# Green and Efficient Synthesis and Characterization of Amino Chromene Derivatives with Add Alkyl Tail

**Madasamy Kumar, Veerappan Jeyachandran, Arumugam Sathamraja, Pandian Paulraj**

***ABSTRACT: The reaction between substituted 4-hydroxybenzaldehyde, active methylene compounds and /or resorcinol yield aminochromene derivatives. Structures of these compounds were established upon the basis of IR,1HNMR,13CNMR,and MASSdata.***

***Keywords: chromenes, imines, amines, antioxidants***

## I. INTRODUCTION

Multicomponent reactions (MCRS) are reactions where numerous reactants involved in single synthetic operation and give new compounds.1 This type of reactions avoids purification process and often wide variety of complex molecule in a single step, inturn it is very useful for saving solvent and reagents. Among many heterocyclic compounds, chromenes are very important due to its biological activity such as antioxidants,2 anticancer,anti-microbial, 3 anti-inflammatory,4 anti-HIV,5 and anti-tumor,6 alzimer disease, 7 antihypotensive8 and antileishmanial.9 There are many reports shown that synthesis of different chromene derivatives and its applications (Figure 1).1, 10, 11 A Knoevenagel condensation is the reaction between salicylaldehyde with active methylene compounds followed by intramolecular cyclisation to give imino derivatives 11. As per reports, different products are obtained by control of a solvent,12 ratio of reagents and temperature13etc., Due to importance of these chromene derivatives, numerous green approaches14 have been developed under distinct conditions like thermal heating,15 microwave,16 ultrasonic,17 electrochemical, infrared, and solvent free conditions. We could not find many reports on variation of an alkyl side chain to see the effect on antioxidant properties of chromene derivatives. So we are motivated to synthesis aminochromenes by taking alkylated aldehyde and malonitrile. Currently, many investigations are going on.18, 19, 20

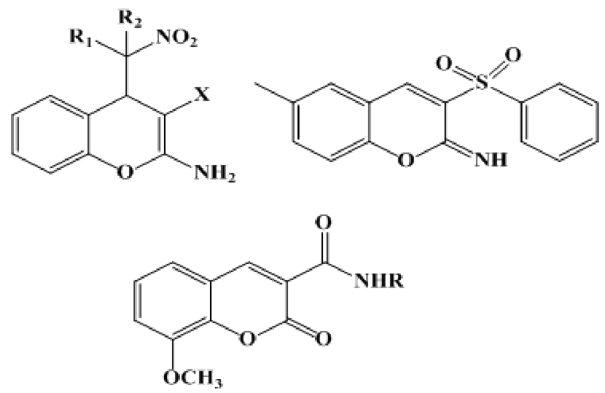


**Figure 1. Examples for different chromene derivatives**

## II. EXPERIMENTAL METHOD AND TECHNIQUES

All NMR spectra were recorded using Bruker (300MHz) spectrometer. JASCO-FTIR spectrometer (4000-400cm$^{-1}$) used for recording Infrared spectra. Electro spray ionization mass spectrometry (ESI-MS) analysis was performed in the negative ion mode on a liquid chromatography-ion trap mass spectrometer (LCQ Fleet, Thermo Fisher Instruments Limited,US).The DPPH radical scavenging action of the compounds was dignified rendering to the method of Blios.[20] The assay of nitric oxide (NO$^{\cdot}$), $H_2O_2$, ($O_2^{\cdot-}$) scavenging activity was determined using the method available in literature.[22, 27, 28]

Aseriesof2-amino-7-hydroxy-4-(4-(alkyloxy) phenyl)-4*H*-chromene-3-carbonitrile havebeensynthesized using calcium hydroxide as efficient and green catalyst.Thestructureswereconfirmedby$^{1}$H-NMR,$^{13}$C-NMR,FT-IRandmassspectroscopictechniques.

## III. RESULTS & DISCUSSION

### A. *General procedure for the synthesis Of 4-alkoxybenzaldehyde: 2a-h*

A mixture of 4-hydroxybenzaldehyde (10mmol,1eq) 1-bromoalkane(15mmol,1.5eq), anhydrous$K_2CO_3$(15mmol,1.5eq) and butanone 20ml, the catalytic amount of KI was added to the mixture was refluxed for 4hours.

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Reaction mixture was concentrated, poured into water and extracted with dichloromethane(DCM)(20mlx2). The combined organic clayer was washed with brine and over anhydrous $Na_2SO_4$. Evaporation of solvent furnished a brown colored mass which was purified by column chromatography on 60-120 mesh silicagel. Elution with a mixture of ethylacetate–petether(1:9)furnished the pure light yellow oilyliquid.[29]

### B. *General procedure for the preparation of 4-alkoxybenzoicacid: 3a-h*

The4-alkoxybenzaldehyde(1g)wasdissolvedinbutanone(20ml )and jones reagent (1.7g$CrO_3$,2ml$H_2SO_4$and6ml$H_2O$)was slowly added to this mixture andstirredfor1hour.After1hour,tothismixturewaterwas added slowly.Thewhiteprecipitatewasfiltered;itwaswashedwithwate randrecrystallizedbyethanolgivepureproduct.[30]

### C. *General procedure for the preparation of 4-formyl-3-hydroxyphenyl-4-(alkoxy)benzoate: 4a-h*

A stirred solution of 4-alkoxybenzoicacid(1eq), 2,4-dihydroxybenzaldehyde (1.1eq),N,N-Dicyclo hexylcarbodiimide(DCC)(3eq) and catalytic amount of (DMAP) dimethy laminopyridinein (DCM) dichloromethane solution was added at the room temperature, mixture was vacuum created and stirred for overnight under $N_2$ atmosphere. The precipitate N,N-dicyclohexylure a was filtered off. The filtrate was diluted with (20ml) DCM and washed with water and dried over anhydrous $Na_2SO_4$.Evaporate solvent by vacuum pump and purified by column chromatography60-120 meshsilicagel.Elution with a mixture of (1:9)ethylacetate–pet ether furnished the pure a product.The product was recrystallized from $CH_2Cl_2$-acetonitrile too obtain a white solid.[24]

### D. *2-amino-7-hydroxy-4-(4-(alkoxy)phenyl)-4H-chromene-3-carbonitrile:5a-h*

A mixture of resorcinol(1.0mmol),2-(4-methoxybenzylidene), malononitrile (1.5mmol), and $Ca(OH)_2$ (1.0mmol) in 5mL of methanol was stirred at room temperature for 5min. After completion of there action monitored by TLC, the crude was washed with ethylacetate, dissolved with THF and filter to separate the catalyst. Solvent was removed from filtrate gave the pure product.

## IV. CONCLUSIONS

Spinel $ZnAl_2O_4$ sample was synthesized successfully by a facile microwave heating route using *H. rosa-sinensis* extract. XRD, EDX and FT-IR results specified that the prepared spinel $ZnAl_2O_4$ sample have spinel structure with well crystalline product and also free from other phase impurities. The HR-SEM result revealed that spinel $ZnAl_2O_4$ sample contain nanoparticle-like morphology. The specific $M_s$ values were obtained to be 0.023 emu/g for spinel $ZnAl_2O_4$ sample.

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