

Figure 1 FT-IR spectra of (a) as-synthesized zinc acetate film, and (b) ZnO NPs thin-film annealed at 400 °C.

from the bridging type metal-acetate bonding (M–OCO–M), those at 1415 cm^{-1} are the C–O stretching frequencies and 1340 cm^{-1} is a weakly C–O mode from an acetic acid molecule ($\text{CH}_3\text{-COOH}$). Figure 1b shows the FT-IR spectrum of ZnO NPs thin-film annealed at 400 °C which shows the absence of absorption bands corresponding to organics and hydroxyl groups, indicating complete removal of organics.

The XRD patterns of annealed thin-films ZnO NPs are crystalline with hexagonal wurtzite structure, and their XRD peaks at 2θ angle 31.9 , 34.6 and 36.2° are corresponding to diffraction from planes (002), (101) and (110), respectively (JCPDS:36-1451) (Fig. 2).

The optical absorption spectra of the thin-film in the UV-visible wavelength range are presented in Fig. 3. It can be seen that the film has high transparency in the visible range. The absorption at higher wavelengths in the visible region is low at wavelength

around 484 nm. Further, a sharp increase of absorption occurs at around 361 nm, indicating the ZnO absorption.

Figure 4 shows the surface morphology of ZnO NPs within the thin-film. In general, the film is homogeneous and continuous. Separate coating layers are not visible for the sintered film. The random distribution of grains suggests a random nucleation mechanism. Film thickness from the SEM image was found to be 366 nm.

For optimization of the reaction conditions, ZnO NPs thin-film was investigated as a catalyst in the model reaction of 3-chlorobenzaldehyde, malononitrile and β -naphthol in various solvents which were chosen for comparison. The best result was obtained in aqueous media (Table 1, entries 2 and 3–5). It is noticeable that in aqueous media and in the absence of catalyst the reaction was very slow and obtained in lower yields (Table 1, entry 1).

An increase of the temperature from 50 °C to 90 °C, showed that further increase of the temperature above 60 °C shortened the reaction time while having no measurable effects on the yield (Table 1, entries 2 and 6–9).

The scalability of the reaction protocol is presented in Table 2. The results showed that the present method is effective for large-scale synthesis (Table 2, entries 2 and 3) as well as routine scale (Table 2, entry 1). It is interesting that the higher yields of products were obtained for large-scale synthesis. All data of Table 2 are provided for optimized conditions.

To expand the efficiency and applicability of our protocol, we used various aromatic aldehydes to produce the corresponding products in high to excellent yields. The results are summarized in Table 3. The structures of products (4a–h) were confirmed by IR, ^1H - and ^{13}C -NMR spectral data and elemental analysis.

A comparison of the efficiency of presented new protocol with several previous methods in the reaction of aromatic aldehydes, malononitrile and β -naphthol for the synthesis of corresponding products is given in Table 4. The results show that this method has some merits in comparison with the known methods on terms of yields, thermal conditions, and reaction times.

A plausible mechanism for the formation of the product is suggested in Scheme 2: the ZnO facilitate Knoevenagel condensation of aromatic aldehyde 1 and malononitrile 2 for the formation of alkene 6, through Lewis acid sites (Zn^{2+}) which are coordinated to the oxygen of the aldehyde and active it for nucleophilic attack of malononitrile. ZnO can also activate methylene group of β -naphthol 3 so that deprotonation occurs in the presence of Lewis basic sites (O^{2-}) to generate intermediate 7 which then ads

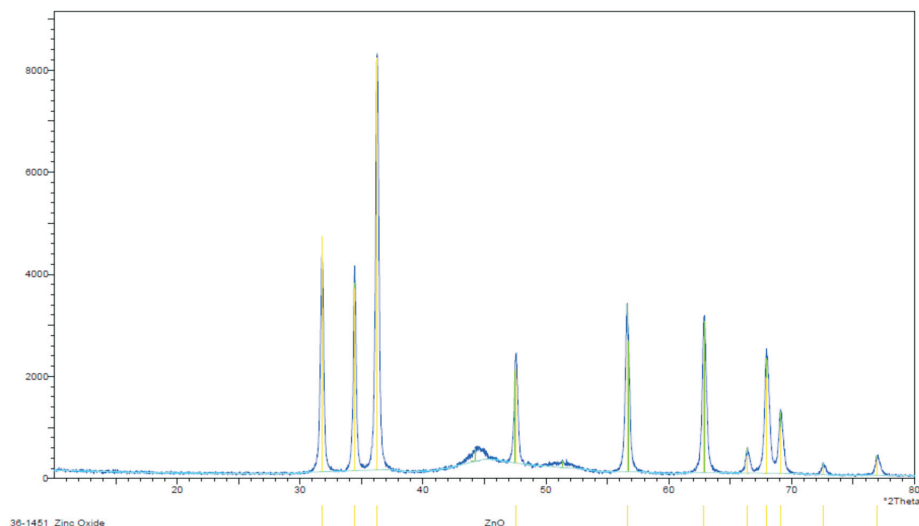


Figure 2 X-ray diffraction analyses of ZnO NPs thin-film annealed at 400 °C.

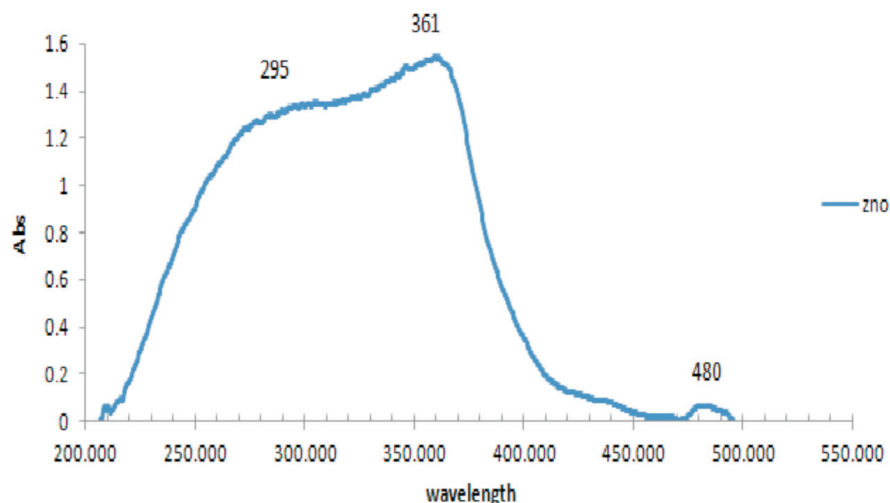


Figure 3 Optical absorption spectra of ZnO NPs thin-film.

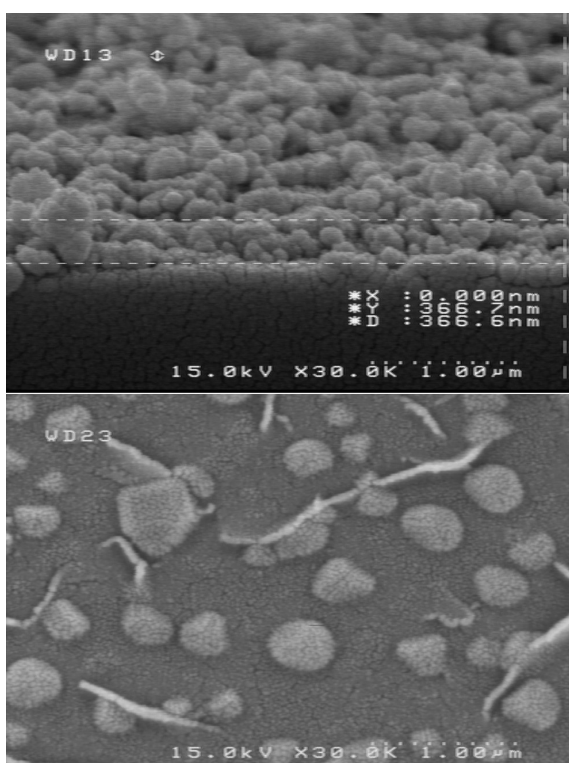


Figure 4 SEM image of ZnO NPs thin-film.

to alkene **6** by Michael type addition to produce the Michael adduct **8**. Intramolecular cyclization of intermediate **9**, which is obtained from the enolization of **8**, gives product **4** after tautomerization.

The recyclability of the catalyst is an important factor from economical and environmental points of view. For this reason, the reusability of the ZnO nanoparticle thin-film was examined in model reaction under the optimized reaction conditions by separating film from the reaction mixture washing with ethanol, and drying *in vacuo*. It was found that the ZnO film could be recycled for at least 15 cycles without significant change in activity.

3. Experimental

3.1. Materials and Methods

All chemicals used in this work purchased from Merck and Fluka in high purity. Melting points were determined with

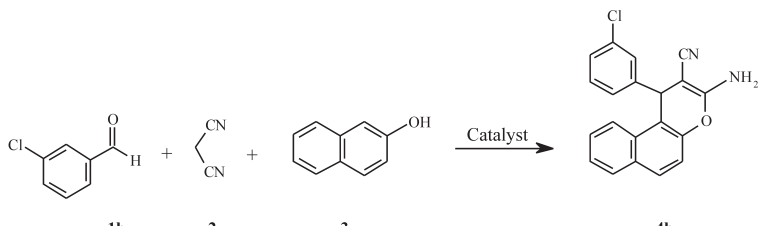
Electrothermal 9100 melting point apparatus and were uncorrected. FT-IR spectra were obtained using a Bruker, Equinox 55, Golden Gate Micro-ATR spectrometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were run on a Bruker DRX-500 AVANCE at 300 and 75 MHz, respectively using TMS as internal standard and, Acetone- d_6 as solvent. Elemental analyses were carried out using a Foss Heraeus CHN-O-Rapid elemental analyser (Foss Heraeus, GmbH, Hanau, Germany). Microscopic morphology of catalyst was visualized by scanning electron microscopy SEM: Philips XL30. Powder X-ray diffraction (XRD) patterns were collected from a diffractometer with X'PertPro monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) operated on 35 mA and 40 kV current, in the range $2\theta = 580^\circ$, from Philips Company. The optical transmittance and reflectance of the films were recorded on an AvaSpec-2048 UV-VIS-NIR spectrometer with drift accessory in the wavelength range from 200 to 500 nm. The TLC plates (silica gel 60 F-254) used in this work were purchased from Merck Inc.

3.2. General Procedure

3.2.1. Preparation of ZnO NPs Thin-film Catalyst

Corresponding preparation of the ZnO film according to conditions of entry 1 in Tables 2 and 3: 1.6 g of zinc acetate dihydrate (99.98 %) was dissolved into 50 mL of methanol, (>99.9 %) and stirred on a magnetic stirrer for 10 min. Then a small amount (0.2 mL) of glacial acetic acid (>99.9 %) was added to the mixture and stirred at 40°C for 10 min, the obtained transparent solution was transferred to an autoclave. The glass substrate ($15 \times 5 \text{ mm}$) was pre-cleaned with water and detergent, and then cleaned in methanol and acetone for 10 min each by using an ultrasonic cleaner and then cleaned with deionized water and dried. The hydrothermal technique⁵¹ was used for the deposition of the sample on the surface of glass substrate. The cleaned glass substrate was transferred to autoclave and aged at 60°C for 48 h, and then the coated film was dried at 100°C in air for 30 min. The process was repeated for a second time to prepare film with desired thickness. Finally, the ZnO NPs thin-film was heat-treated at 400°C in a furnace. The film thickness was found to be 366 nm from the SEM image of ZnO NPs thin-film.

Corresponding preparation of the ZnO film according to conditions of entry 2 in Table 2: 3.2 g of zinc acetate dihydrate (99.98 %) was dissolved into 75 mL of methanol, (>99.9 %) and stirred on a magnetic stirrer for 15 min. Then, a small amount (0.3 mL) of glacial

Table 1 Synthesis of 3-amino-1-(3-chlorophenyl)-1H-benzo[f]chromene-2-carbonitrile (**4b**) under different conditions.


Entry ^a	Catalyst	Solvent	Temp/°C	Time/h ^c	Yield/% ^d
1	No catalyst ^b	H ₂ O	90	6	52
2	ZnO NPs thin-film	H ₂ O	60	2	95
3	ZnO NPs thin-film	EtOH	70	2	70
4	ZnO NPs thin-film	CH ₂ Cl ₂	80	2	68
5	ZnO NPs thin-film	DMF	100	2	65
6	ZnO NPs thin-film	H ₂ O	50	2	75
7	ZnO NPs thin-film	H ₂ O	70	2	95
8	ZnO NPs thin-film	H ₂ O	80	1	96
9	ZnO NPs thin-film	H ₂ O	90	1	96

^a The experiments were treated by mixing 3-chlorobenzaldehyde (2 mmol), malononitrile (2.4 mmol) and β -naphthol (2 mmol) in 20 mL of solvent in the presence of prepared ZnO NPs thin-film according mentioned in general procedure for entry 1 in Tables 2 and 3 (the thickness of ZnO film was 366 nm on both sides of the glass with surface of 0.75 cm²).

^b Experiment conducted without the presence of ZnO NPs thin-film. ^c Reaction times for which maximum yields were achieved. ^d Isolated yield.

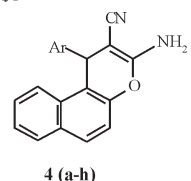
Table 2 Applicability of presented procedure for the synthesis of **4b** with variant amounts of reactants.

Entry	Ratio of the reagents (3-chlorobenzaldehyde:malononitrile: β -naphthol) and conditions for the synthesis of 4b	Conditions for the preparation of ZnO NPs thin-film (time and temperature as given in general procedure)	Film thickness on both sides/nm	Glass surface area/cm ²	Yield/% ^a
1	2:2.4:2 (mmol) in water (20 mL), at 60 °C, 2 h, in 50 mL round-bottom flask	1.6 g of ZnOAc, methanol (50 mL), glass substrate (15 × 5 mm)	366	0.75	95
2	5:6:5 (mmol) in water (30 mL), at 60 °C, 2 h, in 100 mL round-bottom flask	3.2 g of ZnOAc, methanol (75 mL), glass substrate (15 × 7 mm)	366	1.05	97
3	10:12:10 (mmol) in water (60 mL), at 60 °C, 2 h, in 150 mL round-bottom flask	6.4 g of ZnOAc, methanol (100 mL), glass substrate (15 × 15 mm)	366	2.25	98

^a Isolated yield.

acetic acid (>99.9 %) was added to the mixture and stirred at 40 °C for 15 min, the obtained transparent solution was transferred to an autoclave. The glass substrate (15 × 7 mm) was pre-cleaned with water and detergent, and then cleaned in methanol and acetone for 15 min each by using an ultrasonic cleaner and then cleaned with deionized water and dried. The hydrothermal technique⁵¹ was used for the deposition of the sample on the surface of glass substrate. The cleaned glass substrate was transferred to autoclave and aged at 60 °C for 48 h, and then the coated film was dried at 100 °C in air for 30 min. The process was repeated for a second time to prepare film with desired thickness. Finally, the ZnO NPs thin-film was heat treated at 400 °C in a furnace. The film thickness was found to be 366 nm from the SEM image of ZnO NPs thin-film.

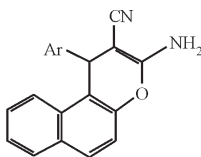
Corresponding preparation of the ZnO film according to conditions of entry 3 in Table 2: 6.4 g of zinc acetate dihydrate (99.98 %) was dissolved into 100 mL of methanol, (>99.9 %) and stirred on a magnetic stirrer for 20 min. Then, a small amount (0.6 mL) of glacial acetic acid (>99.9 %) was added to the mixture and stirred at 40 °C for 20 min, the obtained transparent solution was transferred to an autoclave. The glass substrate (15 × 15 mm) was pre-cleaned with water and detergent, and then cleaned in methanol and acetone for 15 min each by using an ultrasonic cleaner and then cleaned with deionized water and dried. The

Table 3 ZnO NPs thin-film catalyzed three-component synthesis of 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitriles (**4a–h**).


Product	Ar	Yield/% ^{a,b}	M.p/°C	
			Obsd.	Lit.
4a	C ₆ H ₅	97	284–285	286–288 ²²
4b	3-Cl-C ₆ H ₄	95	239–240	236–238 ²²
4c	4-Cl-C ₆ H ₄	98	212–214	210–212 ²²
4d	3-CH ₃ O-C ₆ H ₄	95	255–257	256–258 ²²
4e	4-CH ₃ O-C ₆ H ₄	96	202–204	199–201 ²²
4f	4-CH ₃ -C ₆ H ₄	93	265–267	268–270 ²²
4g	3-NO ₂ -C ₆ H ₄	96	232–234	233–235 ²²
4h	4-NO ₂ -C ₆ H ₄	89	166–168	168–170 ²²

^a Yields refer to those of pure isolated products characterized by IR, ¹H- and ¹³C-NMR spectral data and by elemental analyses.

^b In all cases, the experiments were carried out by mixing aromatic aldehyde (2 mmol), malononitrile (2.4 mmol) and β -naphthol (2 mmol) in 20 mL of water in the presence of prepared ZnO NPs thin-film (the thickness of ZnO film was 366 nm on both sides of the glass with surface of 0.75 cm²) at about 2 h stirring at 60 °C.

Table 4 Comparison of the catalytic efficiency of ZnO NPs thin-film with various known catalysts in the reaction of aromatic aldehydes, malononitrile and β -naphthol.

Conditions	Ar	Yield/% ^a	Ref.
Benzaldehyde (1 mmol), malononitrile (1 mmol) and β -naphthol (1 mmol), in saturated solution of K_2CO_3 (10 mL), under MWI, 2.5 min	C_6H_5	91	19
Aromatic aldehyde (1 mmol), malononitrile (1.1 mmol) and β -naphthol (1.2 mmol), in ethanol (5 mL), in the presence of DABCO (30 mol%), at r.t., 2–4 h	3-Cl- C_6H_4 , 4-Cl- C_6H_4 , 3- NO_2 - C_6H_4	72–80	20
Aromatic aldehyde (5 mmol), malononitrile (5 mmol), β -naphthol (5 mmol) and [bmim]OH (0.5 mmol), in water (2 mL), at reflux, 4–100 min	C_6H_5 , 4-Cl- C_6H_4 , 4- CH_3O - C_6H_4 , 4- CH_3 - C_6H_4 , 4- NO_2 - C_6H_4	80–97	21
Aromatic aldehyde (1 mmol), malononitrile (1 mmol), β -naphthol (1 mmol) and [bmim][PF ₆] (1.5 mL), in water (2 mL), at 80 °C, 2 h	C_6H_5 , 3-Cl- C_6H_4 , 4-Cl- C_6H_4 , 3- CH_3O - C_6H_4 , 4- CH_3O - C_6H_4 , 4- CH_3 - C_6H_4 , 3- NO_2 - C_6H_4 , 4- NO_2 - C_6H_4	70–86	22
Aromatic aldehyde (1 mmol), malononitrile (1 mmol) and β -naphthol (1 mmol), in the presence of CuO-CeO ₂ nanocomposite (0.05 mg), under solvent-free conditions, at 80 °C, 8–25 min	C_6H_5 , 4-Cl- C_6H_4 , 4- CH_3O - C_6H_4 , 4- CH_3 - C_6H_4 , 3- NO_2 - C_6H_4 , 4- NO_2 - C_6H_4	90–94	23
Aromatic aldehyde (5 mmol), malononitrile (5 mmol) and β -naphthol (5 mmol), in ethanol or ethanol/water (1:1) (10 mL), in the presence of Rochelle salt (0.3 g), at reflux, 4–8 h	C_6H_5 , 4-Cl- C_6H_4 , 4- CH_3O - C_6H_4 , 3- NO_2 - C_6H_4 , 3- NO_2 - C_6H_4	81–92	24
Aromatic aldehyde (2 mmol), malononitrile (2.4 mmol) and β -naphthol (2 mmol), in water (20 mL), in the presence of prepared ZnO NPs thin-film (the thickness of ZnO film was 366 nm on both sides of the glass with surface of 0.75 cm ²), at 60 °C, 2 h	C_6H_5 , 3-Cl- C_6H_4 , 4-Cl- C_6H_4 , 3- CH_3O - C_6H_4 , 4- CH_3O - C_6H_4 , 4- CH_3 - C_6H_4 , 3- NO_2 - C_6H_4 , 4- NO_2 - C_6H_4	89–98	This work

^a Isolated yields.

hydrothermal technique⁵¹ was used for the deposition of the sample on the surface of glass substrate. The cleaned glass substrate was transferred to autoclave and aged at 60 °C for 48 h, and then the coated film was dried at 100 °C in air for 30 min. The process was repeated for a second time to prepare film with desired thickness. Finally, the ZnO NPs thin-film was heat-treated at 400 °C in a furnace. The film thickness was found to be 366 nm from the SEM image of ZnO NPs thin-film.

3.2.2. Synthesis of 3-Amino-1-aryl-1H-benzof[chromene]-2-carbonitriles

Corresponding synthesis of compounds (4a–h) according to conditions of entry 1 in Tables 2 and 3: A mixture of aromatic aldehyde (2 mmol), malononitrile (2.4 mmol), β -naphthol (2 mmol) and water (20 mL) were taken in 50 mL round-bottom flask. The ZnO NPs thin-film (15 × 5 mm) was then dipped into the sample and the mixture was stirred at 60 °C for 2 h. The progress of the reaction was monitored with TLC (*n*-hexane: ethyl acetate, 5: 2). Upon completion of the reaction, the ZnO NPs thin-film was removed from the reaction mixture, for reuse by washing with EtOH, and drying *in vacuo* at 80 °C for several hours. The reaction mixture was then filtered. The residue was recrystallized from EtOH 95 % to give the pure product.

Corresponding synthesis of compound (4b) according to conditions of entry 2 in Table 2: A mixture of 3-chlorobenzaldehyde (5 mmol), malononitrile (6 mmol), β -naphthol (5 mmol) and water (30 mL) were taken in 100 mL round-bottom flask. The ZnO NPs thin-film (15 × 7 mm) was then dipped into the sample and the mixture was stirred at 60 °C for 2 h. The progress of the reaction was monitored with TLC (*n*-hexane: ethyl acetate, 5: 2, R_f = 0.48). Upon completion of the reaction, the ZnO NPs thin-film

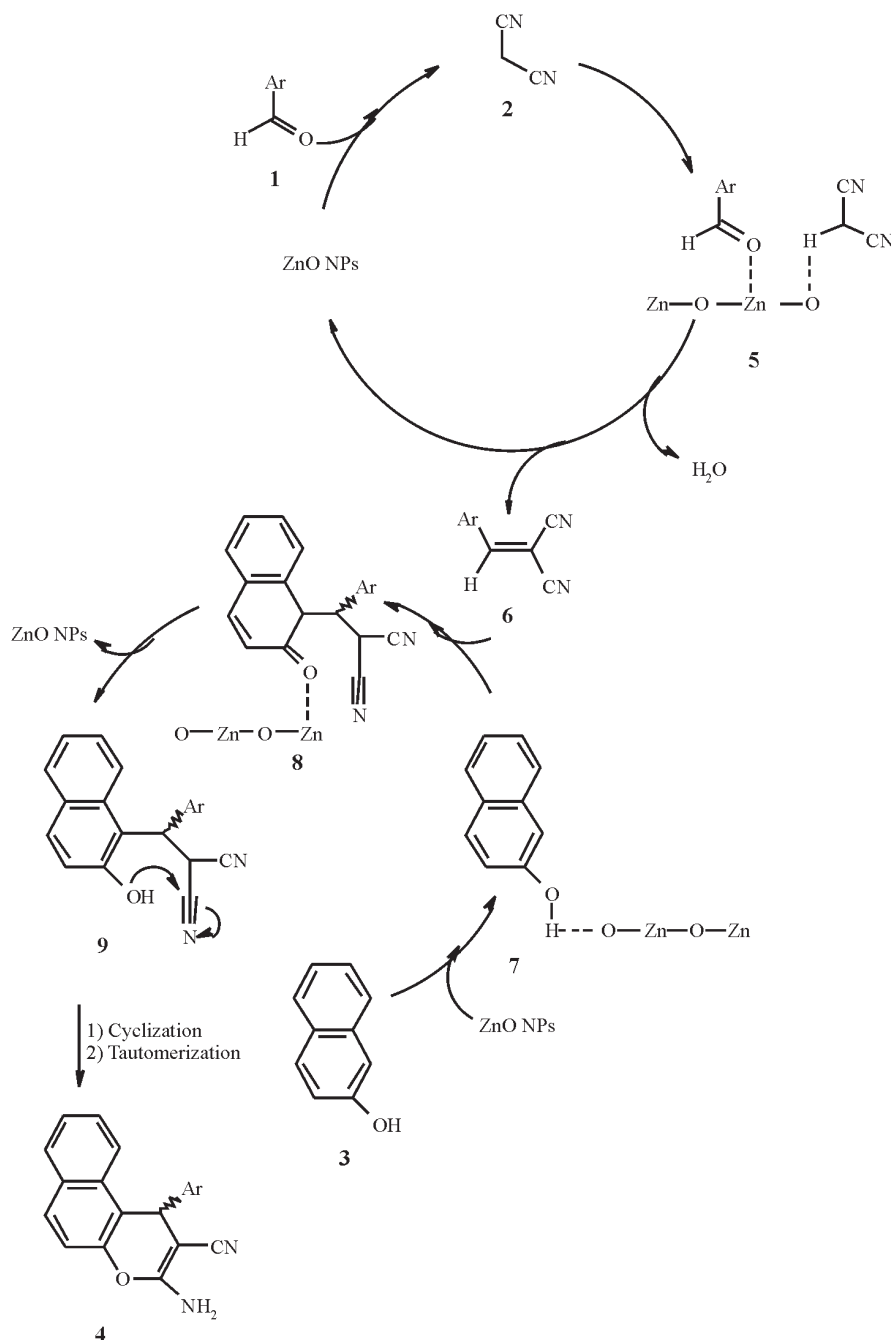
was removed from the reaction mixture, for reuse by washing with EtOH, and drying *in vacuo* at 80 °C for several hours. The reaction mixture was then filtered. The residue was recrystallized from EtOH 95 % to give the pure product.

Corresponding synthesis of compound (4b) according to conditions of entry 3 in Table 2: A mixture of 3-chlorobenzaldehyde (10 mmol), malononitrile (12 mmol), β -naphthol (10 mmol) and water (60 mL) were taken in 150 mL round-bottom flask. The ZnO NPs thin-film (15 × 15 mm) was then dipped into the sample and the mixture was stirred at 60 °C for 2 h. The progress of the reaction was monitored with TLC (*n*-hexane: ethyl acetate, 5: 2, R_f = 0.48). Upon completion of the reaction, the ZnO NPs thin-film was removed from the reaction mixture, for reuse by washing with EtOH, and drying *in vacuo* at 80 °C for several hours. The reaction mixture was then filtered. The residue was recrystallized from EtOH 95 % to give the pure product.

3.2.3. Spectroscopic Data of the Products

3-Amino-1-phenyl-1H-benzof[chromene]-2-carbonitrile (4a) White solid, yield: 0.289 g (97 %), m.p. 284–285 °C (lit: 286–288 °C²²) (*n*-hexane: ethyl acetate, 5: 2, R_f = 0.43). IR (KBr) (ν_{max}/cm^{-1}): 3465, 3346, 2181, 1665, 1600, 1500, 1210, 1076. ¹H-NMR: δ = 5.20 (s, 1 H, H-1), 6.60 (bs, 2 H, NH₂), 7.20 (m, 3 H, H-Ar), 7.38 (m, 2 H, H-Ar), 7.75 (d, *J* = 7.8 Hz, 2 H, H-Ar), 7.82 (d, *J* = 8.1 Hz, 3 H, H-Ar) ppm. ¹³C-NMR: δ = 39.53, 58.37, 116.12, 117.21, 120.95, 124.06, 125.34, 127.03, 127.46, 128.90, 129.12, 129.93, 131.26, 146.15, 147.27, 130.62, 160.14 ppm. Anal. calcd. for C₂₀H₁₄N₂O (298.34): C 80.51, H 4.73, N 9.39; found: C 80.43, H 4.61, N 9.52.

3-Amino-1-(3-chlorophenyl)-1H-benzof[chromene]-2-carbonitrile (4b): White solid, yield: 0.316 g (95 %), m.p. 239–240 °C (lit:



Scheme 2
Proposed reaction mechanism.

236–238 °C²²) (*n*-hexane: ethyl acetate, 5: 2, R_f = 0.48). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3431, 3328, 2181, 1646, 1588, 1515, 1220, 1080. ¹H-NMR: δ = 5.39 (s, 1 H, H-1), 6.34 (bs, 2 H, NH₂), 7.29 (m, 5 H, H-Ar), 7.46 (m, 3 H, H-Ar), 7.92 (m, 2 H, H-Ar), ppm. ¹³C-NMR: δ = 41.27, 55.40, 59.10, 115.08, 118.33, 119.49, 120.66, 120.86, 123.38, 123.93, 126.47, 126.59, 127.67, 133.27, 137.20, 143.06, 145.77, 147.60, 159.89 ppm. Anal. calcd. for C₂₀H₁₃CIN₂O (332.79): C 72.18, H 3.94, N 8.42; found: C 72.13, H 4.15, N 8.52.

3-Amino-1-(4-chlorophenyl)-1H-benzo[f]chromene-2-carbonitrile (4c): White solid, yield: 0.326 g (98 %), m.p. 212–214 °C (lit: 210–212 °C²²) (*n*-hexane: ethyl acetate, 5: 2, R_f = 0.50). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3420, 3330, 2191, 1643, 1591, 1460, 1259, 1112. ¹H-NMR: δ = 4.94 (s, 1 H, H-1), 7.10 (bs, 2 H, NH₂), 7.19 (s, 2 H, H-Ar), 7.28 (d, *J* = 8.5 Hz, 2 H, H-Ar), 7.39 (d, *J* = 8.5 Hz, 2 H, H-Ar), 7.59 (m, 2 H, H-Ar), 7.85 (d, *J* = 8.5 Hz, 1 H, H-Ar), 8.25 (d,

J = 8.5 Hz, 1 H, H-Ar) ppm. ¹³C-NMR: δ = 40.73, 57.88, 115.60, 117.24, 120.78, 122.98, 125.44, 127.61, 128.95, 129.21, 130.14, 130.49, 131.26, 131.62, 145.11, 147.25, 160.16. Anal. calcd. for C₂₀H₁₃CIN₂O (332.79): C 72.18, H 3.94, N 8.42; found: C 72.03, H 3.75, N 8.33.

3-Amino-1-(3-methoxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (4d): White solid, yield: 0.312 g (95 %), m.p. 255–257 °C (lit: 256–258 °C²²) (*n*-hexane: ethyl acetate, 5: 2, R_f = 0.41). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3460, 3350, 2983, 2180, 1665, 1607, 1500, 1234, 1103, 1080. ¹H-NMR: δ = 3.73 (s, 3 H, OCH₃), 5.16 (s, 1 H, H-1), 6.05 (m, 2 H, H-Ar), 6.69 (bs, 2 H, NH₂), 6.74 (d, *J* = 7.7 Hz, 1 H, H-Ar), 7.16 (m, 1 H, H-Ar), 7.27 (d, *J* = 8.8 Hz, 1 H, H-Ar), 7.40 (m, 1 H, H-Ar), 7.72 (m, 2 H, H-Ar), 7.81 (d, *J* = 8.8 Hz, 2 H, H-Ar) ppm. ¹³C-NMR: δ = 41.05, 54.96, 58.23, 111.62, 114.87, 116.03, 117.18, 119.61, 121.92, 124.08, 125.38, 127.53, 128.88, 129.93, 131.29, 131.66,

132.23, 147.16, 147.68, 159.78, 160.18. Anal. calcd. for $C_{21}H_{16}N_2O_2$ (328.37): C 76.81, H 4.91, N 8.53; found: C 76.93, H 4.76, N 8.59.

3-Amino-1-(4-methoxyphenyl)-1H-benzof[chromene-2-carbonitrile (4e): White solid, yield: 0.315 g (96 %), m.p. 202–204 °C (lit: 199–201 °C²²) (*n*-hexane: ethyl acetate, 5: 2, Rf = 0.42). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3450, 3337, 2980, 2180, 1665, 1600, 1500, 1247, 1190, 1075. ¹H-NMR: δ = 3.70 (s, 3 H, OCH₃), 5.16 (s, 1 H, H-1), 5.63 (m, 2 H, H-Ar), 6.76 (bs, 2 H, NH₂), 7.09 (d, *J* = 8.5 Hz, 2 H, H-Ar), 7.25 (d, *J* = 8.5 Hz, 2 H, H-Ar), 7.38 (m, 2 H, H-Ar), 7.70 (t, *J* = 7.3 Hz, 1 H, H-Ar), 7.78 (d, *J* = 8.7 Hz, 1 H, H-Ar) ppm. ¹³C-NMR: δ = 42.49, 60.16, 63.41, 119.23, 121.15, 121.97, 125.76, 128.88, 130.05, 132.19, 133.23, 133.62, 134.54, 135.37, 136.01, 143.10, 151.88, 163.02, 164.74. Anal. calcd. for $C_{21}H_{16}N_2O_2$ (328.37): C 76.81, H 4.91, N 8.53; found: C 76.99, H 5.04, N 8.65.

3-Amino-1-(4-methylphenyl)-1H-benzof[chromene-2-carbonitrile (4f): White solid, yield: 0.291 g (93 %), m.p. 265–267 °C (lit: 268–270 °C²²) (*n*-hexane: ethyl acetate, 5: 2, Rf = 0.47). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3463, 3355, 2960, 2170, 1665, 1605, 1500, 1270, 1190, 1080. ¹H-NMR: δ = 2.20 (s, 3 H, CH₃), 5.16 (s, 1H, H-1), 6.32 (bs, 2 H, NH₂), 7.05 (m, 4 H, H-Ar), 7.26 (d, *J* = 8.7 Hz, 1 H, H-Ar), 7.34 (d, *J* = 5.2 Hz, 2 H, H-Ar), 7.70 (t, *J* = 5.7 Hz, 1 H, H-Ar), 7.82 (d, *J* = 8.7 Hz, 2 H, H-Ar) ppm. ¹³C-NMR: δ = 20.99, 39.20, 58.51, 116.23, 117.21, 120.98, 124.09, 125.31, 127.39, 128.87, 129.67, 129.83, 130.63, 131.25, 136.11, 143.25, 147.20, 160.03. Anal. calcd. for $C_{21}H_{16}N_2O$ (312.37): C 80.75, H 5.16, N 8.97; found: C 80.63, H 5.05, N 9.12.

3-Amino-1-(3-nitrophenyl)-1H-benzof[chromene-2-carbonitrile (4g): White solid, yield: 0.330 g (96 %), m.p. 232–234 °C (lit: 233–235 °C²²) (*n*-hexane: ethyl acetate, 5: 2, Rf = 0.41). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3466, 3340, 2185, 1660, 1610, 1580, 1500, 1334, 1270, 1080, 760. ¹H-NMR: δ = 5.36 (s, 1H, H-1), 6.00 (bs, 2H, NH₂), 7.31 (d, *J* = 9.0 Hz, 1H, ArH), 7.39–7.51 (m, 3H, ArH), 7.61 (d, *J* = 8.28 Hz, 2H, ArH), 7.82–7.87 (m, 2H, ArH), 7.97 (s, 1H, ArH), 8.02 (d, *J* = 8.16 Hz, 1H, ArH) ppm. ¹³C-NMR: δ = 42.54, 62.20, 119.77, 122.05, 125.36, 126.51, 127.01, 128.66, 130.33, 132.58, 133.78, 135.18, 135.62, 136.05, 138.89, 152.17, 153.12, 165.17. Anal. calcd. for $C_{20}H_{13}N_3O_3$ (343.34): C 69.97, H 3.82, N 12.24; found: C 69.88, H 3.75, N 12.12.

3-Amino-1-(4-nitrophenyl)-1H-benzof[chromene-2-carbonitrile (4h): Pale lemon solid, yield: 0.306 g (89 %), m.p. 166–168 °C (lit: 168–170 °C²²) (*n*-hexane: ethyl acetate, 5: 2, Rf = 0.53). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3460, 3320, 2185, 1665, 1600, 1560, 1500, 1325, 1270, 1190, 1080. ¹H-NMR: δ = 5.35 (s, 1H, H-1), 6.05 (bs, 2H, NH₂), 7.30 (d, *J* = 9.0 Hz, 1H, ArH), 7.35–7.42 (m, 4H, ArH), 7.54–7.58 (m, 1H, ArH), 7.82–7.86 (m, 2H, ArH), 8.10 (dd, *J* = 6.96 & 6.92 Hz, 2H, ArH) ppm. ¹³C-NMR: δ = 42.58, 117.45, 120.62, 127.01, 128.17, 129.19, 131.39, 131.90, 132.61, 134.18, 135.29, 151.13, 155.64, 163.77. Anal. calcd. for $C_{20}H_{13}N_3O_3$ (343.34): C 69.97, H 3.82, N 12.24; found: C 69.83, H 4.04, N 12.16.

4. Conclusion

In conclusion, ZnO nanoparticles thin-film was prepared with a mild hydrothermal method and well characterized by various techniques such as XRD, FT-IR and SEM; it was found to catalyze the three-component reaction of aromatic aldehydes, malononitrile and β -naphthol efficiently, affording 3-amino-1-aryl-1H-benzof[chromene-2-carbonitrile derivatives (4) in high to excellent yields. Compared to known methods, satisfactory results were obtained with high yields, mild reaction conditions, short reaction time, reusability of the catalyst, easy work-up, inexpensive reagents and environmentally friendly procedures.

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