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Synthesis of 2-aminothiazoles from methylcarbonyl compounds using a Fe_3O_4 nanoparticle-*N*-halo reagent catalytic system†

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An efficient protocol is developed for the synthesis of 2-aminothiazoles from unfunctionalized methylcarbonyl compounds using Fe_3O_4 nanoparticle-*N*-halo reagent catalytic systems. 1,3-dichloro-5,5-dimethylhydantoin (DCDMH), *N*-bromosuccinimide (NBS) and *N*-iodosuccinimide (NIS) as *N*-halo reagents were explored and the best results were obtained for DCDMH. Fe_3O_4 nanoparticle–DCDMH as an active, reusable, excellent, highly stable magnetic catalyst was used in this process. Advantages of this efficient method include greener and cleaner conditions, shorter reaction time, excellent yield of products, easy separation using a simple external magnetic field, low cost and operational simplicity.

1. Introduction

2-Aminothiazole as a member of the thiazole family has an important place in synthetic and medicinal chemistry (Fig. 1). According to the importance of 2-aminothiazole derivatives, various authors have tried to introduce improved or new methods for the synthesis of these compounds.[1–4]

The first report for the synthesis of 2-aminothiazoles was by Hantzsch and Weber.[5] To date, there are many methods for the preparation of 2-aminothiazole, where the most general method involves condensation of α-haloketones with thiourea in the presence of bromine/iodine or using various homogenous and heterogonous catalysts.[6–12] Recently, nanochitosan as catalyst have been developed for the preparation of 2-aminothiazoles *via* the reaction of ketones and thiourea using I_2 as an iodinating reagent.[12] At the beginning of previous study, the using of Fe_3O_4 nanoparticles (NPs) as a magnetic nanocatalyst were studied, but it was not stable in the presence of I_2. Fe_3O_4 NPs were decomposed and not recyclable in acidic conditions (HI produced during the reaction).

In recent years, magnetic nanostructures such as Fe_3O_4 NPs as ideal supports and nanocatalysts have attracted much attention in catalytic processes, due to their intriguing nanoscale dimensions, high activity, low cost, high surface area, nontoxicity, magnetically separation from the reaction media, and easy modification with other organic or inorganic species.[13,14] So, there is need to design a new method for the synthesis of 2-aminothiazoles using the magnetic nanocatalyst and a new halogenating agent. In this context, *N*-halo reagents 1,3-dichloro-5,5-dimethylhydantoin (DCDMH), *N*-bromosuccinimide (NBS) and *N*-iodosuccinimide (NIS) were tested using Fe_3O_4 NPs. One of the most important targets in this organic reaction was stability, activity, recoverability and reusability of the magnetic nanocatalyst.

N-halo reagents are a large group of substances that is widely used in organic synthesis and the preparation of natural compounds. These include *N*-halo amides, *N*-halo imides, *N*-halo amines, *N*-halo carbamates, *N*-halo sulphonamides, *N*-halo sulphonylmides, *N*-halo ureas, *etc.* In contrast to the halogens (X_2), *N*-halo reagents are easy to use because all of the halogens can be used. *N*-Halosuccinimides have some specific features that determine their broad application in organic synthesis.[15] Moreover, DCDMH is a cheap, efficient, and greener chlorinating reagent than other chlorinating agents such as chlorine, and *N*-chlorosuccinimide (NCS). DCDMH has been extensively used as a disinfectant for domestic and industrial water.[16] There are many protocols which using DCDMH as a mild and effective chlorinating agent.[17,18] To the best of our knowledge, there is no

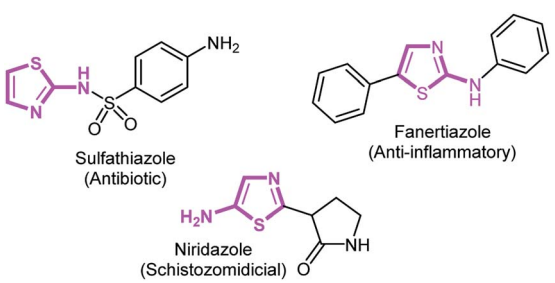

Fig. 1 Some drugs containing the 2-aminothiazole moiety.

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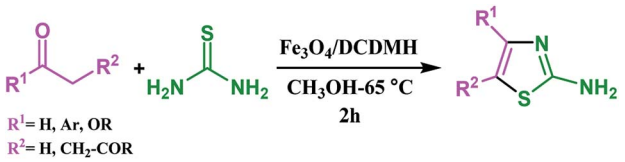


Scheme 1 The synthesis of 2-aminothiazole using chlorinating reagent.

protocol for the synthesis of 2-aminothiazole using organic chlorinating reagent.

In our continued works in this field,[12] here we introduce Fe_3O_4/DCDMH as new, stable and excellent catalytic system for the synthesis of various 2-aminothiazole derivatives in efficient yields (Scheme 1).

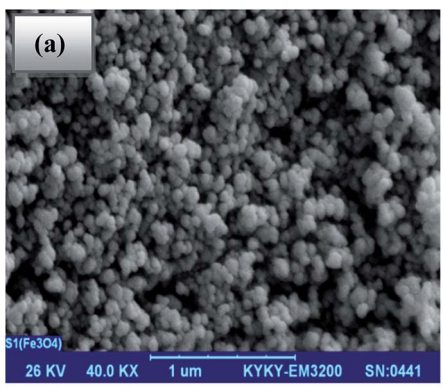
2. Results and discussion

Magnetic Fe_3O_4 NPs were prepared by the coprecipitation technique from the solution of ferrous/ferric mixed salt-solution in alkaline condition. The Fe_3O_4 NPs was characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and vibrating-sample magnetometer (VSM).

Fig. 2 shows the SEM and TEM photographs of Fe_3O_4 NPs. The results showed that the average size of NPs was approximately 10 nm, and the particles are nearly spherical shaped, uniform and monodispersed. The magnetization curves obtained by VSM at room temperature for the Fe_3O_4 NPs are shown in Fig. 3. One can see that the saturation magnetization (M_s) value of the magnetite NPs is 62.76 emu g^{-1} from the magnetization curve.

Fig. 4 presents the XRD-diffraction patterns of the magnetic Fe_3O_4 NPs. The position and relative intensities of all peaks confirm well with standard XRD pattern of Fe_3O_4 (JCPDS card no. 01-1111) indicating retention of the crystalline cubic spinel structure of Fe_3O_4 NPs. The XRD patterns of the particles show seven characteristic peaks reveal a cubic iron oxide phrase (2θ = 30.66, 36.06, 43.72, 54.22, 57.68, 63.18, 74.85). These are related to their corresponding indices (2 2 0), (3 1 1), (4 0 0), (3 3 1), (4 2 2), (5 1 1) and (5 3 1) respectively. The crystallographic parameters calculated using software provided by Panalytical company (Holland) are: $a = b = c$= 8.3941 Å, $\alpha = \beta = \gamma$ = 90.0000°, they are indexed to the cubic spinel phase of Fe_3O_4 NPs.

Our investigation was led by testing thiourea and methylcarbonyl as precursors and Fe_3O_4–I_2 as promising catalytic system. When the reaction was run with 0.5 equiv. of acetophenone, 0.5 equiv. of thiourea, and 1.5 equiv. of iodine in the presence of 10 mol% of Fe_3O_4 NPs as the catalyst, the desired product was obtained in high yield. However, surprisingly the catalyst could not be recovered from the reaction vessel. With regard to the production of HI in the reaction process, it was



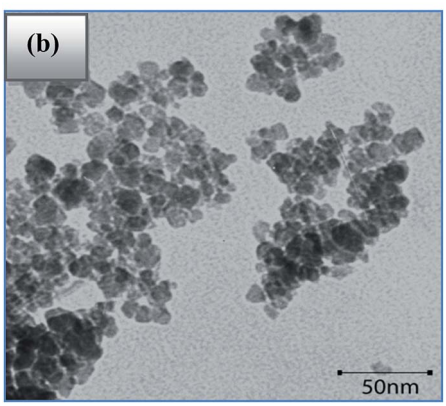


Fig. 2 (a) SEM and (b) TEM photographs of Fe_3O_4 NPs.

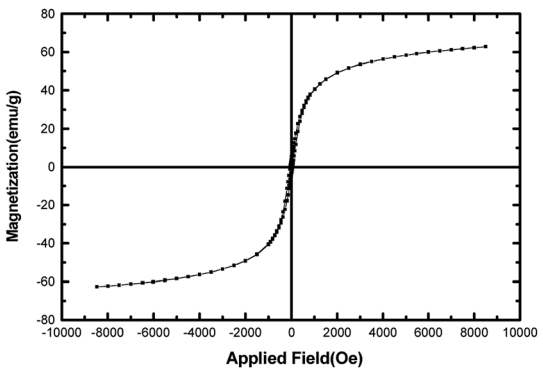


Fig. 3 VSM magnetization curve of Fe_3O_4 NPs.

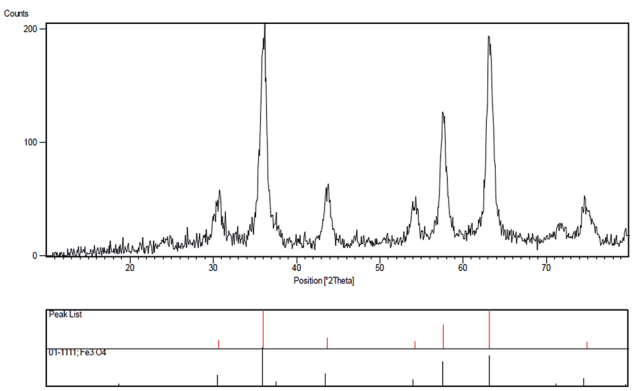


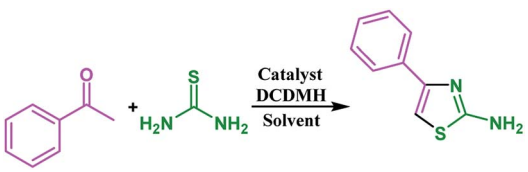
Fig. 4 X-ray powder diffraction (XRD) pattern of Fe_3O_4 NPs.

proposed Fe_3O_4 NPs convert to FeI_3 in the reaction media. By considering this issue (the damaging effect of produced HX from X_2 on metal oxides), the *N*-halo reagents were used as milder halogenating agents to prevent degradation of the catalyst.

DCDMH (a cheaper and more achievable alternative for NCS) as *N*-halo reagent was selected for finding optimal reaction conditions for synthesis of 2-aminothiazole through C_{sp^3}–H bond functionalization of acetophenone (Table 1). The results were promising and there was no damaging effect on the catalyst.

In the first step, the simultaneous use of thiourea and methylcarbonyl for the synthesis of 2-aminothiazole was explored using SiO_2 as the catalyst in CH_3OH at 65 °C which resulted in 20% yield (entry 1). To improve the efficiency of the reaction, the addition of thiourea was postponed. For this reason, it was allowed to the chlorination of methylcarbonyl substrate be occurred, and then thiourea was added to the reaction mixture. When this reaction was carried out in CH_3OH at 65 °C for 2 h, using 5 mol% SiO_2 as the catalyst, in the presence of DCDMH (0.5 eq.), good amounts of 2-aminothiazole were obtained (entry 3). Inspired by the above results, the various catalysts were surveyed and the best result was obtained for Fe_3O_4 NPs (entry 5). In addition to the catalyst, different solvents and the amount of catalyst were then evaluated. Methanol was chosen as an efficient solvent. It was observed that 5 mol% of catalyst was sufficient to carry out the reaction (entry 5).

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Yield (%)
1	—	CH_3OH	30	20
2	SiO_2 (5)	CH_3OH	30	63
3	SiO_2 (5)	CH_3OH	65	75
4	Al_2O_3 (5)	CH_3OH	65	70
5	Fe_3O_4 NPs (5)	CH_3OH	65	93
6	CuO NPs (10)[21]	CH_3OH	65	82
7	Starch NPs (5)[22]	CH_3OH	65	80
8	MMT-K10 (5)	CH_3OH	65	82
9	Fe_3O_4 NPs (5)	H_2O	65	50
10	Fe_3O_4 NPs (5)	EtOH	65	60
11	Fe_3O_4 NPs (5)	DMSO	65	20
12	Fe_3O_4 NPs (5)	EtOAc	65	15
13	Fe_3O_4 NPs (5)	CH_3CN	65	15
14	Fe_3O_4 NPs (1)	CH_3OH	65	83
15	Fe_3O_4 NPs (3)	CH_3OH	65	85
16	Fe_3O_4 NPs (10)	CH_3OH	65	80
17	Fe_3O_4 NPs (20)	CH_3OH	65	75

[a] Reaction condition: acetophenone (1 eq.), thiourea (1 eq.), DCDMH (1.5 eq.), catalyst, and solvent (2 mL) stirred at 65 °C for 2 h.

To compare the type of halogen and its effect on the reaction process and yield, and to choose the best condition and reagent, a series of experiments were carried out (Table 2). For this purpose, DCDMH, NIS, NBS as the *N*-halo reagents were selected. Based on the previous results and to achieve a correct comparison, CH_3OH and Fe_3O_4 were chosen as model solvent and catalyst, respectively. All reactions were performed at 30 (RT) and 65 °C.

As expected, in the cases of NBS and NIS like DCDMH, using catalyst or reflux condition showed better results than the catalyst-free conditions or room temperature, respectively. It was found that in the comparable circumstances, DCDMH showed the best performance in the preparation of 2-aminothiazole. Hence, it was decided to use Fe_3O_4–DCDMH as stable and effective system for the synthesis of various 2-aminothiazole derivatives. The obtained optimized reaction conditions (Table 2, entry 12) were used for variety of methylcarbonyl substrates such as aldehyde, aromatic ketone, β-diketone, β-ketoester and results are summarized in Table 3.

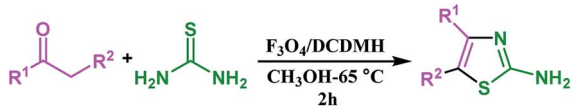
As expected the substrate containing more acidic hydrogen (like β-diketone, β-ketoester, and aldehyde; entries 6–10), showed better results than aromatic ketones (entries 1–5). The more acidic substrate, the more enol forms, and therefore produce more chlorinated product. 2-Hydroxy acetophenone is less efficient than 4-hydroxyacetophenone due to the intramolecular hydrogen bond, and steric hindrance (entries 2 and

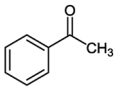
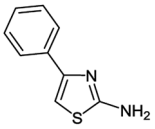
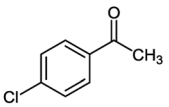
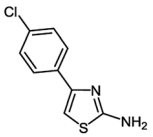
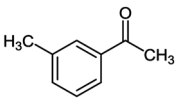
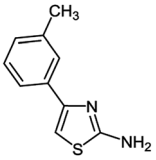
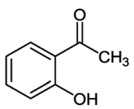
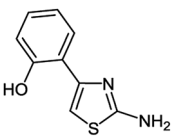
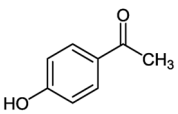
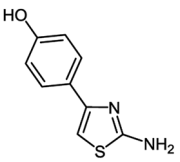
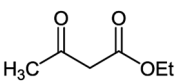
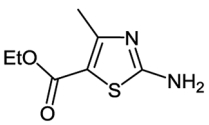
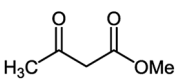
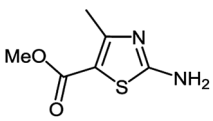
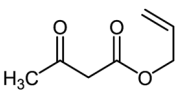
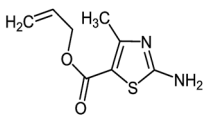
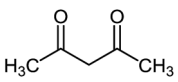
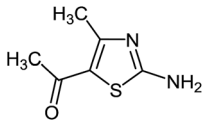
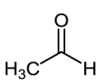
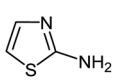
Table 2 Comparison of the halogenating reagents (R_2N-X)[a]

Entry	Catalyst	Reagent	Solvent	Temperature (°C)	Yield (%)
1	—	NIS	CH_3OH	RT	Trace
2	Fe_3O_4 NPs	NIS	CH_3OH	RT	10
3	—	NIS	CH_3OH	65	15
4	Fe_3O_4 NPs	NIS	CH_3OH	65	20
5	—	NBS	CH_3OH	RT	20
6	Fe_3O_4 NPs	NBS	CH_3OH	RT	25
7	—	NBS	CH_3OH	65	50
8	Fe_3O_4 NPs	NBS	CH_3OH	65	70
9	—	DCDMH	CH_3OH	RT	20
10	Fe_3O_4 NPs	DCDMH	CH_3OH	RT	25
11	—	DCDMH	CH_3OH	65	60
12	Fe_3O_4 NPs	DCDMH	CH_3OH	65	93

[a] Reaction condition: acetophenone (1 eq.), thiourea (1 eq.), R_2N-X (1.5 eq.), Fe_3O_4 (5 mol%), and CH_3OH (2 mL) stirred at 65 °C for 2 h.

Table 3 Fe_3O_4 NPs catalyzed synthesis of 2-aminothiazoles[a]



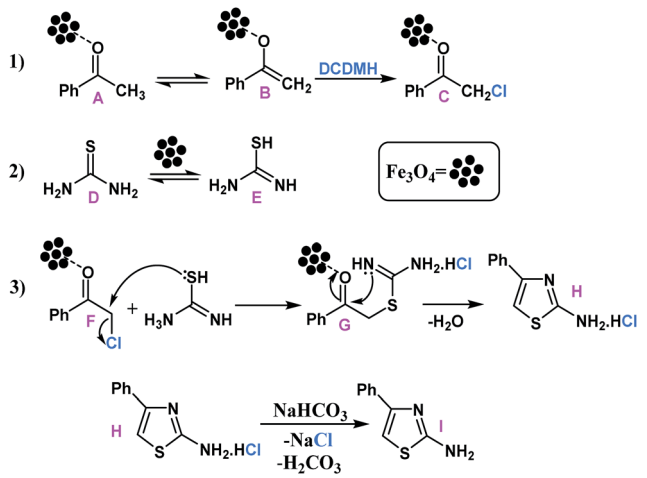
Entry	Methylketone	Product	TON (TOF)	Yield (%)
1			1636 (818)	93
2			1860 (930)	89
3			1672 (836)	88
4			(816)	85
5			1748 (874)	91
6			1822 (911)	98
7			1702 (851)	99
8			1980 (990)	98
9			1544 (772)	99
10			980 (490)	98

[a] Reaction condition: acetophenone (1 eq.), thiourea (1 eq.), DCDMH (1.5 eq.), Fe_3O_4 (5 mol%), and CH_3OH (2 mL) stirred at 65 °C for 2 h.

4). The ketone substrate containing electron donor groups (like Me and OH, entry 3, 4, and 5), showed weaker results than simple acetophenone (entry 1). Excellent selectivity was observed (over 99%) and there was no any by-product (unwanted products).

A proposed mechanism for the production of 2-aminothiazoles is presented in Scheme 2.[12b] Fe_3O_4 NPs as the catalyst can activate the acetophenone to enolize through coordination to the oxygen atom of carbonyl group and accelerate the chlorination of α-position by DCDMH (C). Furthermore, the catalyst can participate in the conversion of D to E. The chlorinated acetophenone react with carbamimidothioic acid species (E) and result in 2-oxo-2-phenylethyl carbamimidothioate intermediate (G). The catalyst participates in this nucleophilic substitution by coordination to the oxygen of carbonyl group. Finally, Fe_3O_4 NPs promoted dehydrogenation of G and followed by the neutralization of H gives 2-aminothiazoles (I).

The nanocatalyst could be magnetically recovered from the reaction mixture during work-up procedure. The reusability of the nanocatalyst was examined for the model reaction. The recovered nanocatalyst was reused for 5 consecutive cycles without any appreciable loss in its efficiency (Fig. 5). Moreover, the SEM micrograph in Fig. 6 display that the morphology of the recovered NPs is stable after reaction. The main reason for the decrease of catalytic activity is the agglomeration of NPs. As the SEM images (after the reaction) are clear, the particles stuck



Scheme 2 Plausible mechanism of the preparation of 2-aminothiazole.

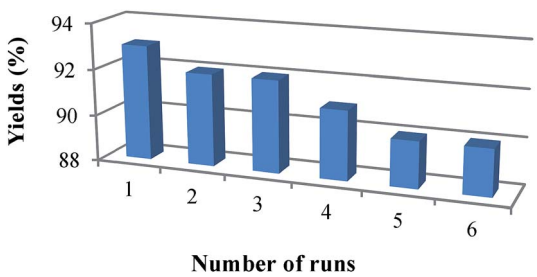


Fig. 5 Recovery cycles of the nanocatalyst.

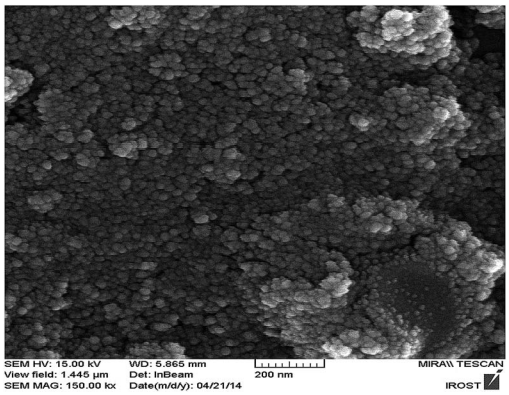


Fig. 6 SEM image of Fe_3O_4 NPs after the reaction.

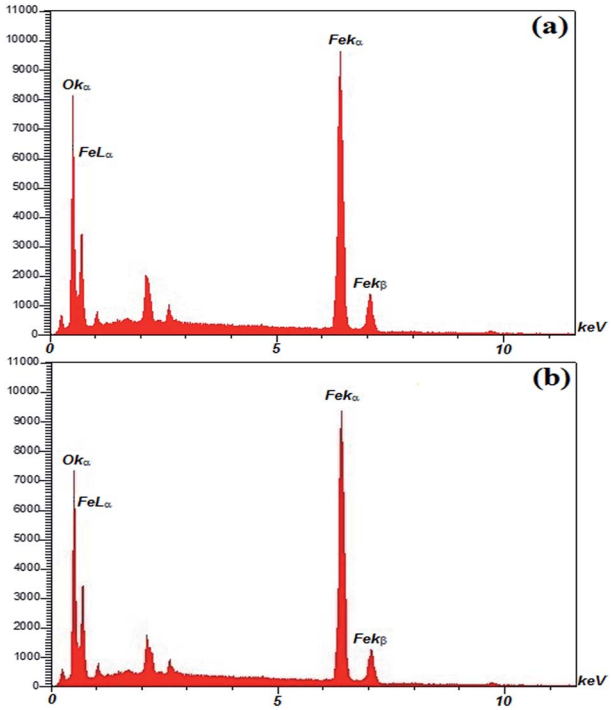


Fig. 7 EDS of Fe_3O_4 NPs before (a) and after the reaction (b).

together and their average size has increased. Increasing the average size of particles decrease the specific surface area and thus reduce the efficiency of the reaction. The EDS (energy-dispersive X-ray spectroscopy) show that the chemical structure of the catalyst has not changed after the reaction (Fig. 7).

3. Experimental

3.1. Chemicals and apparatus

All chemicals were purchased from the Merck, Aldrich and Sigma Chemical Companies. FT-IR spectra were obtained with KBr pellets in the range 400–4000 cm^{-1} with a Perkin-Elmer 550 spectrometer. The magnetic measurement of samples was carried out in a vibrating sample magnetometer (VSM) (4 inch, NDKF, Kashan, Iran) at room temperature. Nanostructures were

characterized using a Holland Philips Xpert X-ray diffraction (XRD) diffractometer (CuK, radiation, $\lambda = 0.154056$ nm), at a scanning speed of 2° min^{-1} from 10° to 100° (2θ). The surface morphology of samples was characterized by scanning electron microscopy (SEM; EM3200) and transmission electron microscopy (TEM; Philips CM10).

3.2. Procedure for preparation of Fe_3O_4 NPs

Typically, 10 mmol of $FeCl_3 \cdot 6H_2O$ and 5 mmol of $FeCl_2 \cdot 4H_2O$ were dissolved in 35 mL of distilled water in a round bottom flask (250 mL) under Ar atmosphere for 1 h. In the next step, 5 mL of NaOH (10 M) was added into the solution within 30 min with vigorous mechanical stirring. After one hour, the resultant black dispersion was heated to 85 °C for 1 h. The black precipitate formed was isolated by magnetic decantation, exhaustively washed with double-distilled water until neutrality, and further washed twice with ethanol and dried at 60 °C in vacuum[19].

3.3. General procedure for the synthesis of 2-aminothiazoles

A mixture of methylcarbonyl (0.5 equiv.), DCDMH (0.5 equiv.) and Fe_3O_4 NPs in CH_3OH (2 mL) at 65 °C was stirred for 1 h. Then thiourea (0.5 equiv.) was added to the mixture and was stirred for 1 h. After the completion of reaction, reaction mixture was filtered off and the filtrate was washed by sodium bicarbonate solution and brine and extracted with ethyl acetate. The organic layer was separated followed by drying using anhydrous sodium sulfate and concentrated under reduced pressure to afford the precipitate. The solid obtained was crystallized from a mixture of water and ethanol.

3.4. Spectroscopic data of representative products

3.4.1. Thiazole-2-amine. Pale yellow powder; mp = 89–90; yield: 98 mg (98%); IR (KBr): 3410, 3289, 3084, 1629, 1521, 1491, 698 (cm^{-1}); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 6.52$ (d, $J = 3.7$ Hz, 1H), 6.75 (s, 2H, NH_2, D_2O exchangeable), 6.90 (d, $J = 3.7$ Hz, 1H).

3.4.2. 4-Phenylthiazol-2-amine. Yellow crystal, mp = 151–153; yield: 163 mg (93%); IR (KBr): 3424, 3256, 2856, 1623, 1519, 1336, 728 (cm^{-1}); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 6.92$ (s, 1H, thiazole), 7.22 (s, 2H, NH_2, D_2O exchangeable), 7.32 (t, $J = 7.9$ Hz, 1H, Ar-H), 7.69 (t, $J = 7.9$ Hz, 2H, Ar-H), 7.71 (m, $J = 7.05$ Hz, 2H, Ar-H).

3.4.3. 5-Acetyl-4-methybhiazole-2-amin. White crystal; mp = 215–217; yield: 154 mg (99%); IR (KBr): 3350, 2920, 1680 (cm^{-1}); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.21–2.29 (2s, 6H, $2CH_3$). 5.32 (s, 2H, NH_2).

3.4.4. 4-(4-Chlorophenyl)thiazol-2-amine. White crystal; mp = 160–162; yield: 186 mg (89%); IR (KBr): 3426, 2924, 1628, 1570, 1495, 744 (cm^{-1}); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 7.24$ (s, 1H, thiazole, D_2O exchangeable), 7.55 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.73 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.43 (s, 2H, NH_2, D_2O exchangeable).

3.4.5. 4-(3-Methylphenyl)thiazol-2-amine. Yellow powder, mp = 88–91, yield; 167 mg (88%); IR (KBr): 3425, 2919, 1605, 1521, 1468, 714 (cm^{-1}); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 2.48$ (s, 3H, CH_3), 6.95 (s, 1H, thiazole), 7.02 (s, 2H, NH_2), 7.05 (d, $J =$ 7.8 Hz, 1H, Ar-H), 7.22 (t, 1H, $J = 7.9$ Hz, Ar-H), 7.56 (d, $J = 7.9$ Hz, 1H, Ar-H), 7.60 (s, 1H, Ar-H).

3.4.6. 4-(2-Hydroxyphenyl)thiazol-2-amine. Yellow powder; mp = 138–139; yield: 163 mg (85%); IR (KBr): 3246, 2064, 1635, 1569, 1461, 743 (cm^{-1}); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 6.88$ (t, 1H, $J = 7.6$ Hz, 1H, ArH), 6.89 (d, $J = 8.24$ Hz, 1H, ArH), 7.16 (s, 1H, thiazole, D_2O exchangeable), 7.24 (t, $J = 8.24$ Hz, 1H, ArH), 7.52 (d, $J = 7.6$ Hz, 1H, ArH), 8.70 (s, 1H, OH, D_2O exchangeable).

3.4.7. 4-(4-Hydroxyphenyl)thiazol-2-amine. Yellow powder; mp = 198–200; yield: 174 mg (91%) IR (KBr): 3447, 2921, 1610, 1504, 1435, 834 (cm^{-1}); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 6.69$ (d, $J = 8.5$ Hz, 2H, Ar-H), 6.70 (s, 1H, thiazole), 6.95 (d, 2H, NH_2), 7.58 (d, $J = 8.5$ Hz, 2H, Ar-H), 9.50 (s, OH).

3.4.8. 4-Methyl-5(ethoxycarbonyl)thiazol-2-amine. White powder, mp = 177–179; yield: 182 mg (98%); IR (KBr): 3374, 3085, 1674, 1515, 1373, 756 (cm^{-1}); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 1.21$ (t, $J = 7.1$, 3H, CH_3), 2.48 (s, 3H, CH_3), 4.12 (q, 2H, CH_2), 7.71 (S, 2H, NH_2).

3.4.9. 4-Methyl-5(methoxycarbonyl)thiazol-2-amine. White powder; mp = 225–226; yield: 170 mg (99%); IR (KBr): 3374, 3085, 1682, 1644, 1504, 1320, 758 (cm^{-1}); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 2.57$ (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 6.12 (S, 2H, NH_2).

3.4.10. 4-Methyl-5(allyloxycarbonyl)thiazol-2-amine. White powder; mp = 148–149; yield: 194 mg (98%); IR (KBr): 3375, 3083, 1672, 1514, 1374, 754 (cm^{-1}); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 2.38$ (s, 3H, CH_3), 4.15 (d, $J = 5.4$ Hz, 2H, CH_2), 5.26 (d, 1H, CH), 7.30 (d, 1H, CH), 5.92 (m, 1H, CH), 7.52 (s, 2H, NH_2).

4. Conclusions

In summary, we have demonstrated an efficient, simple, efficient and sable catalyst-*N*-halo reagent for the synthesis of 2-amintothiazole. We compared DCDMH, NBS, and NIS as *N*-halo reagent for the synthesis of 2-aminothiazole and observed that DCDMH showed best results. This method is quick, and avoids the use of toxic or heavy metal, high temperature, and leads to improved product yields and easy work-up procedure.

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References

1 W. L. Wang, D. Y. Yao, M. Gu, M. Z. Fan, J. Y. Li, Y. C. Xing and F. J. Nan, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 5284–5287.
2 B. A. Fink, D. S. Mortensen, S. R. Stauffer, Z. D. Aron and J. A. Katzenellenbogen, *Chem. Biol.*, 1999, **6**, 205–219.

3 M. D. McReynolds, J. M. Dougherty and P. R. Hanson, *Chem. Rev.*, 2004, **104**, 2239–2258.
4 J. V. Metzger, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees, Pergamon, New York, NY, 1984, vol. 6.
5 A. Hantzsch and J. H. Weber, *Ber. Dtsch. Chem. Ges.*, 1887, **20**, 3118–3132.
6 J. Zhao, J. Xu, J. Chen, M. He and X. Wang, *Tetrahedron*, 2015, **71**, 539–543.
7 J. Noei and A. R. Khosropour, *Ultrason. Sonochem.*, 2009, **16**, 711–717.
8 F. M. Pedro, S. Hirner and F. E. Kühn, *Tetrahedron Lett.*, 2005, **46**, 7777–7779.
9 H. Karade, M. Sathe and M. P. Kaushik, *Catal. Commun.*, 2007, **8**, 741–746.
10 S. M. Ghodse and V. N. Telvekar, *Tetrahedron Lett.*, 2015, **56**, 472–474.
11 T. Keshari, R. Kapoorr and L. D. S. Yadav, *Tetrahedron Lett.*, 2015, **56**, 5623–5627.
12 (*a*) J. Safari, Z. Abedi-Jazini, Z. Zarnegar and M. Sadeghi, *Catal. Commun.*, 2016, **77**, 108–112; (*b*) J. Safari, Z. Abedi-Jazini, Z. Zarnegar and M. Sadeghi, *J. Nanopart. Res.*, 2015, **17**, 495.
13 N. Azgomi and M. Mokhtary, *J. Mol. Catal. A: Chem.*, 2015, **398**, 58–64.
14 Z. Zarnegar and J. Safari, *RSC Adv.*, 2013, **3**, 26094–26101.
15 V. Koval, *Russ. J. Org. Chem.*, 2002, **38**, 301–337.
16 (*a*) T. Mitchenko, P. Stender and N. Makarova, *Solvent Extr. Ion Exch.*, 1998, **16**, 75–149; (*b*) Z. Rao, X. Zhang and W. R. G. Baeyens, *Talanta*, 2002, **57**, 993–998.
17 H. Karade, M. Sathe and M. P. Kaushik, *Catal. Commun.*, 2007, **8**, 741–746.
18 Z. Xu, D. Zhang and X. Zou, *Synth. Commun.*, 2006, **36**, 255–258.
19 J. Safari, Z. Zarnegar and M. Heydarian, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 1332–1338.