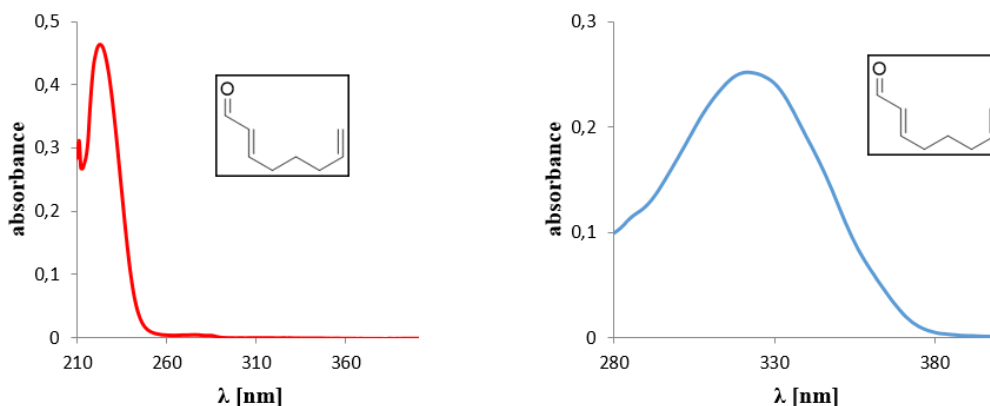


**Exercise 1**

A crucial point in photochemistry are the photophysical properties of a potential photosubstrate.

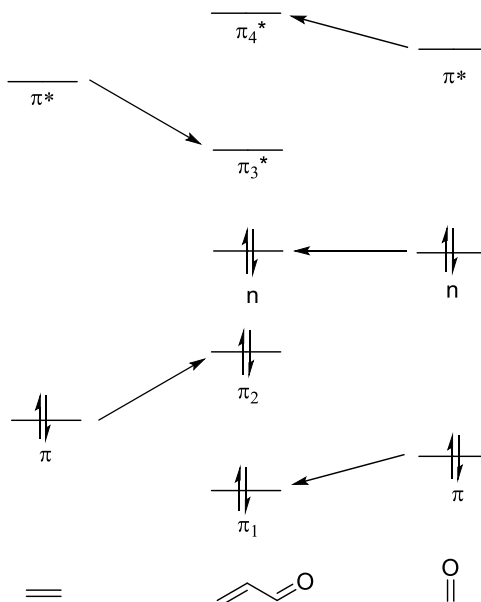
a) UV/Vis-spectroscopy is the method to determine at which wavelength the compound absorbs and therefore at which wavelength it can be promoted to the excited state by direct irradiation. The spectrum of the following aldehyde was recorded using a 1 mm quartz cuvette with  $c = 0.25$  mM for the spectrum on the left and  $c = 75$  mM for the spectrum on the right-hand side. Please assign the type of transition ( $n\pi^*$  and  $\pi\pi^*$ ) using a MO scheme and calculate the corresponding extinction coefficients for the maxima at 223 nm and 322 nm. Why do they differ to each other?



$$\mathcal{E}_{223 \text{ nm}} = 0.45 / 0.25 \cdot 10^{-3} \times 0.1 \text{ cm} = 18000 \text{ L/mol}\cdot\text{cm} (\pi\pi^*) \text{ allowed}$$

$$\mathcal{E}_{322 \text{ nm}} = 0.25 / 75 \cdot 10^{-3} \times 0.1 \text{ cm} = 33 \text{ L/mol}\cdot\text{cm} (n\pi^*) \text{ forbidden}$$

Lower  $\Delta E$  of  $n\pi^*$  transition + lower molar extinction coefficient (quantum mechanically forbidden)



b) Another interesting property of new substrates is luminescence to determine the energy of the respective  $S_1$  and  $T_1$  state. Assuming a compound shows luminescence at 360 nm and 410 nm, please calculate the corresponding energies and state which wavelength corresponds to which type of luminescence and why.

$$E = (h \cdot c) / \lambda$$

$$h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$c = \text{speed of light} = 3 \times 10^8 \text{ m/sec}$$

$\lambda = 360$  and  $410$  nm (given in the question above)

$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

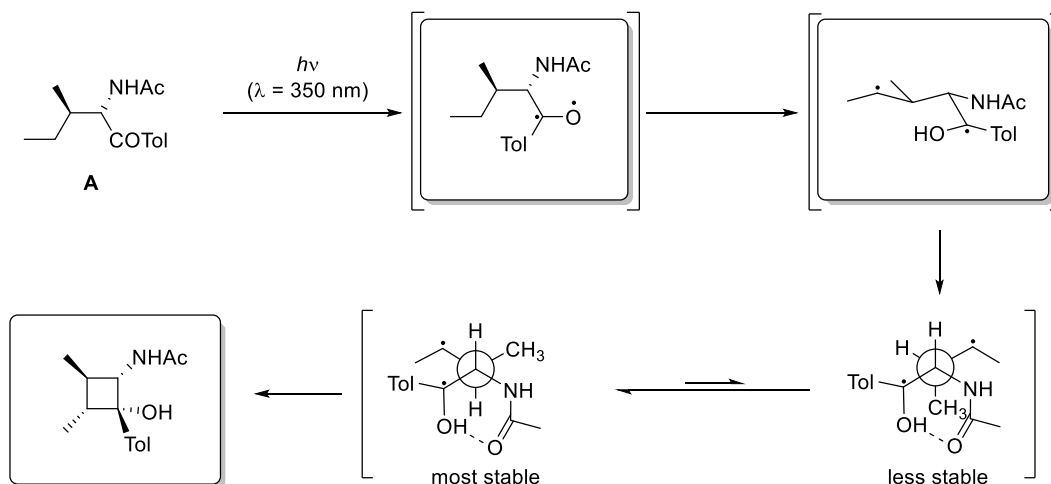
Therefore,  $E(S_1) = 333 \text{ kJ/mol}$ ,  $E(T_1) = 292 \text{ kJ/mol}$ ,

Fluorescence 360 nm, Stokes shift, relaxation of vibrational states

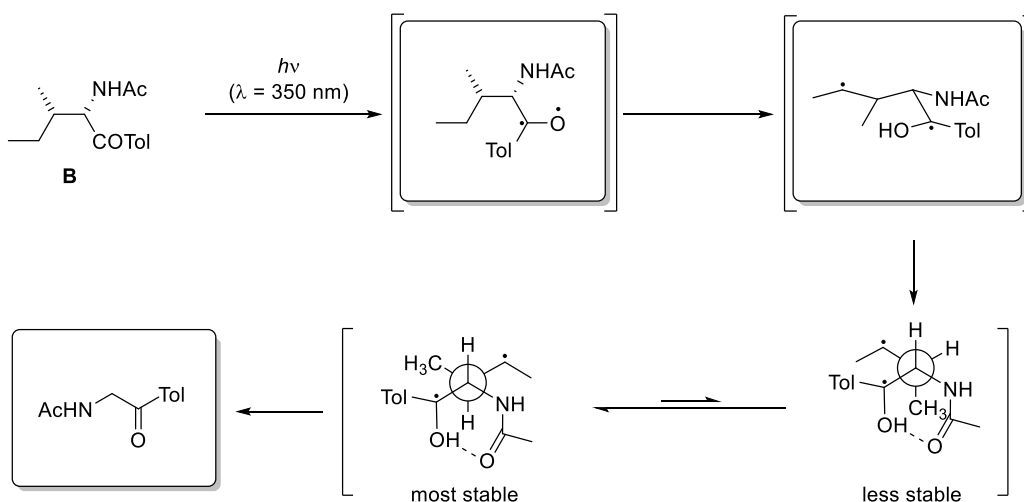
Phosphorescence 410 nm, energy is inversely proportional to wavelength. From the Jablonski diagram, one can see that  $T_1$  is lower in energy compared to that of  $S_1$ . Thus phosphorescence should occur at higher wavelength (lower energy) compared to fluorescence.

### Exercise 2

The two diastereomers **A** and **B** give very different products when irradiated due to different conformational preferences. Draw the excited intermediates and complete the given *Newman* projections. Which products do you expect to be formed as the main products?

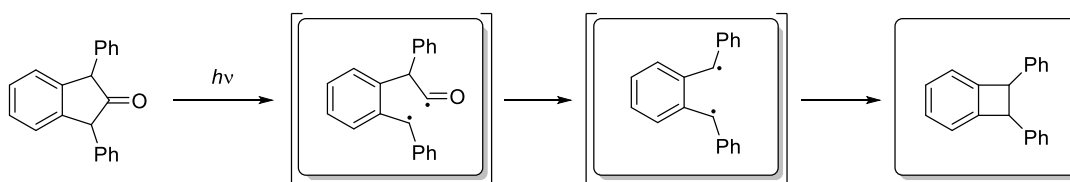


*Org. Biomol. Chem.*, 2016, 14, 7392–7442



### Exercise 3

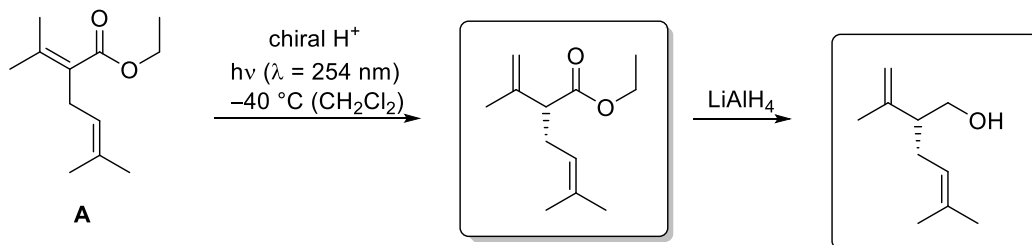
The carbonyl compound shown below was reported to undergo a photo elimination. Complete the sequence by drawing the product and all intermediates.



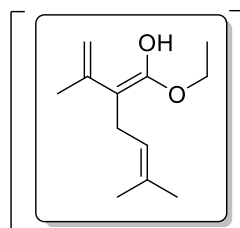
*Angew. Chem.*, 1971, 6, 210–212

**Exercise 1**

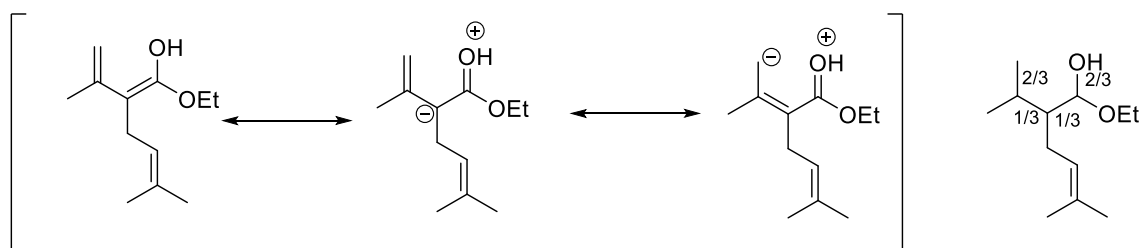
a) In the total synthesis of (*R*)-lavandulol a photochemical key step was employed to generate the stereogenic center. Give the intermediate and the product of the photochemical transformation of ester **A** and explain the regioselectivity with a suitable model. Draw the structure of the final product. (*Hint*: Neglect the configuration of the new formed stereogenic center.)



structure of intermediate:

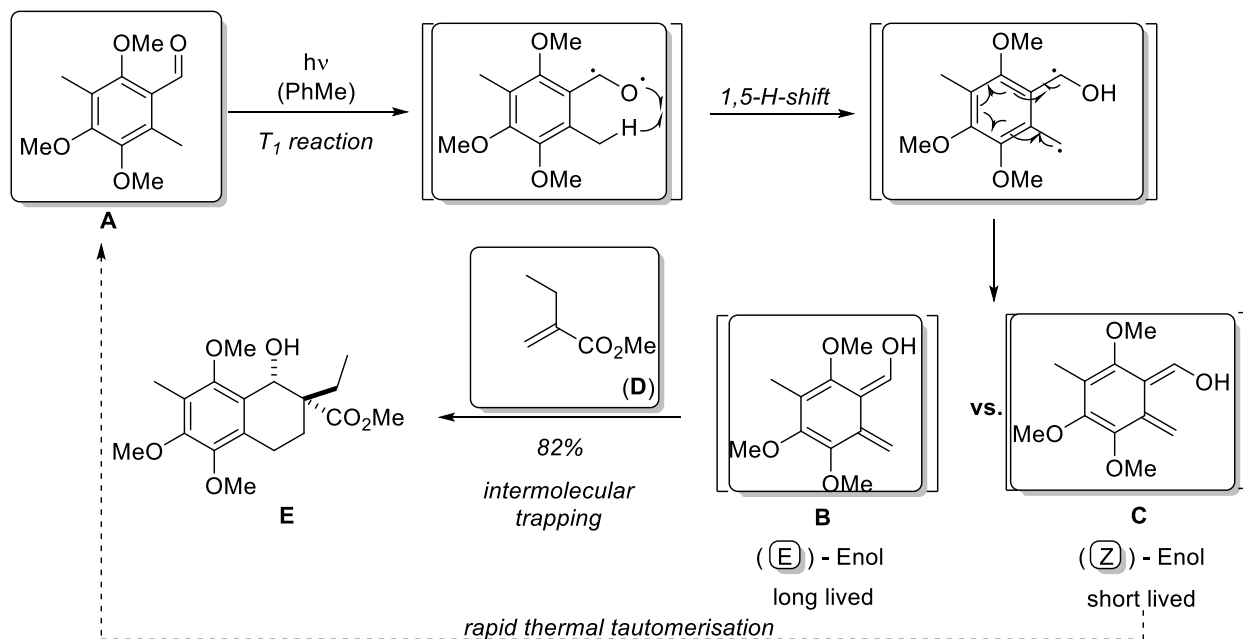


Principle of least motion:



*J. Org. Chem.* **1995**, *60*, 7879-7883.

b) 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.

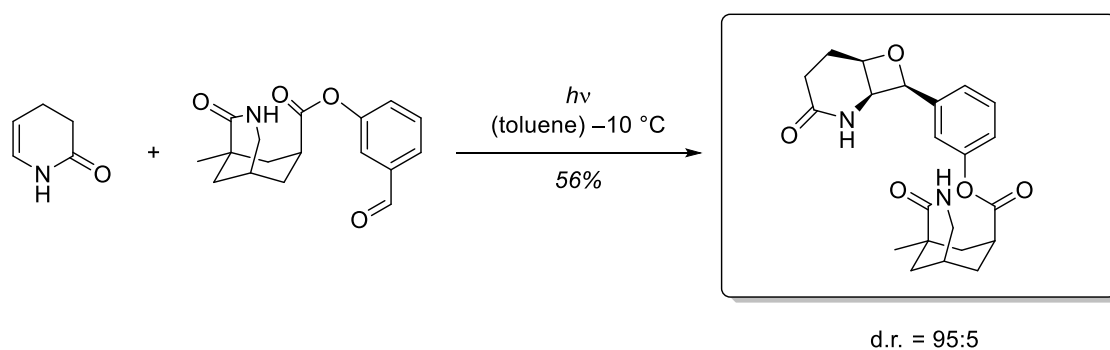


*J. Am. Chem. Soc.* **2004**, 126, 607-612.

### Exercise 2

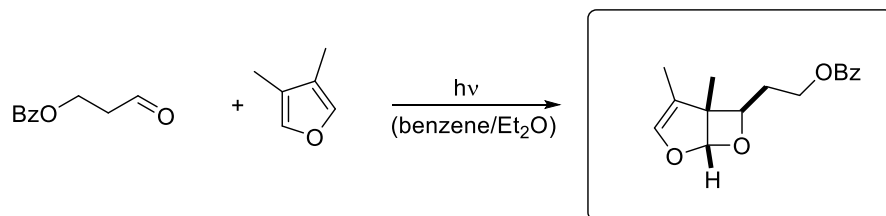
Give the product of the following *Paternò-Büchi* reactions and explain the regio- and stereoselectivity.

a)



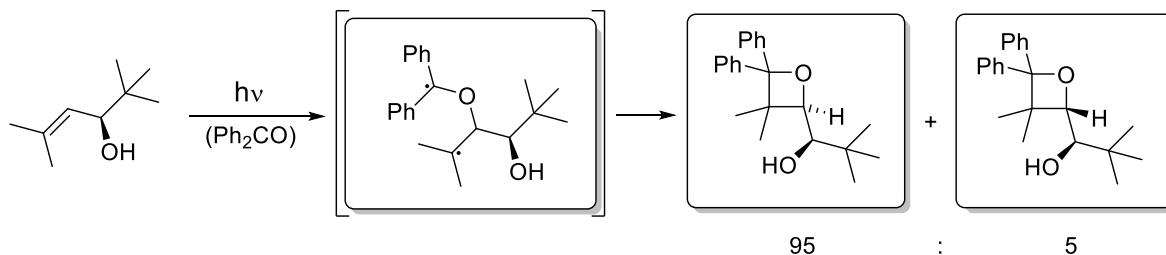
*J. Am. Chem. Soc.* **1999**, 121, 10650-10651.

b)

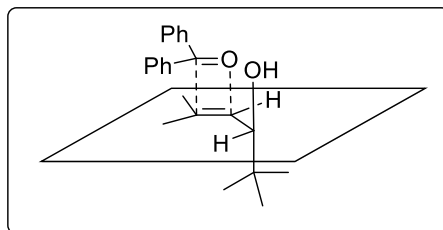


### Exercise 3

The following *Paternò-Büchi* reaction provides one major and one minor diastereomer. Please explain the mechanism of the product formation and rationalize the selectivity by drawing the transition state in case of the major diastereomer. Which effect controls the stereoselectivity?



Intermediate to the major diastereomer:



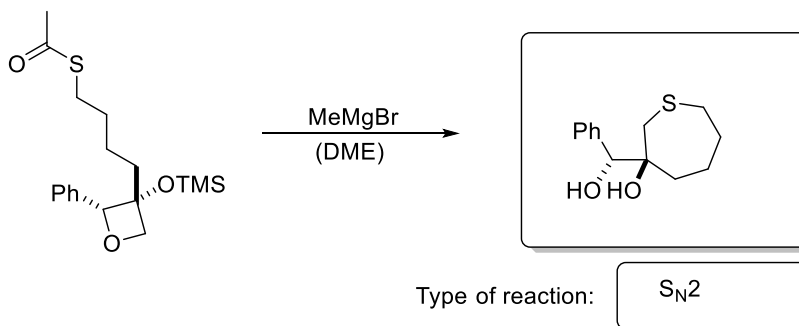
Stereoselectivity due to: 1,3-allylic strain

*Current Organic Chemistry* **2009**, 13, 939-954

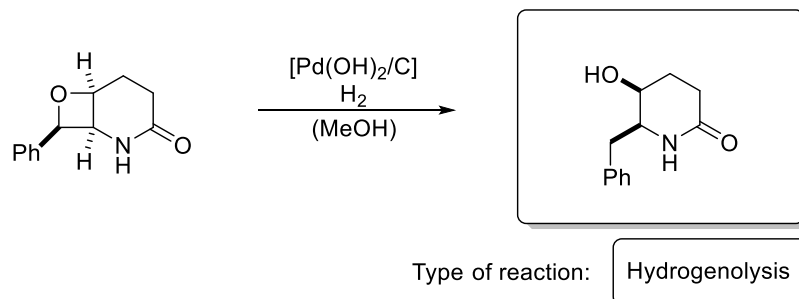
### Exercise 4

Oxetanes can be opened under various reaction conditions. Please complete the following reactions and give the type of reactions.

a)



b)



Exercise 1

a) Anthrylethylene derivatives undergo *E/Z*-isomerization upon irradiation. Irradiation at a wavelength of  $\lambda \geq 400$  nm applied to a solution in hexane yields photostationary ratio of *E/Z* = 6:94. Explain this selectivity considering the following UV-Vis spectra.

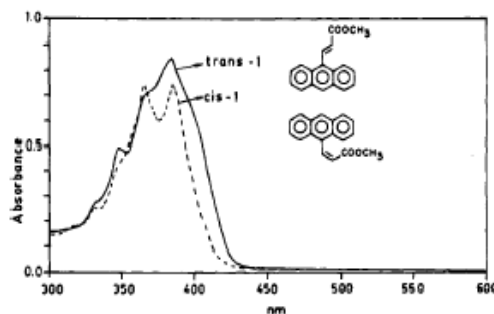
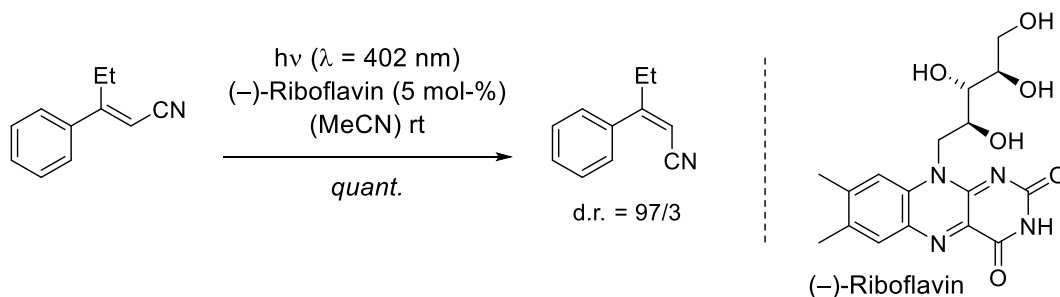


Figure 2. UV-vis absorption spectra of *trans*-1 (solid line) and *cis*-1 (broken line) in hexane solvent.

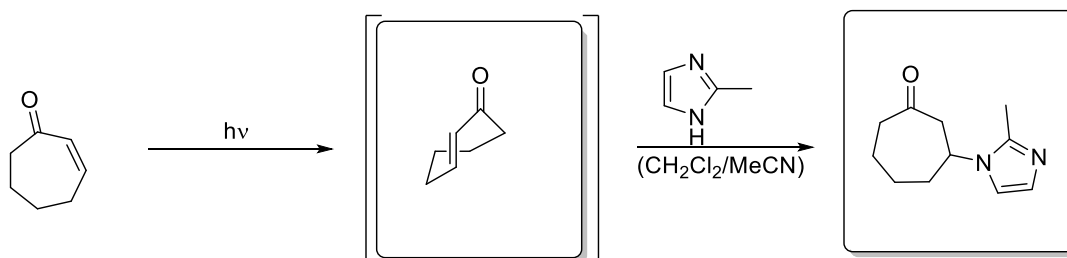
Without sensitizer:  $\epsilon_{400\text{nm}}(\text{trans}) > \epsilon_{400\text{nm}}(\text{cis}) \rightarrow \text{cis-derivative is favoured}$

b) The following photocatalytic *E* → *Z* isomerisation 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.



See script:  $E(T_1)[\text{cis}] > E(T_1)[\text{Sens.}] > E(T_1)[\text{trans}]$

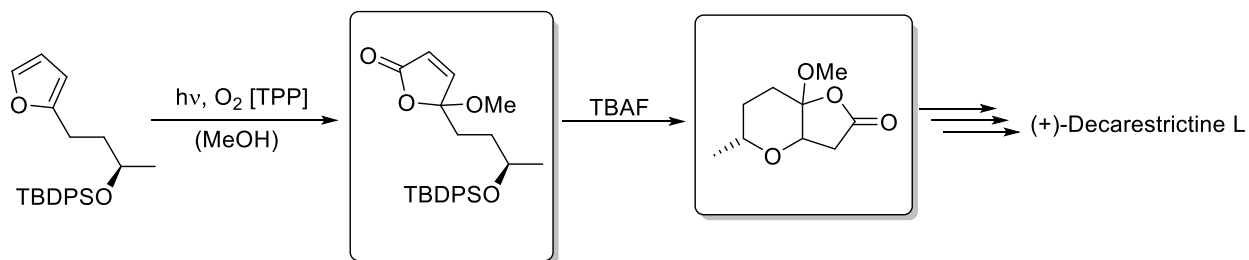
c) UV irradiation of cyclic enones and nitrogen heterocycles lead to the formation of 1,4-adducts. Samples that were not exposed to UV radiation showed no conversion. Complete the following synthesis and propose a structure for the intermediate.



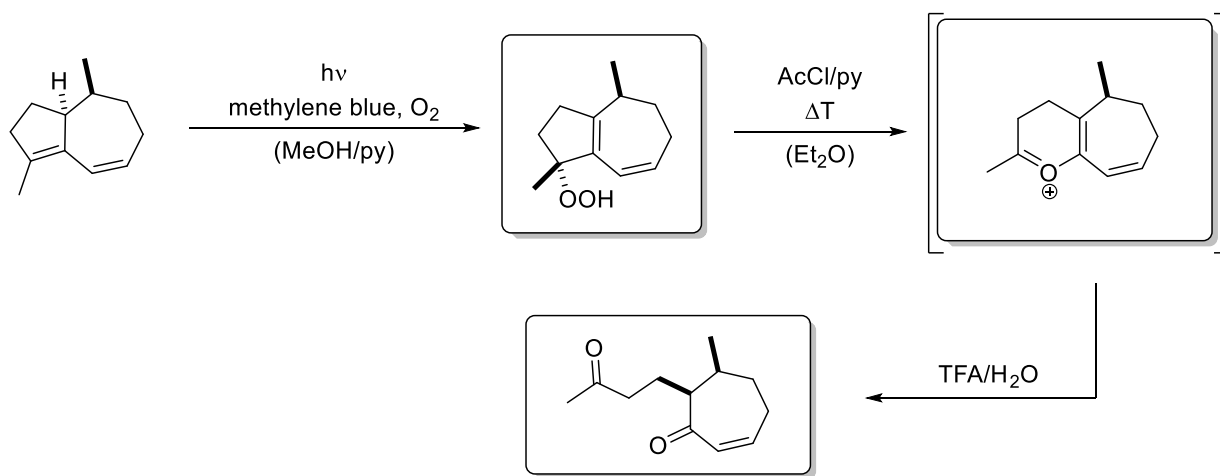
## Exercise 2

In the following reactions singlet oxygen was used to achieve the desired products. Predict the product and complete the sequence for a) and b). Explain the formation of the product for example c).

a)

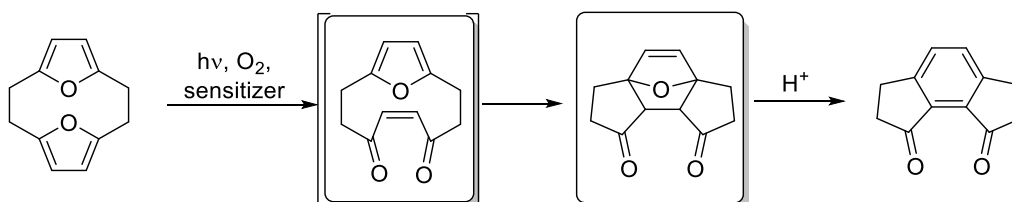


b)



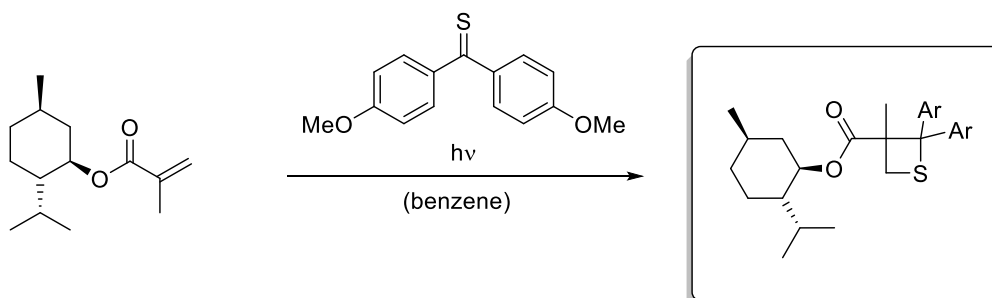
*J. Org. Chem.* **1991**, *24*, 6829-6832.

c)



## Exercise 3

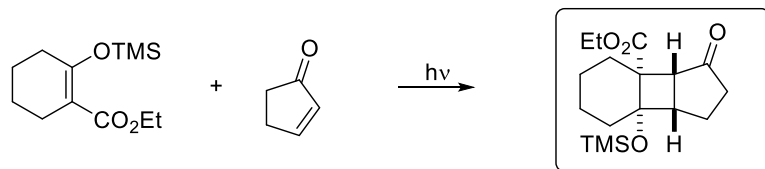
Thiocarbonyls can undergo similar reactions as carbonyl compounds. Given this information draw the obtained product. The stereoconfiguration can be neglected.



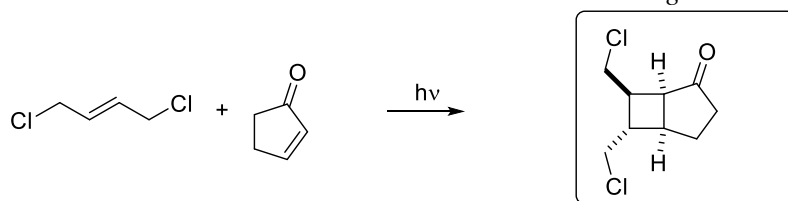
*Photochem. Photobiol. Sci.* **2019**, *18*, 2297–2362.

**Exercise 1**

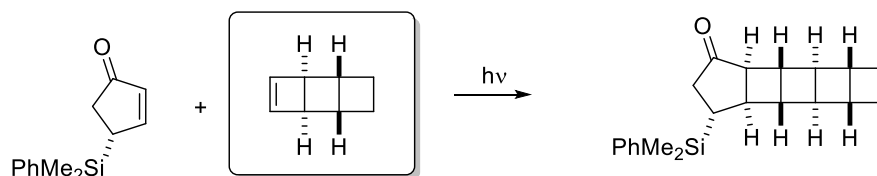
Give the products of the following [2+2] photocycloadditions [a) and b)] and explain the observed regio- and stereoselectivities. For c) give the employed tricyclic alkene and explain the observed stereoselectivity.



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



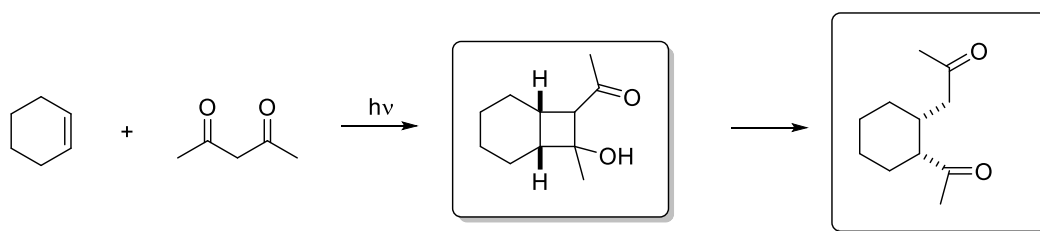
*Tetrahedron Lett.* **2001**, *42*, 7295.



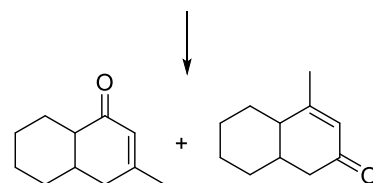
*JACS* **2006**, *128*, 3118.

**Exercise 2**

Give the product of the [2+2] photocycloaddition reaction and the followed ring opening reaction. Specify the relative configuration of the two stereocentres at the cyclohexane-ring. What is the name of this transformation? The product can then undergo a second cyclization shown below. Explain this transformation.



Name of the reaction sequence:



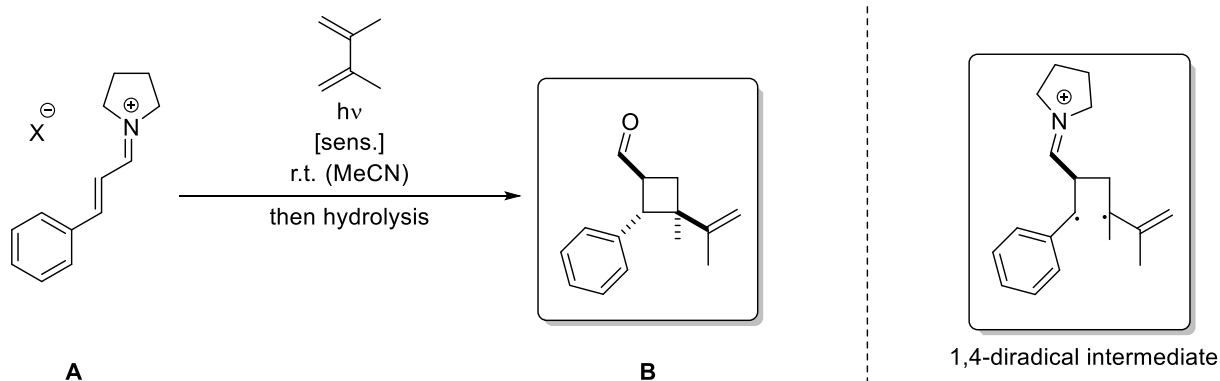
*Proc. Chem. Soc.*, **1962**, 97-132.



### Exercise 3

It is known that iminium ions display a similar reactivity as carbonyl compounds in thermal reactions. In some cases this rule can also be applied to photochemistry.

a) In the following reaction eniminium ion **A** was reacted with 2,3-dimethylbutadiene using sensitization. Give the corresponding 1,4-diradical intermediate, the product aldehyde **B** after hydrolysis and explain the regio- and stereoselectivity.



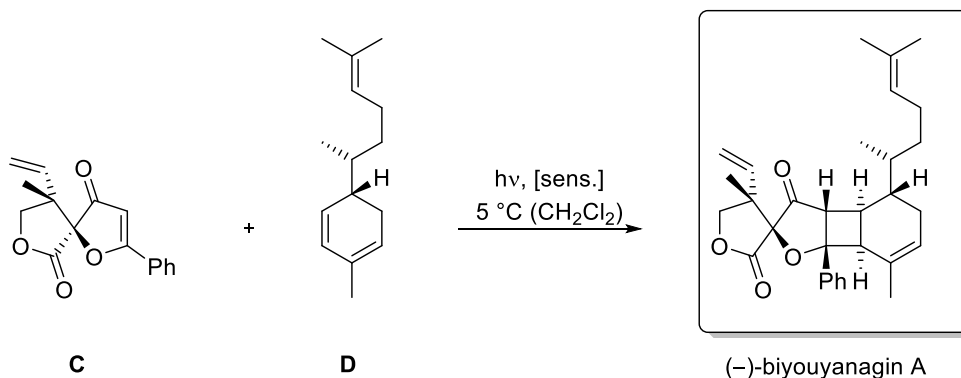
b) Which unproductive side reaction would you expect? Why could a sensitizer be necessary in this case?

*E/Z-isomerization, no  $n\pi^*$ -absorption  $\rightarrow$  no ISC to the T1-state possible*

*Angew. Chem. Int. Ed. 2018, 57, 827-831.*

### Exercise 4

The group of Nicolaou applied a photochemical key step in the total synthesis of (-)-biyouyanagin A. Lactone **C** reacted with alkene **D** under sensitization to give the corresponding cyclobutane. Explain the regio- and diastereoselectivity and give the structure of the natural product. *Hint: The reaction takes place at the more accessible double bond of the alkene D.*

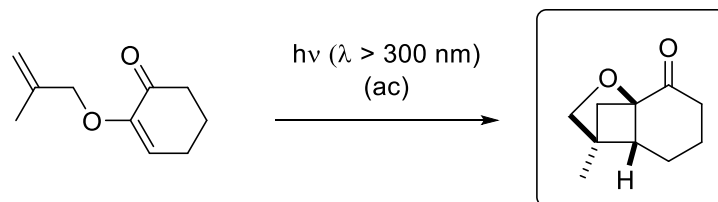
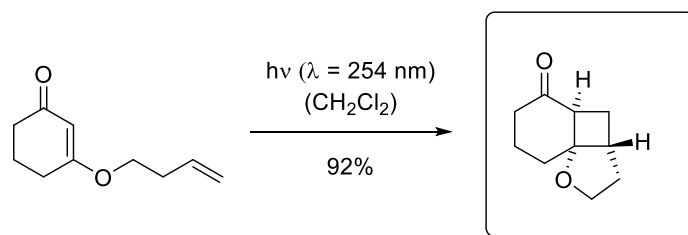


*Cyclic stereocontrol, most stable 1,4-diradical intermediate (benzylic and allylic radical).*

*J. Am. Chem. Soc. 2008, 130, 11114-11121.*

### Exercise 5

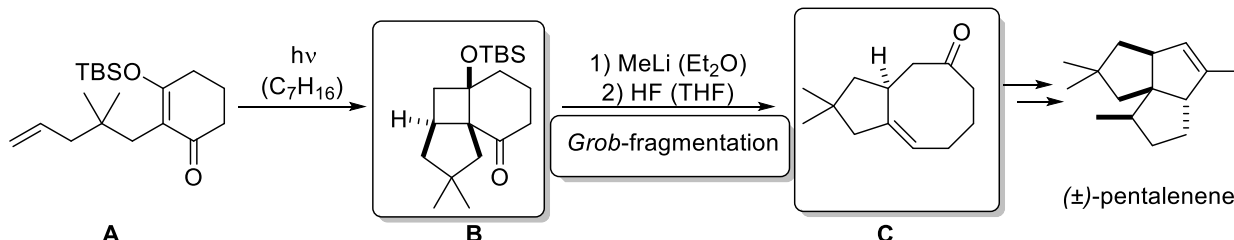
Give the products of the following intramolecular [2+2]-photocycloaddition reactions with the correct relative configuration!



*J.Org.Chem* **1983**, 48, 4241-4247.

**Exercise 1**

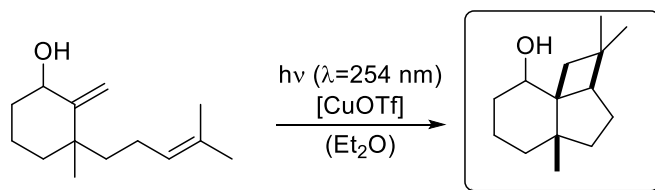
In the total synthesis of (±)-pentalenene a [2+2] photocycloaddition with sequential ring opening was employed as a key step. What product **B** do you expect after irradiation of ketone **A** and which bicyclic product **C** is formed after alkylation and deprotection? Please give the name of the reaction that leads to bicyclic **C**.



*Tetrahedron* **1987**, *43*, 5637-5652.

**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. Why is the addition of a copper salt necessary? For this particular reaction, is it possible to avoid the use of the copper salt? What has to be changed?

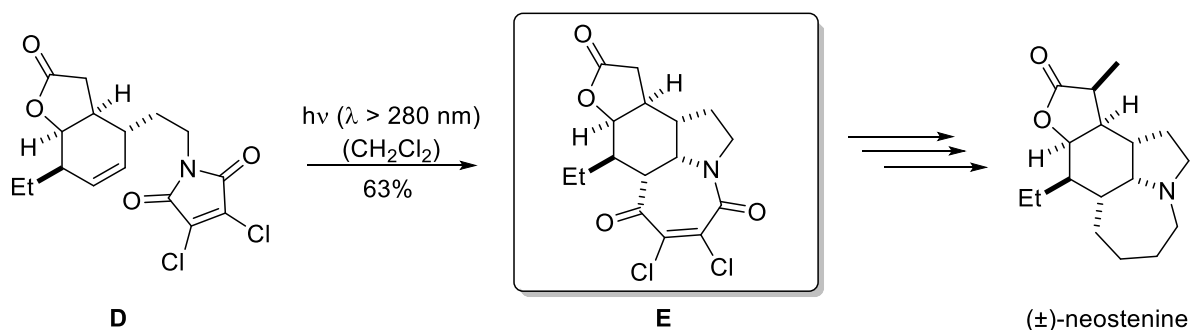


*Copper coordinates double bonds and thus shifts the absorption maximum to 254 nm.*

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

**Exercise 3**

In the total synthesis of stemona alkaloid (±)-neostenine irradiation of maleimide **D** was employed as a photochemical key step. Please give the structure of the obtained tetracyclic product **E** and explain the diastereoselectivity.

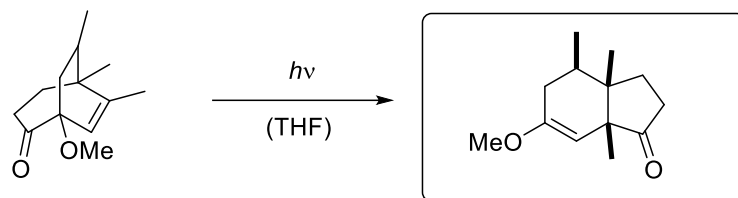
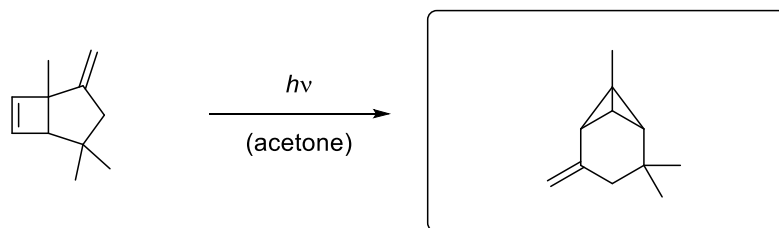
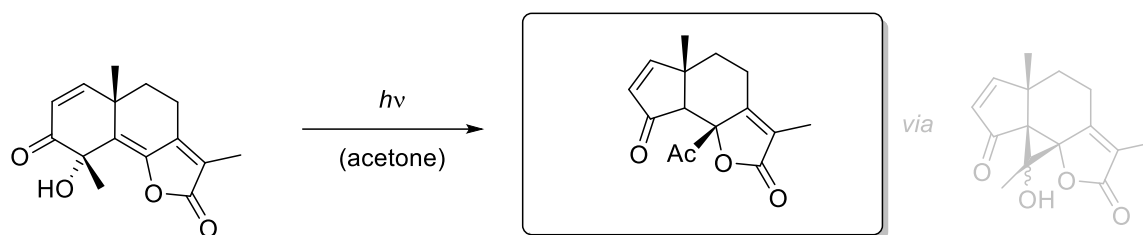


Via  $\alpha$ -cleavage, [5+2]-Cycloaddition, maleimide sterically to hindered, no [2+2]-Cycloaddition

*J. Org. Chem.* **2008**, *73*, 6497-6505.

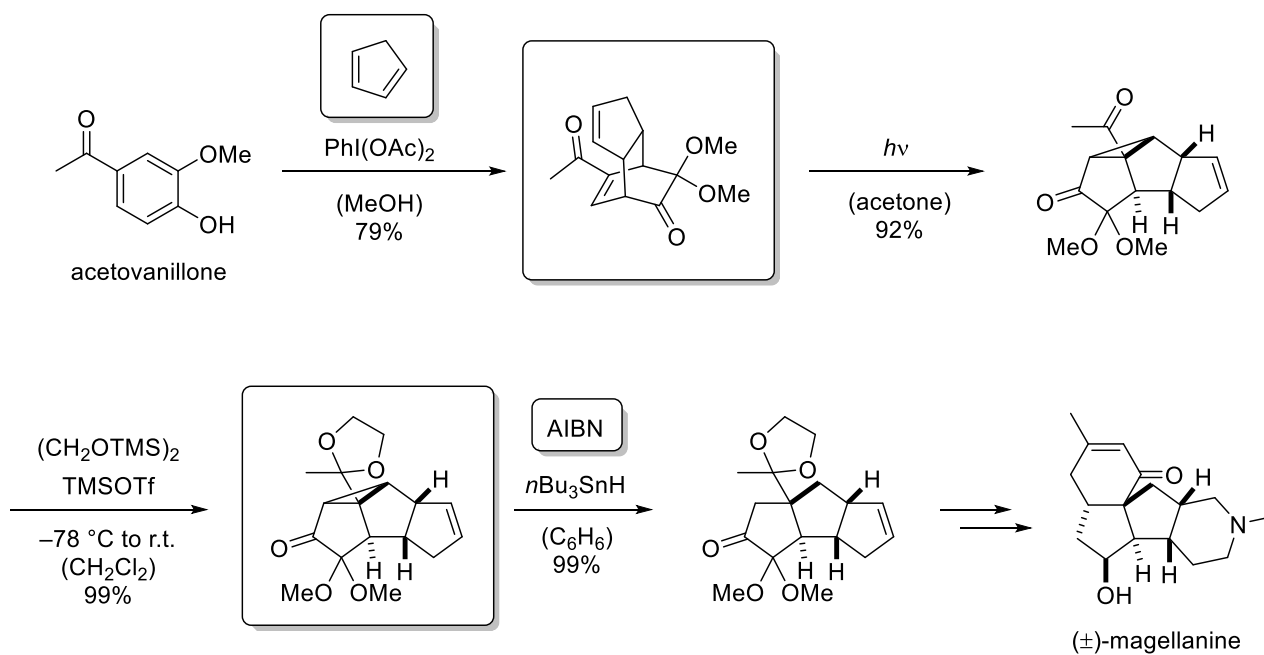
### Exercise 4

Please give the product structures and names of these photochemical transformations. Explain the mechanisms.



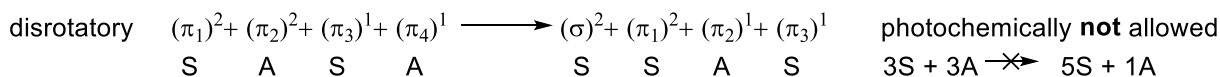
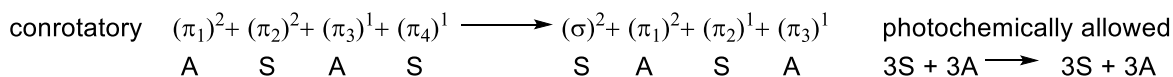
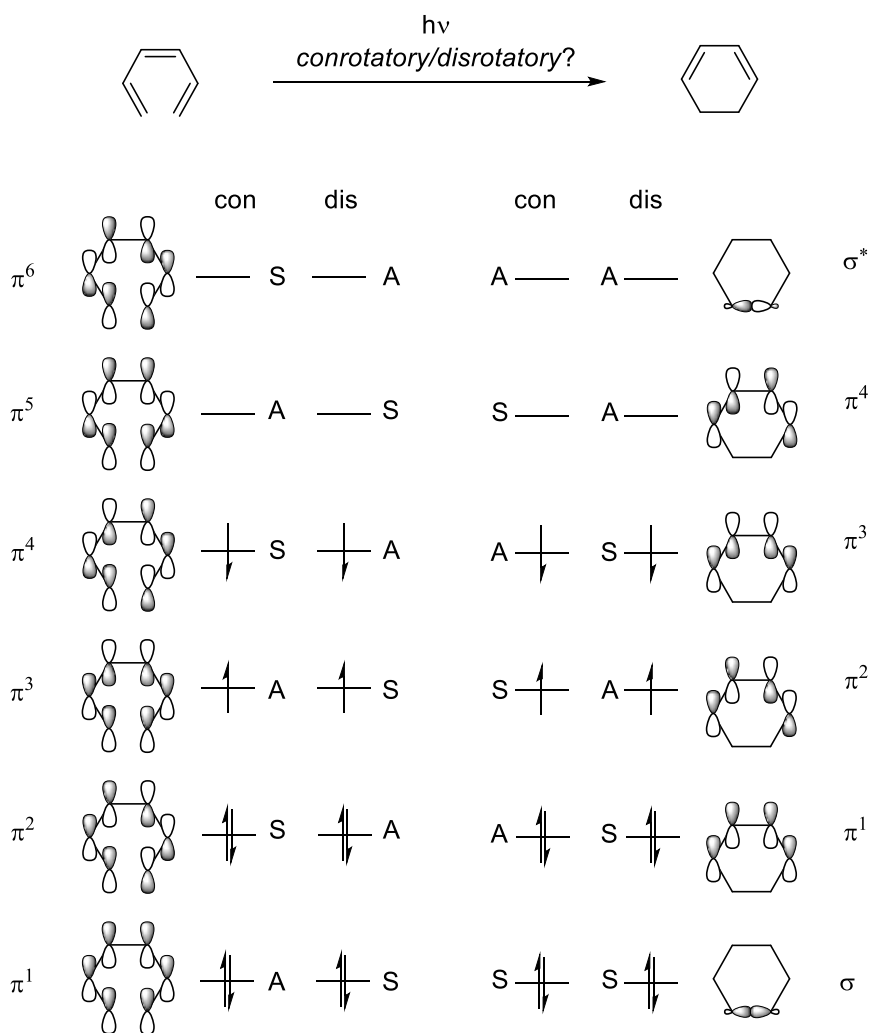
### Exercise 5

The tetracyclic natural product magellanine with six stereogenic centers was efficiently synthesized from commercially available acetovanillone using an oxa-di- $\pi$ -methane rearrangement as a key step. Please fill in the missing products and reagents.



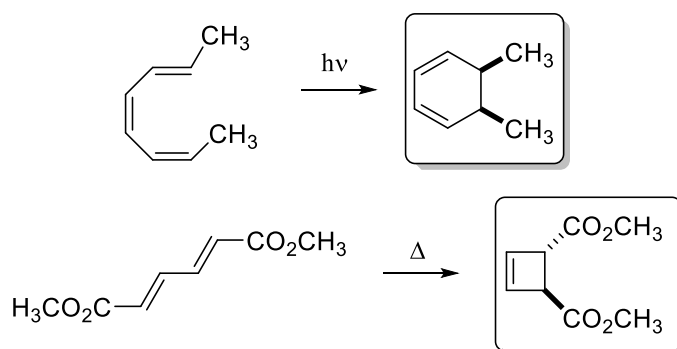
Exercise 1

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?

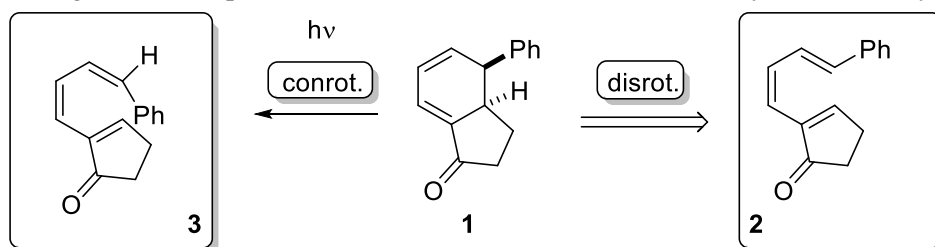


## Exercise 2

a) Fill in both products of the following reactions.



b) Cyclohexadiene **1** was synthesised by a pericyclic reaction under thermal conditions. Which starting material **2** was used? After irradiation of **1** the cyclopentenone **3** was obtained. Explain its different configuration compared to **2**. Do the reactions occur conrotatory or disrotatory?

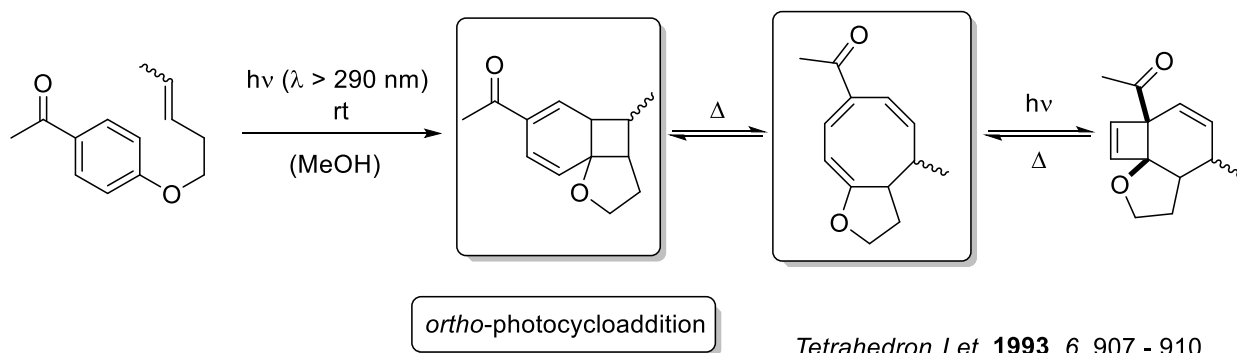


*Synthesis* **2010**, 2233–2244

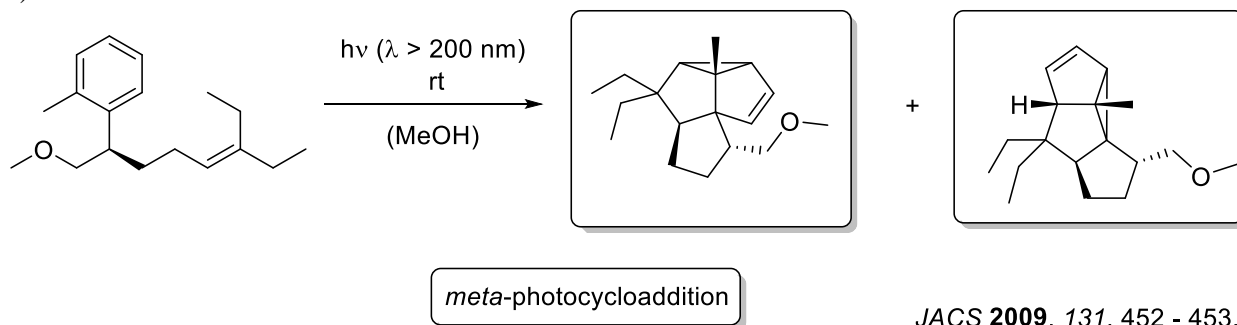
## Exercise 3

Draw the missing structures for the following photochemical reactions. Don't forget to think about the respective mechanisms. Also name the type of reaction [first step for reaction sequence a)].

a)

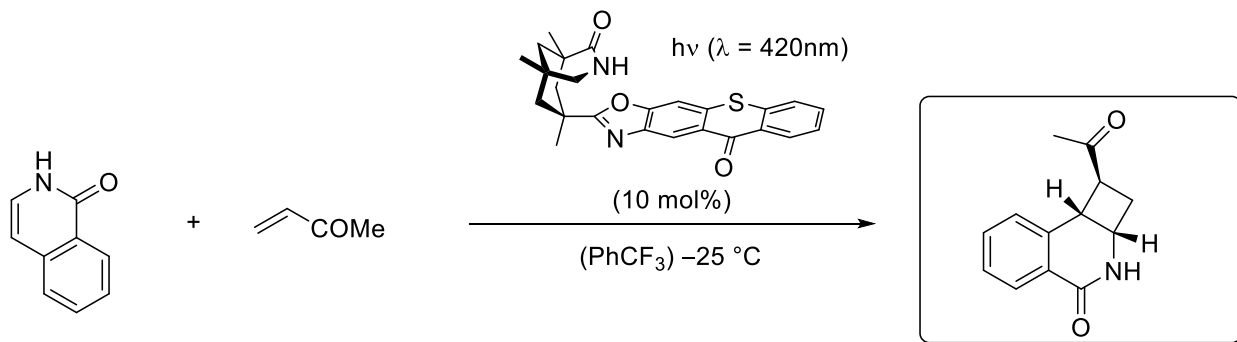


b)



### Exercise 1

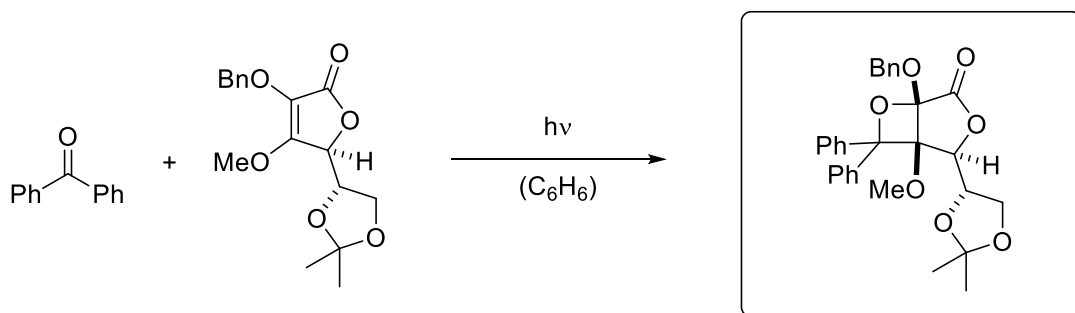
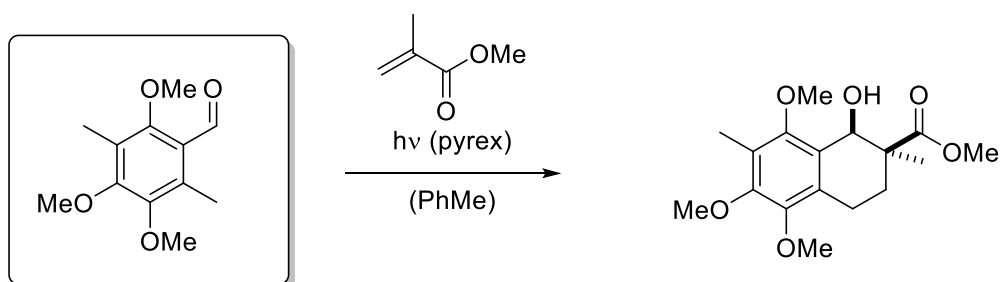
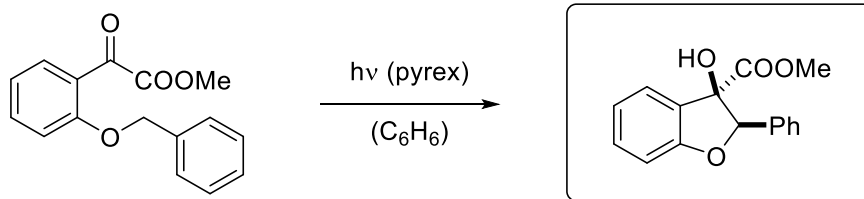
In the presence of the chiral thioxanthone catalyst depicted below, 2(1*H*)-Quinolone undergoes an enantioselective [2+2]-photocycloaddition. Draw the product and predict the absolute stereo configuration.



JACS **2016**, *138*, 7808-7811.

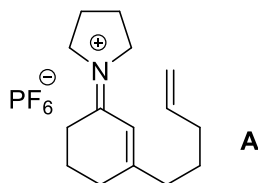
### Exercise 2

Time for some revision: Complete the following reaction schemes by either drawing the starting material or the main product.



### Exercise 3

a) The following redox potential and phosphorescence of iminium ion **A** have been determined, please calculate the redox potential in the ground state and the first excited triplet state. How can the triplet state of **A** be populated?



$$E_{1/2}(\mathbf{A}^+/\mathbf{A}^{\bullet}) = -1.69 \text{ V (vs Ag/AgNO}_3 \text{ in MeCN)}$$

$$\lambda_{\text{em}} = 480 \text{ nm}$$

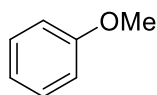
$$E_{1/2}(\mathbf{A}^+/\mathbf{A}^{\bullet}) = -1.69 \text{ V} + 0.30 \text{ V} = -1.39 \text{ V (vs SCE in MeCN)}$$

$$\lambda_{\text{em}} = 480 \text{ nm} \rightarrow E_T = 249 \text{ kJ/mol} = 2.58 \text{ eV}$$

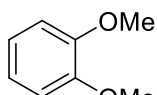
$$\rightarrow E_{1/2}(\mathbf{A}^{+\bullet}/\mathbf{A}^{\bullet}) = +1.19 \text{ V (vs SCE in MeCN)}$$

-population of triplet state only with triplet-sensitizer, no  $n\pi^*$ -transition therefore no ISC possible by direct irradiation.

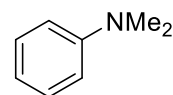
b) Which of the following benzene derivatives undergoes electron transfer with iminium ion **A** in its triplet state? (All redox potentials against SCE in MeCN).



$$E_{1/2}(\mathbf{M}^+/\mathbf{M}) = +1.81 \text{ V}$$



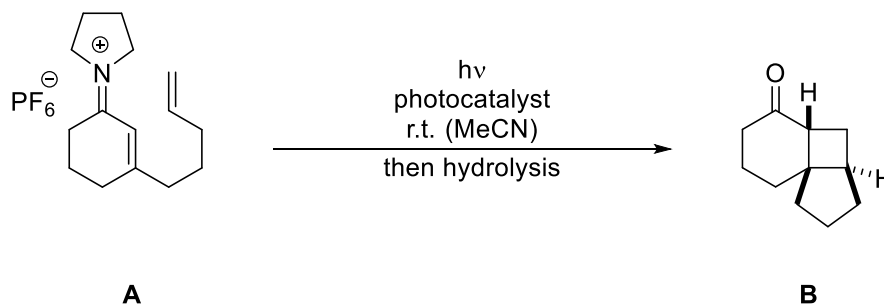
$$E_{1/2}(\mathbf{M}^+/\mathbf{M}) = +1.43 \text{ V}$$



$$E_{1/2}(\mathbf{M}^+/\mathbf{M}) = +0.74 \text{ V}$$

$E^0 > 0$  for SET  $\rightarrow$  only feasible for aniline derivative ( $E_{1/2} < E_{1/2}(\mathbf{A}^{+\bullet}/\mathbf{A}^{\bullet})$ ) redox potential has to be lower for oxidation!

c) From its triplet state iminium ion **A** can undergo a [2+2]-photocycloaddition reaction to give tricyclic ketone **B** after hydrolysis. Which properties of the photocatalyst are required so only energy-transfer is feasible whereas photo-induced electron transfer is not?



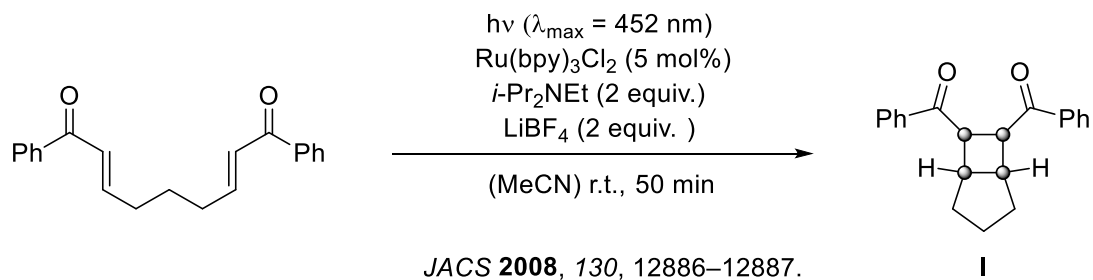
-triplet-energy of photocatalyst has to be higher than 249 kJ/mol

-redox potential in excited state has to be higher than  $-1.39 \text{ V}$   $\rightarrow$  no reduction of iminium ion

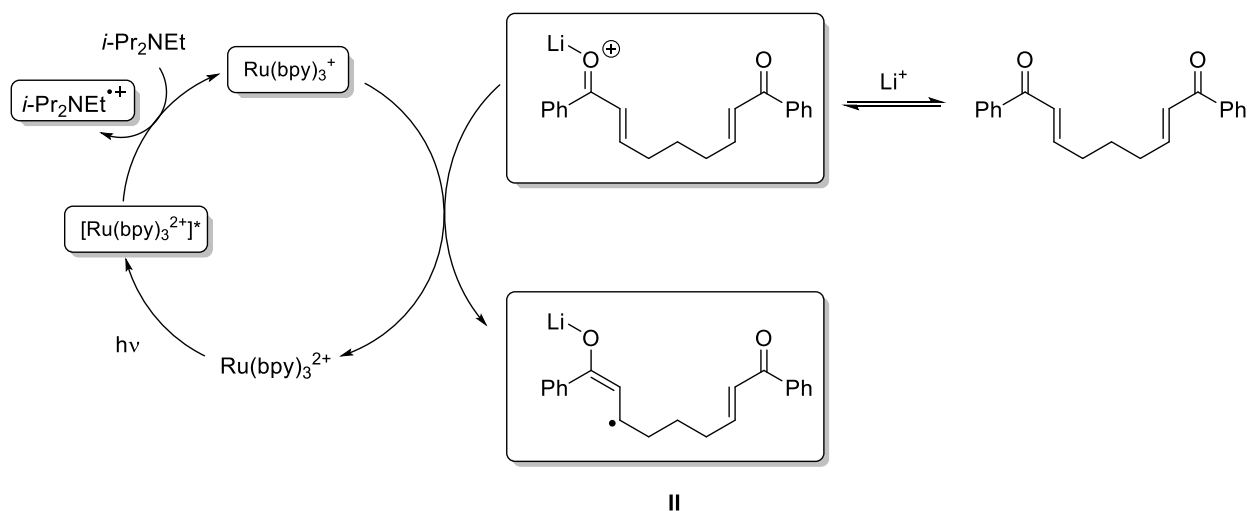


**Exercise 1**

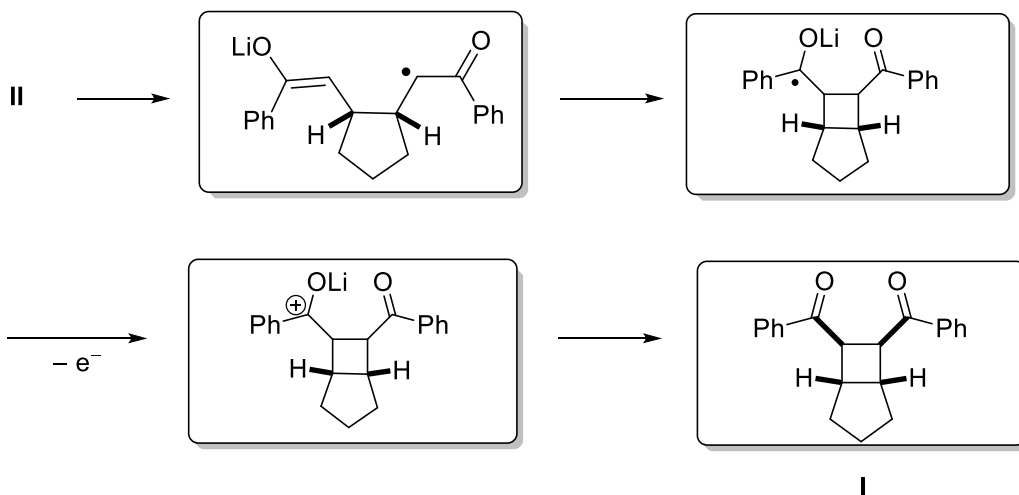
Yoon and co-workers demonstrated that the intramolecular [2+2] cycloaddition of dienones can be promoted by photoredox catalysis. This report showed how photoredox catalysis allows known, redox-mediated processes to proceed under relatively mild conditions to form cyclobutane **I**.



a) Fill out the empty boxes of the photoredox cycle and give the structure of the reactive intermediate **II**. Is the excited catalyst quenched oxidatively or reductively?



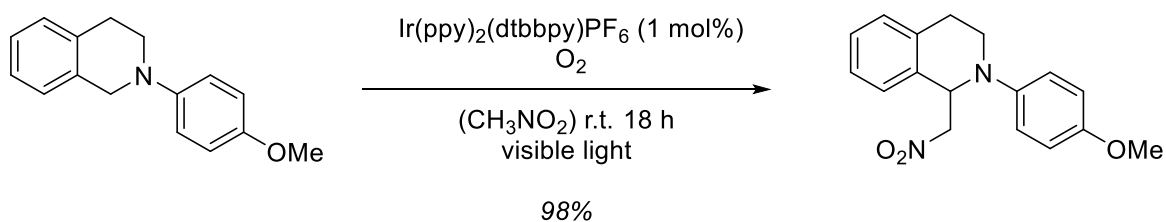
b) How does the reaction proceed from intermediate **II** in order to form product **I**. Show the relative configuration of the formed stereogenic centers.



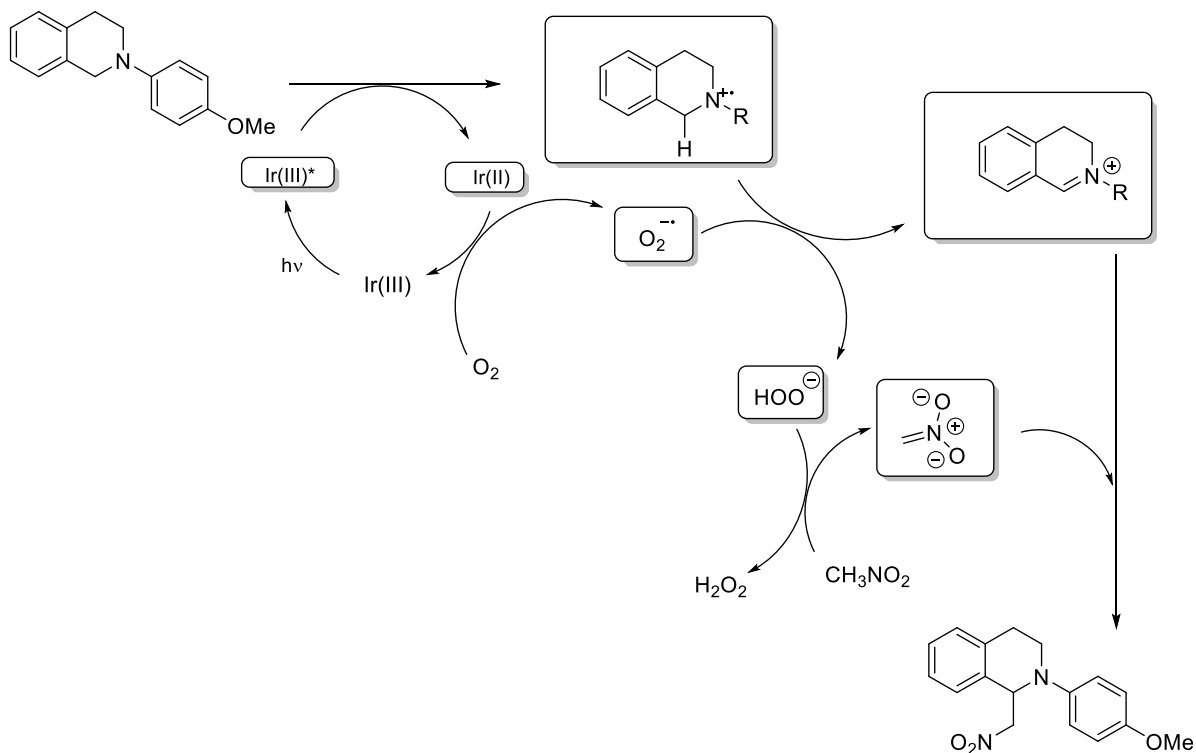
JACS 2008, 130, 12886-12887.

### Exercise 2

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 *via* an iminium ion intermediate. In this case, oxygen acts as the terminal oxidant for this net oxidative process.



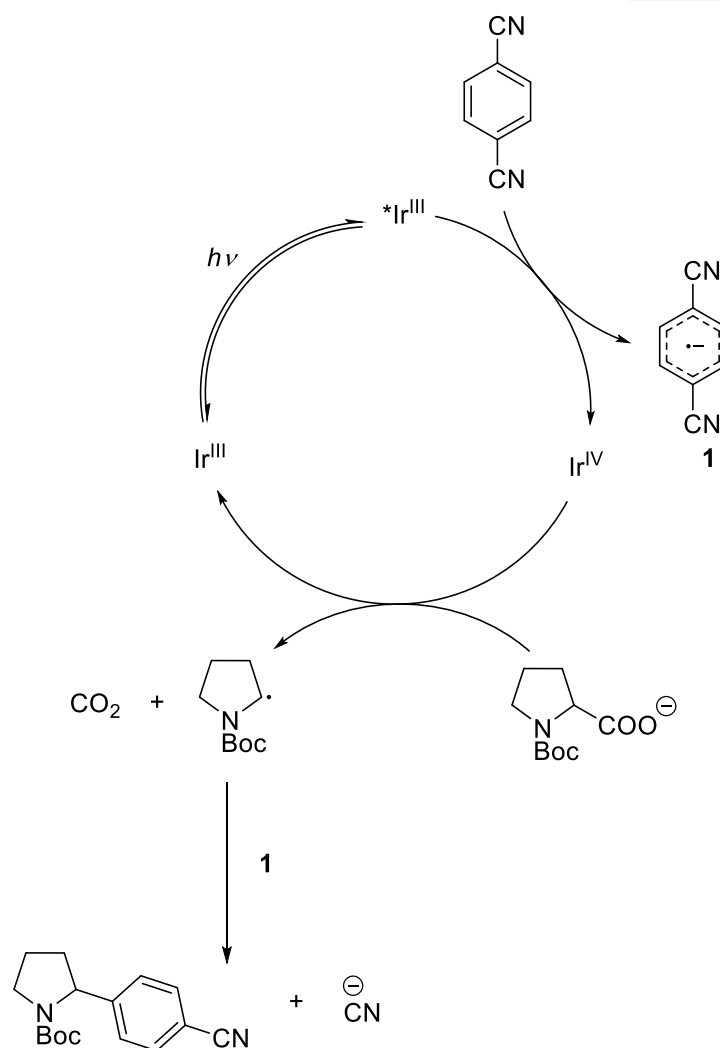
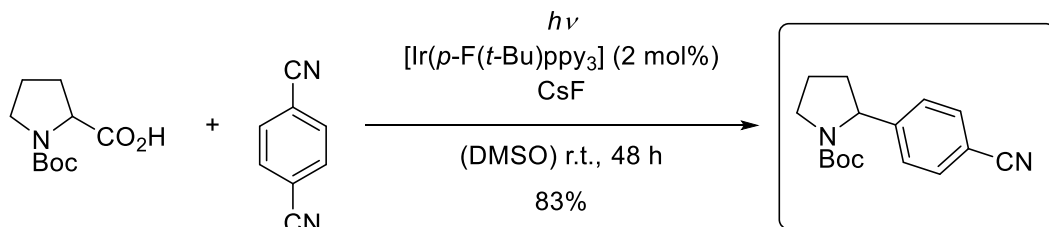
Fill in the missing intermediates, which lead to the formation of the depicted product.



JACS 2010, 132, 1464.

### Exercise 3

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



**Redox neutral:** substrates participate in both the reductive and oxidative steps of the photocatalytic cycle, with no change to the overall oxidation state from starting materials to product.

*J. Am. Chem. Soc.* **2014**, *136*, 5257-5260.

### Exercise 4

The Overman group synthesized the natural product (–)-aplyviolene employing the addition of the tertiary radical generated by photoredox-mediated fragmentation of *N*-(acyloxy)phthalimide **1** to  $\alpha$ -chlorocyclopentenon **2** as the key step. Please give the product of the following reaction and draw the photoredox cycle.

Is the transformation net oxidative, reductive or redox neutral?

*Hint: The alkyl radical attacks the Michael position of 2.*

