Organic Chemistry I
Natural Sciences
Technical University of Munich

Eexam
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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.
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Organic Photochemistry

Exam: CH3038 / Retake **Date:** Tuesday 22nd April, 2025
Examiner: Prof. Dr. 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.
- Allowed resources:
  - one **non-programmable pocket calculator**
  - one **analog dictionary** English ↔ native language
- Subproblems marked by * can be solved without results of previous subproblems.
- **Answers are only accepted if the solution approach is documented.** Give a reason for each answer unless explicitly stated otherwise in the respective subproblem.
- 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.

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) When compared to the triplet state lifetime, singlet state lifetime is typically...

☐ longer by two orders of magnitude.

☐ longer by six oders of magnitude.

☐ shorter.

☐ the same.

b) Which factor determines the regioselectivity of a Paternò-Büchi reaction?

☐ The rotation along the O-C bond to minimize steric interactions of the substituents.

☐ The stability of the transient species after the first bond formation.

☐ The substitution pattern of the olefin, if the carbonyl in question is an aromatic aldehyde.

☐ The distance of the triplet energy of the olefin to that of the carbonyl.

c) What does not happen during a Dexter energy transfer?

☐ The transfer of an electron from the substrate to the sensitizer.

☐ The promotion of the substrate into an electronically excited state.

☐ The reduction of the substrate HOMO-LUMO gap.

☐ The transfer of an electron from the sensitizer to the substrate.

d) For a given ketone RR'C=O, the rate of α-cleavage fragmentation is slowest with R = ?

☐ ^{t}Bu

☐ Me

☐ ^{i}Pr

☐ CH_2Ph

e) For enone photocycloadditions, why is the use of cyclic α,β-unsaturated enones rather than acyclic enones preferred?

☐ Cyclic enones are easier to synthesize than acylic enones.

☐ For acyclic enones, the energy from the absorbed photon is dissipated by *E/Z* isomerization before the photocycloadditon can take place.

☐ For acylic enones, the triplet biradical is too short-lived and returns to the ground state via fluorescence.

☐ Acylic enones give photoproducts that are more difficult to purify.

f) During the oxadi-π-methane rearrangement, the following intermediate is involved:

☐ A macrocycle.

☐ A cyclobutyl-containing species.

☐ An enone.

☐ A 1,4-diradical.

g) A conrotatory [4π] cyclization...

☐ maintains orbital symmetry in the S_1 state.

☐ is photochemically allowed.

☐ is thermally allowed.

☐ all of the other choices.

h) What is a typical solvent used for oxadi-π-methane rearrangements?

☐ Cycloalkenes.

☐ Acetone.

☐ CH_2Cl_2.

☐ $CHCl_3$.

i) What is typically the role of a thiol in a photoredox reaction?

☐ It acts as an oxidant.

☐ It acts as a hydrogen atom shuttle.

☐ It is used to promote the formation of an EDA complex.

☐ It acts as a reductant.

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

☐ Lowering the reduction potential of the starting material.

☐ Increasing the oxidation potential of the starting material.

☐ Lowering the oxidation potential of the starting material.

☐ Increasing the reduction potential of the starting material.

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 = 6.0221×10^{23} /mol, Planck constant = 6.261×10^{-34} Js, speed of light = 299.79×10^{6} m/s, Faraday constant = 96.5 $\text{kJV}^{-1}\text{mol}^{-1}$.
Important: Provide equations for all your calculations and all numbers with three significant digits.

In photochemistry, one possibility to populate the triplet state of a molecule is the direct irradiation to the S_1 state and subsequent intersystem crossing to the T_1 state.

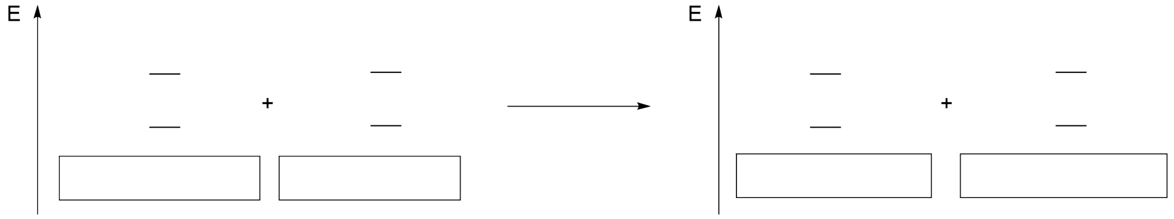
0 ☐ ☐ 1 ☐ ☐ 2 ☐ ☐ 3 ☐ ☐ 4 ☐ ☐ 5 ☐

a) While the triplet state of carbonyl compounds often can be populated by direct irradiation, it often proves difficult for alkenes. Explain this observation, addressing also the character of the excited state.

0 ☐ ☐ 1 ☐ ☐ 2 ☐ ☐ 3 ☐ ☐ 4 ☐ ☐ 5 ☐

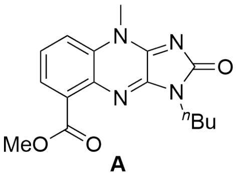
b) Another possibility to populate the T_1 state of alkenes is to employ a triplet sensitizer. Fine-tuning the triplet energy of the sensitizer allows for useful transformations of alkenes. One example is the *E/Z* isomerization of alkenes. Which prerequisite in terms of triplet energies of sensitizer, *E*-alkene, and *Z*-alkene needs to be met?

Use an energy diagram to explain the mechanism of Dexter energy transfer from a sensitizer to a substrate.

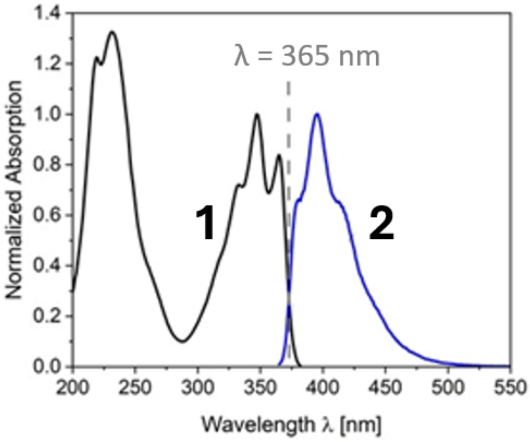


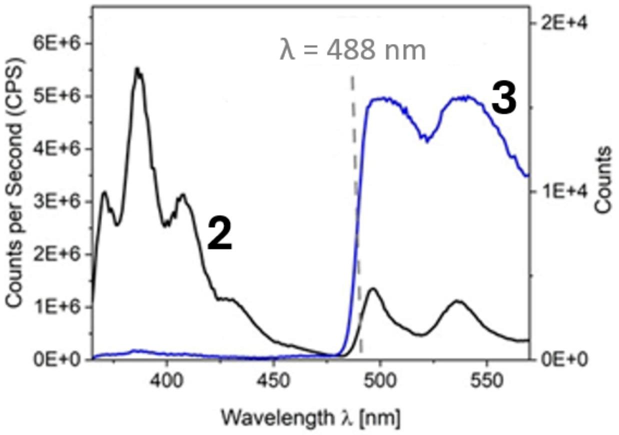
c) For ring-contracted flavin **A**, the following spectroscopic data were measured. Which photochemical processes can be assigned to curves **1**, **2**, and **3**. Explain the term “Stokes shift". What assumptions can be made about the nature of the excited state based on the Stokes shift? Explain your answer.

☐ 0
☐ 1
☐ 2
☐ 3
☐ 4
☐ 5



A



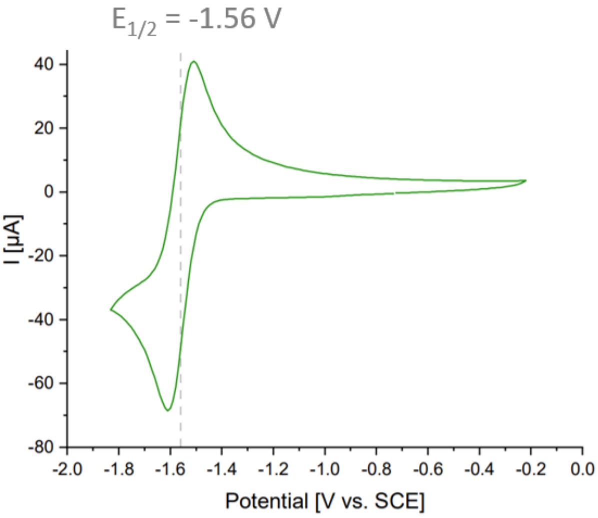


d) Calculate the singlet energy and the triplet energy of **A** in kJmol^{-1}.

☐ 0
☐ 1
☐ 2
☐ 3

0 ☐
☐
1 ☐
☐
2 ☐

e) A cyclic voltammogram of molecule **A** was recorded and the reversible half-wave potential was measured at $E_{1/2}(\mathbf{A}/\mathbf{A}^{\cdot-})$ = -1.56 V *vs.* SCE. Calculate the excited singlet-state redox potential.

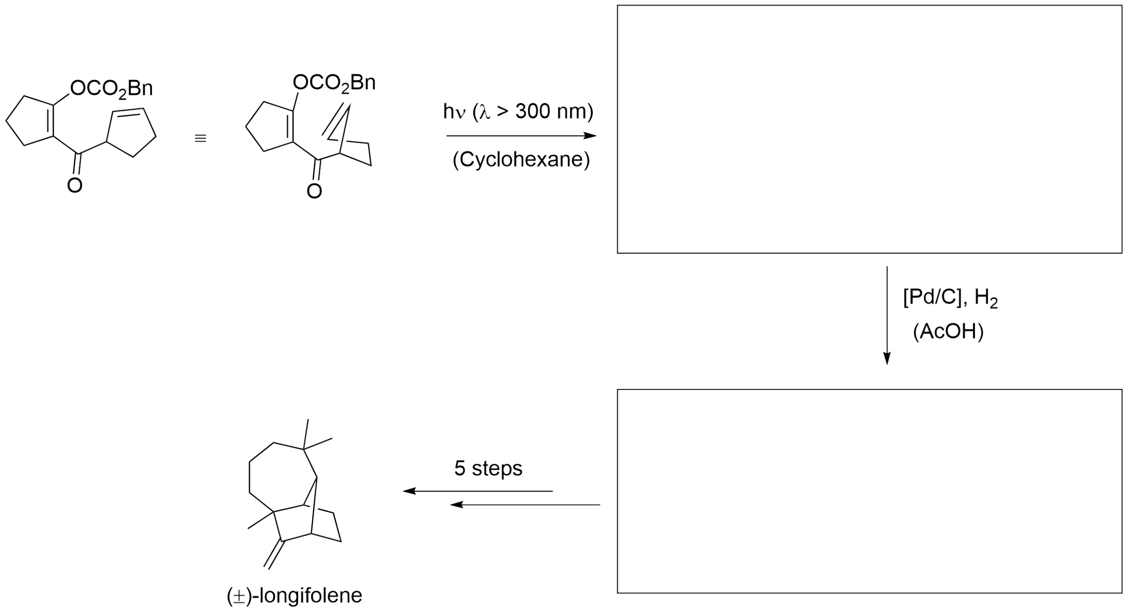


Problem 3 **Direct Excitation (19 credits)**

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

a) In an elegant synthesis of (±)-longifolene, the intricate carbon network was constructed using a photochemical reaction. Draw the missing structures and give the name of the reaction sequence.

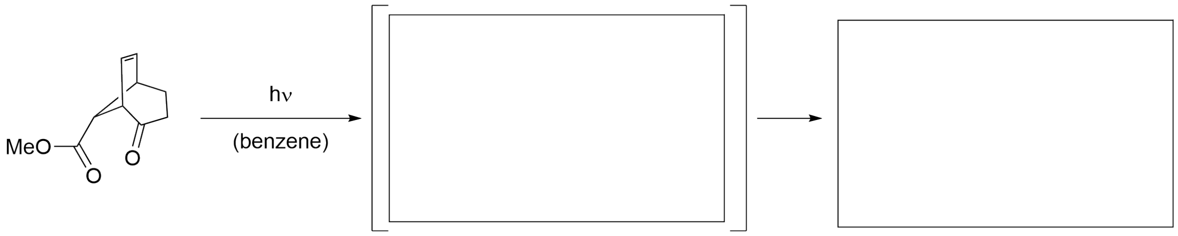
☐ 0
☐ 1
☐ 2
☐ 3
☐ 4
☐ 5
☐ 6



Name of the reaction sequence:

0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7 ☐

b) *Hsu et al.* utilized a photoreaction for the formal synthesis of (±)-mussaenoside and (±)-8-epiloganin. Draw the missing structures. What is the name of the reaction?

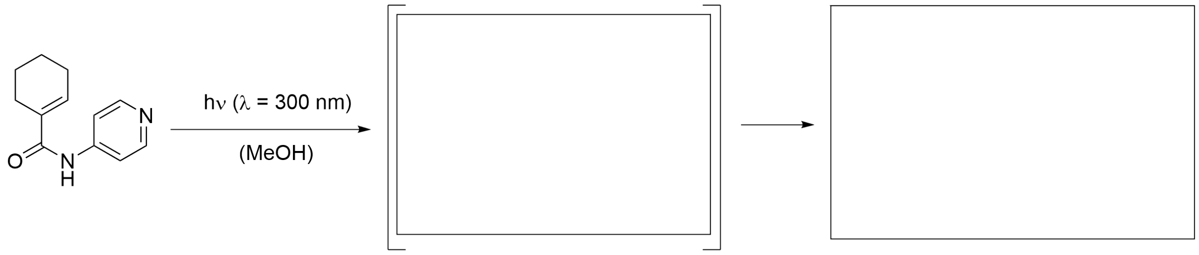


Name of the reaction:

On which potential energy surface does this reaction take place?

0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐

c) Give the structure of the intermediate and the product of the depicted photoreaction. What type of reaction is this? Is the second step antarafacial or suprafacial?



suprafacial ☐
antarafacial ☐

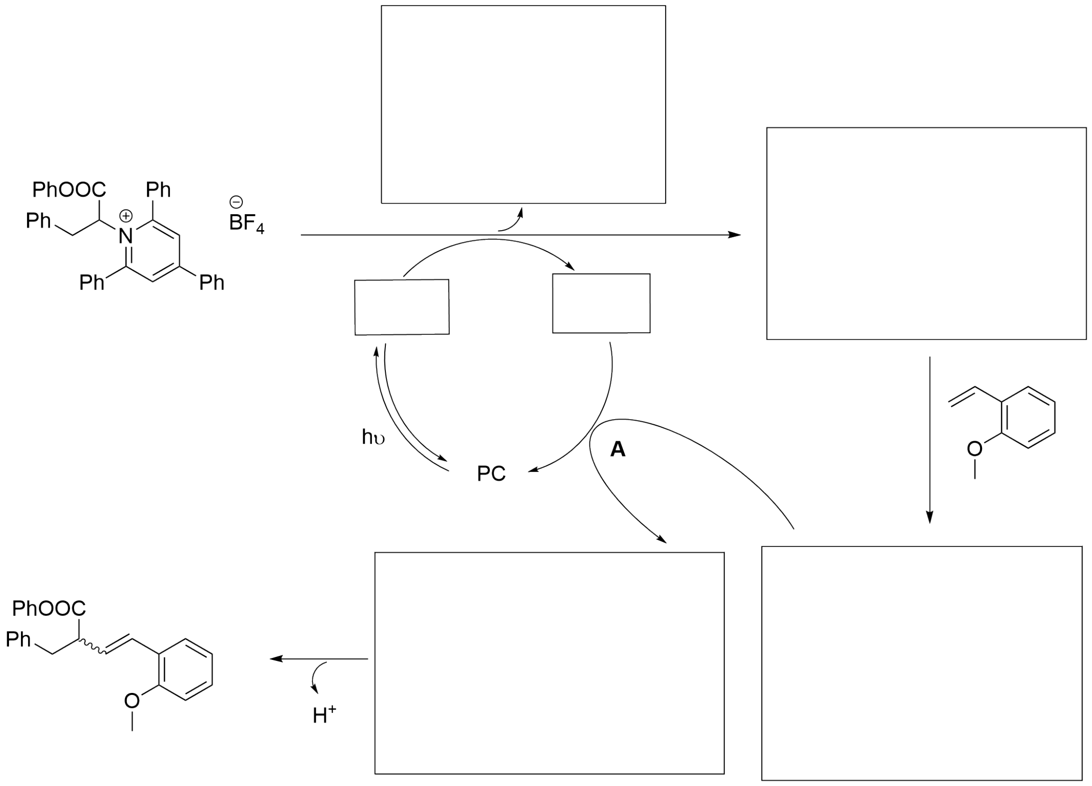
Type of reaction:

Problem 4 **Photoredox Chemistry (19 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 a Katritzky salt using a photoredox catalyst [$Ir(ppy)_3$ or $Ru(bpy)_3(PF_6)_2$]. Fill in the boxes of the reaction mechanism and give the structure of the final product. *Hint:* A heteroaromatic molecule is released in the first step.

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



What is step **A** called?

Depending on the catalyst used in the reaction, the *E/Z* selectivity of the product can be changed.

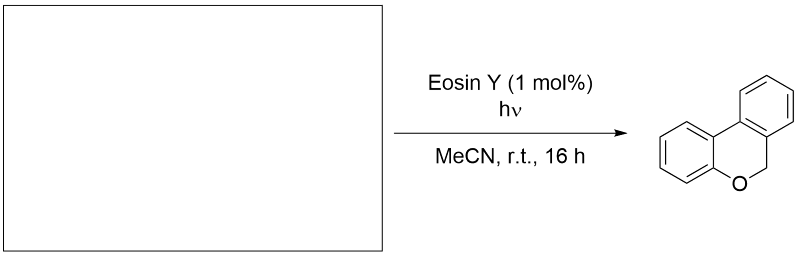
$Ir(ppy)_3$ $Z/E = 96/4$
$Ru(bpy)_3(PF_6)_2$ $E/Z > 99/1$

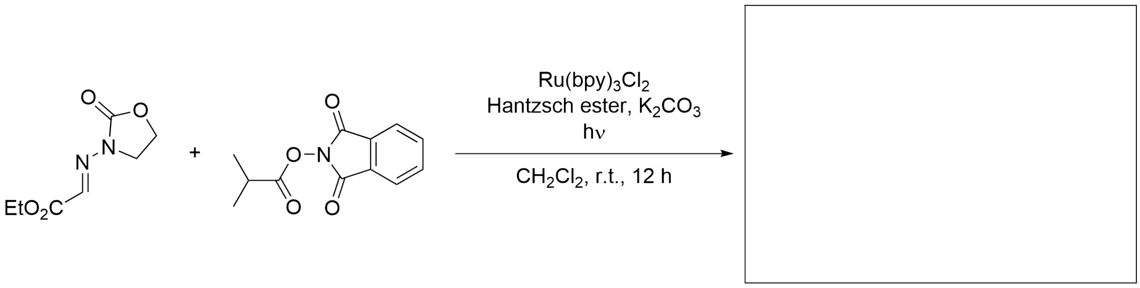
Why is the formation of the *E*-alkene generally favored? Why is an enrichment of the *Z*-isomer observed when an Ir^{III}-catalyst is used instead of a Ru^{II}-catalyst? Which property of the catalyst is responsible for that?

The quantum yields of both reactions were determined to be $\Phi = 0.137$ (Ir) and 0.270 (Ru), respectively. What is the definition of the quantum yield? What conclusion can you draw about a chemical reaction if the measured quantum yield is greater than 1?

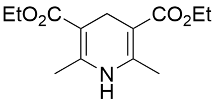
0 ☐
1 ☐
2 ☐
3 ☐
4 ☐
5 ☐
6 ☐
7 ☐

b) What are the products/starting materials of the following reactions? Is the second example a net oxidative, a net reductive, or a redox neutral reaction?





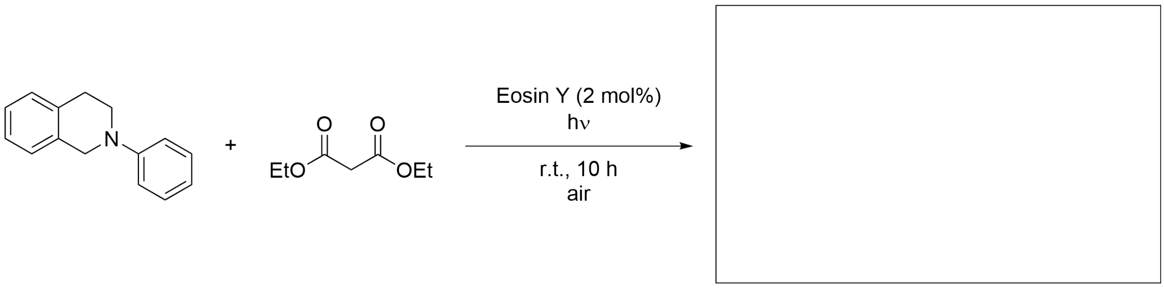
Hantzsch ester:



☐ Net oxidative

☐ Net reductive

☐ Net neutral

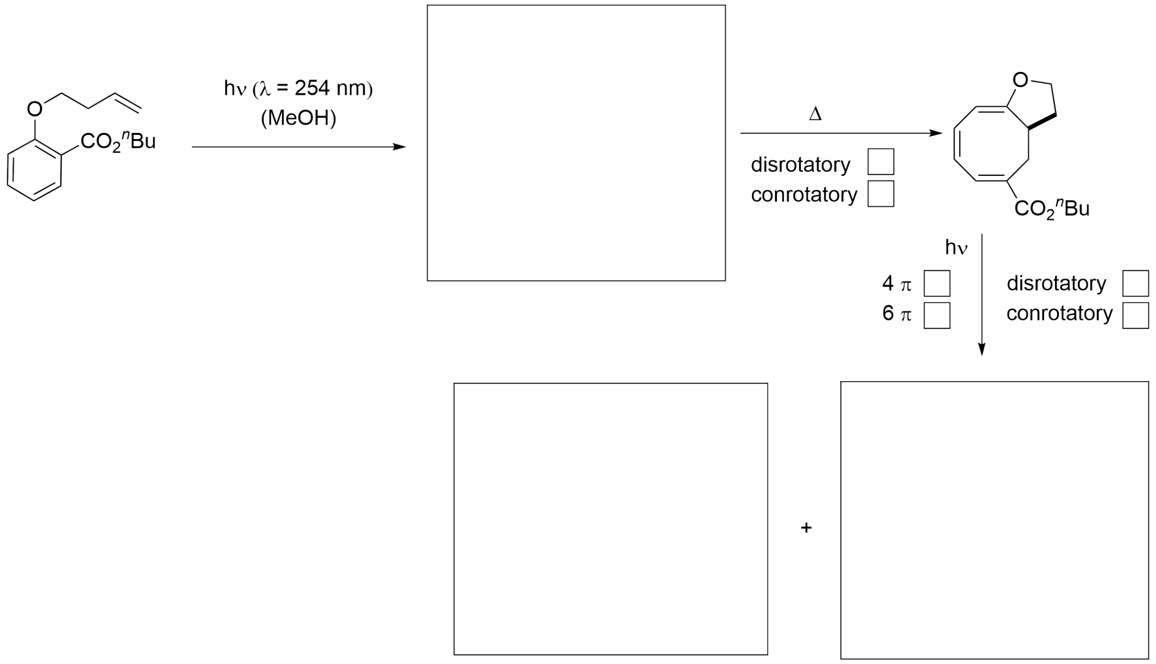


Problem 5 **Diverse Reactivity (32 credits)**

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

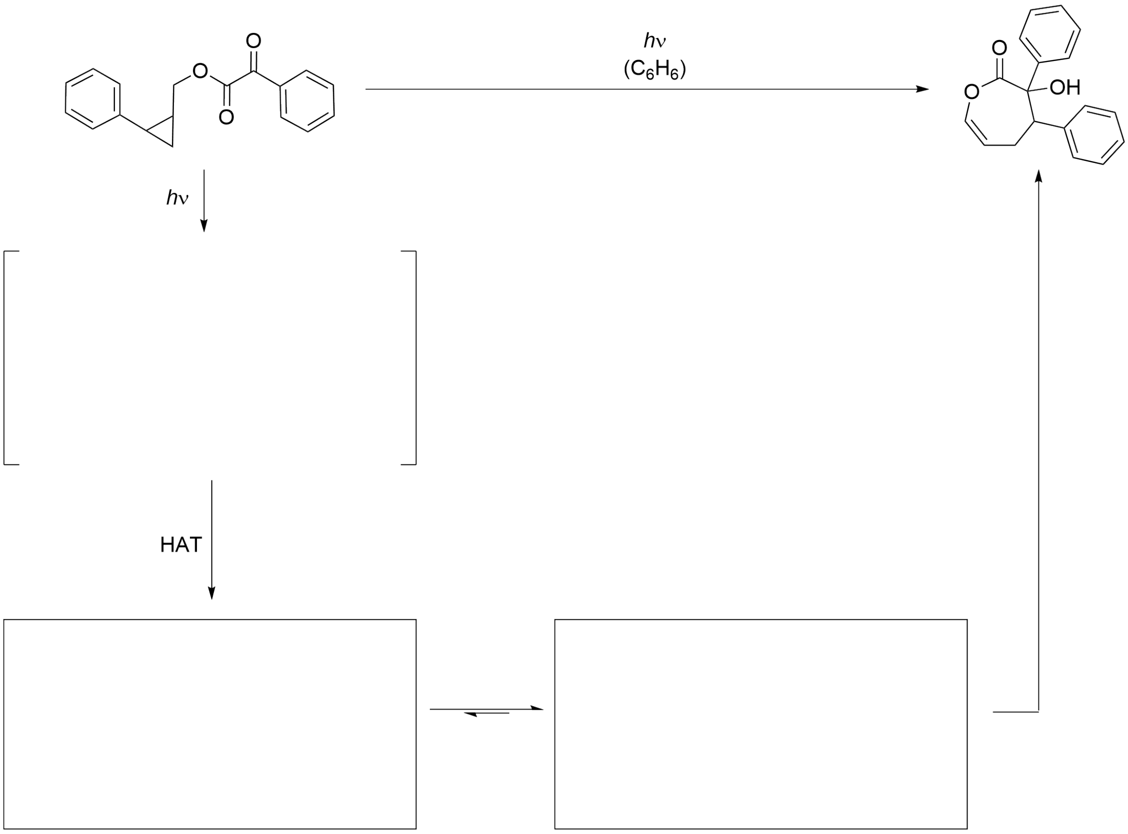
a) Draw the structure of the primary photoproduct. This undergoes a thermally promoted ring opening reaction. Is this a disrotatory on conrotatory process? Tick the correct box. The ring opened product undergoes a photochemically induced process to afford two regioisomeric products. Draw the products and tick the boxes that correctly describe this reaction.

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



☐ 0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6

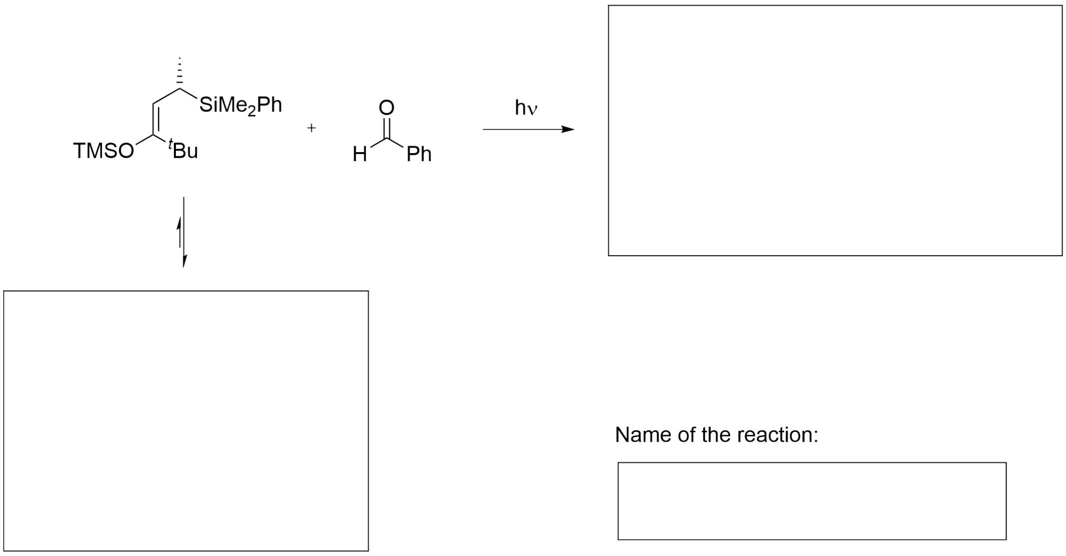
b) Explain the mechanism by giving the intermediates of the following photochemical reaction. What is the name of the reaction? HAT = Hydrogen atom transfer.



Name of the reaction: ☐

☐ 0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5

c) Draw the products of the following reaction and explain the facial diastereoselectivity by giving the preferred conformation of the reacting olefin. *Hint:* ^{t}Bu is sterically more demanding than OTMS.

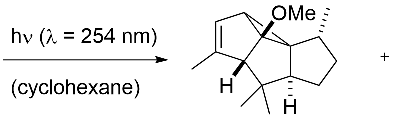


preferred conformation

Name of the reaction: ☐

d) Sesquiterpenes comprise a class of natural products and photochemistry offers elegant ways for the syntheses of their complex carbon skeletons. Give the structure of the starting material and the other product from the reaction. What are the names of the two products obtained? What is the name of this reaction?

☐ 0
☐ 1
☐ 2
☐ 3
☐ 4
☐ 5
☐ 6
☐ 7
☐ 8
☐ 9



Name of reaction:

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