Organic Photochemistry – Exercise 1: 24/10/2024, 11.00 am

German group: CH22210 **English group: CH42306**

1. a) For the determination of the singlet and the triplet energy of iminium ion **9** (Figure 1), the absorption (black), fluorescence (red) and phosphorescence (blue) is measured. The singlet energy is determined from the intersection of the absorption spectrum and the fluorescence spectrum at λ = 380 nm. Phosphorescence can be calculated from the inflection point of the most blue shifted shoulder of the phosphorescence emission (λ_{max} = 562 nm). Calculate the singlet and the triplet energy of iminium ion **9**.

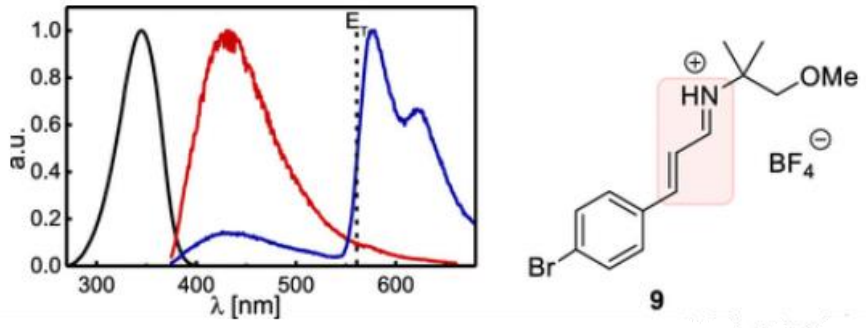


Figure 1. Absorption and luminescence spectra (λ_{exc} = 360 nm) of iminium ion **9** in MeCN. Colors: Absorption, black; fluorescence (rt), red; phosphorescence (77 K), blue. The energy of the (0,0) transition was calculated from the inflection point at λ = 562 nm.

b) In order to know light of which wavelength to choose for the excitation of a compound into one if its excited states, knowledge about the light absorption of the compound is required. For this, UV/Vis spectroscopy is the method of choice. UV/Vis titration is a way to determine the influence of certain additives on the photophysical properties of a compound. Please calculate the corresponding extinction coefficients for *N*,*O*-acetal **7a** with and without Brønsted acid. Explain the effects of the presence of Brønsted acid on the light absorption of **7a**. Name the characteristic points of the UV/Vis titration (Figure 2).

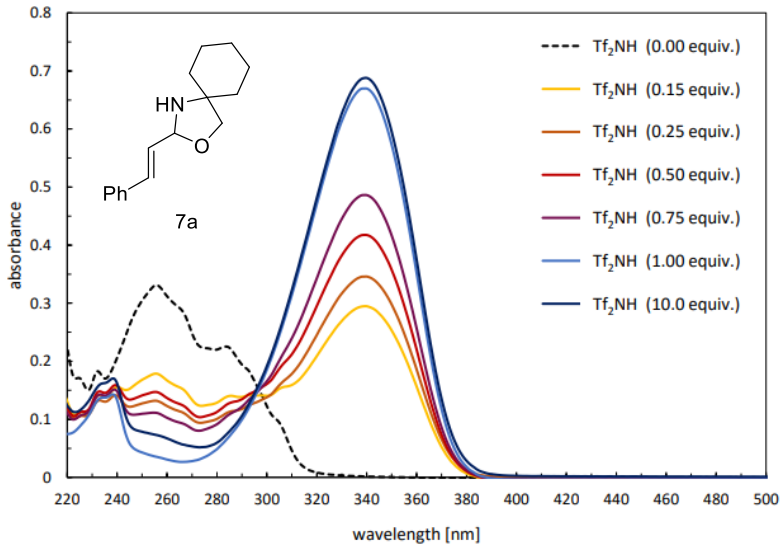
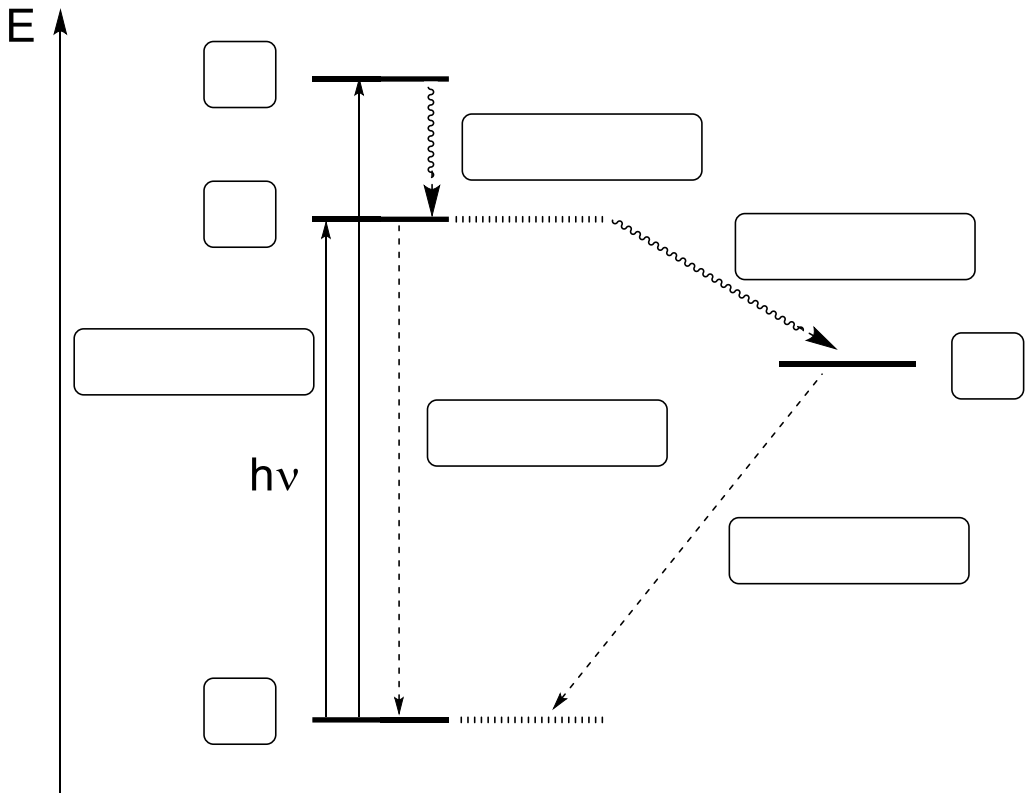


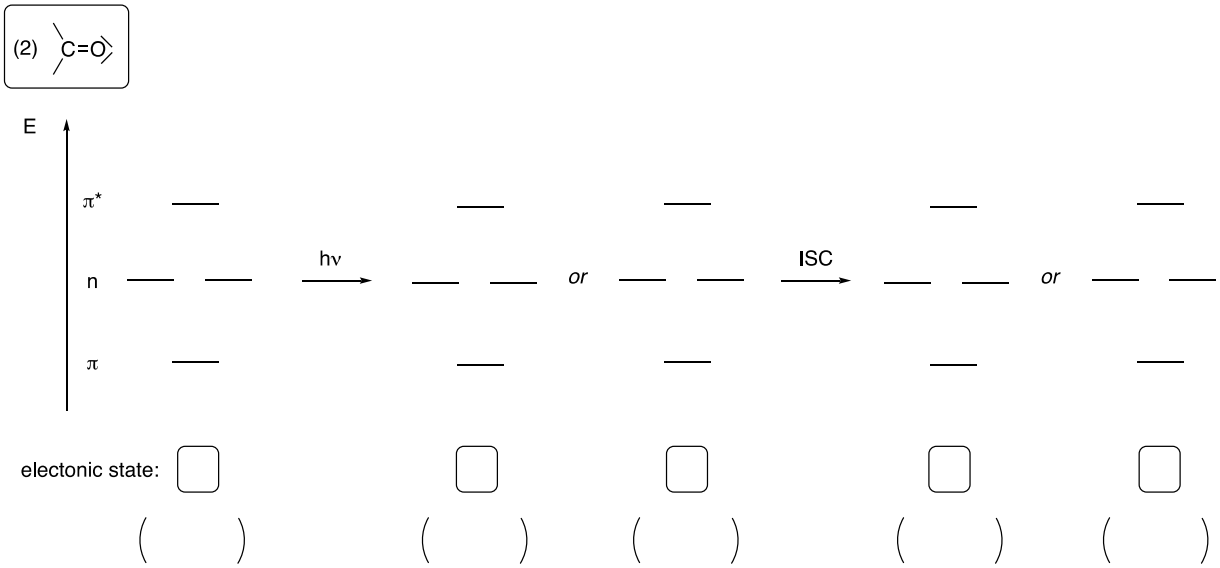
Figure 2. UV-Vis spectrum of *N*,*O*-acetal **7a** in CH_2Cl_2 as the solvent (c = 0.1 mM) without Brønsted acid (••••) and after addition of various equivalents of Tf_2NH (—). Cuvette d = 1mm.

2. a) Complete the following *Jablonski* diagram. Define every energy transfer noted on the diagram.

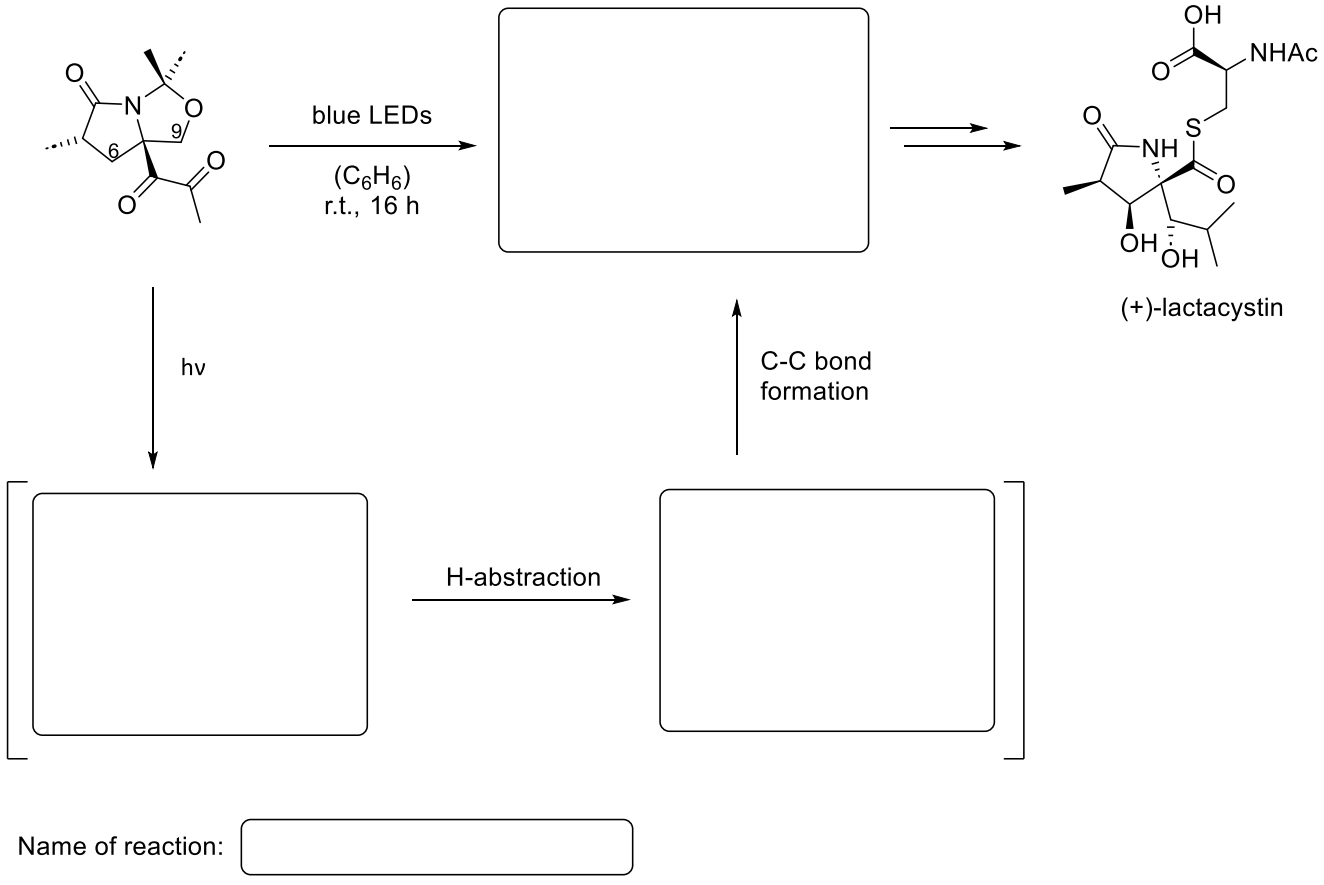


b) Draw an energy diagram to explain the Franck Condon principle and Kasha's rule.

3. Draw the MO diagram for benzophenone (C=O, π-n-π*) in the ground state, after excitation with light and intersystem crossing processes (ISC).



4. An important photo-induced transformation was used in the total synthesis of (+)-lactacystin. Describe the mechanism and analyze the regioselectivity (C6 *vs.* C9) and the diastereoselctivity of the reaction. What is the name of this reaction? Explain why the usage of visible light (instead of higher energy UV light) is crucial for the success of this transformation.



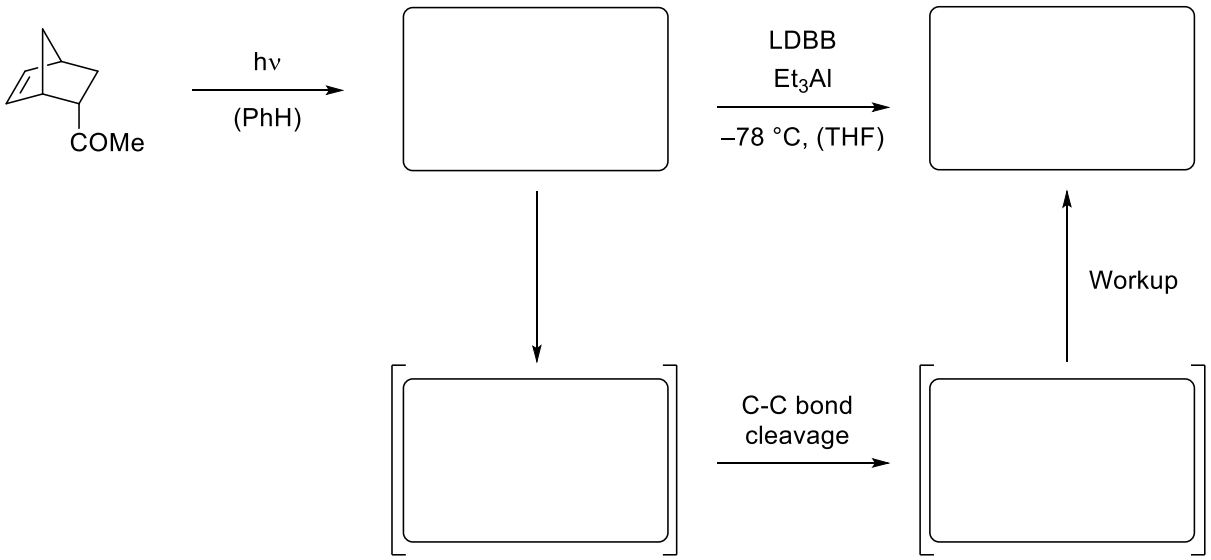
Name of reaction:

Organic Photochemistry – Exercise 2: 07/11/2024, 11.00 am

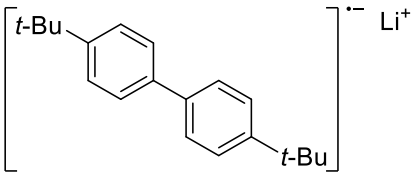
German group: CH22210 **English group: CH42306**

1. Oxetanes present a class of a valuable synthetic targets not only due to their occurrence in a plethora of natural products and biologically active compounds, but also due to their diverse follow up reaction profile. In the following synthesis, the authors utilized an elegant cleavage reaction after the photoreaction, enabling access to substituted diquinanes from norbornene derivatives. Fill in the missing products and intermediates.

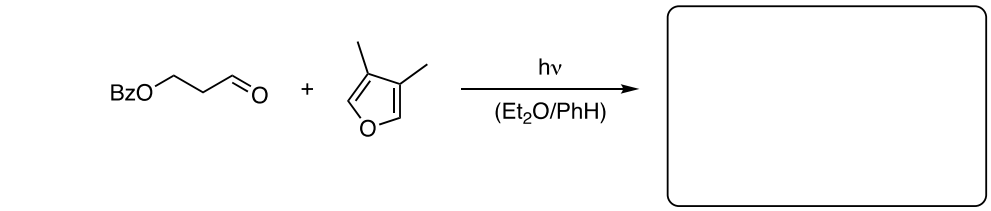
Hint: *In the second step, the Lewis acid coordinates to the oxygen atom, followed by a one-electron reduction mediated radical cleavage of a C-O bond.*

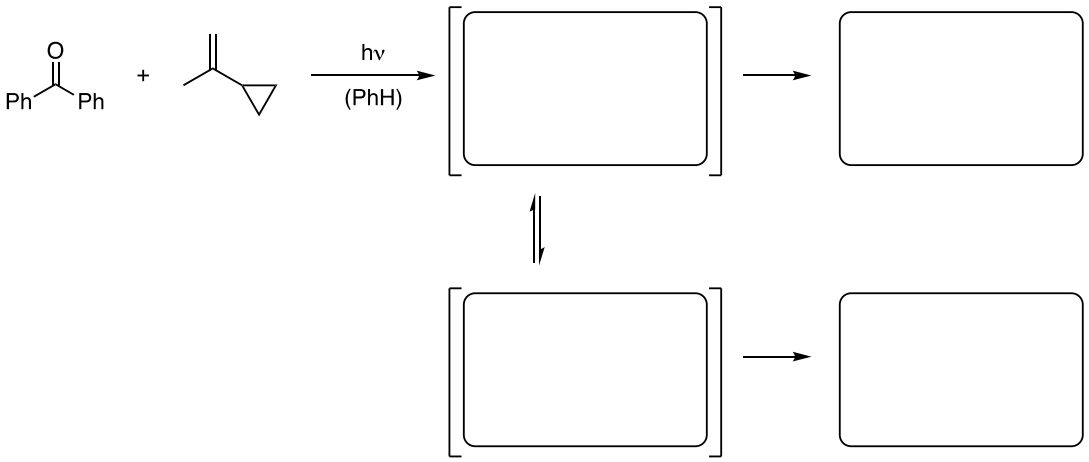


LDBB:

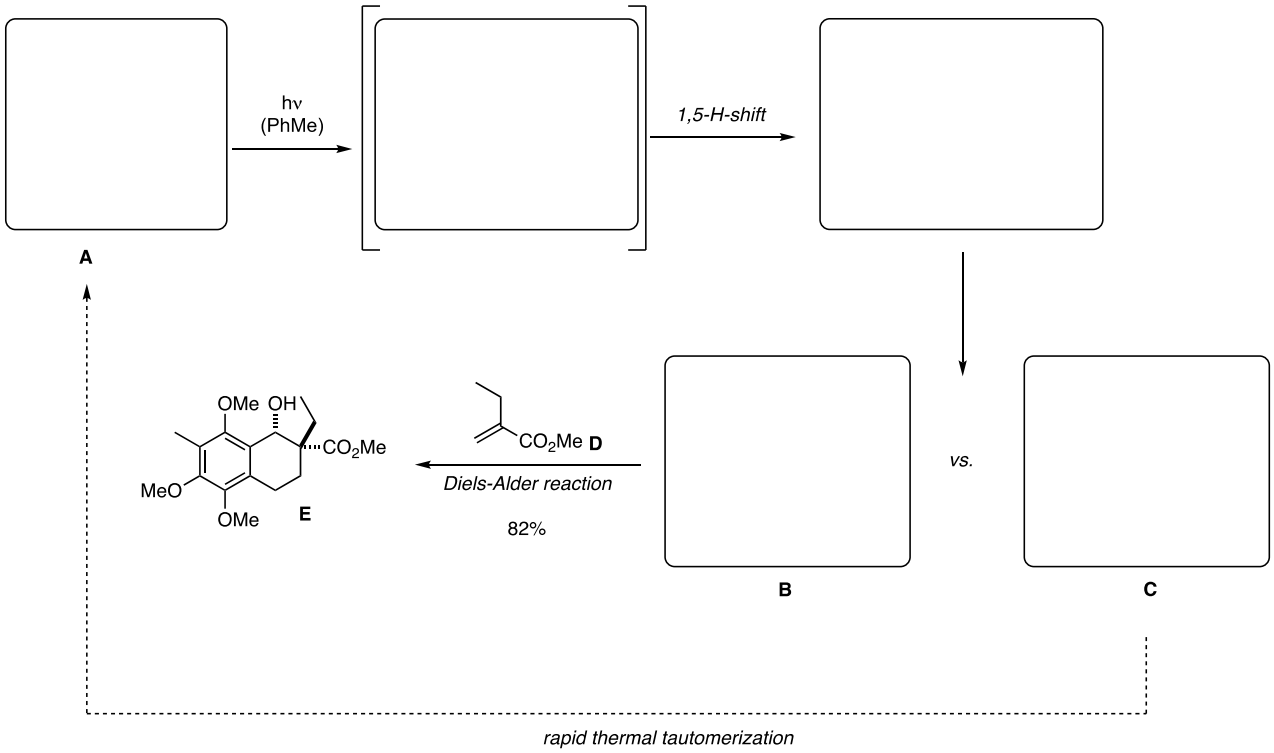


2. Give the structures of the products and intermediates in the following two reactions. In the first case, please also explain the regio- and diastereoselectivity of the reaction.

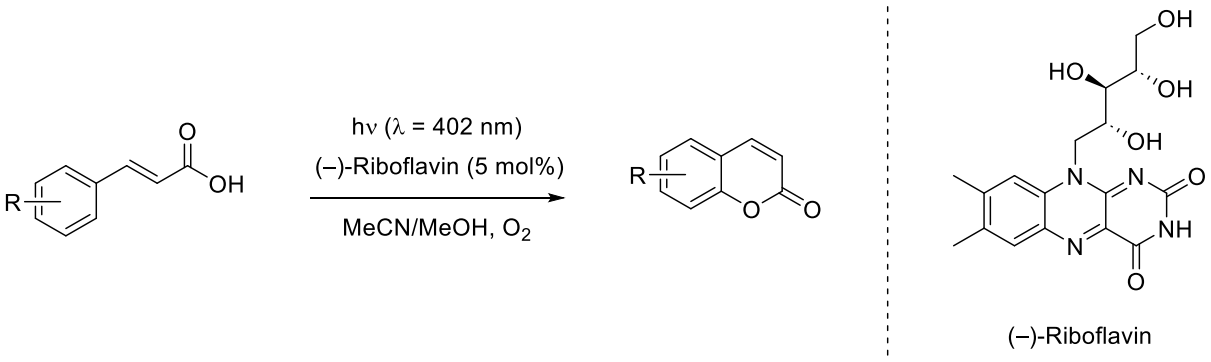




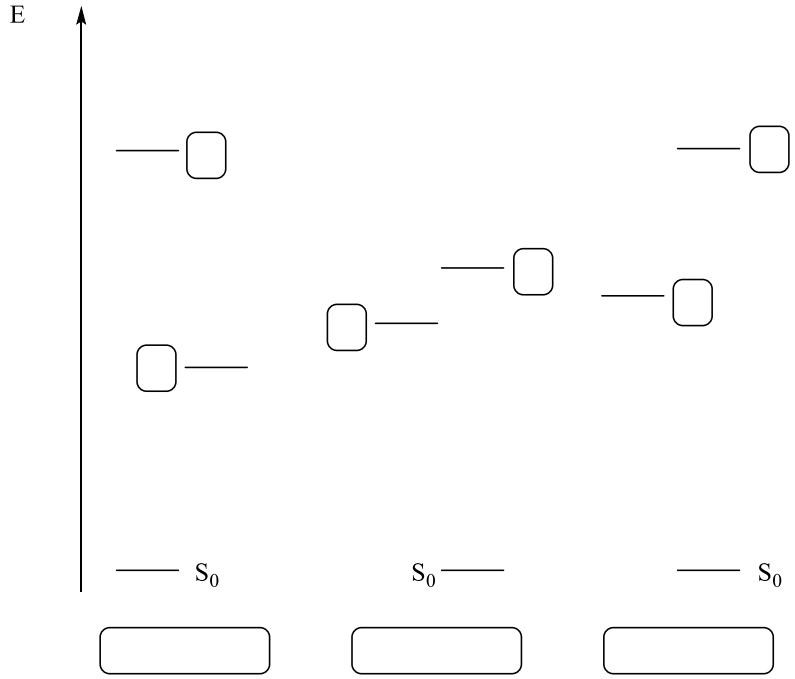
3. Another interesting total synthesis using a photochemical key step was described by the group of Nicolaou. Upon excitation of starting material **A** and subsequent intersystem crossing, two highly reactive intermediates are generated. Only one of the intermediates (**B** or **C**?) can be trapped in an intermolecular reaction with compound **D** to give the product **E** in high yield. Complete the scheme given below (including intermediates and electron arrows) and explain the diastereoselectivity of the final reaction step.



4. One way for the synthesis of complex molecular structures is to use a single catalyst that performs several sequential transformations. A prerequisite for this type of cascade reactivity is that each transformation must follow a different activation mode, by which all preceding and following intermediates remain untouched. In the following reaction, cinnamic acids undergo cyclization to form coumarins.



The depicted catalyst serves a dual purpose, as direct cyclization from the (*E*)-alkene to the coumarin is unfavorable. Explain how the photocatalyst can transform the (E)-alkene into an isomer that is more amenable to cyclization. Elaborate on the reactivity concerning the relative energy levels of the involved electronic states and the relevant energetic transitions.

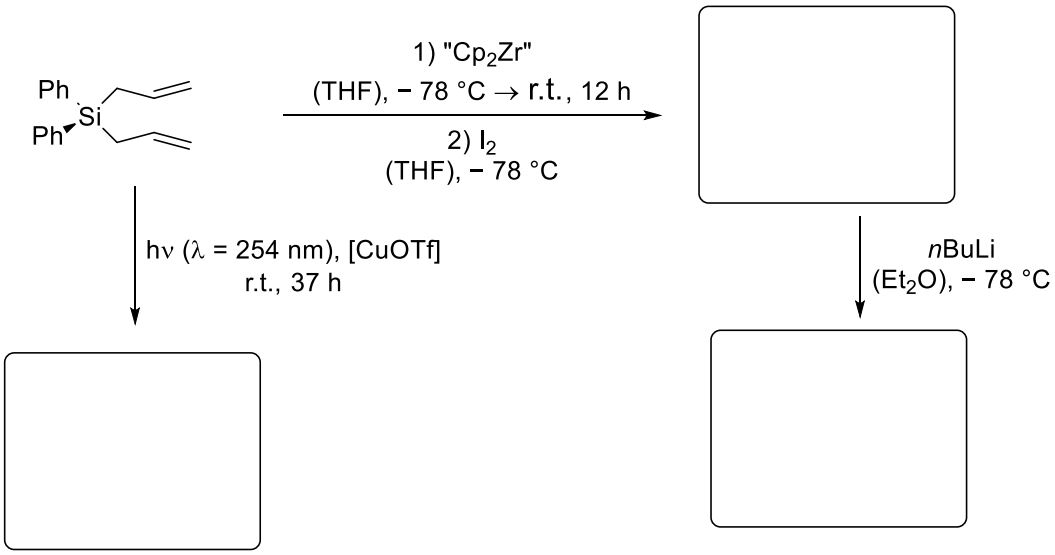

E
S0
S0
S0

Organic Photochemistry – Exercise 3: 21/11/2024, 11.00 am

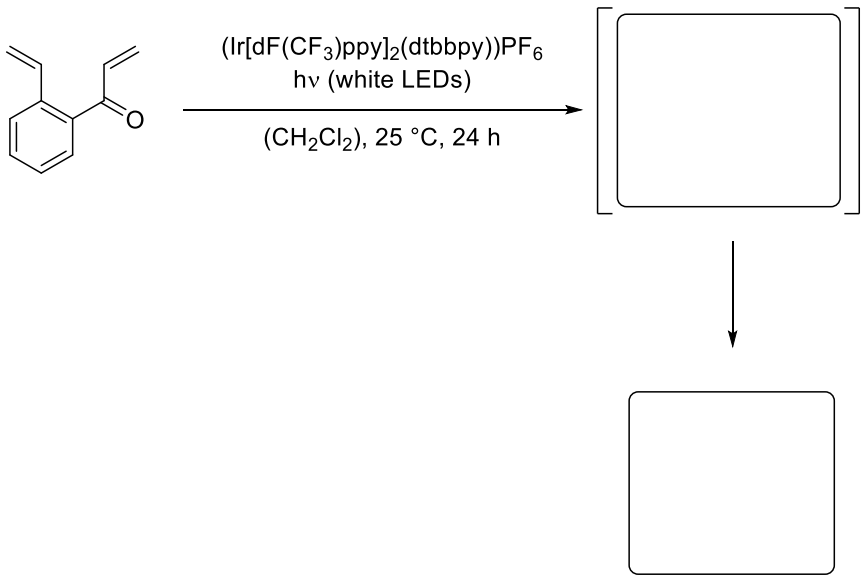
German group: CH22210 **English group: CH42306**

1. Complete the following reactions. Pay attention to the stereoinformation

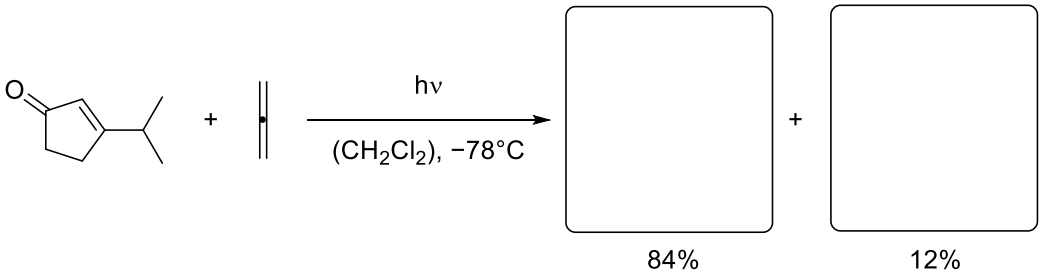
a)



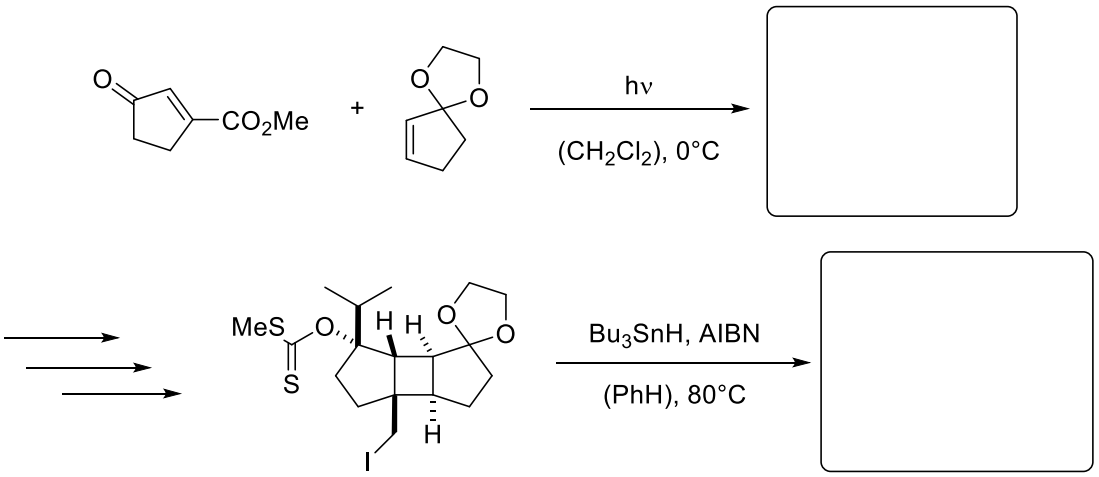
b)



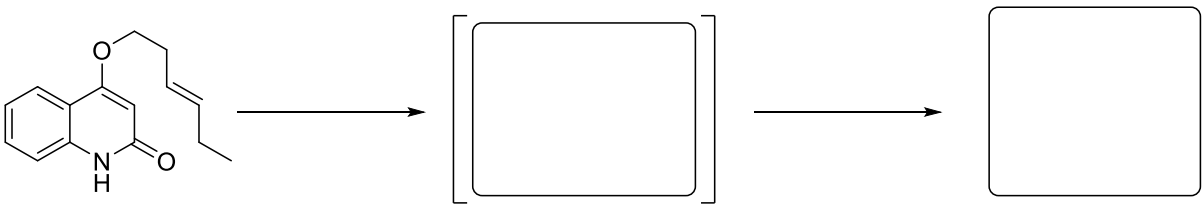
c)



d)



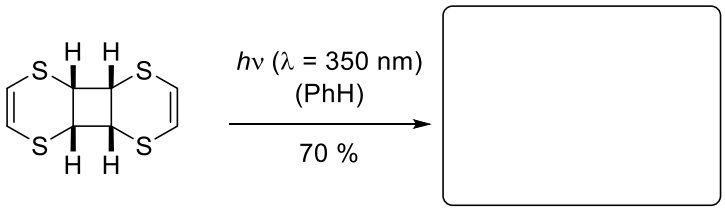
2. The molecule below can undergo a intramolecular [2+2] photocycloaddition.
a) Draw the intermediate 1,4-biradical(s) and the product(s) and try to predict the regio- and diastereomeric outcome.



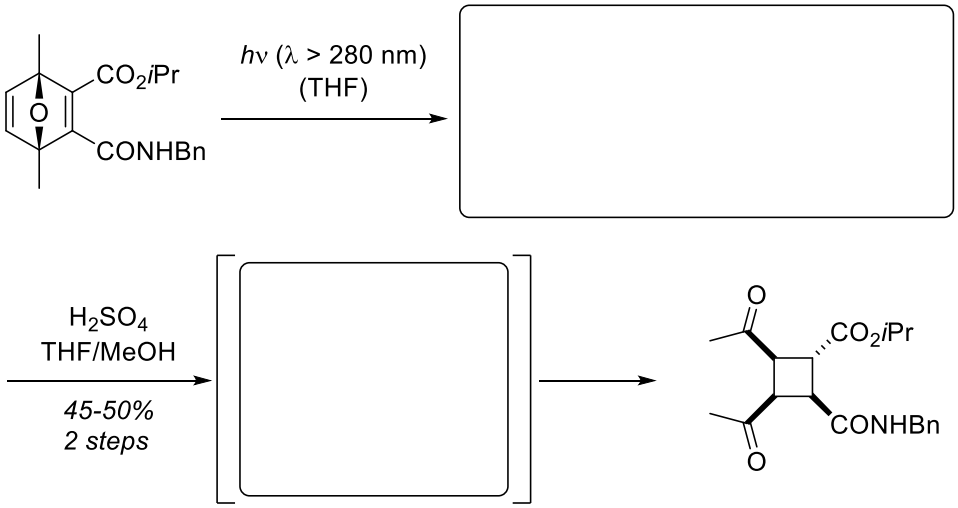
b) If we wanted to prove that this is a triplet reaction, a stereoconvergent reaction outcome is necessary: which similar starting substrate is needed for this? Why are triplet reactions generally stereoconvergent?

3. Fill in the products and intermediates of the following examples.

a)



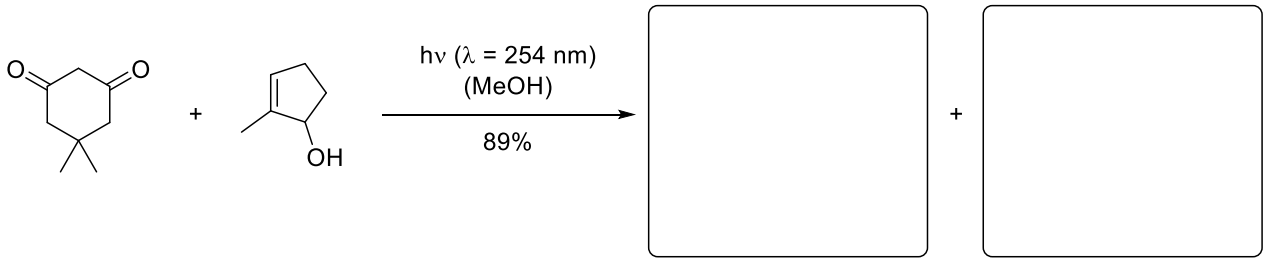
b)

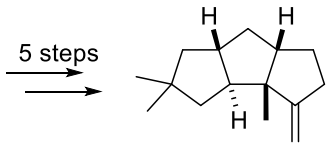


Organic Photochemistry – Exercise 4: 03/12/2024, 09.00 am

German group: CH27402 **English group: CH42306**

1. In their total synthesis of racemic hirsutene, the Weedon group utilized a named photochemical reaction as a key step where two regioisomeric products are obtained in a 1:1 mixture. What are these products and what is the name of the reaction? How does it work mechanistically?

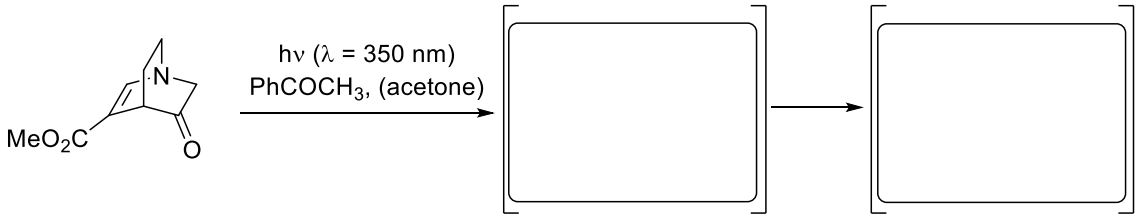


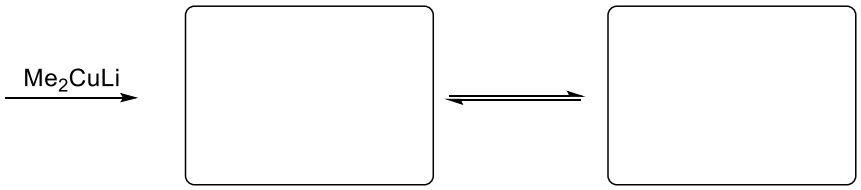


(±)-hirsutene

Name of the reaction:

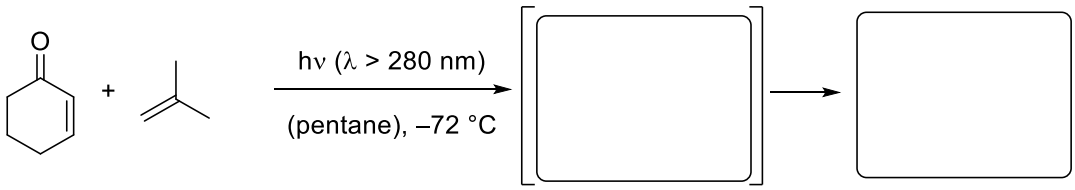
2. The reaction shown below is a staple in organic photochemistry. Give the name of the reaction as well as the structures of the intermediates and products. What role do acetophenone and acetone play? Which hypersurface does the photoreaction occur on?

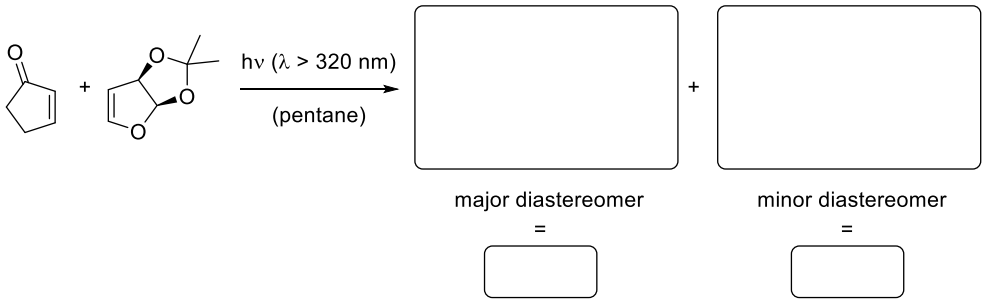


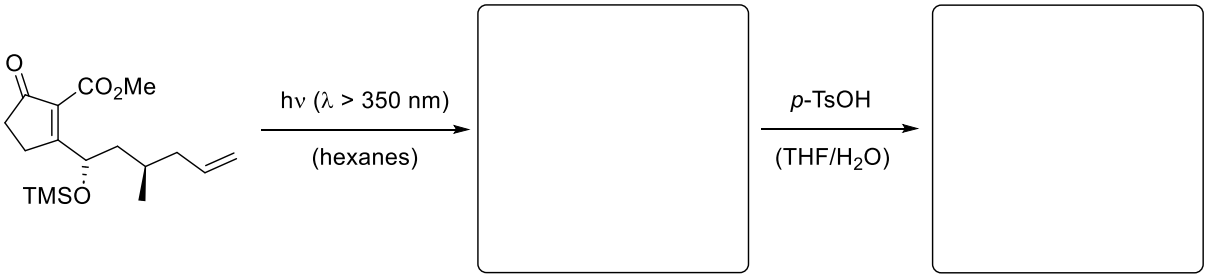


3. Complete the following reaction schemes.

a)





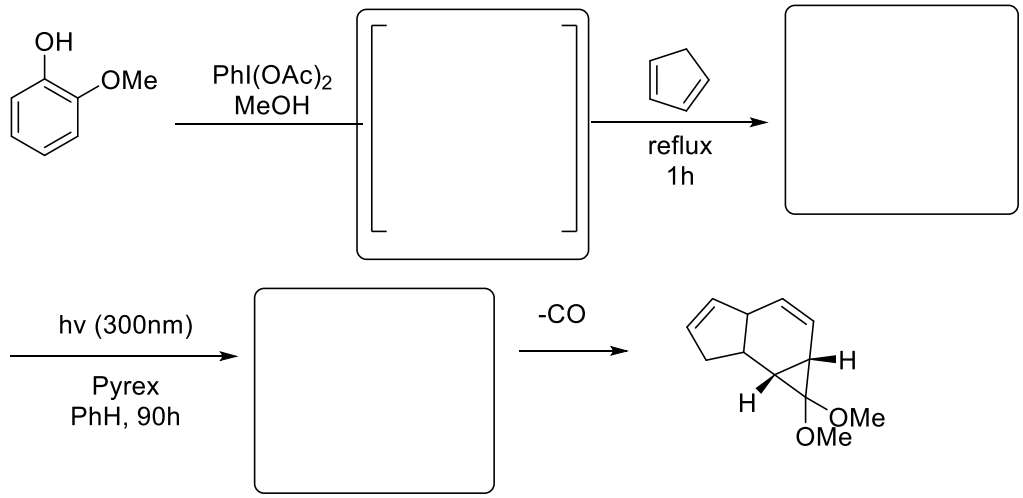


Model for stereoselectivity:

Organic Photochemistry – Exercise 4: 03/12/2024, 09.00 am

German group: CH27402 **English group: CH42306**

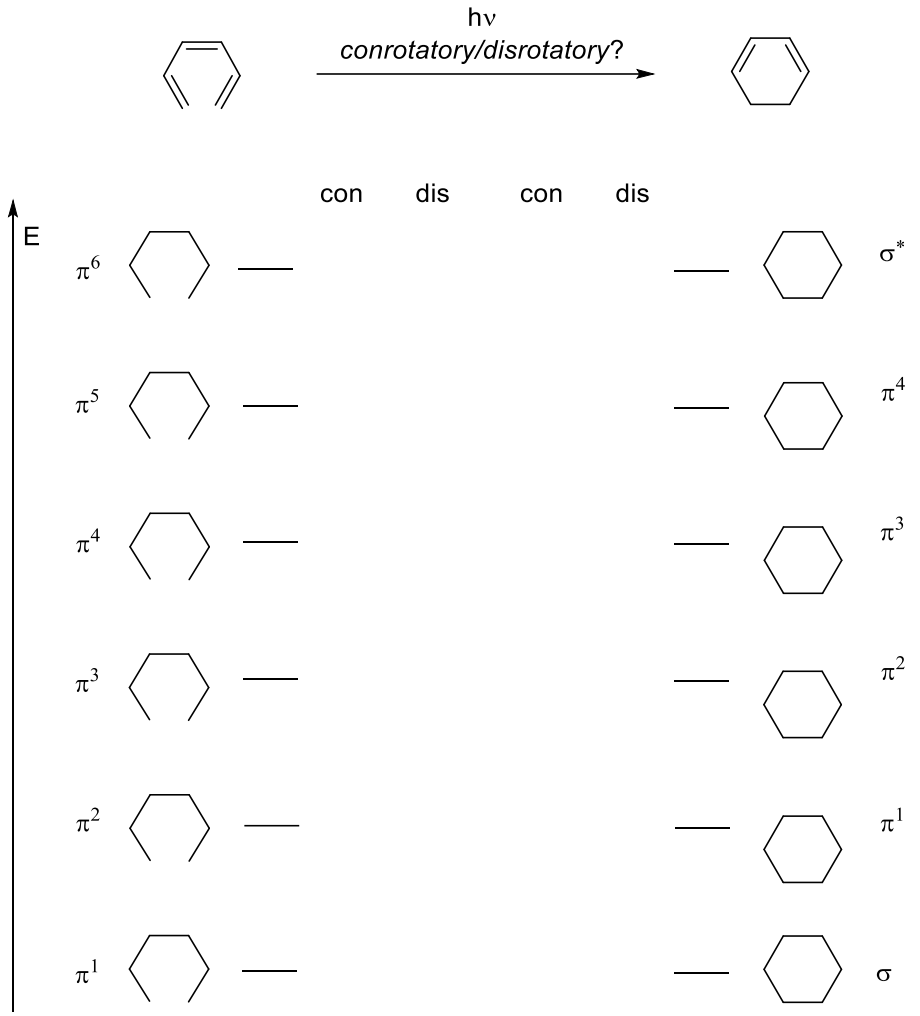
1. Liao and co-workers reported an elegant way of synthesizing the carbon framework of marasmanes. They started from Guajacol, which reacted with cyclopentadiene in a [4+2]-cycloaddition. The product was irradiated triggering a rearragnegement, which aster CO loss afforded the final product. Fill out the boxes and name the rearrangement.



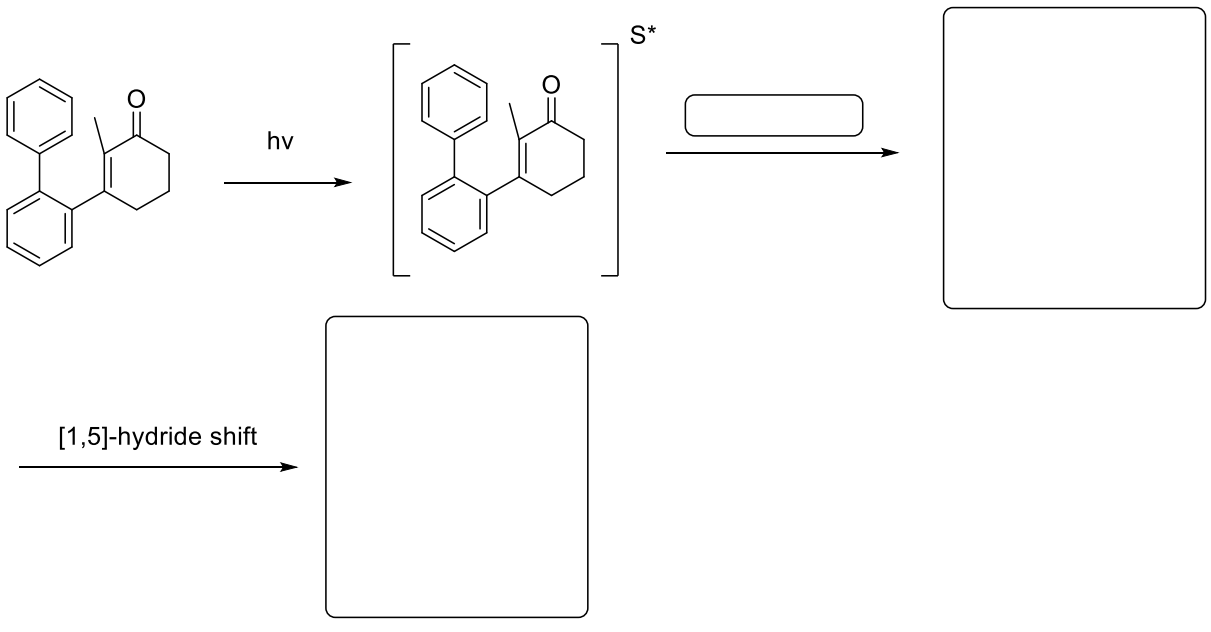
2. Electrocyclic reaction are an important class of reaction in organic chemistry. In this context the Woodward-Hoffman predict the outcome of these.

a) Pericyclic reactions are the consequence of orbital interactions. What are the underlying assumptions for these orbital–orbital interactions?

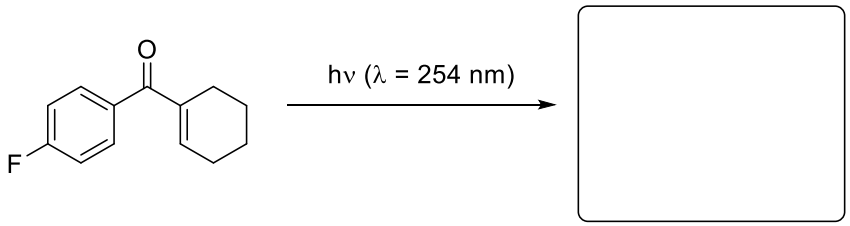
b) Consider hexa-1,3,5-triene as a model system for cyclizations. Does the photochemical [6π] cyclization to cyclohexa-1,3-diene occur in a conrotatory or disrotatory fashion? In the figure below, draw the molecular orbitals of both compounds and fill in the electrons for the S_1 state. Then, analyze the orbital symmetry for both conrotatory and disrotatory cyclization using the Woodward-Hoffmann rules, i.e. if the orbital is symmetric or asymmetric regarding the symmetry operation (conrotatory = C_2-symmetric, disrotatory = mirror-symmetric).



c) A more recent example of a [6π] cyclization was published by Rainer. Fill out the boxes and pay attention to the stereochemical outcome.



3. Give the product of the following reaction. What is the name of the reaction? Does it proceed in a disrotatory or in a conrotatory fashion?



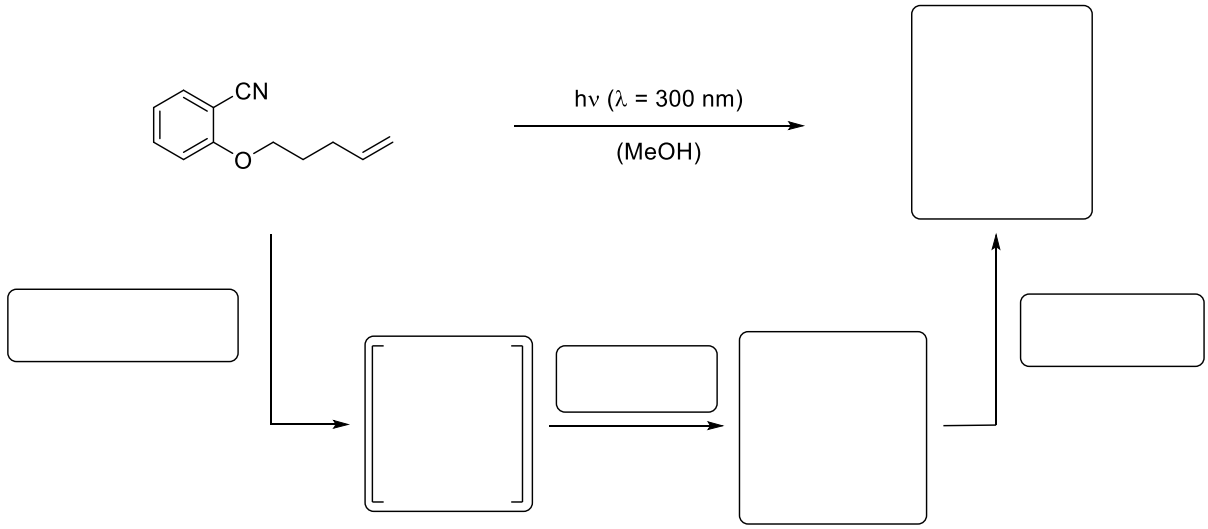
Name of the reaction:

Nature of cyclization:

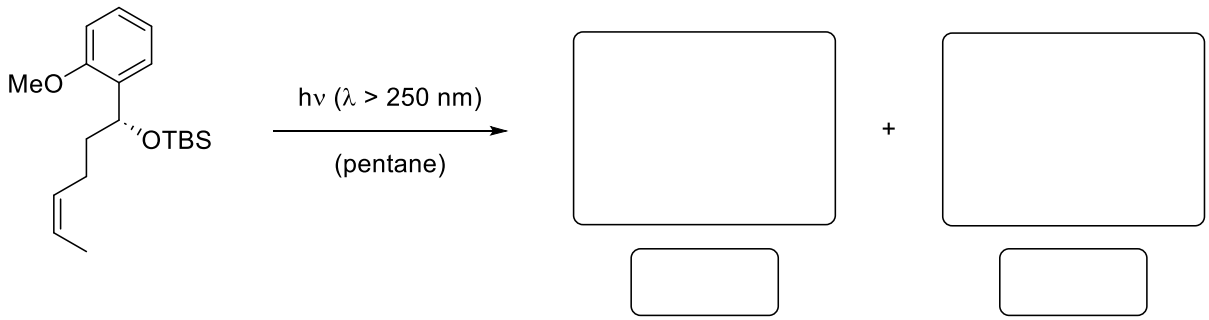
Organic Photochemistry – Exercise 6: 09/01/2025, 11.00 am

German group: CH22210 **English group: CH42306**

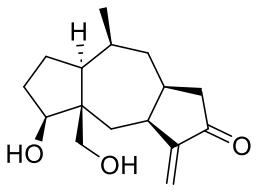
1. The following transformation is the result of a three-component reaction cascade. Please fill in the product along with the two intermediates and label the individual steps.



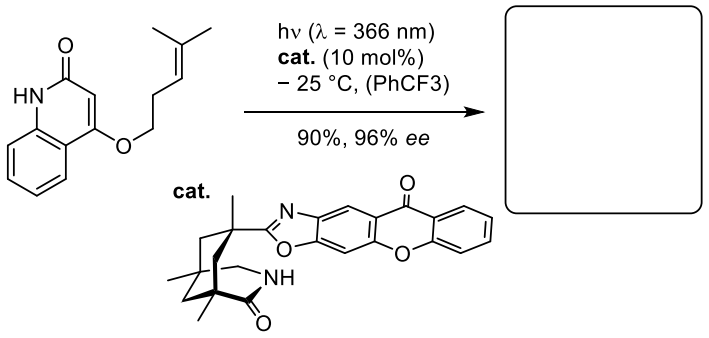
2. In the synthesis of rudmollin, the given starting material was irradiated, resulting in the formation of two isomers. Both isomers were further converted into the natural product. Please fill in the products and the model explaining the observed stereoselectivity. What are the names of the isomers?



Model for stereoselectivity:



3. An enantioselective version of a common reaction in synthetic photochemistry is shown in the reaction below. Give the structure of the product (absolute configuration!) and the name of the reaction. How is enantioselectivity induced by the chiral xanthone catalyst? Draw the catalyst-substrate complex that explains how the enantioface differentiation is achieved in this transformation.



explanation for enantioselectivity:

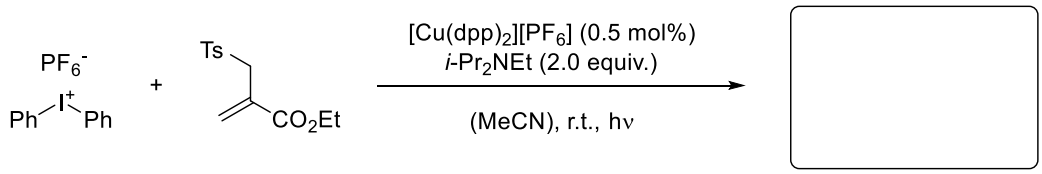
Organic Photochemistry – Exercise 7: 21/01/2025, 09.00 am

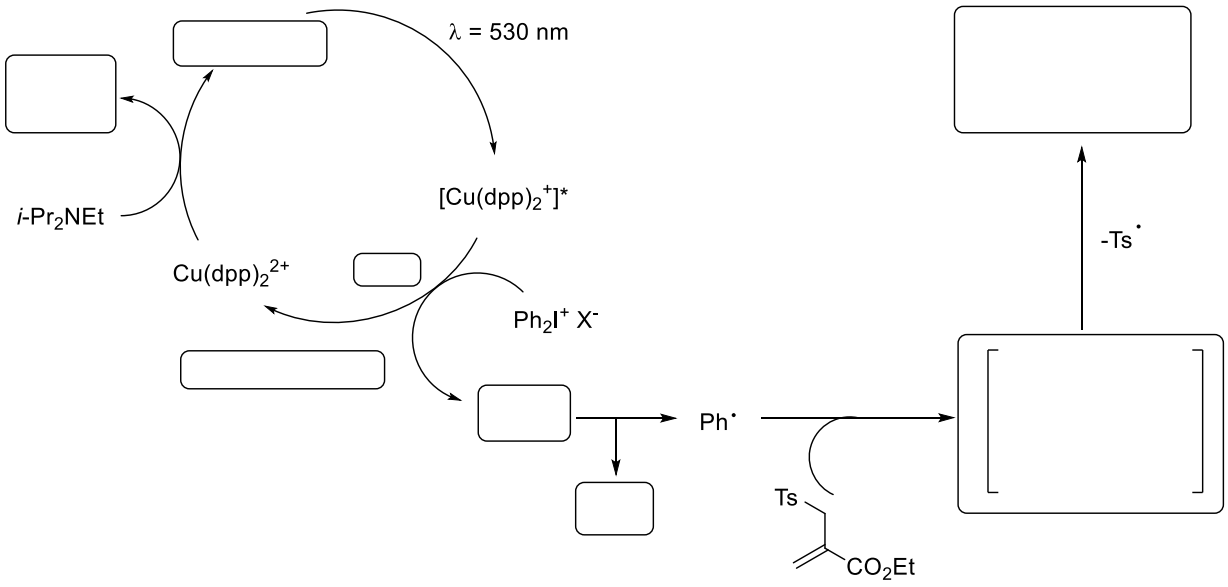
German group: CH27402 **English group: CH42306**

1. Define the term redox (or reduction) potential. What is the general conclusion you can draw if a redox pair has a negative/positive redox potential?

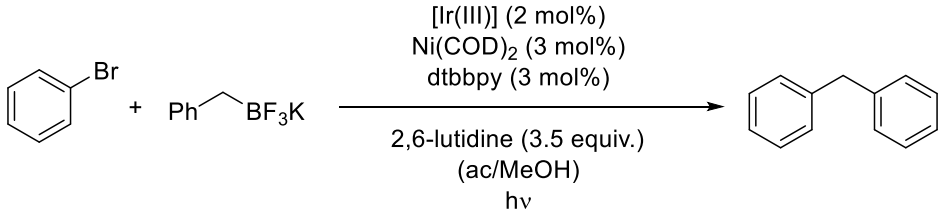
2. Explain why photoexcited transition metal complexes are both stronger oxidants and stronger reductants than their corresponding ground state species.

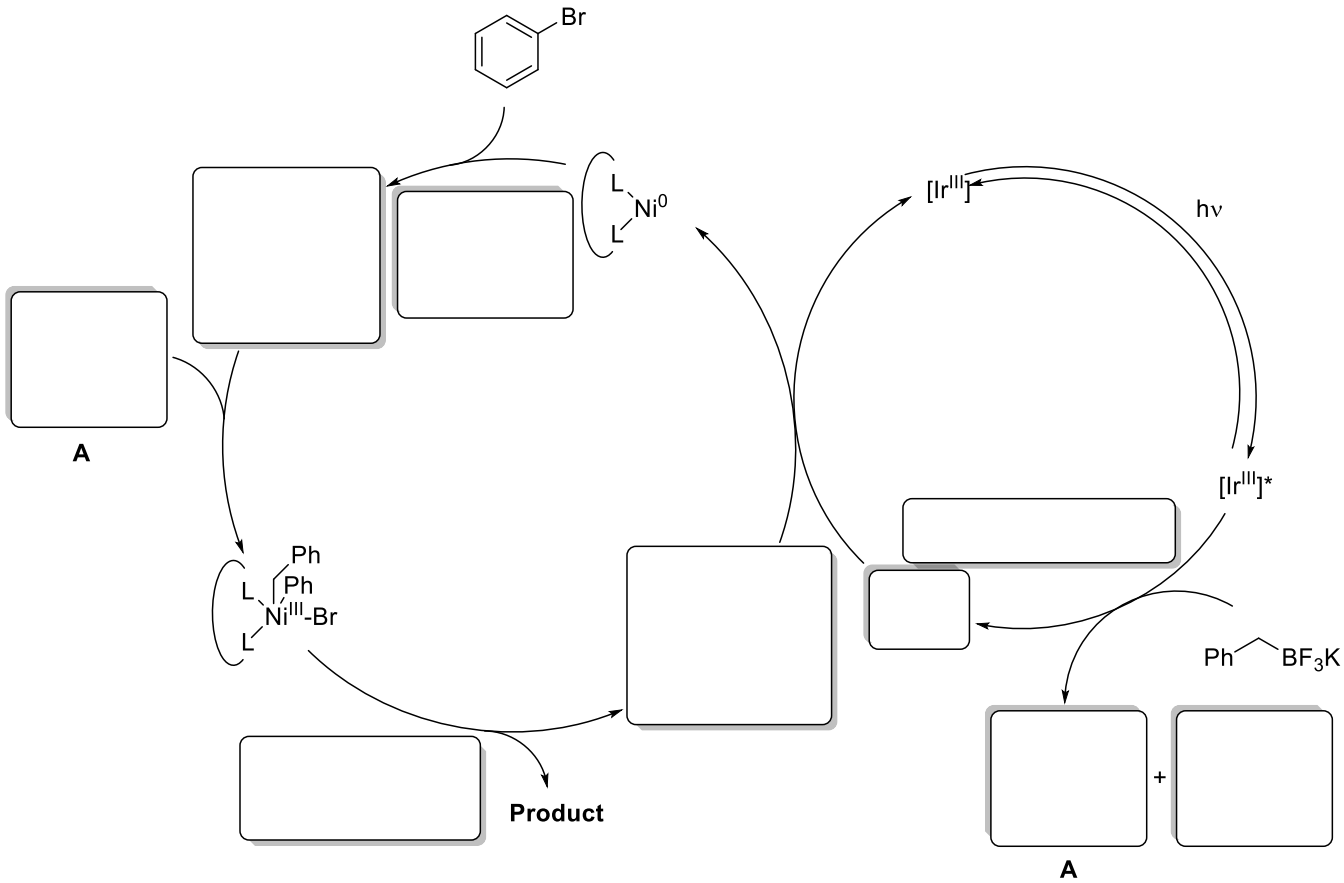
3. Aryl radicals are important synthetic intermediates. Aryl iodonium and aryl diazonium salts behave similarly and can both be used to access the aryl radicals in the presence of a photoredox catalyst. Fill in the boxes, make comments on why aryl iodonium and aryl diazonium salts but not aryl sulfonium salts will react in this reaction.





4. Photoredox catalysis can be paired with transition metals catalysis. This approach presents an alternative to classical cross-coupling reactions. Fill the gaps in the catalytic cycle. Apart from the structures, use labels you learned for cross-coupling reactions.



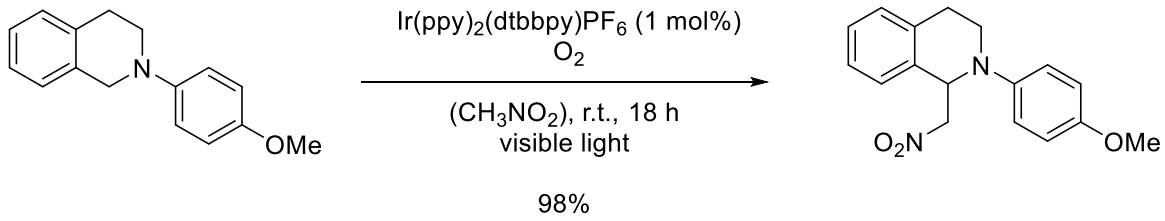


Organic Photochemistry – Exercise 8: 04/02/2025, 09.00 am

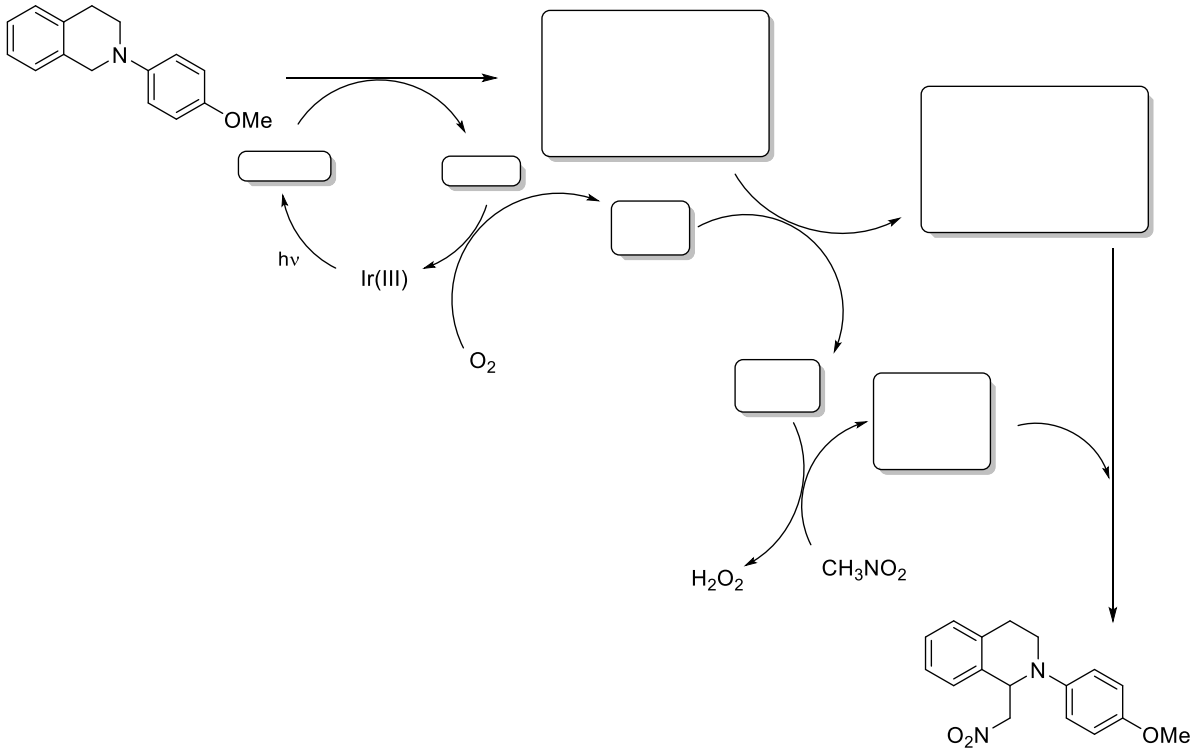
German group: CH27402 **English group: CH42306**

1.

Iminium ions generated by photoredox catalysis can react with nucleophiles to form new carbon-carbon bonds. An early example is the photoredox-catalysed aza-*Henry* reaction shown below.

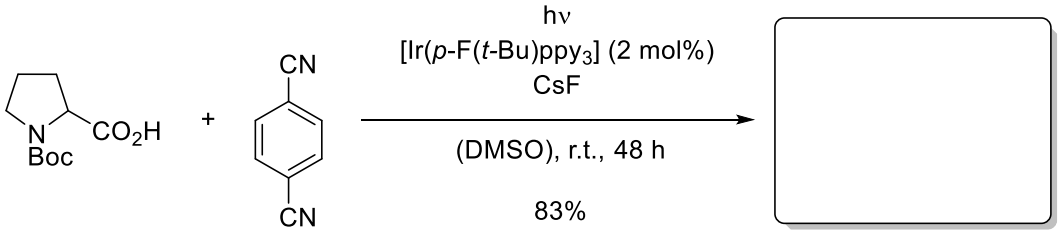


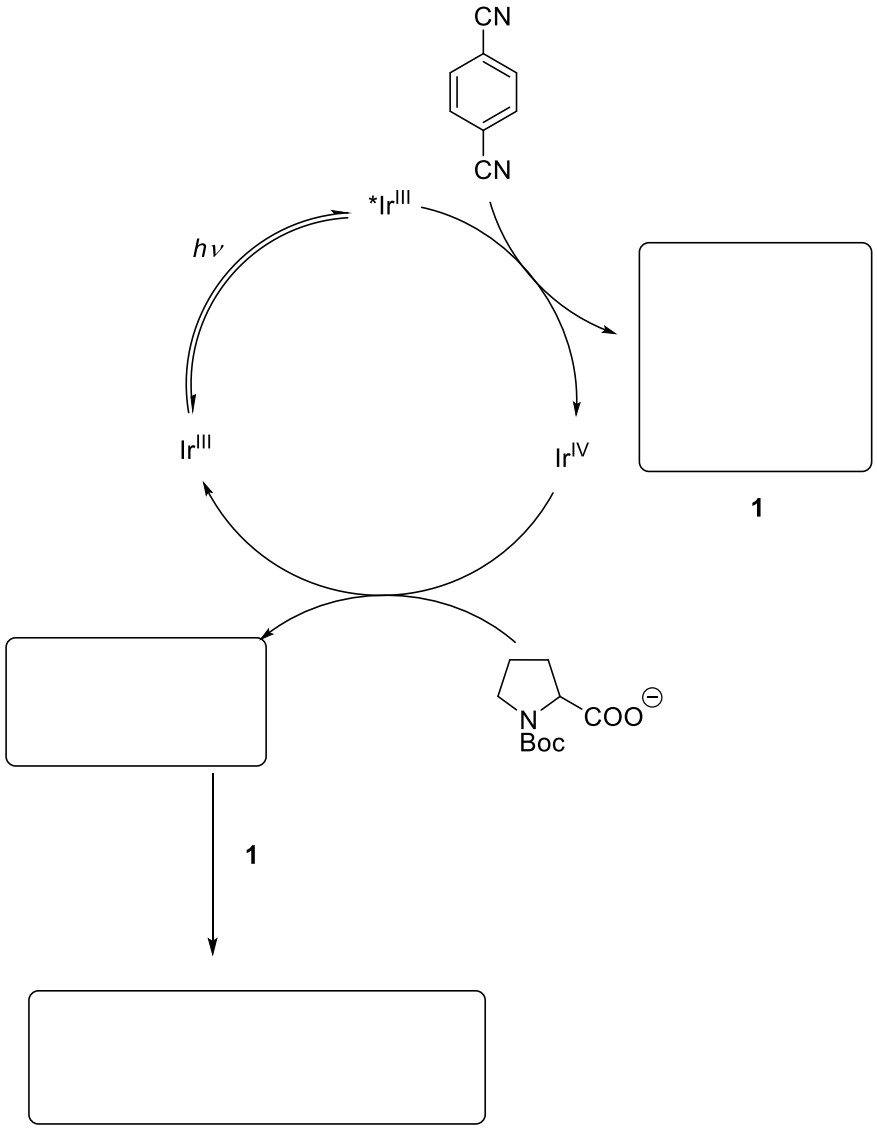
Fill in the missing intermediates, which lead to the formation of the depicted product. What is the role of molecular oxygen in this reaction?



2.

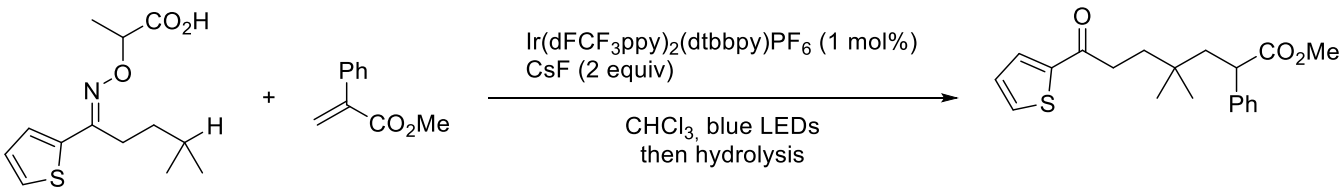
Iridium catalysts [($E_{1/2}^{red}$ [Ir^{IV}/*Ir^{III}] = –1.67 V vs. SCE)] can be employed for the radical decarboxylation of α-amino acids. The radical intermediates generated can be coupled to cyano-substituted aromatic compounds [1,4-dicyanobenzene ($E_{1/2}^{red}$ = –1.61 V vs. SCE)]. Please give the product of the following reaction and draw the photoredox cycle. Is the transformation net oxidative, reductive or redox neutral?

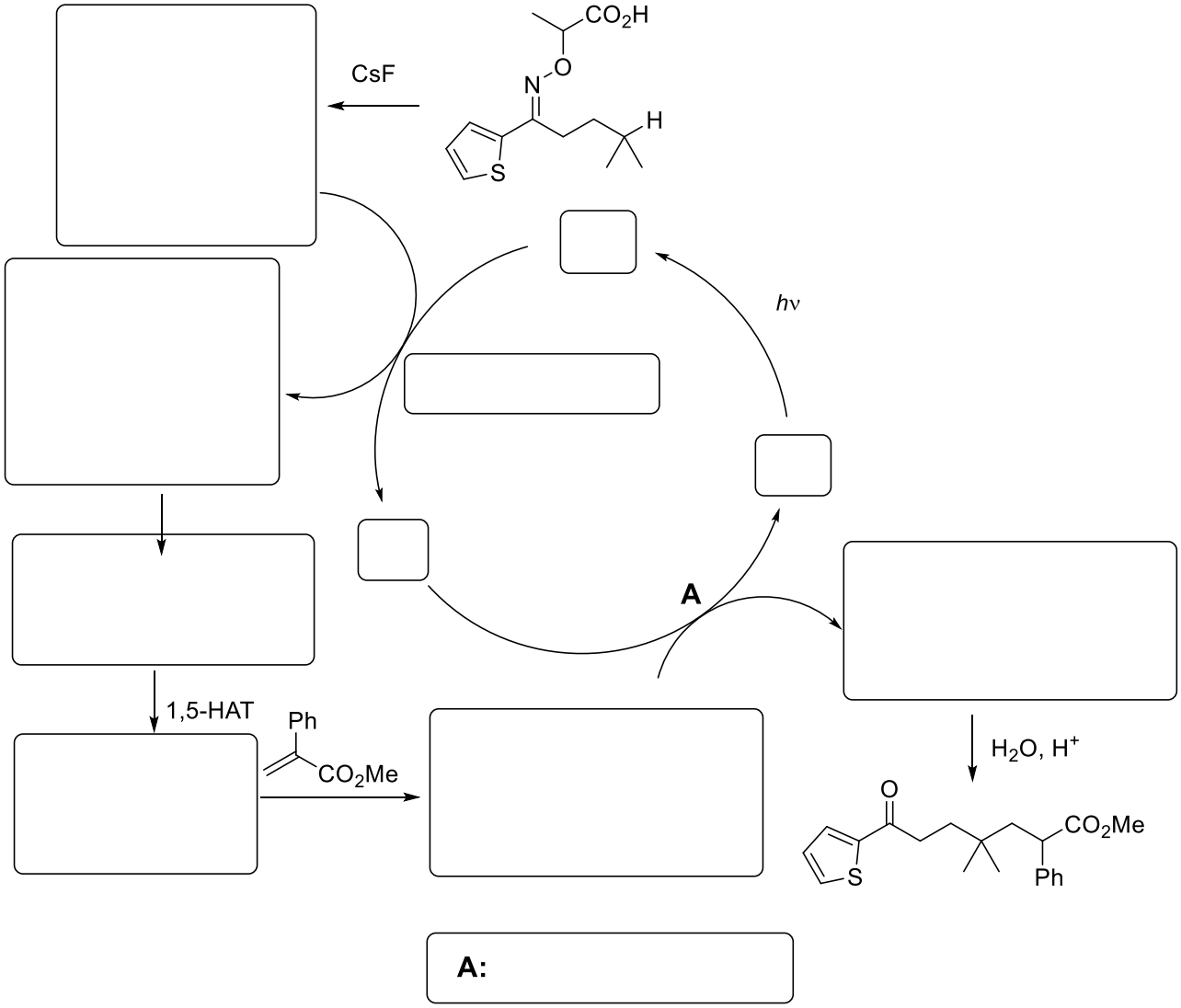

hν
[Ir(p-F(t-Bu)ppy3] (2 mol%)
CsF
(DMSO), r.t., 48 h
83%
CO2H
N
Boc
CN
CN


CN
CN
*Ir^III
hν
Ir^III
Ir^IV
1
COO⊖
N
Boc
1

3.

The following light mediated reaction allows the selective C-H γ-functionalization of various ketones. Fill in the missing intermediates and products of this light mediated transformation. Is this process going through oxidative or reductive quenching? Which term describes what happens in step **A**?





A: