Organic Chemistry I
Natural Sciences
Technical University of Munich

Eexam
Place student sticker here

Note:

- During the attendance check a sticker containing a unique code will be put on this exam.
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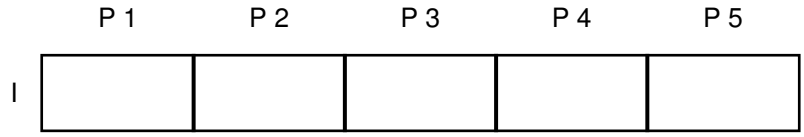
Organic Photochemistry

Exam:	CH3038 / Endterm	**Date:**	Thursday 20th February, 2025
Examiner:	Prof. Dr. Thorsten Bach	**Time:**	08:30 – 10:00



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.
- 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 configurations 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 problems with TUMexam (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 $[Ru(bpy)_3(BF_4)_2]$ photocatalyzed Pschorr reaction, rearomatization occurs via...

- ☐ oxidation of the radical intermediate and deprotonation.
- ☐ reduction of the radical intermediate and tautomerization.
- ☐ reduction of the radical intermediate and deprotonation.
- ☐ oxidation of the radical intermediate and tautomerization.

b) Why do electron-rich amines usually have to be protected for photoredox reactions?

- ☐ To change the redox potential of the amines for a more efficient reductive quench.
- ☐ To prevent light absorption by the amines within the absorption spectrum of the photoredox catalyst.
- ☐ To prevent reduction of the amine.
- ☐ To prevent oxidation of the amine.

c) The Woodward-Hoffmann rules can be applied to predict the outcome of pericyclic reactions. These rules are derived from...

- ☐ determining the spins of electrons in the LUMO.
- ☐ analyzing the polarity of functional groups of the reaction partners.
- ☐ analyzing the symmetry of orbitals.
- ☐ determining the spins of electrons in the HOMO.

d) What is the typical carbon skeleton obtained by an oxa-di-π-methane rearrangement?

- ☐ a cyclopropane.
- ☐ a cyclobutane.
- ☐ a bicyclobutane.
- ☐ a cyclopentane.

e) Which irradiation wavelength is needed to promote Cu(I)-catalyzed [2+2] photocycloadditions of simple alkenes?

- ☐ $\lambda \approx 300$ nm.
- ☐ $\lambda \approx 366$ nm.
- ☐ $\lambda \approx 254$ nm.
- ☐ $\lambda \approx 419$ nm.

f) Intersystem crossing typically happens on a time scale of...

- ☐ microseconds to milliseconds.
- ☐ microseconds to seconds.
- ☐ milliseconds to seconds.
- ☐ nanoseconds to microseconds.

g) In an enone-alkene [2+2] photocycloadditon, which substituents on the alkene will favor a head-to-head regioselectivity?

- ☐ COOMe, CN, OMe, Et.
- ☐ OEt, CN, COOMe, COMe.
- ☐ CN, COOMe, CF_3, COMe.
- ☐ CN, CF_3, COOMe, SMe.

h) The *meta*-photocycloaddition of alkenes to aromatic compounds is generally favored over the *ortho*-photocycloaddition when...

- ☐ the alkene bears a donor substituent and the aromatic compound bears an acceptor substituent.
- ☐ the alkene bears an acceptor substituent and the aromatic compound bears a donor substituent.
- ☐ the alkene bears a donor substituent and the aromatic compound bears a donor substituent.
- ☐ the steric bulk of the substituents of both reaction partners is too high for the *ortho*-photocycloaddition to occur.

i) A photoreaction that forms an excited state intermediate before emitting photons to form a product is called...

- ☐ adiabatic.
- ☐ diabatic.
- ☐ isochoric.
- ☐ diathermal.

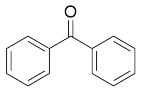
j) Which of the following compounds is generally able to perform a reductive quench on an excited photoredox catalyst?

- ☐ NEt_4Cl.
- ☐ Benzene.
- ☐ PPh_3.
- ☐ Dimethyl sulfoxide.

Problem 2 **Fundamentals of Photochemistry (20 credits)**

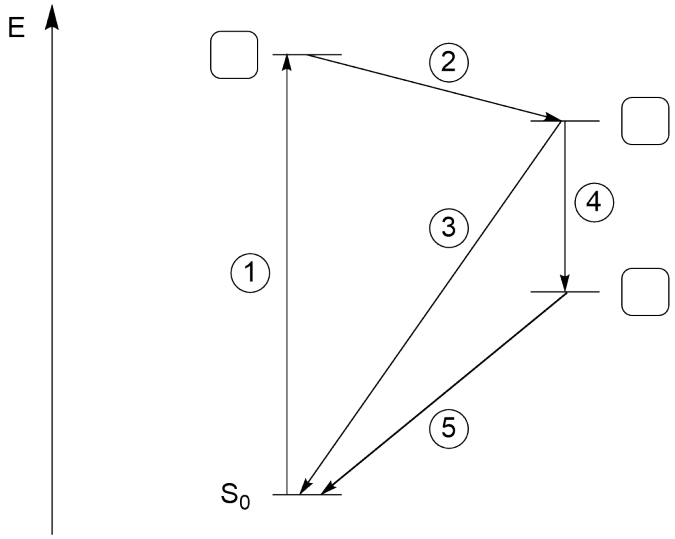
To successfully conduct photochemical reactions, fundamental processes and properties of organic and organometallic compounds upon irradiation need to be studied and understood.
Constants: Avogadro constant = 6.0221 $\times$ 10^{23} /mol, Planck constant = 6.261 $\times$ 10^{-34} Js, speed of light = 299.79 $\times$ 10^{6} m/s.
Important: Provide equations for all your calculations and all numbers with three significant digits.

Benzophenone is a well-known building block in organic synthesis, which due to its absorption properties has a wide variety of applications including its use as a photoinitiator, UV-blocker or as a photophysical probe.



0 1 2 3 4

a) The molecule can be excited into the S_1 state at a wavelength of around 360 nm. After excitation, phosphorescence is typically observed at a wavelength higher than 400 nm. Describe the fate of the molecule after excitation into the S_1 state using the following scheme. Label all electronic states and individual transitions.



1 2 3 4 5

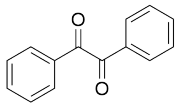
0 1 2 3

b) From which state do you expect the majority of phosphorescence to occur? Please explain your choice with the key principle.

c) Upon excitation, the molecule additionally shows luminescence from the S_1 state. In which area would you estimate the wavelength of this emission to be with respect to the absorption and phosphorescence? Please explain your choice.

0 1 2 3 4 5

d) A common photosensitizer used for E/Z isomerizations is benzil. The wavelength found for the triplet emission spectrum is 522 nm. Calculate the triplet energy in kJ/mol.



λ_{em} = 522 nm

0 1 2

e) What is the definition of the quantum yield of a photochemical reaction? In what range do you expect it to be typically? What conclusion about a photochemical reaction can you draw if the measured quantum yield exceeds that range?

0 1 2 3

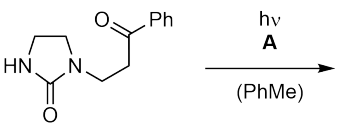
0 1 2 3

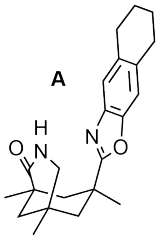
f) Explain why photoexcited metal complexes are both stronger reductants and oxidants than their corresponding ground state species.

Problem 3 **Direct Excitation (23 credits)**

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

a) The photochemical reaction shown below occurs enantioselectively in the presence of chiral host **A**. Fill in the structure of the product and give the name of the reaction. Rationalize the enantioselectivity by showing the interaction of the reactive intermediate with **A**.





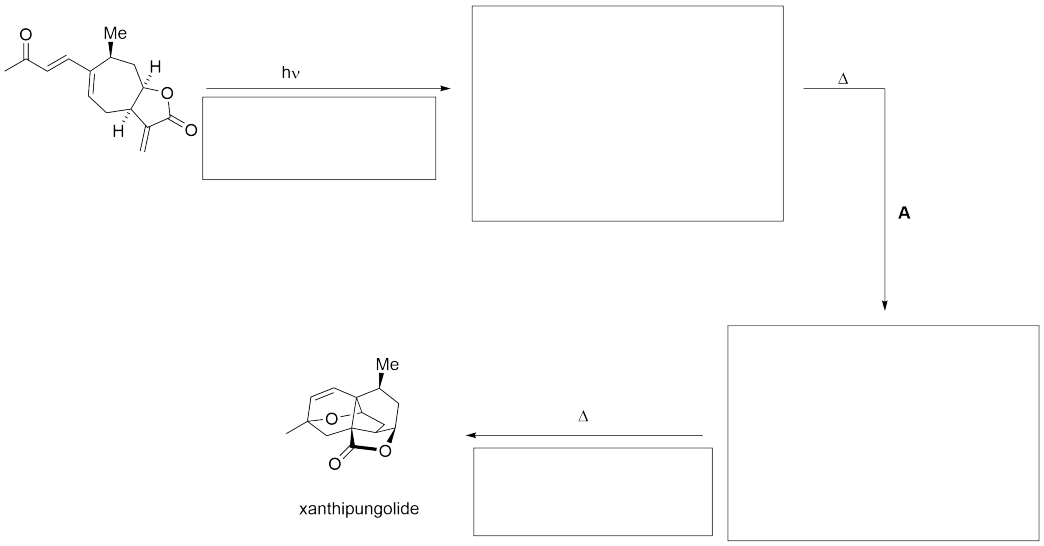
0 1 2 3 4 5 6 7

Rationalization for enantioselectivity:

Name of the reaction:

0 1 2 3 4 5 6 7

b) The sesquiterpene lactone xanthipungolide was isolated from the Egyptian weed Xanthiumpungens, along with xanthatin. The latter can be converted to xanthipungolide by a thermal intramolecular reaction that does not proceed without an initial photochemical step. The final step consists of another intramolecular reaction to furnish the desired xanthipungolide. Fill in the boxes and give the names of the occurring reactions. Classify the second reaction step according to the Woodward-Hoffmann rules. You can disregard the stereoselectivity of this step.



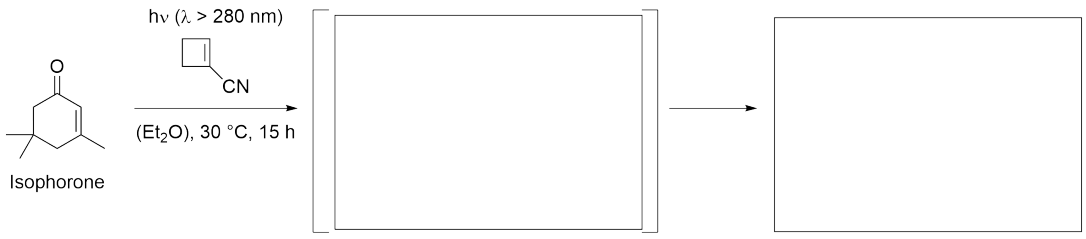
xanthipungolide

Reaction **A**:

Woodward-Hoffmann:

0 1 2 3 4 5 6 7 8 9

c) Fill in the following boxes with the intermediate and the final product of the photocycloaddition reaction of isophorone with the cyclic olefin. Consider regio- and diastereoselectivity. Name the type of regioisomer and diastereoisomer that is predominantly formed. What is the spin multiplicity of the photoexcited substrate that undergoes the reaction?



Isophorone

Spin multiplicity:

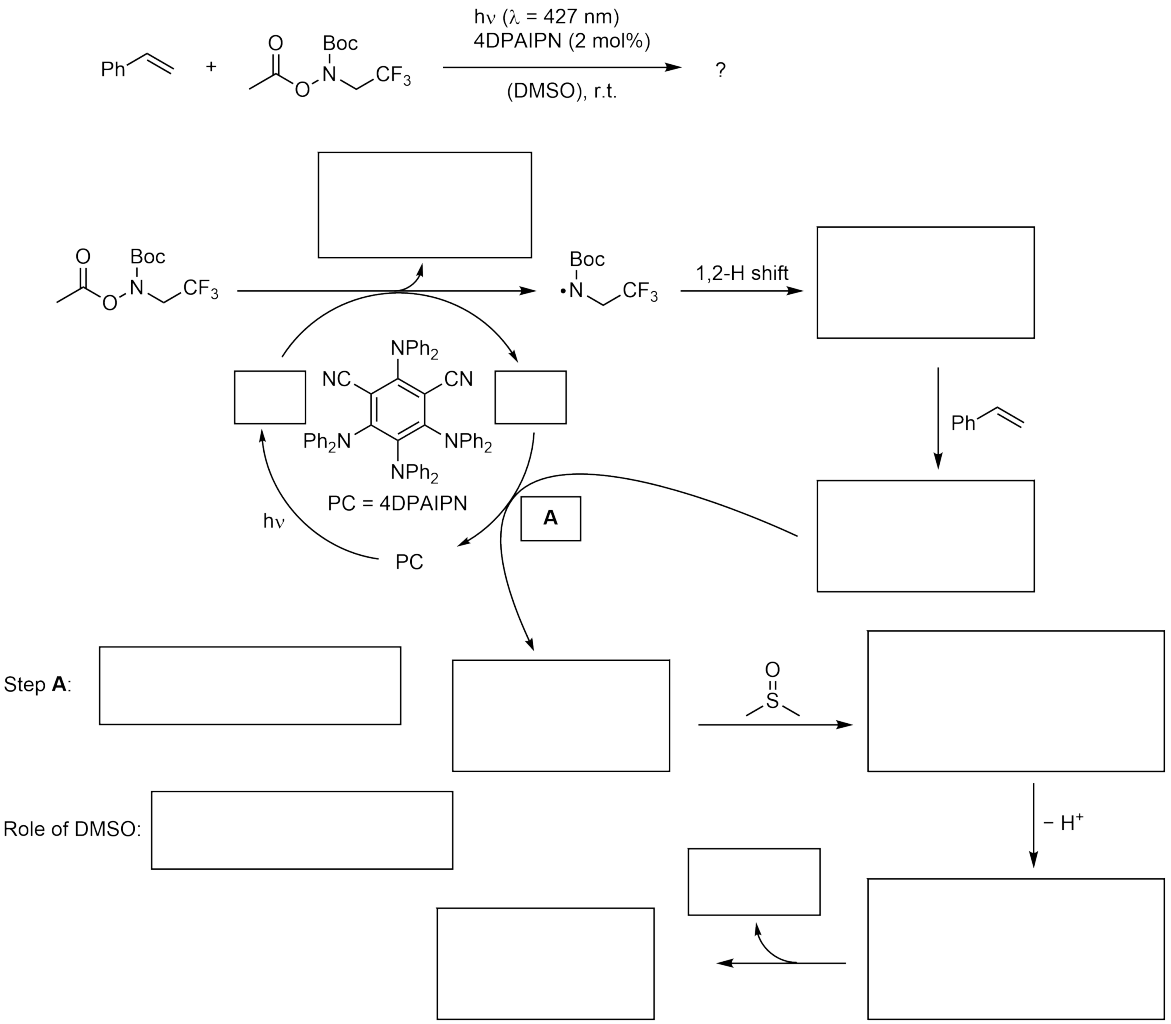
Major regioisomer:

Major diastereoisomer:

Problem 4 **Photoredox Chemistry (18 credits)**

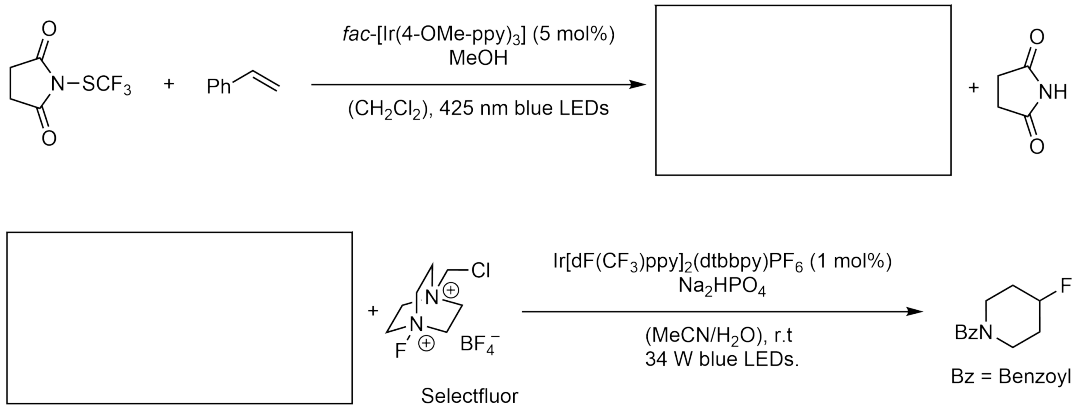
In recent years, the field of photoredox chemistry has experienced a steep gain in importance and attention.

a) Shown below is the photochemical conversion of an acyl hydroxylamine using the organic photoredox catalyst 4DPAIPN. Fill in the boxes of the reaction mechanism and give the structure of the final product. What is the role of DMSO in this reaction?

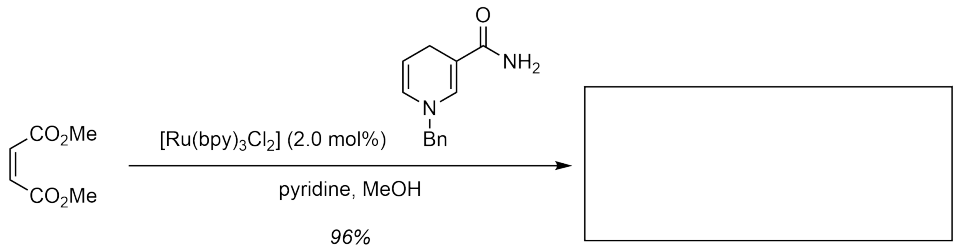


0 1 2 3 4 5 6 7 8 9 10 11 12

b) What are the products/starting materials of the following reactions? Selectfluor is an electrophilic fluorine transfer reagent.



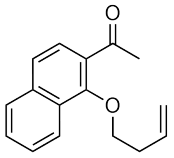
0 1 2 3 4 5 6


CO2Me
CO2Me
[Ru(bpy)3Cl2] (2.0 mol%)
pyridine, MeOH
96%
O
NH2
N
Bn

Problem 5 **Diverse Reactivity (29 credits)**

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

a) What is the product of the following reaction? Give the name of the reaction.



hν (λ = 450 nm)
Lewis Acid catalyst (25 mol%)

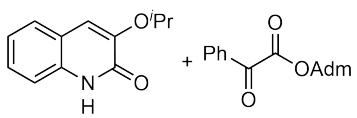
(CH_2Cl_2), −78 °C, 17 h

Name of the reaction:

0 1 2 3 4 5 6

b) Yoon and coworkers recently reported an enantioselective variant of one of the oldest known photochemical reactions. Fill in the boxes with the intermediate and the final product of the reaction and give the name of the reaction. Disregard the enantioselectivity of the reaction, but pay attention to its diastereoselectivity.

Hints: The Ir-catalyst sensitizes the adamantyl (Adm) phenylglyoxylate and not the quinolone. A CO_2Adm group has a larger steric bulk than a phenyl group.



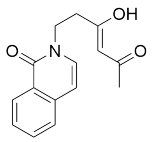
Ir-catalyst (3.5 mol%)
456 nm LED

$(PhCH_3/CH_2Cl_2)$, −78°C, 24 h

Name of the reaction:

0 1 2 3 4 5 6

c) In an attempt to make the carbon skeleton of Galanthan synthetically accessible, a named photoreaction was utilized. Fill in the missing structures and give the name of this reaction sequence.



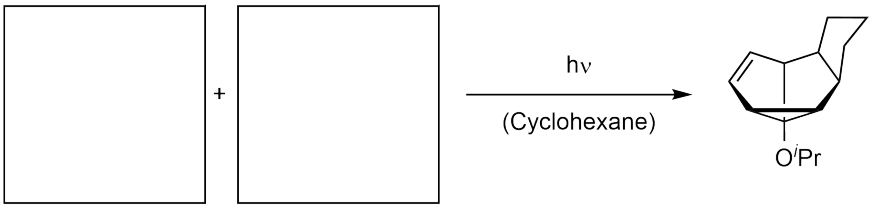
hν (λ > 280 nm)
(MeCN)

Name of reaction sequence:

0 1 2 3 4 5 6

0 1 2 3

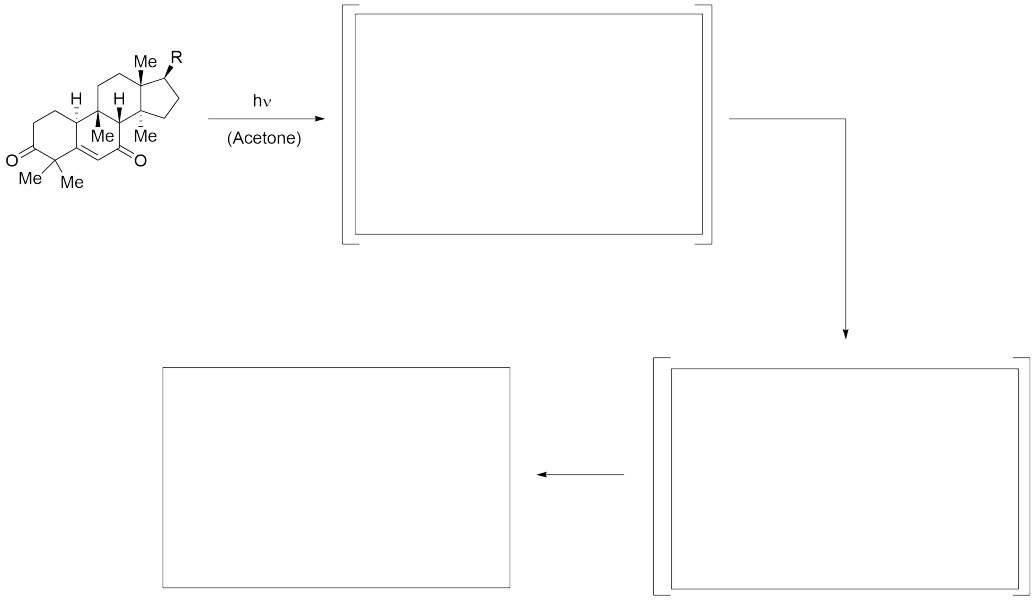
d) Which substrates are required to obtain the product shown below? What is the name of the reaction?



Name of the reaction:

0 1 2 3 4 5 6 7 8

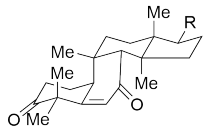
e) Fill in the boxes with the relevant intermediate products and the final product of the photoreaction used in the total synthesis of cucurbalsaminones B and C. The spatial model of the substrate shown below may help you decide for the correct diastereoselectivity of the reaction. What is the name of the reaction? What role does the solvent play in this reaction?



Name of the reaction:

Role of the solvent:

Hint for diastereoselectivity:



Spatial model of the substrate

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