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Preparation and Characterization of Nano-ZnO Catalyst and its Application in Synthesis of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*]chromen Derivatives

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Abstract

An efficient and environmentally adapted synthesis of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*]chromen derivatives by condensation of a wide range of aryl aldehydes, *α*-naphthol and (phenylsulfonyl)acetonitrile and by using a catalytic amount of nano-ZnO under solvent-free condition is explained. This catalyst was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction spectroscopy (EDX) and Thermogravimetric analysis (TG). As a result, 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*] chromens were produced under facile conditions in high yield (89-96%) and high rate (8-15 min), using nano-ZnO as a recyclable catalyst.

Keywords: Nano-ZnO, Nano-catalyst, α-Naphthol,(Phenylsulfonyl)acetonitrile, Solid acid.

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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 [1-6]. Heterocyclic compounds containing oxygen, such as chromens with pyran ring play an important role in pharmaceuticals and biological materials. Moreover, synthesis of chromens through heterocyclic systems is known as an excellent strategy due to their broad spectrum of significant pharmaceutical applications including antimicrobial, antiviral and anticancer [7-11]. On the other hand, nano-catalyst has been utilized to accelerate a number of synthetically valuable reactions. Nowadays, nanoparticle applications as catalysts have attracted researchers due to their unique dimensions, facile recyclability, large specific surface area of nanostructures and short reaction times [12]. Herein, an innovative method for the synthesis of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*]chromens is presented by one-pot three-component condensation of aryl aldehydes, (phenylsulfonyl) acetonitrile and α-naphthol employing a catalytic amount of nano-ZnO in a solvent-free condition.

Experimental

The chemicals applied in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification. An Electrothermal 9100 apparatus determined melting points. ^{1}H and ^{13}C NMR spectra were recorded on Varian-INOVA 500 MHz and 400 MHz spectrometer at solution in DMSO-d_6 using TMS as internal standard. The morphologies of the nanoparticles were observed using scanning electron microscopy (SEM) of MIRA TESCAN microscope with an accelerating voltage of 15 kV. The IR spectra of the catalyst were recorded using a model AVATAR Fourier transform infrared spectroscopy (FT-IR). The x-ray diffraction spectroscopy (EDX) analysis was done using SAMx-analyzer. Thermogravimetric analysis was performed by using a TGA-DSC model Q600 from TA Company.

Preparation of nano-ZnO

Initially, the zinc acetate dihydrate (2.19 g, 0.01 mol) and oxalic acid (1.08g, 0.012 mol) were combined by grinding in a mortar for 35 min at room temperature. Eventually, for obtaining a nice and homogenized ZnO powder (0.78 g), the obtained $ZnC_2O_4.2H_2O$ nanoparticles were calcinated at 450 °C for 30 min under thermal decomposition conditions and then pulverized by mortar.

General procedure for preparation of compounds 4a-k

Synthesis of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*]chromen derivatives (**4a-k**) was carried out in the presence of nano-ZnO catalyst. The nano-catalyst (5.0 mg) was added to a stirred mixture of (phenylsulfonyl) acetonitrile**1** (1.0 mmol), *α*-naphthol**2** (1.0 mmol) and aromatic aldehyde **3** (1.0 mmol). The materials were mixed and heated under solvent-free condition at 80 ºC for the appropriate time as mentioned in Table 4. After completion of the reaction, the reaction mixture was dissolved in hot ethanol and catalyst separated by centrifugation. Finally, the crude product was recrystallized from hot ethanol, filtered, washed several times with ethanol and dried at room temperature.

Analytical data for some products:

*2-Amino-3-(phenylsulfonyl)-4-phenyl-4H-benzo[h]chromen (**4a**)*

White solid, m.p: 219-221 °C; IR (ν_{max}, cm^{-1}): 3418, 3325 (NH_2), 1623(C=C), 1369 and 1138 (SO_2) cm^{-1}; ^1H NMR (500 MHz, DMSO): δ = 4.95 (s, 1H, CH), 7.02–7.75 (m, 16H, aromatic), 8.18 (s, 2H, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO): δ=82.4, 120.8, 121.3, 122.7, 124.1, 125.7, 125.9, 126.3, 126.6, 127.1, 127.6, 128.3, 128.8, 132.1, 132.4, 142.6, 143.7, 145.7, 158.3 ppm. anal. calcd. for $C_{25}H_{19}NO_3S$ (413.5): C, 72.62; H, 4.63; N, 3.39; S, 7.75%; found: C, 72.59; H, 4.65; N, 3.42; S, 7.78%.

*2-Amino-3-(phenylsulfonyl)-4-(4-chlorophenyl)-4H-benzo[h]chromen (**4b**)*

White solid, m.p: 205-206 °C; IR (ν_{max}, cm^{-1}): 3464, 3337 (NH_2), 1624 (C=C), 1368 and 1133 (SO_2); ^1H NMR (500 MHz, DMSO): δ = 4.97 (s, 1H, CH), 7.07–7.75 (m, 15H, aromatic), 8.18 (s, 2H, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO): δ = 82.8, 121.2, 121.4, 123.3, 124.8, 126.3, 126.4, 127.3, 127.4, 128.2, 128.8, 129.4, 129.6, 129.9, 131.5, 132.8, 133.1, 143.2, 144.3, 145.4, 158.8 ppm. anal. calcd. For $C_{25}H_{18}ClNO_3S$ (447.94): C, 67.03; H, 4.05; N, 3.13; S, 7.16%; found: C, 67.00; H, 4.08; N, 3.10; S, 7.19%.

*2-Amino-3-(phenylsulfonyl)-4-(3-chlorophenyl)-4H-benzo[h]chromen (**4c**)*

White solid, m.p: 248-250 °C; IR (ν_{max}, cm^{-1}): 3428, 3323 (NH_2), 1623 (C=C), 1375 and 1142 (SO_2); ^1H NMR (500 MHz, DMSO): δ = 5.09 (s, 1H, CH), 6.86–7.87 (m, 15H, aromatic), 8.27 (s, 2H, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO): δ = 82.3, 120.9, 121.2, 123.1, 124.7, 126.1, 126.2, 126.3, 126.8, 127.1, 127.2, 127.3, 128.1, 129.2, 130.7, 132.7, 133.1, 133.3, 143.1, 144.0, 148.5,

158.8 ppm. anal. calcd. for $C_{25}H_{18}ClNO_3S$ (447.94): C, 67.03; H, 4.05; N, 3.13; S, 7.16%; found: C, 67.06; H, 4.04; N, 3.16; S, 7.15%.

*2-Amino-3-(phenylsulfonyl)-4-(2-chlorophenyl)-4H-benzo[h]chromen (**4d**)*

White solid, m.p: 206-207 °C; IR (ν_{max}, cm^{-1}): 3434, 3307 (NH_2), 1622 (C=C), 1373 and 1138 (SO_2); ^1H NMR (500 MHz, DMSO): δ = 5.55 (s, 1H, CH), 7.06–7.85 (m, 15H, aromatic), 8.30 (s, 2H, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO): δ = 81.6, 119.7, 121.3, 123.0, 124.8, 125.2, 126.0, 127.2, 127.3, 128.0, 128.1, 128.6, 129.2, 129.8, 130.8, 131.6, 132.7, 133.1, 142.8, 143.6, 158.6 ppm. anal. calcd. for $C_{25}H_{18}ClNO_3S$ (447.94): C, 67.03; H, 4.05; N, 3.13; S, 7.16%; found: C, 67.04; H, 4.06; N, 3.09; S, 7.20%.

*2-Amino-3-(phenylsulfonyl)-4-(4-Cyanophenyl)-4H-benzo[h]chromen (**4e**)*

White solid, m.p: 258-259 °C; IR (ν_{max}, cm^{-1}): 3457, 3327 (NH_2), 2230 (CN), 1626 (C=C), 1370 and 1141 (SO_2); ^1H NMR (500 MHz, DMSO): δ = 5.16 (s, 1H, CH), 7.33–7.86 (m, 15H, aromatic), 8.28 (s, 2H, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO): δ = 82.0, 109.5, 119.2, 120.3, 121.3, 123.1, 124.8, 126.1, 126.2, 127.2, 127.3, 128.1, 128.7, 129.3, 132.8, 132.9, 133.1, 143.1, 143.9, 151.7, 158.8 ppm. anal. calcd. for $C_{26}H_{18}N_2O_3S$ (438.5): C, 71.22; H, 4.14; N, 6.39; S, 7.31%; found: C, 71.20; H, 4.12; N, 6.43; S, 7.30%.

*2-Amino-3-(phenylsulfonyl)-4-(3-Nitrophenyl)-4H-benzo[h]chromen (**4f**)*

White solid, m.p: 274-275 °C; IR (ν_{max}, cm^{-1}): 3434, 3300 (NH_2), 1622 (C=C), 1524, 1348 (NO_2), 1273 and 1138 (SO_2); ^1H NMR (500 MHz, DMSO): δ = 5.31 (s, 1H, CH), 7.36–7.95 (m, 15H, aromatic), 8.32 (s, 2H, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO): δ = 81.9, 120.3, 121.3, 121.9, 122.1, 123.1, 124.8, 126.0, 126.1, 127.2, 127.3, 128.1, 129.3, 130.4, 132.6, 133.1, 134.5, 143.1, 144.0, 148.0, 148.1,158.8 ppm. anal. calcd. for $C_{25}H_{18}N_2O_5S$ (458.49): C, 65.49; H, 3.96; N, 6.11; S, 6.99%; found: C, 65.52; H, 3.93; N, 6.14; S, 7.00%.

*2-Amino-3-(phenylsulfonyl)-4-(4-nitrophenyl)-4H-benzo[h]chromen (**4g**)*

White solid, m.p: 219-220 °C; IR (ν_{max}, cm^{-1}): 3462, 3335 (NH_2), 1626 (C=C), 1516, 1349 (NO_2), 1284 and 1133 (SO_2); ^1H NMR (500 MHz, DMSO): δ = 5.24 (s, 1H, CH), 6.69–8.02 (m, 15H, aromatic), 8.29 (s, 2H, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO): δ=82.4, 119.0, 121.0, 121.2, 123.3, 124.6, 126.1, 126.2, 127.1, 127.3, 128.1, 129.3, 129.9, 131.6, 132.6, 133.0, 143.0, 144.1,

145.9, 158.1 ppm. anal. calcd. for $C_{25}H_{18}N_2O_5S$ (458.49): C, 65.49; H, 3.96; N, 6.11; S, 6.99%; found: C, 65.50; H, 3.99; N, 6.10; S, 7.01%.

*2-Amino-3-(phenylsulfonyl)-4-(4-bromophenyl)-4H-benzo[h]chromen (**4h**)*

White solid, m.p: 199-200 °C; IR (ν_{max}, cm^{-1}): 3464, 3340 (NH_2), 1625 (C=C), 1369 and 1134 (SO_2); ^1H NMR (500 MHz, DMSO): δ = 5.04 (s, 1H, CH), 7.15–7.85 (m, 15H, aromatic), 8.26 (s, 2H, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO): δ = 82.5, 119.9, 121.0, 121.2, 123.1, 124.6, 126.1, 126.2, 127.1, 127.2, 128.1, 129.3, 129.9, 131.6, 132.6, 133.0, 143.0, 144.1, 145.7, 158.6 ppm. anal. calcd. for $C_{25}H_{18}BrNO_3S$ (492.39): C, 60.98; H, 3.68; N, 2.84; S, 6.51%; found: C, 60.96; H, 3.71; N, 2.82; S, 6.54%.

*2-Amino-3-(phenylsulfonyl)-4-(4-methylphenyl)-4H-benzo[h]chromen (**4i**)*

White solid, m.p: 226-227 °C; IR (ν_{max}, cm^{-1}): 3420, 3357 (NH_2), 1649 (C=C), 1393 and 1185 (SO_2); ^1H NMR (500 MHz, DMSO): δ = 2.17 (s, 3H, CH_3), 4.97 (s, 1H, CH), 6.92–7.85 (m, 15 H, aromatic), 8.25 (s, 2H, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO): δ = 46.1, 82.5, 121.2, 121.8, 123.1, 124.4, 126.1, 126.3, 127.0, 127.5, 128.0, 129.2, 129.3, 132.5, 132.8, 135.8, 144.2, 155.6 ppm. anal. calcd. for $C_{26}H_{21}NO_3S$ (427.52): C, 73.04; H, 4.95; N, 3.28; S, 7.50%; found: C, 73.06; H, 4.92; N, 3.31; S, 7.48%.

*2-Amino-3-(phenylsulfonyl)-4-(4-fluorophenyl)-4H-benzo[h]chromene (**4j**)*

White solid, m.p: 247-248 °C; IR (ν_{max}, cm^{-1}): 3470, 3339 (NH_2), 1651(C=C), 1371, 1131 (SO_2); ^1H NMR (500 MHz, DMSO) δ: 5.03 (s, 1H, CH), 6.03 (s, 2H, NH_2), 6.68-8.16 (m, 15 H, aromatic) ppm; ^{13}C NMR (125 MHz, DMSO): δ = 4.97 (s, 1H, CH), 6.66-7.86 (m, 15H, aromatic), 8.28 (s, 2H, NH_2) ppm; ^{13}C NMR (125 MHz,DMSO) δ: 83.2, 114.1, 121.2, 121.9, 123.1, 124.4, 126.1, 126.4, 127.0, 127.1, 128.0, 128.6, 129.2, 132.5, 132.9, 138.3, 142.9, 144.3, 158.2, 158.5 ppm. anal. calcd for $C_{25}H_{18}FNO_3S$ (431.48): C 69.59, H 4.21, N 3.25; S 7.43%; found: C 69.51, H 4.27, N 3.29;S 7.45%.

*2-Amino-3-(phenylsulfonyl)-4-(5-bromo-2-hydroxyphenyl)-4H-benzo[h]chromen (**4k**)*

White solid, m.p: 168-170 °C. IR (ν_{max}, cm^{-1}): 3480, 3310 (NH_2), 1688 (C=C), 1361 and 1129 (SO_2);^1H NMR (400 MHz, DMSO) δ: 4.30 (s, 1H, OH), 5.41 (s, 1H, CH), 6.64-8.31 (m, 14H, aromatic), 7.43 (s, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, DMSO) δ: 80.5, 109.9, 117.4, 118.2, 120.2, 122.5, 123.9, 124.4, 125.0, 125.5, 126.3, 126.5, 127.3, 127.5, 128.3, 128.6, 129.8, 130.7,

132.5, 133.7, 142.6, 143.4, 153.4, 158.5, 162.6 ppm. anal. calcd. for $C_{25}H_{18}BrNO_4S$ (508.39): C, 59.06; H, 3.56; N, 2.75; S, 6.31%; found: C, 59.04; H, 3.58; N, 2.73; S, 6.32%.

Results and discussion

As discussed above, the researchers' interest is ever-growing in chromens or benzopyrans, as valuable precursors in numerous natural products such as flavanones [13], catechins [14] and anthocyanins [15] which are used as chemo-preventive and cytotoxic against various cancers. They have a broad spectrum of applications particularly in drug discovery process by containing both biologically and pharmacologically active groups [7-11]. Generally, 2-Aminochromenes are synthesized through Knoevenagel condensation of aldehyde and malononitrile, followed by Michael-type addition-cyclization with dimedone, and activated phenol or naphthols [16]. In addition, 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*] chromens have exhibited various biological activities including antimicrobial [17], antitumor [7], antiviral [11], sex pheromone [18] and mutagenicity activities [19].

Due to the importance and impressive applications of these compounds, providing developing efficient strategies is of special importance. Recently, various methods have been employed for synthesis of these derivatives [20-23], and our team has had many contributions in this regard by applying approaches with the valuable benefits such as less catalyst consumption, shorter reaction time, and higher efficiency [24-28]. To do so, we have designed the novel tandem one-pot procedure for the synthesis of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*]chromen derivatives, which not only has above positive features, but also is able to provide excellent yield with assistance of green and recyclable nano-catalyst via facile workups.

The morphology and particle size of nano-catalyst have been revealed using SEM. As shown in related image (Fig. 1a), the size of nano-ZnO is below 100 nm. As seen in (Fig. 1b), elemental composition of the nano-ZnO was investigated by EDX analysis which is shown in Figure 1b and Table 1. Nano-ZnO is composed of 85.69% Zn and 14.31% of O.

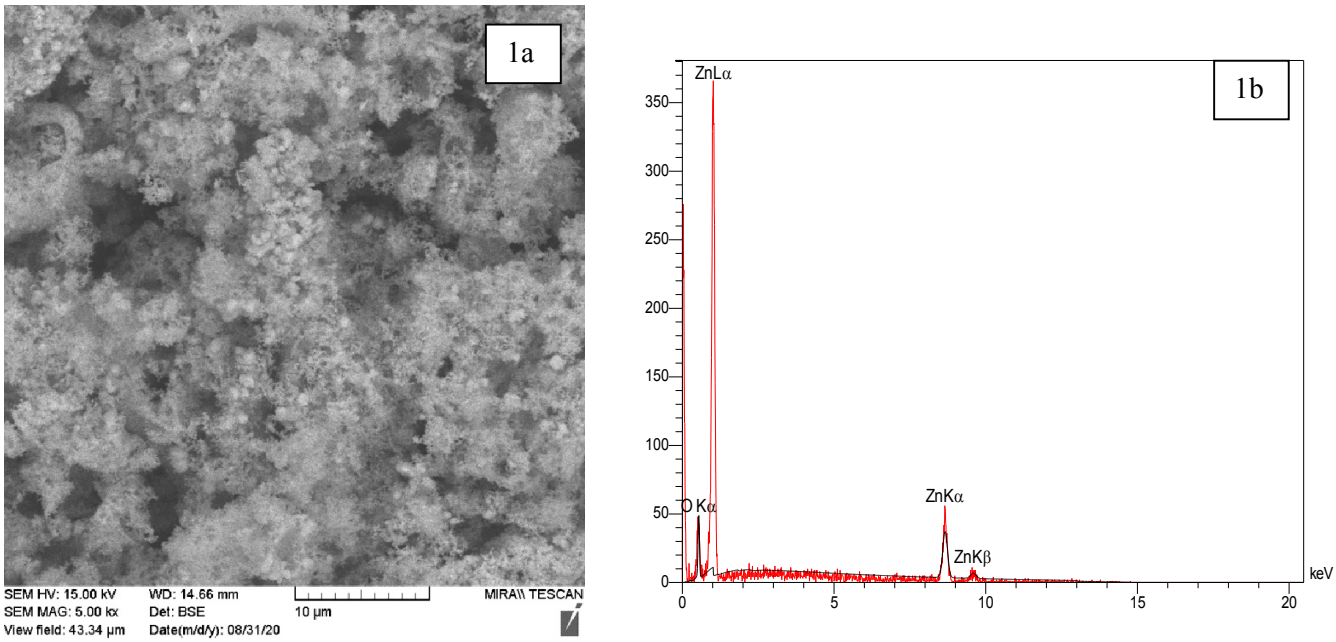


Figure 1. (a)SEM micrograph of nano-ZnO. (b)EDX of nano-ZnO.

Table 1. Chemical analysis of nano-ZnO

Element	nano-ZnO (wt.%)
Zn	85.69
O	14.31

The resulted data by FT-IR spectrum of nano-ZnO exhibited a broad peak for the hydroxyl bands at 3444cm^{-1}(Fig. 2). The absorption bands at nearly 1629 cm^{-1} are due to the O-H bending of water. The Zn-O stretching vibrations revealed at ٤٨٩ cm^{-1} that is represented in the Fig. 2.

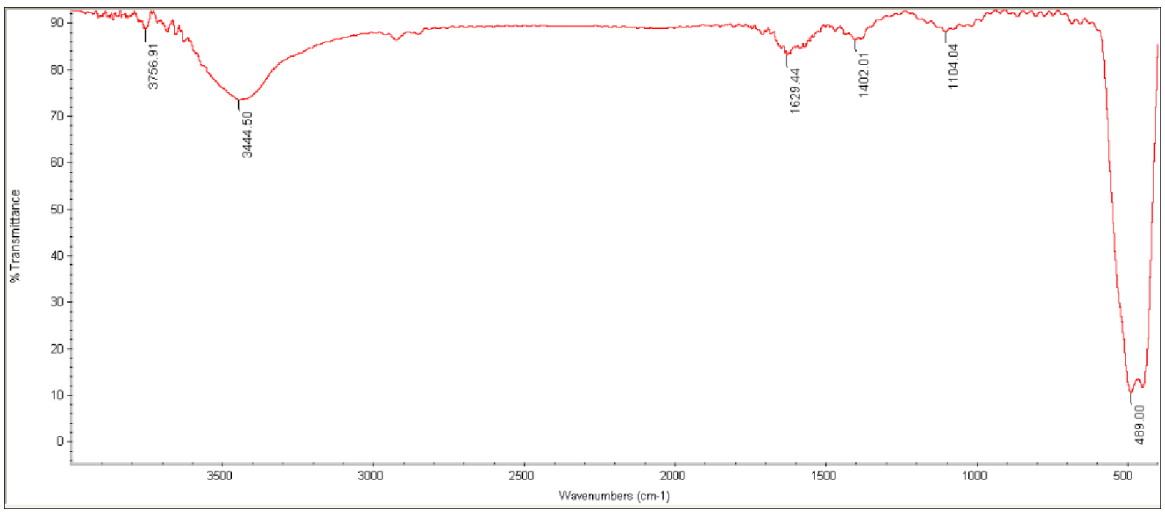


Figure 2. FT-IR spectrum of nano-ZnO catalyst.

Thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed to assess the thermal stability of ZnO (Figure 3). There was a 0.4% weight loss at 100 °C for samples assigned to desorption of H_2O molecules from the surface of ZnO. The further weight loss of ZnO (within 1%) at 150-200 ˚C is due to the renewed dehydration. Based on nano-ZnO TGA-DSC diagram, the substance is stable up to 200 °C hence the catalyst can be used at temperatures below 200 °C for promotion of organic synthesis.

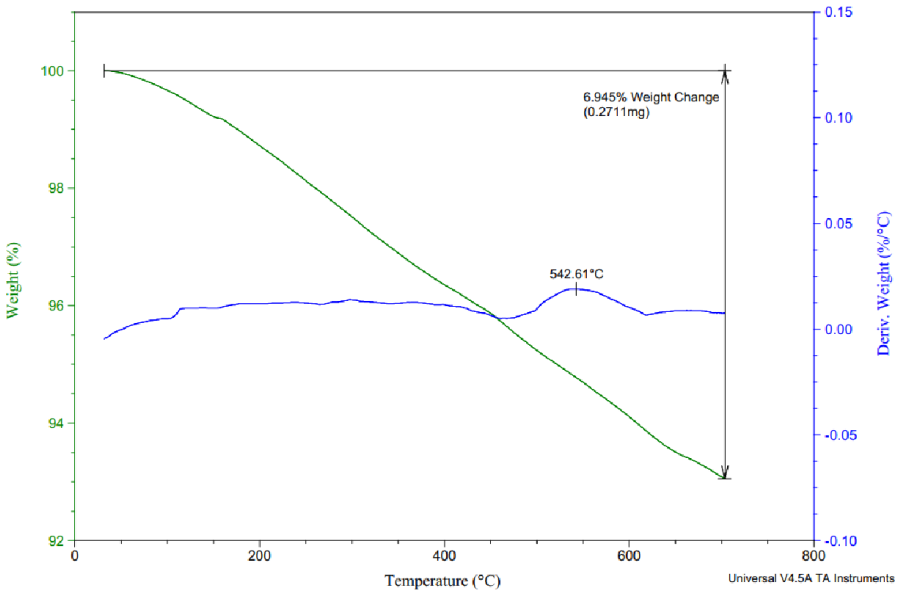
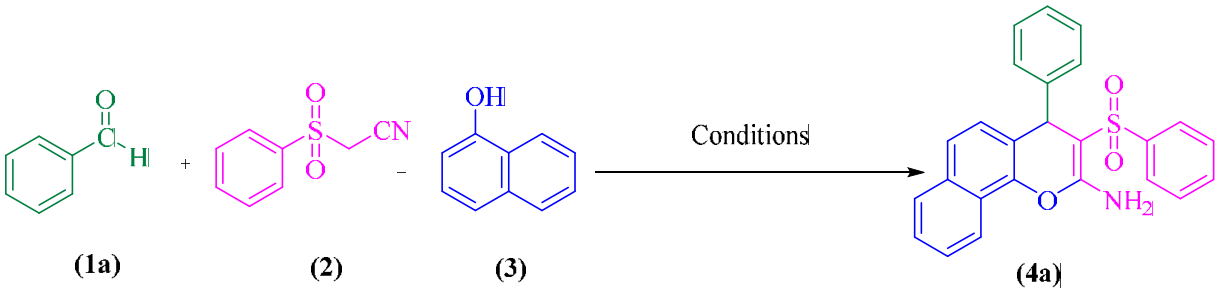


Figure 3. The Thermo-gravimetric analysis (TGA), and differential scanning calorimetry (DSC) curves of nano-ZnO catalyst.

After synthesis and characterization of the nano-ZnO, we investigated the performance of nano-ZnO in synthesis of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*]chromens. The reaction proceeded by 1.0 mmol benzaldehyde, 1.0 mmol (phenylsulfonyl) acetonitrile, and 1.0 mmol *α*-naphthol in the presence of various amounts of nano-ZnO and different solvents. The results of these experiments were listed in Table 2. Accordingly, we figured out that there is no desired product in absence of nano-ZnO (Table 3, entry 1). Furthermore, we examined the effect of various temperatures (such as 25, 40, 60 and 80°C) on reactions (Table 2, entries 2, 9-11). The optimized results were obtained with 5.0 mg nano-ZnO at 80°C under solvent-free condition (Table 2, entry 2).

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

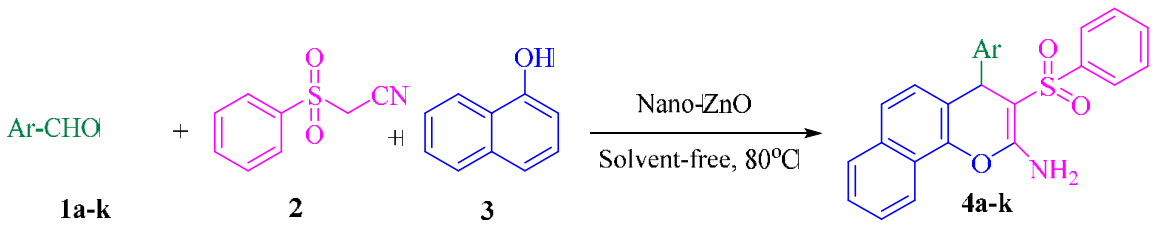


(1a) **(2)** **(3)** **(4a)**

Entry	Catalyst (mg)	Solvent/ Temperature (ºC)	Time (min)	Yield[b] (%)
1	nano-ZnO(0.0)	-/ 80	60	0
2	nano-ZnO(5.0)	-/ 80	10	93
3	nano-ZnO (5.0)	*n*-Hexane/ 80	10	Trace
4	nano-ZnO (5.0)	EtOH/ 80	10	57
5	nano-ZnO (5.0)	CH_3CN/ 80	10	34
6	nano-ZnO (3.0)	-/ 80	10	73
7	nano-ZnO (4.0)	-/ 80	10	81
8	nano-ZnO (6.0)	-/ 80	10	94
9	nano-ZnO(5.0)	-/ 25	10	Trace
10	nano-ZnO(5.0)	-/ 40	10	36
11	nano-ZnO(5.0)	-/ 60	10	48

[a]Reaction condition: benzaldehyde (1.0 mmol),(Phenylsulfonyl)acetonitrile (1.0 mmol) and *α*-naphthol(1.0 mmol) under different temperatures and solvents orsolvent-freecondition.
[b]Isolated yields.

To study the scope of the reaction, a series of substituted aldehydes, (phenylsulfonyl)acetonitrile and *α*-naphthol were mixed using nano-ZnO as catalyst for synthesis of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*]chromen derivatives (Scheme **1**). In all cases, aromatic aldehydes with either electron-donating or electron-withdrawing groups could react with (phenylsulfonyl) acetonitrile and *α*-naphthol smoothly and formed products with good to excellent yields (Table 3,**4a-k**).



1a-k **2** **3** **4a-k**

Scheme 1. Synthesis of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*] chromen derivatives in the presence of nano-ZnO catalyst.

Table 3. Synthesis of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*] chromen derivatives [a].

Entry	Ar	Product	Time (min)	Yield[b]	M.P. (ºC) [Ref.]
1	C_6H_5	**4a**	10	93	219-221 [24]
2	4-Cl-C_6H_4	**4b**	10	94	205-206 [24]
3	3-Cl-C_6H_4	**4c**	10	91	248-250 [24]
4	2-Cl-C_6H_4	**4d**	10	93	206-207 [24]
5	4-CN-C_6H_4	**4e**	8	95	258-259 [24]
6	3-NO_2-C_6H_4	**4f**	8	95	274-275 [24]
7	4-NO_2-C_6H_4	**4g**	8	96	219-220 [24]
8	4-Br-C_6H_4	**4h**	12	92	199-200 [24]
9	4-Me-C_6H_4	**4i**	15	89	226-227 [24]
10	4-F-C_6H_4	**4j**	12	93	247-248 [25]
11	5-Br-2-OH-C_6H_3	**4k**	12	92	168-170

[a]Reaction condition: aldehyde (1.0 mmol), (Phenylsulfonyl)acetonitrile (1.0 mmol), α-naphthol (1.0 mmol) and nano-ZnO (5.0 mg),solvent-free condition.
[b]Isolated yields.

To show the merit of the present study relative to the reported results in the literature, we compared the results of nano-ZnO as catalyst with $SbCl_4O$-coc[24], Potassium phthalimide [25], Fe_3O_4@AP[26], Diethylamine [27] and Nano-Piperidine [28] in the synthesis of 2-Amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*] chromens. As shown in Table 4, entry 6, synthesis of 2-Amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*] chromens catalyzed by nano-ZnO offers production of the corresponding products in shorter time, higher yields and milder condition is done, while other methods require more amounts of catalyst and longer reaction time for synthesis of 2-Amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*] chromens.

Table 4. Comparison of the catalytic performance of nano-ZnO with other catalysts in production of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*] chromen derivatives.

Entry	Catalyst (amount)	Temp. (ºC)/Solvent	Time (min)	Yield (%)	Ref.
1	$SbCl_4O$-coc (15 mg)	70/EtOH	52-60	88-91	[24]
2	Potassium phthalimide (18 mg)	100/-	80-95	85-95	[25]
3	Fe_3O_4@AP (20 mg)	60/Ethanol	10-15	86-93	[26]
4	Diethylamine (30 mol%)	RT/Ethanol	110-300	85-93	[27]
5	Piperidine (0.05 equiv)	80/Ethanol	5	82.1-90.1	[28]
6	nano-ZnO (5.0 mg)	80/-	8-15	89-96	This work

Recycling of the Catalyst

After completion of the reaction, the final mixture was dissolved in heated ethanol. The catalyst was then removed by centrifugation and was washed well with diethyl ether and dried at room temperature for 6 h. The reusability of nano-ZnO was tested by repeating the model study in the presence of nano-ZnO under optimized conditions. The results of these experiments showed that nano-ZnO could be regenerated at the end of the reaction and can be used 4 times without losing too much activity (Table 5).

Table 5. Recoverability of nano-ZnO.

Yield (%)			
First	Second	Third	Fourth
93	92	90	88

Conclusions

We have designed new method for biologically significant 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*] chromens using green chemistry protocols. The solvents and temperature condition were investigated through a novel, stable and eco-friendly nano-solid catalyst *via* one-pot three-component reaction. Short reaction time, inexpensive solid acid catalyst and excellent yield of products under solvent-free condition were among the merits in this study. To sum up, we have developed green method of 2-amino-3-phenylsulfonyl-4-aryl-4*H*-benzo[*h*] chromens without utilizing of toxic solvent.

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