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Synthesis and characterization of a novel Fe_3O_4@SiO_2–BenzIm-Fc[Cl]/BiOCl nano-composite and its efficient catalytic activity in the ultrasound-assisted synthesis of diverse chromene analogs†

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In this study, a novel magnetically recoverable Fe_3O_4@SiO_2–BenzIm-Fc[Cl]/BiOCl nano-composite was synthesized using a simple chemical co-precipitation method. This is the first time that a magnetic nano-catalyst bearing ionic liquid, ferrocene and BiOCl is synthesized. The Fe_3O_4@SiO_2–BenzIm-Fc[Cl]/BiOCl nano-composite was characterized by Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX) and field emission scanning electron microscopy (FE-SEM) techniques. The catalytic activities of the novel magnetic nano-composite were evaluated in one-pot three-component synthesis of a wide variety of 2-amino-3-cyano-4*H*-chromene derivatives under ultrasound irradiation. A simple, facile and highly efficient ultrasound-assisted method was developed to synthesize 4*H*-chromene derivatives *via* one-pot, three-component reaction of aldehyde, malononitrile and active phenolic compounds (2-naphthol, 1-naphthol, 3-(dimethylamino)phenol, resorcinol and orcinol) at room temperature. The reaction of aldehyde, malononitrile and orcinol is newly introduced in this paper. The ultrasound-assisted synthesis protocol that was studied in this article exhibits some notable advantages such as short reaction times, operational simplicity, green reaction conditions, high yields and easy work-up and purification steps. In addition, the novel magnetic nano-composite could be easily recovered by an external magnetic field and reused for six-reaction cycles without significant loss of its catalytic activity.

1. Introduction

Heterocyclic compounds containing a 4*H*-chromene moiety are present in a wide variety of drugs, many natural products and numerous biologically and pharmaceutically active compounds. 2-Amino-4*H*-chromene derivatives are known to exhibit anticancer,[1–3] antioxidant,[4,5] anti-inflammatory,[6,7] antimicrobial,[8,9] anti-tuberculosis,[10] antiviral,[11] anti-proliferative,[12] antibacterial and antifungal,[13] anticoagulant and anti-HIV activities.[14] Hence, the design and synthesis of such compounds is a hot research topic for chemists. Synthetic methods using different catalysts such as K_2CO_3,[15,16] MW/DUB,[17] TFE,[18] amino-silane modified Fe_3O_4 nanoparticles (MNPs-NH_2),[19] potassium phthalimide-*N*-oxyl (POPINO),[20] NaBr,[21] cetyltrimethylammoniumchloride (CTAC),[22] glycine,[23] Fe_3O_4-chitosan nano-particles,[24] 4-dimethylaminopyridine (DMAP),[25] piperidine[26] and Mg/Al hydrotalcite,[27] 2-ethyl imidazolium acetate,[28] and tris-hydroxymethylaminomethane (THAM)[29] were reported. However, because of the importance of 2-amino-4*H*-chromene derivatives, more efficient and environmentally benign methods are still in demand. In order to introduce a simple, green and efficient strategy for the synthesis of these compounds, it is important to use an applied heterogeneous catalyst, an eco-friendly medium for the reactions, and an appropriate source of input energy in order to optimize the reaction duration and product yield and avoid undesirable side-products.

On the other hand, supported heterogeneous catalysts as reusable and environmentally friendly materials play a key role in modern science and technology, especially in organic synthesis.[30–32] Due to the advantages of the immobilization of the catalyst on the solid supports, such as easily handling, non-toxicity, low solubility and increasing the selectivity of the reactions, these types of heterocatalysts are widely used.[33] Catalysts immobilized on nanostructure supports are more

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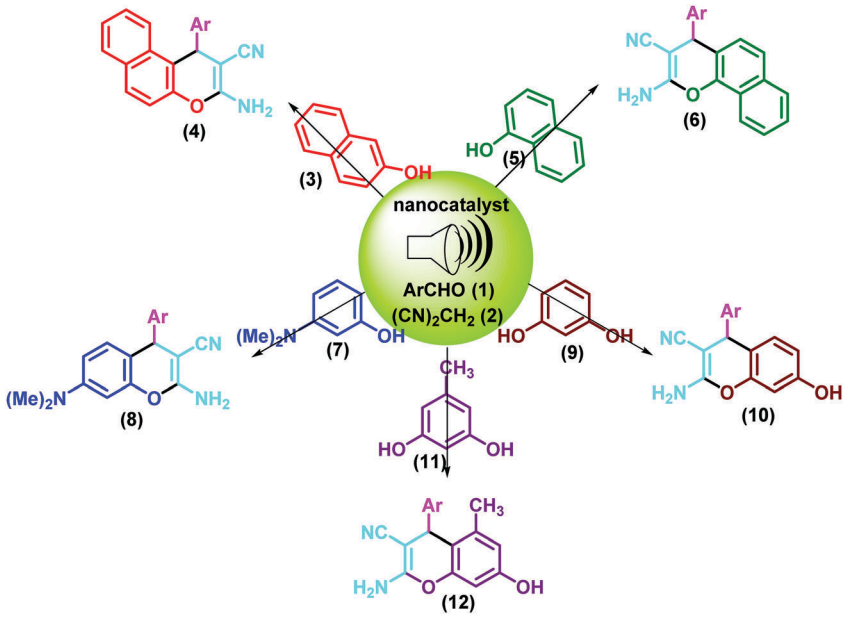


Scheme 1 Ultrasound-assisted synthesis of diverse 2-amino-4*H*-chromenes *via* Fe_3O_4@SiO_2–BenzIm-Fc[Cl]/BiOCl catalyzed three-component reactions.

attractive, because they exhibit higher activity and selectivity.[34–36] Recent studies show that magnetite (Fe_3O_4) nano-particles have unique properties such as superparamagnetism, high surface area, thermal stability, low toxicity, low cost, easy separation from the reaction mixture using an external magnetic field, potential to immobilize different functional groups and excellent recyclability, which make them very applicable and useful supports to design and synthesize reusable heterogeneous catalysts.[37,38] Furthermore, benzimidazolium based ionic liquids (ILs) have received much attention and have been used as environmentally friendly catalysts and solvents, due to their special properties such as negligible volatility, thermal stability, non-inflammability, high activity and selectivity and easy recyclability. Benzimidazole based ILs introduced a new possibility to develop new, efficient and environmentally friendly catalysts for different organic reactions.[39]

In recent years, the development of ultrasound-assisted synthesis reactions has been focused in many scientific and industrial investigations. Sonochemical synthesis has many benefits such as convenience, improved yields and reaction rates, simplicity and controllability of the reaction compared to traditional heating methods which generally require longer reaction times and higher temperatures. Therefore, a large number of organic reactions have been carried out under ultrasonic irradiation in higher yields, shorter reaction times or milder conditions in accordance with the green chemistry principles.[40,41]

In the continuation of our interest towards the development of new efficient synthetic methodologies for various multi-component reactions using nano-magnetic heterogeneous catalysts,[42–46] herein, we report a simple, facile and highly efficient ultrasound-assisted method for the synthesis of 2-amino-4*H*-chromene derivatives. One-pot three-component reactions of aldehyde, malononitrile and active phenolic compounds (2-naphthol, 1-naphthol, 3-(dimethylamino)phenol, resorcinol and orcinol) catalyzed by the Fe_3O_4@SiO_2–BenzIm-Fc[Cl]/BiOCl nano-composite under ultrasonic conditions were investigated (Scheme 1).

2. Experimental

2.1. Materials and apparatus

The chemical reagents used in synthesis were purchased from Merck and Sigma-Aldrich Co. Melting points were determined with a MEL-TEMP model 1202D and are uncorrected. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer as KBr disks. The ^{1}H NMR spectra were recorded using a Bruker Spectrospin Avance 400 spectrometer with DMSO-d_6 as solvent and TMS as an internal standard. ^{13}C NMR spectra were determined on the same instrument at 100 MHz. All chemical shifts were reported as d (ppm) and coupling constants (J) are given in Hz. Elementary analyses (C, H, N) were performed on a Vario EL III analyzer. X-ray diffraction patterns of samples were taken on a Siemens D500 X-ray powder diffraction diffractometer (CuK radiation, λ = 1.5406 Å). FE-SEM images of the products were visualized by a TESCAN MIRA3 Field Emission Scanning Electron Microscope. A multiwave ultrasonic generator (Sonicator 3200; Bandelin, MS 73, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 10–60 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level.

2.2. Synthesis of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite

2.2.1. Synthesis of 1-(4-ferrocenylbutyl)-1*H*-benzimidazole (17). Benzimidazole (2.36 g, 20 mmol) was added to a suspension of

NaH (60%, 0.80 g, 20 mmol) in dry THF (100 mL), and the mixture was stirred at 0 °C for 1 h. Then, 4-chlorobutylferrocene (1.38 g, 5 mmol) was added and the mixture was heated under reflux for 12 h. After cooling, the excess amount of NaH was quenched by the addition of water. After extraction with dichloromethane, the extract was concentrated and the residue was subjected to silica column chromatography eluting with *n*-hexane/ethyl acetate, 9 : 1, to give 1-(4-ferrocenylbutyl)-1*H*-benzimidazole as a brown viscous oil; FT-IR: 3102, 2959, 2877, 1693, 1651, 1526 cm^{-1}; ^1H NMR: δ 1.46–1.54 (m, 2H, $-CH_2-$), 1.84–1.91 (m, 2H, $-CH_2-$), 2.34 (t, J = 7.5 Hz, 2H, $-CH_2-$), 4.01 (m, 2H, $-CH_2-$), 4.04 (m, 7H, Cp-H), 4.14–4.17 (m, 2H, Cp-H), 7.24–7.30 (m, 2H, benzimid-H), 7.47 (m, 2H, benzimid-H), 7.73 (m, 1H, benzimid-H), 8.09 (s, 1H, benzimid-H); ^{13}C NMR: δ 27.2, 27.9, 28.5, 44.0, 66.0, 66.9, 67.3, 86.9, 108.8, 119.4, 120.7, 121.7, 134.6, 144.8 ppm.

2.2.2. Synthesis of Fe_3O_4@SiO_2@BenzIm-Fc[Cl] (19). Fe_3O_4@SiO_2–propyl chloride was prepared according to reported procedures.[43,44] Then, a mixture of Fe_3O_4@SiO_2–$(CH_2)_3Cl$ (1.0 g) and 1-(4-ferrocenylbutyl)-1*H*-benzimidazole (1.0 g) in 10 mL of toluene was heated at 80 °C in an oil bath. After 72 h, the residue was filtered, washed with toluene (3 × 20 mL), MeOH (3 × 20 mL), and CH_2Cl_2 (3 × 20 mL) and dried under reduced pressure at 50 °C for 48 h to afford Fe_3O_4@SiO_2@BenzIm-Fc[Cl].

2.2.3. Synthesis of Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl (20). $BiCl_3$ (0.2 g) was dissolved in 10 mL of water and 30 mL of acetone. Then, 0.2 g of Fe_3O_4@SiO_2@BenzIm-Fc[Cl] nanoparticles was added and the mixture was put in an ultrasonic bath for 15 minutes. The suspension was stirred at room temperature for 24 hours by a mechanical stirrer. Modified nano-particles were separated from the reaction medium *via* an external magnetic field and washed with water, EtOH and acetone. The desired nano-catalyst was dried under vacuum. The modified nano-particles were identified using FT-IR, FE-SEM, EDX and XRD.

2.3. General procedure for the synthesis of 2-amino-4*H*-chromenes derivatives under ultrasound irradiation

A mixture of an aldehyde (1 mmol), malononitrile (1.1 mmol), an appropriate C–H acid 3, 5, 7, 9 or 11 (1 mmol), and Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl (10 mg) in ethanol : water (3 : 2, 5 mL) was sonicated at ambient temperature. When the reaction was completed [monitored by thin layer chromatography (TLC), using *n*-hexane/ethyl acetate (3 : 1) as the eluent], the catalyst was separated using an external magnet and the reaction mixture was cooled and the precipitate was filtered, washed and dried. The crude product was crystallized from ethanol. The structures of the new compounds **12a–f** were characterized by IR, ^1H NMR, ^{13}C NMR and CHN analysis.

2.3.1. 2-Amino-4-(4-chlorophenyl)-7-hydroxy-5-methyl-4*H*-chromene-3-carbonitrile (12a). Cream powder; m.p. 256–258 °C; FT-IR (KBr): 3443, 3351, 3319, 3190, 3028, 2941, 2871, 2073, 1648, 1551 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.88 (s, 3H, CH_3), 4.57 (s, 1H, methin-H), 6.33 (d, 1H, J = 2.2 Hz, Ar-H), 6.39 (d, 1H, J = 2.2 Hz, Ar-H), 6.83 (bs, 2H, NH_2), 7.05 (d, 2H, J = 8.4 Hz, Ar-H), 7.34 (d, 2H, J = 8.4 Hz, Ar-H), 9.68 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 37.7, 57.5, 100.3, 111.9, 113.9, 120.5, 128.2, 128.5, 128.8, 130.9, 137.8, 144.7, 149.9, 156.9, 159.8 ppm; anal. calc. for $C_{17}H_{13}ClN_2O_2$ (%): C, 65.29; H, 4.19; N, 8.96; found: C, 65.02; H, 4.21; N, 8.94.

2.3.2. 2-Amino-7-hydroxy-5-methyl-4-phenyl-4*H*-chromene-3-carbonitrile (12b). Cream powder; m.p. 283–285 °C; FT-IR (KBr): 3501, 3408, 3333, 3213, 2867, 2074, 1646, 1553 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.89 (s, 3H, CH_3), 4.53 (s, 1H, methin-H), 6.35 (s, 1H, Ar-H), 6.39 (s, 1H, Ar-H), 6.77 (bs, 2H, NH_2), 7.04 (d, 2H, J = 7.4 Hz, Ar-H), 7.15–7.29 (m, 3H, Ar-H), 9.63 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 38.5, 58.1, 100.3, 112.5, 113.9, 120.7, 126.4, 126.9, 128.5, 137.7, 145.7, 150.1, 156.8, 159.8 ppm; anal. calc. for $C_{17}H_{14}N_2O_2$ (%): C, 73.37; H, 5.07; N, 10.07; found: C, 73.12; H, 5.08; N, 10.04.

2.3.3. 2-Amino-7-hydroxy-5-methyl-4-(*p*-tolyl)-4*H*-chromene-3-carbonitrile (12c). Light yellow powder; m.p. 236–238 °C; FT-IR (KBr): 3492, 3395, 3366, 3219, 3030, 2953, 2876, 2079, 1646, 1564 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.89 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 4.47 (s, 1H, methin-H), 6.33 (d, 1H, J = 2.2 Hz, Ar-H), 6.38 (d, 1H, J = 2.2 Hz, Ar-H), 6.76 (bs, 2H, NH_2), 6.92 (d, 2H, J = 7.9 Hz, Ar-H), 7.07 (d, 2H, J = 7.9 Hz, Ar-H), 9.64 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 20.6, 38.1, 58.2, 100.2, 112.6, 113.8, 120.7, 126.8, 126.9, 128.7, 129.1, 135.4, 137.7, 142.7, 150.0, 156.7, 159.8 ppm; anal. calc. for $C_{18}H_{16}N_2O_2$ (%): C, 73.95; H, 5.52; N, 9.58; found: C, 73.71; H, 5.55; N, 9.54.

2.3.4. 2-Amino-7-hydroxy-4-(4-isopropylphenyl)-5-methyl-4*H*-chromene-3-carbonitrile (12d). Light yellow powder; m.p. 241–243 °C; FT-IR (KBr): 3451, 3336, 3207, 3117, 2957, 2876, 2081, 1642, 1574 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.15 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.90 (s, 3H, CH_3), 2.77–2.84 (m, 1H, CH), 4.47 (s, 1H, methin-H), 6.34 (d, 1H, J = 2.2 Hz, Ar-H), 6.38 (d, 1H, J = 2.2 Hz, Ar-H), 6.75 (bs, 2H, NH_2), 6.95 (d, 2H, J = 8.1 Hz, Ar-H), 7.13 (d, 2H, J = 8.1 Hz, Ar-H), 9.61 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 23.8, 33.0, 38.1, 58.2, 100.3, 112.8, 113.9, 120.9, 126.1, 126.5, 126.9, 137.7, 143.2, 150.1, 156.8, 159.9 ppm; anal. calc. for $C_{20}H_{20}N_2O_2$ (%): C, 74.98; H, 6.29; N, 8.74; found: C, 74.73; H, 6.31; N, 8.70.

2.3.5. 2-Amino-4-(2-chlorophenyl)-7-hydroxy-5-methyl-4*H*-chromene-3-carbonitrile (12e). Cream powder; m.p. 270–272 °C; FT-IR (KBr): 3500, 3394, 3332, 3219, 2972, 2188, 1650, 1464 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.85 (s, 3H, CH_3), 5.04 (s, 1H, methin-H), 6.32–6.39 (m, 2H, Ar-H), 6.84 (bs, 2H, NH_2), 6.92 (d, 1H, J = 6.2 Hz, Ar-H), 7.17–7.26 (m, 2H, Ar-H), 7.40 (dd, 1H, J = 7.5 Hz, J = 1.4 Hz, Ar-H), 9.68 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.6, 20.9, 56.3, 100.3, 111.8, 113.9, 120.1, 127.9, 128.2, 129.3, 130.2, 131.5, 137.7, 142.7, 150.3, 157.0, 160.2 ppm; anal. calc. for $C_{17}H_{13}ClN_2O_2$ (%): C, 65.29; H, 4.19; N, 8.96; found: C, 65.03; H, 4.22; N, 8.92.

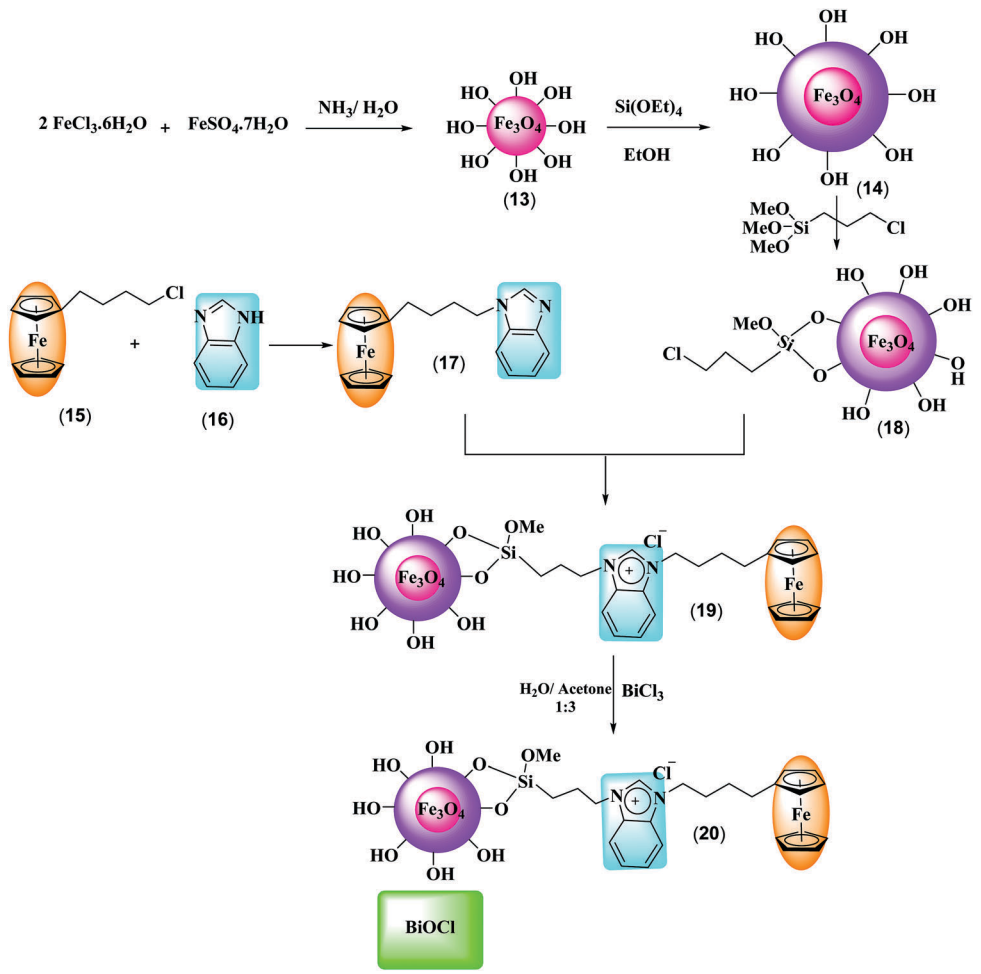
2.3.6. 2-Amino-7-hydroxy-5-methyl-4-(naphthalen-2-yl)-4*H*-chromene-3-carbonitrile (12f). Light yellow powder; m.p. 272–274 °C; FT-IR (KBr): 3490, 3399, 3319, 3206, 2923, 2074, 1642, 1497 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.92 (s, 3H, CH_3), 4.71 (s, 1H, methin-H), 6.35–6.38 (m, 2H, Ar-H), 6.84 (bs, 2H, NH_2), 7.14 (dd, 1H, J = 8.5 Hz, J = 1.6 Hz, Ar-H), 7.44–7.51 (m, 2H, Ar-H), 7.62 (s, 1H, Ar-H), 7.78–7.86 (m, 3H, Ar-H), 9.66 (bs, 1H, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 38.7,

57.8, 100.4, 112.2, 113.9, 120.7, 125.0, 125.6, 125.7, 126.3, 127.5, 127.6, 128.5, 131.8, 132.8, 137.9, 142.9, 150.0, 156.9, 159.9 ppm; anal. calc. for $C_{21}H_{16}N_2O_2$ (%): C, 76.81; H, 4.91; N, 8.53; found: C, 76.58; H, 4.94; N, 8.50.

3. Results and discussion

The new magnetic nano-catalyst Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl was prepared following the multistep protocol shown in Scheme 2. A literature survey showed that Fe_3O_4/BiOCl nano-composites were previously synthesized and their photo-catalytic efficiency was studied,[47–49] but the catalytic activity of these nano-composites has not been investigated. Following our recent studies on the design and synthesis of novel ferrocene containing ionic liquids supported on Fe_3O_4 nano-particles, here we report novel generation of this nano-catalyst as a Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite. Initially, the chemical co-precipitation of Fe^{2+} and Fe^{3+} ions in NH_4OH solution was performed in order to prepare magnetic Fe_3O_4 nano-particles. Subsequently, silica-coated magnetic nano-particles (Fe_3O_4@SiO_2) were easily achieved using the known Stober method. Then, the Fe_3O_4@SiO_2 nano-particles were allowed to react with (3-chloropropyl)trimethoxysilane to obtain chloropropyl containing nano-particles.[50–52] On the other hand, 1-(4-ferrocenylbutyl)-1*H*-benzimidazole was prepared by the reaction of benzimidazole with 4-chlorobutylferrocene. Subsequently 1-(4-ferrocenylbutyl)-1*H*-benzimidazole reacted with Fe_3O_4@SiO_2–$(CH_2)_3Cl$ to afford Fe_3O_4@SiO_2@BenzIm-Fc[Cl] nanoparticles. Finally, the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]-coupled BiOCl nano-composite was prepared by using a simple chemical co-precipitation method using $BiCl_3$ at room-temperature. Chemical analysis of the prepared magnetic nano-particles and Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite was studied by Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD) analysis.

The FT-IR spectra of (a) Fe_3O_4, (b) Fe_3O_4@SiO_2, (c) Fe_3O_4@SiO_2@$(CH_2)_3Cl$, (d) Fe_3O_4@SiO_2@BenzIm-Fc[Cl] and (e) Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl are shown in Fig. 1. In the FT-IR spectroscopy of the nano-particles, the absorption peaks at about 580 cm^{-1} are related to Fe–O bond vibrations. The absorption peaks at about 1080 cm^{-1} in all Fe_3O_4@SiO_2 core–shell MNPs are linked to the asymmetric stretching vibrations of Si–O–Si. In the



Scheme 2 Synthesis of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nanocomposite.

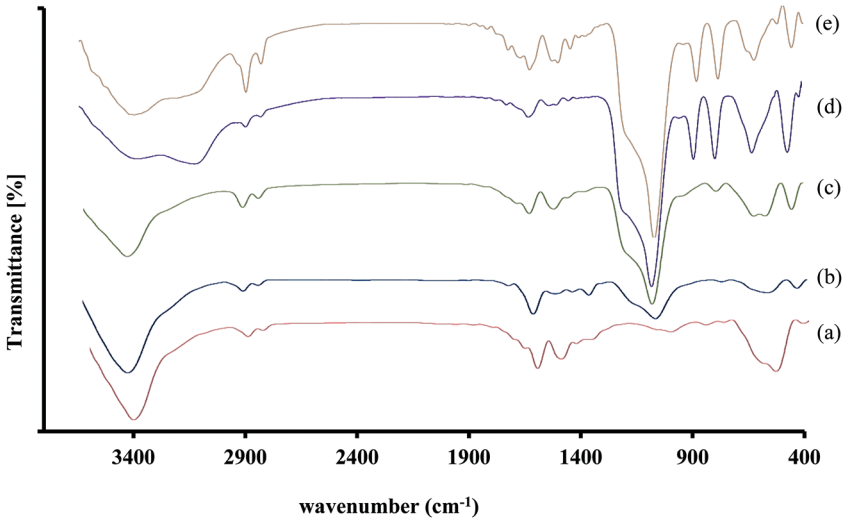
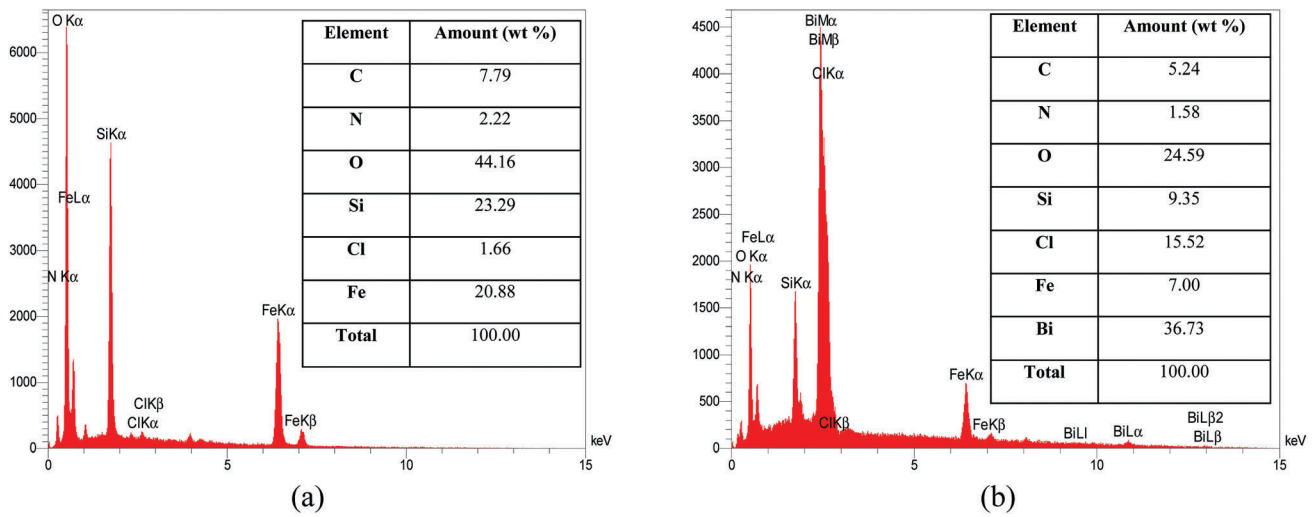


Fig. 1 The FT-IR spectra of (a) Fe_3O_4, (b) Fe_3O_4@SiO_2, (c) Fe_3O_4@SiO_2@$(CH_2)_3Cl$, (d) Fe_3O_4@SiO_2@BenzIm-Fc[Cl] and (e) Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl.

FT-IR spectroscopy of Fe_3O_4@SiO_2–$(CH_3)_3Cl$ MNPs more than Fe–O and Si–O–Si bond vibrations, an absorption peak at 2918 cm^{-1} appeared which is related to the asymmetric stretching vibration of aliphatic C–H. The FT-IR spectroscopy of Fe_3O_4@SiO_2@BenzIm-Fc[Cl] MNPs shows an absorption peak at above 3000 cm^{-1} related to the stretching vibration of aromatic C–H on benzimidazole and ferrocene groups. The absorption peaks at 1643 and 1549 cm^{-1} are also linked to the stretching vibration of C=N and C=C bonds on aromatic rings. Finally, in the FT-IR spectroscopy of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite, the absorption peak at about 530 cm^{-1} is assigned to Bi–O stretching vibration and the absorption peak at 1460 cm^{-1} is assigned to the stretching vibration peak of the Bi–Cl band in the BiOCl structure. These results revealed the successful synthesis of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-catalyst.

Energy-dispersive X-ray spectroscopy (EDX) analysis of Fe_3O_4@SiO_2@BenzIm-Fc[Cl] nano-particles and the newly synthesized one are presented in Fig. 2. The EDX spectrum and data of Fe_3O_4@SiO_2@BenzIm-Fc[Cl] nano-particles introduced the presence of the expected elements (C, N, O, Si, Cl and Fe) in their regions. The EDX spectrum of the novel synthesized Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite indicated the presence of the expected elements (C, N, O, Si, Cl, Fe and Bi) and confirmed the structure of the nano-catalyst. The presence of Bi in the EDX spectrum of the final nano-catalyst confirmed the synthesis of a nano-composite.

The X-ray diffraction (XRD) pattern of the modified Fe_3O_4 nano-particles was measured at 0 to 80 degrees. As shown in Fig. 3, the diffusion pattern of Fe_3O_4@SiO_2@BenzIm-Fc[Cl] nano-particles shows the crystalline dispersions of Fe_3O_4 magnetic nano-particles. The XRD pattern of Fe_3O_4@SiO_2@BenzIm-Fc[Cl] nano-particles exhibited diffraction peaks at 2θ = 31.6°, 35.4°, 43.1°, 53°, 57.3° and 63.9° which are in good agreement with the standard XRD pattern of Fe_3O_4 MNPs (JCPDS card no. 85-1436).



Element	Amount (wt %)
C	7.79
N	2.22
O	44.16
Si	23.29
Cl	1.66
Fe	20.88
Total	100.00

Element	Amount (wt %)
C	5.24
N	1.58
O	24.59
Si	9.35
Cl	15.52
Fe	7.00
Bi	36.73
Total	100.00

Fig. 2 EDX analysis of (a) Fe_3O_4@SiO_2@BenzIm-Fc[Cl] and (b) Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl.

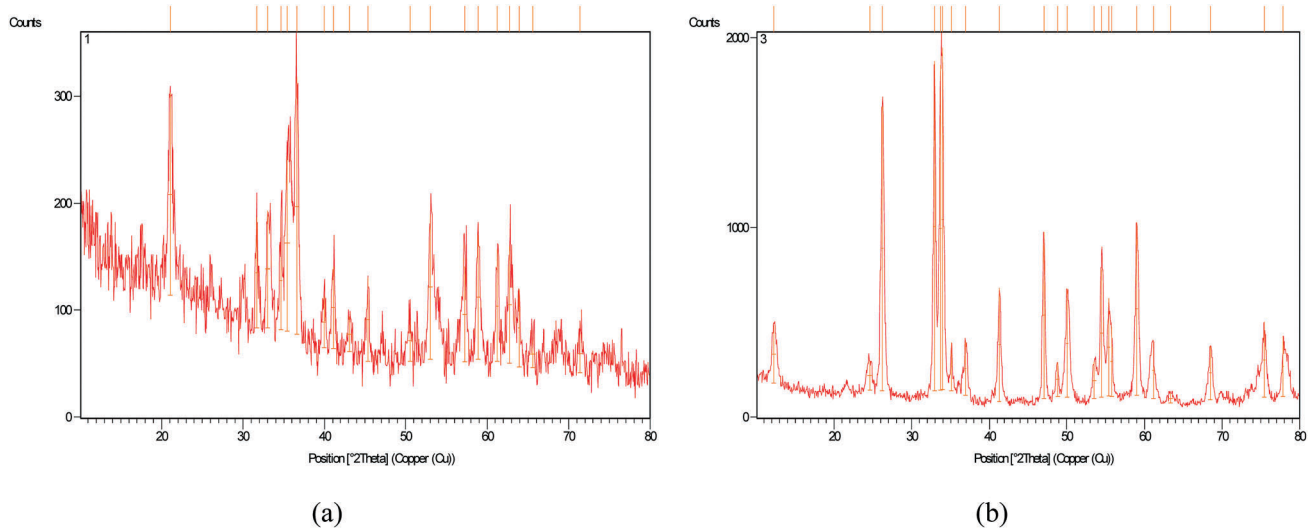


Fig. 3 XRD patterns of (a) Fe_3O_4@SiO_2@BenzIm-Fc[Cl] and (b) Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl.

But the XRD patterns of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite displayed distinctive peaks at $2\theta = 12.2^\circ$, 24.6°, 26.2°, 32.9°, 33.7°, 36.9°, 41.3°, 47.1°, 50.0°, 54.4°, 55.4°, 58.9°, and 77.8° which are well matched with the tetragonal phase JCPDS-ICDD File No. 01-085-0861. These distinctive peaks were very obvious, suggesting the formation and good crystallinity of the novel synthesized Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite.

The surface morphology and size of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl] nano-particles and Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite were evaluated using Field Emission Scanning Electron Microscopy (FE-SEM) analysis (Fig. 4). The FE-SEM images of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl] nano-particles showed that the shapes of these particles are mostly spherical with non-smooth surfaces which increase the surface areas and activity of these particles. The FE-SEM images of Fe_3O_4@SiO_2@BenzIm-Fc[Cl] nano-particles also displayed that the particles are uniformly distributed and the sizes of the magnetic nano-particles are about 40 nm. The FE-SEM images of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite showed that BiOCl was synthesized on the Fe_3O_4@SiO_2@BenzIm-Fc[Cl] nano-particles as irregular plates which are around 150 nm in width and about 50 nm in thickness.

In continuation, we decided to investigate the catalytic activity of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite in the synthesis of 2-amino-4*H*-chromene derivatives. At first, the reaction of 4-chlorobenzaldehyde (**1a**) (1 mmol), malononitrile (**2**) (1.1 mmol) and 2-naphthol (**3**) (1 mmol) under ultrasound irradiation was chosen as a test reaction. The reaction was studied under different conditions and the progress of the reactions was monitored by TLC. In this context, the effects of catalyst loading on the reaction were examined initially. In the absence of catalyst, 3-amino-1-(4-chlorophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (**4a**) was obtained after 60 minutes only in 10% yield. With increase in the amount of catalyst to 10 mg, the yield of the desired product (**4a**) was gradually increased. But more addition

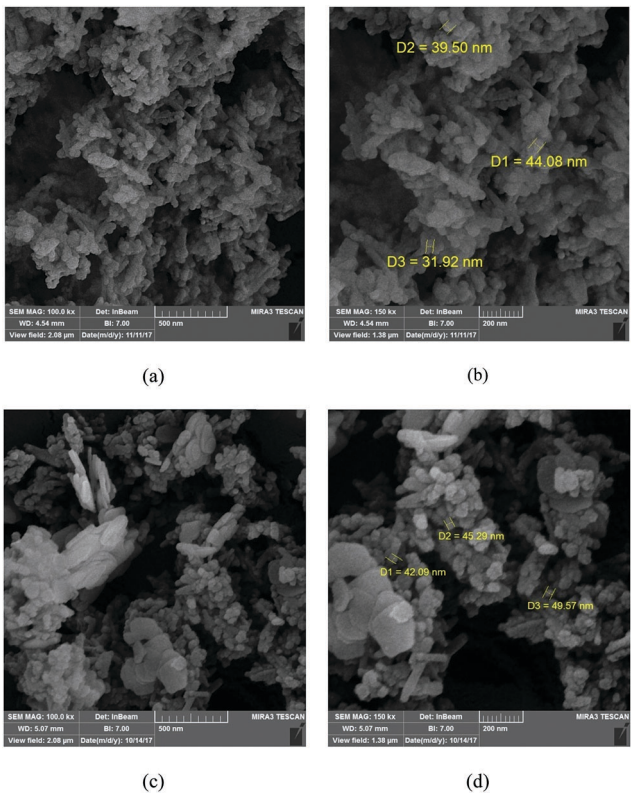
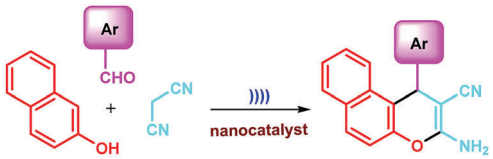


Fig. 4 FE-SEM images of (a and b) Fe_3O_4@SiO_2@BenzIm-Fc[Cl] and (c and d) Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl.

of the catalyst to 15 mg didn't show improvement in the reaction. Then, the subsequent optimization of the reaction conditions affirmed the selection of ethanol–water (3 : 2, v/v) as the best solvent for the synthesis of the desired product (**4a**), in an excellent yield. Finally, we tried to test the effect of ultrasound irradiation power on the reaction of 4-chlorobenzaldehyde, malononitrile and 2-naphthol. Various ranges of irradiation

Table 1 Synthesis of 3-amino-1*H*-benzo[*f*]chromene derivatives using 10 mg of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nanocatalyst



(4a-l)

Entry	Aldehyde	Product	Time (min)	Yield (%)	Obs. m.p. (°C)	Lit. m.p. (°C)
1	4-Chlorobenzaldehyde	(**4a**)	15	96	208–210	207–209[43]
2	Benzaldehyde	(**4b**)	18	93	280–281	279–281[43]
3	4-Bromobenzaldehyde	(**4c**)	18	95	212–214	212–215[43]
4	4-Fluorobenzaldehyde	(**4d**)	18	93	233–235	232–234[43]
5	4-Methylbenzaldehyde	(**4e**)	18	92	272–274	270–273[43]
6	4-Isopropylbenzaldehyde	(**4f**)	20	90	220–222	218–220[43]
7	4-Methoxybenzaldehyde	(**4g**)	20	87	192–194	192–194[43]
8	4-Nitrobenzaldehyde	(**4h**)	15	96	186–188	186–187[43]
9	3-Nitrobenzaldehyde	(**4i**)	18	92	217–219	215–218[43]
10	2-Chlorobenzaldehyde	(**4j**)	20	88	270–272	269–272[43]
11	Thiophene-2-carbaldehyde	(**4k**)	20	84	224–226	224–226[43]
12	4-Pyridinecarboxaldehyde	(**4l**)	20	82	227–229	225–227[43]

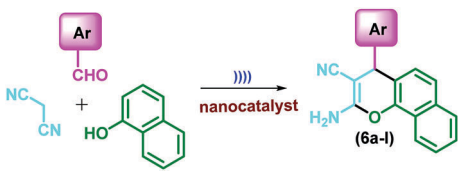
powers (30–60 W) were studied and the best results were obtained when the irradiation power was 50 W.

Subsequently, the method was developed towards various aldehydes to obtain the related 3-amino-1*H*-benzo[*f*]chromene derivatives **4a–l**. Accordingly, a number of aromatic aldehydes with electron-withdrawing groups as well as electron-donating groups and a few heteroaromatic aldehydes were subjected to reaction with malononitrile and 2-naphthol in the presence of a catalytic amount of Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nanocomposite under ultrasonic irradiation. In all cases, the corresponding products **4a–l** were obtained within 15–20 min in excellent yields (Table 1).

After this initial success, the generality of the method for the synthesis of 2-amino-4*H*-benzo[*h*]chromene derivatives was examined. In this context, replacement of the 2-naphthol with 1-naphthol could be expected to furnish 2-amino-4*H*-benzo[*h*]chromenes **6a–l** (Table 2). A literature survey revealed that 4*H*-benzo[*h*]chromene derivatives possess many biological and pharmacological activities such as cytotoxicity and anticancer activity[53] and a number of methods have been reported for the synthesis of these compounds. Here, our new method for the synthesis of these compounds was examined. For this reason three-component reactions between 1-naphthol, malononitrile and a series of aldehydes were performed in the presence of 10 mg of Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite in ethanol–water (3 : 2, v/v) under ultrasonic irradiation. A group of 2-amino-4*H*-benzo[*h*]chromene derivatives (**6a–l**) were synthesized successfully according to this simple and efficient method in high yields.

After establishing a general method for the synthesis of 3-amino-1*H*-benzo[*f*]chromenes **4**, as well as 2-amino-4*H*-benzo[*h*]chromene derivatives **6**, we tried to synthesize another

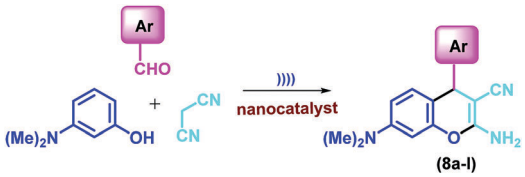
Table 2 Synthesis of 2-amino-4*H*-benzo[*h*]chromene derivatives using 10 mg of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nanocatalyst



(6a-l)

Entry	Aldehyde	Product	Time (min)	Yield (%)	Obs. m.p. (°C)	Lit. m.p. (°C)
1	4-Chlorobenzaldehyde	(**6a**)	15	96	245–247	246–247[54]
2	Benzaldehyde	(**6b**)	15	93	217–219	216–217[54]
3	4-Bromobenzaldehyde	(**6c**)	18	94	240–242	240–241[55]
4	4-Fluorobenzaldehyde	(**6d**)	15	92	233–234	232–234[54]
5	4-Methylbenzaldehyde	(**6e**)	15	90	207–209	205–207[55]
6	4-Isopropylbenzaldehyde	(**6f**)	18	89	204–206	204–205[55]
7	4-Methoxybenzaldehyde	(**6g**)	20	87	192–194	193–194[55]
8	4-Nitrobenzaldehyde	(**6h**)	15	97	238–240	238–239[55]
9	3-Nitrobenzaldehyde	(**6i**)	18	90	217–219	218–220[54]
10	2-Chlorobenzaldehyde	(**6j**)	20	86	251–253	253–254[55]
11	Thiophene-2-carbaldehyde	(**6k**)	25	88	187–189	188–190[55]
12	2-Furancarboxaldehyde	(**6l**)	25	86	170–172	168–170[54]

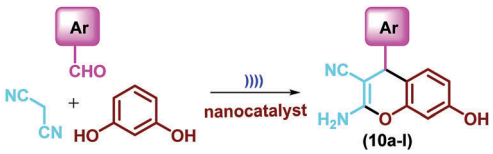
Table 3 Synthesis of 2-amino-7-(dimethylamino)-4*H*-chromene derivatives using 10 mg of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nanocatalyst



(8a-l)

Entry	Aldehyde	Product	Time (min)	Yield (%)	Obs. m.p. (°C)	Lit. m.p. (°C)
1	4-Chlorobenzaldehyde	(**8a**)	20	94	200–202	202–205[56]
2	Benzaldehyde	(**8b**)	22	90	205–205	206–207[56]
3	4-Bromobenzaldehyde	(**8c**)	22	89	214–216	212–214[57]
4	4-Fluorobenzaldehyde	(**8d**)	22	90	180–182	174–178[57]
5	4-Methylbenzaldehyde	(**8e**)	25	91	242–243	240–242[56]
6	4-Isopropylbenzaldehyde	(**8f**)	25	87	225–227	226–228[56]
7	4-Methoxybenzaldehyde	(**8g**)	28	86	175–177	176–178[56]
8	4-Nitrobenzaldehyde	(**8h**)	20	95	225–227	224–226[57]
9	3-Nitrobenzaldehyde	(**8i**)	22	90	206–208	207–209[57]
10	2-Chlorobenzaldehyde	(**8j**)	25	86	193–195	195–197[57]
11	Thiophene-2-carbaldehyde	(**8k**)	28	84	215–217	217–220[56]
12	Pyridine-3-carbaldehyde	(**8l**)	28	85	238–240	240–242[56]

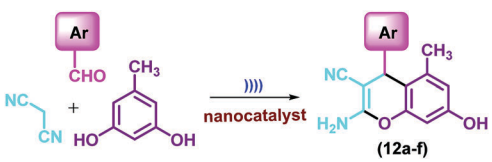
Table 4 Synthesis of 2-amino-4*H*-chromene derivatives using 10 mg of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nanocatalyst



(10a-l)

Entry	Aldehyde	Product	Time (min)	Yield (%)	Obs. m.p. (°C)	Lit. m.p. (°C)
1	4-Chlorobenzaldehyde	(**10a**)	8	98	235–237	239–241[58]
2	Benzaldehyde	(**10b**)	10	95	230–232	231–233[59]
3	4-Bromobenzaldehyde	(**10c**)	10	92	234–236	233–235[59]
4	4-Fluorobenzaldehyde	(**10d**)	10	93	288–290	292–294[59]
5	4-Methylbenzaldehyde	(**10e**)	12	90	186–188	185–187[59]
6	4-Isopropylbenzaldehyde	(**10f**)	12	87	195–197	196–198[60]
7	4-Methoxybenzaldehyde	(**10g**)	15	88	190–192	192–194[60]
8	4-Nitrobenzaldehyde	(**10h**)	8	97	214–216	212–214[60]
9	3-Nitrobenzaldehyde	(**10i**)	12	86	175–177	170–172[59]
10	2-Chlorobenzaldehyde	(**10j**)	15	84	185–187	188–189[61]
11	Thiophene-2-carbaldehyde	(**10k**)	15	85	202–204	204–206[59]
12	2-Furancarboxaldehyde	(**10l**)	15	83	190–192	189–191[62]

Table 5 Synthesis of 2-amino-5-methyl-4*H*-chromene derivatives using 10 mg of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nanocatalyst



(12a-f)

Entry	Aldehyde	Product	Time (min)	Yield (%)	M.p. (°C)
1	4-Chlorobenzaldehyde	(**12a**)	6	98	256–258
2	Benzaldehyde	(**12b**)	8	96	283–285
3	4-Methylbenzaldehyde	(**12c**)	8	95	236–238
4	4-Isopropylbenzaldehyde	(**12d**)	10	93	241–243
5	2-Chlorobenzaldehyde	(**12e**)	10	90	270–272
6	2-Naphthaldehyde	(**12f**)	10	88	272–274

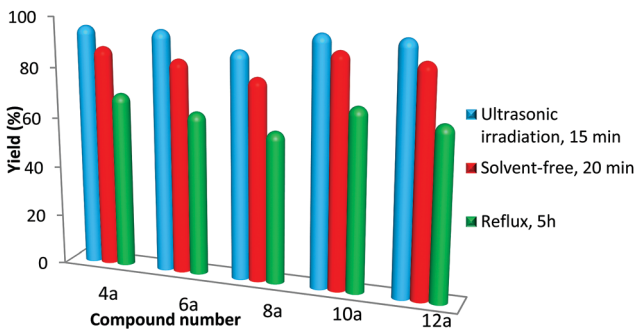


Fig. 5 Comparison of the ultrasonic-assisted method with solvent-free and reflux conditions for the synthesis of 2-amino-4*H*-chromene derivatives catalyzed with Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl.

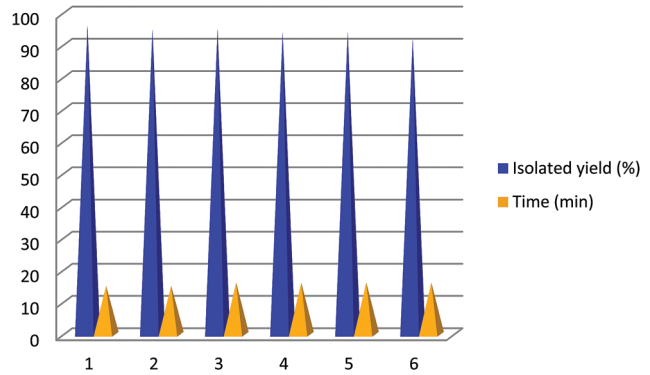


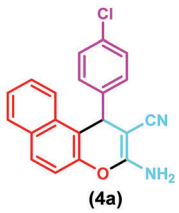
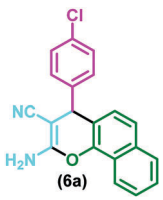
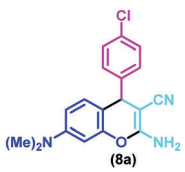
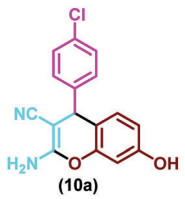
Fig. 6 Recyclability of the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nanocatalyst on the synthesis of **4a**.

important class of chromene-annulated heterocycles, namely 2-amino-7-(dimethylamino)-4*H*-chromenes **8** (Table 3). To achieve this aim, 3-dimethylaminophenol was chosen as the C–H acid in the three-component reaction. We were interested in the synthesis of 2-amino-4-aryl-7-(dimethylamino)-4*H*-chromene-3-carbonitrile derivatives because of their numerous medicinal properties especially anticancer activities. Therefore, various aldehydes containing either electron-withdrawing or electron-donating groups were investigated under the optimized reaction conditions. The results given in Table 3 showed that this one-pot three-component condensation completed within 20–28 min with good isolated yields.

Encouraged by the above mentioned success of a new Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl catalyzed method, we decided to use resorcinol as another enolizable C–H acid derivative. The literature survey showed that due to the versatile biological properties of these 2-amino-4*H*-chromene derivatives, the syntheses of these compounds are well studied and numerous methods for their synthesis are reported. In continuation, three component reactions of various aldehydes, malononitrile and resorcinol catalyzed by Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nano-composite under ultrasonic irradiation are investigated in order to develop and explore the scope and generality of this catalytic method. The results are summarized in Table 4. Aromatic aldehydes containing electron-releasing and electron-withdrawing substituents on their aromatic rings react to give products in high to excellent yields in short reaction times. The reaction times of aromatic aldehydes having electron-withdrawing groups are rather faster than those having electron-donating groups.

Based on the optimized reaction conditions, the reaction was further extended using various aromatic aldehydes with malononitrile and orcinol to synthesize the corresponding

Table 6 Comparison of the present method with the reported methods

Entry	Compound	Catalyst, solvent, condition	Time	Yield (%)	Ref.
1	 (4a)	Triazine-based porous polymer, H_2O, 80 °C	6 h	88	63
		Silica-supported piperazine, $CHCl_3$, reflux	24 h	71	64
		[cmmim]Br, solvent-free, 110 °C	15 min	90	65
		(SiO_2@Im-Fc[OAc]), solvent-free, 90 °C	20 min	92	42
		Nanocatalyst, EtOH/H_2O, sonication	15 min	96	This work
2	 (6a)	Nanostructured diphosphate $Na_2CaP_2O_7$, H_2O, reflux	4 h	90	66
		Nanozeolite clinoptilolite, H_2O, reflux	20 min	95	67
		Sodium-modified hydroxyapatite, H_2O, reflux	3 h	96	68
		Silica-supported piperazine, $CHCl_3$, reflux	7 h	74	64
		[TEA–PEG_{800}–DIL][Cl], H_2O, reflux	15 min	95	54
		Nanocatalyst, EtOH/H_2O, sonication	15 min	96	This work
3	 (8a)	Piperidine, EtOH, 35 °C	12 h	47	69
		Tris-hydroxymethylamino methane, EtOH/H_2O, R.t.	2.5 h	85	29
		Nanocatalyst, EtOH/H_2O, sonication	20 min	94	This work
4	 (10a)	Triazine-based porous polymer, solvent-free, 80 °C	6 h	85	63
		Potassium phthalimide-*N*-oxyl, H_2O, reflux	15 min	92	20
		Amino-appended β-cyclodextrins, H_2O, R.t.	5 h	90	70
		Hydrotalcite, H_2O, 60 °C	5 h	90	27
		2-Ethylimidazolium acetate, solvent-free, 67.5 °C	29 min	94	28
		Nanocatalyst, EtOH/H_2O, sonication	8 min	98	This work

2-amino-5-methyl-4*H*-chromene derivatives (**12a–f**) in excellent yields as shown in Table 5. The new synthesized compounds were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis.

Finally, we decided to combine the sonication method with solvent-free and traditional reflux conditions. For this reason, the synthesis of compounds **4a**, **6a**, **8a**, **10a** and **12a** catalyzed with Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl were studied under different conditions. As summarized in Fig. 5, all 2-amino-4*H*-chromene derivatives were synthesized more efficiently under ultrasonic irradiation with respect to yields and reaction times.

Furthermore, the reusability of the catalyst was investigated with the model reaction under modified conditions and the results are shown in Fig. 6. After completion of the reaction, the catalyst was separated using an external magnet. The collected nano-catalyst was washed several times with EtOH prior to reuse. The recovered nano-catalyst could be reused for six runs without significant decrease in activity.

To highlight the efficiency and applicability of the new method, we compared the results of Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl catalyzed reactions with other reported methodologies. As shown in Table 6, the Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/BiOCl nanocatalyst and new ultrasonic assisted method has a significant impact on the performance of the reactions rather than other catalytic methods.

4. Conclusions

In summary, a new approach for the synthesis of modified magnetic nano-particles was introduced. A novel Fe_3O_4@SiO_2–BenzIm-Fc[Cl]/BiOCl nano-composite was synthesized, characterized and applied as an efficient heterogeneous catalyst for the synthesis of a wide variety of 2-amino-4*H*-chromene derivatives. The reactions were performed under ultrasonic irradiation which has many benefits such as simple operation, reducing the reaction time and improving the product yield. A series of active phenolic compounds (2-naphthol, 1-naphthol, 3-(dimethylamino)phenol, resorcinol and orcinol) were used for the synthesis of 2-amino-4*H*-chromene derivatives *via* one-pot three-component reactions. A general and efficient ultrasound-assisted protocol using a novel recoverable magnetic nano-composite has been demonstrated.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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