1.0 INTRODUCTION

1.1 GENERAL:

In the past decades the tools available to the medicinal chemist to identify, design and test drugs have increased dramatically, both in quantity and sophistication. Computational methods, combinatorial chemistry, biotechnologies and high-throughput screening are among the many powerful techniques that have been harnessed to bring an element of rationality to the search for new drugs. In particular synthetic organic chemistry will continue to play a fundamental role in academic research and in the research and development departments of drug companies of the third millennium.

The role of organic synthesis in drug research and development nowadays and over the next decades was discussed at the 11th Camerino – Noordweijkerhout symposium (11-15 may 1997), in a section dedicated to New Developments in synthetic Medicinal Chemistry. Organic synthesis has made so much progress that it appears as a nature science, ready to face any synthetic problem, however difficult that problem may appear. The mechanistic advance in understanding organic chemistry has made prediction possible of the reactivity of organic compounds towards different reagents, and also to take on more and more complicated synthetic tasks. Retrosynthetic analysis has taught us to disconnect strategic bonds in order to dissect target molecules and identify useful synthetic strategies.
During the past 30 years, many milestones have been attained in the synthesis of natural products with pharmacological interest. The synthesis of prostaglandins, started by Corey in the 1960s and which continued with outstanding results for years; the synthesis of vitamin B_{12} realized by Woodward in the 1970s; the synthesis of the 64-chiral-centers palytoxin, performed by Kishi in the 1980s, and the achievement, almost at the same time, of the synthesis of the much-sought taxol by two different teams in the present era. From the Medicinal Chemistry point of view, it must be stressed that total syntheses, even if not of practical use for commercial production of the drugs, are however very useful in opening the way to analogous and simpler molecules that may help to establish SARs and to design easier to obtain compounds.

Synthesis of bioactive heterocyclic compounds functionalized Multi Walled Carbon Nano Tubes in the field of organic chemistry received significant attention resulting in substantial advances both in the synthetic and medicinal aspects. Generally nitrogen containing heterocycles have been the object of considerable focus because they are structural components of many bioactive natural products such as vitamins, hormones, antibiotics, alkaloids, glycosides and many more compounds which are of significance for human and animal health. There are several generic drugs available in the market contains tetrazoles, pyrimidines and oxazine as their main core of the structure. Pyrimidines are integral components of countless alkaloids; many
pyrimidine alkaloids possess biological and medicinal activity. Some of the tetrazole containing drugs are Irbesartan, used for the treatment of hypertension, Losartan, used to treat high blood pressure and Cefazolin, used to treat bacterial infections of the skin. Due to the increasing interest about the biological activities, solar cell applications of the heterocyclic compounds and catalytic activity of the non-nucleophilic bases, their syntheses are becoming increasingly prevalent and which might be with improved efficiency, simple procedures and quantitative yields of the target molecules.

1.2 LAWSONE DERIVATIVES

Naturally occurring quinones have several different roles in organisms; they are functional constituents of several biochemical systems (e.g. ubiquinones and vitamin K1). 2-Hydroxy-1,4-naphthoquinone (Lawsone) is the principal natural dye in the leaves of henna, Lawsonia inermis. Henna has been used more than 4000 years not only as a hair dye, but also as a body paint and tattoo dye. Today, semi-permanent hair dyes containing Henna as well as its pure dye ingredient are widely used and have become increasingly popular due to their natural origin.\(^1\) Lawsone was first isolated from the leaves of Lawsonia inermis L. in 1959,\(^2\)

1.2.1 BIOLOGICAL APPLICATIONS OF LAWSONE DERIVATIVES

Lawsone and related compounds have been reported to possess interesting biological activities such as antitumor, antibacterial and
antifungal properties.\textsuperscript{3-5} It is also used as a hair dye\textsuperscript{6} and as an ultra-violet (UV) filter in sunscreen formulation.\textsuperscript{7} Naphthoquinones constitute one of the largest and diverse groups of plant secondary metabolites with a broad range of properties\textsuperscript{8,9} antifeedent\textsuperscript{10} and allelopathic activity\textsuperscript{11} which contribute to plant defence. They also possess important pharmacological activities, such as antioxidant,\textsuperscript{12} anti-inflammatory,\textsuperscript{13} anticancer.\textsuperscript{14} With nearly one-third of the global population infected by Mycobacterium tuberculosis (MTB), tuberculosis (TB) is still a major cause of death. Indeed, in 2006 over nine million new cases and 1.7 million deaths occurred due to TB, and there is now a significant concern about the emergence of multi-drug resistant (MDR) strains of TB with an estimated 0.5 million cases worldwide.\textsuperscript{15}

The quinone structure is widespread in nature: for example, quinones play an integral role in many biological electron-transfer processes, particularly respiration and photosynthesis.\textsuperscript{16} Quinones have long been considered for their fungicide, antibacterial, and anticancer properties.\textsuperscript{17} The biological activity of quinones results from their ability to accept one or two electrons to form the corresponding radical anion or dianion species, and also their acid–base properties. Electron-attracting or -donating substituents modulate the redox properties of quinones, i.e. their variable ability to accept electron.\textsuperscript{18} The molecular basis of quinone toxicity is the enzyme-catalysed reduction to semiquinone radicals, which then reduce oxygen to superoxide anion radicals thereby
regenerating the quinone.\textsuperscript{17} A well-studied example is 2-methyl-1,4-naphthoquinone (MNQ, menadione or vitamin K3), which accepts electrons from various flavoproteins acting through a one-electron or mixed (one- and two-electron) mechanism.\textsuperscript{19} Substituted 1,4-naphthoquinones are widespread among natural quinones: for example, menaquinone is involved in the electron-transport chain of bacteria, and lawsone is the 2-hydroxy-1,4-naphthoquinone pigment found in the leaves of Lawsonia alba.\textsuperscript{17}

The benzo[g]quinoline-5,10-dione skeleton is an important structural motif prevalent in natural products with interesting biological properties (Fig. 1). For example, cleistopholine isolated from cleistopholis patens,\textsuperscript{20} oncodostigma monosperma,\textsuperscript{21} meiogyne virgate polyalthia\textsuperscript{22} and annona cherimolia,\textsuperscript{8} exhibits antimicrobial activity\textsuperscript{23,24} and anticancer activity against several cell lines,\textsuperscript{25} besides serving as intermediate in the synthesis of the antifungal agent, sampangine.\textsuperscript{26} Phomazarin, isolated from the cultures of phoma terrestris Hansen,\textsuperscript{27} shows in vitro cytotoxic activity.\textsuperscript{28} Dielsiquinone and marcanines A-E, isolated from the stem bark of goniothalamus marcanii craib, also show cytotoxic activity.\textsuperscript{29}
1.2.3 SYNTHESIS OF LAWSONE DERIVATIVES

The reaction of 2-hydroxy-1,4-naphthaquinone, benzaldehyde, ethyl acetoacetate and ammonium acetate in ethanol.\(^{30}\)

\[
\begin{align*}
\text{Cleistopholine} & \quad \begin{array}{c}
\text{(1)}
\end{array} \\
\text{Phomazarin} & \quad \begin{array}{c}
\text{(2)}
\end{array}
\end{align*}
\]

Marcanines

\[
\begin{align*}
A & \quad R^1, R^2 = H, R^3 = \text{Me}, R^4, R^5 = H \\
B & \quad R^1, R^2 = H, R^3 = \text{OMe}, R^4, R^5 = H \\
C & \quad R^1 = H, R^2 = \text{OMe}, R^3 = \text{CH}_2\text{OH}, R^4 = \text{OH}, R^5 = H \\
D & \quad R^1 = H, R^2 = \text{OMe}, R^3 = \text{Me}, R^4 = \text{OH}, R^5 = H \\
E & \quad R^1 = \text{Me}, R^2 = \text{OMe}, R^3 = \text{Me}, R^4 = \text{OH}, R^5 = H
\end{align*}
\]

\[
\begin{align*}
\text{Scheme-1} \\
\text{Condensation of 1,4-naphthoquinone with mercaptoalkanoic acids to yield S-(1,4-naphthoquinon-2-yl)-mercaptoalkanoic acids, which were converted to amides by reaction with SOCl}_2 \text{ and aromatic amines.}^{31}
\end{align*}
\]
2-Methoxy-3-bromo-1,4-naphthoquinone was obtained by two-step-reaction. Firstly, bromination of lawsone with bromine and hydroperoxide in acidic medium provide 2-hydroxy-3-bromo-1,4-naphthoquinone. This compound was then reacted with dimethylsulfate in acetone to obtain 2-Methoxy-3-bromo-1,4-naphthoquinone. The methylation reaction was catalysed by K$_2$CO$_3$.$^{32}$

Form 2-amino-3-chloro-1,4-naphthoquinone, successfully carried out the synthesis of chloro-1,4-naphthoquinone analogs. 2-Hydroxy-3-chloro-1,4-naphthoquinone was obtained by the diazoniation of 2-amino-3-chloro-1,4-naphthoquinone with sodium nitrite as reagent. Reaction of 2-amino-3-chloro-1,4-naphthoquinone with acid anhydride producing two amino substituted derivatives concentrated H$_2$SO$_4$ was used as catalyst.$^{33}$
The reaction of 2,3-dichloro-1,4-naphthoquinone with arylamine to obtain arylamine analogs of naphthoquinone.\textsuperscript{34}

![Scheme 3](image)

\textbf{Scheme-3}

The Hooker condensation between 2-hydroxynaphthoquinone (lawsone) and an aldehyde.\textsuperscript{35}

![Scheme 4](image)

\textbf{Scheme-4}
Using a halogenated naphthoquinone as the substrate in a palladium catalyzed Heck reaction.\textsuperscript{36}

![Scheme-5]

Three-component condensation reaction of 2-hydroxynaphthalene-1,4-dione, aromatic aldehydes and heterocyclic or carbocyclic amines in the presence of a catalytic amount of InCl\textsubscript{3} in refluxing water.\textsuperscript{37}

![Scheme-6](image)

**1.3 PYRIMIDINE DERIVATIVES**

Barbituric acids are heterocyclic derivatives of pyrimidine trione.\textsuperscript{38-40} They are well-known in medicinal chemistry as hypnotics, sedatives, anticonvulsants and anxiolytic agents. Recently, barbiturates have been used to induce anaesthesia in surgery procedures. C5-substituted and disubstituted barbituric and 2-thiobarbituric acids exhibit a wide spectrum of biological activity and some of them are useful drugs or agrochemicals.
1.3.1 BIOLOGICAL APPLICATIONS OF PYRIMIDINE DERIVATIVES

Organic compounds containing pyrimidine scaffold as a core unit are important targets and are known to exhibit various biological and pharmaceutical activities.\textsuperscript{41} 6-Amino-1,3-dimethyluracil and its fused derivatives\textsuperscript{42} are versatile building blocks for the synthesis of several bioactive heterocycles.\textsuperscript{43} Pyrido[2,3-d]pyrimidines are a class of naturally occurring fused uracils occupying a special place in synthetic and medicinal chemistry due to their wide range of pharmacological activities.\textsuperscript{44} 5-(3-Bromophenyl)-1,3-dimethyl-,11-dihydro-1H-indeno[20,10:5,6]pyrido[2,3-d]pyrimidine-2,4,6-trione (BPIPP) was identified as new potent inhibitor of STa induced cyclic nucleotide synthesis, and as a promising lead for the treatment of acute diarrhea. Moreover, appropriately functionalized pyrido[2,3-d]pyrimidines have also been identified as a new class of fibroblast growth factor receptor (FGFR3) tyrosine kinase inhibitors.\textsuperscript{45}

Tetrahydropyrimidenes are important members of the pyrimidine family, known to possess a wide range of biological activities. Recently, a new series of 5-(3-(1H-indol-3-yl)-substituted phenylallylidene)pyrimidine-4,6(1H,3H,5H)triones were synthesized by Biradar et al. using simple and efficient condensation of chalcones with barbituric acid. The synthesized compounds were screened for their antioxidant (free radical scavenging, total antioxidant capacity and ferric reducing antioxidant power) and DNA cleavage activities. Some of the
synthesized compounds especially 5-((E)-3-(1H-indol-3-yl)-1-p-tolylallylidene)pyrimidine-2,4,6(1H,3H,5H)trione exhibited excellent DNA cleavage activity.\textsuperscript{46} Akue-Gedu et al. synthesized a series of amino-pyridyl indole derivatives and tested them for their in vitro antiproliferative activities toward a human fibroblast primary culture and two human solid cancer cell lines (MCF-7 and PA 1). Among the synthesized compounds 4-(1H-Indol-3-yl)-5-(3-aminophenyl)pyrimidin-2-amine reported to have potential anticancer activity.\textsuperscript{47}

A large number of pyrimidine derivatives were reported to exhibit interesting pharmacological activity.\textsuperscript{48-55} A class of compounds of biological relevance was used in the plant protection area as plant growth regulators.\textsuperscript{56} In continuation of our studies, the development of expedient methods for the synthesis of pyrimido[4,5-d]pyrimidine-2,4-dione, were implemented.\textsuperscript{57} Pyrimidopyrimidines are annulated uracils that have attracted considerable interest in recent years. Derivatives of pyrimidopyrimidine are known to display a wide range of pharmacological activities, and their potent inhibitory properties regarding the tyrosine kinase domain of epidermal growth factor receptor,\textsuperscript{58} 5-phosphoribosyl-1-pyrophosphate synthetase\textsuperscript{59} and dihydrofolate-reductase,\textsuperscript{60} have been fully demonstrated. Numerous reports delineate the antitumour,\textsuperscript{61} antiviral,\textsuperscript{62} antioxidant,\textsuperscript{63} antifungal\textsuperscript{64} and hepatoprotective\textsuperscript{65} activities.
1.3.2 SYNTHESIS OF PYRIMIDINE DERIVATIVES

A ZnCl₂-catalyzed three-component coupling reaction allows the synthesis of various 4,5-disubstituted pyrimidine derivatives in a single step from functionalized enamines, triethyl orthoformate, and ammonium acetate. The procedure can be successfully applied to the efficient synthesis of mono- and disubstituted pyrimidine derivatives, using methyl ketone derivatives instead of enamines.\(^6^6\)

![Scheme 7]

A NaOH catalyzed rearrangement of propargylic hydroxylamines allows a highly stereoselective access to Cbz-protected β-enaminones. A subsequent synthesis of pyrimidines shows the synthetic potential of these β-enaminones.\(^6^7\)

![Scheme 8]

The direct condensation of cyanic acid derivatives with \(N\)-vinyl/aryl amides affords the corresponding C4-heteroatom substituted pyrimidines. The use of cyanic bromide and thiocyanatomethane in this
chemistry provides versatile azaheterocycles poised for further derivatization.\(^{68}\)

\[
\text{H} - \text{N} - \text{C} = \text{C} - \text{R} + 2\text{eq.} \quad 1.1\text{eq. TfO} \\
\quad \text{1.2eq. 2-Cl-Py} \\
\text{CH}_2\text{Cl}_2, 23^\circ\text{C}, 1\text{h or} \quad \text{MW, 140^\circ\text{C}, 5 min} \\
\rightarrow \quad \text{H} - \text{N} - \text{C} = \text{C} - \text{R}''
\]

The coupling of acid chlorides with terminal alkynes using one equivalent of triethylamine under Sonogashira conditions followed by subsequent addition of amines or amidinium salts to the intermediate alkynones allows a straightforward access to enaminoones and pyrimidines under mild conditions and in excellent yields.\(^{69}\)

\[
\text{O} - \text{Cl} + 2\text{mol-% Pd(PPh}_3\text{)}_2\text{Cl}_2 \\
4\text{mol-% CuI} \\
\text{THF, r.t., 1 - 3 h} \\
\rightarrow \quad \text{O} - \text{Cl} + 1.2\text{eq. HN} \quad \text{NH}_2 \\
\quad \text{HN} \quad \text{HN} \\
\quad \text{HN} \quad \text{HN} \\
\quad \text{HN} \quad \text{HN} \\
\quad \text{HN} \quad \text{HN} \\
\text{1.2eq. N}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \\
\text{reflux, 6 h} \\
\rightarrow \quad \text{N} - \text{N} - \text{R}' \quad \text{R}''
\]

A single-step conversion of various N-vinyl and N-aryl amides to the corresponding pyrimidine and quinazoline derivatives involves amide activation with 2-chloropyridine and trifluoromethanesulfonic anhydride followed by nitrile addition into the reactive intermediate and cycloisomerization.\(^{70}\)

\[
\text{R} - \text{N} - \text{C} = \text{C} - \text{R}'''' + 1.1\text{eq.} \quad 1.1\text{eq. TfO} \\
\quad \text{NC-R}'''' \quad \text{1.2eq. 2-Cl-pyridine} \\
\quad \text{CH}_2\text{Cl}_2, -78^\circ\text{C, 5 min, then} \\
\quad 23^\circ\text{C or 45^\circ\text{C, 1 - 18 h}} \\
\rightarrow \quad \text{R} - \text{N} - \text{N} - \text{R}''''
\]

\[\text{Scheme-9}\]
An array of tetrasubstituted saturated fused pyrimidines has been synthesized through a simple and efficient one-pot operation. The strategic utilization of the N-PMB group enabled the construction of a broad range of N-vinyl tertiary enamide starting materials. This stands as a flexible approach to functionalized pyrimidines with the capability of manipulating either ketone, acid chloride, or nitrile reaction partners.\textsuperscript{71}

![Reaction Scheme](image)

**Scheme-10**

### 1.4 CARBON NAONO TUBES

Carbon nanotubes (CNTs), including single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs), have a high surface area, special physicochemical properties and excellent chemical and thermal stability. These unique properties inspire researchers to explore their potential in biological and biomedical applications, such as biosensors, culture substrates, and in particular drug delivery systems. Investigation of the bioactivities of CNTs not only facilitates their potential bio-applications, but also benefits the risk assessment for human exposure to CNTs. Increasing reports have documented the biological activities of CNT both in vitro and in vivo. However, much less work has been done to the bioactivity of MWCNTs and their derivatives, especially their immune activity. SWCNTs and MWCNTs are shows slight cytotoxicity.
1.4.1 FUNCTIONALIZATION OF MWCNTs

In order to produce MWCNTs-COOH, the MWCNTs were sonicated with a mixture of HNO3 and H2SO4 (3:1) for 24 hrs at room temperature or refluxed for 1 hrs.

The carboxylic acid groups (MWCNT-COOH) in MWCNTs were converted to acid chloride (MWCNT-COCl) according to the reported procedure.
1.4.2 TETRAZOLES

Tetrazoles are a class of heterocycles with a wide range of applications which are currently receiving considerable attention,\textsuperscript{75} therefore the literature on tetrazole is expanding rapidly. This functional group has a role in coordination chemistry as a ligand\textsuperscript{76-78} as well as in various materials sciences applications including photography and specialty explosives.\textsuperscript{79} Extensive work has also been carried out in the field of medicinal chemistry, where tetrazoles are frequently used as metabolically stable surrogates for carboxylic acids.\textsuperscript{80-82} Less appreciated, but of enormous potential, are the many useful transformations that make tetrazoles versatile intermediates en route to substituted tetrazoles and especially to other 5-ring heterocycles via Huisgen rearrangement.\textsuperscript{83,84} The prime reason for the scarcity of practical applications for these sophisticated tetrazole-based reactions is the lack of appealing synthetic routes to the key intermediates 5-substituted tetrazoles.

Tetrazoles readily tolerate a wide range of chemical environments and new uses for this unique family of heterocycles continue to emerge in both materials science, and pharmaceutical applications.
1.4.2.1 BIOLOGICAL APPLICATIONS OF TETRAZOLES

Application in medicinal chemistry

5-Substituted 1,2,3,4-tetrazoles are reported to possess antibacterial, antifungal, antiviral, analgesic, anti-inflammatory, antiulcer and antihypertensive activities. The tetrazole function is metabolically stable this feature and a close similarity between the acidic character of the tetrazole group and carboxylic acid group have inspired medicinal chemists to synthesize substituted tetrazoles as potential medicinal agents.

Cis-Amide bond mimic

Marshall et al. have proposed a new use for the tetrazole ring as a cis-amide bond mimic within a peptide chain and this structural motif can be used to pre-organise the amide bonds of peptides, enzyme substrates and inhibitors into a cis-conformation. Incorporation of tetrazole dipeptide analogues into biologically active peptides such as somatostatin and bradykinin has been demonstrated.

![Tetrazole ring as a cis-amide bond mimic](image.jpg)
DNA, RNA synthesis

5-Alkylthiotetrazoles, specifically 5-Benzylthiotetrazole and 5-Ethylthiotetrazole, are powerful activators for DNA and RNA synthesis (Scheme -4).\textsuperscript{101-103} The presence of thio group makes the tetrazole ring more acidic than the corresponding 5-alkytetrazoles;\textsuperscript{104} this improves its ability to act as an activator. In addition, the solubility with biologically active compounds, where reactions are carried out in acetonitrile, is also enhanced. Comparison of 5-(Benzylmercapto)tetrazole (14) to other activators revealed the following order in coupling yield of 2'-O-TBDMS phosphoramidites (15).

\begin{align*}
5\text{-}(\text{Benzylmercapto})\text{tetrazole} & > 5\text{-}(\text{Ethylmercapto})\text{tetrazole} > 4,5\text{-}\text{Dicyanoimidazole} > 1H\text{-tetrazole}. \textsuperscript{101}
\end{align*}

\begin{equation}
\text{(27)}
\end{equation}

\textbf{Scheme-4: RNA phosphoramidite coupling reaction with 5- (Mercapto)-1H-tetrazole activation}

\textbf{Pharmaceutical properties}

Tetrazole itself does not exhibit pharmacological activity; however, many of its derivatives possess interesting biological activities and they are frequently used as metabolically stable surrogates for carboxylic
acids, while tetrazoles generally offer a more favourable pharmacokinetic profile.\textsuperscript{105-108} Like their carboxylic acid analogues, tetrazoles exhibit a planar structure. However, Hansch has shown that anionic tetrazoles are almost 10 times more lipophilic than the corresponding carboxylate,\textsuperscript{109} which is an important factor in allowing the molecule to pass through cell membranes. Hydrogen bonding capability of tetrazolic anions with receptor recognition sites is a key interaction for enhanced binding affinity.\textsuperscript{110} In addition, in the design of drug molecules, one advantage of tetrazoles over carboxylic acids is that they are resistant to many biological metabolic degradation pathways.\textsuperscript{111} Tetrazole derivatives have been investigated in areas as diverse as anti-arrhythmic agents,\textsuperscript{112} anti-diabetic agents,\textsuperscript{113} muscarinic agonists,\textsuperscript{17} anti-cholesterol agents, antifungal agents,\textsuperscript{114} anti-allergic agents,\textsuperscript{18} neurodegenerative diseases\textsuperscript{117} \textsuperscript{19,20,21,22} among others. Some examples are mentioned below.

\begin{align*}
\text{Anti-arrhythmic agents}
\end{align*}

\begin{align*}
&\text{R}^1= \text{p-MeO, p-Me, p-F} \\
&\text{R}^2= \text{p-Cl, -O-Me}
\end{align*}
Muscarinic agonists

Anti-allergenics

Tetrazole derivatives with central nervous system activity

Cardiovascular activity

The 5-((4′-Methyl-1,1′-biphenyl-2-yl)-tetrazole subunit has been used as a carboxylic acid mimic in the class of so-called sartan derivatives (23 & 24). Angiotensin II (AII) is the octapeptide responsible for the peripheral effects of the rennin-angiotensin system\textsuperscript{118-123} which include the regulation of blood pressure and volume homeostasis. Lorsartan (23) was the first nonpeptide angiotensin receptor antagonist to appear on the market\textsuperscript{120,124} followed by Valsartan (24). The 5-((4′-Methyl-1,1′-biphenyl-2-yl)-1H-tetrazole subunit has become ubiquitous in the most potent and bioavailable antagonists disclosed to date.
1.5 NON-NUCLEOPHILIC BASES

With respect to ‘Green Chemistry’, organic synthesis of materials has evoked a lot of interest in the recent past, as it embraces used of environmentally benign procedures such as reusable heterogeneous catalysts and solvent-free syntheses, multicomponent reactions. Recently, several techniques using the reusable heterogeneous catalysts have been developed individually. However excellent green chemistry protocol is awaited.

Catalytic asymmetric addition of stabilized carbanions to α,β-unsaturated enones (Michael reaction) is one of the fundamental C–C bond-forming reactions and useful methods for remote functionalization in organic synthesis. In the case of nitroalkanes, conjugate addition to α,β-unsaturated carbonyl substrates is an important step for the further transformation of masked functionalities. The nitro group, described as a ‘synthetic chameleon’, can undergo Nef reaction, nucleophilic displacements, reduction to an amino group and conversion into nitrile oxide. Several attempts have been made towards achieving asymmetric conjugate addition of nitromethane to chalcones in

![Diagram of Losartan and Valsartan](image)
the presence of lanthanum tris-binaphthoxide,\textsuperscript{136-138} L-proline,\textsuperscript{139} natural cinchona alkaloids,\textsuperscript{140} cinchona alkaloids-derived thiourea,\textsuperscript{141} polymer-anchored chiral catalyst LiAl-poly2A,\textsuperscript{142} chiral quaternary ammonium salts,\textsuperscript{143} Ni(II) complexes\textsuperscript{144} and chiral imidazoline catalysts.\textsuperscript{145}

1.6 **ZnO-ORGANIC THIN FILMS**

In recent years, the scientific and technological interest on zinc oxide thin films has increased phenomenally due to the novel physical and chemical properties reported in the literature. These findings make ZnO thin films good candidates for a wide variety of applications in optoelectronic devices, especially large area, cost-effective thin film solar cells. ZnO is one of the most promising semiconducting materials, suited for the fabrication of the next generation of optoelectronic devices and gas sensors. It is worth mentioning here that the detailed studies on the process parameters such as substrate temperature, doping level, concentration of the source material and aging time of the starting solution, etc., which play crucial roles in affecting the physical properties of the ZnO films, have contributed much to the development of the material.

1.6.1 **ORGANIC SOLAR CELLS**

Organic photovoltaic cells (OPVs) employing electron-donating (p-type) and electron-accepting (n-type) organic semiconducting materials for solar energy harvesting are a promising alternative to silicon solar cells due to their low cost, light weight, mechanical flexibility and solution processing.\textsuperscript{146}
With the increasing demands for clean energy, solar cells have become a foremost device for energy production. The use of solar cells to convert sunlight energy to electricity is becoming rapidly extended but the cost of the existing technologies is far too high to compete on a large scale with the traditional carbon dioxide-producing energy sources. Therefore, the research to improve the efficiency of existing solar cells and to develop new cost-effective technologies has become a major focus of scientific and industrial activities. Dye-sensitized solar cells (DSCs)\textsuperscript{147-149} and organic bulk heterojunction (BHJ)\textsuperscript{150,151} solar cells have evolved to viable devices, with efficiencies above 12\% and 8\%, respectively, and increasing stability on outdoor conditions.\textsuperscript{152-154}
THE SCOPE OF THE PRESENT INVESTIGATION

Ever since the world-shaping discovery of penicillin, nature’s molecular diversity has been extensively screened for new medications and lead compounds in drug discovery. The search for agents intended to combat infectious diseases has been of particular interest and has enjoyed a high degree of success. Indeed, the history of antibiotics is marked with impressive discoveries and drug-development stories, the overwhelming majority of which have their origin in natural products.

Chemistry, and in particular chemical synthesis, has played a major role in bringing naturally occurring antibiotics and their derivatives to the clinic, and no doubt these disciplines will continue to be key enabling technologies. Synthesis of bioactive heterocyclic compounds, functionalized Multi Walled Carbon Nano Tubes in the field of organic chemistry received significant attention resulting in substantial advances both in the synthetic and medicinal aspects. Due to the increasing interest about the biological activities, solar cell applications of the heterocyclic compounds and catalytic activity of the non-nucleophilic bases, their syntheses are becoming increasingly prevalent and which might be with improved efficiency, simple procedures and quantitative yields of the target molecules.

Keeping in mind all these results into account and in continuation of our research program we aimed at synthesizing attractive pharmacological and therapeutic important compounds, herein we report
the synthesis of various structurally diverse heterocyclic compounds having tetrazoles, pyrimidines and oxazine derivatives with the hope to develop some promising antimicrobial agents, catalytic activity of the non-nucleophilic bases and solar cell applications.

In the present study, the following two new series of biolabile heterocyclic compounds, two new series of functionalized Multi Walled Carbon Nano Tubes and one series of thin films are synthesized:

- Lawsone derivatives 42-46
- Pyrimidine derivatives 52-58
- Tetrazole functionalized MWCNTs 62-66
- Amine functionalized MWCNT non-nucleophilic bases 69-75
- ZnO:3,4-dihydro-2H-naphtho[2,3-b][1,4]oxazine-5,10-dione thin films 76-80

The assignment of the structures of the synthesized novel heterocyclic compounds is based on FT-IR, MS, elemental analysis, $^1$H NMR, $^{13}$C NMR, $^1$H-$^{13}$C HSQC, HMBC spectral studies, SEM, EDX, AFM and powder XRD analysis. It is predicted that the new series of synthesized heterocyclic compounds are expected to afford with wide spectrum of biological properties, catalytic activity and solar cell applications. Hence, the possible invitro anti-mycobacterial, anti-breast cancer potencies of the newly synthesized compounds are explored against a spectrum of clinically isolated microbial organisms, catalytic activity and solar cell applications are briefly described.