

DIPYRROMETHANE, ITS DERIVATIVES AND THEIR METAL COMPLEX: APPLICATIONS AS CHEMOSENSORS AND BIOLOGICAL ACTIVITY

Abstract

Pyrrole moiety forms many naturally occurring biologically active compounds and exist in the structure of some biologically active compounds. From this point of view, pyrrole derivatives are very important building blocks in the drug industry and so in organic syntheses. Dipyrromethane derivatives are the building blocks for the syntheses of a variety of calix[n]pyrroles, porphyrins, hexaphyrin and polypyrrolicmacrocycles. The oxidized dipyrromethane derivatives (i.e. dipyrromethenes or dipyrins) have strong coordinating ability towards different metal ions and their metal complexes with trivalent group 13 metal ions show luminescent properties. They work as ligand for the syntheses of organic framework of BODIPY, which are used extensively as molecular probes and dyes. The functionalized C-vinyl pyrroles are prospective new materials for molecular optical switches, nano devices, photo and electro-conducting applications and used as ligands for new photo catalysts, biologically active complexes.

Various hydrazine derivatives such as: (i) hydrazone, (ii) hydrazide-hydrazone, (iii) thiosemicarbazones, (iv) thiocarbazones, (v) semicarbazones, and (vi) carbazones are effective organic compounds, versatile intermediates in their own right and their metal complexes. Hydrazones having an azomethine proton $-\text{CH}=\text{N}-\text{NH}-$ constitute an important class of compounds for new drug development. They are mainly used as antimicrobial, antitubercular, and antidiabetic agents. They have strong coordinating ability towards different metal ions. The chemical stability of hydrazones and their high melting points have recently made them attractive as prospective

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new materials for optic-electronic applications and NLO properties.

Dipyrromethanes are well known synthetic scaffolds for the synthesis of dipyrromethane metal complexes. Advancements have been made in the development of sensors for the detection of heavy-transition-metal ions in biological and environmental systems. Today the development of probes for heavy-transition-metal selective colorimetric and / or fluorescent sensing systems has become a research hotspot because UV-Vis and fluorescence spectroscopy analyses remain the most commonly used detection methods given their high sensitivity and facile operation. Fluorescent probes have been successfully applied to the detection of metal ions in vitro and / or in vivo. This feature is particularly desired for fluorophores with bioimaging applications. Dipyrromethene can be used as fluorescent “turn-on” Zn sensors. The metal complex has found application in various fields. Dipyrromethane-based fluorescent dyes are versatile and valuable probes for many biological systems.

Keywords: Dipyrromethanes, Ligands, Fluorescent Dyes, Photosensitizers.

I. INTRODUCTION

Pyrrole (C_4H_4NH) is a very important five membered heterocyclic aromatic organic compound having five-membered ring [1]. Pyrrole is firstly obtained by the dry distillation of protein by **Rung** in 1834. Electrophilic aromatic substitution occurs primarily at positions 2 and 5 in pyrrole instead of 3 and 4 as given in **Figure 1**.

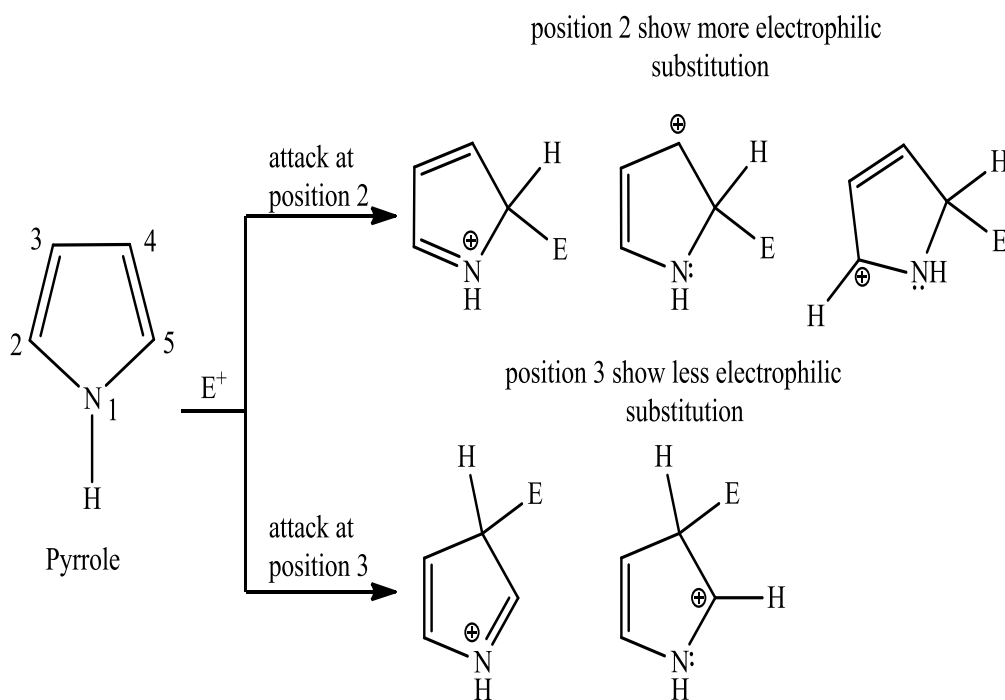


Figure 1: Resonating Structures of Pyrrole

Pyrrole nucleus occurs in many natural compounds and it is a precursor to many natural compounds that are biosynthesized such as porphyrins- heme, chlorins and chlorophylls in **Figure 2**.

The pyrrole-hydrazone and their metal complexes may show different biological activities such as antituberculosis and antimicrobial and utilized as an adaptable starting point for the synthesis of different types of chemical molecules. $-NH-N=CH-$ containing hydrazide-hydrazones are a crucial class of compounds for the creation of novel drugs. Due to the existence of the $>N-N=C<$ functional frame, they are primarily used as antitubercular, antimycobacterial agent and potentially DNA damaging and mutagenic agents. They can effectively coordinate with various metal ions [2-5].

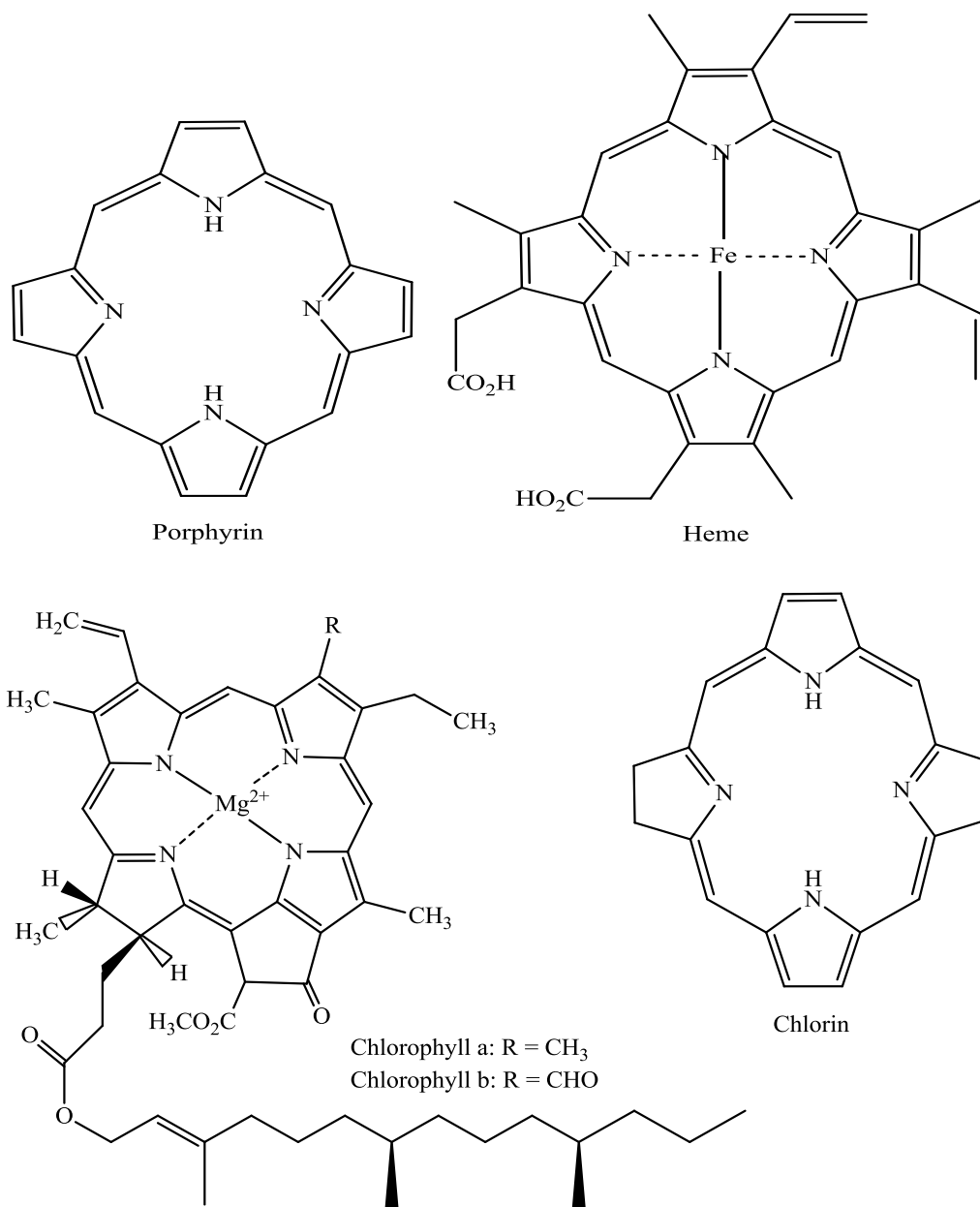


Figure 2: Natural Products Containing Porphyrin Ring

II. DIPYRRROMETHANES

Dipyrromethanes are completely conjugated, planar bipyrrrolic units that function as ligands in supramolecular self-assembly. It includes a vast variety of substances with a broad spectrum of activities. Chemosensors, photo-induced energy, electron transfer, molecular-based memory storage, small-molecule activation, multi-electron redox catalysis, and molecular devices are few areas where they have a lot of potential application. They are the best starting materials for the entire synthesis of pyrrole-containing macromolecules, porphyrins, and boron-dipyrin dyes. The development of novel optical anion sensors, their use in biological systems, and the solution of environmental issues are all potential

applications for derivatives of Dipyrrromethanes [6]. The structure of Dipyrrromethane is given in **Figure 3**.

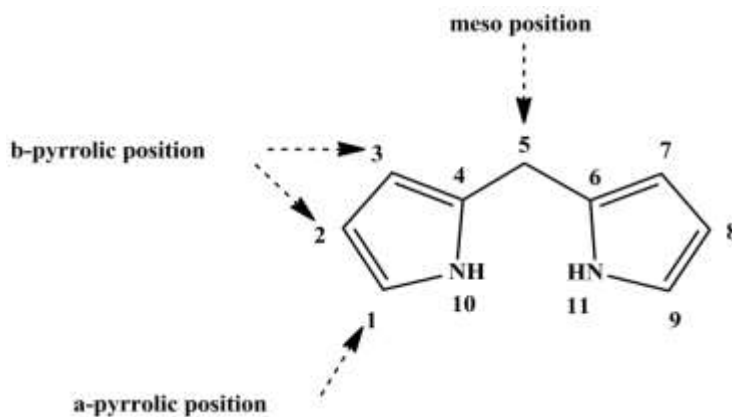


Figure 3: Structure of Dipyrrromethane

1. Dipyrrromethanes types: The compounds which possess two pyrrole units linked direct to each other or via linkers. Dipyrrromethanes play the key role in photo-physical and redox processes in nature. Depending on nature of connecting linkers dipyrrroles have been classified (**Figure 4**) in the following categories such as:

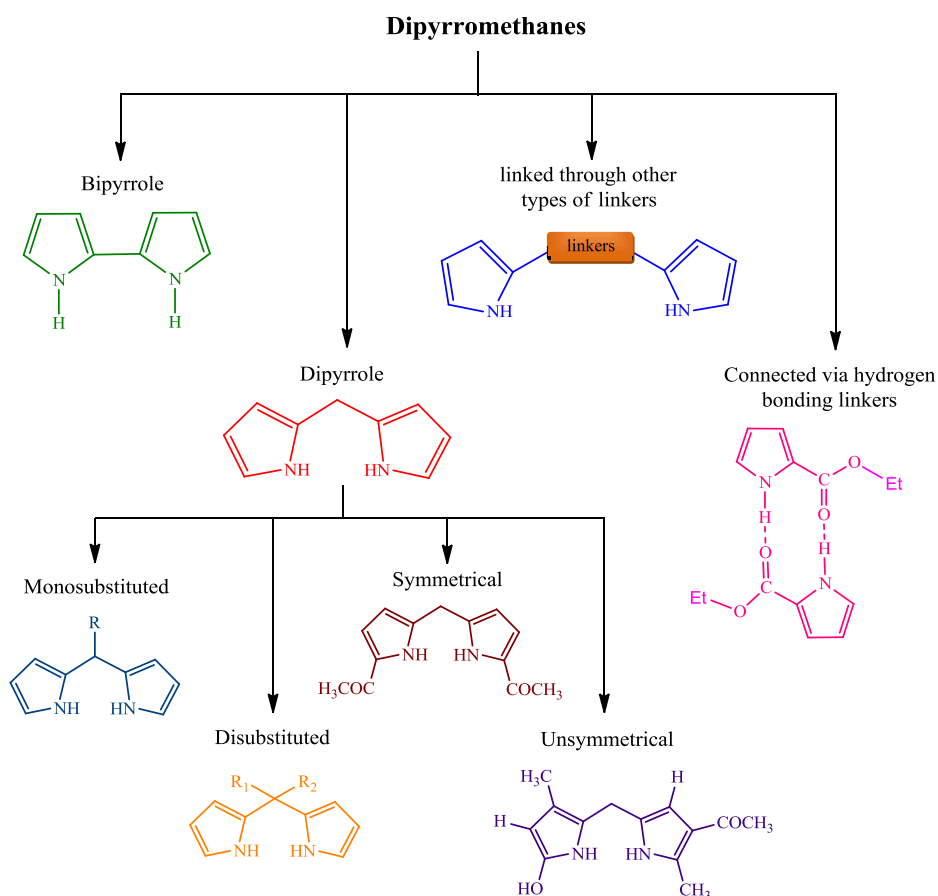
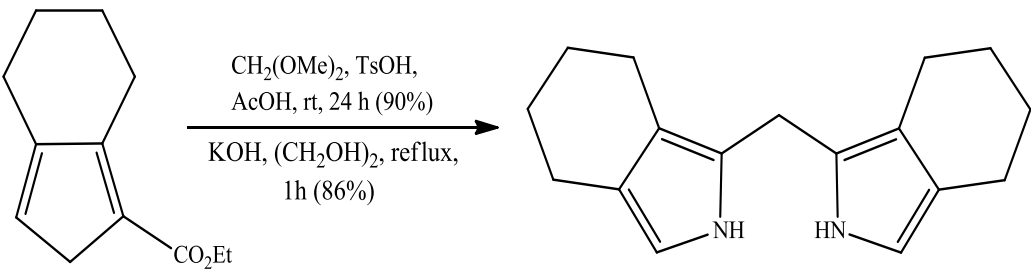
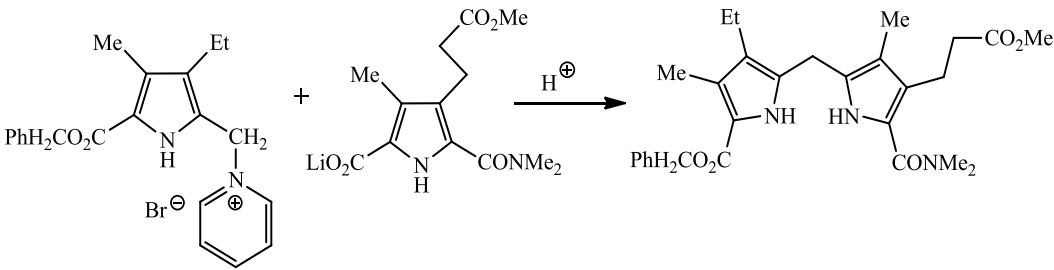


Figure 4: Classification of dipyrrromethane

2. Dipyrrromethanes Derivatives: Dipyrrrolic compounds in which two pyrrole units are linked via *meso*-carbon of (>CH₂ or >CH->C<) as linker. For simplicity, they are categorized as:

- Meso-unsubstituted dipyrrromethanes.
 - Meso-substituted dipyrrromethanes.
 - Symmetrical dipyrrromethanes.
 - Asymmetrical dipyrrromethanes.
- **Meso-Unsubstituted Dipyrrromethanes**

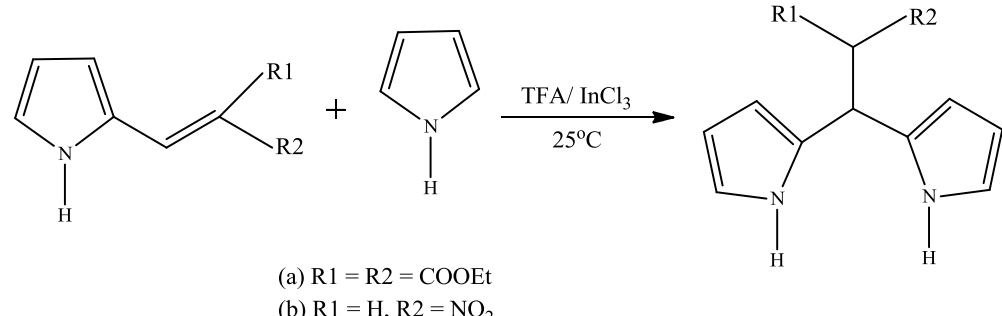
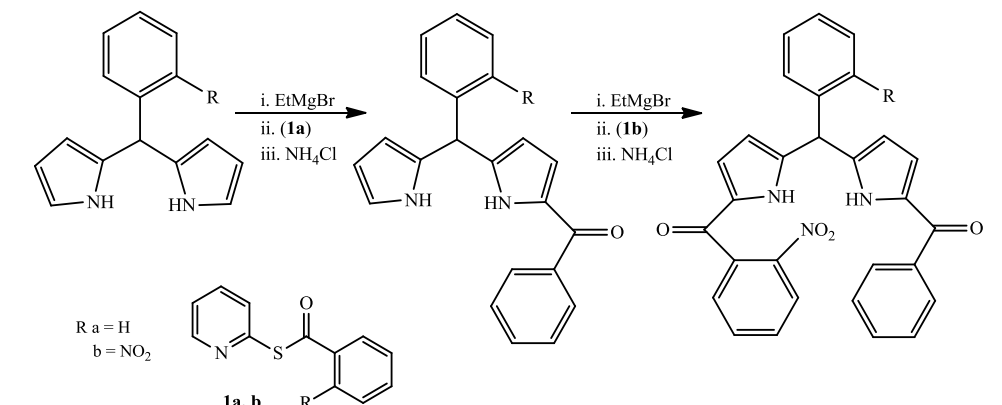
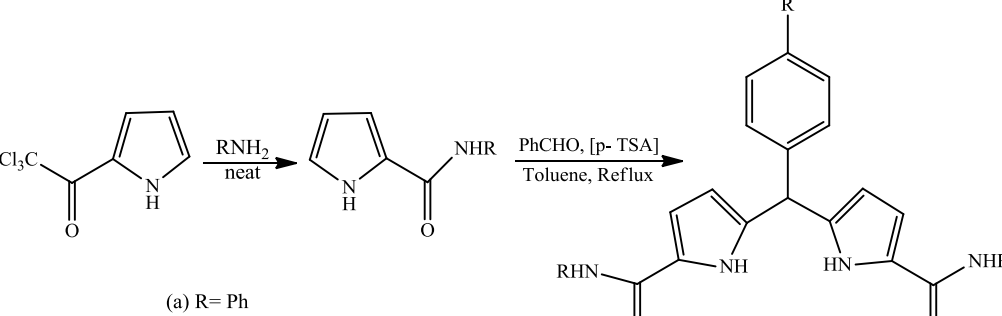
Table 1: Shows Various Meso-Unsubstituted Dipyrrromethanes Derivatives

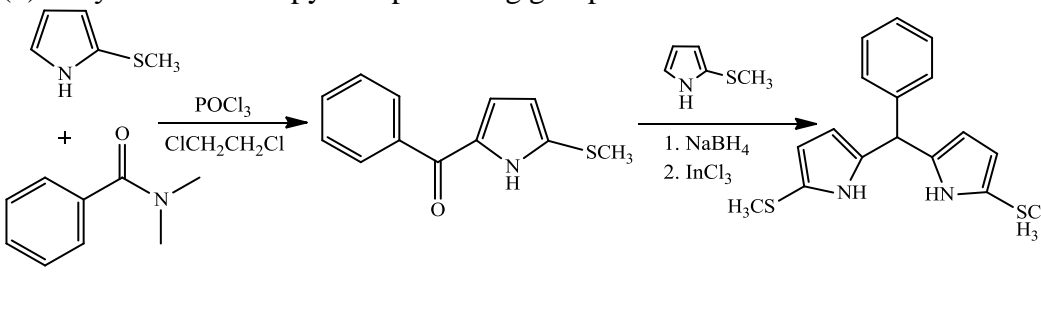
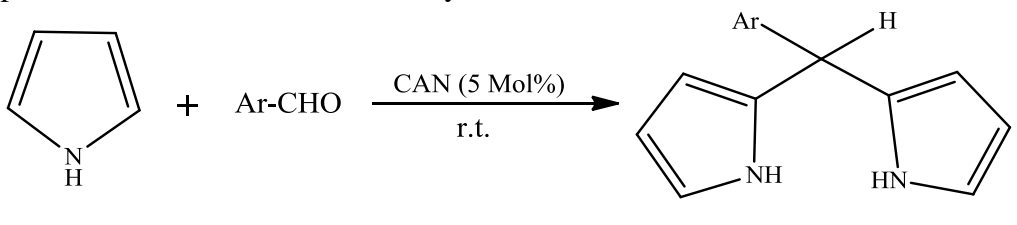
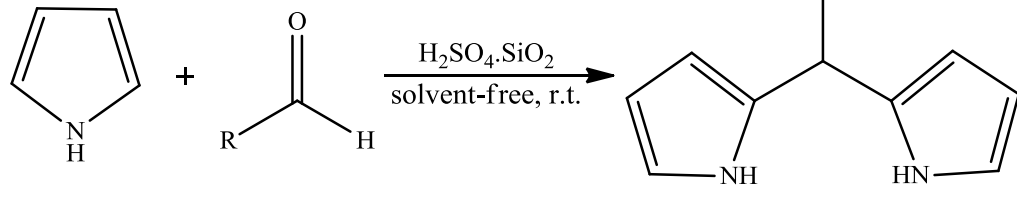
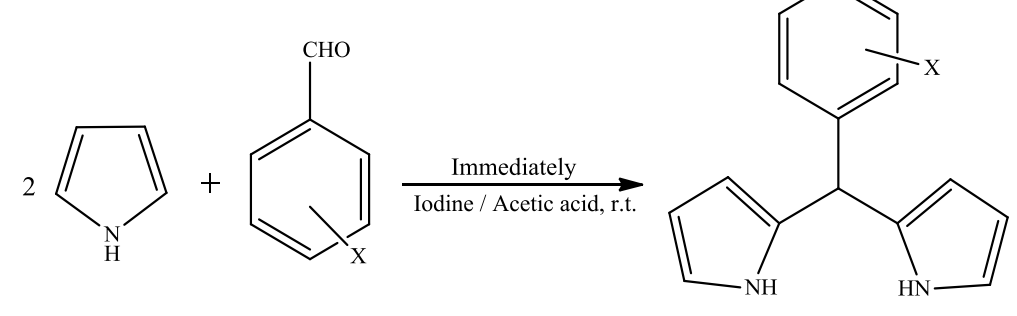
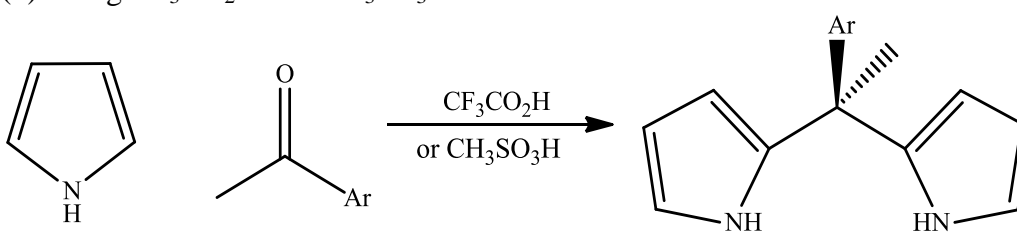
<p>(a) 5-Unsubstituted dipyrrromethane derived from ethyl tetrahydroisoindeole-2-carboxylate and dimethoxymethane.</p> 	<p>[7]</p>
<p>(b) Pyridinium salt of 2-bromomethylpyrroles reacts with lithium salts of pyrrole-2-carboxylic acids in polar solvents.</p> 	<p>[8]</p>

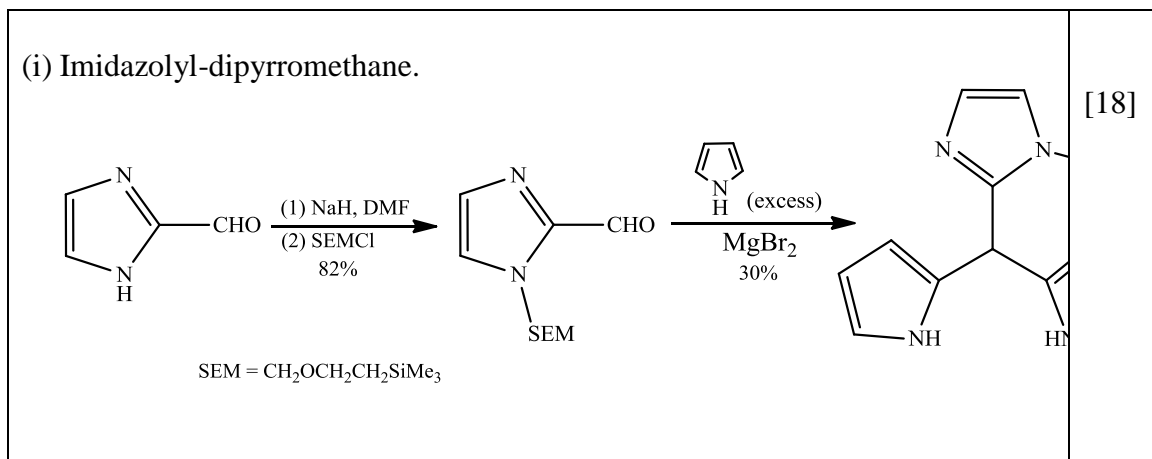
- **Meso-substituted dipyrromethanes:** Synthesis of *meso*-substituted dipyrromethanes can be of two categories: mono and disubstituted. They are as follows:-

➤ **Meso-monosubstituted dipyrromethanes:** *Meso*-monosubstituted dipyrromethanes is shown in **Table 2**.

Table 2: Shows Meso-Monosubstituted Dipyrromethane Derivatives

<p>(a) Using TFA or InCl₃ as a catalyst, from vinyl pyrrole.</p>  <p>(a) R1 = R2 = COOEt (b) R1 = H, R2 = NO₂</p> <p>(b) 2, 2'-substituted dipyrromethanes with EtMgBr and benzoyl pyridenyl sulfide.</p>  <p>R a = H b = NO₂</p> <p>1a, b</p>	<p>[9]</p> <p>[10]</p>
<p>(c) 2, 2'-bis (amido) and <i>meso</i>-substituted dipyrromethanes.</p>  <p>(a) R = Ph (b) R = -C(CH₃)₂</p>	<p>[11]</p>

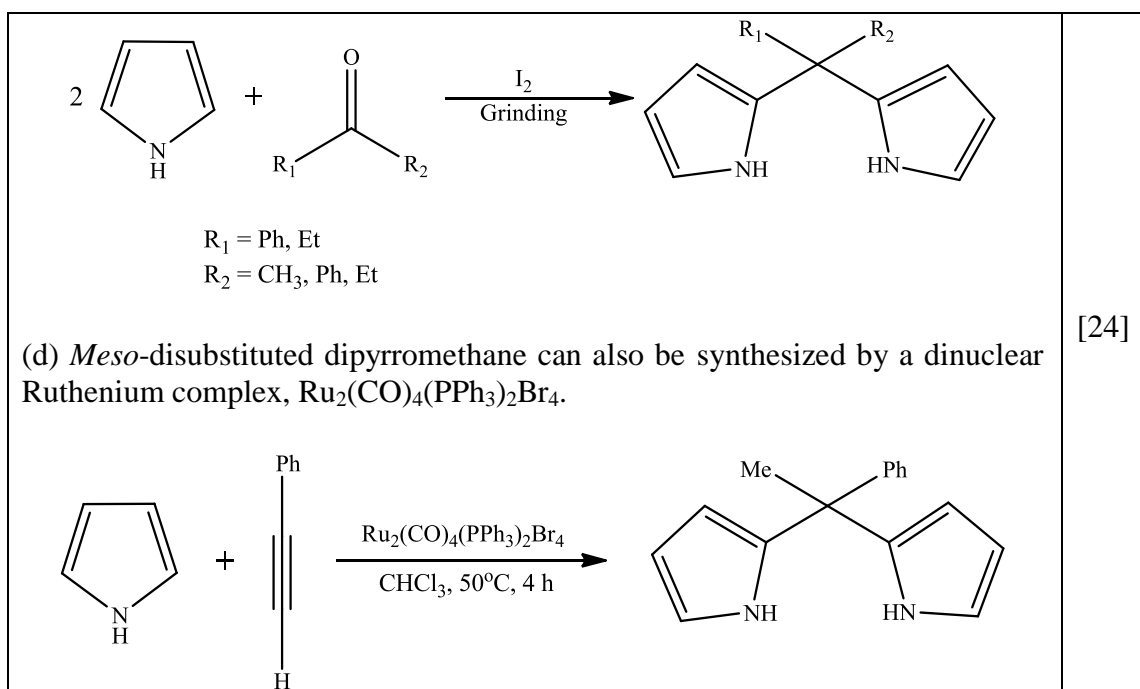
<p>(d) Alkylthio unit is α-pyrrole protecting group.</p> 	<p>[12]</p>
<p>(e) At room temperature, <i>meso</i>-substituted dipyrromethanes are formed in the presence of a non-toxic CAN catalyst.</p> 	<p>[13]</p>
<p>(f) In <i>meso</i>-substituted dipyrromethanes, $H_2SO_4 \cdot SiO_2$ to be used.</p> 	<p>[14]</p>
<p>(g) Using molecular iodine under acetic acid.</p> 	<p>[15, 16]</p>
<p>(h) Using CF_3CO_2H and CH_3SO_3H.</p> 	<p>[17]</p>



➤ **Meso-disubstituted dipyrromethanes:** *Meso*-disubstituted dipyrromethanes are given in **Table 3**.

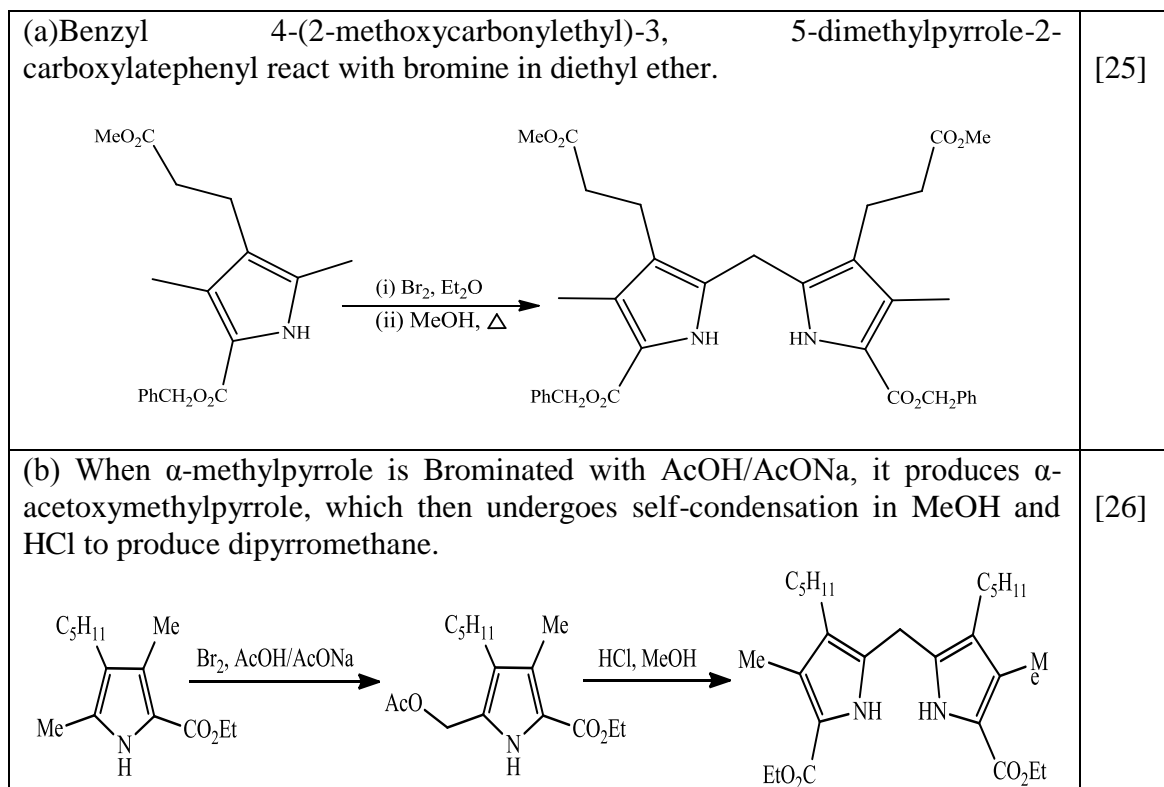
Table 3: Shows *Meso*-Disubstituted Dipyrromethane Derivatives.

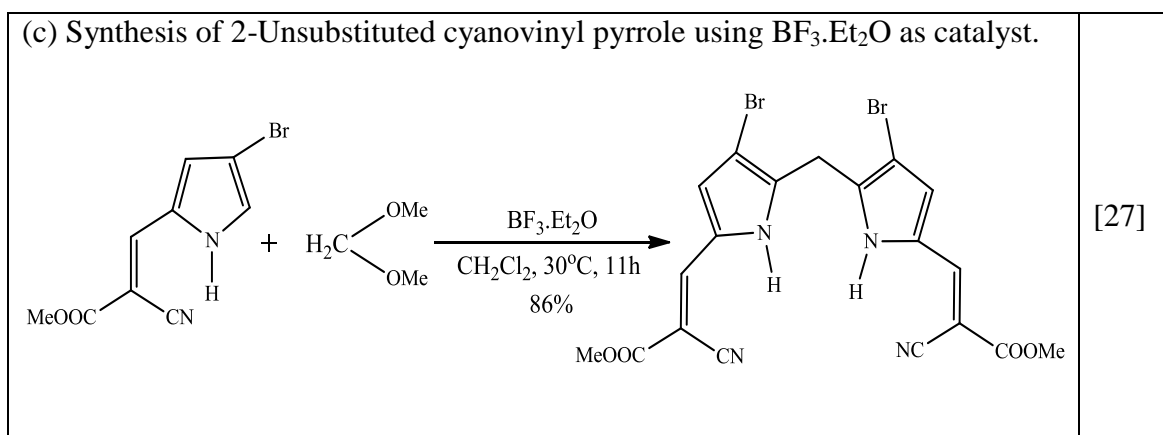
<p>(a) Synthesis of <i>meso</i>-disubstituted dipyrromethanes in the presence of BF₃.Et₂O and EtOH as catalyst. [19]</p> <p>R = </p>	[19]
<p>(b) <i>Meso</i>-disubstituted dipyrromethane synthesized using novel acid as catalyst. [20]</p> <p>R₁ = CH₃, C₂H₅, -(CH₂)₄, -(CH₂)₅, H, etc. R₂ = CH₃, C₂H₅, C₆H₅, C₆F₅, 2,4,6-(CH₃)₃-C₆H₂, etc.</p>	[20]
<p>(c) In a pestle and mortar, mixture of pyrrole, ketone and I₂ was crushed at room temperature. Various catalysts to be used for the synthesis of dipyrromethane such as TiCl₄, TFA, pyrrolidinium tetrafluoroborate, <i>p</i>-toluenesulfonic acid. [21-23]</p>	[21-23]



- **Symmetrical Dipyrromethanes:** Symmetrical dipyrromethane means that both sides are identical and both part matches exactly when one half are like an image of the other half in a mirror. Various types of symmetrical dipyrromethanes are shown in **Table 4**.

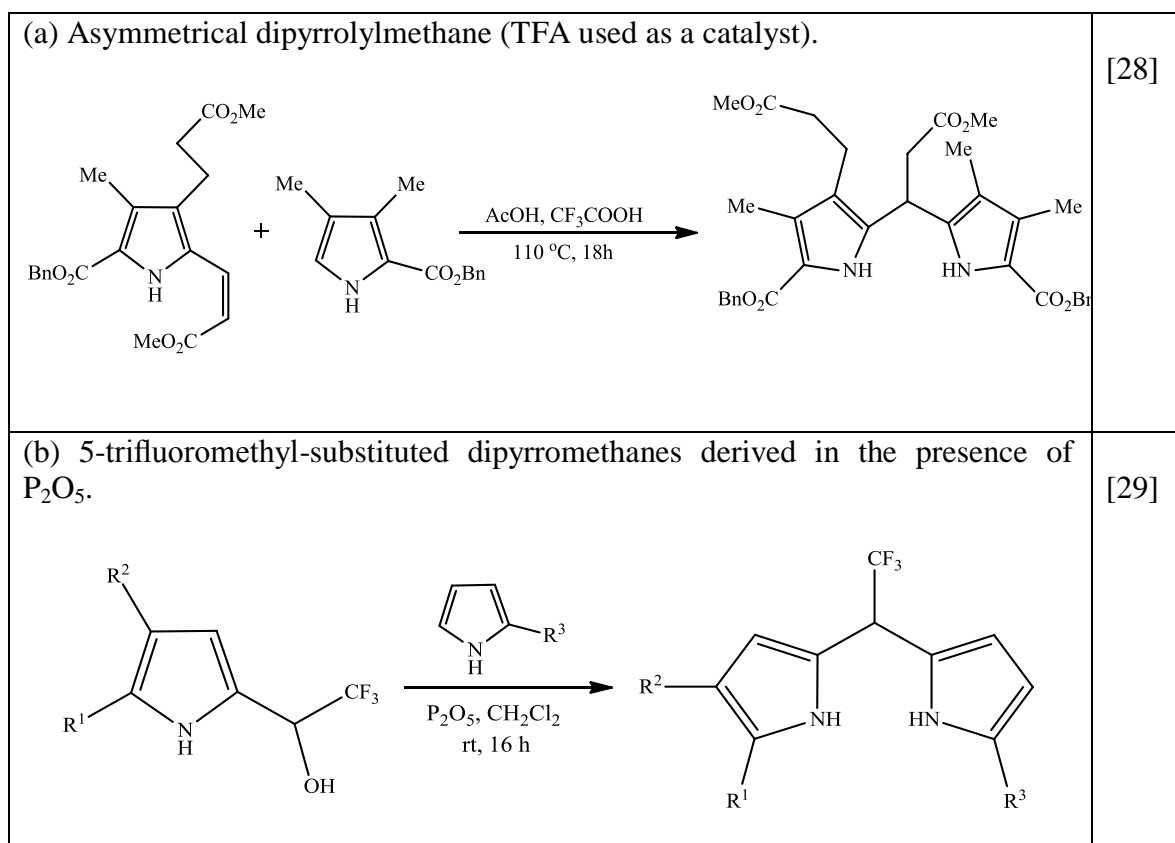
Table 4: Shows Symmetrical Dipyrromethane Derivatives





- **Asymmetrical Dipyrrromethanes:** Asymmetrical dipyrrromethane means that both sides are non-identical in some way. Various types of asymmetrical dipyrrromethanes are shown in **Table 5**.

Table 5: Shows Asymmetrical Dipyrrromethane Derivatives.

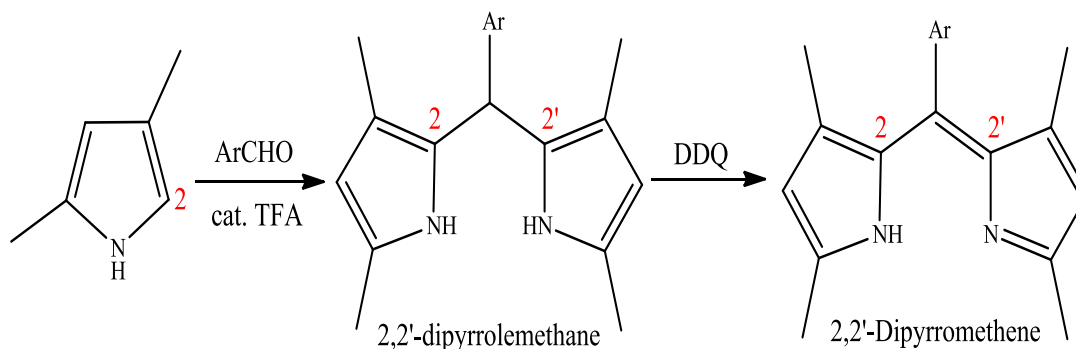


III. DIPYRRROMETHENE

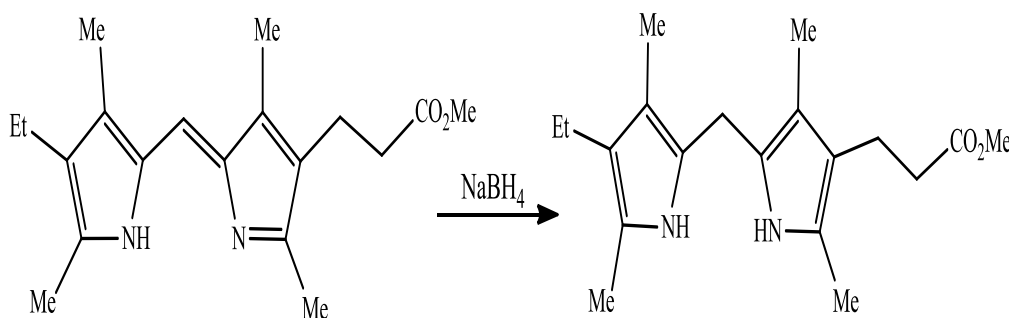
With the chemical formula $\text{C}_9\text{H}_8\text{N}_2$, 2,2'-Dipyrrromethene is also known as Dipyrrromethene or Dipyrrin. Its skeleton can be characterized as two pyrrole rings C_5N linked by a methyne bridge $=\text{CH}-$ through their nitrogen-adjacent (position-2) carbons, with

hydrogen atoms completing the remaining connections. Above $-40\text{ }^{\circ}\text{C}$, it is an easily attacked unstable molecule by nucleophilic chemicals.

- 1. Synthesis:** Oxidation of 2, 2'-Dipyrrolemethane with DDQ at $-78\text{ }^{\circ}\text{C}$ in a dry DCM solution, 2, 2'-Dipyrromethene can be produced [30] is shown in **Scheme 1**.



- 2. Reduction of Dipyrromethene:** Reduction of Dipyrromethene with sodium borohydride also furnishes Dipyrromethane, and establishes that Dipyrromethane and Dipyrromethene are fully interconvertible in the synthetic sense is shown in **Scheme 2**.



IV. APPLICATIONS

- 1. Molecular Probes and Dyes:** The organic framework of BODIPY [31, 32], which is widely used as molecular probes and dyes, is synthesized by dipyrromethanes. The general route for the synthesis of BODIPY is shown in **Figure 5**. Dipyrromethenes (Dipyririn) and BODIPY dyes have separate IUPAC numbering systems. However, the terms α -, β - and *meso*-position are applied to both systems in the same manner [33]. The IUPAC numbering and conventional nomenclature for BODIPY, Dipyririn and Dipyrromethane skeleton is shown in **Figure 6**.

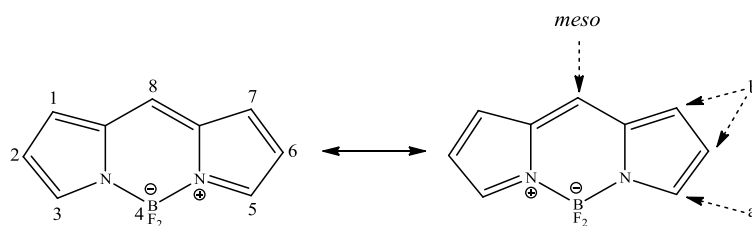


Figure 5: BODIPY dyes (compact, highly fluorescent systems)

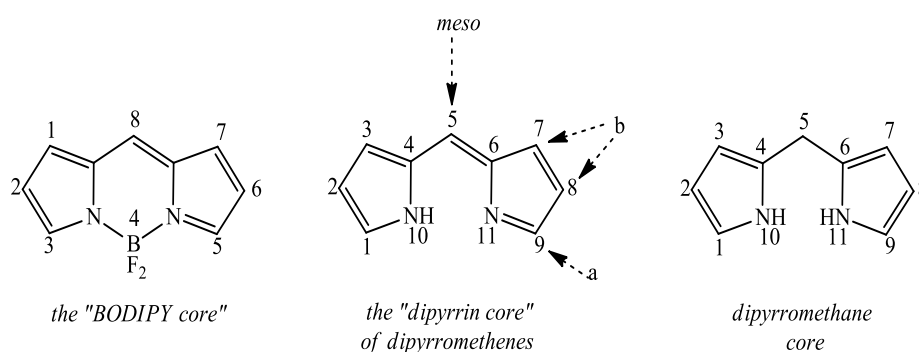
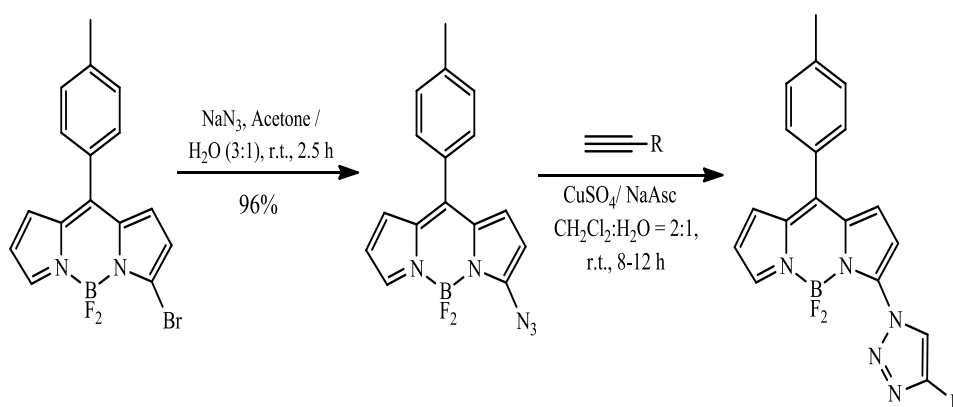


Figure 6: The IUPAC Numbering and Nomenclature for BODIPY, Dipyrriin and Dipyrromethane Skeleton

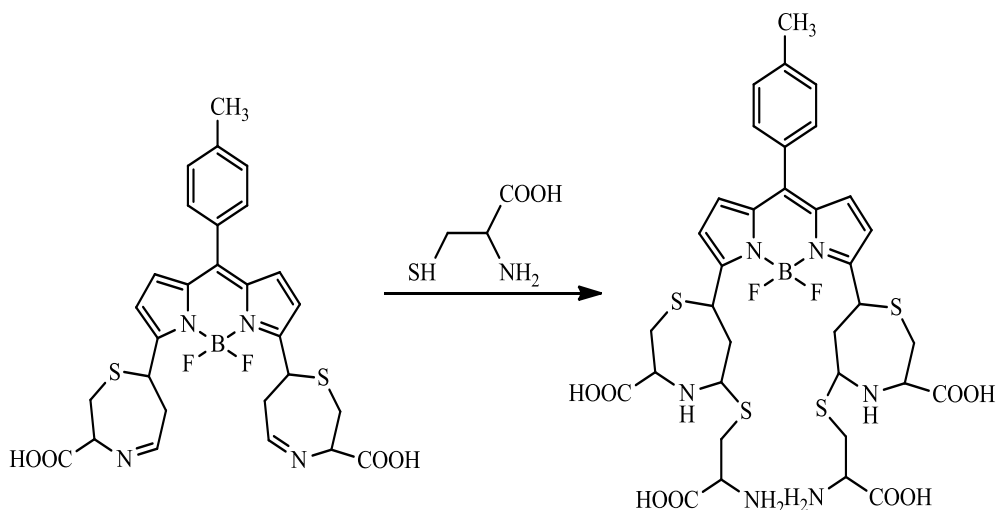
Novel BODIPY-based fluorogenic probe being synthesized, with an azide linked to the 2-position BODIPY ring. We investigated the chemistry of the BODIPY fluorophore due to benefits such as intense absorption in visible light, relatively high molar extinction coefficient (ϵ), biocompatibility, and chemical and photochemical stability [34]. The significance of BODIPY-cholesterol in the trafficking of sterols in living cells and organisms [35], a substituent made up of the side chain of cholesterol. The Synthesis of a new boron-Dipyrromethene (BODIPY) is shown in **Scheme 3** [36].



Scheme 3: Synthesis of a new boron-Dipyrromethene (BODIPY) based fluorogenic probe

- 2. Fluorescent Dyes:** Due to their beneficial photophysical properties, such as photostability, high absorption coefficients and high fluorescence quantum yields, BODIPYs are excellent fluorescent dyes that are used in a variety of research fields as

labeling reagents, fluorescent switches, chemosensors, light harvesting systems, and dye-sensitized solar cells [37]. Homocysteine and cysteine in living cells can be detected using BODIPY [38] is shown in **Scheme 4**.



Scheme 4: BODIPY Show Cysteine And Homocysteine in Living Cells

BODIPY derived hydrazones show fluorescent properties [39] in **Figure 7**. Hydrazone formation in BODIPY would also affect the absorption and emission spectra of the BODIPY fluorophore. This aliphatic hydrazone and aromatic hydrazone [40] are shown in **Figure 8**.

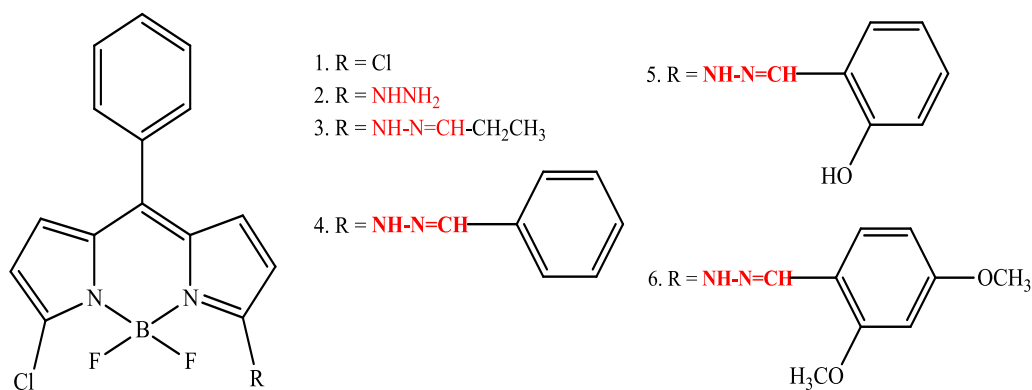


Figure 7: BODIPY Derived Hydrazones Show Fluorescent Properties

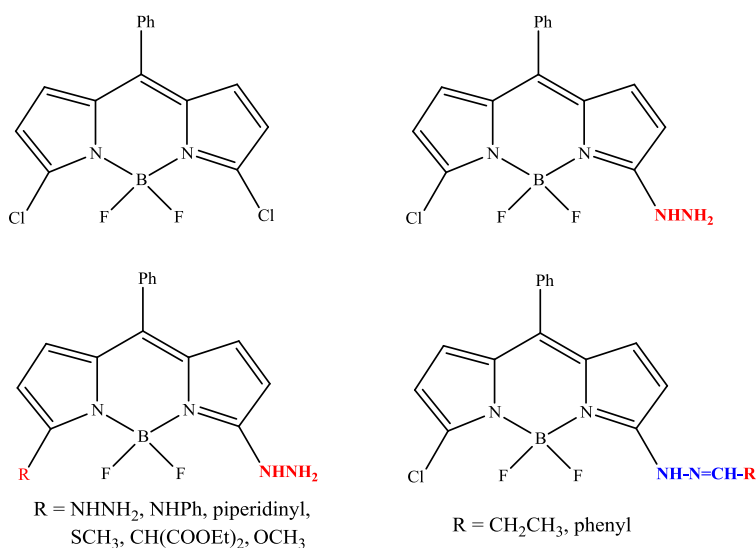
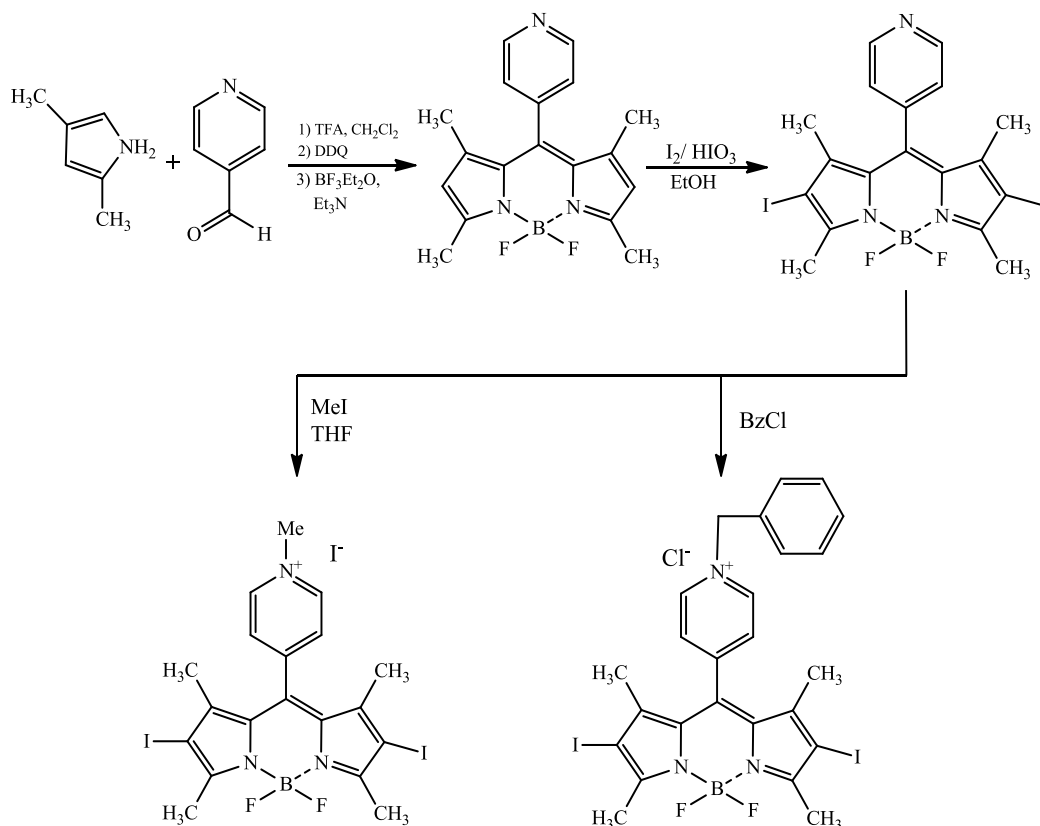


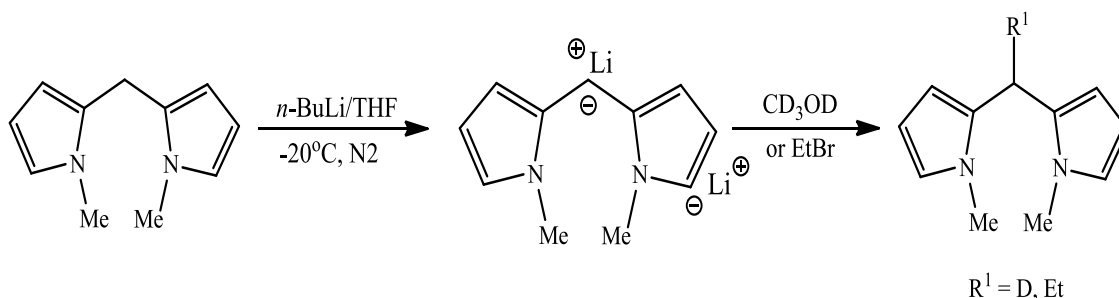
Figure 8: Aliphatic and Aromatic hydrazone Show Fluorescent Properties

- 3. Photosensitizers:** BODIPY photosensitizers are adaptable dyes that have never been used against prokaryotes in a photodynamic application. LED lamps can offer the photosensitizing substance and safe light that are necessary for photodynamic therapy. BODIPY photosensitizers show antimicrobial activity [41, 42] is shown in **Scheme 5**.



Scheme 5: BODIPY Photosensitizers Show Antimicrobial Activity

- 4. Regioselective Lithiation of Dipyrromethanes:** The feasibility of region selective lithiation of *N, N'*-dimethyl dipyrromethanes have been synthesized to avoid the formation of anion at more basic nitrogen centers and also show suitable conditions for lithiation of *meso*-position. This is shown in **Scheme 6**.



Scheme 6: Regioselective Lithiation of *N, N'*-Dimethyl Dipyrromethane

- 5. BODIPY Dyes for Protein Conjugation:** Due to their chemical stability and photophysical characteristics, BODIPYs are extremely important molecules in the field of biomolecule labeling. Several biotechnological applications depend on the conjugation of fluorophores to proteins and BODIPY dyes to be used in this field is shown in **Figure 9** [43].

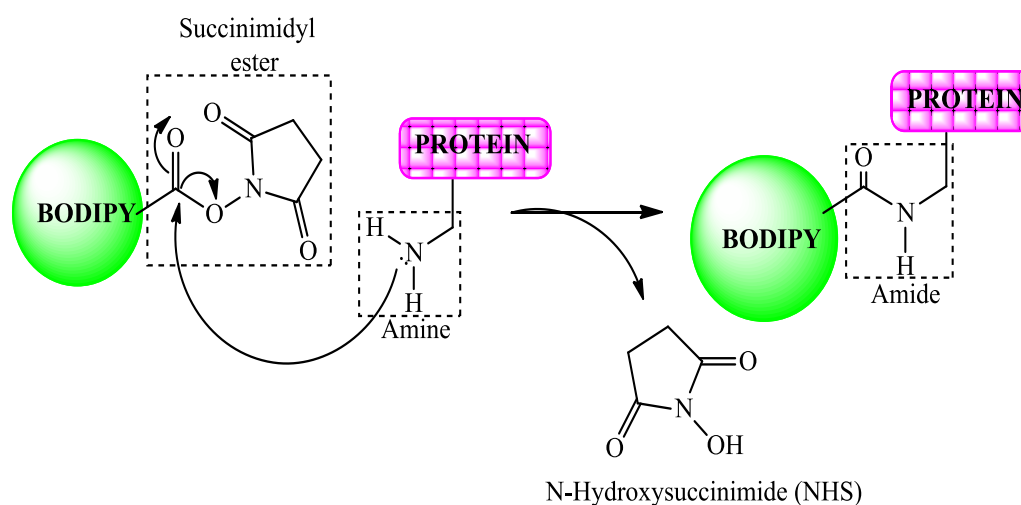
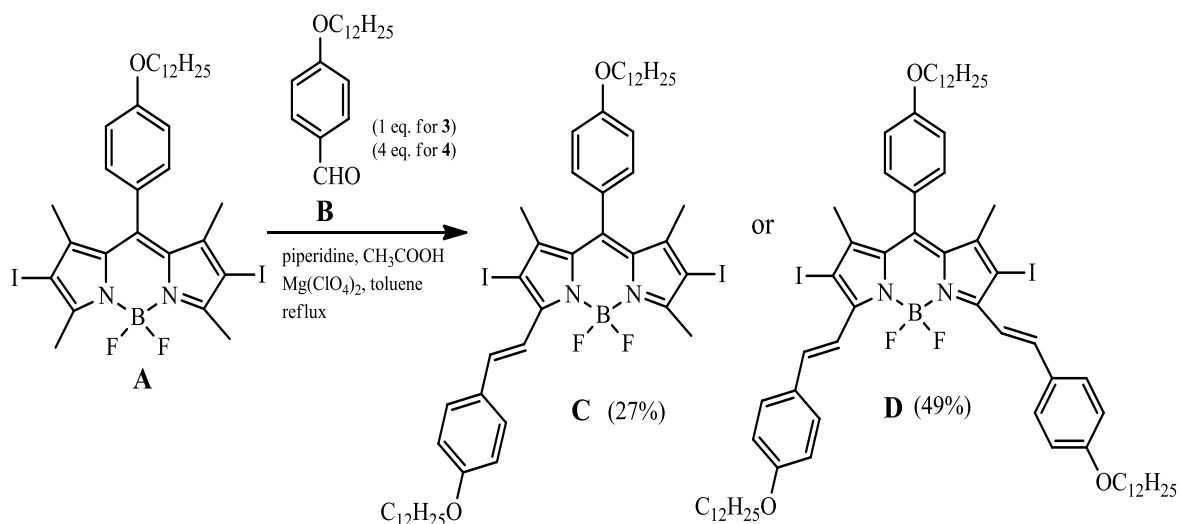


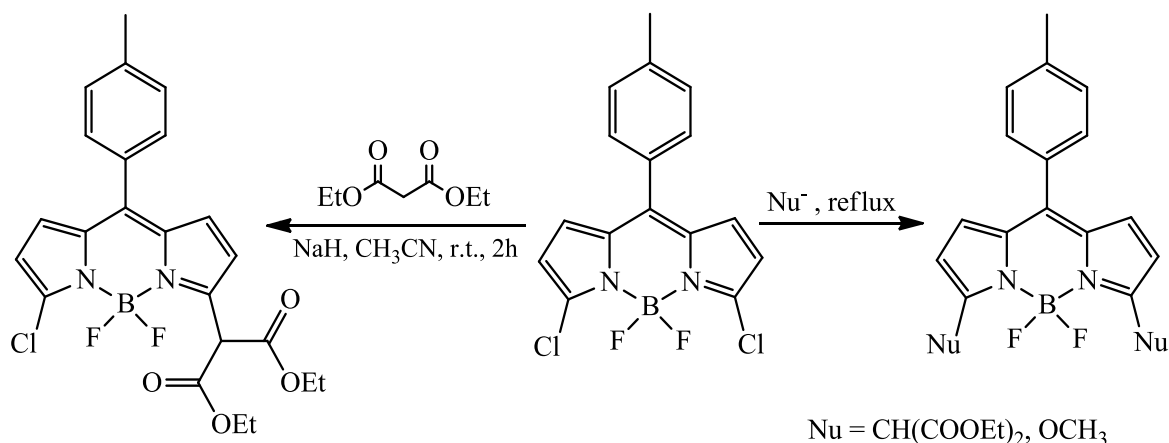
Figure 9: Reaction of Amine Labeling with Succinimidyl Ester Derivatives

- 6. Second-order NLO Properties:** The chromophore comprises a conjugated system with strong electron donor and acceptor groups at the opposite ends, which produce a significant dipole in the molecules and permitting second-order NLO effects [44], are shown in **Scheme 7**.



Scheme 7: BODIPY Show NLO Properties

- 7. Photophysical Properties:** UV-Vis absorption, steady-state, and time-resolved fluorimetry have all been used to examine the solvent-dependent photophysical characteristics of BODIPY is shown in following compounds (**Scheme 8**) [45].



Scheme 8: Solvent-Dependent Photophysical Properties of BODIPY

- 8. Dipyrromethane Chemosensors:** Chemosensors are synthetic analogues of biosensors, the difference being that biosensors incorporate biological receptors such as antibodies, aptamers or large biopolymers. A molecular structure (organic or inorganic complexes) is called a molecular sensor or chemosensor when it is utilized to sense an analyser and generate a measurable change or a signal. In order for a chemosensor to work, a molecular interaction must take place. This interaction often entails the constant monitoring of a chemical species' activity in a specific matrix, such as solution, air, blood, tissue, waste effluents, drinking water, etc. Chemosensing, a type of molecular recognition, is the term used to describe the use of chemosensors [46-48]. Chemosensors may also be electrochemically based on small molecules. Much emphasis has been

focused on the creation of chemosensors for the detection of physiologically and environmentally significant metal ions, such as Cu^{2+} , Zn^{2+} , Hg^{2+} , and Pb^{2+} [49, 50].

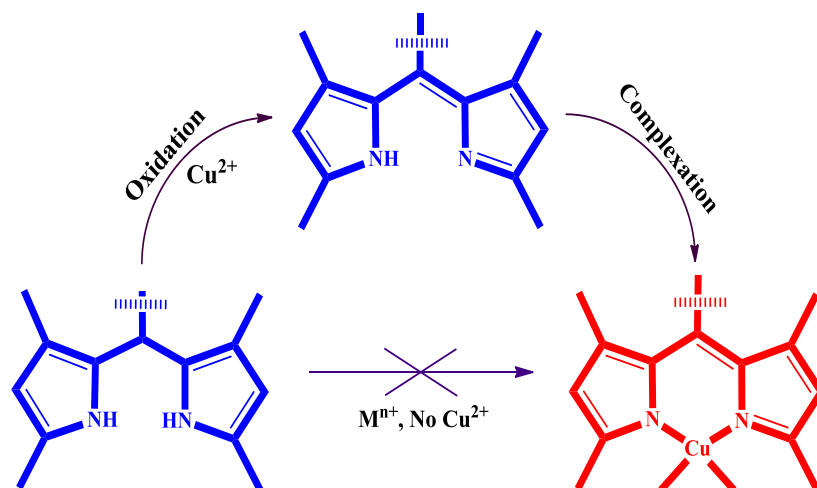


Figure 10: Dipyrromethane's C-H Oxidation and Chelation by Cu Were Used to Create a Quick, Colorimetric, Naked-Eye Cu (II) Chemosensor

Fluorescence chemosensors that detect metal ions via fluorescence enhancement are easier to monitor than those that use fluorescence quenching due to sensitivity issues. Dipyrins are complexes with metal ions using a C-H oxidation-based sensor for dipyrromethane [51].

Charge transfer complexes of dipyrromethanes have also been reported to show excellent selectivity for inorganic anions and neutral molecules [52, 53]. In both biological and environmental systems, sensors for the detection of heavy-transition-metal ions have made advances. Since UV-Vis and fluorescence spectroscopy analyses continue to be the most widely used detection methods due to their high sensitivity and simple operation, the development of probes for heavy-transition-metal selective colorimetric and/or fluorescent sensing systems has emerged as a research hotspot.

To date, various fluorescent probes based on quinoline, anthracenone, [54, 55] fluorescein, [56, 57] and rhodamine coumarin, fluorophores have been successfully applied to the detection of Zn^{2+} in vitro and / or in vivo. However, Zn^{2+} is found in the same elemental group as Cu^{2+} and causes comparable photophysical changes in sensors, using these sensors to distinguish between Zn^{2+} and Cu^{2+} remains difficult [58, 59]. Dipyrromethane is oxidized to dipyrromethene (**Figure 11**). Fluorescent "turn-on" Zn sensors made of dipyrromethene are proposed. The sensitivity of dipyrromethane to Zn^{2+} ions is greater. [60, 61].

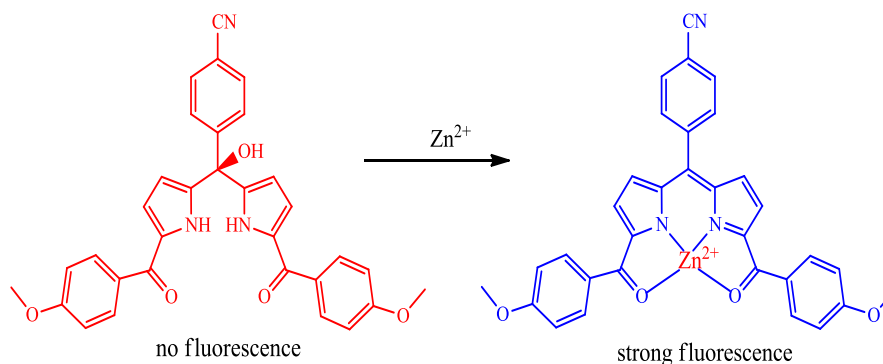


Figure 11: Oxidation of Dipyrromethane Accompanied by Coordination with Zn^{2+}

BODIPYs have a strong track record in the field of diagnostic fluorescent imaging dyes and have many traits with porphyrins and corroles, such as their bright color and fluorescence [62]. The BODIPYs structure is now being improved for absorption at higher wavelengths, with a focus on enhancing excited triplet state production for use in photodynamic treatment [63]. It is possible to achieve this by adding halogen atoms to the BODIPY backbone or by using BODIPY-anthracene dyads that are free of heavy elements.

Dipyrromethanes are frequently used as building blocks for the selective synthesis of meso-substituted BODIPYs and porphyrinoids, which are both of great importance in chemical synthesis [64, 65]. Specifically, BODIPYs are easily available from dipyrromethanes via a three-step one-pot synthesis [66, 67]. *Meso*-positional substitution has a significant impact on the stability of *meso*-substituted dipyrromethanes. In this position, electron-withdrawing substituents prevent the dipyrromethane from breaking down. Additionally, electron withdrawing substituents make the dipyrromethane. BODIPY have also been used as accessory pigments in light-harvesting arrays [68].

9. Biological Applications: Dipyrromethane compound shows various biological applications are as follows:

- **Antibacterial Activity and Antioxidant Activity:** Two gram-negative [*Escherichia coli* (ATCC 25922), *Pseudomonas aeruginosa* (ATCC 27853)] and two gram-positive [*Staphylococcus aureus* (ATCC 25923) and *Bacillus subtilis* (MTCC 121)] bacterial strains were used to test BODIPY's in vitro antibacterial activity (**Figure 12**) show good antibacterial activity. Uncontrolled H_2O_2 accumulates in biological systems result in oxygen free radical production, which severely damages cell membranes. A molecule of water is used to neutralize H_2O_2 after the antioxidant chemicals contribute electrons to it [69].

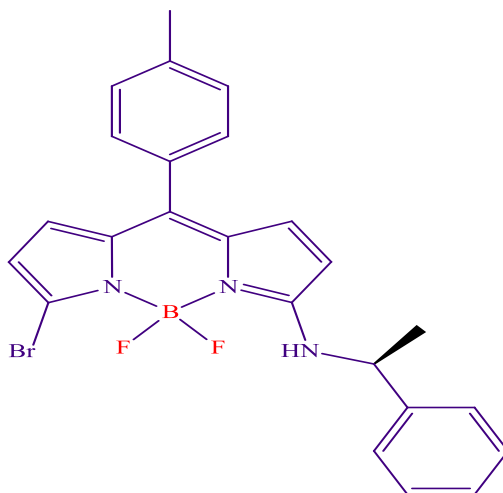


Figure 12: BODIPY Show Antibacterial Activity

- **Antimycobacterial Activity:** The antimycobacterial activity of synthetic drugs against *M. tuberculosis* was evaluated using the MABA method. All the synthesized compounds show good antimycobacterial activity as shown in **Figure 13** [70].

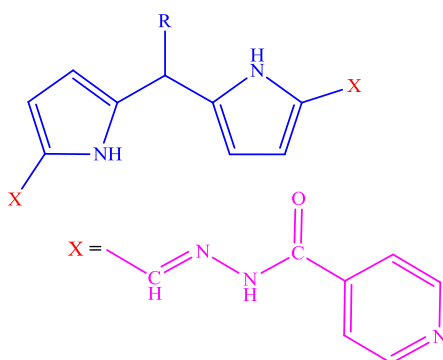


Figure 13: Dipyrromethane Show Antimycobacterial Activity

- **Anti-inflammatory Agents:** Dipyrromethanes used as a structural framework, exhibit promising biological action as anti-inflammatory drugs as shown in **Figure 14**. Nitric oxide synthesis generates the production of a minor free radical called NO. It is a crucial signaling molecule that regulates numerous physiological processes, including host defense, neurotransmission, neurotoxicity, and vasodilation. The tumoricidal and bactericidal effects of macrophages are mediated by the physiological or normal generation. However, tissue damage and inflammation can also be amplified by NO overproduction. As a result, in the formation of an anti-inflammatory drug, inhibiting the production of NO is a very therapeutic target [71].

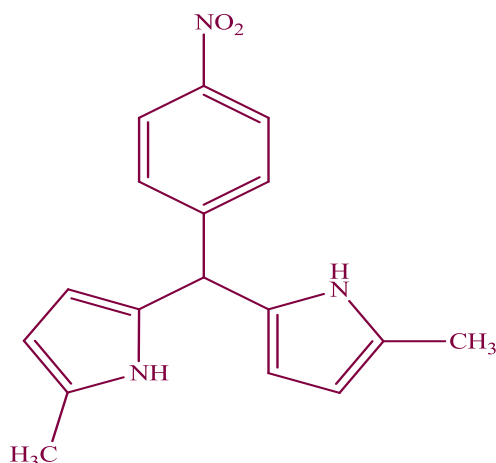
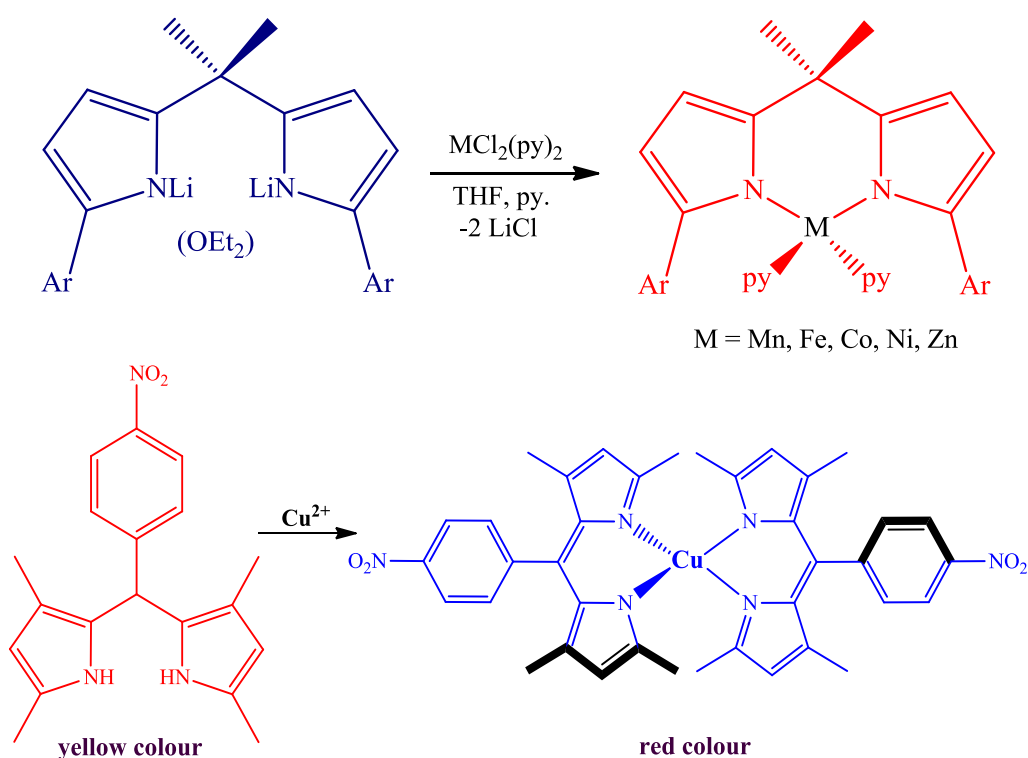


Figure 14: Dipyrromethane show anti-inflammatory activity

- Metal Complex:** A metal complex is made up of a fundamental metal atom or ion that connects to one or more ligands, which are ions or molecules that have one or more pairs of electrons that the metal can share. Lewis acid-base interaction causes a metal ion and ligand to combine to form a complex ion [72-75]. When dipyrromethane reacts with $MCl_2(py)_2$, a divalent metal precursor, it produces metalated species of dipyrromethane metal complex that result upon isolation are pale yellow (Mn), bright orange (Fe), maroon (Co), crimson (Ni), and yellow (Zn) as shown in **Scheme 9**.



Scheme 9: Dipyrromethane Metal Complexes Works as Fluorescent Material

Lewis base are ligand with one or more lone pairs of electrons, while Lewis acid are positively charged metal ions. A central metal atom is surrounded by ligands, which are non-metallic atoms or groups of atoms, in coordination compounds [76-79]. Due to their potential for use in photocatalysis, photovoltaics, electroluminescence, luminescence bioimaging and molecular sensing, photodynamics, fundamental photochemistry studies, and more recently, triplet-triplet annihilation upconversion, transition-metal complexes have received a lot of attention recently [80-82]. The BODIPYs chromophore is included in the Pt (II) Schiff base complex is shown in **Figure 15** [83].

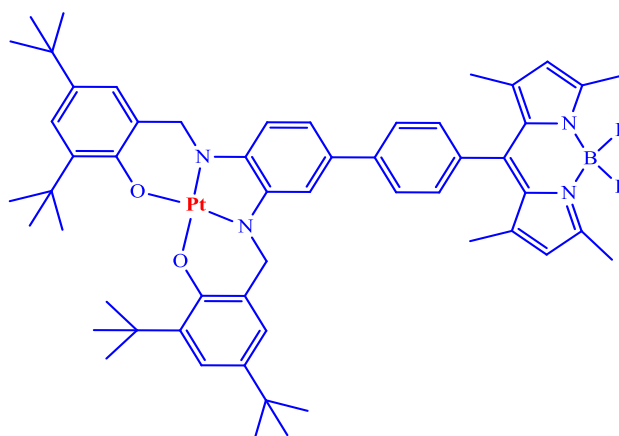
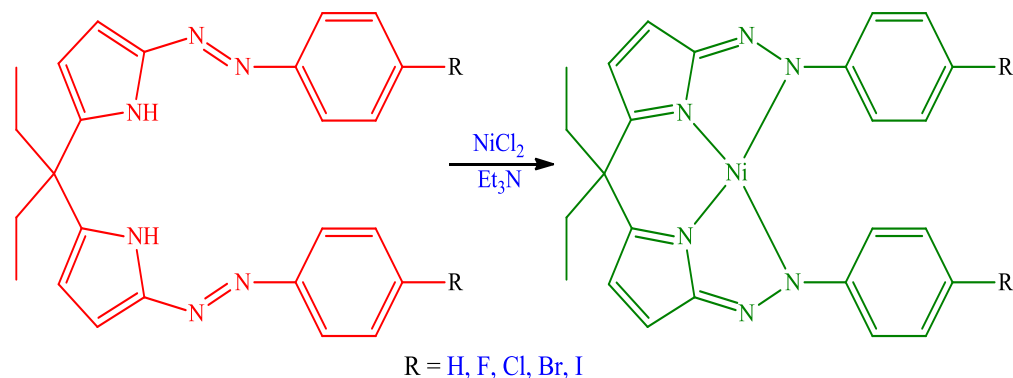


Figure 15: Visible-light-harvesting BODIPYs Chromophore

In the presence of Et_3N , 5, 5'-bis(diazo-dipyrrromethane) and NiCl_2 in methanol were combined to form nickel diazo-dipyrrromethane [84] is shown in **Scheme 10**.



Scheme 10: Synthesis of Nickel Diazo-Dipyrrromethane

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