Chapter 1

1.1 Introduction

As environmental concerns arise, organic chemists are challenged to develop eco-friendly, efficient, selective, and high-yielding processes [1]. "Green chemistry," according to Paul T. Anastas and John C. Warner (1998) is the implementation of a set of guidelines [2] (**Figure 1.1**). The concept of green chemistry is one of the most attractive in chemistry for sustainable development, as it involves using a set of principles to reduce the use or generation of hazardous substances in the design, manufacture, and application of chemical products [3]. Over the past decade, research, implementation, education, and outreach advances have increased the 'state-of-the-art' in green chemistry [4].

Figure 1.1 Principle of Green Chemistry.

Such concepts include designing processes to maximize the amount of raw materials that become the product, using safe, environment-friendly substances like solvents, developing energy-efficient strategies, and minimizing waste products [5,6].

It's worth noting that the field of green synthesis is rapidly evolving, and new developments and approaches are being reported regularly. Consulting recent research articles and journals in the field of organic synthesis, green chemistry, and sustainable chemistry will provide you with the most up-to-date information on current research in the green synthesis of heterocyclic compounds containing sulfur and nitrogen [7–9].

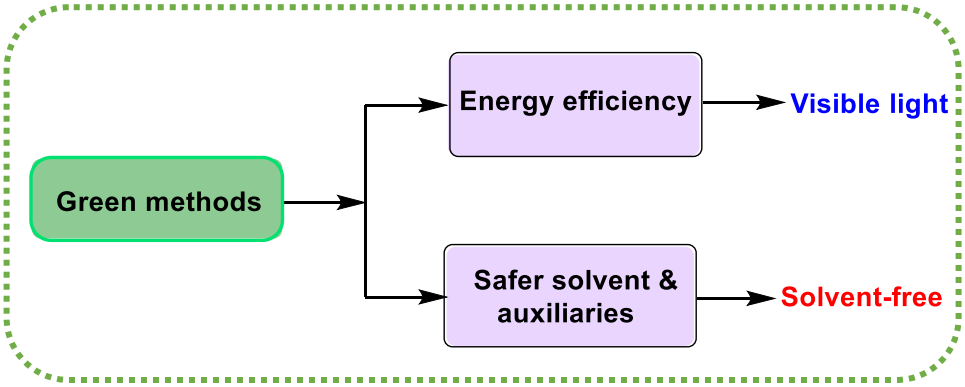


Figure 1.2 Green methods

Green synthesis, also known as sustainable synthesis or eco-friendly synthesis, refers to the development of chemical processes that minimize the use of hazardous substances and reduce the generation of waste, energy consumption, and environmental impact [10–12]. It aims to promote the principles of sustainability, including the efficient use of resources, the reduction of pollution, and the preservation of the environment. The principles of green synthesis align with the broader concept of green chemistry, which aims to design chemical processes that are safer, more sustainable, and less harmful to human health and the environment [13–15].

The focus on utilizing two principles of green chemistry, renewable resources (Energy efficiency), and safer solvents, is another key advantage of green synthesis. (**Figure 1.2**)

1.2 Energy efficiency (visible light)

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 catalysts as catalysts [16–18].

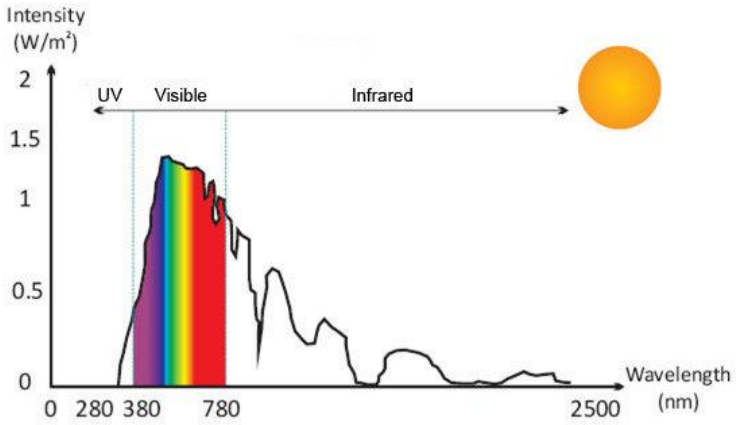


Figure 1.3 visible spectrum

Due to its enormous natural abundance, using visible light as a synthesis promoter is 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 [19].

During his studies, ciamician encountered an experimental challenge as well. A good light source is necessary to conduct photochemical investigations [20]. 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 [21] (**Figure 1.4**).

Figure 1.4 Modern LEDs lights with different wavelengths

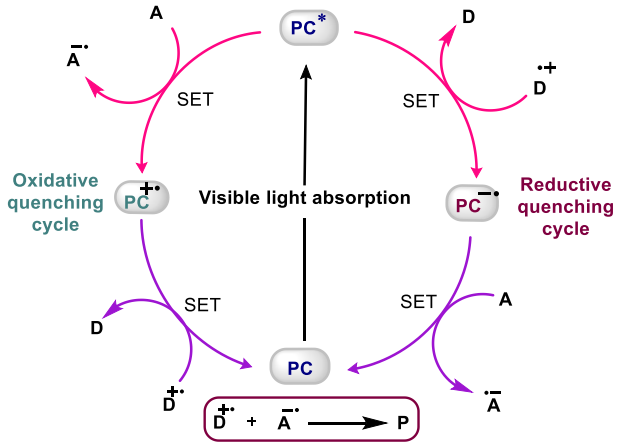
In the early 20th century, photochemical laboratories lacked modern light sources such as halogen, mercury, LED, or laser light sources. Tungsten lamps at the time emitted light that was too dim and red to induce photochemical reactions. Consequently, the institute's balconies, where ciamician conducted his research, were ideal for his laboratory because sunlight was the only viable light source for his experiments. Ciamician also expressed great admiration for the potency of sunlight in his work [22].

1.2.1 Introduction: Mechanistic pathway of photoredox catalysis

1.2.1.1 Photoredox catalysis (Electron transfer)

A typical photoredox catalytic cycle is shown in (**Scheme 1.1**). Usually, the photoredox catalyst (PC) is excited with a photon of a suitable wavelength to generate the excited state

PC*. This new species can then be subjected to a reductive or oxidative step according to the nature of the reaction partners. In the first case, PC* could receive a single electron from reactant D ("donor", reductive quenching cycle) of 1e- to form a PC^{-} species. After a second single electron transfer process, this species can be oxidized to (PC) in the presence of reactant A. In this way, the initial photoredox catalyst is regenerated, closing the catalytic cycle.

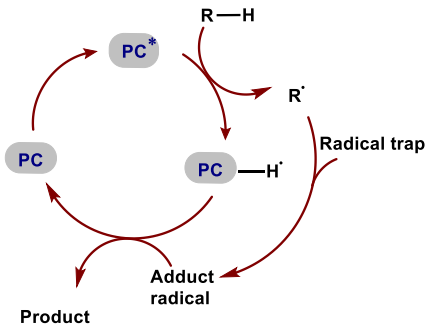


Scheme 1.1 Generic illustration of a molecule photoredox catalysis cyclic: PC = photoredox catalyst, A = acceptor reactant, D = donor reactant, P = product, SET = single electron transfer process.

Conversely, in an oxidative quenching cycle, activated PC* species can be subjected to an abstraction of a single electron in the presence of reactant A ("acceptor"). This generates the oxidized species PC+, which can be reduced by reactant D to regenerate the photoredox catalyst (PC) [16,17,23–28].

1.2.1.2 Hydrogen atom transfer (HAT)

The chemical process known as hydrogen atom transfer (HAT) involves the coordinated movement of two primary particles-a proton and an electron-between two substrates in a single kinetic step [29]. Conversely, HAT presents unique opportunities for organic synthesis since it allows the straightforward activation of (aliphatic) R-H bonds, often with great selectivity, avoids the need to introduce a guiding moiety into a substrate, and allows for careful modification of the reactivity through reaction condition selection (e.g., hydrogen abstractor, solvent, etc.). In the first, the excited state of the photocatalyst (PC*) abstracts a hydrogen atom from a substrate R-H through a direct HAT process (**Scheme 1.2**) [30–37].



Scheme 1.2 Photocatalytic pathway via HAT.

Hydrogen Atom Transfer:

- PS* abstracts a hydrogen atom from a donor (RH), creating an oxidized/reduced photosensitizer and a radical (R•). (PSH or PS−).

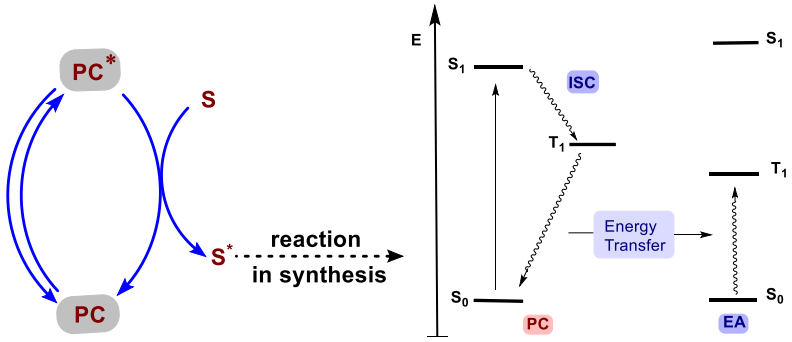
  PS* + RH → PSH + R•

- Alternately, PS* can generate reactive oxygen species (ROS) such as singlet oxygen ($^1O_2$), which can absorb a hydrogen atom.

$$^1O_2 + RH \rightarrow RO^{\bullet} + H_2O$$

1.2.1.3 Energy Transfer

It's important to distinguish between electron transfer and energy transfer processes when discussing visible-light-mediated photocatalysis. The photocatalyst is analogous to the donor, stimulated by the direct absorption of visible light [38].



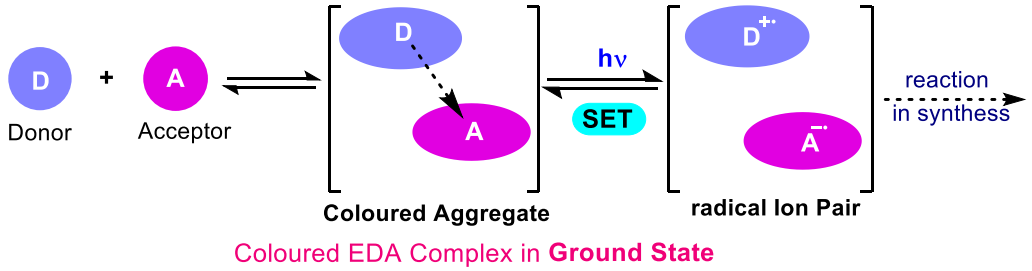
Scheme 1.3 Photochemical reactions with Energy transfer pathways.

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 [39,40] (**Scheme 1.3**).

1.2.1.4 Electron donor-acceptor (EDA) complexes

This process creates a new molecular aggregation in the ground state known as an electron donor-acceptor (EDA) complex by utilizing the interaction of an electron acceptor substrate

A and a donor molecule D (Lewis acids and bases, respectively) (**Scheme 1.4**). The resulting EDA complex absorbs visible light even though components A and D do not.



Scheme 1.4 Photocatalytic pathway via EDA complex

Light excitation induces an intramolecular single-electron transfer (SET) event that can produce radical intermediates under mild circumstances. Since the 1950s, there has been a lot of research on the photophysical properties of EDA complexes, but little of it has been used in chemical synthesis [28,41–45].

1.3 Solvent-free

On the other hand, Solvent-free technology offers numerous benefits for both academic research and industrial applications [45]. These techniques frequently result in higher reaction yields and selectivity, enhancing efficiency and minimizing resource use. Additionally, they cut down on waste by eliminating the need for solvent disposal or purification, which leads to cost savings and a smaller environmental footprint. These approaches enhance workplace safety by reducing exposure to potentially hazardous solvents, promoting a healthier working environment for researchers and operators [13–15]. Overall, adopting green solvents or solvent-free organic synthesis is essential for achieving

more sustainable and environmentally friendly chemical processes. Designing for energy efficiency includes green synthetic methods that lower energy consumption and improve reaction selectivity and yield. These approaches are also characterized by simplicity in set-up, environmental friendliness, cost-effectiveness, and using more eco-friendly energy resources.

1.4 Green approach for the synthesis of nitrogen and sulfur-containing organic compounds

Because of their distinct structural and chemical characteristics, heterocyclic molecules containing sulfur and nitrogen have an enormous biological significance. (**Figure 1.5**)

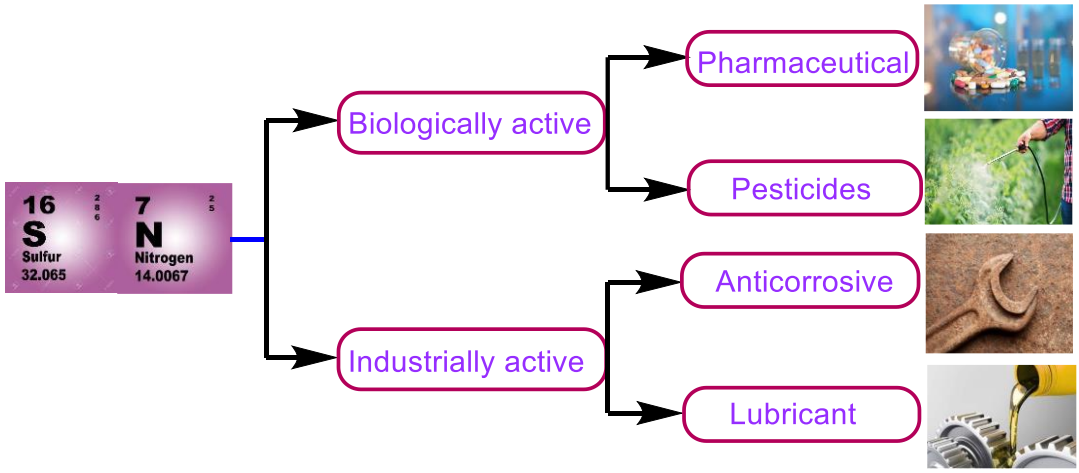


Figure 1.5 Application of nitrogen and sulfur-containing compounds.

These characteristics also make them potentially useful as medicinal agents [46]. These compounds play essential roles in drug discovery, medicinal chemistry, and the development of bioactive molecules. Heterocyclic compounds are acyclic and cyclic structures that contain one or more non-carbon atoms in the ring, like nitrogen (N) and

sulfur (S) (**Figure 1.6**). These atoms add unique characteristics that are frequently essential for biological function. The addition of nitrogen and sulfur atoms to heterocyclic structures confers various electrical, steric, and lipophilic properties that facilitate interactions with biological targets and the regulation of their activities [47].

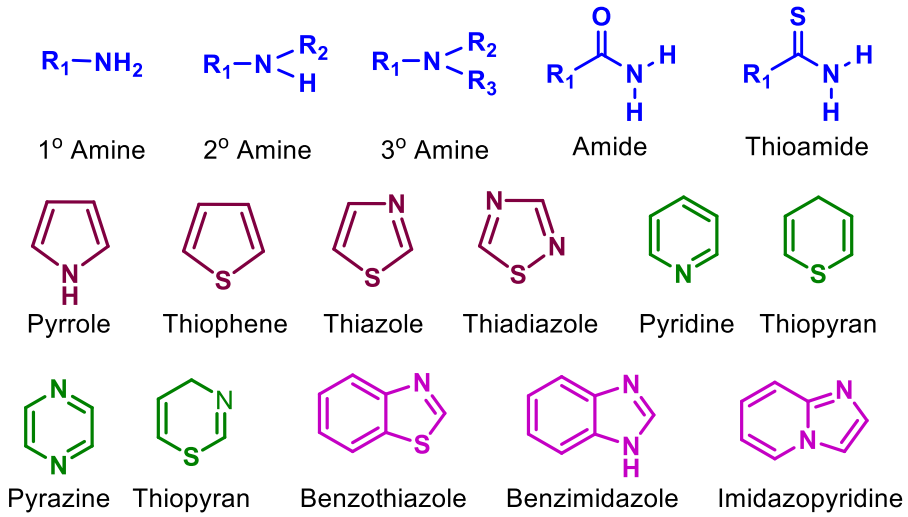


Figure 1.6 Nitrogen and sulphur containing some main class of organic compounds.

The class of heterocyclic compounds that contain biologically significant nitrogen and sulfur is known as nucleosides and nucleotides. The building blocks of DNA and RNA are nucleosides, which are made up of a nitrogenous base attached to a sugar molecule, and nucleotides, which have a phosphate group. The heterocyclic bases (adenine, guanine, cytosine, and thymine/uracil) include nitrogen and sulfur atoms, which are essential for base-pairing interactions that control the genetic code and procedures like transcription, translation, and replication [48].

1.4.1 Nitrogen and sulfur-containing acyclic compounds

1.4.1.1 Amines

Amines are an important class of organic compounds containing nitrogen atoms bonded to carbon atoms and are recognized as the most crucial and extensively studied organic compounds, originating from ammonia through the substitution of one, two, or all three protons with various carbon derivatives [49].

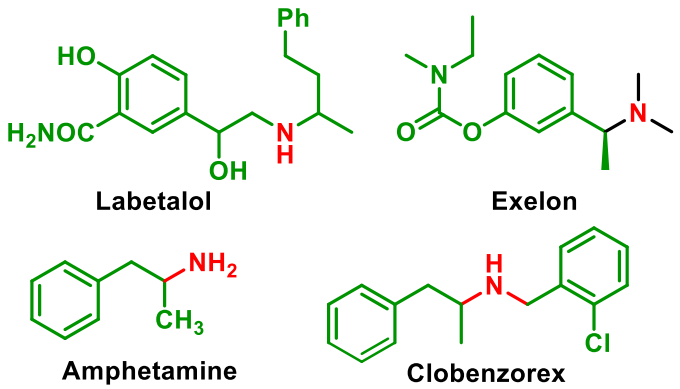


Figure 1.7 Some biologically active compounds containing amine groups.

Their significance is emphasized by their presence in amino acids, in protein synthesis, and their vital role in supporting living organisms. Amines also serve as fundamental building blocks in industries including dyes, pharmaceuticals, surfactants, agrochemicals, and plastics in the rubber, textile, and paper sectors, etc. They can act as both bases and nucleophiles due to the lone pair of electrons on the nitrogen atom [49–53]. Amines find application in the synthesis of various medications. For instance, labetalol is employed in the management of hypertension, including during pregnancy. Exelon serves as a treatment

for Alzheimer's disease, while amphetamines are utilized in the treatment of narcolepsy, obesity, and attention deficit hyperactivity disorder (ADHD), and clobenzorex may be employed to prevent weight gain **(Figure 1.7).**

1.4.1.2 Amides

Amides also known as carboxamides, are the derivatives of carboxylic acids [54]. Carboxamides are significant compounds across diverse industries such as agrochemicals, pharmaceuticals, materials science, and chemical manufacturing [55,56] and serve as essential building blocks in the synthesis of numerous drugs, polymers, and natural products. Consequently, the formation of amide bonds ranks among the most vital and extensively investigated reactions in organic chemistry [57] (**Figure 1.8).**

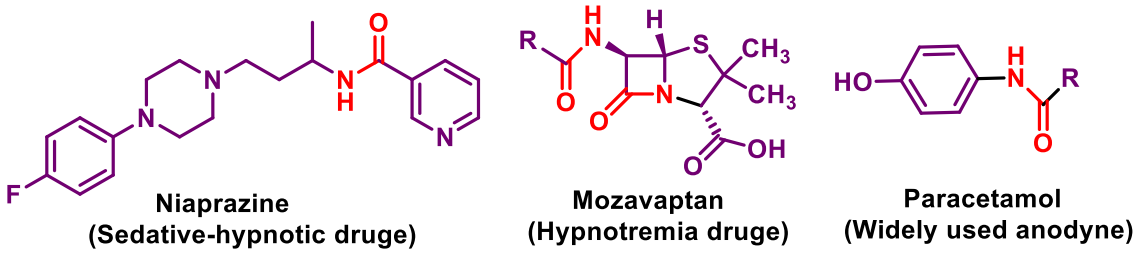


Figure 1.8 Examples of some drugs containing amide groups.

Amides have a generic structure as $RCONH_2$, where the NH_2 group is free and is called a primary amide. When one hydrogen of NH_2 is replaced by an alkyl or aryl group such as RCONHR', it is known as a secondary amide, and tertiary amides are RCONR'R", where both the hydrogens of amine are substituted. In the molecular structure of amides [R-

(C=O)-N], the central carbon atom possesses a double bond with oxygen and also a single bond with nitrogen atoms [54].

1.4.1.3 Thioamides

Sulfur-containing compounds, especially thiocarbonyl, are highly versatile intermediates or precursors which find many applications both in synthetic and biological chemistry [58]. There are many medicinal applications of thioamide functional groups, including antifungal and antibacterial agents, [59] as well as the treatment of diseases such as tuberculosis and leprosy.

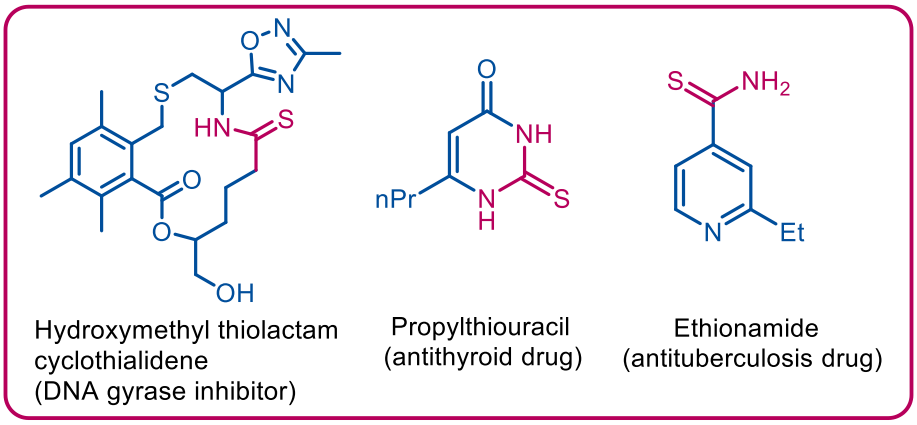
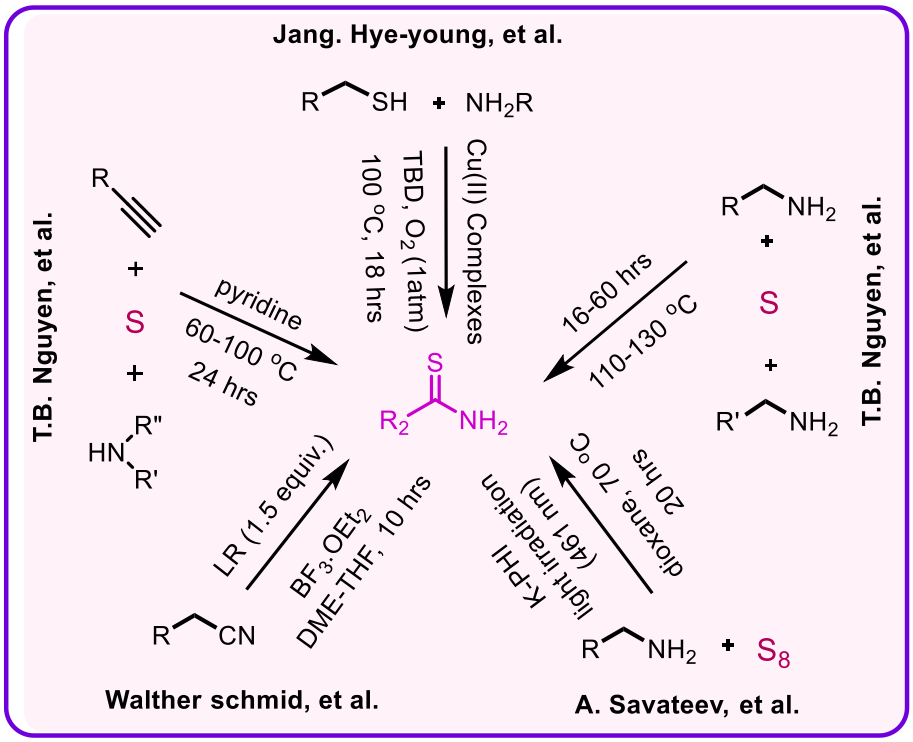


Figure 1.9 Examples of some drugs containing thioamide groups.

Ethion-amide is employed as a second-line treatment when the disease shows resistance to other antibiotics [60] their derivatives have attracted considerable attention because of their utility in the synthesis of a variety of biologically and pharmaceutically relevant moieties such as propylthiouracil and hydroxymethyl thiolactam cyclothialidine, etc. **(Figure 1.9)**.

Among the various procedures available for the synthesis of thioamides, the most general one involves the thionation of amides and nitriles using sulfur-transfer reagents, such as Lawesson reagent [61], P_4S_{10} [62], $(NH_4)_2S$ [63], $(TMS)_2S$ [64], S_8 [65], $PSCl_3$ [66], and some other various methods have also been reported for the synthesis of thioamide derivatives using various catalysts such as Cu (II) complexes, K-PHI under light irradiation (461 nm), pyridine, and $BF_3.OEt_2$ $Cu(OTf)_2$ [67], sodium sulfide ($Na_2S.9H_2O$) [68], cyclodextrin [69].



Scheme 1.5 Synthesis of thioamides.

1.4.2 Nitrogen and sulfur-containing five-membered cyclic compounds

Compounds that have both nitrogen and sulfur atoms are known as heterocyclic compounds. These substances have various chemical and biological characteristics and are used in agrochemicals, materials science, medicinal chemistry, and other domains [70]. These are a few common types of heterocyclic compounds that contain nitrogen and sulfur:

1.4.2.1 Pyrrole

Pyrrole is a five-membered heterocyclic compound and a vital chemical motif in various drugs, natural products, catalysts, and advanced materials [71]. In 1834, Runge isolated pyrrole from coal tar, and the structure was correctly formulated by Baeyer in 1870.

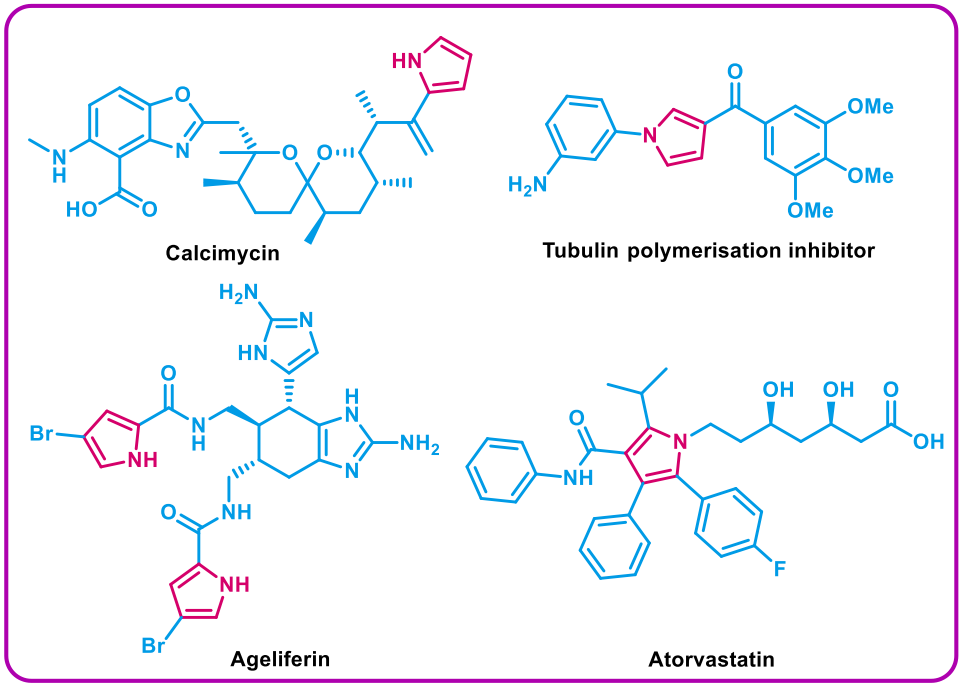
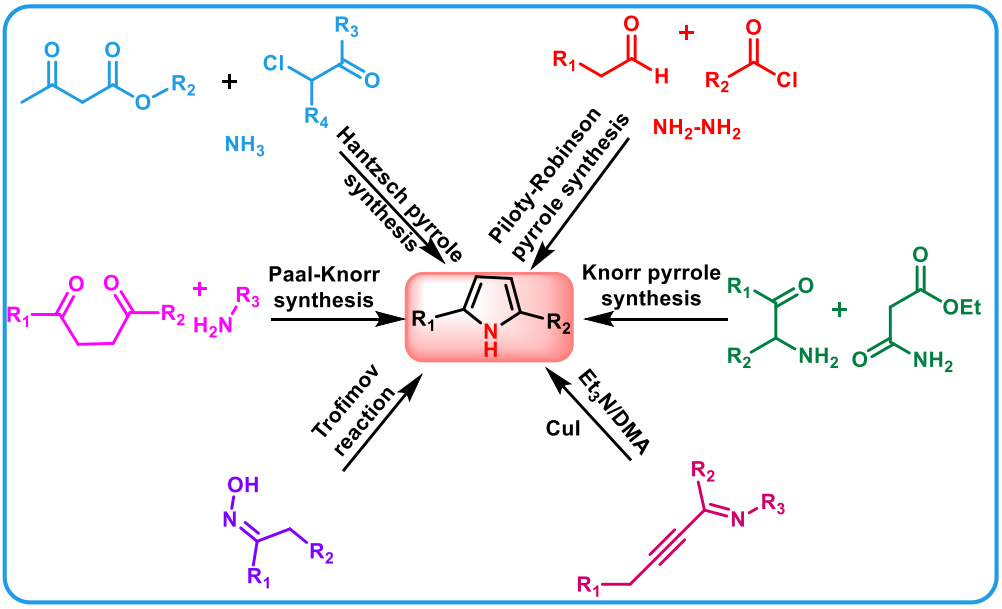


Figure 1.10 A few biologically active compounds containing pyrrole moiety.

Pyrroles are an active compound with suitable metal atoms and from metal complex macrocycles, including the porphyrins of heme, chlorins, bacteriochlorins, chlorophyll, and porphyrinogens [72]. They are an element of polymers, indigoid dyes, and large aromatic rings (**Figure 1.10**). Pyrroles find applications as a solvent for resins, terpenes, corrosion inhibitors, preservatives, and catalysts for polymerization.

It can be used in spectrochemical analysis, luminescence chemistry, transition metal complex catalysts for homogeneous polymerization, and various metallurgical processes [73]. Moreover, certain substances serve as valuable intermediates in the synthesis of synthetic heterocyclic derivatives and physiologically significant naturally occurring alkaloids [74].



Scheme 1.6 Synthesis of pyrrole and its derivatives.

Pyrroles are synthesized by various methods, such as by the reaction of a 1,4-dicarbonyl compound with ammonia or aromatic/aliphatic amines (Paal-Knorr Synthesis), N-butyl-substituted alkynyl imine gave intramolecular cyclization [75], by Knorr pyrrole synthesis in which α-amino-ketone reacts with ethyl acetoacetate [76], ketones or secondary alcohols, and β-amino alcohols [77], ammonia and α-haloketones to give substituted pyrroles known as "Hantzsch pyrrole synthesis", by three-component condensation involving aldehyde, benzoyl chloride, and hydrazine hydrate "Piloty–Robinson pyrrole synthesis" [78] and most importantly from the reaction of oxime with alkynes "Trofimov reaction" [79] (**Scheme 1.6**).

1.4.2.2 Thiophene

Thiophene is a privileged heterocycle containing a five-membered ring of one sulfur as a heteroatom with the formula C_4H_4S. Thiophene and its derivatives are important heterocyclic compounds with a wide range of uses and characteristics, including antimicrobial agent cefoxitin, fungicide agent penthiopyrad, antiinflammatory drug suprofen, anti-hypertensive drug tiamenidine, and herbicide agent dimetheamide [80] (**Figure 1.11).**

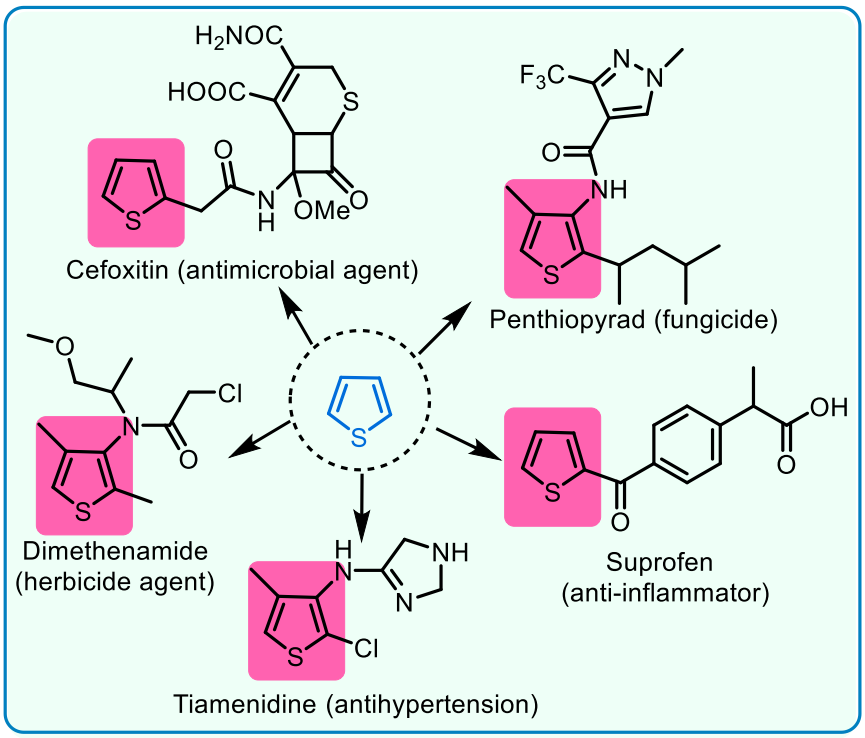


Figure 1.11 Few biologically active compounds containing thiophene moiety.

1.4.2.3 Thiazoles

Heterocyclic compounds with five members that have nitrogen and sulfur atoms in their ring are called thiazoles. They are extensively present in both synthetic and natural items a wide range of biological behaviors, such as antibacterial, antifungal, anticancer, anti-inflammatory, antischistosomal, and antihelmintic effects, are displayed by thiazole derivatives. For instance, the structure of the antibiotic penicillin includes a thiazole ring [6,81–83] (**Figure 1.12).**

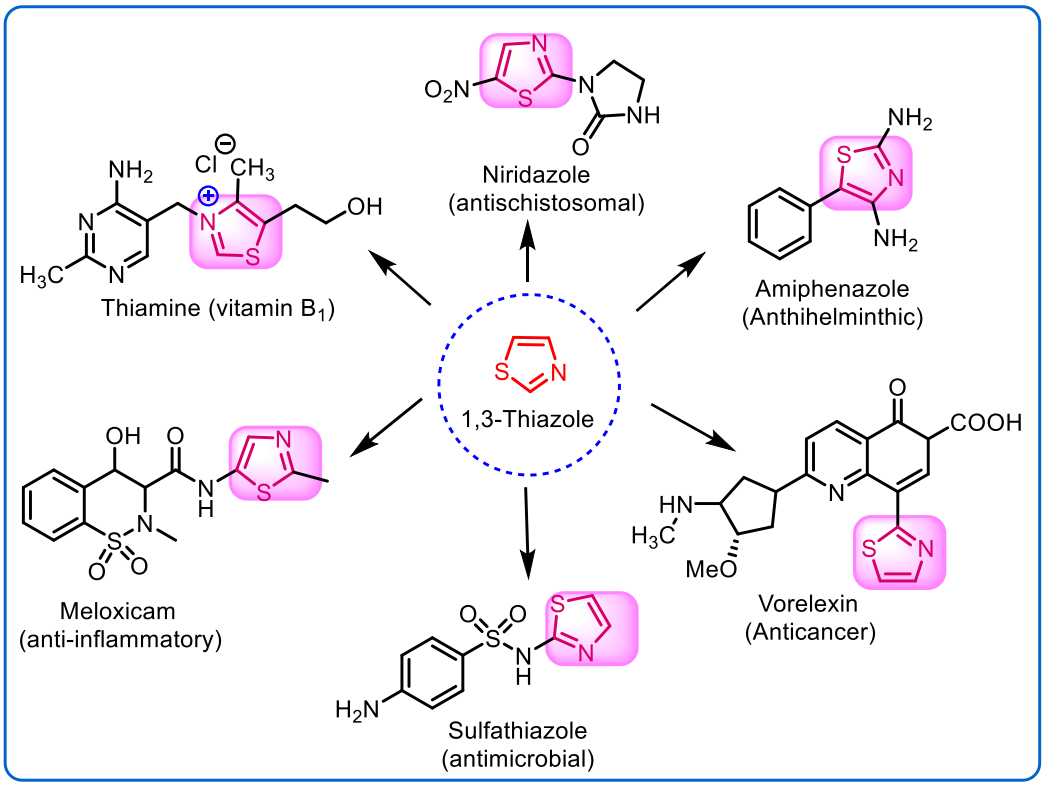
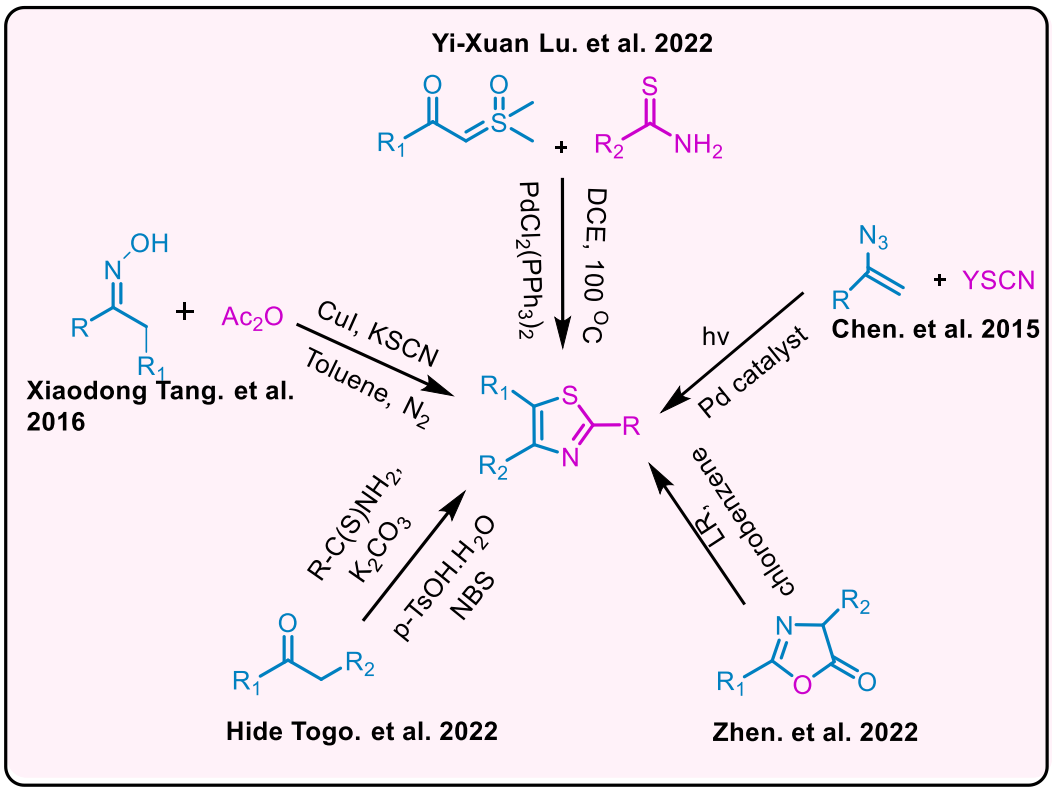


Figure 1.12 A few biologically active compounds containing 1,3-thiazoles moiety.

1.4.3.1.1 Synthesis of 1,3-Thiazoles

Recently, a variety of oxidative systems, such as HX/ DMSO [84], $KI/NH_4NO_3/H_2SO_4/O_2$ [85], $I_2/PTSA/O_2/DMSO$ [86], $CuCl_2/ H_2O$ [87], and $(CH_3)_3SiX\text{-}KNO_3$ [88], have been reported. Lu and co-workers reported the synthesis of 2,4-diphenyl thiazole by the reaction of sulfoxonium ylide and thiobenzamide using palladium as a catalyst in 2022 [89]. G. Zhang and Y. Yu also described the synthesis of 4-phenyl-2-aminothiazole from the reaction of α-azidostyrene and potassium thiocyanate in 2015, using $Pd(OAc)_2$ and n-propanol as solvent [90].



Scheme 1.7 Synthesis of 1,3-thiazoles derivatives.

Specifically, Togo and co-workers successfully synthesized thiazole derivatives in a highly efficient, environmentally safe, and economical process via the α-bromination of various ketones using NBS in an aqueous medium [91].

1.4.2.4 Thiadiazole

Thiadiazoles are a significant class of heterocyclic compounds that contain sulfur and nitrogen. Four isomeric forms of thiadiazole that are found in nature are 1,2,3-thiadiazole, 1,2,5-thiadiazole, 1,2,4-thiadiazole, and 1,3,4-thiadiazole [92].

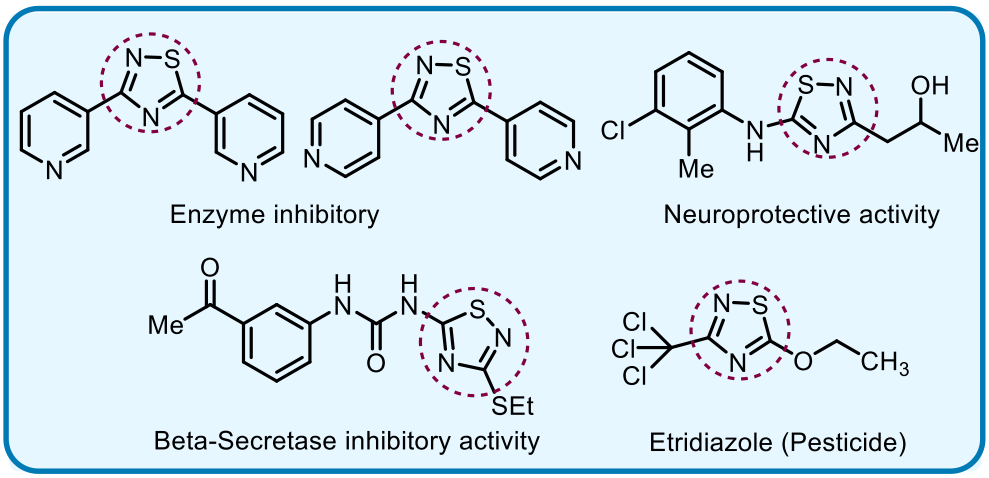
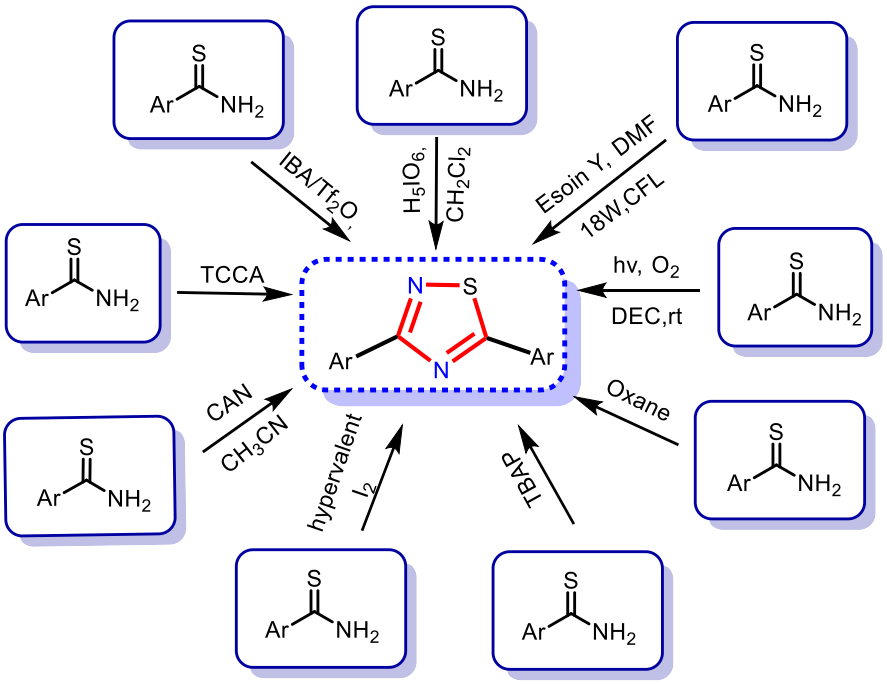


Figure 1.13 A few biologically active compounds containing 1,2,4-thiadiazoles moiety

Among these, we have focused on 1,2,4-thiadiazole. The various biological activities of 1,2,4-thiadiazole core structures and their associated therapeutic applications are the primary reasons for their interest [93]. They are employed in many different industries. Various synthetic 1,2,4-thiadiazole compounds display a range of biological characteristics. (**Figure 1.13**).

1.4.2.4.1 Synthesis of 1,2,4-thiadiazoles by dimerization of thioamides

Another method for creating 1,2,4-thiadiazoles is to dimerize thioamides using various oxidizing agents, like eosin Y in visible light [94], $(IBA/Tf_2O)_2$ [95], 2,4,6-trichloro-1,3,5-triazine (TCCA) [96], Oxane [97], ceric ammonium nitrate [98], H_5IO_6 in CH_2Cl_2 [99], pseudo cyclic hypervalent iodine [100] TBN [101], and chloranil [102][113] (**Scheme 1.8**).



Scheme 1.8 Synthesis of 1,2,4-thiadiazoles by dimerization of thiobenzamides.

1.4.3 Nitrogen and sulfur-containing six-membered and fused heterocyclic compounds

1.4.3.1 Pyridine

Important heteroaromatic chemical pyridine has a wide range of powerful biological effects. Using coal tar distillation, a significant amount of pyridine was extracted from natural sources. Pyridines can also be found in a wide range of important substances, such as the vitamins pyridoxine (vitamin B_6) and niacin (vitamin B_3), as well as other alkaloids like quinine and nicotine. Many medications have pyridine structures, including anti-HIV, anticancer, antidiabetic, and proton pump inhibitor properties (**Figure 1.14).** In 1876,

pyridine was first produced via hydrogen cyanide and acetylene. Chichibabin Pyridine Synthesis is still a process used in industry to synthesize pyridine [103–107].

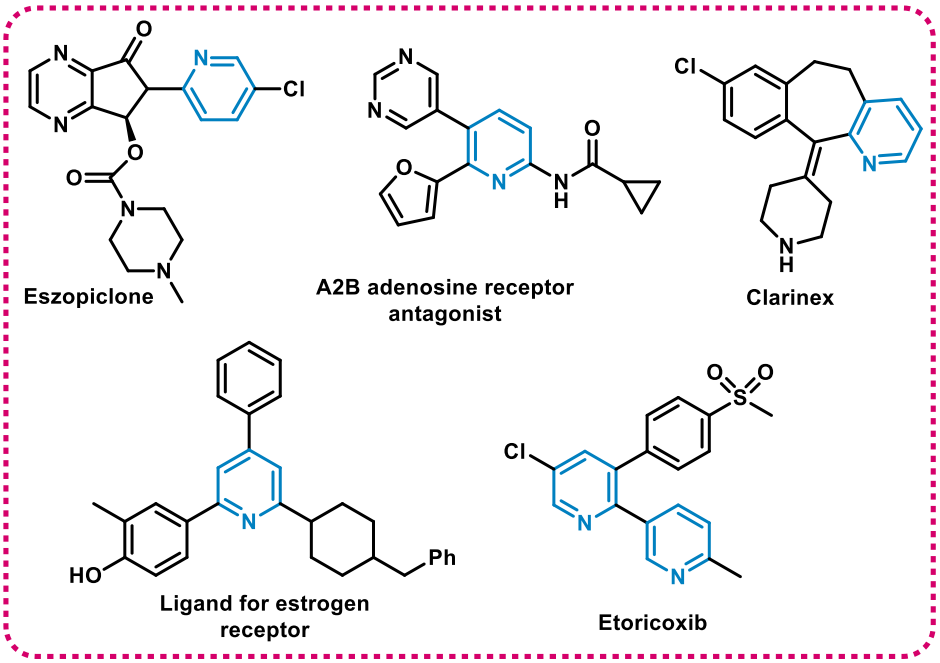
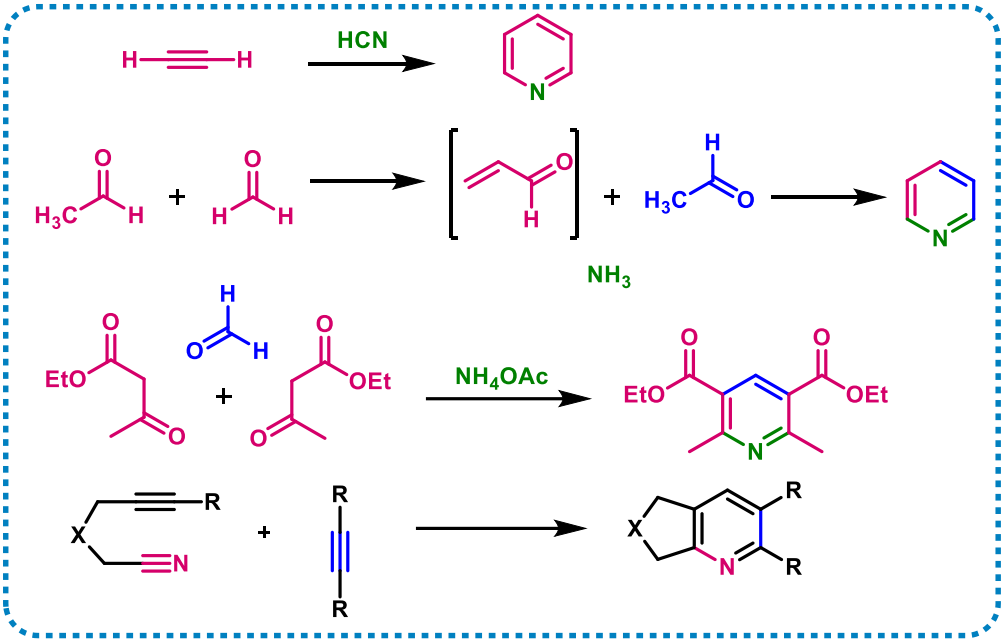


Figure 1.14 Few biologically active compounds containing pyridine moiety.

Acetaldehyde and ammonia react with acrolein to generate dihydropyridine, which is then oxidized with a solid-state catalyst to yield pyridine. This process is known as the Knoevenagel condensation reaction between formaldehyde and aldehyde [108]. A multi-component chemical reaction involving an aldehyde, two equivalents of a β-keto ester, and a nitrogen donor (either ammonium acetate or ammonia) is known as the Hantzsch pyridine synthesis. The cycloaddition of alkynenitriles and alkynes produces pyridine [109,110] (**Scheme 1.9**).



Scheme 1.9 Synthesis of pyridine and its derivatives.

1.4.3.2 Benzothiazole

Due to its numerous biological, pharmacological, and intriguing chemical applications, benzothiazole has attracted much attention [111]. The potential uses of 2-substituted benzothiazole derivatives include imaging agents for $Ca_2þ$ channel antagonist, anti-HIV, antituberculosis, analgesia, diuretic activity, antitumor, antifungal, anti-inflammatory, antiviral, antipsychotic, neurodegenerative, and mosquitocidal properties [112] (**Figure 1.15)**.

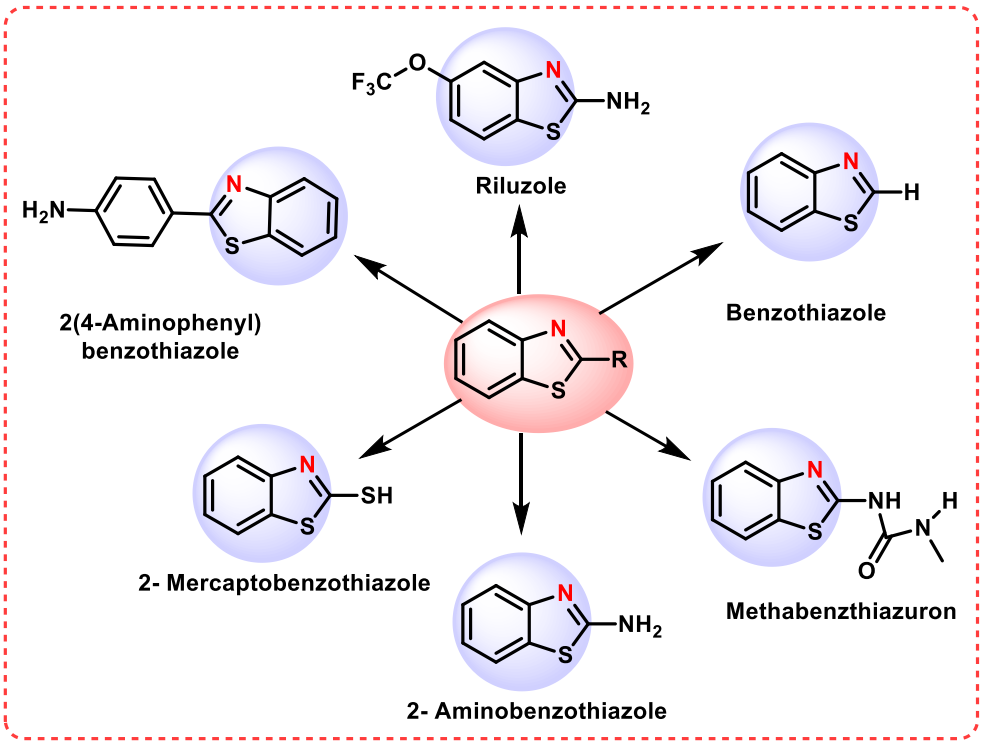
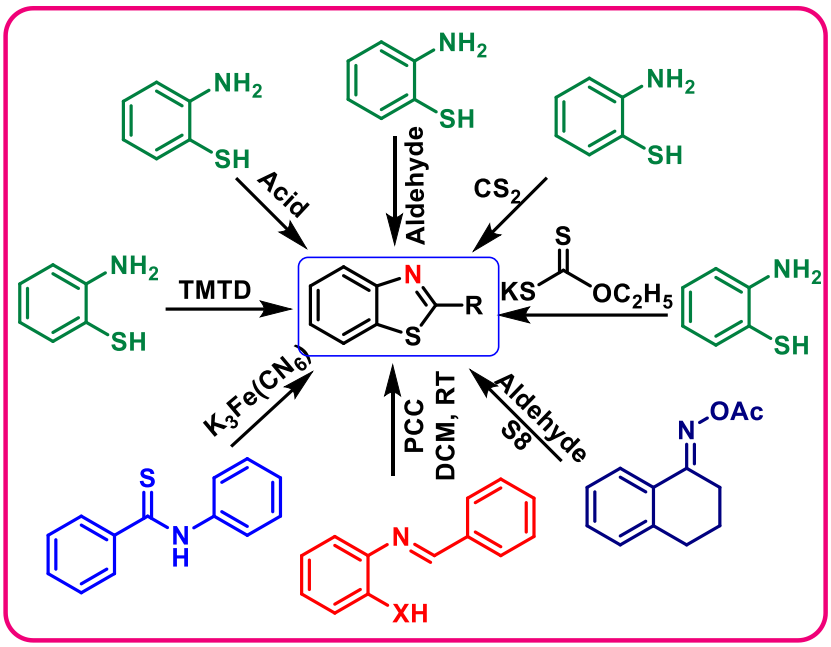


Figure 1.15 Few biologically active compounds containing benzothiazoles moiety.

The primary synthesis of benzothiazoles involves the chemical reaction of 1,2-aminothiophenol with carbonyl molecules [113], 2-halogen substituted anilines, and dithiocarbamates using *t*-BuOK. [114], oxidative cyclization of Schiff's base [115], tetramethylthiuram disulfide (TMTD) and *o*-aminothiophenol [116], arylthioureas undergoes intermolecular oxidative C-H bond functionalization in the presence of pyridine [117] (**Scheme 1.10**).



Scheme 1.10 Synthesis of benzothiazole and its derivatives

1.4.3.3 Benzimidazole

A six-membered benzene ring fused with a five-membered imidazole ring makes up the nitrogen-containing heterocyclic molecule known as benzimidazole. Benzimidazole and its derivatives are constituents of numerous physiologically active compounds and are used as anticoagulants, psychoactive drugs, immunomodulators, hormone modulators, antihypertensive, anti-inflammatory, antibacterial, antiviral, antifungal, antihelmintic, anticancer, antiulcer, antioxidant, and many other biologically active compounds. Derivatives of benzimidazoles work by interacting with essential biological targets such as histamine receptors, β-tubulin, serotonin receptors, and minor grooves in DNA [118–120] (**Figure 1.16)**.

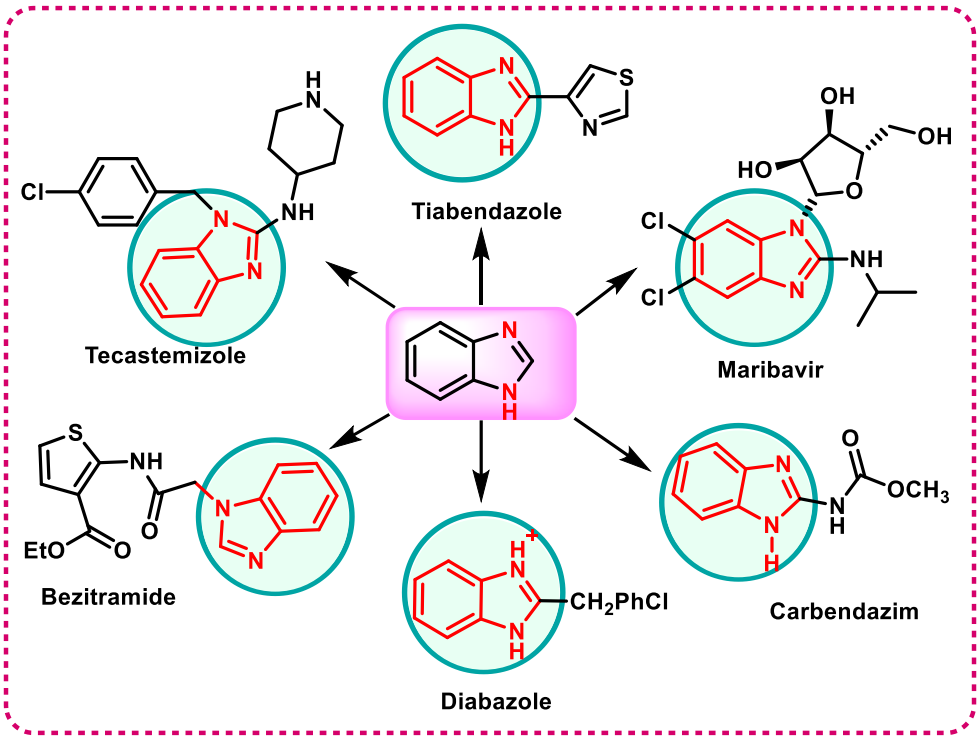
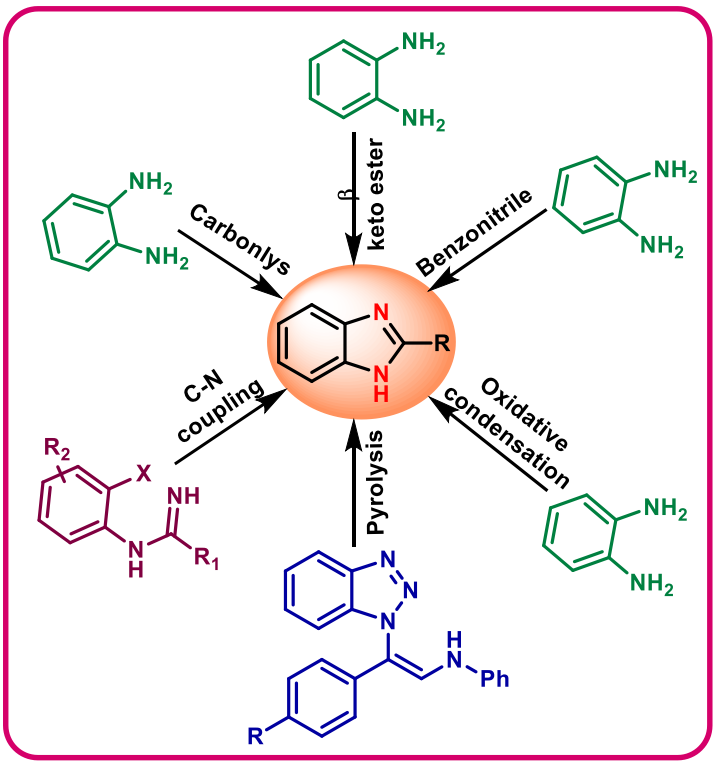


Figure 1.16 A Few biologically active compounds containing benzimidazole moiety.

Several methods were used to produce benzimidazole and its derivatives, including the condensation reaction of *o*-phenylenediamine with carbonyls [121], oxidative condensation reaction of alcohols, methyl arenes derivatives with *o*-phenylenediamine [122], oxidative cyclization of *N*-aryl amidine intermediate resulting from aniline addition to a nitrile [123], and thermolysis of benzotriazole derivatives [124] (**Scheme 1.11**).



Scheme 1.11 Synthesis of benzimidazole and its derivatives.

We are interested in studying the chemistry (synthesis and structural characterization) of benzothiazoles/benzimidazoles, thiazoles, thioamides, and thiadiazoles due to the significance of nitrogen and sulphur containing organic molecules. The ensuing chapters 2-5 describe the research.

1.5 Objectives of Thesis Work

This concise overview makes it abundantly evident that compounds containing nitrogen and sulfur have found widespread use in various sectors, such as organic synthesis, biochemistry, medicinal chemistry, material sciences, agriculture, etc. Thus, our objective is to develop some efficient and greener methodologies for the synthesis of some biologically active nitrogen and sulfur-containing compounds via conventional as well as non-conventional methods, such as renewable energy sources and solvent-free methods, which may make an encouraging contribution to the development of the green and clean chemistry. The main focus of the current thesis work is aimed-

1. Introduction of nitrogen and sulfur-containing compounds.

2. A novel approach towards the synthesis of benzothiazoles and benzimidazoles: Eosin Y catalyzed photo-triggered C-S and C-N bond formation.

3. Visible-light induced C-S bond formation in the synthesis of 2,4-disubstituted thiazoles through cascade functionalization of acetophenone.

4. Synthesis of thioamides from amides using Lawesson reagents in solvent-free conditions: A chromatography-free approach.

5. One-pot, two-step synthesis of 1,2,4-thiadiazoles from primary amides via thiolation and oxidative dimerization under solvent-free conditions.

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