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Construction of C-N Bond *via* Visible-Light-Mediated Difunctionalization of Alkenes

Bhisma K. Patel, Tipu Alam and Amitava Rakshit

Abstract

In the last few years, the photo-redox process via single-electron transfer (SET) has received substantial attention for the synthesis of targeted organic compounds due to its environmental friendliness and sustainability. Of late visible-light-mediated difunctionalization of alkenes has gained much attention because of its step economy, which allows the consecutive installation of two functional groups across the C=C bond in a single operation. The construction of N-containing compounds has always been important in organic synthesis. Molecules containing C-N bonds are found in many building blocks and are important precursors to other functional groups. Meanwhile, C-N bond formation via the addition of the C=C double bond is gaining prominence. Therefore, considering the influence and synthetic potential of the C-N bond, here we provide a summary of the state of the art on visible-light-driven difunctionalizations of alkene. We hope that the construction of the C-N bond *via* visible-light-mediated difunctionalization of alkenes will be useful for medicinal and synthetic organic chemists and will inspire further reaction development in this interesting area.

Keywords: Photocatalysis, Difunctionalization, C-N Bond, Alkenes

1. Introduction

Of late, photo-redox catalysis has been utilized as a flexible and demanding synthetic protocol in the realm of modern organic chemistry due to its environmental friendliness and sustainability [1]. This visible-light-driven protocol essentially affords a large number of nitrogen centred radicals via a single electron transfer (SET) process or energy transfer process under mild reaction conditions, compared to the traditional radical reactions that use high-energy ultraviolet (UV) light or highly toxic and expensive radical initiators [2]. Therefore, visible-light-mediated photo-redox catalysis has been widely applied for the synthesis of natural products, synthetic methodologies, enantioselective catalysis, and polymerization reactions. The success of any photochemical reactions relies on the ability of photocatalysts, usually transition-metal based complexes, organic dyes or heterogeneous semiconductors which promote single-electron transfer (SET) with organic molecules upon excitation with visible light [3]. An alkene difunctionalization can introduce two functional groups in a signal operation across the double bond (**Figure 1**) [4]. In this context, the radical-mediated C-N bond formation has



Figure 1.
Difunctionalization of alkene via visible-light photo-redox catalysis.

emerged as a powerful strategy to construct valuable molecules that have found application in different fields [5]. Therefore, this chapter focuses mainly on the difunctionalization of C=C bonds emphasizing the C-N bond formation using visible-light photo-redox catalysis.

2. Photocatalysts

Photocatalysts are organic or inorganic substances that absorb light and get excited to a higher energy level and transfer this energy to a reacting partner thereby triggering a chemical reaction. Few commonly used photocatalysts for the difunctionalization of alkenes [6] are shown in (**Figures 2 and 3**). These photocatalysts can be divided into two categories: (A) Transition-metal complexes and (B) Organic dyes.

A. Transition-Metal Complex Photocatalysts: The widely used visible-light-mediated photocatalyst are well-defined ruthenium (II) polypyridine complexes or Ir-cyclometalated derivatives. They facilitate redox reactions due to their ability to cause single electron transfer (SET) under a mild reaction condition in the presence of a visible light source [7].

B. Organic Dye: Since the beginning of organic synthesis, the formation of carbon-heteroatom bonds in a controlled and efficient manner is the heart of organic synthesis. Organic dyes using visible light has been playing a key role

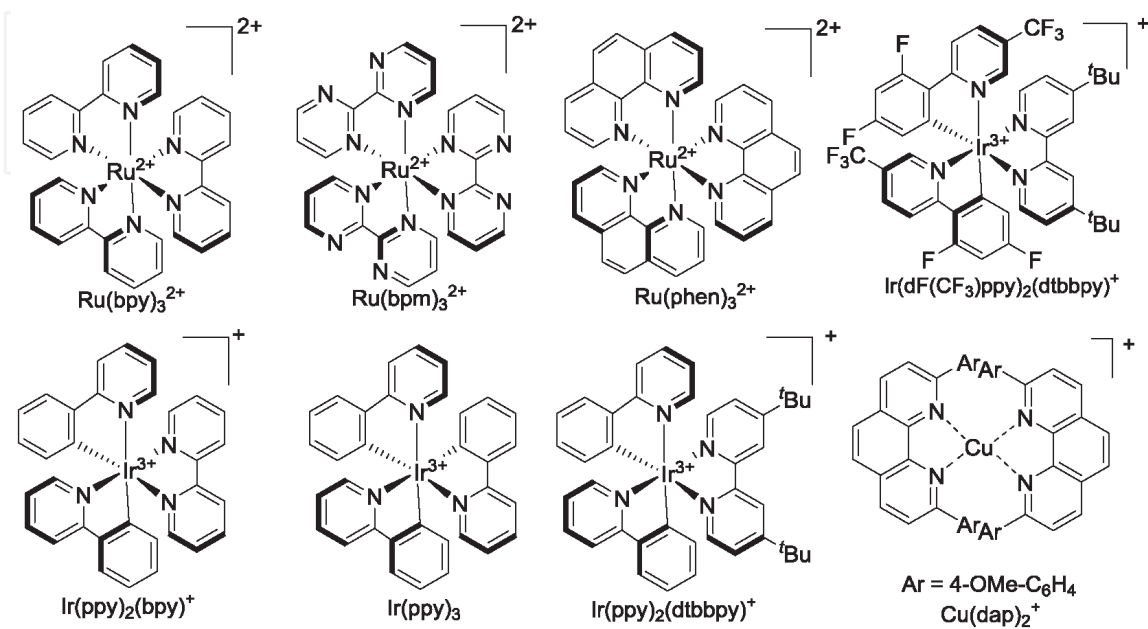


Figure 2.
Commonly used metal-based Photocatalyst for Difunctionalization.

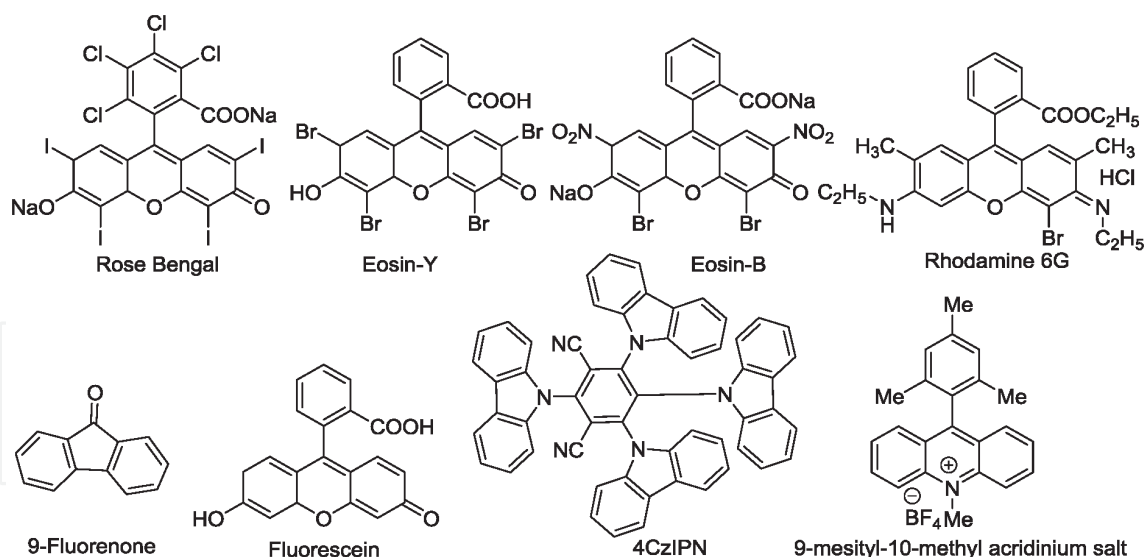


Figure 3.
Commonly used organic dye Photocatalyst for Difunctionalization of alkene.

in the formations of carbon-heteroatom bond in the difunctionalization of alkene. Compared to metal-containing photocatalyst, organic dyes require mild reaction conditions as it uses visible light of low power source and therefore the number of organic dyes have been employed as photo redox catalysts [8].

3. General mechanism

In general, at first, a photocatalyst (P.C) is converted to its excited state (*P.C) by irradiation of visible light and undergoes an energy transfer or a redox path. In the reductive quench path, the (*P.C) absorbs an electron from the electron donor to produce a reduced photo catalyst (P.C⁻). Which is a good reductant for the one-electron reduction of the substrate (S) or transition metal (Mⁿ⁺). Simultaneously, the photocatalyst is regenerate to the ground state and the reduced species radical anion (S^{-•}) or M⁽ⁿ⁻¹⁾⁺ undergo further reaction. In the oxidative quench pathway, the (*P.C) loses an electron to the electron acceptor to generate an oxidized photo catalyst (P.C⁺) which is a good oxidant for the one-electron oxidation of the substrate (S) or transition metal (Mⁿ⁺). The photo catalyst is regenerated and oxidative species radical cation (S^{+•}) or M⁽ⁿ⁺¹⁾⁺ could undergo further transformations. Both of these cycles produce D^{+•} and A^{-•} radicals in a single operation through SET to

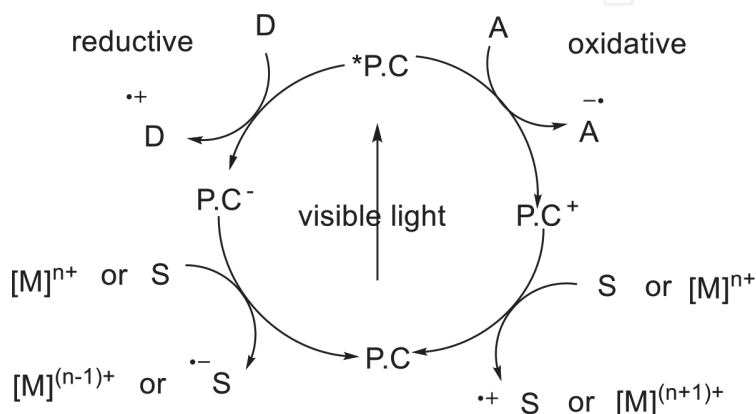


Figure 4.
Redox Photocatalyst via reductive or oxidative pathway.

make the overall process neutral. Here, the reductive path refers to the reduction of the excited photo catalyst (*P.C) where the external electron donor D is oxidized, whereas the oxidative path defines oxidation of the excited photo catalyst (*P.C) with concomitant reduction of the external electron acceptor A (**Figure 4**).

4. Metal-catalyzed C-N bond formations

4.1 Ru-catalyzed C-N bond formations

Several methodologies have been developed for various difunctionalizations of which transition-metal based photocatalytic C-N bond formations is in high demand. Dagousset *et al.* in 2014 reported a metal-catalyzed azido- and aminotri-fluoromethylation of alkenes (**2**) from alkene (**1**), azidotrimethylsilane and Umemoto's reagent (**Figure 5**) [9]. The radical-mediated difunctionalization of alkene is promoted under the irradiations of blue LEDs in the presence of a Ru-catalyst. According to the proposed reaction mechanism in the presence of visible light the catalyst $\text{Ru}(\text{bpy})_3^{2+}$ form an excited species $[\text{Ru}(\text{bpy})_3^{2+}]^*$ which generates the CF_3 radical via a single electron transfer (SET) from Umemoto's reagent. The CF_3 radical reacts with the alkene (**1**) providing the radical species with subsequent oxidation to a cation via a SET process from $[\text{Ru}(\text{bpy})_3^{3+}]$. Finally, the nucleophilic addition of this β -trifluoromethylated carbocation by TMSN_3 or amine afforded the corresponding trifluoro methylated product (**2**).

Yasu *et al.* in 2013 reported a metal-catalyzed facile intermolecular aminotri-fluoromethylation of alkenes (**Figure 6**) [10]. This is a highly efficient bifunctional reaction taking place between alkene (**3**), and Umemoto's reagent in MeCN. Here MeCN acts as a *N*-nucleophile, known as an aminative carbocation trap agent (Ritter-type reaction) and Umemoto's reagent serving as the CF_3 source. The reaction takes place via initial SET processes in the presence of blue LEDs through excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ to $^*[\text{Ru}(\text{bpy})_3]^{2+}$ which reduce the Umemoto's reagent to produce a CF_3 radical. Then this CF_3 radical attacks alkene (**3**) to give a radical which is further oxidized by $[\text{Ru}(\text{bpy})_3]^{3+}$ to form a trifluoromethylated carbocation through another SET process. Finally, the additions of RCN , to the

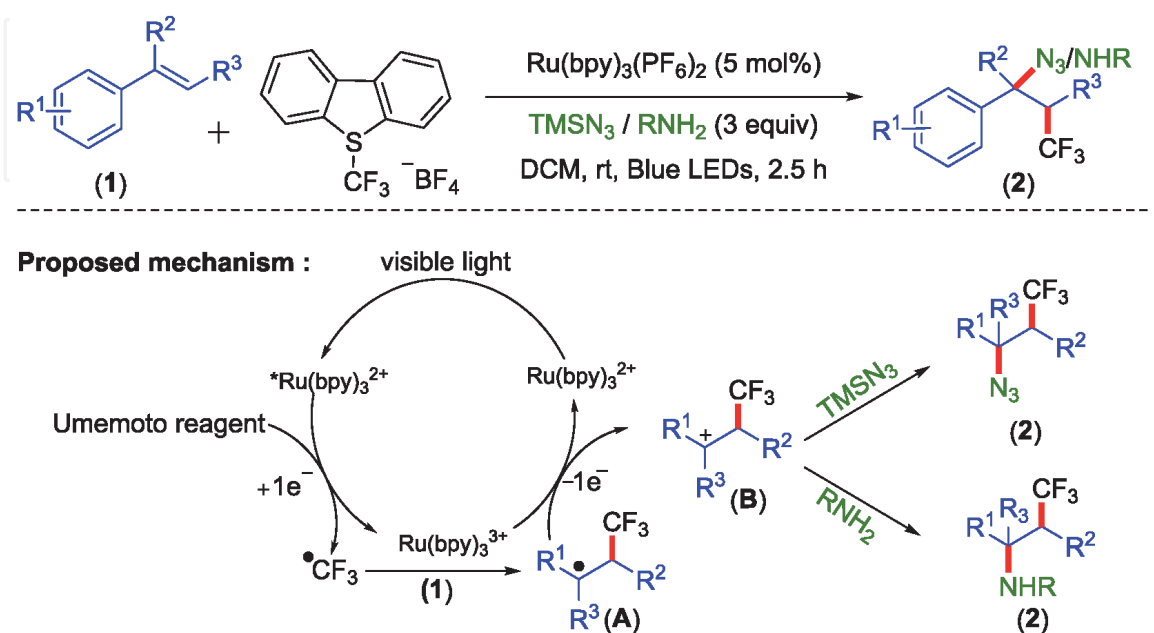


Figure 5.
Synthesis of azido and Aminotrifluoromethylated products.

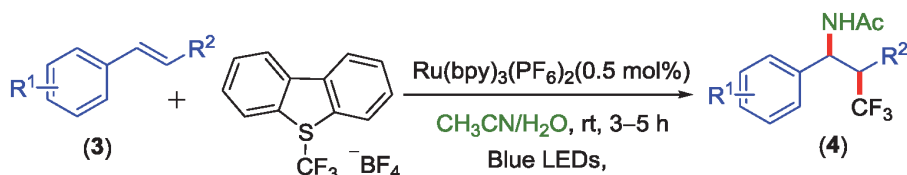


Figure 6.
Synthesis of Aminotrifluoromethylation derivative.

carbocation followed by hydrolysis (Ritter type amination) form the final aminotrifluoromethylated product (4).

Carboni *et al.* in 2014 demonstrated an elegant visible-light-mediated method for the synthesis of carbotrifluoromethylation (6) of enecarbamates using Togni's reagent as the CF_3 source and NaN_3 as the nucleophile (**Figure 7**) [11]. Herein, the CF_3 radical is generated from the Togni reagent via a reductive photo redox path under a single electron transfer process. Then the addition of enecarbamates (5) generates α -amido radical which is rapidly oxidized to an acyliminium cation by a SET process. Finally, nucleophilic additions of NaN_3 affords the product (6).

Bearing the importance of C-N bonds in mind Yang *et al.* in 2020 developed an efficient alkylazidation (8) using alkene (7), sodium azide and heteroarenylium salts as functionalized alkyl reagents for the synthesis of 2-azido-1-(1,4-dihydropyridin-4-yl)-ethane's (8). This reaction permits the incorporation of both azido and 1,4-dihydropyridin-4-yl group via difunctionalization of alkenes to construct C-C and C-N bonds in a single operation (**Figure 8**) [12]. The $[\text{Ru}(\text{bpy})_3]^{2+}$ specie is excited to $[\text{Ru}(\text{bpy})_3]^{2+*}$ by irradiated it with visible-light and undergoes single-electron transfer (SET) with NaN_3 to form an azido radical ($\text{N}_3\cdot$). The addition of azido radical across the C=C bond of alkene (7) generates an alkyl radical which is followed by the addition of the pyridinyl ring of pyridinium and finally, reductions by the $[\text{Ru}(\text{bpy})_3]^+$ species gives a product (8) and regenerates the active catalyst.

Yu *et al.* in 2016 disclose a Ru-catalyzed visible-light-mediated synthesis of azotrifluoromethylation (10) in the presence of alkenes (9) with aryldiazonium salts and sodium trifluoromethanesulfinate (**Figure 9**) [13]. This reaction is successful for unactivated alkene. Both electron-donating and electron-withdrawing groups of alkene and aryldiazonium salts give their product (10) in good yields. These trifluoromethylated azo products are useful building blocks for many heterocycles and nitrogen-containing compounds. As per the suggested mechanism in (**Figure 9**) in the presence of blue light, photoexcitation of the photocatalyst

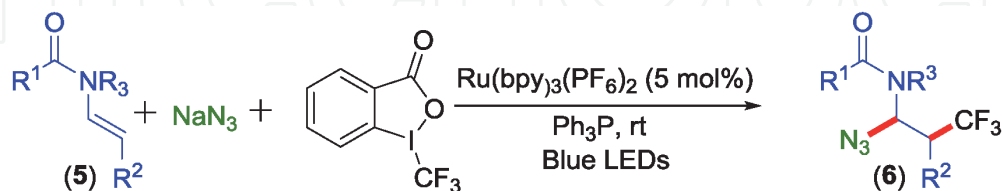


Figure 7.
Synthesis of Carbotrifluoromethylation derivative.

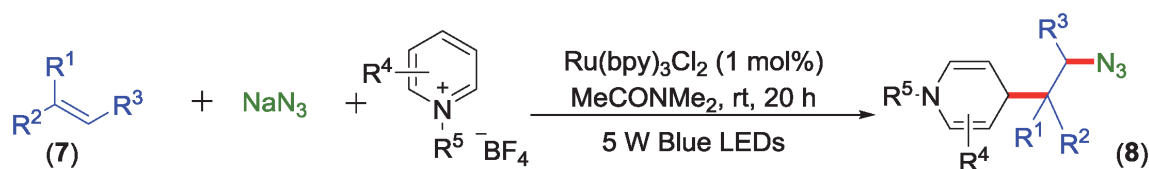


Figure 8.
Synthesis of 2-Azido-1-(1,4-dihydropyridin-4-yl)-ethanes.

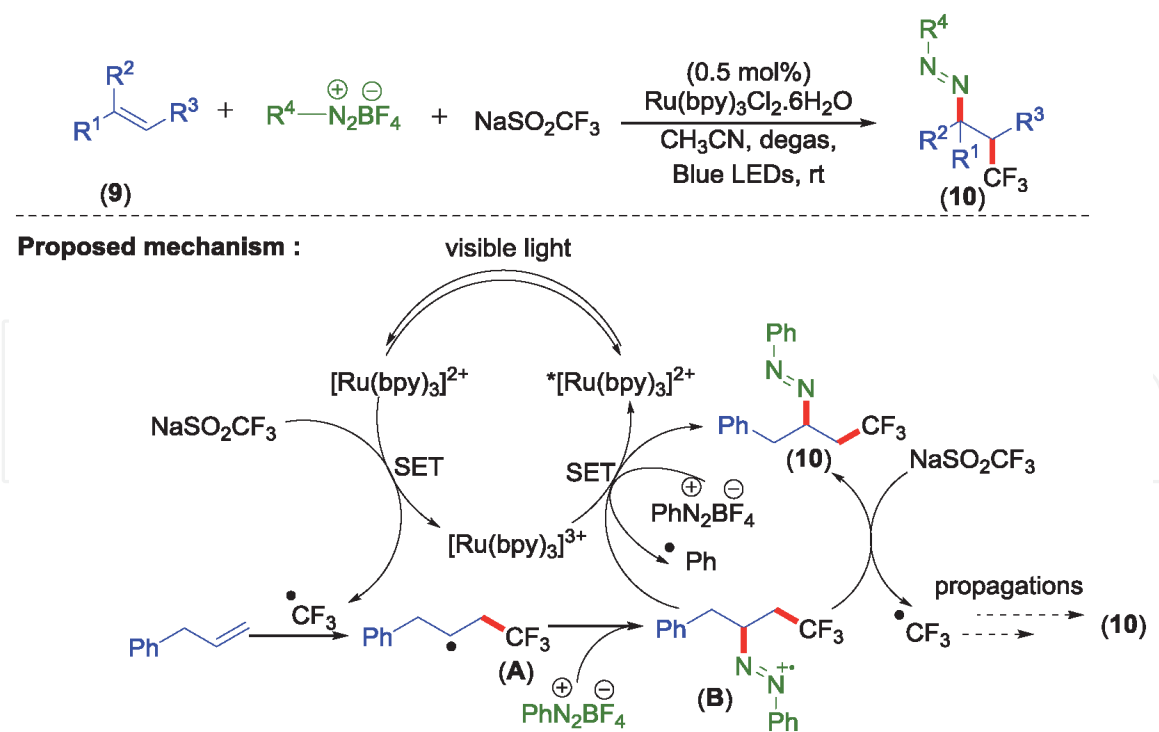


Figure 9.
Synthesis of Trifluoromethylated azo compounds.

$[\text{Ru}(\text{bpy})_3]^{2+}$ generates the excited state $^*[\text{Ru}(\text{bpy})_3]^{2+}$ species. This active species is transferred into the oxidizing photocatalyst $[\text{Ru}(\text{bpy})_3]^{3+}$ via SET oxidation by the phenyldiazonium salt. This active species serves as a strong oxidant to oxidize Langlois' reagent to produce CF_3 radical upon removal of SO_2 and returning the photocatalyst to its ground state. At this time, the CF_3 radical undergoes addition to the alkene (9) to generate the radical intermediate (A), which is easily trapped by the aryldiazonium salt to give the radical cation intermediate (B). Similarly, another SET reduction of intermediate (B) by the reducing $^*[\text{Ru}(\text{bpy})_3]^{2+}$ species gives to the desired product (10).

Since vicinal diamine are found in many pharmaceuticals and various biologically active compounds hence the development of newer methodologies is deemed worthy. Considering their biological importance and ongoing demand Govaerts *et al.* in 2020 demonstrated a Ru-catalyzed diamination of alkene (11) in the presence of blue LEDs (**Figure 10**) [14]. This methodology exploits the generation of aminium radicals from the in situ generated *N*-chloroamines and their capability to react with alkenes via anti-Markovnikov addition.

According to the depicted mechanism (**Figure 10**) initially, chlorination of an alkylamine with NCS occurs followed by the addition of a strong Brønsted acid generates a highly activated *N*-chloroammonium intermediate (A) which upon SET via photoexcited state of $\text{Ru}(\text{bpy})_3^{2+}$ creates the intermediate (B). This aminium radical intermediate (B) adds to the olefin (11) to give anti-Markovnikov intermediate (C). Simultaneously the β -aminium radical intermediate (C) reacts with intermediate (A) restoring the intermediate (B) and provide the protonated β -chloroamine intermediate (D) which gives intermediate (E) followed by ring-opening by a second alkyl amine (e.g., Et_2NH) to give the product (12).

Considering the importance of acyl amide, Hari *et al.* in 2014 established a photochemical method (**Figure 11**) for the synthesis of functionalized amide (14) using diazonium salt as the cheap and environment-friendly arylation partner and alkene (13). [15] The photo Meerwein arylation reaction is applied only for the formation of aryl-alkene coupling products. As suggested in the mechanism,

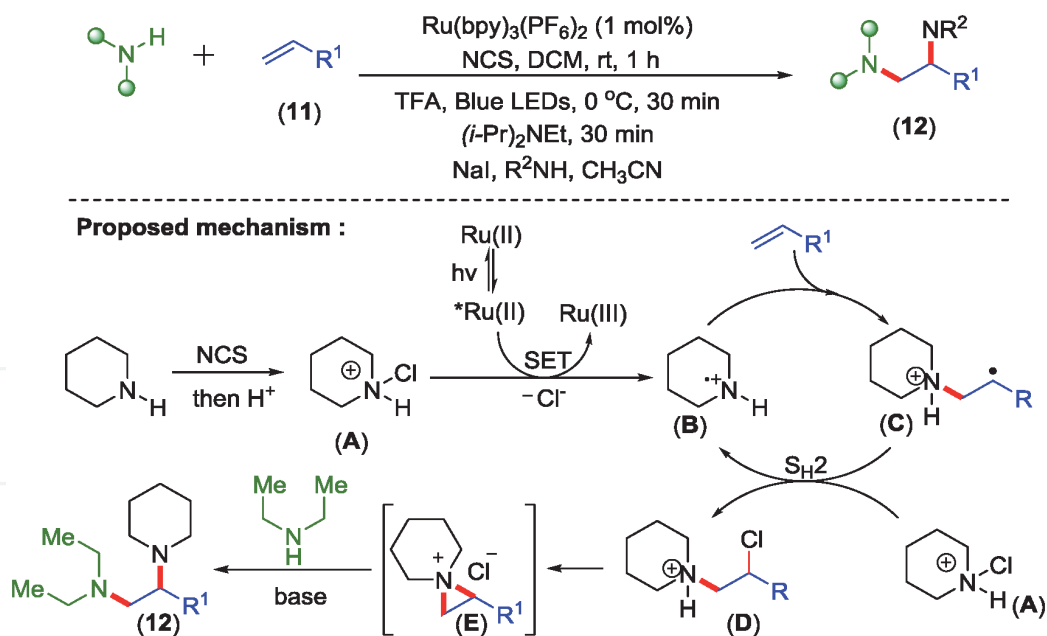


Figure 10.
Synthesis of 1, 2-Diamination product.

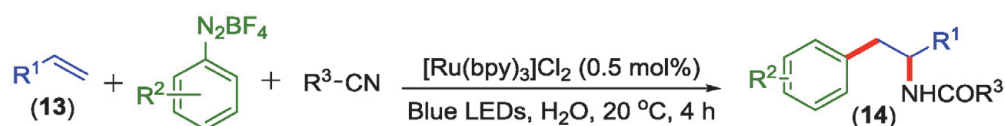


Figure 11.
Synthesis of amino-Arylation product.

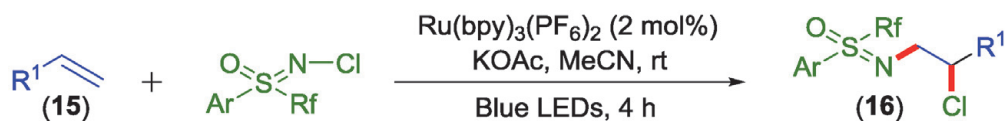


Figure 12.
Synthesis of N-Chloro S-Fluoroalkyl Sulfoximines.

initially an aryl radical is formed via a single-electron transfer (SET) from the excited state of the photocatalyst $[\text{Ru}(\text{bpy})_3]^{2+*}$ to a diazonium salt. Then the addition of aryl radical to alkene (13) generates another radical intermediate which undergoes oxidation to provide a carbenium species. Finally, the attack of a nitrile (R_3CN) to the carbenium species followed by hydrolysis gives the amino-arylated product (14).

Considering the biological importance of sulfoximines containing compounds, Prieto *et al.* in 2019 demonstrated a method for the formation of N-chloro S-fluoroalkyl sulfoximines (16) from alkene (15) and sulfoximine through an atom transfer radical addition (ATRA) mechanism. A broad reaction scope was demonstrated, and various functionalised sulfoximines were well tolerated in the present protocol (Figure 12) [16]. Herein the photoexcited catalyst reacts with sulfoximine by SET reduction to give the sulfoximidoyl radical which is then followed by reaction with the alkene providing the alkyl radical. At this time, two different paths are possible, one is via the radical-chain path and another the catalytic path. In the radical-chain pathway the alkyl radical abstracts a chlorine atom from sulfoximine to give the compound (16) and generate a new sulfoximidoyl radical. In the catalytic pathway, the intermediate alkyl radical undergo oxidation by the

oxidized form of PC into a cationic species and restore the photocatalyst. Finally, the addition of chlorine atom to the cationic species afforded the compound (16).

Ouyang *et al.* in 2018 established an elegant method in which a photo-induced three-component reaction of styrenes (17) with alkyl *N*-hydroxyphthalimide (NHP) esters and amine leads to 1,2-alkylamine (18) (Figure 13) [17]. In this reaction, the alkyl NHP esters act as an alkylating agent to give 1,2-alkyl amine products from their respective alkenes. The plausible mechanism involves a visible-light excitation of the photo redox catalyst thereby decomposing the alkyl NHP ester to an alkyl radical, CO₂, and phthalimide anion. Then the addition of alkyl radical across the C=C bond of arylalkene (17) generates another alkyl radical which upon single electron transfer through oxidation of the [Ru(bpy)₃]³⁺ species provide the alkyl cation. Finally, the nucleophilic attack of amine to the cationic species delivers the final product (18).

4.2 Ir-catalyzed C-N bond formations

Miyazawa *et al.* in 2015 demonstrated a regiospecific synthesis of aminohydroxylation (20) from alkenes (19) by photo redox catalysis (Figure 14) [18]. Here *N*-protected 1-aminopyridinium salt is the key compound that provides an amidyl radical precursor in the presence of Ir-photocatalyst. The reaction proceeds via an Ir-catalyzed radical-mediated path in the presence of acetone and water under the irradiations of blue LEDs providing difunctionalized alkenes. The proposed mechanism is shown in (Figure 14). In the presence of visible light, the photocatalyst Ir^{III} is excited to *Ir^{III}, which undergoes single electron transfer (SET) to an aminopyridinium to provide a stabilized radical (A) and a highly oxidizable Ir species Ir^{IV}. The generated amidyl radical from intermediate (A) reacts with alkene (19) in a regiospecific manner to give a radical intermediate (B). Then Ir^{III} is oxidized to form an Ir^{IV} species and afford β-amino carbocation intermediate (C)

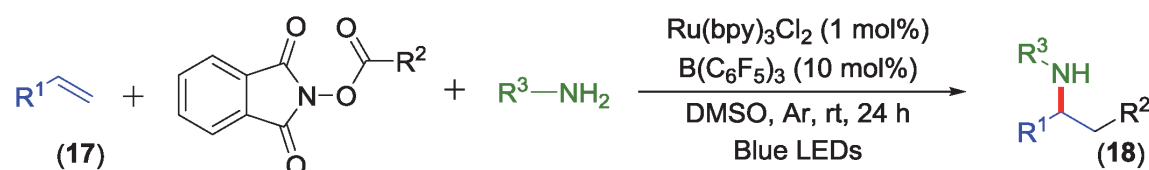


Figure 13.
Synthesis of 1, 2-alkyl amination product.

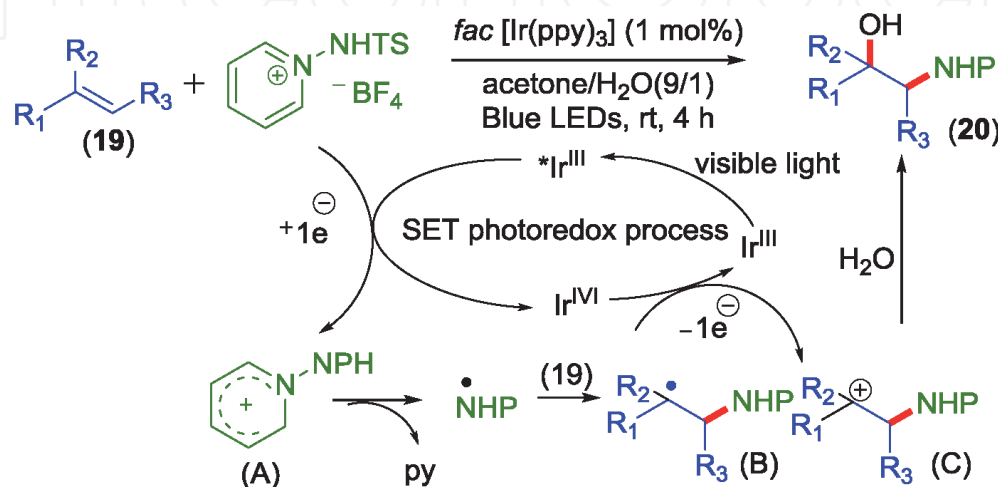


Figure 14.
Synthesis of 1,2-Aminoalcohol.

and regenerate the Ir photocatalyst to its ground state Ir^{III}. Finally, the nucleophilic attack of H₂O to the carbocation intermediate (C) produce the product 1,2-aminoalcohol (20).

Xu and Cai in 2019 reported a metal-catalyzed visible-light-mediated difunctionalization of alkene (21) where BrCF₂CO₂Et and amines are the coupling partner (Figure 15) [19]. The present strategy is equally successful for electron-poor, electron-rich, and internal alkenes. The Csp³-Csp³ and Csp³-N bonds are simultaneously formed under mild conditions. According to the proposed mechanism in (Figure 15) initially, in the presence of visible light, *fac*-Ir^{III}(ppy)₃ is excited to *fac*-Ir^{III}(ppy)₃^{*}, which then reacts with BrCF₂CO₂Et by the SET pathway to generate the ethyl difluoroacetate radical (A) and the oxidized photocatalyst *fac*-Ir^{IV}(ppy)₃. Then, the selective addition of the ethyl difluoroacetate radical (A) to the alkene (21) generate a benzyl radical intermediate (B). This intermediate (B) undergo single-electron oxidation via the cooperative effects of the active Fe (III) species, to form the carbocation intermediate (C). Finally, the attack of an arylamine to the intermediate (C) is followed by base-mediated deprotonation to generate the difluoroalkylamination product (22).

Wu *et al.* in 2019 demonstrated a metal-catalyzed synthesis of β-arylsulfonyl (diarylphosphinoyl)-α,α-diarylethyl-amines (24) from readily available 1,1-diarylethylenes (23), arylazides, and arylsulfinic acids (Figure 16) [20]. This Ir-catalyzed reaction takes place in the presence of blue LEDs and under the nitrogen atmosphere leading to difunctionalizations of alkenes. As per the proposed mechanism (Figure 16) by the irradiations of blue light, the catalyst [Ir(mppy)₃]³⁺ is excited to [Ir(mppy)₃]^{3+*} through energy transfer. Then, arylsulfinic acid and [Ir(mppy)₃]^{3+*} participate in a SET process to generate [Ir(mppy)₃]²⁺ and arylsulfonyl radical (A). Then the addition of alkene (23) to the intermediate (A) form the α α-diarylalkyl radical (B). Simultaneously, [Ir(mppy)₃]^{3+*} transfers its energy to the arylazide resulting in loss of N₂ and the constructions of triplet nitrene intermediate (C). After that via a SET process and protonation, the intermediate (C) is transferred to a nitrogen radical intermediate (D) which then adds to the persistent radical intermediate (B) to give the β-arylsulfonyl(diarylphosphinoyl)-α,α-diarylethyl-amines (24).

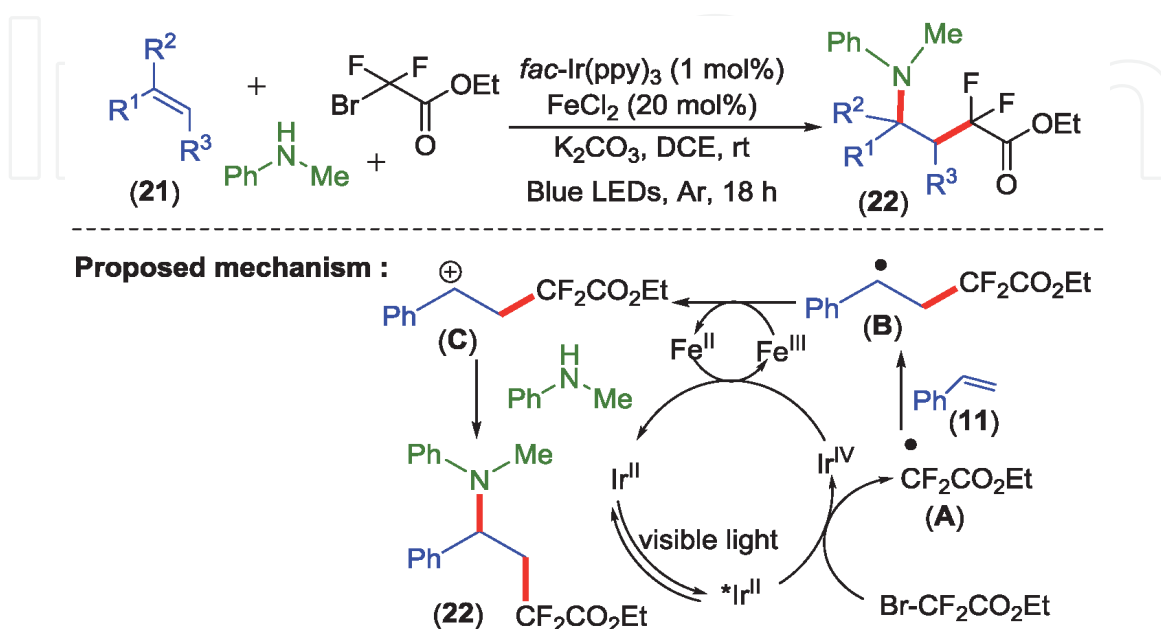


Figure 15.
Synthesis of Difluoroalkylamination product.

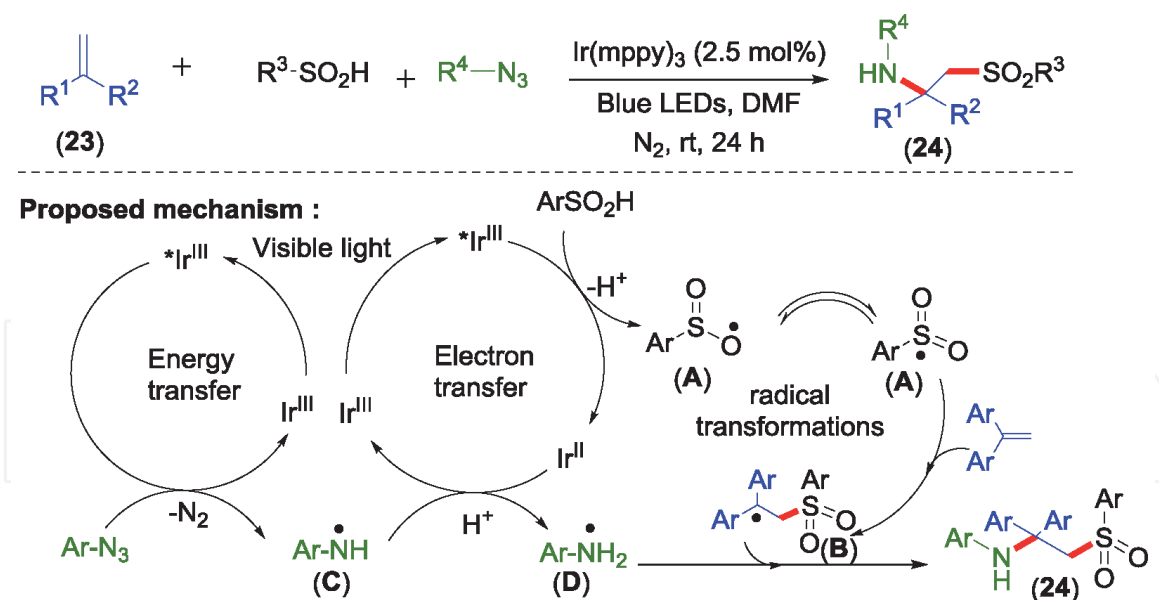


Figure 16.
Synthesis of β -Arylsulfonyl- α , α -diarylethylamines.

Chen *et al.* in 2019 described an Ir-catalyzed visible-light-mediated azidoarylation of alkenes in the presence of pyridines and TMSN_3 (**Figure 17**) [21]. These reactions take place in the presence of *tert*-butanol and irradiations of 90 W blue LEDs. Electron-withdrawing and electron-donating group of alkene and cyanopyridine react smoothly to give the product (26). According to the proposed mechanism, irradiation of $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ produce an excited state Ir^* which would capture a single-electron from azide to generate the azido radical intermediate (A) and reducing photocatalyst Ir^{II} . Then the addition of electrophilic azido radical intermediate (A) to the alkene (25), produce a benzylic radical intermediate (B). A single-electron reduction between Ir^{II} and cyanopyridine generate the pyridyl radical anion intermediate (C) and regenerate the ground-state Ir^{III} catalyst. Simultaneously, a radical-radical coupling between the transient benzylic radical intermediate (B) and the pyridyl radical anion intermediate (C) afford the intermediate (D), which can undergo elimination of a CN^- anion give the product (26).

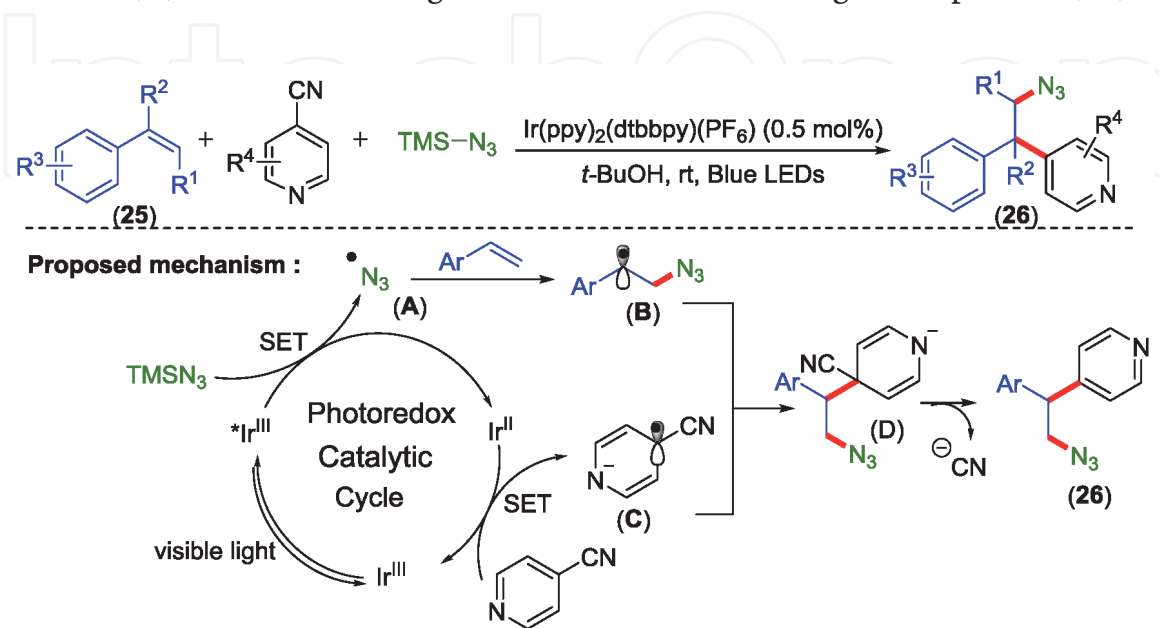


Figure 17.
Synthesis of β -Azidopyridines.

Recently, Guo *et al.* in 2021 demonstrated a photocatalytic 1,2-diamination of 1,3-dienes (27) in the presence of *N*-aminopyridinium and TMSNCS to afford 1,2-aminoisothiocyanation products (28) in high chemo- and regio-selective manner with broad substrate scope and good functional group tolerance (**Figure 18**) [22]. According to the proposed mechanism (**Figure 18**) the visible light excites the Ir-catalyst which reduced *N*-aminopyridinium salt to produce a radical intermediate (A) and underwent dissociations to generate a nitrogen-centered radical (B) and 2,4,6-collidine. Regioselective addition of intermediate (B) to 1,3-diene (27) afford an allylic intermediate (C). Eventually, oxidation of the intermediate (C) by Ir^{IV} afforded a carbocation intermediate (D) with concurrent regeneration of Ir^{III} species. Nucleophilic addition of TMSNCS to the intermediate (D) generated a mixture of 1,2-aminoisothiocyanation (28) and 1,2-aminothiocyanation products.

An elegant method for the synthesis of β -sulfonyl amides (30) is reported by Zong *et al.* in 2019 through an acid promoted photochemical reaction of styrenes (29), aryldiazonium tetrafluoroborates, sulfur dioxide, nitriles, and water (**Figure 19**) [23]. This visible-light-mediated vicinal aminosulfonylation of an alkene with the insertion of SO₂ giving rise to β -sulfonyl amides (30) with high efficiency and excellent chemoselectivity, in moderate to good yields.

As depicted in **Figure 19** the plausible mechanism involves the interaction of aryldiazonium tetrafluoroborate with DABCO·(SO₂)₂ to generate aryl radical, sulfur dioxide, nitrogen, and DABCO radical cation. Then the aryl radical is captured by sulfur dioxide to generate an aryl sulfonyl radical intermediate (A) which subsequently attacks the alkene (29) to furnish a C-centered radical (B). Next with the help of photocatalyst via oxidative SET of C-central radical intermediate (B), provide a cation intermediate (C). Then the attack of nitrile to cation intermediate (C), generated another cation intermediate (D). Water acts as a nucleophile in the presence of a Lewis acid to attack the cation intermediate (D), leading to compound (E). The subsequent isomerization gives β -sulfonyl amide (30).

Ge *et al.* in 2020 developed a metal-catalyzed three-component reaction of alkene (31), using a selenium ylides-based trifluoromethylation reagent, and nucleophiles such as azide, amine, alcohol, water via a radical process to

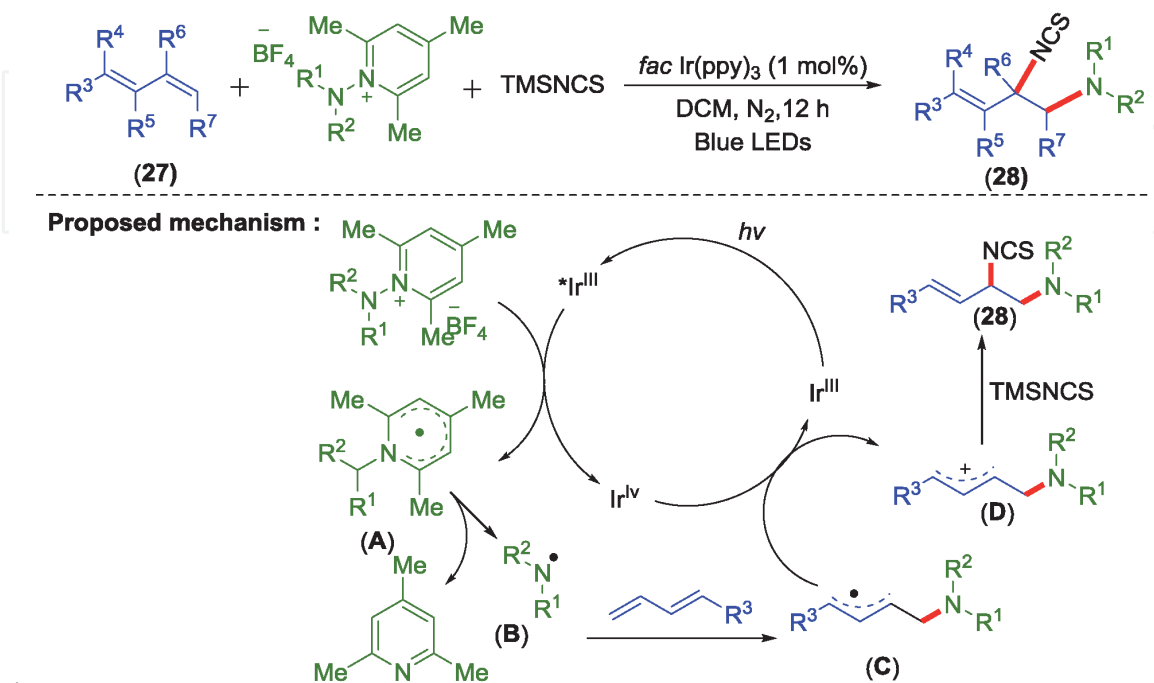


Figure 18.
 Synthesis of 1,2-Diamination product.

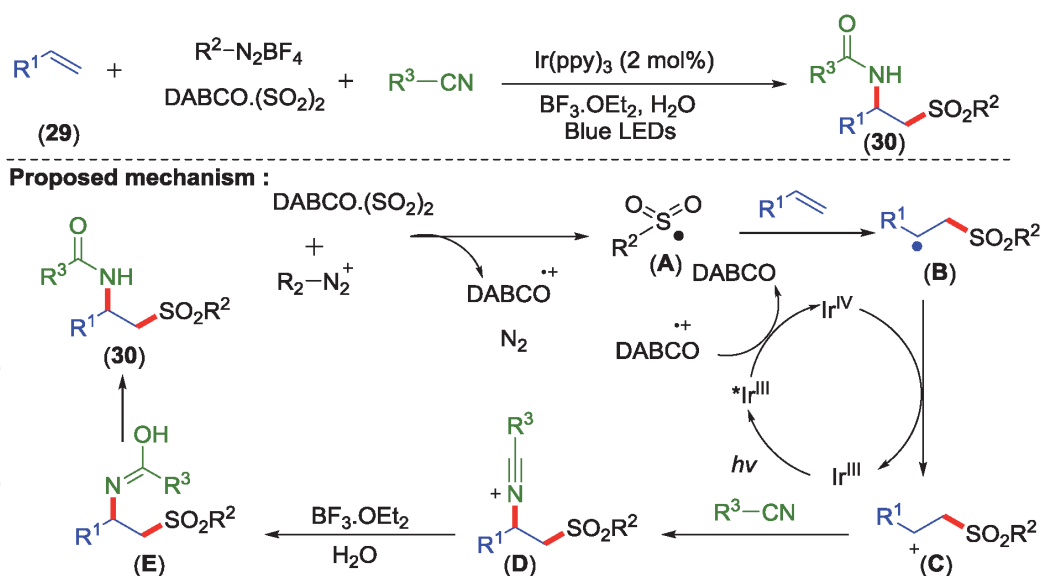


Figure 19.
Synthesis of β -sulfonyl amides.

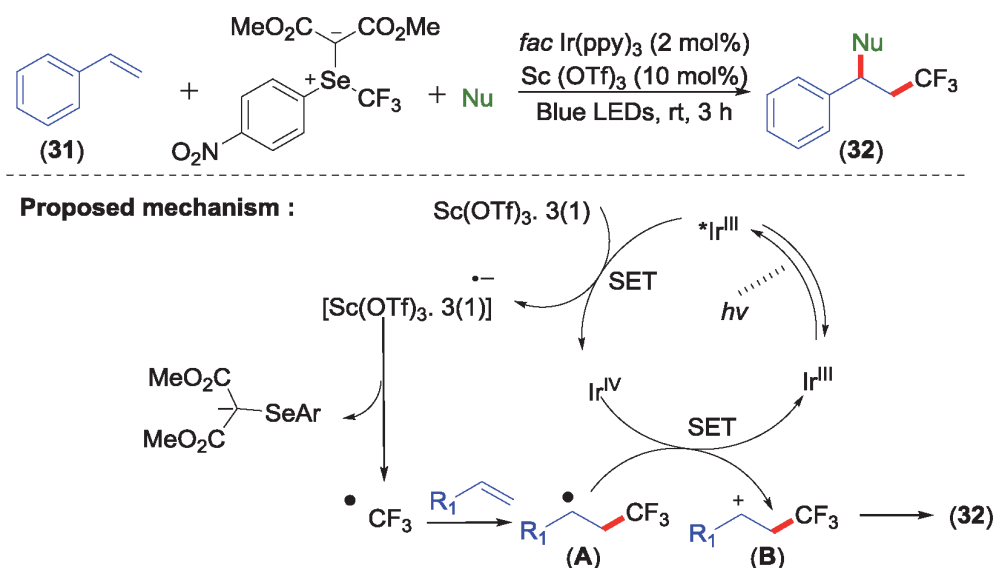


Figure 20.
Synthesis of Trifluoromethylative amination product.

trifluoromethylative amination product (32) under mild conditions (**Figure 20**) [24]. The trifluoromethylation reagent act as a trifluoromethyl radical source. The process takes place in the presence of a Lewis acid scandium(III) trifluoromethanesulfonate Sc(OTf)_3 and a photoredox catalyst $[\text{fac-Ir(ppy)}_3]$. As per the proposed mechanism (**Figure 20**) initially, irradiation of blue light excited the photocatalyst $[\text{fac-Ir}^{\text{III}}(\text{ppy})_3]$ which then transfers one electron to $[\text{Sc(OTf)}_3 \cdot 3(1)]$ (obtained by mixing selenium ylide-based trifluoromethylating reagent with Sc(OTf)_3) via a single electron transfer (SET) process. This radical anion $[\text{Sc(OTf)}_3 \cdot 3(1)]^{\bullet-}$ is unstable and undergoes homolytic cleavage of $\text{Se}-\text{C}(\text{CF}_3)_2$ bond to generate the CF_3^\bullet radical. This CF_3^\bullet radical addition to the styrene (29) gives a trifluoromethylated benzylic radical intermediate (A), which is oxidized by $[\text{Ir}^{\text{IV}}(\text{ppy})_3]$ to a benzylic cation intermediate (B). Finally, the nucleophilic attack at the benzylic cation gives trifluoromethylated product (30).

Qin *et al.* in 2017 demonstrated an Ir-catalyzed protocol for the synthesis of α -amino ketones and diaminations product (34 and 34') from activated olefins (33)

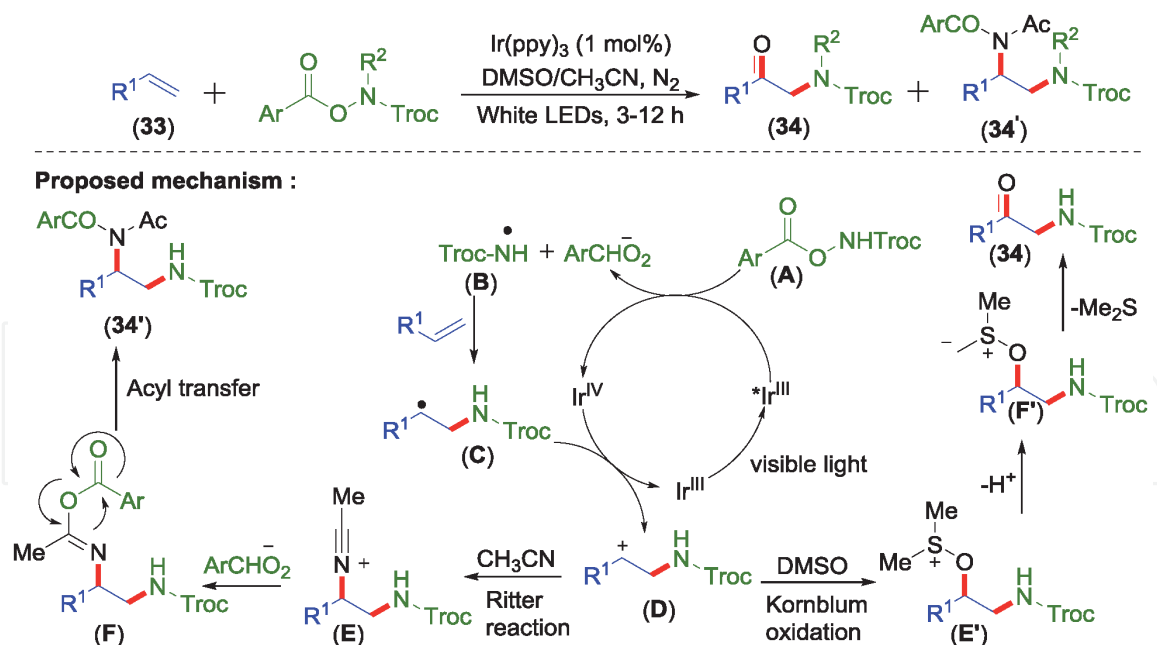


Figure 21.
Synthesis of 1,2-Diamides and α -amino ketones.

(**Figure 21**) [25]. Here *o*-acyl hydroxylamines are the key reacting partner for difunctionalization. Here solvent also play a pivotal role as different solvent gave different products. A plausible mechanism for the Ir-catalyzed radical diamination and α -amino ketone of active olefins is shown in (**Figure 21**). In the presence of visible-light the excited Ir-catalyst induce the reductive cleavage of reactant (A) to generate a radical (B) and a carboxylate anion. The *N*-centered radical (B) adds to the styrene (33) to produce an alkyl radical intermediate (C) with the regeneration of photocatalyst Ir^{III} via oxidation to give a carbocation intermediate (D). In CH_3CN , (D) is trapped by the solvent to give a nitrilium intermediate (E) through a Ritter-type process. Then attack by the intermediate (E) followed by an acyl migration afford the diamidated product (34'). When DMSO is used as the solvent, intermediate (D) can also be trapped by the solvent to provide an alkoxy-sulfonium intermediate (E'), which undergoes Kornblum oxidation to afford the α -amino ketone (34).

Qin *et al.* in 2015 demonstrated an Ir-catalyzed visible-light-mediated synthesis of chloramines (36) from activated olefins (35) (**Figure 22**) [26]. Here *N*-chlorosulfonamides served both as nitrogen and chlorine source. This methodology provides regioselective, efficient, and atom-economic method for the preparation of vicinal halo amines. The reaction goes via the generation of a nitrogen-centered radical from *N*-chlorosulfonamide by oxidative quenching of the Ir-catalyzed which is excited in the presence of blue LEDs. This nitrogen centered radical then adds to the olefin (35) to produce an alkyl radical which is further oxidized to a carbocation intermediate with the regeneration of Ir^{III} . Finally, the addition of chloride anion to the carbocation gives chloraminated product (36).

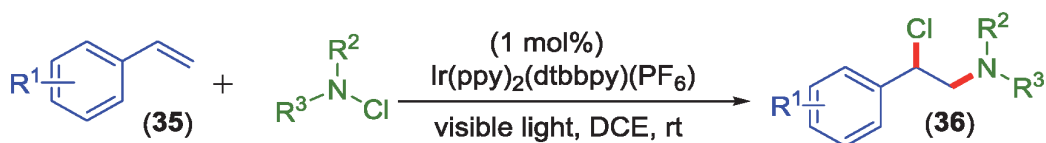


Figure 22.
Synthesis of Chloramination derivative.

4.3 Cu and Pd-catalyzed C-N bond formations

Wu *et al.* in 2019 depicted (**Figure 23**) a visible-light-mediated Cu-catalyzed difunctionalization of alkene (**37**) to give azidation product (**38**) [27]. Here the azidobenziodoxole acts as an azidating agent in the presence of acetonitrile and $[\text{Cu}(\text{dap})_2]\text{PF}_6$ complex as the photocatalyst. While the reactions produced three types of difunctionalized products, which correspond to reaction patterns of amido-azidation, diazidation and benzoyloxy-azidation. The electronic factor of the aryl group attached to the alkene play a vital role in determining the reaction outcome. When the aryl group is rich in electron, the reaction afforded benzoyloxy-azidation product and highly electron-deficient vinyl arenes, generated diazidation products in moderate yields. When the aryl group is electron-deficient or moderately electron-rich, give predominantly amido-azidation product. Based on the proposed mechanism the reaction is initiated via single electron transfer (SET) between IBA- N_3 and $[\text{Cu}(\text{dap})_2]^{++}$, which provided an azidyl radical and $[\text{Cu}(\text{dap})_2]^{2+}$. The azide radical then attacks the alkene to produce a radical which would couple with the $\text{CH}_3\text{CN}-[\text{Cu}]^{2+}$ complex followed by reductive elimination to give Ritter-type intermediate. The latter is readily captured by the *o*-iodo benzoyloxyate anion and further rearrangement formed product (**38**). In another path, the radical generated from alkene is oxidized to the corresponding carbocation by IBA- N_3 . Then addition with *o*-iodo benzoyloxyate anion afforded the oxy-azidation products (**38'**). When the vinyl group is attached to a strong electron-withdrawing group intermediate generated from alkene abstracts an azidyl group from IBA- N_3 to give the diazidation product (**38''**).

Similarly, Fumagalli *et al.* in 2015 demonstrated a method for the synthesis of azidation derivatives (**40** and **40'**) from activate alkenes (**39**) (**Figure 24**) [28]. The reaction is light-switchable, in the presence of light gives methoxyazidated products and in the absence of light, diazidation product is obtained. This methodology uses sustainable and cheap copper-based photocatalyst, to enable electron transfer under mild reaction conditions, thus affecting the formation of double C-N bond in dark, and C-N/C-O formation in the presence of light.

Hossain *et al.* in 2018 developed a visible-light-photocatalytic strategy for the synthesis of azido ketones (**42**) from vinyl arenes (**41**) and TMSN_3 (**Figure 25**) [29]. The reactions proceed via step-economic fashion under an aerobic condition without additional oxidants. As per the mechanism (**Figure 25**) initially in the presence of light $[\text{Cu}(\text{dap})_2]\text{Cl}$ gets excited and form an excited state intermediate (A) via oxidation with dioxygen with the release of an equivalent of ligand (dap).

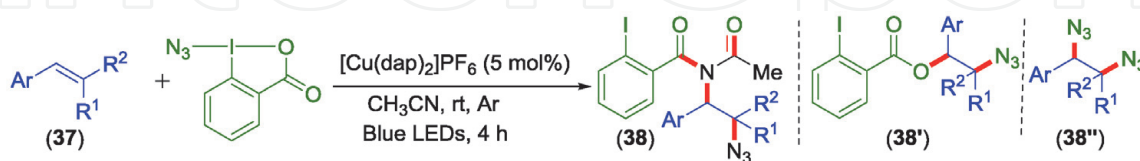


Figure 23.
Synthesis of Azidation derivative.

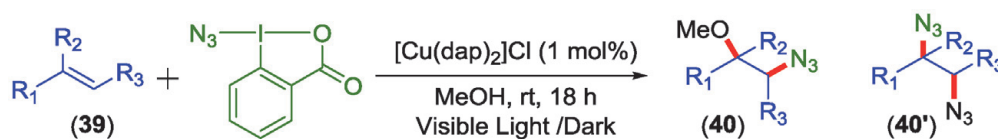


Figure 24.
Synthesis of Azidation derivative.

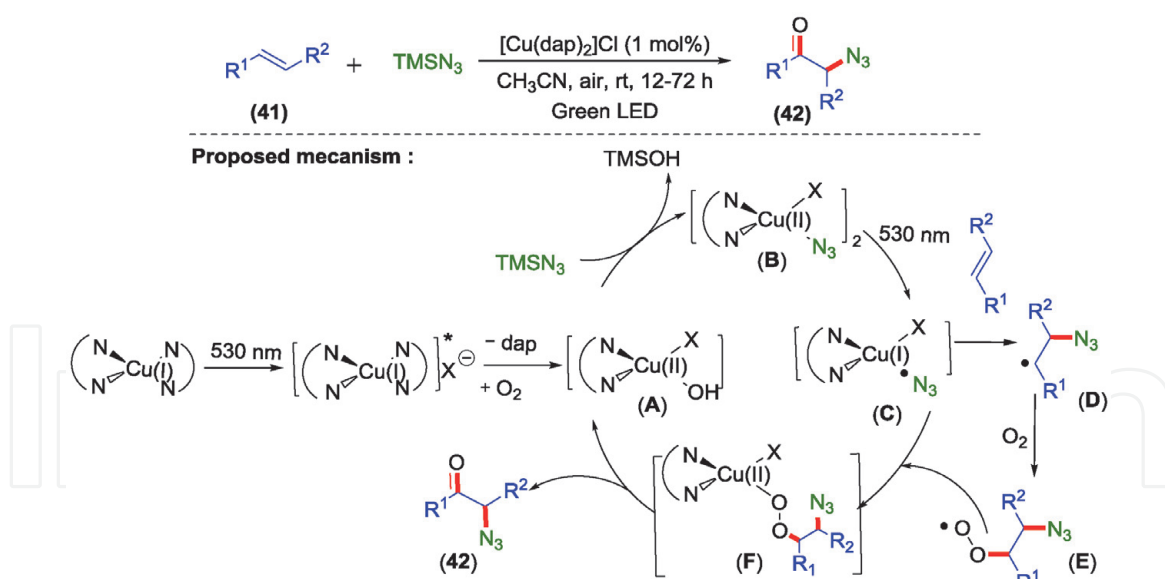


Figure 25.
Synthesis of azido ketones.

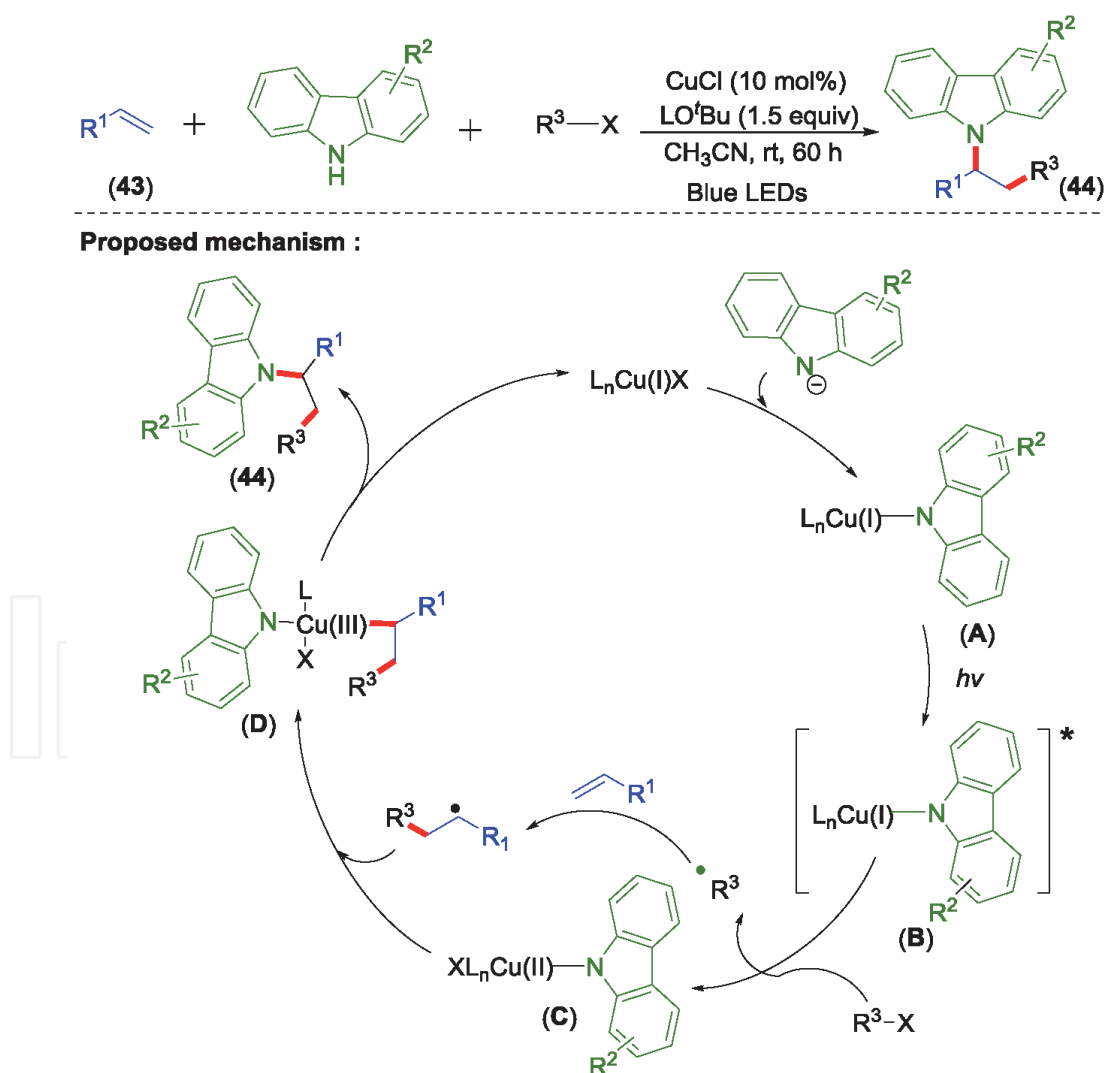


Figure 26.
Synthesis of Carboaminations product.

Then the formation of an intermediate (B) rapidly occurs upon mixing of $[\text{Cu}(\text{dap})\text{Cl}_2]$ with TMSN_3 . The homolytic dissociation of intermediate (B) generates another intermediate (C) and an azide radical. After that the azide radical attacks the alkene

to form a stabilized radical intermediate (D), which further reacts with oxygen to form intermediate (E). Then this radical intermediate binds to intermediate (C) to form a Cu^{II} species intermediate (F). Finally, the release of intermediate (A) gives the ketoazide product (42).

Xiong *et al.* in 2019 reported a Cu-catalyzed visible-light-mediated synthesis of aminoalkylated derivative (44) in the presence of alkene (43), alkyl iodides, and carbazole (**Figure 26**) [30]. According to the proposed mechanism (**Figure 26**) initially, L_nCuCl undergoes ligand exchange with the nucleophile to deliver $\text{L}_n\text{Cu(I)Nu}$ (A). Then it goes to the excited-state adduct intermediate (B) in the presence of LEDs. The excited-state intermediate (B) would then involve an electron transfer with the halide to generate a radical and intermediate (C). Next, the radical attack to the alkene produces an internal radical and intermediate (D). Finally, the product (44) undergo reductive elimination and regenerate the Cu(I) catalyst.

Cheung *et al.* in 2020 disclose a Pd-catalyzed visible-light-mediated synthesis of aminoalkylations derivative (46) via 1,2-carbofunctionalization of conjugated dienes (45) using alkyl iodides and amines as the coupling partners (**Figure 27**) [31]. This methodology is subsequently utilizing for the late-stage derivatization of complex molecules which is useful in drugs discovery. The multi-component reaction uses readily available reaction partners with broad substrate scope and does not require any exogenous photosensitizers or external oxidants.

The proposed mechanism is shown in (**Figure 27**), at first, the photoexcited L_nPd^0 undergo single electron transfer (SET) with alkyl iodide to generate a hybrid alkyl palladium radical intermediate (A), which attack at the terminal position of diene (45) to give the radical intermediate (B). This intermediate exists in equilibrium with the π -allyl complex intermediate (C). A subsequent nucleophilic attack of the amine forms the carbofunctionalization product (46) and regenerates the palladium catalyst.

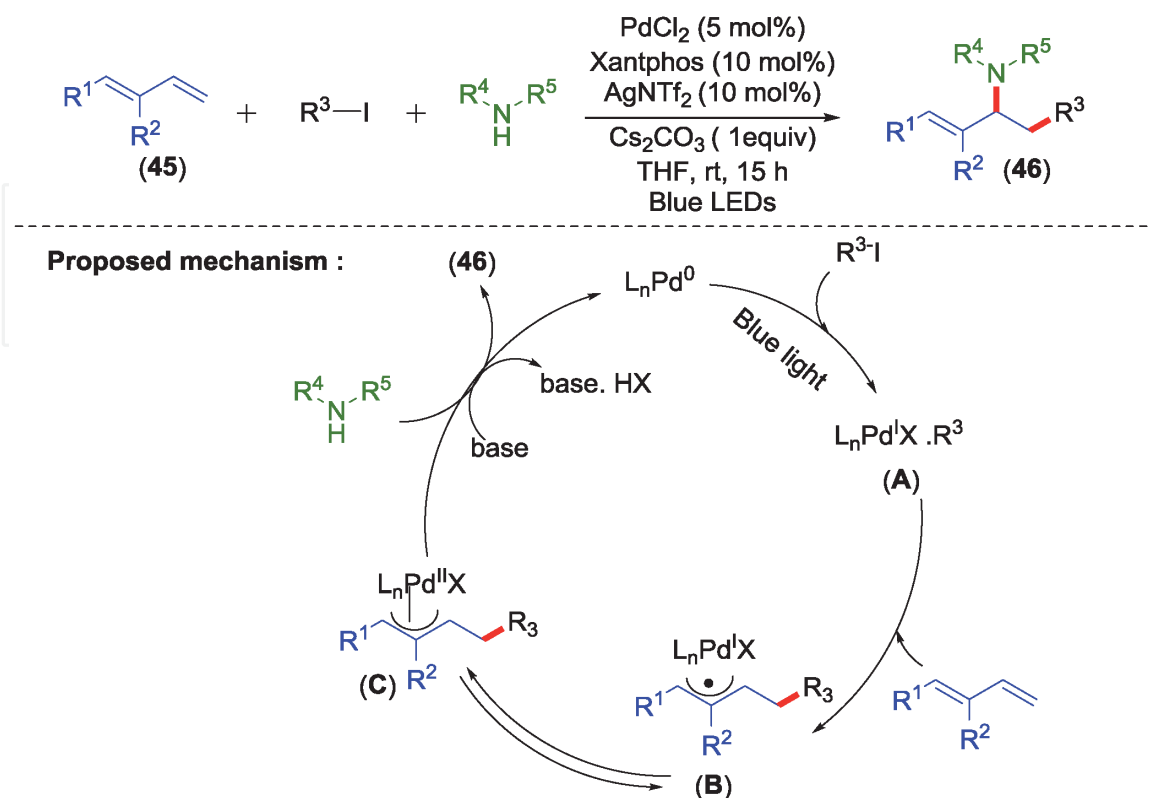


Figure 27.
Synthesis of Aminoalkylations derivative.

5. Organic dye-catalyzed C-N bond formations

5.1 Rose Bengal and 9-Fluorenone catalyzed C-N bond formation

Wei *et al.* in 2018 reported a new and facile visible-light-mediated synthesis of α -azido ketones (**48**) via oxyazidation of alkenes (**47**) with TMSN_3 in the air at room temperature (**Figure 28**) [32]. Rose Bengal is a metal-free photocatalyst, used for the synthesis of α -azido ketones. This difunctionalized products are easily and efficiently obtained in moderate to excellent yields via the formation of C-N and C=O bonds. The proposed mechanism is shown in (**Figure 28**). At first, visible-light irradiation of Rose Bengal generated the excited RB^* . Subsequently, a single electron transfer (SET) process takes place between TMSN_3 and RB^* to produce an azido radical and $\text{RB}^{\bullet-}$ radical anions. Then, the ground state Rose Bengal and $\text{O}_2^{\bullet-}$ is formed through the oxidation of $\text{RB}^{\bullet-}$ by molecular oxygen (air). Furthermore, the attack of azido radical to alkene (**47**) gives the alkyl radical intermediate (A). Next, the interaction between radical intermediate (A) with $\text{O}_2^{\bullet-}$ and H_2O afforded hydroperoxide intermediate (B). The oxidation of $(\text{PhSe})_2$ by hydroperoxide (B) yielded organoselenium intermediate (C) and PhSeOH . Finally, the additions of PhSeOH with reactive intermediate (C) produced the product (**48**) and regenerated $(\text{PhSe})_2$ and elimination of water takes place.

Wang *et al.* in 2019 depicted a visible-light-induce intermolecular azido-hydrazination method for the synthesis of β -azido alkyl hydrazines (**50**) from unactivated alkenes (**49**) (**Figure 29**) [33]. This transformation occurs via metal-free and redox neutral conditions and applies to a wide range of alkenes. The β -azido alkyl hydrazines are used for the preparations of many valuable synthetic building blocks. As per mechanism (**Figure 29**) initially, photo-excited fluorenone generates a N_3 radical via the catalytic oxidation of azide source with the formation of a reductive ketyl radical species (B). Then, the azide radical attacks the alkene to

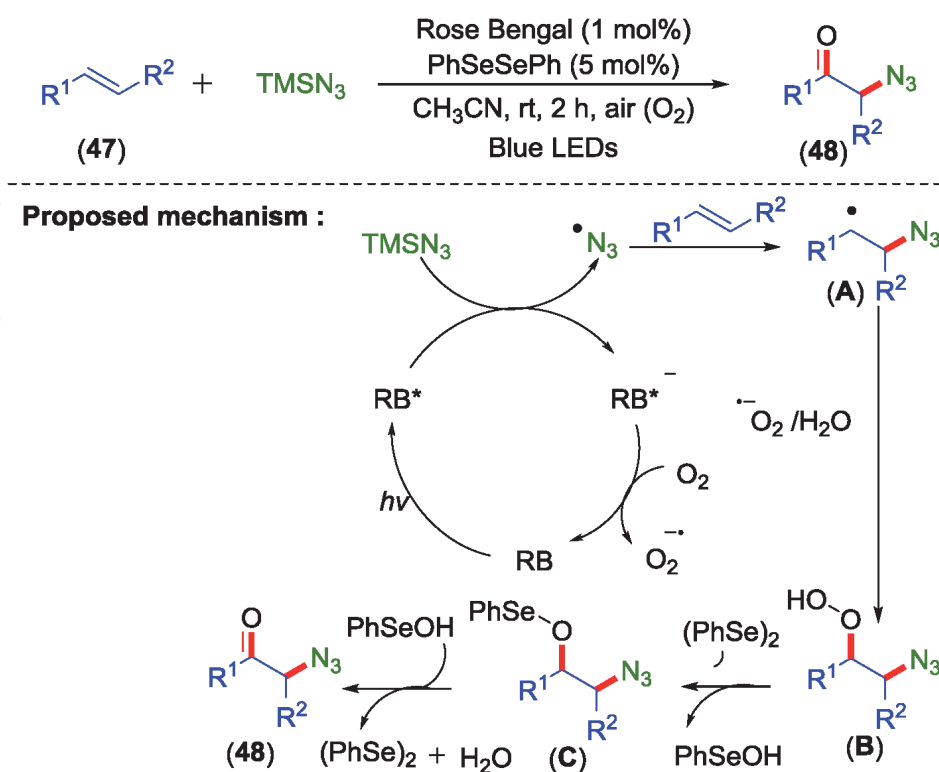


Figure 28.
Synthesis of azido ketones.

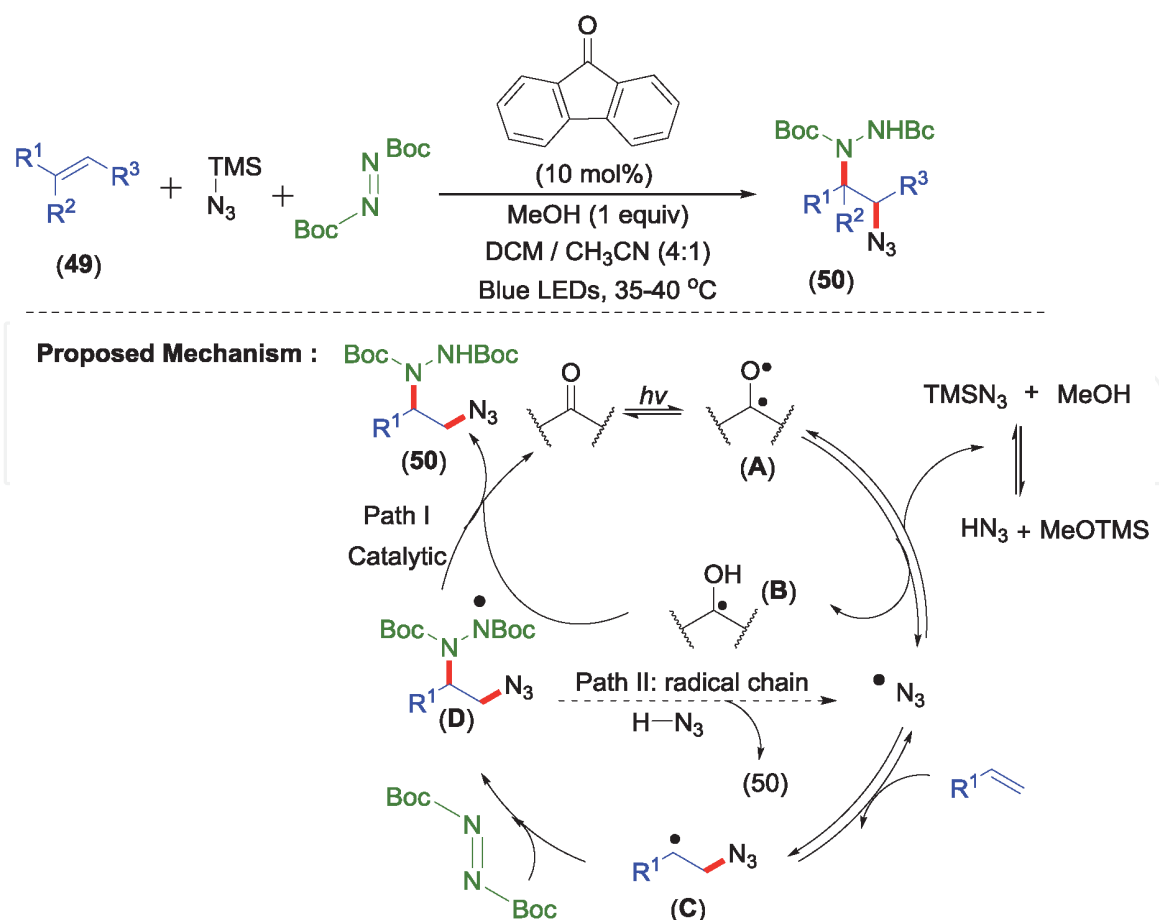


Figure 29.
Synthesis of β -azido alkyl Hydrazines.

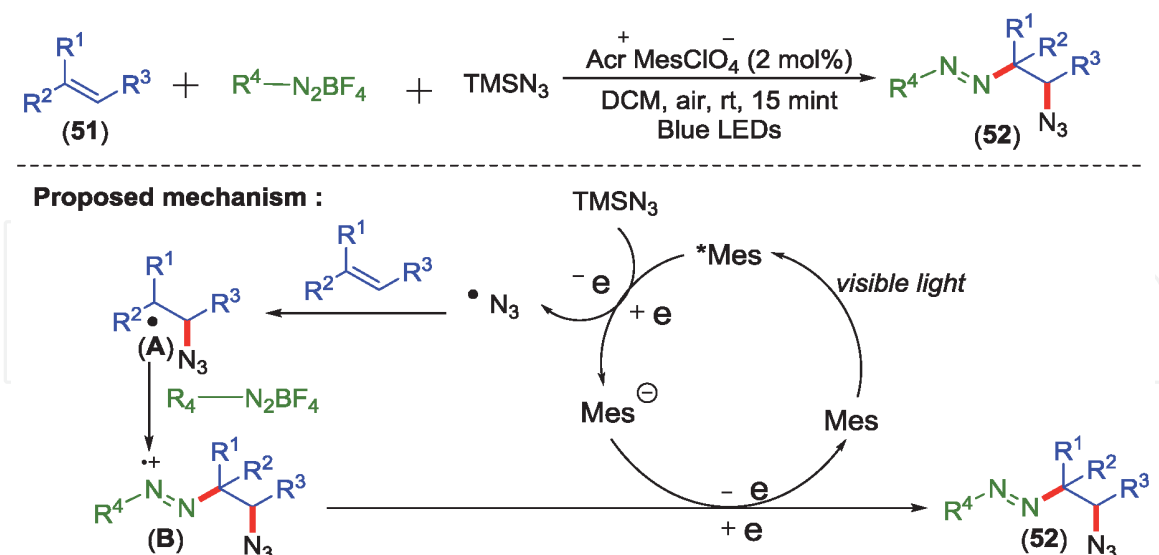


Figure 30.
Synthesis of unsymmetrical azo compounds.

give the alkyl radical intermediate (C). After that, the alkyl radical (C) is trapped by azodicarboxylate giving an *N*-centered radical intermediate (D) which upon the abstraction of a proton give the final product (50) (path I). On the other side, the intermediate (D) is reduced by H-N₃ to regenerate an azide radical and the cycles continue (path II).

5.2 Mes-catalyzed C-N bond formation

Shen *et al.* in 2021 reported a photo-induced multi-component cascade reaction in the presence of aryldiazonium salts with unactivated alkenes (**51**) and trimethylsilyl azide (TMSN₃) under oxidant-free conditions (**Figure 30**) [34]. This protocol provides a new synthetic method for unsymmetrical azo compounds and applies to different aryldiazonium salts and alkenes. According to the proposed mechanism (**Figure 30**) initially, in the presence of visible light, the photocatalyst 'Mes' undergoes an excited state (*Mes) and take parts in a single electron transfer (SET) process with TMSN₃ to generate the azido radical and 'Mes'[•] radical anion. Subsequently, the azido radical attacked the alkene (**51**) to produce an alkyl radical intermediate (A), which is trapped by the aryldiazonium salt to generate a radical cation intermediate (B). Finally, another SET process between the radical cation (B) and the 'Mes'[•] radical anion provide the product (**52**) with simultaneous regeneration of the photocatalyst 'Mes'.

Yang and Lu in 2017 established a suitable method for the formation of hydroxyazidation derivative (**54**) from the reaction of alkenes (**53**) under visible light photo redox catalysis (**Figure 31**) [35]. The important features of the reaction are low catalyst loading, room temperature, broad substrate scope. Readily available starting materials, such as alkenes and air, to construct valuable β -azido alcohols.

Wang *et al.* in 2020, demonstrated a metal-free method for the synthesis of β -trifluoromethyl hydrazines (**56**) by reacting alkene (**55**) with sodium trifluoromethanesulfonate as the CF₃ source. (**Figure 32**) [36]. This methodology enabled a radical cascade that incorporates a trifluoromethyl and a hydrazine group across the C=C double bond.

Moon *et al.* in 2020 demonstrated an atom-economical visible-light-mediated synthesis of aminopyridylationproduct (**58**) in the presence of alkenes (**55**) and *N*-aminopyridinium ylides (**Figure 33**) [37]. This environmentally friendly method

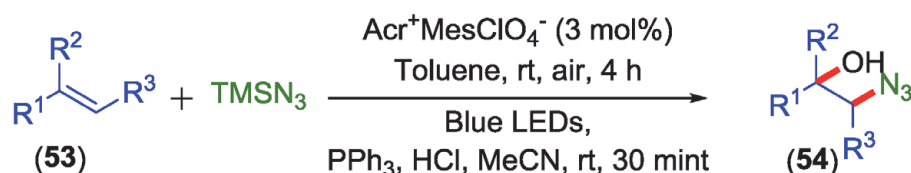


Figure 31.
Synthesis of Hydroxyazidation derivative.

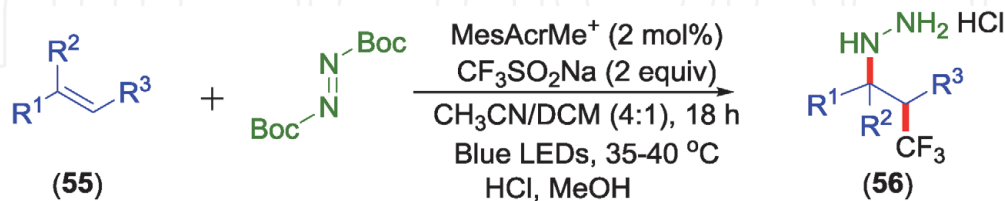


Figure 32.
Synthesis of β -Trifluoromethyl Hydrazines.

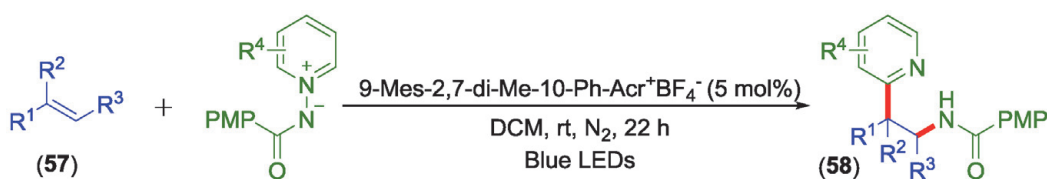


Figure 33.
Synthesis of Aminopyridylation product.

applies to a wide range of substrates with good functional group tolerance. Both activated, unactivated alkenes and pyridine are smoothly reacted and gave their desired products in moderate to good yields at room temperature.

5.3 Eosin-Y-catalyzed C-N bond formation

Moon *et al.* in 2019 demonstrated an Eosin Y mediated photocatalytic strategy for the synthesis of aminoethyl pyridine derivatives (**60**) in the presence of alkenes (**59**) using a variety of *N*-aminopyridinium salts as both aminating and pyridylating agents (**Figure 34**) [38]. Here concomitant incorporations of amino and pyridyl groups take place into alkenes under mild reaction conditions. In this protocol alkene bearing both electron-withdrawing and electron-donating groups are well tolerated. According to the possible mechanism (**Figure 34**) initially, in the presence of LEDs photocatalyst EY excited to the EY*, which subsequently form the unstable *N*-pyridine radical (A) via a single electron transfer (SET). Then the homolytic cleavage of the N-N bond takes place and generate the activated *N*-centered radical intermediate (B) and release the pyridine. The *N*-centered radical intermediate (B), attack the alkene and generate the intermediate (C). After that radical additions take place and produce the intermediate (D). Finally, the product (**60**) is obtained via deprotonations and the radical extrusion process.

Alam *et al.* in 2020 developed an elegant visible-light-mediated synthesis of *N*-hydroxybenzimidoyl cyanides from aromatic terminal alkenes using Eosin Y as a metal-free photocatalyst (**Figure 35**) [39]. DFT calculation supports a biradical pathway with successive incorporation of two nitrogen atoms, one each from *tert*-butyl nitrite (TBN) and ammonium acetate. The difunctionalization product is accomplished by the concomitant installation of an oxime and a nitrile group.

As determined from the DFT calculation and few control experiments a plausible mechanism has been proposed (**Figure 35**). In the influence of visible light Eosin Y (EY) undergoes excitation and generates a PINO radical from NHPI via hydrogen atom transfer (HAT) and returns to the ground state. The PINO radical adds to the

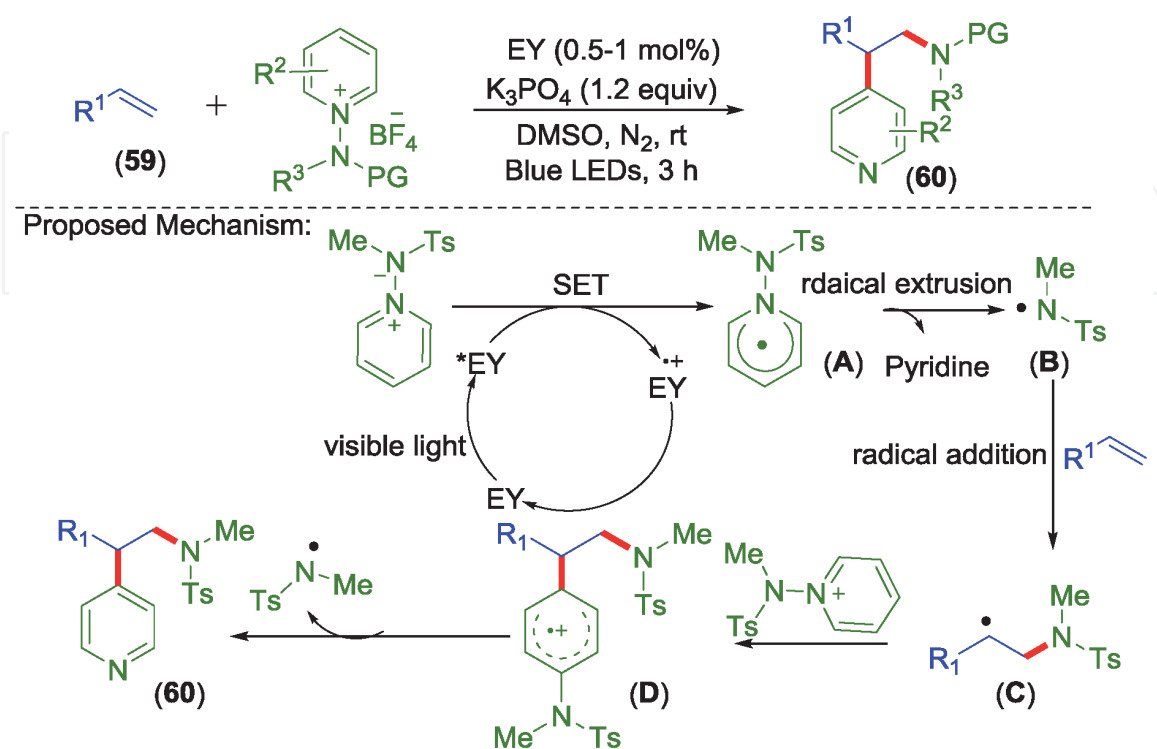


Figure 34.
Synthesis of Aminoethyl pyridine derivatives.

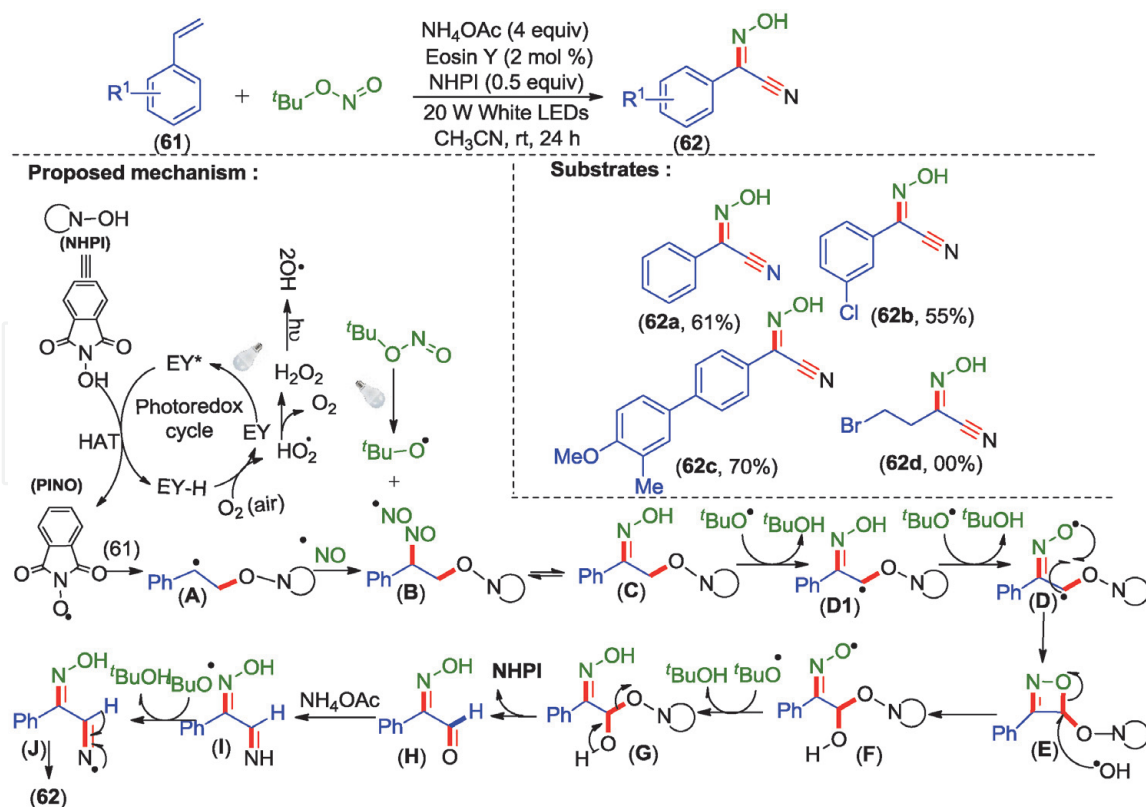


Figure 35.
Synthesis of N-Hydroxybenzimidoyl cyanides.

alkene (61) to give a benzylic radical intermediate (A) which trap the NO radical originating from TBN to give a nitroso intermediate (B) and is tautomerized to an oxime intermediate (C). Subsequent abstraction of two H atoms from the oxime intermediate (C) by in situ *tert*-butoxyl radical give a 1,4-biradical intermediate (D) which upon intramolecular coupling generates a four-membered cyclic intermediate (E). The strained cyclic intermediate (E) undergoes ring-opening via attack of an OH radical to form a hemiacetal radical intermediate (F). The N – O radical intermediate (F) abstracts a proton from *tert*-butanol to generate a neutral hemiacetal intermediate (G). The neutral hemiacetal intermediate loses NHPI providing an oxime aldehyde (H). Condensation between ammonia (generated from ammonium acetate) and the aldehydic intermediate (H) form an iminium intermediate (I). Abstraction of an iminium N – H from the intermediate (I) by the $^t\text{BuO}^\bullet$ radical produce a nitrogen-centered radical (J). Finally, the abstraction of the aldehydic proton from intermediate (J) by *tert*-butoxy radical provided the cyano functionalized product (62).

6. Conclusion

In summary, this chapter focus on the recent advancements in visible-light-mediated transition-metal and organic dye catalyzed difunctionalization of alkene leading to the formation of C-N bond. The utilization of visible light by photo catalysis is a burgeoning field in contemporary organic synthesis. The ubiquitous nature of the C-N bond predominates the synthetic chemist community. In this regard visible-light-mediated difunctionalization of alkene reactions have emerged as an efficient strategy for the synthesis of functionalized molecules, giving a high atom economy. Organic dye mediated C-N bond formations is even more promising compared to metal-catalyzed C-N bond formation because they overcome the


drawbacks associated with transition metals that limits their use in pharmaceutical industries. With the current momentum of development, a greater impact of photocatalytic C–N bond-formations reactions is foreseeable, for example, in the late-stage modifications of natural products, large-scale syntheses and enantioselective C–N bond formations reactions. Visible-light-mediated reactions provide a greener and sustainable approach and mild reaction condition towards the construction of complex molecules. Further developments in this area may open up broad opportunities for straightforward, efficient, and atom economical synthesis of N-compounds from simple alkenes.

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