Chapter -4
Synthesis
Of
4-arylanilinomethyl
Coumarin
Derivatives
INTRODUCTION

The work to be described in this chapter involves the synthesis of various 7-carbethoxyamino-4-arylaminomethylcoumarins from 7-carbethoxyamino-4-bromomethylcoumarin and different primary amines. Coumarins with diverse structural features and versatile biological properties such as anti-microbial, anti-inflammatory and anti-HIV activities have been reviewed. Linkage of various alkyl or aryl moieties at any position of coumarins has resulted in novel molecular matrices which were associated with anti-microbial and anti-inflammatory agents has been reported. In view of this, a brief account of literature on the structure and biological activities of anilinomethyl coumarins is presented below.

Coumarins derivatives containing aniline linkages have been found to be extremely useful as anti-microbial, analgesic and anti-inflammatory agents. A variety of biologically important coumarin derivatives linked with different heterocycles via amine linkage has been reported in last decade. Kulkarni et al.\(^2\) have reported the synthesis and various pharmacological activities of the coumarinyl amines 1, 2 and 3.
Shastri et al.\textsuperscript{3} have reported the anti-inflammatory and analgesic activity of 4-aminophenol condensed ether 4 and amine 5 of 4-bromomethyl coumarins.

![Chemical Structures](image1)

Recently, the luminescent property of europium chealates of acylated 7-amino coumarins 6 has been used to label proteins at cysteine residues on synthetic oligonucleotides containing a free thiols group.\textsuperscript{4}

![Chemical Structures](image2)

The acidic character of coumarin antibiotics was reduced by designing number of 4-alkyl amino methyl coumarins and sulfides. The screening results of biological activity have indicated that the piperazine-condensed compound 7 was potent inhibitor of negative super coiling of DNA gyrase while the imidazolyl sulfide 8 exhibited a balanced activity against different species and resistant bacteria.\textsuperscript{5}
Introduction of above linkages with variety of other substituents into the coumarin ring was employed as a strategy to design anti-bacterial compounds and has resulted the synthesis of 4-arylaminomethyl coumarins. In this series, the most active compound was R= 6-Cl, which showed the growth inhibition of E.coli at 100µg/ml. In this sulphides, the benzthiazolyl sulphides (X= S) were more active than others. In this series, R = 6-Cl and R= 7-OCH₃ were effective against B. Subtilis and S. Aureus respectively.

Hanmantgad et al. synthesized various sulphanilamidomethyl coumarins 11 using 4-aminomethylcoumarins and various arylsufonyl chlorides. These compounds have been characterised by their spectral data and some of them show better anti-bacterial activity against S. aureus and E. coli than the standard (sulphanilamide). Structure activity relationship has also been studied.
Rajesh et al.\textsuperscript{10} reported the synthesis and crystal studies of 7-methyl-4-[(4'-fluoro) anilinomethyl] coumarin. The structure of the molecule reveals the molecule to be on-planar and the phenyl ring to be perpendicular to the coumarin ring.
PRESENT WORK

In the continuation of work, in the present investigation we focused our attention on the synthesis of 4-arylaminomethyl coumarins as showed in Scheme-15. The required 4-bromomethylcoumarins and 4-bromomethylcarbostyrils were prepared by according to reported method. The chemical structures of the compounds were established by elemental analysis; FT-IR and $^1$H NMR spectra and the results are presented in experimental part.

![SCHEME-15](image)

**SCHEME-15**

$X = O, NH$

(i) **Method-1:** xylene, 140°C, reflux (24h), RT

(ii) **Method-2:** DMSO, Stirr (12-14h), RT

RESULTS AND DISCUSSION

**Infrared spectral Studies**

The IR spectrum of compound 161 (Spectrum No.47) exhibited the carbonyl stretching frequency at 1707 cm$^{-1}$. The amide stretching was observed at 3346 cm$^{-1}$. The IR spectrum of all the compounds (156-173) had the characteristic C=O stretching band at 1700 - 1745 cm$^{-1}$ amide stretching frequency at 3200 – 3400 cm$^{-1}$ and C=C stretching band at 1400 – 1500 cm$^{-1}$ was observed in all the compounds respectively. The -CH stretching band is observed at 2920 - 2720 cm$^{-1}$, respectively.
**Synthesis of 4-arylaminoethylcoumarin derivatives**

**1H-NMR spectral studies**

The 1H NMR spectrum of compound 161 (Spectrum No. 49) showed a singlet at 12.39 ppm for NH proton [D2O exchangeable (Spectrum No. 50)]. A singlet resonated for C-5 proton of 6-methoxy substituted coumarin at δ 7.68 ppm, a multiplet for six protons at δ 7.14 – 7.55 ppm was observed for aromatic protons and another singlet at δ 6.43 ppm was observed for C-3 proton of 6-methoxy substituted coumarin, respectively. The spectrum showed a sharp singlet for methylene protons at δ 4.46 ppm. Two singlets were exhibited at δ 3.37 ppm and δ 2.09 ppm for methoxy and methyl protons respectively. The 1H NMR spectra of all the compounds (156-173) exhibited structure revealing proton signals at δ 8.50 - 6.20 ppm (m, t, dd, d for aromatic protons), δ 4.10 - 5.30 ppm (C4-CH2 protons), respectively with DMSO-d6 solvent peaks.

**13C-NMR spectral studies**

The 13C NMR spectrum of compound 161 (Spectrum No. 51) exhibited a peaks at δ 160.51 ppm, δ 159.96 ppm for carbonyl carbon atoms. The signals at δ 151.66 ppm, δ 152.25 ppm, δ 152.25 ppm, δ 147.38 ppm, δ 126.91 ppm, δ 126.12 ppm, δ 119.19 ppm, δ 117.53 ppm, δ 111.85 ppm, δ 108.62 ppm, δ 107.71 ppm, δ 104.07 ppm and δ 96.21 ppm were resonated for aromatic carbon atoms of coumarin rings, respectively. The peaks observed at δ 56.80 ppm for C4 - CH2 and methoxy carbon atoms. Two methyl carbon exhibited peak at δ 18.98 ppm. The 13C
NMR spectra of all the compounds (156-173) showed peaks at δ 190-150 ppm for carbonyl carbon and peaks showed between δ 95 - 152 ppm for aromatic carbon atoms, at δ 1 - 60 ppm methyl and methylene carbon atoms with DMSO-\(_d_6\) solvent peaks.

**GC-MS Studies**

The mass spectrums by electron ionization (EI) have been recorded for the synthesized compounds. The GC - MS of compound 161 (Spectrum No. 49) showed the moderate intensities of the molecular ion fragmentation peaks. In the chemical ionization mode the protonated molecular ion [m/z 174 (7-amino-4-methy coumarin ion)] was observed as the base peak. Mass fragmentation at 363 showed the formation of the compound 6-Methoxy-4-{{[(4-methyl-2-oxo-2H-chromen-7-yl)amino]methyl}-2H-chromen-2-one (161). The mass spectra of the compounds (156-173) showed peaks corresponding to their molecular ion.

The IR, GC-MS, \(^1\)H NMR, and \(^{13}\)C NMR spectra of compounds 156 and 173 are enclosed as Spectrum No. 47-51.

**EXPERIMENTAL SECTION:**

1. **General experimental procedure for the synthesis of 4-arylaminomethyl coumarins (156-173):**

   **Method-1:** A mixture of 4-bromomethyl coumarins / 4-bromomethyl carbostyril derivatives (0.004 mol) and 7-amino-4-methylcoumarin (0.004 mol) in super dry xylene (30 mL) were refluxed on an oil bath for 24 hr (135-148\(^0\)C). After the completion of the reaction, the separated solid was filtered, washed with excess of cold ethanol, dried and crystallized from suitable solvent.

   **Method-2:** A mixture of 4-bromomethyl coumarin / 4-bromomethyl carbostyril derivatives (0.004 mol) and 7-amino-4-methylcoumarin (0.004 mol) in DMSO (25
mL) were stirred at RT for 14 hr. After the completion of the reaction, the contents were poured to crushed ice and the separated solid was filtered, washed with excess of cold ethanol, dried and crystallized from suitable solvent.

The yields of the compounds obtained by these two methods are shown in Table -4.1.

**Table -4.1**

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Yield (%)</th>
<th>Method-1</th>
<th>Method-2</th>
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<tr>
<td>156</td>
<td>71</td>
<td>86</td>
<td></td>
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<tr>
<td>157</td>
<td>68</td>
<td>75</td>
<td></td>
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<td>158</td>
<td>63</td>
<td>94</td>
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<tr>
<td>159</td>
<td>68</td>
<td>89</td>
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<td>160</td>
<td>62</td>
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<td>60</td>
<td>87</td>
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<td>162</td>
<td>78</td>
<td>92</td>
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<tr>
<td>163</td>
<td>70</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>164</td>
<td>71</td>
<td>87</td>
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<td>165</td>
<td>62</td>
<td>90</td>
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<tr>
<td>166</td>
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<td>92</td>
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<td>167</td>
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<tr>
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</tr>
<tr>
<td>173</td>
<td>62</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>

The physical constants and analytical data of synthesized compounds (150-173) have been given below.

7-Methyl-4-([(4-methyl-2-oxo-2H-chromen-7-yl) amino] methyl)-2H-chromen-2-one 156:

- **Molecular Formula**: C_{21}H_{17}NO_{4}
- **Physical State**: Brown colour amorphous powder
- **mp[^{°}C]** : 218
- **GC-MS (m/z)** : 347
- **IR (KBr, cm^{-1})** : 3434, 1712 (C=O), 1698 (C=O).
Synthesis of 4-arylaminomethylcoumarin derivatives

$^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ : 7.81 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.56 (d, $J = 8.7$ Hz, 1H, Ar-H), 7.32 (s, 1H, Ar-H), 7.28 (d, $J = 2.8$ Hz, 1H, Ar-H), 7.15 (dd, $J = 2.8, 8.0$ Hz, 1H, Ar-H), 6.60 (s, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 6.12 (s, 1H, Ar-H), 5.90 (s, 1H, NH), 4.68 (s, 2H, CH$_2$), 2.30 (s, 3H, CH$_3$), 2.08 (s, 3H, CH$_3$).

$^{13}$C NMR (DMSO-$d_6$, 400 MHz) $\delta$ : 161.04, 160.53, 155.98, 154.15, 153.74, 153.67, 152.22, 143.49, 126.71, 125.91, 125.09, 117.13, 115.91, 111.23, 110.87, 110.13, 108.74, 97.69, 43.09, 21.57, 18.51.

Elemental analysis for C$_{21}$H$_{17}$NO$_4$ : Calcd - C, 72.61; H, 4.93; N, 4.03; found - C, 72.65; H, 4.97; N, 4.06.

6-Methyl-4-[[4-methyl-2-oxo-2H-chromen-7-yl) amino] methyl]-2H-chromen-2-one 157:

Molecular Formula : C$_{21}$H$_{17}$NO$_4$

Physical State : Light brown colour amorphous powder

mp[°C] : 184

GC-MS (m/z) : 347

IR (KBr, cm$^{-1}$) : 3346, 1707 (C=O), 1692 (C=O).

$^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ : 7.74 (d, $J = 8.2$ Hz, 1H, Ar-H), 7.45 (d, $J = 8.7$ Hz, 1H, Ar-H), 7.04 (dd, $J = 2.3, 8.21$ Hz, 1H, Ar-H), 6.99 (t, $J = 2.5$ Hz, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 6.65 (s, 1H, Ar-H), 6.34 (s, 1H, Ar-H), 6.12 (s, 1H, NH), 6.02 (s, 1H, Ar-H), 4.63 (s, 2H, CH$_2$), 2.83 (s, 3H, CH$_3$), 2.28 (s, 3H, CH$_3$).

Elemental analysis for C$_{21}$H$_{17}$NO$_4$ : Calcd - C, 72.61; H, 4.93; N, 4.03; found - C, 72.66; H, 4.96; N, 4.05.
6-Chloro-4-[(4-methyl-2-oxo-2\textit{H}-chromen-7-yl) amino] methyl]-2\textit{H}-chromen-2-one 158:

**Molecular Formula**: C\textsubscript{20}H\textsubscript{14}NClO\textsubscript{4}  
**Physical State**: Yellow colour amorphous powder  
**\(mp[^{\circ}C]\)**: 158

**GC-MS (m/z)**: 367 (M+), 369 (M+2)  
**IR (KBr, cm\textsuperscript{-1})**: 3373, 1717 (C=O), 1702 (C=O).

**\(^{1}\text{H} \text{NMR (DMSO-d\textsubscript{6}, 400 MHz)} \delta****: 7.78 (d, \(J = 8.0 \text{ Hz}, 1\text{H, Ar-H}\)), 7.69 (d, \(J = 8.7 \text{ Hz}, 1\text{H, Ar-H}\)), 7.30 (s, 1\text{H, Ar-H})), 7.21 (dd, \(J = 2.8, 8.0 \text{ Hz}, 1\text{H, Ar-H}\)), 7.14 (dd, \(J = 2.8, 8.0 \text{ Hz}, 1\text{H, Ar-H}\)), 6.68 (s, 1\text{H, Ar-H})), 6.31 (s, 1\text{H, Ar-H})), 6.11 (s, 1\text{H, Ar-H})), 5.94 (s, 1\text{H, NH})), 4.70 (s, 2\text{H, CH}_2)), 1.84 (s, 3\text{H, CH}_3)).

**Elemental analysis for C\textsubscript{20}H\textsubscript{14}NClO\textsubscript{4}**: Calcd - C, 65.31; H, 3.84; N, 3.81; found - C, 65.35; H, 3.87; N, 3.85.

7-Chloro-4-[(4-methyl-2-oxo-2\textit{H}-chromen-7-yl) amino] methyl]-2\textit{H}-chromen-2-one 159:

**Molecular Formula**: C\textsubscript{20}H\textsubscript{14}NClO\textsubscript{4}  
**Physical State**: Brown colour amorphous powder  
**\(mp[^{\circ}C]\)**: 172

**GC-MS (m/z)**: 367 (M+), 369(M+2)  
**IR (KBr, cm\textsuperscript{-1})**: 3420, 1720 (C=O), 1701 (C=O).

**\(^{1}\text{H} \text{NMR (DMSO-d\textsubscript{6}, 400 MHz)} \delta****: 7.58-7.66 (m, 2\text{H, Ar-H})), 7.62 (d, \(J = 8.7 \text{ Hz}, 1\text{H, Ar-H})), 7.45 (t, \(J = 2.8, 8.0 \text{ Hz}, 1\text{H, Ar-H})), 6.91 (s, 1\text{H, Ar-H})), 6.36 (s, 1\text{H, Ar-H})), 6.21
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Elemental analysis for \( \text{C}_{20}\text{H}_{14}\text{NClO}_{4} \) : Calcd - C, 65.31; H, 3.84; N, 3.81; found - C, 65.36; H, 3.87; N, 3.84.

7-Methoxy-4-[(4-methyl-2-oxo-2H-chromen-7-yl) amino] methyl]-2H-chromen-2-one 160:

Molecular Formula : \( \text{C}_{21}\text{H}_{17}\text{NO}_{5} \)

Physical State : Brown colour amorphous powder

\( mp[^{\circ}C] \) : 268

\( \text{GC-MS (m/z)} \) : 363

\( \text{IR (KBr, cm}^{-1}) \) : 3439, 1732 (C=O), 1708 (C=O).

\( ^{1}\text{H NMR (DMSO-d}_6, 400 \text{ MHz)} \) \( \delta \) : 7.71 (d, \( J = 8.7 \text{ Hz, 1H, Ar-H} \)), 7.40 (d, \( J = 8.7 \text{ Hz, 1H, Ar-H} \)), 7.16 (t, \( J = 5.4 \text{ Hz, 1H, Ar-H} \)), 6.92 (dd, \( J = 2.5, 8.7 \text{ Hz, 1H, Ar-H} \)), 6.88 (s, 1H, Ar-H), 6.61 (s, 1H, Ar-H), 6.42 (s, 1H, Ar-H), 6.08 (s, 1H, Ar-H), 5.98 (s, 1H, NH), 4.72 (s, 2H, CH\(_2\)), 3.68 (s, 3H, OCH\(_3\)), 2.26 (s, 3H, CH\(_3\)).

\( ^{13}\text{C NMR (DMSO-d}_6, 400 \text{ MHz)} \) \( \delta \) : 162.97, 161.06, 160.74, 155.97, 155.54, 154.19, 153.92, 152.25, 126.73, 126.49, 112.70, 111.74, 110.87, 110.09, 108.98, 108.71, 101.37, 97.65, 56.47, 43.11, 18.52.

Elemental analysis for \( \text{C}_{21}\text{H}_{17}\text{NO}_{5} \) : Calcd - C, 69.41; H, 4.72; N, 3.85; found - C, 69.45; H, 4.75; N, 3.88.

6-Methoxy-4-[(4-methyl-2-oxo-2H-chromen-7-yl) amino] methyl]-2H-chromen-2-one 161:

Molecular Formula : \( \text{C}_{21}\text{H}_{17}\text{NO}_{5} \)

Physical State : Brown colour amorphous powder
Synthesis of 4-arylaminomethylcoumarin derivatives

mp[°C] : 228
GC-MS (m/z) : 363
IR (KBr, cm⁻¹) : 3330, 1710 (C=O), 1698 (C=O).

\(^1\)H NMR (DMSO-d₆, 400 MHz) δ : 7.79 (d, J = 8.7 Hz, 1H, Ar-H), 7.62 (d, J = 8.7 Hz, 1H, Ar-H), 7.45 (t, J = 5.4 Hz, 1H, Ar-H), 7.15 (dd, J = 2.5, 8.7 Hz, 1H, Ar-H), 6.92 (s, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 6.56 (s, 1H, Ar-H), 6.32 (s, 1H, Ar-H), 5.90 (s, 1H, NH), 4.58 (s, 2H, CH₂), 3.72 (s, 3H, OCH₃), 2.32 (s, 3H, CH₃).

Elemental analysis for C₂₁H₁₇NO₅ : Calcd - C, 69.41; H, 4.72; N, 3.85 ; found - C, 69.44; H, 4.75; N, 3.89.

6-Flouro-4-\{[(4-methyl-2-oxo-2H-chromen-7-yl) amino] methyl\}-2H-chromen-2-one 162:

\begin{center}
\textbf{Molecular Formula} : C₂₀H₁₄NFO₄  \\
\textbf{Physical State} : Brown colour amorphous powder  \\
mp[°C] : 148
\end{center}

GC-MS (m/z) : 351
IR (KBr, cm⁻¹) : 3359, 1725 (C=O), 1699 (C=O).

\(^1\)H NMR (DMSO-d₆, 400 MHz) δ : 7.60-7.72 (m, 2H, Ar-H), 7.45-7.52 (m, 2H, Ar-H), 6.95 (s, 1H, Ar-H), 6.32 (s, 1H, Ar-H), 6.25 (s, 1H, Ar-H), 6.11 (s, 1H, Ar-H), 5.96 (s, 1H, NH), 4.55 (s, 2H, CH₂), 1.86 (s, 3H, CH₃).

Elemental analysis for C₂₀H₁₄NFO₄ : Calcd - C, 68.37; H, 4.02; N, 3.99 ; found – C, 68.42; H, 4.05; N, 4.04.

7-Flouro-4-\{[(4-methyl-2-oxo-2H-chromen-7-yl) amino] methyl\}-2H-chromen-2-one 163:

\textbf{Molecular Formula} : C₂₀H₁₄NFO₄
Physical State: Brown colour amorphous powder

mp[°C] : 176

GC-MS (m/z) : 351

IR (KBr, cm\(^{-1}\)) : 3373, 1717 (C=O), 1702 (C=O).

\(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) : 7.68 (dd, 1H, Ar-H), 7.51 (d, 21H, Ar-H), 7.12 (t, 1H, Ar-H), 6.95 (t, 1H, Ar-H), 6.66 (s, 1H, Ar-H), 6.42 (s, 1H, Ar-H), 6.20 (s, 1H, Ar-H), 6.04 (s, 1H, Ar-H), 5.92 (s, 1H, NH), 4.32 (s, 2H, CH\(_2\)), 1.80 (s, 3H, CH\(_3\)).

Elemental analysis for C\(_{20}\)H\(_{14}\)NFO\(_4\) : Calcd - C, 68.37; H, 4.02; N, 3.99; found – C, 68.40; H, 4.06; N, 4.02.

5, 7-Dimethyl-4-[(4-methyl-2-oxo-2\(H\)-chromen-7-yl) amino] methyl]-2\(H\)-chromen-2-one 164:

Molecular Formula : C\(_{22}\)H\(_{19}\)NO\(_4\)

Physical State: Cream colour amorphous powder

mp[°C] : 210

GC-MS (m/z) : 361

IR (KBr, cm\(^{-1}\)) : 3363, 1711 (C=O), 1695 (C=O).

\(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) : 7.44-7.56 (m, 2H, Ar-H), 6.81 (s, 1H, Ar-H), 6.72 (s, 1H, Ar-H), 6.30 (s, 1H, Ar-H), 6.26 (s, 1H, Ar-H), 6.10 (s, 1H, Ar-H), 5.98 (s, 1H, NH), 4.58 (s, 2H, CH\(_2\)), 2.76 (s, 3H, CH\(_3\)), 2.38 (s, 3H, CH\(_3\)), 1.35 (s, 3H, CH\(_3\)).

Elemental analysis for C\(_{22}\)H\(_{19}\)NO\(_4\) : Calcd - C, 73.12; H, 5.30; N, 3.88; found - C, 73.16; H, 5.34; N, 3.91.
7, 8-Dimethyl-4-[[4-methyl-2-oxo-2H-chromen-7-yl] amino] methyl]-2H-chromen-2-one 165:

**Molecular Formula**: $C_{22}H_{19}NO_4$

**Physical State**: Cream colour amorphous powder

$mp[^{\circ}C]$ : 184

**GC-MS ($m/z$)** : 361

**IR (KBr, cm$^{-1}$)** : 3384, 1720 (C=O), 1701 (C=O).

$^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ : 7.52-7.67 (m, 2H, Ar-H), 7.47 (d, 1H, $J = 7.83$ Hz, Ar-H), 7.11 (d, 1H, $J = 8.31$ Hz, Ar-H), 6.50 (s, 1H, Ar-H), 6.42 (s, 1H, Ar-H), 6.25 (s, 1H, Ar-H), 6.12 (s, 1H, NH), 4.70 (s, 2H, CH$_2$), 2.37 (d, 6H, $J = 9.29$ Hz, CH$_3$), 1.72 (s, 3H, CH$_3$).

Elemental analysis for $C_{22}H_{19}NO_4$ : Calcd - C, 73.12; H, 5.30; N, 3.88; found - C, 73.15; H, 5.35; N, 3.93.

1-((4-Methyl-2-oxo-2H-chromen-7-ylamino)methyl)-3H-benzo[f] chromen-3-one 166:

**Molecular Formula**: $C_{24}H_{17}NO_4$

**Physical State**: Cream colour amorphous powder

$mp[^{\circ}C]$ : 206

**GC-MS ($m/z$)** : 383

**IR (KBr, cm$^{-1}$)** : 3363, 1730 (C=O), 1711 (C=O).

$^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ : 8.50 - 8.58 (m, 1H, Ar-H), 7.87 (d, $J = 6.02$ Hz, 1H, Ar-H), 7.74 (m, 2H, Ar-H), 7.60 - 7.68 (m, 4H, Ar-H), 6.65 (s, 1H, Ar-H), 6.50 (s, 1H, Ar-H), 6.32 (s, 1H, Ar-H), 6.12 (s, 1H, NH), 4.78 (s, 2H, CH$_2$), 1.84 (s, 3H, CH$_3$).
Elemental analysis for C_{24}H_{17}NO_{4} : Calcd - C, 75.19; H, 4.47; N, 3.65; found - C, 75.23; H, 4.50; N, 3.68.

4-((4-Methyl-2-oxo-2H-chromen-7-ylamino)methyl)-2H-benzo[h] chromen-2-one 167:

**Molecular Formula** : C_{24}H_{17}NO_{4}

**Physical State** : Gray colour amorphous powder

mp[^oC] : 232

**GC-MS (m/z)** : 383

**IR (KBr, cm^{-1})** : 3386, 1731 (C=O), 1706 (C=O).

^1H NMR (DMSO-d_6, 400 MHz) δ : 8.40 (d, J = 8.53 Hz, 1H, Ar-H), 8.11 (d, J = 9.03 Hz, 1H, Ar-H), 7.92 (d, J = 8.03 Hz, 1H, Ar-H), 7.68 (t, J = 8.20 Hz, 1H, Ar-H), 7.52 (t, J = 7.84 Hz, 1H, Ar-H), 7.40 (d, J = 8.03 Hz, 1H, Ar-H), 7.36 (dd, J = 2.0, 8.03 Hz, 2H, Ar-H), 6.68 (s, 1H, Ar-H), 6.39 (s, 1H, Ar-H), 6.10 (s, 1H, Ar-H), 5.84 (s, 1H, NH), 5.12 (s, 2H, CH_2), 1.72 (m, 3H, CH_3).

Elemental analysis for C_{24}H_{17}NO_{4} : Calcd - C, 75.19; H, 4.47; N, 3.65; found – C, 75.22; H, 4.50; N, 3.69.

Methyl 4-((4-methyl-2-oxo-2H-chromen-7-ylamino) methyl)-2-oxo-2H-chromen-7-ylcarbamate 168:

**Molecular Formula** : C_{22}H_{18}N_{2}O_{6}

**Physical State** : Yellow colour amorphous powder

mp[^oC] : 188

**GC-MS (m/z)** : 406

**IR (KBr, cm^{-1})** : 3420, 3356, 1726 (C=O), 1710 (C=O), 1688 (NHC=O).

^1H NMR (DMSO-d_6, 400 MHz) δ : 7.74 (d, J = 6.84 Hz, 1H, Ar-H), 7.68 (d, J =
Synthesis of 4-arylaminomethylcoumarin derivatives

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6.84 Hz, 1H, Ar-H), 7.48 (s, 1H, Ar-H), 7.36 (t, J = 6.88 Hz, 1H, Ar-H), 7.22 (t, J = 6.88 Hz, 1H, Ar-H), 7.09 (s, 1H, NH), 6.42 (s, 1H, Ar-H), 6.30 (s, 1H, Ar-H), 6.20 (s, 1H, Ar-H), 5.94 (s, 1H, NH), 4.78 (s, 2H, CH₂), 3.81 (s, 3H, OCH₃), 1.80 (s, 3H, CH₃).

Elemental analysis for C₂₂H₁₈N₂O₆: Calcd - C, 65.02; H, 4.46; N, 6.89; found - C, 65.05; H, 4.49; N, 6.94.

Ethyl 4-((4-methyl-2-oxo-2H-chromen-7-ylamino) methyl)-2-oxo-2H-chromen-7-ylcarbamate 169:

Molecular Formula: C₂₃H₂₀N₂O₆
Physical State: Brown colour amorphous powder
mp[°C]: 206
GC-MS (m/z): 420
IR (KBr, cm⁻¹): 3411, 3390, 1730 (C=O), 1713 (C=O), 1692 (NHC=O).

¹H NMR (DMSO-d₆, 400 MHz) δ: 7.72 (d, J = 6.96 Hz, 1H, Ar-H), 7.49 (s, 1H, Ar-H), 7.41 (t, J = 6.88 Hz, 1H, Ar-H), 7.32 (dd, J = 1.92, 6.82 Hz, 2H, Ar-H), 7.23 (t, J = 6.88 Hz, 1H, Ar-H), 6.91 (s, 1H, NH), 6.46 (s, 1H, Ar-H), 6.28 (s, 1H, Ar-H), 5.92 (s, 1H, NH), 4.72 (s, 2H, CH₂), 4.24 (q, J = 6.72 Hz, 2H, CH₂), 1.82 (s, 3H, CH₃), 1.41 (t, 3H, CH₃).

Elemental analysis for C₂₃H₂₀N₂O₆: Calcd - C, 65.71; H, 4.79; N, 6.66; found - C, 65.75; H, 4.83; N, 6.69.

4-((4-Methyl-2-oxo-2H-chromen-7-ylamino) methyl)quinolin-2(1H)-one 170:

Molecular Formula: C₂₀H₁₆N₂O₃
Physical State: Brown colour amorphous powder
mp[°C]: 226
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GC-MS (m/z) : 332

IR (KBr, cm⁻¹) : 3420, 3280, 1720 (C=O), 1698 (C=O) 1655 (NHC=O).

¹H NMR (DMSO-d₆, 400 MHz) δ : 12.21 (s, 1H, NH), 7.80 (dd, J = 2.0, 8.20 Hz, 2H, Ar-H), 7.44 - 7.53 (m, 2H, Ar-H), 7.28 - 7.37 (m, 2H, Ar-H), 6.78 (s, 1H, Ar-H), 6.67 (s, 1H, Ar-H), 6.45 (s, 1H, Ar-H), 5.98 (s, 1H, NH), 2.12 (s, 2H, CH₂), 1.78 (s, 3H, CH₃).

Elemental analysis for C₂₀H₁₆N₂O₃ : Calcd - C, 72.28; H, 4.85; N, 8.43; found – C, 72.32; H, 4.88; N, 8.47.

8-Methyl-4-((4-methyl-2-oxo-2H-chromen-7-ylamino) methyl) quinolin-2(1H)-one 171:

Molecular Formula : C₂₁H₁₈N₂O₃

Physical State : Gray colour amorphous powder

mp[^°C] : 234

GC-MS (m/z) : 346

IR (KBr, cm⁻¹) : 3421, 3274, 1733 (C=O), 1698 (NHC=O).

¹H NMR (DMSO-d₆, 400 MHz) δ : 10.00 (s, 1H, NH), 7.65-7.72 (m, 2H, Ar-H), 7.38 (t, J = 7.28 Hz, 1H, Ar-H), 7.21 - 7.32 (m, 2H, Ar-H), 6.70 (s, 1H, Ar-H), 6.57 (s, 1H, Ar-H), 6.32 (s, 1H, Ar-H), 6.10 (s, 1H, NH), 4.72 (s, 2H, CH₂), 2.56 (s, 3H, CH₃), 1.72 (s, 3H, CH₃).

Elemental analysis for C₂₁H₁₈N₂O₃ : Calcd - C, 72.82; H, 5.24; N, 8.09; found – C, 72.85; H, 5.28; N, 8.14.

5, 8-Dimethyl-4-((4-methyl-2-oxo-2H-chromen-7-ylamino) methyl) quinolin-2(1H)-one 172:

Molecular Formula : C₂₂H₂₀N₂O₃

Physical State : Cream colour amorphous powder
Synthesis of 4-arylaminomethylcoumarin derivatives

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\text{mp}[^{\circ}\text{C}] : 246
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\text{GC-MS (m/z)} : 360
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\text{IR (KBr, cm}^{-1}) : 3392, 3245, 1720 (\text{C}=\text{O}), 1691 (\text{NHC}=\text{O}).
\]

\[\text{H NMR (DMSO-}d_6, 400 \text{ MHz)} \delta : 10.22 (s, 1H, NH), 7.70 (dd, J = 7.42Hz, 2H, Ar-H), 6.92 (m, 2H, Ar-H), 6.78 (s, 1H, Ar-H), 6.50 (s, 1H, Ar-H), 6.26 (s, 1H, Ar-H), 6.14 (s, 1H, NH), 4.74 (s, 2H, CH₂), 2.86 (s, 3H, CH₃), 2.32 (s, 3H, CH₃), 1.80 (s, 3H, CH₃).\]

Elemental analysis for \(\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_3\) : Calcd - C, 73.32; H, 5.59; N, 7.77; found - C, 73.35; H, 5.63; N, 7.80.

7-Chloro-4-((4-methyl-2-oxo-2H-chromen-7-ylamino) methyl) quinolin-2(1H)-one 173:

\[
\text{Molecular Formula} : \text{C}_{20}\text{H}_{15}\text{N}_2\text{ClO}_3
\]

\[
\text{Physical State} : \text{Cream colour amorphous powder}
\]

\[
\text{mp}[^{\circ}\text{C}] : 228
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\[
\text{GC-MS (m/z)} : 366 (M+), 368(M+2)
\]

\[
\text{IR (KBr, cm}^{-1}) : 3455, 3366, 1718 (\text{C}=\text{O}), 1662 (\text{NHC}=\text{O}).
\]

\[\text{H NMR (DMSO-}d_6, 400 \text{ MHz)} \delta : 11.94 (s, 1H, NH), 7.81 (d, J = 8.78 Hz, 1H, Ar-H), 7.44 (s, 1H, Ar-H), 7.32 (t, J = 8.53 Hz, 1H, Ar-H), 7.21 (d, J = 8.70 Hz, 1H, Ar-H), 6.92 (t, J = 8.52 Hz, 1H, Ar-H), 6.85 (s, 1H, Ar-H), 6.31 (s, 1H, Ar-H), 6.24 (s, 1H, Ar-H), 6.10 (s, 1H, NH), 5.90 (s, 1H, NH), 4.79 (s, 2H, CH₂), 1.80 (s, 3H, CH₃).\]

Elemental analysis for \(\text{C}_{20}\text{H}_{15}\text{N}_2\text{ClO}_3\) : Calcd - C, 65.49; H, 4.12; N, 7.64; found – C, 65.53; H, 4.15; N, 7.68.
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REFERENCE


