Question 1 (overall 10 points)

Topic: The photoredox catalyst

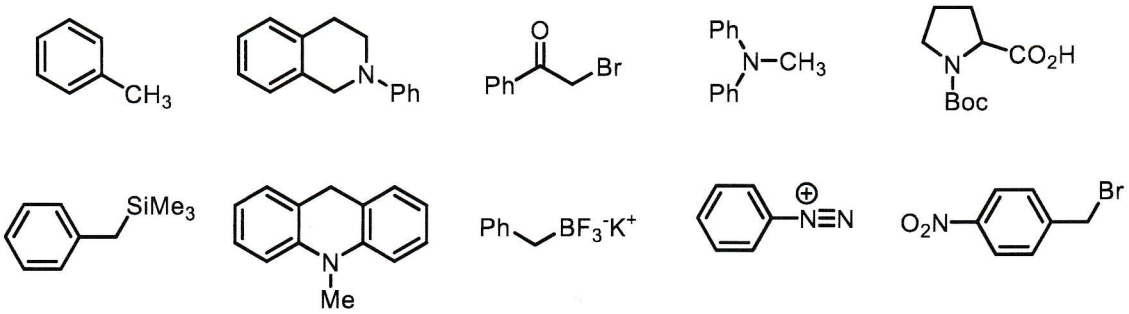
(a) Give an example of a typical photoredox catalyst and provide its chemical structure. (3 P)

(b) Explain the principle of photoredox catalysis and the role of the photoredox catalyst. Please include both oxidative and reductive processes. (6 P)

(c) For which types of photoredox reactions is the term "photoredox catalyst" not accurate? Explain. (1 P)

Question 2 (overall 20 points)

How can the following compounds be converted into carbon radicals using single electron transfer (SET)? Please show the intermediates after the initial SET and the radical products for each compound. (10 x 2 P)



Question 3 (overall 10 points)

Topic: Proton-coupled electron transfer (PCET)

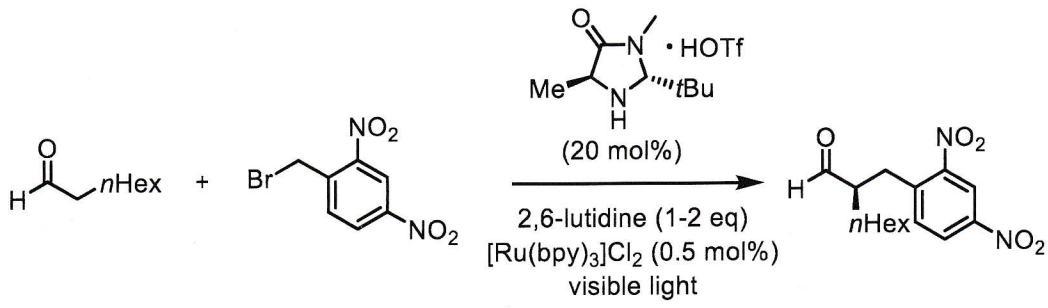
(a) What is PCET? Explain the concept. (2 P)

(b) Provide an example for <u>oxidative</u> PCET and explain. (4 P)

(c) Provide an example for <u>reductive</u> PCET and explain. (4 P)

Question 4 (overall 10 points)

Provide the detailed reaction mechanism for the reaction shown below. Give brief explanations for the individual mechanistic steps. Explain also the stereoselectivity. (8 P)



Additional quest. .: Under certain circumstances, related reactions can be performed by just using the secondary amine and visible light but without any additional photoredox catalyst! What species absorbs the visible light in such systems? (2 P)

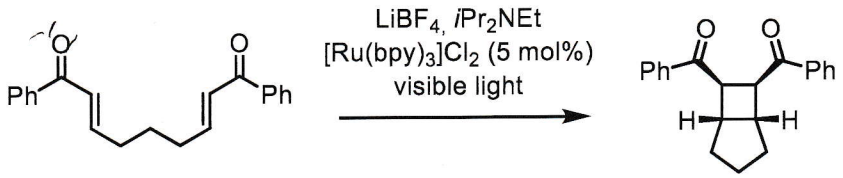
Question 5 (overall 10 points)

Please provide the reaction conditions and mechanism for the nickel-catalyzed cross-coupling of organotrifluoroborates with aryl halides under photoredox conditions.

Question 6 (overall 10 points)

Yoon recently reported an intramolecular [2+2] photocycloaddition catalyzed by $[Ru(bpy)_3]Cl_2$ as shown below.

Explain the detailed stepwise mechanism! Please also provide an explanation for the requirements of $LiBF_4$ and iPr_2NEt as additives.



Question 7 (overall 10 points)

How does photosensitization of [2+2] photocycloadditions work? Provide an example with a detailed mechanism!

Question 8 (overall 10 points)

(a) **Explain a photochemical method to generate singlet oxygen. (4 P)**

(b) **What are the three main reaction pathways of single oxygen with alkenes? Provide an example for each. (3 x 2P)**

Question 9 (overall 10 points)

What is the Hoffmann-Löffler-Freytag reaction? Provide an example and show the detailed mechanism.