CHAPTER 1

Introduction

Overview of Some Main Class of Nitrogen, Oxygen and Sulphur Containing Heterocyclic Compounds

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Heterocyclic compounds are a class of cyclic organic compounds in which one or more of the carbon atoms inside the backbone of the molecule is changed apart from carbon. The most commonly found heteroatoms in heterocyclic compounds are nitrogen, oxygen and sulphur. Heterocyclic compounds are divided into different categories on the basis of total number of atoms in the cyclic structure they have like three, four, five, six, seven and eight membered and also fused types of heterocyclic compounds are known. Out of them nitrogen, oxygen and sulphur containing five, six membered and fused heterocyclic compounds maintained the curiosity of researchers throughout the decades of historical development of organic synthesis.

Five Membered Heterocyclic Compounds: Pyrrole, furan and thiophene are the important single heteroatom containing five membered heterocyclic compounds. The common five membered heterocyclic compounds having more than one heteroatoms are isoxazole, pyrazole, imidazole, azole, thiazole, thiadiazole, oxadiazole, triazene, etc. Heterocyclic compounds which are partially reduced are often referred to as dihydro or tetrahydro derivatives of the parent unsaturated compound (**Figure 1.1**).

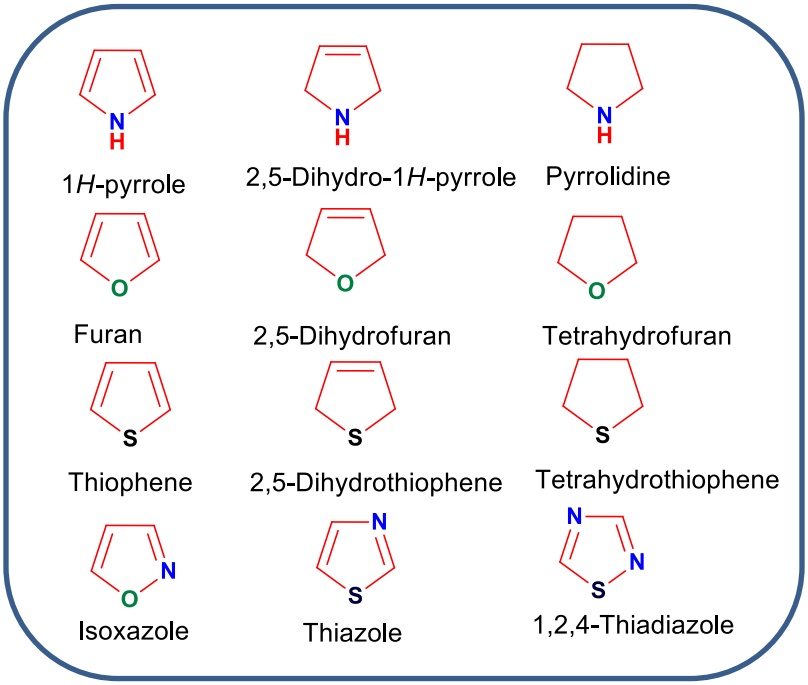


Figure 1.1: Some important five membered heterocyclic compounds.

Six Membered Heterocyclic Compounds: Pyridine, pyran and thiopyran are some common six membered heterocyclic compounds containing single heteroatom in the ring. The six membered heterocycles which comprises more than one heteroatoms are pyrazine, dioxane, dithine**,** oxazine, thiazine etc. Thiadiazine is a heterocyclic compound having two nitrogen atoms and one sulfur atom in six-membered ring skeleton and triazine also contains three nitrogen atoms in a six member ring (**Figure 1.2**).

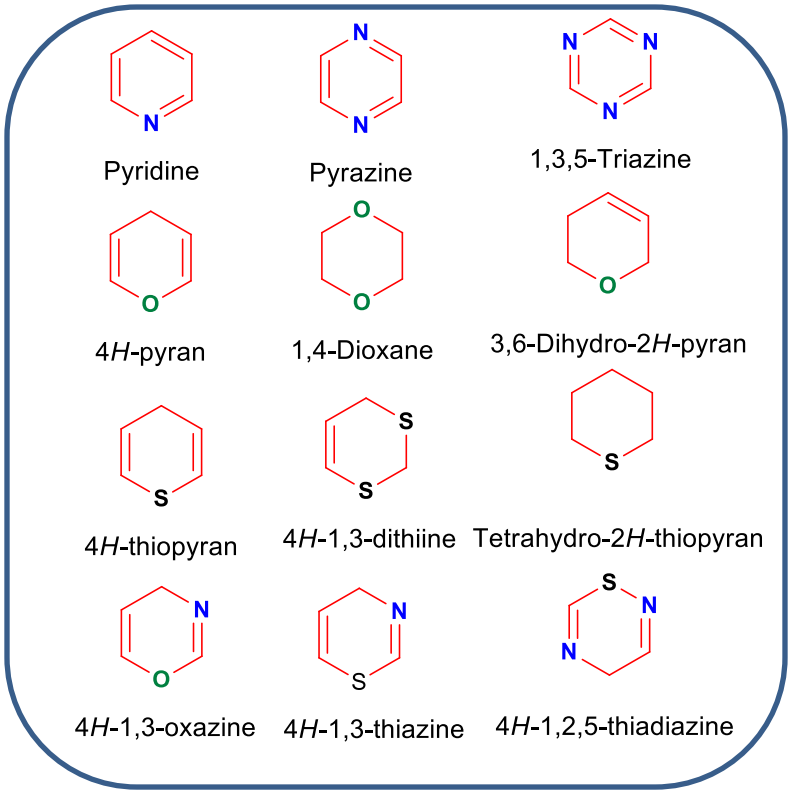


Figure 1.2: Some important six membered heterocyclic compounds.

Fused Heterocyclic Compounds: Fused heterocyclic ring structures are obtained by the fusion of one ring with other rings. Quinoline, 1*H*-indole, coumarin and benzothiophene are some important single heteroatom containing fused heterocyclic compounds. The common fused heterocyclic ring contains more than one heteroatoms such as imidazo[1,2-a]pyridine, benzothiazole, benzooxathiole and furopyran etc. Pyrazolooxazole is a heterocyclic compound holding one oxygen atom and three nitrogen atoms as share of the fused heterocyclic compound (**Figure 1.3**).

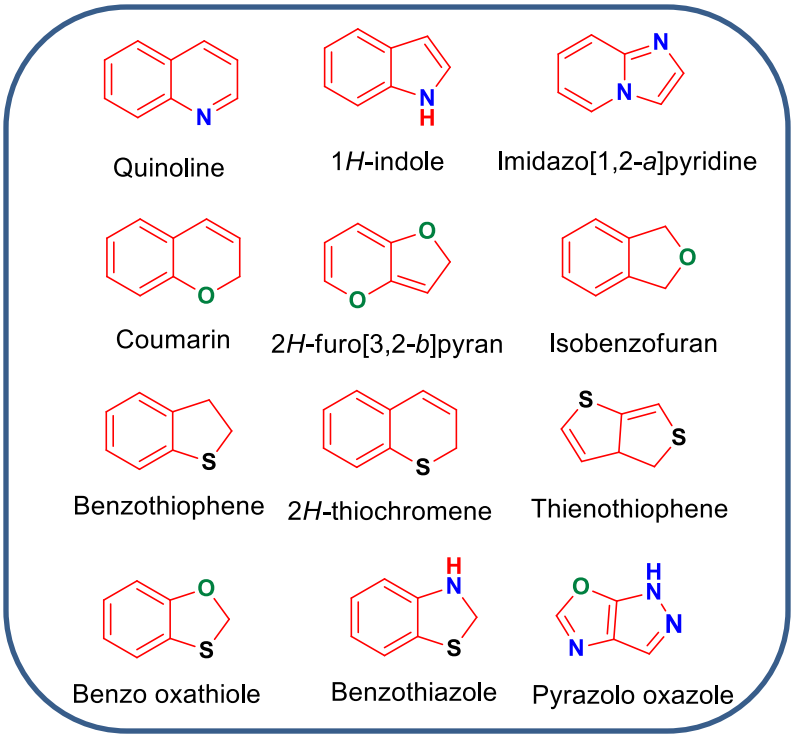


Figure 1.3: Some important fused heterocyclic compounds.

The chemical substances which comprise at least one heterocyclic moiety make them the most important class of compounds in organic chemistry. Heterocyclic compounds have attracted the attention of scientists over the years due to its vitality in human life and abundance in nature (Nagaraj et al. 2008) due to the fact that they are important structural subunits present in many herbal merchandise consisting of vitamins, hormones, antibiotics and pigments (Ju et al. 2006, Yadav et al. 2011). Thus, these derivatives have attracted considerable attention in the designing of biologically active molecules. Modern society depends on man-made heterocycles for many purposes together with drugs, pesticides,

dyes, plastics, cosmetics, solvents, antioxidants and vulcanization accelerators (Li et al. 2011, Martins et al. 2004) (**Figure 1.4**).

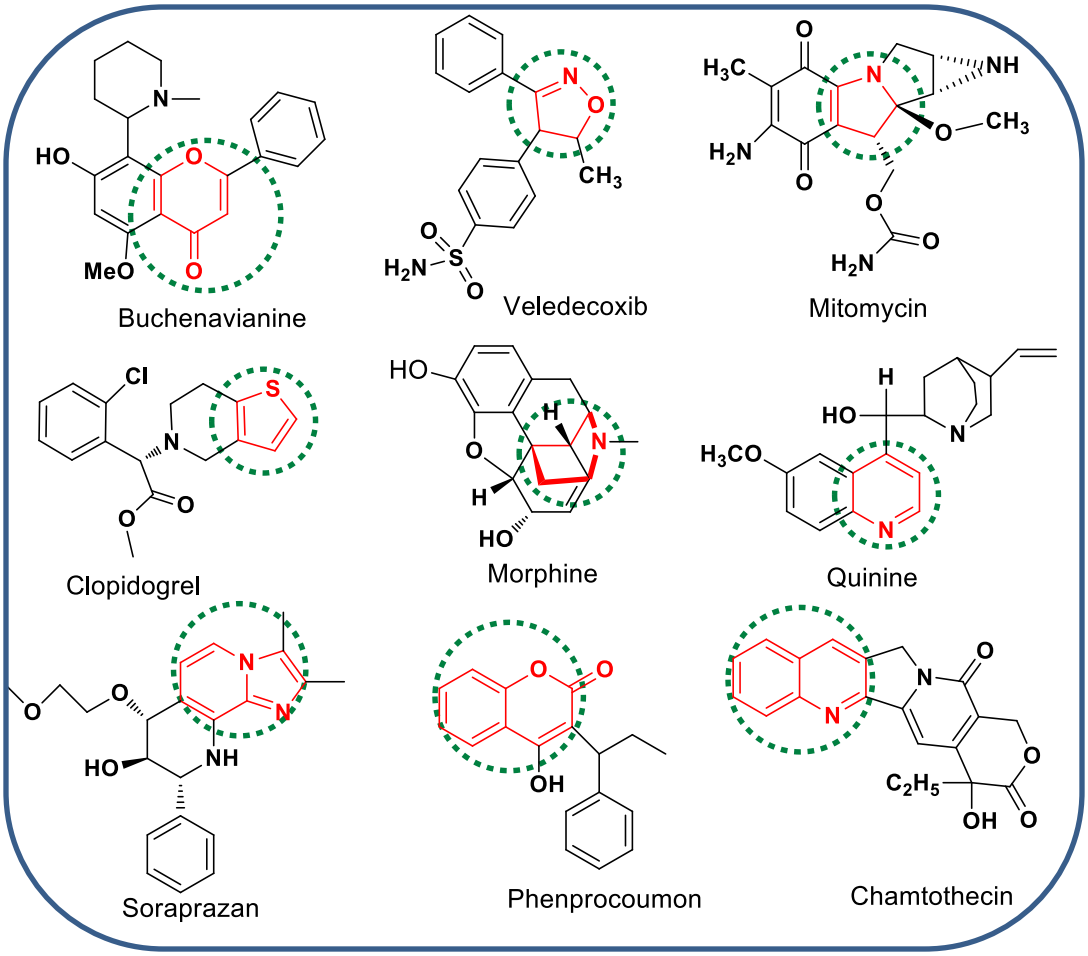


Figure 1.4: Some example of natural products and drugs containing different heterocyclic moieties.

Synthesis of heterocyclic skeleton with biologically ubiquitous functionalities is a lucrative aim for chemists. The five, six membered, fused heterocycles and related compounds have been the subject of major attraction for the researchers in the area of

synthetic organic chemistry. Therefore, chemists have been involved in extensive efforts to produce these heterocyclic compounds by rising new and effective synthetic transformation. Our main focus is on the study of 1,2,4-thiadiazole, coumarin, imidazo[1,2-a]pyridine and 4*H*-pyran scaffold.

1.1 Thiadiazole

Thiadiazoles are very important class of nitrogen and sulphur containing heterocyclic compounds. 1,2,3-thiadiazole, 1,2,5-thiadiazole, 1,2,4-thiadiazole and 1,3,4-thiadiazole are four isomeric forms of thiadiazole found in nature (Siddiqui et al. 2009). Out of them, we have focused on 1,2,4-thiadiazole. 1,2,4-Thiadiazole core structure are of great interest mainly because of their various biological activities and associated clinical applications (Iizawa et al. 1993, Donkor et al. 2000, Gurjar et al. 2014). They have diverse applications in different fields. A large number of synthetic 1,2,4-thiadiazole derivatives show wide range of biological activities such as thiadiazole KC 12291 which displayed the foremost proof of its cardioprotective activity (Hartmann et al. 1998), 6-(1,2,4-thiadiazol-5-yl)-3-amino pyridazine derivatives are recognized as unique angiogenesis inhibitors (Bongartz et al. 2002) and monocyclic 1,2,4-thiadiazoles have been found as useful insecticidal, herbicidal and fungicidal agents. Additionally, the properties of 1,2,4-thiadiazole as thioltrapping representatives has been reviewed recently (Tam et al. 2005) (**Figure 1.5**).

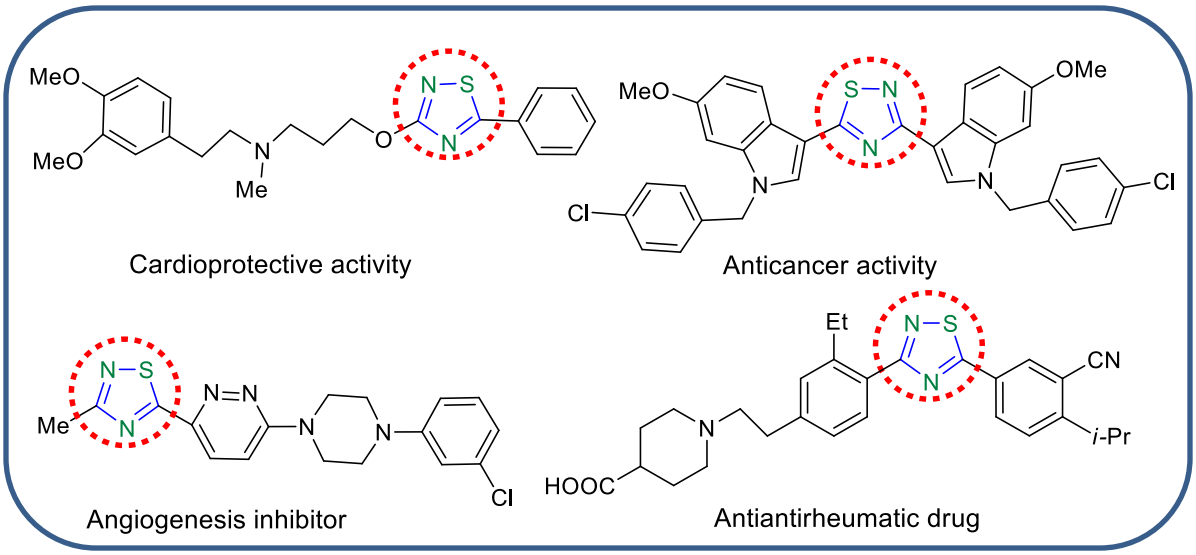
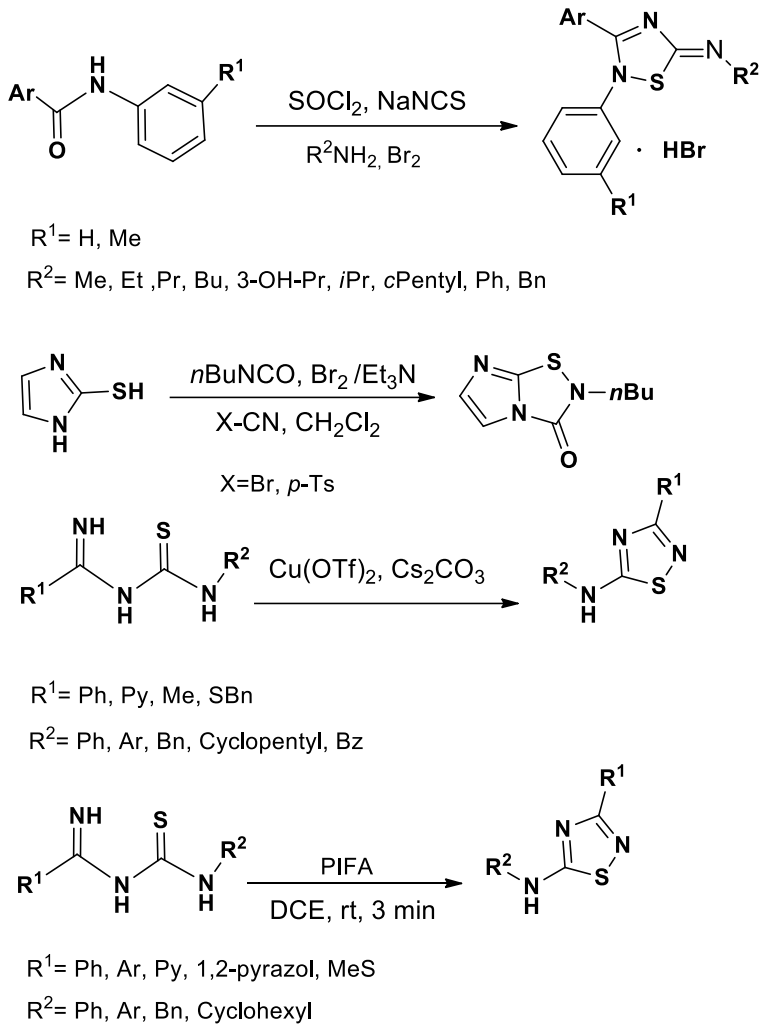


Figure 1.5: Some biological active compounds containing thiadiazole scaffold.

In this context, enormous efforts have been dedicated by chemists to establish many concise synthetic paths accessing thiadiazole framework. Synthesis of thiadiazole has been sub categorized in cyclization, dimerization and condensation reactions.

1.1.1 Synthesis of 1,2,4-Thiadiazoles by Cyclization

1,2,4-Thiadiazoles have been synthesized by cyclization of different starting materials in the presence of catalysts such as from benzamides in the presence of $SOCl_2$, NaNCS, RNH_2, Br_2 (Goblyos et al. 2005), from 2-mercaptoimidazole and *n*-butyl isocyanate via oxidative ring closure with Br_2 and triethylamine (Leung et al. 2005), from imidoylthioureas catalyzed by copper (Kim et al. 2014), imidoylthioureas mediated by phenyliodine(III) bis(trifluoroacetate) (PIFA) (Mariappan et al. 2016) (**Scheme 1.1**).

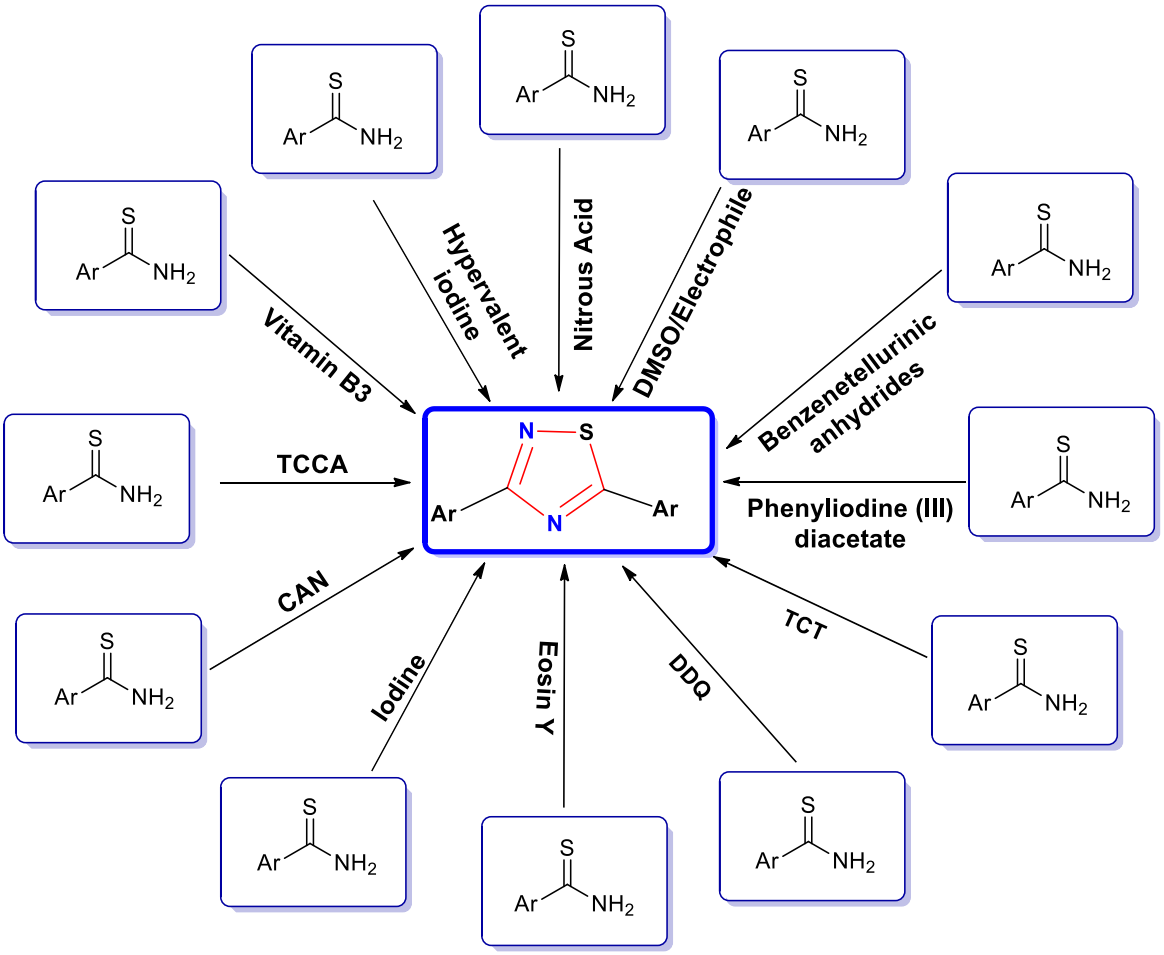


Scheme 1.1: Synthesis of 1,2,4-thiadiazoles by cyclization.

1.1.2 Synthesis of 1,2,4-Thiadiazoles by Dimerization of Thioamides

1,2,4-Thiadiazoles are also synthesized by dimerization of thioamides by using different oxidizing agents such as nitrous acid (Cronyn et al. 1952), DMSO/electrophile (Takikawa et al. 1985), benzene tellurinic mixed anhydrides

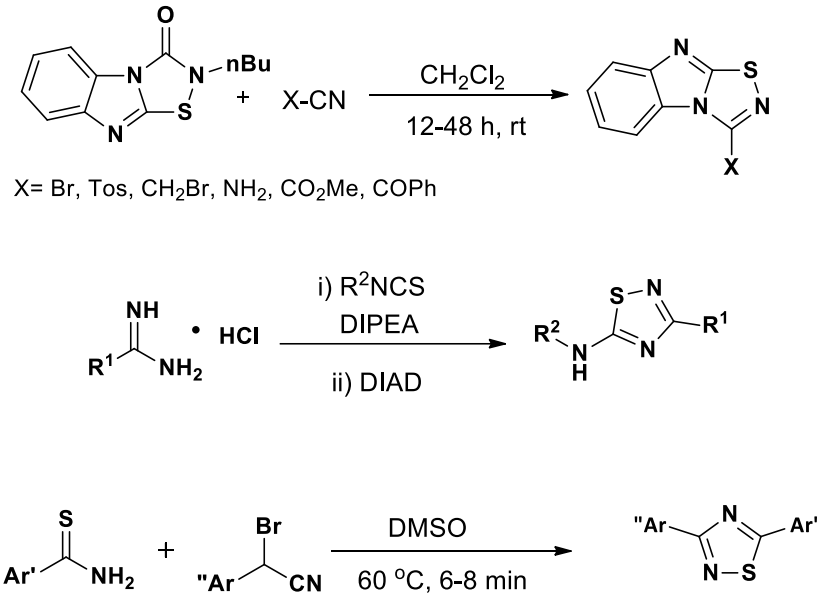
(Fukumoto et al. 1990), phenyliodine (III) diacetate (Yan et al. 2003), 2,4,6-trichloro-1,3,5-triazine (TCT) (Khosropour et al. 2010), 2,3-dichloro-5,6-dicyanobenzoquinone (Cheng et al. 2012), eosin Y in visible light (Srivastava et al. 2013), iodine (Zhao et al. 2014), ceric ammonium nitrate (Vanajatha et al. 2016), trichloroisocyanuric acid (TCCA) (Bose et al. 2017), organocatalytic approach by using vitamin B_3 (Putta et al. 2018), pseudo cyclic hypervalent iodine (Quarban et al. 2019) (**Scheme 1.2**).



Scheme 1.2: Synthesis of 1,2,4-thiadiazoles by dimerization of thiobenzamides.

1.1.3 Synthesis of 1,2,4-Thiadiazoles through Condensation Reactions

Another synthetic path to produce the useful 1,2,4-thiadiazole framework is through condensation or exchange reactions by using various precursors such as 1,2,4-thiadiazol-3(2*H*)one derivatives and substituted nitriles (e.g. cyanogen bromide or *p*-toluenesulfonyl cyanide) (Leung et al. 2005), from isothiocyanates, amidine hydrochlorides and *N*,*N*-diisopropylethylamine (DIPEA) followed by the addition of diisopropylazodicarboxylate (Wu et al. 2008), from benzothioamides with arylacetonitrile (Boeini et al. 2011) (**Scheme 1.3**).



Scheme 1.3: Synthesis of 1,2,4- thiadiazoles by condensation.

1.2 Coumarin

Coumarin compounds are important naturally occurring and synthetic oxygen containing heterocyclic compounds and it has benzopyrone framework. In 1820, Vogel isolated coumarin from tonka beans also known as coumarou in French (Gleye et al. 2003). This special benzopyrone structural moiety permits its derivatives to interact with a variety of enzymes and receptors in organisms through weak bond interactions and due to this property they are widely used in medicinal chemistry. Coumarins play an important role in numerous natural processes like plant physiology and also elaborate in the actions of plant growth hormones, growth regulators, control of respiration and photosynthesis (Vekariya et al. 2014). In the field of supramolecular chemistry which is important in pharmaceutical

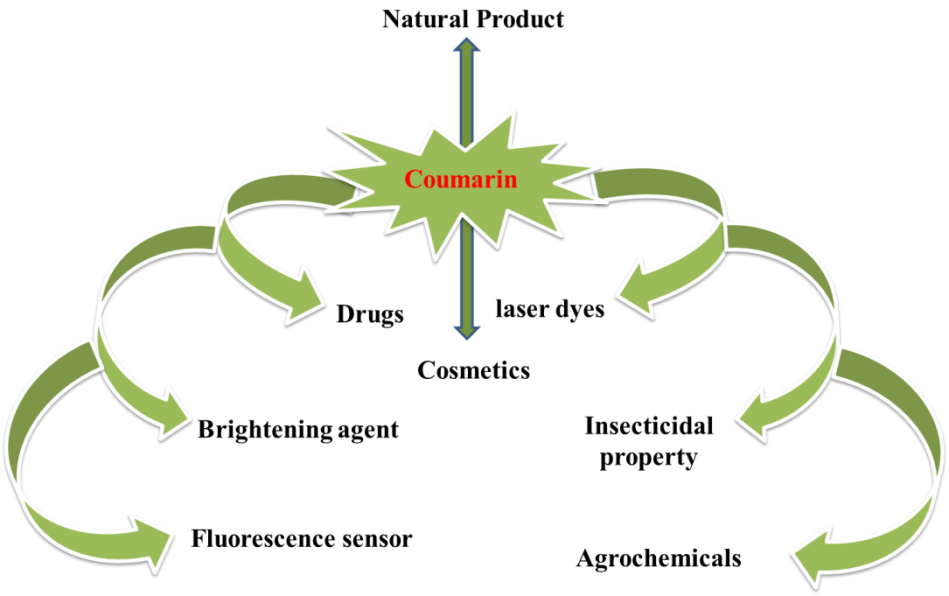


Figure 1.6: Applications of coumarin in different fields.

science, coumarin containing supramolecular medicine emerged as a new class of drugs in recent years. Coumarin has been investigated for a wide range of properties in different fields such as in fragrance & perfume, additive in food & cosmetics, laser dyes, agrochemicals, cosmetics, brightening agents, insecticides, fluorescence sensor and in drugs (Brahmachari et al. 2015) (**Figure 1.6**).

Figure 1.7 shows some coumarin containing biologically active natural products and drugs like Umbelliferone is used as sunscreen, Dicoumarol as anticoagulant drug, Seselin plays an important role as a metabolite, Calanolide A shows anti-tuberculosis activities, Chlorobiosin use as antibacterial and Lamellarin D shows cytotoxic activity against tumor cell lines.

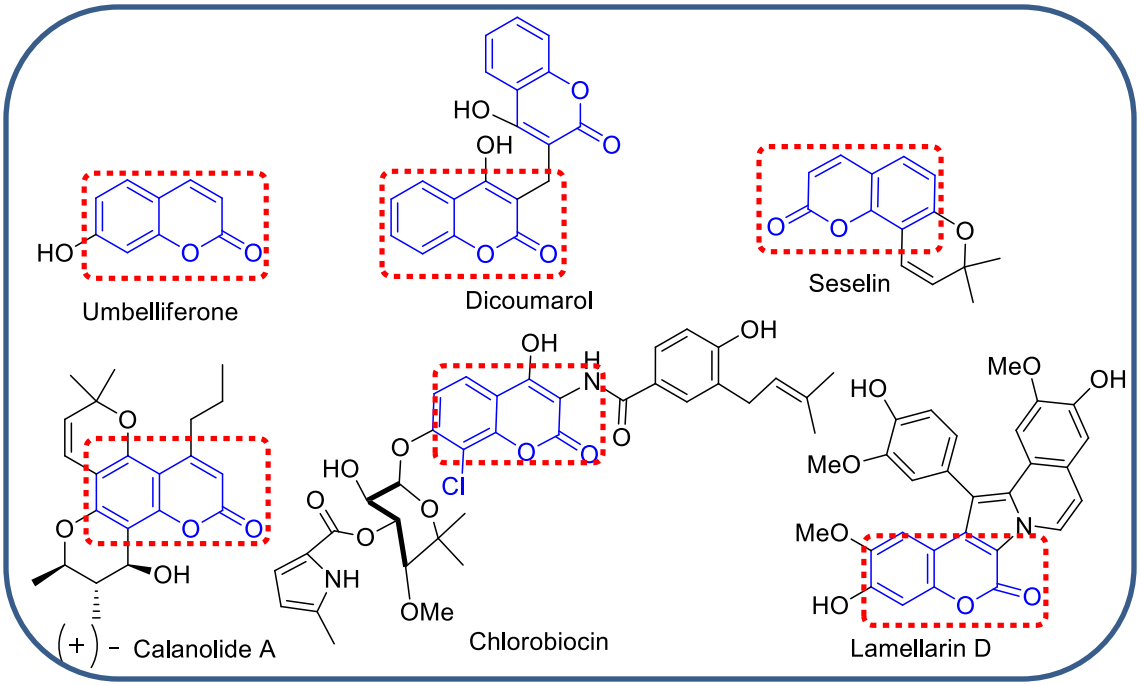
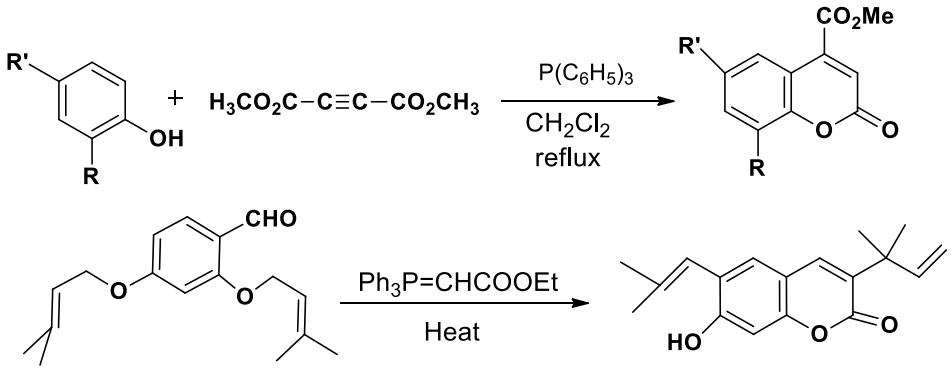


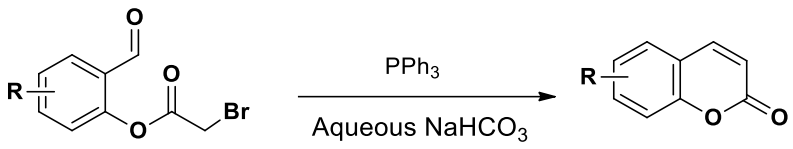
Figure 1.7: Coumarin containing biologically active compounds.

In view of the numerous applications in different fields, numerous natural coumarins are isolated from fungi, bacteria, plants and as well as obtained from chemical synthesis (Murray et al. 1991, Stefanachi et al. 2018). Synthesis of coumarin is always the subject of interest for the organic chemists. They have developed different methodologies for synthesis of this biologically important moiety. In literature, lots of methods have been described for the synthesis of coumarins by using different starting materials with different catalysts like Wittig reaction, Perkin reaction, Baylis-Hilmann reaction, Pechmann condensation and Knoevenagel condensation.

1.2.1 Wittig Reaction

Wittig reaction is tremendously used for C–C bond formation in the synthesis of natural products. Coumarins have been synthesized through Wittig reaction under different reaction conditions (Yavari et al. 1998, Patre et al. 2009, Belavagi et al. 2014) (**Scheme 1.4**).

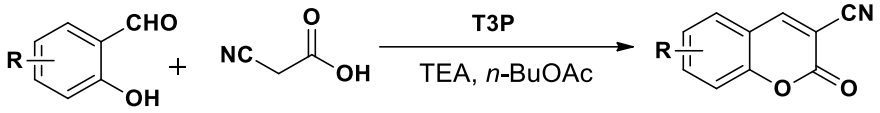




Scheme 1.4: Synthesis of coumarin by Wittig reaction.

1.2.2 Perkin Reaction

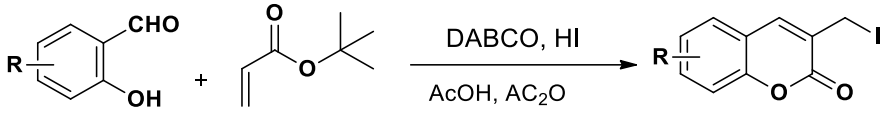
Perkin reaction is another method to synthesize coumarins. Augustine and co-workers described the synthesis of coumarins from salicylaldehyde and cyano acetic acid mediated by propylphosphonic anhydride (T3P) by Perkin reaction (Augustine et al. 2012) (**Scheme 1.5**).



Scheme 1.5: Synthesis of coumarin by Perkin reaction.

1.2.3 Baylis-Hilmann Reaction

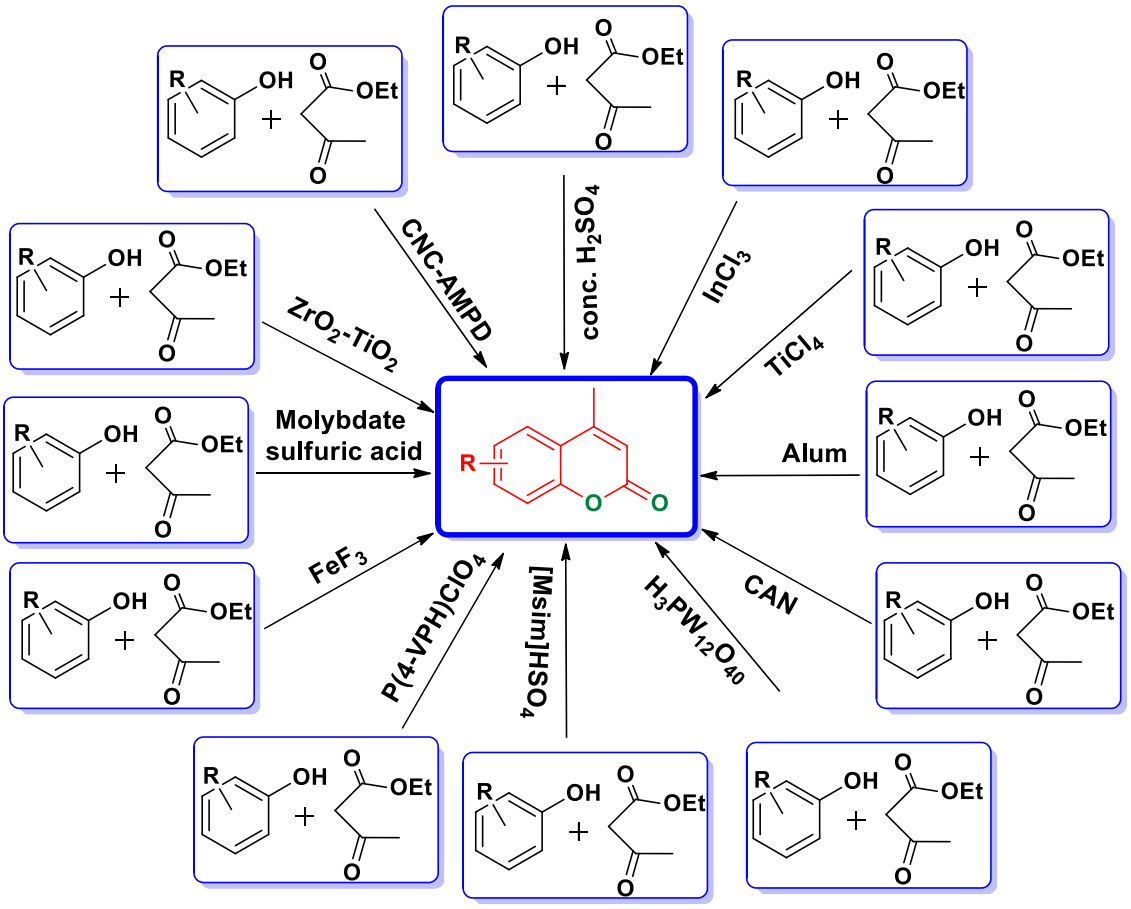
In Baylis-Hilmann methodology, coumarins are synthesized by the reaction of salicylaldehyde with *t*-butyl acrylate in the presence of DABCO, HI and acetic acid (Kaye et al. 2003) (**Scheme 1.6**).



Scheme 1.6: Synthesis of coumarin by Baylis-Hilmann reaction.

1.2.4 Pechmann Condensation

Traditionally coumarins have been synthesized over a decade by Pechmann reaction. In this protocol coumarins are synthesized by the reaction of phenol with β– keto esters or maleic acid in the presence of different catalysts such as conc. H_2SO_4 (Pechmann et al. 1884),

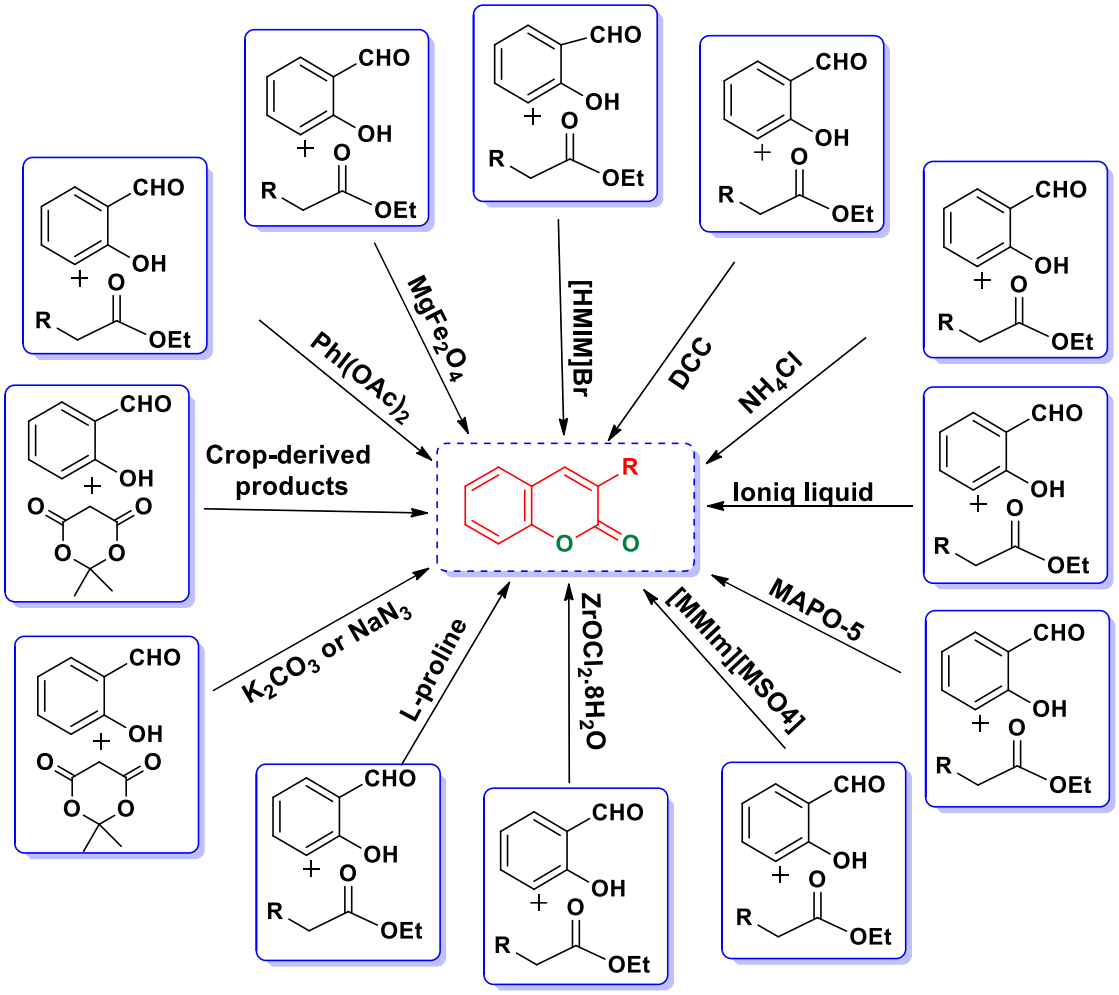


Scheme 1.7: Synthesis of coumarin by Pechmann reaction.

indium (III) chloride (Bose et al. 2002), $TiCl_4$ (Valizadeh et al. 2005), Alum (Dabiri et al. 2007), ceric ammonium nitrate (CAN) (Reddy et al. 2008), phosphotungstic acid (Keri et al. 2009), acidic ionic liquid (Khaligh et al. 2012), poly(4-vinylpyridinium)perchlorate (Khaligh et al. 2013), FeF_3 (Vahabi et al. 2014), molybdate sulfuric acid (Moradi et al. 2015), zirconia-based heterogeneous (Khan et al. 2016), cellulose nanocrystal supported palladium nanoparticles (Mirosanloo et al. 2018) (**Scheme 1.7**).

1.2.5 Knoevenagel Condensation

Knoevenagel condensation is most common process for the synthesis of coumarins. In this methodology coumarin have been synthesized by the reaction of *o*-hydroxybenzaldehydes *i.e.* salicylaldehyde derivatives and active methylene compounds in the presence of different catalyst such as DCC (Bonsignore et al. 1995), ammonium chloride (Valizadeh et al. 2001), ionic liquid (Ranu et al. 2006), Lewis acid metal ion-exchanged MAPO-5 molecular sieves (Gopalakrishnan et al. 2008), [MMIm][MSO4] containing proline (Verdia et al. 2011), $ZrOCl_2.8H_2O$ (Tasqeeruddin et al. 2013), L-proline (Srikrishna et al. 2014), K_2CO_3 or NaN_3 (Brahmachari et al. 2015), crop-derived products (Fiorito et al. 2016), $PhI(OAc)_2$ (Khan et al. 2017), $MgFe_2O_4$ nanocatalyst (Ghomi et al. 2018), [HMIM]Br, piperidene and AcOH (Dinparast et al. 2019) (**Scheme 1.8**).



Scheme 1.8: Synthesis of coumarin by Knoevenagel condensation.

1.3 Imidazo[1,2-a]pyridine

The imidazo[1,2-a]pyridine ring system was described by Chichibabin in 1925. Imidazo[1,2-a]pyridines are an important class of nitrogen ring junction heterocyclic compounds, in this imidazole moiety is fused with the pyridine ring.

Imidazo[1,2-a]pyridine is one of the imperative fused bicyclic 5–6 heterocycles with the applications ranging from medicinal and combinatorial chemistry to material chemistry. It is also known as a 'drug prejudice' framework due to its broad applications in pharmaceutical chemistry. Furthermore, this scaffold is beneficial in material science due to its unique structural features. These derivatives show a wide range of biological activities like antibacterial, antitumor, antifungal, antiviral, antipyretic, analgesic activities (Bagdi et al. 2015) **(Figure 1.8)**.

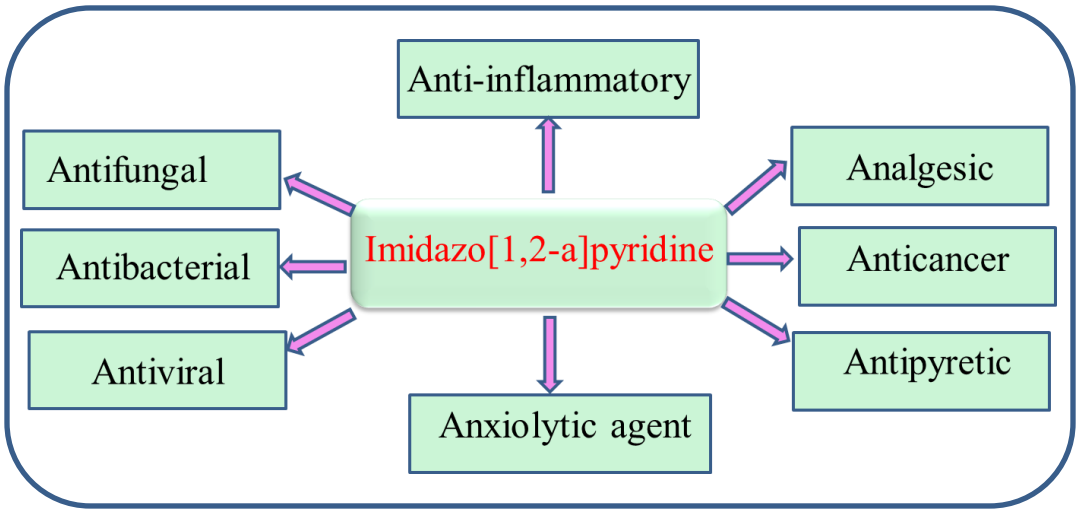


Figure 1.8: Biological activities of imidazo[1,2-a]pyridines.

Imidazo[1,2-a]pyridine moiety is present in many drugs and are used against various diseases **(Figure 1.9)**. Zolpidem was the first drug launched in the market as a hypnotic, Zolimidin as antiulcer, Saripidem is commercially available drug works as an anxiolytic

agent, Miroprofen an analgesic, GSK812397 as HIV infection and P13 K alpha inhibitor as an anti-cancer agent.

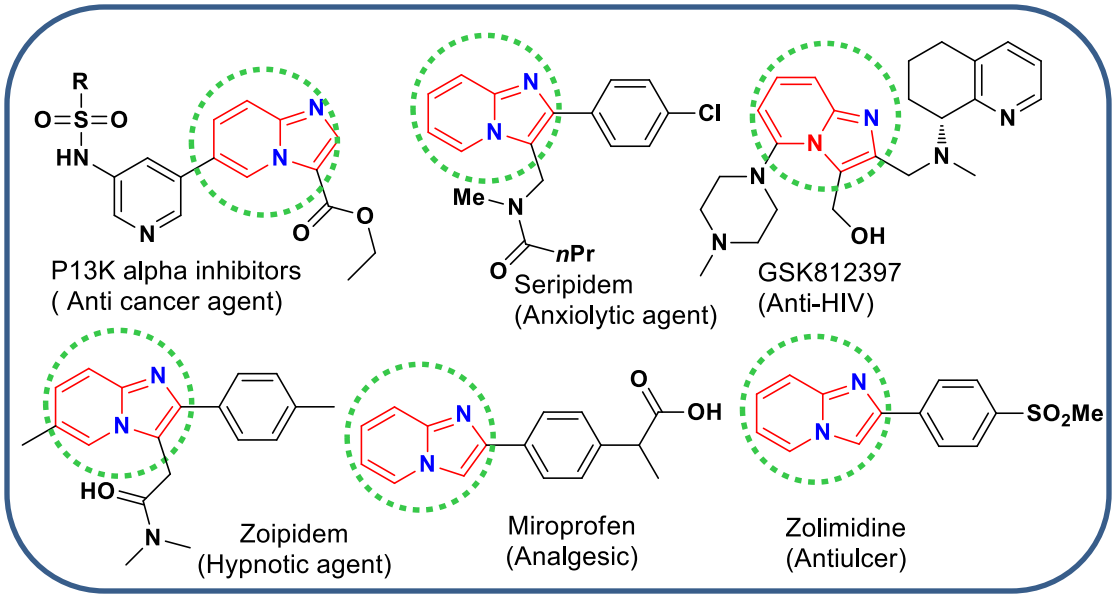


Figure 1.9: Imidazo[1,2-a]pyridine scaffold containing drugs.

Excited-state intramolecular proton transfer (ESIPT) property is observed in 2-substituted hydroxylphenyl imidazo[1,2-a]pyridines (**A**) in the majority of solvents which is responsible for strong, solid-state emission (Douhal et al. 1997). Imidazo[1,2-a]pyridines have established wide application as fluorescence sensors, laser dyes and also in molecular switches. Imidazo[1,2-a]pyridines (**B**) scaffold containing fluorescent dopamine D3 receptor ligands used as important probes for receptor visualization (Leopoldo et al. 2014).

In addition to this, metal complexes of imidazo[1,2-a]pyridine (**C**) are used in the area of electronic devices. Furthermore, 2-carbonyl-3-(pyridylamino)imidazo[1,2-a]pyridine (**D**) has been recognized as a luminous probe for mercury ion (Roopan et al. 2016) (**Figure 1.10**).

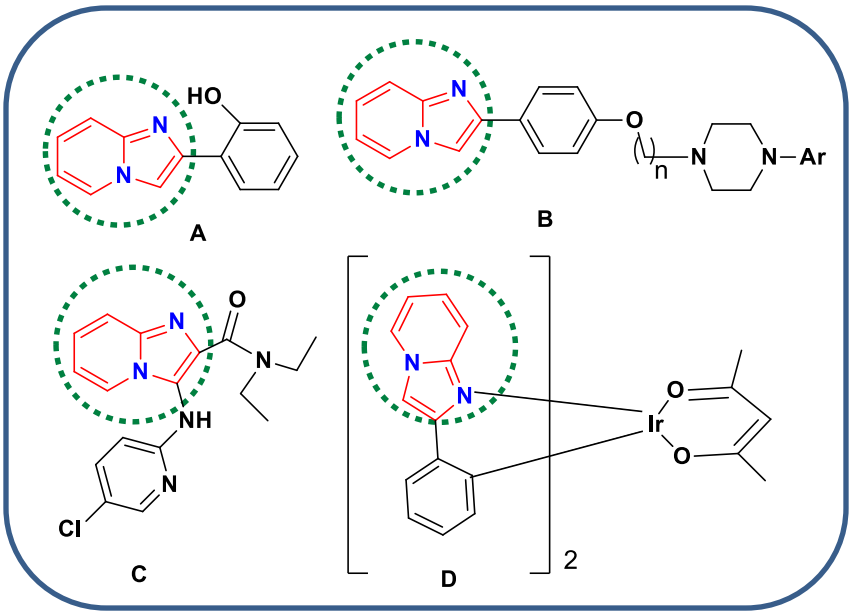


Figure 1.10: Material science application of imidazo[1,2-a]pyridine.

Due to its wide applicability in different branches of chemistry, it is desirable to synthesize this moiety from the readily available chemicals. Efforts have been focused to improve diverse synthetic approaches for the synthesis of imidazo[1,2-a]pyridines and numerous methods have been established. There are lots of methods described in literature for the synthesis of imidazo[1,2-a]pyridines and these methods can be categorized into multicomponent, tandem reaction, aminooxygenation, hydroamination, oxidative coupling

and condensation reaction. Different synthetic strategies of imidazo[1,2-a]pyridines by using various type of starting material is shown in **Figure 1.11**.

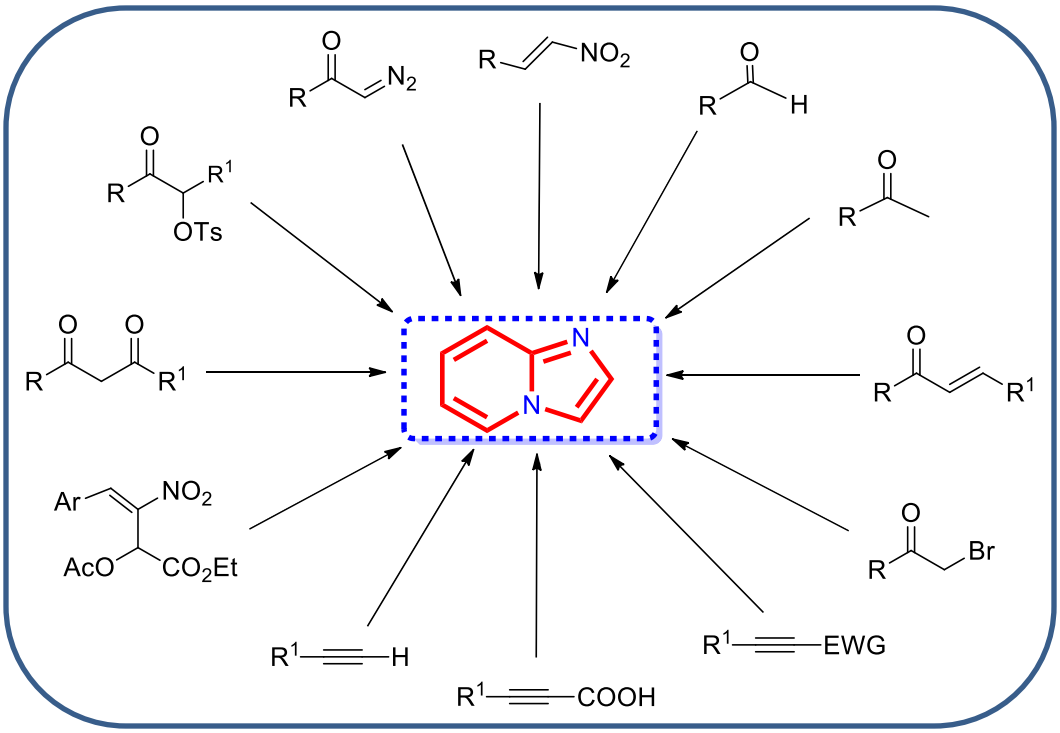
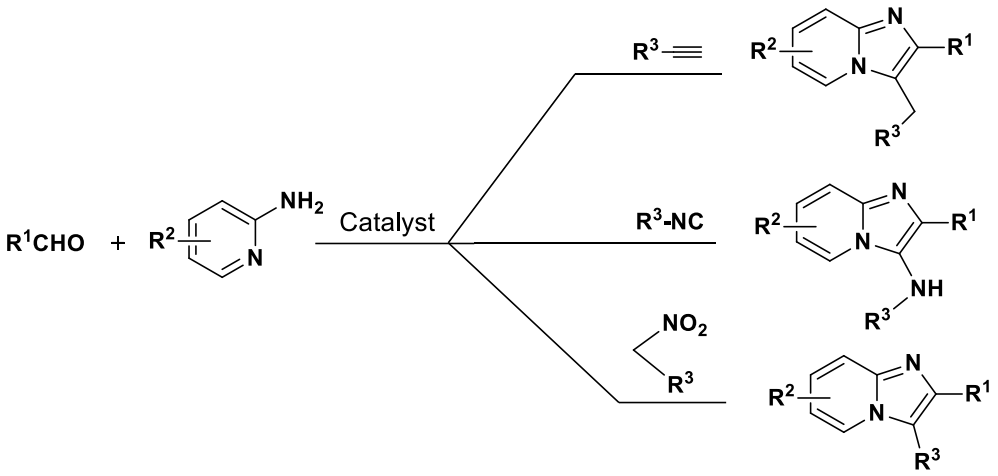


Figure 1.11: Synthesis of imidazo[1,2-a]pyridines by various starting material.

1.3.1 Multicomponent Approach

Imidazo[1,2-a]pyridines have been synthesized by the multicomponent approach through the reaction of 2-aminopyridine, aldehyde and cyanide or isocynide in the presence of various catalysts: scandium triflate (Schwerkoske et al. 2005), copper-catalyzed (Chernyak et al. 2010), K_2CO_3 (Adib et al. 2011), bromodimethylsulfonium bromide

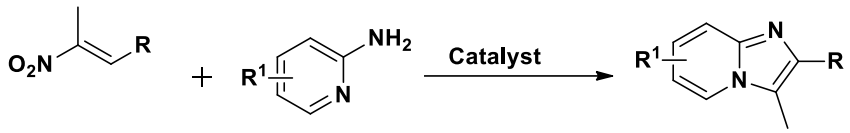
(BDMS) (Khan et al. 2012). Imidazo[1,2-a]pyridines were also achieved by the reaction of 2-aminopyridine, aldehyde and terminal alkyne catalyzed by $Cu(OTf)_3$ (Chernyak et al. 2010), $CuSO_4$ (Liu et al. 2010), nano-Fe_3O_4–$KHSO_4 \cdot SiO_2$ (Guntreddi et al. 2012) and from the reaction of 2-aminopyridine, aldehyde and nitro methane (Yan et al. 2014) (**Scheme 1.9)**.



Scheme 1.9: Synthesis of imidazo[1,2-a]pyridines by multicomponent approach.

1.3.2 Tandem Reaction

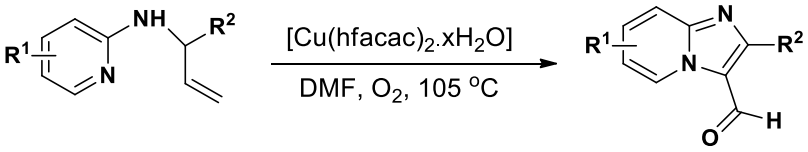
Imidazo[1,2-a]pyridines were synthesized by Tandem reaction of 2-aminopyridine with nitroalkenes in the presence of different catalyst such as iron (II) (Yan et al. 2012), iron (III) (Santra et al. 2013) (**Scheme 1.10)**.



Scheme 1.10: Synthesis of imidazo[1,2-a]pyridines by Tandem reaction.

1.3.3 Aminooxygenation

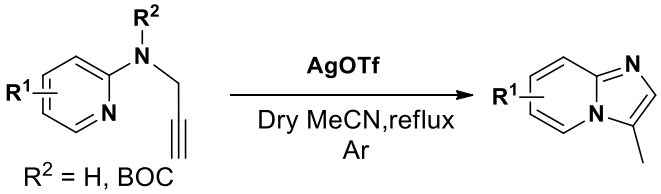
Imidazo[1,2-a]pyridines were also synthesized by copper-catalyzed intramolecular dehydrogenative aminooxygenation (Wang et al. 2011) (**Scheme 1.11)**.



Scheme 1.11: Synthesis of imidazo[1,2-a]pyridines by Aminooxygenation.

1.3.4 Hydroamination

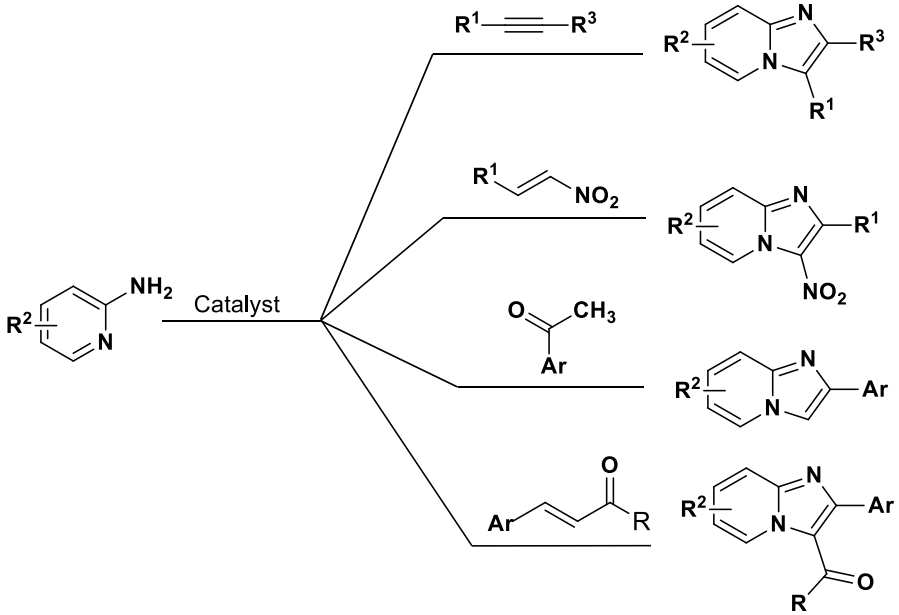
Chioua developed a method for the synthesis of 3-methylimidazo[1,2-a]pyridines through Ag-catalyzed cyclization of the N-(prop-2-yn-1-yl)pyridine-2-amines (Chioua et al. 2012) **(Scheme 1.12)**.



Scheme 1.12: Synthesis of imidazo[1,2-a]pyridines by Hydroamination.

1.3.5 Oxidative Coupling

Imidazo[1,2-a]pyridines were also synthesized by oxidative coupling of 2-aminopyridine with various substrates like alkynes (Zeng et al. 2012, He et al. 2012, Gao et al. 2013), nitroolefines (Yan et al. 2012), aryl methyl ketones (Chandra et al. 3013, Pericherla et al. 2013, Meng et al 2018), chalcones (Monir et al. 2014) etc. using different metal catalyst **(Scheme 1.13)**.

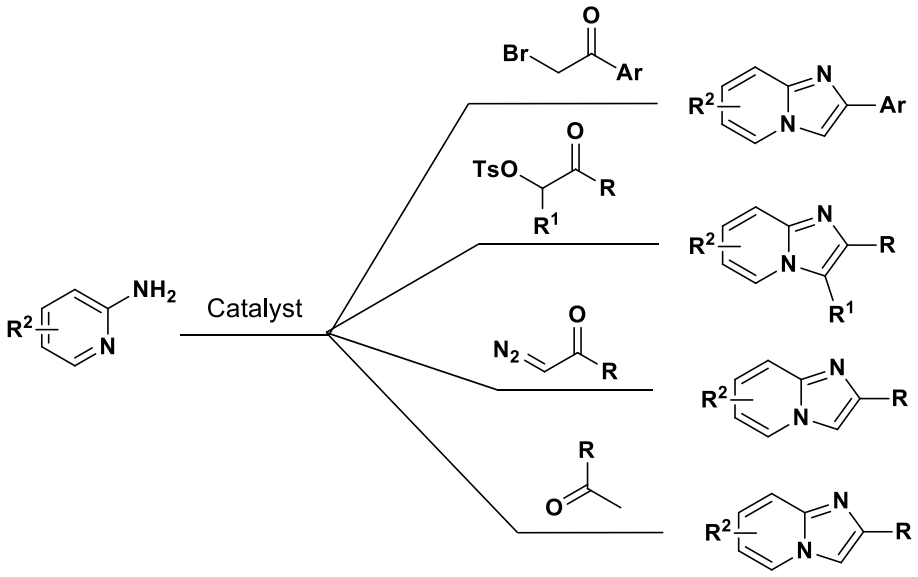


Scheme 1.13: Synthesis of imidazo[1,2-a]pyridines by oxidative coupling.

1.3.6 Condensation Reaction

Imidazo[1,2-a]pyridines were synthesized by the condensation of α-haloketones and 2-aminopyridines in the presence of different catalysts like neutral Al_2O_3 (Ponnala et al. 2005), $NaHCO_3$ (Hiebe et al. 2014), MgO (Patil et al. 2016), $NaHCO_3$ in eucalyptol

(Campos et al. 2019) and also in catalyst free condition (Burkholder et al. 2001, Zhu et al. 2009, Kong et al. 2016). Imidazo[1,2-a]pyridines were also synthesized by the reaction of 2-aminopyridine with different substrate such as α-tosyloxyketones catalyzed by $BPyBF_4$, Na_2CO_3 (Xie et al. 2002), α-diazoketones catalyzed by Cu (Yadav et al. 2007), methyl aryl ketones in the presence of different catalysts such as iodobenzene (Chang et al. 2010), I_2/NaOH (Stasyuk et al. 2012), graphene oxide (GO)/NaI (Kundu et al. 2015), iodine-ammonium acetate (Kour et al. 2016), NBS (Bhagat et al. 2017), I_2 in cyclohexane (Ghosh et al. 2018), HI (Feng et al. 2019), $FeCl_3/I_2$ (Ujwaldev et al. 2019) etc. (**Scheme 1.14**).



Scheme 1.14: Synthesis of imidazo[1,2-a]pyridines by condensation reaction.

1.4 4*H*-pyran

4*H*-pyran is oxygen containing heterocyclic compound which displays significant biological and pharmacological activities and also constitute a structural unit of a series of natural products. A number of 2-amino-4*H*-pyrans played imperative role in the discipline of drugs, photoactive materials, agrochemicals, cosmetics and pigment industries shown in Figure 1.12 (Fotouhi et al. 2007).

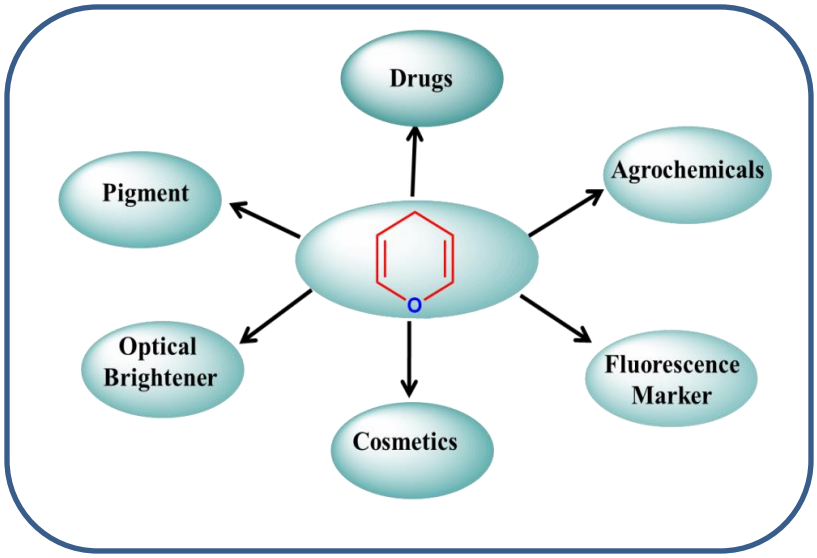


Figure 1.12: Applications of 4*H* -pyrans in different fields.

4*H*-pyrans are ubiquitous structural moiety in bioactive molecules due to their good biocompatibility. Mainly cyano functionality in 2-amino-4*H*-pyrans derivatives has an impending utility in the treatment of various diseases like cancer, rheumatoid, psoriasis (Azath et al. 2012) and also in the treatment of various neurodegenerative disease such as

alzheimer's disease, AIDS-associated dementia and down syndrome also for the treatment of schizophrenia and huntington's diseases (Thanaraj et al. 2019) (**Figure 1.13**).

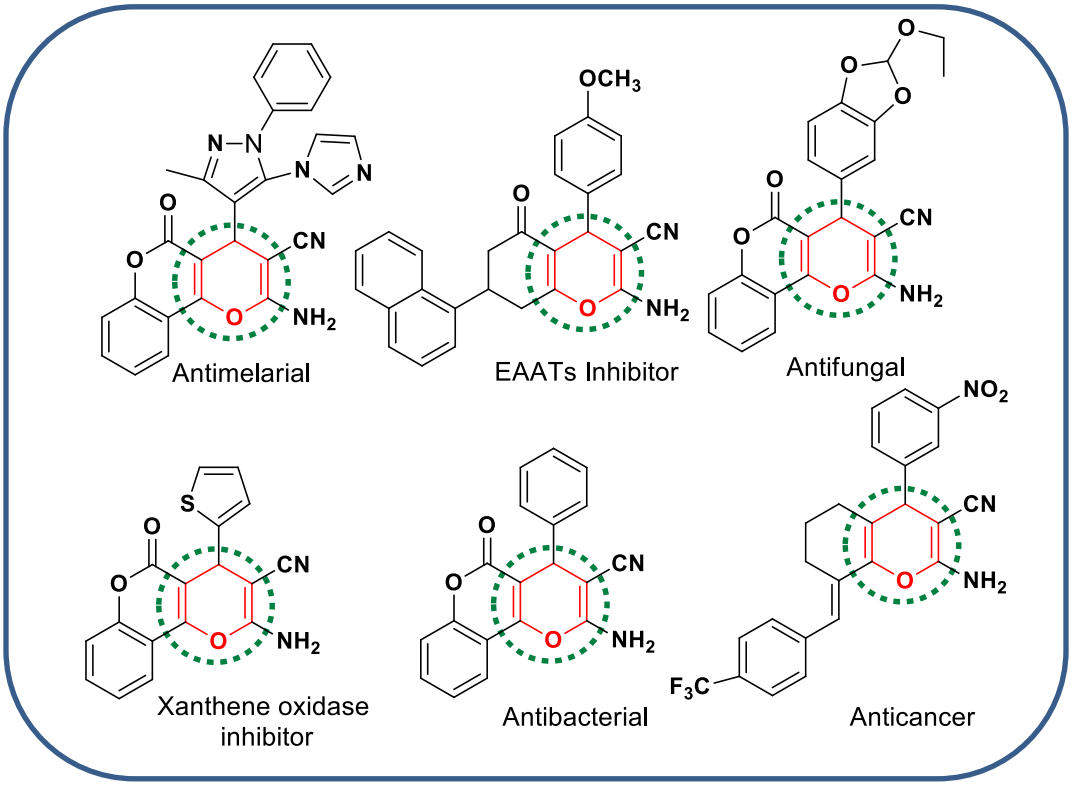
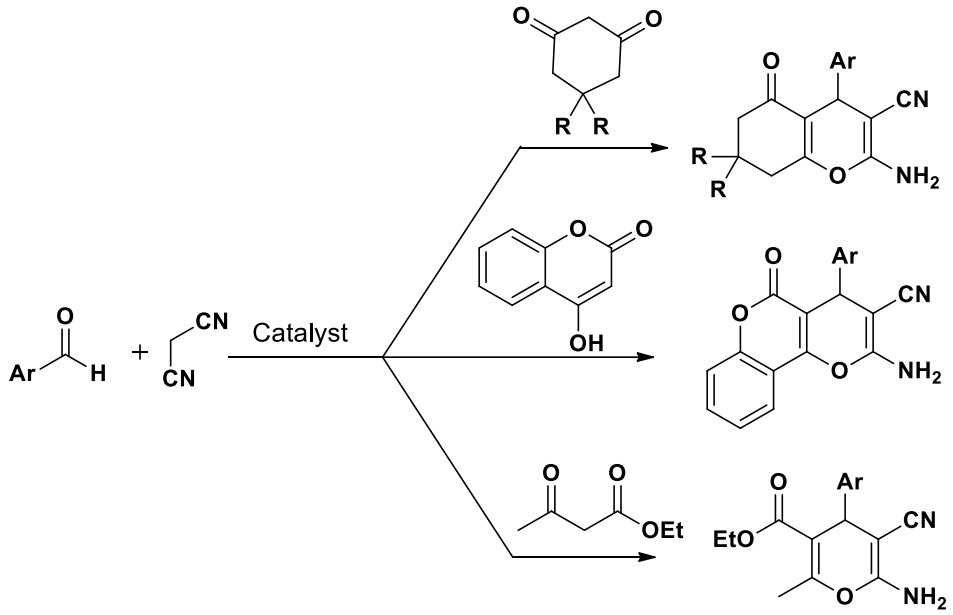


Figure 1.13: Drugs containing 4*H*-pyran moiety.

Considering the importance of these compounds, many methods have been reported for the synthesis of tetrahydro-4*H*-benzo[b]pyran derivatives. Out of the several approaches for the synthesis of 2-amino-4*H*-pyran, multicomponent reaction (MCR) is the most useful and preferred method for the construction of these heterocyclic compounds. The best protocol to synthesize 4*H*-pyrans is the Knoevenagel condensation-Michael cyclization

reaction by using aldehyde, carbonitrile and 1,3-dicarbonyl compound by one-pot multicomponent reaction.

Synthesis of 4*H*-pyran can be achieved by the reaction of benzaldehyde, malononitrile with different 1,3-dicarbonyl compounds in the presence of different catalyst such as triethyl amine (Elnagdi et al. 1989), ammonium acetate (Tu et al. 2002), KF-Al_2O_3 (Wang et al. 2003), S-proline (Balalaie et al. 2006), electrogenated base (Fotouhi et al. 2007), tetrabutylammonium bromide (Gurumurthi et al. 2009), per-6-amino-β-cyclodextrin (Azath et al. 2012), potassium tertiary butoxide (Rao et al. 2018), $TiO_2/H_{14}[NaP_5W_{30}O_{110}]$ (Azarifar et al. 2014), AuNPs@RGO-SH (Naeimi et al. 2017), $NiFe_2O_4$ nanoparticle-supported (Maleki et al. 2016), [pyridine-SO_3H]Cl (Sonyanaik et al. 2018),



Scheme 1.15: Common acid base catalyzed synthesis of 4*H*-pyran.

CuO-CNs (Thanaraj 2019), Cu@MNPs (Wanzheng et al. 2019). 4-*H* pyran can also be synthesized under catalyst free condition (Bandgar et al. 2007, Ponpandian et al. 2014, Elinson et al. 2015, Bakherad et al. 2019) (**Scheme 1.15**).

1.5 Objectives of Thesis Work

From this brief introduction, it is clear that heterocyclic compounds have found wide applications in various fields including organic synthesis, biochemistry, medicinal chemistry, material sciences and agriculture etc. Thus, our objective is to develop some efficient and greener methodology for synthesis of some biologically active heterocyclic compounds via conventional as well as non-conventional methods such as ultrasound, solar energy and grinding techniques 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. To investigate oxidative dimerization of primary thiobenzamides and selenamides into 1,2,4-thiadiazole and 1,2,4-selenadiazole by different methods under metal and catalyst-free condition using green oxidants TBN and Chloranil.

2. To develop a practical method for the synthesis of 3-functionalized coumarins by oxidative coupling of *o*-cresols and active methylene compounds under metal and catalyst-free condition in the presence of *tert*-butyl hydrogen peroxide (TBHP).

3. To explore a novel, facile, efficient and scalable route for the synthesis of imidazo[1,2-a]pyridines in solvent free conditions under grinding at room temperature using KI/TBHP.

4. To demonstrate a solar energy mediated environmentally benign, simple and efficient method for one pot multicomponent synthesis of tetrahydrobenzo[b]pyran using L-Ascorbic acid as a green biodegradable catalyst.

1.6 References

Adib, M., E. Sheikhi and N. Rezaei, "One-pot synthesis of imidazo[1,2-a]pyridines from benzyl halides or benzyl tosylates, 2-aminopyridines and isocyanides," *Tetrahedron letters*, **52**(25) (2011) 3191-3194.

Augustine, J. K., A. Bombrun, B. Ramappa and C. Boodappa, "An efficient one-pot synthesis of coumarins mediated by propylphosphonic anhydride (T3P) via the Perkin condensation,"*Tetrahedron Letters*, **53**(33) (2012) 4422-4425.

Azarifar, D., S.-M. Khatami and R. N.-Yami, "Nano-titania-supported Preyssler-type heteropolyacid: An efficient and reusable catalyst in ultrasound-promoted synthesis of 4*H*-chromenes and 4*H*-pyrano[2,3-c]pyrazoles," *Journal of Chemical Sciences*, **126**(1) (2014) 95-101.

Azath, I. A., P. Puthiaraj and K. Pitchumani, "One-pot multicomponent solvent-free synthesis of 2-amino-4 H-benzo[b]pyrans catalyzed by per-6-amino-β-cyclodextrin," *ACS Sustainable Chemistry & Engineering*, **1**(1) (2012) 174-179.

Bagdi, A. K., S. Santra, K. Monir and A. Hajra, "Synthesis of imidazo [1,2-a] pyridines: a decade update," *Chemical Communications*, **51**(9) (2015) 1555-1575.

Bakherad, M., F. Moosavi, A. Keivanloo, R. Doosti, E. Moradian and M. Armaghan, "Catalyst-free green synthesis of tetrahydro-benzo[b]pyrans in magnetized water: experimental aspects and molecular dynamics simulation," *Research on Chemical Intermediates*, **45**(5)(2019) 2981-2997.

Balalaie, S., M. Bararjanian, A. M. Amani and B. Movassagh, "(S)-Proline as a neutral and efficient catalyst for the one-pot synthesis of tetrahydrobenzo[b]pyran derivatives in aqueous media," S*ynlett*, **2006**(02) (2006) 263-266.

Bandgar, S. B., B. P. Bandgar, B. L. Korbad, J. V. Totre and S. Patil, "Uncatalyzed reactions in aqueous media: Three-component, one-pot, clean synthesis of tetrahydrobenzo [b]pyran derivatives," *Australian journal of chemistry*, **60**(4) (2007) 305-307.

Belavagi, N. S., N. Deshapande, M. G. Sunagar and I. A. M. Khazi, "A practical one-pot synthesis of coumarins in aqueous sodium bicarbonate via intramolecular Wittig reaction at room temperature," *RSC Advances*, **4**(75) (2014) 39667-39671.

Bhagat, S. B. and V. N. Telvekar, "NBS mediated protocol for the synthesis of N-bridged fused heterocycles in water," *Tetrahedron Letters*, **58**(37) (2017) 3662-3666.

Boeini, H. Z. and M. Mobin, "An Unexpected Result of the Reaction of Benzothioamide Derivatives with 2-Aryl-2-bromoacetonitriles," *Helvetica Chimica Acta*, **94**(11) (2011) 2039-2044.

Bongartz, J.-P., R. Stokbroekx, M. V. Aa, M. Luyckx, M. Willems, M. Ceusters and L. Meerpoel, "Synthesis and anti-angiogenic activity of 6-(1, 2, 4-thiadiazol-5-yl)-3-amino pyridazine derivatives," *Bioorganic & medicinal chemistry letters*, **12**(4) (2002) 589-591.

Bonsignore, L., F. Cottiglia, A. M. Maccioni, D. Secci and S. M. Lavagna, "Synthesis of coumarin-3-O-acylisoureas by dicyclohexylcarbodiimide," *Journal of heterocyclic chemistry*, **32**(2) (1995) 573-577.

Bose, D. S., A. P. Rudradas and M. H. Babu, "The indium(III)chloride-catalyzed von Pechmann reaction: a simple and effective procedure for the synthesis of 4-substituted coumarins,"*Tetrahedron letters*, **43**(50) (2002) 9195-9197.

Bose, S. D. and K. R. Reddy, "A Simple and Convenient Method for the Synthesis of 3,5-disubstituted-1,2,4-thiadiazoles via Oxidative Dimerization of Primary Thioamides," *Journal of Heterocyclic Chemistry*, **54**(1) (2017) 769-774.

Brahmachari, G., "Room temperature one-pot green synthesis of coumarin-3-carboxylic acids in water: a practical method for the large-scale synthesis," *ACS Sustainable Chemistry & Engineering*, **3**(9) (2015) 2350-2358.

Burkholder, C., W. R. D. Jr, M. Medebielle and S. A.-Mohand, "Synthesis and electron-transfer reactions of some 3-difluoroacetylated imidazo[1,2-a]pyridine derivatives," *Tetrahedron Letters*, **42**(17) (2001) 3077-3080.

Campos, J. F., M.-C. Scherrmann and S. B. Raboin, "Eucalyptol: a new solvent for the synthesis of heterocycles containing oxygen, sulfur and nitrogen," *Green chemistry*, **21**(6) (2019) 1531-1539.

Chandra, M., D. Ramachandra R. Donthiri, S. N. Rao and S. Adimurthy, "Copper (I) Iodide-Catalyzed Aerobic Oxidative Synthesis of Imidazo[1,2-a]pyridines from 2-Aminopyridines and Methyl Ketones," *Advanced Synthesis & Catalysis*, **355**(11-12) (2013) 2217-2221.

Chang, Y.-L., H.-M. Wang, R.-S. Hou, I.-J. Kang and L.-C. Chen, "Iodobenzene-Catalyzed Synthesis of Imidazo[1,2-a]pyridines from Aryl Ketones with mCPBA in Ionic Liquid," *Journal of the Chinese Chemical Society*, **57**(2) (2010) 153-156.

Cheng, D., R. Luo, W. Zheng and J. Yan, "Highly Efficient Oxidative Dimerization of Thioamides to 3,5-Disubstituted-1,2,4-Thiadiazoles Mediated by DDQ," *Synthetic Communications*, **42**(13) (2012) 2007-2013.

Chernyak, N. and V. Gevorgyan, "General and efficient copper-catalyzed three-component coupling reaction towards imidazoheterocycles: one-pot synthesis of alpidem and zolpidem," *Angewandte Chemie International Edition*, **49**(15) (2010) 2743-2746.

Chioua, M., E. Soriano, L. Infantes, M. L. Jimeno, J. M. Contelles and A. Samadi, "Silver-Catalyzed Cyclization of N-(Prop-2-yn-1-yl)pyridin-2-amines," *European Journal of Organic Chemistry*, **2013**(1) (2013) 35-39.

Cronyn, M. W. and T. W. Nakagawa, "The reaction of nitrous acid with thiobenzamides," *Journal of the American Chemical Society*, 74(14) (1952) 3693-3693.

Dabiri, M., M. Baghbanzadeh, S. Kiani and Y. Vakilzadeh, "Alum ($KAl(SO_4)_2 \cdot 12H_2O$) Catalyzed One-Pot Synthesis of Coumarins under Solvent-Free Conditions," *Monatshefte für Chemie-Chemical Monthly*, **138**(10) (2007) 997-999.

Dinparast, L., S. Hemmati, G. Zengin, A. A. Alizadeh, M. B. Bahadori, H. S. Kafil and S. Dastmalchi, "Rapid, Efficient, and Green Synthesis of Coumarin Derivatives via Knoevenagel Condensation and Investigating Their Biological Effects," *ChemistrySelect*, **4**(31) (2019) 9211-9215.

Donkor, I. O., "A survey of calpain inhibitors," *Current medicinal chemistry*, **7**(12) (2000) 1171-1188.

Douhal, A., F. A.-Guerri and A. U. Acuña, "Probing Nanocavities with Proton-Transfer Fluorescence," *Angewandte Chemie International*, **36**(13-14) (1997) 1514-1516.

Elinson, M. N., F. V. Ryzhkov, T. A. Zaimovskaya and M. P. Egorov, "Non-catalytic solvent-free synthesis of 5,6,7,8-tetrahydro-4*H*-chromenes from aldehydes, dimedone and malononitrlie at ambient temperature," *Mendeleev Communications*, **25**(3) (2015) 185-187.

Elnagdi, M. H., F. A. Maksoud, A. Aal and Y. M. Yassin, "Synthesis of Condensed 4*H*-Pyrans: The reaction of 1,1-dimethyl-3,5-diketocyclohexane with cinnamonitriles," *Journal für Praktische Chemie*, **331**(6) (1989) 971-976.

Feng, M. -L., S.-Qi Li, H.-Z. He, L.-Y. Xi, S.-Y. Chen and X.-Qi Yu, "Electrochemically initiated intermolecular C–N formation/cyclization of ketones with 2-aminopyridines: an efficient method for the synthesis of imidazo[1,2-a]pyridines," *Green chemistry*, **21**(7) (2019) 1619-1624.

Fiorito, S., V. A. Taddeo, S. Genovese and F. Epifano, "A green chemical synthesis of coumarin-3-carboxylic and cinnamic acids using crop-derived products and waste waters as solvents," *Tetrahedron Letters*, **57**(43) (2016) 4795-4798.

Fotouhi, L., M. M. Heravi, A. Fatehi and K. Bakhtiari, "Electrogenerated base-promoted synthesis of tetrahydrobenzo[b]pyran derivatives," *Tetrahedron letters*, **48**(31) (2007) 5379-5381.

Fukumoto, T., T. Matsuki, N. X. Hu, Y. Aso, T. Otsubo and F. Ogura, "Organotelluriums Part XXIII. Benzenetellurinic mixed anhydrides as mild oxidizing agents," *Chemistry Letters*, **12** (1990) 2269-2272.

Gao, Y., M. Yin, W. Wu, H. Huang and H. Jiang, "Copper-Catalyzed Intermolecular Oxidative Cyclization of Halo-alkynes: Synthesis of 2-Halo-substituted Imidazo[1,2-a] pyridines, Imidazo[1,2-a]pyrazines and Imidazo[1,2-a]pyrimidines," *Advanced Synthesis & Catalysis*, **355**(11-12) (2013) 2263-2273.

Ghomi, J. S. and Z. Akbarzadeh, "Ultrasonic accelerated Knoevenagel condensation by magnetically recoverable $MgFe_2O_4$ nanocatalyst: A rapid and green synthesis of coumarins under solvent-free conditions," *Ultrasonics sonochemistry*, **40** (2018) 78-83.

Ghosh, P., B. Ganguly, B. Kar, S. Dwivedi and S. Das, "Green procedure for highly efficient, rapid synthesis of imidazo[1,2-a]pyridine and its late stage functionalization," *Synthetic Communications*, **48**(9) (2018) 1076-1084.

Gleye, C., G. Lewin, A. Laurens, J.-C. Jullian, P. Loiseau, C. Bories and R. Hocquemiller, "Acaricidal activity of tonka bean extracts synthesis and structure activity relationships of bioactive derivatives," *Journal of natural products*, **66**(5) (2003) 690-692.

Goblyos, A., H. D. Vries, J. Brussee and A. P. IJzerman, "Synthesis and biological evaluation of a new series of 2,3,5-substituted[1,2,4]-thiadiazoles as modulators of adenosine A1 receptors and their molecular mechanism of action," *Journal of medicinal chemistry*, **48**(4) (2005) 1145-1151.

Gopalakrishnan, S., K. R. Viswanathan, S. V. Priya, J. H. Mabel, M. Palanichamy and V. Murugesan, "Lewis acid metal ion-exchanged MAPO-5 molecular sieves for solvent free synthesis of coumarin derivative," *Catalysis Communications*, **10**(1) (2008) 23-28.

Guntreddi, T., B. K. Allam and K. N. Singh, "Simple and efficient one-pot synthesis of imidazo[1,2-a]pyridines catalyzed by magnetic nano-Fe_3O_4–$KHSO_4$· SiO_2," *Synlett*, **23** (18) (2012) 2635-2638.

Gurjar, A. S., V. Andrisano, A. D. Simone and V. S. Velingkar, "Design, synthesis, in silico and in vitro screening of 1,2,4-thiadiazole analogues as non-peptide inhibitors of beta-secretase," *Bioorganic chemistry*, **57**(2014) 90-98.

Gurumurthi, S., V. Sundari and R. Valliappan, "An efficient and convenient approach to synthesis of tetrahydrobenzo[b]pyran derivatives using tetrabutylammonium bromide as catalyst," *Journal of Chemistry*, **6**(S1) (2009) S466-S472.

Hartmann, M., U. K. M. Decking and J. Schrader, "Cardioprotective actions of KC 12291 II. Delaying Na+ overload in ischemia improves cardiac function and energy status in reperfusion," *Naunyn-Schmiedeberg's archives of pharmacology*, **358**(5) (1998) 554-560.

He, C., J. Hao, H. Xu, Y. Mo, H. Liu, J. Han and A. Lei, "Heteroaromatic imidazo[1,2-a] pyridines synthesis from C–H/N–H oxidative cross-coupling/cyclization," *Chemical Communications*, **48**(90) (2012) 11073-11075.

Hiebel, M.-A., Y. Fall, M.-C. Scherrmann and S. Berteina-Raboin, "Straightforward Synthesis of Various 2, 3-Diarylimidazo[1,2-a]pyridines in PEG 400 Medium through One-Pot Condensation and C–H Arylation," *European Journal of Organic Chemistry*, **2014**(21) (2014) 4643-4650

Iizawa, Y., K. Okonogi, R. Hayashi, T. Iwahi, T. Yamazaki and A. Imada, "Therapeutic effect of cefozopran (SCE-2787), a new parenteral cephalosporin, against experimental infections in mice," *Antimicrobial agents and chemotherapy*, **37**(1) (1993) 100-105.

Ju, Y. and R. S. Varma, "Aqueous N-heterocyclization of primary amines and hydrazines with dihalides: microwave-assisted syntheses of N-azacycloalkanes, isoindole, pyrazole, pyrazolidine and phthalazine derivatives," *The Journal of organic chemistry*, **71**(1) (2006) 135-141.

Kaye, P. T., M. A. Musa and X. W. Nocanda, "Efficient and chemoselective access to 3-(chloromethyl)coumarins via direct cyclisation of unprotected Baylis-Hillman adducts," *Synthesis*, **2003**(04) (2003) 0531-0534.

Keri, R. S., K. M. Hosamani and H. R. S. Reddy, "A solvent-free synthesis of coumarins using Phosphotungstic acid as catalyst," *Catalysis letters*, **131**(1-2) (2009) 321-327.

Khaligh, N. G. and F. Shirini, "Introduction of poly(4-vinylpyridinium)perchlorate as a new, efficient, and versatile solid acid catalyst for one-pot synthesis of substituted coumarins under ultrasonic irradiation,"*Ultrasonics sonochemistry*, **20**(1) (2013) 26-31.

Khaligh, N. G., "Synthesis of coumarins via Pechmann reaction catalyzed by 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate as an efficient, halogen-free and reusable acidic ionic liquid,"*Catalysis Science & Technology*, **2**(8) (2012) 1633-1636.

Khan, A. T., R. S. Basha and M. Lal, "Bromodimethylsulfonium bromide (BDMS) catalyzed synthesis of imidazo[1,2-a]pyridine derivatives and their fluorescence properties," *Tetrahedron Letters*, **53**(17) (2012) 2211-2217.

Khan, D., S. Mukhtar, M. A. Alsharif, M. I. Alahmdi and N. Ahmed, "$PhI(OAc)_2$ mediated an efficient Knoevenagel reaction and their synthetic application for coumarin derivatives," *Tetrahedron Letters*, **58**(32) (2017) 3183-3187.

Khan, S. A., S. B. Khan, A. M. Asiri and I. Ahmad, "Zirconia-based catalyst for the one-pot synthesis of coumarin through Pechmann reaction," *Nanoscale research letters*, **11**(1) (2016) 345.

Khosropour, A. R. and J. Noei, "TCT-DMSO/[bmim]BF_4: A novel promoter system for the synthesis of 3,5-diaryl-1,2,4-thiadiazoles at ambient temperature," *Journal of Heterocyclic Chemistry*, **48**(1) (2011) 226-229.

Kim, H.-Y., S. H. Kwak, G.-H. Lee and Y.-D. Gong, "Copper-catalyzed synthesis of 3-substituted-5-amino-1,2,4-thiadiazoles via intramolecular N–S bond formation," *Tetrahedron*, **70** (45) (2014) 8737-8743**.**

Kong, D., X. Wang, Z. Shi, M. Wu, Q. Lin and X. Wang, "Solvent-and catalyst-free synthesis of imidazo[1,2-a]pyridines under microwave irradiation," *Journal of Chemical Research*, **40**(9) (2016) 529-531.

Kour, D., R. Khajuria and K. K. Kapoor, "Iodine–ammonium acetate promoted reaction between 2-aminopyridine and aryl methyl ketones: a novel approach towards the synthesis of 2-arylimidazo[1,2-a]pyridines," *Tetrahedron Letters*, **57**(40) (2016) 4464-4467.

Kundu, S. and B. Basu, "Graphene oxide (GO)-catalyzed multi-component reactions: green synthesis of library of pharmacophore 3-sulfenylimidazo[1,2-a]pyridines," *RSC Advances*, **5**(62) (2015) 50178-50185.

Leopoldo, M., E. Lacivita, E. Passafiume, M. Contino, N. A. Colabufo, F. Berardi and R. Perrone,"4-[ω-[4-Arylpiperazin-1-yl] alkoxy] phenyl)imidazo[1,2-a]pyridine derivatives: fluorescent high-affinity dopamine D3 receptor ligands as potential probes for receptor visualization," *Journal of medicinal chemistry*, **50**(20) (2007) 5043-5047.

Leung-Toung, R., T. F. Tam, Y. Zhao, C. D. Simpson, W. Li, D. Desilets and K. Karimian, "Synthesis of 3-Substituted Bicyclic Imidazo[1,2-d][1,2,4]thiadiazoles and Tricyclic Benzo [4,5] imidazo[1,2-d][1,2,4]thiadiazoles," *The Journal of organic chemistry*, **70** (16) (2005) 6230-6241.

Li, D., Y. Huang and J. Su, "Dyeing behaviours of amino heterocyclic compounds as blue oxidative hair dye precursors applied to keratin fibres," *International journal of cosmetic science*, **33**(2) (2011) 183-189.

Liu, P., L.-S. Fang, X. Lei and G.-Q. Lin, "Synthesis of imidazo[1,2-a]pyridines via three-component reaction of 2-aminopyridines, aldehydes and alkynes," *Tetrahedron Letters*, **51** (35) (2010) 4605-4608.

Maleki, B., M. Baghayeri, S. A. J. Abadi, R. Tayebee and A. Khojastehnezhad, "Ultrasound promoted facile one pot synthesis of highly substituted pyran derivatives catalyzed by silica-coated magnetic $NiFe_2O_4$ nanoparticle-supported $H_{14}[NaP_5W_{30}O_{11}0]$ under mild conditions," *RSC Advances*, **6**(99) (2016) 96644-96661.

Mariappan, A., K. Rajaguru, N. M. Chola, S. Muthusubramanian and N. Bhuvanesh, "Hypervalent Iodine (III) Mediated Synthesis of 3-Substituted 5-Amino-1, 2, 4-thiadiazoles through Intramolecular Oxidative S–N Bond Formation," *The Journal of organic chemistry*, **81**(15) (2016) 6573-6579.

Martins, M. A. P, W. Cunico, C. M. P. Pereira, A. P. Sinhorin, A. F. C. Flores, H. G. Bonacorso and N. Zanatta, "4-Alkoxy-1,1,1-trichloro-3-alken-2-ones: preparation and applications in heterocyclic synthesis," *Current Organic Synthesis*, **1**(4) (2004) 391-403.

Meng, X., Y. Wang, C. Yu and P. Zhao, "Heterogeneously copper-catalyzed oxidative synthesis of imidazo[1,2-a]pyridines using 2-aminopyridines and ketones under ligand-and additive-free conditions," *RSC advances*, **4**(52) (2014) 27301-27307.

Mirosanloo, A., D. Zareyee and M. A. Khalilzadeh, "Recyclable cellulose nanocrystal supported Palladium nanoparticles as an efficient heterogeneous catalyst for the solvent-free synthesis of coumarin derivatives via von Pechmann condensation," *Applied Organometallic Chemistry*, **32**(12) (2018) 4546.

Monir, K., A. K. Bagdi, S. Mishra, A. Majee and A. Hajra, "Copper (II)-Catalyzed Aerobic Oxidative Coupling between Chalcone and 2-Aminopyridine via C-H Amination: An Expedient Synthesis of 3-Aroylimidazo[1,2-a]pyridines," *Advanced Synthesis & Catalysis*, **356**(5) (2014) 1105-1112.

Moradi, L. and F. Belali,"Solvent-free one-pot synthesis of coumarins using molybdate sulfuric acid as highly efficient catalyst," *Journal of the Iranian Chemical Society*, **12**(11) (2015) 1927-1934.

Murray, R. D. H., "Naturally occurring plant coumarins," In Fortschritte der Chemie organischer Naturstoffe/Progress in the Chemistry of Organic Natural Products," (1991) 83-316.

Naeimi, H. and M. F. Zarabi,"Gold nanoparticles supported on thiol-functionalized reduced graphene oxide as effective recyclable catalyst for synthesis of tetrahydro-4*H*-chromenes in aqueous media,"*Applied Organometallic Chemistry*, **32**(4) (2018) 4225.

Nagaraj, A. and C. S. Reddy, "Synthesis and biological study of novel bis-chalcones, bis-thiazines and bis-pyrimidine," *Journal of the iranian chemical society*, **5**(2) (2008) 262-267.

Pechmann, H. V., "New Formation of Coumarins. Synthesis of Daphnetin. I," *Reports of the German Chemical Society*, **17**(1) (1884) 929-936.

Patil, S. V., N. D. Gaikwad and V. D. Bobade, "A simple and efficient synthesis of imidazolo[1,2-a]pyridines using MgO in aqueous medium," *Arabian Journal of Chemistry*, **9** (2016) S1649-S1653.

Patre, R. E., J. B. Shet, P. S. Parameswaran and S. G. Tilve, "Cascade Wittig reaction-double Claisen and Cope rearrangements: one-pot synthesis of diprenylated coumarins gravelliferone, balsamiferone, and 6,8-diprenylumbelliferone," *Tetrahedron Letters*, **50** (47) (2009) 6488-6490.

Pericherla, K., P. Kaswan, P. Khedar, B. Khungar, K. Parang and A. Kumar, "Copper catalyzed tandem oxidative C–H amination/cyclizations: Direct access to imidazo[1,2-a] pyridines," *RSC Advances*, **3**(41) (2013) 18923-18930.

Ponnala, S., S. T. V. S. K. Kumar, B. A. Bhat and D. P. Sahu, "Synthesis of bridgehead nitrogen heterocycles on a solid surface," *Synthetic communications*, **35**(7) (2005) 901-906

Ponpandian, T. and S. Muthusubramanian, "One-pot, catalyst-free synthesis of spirooxindole and 4*H*-pyran derivatives,"*Synthetic Communications*, **44**(6) (2014) 868-874.

Putta, V. P. R. K., R. Gujjarappa, N. Vodnala, R. Gupta, P. P. Pujar and C. C. Malakar, "The facile and efficient organocatalytic platform for accessing 1,2,4-selenadiazoles and thiadiazoles under aerobic conditions," *Tetrahedron Letters*, **59**(10) (2018) 904-908.

Qurban, J., M. Elsherbini, H. Alharbi and T. Wirth, "Synthesis, characterisation, and reactivity of novel pseudocyclic hypervalent iodine reagents with heteroaryl carbonyl substituents," *Chemical Communications*, **55**(55) (2019) 7998-8000.

Ranu, B. C. and R. Jana, "Ionic Liquid as Catalyst and Reaction Medium–A Simple, Efficient and Green Procedure for Knoevenagel Condensation of Aliphatic and Aromatic Carbonyl Compounds Using a Task-Specific Basic Ionic Liquid," *European journal of organic chemistry*, **2006**(16) (2006) 3767-3770.

Rao, N. K., T. N. Rao, B. Parvatamma, K. P. Devi and S. C. Setty, "Multi component one pot synthesis and characterization of derivatives of 2-amino-7, 7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile and study of anti-microbial activity," *Bulletin of the Chemical Society of Ethiopia*, **32**(1) (2018) 133-138.

Reddy, Y. T., V. N. Sonar, P. A. Crooks, P. K. Dasari, P. N. Reddy and B. Rajitha, "Ceric ammonium nitrate (CAN): An efficient catalyst for the coumarin synthesis via Pechmann condensation using conventional heating and microwave irradiation," *Synthetic Communications*, **38**(13) (2008) 2082-2088.

Rival, Y., G. Grassy and G. Michel, "Synthesis and antibacterial activity of some Imidazo [1,2-α]pyrimidine derivatives," *Chemical and pharmaceutical bulletin*, **40**(5) (1992) 1170-1176.

Roopan, S. M., S. M. Patil and J. Palaniraja, "Recent synthetic scenario on imidazo[1,2-a] pyridines chemical intermediate," *Research on Chemical Intermediates*, **42**(4) (2016) 2749-2790.

Santra, S., S. Mitra, A. K. Bagdi, A. Majee and A. Hajra, "Iron (III)-catalyzed three-component domino strategy for the synthesis of imidazo[1,2-a]pyridines," *Tetrahedron Letters*, **55**(37) (2014) 5151-5155.

Schwerkoske, J., T. Masquelin, T. Perun and C. Hulme, "New multi-component reaction accessing 3-aminoimidazo[1,2-a]pyridines," *Tetrahedron letters*, **46**(48) (2005) 8355-8357.

Siddiqui, N., P. Ahuja, W. Ahsan, S. N. Pandeya and M. S. Alam, "Thiadiazoles: progress report on biological activities," *Journal of Chemical and Pharmaceutical Research*, **1**(1) (2009) 19-30.

Sonyanaik, B., B. Sakram, A. Kurumanna and P. Madhu, "Green, expeditious and recyclable specific acidic ionic liquid[pyridine-SO_3H]Cl catalyzed one-pot synthesis of 2-amino-4-aryl-4H-chromene-3-carbonitrile scaffolds under microwave irradiation," *Heterocyclic letters*, **8**(2) (2018) 375-384.

Srikrishna, D., S. Tasqeeruddin and P. K. Dubey, "Synthesis of 3-substituted Coumarins: An Efficient Green Approach Using L-proline as Catalyst in Triethanolamine Medium," *Letters in Organic Chemistry*, **11**(8) (2014) 556-563.

Srivastava, V. P., A. K. Yadav and L. D. S. Yadav, "Eosin Y catalyzed visible-light-driven aerobic oxidative cyclization of thioamides to 1,2,4-thiadiazole," *Synlett*, **24**(04) (2013) 465-470.

Stasyuk, A. J., M. Banasiewicz, M. K. Cyranski and D. T. Gryko, "Imidazo[1,2-a] pyridines susceptible to excited state intramolecular proton transfer: one-pot synthesis via an Ortoleva–King reaction," *The Journal of organic chemistry*, **77**(13) (2012) 5552-5558.

Stefanachi, A., F. Leonetti, L. Pisani, M. Catto and A. Carotti, "Coumarin: A natural, privileged and versatile scaffold for bioactive compounds," *Molecules*, **23**(2) (2018) 250.

Takikawa, Y., K. Shimada, K. Sato, S. Sato and S. Takizawa, "Convenient preparations of 3,5-disubstituted 1,2,4-thiadiazoles by oxidative dimerization of thioamides," *Bulletin of the Chemical Society of Japan*, **58**(3) (1985) 995-999.

Tam, T. F., R. Leung -Toung, W. Li, M. Spino and K. Karimian, "Medicinal chemistry and properties of 1,2,4-thiadiazoles," *Mini reviews in medicinal chemistry*, **5**(4) (2005) 367-379.

Tasqeeruddin, S., A. S. A.-Arifi and P. K. Dubey, "An Efficient Solid-Phase Green Synthesis of Chromen-2-one Derivatives," *Asian Journal of Chemistry*, **25**(12) (2013).

Thanaraj, C., G. R. P. Dharsini, N. Ananthan and R. Velladurai, "Facile route for the synthesis and cytotoxic effect of 2-amino-4 H-benzo[b]pyran derivatives in aqueous media using copper oxide nanoparticles decorated on cellulose nanocrystals as heterogeneous catalyst," *Inorganic and Nano-Metal Chemistry*, **49**(9) (2019) 313-321.

Tu, S.-J., C.-B. Miao, Y. Gao, Y.-J. Feng and J.-C. Feng, "Microwave-prompted reaction of cinnamonitrile derivatives with 5, 5-dimethyl-1, 3-cyclohexanedione," *Chinese Journal of Chemistry*, **20**(7) (2002) 703-706.

Ujwaldev, S. M., K. R. Rohit, N. A. Harry and G. Anilkumar, "Novel one step synthesis of imidazo[1,2-a]pyridines and Zolimidine via iron/iodine-catalyzed Ortoleva-King type protocol," *Tetrahedron Letters*, **60**(33) (2019) 150950.

Vahabi, V. and F. Hatamjafari, "Microwave assisted convenient one-pot synthesis of coumarin derivatives via Pechmann condensation catalyzed by FeF_3 under solvent-free conditions and antimicrobial activities of the products, "*Molecules*, **19**(9) (2014) 13093-13103.

Valizadeh, H. and A. Shockravi, "An efficient procedure for the synthesis of coumarin derivatives using $TiCl_4$ as catalyst under solvent-free condition," *Tetrahedron letters*, **46** (20) (2005) 3501-3503.

Vanajatha, G. and V. P. Reddy, "High yielding protocol for oxidative dimerization of primary thioamides: a strategy toward 3,5-disubstituted-1,2,4-thiadiazoles," *Tetrahedron Letters*, **57(**22) (2016) 2356-2359.

Vekariya, R. H. and H. D. Patel, "Recent advances in the synthesis of coumarin derivatives via knoevenagel condensation: A review," *Synthetic Communications*, **44**(19) (2014) 2756-2788.

Verdía, P., F. Santamarta and E. Tojo, "Knoevenagel reaction in [MMIm][MSO4]: Synthesis of coumarins," *Molecules*, **16**(6) (2011) 4379-4388.

Wang, H., Y. Wang, D. Liang, L. Liu, J. Zhang and Q. Zhu, "Copper-Catalyzed Intramolecular Dehydrogenative Aminooxygenation: Direct Access to Formyl-Substituted Aromatic N-Heterocycles," *Angewandte Chemie International Edition*, **50**(25) (2011) 5678-5681.

Wanzheng, M. A., A. G. Ebadi, R. Javahershenas and G. Jimenez, "One-pot synthesis of 2-amino-4*H*-chromene derivatives by MNPs@Cu as an effective and reusable magnetic nanocatalyst," *RSC Advances*, **9**(23) (2019) 12801-12812.

Wu, Y.-J. and Y. Zhang, "An efficient one-pot synthesis of 3-substituted-5-amino-1,2,4-thiadiazoles from isothiocyanates and amidines," *Tetrahedron Letters*, **49**(18) (2008) 2869-2871.

Xie, Y.-Y., Z.-C. Chen and Q.-G. Zheng, "Organic reactions in ionic liquids: cyclocondensation of α-bromoketones with 2-aminopyridine," *Journal of Chemical Research*, **2003**(10) (2003) 614-615.

Yadav, J. S., B. V. S. Reddy, Y. G. Rao, M. Srinivas and A. V. Narsaiah, "$Cu(OTf)_2$-catalyzed synthesis of imidazo[1,2-a]pyridines from α-diazoketones and 2-aminopyridines," *Tetrahedron Letters*, **48**(43) (2007) 7717-7720.

Yadav, P. S., D. Devprakash and G. P. Senthilkumar, "Benzothiazole: Different methods of synthesis and diverse biological activities," *International Journal of Pharmaceutical Sciences and Drug*, **3** (2011) 1-7.

Yan, H., S. Yang, X. Gao, K. Zhou, C. Ma, R. Yan and G. Huang, "Iron (II)-catalyzed denitration reaction: synthesis of 3-methyl-2-arylimidazo[1,2-a]pyridine derivatives from aminopyridines and 2-methylnitroolefins," *Synlett*, **23**(20) (2012) 2961-2964.

Yan, H., Y. Wang, C. Pan, H. Zhang, S. Yang, X. Ren, J. Li and G. Huang, "Iron (III)-Catalyzed Denitration Reaction: One-Pot Three-Component Synthesis of Imidazo[1,2-a] pyridine Derivatives," *European Journal of Organic Chemistry*, **2014**(13) (2014) 2754-2763.

Yan, M., Z.-C. Chen and Q.-G. Zheng, "Organic reactions in ionic liquids: oxidative dimerisation of thioamides with phenyliodine (III) diacetate," *Journal of Chemical Research*, **2003**(10) (2003) 618-619.

Yan, R.-L., H. Yan, C. Ma, Z.-Y. Ren, X.-A. Gao, G.-S. Huang and Y.-M. Liang, "Cu (I)-catalyzed synthesis of imidazo[1,2-a]pyridines from aminopyridines and nitroolefins using air as the oxidant," *Journal of organic chemistry*, **77**(4) (2012) 2024-2028.

Yavari, I., R. Hekmat-Shoar and A. Zonouzi, "A new and efficient route to 4-carboxymethyl coumarins mediated by vinyltriphenylphosphonium salt," *Tetrahedron Letters*, **39**(16) (1998) 2391-2392.

Zeng, J., Y. J. Tan, M. L. Leow and X.-W. Liu, "Copper (II)/iron (III) Co-catalyzed intermolecular diamination of alkynes: facile synthesis of imidazopyridines," *Organic letters*, **14**(17) (2012) 4386-4389.

Zhao, J.-W., J.-X. Xu and X.-Z. Guo, "Green synthesis of 1,2,4-thiadizoles from thioamides in water using molecular oxygen as an oxidant," *Chinese Chemical Letters*, **25** (11) (2014) 1499-1502.

Zhu, D., J. Chen, D. Wu, M. Liu, J. Ding and H. Wu, "An efficient, catalyst-and solvent - free synthesis of imidazo[1,2-a]pyridines and 2, 4-disubstituted thiazoles on grinding," *Journal of Chemical Research*, **2009**(2) (2009) 84-86.