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Efficient One-Pot Synthesis of 2-Amino-4*H*-chromenes Catalyzed by Ferric Hydrogen Sulfate and Zr-Based Catalysts of FI

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$Fe(HSO_4)_3$ efficiently catalyzes the synthesis of 2-amino-4*H*-chromenes. The reactions proceed through a one-pot, three-component condensation of α- or β-naphthol, aromatic aldehyde derivatives, and malonitrile in the presence of a catalytic amount of ferric hydrogen sulfate. Also, three-component condensation of resorcinol, malononitrile, and various aldehydes using the catalyst gave the corresponding 2-amino-4*H*-chromenes in good yields. The catalyst displayed high activity and recyclability without loss of its catalytic activity. Additionally, three Zr-based FI catalysts were applied for the one-pot synthesis of chromene derivatives. Although the chemical yield was not high, it is the first report of using such catalysts in the field.

Keywords amino-4*H*-chromenes, ferric hydrogen sulfate, three-component condensation

INTRODUCTION

Multicomponent coupling reactions (MCRs) are emerging as useful tools for the carbon–carbon and carbon–heteroatom bond-forming reactions and for the synthesis of small drug-like molecules with several degrees of structural diversity.[1] One-pot multicomponent reactions provide the possibility of directly synthesizing a complex molecule without needing to isolate the intermediates, which has aroused researchers to design such reactions using different catalysts.[2,3] Benzopyrans have firmly attracted the researchers' attention due to their useful biological and pharmacological properties.[3] The value of 2-amino-4*H*-chromene compounds can be realized by their unique pharmacological activities including antimicrobial,[4] antiviral,[5] mutagenic,[3] antiproliferative,[6] antitumor,[7] cancer therapy, and central nervous system activity.[8]

Although several protocols for the synthesis of 2-amino-4*H*-pyran derivatives using various catalysts such as piperidine,[9] morpholine,[10] CTACl (cetyltrimethylammonium chloride),[11] TEBA (triethylbenzylammonium chloride),[12] alumina,[13] methanesulfonic acid,[14] and K_2CO_3 in water under microwave irradiation[15] have been reported previously, most of them require long reaction time as well as high temperatures. In spite of advent of the recent efficient catalysts such as CAN (ceric ammonium nitrate),[16] *N,N*,dimethylaminoethylbenzyldimethylammonium chloride,[17] Mg/Al hydrotalcite,[18] and CTABr (cetyltrimethylammonium bromide),[19] which are claimed to be efficient in synthesis 2-amino-4*H*-chromene compounds, these catalysts are either expensive or not applicable to various compounds; also, in some cases ultrasonic irradiation is needed to achieve high yields. Therefore, the development of a new method with better profitability, higher yield, and a simpler and convenient procedure using an inexpensive catalyst is highly desirable.

In this work, we report the efficient synthesis of 2-amino-4*H*-chromene derivatives through a one-pot, three-component condensation of activated phenols, aromatic aldehydes, and malononitrile catalyzed by ferric hydrogen sulfate as an efficient, bifunctional, heterogeneous, inexpensive, and easy-to-prepare catalyst (Scheme 1). Additionally, to extend the scope and also to introduce possible useful catalysts for this transformation, three Zr-based FI catalyst swere applied to the one-pot synthesis of chromene derivatives.

EXPERIMENTAL

Chemicals were either prepared or purchased from Merck, Fluka, and Aldrich chemical companies. All yields refer to isolated products. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. Infrared (IR) spectra were recorded on a Shimadzu-IR 470 spectrophotometer. ^{1}H-Nuclear magnetic resonance (NMR) spectra was recorded on a Bruker 100-MHz spectrometer in chloroform as the solvent with trimethylsilane (TMS) as internal standard. Ferric hydrogen sulfate was prepared according to a previously reported procedure.[20,21]

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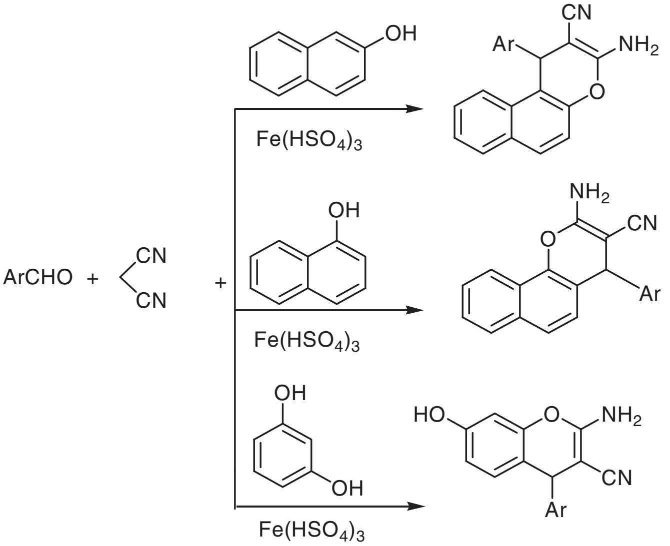


SCH. 1. Ferric hydrogen sulfate-catalyzed three-component synthesis of 2-amino-4*H*-chromenes.

General Procedure for Synthesis of 2-Amino-3-cyano-4-substituted-4*H*-benzo[e]chromene Derivatives (1–8) and 2-Amino-3-cyano-7-hydroxy-4-substituted-4*H*-chromene (9–12)

A reaction mixture of 2-naphthol (144 mg, 1.0 mmol), benzaldehyde (106 mg, 1.0 mmol), malononitrile (61 μL, 1.1 mmol), and $Fe(HSO_4)_3$ (0.034 mg, 0.1 mmol) in MeCN (10 mL) was refluxed for 4.5 h. Thin-layer chromatography (TLC) showed completion of the reaction. The reaction mixture was filtered to recover the catalyst. The catalyst was further washed with an additional portion of MeCN (2 × 5 mL). The combined filtrates were concentrated *in vacuo* to give Entry 1 as an amorphous, off-white-colored solid (271 mg). NMR evaluation of this solid shows the obianed compound is almost pure. Crystallization of this solid from hot EtOH gives pure product (256 mg, 86% yield) as colorless needles (melting point [mp] 278°C). The recovered $Fe(HSO_4)_3$ catalyst could be reused without further treatment.

Representative spectral data for the selected products are:

(Entry **3**): IR (KBr) (υ_{max}, cm^{-1}): 3440, 3325, 2185, 1680, 1665, 1595, 1550, 1502, 1365, 1255, 1200, 995, 840. δ_H (ppm): 3.50 (s, 3H), 5.40 (s, 1H), 6.75 (s, 2H, NH_2), 7.0–7.50 (m, 10H).

(Entry **4**): IR (KBr) (υ_{max}, cm^{-1}): 3430, 3116, 3045, 2965, 2194, 1709, 1551, 1460, 1375, 1273, 1097, 830, 750. δ_H (ppm): 5.30 (s, 1H), 6.80–7.05 (m, 3H), 7.10–7.75 (m, 9H).

(Entry **5**): IR (KBr) (υ_{max}, cm^{-1}): 3445, 3180, 2196, 1654, 1585, 1555, 1536, 1500, 1386, 1258, 1159, 1013, 805, 770. δ_H (ppm): 5.25 (s, 1H), 7.10 (s, 2H, NH_2), 7.60–7.80 (m, 3H), 7.90–8.15 (m, 5H).

(Entry **6**): IR (KBr) (υ_{max}, cm^{-1}): 3456, 3166, 3091, 2171, 1585, 1572, 1548, 1493, 1372, 1233, 1145, 987, 875. δ_H (ppm): 5.15 (s, 1H), 6.65 (s, 2H, NH_2), 7.0–7.70 (m, 8H), 7.85 (d, 2H, $J = 8$ Hz).

(Entry **7**): IR (KBr) (υ_{max}, cm^{-1}): 3444, 3305, 3192, 2738, 2194, 1617, 1537, 1317, 1258, 1086, 808; δ_H (ppm): 3.65 (s, 3H), 5.60 (s, 1H), 7.35 (m, 6H), 7.4–7.8 (m, 6H).

(Entry **9**): IR (KBr) (υ_{max}, cm^{-1}): 3437, 3057, 3006, 2930, 2195, 1570, 1482, 1375, 1216, 1087, 866. δ_H (ppm): δ_H 4.85 (s, 1H), 6.40–7.40 (m, 10H), 9.9 (s, 1H, OH).

(Entry **10**): IR (KBr) (υ_{max}, cm^{-1}): 3400, 3108, 2970, 2196, 1713, 1460, 1094, 1020, 736. δ_H (ppm): δ_H 4.80 (s, 1H), 6.90–7.10 (m, 2H, NH_2), 7.30–7.50 (m, 4H), 7.55–7.95 (m, 3H), 9.75 (bs, 1H, OH).

(Entry **11**): IR (KBr) (υ_{max}, cm^{-1}): 3445, 3133, 2195, 1736, 1660, 1452, 1301, 1117, 958, 752. δ_H (ppm): δ_H 4.75 (s, 1H), 7–7.30 (m, 7H), 7.40–7.55 (m, 2H), 9.70 (s, 1H, OH).

RESULTS AND DISCUSSION

Using β-naphthol, malononitrile, and benzaldehyde in a stoichiometric ratio of 1:1.1:1 and 0.1 equivalents ferric hydrogen sulfate (based on the aldehyde component), a reaction was designed as a model in order to find out the optimum solvent, and the results are shown in Table 1.

As it can be seen in Table 1, among the various solvents investigated, CH_3CN was found to be the best choice. However, ethanol, toluene, and benzene afforded satisfying yields. Moderate and poor yields were obtained when the reactions were carried out in THF and hexane respectively. As can be seen in Table 1, the catalyst could be reused without significant loss of its catalytic activity until at least five times.

TABLE 1

Influence of solvent on $Fe(HSO_4)_3$-catalyzed reaction of β-naphthol, malononitrile, and benzaldehyde and reusability study

Solvent	Acetonitril	Dichloroethane	Ethanol	Toluene	Benzene	THF	Hexane
Yield[a,b]	86	82	78	75	70	~42	<20
Reusability[c]	86[d]	85[e]	83[f]	83[g]	~80[h]	—	—

[a] All the reactions were carried out under reflux condition for 4 h.

[b] Isolated yields.

[c] Reusability of the recovered catalyst was investigated in CH_3CN as the optimum solvent.

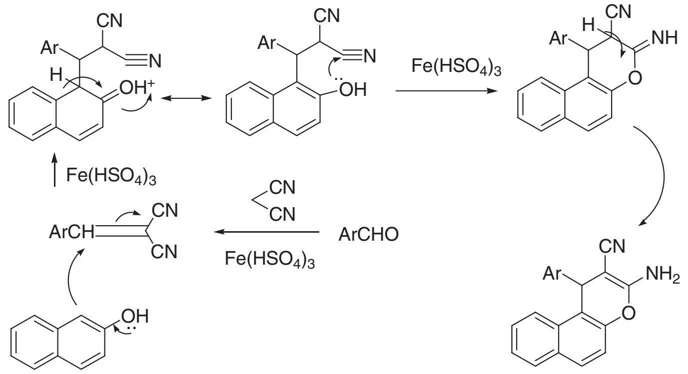
[d-h] Reusability of the recovered catalyst in new runs (from run 2 [d] to run 6 [h]).

TABLE 2
Comparison of efficiency between ferric hydrogen sulfate (FHS) and $\mathrm{FeCl_3}$ or $\mathrm{NaHSO_4}$

$\mathrm{FeCl_3}$ (10%) + $\mathrm{NaHSO_4}$ (30%)	$\mathrm{NaHSO_4}$ (30%)	$\mathrm{FeCl_3}$ (10%)	FHS (10%)	Catalyst
80	20	52	86	Yield[a,b]

[a] All the reactions were carried out under reflux condition for 4 h in $\mathrm{CH_3CN}$.

[b] Isolated yields.



SCH. 2. The proposed mechanism.

In order to show what is so special about $\mathrm{Fe(HSO_4)_3}$ and also to find out that which part of the catalyst is responsible to promote the reaction, we studied the reaction in the presence of catalytic amount of $\mathrm{FeCl_3}$ and $\mathrm{NaHSO_4}$ at the same conditions. Comparing of catalytic efficiency of $\mathrm{Fe(HSO_4)_3}$ (10%) with $\mathrm{NaHSO_4}$ (10% and 30%) and $\mathrm{FeCl_3}$ (10%) or a combination of them showed that ferric hydrogen sulfate was acting even better than a mixed catalyst (Table 2). Furthermore, it was revealed that both parts of the catalyst are involved in catalyzing the reaction.

To generalize the study, several substituted benzaldehydes were reacted with malononitrile and α- or β-naphthol in the multicomponent one-pot reaction to afford substituted 2-amino-4*H*-chromenes derivatives in high yields. The results are illustrated in Table 2. The reactions proceeded easily under reflux condition to afford the corresponding products in high yields using aromatic aldehydes containing electron-withdrawing groups (such as nitro and halide groups) or electron-donating groups (such as methoxy groups). Although no significant differences in terms of yields in such a one-pot three-component reaction has been reported,[14] in the present study it was revealed that the yield of the reaction of aromatic aldehyde with malononitrile and α-naphthol is almost better than that of β-naphthol. As can be seen in Table 2, 4-nitrobenzaldehyde (entry 2) and 4-chlorobenzaldehyde (entry 4) were reacted with malononitrile and β-naphthol for 4 h, and they gave isolated yields of the corresponding compounds 2 (88%) and 4 (85%), while 4-nitrobenzaldehyde (entry 6) and 4-chlorobenzaldehyde (entry 8) were treated with malononitrile and α-naphthol for 3 h and the yields of the corresponding compounds are 92% and 94%, respectively. The results indicate that α-naphthol exhibits higher reactivity than β-naphthol at the same reaction conditions.

To investigate more aspects of the new synthetic approach to substituted 2-amino-4*H*-chromenes, and to find out the probable limitations of the scope, we also studied the one-pot three-component reaction of aldehyde, malononitrile, and resorcinol under similar conditions (Table 3, entries 9–12). The corresponding products were obtained in good yields. It should be mentioned that the reaction of benzaldehyde, malononitrile, and phenol was carried out at the same conditions and no corresponding product was detected. It is notworthy that no detectable chromene was found in the case of reaction between resorcinol, malononitrile, and *para*-methoxybenzaldehyde and *para-N,N*-dimethylbenzaldehyde.

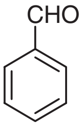
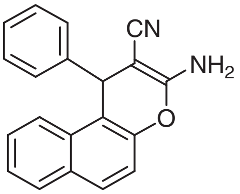
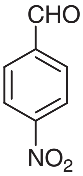
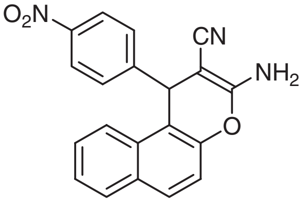
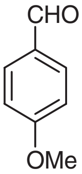
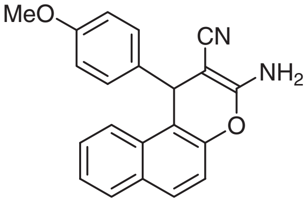
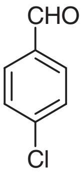
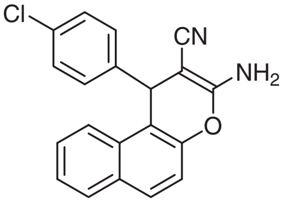
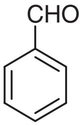
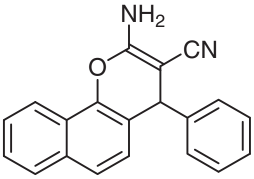
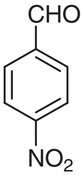
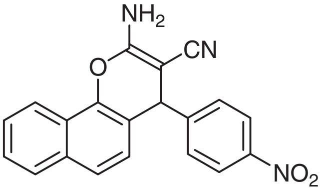
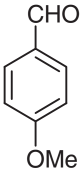
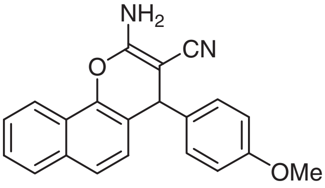
The proposed mechanism[19,22] for three-component synthesis of 2-amino-4*H*-chromene derivatives is shown in Scheme 2. The aldehyde first condenses with malononitrile to afford α-cyanocinnamonitrile derivatives by Knoevenagel addition. Naphthol or phenol *ortho* C-alkylation gives an intermediate which cyclizes via nucleophilic attack of O atom on the cyano moiety following protonation and rearrangement to produce the corresponding 2-amino-4*H*-chromene (Scheme 2).

It is noteworthy that in the case of using resorcinol, aromatic aldehydes with electron- donating substituents (*para*-methoxybenzaldehyde and *para-N,N*-dimethylbenzaldehyde) didn't afford the expected corresponding compounds but obtained the α-cyanocinnamonitrile compound. We propose that electron-donating substituents on the aromatic ring increase the electron density of $\mathrm{C{-}C}$ double bonds in the intermediate (cyanocinnamonitrile), which may retard the reaction of the phenol *ortho* C-alkylation with the electrophilic $\mathrm{C{-}C}$ double bond. In addition, we believe that the substituted cyanocinnamonitrile intermediate shows low reactivity due to the full conjugation resulting in suppression of further reaction with phenol (Scheme 3).

Recently, we have reported the synthesis of FI-like Zr-based catalysts and their application in polymerization of ethylene.[23] Encouraged by the results in the present study and also in order to further extend the scope, we intended to use the phenoxyimine-based catalysts of bis[1-[(phenylimino)methyl]-2-naphtholato]zirconium(IV) dichloride (**1**), bis[1-[(mesity limino)methyl]-2-naphtholato]zirconium(IV) dichloride (**2**), and bis[1-[(2,6-diisopropylphenyl)imino]methyl-2-naphtho lato]zirconium(IV) dichloride (**3**) for the synthesis of 2-amino-4*H*-chromene derivatives. To the best of our knowledge, this is the first report of using such catalysts in the field of one-pot multicomponenet reactions.

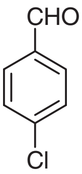
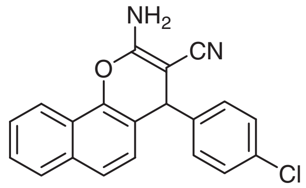
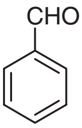
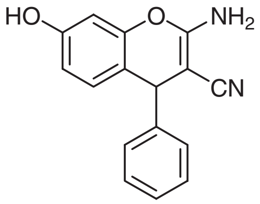
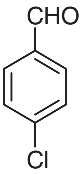
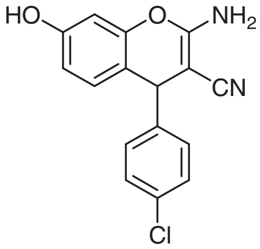
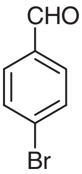
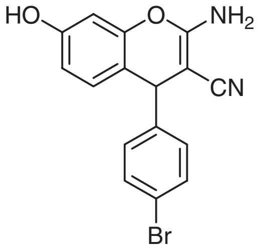
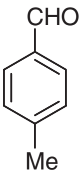
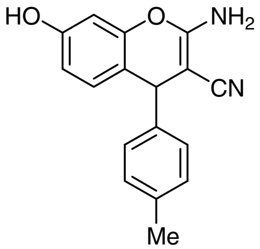
The catalysts preparation procedure and their characterization have been reported elsewhere.[23] It should be mentioned that due to the extreme sensitivity of the catalysts to moisture and

TABLE 3
Results of one-pot three-component synthesis of 2-amino-4H-chromenes

						Melting point (°C)	
Entry	Naphthol	Aldehyde	Product^a	Time (h)	Yield(%)^b	Found	Reported
1	β-Naphthol			4.5	86	278	278–280[14]
2	β-Naphthol			4	88	186	185–186[14]
3	β-Naphthol			5	80	181	182[17]
4	β-Naphthol			4	85	210	208[17]
5	α-Naphthol			3.5	87	210	210–211[18]
6	α-Naphthol			3	92	240–242	239–241[18]
7	α-Naphthol			4	86	188–190	190–192[18]

(Continued on next page)

TABLE 3
Results of one-pot three-component synthesis of 2-amino-4*H*-chromenes *(Continued)*

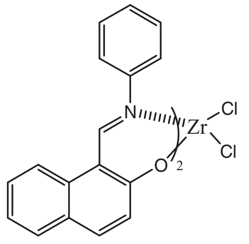
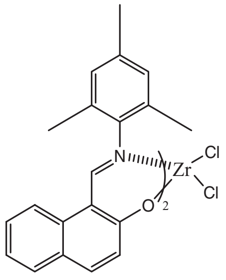
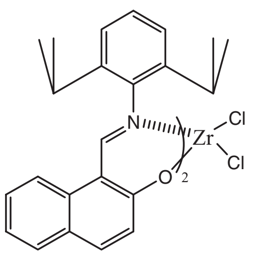
Entry	Naphthol	Aldehyde	Product[a]	Time (h)	Yield(%)[b]	Melting point (°C)	
						Found	Reported
8	α-Naphthol			3	94	230	232[18]
9	Resorcinol			4	83	233	232–234[15,18]
10	Resorcinol			3	86	163	161–162[15]
11	Resorcinol			3	87	228	225–227[15]
12	Resorcinol			3.5	82	187	185–187[15]

[a] The products were identified by ^{1}HNMR and IR spectra.
[b] Isolated yields.

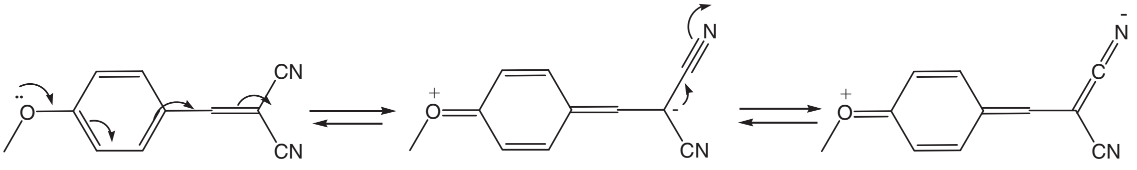
air, all the chemical reactions were done under an atmosphere of nitrogen in toluene.

The one-pot reaction of aromatic aldehyde, malononitrile, and beta-naphthol using the bis-phenoxyimine catalysts was carried out under the same conditions employed for the ferric hydrogen sulfate. As can be seen in Table 4, the reaction in the presence of a catalytic amount of FI-like catalysts of **1–3** succeeded and the corresponding products were isolated in moderate yields. This is the first report of a Mannich reaction via three-component one-pot reactions in the presence of phenoxyimine Zr-based catalysts.

TABLE 4
Results of one-pot, three-component synthesis of 2-amino-4H-chromenes

Catalysts **1–3**(left to rioght)			
Product/yield[a]	1/30	1/30	1/40
Product/yield	5/30	5/35	5/45

[a]Yields refer to isolated yield, reaction time = 4 h.



SCH. 3. Effect of electron-donating substitutions on stability of the cyanocinnamonitrile.

It should be pointed out that the purification procedure and workup were extremely simple. After completion of the reaction, the heterogeneous catalyst was easily removed through filtration and the product was obtained after solvent evaporation. The purified products were obtained by crystallization from ethanol.

CONCLUSION

One-pot synthesis of substituted 2-amino-4H-chromene derivatives has been reported. $Fe(HSO_4)_3$ was found to be an efficient catalyst due to its applicability to the various compounds, heterogeneity of the catalyst, high reusability, bifunctionality, reasonable reaction times, and high yields of the products. Three FI-like catalysts bearing phenoxyimine chelate ligands were examined and the corresponding products were obtained in moderate yields.

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