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Chapter 1

Organic Reactions Promoted by Metal-Free Organic Dyes Under Visible Light Irradiation

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Additional information is available at the end of the chapter

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Abstract

Although dyes have received much attention as the visible light-activated photocatalysts, the use of metal-free organic dyes in synthetic organic chemistry is still limited. This chapter summarizes the recent progress in the visible light photocatalysis promoted by metal-free organic dyes. Eosin Y is the typical organic dyes to induce the photoredox catalysis. Recently, other organic dyes such as Rose Bengal, fluorescein, and methylene blue have been studied as photocatalysts to promote the single-electron transfer processes.

Keywords: photocatalyst, organocatalyst, dye, catalysis, visible light, radical

1. Introduction

The use of abundant sunlight as a clean source of energy is an important aim of green chemistry. In recent years, dyes have attracted a great deal of attention as the visible light-activated photocatalysts in synthetic organic chemistry. However, these studies have mainly concentrated on the redox transformations using transition metal dyes such as ruthenium or iridium photocatalysts [1–9]. In contrast, the use of metal-free dyes still remains rather underdeveloped, although organic dyes are more environmentally friendly and cheaper. Eosin Y is the typical organic dyes to induce the photoredox catalysis [10]. Recently, Rose Bengal, fluorescein, methylene blue, and other organic dyes have been studied as photocatalysts to promote the single-electron transfer processes [11–13]. Additionally, 3-cyano-1-methylquinolinium, 9-mesityl-10-methylacridinium ion, and acridinium salts were developed as organic photocatalysts [12, 13].

The photoredox cycle is initiated by the visible light irradiation of dye in the ground state to produce the high-energy excited state of dye (Dye*) (**Figure 1**). Two distinctive pathways

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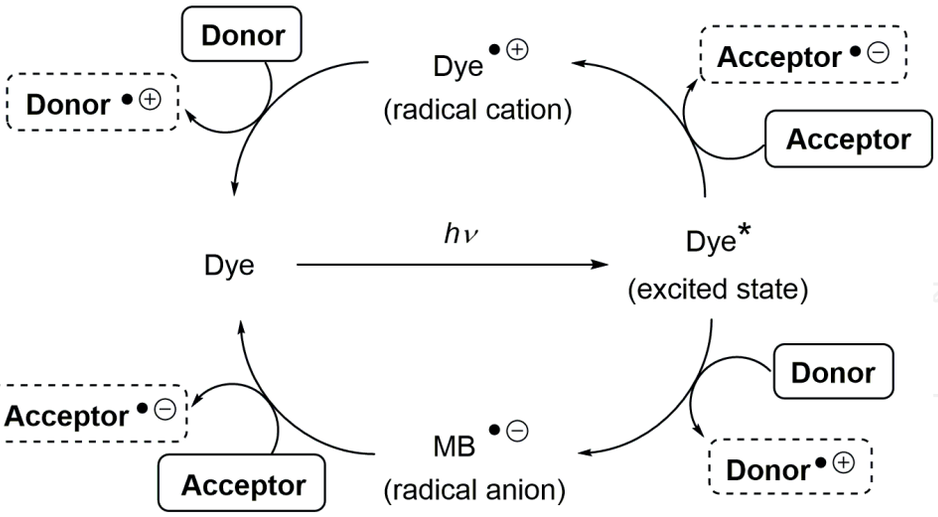


Figure 1. Dye-catalyzed photoredox cycle.

from dye in the excited state (Dye*) are described for the mechanism of visible light photoredox catalysis. The reductive property of Dye* can be used in the presence of a sacrificial electron acceptor. In other words, Dye* serves as an electron donor leading the radical cation species of Dye. In contrast, Dye* also acts as an electron acceptor in the presence of a sacrificial electron donor.

2. Eosin Y and eosin B

Eosin Y (EY) is the typical organic dye to induce the synthetically useful photoredox transformations [14–30]. EY that absorbed visible light populates in the lowest excited singlet state. The subsequent spin-forbidden singlet-triplet intersystem crossing affords EY in the excited triplet state. A variety of photoredox transformations are induced by the single-electron transfer from EY in the excited triplet state. In 2014, König provides the review article concerning the utility of EY as a photocatalyst in synthetic organic chemistry [10]. Therefore, this section highlights the recent remarkable progress in the EY-catalyzed photoredox transformations.

The EY-catalyzed generation of aryl radicals from aryl diazonium salts was studied by König's group [14]. The direct C–H bond arylation of heteroarenes with aryl diazonium salts was achieved by employing only 1 mol% of EY (**Figure 2**). The arylation of furan with diazonium salt **1** in dimethyl sulfoxide (DMSO) proceeded smoothly under the visible light irradiation to give the desired coupling product **2** in 85% yield. This transformation proceeds through the radical mechanism. Initially, aryl radical is produced by the single-electron transfer from the excited EY (EY*) to aryl diazonium salt **1**. The addition of aryl radical to furan leads to the formation of the radical intermediate **A**, which is further oxidized to cation intermediate **B**. Final deprotonation gives the coupling product **2**. Next, the EY-catalyzed arylation of simple arenes with fluorinated aryl bromides was developed [15]. In the presence of EY (5 mol%) and triethylamine as an electron donor, the direct arylation using 1-bromo-2,3,4,5,6-pentafluorobenzene **3** and benzene gave the coupling product **4** in 85% yield. The mechanistic investigations reveal that the photooxidation of

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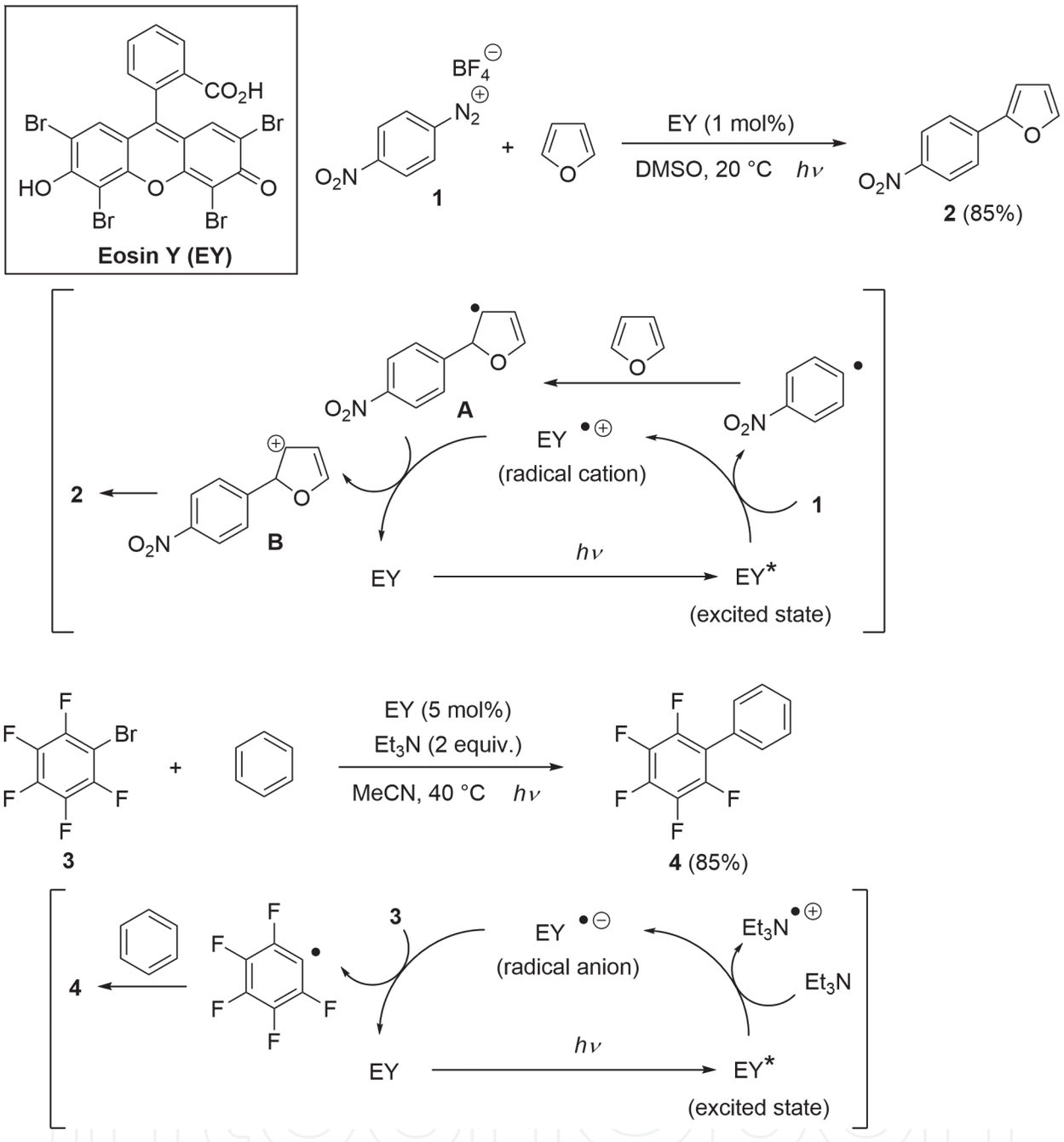


Figure 2. EY-catalyzed generation of aryl radicals and coupling reactions.

triethylamine by the excited EY (EY*), and the subsequent single-electron transfer from the radical anion species of EY to **3** leads to the formation of the polyfluorinated aryl radical. The mild visible light-mediated generation of aryl radicals from diazonium salts was also investigated by Wangelin's group [16–18]. The coupling reaction catalyzed by EY was investigated with no use of any sacrificial oxidants [19, 20].

The vinyl sulfones were synthesized by the EY-catalyzed reaction of alkenes with sodium aryl sulfinates [21]. The reaction of 1,2-dihydronaphthalene **6** with sodium benzenesulfinate **5** was performed in the presence of EY (10 mol%) and nitrobenzene as a terminal oxidant (**Figure 3**).

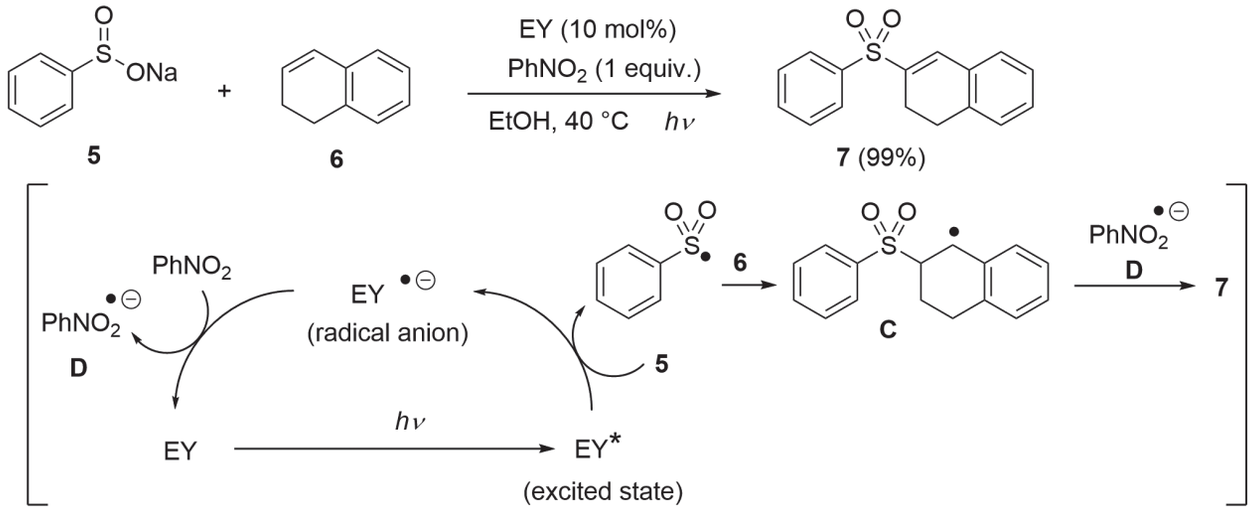


Figure 3. EY-catalyzed reaction using sodium benzenesulfinate.

The desired vinyl sulfone **7** was obtained in 99% yield. In this reaction, sodium sulfinate **5** is oxidized by the excited EY (EY*) to give the sulfonyl radical, which attacks the double bond of **6** to form the radical intermediate **C**. Nitrobenzene oxidizes the radical cation species of EY to give EY in the ground state and the radical anion species **D** of nitrobenzene, which reacts with radical intermediate **C** to give the vinyl sulfone **7**.

The oxidative cyclization reaction between 3-phenylpropiolate **8** and 4-methylbenzenesulfinic acid **9** was studied (**Figure 4**) [22]. In the presence of EY (1 mol%) and *tert*-butyl hydroperoxide (TBHP), the reaction between **8** and **9** was performed in MeCN–H_2O (1:1, v/v) under the

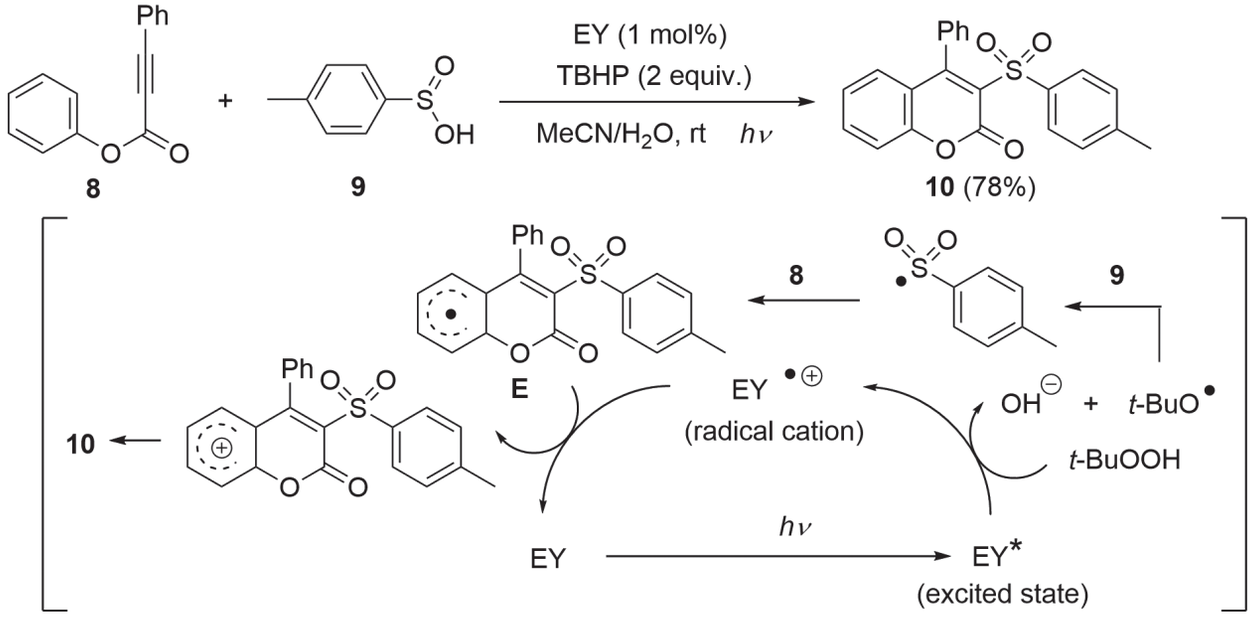


Figure 4. EY-catalyzed reaction using 4-methylbenzenesulfinic acid.

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visible light irradiation. The desired coumarin **10** was obtained in 78% isolated yield. Initially, *tert*-butoxyl radical is produced by the single-electron transfer from the excited EY (EY*) to TBHP. The cyclization reaction is promoted by the addition of sulfonyl radical, generated from sulfinic acid **9** and *tert*-butoxyl radical, to alkyne moiety of **8**. The coumarin **10** is formed *via* the oxidation of the cyclized radical intermediate **E** by the radical cation species of EY.

The EY-catalyzed cyclization of 2-isocyanobiphenyls with arylsulfonyl chlorides took place under the oxidant-free visible light irradiation conditions [23]. In the presence of K_2HPO_4 as a base, the EY-catalyzed reaction of benzenesulfonyl chloride **11** and 2-isocyanobiphenyl **12** proceeded smoothly to give the 6-phenyl-substituted phenanthridine **13** in 79% yield (**Figure 5**). Initially, the single-electron transfer from the excited EY (EY*) to sulfonyl chloride **11** gives the phenyl radical, which adds to isocyanide **12** to form the imidoyl radical intermediate **F**. The subsequent cyclization gives the cyclized radical intermediate **G**, which is oxidized by the radical cation species of EY. Finally, the deprotonation leads to **13**.

EY could be used as the photocatalyst for the 5-*exo*-trig cyclization of iminyl radicals generated from *O*-aryl oximes [24]. Among several aryl oximes evaluated, 2,4-dinitro-substituted aryl oxime **14** has the excellent reactivity due to its low reduction potential (**Figure 6**). In the presence of cyclohexadiene (CHD) as a H-donor, EY-catalyzed photoreaction of **14** gave the cyclized product **15** in 78% yield. In this transformation, the iminyl radical **I** is generated *via* the reduction of **14** by the excited EY (EY*) followed by the fragmentation of radical anion **H**. The cyclization of **I** gives the cyclized *C*-centered radical **J**, which abstracts H-atom from CHD to give the desired product **15**. Furthermore, the formation of product **15** was observed even in the absence of EY, when the MeCN solution of **14** was treated with Et_3N under the visible

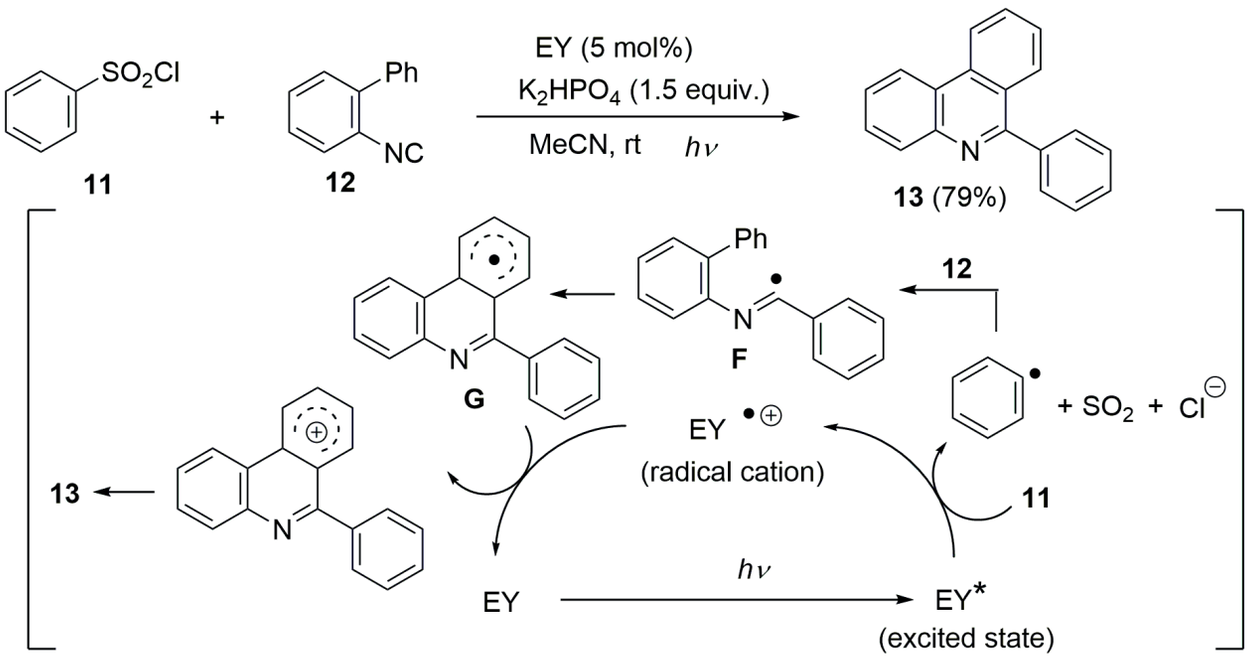


Figure 5. EY-catalyzed cyclization of 2-isocyanobiphenyl.

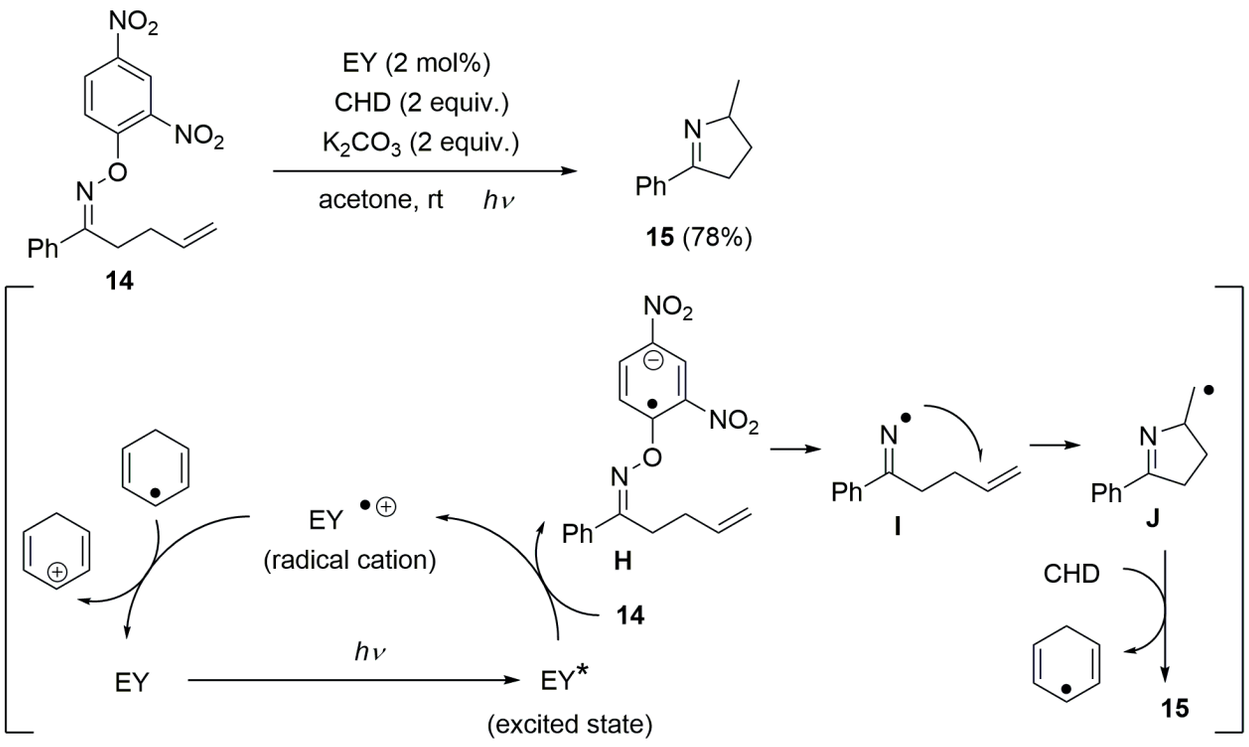


Figure 6. EY-catalyzed cyclization of 2,4-dinitro-substituted aryl oxime.

light irradiation. In this case, the visible light-mediated electron transfer would be induced by the formation of donor-acceptor complex between Et_3N and 2,4-dinitrophenyl group of **14**.

The EY-induced photocatalysis was applied to the radical cascade cyclization of polyenes [25]. The photocatalytic cascade cyclization of polyene **16** proceeded by employing EY (**Figure 7**). Hexafluoro-2-propanol (HFIP) was identified as the optimal solvent. The cyclized product **17** was obtained in 93% yield with the excellent diastereoselectivity *via* the radical cation intermediate **K** generated by the single-electron transfer from **16** to the excited EY (EY*). In this process, the OH moiety of **16** would act as a terminator.

Eosin B is also the active catalyst under the visible light irradiation [31]. The C–H functionalization of thiazole derivatives with diarylphosphine oxides was achieved by the eosin B-catalyzed photoredox process. When eosin B was employed as a photocatalyst, the phosphorylation of benzothiazole **18** with diphenylphosphine oxide proceeded effectively to give the phosphorylation product **19** in 87% yield (**Figure 8**). In this transformation, hydrogen (H_2) is the only by-product.

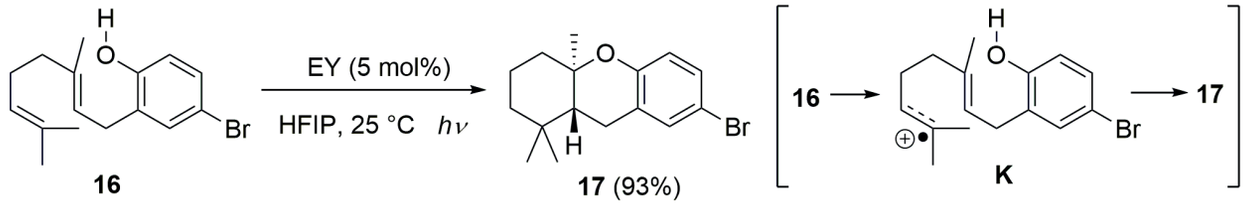


Figure 7. EY-catalyzed cascade cyclization of polyene.

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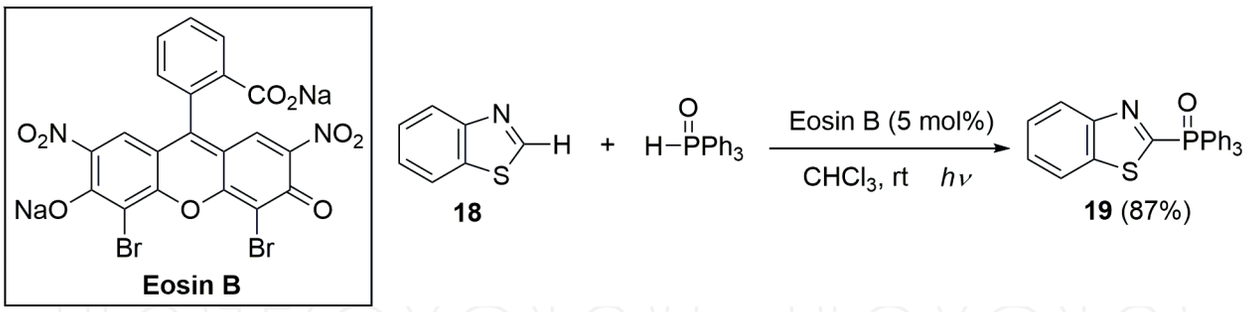


Figure 8. Eosin B-catalyzed phosphorylation of benzothiazole.

3. Rose Bengal

Rose Bengal (RB) was widely used as a visible light-activated photocatalyst [32–44]. Tan's group studied the photoredox catalysis using RB [32–36]. RB was a good catalyst for the dehydrogenative coupling reaction between tetrahydroisoquinolines and nitroalkanes (**Figure 9**) [33]. In the presence of RB (5 mol%), the reaction of *N*-phenyl-tetrahydroisoquinoline **20** with nitromethane gave the adduct **21** in 92% yield. In the absence of O_2, a much lower yield was obtained relative to the reaction performed in open air; thus, air is important for this reaction as an oxidant. Additionally, this reaction was expanded to the dehydrogenative Mannich reaction using enamine nucleophiles generated from ketones and pyrrolidine.

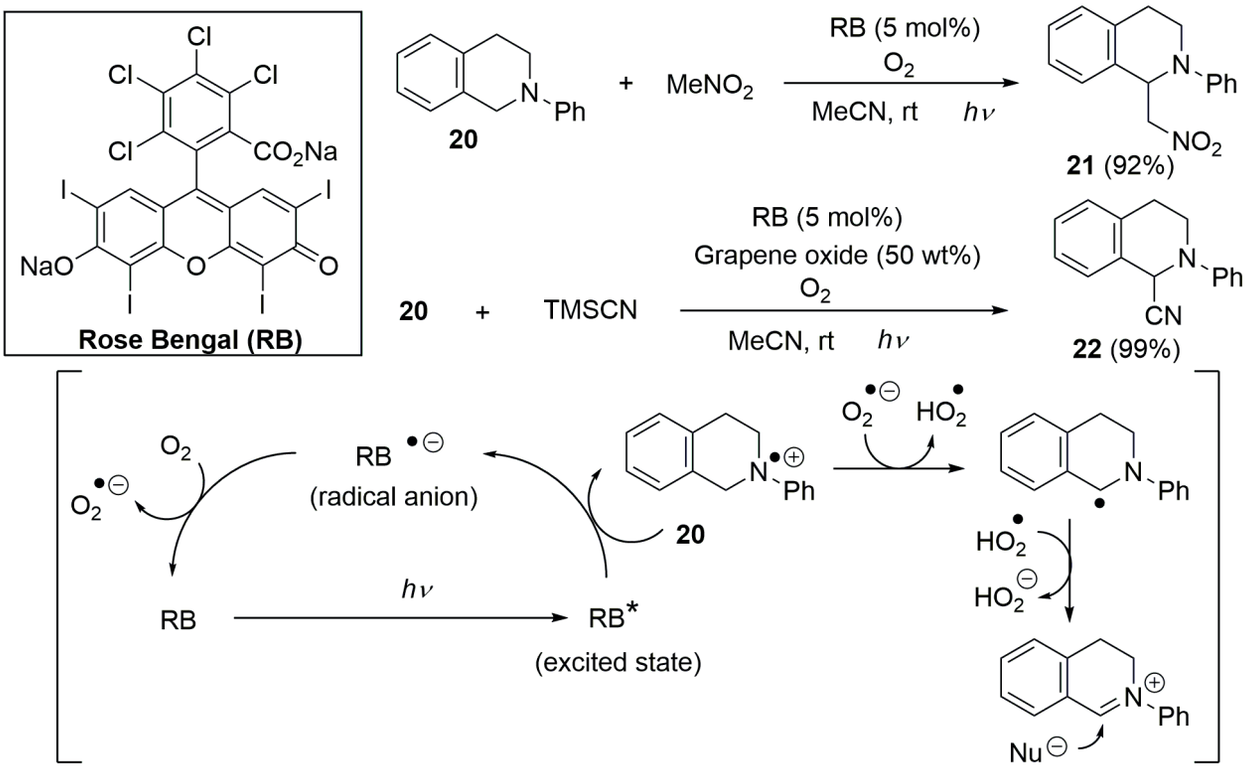


Figure 9. RB-catalyzed reaction of tetrahydroisoquinoline.

Next, the combination of graphene oxide and RB was studied in the reaction between tetrahydroisoquinolines with TMSCN or $TMSCF_3$ [34]. In the presence of RB (5 mol%) and graphene oxide (50 wt%), the reaction of **20** with TMSCN proceeded effectively to give the adduct **22** in 99% yield, while the yield of **22** decreased to 45% in the absence of graphene oxide. The use of graphene oxide as a cocatalyst improves the reaction rates and yields.

New method for the synthesis of Meyers's bicyclic lactams was developed by using RB photocatalysis [37–39]. This cascade transformation is the one-pot reaction which begins from furan substrates (**Figure 10**) [37]. Despite the extraordinary complexity of reaction cascade, the reaction between 2-methylfuran **23** and L-serine ethyl ester **24** led to the formation of bicyclic lactam **25** in 68% yield. At first, RB promotes the photooxidation of methylfuran **23** with singlet oxygen in MeOH. The intermediate **L** is formed by the in situ reduction of hydroperoxy with Me_2S. The next reaction of **L** with L-serine ethyl ester **24** gives the intermediate **M**, which is converted to 2-pyrrolidinone **N** *via* imino enal. Actually, 2-pyrrolidinone **N** could be isolated by the flash column chromatography using silica gel neutralized by trimethylamine. Finally, treatment of **N** with TFA gives the bicyclic lactam **25** as the final product of one-pot reaction cascade.

The aerobic visible light-promoted indole C3 formylation reaction was achieved by using RB as a photocatalyst and *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMEDA) as a one-carbon source (**Figure 11**) [40]. Upon the irradiation of visible light, the reaction of *N*-methylindole **26** with TMEDA in the presence of RB (5 mol%) and KI as an additive under air afforded 3-formyl-*N*-methylindole **27** in 70% yield. This transformation proceeds *via* the addition of *N*-methylindole **26** to iminium ion **O** generated by the oxidation of TMEDA. Next, the C3 thiocyanation reaction of indoles was developed by using ammonium thiocyanate (NH_4SCN) as a thiocyanate radical source [41]. In the presence of RB (1 mol%), the reaction of indole **28** with NH_4SCN gave the adduct **29** in 98% yield. In this reaction, thiocyanate radical is generated by the single-electron transfer between thiocyanate anion and the excited RB (RB*). The thiocyanate radical adds to indole **28**. The subsequent oxidation leads to **29**.

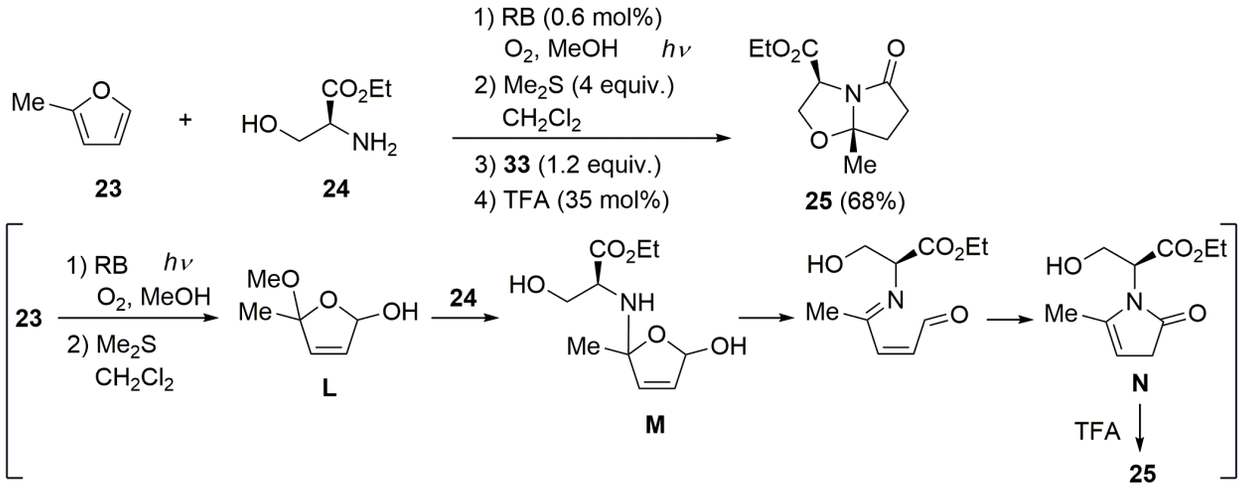


Figure 10. RB-catalyzed synthesis of bicyclic lactam.

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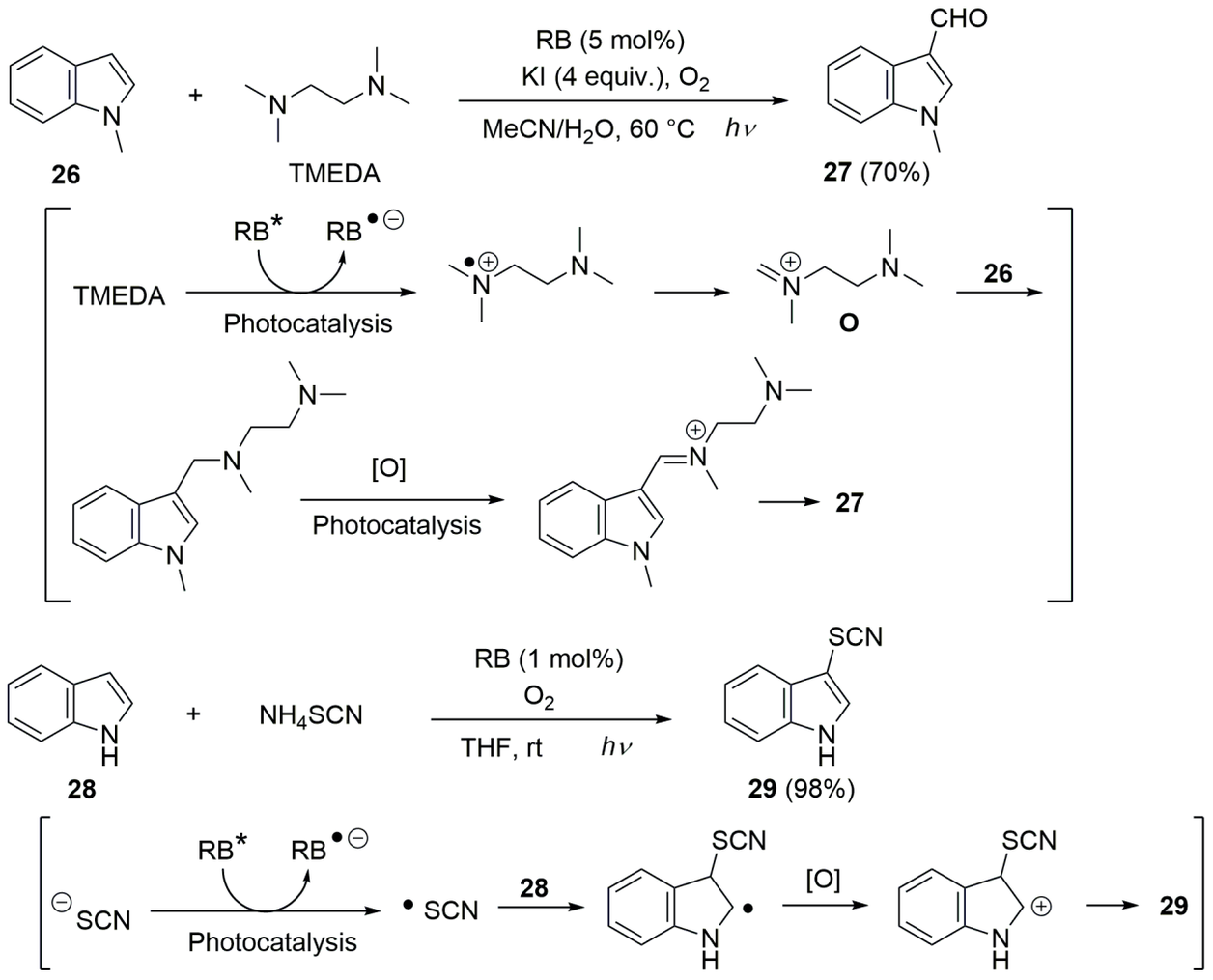


Figure 11. RB-catalyzed functionalization of C3 in indoles.

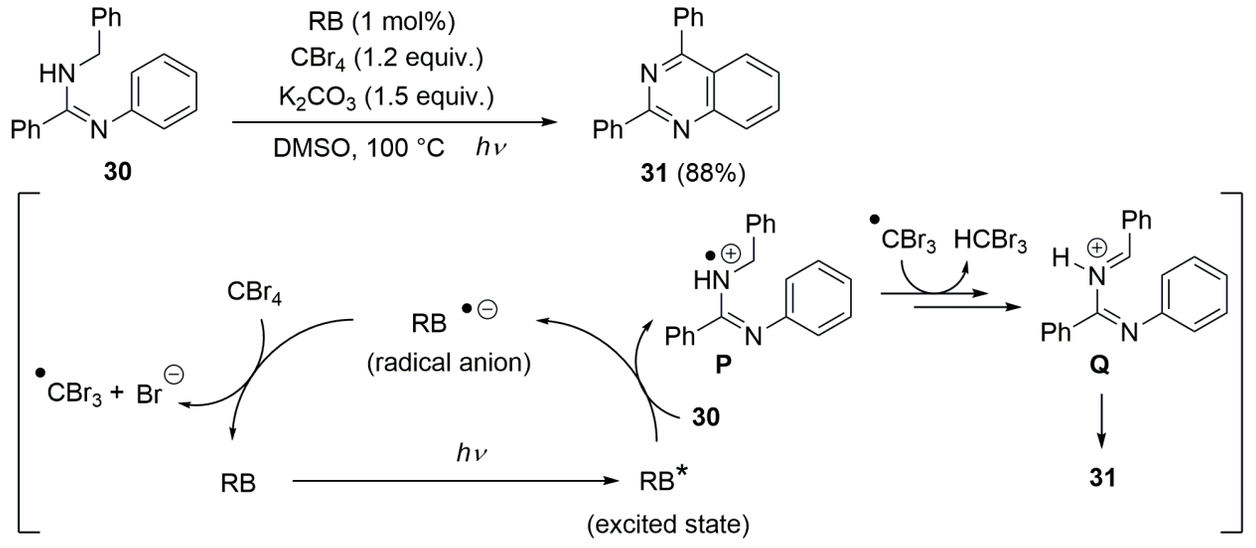


Figure 12. RB-catalyzed oxidative cyclization of benzimidamide.

The new method for the synthesis of quinazolines was developed by using RB as a photocatalyst (**Figure 12**) [42]. In the presence of RB (1 mol%), CBr_4 as an oxidant, and K_2CO_3 as a base, the oxidative carbon-carbon bond-forming cyclization of *N*-benzyl-*N*′-phenyl benzimidamide **30** proceeded smoothly under the visible light irradiation. The desired quinazoline **31** was obtained in 88% yield. In this transformation, CBr_3 radical is generated by the reaction between CBr_4 and the radical anion species of RB. Next, the iminium ion intermediate **Q** is formed from the radical cation intermediate **P** by the association of CBr_3 radical. Finally, the intramolecular Friedel-Craft reaction of iminium ion **Q** leads to quinazoline **31**.

4. Fluorescein and rhodamine B

The utility of fluorescein was demonstrated in the alkoxycarboxylation of aryldiazonium salts using CO gas [45]. In the presence of 0.5 mol% of fluorescein as a photocatalyst, treatment of diazonium tetrafluoroborate **32** with CO (80 atm pressure) in methanol under the irradiation of visible light gave methyl ester **33** in 80% yield (**Figure 13**). Initially, the phenyl radical is generated from diazonium **32** by the single-electron transfer from the excited state of fluorescein (Dye*). Next, benzoyl radical **R** is formed *via* trapping of CO molecule by phenyl radical. The methyl ester **33** is obtained *via* the oxidation of benzoyl radical **R** by the reactive radical cation species of dye followed by trapping of the resulting benzylidyneoxonium **S** with methanol. Furthermore, the dual catalytic system using photocatalyst and gold catalyst was studied by Glorius's group [46].

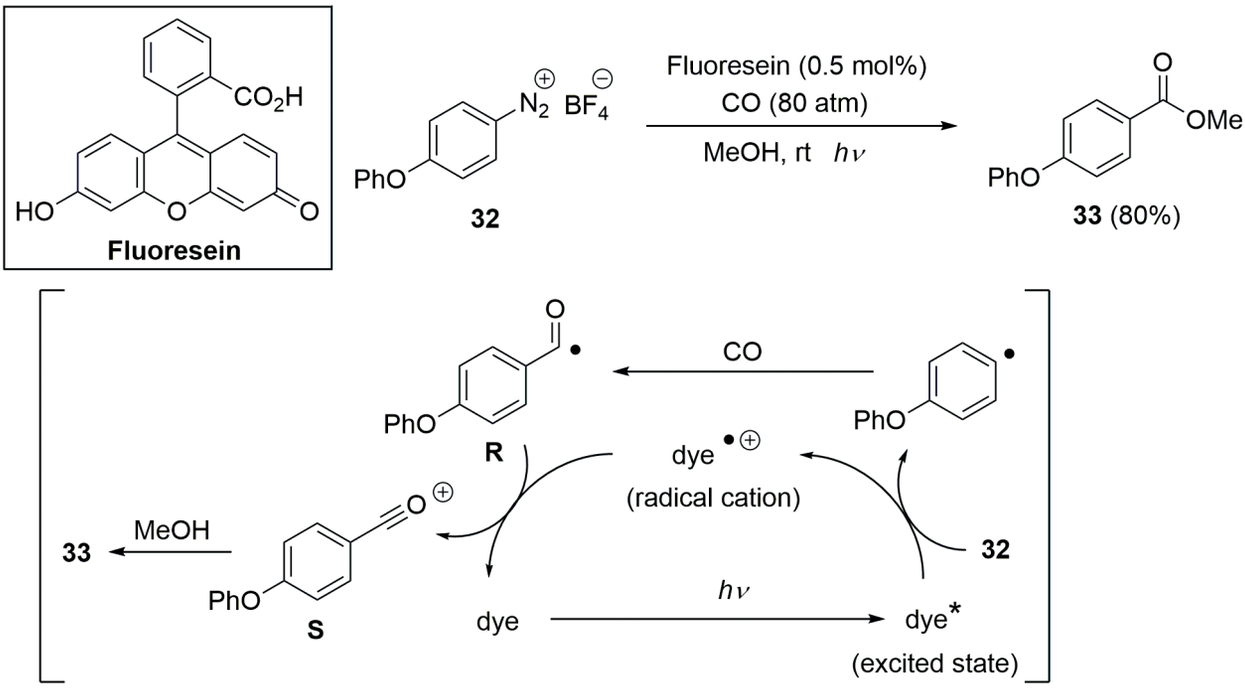


Figure 13. Fluorescein-catalyzed alkoxycarboxylation of aryldiazonium.

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The utility of rhodamine B as a water-soluble photocatalyst was demonstrated in the aqueous-medium carbon-carbon bond-forming radical reactions [47]. In the presence of $(i\text{-Pr})_2NEt$ as a reductive quencher, the rhodamine B-catalyzed reaction of alkene **34** with $i\text{-}C_3F_7I$ in H_2O proceeded smoothly to give the product **35** in 90% yield (**Figure 14**). In this transformation, the photo-induced electron transfer from the excited singlet state (S_1) of rhodamine B to $i\text{-}C_3F_7I$ was proposed. This electron transfer process was supported by the fluorescence quenching of rhodamine B with addition of $i\text{-}C_3F_7I$. Additionally, the aqueous-medium radical addition-cyclization-trapping reaction of **36** proceeded effectively even in the absence of $(i\text{-Pr})_2NEt$. In this transformation, the single-electron transfer from iodine ion (I^-) to the radical cation species of rhodamine B in an ion pair would proceed to give I_2, because the oxidation potential of rhodamine B is positive enough to oxidize I^- into I_2.

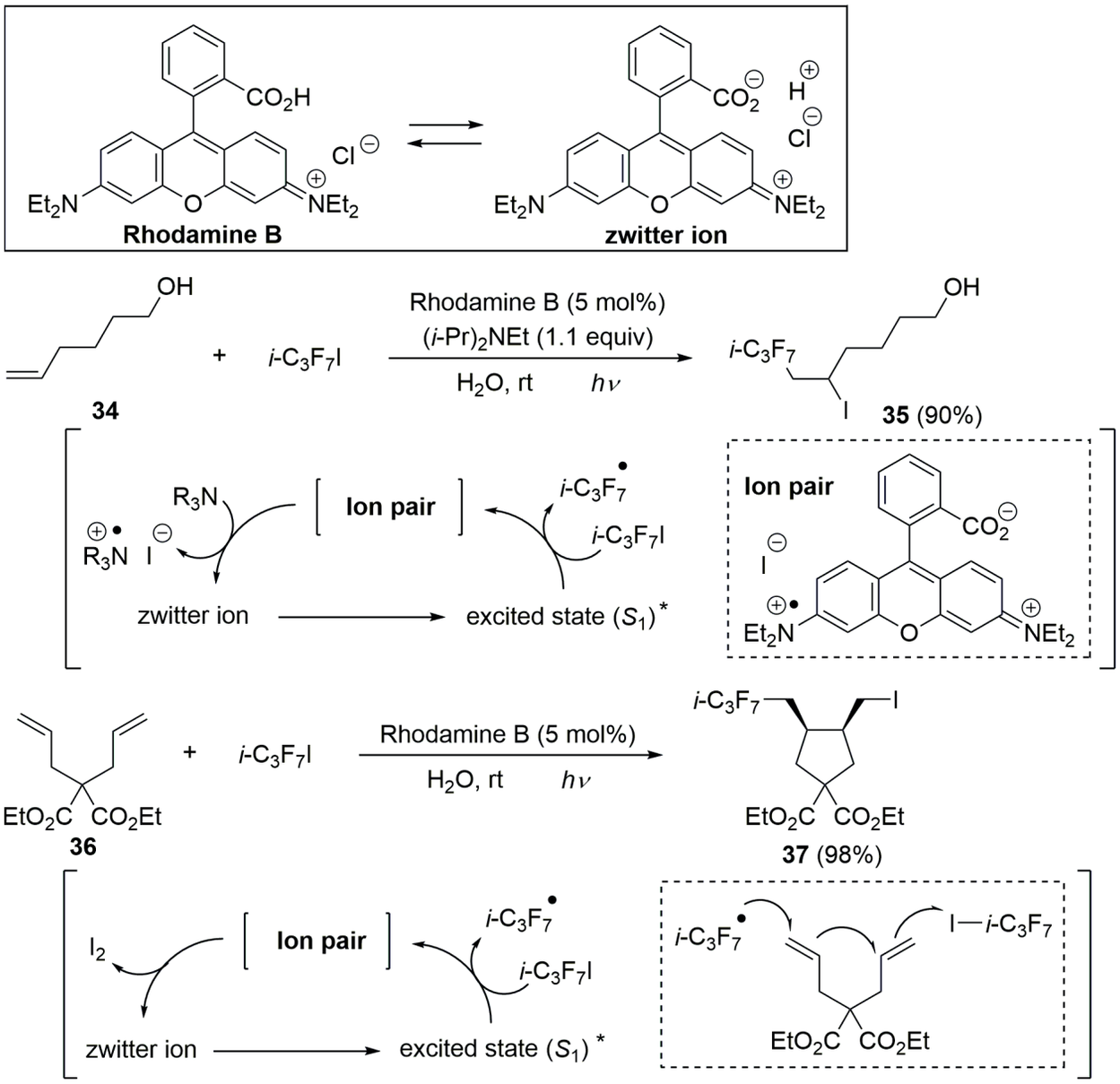


Figure 14. Rhodamine B-catalyzed aqueous-medium radical reactions.

5. Methylene blue and acridine red

Methylene blue (MB) is a member of the thiazine dye family. Scaiano's group used MB as a photocatalyst under the visible light irradiation [48]. The radical trifluoromethylation of electron-rich heterocycles was studied by the use of Togni's reagent **39** as a CF_3 radical source (**Figure 15**). The trifluoromethylation of 3-methylindole **38** proceeded with good yield at low catalyst concentration, when *N*,*N*,*N′*,*N′*-tetramethylenediamine (TMEDA) was used as an electron donor. In the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as an electron donor, the reaction of terminal alkene **41** with Togni's reagent **39** also gave the hydrotrifluoromethylation product **42** in 67% yield as a major product, because the fully reduced form of MB, leuco-MB, acts as a hydrogen source [49]. The possible mechanism for the catalytic formation of CF_3 radical is shown. The visible light-excited MB (MB*) is readily quenched by aliphatic amines such as TMEDA or DBU to form the semi-reduced MB as a radical anion and an α-amino radical. CF_3 radical is generated *via* the reduction of Togni's reagent **39** with semi-reduced MB and/or an α-amino radical.

The one-pot transformation of furans into 5-hydroxy-1*H*-pyrrol-2(5*H*)-ones was investigated by using MB as a photocatalyst [50]. In the presence of MB (2 mol%) and oxygen, the reaction of furan **43** with benzylamine gave lactam **44** in 72% yield *via* the reduction of the intermediate by

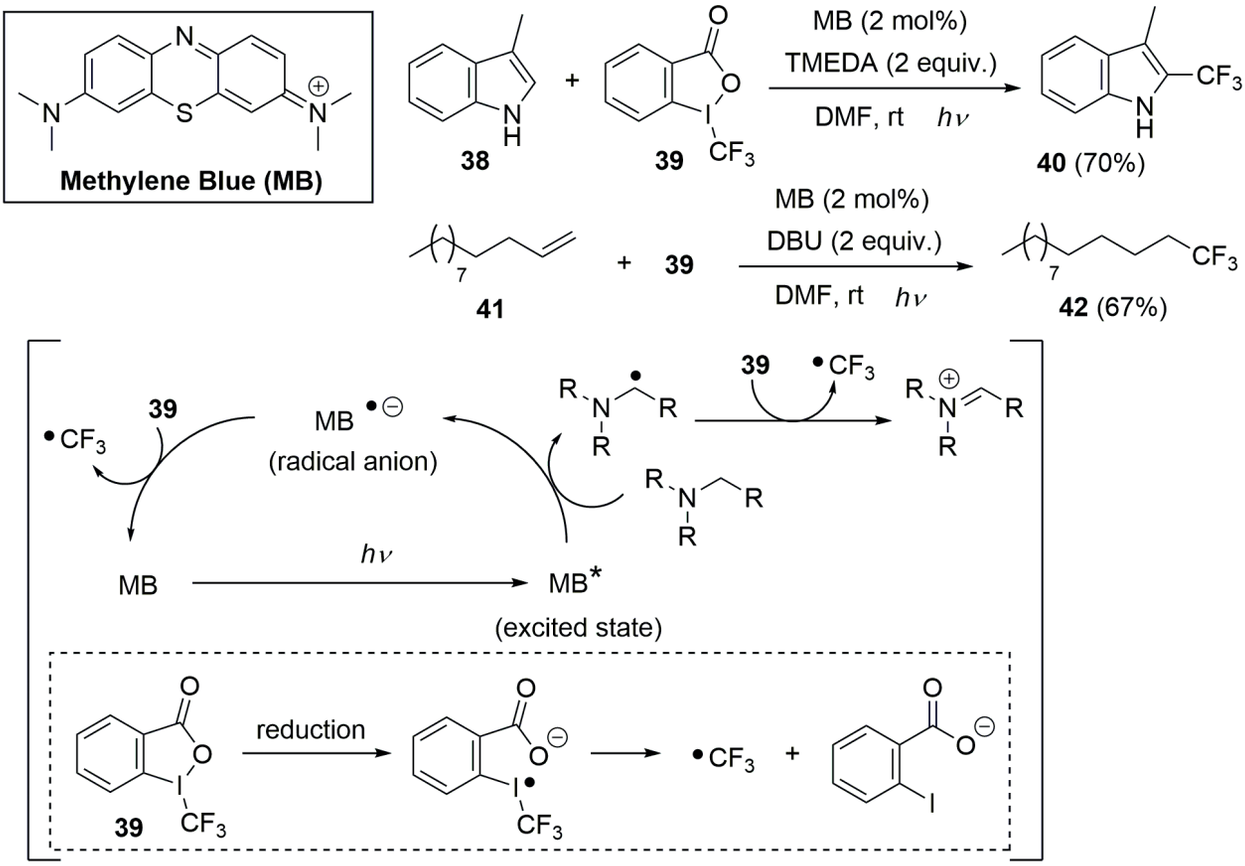


Figure 15. MB-catalyzed trifluoromethylation using Togni's reagent.

Me_2S (**Figure 16**). The use of 2-(3,4-dimethoxyphenyl)ethanamine **45** instead of benzylamine led to the formation of tricycle **46** *via* Pictet-Spengler cyclization process. For Pictet-Spengler cyclization, HCOOH was added as an acid leading to *N*-acyliminium ion, which spontaneously cyclized to form **46**.

New phenothiazine-based organic dye was also developed as a visible light-activated photocatalyst [51].

Acridine red was used as a photocatalyst for the visible light-induced direct thiolation of ethers (**Figure 17**) [52]. The thiolation of tetrahydrofuran (THF) using diphenyl disulfide **47** was carried out in the presence of acridine red (2 mol%) and *tert*-butyl hydroperoxide (TBHP) as an oxidant. The reaction occurred at ambient conditions to give α-arylthioether **48** in 82% yield. This transformation proceeds *via* the generation of radical intermediate from THF, which reacts with diphenyl disulfide **47** to afford 2-(phenylthio)-tetrahydrofuran **48**.

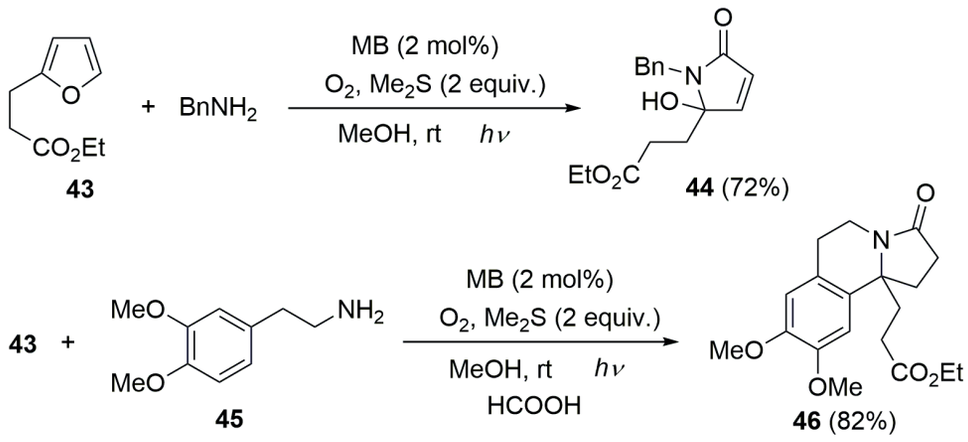


Figure 16. MB-catalyzed reactions of furan with amines.

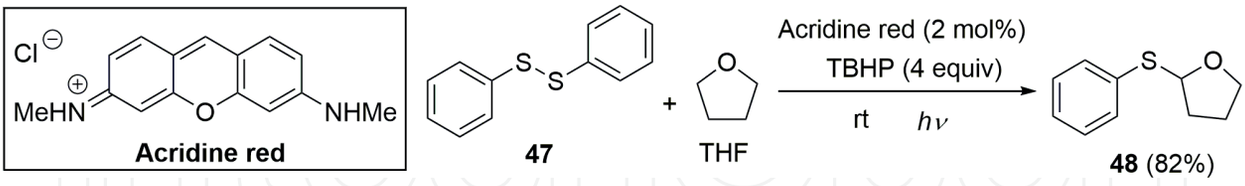


Figure 17. Acridine red-catalyzed thiolation of tetrahydrofuran.

6. Riboflavin tetraacetate

Riboflavin tetraacetate (RFT) is an effective photocatalyst for the visible light-driven organic reactions. The aerobic oxidation of alkyl benzenes to ketones and carboxylic acids was investigated through a dual catalysis using RFT and the tris(2-pyridylmethyl)amine-iron complex $[Fe(TPA)(MeCN)_2](ClO_4)_2$ (TPA=tris(2-pyridylmethyl)amine) [53]. When a mixture of RFT (10 mol%) and $[Fe(TPA)(MeCN)_2](ClO_4)_2$ (2 mol%) was employed, the oxidation of 4-ethylanisole

49 proceeded effectively under the visible light irradiation to give 4-acetylanisole **50** in 80% yield (**Figure 18**). In this oxidation, the iron complex acts as a catalyst for not only oxidation of **49** but also disproportionation of hydrogen peroxide H_2O_2 which is obtained in the RFT-catalyzed oxidation of **49**.

RFT also catalyzed the aerobic oxidation of sulfides to sulfoxides without overoxidation to sulfones [54]. In the presence of RFT (2 mol%), sulfide **51** was transformed chemoselectively to the corresponding sulfoxide **52** in 91% yield (**Figure 19**).

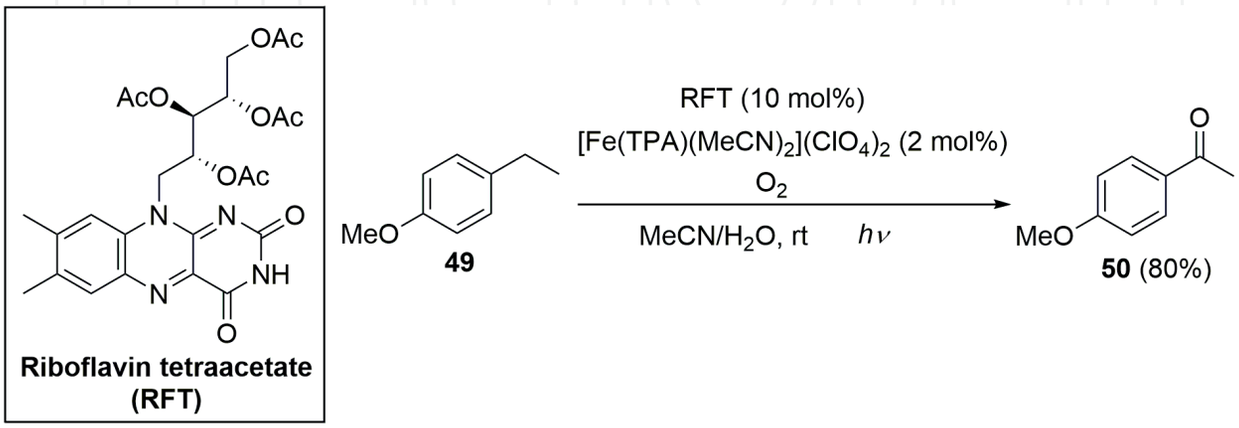


Figure 18. RFT-catalyzed oxidation of 4-ethylanisole.

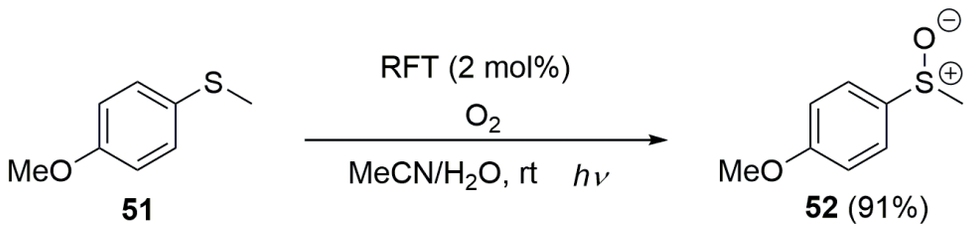


Figure 19. RFT-catalyzed oxidation of sulfide.

7. Concluding remarks

Organic dyes that absorbed visible light induce the synthetically valuable photochemical transformations. The metal-free photocatalysis using organic dyes rapidly progresses in the last few years. In addition to the organic dyes shown in this chapter, Fukuzumi' group has developed 3-cyano-1-methylquinolinium and 9-mesityl-10-methylacridinium ions as photocatalysts [13]. More recently, Nicewicz' group has studied the photocatalysis using acridinium salts [12]. These visible light-induced catalysis disclosed a broader aspect of the utility of organic photocatalysts for synthetic organic chemistry. This chapter will inspire creative new contributions to organic chemists.

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