# A Green and Efficient Method for the Synthesis of 3,4-Dihydropyrano[c]chromene using Phosphate Fertilizers (MAP, DAP and TSP) as Heterogeneous Catalysts

**Soukaina CHEHAB**[1], **Youssef MERROUN**[1], **Touriya GHAILANE**[1], **Rachida GHAILANE**[1], **Said BOUKHRIS**[1] **and Abdelaziz SOUIZI***

Laboratory of Organic, Organometallic and Theoretical Chemistry, University of Ibn Tofail, Faculty of Science, B.P. 133, 14000 Kenitra, Morocco

**Abstract:** This article presents a simple and green method for the synthesis of 3,4-dihydropyrano[c]chromenes, they have been obtained by the condensation of an aromatic aldehyde, malononitrile and 4-hydroxycoumarin in presence of phosphate fertilizers (Monoammonium phosphate MAP, Diammonium phosphate DAP and Triple superphosphate TSP) as heterogeneous catalysts and ethanol as an ecological solvent. This method has remarkable advantages, such as excellent catalytic performance of the catalysts used in the ethanol and the facility of preparation of the desired products with high to excellent yields (>92%) in short reaction times varying from 30 to 45 min, the long-term durability and easy recovery of catalysts, constitute a good heterogeneous system. All these advantages added to the low cost of these catalysts and their ecological profile have allowed them to be an alternative to the other synthetic and toxic catalysts used previously.

**Keywords:** Heterogeneous catalysts, MAP, DAP, TSP, 3,4-dihydropyrano[c]chromene, phosphate fertilizers.

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***Corresponding author. E-mail**: souizi@yahoo.com

## INTRODUCTION

Awareness of the harmful effects of certain practices used in chemical synthesis and the need to protect the environment was the reason why research in the chemical area was directed for developing some synthesis strategies that are environmentally friendly (1-2). Consequently, the main aim of chemists is to find the procedures of synthesis using different kinds of catalysts to reduce the cost and time of reaction with good yields of desired products (3). Indeed, the use of heterogeneous phosphate-based catalysts takes great importance in chemical synthesis due to their availability essentially in Morocco which is considered as the most known country in the production of natural phosphate (4-9). Other heterogeneous catalysts as hydroxyapatite (10-13) and fluoroapatite (14-16) are also used in organic synthesis. In particular our work is aimed to 3,4-dihydropyrano[c]chromene synthesis, which gains a lot of attention due to their various biological activities (17-22), they are well known as spasmolytic, diuretic, anticoagulant, anti-cancer and anti-anaphylactic, they can also be used as cognitive enhancers, for the treatment of neurodegenerative diseases, including Alzheimer's disease, amyotrophic lateral sclerosis, Huntington's disease, Parkinson's disease, AIDS-associated dementia and Down syndrome as well as for the treatment of schizophrenia and myoclonus (23) . Following the importance and usefulness of dihydropyrano[c]chromene derivatives, numerous synthetic pathways have been described, including electrolysis (24) microwave and ultrasonic irradiation (25-26) by piperidine/pyridine in ethanol (27), $H_6P_2W_{18}O_{62} \cdot 18H_2O$, tetrabutylammonium bromide, copper oxide nanoparticles, sodium dodecyl sulfate (SDS), trisodium citrate, selectfluor chloride triethylbenzylammonuim DABCO in aqueous media (28-35). Tetramethylguanidinium trifluoroacetate (TMGT) (36), rare earth perfluorooctanoates (37), $Na_2SeO_4$ (38), $SiO_2$-Pr-$SO_3$ (39), functionalized sulfonic acid silica (40), hexamethylenetetramine (41), $Fe_2O_3$ nanoparticles (42), the complexes of silica gel (43), Ru (II)(44), Urea (45), $NH_4VO_3$ (46), starch solution (47), grindstone chemistry (48), SBPPSP (49), MgO nanoparticle (50), ammonium acetate (51), 4-(dimethylamino)pyridine (DMAP) (52). Some synthetic catalysts of phosphate have also been reported in the literature for 3,4-dihydropyrano[c]chromenes synthesis; one found the Disodium hydrogen phosphate (53) and DHAP which has been described once as a homogeneous catalyst in the presence of ethanol-water (54). The majority of these methods use the expensive or homogenous catalysts that present certain disadvantages such as deactivation of the catalyst, difficult work and toxic effluents, not forgetting in some cases the low yields of the desired product, the long reaction time, and the most of them are synthetic and they require special efforts in their preparation. For these reasons, the development of a new and mild method that overcomes the drawbacks of previous procedures. In this context, this is the first time that phosphate fertilizers (MAP, DAP and

TSP) are used directly as heterogeneous catalysts in their granule form for the synthesis of 3,4-dihydropyrano [c] chromene, in order to valorize one of the important natural resources in Morocco that is considered among the first countries producer of the natural phosphate.

The present work is oriented in particular on the direct application of phosphate monoammonium phosphate (MAP), di-ammonium phosphate (DAP) and triple super phosphate (TSP) as heterogeneous catalysts that they are already used in some researchers developed in our laboratory focused on synthesis in organic chemistry (55). Thus, we projected to the synthesis of 3,4-dihydropyrano[c]chromene in the presence of these heterogeneous catalysts, It was shown that they could be easily recovered and reused, as a consequence they can be considered among the most efficient catalysts in organic synthesis from the multicomponent reactions (MCRs) (56-57). The novelty of this study is the use of new catalysts, available in large quantities and inexpensive because Morocco is considered as a leader in the phosphate production. For this reason, this work is focused on the valorization of the fertilizer phosphate in the catalytic area. It is well known as reported before that these catalysts led to the desired products with excellent yields in short reaction times. The contribution of this work in the development of Moroccan natural resources for participating to economize of the cost of manipulation and energy of the reaction as well as to the development of green chemistry. In addition, the besides one of the strong point of these catalysts is that they are used as a heterogeneous catalyst in their natural shape without further preparation.

## MATERIALS AND METHODS

The chemicals used in this work were purchased from Sigma-Aldrich Chemical Companies. The known products were identified by comparison of their melting points and their spectral data with those reported in the literature. Monitoring of the evolution of the reactions was carried out by TLC on silica gel SILG / UV 254 plates. The melting points were taken on a hot Kofler and are not corrected. $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a 300 MHz Bruker spectrometer in DMSO-d6.

### General procedure for the synthesis of 3,4-dihydropyrano [c] chromene

A mixture of malononitrile (1 mmol), aromatic aldehyde (1 mmol) and 4-hydroxycoumarin (1 mmol) in ethanol (1 mL), in the presence of 0.01 g of catalyst, was brought to reflux, the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature, the solid thus formed was collected by filtration, washed with ethanol and purified by recrystallization from hot ethanol to give pure products **4a-**

**4f**. The product obtained was characterized on the basis of their melting points reported in Table 5 and spectroscopic data that are given below and their comparison with the ones given in the literature show a good agreement.

*2-Amino-4-phenyl-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile* **4a**:
$^1$H NMR (300 MHz, DMSO-$d_6$, delta, ppm): 7.91 (1H, d, Ar-H), 7.70 (1H, t, Ar-H), 7.49 (1H, t, Ar-H), 7.45 (1H, d, Ar-H), 7.42 (2H, s, $NH_2$), 7.35 -7.24 (5H, m, Ar-H), 4.45 (1H, s, CH). $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ 160, 158.46, 153.89, 152.61, 143.80, 133.38, 128.99, 128.10, 127.59, 125.13, 122.94, 119.70, 117.03, 113.43, 104.48, 58.48.

*2-Amino-4-p-tolyl-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile* **4b**:
$^1$H NMR (300 MHz, DMSO-$d_6$, delta, ppm): 7.91 (1H, d, Ar-H), 7.72 (1H, t, Ar-H), 7.50-7.42 (2H, m, Ar-H), 7.38 (2H, s, $NH_2$), 7.17-7.10 (4H, m, Ar-H), 4.40 (1H, s, CH), 2.26 (3H, s, $CH_3$). $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ 159.97, 158.41, 153.72, 152.57, 140.87, 136.75, 133.32, 129.53, 127.99, 125.10, 122.91, 119.72, 117, 113.43, 104.61, 58.60, 21.09.

*2-Amino-4-(4-diméthylaminophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile* **4c**: $^1$H NMR (300 MHz, DMSO-$d_6$, delta, ppm): 7.83 (1H, d, Ar-H), 7.72 (1H, t, ArH), 7.50 -7.42 (2H, m, Ar-H), 7.19 (2H, s, $NH_2$), 7.08-6.65 (4H, m, Ar-H), 4.33 (1H, s, CH), 2.86 (6H, s, N $(CH_3)_2$). $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ 159.97, 158.44, 154.88, 152.54, 134.04, 131.41, 128.63, 125.05, 122.89, 119.73, 116.96, 113.56, 105.22, 59.27.

*2-Amino-4-(4-nitrophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile* **4d**:
$^1$H NMR (300 MHz, DMSO-$d_6$, delta, ppm): 8.17 (1H, d, Ar-H), 7.91 (1H, d, Ar-H), 7.77 (1H, t, Ar-H), 7.74 (1H, t, Ar-H), 7.57 (2H, s, $NH_2$), 7.55-7.46 (4H, m, Ar-H), 4.68 (1H, s, CH). $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ 160.05, 158.52, 154.43, 152.75, 151.23, 147.09, 133.66, 129.65, 125.23, 124.20, 123.06, 119.35, 117.11, 113.38, 103.28, 57.24.

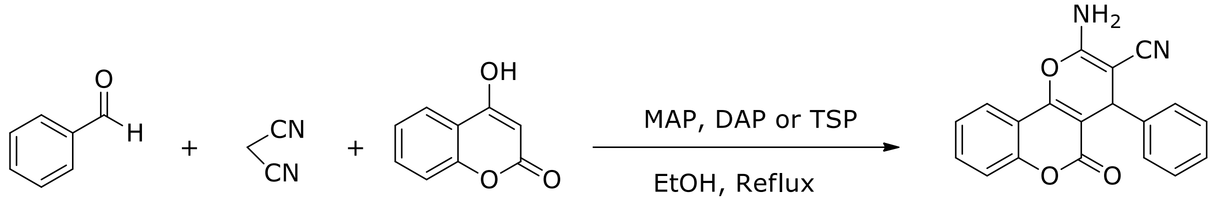
*2-Amino-4-(4-bromophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile* **4e**:
$^1$H NMR (300 MHz, DMSO-$d_6$, delta, ppm): 7.93(1H,d, ArH), 7.73 (1H, t, Ar-H), 7.68 (1H, t, Ar-H), 7.52-7.48 (3H, m, Ar-H), 7.45(2H, s, NH2), 7.26 (2H, d, Ar-H), 4.48 (1H, s, CH). $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ 159.95, 158.53, 154.07, 152.70, 143.17, 133.43, 131.82, 130.42, 125.09, 123.02, 120.70, 119.39, 117, 113.43, 103.97, 58.22.

*2-Amino-4-(4-chlorophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile* **4f**:
$^1$H NMR (300 MHz, DMSO-$d_6$, delta, ppm): 7.92 (1H, d, Ar-H), 7.71 (1H, t, Ar-H), 7.48 (1H, t, Ar-H), 7.43 (1H, d, Ar-H), 7.40 (2H, s, NH2), 7.37-7.30 (4H, m, Ar-H), 4.50 (1H,

s, CH). $^{13}$C NMR (75 MHz, DMSO-d$_6$): δ 159.94, 158.54, 154.05, 152.69, 142.73, 133.39, 132.25, 130.05, 129.14, 125.06, 123, 119.40, 116.97, 113.43, 104.04, 58.31.

## RESULTS AND DISCUSSION

In order to test the catalytic activity of the phosphate heterogeneous catalysts MAP, DAP, and TSP used herein, we have chosen the synthesis of 3,4-dihydropyrano[c]chromene, which is a condensation between an aromatic aldehyde, malononitrile, and 4-hydroxycoumarin (MCR) (Scheme 1).



**1** **2** **3** **4a**

**Scheme 1.** Synthesis of 3,4-dihydropyrano[c]chromene.

**Table 1.** Catalytic Test for the Synthesis of the 3,4-Dihydropyran[c]Chromene[a].

| Entry | Catalyst | Amount of catalyst (g) | Time | Yield (%)[b] |
|---|---|---|---|---|
| 1 | - | 0 | 24 h | 25 |
| 2 | MAP | 0.01 | 30 min | 86 |
| 3 | DAP | 0.01 | 45 min | 82 |
| 4 | TSP | 0.01 | 35 min | 82 |

[a]Reaction conditions: Benzaldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol), EtOH (3 mL), 0.01 g of MAP, DAP and TSP, Reflux.

[b]Isolated yield.

First, the reaction was tested in the absence of the catalyst, when the experiment had started no product was observed, but after prolonged reaction time (24 h), the desired product was obtained with a yield of 25%, while the reaction in the presence of the catalysts MAP, DAP and TSP improve the reactivity and provide products with reasonable yields which were respectively 86, 82 and 82%. The reaction times are short as 30 min for the MAP, 45 min for the DAP and 35 min for the TSP. These results confirm that the used catalysts possess catalytic activity efficient for the synthesis of the 3,4-dihydropyrano[c]chromene (Table 1).

In order to optimize the reaction conditions of the 3,4-dihydropyrano[c]chromene synthesis catalyzed by MAP, DAP, and TSP, it seems interesting for us to examine the effect of different parameters namely the of the reaction time, the amount of catalyst as well as the nature and volume of the solvent.

We have opted to examine the influence of the reaction time which is the fundamental parameter providing a straight effect on of the reaction yield. The yield of the desired product **4a** was determined in function of the reaction time that was varied by a step of 5 min starting from 30, 45 and 35 min, respectively for the MAP, DAP and TSP catalysts, these times are those obtained under the same conditions described previously ((a) given after Table 1). The results of this study are presented in Figure 1.

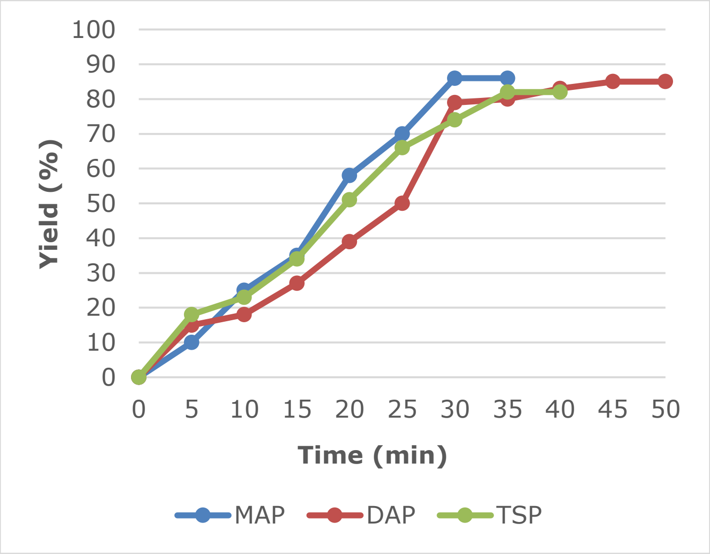


**Figure 1.** Time reaction optimization of the synthesis of 3,4-dihydropyran[c]chromene.

Figure 1 shows that the yield increases when the reaction time increases until the platform where the yield remains constant in function of time, indeed the yield of synthesis product reaches 86% after 30 min for the MAP. Whereas, both DAP and TSP catalysts give the same yield by 82% with 45 and 35 min as reaction times respectively.

After having optimized the reaction time, we consider useful to study the amount effect of the catalysts MAP, DAP and TSP used herein. For that, the amount of each catalyst has been varied from 0.002 g to 0.01 g. The obtained yields are collected in Table 2.

**Table 2.** The catalysts mass optimization for the synthesis of 3,4-dihydropyrano[c] chromene[a].

| Entry | Amount of catalyst (g) | Time (min) | | | Yield (%)[b] | | |
|---|---|---|---|---|---|---|---|
| | | MAP | DAP | TSP | MAP | DAP | TSP |
| 1 | 0.002 | 30 | 45 | 35 | 80 | 86 | 87 |
| 2 | 0.004 | 30 | 45 | 35 | 85 | 90 | 92 |
| 3 | 0.006 | 30 | 45 | 35 | 93 | 87 | 88 |
| 4 | 0.008 | 30 | 45 | 35 | 89 | 83 | 85 |
| 5 | 0.01 | 30 | 45 | 35 | 86 | 82 | 82 |

[a]Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol), EtOH (3 mL), (xg) mass of MAP, DAP and TSP, Reflux.

[b]Isolated yield.

From the table above, it is noticeable that the amount of 0.006 g for the MAP and 0.004 g for both DAP and TSP catalysts are sufficient to provide excellent yields in case of the reaction leading to product **4a**. The obtained yields are 93, 90 and 92% for MAP, DAP and TSP, respectively. Beyond these amounts, the observation of a remarkable decrease in yields, parallel to the increase in the quantity of the catalyst, is justified by the dispersive effect of the reagent on the surface of the catalysts.

The influence of the solvent nature on the catalytic activity of MAP, DAP, and TSP was studied in case of the model reaction while maintaining the same optimized parameters, namely reaction time and catalyst amount, described previously. For this, solvents of different nature, protic polar (EtOH, MeOH), aprotic ($CH_3CN$, THF), as well as solvents of apolar nature (toluene, dioxane), were used, the reaction was also performed in absence of the solvent. Table 3 summarizes all the results obtained in this study.

**Table 3.** Reaction yield of the synthesis of 3,4-dihydropyrano[c]chromene [a] in presence of a different kind of solvent.

| Entry | Solvent | Time (min) | | | Yield (%)[b] | | |
|---|---|---|---|---|---|---|---|
| | | MAP | DAP | TSP | MAP | DAP | TSP |
| 1 | Solvent-free | 30 | 45 | 35 | 78 | 74 | 74 |
| 2 | EtOH | 30 | 45 | 35 | 93 | 90 | 92 |
| 3 | MeOH | 30 | 45 | 35 | 75 | 77 | 83 |
| 4 | $CH_3CN$ | 30 | 45 | 35 | 74 | 77 | 79 |
| 5 | THF | 30 | 45 | 35 | 61 | 75 | 80 |
| 6 | Dioxane | 30 | 45 | 35 | 63 | 60 | 77 |
| 7 | Toluene | 30 | 45 | 35 | 59 | 55 | 70 |

[a] Reaction conditions: Benzaldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol), (3 mL) of solvent, 0.006 g of MAP, 0.004 g of DAP and TSP, Reflux.

[b]Isolated yield.

The results given in Table 3 show that the reaction is clearly favored in protic polar solvents and more specifically in ethanol, this is available for the model reaction where the MAP, DAP, and TSP catalysts were applied, the product **4a** is obtained with yields which are 93, 90 and 92% respectively. However, in the case of methanol it is noted that it allows obtaining the product with a lower yield than ethanol even though its dielectric constant is greater compared to the ethanol one, which may be explained by the fact that the methanol is more acidic than the ethanol, thus the O-H bond is more polar in methanol than in ethanol. Therefore, the methanol tends to liberate the proton more easily, unlike to the ethanol which just allows the polarization of the reagents leading to the formation of the desired product 4a with a good yield. Moreover, the appropriate solvent for each organic synthesis depends on the nature of the reaction mixture. Therefore, the use of ethanol as a solvent facilitates the formation and the separation of the charges on the active sites of the reagents, indeed this process is caused by the electrostatic interaction involved between the atomic charge on the atom forming polar bond of the solvent with the active atomic center which possesses the opposite sign of charge, in the reagent, this interaction makes easy the formation of the final product 4a.

As regards on the aprotic polar solvents ($CH_3CN$, THF) and nonpolar (toluene, dioxane), used in this part of our study, one can notice that the yield obtained in presence of each solvent is lower than that obtained in ethanol. One can deduce that the ethanol is the appropriate solvent allowing to obtain the desired product with excellent yields.

The volume of the solvent can also be a determining factor that can influence the yield of the 3,4-dihydropyrano[c]chromene synthesis, for this reason, it would be interesting to study the volume effect that was carried out by taking into account of the optimized parameters obtained previously, for this, the volume of ethanol was decreased from 3 to 1 ml, and Table 4 summarizes the obtained results.

**Table 4**. Optimization of the ethanol volume on the synthesis of 3,4-dihydropyrano[c]chromene [a].

| Entry | Volume of ethanol | Time (min) | | | Yield (%)[b] | | |
|---|---|---|---|---|---|---|---|
| | | MAP | DAP | TSP | MAP | DAP | TSP |
| 1 | Solvent-free | 30 | 45 | 35 | 78 | 74 | 74 |
| 2 | 1mL | 30 | 45 | 35 | 95 | 92 | 93 |
| 3 | 2mL | 30 | 45 | 35 | 94 | 91 | 93 |
| 4 | 3mL | 30 | 45 | 35 | 93 | 90 | 92 |

[a] Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarine (1 mmol), (x mL) of EtOH, 0.006 g of MAP, 0.004 g of DAP and TSP, reflux.

[b]Isolated yield.

From Table 4, it can be shown that 1 mL of ethanol appears to be the sufficient volume to achieve a yield of 95, 92 and 93% for the model reaction catalyzed by the MAP, DAP and

TSP respectively, whereas beyond 1 mL a decrease in yield has been observed, this is due the dispersion phenomenon of the reagents on the catalyst surface.

One of the most important factors that determine the efficiency of the catalytic activity of the catalyst is its ability to be reused for several times and its reliability to give a good reaction yield for each reuse, this allows to ensure sustainable chemistry. In this context the recovery and study of the reuse of MAP, DAP and TSP catalysts were carried out under the optimum reaction conditions already determined, the catalysts recovered by simple filtration and reused in a second reaction involving the same reagents and under the same operating conditions. This operation was repeated for four times, Figure 2 presents the results obtained.

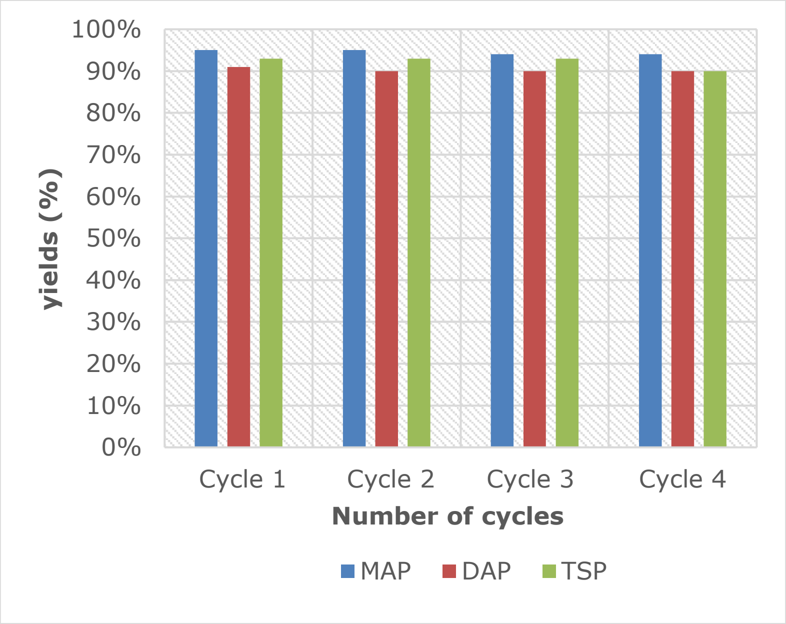
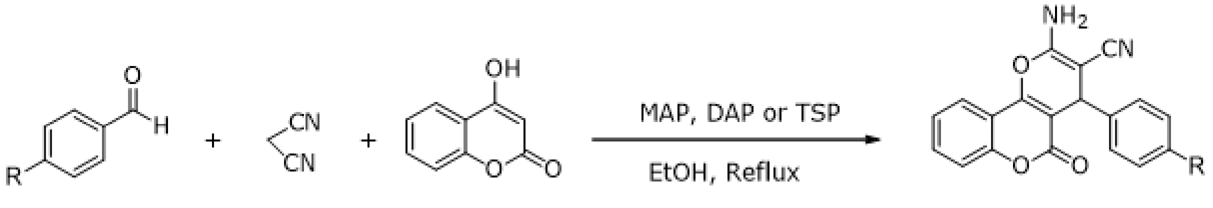


**Figure 2.** Reusability of the MAP, DAP, and TSP catalysts in case of the synthesis of 3,4-dihydropyrano [c] chromene.

The results clearly show that MAP, DAP and TSP catalysts can be reused several times without significant loss of their catalytic activities even after 4 cycles of application. After optimization of the reactional conditions for the synthesis of a product (**4a** 3,4-dihydropyrano[c]chromene), a generalization study of the reaction was carried out in order to synthesize other derivatives belonging to the same family of 3,4-dihydropyrano [c] chromene. These derivatives have been synthesized from various aromatic aldehydes, malononitrile and 4-hydroxycoumarin under the optimum operating conditions already determined, the obtained yields are given in Table 5.



**1** **2** **3** **4a-4f**

**Scheme 2.** Synthesis of 3,4-dihydropyrano[c]chromene derivatives.

**Table 5**. Reaction times and yields of the synthesis reactions of 3,4-dihydropyrano[c] chromene[a]

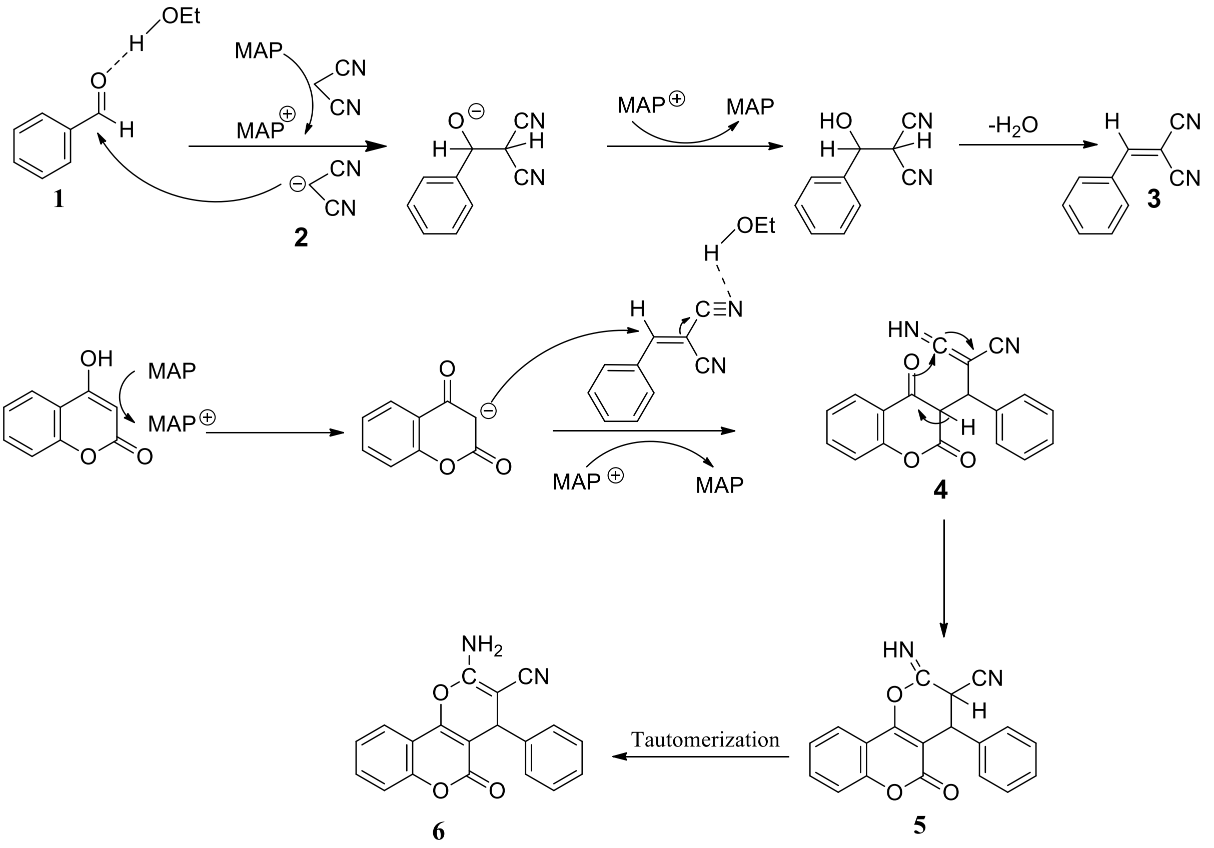
| Entry | R | Time (min) | | | Yield (%)[b] | | | Mp (°C) | |
|---|---|---|---|---|---|---|---|---|---|
| | | MAP | DAP | TSP | MAP | DAP | TSP | Found | Reported |
| 4a | H | 30 | 45 | 35 | 95 | 92 | 93 | 256-258 | 256-258(58) |
| 4b | $CH_3$ | 30 | 30 | 35 | 88 | 80 | 81 | 251-253 | 250-252 (32) |
| 4c | $(CH_3)N$ | 45 | 45 | 45 | 97 | 87 | 94 | >260 | 266-268 (32) |
| 4d | $NO_2$ | 15 | 15 | 15 | 98 | 85 | 84 | 258-260 | 258-260(58) |
| 4e | Br | 15 | 15 | 15 | 84 | 83 | 87 | 248-250 | 247-249 (58) |
| 4f | Cl | 15 | 15 | 15 | 77 | 79 | 85 | 256-258 | 258-260 (32) |

[a] Reaction conditions: aromatic aldehyde (1 mmol), malononitrile (1 mmol), 4- hydroxycoumarin (1 mmol), (1 mL) ethanol, 0.006 g of MAP, 0.004 g of DAP and TSP, reflux.

[b] Isolated yield.

The yields of desired products presented in Table 5 remains better regardless of the nature of the group, used as a substituent on the aromatic aldehyde, that is electron attractor in case of $NO_2$ or electron donor in cases of $CH_3$, $N(CH_3)_2$, Br and Cl groups. The best-obtained yield is 98% for the entry **4d** when the MAP catalyst is used while it is by 92% for entry **4a** using DAP catalyst and it is 94% for entry **4c** using TSP as a catalyst. Whereas the reaction times vary between 15 min and 45 min for the six synthesis reactions in presence of MAP, DAP and TSP catalysts used in this study.

To understand the interaction involved, between the catalyst and the reagents as well as between the solvent and the reagents, during the reaction process, the following mechanism is proposed to describe the condensation of an aromatic aldehyde, malononitrile and 4-hydroxycoumarin, using MAP catalyst and EtOH as solvent, for the synthesis of 2,3-dihydroquinazolin-4 (1H)-One (Scheme 3).



**Scheme 3.** A plausible mechanism (catalyst and solvent) for the formation of 3,4-Dihydropyrano[c]Chromene.

Scheme 3 shows the proposed mechanism for the synthesis of 3,4 Dihydropyrano [c] chromene, firstly the condensation of knoevenagal between benzaldehyde **1** and malononitrile **2** in the presence of MAP (proposed as an ampholyte catalyst, in this mechanism plays the role of a base), which removes the proton from the malononitrile, and the ethanol which allows activation of the carbonyl group, followed by dehydration to produce the 2-benzylidenemalononitrile **3**, And then, the nucleophilic addition of 4-hydroxycoumarin at intermediate 3, followed by intramolecular cyclization **4** and tautomerization for formation of corresponding product **6**.

In order to conclude about the effectiveness of MAP, DAP and TSP catalysts used herein, Table 6 collect the results of this work and some data from the literature concerning the same synthesis reaction and using another type of catalysts.

**Table 6**. Comparative table of the reaction conditions for the synthesis of 3, 4-dihydropyrano[c]chromene

| Entry | Catalyst | Catalyst amount | Solvent | T (°C) | time | Yield (%) | Ref |
|---|---|---|---|---|---|---|---|
| **1** | $Al_2O_3$ | 10 mol% | Ethanol | Reflux | 2 h | 71 | (39) |
| **2** | SDS | 20 mol% | Water | Reflux | 2.5 h | 88 | (32) |
| **3** | $RuBr_2(PPh_3)_4$ | 5 mol% | Water | Reflux | 60 min | Trace | (44) |
| **4** | $RuBr_2(PPh_3)_4$ | 5 mol% | Ethanol | Reflux | 45 min | 45 | (44) |
| **5** | Silica gel | 300 wt% | Ethanol | 25 | 4 h | 95 | (43) |
| **6** | TEBA | 0.15 g | Water | Reflux | 10 h | 96 | (35) |
| **7** | DBSA | 25 mol% | Water | 90 | 4 h | 90 | (59) |
| **8** | $Na_2HPO_4$ | 10 mol% | $H_2O$:EtOH | Reflux | 10 min | 93 | (53) |
| **9** | Piperidine | 10 mol% | Ethanol | 25 | 30 min | 90 | (60) |
| **10** | OBS | 50 mol% | Solvent-free | 120 | 50 min | 85 | (61) |
| **11** | $NH_4OAc$ | 15 mol% | Ethanol | Reflux | 3 min | 94 | (51) |
| **12** | EDTA-4Na | 2mol% | $H_2O$:EtOH | 50 | 20 min | 91 | (62) |
| **13** | SBS | 10 mol% | $H_2O$:EtOH | Reflux | 23 min | 89 | (63) |
| **14** | MAP | 0.006 g/ 2.5 mol% | Ethanol | Reflux | 30 min | 95 | this work |
| **15** | DAP | 0.004 g/ 3.1 mol% | Ethanol | Reflux | 45 min | 92 | this work |
| **16** | TSP | 0.004 g/1.7 mol% | Ethanol | Reflux | 35 min | 93 | this work |

Recently several works have been developed concerning the use of different kinds of catalyst for the synthesis studied herein. From the table 6, it can be seen that the catalysts MAP, DAP and TSP show interesting catalytic activities for the 3,4-dihydropyrano[c]chromene synthesis, they lead high yields of the desired products in short reaction times even with smaller amounts of the catalyst compared to the that given in the literature. Nevertheless, some of these catalysts have a shorter reaction time and good yields compared to the results obtained in this work but have certain drawbacks as NH4OAc which is a homogeneous catalyst, piperidine which is a corrosive product and EDTA-4Na is a synthetic catalyst. To sum up, the catalysts used herein present several advantages, they resent interesting catalytic activities and they can be reused for at least 4 times.

## CONCLUSION

To sum up, six 3, 4-dihydropyrano[c]chromenes have been successfully synthesized, using MAP, DAP and TSP phosphate fertilizers as heterogeneous catalysts which are available, inexpensive, non-toxic, and recyclable. The reactional conditions optimized in this work, namely, reaction time, catalyst amount, solvent nature and its volume, show that method has been characterized by simplicity of operation by reducing the cost of handling for organic synthesis, soft working conditions, short reaction times, excellent yields, and respect to the environment.

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