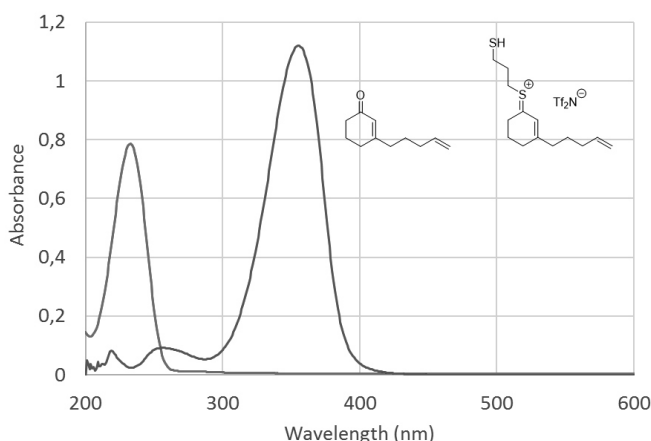


Exercise 1

UV/Vis spectra allow for the fast and easy calculations of extinction coefficients as well as the interpretation of different electronic transitions of the molecule.

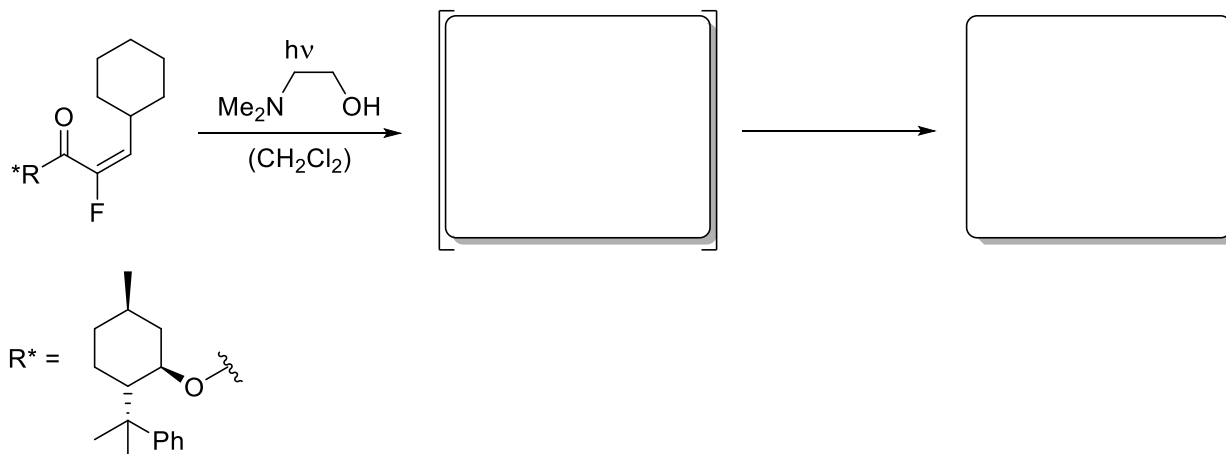
- a) The UV/Vis spectra of the enone and sulfonium ion are shown below, respectively. Assuming the spectra were recorded using a 1 mm quartz cuvette and 0.5 mM concentration for both samples, calculate the absorption coefficient for the enone at 233 nm and the sulfonium ion at 357 nm. The absorbance for the enone at 233 nm is 0.77 and the absorbance of the sulfonium ion at 357 nm is 1.11. To what transition do you assign the absorption?



- b) The enone shown above shows phosphorescence at $\lambda = 410$ nm. Calculate the triplet energy of the enone.
- c) Using a Jablonski diagram, qualitatively explain why one observes fluorescence at lower wavelengths compared to phosphorescence (no mathematics required).
- d) The enone shown above is reported to undergo rapid intersystem crossing to the triplet state (T_1) when the $n\pi^*$ transition is excited at 320 nm. Explain what causes intersystem crossing for the above enone.

Exercise 2

α,β -Unsaturated esters can be photochemically deconjugated and by use of chiral auxiliaries, such as 8-phenylmenthol, diastereoselectivity can be induced. Draw the intermediate and the product and give the configuration of the formed stereogenic center.

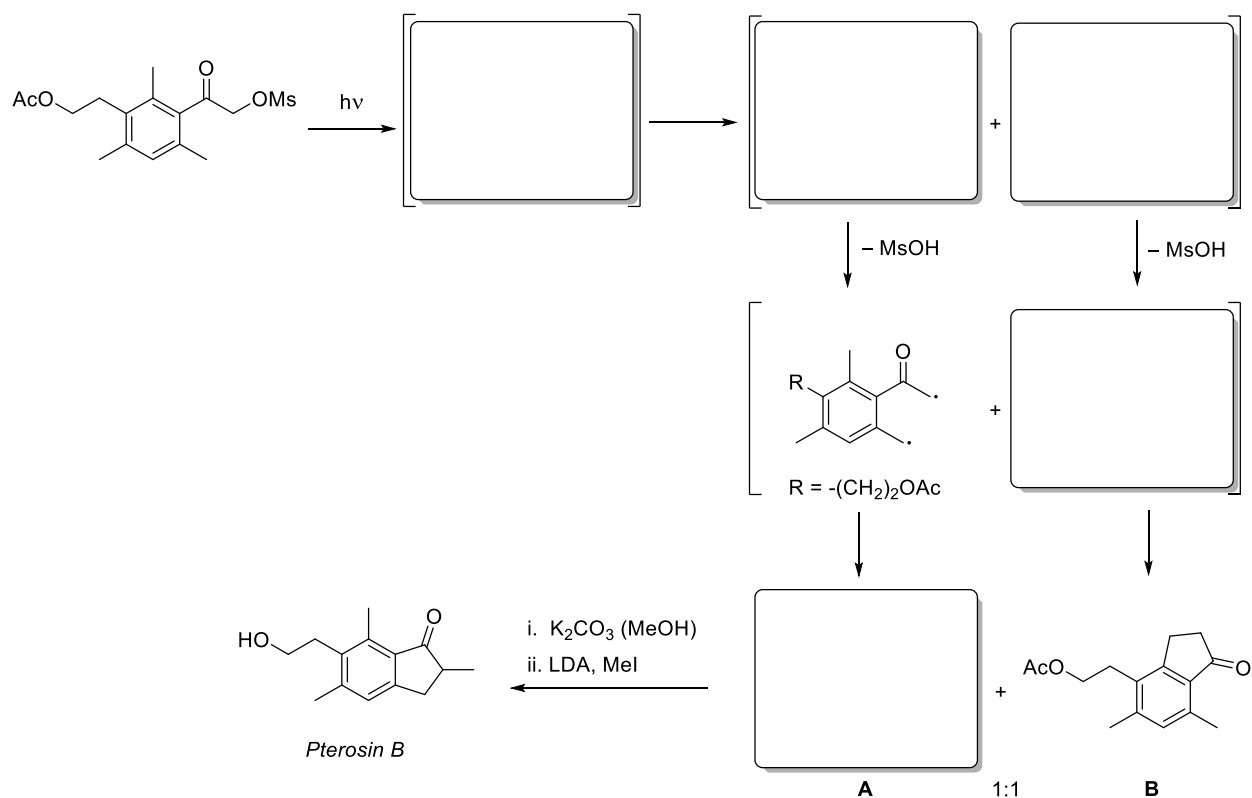


Draw the intermediate with the auxiliary in a chair conformation in the box below to help you visualize the selectivity for one diastereomer.



Exercise 3

In the total synthesis of *Pterosin B*, a photochemical step was implied in order to obtain an important precursor of the natural product. However, the photoreaction gave a 1:1 mixture of the desired product **A** and an unwanted regioisomer **B**. Explain the formation of both products by drawing all intermediates.



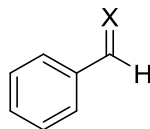
Organic Photochemistry – 2nd exercise 21.11.2017 9.00 a.m.

Group I: room 22210

Group II: room 42306

Exercise 1

Benzaldehyde and styrene have structural similarities. However, their energy gap between their singlet and triplet energies differ ($\Delta E_{(X=O)} = 21 \text{ kJ mol}^{-1}$, $\Delta E_{(X=CH_2)} = 157 \text{ kJ mol}^{-1}$).



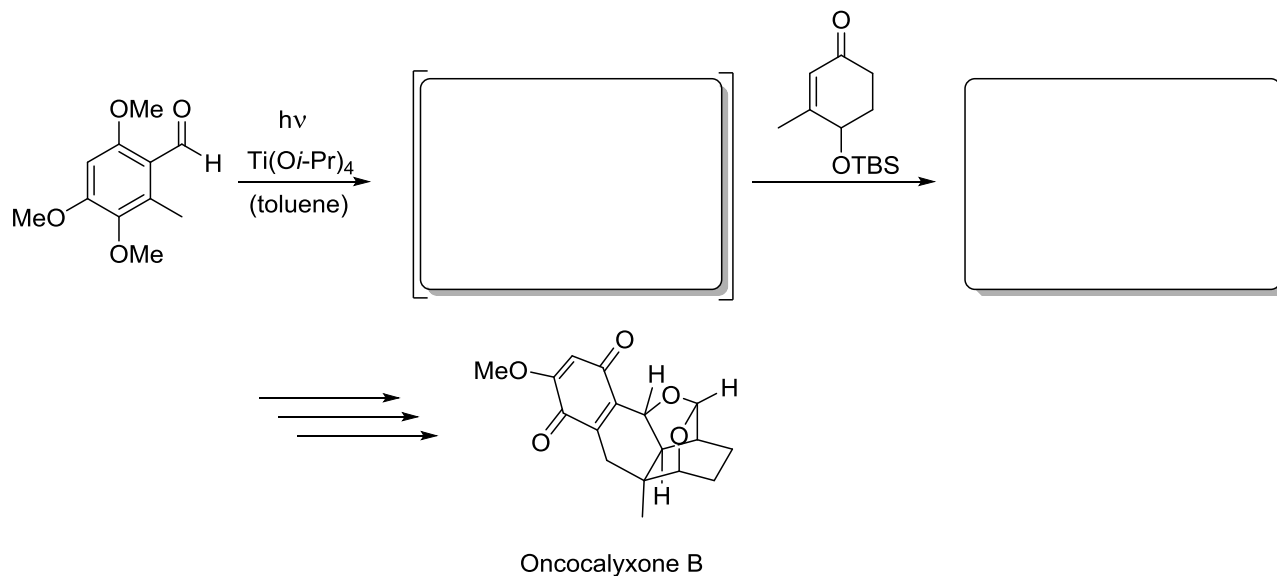
$$X = O \quad E(S_1) = 320 \text{ kJ mol}^{-1} \quad E(T_1) = 299 \text{ kJ mol}^{-1}$$

$$X = CH_2 \quad E(S_1) = 415 \text{ kJ mol}^{-1} \quad E(T_1) = 258 \text{ kJ mol}^{-1}$$

- Explain the occurrence of the energy gap between singlet and triplet states (singlet triplet splitting).
- Assign the configuration of the lowest singlet (S_1) and triplet state (T_1) in the case of benzaldehyde and in the case of styrene.
- Why is the singlet triplet splitting significantly larger in the case of styrene compared to benzaldehyde? Draw the n -, π - and π^* - orbitals of the important ($C=O$, $C=C$) bond to help you explain your answer.

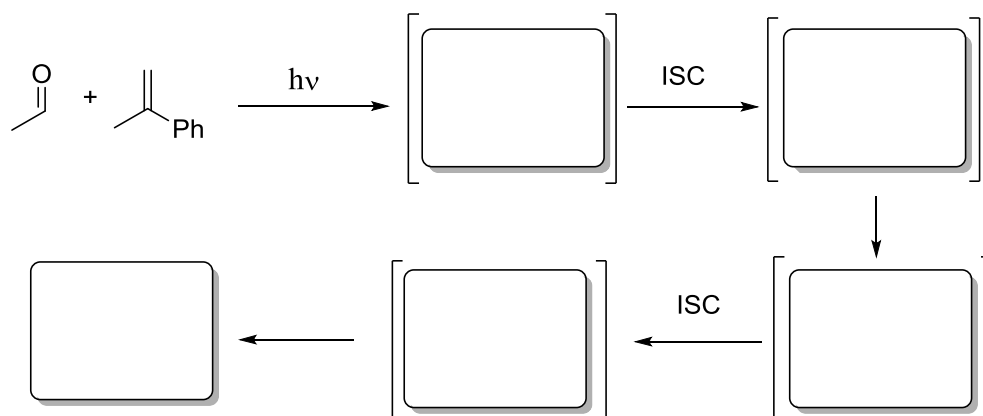
Exercise 2

The total synthesis of Oncocalyxone B features a photochemical step, where the intermediate is trapped by a cyclohexanone derivative. Draw the intermediate and the final product. Assign the relative configuration of all stereogenic centers formed.



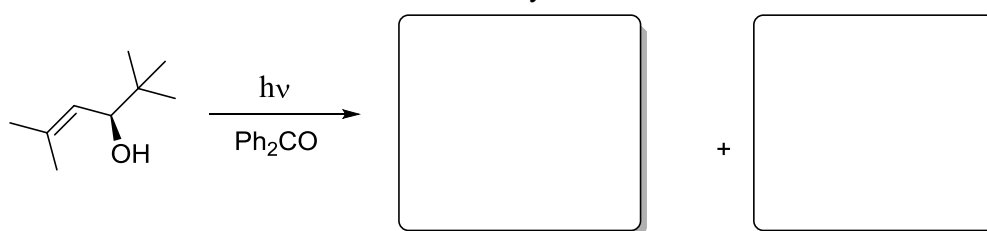
Exercise 3

The Paternò-Büchi reaction is a very common method for the generation of highly substituted oxetanes that can be further functionalized using a variety of different reactions. Provide all intermediates and the final product from the Paternò-Büchi reaction shown below. Why do you observe one diastereomer in the final product?



Exercise 4

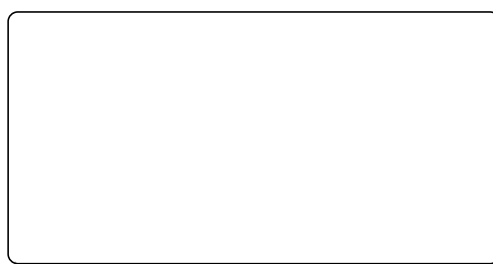
The following Paternò-Büchi reaction provides one major diastereomer and one minor diastereomer. Draw the two products and rationalize the selectivity by drawing the transition state in the case of the major diastereomer. Which effect controls the stereoselectivity?



Major

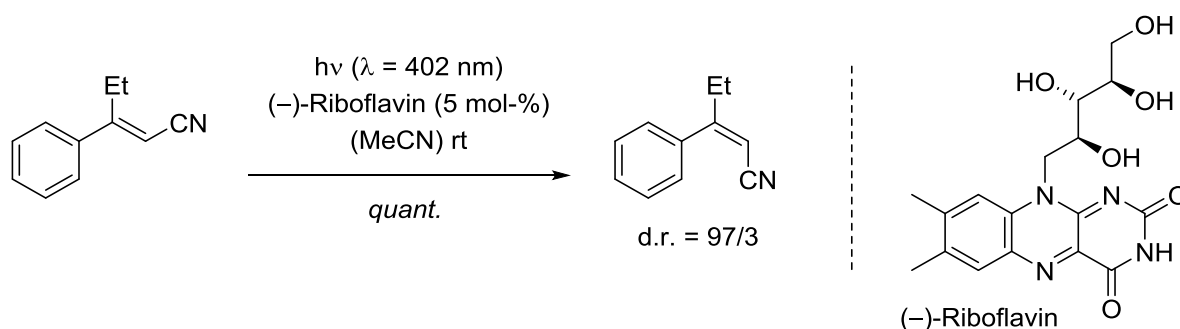
Minor

Intermediate to the major diastereomer:



Exercise 5

Please explain the following photocatalytic $E \rightarrow Z$ isomerisation of cinnamionitriles in the presence of (-)-Riboflavin.



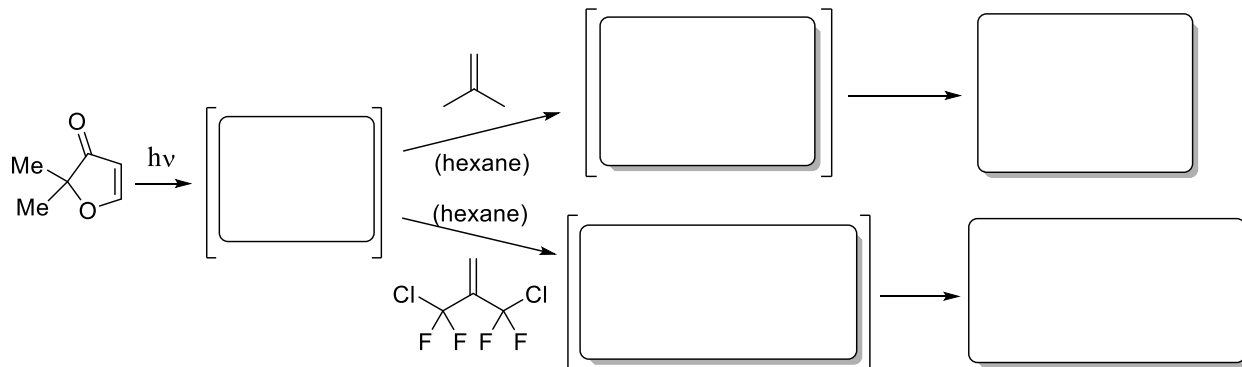
Organic Photochemistry – 3rd exercise 12.12.17 9.15 a.m.

Group I: room 27402

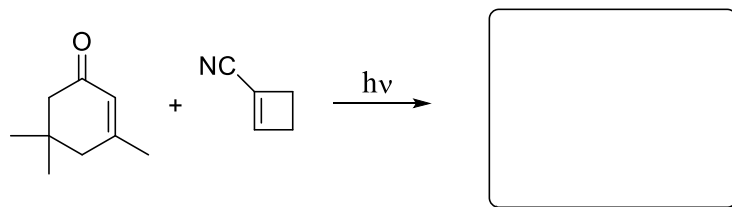
Group II: room 42306

Exercise 1

a) Explain the outcome of irradiation of the following enone in the presence of different olefins. Rationalize the regioselectivity by drawing the mechanism.



b) Draw the product of the [2+2] photocycloaddition reaction shown below and explain the regio- and diastereoselectivity.



Intermediate:



Exercise 2

Draw the two products for the photoreaction shown below and rationalize the diastereoselectivity of the major product by cyclic stereocontrol.



MOM = $-\text{CH}_2\text{OCH}_3$

Major

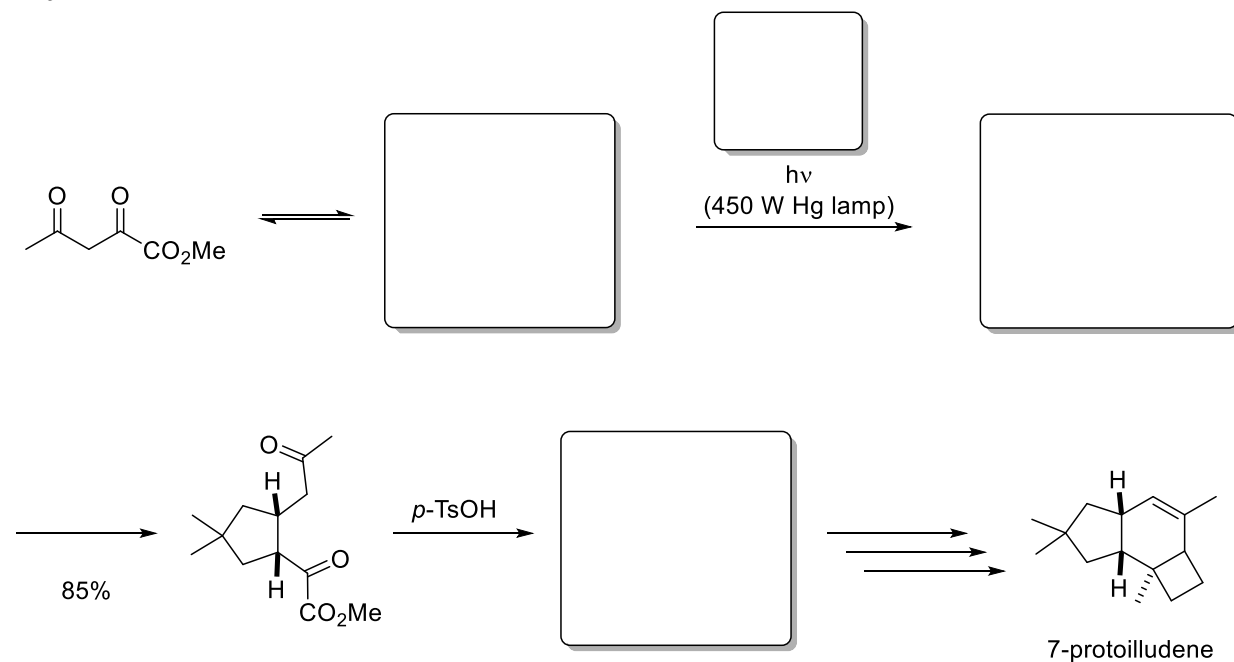
Minor

Diastereoface differentiation:



Exercise 3

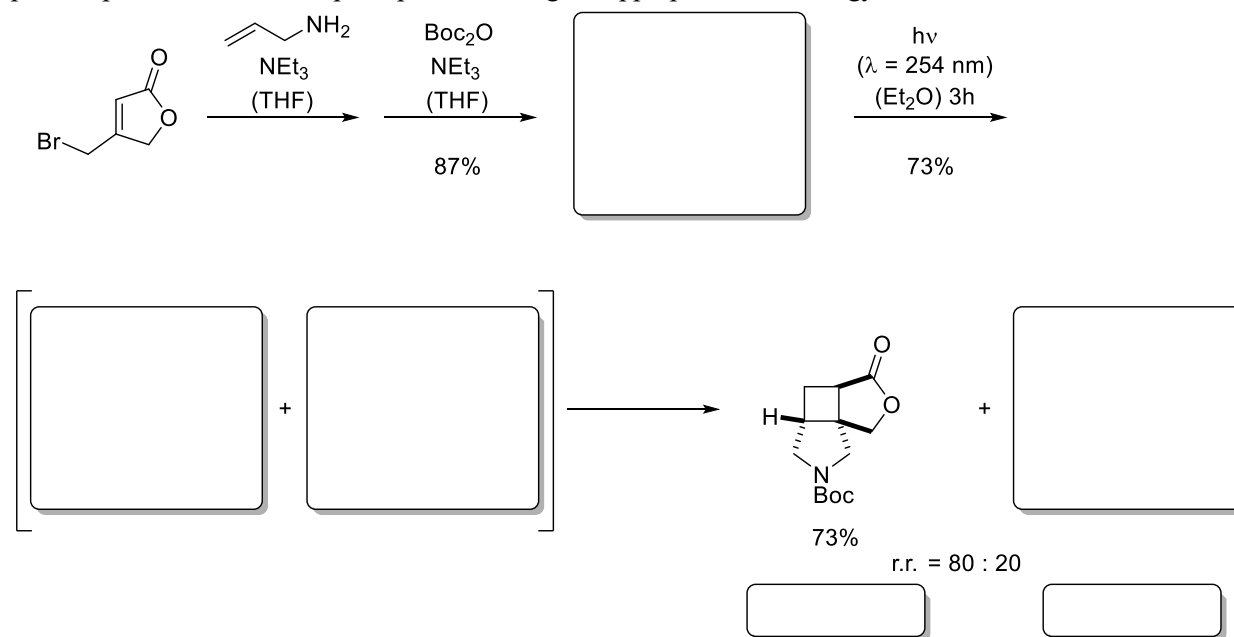
The total synthesis of 7-protoilludene starts with a photoreaction of the diketoester shown below. Which form of the diketoester is capable of undergoing the shown photoreaction? Fill in the missing olefin. Draw the product of the photoreaction and state the name of the reaction sequence. What happens when the resulting compound is subjected to acidic conditions?



Reaction sequence:

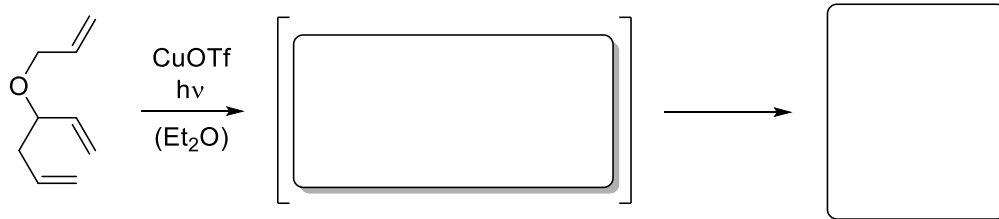
Exercise 4

3-Azabicyclo[3.2.0]heptane scaffolds can be built up by using intramolecular [2+2] photocycloaddition reactions. Draw the irradiation precursor and the minor product that is formed in the photoreaction. In addition, draw possible intermediates that lead to the respective photocycloaddition products. Why is the formation of the given product preferred? Label the photoproducts using the appropriate terminology.

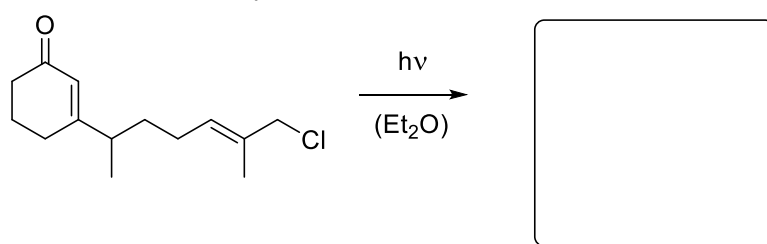


Exercise 1

Draw the product of the following photocycloaddition and explain the regio- and stereoselectivity.

**Exercise 2**

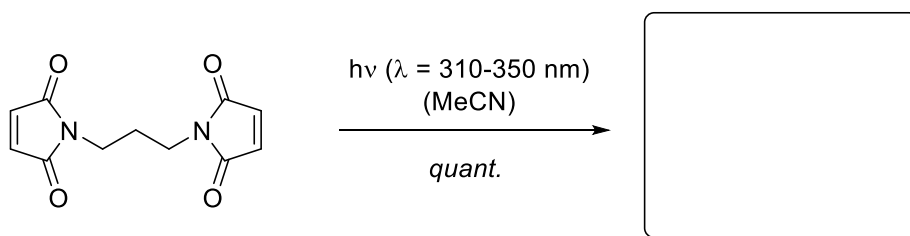
Draw the product of the below [2+2] photocycloaddition and rationalize the stereochemical outcome. Which effect controls the stereoselectivity?



Stereoface differentiation:

**Exercise 3**

Imides can react photochemically in a similar fashion as enones. In this case, irradiation of the shown dimaleimide gives a single product quantitatively. Draw the product with the relative configuration. Which type of photochemical reaction occurs.

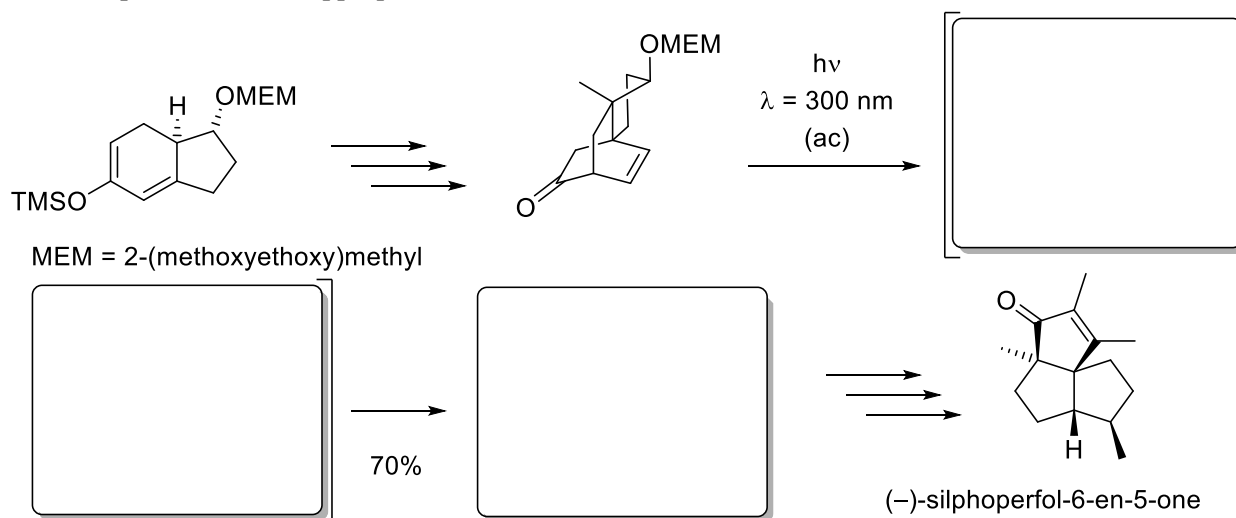


Type of reaction:



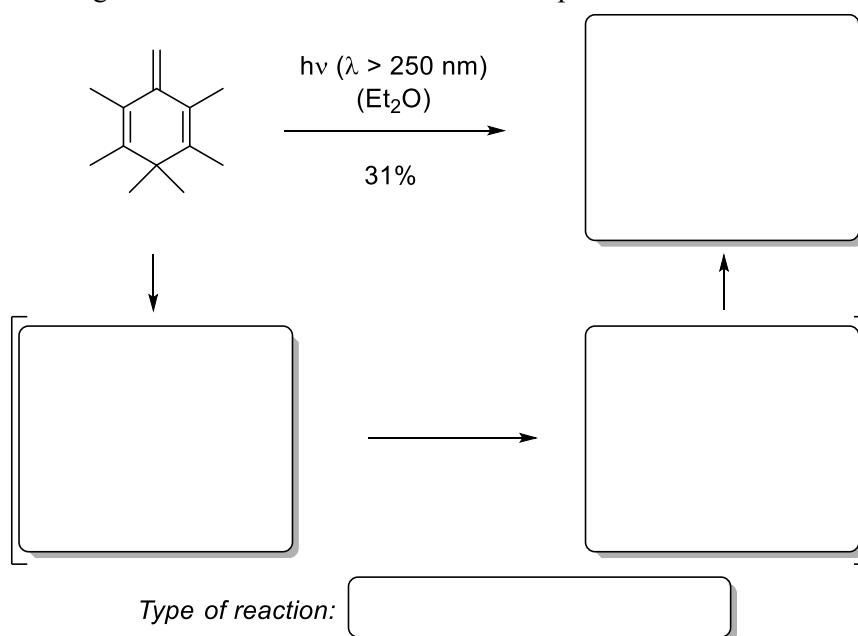
Exercise 4

(-)-Silphiperfol-6-en-5-one was synthetically accessible by using an oxadi- π -methane rearrangement. Draw the product and the appropriate intermediates.



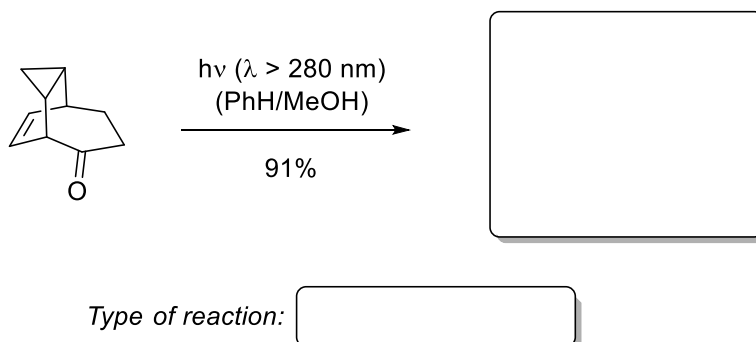
Exercise 5

Methylene-2,5-cyclohexadiene reacts when irradiated at short wavelength. Draw the product and explain its formation by drawing the intermediates. What reaction is depicted?



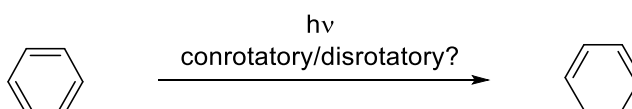
Exercise 6

β,γ -unsaturated carbonyl compounds isomerize when irradiated under suitable conditions. Which reaction takes place? Draw the product including the relative configuration.



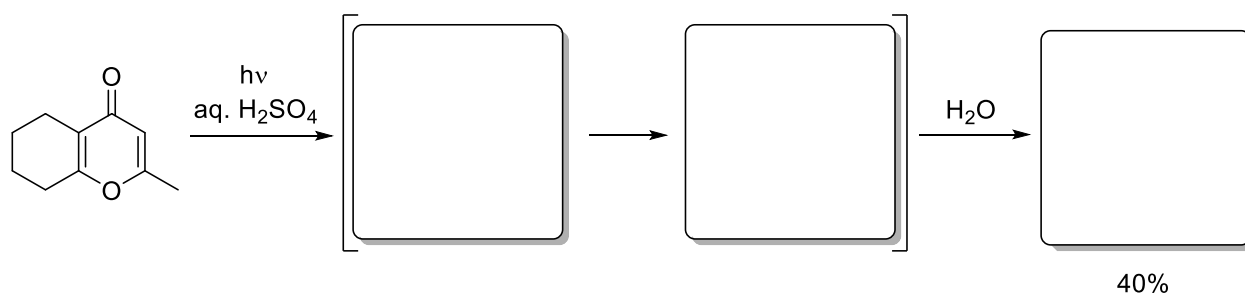
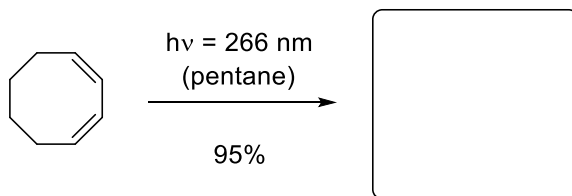
Exercise 1

Consider hexatriene as a model system for cyclisations. Does the photochemical $[6\pi]$ cyclisation occur conrotatory or disrotatory? Analyse the symmetry of the reaction using the Woodward-Hoffmann rules. Therefore draw the molecular orbitals of hexatriene and analyse their orbital symmetry for both cases, conrotatory and disrotatory. Which symmetry operation is important in the conrotatory, respectively disrotatory case?



Exercise 2

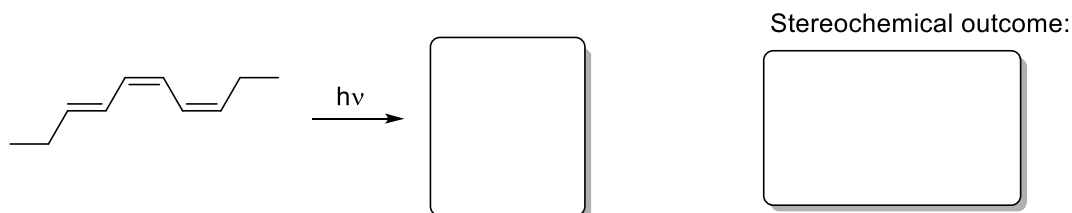
Draw the expected product formed for each reaction.



Exercise 3

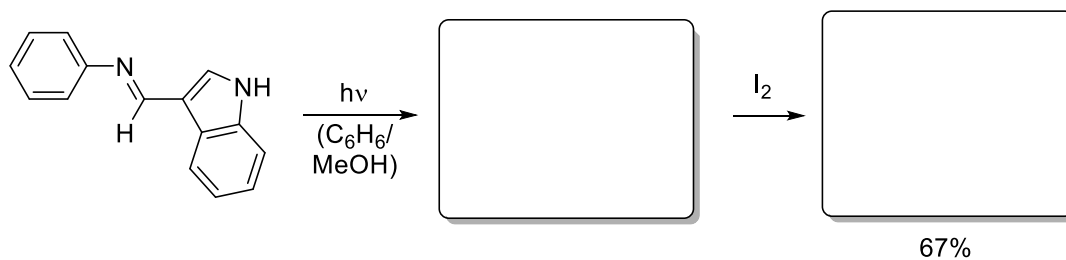
The triene shown below undergoes a $[6\pi]$ cyclisation. Draw the product and rationalize the stereochemical outcome.

Hint: Photoisomerisation is necessary



Exercise 4

Cryptosanguinolentine was synthesized from the indole shown below. Draw both the intermediate and the final product. Describe the reactive chromophore. Which types of photoreactions occur.



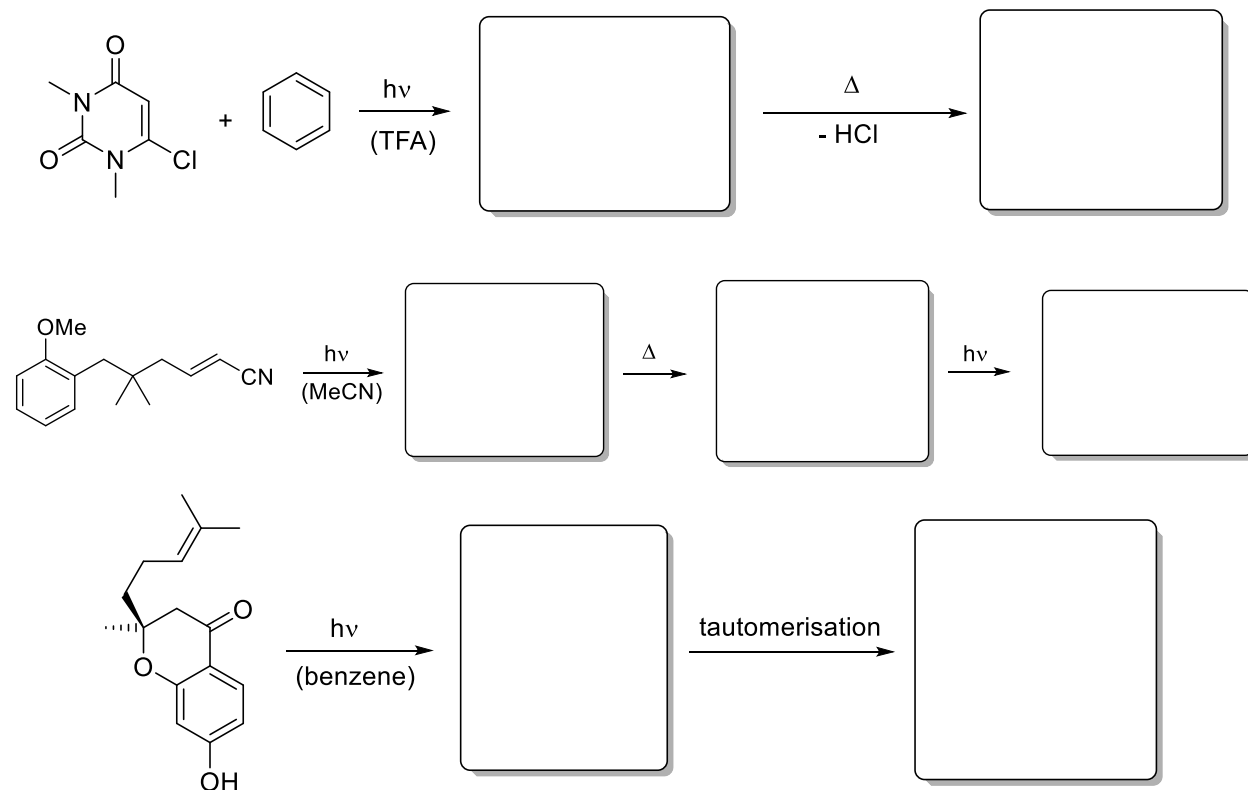
Reactive chromophore:

Type of photoreactions:

Exercise 5

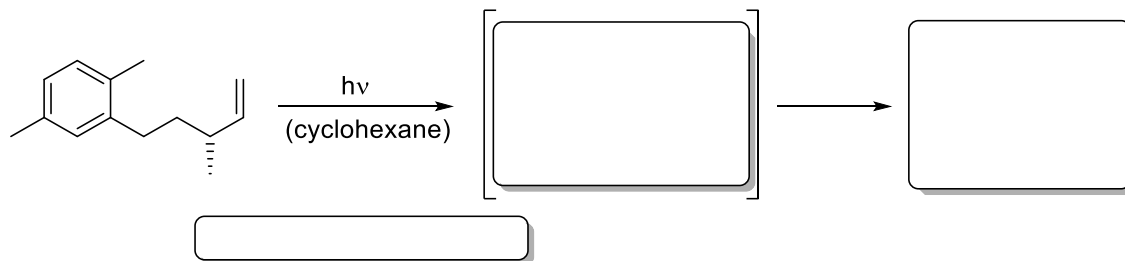
In the ortho-photocycloaddition shown below, draw all intermediates and the final product. Rationalize, if necessary the stereochemical outcome of the product.

Hint: " Δ " indicates a thermally allowed pericyclic reaction.

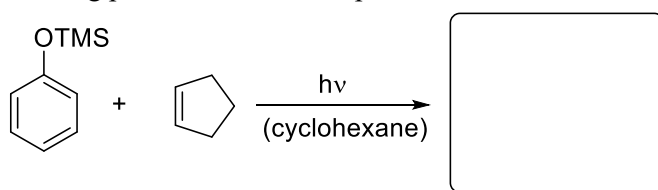


Exercise 1

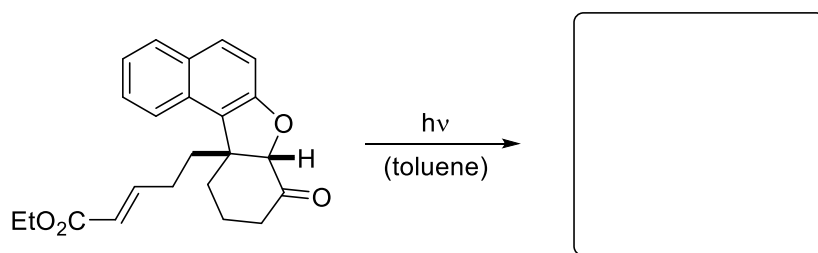
a) The following photoreaction was used towards the total synthesis of retigeranic acid. Draw the product and name the type of reaction.



b) Draw the product of the following photoreaction and explain the endo or exo selectivity.



c) Determine whether the following reaction would proceed via an *ortho*- or *meta*-photocycloaddition and draw the product.



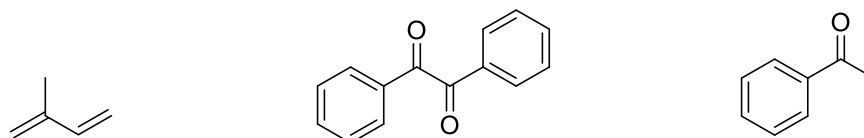
Short Repetition:

Exercise 2

In general, one observes fluorescence emission at higher wavelengths compared to that of absorption. Using the Jablonski Diagram, explain why this is observed.

Exercise 3

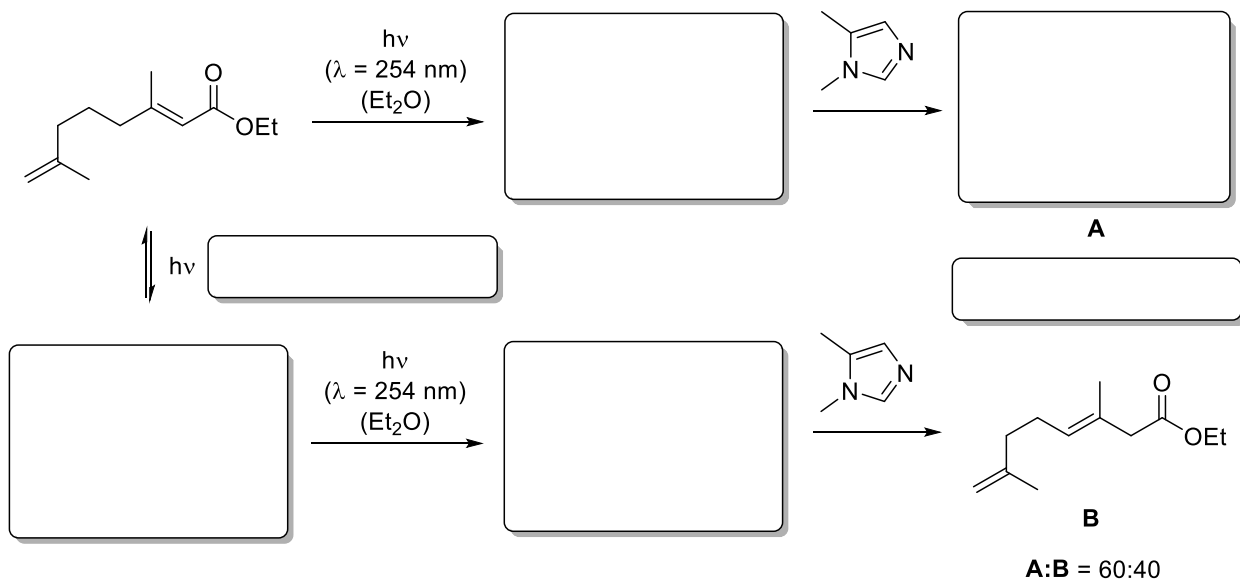
For the three molecules shown, indicate at which wavelength you would irradiate the molecule (220 nm, 310 nm, and/or 400 nm).



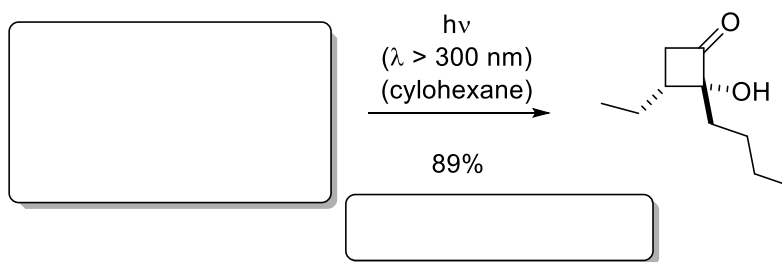
Exercise 4:

Draw the missing products and reactants and state the respective reaction names or specify the formed photoproducts.

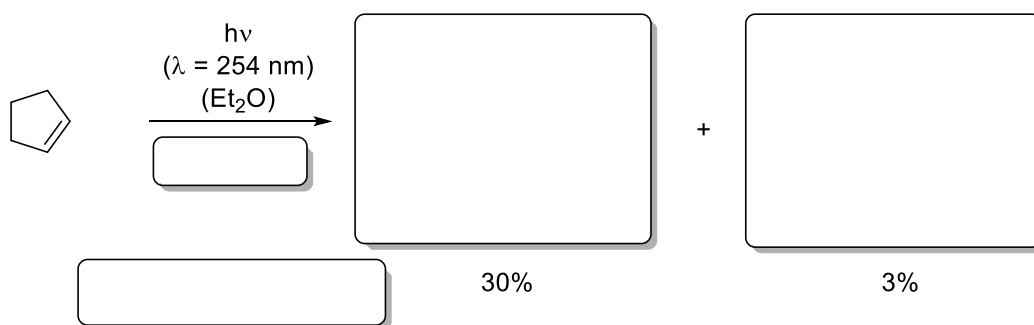
a) *Hint: 1,2-Dimethylimidazole acts equally as N,N-dimethylethanol*



b)



c)



d)

