

***p*-Dimethylaminopyridine (DMAP): A highly efficient catalyst for one pot, solvent free synthesis of substituted 2-amino-2-chromenes under microwave irradiation**

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Abstract: A highly efficient, green and expeditious method is described for the synthesis of substituted 2-amino-2-chromenes employing one pot three component condensation of aromatic aldehydes, malononitrile and activated phenol in presence of *p*-dimethylaminopyridine (10 mol %) as a catalyst under microwave irradiation. The present method is operationally simple and offers many advantages such as high yield, short reaction time and simple workup.

Keywords: 2-amino-2-chromenes; multicomponent; *p*-dimethylaminopyridine; microwave irradiation.

1. Introduction

The increasing attention during the last decades towards the environmental protection; forced both modern academic and industrial groups to develop the chemical processes which gives maximum yield, reduce the cost of raw material, utilize the non-toxic reagents and non-hazardous solvents. So one of the tools for such need of time is multicomponent reaction (MCR); this process consist of two or more synthetic steps which are carried out without isolation of any intermediate thus reducing time, saving money, energy and raw materials¹.

Microwave assisted solvent free reactions have received great importance due to their simplicity in operation, elimination of solvents at source by preventing pollution in organic synthesis, enhanced rate of reaction and better yields with high purity as compared to those carried out by conventional heating². Microwave assisted solventless protocols has been applied in various useful transformations involving condensation, oxidation-reduction, protection-deprotection, rearrangement reactions and synthesis of different heterocyclic systems³. Further, the use of solvent free synthesis in conjugation with microwave irradiation (MWI) develops an efficient procedure associated with many advantages such as short reaction time, uniform heating and higher yields for the synthesis of various synthetic scaffolds.

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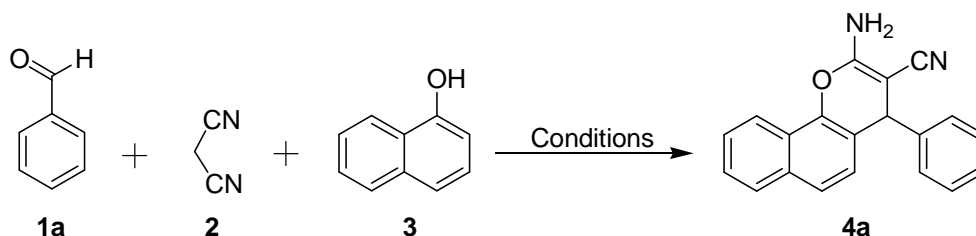
2-amino-2-chromenes are an important class of heterocyclic compounds as they are the main constituents of many natural products. They are widely used as cosmetics, pigments⁴ and potential biodegradable agrochemicals⁵. Also fused chromenes are biologically active compounds with a wide range of activities such as antimicrobial⁶, mutagenic⁷, antiviral⁸, sex pheromonal⁹, antitumoral¹⁰ and central nervous system activities¹¹.

The development of an efficient methodology for the synthesis of substituted 2-amino-2-chromenes is highly essential. The most straightforward synthesis of substituted 2-amino-2-chromenes involves a three component condensation of aromatic aldehyde, malononitrile and an activated phenol traditionally this condensation was carried out by using a base such as piperidine¹² which are frequently utilized in stoichiometric amounts and refluxing in several hours. Also various modified procedures have been reported for the synthesis of substituted 2-amino-2-chromenes using CTACl¹³, TEBA¹⁴, γ -alumina¹⁵, K₂CO₃ [16], H₁₄ [NaP₅W₃₀O₁₁₀] [17], p-TSA¹⁸ and KF/Al₂O₃¹⁹ as a catalyst. However, most of these methods suffer from one or more drawbacks such as moderate yield of the products, the use of toxic solvents, longer reaction time and tedious workup procedure.

2. Results and discussion

Herein, we wish to report synthesis of substituted 2-amino-2-chromenes by one pot three component condensation of aromatic aldehydes, malononitrile and activated phenol in presence of *p*-dimethylaminopyridine (10 mol %) as a catalyst under microwave irradiation. The corresponding product obtained with good to excellent yields (85-96 %).

Initially, benzaldehyde (**1a**) was selected as a probe aldehyde to optimize the condensation reaction between malononitrile (**2**) and 1-naphthol (**3**) for the synthesis of 2-amino-2-chromenes (**Scheme 1**). To improve the eco-compatibility of organic processes, among the several catalysts were screened at variable conditions and results are summarized in Table 1. At first the reaction was carried out in absence of catalyst and solvent (Table 1, entry 1) at 60 °C no product formation was observed. We screened other catalyst such as β -CD, Alum, Bi(NO₃)₃.5H₂O, SrCl₂.6H₂O, SnCl₂.2H₂O, SnCl₄.SiO₂, HClO₄.SiO₂, for the condensation reaction at room temperature, conventional heating and microwave irradiation (Table 1, entries 2-12) but we did not detect the desired product formation. However, the addition of a catalytic amount of base (10 %) such as *t*-BuOK, *t*-BuONa and DBU (Table 1, entries 13-15) results in formation of product **4a** under microwave irradiation with < 60 % yields. By addition of 10 mol % DMAP in ethanol and under solvent free conditions (Table 1, entry 16, 17) under MW irradiation results in formation of product **4a**. To compare the efficiency of solvent free condition with respect to solution condition, it was found that the solvent free condition is most efficient (Table 1, entry 17) give excellent yield (95 %).



Scheme 1. Reaction between benzaldehyde (**1a**), malononitrile (**2**) and 1-naphthol (**3**) under variable conditions.

Table 1. Screening of different catalyst for synthesis of **4a**^a

Entry	Catalyst	Solvent	Time	Temp. (°C)	Yields [%] ^b
1	No Catalyst	No Solvent	2 h	60	-
2	β-CD	Water	12 h	Reflux	-
3	β-CD	aq. C ₂ H ₅ OH	20 min	MW	-
4	Alum	Water	12 h	RT	-
5	Alum	Water	2 h	Reflux	-
6	Bi (NO ₃) ₃ .5H ₂ O	C ₂ H ₅ OH	12 h	RT	-
7	Bi (NO ₃) ₃ .5H ₂ O	C ₂ H ₅ OH	6 h	Reflux	-
8	SrCl ₂ .6H ₂ O	Neat	5.0 min	MW	-
9	SnCl ₂ .2H ₂ O	Neat	5.0 min	MW	-
10	SnCl ₄ .SiO ₂	Neat	10.0 min	MW	-
11	SnCl ₄ .SiO ₂	CH ₃ CN	10.0 min	MW	-
12	HClO ₄ .SiO ₂	Neat	5.0 min	MW	-
13	<i>t</i> -BuOK	C ₂ H ₅ OH	4.8 min	MW	50
14	<i>t</i> -BuONa	C ₂ H ₅ OH	3.6 min	MW	45
15	DBU	C ₂ H ₅ OH	3.6 min	MW	60
16	DMAP	C ₂ H ₅ OH	3.0 min	MW	80
17	DMAP	Neat	0.6 min	MW	95

^aReaction condition: Benzaldehyde (1 mmol), malononitrile (1 mmol), 1-naphthol (1 mmol) and catalyst (10 mol %). ^bYields of isolated pure products. (-) No reaction takes place.

This clearly indicates the catalytic effect of DMAP for the synthesis of **4a**. The activity of *p*-dimethylaminopyridine (DMAP) for this condensation is remarkable than that of all the other tested catalyst. We also investigated the effect of catalytic amount on yield and rate of the reaction for the synthesis of **4a** and summarized in Table 2. It was found that 10 mol% of catalyst for solventless synthesis of **4a** under MW irradiation gives excellent yield. A controlled reaction was also carried out to confirm that no desired product was obtained in the absence of the catalyst (Table 2, entry 7).

Table 2. Optimization of amount of catalyst for the synthesis of **4a**^a

Entry	Catalyst (mol%)	Solvent	Time (min.)	Temp. (°C)	Yields [%] ^b
1	5	aq. C ₂ H ₅ OH	5.8	MW	60
2	5	C ₂ H ₅ OH	4.8	MW	65
3	5	Neat	1.2	MW	68
4	10	aq. C ₂ H ₅ OH	3.6	MW	78
5	10	C ₂ H ₅ OH	3.0	MW	80
6	10	Neat	0.6	MW	95
7	-	Neat	0.6	MW	-

^aReaction condition: Benzaldehyde (1 mmol), malononitrile (1 mmol), 1-naphthol (1 mmol), catalyst.

^bYields refer to isolated pure products. (-) No reaction takes place.

With these results in our hands, we examine the generality of these conditions to other aromatic aldehydes including electron donating, electron withdrawing and heterocyclic and the results are as shown in Table 3. The catalyst plays important role in the success of the reaction in terms of the rate and the yields.

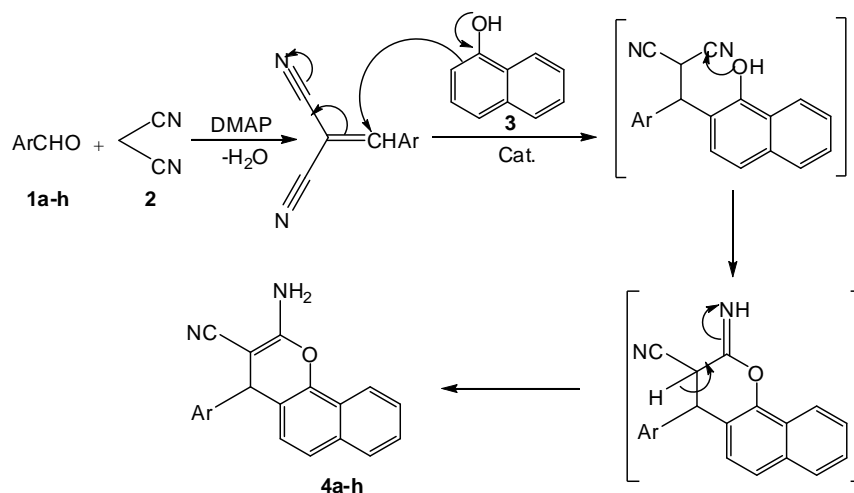
Table 3. Synthesis of 2-amino-2-chromenes under solvent free condition catalyzed by *p*-dimethylamino pyridine (DMAP)^a

Entry	Ar	Product	Time (h)	Yields [%] ^b	M.P. (Lit M. P.) (°C)
1	C ₆ H ₅	4a	1.2	95	212-214 (210-211) ²⁰
2	3,4-OCH ₃ C ₆ H ₃	4b	1.5	87	208-210 (210-211) ²¹
3	3,4,5-OCH ₃ C ₆ H ₂	4c	1.5	89	185-186 (186-187) ²¹
4	4-BrC ₆ H ₄	4d	1	94	240-241 (241-243) ²²
5	2-ClC ₆ H ₄	4e	1	85	235-237 (236-237) ¹³
6	2-NO ₂ C ₆ H ₄	4f	1	93	209-210 (208-210) ²¹
7	4-NO ₂ C ₆ H ₄	4g	1	96	241-242 (240-241) ²³
8	Pyridine-4-carbaldehyde	4h	1	90	240-242

^ammol ratio of aromatic aldehyde, malononitrile, 1-naphthol and catalyst is 1:1:1:0.1

^bYields refer to isolated pure products.

It is evident that there is a highly influential substitution and steric factor, meta and para-substituted aldehydes afforded higher conversion (Table 3, entries 2- 4, 7) as compared to ortho-substituted aldehydes (Table 3, entries 5, 6). Similarly electron donating substituent's somewhat decrease the rate of the reaction and yield (Table 3, entry 2, 3) while electron withdrawing substituent's cleanly converted in to corresponding 2-amino-2-chromenes in excellent yield (Table 3, entries 6 and 7). Remarkably, Pyridine-4-carbaldehyde (Table 3, entry 8) also reacted with malononitrile and 1-naphthol under similar reaction conditions and gives the expected product in excellent yield (90%). This pattern was consistently observed with all other substituents. All the synthesized compounds were characterized by IR, ¹H-NMR and Mass spectroscopic technique.

**Scheme 2.** Mechanistic pathway for the formation of substituted 2-amino-2-chromenes

The mechanism of formation of the product is a sequence of reactions involving Knoevenagel condensation of malononitrile with aromatic aldehyde by loss of water molecule, followed by Michael addition of 1-naphthol from β -position on electron deficient C-atom and an intra molecular cyclisation that leads to the formation of the desired product. The probable mechanism is given in Scheme 2.

3. Conclusion

In conclusion, we have developed a novel, practically efficient solvent free protocol for the synthesis of substituted 2-amino-2-chromenes via one-pot three component reaction of aromatic aldehyde, malononitrile and 1-naphthol using a catalytic amount of *p*-dimethylaminopyridine (10 mol %) under microwave irradiation. The present protocol offers several advantages such as solvent free condition, operational simplicity, short reaction time, easy work up and easy purification of products simply by recrystallization.

4. Experimental

Melting points of the synthesized compounds were measured by open capillary method and are uncorrected. Infrared spectra were recorded using KBr pellets on Shimadzu fourier transform infrared spectrophotometer in the region 4000-400 cm^{-1} . $^1\text{H-NMR}$ spectra were recorded on Varian mercury plus 300 MHz spectrophotometer in CDCl_3 as solvent and TMS as an internal standard with ^1H resonant frequency of 300 MHz. The chemical shifts were measured in *ppm* downfield from internal TMS at $\delta=0$. The mass spectra were recorded on Varian Inc. 410 prostar binary with 500 MS IT. TLC was performed on Fluka[®] silica gel plates (5-17 μm , F₂₅₄). The mobile phase was ethyl acetate and n-hexane (2:8) and detection was made using UV light. Chemicals used were of commercial grade and used without further purification. All products are known compounds and were identified by comparing of their physical and spectral data with those reported in the literature.

4.1. General procedure for the synthesis of 2-amino-2-chromenes

In a round bottom flask *p*-dimethylaminopyridine (10 mol%, 0.1 mmol) was added to a mixture of aromatic aldehyde (1 mmol), malononitrile (1 mmol) and 1-naphthol (1 mmol). The resulting mixture was irradiated with microwaves under solvent free condition for the appropriate time as motioned in Table 3. After completion of the reaction, as indicated by TLC, the mixture of ethanol-water (2:1, 5 ml) was added to the reaction mixture and then the solution was filtered. The crude product was washed with water and further purified by recrystallization using ethanol. The products were obtained in 85-96 % yields.

4.2. Spectroscopic data

2-amino-4-phenyl-4H-benzo[h]chromene-3-carbonitrile (4a): White solid, IR (KBr), ν (cm^{-1}): 3448, 2204, 1654, 1099; $^1\text{H-NMR}$ (CDCl_3 , 300MHz), δ (ppm): 1.55 (s, 2H, NH_2), 4.73 (s, 1H, CH), 7.03 (d, 1H, $J=8.6$ Hz, ArH), 7.22 -7.61(m, 8H, ArH), 7.79 (d, 1H, $J=7.6$ Hz, ArH), 8.18 (d, 1H, $J=8.1$ Hz, ArH); MS (ESI): 297.39 (M^+-1).

2-amino-4-(3, 4-dimethoxyphenyl)-4H-benzo[h]chromene-3-carbonitrile (4b): Light yellow solid, IR (KBr), ν (cm^{-1}): 3381, 2222, 1660, 1273; $^1\text{H-NMR}$ (CDCl_3 , 300MHz), δ (ppm): 1.55 (s, 2H, NH_2), 3.93 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 4.83 (s, 1H, CH), 6.71-6.97 (m, 3H, ArH), 7.03 (d, 1H, $J=8.6$ Hz, ArH), 7.36 -7.68 (m, 3H, ArH), 7.79 (d, 1H, $J=7.6$ Hz, ArH), 8.17 (d, 1H, $J=8.1$ Hz, ArH); MS (ESI): 357.25 (M^+-1).

2-amino-4-(3, 4, 5-trimethoxyphenyl)-4H-benzo[h]chromene-3-carbonitrile (4c): Dark yellow solid, IR (KBr), ν (cm^{-1}): 3342, 2220, 1664, 1130; $^1\text{H-NMR}$ (CDCl_3 , 300MHz), δ (ppm): 1.56 (s, 2H, NH_2), 3.80 (s, 6H, OCH_3), 3.82 (s, 3H, OCH_3), 4.83 (s, 1H, CH), 6.43 (s, 2H, ArH), 7.07 (d, 1H, $J=8.5$ Hz, ArH), 7.53-7.60 (m, 3H, ArH), 7.82 (d, 1H, $J=7.6$ Hz, ArH), 8.19 (d, 1H, $J=7.6$ Hz, ArH); MS (ESI): 388.97 (M^+).

2-amino-4-(4-bromophenyl)-4H-benzo[h]chromene-3-carbonitrile (4d): Dark yellow solid, IR (KBr), ν (cm^{-1}): 3350, 2191, 1651, 1101; $^1\text{H-NMR}$ (CDCl_3 , 300MHz), δ (ppm): 1.55 (s, 2H, NH_2),

5.03 (s, 1H, CH), 6.96 (d, 1H, $J=8.6$ Hz, ArH), 7.64-6.94 (m, 7H, ArH), 7.82 (d, 1H, $J=8.5$ Hz, ArH), 8.20 (d, 1H, $J=8.5$ Hz, ArH); MS (ESI): 376.23 (M^+-1).

2-amino-4-(2-chlorophenyl)-4H-benzo[h]chromene-3-carbonitrile (4e): White solid, IR (KBr), ν (cm^{-1}): 3327, 2198, 1662, 1103, 752; $^1\text{H-NMR}$ (CDCl_3 , 300MHz), δ (ppm): 1.55 (s, 2H, NH_2), 4.78 (s, 1H, CH), 7.07 (d, 1H, $J=8.6$ Hz, ArH), 7.17-7.61 (m, 7H, ArH), 7.79 (d, 1H, $J=7.2$ Hz, ArH), 8.18 (d, 1H, $J=8.1$ Hz, ArH); MS (ESI): 331.35 (M^+-1).

2-amino-4-(2-nitrophenyl)-4H-benzo[h]chromene-3-carbonitrile (4f): Dark yellow solid, IR (KBr), ν (cm^{-1}): 3332, 2194, 1660, 1523, 1105; $^1\text{H-NMR}$ (CDCl_3 , 300MHz), δ (ppm): 1.54 (s, 2H, NH_2), 4.82 (s, 1H, CH), 7.07 (d, 1H, $J=8.6$ Hz, ArH), 7.30-7.80 (m, 7H, ArH), 7.88 (d, 1H, $J=8.1$ Hz, ArH), 8.18 (d, 1H, $J=8.1$ Hz, ArH); MS (ESI): 344.40 (M^++1).

2-amino-4-(4-nitrophenyl)-4H-benzo[h]chromene-3-carbonitrile (4g): Dark yellow solid, IR (KBr), ν (cm^{-1}): 3350, 2191, 1651, 1510, 1350, 1101; $^1\text{H-NMR}$ (CDCl_3 , 300MHz), δ (ppm): 1.54 (s, 2H, NH_2), 4.85 (s, 1H, CH), 6.96 (d, 1H, $J=8.5$ Hz, ArH), 7.40-7.80 (m, 7H, ArH), 7.82 (d, 1H, $J=7.2$ Hz, ArH), 8.19 (d, 1H, $J=8.5$ Hz, ArH); 342.19 (M^+-1).

2-amino-4-(pyridin-4-yl)-4H-benzo[h]chromene-3-carbonitrile (4h): Light yellow solid, IR (KBr), ν (cm^{-1}): 3344, 2206, 1668, 1105; $^1\text{H-NMR}$ (CDCl_3 , 300MHz), δ (ppm): 1.56 (s, 2H, NH_2), 4.84 (s, 1H, CH), 6.99 (d, 1H, $J=8.6$ Hz, ArH), 7.16-7.63 (m, 5H, ArH), 7.82 (d, 1H, $J=7.2$ Hz, ArH), 8.18 (d, 1H, $J=7.6$ Hz, ArH), 8.56 (d, 2H, $J=7.6$ Hz, 2ArH); MS (ESI): 300.12 (M^++1).

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