CHAPTER 2

Synthesis of Novel pyrrolo [2,3-b]quinolin-2-one and

Pictet Spengler type synthesis of pyrrolebenz [b] and evaluation of their

biological activity

In this chapter, we describe the synthesis of 1-phenyl-1H-pyrrolo [2, 3-b]quinolin-2(3H)-one 116a-h and Benzo [b] pyrrolo [3, 4-e azepine] 1,3 (2H,3aH)-dione 121a-c, 122a-d, 123a-b, 124a-c and 125a-j by using Brownsted acid catalyzed (AcOH) Pictet-Spengler type reaction. Synthesized compounds were studied for their biological activity.

This chapter is divided into two sections.


Section B: Pictet-Spengler type synthesis of Benzo [b] pyrrolo [3, 4-e] azepine derivatives and evaluation of pesticidal activity against Dysdercus cingulatus (Red cotton bug).

2.1 Introduction

The construction of ring structures beginning from compound having ortho nitro or ortho amino functionality has wide applicability for the synthesis of enormous number of heterocyclic ring systems. This method leads the direction of five, six and seven membered ring system having nitrogen as a heteroatom with ring growth (linear/angular) and generally permits the direct and regiospecific introduction of functional groups in the newly formed heterocyclic ring. Among numerous possibilities for ortho joined
functionalities those containing carbon and nitrogen are of particular interest. From literature it was noted that compound having o-amino/nitro functionality has been utilized for synthesis of various heterocycles like quinoline, isoquinoline, indole, pyrrole, azepine, benzazepine, etc. Polynuclear heterocycles derived from quinolines represent an important class of compounds and have attracted a great deal of attention in recent years because of their wide range of pharmacological properties [1] such as antitumor agents [2], gastric acid secretion inhibitors [3-4], antileishmanial agents, [5] hypotensive. [6] This scaffold affords a wide range of modulation allowing its chemical structure to fit with a variety of targets involved in tumor progression, such as kinases, growth factor receptors or DNA itself. Also quinoline fused with pyrrole ring has important scaffold in many natural and synthetic compounds [7-13]. Therefore development of new strategy for the synthesis of such types of nitrogen containing heterocycle is more important in the field of heterocyclic chemistry.
Quinoline derivatives have been widely used for the treatment of malaria [14-16]. Systematic modification of quinoline led to the potent antimalarial chloroquine drugs 1. Encouraged with these findings, chemists focused on synthesizing other new compounds which contain the quinoline scaffold. The screening efforts produced quinine 2, pamaquine and primaquine 3 and other several reports of new potent quinoline compounds exhibit good activity against malaria. The functionalized quinolines and their hetero-fused analogs are present in numerous natural products [17-20] such as marinoquinoline-A 4 showed antibacterial and antifungal activities [17], camptothecin 5 [18] and luotonin-A 6 [19], along with the wide spectrum of physiological activities.

The Pictet Spengler reaction is one of the simplest methods for the synthesis of tetrahydro β-carboline [21-25] tetrahydro isoquinoline [26, 27] and indolo benzazepines [28-31] derivatives. In recent years, the literature has grown significantly and modified methods describing the use of Bronsted acids (protic acid) catalysts such as HCl, AcOH, H_2SO_4 TFSA (trifluoromethane sulphonic acid), TFA, chiral phosphoric acid [25,28, 32] as well as Lewis acid catalysts such as AlCl_3, ZnCl_2, AuCl, PdCl_2, AuCl_3, AuBr_3, Sc(OTf)_3, Sm(OTf)_3, In(OTf)_3, [21, 22] and ionic liquids ([bmim]BF_4, [bmim]Cl-AlCl_3, etc.) have been reported [33-34]. Literature revealed that the synthesis of benzazepine scaffolds is an interest to synthetic and medicinal chemistry due to their presence in natural products[35,36] and broad spectrum of biological active compounds such as immobilized inhibitor [37], nNOS inhibitor [38], growth hormone secretagogue (L-692,429) [39], antileishmanial chemo type [40], antiproliferative [41], 5-HT_2c and 5-HT_2a/2c receptor antagonist [42-43], non-peptide vasopressin V_2 receptor antagonist [44-45], antioxidant [46], antiparasitic [47], antitumor agents [48], AVP antagonist [49], Anti-HIV-1 agents.
arginine vasopressin antagonist[54-55]. Fused benzazepines is an important class showing similar structural motif of many medicinally relevant compounds. The preparation of these structural scaffolds needs multi steps synthesis and this requirement invites more efficient methodologies for the construction of such functionalized units. In recent years, a number of catalysts have emerged as powerful approaches to the construction of benzazepine-fused ring systems [56] are limited to synthesis of fused benzazepine derivatives. Pictet-Spengler Reaction [57] is widely applicable for the construction of various nitrogen containing heterocycles [58]. This transformation is generally accomplished by treatment of aldehydes with β-(hetero) aryl ethylamine in the presence of acidic catalyst, which promotes the imine formation and subsequent cyclization through an intramolecular Friedel-Craft reaction. Limited reports have been exploited for the construction of chiral seven membered ring systems by Pictet-Spengler-type reaction. Herein, we wish to report two steps synthetic efficient route for the synthesis of Pyrollo[2,3-b] quinoline starting from maleimide and the synthesis of 2, 3-dihydro Benzo[b]pyrrolo [3, 4-e azepines] derivatives, through an acetic acid catalyzed Pictet-Spengler-type reaction. Much attention has been paid for the construction of pyrrole fused with quinoline and benzazepine ring systems due to their biological properties [59].

- **Literature updates** for the synthesis of linear vs angular pyrrolo [2, 3-b] quinoline

Saito T. *et al.* [60] reported the synthesis of pyrrolo [2,3-b]quinolines via Rh(I) catalyzed carbodiimide-Pauson-Khand-type reaction. Reaction of compound 2-azidobenzaldehyde or 1-(2-azidophenyl)ethanone with lithium acetylene at -78°C temperature in THF
afforded compound 8, which on O-methylation gives compound 9, further compound 9 on reaction with TPP afforded iminophosphorane compound 10 by Staudinger reaction, which on aza-wittig reaction with isocyanate afforded carbodiimide 11, the catalytic Pauson-Khand reaction is carried out using carbodiimide 11 in presence of \([\text{RhCl(CO)}_2\text{dppp}]_2\) in refluxing toluene afforded compound 12 in low to good yield.

Shanmugam et al. [61] reported the synthesis of 1-Aryl-2-Chloro-1-H-pyrolo[2,3-b]quinolines 16. The compound quinolone-3-acetic acid 13 on reaction with N, N-bis[iodomagnetium] aniline 14 afforded the anilides 15, which on further heating with POCl₃ afforded the 1-Aryl-2-Chloro-1-H-pyrolo[2,3-b]quinolines 16 in 60-65% yield.

Mphahlele et al. [62] reported palladium-catalyzed heteroannulation of 2-aryl-3-iodo-4-(phenylamino) quinolines and 4-(N, N-allylphenylamino)-2-aryl-3-iodoquinoines to 1H-pyrrolo [3,2-c]quinoline derivatives. Quinoline 17 subjected to Palladium(0)/copper iodide catalyzed Sonogashira cross-coupling with phenylacetylene to afford 4-chloro-2-
phenyl-3-(phenylethynyl)quinoline 18, which was further reacted with aniline in refluxing ethanol to yield 2-phenyl-4-(phenylamino)-3-(phenylethynyl)quinoline 19, which was cyclized by refluxing compound in dioxane/water to 20.

Testa et al. [63] reported the synthesis of pyrrolo [3, 2-c] quinoline derivatives via imine formation. Paal Knorr reaction between 1, 4-diketone 21 and alkyl or aryl amines by in acetic acid at reflux temperature for 3-8 h, afforded the corresponding 5-(o-nitro phenyl)-1-substituted pyrroles 22 in 60–87% yield, which was reduced in to 5-(o-amino phenyl)-1-substituted pyrroles 23 in H₂ in Pd/C in good to excellent. Treatment of amine with aldehydes in the presence of p-toluenesulphonic acid (p-TsOH) in DMF at 100°C afforded compounds 26 in good yields 72–94%, within 3 h, through intermediate 24 and 25.
Kravchenko et al. [64] reported the synthesis of 4-Substituted 2-(2-Acetyloxyethyl)-8-(morpholine 4-sulfonyl)pyrrolo[3,4-c]quinoline 1,3-diones as potent caspase-3 inhibitors. The chloride compound 27 was reacted with morpholine in 1, 4-dioxane to give sulfonyl amide 28, which was further refluxed in a AcOH/water (1:1) mixture to afford 8-sulfamoyl isatin 29. Dicarboxylic acids 30 were prepared by reaction of isatin with aq. KOH at room temperature for 12 h in 60-87% yield. Acids 30 were converted into furandiones 31 upon the reaction with acetic anhydride. Reactions of anhydrides 31 with 2-aminoethanol in Ac2O and pyridine smoothly led to imides 32.

Boisse et al. [65] reported three steps synthetic route for the synthesis of pyrrolo quinoline. Ketoester 33 was obtained one-pot by Michael addition of glycine to methyl acrylate followed by Dieckmann cyclization. Unsubstituted or acylated analogs of enaminoesters 34 have been obtained by using ammonium formate, possibly in the presence of acetic anhydride. In order to examine this reaction sequence, Bredereck’s reagent was heated with β-enaminoester 35 (R=4-OMe). The reaction on the activated methylene group started very slowly, leading to dimethylenamine 36. Strong basic alkoxide was necessary, with better results observed with t-BuOK than with sodium...
methoxide. The key intermediate 36 was not isolated, but in situ led to condensed pyrrolidinoquinoline 37 and dimethylamine.

Lee et al. [66] reported the synthesis of dihydropyrroloquinolines and evaluation selectively Antagonise p-Glycoprotein. The imine compound 40 was obtained by reacting compound 38 with imide compound 39 having α-methylene group. Compound 40 undergoes cyclization to 41. The free amine functionality on reaction with alkyl halide gives compound 42 while on reacting with acyl halide gives 43.

Parvatkar et al. [67] reported double reductive cyclization to indoloquinoline alkaloid cryptotackieine. Indoloquinoline 47 was synthesized in two steps procedure. Condensation reaction between o-nitrobenzaldehyde 44 and o-nitrophenylacetic acid 45
in Ac₂O and NEt₃ followed by refluxing obtained acid in EtOH and catalytic H₂SO₄ for 24 h afforded compound 46 in 71% yield, which on reduction with Fe/AcOH in presence of HCl afforded compound 47 in 74% yield. During reduction four reaction took place in a concerted manner i.e. reduction of both nitro groups, cyclization, isomerization of double bond (E-amide to Z-amide) and second cyclization. Compound 47 on further methylation on quinoline nitrogen afforded the alkaloid cryptotackieine 48 in 84% yield.

Nishino et al. [68] reported efficient Copper-Catalyzed Oxidative Direct Cyclization of N-Methyl anilines with Electron-Deficient Alkenes Using Molecular Oxygen. Compound Tetrahydroquinoline 51 was obtained by one pot reaction. Stirring the compound N, N-dimethylaniline 49 with N-phenylmaleimide 50 in the presence of 20 mol % of CuCl₂ catalyst in MeCN at room temperature for 24 h using molecular oxygen afforded the skeleton 51 in good yield.
**Literature updates** for the synthesis of Benzo[b]azepines

Wang et al. [69] reported palladium catalyzed synthesis of benzazepines. Reaction of Isatin 52 and diphenylacetylene 53 to give the corresponding benzazepine 54. Based on optimization experiments, the best results were obtained using Pd(OAc)$_2$ as catalyst with stoichiometric amounts of AgOAc as the oxidant in a mixed solvent of MeCN/1,4-dioxane. Under these conditions, conversion was complete within 24 h at 120$^\circ$C in an inert N$_2$ condition.

\[
\text{NHO}_2 + \text{Ph} + \text{Pd(OAc)}_2 (10 \text{ mol} \%) \xrightarrow{\text{AgOAc, 100$^\circ$C}} \text{NHO}_2 + \text{Ph}
\]

Cheng et al. [27] reported synthesis of indolo [3, 4-cd] [1]benzazepines by catalytic asymmetric Pictet Spengler reaction. Reaction of amine compound 55 with aldehydes or imines 56 in presence of chiral phosphoric acid catalyst, at room temperature for 24 h afforded the compound 57 in 99% yield. In this report imine was used instead of aldehydes, for Pictet Spengler reaction.
Ikemoto et al. [70] reported the synthesis of benzazepine having chiral sulphoxide moiety which act as a candidate for an orally active HIV-1 therapeutic agent. Compound butyric acid 60 was obtained in one-pot by the hydrolysis of 1-isobutylpyrrolidin-2-one 58 with aqueous MsOH followed by neutralization and anilination of 59. Compound 60 was esterified with MeI and K₂CO₃, which was treated with the combination of NaOMe and dimethyl carbonate followed by hydrolysis to give 61 in 52% Yield. The Suzuki–Miyaura reaction of 61 with boronate complex led from aryl bromide gave 63 in 86% yields. The treatment of carboxylic acid 63 with 1.1 equiv of oxalyl chloride and a catalytic amount of DMF in THF, followed by amidation with 1.3 equiv of 64 and 3.5 equiv of i-Pr₂NEt, gave crude 65 without the Pummerer rearrangement.
Cossy et al. [71] reported the synthesis of Spiro [benzazepine-2,4'-piperidine. The synthetic approach based on a Heck reaction and an intramolecular aldol condensation. Compound amine 67 radially obtained by reaction of imine 66 with homoallylmagnesium bromide, allyl magnesium bromide in toluene. After deprotection of 68 in HCl/EtOH, at reflux condition, for 2 h and treatment of the resulting diamine 68 with acetic anhydride in the presence of DMAP, the monoprotected amine 70, with an overall yield of 47%. Heck reaction was applied to 69 in Pd(OAc)$_2$ PPh$_3$, Et$_3$N, mixture of 70 and 71 was obtained, this mixture was treated with an excess of acetyl chloride (16 equiv) in refluxing chloroform for 20 h, the more thermodynamically stable N,N-diacetylated spiro[benz-azepine-2,4'-piperidine] 72. The compound 74 keto aldehyde was obtained by ozonolysis of compound 73 followed by Me$_2$S reduction of the ozonide (73% yields). The construction of the seven-membered ring of 76 was achieved from 74 by using an intramolecular aldol condensation. When compound 74 is treated with an aqueous methanolic solution of KOH, three products are obtained, 75-a (aldolisation-crotonisation...
product), 75-b (aldolisation product) and 75-c (addition of methyleate on 75-a), were isolated in an 8/1/1 ratio (48% yield). When the reaction was performed in THF in the presence of an aqueous solution of KOH, only the two products 74-b and 75 were obtained, 74-b could be transformed to 75 by treating compound 74-b was treated with mesyl chloride in the presence of DMAP at room temperature. After hydrogenation of 26 in H₂, Pd/C, the desired spiro [benzazepine-2, 4'-piperidine] 76 was isolated in 74% yield.

Kundu et al. [30] reported the novel synthetic strategy for the synthesis of benzo fused diazepine compounds by Pictet Spengler reaction. In the first instance, imidazoles 80 with aryl- NH₂ originating from N-1 of the ring was synthesize by treating 2,4 disubstituted imidazoles 77 with o-nitrobenzyl bromide 78 in the presence of NaH to get
The resulting N-1 linked aryl nitro 79 was then reduced to NH$_2$ to obtained 80 functionality via catalytic hydrogenation. The compound 80 was utilized for further Pictet Spengler reaction. This led to carry out the Pictet Spengler reaction under a variety of reaction conditions such as acid-catalyzed and neutral conditions in order to optimize the cyclization via C-C bond formation. Treatment of imidazole derivative 80 with p-ethoxybenzaldehyde in the presence of p-TsOH in toluene at reflux for 18 to 20 h gives Schiff’s base 81, which undergoes intramolecular cyclisation to 82.

He et al. [72] reported Iridium-Catalyzed Tandem Enantioselective Synthesis of 2,3-Dihydro-1H-benzo[b]azepines. Compound 83 on treatment with (E)-but-2-ene-1, 4-diyldimethyl dicarbonate 84 in [(Ir(cod)Cl)$_2$] (cod=1,5-cyclo-octadiene) and the phosphoramidite ligand L1 and DABCO as a base, in THF at 50°C for 12 hours to give 85 in 73% yield. The formation of 85 indicates that the intramolecular allylic amination reaction proceeds faster than the allylic vinylation reaction.
Palma et al. [46] reported the synthesis and in vitro activity of new tetrahydronaphtho [1, 2-b] azepine derivatives against Trypanosoma cruzi and Leishmania chagasi parasites. N-benzyl-a-naphthylamines, on reaction with an excess of allyl bromide in the presence of potassium carbonate in dry acetone under reflux, were converted into N-allyl-N-benzyl-substituted-a-naphthylamines 86 in good yields 70–85%. The introduction of an allyl moiety at the ortho-position of the amino group was carried out via an aromatic amino-Claisen rearrangement of the N-allyl derivatives 86. Thus, rearrangement of these derivatives by heating in the presence of stoichiometric amounts of boron trifluoride diethyl ether (BF₃·Et₂O), as acid catalyst, at 115–125°C gave the rearranged products 87 in excellent yields 61–88%. Oxidation and subsequent intramolecular 1,3-dipolar cycloaddition of 88 to obtain the corresponding 1,4-epoxytetrahydronaphtho[1,2-b]azepines 89 was carried out by reacting compounds 87 with an excess of hydrogen peroxide (30%H₂O₂) in the presence of catalytic amounts of sodium tungstate (Na₂WO₄·2H₂O) and by heating generated in-situ nitrones in toluene under reflux. Finally, reductive cleavage of the N–O bond of 89 by treating with Zn in 80% acetic acid at 80–82°C for 2–5 h, gave, as expected, exclusively cis-2-aryl-4-hydroxytetrahydronaphtho[1,2-b]azepines 90 in 64–78% yields and study in vitro anti-parasitic activity of compounds 89 and 90 against T. cruzi, L. chagasi.
Sharma et al. [28] reported a synthesis of benzazepinoindoles by Pictet-Spengler cyclisation. Synthesis of substrate 94 was carried out by reacting indole 91 with 2-nitro benzyl bromide 92 in the presence of Na$_2$CO$_3$, resultant nitro intermediate 93 was reduced in Fe/HCl afford the compound 94. Compound 99 was obtained in two steps from 2-nitro phenyl acetic acid 97 by literature procedure [26]. The substrate 94 and 99 has ability to undergo Pictet Spengler cyclisation with aldehydes and ketones. Compound 94 and 99 on reaction with aldehydes and ketones in 2% TFA in DCM at room temperature for 15 min afforded the cyclized product 101 and 96, reaction goes through imine intermediate 95 and 102.
Padwa et al. [73] reported an approach for the preparation of benzazepin-4 one via a hetero Cope rearrangement. Isoxazolidine 104 is readily prepared by a [3+2] cycloaddition from the corresponding N-phenyl-C- phenylnitron 103 in 92% yield as a single stereoisomer. The high pressure technique was particularly rewarding, owing to the commonly encountered reversibility of such cycloaddition reactions at high temperatures. The high pressure is also reverses the selectivity in the cycloaddition reaction . Treatment of 104 with DBU leads to 105, which undergoes the key hetero-Cope process, ultimately giving the ring-expanded product 106 as a 1:2 mixture of Cis and Trans stereoisomers.
Lin et al. [74] reported the azepine framework can be constructed from enamine derivatives and electrophilic acetylene compounds. When 1-acetyl-3-piperidinoindole 107 and dimethyl acetylenedicarboxylate 108 are refluxed in dioxane for one day, the 1:1 adduct 109 is isolated in 96% yield. Cyclobutene (R=CO₂CH₃) is implicated in this two-carbon ring expansion process, although not isolated in this case. Cyclobutene (R=H), however, was isolated when methyl propiolate was employed as the electrophile. The ring expansion product 110 is formed in 68% yield after refluxing for 11 days in dioxane. In both cases, the substitution around the periphery of the seven-membered ring can be exploited for further chemical transformations.

Hossini et al. [75] reported ring expansion of heterocyclic ketone and related systems utilized via a Wittig Preavost sequence. Proctor has prepared several exocyclic alkenes 111 from a variety of heterocyclic ketone derivatives that were subsequently treated with Preavost reaction conditions (AgNO₃, I₂, and CH₃OH). The seven-membered adduct is
obtained as the acetal 112 that was hydrolyzed to the corresponding ketone in good yields (60%). These expansions are highly dependent on the substituents present.

2.2. A. Present work


In this section we describe our approach to synthesize of pyrrolo [2, 3-b] quinoline heterocycles. General approach for the synthesis of pyrrolo [2, 3-b] quinoline is outlined in scheme- 1.
Retrosynthetic approach

\[
\begin{array}{c}
\text{116} \\
\text{118} \\
\text{115} \\
\text{113} \\
\text{120}
\end{array}
\]

Scheme-2

2.3. A. Results and Discussion

2.3.1. A. One pot synthesis of \((E)\)-3-(2-nitrobenzylidene)-1-phenylpyrrolidine-2, 5-dione, 115a-b

\[
\begin{array}{c}
\text{113a-g} \\
\text{114a-g} \\
\text{120} \\
\text{115a-g}
\end{array}
\]

Scheme-3

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Ar</th>
<th>Sr. No.</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>C_6H_5</td>
<td>e</td>
<td>4-ClC_6H_4</td>
</tr>
<tr>
<td>b</td>
<td>4-CH_3C_6H_4</td>
<td>f</td>
<td>4-BrC_6H_4</td>
</tr>
<tr>
<td>c</td>
<td>4-CH_3OC_6H_4</td>
<td>g</td>
<td>CH_3C_6H_5</td>
</tr>
<tr>
<td>d</td>
<td>4-FC_6H_4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The synthesis of compound 115a-g was achieved by the reaction of maleimide 113a-g with TPP in ethanol at room temperature to afford the TPP-Maleimide adduct 114a-g (not isolated), which on further reaction with o-nitro benzaldehyde in situ at room temperature for 30 min afforded product 115a-g in 98-99% yield. All the synthesized compounds were characterized by spectral and analytical methods.
Such as IR spectra of compound 115a showed characteristic absorption bands at 1565 and 1525 cm$^{-1}$ corresponded to NO$_2$ stretching. Whereas, the absorption band for two amide carbonyl appeared at 1757 and 1716 cm$^{-1}$ respectively. The $^1$H NMR spectrum (DMSO-$d_6$) of this compound showed doublet ($J=1.5$ Hz, 2H) at $\delta$ 3.77 for aliphatic CH$_2$, triplet ($J=5.4$ & 1.5 Hz, 2H) at $\delta$ 7.36, triplet ($J=5.4$ Hz, 1H) at $\delta$ 7.43, triplet ($J=5.4$ & 5.7 Hz, 2H) at $\delta$ 7.51, multiplet ($J=5.1$ & 1.5 Hz, 1H) at $\delta$ 7.71-7.62, triplet (1H) at $\delta$ 7.79, multiplet ($J=6.6$, 4.5 & 1.5 Hz, 2H) at $\delta$ 7.88-7.82, corresponded to aromatic protons respectively. The doublet at 8.18 corresponded to protons at vinylic carbon. Further, the mass spectrum of this compound showed characteristic M$^+$ peak at 308 m/z and the elemental analysis was in agreement with molecular formula C$_{17}$H$_{12}$N$_2$O$_4$. On the
basis of these spectral data structure of 115 was settled \( i.e., \) \((E)-3-(2\text{-nitrobenzylidene})\text{-}1\text{-phenylpyrrolidine-2,5-dione}\).

2.3.2. A. \((E)-3-(2\text{-aminobenzylidene})\text{-}1\text{-phenylpyrrolidine-2,5-dione, 118a-g}\)

Amino compound 118a-g was obtained from nitro compound 115a-g by reduction. The nitro compound 115a-g on heating with Fe in AcOH, at \(100^0\text{C}\) temperature for 10 min afforded the amino compound 118a-g in 97-99% yield (Method-A). Synthesis of 118a-g was also achieved stirring from phosphorous ylide 114a-g with o-amino aldehyde 126 in ethanol at room temperature for 45 min gives 118 in 94-98% yield. O-aminobenzaldehyde 126 was obtained by reduction of O-nitrobenzaldehyde 120 in FeSO\(_4\), HCl and NH\(_4\)Cl in H\(_2\)O at \(90^0\text{C}\) for 8-10 min.

![Scheme-4](image)

**Figure No. 3: \(^1\text{H NMR Spectra of } (E)-3-(2\text{-aminobenzylidene})\text{-}1\text{-phenylpyrrolidine-2,5-dione, 118a-g)**
The IR spectra of this compound 118a showed characteristic absorption bands at 3444 and 3363 cm\(^{-1}\) corresponded to NH\(_2\) stretching respectively. Whereas, the absorption band for two amide carbonyl apppeared at 1766 and 1693 cm\(^{-1}\) respectively. The \(^1\)H NMR spectrum (DMSO-\(d_6\)) of this compound showed doublet (\(J= 2.4\) Hz, 2H) at \(\delta 3.69\) for aliphatic CH\(_2\), broad singlet (2H) at \(\delta 4.02\) for NH\(_2\) proton, multiplet (9H) at \(\delta 6.85-7.19\) for aromatic proton and singlet (1H) at \(\delta 7.81\) for vinylic proton. In \(^{13}\)C NMR spectra (DMSO-\(d_6\)) the peaks at \(\delta 34.0\) represented methylene carbons at C\(_3\) position. Whereas, the carbonyl carbon appear at \(\delta 173.2\) and 169.9. All other aromatic carbons appeared at their respective chemical shift positions in between \(\delta 116.6\) and 146.3. Further, the mass spectrum of this solid showed characteristic M\(^+\) peaks at 279 m/z. Also, the elemental analysis obtained was in agreement with the molecular formula C\(_{17}\)H\(_{14}\)N\(_2\)O\(_2\). On the basis of above spectral and analytical data structure 118 was assigned to this solid. \(i.e., (E)-3-(2\text{-aminobenzylidene})-1\text{-phenylpyrrolidine}-2,5\text{-dione.}

2.3.3. A. Synthesis of 1-phenyl-1H-pyrrolo [2,3-b]quinolin-2(3H)-one, 116a-h and 117a-h

![Scheme 5](image)

Refluxing compound 115a-g with Fe in acetic acid for 22 h gives the mixture of products 116a-h and 117a-g (TLC Checked), reaction mixture was cooled and filtered through celite and the excess of acetic acid was removed at reduced pressure on the rotary evaporator and pour it on crushed ice to obtained white solid, which was filtered and
dried. The obtained compound was purified by column chromatography using Hexane: Ethyl acetate (8:2) as an eluent to give 116a-g in 70-75% and 117a-g 25-30%.

The IR spectra of this compound showed characteristic absorption bands at 3058 cm$^{-1}$ corresponded to CH$_2$ stretching. Whereas, the absorption band for amide carbonyl appeared at 1735 cm$^{-1}$ the band absorption at 1436 cm$^{-1}$ for C=N. The $^1$H NMR spectrum (DMSO-$d_6$) of this solid showed two singlet (2H) at δ 3.81 for two CH$_2$ proton, all aromatic proton attached to carbon absorb (10H) at δ 7.41-7.93 In $^{13}$C NMR spectra (DMSO-$d_6$) the peaks at δ 34.3 represented methylene carbons, all other aromatic carbons appeared at their respective chemical shift positions in between δ 119.3 and 157.0, and peak at δ 173.6 is for carbonyl carbon. Further, the mass spectrum of this solid showed characteristic M$^+$ peaks at 260 m/z. Also, the elemental analysis obtained was in
agreement with the molecular formula $\text{C}_{17}\text{H}_{12}\text{N}_{2}\text{O}$. On the basis of above spectral and
analytical data structure 116a was assigned to this solid. i.e., 1-phenyl-1H-pyrrolo[2,3-
b]quinolin-2(3H)-one.

2.3.4. A: Evaluation of antibacterial activity and antifungal activity of pyrrolo [2, 3-
b] quinoline derivatives.

The antimicrobial activity of the synthesized compounds was evaluated by the
agar cup plate method. The antibacterial and antifungal assays were performed in Muller-
Hinton broth and Czapek Dox broth respectively. Evaluation was performed using the
bacteria reseeded in broth for 24 h at 37 °C, and the fungi were reseeded in broth for 48 h
at 25 °C. The antibacterial activity of tested samples was studied against one Gram
positive bacteria Bacillus subtilis NCIM 2250, one Gram negative bacteria Escherichia
Coli ATCC 25922 while Candida albicans MTCC 277, Candida tropicalis MTCC 184,
Aspergillus niger MCIM 545 and Aspergillus clavatus MTCC 1323 were used as
standard fungal strain. The compounds were diluted in DMF with required concentration
for bioassay. DMF was also loaded as control. Streptomycin and griseofluvin was used as
standard to evaluate the potency of the tested compounds under same conditions. The
zone of inhibition was determined from the diameter of the zone of inhibition using
caliper. Each inhibition zone was measured three times to get average value. The
minimum inhibitory concentration (MIC) values were determined on MH agar plates by
pouring the molted agar in Petri dishes according to National Committee for Clinical
Laboratory Standards (NCCLS, M7-A5 January 2000), containing the following
concentrations (mg/mL): 0 (control), 5, 10, 15, 20, 25. The MIC was defined as the
lowest concentration tested samples showing no visible bacterial growth after 24 h
incubation period at 37°C.
In vitro antibacterial and antifungal activity of all newly synthesized compounds was screened by considering zone of inhibition of growth. The synthesized compounds (116a-h) were screened with their different concentrations along with standard antibiotics such as Streptomycin (5 µg/mL) and Griseofluvin (5 µg/mL) (Table-1). The results showed that compounds (116a, 116b, 116c and 116h) had very low antimicrobial activity while compounds (116d-g) showed excellent antibacterial and antifungal activity with MIC value in between (10 and 15 µg/mL). From the data it is clear that antimicrobial activity of the compounds (116d-g) influences by changing the substituent’s on the aromatic ring. Compound 116d having fluorine substituent while, 116e having trifluoro, 116f having chloro, 116g having bromo substituent. Hence, F, Cl, Br and CF₃ substituent’s was showed consistently excellent antimicrobial activity against antibacterial and antifungal strains.

Table-1: Antibacterial and antifungal activity of compounds (116a-h)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Bacillus subtilis NCIM 2250 ZIa (MIC)b</th>
<th>Escherichia Coli ATCC 25922 ZI (MIC)</th>
<th>Candida albicans MTCC 277 ZI (MIC)</th>
<th>Candida tropicalis MTCC 184 ZI (MIC)</th>
<th>Aspergillus niger MCIM 545 ZI (MIC)</th>
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<td>17.3(20)</td>
<td>-</td>
<td>13.7(20)</td>
<td>-</td>
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<tr>
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<td>16.1(20)</td>
<td>14.2(20)</td>
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<td>17.1(10)</td>
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<tr>
<td>116f</td>
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<td>12.4(10)</td>
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<td>16.9(15)</td>
<td>15.3(15)</td>
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<tr>
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<td>n.t.</td>
<td>n.t.</td>
<td>16.8(05)</td>
<td>17.3(05)</td>
<td>16.9(05)</td>
<td>17.6(05)</td>
</tr>
</tbody>
</table>

Bold values indicates better results  
Minimum inhibitory concentration in µg/ml  
Zone of inhibition in mm  
n.t. not tested
2.2.B. Present work

Section: B

In this section we describe the synthesis of benz[b]azepine derivatives by Brownsted acid catalyzed Pictet Spengler reaction. General approach for the synthesis of benz[b]azepines is outlined in scheme- 3. All the synthesized compound ware studied for their in vitro activity against Red cotton bug.

Scheme-6
The retrosynthetic pathway for the synthesis of benz[b]azepines

Scheme-7

2.3. B. Result and discussion

2.3.1. B. 4, 4-dimethyl-2-phenyl-4, 5-dihydro Benzo [b]pyrrolo [3, 4-e azepine] 1, 3 (2H, 3aH)-dione, 121a-c

Scheme-8

<table>
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<th>Ar</th>
<th>R</th>
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<tr>
<td>a</td>
<td>C₆H₅</td>
<td>H</td>
</tr>
<tr>
<td>b</td>
<td>4-CH₃C₆H₄</td>
<td>H</td>
</tr>
<tr>
<td>c</td>
<td>4-CH₃C₆H₄</td>
<td>CH₃</td>
</tr>
</tbody>
</table>
Possible Mechanism:

[Chemical structures and reaction pathways are shown here.]

Scheme-9

Reaction of 118a-b with various aldehydes or ketones gave the unisolated imine intermediates 127, which are converted into iminium ion intermediate 128 by N-protonation with Brownsted acid. It is the electrophilicity of iminium double bond that is the driving force of the cyclization. The reaction mechanism occurs by the initial formation of the imine ion 127 followed by the electrophilic substitution after deprotonation desired product 128 is formed. The reaction is driven by the nucleophilicity of the 3-position of the pyrrole 2, 5-dione instantaneously attack in S_N2’ fashion on carbon atom of the imine (C=N) with carbon-carbon single bond formation leading intramolecular cyclization to form dihydro Benzo[b]pyrrolo [3, 4-e azepines] derivatives 121a-c was in excellent yield of 93-97%.

Figure No. 4: ^1^H NMR Spectra of 4, 4-dimethyl-2-phenyl-4, 5-dihydro Benzo [b]pyrrolo [3, 4-e azepine] 1, 3 (2H, 3aH)-dione. 121a
The IR spectra of this compound showed characteristic absorption bands at 3473 cm\(^{-1}\) corresponded to NH stretching. Whereas, the absorption band for two amide carbonyl appeared at 1758 and 1704 cm\(^{-1}\) respectively. The \(^1\)H NMR spectra (DMSO-\(d_6\)) of this compound showed two singlet (3H) at \(\delta\) 1.05 and 1.88 for two CH\(_3\) proton attached to aliphatic carbon, singlet (1H) at \(\delta\) 3.52 for aliphatic CH, singlet (1H) at \(\delta\) 4.56 for NH proton and all aromatic proton attached to carbon absorb (9H) at \(\delta\) 6.65-7.48, singlet (1H) at \(\delta\) 7.76 for vinylic proton. In \(^{13}\)C NMR spectrum (DMSO-\(d_6\)) the peaks at \(\delta\) 22.6 and 29.3 represented methyl carbons attached to C\(_2\) position, Whereas, the aliphatic carbon C\(_2\) and C\(_3\) appeared at \(\delta\) 52.1 and 55.6. All other aromatic carbons appeared at their respective chemical shift positions in between \(\delta\) 117.3 and 146.2.
DEPT study shows the absence of peak at $\delta$ 52.1 for C$_2$ for quaternary carbon. Further, the mass spectrum of this solid showed characteristic $\text{M}^+$ peaks at 317 m/z. Also, the elemental analysis obtained was in agreement with the molecular formula C$_{20}$H$_{18}$N$_2$O$_2$. On the basis of above spectral and analytical data structure 121a was assigned to this compound. i.e., 4, 4-dimethyl-2-phenyl-4, 5-dihydro Benzo [b]pyrrolo [3, 4-e azepine] 1, 3 (2H, 3aH)-dione. Similarly compound 122a-d, 124a-c and 125a-j were prepared and characterised.
2.3.2.B. 2-(p-tolyl) 3a, 5-dihydro-1H-spiro [benzo[b] pyrrolo(3,4-e)azepine-4,1’-cyclopentane] 1,3-dione, 123a-b

![Reaction scheme](image)

Scheme-10

<table>
<thead>
<tr>
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<th>n</th>
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</thead>
<tbody>
<tr>
<td>a</td>
<td>-CH₂-</td>
</tr>
<tr>
<td>b</td>
<td>-CH₂-CH₂-</td>
</tr>
</tbody>
</table>

Reaction of the amino compound 118b with cyclic ketone like cyclopentanone 129a and cyclohexanone 119b in ethanol and catalytic acetic acid at reflux temperature for 5-8 h, afforded the spiro compound 123a-b in high yield.

![NMR spectrum](image)

**Figure No. 7:** $^1$H NMR Spectra of 2-(p-tolyl) 3a, 5-dihydro-1H-spiro [benzo[b]pyrrolo(3,4-e)azepine-4,1’-cyclopentane] 1,3-dione, 123a
The IR spectrum of this compound showed characteristic absorption bands at 3488 cm$^{-1}$ corresponded to NH stretching. Whereas, the absorption band for two amide carbonyl appeared at 1754 and 1708 cm$^{-1}$ respectively. The $^1$H NMR spectrum (DMSO-$d_6$) of this compound showed dd at $\delta$1.08 (1H), singlet at 1.68 (4H), doublet at $\delta$ 1.84 (2H), singlet at $\delta$2.39 (CH$_3$), multiplet at $\delta$3.39 (1H), singlet at $\delta$2.69 (1H) and singlet at $\delta$2.62 (1H) for NH proton, all aromatic proton attached to carbon absorb (9H) at $\delta$ 6.67-7.80. In $^{13}$C NMR spectrum (DMSO-$d_6$) the peaks at $\delta$ 24.5 represented methyl carbons attached to aromatic ring, all the aliphatic carbon appeared seperately at $\delta$ 20.4-63.0. Whereas, the aliphatic carbon C$_2$ and C$_3$ appeard at $\delta$ 52.1 and 55.6. All other aromatic carbons

Figure No. 8: $^{13}$C NMR Spectra of 2-(p-tolyl) 3a, 5-dihydro-1H-spiro [benzo[b]pyrrolo(3,4-e)azepine-4,1'-cyclopentane] 1,3-dione, 123a
appeared at their respective chemical shift positions in between δ 119.3 and 146.5, while two amide carbonyl carbon observed at δ169.8 and 173.6 respectively.

2.3.3.B. Evaluation of pesticidal activities of newly synthesized Benzo [b] pyrrolo [3, 4-e] azepine derivative against Dysdercus cingulatus (Red cotton bug),

Dysdercus cingulatus is commonly called as red cotton bug and is pest of cotton, okra, pods. Its life cycle is completed in 35-38 days. There are five instars stages in the life cycle. These insects are collected from nearby fields (of sinner) and treated in plastic jar. Nine synthetic compounds coded as 125a, 125b, 125c, 125d, 125e, 125f, 125i, 125j and 125k was used to study growth and metamorphosis in 4th and 5th instar nymphs of Dysdercus cingulatus. These were freshly moulted 24-36 hours old nymph. All nine compounds were acetone soluble, to begin with the study these compounds were used to find out LD$_{50}$ value. These unable set to the dosages for further. It was observed that there was a different LD$_{50}$ value for different compounds and so in experimentation it was not possible to use same dosages for different compounds. Acetone solution containing compound was used on ventiolateral margin of body different dosage were topically applied by Haniloton microliter syringe. Along with liited count of group was maintained each dose contain 5 nymphs (irrespective of their sex). They were observed daily and record was maintained. The completed results show percentage mortality.

It is observed that compound 125b is most toxic followed by compound 125k, 125f, 125j and 125i. This was common pattern observed with reference to growth and melainoephosis. In all the compounds it is observed that percent mortality increases with increase in dosage and post treatment period of the nine compounds under investigation, compound 125b shows lowest LD$_{50}$ for 4th and 5th instar nymphs as 15.15 µg/mL and
10.02 µg/mL respectively. Moles over the sub lethal doses which are decided on the basis of LD50 were also least. These enable us to be most toxic (Ref Table). On the contrary compound 125k showed maximum LD50 value for both 4th and 5th instar nymphs (Ref. Table-1 and 2).

The general observation which was observed regarding treated insect

a) They showed prolonged inter ecclesial period and
b) Percent mortality increased with increase in dosage

c) No uniform dosage could be set (due to different LD50 values)

d) Morphological abnormalities were least (almost negligible)

Compound 125b most toxic, compound 125f having OH functionality at para position and compound 125k, 125j, 125i appear to be structurally similar. It shows presence of three, two and one aryl-OMe group respectively.

Table-1, Study of invitro pesticidal activity against Dysdercus cingulatus (Red cotton bug).

<table>
<thead>
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<th>Compound</th>
<th>LD50=28.27 µg 4th Instar</th>
<th>LD50=26.33 µg 5th Instar</th>
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<tbody>
<tr>
<td>Dose µg</td>
<td>% mortality</td>
<td>% moult to 5th instar (day)</td>
</tr>
<tr>
<td>125a</td>
<td>1.0</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>39</td>
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<td>28</td>
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Table-2, Dose in µg/mL and killing the bug in 4th and 5th instar.

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<th>5th (days)</th>
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<td>30.28 (8)</td>
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<td>b</td>
<td>1-7</td>
<td>15.15 (9)</td>
<td>10.02 (10)</td>
</tr>
<tr>
<td>c</td>
<td>1-20</td>
<td>54.63 (8)</td>
<td>48.31 (11)</td>
</tr>
<tr>
<td>d</td>
<td>3-20</td>
<td>33.16 (9)</td>
<td>30.18 (8)</td>
</tr>
<tr>
<td>e</td>
<td>1-18</td>
<td>37.42 (9)</td>
<td>34.26 (11)</td>
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<td>f</td>
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<td>21.49 (9)</td>
<td>19.19 (10)</td>
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<td>i</td>
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<td>j</td>
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<tr>
<td>k</td>
<td>1-10</td>
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<td>15.32 (10)</td>
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2.4 Conclusion

Synthesized N-Aryl Pyrrolo[2,3-b]quinoline derivatives by the reductive isomerization of (E)-3-(2-nitrobenzylidene)-1-phenylpyrrolidine-2, 5-dione, in iron and acetic acid, this compounds was studied for their antimicrobial activity and it showed good to excellent antibacterial as well as antifungal activity. Also Benz[b]azepine compounds was synthesized by Pictet-Spengler reaction and thus the obtained new class of compound was studied for their invitro activity against Dysdercus Cingulatus (Red
Cotton Bug) and shows good to excellent result. All this synthesized compounds are new addition in heterocyclic chemistry library.

2.5 Experimental

Synthesis of (E)-3-(2-nitrobenzylidene)-1-phenylpyrrolidine-2, 5-dione, 115a-h

![Chemical structure](image)

<table>
<thead>
<tr>
<th>113, 114</th>
<th>Ar</th>
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</thead>
<tbody>
<tr>
<td>115</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>C₆H₅</td>
</tr>
<tr>
<td>b</td>
<td>4-CH₃C₆H₄</td>
</tr>
<tr>
<td>c</td>
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<td>d</td>
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<td>g</td>
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</tr>
<tr>
<td>h</td>
<td>CH₂C₆H₅</td>
</tr>
</tbody>
</table>

General Procedures
To a solution of compound 113a (1.31 g, 7.01 mmol) in Ethanol (10 ml), was an added portion wise Triphenylphosphine (0.935 g, 7.01 mmol) white solid get separated within 3-5 min, continue the stirring for further 30 min for completion of the reaction (TLC Checked). To this same suspension was added a solution of 2-Nitrobenzaldehyde 120 in ethanol (mL) and stir for 30 min for the reaction completion (TLC Checked). The separated solid was filtered washed with Ethanol, dried and recrystallized from Acetone: DMF=9: 1, to afford the 118a in 94% yield.
(E)-3-(2-nitrobenzylidene)-1-phenylpyrrolidine-2, 5-dione, 115a

Yield: 3.45 g (97%); white solid; M.p. 223-224°C; Rf = 0.32 (hexane: ethyl acetate, 9:1); IR: \( \bar{\nu} = 1757, 1716, 1658, 1565, 1525, 1120 \). \(^1\)H NMR (300 MHz, \( d_6 \)-DMSO) \( \delta \) : 3.77(d, \( J = 1.5 \) Hz, 2H), 7.36 (t, \( J = 5.4 & 1.5 \) Hz, 2H), 7.45-7.41(t, \( J = 5.4 \) Hz, 1H), 7.53-7.49(t, \( J = 5.4 & 5.7 \) Hz, 2H), 7.71-7.62(m, \( J = 5.1 & 1.5 \) Hz, 1H), 7.79(t, 1H), 7.88-7.82 (m, \( J = 6.6, 4.5 & 1.5 \) Hz, 2H), 8.16(d, \( J = 6 \) Hz, 1H); MS (70 eV): \( m/z = 306.9 \) [M-1]⁺; Analysis Calculated for C\(_{17}\)H\(_{12}\)N\(_2\)O\(_4\): Calcd:C, 66.23; H, 3.92; N, 9.09%; Found: C, 66.07; H, 4.10; N, 8.93%.

(E)-3-(2-nitrobenzylidene)-1-p-tolylpyrrolidine-2, 5-dione, 115b

Yield: 3.37 g (98%); white solid; M.p. 198-199°C; Rf = 0.43 (hexane: ethyl acetate, 9:1); IR: \( \bar{\nu} = 1764, 1712, 1664, 1577, 1521, 1184 \). \(^1\)H NMR (300 MHz, \( d_6 \)-DMSO) \( \delta \) : 2.68(s, 3H), 3.79 (s, 2H), 7.25 (t, \( J = 8.1 \) Hz, 2H), 7.30 (t, \( J = 8.1 \) Hz, 2H), 7.7(t, \( J = 6.8 \) Hz, 1H), 7.86-7.79(m, 3H), 8.18(d, \( J = 8.1Hz \) , 1H); MS (70 eV): \( m/z = 323 \) [M+1]⁺; Analysis Calculated for C\(_{18}\)H\(_{14}\)N\(_2\)O\(_4\): Calcd:C, 67.07; H, 4.38; N, 8.69%; Found: C, 67.25; H, 4.26; N, 8.53%.

(E)-3-(2-nitrobenzylidene)-1-(4-methoxyphenyl)pyrrolidine-2,5-dione, 115c

White solid; Yield: 3.23(97%); M. p. 212-214°C; Rf = 0.45 (hexane: ethyl acetate, 9:1); IR (KBr) 3055(C-H), 1769 (C=O), 1716 (C=O), 1660 (C=C), 1564- 1525 (NO\(_2\)), 1380 (C-O) cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) ppm: \(^1\)H NMR : 3.49(s, 3H, OCH\(_3\)), 3.80 (s, 2H, CH\(_2\)), 6.68(d, \( J = 8.1 \) Hz, 2H, Ar-H), 7.29 (d, \( J = 8.1 \) Hz, 2H, Ar-H), 7.64-7.63 (t, \( J = 6.9 & 1.2 \) Hz, 1H, Ar-H), 7.79-7.67 (m, \( J = 6.9 & 1.2 \) Hz, 3H, Ar-H), 8.16 (d, \( J = 8.1 \) Hz, 1H, =CH); MS (m/z): 338[M⁺]; Analysis Calculated for C\(_{18}\)H\(_{14}\)N\(_2\)O\(_5\): Calcd:C, 63.90; H, 4.17; N, 8.28%; Found: C, 64.04; H, 4.33; N, 8.47%.

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(E)-3-(2-nitrobenzylidene)-1-(4-fluorophenyl) pyrrolidine-2, 5-dione, 115d

White solid; Yield: 3.27(96%); M. p. 210-212^0C; R_f = 0.47 (hexane: ethyl acetate, 9:1);
IR (KBr) 1773 (C=O), 1715 (C=O), 1665 (C=C), 1565-1535 (NO_2), 1361 (C-O), 925 (C-F) cm\(^{-1}\);
\(^1\)H NMR (CDCl\(_3\)) \(\delta\) ppm: 3.78(s, 2H, CH\(_2\)), 7.41 (d, J= 6.8 Hz, 2H, Ar-H), 7.73(s, 1H, Ar-H), 7.77(d, J=6.8 Hz, 2H, Ar-H), 7.89(m, 3H, Ar-H), 8.17(d, J= 6.8 Hz, 1H, =CH); MS (m/z): 326 [M^+] , 328[M+2]; Analysis Calculated for C\(_{17}\)H\(_{11}\)FN\(_2\)O\(_4\):
Calcd: C, 62.58; H, 3.40; N, 8.59%.; Found: C, 62.75; H, 3.28; N, 8.71%.

(E)-3-(2-nitrobenzylidene)-1-(3-(trifluoromethyl) phenyl) pyrrolidine-2,5-dione, 115e

White solid; Yield: 3.12(95%); M. p. 186-188^0C; R_f = 0.42 (hexane: ethyl acetate, 9:1); IR (KBr) 1770 (C=O), 1716 (C=O), 1560-1532 (NO_2), 1366 (C-O), 629 (C-F) cm\(^{-1}\);
\(^1\)H NMR (CDCl\(_3\)) \(\delta\) ppm: 3.68 (s, 2H, CH\(_2\)), 7.47-7.29 (m, 4H, Ar-H), 7.72-7.60 (m, 4H, Ar-H), 8.17 (s, 1H, =CH-); MS (m/z): 376 [M^+]; Analysis Calculated for C\(_{18}\)H\(_{11}\)F\(_3\)N\(_2\)O\(_4\):
Calcd: C, 57.45; H, 2.95; N, 7.44%; Found: C, 57.63; H, 3.08; N, 7.31%.

(E)-3-(2-nitrobenzylidene)-1-(4-chlorophenyl) pyrrolidine-2, 5-dione, 115f

White solid; Yield: 3.17(96%); M. p. 179-181^0C; R_f = 0.53 (hexane: ethyl acetate, 9:1);
IR (KBr) 1769 (C=O), 1719 (C=O), 1662 (C=C), 1557-1532 (NO_2), 1358 (C-O), 727 (C-Cl) cm\(^{-1}\);
\(^1\)H NMR (CDCl\(_3\)) \(\delta\) ppm: 3.76(s, 2H, CH\(_2\)), 7.42(d, J= 6.8 Hz, 2H, Ar-H), 7.59(d, J=6.8 Hz, 2H, Ar-H), 7.69(s, 1H, Ar-H), 7.85(m, 3H, Ar-H), 8.15(d, J= 6.8 Hz, 1H, =CH-); MS (m/z): 341[M^+], 343[M+2]; Analysis Calculated for C\(_{17}\)H\(_{11}\)ClN\(_2\)O\(_4\):
Calcd: C, 59.57; H, 3.23; N, 8.17%.; Found: C, 59.73; H, 3.39; N, 8.33%.
(E)-3-(2-nitrobenzylidene)-1-(4-bromophenyl) pyrrolidine-2, 5-dione, 115g

White solid; Yield: 2.99 (97%); M. p. 153-155 °C; Rf = 0.51 (hexane: ethyl acetate, 9:1);
IR (KBr) 1772 (C=O), 1715 (C=O), 1570-1535 (NO2), 1357 (C-O), 525 (C-Br) cm⁻¹: ¹H NMR (CDCl₃) δ ppm: 3.56 (d, J = 2.4 Hz, 2H, CH₂), 7.32 (d, J = 8.8 & 2.4 Hz, 2H, Ar-H), 7.52 (d, J = 7.6 Hz, 1H, Ar-H), 7.62 (dt, J = 8.8 & 2.4 Hz, 3H, Ar-H), 7.74 (dt, J = 8 & 0.8 Hz, 1H, Ar-H), 8.09 (t, J = 2.4 Hz, 1H, Ar-H), 8.18 (dd, J = 7.2 Hz, 1H, =CH); MS (m/z): 385[M⁺], 387[M+2]; Analysis Calculated for C₁₇H₁₁BrN₂O₄: Calcd: C, 60.20; H, 3.27; N, 8.26%; Found: C, 60.35; H, 3.44; N, 8.09%.

(E)-3-(2-nitrobenzylidene)-1-benzylpyrrolidine-2, 5-dione, 115h

White solid; Yield: 3.34 (97%); M. p. 173-175 °C; Rf = 0.47 (hexane: ethyl acetate, 9:1);
IR (KBr) 3053 (CH₂), 1759 (C=O), 1718 (C=O), 1650 (C=C), 1563-1520 (NO₂), 1118 (C-O) cm⁻¹: ¹H NMR (CDCl₃) δ ppm: 3.74 (d, J = 1.5 Hz, 2H, CH₂), 4.57 (s, 2H, CH₂), 7.22 (t, J = 5.4 & 1.5 Hz, 2H, Ar-H), 7.34-7.29 (t, J = 5.4 Hz, 1H, Ar-H), 7.54-7.43 (t, J = 5.4 & 5.7 Hz, 2H, Ar-H), 7.66-7.57 (m, J = 5.1 & 1.5 Hz, 1H, Ar-H), 7.68 (t, 1H, Ar-H), 7.89-7.74 (m, J = 6.6, 4.5 & 1.5 Hz, 2H, Ar-H), 8.18 (d, J = 6 Hz, 1H, =CH); MS (m/z): 322[M⁺]; Analysis Calculated for C₁₈H₁₄N₂O₄: Calcd: C, 67.07; H, 4.38; N, 8.69%; Found: C, 67.23; H, 4.55; N, 8.57%.

Synthesis of ortho aminobenzaldehyde, 130[76]
Procedures

In a round bottom flask was charged with ferrous sulfate heptahydrate (5.25g, 20 mmol), conc. hydrochloric acid (0.025 mL) and of o-nitrobenzaldehyde 120 (5.0g, 2 mmol) in the order given. It was stirred and the flask was heated by means of the steam bath. When the temperature of the mixture reaches 90°, 1.3 ml. of concentrated ammonium hydroxide was added in one portion, and at 2-minute intervals three 0.7 ml. portions of ammonium hydroxide was added. Stirring and heating was continued throughout. The total reaction time is 8–10 minutes. Immediately after the addition of the last portion of ammonium hydroxide, the reflux condenser and stirrer were removed and the flask was connected to the steam-distillation assembly. The mixture was steam-distilled as rapidly as possible and two 50 ml. fractions of distillate are collected during a period of 10–13 minutes. The first fraction was saturated with sodium chloride, and the solution was stirred at 5° until precipitation appears to be complete. The solid was collected on a Buchner funnel and dried in the air. The product weighs 2.72–3.11 g. (57–65%) and melts at 38–39°. The second fraction of the distillate was saturated with sodium chloride and combined with the filtrate remaining from the first fraction. The combined solution was extracted with two 45-ml. portions of ether. The combined ether extract was filtered, dried over anhydrous sodium sulfate, and concentrated by distillation, finally under reduced pressure. The residue solidifies on cooling and weighs 0.6–1.0 g, it was purified by steam distillation from 40–50 ml. of saturated sodium chloride solution. Saturation of the distillate with sodium chloride, cooling, and filtration. The pure product 130 so obtained weighs 0.42–0.87 g. The total yield is 3.3–3.6 g. (69–75%).
Synthesis of \((E)-3\-(2\text{-aminobenzylidene})\)-1-phenylpyrrolidine-2, 5-dione, 118a-b

\[
\begin{align*}
\text{Method A: To a solution of 115 (2.0 g, 6.5 mmol) in acetic acid (30 mL) was added Fe (2.18, 39 mmol, >250-300 mesh size) and resultant reaction mixture was heated at reflux temperature for 10 min. After cooling this reaction mixture was filtered through celite and the filtrate was poured on to crushed ice (50 g). The yellow solid separated was extracted in ethyl acetate, and organic layer was washed with brine (3x50 mL) and then dried over anhydrous Na}_2\text{SO}_4. The solvent was evaporated under reduced pressure and the residue was recrystallized from acetone to afford 118 as a yellow solid (95%).}
\end{align*}
\]

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<th>115, 118 Ar</th>
<th>C\textsubscript{6}H\textsubscript{5}</th>
<th>4-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}</th>
<th>4-OCH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}</th>
<th>4-FC\textsubscript{6}H\textsubscript{4}</th>
<th>4-CF\textsubscript{3}C\textsubscript{6}H\textsubscript{4}</th>
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<td>CH\textsubscript{2}C\textsubscript{6}H\textsubscript{5}</td>
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**Method B:** Nitro compound 115 (1.3 gm, 4 mmol) dissolved in ethyl acetate (41 ml), water (25 ml), iron powder (0.845 gm, 15 mmol) [partical size <100 mesh] was added followed by ammonium chloride (1.4 gm,25 mmol). It was stirred vigoursly at room temperature for a time 24 hr Reaction mixture was filtered through celite and the inorganic residue was washed with ethyl acetate. The ethyl acetate phase was separated and washed with water (3X25mL) followed by brine. Evaporation of solvent on drying with anhydrous Na\textsubscript{2}SO\textsubscript{4} afforded the yellow solid (98%).
Synthesis of (E)-3-(2-aminobenzylidene)-1-phenylpyrrolidine-2, 5-dione, 118a-b

![Chemical structure](image)

<table>
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<tr>
<th>114, 118 Ar</th>
<th>a C₆H₅</th>
<th>b 4-CH₃C₆H₄</th>
</tr>
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</table>

**General procedure**

To a suspension of compound 114a (1.0g, 2.3mmol) in ethanol (5mL) was added a solution o-aminobenzaldehyde 130 (0.28g, 2.3mmol) in ethanol (2ml) and the reaction mixture was stirred for 90 min at room temperature (TLC Checked). The solid was washed with ethanol (3x20) and dried, recrystallized in ethanol afford 118a in 95% yield. Similarly 114b-h were prepared using appropriate TPP adduct.

**(E)-3-(2-aminobenzylidene)-1-phenylpyrrolidine-2, 5-dione, 118a**

Yellow solid; yield: 1. 71 g (95%); M.p. 213-214°C; \( R_f = 0.45 \) (Hexane: Ethyl acetate, 8:2); IR (KBr): 3444, 3363, 3244, 1766, 1693, 1386, 1176, 699 cm\(^{-1}\). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \( \delta = 3.69 \) (d, \( J = 2.4 \) Hz, 2H), 4.02 (bs, 2H), 6.85-6.73 (m, 2H), 7.52-7.19 (m, 7H), 7.81 (s, 1H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): \( \delta = 34.0, 116.6, 118.7, 119.0, 123.2, 126.4, 128.5, 128.6, 129.1, 130.2, 131.4, 132.0, 146.3, 169.9, 173.2 \) ppm; MS (EI): \( m/z 279 \) [M+1]\(^+\); Analysis Calculated for C\(_{17}\)H\(_{14}\)N\(_2\)O\(_2\): Calcd:C, 73.37; H, 5.07; N, 10.07%; Found: C, 73.19; H, 5.25; N, 10.28%.

**(E)-3-(2-aminobenzylidene)-1-p-tolylpyrrolidine-2, 5-dione, 118b**

Yellow solid; yield: 1.86 g (98%); M.p. 195-196°C; \( R_f = 0.55 \) (Hexane: Ethyl acetate, 8:2); IR (KBr): 3444, 3363, 3242, 1766, 1695, 1178, 754 cm\(^{-1}\). \(^1\)H NMR (400 MHz,
CDCl$_3$): $\delta$ = 2.39(s, 3H), 3.67(s, 2H), 4.02 (bs, 2H), 6.83-6.72 (s, 2H), 7.28-7.18 (m, 6H), 7.79 (s, 1H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ = 21.2, 34.0, 116.6, 118.6, 119.0, 123.2, 126.2, 128.5, 129.3, 129.7, 130.1, 131.4, 138.6, 146.3, 170.1, 173.4 ppm; MS (EI): $m/z$ 293 [M+1]$^+$; Analysis Calculated for C$_{18}$H$_{16}$N$_2$O$_2$: Calcd: C, 73.95; H, 5.52; N, 9.58%; Found: C, 74.13; H, 5.32; N, 9.42%.

**Synthesis of 1-phenyl-1H-pyrrolo[2,3-b]quinolin-2(3H)-one, 116a-h and 117a-h**

![Chemical structure](image)

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<th>115, 113 Ar</th>
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<th>(4-\text{OMeC}_6\text{H}_4)</th>
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<th>(3-\text{BrC}_6\text{H}_4)</th>
<th>(\text{CH}_2-\text{C}_6\text{H}_5)</th>
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<td>a</td>
<td>(\text{C}_6\text{H}_5)</td>
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<td>(3-\text{BrC}_6\text{H}_4)</td>
<td>(\text{CH}_2-\text{C}_6\text{H}_5)</td>
</tr>
</tbody>
</table>

**Synthesis of 1-phenyl-1H-pyrrolo[2,3-b]quinolin-2(3H)-one, 116a-h and 117a-h**

To a stirring solution of compounds 115a-h (2.0 g, 6.8 mmol) in acetic acid (20ml) was added Fe (2.23 g, 40.8 mmol) (>200-250 mesh size) and the resultant reaction mixture was heated at 100$^\circ$C for 24 hours, and was filtered through celite and washed with acetic acid, the filtrate was concentrated and poured onto crushed ice. The white solid obtained was filtered and dried. The mixture of product was separated by column chromatography using Hexane: Ethyl acetate as an eluent to give 116a-h in 75% and 117a-h 25%.
1-phenyl-1H-pyrrolo[2,3-b]quinolin-2(3H)-one, 116a

White solid; Yield: 1.21g (72%); M. p. 198-200 °C; R_f = 0.54 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3058 (CH_2), 1735 (C=O), 1436 (C=N) cm^{-1}; ^1H NMR (CDCl_3) δ ppm:
3.81(s, 2H, -CH_2), 7.47-7.41(m, J = 7.5 & 8.7 Hz, 2H, Ar-H), 7.66-7.54(m, 5H, Ar-H), 7.73(d, J = 7.5 Hz, 1H, Ar-H), 7.89(d, J = 8.7 Hz, 1H, Ar-H), 7.93(s, 1H, =CH-); ^13C NMR (75 MHz, CDCl_3) δ: 34.3, 119.3, 124.8, 126.2, 126.7, 127.5, 128.0, 128.1, 129.0, 129.3, 131.4, 133.2, 146.5, 157.0, 173.6 ppm; MS (m/z): 260 [M^+] ; Analysis Calculated for C_{17}H_{12}N_2O: Calcd: C, 78.44; H, 4.65; N, 10.76%; Found: C, 78.60; H, 4.83; N, 10.55%.

1-p-tolyl-1H-pyrrolo[2,3-b]quinolin-2(3H)-one, 116b

White solid; Yield: 1.20g (71%); M. p. 167-169 °C; R_f = 0.48 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3057 (CH_2), 1737 (C=O), 1445 (C=N) cm^{-1}; ^1H NMR (CDCl_3) δ ppm:
2.43(s, 3H, CH_3), 3.82(d, J = 0.9 Hz, 2H, Ar-H), 7.37(d, J = 6.0 Hz, 2H, Ar-H), 7.41(t, J = 6.3 & 5.1 Hz, 1H, Ar-H), 7.48(d, J = 6.0 Hz, 2H, Ar-H), 7.60(t, J = 5.1 & 0.9 Hz, 1H, Ar-H), 7.75(d, J = 6.0 Hz, 1H, Ar-H), 7.88(d, J = 6.3 Hz, 1H, Ar-H), 7.94(s, 1H, =CH); MS (m/z): 247 [M^+] ; Analysis Calculated for C_{18}H_{14}N_2O: Calcd: C, 78.81; H, 5.14; N, 10.21%; Found: C, 78.68; H, 5.25; N, 10.37%.

1-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]quinolin-2(3H)-one, 116c

White solid; Yield: 1.23g (72%); M. p. 141-143 °C; R_f = 0.45 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3062 (CH_2), 1737 (C=O), 1432 (C=N) cm^{-1}; ^1H NMR (CDCl_3) δ ppm:
3.79(s, 3H, -CH_3), 3.83(d, J = 0.9 Hz, 2H, -CH_2), 7.12(d, J = 6.0 Hz, 2H, Ar-H), 7.42(t, J = 6.3 & 5.1 Hz, 1H, Ar-H), 7.49(d, J = 6.0 Hz, 2H, Ar-H), 7.63(t, J = 5.1 & 0.9 Hz, 1H, Ar-
H), 7.78(d, J= 6.0 Hz, 1H, Ar-H), 7.87(d, J= 6.3 Hz, 1H, Ar-H), 7.92(s, 1H, =CH-); MS (m/z): 290[M⁺]; Analysis Calculated for C₁₈H₁₄N₂O₂: Calcd:C, 74.47; H, 4.86; N, 9.65%. Found: C, 74.64; H, 5.01; N, 9.50%.

1-(4-fluorophenyl)-1H-pyrrolo[2,3-b]quinolin-2(3H)-one, 116d

White solid; Yield: 1.26g (74%); M. p. 157-159° C; Rf = 0.42 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3050 (CH₂), 1713 (C=O), 1645 (C=C), 1450 (C=N) cm⁻¹: ¹H NMR (CDCl₃) δ ppm: 3.91(d, J= 1.2 Hz, 2H, CH₂), 7.57-7.25 (m, 4H, Ar-H), 7.68 (d, J= 8.4 Hz, 2H, Ar-H), 7.83 (d, J= 8.4 Hz, 2H, Ar-H), 7.87(s, 1H, =CH-); MS (m/z): 278[M⁺] 280[M+2]; Analysis Calculated for C₁₇H₁₁FN₂O: Calcd: C, 73.37; H, 3.98; N, 10.07%; Found: C, 73.52; H, 4.07; N, 9.93%.

1-(3-(trifluoromethyl)phenyl)-1H-pyrrolo[2,3-b]quinolin-2(3H)-one, 116e

White solid; Yield: 1.25g (72%); M. p. 173-175° C; Rf = 0.47 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3083 (CH₂), 1716 (C=O), 1647 (C=C), 1455 (C=N) cm⁻¹: ¹H NMR (CDCl₃) δ ppm: 3.91(d, J= 1.2 Hz, 2H, CH₂), 7.47(t, J= 7.2 Hz, 1H, Ar-H), 7.57(t, J= 8.4 & 1.2 Hz, 2H, Ar-H), 7.67-7.60(m, J= 8.4, 2 & 1.2 Hz, 3H, Ar-H), 7.78(d, J= 7.6 Hz, 1H, Ar-H), 7.90 (d, J= 8.1 Hz, 1H, Ar-H), 7.98(s, 1H, =CH-); MS (m/z): 329[M⁺]; Analysis Calculated for C₁₈H₁₁F₃N₂O: Calcd: C, 65.85; H, 3.38; N, 8.53%; Found: C, 65.68; H, 3.43; N, 8.37%.

1-(4-chlorophenyl)-1H-pyrrolo[2,3-b]quinolin-2(3H)-one, 116f

White solid; Yield: 1.25g (73%); M. p. 168-170° C; Rf = 0.54 (Hexane: Ethyl acetate, 9:1); IR (KBr) 2954 (CH₂), 1743 (C=O), 1663 (C=Cl) 725 (C-Cl) cm⁻¹: ¹H NMR (CDCl₃)
δ ppm: 3.84(d, J= 1.2 Hz, 2H, CH₂), 7.44(t, J= 7.2 Hz, 1H, Ar-H), 7.53(d, J= 8.4 & 1.2 Hz, 2H, Ar-H), 7.64-7.51(m, J= 8.4, 2 & 1.2 Hz, 3H, Ar-H), 7.76(d, J= 7.6 Hz, 1H, Ar-H), 7.88(d, J= 8.1 Hz, 1H, Ar-H), 7.97(s, 1H, =CH-); ¹³C NMR (75 MHz, CDCl₃) δ:
34.2, 119.0, 125.0, 126.2, 127.6, 127.9, 128.1, 129.2, 129.5, 131.6, 131.7, 133.5, 146.5, 156.6, 173.3 ppm;

MS (m/z): 295[M⁺] 297[M+2]; Analysis Calculated for C₁₇H₁₁ClN₂O:
Calcd:C, 69.28; H, 3.76; N, 9.50%; Found: C, 69.47; H, 3.83; N, 9.32%.

1-(4-bromophenyl)-1H-pyrrolo[2,3-b]quinolin-2(3H)-one, 116g

White solid; Yield: 1.26g (72%); M. p. 153-155 °C; Rf = 0.49 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3058 (CH₂), 1737 (C=O), 1639 (C=C), 1490 (C=N), 825 (C-Br) cm⁻¹: ¹H NMR (CDCl₃) δ ppm: 3.81(s, 2H, CH₂), 7.44(t, J= 8 Hz, 1H, Ar-H), 7.58(d, J= 8.4Hz, 2H, Ar-H), 7.62(t, J= 7.2 Hz, 1H, Ar-H), 7.67(d, J= 8.4 Hz, 2H, Ar-H), 7.76 (d, J= 8 Hz, 1H, Ar-H), 7.88 (d, J= 8.4 Hz, 1H, Ar-H), 7.96(s, 1H, =CH-); MS (m/z): 339[M⁺] 341[M+2]; Analysis Calculated for C₁₇H₁₁BrN₂O: Calcd: C, 60.20; H, 3.27; N, 8.26%; Found: C, 60.35; H, 3.44; N, 8.09%.

1-benzyl-1H-pyrrolo[2,3-b]quinolin-2(3H)-one, 116h

White solid; Yield: 1.27g (75%); M. p. 132-134 °C; Rf = 0.44 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3034 (-CH₂), 1732 (C=O), 1443 (C=N) cm⁻¹: ¹H NMR (CDCl₃) δ ppm: 3.83(s, 2H, CH₂), 5.27(s, 2H, CH₂), 7.43-7.39(m, 2H, Ar-H), 7.64-7.47(m, 5H, Ar-H), 7.79 (d, J= 8 Hz, 1H, Ar-H), 7.84 (d, J= 8.4 Hz, 1H, Ar-H), 7.98(s, 1H, =CH-); MS (m/z): 274[M⁺]; Analysis Calculated for C₁₈H₁₄N₂O: Calcd:C, 78.81; H, 5.14; N, 10.21%; Found: C, 78.94; H, 5.32; N, 10.05%.
N-(2-((E)-(2,5-dioxo-1-phenylpyrrolidin-3-ylidene)methyl)phenyl)acetamide, 117a

White solid; Yield: 1.13 g (99%); M. p. 178-179°C; \( R_f = 0.27 \) (Hexane: Ethyl acetate, 9:1);
IR (KBr) 3238 (\(-\text{NH}\)), 3029 (\(-\text{CH}_3\)), 1764 (C=O), 1708 (C=O), 1662 (C=O), 1596 (C=C), 1369 (C-O) cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) ppm: 2.10(s, 3H, -\text{CH}_3), 3.62(s, 2H, -\text{CH}_2), 7.38-7.26(m, 8H, Ar-H), 7.71(d, \( J = 7.5 \) Hz, 1H, Ar-H), 7.78(s, 1H, =\text{CH}-), 7.86(s, 1H, -NH); D\(_2\)O: 2.13(s, 3H, -\text{CH}_3), 3.65(d, \( J = 2.1 \) Hz, 2H, -\text{CH}_2), 7.45-7.21(m, 8H, Ar-H), 7.76(d, \( J = 8.7 \) Hz, 1H, Ar-H), 7.80(s, 1H, =\text{CH}-); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 23.8, 33.8, 124.8, 125.5, 126.3, 126.9, 128.1, 128.6, 129.0, 130.4, 130.8, 131.6, 137.1, 130.1, 169.2, 169.9, 172.8 ppm; MS (m/z): 320 [M\(^+\)]; Analysis Calculated for C\(_{19}\)H\(_{16}\)N\(_2\)O\(_3\): Calcd: C, 71.24, H, 5.03, N, 8.74%; Found: C, 71.41, H, 4.87, N, 8.90%.

N-(2-((E)-(2,5-dioxo-1-p-tolylpyrrolidin-3-ylidene)methyl)phenyl)acetamide, 117b

White solid; Yield: 1.10 g (97%); M. p. 193-195°C; \( R_f = 0.32 \) (Hexane: Ethyl acetate, 9:1);
IR (KBr) 3238 (-\text{NH}), 1764 (C=O), 1710 (C=O), 1650 (C=O), 1514 (C=C), 1388 (C-O) cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) ppm: 2.19(s, 3H, -\text{CH}_3), 2.38(s, 3H, -\text{CH}_3), 3.67(d, \( J = 2.1 \) Hz, 2H, -\text{CH}_2), 7.30(m, \( J = 8.1 \) & 7.5 Hz, 5H, Ar-H), 7.47-7.42(t, \( J = 7.2 \) & 7.5 Hz, 2H, Ar-H), 7.56(bs, 1H, -NH), 7.80(s, 1H, =\text{CH}-); MS (m/z): 335 [M\(^+\)]; Analysis Calculated for C\(_{20}\)H\(_{18}\)N\(_2\)O\(_3\): Calcd: C, 71.84, H, 5.43, N, 8.38%; Found: C, 72.01, H, 5.23, N, 8.49%.

N-(2-((E)-(1-(4-methoxyphenyl)-2,5-dioxopyrrolidin-3-ylidene)methyl)phenyl)acetamide 117c

White solid; Yield: 1.10 g (97%); M. p. 165-167°C; \( R_f = 0.36 \) (Hexane: Ethyl acetate, 9:1);
IR (KBr) 3344 (-\text{NH}), 3055 (-\text{CH}_3), 1767 (C=O), 1709 (C=O), 1655 (C=O), 1378 (C-O) cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) ppm: 2.15(s, 3H, -\text{CH}_3), 3.69(d, \( J = 2.1 \) Hz, 2H, -\text{CH}_2), 3.78 (s, 3H, -\text{OCH}_3), 7.12 (d, \( J = 7.5 \) Hz, 2H, Ar-H), 7.37-7.33(m, 3H, Ar-H), 7.49-7.41(t, \( J = 7.2 \) &
7.5 Hz, 2H, Ar-H), 7.57 (bs, 1H, -NH), 7.79 (s, 1H, =CH-); MS (m/z): 350[M⁺]; Anal.
Analysis Calculated for C₂₀H₁₈N₂O₄: Calcd: C, 68.56, H, 5.18, N, 8.00%; Found: C, 68.39, H, 5.35, N, 7.84%.

N-(2-((E)-(1-(4-fluorophenyl)-2,5-dioxopyrrolidin-3-ylidene)methyl)phenyl)acetamide, 117d.
White solid; Yield: 1.09g (96%); M. p. 187-189 °C; R_f = 0.35 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3344 (-NH), 3055 (-CH₃), 1767 (C=O), 1709 (C=O), 1655 (C=O), 1378 (C-F), 1150 (C-O) cm⁻¹; ¹H NMR (CDCl₃) δ ppm: 2.26 (s, 3H, -CH₃), 3.71 (d, J = 2.4 Hz, 2H, -CH₂), 7.32-7.28 (m, 4H, Ar-H), 7.53-7.47 (m, 4H, Ar-H), 7.78 (s, 1H, -NH), 7.82 (s, 1H, =CH-); MS (m/z): 338[M⁺]; Analysis Calculated for C₁₉H₁₅FN₂O₃: Calcd: C, 67.45; H, 4.47; N, 8.28%; Found: C, 67.57; H, 4.61; N, 8.09%.

N-(2-((E)-(1-(3-trifluoromethyl)phenyl)-2,5-dioxopyrrolidin-3-ylidene)methyl)phenyl)acetamide, 117e.
White solid; Yield: 1.07g (96%); M. p. 190-192 °C; R_f = 0.37 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3231 (-NH), 3034 (-CH₃), 1767 (C=O), 1708 (C=O), 1655 (C=O), 1387 (C-F), 1156 (C-O) cm⁻¹; ¹H NMR (CDCl₃) δ ppm: 2.29 (s, 3H, -CH₃), 3.64 (s, 2H, -CH₂), 7.29-7.18 (m, 4H, Ar-H), 7.65-7.45 (m, 4H, Ar-H), 7.74 (s, 1H, -NH), 7.81 (s, 1H, =CH-); MS (m/z): 388[M⁺]; Analysis Calculated for C₂₀H₁₅F₃N₂O₃: Calcd: C, 61.86; H, 3.89; N, 7.21%; Found: C, 61.96; H, 4.03; N, 7.37%.

N-(2-((E)-(1-(4-chlorophenyl)-2,5-dioxopyrrolidin-3-ylidene)methyl)phenyl)acetamide, 117f.
White solid; Yield: 1.11g (98%); M. p. 177-179 °C; R_f = 0.26 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3234 (-NH), 1768 (C=O), 1710 (C=O), 1652 (C=O), 1490 (C=C), 1386
(C-O), 655 (C-Cl) cm⁻¹: ¹H NMR (CDCl₃) δ ppm: 2.23 (s, 3H, N-CH₃), 3.69 (d, J= 2.4 Hz, 2H, -CH₂), 7.35-7.24 (m, 4H, Ar-H), 7.47-7.43 (m, 4H, Ar-H), 7.76 (s, 1H, -NH), 7.79 (s, 1H, =CH-); MS (m/z): 255[M⁺] 257[M+2]; Analysis Calculated for C₁₉H₁₅ClN₂O₃: Calcd:C, 64.32; H, 4.26; N, 7.90%; Found: C, 64.19; H, 4.12; N, 8.04%.

N-(2-((E)-(1-(4-bromophenyl)-2, 5-dioxopyrrolidin-3-ylidene)methyl)phenyl)acetamide, 117g

White solid; Yield: 1.08 g (97%); M. p: 189-191 °C; R f = 0.27 (Hexane: Ethyl acetate, 9:1); IR 3234 (-NH), 3014 (-CH₃), 1766 (C=O), 1708 (C=O), 1490 (C=C), 1176 (C-O), 763 (C-Br). (KBr) cm⁻¹; ¹H NMR (CDCl₃) δ ppm: 2.25 (s, 3H, -CH₃), 3.72 (d, J= 2.4 Hz, 2H, -CH₂), 7.37-7.27 (m, 4H, Ar-H), 7.48-7.45 (m, 4H, Ar-H), 7.72 (s, 1H, -NH), 7.76 (s, 1H, =CH-); MS (m/z): 397[M⁺], 399 [M+H]; Analysis Calculated for C₁₉H₁₅BrN₂O₃: Calcd:C, 57.16; H, 3.79; N, 7.02%; Found: C, 57.33; H, 3.92; N, 6.87%.

N-(2-((E)-(1-benzyl-2, 5-dioxopyrrolidin-3-ylidene)methyl)phenyl)acetamide, 117h

White solid; Yield: 1.09 g (96%); M. p.: 210-212 °C; R f = 0.32 (Hexane: Ethyl acetate, 9:1); IR (KBr) 3268 (-NH), 3034 (-CH₃), 1770 (C=O), 1712 (C=O), 1655 (C=O), 1390 (C-O) cm⁻¹; ¹H NMR (CDCl₃) δ ppm: 2.26 (s, 3H, -CH₃), 3.78 (s, 2H, -CH₂), 4.37 (s, 2H, -CH₂), 7.39-7.31 (m, 4H, Ar-H), 7.50-7.43 (m, 4H, Ar-H), 7.73 (s, 1H, -NH), 7.77 (s, 1H, =CH-); MS (m/z): 334[M⁺]; Analysis Calculated for C₂₀H₁₈N₂O₃: Calcd:C, 71.84; H, 5.43; N, 8.38%; Found: C, 71.65; H, 5.59; N, 8.51%.
Synthesis of N-(2-((E)-2,5-dioxo-1-phenylpyrrolidin-3-ylidene) methyl) phenyl acetamide, 117a-h

An amino compound 118a-h (1 g, 3.8 mmol) was dissolved in acetic anhydride and further stirred for 5 min. The reaction mixture was poured on to crushed ice. The white solid separated was filtered, dried and recrystallized in ethanol, yield quantitative.

Synthesis of 4, 4-dimethyl-2-phenyl-4, 5-dihydro Benzo [b]pyrrolo [3, 4-e]azepine 1, 3 (2H, 3aH)-dione, 118a
General procedure

To a solution of compound 118b (3.4mmol) in ethanol (5 mL) was added 126a-b (3.4mmol) and catalytic acetic acid, the resultant reaction mixture was refluxed for 5-8 h for completion of reaction (TLC Checked). Cool the reaction mixture and excess of solvent removed under reduced pressure on rotary evaporator, obtained compound was recrystallised in acetone.

4, 4-dimethyl-2-phenyl-4, 5-dihydro Benzo [b]pyrrolo [3, 4-e azepine] 1, 3 (2H, 3aH)-dione, 121a

Golden yellow solid; yield: 1.44 g (90%); M.p. 210-211°C; Rf = 0.45 (Hexane: Ethyl acetate, 9:1); IR (KBr, cm⁻¹): 3373, 3060, 2974, 1758, 1704, 1658, 1485, 1380, 1141, 754. ¹H NMR (400 MHz, CDCl₃) δ: 1.05(s, 3H), 1.88(s, 3H), 3.52(s, 1H), 4.56(s, 1H), 6.65(d, J=8 Hz, 1H), 6.80 (t, J=8 Hz, 1H), 7.20 (t, J=8 & 8Hz, 1H), 7.41-7.34 (dd, J=8 & 8Hz 4H), 7.48 (t, J=8 & 8Hz, 2H), 7.76 (s, 1H); ¹³C NMR (100 MHz, CDCl₃ d₆- DMSO) δ: 22.6, 29.3, 52.1, 55.6, 117.3, 118.3, 118.9, 121.8, 126.5, 128.4, 129.0, 131.7, 132.0, 135.6, 136.4, 146.2, 169.2, 172.9 ppm; DEPT: 22.6, 29.3, 55.6, 117.3, 118.3, 118.9, 121.8, 126.5, 128.4, 129.0, 131.7, 132.0, 135.6, 136.4, 146.2, 169.2, 172.9 ppm; D₂O: 0.86(s, 3H), 1.71(s, 3H), 2.05(s, 1H), 3.56(s, 1H), 6.86-6.69(m, 2H), 7.56-7.15(m, 7H); Mass Spectrum (EI): 317(M-H)⁺; Analysis Calculated for C₂₀H₁₈N₂O₂: Calcd:C, 75.45; H, 5.70; N, 8.80%; Found: C, 75.64; H, 5.57; N, 8.64%.
4, 4-dimethyl-2-(p-tolyl) 4, 5-dihydro Benzo [b] pyrrolo [3, 4-e azepine]1, 3 (2H, 3aH)-dione, 121b

Golden yellow solid; yield: 1.52 g (91%); M.p. 204-205°C; \( R_f = 0.53 \) (Hexane: Ethyl acetate, 9:1); IR (KBr, cm\(^{-1}\)): 3332, 2937, 1762, 1699, 1650, 1230, 759. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \): 0.90 (s, 3H), 1.76 (s, 3H), 2.34 (s, 3H), 2.48 (s, 1H), 3.34 (s, 4H), 3.59 (d, \( J = 0.9 \) Hz, 1H), 6.58 (s, 1H), 6.65 (t, \( J = 7.8 \) Hz, 1H), 6.94 (d, \( J = 8.4 \) Hz, 1H), 7.19 (m, 3H), 7.28 (d, \( J = 8.1 \) Hz, 2H), 7.37 (d, \( J = 7.5 \) Hz, 1H), 7.58 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \): 20.6, 22.4, 28.1, 51.5, 55.3, 116.6, 116.8, 118.8, 122.0, 126.8, 129.2, 129.7, 131.0, 134.7, 135.1, 137.6, 147.3, 168.8, 172.8 ppm; Mass Spectrum (EI): 331 (M-H); Analysis Calculated for C\(_{21}\)H\(_{20}\)N\(_2\)O\(_2\): Calcd: C, 75.88; H, 6.06; N, 8.43%; Found: C, 75.69; H, 6.23; N, 8.61%.

4-ethyl-4-methyl-2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo [3,4-e azepine]1,3 (2H,3aH)-dione, 121c

Golden yellow solid; yield: 1.58 g (91%); M.p. 182-183°C; \( R_f = 0.42 \) (Hexane: Ethyl acetate, 9:1); IR (KBr, cm\(^{-1}\)): 3363, 2972, 1757, 1704, 1699. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \): 0.81 (t, 3H), 1.45-1.33 (q, 2H), 2.39 (s, 3H), 3.55 (s, 1H), 4.60 (s, 1H), 6.79-6.65 (m, 2H), 7.30-7.24 (m, 6H), 7.41 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \): 7.5, 21.1, 25.3, 27.0, 54.8, 55.9, 118.0, 118.2, 118.9, 119.0, 121.6, 126.2, 129.4, 129.6, 131.7, 135.6, 136.0, 138.3, 146.2, 169.3, 173.2 ppm; Mass Spectrum (EI): 347.5 (M+H); Analysis Calculated for C\(_{22}\)H\(_{22}\)N\(_2\)O\(_2\): Calcd: C, 76.28; H, 6.40; N, 8.09%; Found: C, 76.43; H, 6.52; N, 7.87%.
Synthesis of 4-methyl-4-phenyl-2-(p-tolyl) 4, 5-dihydro Benzo [b] pyrrolo [3, 4-e azepine]1,3 (2H,3aH)-dione, 122a-d

\[
\begin{align*}
\text{118b} & \quad \text{EtOH, cat AcOH} \quad \text{reflux, 7-8 h} \quad \text{127a-d} \\
& \quad \text{122a-d}
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**General procedure**

To a solution of compound 118b (3.4mmol) in ethanol (5 mL) was added 127a-d (3.4mmol) and catalytic acetic acid, the resultant reaction mixture was refluxed for 7-8 h for completion of reaction (TLC Checked). Cool the reaction mixture and excess of solvent removed under reduced pressure on rotary evaporator, obtained compound was recrystallised in acetone.

4-methyl-4-phenyl-2-(p-tolyl) 4, 5-dihydro Benzo [b] pyrrolo [3, 4-e azepine]1,3 (2H,3aH)-dione, 122a

Golden yellow solid; yield: 1.76 g (89%); M.p. 237-238\(^{\circ}\)C; \(R_f = 0.66\) (Hexane: Ethyl acetate, 9:1); IR (KBr, cm\(^{-1}\)): 3334, 2956, 1758, 1699, 1656, 1253, 802, 757. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 0.96 (s, 3H), 2.28 (s, 3H), 3.80 (s, 1H), 5.54(s, 1H), 6.65(m, 3H), 6.74(t, \(J=7.4\) Hz, 1H), 6.92 (dd, \(J=8\) & 6.8Hz, 5H), 7.14 (dd, \(J=8\) & 6.9Hz 3H), 7.27 (d,
J = 6.9Hz (1H), 7.63 (d, J = 2.1 Hz, 1H); Mass Spectrum (EI): 395 (M+H); Analysis Calculated for C26H22N2O2: Calcd: C, 79.16; H, 5.62; N, 7.10%; Found: C, 79.36; H, 5.43; N, 7.27%.

4-methyl-4-(p-tolyl) phenyl-2-(p-tolyl) 4, 5-dihydro Benzo [b] pyrrolo [3, 4-e azepine]1, 3 (2H,3aH)-dione, 122b

Golden yellow solid; yield: 1.94 g (90%); M.p. 253-255°C; Rf = 0.42 (Hexane: Ethyl acetate, 9:1); IR (KBr, cm⁻¹):3338, 2950, 1763, 1702, 1652, 1179, 757; ¹H NMR (400 MHz, CDCl₃) δ: 1.05 (s, 3H), 2.26 (s, 3H), 3.84 (s, 1H), 5.74 (s, 1H), 6.85-6.71 (m, 4H), 7.41-7.09 (m, 4H), 7.42-7.25 (m, 4H), 7.67 (s, 1H); Mass Spectrum (EI): 408 (M+H); Analysis Calculated for C27H24N2O2: Calcd: C, 79.39; H, 5.92; N, 6.86%; Found: C, 79.13; H, 6.02; N, 6.64%.

4-methyl-4-chloro phenyl-2-(p-tolyl) 4, 5-dihydro Benzo [b] pyrrolo [3, 4-e azepine]1, 3 (2H,3aH)-dione, 122c

Golden yellow solid; yield: 1.94 g (90%); M.p. 218-219°C; Rf = 0.46 (Hexane: Ethyl acetate, 9:1); IR (KBr, cm⁻¹):3335, 2947, 1767, 1701, 1655, 1250, 757, 525.¹H NMR (400 MHz, CDCl₃) δ: 1.05 (s, 3H), 2.26 (s, 3H), 3.87 (s, 1H), 5.74 (s, 1H), 6.81-6.65 (m, 4H), 7.36-7.01 (m, 4H), 7.40-7.21 (m, 4H), 7.66 (s, 1H); Mass Spectrum (EI): 429 (M+H); Analysis Calculated for C27H24ClN2O2: Calcd: C, 72.81; H, 4.94; N, 6.53%; Found: C, 72.65; H, 5.11; N, 6.71%.

4-methyl-4-bromo phenyl-2-(p-tolyl) 4, 5-dihydro Benzo [b] pyrrolo [3, 4-e azepine]1, 3 (2H,3aH)-dione, 122d

Golden yellow solid; yield: 2.01 g (93%); M.p. 277-279°C; Rf = 0.54 (Hexane: Ethyl acetate, 9:1); IR (KBr, cm⁻¹):3342, 2937, 1762, 1705, 1665, 1252, 755, 625.¹H NMR
(400 MHz, CDCl₃) δ: 1.04 (s, 3H), 2.29 (s, 3H), 3.89 (s, 1H), 5.79 (s, 1H), 6.75-6.53 (m, 4H), 7.42-6.91 (m, 4H), 7.47-7.35 (m, 4H), 7.73 (s, 1H); Mass Spectrum (EI): 472(M+H), 474(M+2); Analysis Calculated for C₂₆H₂₁BrN₂O₂: Calcd: C, 65.97; H, 4.47; N, 5.92%; Found: C, 65.78; H, 4.34; N, 6.01%.

Synthesis of 2-(p-tolyl) 3a,5-dihydro-1H-spiro [benzo[b]pyrrolo(3,4-e)azepine-4,1’-cyclopentane] 1,3- (2H)-dione, 123a-b

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<td>b</td>
<td>-CH₂-CH₂-</td>
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To a solution of compound 118b (3.4mmol) in ethanol (5 mL) was added 129a-b (3.4mmol) and catalytic acetic acid, the resultant solution was refluxed for 5-8 h for completion of reaction (TLC Checked). Cool the reaction mixture and excess of solvent removed under reduced pressure on rotary evaporator, obtained compound was recrystallised in acetone.

2-(p-tolyl) 3a,5-dihydro-1H-spiro [benzo[b]pyrrolo(3,4-e)azepine-4,1’-cyclopentane] 1,3- (2H)-dione, 123a

Golden yellow solid; yield: 1.64 g (91%); M.p. 186-187°C; Rf = 0.43 (Hexane: Ethyl acetate, 9:1); IR (KBr, cm⁻¹): 3409, 2948, 1760, 1701. ¹H NMR (400 MHz, CDCl₃) δ:
1.07-1.05 (m, 1H), 1.62-1.58 (m, 4H), 1.93-1.86 (m, 2H), 2.39 (s, 3H), 3.36 (q, 1H), 3.66 (s, 1H), 4.61 (s, 1H), 6.65 (d, J= 8.1Hz, 1H), 6.81 (t, J= 7.5Hz, 1H), 7.37-7.18 (m, 6H), 7.72 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$ $d_6$- DMSO) δ: 21.2, 23.7, 24.4, 33.7, 38.3, 53.6, 63.3, 118.1, 118.4, 119.0, 122.8, 126.3, 129.4, 129.7, 131.6, 135.6, 135.8, 138.4, 145.9, 169.5, 173.0 ppm; Mass Spectrum (EI): 358 (M+H). Analysis Calculated for C$_{23}$H$_{22}$N$_2$O$_2$: Calcd: C, 77.07; H, 6.19; N, 7.82%; Found: C, 76.91; H, 6.34; N, 7.65%.

2-(p-tolyl) 3a, 5-dihydro-1H-spiro [benzo[b] pyrrolo (3,4-e)azepine-4,1’-cyclohexane]

1,3- (2H)-dione, 123b

Golden yellow solid; yield: 1.68 g (90%); M.p. 215-216°C; $R_f$ = 0.47 (Hexane: Ethyl acetate, 9:1); IR (KBr, cm$^{-1}$): 3413, 2920, 1757, 1703, 1649. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.92-1.01 (m, 9H), 2.39 (s, 3H), 3.08-2.99 (m, 1H), 3.49 (s, 1H), 4.73 (s, 1H), 6.74 (d, J= 8.1Hz, 1H), 6.82 (t, J= 7.5Hz, 1H), 7.73-7.21 (m, 6H), 7.74 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$ $d_6$- DMSO) δ: 21.1, 21.7, 25.2, 28.5, 34.5, 53.8, 56.5, 118.6, 118.9, 121.5, 126.3, 129.4, 129.6, 131.7, 135.5, 135.8, 138.3, 145.6, 169.5, 173.1 ppm; Mass Spectrum (EI):373.5 (M+H); Analysis Calculated for C$_{24}$H$_{24}$N$_2$O$_2$: Calcd:C, 77.39; H, 6.49; N, 7.52%; Found: C, 77.21; H, 6.67; N, 7.69%.

Synthesis of 2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo [3,4-e azepine]1,3 (2H,3aH)-dione, 121a-c

<table>
<thead>
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<tbody>
<tr>
<td>a</td>
<td>H</td>
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<tr>
<td>b</td>
<td>CH$_3$</td>
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<tr>
<td>c</td>
<td>CH(CH$_3$)$_2$</td>
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General procedure

To a solution of compound 118b (3.4mmol) in ethanol (5 mL) was added 131a-c (3.4mmol) and catalytic acetic acid, the resultant reaction mixture was refluxed for 4-6 h for completion of reaction (TLC Checked). Cool the reaction mixture and excess of solvent removed under reduced pressure on rotary evaporator, obtained compound was recrystallised in acetone.

2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo [3,4-e azepine]1,3 (2H,3aH)-dione, 124a

Golden yellow solid; yield: 1.63 g (91%); M.p. 218-220°C; \( R_f = 0.42 \) (Hexane: Ethyl acetate, 9:1); IR (KBr, cm\(^{-1}\)): 3351, 1764, 1698, 772, 760. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 2.38(s, 3H), 3.62(m, 1H), 3.68(m, 1H), 3.92(m, 1H), 5.33(s, 1H), 6.70(d, \( J=8.1 \) Hz, 1H), 6.74(t, \( J=1.8 \) & 6.9, 1H), 7.32-7.19(m, 6H), 7.60(d, \( J=2.4 \)Hz, 1H); Mass Spectrum (EI): 304 (M+H); Analysis Calculated for C\(_{19}\)H\(_{16}\)N\(_2\)O\(_2\): Calcd: C, 74.98; H, 5.30; N, 9.20%; Found: C, 75.12; H, 5.11; N, 9.02%.

4-methyl-2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo [3,4-e azepine]1,3 (2H,3aH)-dione, 124b

Golden yellow solid; yield: 1.66 g (94%); M.p. 243-245°C; \( R_f = 0.46 \) (Hexane: Ethyl acetate, 9:1); IR (KBr, cm\(^{-1}\)): 3350, 1762, 1696, 1648, 771, 758. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 1.04(d, \( J=6.9 \)Hz, 3H), 2.38(s, 3H), 3.88(t, 1H), 3.93(d, 1H), 5.35(d, \( J=6.6 \) Hz, 1H), 6.68(d, \( J=8.1 \) Hz, 1H), 6.72(t, \( J=1.8 \) & 6.9, 1H), 7.29-7.18(m, 6H), 7.65(d, \( J=2.4 \)Hz, 1H); Mass Spectrum (EI): 318 (M+H); Analysis Calculated for C\(_{20}\)H\(_{18}\)N\(_2\)O\(_2\): Calcd: C, 75.45; H, 5.70; N, 8.80%; Found: C, 75.23; H, 5.91; N, 8.63%. 
4-isopropyl-2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo [3,4-e azepine]1,3 (2H,3aH)-dione, 124c

Golden yellow solid; yield: 1.60 g (92%); M.p. 226-227°C; \( R_f = 0.42 \) (Hexane: Ethyl acetate, 9:1); IR (KBr, cm\(^{-1}\)): 3359, 2970, 1764, 1695, 1645, 1514, 1380, 1157, 1139, 771, 756. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 0.84(d, \( J=6.9\)Hz, 3H), 0.95(d, \( J=7.2\)Hz, 3H), 1.81(m, 1H), 2.38(s, 3H), 3.86(t, 1H), 3.93(m, 1H), 5.30(d, \( J=6.6 \)Hz, 1H), 6.67(d, \( J=8.1 \)Hz, 1H), 6.77(t, \( J=1.8 \& 6.9 \) 1H), 7.31-7.16(m, 6H), 7.66(d, \( J=2.4\)Hz, 1H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\) \( d_6\)- DMSO) \( \delta \): 18.6, 20.7, 21.1, 28.9, 51.1, 57.6, 118.1, 118.8, 121.4, 125.9, 129.4, 129.7, 136.1, 138.4, 146.4, 151.1, 160.9, 168.9, 173.8 ppm; Mass Spectrum (El): 347.5 (M+H); Analysis Calculated for C\(_{22}\)H\(_{22}\)N\(_2\)O\(_2\): Calcd:C, 76.28; H, 6.40; N, 8.09%; Found: C, 76.43; H, 6.57; N, 7.88%.

**Synthesis of dihydro Benzo[b]pyrrolo [3, 4-e azepines], 125a-j**

\[ \text{118b} + \text{ArCHO} \xrightarrow{\text{EtOH, cat.AcOH, reflux, 3-5 h}} \text{125a-j} \]

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General procedure

Synthesis of dihydro Benzo[b]pyrrolo [3, 4-e azepines], 125a-j

To a solution of 118b (1.4 g, 5.0 mmol) in dry ethanol (10 mL) was added aromatic aldehydes 132 (5.0 mmol) and catalytic amount of glacial acetic acid and resultant reaction mixture was refluxed for 3-5 hr (TLC checked). It was cooled and poured on to crushed ice. The golden yellow solid separated was filtered, dried and recrystallized from acetone.

4-phenyl-2-(p-toly] 4, 5-dihydro Benzo [b]pyrrolo [3,4-e azepine]1,3 (2H,3aH)-dione, 125a

Golden yellow solid; yield: 1.78 g (93%); M.p. 141-143°C; R$_f$ = 0.42 (Hexane: Ethyl acetate, 9:1); IR (KBr, cm$^{-1}$): 3371, 3060, 1760, 1701, 1658, 1515, 1386, 1151, 756. $^1$H NMR (400 MHz, CDCl$_3$) δ: 2.36 (s, 3H), 3.90 (t, $J=2.3$ Hz, 1H), 5.41 (d, $J=6.5$ Hz, 1H), 5.67(dd, $J=6.4$, 3.3 Hz, 1H), 6.76 (d, $J=8.4$ Hz, 1H), 6.83 (t, $J=7.1$ Hz, 1H), 6.94 (d, $J=8.3$ Hz, 2H), 7.09 (dd, $J=7.5$, 2.0 Hz, 2H), 7.25-7.16 (m, 6H), 7.35 (d, $J=7.9$ Hz, 1H), 7.70 (d, $J=2.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, $d_6$- DMSO) δ: 20.5, 49.9, 56.8, 115.6, 116.4, 118.2, 121.5, 122.3, 125.7, 128.2, 128.3, 128.5, 130.0, 130.3, 130.8, 134.2, 138.6, 141.3, 148.6, 168.0, 172.8 ppm; Mass Spectrum (EI): 381.5 (M+H); Analysis Calculated for C$_{25}$H$_{20}$N$_2$O$_2$: Calcd:C, 78.93; H, 5.30; N, 7.36%; Found: C, 79.06; H, 5.49; N, 7.57%.

4-(4-fluorophenyl]-2-(p-toly] 4, 5-dihydro Benzo [b] pyrrolo [3, 4-e azepine]1,3 (2H,3aH)-dione, 125b

Golden yellow solid; yield: 1.86 g (93%); M.p. 221-222°C R$_f$ = 0.47 (Hexane: Ethyl acetate, 9:1); IR (KBr, cm$^{-1}$): 3353, 3058, 1763, 1699, 1657, 1158, 725. $^1$H NMR (400
MHz, CDCl$_3$) $\delta$: 2.36 (s, 3H), 3.85 (s, 1H), 5.46 (d, $J= 7.5$ Hz, 1H), 5.60 (s, 1H), 6.95-6.64 (m, 6H), 7.25-7.02 (m, 4H), 7.32 (d, $J= 7.5$ Hz, 2H), 7.69 (d, $J= 1.5$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 21.1, 50.7, 58.3, 114.9, 115.2, 117.8, 118.3, 121.5, 126.1, 128.2, 129.0, 129.5, 129.7, 131.7, 135.6, 135.7, 136.7, 138.7, 147.6, 168.3, 173.1; Mass Spectrum (EI): 399 (M+H); Analysis Calculated for C$_{25}$H$_{19}$FN$_{2}$O$_{2}$: Calcd: C, 75.36; H, 4.81; N, 7.03%; Found: C, 75.56; H, 4.96; N, 6.90%.

4-(3-chlorophenyl)-2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo [3, 4-e azepine]1,3 (2H,3aH)-dione, 125c

Golden yellow solid; yield: 2.37 g (95%); M.p. 266-268°C; $R_f = 0.57$ (Hexane: Ethyl acetate, 9:1); IR (KBr, cm$^{-1}$): 3358, 1763, 1703, 1658, 1153, 725; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 2.36(s, 3H), 3.80(s, 1H), 5.49(d, $J=6.3$ Hz,1H), 5.54(s, 1H), 6.78(d, , 1H), 6.86(t, , 1H), 6.84-7.15 (m, 4H), 7.38-7.45(m, 6H), 7.70(s, 1H); Mass Spectrum (EI): 414(M-H); Analysis Calculated for C$_{25}$H$_{19}$ClN$_{2}$O$_{2}$: Calcd: C, 72.37; H, 4.62; N, 6.75%; Found: C, 72.56; H, 4.39; N, 6.96%.

4-(4-chlorophenyl)-2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo [3, 4-e azepine]1,3 (2H,3aH)-dione, 125d

Golden yellow solid; yield: 2.02 g (97%); M.p. 213-214°C $R_f = 0.47$ (Hexane: Ethyl acetate, 9:1); IR (KBr, cm$^{-1}$): 3367, 3047, 1760, 1702, 1660, 525. $^1$H NMR (300 MHz, $d_6$-DMSO) $\delta$: 2.32 (s, 3H), 3.98 (s, 1H), 5.48 (s, 1H), 6.69-6.62 (m, 1H), 7.14-6.71 (m, 3H), 7.47-7.26 (m, 8H), 7.59 (S, 1H), 7.88(s, 1H); $^{13}$C NMR (75 MHz, $d_6$- DMSO) $\delta$: 20.6, 50.3, 56.8, 116.4, 116.6, 118.2, 120.6, 121.4, 126.3, 128.0, 129.3, 129.4, 130.8, 131.0, 131.3, 135.4, 137.8, 140.5, 148.5, 167.9, 172.9; Mass Spectrum (EI): 415 (M+H);
Analysis Calculated for C_{25}H_{19}ClN_{2}O_{2}: Calcd:C, 72.37; H, 4.62; N, 6.75%; Found: C, 72.53; H, 4.79; N, 6.55%.

4-(3-bromophenyl)-2-(p-tolyl) 4, 5-dihydro Benzo[b]pyrrolo[3, 4-e azepine]1, 3 (2H,3aH)-dione, 125e

Golden yellow solid; yield: 2.19 g (95%); M.p. 210-211\(^{\circ}\)C; \(R_f = 0.53\) (Hexane: Ethyl acetate, 9:1); IR (KBr, cm\(^{-1}\)): 3355, 3043, 1760, 1704, 1656, 1517, 1384, 1153, 777, 514. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 2.36(s, 3H), 3.83(s, 1H), 5.47(d, \(J=6.3\) Hz,1H), 5.6(s, 1H), 6.75(d, \(J=6.3\) Hz, 1H), 6.82(t, \(J=6.3\) Hz, 1H), 7.05-6.84(m, 4H), 7.36-7.38(m, 6H), 7.69(s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 21.4, 52.1, 59.3, 117.5, 118, 118.4, 121.5, 122.4, 125, 126.3, 129.2, 129.8, 129.9, 131.1, 131.8, 135.7, 136.8, 138.8, 142.5, 147.5, 159.4, 168.2, 173.1; Mass Spectrum (EI): 457 (M-H), 459(M+2); Analysis Calculated for C_{25}H_{19}BrN_{2}O_{2}: Calcd:C, 65.37; H, 4.17; N, 6.10%; Found: C, 65.51; H, 4.31; N, 5.93%.

4-(3-nitrophenyl)-2-(p-tolyl) 4, 5-dihydro Benzo[b]pyrrolo[3, 4-e azepine]1, 3 (2H,3aH)-dione, 125f

Golden yellow solid; yield: 2.12 g (96%); M.p. 243-245\(^{\circ}\)C; \(R_f = 0.57\) (Hexane: Ethyl acetate, 9:1); IR (KBr, cm\(^{-1}\)): 3350, 1764, 1705, 1650, 1510, 1380; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 2.39(s, 3H), 3.86(s, 1H), 5.49(d, \(J=6.3\) Hz,1H), 5.71(s, 1H), 6.77(d, \(J=6.3\) Hz,1H), 6.86(t, \(J=6.3\) Hz,1H), 6.84-7.37 (m, 4H), 7.39-7.54(m, 6H), 7.72 (s, 1H); Mass Spectrum (EI): 425 (M-H); Analysis Calculated for C_{25}H_{19}N_{3}O_{4}: Calcd: C, 70.58; H, 4.50; N, 9.88%; Found: C, 70.76; H, 4.32; N, 9.79%.
4-(4-hydroxyphenyl)-2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo [3, 4-e azepine]1, 3 (2H,3aH)-dione, 125g

Golden yellow solid; yield: 1.89 g (95%); M.p. 242-243°C; $R_f = 0.45$ (Hexane: Ethyl acetate, 9:1); IR (KBr, cm$^{-1}$): 3357, 3340, 3043, 1755, 1699, 1647, 1512, 1367, 1151, 754. $^1$H NMR (300 MHz, $d_6$-DMSO) $\delta$: 2.34 (s, 3H), 3.87 (dd, $J = 7.5$ & 1.8 Hz, 1H), 4.07 (d, $J = 7.5$ Hz, 1H), 5.32 (s, 1H), 6.89-6.75 (m, 4H), 7.22-7.13 (m, 7H), 7.34 (d, $J = 7.5$ Hz, 1H), 7.67 (s, 1H), 7.68 (bs, 1H); $^{13}$C NMR (75 MHz, $d_6$-DMSO) $\delta$: 21.0, 53.2, 58.0, 115.6, 116.9, 118.1, 118.5, 124.5, 126.2, 128.9, 129.2, 129.4, 130.8, 131.2, 135.3, 135.4, 137.9, 147.8, 157.4, 168.8, 171.3; Mass Spectrum (EI): 397 (M+H); Analysis Calculated for C$_{25}$H$_{20}$N$_2$O$_3$: Calcd: C, 75.74; H, 5.08; N, 7.07%; Found: C, 75.57; H, 4.91; N, 7.24%.

4-(4-methoxyphenyl)-2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo [3,4-e azepine]1,3 (2H,3aH)-dione, 125g

Golden yellow solid; yield: 1.91 g (93%); M.p. 166-167°C; $R_f = 0.47$ (Hexane: Ethyl acetate, 9:1); IR (KBr, cm$^{-1}$): 3334, 2956, 1758, 1699, 1656, 1514, 1384, 1253, 1153, 1026, 802, 757. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 2.28 (s, 3H), 3.66 (s, 3H), 3.82-3.76 (m, 1H), 5.33 (d, $J = 6.7$ Hz, 1H), 5.54 (dd, $J = 6.3$, 3.1 Hz, 1H), 6.65 (dd, $J = 14.4$, 8.6 Hz, 3H), 6.74 (t, $J = 7.4$ Hz, 1H), 6.92 (dd, $J = 7.6$, 8.5 Hz, 4H), 7.14 (dd, $J = 6.9$, 5.6 Hz, 3H), 7.27 (d, $J = 6.9$ Hz, 1H), 7.63 (d, $J = 2.1$ Hz, 1H); Mass Spectrum (EI): 411.5 (M-H); Analysis Calculated for C$_{26}$H$_{22}$N$_2$O$_3$: Calcd: C, 76.08; H, 5.40; N, 6.82%; Found: C, 75.89; H, 5.57; N, 7.01%.
4-(3,4-dimethoxyphenyl)-2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo[3,4-e azepine]1,3 (2H,3aH)-dione, 125i

Golden yellow solid; yield: 2.12 g (96%); M.p. 186-187°C; $R_f = 0.52$ (Hexane: Ethyl acetate, 9:1); IR (KBr, cm$^{-1}$): 3375, 3043, 1764, 1708, 1662, 1514, 1384, 1236, 1139, 1026, 759. $^1$H NMR (400 MHz, CDCl$_3$) δ: 2.39(s, 3H), 3.72 (s, 1H), 3.38 (s, 3H), 3.39 (s, 3H), 5.39 (d, $J=2.4$ Hz, 1H), 5.68 (s, 1H), 6.90-6.62 (m, 3H), 7.24-7.11 (m, 6H), 7.39 (d, $J=8$Hz, 1H), 7.61(s, 1H), 7.73 (s, 1H); Mass Spectrum (EI): 441 (M+H); Analysis Calculated for C$_{27}$H$_{24}$N$_{2}$O$_{4}$: Calcd: C, 73.62; H, 5.49; N, 6.36%; Found: C, 73.83; H, 5.69; N, 6.53%.

4-(2,4,6-trimethoxyphenyl)-2-(p-tolyl) 4, 5-dihydro Benzo [b]pyrrolo[3,4-e azepine]1,3 (2H,3aH)-dione, 125j

Golden yellow solid; yield: 2.24 g (95%); M.p. 247-248°C; $R_f = 0.54$ (Hexane: Ethyl acetate, 9:1); IR (KBr, cm$^{-1}$): 3355, 3016, 1762, 1706, 1652, 1487, 1373, 1095,765. $^1$H NMR (400 MHz, CDCl$_3$) δ: 2.37 (s, 3H), 3.59 (s, 3H), 3.81 (s, 3H), 3.90 (s, 3H), 3.99-3.41 (m, 1H), 5.41 (d, $J=6.7$ Hz, 1H), 5.61 (dd, $J=6.4$, 3.2 Hz, 1H), 6.69-6.61 (m, 3H), 6.81 (t, $J=7.5$ Hz, 1H), 6.95 (dd, $J=14.3$, 4.6 Hz, 2H), 7.21 (dt, $J=11.9$, 8.6 Hz, 3H), 7.34 (d, $J=7.9$ Hz, 1H), 7.69 (d, $J=2.2$ Hz, 1H); Mass Spectrum (EI): 471 (M+H); Analysis Calculated for C$_{28}$H$_{26}$N$_{2}$O$_{5}$: Calcd:C, 71.47; H, 5.57; N, 5.95%; Found: C, 71.21; H, 5.39; N, 6.12%.
References:


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Brown, A. D.; Bungay, P. J.; Conlon, K. M.; Edmunds, N. J.; Forselles, K.;


