Chair of Organic Chemistry I
Department of Chemistry
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 / Endterm	**Date:**	Tuesday 28th February, 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 ×■

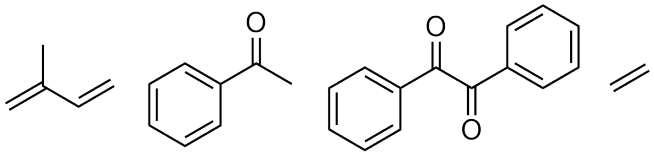
a) The Franck Condon principle...

- ☐ states that all vibronic transitions have the same probability.
- ☐ describes whether an electronic transition is photochemically allowed.
- ☐ describes whether a reaction is thermally allowed.
- ☐ states that a transition is more likely the more the wave functions of the two states overlap.

b) Intersystem crossing often happens on the time scale of...

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

c) Arrange the following molecules in order of increasing wavelength of maximum absorption:



1 **2** **3** **4**

- ☐ **4** < **1** < **3** < **2**
- ☐ **1** < **4** < **3** < **2**.
- ☐ **4** < **1** < **2** < **3**.
- ☐ **1** < **4** < **2** < **3**.

d) The use of Cu(I) catalysis in [2+2] photocycloaddition reactions allows to:

- ☐ increase the wavelength of the absorption maximum of the substrate.
- ☐ avoid photodimerization as a side reaction.
- ☐ change the reaction solvent.
- ☐ lower the wavelength of the absorption maximum of the substrate.

e) Which of the following statements regarding sensitization is true?

- ☐ All of the other choices.
- ☐ Sensitization is only feasible if the sensitizer and the substrate are in close proximity and have suitable triplet energies.
- ☐ Sensitization is necessary for synthetic purposes if an alkene has a low intersystem crossing rate.
- ☐ Sensitization is useful for α,β-unsaturated systems if they only absorb short wavelength photons.

f) Photochemical [1,3]-sigmatropic acyl shifts...

- ☐ proceed intarafacially.
- ☐ are forbidden.
- ☐ proceed antarafacially.
- ☐ proceed suprafacially.

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

- ☐ the alkene bears an acceptor substituent and the aromatic an acceptor substituent.
- ☐ the alkene bears a donor substituent and the aromatic an acceptor substituent.
- ☐ the alkene bears an acceptor substituent and the aromatic a donor substituent.
- ☐ the alkene bears a donor substituent and the aromatic a donor substituent.

h) What kind of Lewis acidic compound can be used for asymmetric photocatalysis of benzaldehyde derivatives?

- ☐ Borate salts.
- ☐ Unsubstituted oxazaborolidines.
- ☐ Pincacol boronic esters.
- ☐ Activated oxazaborolidine complexes.

i) *N*-Hydroxyphthalimide esters are often used to photochemically generate...

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

j) Which statement regarding thiols in photoredox reactions is true?

- ☐ Thiols act as hydrogen atom shuttles.
- ☐ Thiols act as Brønsted bases.
- ☐ Thiols act as external oxidants.
- ☐ All of the other choices.

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

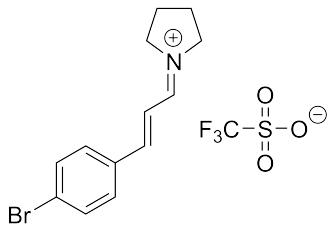
To successfully conduct photochemical reactions, fundamental processes and properties of organic and organometallic compounds upon irradiation need to be studied and understood.
Constants: Avogadro constant = 6.0221 $\times$ 10^{23}/mol, Planck constant = 6.6261 $\times$ 10^{-34} J s, speed of light = 299.79 $\times$ 10^{6} m/s.
Important: Provide equations for all your calculations and all numbers with three significant digits.

0 1 2 3

a) Explain the process of phosphorescence in comparison to fluorescence.

0 1 2

b) This iminium ion shows phosphorescence at λ = 580 nm. Calculate the triplet energy in kJ/mol.



0 1 2 3 4

c) You would like to determine the quantum yield of a photocatalyzed reaction. Therefore, you irradiate a sample solution in a cuvette (volume = 2.50 mL) with a suitable LED and detect the energy of the light that has passed the solution (i.e. transmitted). After exactly 60.0 min, you take a sample of the solution and determine via calibrated GC analysis that the product concentration was 42.1 µmol/mL. As you know the energy output of the LED, you determine that, within these 60.0 min, energy of approximately 414 J was absorbed. You also know that one photon at λ_{max} has an energy of 4.73 $\times$ 10^{-19} J.
Calculate 1) the amount of product that was formed in µmol, 2) the amount of absorbed photons in mmol, and 3) the quantum yield of product formation ϕ.

1. $n_{product}$ =

2. $n_{photons}$ =

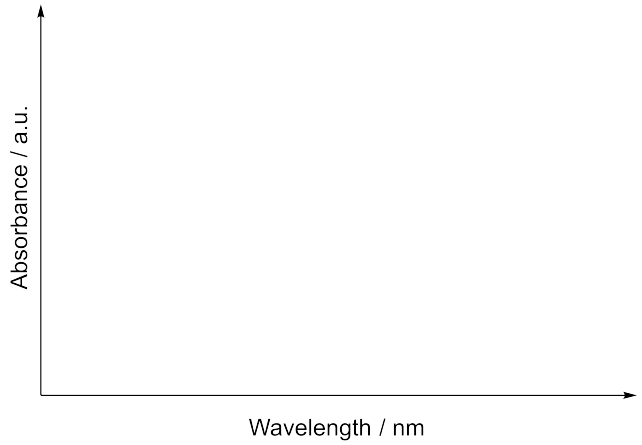
3. ϕ =

d) You study the α-alkylation of 1-octanal with diethyl 2-bromomalonate as well as $[Ru(bpy)_3]Cl_2$ and a chiral imidazolidinone as catalysts. As your collegues propose different plausible mechanisms, you determine the quantum yield and find that ϕ = 18. What does this finding tell you regarding the mechanism?

0 1

e) Consider an *E/Z* isomerization (via S_1) started by direct excitation, in which the ***Z* isomer predominates** in the photostationary state. In the diagram below, schematically draw UV–vis spectra in which the absorption behavior of both the *E* and *Z* diastereomer is depicted (one curve per diastereomer). Also indicate with a vertical line the optimal wavelength of a light source that should be employed in this reaction. *Hint: Consider the absorptivity and the wavelength of maximum absorption.*

0 1 2 3



f) Non-conjugated alkenes normally absorb weakly over 200 nm, which would make their excitation hard to achieve under direct irradiation, but a photosensitized isomerization from the triplet state can be a solution. 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

g) How does the reduction potential of a metal complex generally change upon the introduction of more electron-deficient ligands? What is the reason for this?

0 1 2

h) $[Ru(bpy)_3]^{2+*}$ can be converted into a stronger reductant upon addition of certain organic reagents. What is the name of this process? Give an example for such a reagent! Why does the reduction potential of the complex decrease significantly?

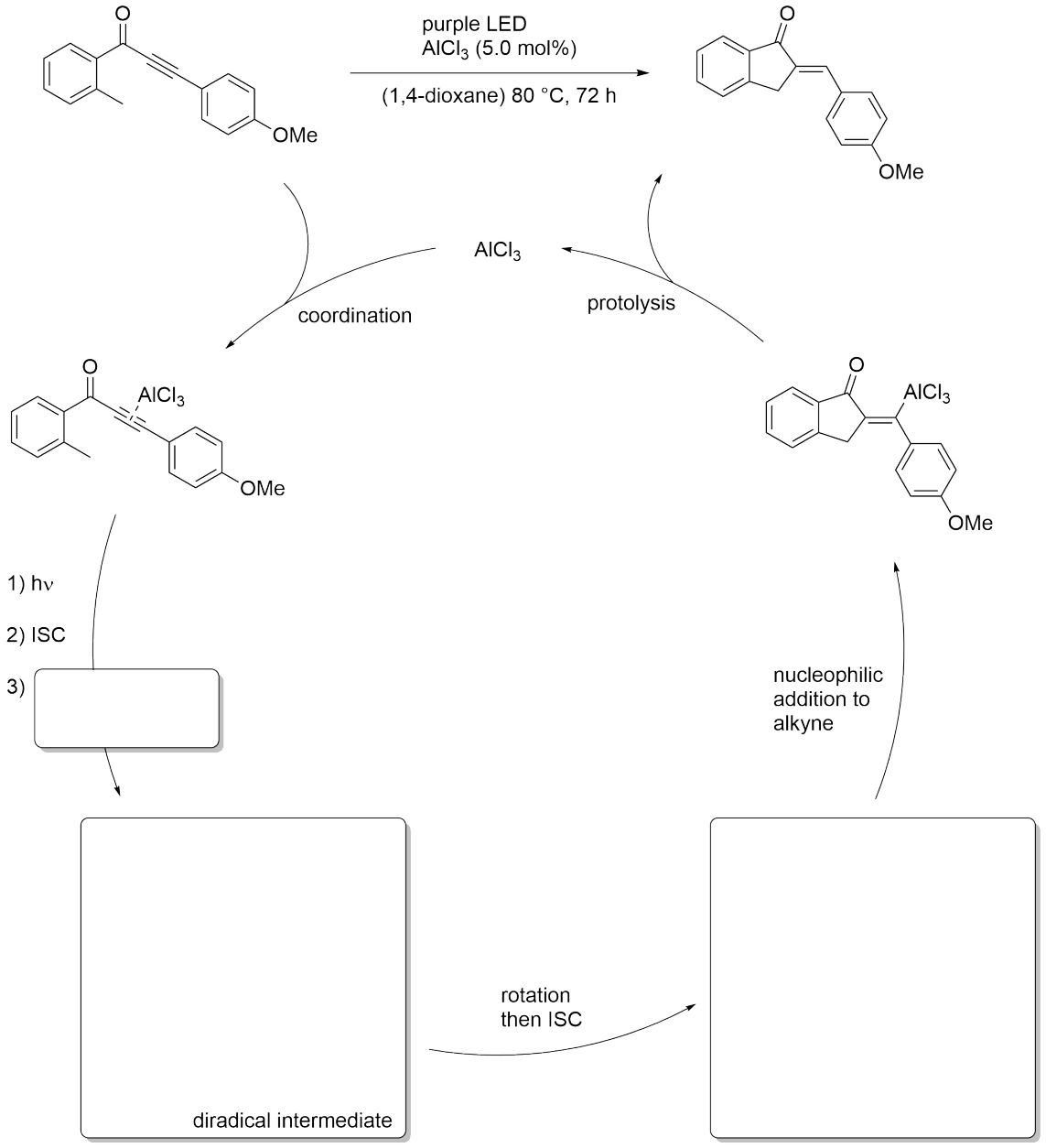
0 1 2 3

Problem 3 **Direct Excitation (29 credits)**

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

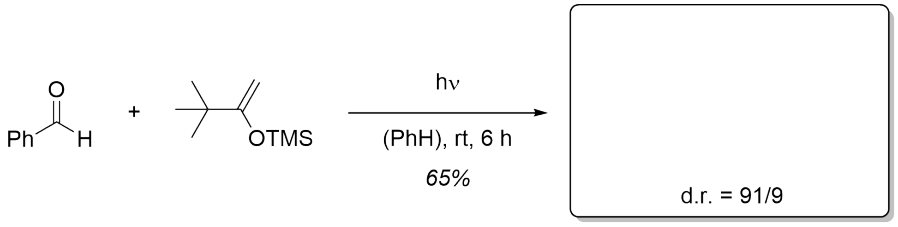
0 1 2 3 4 5

a) The Guo group published the following photochemical cyclization, in which they found $AlCl_3$ to be a useful catalyst. Complete the catalytic cycle by providing the correct structures of the missing intermediates and the name of the process after excitation and intersystem crossing (ISC). *Hint: Remember which primary reaction you have learned to occur upon excitation of ortho-substituted aromatic ketones!*



b) Please fill in the major product of this transformation with its expected relative configuration and give a brief explanation why this diastereomer is predominantly formed.

0 1 2 3 4

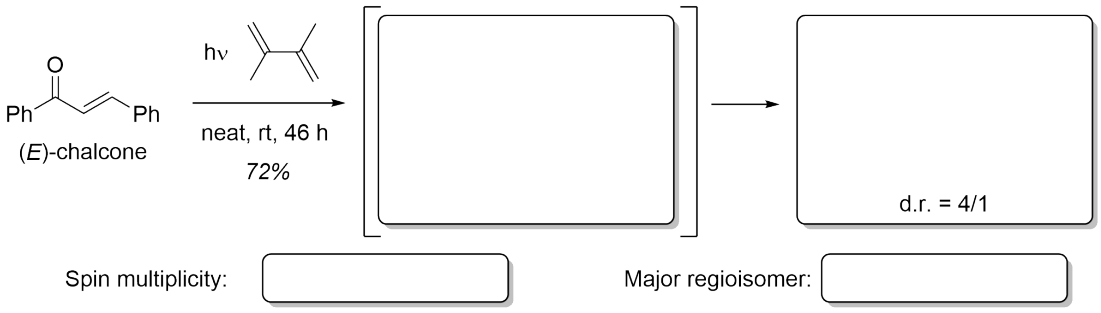


Explanation for diastereoselectivity:

Name of reaction:

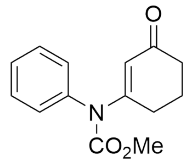
c) Fill the following boxes with the diradical intermediate and final product of the photocycloaddition reaction of (*E*)-chalcone with 2,3-dimethylbutadiene. Consider regio- and diastereoselectivity. Name the type of regioisomer that is predominantly formed. What is the spin multiplicity of the photoexcited substrate that is undergoing the reaction?

0 1 2 3 4 5 6 7 8



0 1 2 3 4 5 6

d) The given starting material undergoes a photochemical transformation to form a primary photoproduct. However, the acidity of silica is sufficient for quantitative epimerization of the photoproduct. Depict the reaction mechanism, the primary and final product and explain the configuration of the **primary product**.



hν (λ = 366 nm), rt, 48 h

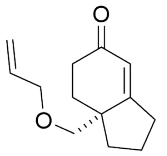
(CH_2Cl_2)

silica

Explanation for configuration of primary product:

0 1 2 3 4 5 6

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



hν (λ > 300 nm) (hexane)

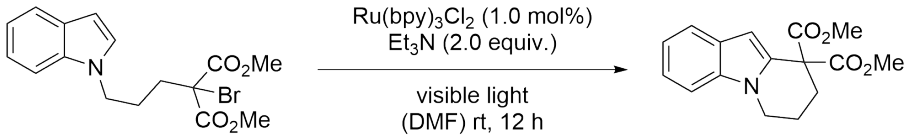
80%

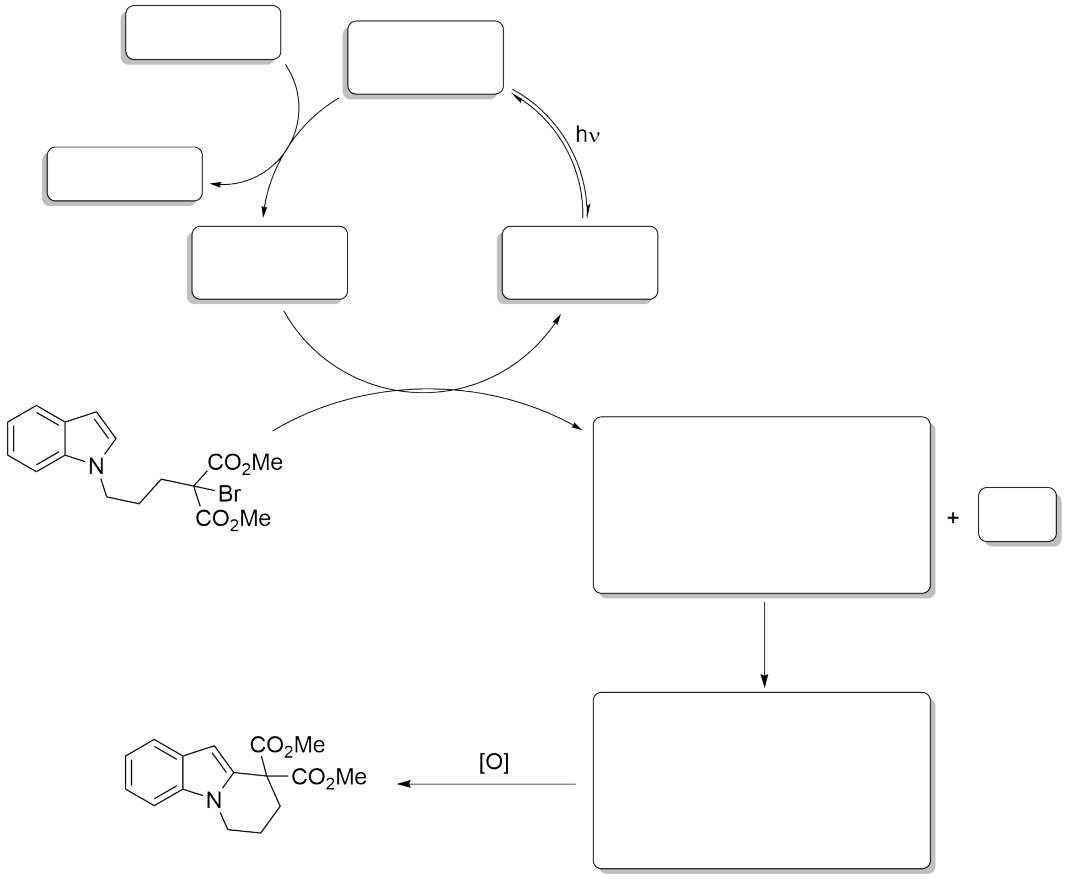
d.r. > 95/5

Problem 4 **Photoredox Chemistry (20 credits)**

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

a) Indoles are an important structural fragment in a variety of natural as well as pharmaceutical compounds. Tryptamine alkaloids such as the neurotransmitter serotonin and the psychedelic drug dimethyltryptamine are derived from substituted indoles. In 2010, Stephenson and co-workers reported the visible light mediated intramolecular alkylation of indoles using $Ru(bpy)_3Cl_2$ as a photoredox catalyst. Please complete the catalytic cycle of the reaction. [O] = oxidation

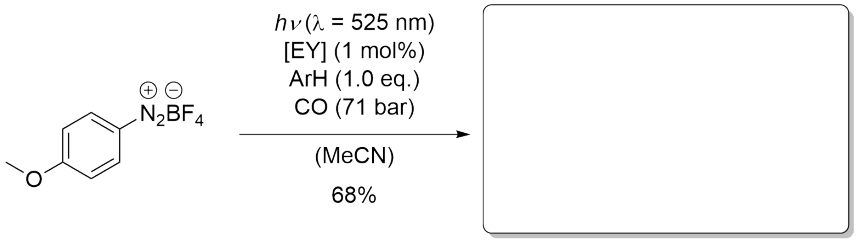




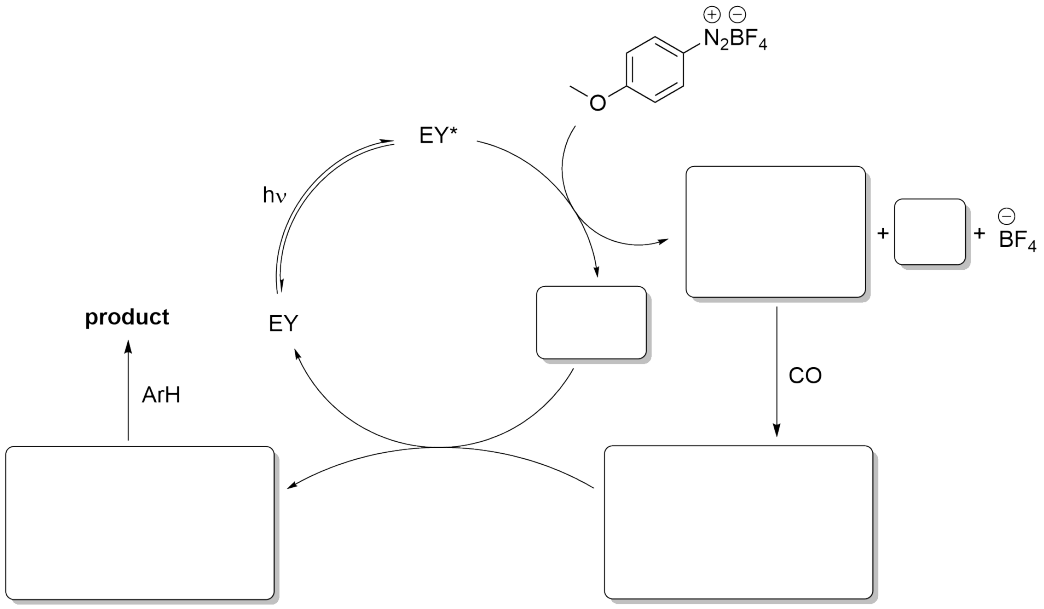
0 1 2 3 4 5 6 7 8 9 10

0 1 2 3 4 5 6 7 8

b) Aryldiazonium salts are an interesting substrate class for carbon-carbon bond formation. In the following example eosin Y (EY) is used as photoredox catalyst. Please give the final product of the reaction.

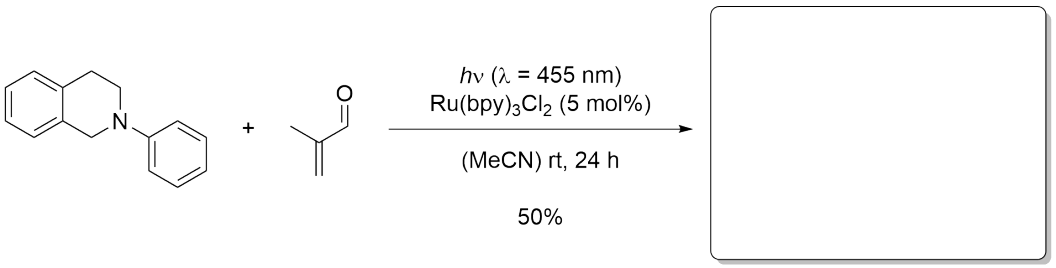


Explain the mechanism by filling in the boxes below.



0 1 2

c) Give the product of the following reaction. Ignore any stereocenters.

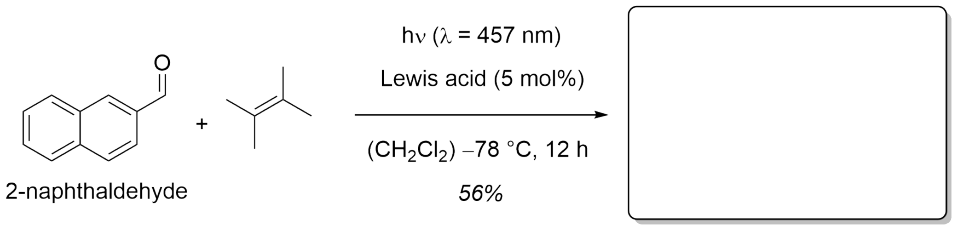


Problem 5 **Diverse Reactivity (21 credits)**

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

a) Stegbauer *et al.* found that adding a Lewis acid to 2-naphthaldehyde changed its photoreactivity. No carbonyl reactivity was observed; instead, 2-naphthaldeyhde behaved similarly to acceptor-substituted benzenes. Draw the product and name the type of reaction.

0 1 2 3 4

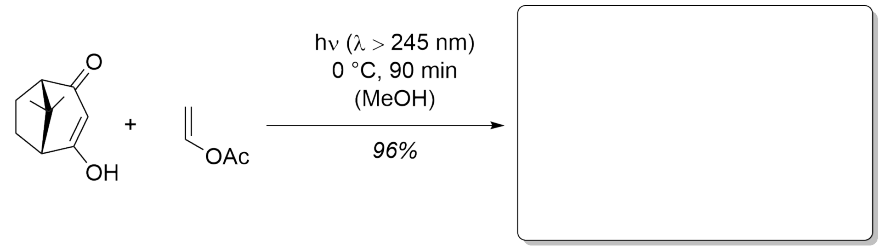


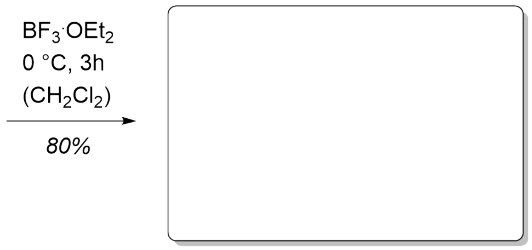
2-naphthaldehyde

Reaction Type:

b) The following photocycloaddition led to a mixture of two diastereoisomers. Further reaction with $BF_3 \cdot OEt_2$ led to the rearrangement of these compounds. Fill in the box with the appropriate major diastereoisomer and its rearrangement product. What is the name of this reaction sequence? You can disregard the stereoinformation of the acetoxy group of both the intermediate and the product.

0 1 2 3 4 5 6

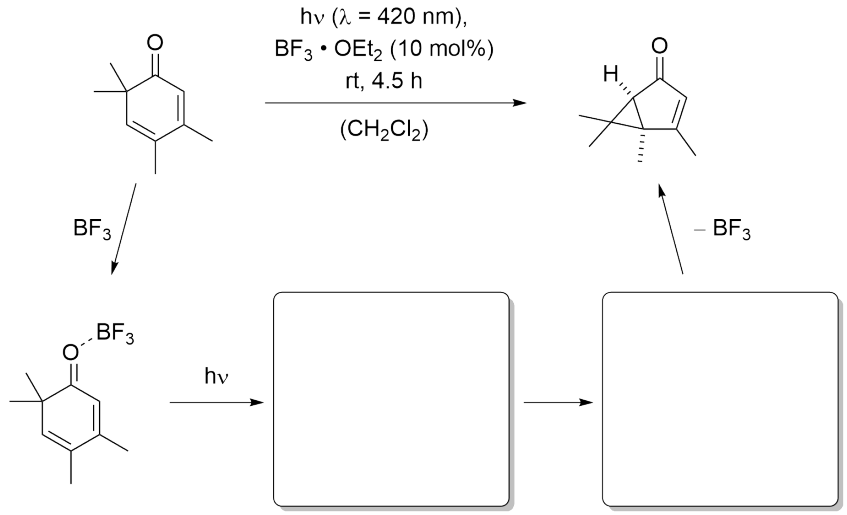




Name of the reaction sequence:

0 1 2 3 4 5

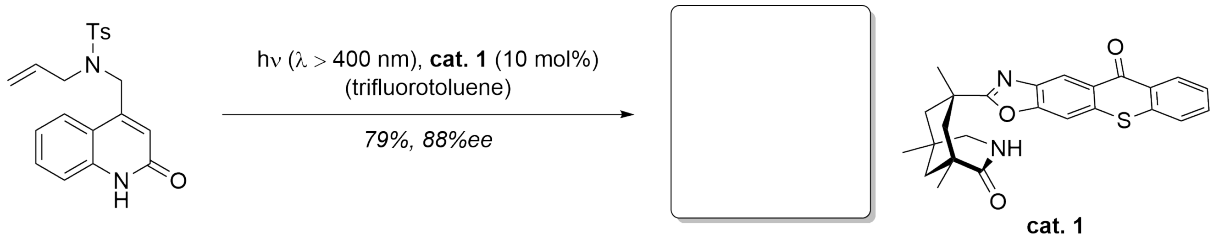
c) Upon irradiation of 3,4,6,6-tetramethylcyclohexa-2,4-dien-1-one under the given conditions, the following bicyclic product is formed. $BF_3 \cdot OEt_2$ acts as a Lewis acid catalyst that induces a bathochromic shift so that irradiation with visible light leads to an efficient reaction. Give a mechanistic explanation by providing the intermediates in the boxes below. What is the name of this reaction?



Name of the reaction:

0 1 2 3 4 5 6

d) 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 **1** with high enantioselectivity. Draw the final compound with the correct absolute configuration.



cat. 1

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

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