4.1. Introduction:

Aryl substituted 3,4-dihydropyrimidin-2-ones (DHPMs) and their derivatives have been receiving much attention in the recent years owing to their enormous application in the field of drugs and pharmaceuticals.\(^1\) They also exhibit a wide range of biological activities\(^2\) and are extensively used in the pharmaceutical industry as calcium channel blockers, antihypertensive, \(\alpha\)-antagonist, antibacterial, antiviral, antitumour, antiinflammatory and HIV agents.\(^3,4\) DHPMs are generally synthesized by the Biginelli reaction pathway, which involves the one-pot condensation of an aldehyde, \(\beta\)-keto ester and urea or thiourea\(^5\) using acidic catalysts. Several reports are available on the synthesis of DHPMs. In most of the cases, catalysts such as concentrated HCl, BF\(_3\).OEt\(_2\), clays, InCl\(_3\), LaCl\(_3\), lanthanide triflate, H\(_2\)SO\(_4\), ceric ammonium nitrate, Mn(OAc)\(_3\), ion-exchange resin, 1-\(n\)-butyl-3-methylimidazolium tetra fluoroborate, BiCl\(_3\), LiClO\(_4\), InBr\(_3\), FeCl\(_3\), ZrCl\(_4\), Cu(OTf)\(_2\), Bi(OTf)\(_3\), LiBr, ytterbium triflates, NH\(_4\)Cl, MgBr\(_2\) and other reagents have been used for this transformation.\(^6\)\textsuperscript{-25} Homogenous catalyst supported on the solid matrix has also been used for the synthesis of DPHMs.\(^21\) Unfortunately, many of these catalysts suffer from one or more limitations, such as long reaction times, occurrence of several side
reactions, drastic reaction conditions, tedious workup procedure and low yields. In addition, the solid oxide catalyst used previously had poor textural parameters such as low surface area and pore volume, which do not support a better performance in the synthesis of DHPMs. These factors stimulate us to search for a better catalyst, which has to offer a high activity for the synthesis of DHPMs under mild reaction conditions.

Recently, the use of heterogeneous catalysts has received considerable importance in organic synthesis because of their easiness of handling, enhanced reaction rates, better selectivity, easy workup and recoverability of catalysts. Especially, mesoporous heterogenous catalysts have been receiving much attention in the field of organic syntheses and catalysis owing to their excellent textural characteristics and well-ordered mesostructure with uniform pores. Among the mesoporous solid acid catalysts, materials with three-dimensional (3D) mesopore structures are found to be more advantageous than the catalysts with one-dimensional (1D) mesoporous structure as the former can offer more resistant to pore locking and allow faster diffusion of reactants, which are highly necessary to obtain a stable and a high catalytic activity. Dubey et al. reported the synthesis of DHPMs in the liquid phase using SBA-15 impregnated with Aluminium as catalyst, which was prepared by postsynthetic grafting method. As the catalyst was prepared by postsynthesis grafting method, there is a possibility that the Al⁺³
species may be leached out during the reaction. Recently, Vinu et al. reported the direct synthesis of aluminium incorporated mesoporous KIT-5 material (AlKIT-5), which possesses 3D mesostructure with \( Fm3m \) symmetry and a high acidity and a large pore diameter.\(^{39,40}\) Although these materials possess interesting textural and catalytic properties, with the best of our knowledge, there has been no report available on the synthesis of DHPMs using such materials as catalysts in the literature so far. Here, we demonstrate a simple, convenient and efficient method for the synthesis of DHPMs in acetonitrile solvent using AlKIT-5 catalyst through one-pot condensation of aldehyde, \( \beta \)-keto ester and urea/thiourea.

4.2. Present work:

This chapter describes the synthesis of biologically active 3,4-dihydropyrimidin-2-ones (DHPMs) \( \textbf{4} \) through a three component condensation of aldehyde \( \textbf{1} \), \( \beta \)-keto ester \( \textbf{2} \) and urea/thiourea \( \textbf{3} \) using Dichloro Dicyano Quinone (DDQ)\(^{42}\) and mesoporous aluminosilicate (AlKIT-5)\(^{43}\) catalysts in acetonitrile as solvent under reflux conditions.

Initially we performed the Biginelli’s one-pot reaction of benzaldehyde (0.106 g, 1.0 mmol) with ethyl acetoacetate (0.156 g, 1.2 mmol) and urea (0.072 g, 1.2 mmol) using 5 mol% DDQ in acetonitrile under reflux conditions (Scheme 1) and 92% yield achieved and later remaining compounds were synthesized and results are presented in Table 4.3. The proposed plausible reaction mechanism is given in Scheme 2.
Scheme 1: Synthesis of DHPMs using DDQ

Scheme 2: Plausible mechanism for the synthesis of DHPMs using DDQ

We also performed the Biginelli’s one-pot reaction of benzaldehyde (0.106 g, 1.0 mmol) with ethyl acetoacetate (0.156 g, 1.2 mmol) and urea (0.072 g, 1.2 mmol) using AlKIT-5(10) catalyst (150 mg) under reflux in acetonitrile solvent for 3h (Scheme 3).

Scheme 3: Synthesis of DHPMs using AlKIT-5
The AlKIT-5 catalyst was found to be highly active, affording 96% yield of 4a in 3 h. It must be noted that no product was obtained when the reaction was carried out without catalyst.

These results indicate that the acidity of the catalyst plays a critical role in this transformation and dictates the activity of the catalyst. The role of the Brönsted acid site of the AlKIT-5 catalyst on the formation of DHPMs and the reaction mechanism are clearly depicted in Scheme 4. This first step begins with rate determining nucleophilic addition by the urea 3 to the aldehyde 1. The ensuring condensation step is catalyzed by the addition of acid, resulting in the imine nitrogen A (electrophile). The β-ketoester 2 then adds to the imine bond and consequently the ring closed by B by the nucleophilic attack by the amine onto the carbonyl group. This final step ensues a second condensation and results in the Biginelli compound 4.

Scheme 4: Plausible mechanism for the synthesis of DHPMs using AlKIT-5 catalyst
In order to understand the role of acidity of AlKIT-5 on the yield of the final product, we carried out the synthesis of DPHMs using AlKIT-5 with different acidity. The acidity of the materials was controlled by adjustment of the amount of ‘Al’ content in the silica framework of KIT-5. As can be seen in Table 4.1, the acidity of the materials increases with increasing the ‘Al’ content in the silica matrix. Table 4.1 also shows the textural parameters including specific surface area, pore volume and pore diameter of the AlKIT-5 catalysts with different ‘Al’ contents. The specific surface area, pore volume, pore diameter, cage diameter and the acidity of the AlKIT-5(10) are found to be 989 m²/g, 0.68 cm³/g, 6 nm, 12 nm, and 0.51 mmol of NH₃/g, respectively. The detailed characterization results of the materials and their discussion can be found in earlier reports. As expected, the activity of the catalyst increases with increasing the amount of Aluminium content in AlKIT-5, confirming the role of acidity of the catalyst in this transformation. Among the AlKIT-5 catalysts studied, AlKIT-5(10) was found to be highly active, which exhibits better textural parameters and higher acidity than those of other materials used in the study and has been used for the remaining catalytic studies under the optimized reaction conditions. It has been also found that the activity of our catalyst is much better than the reported catalysts such as AlSBA-15, Amberlyst-70 and MCM-41-R-SO₃H. The effect of the catalyst concentration on the synthesis of DHPMs was also investigated over different amounts of AlKIT-5(10) at reflux temperature for 3.0 h and the results are presented in Table
4.2. It has been found that the concentration of the catalyst significantly alters the outcome of the final product. The yield of the final product increases from 40 to 96% with increasing the weight of the catalyst from 50 to 200 mg, respectively. This could be mainly due to the availability of huge number of surface acidic sites in the reactant mixture as the weight of the catalyst is increased.

The synthesis of various DHPMs using several aromatic and aliphatic aldehydes under the optimized conditions was also carried out using AlKIT-5(10) catalyst (150 mg) and results are summarized in Table 4.3. The reaction proceeded very smoothly in refluxing conditions with the AlKIT-5(10) catalyst and all the reactions were almost completed within 3–4 h of reaction time. The catalyst showed an excellent activity in all the cases, showing 80–96% isolated yield of the corresponding derivatives of DHPMs. Another important feature of this procedure is the stability of a variety of functional groups such as ether, hydroxy, halides, nitro, etc., under these reaction conditions. This procedure not only preserves the simplicity of Biginelli reaction but also produces DHPMs in excellent yields. Thus this procedure offers an easy access to substituted DHPMs with a variety of substitution patterns.

The effect of solvents on the synthesis of DPHMs was also investigated. Among various solvents like acetonitrile, methanol, methylene chloride and THF studied, methanol and acetonitrile were found to be the excellent solvents for this transformation. Thiourea
has also been used to obtain the corresponding thio derivatives of dihydropyrimidinones, which were reported to have good biological activities.\textsuperscript{3} Thiophene carboxaldehyde, furfural, cinnamal aldehyde and 3-phenoxy benzaldehyde also worked well to synthesize multifunctionalised DHPMs using AlKIT-5(10).
Table.4.1. Textural parameters, acidity and catalytic activity of the AlKIT-5 catalysts with different Aluminium content and catalytic activity of the DDQ

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Catalyst</th>
<th>a₀ (nm)</th>
<th>n_{Si}/n_{Al}</th>
<th>S_{BET} (m²/g)</th>
<th>Vₚ (cm³/g)</th>
<th>D_{pads, BJH} (nm)</th>
<th>Cage diameter (nm)</th>
<th>Acidity (mmol/g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlKIT-5(10)</td>
<td>18.44</td>
<td>7</td>
<td>10</td>
<td>989</td>
<td>0.68</td>
<td>6.0</td>
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<td>2</td>
<td>AlKIT-5(28)</td>
<td>17.76</td>
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<td>28</td>
<td>815</td>
<td>0.56</td>
<td>5.6</td>
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<td>0.32</td>
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<tr>
<td>3</td>
<td>AlKIT-5(44)</td>
<td>16.97</td>
<td>12</td>
<td>44</td>
<td>713</td>
<td>0.45</td>
<td>5.2</td>
<td>10.3</td>
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<td>4</td>
<td>DDQ (5 mol %)</td>
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</tr>
</tbody>
</table>

a₀ unit cell constant; S_{BET} specific surface area; Vₚ specific pore volume; D_{pads, BJH} pore diameter; Reaction conditions: substrate = OPDA and acetone, weight of the catalyst = 150 mg, reaction temperature = Reflux, solvent = acetonitrile.

Table.4.2. Effect of the weight of AlKIT-5(10) on the synthesis of DHPMs

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Weight of AlKIT-5(10) (mg)</th>
<th>Reaction time (h)</th>
<th>Yield (%)</th>
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<td>96</td>
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<tr>
<td>4</td>
<td>200</td>
<td>3.0</td>
<td>96</td>
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</table>

Reaction conditions: substrate = Aldehydes, β-keto ester, urea/thiourea, reaction temperature = Reflux, solvent = acetonitrile.
**Table 4.3.** Synthesis of dihydropyrimidinones and thio derivatives using DDQ and Mesoporous aluminosilicate (AlKIT-5(10) catalyst)

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<th>Entry</th>
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<th>X</th>
<th>R¹</th>
<th>R²</th>
<th>Product (4)</th>
<th>Time⁷ (h)</th>
<th>Yield⁸ (%)</th>
<th>Time⁹ (h)</th>
<th>Yield¹⁰ (%)</th>
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<td>![Structure 4d]</td>
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- Reaction time for the DHPMs derivatives with DDQ
- Isolated yields for the DHPMs derivatives with DDQ
- Reaction time for the DHPMs derivatives with AlKIT-5
- Isolated yields for the DHPMs derivatives with AlKIT-5
It is also important to note that the workup of the reaction mixture is very simple. The catalyst can be filtered out easily and the solvent was evaporated. Recycling experiments were conducted to find out the stability of the catalyst after the reaction. The catalyst was easily separated by centrifugation and reused after activation at 500°C for 3.0–4.0 h. The efficiency of the recovered catalyst was verified with the Biginelli reaction (entry 1). Using the fresh catalyst, the yield of product (4a) was 96%, while the recovered catalyst in the three subsequent recycling experiments gave the yields of 95, 92 and 90%, respectively. These results reveal that the catalyst can be recycled several times without losing much activity.

Structural assignment of compounds 1-30 (4a-4z & 4a₁-4d₁) were made based on IR, ¹H NMR and MALDI-MS spectral data.

The compound 4a IR spectrum (Fig.4.1) showed absorption peaks at 3240, 3117, 2981, 2880, 1691, 1656, 1600, 1465, 1422, 1291, 1227, 1090, 782 and 699 cm⁻¹. The peak at 3240, 3117 cm⁻¹ indicates the occurrence of –NH stretching in pyridiminone ring, peak at 2981 cm⁻¹ indicates aryl -CH stretching, peak at 2880 cm⁻¹ indicates alkyl -CH stretching, peak at 1691 cm⁻¹ indicates the presences of >C=O-ester stretching, peak at 1656 cm⁻¹ indicates presence of >C=O-stretching in pyrimidinone ring, peak at 1600 cm⁻¹ indicates the presence of –NH bending, peak at 1465 cm⁻¹ indicates the presence of >C=C< conjugated aromatic streching, peak at 1422 cm⁻¹ indicates the presence of isolated >C=C< streching, peak at 1291 cm⁻¹ indicates
the presence of aliphatic –CH bending, peak at 1227 cm\(^{-1}\) indicates >C-O- stretching, peak at 1090 cm\(^{-1}\) indicates >C-N- stretching, peak at 782 cm\(^{-1}\) assigns the aromatic -CH bending, peak at 699 cm\(^{-1}\) assigns the aromatic -CH bending and these peaks are confirmed the formation of pyrimidinone ring.

The \(^1\)H NMR (300 Hz, DMSO-d\(_6\)) for compound \(4a\) (Fig.4.2) showed the signals at \(\delta\) 1.15 (t, \(J = 7.1\) Hz, 3H, -OCH\(_2\)CH\(_3\)), which is a triplet assigned to methyl group. The signal at \(\delta\) 2.25 (s, 3H, -CH\(_3\)) was a singlet of three protons of -CH\(_3\) group at 6\(^{th}\) position, signal at \(\delta\) 3.96 (q, 2H, -OCH\(_2\)-CH\(_3\)) a quartet of two protons and signal at 5.15 (s, 1H, -CH-) indicates one proton at 4\(^{th}\) postion in the ring. The remaining signals at \(\delta\) 7.20-7.30 (m, 5H, Ar-H) confirms the presence of five aromatic protons and signal at 7.72 (brs, 1H, -NH), 9.13 (brs, 1H,-NH) indicates the presence of -NH protons in ring.

MALDI-Mass spectrum (Fig.4.3) for compound \(4a\) showed molecular ion peak at m/z [M\(^+\)] = 260, corresponds to molecular formula C\(_{14}\)H\(_{16}\)N\(_2\)O\(_3\) and which is equal to calculated mass 260.28 g/mol.

All other compounds spectral data results are presented in experimental section.

**4.3. Conclusions:**

DHPMs are synthesized by using DDQ reagent and AlKIT-5 catalyst. These two are valuable and additional to the present existing procedures. Among the two catalyts, AlKIT-5 is heterognous and
showed better performance than DDQ in terms of yields and recyclability. We designed and synthesized some biologically active chloro and thiophene derivatives of DHPMs.

We have developed a simple, convenient and effective method for the synthesis of DPHMs and their derivatives using substituted aldehydes, β-keto ester, urea/thiourea at reflux temperature using 3D mesoporous aluminosilicate catalyst with cage type pore under acetonitrile conditions. This method is applicable to a wide range of substrates including aromatic, aliphatic, α,β-unsaturated and heterocyclic aldehydes. The catalyst was found to be highly active and selective, affording a high yield of DHPMs with good recyclability. Compared to the classical Biginelli reaction conditions, this new approach consistently has the advantage of excellent yields (80–96%) and short reaction times, 3.0–4.0 h. The effect of the acidity and the concentration of the catalyst were investigated. We also demonstrate the synthesis of multifunctional Biginelli compounds using the highly active AlKIT-5 catalysts. The mesoporous AlKIT-5 catalysts are promising heterogenous catalysts in all circumstances where the aluminosilicate matrix is highly stable and we strongly hope that this catalyst could also be used for other acid catalyzed organic transformation and help to replace the existing toxic, corrosive and expensive homogenous catalysts. We designed and synthesized some biologically active thio derivatives of DHPMs.
4.4. Experimental:

General procedure for the synthesis of DHPMs: A solution of aldehyde (1.0 mmol), β-keto ester (1.2 mmol), and urea/thiourea (1.2 mmol) in acetonitrile (6 ml) was heated under reflux conditions in the presence of AlKIT-5(10) catalyst (150 mg) for 3.0–4.0 h. Completion of the reaction was monitored by TLC. Ethyl acetate (20%) in hexane was used as the mobile phase and both the reactant and the final product were spotted on the TLC plate. The product retention factor (Rf) was observed at around 0.25-0.35. The disappearance of the reactant spot on the TLC plate indicates the completion of the reaction. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and recrystallised from methanol. All products were characterized by spectral data (1H NMR, IR and MALDI-MS) and also the melting points of the samples. The spectral data of all the compounds are given below.

Entry 1: Ethyl 6-methyl-2-oxo-4-phenyl-3,4-dihydropyrimidine-5-carboxylate (4a): A mixture of benzaldehyde (0.106 g, 1.0 mmol), ethylacetoacetate (0.156g, 1.2 mmol), urea (0.072 g, 1.2 mmol), AlKIT-5 (0.150 g) and acetonitrile (6 mL) was stirred at reflux temperature for 3 h. On completion of the reaction, as indicated by TLC, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and recrystallised from methanol to yield dihydropyrimidinone 4a as a milky white solid (0.250 g, 96% yield): m.p. 209-
210°C. IR (KBr): ν
max
3240, 3117, 2981, 2880, 1691, 1656, 1600, 1465, 1422, 1291, 1227, 1090, 782, 699 cm
-1
(Fig.4.1). ¹H NMR (300 MHz, DMSO-d₆): δ 1.15 (t, J = 7.1 Hz, 3H, -OCH₂CH₃), 2.25 (s, 3H, -CH₃), 3.96 (q, J = 7.1 Hz, 2H, -OCH₂-), 5.15 (brs, 1H, -CH-), 7.20-7.30 (m, 5H, Ar-H), 7.72 (brs, 1H, -NH), 9.13 (brs, 1H, -NH) ppm (Fig.4.2).
MALDI-MS: m/z [M⁺] = 260 (Fig.4.3). M.F. C₁₄H₁₆N₂O₃.

Entry 2: Ethyl 6-methyl -4-(2-nitrophenyl) -2-oxo-3,4-dihydro pyrimidine-5-carboxylate (4b): A mixture of 2-nitro benzaldehyde (0.151 g, 1.0 mmol), ethylacetoacetate (0.156g, 1.2 mmol), urea (0.072 g, 1.2 mmol), AlKIT-5 (0.150 g) in acetonitrile (6 mL) was stirred at reflux temperature for 3 h. On completion of reaction, as indicated by TLC, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and recrystallised from methanol to yield product 4b as a white solid (0.293 g, 96% yield): m.p. 208-210°C. IR (KBr): ν
max
3472, 3285, 2976, 2876, 1667, 1660, 1599, 1543, 1540, 1364, 1300, 1135, 1076, 785, 693 cm
-1
(Fig.4.4). ¹H NMR (300 MHz, DMSO-d₆): δ 1.87 (t, J = 7.1 Hz, 3H, -OCH₂CH₃), 2.26 (s, 3H, -CH₃), 4.0 (q, J = 7.1 Hz, 2H, -OCH₂-), 4.84-4.94 (brs, 1H, -NH), 7.10-7.47 (m, 4H, Ar-H), 7.57 (brs, 1H, -NH), 8.17 (brs, 1H, -NH) ppm (Fig.4.5).
MALDI-MS: m/z [M⁺] = 305 (Fig.4.6). M.F. C₁₄H₁₅N₃O₅.

Entry 3: Ethyl 6-methyl -4-(4-nitrophenyl) -2-oxo-3,4-dihydro pyrimidine-5-carboxylate (4c): This compound was prepared as described in general procedure from a mixture of 4-nitro benzaldehyde (0.151 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol), urea
(0.072 g, 1.2 mmol) and AlKIT-5 (0.150 g) was stirred at reflux temperature for 3 h in 6 mL of acetonitrile. Up on completion as monitored by TLC, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and recrystalised from methanol, to give dihydropyrimidinone 4c as an off white solid (0.283 g, 93% yield): m.p. 209-211°C. IR (KBr): ν_{max} 3241, 3119, 2990, 2980, 1729, 1708, 1648, 1524, 1465, 1348, 1292, 1225, 1097, 786, 698 cm^{-1} (Fig.4.7). ^1H NMR (300 MHz, DMSO-d_{6}): δ 1.09 (t, J = 7.1 Hz, 3H, -OCH\textsubscript{2}CH\textsubscript{3}), 2.26 (s, 3H, -CH\textsubscript{3}), 4.01 (q, J = 7.0 Hz, 2H, -OCH\textsubscript{2}C), 5.27 (s, 1H, -CH-) ppm (Fig.4.8). MALDI-MS: m/z [M^+] = 305 (Fig.4.9). M.F. C\textsubscript{14}H\textsubscript{15}N\textsubscript{3}O\textsubscript{5}.

**Entry 4:** Ethyl 6-methyl 4-(3-nitrophenyl) -2-oxo-3,4-dihydro pyrimidine-5-carboxylate (4d): A mixture of 3-nitrobenzaldehyde (0.151 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol), urea (0.072 g, 1.2 mmol) and AlKIT-5 (0.150 g) in 6 mL of acetonitrile was stirred for 3 h at reflux temperature. The progress of the reaction was monitored by TLC. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and recrystalised from methanol, to get desired dihydropyrimidinone 4d as a white solid (0.262 g, 86% yield): m.p. 230-231°C. IR (KBr): ν_{max} 3444, 3337, 2968, 2810, 1690, 1662, 1609, 1534, 1453, 1348, 1295, 1225, 1089, 737, 693 cm^{-1} (Fig.4.10). ^1H NMR (300 MHz, DMSO-d_{6}): δ 1.10 (t, J = 7.1 Hz, 3H, -
OCH₂CH₃), 2.26 (s, 3H, -CH₃), 4.04 (q, J = 7.1 Hz, 2H, -OCH₂-), 5.40 (s, 1H, -CH-), 7.63-8.16 (m, 4H, Ar-H), 7.75 (brs, 1H, -NH), 9.35 (brs, 1H, -NH) ppm (Fig.4.11). MALDI-MS: m/z [M⁺] = 305 (Fig.4.12). M.F. C₁₄H₁₅N₃O₅.

**Entry 5: Ethyl 4-(4-chlorophenyl) -6-methyl -2-oxo-3,4-dihydro pyrimidine-5-carboxylate (4e):** 4-chlorobenzaldehyde (0.140 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol) and urea (0.072 g, 1.2 mmol) was dissolved in acetonitrile (6 mL) and then AlKIT-5 (0.150 g) was added. The resulting mixture was allowed to stir at reflux temperature for 3 h. The progress of the reaction was monitored by TLC. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the product was separated by filtration and then recrystallised from methanol to give the desired dihydropyrimidinone 4e as off white solid (0.258 g, 88% yield): m.p. 209-212°C. IR (KBr): νmax 3244, 3119, 2982, 2980, 1728, 1704, 1651, 1491, 1463, 1292, 1224, 1092, 784, 607 cm⁻¹ (Fig.4.13). ¹H NMR (300 MHz, DMSO-d₆): δ 1.05 (t, J = 7.1 Hz, 3H, -OCH₂CH₃), 2.22 (s, 3H, -CH₃), 3.95 (q, J = 7.1 Hz, 2H, -OCH₂-), 5.13 (brs, 1H, -CH-), 7.20-7.38 (m, 4H, Ar-H), 7.73 (brs, 1H, -NH), 9.17 (brs, 1H, -NH) ppm (Fig.4.14). MALDI-MS: m/z [M⁺] = 294 (Fig.4.15). M.F. C₁₄H₁₅ClN₂O₃.

**Entry 6: Ethyl 4-(4-methoxyphenyl) -6-methyl -2-oxo-3,4-dihydro pyrimidine-5-carboxylate (4f):** To a mixture of 4-methoxy benzaldehyde (0.136 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol) and urea (0.072 g, 1.2 mmol) in 6 mL of acetonitrile, AlKIT-5
(0.150 g) was added and the resulting mixture was stirred at reflux temperature for 3 h. The progress of the reaction was monitored by TLC. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol to afford product 4f as a yellow solid (0.258 g, 89% yield): m.p. 205°C. IR (KBr): ν_{max} 3236, 3118, 2958, 2880, 1726, 1699, 1655, 1514, 1460, 1283, 1233, 1091, 792, 659 cm^{-1} (Fig.4.16). {^1}H NMR (300 MHz, DMSO-d_6): δ 1.05 (t, J = 7.1 Hz, 3H, -OCH_2CH_3), 2.22 (s, 3H, -CH_3), 3.75 (s, 3H, -OCH_3), 3.95 (q, J = 7.1 Hz, 2H, -OCH_2-), 5.08 (s, 1H, -CH-), 6.81-7.15 (m, 4H, Ar-H), 7.59 (brs, 1H, -NH), 9.07 (brs, 1H, -NH) ppm (Fig.4.17). MALDI-MS: m/z [M^+] = 290 (Fig.4.18). M.F. C_{15}H_{18}N_2O_4.

**Entry 7: Ethyl 6-methyl-2-oxo-4-(3-phenoxyphenyl)-3,4-dihydro pyrimidine-5-carboxylate (4g):** The title compound was prepared from 3-phenoxybenzaldehyde (0.198 g, 1.0 mmol), etylacetoacetate (0.156 g, 1.2 mmol) and urea (0.072 g, 1.2 mmol) in 6 mL of acetonitrile using AlKIT-5 (0.150 g) as catalyst, were combined in a 100mL round-bottom flask. The resulting mixture was stirred at reflux temperature for 3 h. The progress of the reaction was monitored by TLC. The catalyst was recovered by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol, to afford the product 4g as a pure white solid (0.295 g, 84% yield): m.p. 193-194°C. IR (KBr): ν_{max} 3242, 3112, 2981, 1712,1654, 1582, 1487,
1245, 1097, 786 cm$^{-1}$ (Fig.4.19). \(^1\)H NMR (300 MHz, DMSO-d$_6$): \(\delta\) 1.15 (t, 3H, \(J = 6.8\) Hz), 2.37 (s, 3H), 4.10 (q, 2H, \(J = 6.8\) Hz), 5.35 (s, 1H), 5.82 (brs, NH), 6.84 (m, 1H), 7.05–7.10 (m, 5H), 7.45 (m, 3H), 8.40 (brs, -NH) ppm (Fig.4.20). Anal. Calcd. for C$_{20}$H$_{22}$N$_2$O$_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.79; H, 6.26; N, 7.94. MALDI-MS: m/z [M$^+$] = 352 (Fig.4.21). M.F. C$_{20}$H$_{20}$N$_2$O$_4$.

**Entry 8: Ethyl 4-(2-hydroxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4h):** According to the general procedure, a mixture of 2-hydroxy benzaldehyde (0.122 g, 1.0 mmol), ethyl acetoacetate (0.156 g, 1.2 mmol), urea (0.072 g, 1.2 mmol) and AlKIT-5 (0.150 g) in acetonitrile (6 mL) was stirred at reflux temperature for 3 h. On completion of the reaction, as indicated by TLC, the catalyst was recovered by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol, to yield the corresponding dihydropyrimidinone 4h as a pure white solid (0.243 g, 88% yield): m.p. 190-192°C. IR (KBr): \(\nu_{\text{max}}\) 3233, 3084, 2960, 2943, 1749, 1693, 1584, 1509, 1461, 1272, 1247, 1191, 1091, 762, 615 cm$^{-1}$ (Fig.4.22). \(^1\)H NMR (300 MHz, DMSO-d$_6$): \(\delta\) 1.22 (t, \(J = 7.1\) Hz, -OCH$_2$CH$_3$), 1.73 (s, 3H, -CH$_3$), 4.15 (q, \(J = 7.1\) Hz, 2H, -OCH$_2$-), 4.49 (brs, 1H, -CH-), 6.76-7.21 (m, 4H, Ar-H), 7.85 (brs, 1H, -NH), 9.13 (brs, 1H, -NH) ppm (Fig.4.23). MALDI-MS: m/z [M$^+$] = 276 (Fig.4.24). M.F. C$_{14}$H$_{16}$N$_2$O$_4$. 


**Entry 9: Ethyl 4-(3-hydroxyphenyl) -6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4i):** A solution of 3-hydroxy benzaldehyde (0.122 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol) and urea (0.072 g, 1.2 mmol) in acetonitrile (6 ml) was heated under reflux conditions in the presence of AlKIT-5(10) catalyst (0.150 g) for 3 h. Completion of the reaction was monitored by TLC. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and then the resulting solid was separated by filtration and recrystalised from methanol, to yield the desired product 4i as a pure white solid (0.229 g, 83% yield): m.p. 259-260°C. IR (KBr): \( \nu_{\text{max}} \) 3355, 3247, 3121, 2981, 1724, 1645, 1600, 1455, 1430, 1315, 1225, 1093, 779, 704 cm\(^{-1}\) (Fig.4.25). \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \( \delta \) 1.10 (t, \( J = 7.1 \) Hz, 3H, -OCH\(_2\)CH\(_3\)), 2.25 (s, 3H, -CH\(_3\)), 4.02 (q, \( J = 7.1 \) Hz, 2H, -OCH\(_2\)-), 5.07 (s, 1H, -CH\(_2\)-), 6.43-7.14 (m, 4H, Ar-H), 7.70 (brs, 1 H, -NH), 9.17 (brs, 1H, -NH) 9.38 (brs, 1H, -OH) ppm (Fig.4.26). MALDI-MS: m/z [M\(^+\)] = 276 (Fig.4.27). M.F. C\(_{14}\)H\(_{16}\)N\(_2\)O\(_4\).

**Entry 10: Ethyl 4-(5-chloro-2-hydroxyphenyl) -6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4j):** To a mixture of 5-chloro-2-hydroxybenzaldehyde (0.156 g, 1.0 mmol) ethylacetoacetate (0.156 g, 1.2 mmol) and urea (0.072 g, 1.2 mmol), AlKIT-5 (0.150 g) was added and then allowed to stir at reflux temperature for 3 h in 6 mL of acetonitrile. The progress of the reaction was monitored by TLC. The catalyst was recovered by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by
filtration and then recrystalised from methanol, to give the desired product 4j as a pure white solid (0.254 g, 82% yield): m.p. 208-210°C. IR (KBr): v_max 3300, 3235, 3091, 2960, 2948, 1745, 1695, 1584, 1505, 1481, 1344, 1249, 1199, 1082, 773, 673 cm\(^{-1}\) (Fig.4.28). \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta\) 1.08 (t, \(J = 7.1\) Hz, 3H, -OCH\(_3\)CH\(_3\)), 1.75 (s, 3H, -CH\(_3\)), 4.20 (q, \(J = 7.1\) Hz, 2H, -OCH\(_2\)CH\(_3\)), 4.54 (s, 1H, -CH-), 6.82-7.27 (m, 3H, Ar-H), 7.71 (brs, 1H, -NH) ppm (Fig.4.29). MALDI-MS: m/z [M\(^+\)] = 310 (Fig.4.30). M.F. C\(_{14}\)H\(_{15}\)ClN\(_2\)O\(_4\).

**Entry 11: Ethyl 6-methyl-2-oxo-4-styryl-3,4-dihydropyrimidine-5-carboxylate (4k):** To a solution of cinnamaldehyde (0.132 g, 1.0 mmol, ethylacetoacetate (0.156 g, 1.2 mmol), and urea (0.072 g, 1.2 mmol) in 6 mL of acetonitrile, AlKIT-5 (0.150 g) was added. The resulting mixture was stirred for 3 h at reflux temperature. The completion of reaction was monitored by TLC. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystalised from methanol, to give the desired dihydropyrimidinone 4k as a pure white solid (0.251 g, 88% yield): m.p. 229-231°C. IR (KBr): v_max 3335, 3242, 3098, 2978, 1689, 1642,1492, 1373, 1218, 1121, 785 cm\(^{-1}\) (Fig. 4.31). \(^1\)HNMR (300 MHz, DMSO-d\(_6\)): \(\delta\) 1.06 (t, 3H, \(J = 7.0\) Hz), 2.50 (s, 3H), 3.95 (q, 2H, \(J = 7.0\) Hz), 4.24 (d, 1H, \(J = 6.0\) Hz), 6.0 (d, 1H, \(J = 16.4\) Hz), 6.2 (d, 1H, \(J = 16.4\) Hz), 7.20 ~ 7.25 (m, 5H), 7.45 (d, -NH, \(J = 1.7\) Hz), 8.95 (brs, -NH) ppm (Fig. 4.32). MALDI-MS: m/z [M\(^+\)] = 286 (Fig.4.33). Anal. Calcd. for C\(_{16}\)H\(_{20}\)N\(_2\)O\(_3\): C, 66.65; H, 6.99; N, 9.72. Found: C, 66.68; H, 6.99; N, 9.75. M.F. C\(_{16}\)H\(_{18}\)N\(_2\)O\(_3\).
Entry 12: Ethyl 6-methyl-2-oxo-4-(thiophen-2-yl)-3,4-dihydro pyrimidine-5-carboxylate (4l): 2-Thiophenecarboxaldehyde (0.112 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol) and urea (0.072 g, 1.2 mmol) was dissolved in acetonitrile (6 mL) and AlKIT-5 (0.150 g) were added. The resulting mixture was allowed to stir at reflux temperature for 3 h. The progress of the reaction was monitored by TLC. Upon completion, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and recrystallised from methanol, to give the desired product 4l as off white solid (0.244 g, 92% yield): m.p. 215-217°C. IR (KBr): \( \nu_{\text{max}} \) 3242, 3118, 2981, 2980, 1726, 1711, 1653, 1464, 1422, 1291, 1224, 1093, 790, 693 cm\(^{-1} \) (Fig.4.34). \(^1\)H NMR (300 MHz, DMSO-\( d_6 \)): \( \delta \) 1.16 (t, \( J = 7.1 \) Hz, 3H, -OCH\(_2\)CH\(_3\)), 2.22 (s, 3H, -CH\(_3\)), 4.05 (q, \( J = 7.1 \) Hz, 2H, -OCH\(_2\)-), 5.41 (s, 1H, -CH-), 6.87-7.37 (m, 3H, Ar-H), 7.91 (brs, 1H, -NH), 9.32 (brs, 1H, -NH) ppm (Fig.4.35). MALDI-MS: m/z [M\(^+\)] = 266 (Fig.4.36). M.F. C\(_{12}\)H\(_{14}\)N\(_2\)O\(_3\)S.

Entry 13: Ethyl 4-(furan-2-yl)-6-methyl-2-oxo-3,4-dihydro pyrimidine-5-carboxylate (4m): To a 6 mL of acetonitrile, furfuraldehyde (0.096 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol) and urea (0.072 g, 1.2 mmol), AlKIT-5 (0.150 g) was added. The resulting mixture was stirred at reflux temperature for 3 h. The completion of reaction was monitored by TLC. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol, to give desired product 4m as a pale yellow solid
(0.230 g, 92% yield): m.p. 209-211°C. IR (KBr): ν_{max} 3245, 3120, 2988, 2980, 1694, 1650, 1650, 1630, 1458, 1420, 1317, 1217, 1095, 798, 738 cm⁻¹ (Fig. 4.37). ¹H NMR (300 MHz, DMSO-d₆): δ 1.15 (t, J = 7.1 Hz, 3H, -OCH₂CH₃), 2.23 (s, 3H, -CH₃), 4.02 (q, J = 7.1 Hz, 2H, -OCH₂-), 5.21 (s, 1H, -CH-), 6.08-7.55 (m, 3H, Ar-H), 7.75 (brs, 1H, -NH), 9.24 (brs, 1H, -NH) ppm (Fig. 4.38). MALDI-MS: m/z [M⁺] = 250 (Fig. 4.39).

M.F. C₁₂H₁₄N₂O₄.

**Entry 14:** Methyl 6-methyl-2-oxo-4-phenyl-3,4-dihydropyrimidine-5-carboxylate (4n): The title compound was prepared from benzaldehyde (0.106 g, 1.0 mmol), methylacetoacetate (0.139 g, 1.2 mmol), urea (0.072 g, 1.2 mmol) using AlKIT-5 (0.150 g) in 6 mL of acetonitrile. The resulting mixture was stirred at reflux temperature for 4 h. The completion of reaction was monitored by TLC. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol, to afford pure product 4n as a white solid (0.211 g, 86% yield): m.p. ~300°C. IR (KBr): ν_{max} 3444, 3335, 2990, 2890, 1669, 1625, 1456, 1360, 1225, 1189, 1095, 790, 600 cm⁻¹ (Fig. 4.40). ¹H NMR (300 MHz, DMSO-d₆): δ 2.23 (s, 3H, -CH₃), 3.50 (s, 3H, -CH₃), 5.23 (s, 1H, -CH-), 7.20-7.45 (m, 5H, Ar-H), 7.79 (brs, 1H, -NH), 9.00 (brs, 1H, -NH) ppm (Fig. 4.41). MALDI-MS: [M⁺] = 246 (Fig. 4.42). M.F. C₁₃H₁₄N₂O₃.

**Entry 15:** Ethyl 2-oxo-4,6-diphenyl-3,4-dihydropyrimidine-5-carboxylate (4o): A solution of benzaldehyde (0.106 g, 1.0 mmol), ethyl-3-oxo-3-phenylpropanoate (0.230 g, 1.2 mmol), urea (0.072
g, 1.2 mmol) in acetonitrile (6 ml) was heated under reflux conditions in the presence of AlKIT-5(10) (0.150 g) for 4 h. Upon completion of reaction was monitored by TLC, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol, to give the desired product 4o as a white solid (0.289 g, 90% yield): m.p. 162-164°C. IR (KBr): $\nu_{\text{max}}$ 3448, 3348, 3190, 2800, 1669, 1623, 1530, 1452, 1374, 1225, 1158, 1020, 784, 697 cm$^{-1}$ (Fig.4.43). $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ 0.75 (t, $J = 7.1$ Hz, -OCH$_3$), 3.85 (q, $J = 7.1$ Hz, 2H, -OCH$_2$-), 5.50 (s, 1H, -CH-), 7.16-7.35 (m, 10H, Ar-H), 7.82 (brs, 1H, -NH), 8.97 (brs, 1H, -NH) ppm (Fig.4.44). MALDI-MS: m/z [M$^+$] = 322 (Fig.4.45). M.F. C$_{19}$H$_{18}$N$_2$O$_3$.

**Entry 16:** Ethyl 6-methyl-4-phenyl-2-thioxo-3,4-dihydro pyrimidine-5-carboxylate (4p): A mixture of benzaldehyde (0.106 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol), thiourea (0.091 g, 1.2 mmol), and AlKIT-5 (0.150 g) in acetonitrile (6 mL) was stirred at reflux temperature for 4 h. Upon completion of the reaction, as indicated by TLC, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol to give pure product 4p as a white solid (0.251 g, 91% yield): m.p. 188-190°C. IR (KBr): $\nu_{\text{max}}$ 3330, 3176, 3106, 2981, 1671, 1670, 1576, 1466, 1420, 1284, 1196, 1119, 761, 694 cm$^{-1}$ (Fig.4.46). $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ 1.10 (t, $J = 7.1$ Hz, 3H, -OCH$_3$), 2.29 (s, 3H, -CH$_3$), 4.02 (q, $J = 7.1$ Hz, 2H, -OCH$_2$-), 5.14 (s, 1H, -CH-),
7.23-7.35 (m, 5H, Ar-H), 9.67 (brs, 1H, -NH), 10.34 (brs, 1H, -NH) ppm (Fig.4.47). MALDI-MS: m/z [M'] = 276 (Fig.4.48). Anal. Calcd. for C_{14}H_{16}N_{2}O_{2}: 60.85; H, 5.84; N, 10.14. Found: C, 60.85; H, 5.84; N, 10.14.

**Entry 17: Ethyl 6-methyl-4-(2-nitrophenyl)-2-thioxo-3,4-dihydro pyrimidine-5-carboxylate (4q):** This compound was prepared as described in general procedure from a solution of 2-nitrobenzaldehyde (0.151 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol) and thiourea (0.091 g, 1.2 mmol) in acetonitrile (6 ml) using AlKIT-5(10) (0.150 g) was stirred for 4 h under reflux conditions. Upon completion of the reaction was monitored by TLC, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the product was separated by filtration and then recrystallised from methanol, to give the desired product 4q as off white solid (0.292 g, 91% yield): m.p. 209-211°C. IR (KBr): \nu_{max} 3293, 3111, 2983, 2950, 1722, 1660, 1576, 1524, 1467, 1355, 1250, 1195, 1094, 710, 580 cm^{-1} (Fig.4.49). \textsuperscript{1}H NMR (300 MHz, DMSO-d\textsubscript{6}): \delta 1.00 (t, J = 7.1 Hz, 3H, -OCH\textsubscript{2}CH\textsubscript{3}), 2.42 (s, 3H, -CH\textsubscript{3}), 3.95 (q, J = 7.1 Hz, 2H, -OCH\textsubscript{2}-), 5.90 (s, 1H, -NH), 7.48-7.94 (m, 4H, Ar-H), 8.60 (brs, 1H, -NH), 10.31 (brs, 1H, -NH) ppm (Fig.4.50). MALDI-MS: m/z [M'] = 321 (Fig.4.51). Anal. Calcd. for C_{14}H_{15}N_{3}O_{4}: S, 52.33; H, 4.70; N, 13.08. Found: C, 52.30; H, 4.68; N, 13.04.

**Entry 18: Ethyl 6-methyl-4-(4-nitrophenyl)-2-thioxo-3,4-dihydro pyrimidine-5-carboxylate (4r):** To a mixture of 4-nitrobenzaldehyde (0.151 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol), thiourea
(0.091 g, 1.2 mmol), AlKIT-5 (0.150 g) was added and allowed to stir at reflux temperature for 4 h in 6 mL of acetonitrile. The completion of reaction was monitored by TLC. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol to give the desired product 4r as a yellow solid (0.282 g, 88% yield): m.p. 160-162 °C. IR (KBr): ν\text{max} 3288, 3187, 2985, 2823, 1650, 1620, 1609, 1519, 1422, 1349, 1245, 1160, 1108, 856, 699 cm\(^{-1}\) (Fig.4.52). \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): δ 1.05 (t, J = 7.1 Hz, 3H, -OCH\(_2\)CH\(_3\)), 2.08 (s, 3H, -CH\(_3\)), 4.10 (q, J = 7.1 Hz, 2H, -OCH\(_2\)-), 6.66 (s, 1H, -CH-), 7.64-7.68 (m, 4H, Ar-H), 8.27 (brs, 1H, -NH), 8.87 (brs, 1H, -NH) ppm (Fig.4.53). MALDI-MS: m/z [M\(^+\)] = 321 (Fig.4.54). Anal. Calcd. for C\(_{14}\)H\(_{15}\)N\(_3\)O\(_4\)S: C, 52.33; H, 4.70; N, 13.08. Found: C, 52.29; H, 4.66; N, 13.05.

**Entry 19: Ethyl 6-methyl -4-(3-nitrophenyl) -2-thioxo-3,4-dihydro pyrimidine-5-carboxylate (4s):** To a solution of 3-nitrobenzaldehyde (0.151 g, 1.0 mmol), ethylacetooacetate (0.156 g, 1.2 mmol) and thiourea (0.091 g, 1.2 mmol) in 6 mL of acetonitrile, AlKIT-5 (0.150 g) was added. The resulting mixture was stirred for 4 h at reflux temperature. The completion of reaction was monitored by TLC. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol, to give the desired product 4s as a pure white solid (0.256 g, 80% yield): m.p. 203-205°C. IR (KBr): ν\text{max} 3180, 3160, 2990, 2920, 1717, 1662, 1596, 1533, 1477,
1345, 1276, 1192, 1104, 737, 670 cm⁻¹ (Fig.4.55). ¹H NMR (300 MHz, DMSO-d₆): δ 1.11 (t, J = 7.1 Hz, 3H, -OCH₂CH₃), 2.32 (s, 3H, -CH₃), 4.03 (q, J = 7.1 Hz, 2H, -OCH₂-), 5.33 (s, 1H, -CH-), 7.68-8.18 (m, 4H, Ar-H), 9.78 (brs, 1H, -NH), 10.52 (brs, 1H, -NH) ppm (Fig.4.56). MALDI-MS: m/z [M⁺] = 321 (Fig.4.57). Anal. Calcd. for C₁₄H₁₅N₃O₄S: C, 52.33; H, 4.70; N, 13.08. Found: C, 52.29; H, 4.66; N, 13.03.

**Entry 20: Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-3,4-dihydro pyrimidine-5-carboxylate (4t):** A mixture of 4-chloro benzaldehyde (0.140 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol) and thiourea (0.091 g, 1.2 mmol) was dissolved in acetonitrile (6 mL) and AlKIT-5 (0.150 g) was added. The resulting mixture was allowed to stir at reflux temperature for 4 h. The completion of the reaction was monitored by TLC. The catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol, to give the desired dihydropyrimidinone 4t as a pure white (0.272 g, 88% yield): m.p. 192-194°C. IR (KBr): νmax 3378, 3275, 3178, 2950, 1733, 1630, 1609, 1517, 1492, 1415, 1280, 1182, 1091, 822, 731 cm⁻¹ (Fig.4.58). ¹H NMR (300 MHz, DMSO-d₆): δ 1.05 (t, J = 7.1 Hz, 3H, -OCH₂CH₃), 1.45 (s, 3H, -CH₃), 3.90 (q, 2H, -OCH₂-), 4.75 (s, 1H, -CH-), 7.31-7.48 (m, 4H, Ar-H), 8.44 (brs, 1H, -NH), 8.81 (brs, 1H, -NH) ppm (Fig.4.59). MALDI-MS: m/z [M⁺] = 310 (Fig.4.60). Anal. Calcd. for C₁₄H₁₅ClN₂O₂S: C, 54.10; H, 4.86; N, 9.01. Found: C, 54.07; H, 4.83; N, 9.00.
**Entry 21:** Ethyl 4-(4-methoxyphenyl) -6-methyl-2-thioxo-3,4-dihydropyrimidin-5-carboxylate (4u): To a 6 mL of acetonitrile, 4-methoxybenzaldehyde (0.136 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol), thiourea (0.091 g, 1.2 mmol) and AlKIT-5 (0.150 g) were added in a 100mL round-bottom flask. The reaction mixture was stirred at reflux temperature for 4 h. The completion of reaction was monitored by TLC and the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol, to give pure product 4u as a white solid (0.251 g, 82% yield): m.p. 150-152°C. IR (KBr): $v_{\text{max}}$ 3315, 3173, 2985, 2880, 1668, 1630, 1576, 1510, 1464, 1270, 1183, 1123, 1028, 767 cm$^{-1}$ (Fig.4.61).

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 1.10 (t, $J = 7.1$ Hz, 3H, -OCH$_2$CH$_3$), 2.27 (s, 3H, -CH$_3$), 3.71 (s, 3H, -OCH$_3$), 4.00 (q, $J = 7.1$ Hz, 2H, -OCH$_2$-), 5.10 (s, 1H, -CH$_2$-), 6.87-7.13 (m, 4H, Ar-H), 9.58 (brs, 1H, -NH), 10.27 (brs, 1H, -NH) ppm (Fig.4.62). MALDI-MS: m/z [M$^+$] = 306 (Fig.4.63). *Anal.* Calcd. for C$_{15}$H$_{18}$N$_2$O$_3$S: C, 58.80; H, 5.92; N, 9.14. Found: C, 58.76; H, 5.88; N, 9.10.

**Entry 22:** Ethyl 6-methyl -4-(3-phenoxyphenyl) -2-thioxo-3,4-dihydropyrimidin-5-carboxylate (4v): The title compound was prepared from 3-phenoxybenzaldehyde (0.198 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol), thiourea (0.091 g, 1.2 mmol) in 6 mL of acetonitrile using AlKIT-5 (0.150 g). The resulting mixture was stirred at 80°C temperature for 4 h. The completion of reaction was
monitored by TLC and the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and recrystallised from methanol, to afford pure product 4v as a light greenish white solid (0.309 g, 84% yield): m.p. 145-147°C. IR (KBr): \( \nu_{\text{max}} \) 3312, 3179, 2998, 2960, 1668, 1650, 1580, 1485, 1463, 1286, 1187, 1115, 756, 697 cm\(^{-1}\) (Fig.4.64).

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \( \delta \) 1.07 (t, \( J = 7.1 \) Hz, 3H, -OCH\(_2\)CH\(_3\)), 2.27 (s, 3H, -CH\(_3\)), 4.00 (q, \( J = 7.1 \) Hz, 2H, -OCH\(_2\)-), 5.14 (s, 1H, -CH-), 6.86-7.40 (m, 9H, Ar-H), 9.61 (brs, 1H, -NH), 10.38 (brs, 1H, -NH) ppm (Fig.4.65). MALDI-MS: m/z [M\(^+\)] = 368 (Fig.4.66).

**Anal. Calcd. for C\(_{20}\)H\(_{20}\)N\(_2\)O\(_3\)S: C, 65.20; H, 5.47; N, 7.60. Found: C, 65.16; H, 5.45; N, 7.56.**

**Entry 23: Ethyl 4-(2-hydroxyphenyl)-6-methyl -2-thioxo-3,4-dihydro pyrimidine-5-carboxylate (4w):** A mixture of 2-hydroxy benzaldehyde (0.122 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol), thiourea (0.091 g, 1.2 mmol) and AlKIT-5 (0.150 g) in acetonitrile (6 mL) was stirred at reflux temperature for 4 h. Up on completion of reaction, as indicated by TLC, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol, to give the product 4w as a white solid (0.245 g, 84% yield): m.p. 210-212°C. IR (KBr): \( \nu_{\text{max}} \) 3327, 3193, 2990, 2977, 1723, 1600, 1564, 1509, 1460, 1290, 1260, 1180, 1088, 912, 758 cm\(^{-1}\) (Fig.4.67). \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \( \delta \) 1.23 (t, \( J = 7.1 \) Hz, 3H, -OCH\(_2\)CH\(_3\)), 1.78 (s, 3H, -CH\(_3\)), 4.15 (q, \( J = 7.1 \) Hz, 2H, -
OCH2-), 4.57 (s, 1H, -CH3), 6.76-7.27 (m, 4H, Ar-H), 9.14 (bri, 1H, -NH), 9.63 (bri, 1H, -NH), 10.21 (bri, 1H, -OH) ppm (Fig.4.68). MALDI-MS: m/z [M+1] = 292 (Fig.4.69). Anal. Calcd. for C14H16N2O3S: C, 57.52; H, 5.52; N, 9.58. Found: C, 57.48; H, 5.49; N, 9.55.

**Entry 24: Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4x):** A solution of 3-hydroxy benzaldehyde (0.122 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol) and thiourea (0.091 g, 1.2 mmol) in acetonitrile (6 ml) was heated under reflux conditions in the presence of AIKIT-5(10) (0.150 g) for 4 h. Up on completion of reaction was monitored by TLC, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol to give the desired product 4x as a white solid (0.239 g, 82% yield): m.p. 210-212°C. IR (KBr): νmax 3312, 3187, 2985, 2880, 1668, 1620, 1576, 1475, 1425, 1288, 1260, 1195, 1116, 765 cm⁻¹ (Fig.4.70). ¹H NMR (300 MHz, DMSO-d6): ω 1.18 (t, J = 7.1 Hz, 3H, -OCH2CH3), 2.16 (s, 3H, -CH3), 4.05 (q, J = 7.1 Hz, 2H, -OCH2-), 5.25 (s, 1H, -CH3), 6.73-7.59 (m, 4H, Ar-H), 8.94 (bri, 1H, -NH), 8.96 (bri, 1H, -NH), 9.69 (bri, 1H, -OH) ppm (Fig.4.71). MALDI-MS: m/z [M+] = 292 (Fig.4.72). Anal. Calcd. for C14H16N2O3S: C, 57.52; H, 5.52; N, 9.58. Found: C, 57.48; H, 5.48; N, 9.54.

**Entry 25: Ethyl 4-(5-chloro-2-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4y):** A mixture of 5-chloro-2-hydroxybenzaldehyde (0.156 g, 1.0 mmol), ethyl acetoacetate (0.156 g,
1.2 mmol), thiourea (0.091 g, 1.2 mmol) and AlKIT-5 (0.150 g) was stirred at reflux temperature for 4 h in 6 mL of acetonitrile. The completion of reaction was monitored by TLC. Up on completion, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol to give the desired product 4y as a pure white solid (0.267 g, 82% yield): m.p. 213-215°C. IR (KBr): ν̂max 3246, 3237, 2960, 2958, 1721, 1630, 1557, 1499, 1470, 1373, 1205, 1094, 819, 652 cm⁻¹ (Fig. 4.73). ¹H NMR (300 MHz, DMSO-d₆): δ 1.23 (t, J = 7.1 Hz, 3H, -OCH₂CH₃), 1.78 (s, 3H, -CH₃), 3.99 (q, J = 7.1 Hz, 2H, -OCH₂-), 4.62 (s, 1H, -CH-), 6.84-7.25 (m, 3H, Ar-H), 9.10 (brs, 1H, -NH), 9.26 (brs, 1H, -NH), 10.01 (brs, 1H, -OH) ppm (Fig. 4.74). MALDI-MS: m/z [M⁺] = 326 (Fig. 4.75). Anal. Calcd. for C₁₄H₁₅ClN₂O₃S:C,51.45; H,4.63; N,8.57. Found:C,51.40; H,4.60; N,8.54.

**Entry 26: Ethyl 6-methyl -4-styryl -2-thioxo -3,4-dihydro pyrimidine-5-carboxylate (4z):** To a solution of cinnamaldehyde (0.132 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol and thiourea (0.091 g, 1.2 mmol) in 6 mL of acetonitrile, AlKIT-5 (0.150 g) was added. The resulting mixture was stirred for 4 h at reflux temperature. The completion of the reaction was monitored by TLC. Up on completion, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol to give the desired product 4z as a light yellow solid (0.259 g, 86% yield): m.p. 190-192°C. IR (KBr): ν̂max 3160, 3155, 2981, 2904, 1707, 1681,
1595, 1474, 1465, 1263, 1193, 1108, 754, 695 cm⁻¹ (Fig.4.76). ¹H NMR (300 MHz, DMSO-d₆): δ 1.20 (t, J = 7.1 Hz, 3H, -OCH₂CH₃), 2.25 (s, 3H, -CH₃), 4.10 (q, J = 7.1 Hz, 2H, -OCH₂-), 4.75 (s, 1H, -CH), 6.18 (dd, 1H, J = 14.5 Hz, 4.1 Hz, -CH=CH-), 6.35 (d, 1H, J = 4.1 Hz, -CH=CH-), 7.21-7.42 (m, 5H, Ar-H), 9.50 (brs, 1H, -NH), 10.30 (brs, 1H, -NH) ppm (Fig.4.77). MALDI-MS: m/z [M⁺] = 302 (Fig.4.78). Anal. Calcd. for C₁₆H₁₈N₂O₂S: C, 63.55; H, 6.00; N, 9.26. Found: C, 63.51; H, 5.96; N, 9.22.

**Entry 27: Ethyl 6-methyl -4-(thiophen-2-yl) -2-thioxo-3,4-dihydro pyrimidine-5-carboxylate (4a₁):** 2-Thiophenecarboxaldehyde (0.112 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol) and thiourea (0.091 g, 1.2 mmol) was dissolved in acetonitrile (6 mL) and AlKIT-5 (0.150 g) was added. The reaction mixture was then allowed to stir at reflux temperature for 4 h. The completion of the reaction was monitored by TLC. Up on completion, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and recrystallised from methanol to give the desired product 4a₁ as off white solid (0.254 g, 90% yield): m.p. 215-217°C. IR (KBr): vₘₐₓ 3305, 3185, 2987, 2960, 1664, 1659, 1571, 1460, 1374, 1278, 1185, 1115, 767, 705 cm⁻¹ (Fig.4.79). ¹H NMR (300 MHz, DMSO-d₆): δ 1.15 (t, J = 7.1 Hz, 3H, -OCH₂CH₃), 2.27 (s, 3H, -CH₃), 4.10 (q, J = 7.1 Hz, 2H, -OCH₂-), 5.42 (s, 1H, -CH), 6.89-7.42 (m, 3H, Ar-H), 9.74 (brs, 1H, -NH), 10.43 (brs, 1H, -NH) ppm (Fig.4.80). MALDI-MS: m/z [M⁺] = 282 (Fig.4.81). Anal.
Calcd. for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2\text{S}_2$: C, 51.04; H, 5.00, N, 9.92. Found: C, 51.00; H, 4.96; N, 9.90.

**Entry 28:** Ethyl 4-(furan-2-yl)-6-methyl -2-thioxo-3,4-dihydro pyrimidine-5-carboxylate ($4b_1$): In 6 ml of acetonitrile, furfuraldehyde (0.096 g, 1.0 mmol), ethylacetoacetate (0.156 g, 1.2 mmol) and thiourea (0.091 g, 1.2 mmol) and AlKIT-5 (0.150 g) were combined in 100mL round-bottom flask. The reaction mixture was stirred at reflux temperature for 4 h. Upon completion of the reaction, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol to give the desired product $4b_1$ as a light yellow solid (0.239 g, 90% yield): m.p. 220-222°C. IR (KBr): $\nu_{\text{max}}$ 3316, 3177, 2985, 2960, 1661, 1659, 1576, 1451, 1377, 1277, 1187, 1116, 760 cm$^{-1}$ (Fig.4.82). $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ 1.14 (t, $J = 7.1$ Hz, 3H, $-\text{OCH}_2\text{CH}_3$), 2.28 (s, 3H, $-\text{CH}_3$), 4.05 (q, $J = 7.1$ Hz, 2H, $-\text{OCH}_2\text{-}$), 5.23 (s, 1H, $-\text{CH}$), 6.14-7.59 (m, 3H, Ar-$\text{H}$), 9.65 (brs, 1H, $-\text{NH}$), 10.41 (brs, 1H, $-\text{NH}$) ppm (Fig.4.83). MALDI-MS: m/z $[\text{M}^+]=266$ (Fig.4.84). Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$: C, 54.12; H, 5.30; N, 10.52. Found: C, 54.09; H, 5.26; N, 10.48.

**Entry 29:** Methyl 6-methyl-4-phenyl -2-thioxo-3,4-dihydro pyrimidine-5-carboxylate ($4c_1$): The title compound was prepared from benzaldehyde (0.106 g, 1.0 mmol), methylacetoacetate (0.139 g, 1.2 mmol), thiourea (0.091 g, 1.2 mmol), using AlKIT-5 (0.150 g) in 6 mL of acetonitrile. The reaction mixture was stirred at reflux temperature for 4 h. The completion of reaction was monitored by TLC
and the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol to afford pure product 4c as off white solid (0.215 g, 82% yield): m.p. \(\approx 300^\circ \text{C}\). IR (KBr): \(\nu_{\text{max}}\) 3276, 3174, 2990, 1665, 1640, 1615, 1473, 1416, 1200, 1084, 731, 634 \text{ cm}^{-1} \text{ (Fig.4.85)}. \text{^1H NMR} (300 MHz, DMSO-d_6): \delta 2.29 \text{ (t, } J = 7.1 \text{ Hz, 3H, -OCH}_3), 3.56 \text{ (s, 3H, -CH}_3), 5.37 \text{ (s, 1H, -CH-)}, 7.47-7.52 \text{ (m, 5H, Ar-H)}, 7.93 \text{ (brs, 1H, -NH)}, 7.95 \text{ (brs, 1H, -NH)} ppm \text{ (Fig.4.86). MALDI-MS: m/z \([M^+]\) = 262 \text{ (Fig.4.87). Anal. Calcd. for C}_{13}H_{14}N_2O_2S: C, 59.52; H, 5.38; N, 10.68. Found: C, 59.49; H, 5.34; N, 10.64.}

**Entry 30:** Ethyl 4,6-diphenyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4d): A solution of benzaldehyde (0.106 g, 1.0 mmol), ethyl-3-oxo-3-phenylpropanoate (0.230 g, 1.2 mmol) and thiourea (0.091 g, 1.2 mmol) in acetonitrile (6 ml) was heated under reflux conditions in the presence of AlKIT-5(10) (0.150 g) for 4 h. Upon completion of reaction was monitored by TLC, the catalyst was separated by filtration. The reaction mixture was then poured onto crushed ice and the solid product was separated by filtration and then recrystallised from methanol to give the desired product 4d as off white solid (0.297 g, 88% yield): m.p. \(> 300^\circ \text{C}\). IR (KBr): \(\nu_{\text{max}}\) 3377, 3276, 2830, 2810, 1640, 1612, 1590, 1469, 1417, 1250, 1088, 731, 635 \text{ cm}^{-1} \text{ (Fig.4.88)}. \text{^1H NMR} (300 MHz, DMSO-d_6): \delta 1.05 \text{ (t, } J = 7.1 \text{ Hz, 3H, -OCH}_2\text{CH}_3), 3.90 \text{ (q, } J = 7.1 \text{ Hz, 2H, -OCH}_2\text{-}), 5.30 \text{ (s, 1H, -CH-)}, 6.93-6.94 \text{ (m, 10H, Ar-H)}, 8.00 \text{ (brs, 1H, -NH)}, 9.13 \text{ (brs, 1H, -NH)}
ppm (Fig.4.89). MALDI-MS: m/z[M⁺] = 338 (Fig.4.90). Anal. Calcd. for C₁₉H₁₈N₂O₂: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.40; H, 5.32; N, 8.24.
Fig. 4.1. IR spectrum of Ethyl 6-methyl-2-oxo-4-phenyl-3,4-dihydropyrimidine-5-carboxylate (4a)

Fig. 4.2. $^1$H NMR spectrum of Ethyl 6-methyl-2-oxo-4-phenyl-3,4-dihydropyrimidine-5-carboxylate (4a)
Fig: 4.3. Mass spectrum of Ethyl 6-methyl-2-oxo-4-phenyl-3,4-dihydropyrimidine-5-carboxylate (4a) (MW=260)

Fig: 4.4. IR Spectrum of Ethyl 6-methyl-4-(2-nitrophenyl)-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4b)
Fig: 4.5. $^1$H NMR spectrum of Ethyl 6-methyl-4-(2-nitrophenyl)-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4b)

Fig: 4.6. Mass spectrum of Ethyl 6-methyl-4-(2-nitrophenyl)-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4b) (MW=305(o))
Fig: 4.7. IR Spectrum of Ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4c)

Fig: 4.8. $^1$H NMR spectrum of Ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4c)
Fig: 4.9. Mass spectrum of Ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4c) (MW=305(p))

Fig: 4.10. IR Spectrum of Ethyl 6-methyl-4-(3-nitrophenyl)-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4d)
Fig: 4.11. $^1$H NMR spectrum of Ethyl 6-methyl-4-(3-nitrophenyl)-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4d)

Fig: 4.12. Mass spectrum of Ethyl 6-methyl-4-(3-nitrophenyl)-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4d) (MW=305(m))
Fig: 4.13. IR Spectrum of Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4e)

Fig: 4.14. $^1$H NMR spectrum of Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4e)
Fig: 4.15. Mass spectrum of Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4e) (MW=294)

Fig: 4.16. IR Spectrum of Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4f)
Fig: 4.17. $^1$H NMR spectrum of Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4f)

Fig: 4.18. Mass spectrum of Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4f) (MW=290)
Fig: 4.19. IR Spectrum of Ethyl 6-methyl-2-oxo-4-(3-phenoxyphenyl)-3,4-dihydropyrimidine-5-carboxylate (4g)

Fig: 4.20. $^1$H NMR spectrum of Ethyl 6-methyl-2-oxo-4-(3-phenoxyphenyl) - 3,4-dihydropyrimidine-5-carboxylate (4g)
Fig: 4.21. Mass spectrum of Ethyl 6-methyl-2-oxo-4-(3-phenoxyphenyl) - 3,4-dihydropyrimidine-5-carboxylate (4g) (MW=352)

Fig: 4.22. IR spectrum of Ethyl 4-(2-hydroxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4h)
Fig: 4.23. $^1$H NMR spectrum of Ethyl 4-(2-hydroxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4h)

Fig: 2.24. Mass spectrum of Ethyl 4-(2-hydroxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4h) (MW=276(o))
Fig: 4.25. IR Spectrum of Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4i)

Fig: 4.26. $^1$H NMR spectrum of Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4i)
Fig: 4.27. Mass spectrum of Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4i) (MW=276(m))

Fig: 4.28. IR Spectrum of Ethyl 4-(5-chloro-2-hydroxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4j)
Fig: 4.29. $^1$H NMR spectrum of Ethyl 4-(5-chloro-2-hydroxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4j)

Fig: 4.30. Mass spectrum of Ethyl 4-(5-chloro-2-hydroxyphenyl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4j) (MW=310)
Fig: 4.31. IR spectrum of (E)-ethyl 6-methyl-2-oxo-4-styryl-3,4-dihydropyrimidine-5-carboxylate (4k)

Fig: 4.32. \(^1H\) NMR spectrum of (E)-ethyl 6-methyl-2-oxo-4-styryl-3,4-dihydropyrimidine-5-carboxylate (4k)
Fig: 4.33. Mass spectrum of (E)-ethyl 6-methyl-2-oxo-4-styryl-3,4-dihydropyrimidine-5-carboxylate (4k) (MW=286)

Fig: 4.34. IR spectrum of Ethyl 6-methyl-2-oxo-4-(thiophen-2-yl)-3,4-dihydropyrimidine-5-carboxylate (4l)
Fig: 4.35. $^1$H NMR spectrum of Ethyl 6-methyl-2-oxo-4-(thiophen-2-yl)-3,4-dihydropyrimidine-5-carboxylate (4l)

Fig: 4.36. Mass spectrum of Ethyl 6-methyl-2-oxo-4-(thiophen-2-yl)-3,4-dihydropyrimidine-5-carboxylate (4l) (MW=266)
Fig: 4.37. IR spectrum of Ethyl 4-(furan-2-yl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4m)

Fig: 4.38. $^1$H NMR spectrum of Ethyl 4-(furan-2-yl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate (4m)
Fig: 4.39. Mass spectrum of Ethyl 4-(furan-2-yl)-6-methyl-2-oxo-3,4-dihydropyrimidine-5-carboxylate \((4m)\) (MW=250)

Fig: 4.40. IR spectrum of Methyl 6-methyl-2-oxo-4-phenyl-3,4-dihydropyrimidine-5-carboxylate \((4n)\)
Fig: 4.41. $^1$H NMR spectrum of Methyl 6-methyl-2-oxo-4-phenyl-3,4-dihydropyrimidine-5-carboxylate (4n)

Fig: 4.42. Mass spectrum of Methyl 6-methyl-2-oxo-4-phenyl-3,4-dihydropyrimidine-5-carboxylate (4n) (MW=246)
Fig: 4.43. IR spectrum of Ethyl 2-oxo-4,6-diphenyl-3,4-dihydropyrimidine-5-carboxylate (4o)

Fig: 4.44. $^1$H NMR spectrum of Ethyl 2-oxo-4,6-diphenyl-3,4-dihydropyrimidine-5-carboxylate (4o)
Fig: 4.45. Mass spectrum of Ethyl 2-oxo-4,6-diphenyl-3,4-dihydropyrimidine-5-carboxylate (4o) (MW = 322)

Fig: 4.46. IR spectrum of Ethyl 6-methyl-4-phenyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4p)
Fig: 4.47. $^1$H NMR spectrum of Ethyl 6-methyl-4-phenyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4p)

Fig: 4.48. Mass spectrum of Ethyl 6-methyl-4-phenyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4p) (MW=276)
Fig: 4.49. IR spectrum of Ethyl 6-methyl-4-(2-nitrophenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4q)

Fig: 4.50. $^1$H NMR spectrum of Ethyl 6-methyl-4-(2-nitrophenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4q)
Fig: 4.51. Mass spectrum of Ethyl 6-methyl-4-(2-nitrophenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4g) (MW=321(o))

Fig: 4.52. IR spectrum of Ethyl 6-methyl-4-(4-nitrophenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4r)
Fig: 4.53. $^1$H NMR spectrum of Ethyl 6-methyl-4-(4-nitrophenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate ($4r$)

Fig: 4.54. Mass spectrum of Ethyl 6-methyl-4-(4-nitrophenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate ($4r$) (MW=321(p))
Fig: 4.55. IR spectrum of Ethyl 6-methyl-4-(3-nitrophenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4s)
Fig: 4.57. Mass spectrum of Ethyl 6-methyl-4-(3-nitrophenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4s) (MW=321(m))

Fig: 4.58. IR spectrum of Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4t)
Fig: 4.59. $^1$H NMR spectrum of Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4t)

Fig: 4.60. Mass spectrum of Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4t) (MW=310)
Fig: 4.61. IR spectrum of Ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4u)

Fig: 4.62. $^1$H NMR spectrum of Ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4u)
Fig: 4.63. Mass spectrum of Ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate *(4u)* (MW=306)

Fig: 4.64. IR spectrum of Ethyl 6-methyl-4-(3-phenoxyphenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate *(4v)*
Fig: 4.65. $^1$H NMR spectrum of Ethyl 6-methyl-4-(3-phenoxyphenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4v)

Fig: 4.66. Mass spectrum of Ethyl 6-methyl-4-(3-phenoxyphenyl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4v) (MW=368)
Fig: 4.67. IR spectrum of Ethyl 4-(2-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4w)

Fig: 4.68. $^1$H NMR spectrum of Ethyl 4-(2-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4w)
Fig: 4.69. Mass spectrum of Ethyl 4-(2-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate \((4w)\) (MW=292(o))

Fig: 4.70. IR spectrum of Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate \((4x)\)
Fig: 4.71. $^1$H NMR spectrum of Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4x)

Fig: 4.72. Mass spectrum of Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4x) (MW=292(m))
Fig: 4.73. IR spectrum of Ethyl 4-(5-chloro-2-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4y)

Fig: 4.74. $^1$H NMR spectrum of Ethyl 4-(5-chloro-2-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4y)
Fig: 4.75. Mass spectrum of Ethyl 4-(5-chloro-2-hydroxyphenyl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate ($4_y$) (MW=326)

Fig: 4.76. IR spectrum of (E)-ethyl 6-methyl-4-styryl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate ($4_z$)
Fig: 4.77. $^1$H NMR spectrum of (E)-ethyl 6-methyl-4-styryl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate ($4z$)

Fig: 4.78. Mass spectrum of (E)-ethyl 6-methyl-4-styryl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate ($4z$) (MW=302)
Fig: 4.79. IR spectrum of Ethyl 6-methyl-4-(thiophen-2-yl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4a₁)

Fig: 4.80. ¹H NMR spectrum of 6-methyl-4-(thiophen-2-yl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4a₁)
Fig: 4.81. Mass spectrum of 6-methyl-4-(thiophen-2-yl)-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4a₁) (MW=282)

Fig: 4.82. IR spectrum of Ethyl 4-(furan-2-yl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4b₁)
Fig. 4.83. $^1$H NMR spectrum of Ethyl 4-(furan-2-yl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4b₁)

Fig. 4.84. Mass spectrum of Ethyl 4-(furan-2-yl)-6-methyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4b₁) (MW=266)
Fig: 4.85. IR spectrum of Methyl 6-methyl-4-phenyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4c₁)

Fig: 4.86. ¹H NMR spectrum of Methyl 6-methyl-4-phenyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4c₁)
Fig: 4.87. Mass spectrum of Methyl 6-methyl-4-phenyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4c₁) (MW=262)

Fig: 4.88. IR spectrum of Ethyl 4,6-diphenyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4d₁)
Fig: 4.89. $^1$H NMR spectrum of Ethyl 4,6-diphenyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4d$_1$)

Fig: 4.90. Mass spectrum of Ethyl 4,6-diphenyl-2-thioxo-3,4-dihydropyrimidine-5-carboxylate (4d$_1$) (MW=338)
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