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FULL PAPER

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$Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs: A novel magnetic catalyst for the clean and efficient cascade synthesis of 1-(benzothiazolylamino)methyl-2-naphthol derivatives in the absence of solvent

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A green, simple and eco-friendly three-component condensation for the synthesis of 1-(benzothiazolylamino)methyl-2-naphthols using new magnetic nanoparticles formulated as $Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs is described. Considering the economic and environmental aspects, the method provides some advantages such as clean procedure, solvent-free conditions, simple operation and work-up, relatively short reaction times and high yields of the products. Moreover the introduced catalyst can be readily recovered up to 4 consecutive runs with consistent activity using an external magnet.

KEYWORDS

2-Aminobenzothiazole, mild reaction conditions, nano catalyst, one-pot three-component condensation, solvent-free conditions

1 | INTRODUCTION

The development of eco-friendly, effectual, and economical methodologies for the synthesis of biologically important compounds is still a great challenge in organic chemistry. Multi-component reactions have newly attracted much attention as a diversity oriented synthetic methodologies due to their high efficiency, the creation of several new bonds in a one-pot reaction, time and energy saving and environmental friendliness.[1] Accordingly, academic and industrial research groups have increasingly emphasized on the use of MCRs to synthesize a broad range of structural variations.[2]

In recent years, accomplishment of MCRs in the absence of solvent have attracted great interest. These methods have many benefits such as high efficiency and selectivity, operational easiness, mild reaction conditions, and waste reduction.[3]

Benzothiazole and its derivatives are of interesting compounds because they found in many natural products and pharmaceuticals.[4] These compounds were reported to possess anti-inflammatory,[5] anti-tumor,[6] anti-convulsant,[7] anti-bacterial,[8] anti-fungal,[9] and topoisomerase II inhibitory activities.[10] Among them, 1-(benzothiazolylamino)phenyl- methyl-2-naphthols have two biologically active parts, 2-aminobenzothiazole and Betti′s base. Betti′s base derivatives [1-(a-aminoalkyl)-2-naphthols] have provided comfortable access to many effective synthetic building blocks *via* the amino and phenolic hydroxy functional groups.[11] Because of this, the synthesis of 1-(benzothiazolylamino)methyl-2-naphthols is a significant and beneficial duty in organic chemistry processes.

The majority of the novel heterogenized catalysts are based on magnetic nanoparticles (MNPs) Fe_3O_4 supports, primarily because Fe_3O_4 displays some advantageous properties, such as readily availability, relatively large surface area to volume ratio, heterogeneous characteristics and recoverability using an external permanent magnet. In characteristic, Fe_3O_4 nanoparticles coated with a layer of silica have advantageous properties, such as constant catalytic activity and stability.[12–15]

The susceptibility of transition elements to mediate organic synthesis constitutes one of the most efficient strategies to attain both selectivity and efficiency in synthetic chemistry.[16] Zirconium pertain to group IV transition elements that can be considered as efficient catalysts due to easy availability, low cost and low toxicity. Despite these advantages, this metal is also unstable to moisture, corrosive and difficult to handle. Considering these limitations and in continuation of our previous reports on the application of zirconium based and supported reagents in organic transformations,[17–20] we were interested to investigate the stabilization of $ZrCl_4$ on magnetic supports. In this regard, $Fe_3O_4@SiO_2ZrCl_2$-MNPs is successfully prepared, characterized and used as an efficient catalyst in the promotion of one-pot three-component condensation of aryl aldehydes, β-naphthol and 2-aminobenzothiazole to obtain 1-(benzothiazolylamino)methyl-2-naphthols in the absence of solvent.

2 | EXPERIMENTAL

2.1 | Chemicals

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. The purity determination of the substrate and reaction monitoring were accompanied by thin-layer chromatography (TLC) on a silica gel Polygram SILG/UV 254 plate. The products were separated and purified by different chromatographic techniques and were identified by the comparison of their IR, NMR and refractive index with those reported for the authentic samples. All yields refer to the isolated products. The IR spectra were run on a Perkin–Elmer bio-spectrometer. The ^{1}H NMR and ^{13}C NMR (300 MHz) were run on a Bruker Avance DPX-300 FTNMR spectrometer (d in ppm). Melting points were recorded on a Bu¨ chi B-545 apparatus in open capillary tubes. A Philips PW1840 diffractometer with Cu K_α radiation was used to record the X-ray patterns of the synthesized nanoparticles. Scanning electron microscope images were obtained with LEO 1430 VP. The chemical composition was obtained using energy dispersive Xray spectroscopy (EDX) (ESEM, Philips, XL30). The magnetic properties were determined using vibrating sample magnetometry (VSM; Lake Shore 7200 at 300 kVsm Rasht, Iran).

2.2 | Catalyst preparation

2.2.1 | Preparation of Fe_3O_4 magnetic nanoparticles

Firstly, a mixture of 2 g of $FeCl_2.4H_2O$, 5.2 g of $FeCl_3.6H_2O$ in 25 ml of deionized water containing 0.85 ml of HCl was added dropwise to a solution of 15 g of sodium hydroxide (NaOH) in 25 ml of deionized water with vigorous stirring to make a black solid product. Then the resultant mixture was heated in a water bath for 4 h at 80 °C. The black solid MNPs were isolated using an external magnet and washed with deionized water and ethanol three times and then dried at 80 °C for 10 h.[21]

2.2.2 | Preparation of $Fe_3O_4@SiO_2$ magnetic nanoparticles

300 mg Fe_3O_4-MNPs were dispersed in a mixture of 40 ml of EtOH and 4 ml of deionized water by ultrasonication for 15 min, followed by the addition of 5 ml of $NH_3.H_2O$ (28 wt.%) and 2 ml of tetraethylorthosilicate (TEOS). The mixture was stirred at 400 rpm for 12 h at room temperature. The products were collected by magnetic separation, washed with diluted hydrochloric acid and deionized water, and dried under vaccum.[22]

2.2.3 | Preparation of $Fe_3O_4@SiO_2–ZrCl_2$ magnetic nanoparticles

$Fe_3O_4@SiO_2$ (0.5 g) was dispersed in dry chloroform (15 ml) and sonicated for 30 min. Then, $ZrCl_4$ (0.5 g) was added to the dispersed solution of $Fe_3O_4@SiO_2$ at room temperature and stirred for 60 min. The suspended substance was separated using an external magnet and washed with chloroform (60 ml) and dried at room temperature.

Because that $Fe_3O_4@SiO_2–ZrCl_2$-MNPs procreates HCl in water, we have specified the concentration of the acquired acidic aqueous solution by titration. For this purpose 0.1 g $Fe_3O_4@SiO_2–ZrCl_2$-MNPs placed in conical flask. Then 10 ml of water and 3 drops of phenolphthalein was added and titrated with NaOH (0.1 M). The obtained results clarified that 0.1 g of catalyst manufactured a 0.5 mmol of H^+.

2.3 | Catalytic activity

2.3.1 | General procedure for the preparation of 1-(benzothiazolylamino)methyl-2-naphthol derivatives

A mixture of 2-aminobenzothiazole (1 mmol), β–naphtol (1 mmol), aldehyde (1 mmol) and $Fe_3O_4@SiO_2–ZrCl_2$-MNPs (0.030 g) was heated in an oil bath at 100 °C for an appropriate time [TLC: *n*-hexane: ethyl acetate (10:5)]. After completion of the reaction, the mixture was cooled to room temperature, acetone (10 ml) was added and the catalyst was removed using an external magnet. Evaporation of the solvent from mixture gave the solid residue which recrystallized from EtOH to afford the pure product. Finally Fe_3O_4@SiO_2–$ZrCl_2$-MNPs washed with chloroform and be used for the next run.

2.4 | Spectroscopic data

2.4.1 | 1-(benzo[d]thiazol-2-ylamino)(phenyl)methyl)naphthalene-2-ol (a)

^{1}H NMR (DMSO-d$_6$, 400 MHz): d = 6.96–7.93 (16H, m, 15H arom and 1H–CH), 8.67 (1H, s, NH), 10.11 (1H, s, OH); ^{13}C NMR (DMSO-d$_6$, 100 MHz): d = 53. 36, 118.02, 118.57, 118.81, 120.49, 120.84, 122.27, 123.58, 125.23, 126.04, 127.83, 128.34, 128.56, 129.28, 130.59, 132.12, 142.25, 151.96, 153.19, 166.33.

2.4.2 | 1-(benzo[d]thiazol-2-ylamino)(2-chloro phenyl)naphthalene-2-ol (b)

^{1}H NMR (DMSO-d$_6$, 500 MHz): d = 6.97–8.01 (15H, m, 14H arom and 1H–CH), 8.89 (1H, s, NH), 9.91 (1H, s, OH); ^{13}C NMR (DMSO-d$_6$, 125 MHz,): d = 52.59, 118.62, 119.47, 121.45, 121.68, 122.45, 122.68, 123.19, 123.69, 126.32, 126.60, 126.99, 129.13, 129.16, 129.49, 129.81, 131.16, 142.52, 153.20, 154.29, 167.17.

2.4.3 | 1-((benzo[d]thiazol-2-ylamino)(3-chlorophenyl)methyl)naphthalen-2-ol (c)

^{1}H NMR (DMSO-d$_6$, 400 MHz): d = 7.04–8.06 (15H, m, 14H arom and 1H–CH), 8.49 (1H, s, NH), 10.25 (1H, s, OH); ^{13}C NMR (DMSO-d$_6$, 100 MHz): d = 53.13, 118.53, 118.70, 118.82, 121.42, 121.61, 123.01, 123.87, 125.30, 125.94, 126.16, 126.66, 126.99, 129.01, 129.11, 130.35, 130.52, 131.29, 132.46, 133.32, 145.86, 152.40, 153.68, 166.62.

2.4.4 | 1-(benzo[d]thiazol-2-ylamino)(4-chloro phenyl)naphthalene-2-ol (d)

^{1}H NMR (DMSO-d$_6$, 400 MHz): d = 6.67–7.78 (15H, m, 14H arom and 1H–CH), 8.57 (1H, s, NH); 10.27 (1H, s, OH); ^{13}C NMR (DMSO-d$_6$, 100 MHz): 53.48, 117.71, 118.13, 118.96, 120.95, 121.12, 122.43, 122.47, 125.81, 126.82, 127.30, 127.78, 128.22, 129.54, 130.32, 134.52, 138.16, 151.61, 153.28, 166.89.

2.4.5 | 1-((benzo[d]thiazol-2-ylamino)(3-bromo-phenyl)methyl)naphthalen-2-ol (e)

^{1}H NMR (DMSO-d$_6$, 500 MHz): d = 7.01–7.89 (15H, m, 14H arom and 1H–CH), 8.83 (1H, s, NH), 10.21 (1H, s, OH); ^{13}C NMR (DMSO-d$_6$, 125 MHz): d = 53.08, 118.54, 118.71, 118.83, 121.41, 121.60, 122.02, 123.02, 123.90, 125.68, 125.93, 127.00, 129.03, 129.12, 129.55, 130.36, 130.82, 131.30, 132.46, 146.10, 152.44, 153.67, 166.59.

2.4.6 | 1-((benzo[d]thiazol-2-ylamino)(4-bromophenyl) methyl)naphthalen-2-ol (f)

^{1}H NMR (DMSO-d$_6$, 400 MHz): d = 7.04–7.85 (15H, m, 14H arom and 1H–CH), 8.84 (1H, s, NH), 10.21 (1H, s, OH); ^{13}C NMR (DMSO-d$_6$, 100 MHz): d = 53.1, 118.6, 118.7, 118.8, 119.6, 121.4, 121.6, 123.0, 124.1, 125.9, 126.9, 128.8, 129.1, 130.3, 131.3, 131.4, 132.5, 142.7, 152.5, 153.7, 166.6.

2.4.7 | 1-((benzo[d]thiazol-2-ylamino)(4-fluoro-phenyl)methyl)naphthalen-2-ol (g)

^{1}H NMR (DMSO-d$_6$, 500 MHz): d = 6.99–7.85 (15H, m, 14H arom and 1H–CH), 8.80 (1H, s, NH), 10.17 (1H, s, OH); ^{13}C NMR (DMSO-d$_6$, 125 MHz): d = 53.13, 115.21, 115.38, 118.55, 118.80, 118.84, 121.40, 121.57, 122.93, 124.11, 125.94, 126.80, 128.37, 128.43, 129.07, 130.18, 131.14, 132.50, 138.98, 152.28, 153.65, 160.25, 162.17, 166.71.

2.4.8 | 1-(benzo[d]thiazol-2-ylamino)(3-nitro phenyl)naphthalene-2-ol (h)

^{1}H NMR (DMSO-d$_6$, 400 MHz): d = 7.05–7.88 (15H, m, 14H arom and 1H–CH), 8.90 (1H, s, NH), 10.12 (1H, s, OH); ^{13}C NMR (DMSO-d$_6$, 100 MHz): d = 54.38, 116.12, 118.72, 119.41, 119.62, 119.82, 121.84, 121.91, 123.28, 126.43, 126.99, 129.41, 129.55, 130.27, 131.23, 133.12, 146.14, 152.48, 154.06, 167.22.

2.4.9 | 1-(benzo[d]thiazol-2-ylamino)(4-nitro phenyl)methyl)naphthalene-2-ol (i)

^{1}H NMR (DMSO-d$_6$, 400 MHz): d = 6.73–7.30 (15H, m, 14H arom and 1H–CH), 8.65 (1H, s, NH), 10.00 (1H, s, OH); ^{13}C NMR (DMSO-d$_6$, 100 MHz): d = 53.43, 117.81, 118.31, 118.58, 119.59, 120.41, 122.54, 123.24, 125.20, 125.33, 126.65, 127.32, 128.57, 128.98, 129.89, 145.99, 150.68, 153.38, 166.69.

2.4.10 | 1-((benzo[d]thiazol-2-ylamino)(3-methoxy-phenyl)methyl)naphthalen-2-ol (j)

^{1}H NMR (DMSO-d$_6$, 400 MHz): d = 3.65 (3H, s, OCH_3), 6.76–7.88 (15H, m, 14H arom and 1H–CH), 8.79 (1H, s, NH), 10.17 (1H, s, OH); ^{13}C NMR (DMSO-d$_6$, 100 MHz):

d = 53.43, 55.33, 111.11, 113.08, 118.56, 118.83, 118.94, 119.09, 121.35, 121.45, 122.88, 125.90, 126.68, 128.99, 129.07, 129.68, 130.01, 131.22, 132.58, 144.67, 152.54, 153.60, 159.60, 166.72.

2.4.11 | 1-(benzo[d]thiazol-2-ylamino)(4-methoxy phenyl)methyl)naphthalene-2-ol (k)

^1H NMR (DMSO-d_6, 400 MHz): d = 3.69 (3H, s, OCH_3), 6.69–7.97 (15H, m, 14H arom and 1H–CH), 8.51 (1H, s, NH), 10.53 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): d = 54.81, 67.47, 118.11, 119.03, 119.12, 120.58, 122.53, 125.52, 126.22, 127.42, 128.47, 128.79, 129.38, 130.22, 132.16, 133.56, 132.12, 142.25, 151.69, 153.35, 166.84.

2.4.12 | 1-(benzo[d]thiazol-2-ylamino)(p-tolyl)methyl)methyl)naphthalene-2-ol (l)

^1H NMR (DMSO-d_6, 400 MHz): d = 2.23 (3H, s, CH_3), 6.95–7.39 (15H, m, 14H arom and 1H–CH), 8.66 (1H, s, NH), 10.14 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): d = 20.60, 53.33, 118.00, 118.66, 118.92, 120.51, 120.85, 122.27, 125.26, 126.03, 128.34, 128.50, 128.60, 129.22, 130.55, 132.13, 135.17, 139.13, 151.97, 153.20, 166.39.

2.4.13 | 1-((benzo[d]thiazol-2-ylamino)(otolyl) methyl)naphthalen-2-ol (m)

^1H NMR (DMSO-d_6, 400 MHz): d = 2.10 (3H, s), 6.97–7.96 (15H, m, 14H arom and 1H–CH), 8.81 (1H, s, NH), 10.08 (1H, s,OH); ^{13}C NMR (DMSO-d_6, 100 MHz): d = 19.5, 53.1, 117.4, 118.5, 118.6, 121.3, 121.5, 123.0, 123.9, 125.9, 126.1, 126.7, 127.4, 127.5, 129.0, 129.1, 130.1, 130.7, 131.1, 133.0, 136.6, 139.8, 152.5, 153.7, 166.0.

2.4.14 | 1-((benzo[d]thiazol-2-ylamino)(2-methoxyphenyl)methyl)naphthalen-2-ol (n)

^1H NMR (DMSO-d_6, 400 MHz): d = 3.79 (3H, s, OCH_3), 6.83–7.73 (15H, m, 14H arom and 1H–CH), 8.16 (1H, s, NH), 10.47 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): d = 50.63, 55.82, 111.38, 118.40, 118.68, 119.03, 120.15, 121.14, 121.23, 122.60, 123.97, 125.79, 125.96, 126.33, 128.40, 128.71, 128.81, 129.45, 130.09, 131.06, 133.09, 152.79, 153.84, 157.20, 166.16.

3 | RESULTS AND DISCUSSION

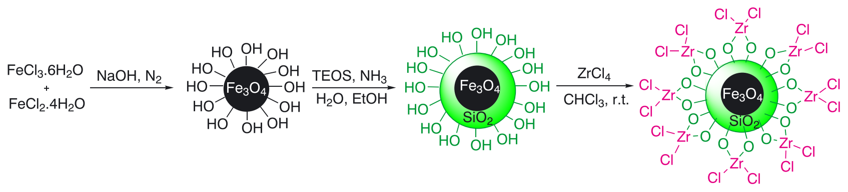
As we have mentioned previously, the focus of this article is on the preparation of $Fe_3O_4@SiO_2$–$ZrCl_2$ as a new and stable nano-magnetic derivative of zirconium (Scheme 1) and its applicability in the acceleration of the synthesis of 1-(benzothiazolylamino)methyl-2-naphthols as a model organic reaction.

3.1 | Characterization of $Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs

The synthesized catalyst was characterized by FT-IR, XRD, SEM, EDX and VSM techniques.

3.1.1 | FT-IR study

Successful coating of $ZrCl_4$ on the surface of $Fe_3O_4@SiO_2$ core could be proven by FT-IR spectroscopy. Figure 1 shows the FT-IR spectra of $ZrCl_4$, Fe_3O_4-MNPs, $Fe_3O_4@SiO_2$-MNPs and $Fe_3O4@SiO_2$–$ZrCl_2$-MNPs. In all of the spectra, the broad absorption around the 3350 cm^{-1} due to O-H stretching vibrations are observed with a strong intermolecular hydrogen bonding. FT-IR spectrum of Fe_3O_4-MNPs (Figure 1a) showed characteristic absorption at 590 and 443 cm^{-1} due to the Fe–O–Fe vibration related to the magnetite phase. After coating with a layer of SiO_2, FT-IR spectrum of $Fe_3O_4@SiO_2$-MNPs (Figure 1b) exhibits new peaks at 1090 and 960 cm^{-1} which are assigned to Si–O–Si and Si–OH stretching vibrations, respectively. Weak band at 475 cm^{-1} is attributable to the Si–O–Fe stretching vibrations of $Fe_3O_4@SiO_2$-MNPs. The $ZrCl_4$ is adsorbed on the $Fe_3O_4@SiO_2$ surface by Si–O–Zr bonds. This adsorption band cannot be seen in the FT-IR spectrum because it appears at around 982 cm^{-1} and therefore overlaps with the Si–OH vibration of $Fe_3O_4@SiO_2$ nanoparticles (Figure 1c).



SCHEME 1 Preparation of $Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs

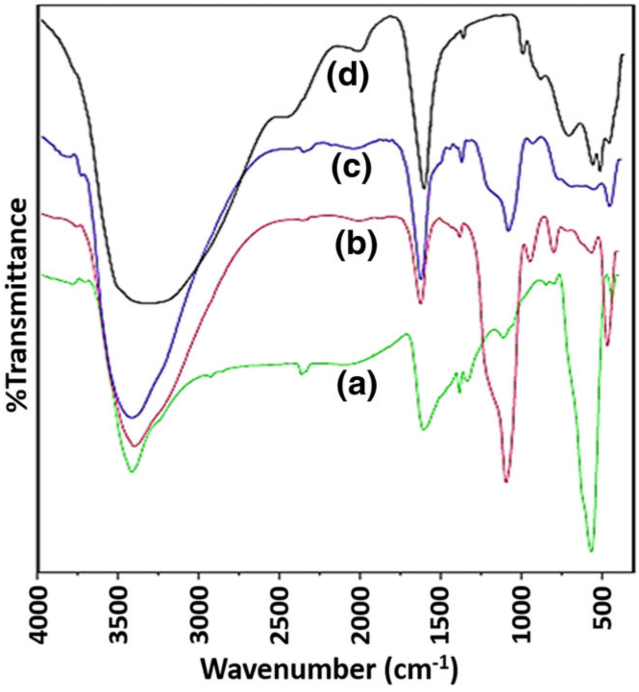


FIGURE 1 FT-IR spectra of (a) Fe_3O_4-MNPs and (b) Fe_3O_4@SiO_2-MNPs (c) Fe_3O_4@SiO_2–$ZrCl_2$-MNPs (d) $ZrCl_4$

3.1.2 | EDX study

The energy-dispersive Xray analysis (EDX) spectrum of Fe_3O_4@SiO_2–$ZrCl_2$-MNPs also indicates the presence of all expected elements (Fe, Si, Zr, Cl and O) and confirm the supporting of $ZrCl_4$ on Fe_3O_4@SiO_2-MNPs (Figure 2). The elemental compositions of Fe_3O_4@SiO_2–$ZrCl_2$ were found to be 43.49, 13.15, 13.92, 17.79 and 11.56% for Fe, O, Si, Zr and Cl respectively. Pursuant to EDX data, the molar ratio of Zr:Cl, was 1:2 and for this reason the possible structure of Fe_3O_4@SiO_2–$ZrCl_2$-MNPs was suggested as shown in Scheme 1.

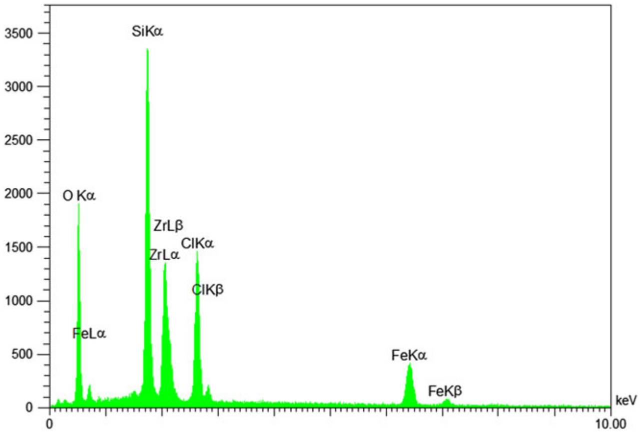


FIGURE 2 EDX data for Fe_3O_4@SiO_2–$ZrCl_2$-MNPs

3.1.3 | SEM study

The morphologies and structures of the synthesized Fe_3O_4@SiO_2-MNPs and Fe_3O_4@SiO_2–$ZrCl_2$-MNPs were investigated by the scanning electron microscopy (SEM). The SEM images indicate that Fe_3O_4@SiO_2-MNPs are spherical and their average size is about 70 ± 18 nm (Figure 3a). Atfer interaction with $ZrCl_4$, the typical core–shell structure of Fe_3O_4@SiO_2-MNPs can be observed and the average size increases to about 100 ± 20 nm (Figure 3b).

3.1.4 | XRD study

Figure 4 shows the X-ray diffraction pattern for pure Fe_3O_4-MNPs (Figure 4a), Fe_3O_4@SiO_2-MNPs (Figure 4b) and Fe_3O_4@SiO_2–$ZrCl_2$-MNPs (Figure 4c). In XRD patterns of Fe_3O_4-MNPs diffraction peaks with 2θ at 30.0°, 35.6°, 43.2°, 57.2°, and 62.5° are observed which confirm the structure of the magnetite material (JCPDS

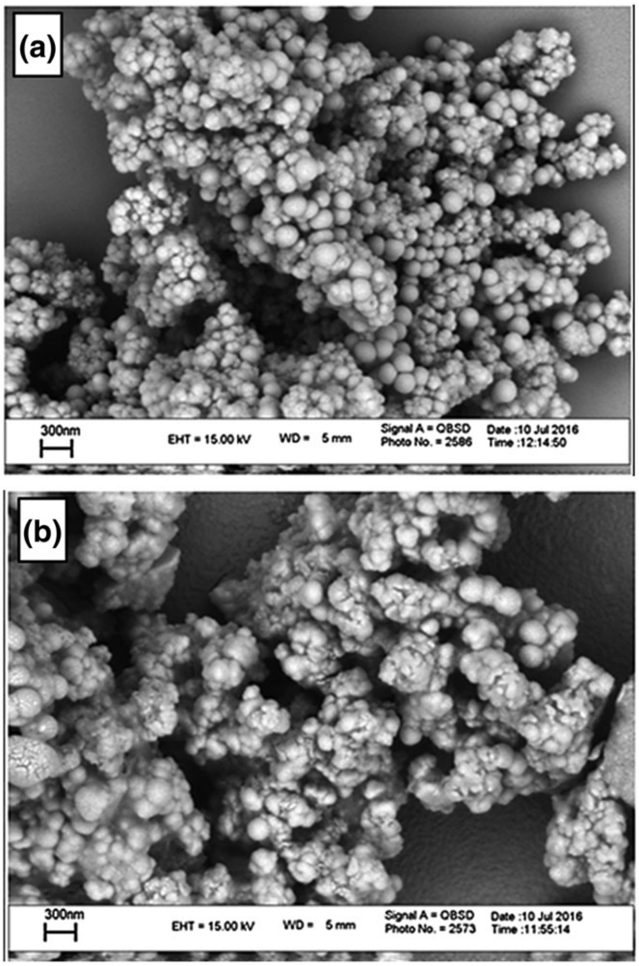


FIGURE 3 SEM images of (a) Fe_3O_4@SiO_2-MNPs (b) Fe_3O_4@SiO_2–$ZrCl_2$-MNPs

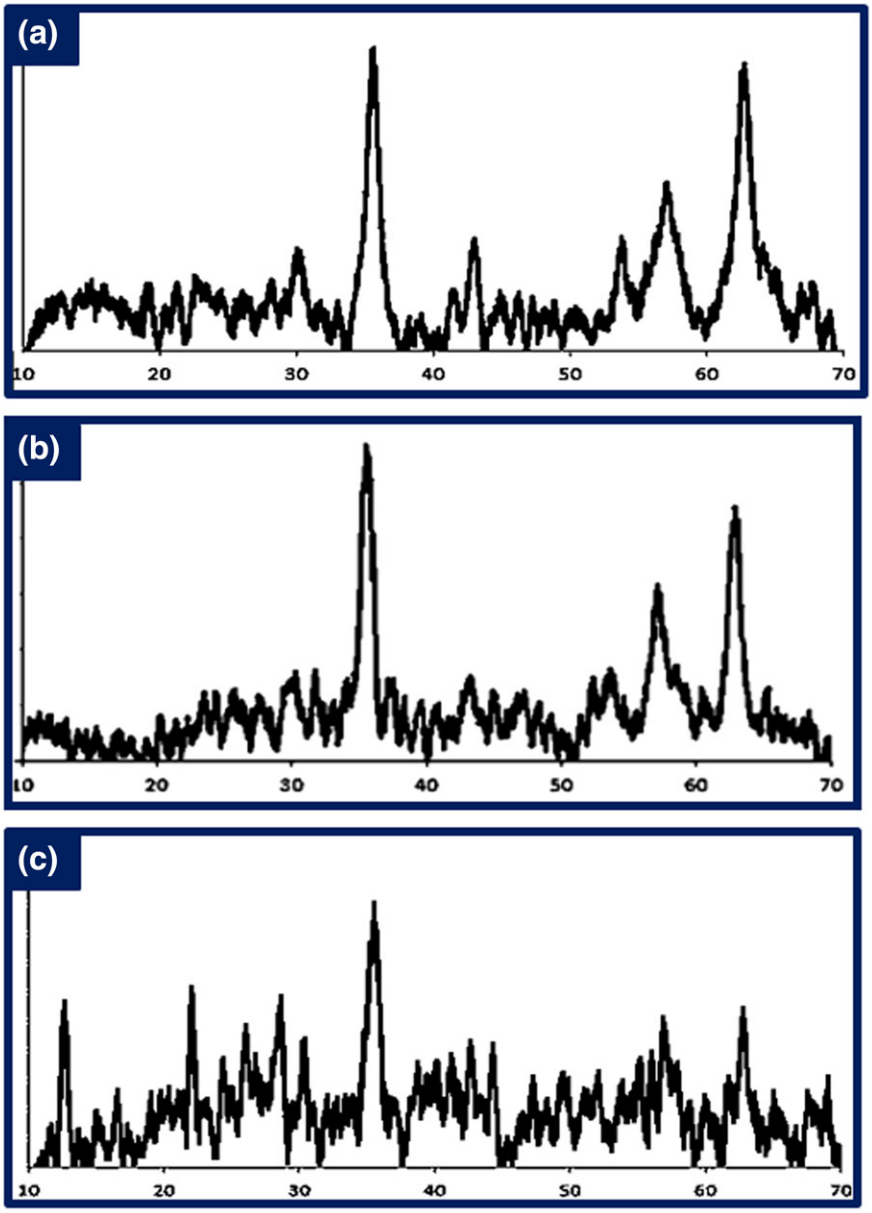


FIGURE 4 XRD pattern of Fe_3O_4-MNPs (a), $Fe_3O_4@SiO_2$-MNPs (b) and $Fe_3O_4@SiO_2–ZrCl_2$-MNPs (c)

card no. 79–0418). The characteristic peaks for pure Fe_3O_4-MNPs also observed for $Fe_3O_4@SiO_2$-MNPs. This revealed that the surface modification of Fe_3O_4 nanoparticles with SiO_2 did not lead to their phase change. In Figure 4c, the XRD pattern of $Fe_3O_4@SiO_2–ZrCl_2$-MNPs showed a much broader diffraction pattern and increased the noise to that of Figure 4b, which can be attributed to linking $ZrCl_2$ on the surface of $Fe_3O_4@SiO_2$.

3.1.5 | VSM study

The magnetization hysteresis for the synthesized $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$-$ZrCl_2$ nanoparticles are shown in Figure 5. The saturation magnetization (M_s) of $Fe_3O_4@SiO_2$ nanoparticles (curve a) was about 39.37 emu/g, which decreased to 15.82 emu/g after supporting $Fe_3O_4@SiO_2$ with $ZrCl_2$ (curve b). The obtained M_s value is lower than that of $Fe_3O_4@SiO_2$ nanoparticles, which confirms the presence of a diamagnetic outer shell ($ZrCl_2$). Such magnetizations are sufficient for performing magnetic separation.

3.2 | Application of $Fe_3O_4@SiO_2–ZrCl_2$-MNPs

The catalytic activity of $Fe_3O_4@SiO_2–ZrCl_2$-MNPs was explored in the synthesis of 1-(benzothiazolylamino)

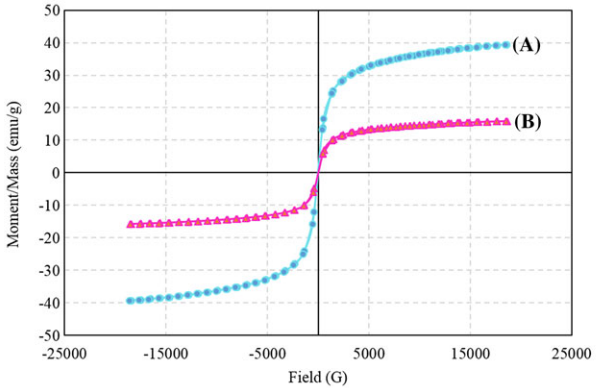


FIGURE 5 VSM pattern of $Fe_3O_4@SiO_2$-MNPs (a) and $Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs (b)

methyl-2-naphthols. In our primary study, the best reaction conditions were surveyed by using the reaction between 2-aminobenzothiazole (1 mmol), *β*–naphtol (1 mmol) and 4-chlorobenzaldehyde (1 mmol) as a model reaction. The best results were obtained under solvent-free conditions. In the next step, the effect of temperature on completion of the reaction in the absence of solvent was studied by performing the reaction at 60, 80, 100, and 110 °C. When the model reaction was carried out in 100 °C, the good yield was obtained in a short time. Moreover, the effect of the catalyst amounts on the reaction output was explored. The results showed that 0.030 g $Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs was enough to promote the reaction (Table 1, Scheme 2).

Using these optimized reaction conditions, a series of 1-(benzothiazolylamino)methyl-2-naphthols were synthesized in high yields by utilization of one-pot condensation of aromatic aldehydes, *β*-naphtol and 2-aminobenzothiazole in the presence of $Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs and the results are tabulated in Table 2. The obtained results showed that the reaction work well with aromatic aldehydes containing electron-donating and electron-withdrawing substituents on the aromatic ring. Because of the formation of a mixture of unidentified products the method is not recommended for aliphatic aldehydes.

The plausible mechanism of the reaction in the presence of $Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs is shown in Scheme 3. On the basis of this mechanism $Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs plays an important role in activating of aromatic aldehyde. Then activated aldehyde in reaction with *β*–naphtol produces the

TABLE 1 Optimization of three-component reaction of *β*–naphthol, 4-chlorobenzaldehyde, and 2-aminobenzothiazole under various conditions[a]

Entry	Catalyst (g)	Conditions	Time (min)	Yield (%)[b]
1	None	Solvent free, 70 °C	100	Trace
2	$Fe_3O_4@SiO_2$-MNPs (0.035)	Solvent-free, 100 °C	70	60
3	$Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs (0.035)	Solvent-free, 60 °C	50	75
4	$Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs (0.030)	Solvent-free, 80 °C	25	86
5	$Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs (0.030)	Solvent-free, 100 °C	7	95
6	$Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs (0.030)	Solvent-free, 110 °C	7	95
7	$Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs (0.025)	H_2O (3 ml), 70 °C	75	65
8	$Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs (0.025)	CH_3CN, 60 °C	70	50
9	$Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs (0.025)	EtOH, 70 °C	60	58
10	$Fe_3O_4@SiO_2$–$ZrCl_2$-MPs (0.025)	*n*-hexane, 60 °C	120	Trace

[a] Reaction conditions: *β*–naphthol (1 mmol), 2-aminobenzothiazole (1 mmol), 4-chlorobenzaldehyde (1 mmol) and $Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs under different condition.

[b] The yield refers to pure isolated product.

SCHEME 2 One-pot three-component reaction of 2-aminobenzothiazole, *β*–naphtol and different aromatic aldehydes catalyzed by $Fe_3O_4@SiO_2$–$ZrCl_2$-MNPs in the absence of solvent

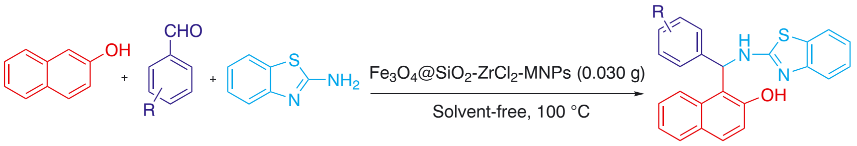
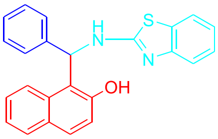
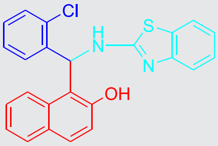
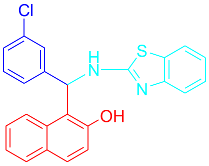
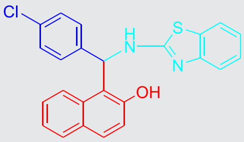
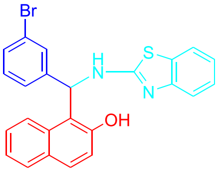
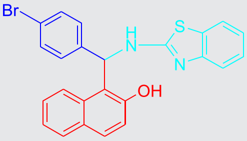
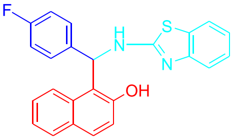
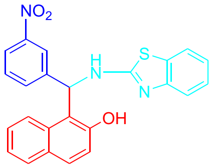
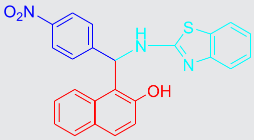
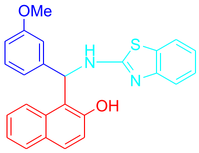
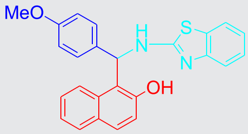
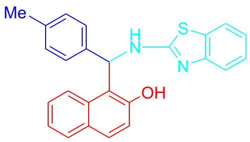
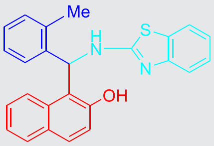
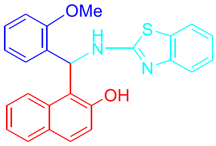


TABLE 2 Scope of catalytic activity of $Fe_3O_4@SiO_2–ZrCl_2$-MNPs in the synthesis of 1-(benzothiazolylamino)methyl-2-naphthol derivatives[a]

Entry	ArCHO	Product	Time (min)	Yield (%) [b,c]	Mp (°C)	
					Found	reported [ref.]
1		 (a)	15	90	204–205	202–203[23]
2		 (b)	12	92	188–190	189–190[23]
3		 (c)	10	90	193–194	193–195[26]
4		 (d)	7	95	210–211	209–210[23]
5		 (e)	10	90	203–204	200–202[24]
6		 (f)	9	93	198–199	200–202[26]
7		 (g)	10	90	186–187	188–189[23]

(Continues)

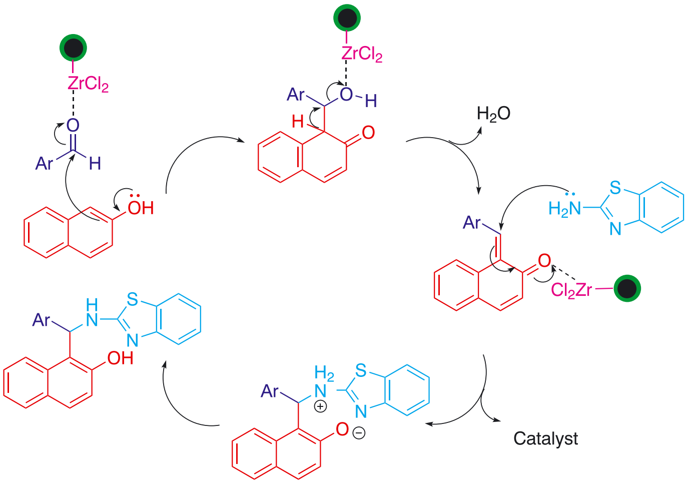
TABLE 2 (Continued)

Entry	ArCHO	Product	Time (min)	Yield (%) [b,c]	Mp (°C)	
					Found	reported [ref.]
8		 (h)	15	90	197–199	198–199[25]
9		 (i)	14	90	190–192	188–190[24]
10		 (j)	20	90	184–186	185–187[24]
11		 (k)	20	89	174–175	175–176[25]
12		 (l)	23	90	181–183	182–183[25]
13		 (m)	20	88	191–193	191–193[26]
14		 (n)	25	90	164–166	168–170[26]

[a] Reaction conditions: aldehyde (1 mmol), 2-aminobenzothiazole (1 mmol), β-naphtol (1 mmol) and $Fe_3O_4@SiO_2–ZrCl_2$-MNPs (0.030 g); reactions conducted under solvent-free conditions at 100 °C.

[b] Isolated yields.

[c] All the products are known compounds and are identified by the comparison of their spectroscopic data with the authentic samples.



SCHEME 3 Plausible mechanism for the formation of 1-(benzothiazolylamino)methyl-2-naphthol derivatives in the presence of $Fe_3O_4@SiO_2–ZrCl_2$-MNPs

FIGURE 6 Magnetic separation and reuse

intermediate (I) that subsequently undergoes elimination reaction to afford intermediate (II). This compound undergoes further addition with the 2-aminobenzothiazole to produce 1-(benzothiazolylamino) methyl-2-naphthol derivatived.

The reusability of the catalyst in the model reaction of the preparation of 1-(benzothiazolylamino) methyl-2-naphthol derivatives under the optimized reaction conditions was also investigated for at least four runs. For this purpose and because of the solubility of the products in acetone, after completion of the reaction, acetone (10 ml) was added, the mixture was stirred for 5 minute and then the catalyst was removed using an external magnet (Figure 6). In continue evaporation of the acetone from mixture gave the solid residue which recrystallized from EtOH to afford the pure product. Finally $Fe_3O_4@SiO_2–ZrCl_2$-MNPs was washed with chloroform which can be used for four successive runs without a considerable loss of its catalytic activity (Figure 7). The same FT-IR of the recovered catalyst with the freshly prepared one confirms the stability of the catalyst in reaction media.

In order to show the merit of the above mentioned method we further compared the efficiency of the prepared catalyst with some of those reported in the literature, for the reaction of *β*–naphtol, 2-aminobenzothiazole and 4-Chlorobenzaldehyde. As shown in Table 3, $Fe_3O_4@SiO_2–ZrCl_2$-MNPs can act as a useful catalyst and lead to an improved protocol in terms of compatibility with environment, yields of the products and reaction times compared to the other reported systems.

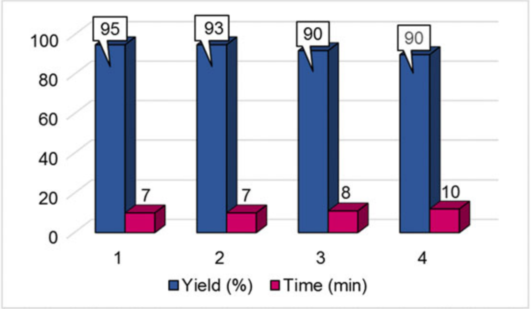


FIGURE 7 Recycling of the catalyst in the synthesis of 1-(benzothiazolylamino)methyl-2-naphthol derivatives

TABLE 3 Comparison of the results obtained in the presence of Fe_3O_4@SiO_2–$ZrCl_2$-MNPs under solvent-free conditions with other catalysts reported in the literature in the synthesis 1-(benzo[d]thiazol-2-ylamino)(4-chloro phenyl)naphthalene-2-ol

Entry	Catalyst	Conditions	Time (min)	Yield (%)	[ref.]
1	HPA (0.12 g)	Ultrasound, H_2O (3 ml), 45 °C	110	90	[27]
2	$NaHSO_4.H_2O$ (10 mol %)	Solvent-free, 100 °C	6	83	[26]
3	SDS (20 mol %)	H_2O (3 ml), 100 °C	60	88	[30]
4	NBS (0.1 mmol)	Neat, 60 °C	8	95	[28]
5	Triton X-100 (10 mol %)	H_2O (10 ml) 60 °C	72	95	[29]
6	$ZnCl_2$ (10 mol %)	Solvent-free, 70 °C	120	39	[26]
7	$YbCl_3$ (20 mol %)	H_2O (3 ml), 100 °C	6 h	40	[30]
8	$Sc(OTf)_3$ (20 mol %)	H_2O (3 ml), 100 °C	60	55	[30]
9	$Al(H_2PO_4)_3$ (10 mol %)	Solvent-free, 70 °C	53	62	[26]
10	$MgCl_2$ (10 mol %)	Solvent-free, 70 °C	19	71	[26]
11	LiCl (0.5 g, 71 mmol)	H_2O (3 ml), 90 °C	6 h	92	[25]
12	Fe_3O_4@SiO_2–$ZrCl_2$-MNPs (0.030 g)	Solvent free, 100 °C	7	95	This work

4 | CONCLUSION

In conclusion, in this study a simple method for the synthesis of the Fe_3O_4@SiO_2–$ZrCl_2$-MNPs as a magnetically heterogeneous nano catalyst was demonstrated. This catalyst can effectively promote the synthesis of 2′-aminobenzothiazolo-arylmethyl-2-naphthols through three-component condensation of various aromatic aldehydes, β-naphtol and 2-aminobenzothiazole under solvent-free conditions. The protocol is simple, efficient and eco-friendly because it has some advantages such as simple catalyst preparation, short reaction times, high yields, mild reaction conditions and use of a reusable catalyst.

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