CHAPTER-2

SYNTHESIS AND CHARACTERIZATION OF DISPERSE DISAZO DYES

2.1 Background

During the last 40 years a significant effort has been made to replace red and blue anthraquinone disperse dyes with technically equivalent azo dyes, for both environmental and economic reasons. In this regard, azo dyes based on heterocyclic amines have been developed, and the resultant dyes have higher tinctorial strength and give brighter dyeings than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, isothiazole, thiophene compounds afford very electronegative diazo components and, consequently, provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds. Moreover, it is well known that the ring systems of this type are useful for providing blue and green azo dyes. Azo dyes for polyester are normally of the monoazo type however a number of disazo compounds have reached commercial status.

In this context, Iroh and coworkers have reported the synthesis of reactive dyes of Mannich base containing ω-(dimethylamino) propiophenone groups and their applicabilities in dyeing nylon-6, viscose rayon fibers by studying fixation and fastness properties. Mannich bases have also been reported in patents as coupling components for synthesis of light sensitive diazo materials employed in photoprinting technology. These compounds give a stable dye-image of dark color tone by reaction with diazonium compound and improved water solubility.

T. B. Shah and coworkers in our laboratory have synthesized Mannich Base polymers by condensation of four different phenols with formaldehyde and piperazine using Mannich reaction. These Mannich base polymers have been used as a coupling component in coupling reaction with six diazonium salts of aromatic amines to yield novel polymeric disperse azo dyes. The applicabilities of these polymeric dyes in textile dyeing have been assessed by dyeing polyester and nylon fabrics and examining their fastness properties.
Moreover, recently T.B. Shah and coworkers\textsuperscript{17} in our laboratory have reported the application of Mannich bases of benzimidazole as dye precursors in the synthesis of disperse and acid azo dyes. They have prepared the N-Mannich bases of benzimidazole, respectively with m-aminophenol and o-tolidine using Mannich reaction as shown in \textbf{Scheme 2.1}. The dyeability of the two series dyes have been assessed and are found to be 80-90\% on polyester and nylon with good wash fastness and moderate light fastness properties.

\textbf{Scheme 2.1: Synthesis of Disperse Azo Dyes of Mannich Bases}

Besides this, they have recently reported the synthesis of N-Mannich bases derived from nitrogen containing five membered heterocyclic compounds viz; benzimidazole, benzotriazole, and 2-methylbenzimidazole with formaldehyde and different diamines such as m-phenylenediamine, p-phenylenediamine and benzidine \textbf{Scheme 2.2} and
used as diazonium component in synthesis of disperse azo dyes by coupling with different phenols. The dyeing characteristics of these disperse azo dyes have been investigated by dyeing polyester and nylon fabrics and studying their fastness properties.\(^\text{18}\)

**Scheme 2.2: Synthesis of Disperse Azo Dyes of Mannich Bases**

Prompted by these reports and in continuation of this work, it was contemplated to design, synthesize and evaluate dyeing properties of new heterocyclic disperse disazo dyes derived from Mannich bases of dihydropyrimidine (DHPMs) as diazonium component and different substituted phenols as coupling components. The dyeing characteristics of these disperse disazo dyes have been investigated by dyeing polyester and nylon fabrics and studying their fastness properties. The outlines of work performed in the field of synthesis and dyeing properties of new disperse disazo dyes derived from N-Mannich base of DHPM are given in the following.
A. Synthesis and Characterization of N-Mannich Bases:

- Synthesis of eight hydrogen active substrates 3,4-Dihydropyrimidiones (DHPMs) by Biginelli reaction of four aromatic aldehydes with ethyl acetoacetate and urea or thiourea. Characterization of these DHPMs in terms of their general properties, elemental analysis and spectral studies (FT-IR, \(^1\text{H}\) NMR, \(^{13}\text{C}\) NMR and Mass).

- Mannich reaction of each of the 3,4-Dihydropyrimidiones (DHPMs) with p-phenylenediamine and formaldehyde in presence of hydrochloric acid as catalyst to afford eight N-Mannich bases. These Mannich bases are characterized in terms of their general properties and elemental analysis and spectral studies (FT-IR, \(^1\text{H}\) NMR, \(^{13}\text{C}\) NMR and Mass) for structure determination.

B. Synthesis and Characterization of Disperse Disazo Dyes

- Application of each of eight Mannich base as a diazonium component in the synthesis of disperse disazo dyes by diazotization and subsequent coupling reaction respectively with ten different phenolic coupling components to yield eight series disperse disazo dyes.

- Characterization of all disperse disazo dyes for determining chemical composition, chemical structure by estimating number of azo groups, studying general properties, elemental analysis and spectral studies (UV-visible, FT-IR, \(^1\text{H}\) NMR, \(^{13}\text{C}\) NMR and mass).

2.2 An Overview of Reactions

Prior to giving actual experimental details of synthesis of disperse disazo dyes, it would be more reasonable to discuss the important chemical aspects of the three main chemical reactions involved in these syntheses.

- Biginelli reaction an important “Multicomponent reaction” for the synthesis of dihydropyrimidines.

- Mannich reaction of heterocyclic compounds containing active hydrogen on nitrogen atom of the heterocyclic ring to yield N-Mannich bases.

- Diazotization and coupling reaction used for synthesis of azo dyes.
Biginelli reaction

Biginelli condensation is an important “Multicomponent Reaction” for the synthesis of dihydropyrimidine (DHPMs). The classical reaction was first reported by pietro Biginelli reaction in 1893. This is very simple one-pot, acid catalyzed condensation reaction of ethylacetoacetate, benzaldehyde, and urea to yield dihydropyrimidine (Scheme 2.3).\(^{19}\)

![Scheme 2.3: Biginelli Reaction](image)

The original cyclocondensation reaction has been extended widely to include variations in all the three components. Of these, the aldehyde component has been varied to the large extent to many aromatic, aliphatic and heterocyclic aldehydes.\(^ {19-22}\) Another unusual for aldehyde used is \(\alpha, \beta\) – dichloroethyl ether which yields 4-chloromethyl derivatives. A part from common alkyl acetoacetate as \(\beta\)-keto ester components, other acetoacetic acid ester such as benzyl acetoacetate, (-)-menthyl acetoacetate, \(\beta\)-chloroethyl acetoacetate, 2-furanylmethyl acetoacetate and ethylthioacetoacetates have been used successfully in the Biginelli reaction.\(^ {23-25}\) Primary, secondary and tertiary acetoacetatemides have been used in place of ester to produce pyrimidine-5-carboxamide and monosubstituted ureas or thioureas from exclusively N-1 substituted dihydropyrimidines.\(^ {26}\)

The mechanism of the Biginelli reaction has been investigated by several research groups. More recently Sweet and Fissekis\(^ {27}\) suggested the reaction mechanism that an aldol condensation reaction is the first and limiting step of the reaction eventually leading to carbenium ion 5 as the key intermediate in the reaction. Interception of cation 5 by urea forms another intermediate 7 which undergo cyclization to dihydropyrimidine 8 (Scheme 2.4).
Traditionally Biginelli reactions were conducted under strongly acidic conditions which suffer from poor yield and long reaction time period especially in the case of sterically substituted aldehydes. This has led to the development of several new synthetic methodologies which improved the yields compared to the original procedure. These new protocols involve the use of Lewis acid, and/or transition metal salts. However, these catalysis have limitation like high cost and use of strong acids. Therefore search for a milder and more efficient protocol for the synthetic DHPMs continues to draw the attention of researchers.

The current importance and interest in DHPMs of Biginelli type is mainly due to their therapeutic and pharmacological properties. Biginelli compounds show a diverse range of biological activities such antihypertensive, calcium channel blockers, cardiovascular activity. Since 1986, a number of publications and patents dealing with the studies of DHPMs has grown rapidly. In recent publications, the study stereo chemical aspects of dihydropyrimidine are also well documented. Fikret Karci et.al reported the synthesis of some new disazo pyrazolo [1,5-a] pyrimidine derivatives.

**Mannich reaction**

Mannich reaction also referred as aminomethylation in general is a three component condensation reaction in which a substrate containing acidic hydrogen atom (RH), reacts with formaldehyde and an amine to form the product called Mannich base. In this Mannich base, nitrogen atom of the amine is linked to the substrate through methylene group. There have been extensive investigations on the mechanism of Mannich reaction. The reaction proceeds via initial nucleophilic...
reaction of amine 9 with formaldehyde 10 to give adduct 11, which are converted into an iminium ion species 12 through protonation and subsequent loss of water. The iminium ion species 12 then reacts with enol 13 of the CH-acidic substrate by overall loss of proton to give a product 14. (Scheme 2.5)

**Scheme 2.5: Mannich Reaction**

The acidic hydrogen atom of the substrate (R-H) could be present at a carbon atom or heteroatom such as nitrogen, sulfur, oxygen, phosphorus, the aminomethylation may lead to the corresponding C-, N-, S-, O- and P- Mannich base respectively. Though the substrate R-H employed in Mannich reaction are of structurally different class of compounds, they have a common feature of high degree of nucleophilicity. The structural variations performed were of three types, aromatic substitution, side chain modification, and terminal modification as shown in 15. 

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The aminomethylation of aromatic substrates and heterocyclic substrates either nitrogen containing or sulfur containing or both hetero atoms have been widely studied for the synthesis and modification of biologically active compounds. It also provides a convenient access to many useful synthetic building blocks as amino group can be easily converted into a variety of other functionalities. Consequently Mannich bases are very useful intermediates in the synthetic chemistry for number of reactions like deaminomethylation, deamination, reduction, cyclization, hydrogenation, alkylation etc.

The amine reagents are mostly employed as free bases in presence of acetic acid or as the easily accessible hydrochloride. In addition to this, aliphatic amines, hydroxylamine or hydrazine can be used. The extensive research deals predominantly with secondary amines mainly because the use of primary amine in aminomethylation may lead to a mixture of secondary and tertiary Mannich bases. Tertiary amines can not be used because of lack of protons on the tertiary nitrogen atom. Mannich reaction with the secondary cyclic amines such as morpholine, piperidine and pyrrolidine to afford aminomethyl derivatives. Besides this, the other heterocyclic amines like benzotriazole, imidazole, indole, pyrazole, thiazole etc have also been employed in Mannich reaction.

Formaldehyde, both in the form of formalin solution or as paraformaldehyde, is the most used aldehyde component in the synthesis of Mannich bases. The other aldehydes or ketones used are either aliphatic or aromatic. Acetaldehyde was used in a limited number of cases and that of aromatic aldehydes were used in presence of appropriate catalyst. Recently the successful replacement of formaldehyde with dichloromethane or methylene dihalides for the aminomethylation of several substrates, have also been reported in literature.

Far from being only important to theoretical research, Mannich bases also exhibit a wide range of applications in organic synthesis. The most significant contributions of Mannich reaction to applied research lie in the field of pharmaceutical chemistry, biomimetics and the other technological applications ranging from detergent, flocculants chelators, anticorrosion chemicals and crosslinking agents. Because of their manifold reactivity, Mannich bases are useful
intermediates in a number of organic reactions such as in synthesis of azo dyes, elimination of amine to form an α,β-unsaturated carbonyl compound, substitution reaction of amino group used as alkylation agent and addition reaction with organolithium or organomagnesium yield β-aminoalcohols 49-51.

At present the great potentialities of Mannich reactions are far from being exhausted and are still of interest for researchers. A number of recent studies are devoted to “non-classical” Mannich reactions using new substrates, modified methods for the synthesis and chemical transformations using several novel catalytic systems.52 The main advantages of such developments are the higher yield and purity of the products; safe, ecofriendly and economically feasible technology.

In conclusion, understanding of Mannich reaction and use of Mannich bases for large scale production of chemicals as well as for synthesis of exotic materials are some of the intellectual challenges of chemist, scientist and pharmacist. Consequently over the last two decades, a large number of literature reports and patents have been documented for the synthesis and pharmacological activity of Mannich bases derived from various heterocyclic compounds.

**Diazotization and Coupling Reactions**

There have been three major developments in the chemistry of diazonium salts: elucidation of complex mechanism of diazotization, development of the method for “the direct introduction of the diazonium group” and the mechanism of coupling reaction of diazonium salts. It has reported that under normal reaction conditions diazotization with nitrous acid leads to a diazonium salt in two steps by scrambling of nitrogen atom in a diazonium salt and the rate determining step is N-nitrosation. In other words, amine behaves as a nucleophile, donating the lone-pair of electrons of nitrogen to the electrophilic derivatives of nitrous acid as shown in following

\[
\begin{align*}
\text{ArNH}_2 + \text{NO}_2^- & \rightarrow \text{ArN}_2^+ + \text{H}_2\text{O} \\
\text{ArN}_2^+ + \text{X}^- & \rightarrow \text{ArN}_2\text{X} \\
\text{X} = \text{HO} & \quad \text{Nitrosic acid} \\
\text{NO}_2 & \quad \text{Nitrous acid anhydride} \\
\text{Cl} & \quad \text{Nitrosyl chloride}
\end{align*}
\]
Inspite of the wide variety of conditions employed in diazotization reactions, an aromatic compound is converted into a diazonium salt by a nitrous acid solution through formation of aromatic nitroso compound intermediate. The mechanism of the nitrosation process depends on the nature of nitrosating medium. Weakly basic amines such as p-nitro aniline and 2,4-dinitro aniline are normally diazotized by using moderately strong acid. The methods of diazotization of aromatic amines are described by Saunders and Allen and by Zollinger.

Diazotization involves the initial N-nitrosation of the aromatic amine. There are a number of nitrous acid derivatives which can effect nitrosation and these include $\text{N}_2\text{O}_3$, $\text{NOX}$ (X= Cl, Br, I), $\text{H}_2\text{NO}_2^+$ and $\text{NO}^+$. In dilute neutral medium, nitrous anhydride ($\text{N}_2\text{O}_3$) is the main agent. Halide ions can effectively catalyzed the diazotization by forming nitrosyl halides. In more acidic medium the nitrous acidium ion is the predominant nitrosation agent.

Diazotization of aromatic carbocyclic compounds, phenols, and their derivatives, tertiary aromatic amines can be effectively performed using nitrosylchloride while for aromatic sulfonic acids, carboxylic acids and nitro compounds, catalytic amount of mercuric sulfate is added to sodium nitrite solution in excess nitrosyl sulfuric acid. The diazotization of heteroaromatic amines are somewhat ticklish. In spite of the great increase in interest for disperse dyes based on heterocyclic dazocomponents, little systematic knowledge is available. The difficulties in the diazotization of hetero aromatic amine is the protonation at the nitrogen containing hetero ring which decreases the nucleophilicity of the amine group and the diazotization of heterocyclic amines in contrast to that of aromatic amines does not go to completion but to an equilibrium between the amine and the diazonium ion. This equilibrium favors the protonated amine when the acidity is increased. In spite of this, the simplest method of diazotizing heteroaromatic amines involves the use of nitrosyl sulfuric acid and improved by addition of a mixture of concentrated acetic acid and propionic acids. The aromatic and heteroaromatic diazonium ions formed are susceptible to irreversible decomposition reaction and therefore diazotization and azo coupling reactions need to be carried out at as low temperature as possible (generally < $5^0$C). Heterocyclic amines such as pyrroles and pyrazole can be diazotized in a similar manner to that of phenols to form
“diazopyrroles” and “diazopyrazoles” which are extremely stable substance using parent heterocyclic amino compound.

Coupling reaction of diazonium salts with aromatic nuclei was recognized as an electrophilic substitution, analogous to aromatic nitration sulfonation etc. The coupling reaction has been the subject of extensive study. It involves an electrophilic attack by the diazonium ion at a highly nucleophilic centre in the coupling agent. i.e. at a position of high electron density. The coupling compounds include phenols, naphthols, aromatic amines and organic compounds containing reactive methylene groups and they undergoes coupling reaction visualized in Scheme 2.6

The coupling reaction may be accompanied by competing side reactions where in the diazonium salt may decompose with evolution of nitrogen or may form diazonium compounds. For laboratory synthesis, the optimum condition for coupling depends largely on the nature of coupling component and diazonium component. As the present work deals with the diazotization of N-Mannich Bases and coupling with different phenolic components, it would be more appropriate to discuss the position of coupling i.e. attachment of azo group in the phenols. The position of the attachment of azo group follows o- or p- to the directing group. The para position is favored over the ortho. The following are the preferred position for coupling reaction:
The coupling reaction of phenols is carried out in the alkaline medium and that of amines is carried out in acidic medium. Phenol coupled faster than amines. The presence of electron withdrawing groups such as $\text{-NO}_2$, $\text{-SO}_3\text{H}$, $\text{-COOH}$ in diazonium component favor the coupling reaction whereas that of electron releasing groups like $\text{-CH}_3$, $\text{-Cl}$, $\text{-OCH}_3$ in coupling component makes the coupling reaction more easier.

Various heterocyclic amines such as 5-pyrazole, 2-methyl and phenylindole, 1,3,3-trimethylene indolenine, imidazole, barbituric acid and pyridone derivatives, hydroxyquinolines and quinolines are reported in patents as coupling components. Most important yellow disperse dyes based on pyridone derivatives as coupling components are reported for dyeing polyesters\textsuperscript{30,57}.

2.3 Synthesis and Characterization of Dihydropyrimidones

N-Mannich bases required for the synthesis of disperse disazo dyes were synthesized in two steps. The first step involved the preparation of hydrogen active precursors 3,4-Dihydropyrimidones (DHPMs) by Biginelli reaction of aromatic aldehydes with ethylacetooacetate and urea or thiourea according to procedure reported in literature\textsuperscript{58}. The second step followed was the Mannich reaction of each of the DHPMs with p-phenylenediamine and formaldehyde to give eight different Mannich bases. All of these chemical compounds were characterized by analyzing their general properties, elemental analysis and spectral studies.

Experimental

Materials

Ethylacetoacetate, aromatic aldehydes namely benzaldehyde, salicyaldehyde, p-anisaldehyde, vanillin and urea/thiourea were used of commercial L.R. grade after purification. All other chemicals and solvents were used of L.R. grade.

2.3.1 Synthesis

3, 4-Dihydropyrimidin-2(1H)-ones: ($BU_1$)

A mixture of benzaldehyde (5.3 gm, 0.05 mol), ethyl acetoacetate (5ml, 0.05 mol), and urea (3 gm, 0.05 mol) and a few drops of HCl as catalyst was refluxed in methanol for about 55 min. The progress of the reaction was monitored continuously by TLC. After completion of reaction, the resulting mixture was cooled. The solid
was filtered off and washed several times with methanol. The product was further recrystallization by methanol. In a similar manner the other three dihydropyrimidinones BU₂, BU₃ and BU₄ were prepared by using salicyaldehyde, p-anisaldehyde and vanillin respectively.

### 3, 4-Dihydropyrimidin-2(1H)-thiones (BT₁)

The dihydropyrimidinethione (BT₁₋₄) were synthesized by the Biginelli reaction of above mentioned aromatic aldehydes with ethyl acetoacetate and thiourea according to the procedure used for dihydropyrimidinones.

**Scheme 2.7** shows the synthetic protocol involved in the synthesis of DHPMs (BU₁₋₄, BT₁₋₄). The chemical structure and IUPAC names of DHPMs are furnished in **Table 2.1** and their analytical and spectral data are given following section.

![Scheme 2.7: Synthetic Protocol for 3,4-Dihydropyrimidinones (DHPMs)](image)

#### 2.3.2 Characterization

All the melting points (°C) were determined on a melting point apparatus and are uncorrected. C, H, N analysis was carried out on Perkin Elmer (USA) 2400, Series II. The FT-IR spectra were obtained with “NICOLET-400 D” FT-IR Spectrometer in KBr pellets. ¹H NMR and ¹³C NMR spectra were scanned on “FT-NMR, BRUKER, 400 MHz Instrument” in DMSO-d₆ and CDCl₃ solvent using TMS as an internal standard. Mass spectra were recorded on Shimadzu GCMS QP 2010 instrument. The spectral characterization data of all DHPM precursors are furnished and interpreted in the following section.
Table 2.1: Chemical Structure of 3,4-Dihydropyrimidones (BU- and BT-series)

<table>
<thead>
<tr>
<th>BU-series</th>
<th>BT-series</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BU&lt;sub&gt;1&lt;/sub&gt;</strong></td>
<td><strong>BT&lt;sub&gt;1&lt;/sub&gt;</strong></td>
</tr>
<tr>
<td><img src="image" alt="BU1 structure" /></td>
<td><img src="image" alt="BT1 structure" /></td>
</tr>
<tr>
<td>ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
<td>ethyl 6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><strong>BU&lt;sub&gt;2&lt;/sub&gt;</strong></td>
<td><strong>BT&lt;sub&gt;2&lt;/sub&gt;</strong></td>
</tr>
<tr>
<td><img src="image" alt="BU2 structure" /></td>
<td><img src="image" alt="BT2 structure" /></td>
</tr>
<tr>
<td>ethyl 4-(2-hydroxyphenyl)6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
<td>ethyl 4-(2-hydroxyphenyl)6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><strong>BU&lt;sub&gt;3&lt;/sub&gt;</strong></td>
<td><strong>BT&lt;sub&gt;3&lt;/sub&gt;</strong></td>
</tr>
<tr>
<td><img src="image" alt="BU3 structure" /></td>
<td><img src="image" alt="BT3 structure" /></td>
</tr>
<tr>
<td>ethyl 4-(4-methoxyphenyl)6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
<td>ethyl 4-(4-methoxyphenyl)6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><strong>BU&lt;sub&gt;4&lt;/sub&gt;</strong></td>
<td><strong>BT&lt;sub&gt;4&lt;/sub&gt;</strong></td>
</tr>
<tr>
<td><img src="image" alt="BU4 structure" /></td>
<td><img src="image" alt="BT4 structure" /></td>
</tr>
<tr>
<td>ethyl 4-(3-hydroxy-4-methoxyphenyl)6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
<td>ethyl 4-(3-hydroxy-4-methoxyphenyl)6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
</tbody>
</table>
• **Analytical and Spectral data of DHPMs (BU-Series)**

**BU₁:** White solid, mp 202-203°C, Yield 85%, Anal. Calcd for C₁₄H₁₆N₂O₃, M.W.: 260, Calc. C, 64.60; H, 6.20; N, 10.76; found C, 60.40; H, 6.18; N, 10.75. IR (υ cm⁻¹): Benzene ring: 1620, 1480, 1430 (skeletal vibration), 3110 (C-H stretching), 750 and 700 (C-H and C=C bending for mono substituted ring), 1110 (C-H in-plane bending); aliphatic methyl group (-CH₃): 2910 (C-H asymm and symm stretching), 1480 (C-H bending); carbonyl of ester group (CH₃-C=O-O): 1730 (-C=O stretching), 1190 (-C=O-C stretching of propionate); Secondary amide (-NH-C=O-H): 1700 (-C=O stretching), 3240 (N-H asymm and symm stretching), 1650 (-NH in plane bending), 1270, 1500 (coupling of N-H bending and -C-N stretching), 650 (O-C-N bending), 690 (N-H out of plane bending). ¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 4.0 (2H, q, CH₂ of ester group), 5.1 (1H, s, H on pyrimidine ring), 7.7 (1H, s, NH of pyrimidine ring), 9.2 (1H, s, NH of pyrimidine ring), 7.2-7.3 (5H, m, aromatic proton). ¹³C NMR: 14.5, 17.2, 54.4, 59.6, 101.75, 128.8, 129.0, 129.4, 139.7, 145.3, 160.4, 165.8. Mass (m/z): 260 (M⁺), 245, 231, 214, 183, 155, 137, 110, 96, 77, 67, 42.

**BU₂:** White solid, m.p.227-228°C, Yield 82%, Anal. Calcd for C₁₄H₁₆N₂O₄, M.W.: 276, Calc C, 60.80; H, 5.84; N, 10.14; found C, 60.40; H, 5.80; N, 10.12; IR (υ cm⁻¹): benzene ring: 1605, 1460, 1510 (skeletal vibration), 3000 (C-H stretching), 760 and 720 (C-H and C=C bending for mono substituted ring) 1090 (C-H in-plane bending); aliphatic methyl group (-CH₃): 2890 (C-H asymm and symm stretching), 1415 (C-H bending); carbonyl of ester group (CH₃-C=O-O): 1710 (-C=O stretching), 1190 (-C=O-C stretching of propionate); Secondary amide (-NH-C=O-H): 1690 (-C=O stretching), 3290 (N-H asymm and symm stretching), 1605 (-NH in plane bending), 1240, 1510 (coupling of N-H bending and -C-N stretching), 660 (O-C-N bending), 720 (N-H out of plane bending). functional group: 3350 (O-H stretching), ¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 4.0 (2H, q, CH₂ of ester group), 5.1 (1H, s, H on pyrimidine ring), 8.9 (1H, s, NH of pyrimidine ring), 9.2 (1H, s, NH of pyrimidine ring), 7.2-7.3 (4H, m, aromatic proton), 7.7 (1H, s, OH group). ¹³C NMR: 13.5, 17.5, 48.1, 59.6, 102.7, 117.6, 118.6, 121.4, 127.6, 129.3, 146.1, 152.6, 155.4, 165.81.
**BU₃**: Creamy white solid, m.p. 200 - 201 °C, Yield 79%. Anal. Calcd for C₁₅H₁₈N₂O₄, M.W.: 290 Calc C, 62.06; H, 6.25; N, 9.65; found C, 62.05; H, 6.21; N, 9.63; IR (υ cm⁻¹): benzene ring: 1640, 1520, 1450 (skeletal vibration), 3100 (C-H stretching), 860 and 700 (C-H and C-C bending for mono substituted ring), 1100 (C-H in-plane bending); aliphatic methyl group (-CH₃): 2890 (C-H asymm and symm stretching), 1440 (C-H bending); carbonyl of ester group (CH₃-C=O-O): 1720 (-C=O stretching), 1200 (-C-O-C stretching of propionate); Secondary amide (-NH-C=O-H): 1705 (-C=O stretching), 3250 (N-H asymm and symm stretching), 1640 (-NH in plane bending), 1260, 1510 (coupling of N-H bending and -C-N stretching), 660 (O-C-N bending), 690 (N-H out of plane bending) functional group: 1060, 1280 (-C-O-C- symm. and asymm stretching of -OCH₃). $^1$H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.2 (3H, s, CH₃ of pyrimidine ring), 4.0 (2H, q, CH₂ of ester group), 5.0 (1H, s, H on pyrimidine ring), 7.7 (1H, s, NH of pyrimidine ring), 9.3 (1H, s, NH of pyrimidine ring), 6.9 - 7.2 (4H, m, aromatic proton), 3.7 (3H, s, OCH₃ group). $^{13}$C NMR: 14.5, 17.2, 53.7, 55.5, 60.6, 101.1, 113.1, 113.6, 131.5, 131.7, 133.8, 147.3, 154.5, 158.6, 167.8.

**BU₄**: Light yellow solid, m.p., 202-203 °C, Yield 80% Anal. Calc for C₁₅H₁₈N₂O₅, M.W.: 306, Calc C, 58.82; H, 5.92; N, 9.15; found C, 58.60; H, 5.91; N, 9.10; IR (υ cm⁻¹): benzene ring: 1630, 1520, 1460 (skeletal vibration), 3110 (C-H stretching), 860 and 680 (C-H and C-C bending for mono substituted ring), 1100 (C-H in-plane bending); aliphatic methyl group (-CH₃): 2890 (C-H asymm and symm stretching), 1430 (C-H bending); carbonyl of ester group (CH₃-C=O-O): 1700 (-C=O stretching), 1210 (-C-O-C stretching of propionate); Secondary amide (-NH-C=O-H): 1650 (-C=O stretching), 3210 (N-H asymm and symm stretching), 1650 (-NH in plane bending), 1280, 1520 (coupling of N-H bending and -C-N stretching), 610 (O-C-N bending), 680 (N-H out of plane bending), functional group: 3510 (O-H stretching), 1020, 1220 (-C-O-C- symm. and asymm stretching of -OCH₃). $^1$H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.2 (3H, s, CH₃ of pyrimidine ring), 4.0 (2H, q, CH₂ of ester group), 5.0 (1H, s, H on pyrimidine ring), 8.9 (1H, s, NH of pyrimidine ring), 9.5 (1H, s, NH of pyrimidine ring), 6.6 - 6.7 (3H, m, aromatic proton), 3.7 (3H, s, OCH₃ group), 7.7 (1H, s, OH group). $^{13}$C NMR: 13.5, 17.5, 52.12, 56.04, 61.18, 101.9, 112.9, 115.88, 123.63, 127.07, 146.8, 155.6, 158.63, 166.1
• **Analytical and Spectral data of DHPMs (BT-Series)**

**BT\(_1\):** White solid, m.p. 207-208 °C, Yield 85%, Anal. Calcd for C\(_{14}\)H\(_{16}\)N\(_2\)O\(_2\)S. M.W.:276, Calc C, 60.85; H, 5.84; N, 10.14; found C, 60.80; H, 5.82; N, 10.12; IR (\(v\) cm\(^{-1}\)): benzene ring: 1550,1490,1420 (skeletal vibration), 3000 (C-H stretching), 750 and 700(C-H and C-C bending for mono substituted ring), 1120 (C-H in-plane bending ); aliphatic methyl group (-CH\(_3\) ): 2890 (C-H asymm and symm stretching), 1470 (C-H bending) ; carbonyl of ester group (CH\(_3\)-C=O-O): 1690 (-C=O stretching), 1180 (-C-O-C stretching of propionate); Secondary amide (-NH-C=S-H): 1260 (-C=S stretching), 3200 (N-H asymm and symm stretching), 1610 (-NH in plane bending), 1280 (coupling of N-H bending and -C-N stretching), \(^1\)H NMR: \(\delta\) 1.0 (3H, t, CH\(_3\) of ester group), 2.2 (3H, s, CH\(_3\) of pyrimidine ring), 4.0 (2H, q, CH\(_2\) of ester group), 5.1 (1H, s, H on pyrimidine ring), 9.7 (1H, s, NH of pyrimidine ring), 10.3(1H, s, NH of pyrimidine ring),7.2-7.3 (5H, m, aromatic proton).\(^1\)C NMR: 14.4, 17.6, 54.5, 60.0, 101.1, 126.8, 128.1, 129.1, 140.9, 165.5, 174.7. Mass (m/z): 276 (M\(^+\)), 247, 231, 199, 186, 155, 137, 116, 111, 96, 77, 67, 51, 42.

**BT\(_2\):** White solid, m.p. 199-200 °C, Yield 83%, Anal. Calcd for C\(_{14}\)H\(_{16}\)N\(_2\)O\(_3\)S, M.W.: 292, Calc C, 57.52; H, 5.52; N, 9.58; found C, 56.92; H, 5.43; N, 9.11; IR (\(v\) cm\(^{-1}\)): benzene ring: 1590, 1550, 1500 (skeletal vibration), 3110 (C-H stretching), 760 and 710 (C-H and C-C bending for mono substituted ring), 1110 (C-H in-plane bending ); aliphatic methyl group (-CH\(_3\) ): 2930 (C-H asymm and symm stretching), 1430 (C-H bending) ; carbonyl of ester group (CH\(_3\)-C=O-O): 1720 (-C=O stretching), 1210 (-C-O-C stretching of propionate); Secondary amide (-NH-C=S-H): 1240 (-C=S stretching), 3140 (N-H asymm and symm stretching), 1610 (-NH in plane bending), 1290 (coupling of N-H bending and -C-N stretching), functional group: 3410 (O-H stretching). \(^1\)H NMR: \(\delta\) 1.0 (3H, t, CH\(_3\) of ester group), 2.2 (3H, s, CH\(_3\) of pyrimidine ring), 4.0 (2H, q, CH\(_2\) of ester group), 5.1 (1H, s, H on pyrimidine ring), 8.9 (1H, s, NH of pyrimidine ring), 9.2 (1H, s, NH of pyrimidine ring), 7.2-7.3 (4H, m, aromatic proton), 8.7 (1H, s, OH group). \(^1\)C NMR: 13.5, 17.2, 52.7, 59.4, 104.8, 119.0, 120.2, 122.0, 127.0, 128.8, 154.7, 165.5, 175.8
**BT₃:** Off white solid, m.p. 150-151⁰C, Yield 85%. Anal. Calcd for C₁₅H₁₈N₂O₃S, M.W.: 306, Calc C, 58.80; H, 5.92; N, 9.14; found C, 58.75; H, 5.91; N, 9.12; IR (ν cm⁻¹): benzene ring: 1590, 1500, 1440 (skeletal vibration), 3010 (C-H stretching), 860 and 690 (C-H and C-C bending for mono substituted ring), 1130 (C-H in-plane bending); aliphatic methyl group (-CH₃): 2910 (C-H asymm and symm stretching), 1440 (C-H bending); carbonyl of ester group (CH₃-C=O-O): 1690 (-C=O stretching), 1180 (-C-O-C stretching of propionate); Secondary amide (-NH-C=S-H): 1270 (-C=S stretching), 3160 (N-H asymm and symm stretching), 1610 (-NH in plane bending), 1290 (coupling of N-H bending and -C-N stretching), functional group: 1030, 1270 (-OCH₃).¹H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.2 (3H, s, CH₃ of pyrimidine ring), 4.0 (2H, q, CH₂ of ester group), 5.1 (1H, s, H on pyrimidine ring), 9.0 (1H, s, NH of pyrimidine ring), 9.2 (1H, s, NH of pyrimidine ring), 6.9 -7.2 (4H, m, aromatic proton), 3.7 (3H, s, OCH₃ group).¹³C NMR: 14.5, 17.2, 54.4, 58.2, 60.6, 110.4, 116.1, 116.2, 131.4, 131.7, 134.5, 146.6, 154.6, 167.8, 175.8.

**BT₄:** Light yellow solid, m.p. 206-207⁰C, Yield 88%. Anal. Calcd for C₁₅H₁₈N₂O₄S, M.W.: 322, Calc C, 55.89; H, 5.83; N, 8.69; found C, 55.40; H, 5.82; N, 8.55; IR (ν cm⁻¹): benzene ring: 1600, 1520, 1490 (skeletal vibration), 3000 (C-H stretching), 890 and 690 (C-H and C-C bending for mono substituted ring), 1110 (C-H in-plane bending); aliphatic methyl group s(-CH₃): 2890 (C-H asymm and symm stretching), 1460 (C-H bending); carbonyl of ester group (CH₃-C=O-O): 1710 (-C=O stretching), 1200 (-C-O-C stretching of propionate); Secondary amide (-NH-C=S-H): 1300 (-C=S stretching), 3190 (N-H asymm and symm stretching), 1600 (-NH in plane bending), 1290 (coupling of N-H bending and -C-N stretching), functional group: 3400 (O-H stretching), 1030, 1270 (-C-O-C- symm. and asymm stretching of -OCH₃).¹H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.2 (3H, s, CH₃ of pyrimidine ring), 4.0 (2H, q, CH₂ of ester group), 5.0 (1H, s, H on pyrimidine ring), 10.2 (1H, s, NH of pyrimidine ring), 9.7 (1H, s, NH of pyrimidine ring), 6.6 -6.7 (3H, m, aromatic proton), 3.8 (3H, s, OCH₃ group), 9.5 (1H, s, OH group).¹³C NMR: 14.5, 1.5 52.1, 56.0, 60.0, 103.4, 111.1, 112.9, 123.15, 145.0, 156.6, 157.8, 165.7, 174.5.
2.3.3 Results and Discussion

The synthetic route followed for the DHPMs is outlined in Scheme 2.7. The reaction of aromatic aldehydes namely benzaldehyde, salicyaldehyde, anisaldehyde and vanillin with urea in ethanolic medium containing few drops of conc. HCl gave dihydropyrimidinones (BU₁-₄) and with thiourea dihydropyrimidinethiones (BT₁-₄) in good yields of 80% to 89%. The purity of these compounds was checked by melting point, TLC and elemental analysis. The analytical data of C, H and N content of all DHPMs are in good agreement with calculated values (Table 2.1) based on proposed structure shown in the scheme. The structure of DHPMs was established on the basis of spectral data (FT-IR, ¹H NMR, and ¹³C NMR). FT-IR, ¹H NMR, ¹³C NMR and Mass spectra of these compounds are shown in Fig. 2.1-2.5. The FT-IR spectra of BU- and BT-series showed the following common characteristic absorption bands.

**Benzene ring**
- Skeletal vibration: 1640-1550, 1550-1460, 1510-1420 cm⁻¹
- C-H stretching: 3110-3000 cm⁻¹
- C-H in-plane bending: 1130-1090 cm⁻¹

**Aliphatic methyl group (-CH₃)**
- C-H stretching: 2930-2890 cm⁻¹
- C-H bending: 1480-1415 cm⁻¹

**Carbonyl of ester group (C=O)**
- C-O-C stretching: 1210-1180 cm⁻¹
- C=O stretching: 1730-1690 cm⁻¹

**Secondary amide (NH-C=O-NH) of pyrimidine ring (BU series)**
- C=O stretching of amide: 1705-1650 cm⁻¹
- O-C-N bending: 660-610 cm⁻¹
- N-H stretching: 3290-3210 cm⁻¹
- N-H in plane bending: 1650-1605 cm⁻¹
- N-H out of plane bending: 720-680 cm⁻¹
- C-N-H stretching (Due to Coupling of N-H bending and C-N stretching): 1520-1500 cm⁻¹

**Secondary thioamide (NH-C=S-NH) of pyrimidine ring (BT series)**
- C=S stretching: 1300-1240 cm⁻¹
- N-H stretching: 3200-3140 cm⁻¹
- N-H in plane bending: 1610-1600 cm⁻¹
- C-N-H stretching (Due to Coupling of N-H bending and C-N stretching): 1290-1240 cm⁻¹
Fig. 2.1: IR, $^1$H NMR and $^{13}$C NMR Spectra of BU$_1$ and BT$_1$ DHPMs
Fig. 2.2: Mass Spectra of $\text{BU}_1$ and $\text{BT}_1$ DHPMs
Fig. 2.3: IR, $^1$H NMR and $^{13}$C NMR Spectra of BU$_2$ and BT$_2$ DHPMs
Fig. 2.4: IR, $^1$H NMR and $^{13}$C NMR Spectra of BU$_3$ and BT$_3$ DHPMs
Fig. 2.5: IR, $^1$H NMR and $^{13}$C NMR Spectra of BU$_4$ and BT$_4$ DHPMs
Interpretation of $^1$H and $^{13}$C NMR spectra of two representative DHPMs (BU$_1$ and BT$_1$) is discussed here in detail. The chemical structure of BU$_1$ (16) and BT$_1$ (17) are shown below

![Chemical structures of BU1 (16) and BT1 (17)]

In $^1$H NMR spectrum of BU$_1$ (16), two singlet were observed at $\delta$ 2.3 and 1.0 ppm integrating for 3H of C$_7$ and C$_{10}$ of ester group. One quartet was observed at $\delta$ 4.0 ppm for 2H of C$_9$ proton. The 1H of C$_4$, N$_1$ and N$_3$ atoms of pyrimidine ring appeared as a singlet at $\delta$ 5.1, 7.7 and 9.2 ppm respectively and that of 5H of aromatic ring were observed as multiplate in the region $\delta$ 7.2-7.3 ppm. In $^{13}$C NMR spectrum of BU$_1$, methyl carbons C-7 and C-10 at $\delta$ 13.7 and 17.3 ppm, methylene carbon C-9 at $\delta$ 54.4 ppm, pyrimidine ring carbons C-4, C-5 and C-6 at $\delta$ 54.4, 101.7 and 145.3 ppm, aromatic carbons C-11 to C-16 at $\delta$ 126.7, 127.7, 128.8 and 129.3 ppm, carbonyl carbons C-2 and C-8 at $\delta$ 160.4 and 165.8 ppm observed are in agreement with the literature $^{58,59}$.

In addition to this, the mass spectrum of BU$_1$ the molecular ion peak (M$^+$) at m/z 260 is in agreement with the molecular weight (C$_{14}$H$_{16}$N$_2$O$_3$). The base peak observed at m/z 183 may be due to the loss of phenyl radical (C$_6$H$_5^-$, m/z 77). Other important mass peaks obtained at m/z 245 and 231 may be due to the loss of methyl (CH$_3^-$) and ethyl (C$_2$H$_5^-$) radicals respectively. The formation of fragmented ions at m/z 42 and 77 may have composition C$_2$H$_4$N$^+$ and C$_6$H$_5^+$ respectively.

Analogously, $^1$H NMR spectrum of BT$_1$ (17), showed two singlet observed at $\delta$ 2.2 and 1.0 ppm integrating for three protons of C$_7$ and C$_{10}$ of ester group. One quartet is observed at $\delta$ 4.0 ppm for two of C$_9$ proton. The 1H of C$_4$, N$_1$ and N$_3$ proton appeared as a singlet at $\delta$ 5.1, 9.7 and 10.3 ppm respectively. 5H of aromatic ring were observed as multiplate in the region $\delta$ 7.2-7.3 ppm. In $^{13}$C NMR spectrum of BT$_1$ the molecular ion peak (M$^+$) at m/z 256 is in agreement with the molecular weight (C$_{13}$H$_{16}$N$_2$O$_2$). The base peak observed at m/z 179 may be due to the loss of phenyl radical (C$_6$H$_5^-$, m/z 77). Other important mass peaks obtained at m/z 231 and 219 may be due to the loss of methyl (CH$_3^-$) and ethyl (C$_2$H$_5^-$) radicals respectively. The formation of fragmented ions at m/z 42 and 77 may have composition C$_2$H$_4$N$^+$ and C$_6$H$_5^+$ respectively.
methyl carbons C-7 and C-10 at $\delta$ 114.5 and 18.6 ppm, methylene carbon C-9 at $\delta$ 60.0 ppm, pyrimidine ring carbons C-4, C-5 and C-6 at $\delta$ 54.5, 101.7 and 145.9 ppm, aromatic carbons C-11 to C-16 at $\delta$ 126.7, 128.8, 129.3 and 140.9 ppm, thiocarbonyl carbons C-2 at $\delta$ 174.7 ppm and carbonyl carbon C-8 at $\delta$ 165.6 ppm observed are in agreement with the literature\textsuperscript{58}.

In addition to this, the mass spectrum of \( \text{BT}_1 \) the molecular ion peak (\( M^+ \)) at m/z 276 is in agreement with the molecular weight (\( \text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2\text{S} \)). The formation of base peak observed at m/z 199 is similar to that of \( \text{BU}_1 \) obtained due to the loss of phenyl radical (\( \text{C}_6\text{H}_5^- \), m/z 77). Other important mass peaks obtained at m/z 247 and 231 may be due to the loss of ethyl (\( \text{C}_2\text{H}_5^- \)) and ethyloxy (\( \text{CH}_3\text{CH}_2\text{O}^- \)) radicals respectively. The formation of fragmented ions at m/z 42 and 77 may have composition \( \text{C}_2\text{H}_4\text{N}^+ \) and \( \text{C}_6\text{H}_5^+ \) respectively.

In conclusion, the spectral data of \( \text{BU}_1 \) and \( \text{BT}_1 \) are in accordance with proposed chemical structure and are in agreement with literature report\textsuperscript{60-62}.
2.4 Synthesis and characterization of N-Mannich bases

Each of the eight DHPM precursors (BU and BT series) reported earlier was used as substrate (H-active compound) in Mannich reaction respectively with formaldehyde and p-phenylenediamine to give a eight N-Mannich compounds.

Experimental

Materials

Each of the DHPMs (BU and BT series) was used after recrystallization from appropriate solvents. p-phenylenediamine was used of commercial L.R grade after purification. While all other chemicals and solvents were used of LR grade.

2.4.1 Synthesis

Mannich base of 3,4-Dihydropyrimidin-2(1H)-ones: (MBU-Series)

The detail procedure for preparation of Mannich bases is given in the following section typically from BU₁ as substrate.

In a three necked flask equipped with a stirrer and dropping funnel, DMF solution of BU₁ (0.05 mol) and 37% formaldehyde (0.1 mol) were added under stirring. The reaction mixture was stirred at room temperature for half an hour to complete the reaction and to form methylol derivative of BU₁. To the resulting solution, a solution of p-phenylenediamine (0.1 mol) in DMF containing conc. HCl as catalyst was added dropwise with stirring during half an hour at room temperature and refluxed. The reaction was monitored continuously by TLC. After completion of reaction, the resulting mixture was cooled to room temperature and poured into crushed ice with continuous stirring. The solid separated was filtered off, washed thoroughly with hot water, air-dried and recrystallized from appropriate solvent to give N-Mannich base of BU₁ (1a). Other Mannich base of each of DHPMs (BU₂-BU₄) with p-phenylenediamine was prepared by following the same procedure resulted into formation a series of Mannich bases of dihydropyrimidinones 1b-d (MBU-Series). The purity of this Mannich bases was examined by TLC.
Mannich base of 3,4-Dihydropyrimidin-2(1H)-thiones (MBT-Series)

Analogously Mannich reaction of dihydropyrimidinethiones (BT<sub>1</sub>-BT<sub>4</sub>) with p-phenylenediamine afforded four Mannich bases of dihydropyrimidinethiones 2a-d (MBT-Series) and their purity was also checked by TLC.

Scheme 2.8 shows the general reaction protocol for both the series of Mannich bases. The chemical structures and IUPAC names of N-Mannich base compounds MBU- and MBT-Series are furnished in Table 2.2.

(a) N-Mannich base of 3,4-Dihydropyrimidin-2(1H)-ones (MBU-Series)

(b) N-Mannich base of 3,4-Dihydropyrimidin-2(1H)-thiones (MBT-Series)

Scheme 2.8: Reaction Protocol for Synthesis of N-Mannich Bases
Table 2.2: Chemical Structure of N-Mannich bases (MBU- and MBT-series)

<table>
<thead>
<tr>
<th>MBU series</th>
<th>MBT series</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1a</strong></td>
<td><strong>2a</strong></td>
</tr>
<tr>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>ethyl 1,3-bis((4-aminophenylamino)methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
<td>ethyl 1,3-bis((4-aminophenylamino)methyl)-6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><strong>1b</strong></td>
<td><strong>2b</strong></td>
</tr>
<tr>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>ethyl 1,3-bis((4-aminophenylamino)methyl)-4-(2-hydroxyphenyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
<td>ethyl 1,3-bis((4-aminophenylamino)methyl)-4-(2-hydroxyphenyl)-6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><strong>1c</strong></td>
<td><strong>2c</strong></td>
</tr>
<tr>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>ethyl 1,3-bis((4-aminophenylamino)methyl)-4-(2-methoxyphenyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
<td>ethyl 1,3-bis((4-aminophenylamino)methyl)-4-(2-methoxyphenyl)-6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><strong>1d</strong></td>
<td><strong>2d</strong></td>
</tr>
<tr>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>ethyl 1,3-bis((4-aminophenylamino)methyl)-4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
<td>ethyl 1,3-bis((4-aminophenylamino)methyl)-4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
</tbody>
</table>
2.4.2 Characterization

- **Analytical and Spectral data of N-Mannich bases (MBU Series)**

1a: Off white solid, m.p. 177-179\(^\circ\)C, Yield 68%, Anal. Calcd for C\(_{28}\)H\(_{32}\)N\(_6\)O\(_3\) M.W.500, Calc.: C, 67.18; H, 6.44; N, 16.79; found: C, 68.05; H, 6.34; N, 17.10. IR (v cm\(^{-1}\)): Benzene ring: 1640, 1510, 1470 (skeletal vibration), 3090 (C-H stretching), 750 and 680 (C-H and C-C bending for mono substituted ring), 1020 (C-H in-plane bending); aliphatic methyl group (-CH\(_3\)) : 2910 (C-H asymm and symm stretching), 1470 (C-H bending); carbonyl of ester group (CH\(_3\)-C=O-O): 1735 (-C=O stretching), 1180 (-C-O-C stretching of propionate); Aminomethylene bridge: 2950,2820 (-CH\(_2\) asymm. and symm. stretching), Primary amine (-NH\(_2\)): 3360 (N-H stretching), 1620 (N-H in plane bending), 1270 (-C-N stretching). Secondary amine (-NH): 3220 (N-H stretching), 1510 (-N-H in plane bending), 1290 (-C-N stretching) tert. Amide (N-C=O-N): 1710 (amide (I) band- C=O stretching), 1260 (amide (III) band –C-N bending), 620 and 530 (amide (IV) and (VI) OCN deformation). \(^1\)H NMR: δ 1.0 (3H, t, CH\(_3\) of ester group), 2.3 (3H, s, CH\(_3\) of pyrimidine ring), 3.5 (4H, s, two –NH\(_2\) of p-phenylene ring motifs) 4.0 (2H, q, CH\(_2\) of ester group), 4.8 (2H, s, two secondary –NH), 5.1 (2H, s, 2\(^{\text{nd}}\) methylene bridge), 5.3 (2H, s, 1\(^{\text{st}}\) methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.8 -7.3 (13H, m, three aromatic proton). \(^{13}\)C NMR: 14.5, 17.3, 39.4, 52.7, 60.3, 61.9, 99.9, 114.4, 114.5, 115.0, 118.0, 128.8, 128.9, 130.3, 131.2, 139.4, 141.4, 146.8, 167.5, Mass (m/z): 500 (M\(^+\)), 485, 471, 427, 424, 380, 378, 303, 289, 275, 259, 245, 229, 183, 155, 137, 110, 96, 77, 56, 42.

1b: White solid, m.p. 202-204\(^\circ\)C, Yield 72%, Anal. Calcd for C\(_{28}\)H\(_{32}\)N\(_6\)O\(_4\) M.W. 516, Calc.: C, 65.10; H, 6.24; N, 16.27; found: C, 65.42; H, 6.46; N, 16.79. IR (v cm\(^{-1}\)): Benzene ring: 1610, 1470, 1450 (skeletal vibration), 3000 (C-H stretching), 760 and 710 (C-H and C-C bending for mono substituted ring), 1020 (C-H in-plane bending); aliphatic methyl group (-CH\(_3\)) : 2810 (C-H asymm and symm stretching), 1470 (C-H bending); Carbonyl of ester group (CH\(_3\)-C=O-O): 1720 (-C=O stretching), 1200 (-C-O-C stretching of propionate); Aminomethylene bridge: 2910, 2810 (-CH\(_2\) asymm. and symm. stretching), Primary amine (-NH\(_2\)): 3310 (N-H stretching), 1610 (N-H in plane bending), 1260 (-C-N stretching). Secondary amine (-NH): 3250 (N-H stretching), 1510 (-N-H in plane bending), 1300 (-C-N stretching).
tert. Amide (N-C=O-N): 1630 (amide (I) band- C=O stretching), 1260 (amide (III) band –C-N bending), 630 and 580 (amide (IV) and (VI) OCN deformation), functional group: 3360 (O-H stretching). $^1$H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 3.5 (4H, s , two –NH$_2$ of p-phenylene ring motifs) 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.2 (2H, s, 2nd methylene bridge), 5.4 (2H, s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.9 -7.2 (12H, m, three aromatic proton), 8.3 (1H, s, OH group). $^{13}$C NMR: 14.5, 17.3, 38.5, 52.3, 53.2, 60.1, 100.0, 114.3, 114.4, 115.0, 115.2, 115.4, 115.7, 116.5, 117.6, 118.9, 119.0, 121.6, 127.6, 130.0, 138.1, 139.8, 140.6, 145.9,149.8, 153.0, 167.5.

**1c:** Light brown solid, m.p. 156-158 °C, Yield 70%, Anal. Calcd for C$_{29}$H$_{34}$N$_6$O$_4$ M.W.530, Calc.: C, 65.64; H, 6.46; N, 15.84; found: C, 65.78; H, 6.56; N, 16.02.

IR (υ cm$^{-1}$): Benzene ring: 1680, 1620, 1450 (skeletal vibration), 3110 (C-H stretching), 810 and 710 (C-H and C-C bending for mono substituted ring), 1020 (C-H in-plane bending ); Aliphatic methyl group(-CH$_3$ ) : 2800 (C-H asymm and symm stretching), 1480 (C-H bending ); Carbonyl of ester group (CH$_3$-C=O-O): 1725 (-C=O stretching), 1170 (-C-O-C stretching of propionate); Aminomethylene bridge: 2940, 2860 (-CH$_2$ asymm. and symm. stretching), Primary amine (-NH$_2$): 3260 ( N-H stretching), 1620 (N-H in plane bending), 1290 (-C-N stretching). Secondary amine (-NH): 3010 (N-H stretching), 1510 (-N-H in plane bending), 1340 (-C-N stretching) tert. Amide (N-C=O-N): 1640 (amide (I) band- C=O stretching), 1260 (amide (III) band –C-N bending), 660 and 580 (amide (IV) and (VI) OCN deformation), functional group: 1090, 1290 (-C-O-C- symm. and asymm stretching of -OCH$_3$). $^1$H NMR: δ 1.1 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 3.9 (4H, s , two –NH$_2$ of p-phenylene ring motifs) 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.1 (2H, s, 2nd methylene bridge), 5.4 (2H, s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.8 -7.3 (12H, m, three aromatic proton), 3.7 (3H, s, OCH$_3$ group), $^{13}$C NMR: 13.4, 17.3, 38.5, 52.3, 55.0, 56.2, 60.9, 99.5, 113.0, 113.1, 114.2, 114.5, 115.0, 118.0, 118.3, 130.0, 130.5, 130.9, 138.4, 139.5, 146.8, 149.1, 159.9, 167.5
1d: Off white solid, m.p. 210-212° C, Yield 78%, Anal. Calcd for C_{29}H_{34}N_{6}O_{5} M.W.546, Calc.: C, 63.72; H, 6.27; N, 15.37; found: C, 63.66; H, 6.19; N, 15.48. IR (υ cm⁻¹): Benzene ring: 1590, 1540, 1480 (skeletal vibration), 3110 (C-H stretching), 890 and 710 (C-H and C-C bending for mono substituted ring), 1010 (C-H in-plane bending ); aliphatic methyl group (-CH₃): 2860 (C-H asymm and symm stretching), 1460 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1735 (-C=O stretching), 1190 (-C-O-C stretching of propionate); Aminomethylene bridge: 2920, 2800 (-CH₂ asymm. and symm. stretching), Primary amine (-NH₂): 3200 (N-H stretching), 1590 (N-H in plane bending), 1280 (-C-N stretching). Secondary amine (-NH): 3110 (N-H stretching), 1540 (-N-H in plane bending), 1340 (-C-N stretching) tert. Amide (N-C=O-N): 1700 (amide (I) band- C=O stretching), 1280 (amide (III) band –C-N bending), 640 and 590 (amide (IV) and (VI) OCN deformation), functional group: 3550 (O-H stretching), 1050, 1220 (-C-O-C- symm. and asymm stretching of -OCH₃). \(^1\)H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 3.7 (4H, s, two –NH₂ of p-phenylene ring motifs) 4.0 (2H, q, CH₂ of ester group), 4.8 ( 2H, s, two secondary –NH), 5.1 (2H, s, 2nd methylene bridge), 5.3 (2H, s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.9 -7.3 (11H, m, three aromatic proton), 3.7 (3H, s, OCH₃ group), 8.5 (1H, s, OH group). \(^{13}\)C NMR: 13.3, 39.1, 52.3, 55.2, 56.8, 60.6, 99.1, 106.0, 107.0, 114.0, 115.1, 115.2, 115.5, 115.7, 118.0, 118.3, 128.2, 138.2, 139.7, 140.8, 145.1, 149.9, 156.3, 159.3, 167.5

- **Analytical and Spectral study of N-Mannich bases (MBT-Series)**

2a: Off white solid, m.p. 124-126° C, Yield 77%, Anal. Calcd for C_{28}H_{32}N_{6}O_{2}S M.W.516: C, 65.09; H, 6.24; N, 16.27; found: C, 65.58; H, 6.48; N, 14.20. IR (υ cm⁻¹): Benzene ring: 1580, 1470, 1440 (skeletal vibration), 3090 (C-H stretching), 750 and 710 (C-H and C-C bending for mono substituted ring), 1030 (C-H in-plane bending ); aliphatic methyl group (-CH₃): 2900 (C-H asymm and symm stretching), 1470 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1690 (-C=O stretching), 1200 (-C-O-C stretching of propionate); Aminomethylene bridge: 2960,2820 (-CH₂ asymm. and symm. stretching), Primary amine (-NH₂): 3300 (N-H stretching), 1580 (N-H in plane bending), 1260 (-C-N stretching). Secondary amine (-NH): 3160 (N-H stretching), 1510 (-N-H in plane bending), 1320 (-C-N stretching)
tert. thioamide (N-C=S-N): 1380 (C=S stretching), 641260 (C-N stretching). \(^1\)H NMR: \(\delta\) 1.1 (3H, t, CH\(_3\) of ester group), 2.4 (3H, s, CH\(_3\) of pyrimidine ring), 3.6 (4H, s, two \(-\text{NH}_2\) of p-phenylene ring motifs) 4.0 (2H, q, CH\(_2\) of ester group), 4.7 (2H, s, two secondary \(-\text{NH}\), 5.7 (2H, s, 2\(^{\text{nd}}\) methylene bridge), 5.9 (2H, s, 1\(^{\text{st}}\) methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 6.9-7.1 (13H, m, three aromatic proton).

\(^1^3\)C NMR: 14.4, 17.1, 42.4, 47.7, 60.0, 64.5, 96.7, 114.1, 118.0, 119.0, 131.3, 137.5, 139.3, 140.4, 140.7, 140.8, 145.1, 168.6, 184.7, Mass (m/z): 514 (M\(^+\)), 498, 441, 425, 409, 395, 318, 303, 289, 255, 245, 199, 155, 187, 174, 137, 110, 94, 77, 67, 42.

**2b:** Light yellow solid, m.p. 135-137\(^0\)C, Yield 67\%, Anal. Calcd for C\(_{28}\)H\(_{32}\)N\(_6\)O\(_3\)S M.W.532: C, 63.14; H, 6.06; N, 15.78; found: C, 63.19; H, 6.26; N, 15.89. IR (\(\nu\) cm\(^{-1}\)): Benzene ring: 1630, 1590, 1510 (skeletal vibration), 3190 (C-H stretching), 770 and 720 (C-H and C-C bending for mono substituted ring), 1030 (C-H in-plane bending); aliphatic methyl group (-CH\(_3\) ) : 2850 (C-H asymm and symm stretching), 1410 (C-H bending); Carbonyl of ester group (CH\(_3\)-C=O-O): 1730 (-C=O stretching), 1180 (-C-O-C stretching of propionate); Aminomethylene bridge: 2950, 2850 (-CH\(_2\) asymm. and symm. stretching), Primary amine (-NH\(_2\)): 3360 (N-H stretching), 1590 (N-H in plane bending), 1250 (-C-N stretching). Secondary amine (-NH): 3280 (N-H stretching), 1500 (-N-H in plane bending), 1320 (-C-N stretching) tert. thioamide (N-C=S-N): 1370 (C=S stretching), 641260 (C-N stretching). \(^1\)H NMR: \(\delta\) 1.1 (3H, t, CH\(_3\) of ester group), 2.2 (3H, s, CH\(_3\) of pyrimidine ring), 3.6 (4H, s, two \(-\text{NH}_2\) of p-phenylene ring motifs) 4.0 (2H, q, CH\(_2\) of ester group), 4.8 (2H, s, two secondary \(-\text{NH}\), 5.6 (2H, s, 2\(^{\text{nd}}\) methylene bridge), 5.9 (2H, s, 1\(^{\text{st}}\) methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 6.8 -7.1 (12H, m, three aromatic proton), 8.9 (1H, s, OH group). \(^1^3\)C NMR: 13.7, 17.3, 43.8, 45.7, 54.5, 61.9, 98.8, 114.1, 114.3, 114.5, 119.4, 119.6, 120.5, 129.6, 139.4, 140.2, 140.3, 140.8, 145.1, 153.6, 165.5, 184.5

**2c:** Light brown solid, m.p. 163-165\(^0\)C, Yield 80\%, Anal. Calcd for C\(_{29}\)H\(_{34}\)N\(_6\)O\(_3\)S M.W. 546, Calc.: C, 63.71; H, 6.27; N, 15.37; found: C, 63.50; H, 6.22; N, 14.94 IR (\(\nu\) cm\(^{-1}\)): Benzene ring: 1680, 1580, 1410 (skeletal vibration), 3080 (C-H stretching), 820 and 710 (C-H and C-C bending for mono substituted ring), 1030 (C-H in-plane bending); aliphatic methyl group (-CH\(_3\) ) : 2850 (C-H asymm and
symm stretching), 1450 (C-H bending); Carbonyl of ester group (CH$_3$C=O-O): 1730 (-C=O stretching), 1180 (-C-O-C stretching of propionate); Aminomethylene bridge: 2920, 2860 (-CH$_2$ asymm. and symm. stretching), Primary amine (-NH$_2$): 3300 (N-H stretching), 1610 (N-H in plane bending), 1270 (-C-N stretching). Secondary amine (-NH): 3120 (N-H stretching), 1500 (-N-H in plane bending), 1320 (-C-N stretching) tert. thioamide (N-C=S-N): 1360 (C=S stretching), 1270 (C-N stretching), functional group: 1030, 1250 (-C-O-C symm. and asymm stretching of -OCH$_3$). $^1$H NMR: δ 1.1 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 3.7 (4H, s, two –NH$_2$ of p-phenylene ring motifs) 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.6 (2H, s, 2$^\text{nd}$ methylene bridge), 5.8 (2H, s, 1$^\text{st}$ methylene bridge). 6.1 (1H, s, H on pyrimidine ring), 6.9 - 7.3 (12H, m, three aromatic proton), 3.9 (3H, s, OCH$_3$ group), $^{13}$C NMR: 13.3, 17.3, 45.1, 47.1, 57.3, 61.8, 65.8, 97.9, 114.0, 115.8, 118.3, 118.5, 119.1, 130.4, 139.2, 140.7, 145.1, 161.7, 168.1, 184.0.

2d: Off white solid, m.p. 186-188°C, Yield 75%. Anal. Calcd for C$_{29}$H$_{34}$N$_6$O$_4$S M.W.562 Calc.: C, 61.90; H, 6.09; N, 14.94; found: C, 61.63; H, 6.19; N, 14.74. IR (υ cm$^{-1}$): Benzene ring: 1590, 1510, 1480 (skeletal vibration), 3110 (C-H stretching), 830 and 710 (C-H and C-C bending for mono substituted ring), 1020 (C-H in-plane bending); aliphatic methyl group (-CH$_3$): 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH$_3$C=O-O): 1700 (-C=O stretching), 1190 (-C-O-C stretching of propionate); Aminomethylene bridge: 2910, 2840 (-CH$_2$ asymm. and symm. stretching), Primary amine (-NH$_2$): 3300 (N-H stretching), 1610 (N-H in plane bending), 1280 (-C-N stretching). Secondary amine (-NH): 3220 (N-H stretching), 1510 (-N-H in plane bending), 1320 (-C-N stretching) tert. thioamide (N-C=S-N): 1370 (C=S stretching), 1280 (C-N stretching), functional group: 3400 (O-H stretching), 1020, 1260 (-C=O-C symm. and asymm stretching of -OCH$_3$). $^1$H NMR: δ 1.1 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 3.7 (4H, s, two –NH$_2$ of p-phenylene ring motifs) 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.6 (2H, s, 2$^\text{nd}$ methylene bridge), 5.9 (2H, s, 1$^\text{st}$ methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 6.9 - 7.3 (11H, m, three aromatic proton), 3.9 (3H, s, OCH$_3$ group), 9.1 (1H, s, OH group). $^{13}$C NMR: 13.0, 17.1, 45.1, 47.1, 55.8, 56.3, 61.8, 97.9, 109.3, 111.4, 114.0, 114.1, 118.3, 118.5, 119.1, 122.2, 127.1, 139.4, 140.2, 140.7, 145.1, 155.2, 158.0 168.1, 184.4.
2.4.3 Results and Discussion

The synthetic route followed for the synthesis of N-Mannich base is outlined earlier in Scheme 2.8. The eight DHPMs (BU\textsubscript{1-4}, BT\textsubscript{1-4}) discussed in earlier section (2.4.1) were used in preparation of Mannich bases. The reaction conditions for the Mannich reaction were optimized by varying molar ratio of reactants, solvents and acidity level. It was observed that the most suitable molar ratio of DHPM, p-phenylenediamine and formaldehyde was 1:2:2 and the most suitable reaction medium was DMF containing concentrated HCl as catalyst. Each of DHPMs of BU and BT series was reacted with formaldehyde and p-phenylenediamine in DMF containing few drops of HCl to form corresponding Mannich base of dihydropyrimidinones \textbf{1a-d} and dihydropyrimidinethiones \textbf{2a-d} respectively. The reaction yields were between 70-80\% while the reaction time period was about 4 h. All Mannich base compounds are new and analyzed for their purity by m.p., TLC and C, H, N analysis. The structure of these compounds was assigned on the basis of analytical and spectral data. FT-IR, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and Mass spectra of these compounds are shown in Fig. 2.6-2.11. These data are interpreted typically for two Mannich bases \textbf{1a} and \textbf{2a} respectively derived from BU\textsubscript{1} and BT\textsubscript{1}. For the sake of better understanding Mannich base is considered as made up of three parts particularly of DHPM, aminomethylene bridge (-CH\textsubscript{2}-NH-) and primary aromatic diamine. FTIR spectra of both series of N-Mannich bases showed all the characteristics absorption bands of DHPM reported in earlier section (2.4.2). Whereas the other two parts aromatic diamine and aminomethylene bridge of Mannich base showed the following common absorption bands.

\textit{Primary amino group (-NH\textsubscript{2})}

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<tbody>
<tr>
<td>N-H stretching</td>
<td>3380-3200 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>N-H in plane bending</td>
<td>1620-1520 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>C-N stretching</td>
<td>1290-1270 cm\textsuperscript{-1}</td>
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</tbody>
</table>

\textit{Aminomethylene bridge (-CH\textsubscript{2}-NH-)}

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<tbody>
<tr>
<td>CH\textsubscript{2} asymmetric stretching</td>
<td>2960-2910 cm\textsuperscript{-1}</td>
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<tr>
<td>CH\textsubscript{2} symmetric stretching</td>
<td>2860-2810 cm\textsuperscript{-1}</td>
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\textit{Secondary amino group (-NH)}

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<td>N-H stretching</td>
<td>3300-3010 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>N-H in plane bending</td>
<td>1540-1500 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>C-N stretching</td>
<td>1340-1290 cm\textsuperscript{-1}</td>
</tr>
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</table>
Fig. 2.6: IR, $^1$H NMR and $^{13}$C NMR Spectra of 1a and 1b Mannich bases
Fig. 2.7: Mass Spectra of 1a and 2a Mannich base
Fig. 2.8: IR, $^1$H NMR and $^{13}$C NMR Spectra of 1b and 2b Mannich base
Fig. 2.9: IR, $^1$H NMR and $^{13}$C NMR Spectra of 1c and 2c Mannich base
Fig. 2.10: IR, $^1$H NMR and $^{13}$C NMR Spectra of 1d and 2d Mannich base
Fig. 2.11: Mass Spectra of 1b, 1c and 1d Mannich base
Tertiary amide (-N-C=O-N-) (MBU-Series)

C=O stretching 1710-1630 cm\(^{-1}\)
C-N stretching (amide III) band 1290-1260 cm\(^{-1}\)
O-CN deformation (amide IV band) 660-530 cm\(^{-1}\)
O-CN deformation (amide VI band) 590-530 cm\(^{-1}\)

Tertiary thioamide (−N-C=S-N−) (MBT-Series)

C=S stretching 1380-1360 cm\(^{-1}\)
C-N stretching (amide III) band 1250-1260 cm\(^{-1}\)

\(^1\)H NMR, \(^{13}\)C NMR spectral data for N-Mannich bases (1a and 2a) are interpreted in the following. The general structures of 1a and 2a Mannich base are:

\[^1\text{H NMR spectrum of 1a (18), showed all proton signals of DHPMs (section 2.4.3) except that of secondary amine (-NH) of pyrimidine ring system. In addition this, the other proton signals of aminomethylene bridge and that of the aromatic ring are:
\]^1\text{H NMR spectrum of 1a (18), showed all proton signals of DHPMs (section 2.4.3) except that of secondary amine (-NH) of pyrimidine ring system. In addition this, the other proton signals of aminomethylene bridge and that of the aromatic ring are:}

- A singlet at δ 3.5 ppm equivalent to 4H indicated 2H of two identical amino group (-NH\(_2\)) of N\(_{23}\) and N\(_{32}\) proton of 1a. Similarly a singlet observed at δ 4.8 ppm was equivalent to 2H of two secondary amino groups (-NH) of aminomethylene bridge on (N\(_{18}\) and N\(_{27}\))
- Further two singlets appeared at δ 5.1 and 5.3 ppm were integrating for 2H of methylene groups (-CH\(_2\)) at C\(_{17}\) and C\(_{26}\) atoms of amino methylene bridge.
- A multiplet in the region δ 6.3-7.3 ppm was equivalent to 13H indicates 8H of two identical benzene ring of p-phenylenediamine and 5H of phenyl ring of DHPM.

Analogously in \(^{13}\)CNMR spectrum of 1a, besides the carbon signals of DHPM (section 2.4.3), the \(^{13}\)C NMR signals at δ 39.4 and 52.7 ppm were due to C-17 and C-26 atoms of two amino methylene bridge (-CH\(_2\)-NH-) between pyrimidine ring and aromatic ring of p-phenylenediamine. Further, more number of signals due to carbon atoms of two phenyl ring of p-phenylenediamine resonated upfield in the region of δ 114-145 ppm in \(^{13}\)C NMR spectrum of 1a compared to that of DHPMs (δ128-145 ppm).
A mass spectrum of 1a showed molecular ion peak (M⁺) at m/z 500 is in agreement with its molecular weight (C₂₈H₃₂N₆O₃). The formation of base peak at m/z 183 reveals formation of same stable fragmentated ion of 1a as that of its parent BU₁ (20).

This shows the similar fragmentation pattern (Fig.3). The other important fragmentated ion peaks observed at m/z values due to loss of different groups are mentioned in the following:

<table>
<thead>
<tr>
<th>m/z</th>
<th>Loss of radical</th>
<th>m/z</th>
<th>Loss of radical</th>
</tr>
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<tbody>
<tr>
<td>485</td>
<td>CH₃⁺</td>
<td>380</td>
<td>CH₂-N-C₆H₄NH₂⁺</td>
</tr>
<tr>
<td>471</td>
<td>C₂H₅⁺</td>
<td>289</td>
<td>CH₂-NH-C₆H₄NH₂⁺</td>
</tr>
<tr>
<td>427</td>
<td>C₂H₂COO⁻</td>
<td>259</td>
<td>NH-C₆H₄NH₂ and N-C₆H₄NH₂⁺</td>
</tr>
<tr>
<td>424</td>
<td>C₆H₄⁻</td>
<td></td>
<td>p-phenylendiamine aromatic ring</td>
</tr>
</tbody>
</table>

All proton signals of DHPMs were observed except that of secondary amine (-NH) of pyrimidine ring system in ¹H NMR spectrum of 2a. In addition to this, the other proton signals of aminomethylene bridge and that of the aromatic rings are:

- A singlet at δ 3.6 equivalent to 4H indicated 2H of two identical amino group (-NH₂) on N₂₃ and N₃₂ proton of 2a. Similarly a singlet observed at δ 4.7 ppm was equivalent to 2H of two secondary amino group (-NH) of aminomethylene bridge (N₁₈ and N₂₇).
- Further two singlet appeared at δ 5.7 and 5.9 ppm were integrating for 2H of methylene groups (-CH₂) at C₁₇ and C₂₆ atoms of amino methylene bridge.
- A multiplet in the region δ 6.9-7.1 ppm was equivalent to 13H indicated 8H of two identical benzene ring of p-phenylendiamine and 5H of phenyl ring of DHPM.

¹³C NMR data for N-Mannich base are reported in earlier section showed the chemical shifts for the C=S peak down field at 184 ppm as compared with their 174-176 ppm starting DHPM (BT₁₄). In ¹³C NMR spectrum of 2a, besides the carbon signals of DHPM (section 2.4.3), the ¹³C NMR signals at δ 42.7 and 47.7 ppm were due to C-17 and C-26 atoms of two aminomethylene bridge (-CH₂-NH-) between pyrimidine ring and aromatic ring of p-phenylendiamine. Further, more number of the signals due to carbon atoms of two phenyl ring of p-phenylendiamine resonated...
upfield in the region of $\delta$ 114-145 ppm in $^{13}$C NMR spectrum of 2a compared to that of DHPMs ($\delta$ 123-145 ppm).

A mass spectrum of 2a showed molecular ion peak at m/z 516 is in agreement with its molecular weight (C$_{28}$H$_{32}$N$_6$O$_3$). The peak (M$^+$-2) at m/z 514 may be due to the loss of two protons (H$^-$) of primary –NH$_2$ groups in the molecular ion (M$^+$) peak formation. The formation of base peak at m/z 199 reveals the formation of same stable fragmentated ion of 2a as that of its parent BT$_1$ (21) and shows the similar fragmentation pattern (Fig.2.2). The other important fragmentated ion peaks observed at m/z values due to loss of different groups are mentioned in following:

<table>
<thead>
<tr>
<th>m/z</th>
<th>Loss of radical</th>
<th>m/z</th>
<th>Loss of radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>498</td>
<td>CH$_3$</td>
<td>303</td>
<td>N-C$_6$H$_4$NH$_2^-$</td>
</tr>
<tr>
<td>441</td>
<td>C$_2$H$_4$COO$^-$</td>
<td>289</td>
<td>CH$_2$-NH-C$_6$H$_4$NH$_2^-$</td>
</tr>
<tr>
<td>425</td>
<td>C$_6$H$_4$NH$^-$</td>
<td>259</td>
<td>NHC$_6$H$_4$NH$_2$ and N-C$_6$H$_4$NH$_2^-$</td>
</tr>
<tr>
<td>409</td>
<td>NH-C$_6$H$_4$-NH$_2^-$</td>
<td></td>
<td>p-phenylenediamine aromatic ring</td>
</tr>
</tbody>
</table>

Evidences for the formation N-disubstituted Mannich bases:

- Analytical data of C, H, and N content of N-Mannich bases compounds are in agreement with the calculated values based on the proposed structure (Scheme 2.8).
- The FTIR spectra of N-Mannich bases have shown absorption bands in the region 2960-2910 cm$^{-1}$ indicates the formation of methylene bridge (>N-CH$_2$-N<) between the nitrogen atom of the pyrimidine ring and p-phenylenediamine. In addition to this, the presence of absorption band at 3380-3300 cm$^{-1}$ may be due to primary amino group (-NH$_2$).
- $^1$H NMR spectra of the N-Mannich showed the absence of two (1H,-NH) singlet ($\delta$ 7.7 and 9.2 ppm) of secondary amino group of DHPM suggesting the participation these two secondary amino groups in Mannich reaction with formaldehyde and p-phenylenediamine.
- At the same time, the presence of two singlet at $\delta$ 5.0-5.5 and 5.3-5.8 ppm corresponding to 2H of methylene group and a singlet $\delta$ 4.5-5.0 ppm of 2H of two identical secondary amino groups indicate the formation of amino methylene bridge between DHPMs and p-phenylenediamine.
- Eventually this is further confirmed by the occurrence of a singlet at $\delta$ 3.5-4.0 ppm equivalent to 4H of primary amino groups of two p-phenylenediamine moiety and $^{13}$C NMR and mass spectral data.
2.5 Synthesis and Characterization of Disperse Disazo Dyes

Literature survey reveals Mannich base used as reactive intermediates in a number of syntheses of organic compounds. With reference to this, attempts have been made to employ N-Mannich base discussed in the earlier section 2.4.4 as diazonium components in synthesis of disazo disperse dyes by coupling reaction with different phenolic compounds. The details of procedure followed in the synthesis of new disazo disperse dyes are furnished here. Each of the two series of N-Mannich bases (MBU- and MBT-Series) has been diazotized and coupled respectively with ten phenolic coupling components to afford a family of two groups of disazo disperse dyes.

Experimental

Materials

Mannich Bases (MBU- and MBT-Series) were used as a diazonium component. Ten different phenolic compounds listed in Table 2.3-2.7 were used as a coupling component after their purification. All the other chemicals and solvents were used of L.R. grade.

2.5.1 Synthesis

Ethyl 1,3-bis((4-(4-hydroxyphenyl) diazenyl) phenylamino) methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (1aD)

The general procedure used in the synthesis is typically presented for the preparation of a disperse dye using N-Mannich base 1a as diazonium component and phenol as coupling component.

Diazotization

A solution of Mannich Base (1a) (0.1 mol) in HCl (25 ml, 2N) was cooled in ice-bath to a temperature of 0–2 °C. To this cooled solution, NaNO₂ (100 ml, 2N) solution was added dropwise during half an hour such that the temperature of reaction mixture should not increase more than 2–3 °C. The test for completion of diazotization reaction was carried out by congo-red paper giving deep blue color. If the diazotization was not completed more nitrite solution was added until the positive
test for completion of diazotization was obtained. This diazonium salt solution was used immediately in coupling reaction of phenol.

**Coupling reaction**

To a cooled alkaline solution of phenol (0.2 mol), the above diazonium salt solution was added dropwise with continuous stirring at 0–5°C. The reaction mixture was then allowed to stand for 1 h at this temperature with stirring. The pH of the solution was adjusted at pH 6.0–6.5. The precipitated disperse disazo dye was filtered, washed several times with water until the washings were neutral, air-dried and recrystallized from appropriate solvent to give a dye 1aD₁.

Diazotization of other Mannich bases by using the same procedure and their subsequent coupling reactions with each of the coupling phenols resulted into a formation of a family of two groups of disazo disperse dyes (MBUD- and MBTD-groups) consisting of four series of disperse disazo dyes in each group. They are assigned as 1a-, 1b-, 1c-, and 1d-series (MBUD-group) and 2a-, 2b-, 2c-, and 2d-series (MBTD-group).

**Scheme 2.9** shows the general reaction protocol for synthesis of two group of disperse disazo dyes. The chemical structures and IUPAC names of 1a- and 2b-series of disperse disazo dyes as a representative of each groups are furnished in **Tables 2.3-2.7**.
Scheme 2.9: Synthetic Protocol for Disperse Disazo Dyes. (MBUD- and MBTD-group)
Table 2.3: Chemical Structure of Disperse Disazo Dye of 1aD₁₋₁₀ (MBUD group)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>ethyl 1,3-bis((4-((4-hydroxyphenyl) diazenyl) phenylamino) methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>ethyl 1,3-bis((4-((3-chloro-4-hydroxyphenyl) diazenyl) phenylamino)methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>ethyl 1,3-bis((4-((2,4-dihydroxyphenyl)diazenyl) phenylamino)methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>ethyl 1,3-bis((4-((4-hydroxy-3-methyl phenyl) diazenyl) phenylamino)methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>ethyl 1,3-bis((4-((4-amino-5-hydroxyphenyl) diazenyl) phenylamino)methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>ethyl 1,3-bis((4-((4-hydroxy-2-methyl phenyl) diazenyl) phenylamino)methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image7.png" alt="Structure 7" /></td>
<td>ethyl 1,3-bis((4-((5-hydroxy-2-methyl phenyl) diazenyl) phenylamino)methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image8.png" alt="Structure 8" /></td>
<td>ethyl 1,3-bis((4-((4-hydroxynaphthalen-1-yl) diazenyl) phenylamino)methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image9.png" alt="Structure 9" /></td>
<td>ethyl 1,3-bis((4-((4-hydroxy-5-methyl phenyl) diazenyl) phenylamino)methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image10.png" alt="Structure 10" /></td>
<td>ethyl 1,3-bis((4-((2-hydroxynaphthalen-1-yl) diazenyl) phenylamino)methyl)-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
</tbody>
</table>
### Table 2.4: Chemical Structure of Disperse Disazo Dye of 2aD<sub>1-10</sub> (MBTD group)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure 2aD&lt;sub&gt;1&lt;/sub&gt;" /></td>
<td>ethyl 1,3-bis((4-((4-hydroxyphenyl) diazenyl) phenylamino)methyl)-6-methyl-2-thio-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 2aD&lt;sub&gt;2&lt;/sub&gt;" /></td>
<td>ethyl 1,3-bis((4-((2,4-dihydroxyphenyl) diazenyl) phenylamino)methyl)-6-methyl-2-thio-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image3" alt="Structure 2aD&lt;sub&gt;3&lt;/sub&gt;" /></td>
<td>ethyl 1,3-bis((4-((4-hydroxy-3-methyl phenyl) diazenyl) phenylamino)methyl)-6-methyl-2-thio-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image4" alt="Structure 2aD&lt;sub&gt;4&lt;/sub&gt;" /></td>
<td>ethyl 1,3-bis((4-((4-hydroxy-2-methyl phenyl) diazenyl) phenylamino)methyl)-6-methyl-2-thio-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image5" alt="Structure 2aD&lt;sub&gt;5&lt;/sub&gt;" /></td>
<td>ethyl 1,3-bis((5-hydroxy-2-methyl phenyl) diazenyl) phenylamino)methyl)-6-methyl-2-thio-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image6" alt="Structure 2aD&lt;sub&gt;6&lt;/sub&gt;" /></td>
<td>ethyl 1,3-bis((4-((3-chloro-4-hydroxyphenyl) diazenyl) phenylamino)methyl)-6-methyl-2-thio-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image7" alt="Structure 2aD&lt;sub&gt;7&lt;/sub&gt;" /></td>
<td>ethyl 1,3-bis((4-((2-chloro-4-hydroxyphenyl) diazenyl) phenylamino)methyl)-6-methyl-2-thio-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image8" alt="Structure 2aD&lt;sub&gt;8&lt;/sub&gt;" /></td>
<td>ethyl 1,3-bis((4-((4-amino-5-hydroxyphenyl) diazenyl) phenylamino)methyl)-6-methyl-2-thio-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image9" alt="Structure 2aD&lt;sub&gt;9&lt;/sub&gt;" /></td>
<td>ethyl 1,3-bis((4-((4-hydroxynaphthalen-1-yl) diazenyl) phenylamino)methyl)-6-methyl-2-thio-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
<tr>
<td><img src="image10" alt="Structure 2aD&lt;sub&gt;10&lt;/sub&gt;" /></td>
<td>ethyl 1,3-bis((4-((2-hydroxynaphthalen-1-yl) diazenyl) phenylamino)methyl)-6-methyl-2-thio-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate</td>
</tr>
</tbody>
</table>
2.5.2 Characterization

The chemical compositions and chemical structures of all of the disperse azo dyes were established by estimation of number of azo groups, in addition to elemental analysis and spectral studies (IR, NMR, UV-VISIBLE and Mass).

Measurements

All the melting points (°C) were determined on a melting point apparatus and are uncorrected. C, H, N analysis was carried out on Perkin Elmer (USA) 2400, Series II. The FT-IR spectra were obtained with “NICOLET-400 D” FTIR Spectrometer in KBr pellets. $^1$H NMR and $^{13}$C NMR spectra were scanned on “FT-NMR, BRUKER, 400 MHz Instrument” in DMSO-d$_6$ and CDCl$_3$ solvent using TMS as an internal standard. Mass spectra were recorded on Shimadzu GC MS QP 2010 instrument.

The number of azo group in the dye was estimated by a method reduction of azo group with excess of titanous salt and back titration of unreacted salt using ferrous ammonium sulfate reported in literature $^6$.$^3$. This method is very suitable for estimation of azo group in the dyestuff. Azo compounds are quantitatively reduced by titanous salt as

$$\text{R-N}=\text{N-R'} + 4\text{TI}^{+3} + 4\text{H}^+ \rightarrow \text{R-NH}_2 + \text{R'-NH}_2 + 4\text{TI}^{+4}$$

Insoluble disperse disazo dyes was first dissolved in DMF and then diluted with 20-25ml water. Then excess of the titanous solution added and the solution was boiled in a stream of carbon dioxide for 3-5 minutes, and the excess of titanous salt was determined by titration with standard 0.1 N ferric ammonium sulphate solutions, using ammonium thiocynate solution as an indicator. A blank was also run without sample. Number of azo group for each disperse dye was estimated by this method indicated the presence of two azo group (–N=N-) in each disperse dye molecule.

Electronic absorption spectra of eight series of disperse dyes and those of model disperse disazo dyes were recorded on “SHIMADZU A – 20” spectrophotometer by using a solution of dye in DMF solvent. The concentration of the dye in the solution was 16 ppm. These spectra are shown in Fig. 1 From these spectra, the values of $\lambda_{\text{max}}$ and the absorbance corresponding to the $\lambda_{\text{max}}$ were read and molar extinction coefficient ($\varepsilon$) values are estimated using Lambert–Beer’s equation. These data are presented in Table 2.8.
Analytical and Spectral data of Disazo Disperse Dyes (MBUD- group)

- **1a-Series**

**1aD₁:** orange solid, m.p. 267-269°C, Yield 68%. Anal. Calcd for C₄₀H₃₈N₈O₅
M.W.710, Calc.: C, 67.59; H, 5.39; N, 15.76; found: C, 67.43; H, 5.20; N, 15.1
No. of azo group: 1.90 IR (υ cm⁻¹): Benzene ring: 1630, 1580, 1450 (skeletal vibration), 3070 (-C-H- stretching), 730 and 690 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2910 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃ ) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1750 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (-NH): 3380 (N-H stretching), 1510 (-N-H in plane bending), 1240 (-C-N stretching) tert. Amide (N-C=O-N): 1710 (amide (I) band- C=O stretching), 1240 (amide (III) band –C-N bending), 760 and 570 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching) –OH group: 3550 (O-H stretching), 1360, 1270 (O-H in plane bending), 1250 (O-H and C-O coupled). ¹H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.2 (2H, s, 2nd methylene bridge), 5.4 (2H, s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.7-7.6 (21H, m, five aromatic proton), 8.2 (2H, s, OH group). ¹³C NMR: 13.9, 17.3, 38.4, 52.3, 60.9, 61.1, 99.5, 109.7, 113.4, 116.2, 116.4, 125.1, 125.2, 126.4, 126.7, 129.8, 130.5, 131.2, 136.3, 138.9, 139.6, 145.5, 145.8, 146.8, 149.4, 161.0, 167.1 Mass (m/z): 708 (M⁺), 695, 681, 665, 637, 633, 617, 589, 562, 536, 524, 513, 484, 468, 258, 183, 157, 137, 116, 108, 88, 77, 56, 43.

**1aD₂:** Brown solid, m.p. 310-311°C, Yield 60%. Anal. Calcd for C₄₀H₃₈N₈O₇
M.W.742, Calc.: C, 64.68; H, 5.16; N, 15.09; found: C, 64.83; H, 5.17; N, 14.98.
No. of azo group: 2.21. IR (υ cm⁻¹): Benzene ring: 1620, 1580, 1470 (skeletal vibration), 3020 (-C-H- stretching), 730 and 1080 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2910 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃ ) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1720 (C=O stretching), 1120 (C-O-C stretching of propionate), Secondary amine (-NH): 3320 (N-H stretching), 1520 (-N-H in plane bending), 1260 (-C-N stretching) tert. Amide (N-C=O-N): 1710 (amide (I) band- C=O stretching), 1220 (amide (III) band –C-N bending), 760 and
580 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching) –OH group: 3480 (O-H stretching), 1390, 1320 (O-H in plane bending), 1220 (O-H and C-O coupled). $^1$H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.2 (2H, s, 2$^{nd}$ methylene bridge), 5.3 (2H, s, 1$^{st}$ methylene bridge), 5.8 (1H, s, H on pyrimidine ring), 6.7-7.3 (19H, m, five aromatic proton) 8.2 (4H, s, OH group). $^{13}$C NMR: 13.9, 17.5, 38.0, 52.4, 60.8, 61.1, 99.5, 103.3, 109.2, 109.7, 113.3, 126.2, 126.3, 126.4, 126.7, 129.4, 130.5, 131.1, 131.9, 133.6, 140.1, 140.9, 145.5, 145.8, 145.9, 146.7, 149.4, 154.5, 164.8, 167.7 Mass (m/z): 742 (M$^+$), 727, 713, 697, 669, 665, 633, 605, 562, 529, 524, 500, 484, 468, 439, 389, 360, 316, 258, 183 157, 137, 116, 108, 88, 77, 56, 43

1aD$_3$, 1aD$_4$, and 1aD$_5$ (o-CH$_3$, m-CH$_3$, and p-CH$_3$): light orange solid, Orange solid, and Orange solid, m.p. 257-259$^0$C, 271-273$^0$C, and 269-271$^0$C, Yield 78%, 64%, and 84%. Anal. Calcd for C$_{42}$H$_{42}$N$_8$O$_5$ M.W.738, Calc.: C, 68.28; H, 5.73; N, 15.17; found: C, 68.21, 68.08, and 68.44; H, 5.66, 5.86, and 5.56; N, 15.40, 15.20, and 15.01. No. of azo group: 1.89, 2.10 and 2.05 respectively .IR (υ cm$^{-1}$): Benzene ring: 1650, 1590, 1480 (skeletal vibration), 3180 (-C-H- stretching), 730 and 1090 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2930 (-CH$_2$ asymm. and symm. stretching), aliphatic methyl group (-CH$_3$ ) : 2850 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH$_3$-C=O-O): 1750 (C=O stretching), 1170 (C-O-C stretching of propionate), Secondary amine (-NH): 3390 (N-H stretching), 1520 (-N-H in plane bending), 1310 (-C-N stretching) tert. Amide (N-C=O-N): 1700 (amide (I) band- C=O stretching), 1250 (amide (III) band –C-N bending), 700 and 570 (amide (IV) and (VI) OCN deformation) Azo group: 1520 (-N=N- stretching), -OH group: 3480 (O-H stretching), 1360, 1330, (O-H in plane bending), 1200 (O-H and C-O coupled). $^1$H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.2 (3H, s, CH$_3$ of pyrimidine ring), 2.8 (6H, s , CH$_3$ on aromatic ring) 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.2 (2H, s, 2$^{nd}$ methylene bridge), 5.5 (2H, s, 1$^{st}$ methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.2 -7.8 (19H, m, five aromatic ring proton), 8.2 (2H, s, OH group). $^{13}$C NMR: 13.7, 17.5, 19.5, 19.9, 38.0, 52.3, 60.6, 61.5, 99.6, 109.2, 109.7, 113.4, 115.4, 117.9, 122.6, 126.2, 126.3, 126.4, 126.7, 129.4, 130.5, 131.9, 136.3, 136.6, 138.2, 138.9, 145.5,
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145.8, 146.6, 146.7, 148.5, 149.4, 161.6, 167.7 Mass (m/z): 736 (M^+), 723, 709, 693, 665, 661, 631, 603, 562, 527, 524, 498, 468, 389, 374, 360, 316, 258, 183 157, 137, 116, 108, 88, 77, 56, 43

1aD_6 and 1aD_7 (o-Cl and p-Cl): Brown solid, Dark brown solid, m.p. 265-267°C, 277-279°C, Yield 67%, 77%, Anal. Calcd for C_{40}H_{36}Cl_{2}N_{8}O_{5} M.W.778, Calc.: C, 61.62; H, 4.65; N, 14.37; found: C, 61.14, 61.62; H, 4.10, 4.65; N, 14.10, 14.37. No. of group: 1.93, 2.14 respectively. IR (v cm^{-1}): Benzene ring: 1630, 1580, 1540 (skeletal vibration), 3050 (-C-H- stretching), 730 and 1090 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2950 (-CH\_2 asymm. and symm. stretching), aliphatic methyl group (-CH\_3): 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH\_3-C=O-O): 1750 (C=O stretching), 1160 (C-O-C stretching of propionate), Secondary amine (-NH): 3380 (N-H stretching), 1500 (-N-H in plane bending), 1280 (-C-N stretching) tert. Amide (N-C=O-N): 1700 (amide (I) band- C=O stretching), 1280 (amide (III) band –C=N bending), 760 and 580 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching) –OH group: 3410 (O-H stretching), 1390, 1330, 1280 (O-H in plane bending), 1240 (O-H and C-O coupled). \(^1\)H NMR: \(\delta\) 1.0 (3H, t, CH\_3 of ester group), 2.3 (3H, s, CH\_3 of pyrimidine ring), 4.0 (2H, q, CH\_2 of ester group), 4.8 (2H, s, two secondary –NH), 5.1 (2H, s, 2\(^{nd}\) methylene bridge), 5.3 (2H, s, 1\(^{st}\) methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.7-7.3 (19H, m, five aromatic ring proton), 8.1 (2H, s, OH group). \(^13\)C NMR: 13.9, 17.5, 38.0, 52.3, 60.9, 61.2, 99.5, 109.2, 109.7, 113.3, 118.5, 123.6, 123.4, 126.3, 126.5, 126.6, 126.7, 127.8, 129.4, 130.5, 131.6, 131.9, 136.4, 140.1, 145.5, 145.8, 146.6, 146.7 149.2, 149.4, 157.5, 167.3. Mass (m/z): 778 (M^+), 779 (M+1), 763, 749, 733, 705, 701, 651 623, 547, 524, 518, 468, 449, 389, 360, 316, 258, 183, 157, 137, 116, 108, 88, 77, 56, 43

1aD_8: Dark brown solid, m.p. 267-269°C, Yield 68%, Anal. Calcd for C_{40}H_{40}N_{10}O_{5} M.W.740, Calc.: C, 64.85; H, 5.44; N, 18.91; found: C, 63.93; H, 5.30; N, 18.74. No. of azo group: 1.97 IR (v cm^{-1}): Benzene ring: 1630, 1580, 1450 (skeletal vibration), 3070 (-C-H- stretching), 730 and 690 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2910 (-CH\_2 asymm. and symm. stretching), aliphatic methyl group (-CH\_3): 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH\_3-C=O-O): 1750 (C=O stretching), 1150
(C-O-C stretching of propionate), Secondary amine (-NH): 3380 (N-H stretching), 1510 (-N-H in plane bending), 1240 (-C-N stretching) tert. Amide (N-C=O-N): 1710 (amide (I) band- C=O stretching), 1240 (amide (III) band –C-N bending), 760 and 570 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching) –OH group: 3550 (O-H stretching), 1360, 1320, 1270 (O-H in plane bending), 1250 (O-H and C-O coupled). 1H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 3.7 (2H, s, two primary -NH$_2$), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.1 (2H, s, 2$^{nd}$ methylene bridge), 5.3 (2H, s, 1$^{st}$ methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.7-7.4 (19H, m, five aromatic ring proton), 8.1 (2H, s, OH group). 13C NMR: 13.9, 17.3, 38.4, 52.3, 60.9, 61.1, 99.5, 109.7, 113.4, 116.2, 116.4, 125.1, 125.2, 126.4, 126.7, 129.8, 130.5, 131.2, 136.3, 138.9, 139.6, 145.5, 145.8, 146.8, 149.4, 161.0, 167.1 Mass (m/z): 738 (M$^+$), 725, 711, 695, 667, 663, 633, 604, 562, 528,524, 499, 484, 468, 439, 389, 360, 326, 258, 183 157, 137, 116, 108, 88, 77, 56, 43

1aD$_9$ and 1aD$_{10}$ (α-naphthol and β-naphthol): Red Brown solid, Brown solid m.p. 327-329°C, 297-299°C, Yield 61%, 74%, Anal. Calcd for C$_{48}$H$_{42}$N$_8$O$_5$ M.W.: 810, Calc.: C, 71.10; H, 5.22; N, 13.82; found: C, 70.89, 71.23; H, 5.08, 5.20; N, 13.80, 13.50, No. of azo group: 2.14, 2.07 respectively. IR (υ cm$^{-1}$): Benzene ring: 1650, 1580, 1460 (skeletal vibration), 3080 (-C-H- stretching), 730 and 1030 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2970 (-CH$_2$ asymm. and symm. stretching), aliphatic methyl group (-CH$_3$ asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH$_3$-C=O-O): 1740 (C=O stretching), 1160 (Carbon of ester group), 730 (C-O-C stretching of propionate), Secondary amine (N-H): 3340 (N-H stretching), 1510 (-N-H in plane bending), 1290 (-C-N stretching) tert. Amide (N-C=O-N): 1710 (amide (I) band- C=O stretching), 1240 (amide (III) band –C-N bending), 700 and 580 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching) –OH group: 3220 (O-H stretching), 1380, 1360, 1270 (O-H in plane bending), 1210 (O-H and C-O coupled) 770 (4H CH- out of plane banding). 1H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.2 (3H, s, CH$_3$ of pyrimidine ring), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.1 (2H, s, 2$^{nd}$ methylene bridge), 5.5 (2H, s, 1$^{st}$ methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.1-7.6 (25H, m, seven aromatic ring proton), 8.3 (2H, s, OH group). 13C NMR: 13.6, 17.4,
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38.3, 52.5, 60.8, 61.3, 99.8, 109.4, 113.3, 121.4, 124.4, 125.3, 127.7, 128.2, 128.3, 128.4, 128.7, 129.6, 130.5, 131.1, 131.9, 133.2, 136.3, 139.6, 140.4, 141.1, 145.5, 146.6, 146.7 149.4, 164.8, 167.7. Mass (m/z): 810 (M⁺), 795,781, 737, 733, 667, 639, 563, 534, 468, 449, 389, 360, 316, 258, 183 157, 137, 116, 108, 88, 77, 56, 43

- 1b-series

1bD₁: Orange solid, m.p. 234-236°C, Yield 81%. Anal. Calcd for C₄₀H₃₈N₈O₆ M.W.726, Calc.: C, 66.10; H, 5.27; N, 15.42; found: C, 66.16; H, 5.30; N, 15.32. No. of azo group: 2.12. IR (υ cm⁻¹): Benzene ring: 1610, 1490, 1450 (skeletal vibration), 3080 (-C-H- stretching), 780 and 1210 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2950 (-CH₂ aymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃=C=O-O): 1710 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (-NH): 3300 (N-H stretching), 1520 (-N-H in plane bending), 1320 (-C-N stretching) tert. Amide (N-C=O-N): 1630 (amide (I) band- C=O stretching), 1210 (amide (III) band –C-N bending), 730 and 550 (amide (IV) and (VI) OCN deformation) Azo group: 1520 (-N=N- stretching) –OH group: 3350 (O-H stretching), 1390, 1320, (O-H in plane bending), 1250 (O-H and C-O coupled). ¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.1 (2H, s, 2nd methylene bridge), 5.3 (2H, s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.0-7.7 (20H, m, five aromatic ring proton), 8.3 (3H, s, OH group). ¹³C NMR: 13.9, 17.6, 38.0, 52.4, 53.6, 60.9, 99.8, 109.7, 113.3, 116.0, 116.2, 117.7, 121.4, 125.0 126.4, 126.7, 127.2, 130.5, 138.9, 139.3, 145.1, 145.9, 146.6, 146.7 149.4, 153.5, 161.03, 162.8, 167.7

1bD₂: Dark brown solid, m.p. 256-258°C, Yield 72%. Anal. Calcd for C₄₀H₃₈N₈O₈ M.W.758, Calc.: C, 63.82; H, 5.05; N, 14.77; found: C, 63.67; H, 5.29; N, 14.79. No. of azo group: 1.86. IR (υ cm⁻¹): Benzene ring: 1660, 1620, 1520 (skeletal vibration), 3025 (-C-H- stretching), 780 and 1230 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2950 (-CH₂ aymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃=C=O-O): 1730 (C=O stretching), 1160
(C-O-C stretching of propionate), Secondary amine (-NH): 3350 (N-H stretching), 1520 (-N-H in plane bending), 1300 (-C-N stretching) tert. Amide (N-C=O-N): 1720 (amide (I) band- C=O stretching), 1260 (amide (III) band –C-N bending), 760 and 590 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching) –OH group: 3420 (O-H stretching), 1380, 1260 (O-H in plane bending), 1230 (O-H and C-O coupled).$^1$H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 4.0 (2H, q, CH$_2$ of ester group), 4.7 (2H, s, two secondary –NH), 5.2 (2H, s, 2$^{\text{nd}}$ methylene bridge), 5.5 (2H, s, 1$^{\text{st}}$ methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.1-7.7 (18H, m, five aromatic ring proton), 8.3 (5H, s, OH group).$^{13}$C NMR: 13.8, 17.5, 38.1, 52.4, 53.8, 60.1, 100.2, 103.3, 109.2, 109.7, 113.3, 116.2, 117.7, 121.4, 126.4, 126.7, 127.2, 127.8, 129.4, 130.5, 131.1, 131.9, 136.3, 140.1, 140.9, 145.5, 145.8, 146.6, 146.7 149.4, 154.5, 164.8, 167.7

$^{1b}$D$_4$: Yellow orange solid, m.p. 296-298$^0$C, Yield 78%, Anal. Calcd for C$_{42}$H$_{42}$N$_8$O$_6$ M.W.: 754, Calc.: C, 66.83; H, 5.61; N, 14.84; found: C, 66.89; H, 5.80; N, 14.62. No. of azo group: 1.90. IR (v cm$^{-1}$): Benzene ring: 1610, 1480, 1440 (skeletal vibration), 3060 (-C-H- stretching), 760 and 1240 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2960 (-CH$_2$ asymm. and symm. stretching), aliphatic methyl group (-CH$_3$) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH$_3$-C=O-O): 1670 (C=O stretching), 1180 (C-O-C stretching of propionate), Secondary amine (-NH): 3260 (N-H stretching), 1480 (-N-H in plane bending), 1310 (-C-N stretching) tert. Amide (N-C=O-N): 1640 (amide (I) band- C=O stretching), 1250 (amide (III) band –C-N bending), 760 and 590 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching) –OH group: 3420 (O-H stretching), 1380, 1260 (O-H in plane bending), 1230 (O-H and C-O coupled).$^1$H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 2.8 (6H, s, CH$_3$ of aromatic ring), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.1 (2H, s, 2$^{\text{nd}}$ methylene bridge), 5.3 (2H, s, 1$^{\text{st}}$ methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.0-7.7 (18H, m, five aromatic ring proton), 8.3 (3H, s, OH group).$^{13}$C NMR: 13.8, 17.5, 19.3, 19.8, 38.1, 52.4, 53.8, 60.1, 99.7, 109.2, 109.7, 113.3, 115.2, 117.9, 121.4, 122.5, 126.4, 126.7, 127.2, 130.0, 136.3, 138.4, 138.9, 145.5, 146.6, 148.7 149.4, 161.8, 167.7
1bD₉: Brown solid, m.p. 285-287°C, Yield 76%. Anal. Calcd for C₄₀H₃₆Cl₂N₈O₆
M.W.795, Calc.: C, 60.38; H, 4.56; N, 14.08, found: C, 60.57; H, 4.42; N, 14.43.
No. of azo group: 2.23. IR (υ cm⁻¹): Benzene ring: 1670, 1510, 1480 (skeletal
vibration), 3050 (-C-H- stretching), 750 and 1230 (C-H and C-C bending for mono
substituted ring); Aminomethine bridge: 2960 (-CH₂ asymm. and symm. stretching),
Aliphatic β-keto ester group : 1750 (C=O stretching), 1180 (C-O-C stretching of
propionate), Secondary amine (-NH): 3340 (N-H stretching), 1510 (-N-H in plane
bending), 1310 (-C-N stretching) tert. Amide (N-C=O-N): 1740 (amide (I) band-
C=O stretching), 1260 (amide (III) band –C-N bending), 750 and 590 (amide (IV) and
(VI) OCN deformation) Azo group: 1550 (-N=N- stretching) –OH group: 3340 (O-H
stretching), 1390, 1330, 1270 (O-H in plane bending), 1230 (O-H and C-O coupled).
¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 4.1
(2H,q, CH₂ of ester group), 4.7 (2H, s, two secondary –NH), 5.1 (2H, s, 2nd
methylene bridge), 5.3 (2H,s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.0-7.6
(18H, m, five aromatic ring proton), 8.3 (3H, s, OH group). ¹³C NMR: 13.9, 17.5,
38.2, 52.6, 53.6, 60.9, 100.5, 109.2, 113.3,116.2, 117.7, 118.3, 121.4, 123.4, 126.4,
126.7, 127.2, 138.3, 139.4, 145.8, 146.6, 146.2, 147.4, 149.4, 154.5, 157.8, 167.7

1bD₅: Red brown solid, m.p. 274-276°C, Yield 65%. Anal. Calcd for C₄₈H₄₂N₈O₆
M.W.: 826, Calc.: C, 69.72; H, 5.12; N, 13.55; found: C, 69.28; H, 5.24; N, 13.75.
No. of azo group: 2.04. IR (υ cm⁻¹): Benzene ring: 1680, 1500, 1430 (skeletal
vibration), 3040 (-C-H- stretching), 740 and 1220 (C-H and C-C bending for mono
substituted ring); Aminomethylene bridge: 2920 (-CH₂ asymm. and symm. stretching),
aliphatic methyl group (-CH₃) : 2840 (C-H asymm and symm stretching), 1430 (C-H
bending) ; Carbonyl of ester group (CH₂-C=O-O): 1740 (C=O stretching), 1180
(C-O-C stretching of propionate), Secondary amine (-NH): 3300 (N-H stretching),
1500 (-N-H in plane bending), 1280 (-C-N stretching) tert. Amide (N-C=O-N): 1730
(amide (I) band- C=O stretching), 1260 (amide (III) band –C-N bending), 750 and
600 (amide (IV) and (VI) OCN deformation) Azo group: 1520 (-N=N- stretching)
–OH group: 3190 (O-H stretching), 1350, 1310, 1280 (O-H in plane bending), 1260
(O-H and C-O coupled) 770 ( 4H CH- out of plane banding). ¹H NMR: δ 1.0 (3H, t,
CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 4.1 (2H, q, CH₂ of ester
group), 4.7 (2H, s, two secondary –NH), 5.1 (2H, s, 2nd methylene bridge), 5.3 (2H,s,
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1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.0-7.6 (24H, m, five aromatic ring proton), 8.3 (3H, s, OH group). $^{13}$C NMR: 13.8, 17.5, 38.1, 52.4, 53.8, 60.1, 100.5, 109.7, 110.4, 113.3, 116.2, 117.7, 121.4, 122.3, 124.8, 125.5, 126.8, 127.2, 129.4, 130.5, 131.1, 131.9, 139.3, 149.8, 145.7, 145.8, 146.6, 146.7, 149.4, 153.5, 157.3, 159.8, 167.7

- **1c-series**

**1cD$_1$:** Yellow orange solid, m.p. 260-262°C, Yield 73%, Anal. Calcd for C$_{41}$H$_{40}$N$_8$O$_6$ M.W.740, Calc.: C, 66.47; H, 5.44; N, 15.13; found: C, 66.64; H, 5.39; N, 15.20. No. of azo group: 2.10. IR ($\nu$ cm$^{-1}$): Benzene ring: 1630, 1550, 1470 (skeletal vibration), 3060 (-C-H- stretching), 810 and 980 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2920 (-CH$_2$ asymm. and symm. stretching), aliphatic methyl group (-CH$_3$) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH$_3$-C=O-O): 1770 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (-NH): 3260 (N-H stretching), 1510 (-N-H in plane bending), 1350 (-C=N stretching) tert. Amide (N-C=O-N): 1710 (amide (I) band- C=O stretching), 1250 (amide (III) band –C=N bending), 770 and 590 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching) –OH group: 3320 (O-H stretching), 1350, 1270 (O-H in plane bending), 1250 (O-H and C-O coupled). $^1$H NMR: $\delta$ 1.0 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 3.8 (3H of OCH$_3$ group), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.2 (2H, s, 2nd methylene bridge), 5.4 (2H, s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.2-7.7 (20H, m, five aromatic ring proton), 8.5 (2H, s, OH group). $^{13}$C NMR: 13.9, 17.4, 38.5, 52.6, 55.8, 60.7, 61.6, 99.5, 109.5, 113.3, 116.0, 125.9, 126.4, 126.7, 130.5, 130.9, 138.1, 139.6, 145.8, 146.6, 146.7, 149.4, 160.6, 161.0, 167.3

**1cD$_2$:** Dark brown solid, m.p. 273-275$^0$C, Yield 68%, Anal. Calcd for C$_{41}$H$_{40}$N$_8$O$_8$ M.W.772, Calc.: C, 63.72; H, 5.22; N, 14.50; found: C, 63.81; H, 5.10; N, 14.48. No. of azo group: 1.91. IR ($\nu$ cm$^{-1}$): Benzene ring: 1640, 1550, 1470 (skeletal vibration), 3040 (-C-H- stretching), 810 and 980 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2910 (-CH$_2$ asymm. and symm. stretching), aliphatic methyl group (-CH$_3$) : 2840 (C-H asymm and symm stretching), 1430 (C-H
bending) ; Carbonyl of ester group (CH$_3$-C=O-O): 1750 (C=O stretching), 1140 (C-O-C stretching of propionate), Secondary amine (-NH): 3150 (N-H stretching), 1510 (-N-H in plane bending), 1350 (-C-N stretching) tert. Amide (N-C=O-N): 1680 (amide (I) band- C=O stretching), 1260 (amide (III) band –C-N bending), 760 and 590 (amide (IV) and (VI) OCN deformation) Azo group: 1570 (-N=N- stretching) –OH group: 3340 (O-H stretching), 1380, 1280 (O-H in plane bending), 1240 (O-H and C-O coupled). $^1$H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 3.8 (3H of OCH$_3$ group), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.2 (2H, s, 2$^{nd}$ methylene bridge), 5.3 (2H, s, 1$^{st}$ methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.8-7.3 (18H, m, five aromatic ring proton), 8.1 (4H, s, OH group). $^{13}$C NMR: 13.9, 17.5, 38.4, 52.8, 55.4, 60.1, 61.6, 99.5, 103.3, 109.2, 109.7, 113.2, 113.3, 126.4, 126.7, 127.4, 130.5, 130.9, 131.6, 140.4, 140.9, 145.8, 146.6, 146.7 149.4, 154.5, 160.6, 164.4, 167.5

1cD$_2$: Yellow orange solid, m.p. 264-266$^0$C, Yield 73%, Anal. Calcd for C$_{43}$H$_{44}$N$_8$O$_6$ M.W.768, Calc.: C, 67.17; H, 5.77; N, 14.57; found: C, 67.19; H, 5.74; N, 14.30. No. of azo group: 2.16. IR (υ cm$^{-1}$): Benzene ring: 1650, 1540, 1440 (skeletal vibration), 3050 (-C-H- stretching), 820 and 970 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2920 (-CH$_2$ aymmm. and symm. stretching), aliphatic methyl group (-CH$_3$ ) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH$_3$-C=O-O): 1750 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (-NH): 3330 (N-H stretching), 1510 (-N-H in plane bending), 1340 (-C-N stretching) tert. Amide (N-C=O-N): 1700 (amide (I) band- C=O stretching), 1260 (amide (III) band –C-N bending), 760 and 590 (amide (IV) and (VI) OCN deformation) Azo group: 1560 (-N=N- stretching) –OH group: 3470 (O-H stretching), 1360, 1340, 1260 (O-H in plane bending), 1230 (O-H and C-O coupled). $^1$H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 2.7 (6H, s, of CH$_3$ of aromatic ring), 3.8 (3H of OCH$_3$ group), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.3 (2H, s, 2$^{nd}$ methylene bridge), 5.4 (2H, s,1$^{st}$ methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.2-7.7 (18H, m, five aromatic ring proton), 8.3 (2H, s, OH group). $^{13}$C NMR: 13.9, 17.5, 19.4, 38.0, 52.2, 55.8, 60.1, 61.6, 99.5, 109.2, 115.3, 117.9, 122.2, 126.4, 126.7, 130.5, 136.4, 138.3, 138.9, 145.8, 146.7 149.4, 160.6, 161.4, 167.7
**1cD₆:** Orange solid, m.p. 289-291° C, Yield 72%. Anal. Calcd for C₄₁H₃₈Cl₂N₆O₃
M.W.: 808, Calc.: C, 60.82; H, 4.73; N, 13.84; found: C, 60.89; H, 4.70; N, 13.80.
No. of azo group: 2.08. IR (ν cm⁻¹): Benzene ring: 1630, 1530, 1470 (skeletal vibration), 3060 (-C-H- stretching), 820 and 950 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2920 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1760 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (-NH): 3320 (N-H stretching), 1510 (-N-H in plane bending), 1340 (-C-N stretching) tert. Amide (N-C=O-N): 1730 (amide (I) band- C=O stretching), 1250 (amide (III) band –C-N bending), 750 and 590 (amide (IV) and (VI) OCN deformation) Azo group: 1560 (-N=N- stretching) –OH group: 3420 (O-H stretching), 1360, 1340, 1260 (O-H in plane bending), 1230 (O-H and C-O coupled). ¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 3.8 (3H of OCH₃ group), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.2 (2H, s, 2nd methylene bridge), 5.4 (2H, s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.6 -7.6 (18H, m, five aromatic ring proton), 8.4 (2H, s, OH group). ¹³C NMR: 13.9, 17.5, 19.4, 38.0, 52.2, 55.8, 60.9, 61.5, 99.7, 109.7, 113.2 113.3, 115.4, 116.4, 126.7, 126.9, 129.7, 130.5, 130.9, 138.1, 138.9, 145.8, 146.6, 146.7, 148.4, 149.4, 158.3, 160.6, 161.4, 167.7

**1cD₇:** Dark brown solid, m.p. 277-279° C, Yield 71%. Anal. Calcd for C₄₉H₄₄N₈O₆
No. of azo group: 1.84. IR (ν cm⁻¹): Benzene ring: 1680, 1570, 1470 (skeletal vibration), 3100 (-C-H- stretching), 810 and 9840 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2910 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1780 (C=O stretching), 1160 (C-O-C stretching of propionate), Secondary amine (-NH): 3360 (N-H stretching), 1510 (-N-H in plane bending), 1350 (-C-N stretching) tert. Amide (N-C=O-N): 1700 (amide (I) band- C=O stretching), 1260 (amide (III) band –C-N bending), 760 and 590 (amide (IV) and (VI) OCN deformation) Azo group: 1590 (-N=N- stretching) –OH group: 3240 (O-H stretching), 1390, 1350, 1280 (O-H in plane bending), 1260 (O-H and C-O coupled) 770 (4H CH- out of plane banding). ¹H NMR: δ 1.0 (3H, t,
CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 3.9 (3H of OCH$_3$ group), 4.0
(2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.1 (2H, s, 2$^{nd}$
methylene bridge), 5.4 (2H, s, 1$^{st}$ methylene bridge), 5.9 (1H, s, H on pyrimidine
ring), 7.2-7.6 (24H, m, five aromatic ring proton), 8.4 (2H, s, OH group). $^{13}$C NMR:
13.9, 17.2, 38.0, 52.2, 55.8, 60.1, 61.6, 99.5, 109.2, 110.7, 113.3, 122.2, 123.7, 124.4,
124.9, 126.4, 126.7, 128.2, 129.4, 130.5, 139.1, 139.9, 145.8, 145.9, 146.6, 146.7
149.4, 157.5, 159.4, 160.6, 167.7

**1d-series**

**1dD$_1$:** Orange solid, m.p. 284-286$^0$C, Yield 71%, Anal. Calcd for C$_{41}$H$_{40}$N$_8$O$_7$
M.W.756, Calc.: C, 65.07; H, 5.33; N, 14.81; found: C, 65.18; H, 5.41; N, 14.72.
No. of azo group: 1.97. IR (υ cm$^{-1}$): Benzene ring: 1640, 1530, 1490 (skeletal
vibration), 3000 (-C-H- stretching), 700 and 950 (C-H and C-C bending for mono
substituted ring); Aminomethylene bridge: 2900 (-CH$_2$ asymm. and symm. stretching),
aliphatic methyl group (-CH$_3$): 2840 (C-H asymm and symm stretching), 1430 (C-H
bending); Carbonyl of ester group (CH$_3$-C=O-O): 1710 (C=O stretching), 1120
(C-O-C stretching of propionate), Secondary amine (-NH): 3360 (N-H stretching),
1510 (-N-H in plane bending), 1300 (-C-N stretching) tert. Amide (N-C=O-N): 1620
(amide (I) band- C=O stretching), 1240 (amide (III) band –C-N bending), 770 and
580 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching)
–OH group: 3440 (O-H stretching), 1370, 1350 (O-H i n plane bending), 1250 (O-H
and C-O coupled). $^1$H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$
of pyrimidine ring), 3.7 (3H of OCH$_3$ group), 4.1 (2H, q, CH$_2$ of ester group), 4.7 (2H, s,
two secondary –NH), 5.1 (2H, s, 2$^{nd}$ methylene bridge), 5.3 (2H, s, 1$^{st}$ methylene
bridge), 5.9 (1H, s, H on pyrimidine ring), 7.0-7.6 (19H, m, five aromatic ring
proton), 8.2 (3H, s, OH group). $^{13}$C NMR: 14.2, 17.7, 39.4, 52.7, 55.9, 60.3, 62.0,
99.5, 109.7, 110.2, 113.3, 114.4, 116.0, 122.8, 125.6, 126.4, 126.7, 138.9, 139.4,
145.4, 146.8, 149.7, 161.3, 167.5.

**1dD$_2$:** Dark brown solid, m.p. 274-275$^0$C, Yield 78%, Anal. Calcd for C$_{41}$H$_{40}$N$_8$O$_9$
No. of azo group: 2.07. IR (υ cm$^{-1}$): Benzene ring: 1600, 1560, 1440 (skeletal
vibration), 3020 (-C-H- stretching), 700 and 960 (C-H and C-C bending for mono
substituted ring); Aminomethylene bridge: 2920 (-CH₂ aymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H aymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (-NH): 3300 (N-H stretching), 1500 (-N-H in plane bending), 1310 (-C-N streching) tert. Amide (N-C=O-N): 1650 (amide (I) band- C=O stretching), 1250 (amide (III) band –C-N bending), 740 and 570 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching) –OH group: 3400 (O-H stretching), 1380, 1360 (O-H in plane bending), 1250 (O-H and C-O coupled). ¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 3.8 (3H of OCH₃ group), 4.0 (2H, q, CH₂ of ester group), 4.7 (2H, s, two secondary –NH), 5.2 (2H, s, 2nd methylene bridge), 5.5 (2H, s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.1-7.7 (17H, m, five aromatic ring proton), 8.3-8.5 (5H, s, OH group). ¹³C NMR: 13.9, 17.5, 38.4, 52.3, 55.8, 60.9, 62.3, 99.8, 109.1, 109.7, 110.2, 113.3, 114.4, 116.0, 122.8, 126.4, 126.7, 12.8, 131.9, 140.3, 140.9, 145.8, 146.2, 146.5, 146.7, 149.7, 154.5, 164.3, 167.5.

1dD₄₂: Orange solid, m.p. 270-272°C, Yield 83%, Anal. Calcd for C₄₃H₄₄N₈O₇ M.W.:784, Calc.: C, 65.82; H, 5.65; N, 14.81; found: C, 65.72; H, 4.71; N, 13.34. No. of azo group: 2.04. IR (υ cm⁻¹): Benzene ring: 1610, 1550, 1480 (skeletal vibration), 3080 (-C-H- stretching), 720 and 990 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2910 (-CH₂ aymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H aymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH₃-C=O-O): 1740 (C=O stretching), 1140 (C-O-C stretching of propionate), Secondary amine (-NH): 3320 (N-H stretching), 1500 (-N-H in plane bending), 1310 (-C-N streching) tert. Amide (N-C=O-N): 1700 (amide (I) band- C=O stretching), 1260 (amide (III) band –C-N bending), 760 and 550 (amide (IV) and (VI) OCN deformation) Azo group: 1570 (-N=N- stretching) –OH group: 3400 (O-H stretching), 1350 (O-H in plane bending), 1250 (O-H and C-O coupled). ¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 2.8 (6H, s, CH₃ of aromatic ring), 3.8 (3H of OCH₃ group), 4.0 (2H, q, CH₂ of ester group), 4.7 (2H, s, two secondary –NH), 5.2 (2H, s, 2nd methylene bridge), 5.5 (2H, s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.1-7.7 (17 H, m, five aromatic ring proton), 8.4 (3H, s, OH group). ¹³C NMR: 13.4, 17.4, 19.7, 38.4,
52.3, 55.9, 60.5, 62.3, 99.6, 109.5, 110.2, 113.4, 114.8, 115.4, 117.9, 122.8, 126.2.6, 126.4, 126.7, 138.2, 138.4, 145.4, 146.2, 146.4, 146.7, 146.9, 149.7, 161.3, 167.5.

1dD₆: Dark orange solid, m.p. 322-323°C, Yield 79%, Anal. Calcd for C₄₁H₃₈Cl₂N₈O₇ M.W.:824, Calc.: C, 59.63; H, 4.64; N, 13.59; found: C, 59.55; H, 4.71; N, 13.34. No. of azo group: 2.25. IR (υ cm⁻¹): Benzene ring: 1640, 1595, 1470 (skeletal vibration), 3060 (-C-H- stretching), 710 and 910 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2940 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃): 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1130 (C-O-C stretching of propionate), Secondary amine (-NH): 3290 (N-H stretching), 1510 (-N-H in plane bending), 1300 (-C-N stretching) tert. Amide (N-C=O-N): 1620 (amide (I) band- C=O stretching), 1260 (amide (III) band –C-N bending), 770 and 540 (amide (IV) and (VI) OCN deformation) Azo group: 1570 (-N=N- stretching) –OH group: 3390 (O-H stretching), 1380, 1350, 1280 (O-H in plane bending), 1230 (O-H and C-O coupled). ¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 3.8 (3H of OCH₃ group), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.1 (2H, s, 2nd methylene bridge), 5.3 (2H, s, 1st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.0-7.7 (17H, m, five aromatic ring proton), 8.2 (3H, s, OH group). ¹³C NMR: 14.2, 17.7, 39.4, 52.7, 55.9, 60.3, 62.0, 99.5, 109.7, 110.2, 113.3, 114.5, 116.7, 122.9, 125.6, 126.2, 126.4, 126.7, 139.2, 139.4, 145.8, 146.6, 146.7, 146.8, 148.4, 149.7, 158.3, 167.5.

1dD₉: Brown solid, m.p. 263-265°C, Yield 85%, Anal. Calcd for C₄₉H₄₄N₈O₇ M.W.500, Calc.: C, 67.18; H, 6.44; N, 16.79; found: C, 68.05; H, 6.34; N, 17.10. No. of azo group: 1.92. IR (υ cm⁻¹): Benzene ring: 1670, 1560, 1440 (skeletal vibration), 3020 (-C-H- stretching), 710 and 910 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2910 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃): 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1120 (C-O-C stretching of propionate), Secondary amine (-NH): 3470 (N-H stretching), 1520 (-N-H in plane bending), 1300 (-C-N stretching) tert. Amide (N-C=O-N): 1620 (amide (I) band- C=O stretching), 1290 (amide (III) band –C-N bending), 750 and 580 (amide (IV) and (VI) OCN deformation) Azo group: 1580 (-N=N- stretching)
–OH group: 3260 (O-H stretching), 1390, 1380 (O-H in plane bending), 1260 (O-H and C-O coupled). $^1$H NMR: δ 1.0 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 3.8 (3H of OCH$_3$ group), 4.1 (2H, q, CH$_2$ of ester group), 4.7 (2H, s, two secondary –NH), 5.1 (2H, s, 2$^{nd}$ methylene bridge), 5.3 (2H, s, 1$^{st}$ methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 7.0-7.7 (19H, m, five aromatic ring proton), 8.3 (3H, s, OH group). $^{13}$C NMR: 14.2, 17.7, 39.4, 52.7, 55.9, 60.3, 62.0, 99.5, 109.7, 110.2, 110.7, 113.3, 114.5, 122.3, 122.8, 123.8, 124.8, 124.9, 125.6, 126.7, 129.0, 139.4, 139.8, 145.4, 146.2, 146.4, 146.7, 149.7, 157.4, 159.3, 167.5.

**Analytical and Spectral data of Disazo Disperse Dyes (MBUD-group)**

- **2a-series**

  **2aD$_1$:** Orange solid, m.p. 276-278°C, Yield 65%. Anal. Calcd for C$_{40}$H$_{38}$N$_8$O$_6$S M.W.726, Calc.: C, 66.10; H, 5.27; N, 15.42; found: C, 66.26; H, 5.40; N, 15.10. No. of azo group 2.04. IR (υ cm$^{-1}$): Benzene ring: 1640, 1610, 1450 (skeletal vibration), 3100 (-C-H- stretching), 740 and 1020 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2900 (-CH$_2$ asymm. and symm. stretching), aliphatic methyl group (-CH$_3$) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH$_3$-C=O-O): 1710 (C=O stretching), 1170 (C-O-C stretching of propionate), Secondary amine (-NH): 3360 (N-H stretching), 1450 (-N-H in plane bending), 1450 (-N-H in plane bending), 1290 (-C-N stretching) tert. thioamide (N-C=S-N): 1410 (C=S stretching), 650 (C-S stretching) 1210 (–C-N bending), Azo group: 1540 (-N=N- stretching) –OH group: 3480 (O-H stretching), 1360, 1350, 1290 (O-H in plane bending), 1270 (O-H and C-O coupled). $^1$H NMR: δ 1.1 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.5 (2H, s, 2$^{nd}$ methylene bridge), 5.7 (2H, s, 1$^{st}$ methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 6.6-7.6 (21H, m, five aromatic ring proton), 8.5 (2H, s, OH group). $^{13}$C NMR: 13.5, 17.5, 45.9, 49.9, 60.9, 64.1, 97.6, 112.3, 114.7, 116.0, 125.3, 126.4, 126.7, 130.13, 131.9, 137.4, 139.6, 145.1, 145.5, 145.8, 146.6, 146.8 161.03, 168.1, 184.1. Mass (m/z): 724 (M$^+$), 711, 697, 681, 653, 649, 633, 605, 540, 500, 484, 332, 274, 199, 186,174, 155, 137, 116, 96, 77, 54, 42

  **2aD$_2$:** Orange solid, m.p. 269-272°C, Yield 73%. Anal. Calcd for C$_{40}$H$_{38}$N$_8$O$_6$S M.W.758, Calc.: C, 63.31; H, 5.05; N, 14.77; found: C, 62.87; H, 5.40; N, 14.79. No. of azo group 2.07. Benzene ring: 1620, 1580, 1470 (skeletal vibration), 3020
(-C-H stretching), 730 and 1080 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2910 (-CH\textsubscript{2} asymm. and symm. stretching), aliphatic methyl group (-CH\textsubscript{3} ) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH\textsubscript{3}-C=O-O): 1720 (C=O stretching), 1120 (C-O-C stretching of propionate), Secondary amine (-NH): 3360 (N-H stretching), 1450 (-N-H in plane bending), 1290 (-C-N stretching) tert. thioamide (N-C=S-N): 1410 (C=S stretching), 650 (C-S stretching) 1210 (–C-N bending), Azo group: 1580 (-N=N-stretching) –OH group: 3480 (O-H stretching), 1390, 1320 (O-H in plane bending), 1220 (O-H and C-O coupled).\textsuperscript{1}H NMR: \(\delta\) 1.0 (3H, t, CH\textsubscript{3} of ester group), 2.3 (3H, s, CH\textsubscript{3} of pyrimidine ring), 4.0 (2H, q, CH\textsubscript{2} of ester group), 4.8 (2H, s, two secondary –NH), 5.2 (2H, s, 2\textsuperscript{nd} methylene bridge), 5.7 (2H, s, 1\textsuperscript{st} methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 6.7-7.3 (19H, m, five aromatic proton) 8.2 (4H, s, OH group). \textsuperscript{13}C NMR: 13.9, 17.5, 38.0, 52.4, 60.8, 61.1, 99.5, 103.3, 109.2, 109.7, 113.3, 126.2, 126.3, 126.4, 126.7, 127.8, 129.4, 130.5, 131.1, 131.9, 136.3, 140.1, 140.9, 145.5, 145.8, 146.6, 146.7 149.4, 154.5, 167.7, 184.8. Mass (m/z): 758 (M\textsuperscript{+}), 743, 729, 713, 685, 681, 650, 621, 545, 540, 516, 484, 439, 389, 374, 332, 274, 199, 186,174, 155, 137, 116, 96, 77, 54, 42

2aD\textsubscript{3}, 2aD\textsubscript{4} and 2aD\textsubscript{5} (o-CH\textsubscript{3}, m-CH\textsubscript{3}, and p-CH\textsubscript{3}): Orange solid, Light orange solid, and Orange solid, m.p. 291-293\textdegree C, 271-273\textdegree C, and 259-261\textdegree C, Yield 69%, 79%, and 63%, Anal. Calcd for C\textsubscript{42}H\textsubscript{42}N\textsubscript{8}O\textsubscript{4}S M.W. 754, Calc.: C, 66.82; H, 5.19; N, 14.84; found: C, 66.71, 66.13, and 66.41; H, 5.59, 5.19 and 5.49; N, 14.79, 14.84, 14.69. No. of azo group: 2.12, 1.92 and 2.02 respectively. IR (\(\nu\) cm\textsuperscript{-1}): Benzene ring: 1670, 1610, 1470 (skeletal vibration), 3100 (-C-H- stretching), 710 and 1020 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2940 (-CH\textsubscript{2} asymm. and symm. stretching), aliphatic methyl group (-CH\textsubscript{3} ) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH\textsubscript{3}-C=O-O): 1710 (C=O stretching), 1180 (C-O-C stretching of propionate), Secondary amine (-NH): 3300 (N-H stretching), 1520 (-N-H in plane bending), 1280 (-C-N stretching) tert. thioamide (N-C=S-N): 1420 (C=S stretching), 680 (C-S stretching) 1200 (–C-N bending), Azo group: 1580 (-N=N-stretching) –OH group: 3420 (O-H stretching), 1320, 1350, 1290 (O-H in plane bending), 1280 (O-H and C-O coupled). \textsuperscript{1}H NMR: \(\delta\) 1.1 (3H, t, CH\textsubscript{3} of ester group), 2.3 (3H, s, CH\textsubscript{3} of pyrimidine ring), 2.7 (6H, s, CH\textsubscript{3} of
aromatic ring group), 4.0 (2H, q, CH\textsubscript{2} of ester group), 4.7 (2H, s, two secondary –NH), 5.6 (2H, s, \textsuperscript{2nd} methylene bridge), 5.7 (2H, s, \textsuperscript{1st} methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.2-7.6 (19 H, m, five aromatic ring proton), 8.8 (2H, s, OH group). \textsuperscript{13}C NMR: 13.7, 16.3, 16.8, 17.5, 45.9, 47.9, 60.8, 64.8, 97.8, 112.3, 114.4, 114.7, 116.20, 123.9, 126.4, 126.7, 130.1, 130.9, 131.2, 131.8, 137.4, 139.6, 145.1, 145.6, 146.2, 146.8, 158.8, 168.8, 184.4. Mass (m/z): 752 (M\textsuperscript{+}), 739, 725, 709, 681, 677, 647, 619, 602, 578, 543, 541, 514, 476, 415, 389, 374, 345, 332, 274, 199, 186,174, 155, 137, 116, 96, 77, 54, 42

\textbf{2aD\textsubscript{6} and 2aD\textsubscript{7} (o-Cl and p-Cl):} Orange solid, Red brown solid, m.p. 276-278\textdegree C, 256-258\textdegree C, Yield 65\%, 74\%. Anal. Calcd for C\textsubscript{40}H\textsubscript{38}N\textsubscript{8}O\textsubscript{4}S M.W.726, Calc.: C, 66.10; H, 5.27; N, 15.42; found: C, 66.26, 60.28; H, 5.40, 4.60; N, 15.10, 14.88. No. of azo group 2.04, 1.89 respectively.IR (υ cm\textsuperscript{-1}): Benzene ring: 1640, 1610, 1450 (skeletal vibration), 3100 (-C-H- stretching), 740 and 1020 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2900 (-CH\textsubscript{2} asymm. and symm. stretching), aliphatic methyl group (-CH\textsubscript{3} ) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH\textsubscript{3}-C=O-O): 1710 (C=O stretching), 1170 (C-O-C stretching of propionate), Secondary amine (-NH): 3360 (N-H stretching), 1450 (-N-H in plane bending), 1290 (-C-N stretching) tert. thioamide (N-C=S-N): 1410 (C=S stretching), 650 (C-S stretching) 1210 (–C-N bending), Azo group: 1540 (-N=N- stretching) –OH group: 3480 (O-H stretching), 1360, 1350, 1290 (O-H in plane bending), 1270 (O-H and C-O coupled). \textsuperscript{1}H NMR: δ 1.1 (3H, t, CH\textsubscript{3} of ester group), 2.3 (3H, s, CH\textsubscript{3} of pyrimidine ring), 4.0 (2H, q, CH\textsubscript{2} of ester group), 4.8 (2H, s, two secondary –NH), 5.5 (2H, s, \textsuperscript{2nd} methylene bridge), 5.7 (2H, s, \textsuperscript{1st} methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 6.6-7.6 (21H, m, five aromatic ring proton), 8.5 (2H, s, OH group). \textsuperscript{13}C NMR: 13.5, 17.5, 45.9, 49.9, 60.9, 64.1, 97.6, 112.3, 114.7, 116.0, 125.3, 126.4, 126.7, 130.13, 131.9, 137.4, 139.6, 145.1, 145.5, 145.8, 146.6, 146.8 161.03, 168.1, 184.1. Mass (m/z): 795(M\textsuperscript{+}), 796(M+1), 780, 766, 750, 722, 718, 668, 640, 564, 540, 535, 485, 449, 333, 274, 199, 186,174, 155, 137, 116, 96, 77, 54, 42

\textbf{2aD\textsubscript{8}}: Dark red solid, m.p. 282-284\textdegree C, Yield 73\%. Anal. Calcd for C\textsubscript{40}H\textsubscript{40}N\textsubscript{10}O\textsubscript{4}S M.W.756, Calc.: C, 63.48; H, 5.33; N, 18.51; found: C, 63.33; H, 5.10; N, 18.62. No. of azo group: 1.92. IR (υ cm\textsuperscript{-1}): Benzene ring: 1630, 1570, 1480 (skeletal
vibration), 3000 (-C-H- stretching), 720 and 1020 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2970 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1190 (C-O-C stretching of propionate), Secondary amine (-NH): 3320 (N-H stretching), 1520 (-N-H in plane bending), 1280 (-C-N stretching) tert. thioamide (N-C=S-N): 1400 (C=S stretching), 660 (C-S stretching) 1250 (-C=N- bending) –OH group: 3490 (O-H stretching), 1370, 1320, 1280 (O-H in plane bending), 1250 (O-H and C-O coupled). ¹H NMR; δ 1.1 (3H, t, CH₃ of ester group), 2.4 (3H, s, CH₃ of pyrimidine ring), 3.9 (4H, s, NH₂ of aromatic ring ), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.7 (2H, s, 2nd methylene bridge), 5.8 (2H, s, 1st methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.2-7.6 (19H, m, five aromatic ring proton), 8.1 (2H, s, OH group). ¹³C NMR: 13.7, 17.0, 45.0, 46.9, 61.8, 65.3, 97.8, 112.3,113.7, 114.4, 114.7, 119.20, 121.9, 123.4, 126.7, 130.9, 131.2, 131.8, 137.4, 141.2, 145.1, 145.6, 145.8, 149.2, 156.8, 168.1, 184.0. Mass (m/z): 754 (M⁺), 727, 711, 683, 679, 642, 620, 605, 575, 540, 541, 500, 462, 439, 425, 389, 374, 342,274, 199, 186,174, 155, 137, 116, 96, 77, 54, 42

2aD₉ and 2aD₁₀ (α-naphthol and β-naphthol): Orange solid, Dark brown solid m.p. 276-278°C, 177-179°C, Yield 65%, 68%, Anal. Calcd for C₄₀H₃₈N₈O₄S M.W.726, Calc.: C, 66.10; H, 5.27; N, 15.42; found: C, 66.26, 69.71; H, 5.40, 5.62; N, 15.10, 15.55. No. of azo group 2.04, 2.10 respectively. IR (υ cm⁻¹): Benzene ring: 1640, 1610, 1450 (skeletal vibration), 3100 (-C-H- stretching), 740 and 1020 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2900 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1170 (C-O-C stretching of propionate), Secondary amine (-NH): 3360 (N-H stretching), 1450 (-N-H in plane bending), 1290 (-C-N stretching) tert. thioamide (N-C=S-N): 1410 (C=S stretching), 650 (C-S stretching) 1210 (-C-N bending), Azo group: 1540 (-N=N- stretching) –OH group: 3480 (O-H stretching), 1360, 1350, 1290 (O-H in plane bending), 1270 (O-H and C-O coupled). ¹H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.5 (2H, s, 2nd methylene bridge),
5.7 (2H, s, 1st methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 6.6-7.6 (21H, m, five aromatic ring proton), 8.5 (2H, s, OH group). $^{13}$C NMR: 13.5, 17.5, 45.9, 49.9, 60.9, 64.1, 97.6, 112.3, 114.7, 116.0, 125.3, 126.4, 126.7, 130.13, 131.2, 131.9, 137.4, 139.6, 145.1, 145.5, 145.8, 146.6, 146.8 161.03, 168.1, 184.1. Mass (m/z): 826 (M$^+$), 811, 797, 781, 753, 749, 683, 655, 579, 550, 540, 484, 540, 462, 439, 389, 374, 332, 274, 199, 186, 174, 155, 137, 116, 96, 77, 54, 42

- **2b-series**

2bD$_1$: Orange solid, m.p. 298-300$^0$C, Yield 67%, Anal. Calcd for C$_{40}$H$_{38}$N$_8$O$_5$S M.W.742, Calc.: C, 64.67; H, 5.16; N, 16.79; found: C, 64.51; H, 5.23; N, 15.13. No. of azo group: 1.91. IR (υ cm$^{-1}$): Benzene ring: 1620, 1540, 1450 (skeletal vibration), 3050 (-C-H- stretching), 770 and 1230 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2960 (-CH$_2$ asymm. and symm. stretching), aliphatic methyl group (-CH$_3$ ) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH$_3$-C=O-O): 1710 (C=O stretching), 1170 (C-O-C stretching of propionate), Secondary amine (-NH): 3250 (N-H stretching), 1480 (-N-H in plane bending), 1330 (-C-N strencching) tert. thioamide (N-C=S-N): 1410 (C=S stretching), 660 (C-S stretching) 1230 (–C-N bending), Azo group: 1590 (-N=N- stretching) –OH group: 3480 (O-H stretching), 1360, 1330 (O-H in plane bending), 1260 (O-H and C-O coupled). $^1$H NMR: δ 1.1 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.7 (2H, s, 2nd methylene bridge), 5.8 (2H, s, 1st methylene bridge), 6.1 (1H,s, H on pyrimidine ring), 7.2-7.7 (20H, m, five aromatic ring proton), 8.8 (3H, s, OH group). $^{13}$C NMR: 13.5, 17.5, 45.9, 49.9, 60.9, 64.1, 97.6, 112.3, 114.7, 116.0, 125.3, 126.4, 126.7, 130.13, 131.2, 131.9, 137.4, 139.6, 145.1, 145.5, 145.8, 146.6, 146.8 161.03, 168.1, 184.1.

2bD$_3$: Yellow orange solid, m. p. 287-289$^0$C, Yield 73%, Anal. Calcd for C$_{42}$H$_{42}$N$_8$O$_5$S M.W.770, Calc.: C, 65.44; H, 5.49; N, 14.54; found: C, 65.40; H, 5.43; N, 14.57. No. of azo group: 2.10. IR (υ cm$^{-1}$): Benzene ring: 1660, 1550, 1500 (skeletal vibration), 3050 (-C-H- stretching), 770 and 1230 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2910 (-CH$_2$ asymm. and symm. stretching), aliphatic methyl group (-CH$_3$ ) : 2840 (C-H asymm and symm stretching),
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1430 (C-H bending); Carbonyl of ester group (CH$_3$-C=O-O): 1740 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (–NH): 3240 (N-H stretching), 1500 (-N-H in plane bending), 1340 (-C-N stretching) tert. thioamide (N-C=S-N): 1370 (C=S stretching), 680 (C-S stretching) 1230 (–C-N bending), Azo group: 1570 (-N=N- stretching) –OH group: 3430 (O-H stretching), 1370, 1340 (O-H in plane bending), 1280 (O-H and C-O coupled). $^1$H NMR: $\delta$ 1.1 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 2.8 (6H, s, CH$_3$ of aromatic ring), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.6 (2H, s, 2nd methylene bridge), 5.8 (2H, s, 1st methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.2-7.7 (18H, m, five aromatic ring proton), 8.5 (3H, s, OH group). $^{13}$C NMR: 13.7, 16.3, 16.8, 17.5, 45.9, 47.9, 60.8, 64.8, 97.8, 112.3, 114.4, 114.7, 116.20, 123.9, 126.4, 126.7, 130.1, 130.9, 131.2, 131.8, 137.4, 139.6, 145.1, 145.6, 146.2, 146.8, 158.8, 168.8, 184.4


No. of azo group: 2.20. IR (υ cm$^{-1}$): Benzene ring: 1680, 1540, 1480 (skeletal vibration), 3090 (-C-H- stretching), 780 and 1240 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2920 (-CH$_2$ asymm. and symm. stretching), aliphatic methyl group (-CH$_3$ ) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH$_3$-C=O-O): 1780 (C=O stretching), 1170 (C-O-C stretching of propionate), Secondary amine (–NH): 3150 (N-H stretching), 1510 (-N-H in plane bending), 1320 (–C-N stretching) tert. thioamide (N-C=S-N): 1380 (C=S stretching), 660 (C-S stretching) 1240 (–C-N bending), Azo group: 1580 (-N=N-stretching) –OH group: 3430 (O-H stretching), 1380, 1350 (O-H in plane bending), 1240 (O-H and C-O coupled). $^1$H NMR: $\delta$ 1.1 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.7 (2H, s, 2nd methylene bridge), 5.8 (2H, s, 1st methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.1-7.7 (18H, m, five aromatic ring proton), 8.5 (3H, s, OH group). $^{13}$C NMR: 13.2, 17.7, 44.9, 48.2, 60.8, 64.2, 98.1, 112.6, 114.4, 114.7, 116.20, 123.9, 126.2, 126.7, 129.9, 130.9, 131.2, 131.8, 137.4, 139.6, 145.1, 145.6, 146.2, 146.8, 150.8, 157.7, 167.9, 183.9
2bD₈: Dark red solid, m.p. 268-269⁰C, Yield 75%. Anal. Calcd for C₄₀H₃₀N₁₀O₅S M.W.772, Calc.: C, 62.16; H, 5.22; N, 18.12; found: C, 62.10; H, 5.18; N, 18.24. No. of azo group: 2.09. IR (υ cm⁻¹): Benzene ring: 1670, 1510, 1480 (skeletal vibration), 3100 (-C-H stretching), 780 and 1220 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2920 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃): 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (-NH): 3250 (N-H stretching), 1510 (-N-H in plane bending), 1310 (-C-N stretching) tert. thioamide (N-C=S-N): 1410 (C=S stretching), 690 (C-S stretching) 1260 (–C-N bending). Azo group: 1550 (–N=N- stretching) –OH group: 3400 (O-H stretching), 1380, 1350 (O-H in plane bending), 1260 (O-H and C-O coupled). ¹H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.2 (3H, s, CH₃ of pyrimidine ring), 3.7 (4H, s, NH₂ of aromatic ring), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.6 (2H, s, 2nd methylene bridge), 5.9 (2H, s, 1st methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.0-7.4 (18H, m. five aromatic ring proton), 8.8 (3H, s, OH group). ¹³C NMR: 13.7, 17.0, 45.0, 46.9, 61.8, 65.3, 97.8, 112.3, 113.7, 114.4, 114.7, 119.20, 121.9, 123.4, 126.7, 130.1, 131.2, 131.8, 137.4, 141.2, 145.1, 145.6, 145.8, 149.2, 156.8, 168.1, 184.0

2bD₁₀: Brown solid, m.p. 237-239⁰C, Yield 76%. Anal. Calcd for C₄₈H₄₂N₈O₅S M.W.842, Calc.: C, 68.39; H, 5.02; N, 13.29; found: C, 62.10; H, 5.14; N, 13.43. No. of azo group: 2.10. IR (υ cm⁻¹): Benzene ring: 1680, 1570, 1450 (skeletal vibration), 3010 (-C-H stretching), 720 and 1240 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2920 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃): 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1180 (C-O-C stretching of propionate), Secondary amine (-NH): 34000 (N-H stretching), 1480 (-N-H in plane bending), 1310 (-C-N stretching) tert. thioamide (N-C=S-N): 1380 (C=S stretching), 690 (C-S stretching) 1240 (–C-N bending). Azo group: 1590 (–N=N- stretching) –OH group: 3210 (O-H stretching), 1370, 1350 (O-H in plane bending), 1240 (O-H and C-O coupled) 760 ((4H) CH of out of plane bending). ¹H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.7 (2H, s, 2nd methylene
bridge), 5.8 (2H, s, 1st methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.1-7.6 (20H, m, five aromatic ring proton), 8.5 (3H, s, OH group). $^{13}$C NMR: 13.5, 17.5, 45.9, 49.9, 60.9, 64.1, 97.6, 112.3, 114.7, 116.0, 125.3, 126.4, 126.7, 130.13, 131.2, 131.9, 137.4, 139.6, 145.1, 145.5, 145.8, 146.6, 146.8 161.03, 168.1, 184.1

- 2c-series

2cD₁: Orange solid, m.p. 241-243°C, Yield 73%, Anal. Calcd for C₄₁H₄₀N₈O₅S M.W.756, Calc.: C, 65.06; H, 5.33; N, 14.80; found: C, 65.02; H, 5.30; N, 14.78 No. of azo group: 1.86. IR (υ cm⁻¹): Benzene ring: 1610, 1500, 1450 (skeletal vibration), 3080 (-C-H- stretching), 800 and 940 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2920 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (-NH): 3220 (N-H stretching), 1500 (-N-H in plane bending), 1320 (-C-N stretching) tert. thioamide (N-C=S-N): 1380 (C=S stretching), 770 (C-S stretching) 1230 (--C-N bending), Azo group: 1530 (-N=N- stretching) –OH group: 3430 (O-H stretching), 1380, 1320, (O-H in plane bending), 1230 (O-H and C-O coupled). $^1$H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 3.9 (3H of OCH₃ group), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.7 (2H, s, 2nd methylene bridge), 5.8 (2H, s, 1st methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.2-7.6 (20H, m, five aromatic ring proton), 8.8 (2H, s, OH group). $^{13}$C NMR: 13.5, 17.5, 45.9, 49.9, 60.9, 64.1, 97.6, 112.3, 114.7, 116.0, 125.3, 126.4, 126.7, 130.13, 131.2, 131.9, 137.4, 139.6, 145.1, 145.5, 145.8, 146.6, 146.8 161.03, 168.1, 184.

2cD₃: Red orange solid, m.p. 263-265°C, Yield 74%, Anal. Calcd for C₄₃H₄₄N₈O₅S M.W.784, Calc.: C, 65.80; H, 5.65; N, 14.28; found: C, 65.79; H, 5.62; N, 14.37. No. of azo group: 1.88. IR (υ cm⁻¹): Benzene ring: 1610, 1510, 1450 (skeletal vibration), 3080 (-C-H- stretching), 800 and 940 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2910 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH₃-C=O-O): 1750 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (-NH): 3380 (N-H stretching),
1510 (-N-H in plane bending), 1320 (-C-N stretching) tert. thioamide (N-C=S-N): 1380 (C=S stretching), 780 (C-S stretching) 1280 (-C-N bending), Azo group: 1570 (-N=N- stretching) –OH group: 3390 (O-H stretching), 1350, 1320, 1570 (C=S stretching), 790 (C-S stretching) 1280 (–C-N bending), Azo group: 1570 (-N=N- stretching) –OH group: 3390 (O-H stretching), 1350, 1320, 1280 (O-H and C-O coupled). ^1^H NMR: δ 1.1 (3H, t, CH$_3$ of ester group), 2.3 (3H, s, CH$_3$ of pyrimidine ring), 2.7 (6H, of CH$_3$ of aromatic ring), 3.8 (3H of OCH$_3$ group), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.6 (2H, s, 2$^{nd}$ methylene bridge), 5.8 (2H, s, 1$^{st}$ methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.2-7.6 (19H, m, five aromatic ring proton), 8.5 (2H, s, OH group). ^13^C NMR: 13.7, 16.3, 16.8, 17.5, 45.9, 47.9, 60.8, 64.8, 97.8, 112.3, 114.4, 114.7, 116.20, 123.9, 126.4, 126.7, 130.1, 130.9, 131.2, 131.8, 137.4, 139.6, 145.1, 145.6, 146.2, 146.8, 158.8, 168.8, 184.4

2cD$_7$: Red orange solid, m.p. 270-272°C, Yield 67%. Anal. Calcd for C$_{41}$H$_{36}$Cl$_2$N$_8$O$_5$S M.W.824, Calc.: C, 59.63; H, 4.64; N, 13.57; found: C, 59.66; H, 4.63; N, 13.50. No. of azo group: 2.18. IR (υ cm$^{-1}$): Benzene ring: 1620, 1470, 1440 (skeletal vibration), 3060 (-C-H- stretching), 850 and 940 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2950 (-CH$_2$ asymm. and symm. stretching), aliphatic methyl group (-CH$_3$) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH$_3$-C=O-O): 1680 (C=O stretching), 1180 (C-O-C stretching of propionate), Secondary amine (-NH): 3290 (N-H stretching), 1400 (-N-H in plane bending), 1320 (-C-N stretching) tert. thioamide (N-C=S-N): 1350 (C=S stretching), 790 (C-S stretching) 1250 (-C-N bending), Azo group: 1590 (-N=N- stretching) –OH group: 3400 (O-H stretching), 1340, 1300, (O-H in plane bending), 1280 (O-H and C-O coupled). ^1^H NMR: δ 1.1 (3H, t, CH$_3$ of ester group), 2.4 (3H, s, CH$_3$ of pyrimidine ring), 3.8 (3H of OCH$_3$ group), 4.0 (2H, q, CH$_2$ of ester group), 4.8 (2H, s, two secondary –NH), 5.7 (2H, s, 2$^{nd}$ methylene bridge), 5.8 (2H, s, 1$^{st}$ methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.2-7.7 (19H, m, five aromatic ring proton), 8.5 (3H, s, OH group). ^13^C NMR: 13.2, 17.7, 44.9, 48.2, 60.8, 64.2, 98.1, 112.6, 114.4, 114.7, 116.20, 123.9, 126.2, 126.7, 129.9, 130.9, 131.8, 137.4, 139.6, 145.1, 145.6, 146.2, 146.8, 150.8, 157.7, 167.9, 183.9

2cD$_8$: Dark red solid, m.p. 318-320°C, Yield 73%. Anal. Calcd for C$_{41}$H$_{42}$N$_{10}$O$_5$S M.W.786, Calc.: C, 62.58; H, 5.38; N, 17.80; found: C, 62.40; H, 5.14; N, 17.73. No. of azo group: 2.05. IR (υ cm$^{-1}$): Benzene ring: 1650, 1540, 1450 (skeletal
vibration), 3050 (-C-H- stretching), 810 and 940 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2940 (-CH₂ asymm. and symm. stretching), Aliphatic β-keto ester group : 1770 (C=O stretching), 1170 (C-O-C stretching of propionate), Secondary amine (-NH): 3350 (N-H stretching), 1500 (-N-H in plane bending), 1300 (-C-N stretching) tert. thioamide (N-C=S-N): 1340 (C=S stretching), 780 (C-S stretching) 1250 (-C-N bending), Azo group: 3350 (O-H stretching), 1350, 1310, (O-H in plane bending), 1270 (O-H and C-O coupled). ¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 3.5 (4H, s, two –NH₂ of p-phenylene ring motifs) 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, secondary –NH), 5.1 (2H, s, ²nd methylene bridge), 5.3 (2H, s, ¹st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.8 -7.3 (13H, m, three aromatic proton). ¹³C NMR: 13.7, 17.0, 45.0, 46.9, 61.8, 65.3, 97.8, 112.3, 113.7, 114.4, 114.7, 119.20, 121.9, 123.4, 126.7, 130.1, 130.9, 131.2, 131.8, 137.4, 141.2, 145.1, 145.6, 145.8, 149.2, 156.8, 168.1, 184.0

2cD₁₀: Dark Brown solid, m.p. 306-308°C, Yield 70%, Anal. Calcd for C₄₀H₄₄N₈O₅S M.W.856, Calc.: C, 68.67; H, 5.18; N, 13.08.79; found: C, 68.0; H, 5.28; N, 13.19. No. of azo group: 2.01. IR (υ cm⁻¹): Benzene ring: 1610, 1510, 1450 (skeletal vibration), 3090 (-C-H- stretching), 850 and 950 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2920 (-CH₂ asymm. and symm. stretching), Aliphatic methyl group (-CH₃ ) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH₃-C=O-O): 1750 (C=O stretching), 1180 (C-O-C stretching of propionate), Secondary amine (-NH): 3370 (N-H stretching), 1510 (-N-H in plane bending), 1330 (-C-N stretching) tert. thioamide (N-C=S-N): 1350 (C=S stretching), 770 (C-S stretching) 1260 (-C-N bending), Azo group: 1610 (-N=N- stretching) –OH group: 3290 (O-H stretching), 1350, 1330, (O-H in plane bending), 1280 (O-H and C-O coupled) 770 (4H, CH out of plane bending). ¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 3.5 (4H, s, two –NH₂ of p-phenylene ring motifs) 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, secondary –NH), 5.1 (2H, s, ²nd methylene bridge), 5.3 (2H, s, ¹st methylene bridge), 5.9 (1H, s, H on pyrimidine ring), 6.8 -7.3 (13H, m, three aromatic proton). ¹³C NMR: 13.5, 17.5, 45.9, 49.9, 60.9, 64.1, 97.6, 112.3, 114.7, 116.0, 125.3, 126.4, 126.7, 130.1, 131.9, 137.4, 139.6, 145.1, 145.5, 145.8, 146.6, 146.8 161.03, 168.1, 184.1
• 2d-series

2dD₁: Yellow orange solid, m.p. 252-254°C, Yield 75%. Anal. Calcd for C₄₁H₄₀N₈O₆S M.W.772 Calc.: C, 63.72; H, 5.22 N, 14.50; found: C, 63.64; H, 5.17; N, 14.43. No. of azo group: 2.02. IR (υ cm⁻¹): Benzene ring: 1620, 1510, 1450 (skeletal vibration), 3080 (C-H stretching), 780 and 970 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2920 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃): 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1110 (C-O-C stretching of propionate), Secondary amine (-NH): 3370 (N-H stretching), 1510 (-N-H in plane bending), 1320 (-C-N stretching) tert. thioamide (N-C=S-N): 1420 (C=S stretching), 760 (C-S stretching) 1250 (-C-N bending), Azo group: 1560 (-N=N- stretching) –OH group: 3420 (O-H stretching), 1390, 1350, 1270 (O-H in plane bending), 1250 (O-H and C-O coupled).¹H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.4 (3H, s, CH₃ of pyrimidine ring), 3.8 (3H of OCH₃ group), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.6 (2H, s, 2nd methylene bridge), 5.8 (2H, s, 1st methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.2-7.7 (19H, m, five aromatic ring proton), 8.6 (3H, s, OH group).¹³C NMR: 13.5, 17.5, 45.9, 49.9, 60.9, 64.1, 97.6, 112.3, 114.7, 116.0, 125.3, 126.4, 126.7, 130.13, 131.2, 131.9, 137.4, 139.6, 145.1, 145.5, 145.8, 146.6, 146.8, 161.03, 168.1, 184.

2dD₂: Orange solid, m.p. 252-254°C, Yield 75%. Anal. Calcd for C₄₃H₄₄N₈O₆S M.W.800, Calc.: C, 64.48; H, 5.54; N, 13.99; found: C, 64.43; H, 5.42; N, 13.76. No. of azo group: 1.95. IR (υ cm⁻¹): Benzene ring: 1630, 1500, 1460 (skeletal vibration), 3090 (-C-H- stretching), 780 and 940 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2940 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃): 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1170 (C-O-C stretching of propionate), Secondary amine (-NH): 3400 (N-H stretching), 1500 (-N-H in plane bending), 1320 (-C-N stretching) tert. thioamide (N-C=S-N): 1410 (C=S stretching), 760 (C-S stretching) 1220 (-C-N bending), Azo group: 1580 (-N=N- stretching) –OH group: 3470 (O-H stretching), 1390, 1350 (O-H in plane bending), 1280 (O-H and C-O coupled).¹H NMR: δ 1.0 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 2.7 (6H, s, CH₃ of aromatic ring), 3.9 (3H of
OCH₃ group), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.6 (2H, s, 2nd methylene bridge), 5.8 (2H, s, 1st methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.2-7.7 (17H, m, five aromatic ring proton), 8.2 (3H, s, OH group). ¹³C NMR: 13.7, 16.3, 16.8, 17.5, 45.9, 47.9, 60.8, 64.8, 97.8, 112.3, 114.4, 114.7, 116.20, 123.9, 126.4, 126.7, 130.1, 130.9, 131.2, 131.8, 137.4, 139.6, 145.1, 145.6, 146.2, 146.8, 158.8, 168.8, 184.4

2dD₇: Red orange solid, m.p. 319-321°C, Yield 65%. Anal. Calcd for C₄₁H₃₈Cl₂N₈O₆S M.W.840. Calc.: C, 58.50; H, 4.55.; N, 13.31; found: C, 58.48; H, 4.35; N, 13.38. No. of azo group: 1.94. IR (υ cm⁻¹): Benzene ring: 1640, 1530, 1470 (skeletal vibration), 3060 (-C-H- stretching), 50 and 980 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2930 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃): 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1720 (C=O stretching), 1160 (C-O-C stretching of propionate), Secondary amine (-NH): 3350 (N-H stretching), 1510 (-N-H in plane bending), 1320 (-C-N stretching) tert. thioamide (N-C=S-N): 1400 (C=S stretching), 750 (C-S stretching) 1230 (-C-N bending), Azo group: 1560 (-N=N- stretching) –OH group: 3430 (O-H stretching), 1370, 1340, 1270 (O-H in plane bending), 1250 (O-H and C-O coupled).

1H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.3 (3H, s, CH₃ of pyrimidine ring), 3.8 (3H of OCH₃ group), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.7 (2H, s, 2nd methylene bridge), 5.8 (2H, s, 1st methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.2-7.6 (17H, m, five aromatic ring proton), 8.8 (3H, s, OH group). ¹³C NMR: 13.2, 17.7, 44.9, 48.2, 60.8, 64.2, 98.1, 112.6, 114.4, 114.7, 116.20, 123.9, 126.2, 126.7, 129.9, 130.9, 131.2, 137.4, 139.6, 145.1, 145.6, 146.2, 146.8, 150.8, 157.7, 167.9, 183.9

2dD₈: Brown solid, m.p. 284-285°C, Yield 87%. Anal. Calcd for C₄₁H₄₂N₁₀O₆S M.W.802. Calc.: C, 61.33; H, 5.27; N, 17.45; found: C, 61.26; H, 5.31; N, 17.44. No. of azo group: 2.12. IR (υ cm⁻¹): Benzene ring: 1620, 1540, 1480 (skeletal vibration), 3080 (-C-H- stretching), 750 and 950 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2930 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃): 2840 (C-H asymm and symm stretching), 1430 (C-H bending); Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1150 (C-O-C stretching of propionate), Secondary amine (-NH): 3320 (N-H stretching),
1520 (-N-H in plane bending), 1300 (-C-N stretching) tert. thioamide (N-C=S-N): 1430 (C=S stretching), 760 (C-S stretching) 1240 (–C-N bending), Azo group: 1550 (-N=N- stretching) –OH group: 3400 (O-H stretching), 1380, 1320, 1250 (O-H and C-O coupled). ¹H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.4 (3H, s, CH₃ of pyrimidine ring), 3.7 (4H, s, of NH₂ group), 3.9 (3H of OCH₃ group), 4.0 (2H, q, CH₂ of ester group), 4.7 (2H, s, two secondary –NH), 5.6 (2H, s, 2ⁿ methylene bridge), 5.8 (2H, s, 1ˢ methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.2-7.7 (19H, m, five aromatic ring proton), 8.5 (3H, s, OH group). ¹³C NMR: 13.5, 17.0, 45.0, 46.9, 61.8, 65.3, 97.8, 112.3, 113.7, 114.4, 114.7, 119.20, 121.9, 123.4, 126.7, 130.1, 130.9, 131.2, 131.8, 137.4, 141.2, 145.1, 145.6, 145.8, 149.2, 156.8, 161.9, 184.0

2dD₁₀: Red brown solid, m.p. 296-297°C, Yield 81%. Anal. Calcd for C₄₃H₄₄N₈O₆S M.W.856, Calc.: C, 67.41; H, 5.08; N, 12.84; found: C, 67.39; H, 5.13; N, 12.77. No. of azo group: 2.07. IR (ν cm⁻¹): Benzene ring: 1630, 1500, 1430 (skeletal vibration), 3070 (-C-H stretching), 760 and 960 (C-H and C-C bending for mono substituted ring); Aminomethylene bridge: 2920 (-CH₂ asymm. and symm. stretching), aliphatic methyl group (-CH₃) : 2840 (C-H asymm and symm stretching), 1430 (C-H bending) ; Carbonyl of ester group (CH₃-C=O-O): 1710 (C=O stretching), 1180 (C-O-C stretching of propionate), Secondary amine (-NH): 3380 (N-H stretching), 1500 (-N-H in plane bending), 1310 (-C-N stretching) tert. thioamide (N-C=S-N): 1430 (C=S stretching), 780 (C-S stretching) 1220 (–C-N bending), Azo group: 1580 (-N=N- stretching) –OH group: 3240 (O-H stretching), 1380, 1320, 1250 (O-H and C-O coupled). ¹H NMR: δ 1.1 (3H, t, CH₃ of ester group), 2.4 (3H, s, CH₃ of pyrimidine ring), 3.8 (3H of OCH₃ group), 4.0 (2H, q, CH₂ of ester group), 4.8 (2H, s, two secondary –NH), 5.7 (2H, s, 2ⁿ methylene bridge), 5.9 (2H, s, 1ˢ methylene bridge), 6.1 (1H, s, H on pyrimidine ring), 7.1-7.6 (23H, m, five aromatic ring proton), 8.6 (3H, s, OH group). ¹³C NMR: 13.5, 17.5, 45.9, 49.9, 60.9, 64.1, 97.6, 112.3, 114.7, 116.0, 125.3, 126.4, 126.7, 130.13, 131.2, 131.9, 137.4, 139.6, 145.1, 145.5, 145.8, 146.6, 146.8 161.03, 168.1, 184.1
Fig. 2.12: IR, $^1$H NMR and $^{13}$C NMR Spectra of Disazo Disperse Dyes
($1aD_1$ and $2aD_1$)
Fig. 2.13: IR, $^1$H NMR and $^{13}$C NMR Spectra of Disazo Disperse Dyes (1aD$_2$ and 2aD$_2$)

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Fig. 2.14: IR, $^1$H NMR and $^{13}$C NMR Spectra of Disazo Disperse Dyes (1aD$_3$ and 2aD$_3$)
Fig. 2.15: IR, $^1$H NMR and $^{13}$C NMR Spectra of Disazo Disperse Dyes (1aD$_4$ and 2aD$_4$)
Fig. 2.16: IR, $^1$H NMR and $^{13}$C NMR Spectra of Disazo Disperse Dyes (1aD$_S$ and 2aD$_S$)
Fig. 2.17: IR, $^1$H NMR and $^{13}$C NMR Spectra of Disazo Disperse Dyes 
($1aD_6$ and $2aD_6$)
Fig. 2.18: IR, $^1$H NMR and $^{13}$C NMR Spectra of Disazo Disperse Dyes (1aD and 2aD$_7$)
Fig. 2.19: IR, $^1$H NMR and $^{13}$C NMR Spectra of Disazo Disperse Dyes (1aD$_8$ and 2aD$_8$)
Fig. 2.20: IR, $^1$H NMR and $^{13}$C NMR Spectra of Disazo Disperse Dyes (1aD$_9$ and 2aD$_9$)
Fig. 2.21: IR, $^1$H NMR and $^{13}$C NMR Spectra of Disazo Disperse Dyes
$(1aD_{10}$ and $2aD_{10}$)
Fig. 2.22: Mass Spectra of Disazo Disperse Dyes

(1aD₁, 1aD₂ and 1aD₃)
Fig. 2.23: Mass Spectra of Disazo Disperse Dyes

$(1aD_6, 1aD_8$ and $1aD_9$)
Fig. 2.24: Mass Spectra of Disazo Disperse Dyes

(2aD₁, 2aD₂ and 2aD₃)
Fig. 2.25: Mass Spectra of Disazo Disperse Dyes

(2aD₆, 2aD₈ and 2aD₉)
2.5.3 Results and Discussion

The synthetic route followed for the synthesis of disperse disazo dyes is outlined earlier in Scheme 2.9. The Mannich bases (1a-d, 2a-d) used in preparation of disazo disperse dyes have already been described in earlier section (2.4.4). The Mannich base (1a-d, 2a-d) was diazotized and the diazonium solution was immediately used in coupling reaction with different phenols to give a eight series of disperse disazo dyes. The reaction yields were between 65-90%. The introduction of substituents (-OH, -OCH₃ or both) in the phenyl ring of diazonium salt of Mannich base, gave relatively higher yield of dyes as compared to the dyes derived from Mannich base of unsubstituted phenyl ring in both groups (MBUD- and MBTD-group). The presence of electron-donating groups is believed to account for higher yield obtained for dyes. Thus the yield obtained for the dyes of 1d-and 2d-series was highest (> 80%) in each group. These dyes were purified by recrystallization from suitable solvents and their purity was checked by TLC. The value of number of azo groups estimated in each dye was found to be almost two indicating the formation of disazo dyes. The analytical data of C, H and N content of all disperse disazo dyes are in good agreement with calculated values. The important bands in the IR spectra as well as main signals of ¹H NMR and ¹³C NMR spectra are assigned. The observed UV-visible absorption bands are assigned to the corresponding electronic transitions.

The important diagnostic bands in IR spectra of dyes were assigned and the characteristic frequencies of absorption bands are reported in earlier section 2.5.2. The characteristic absorption bands of Mannich base moiety of a disperse dye resemble to those of corresponding parent Mannich base (reported section 2.4.5) Fig 2.26 except that of primary amino (−NH₂) groups of p-phenylenediamine rings. It is seen that primary amino (−NH₂) stretching vibration of p-phenylenediamine ring at 3380-3300 cm⁻¹ disappeared and two new bands at 1520 cm⁻¹ and 1450 cm⁻¹ appeared due to asymmetric and symmetric stretching vibration of azo group (N=N) in FT-IR spectrum of each dye. Significant shifts in the absorption band of azo group (N=N) at 1520 cm⁻¹ were observed in the spectra of dyes which may be due to occurrence of resonance between azo group and the phenyl ring. Besides this, other characteristics absorption bands of phenolic component are summarized in the following:
Fig.: 2.26 IR Spectra of Parent **DHPM, Mannich Base** and its **Disperse Disazo Dyes**
FT-IR spectra of all dyes showed a broad characteristic absorption band of phenolic (-OH) in the range 3550-3220 cm\(^{-1}\). The low frequency values of –OH stretching band may be due to intra-molecular hydrogen bond formation with the lone pair of electrons on the nitrogen atoms of azo groups. Further the characteristic absorption peak of different substituent groups such as 720 cm\(^{-1}\) (chlorine (-Cl)), and 1480 cm\(^{-1}\) methyl (-CH\(_3\)), of phenolic coupler in relevant dyes are observed at particular frequencies which are in good agreement with the literature data\(^6\). Besides this, the FT-IR spectra of dyes show strong or medium absorption bands corresponding to out of plane deformation of C-H bonds of aromatic ring in the range 890-720 cm\(^{-1}\) according to types of substitution in the aromatic ring. (di, or trisubstituted etc.).

\(^1\)H NMR and \(^{13}\)C NMR spectral data are interpreted typically for 1aD\(_{1-10}\) and 2aD\(_{1-10}\) as a representative of each group of dyes.

The general structure of dyes in 1aD\(_{1-10}\) series is

As shown in Fig. 2.27, comparison between the \(^1\)H NMR of the disperse disazo dye 1aD\(_1\) and its starting Mannich base 1a it was observed that:

- A singlet at \(\delta\) 3.5ppm equivalent to 4H of two primary amino groups of aromatic diamine rings of Mannich base was disappeared and

- A new singlet integrating for 2H of OH group of two phenolic coupling components was appeared in the \(^1\)H NMR spectrum of a dye.

- As well as, all the aromatic protons of azo dyes showed the multiplets at downfield value \(\delta\) 6.7-7.6 integrating for 21H and it is in agreement with number of protons of five benzene rings shown in above structure.
Fig.: 2.27 $^1$H NMR Spectra of Parent DHPM, Mannich Base and its Disperse Disazo Dyes
• A singlet due to phenolic (–OH) of dyes was observed at δ 8.2 ppm equivalent 2H for all the dyes except that of 1aD₂ (4H equivalent) which was derived from resorcinol.

• The ¹H NMR signal due to substituents present in the phenyl ring of coupling components are in agreement with literature. (δ 3.9 ppm, s, 3H for two –CH₃ groups and δ 3.7 ppm, s, 2H for two –NH₂ groups).

Analogously the comparison (Fig. 2.28) between the ¹³C NMR data of dyes and parent Mannich base reveals the same pattern of ¹³C NMR signals with the occurrence of two more signals in the region 161-164 due to two C-OH of phenolic groups of coupling components in dye. However the carbon atoms of phenol aromatic ring in the dye resonated upfield and appeared in the region 109-146 ppm, from 114-146 ppm and 128-145 ppm for N-Mannich bases and DHPMs respectively.

The general structure of dyes in 2aD₁-10 series is

As shown in Fig. 2.27, comparison between the ¹H NMR of the disperse disazo dye 1aD₁ and its starting Mannich base 1a it was observed that:

• A singlet at δ 3.6ppm equivalent to 4H of two primary amino groups of aromatic diamine rings of Mannich base was disappeared and

• A new singlet integrating for 2H of OH group of two phenolic coupling components was appeared in the ¹H NMR spectrum of a dye.
Fig.: 2.28 $^{13}$C NMR Spectra of Parent DHPM, Mannich Base and its Disperse Disazo Dyes
• As well as, all the aromatic protons of azo dyes showed the multiplets at downfield value \( \delta \) 6.9-7.6 integrating for 21H and it is in agreement with number of protons of five benzene rings shown in above structure.

• A singlet due to phenolic (–OH) of dyes was observed at \( \delta \) 8.2 ppm equivalent 2H for all the dyes except that of \textit{2aD}_2 (4H equivalent) which was derived from resorcinol.

• The \(^1\)H NMR signal due to substituents present in the phenyl ring of coupling components are in agreement with literature report. (\( \delta \) 3.9 ppm, s, 3H for two –CH\(_3\) groups and \( \delta \) 3.7 ppm, s, 2H for two –NH\(_2\) groups).

Analogously the comparison (Fig. 2.28) between the \(^{13}\)C NMR data of dyes and parent Mannich base reveals the same pattern of \(^{13}\)C NMR signals with the occurrence of two more signals in the region 162-164 due to two C-OH of phenolic groups of coupling components in dye. However the carbon atoms of phenol aromatic ring in the dye resonated upfield and appeared in the region 111-146 ppm, from 114-146 ppm and 128-145 ppm for N-Mannich bases and DHPMs respectively.

Finally the mass spectra of \textit{1aD}_1 and \textit{2aD}_1 dyes (Fig. 2.29) show the formation of base peaks at m/z 183 and 199 and they are similar to those of stable ions obtain from corresponding parent Mannich bases (\textit{1a} and \textit{2a}) and DHPMs (\textit{BU}_1 and \textit{BT}_1). Further the fragmentation pattern of \textit{1aD}_1 and \textit{2aD}_1 resembles each other as described in following.

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<td>C(_6)H(_5)OH(^-)</td>
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<td>274</td>
<td>2(CH(_2)NHC(_6)H(_4)N=NC(_6)H(_5)OH(^-))</td>
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Fig.: 2.29 Mass Spectra of Parent DHPM, Mannich Base and its Disperse Disazo Dyes
Electronic Absorption spectra

Substituent effects

Absorption spectra of the disazo dyes (Fig. 2.30) were recorded over range of \( \lambda \) between 300-700 nm in DMF at concentration \( 1.6 \times 10^{-3} \) M and results are summarized in Table 2.8. While the replacement of pyrimidinone (C=O) to pyrimidinethione (C=S) on pyrimidine ring of diazonium Mannich base exerted a negligible change \( \lambda_{\text{max}} \) on comparing azo dyes of two groups (MBUD- and MBTD-group)

Fig.: 2.30 Absorption Spectra of Disperse Disazo Dyes in DMF
Table 2.8 Absorption Spectral Data of Disperse Disazo Dyes in DMF

**MBUD- group**

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<th>1c-series</th>
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**MBTD- group**

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<th>2b-series</th>
<th>2c-series</th>
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The effects of substituents in phenolic components were evaluated relative to the dye \( D_1 \) derived from unsubstituted phenol coupling component in each series of dyes of two groups (**MBUD- and MBTD- groups**).

- The values of the logaritham of molar extinction coefficient (\( \log \varepsilon \)) for all the dyes were in the range 4.1- 4.8 (except \( 1bD_1, 1bD_2, 2bD_1, 2aD_2 \)) consistent with their high intensity of absorption.

- Bathochromic shifts in the region 93-194 nm and 70-180 nm were observed respectively for dyes \( D_9 \) and \( D_{10} \) of all series and it may be due to increase in aromaticity of naphthalene ring as compared to benzene ring of phenol.

- Dyes \( D_2 \) and \( D_8 \) in each series containing electron donating groups –OH and –NH\(_2\) in meta and para position to azo group showed bathochromic shifts of 44-140 nm and 15-94 nm respectively as expected due to auxochromic nature of these groups.

- Whereas dyes \( D_6 \) and \( D_7 \) containing weak electron acceptor chloro group (o- and p-) respectively showed a bathochromic shifts of 17-45 nm and 17-80 nm.

- Mean while the presence of methyl group in ortho, para and meta position of phenol exerted small bathochromic shifts of 3-40 nm for dyes \( D_3, D_4, \) and \( D_5 \) of two groups.

- Similar effects of the substituent of phenyl ring of DHPM of diazonium Mannich base were also observed in absorption maxima of dyes of two groups. The absorption maxima of following dyes showed hypsochromic shifts of -3 to -24 nm relative to corresponding dyes derived from diazonium components of **1a-series** and **2a-series** and this is indicating antiauxochromic nature of substituents present in the DHPM.

**Solvent effects**

Absorption spectra of the selected disazo dyes \( 1aD_1, 1aD_8, 1aD_{10} \) (**MBUD-group**) and \( 2aD_1, 2aD_8, 2aD_{10} \) (**MBTD-group**) (Fig.2.31) were recorded over range of \( \lambda \) between 300-700 nm using five solvents viz; acetone, acetonitrile, methanol, dimethylformide (DMF) and dimethylsulphoxide (DMSO), at concentration \( 1.6 \times 10^{-3} \) M and results are summarized in **Table 2.9-2.10**
Fig.: 2.31 Absorption Spectra of Disperse Disazo Dyes in Various Solvent

$\textbf{1aD}_1, \textbf{1aD}_8, \textbf{1aD}_{10}$ and $\textbf{2aD}_1, \textbf{2aD}_8, \textbf{2aD}_{10}$
Table 2.9  Influence of Solvents on $\lambda_{\text{max}}$ (nm) of Dyes

### 1a and 2a-Series

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### Table 2.10: Influence of Solvents on $\lambda_{\text{max}}$ (nm) of Dyes

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#### 1d- and 2d-Series

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• The electronic spectra of these dyes showed an absorption band in the region 331-498 nm in acetone, 330-480 nm acetonitrile, 365-561 nm in dimethylsulphoxide (DMSO), and 330-497 nm in methanol and 361-553 nm in dimethylformide (DMF). This band was due to electronic transitions involving the whole conjugate system (both of the phenyl and pyrimidine) and the azo groups are assigned to a transition of $\pi \rightarrow \pi^*$ type.

• Bathochromic shifts of the visible absorption band were also observed for the dyes $1aD_1, 1aD_8, 1aD_{10}$ (MBUD-group) and $2aD_1, 2aD_8, 2aD_{10}$ (MBTD-group) on increasing the solvent polarity. The absorption maxima of these dyes showed bathochromic shifts considerably in this order: DMSO > DMF > acetonitrile > methanol > acetone.

• However the visible absorption spectra of other dyes did not show regular variation with the polarity of solvent and this may be due to effect of substituent.
References


[54]. Zolinger H. *Azo and Diazo-Chemistry*. New york: wiley (Inter science); 1961:221-83.


