Chapter –2

Synthesis of $\beta$-amino carbonyl derivatives containing coumarin and benzofuran nucleus
Chapter-2 \( \beta \)-amino carbonyl derivatives of coumarin and benzofuran

2.1 Introduction

The Mannich reaction is a three-component condensation reaction involving active hydrogen and is one of the most important carbon-carbon bond forming reactions in organic synthesis [1, 2]. It affords synthetically and biologically important \( \beta \)-amino carbonyl compounds which are important intermediates for the construction of various nitrogen-containing natural products and pharmaceuticals [3]. They are also used as synthetic building blocks and precursors of pharmaceutically valuable heterocyclic compounds [4]. \( \beta \)-Amino ketones find use as photo initiators in printing applications and as intermediates for the preparation of antibiotics, antibiotic enhancers or enzyme inhibitors. In recent years, Mannich bases have gained importance due to their application in pharmaceutical chemistry. They have been found to possess antibacterial, antifungal, anticancer [5, 6], antitubercular [7] analgesic and anti-inflammatory [8] properties. Now a days, the use of Mannich bases in cancer therapy is one of the several current areas of research. On the other hand, they have many attractive applications in paint and polymer chemistry [9].

One-pot Mannich reactions using the unmodified aldehydes or ketone as reactants have been reported, and a variety of Bronsted or Lewis acid catalysts such as Zn (OTf)_2 [10, 11], H_3PW_{12}O_{40}, ZrOCl_2.8H_2O, DBSA, Salen Zn complex, SSA, HClO_4–SiO_2, and NbCl_5 [12], have been investigated. However, they often suffer from the drawbacks of long reaction times and harsh reaction conditions, toxicity, and difficulty in product separation, which limit its use in the synthesis of complex molecules. Furthermore, some of them are corrosive and volatile, and often cause the environment problems. Therefore, the development of simple, efficient, high yielding and environmental friendly methods using new catalysts for the Mannich reaction is still necessary.

Ceric (IV) ammonium nitrate (CAN)

Ceric (IV) ammonium nitrate (CAN) is a convenient and widely used reagent for affecting wide array of synthetic transformations. CAN has emerged as an important reagent for the construction of carbon-carbon and carbon–heteroatom bonds and has great deal of attention. In addition, many advantages such as excellent solubility in water, cost-effectiveness, eco-friendly nature, easy handling, high reactivity, and easy work-up procedures make CAN a potent catalyst in organic synthesis. Besides, CAN is able to
catalyze various organic transformations not only based on its electron transfer capacity but also with its Lewis acidic property [13]. Due to the numerous advantages associated with this eco-friendly compound, CAN has been explored as a powerful catalyst for different reactions such as oxidation, nitration, 1, 3-dipolar cycloaddition, thiocyanation, protection, esterification, 1, 4-addition, and the Biginelli reaction [14].

Indeed, the Lewis acidity of CAN has recently allowed many synthetically important organic transformations using catalytic amounts of the reagent [15] to be carried out, and if this chemistry continues to be successfully implemented, CAN will become an alternative to the hygroscopic and highly expensive lanthanide triflate Lewis acids.

**CAN catalyzed reactions**

Mazaahir et al reported Ceric ammonium nitrate (CAN) catalyzed three component Mannich reaction of acetophenone with aromatic aldehydes and aromatic amines in polyethylene glycol 1. This protocol has advantages of high yield, mild reaction conditions, no environmental pollution and simple work up procedure [16].

\[
\text{\textbf{R}} - \text{H, 4-CH}_3, 4-\text{OCH}_3, 4-\text{NO}_2, 4-\text{Br}
\]

Hong-Juan Wang et al reported the synthesis of functionalized tetrahydropyridines 2 by a multicomponent condensation reaction of \(\beta\)-keto ester with two equivalents of aromatic aldehyde, and two equivalents of amine in the presence of a catalytic amount of cerium ammonium nitrate (CAN) [17].
Recently, Hua et al synthesized a series of Bismuth (III) chloride catalyzed β-amino carbonyl compounds 3(a-z) using aromatic ketone, aldehyde and amine [18].

\[
\text{Ar} - \text{CHO} + \text{NH}_2 \xrightarrow{\text{BiCl}_3} \text{Ar} - \text{CHN} \text{Ar} + \text{CHO}
\]

Pawel et al synthesized a series of acid-catalyzed β-amino carbonyl compounds 4(a-h) using dihydroxyacetone, p-anisidine, and aldehydes in high yield [19].

\[
\text{OH} + \text{Ar} - \text{NH}_2 + \text{H} - \text{CHO} \xrightarrow{\text{Amino acid}} \text{HO} + \text{HO} + \text{CH}_3
\]

Suman et al reported the β-amino carbonyl compound 5 by Mannich reaction using ionic liquid as a catalyst. The ionic liquid was easily separated from the reaction mixture by water extraction and was recycled four times without any loss in activity [20].

\[
\text{CH}_3 + \text{CHO} + \text{NH}_2 \xrightarrow{\text{Ionic liquid}} \text{HO} + \text{HO} + \text{CH}_3
\]

**Benzofurans**

Benzo[b]furan derivatives are an important class of organic compounds, which are known to be present in many natural products and possess physiological activity [21]. Several benzofuran ring systems bearing various substituents at the C-2 position are widely distributed in nature, e.g., ailanthoidol, a neolignan derivative, has been reported to have antiviral, antioxidant and antifungal activities [22]. Furthermore, most of compounds prepared from 2-acetylbenzofurans have antimicrobial, antitumor, anti-inflammatory, fungicidal weed-killing activity, and used for treatment of cardiac
arrhythmias [23-27]. Moreover, benzofurans are building blocks for fluorescent sensors [28] and are used as brighteners. Many of natural benzofurans have physiological, pharmacological and toxic properties, and therefore there is continuing interest in their chemical synthesis [29].

Murti et al reported Mannich reaction of 2-acetyl benzofuran with various amines which upon reduction with NaBH₄ gave corresponding benzofuranoaminopropan-1-ols 6(a-d) [30].

\[
\text{NR}_{2}= 4\text{-phenylpiperazino, piperidine, morpholino, 4\text{-}(2\text{-methylphenyl}) piperazino}
\]

John B. Wright et al in 1960 synthesized benzofuran Mannich base analogues by the reaction of 3-(dichloroamino)-2-phenoxy-1-phenylpropan-1-one with polyphosphoric acid 7(a-h) [31].

George et al synthesized benzofuran Mannich bases 8(a-k) by condensation-cyclisation of o-ethyl phenol with secondary amines and paraformaldehyde on cuprous iodide doped alumina under solvent free and microwave irradiation conditions which generated the 2-(dialkylaminomethyl)-benzo[b]furans in good yield [32].
Rao et al reported benzofuran Mannich bases 9(a-h) under solvent free, PTSA/PTC catalytic conditions assisted by microwave irradiation [9].

Coumarins

Coumarins are compounds that display a special role in nature. Pharmacologically, coumarins and their derivatives are included in the family of the flavonoids and exhibit a variety of interesting biological and pharmacological activity. Therefore, coumarins and their derivatives have raised considerable interest because of their potential beneficial effects on human health [33]. They have been reported to possess antibacterial [34, 35], antioxidant [36], anti-HIV [37-39], anticoagulant [40], anticancer [41], anthelmintic [42] and anti-inflammatory [43, 44] activities. As a result, coumarin and their derivatives have been the subject of extensive investigations. Coumarins contain the parent nucleus of benzo-α-pyrone and occur in plants of the families like Orchidaceae, Leguminaceae, Rutaceae, Umbelliferae and Libiatae [45]. A number of synthetic protocols have been applied for the synthesis of nitrogen containing coumarin derivatives [46-49]. Mannich reaction [50] is the best way to synthesize such type of compounds.

Atul et al reported the synthesis of novel benzyl amino coumarin derivatives 10(m-n) via Mannich type reaction in aqueous media catalyzed by non-ionic surfactant [51].
Yashumati et al synthesized coumarin Mannich bases 11(a-d) by the reaction of 7-hydroxy-4-methyl coumarin, paraformaldehyde and appropriate amine using conventional as well as microwave methods [52].

![Chemical structure](image)

**11(a-d)**

β-Amino carbonyl compounds obtained by Mannich reaction have been known to be crucial intermediates in the synthesis of pharmaceutical ingredients and natural products [53]. Therefore, much consideration has been drawn for the development of new synthetic methods to prepare these compounds.

### 2.2 Present work

In view of above facts, and with the belief that the assimilation of more than one bio-potent nucleus into a single structure may furnish novel heterocycles with stimulating antimicrobial and antioxidant activity, we have made an attempt to synthesize highly atom-economic functionalized β-amino carbonyl compounds of coumarin and benzofuran by one-pot, three component reaction using CAN as an efficient catalyst.

In the present investigation, coumarins 4(a-h)/benzofuran 6(a-i) containing β-amino carbonyl derivatives were synthesized through one pot, three component reaction between p-substituted aromatic aldehydes, aniline/p-amino benzoic acid and 3-acetyl-2H-chromen-2-one (1)/1-(1-benzofuran-2-yl) ethanone (5) in the presence of catalytic amount of CAN respectively. In the initial studies, this reaction was performed using common Lewis acids such as ZnCl2, CuCl2, AlCl3, FeCl3, LaCl3, InCl3 and CAN. Among these, CAN was found to be the most efficient catalyst for this transformation resulting in highest conversion to the desired product.

With the intention to optimize the reaction condition, experiments were focused on the effect of solvents on reaction time (Table 2.1). Methanol, Ethanol, acetonitrile, water and solvent free media were tried and ethanol was observed to be the preferred solvent in this reaction.
We also studied the amount of CAN catalyst required to get the desired compounds in good yield. Generally, there was no reaction in the absence of catalyst. Using 1 equivalent of benzaldehyde, 1 equivalent of 3-acetyl-2H-chromen-2-one, 1 equivalent of aniline and variable amount of CAN, the experiments showed that 10 mol % of CAN (based on benzaldehyde) could effectively catalyze the reaction. Increase in the amount of CAN (20 mol %) had no substantial improvement in the yield (Table 2.2).

The optimum ratio of benzaldehyde, 3-acetyl-2H-chromen-2-one, aniline and CAN was found to be 1:1:1:0.1. Encouraged from the above results, we extended this method for the synthesis of 1-(1-benzofuran-2-yl)-3-phenyl-3-(phenyl amino) propan-1-one 6(a-i) derivatives. The optimum ratio of benzaldehyde, 1-(1-benzofuran-2-yl) ethanone, aniline and CAN was found to be 1:1:1:0.07. Effect of solvents and reaction conditions for the synthesis of compounds 4(a-h) and 6(a-i) derivatives have been given in Table 2.2.

Table 2.1 Effect of solvent on the synthesis of compounds 4(a-h) and 6(a-i)

<table>
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<th>Time(h)</th>
<th>Yield (%)</th>
<th>Entry</th>
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Table 2.2 Synthesis of compounds 4(a-h) and 6(a-i) at different molar ratio of catalyst and reactants

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<th>No.</th>
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<th>PhNH₂ (mmol)</th>
<th>CAN (mmol)</th>
<th>Yield %</th>
<th>No.</th>
<th>PhCOCH₃ (mmol)</th>
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Page 50
Chapter-2  \( \beta \)-amino carbonyl derivatives of coumarin and benzo furan

The synthesis of \( \beta \)-amino carbonyl compounds of Coumarin 4(a-h) and benzofuran 6(a-i) involved the following steps.

1. Synthesis of 3-acetyl-2\(H\)-chromen-2-one (1) from salicylaldehyde and ethyl acetoacetate
2. Reaction of 3-acetyl-2\(H\)-chromen-2-one (1) with \( p \)-substituted aromatic aldehydes 2(a-g) and aromatic amines 3(a-b) to give 4(a-h).
4. Reaction of 1-(1-benzofuran-2-yl) ethanone (5) with \( p \)-substituted aromatic aldehydes 2(a-g) and aromatic amines 3(a-b) to give 6(a-i).

The schematic representation of the synthesized molecules is given in Scheme-1 and 2.

2.2.1 Synthesis of 3-acetyl-2\(H\)-chromen-2-one (1)

A mixture of salicylaldehyde and ethyl acetoacetate was taken in a round bottom flask and stirred at 0-5°C in ethanol with catalytic amount of piperidine to furnish the compound 3-acetyl coumarin.

\[
\text{OH} + \text{O} \quad \text{piperidine/EtOH} \quad \text{Stirring/0-5°C} \quad \text{O} \quad \text{1}
\]

The formation of compound 1 was confirmed by comparing its m.p with literature value [55].

2.2.2 Synthesis of \( \beta \)-amino carbonyl compounds containing coumarin nucleus (4a-h)

When a mixture of 3-acetyl-2\(H\)-chromen-2-one (1), \( p \)-substituted aromatic aldehydes (2a-g) and aniline/p-aminobenzoic acid (3a-b) was stirred at 60°C in the presence of ceric ammonium nitrate as a catalyst, we got the title compounds (4a-h).
The structure of newly synthesized compounds 4(a-h) was confirmed by IR, $^1$H NMR, $^{13}$C NMR and Mass spectral studies. The IR spectrum of compound 4e exhibited broad absorption band at 3327 cm$^{-1}$ attributed to carboxylic O-H group and the band at 1740 cm$^{-1}$ corresponds to C=O group. The two absorption bands at 1677 and 1680 cm$^{-1}$ corresponds to lactone C=O and acetyl C=O groups. The $^1$H NMR spectrum of compound 4e displayed a broad singlet at δ 10.68 ppm due to carboxylic -OH proton and a multiplet between δ 6.48-7.83 ppm due to aromatic protons. The compound showed a triplet at δ 4.72 ppm and a broad singlet at δ 4.3 ppm due to -CH and NH proton. Compound 4e displayed a doublet at δ 3.47 ppm which corresponds to two methylene (-CH$_2$) protons. Further, the formation of compound 4e confirmed by $^{13}$C NMR spectrum. The compound 4e showed a signal at δ 200.40 and 194.61 ppm corresponds to acetyl C=O and lactone C=O group. Another signal at δ 170.09 ppm corresponds to carbon of carboxylic C=O group. Mass spectrum of the compound 4e displayed a molecular ion peak [M$^+$] at m/z 447 corresponding to the molecular mass of the compound and isotopic peak at m/z 449 [M+2].
Chapter-2

β-amino carbonyl derivatives of coumarin and benzofuran

IR spectrum of compound 4e

'H NMR spectrum of compound 4e
Chapter 2

β-amino carbonyl derivatives of coumarin and benzofuran

$^{13}$C NMR spectrum of compound 4e
**β-amino carbyl derivatives of coumarin and benzofuran**

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**Location:** Vial 53

**Injection Time:** 11:19:45 AM  
**Inj. Vol.:** 10 µl

**Sample Name:** B-040211-3,0023

**Acq. Operator:**  
**Acq. Method:** ACIDIC

**Sample Info:** Ka,B-040211-3,0023

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### Mass spectrum of compound 4e

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**Instrument:** Agilent 6330 Ion Trap  
**Instrument Code:** BIL/LAB/RND/001

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**Signal 1:** DAD 1, Sig=220, Ref-off

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**Print Date:** 08/02/2011 6:39:49 PM

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**Intens. [x10^5]**

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**Mass spectrum of compound 4e**

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2.2.3 Synthesis of 2-acetyl benzofurans 5

The compound, 2-acetyl benzofuran 5 was synthesized according to reported method and the formation of compounds 5 was confirmed by comparing its melting point with literature value [54].

2.2.4 Synthesis of β-amino carbonyl compounds containing benzofuran nucleus 6(a-i)

A mixture of 3-acetyl-2H-chromen-2-one 5, \( p \)-substituted aromatic aldehydes 2(a-g) and aniline/\( p \)-aminobenzoic acid 3(a-b) was stirred at 60 °C in the presence of ceric ammonium nitrate as a catalyst to furnish title compounds 6(a-i).

![Scheme-2](image)

<table>
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<th>( R' )</th>
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</table>

The structure of newly synthesized compounds 6(a-i) was confirmed by IR, \(^1\)H NMR, \(^{13}\)C NMR and Mass spectral studies. The IR spectrum of compound 6f displayed broad absorption band at 3450 cm\(^{-1}\) attributed to carboxylic O-H group and the band at 3210 cm\(^{-1}\)corresponds to NH stretching vibration. The other two absorption bands.
at 1739 and 1620 cm\(^{-1}\) corresponds to two C=O groups. The \(^1\)H NMR spectrum of compound 6f exhibited a broad singlet at \(\delta\) 10.41 ppm corresponds to carboxylic –OH proton and a multiplet between \(\delta\) 6.54-7.90 ppm due to aromatic protons. The compound 6f showed a triplet at \(\delta\) 5.22 ppm and a broad singlet at \(\delta\) 4.76 ppm corresponds to -CH and NH proton. The doublet appeared at \(\delta\) 3.53 ppm due to two methylene (-CH\(_2\)) protons. Further, the formation of compound 6f confirmed by \(^{13}\)C NMR spectrum. The compound 6f showed a signal at \(\delta\) 200.40 and 170.69 ppm corresponds to acetyl C=O and carboxylic C=O group respectively. Mass spectrum of the compound 6f displayed a molecular ion peak at m/z 419 [M\(^+\)] corresponding to the molecular mass of the compound and isotopic peak at m/z 421 [M+2].

**General mechanism for synthesis of \(\beta\)-amino carbonyl derivatives of coumarin and benzofuran**
IR spectrum of compound 6f

^1H NMR spectrum of compound 6f
$^{13}$C NMR spectrum of compound 6f
Chapter 2

β-amino carbonyl derivatives of coumarin and benzofuran

Sample Report:

Sample Name: FT053-097
Date File: 04/09/2011
Report Code: 0824D17-004

UPLC Report

Sample Report:

3: UV Detector: TIC Smooth (R, 3x3)

Peak ID | Time | M/z | Area
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2       | 0.66  | 223 | 88.4
3       | 0.82  | 223 | 88.4
4       | 1.67  | 223 | 88.4
5       | 1.83  | 223 | 88.4
6       | 2.00  | 223 | 88.4
7       | 2.16  | 223 | 88.4
8       | 2.32  | 223 | 88.4
9       | 2.48  | 223 | 88.4
10      | 2.64  | 223 | 88.4

Peak ID | Time | M/z | Area
------- | ----- | ---- | ----
1       | 0.40  | 223 | 88.4
2       | 0.66  | 223 | 88.4
3       | 0.82  | 223 | 88.4
4       | 1.67  | 223 | 88.4
5       | 1.83  | 223 | 88.4
6       | 2.00  | 223 | 88.4
7       | 2.16  | 223 | 88.4
8       | 2.32  | 223 | 88.4
9       | 2.48  | 223 | 88.4
10      | 2.64  | 223 | 88.4

Sample Report (continued):

Peak ID | Time | M/z | Area
------- | ----- | ---- | ----
9       | 0.91  | 223 | 88.4
10      | 1.06  | 223 | 88.4

Mass spectrum of compound 6f
2.3 Experimental

2.3.1 3-Acetyl-2H-chromen-2-one (1)

A mixture of salicylaldehyde (0.5g, 0.0041 mol) and ethyl acetoacetate (0.53g, 0.0041mol) was taken in a round bottom flask containing 10-15 ml of dry ethanol. To this, 1ml of piperidine was added. The mixture was stirred at 0°C for about 7-8 h. The completion of the reaction mixture was monitored by TLC. The residue was filtered and dried. It was recrystallized from dry ethanol, the pure compound separates out (m.p. 119-121 °C).

2.3.2 Synthesis of compounds 4(a-h)

General procedure:

An equimolar quantity of 3-acetyl-2H-chromen-2-one (1) (0.0026 mol), p-substituted aromatic aldehyde (0.0026 mol) and aromatic amine (0.0026 mol) in ethanol (50 mL) was taken in 100 mL round bottomed flask and stirred at 60°C. To this, 10 mol% of ceric ammonium nitrate was added and the stirring was continued for 6 h. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled, poured into crushed ice and neutralized using 10% NaHCO₃ solution. The precipitated product was filtered, dried and recrystallized from ethanol. The product was further purified by column chromatography eluting with petroleum ether, ethyl acetate mixture (80:20, v/v).

3-[3-Phenyl-3-(phenyl amino) propanoyl]-2H-chromen-2-one (4a)

Yellow solid; Yield-79%, m.p. 160-163 °C; IR (KBr, v max, cm⁻¹): 3290 (NH), 2850 (Ar-CH), 1677 (coumarin C=O), 1710 (C=O free ketone); ¹H NMR (400 MHz, DMSO, δ ppm) 7.93 (d, J = 9.2 Hz, 2H, Ar-H), 7.54-7.0 (m, lOH), 7.03 (t, J = 7.6 Hz, 2H), 6.63 (t, J = 7.4 Hz, 1H), 4.43 (t, J = 6.64 Hz, 1H, CH), 4.3 (br s, 1H, NH), 3.42 (dd, J₁ = 6.8, J₂ = 13.3 Hz); ¹³CNMR (300 MHz, DMSO, δ ppm): 200.01 (C=O), 194.61, 174.78, 173.74, 172.54, 162.74, 158.61, 153.53, 151.17, 140.88, 140.10, 133.20, 130.78, 119.97, 118.17, 116.50, 108.20, 107.78, 64.00, 45.00; MS (LCMS): m/z 370 [M+1]. Mol.Formula: C₂₄H₁₉NO₃.
4-([3-Oxo-3-(2-oxo-2H-chromen-3-yl)-1-phenylpropyl] amino) benzoic acid (4b)

Colorless solid, Yield-90%, m.p. 162-165 °C; IR (KBr, $\nu_{\text{max}}, \text{cm}^{-1}$): 3463 (O-H), 3280 (NH), 2850 (Ar-CH), 1773 (C=O of carboxylic), 1677 (coumarin C=O), 1695 (free C=O); $^1$H NMR (400 MHz, DMSO, $\delta$ ppm): 10.41 (s, 1H, OH), 7.87 (d, J = 9 Hz, 2H, Ar-H), 7.41-7.30 (m, 5H), 7.21-7.01 (m, 5H), 6.48 (d, J = 7.56 Hz, 2H), 4.45 (t, J = 5.72 Hz, 1H, CH), 4.2 (br s, 1H, NH), 3.41 (dd, J1 = 6.9 Hz, J2 = 13.4 Hz); $^{13}$CNMR (300 MHz, DMSO, $\delta$ ppm): 200.33 (C=O), 194.61, 174.78, 173.74, 172.54, 170.09 (C=O, carboxylic), 162.74, 158.61, 153.53, 142.00, 140.10, 137.00, 133.20, 129.03, 119.97, 118.17, 107.78, 64.00, 45.00; MS (LCMS): m/z 413. Mol.Formula: C$_{25}$H$_{19}$NO$_5$.

4-([1-(4-Methylphenyl)-3-oxo-3-(2-oxo-2H-chromen-3-yl) propyl] amino) benzoic acid (4c)

Off-white solid, Yield-86%, m.p. 158-162 °C; IR (KBr, $\nu_{\text{max}}, \text{cm}^{-1}$): 3459 (O-H), 3250 (NH), 2851 (Ar-CH), 1740 (C=O of carboxylic), 1679 (coumarin C=O), 1699 (free C=O); $^1$H NMR (400 MHz, DMSO, $\delta$ ppm): 10.41 (s, 1H, OH), 7.87 (d, J = 9 Hz, 2H, Ar-H), 7.41-7.30 (m, 5H), 7.28 (d, J = 8.7 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 6.48 (d, J = 7.56 Hz, 2H), 5.42 (t, J = 6.87 Hz, 1H, CH), 4.0 (br s, 1H, NH), 3.41 (dd, J1 = 6.6 Hz, J2 = 13.2 Hz), 2.261 (s, 3H); $^{13}$CNMR (300 MHz, DMSO, $\delta$ ppm): 200.40 (C=O), 195.61, 174.78, 173.74, 172.54, 171.09 (C=O, carboxylic), 163.74, 158.61, 153.53, 142.00, 141.10, 137.00, 131.20, 130.78, 129.03, 118.17, 114.06, 64.00, 45.00, 22.10; MS (LCMS): m/z 425. Mol.Formula: C$_{26}$H$_{21}$NO$_5$.

4-([1-(4-Methoxyphenyl)-3-oxo-3-(2-oxo-2H-chromen-3-yl) propyl] amino) benzoic acid (4d)

Colorless solid, Yield-83%, m.p. 160-164 °C; IR (KBr, $\nu_{\text{max}}, \text{cm}^{-1}$): 3439 (O-H), 3310 (NH), 2855 (Ar-CH), 2850 (C=O), 1740 (C=O of carboxylic), 1678 (coumarin C=O), 1695 (free C=O); $^1$H NMR (400 MHz, DMSO, $\delta$ ppm): 10.76 (s, 1H, OH), 7.86 (d, J = 9 Hz, 2H, Ar-H), 7.43-7.32 (m, 5H), 7.26 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 6.48 (d, J = 7.56 Hz, 2H), 5.42 (t, J = 6.87 Hz, 1H, CH), 4.3 (br s, 1H, NH), 3.47 (dd, J1 = 6.5 Hz, J2 = 13.0 Hz), 2.27 (s, 3H); $^{13}$CNMR (300 MHz, DMSO, $\delta$ ppm): 200.21 (C=O), 195.61, 175.78, 173.74, 171.54, 169.09 (C=O, carboxylic), 162.74, 155.61, 153.53, 142.00, 140.10, 136.00, 132.20, 130.78, 118.17, 114.06, 52.00, 45.03, 34.20; MS (LCMS): m/z 444 [M+1]. Mol.Formula: C$_{26}$H$_{21}$NO$_6$. 
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4-[[1-(4-Chlorophenyl)-3-oxo-3-(2-oxo-2H-chromen-3-yl) propyl] amino] benzoic acid (4e)

Off-white solid, Yield-85%, m.p.165-169 °C; IR (KBr, $\nu_{max}$, cm$^{-1}$): 3327 (O-H), 3200 (NH), 2855 (Ar-CH), 1740 (C=O of carboxylic), 1677 (coumarin C=O), 1680 (free C=O); $^1$H NMR (400 MHz, DMSO, δ ppm): 10.68 (s, 1H, OH), 7.83 (d, J = 8.6 Hz, 2H, Ar-H), 7.41-7.29 (m, 5H), 7.23 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 6.48 (d, J = 7.56 Hz, 2H), 4.72 (t, J = 4.93 Hz, 1H, CH), 4.3 (br s, 1H, NH), 3.47 (dd, J1 = 6.5 Hz, J2 = 13.0 Hz); $^{13}$CNMR (300 MHz, DMSO, δ ppm): 200.35 (C=O), 194.61, 175.78, 173.74, 172.54, 170.90 (C=O, carboxylic), 162.74, 157.61, 153.53, 142.00, 140.10, 137.02, 133.20, 130.78, 129.06, 127.05, 114.17, 64.00, 45.00; MS (LCMS): m/z 449 [M], 451[M+2]. Mol.Formula: C$_{25}$H$_{17}$ClNO$_5$.

4-[[1-(4-Fluorophenyl)-3-oxo-3-(2-oxo-2H-chromen-3-yl) propyl] amino] benzoic acid (4f)

Pale yellow solid, Yield-76%, m.p.161-164 °C; IR (KBr, $\nu_{max}$, cm$^{-1}$): 3325 (O-H), 3270 (NH), 2865 (Ar-CH), 1743 (C=O of carboxylic), 1683 (coumarin C=O), 1681 (free C=O); $^1$H NMR (400 MHz, DMSO, δ ppm): 10.65 (s, 1H, OH), 7.85 (d, J = 8.4 Hz, 2H, Ar-H), 7.41-7.26 (m, 5H), 7.27 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 6.70 (d, J = 7.56 Hz, 2H), 4.75 (t, J = 4.93 Hz, 1H, CH), 4.6 (br s, 1H, NH), 3.43 (dd, J1 = 6.4 Hz, J2 = 12.30 Hz ); $^{13}$CNMR (300 MHz, DMSO, δ ppm): δ 200.39 (C=O), 194.61, 174.78, 173.74, 172.54, 170.90 (C=O, carboxylic), 162.74, 157.61, 153.53, 142.00, 140.10, 137.02, 133.20, 130.78, 129.06, 127.05, 114.17, 64.00, 45.00; MS (LCMS): m/z 431 [M]. Mol.Formula: C$_{25}$H$_{18}$FNO$_5$.

4-[[1-(4-Nitrophenyl)-3-oxo-3-(2-oxo-2H-chromen-3-yl) propyl] amino] benzoic acid (4g)

Colorless solid, Yield-91%, m.p.75-80 °C; IR (KBr, $\nu_{max}$, cm$^{-1}$): 3459 (O-H), 3260 (NH), 2865 (Ar-CH), 1746 (C=O of carboxylic), 1678 (coumarin C=O), 1682 (free C=O), 1557 (NO$_2$); $^1$H NMR (400 MHz, DMSO, δ ppm): 10.74 (s, 1H, OH), 7.84 (d, J = 8.6 Hz, 2H, Ar-H), 7.43-7.28 (m, 5H), 7.25 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 7.55 Hz, 2H), 4.80 (t, J = 4.93 Hz, 1H, CH), 4.6 (br s, 1H, NH), 3.47 (dd, J1 = 6.5 Hz, J2 = 11.20 Hz, 2H); $^{13}$CNMR (300 MHz, DMSO, δ ppm): 200.35 (C=O), 194.61, 175.78, 173.74, 171.54, 170.90 (C=O, carboxylic), 162.74, 157.61, 153.53, 142.00,
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139.10, 137.021, 133.20, 130.78, 129.06, 127.05, 113.17, 64.00, 45.00; MS (LCMS): m/z 459 [M +1]. Mol.Formula: C\(_{25}\)H\(_{18}\)N\(_2\)O\(_7\).

4-\{(1-(4-Dimethylaminophenyl)-3-oxo-3-(2-oxo-2H-chromen-3-yl) propyl] amino\] Benzoic acid (4h)

Brown solid, Yield-75%, m.p. 155-158 °C; IR (KBr, \(v_{max}\), cm\(^{-1}\)): 3455 (O-H), 3310 (NH), 2860 (Ar-CH), 1741 (C=O of carboxylic), 1675 (coumarin C=O), 1685 (free C=O); \(^1\)H NMR (400 MHz, DMSO, \(\delta\) ppm): 10.74 (s, 1H, OH), 7.83 (d, J = 8.9 Hz, 2H, Ar-H), 7.49-7.35 (m, 5H), 7.26 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.53 Hz, 2H), 6.49 (d, J = 7.55 Hz, 2H), 5.28 (t, J = 6.91 Hz, 1H, CH), 4.6 (br s, 1H, NH), 3.47 (dd, J\(_1\) = 6.5 Hz, J\(_2\) = 13.0 Hz), 2.75 (s, 6H, H\(_3\)C-N-CH\(_3\)); \(^{13}\)CNMR (300 MHz, DMSO, \(\delta\) ppm): 200.26 (C=O), 194.61, 175.78, 173.74, 171.54, 170.09 (C=O, carboxylic), 162.74, 157.61, 153.53, 142.00, 139.10, 137.021, 133.20, 130.78, 129.06, 127.05, 37.51, 34.20, 32.50, 22.10 (H\(_3\)C-N-CH\(_3\)); MS (LCMS): m/z 457 [M+1]. Mol.Formula: C\(_{27}\)H\(_{24}\)N\(_2\)O\(_5\).

2.3.3 Synthesis of 1-(1-benzofuran-2-yl) ethanone (5)

Salicylaldehyde (0.08 mol) was taken in 50 ml of absolute ethanol. To this, KOH (0.08 mol) pellets were added and the reaction mixture was stirred for 5 minutes. Then chloroacetone (0.08 mol) was added drop-wise in about 10 minutes and the resulting reaction mixture was allowed to stir for 20 minutes. Catalytic amount of potassium iodide was used in the reaction. The reaction mass was poured into the crushed ice, the solid obtained was filtered and recrystallized from ethanol to get pale yellow crystalline solid (5).

2.3.4 Synthesis of compounds 6(a-i)

General procedure:

In 100ml round bottom flask, 1-(1-benzofuran-2-yl) ethanone (5) (0.003mol), \(p\)-substituted aromatic aldehyde (0.003mol) and aromatic amine (0.003mol) in absolute ethanol (50mL) were taken stirred at 60 °C. To this, 7 mol% CAN was added and the stirring was continued for 5-6 that that temperature. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled, poured into crushed ice and neutralized using 10% NaHCO\(_3\) solution. The precipitated product was filtered, dried and recrystallized using ethanol. The product was further purified by
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Silica gel column chromatography eluting with petroleum ether, ethyl acetate mixture (80:20, v/v) to yield the β-amino carbonyl compounds 6(a–i).

1-(1-Benzofuran-2-yl)-3-phenyl-3-(phenyl amino) propan-1-one (6a)

Green solid, Yield-83%, m.p.90-95 °C; IR (KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3300 (NH), 2850 (Ar-CH), 1695 (free C=O); $^1$H NMR (400 MHz, DMSO, $\delta$ ppm): 7.83 (d, J = 9.3 Hz, 2H, Ar-H), 7.56-7.10 (m, 10H), 7.03 (t, J = 7.2 Hz, 1H), 5.32 (t, J = 6.56 Hz, 1H, CH), 4.6 (br s, 1H, NH), 3.45 (dd, $J_1 = 6.5$, $J_2 = 11.3$ Hz, 2H); $^{13}$C NMR (300 MHz, DMSO, $\delta$ ppm): 339.00 (C=O), 193.61, 175.78, 174.74, 172.54, 163.74, 157.61, 153.53, 151.17, 140.88, 140.10, 133.20, 127.78, 119.97, 118.17, 115.50, 108.78, 78.28, 78.28; MS (LCMS): m/z 341. Mol. Formula: C$_{23}$H$_{19}$NO$_2$.

1-(1-Benzofuran-2-yl)-3-(4-methoxyphenyl)-3-(phenyl amino) propan-1-one (6b)

Brown solid, Yield-79%, m.p.101-105 °C; IR (KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3280 (NH), 2858 (Ar-CH), 1701 (free C=O); $^1$H NMR (400 MHz, DMSO, $\delta$ ppm): 7.84 (d, J = 9.3 Hz, 2H, Ar-H), 7.45-7.33 (m, 5H), 7.31-7.28 (m, 5H), 6.48 (d, J = 7.56 Hz, 2H), 4.49 (t, J = 5.71 Hz, 1H, CH), 4.8 (br s, 1H, NH), 3.41 (dd, $J_1 = 6.9$ Hz, $J_2 = 13.4$ Hz, 2H), 2.25 (s, 3H); $^{13}$C NMR (300 MHz, DMSO, $\delta$ ppm): 339.00 (C=O), 193.61, 175.78, 174.74, 172.54, 163.74, 157.61, 153.53, 151.17, 142.20, 140.10, 133.20, 127.78, 119.50, 118.17, 115.50, 108.78, 60.50, 52.10, 41.80; MS (LCMS): m/z 372 [M+1]. Mol. Formula: C$_{24}$H$_{21}$NO$_3$.

4-[(3-(1-Benzofuran-2-yl)-3-oxo-1-phenylpropyl) amino] benzoic acid (6c)

Yellow solid, Yield-89%, m.p.90-95 °C; IR (KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3455 (OH), 1693 (free C=O); $^1$H NMR (400 MHz, DMSO, $\delta$ ppm): 10.43 (s, 1H, OH), 7.89 (d, J = 9.2 Hz, 2H, Ar-H), 7.48-7.30 (m, 5H), 7.32-7.29 (m, 5H), 6.46 (d, J = 7.51 Hz, 2H), 4.50 (t, J = 5.71 Hz, 1H, CH), 4.6 (br s, 1H, NH), 3.43 (dd, $J_1 = 6.6$ Hz, $J_2 = 10.4$ Hz, 2H); $^{13}$C NMR (300 MHz, DMSO, $\delta$ ppm): 200.30 (C=O), 195.61, 174.58, 173.00, 172.64, 170.01 (C=O, carboxylic), 162.74, 158.61, 153.53, 142.00, 140.10, 133.20, 137.00, 130.78, 129.03, 121.58, 118.17, 63.00, 42.00; MS (LCMS): m/z 386 [M+1]. Mol. Formula: C$_{24}$H$_{21}$NO$_4$.

4-(3-(Benzofuran-2-yl)-1-(4-methylphenyl)-3-oxopropylamin) benzoic acid (6d)

Pale yellow solid, Yield-77%, m.p. 99-103 °C; IR (KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3420 (OH), 1697 (free C=O); $^1$H NMR (400 MHz,
4-(3-(Benzo[1-furan-2-yl]-1-(4-methoxyphenyl)-3-oxopropylamino) benzoic acid (6e)
Brown solid, Yield-84%, m.p.110-114°C; IR (KBr, \( \nu_{\text{max}} \), cm\(^{-1} \)): 3415 (O-H), 3200 (NH), 2859 (Ar-CH), 1776 (C=O of carboxylic), 1698 (free C=O); \(^1\)H NMR (400 MHz, DMSO, \( \delta \) ppm): 10.69 (s, 1H, OH), 7.93 (d, J = 9.5 Hz, 2H, Ar-H), 7.56-7.43 (m, 5H), 7.35 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 6.48 (d, J = 7.50 Hz, 2H), 3.49 (dd, J\(_1\) = 6.3 Hz, J\(_2\) = 9.6 Hz, 2H), 2.31 (s, 3H); \(^1^3\)C NMR (300 MHz, DMSO, \( \delta \) ppm): 200.40 (C=O), 195.61, 174.78, 173.74, 171.54, 169.09 (C=O, carboxylic), 162.74, 158.61, 153.53, 141.00, 132.20, 127.30, 119.07, 114.06, 91.40, 89.50, 60.80, 41.80, 34.20; MS (LCMS): m/z 416 [M+1]. Mol. Formula: C\(_{25}\)H\(_{21}\)NO\(_5\).

4-(3-(Benzo[1-furan-2-yl]-1-(4-chlorophenyl)-3-oxopropylamino) benzoic acid (6f)
Colorless solid, Yield-76%, m.p.107-110°C; IR (KBr, \( \nu_{\text{max}} \), cm\(^{-1} \)): 3450 (O-H), 3210 (NH), 2855 (Ar-CH), 1739 (C=O of carboxylic), 1620 (free C=O); \(^1\)H NMR (400 MHz, DMSO, \( \delta \) ppm): 10.41 (s, 1H, OH), 7.90 (d, J = 8.50 Hz, 2H, Ar-H), 7.71-7.59 (m, 5H), 7.48 (d, J = 8.61 Hz, 2H), 7.37 (d, J = 8.42 Hz, 2H), 6.54 (d, J = 7.64 Hz, 2H), 3.53 (dd, J\(_1\) = 6.3 Hz, J\(_2\) = 9.70 Hz, 2H); \(^1^3\)C NMR (300 MHz, DMSO, \( \delta \) ppm): 200.40 (C=O), 194.61, 174.78, 173.74, 172.54, 170.69 (C=O, carboxylic), 162.74, 158.61, 153.53, 142.00, 140.10, 137.00, 134.50, 130.78, 129.06, 127.03, 121.17, 63.00, 41.00; MS (LCMS): m/z 419 [M], 421[M+2]. Mol. Formula: C\(_{24}\)H\(_{18}\)ClNO\(_4\).

4-((3-[1-Benzofuran-2-yl]-1-(4-fluorophenyl)-3-oxopropyl] amino) benzoic acid (6g)
Brown solid, Yield-81%, m.p.103-106°C; IR (KBr, \( \nu_{\text{max}} \), cm\(^{-1} \)): 3470 (br, O-H), 3305 (narrow strong, NH), 2875 (Ar-CH), 1743 (C=O of carboxylic), 1659 (free C=O); \(^1\)H NMR (400 MHz, DMSO, \( \delta \) ppm): 10.68 (s, 1H, OH), 7.88 (d, J = 8.82 Hz, 2H,
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4-(3-(Benzofuran-2-yl)-1-(4-nitrophenyl)-3-oxopropylamino) benzoic acid (6h)
Pale yellow solid, Yield-75%, m.p. 105-108 °C; IR (KBr, v_max, cm⁻¹): 3249 (NH), 2873 (Ar-CH), 1726 (C=O of carboxylic), 1667 (free C=O), 1552 (NO₂);

1H NMR (400 MHz, DMSO, δ ppm): 10.54 (s, 1H, OH), 7.87 (d, J = 8.54 Hz, 2H, Ar-H), 7.46-7.32 (m, 5H), 7.28 (d, J = 8.92 Hz, 2H), 7.26 (d, J = 8.42 Hz, 2H), 6.75 (d, J = 7.53 Hz, 2H), 4.93 (t, J = 4.93 Hz, 1H, CH), 4.82 (br s, 1H, NH), 3.43 (dd, J₁ = 7.5 Hz, J₂ = 10.20 Hz, 2H);

13CNMR (300 MHz, DMSO, δ ppm): 200.30 (C=O), 194.61, 175.78, 173.74, 170.89 (C=O, carboxylic), 162.74, 157.61, 149.00, 139.10, 137.02, 133.20, 130.78, 129.06, 127.05, 114.17, 65.00, 42.00; MS (LCMS): m/z 430. Mol. Formula: C₂₄H₁₈N₂O₆.

4-(3-(Benzofuran-2-yl)-1-(4-(dimethyl amino) phenyl)-3-oxopropylamino) benzoic acid (6i)
Brown solid, Yield-87%, m.p. 110-114 °C; IR (KBr, v_max, cm⁻¹): 3431 (O-H), 2870 (Ar-CH), 1721 (C=O of carboxylic), 1659 (free C=O);

1H NMR (400 MHz, DMSO, δ ppm): 10.53 (s, 1H, OH), 7.89 (d, J = 8.68 Hz, 2H, Ar-H), 7.52-7.38 (m, 5H), 7.29 (d, J = 8.43 Hz, 2H), 7.23 (d, J = 8.56 Hz, 2H), 6.52 (d, J = 7.65 Hz, 2H), 5.29 (t, J = 6.92 Hz, 1H, CH), 4.72 (br s, 1H, NH), 3.50 (dd, J₁ = 6.45 Hz, J₂ = 11.10 Hz), 2.73 (s, 6H, H₃C-N-CH₃);

13CNMR (300 MHz, DMSO, δ ppm): 200.40 (C=O), 196.61, 176.68, 173.74, 171.54, 170.09 (C=O, carboxylic), 161.74, 156.61, 153.53, 142.00, 139.10, 137.20, 136.021, 132.20, 130.78, 129.06, 114.00, 64.00, 44.60 (H₃C-N-CH₃), 41.76; MS (LCMS): m/z 429 [M+1]. Mol. Formula: C₂₆H₂₄N₂O₄.
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