Chapter-1

Introduction

1.1 Introduction

The phrase "Green Chemistry" was first used by the US EPA (United States Environmental Protection Agency) in 1990 to refer to chemical processes that do not include synthesizing or manufacturing poisonous or damaging materials [1, 2].

"Green chemistry," according to Paul T. Anastas and John C. Warner (1998) [3] is the implementation of a set of guidelines (Figure 1.1) that minimizes or completely avoids the use of dangerous chemicals in the design of reaction mechanisms, waste prevention, optimization of the atom economy, use of cleaner solvents, decreased synthesis of byproducts, and energy efficiency techniques. Because of this, it was crucial to develop synthetic processes based on these ideas to produce valuable organic molecules with little to no harm to the Earth [4-6].

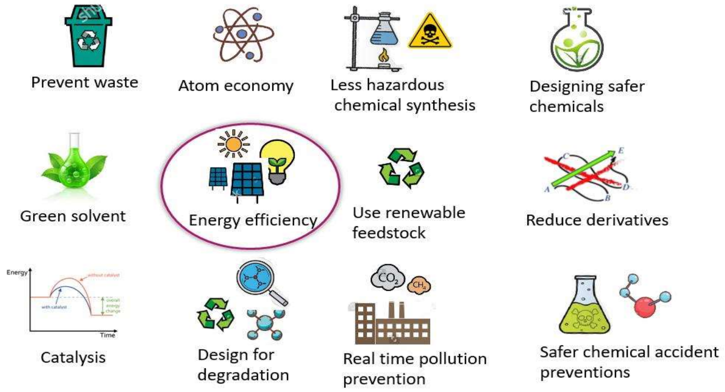


Figure 1.1 Principle of Green Chemistry.

Two most critical green chemistry ideas for synthetic chemists are using cleaner solvents and designing for energy efficiency. The advantages of green synthetic methodology include easy set-up, environmental friendliness, economics, safer chemicals, and more environmentally friendly energy resources, it was necessary to replace thermal methods in synthesizing organic compounds with other unconventional techniques like microwave, ultrasonic radiations and visible light-mediated reactions combined with traditional resources, and the use of photoredox catalyst as catalysts.

Visible light and green reaction conditions have been taken into account in our synthetic methodology [7-9]. A comparison of synthetic processes for related or identical reactions was also conducted. It was believed that these processes would make use of different inorganic and organic catalysts, different non-polar and polar solvents, and other variables. The use of environmentally friendly green solvents, catalysts, renewable feedstocks, and decreased waste generation are significant aspects of achieving more environmentally friendly procedures in light of this goal [4, 6].

1.2 Historical background and basic concept of visible-light mediated organic reactions/synthesis (Photochemistry)

Modern society was founded on the usage of fossil fuels. However, despite several technological developments that have improved their efficiency, they are still not a sustainable energy source, it is true. Although the limited fuel supply is no longer the primary cause for concern, experts have long recognized this [10, 11]. Transport, heavy industry, building heating, and the creation of electricity are all made possible by fossil fuels. Therefore, burning fossil fuels contributes to pressing problems like global warming, resource depletion, and environmental damage. The deposits of coal, oil, and natural gas are constrained and referred to as non-renewable energy sources since they cannot be replenished after they are depleted. Over the next century, it is predicted that oil and natural gas reserves will drastically decrease at the current energy consumption rate. Although coal is more readily available, its use can worsen environmental issues like global warming (the gradual rise in Earth's temperature). In the future, adopting alternative energy sources will be more vital due to the rising energy needs of industrialized civilizations and developing countries. Other approaches to solving the energy issue include energy conservation and more effective energy use. To reduce the effects and perhaps even stop the development, there must be an international effort to impose changes in conduct, policy, and consumption. The Paris Agreement, where participating nations create policies to fight climate change, set goals that restrict the global temperature increase to 1.5 °C. Each nation has a variety of options for achieving these objectives. Still, a concentrated effort in creating and using renewable energy is necessary to reduce some of the stress on modern industry. The negative consequences of fossil fuels can be mitigated with more effective and accessible alternative fuel sources. A possible strategy is to employ solar energy inspired by nature and photosynthesis. This is because more solar radiation hits the Earth daily than is needed to meet the entire world's annual energy needs.

Giacomo Ciamician, a chemistry professor at the university of Bologna in Italy from 1889–1922, (Figure 1.2a) was the first researcher to examine the photochemical reaction thoroughly. He was motivated by the capacity of plants to utilize solar energy [12]. He is credited with founding photochemistry. His statement that "*there is another agent that has a major effect on the activities of life and that deserves to be extensively investigated: that is light*" shows how well he recognized the significance of sunshine [13, 14].

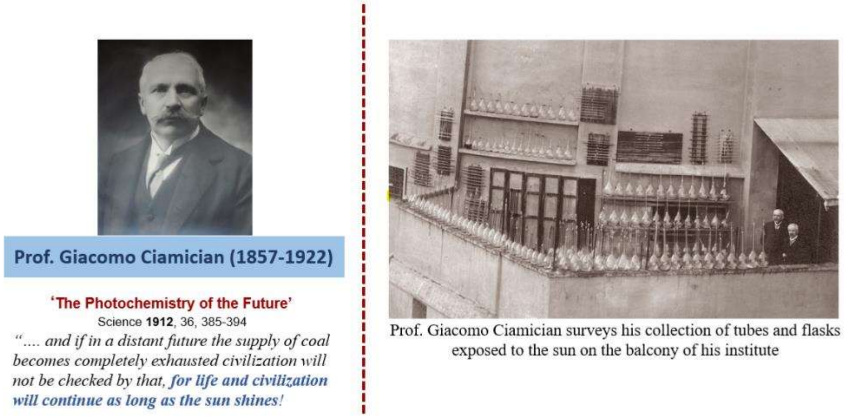


Figure 1.2 (a) Prof. Giacomo Ciamician (1857-1922), (b) Giacomo Ciamician surveys his collection of tubes and flasks exposed to the sun on the balcony of his institute (Images are taken from https://chemistry.unibo.it/en Department of chemistry "Giacomo Ciamician" Alma Mater Studiorum - Università di Bologna - Via Zamboni, Bologna and statements are taken from reference 14

He was a staunch supporter of utilizing the energy that the Earth receives from the sun on a daily basis to replace fossil fuels (such as coal). He precisely predicted the creation of fuels by simulated photochemical processes (artificial photosynthesis), which is still one of the key objectives of current chemistry research [10, 11].

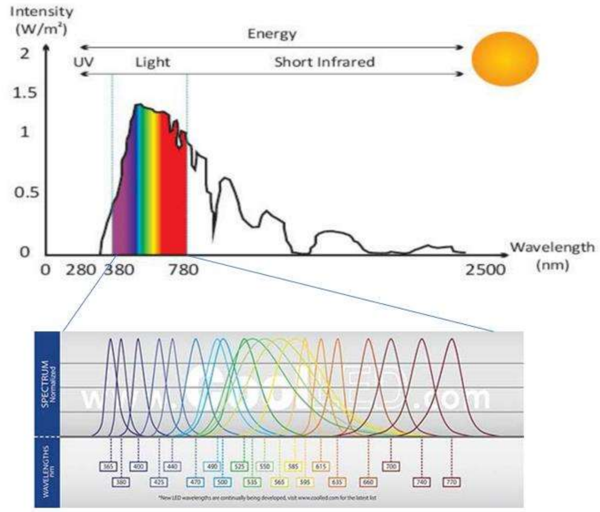


Figure. 1.3: Solar radiation spectrum

In the upper atmosphere, the Earth gets 174 petawatts of solar energy (1 petawatt = 1015 watts). Clouds and oceans absorb the remaining 30%, and land masses, with just about 30% reflected space. At the Earth's surface, the solar light spectrum is primarily distributed in the visible and near-infrared regions, with a tiny portion in the near ultraviolet (Figure. 1.3). Due to its enormous natural abundance, the use of visible light as a promoter in synthesis is therefore particularly intriguing. In contrast to UV light, handling visible light is very simple, safe, and has the potential to be used on an industrial scale [15, 16].

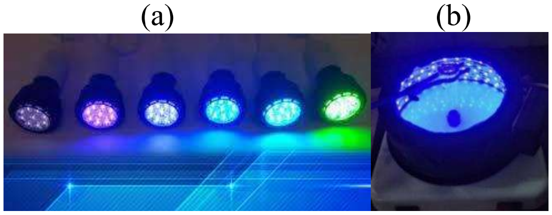


Figure 1.4 (a) Modern LEDs with different wavelengths (b) Reaction setup in our lab

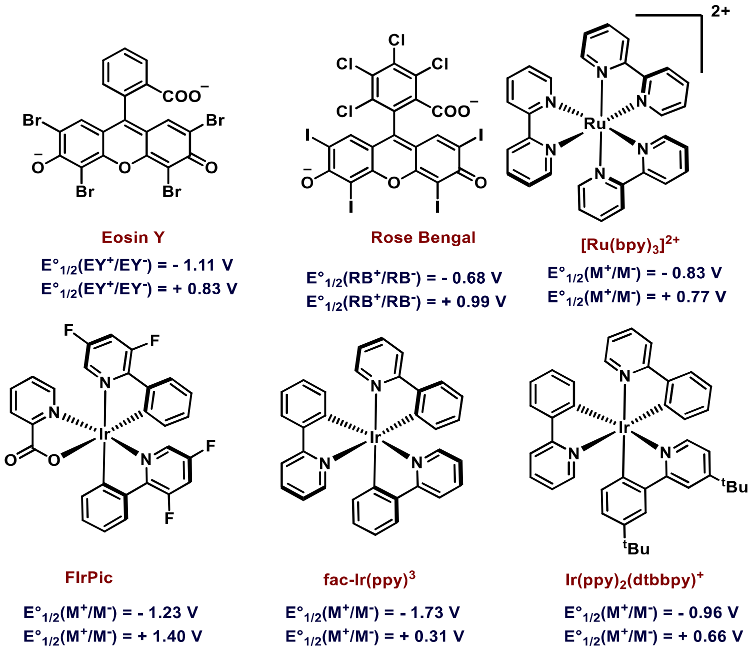
During his studies, Ciamician encountered an experimental challenge as well. A good light source is necessary to conduct photochemical investigations. Today's researchers work with powerful halogen, mercury, and tungsten lamps that include light filters that let them choose from nearly monochromatic light beams or LEDs (Figure 1.4). Laser sources, continuous or pulsed, are increasingly frequently found in photochemical laboratories. But at the beginning of the 20th century, there were no halogen, mercury, LED, or laser light sources, and the tungsten lamps' light was too dim and too "red" to cause photochemical reactions. The balconies of the institute where Ciamician worked were the most appropriate location for his laboratory because the sun was the sole practical light source for his photochemical research. He also used words that showed how much he appreciated the power of sunlight *"....and if in a distant future the supply of coal becomes completely exhausted civilization will not be checked by that, for life and civilization will continue as long as the sun shines!"* (Figure 1.2b) [14].

1.3 Mechanistic pathways of photoredox catalysis

The study of photochemistry focuses on chemical processes triggered by light absorption. Different species can harness the photon's energy and enter an electrically excited state, which starts a chemical reaction. There are two ways to start the chemical reaction by;

i) direct excitation of the substrates or reaction intermediates (direct photochemistry), or

ii) the ability of colored catalysts to absorb light and then activate non-absorbing substrates (Scheme1.1). If the catalyst is replaced during the process, the latter circumstance is considered photocatalysis [7-9, 17-21].

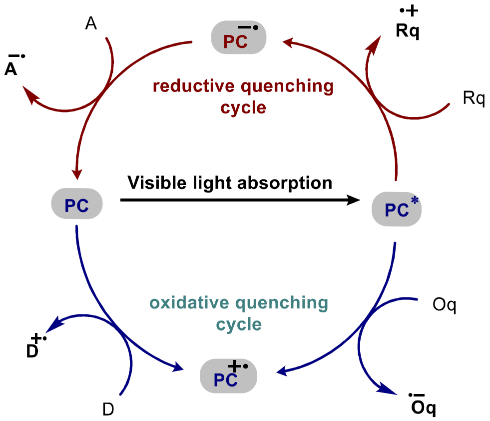


Scheme 1.1: Inorganic and organic photoredox catalysts**.**

The term "photocatalytic reaction" thus refers to a reaction that needs both a catalyst (that is not consumed) and light. Photoexcited species interact with other reaction constituents via a variety of mechanisms, including Photoredox catalysis (Electron transfer):, Hydrogen atom transfer, energy transfer (sensitization) and, EDA complex

1.3.1 Photoredox catalysis (Electron transfer)

Because excited states can be reduced and oxidized more readily than their corresponding ground states, photoredox catalysis depends on this general property. As a result, the photocatalyst can act as either an electron donor or an electron acceptor to be renewed in the catalytic cycle (Scheme 1.2) [20-24].



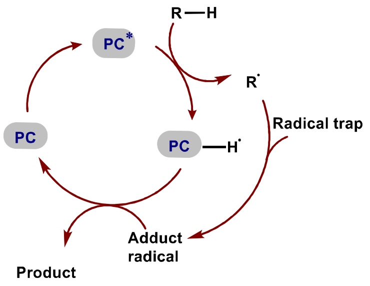
Scheme 1.2 Photoredox catalysis by oxidative and reductive pathways with the electronic state of the catalyst. PC = photocatalyst, Rq = Reductive quencher, Oq = Oxidative quencher D = donor, A = acceptor

A suitable wavelength of light can excite a photocatalyst (PC) to produce an excited species (PC^{*}) with a higher energy electron, which can then be changed into a radical cation ($PC^{\bullet +}$) by donating an electron to the quencher (Q). The quencher produces a stable anionic radical ($Q\bullet^{-}$) after 1e-reduction, which passes through reductive transformation.

The cationic radical species of the photocatalyst (PC^{+}), to complete the photocatalytic cycle, absorbs an electron from the donor molecule (D), returns to the ground state, and prepares for the subsequent cycle (oxidative quenching). When the process is reversed, the photoexcited catalyst (PCat*) collects an electron from the quencher and then donates it to an acceptor molecule (A), returning to the ground state and ending the catalytic cycle, the oxidative transformation happens (reductive quenching). Both oxidative and reductive routes can utilize the photocatalyst, depending on the type of quenchers, such as donor or acceptor [23-26].

1.3.2 Hydrogen Atom Transfer (HAT)

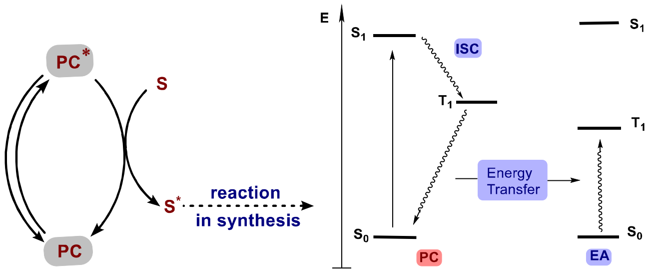
Hydrogen atom transfer (HAT) is a chemical transformation consisting of the concerted movement of two elementary particles – a proton and an electron – between two substrates in a single kinetic step [27]. Significantly, HAT represents a key step in various chemical reactions, including the combustion of hydrocarbons and aerobic oxidations. Additionally, it affects several atmospheric phenomena. Numerous metalloenzymes in biology are known to function through a HAT step, and extensive research has been done on the function of such processes in the harmful effects of reactive oxygen species (ROS) in vivo and the mechanism of action of antioxidants [27-30]. HAT, on the other hand, offers uncommon possibilities for organic synthesis because it permits the simple activation of (aliphatic) R-H bonds, frequently in a highly selective manner, allows skipping the introduction of a guiding moiety into a substrate, and the reactivity may be modified by carefully selecting the reaction conditions (e.g., hydrogen abstractor, solvent, etc.) [31]. In the first, a hydrogen atom is abstracted from a substrate R-H by the excited state of the photocatalyst (PC*) in a direct HAT process [32]. A back-HAT step to one of the intermediates created during the catalytic cycle then closes it (scheme1.3) [25, 33-35].



Scheme 1.3 Photocatalytic pathway via HAT

1.3.3 Energy Transfer

It's important to distinguish between electron transfer and energy transfer processes when discussing visible-light-mediated photocatalysis. The strong redox activity of an excited state molecule is used in electron transfer photocatalysis to trigger a single electron transfer (SET) event. While this sub-discipline has seen a lot of attention in the recent decade. Energy transfer [25, 26, 36-38] is formally defined as "the photophysical process in which an excited state of one molecular entity (the donor D) is deactivated to a lower-lying state by transferring energy to a second molecular entity (the acceptor A), which is thereby raised to a higher energy state."



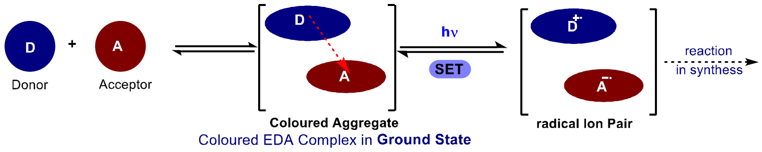
Scheme 1.4 Photocatalysts used in photochemical reactions with EnT pathways

In this way, the photocatalyst is analogous to the donor, stimulated by the direct absorption of visible light. The excited photocatalyst can then transfer its excited state energy to the corresponding substrate (the acceptor), which is "indirectly excited" or "sensitized". To be clear, excited photocatalysts that undergo SET or EnT might be referred to as photoredox catalysts or photosensitizers (Scheme 1.4). Because of their relatively high triplet energies and long lives of their triplet states, various ruthenium- and iridium-based polypyridyl complexes and organic dyes are excellent photocatalysts (sensitizers) for such reactions.

1.3.4 Electron Donor-Acceptor (EDA) Complexes

This scenario has altered drastically in recent years, with various photochemical procedures being discovered, significantly increasing the synthetic toolbox of modern chemists. Progress within the discipline has been chiefly encouraged by photoredox catalysis [26]. This method makes use of colourful photocatalysts that gather visible light energy to activate readily available bench-stable substrates and create reactive radicals under very moderate reaction conditions.

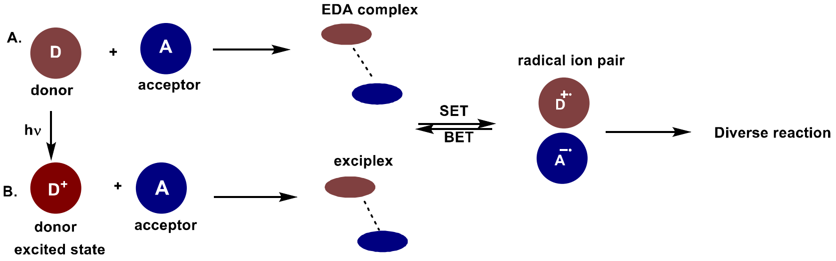
The synthetic community has recently realized the significance of a photochemical technique that varies from photoredox catalysis because it does not rely on an exogenous photoredox catalyst [39-43]. This method uses the interaction of an electron acceptor substrate A and a donor molecule D (Lewis acids and bases, respectively) to produce a new molecular aggregation in the ground state known as an electron donor-acceptor (EDA) complex (Figure 1a). Although components A and D do not absorb visible light,



Scheme 1.5 Photocatalytic pathway via EDA complex

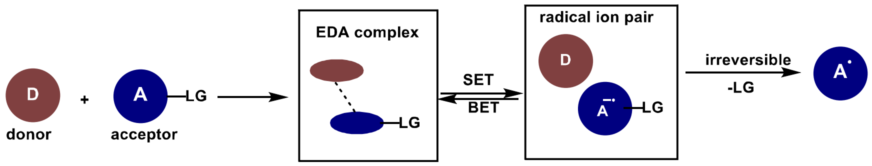
the resulting EDA complex does. Under mild conditions, light excitation causes an intramolecular single-electron-transfer (SET) event that can yield radical intermediates. Despite substantial research into the photophysical characteristics of EDA complexes since the 1950s, their application to chemical synthesis has been limited.

Conferring to Hildebland, iodine interaction with aromatic hydrocarbons resulted in spectroscopic changes [44]. Mulliken then proposed a quantum mechanics hypothesis for the creation of EDA complexes [45]. In the ground state, stable charge-transfer complexes have a large contribution from the non-bonded structure and a moderate contribution from the charge-transfer structure.



Scheme 1.6 Schematic pathway of EDA complex (A) and exciplex (B)

On the other hand, photo-excitation of EDA complexes results in polarised charge-transfer states that cannot be attained thermally, from which the SET process yields a radical ion pair (Scheme 1.6 A). Alternatively, Leonhart and Weller revealed how, while no charge-transfer interaction is observable in the ground state, an exciplex[46] can be generated in the excited state of a donor or acceptor (Scheme 1.6 B).



Scheme 1.7 A radical generation strategy based on LG-installed EDA complex

Both processes generate radical species that can participate in various reactions. Even when the SET event is successful, and a radical ion pair is formed from an EDA complex, back electron transfer (BET) frequently impedes the formation of radical species as an ideal path and, as a result, the application of EDA complexes to organic synthesis.

Using a leaving group (LG)-installed acceptor removed this BET-derived limitation. The removal of the departing group competes with BET, preventing a restoration to the original EDA complex. If the elimination efficiency, an irreversible process, is sufficiently high, the equilibrium is disturbed, resulting in the generation of radical species, which is then implicated in chemical synthesis. Several groups pioneered this concept of an EDA complex created from a donor substrate with LG-installed acceptors, but no specific experimental evidence of the EDA complex was found [47].

1.4 Visible light-mediated synthesis of Nitrogen and Sulfur-containing Compounds

Nitrogen-containing compounds are abundant in a wide range of bioactive molecules, including peptides, alkaloids, nucleic acids, and other natural products, as well as in a large range of routinely used medications [48-53]. Such compounds are important chemical building blocks that are widely used in the manufacture of medicines, food additives, detergents, polymer materials, and agrochemicals.

Sulfur-containing compounds (SCCs) are essential components of human bodies as well as other living species [54-62]. They exist as amino acids, peptides, proteins, enzymes, and vitamins implying that sulfur-containing molecules have already catalyzed or participated in many types of reactions in nature. Furthermore, they perform distinct roles in everyday life including materials science, ood chemistry, clinical chemistry, and synthetic chemistry.

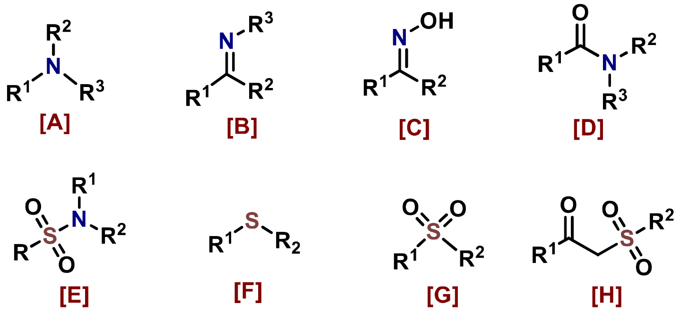


Figure1.5 Nitrogen and sulfur containing some main class of organic compounds.

The recent applications of visible-light-induced photocatalytic trends for the synthesis of pharmaceutically potent biologically active Nitrogen and sulfur-containing compounds like amines(A) imines(B), oxime(C) amide(D), sulfonamides(E) sulfides(F) sulfones(G) β-keto sulfones(H) via different modes of chemical bond formation are discussed below.

1.4.1 Amine

Amines are the most important and commonly utilized organic chemicals, and their prevalence in pharmaceutical and agrochemical agents, natural products, and small-molecule biological probes has fueled efforts to expedite their manufacture. Amines are also used in the synthesis of many drugs like Amphetamine, Chlorpheniramine and Salmeterol etc. (Figure 1.2).

Photoredox catalysis is widely used in the synthesis of amines. In this section, we shall discuss recent exemplary cases of amine synthesis by visible-light-mediated reactions.

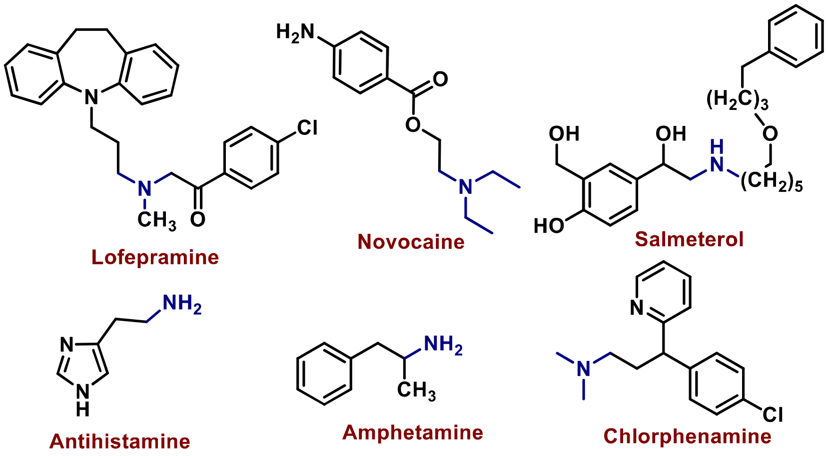
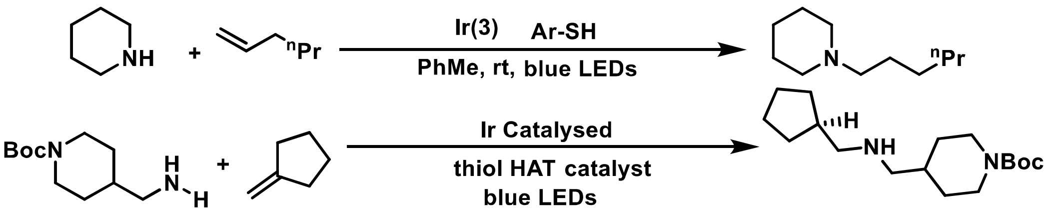


Figure 1.6 Some biological active drugs containing amine functional group

1.4.1.1 Synthesis of amine with alkenes

Under visible light conditions, olefin amination is an effective method for forming C-N bonds (amines) with substituted and terminal alkenes.

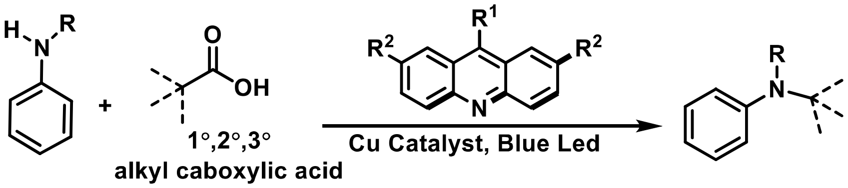
Musacchio, et al. discovered this transition for unactivated olefins with cyclic secondary alkylamines in an intermolecular environment Ir-3 catalyzed under visible light irradiations [63]. David C. Miller et al. published a photocatalytic approach for the intermolecular anti-Markovnikov hydroamination of unactivated olefins with primary alkyl amines to yield selective secondary amine products [64].



Scheme 1.8 Synthesis of amine with alkenes

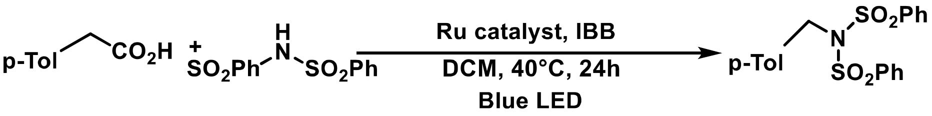
1.4.1.2 Amine from decarboxylation of carboxylic acid

The MacMillan and Larionov groups develop drecent advances in photoredox chemistry to enable the synthesis of carbon-centered radicals from feedstock 1°, 2°, and 3° carboxylic acids via carboxylate single electron oxidation [65]. The generated nucleophile carbon-centered radicals easily react with various electrophilic heteroatoms or other radical acceptors in this context.



Scheme 1.9 Synthesis of amine from carboxylic acid via single electron oxidation

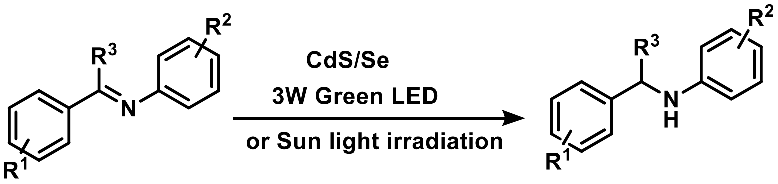
Murakami, Itami, and colleagues reported an alternative strategy [66]. This study used aryl acetic acids and the hypervalent iodine-based oxidant IBB to synthesize sulfonamide, which was reported as a suitable Ritter-type amination approach for the synthesis of tertiary amine derivatives.



Scheme 1.10 Synthesis of amine from carboxylic acid via iodine based oxidant

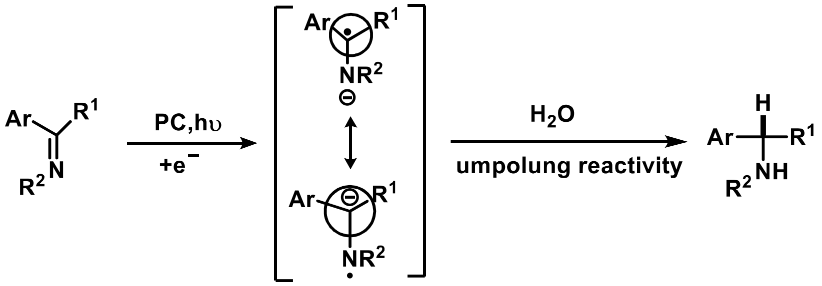
1.4.1.3 Synthesis of amine from imine

Various imines are compatible, resulting in excellent yields of desirable amines under visible light circumstances using CdSe/CdS core/shell quantum dots (QDs) as stable and highly active photoredox catalysts. Zi-Wei et al. reported that this reaction takes place through PCET from the QDs conduction band [67].



Scheme 1.11 Synthesis of amine from imine using CdSe/CdS core/shell QDs

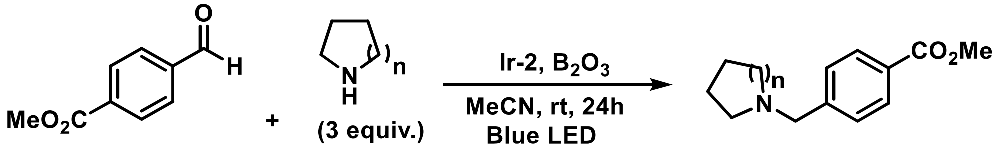
Rui Wang et.al. also reported the synthesis of amine from benzophenone ketiminines using photoredox catalyst via the carbanionic reactivity of imines [68].



Scheme 1.12 Synthesis of amine from benzophenone ketiminines

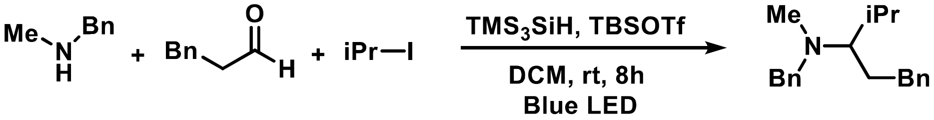
1.4.1.4 Amination of carbonyl compounds

Reductive conversion of aryl aldehydes into benzylamines was reported utilizing Ir-2, photocatalyst, Lewis acid, and the water scavenger additive boron trioxide [69].



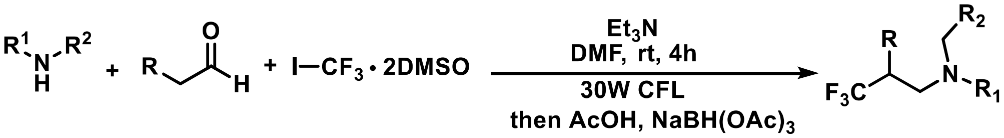
Scheme 1.13 Photocatalyzed direct reductive amination of aldehydes

The Gaunt groupreported carbonyl alkylative amination using *in situ* enamine production in the presence of super silane, TBSOTf, and visible light [70].



Scheme 1.14 Synthesis of complex tertiary alkyl amines via carbonyl alkylative amination

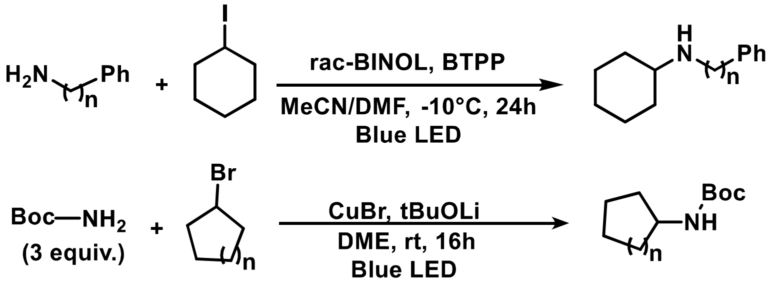
Also, the Gaunt group revealed the trifluoromethylation form of this process to obtain - trifluoromethyl tertiary alkylamines. In a reductive aminocyclization of feedstock ketones and secondary amines, which produce iminium *in situ,* valuable N-heterospirocycles were synthesized [71].



Scheme1.15 Synthesis of trifluoromethyl tertiary alkylamines

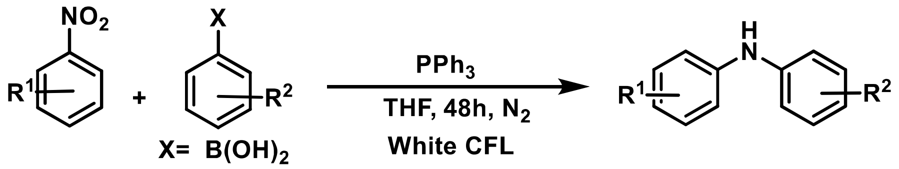
1.4.1.5 From dehydrohalogenation couplings.

Fu, Peters, and colleagues described photoinduced dehydrohalogenation coupling to generate primary amineusing copper photocatalyst, primary alkylamines, and haloalkanes.



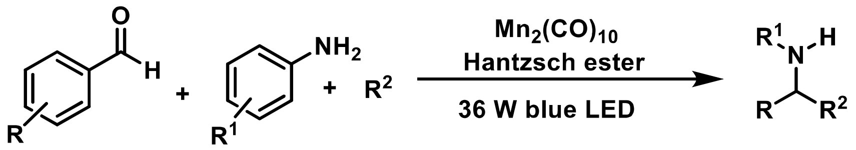
Scheme 1.16 Synthesis of amines by dehydrohalogenative couplings

Metal-free, visible-light and triphenylphosphine-mediated intermolecular, reductive amination of nitroarenes and boronic acids at room temperature without the use of a photocatalyst were recently reported by Kartic Manna [72].



Scheme 1.17 Synthesis of amine by reductive amination of nitroarenes and boronic acids

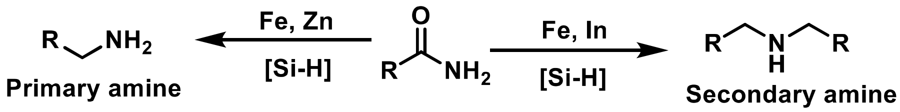
Xiaochen Wang described the visible-light-mediated multicomponent synthesis of secondary amine by three-component alkylation reactions of imines (generated *in situ* by condensation of benzaldehydes and anilines) with unactivated alkyl iodides using cheap and readily available $Mn_2(CO)_{10}$ [73].



Scheme 1.18 Synthesis of amine by three-component alkylation reactions of imines

1.4.1.6 Synthesis of amine by the reduction of amide

Jiajun Wu reported Tandem iron/zinc or iron/indium-catalyzed hydrosilylation of primary amides under visible light activation. The type of the co-catalyst ($Zn(OTf)_2$ vs $In(OTf)_3$) was critical in the selectivity of the $Fe(CO)_4(IMes)$ catalyzed reduction of primary amides: Zn favoured the synthesis of primary amines, where as indium co-catalyzed the formation of secondary amines [74].



Scheme1.19 Synthesis of amine Fe/Zn or Fe/In-catalyzed hydrosilylation of amides

1.4.2 Imine

An imine is a functional group that is frequently referred to as azomethines or Schiff’s bases. Albert Ladenburg, a German scientist, created the name "imine" in 1883. Imines and their derivatives have been identified as key intermediates in the synthesis of physiologically active heterocycles and alkaloids containing nitrogen [75,76]. A particularly intriguing technique for the manufacture of imines is the homogenous oxidative dehydrogenation of amines by air or pure O_2. In recent years, several techniques have been tested.

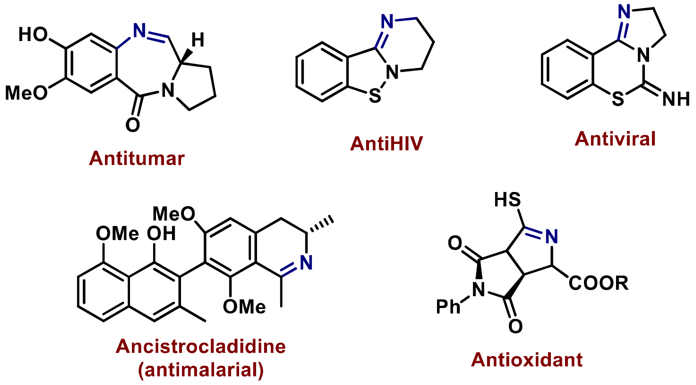
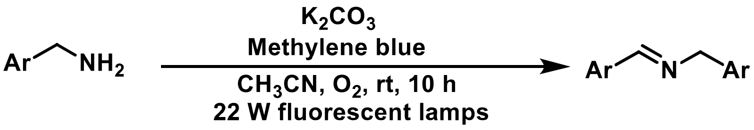


Figure 1.7 Some biological active drugs containing imine functional group

1.4.2.1 From aerobic oxidative coupling of benzylamines

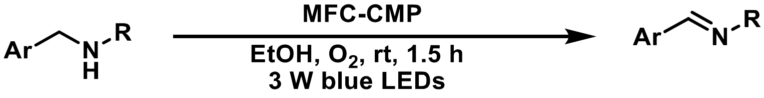
An organic dye, methylene blue, was used as a photocatalyst in the photo-organocatalytic aerobic oxidative coupling of benzylamines to give N-benzylidene benzylamines [77].



Scheme 1.20 Synthesis of imine by aerobic photo-oxidative coupling of benzyl amines

1.4.2.2 From aerobic dehydrogenation of amines

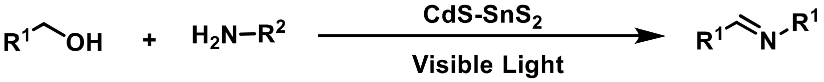
Aerobic dehydrogenation of secondary amines to imines was also carried out under visible light irradiation using metal-free, recyclable carbazole-based CMP with a fluorene moiety (MFC-CMP, 23) as heterogeneous photocatalysts [78].



Scheme 1.21 Synthesis of imine by dehydrogenation of secondary amines

1.4.2.3 From coupling of alcohols and amines

The current study presents an efficient, adaptable, and atom-efficient method for the synthesis of imines by cross-coupling of alcohols and amines under visible light irradiation with CdS-SnS_2 composites as photocatalysts and air as an oxidant.



Scheme 1.22 Synthesis of imine by cross-coupling of alcohol ls and amines

1.4.3 Oxime

Oxime is a critical structural ingredient used in the manufacture of pharmaceuticals and agrochemicals [79]. Oxime compounds have numerous applications, including nerve agent antidotes such as pralidoxime, obidoxime, methoxime, asoxime, and trimedoxime (Figure 1.5). Oximes can also be found in antioxidants, insecticides, vasodilators, antibacterial agents, and P450 inhibitors. Diacetyloxime is an ATP-sensitive potassium ion channel inhibitor.

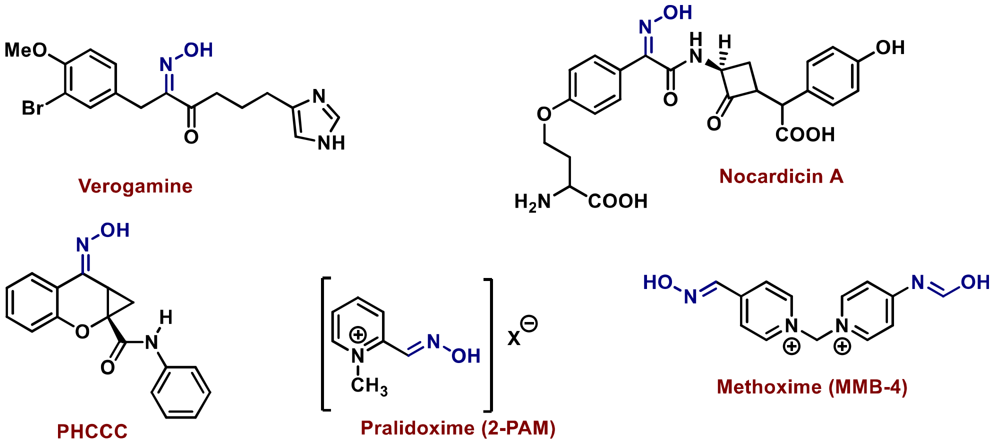
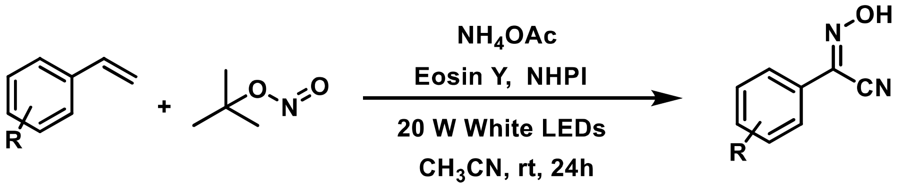


Figure 1.8 Some biological active drugs containing oxime functional groups

1.4.3.1 From aromatic terminal alkene

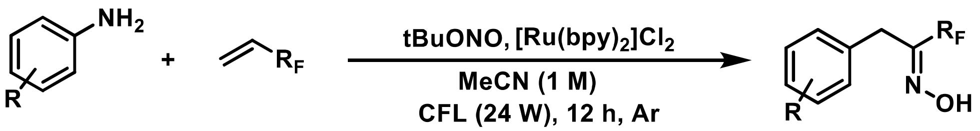
Tipu Alam, reported, the synthesis of N-hydroxybenzimidoyl cyanides from aromatic terminal alkenes was reported using Eosin Y as an organic photoredox catalyst, *tert*-butyl nitrite, and ammonium acetate [80].



Scheme 1.23 Synthesis of oxime by cyanation of Terminal Alkene

1.4.3.2 From amine

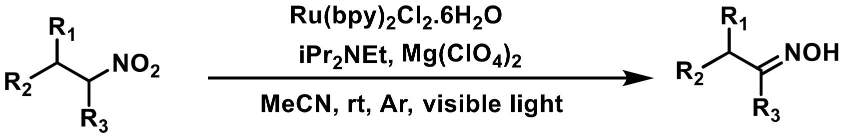
Da seul, lee and co workers described a light-promoted tandem approach for the synthesis of fluoroalkylated oximes. This approach could be used on aromatic compounds that are both electron-rich and electron-deficient [81].



Scheme 1.24 Synthesis of fluoroalkylated oxime

1.4.3.3 From nitro compounds

D. Z. Wang described the synthesis of oximes from a variety of nitro compounds under the synergistic effects of visible light irradiation, the $Ru(bpy)_3Cl_2$ photocatalyst, Hünig's base, $Mg(ClO4)_2$ activation, and MeCN solvent[82].



Scheme 1.25 Synthesis of oxime from nitro compounds

1.4.4 Amide

Amides [83] are a class of molecules that are important in the pharmaceutical industry, materials science, agrochemicals, and chemical biology. Many pharmaceuticals, natural compounds, and polymers contain carboxyamide functional groups. According to the statistics in a 2006 survey, amides are found in two-thirds of drug candidates [84] and present in 25% of all pharmaceuticals currently in the market [85]. In addition, in 2014, more than 50% of the reported processes used amidation reactions [86]. Figure 1.3 depicts some examples. Their wide range of applications is strongly related to the structure of the amidic moiety, which confers unique properties to these compounds. As a result, the production of amide bonds is one of the most important and investigated organic chemistry reactions.

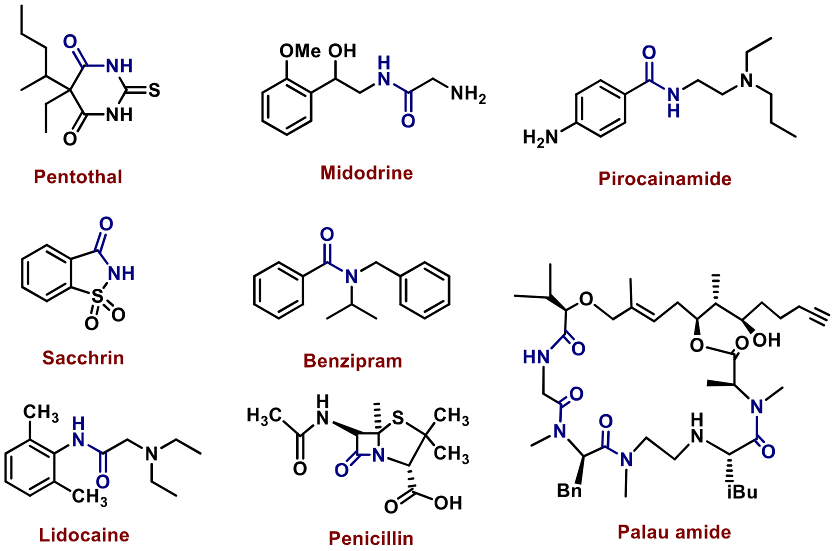
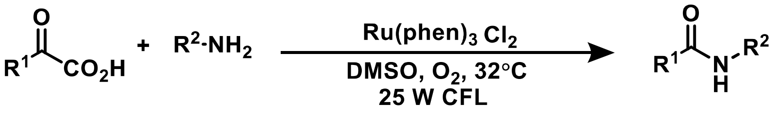


Figure 1.9 Some biological active drugs containing amide functional groups

1.4.4.1 Synthesis of amide from keto acids

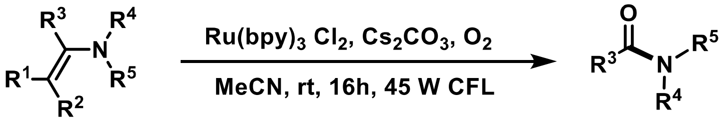
Lei and Lan [87] described early efforts to use visible-light photoredox catalysis for the radical oxidative decarboxylative coupling of α -keto acids with amines .



Scheme 1.26 Synthesis of amide from keto acids

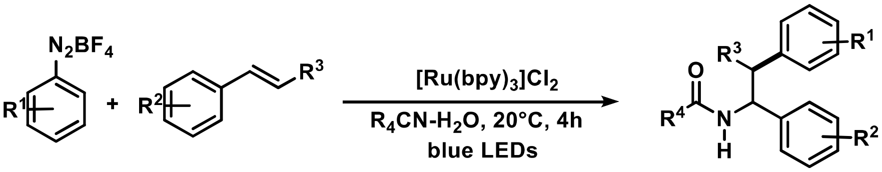
1.4.4.2 From enamines

Wang and co-workers [88] described the synthesis of amide from oxidative amidation of enamines utilizing Ru photocatalyst and molecular oxygen as oxidant under irradiation of 45 W household bulb in 2014.



Scheme 1.27 Synthesis of amide from enamines utilizing Ru photocatalyst

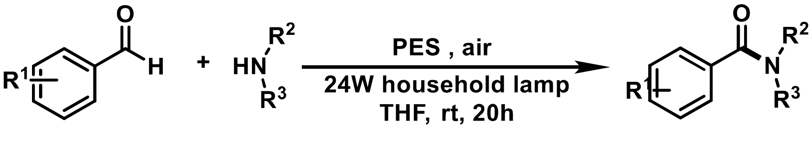
König's group [89] originally published a novel visible-light-driven aryl radical-mediated Meerwein addition process, namely intermolecular amino-arylation of alkenes.



Scheme 1.28 Synthesis of amide from enaminesvia aryl radical

1.4.4.3 From aldehyde

Leow described the oxidative amidation of aromatic aldehydes with amines using a low-cost phenazine ethosulfate as an organic photocatalyst and air as the sole oxidant [90].

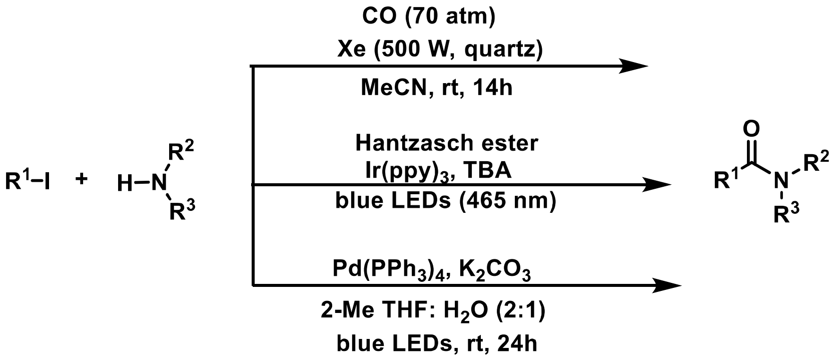


Scheme 1.29 Synthesis of amide from oxidative amidation of aromatic aldehydes

1.4.4.4 Radical aminocarbonylation

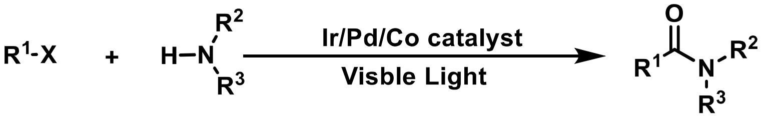
Despite several breakthroughs in transition metal-catalyzed CO-based aminocarbonylations [91-94] in recent years, the use of visible-light photoredox catalysis to radical carbonylation has provided a new route for the synthesis of amides.

Ryu's group [95] described a photoinduced catalyst-free aminocarbonylation of aryl iodides with amines employing a Xe-lamp as a basic light source, in the presence of CO gas. In 2016, the Odell group [96] devised an effective, low-pressure visible-light-mediated radical aminocarbonylation of unactivated alkyl iodides for the production of alkyl amides using $Mo(CO)_6$ as an efficient CO surrogate. Sardana's group [97] described a palladium-catalyzed aminocarbonylation of unactivated alkyl iodides with stoichiometric quantities of carbon monoxide



Scheme 1.30 Synthesis of amide by radical aminocarbonylation

Arndtsen's group recently devised an ingenious method involving visible light excitation of a palladium catalyst to drive both the oxidation addition and the reductive elimination steps with minimal barriers [98, 99]. Alexanian's group described a broadly applicable visible-light-driven cobalt catalyzed amino carbonylation of (hetero)aryl halides [100]. The utilization of a simple carbonyl complex $Co_2(CO)_8$ in conjunction with carbon monoxide (2 atm) and visible light (390 nm LEDs) enables the synthesis of important amides in good to quantitative yields.

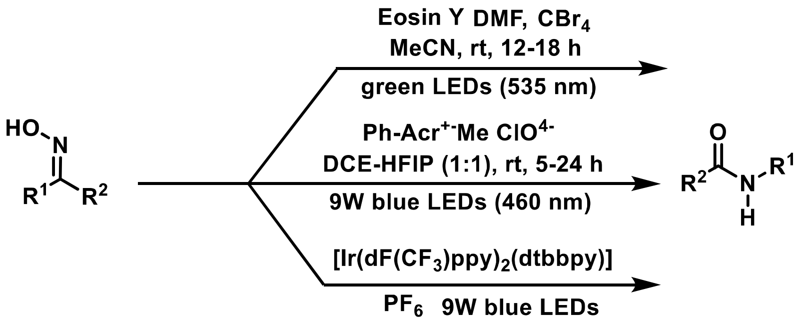


Scheme 1.31 Synthesis of amide using Ir/Pd/Co photocatalyst

1.4.4.5 From oxime

The Beckmann rearrangement is a well-known procedure for generating amides and lactams from widely available oximes [101].

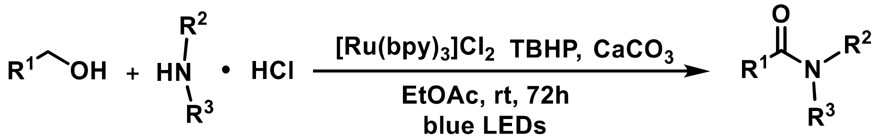
Yadav's group described an efficient visible-light-induced Beckmann rearrangement of oximes utilizing the Vilsmeier-Haack reagent, which is generated *in situ* by a photoredox-catalyzed reaction of carbon tetrabromide with DMF [102]. Guan and He described a visible-light-induced organic photocatalyzed more atom-economical and novel Beckmann rearrangement of oximes under mild conditions [103]. The Rovis' group recently achieved the synthesis of the Z isomer of oxime by photoisomerization using visible-light-mediated energy transfer catalysis [104].



Scheme 1.32 Synthesis of amide from oxime

1.4.4.6 From alcohol

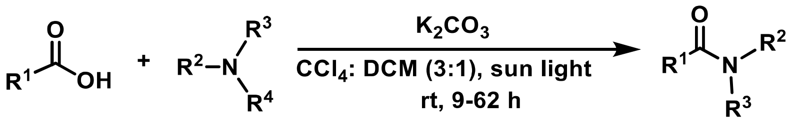
Luca's group published a photocatalyzed route to amides from alcohols and amines [105].



Scheme 1.33 Synthesis of amide from alcohol

1.4.4.7 From acids

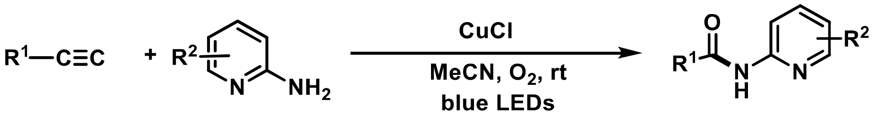
Szpilman et al. [106] established a visible-light-assisted direct amide synthesis from carboxylic acids and amines. They discovered that trimethylamine and tetrachloromethane form a charge-transfer complex that absorbs light.



Scheme 1.34 Synthesis of amide from carboxylic acids and amines.

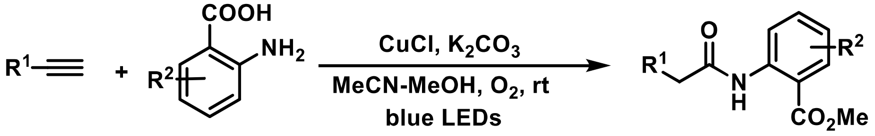
1.4.4.8 From alkyne

Hwang et al. reported [107] a new aerobic oxidative C–N coupling via C≡C triple bond cleavage using copper-catalyst under visible light irradiation.



Scheme 1.35 Synthesis of amide via C≡C triple bond cleavage using copper-catalyst

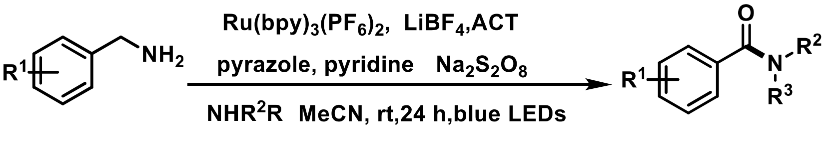
Subsequently, the same author reported under the same visible light promoted copper-catalyzed regioselective acetamidation of terminal alkyne with different aryl amines to an amide.



Scheme 1.36 Synthesis of amide via C≡C triple bond cleavage using Cu-catalyst

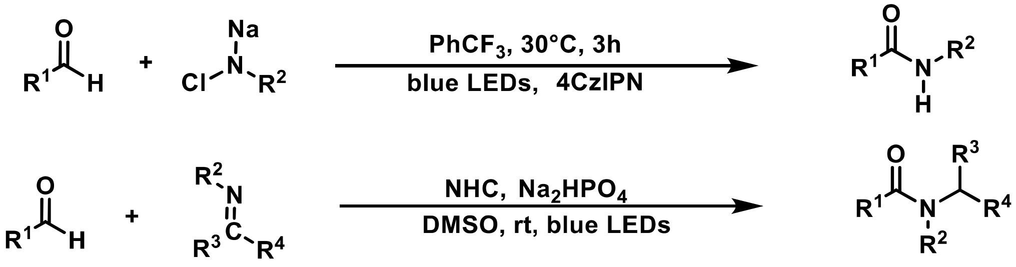
1.4.4.9 From amines

Leadbeater's group [108] described visible-light-promoted oxidative amidation and transamidation for the synthesis of amides using sodium persulfate as a terminal oxidant.



Scheme 1.37 Synthesis of amide using sodium persulfate as a terminal oxidant

Seo and Chang recently showed that nitrogen-centered radicals [109-112] produced photocatalytically from initially photostable N-chloro-N-sodio carbamates under blue LED irradiation. Shu's group [113] described dual *N*-heterocyclic carbine and photoredox catalyzed 100% atom-economical and metal-free synthesis of amides from aldehydes and imine esters under redox-neutral conditions



Scheme 1.38 Synthesis of amide from aldehydes

1.4.5 Sulfonamides

Sulfonamides (sulfa medicines) were the first synthetic drugs that were widely and consistently utilized as preventative and chemotherapeutic medicines against a wide range of disorders . Over 30 medicines with this activity are in clinical use, including the antihypertensive agent bosentan, antibacterial, antiprotozoal, antifungal, anti-inflammatory, nonpeptidic vasopressin receptor antagonist, translation initiation inhibitors and other biological activit [114]. Sulfonamides have lately been employed as an anticancer drug, as the antiviral HIV protease inhibitor amprenavir and in Alzheimer's disease. Because of the above, photoredox catalysis has recently gained popularity in the synthesis of sulphonamides [115-120].

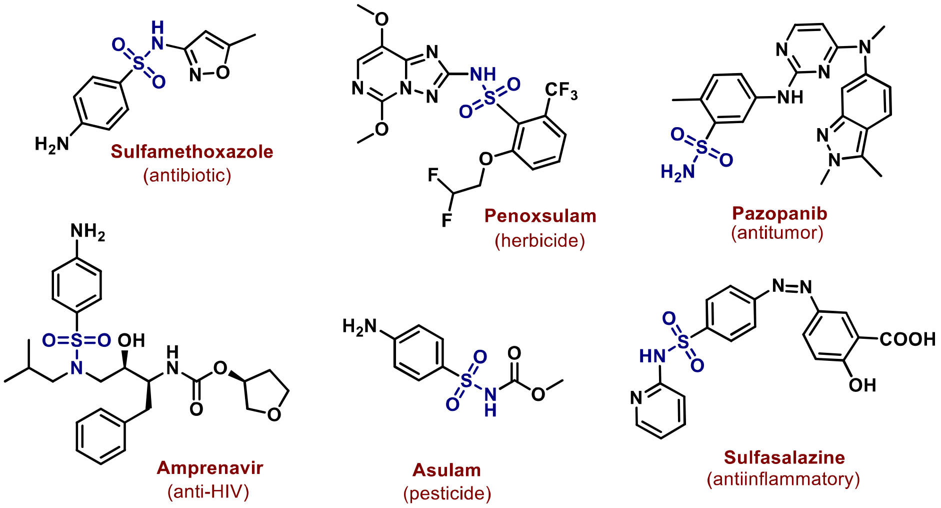
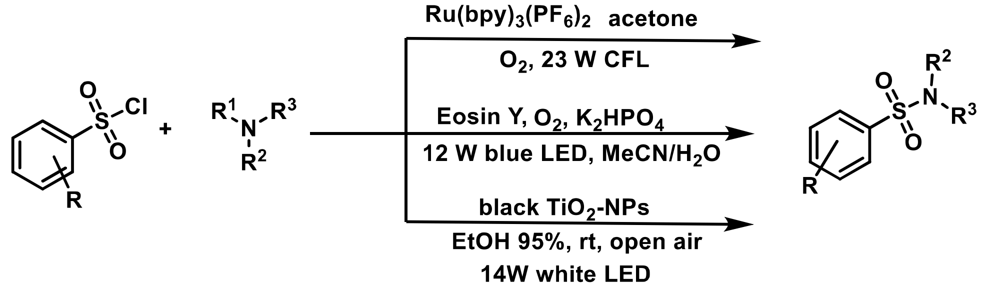


Figure 1.10 Some biologically relevant sulfonamide compounds

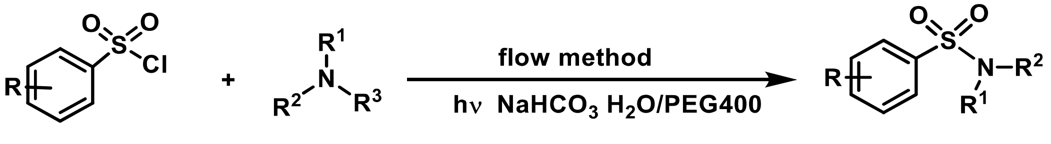
1.4.5.1 Synthesis of sulfonamides from sulfonyl chlorides

M. Chen described visible light-mediated dehydrogenative arylsulfonylation of tertiary aliphatic amines with arylsulfonyl chlorides to a new synthesis of arylsulfonyl enamines [121]. Based on the reaction of aliphatic amines with arenesulfonyl chlorides in the presence of eosin Y as a photocatalyst under visible light, a mild, practicable, and ecologically acceptable approach to sulfonamides was established by Zhan [122]. Hosseini-Sarvari presented a unique heterogeneous technique in 2020, beginning with tertiary amines and arenesulfonyl chlorides and utilising black TiO_2 nanoparticles with photocatalytic activity to produce sulfonamides under visible light in mild circumstances [123].



Scheme 1.39 Synthesis of sulfonamide from sulfonyl chloride with tertiary amines

The study demonstrates the effect of flow technologies in drug development by establishing an efficient, safe, and easily scalable production of sulfonamides using a meso-reactor device [124].



Scheme 1.40 Synthesis of sulfonamide under flow conditions

1.4.6 Thioether(Sulfides)

Because of the possibility of working under moderate circumstances at room temperature and utilizing convenient less poisonous and odourless sulfur sources, photocatalysis has been used for the manufacture of thioethers in recent years, both in the presence of metal- and organo-photocatalysts. Organosulfur compounds/sulfides are the building blocks of many commercially available medications that are used to treat a variety of ailments such as cancer, diabetes, Alzheimer's disease, and AIDS (Figure 1.11).

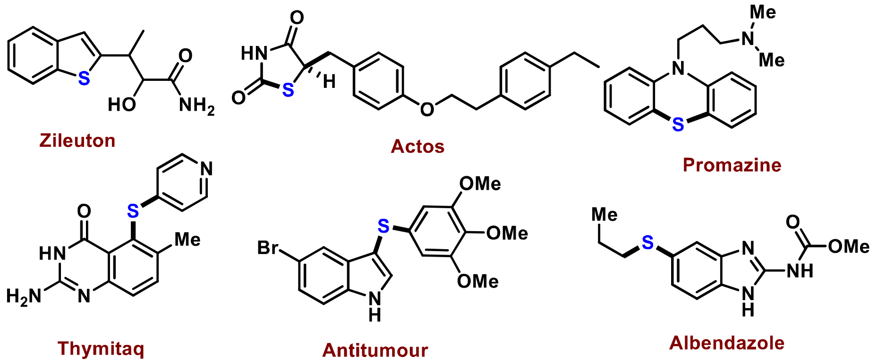
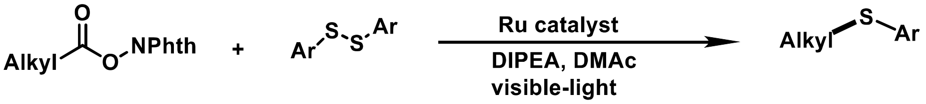


Figure 1.11 Some biological active drugs containing sulfide functional groups

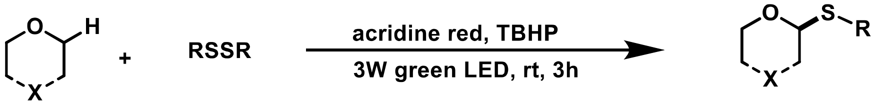
1.4.6.1 From disulfides

Xiao and co-workers was described visible-light-promoted synthesis of sulfide through a decarboxylative coupling reaction between N-hydroxyphthalimide esters and diaryl disulfides [125].



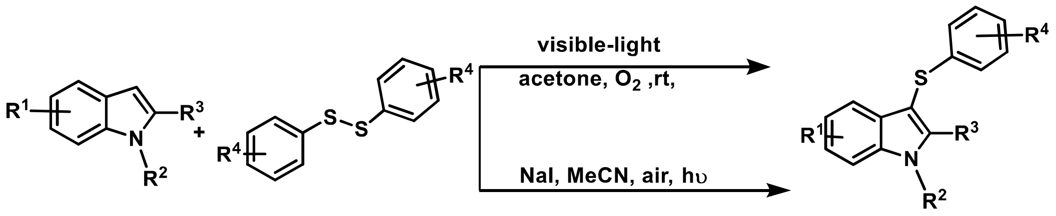
Scheme1.41 Synthesis of sulfide through decarboxylative coupling

A well-designed and competent method for the synthesis of α-arylthioethers was reported by Zhu's group through visible light-induced direct thiolation α-C(sp3)−H of ethers with diaryl disulfides using acridine red as energy transfer photocatalyst [126].



Scheme 1.42 Synthesis of sulfide by direct thiolation of ethers with disulfides

Kumar's group and Ye's group also reported a similar approach i.e. visible light-promoted synthesis of 3-arylthioindoles from indoles and diaryl disulfides employing oxygen as a safe oxidant and using the catalytic amount of sodium iodide respectively [127].



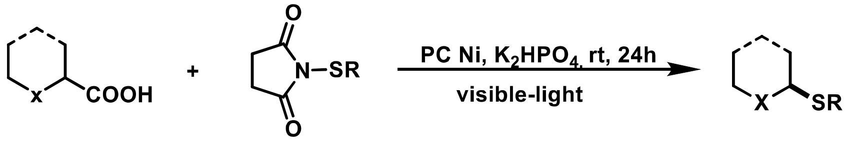
Scheme 1.43 Synthesis of sulfide C-3 sulfenylation of indoles with diaryl disulfides.

An efficient visible-light-induced sulfidation of arylhydrazines for the synthesis of aromatic sulfides was reported by Li and co-workers via a cross-coupling reaction [128].

$$Ar^1NHNH_2 \quad + \quad Ar^2SSAr^2 \xrightarrow[H_2O_2,\ \text{Blue LEDs, 8h}]{Na_2\text{-eosin Y}} Ar^1\text{-}SAr^2$$

Scheme 1.44 Synthesis of sulfide by sulfidation of arylhydrazine

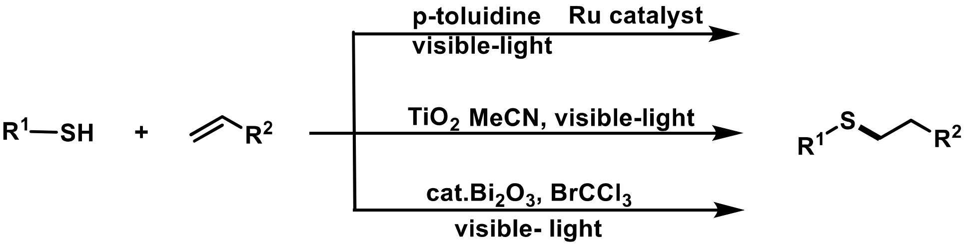
Wei and co-workers described a thiolation reaction from carboxylic acids using the combination of photoredox catalyst and nickel catalyst[129].



Scheme 1.45 Synthesis of sulfide by decarboxylative sulfenylation of amino acids

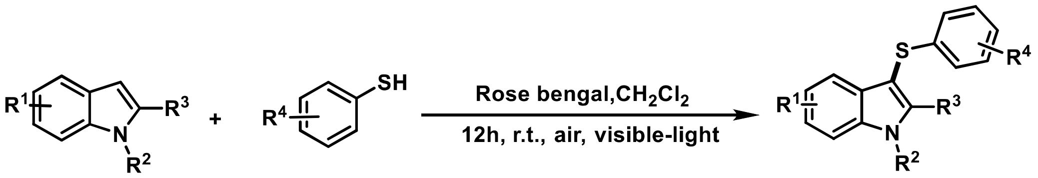
1.4.6.2 From thiol

The synthesis of sulfides was reported by Tyson et al., Bhat's group, and Fadeyi and co-workers through the conjugation of different alkenes with thiols under visible light irradiation using different photocatalyst [130-132].



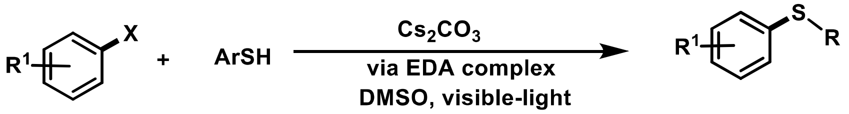
Scheme 1.46 Synthesis of sulfide thiol−ene reaction, using Ru/TiO_2/Bi_2O_3 as catalyst

Fan's group reported a visible-light-induced synthesis of 3-sulfenylindoles from indoles, via easily available thiophenols as sulfenylating agents using readily available and cheap rose bengal as a photocatalyst and air as the green oxidant.



Scheme 1.47 Synthesis of sulfide by C-3 sulfenylation of indoles with thiophenols

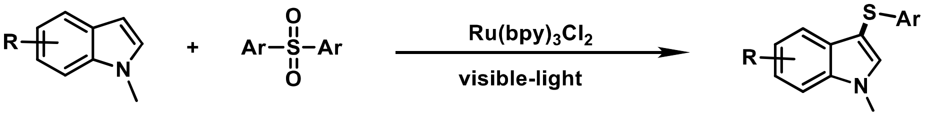
A mild and facile visible-light-induced construction of C−S bonds via cross-coupling reaction between thiols and arylhalides was reported by Liu et al. without either a transition metal or photoredox catalysts [133].



Scheme 1.48 Synthesis of sulfide from thiol via intermolecular charge transfer.

1.4.6.3 From sulfones

An efficient visible-light-induced 3-sulfenylation of N-methylindoles with arylsulfonyl chlorides was reported by Chen et al. under mild conditions [134].



Scheme 1.49 Synthesis of sulfide by 3-sulfenylation of N-methylindoles

1.4.7 Sulfones

Sulfones are common structural motifs in medicines and agrochemicals, as well as versatile synthetic intermediates in organic chemistry. Eletriptan, for example, is a serotonin that is effective in the treatment of migraine attacks. Ceritinib is a medication that has been approved by the FDA to treat anaplastic lymphoma kinase (ALK) positive non-small cell lung cancer. MK0752 is a moderately effective secretase inhibitor that can lower A40 output (Figure 1.12) [135, 136].

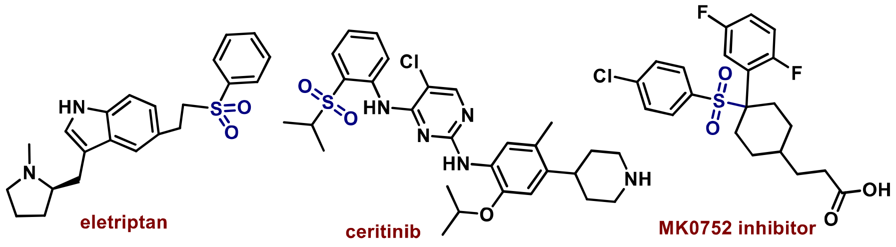
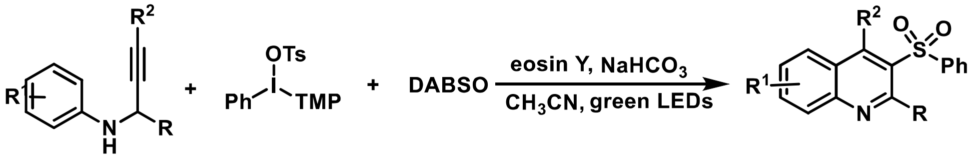


Figure 1.12 Few biological active drugs containing sulfone functional groups

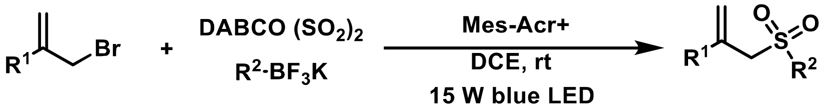
1.4.7.1 Synthesis of sullfones from DABSO

A visible-light mediated, three-component synthesis of 3-arylsulfonyl quinoline derivatives was reported by Zhang et al. [137] from N-propargyl aromatic amines diaryliodonium salts and sulphur dioxide using eosin Y as a photocatalyst.



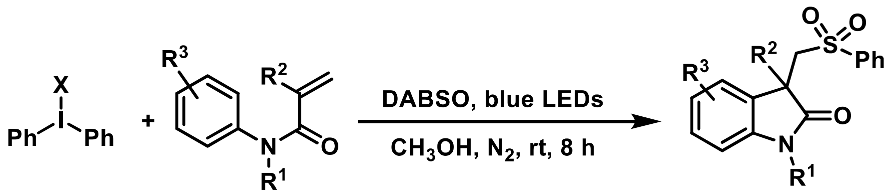
Scheme 1.50 Synthesis of sulfone from N-propargyl amines, iodonium salts and DABSO

Wu and co-workers [138] reported the insertion of sulfur dioxide in sulfonylation reaction via photoredox catalysis by using potassium alkyltriuoroborates as radical reservoirs.



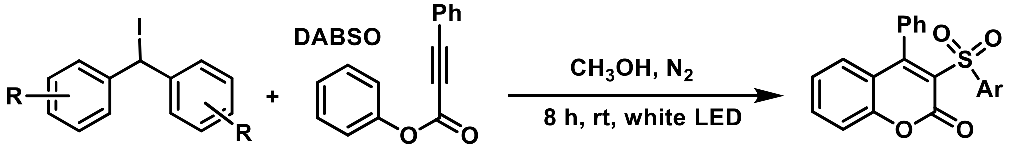
Scheme 1.51 Synthesis of sulfone by using potassium alkyltriuoroborates

Manolikakes et al. [139] developed a new catalyst-free, visible-light mediatedsynthesis of sulfonylated oxindoles from three-component reaction of N-arylacrylamides diaryliodonium salts and sulfur dioxide.



Scheme 1.52 Synthesis of sulfone from N-arylacrylamides

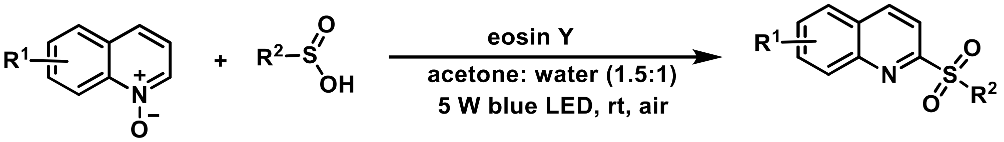
A catalyst-free visible-light-induced three-component synthesis of sulfonylated coumarins was developed by Manolikakes et al. utilizing diaryliodonium salts as radical precursors and sulfur dioxide as a key building block [140].



Scheme 1.53 Synthesis of sulfonylated coumarins

1.4.7.2 Synthesis of sullfones from sulfinic acids

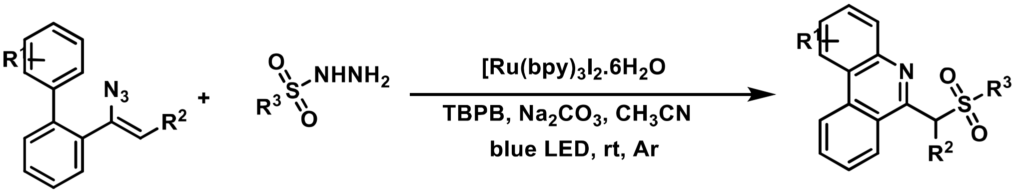
A visible-light-induced synthesis of 2-sulfonylquinolineswas reported by He et al. via deoxygenative C2- sulfonylation of quinoline N-oxides with sulfinic acids using eosin Y as a photocatalyst [141].



Scheme 1.54 Synthesis of sulfone by sulfonylation of quinolone N oxide

1.4.7.3 Synthesis of sullfones from sulfonyl hydrazines

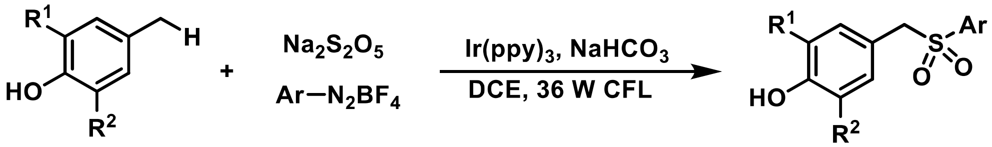
Under mild reaction conditions, Zhou et al. [142] described an effective and easy procedure for the synthesis of functionalized phenanthridinesn by visible-light-mediated tandem sulfonylation/annulation of vinyl azides and sulfonyl hydrazines.



Scheme 1.55 Synthesis of sulfone by annulation of vinyl azides and sulfonyl hydrazines.

1.4.7.4 Synthesis of sullfones from sodium metabisulfite

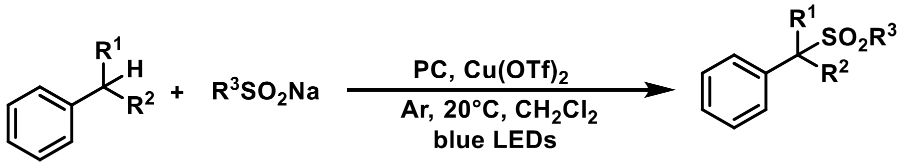
The photocatalyzed sulfonylation of benzylic C–H bonds was developed by Wu et al. [143] via the three-component reaction of aryldiazonium tetrafluoroborates, 4-methylphenols, and sodium metabisulphites under visible light irradiation. As a substitute for SO_2, sodium metabisulfite is utilized in this procedure.



Scheme 1.56 Synthesis of sulfone by sulfonylation of benzylic C–H bonds

1.4.7.5 Synthesis of sullfones from in-organic sulfinates

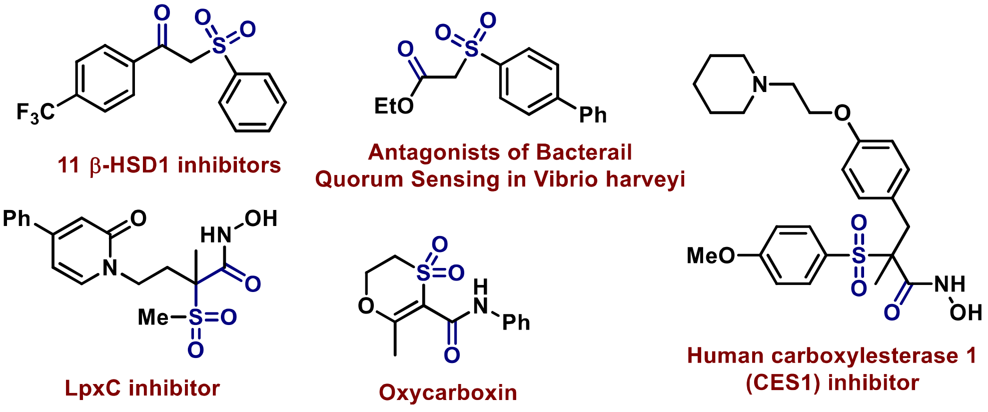
The direct and selective C(sp3)–H sulfonylation of hydrocarbons was reported using a conjugated polycyclic quinone as a direct HAT photocatalyst, copper triflate as an inexpensive oxidant, and commercially available in-organic sulfinates as the sulfonylation source [135].



Scheme 1.57 Synthesis of sulfone from in-organic sulfinates

1.4.8 *β*-Keto sulfones

β-keto sulfones (2-oxo sulfones) [136, 144, 145] and related sulfones have piqued the interest of researchers due to their promising biological actions such as anti-hepatitis, anti-bacterial, antifungal, and non-nucleoside inhibitors [146]. Surprisingly, β-keto sulfones have versatile functional groups such as sulfonyl, carbonyl, and active methylene (α-acidic protons) moieties, which can be easily manipulated in a variety of synthetic reactions. As a result, various appealing qualities were envisioned, such as the ease of manufacturing β-keto sulfones and the proximity of three functions, which would speed up a wide range of valuable synthetic transformations (Figure 1.13).


11 β-HSD1 inhibitors

Antagonists of Bacterail Quorum Sensing in Vibrio harveyi

LpxC inhibitor

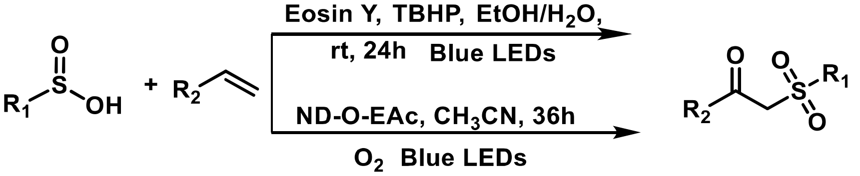
Oxycarboxin

Human carboxylesterase 1 (CES1) inhibitor

Figure 1.13 Few biological active drugs containing β-keto sulfones functional groups

1.4.8.1 Synthesis of *β*-keto sulfones from sulfinic acids

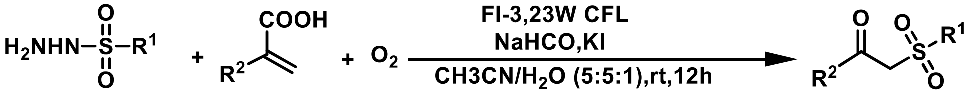
Yang, Wang, and colleagues reported visible-light irradiation oxidative-sulfonylation of alkenes with sulfinic acids at room temperature using eosin-Y as the photocatalyst and TBHP to produce*β*-keto sulfones [147].



Scheme 1.58 Synthesis of β-keto sulfones using alkenes and sulfinic acids

1.4.8.2 Synthesis of *β*-keto sulfones from aryl sulfonyl hydrazides

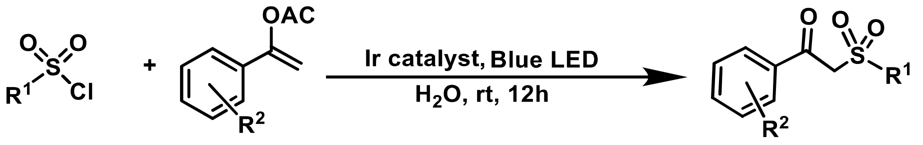
Very recently, Guan, He and co-workers explored a new synthesis of β-keto sulfones using fluorescein (Fl-3) as a photocatalyst for the decarboxylative process under visible-light irradiation [148].



Scheme 1.59 Synthesis of β-keto sulfones from aryl sulfonyl hydrazides

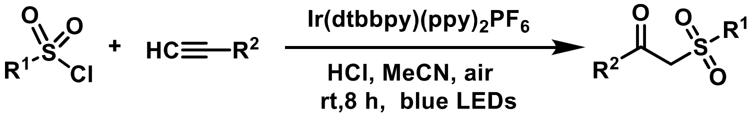
1.4.8.3 Synthesis of *β*-keto sulfones from aryl sulfonyl chloride

Visible-light promoted synthesis of β-Keto sulfones was reported via oxidative-sulfonylation of alkynes with sulfonyl chlorides under the catalytic influence of Ir(dtbbpy)(ppy)2PF$_6$ and HCl in air as the oxidant by Ni et al. [149]



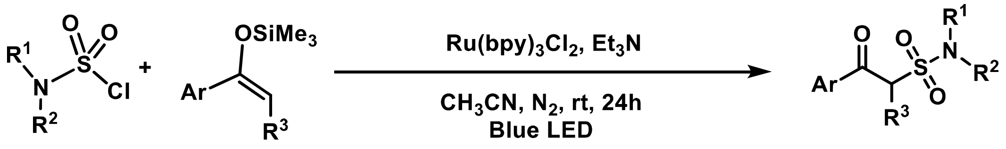
Scheme 1.60 Synthesis of β-keto sulfones from enol acetates with sulfonyl chloride

Lipshutz and colleagues then effectively developed an Ir-based amphoteric PQS-attached photocatalyst. This newly developed photocatalyst was used for visible light-mediated sulfonylation of enol acetates with sulfonyl chlorides to generate β-keto sulfones [150].



Scheme 1.61 Synthesis of β-keto sulfones from alkynes with sulfonyl chlorides

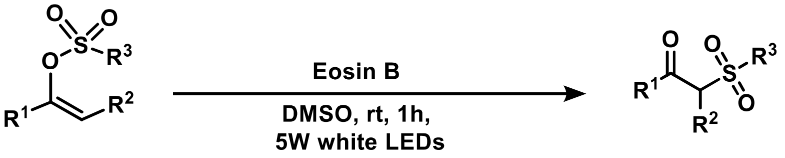
Wang et al. reported a novel photoredox-catalyzed synthesis of highly functionalized β-keto sulfonamides via S-N bond formation from chlorosulfonamides and enol silyl ethers.



Scheme 1.62 Synthesis of β-keto sulfones from cholosulfonyl chloride

1.4.8.4 Synthesis of *β*-keto sulfones by rearrangement of vinyl tosylates

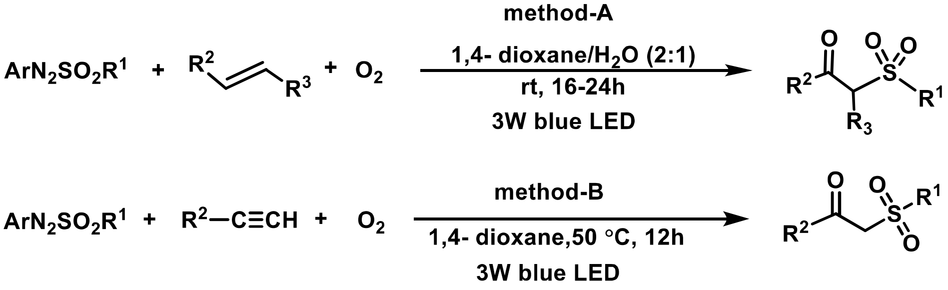
Xie and co-workers reported the synthesis of β-keto sulfones via visible light-induced rearrangement of vinyl tosylates using eosin B as photocatalyst [151].



Scheme 1.63 Synthesis of β-keto sulfones by rearrangement of vinyl tosylates

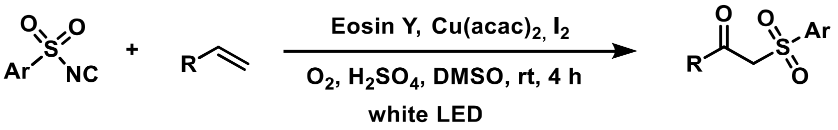
1.4.8.5 Synthesis of *β*-keto sulfones via oxosulfonylation of alkenes or alkynes

The synthesis of β-keto sulfones was recently developed by Wei and colleagues via visible light-induced aerobic oxosulfonylation of alkenes or alkynes and arylazo sulfones in the absence of a photocatalyst [152] (Scheme 1.63; method-A). Subsequently under identical conditions, the same group effectively extended to other arylalkynes employing arylazo alkyl/arylsulfones [153] (Scheme 1.63; method-B). A series of β-keto sulfones were synthesised with comparable yields.



Scheme 1.64 Synthesis of β-keto sulfones oxosulfonylation of alkenes or alkynes with arylazo sulfones

Guo, Huo, and co-workers reported the visible light-initiated synthesis of β-keto sulfones via oxosulfonylation of alkenes using TosMIC and eosin Y as a photocatalyst [154].



Scheme 1.65 Synthesis of β-keto sulfones oxosulfonylation of alekens with TosMIC

In view of the importance of Nitrogen and Sulfur containing organic compounds and visible light as a renewable, sustainable, and benign source of energy, our interest is to explore the chemistry (synthesis and structural characterization) of Schiff's Base, Sulfonamides, N-aryl sulfonamides and amine sulfonate salts derivaties under visible light irradiation. The studies have been described in subsequent **chapter 2-5**.

1.5 References

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