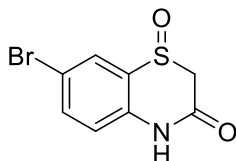


Organic Photochemistry – Exercise 1: 27/10/2022, 11.00 am

German group: CH22210

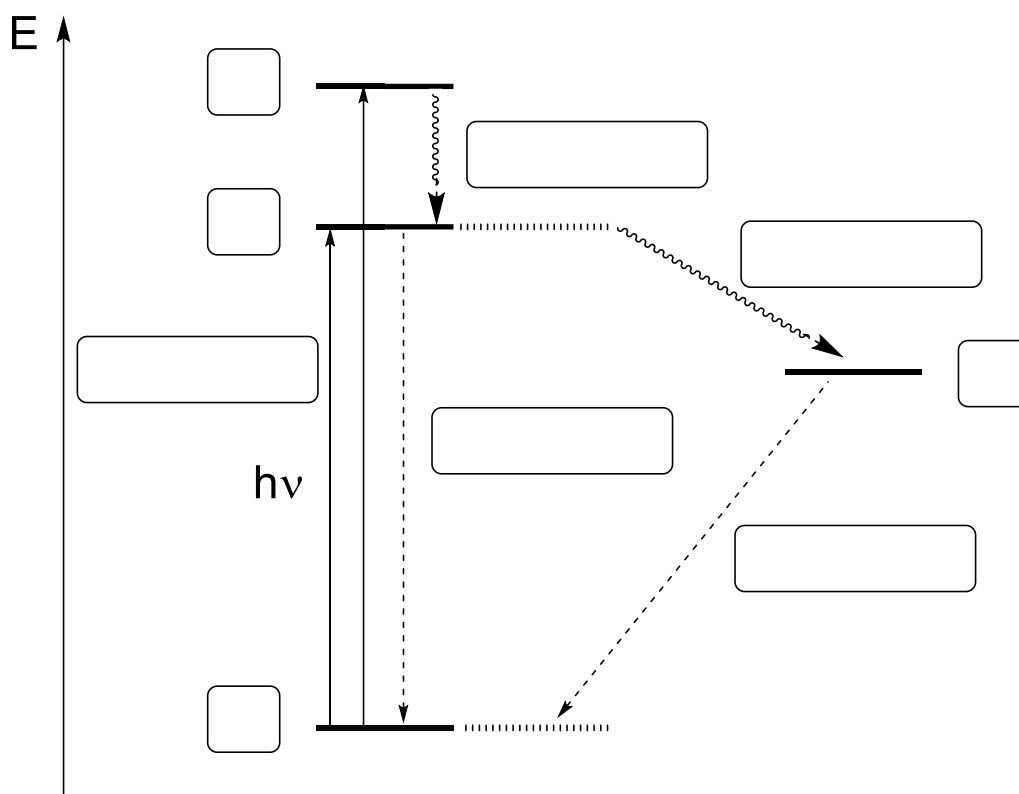
English group: CH42306

1. The benzothiazine derivative below shows phosphorescence at $\lambda = 413$ nm.



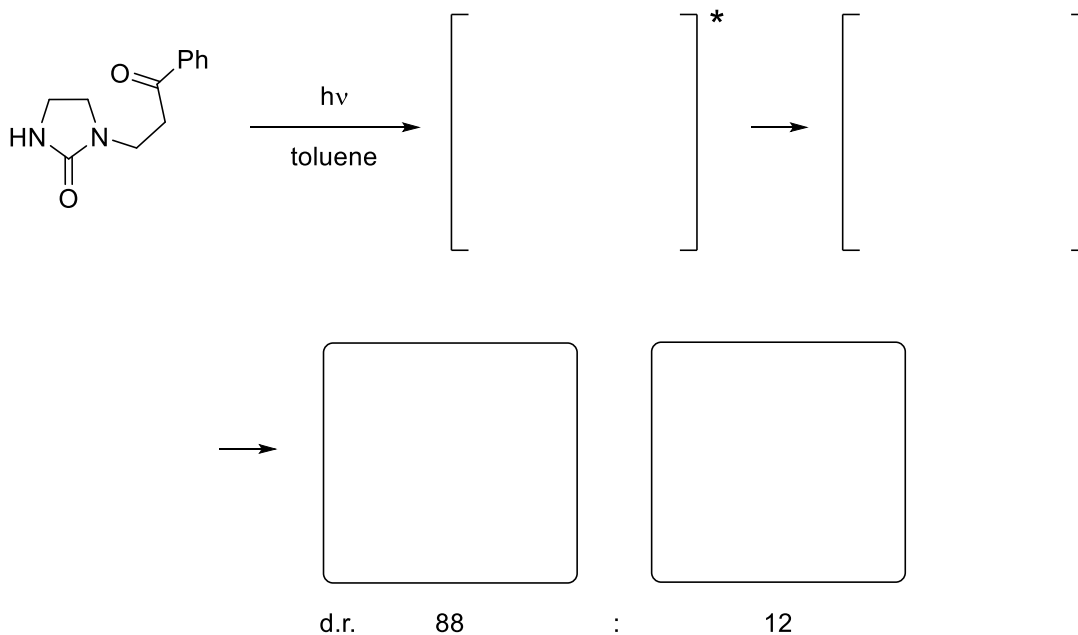
a) Calculate the triplet energy (in kJ/mol).

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

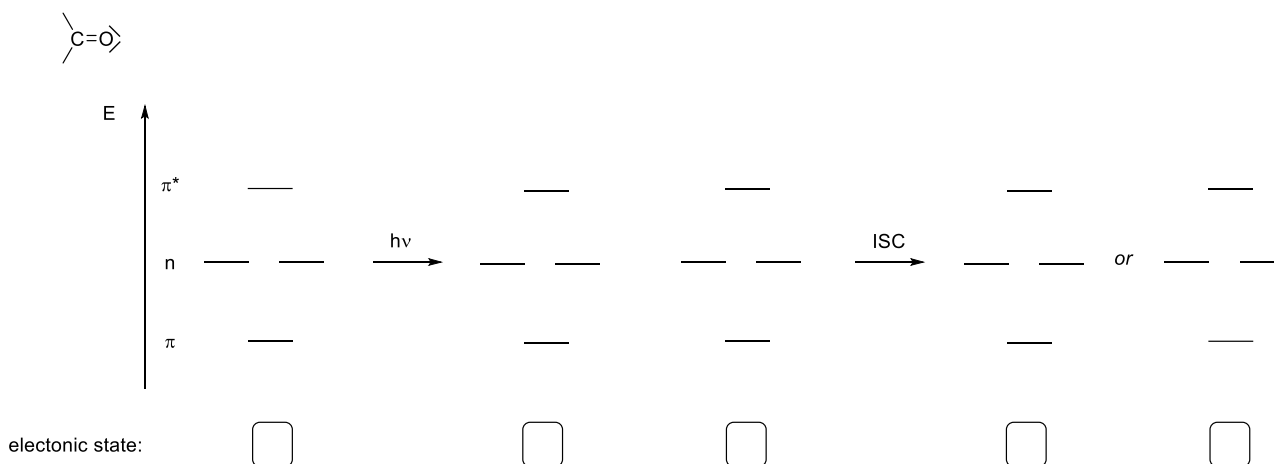


c) Draw an energy diagram to explain the Kasha's rule.

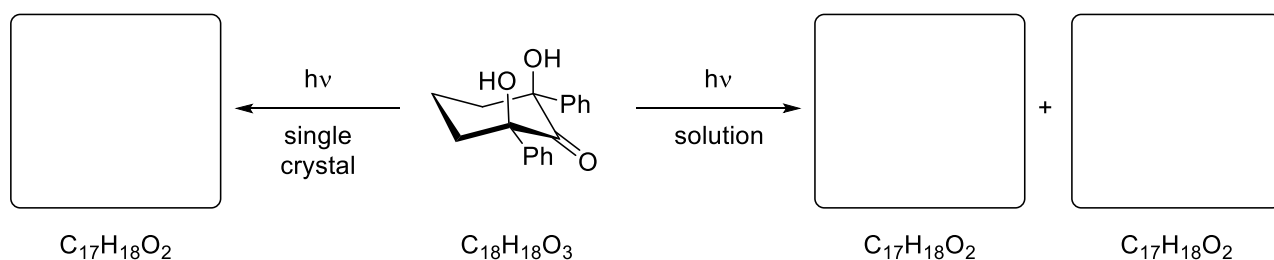
2. a) Provide the mechanism and the two diastereoisomers formed in this reaction. Explain the diastereoselectivity.



b) Draw the MO diagram for the ketone (not the urea) ($\text{C}=\text{O}$, π - n - π^*) in the ground state, after excitation with light and intersystem crossing processes (ISC).



3. The irradiation of this ketone derivative was performed both in solution and in a single-crystal form. In the latter case, only one isomer was obtained, while two different stereoisomers were obtained when irradiation was performed in solution. Complete the scheme with the appropriate compounds, and explain the difference in reactivity.

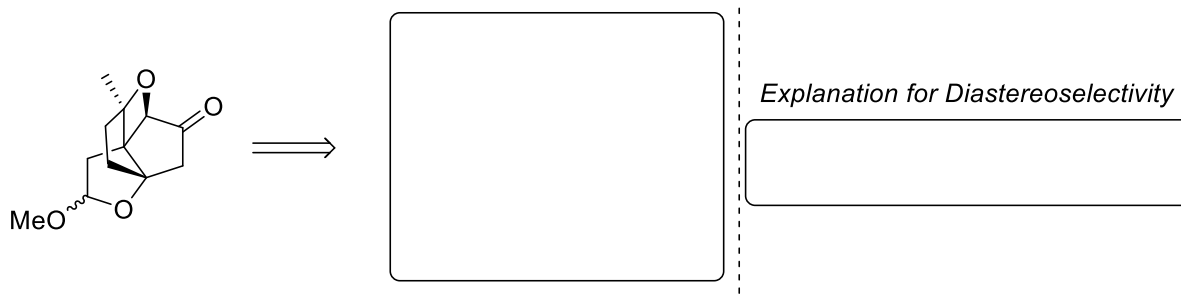


Organic Photochemistry – Exercise 2: 17/11/2022, 11.00 am

German group: CH22210

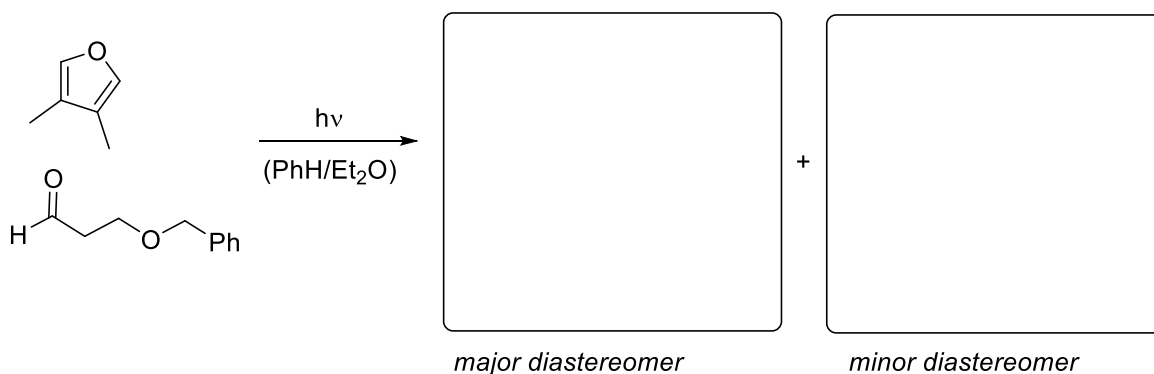
English group: CH42306

1. The tetracyclic core of the merrilactone A was synthesized by *Greaney* and coworkers utilizing an elegant intramolecular Paternò-Büchi reaction. Please provide the structure of the irradiation precursor and an explanation for the observed diastereoselectivity.

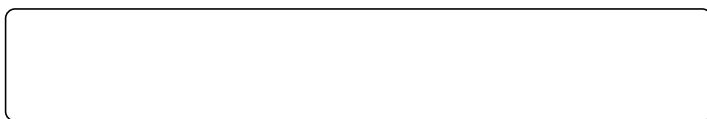


2. The synthetic utility of the Paternò-Büchi reaction originates not only from the possibility to access densely functionalized furans, but also from the option to further transform these products. Please fill in the missing structures and provide an explanation for the observed selectivity.

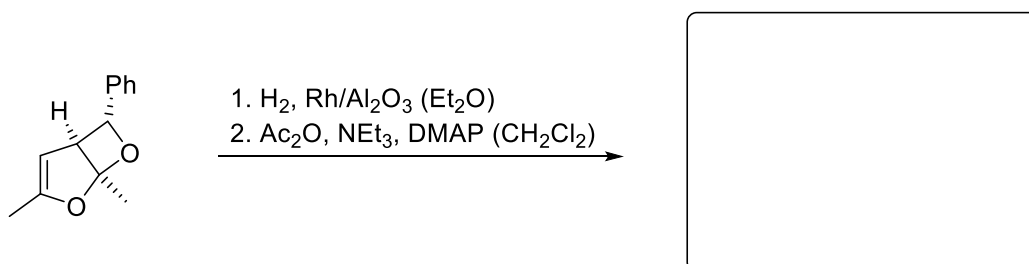
a)



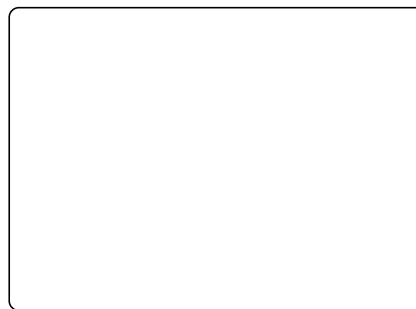
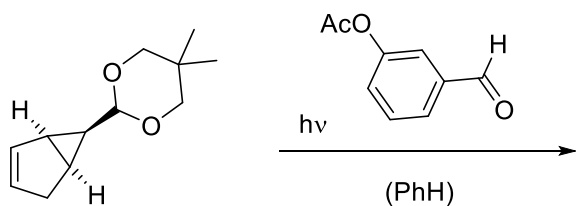
Explanation for regioselectivity and diastereoselectivity:



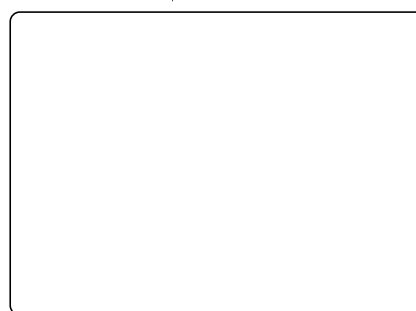
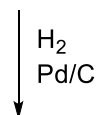
b)



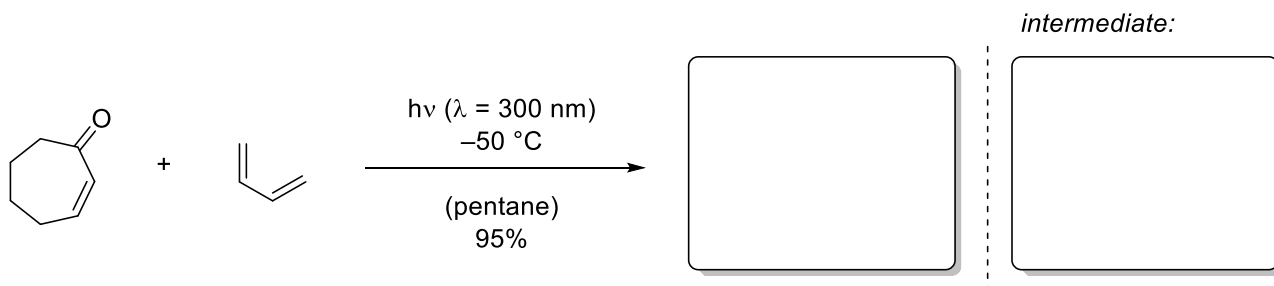
c)



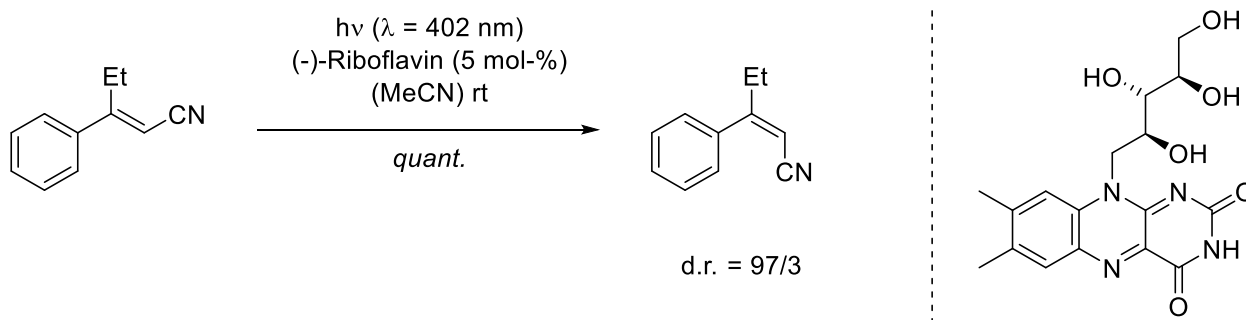
Explanation for diastereoselectivity:



3. In 2022 the Bach group published a paper on Diels-Alder reactions of cyclohept-2-enones. The depicted cyclic enone does not undergo a reaction without irradiation. Upon irradiation, a reactive intermediate leads to a Diels-Alder reaction. Please explain this observation and fill in the blanks.



4. a) The following photocatalytic *E* → *Z* isomerization of cinnamitriles in the presence of (–)-riboflavin was observed. Explain this phenomenon by drawing a rough scheme of the possible energy distribution of the electronic states involved in the reaction.



b) What is the role of (–)-riboflavin? Explain the mechanism behind it (name of mechanism?).

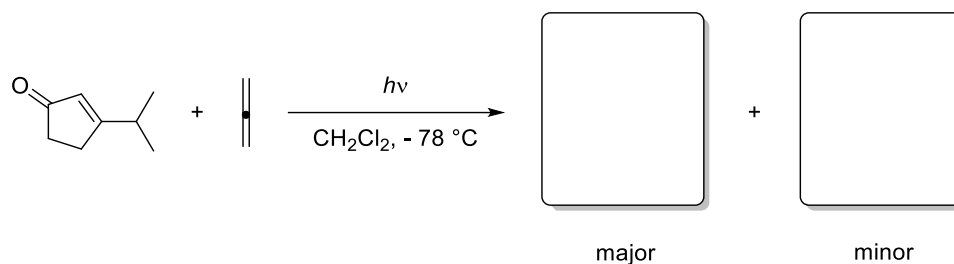
Organic Photochemistry – Exercise 3: 06/12/2022, 9.00 am

German group: CH27402

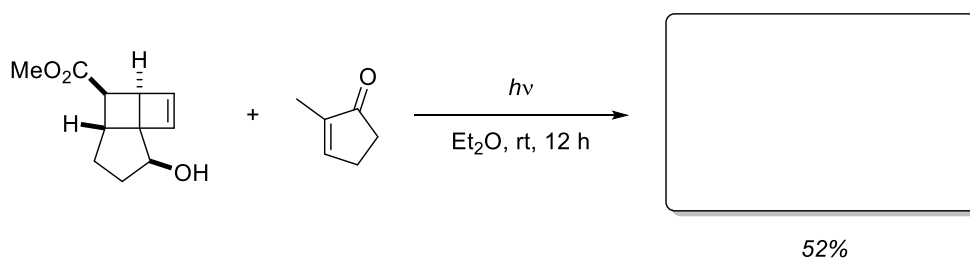
English group: CH42306

1. Give the products of the following [2+2] photocycloadditions.

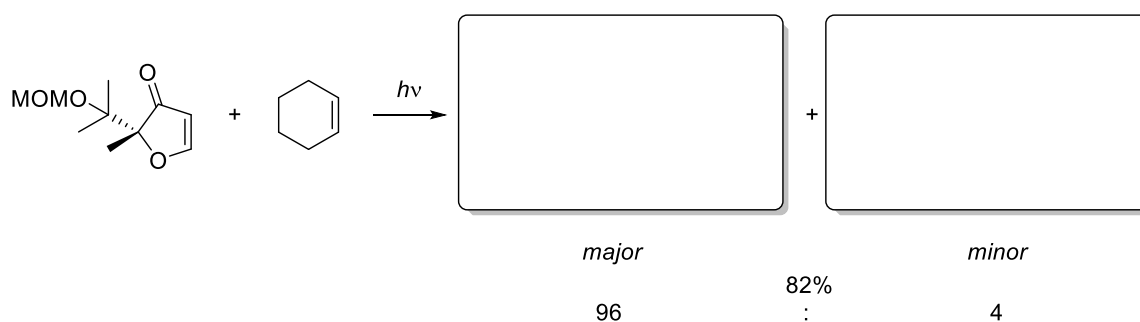
a) *Hint: Allenes react similar to acceptor-substituted olefins.*



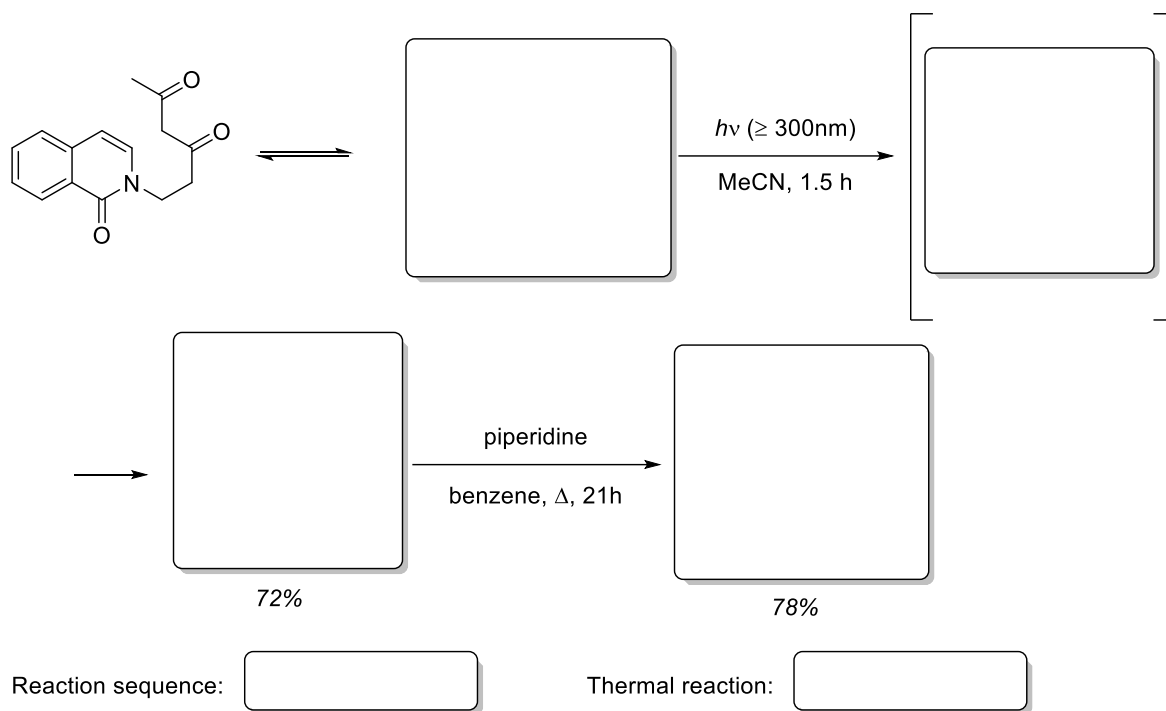
b)



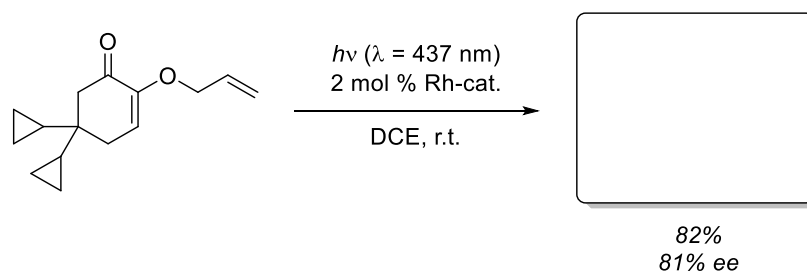
c)



2. The following reaction sequence is a great way to build up Galanthan-type tetracyclic skeletons. Which form of the diketone is capable of undergoing [2+2] photocycloadditions? Draw the correct form of the diketone and the reaction intermediate. The photoproduct then undergoes a subsequent thermal reaction to the final compound. Name the reaction sequence and the following thermal reaction.

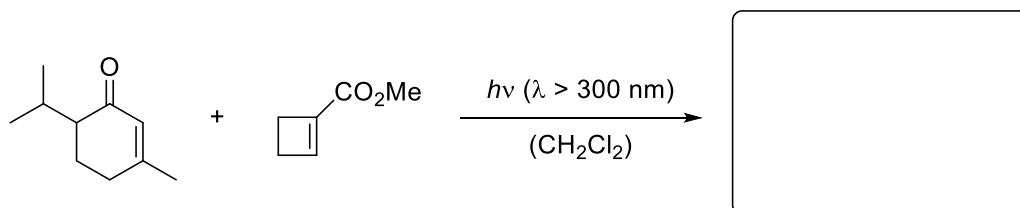


3. The following cyclic enone was shown to undergo enantioselective sensitized [2+2] photocycloaddition in the presence of a chiral rhodium-based triplet sensitizer. Draw the product of the reaction (either enantiomer will be accepted).

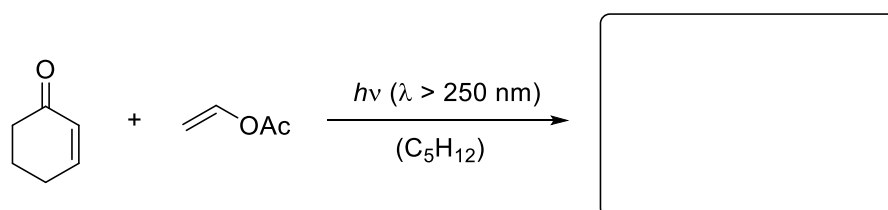


4. Give the products of the following [2+2] photocycloaddition reactions and explain the regioselectivity.

a)



b)

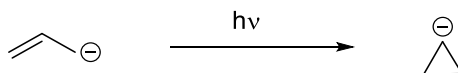


Organic Photochemistry – Exercise 4: 15/12/2022, 11.00 am

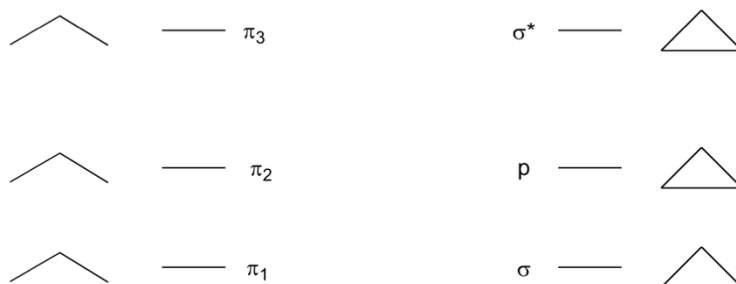
German group: CH22210

English group: CH42306

1. Upon irradiation, the allyl anion may cyclize to the cyclopropyl anion as depicted in the scheme below.

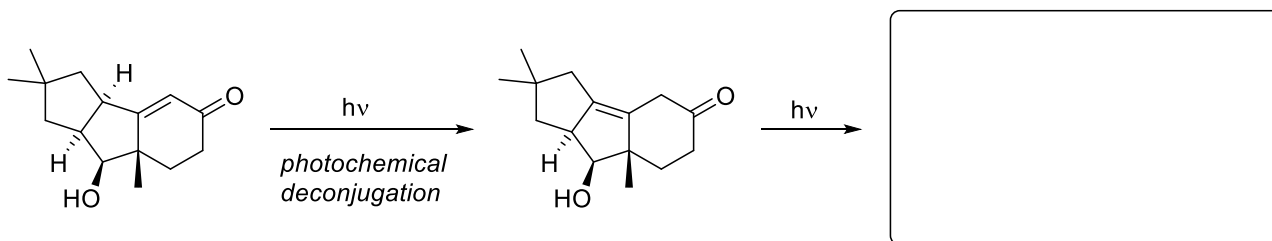


To analyze the reaction, draw the molecular orbitals of the starting material and the corresponding orbitals in the product. Determine if they are symmetric (S) or antisymmetric (A) regarding the symmetry operation of a conrotatory ring closure (C_2 axis). How many electrons occupy the symmetric and antisymmetric molecular orbitals in the starting material and in the product in the first excited singlet state? Is the conrotatory ring closure photochemically allowed? Justify your decision.



2. Rearrangement reactions of β,γ -unsaturated molecules can lead to a broad range of complex structures: Please provide the missing molecules.

a)

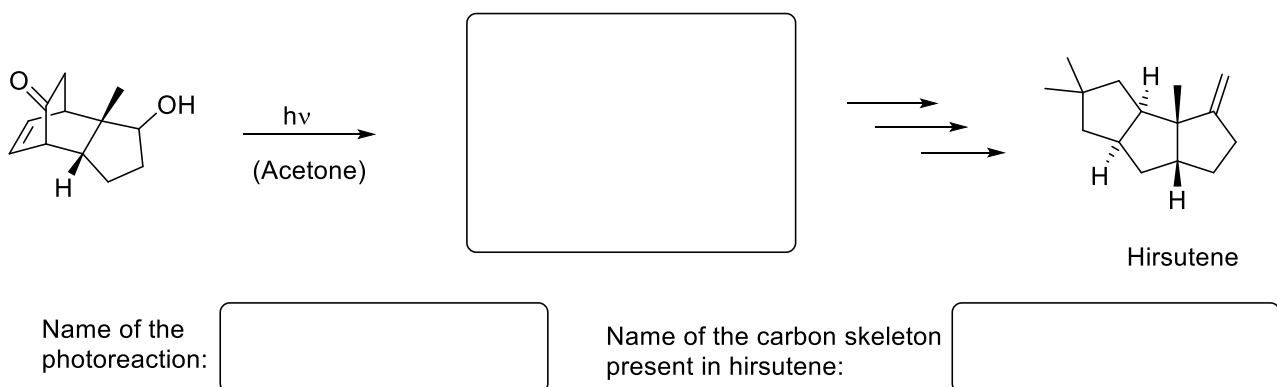


Name of the photoreaction:

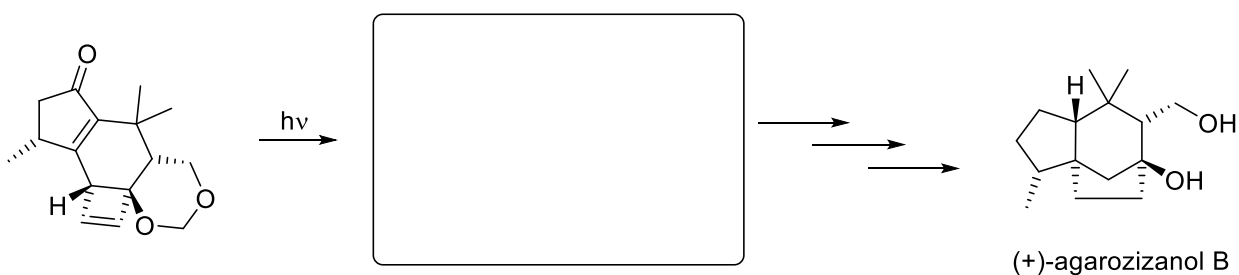
b)



c)



3. The total synthesis of (+)-agarozizanol B was accomplished by a complex photochemical cascade reaction. One of the steps of the photochemical cascade involves a di- π -methane rearrangement, which leads to a key compound that later could be converted to the desired natural product. Please provide the structure of the missing compound.



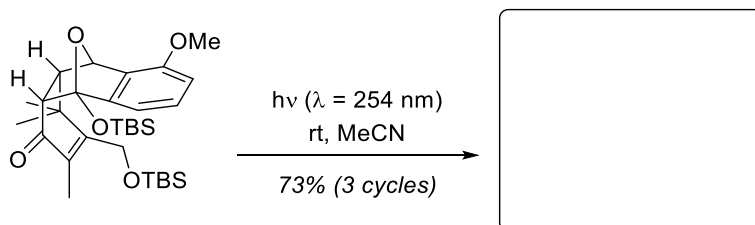
Organic Photochemistry – Exercise 5: 12/01/2023, 11.00 am

German group: CH22210

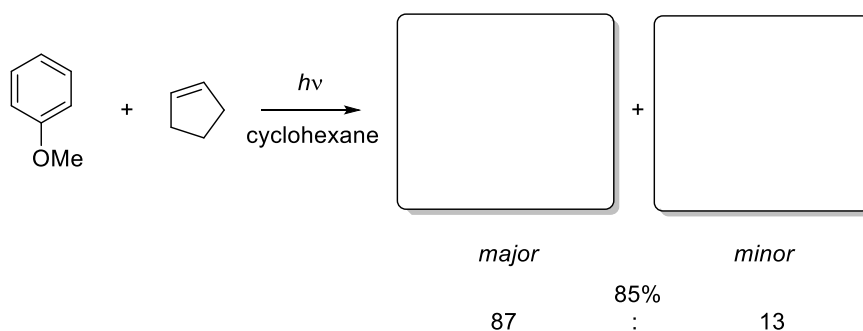
English group: CH42306

1. Give the products of the following arene photocycloadditions.

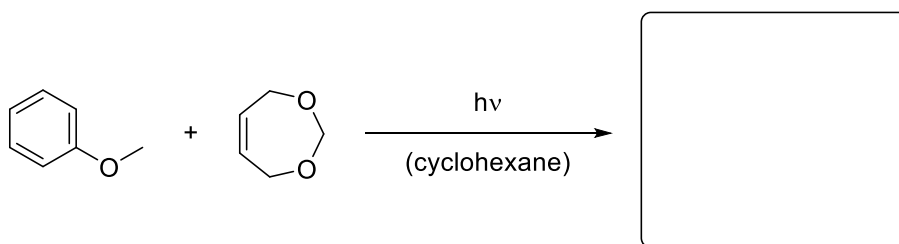
a)



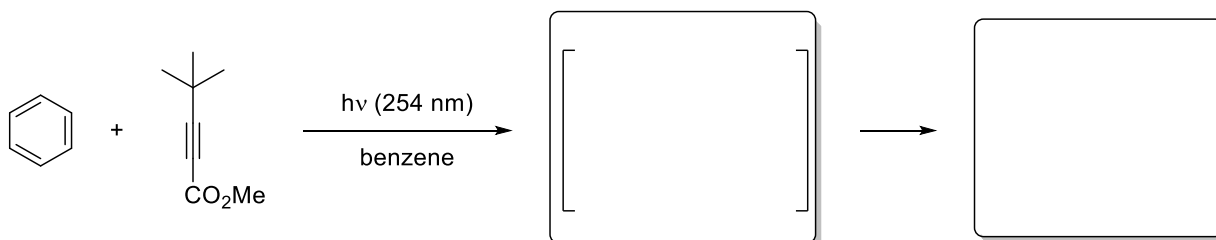
b)



c)



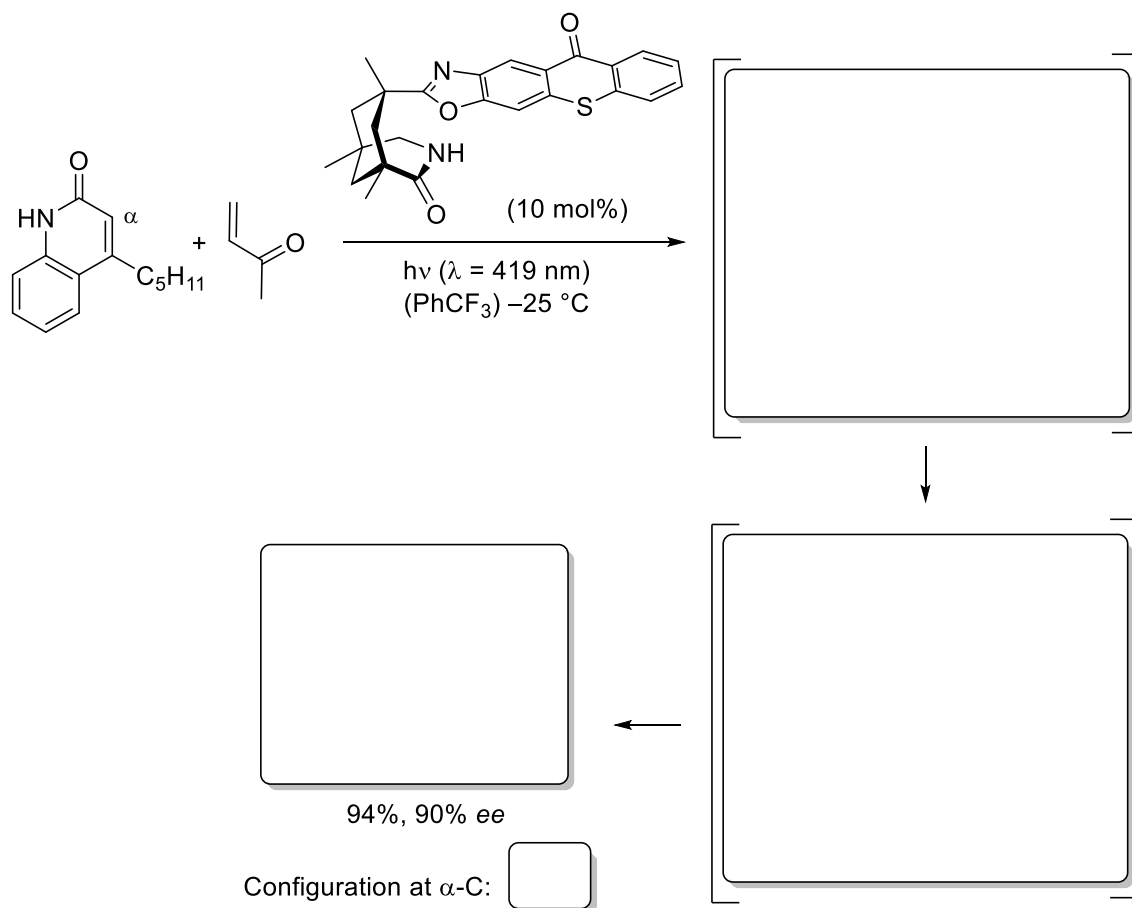
2. Give the intermediate and the product of the following arene photocycloaddition.



3.

a) Enantioselective photocycloadditions are a major research topic in recent studies. One opportunity for enantioselective photocycloaddition is a reaction with a chiral organocatalyst.

Draw the hydrogen bond complex of the substrate and the catalyst, the resulting 1,4-diradical and the preferred enantiomer of the product. Determine the configuration of the newly formed stereogenic centre at the α -carbon atom according to the *Cahn-Ingold-Prelog* sequence rules (CIP priority rules).



b) The used chiral catalyst has a sensitizer as shield. What is the sensitizer? Please draw the structure of the sensitizer and explain briefly the principle of a sensitized photoreaction.

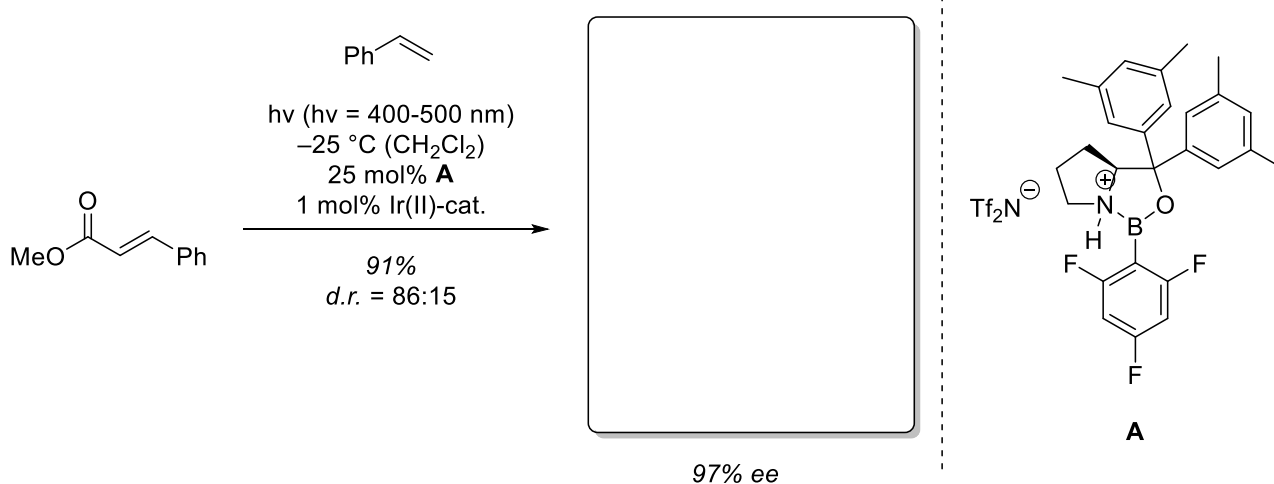
Organic Photochemistry – Exercise 6: 26/01/2023, 11.00 am

German group: CH22210

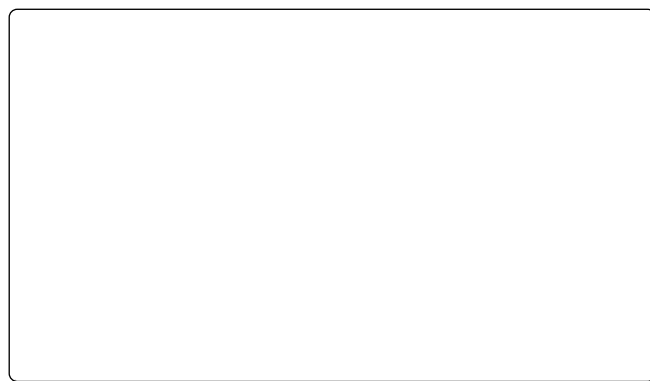
English group: CH42306

1. Yoon, Baik and co-workers studied the activation of cinnamic acid esters by chiral Lewis acids. Lewis acid **A** was able to enantioselectively catalyze the triplet sensitized reaction depicted below. An iridium complex served as an achiral sensitizer in this dual catalytic reaction.

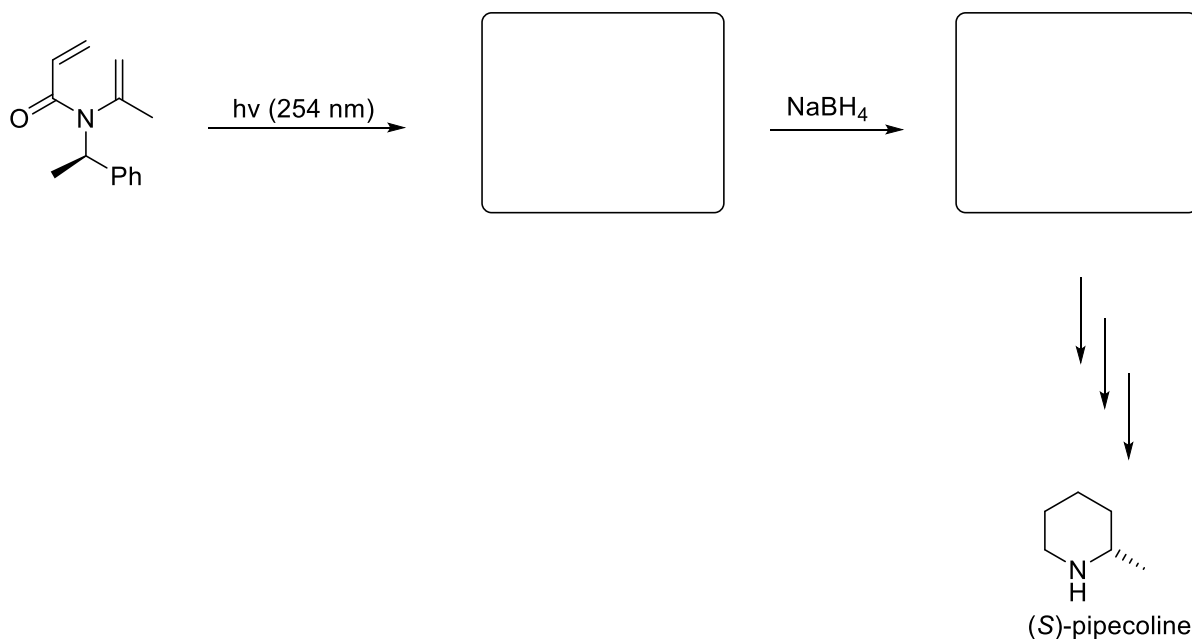
a) Draw the product in its correct relative and absolute configuration.



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

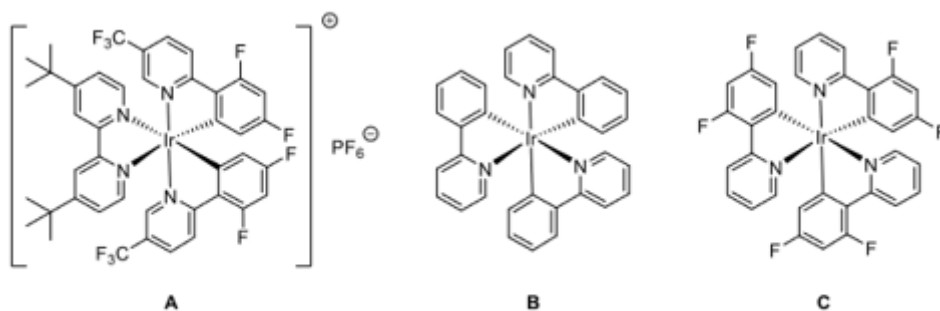


c) Not only catalytic methods can lead to enantioenriched products: In the following example an auxiliary assisted diastereoselective reaction was used for the total synthesis of (*S*)-pipercoline. Please provide the missing structures. *Hint: The diastereoselectivity of the reduction should lead to (*S*)-pipercoline.*



2. The *MacMillan* group described useful applications for ruthenium complexes in the field of visible light photoredox catalysis. A commonly used catalyst is the polypyridyl complex of ruthenium $\text{Ru}(\text{bpy})_3^{2+}$.

- Explain what photo- and electrochemical properties of $\text{Ru}(\text{bpy})_3^{2+}$ make the complex a good photoredox catalyst.
- Draw a MO-scheme of $\text{Ru}(\text{bpy})_3^{2+}$, before and after excitation, illustrating its oxidant and reductant properties.
- What effect has a more electron rich ligand as tmb?
- Please order the iridium photoredox catalysts depicted below according to their redox potential $E_{1/2}(\text{M}/\text{M}^-)$. Give a short explanation for the observed trend.

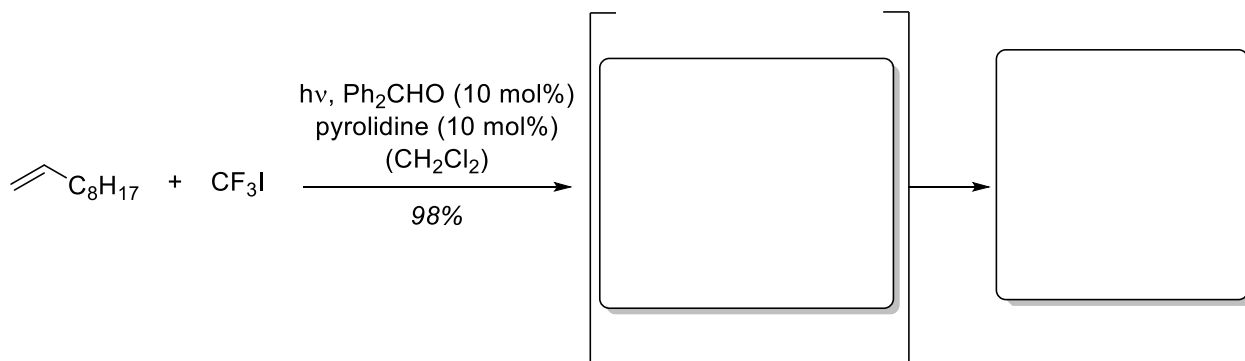


Organic Photochemistry – Exercise 7: 09/02/2023, 11.00 am

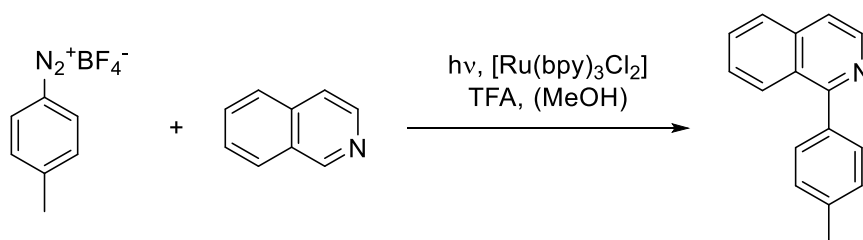
German group: CH22210

English group: CH42306

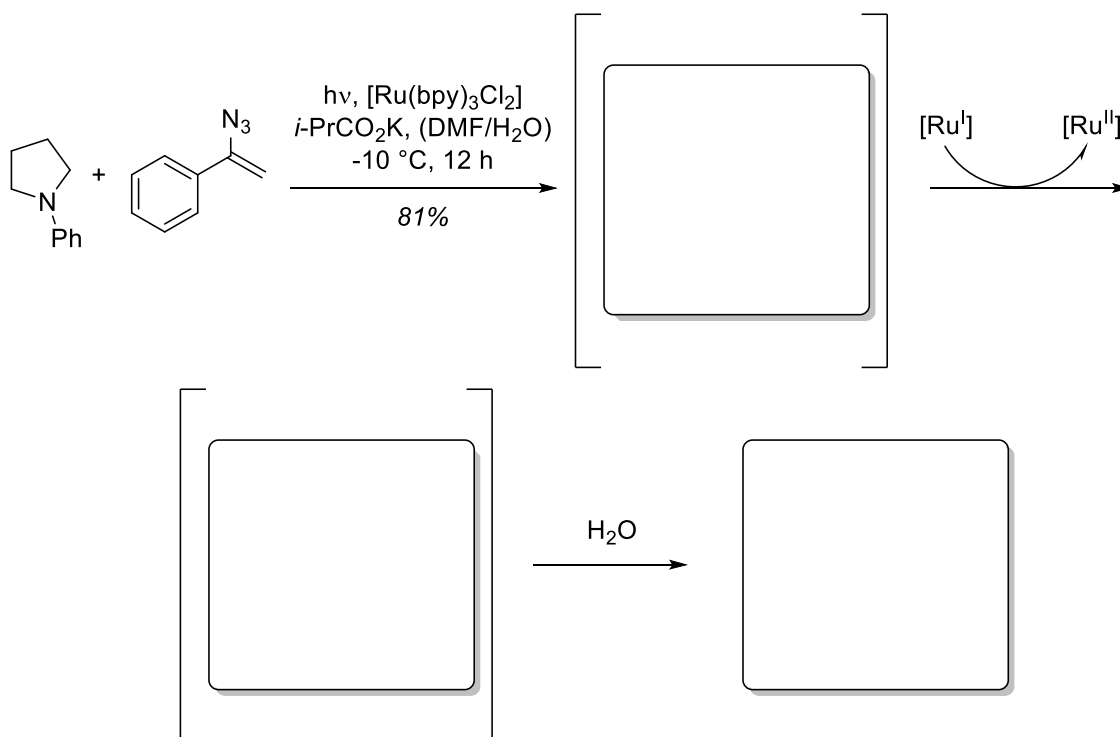
1. The following ATRA reaction was accomplished by irradiation of the alkene and trifluoroiodide in the presence of an amine and an aldehyde. Draw the EDA-complex formed by the enamine and the alkylating reagent, and draw the structure of the final compound.



2. Draw the mechanism of the following reaction.



3. Fill out the following boxes with the appropriate reaction intermediates and final product. Is this reaction a redox neutral, net oxidative or net reductive process?



4. Combined organocatalysis and photoredox chemistry is a great way to build up new molecules with high enantioselectivity. Draw the product of the reaction below considering its absolute configuration. Explain the enantioselectivity using intermediates formed during the reaction.

