Chapter I
General Introduction

By definition, transition metals are those which have incomplete d-orbitals in any of their oxidation states.[1] Transitional metals are kept in between the s and p-block elements in the modern periodic table because of their transitional properties of the formal elements.[2] These transitional metals are important over the s and p-block elements in several ways such as transitional metals have higher charge/radius ratio, formed coloured complexes, show interesting magnetic behaviors, show variable oxidation states and so on.[3,4] The chemistry of biological systems also relies on a number of transition metals; the most well-known examples are iron, cobalt, copper, and molybdenum.[5-7] The two main processes involved in oxygen transport and electron transfer (also known as oxidation-reduction reactions) reactions are carried out by proteins carrying iron and copper which is by far the most prevalent and significant transition metal to play such a role in biological systems.[8,9] These transition metals in combination with the ligands formed transition metal complexes.[10] The ligand may be different types of chelators like bidentate, tridentate, tetradentate, pentadentate and hexadentate also. The donation property and the selectivity of the ligand towards the different metal ions may be varied by employing the donor atoms like nitrogen (N), oxygen (O), sulphur (S), and phosphorous (P) in the ligand skeleton.[11-13] Literature survey suggests that the chelating ligands like 2,2′-bipyridine (bpy), 2,2′-dipyridylamine (dpa), 2,6-Bis-(benzimidazol-2-yl)-pyridine (bzimpy) are exist in different conformer such as cis-cis, cis-trans, trans-trans.[14,15] Depending upon the metal centres and the stability of the transition metal complexes the coordinational modes can be different. Setifi *et al.* reported the various conformations and different binding motifs of 2,2′-dipyridylamine (dpa) which is shown in **Fig. I.1**. Targeting transition-metal complexes makes sense when creating useful materials and catalysts. Coordination compounds have importance in qualitative and quantitative analysis, the chemical industry, the synthetic polymer industry, the dye industry, and technological processes.[13,16] Transition metal complexes play crucial to the biological systems that support human and plant life also.[17] Anti-cancer medications include coordination chemicals including complexes of platinum, palladium, and ruthenium.[18,19] Additionally, several transition metal complexes have antibacterial and antifungal properties.[20-22] The coordination

compounds have demonstrated effective behaviour against a variety of illnesses, including malaria and Alzheimer's.[23,24] Recently, coordination compounds have been employed for the treatment of anti-viruses like coronaviruses.[25,26] The gram amounts of potentially lethal gadolinium ions can be safely injected into a patient undergoing an MRI scan, in fact into millions of patients each year, is a testament to sophisticated coordination chemistry.[27]

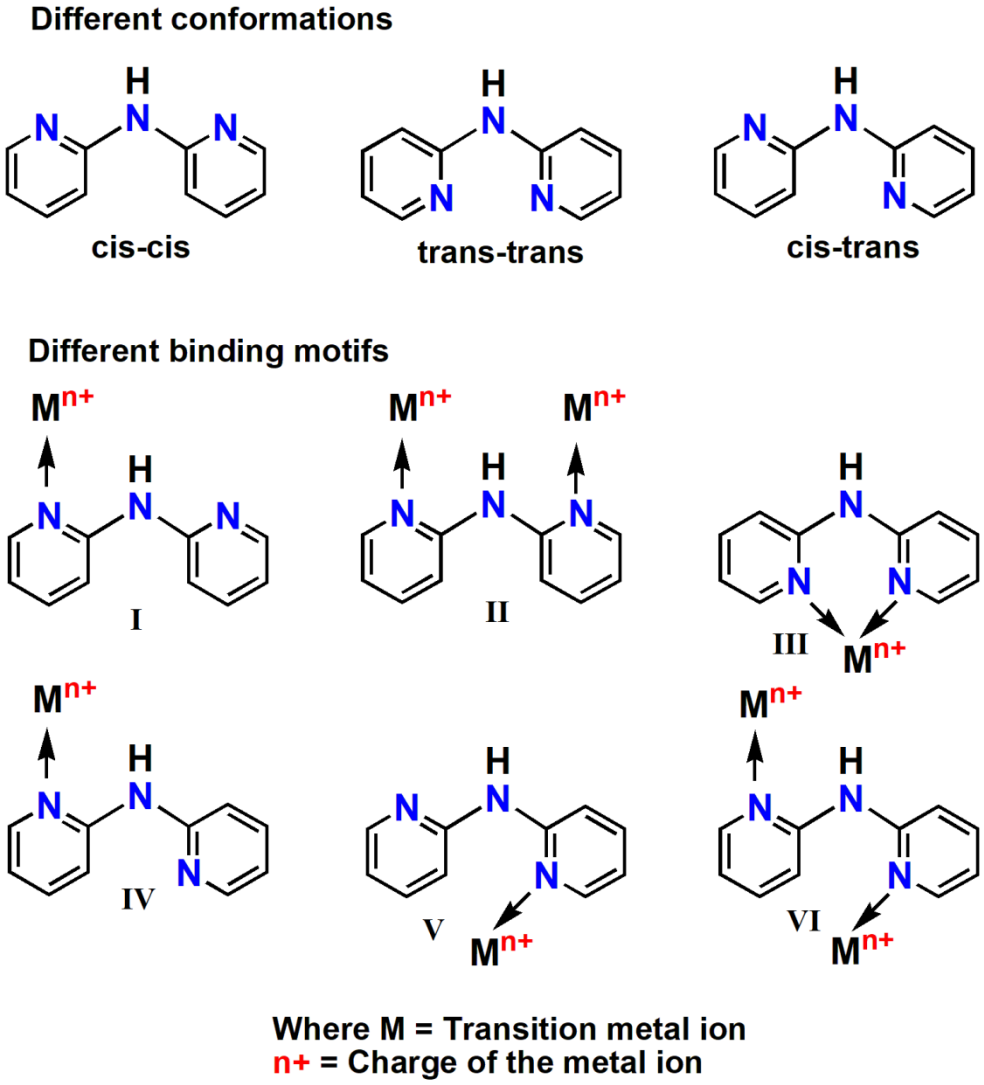


Fig. I.1. Different conformers and binding motifs of 2,2'-dipyridylamine

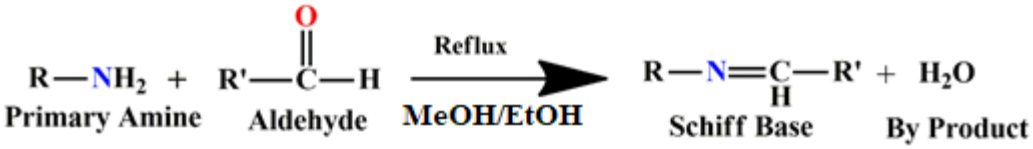
On the flip side, food, vegetables and mother nature contain bioactive substances that can work on the body to improve good health as bioactive compounds are act as secondary metabolites.[28-30] Numerous of these bioactive substances are supposed to have antioxidant, immunomodulatory, anti-osteoporotic, anti-hypertensive, antibacterial, antidiabetic, and anti-cancer characteristics. They are also said to be useful in lowering cardiovascular problems.[31] Therefore, paramount research is going on to

synthesis the valuable bioactive compounds.[32] Among them, catalytic pathway by employing the transition metal complex gained the most attention because the estimated global commercial value of all catalysts in 2014 was 17.2 billion US dollars. The North American Catalytic Society (NACS) claimed that roughly 35% of the world's GDP depends on catalysts and that their use in industry is growing by 5% annually. Additionally, according to a recent report, catalysts are required for more than 60% of chemical synthesis and 90% of chemical transformation in the various chemical industries around the world.[33] The green synthesis protocol through metal-free, catalysts free sustainable route to the synthesis these bioactive compounds also have been developed day by day around the globe for enhancing human well-being.[34]

I.1. Schiff base ligand and its importance

Hugo Schiff, a German chemist, synthesized Schiff base for the first time in 1864.[35] Having an azomethine (-C=N-) functional group, Schiff bases are polydentate chelators with a wide range of significant uses in many disciplines of science, such as the fields of medicine, biology, physics, materials science and in many industries also.[36-38]

The general synthesis of Schiff base ligand is the condensation of aldehydes or ketone with the amine compounds in ethanol or methanol medium.[39-41] The synthetic diagram is shown in **Scheme I.1**.



Scheme I.1: Synthesis procedure of Schiff base ligand

According to scientific research, the lone pair of electrons in the sp^2 hybridised orbital of the nitrogen atom of the azomethine (-C=N-) group is the prime reason for the physicochemical properties of the Schiff base. In the presence of the azomethine nitrogen and addition to the functional groups like (–OH), (–SH), ($–NO_2$), (–COOH), ($–OCH_3$) etc. make the Schiff base a promising chelating agent that can bind with the metal ion and form the Schiff base coordination complexes.[42] Schiff bases are widely used in the agrochemical, catalysis, fungicidal, and dye industries.[43] Scientific literature also tells that a number of Schiff bases exhibit exceptional antibacterial, antifungal, and anticancer properties. The C=N moiety in this class of molecules is crucial for biological activity. Due to numerous pharmacological applications, including

antifungal, antiviral, antimalarial, antimicrobial, anticancer, antituberculosis, anti-HIV, nanotechnology and catalytic application in the oxidation of organic compounds, researchers have recently given Schiff bases and their metal complexes a great deal of attention.[44-46] One of the pioneers of the Schiff base and reduced Schiff base and their complexes research is Prof. Debasis Das, University of Calcutta, West Bengal, India. Prof. Das and co-workers synthesise the structurally distinct homologous Schiff bases and their mono and binuclear zinc complexes. The Schiff base complexes showed anti-oxidant activity (radical scavenging agent), and antimicrobial activity for both Gram-positive and Gram-negative bacteria activity and one of the complex is said to be the prominent phosphatase model from their study.[47] From the laboratory of Professor Ashutosh Ghosh from the University of Calcutta, West Bengal, India comes another significant piece of research in this discipline. On the basis of specially crafted synthetic asymmetric Schiff base ligands and their Ni(II)-Mn(II) heterometallic Schiff base complexes, Prof. Ghosh and co-workers synthesized quinone, an important class of bioactive compounds.[48] Prof. Thomas J Meade from Northwestern University, US reported histidine-containing proteins inhibition by cobalt(III) Schiff base complexes through a dissociative exchange mechanism. The design of a novel dinuclear Co(III) Schiff base complex with bridging diimidazole ligands was influenced by these fluorescent imidazole reporters. This complex exhibits improved stability against ligand exchange with competing imidazoles in a biological pH range.[49] A new technique for making hydrophilic amino acid gossypol Schiff bases, which are challenging to make using current techniques, was created by another renowned scientist from Collaborative Innovation Centre of Chemical Science and Engineering, Republic of China by Prof. Quingmin Wang. A number of amino acid gossypol Schiff bases were designed, synthesised, and tested for their anti-TMV properties. Most of these compounds showed positive activities.[50] Some of the various types of Schiff base ligands are represented in **Fig. I.2**.

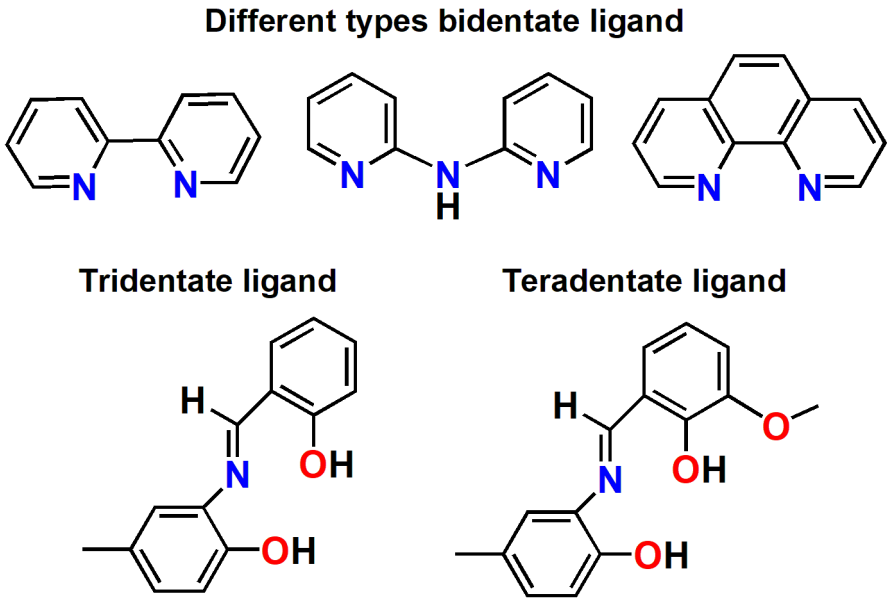


Fig. I.2. Some of various types of Schiff base ligands

I.2. Bioactive compound and its importance

The words "bioactive" are made up of the prefix "bio" and the suffix "-active." In etymology, the prefix bio- relates to life and comes from the Greek word "bios" and active, derived from the Latin "activus," which means: active, lively, full of energy, or having energy.[51] This activity displays every phenomenon that gives rise to a type of life, a working system, or a process. Many naturally occurring substances have been investigated for various purposes, particularly in the food and pharmaceutical industries. These substances have bioactive properties.[52-54] These compounds have chemical structures that carry out certain biological functions. These metabolites can be broadly categorized into three groups: alkaloids, phenolic chemicals, and terpenes and terpenoids. Carotenoids, sterols, and flavonoids are common examples among them. Tetraterpenes with C_{40} skeletons, constructed from eight isoprenoid units (C_5), and distinguished by a core sequence of conjugated double bonds, make up the majority of the bioactive terpenes that have been studied.[55,56] Sterols, which are triterpenes (C_{30}) with a fundamental structure made up of a tetracyclic ring and a C_{17} side chain, also fall under the category of terpenes.[57] The flavonoids, which are phenolic chemicals, have a low molecular weight, 15 carbon atoms, and are arranged in the fundamental configuration C_6-C_3-C_6.[58] Alkaloids, on the other hand, are often heterocyclic organic molecules with a basic pH and include nitrogen atoms in their structural features.[56]

Other molecules, such as polysaccharides, amino acids, and peptides, have also

demonstrated some bioactivity in addition to the major groups, showing that there are a wide variety of bioactive compounds that are being explored and studied in a variety of sources.[58] Numerous bioactive substances with considerable potential for use in the food and pharmaceutical industries are produced by microorganisms, plants, and animals. More than 80% and 30% of the active ingredients used in food and medication, respectively which come from natural sources.[59] Growing interest is being shown in bioactive molecules across a variety of fields, including geomedicine, plant science, contemporary pharmacology, agrochemicals, cosmetics, the food industry, nanobioscience, etc.[60] Phenazine, caffeine, phenoxazinone, benzimidazole, coumarin, resveratrol are the some important bioactive compounds. A Literature survey suggests that more than 100 and over 6000 synthetic phenazine derivatives are studied to date. Phenazine natural products having antibiotic properties are known to be produced by both marine and soil-dwelling bacteria, and this class of metabolites holds tremendous promise for the identification of novel anti-infective agents.[61] Caffeine is another bioactive compound used in our daily life which stimulates (increases activity in) our nerve system and brain. The adenine and guanine bases of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) are chemically related to caffeine, which is a bitter, white crystalline purine and methylxanthine alkaloid. Numerous beverages, including coffee, tea, soft drinks, and energy drinks, contain caffeine. Caffeine is also present in chocolate.[62] The substance phenoxazine is a heterocyclic compound. Phenoxazine is made up of two benzene rings attached to an oxazine. It can be found as the main component of several naturally occurring chemical substances, including dactinomycin and litmus. A phenoxazine core also serves as the foundation for the colours Nile blue and Nile red.[63] Benzimidazole is also a heterocyclic bioactive compound. Most of the drugs which have a highly impact in pharmaceutical science such as lerisetron, telmisartan, bilastain, albendazole etc. contain the basic benzimidazole moiety in their structure. It is one of the listed drugs by the United States Food and Drug Administration.[64] A stilbenoid, or natural phenol, called resveratrol (3,5,4′-trihydroxy-trans-stilbene), is a phytoalexin produced by a number of plants in reaction to injury or when the plant is being attacked by pathogens like bacteria or fungi. The skin of grapes, blueberries, raspberries, mulberries, and peanuts are among the food sources of resveratrol.[65] Lastly, a lactone-like chain (CH)=(CH)−(C=O)−O−, generating a second six-membered heterocycle that shares two carbons with the benzene ring, is said to replace two neighbouring hydrogen atoms in the benzene molecule to produce

coumarin. It can be categorised as a lactone and belongs to the chemical family of benzopyrones. In addition to being frequently used to treat leukaemia, prostate cancer, and renal cell carcinoma, coumarins also have the power to mitigate the negative effects of radiotherapy. Due to its use in photochemotherapy and other cancer treatments, coumarin derivatives, both natural and synthetic, are in demand.[65] Some important bioactive compounds are shown in **Fig. I.3**.

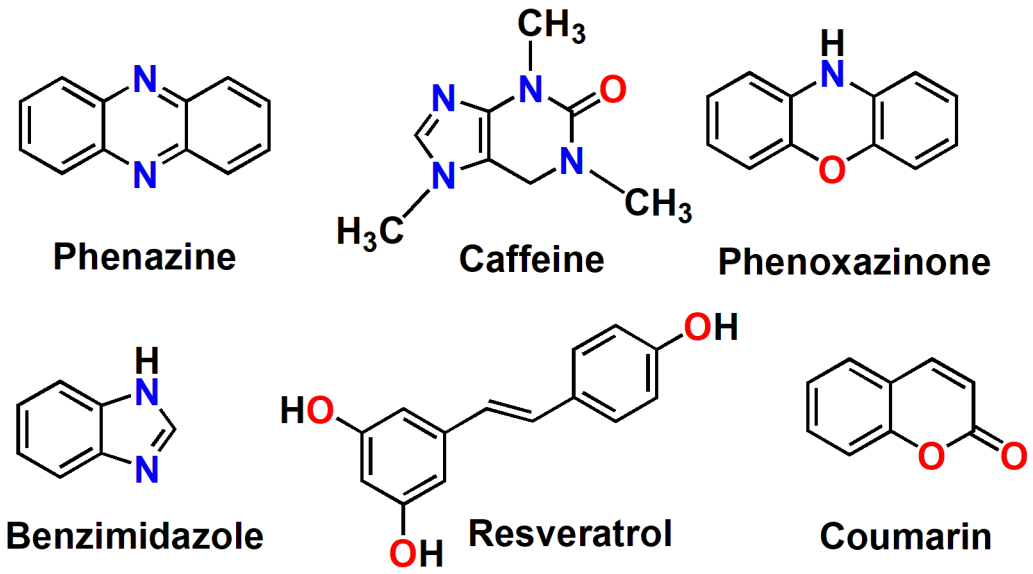


Fig. I.3. Some bioactive compounds

I.3. Synthesis of bioactive compounds by transition metal complex

During the past 50 years, transition metal catalysis has probably developed into one of the most significant aspects of contemporary synthetic organic, bioinorganic and medicinal chemists.[67] The new chemical reactivity provided by transition metal complexes has enabled creative responses to concerning synthetic problems because these compounds have access to a variety of oxidation states, bonding modes, and their coordination environments.[67] Undoubtedly, the particular reactivity and selectivity of metal-based complexes greatly expand the possibilities for biomolecule modification and for the production of significant bioactive compounds day by day.[68-70] Transition metal-mediated and transition metal complex-mediated processes have the potential to be used in biological sensing, imaging, caging, pharmaceutical and therapeutic applications also.[71]

A renowned synthetic organic chemist from the Indian Institute of Technology (IIT), Guwahati Prof. Anil K. Saikia regioselectively synthesized 2*H*-indazole derivatives by

using copper and zinc salts. 2*H*-indazoles are a significant class of heterocyclic compounds. The 2*H*-indazole motif is prevalent in medicinal compounds and bioactive natural materials with unique bioactivities like estrogen receptor β, 5-HT_{1A} receptor, antiangiogenic, anti-cancer activities.[72] Another popular scientist who is enormously contributing to the synthetic bioactive compounds library is Prof. Sabuj Kundu of Indian Institute of Technology (IIT), Kanpur. Prof. Kundu and co-workers synthesized the huge number of bioactive alcohol derivative compounds which act as an anti-allergic, anti-bacterial, food additives and acetylcholinesterase inhibitors by hydrogenation method using low loading of iridium-based catalyst.[73] The pioneer of the catalyst-driven synthesis of biologically important molecules is Prof. Debabrata Maiti from IIT, Bombay. The group explored the catalytic fate of late-transition Rh-catalyst for the synthesis of bioactive alkene-based compounds by the ortho-alkynylation in ambient conditions and successfully isolated estrone, menthone. camphor, and menthone like significant compounds. Derivatives of cinnamic acid are favoured scaffolds that are a crucial component of numerous natural products and physiologically active compounds. It has been demonstrated that cinnamic acid derivatives such sinapic acid, caffeic acid, ferulic acid, and isoferulic acid have a range of pharmacological properties, including anticancer, antioxidant, immunomodulation, and anti-inflammation effects.[74] Prof. Manickam Bakthadoss and co-workers designed and development of a novel method using nitrile as a directing group (DG) for the palladium-catalyzed selective meta-C-H activation of α-substituted cinnamates and their heterocyclic analogues with different alkenes.[75]

Transition metal complex-mediated synthesis of bioactive compounds has gained attention not only in India but also to the global synthetic chemist. Prof. Wolff and his team from Michigan State University, US reported the synthesis of carbonylative benzannulations products by [5+1] cycloaddition reaction using a cost-effective $Fe_2(CO)_9$ catalyst. The same group also reported the synthesis of carbazole-3,4-quinone by a robust Cr-based catalyst. These carbonylative benzannulations play a vital role in the pharmaceutical industry.[76] It is well known in the world of medicinal chemistry that adding a fluorine atom in place of a hydrogen atom or a hydroxyl group frequently enhances the pharmacological action of the parent compound and there are several therapeutic candidates containing fluorine such as florinef acetate, levofloxacin and Lipitor. Prof. Mikiko Sodeoka from Advanced Science Institute, Japan synthesized a series of optically active fluorinating α-Keto esters in the presence of hydroxyl bridged

palladium catalyst.[77] The discovery of pharmaceuticals incorporating nitrile (-CN) has recently attracted much more attention in the medical science due to the huge applicability of vildagliptin, letrozole, pericyazine etc. as an antidiabetic drug, anti-breast cancer drug. Prof. Bill Morandi group from Max-Planck Institute, Germany reported nickel complex catalyzed synthesis of medicinally significant cyanation derivatives through cross-coupling reaction.[78]

I.3. Transition metal-free synthesis of bioactive compound

For the concern of sustainable development, green synthesis is considered as a crucial protocol for lowering the negative impacts connected to the conventional synthesis techniques frequently used in laboratories and industries.[79] Recent trends have demonstrated that transition-metal-free reactions are an effective and environmentally friendly method for producing bioactive molecules and become one of the most fascinating fields to synthetic chemists.[80] Major limitations of transition metal catalysis include the high cost associated with the manufacture of the catalyst, stability factor to moisture and air, difficult and expensive separation techniques of transition metal catalysts from reaction mixtures, which are particularly important to the pharmaceutical industry and also requirements of co-catalysts and additives in some circumstances for boosting the effectiveness and reactivity of the transition metal-catalyzed transformation to produce the value-added products.[80] Therefore, additive-free, metal-free synthetic protocols for the development of medicinally and pharmaceutically significant bioactive compounds is a cutting edged topic for scientists around the globe in recent decades.[81] Prof. Santanu Panda from IIT, Kharagpur, India is a well-known researcher in the field of metal-free synthesis of bioactive chemicals. The team claimed to have created bioactive heterobiaryl derivatives of benzofuran and benzothiophene. These substances can be used to treat breast cancer and chagas illnesses.[82] One of the renowned scientists in this area is Prof. Dilip Kumar Maiti from the University of Calcutta, India. Prof. Maiti and co-workers moved forward the sustainable protocols and synthesized large number of annulated products of isoquinolines by using N-heterocyclic carbene (NHC) as a catalyst and achieved the isoquionoline derivatives from good to excellent yields.[83] From the medicinal point of view, these isoquinoline alkaloids are the second largest important drug which functions as an antifungal, antiviral, antioxidant, anticancer, antispasmodic, and an enzyme inhibitor agent. Prof. Alkananda Hajra from

Visva-Bharati introduced the visible-light in this synthetic method which is one of the most sophisticated techniques in modern days. The group successfully isolated the quinazoline, phenanthridine, purine and its derivatives, bioactive quinoxyfen, roflumilast and fasudil compounds through effective, commercially feasible, and environmentally friendly synthetic technique.[84] Professor Asish Ranjan Das, another well-known scientist at the University of Calcutta in India, expanded the venture of the photocatalytically assisted synthesis. Prof. Das and the group described a practical and straightforward mono- and di-C(sp3)-O cross-coupling with ketones, dicarbonyl compounds, and nitroalkane to produce substituted imidate derivatives from tautomerizable N-heterocycles (dihydrophthalazine-1,4-diones, quinoxalinone, pyridone and pyrimidinone) under visible light. Numerous substituted quinazoline and quinazolinone derivatives have a variety of biological effects, including those that are acaricidal, weedicide, antimalarial, anticancer, antimicrobial, antifungal, antiviral, antiprotozoan, diuretic, muscle relaxant, antitubercular, antidepressant, and many others.[85]

Additionally, many research groups around the world showed their intense interest in the approach without transition metals or any additives for the production of bioactive pharmacophores. Very prestigious chemist Prof. Chien-Hong Cheng from Tsing Hua University, Taiwan reported the synthesis of bioactive sulfonamide derivatives by transition metal-free tandem cyclization via diradical pathway. Huge number of the sulfonamide products, also known as sultam derivatives are achieved by Prof. Cheng and coworkers. These sulfonamide products have crucial bioactive properties like antithyroid, diuretic, antitumor, hypoglycemic, protease inhibitors etc.[86] Medicinally important Benzofurylethylamine derivatives which are a subclass of benzofurans are synthesized by Patrick J Walsh and his associates by a novel cascade mechanism of radical cyclization.[87] Prof. Takumi Mizuno, a remarkable scientist from the Osaka Research Institute of Industrial Science and Technology in Japan, extended the environmentally friendly synthesis of diaryl sulphide derivatives without the need for transition metal complexes or any oxidants. The group described the base-promoted synthesis of diaryl sulphides derivatives, which are extremely important as drugs for the treatment of a variety of illnesses including cancer, Alzheimer's, Parkinson's, AIDS, neoplastic, HCV, diabetic, and parasitic diseases. Lastly, metraminol is an important class of drug treated in serious hypotension and is used as a precursor of many bioactive compounds. It has also been used as a vasoconstrictor through intracavernosal injection

to treat vasodilator-induced priapism and also used as a test for familial Mediterranean fever diagnosis.[88] Prof. Stephen Noack from the Institute of Bio- and Geosciences (IBG-1), Germany established decoupled transamination pathway to synthesise metaraminol from biobased L-alanine. Their study emphasised implications for the integration of novel biobased processes and clarifies how biocatalytic conversions work in intricate fermentation matrices. This is really a high degree of environmentally friendly and sustainable approach for the production of bioactive compounds.[89]

I.5. Scope and objectives of the present study

This research examines the features of several new coordination complexes and explores their possible usage in a number of catalytic transformations for the production of bioactive compounds. The synthetic protocol of an important class of bioactive compounds by a sustainable route also has been elaborated and their biological applications are studied. The characterization of the newly designed compounds is performed by a suite of various spectroscopic techniques. Below is the summary of main the themes of this dissertation:

(i) Synthetic procedure of the newly designed Schiff base ligands.

(ii) The characterization of those compounds is performed using various analytical techniques.

(iii) X-ray structures of the synthetic compounds and their supramolecular frameworks to show the primary and secondary zone of coordination and non-covalent interactions are discussed in the thesis.

(iv) Clarification of the stereochemical, geometrical, and electronic structure of these newly synthesized compounds using spectroscopic findings and computational calculations are thoroughly explained.

(v) Examination of bio-inspired phenazine oxidase reactions was done.

(vi) Through a green chemical approaches, bioactive compounds are synthesized by a newly established methodology.

(vii) The synthesized compounds are applied to the drug delivery for various biological applications including cancer.

(viii) Our findings from all of these experiments were thoroughly compared with previously published literature.

The references in my PhD thesis are organized in the manner described below: name of authors, abbreviated journal name in italic, year in bold, volume in italic, page/article number.

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