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Microwave Assisted Multi-component Synthesis of 4*H*-chromene Derivatives by Nano-coconut Shell-BF_3 as a New Heterogeneous Catalyst

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Abstract

Microwave assisted reactions have gained considerable attention, due to versatility and reduction of solvent and reaction time. The reaction of a nano-coconut shell and *boron tri-fluoride* in diethyl ether solvent resulted in preparation of nano-coconut shell-BF_3 as a catalyst. The nano-coconut shell-BF_3 catalyst has been characterized by fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Nano-coconut shell-BF_3 has been applied as a new heterogeneous catalyst for synthesis of 4*H*-chromene derivatives from the simple one-pot reaction *between* aryl aldehydes, cyclic 1,3-diketone and, malononitrile under microwave reaction. Cleanliness, simple methodology, short time, and excellent yields of products are some advantages of this method.

Keywords: *4H-chrmoene,* Boron trifluoride, *Nano-catalyst, Multi-component reaction, Coconut shell.*

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Introduction

Conventionally, microwave chemistry [1] was used only when all other options to perform a particular reaction remain unsuccessful like long reaction times or high temperatures to complete the synthetic reactions [2]. These days the practice has changed a lot due to the growing availability of microwave reactors in laboratories and therefore the routine synthetic chemical transformations are also being carried out by using microwave irradiation [3]. Microwave irradiation has the capability to convert electromagnetic radiations into heat to initiate the chemical reactions [4].

In general, 4*H*-chromenes which are tetrahydrobenzo[b]pyrans [5] are heterocyclic compounds known for their diverse important biological activities like anticancer, anticoagulant and anti-anaphylactic, diuretic and spasmolytic since long time [6, 7]. These 4*H*-chromenes have wide usability in cosmetics and agrochemicals [8].

Numerous attempts have recently been made to achieve the synthesis of 4*H*-chromene derivatives through the use of protocols including $CeCl_3 \cdot 7H_2O$ [9], N-Methylimidazole [10], tetra-methylammonium hydroxide [11], MgO [12], amines [13], 2,2,2-trifluoroethanol [14], TiO_2 [15], starch solution [16], $Zn(Phen)_2Cl_2$ [17], Fluoride ion [18]. In addition, microwave [19, 20], ultrasonic irradiation [21], and electro-synthesis [22] as subsidiary conditions also give satisfactory yields for the pyrans synthesis.

In recent years, there has been growing interest in finding inexpensive and effective solid acid nano catalyst such as nano-crystalline TiO_2-$HClO_4$ [23], nano-$TiCl_4.SiO_2$ [24, 25] nano-$SnCl_4.SiO_2$ [26-28] nano-$BF_3.SiO_2$ [29-31] $HClO_4$-SiO_2 nano-particles [32], nano-silica sulfuric acid [33-38] and nano-sawdust-BF_3 [39].

Nowadays, support materials include cellulose, synthetic polymers, and silica gel, and sample-immobilization methods include adsorption, and covalent binding have been used in different fields [40-42]. The coconut shell consists of cellulose, lignin, and hemi-celluloses. The ligno-cellulosic material includes a wide variety of hydroxyl groups that can be used as active sites for the preparation of solid acid catalysts [43]. In this study, the nano-coconut shell has been used as an adsorbent for the preparation of nano-coconut shell-BF_3 whose average size is small and is well distributed. The presence of functional groups on the surface of nano-coconut shell-BF_3 resulted in a dramatic increase in the surface polarity and acidity, and as a result, raised the catalytic efficiency of the nano-coconut shell-BF_3.

Thus, in the present study, the green synthetic procedure for the synthesis of 4*H*-chromene derivatives in the presence of nano-coconut shell-BF_3 as an efficient heterogeneous catalyst has been reported. This methodology using nano-coconut shell-BF_3 has not been previously found in literature survey for the synthesis of such novel compounds.

Experimental

Materials and Instrumentation

All chemicals were purchased from Fluka or Merck Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer. The ^{1}H NMR spectra were recorded on Bruker DRX-400 Avance instrument (400 MHz for ^{1}H, 100 MHz for ^{13}C) in solution state in DMSO-d_6 using TMS as an internal standard. The morphologies of the nanoparticles were observed using transmission electron microscopy (TEM) of a Philips EM 208 electron microscope and field emission scanning electron microscopy (FESEM) of a Mira 3 TESCAN microscope with an accelerating voltage of 15 kV.

Synthesis of nano-coconut shell-BF_3

At first, the outer brown shell of coconut was separated and washed several times with deionized water to remove adhering dirt and then dried at 60 °C for 24 h. The dried coconut shell was ground to pass through a 1 mm sieve and labeled as the coconut shell. The nano-coconut shell-BF_3 was prepared by the combination of $BF_3.OEt_2$ (0.6 g, 4.2 mmol) drop by drop over 10 min via a syringe to coconut shell powder (0.4 g) in a 50 ml flask include 5ml diethyl ether at room temperature. The reaction mixture was stirred, and then after 30 min, the brown powder was separated and dried in an oven at 60°C for 4h and pulverized in the mortar. The size of particles was obtained below 50 nm using SEM and TEM.

*General procedure for the preparation of compounds (**4a-j**)*

As shown in scheme 1, an equal mol of aromatic aldehyde (**1a-j**), malononitrile (**2**) and dimedone (**3**), in 5 mL of EtOH and 5 mL H_2O in the presence of 0.07g nano-coconut shell-BF_3 was taken and the mixture was transferred into a reaction tube, irradiated in a microwave reactor under continuous stirring in an open system under inert atmospheric pressure at 900 °C for 4-5 minutes. The reaction was monitored by TLC (*n*-hexane: ethyl acetate 3:1). The reaction mixture was cooled to room temperature, diluted with hot ethanol (5 mL), and stirred for 10 min. Finally, isolation of the catalyst was done by filtration and recovered. After evaporation of the solvent, the crude product was re-crystallized from hot ethanol to obtain the pure compound (as shown in Table 1).

Characterization data of the compounds

2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4a)***

Yellow solid; IR (KBr, cm^{-1}) *v*: 3393, 3332, 2186, 1685, 1214; ^1H NMR (400MHz, $CDCl_3$): *δ* 7.24-7.32(m, 5H, aromatic), 4.57(s, 2H, NH_2), 4.43(s, 1H, CH), 2.49(s, 2H, CH_2), 1.62(s, 2H, CH_2), 1.14(s, 3H, CH_3), 1.07(s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 195.9, 162.3, 158.1, 144.6, 128.1, 127.9, 127.8, 120.2, 113.5, 58.4, 50.2, 39.8, 35.9, 32.4, 28.5, 27.6.

2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4b)***

Yellow solid; IR (KBr, cm^{-1}) *v*: 3394, 3324, 2186, 1682, 1215; ^1H NMR (400MHz, $CDCl_3$): *δ* 7.35(d, *J*=7.6Hz, 1H, aromatic), 7.21-7.24(m, 2H, aromatic), 7.14-7.18(m, 1H, aromatic), 4.86(s, 1H, CH), 4.65(s, 2H, NH_2), 2.47(s, 2H, CH_2), 2.18-2.27(m, 2H, CH_2), 1.14(s, 3H, CH_3), 1.09(s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 196.2, 164.3, 159.6, 142.1, 133.1, 131.2, 130.8, 128.7, 128.5, 120.6, 112.7, 57.8, 50.7, 40.5, 34.2, 32.2, 29.3, 27.9.

2-Amino-4-(3-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitril ***(4c)***

White solid; IR (KBr, cm^{-1}) *v*: 3393, 3328, 2179, 1681, 1217; ^1H NMR (400MHz, $CDCl_3$): *δ* 7.21-7.26(m, 1H, aromatic), 6.85(d, *J*=7.6Hz, 1H, aromatic), 6.75-6.78(m, 2H, aromatic), 4.62(s, 2H, NH_2), 4.38(s, 1H, CH), 3.82(s, 3H, OCH_3), 2.47(s, 2H, CH_2), 2.25(d, *J*=2.4Hz, 2H, CH_2), 1.14(s, 3H, CH_3), 1.07(s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 196.2, 164.1, 159.4, 142.1, 133.1, 130.7, 128.6, 120.6, 112.8, 57.5, 50.5, 40.5, 34.2, 32.3, 29.3, 27.5.

2-Amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitril ***(4d)***

White solid; IR (KBr, cm^{-1}) *v*: 3384, 3245, 2185, 1681, 1217; ^1H NMR (400MHz, $CDCl_3$): *δ* 7.18(d, *J*=8.4Hz, 2H, aromatic), 6.85(d, *J*=8.4Hz, 2H, aromatic), 4.54(s, 2H, NH_2), 4.39(s, 1H, CH), 3.79(s, 3H, OCH_3), 2.47(s, 2H, CH_2), 2.24(d, *J*=5.2Hz, 2H, CH_2), 1.13(s, 3H, CH_3), 1.07(s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 195.9, 162.1, 158.7, 137.1, 128.2, 120.4, 113.8, 58.6, 55.2, 49.8, 40.6, 34.2, 32.6, 28.3, 27.2.

2-Amino-4-(2-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitril ***(4e)***

White solid; IR (KBr, cm^{-1}) *v*: 3387, 3229, 2175, 1682, 1215; ^1H NMR (400MHz, $CDCl_3$): *δ* 7.18-7.23(m, 1H, aromatic), 7.11-7.14(m, 1H, aromatic), 6.88-6.92(m, 2H, aromatic), 4.74(s, 1H, CH), 4.47(s, 2H, NH_2), 3.87(s, 3H, OCH_3), 2.47(s, 2H, CH_2), 2.23(d, J=8.4Hz, 2H, CH_2), 1.15(s, 3H, CH_3), 1.08(s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 196.2, 163.3, 158.7, 142.3, 133.1, 130.7, 127.6, 120.5, 113.3, 56.6, 50.3, 40.7, 34.3, 32.2, 28.3, 27.4.

2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4f)***Yellow solid; IR (KBr, cm^{-1}) *v*: 3394, 3326, 2175, 1681, 1224; ^1H NMR (400MHz, $CDCl_3$): *δ* 8.18(d, *J*=8.8Hz, 2H, Aromatic), 7.43(d, *J*=8.4Hz, 2H, aromatic), 4.68(s, 2H, NH_2), 4.53(s, 1H, CH), 2.52(s, 2H, CH_2), 2.24-2.28(m, 2H, CH_2), 1.16(s, 3H, CH_3), 1.07(s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 195.8, 162.9, 158.7, 146.2, 128.9, 128.6, 124.2, 124.0, 119.8, 119.6, 112.1, 57.6, 49.8, 39.7, 35.9, 32.2, 28.4, 28.2.

2-Amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4g)***Yellow solid; IR (KBr, cm^{-1}) *v*: 3393, 3327, 2185, 1681, 1217; ^1H NMR (400MHz, $CDCl_3$): *δ* 8.11(d, *J*=8.4Hz, 1H, aromatic), 8.07(s, 1H, aromatic), 7.71 (d, *J*=8.4Hz, 1H, aromatic), 7.48-7.53(m, 1H, aromatic), 4.75(s, 2H, NH_2), 4.54(s, 1H, CH), 2.48-2.57(m, 2H, CH_2), 2.20-2.29(m, 2H, CH_2), 1.16(s, 3H, CH_3), 1.08(s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 196.3, 163.8, 157.7, 150.4, 143.2, 136.4, 130.2, 125.9, 121.6, 119.8, 119.3, 59.2, 49.7, 39.6, 35.7, 32.2, 28.3, 27.6.

*2-Amino-4-(4-hydroxy-3,5-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (****4h****)*

Yellow solid; IR (KBr, cm^{-1}) *v*: 3389, 3229, 2177, 1680, 1215;^1H NMR (400MHz, $CDCl_3$): *δ* 6.47(s, 2H, aromatic), 5.48(s, 1H, CH), 4.63(s, 2H, NH_2), 4.35(s, 1H, OH), 3.87(s, 6H, OCH_3), 2.43-2.55(m, 2H, CH_2), 2.22-2.34(m, 2H, CH_2), 1.15(s, 3H, CH_3), 1.09(s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 196.2, 163.1, 157.7, 138.5, 128.3, 127.1, 125.3, 120.3, 113.9, 57.6, 55.8, 49.9, 39.6, 34.6, 32.3, 28.1, 27.4.

2-Amino-7,7-dimethyl-4-(naphthalen-1-yl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4i)***

Yellow solid; IR (KBr, cm^{-1}) *v*: 3395, 3236, 2187, 1682, 1219; ^1H NMR (400MHz, $CDCl_3$): *δ* 8.41(d, *J*=8.4Hz, 1H, aromatic), 7.86(d, *J*=8.0Hz, 1H, aromatic), 7.75(d, *J*=8.0Hz, 1H, aromatic), 7.59-7.62(m, 1H, aromatic), 7.56(s, 1H, aromatic), 7.48-7.53(m, 1H, aromatic), 7.25-7.44(m, 1H, aromatic), 5.23(s, 1H, CH), 4.54(s, 2H, NH_2), 2.54-2.60(m, 2H, CH_2), 2.17-2.27(m, 2H, CH_2),

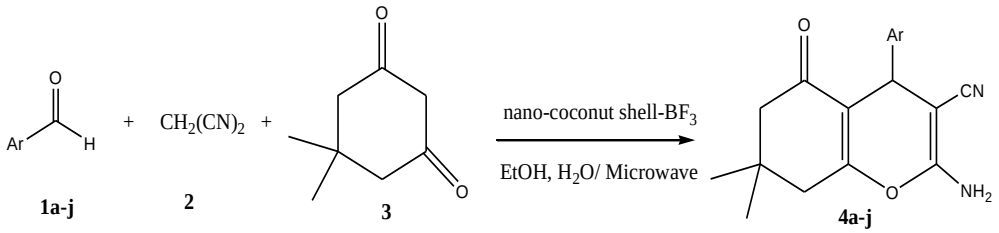
1.16(s, 3H, CH_3), 1.08(s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 195.9, 162.6, 155.5, 135.8, 133.2, 132.9, 128.7, 127.6, 127.5, 125.4, 125.3, 125.1, 123.6, 120.4, 113.6, 54.5, 51.8, 40.2, 34.9, 32.2, 28.2, 27.4.

2-Amino-4-(1H-indol-3-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4j)***

Yellow solid; IR (KBr, cm^{-1}) *v*: 3396, 3239, 2176, 1681, 1215; ^1H NMR (400MHz, $CDCl_3$): *δ* 8.11(s, 1H, NH), 7.42(d, *J*=8.0Hz, 1H, aromatic), 7.36(d, *J*=8.0Hz, 1H, aromatic), 7.21(s, 1H, aromatic), 7.14-7.19(m, 1H, aromatic), 7.05-7.10(m, 1H, aromatic), 4.75(s, 1H, CH), 4.55(s, 2H, NH_2), 2.43-2.55(d, 2H, CH_2), 2,15-2,24(m, 2H, CH_2), 1.13(s, 3H, CH_3), 0.97(s, 3H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 195.9, 161.5, 155.4, 136.7, 127.6, 123.6, 122.3, 120.4, 119.7, 118.2, 113.6, 110.8, 108.6, 54.5, 51.8, 40.3, 34.8, 32.2, 28.2, 27.5.

Results and discussion

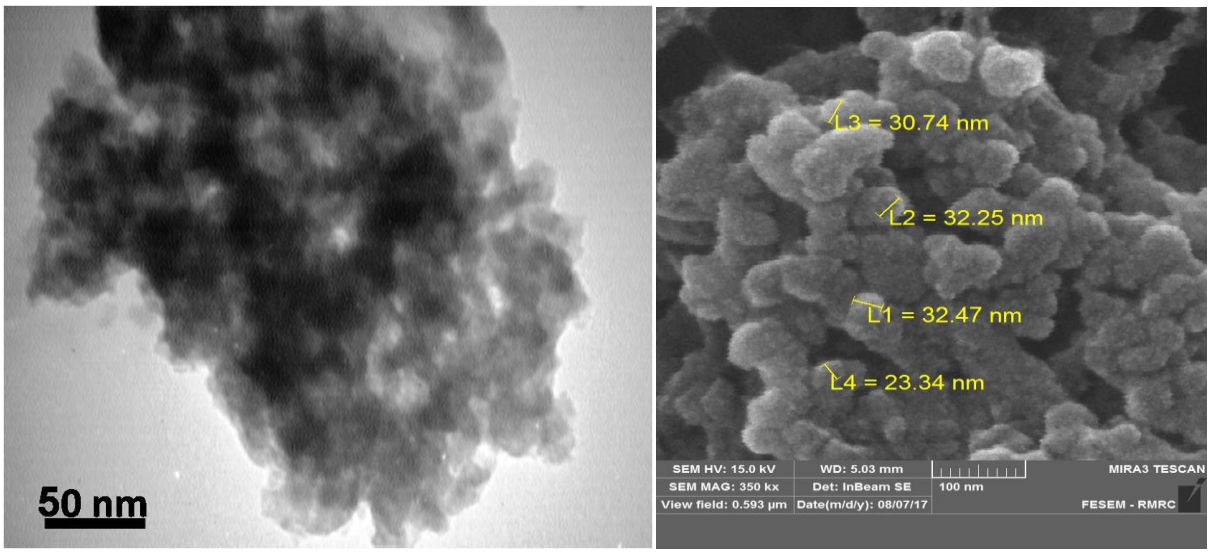
In continuation of our previous research on the use of nano solid acids in organic synthesis [30-35], nano-coconut shell-BF_3, as a new nano-catalyst, has been applied for the synthesis of 4*H*-chromene derivatives. The catalytic activity of nanoparticles was investigated for the synthesis of 4*H*-chromene derivatives, by the condensation of an aldehyde **1a-j**, malononitrile **2** and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) **3** (Scheme 1).



1a-j **2** **3** **4a-j**

Scheme 1. Synthesis of 4H-chromene derivativesin the presence of nano-coconut shell-BF_3 as the catalyst.

The morphology and particle size of nano-coconut shell-BF_3 was investigated by Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM), in which the dimensions of catalyst were obtained below 50 nm (Figure 1).



(a) (b)

Figure 1. (a) TEM and (b) SEM micrograph of nano-coconut shell-BF_3.

The FT-IR spectrum (Figure 2) of the coconut shell-BF_3 exhibited a broad peak for an OH absorption band at 3425 cm^{-1}.The appearance of the band at 1444cm^{-1} demonstrated B–O stretching vibration, clearly. The peak at 1113cm^{-1} represented C–O stretching vibration of the glucose unit. The absorption band of B–F was hidden under C–O band.

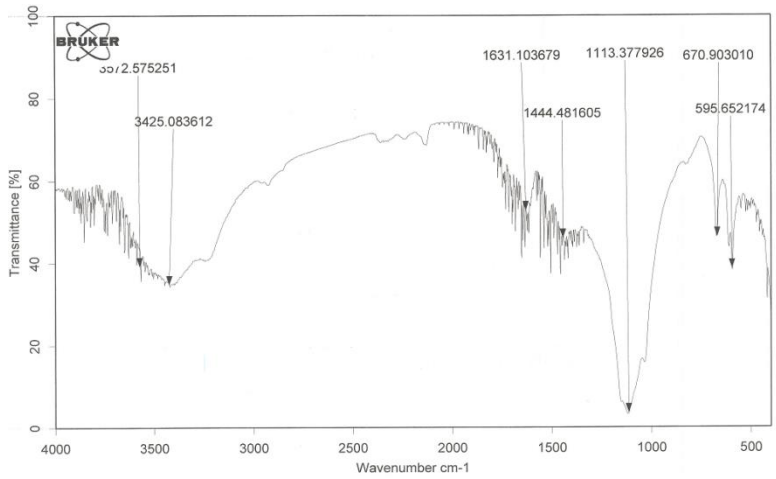


Figure 2. FTIR spectrum of nano-coconut shell-BF_3.

To identify the quantity of nano-coconut shell-BF_3 required for organic reactions, we carried out the reaction of benzaldehyde, malononitrile, and dimedone as a model reaction for determining the parameters in a one-pot, three-component synthesis under microwave condition to synthesize 4*H*-chromene derivatives. Investigation of the results prove that (Table 1), the best results are obtained

regarding the reaction rates and yields when equal volumes of EtOH and H_2O are mixed, and the reaction was carried out at 90 °C for 4 min under microwave conditions using 0.07 g catalyst (entry3). To further enlarge the scope of this condition, we conducted reaction with a variety of substituted aldehydes under the optimized condition for the synthesis of 4*H*-chromenes (**4a-j**). There is a smooth progression in the reaction for various substituents to afford the products in high yields. The results are summarized in(Table1).

Table 1. Optimization of the reaction conditions for synthesis of **4a.**

Entry	Catalyst (amount)	Temperature	Time(min)	Yield
1	nano-coconut shell-BF_3 (0.03 g)	90	6	79
2	nano-coconut shell-BF_3 (0.05 g)	90	4	86
3	nano-coconut shell-BF_3 (0.07 g)	90	4	94
4	nano-coconut shell-BF_3 (0.08 g)	90	4	95
5	nano-coconut shell-BF_3 (0.09 g)	90	5	92
6	nano-coconut shell-BF_3 (0.07 g)	70	4	81
8	nano-coconut shell-BF_3 (0.07 g) 2^{nd} run	90	4	91
9	nano-coconut shell-BF_3 (0.07 g) 3^{rd} run	90	4	87
10	No Catalyst	100	4	Trace

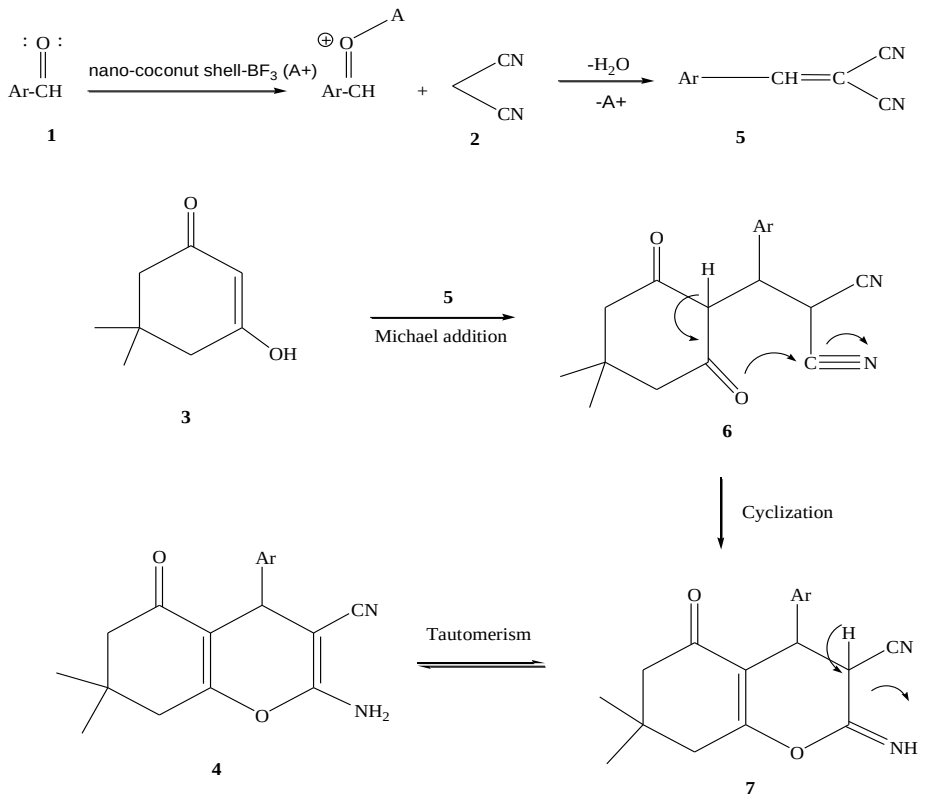
Nano-coconut shell-BF_3 catalyst reaction potentiality was examined for the model reaction. Recycling involves the isolation of the catalyst from the reaction mixture by usual filtration. The recovered catalyst was purified by washing with ethyl acetate followed by drying in an oven. The results shown in (Table 1, entries 8, 9) indicated that the catalyst can be used for three successive times without any significant loss of activity.

As revealed from the above study, aldehydes carrying electron-donating and electron-withdrawing groups undergo these reactions to get the analogous products in good yield irrespective of the nature of the substituent groups. The products are identified, characterized by their melting points and spectral (FT-IR, ^1H and ^{13}C NMR) investigations and associated with literature data (Table 2).

Table 2. Synthesis of 4*H*-chromene analogs catalyzed by nano-coconut shell-BF_3 under optimized condition.

Entry	**Ar**	**Product**	**Yield%**	**m.p./ºC**	
				Found	**Reported[Ref]**
1	C_6H_5	4a	94	229-230	225-227[44]
2	2-ClC_6H_4	4b	93	215-216	216-218[44]
3	3-$MeOC_6H_4$	4c	89	187-189	188-190[17]
4	4-$MeOC_6H_4$	4d	90	197-198	195-196[44]
5	2-$MeOC_6H_4$	4e	87	205-206	203-205[17]
6	4-$NO_2C_6H_4$	4f	95	178-180	177-178[44]
7	3-$NO_2C_6H_4$	4g	94	213-214	214-215[44]
8	3,5-diMeO-4-OHC_6H_2	4h	85	191-192	189-192[20]
9	1-naphthyl	4i	86	213-215	214-215[18]
10	3-indolyl	4j	78	183-185	185-186[18]

The most probable mechanism is depicted in Scheme 2. Condensation of aldehyde **1** and malononitrile **2** in the presence of the acidic catalyst of nano-coconut shell-BF_3 (A^+) products an intermediate **5**. Then the Michael addition of dimedone **3** to intermediate **5** would furnish intermediate **6**. Finally, the product **4** was obtained by an intra-molecular cyclization and tautomerization.



Scheme 2.A plausible mechanism for the formation of 4*H*-chromene derivatives.

Conclusion

Highly effective pharmacologically active scaffolds were synthesized by using nano-coconut shell-BF_3 as a heterogeneous catalyst, which activates the one-pot, three-component derivatives. The present synthetic methodology is significantly responsible for efficient, short reaction times, cleaner reaction profile, convenient work-up, easy catalystic recyclability, reusability and excellent yield with no loss of catalytic activity, which makes this protocol valuable and versatile for carrying benign chemical processes.

Acknowledgements

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