

Nano-cellulose-OSnCl_{4-x}: Green and natural-based renewable nanocatalyst for one-pot synthesis of 2-amino-3-phenylsulfonyl-4H-pyran derivatives

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ABSTRACT

A highly efficient, eco-friendly procedure has been proposed for the synthesis of 2-amino-3-phenylsulfonyl-4H-pyran derivatives via nano-cellulose-OSnCl_{4-x} catalyst prepared from cotton as support treated with tin tetrachloride (SnCl₄). This catalyst is characterized by FT-IR, FESEM, TEM, TGA, and EDX. The TEM results confirmed the size of the nano-cellulose-OSnCl_{4-x} catalyst was below 30 nm. The efficiency of this solid acid catalyst was investigated in one-pot, three-component condensation reactions with aromatic aldehydes, dimedone, and phenylsulfonylacetonitrile under reflux conditions. As a result, 2-amino-3-phenylsulfonyl-4H-pyran derivatives were produced under facile conditions in high yield (84-95%) and high rate (30-50 min) using nano-cellulose-OSnCl_{4-x} as a recyclable catalyst.

Keywords: Phenylsulfonylacetonitrile, pyran derivatives, dimedone, green chemistry, nano-cellulose-OSnCl_{4-x}

1. Introduction

Recently, multicomponent reactions (MCRs) have become a special and dedicated procedure in pharmaceutical chemistry for the discovery of new drugs and the production of biologically active products due to their excellent selectivity, simple, rapid, and extensive applications [1-7].

Heterocyclic compounds containing oxygen, such as pyran ring play an important role in pharmaceuticals and biological materials. In addition, the incorporation of pyran derivatives via the heterocyclic system has proven to be an impressive technique owing to their pharmacological factors, e.g., antimicrobial, antiviral, and anticancer [8-12]. Over the last few years, nano solids have been employed to accelerate numerous synthetically high-value reactions. Therefore, their dimensions, facile recyclability, high specific surface area, and time should be considered for their application as catalysts [13].

Lately, studies have revealed that using plenty of heterogeneous nanocatalysts in organic synthesis, e.g., nano-SiO₂-OSO₃H [14], nano-sawdust-OSO₃H [15], TiCl₄/nano Sawdust [16], nano-cellulose-OSO₃H [17], nano kaolin/TiCl₄ [18], nano-SbCl₄O-coc [19], nano-pistachio hull-O_xTiCl_{4-x} [20], nano-pistachio hull-OSO₃H [21], SnCl₄/Nano-Sawdust [22] and SnCl₄/nano SiO₂ [23] can be easily fractionated by a simple filtration process and reused in a primitive reaction.

There are several approaches for the synthesis of 2-amino-3-phenylsulfonyl-4H-pyrans, but some of them are characterized by difficult handling methods, long reaction times, and low yields [18, 24, 25]. Therefore, the need for a new tandem one-pot system for the synthesis of 2-amino-3-phenylsulfonyl-4H-pyrans that can not only solve these problems but also give excellent results and produce a solid product with simple work-up techniques has been recognized.

In continuation of our research concerning the synthesis of novel catalysts for biological active heterocycles, we unveil cotton as an economically important natural fiber in the world which would be an excellent bio-resource

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candidate for preparing solid acids. The fundamental value of this catalyst is because of a vast variety of hydroxyl groups through its great composition of lignin, cellulose, and hemicellulose [26]. Herein, we are reporting the utility of an innovative method for the synthesis of 2-amino-3-phenylsulfonyl-4*H*-pyrans. This process takes place through one-pot three-component condensation of aromatic aldehydes, (phenylsulfonyl)acetonitrile, and dimedone in the presence of nano-cellulose-OSnCl_{4-x} as a readily available, highly efficient catalyst under reflux in ethanol.

2. Experimental

2.1 Material and instrumentation

The chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were determined with an Electrothermal 9100 apparatus. Elemental analyses were performed using a Costech ECS 4010 CHNS-O analyzer at the analytical laboratory of the Science and Research Unit of Islamic Azad University. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ¹H and ¹³C NMR spectra were recorded on Bruker DRX-400 Avance spectrometer at a solution in DMSO using TMS as internal standard. The morphologies of the nanoparticles were observed using Field Emission Scanning Electron Microscopy (FESEM) of a MIRA3 TESCAN microscope with an accelerating voltage of 15 kV and transmission electron microscopy (TEM) of Philips CM120. Thermogravimetric analysis was performed by using a TG of Netzsch STA 409 PC. The stable nano-cellulose is prepared [27] and used for the preparation of catalyst (nano-cellulose-OSnCl_{4-x}).

2.2. Preparation of nano-cellulose-OSnCl_{4-x}

At first, tin tetrachloride (1 mL) was dropwise applied to powdered nano-cellulose (1.0 g) in 5 mL chloroform at 0 °C for 15 min to prepare nano-cellulose-OSnCl_{4-x}. After stirring the compound for 30 min, the powder was separated and rinsed with chloroform (15 mL) and *n*-hexane (15 mL), respectively. Finally, the resulting resulted solid was dried at 60 °C for 5 h and milled in a mortar to obtain a fine homogenized nano-cellulose-OSnCl_{4-x} powder. The TEM results confirmed that the size of the nano-cellulose-OSnCl_{4-x} catalyst was below 30 nm.

2.3. General procedure for preparation of 2-amino-7,8-dihydro-7,7-dimethyl-4-phenyl-3-(phenylsulfonyl)-4*H*-chromen-5(6*H*)-ones

2-amino-3-phenylsulfonyl-4*H*-pyrans (**4a-k**) were synthesized in the constant presence of cellulose-OSnCl_{4-x} as a nanocatalyst. For this purpose, nano-cellulose-OSnCl_{4-x} (5.0 mg) was incorporated into a mixed combination of aromatic aldehyde (1 mmol), dimedone (1 mmol), phenylsulfonylacetonitrile (1 mmol) and ethanol (5 mL). The materials were mixed and refluxed at 78 °C for 30-50 min. The progress of the reaction was monitored by TLC (*n*-hexane: ethyl acetate 3:1). After completion of the reaction, the catalyst was removed by centrifugation, and the untreated product was recrystallized from the hot solution to afford the pure compound.

2.4. Spectral data of some selected products are given below:

2-amino-7,7-dimethyl-4-(2-nitrophenyl)-3-(phenylsulfonyl)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (**4b**)

White, solid, m.p. 184-186 °C; IR (ν_{max}, cm⁻¹): 3360 (NH₂), 1663 (C=O), 1547, 1350 (NO₂), 1374 and 1136 (SO₂); ¹H NMR (400 MHz, DMSO-d₆): δ 0.72 (s, 3H, CH₃), 0.96 (s, 3H, CH₃), 1.91-2.59 (m, 4H, CH₂), 5.39 (s, 1H, CH_{aliphatic}), 7.58 (s, 2H, NH₂), 7.20-7.78 (m, 9H, CH_{aromatic}) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ 25.8, 28.7, 29.9, 31.7, 48.6, 49.5, 82.6, 114.6, 124.1, 125.8, 127.3, 127.6, 128.9, 129.2, 130.2, 132.6, 133.0, 139.5, 142.8, 148.2, 156.7, 162.2, 195.4 ppm.

2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-3-(phenylsulfonyl)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (**4e**)

White, solid, m.p. 167-169 °C; IR (ν_{max}, cm⁻¹): 3455 (NH₂), 1659 (C=O), 1323 and 1137 (SO₂); ¹H NMR (400 MHz, DMSO-d₆): δ 0.78 (s, 3H, CH₃), 0.98 (s, 3H, CH₃), 2.01-2.56 (m, 4H, CH₂), 3.66 (s, 3H, OCH₃), 4.42 (s, 1H, CH_{aliphatic}), 7.31 (s, 2H, NH₂), 6.65-7.59 (m, 9H, CH_{aromatic}) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ 26.1, 27.7, 28.7, 31.4, 31.8, 33.6, 49.8, 54.9, 84.4, 113.2, 115.8, 125.7, 128.6, 128.7, 128.8, 128.9, 129.5, 132.1, 136.3, 143.3, 156.4, 157.6, 161.6, 195.2 ppm.

2-amino-4-(4-chlorophenyl)-7,7-dimethyl-3-(phenylsulfonyl)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (**4h**)

White, solid, m.p. 182-183 °C; IR (ν_{max}, cm⁻¹): 3457 (NH₂), 1666 (C=O), 1332 and 1134 (SO₂); ¹H NMR (400 MHz, DMSO-d₆): δ 0.76 (s, 3H, CH₃), 0.96 (s, 3H, CH₃), 2.01-2.57 (m, 4H, CH₂), 4.45 (s, 1H, CH_{aliphatic}), 7.48 (s, 2H, NH₂), 7.05-7.63 (m, 9H, CH_{aromatic}) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ 26.0, 28.7, 31.8, 34.1, 48.6, 49.8, 83.7, 115.1, 125.7, 126.4, 127.7, 128.2,

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128.8, 129.0, 129.4, 129.6, 130.7, 132.3, 143.1, 143.3, 156.4, 162.1, 195.3 ppm.

2-amino-4-(4-chloro-3-nitrophenyl)-7,8-dihydro-7,7-dimethyl-3-(phenylsulfonyl)-4H-chromen-5(6H)-one (4j)

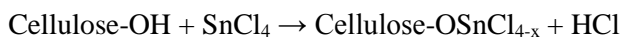
White, solid; m.p. 212-214 °C; IR (ν_{\max} , cm^{-1}): 3305 (NH_2), 1666 ($\text{C}=\text{O}$), 1530, 1361 (NO_2), 1332 and 1139 (SO_2); ^1H NMR (400 MHz, DMSO-d_6): δ 0.77 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 2.02-2.62 (m, 4H, CH_2), 4.58 (s, 1H, $\text{CH}_{\text{aliphatic}}$), 7.63 (s, 2H, NH_2), 7.32-8.01 (m, 8H, $\text{CH}_{\text{aromatic}}$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.3, 28.8, 31.9, 34.7, 48.7, 49.5, 84.1, 114.7, 124.1, 125.6, 126.9, 128.9, 129.3, 129.5, 129.8, 131.7, 132.9, 144.7, 146.7, 152.9, 157.9, 163.3, 195.4 ppm; Anal. Calcd. For $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_6\text{S}$: C, 56.50; H, 4.32; N, 5.72; S, 6.55 Found: C, 56.48; H, 4.29; N, 5.68; S, 6.50%.

2-amino-7,8-dihydro-4-(2-hydroxy-5-nitrophenyl)-7,7-dimethyl-3-(phenylsulfonyl)-4H-chromen-5(6H)-one (4k)

White, solid; m.p. 234-236 °C; IR (ν_{\max} , cm^{-1}): 3390 (NH_2), 1662 ($\text{C}=\text{O}$), 1524, 1383 (NO_2), 1338 and 1129 (SO_2); ^1H NMR (400 MHz, DMSO-d_6): δ 0.79 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 2.06-2.65 (m, 4H, CH_2), 4.64 (s, 1H, $\text{CH}_{\text{aliphatic}}$), 7.69 (s, 2H, NH_2), 7.91 (s, 1H, OH), 7.57-8.07 (m, 8H, $\text{CH}_{\text{aromatic}}$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.9, 28.9, 30.1, 31.6, 48.5, 49.7, 83.8, 114.7, 124.2, 125.8, 127.2, 127.5, 128.9, 129.5, 130.3, 132.7, 134.1, 141.7, 143.9, 151.9, 156.9, 162.5, 195.4 ppm; Anal. Calcd. For $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_7\text{S}$: C, 58.71; H, 4.71; N, 5.95; S, 6.81 Found: C, 58.68; H, 4.69; N, 5.92; S, 6.75%.

3. Results and Discussion

The nano-cellulose- OSnCl_{4-x} catalyst was simply prepared as shown in the following (Scheme 1) and evaluated with FTIR, FE-SEM, TEM, EDX, and TGA techniques.



Scheme 1. Preparation of nano-cellulose- OSnCl_{4-x}

The FT-IR spectrum of the nano-cellulose exhibited a broad peak for an OH absorption band at 3346 cm^{-1} . The C-H stretching vibrations of the aliphatic systems for cellulose were observed at 2901 cm^{-1} . The peaks at 1165 and 1059 cm^{-1} represented the C-O stretching vibration of the glucose unit (Fig. 1a).

The FTIR spectra of nanocrystalline cellulose- OSnCl_{4-x} in Fig. 1b demonstrated dominant peaks at

approximately $3300\text{-}3500 \text{ cm}^{-1}$ and 2922 cm^{-1} , were corresponded to the stretching vibrations of OH and aliphatic CH groups, respectively. The appearance of the band at 1637 cm^{-1} clearly demonstrated Sn-Cl stretching vibration. The bridge asymmetric C-O-C stretching vibrations were observed within the range of $1059\text{-}1158 \text{ cm}^{-1}$. The Sn-O stretching vibration was observed at 673 cm^{-1} , indicating that tin tetrachloride is supported on nano-cellulose [22, 23].

A field emission scanning electron microscope (FE-SEM) was used to study the morphology of the nanocatalysts and to evaluate the average particle size and distribution of cellulose and nano-cellulose- OSnCl_{4-x} , as shown in Fig. 2. The size of cellulose- OSnCl_{4-x} is about 72-93 nm, and the spots on the surface of cellulose can be assigned to tin tetrachloride groups (Fig. 2b). Moreover, the data obtained by spot EDX confirmed these results.

As can be seen in Fig. 3, EDX analysis revealed the fundamental composition of the cellulose and nano-cellulose- OSnCl_{4-x} . The obtained results are presented in Table 1, which shows that cellulose consists of C and O (Fig. 3a) and cellulose- OSnCl_{4-x} (Fig. 3b) contains elements C, O, Cl and Sn. The presence of Sn and Cl in the EDX (Fig. 3b) imply a chemical interaction of tin tetrachloride with the surface of cellulose.

Fig. 4 shows the TEM of the image related to SnCl_4 supported on cellulose (nano-cellulose- OSnCl_{4-x}). As it can be seen from the TEM image, the average particle size distribution is below 100 nm that is near to obtained results by FE-SEM images.

The thermal decomposition of the nano-cellulose- OSnCl_{4-x} has been studied using a combination of thermogravimetry (TGA) and derivative thermogravimetry (DTG) methods up to 800°C . Three thermal decomposition mass loss steps are observed for the nano-cellulose- OSnCl_{4-x} (a) 11.06% mass loss at 167°C related to loss of physically adsorbed solvent, adsorbed surface hydroxyl groups, and water, (b) 58.5% mass loss at 508°C related to loss of the covalently bond organic group to the cellulose surface and (c) The mass loss of 25.54% at the third step associated with T_{DTG} peak at 802°C , corresponds to the residual mass. The total weight loss is 95.1% (Fig. 5).

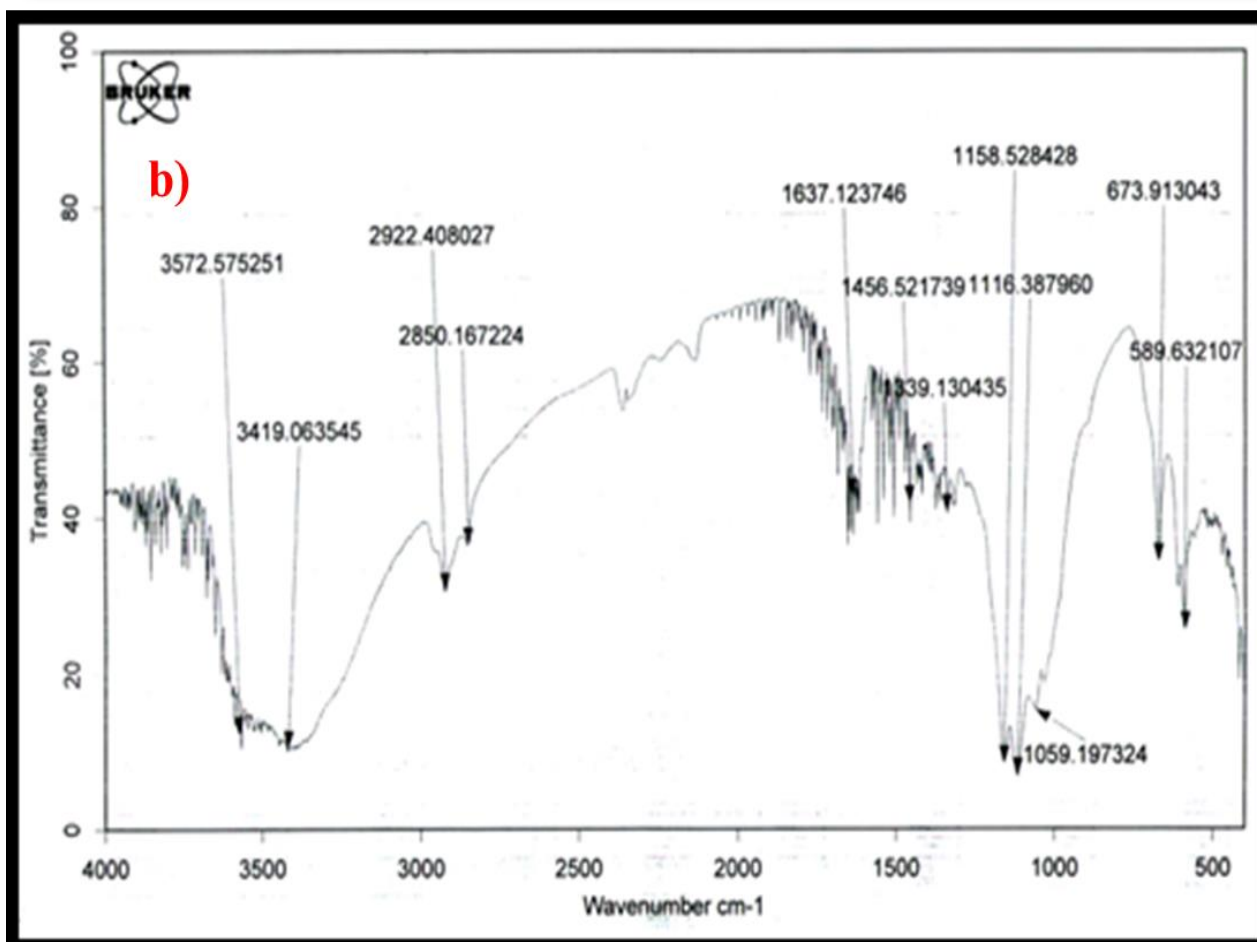
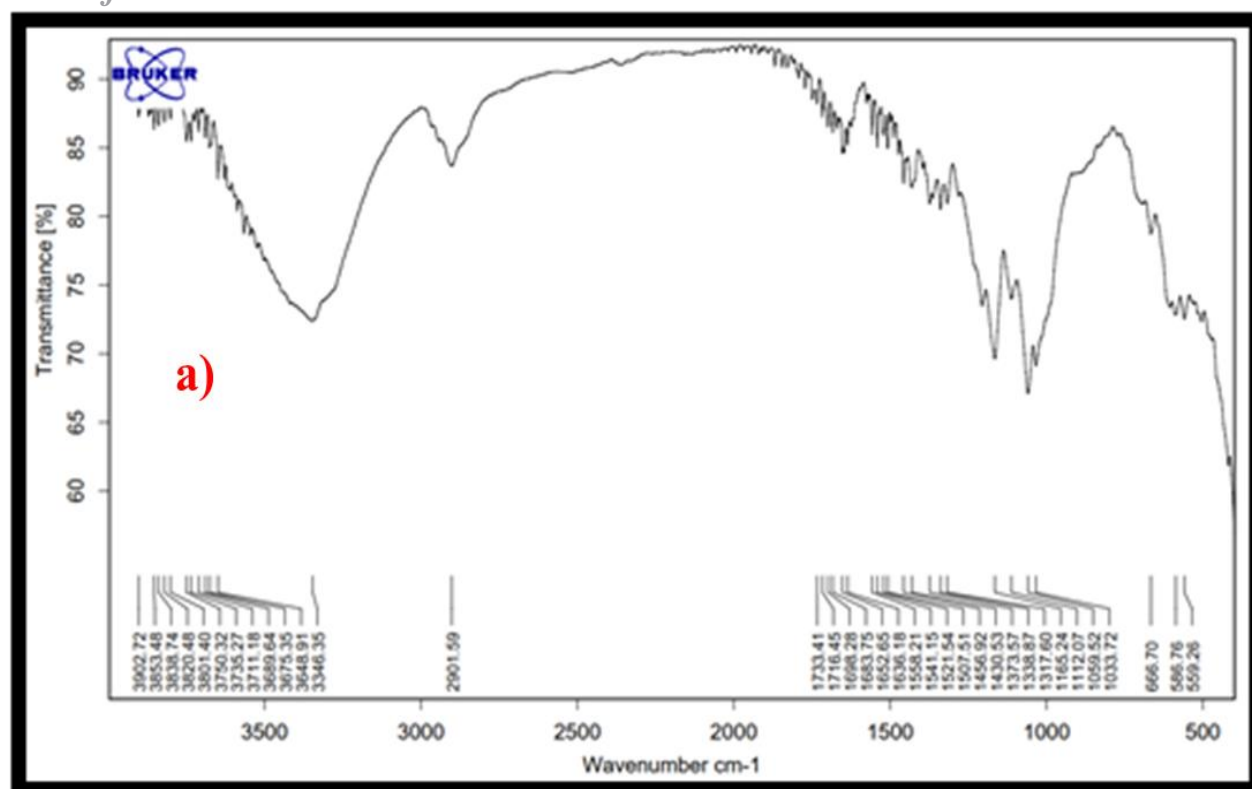


Fig. 1. FTIR spectrum of a) nano-cellulose, b) nano-cellulose-OSnCl_{4-x}

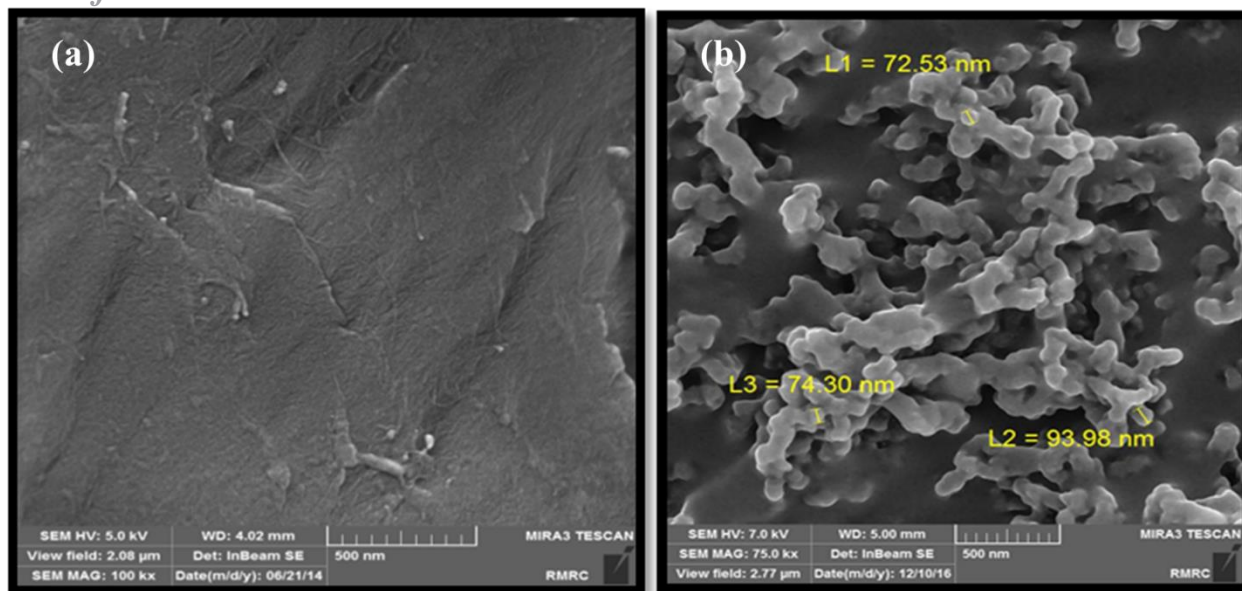


Fig. 2. (a) FE-SEM of Cellulose and (b) FE-SEM of nano-cellulose-OSnCl_{4-x}

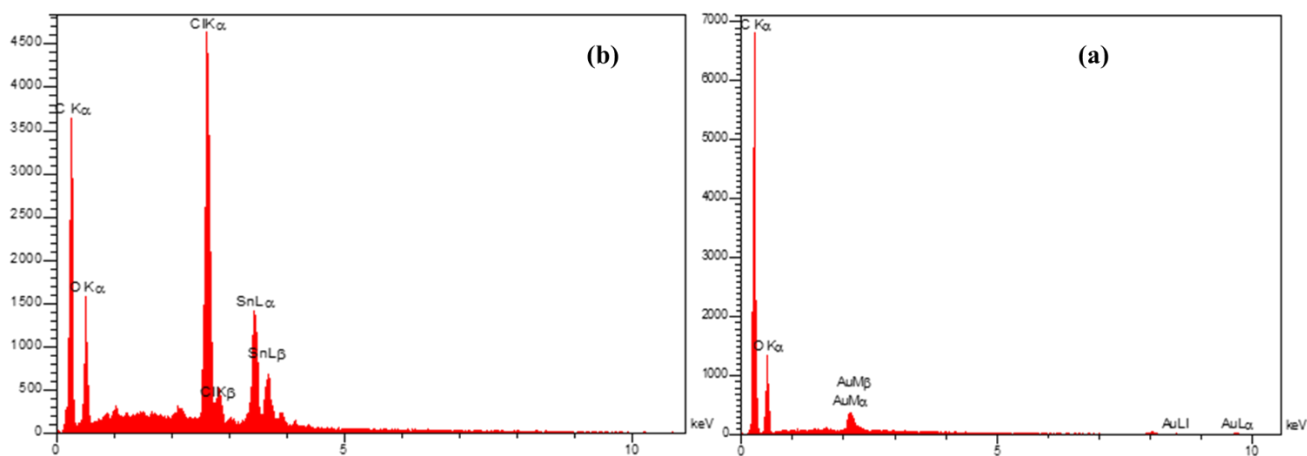


Fig. 3. (a) EDX of Cellulose and (b) EDX of nano-cellulose-OSnCl_{4-x}

Table 1. Chemical analysis of cellulose and nano-cellulose-OSnCl_{4-x}

Element	Cellulose (W%)	Nano-cellulose-OSnCl _{4-x} (W%)
C	69.20	55.34
O	22.84	22.19
Cl	-	10.77
Sn	-	11.70

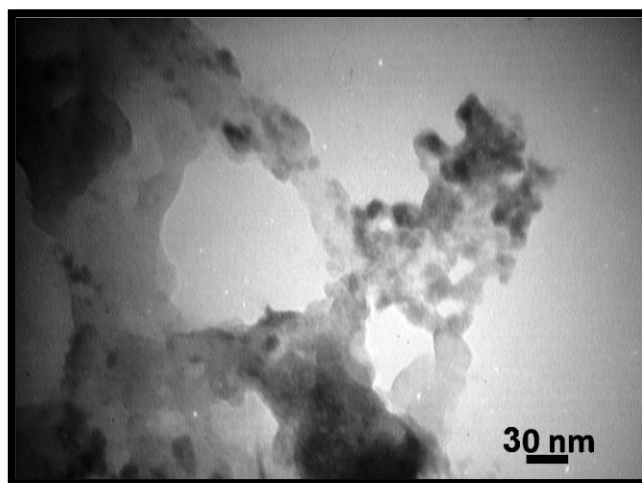


Fig. 4. TEM image of nano-cellulose-OSnCl_{4-x}

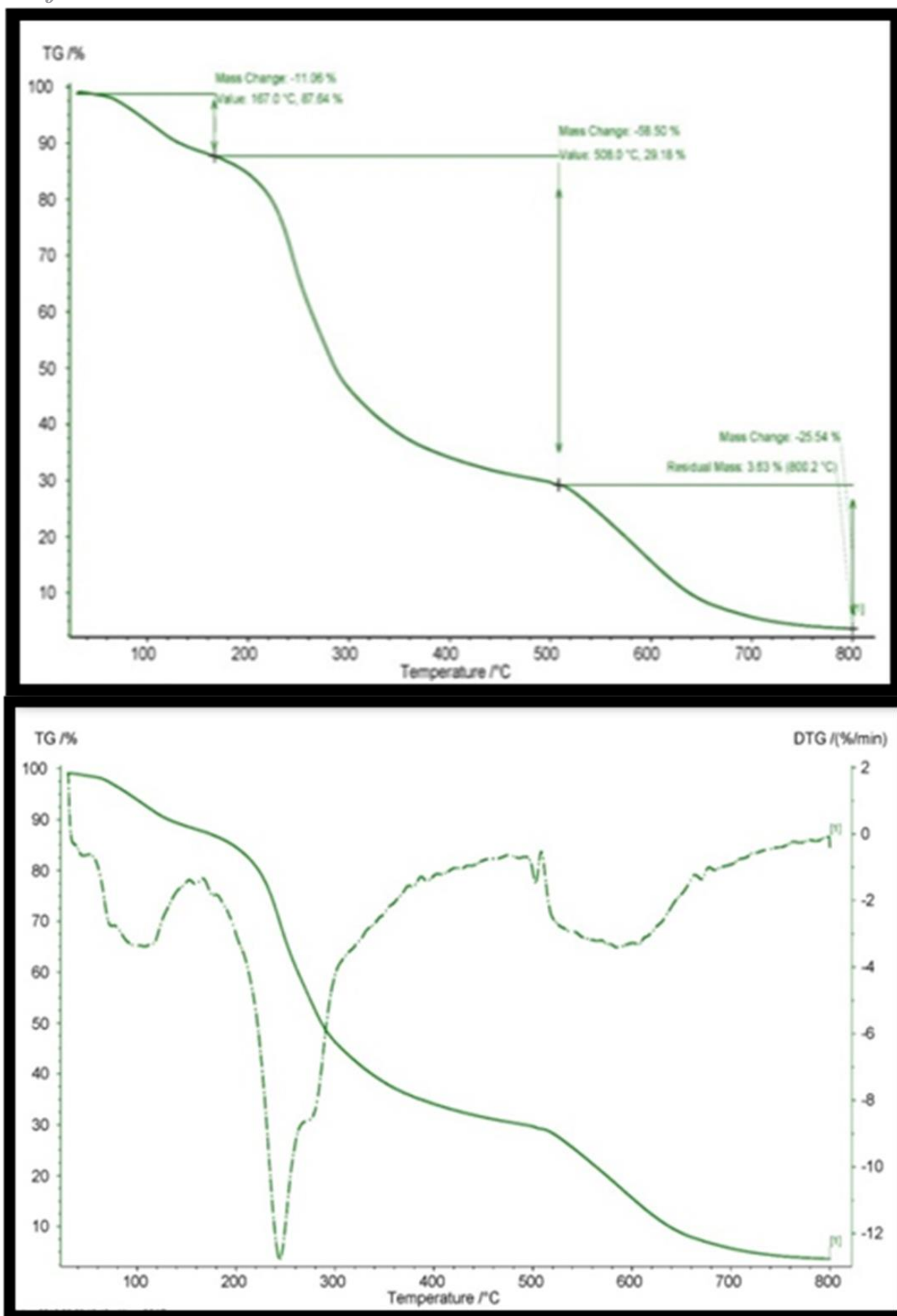


Fig. 5. The TGA/DTG curves of nano-cellulose-OSnCl_{4-x} samples

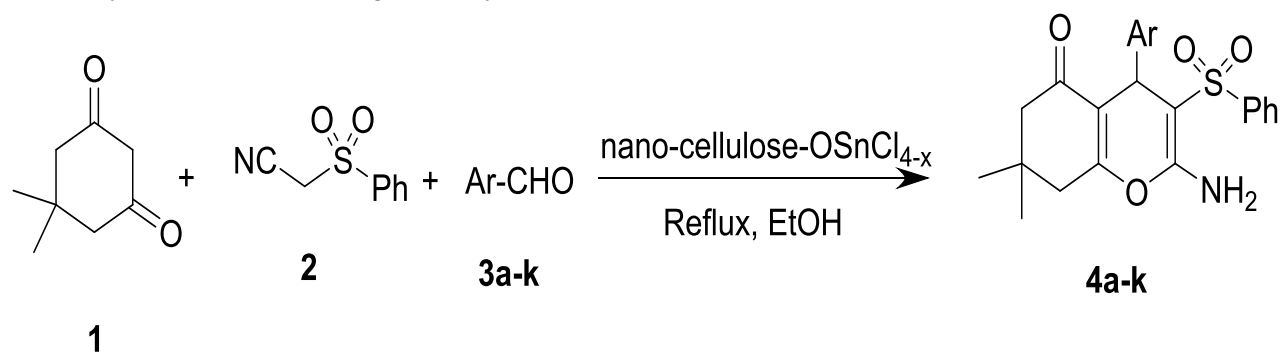
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In extension to the studies of nano solid acids application in organic synthesis [14-21], we have explored the synthesis of 2-amino-7,8-dihydro-7,7-dimethyl-4-phenyl-3-(phenylsulfonyl)-4*H*-chromen-5(6*H*)-one derivatives by the one-pot three-component condensation of, dimedone **1**, phenylsulfonylacetonitrile **2** and an aromatic aldehyde **3** with 5 mg nano-cellulose-OSnCl_{4-x} as catalyst (**Scheme 2**).

The study was commenced by using benzaldehyde, phenylsulfonylacetonitrile, and dimedone as model substrates for the preparation of **4a**. The experiments revealed that in the absence of nano-cellulose-OSnCl_{4-x}, we will subsequently not see any progress in EtOH under reflux (**Table 2**, entry 1). The transformation of benzaldehyde, dimedone, and phenylsulfonylacetonitrile proceeded smoothly with nano-cellulose-OSnCl_{4-x} (5 mg) in EtOH (5mL), and at the end of the reaction (about 30 min later), the product was collected by filtration and recrystallized from ethanol, affording the nicely crystalline **4a** in good yield (92%, **Table 2**, entry 2). Different solvents and catalysts were examined in the model reaction, and the results are tabulated in **Table 2**. A wide range of Lewis acid catalysts including SbCl₅, SnCl₄, BF₃, and TiCl₄ was investigated to improve the yield for the synthesis of 2-amino-7,8-dihydro-7,7-dimethyl-4-phenyl-3-(phenylsulfonyl)-4*H*-chromen-5(6*H*)-one. It is noteworthy, that all of these Lewis acids (**Table 2**, entries 2-5) could simply catalyze this reaction in EtOH but nano-cellulose-OSnCl_{4-x} gave the highest yield (92%, **Table 2**, entry 2), and 5 mg loading was sufficient for this reaction. Different solvents, for example, CH₂Cl₂, CH₃CN, and H₂O were verified in the presence of nano-cellulose-OSnCl_{4-x} as the catalyst, but conversely, they caused low yields (**Table 2**, entries 6-8). Decreasing the catalyst loading from 5 to 1 mg, lowered the yield of the reaction significantly (**Table 2**,

entries 9, 10). The yields of **4a** were not further enhanced with an increased amount of the catalyst (**Table 2**, entry 11). Therefore, it is obvious from the results that the best situation for **4a** could be entry 2, using nano-cellulose-OSnCl_{4-x} (5 mg) as solid acid and EtOH as solvent under reflux. A remarkable advantage of this technique is that the reagent can be recovered at the end of the reaction and can be used several times without losing its activity. To regenerate the catalyst, after completion of the reaction, the mixture was filtered and recrystallized from hot ethanol; the catalyst was separated and washed with ethanol and then dried to obtain the solid remainder. This procedure repeated for two cycles and the yield of product **4a** did not change significantly (**Table 2**, entries 12, 13). The experiments revealed that in the presence of free nano-cellulose, the product is slightly observed (**Table 2**, entry 14).

Encouraged by these remarkable results, and in order to investigate the generality and scope of this new protocol, a variety of 2-amino-7,8-dihydro-7,7-dimethyl-4-phenyl-3-(phenylsulfonyl)-4*H*-chromen-5(6*H*)-one derivatives (**4a-k**) were synthesized by treating substituted benzaldehyde with dimedone and phenylsulfonylacetonitrile in presence of a catalytic amount of nano-cellulose-OSnCl_{4-x} under the optimized condition. When dimedone and phenylsulfonylacetonitrile reacted with aromatic aldehydes including the halogen group or other electron-withdrawing group on the phenyl ring, the corresponding product was formed with 87-95% yields under reaction conditions (**Table 3**, entries 2, 3 and 6-11). Aromatic aldehydes bearing electron-donating gave high yields of the corresponding products (**Table 3**, entries 4, 5), but within longer reaction time than aromatic aldehydes containing electron-withdrawing group.



Scheme 2. Synthesis of 2-amino-7,8-dihydro-7,7-dimethyl-4-phenyl-3-(phenylsulfonyl)-4*H*-chromen-5(6*H*)-one derivatives in the presence of nano-cellulose-OSnCl_{4-x} as catalyst

Table 2. Optimization of the reaction conditions for the synthesis of **4a**^a

Entry	Catalyst (mg)	Solvent	Time (min)	Yield ^b (%)
1	nano-cellulose-OSnCl _{4-x} (0)	EtOH	90	0
2	nano-cellulose-OSnCl _{4-x} (5)	EtOH	30	9 ²
3	nano-cellulose-SbCl ₅ (5)	EtOH	30	63
4	nano-cellulose-BF ₃ (5)	EtOH	30	75
5	nano-cellulose-TiCl ₄ (5)	EtOH	30	80
6	nano-cellulose-OSnCl _{4-x} (5)	CH ₂ Cl ₂	30	Trace
7	nano-cellulose-OSnCl _{4-x} (5)	H ₂ O	30	52
8	nano-cellulose-OSnCl _{4-x} (5)	CH ₃ CN	30	45
9	nano-cellulose-OSnCl _{4-x} (1)	EtOH	30	79
10	nano-cellulose-OSnCl _{4-x} (3)	EtOH	30	82
11	nano-cellulose-OSnCl _{4-x} (7)	EtOH	30	96
12	nano-cellulose-OSnCl _{4-x} (5) 2 nd run	EtOH	30	91
13	nano-cellulose-OSnCl _{4-x} (5) 3 rd run	EtOH	30	89
14	nano-cellulose (5)	EtOH	30	Trace

^a Reaction condition: 5 mL of solvent under reflux, 1 mmol of benzaldehyde, 1 mmol of dimedone, and 1 mmol of phenylsulfonylacetonitrile

^b Isolated yields.

Table 3. Synthesis of 2-amino-7,8-dihydro-7,7-dimethyl-4-phenyl-3-(phenylsulfonyl)-4H-chromen-5(6H)-one derivatives^a

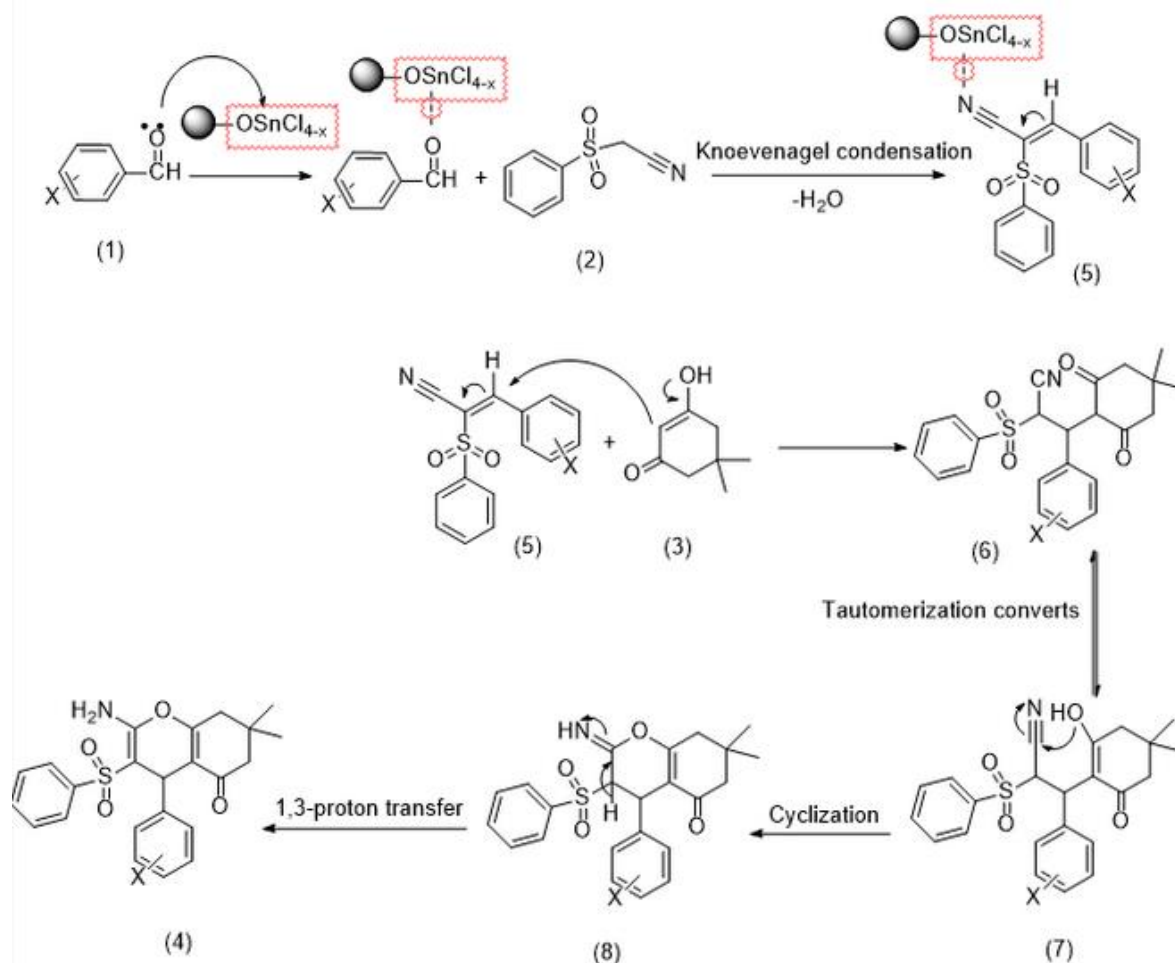
Entry	Ar	Product	Time (min)	Yield ^b (%)	m.p. °C	m.p. °C [Ref.]
1	C ₆ H ₅	4a	40	92	157-158	157-159 [24]
2	2-O ₂ NC ₆ H ₄	4b	30	93	184-186	185-187 [24]
3	4-O ₂ NC ₆ H ₄	4c	30	95	188-190	185-187 [24]
4	4-CH ₃ C ₆ H ₄	4d	50	84	190-192	189-192 [24]
5	4-CH ₃ OC ₆ H ₄	4e	50	86	167-169	165-169 [24]
6	3-BrC ₆ H ₄	4f	45	87	114-116	113-115 [24]
7	2-ClC ₆ H ₄	4g	30	90	188-190	188-190 [24]
8	4-ClC ₆ H ₄	4h	30	91	182-183	181-183 [24]
9	2,4-diClC ₆ H ₃	4i	35	89	202-204	201-203 [24]
10	4-Cl-3-O ₂ NC ₆ H ₃	4j	30	94	212-214	-
11	2-OH-5-O ₂ NC ₆ H ₃	4k	30	92	234-236	-
12	<i>n</i> -C ₃ H ₇	4l	120	N.R.	-	-

^a Reaction condition: 1 mmol of aldehyde, 1 mmol of dimedone, 1 mmol of phenylsulfonylacetonitrile, and 5 mL of ethanol under reflux condition.

^b Isolated yields.

The mechanism of 2-amino-7,8-dihydro-7,7-dimethyl-4-phenyl-3-(phenylsulfonyl)-4H-chromen-5(6H)-ones (**4**) synthesis using nano-cellulose-OSnCl_{4-x} is outlined in **Scheme 3**. At the beginning of the reaction, aldehyde (**1**) is attached to the surface of nano-cellulose-OSnCl_{4-x}. This is an interaction between the tin atom of Lewis acid supported on nano-cellulose and oxygen of the carbonyl group in aldehyde. Then, the 3-Aryl-2-(phenylsulfonyl)acrylonitrile (**5**), comprising the electron-poor C=C double bond, is formed

quantitatively by Knoevenagel condensation of phenylsulfonylacetonitrile (**2**) to the aromatic aldehyde (**1**) in the presence of nano-cellulose-OSnCl_{4-x} as nanocatalyst. Afterward, the dimedone (**3**) C-alkylation by reaction with the electrophilic C=C double bond gives the intermediate (**7**). Then, it makes the inner molecular ring (**8**), and after 1,3-proton transfer the corresponding product (**4**) was provided.



Scheme 3. Suggested mechanism for the synthesis of 2-amino-7,8-dihydro-7,7-dimethyl-4-phenyl-3-(phenylsulfonyl)-4H-chromen-5(6H)-ones in the presences of nano-cellulose-OSnCl_{4-x} as catalyst

● :Nano-cellulose

4. Conclusions

In conclusion, a well-organized, environmentally friendly, atom-economical, and simple procedure for the preparation of 2-amino-7,8-dihydro-7,7-dimethyl-4-phenyl-3-(phenylsulfonyl)-4H-chromen-5(6H)-one derivatives in a three-component reaction in ethanol is described. Nano-cellulose-OSnCl_{4-x} as a novel, heterogeneous and reusable nanocatalyst is prepared in a very simple procedure. Prominent among the advantages of this method are working simplicity, mild reaction conditions, short reaction times, higher yields, and environmental friendliness. Meanwhile, solid phase acidic catalyst could be reused for a number of times without appreciable loss of activity. The current technique does not involve any dangerous organic solvent. Consequently, this procedure could be considered as green chemistry.

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