

Multicomponent Synthesis Of 2-Amino-4H-Chromenes Using SLS As Catalyst Under Solvent Free Condition.

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Abstract

An improved, simple and facile synthesis of 2-amino-4H-chromene derivatives by applying one-pot, three-component condensation reaction of substituted aromatic aldehydes, β -naphthol and malononitrile in solvent free condition has been carried out in the presence of catalyst Sodium Lauryl Sulphate (SLS). These chromenes derivatives need short reaction times, are non-toxic and easy to work-up, hence making this process environment friendly. A detail mechanistic study shows that the reaction using malononitrile proceeds through intermediate.

Key words: Multicomponent synthesis, SLS-catalyst, solvent free condition, non-toxic, environmental friendly.

1- INTRODUCTION

In chemistry, Multicomponent reaction (MCR) is one of the most important processes for the preparation of highly functionalized organic compounds. In modern synthetic chemistry, a multicomponent reaction is referred as a "Multicomponent Assembly Process". According to Ugi, "Multicomponent reaction convert more than two adducts directly into their product by one pot-reaction" ⁽¹⁾.

Multicomponent reactions (MCRs) constitute an especially attractive synthetic strategy, since they provide easy and rapid access to large libraries of organic compounds with diverse substitution patterns. As MCRs are one-pot reaction, they are easier to carry out than multistep synthesis coupled with high-throughput library screening. This strategy was an important development in the drug discovery in the context of rapid identification and optimization of biologically active lead compounds ⁽²⁾. In particular, transition metal-catalyzed, multicomponent sequences has recently gained considerable interest. Based upon the Sonogashira entry to alkynones, alkenones and intermediates of allenes have opened a new path to the one-pot synthesis of

numerous classes of heterocyclic compounds in a multicomponent reactions pattern ⁽³⁾. These methodological approaches have now found various applications in one-pot synthesis of functional chromophores, dyes, pharmaceutically active compounds and marine alkaloids and their derivatives ⁽⁴⁾.

However, in last decade, with the introduction of high-throughput biological screening, the importance of multicomponent reactions for drug discovery have been recognized and considerable efforts from both academic and industrial. Researchers have been focused specially on the design and development of multicomponent reactions for the generation of libraries of heterocyclic compound ⁽⁵⁾.

Furthermore, the usefulness of the rigid and well defined structures of heterocyclic compounds were represented many detailed structure activity relationship (SAR)-studies. One step process is more suitable as compared to multistep process, since they are requiring shorter reaction time, and gives excellent yield with easy workup. Heterocyclic compounds are ubiquitous among pharmaceutical compounds ^(6,7).

Accordingly, many efficient and practical synthesis procedures are noticed for the synthesis of versatile siprooxindole-fused heterocycles. From last few years, the prominence of the development of green and sustainable chemistry. Heterocyclic compounds as a results of multicomponent chemical reactions having interesting pharmacological activities such as anti hypertensive, antibacterial, anticancer and anti HIV-activities⁽⁸⁻¹⁰⁾.

Synthesis of structurally novel and diverse compounds for biological screening is an important task of discovery chemistry. Diversity-oriented synthesis (DOS) are aimed on the preparation of compounds libraries with substitutional, skeletal and stereo-chemical variations⁽¹¹⁾. Multicomponent reactions provided many powerful tools for diversity-oriented synthesis to produce molecules with complexity and diversity⁽¹²⁾. Since the numbers of multicomponent reactions are inadequate, post-multicomponent reactions modifications are required for the development of new library scaffolds.

An ideal multicomponent reaction is involve in the simultaneous addition of reactant, reagents and catalyst at the starting of the reaction and required that all reactants couple in an exclusive ordered mode under the same reaction conditions⁽¹³⁾. An achievement of the multi-step consequence or multicomponent one-pot transformations are required a balance of equilibrium and a congenial sequence of reversible and irreversible processes. Thus, the know that multicomponent reactions are two types of reactions i.e.⁽¹⁴⁾ (a) Type-1 MCRs in which there are an equilibrium reactants, intermediates and final products; (b) Type-2 in which, an equilibrium exists between reactants and intermediates with the final product being irreversibly formed.

The multicomponent reactions are important in combinatorial chemistry predicted to exhibit negative activation volume owing to the condensation of a single reaction intermediate and product. This method introduced rapid synthesis of compounds libraries⁽¹⁵⁾. The atom economy and convergent character of this one-pot method are perfectly amenable to automation of combinatorial synthesis. They are powerful tools in modern drug discovery

processes allowing rapid, automated and high throughput generation of organic compounds. Additionally, this one pot character delivers fewer by-products compared to classical stepwise synthetic routes, with lower costs, time and energy⁽¹⁶⁾.

Sodium Louryl Sulfate (SLS) is an inexpensive and very effective foaming agent⁽¹⁷⁾. It is used under the name SLS in some food products as an emulsifying agent and whipping aid. Test in the US indicated that it is safe for consumers use. The Australian government's Department of Health and Ageing and its National Industrial Chemicals Notification and Assessment Scheme (NICNAS) have determined SLES does not react with DNA⁽¹⁸⁾.

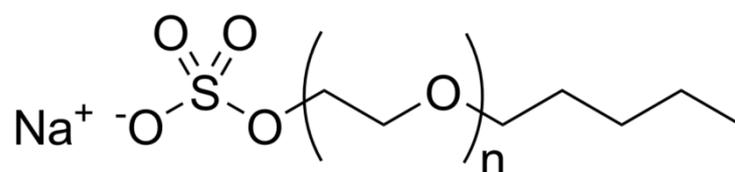


Fig.1 Sodium lauryl sulfate (SLS)

The rising attention from the last few decades towards the green chemistry and environmental protection, that forced both present academic and industrial groups to develop the lot of chemical processes which gives excellent yield, reduced the cost of raw materials; utilize the non-toxic reagents and non-hazardous organic solvents. Thus, developed one of the most important tools for such need of time are multicomponent reactions (MCRs); this process contain of two or more synthetic procedures which is carried out without isolation of any intermediate so reduced time saving energy and money and raw materials⁽¹⁹⁾. A privileged structure is defined as “a single molecular framework able to provide ligande for diverse reporters”. Since then, increasing numbers of sub-structural frameworks are described as privileged structures including 3-amino-4H-chromene⁽²⁰⁾. These compounds have been used extensively in medicinal chemistry. It is themain component of many naturally occurring products, and is widely used as cosmetics, pigments and potential biodegradable agrochemicals⁽²¹⁾. More recently **Zhu et al**⁽²²⁾ have been synthesized 3-amino-1h-chromene on the use of cetyltrimethyl-ammonium chloride in the presence solvent of water. These compounds

are usually prepared by reacting aromatic aldehydes, malononitrile, and activated phenol in the presence of organic solvent.

2-amino-4H-chromenes are an important group of heterocyclic compounds having important biological activities⁽²³⁾. From the last few decades, these compounds have been shown interesting pharmacological properties including, antiviral, mutagenicity, antiproliferative, antimicrobial, sex-pheromone, antitumor, cancer-therapy and central-nervous system activity⁽²⁴⁻³¹⁾. 3-Amino-1H-chromens and their derivatives are also used as anti-coagulants, anti-anaphylactics and antispasmodic agents⁽³²⁻³⁵⁾.

For these reasons, development of an environmentally benevolent and simple procedure for the synthesis of 3-Amino-1H-chromenes, in this place we have reported condensation of three component reactions like substituted aromatic aldehydes, β -naphthols and malononitrile in the presence of SLS as

2.2- List of chemicals used and their sources

Chemicals

Benzaldehyde
3-Chlorobenzaldehyde
2,4- dichlorobenzaldehyde
2-nitrobenzaldehyde
4-methoxybenzaldehyde
3-Hydroxybenzaldehyde
4- nitrobenzaldehyde
 β – naphthol
Malononitrile
SLS
2-Tolualdehyde
Sodium carbonate
Manganesechloride
Zinc chloride
Cupric nitrate
Cerium nitrate

catalyst with excellent yield, very simple procedure and short time duration.

2- EXPERIMENTAL SECTION

2.1- Characterization Techniques

IR spectra were recorded by SHIMADZU IR spectrometer by sample dispersed in KBr pellet and are reported in terms of frequency of absorption (cm^{-1}). The ^1H NMR spectra were measured by Bruker Avance II 500 NMR spectrometer with tetramethylsilane as an internal standard, ^1H NMR have been reported as follows; Chemical shift (ppm), integration, multiplicity, (s-singlet, d-doublet, t-triplet, q-quarter, m-multiplet and br-broad) and Coupling constant (Hz). Melting points were determined in open capillaries and are uncorrected. Pre-coated TLC plates, Rankem silica gel G was used for preparation of thin layer liquid chromatography.

Commercially available reagents were used without further purification.

Source

Rankem
Himedia
Himedia
Himedia
Himedia
Himedia
Rankem
CDH
Rankem
Himedia
Rankem
Himedia
Qualigens
Qualigens
Merck

2.3- Synthesis of 2-amino 1H-chromene derivatives using of sodium lauryl sulfate (SLS) as catalyst

A mixture of aromatic aldehyde (0.05mmol), β -naphthol (0.05mmol), and malononitrile (0.05mmol) was refluxed in ethanol at 70°C in the presence of SLS. The reaction was monitored by TLC. After completion the reaction, reaction mixture was cooled at room temperature and filtered. Reaction product was purified by column chromatography with ethyl acetate and hexane (6:4). The solid product

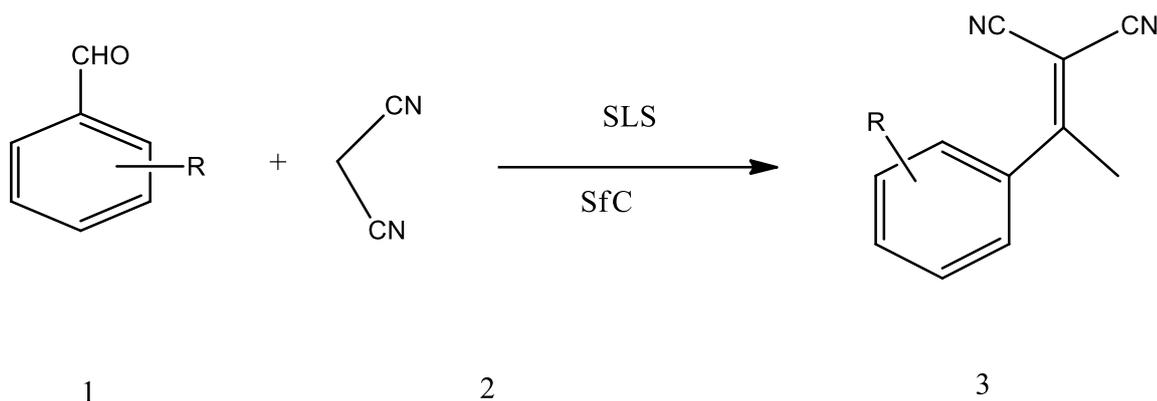
was recrystallized by ethanol. The product of 2-amino chromene derivatives are collected as pinkish white crystals.

2.4- Synthesis of intermediate

A mixture of aromatic aldehyde (0.05mmol) and malononitrile (0.05mmol) was heated at 70°C in solvent ethanol in the presence of sodium lauryl sulfate (SLS) as a catalyst (Scheme 2.1). The reaction was monitored by TLC. After completion of the reaction, the product was purified by column chromatography using hexane and ethyl acetate

(6:4). The solid was recrystallized by ethanol. The product was characterized by mass, IR, ¹H

NMR.



Scheme 2.1 proposed intermediate reaction using SLS as catalyst

3- RESULTS AND DISCUSSION

One -pot three component condensation reactions of aromatic aldehyde, β -naphthol and malanonitrile using various catalysts in ethanol as a solvent at 70°C have been studied.

3.1- Effect of Catalyst

In the initial experiments, in the absence of catalyst no product was obtained, when aromatic aldehyde (0.005mmol), β -naphthol

(0.005mmol) and malanonitrile (0.005mmol) was refluxed at 70°C in solvent ethanol. The reactions show (table 3.1) that the yields of the products are dependent on the nature of the catalyst. In the presence of 0.1g of catalyst SLS highest yield (86%) was obtained. From the table 3.1 is clear that minimum yield (20%) was obtained when ZnCl₂ was used. Other catalyst gave yield in the range of 30-58%.

Table 3.1 Optimization of reaction condition using various catalysts

Entry	Catalyst	Time (min)	Yield (%)
1	No catalyst	120	No product
2	ZnCl ₂	190	20
3	NaCO ₃	155	30
4	Al-Ni-NO ₃	80	36
5	Mn-Al-CO ₃	240	45
6	Ce-Ni-CO ₃	90	58
7	SLS	65	86

3.2- Effect of solvents on the reaction

One –pot three component condensation reactions of substituted aromatic aldehyde (0.005mmol), β -naphthol (0.005mmol) and malanonitrile (0.005mmol) using various solvents in the presence of catalyst SLS at 70°C have been studied and given in table 3.2. The reactions were very sensitive to the nature

of solvents (Table 3.2). It was observed that in it gave 86% of product yield. No products yields were obtained when reactions were carried out in the presence of toluene, hexane and dichloromethane. In the presence of pure water no product yield was obtained due to lack of solubility of the reactant. 50% product yield was obtained in methanol.

Table 3.2 Optimization of reaction condition using various organic solvent

Entry	Solvent (ml)	Yield (%)
1	Water	00
2	Methanol	50
3	Hexane	00
4	Acetone	25
5	Toluene	05
6	Dichloromethane	18
7	Ethanol	86

3.3 Effect of catalyst concentration on the reaction

In the initial experiment, the reaction was carried out in the absence of catalyst product yield 5% was obtained. After this different catalyst concentration effect was observed

(table 3.3) which shows that 0.1g of SLS was enough to catalyze the reaction. Further when increase in catalyst concentration did not show any improvement in the yield. However 86% yield was obtained when 100 mg catalyst was used (table 3.3).

Table 3.3: The effect of catalyst concentration on the synthesis of 3-amino-1H chromene

Entry	Catalyst conc. (mg)	Yield (%)
1	Free	5
2	5	15
3	10	30
4	25	48

5	50	65
6	100	86
7	110	86

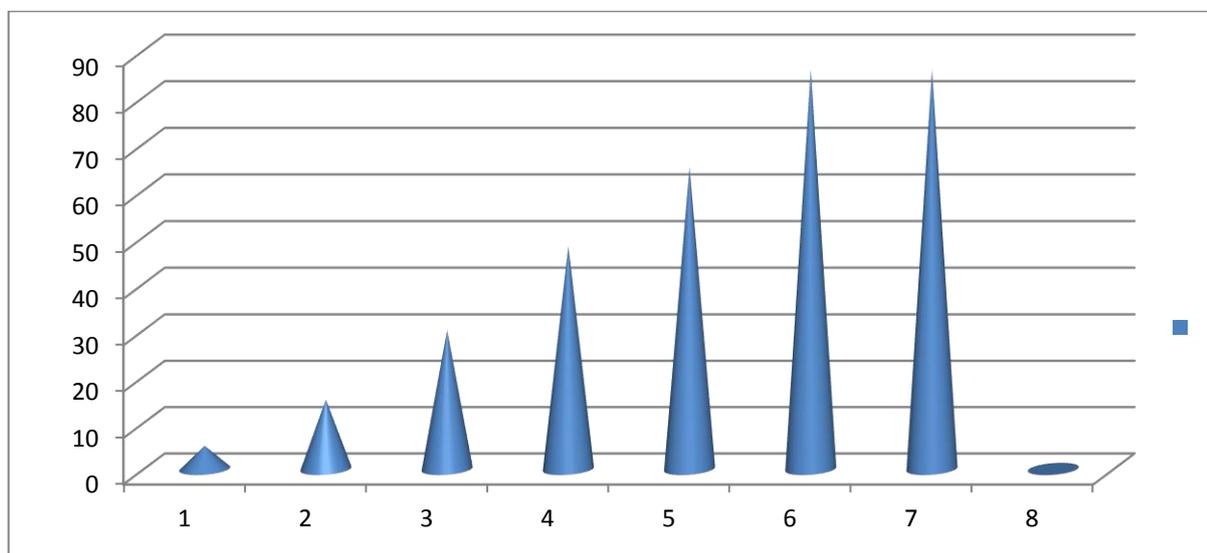
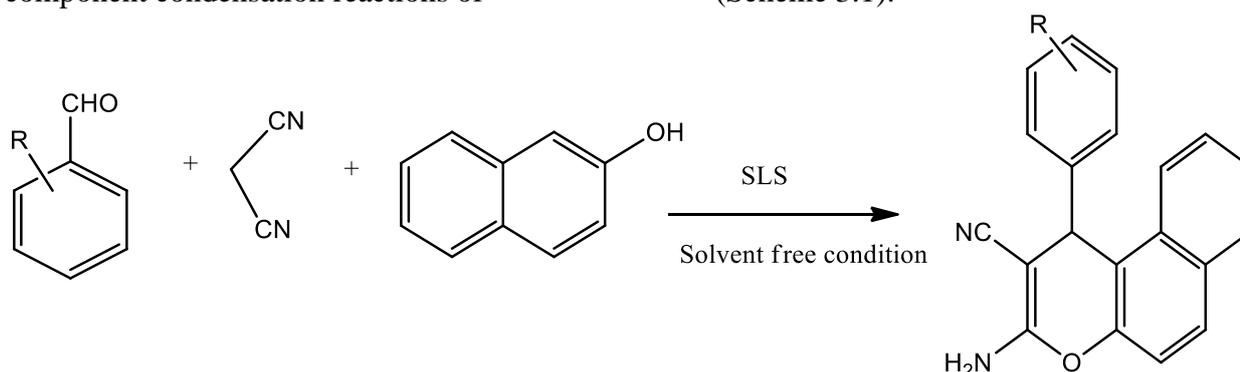


Fig. 2 Effect of catalyst concentration on the product yield

3.4 Synthesis and characterization of 3-amino-1H-chromene derivatives using SLS as catalyst

Under optimized reaction conditions, three component condensation reactions of

substituted aromatic aldehyde, β -naphthol and malanonitrile in the presence of catalyst SLS in ethanol solvent at 70°C have been carried out to give 3-amino-1H-chromene derivatives (Scheme 3.1).

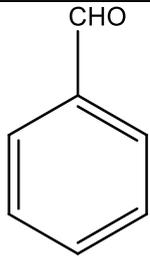
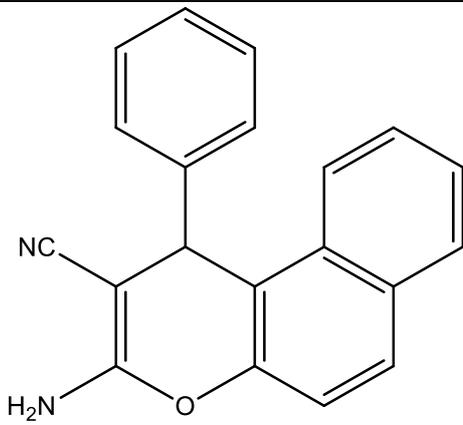
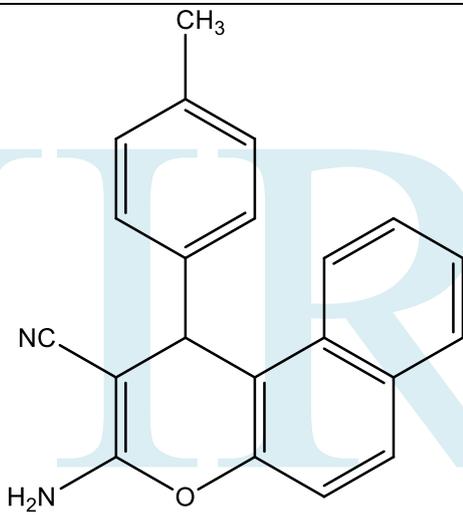
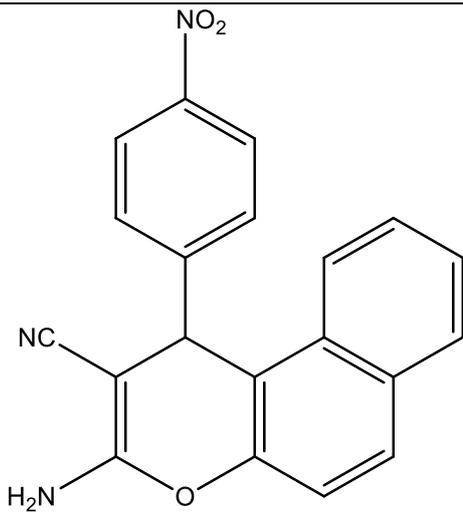


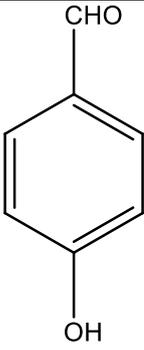
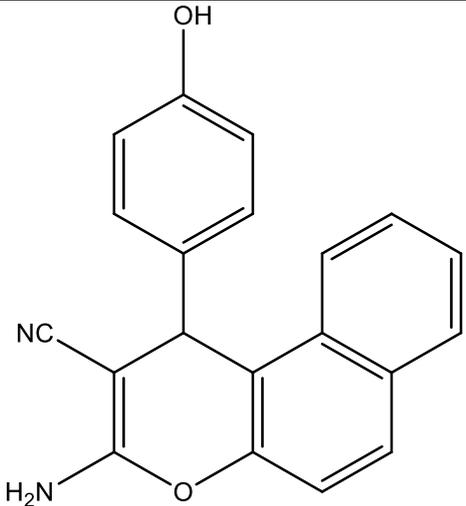
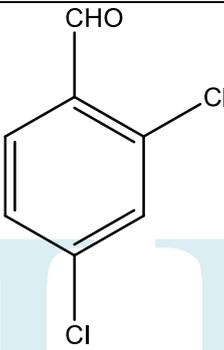
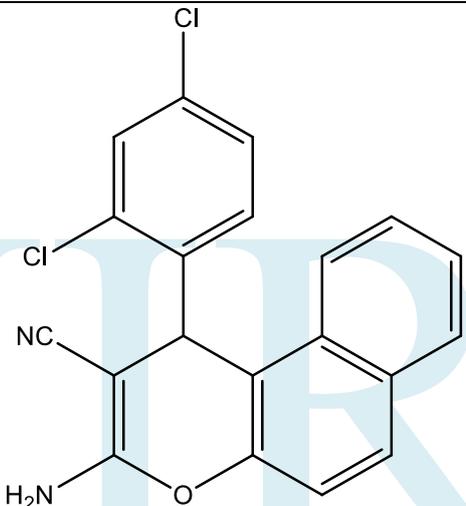
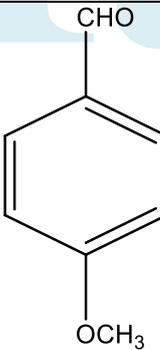
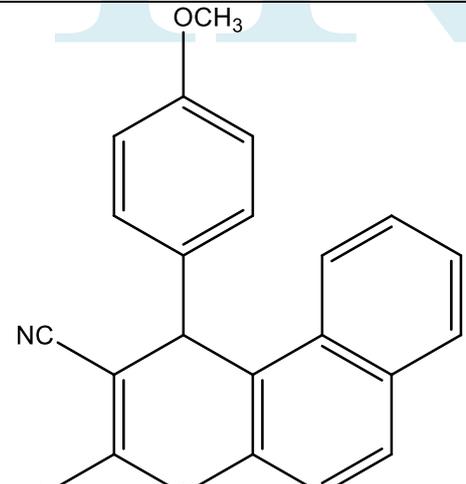
R= H, 2-NO₂, 2-OH, 2- Cl, 4-OMe etc.

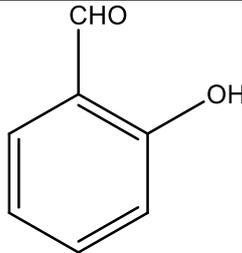
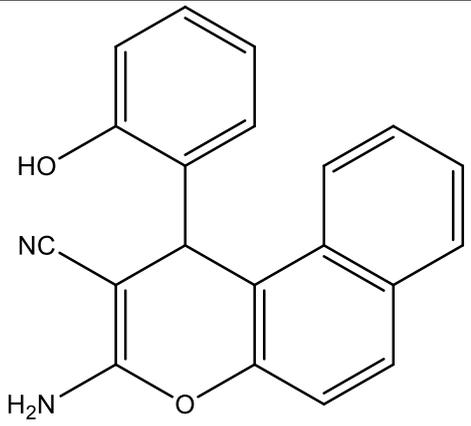
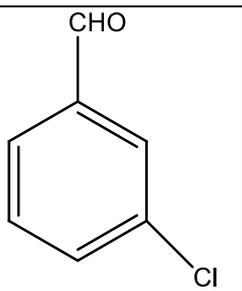
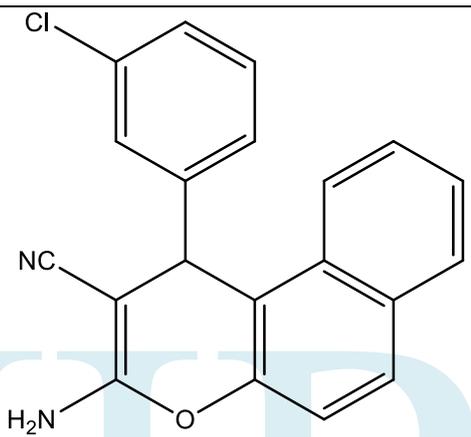
Scheme 3.1 preparation of 3-amino-1H-chromene derivatives using SLS

Therefore, we have synthesized the derivatives of 3-amino-1H-chromene by using substituted aromatic aldehydes, β -naphthol and malanonitrile in the presence of catalyst SLS in ethanol solvent which is summarized in table 3.4.

Table 3.4 One-pot three component synthesis of 3-amino 1H-chromene derivatives using SLS as catalyst

Entry	Reactant	Product	Time (min)	Yield (%)	M.P.(⁰ C)
4a			90	71	208-209
4b			120	69	200 – 202
4c			65	86	214 - 215

4d			210	79	209 – 211
4e			207	80	210-212
4f			80	75	193-195

4g			250	78	210 – 212
4h			210	82	232-234

On increase in the amount of catalyst the reaction time is reduced. Various aromatic aldehydes are containing electron donating and electron withdrawing substituted at ortho, meta, para position show equal effect toward the product yields. From the above it is clear that electronic effect is not controlling the rate determining steps. Both, the electron-rich and electron-deficient aromatic aldehydes are worked well under the reaction condition and conducting to high yields of the products. In the series of reaction, β -naphthol was utilized under the reaction condition to give the corresponding product 3-amino-1H-chromenes. The structure of 3-amino 1H-chromenes derivatives of β -naphthol was confirmed by mass, IR and NMR spectral analysis. The NMR spectra of the product 2-amino 1H chromenes derivatives were characterized by obtained singlet at δ 7.27 due to asymmetric C-H hydrogen and multiplets δ 7.5-1.66 due to aromatic hydrogen of β -naphthol and benzene ring of aromatic aldehyde which is not affected by β -naphthol. Mass spectra of compound 4a shows molecular ion peak which was confirmed the proposed structure of compound

4a. Therefore, a variety of substitute aromatic aldehydes have been studied in table 3.4.

4- MECHANISM

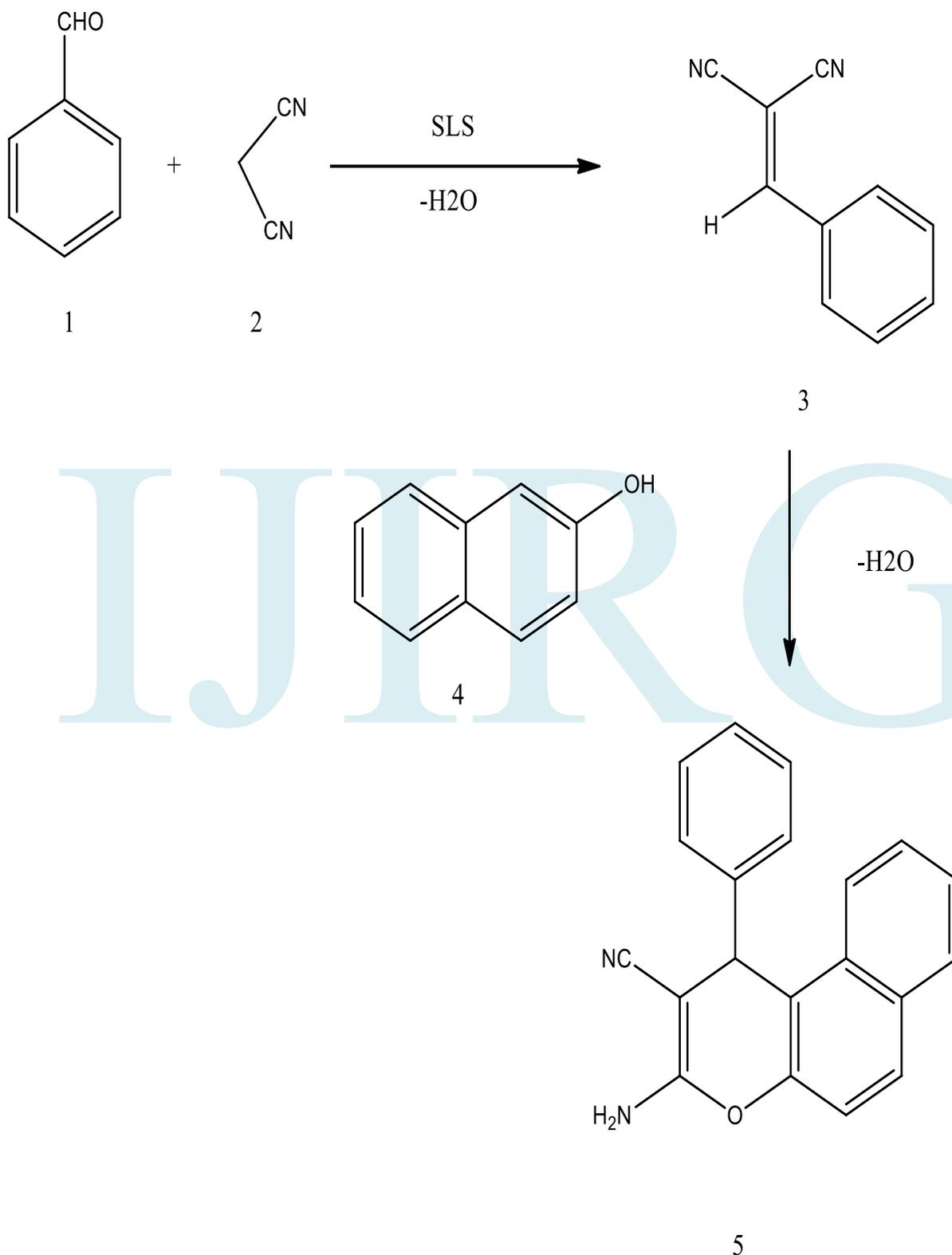
The mechanistic pathway of three component condensation reactions has been studied by using substituted aromatic aldehydes, malononitrile and β -naphthol in the presence of catalyst SLS in ethanol solvent. This is for the first time this reaction proceeds well in surfactant SLS.

A possible mechanism has been suggested in Scheme 4.1 for this reaction. On the basis of this proposed mechanism, in the initially aromatic aldehyde (1) is condensed with malononitrile (2) in the presence of catalyst SLS which conducts to the formation of arylidenemalononitrile-2 (3) with the loss of a water molecule (36). The nucleophilic addition of the enolized β -naphthol(4) to arylidenemalononitrile-2 pursued by cyclization of the intermediate molecule (3) resulting a desired species of 3-amino 1H-chromene (5).

Therefore, we have developed a very clean and cost-effective method for the synthesis of 3-amino 1H-chromene by the condensation of

aromatic aldehydes, malononitrile and β -naphthol using surfactant SLS as catalyst and ethanol as dissolving solvent. This process is very simple, short time duration, easy work-up, together with the use of non toxic,

commercially available and inexpensive catalyst is used. All the synthesized compounds were characterized by mass, IR, ^1H NMR and C^{13} NMR spectroscopic techniques.



Scheme 4.1 plausible reaction mechanism by using catalyst surfactant SL

We have studied three set of reactions of aromatic aldehyde, malononitrile and β -naphthol under the reaction condition for prove the mechanism of one-pot three component condensation reaction. Under the present condition obtained intermediate has been isolated and characterized by mass, IR, and NMR spectra. The intermediate consequently reacts with β -naphthol. It is clear that the intermediate provides the target molecule with excellent 86% yield. This reaction is developed in two steps first condensation of aromatic aldehyde (1) and malononitrile (2) according to Knoevenagel type reaction formed intermediate (3) which then react with β -naphthol to give final product. The plausible reaction mechanism is given in Scheme 4.1. Balliniet *al* have reported⁽³⁷⁾ that the reaction is easily occurring without catalyst under solvent free condition. It is proceeded the C-alkylation of the phenolic ring at the o-position and provide the intermediate. When we examined this process

without using catalyst under solvent free condition for 6 hours at 70°C then found that there no reaction is developed. The nucleophilic bombard of the phenolic OH on the CN-group is the final process to give intermediate benzalidenemalanonitrile (3)⁽³⁸⁾. During the mechanistic study, we have excluded out the involvement of the reaction intermediates. It was found that the mechanistic pathway of reaction is basically depended on the reaction conditions.

5- CHARACTERIZATION OF THE PRODUCT 3-AMINO-1-PHENYL-1H-BENZO [F] CHROMENE-3-CARBONITRILE

In the mass spectra of compound (4a), the molecular ion peak is obtained at 298 m/z which matched to the calculated molecular ion weight of the molecule having assigned structure as follows. An expected drawing of the product (4a) with the carbon atom labeling scheme is presented below.

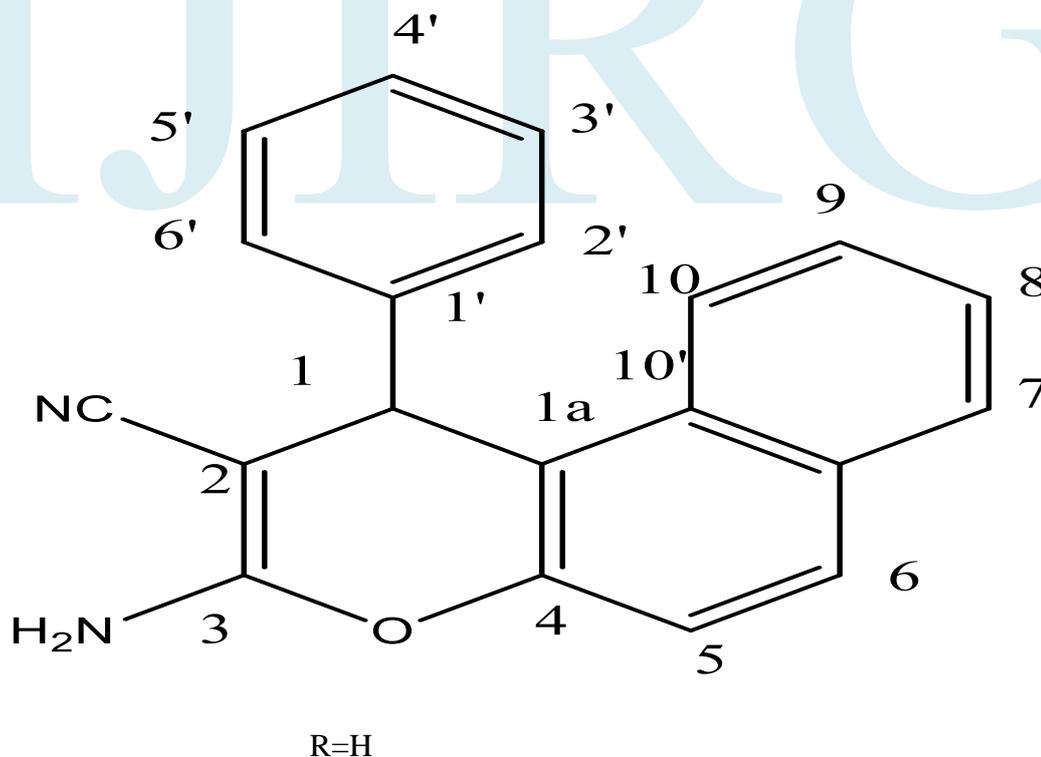


Fig. 3 Structure of 3-amino-1-phenyl-1H- benzo[f]chromene-3-carbonitrile

In the IR spectra of compound (4a), the bond due to ν (NH_2) group stretching vibration was appeared at 3360cm^{-1} . The bond due to ν (CN) group was observed at 2208cm^{-1} (39). The other characteristics groups like ν (C-C), ν (C-H) and ν (C-O) were appeared at 3450, 1600, 1200 cm^{-1} respectively.

In the ^1H NMR spectra of compound (4a), the two singlets were appearing at 4.59 and 5.24ppm which are assigned to NH_2 and H-1 proton respectively. The multiplets were appeared due to aromatic protons (H-5, H-10 and H-1'- H-6') as expected and observed in the range of 7.10-7.90ppm (40).

In the ^{13}C NMR spectra of all the compounds (4a-4g), the assignment has been made on the basis of literature survey reports of the related compounds and according to the principle (41).

The ^{13}C NMR spectra of compound (4a), the signal appearance is observed at 117.95ppm due to carbon which is attached to carbonitrile. The peacks are obtained from ^{13}C NMR spectra further authentic with the finding of IR and ^1H NMR spectra (42).

6- CONCLUSION

In the continuation of our efforts to develop an efficient environmentally benign process for the synthesis of various heterocycles atoms, we reported herein our result with catalyst SLS that effectively catalyzed the three components condensation reaction of substituted aromatic aldehydes, malononitrile and β -naphthole in solvent ethanol are giving excellent yield. The present protocol shows several advantages such as simple reaction condition, short time duration, easy work up and simple purification of the products by easy recrystallization. The reaction shows that the products yields are depend on the nature of the catalyst.

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