3.1. Introduction

Fries rearrangement, a hundred year old odyssey, is one of the most significant synthetic strategies for the preparation of versatile acylated scaffolds of biological and medicinal interest.\textsuperscript{1,2} The Lewis acid catalyzed Fries rearrangement, discovered by Fries in 1908, transforms an aryl ester 1 into a mixture of \textit{o}- and \textit{p}-hydroxycarbonyl compounds 5 and 6, the ratio strongly depending on the reaction conditions, such as temperature, medium and most importantly, Lewis acid catalyst used.\textsuperscript{3} Despite of many efforts, a definitive reaction mechanism for the Fries rearrangement is not available. Evidence for inter- and intramolecular mechanisms have been obtained by cross-experiments with mixed reactants and it has been observed that the progress of the reaction is not dependent on solvent or substrate. The most widely accepted mechanism involves the complexation of Lewis acid, such as AlCl\textsubscript{3}, with the carbonyl oxygen of the aryl ester 1. This oxygen atom, being more electron rich, is the preferred Lewis base and hence Lewis acid binds here in preference to the phenolic oxygen atom generating intermediate 2. This interaction polarizes the bond between the acyl residue and the phenolic oxygen atom generating intermediate 3 leading to the formation of free acylium cation 4, which reacts as in a classical electrophilic substitution with the aromatics. The abstracted proton is released as hydrochloric acid where the chlorine is derived from aluminium chloride (Scheme 1).

![Scheme 1](image)

The orientation of the substitution pattern is proposed to be temperature dependent. Low reaction temperature favors \textit{para} substituted product 6 while high temperatures favour...
the ortho product 5. Lewis acids such as boron trifluoride and bismuth triflate or strong protic acids such as hydrogen fluoride and methanesulphonic acid have been used as catalysts in the above transformation. In order to avoid the use of corrosive catalysts, the search for alternative heterogeneous catalysts has been actively pursued.

Wigal et. al. have studied the synthetic utility and mechanistic implications of Fries rearrangement of hydroquinone diesters 7/9 in boron trifluoride complexes. Reactions of boron trifluoride methyl and ethyl etherate complexes with hydroquinone diesters yielded monomethyl and monoethyl derivatives of acetylhydroquiones 8/10 which are important building blocks for a variety of synthetic applications (Scheme 2).

Recently, Stoyanov et. al. have reported the mechanistic studies of boron trichloride promoted Fries Rearrangement of aryl Formates 11 by means of $^1$H, $^2$H and $^{11}$B NMR spectroscopy which is further supported by DFT calculations. The reaction as reported proceeds in two main steps involving the formation of an initial 1:1 substrate-Lewis acid adduct, producing formyl chloride in the reaction mixture followed by the introduction of the aldehyde functionality in the aromatic ring through an electrophilic acylation. The ortho position was strongly favored because of the stability of the transition state due to the chelating effect of the two ortho oxygen atoms on the boron atom. Such an interaction
was projected to significantly lower the energy barrier in contrast to the case of the para isomer, DFT calculations have further supported the proposed mechanism for the formation of the ortho rearranged product 12 with $^1$H and $^{11}$B chemical shifts in agreement with the observed resonances in the NMR spectra (Scheme 3).

Methanesulphonic acid (MSA) has also been reported to catalyze Fries rearrangement. The rearrangement of phenyl acetate 13 was usually performed in hydrofloric acid (HF). Commarieu et.al. have optimized this reaction with methanesulfonic acid (MSA) to give para-hydroxyacetophenone 14 with high conversion and selectivity (up to 92% of para-isomer 14 and 8% of ortho-isomer 15 at 100% conversion) as shown in Scheme 4.
The literature rationale also reveals the utility of anilides and related substrate in Fries rearrangement, however, the reactions were found to be sluggish. Dippy et al. studied the rearrangement of \( N,N \)-diacylanilides using freshly fused Zinc chloride.\(^7\) The rearrangement was shown to be slow and led to lower yields of the products. The rearrangement of \( N \)-monoacylanilides was shown to be even more difficult. The treatment of \( N \)-monoacylanilides with anhydrous aluminium chloride at high temperature yielded the \( o \)-amino-acylphenone or \( p \)-amino-acylphenone in low yields. In addition esters were obtained as by-products in this reaction.\(^8\) Das et al. have developed a method for facile rearrangement of sulfonanilides under the microwave irradiation in the presence of excess of aluminium chloride.\(^9\) Jin et al. have employed Ytterbium triflate with lithium perchlorate as co-catalyst to catalyse the Fries-type rearrangement of various acylanilides 16 with moderate yields of amino ketones (Scheme 5).\(^10\)

![Scheme 5](image)

**Scheme 5**

Recently, Abedi and co-workers have examined the rearrangement of anilides 18 in the presence of Phosphorous pentaoxide in methanesulphonic acid. The \( P_2O_5/\text{methanesulfonic acid} \) (1:7) was shown as an efficient reagent for the rearrangement to \( p \)-aminoaryl ketones 20 via \( p \)-acylated anilide 19 (Scheme 6).\(^11\)

![Scheme 6](image)

**Scheme 6**
Some of the major advantages of this protocol were good yields, inexpensive and non-toxic catalyst, mild reaction conditions and high selectivity. In view of the difficulty in achieving the rearrangements of N-monoacylanilides, various photochemical methods has also been widely used.\textsuperscript{12-19}

Thus, there are also numerous reports in the literature highlighting variants in the conventional thermal Fries reaction \textit{viz.} photochemical version called Photo-Fries rearrangement and anionic version called Anionic Fries rearrangement. Literature rationale also suggests the substrate expansion moving from the conservative aryl esters to anilides, thioesters, carbamates, conjugated aryl esters and anilides.

A photochemical variant of the Fries rearrangement involved a radical reaction mechanism proceeding through the homolytic cleavage of the phenolic oxygen and carbonyl carbon bond of ester $\text{I}$ generating an acyl radical $\text{21}$ and a phenoxide radical $\text{I}$, first described in 1960.\textsuperscript{20} The phenoxide radical isomerizes to \textit{ortho} $\text{II}$ or \textit{para} radical $\text{III}$ before combining with the acyl radical $\text{21}$ to form \textit{para} and \textit{ortho} rearranged products $\text{22a}$ and $\text{22b}$ and as shown in Scheme 8.

![Scheme 8](image)

The Photo-Fries rearrangement was also reported to occur naturally, for example, exposure of the plastic bottle made of polyethylene terephthalate (PET) to the sun, particularly to UV light at a wavelength of about 310nm led to the leaching of phthalate from the plastic.\textsuperscript{21}

Many biologically important scaffolds have reportedly been synthesized using this technology. Taddei \textit{et. al.} have developed a simple and facile route for the synthesis of 2,4-disubstituted quinazolines $\text{26}$ derived from naturally occurring amino acids. 2,4-dialkyl or aryl quinazolines $\text{26}$ have been prepared in three steps starting from easily available anilides $\text{23}$. A photochemically induced Fries rearrangement of the anilides gave several \textit{ortho}-aminoacylbenzene derivatives $\text{24}$ that were acylated at the NH$_2$. These
acylamides 25 underwent rapid cyclization to 2,4-disubstituted quinazolines (and benzoquinazolines) in the presence of ammonium formate under microwave activation. This procedure was compatible with different functional groups and it also allowed the preparation of new quinazolines derived from naturally occurring amino acids (Scheme 9).

Scheme 9
Taddie et. al. have also demonstrated that photo-Fries rearrangement of anilides 27 resulted in the corresponding o-amino phenones 28. These compounds are useful building blocks for the preparation of benzoannelated heterocycles.

Scheme 10
The products 29, obtained after coupling of 28 with N-Boc protected amino acids on TFA mediated deprotection cyclized to 3,5-disubstituted 1,4-benzodiazepin-2-ones 30 (Scheme 10). Similar results were obtained by coupling with N-Cbz-protected R-amino acids followed by microwave assisted hydrogenolysis. The Fries rearrangement of anilides derived from N-Boc-Ala-OH followed by coupling with N-Cbz-(OMe)Asp-OH, yielded benzodiazepines which could be inserted in a peptide chain for the preparation of conformationally constrained peptidomimetics.

The anionic variant of Fries rearrangement was first reported by Melvin in 1981. Thereafter, a number of reports have appeared on anionic Fries rearrangement in which the aryl ester undergoes ortho metallation with a strong base, which then rearranges through a nucleophilic attack. Lu et al. have developed a superior one-pot process for rapid preparation of oxo anilides 34, involving iodine magnesium exchange, regiospecific ortho N-Fries rearrangement and in situ trapping of the formed aniline anion 33 prepared by ortho metallation of 31 via 32. The acyl groups capable of migration possess a sp³ tertiary carbon center with carbon or heteroatom substituents. The acyl migration, coupled with acylation and McMurry cyclization, allows ready access to 1,2,3-trisubstituted indoles 35 with tertiary carbon substituent at the C³ position (Scheme 11).
Strained cyclic amides, $\beta$-lactams have also been reported as potential substrates for Fries rearrangement. These cyclic amides bearing an aromatic substituent at N-1 undergoes facile Fries rearrangement generating novel heterocyclic compounds. In recent years a number of reports have appeared in the literature concerning the transformation of azetidin-2-ones to tetrahydroquinolines by photolysis\textsuperscript{26} and to dihydrocarbostyrils via acidic rearrangement (Scheme 12).\textsuperscript{27}

\[ \text{Azetidin-2-one} \xrightarrow{\text{hv}} \text{Tetrahydroquinoline} \]

\[ \text{Azetidin-2-one} \xrightarrow{\text{H}^+} \text{Tetrahydroquinoline} \]

Scheme 12

$\beta$-lactams are also known to undergo 1,4-heterolytic cleavage and subsequent prototropic shift to generate corresponding amides.\textsuperscript{28} Kano et al. have reported the trifluoroacetic acid mediated easy access to novel 1,2,3,4-tetrahydroquinolin-4-ones via Fries rearrangement of 1-aryl-azetidin-2-ones.\textsuperscript{29} Thus, 1-(4-methoxy)-azetidin-2-ones 36 on heating in trifluoroacetic acid resulted in tetrahydroquinolin-4-ones 37 in quantitative yields. However, the treatment of 1-(3-methoxyphenyl)-azetidin-2-one 38 with trifluoroacetic acid under similar conditions, resulted in the mixture of ortho and para rearranged products 7-metox 1,2,3,4-tetrahydroquinolin-4-ones 39 and 5-metox 1,2,3,4-tetrahydroquinolin-4-ones 40. The Fries rearrangement of 1-$\alpha$-napthyl- azetidin-2-one 41 lead to the formation of expected benz[$h$]-quinolin-4-one 42 in quantitative yield (Scheme 13).\textsuperscript{29}
Scheme 13

Different acids viz. conc. Sulphuric acid, boron triflouro-etherate, methanesulphonic acid, triflouroacetic acid at room and elevated temperatures were gauged to catalyse the Fries rearrangement of azetidin-2-ones. The best results, in terms of reaction times and yields were reported with methanesulphonic acid at room temperature and triflouroacetic acid under refluxing conditions.\(^{30}\) Kano et. al. have also devised an easy, single step entry to furo[3,2-c]quinoline derivatives \(^{45}\) by means of triflouroacetic acid mediated Fries rearrangement of 1-aryl-3-(2-oxoalkyl)azetidin-2-ones \(^{43}\). The reaction was reported to proceed through 2,3-dihydro-3-\(\beta\)-ketoalkyl-4(1\(H\))-quinolone intermediates \(^{44}\) (Scheme 14).\(^{31}\)

Scheme 14
Tepe et al. have also reported a significantly milder method for the preparation of quinolin-4-ones 47 by treatment of N-aryl azetidin-2-ones 46 with trifluoromethanesulfonic acid in 1,2-dichloroethane (Scheme 15). The ring expansion was attributed solely to the inherent ring strain in \( \beta \)-lactams as \( \delta \)-lactams failed to undergo rearrangement under similar reaction conditions.

![Scheme 15](image)

Thus there are numerous reports in the literature highlighting the Fries rearrangement in various substrates viz. aryl esters, anilides, thioesters, carbamates, conjugated aryl esters and anilides. The use of different catalysts like aluminium chloride, boron trifluoride, bismuth triflate and even strong protic acids such as hydrogen fluoride, methanesulphonic acid, trifluoroacetic acid and trifluoromethanesulphonic acid has also been highlighted. However, the literature validation suggests that there are only a few reports of Fries rearrangement using \( \beta \)-lactams as substrates and there is hardly any report concerning the Fries rearrangement of C-3 functionalized \( \beta \)-lacatms and \( \alpha, \beta \)-unsaturated anilides.
3.2. Facile Fries Rearrangement of 3-dienyl-β-lactams and 3-carbocyclic/heterocyclic ring substituted β-lactams: Synthesis of novel quinolin-4-ones:

3.2.1 Result and Discussion

The trans 3-butadienyl-2-azetidinones 48a-l required for the present studies were easily obtained by the reported procedure viz the reactions of the in situ generated butadienyl ketene with N-aryl imines.\textsuperscript{34} The treatment of 3-dienyl azetidin-2-ones 48a-l with 1.0 eq of trifloromethanesulphonic acid (triflic acid) in dry 1,2-dichloroethane for 10-15 min resulted in the formation of 3-(but-2-enylidene)-2-arylquinolin-4(3\textit{H})-one 49a-l in moderate to good yields of 55-65\% (Scheme 17, Table 1).

![Scheme 17](image)

The compound 49a, for example, analyzed for C\textsubscript{19}H\textsubscript{15}NO showed a molecular ion peak at \textit{m/z} 273. Its IR spectrum exhibited sharp absorptions 1627 and 1684 cm\textsuperscript{-1}. The salient features of its \textsuperscript{1}H spectrum include a doublet at \(\delta 1.86(J=5.4 \text{ Hz})\) corresponding to the three methyl protons, a doublet at \(\delta 5.88(J=15.0 \text{ Hz})\) due to H\textsubscript{2}, a multiplet at \(\delta 6.17(J=5.1\text{Hz and 14.71 Hz})\) corresponding to H\textsubscript{1} and an unresolved doublet at \(\delta 7.25\) due to H\textsubscript{3}. Its \textsuperscript{13}C spectrum showed the presence of the required carbons including the characteristic methyl carbon and quinolinone rings iminic carbon at \(\delta 20.1\) and \(\delta 161.4\) respectively. The absorption of carbonyl carbon at \(\delta 176.3\) further corroborates the assigned structure (Figure 1).
The plausible mechanism underlying the above transformation is believed to involve the initial protonation of 3-dienyl-β-lactam 48 generating intermediate 50 which isomerizes to intermediate 51. The carbocation intermediate 51, being unstable, readily undergoes Fries rearrangement through an ortho attack of the aromatic substituent on the nitrogen atom, generating ring expanded intermediate 52. Its aromatization accompanied by oxidation generates intermediate 53 which on tautomerization results in the desired quinolin-4(3H)-ones 49 as shown in Scheme 18.
In an attempt to generalize these reactions, it was considered worthwhile to examine the triflic acid mediated Fries rearrangement of 3-dienyl-\(\beta\)-lactams DA cycloadducts with symmetrical, unsymmetrical carbon and heterodienophiles. The cycloadducts of 3-dienyl azetidin-2-ones 54a-i required for the present study were easily obtained following the previous reported procedure.\(^{35}\) Thus, the treatment of 54, with 1.1 eq of triflic acid in dry 1,2-dichloroethane for 2-3 hr resulted in the formation of 2-(4-oxo-2-aryl-1,2,3,4-tetrahydroquinolin-3-yl)cyclohex-3-enecarboxylic acid derivatives 55 in excellent yields of 80-90% (Scheme 19, Table 2).
Table 2: Triflic acid mediated Fries rearrangement of cycloadducts 54.

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<td>OCH₃</td>
<td>NH₂</td>
<td>3.0</td>
<td>81</td>
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</tbody>
</table>

a All the reactions were conducted using 1,2 dichloroethane as solvent. b Yields of adducts were measured prior to crystallization.

The diastereomERICally pure, rearranged products 55a-i thus obtained, were characterised with the help of analytical data and spectral evidences, the details of which are described in the experimental section while the salient features are discussed here. The compound 55a, for example, analysed for C₂₃H₂₃NO₃ showed a molecular ion peak at m/z 361 in its mass spectrum. Its IR spectrum showed a strong absorption peak at 1682 and 1700 cm⁻¹ due to the carbonyl groups of ester and quinolin-4-one ring. Its high resolution ¹H NMR (300MHz) spectrum showed a multiplet at δ 2.05 corresponding to H₆a, H₆b, H₇a and H₇b, another multiplet at δ 2.78 due to H₈, a doublet of a doublet at δ 2.90(J=1.8 Hz, 3.0 Hz) corresponding to H², a doublet of a doublet of a doublet at δ 3.15(J=1.8 Hz, 5.4 Hz, 9.6 Hz) due to H₁, a singlet at δ 3.64 due to three methoxy protons, a doublet at δ 4.66(J=3.0 Hz) corresponding to H₁, a triplet of a doublet at δ 5.60 (J=3.0Hz, 9.6 Hz) due to H⁵, a doublet of a doublet of a doublet at δ 6.03 (J=2.7Hz, 5.7 Hz, 9.6 Hz) corresponding to H⁴. The coupling constant of J=1.8 Hz between H² and H³ established the cis stereochemistry between these protons and the coupling constant of J=9.6 Hz also confirms the cis stereochemical assignment between H³ and H⁸ protons. Its ¹³C NMR spectrum showed the presence of required number of carbons along with absorptions at δ 173.8 and 182.4 corresponding ester and quinolinone ring carbonyl (Figure 2).

The stereochemistry of the starting DA cycloadducts is retained in the Fries rearranged products as is evident from the coupling constant values between H⁴ & H², H² & H³ and H³ & H⁸ protons. ³⁵
In an attempt to further rationalize the results, we have examined the Fries rearrangement of the DA cycloadducts of 3-dienyl-2-azetidinones with symmetrical dienophiles viz. maleic anhydride, N-phenyl maleimide, obtained by the earlier reported procedure. 35 Thus, the treatment of DA cycloadducts 56a-f with triflic acid under the reaction condition described above also resulted in desired rearrangement leading to the formation of 4-(4-oxo-2-aryl-1,2,3,4-tetrahydroquinolin-3-yl)-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione(X=O) and 4-(4-oxo-2-aryl-1,2,3,4-tetrahydroquinolin-3-yl)-2-phenyl-3a,4,7,7a-tetrahydro-1H-isoindole-1,3(2H)-dione derivatives(X=NPh) 57a-f in excellent yields (80-90%) (Scheme 20, Table 3).

Table 3: Triflic acid mediated Fries rearrangement of cycloadducts 56.

<table>
<thead>
<tr>
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<th>R</th>
<th>X</th>
<th>Reaction Time(h)</th>
<th>% Yield of 57</th>
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<td>57b</td>
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<td>57c</td>
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</tr>
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<td>57f</td>
<td>OCH₃</td>
<td>NPh</td>
<td>4.0</td>
<td>80</td>
</tr>
</tbody>
</table>

*All the reactions were conducted using 1,2 dichloroethane as solvent. *Yields of adducts were measured prior to crystallization.
The diastereomERICally pure products thus obtained, were also characterised as usual with the help of analytical data and spectral evidences, the details of which are described in the experimental section while the salient features are discussed here. The compound 57a, for example, analysed for C$_{23}$H$_{19}$NO$_4$ showed a molecular ion peak at $m/z$ 373 in its mass spectrum. Its IR spectrum showed a strong absorption peak at 1700 and 1771 cm$^{-1}$ due to the carbonyl groups of quinoline and tetrahydroisobenzofuran-1,3-dione ring. Its high resolution $^1$H NMR (300MHz) spectrum showed a multiplet at $\delta$ 2.01 corresponding to H$^{6b}$, another multiplet at $\delta$ 2.30 due to H$^{6a}$, a doublet of a doublet at $\delta$ 2.89(J=4.5 Hz, 14.9 Hz) corresponding to H$^2$, a doublet of a doublet of a doublet at $\delta$ 3.21(J=1.5 Hz, 5.7 Hz, 14.9 Hz) due to H$^3$, a doublet of a doublet at $\delta$ 3.36(J=5.7 Hz, 8.7 Hz) corresponding to H$^8$, a doublet of a doublet of a doublet at $\delta$ 3.68(J=2.7Hz, 3.0Hz, 8.7Hz) due to H$^7$, a doublet at $\delta$ 4.65(J=4.5 Hz) corresponding to H$^1$, a multiplet at $\delta$ 6.01 due to H$^5$, another multiplet at $\delta$ 6.03 corresponding to H$^4$. The coupling constant of J=14.9 Hz between H$^2$ and H$^3$ established the trans stereochemistry between these protons and the coupling constant of J=5.7 Hz confirms the cis stereochemical assignment between H$^3$ and H$^8$ protons. Its $^{13}$C NMR spectrum showed the presence of required number of carbons along with characteristic of carbonyls at $\delta$ 170.7, 173.2 and 183.2 corresponding to tetrahydroisobenzofuran-1,3-dione and quinazoline ring (Figure 3).

The stereochemistry of the starting dienyl lactam cycloadducts is again retained in the Fries rearranged products as is evident from the coupling constant values between H$^1$ & H$^2$, H$^2$&H$^3$ and H$^3$&H$^8$ protons.35

![Figure 3]
These results were further validated by the Fries rearrangement of NDA cycloadducts of 3-dienyl-2-azetidinones with nitrosobenzene. The treatment of NDA cycloadducts 58a-c with 1.1 eq of triflic acid in dry 1,2-dichloroethane for 3-4hr resulted in the formation of 2-aryl-3-(2-phenyl-3,6-dihydro-2H-1,2-oxazin-6-yl)-2,3-dihydroquinolin-4(1H)-one derivatives 59a-c in good to excellent yields (75-85%) (Scheme 21, Table 4).

Scheme 21

<table>
<thead>
<tr>
<th>Entry</th>
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<th>% Yield of 59</th>
</tr>
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<tbody>
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<td>59c</td>
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<td>84</td>
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</table>

*All the reactions were conducted using 1,2 dichloroethane as solvent. *Yields of adducts were measured prior to crystallization.

The diastereomERICALLY pure Fries rearranged products thus obtained, were characterised again with the help of analytical data and spectral evidences, the details of which are described in the experimental section while the salient features are discussed here. The compound 59a, for example, analysed for C₂₅H₂₂N₂O₂ showed a molecular ion peak at m/z 382 in its mass spectrum. Its IR spectrum showed a strong absorption peaks at 1460 and 1498 cm⁻¹ due cyclic nitroso compounds and absorption at 1680 cm⁻¹ due to the carbonyl group of the quinolinone ring. Its high resolution ¹H NMR (300MHz) spectrum showed a doublet of a doublet at δ 3.72(J=3.3 Hz, 10.2 Hz) corresponding to H², a doublet of an AB quartet at δ 3.85(J=2.1Hz, 2.4 Hz, 16.2 Hz) due to H⁶a and H⁶b, a doublet of a doublet at δ 4.52(J=1.5 Hz, 10.2 Hz) corresponding to H³, a doublet at δ 4.63 (J=3.3 Hz) due to H¹, a multiplet at δ 6.01 corresponding to olefenic H⁴ and H⁵ protons (Figure 4).
The coupling constant of $J=10.2$ Hz between $H_2$ and $H_3$ established the trans stereochemical assignment between these protons. Its $^{13}$C NMR spectrum showed the presence of required number of carbons along with characteristic carbonyl at $\delta 183.5$ corresponding to the quinazoline ring (Figure 4).

In an effort to optimize the reaction conditions, all the reactions were attempted in a number of solvents under varying temperature conditions. The reactions in dichloromethane, benzene, chloroform and tetrahydrofuran at 0°C and room temperature were found to be slower with lower yields of the isolated product. Best results in terms of yields and reaction times were observed when 1,2-dichloroethane was employed for the rearrangement at 0°C. Different Lewis acids viz. AlCl$_3$, TiCl$_4$, BF$_3$-Et$_2$O, CH$_3$SO$_3$H were also attempted to catalyze the Fries rearrangement of C-3 functionalized $\beta$-lactams. With the exception of methanesulphonic acid, no other catalyst was able to conceive this rearrangement and even with methanesulphonic acid, the reaction took 2-3 days for completion. The best results were observed with the use of trifloromethanesulphonic acid as a catalyst.
3.3 Triflic acid catalysed Fries Rearrangement of Sorbyl anilides to novel benzazocinones:

3.3.1. Results and Discussion

The lack of substantial evidence on the Fries rearrangement of $\alpha,\beta$-unsaturated anilides and in continuation of our pursuits for the synthesis of biologically imperative heterocyclics utilizing the synthetic transformations of sorbyl based precursors, it was thought worthwhile to explore the Fries rearrangement of sorbyl anilides. Interestingly, the treatment of $60$, prepared by the reported procedure, with 1.0 eq. of triflic acid in dry dichloroethane for 3-4hr led to the exclusive formation of novel benzo[b]azocin-6-one derivatives $61$ in excellent yields (80-90%) (Scheme 22, Table 5).

![Scheme 22](image)

**Table 5**: Triflic acid mediated rearrangement of sorbyl anilides $60$.

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<td>61h</td>
<td>$m$-CH$_3$</td>
<td>3.5</td>
<td>83</td>
</tr>
<tr>
<td>61i</td>
<td>$m$-Cl</td>
<td>3.2</td>
<td>81</td>
</tr>
<tr>
<td>61j</td>
<td>$m$-OCH$_3$</td>
<td>3.8</td>
<td>86</td>
</tr>
</tbody>
</table>

*All the reactions were conducted using 1,2 dichloroethane as solvent. *Yields of adducts were measured prior to crystallization.

The structure was assigned to the products on the basis of spectral studies and analytical evidences. The compound $61a$, for example, characterized as (Z)-2,8-
dimethyl-1,2-dihydrobenzo[b]azocin-6(5H)-one was analyzed for C\textsubscript{13}H\textsubscript{15}NO and showed a molecular ion peak at \textit{m/z} 202(M\textsuperscript{+}) in its mass spectrum. Its IR spectrum exhibited sharp absorption at 1680 cm\textsuperscript{-1} due to the carbonyl of the azocinone ring. The salient features of its \textsuperscript{1}H NMR spectrum include a doublet at \(\delta\) 1.73(\(J=4.8\)Hz) corresponding to azocinone ring methyl protons, a singlet at \(\delta\) 2.29 corresponding to aromatic methyl protons, doublet of an AB quartet at \(\delta\) 3.46(\(J=6.3\) Hz, 7.8Hz, 16.2 Hz) due to \(H^4a,4b\) methylene protons, a quartet at \(\delta\) 3.58(\(J=4.8\)Hz) corresponding to methine proton, unresolved multiplet at \(\delta\) 5.48 corresponding to two olefinic protons, a doublet at \(\delta\) 6.68(\(J=8.0\) Hz) corresponding to \(H_8\) proton, a singlet at \(\delta\) 6.93 corresponding to \(H_5\) proton and a doublet at \(\delta\) 6.95(\(J=8.0\)Hz) corresponding to \(H_7\). Its \textsuperscript{13}C NMR shows absorptions at \(\delta\) 17.8(-CH\textsubscript{3}), 20.8(-CH\textsubscript{3}), 36.9(-CH\textsubscript{2}), 39.2(-CH), 170.6 (C=O) along with the requisite number carbons for aromatic and olefinic carbons (Figure 5).

The plausible mechanism for the formation of benzo[b]azocin-6-one 61 is depicted in Scheme 23 and may follow either Path A involving an initial [6-\textit{endo-trig}] Michael addition to 6-methyl-1-aryl-3,6-dihydro-1\textsubscript{H}-pyridin-2-one 62 which undergoes Fries rearrangement to yield the desired product 61. Alternatively, the sorbyl anilides may follow Path B involving an initial Fries rearrangement to form substituted 1-(2-aminoaryl)-hexa-2,4-dien-1-one 63 which upon intramolecular [8-\textit{endo-trig}] Michael addition results in 61. However, 63 may prefer a more favored [6-\textit{endo-trig}] process favoring the formation of 64 over a [8-\textit{endo-trig}] process to form 65. The formation of 64 may also be preferred due to the higher stability of 6-membered ring over an alternative medium sized eight membered ring (Path B). Hence, the Michael-Fries rearrangement Path A appears to be favored for the formation of 61 over the alternative Path B.
In order to further support the proposed mechanism, we have examined the reactions of $\alpha,\beta$-unsaturated anilides 66 under similar reaction conditions. It was felt that in this case, the tandem Michael-Fries rearrangement, involving an unfavorable [4-endo-trig] cyclization will be inhibited due to the initial formation of strained $\beta$-lactam ring 67, while the Fries-Michael process involving a favourable [6-endo-trig] cyclization would be facilitated to yield dihydro-$1H$-quinolin-4-ones 69 via 1-(2-amino-aryl)-alk-2-en-1-one 68 (Figure 6). However, the inability of $\alpha,\beta$-unsaturated anilides to undergo any transformation especially the favored Fries-Michael rearrangement, indirectly supports the Michael-Fries Path A for the formation of 61.
Recently, Abedi and co-workers attempted the Fries rearrangement of $N$-phenylcinnamamide 66 and obtained the substituted quinolin-2(1H)-one 70 as the major product via intramolecular cyclization. A sulphonated product 71 was also obtained as a side product in the reaction mixture (Scheme 24).\textsuperscript{11}

Accordingly, it was felt that the product formed in the reaction of sorbyl anilide 60 with triflic acid might result from an intramolecular cyclization leading to 6-methyl-3,6-dihydrobenzo[b]azocin-2(1H)-one 72 instead of the earlier characterized 2-methyl-1,2-
dihydrobenzo[b]azocin-6(5H)-one 61. However, such an intramolecular cyclization may be ruled out because:

(i) Sorby anilide 60 did not undergo any transformation under the reaction conditions for intramolecular cyclization viz. P2O5/CH3SO3H reported by Abedi and co-workers.

(ii) The intramolecular cyclization of sorbyl anilide 60 would have preferred the [6-endo-trig] process to yield more stable 6-membered product 64 over the [8-endo-trig] process to form relatively less stable eight membered product 72 (Scheme 25).

Scheme 25

The observations described above also provide circuitous evidences in favor of the Michael-Fries mechanism leading to the formation of Benzo[b]azocin-6-ones in the reactions of sorbylanilides 60 with trifluoromethanesulphonic acid. Further, the approach assumes significance as it entails an unprecedented Michael-Fries rearrangement of sorbyl anilides perhaps via a δ-lactam intermediate, earlier considered unreactive under the comparable and even drastic reaction conditions.32,33

The proposed structure is planned to be unambiguously supported with the help of X-ray diffraction studies.
3.4 Conclusion:
The present chapter summaries the thermal Fries rearrangement of trans 3-dienyl-2-azetidinones and 3-carbo/heterocyclic substituted β-lactams employing triflic acid as the catalyst to generate novel quinolinone derivatives in a facile and fast process. The methodology further assumes significance as it appears to be the first report on Fries rearrangement of a dienyl tethered heterocyclic systems. The chapter also explicates a convenient one pot synthesis of novel Benzo[b]azocin-6-ones via an unprecedented tandem Michael-Fries rearrangement of sorbyl anilides. The present work further assumes significance as this appears to be the first report on synthesis of novel benzo[b]azocin-6-ones from sorbyl anilides.
3.5 Experimental Section

Melting points were determined by open capillary using Veego Precision Digital Melting Point apparatus (MP-D) and are uncorrected. IR spectra were recorded on a Shimadzu D-8001 spectrophotometer. $^1$H NMR spectra were recorded in deuterochloroform with Joel (300 MHz) spectrometers using TMS as internal standard. Chemical shift values are expressed as ppm downfield from TMS and $J$ values are in Hz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, m: multiplet, q: quartet, br: broad peak and brs: broad singlet. $^{13}$C NMR spectra were also recorded on Joel 300 (75.0 MHz) spectrometers in deuterochloroform using TMS as internal standard. Mass spectra were recorded on Shimadzu GCMS-QP-2000 mass spectrometer. Elemental analyses were performed on Heraus CHN-O-Rapid Elemental Analyzer. Column chromatography was performed on silica gel (60–120) mesh Harrison Research Chromatotron using 2 mm plates (Silica gel 60 PF254).

General procedure for the synthesis of quinolin-4(3H)-one 49a-l:

The synthesis of quinolin-4(3H)-one was realized by slow addition of triflic acid (15mmol) to ice cold solution of 1,2-dichloroethane (20 mL) solution of trans-3-butadienyl-2-azetidinones (10mmol) 48a-l. After completion of the reaction, (monitored through tlc) reaction mixture was washed with water and extracted with dichloroehane. The removal of solvent under reduced pressure resulted in crude product, which was purified through silica gel column chromatography resulted in isolation of compound 49a-l in excellent yields.

49a. 3-(but-2-enylidene)-2-phenylquinolin-4(3H)-one:

Pale yellow solid, M. p.: 92-93 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H = 1.86$(d, $J = 5.4$ Hz, 3H, -CH$_3$), 5.88(d, 1H, $J$=15.0 Hz, H$_2$), 6.17(m, 2H, H$_1$), 7.25(m, 1H, H$_3$), 6.92-7.68(m, 9H, ArH, aromatic), $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C = 19.5$, 127.0, 127.1, 127.7, 128.2, 128.8, 129.2, 130.2, 130.4, 131.0, 131.2, 135.8, 138.9, 143.1, 153.5, 164.8, 177.4 ppm.
49b. 3-(but-2-enylidene)-2-(4-chlorophenyl)quinolin-4(3H)-one:
Pale yellow solid, M. p.: 93-94 °C. \(^1^H\) NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 1.85 (d, J = 5.4\) Hz, 3H, -CH\(_3\)), 5.86(d, 1H, \(J=15.0\) Hz, H\(_2\)), 6.15(m, 2H, H\(_1\)), 7.24(m, 1H, H\(_3\)), 6.86-7.64(m, 8H, ArH, aromatic), \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 19.7, 127.2, 127.3, 127.8, 128.3, 128.9, 130.1, 130.6, 131.3, 131.4, 135.8, 136.0, 137.3, 143.2, 153.6, 164.6, 177.2\) ppm. MS \(m/z\) 307 \([M]^+\). IR (KBr): \(v_{\text{max}} = 1434, 1536, 1588, 1629, 1688\) cm\(^{-1}\). Anal. Calcd for C\(_{19}\)H\(_{15}\)NO: C, 83.49; H, 5.53; N, 5.12. Found: C 83.67, H 5.75, N 5.02.

49c. 3-(but-2-enylidene)-2-(4-methoxyphenyl)quinolin-4(3H)-one:
Pale yellow solid, M. p.: 95-96 °C. \(^1^H\) NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 1.86 (d, J = 5.7\) Hz, 3H, -CH\(_3\)), 3.82(s, 3H, -OCH\(_3\)), 5.85(d, 1H, \(J=15.0\) Hz, H\(_2\)), 6.16(m, 2H, H\(_1\)), 7.25(m, 1H, H\(_3\)), 6.90-7.67(m, 8H, ArH, aromatic), \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 19.7, 55.2, 115.6, 127.3, 127.4, 127.9, 128.1, 130.1, 130.2, 130.4, 131.3, 131.4, 131.6, 135.9, 143.2, 153.5, 164.7, 177.2\) ppm. MS \(m/z\) 303 \([M]^+\). IR (KBr): \(v_{\text{max}} = 1434, 1536, 1588, 1629, 1688\) cm\(^{-1}\). Anal. Calcd for C\(_{20}\)H\(_{17}\)NO\(_2\): C, 79.19; H, 5.65; N, 4.62. Found: C, 79.31; H, 5.79; N, 4.50.

49d. 3-(but-2-enylidene)-2-p-tolylquinolin-4(3H)-one:
Pale yellow solid, M. p.: 96-97 °C. \(^1^H\) NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 1.86 (d, J=5.4\) Hz, 3H, -CH\(_3\)), 2.25(s, 3H, -CH\(_3\)C\(_6\)H\(_4\)), 5.86(d, 1H, \(J = 15.0\) Hz, H\(_2\)), 6.16(m, 2H, H\(_1\)), 7.26(m, 1H, H\(_3\)), 6.90-7.63(m, 8H, ArH, aromatic), \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 19.6, 21.5, 127.0, 127.2, 127.8, 128.3, 129.0, 129.2, 130.2, 130.5, 131.2, 135.8, 136.6, 140.3, 143.3, 153.2, 164.6, 177.2\) ppm. MS \(m/z\) 287 \([M]^+\). IR (KBr): \(v_{\text{max}} = 1435, 1537, 1589, 1626, 1683\) cm\(^{-1}\). Anal. Calcd for C\(_{20}\)H\(_{17}\)NO: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.74; H, 6.06; N, 4.72.
49e. 3-(but-2-enylidene)-6-chloro-2-phenylquinolin-4(3H)-one:
Pale yellow solid, M. p.: 95-96 °C. ¹H NMR (CDCl₃, 300 MHz): δ_H = 1.84(d, J=5.4 Hz, 3H, -CH₃), 5.86(d, 1H, J=15.0 Hz, H₂), 6.15(m, 2H, H₁, H₃), 7.25(m, 1H, H₃), 6.92-7.68(m, 8H, ArH, aromatic). ¹³C NMR (CDCl₃, 75 MHz): δ_C = 19.6, 127.1, 128.2, 128.3, 128.9, 129.1, 130.2, 130.4, 131.0, 131.3, 133.3, 135.9, 138.9, 143.0, 151.5, 164.6, 177.2 ppm. MS m/z 307 [M]⁺. IR (KBr): ν_max = 1435, 1532, 1586, 1629, 1686 cm⁻¹. Anal. Calcd for C₁₀H₁₄ClNO: C, 74.15; H, 4.58; N, 4.55. Found: C, 74.27; H, 4.69; N, 4.42.

49f. 3-(but-2-enylidene)-6-chloro-2-(4-chlorophenyl)quinolin-4(3H)-one:
Pale yellow solid, M. p.: 93-94 °C. ¹H NMR (CDCl₃, 300 MHz): δ_H = 1.86(d, J=5.4 Hz, 3H, -CH₃), 5.85(d, 1H, J=15.0 Hz, H₂), 6.16(m, 2H, H₁, H₃), 7.23(m, 1H, H₃), 6.86-7.65(m, 7H, ArH, aromatic). ¹³C NMR (CDCl₃, 75 MHz): δ_C = 19.7, 127.2, 127.5, 128.3, 128.9, 130.6, 131.3, 131.4, 131.6, 133.3, 135.9, 136.0, 137.2, 143.4, 153.6, 164.6, 177.2 ppm. MS m/z 341 [M]⁺. IR (KBr): ν_max = 1432, 1532, 1584, 1628, 1689 cm⁻¹. Anal. Calcd for C₁₉H₁₃Cl₂NO: C, 66.68; H, 3.83; N, 4.09. Found: C, 66.82; H, 3.96; N, 4.01.

49g. 3-(but-2-enylidene)-6-chloro-2-(4-methoxyphenyl)quinolin-4(3H)-one:
Pale yellow solid, M. p.: 97-98 °C. ¹H NMR (CDCl₃, 300 MHz): δ_H = 1.86(d, J=5.7 Hz, 3H, -CH₃), 3.83(s, 3H, -OCH₃), 5.86(d, 1H, J = 15.0 Hz, H₂), 6.16(m, 2H, H₁, H₃), 7.24(m, 1H, H₃), 6.91-7.67(m, 7H, ArH, aromatic). ¹³C NMR (CDCl₃, 75 MHz): δ_C = 19.7, 55.2, 115.3, 127.3, 127.2, 128.1, 130.1, 130.9, 131.2, 131.4, 131.6, 133.5, 135.9, 143.3, 153.7, 164.5, 177.3 ppm. MS m/z 337 [M]⁺. IR (KBr): ν_max = 1435, 1532, 1586, 1629, 1682 cm⁻¹. Anal. Calcd for C₁₉H₁₅ClNO₂: C, 71.11; H, 4.77; N, 4.15. Found: C, 71.29; H, 4.89; N, 4.02.

49h. 3-(but-2-enylidene)-6-chloro-2-p-tolylquinolin-4(3H)-one:
Pale yellow solid, M. p.: 93-94 °C. ¹H NMR (CDCl₃, 300 MHz): δ_H = 1.85(d, J=5.4 Hz, 3H, -CH₃), 2.24(s, 3H, -CH₃C₆H₄), 5.89(d, 1H, J=15.0 Hz, H₂), 6.16(m, 2H, H₁, H₃), 7.25(m, 1H, H₃), 6.92-7.68(m, 8H, ArH, aromatic). ¹³C NMR (CDCl₃, 75 MHz): δ_C = 19.6, 127.1, 128.2, 128.3, 128.9, 130.2, 130.4, 131.0, 131.3, 133.3, 135.9, 138.9, 143.0, 151.5, 164.6, 177.2 ppm. MS m/z 325 [M]⁺. IR (KBr): ν_max = 1435, 1532, 1586, 1629, 1686 cm⁻¹. Anal. Calcd for C₁₉H₁₅ClNO: C, 74.15; H, 4.58; N, 4.55. Found: C, 74.27; H, 4.69; N, 4.42.
7.26 (m, 1H, H$_3$), 6.92-7.62 (m, 7H, ArH, aromatic), $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C$ = 19.6, 21.3, 127.2, 128.2, 128.3, 128.9, 129.3, 130.5, 130.4, 131.2, 133.3, 135.9, 138.9, 140.6, 143.2, 151.3, 164.6, 177.3 ppm. MS $m/z$ 321 [M]$^+$. IR (KBr): $\nu_{max}$ = 1435, 1532, 1584, 1626, 1682 cm$^{-1}$. Anal. Calcd for C$_{20}$H$_{16}$ClNO: C, 74.65; H, 5.01; N, 4.35. Found: C, 74.84; H, 5.18; N, 4.21.

**49i. 3-(but-2-enylidene)-6-methyl-2-phenylquinolin-4(3H)-one:**
Pale yellow solid, M. p.: 97-98 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H$ = 1.85 (d, $J$=5.4 Hz, 3H, -CH$_3$), 2.32 (s, 3H, -CH$_3$C$_6$H$_3$), 5.88 (d, 1H, $J$=15.0 Hz, H$_2$), 6.15 (m, 2H, H$_1$), 7.25 (m, 1H, H$_3$), 6.91-7.62 (m, 8H, ArH, aromatic), $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C$ = 19.5, 21.6, 125.7, 127.0, 128.2, 128.8, 130.2, 130.4, 131.0, 131.2, 131.4, 136.1, 137.4, 138.9, 143.1, 150.5, 164.8, 177.4 ppm. MS $m/z$ 287 [M]$^+$. IR (KBr): $\nu_{max}$ = 1436, 1531, 1588, 1629, 1684 cm$^{-1}$. Anal. Calcd for C$_{20}$H$_{17}$NO: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.76; H, 6.09; N, 4.73.

**49j. 3-(but-2-enylidene)-2-(4-chlorophenyl)-6-methylquinolin-4(3H)-one:**
Pale yellow solid, M. p.: 94-95 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H$ = 1.85 (d, $J$=5.4 Hz, 3H, -CH$_3$), 2.32 (s, 3H, -CH$_3$C$_6$H$_3$), 5.88 (d, 1H, $J$=15.0 Hz, H$_2$), 6.16 (m, 2H, H$_1$), 7.25 (m, 1H, H$_3$), 6.90-7.63 (m, 7H, ArH, aromatic), $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C$ = 19.6, 21.6, 125.8, 127.0, 128.2, 130.4, 130.6, 130.7, 131.3, 131.4, 136.5, 136.8, 137.3, 137.6, 143.1, 150.35, 164.4, 177.5 ppm. MS $m/z$ 321 [M]$^+$. IR (KBr): $\nu_{max}$ = 1436, 1531, 1588, 1629, 1684 cm$^{-1}$. Anal. Calcd for C$_{20}$H$_{16}$ClNO: C, 74.65; H, 5.01; N, 4.35. Found: C, 74.80; H, 5.18; N, 4.20.

**49k. 3-(but-2-enylidene)-2-(4-methoxyphenyl)-6-methylquinolin-4(3H)-one:**
Pale yellow solid, M. p.: 95-96 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H$ = 1.85 (d, $J$=5.4 Hz, 3H, -CH$_3$), 2.32 (s, 3H, -CH$_3$C$_6$H$_3$), 3.83 (s, 3H, -OCH$_3$), 5.85 (d, 1H, $J$ = 15.0 Hz, H$_2$), 6.16 (m, 2H, H$_1$), 7.24 (m, 1H, H$_3$), 6.91-7.62 (m, 7H, ArH, aromatic), $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C$ = 19.6, 21.6, 125.8, 127.0, 128.2, 130.4, 130.6, 130.7, 131.3, 131.4, 136.5, 136.8, 137.3, 137.6, 143.1, 150.35, 164.4, 177.5 ppm. MS $m/z$ 321 [M]$^+$. IR (KBr): $\nu_{max}$ = 1436, 1531, 1588, 1629, 1684 cm$^{-1}$. Anal. Calcd for C$_{20}$H$_{16}$ClNO: C, 74.65; H, 5.01; N, 4.35. Found: C, 74.80; H, 5.18; N, 4.20.
75 MHz): $\delta_C = 19.5, 21.6, 55.6, 114.9, 125.8, 127.1, 128.2, 130.2, 130.4, 131.2, 131.3, 131.4, 136.1, 143.2, 150.6, 162.9, 164.9, 177.5$ ppm. MS $m/z$ 317 $[M]^+$. IR (KBr): $\nu_{max} = 1432, 1530, 1585, 1629, 1684$ cm$^{-1}$. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.72; H, 6.10; N, 4.70.

49l. 3-(but-2-enylidene)-6-methyl-2-p-tolylquinolin-4(3H)-one:
Pale yellow solid, M. p.: 97-98 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H = 1.85$ (d, $J=5.4$ Hz, 3H, -CH$_3$), 2.32 (s, 3H, -CH$_3$C$_6$H$_3$), 2.34 (s, 3H, -CH$_3$C$_6$H$_4$), 5.86 (d, 1H, $J=15.0$ Hz, H$_2$), 6.15 (m, 2H, H$_1$), 7.26 (m, 1H, H$_3$), 6.93-7.62 (m, 7H, ArH, aromatic), $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C = 19.5, 21.4, 21.6, 125.7, 127.2, 128.2, 128.9, 130.3, 130.4, 131.2, 131.4, 135.9, 136.1, 137.4, 140.7, 143.2, 150.5, 164.9, 177.5$ ppm. MS $m/z$ 301 $[M]^+$. IR (KBr): $\nu_{max} = 1434, 1530, 1584, 1629, 1685$ cm$^{-1}$. Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, C, 83.82; H, 6.50; N, 4.48.

General procedure for the synthesis of quinolinones:
The synthesis of substituted quinolinones was realized by slow addition of triflic acid (15mmol) to ice cold 1,2-dichloroethane (20 mL) solution of trans-3-butadienyl-2-azetidinones cycloadducts (10mmol) 54a-i, 56a-f and 58a-c. After completion of the reaction, (monitored through tlc) reaction mixture was washed with water and extracted with dichloroethane. The removal of solvent under reduced pressure resulted in crude product, which was purified through silica gel column chromatography resulted in isolation of compounds 55a-i, 57a-f and 59a-c in excellent yields.

55a. methyl 2-(4-oxo-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)cyclohex-3-ene carboxylate:
White solid, M. p.: 104-105 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H = 2.05$ (m, 4H, H$_{6a,6b,7a,7b}$), 2.78 (m, 1H, H$_8$), 2.90 (dd, $J=1.8$ Hz, 3.0Hz, 1H, H$_2$), 3.15 (ddd, $J=1.8$ Hz, 5.4Hz, 9.6Hz, 1H, H$_3$), 3.64 (s, 3H, -OCH$_3$), 4.66 (d, $J=3.0$ Hz, 1H, H$_1$), 5.60 (ddd, $J=2.7$
Hz, 3.0Hz, 9.6Hz, 1H, H₅), 6.03(ddd, J=2.7 Hz, 5.7Hz, 9.6Hz, 1H, H₄), 6.85-7.48(m, 9H, ArH, aromatic), ¹³C NMR (CDCl₃, 75 MHz): δC = 24.6, 24.9, 36.4, 40.1, 52.2, 52.5, 55.3, 115.3, 115.9, 117.0, 125.6, 125.9, 128.1, 128.5, 129.6, 130.3, 133.9, 140.5, 151.5, 173.8, 182.4 ppm. MS m/z 361 [M]+. IR (KBr): νmax = 1492, 1635, 1653, 1700, 1771, 3454 cm⁻¹.
Anal. Calcd for C₂₃H₂₃NO₃: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.67; H, 6.62; N, 3.70.

55b. methyl 2-(2-(4-chlorophenyl)-4-oxo-1,2,3,4-tetrahydroquinolin-3-yl)cyclohex-3-enecarboxylate:
White solid, M. p.: 107-108 °C. ¹H NMR (CDCl₃, 300 MHz): δH = 2.06(m, 4H, H₆a,6b,7a,7b), 2.77(m, 1H, H₈), 2.92(dd, J=1.8Hz, 3.0Hz, 1H, H₂), 3.14(ddd, J=1.8 Hz, 5.4Hz, 9.6Hz, 1H, H₃), 3.66(s, 3H, -OCH₃), 4.68(d, J=3.0 Hz, 1H, H₁), 5.61(ddd, J=2.7 Hz, 3.0Hz, 9.6Hz, 1H, H₄), 6.05(ddd, J=2.7 Hz, 5.7Hz, 9.6Hz, 1H, H₅), 6.80-7.48(m, 8H, ArH, aromatic), ¹³C NMR (CDCl₃, 75 MHz): δC = 24.7, 24.9, 36.3, 40.2, 52.1, 52.4, 55.2, 115.3, 115.9, 117.1, 125.7, 128.1, 128.5, 129.5, 130.2, 130.6, 133.9, 139.1, 151.3, 173.6, 182.3 ppm. MS m/z 395 [M]+. IR (KBr): νmax = 1491, 1634, 1652, 1702, 1770, 3450 cm⁻¹.
Anal. Calcd for C₂₃H₂₂ClNO₃: C, 69.78; H, 5.60; N, 3.54. Found: C, 69.91; H, 5.80; N, 3.44.

55c. methyl 2-(2-(4-methoxyphenyl)-4-oxo-1,2,3,4-tetrahydroquinolin-3-yl)cyclohex-3-enecarboxylate:
White solid, M. p.: 110-112 °C. ¹H NMR (CDCl₃, 300 MHz): δH = 2.03(m, 4H, H₆a,6b,7a,7b), 2.77(m, 1H, H₈), 2.89(dd, J=1.8Hz, 3.0Hz, 1H, H₂), 3.14(ddd, J=1.8 Hz, 5.4Hz, 9.6Hz, 1H, H₃), 3.63(s, 3H, -OCH₃), 3.82(s, 3H, -OCH₃C₆H₄), 4.65(d, J=3.0 Hz, 1H, H₁), 5.61(ddd, J=2.7 Hz, 3.0Hz, 9.6Hz, 1H, H₄), 6.02(ddd, J=2.7 Hz, 5.7Hz, 9.6Hz, 1H, H₅), 6.83-7.48(m, 8H, ArH, aromatic), ¹³C NMR (CDCl₃, 75 MHz): δC = 24.5, 24.8, 36.3, 40.2, 52.1, 52.6, 55.2, 55.6, 114.2, 115.2, 115.9, 117.1, 125.5, 127.9, 129.5, 130.2, 132.3, 133.9, 151.6, 156.5, 173.7, 182.2 ppm. MS m/z 391 [M]+. IR (KBr): νmax = 1490,
55d. 2-(4-oxo-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)cyclohex-3-enecarboxylic acid:

White solid, M. p.: 106-107 °C. \[^1^H\text{NMR (CDCl}_3\text{, 300 MHz)}: \delta_H = 2.12(m, 4H, H_{6a,6b,7a,7b}), 2.85(m, 1H, H_8), 2.91(dd, J=1.8Hz, 3.0Hz, 1H, H_2), 3.18(ddd, J=1.8 Hz, 5.4Hz, 9.6Hz, 1H, H_3), 4.64(d, J=3.0 Hz, 1H, H_1), 5.62(ddd, J=2.7 Hz, 3.0Hz, 9.6Hz, 1H, H_5), 6.02(ddd, J=2.7 Hz, 5.7Hz, 9.6Hz, 1H, H_4), 6.85-7.48(m, 9H, ArH, aromatic), \[^{13}\text{C NMR (CDCl}_3\text{, 75 MHz)}: \delta_C = 24.2, 24.7, 36.1, 42.7, 52.3, 55.2, 115.1, 115.7, 117.2, 125.3, 125.6, 128.0, 128.4, 129.5, 130.2, 133.9, 140.4, 151.6, 177.9, 182.4 ppm. MS \text{m/z} 347 [M]^+. IR (KBr): \nu_{\text{max}} = 1422, 1534, 1640, 1680, 1734, 3444 cm\textsuperscript{-1}. Anal. Calcd for C\textsubscript{24}H\textsubscript{25}NO\textsubscript{4}: C, 73.64; H, 6.44; N, 3.58. Found: C, 73.80; H, 6.61; N, 3.42.

55e. 2-(2-(4-chlorophenyl)-4-oxo-1,2,3,4-tetrahydroquinolin-3-yl)cyclohex-3-enecarboxylic acid:

White solid, M. p.: 109-110 °C. \[^1^H\text{NMR (CDCl}_3\text{, 300 MHz)}: \delta_H = 2.11(m, 4H, H_{6a,6b,7a,7b}), 2.86(m, 1H, H_8), 2.90(dd, J=1.8Hz, 3.0Hz, 1H, H_2), 3.17(ddd, J=1.8 Hz, 5.4Hz, 9.6Hz, 1H, H_3), 4.63(d, J=3.0 Hz, 1H, H_1), 5.63(ddd, J=2.7 Hz, 3.0Hz, 9.6Hz, 1H, H_5), 6.03(ddd, J=2.7 Hz, 5.7Hz, 9.6Hz, 1H, H_4), 6.80-7.48(m, 8H, ArH, aromatic), \[^{13}\text{C NMR (CDCl}_3\text{, 75 MHz)}: \delta_C = 24.1, 24.6, 36.2, 42.6, 52.4, 55.1, 115.3, 115.9, 117.1, 125.7, 128.1, 128.5, 129.5, 130.2, 130.6, 133.9, 139.1, 151.3, 177.6, 182.2 ppm. MS \text{m/z} 381 [M]^+. IR (KBr): \nu_{\text{max}} = 1423, 1536, 1642, 1685, 1732, 3442 cm\textsuperscript{-1}. Anal. Calcd for C\textsubscript{22}H\textsubscript{21}ClNO\textsubscript{3}: C, 69.20; H, 5.28; N, 3.67. Found: C, 69.38; H, 5.42; N, 3.50.
55f. 2-(2-(4-methoxyphenyl)-4-oxo-1,2,3,4-tetrahydroquinolin-3-yl)cyclohex-3-enecarboxylic acid:

White solid, M. p.: 105-106 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 2.13\)(m, 4H, H\(_{6a,6b,7a,7b}\)), 2.86(m, 1H, H\(_8\)), 2.90(dd, \(J=1.8\) Hz, 3.0Hz, 1H, H\(_2\)), 3.17(ddd, \(J=1.8\) Hz, 5.4Hz, 9.6Hz, 1H, H\(_3\)), 3.86(s, 1H, -OCH\(_3\)), 4.63(d, \(J=3.0\) Hz, 1H, H\(_1\)), 5.62(ddd, \(J=2.7\) Hz, 3.0Hz, 9.6Hz, 1H, H\(_5\)), 6.03(ddd, \(J=2.7\) Hz, 5.7Hz, 9.6Hz, 1H, H\(_4\)), 6.83-7.48(m, 8H, ArH, aromatic), \(^1^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 24.1, 24.9, 36.3, 42.6, 52.1, 55.2, 55.6, 114.3, 115.1, 115.9, 117.2, 125.6, 127.8, 129.5, 130.3, 132.1, 133.9, 151.7, 156.5, 177.9, 182.3\) ppm. MS \(m/z 377 [M]^+\). IR (KBr): \(\nu_{max} = 1424, 1537, 1641, 1688, 1735, 3444\) cm\(^{-1}\). Anal. Calcd for C\(_{23}\)H\(_{23}\)NO\(_4\): C, 73.19; H, 6.14; N, 3.71. Found: C, 73.36; H, 6.33; N, 3.58.

55g. 2-(4-oxo-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)cyclohex-3-enecarboxamide:

White solid, M. p.: 104-105 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 2.08\)(m, 4H, H\(_{6a,6b,7a,7b}\)), 2.76(m, 1H, H\(_8\)), 2.92(dd, \(J=1.8\) Hz, 3.0Hz, 1H, H\(_2\)), 3.16(ddd, \(J=1.8\) Hz, 5.4Hz, 9.6Hz, 1H, H\(_3\)), 4.64(d, \(J=3.0\) Hz, 1H, H\(_1\)), 5.64(ddd, \(J=2.7\) Hz, 3.0Hz, 9.6Hz, 1H, H\(_5\)), 6.03(ddd, \(J=2.7\) Hz, 5.7Hz, 9.6Hz, 1H, H\(_4\)), 6.84-7.48(m, 9H, ArH, aromatic), \(^1^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 24.2, 24.7, 36.2, 47.4, 52.4, 55.3, 115.2, 115.7, 117.3, 125.4, 125.8, 128.2, 128.5, 129.7, 130.2, 133.9, 140.3, 151.5, 175.6, 182.3\) ppm. MS \(m/z 346 [M]^+\). IR (KBr): \(\nu_{max} = 1435, 1537, 1654, 1690, 1744, 3442\) cm\(^{-1}\). Anal. Calcd for C\(_{22}\)H\(_{22}\)N\(_2\)O\(_2\): C, 76.28; H, 6.40; N, 8.09. Found: C, 76.45; H, 6.57; N, 8.00.

55h. 2-(2-(4-chlorophenyl)-4-oxo-1,2,3,4-tetrahydroquinolin-3-yl)cyclohex-3-enecarboxamide:

White solid, M. p.: 110-111 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 2.08\)(m, 4H, H\(_{6a,6b,7a,7b}\)), 2.83(m, 1H, H\(_8\)), 2.92(dd, \(J=1.8\) Hz, 3.0Hz, 1H, H\(_2\)), 3.17(ddd, \(J=1.8\) Hz, 5.4Hz, 9.6Hz, 1H, H\(_3\)), 4.62(d, \(J=3.0\) Hz, 1H, H\(_1\)), 5.64(ddd, \(J=2.7\) Hz, 3.0Hz, 9.6Hz, 1H, H\(_5\)), 6.02(ddd, \(J=2.7\) Hz, 5.7Hz, 9.6Hz, 1H, H\(_4\)), 6.80-7.48(m, 8H, ArH, aromatic), \(^1^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 24.1, 24.6, 36.2, 47.6, 52.4, 55.2, 115.3, 115.9, 117.2, 117.3, 125.4, 125.8, 128.2, 128.5, 129.7, 130.2, 133.9, 140.3, 151.5, 175.6, 182.3\) ppm. MS \(m/z 346 [M]^+\). IR (KBr): \(\nu_{max} = 1435, 1537, 1641, 1688, 1735, 3444\) cm\(^{-1}\). Anal. Calcd for C\(_{22}\)H\(_{22}\)N\(_2\)O\(_2\): C, 76.28; H, 6.40; N, 8.09. Found: C, 76.45; H, 6.57; N, 8.00.
125.7, 128.0, 128.5, 129.7, 130.3, 130.6, 133.9, 139.2, 151.3, 175.4, 182.3 ppm. MS m/z 380 [M]+. IR (KBr): $\nu_{\text{max}} = 1436, 1536, 1655, 1692, 1745, 3441 \text{ cm}^{-1}$. Anal. Calcd for C$_{22}$H$_{21}$ClN$_2$O$_2$: C, 69.38; H, 5.56; N, 7.36. Found: C, 69.47; H, 5.71; N, 7.22.

55i. **2-(2-(4-methoxyphenyl)-4-oxo-1,2,3,4-tetrahydroquinolin-3-yl)cyclohex-3-ene carboxamide:**

White solid, M. p.: 109-110 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H = 2.07$(m, 4H, H$_{6a,6b,7a,7b}$), 2.84(m, 1H, H$_8$), 2.91(dd, $J=1.8$ Hz, 3.0Hz, 1H, H$_2$), 3.16(ddd, $J=1.8$ Hz, 5.4Hz, 9.6Hz, 1H, H$_3$), 3.85(s, 1H, -OCH$_3$), 4.62(d, $J=3.0$ Hz, 1H, H$_1$), 5.63(ddd, $J=2.7$ Hz, 3.0Hz, 9.6Hz, 1H, H$_5$), 6.03(ddd, $J=2.7$ Hz, 5.7Hz, 9.6Hz, 1H, H$_4$), 6.83-7.48(m, 8H, ArH, aromatic), $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C = 24.2, 24.7, 36.2, 47.5, 52.2, 55.3, 55.5, 114.2, 115.2, 115.9, 125.6, 127.8, 129.6, 130.2, 132.2, 133.9, 151.7, 156.5, 175.5, 182.1 ppm. MS m/z 376 [M]+. IR (KBr): $\nu_{\text{max}} = 1435, 1535, 1655, 1691, 1746, 3440 \text{ cm}^{-1}$. Anal. Calcd for C$_{23}$H$_{24}$N$_2$O$_3$: C, 73.38; H, 6.43; N, 7.44. Found: C, 73.54; H, 6.59; N, 7.29.

57a. **4-(4-oxo-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione:**

White solid, M. p.: 194-196 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H = 2.01$(m, 1H, H$_{6b}$), 2.30(m, 1H, H$_{6a}$), 2.89(dd, $J=4.5$ Hz, 14.9Hz, 1H, H$_2$), 3.21(ddd, $J=1.5$ Hz, 5.7Hz, 14.9Hz, 1H, H$_3$), 3.36(dd, $J=5.7$ Hz, 8.7Hz, 1H, H$_8$), 3.68(m, $J=2.7$ Hz, 3.0 Hz, 8.7Hz, 1H, H$_7$), 4.65(d, $J=4.5$ Hz, 1H, H$_1$), 6.01(m, 1H, H$_5$), 6.03(m, 1H, H$_4$), 6.80-7.42(m, 9H, ArH, aromatic), $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C = 25.6, 33.4, 42.6, 43.7, 52.5, 55.4, 115.3, 115.9, 117.0, 125.2, 125.9, 128.1, 128.5, 128.7, 129.6, 133.9, 140.5, 151.5, 170.7, 173.2, 183.2 ppm. MS m/z 373 [M]+. IR (KBr): $\nu_{\text{max}} = 1560, 1636, 1654, 1700, 1771, 3446 \text{ cm}^{-1}$. Anal. Calcd for C$_{23}$H$_{19}$NO$_4$: C, 73.98; H, 5.13; N, 3.75. Found: C, 73.10; H, 5.28; N, 3.61.
57b. 4-(2-(4-chlorophenyl)-4-oxo-1,2,3,4-tetrahydroquinolin-3-yl)-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione:
White solid, M. p.: 196-197 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 2.02\) (m, 1H, H\(_{6b}\)), 2.31 (m, 1H, H\(_{6a}\)), 2.90 (dd, \(J = 4.5\) Hz, 14.6 Hz, 1H, H\(_2\)), 3.21 (ddd, \(J = 1.5\) Hz, 5.7 Hz, 14.6 Hz, 1H, H\(_3\)), 3.35 (dd, \(J = 5.7\) Hz, 8.7 Hz, 1H, H\(_8\)), 3.67 (m, \(J = 2.7\) Hz, 3.0 Hz, 8.7 Hz, 1H, H\(_7\)), 4.66 (d, \(J = 4.5\) Hz, 1H, H\(_1\)), 6.01 (m, 1H, H\(_4\)), 6.03 (m, 1H, H\(_4\)), 6.79-7.40 (m, 8H, ArH, aromatic). \(^1^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 25.6, 33.2, 42.5, 43.5, 52.6, 55.3, 115.2, 115.9, 117.1, 125.2, 128.3, 128.6, 128.7, 129.6, 131.3, 133.9, 138.2, 151.6, 170.3, 173.2, 183.4 ppm. MS \(m/z\) 407 \([M]^+\). IR (KBr): \(v_{\text{max}} = 1562, 1632, 1655, 1702, 1773, 3444\) cm\(^{-1}\). Anal. Calcd for C\(_{23}\)H\(_{18}\)ClNO\(_4\): C, 67.73; H, 4.45; N, 3.43. Found: C, 67.89; H, 4.59; N, 3.30.

57c. 4-(2-(4-methoxyphenyl)-4-oxo-1,2,3,4-tetrahydroquinolin-3-yl)-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione:
White solid, M. p.: 190-192 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 2.01\) (m, 1H, H\(_{6b}\)), 2.31 (m, 1H, H\(_{6a}\)), 2.88 (dd, \(J = 4.5\) Hz, 14.9 Hz, 1H, H\(_2\)), 3.22 (ddd, \(J = 1.5\) Hz, 5.7 Hz, 14.9 Hz, 1H, H\(_3\)), 3.35 (dd, \(J = 5.7\) Hz, 8.7 Hz, 1H, H\(_8\)), 3.67 (m, \(J = 2.7\) Hz, 3.0 Hz, 8.7 Hz, 1H, H\(_7\)), 3.81 (s, 3H, -OCH\(_3\)), 4.66 (d, \(J = 4.5\) Hz, 1H, H\(_1\)), 6.02 (m, 1H, H\(_4\)), 6.04 (m, 1H, H\(_4\)), 6.81-7.43 (m, 8H, ArH, aromatic). \(^1^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 25.5, 33.2, 42.6, 43.6, 52.3, 55.3, 55.7, 114.0, 115.2, 115.9, 117.1, 125.3, 127.5, 128.1, 129.6, 132.6, 133.9, 151.3, 157.2, 170.8, 173.1, 183.3 ppm. MS \(m/z\) 403 \([M]^+\). IR (KBr): \(v_{\text{max}} = 1562, 1632, 1656, 1702, 1773, 3444\) cm\(^{-1}\). Anal. Calcd for C\(_{24}\)H\(_{21}\)NO\(_5\): C, 71.45; H, 5.25; N, 3.47. Found: C, 71.59; H, 5.40; N, 3.32.

57d. 4-(4-oxo-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-phenyl-3a,4,7,7a-tetrahydro-1\(H\)-isoindole-1,3(2\(H\))-dione:
White solid, M. p.: 189-190 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 2.10\) (m, 1H, H\(_{6b}\)), 2.36 (m, 1H, H\(_{6a}\)), 2.91 (dd, \(J = 4.2\) Hz, 14.6 Hz, 1H, H\(_2\)), 3.23 (ddd, \(J = 1.5\) Hz, 5.4 Hz, 14.6 Hz, 1H, H\(_3\)), 3.40 (dd, \(J = 5.4\) Hz, 8.7 Hz, 1H, H\(_8\)), 3.70 (m, \(J = 2.7\) Hz, 3.0 Hz, 8.7 Hz,
1H, H₇), 4.66(d, J=4.2Hz, 1H, H₁), 6.03(m, 1H, H₃), 6.05(m, 1H, H₄), 6.82-7.42(m, 14H, ArH, aromatic), ¹³C NMR (CDCl₃, 75 MHz): δC = 25.6, 34.3, 39.5, 47.6, 52.5, 55.4, 115.3, 115.9, 117.0, 125.2, 125.9, 128.0, 128.1, 128.2, 128.5, 128.7, 128.9, 129.6, 131.9, 133.9, 140.5, 151.5, 176.8, 177.8, 183.5 ppm. MS m/z 448 [M⁺]. IR (KBr): vmax = 1562, 1635, 1658, 1705, 1773, 3440 cm⁻¹. Anal. Calcd for C₂₉H₂₄N₂O₃: C, 77.66; H, 5.39; N, 6.25. Found: C, 77.82; H, 5.54; N, 6.11.

57e. 4-(2-(4-chlorophenyl)-4-oxo-1,2,3,4-tetrahydroquinolin-3-yl)-2-phenyl-3a,4,7,7a-tetrahydro-1H-isindole-1,3(2H)-dione:
White solid, M. p.: 197-198 °C. ¹H NMR (CDCl₃, 300 MHz): δH = 2.11(m, 1H, H₆b), 2.35(m, 1H, H₆a), 2.90(dd, J=4.2Hz, 14.9Hz, 1H, H₂), 3.22(dd, J=1.5 Hz, 5.4Hz, 14.9Hz, 1H, H₃), 3.41(dd, J=5.4 Hz, 8.7Hz, 1H, H₈), 3.71(m, J=2.7Hz, 3.0 Hz, 8.7Hz, 1H, H₇), 4.65(d, J=4.2Hz, 1H, H₁), 6.02(m, 1H, H₅), 6.05(m, 1H, H₄), 6.80-7.43(m, 13H, ArH, aromatic), ¹³C NMR (CDCl₃, 75 MHz): δC = 25.5, 34.2, 39.6, 47.6, 52.4, 55.5, 115.2, 115.9, 117.1, 125.2, 128.0, 128.1, 128.4, 128.6, 128.7, 128.9, 129.6, 131.4, 131.9, 133.9, 138.5, 151.6, 176.7, 177.6, 183.4 ppm. MS m/z 482 [M⁺]. IR (KBr): vmax = 1560, 1633, 1656, 1704, 1772, 3442 cm⁻¹. Anal. Calcd for C₂₉H₂₃ClN₂O₃: C, 72.12; H, 4.80; N, 5.80. Found: C, 72.25; H, 4.93; N, 5.66.

57f. 4-(2-(4-methoxyphenyl)-4-oxo-1,2,3,4-tetrahydroquinolin-3-yl)-2-phenyl-3a,4,7,7a-tetrahydro-1H-isindole-1,3(2H)-dione:
White solid, M. p.: 194-195 °C. ¹H NMR (CDCl₃, 300 MHz): δH = 2.11(m, 1H, H₆b), 2.34(m, 1H, H₆a), 2.90(dd, J=4.2Hz, 14.6Hz, 1H, H₂), 3.22(dd, J=1.5 Hz, 5.4Hz, 14.6Hz, 1H, H₃), 3.41(dd, J=5.4 Hz, 8.7Hz, 1H, H₈), 3.72(m, J=2.7Hz, 3.0 Hz, 8.7Hz, 1H, H₇), 3.82(s, 1H, -OCH₃), 4.65(d, J=4.2Hz, 1H, H₁), 6.02(m, 1H, H₅), 6.05(m, 1H, H₄), 6.84-7.42(m, 13H, ArH, aromatic), ¹³C NMR (CDCl₃, 75 MHz): δC = 25.5, 34.2, 39.6, 47.2, 52.3, 55.3, 55.7, 114.1, 115.3, 115.9, 117.0, 125.2, 127.6, 128.0, 128.2, 128.7, 128.9, 129.6, 131.9, 132.8, 133.9, 151.5, 157.2, 176.7, 177.6, 183.4 ppm. MS m/z 478
[M]⁺. IR (KBr): v<sub>max</sub> = 1560, 1634, 1659, 1704, 1772, 3443 cm⁻¹. Anal. Calcd for C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.48; H, 5.60; N, 5.72.

59a. 2-phenyl-3-(2-phenyl-3,6-dihydro-2H-1,2-oxazin-6-yl)-2,3-dihydroquinolin-4(1H)-one:
White solid, M. p.: 183-184 °C. ¹H NMR (CDCl<sub>3</sub>, 300 MHz): δ<sub>H</sub> = 3.72(dd, J=3.3Hz, 10.2Hz, H<sub>2</sub>), 3.85(dABq, J=2.1Hz, 2.4Hz, 16.2Hz, 2H, H<sub>6a,6b</sub>), 4.52(dd, J=1.5Hz, 10.2Hz, 1H, H<sub>3</sub>), 4.63(d, J=3.3Hz, 1H, H<sub>1</sub>), 6.01(m, 2H, H<sub>4,5</sub>), 6.70-7.51(m, 14H, ArH, aromatic), ¹³C NMR (CDCl<sub>3</sub>, 75 MHz): δ<sub>C</sub> = 48.5, 56.2, 57.1, 64.6, 115.3, 115.9, 116.6, 117.0, 126.0, 126.5, 126.6, 127.1, 127.5, 128.1, 128.8, 129.6, 133.9, 139.6, 150.0, 151.5, 183.5 ppm. MS m/z 382 [M]<sup>+</sup>. IR (KBr): v<sub>max</sub> = 1460, 1498, 1538, 1624, 1655, 1680, 3436 cm⁻¹. Anal. Calcd for C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 78.51; H, 5.80; N, 7.32. Found: C, 78.69; H, 5.96; N, 7.20.

59b. 2-(4-chlorophenyl)-3-(2-phenyl-3,6-dihydro-2H-1,2-oxazin-6-yl)-2,3-dihydroquinolin-4(1H)-one:
White solid, M. p.: 186-187 °C. ¹H NMR (CDCl<sub>3</sub>, 300 MHz): δ<sub>H</sub> = 3.71(dd, J=3.3Hz, 10.2Hz, H<sub>2</sub>), 3.83(dABq, J=2.1Hz, 2.4Hz, 16.2Hz, 2H, H<sub>6a,6b</sub>), 4.51(dd, J=1.5Hz, 10.2Hz, 1H, H<sub>3</sub>), 4.62(d, J=3.3Hz, 1H, H<sub>1</sub>), 6.00(m, 2H, H<sub>4,5</sub>), 6.68-7.50(m, 13H, ArH, aromatic), ¹³C NMR (CDCl<sub>3</sub>, 75 MHz): δ<sub>C</sub> = 48.6, 56.2, 57.2, 64.7, 115.2, 115.9, 116.7, 117.01, 126.5, 126.6, 127.2, 127.5, 128.7, 128.9, 129.6, 131.5, 133.9, 138.8, 150.1, 151.7, 183.4 ppm. MS m/z 416 [M]<sup>+</sup>. IR (KBr): v<sub>max</sub> = 1462, 1497, 1536, 1623, 1656, 1684, 3440 cm⁻¹. Anal. Calcd for C<sub>25</sub>H<sub>22</sub>ClN<sub>2</sub>O<sub>2</sub>: C, 72.02; H, 5.08; N, 6.72. Found: C, 72.18; H, 5.22; N, 6.61.
59c. 2-(4-methoxyphenyl)-3-(2-phenyl-3,6-dihydro-2H-1,2-oxazin-6-yl)-2,3-dihydroquinolin-4(1H)-one:
White solid, M. p.: 188-189 °C. 1H NMR (CDCl$_3$, 300 MHz): $\delta_H = 3.74$ (dd, $J=3.3$Hz, 10.2Hz, H$_2$), 3.82 (s, 3H, -OCH$_3$), 3.84 (dABq, $J=2.1$Hz, 2.4Hz, 16.2Hz, 2H, H$_{6a,6b}$), 4.51 (dd, $J=1.5$Hz, 10.2Hz, 1H, H$_3$), 4.64 (d, $J=3.3$Hz, 1H, H$_1$), 6.01 (m, 2H, H$_{4,5}$), 6.74-7.50 (m, 13H, ArH, aromatic). 13C NMR (CDCl$_3$, 75 MHz): $\delta_C = 48.6$, 55.2, 56.3, 57.2, 64.5, 114.5, 115.3, 115.9, 116.6, 117.0, 126.5, 126.6, 127.1, 127.5, 127.8, 129.6, 132.8, 133.7, 150.2, 151.5, 157.7, 183.2 ppm. MS m/z 412 [M$^+$]. IR (KBr): $\nu_{max} = 1462$, 1496, 1537, 1622, 1658, 1683, 3438 cm$^{-1}$. Anal. Calcd for C$_{26}$H$_{24}$N$_2$O$_3$: C, 75.71; H, 5.86; N, 6.79. Found: C, 75.88; H, 5.98; N, 6.65.

General procedure for the synthesis of benzo[b]azocinones:
The synthesis of substituted dihydrobenzo[b]azocin-6(5H)-ones 61 was realized by slow addition of triflic acid (15mmol) to 1,2-dichloroethane(20 mL) solution of sorbyl anilides 60(10mmol). After completion of the reaction, (monitored through tlc) reaction mixture was washed with water and extracted with dichloroethane. The removal of solvent under reduced pressure resulted in crude product, which was purified through silica gel column chromatography resulted in isolation of compounds 61a-j in excellent yields.

61a. 2,8-dimethyl-1,2-dihydrobenzo[b]azocin-6(5H)-one:
White solid, M. p.: 109-110 °C. 1H NMR (CDCl$_3$, 300 MHz): $\delta_H = 1.73$ (d, 3H, $J=4.2$Hz, -CH$_3$), 2.29 (s, 3H, -CH$_3$C$_6$H$_3$), 2.62 (dABq, $J=6.3$Hz, 7.8Hz, 16.2Hz, 2H, H$_{4a,4b}$), 3.57 (q, $J=6.3$Hz, 1H, H$_1$), 5.49 (m, 2H, H$_{2,3}$), 6.68 (d, $J=7.8$Hz, 1H, H$_8$), 6.97-7.01 (m, 2H, $J=7.8$Hz, H$_{5,7}$). 13C NMR (CDCl$_3$, 75 MHz): $\delta_C = 17.8$, 20.8, 36.9, 39.4, 115.3, 126.3, 127.3, 128.1, 128.3, 130.7, 132.8, 134.0, 170.6 ppm. MS m/z 201 [M$^+$]. IR (KBr): $\nu_{max} = 1378$, 1505, 1558, 1680, 3208 cm$^{-1}$. Anal. Calcd for C$_{13}$H$_{15}$NO: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.71; H, 7.66; N, 6.82.
61b. 2-methyl-1,2-dihydrobenzo[b]azocin-6(5H)-one:
White solid, M. p.: 100-101 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H = 1.73$(d, 3H, $J=4.2$Hz, -CH$_3$), 2.61(dABq, $J=6.3$Hz, 7.8Hz, 16.2Hz, 2H, H$_{4a,4b}$), 3.57(q, $J=6.0$Hz, 1H, H$_1$), 5.48(m, 2H, H$_{2,3}$), 6.82(d, $J=7.8$Hz, 1H, H$_8$), 7.01(t, $J=7.5$Hz, 1H, H$_6$), 7.16-7.33(m, 2H, $J=7.8$Hz, H$_{5,7}$). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C = 20.9, 36.8, 39.5, 115.4, 126.3, 127.3, 128.1, 128.3, 130.7, 132.8, 134.0, 170.7$ ppm. MS $m/z$ 187 [M$^+$]. IR (KBr): $v_{max} = 1379, 1504, 1558, 1680, 3209$ cm$^{-1}$. Anal. Calcd for C$_{12}$H$_{13}$NO: C, 76.98; H, 7.00; N, 7.48. Found: C, 77.12; H, 7.16; N, 7.31.

61c. 8-chloro-2-methyl-1,2-dihydrobenzo[b]azocin-6(5H)-one
White solid, M. p.: 110-111 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H = 1.73$(d, 3H, $J=4.2$Hz, -CH$_3$), 2.63(dABq, $J=6.3$Hz, 7.8Hz, 16.2Hz, 2H, H$_{4a,4b}$), 3.59(q, $J=6.3$Hz, 1H, H$_1$), 5.48(m, 2H, H$_{2,3}$), 6.65(d, $J=7.8$Hz, 1H, H$_8$), 6.97-7.00(m, 2H, $J=7.8$Hz, H$_{5,7}$). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C = 20.8, 36.9, 39.4, 115.2, 126.3, 127.4, 128.3, 130.7, 130.8, 132.7, 134.2, 170.5$ ppm. MS $m/z$ 221 [M$^+$]. IR (KBr): $v_{max} = 1377, 1504, 1559, 1681, 3206$ cm$^{-1}$. Anal. Calcd for C$_{12}$H$_{12}$ClNO: C, 65.02; H, 5.46; N, 6.32. Found: C, 65.18; H, 5.62; N, 6.20.

61d. 8-methoxy-2-methyl-1,2-dihydrobenzo[b]azocin-6(5H)-one:
White solid, M. p.: 102-103 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta_H = 1.72$(d, 3H, $J=4.2$Hz, -CH$_3$), 2.63(dABq, $J=6.3$Hz, 7.8Hz, 16.2Hz, 2H, H$_{4a,4b}$), 3.56(q, $J=6.0$Hz, 1H, H$_1$), 5.48(m, 2H, H$_{2,3}$), 6.68(d, $J=7.8$Hz, 1H, H$_8$), 6.96-7.01(m, 2H, $J=7.8$Hz, H$_{5,7}$). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta_C = 20.9, 36.7, 39.6, 55.4, 114.3, 115.3, 126.5, 127.5, 128.5, 130.3, 132.9, 134.2, 170.6$ ppm. MS $m/z$ 217 [M$^+$]. IR (KBr): $v_{max} = 1378, 1503, 1558, 1681, 3210$ cm$^{-1}$. Anal. Calcd for C$_{13}$H$_{15}$NO$_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.99; H, 7.10; N, 6.32.
61e. 2,10-dimethyl-1,2-dihydrobenzo[b]azocin-6(5H)-one:
White solid, M. p.: 104-105 °C. \(^1\)H NMR (CDCl₃, 300 MHz): \(\delta_H = 1.72\) (d, 3H, \(J=4.2\) Hz, -CH₃), 2.15 (s, 3H, -CH₃CH₃), 2.61 (d ABq, \(J=6.3\) Hz, 7.8 Hz, 16.2 Hz, 2H, H₄a,₄b), 3.58 (q, \(J=6.3\) Hz, 1H, H₁), 5.48 (m, 2H, H₂, H₃), 6.64 (t, \(J=7.5\) Hz, 1H, H₅), 6.99-7.01 (m, 2H, J₅,₇). \(^{13}\)C NMR (CDCl₃, 75 MHz): \(\delta_C = 17.6\), 20.7, 36.9, 39.7, 115.2, 126.4, 127.2, 128.1, 128.3, 130.5, 132.7, 134.1, 170.5 ppm. MS \(m/z\) 201 [M]. IR (KBr): \(v_{max} = 1377, 1504, 1560, 1682\) cm\(^{-1}\). Anal. Calcd for C₁₃H₁₅NO: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.70; H, 7.64; N, 6.86.

61f. 10-chloro-2-methyl-1,2-dihydrobenzo[b]azocin-6(5H)-one:
White solid, M. p.: 106-107 °C. \(^1\)H NMR (CDCl₃, 300 MHz): \(\delta_H = 1.73\) (d, 3H, \(J=4.2\) Hz, -CH₃), 2.61 (d ABq, \(J=6.3\) Hz, 7.8 Hz, 16.2 Hz, 2H, H₄a,₄b), 3.59 (q, \(J=6.3\) Hz, 1H, H₁), 5.46 (m, 2H, H₂, H₃), 6.63 (t, \(J=7.5\) Hz, 1H, H₆), 6.96-7.01 (m, 2H, J₆,₇). \(^{13}\)C NMR (CDCl₃, 75 MHz): \(\delta_C = 20.6\), 36.8, 39.6, 115.3, 126.6, 127.7, 128.3, 130.5, 131.4, 132.6, 134.2, 170.7 ppm. MS \(m/z\) 221 [M]. IR (KBr): \(v_{max} = 1376, 1505, 1559, 1682\) cm\(^{-1}\). Anal. Calcd for C₁₂H₁₂ClNO: C, 65.02; H, 5.46; N, 6.32. Found: C, 65.20; H, 5.60; N, 6.22.

61g. 10-methoxy-2-methyl-1,2-dihydrobenzo[b]azocin-6(5H)-one:
White solid, M. p.: 102-103 °C. \(^1\)H NMR (CDCl₃, 300 MHz): \(\delta_H = 1.73\) (d, 3H, \(J=4.2\) Hz, -CH₃), 2.62 (d ABq, \(J=6.3\) Hz, 7.8 Hz, 16.2 Hz, 2H, H₄a,₄b), 3.57 (q, \(J=6.0\) Hz, 1H, H₁), 3.83 (s, 3H, -OCH₃), 5.46 (m, 2H, H₂, H₃), 6.65 (t, \(J=7.5\) Hz, 1H, H₆), 6.96-7.01 (m, 2H, J₆,₇). \(^{13}\)C NMR (CDCl₃, 75 MHz): \(\delta_C = 20.6\), 36.7, 39.6, 55.4, 114.2, 115.5, 126.6, 127.7, 128.5, 130.2, 132.9, 134.4, 170.4 ppm. MS \(m/z\) 217 [M]. IR (KBr): \(v_{max} = 1378, 1503, 1559, 1683\) cm\(^{-1}\). Anal. Calcd for C₁₃H₁₅NO₂: C, 71.87; H, 6.96; N, 6.45. Found: C, 72.01; H, 7.06; N, 6.30.
61h. 2,8-dimethyl-1,2-dihydrobenzo[b]azocin-6(5H)-one:
White solid, M. p.: 106-107 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 1.72\) (d, 3H, \(J=4.2\) Hz, -CH\(_3\)), 2.30 (s, 3H, -CH\(_3\)C\(_6\)H\(_5\)), 2.62 (dABq, \(J=6.3\) Hz, 7.8 Hz, 16.2 Hz, 2H, H\(_{4a,4b}\)), 3.58 (q, \(J=6.3\) Hz, 1H, H\(_1\)), 5.48 (m, 2H, H\(_{2,3}\)), 6.64 (q, \(J=7.5\) Hz, 1H, H\(_8\)), 6.68 (d, \(J=7.5\) Hz, 1H, H\(_5\)), 7.08 (m, 1H, \(J=7.5\) Hz, H\(_6\)). \(^1^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 19.5, 20.8, 36.8, 39.5, 115.2, 126.2, 127.1, 128.2, 128.4, 130.6, 132.9, 134.1, 170.5\) ppm. MS \(m/z\) 201 [\(M^+\)]. IR (KBr): \(v_{max} = 1376, 1503, 1559, 1682, 3206\) cm\(^{-1}\). Anal. Calcd for C\(_{13}\)H\(_{15}\)NO: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.68; H, 7.68; N, 6.80.

61i. 9-chloro-2-methyl-1,2-dihydrobenzo[b]azocin-6(5H)-one:
White solid, M. p.: 108-109 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 1.73\) (d, 3H, \(J=4.2\) Hz, -CH\(_3\)), 2.62 (dABq, \(J=6.3\) Hz, 7.8 Hz, 16.2 Hz, 2H, H\(_{4a,4b}\)), 3.57 (q, \(J=6.3\) Hz, 1H, H\(_1\)), 5.47 (m, 2H, H\(_{2,3}\)), 6.63 (q, \(J=7.5\) Hz, 1H, H\(_8\)), 6.69 (d, \(J=7.5\) Hz, 1H, H\(_5\)), 7.06 (m, 1H, \(J=7.5\) Hz, H\(_6\)). \(^1^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 20.8, 36.9, 39.6, 115.1, 126.4, 127.4, 128.6, 130.6, 131.4, 132.9, 134.1, 170.6\) ppm. MS \(m/z\) 221 [\(M^+\)]. IR (KBr): \(v_{max} = 1376, 1507, 1560, 1680, 3206\) cm\(^{-1}\). Anal. Calcd for C\(_{12}\)H\(_{12}\)ClNO: C, 65.02; H, 5.46; N, 6.32. Found: C, 65.18; H, 5.62; N, 6.20.

61j. 9-methoxy-2-methyl-1,2-dihydrobenzo[b]azocin-6(5H)-one:
White solid, M. p.: 112-113 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta_H = 1.72\) (d, 3H, \(J=4.2\) Hz, -CH\(_3\)), 2.63 (dABq, \(J=6.3\) Hz, 7.8 Hz, 16.2 Hz, 2H, H\(_{4a,4b}\)), 3.56 (q, \(J=6.3\) Hz, 1H, H\(_1\)), 3.82 (s, 3H, -OCH\(_3\)), 5.48 (m, 2H, H\(_{2,3}\)), 6.62 (q, \(J=7.5\) Hz, 1H, H\(_8\)), 6.70 (d, \(J=7.5\) Hz, 1H, H\(_5\)), 7.08 (m, 1H, \(J=7.5\) Hz, H\(_6\)). \(^1^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta_C = 20.8, 36.9, 39.6, 55.4, 114.2, 118.2, 126.4, 127.4, 130.6, 131.6, 132.9, 134.2, 170.5\) ppm. MS \(m/z\) 217 [\(M^+\)]. IR (KBr): \(v_{max} = 1376, 1504, 1562, 1682, 3210\) cm\(^{-1}\). Anal. Calcd for C\(_{13}\)H\(_{15}\)NO\(_2\): C, 71.87; H, 6.96; N, 6.45. Found: C, 72.06; H, 7.05; N, 6.30.
3.6 Bibliography


