpy})_3]^{2+}$?

- All of the other options
- metal-to-ligand charge-transfer (MLCT)
- ligand-field (LF)
- intraligand (IL)

h) Which of the following transition states is usually involved during the hydrogen atom transfer (HAT) event in Norrish type II reactions?

- 5-membered ring
- 4-membered ring
- 6-membered ring
- 7-membered ring

i) Tertiary amine bases, like triethylamine, diisopropylethylamine and DBU, are often used in photoredox reactions. What role(s) can they play in the reaction?

- They readily undergo one-electron reduction, and the resulting radical anion can also transfer an electron to the substrate to complete the catalytic cycle.
- They are mostly used as bases to deprotonate and activate photocatalysts in photoredox reaction.
- All of the other choices.
- They readily undergo one-electron oxidation, and the resulting radical cation can also transfer an H-atom to complete the catalytic cycle.

j) Multifunctional catalysis describes...

- regimes where two or more reactants are simultaneously and independently activated by an equal number of distinct catalytically active site within one catalyst.
- regimes where two or more catalysts are simultaneously and independently activated.
- none of the other options.
- regimes where two or more reactants are simultaneously and independently activated by an equal number of distinct catalysts.

k) In which photoelectrochemical process do we observe a level inversion of the HOMO and SOMO photocatalyst (PC) orbitals?

- $PC^{\bullet-} \rightarrow [PC]^*$
- $PC \rightarrow [PC]^*$
- $PC^{\bullet-} \rightarrow [PC^{\bullet-}]^*$
- $PC \rightarrow PC^{\bullet-}$
- $PC \rightarrow [PC^{\bullet-}]^*$

l) What are the advantages of using Ce catalysts for remote C–H bond functionalization?

- Cerium catalysts are unstable but this makes them more reactive and gives high yields of products in photocatalyzed reactions.
- Cerium is inexpensive and abundant, and the reaction conditions are mild (base free, room temperature).
- $CeCl_3$ is soluble in many organic solvents and it is not hygroscopic.
- All of the other options.

m) In the context of radical photochemistry, alkyl amines may react with a base or other reactants to form...

- α -amino radicals or aminium ions.
- α -amino radicals, iminium or aminium ions.
- α -amino radicals, imines or iminium ions.
- exclusively α -amino radicals.

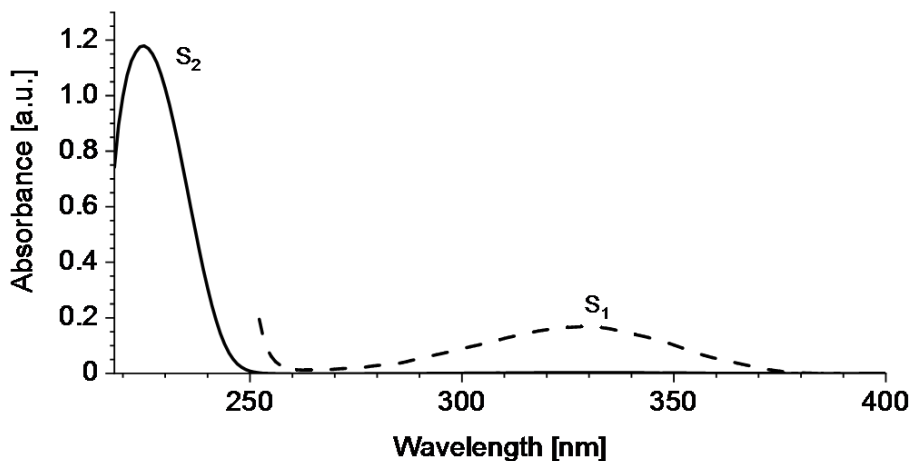
n) Which of these enzymes is a naturally occurring photoenzyme?

- Alcohol dehydrogenase
- Amylase
- Cytochrome P450
- None of the other options
- Reverse transcriptase

Problem 2 Fundamentals of Theory and Spectroscopy (18 credits)

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

a) Below you can find an UV/vis spectrum of 2-cyclohexen-1-one in dichloromethane (solid line: $c = 1.0$ mM; dashed line: $c = 50$ mM) measured in a 1.0 mm quartz cuvette at room temperature. Two absorption bands are noticeable: one with $\lambda_{max} = 330$ nm and one with $\lambda_{max} = 224$ nm.



Given the UV/vis spectrum of 2-cyclohexen-1-one, calculate the molar attenuation coefficient (also called molar extinction coefficient) for the maximum of S_2 using the Lambert–Beer law. Give the formula of the law and calculate the value for the molar attenuation coefficient to two significant digits in the typically used SI units.

b) Briefly explain "thermally activated delayed fluorescence" and provide a typical commercial application of this phenomenon.



c) The theory described by Woodward and Hoffmann was the first model that successfully explained and predicted the outcome of pericyclic reactions. What is the basic principle of the Woodward–Hoffmann rules? In addition, give **one** aspect of a pericyclic reaction that may be predicted with this theory?



- basic principle:

- predicted aspect:

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1 d) Transient absorption spectroscopy is a useful method to understand photophysics and -chemistry. Give **one** specific example that has been / could be studied by transient absorption spectroscopy.

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2 e) What are conical intersections and for which processes on a potential energy surface are they relevant?

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3 f) You would like to determine the quantum yield of a photocatalyzed reaction. Therefore, you want to irradiate a sample solution (volume = 2.5 mL) in a cuvette with a suitable LED with $\lambda_{max} = 400$ nm (irradiated area = 1.0 cm²) and detect the energy of the light that has passed the solution (i.e. transmitted).

With only solvent in the cuvette (without substrate and catalyst), you measure an energy output of the LED of 160 120 $\mu\text{W cm}^{-2}$. With your sample solution (substrate and catalyst), you measure an energy of 10 190 $\mu\text{W cm}^{-2}$. After exactly 60 min, you take a sample of the solution and determine via calibrated GC analysis that the product concentration was 22.1 $\mu\text{mol mL}^{-1}$.

Calculate the energy of a photon at 400 nm, the mol of absorbed photons after 60 min and the quantum yield of product formation. Provide all numbers with three significant digits.

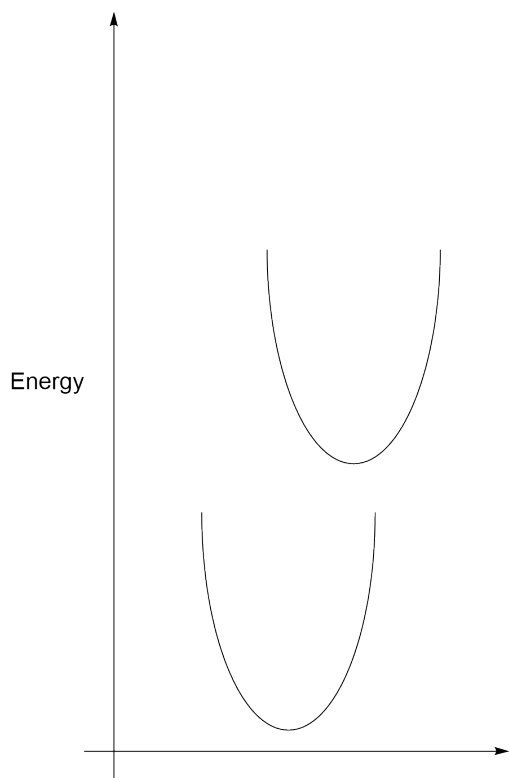
Useful constants: Avogadro constant = $6.0221 \times 10^{23} \text{ mol}^{-1}$, Planck constant = $6.6261 \times 10^{-34} \text{ J s}$, speed of light = $299.79 \times 10^6 \text{ m s}^{-1}$.

• $E_{\text{photon}}(400 \text{ nm}) =$

• $n_{\text{photons}} =$

• $\phi =$

g) Briefly explain the Franck-Condon principle and the Stokes shift. To illustrate your explanation, draw some vibrational energy levels into the given parabolas that represent the S_0 and S_1 energy surfaces, and draw arrows representing the photoexcitation of a molecule from S_0 to S_1 as well as following radiative or non-radiative processes to the S_0 minimum. Properly label the energy surfaces and *all* arrows.



short explanation:

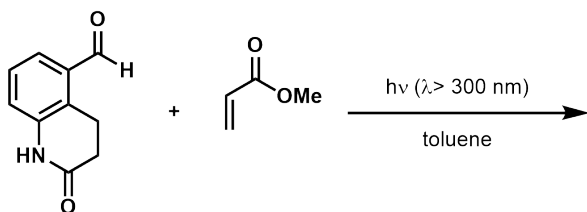
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Problem 3 Direct Excitation (7 credits)

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

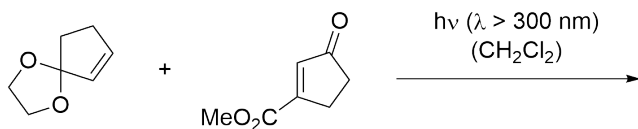
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a) Draw the structure of the product. *Hint: The endo-diastereomer is obtained.*



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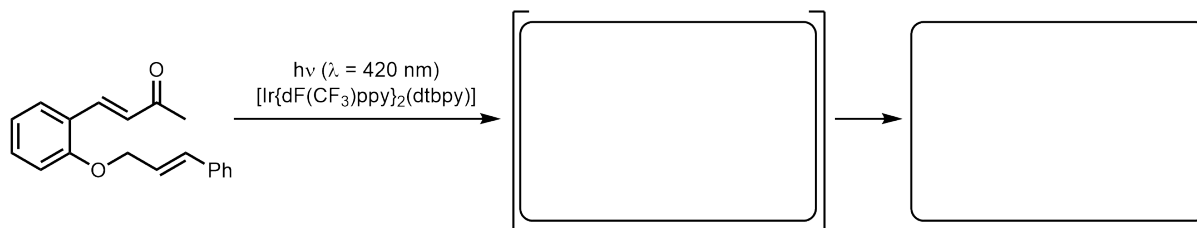
b) Give the missing structure in the shown photochemical transformation after direct irradiation under consideration of the diastereo- and regioselectivity. *Hint: The acetal has an electron-withdrawing effect on the olefin.*



Problem 4 Photocatalysis (9 credits)

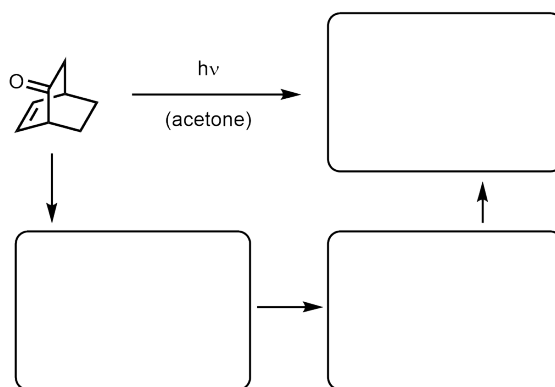
Both organic and organometallic catalysts have significantly expanded the repertoire of photochemical reactions.

a) Draw the structures of the diradical intermediate and the product of this reaction. *Hint: The thermodynamically most stable diradical is being formed.*



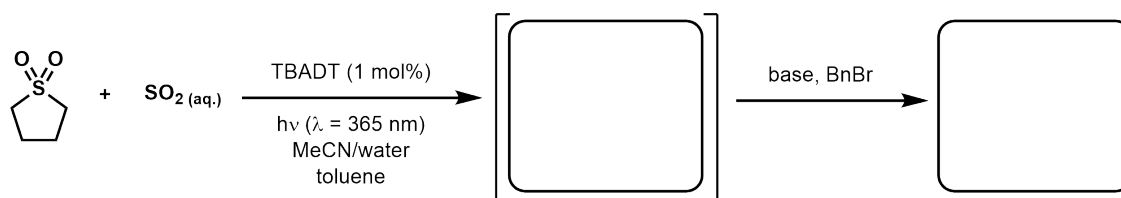
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b) Give the structures of the diradical intermediates and the product of this rearrangement reaction.



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c) Complete the following reaction scheme. *Hint: In the second step, the crude acid is directly transformed into a derivative to facilitate its isolation.*



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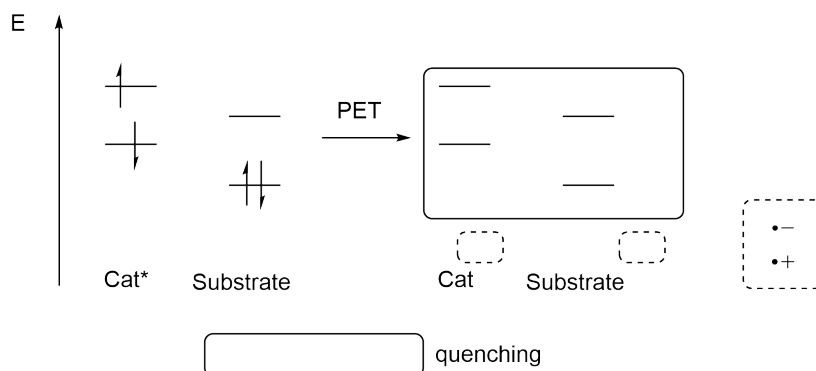
Problem 5 Basics of Photoredox Catalysis (11 credits)

Some fundamental aspects are relevant for various photoredox-catalyzed reactions.

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- a) The transition metal photocatalyst $[\text{Ru}(\text{bpy})_3]^{2+}$ is one of the most frequently applied catalyst for photoredox and sensitization processes in organic synthesis. Give **one** advantage and **one** disadvantage of this catalyst. Also name the main difference between a 4d complex like $[\text{Ru}(\text{bpy})_3]^{2+}$ and a 3d complex like $[\text{Fe}(\text{bpy})_3]^{2+}$ regarding their excited states.

- advantage and disadvantage of $[\text{Ru}(\text{bpy})_3]^{2+}$:
- difference of $[\text{Fe}(\text{bpy})_3]^{2+}$:

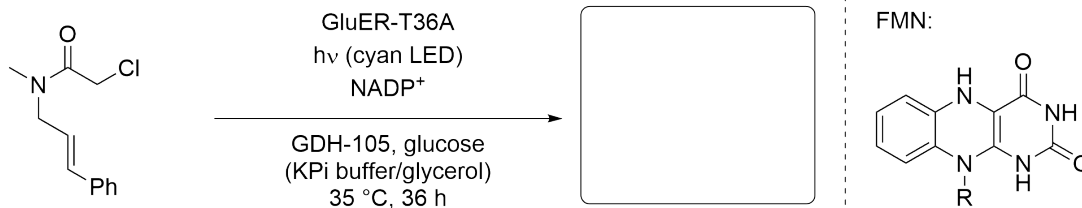
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- b) Transition metal and organic photocatalysts (e.g. $[\text{Ru}(\text{bpy})_3]^{2+}$ or eosin Y) can participate in photoredox processes. Below you find a scheme demonstrating a photoinduced electron transfer (PET) between an excited catalyst (Cat^*) and a general substrate. Please complete the scheme by filling in electrons (as arrows) and the elements given in the dashed box on the right. Name the type of quenching represented in this scheme.



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- c) Amine radical cations are highly reactive and can be found in photoredox reactions. Draw **one** typical amine radical cation that acts as a HAT or a SET agent. State to which type of agent your drawn molecule belongs.

_____ agent

d) The following amide undergoes a reaction when irradiated with visible light in the presence of the flavin-dependent "ene"-reductase GluER-T36A (and the glucose dehydrogenase GDH-105). This enzyme has flavinmononucleotide (FMN) in its active site. Under the reaction conditions, the promiscuous photoenzymatic activity gives predominantly the (*R*)-enantiomer. Draw the product, and briefly explain why the stereoselectivity is observed and why visible light can be used instead of UV light.



Explanation:

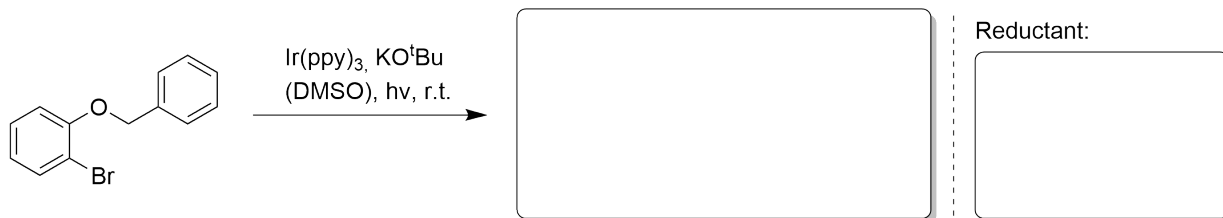


Problem 6 Photoredox Chemistry (15.5 credits)

Through photoredox catalysis, a plethora of chemical reactions are made feasible.

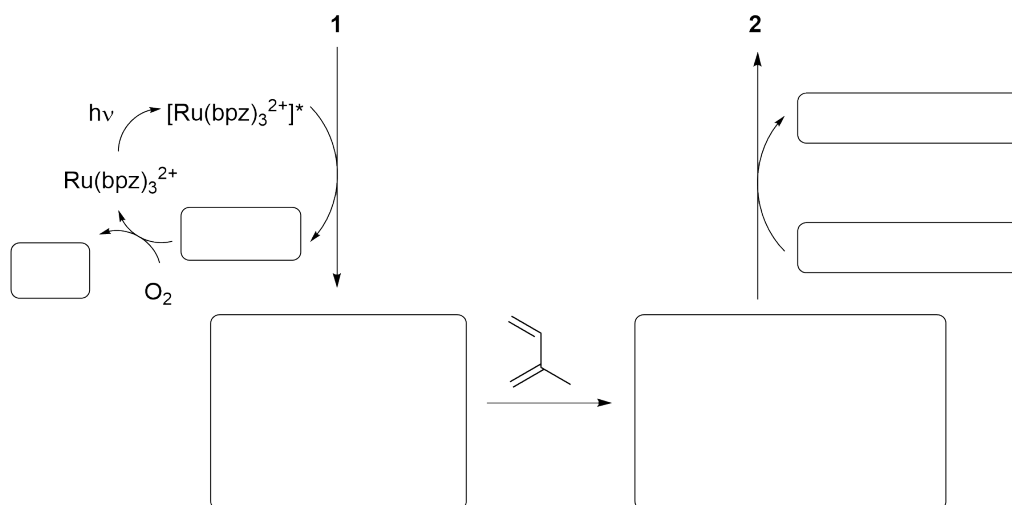
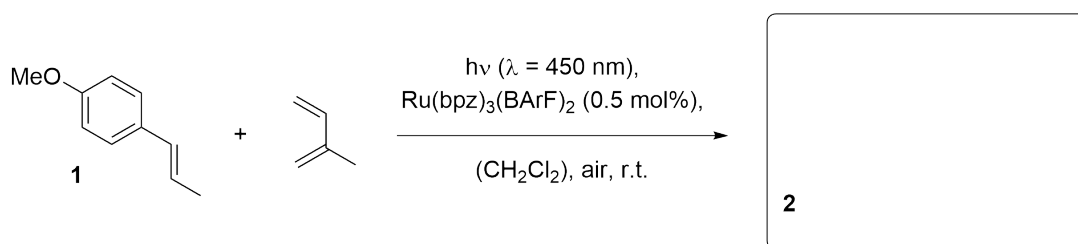
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a) One of the oldest known cross-coupling reactions is the Ullmann reaction, in which two aryl halides are coupled via the addition of copper under harsh conditions. In the following intramolecular photoredox cross-coupling reaction, the same product moiety is obtained. Give the structure of the product. Which compound is most likely the reductant that initiates the reaction?



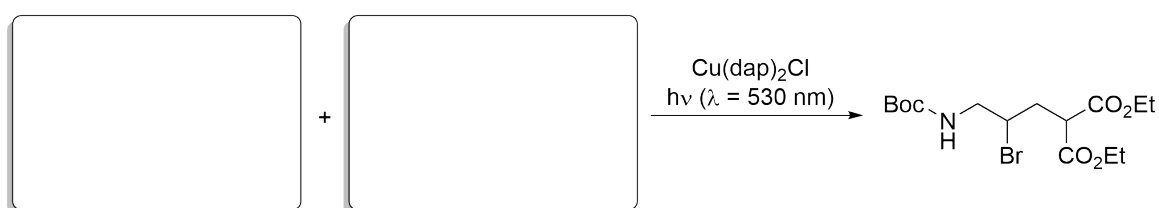
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b) A styrene derivative and a diene are irradiated in the presence of a ruthenium catalyst and undergo a cycloaddition. Draw the product with the correct relative configuration and give a mechanistic explanation.



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c) Certain copper catalysts are able to act as photoredox catalysts after being irradiated with green light. Give the structures of the starting materials. What type of reaction is happening here?

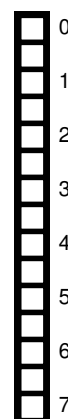
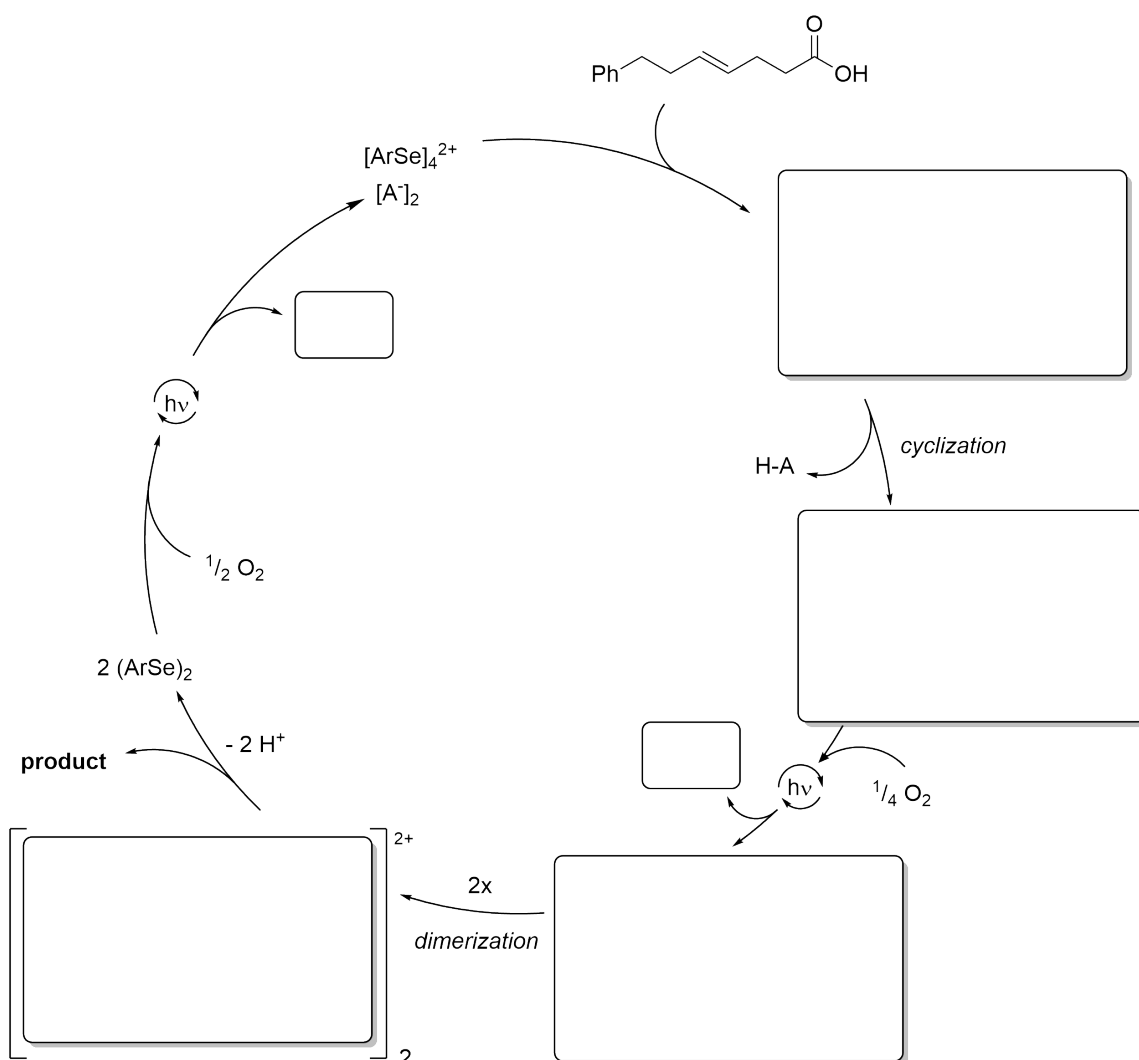
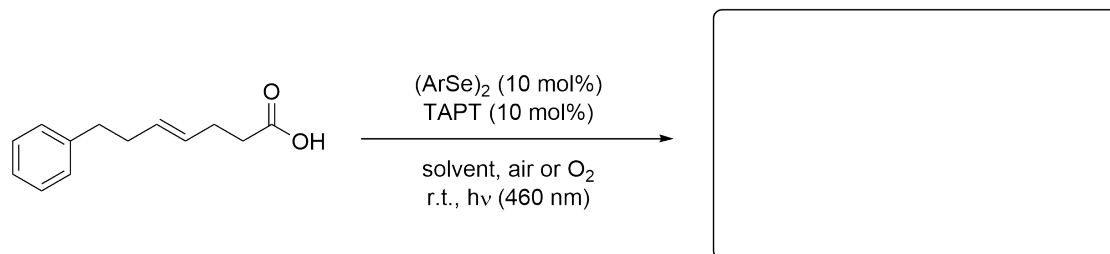


Type of reaction:

Problem 7 Multicatalysis (13 credits)

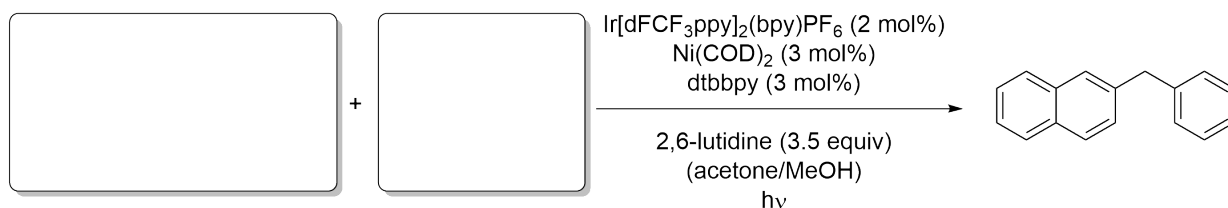
In some cases, a multicatalysis approach is employed for specific reactivity in photochemistry.

a) There has been an increasing number of reports on photo-oxidative functionalizations of simple olefins with nucleophiles by means of selenium- π -acid catalysis. The first example of such a SET-enabled multicatalytic transformation was disclosed in 2016 by Breder and co-workers. The authors employed aryl diselenanes and pyrylium salts as an integratively cooperating catalytic pair for the light-driven electrophilic activation of alkenes under aerobic conditions. Interestingly, they were able to carry out intramolecular ringclosure reactions with this method. Please fill out the following boxes with products and intermediates of the catalytic cycle. Neglect the absolute configuration. *Hint: Aliquots of the reactions mixture gave negative starch-potassium iodide tests.*

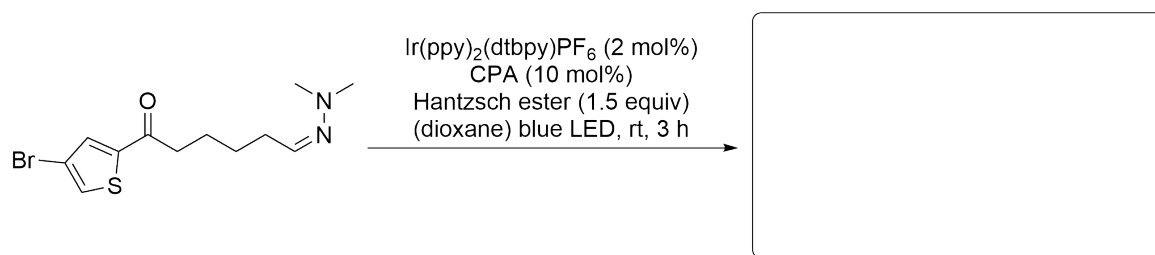


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b) Several examples for combining photoredox with cross-coupling catalysis have been published in literature. Give the structures of suitable starting materials to form the aromatic compound below.

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c) Proton coupled electron transfer reactions provide an excellent opportunity to form chiral molecules by using chiral phosphoric acids (CPAs). What is the structure of the product? It is sufficient to draw the expected major diastereoisomer without absolute configuration.

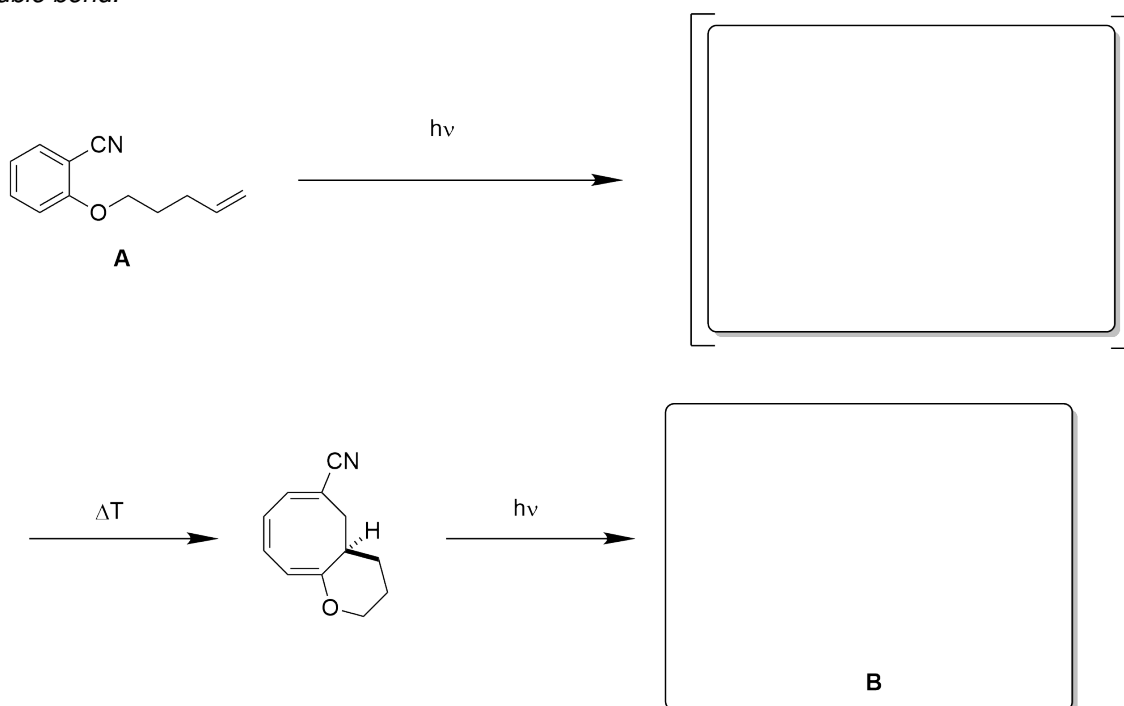


Problem 8 Diversity in Reactivity (12.5 credits)

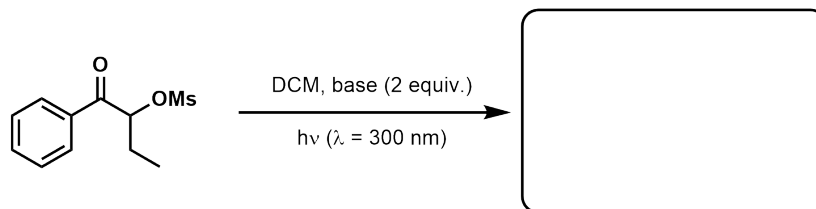
Organic photochemistry gives rise to a diverse set of chemical reactions.

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a) In the Bach group, photochemical reaction cascades have been studied for several years, starting with the publication by A. Zech in 2018 regarding the transformation of *O*-pent-4-enyl-substituted salicylates to complex multifunctional scaffolds. Also investigated was the cyanide derivative **A**, which successfully underwent the reaction cascade to product **B** that contains a tricyclic carbon skeleton. Draw the missing intermediate and the final product (with the correct relative configuration). *Hint: B features a conjugated double bond.*

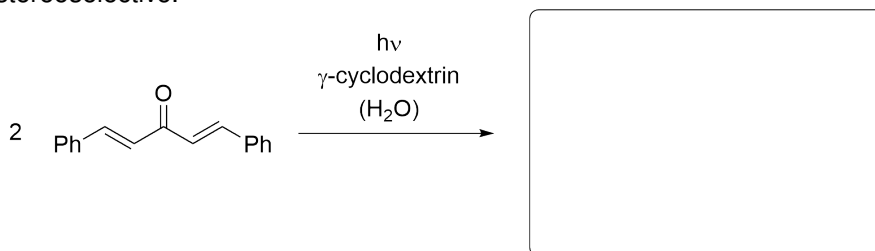


b) Hydrogen abstraction is a useful process in photochemistry. Draw the structure of the following reaction.



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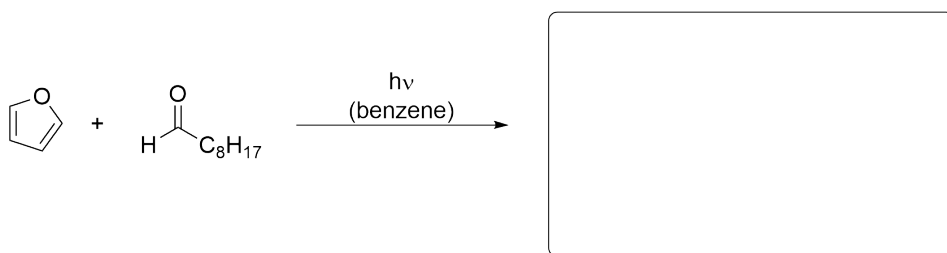
c) In the presence of γ -cyclodextrin, two molecules of the following symmetric chalcone dimerize via two cycloadditions to the *syn*-product upon irradiation with UV-light. Draw the product and explain why this reaction is diastereoselective.



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Explanation:

d) Irradiation of nonanal in the presence of furan yields a single diastereoisomer. Give the structure of the product.



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

A large, empty rectangular box with a thin black border, occupying most of the page. It is intended for students to write their solutions to the problems on the page.