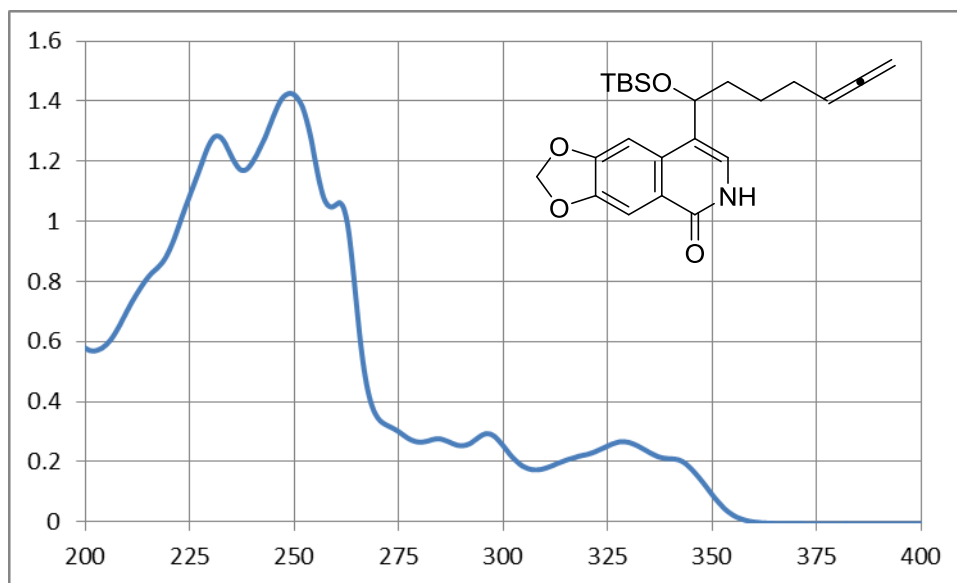


### Exercise 1

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.

- In the spectrum below, assign the absorption bands at 250 nm and 330 nm to  $n\pi^*$  and  $\pi\pi^*$  transitions. Justify your decision.
- Calculate the molar extinction coefficient at 330 nm, if the spectrum was obtained in a cell with a path length of 1 mm and a concentration of  $0.55 \text{ mmol L}^{-1}$ .

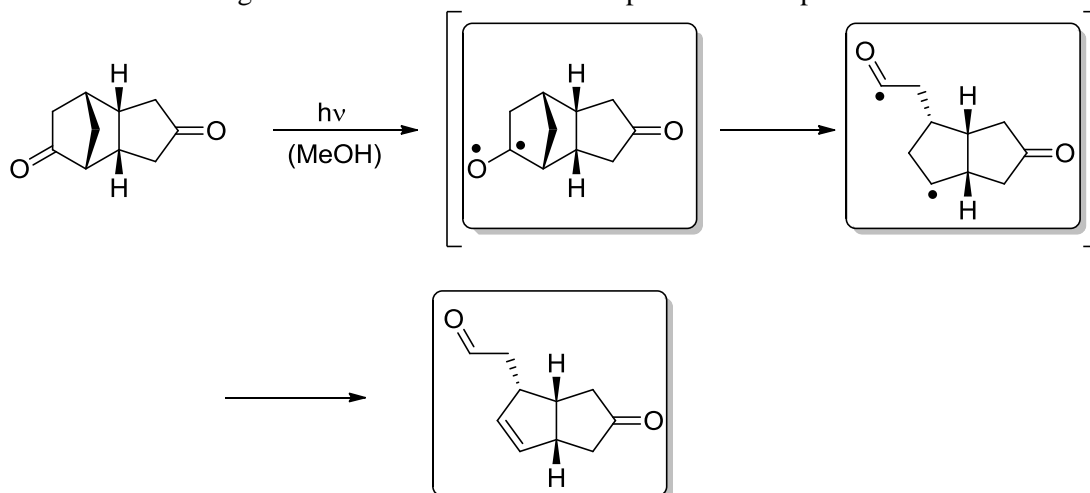


$$A = \epsilon c d$$

$$\epsilon = A/(c d) = 0.27 / (0.55 \cdot 10^{-3} \text{ mol/L} \cdot 0.1 \text{ cm}) = 4909 \text{ L mol}^{-1} \text{ cm}^{-1}$$

### Exercise 2

In his total synthesis of the tetracycle Triquinacene, Deslongchamps used the following photochemical reaction. Fill in the missing intermediates and the obtained product and explain the observed selectivity.

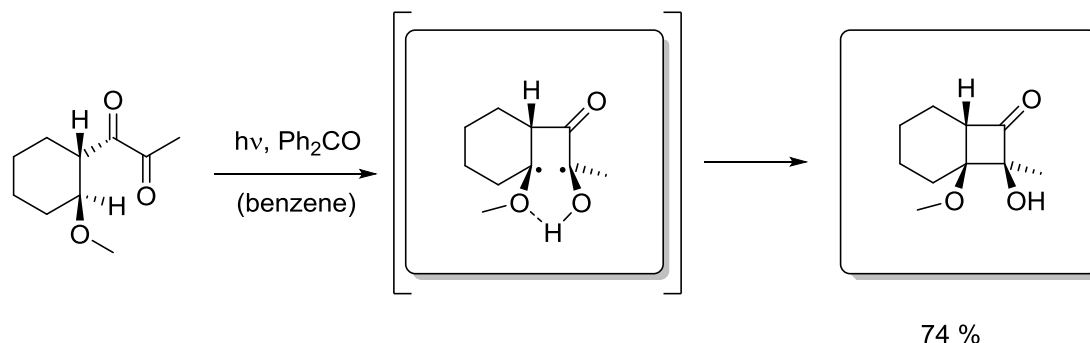


Secondary radicals > primary ones

[Synth. Commun. **1973**, 3, 161.]

### Exercise 3

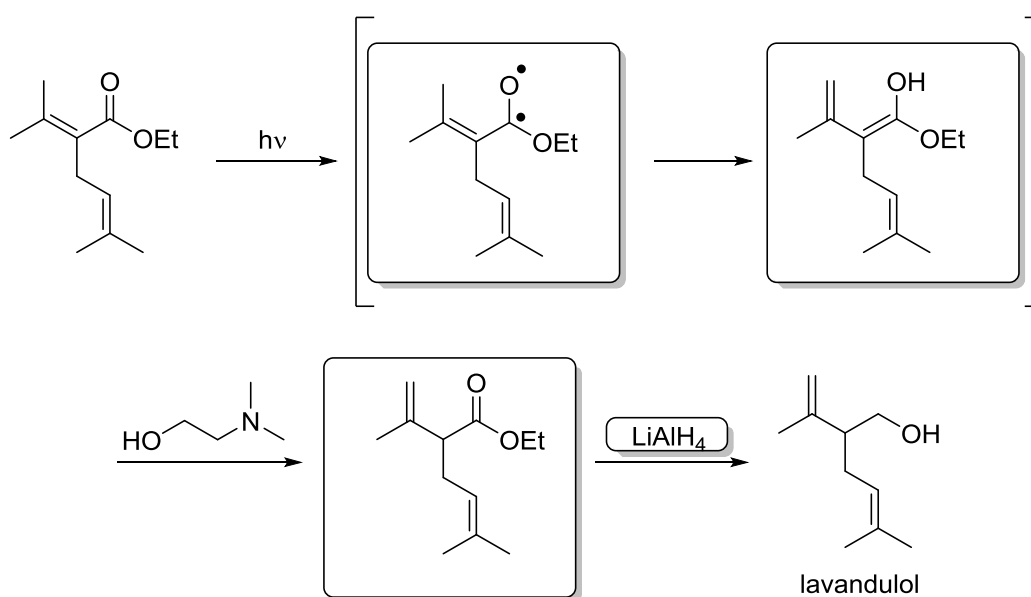
Draw the structures of the intermediate and the product for the following photosensitized reaction.



*Tetrahedron Lett.* **2010**, 51, 872–874

### Exercise 4

The total synthesis of lavandulol uses a photochemical deconjugation. Give the missing intermediates and the reagent for the final step. By what means can the generated stereocenter be defined?

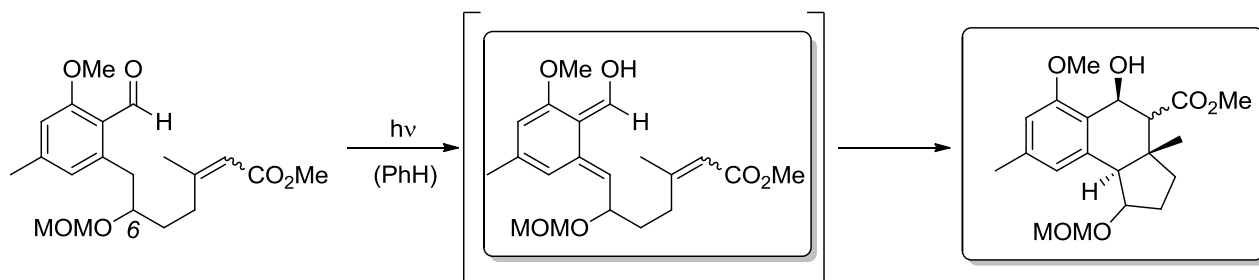


Use of chiral amino alcohol or use of chiral auxiliary instead of OEt

[J. Org. Chem. **1995**, 60, 7879 – 7883.]

### Exercise 5 (Additional exercise)

Ortho-Quinodimethanes are valuable intermediates in photochemical reactions, as they provide numerous methods of further use. The most frequently used method is trapping the intermediate in a Diels-Alder reaction. Give the intermediate and the product of the following reaction with the correct relative stereochemistry (ignore the effect of the stereogenic center at C-6 at the moment).

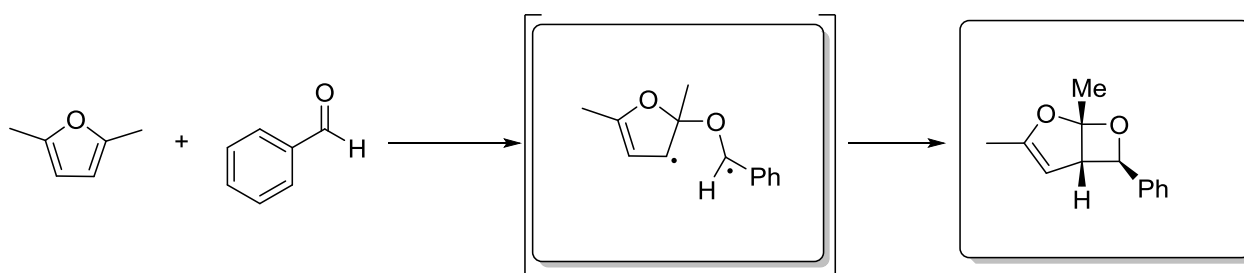


Additional task: draw the transition state that governs the stereochemical outcome of the reaction.

**Exercise 1**

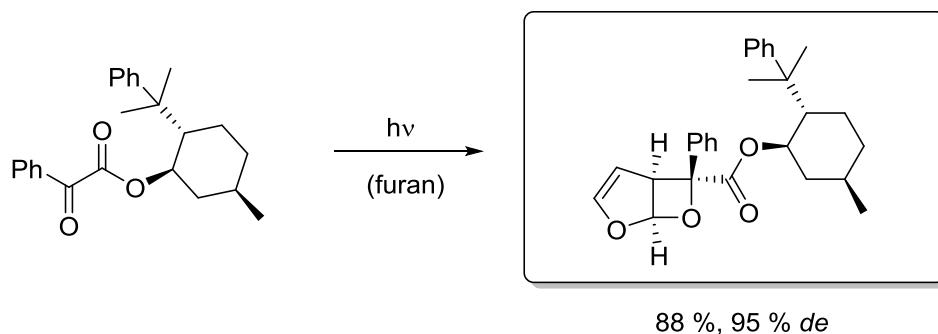
The Paternò-Büchi reaction is a very common reaction for the generation of highly substituted oxetanes that can be further functionalized using a variety of different reactions. Give the products obtained from the following reactions and discuss regio- and stereoselectivity (if necessary, draw the transition state that governs the stereochemical outcome of the reaction). What effect determines the regioselectivity of the first addition step?

a)



*J. Am. Chem. Soc.*, **1983**, *105*, 660–661.

b)

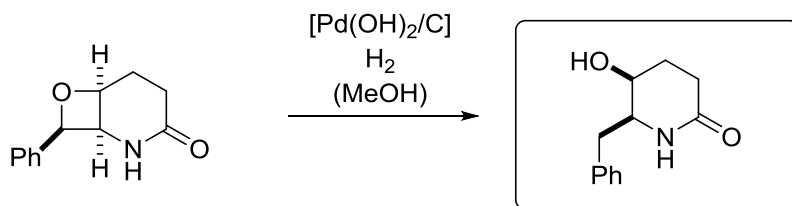


*Photochem. Photobiol. Sci.*, **2003**, *2*, 904–913.

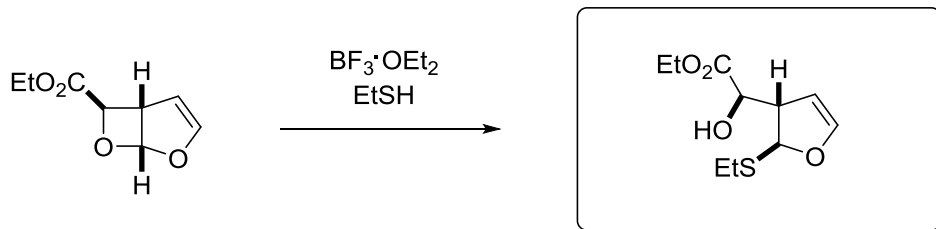
**Exercise 2**

As already stated, Paternò-Büchi products allow for further functionalizations by different means. Give the products of the following opening reactions and explain their regioselectivity. Also, for parts a) and b), give the starting materials for the Paternò-Büchi reactions.

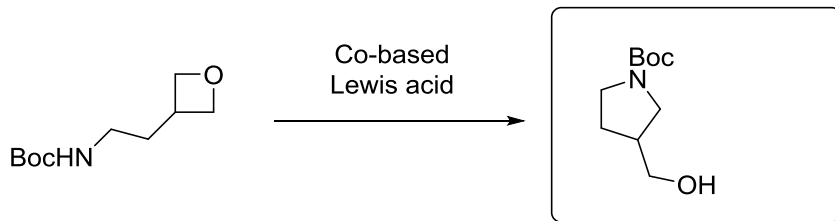
a)



b)

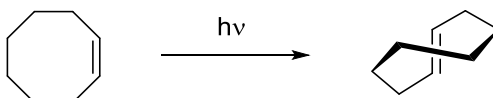


c)



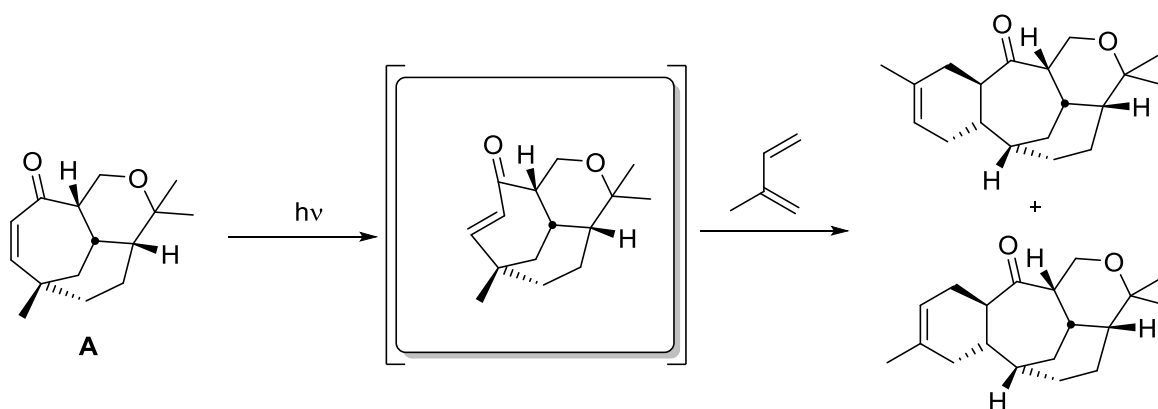
### Exercise 3

Although of low preparative importance, *E/Z* isomerization can be of interest for synthetic organic chemistry. The most prominent example is the photochemical isomerization of *Z*-cyclooctene, leading to *E*-cyclooctene which can be isolated in spite of the high intrinsic ring strain. Explain the mechanism of the reaction that can proceed from both the  $S_1$  and the  $T_1$  state.



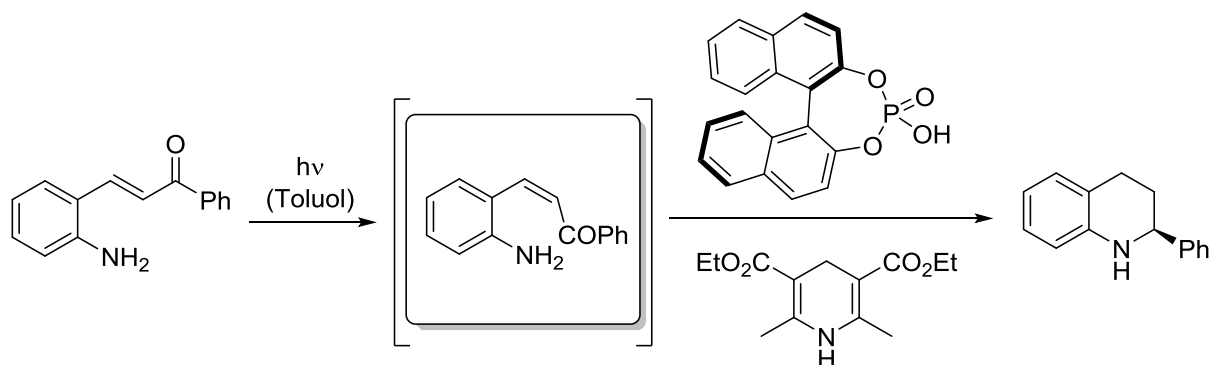
### Exercise 4

Upon irradiation, the 7-membered enone system **A** forms an intermediate which then reacts with isoprene in a diastereoselective Diels-Alder reaction to the product given below. Explain the relative configuration of the newly formed stereogenic centers by the structure of the photochemical intermediate.



**Exercise 1**

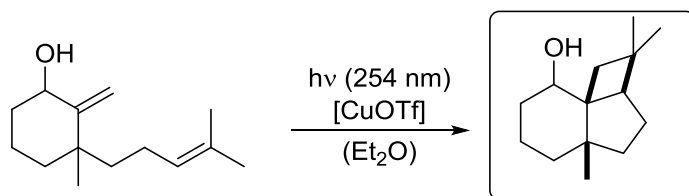
In the following one-pot reaction the styrene given below is irradiated in the presence of a chiral phosphoric acid and a Hantzsch ester. By irradiation, an intermediate is formed which can be reduced in presence of these two reagents to form a chiral tetrahydroquinoline. Draw the structure of the intermediate and explain why light is necessary to induce its formation!



Photochemical E/Z isomerization makes reaction possible

**Exercise 2**

Intramolecular [2+2] photocycloadditions allow for the rapid generation of complex skeletons from rather simple precursors. Give the product of the following copper(I) catalyzed transformation and explain the stereochemical outcome. Why is the addition of a copper salt necessary? For this particular reaction, how could the copper salt have been avoided?

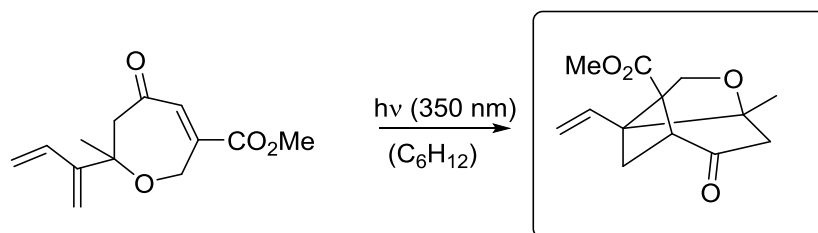


Copper coordinates double bonds and thus reduces the absorption maximum to 254 nm.

If the corresponding ketone is used instead, copper-OTf can be left out (usual 2+2 to enones).

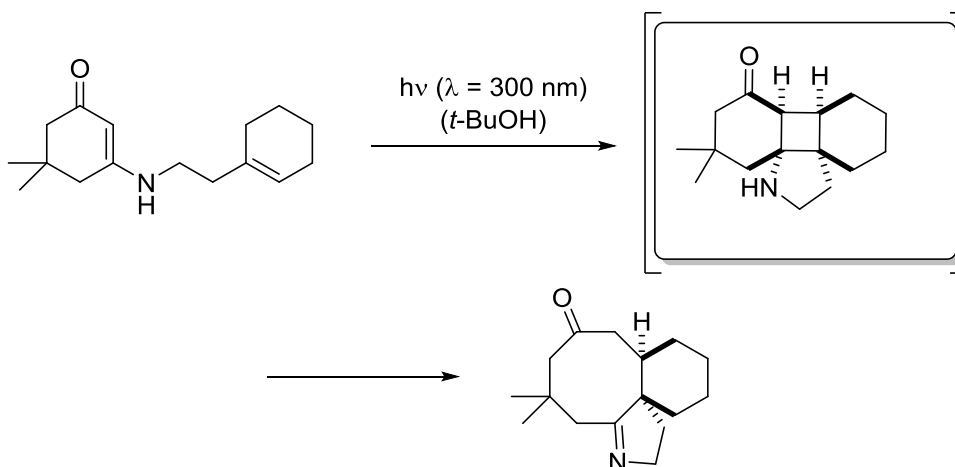
**Exercise 3**

If the following 7-membered ring is irradiated, a single tricyclic photocycloaddition product forms. Give the structure of the product and explain the regioselectivity of the photoreaction.



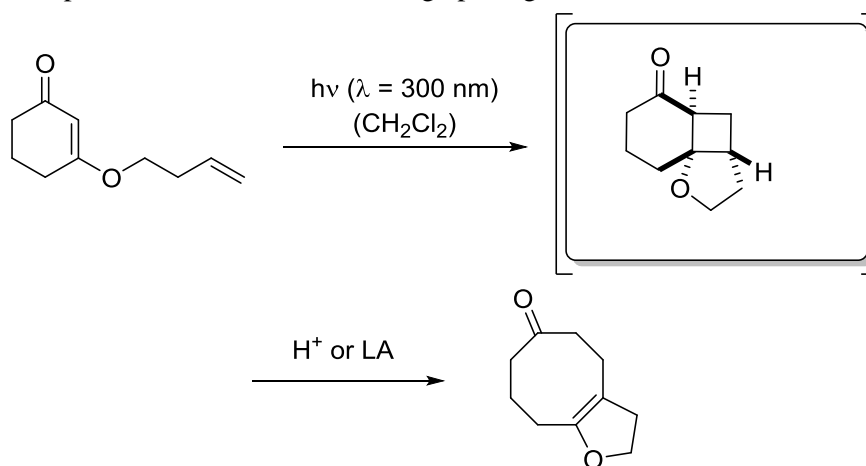
#### Exercise 4

a) Irradiation of the following enamine type precursor leads to a [2+2] photocycloaddition product. However, the cyclobutane cannot be isolated and undergoes rapid fragmentation to a tricyclic product. Draw the structure of the [2+2] photocycycloaddition product and explain the mechanism of its fragmentation reaction. Consider the stereogenic information! What is the name of this ring opening reaction?



Retro-Mannich reaction

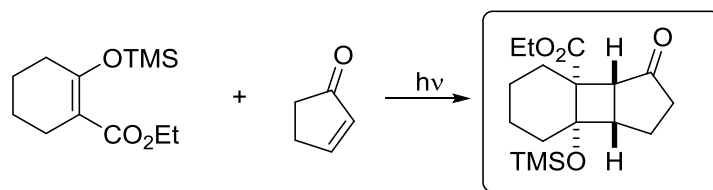
b) The given enol type precursor can undergo a [2+2] photocycloaddition reaction to form an isolable product. Treatment of the cyclobutane with Lewis or Bronsted acids leads to facile fragmentation of the cyclobutane to form a bicyclic dihydrofuran. Draw the structure of the photoproduct in the correct relative configuration and explain the mechanism of the ring opening reaction! What is the name of the last step?



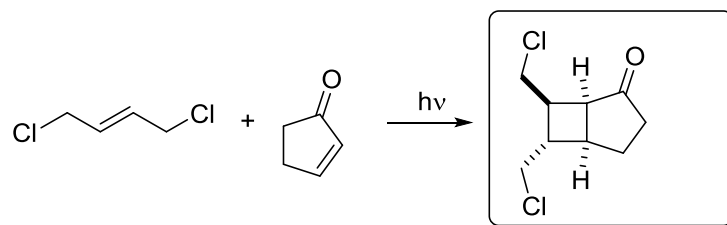
Retro-Aldol reaction

#### Exercise 5

Give the products of the following [2+2] photocycloadditions and explain the observed regio- and stereoselectivities.



*J. Org. Chem.* **1996**, *61*, 5358.



*Tetrahedron Lett.* **2001**, 42, 7295.

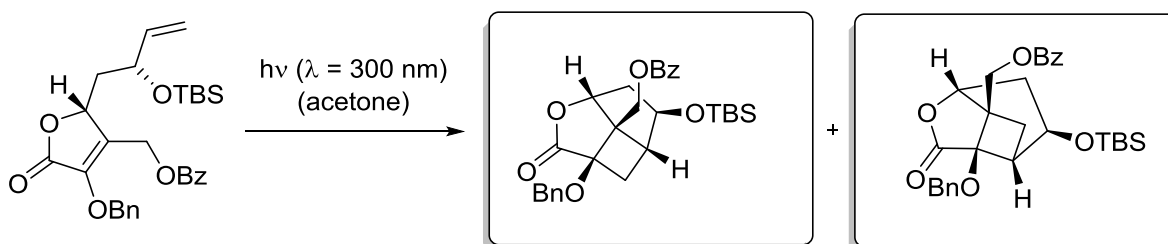


**Exercise 1**

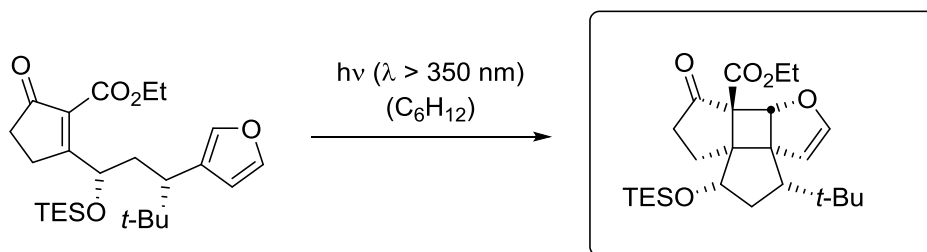
The following diastereoselective intramolecular [2+2] photocycloadditions were used as key steps in the total synthesis of natural products. Draw the corresponding products in the correct relative configuration!

*Hint: chiral induction does not occur from a stereogenic center in  $\alpha$ -position to a furan moiety!*

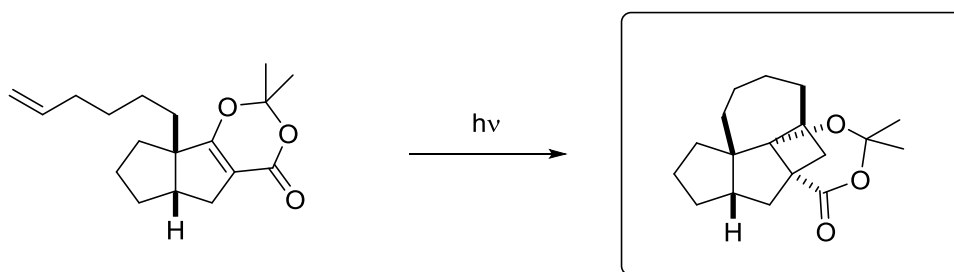
a)



b)



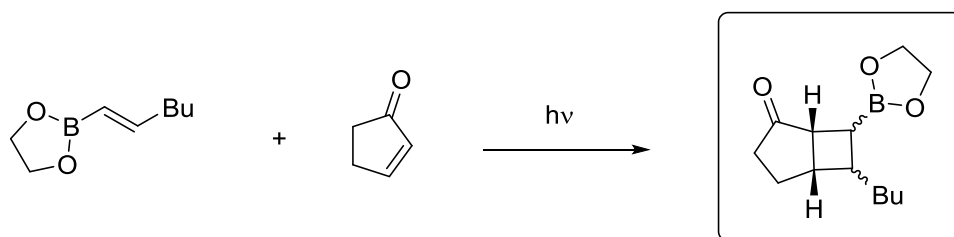
c)



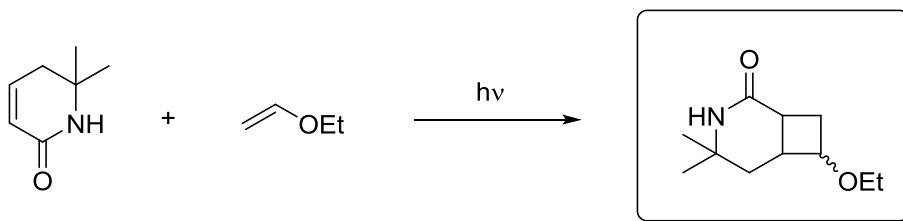
**Exercise 2**

Give the products of the following intermolecular [2+2] photocycloadditions and discuss the observed regioselectivity. How can the boronic ester from part a) be synthesized?

a)



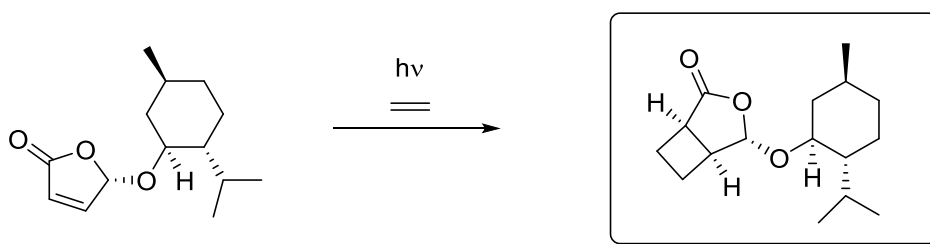
b)



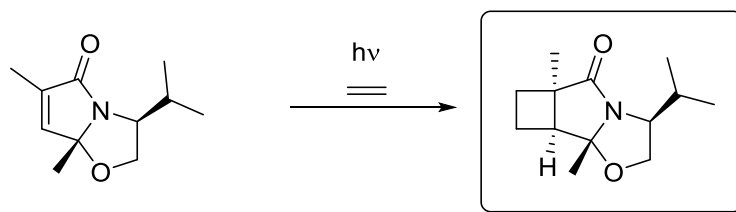
### Exercise 3

In order to conduct photocycloadditions enantioselectively, cyclic stereocontrol can be used amongst others. Give the products of the following reactions and explain the diastereoselectivity.

a)

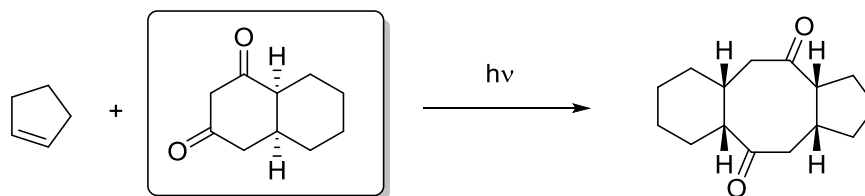


b)



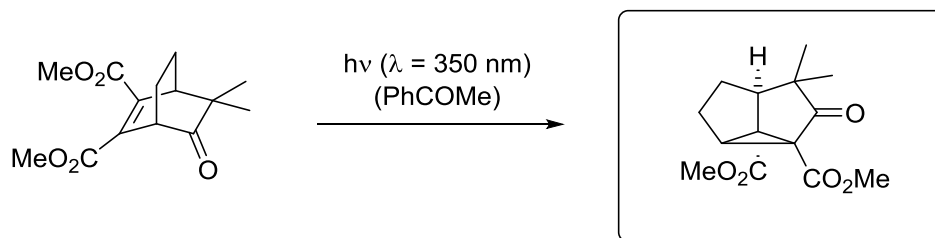
### Exercise 4

Upon irradiation of a two component mixture, the following product is observed as the major product of a [2+2] photocycloaddition and a consecutive reaction. Explain the formation of the given product and give the starting material used for this transformation.



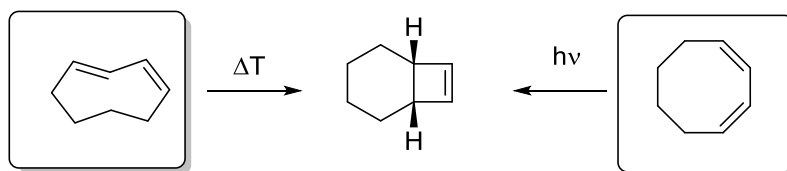
### Exercise 5

Draw the structure of the following oxa-di- $\pi$ -methane rearrangement product in the correct relative configuration!



**Exercise 1**

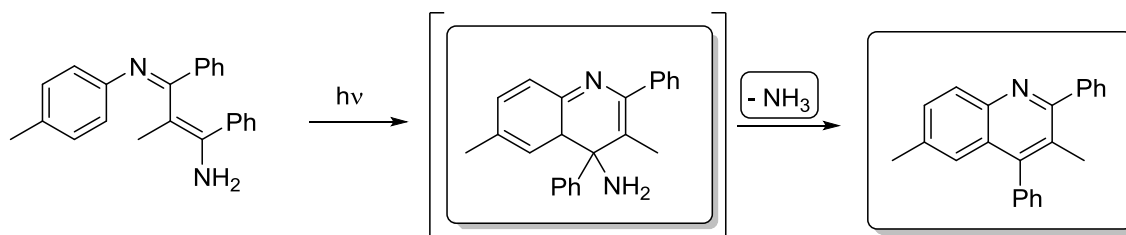
The following bicyclo[4.2.0]octene can be made from different (but similar) starting materials using different conditions for the reaction. Give the corresponding starting materials and discuss the stereoselectivity of the reactions.



**Exercise 2**

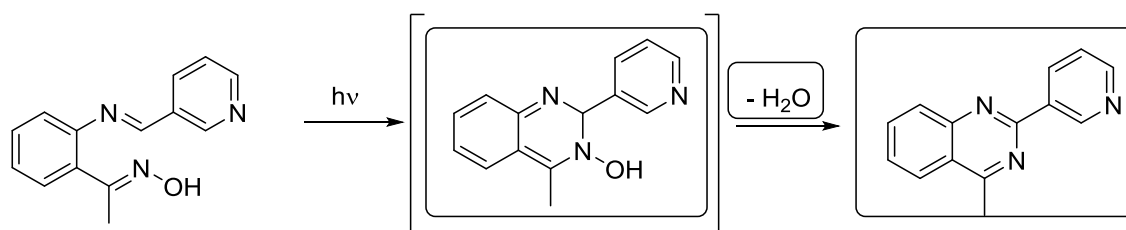
Upon irradiation of the given imines, one single aromatic product is formed in each case. Give the intermediary structures and the expected products.

a)



*Tetrahedron Lett.*, **1993**, 34, 5321.

b)



*Tetrahedron*, **2010**, 66, 4469.

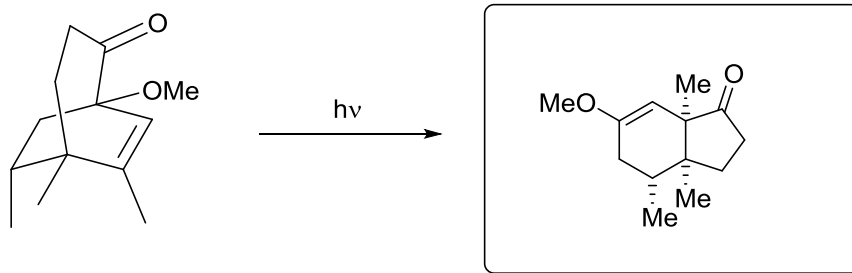
**Exercise 3**

Consider the cyclopentadienyl anion as a model system for cyclisations. Does the conrotatory cyclisation occur under thermal or photochemical conditions? Analyze the symmetry of the reaction using the Woodward-Hoffmann rules.

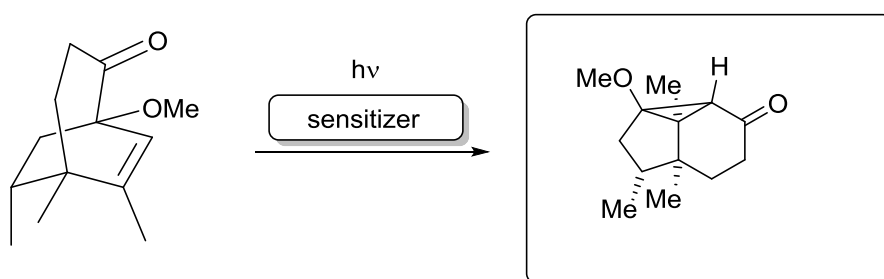
### Exercise 1

The following photochemical 1,3-acyl shift was used as a key step in the total synthesis of pinguisone.

- a) Draw the rearrangement product in the correct configuration!

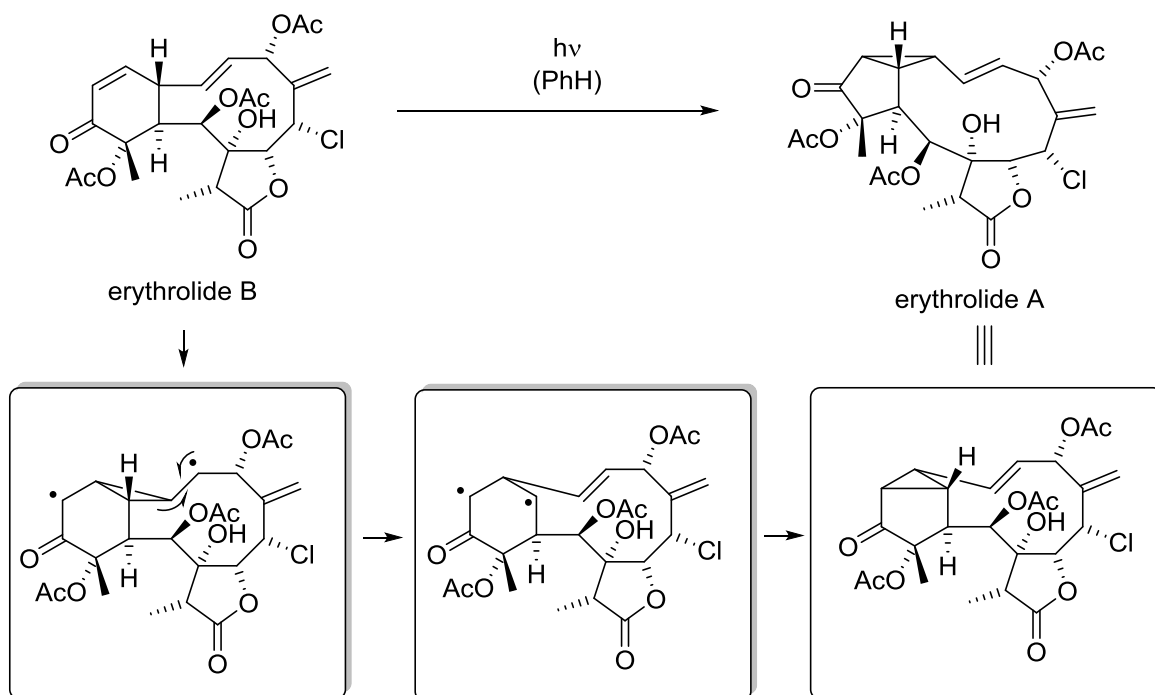


- b) The same irradiation precursor might be reacted in a oxa-di- $\pi$ -rearrangement. Draw the expected product in the correct configuration! What kind of reagent has to be added to favour the oxa-di- $\pi$ -rearrangement? Explain your choice!



### Exercise 2

The natural products given below can be transformed into each other via a photochemically induced di- $\pi$ -rearrangement. Explain the mechanism of the reaction by drawing the intermediates leading to erythrolide A starting from erythrolide B!



# Organic Photochemistry – 6<sup>th</sup> exercise 6.2.2014 11.05 a.m.

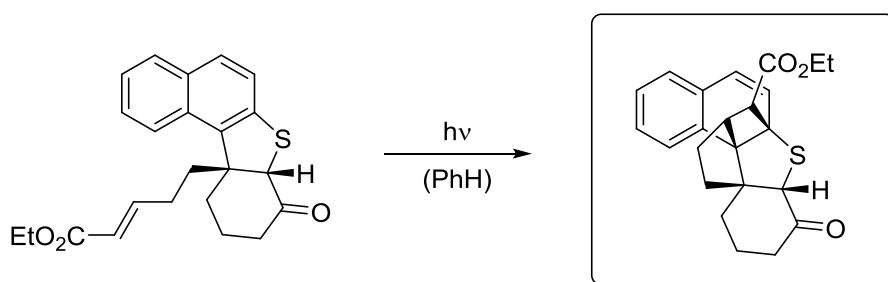
The exercise takes place in room 22210 exclusively!

## Exercise 1

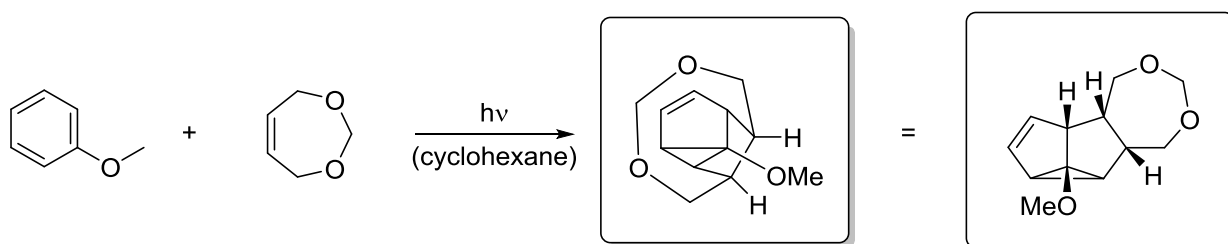
Arene photocycloadditions are one of the few possibilities of dearomatization. In the following exercises, consider the following aspects before drawing the expected product(s).

- Determine the substitution pattern of the arene and the alkene. Consequently, what reaction is likely to occur?
- Determine the facial preference of the alkene and the *endo/exo* selectivity.
- Draw the product(s).

i)



ii)



## Exercise 2

Any questions?

If you haven't already done so, please register for **the exam on Tuesday, Feb 11 at 10 a.m. in 27402!**