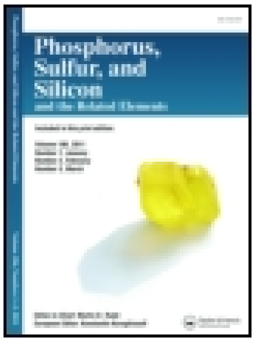

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Fe_3O_4 MNPs-DETA/Benzyl-Br_3: A new magnetically reusable catalyst for the oxidative coupling of thiols

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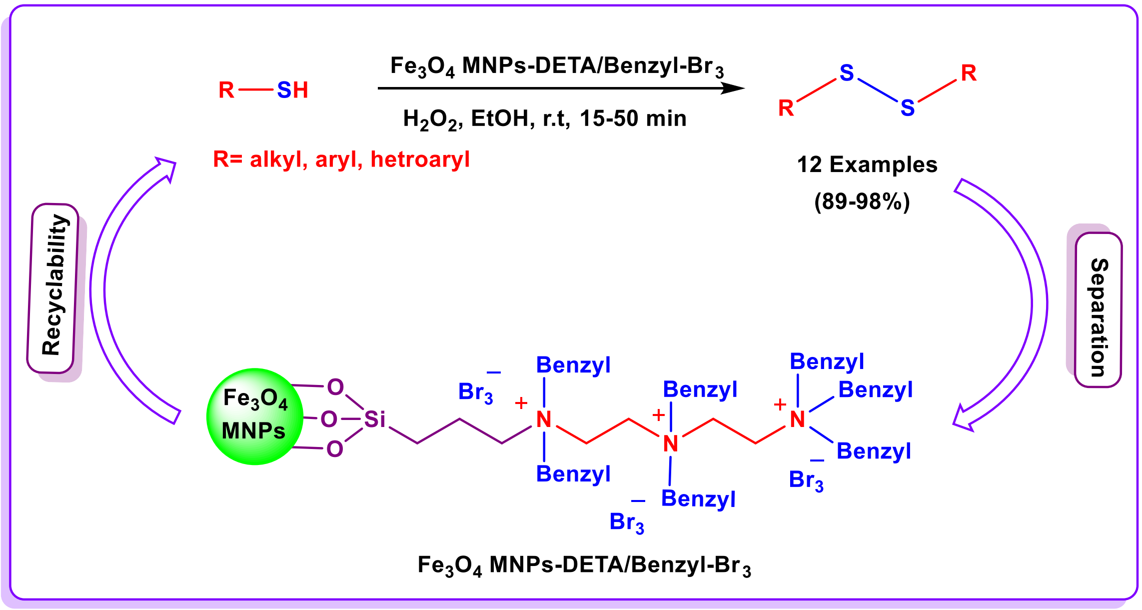
Abstract

We report a new strategy to immobilize a bromine source on the surface of magnetic Fe_3O_4 nanoparticles (Fe_3O_4 MNPs-DETA/Benzyl-Br_3) leading to a magnetically recoverable catalyst, which exhibits high catalytic efficiency in oxidative coupling of thiols to the disulfides (89-98%). The Fe_3O_4 MNPs-DETA/Benzyl-Br_3 catalyst was fabricated by anchoring 3-chloropropyltrimethoxysilane (CPTMS) on magnetic Fe_3O_4 nanoparticles, followed with *N*-benzylation and reaction with bromine in tetrachloridecarbon. The resulting nanocomposite was analyzed by a series of characterization techniques such as FT-IR, SEM, TGA, VSM and XRD. The catalyst could be recovered via magnetic attraction and could be recycled at least 5 times without appreciable decrease in activity.



Key words

Fe_3O_4 MNPs-DETA/Benzyl-Br_3, Bromine source, Oxidative coupling of thiols, Magnetically separation, Disulfides

Introduction

Oxidative coupling of thiols to the disulfides is a key and valuable transformation in organic synthesis, because compounds containing S-S bond (disulfides) are prevalent in nature and present in the structural backbones of a broad spectrum of biological and pharmaceutical active molecules [1-4]. From the medicinal point of view, interest in disulfides has amplified when researchers found that compounds containing the S-S bond play an important role in the stabilization of the folded form of proteins [5-6]. The biological and pharmaceutical activities of disulfide derivatives have encouraged organic chemists to develop new, efficient and green catalytic systems for their preparation.

During the last decade, a diverse range of reagents, catalysts and oxidants have been reported for the oxidative coupling of thiols to the disulfides [1-2].

In recent times, magnetic separation have been received profound attention in modern research in catalysis, because catalysts immobilized on magnetic nanoparticles can be readily separated from reaction medium by using an external magnet, without the need for filtration, centrifugation or other tedious workup processes [7-10]. The magnetic separation not only prevents the loss of the catalyst in this process and is not time-consuming but also it improves product purity and optimizes operational costs [11]. Recent literature publications clearly have shown that magnetic nanoparticles possess a series of admirable advantages such as high surface area to bulk ratios, low toxicity, high activity and thermal stability and the capability of surface modifications and easy dispersion [12-15]. In fact, magnetic separation is a nice strategy to link the gap between heterogeneous and homogenous catalysis [16]. Among the various employed magnetic NPs as the core magnetic support, Fe_3O_4 nanoparticles have been widely studied both for their scientific interests and technological applications [17].

Catalysis research using bromine is a well-known topic in organic synthesis [18]. However, the hazardous and toxic nature of bromine and its negative and deleterious effects on human health has caused organic chemists to cautiously work with bromine [18-20]. Furthermore, the separation of bromine source catalysts from the desired products or reaction media is a difficult, tedious and time consuming task and needs a series of costly and specific techniques [21-22]. The development of heterogenous bromine reagents on magnetic nanoparticles can be considered as an efficient and fascinating catalytic system to overcome this drawback, because the catalyst can be readily separated from the reaction mixture by an external magnet [4, 7]. Inspired by this catalytic strategy, in this paper, we report that tribromide ion immobilized on the surface of magnetic Fe_3O_4 nanoparticles (Fe_3O_4 MNPs-DETA/Benzyl-Br_3) is a new magnetically recoverable catalyst for the oxidative coupling of thiols to the disulfides.

2. Result and discussion

2.1. Preparation and characterization of Fe_3O_4 MNPs-DETA/Benzyl-Br_3:

Tribromide ion immobilized on the surface of magnetic Fe_3O_4 nanoparticles (Fe_3O_4 MNPs-DETA/Benzyl-Br_3) was successfully fabricated by using the surface modification strategy as depicted in Scheme 1. Initially, naked Fe_3O_4 MNPs were prepared and functionalized with (3-chloropropyl)-trimehoxysilane (CPTMS) by a previously procedure according to the literature method [22]. The reaction of Fe_3O_4 MNPs-propyl chloride with diethylenetriamine (DETA) in refluxing toluene led to the formation of the Fe_3O_4 MNPs-DETA [17]. Subsequent, the *N*-

benzylation of Fe_3O_4 MNPs-DETA was performed in the presence of K_2CO_3 in DMF to obtain Fe_3O_4 MNPs-DETA/Benzyl-Br. Finally, the Fe_3O_4 MNPs-DETA/Benzyl-Br_3 was prepared through the reaction of Fe_3O_4 MNPs-DETA/Benzyl-Br with Br_2 in chloroform at room temperature.

The structure of Fe_3O_4 MNPs-DETA/Benzyl-Br_3 was analyzed by a series of characterization techniques such as FT-IR, SEM, VSM, TGA and XRD.

The FT-IR spectra for the Fe_3O_4 MNPs (a), Fe_3O_4 MNPs-CPTMS (b), Fe_3O_4 MNPs-DETA (c), Fe_3O_4 MNPs-DETA/Benzyl-Br (d) and Fe_3O_4 MNPs-DETA/Benzyl-Br_3 (e) are displayed in Fig 1. The FT-IR spectrum for the Fe_3O_4 MNPs shows a stretching vibration at 3440 cm^{-1} which incorporates the contributions from both symmetrical and asymmetrical modes of the O-H bonds which are attached to the surface iron atoms. The presence of Fe_3O_4 was confirmed by strong absorption band at around 560 cm^{-1}, in which is attributed to the Fe--O bond of Fe_3O_4 (Fig. 1a) [15]. The formation of Fe_3O_4 MNPs-CPTMS is confirmed by C--H stretching vibrations that appear at 2855-2956 cm^{-1} (Fig. 1b). Also the absorption around at 1034 cm^{-1} corresponds to Si--O stretching vibration (Fig. 1b) [16]. As shown in Fig. 1c, the replacement of DETA instead of chlorine in Fe_3O_4 MNPs-CPTMS is confirmed by N--H stretching vibrations that appear at 3400 cm^{-1}. In the curve of Fe_3O_4 MNPs-DETA/Benzyl-Br (Fig. 1d), the presence of the anchored benzyl groups are confirmed by C--H stretching vibrations that appear at 2925 cm^{-1} and also C = C stretching vibration modes as a broad band that appear at 1600 cm^{-1}. Also the broad peak at nearly 1345-1400 cm^{-1} in the Fe_3O_4 MNPs-DETA/Benzyl-Br is attributed to C-N^+ stretching vibration [23]. But, Br_3 exhibits a signal between 180 and 200 cm^{-1} [22], which is not recognizable with the FT-IR spectrum.

The SEM images of Fe_3O_4 MNPs-DETA/Benzyl-Br_3 at different magnification are presented in Fig. 2. The SEM images confirmed that the catalyst has made up of uniform nanometer-sized particles with the average size of 10 nm.

The magnetic property of the catalyst was investigated by a vibrating sample magnetometer (VSM) at ambient temperature. The curves of magnetization for the Fe_3O_4 MNPs (red line) and Fe_3O_4 MNPs-DETA/Benzyl-Br_3 (green line) are depicted in Figure S 1 (Supplemental Materials). According to the magnetization curves, the saturation of the nanoparticles decreased from 75.21 emu/g (in the Fe_3O_4 MNPs to 45.89 emu/g in the final catalyst. The decrease of the saturation magnetization can be related to the presence of DETA/Benzyl-Br_3 on the surface of the magnetic Fe_3O_4 nanoparticles.

Thermogravimetric analysis (TGA) was used to determine the percent of functional groups chemisorbed onto the surface of magnetic nanoparticles. Figure S 2 (Supplemental Materials) shows the TGA curves for bare Fe_3O_4 MNPs (black line), Fe_3O_4 MNPs-CPTMS (blue line), Fe_3O_4 MNPs-DETA (green line) and Fe_3O_4 MNPs-DETA/Benzyl-Br_3 (red line). The TGA curve of the all samples shows the small amount of weight loss below 200°C is due to desorption of physically adsorbed solvents and surface hydroxyl groups [3]. Organic groups have been reported to desorb at temperatures above 260°C [3]. The organic groups on the catalyst are found to have a mass percentage loss about of 15%, while the CPTMS-Fe_3O_4 and Fe_3O_4 MNPs-DETA have the mass loss, at 5% and 9%, respectively. As shown in Figure S 2, the catalyst was stable even at 200 °C.

The XRD-diffraction pattern of the prepared catalyst (Fe_3O_4 MNPs-DETA/Benzyl-Br_3) is shown in Figure S 3. In the XRD pattern of Fe_3O_4 MNPs-DETA/Benzyl-Br_3, several characteristic peaks at 2θ = 35.1°, 41.5°, 50.6°, 63.1°, 67.5° and 74.6° were observed, which are assigned to the (220), (311), (400), (422), (511) and (440) crystallographic faces of magnetite (in good agreement with the standard Fe_3O_4 XRD spectrum reported in the literature) [17]. This analysis clearly affirmed this theme that the surface modification and conjugation of the Fe_3O_4 nanoparticles did not lead to phase change.

2.2. Catalytic study

After characterization of catalyst, the catalytic activity of Fe_3O_4 MNPs-DETA/Benzyl-Br_3 in the oxidative coupling of thiols to the disulfides at ambient temperature was studied. To find the optimum reaction conditions, the effect of various parameters (such as solvent type, catalyst and hydrogen peroxide amounts) on the room temperature oxidative coupling of benzo[d]thiazole-2-thiol (as a model substrate) was studied. The results are summarized in Table 2. First, the effect of catalyst loading on the model reaction was studied by varying the amount of Fe_3O_4 MNPs-DETA/Benzyl-Br_3 in EtOH at room temperature (Table 2, Entries 1-4). The results show that 12.5×10^{-3} mol% of Fe_3O_4 MNPs-DETA/Benzyl-Br_3 is the optimal amount of catalyst for all subsequent condensations. To clarify the role of catalyst in the process, the reaction was carried out at in the absence of catalyst. But, only 5% of product 2d was observed after 120 min (Table 1, Entry 5). Next, to evaluate the solvent effect on product yield and reaction time, the model reaction was carried out with 10 mg of catalyst in several solvent such as EtOH, CH_3CN, acetone, CH_2Cl_2 and THF (Table 3, Entries 3 and 6-9). As shown in Table 1, the best results (highest yield and shortest time) were observed in EtOH. Finally, the effect of oxidant loading on the reaction was then studied. The reaction was carried out in the presence of different amounts of hydrogen peroxide (Table 1, Entries 3 and 10-12). As shown in Table 1, the highest yield and shortest reaction time of product 2d was obtained in the presence of 12.5×10^{-3} mol% of Fe_3O_4 MNPs-DETA/Benzyl-Br_3 and 0.5 mL of hydrogen peroxide in EtOH at ambient temperature (Table 1, Entry 3).

With the optimized reaction conditions in hand, to further study the scope and generality of this catalytic system, the applicability of a series of thiols was then subjected to the oxidation reaction (Scheme 2). The results of this study are listed in Table 2. The obtained results shown well that a diverse range of thiols could be successfully oxidized to the corresponding disulfides in high to excellent yields. It is noteworthy that aromatic and heteroaromatic thiols with electron-donating as well as electron-withdrawing substituents at ortho and para position were well tolerated and did not exert any tangible effect on the yield of reactions.

The efficiency of Fe_3O_4 MNPs-DETA/Benzyl-Br_3 is shown by comparison our results on the oxidative coupling of 4-methylbenzenethiol with the previously reported protocols in the literature (Table 3). The results showed that Fe_3O_4 MNPs-DETA/Benzyl-Br_3 is a better catalyst with respect to reaction times and yields of the products.

The reusability of the Fe_3O_4 MNPs-DETA/Benzyl-Br_3 catalyst was studied in the oxidative coupling of 4-methylbenzenethiol as a model reaction. After completion of the reaction, the Fe_3O_4 MNPs-DETA/Benzyl-Br_3 catalyst was readily separated from the reaction mixture by an external magnet, washed several times with ethanol and dried to remove residual product. It is noteworthy that the recovered catalyst was reused at least five times without significant loss of its catalytic efficiency (Figure S 4).

3. Conclusion

In summary, we developed a novel magnetically recoverable catalyst based on immobilization of tribromide ion on the surface of silica-coated magnetic Fe_3O_4 nanoparticles functionalized with DETA/Benzyl. The structure of Fe_3O_4 MNPs-DETA/Benzyl-Br_3 was characterized by FT-IR, SEM, VSM, TGA and XRD analysis techniques. The Fe_3O_4 MNPs-DETA/Benzyl-Br_3 showed high catalytic activity in the oxidative coupling of thiols to disulfides. It is noteworthy that this nanosolid catalyst can be readily synthesized by a very simple strategy using inexpensive precursors, and the recoverable catalyst can be reused at least five times without significant loss of its catalytic activity. Therefore, this procedure can act as an effective alternative in the oxidative coupling of thiols to disulfides.

4. Experimental

Materials

Chemicals were purchased from Fisher and Merck. The reagents and solvents used in this work were obtained from Sigma-Aldrich, Fluka or Merck and used without further purification. The infrared spectra (IR) of samples were recorded in KBr disks using a NICOLET impact 410 spectrometer. ^{1}HNMR and ^{13}CNMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. Nanostructures were characterized using a Holland Philips X, pert X-ray powder diffraction (XRD) diffractometer (Co Kα, radiation = 0.154056 nm), at a scanning speed of 2° min^{-1} from 10° to 80°. Scanning electron microscope (SEM) was performed on a FEI Quanta 200 SEM operated at a 20 kV accelerating voltage. The thermogravimetric analysis (TGA) curves are recorded using a PL-STA 1500 device manufactured by Thermal Sciences. The magnetic measurements were carried out in a vibrating sample magnetometer (VSM, BHV-55, Riken, Japan) at room temperature. The Supplemental Materials contains additional characterization data for the catalyst (Figures S 1 -- S 4).

General procedure for the oxidative coupling of thiols to the disulfides:

A mixture of thiol (1 mmol), hydrogen peroxide (0.5 mL) and Fe_3O_4 MNPs-DETA/Benzyl-Br_3 (12.5×10^{-3} mol%) in ethanol (2 mL) was stirred at ambient temperature. Reaction progress was monitored by TLC (acetone: n-hexane, 2:8). After completion of the reaction, catalyst was separated by external magnet and washed with ethyl acetate, and next, the product was extracted with ethyl acetate (4 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4 (1.5 g). Finally, the organic solvents were evaporated, and the corresponding disulfides were obtained in high to excellent yields (89-98%).

All the products are known compounds and were characterized by comparison of their IR and NMR spectral data and physical properties with those reported in the literature.

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References

1) Mandal, B.; Basu, B. RSC Adv. 2014, 4, 13854.

2) Shiri, L.; Ghorbani-Choghamarani, A.; Kazemi, M. *Aust. J. Chem.* 2017, 70, 9.

3) Shiri, L.; Ghorbani-Choghamarani, A.; Kazemi, M. *Appl. Organometal. Chem*. 2016, DOI: 10.1002/aoc.3596.

4) Shiri, L.; Ghorbani-Choghamarani, A.; Kazemi, M. *Res. Chem. Intermed.* 2017, 43, 2707.

5) Ghorbani-Choghamarani, A.; Darvishnejad, Z.; Tahmasbi, B. *Inorganica Chimica Acta*. 2015, 435, 223.

6) Hajjami, M.; Rahmani, S. *J. Porous. Mater*. 2015, 22, 1265.

7) Shiri, L.; Ghorbani-Choghamarani, A.; Kazemi, M. *Appl. Organometal. Chem*. 2017, DOI: 10.1002/aoc.3634.

8) Zhang, L.; Li, P.; Liu, C.; Yang, J.; Wang, M.; Wang, L. ***Catal. Sci. Technol.*** 2014, **4**, 1979.

9) Zhang, X.; Li, P.; Ji, Y.; Zhang, L.; Wang, L. *Synthesis*. 2011, 2975.

10) Shiri, L.; Rahmati, S.; Ramezani-Nejad, Z.; Kazemi, M. *Appl. Organomet. Chem.* 2017, DOI: 10.1002/aoc.3687.

11) Ying, A.; Hou, H.; Liu, S.; Chen, G.; Yang, J.; Xu, S. *ACS Sustainable Chem. Eng.* 2016, 4, 392.

12) Shiri, L.; Ghorbani-Choghamarani, A.; Kazemi, M. *Aust. J. Chem.* 2016, 69, 585.

13) Ying, A.; Liu, S.; Li, Z.; Chen, G.; Yang, J.; Yan, H.; Xu, S. *Adv. Synth. Catal.* 2016, 358, 2116.

14) Shiri, L.; Kazemi, M. *Res. Chem. Intermed.* 2017, DOI 10.1007/s11164-017-2914-7.

15) Zhang, L.; Li, P.; Li, H.; Wang, L. ***Catal. Sci. Technol.*** 2012, **2**, 1859.

16) Zhang, L.; Li, P.; Yang, J.; Wang, M.; Wang, L. *Chem. Plus. Chem.* 2014, 79, 217.

17) Shiri, L.; Ghorbani-Choghamarani, A.; Kazemi, M. *Monatsh. Chem.* 2017, DOI 10.1007/s00706-016-1906-4.

18) Shiri, L.; Kazemi, M. **Mini** Rev Org Chem. 2017, 14, DOI: 10.2174/1570193X14666170518114613.

19) Jitareanu, A.; Zbancioc, A. M.; Tuchilus, C.; Balan, M.; Stanescu, U.; Tataringa, G. *Rev. Med. Chir. Soc. Med. Nat. Iasi.* 2015, 119, 1180.

20) Saikia, I.; Borah, A.J.; Phukan, P. *Chem. Rev.* **2016**, *116*, 6837.

21) Ghorbani-Choghamarani, A.; Pourbahar, N. *Chin. J. Catal.* 2012, 33, 1470.

22) Ghorbani-Choghamarani, A.; Goudarziafshar, H.; Zamani, P. *Chin. Chem. Lett.* 2011, 22, 1207.

23) Rostami, A.; Navasi, Y.; Moradi, D.; Ghorbani-Choghamarani, A. *Catal Commun.* 2014, 43, 16.

24) Moghaddam, F. M.; Masoud, N.; Foroushani, B. K.; Saryazdi, S.; Ghonouei, N.; Daemi, E. *Scientia Iranica*. 2013, 20, 598.

25) Nikoorazm, M.; Ghorbani-Choghamarani, A.; Mahdavi, H.; Esmaeili, S.M. *Microporous. Mesoporous. Mater*. 2015, 211, 174.

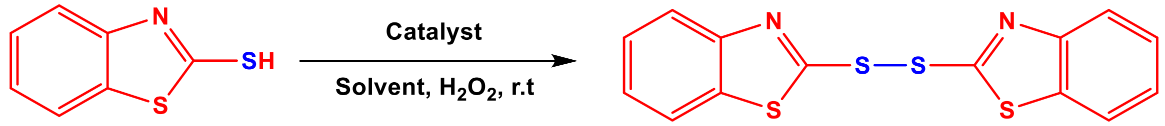
26) Rajabi, F.; Kakeshpour, T.; Saidi, M.R. *Catal. Commun*. 2013, 40, 13.

27) Bagherzadeh, M.; Haghdoost, M.M.; Moghaddam, F.M.; Koushki-Foroushani, B.; Saryazdi, S.; Payab, E. *J. Coord. Chem.* 2013, 66, 3025.

28) Nikoorazm, M.; Ghorbani-Choghamarani, A.; Noori, N. *J. Porous Mater.* 2015, 22, 877.

29) Patra, A.K.; Dutta, A.; Pramanik, M.; Nandi, M.; Uyama, H.; Bhaumik, A. *Chem. Cat. Chem.* 2014, 6, 220.

Table 1. Optimization of the reaction conditions [a]



2d

Entry	Catalyst (mol%)	H_2O_2 (mL)	Solvent	Time/min	Yield (%) [b]
1	3.75×10^{-3}	0.5	EtOH	30	91
2	6.25×10^{-3}	0.5	EtOH	20	95
3	12.5×10^{-3}	0.5	EtOH	15	98
4	18.75×10^{-3}	0.5	EtOH	15	97
5	--	0.5	EtOH	120	5
6	12.5×10^{-3}	0.5	CH_3CN	25	92
7	12.5×10^{-3}	0.5	Acetone	35	94
8	12.5×10^{-3}	0.5	THF	115	90
9	12.5×10^{-3}	0.5	CH_2Cl_2	80	91
10	12.5×10^{-3}	0.3	EtOH	50	89
11	12.5×10^{-3}	0.4	EtOH	30	94
12	12.5×10^{-3}	0.6	EtOH	15	98

[a] Reaction conditions: The oxidative coupling of benzo[d]thiazole-2-thiol (1 mmol) by using H_2O_2 in the presence of catalyst and solvent (2 mL). [b] Isolated yield.

Table 2. Fe_3O_4 MNPs-DETA/Benzyl-Br_3 catalyzed the oxidative coupling of thiols into disulfides in ethanol at room temperature.

Entry	Thiol	Product	Time (min)	Yield (%)[a]	Mp (°c) [Ref.]
1	Benzenethiol	2a	50	90	60-61 [4]
2	4-Methylbenzenethiol	2b	15	98	40-42 [4]
3	Naphthalene-2-thiol	2c	20	91	133-134 [4]
4	Pyridine-2-thiol	2d	50	92	54-56 [4]
5	Benzo[d]thiazole-2-thiol	2e	15	98	171-172 [3]
6	4-Fluorobenzenethiol	2f	15	93	Oil [4]
7	4-Bromobenzenethiol	2g	25	96	88-89 [6]
8	2-Aminobenzenethiol	2h	30	94	80-82 [4]
9	2-Mercaptobenzoic acid	2i	30	93	285-287 [3]
10	Phenylmethanethiol	2j	55	95	70-71 [4]
11	2-Mercaptoethanol	2k	35	90	Oil [6]
12	2-Mercaptoacetic acid	2l	45	89	Oil [6]

[a] Isolated yield

Table 3 Comparison of the activity of various catalysts in the oxidative coupling of 4-methylbenzenethiol.

Entry	Substrate	Catalyst	Time (min)	Yield (%)[a]	[Ref.]
1	4-Methylbenzenethiol	Ni-salen-MCM-41	25	95	[24]
2	4-Methylbenzenethiol	Fe NPs@SBA-15	45	94	[25]
3	4-Methylbenzenethiol	Fe_3O_4@SiO_2--NH_2@Mn(III)	120	83	[26]
4	4-Methylbenzenethiol	Cu(II) Schiff base MCM-41	72	83	[27]
5	4-Methylbenzenethiol	Mn--ZSM-5	360	82	[28]
6	4-Methylbenzenethiol	This catalyst	15	98	This work

[a] Isolated yield

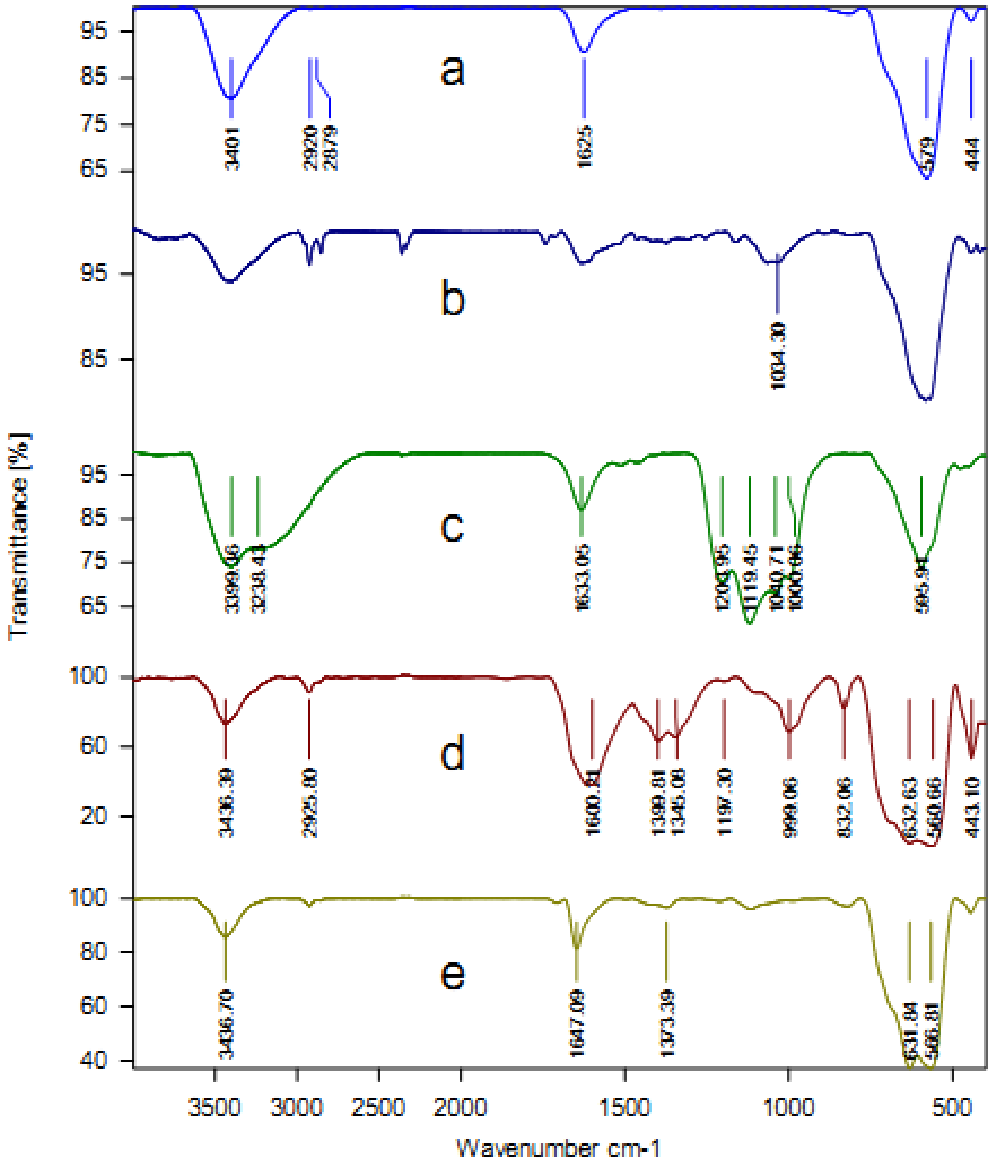


Figure 1. FT-IR spectra of Fe_3O_4 MNPs (a), Fe_3O_4 MNPs-CPTMS (b), Fe_3O_4 MNPs-DETA (c), Fe_3O_4 MNPs-DETA/Benzyl-Br (d) and Fe_3O_4 MNPs-DETA/Benzyl-Br_3 (e)..

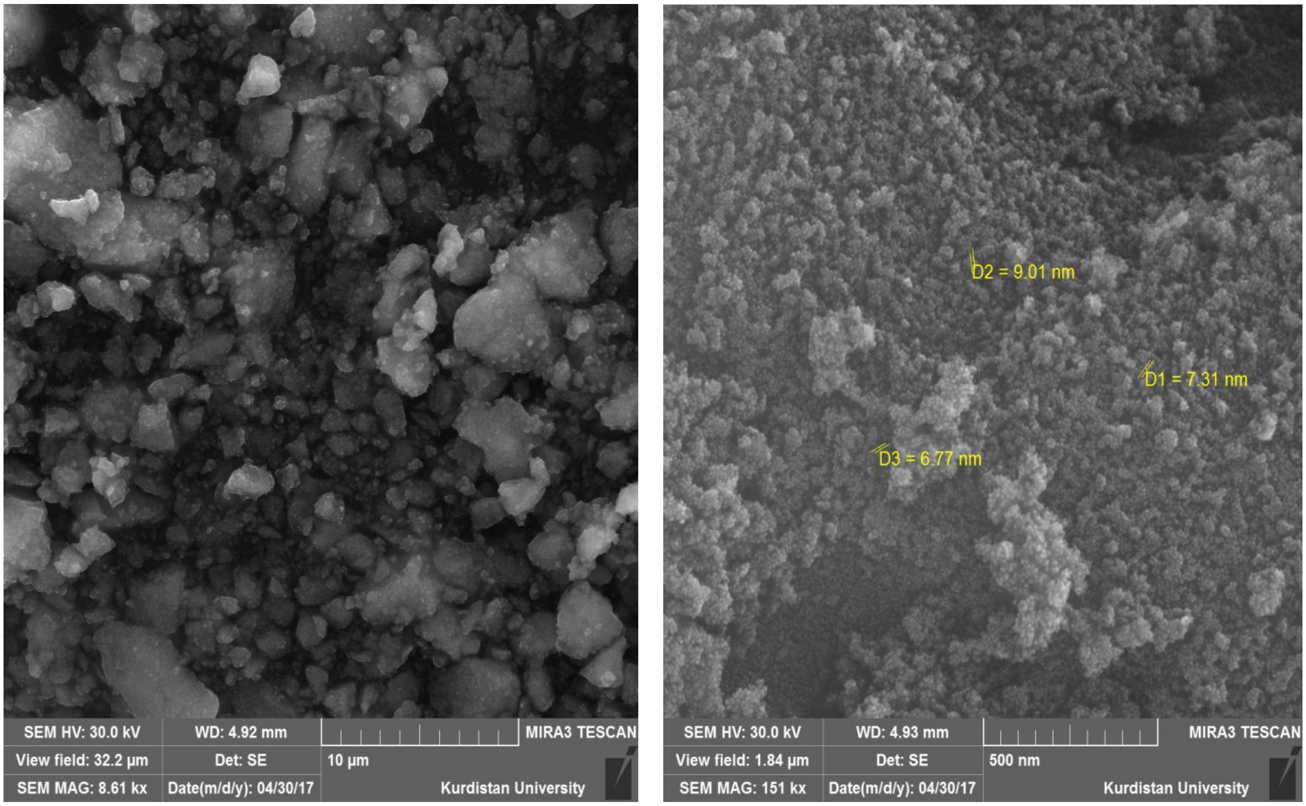
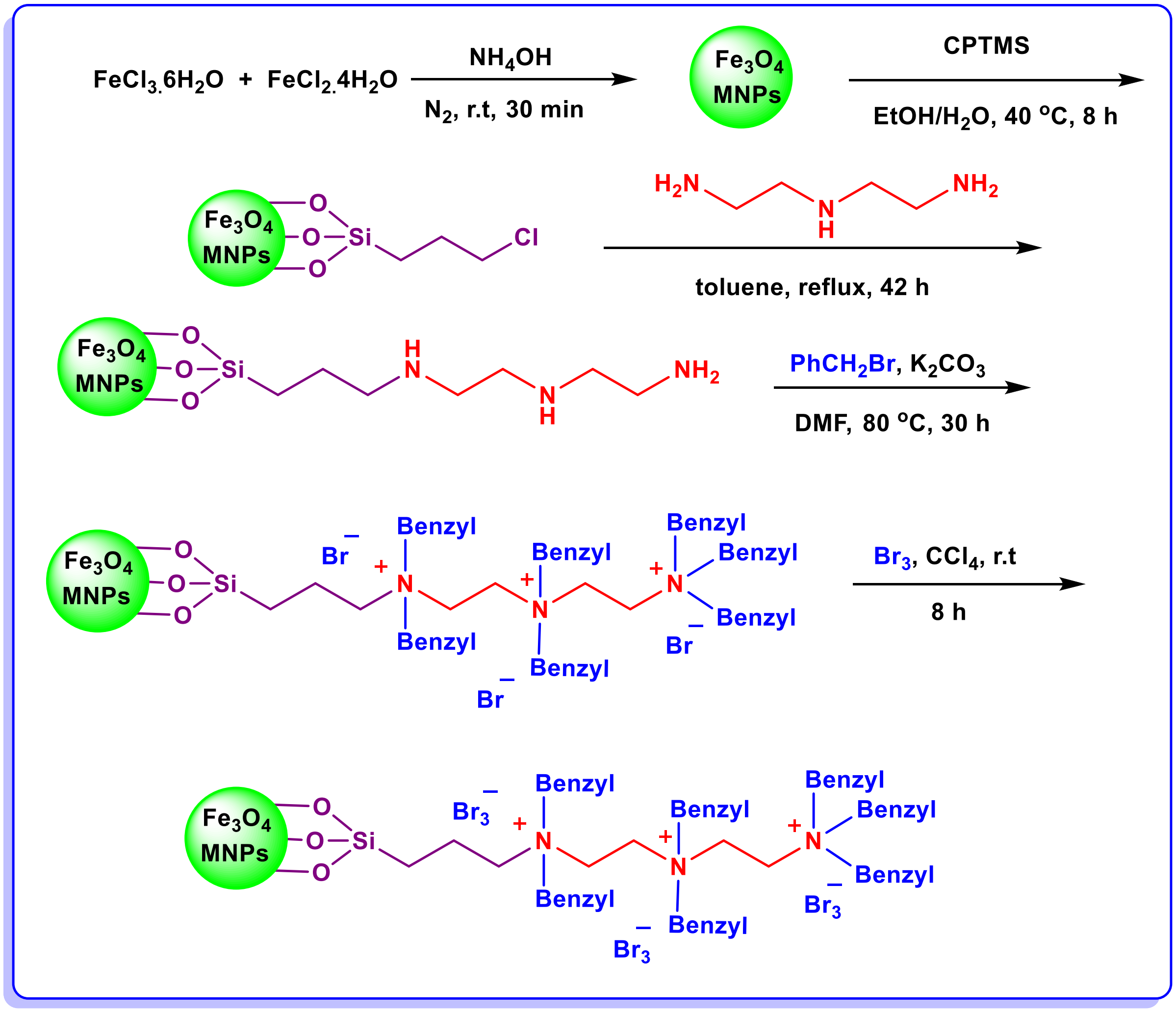
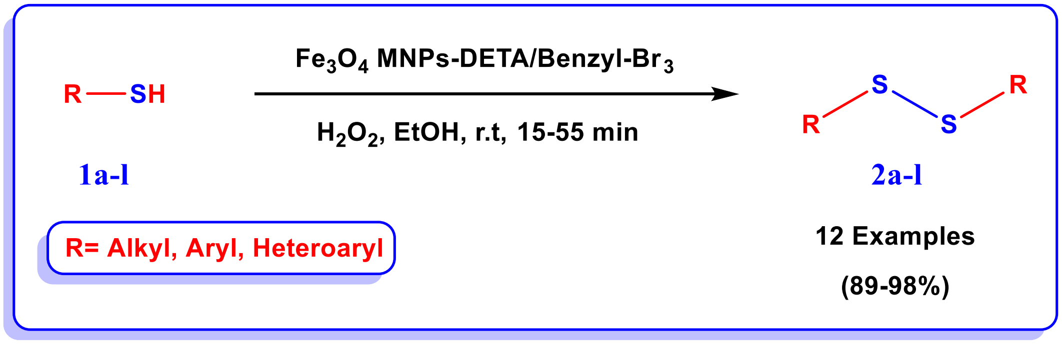


Fig 2. SEM images of the Fe_3O_4 MNPs-DETA/Benzyl-Br_3 at different magnification.



Scheme 1. Stepwise preparation of Fe_3O_4 MNPs-DETA/Benzyl-Br_3.



Scheme 2. Fe_3O_4 MNPs-DETA/Benzyl-Br_3 catalyzed the oxidative coupling of thiols to the disulfides.