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# Novel Anilino Coumarins' Multistep Production And In Vitro Bio-Evaluation

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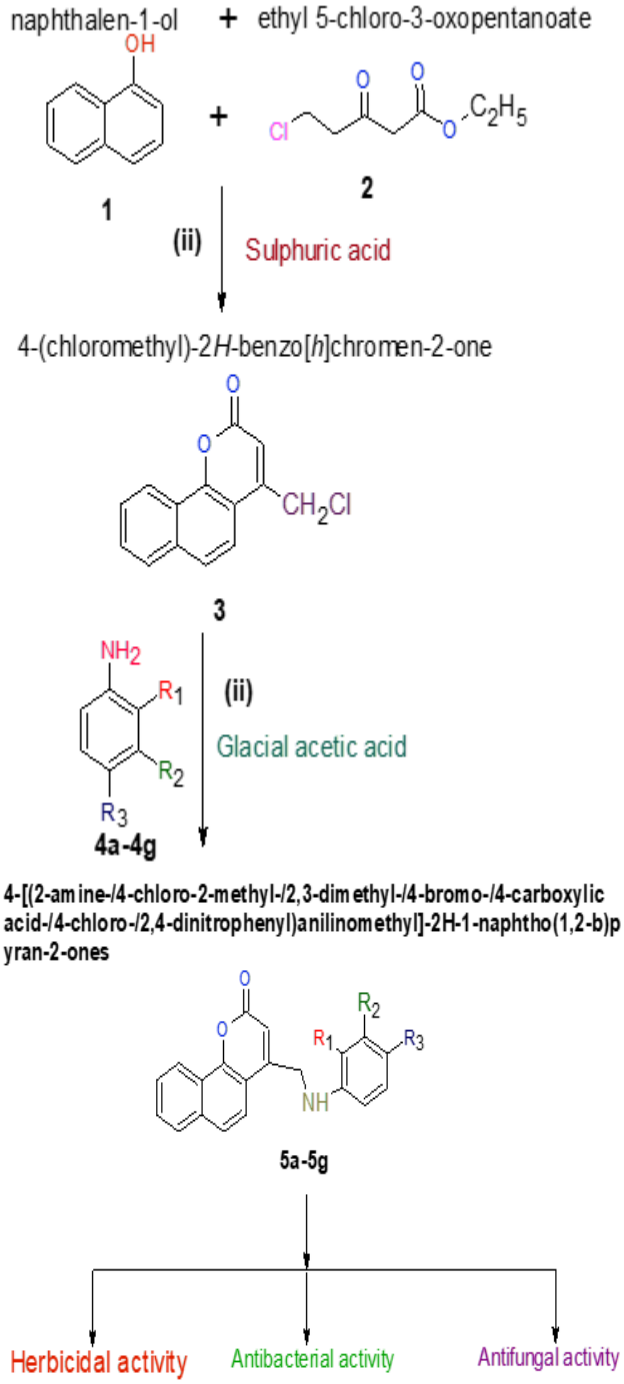
**Abstract:**

This research provides a simple and environmentally friendly multistep process for the synthesis of amino substituted coumarin (**5a-5g**) using glacial acetic acid, 73% $H_2SO_4$, and 5% HCl as solvents in the condensation reaction between -naphthol (**1**) and ethyl-4-chloroacetoacetate (**2**). Through thin layer chromatography and melting point, the purity of the chemicals that were converted was shown. All synthetic compounds have undergone thorough characterization using Data from NMR and FTIR spectroscopy and their effectiveness as an in vitro herbicide against seeds of Raphanus sativus L. (Radish) has also been evaluated. The substances antibacterial activity against Bacillus had also been shown. Antifungal activity turned into also determined towards strategies technique. From result of activity data, it became determined that compounds **5c** and **5g** had been confirmed highest growth inhibition against R. sativus L. (root) and R. sativus L. (shoot), respectively. Compounds **5b**, **5c** and **5g** were located maximum energetic against Bacillus species at all of the concentrations. Compound **5c** become confirmed maximum fungal toxicity in opposition to Rhizoctonia solani.

## Graphic abstract:




**Keywords:**Coumarin, substituted anilines, $H_2SO_4$, glacial acetic acid, antifungal, antibacterial, herbicidal activity

## Introduction:

Agrochemicals had played a significant role to increase the yields of various food commodities by protecting crops from insects and pests. Without these chemicals it would have not been possible to provide food for ever increasing population of our country since independence. Carvalho, (2017) studied the current demand of agrochemicals to increases the food production to feed a rapid growing human population to maintain pressure on the intensive use of pesticides and fertilizers. Bhandari, (2014) reported the pesticides involve chemically synthesized compounds, devices or organisms that are routinely utilized in agriculture to manage, destroy or repel pests, pathogens or parasites. The development of synthetic methods has helped a lot in this direction by synthesizing large number of molecules. Heterocyclic compounds are an important class of naturally occurring substances that contain at least one atom in addition to the carbon atom in their ring. Numerous biological activities are displayed by heterocyclic compounds with nitrogen, sulphur, and oxygen atoms, and these activities rely on the number of heteroatoms, the size of the ring, and the

shape of the compound. Anilino substituted coumarins, a bicyclic molecule with a coumarin ring fused to a substituted aniline nucleus, are unquestionably one of the most significant nitrogen and oxygen-containing moiety. The oxygen and nitrogen in the rings of amino coumarin molecules are what gives them their biological action. Many coumarin compounds have a variety of biological effects, including antibacterial, antifungal, herbicidal, antiviral, anticancer, antimalarial, and antitumor properties. There are numerous artificial methods available for creating coumarin derivatives.

## Experimental

Onboard the electric device, the melting point is tested for the Gensen melting factor. On silica gel G TLC plates, the homogeneity of the compounds is frequently checked using ethyl acetate:hexane (3:7) as the eluent. At the "Perkin Elmer FTIR" spectrophotometer in KBr, FTIR spectra were captured, and frequencies were recorded in $cm^{-1}$. Tetramethylsilane (TMS) was used as an internal reference for recording $^1$HNMR spectra on a "BrukerAvance II 400F" (400MHz) 1HNMR spectrophotometer in $CDCl_3$ or DMSO-$d_6$. While the value of J is expressed in Hz, the value of the chemical shift is expressed in units (ppm).

## Bio evaluation

## Herbicidal activity

The test chemical was produced as a solution in DMSO at 50, 100, and 150 μg/ml concentrations. After being dissolved, the agar powder (5 g) is added to 1 L of distilled water that has been heated to a rolling boil. Solution (2 ml) containing test chemicals was combined with molten agar (18 ml) and put in a 4.5 cm diameter Petri dish. Untreated controls have included agar plates without look at substances. On the agar plate's surface were seeds from the radish plant *Raphanus sativus* L. The cultivation conditions were maintained alternatively for 7 days at 25°C, 12 hours of light, and 12 hours of darkness in a petri dish covered with a glass lid in the night. *Raphanus sativus* L. roots and shoots were measured seven days later. A predetermined formula was used to calculate the rate of growth inhibition bound to the untreated control.

$$\% \text{ inhibition} = \frac{C - T}{C} \times 100$$

Mycelia development in the control dish, C
T = Mycelia growth following treatment in a dish.

## Antibacterial activity

On Luria-Bertanimedium, the Bacillus strain was cultured in the laboratory. The zone inhibition approach was used to assess antibacterial activity. A suitable amount of a manufactured substance at a concentration of 50, 100, 150, or 200 μg/ml was obtained from the stock solution and diluted with DMSO. DMSO served as the adverse control. Whatman's No. 1 filter paper was used to create circular paper discs with a 10 mm diameter. Discs were placed in a Petri dish and autoclaved at 15 lbs of pressure for 20 minutes. For each concentration of the synthetic substance, two paper discs were employed. Holding the paper disc vertically with sterile forceps allowed excess solution absorbed by the paper disc to be removed.

## Anti-fungal properties

The antifungal efficacy of the produced compounds (**5a–5g**) against Rhizoctonia *solani* and Aspergillusniger, respectively, has been tested. On potato dextrose agar, the fungi have been cultured in a lab (PDA). The food poisoning approach was used to gauge the antifungal activity. An aliquot of 99 ml of sterile potato dextrose agar was aseptically mixed with the needed quantity of synthetic chemical, which was dissolved in 1 mL of DMSO. After a brief period of stirring, the mixture was chilled to 45 ° C. The 23-day-old fungal colony's surrounding 5 mm of mycelium was centrally implanted onto each plate. Colony diameters were periodically measured while for 48–72 hours, inoculation Petri plates were kept in the dark at 25 ° C, almost fully covering the control plate. Three times each observation has been made. Using the equation

$$\% \text{ inhibition} = \frac{C - T}{C} \times 100$$

Mycelia development in the control dish is represented by the letter C.
T stands for mycelia growth in the test dish.

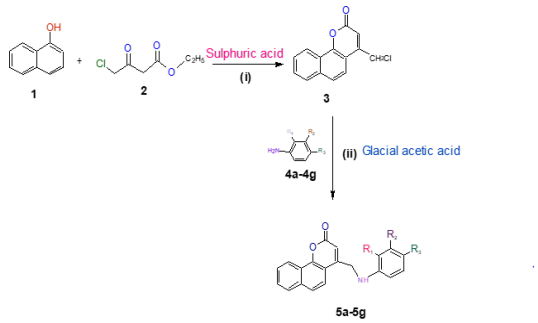
## Statistic evaluation

For each treatment, the experiment was carried out three times. The average was noted and represented as mean standard deviation.

## A multistep process is used to make coumarin derivatives.

In a flask with a round bottom, Ethyl-4-chloroacetoacetate (2, 3.25 g, 20 mmol) and naphthol (1, 2.88 g, 20 mmol) were combined before being consistently stirred with a magnetic

stirrer to add sulphuric acid (20 ml, 73%). TLC was used to verify that the reaction had finished. The reaction between substituted anilines (**4a-4g**, 10 mmol) and 4-Chloromethyl-2H-1-naphtho(1,2-b)pyran-2-one (**3**, 2.44 g, 10 mmol) took place in a cup with a circular base. The product was worked up in ice water, then filtered and crystallised from methanol to yield **3**. Ice was used to chill the cup Before adding 5 cc of glacial acetic acid, bring the mixture to room temperature.The response mixture was then warmed on an oil bath for one hour at 120 to 130 degrees Celsius. With 200 cc of 5% hydrochloric acid, the mixture was agitated on a magnetic stirrer after cooling. TLC noted that the reaction had ended. Ice water was used to filter the response product. To get **5a-5g** from benzene, a solid product was separated, washed with water, dried, and recrystallized. By using 1HNMR and FTIR spectroscopy, all substances (**5a-5g**) were identified.




Scheme 1

## Reagents and Reaction Conditions:

**(**i) 73% $H_2SO_4$
(ii) Glacial Acetic acid, 5%HCl, 120-130$^{o}$C.

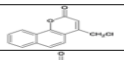
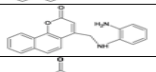
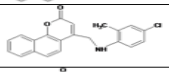
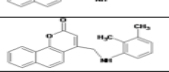
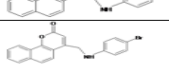
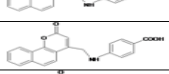
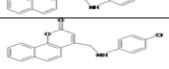
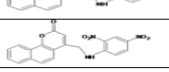
**Table. 1:**Substituents of compounds (5a-5g)

| Compound Number | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| 4a,5a | $NH_2$ | H | H |
| 4b,5b | $CH_3$ | H | Cl |
| 4c,5c | $CH_3$ | $CH_3$ | H |
| 4d,5d | H | H | Br |
| 4e,5e | H | H | COOH |
| 4f,5f | H | H | Cl |
| 4g,5g | $NO_2$ | H | $NO_2$ |

## Results and discussion

When ethyl-4-chloroacetoacetate (**2**) and -naphthol (**1**) were combined via Pechmann condensation in an equimolar ratio with 73% $H_2SO_4$, the result was 4-Chloromethyl-2H-1-naphtho (1,2-b)pyran-2-one (**3**). (**scheme 1**). TLC monitored the reaction's development and discovered that it had reached its conclusion. The compound (**3**) was then further reacted with 2-amine aniline (**4a**), 4-chloro-2-methyl aniline (**4b**), 2,3-dimethyl aniline (**4c**), 4-bromo-aniline (**4d**), 4-carboxylic acid (**4e**), 4-chloraniline (**4f**), and 2,4-dinitro aniline (**4g**) by refluxing on an oil bath at 120–130 °C for an hour in glacial acetic acid. After the mixture cooled, it was stirred As a starting point, we will use the production of 4[(2-Aminephenyl)anilinomethyl]-2H-1-naphtho(1,2-b)pyran-2-one (**5a**). In this procedure, 4-Chloromethyl-2H-1-naptho(1,2-b)pyran-2-one (3) and 2-amine aniline (**4a**) were refluxed on an oil bath for an hour while being mixed with glacial acetic acid, and after cooling, the mixture was agitated on a magnetic stirrer with 200 ml of 5% HCL. TLC was used to verify that the reaction had finished. The produced product was put into ice water, filtered, washed with water, dried, and recrystallized with benzene to produce a crystalline solid with a corresponding melting point of 202-204 $^{o}$C and 82% yield. In the molecule (**5a**) $^{1}$HNMR spectra in $CDCl_3$, a doublet at 4.22 integrating for two protons for methylene functionality was visible. At 4.73 for NH, a feature singlet could be seen. At 6.78, the sole aromatic proton, $C_3$-H, was visible downfield as a singlet. The when there is NH, C=Ostretching, and C=C aromatic compounds were indicated by the compound's IR absorption peaks at 3370, 1703, and 1550 $cm^{-1}$, respectively. The chemical was given the form 4[(2-Aminephenyl)anilinomethyl]-2H-1-naphtho(1,2-b)pyran-2-one primarily based on the aforementioned records. Alternative compounds (**5b–5g**) had also been arranged similarly.

**Table. 2:**Physical and analytical data of 4-Chloromethyl-2H-1-naphtho(1,2-b)pyran-2-one (3) and 4-[(substituted phenyl)anilinomethyl]-2H-1-naphtho(1,2-b) pyran -2-ones (5a-5g).

| Compound Number | Molecular Formula | Structure | IR ($cm^{-1}$) | Yield (%) | Melting Point (°C) |
|---|---|---|---|---|---|
| 3 | $C_{14}H_9O_2Cl$ |  | 1704 (C=O), 790 (C-Cl) | 87 | 170=C |
| 5a | $C_{23}H_{16}O_2N_2$ |  | 1703 (C=O), 3370 (N-H) | 82 | 202-204=C |
| 5b | $C_{24}H_{17}O_2NCl$ |  | 1695 (C=O), 800 (C-Cl), 3372 (N-H) | 78 | 200-202=C |
| 5c | $C_{25}H_{19}O_2N$ |  | 1720 (C=O), 3390 (N-H) | 81 | 199-200=C |
| 5d | $C_{23}H_{14}O_2NBr$ |  | 1730 (C=O), 730 (C-Br), 3400 (N-H) | 75 | 205-206=C |
| 5e | $C_{25}H_{17}O_4N$ |  | 1740 (C=O), 3380 (N-H) | 77 | 190-192=C |
| 5f | $C_{23}H_{14}O_2Cl$ |  | 1680 (C=O), 810 (C-Cl) | 81 | 198-200=C |
| 5g | $C_{23}H_{13}N_3O_6$ |  | 1720 (C=O), 3380 (N-H) | 84 | 162-164=C |

## Characterization data of synthesized compounds

### 4-Chloromethyl-2H-1-naphtho (1,2-b)pyran-2-one (3)

M.p. 170°C [Lit. 165-166°C, Jagdeep, (2001)], IR (KBr) 790(**C-Cl**)), 1560(**C=C**, aromatic), 1704(**C = O**) $^1$HNMR ($CDCl_3$) 5.03(s, 2H, **$CH_2Cl$**), 6.72(s, 1H, **$C_3$-H**), 7.34-7.89(m, 4H, **Ar-H**), 7.98(d, 1H, **$C_6$-H**), 8.25(d, 1H, **$C_5$-H**)

### 4-[(2-Aminephenyl)anilinomethyl]-2H-1-naphtho(1,2-b) pyran-2-one (5a)

M.p. 202-204°C, IR (KBr) 1550(**C =C**, aromatic), 1703(**C = O**), 3370(**N-H**), $^1$HNMR (DMSO-$d_6$ 4.52(s, 2H, **NH**), 5.04(t, 2H, **$CH_2$-NH**), 6.78(s, 1H, **$C_3$-H**),7.64-7.96(m, **Ar-H**)

### 4-[(4-Chloro-2-methylphenyl)anilinomethyl]-2H-1-naphtho(1,2-b) pyran-2-one (5b)

M.p. 200-202°C, IR (KBr) 800(**C-Cl**), 1560(**C =C**, aromatic), 1695(**C = O**), 3372(**NH**), $^1$HNMR (DMSO-$d_6$) 2.31(s, 3H, **$CH_3$**), 4.69(s, 1H, **NH**), 5.01(d, **J=8.0 Hz**, 2H,**$CH_2$-NH**), 6.85(s, 1H, **$C_3$-H**),7.02(d, **J=9.0 Hz**, 1H, **$C_5$-H**), 6.95(d, **J=8.0 Hz**, 1H, **$C_6$-H**), 7.70-7.87(m, 6H, **Ar-H**)

### 4-[(2,3-Dimethylphenyl)anilinomethyl]-2H-1-naphtho(1,2-b)pyran-2-one (5c)

M.p. 199-200°C, IR (KBr) 1400(**C-$CH_3$**), 1590(**C=C**, aromatic), 1720(**C = O**), 3390(**NH**), $^1$HNMR (DMSO-$d_6$) 2.82(s, 3H, **$CH_3$**), 4.75(s, 1H, **NH**), 5.02(d, **J=8.0 Hz**, 2H, **$CH_2$-NH**), 6.87(s, 1H,**$C_3$-H**), 7.04(d, **J=9.0 Hz**, 1H, **$C_5$-H**), 7.62(d, **J=8.0 Hz**, 1H, **$C_6$-H**), 7.69-7.98(m, 6H, **Ar-H**).

### 4-[(4-Bromophenyl) anilinomethyl]-2H-1-naphtho(1,2-b)pyran-2-one (5d)

M.p. 205-206°C, IR (KBr) 730(**C-Br**), 1560(**C = C**, aromatic), 1730(**C = O**), 3400(**NH**), $^1$HNMR (DMSO-$d_6$) 5.02(s, 1H, **NH**), 5.03(d, **J=9.0 Hz**, 2H, **$CH_2$-NH**), 6.89(s, 1H, **$C_3$-H**), 6.95(d, **J=8.0 Hz**, 1H, **$C_5$-H**), 7.67(d, **J=9.0 Hz**, 1H, **$C_6$-H**), 7.72-8.03(m, 6H, **Ar-H**).

### 4-[(4-Carboxylic acid phenyl) anilinomethyl]-2H-1-naphtho(1,2-b)pyran-2-one (5e)

M.p. 190-192°C, IR (KBr) 1560(**C =C**, aromatic), 1740(**C = O**), 3380(**NH**), $^1$HNMR ($CDCl_3$) 5.03 (s, 1H, **NH**), 4.98 (d, **J=9.0 Hz**, 2H, **$CH_2$-NH**), 6.80(s, 1H, **$C_3$-H**), 7.02(d, **J=8.0 Hz**, 1H, **$C_5$-H**), 7.59(d, **J=8.0 Hz**, 1H, **$C_6$-H**), 7.81-8.43(m, 6H, **Ar-H**), 11.24(s, 1H,**COOH**).

### 4-[(4-Chlorophenyl) anilinomethyl]-2H-1-naphtho (1,2-b)pyran-2-one (5f)

M.p. 198-200°C, IR (KBr) 810(**C-Cl**), 1560(**C = C**, aromatic), 1680(**C = O**), 3405(NH), $^1$HNMR ($CDCl_3$) 4.80(s, 1H, **NH**), 5.02(d, **J=9.0 Hz**, 2H, **$CH_2$-NH**), 6.88(s, 1H, **$C_3$- H**), 7.02(d, **J=8.0 Hz**, 1H, **$C_5$-H**), 7.61(d, **J=8.0 Hz**, 1H, **$C_6$-H**), 7.64-8.21(m, 6H, **Ar-H**).

### 4-[(2, 4-Dinitrophenyl) anilinomethyl]-2H-1-naphtho(1,2-b)pyran-2-one (5g)

M.p. 162-164°C, IR (KBr) 1550(**$NO_2$**), 1560(**C = C**, aromatic), 1720(**C = O**), 3010(**C = CH**), 3380(**NH**), $^1$HNMR ($CDCl_3$) 5.02(s, 1H, **NH**), 5.13(d, **J=9.0 Hz**, 2H, **$CH_2$-NH**), 6.83(s, 1H, **$C_3$-H**), 6.99(d, **J=8.0 Hz**, 1, $C_5$-H), 7.62(d, **J=8.0 Hz**, 1H, **$C_6$-H**), 7.69-7.98(m, 6H, **Ar-H**).

## Herbicidal activity

At several concentrations, including 200, 150, 100, and 50 µg/ml, all compounds (**5a**–**5g**) were examined for their ability to control RaphanussativusL.The results are provided in the table. The outcomes were presented as primary screening results. As a stock solution, all substances were diluted to a concentration of 1000 g/ml. By inhibiting the growth of weed roots and shoots, chemicals' herbicidal effects against Raphanussativus L. were assessed. The mean difference between treatment and control groups was used to compute the percentage of growth inhibition. According to the data on herbicidal activity shown in figure **1**, compound (**5c**) was active in roots at doses of 50, 100, 150, and 200 µg/ml and showed percentage growth inhibition of 72.36, 79.53, 85.47, and 93.45%. Inhibition of percentage increase was seen for compound (**5f**) at concentrations of 50, 100, 150, and 200 µg/ml, 68.90, 75.49, 80.46, and 90.64. In roots with 50, 100, 150, and 200 µg/ml of compound (**5e**), growth inhibition was inhibited by 63.56, 67.54, 75.68, and 88.00%, respectively. The root growth of the compound (**5g**) was inhibited by 73.70, 78.50, 88.95, and 94.63% at various concentrations of 50, 100, 150, and 200 µg/ml. Figure **2** perusal of activity data reveals that chemicals **5c** and **5d** were both discovered to be active in shoots. At various concentrations of 50, 100, 150, and 200 µg/ml, compound no. (**5c**) has been demonstrating a percentage growth inhibition of 70.00, 74.86, 77.00, and 91.57%, whereas compound no. (**5d**) demonstrated a percentage growth inhibition of 51.13, 63.78, 70.04, and 84.00% in a shoot. The percentage growth inhibition for compound no. (**5g**) was 69.89, 74.35, 83.76, and 92.95 at 50, 100, 150, and 200µg/ml in shoot. The compounds **5c**

and **5g** demonstrated the maximum percentage growth inhibition of both Roots and Shoots of Raphanussativus L. at all the tested concentrations, according to the activity data presented in table **3**. The substitution of nitro and methyl substituents on benzene rings may be the cause of the growth inhibition.

**Table. 3:**Herbicidal activity of 4-[(substituted phenyl) anilinomethyl]-2H-1-naphtho(1,2-b) pyran -2-ones(5a-5g).

| Compound No. | % Inhibition | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Root | | | | Shoot | | | |
| | 50 (µg/ml) | 100 (µg/ml) | 150 (µg/ml) | 200 (µg/ml) | 50 (µg/ml) | 100 (µg/ml) | 150 (µg/ml) | 200 (µg/ml) |
| 5a | 54.00 | 59.90 | 68.96 | 76.94 | 53.65 | 55.50 | 65.54 | 73.96 |
| 5b | 68.80 | 73.80 | 76.89 | 86.50 | 65.90 | 67.74 | 74.36 | 83.64 |
| 5c | 72.36 | 79.53 | 85.47 | 93.45 | 70.00 | 74.86 | 77.00 | 91.57 |
| 5d | 52.07 | 65.43 | 73.26 | 86.89 | 51.13 | 63.78 | 70.04 | 84.00 |
| 5e | 63.56 | 67.54 | 75.68 | 88.00 | 59.80 | 62.09 | 73.05 | 82.95 |
| 5f | 68.90 | 75.49 | 80.46 | 90.64 | 63.46 | 74.50 | 78.49 | 78.57 |
| 5g | 73.70 | 78.50 | 88.95 | 94.63 | 69.89 | 74.35 | 83.76 | 92.95 |

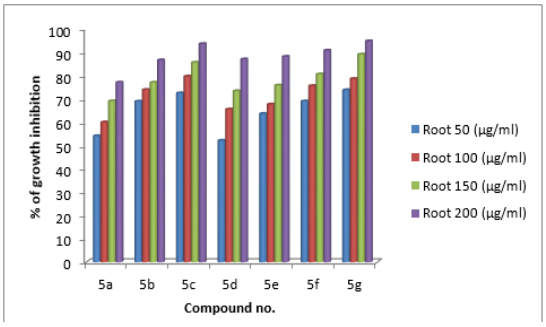



**Fig. 1**-Herbicidal activity of 4-[(substitutedphenyl) anilinomethyl]-2H-1-naphtho(1,2-b) pyran -2-ones (5a-5g) in root

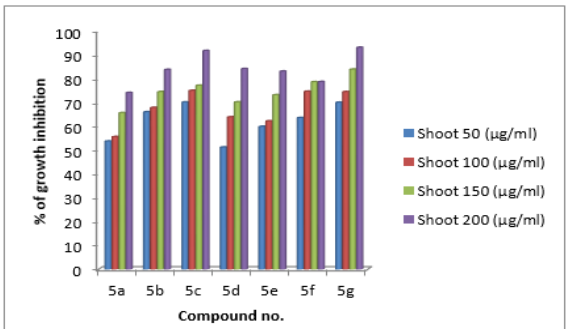
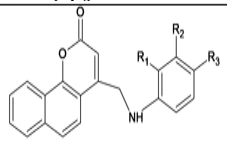



**Fig. 2**-Herbicidal activity of 4-[(substitutedphenyl)anilinomethyl]-2H-1-naphtho(1,2-b) pyran -2-ones (5a-5g) in shoot

## Antibacterial activity

By employing the Zone inhibition method and DMSO as a negative control, all synthesized compounds (**5a**–**5g**) were evaluated for their antibacterial efficacy against bacterial strains in vitro of the Bacillus species. Table **4** and Fig. **3** display the results of the synthetic compounds' antibacterial activities. The antibacterial activity data presented in figure **3** revealed that compound (**5c**) was found active against Bacillus species at 50, 100, 150 and 200 µg/ml concentrations and showing percentage growth inhibition 11.00, 17.50, 29.00 and 46.00%. Compound (**5a**) and (**5d**) exhibited 16.00, 32.00 and 11.00, 16.50% growth inhibition against Bacillus species at concentrations 150 and 200 µg/ml respectively. Compound (**5f**) has been given growth inhibition 9.00, 16.50, 24.00 and 40.00% against Bacillus species at different concentrations 50, 100, 150 and 200 µg/ml. Compound (**5g**)showed maximum inhibition at 200 µg/ml concentration then other compounds of the series (**5a-5g**) due to presence of nitro group on aniline.

**Table. 4:**Antibacterial activity of 4-[(substitutedphenyl)anilinomethyl]-2H-1-naphtho(1,2-b) pyran -2-ones (5a-5g).

| Compound No. |  | | | *Bacillus species* Zone inhibition in mm. | | | |
|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | 50 µg/ml | 100 µg/ml | 150 µg/ml | 200 µg/ml |
| 5a | $NH_2$ | H | H | a | A | 16.00 | 32.00 |
| 5b | $CH_3$ | H | Cl | 11.50 | 17.00 | 23.00 | 31.00 |
| 5c | $CH_3$ | $CH_3$ | H | 11.00 | 17.50 | 29.00 | 46.00 |
| 5d | H | H | Br | a | A | 11.00 | 16.50 |
| 5e | H | H | COOH | a | A | A | a |
| 5f | H | H | Cl | 9.00 | 16.50 | 24.00 | 40.00 |
| 5g | $NO_2$ | H | $NO_2$ | 15.00 | 23.50 | 39.00 | 57.50 |

A: No growth inhibition

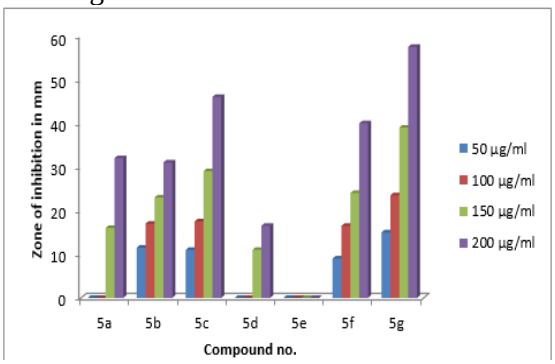



**Fig. 3**-Antibacterial activity of 4-[(substitutedphenyl)anilinomethyl]-2H-1-naphtho(1,2-b) pyran -2-ones (5a-5g) against Bacillus species

## Anti-fungal properties

By using the methodology of poisoned food, all produced compounds (**5a–5g**) were tested for their antifungal efficacy against two different fungal strains. A negative control against fungus strains was DMSO. Table **5** and Figs. **4,5** display the results of the investigated drugs' antifungal activity. The findings in figure **4** showed that compound (**5c**) was shown to be active against Rhizoctonia solani fungus and showed 48.62, 72.35, 75.32, and 79.63% at 50, 100, 150, and 200

µg/ml concentrations. Most synthetic compounds have moderate to good activity against antifungal toxicity. Antifungal toxicity data given in figure **4** revealed that compound (**5c**) shown fungal activity Rhizoctonia solani and showed 48.62, 72.35, 75.32 and 79.63% at 50, 100, 150 and 200 µg/ml concentrations. This compound (**5c**) was also active against the tested fungus Aspergillus niger andshowed the percentage growth inhibition 40.32, 54.73, 61.00 and 72.73 at 50, 100, 150 and 200 µg/ml concentration. Compound (**5f**) has not demonstrated any growth inhibition at any concentration. At lower concentrations, compound (**5e**) has not exhibited any growth inhibition. At 50 and 200 µg/ml doses, compound (**5e**) showed 26.00 and 52.00% growth suppression against Rhizoctonia solani and no percentage inhibition even at 200 mg/ml against the tested fungus Aspergillus niger, respectively. Compound (**5g**)has been found moderate active against Rhizoctonia solani. Compound (**5c**) was found most against Rhizoctonia solani fungus active due to presence of methyl group on phenoxy ring if this group replace with carboxylic acid group on aniline ring then activity will be decreases i.e the compound (**5e**). Compound no. (**5d**) exhibited no activity at lower concentration but this shown the percentage growth inhibition 36.00 and 55.00 at higher concentrations i.e. 150 and 200 µg/ml against the tested fungus Aspergillus niger. Compound (**5c**) also found active against Aspergillus niger fungus due to methyl group on aniline ring.

**Table. 5:**Antifungal activity of 4-[(substitutedphenyl)anilinomethyl]-2H-1-naphtho(1,2-b) pyran -2-ones (5a-5g).

| Compound No. | % age growth inhibition | | | | | | | | Rhizoctonia solani | Aspergillus niger |
|---|---|---|---|---|---|---|---|---|---|---|
| | Fungi | | | | | | | | | |
| | Rhizoctonia solani | | | | Aspergillus niger | | | | | |
| | 50 µg/ml | 100 µg/ml | 150 µg/ml | 200 µg/ml | 50 µg/ml | 100 µg/ml | 150 µg/ml | 200 µg/ml | $EC_{50}$ µg/ml | $EC_{50}$ µg/ml |
| 5a | 42.50 | 48.63 | 59.72 | 67.43 | 30.00 | 33.00 | 51.20 | 69.34 | 106.18 | 146.71 |
| 5b | 41.65 | 52.32 | 61.79 | 69.21 | 36.72 | 43.45 | 49.67 | 58.93 | 89.13 | 151.78 |
| 5c | 48.62 | 72.35 | 75.32 | 79.63 | 40.32 | 54.73 | 61.00 | 72.73 | 52.91 | 71.88 |
| 5d | 40.57 | 48.98 | 62.23 | 69.47 | a | a | 36.00 | 55.00 | 103.85 | 186.84 |
| 5e | a | a | 26.00 | 52.00 | a | a | a | a | 196.16 | a |
| 5f | a | a | a | a | 32.37 | 37.23 | 45.24 | 54.87 | A | 174.72 |
| 5g | 47.14 | 54.28 | 61.42 | 68.57 | a | a | 46.57 | 54.28 | 70.03 | 172.25 |

A: No growth inhibition

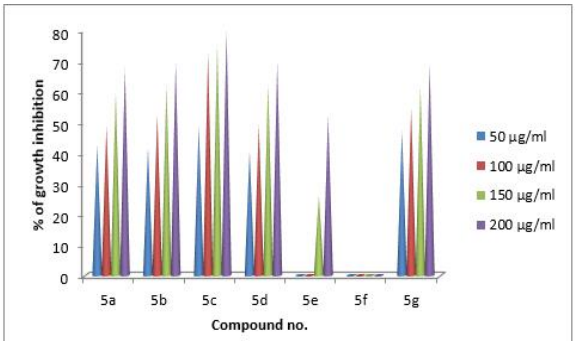



**Fig. 4**-Antifungal activity of 4-[(substitutedphenyl)anilinomethyl]-2H-1-naphtho(1,2-b) pyran -2-ones (5a-5g) against Rhizoctonia solani

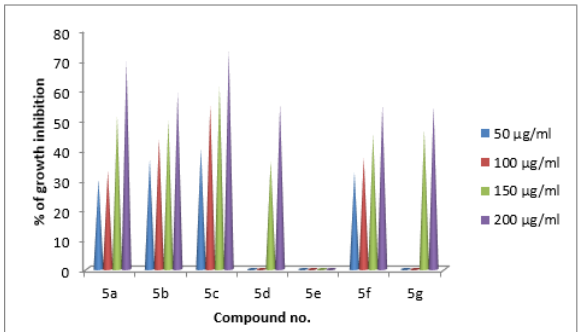



**Fig. 5**-Antifungal activity of 4-[(substitutedphenyl)anilinomethyl]-2H-1-naphtho(1,2-b) pyran -2-ones (5a-5g) against Aspergillus Niger

## Conclusions

For the quick synthesis of biological energetic substituted coumarin derivatives, a multistep approach has been established. NMR and FTIR spectral analysis were used to comprehensively analyse each produced substance. Mild reaction conditions, no additional energy input, no toxic byproducts, and inexpensive reactants are a few advantages of the current technique. Additionally, the herbicidal activity against Raphanus sativus L. (radish) seeds, the antibacterial activity against Bacillus species, and the antifungal activity against Rhizoctonia solani and Aspergillus niger were all used to evaluate the bio-efficacy of the synthesised compounds (**5a**–**5g**). Based on biological facts, we got to the conclusion that strong electronegative groups at the phenyl ring have an excellent activity profile when compared to electropositive groups.

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## Adherence to moral principles
## Competing interests

There are no conflicts of interest that the authors can disclose regarding the publishing of this manuscript.

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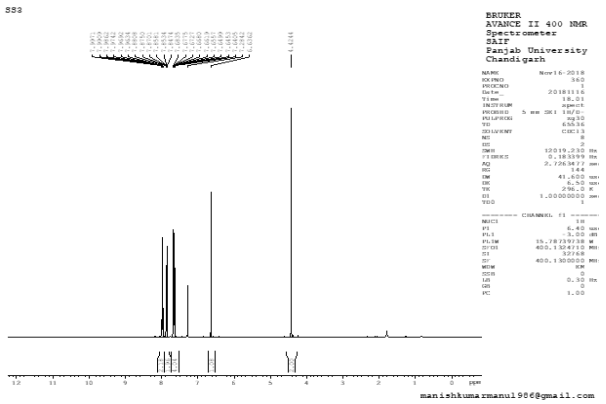
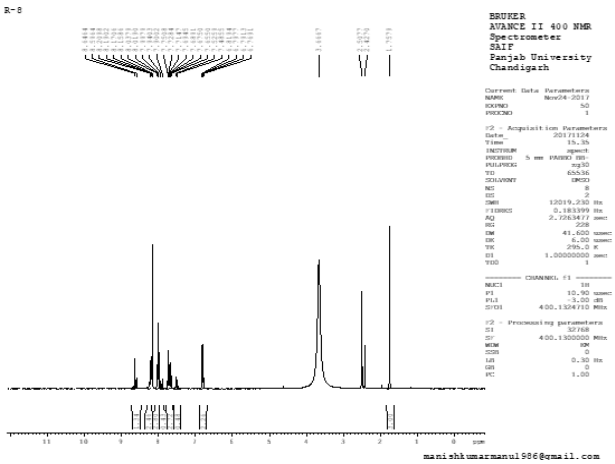
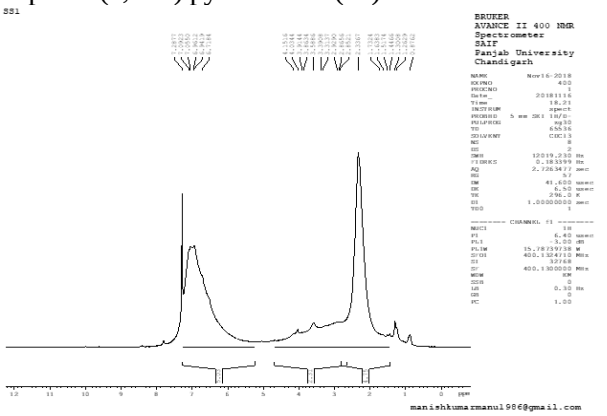


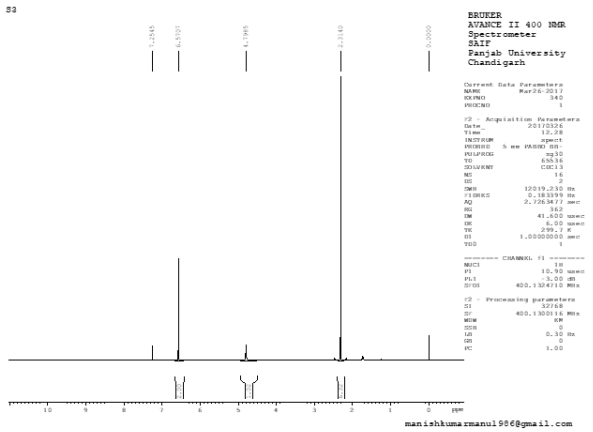
4-[(2-Aminephenyl)anilinomethyl]-2H-1-naphtho(1,2-b)pyran-2-one (5a)



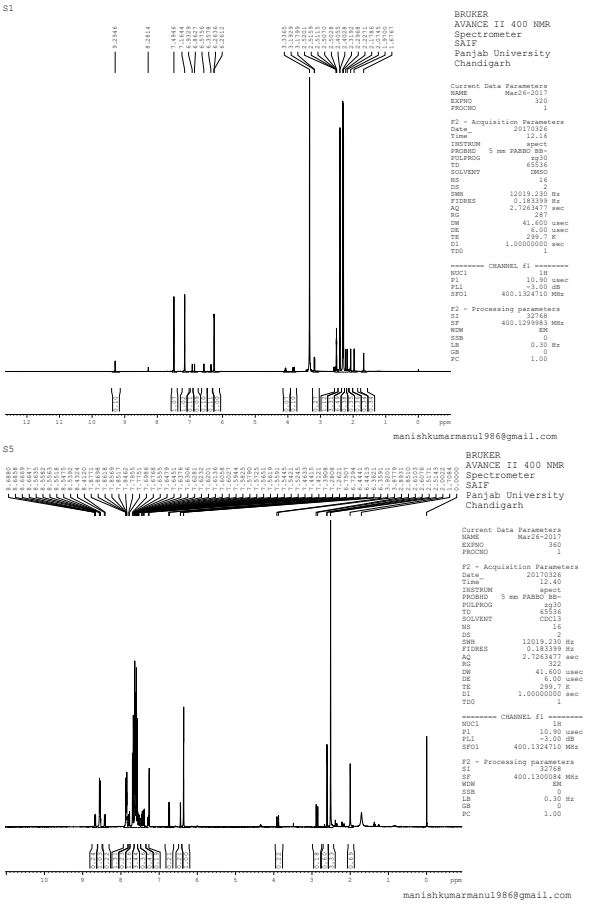
4-[(4-Chloro-2-methylphenyl) anilinomethyl]-2H-1-naphtho (1, 2-b) pyran-2-one (5b)



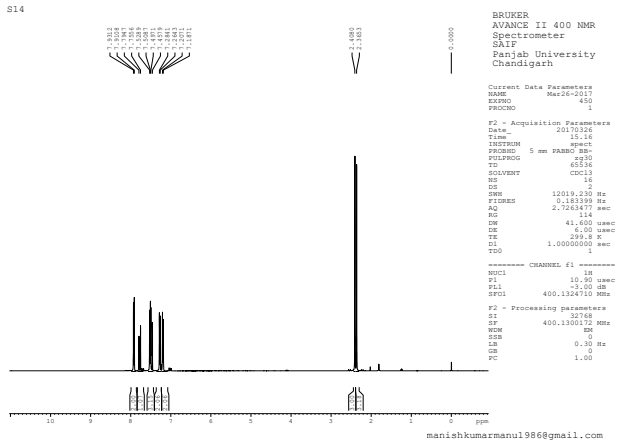
4-[(2, 3-Dimethylphenyl) anilinomethyl]-2H-1-naphtho(1,2-b)pyran-2-one (5c)



4-[(4-Bromophenyl) anilinomethyl]-2H-1-naphtho(1,2-b) pyran-2-one (5d)



**4**-[(4-Chlorophenyl)anilinomethyl]-2H-1-naphtho(1,2-b) pyran-2-one (5f)




4-[(4-Carboxylic acid phenyl)anilinomethyl]-2H-1-naphtho (1, 2-b) pyran-2-one (5e)

4-[(2,4-Dinitrophenyl)anilinomethyl]-2H-1-naphtho(1,2-b)pyran-2-one (5g)