Received: 2 October 2019 | Revised: 5 February 2020 | Accepted: 7 February 2020

DOI: 10.1002/aoc.5641

FULL PAPER

Applied Organometallic Chemistry WILEY

3-Amino-5-mercapto-1,2,4-triazole-functionalized Fe_3O_4 magnetic nanocomposite as a green and efficient catalyst for synthesis of bis(indolyl)methane derivatives

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A core–shell Fe_3O_4@silica magnetic nanocomposite functionalized with 3-amino-5-mercapto-1,2,4-triazole (Fe_3O_4/SiO_2/PTS/AMTA) was prepared using Fe_3O_4 with silica layer, and its surface was modified with 3-amino-5-mercapto-1,2,4-triazole. The novel synthesized magnetite nanocomposite was characterized using various techniques. The catalytic activity of Fe_3O_4/SiO_2/PTS/AMTA was demonstrated in the synthesis of bis(indolyl)methane derivatives under solvent-free conditions. Some of the bis(indolyl)methane derivatives were synthesized through one-pot, three-component reaction of 1 mol of various benzaldehydes or ketones with 2 mol of indole in the presence of Fe_3O_4/SiO_2/PTS/AMTA in good to excellent isolated yields. In addition, the catalyst could be recovered and used for several reaction runs without loss of catalytic activity. The stability of recycled catalyst was investigated. This method has some advantages including experimental simplicity, good to excellent yields, solvent-free conditions and stability and reusability of the catalyst.

KEYWORDS

bis(indolyl)methanes, green chemistry, heterogeneous catalyst, magnetic nanocatalyst, solvent free

1 | INTRODUCTION

In the recent years, magnetic nanoparticles (MNPs) have been employed in various scientific fields including catalysis,[1, 2] semiconductors,[3] sensors,[4] pigments, wastewater treatments,[5, 6] adsorbents,[7] magnetic resonance imaging,[8] magnetic data storage devices,[9] bioseparations[10] and medicines.[11, 12] Recently, some MNPs have been used as highly useful supports for immobilization of homogeneous catalysts in order to obtain heterogeneous catalysts and enable them to be recovered using an external magnet.[13–15] Among MNP materials, magnetite (Fe_3O_4) has received more attention in biomedical and chemical fields because of its unique physical and chemical properties.[16, 17] Hopping of electrons between Fe^{2+} and Fe^{3+} results in development of the magnetic properties of Fe_3O_4.[18] The surface of Fe_3O_4 often releases toxic Fe^{2+} ions and is oxidized by the air. Hence, various procedures have been developed to modify and coat the surface of the particles. Magnetic core–shell Fe_3O_4@SiO_2 with hydroxyl groups can be coupled with functional groups such as amines, carboxylates and thiols using appropriate organosilicon precursors.[19, 20] Therefore, surface-functionalized Fe_3O_4@SiO_2 nanocomposites can be applied as convenient nanomagnetic catalysts, which can be separated using an external magnet.

3-Amino-5-mercapto-1,2,4-triazole (AMTA) with sulfur and nitrogen atoms is an interesting compound commonly used in the processing of silver halide photographic material, in the synthesis of organic compounds, as a modifier of Au and Ag electrodes, as an antioxidant and as a viscosity index improver.[21–23] As a base group, AMTA can be applied successfully for the functionalization of silica-coated Fe_3O_4 nanoparticles. In the work reported herein, Fe_3O_4/SiO_2/PTS/AMTA, as a novel magnetically reusable catalyst, was prepared and used for the synthesis of bis(indolyl)methane derivatives under solvent-free conditions.

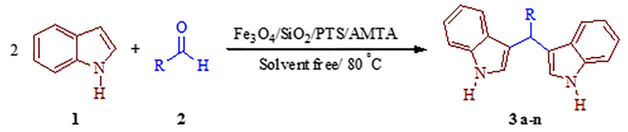
Recently, bis(indolyl)alkanes have attracted a great deal of interest due to their synthetic as well as biological applications as a result of their antitumor,[24] antileishmanial,[25] antihyperlipidemic[26] and anticancer activities.[27] Several products containing bis(indolyl) alkane derivatives have been separated previously from marine sources.[28, 29] In this regard, various methods have been reported for the synthesis of bis(indolyl)alkane derivatives, especially bis(indolyl)methanes, through electrophilic substitution of indole with carbonyl compounds in the presence of various acid or base catalytic reagents such as ZrO_2–MgO,[30] tetrabutylammonium hydrogen sulfate,[31] montmorillonite K-10,[32] zeolite,[33] ammonium chloride,[34] tungstophosphoric acid supported on zirconia,[35] Fe_3O_4@silica sulfuric acid,[36] $H_5PW_{10}V_2O_{40}$/pyridino-Fe_3O_4,[37] nano-Fe_3O_4,[38] ZrO_2–Al_2O_3–Fe_3O_4,[39] and $[\{Ti(salophen)H_2O\}_2O][OSO_2C_8F_{17}]_2$.[40] Although these procedures are valuable, some of them have disadvantages.

2 | RESULTS AND DISCUSSION

Following increasing interest in the green and efficient synthesis of heterocyclic compounds,[41–44] in the study presented here a convenient method was introduced for the synthesis of bis(indolyl)methane derivatives in the presence of Fe_3O_4/SiO_2/PTS/AMTA as a novel magnetic catalyst (Scheme 1).

First, the catalyst was synthesized by coating Fe_3O_4 with a layer of silica, followed by condensation with chloropropyltrimethoxysilane (CPTMS) and substitution of chlorine atom with AMTA as described in Section 3 (Scheme 2).

Subsequently, the obtained nanocatalyst was characterized using Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (SEM), powder X-ray diffraction (XRD) and vibrating sample magnetometry (VSM).



SCHEME 1 Synthesis of bis(indolyl)methanes catalyzed by Fe_3O_4/SiO_2/PTS/AMTA

Figure 1 shows the powder XRD patterns of Fe_3O_4, Fe_3O_4/SiO_2, Fe_3O_4/SiO_2/PTS and Fe_3O_4/SiO_2/PTS/AMTA in the range 10–80°. Peaks observed at 30.1°, 35.5°, 43.1°, 53.4°, 57.0° and 62.6° in the patterns of all nanocomposites corresponded to the crystalline state of cubic Fe_3O_4 MNPs. Results indicated that the Fe_3O_4 structure remained unchanged after modification and attachment of AMTA.

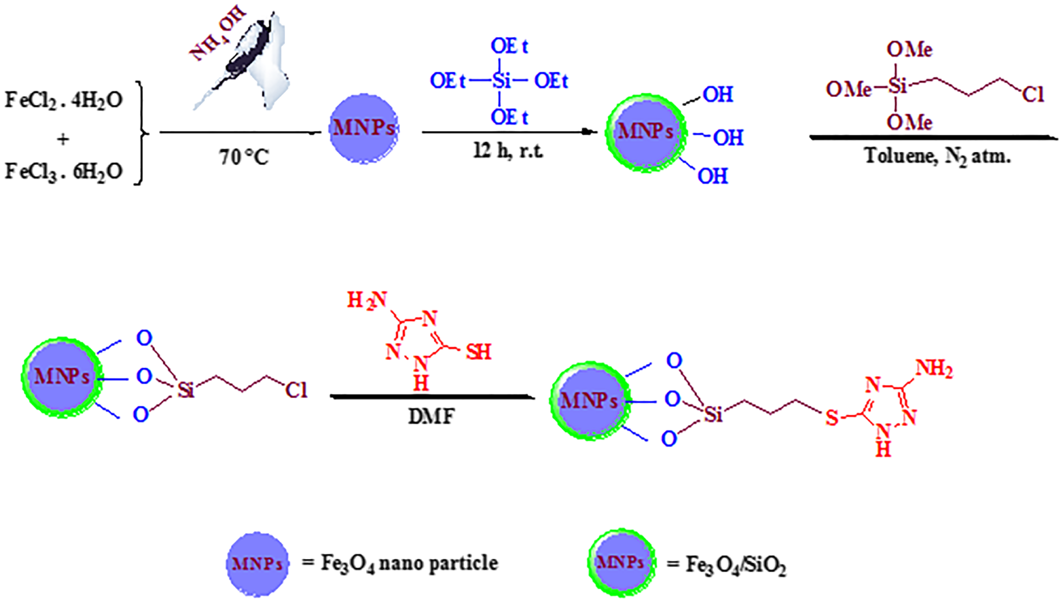
Figure 2 shows the FT-IR spectra of Fe_3O_4, Fe_3O_4/SiO_2, Fe_3O_4/SiO_2/PTS, AMTA and Fe_3O_4/SiO_2/PTS/AMTA. Comparison of the spectra indicated that peaks at 570 cm^{-1} were attributed to Fe&bond;O stretching vibration of Fe_3O_4. The peak at 1080 cm^{-1} was assigned to Si&bond;O bond of the silica layer (Figure 2b, c,e).[14] Comparison of FT-IR spectra presented in Figure 2d,e showed that the peaks at 1594 and 1395 cm^{-1} corresponded to C&dbond;N and C&bond;N stretching vibrations of AMTA heterocyclic ring of Fe_3O_4/SiO_2/PTS/AMTA, respectively, while the absorption peak of S&bond;H at 2614 cm^{-1} disappeared in the spectrum of Fe_3O_4/SiO_2/PTS/AMTA showing a nucleophilic substitution of Cl by SH group of AMTA.[45]

Morphology and particle size of synthesized Fe_3O_4/SiO_2/PTS/AMTA were evaluated using SEM. As shown in Figure 3, Fe_3O_4/SiO_2/PTS/AMTA exhibited a uniform and spherical morphology with an average particle size of about 17 nm. Furthermore, energy-dispersive X-ray (EDX) analysis showed characteristic peaks of Fe, Si, O, C, N and S atoms confirming that Fe_3O_4 was coated with SiO_2 and functionalized with AMTA (Figure 4).

Figure 5 shows field-dependent magnetization curves of uncoated Fe_3O_4 powder, Fe_3O_4/SiO_2 powder, Fe_3O_4/SiO_2/PTS powder and Fe_3O_4/SiO_2/PTS/AMTA powder at ambient temperature. All samples were superparamagnetic with saturation magnetizations of 63.7, 56.6, 53.19 and 49.60 emu g^{-1}, respectively. The results showed a reduction of saturation magnetization for Fe_3O_4/SiO_2, Fe_3O_4/SiO_2/PTS and Fe_3O_4/SiO_2/PTS/AMTA in comparison with Fe_3O_4, attributed to the diamagnetic contribution of SiO_2 and organic group on the surface of Fe_3O_4 nanoparticles. However, Fe_3O_4/SiO_2/PTS/AMTA still had sufficient magnetic properties and could be separated from a reaction mixture using an external magnet.

Thermogravimetric analysis (TGA) was used to investigate the thermal stability of the synthesized Fe_3O_4/SiO_2/PTS/AMTA from room temperature to 800°C under a nitrogen atmosphere (Figure 6). Weight loss (14.1%) was observed attributed to loss of adsorbed water and decomposition of propyl and AMTA as organic functional groups.

After the synthesis and characterization of Fe_3O_4/SiO_2/PTS/AMTA, its catalytic activity was investigated for the preparation of bis(indolyl)methane derivatives. At



SCHEME 2 Preparation of $Fe_3O_4/SiO_2/PTS/AMTA$

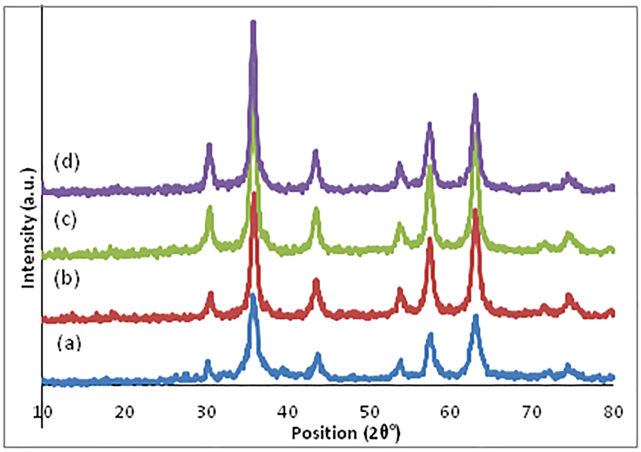


FIGURE 1 XRD patterns of Fe_3O_4 (a), Fe_3O_4/SiO_2 (b), $Fe_3O_4/SiO_2/PTS$ (c) and $Fe_3O_4/SiO_2/PTS/AMTA$ (d)

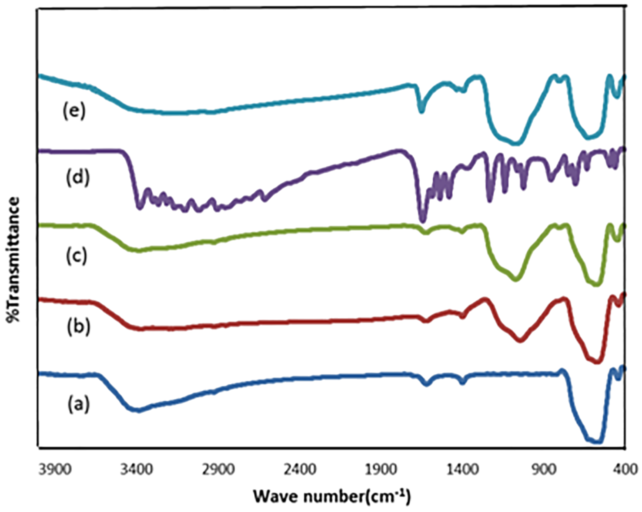


FIGURE 2 FT-IR spectra of Fe_3O_4 (a), Fe_3O_4/SiO_2 (b), $Fe_3O_4/SiO_2/PTS$ (c), AMTA (d) and $Fe_3O_4/SiO_2/PTS/AMTA$ (e)

first, a mixture of benzaldehyde (1 mmol) and indole (2 mmol) was stirred as a model reaction in the presence of various amounts of the catalyst under different conditions, and the results are presented in Table 1. According to Table 1, the presence of catalyst was essential for the reaction (entry 1) and an amount of more than 10 mg of $Fe_3O_4/SiO_2/PTS/AMTA$ did not have much effect on yield and reaction time (entry 10). In addition, the presence of solvent reduced the completion of the reaction. Consequently, it was found that an amount of 10 mg of $Fe_3O_4/SiO_2/PTS/AMTA$ at 80°C under solvent-free conditions were optimal for the preparation of bis(indolyl) methanes (entry 8). When the reaction was carried out in the presence of Fe_3O_4 MNPs or AMTA instead of $Fe_3O_4/SiO_2/PTS/AMTA$ under identical conditions (entries 13 and 14), yields of reaction were approximately the same. In this study, AMTA played the primary role as a catalyst in $Fe_3O_4/SiO_2/PTS/AMTA$ and was supported on Fe_3O_4 MNPs, which can be easily separated using an external magnet.

Optimized reaction conditions were used for synthesis of some bis(indolyl)methane derivatives by the three-component reaction between various aldehydes and ketones with indole to investigate the generality of this procedure (Table 2). As evident from Table 2, this method is useful for the reaction of indole with various aromatic aldehydes bearing electron-withdrawing or electron-donating groups to afford corresponding

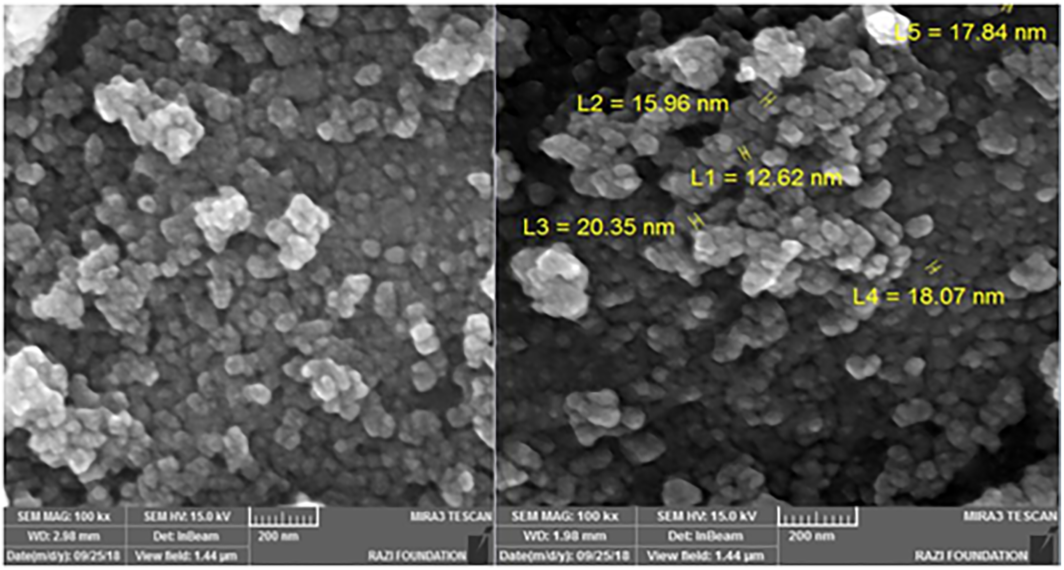


FIGURE 3 SEM images of Fe_3O_4/SiO_2/PTS/AMTA

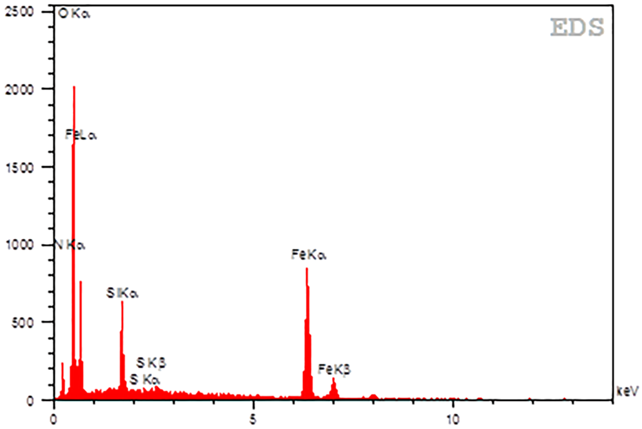


FIGURE 4 EDX analysis of Fe_3O_4/SiO_2/PTS/AMTA

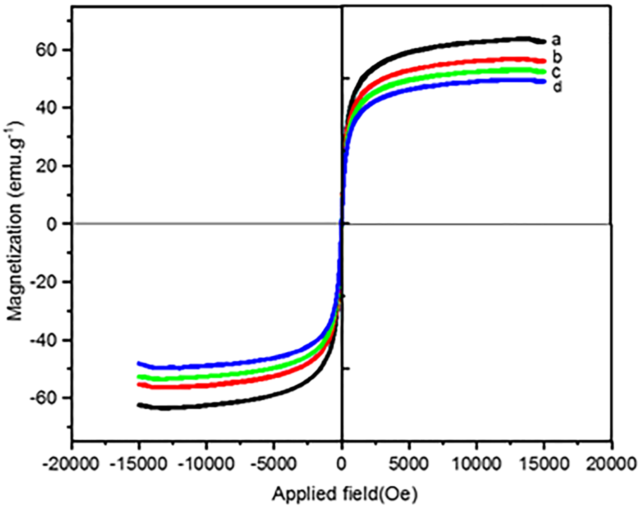


FIGURE 5 VSM analyses of Fe_3O_4 (a), Fe_3O_4/SiO_2 (b), Fe_3O_4/SiO_2/PTS (c) and Fe_3O_4/SiO_2/PTS/AMTA (d)

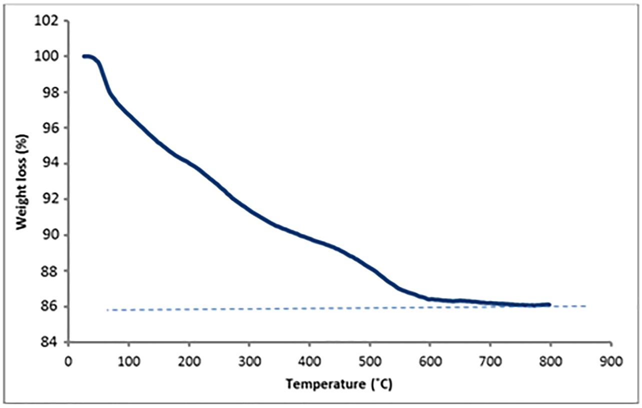


FIGURE 6 TGA of Fe_3O_4/SiO_2/PTS/AMTA

bis(indolyl)methane derivatives. Furthermore, the reaction of isatin and cyclohexane with indole was carried out under optimum conditions, which resulted in the generation of corresponding products in good to excellent yields.

Scheme 3 shows a plausible mechanism for the synthesis of bis(indolyl)methane derivatives catalyzed by Fe_3O_4/SiO_2/PTS/AMTA. It is believed that Fe_3O_4/SiO_2/PTS/AMTA acts as an efficient base catalyst with nitrogen atoms of AMTA. So that, first, indole reacts with the carbonyl group of aldehyde or ketone, and generates intermediate **IV** through abstraction of a proton using the catalyst. Then, the catalyst helps in loss of H_2O from indolyl carbinol (**IV**) and forms 3-arylidene-3*H*-indole (**V**). Finally, the nucleophilic attack of the second mole of indole to intermediate **V** and abstraction of a proton from intermediate **VII** result in the production of corresponding bis(indolyl)methane. The catalyst is reused

TABLE 1 Optimization of reaction conditions

Entry	Solvent	Temperature (°C)	Catalyst (mg)	Time (h)	Yield (%)
1	—	r.t.	Fe_3O_4/SiO_2/PTS/AMTA (0)	8	—
2	EtOH	r.t.	Fe_3O_4/SiO_2/PTS/AMTA (10)	8	20
3	MeOH	r.t.	Fe_3O_4/SiO_2/PTS/AMTA(10)	8	20
4	EtOAc	r.t.	Fe_3O_4/SiO_2/PTS/AMTA (10)	8	5
5	—	60	Fe_3O_4/SiO_2/PTS/AMTA (5)	5	50
6	—	60	Fe_3O_4/SiO_2/PTS/AMTA (10)	5	95
7	—	80	Fe_3O_4/SiO_2/PTS/AMTA (5)	4	70
8	—	80	Fe_3O_4/SiO_2/PTS/AMTA (10)	1.5	96
9	—	100	Fe_3O_4/SiO_2/PTS/AMTA (10)	1.5	96
10	—	80	Fe_3O_4/SiO_2/PTS/AMTA (13)	1.5	97
11	EtOH	60	Fe_3O_4/SiO_2/PTS/AMTA (10)	5	80
12	EtOH	80	Fe_3O_4/SiO_2/PTS/AMTA (10)	3	85
13	—	80	Fe_3O_4 (10)	2	95
14	—	80	AMTA (10)	1.75	95

in the next reaction cycle, and increases the electrophilicity of the carbonyl group with adsorbed hydrogen.[30, 50]

Reusability and recovery of Fe_3O_4/SiO_2/PTS/AMTA were investigated in the synthesis of 4-chlorophenylmethane-3,3′-bis(indolyl) (**3f**) under optimized conditions. At the end of the reaction, the mixture was diluted with ethanol, and the catalyst was magnetically removed from the mixture using an external magnet, and then washed with ethanol and dried. Then, the separated catalyst was used in a fresh reaction for five runs without notable loss of activity (Figure 7).

The stability of the recycled catalyst was investigated using SEM and TGA (Figures 8 and 9). Results of TGA showed no change in the thermal stability of the catalyst after five cycles. A comparison of the results obtained from SEM analysis showed that the shape and size of recycled catalyst particles and fresh catalyst particles were identical.

A hot filtration test was also performed to investigate the heterogeneity of the catalyst. In this regard, synthesis of 4-chlorophenylmethane-3,3′-bis (indolyl) (**3f**) was carried out in the presence of Fe_3O_4/SiO_2/PTS/AMTA under optimized conditions for 1 hour. Then, the catalyst was filtered off at the reaction temperature. The reaction progress was followed by GC, and the yield of **3f** was equal to 56%. The reaction with the filtrate was allowed to continue without using the catalyst for 2 hours, and no further conversion was observed.

Finally, the performance of this procedure regarding the preparation of bis(indolyl)phenylmethane was compared with that of various methods reported in the literature (Table 3). Results obtained from this comparison showed a preference for the current method due to it being solvent-free and involving mild conditions, and also its use of a small amount of nontoxic and recoverable catalyst.

3 | EXPERIMENTAL

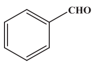
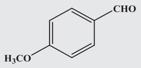
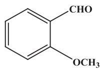
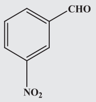
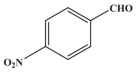
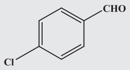
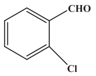
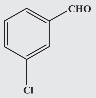
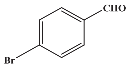
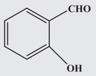
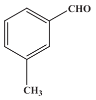
3.1 | General

All chemicals and reagents were purchased from Sigma-Aldrich and were used without further purification. The progress of the organic reactions was monitored using TLC. Melting points were determined with an Electrothermal digital melting point apparatus (Bornstead). ^1H NMR spectra were recorded using a Bruker 400 MHz spectrometer in pure $CDCl_3$. FT-IR spectra were recorded with a Shimadzu IR-470 spectrometer using KBr disks. Powder XRD measurements were made with an X'Pert Pro X-ray diffractometer using a Cu tube over the 2θ range from 10° to 80°. Elemental composition and surface morphology were investigated using a field emission SEM instrument (Tescan Mira III). Magnetization was assessed with a vibrating sample magnetometer (MDK-VSM, model MDKB).

3.2 | Synthesis of nanomagnetic Fe_3O_4

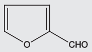
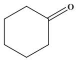
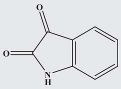
The Fe_3O_4 MNPs were prepared using a previously reported chemical co-precipitation method with minor

TABLE 2 Synthesis of bis(indolyl)methane derivatives in presence of Fe_3O_4/SiO_2/PTS/AMTA

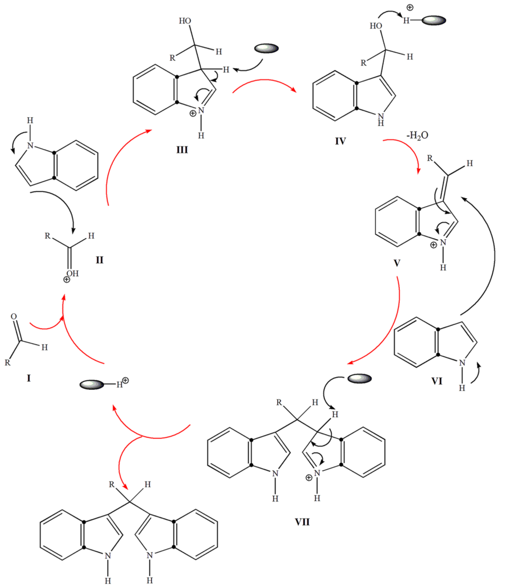
					M.p. (°C)	
Entry	**Product**	**Aldehyde/ketone**	**Time (h)**	**Yield (%)^{aa}**	**Found**	**Reported**
1	**3a**		1.5	96	139–140	140–142[46]
2	**3b**		7.5	93	182–184	180–182[46]
3	**3c**		6.75	95	135–137	134–135[47]
4	**3d**		7	90	260–263	261–263[47]
5	**3e**		6	83	217–219	218–220[47]
6	**3f**		2	90	76–79	74–76[46]
7	**3g**		1	98	73–75	73–75[46]
8	**3h**		1.5	95	87–89	89–91[48]
9	**3i**		5	85	112–114	110–112[47]
10	**3j**		8	70	340–343	340–342[47]
11	**3k**		2.75	85	100–102	98–99[49]

(Continues)

TABLE 2 (Continued)

Entry	Product	Aldehyde/ketone	Time (h)	Yield (%)[aa]	M.p. (°C) Found	M.p. (°C) Reported
12	**3l**		6	75	318–320	320–322[48]
13	**3m**		6	80	158–160	160–162[46]
14	**3n**		2.75	97	312–315	312–314[31]

[a] Isolated yield.



SCHEME 3 Plausible mechanism for synthesis of bis(indolyl) methane derivatives catalyzed by Fe_3O_4/SiO_2/PTS/AMTA

modifications.[55] First, 5.4 g of $FeCl_3{\cdot}6H_2O$ and 2.0 g of $FeCl_2{\cdot}4H_2O$ were dissolved in 2 ml of concentrated hydrochloric acid and 20 ml of double-distilled water. The solution was stirred vigorously under a nitrogen gas flow at 80°C. Subsequently, a solution of ammonium hydroxide (2 M) was added dropwise to the solution under vigorous stirring to adjust the pH value to 10 and a black precipitate was formed. The final product was separated using an external magnet, was washed several times using double distilled water and was dried at room temperature to afford black nanomagnetic Fe_3O_4.

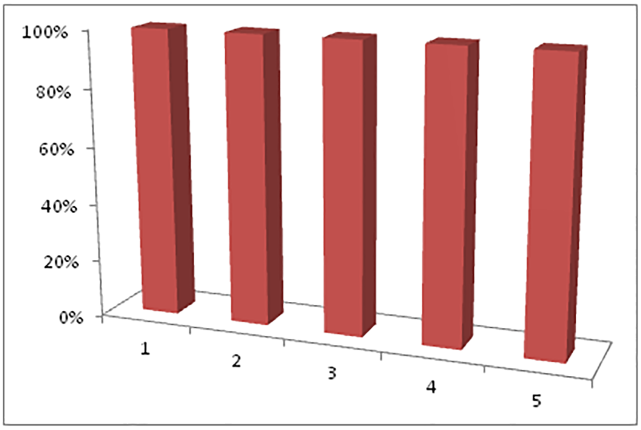


FIGURE 7 Recyclability of Fe_3O_4/SiO_2/PTS/AMTA in the reaction between 4-chlorobenzaldehyde and indole under optimized conditions

3.3 | Synthesis of Fe_3O_4/SiO_2 nanocomposite

SiO_2 shells were coated on the prepared Fe_3O_4 MNPs via condensation and hydrolysis of tetraethyl orthosilicate (TEOS). Briefly, 2 g of synthesized Fe_3O_4 powder was added to 200 ml of a solution containing water and ethanol (1:4), followed by ultrasonication for 30 minutes. Afterwards, TEOS (2.5 ml) and concentrated ammonia aqueous solution (10 ml) were added to the mixture under continuous stirring at room temperature for 12 hours. Finally, the product was collected using an external magnet, was rinsed several times using ethanol and double-distilled water and then was dried.[56]

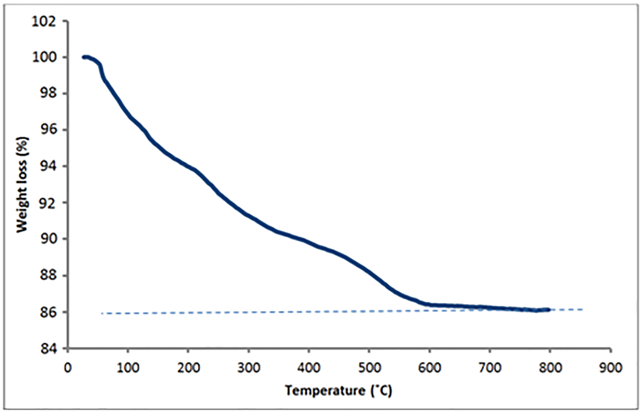


FIGURE 8 TGA of recycled Fe_3O_4/SiO_2/PTS/AMTA

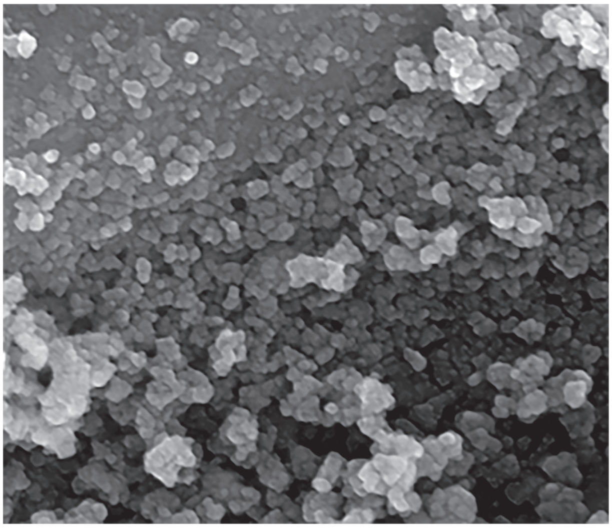


FIGURE 9 SEM image of recycled Fe_3O_4/SiO_2/PTS/AMTA

3.4 | Synthesis of chloropropyl-modified Fe_3O_4/SiO_2 nanocomposite (Fe_3O_4/SiO_2/PTS)

Chloropropyl-modified Fe_3O_4@SiO_2 nanocomposite was prepared according to a previously reported method.[57] An amount of 2 g of synthesized silica-coated MNPs was dispersed in 100 ml of toluene by ultrasonic treatment, and then 2 ml of CPTMS was added dropwise to the mixture. The mixture was refluxed under nitrogen atmosphere for 2 hours. The resulting solid was separated using an external magnet, was washed twice using double-distilled water and ethanol and then was dried.

3.5 | Synthesis of Fe_3O_4/SiO_2/PTS/AMTA

An amount of 0.1 g of AMTA was added to a suspension containing 1.0 g of synthesized Fe_3O_4/SiO_2/PTS in 70 ml of dimethylformamide (DMF) and was refluxed under nitrogen atmosphere at 60°C for 6 hours. The magnetically collected solid product then was washed with DMF and was dried at room temperature to afford the Fe_3O_4/SiO_2/PTS/AMTA nanocatalyst.

3.6 | General procedure for synthesis of bis(indolyl)methane derivatives using Fe_3O_4/SiO_2/PTS/AMTA

A mixture containing indole (2 mmol), aldehyde (1 mmol) and Fe_3O_4/SiO_2/PTS/AMTA (0.01 g) was stirred vigorously at 80°C under solvent-free conditions. The progress of reaction was followed by TLC (*n*-hexane–ethyl acetate, 4/1). After complete conversion, the reaction mixture was diluted with ethanol, an

TABLE 3 Comparison of results with those reported in the literature regarding preparation of 1 mmol of bis(indolyl)methane derivatives

Entry	Catalyst	Time	Yield (%)	Catalyst amount	Condition
1	Fe_3O_4/SiO_2/PTS/AMTA	1–8 h	70–98	10 mg	Solvent free, 80°C (this work)
2	Zeolite HY	1–1.5 h	65–85	50 mg	CH_2Cl_2, r.t.[33]
3	$FeCl_3\cdot 6H_2O$	0.5–5 h	78–98	5 mol%	[omim]PF_6[51]
4	Silica sulfuric acid (SSA)	10 min–6 h	67–95	50 mg	Solvent free, r.t.[52]
5	Schiff base + $Cu_SO_4\cdot 5H_2O$	15 h	80–98	5 mol%	EtOH, r.t.[53]
6	*N,N,N,N*-Tetrabromobenzene-1, 3-disulfonamide (TBBDA)	1 min–2 h	78–95	50 mg	Solvent free, r.t.[47]
7	$ZrCl_4$	10 min–6 h	81–97	23 mg	CH_3CN, r.t.[48]
8	Cellulose-supported perchloric acid (CSPA)	10–40 min	80–94	100 mg	Solvent free, r.t.[54]
9	ZrO_2–MgO	20 min	94.5–99.2	100 mg	Solvent free, 70°C[30]
10	Nano-Fe_3O_4	1 min–24 h	40–99	10 mol%	Solvent free, r.t.[38]

external magnet was used to remove the catalyst and crushed ice was added to the mixture. The precipitate was filtered, was washed using distilled water and then was dried at room temperature. The crude product was purified by recrystallization from hexane and ethyl acetate to afford a high-purity product.

3.7 | Selected spectroscopic data

3.7.1 | 3,3′-Bis(indolyl)phenylmethane (3a)

IR (KBr, ν_{max}, cm^{-1}): 3400 (N&bond;H), 3100 (aromatic C&bond;H), 2932 (aliphatic C&bond;H), 1599 and 1493 (aromatic C&dbond;C), 1339 (C&bond;N). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 5.80 (1H, s, C&bond;H), 6.55 (2H, s, Ar&bond;H), 6.95 (2H, t, J = 7.4 Hz), 7.05–7.32 (11H, m, Ar&bond;H), 7.90 (2H, brs, NH). Anal. Calcd for $C_{23}H_{18}N_2$ (%): C, 85.68; H, 5.63; N, 8.69. Found (%): C, 85.64; H, 5.66; N, 8.70.

3.7.2 | 3,3′-Bis(indolyl)-4-methoxyphenylmethane (3b)

IR (KBr, ν_{max}, cm^{-1}): 3398 (N&bond;H), 3110 (aromatic C&bond;H), 2927 (aliphatic C&bond;H), 1615 and 1490 (aromatic C&dbond;C), 1334 (C&bond;N), 1246 (C&bond;O). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 3.79 (3H, s, OCH$_3$), 5.80 (1H, s, CH), 6.70 (2H, s, ArH), 6.84 (2H, d, J = 8.0 Hz, ArH), 7.00 (2H, t, J = 7.3 Hz, ArH), 7.17 (2H, t, J = 7.1 Hz, ArH), 7.39–7.45 (4H, dd, J = 15.0, 8.0 Hz, ArH), 7.92 (2H, brs, NH). Anal. Calcd for $C_{24}H_{20}N_2O$ (%): C, 81.79; H, 5.72; N, 7.95. Found (%): C, 81.90; H, 5.76; N, 8.07.

3.7.3 | 3,3′-Bis(indolyl)-3-nitrophenylmethane (3d)

IR (KBr, ν_{max}, cm^{-1}): 3430 (N&bond;H), 3100 (aromatic C&bond;H), 2936 (aliphatic C&bond;H), 1526, 1347 (N&dbond;O), 1610, 1455 (aromatic C&dbond;C), 1245 (C&bond;N). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 6.00 (1H, s, CH), 6.70 (2H, s, ArH), 7.07 (2H, t, J = 7.5 Hz, ArH), 7.23–7.49 (7H, m, ArH), 7.72 (1H, d, J = 7.5, ArH), 8.01 (2H, brs, NH), 8.15 (1H, d, J = 7.5, ArH), 8.25 (1H, s, ArH). Anal. Calcd for $C_{23}H_{17}N_3O_2$ (%): C, 75.19; H, 4.66; N, 11.44. Found (%): C, 75.20; H, 4.70; N, 11.37.

3.7.4 | 4-Chlorophenylmethane-3,3′-bis(indolyl) (3f)

IR (KBr, ν_{max}, cm^{-1}): 3411 (N&bond;H), 3121 (aromatic C&bond;H), 2932 (aliphatic C&bond;H), 1680 and 1487 (aromatic C&dbond;C), 1343 (C&bond;N). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 5.81 (1H, s, CH), 6.57 (2H, s, ArH), 6.92 (2H, t, J = 7.6 Hz, ArH), 7.09 (2H, t, J = 7.6 Hz, ArH), 7.13–7.32 (8H, m, ArH), 7.80 (2H, brs, NH). Anal. Calcd for $C_{23}H_{17}ClN_2$ (%): C, 77.41; H, 4.80; N, 7.85. Found (%): C, 77.45; H, 4.78; N, 7.90.

3.7.5 | Cyclohexyl-3,3′-bis(indolyl)methane (3m)

IR (KBr, ν_{max}, cm^{-1}): 3409 (N&bond;H), 3100 (aromatic C&bond;H), 2932 (aliphatic), 1600 and 1455 (aromatic C&dbond;C), 1336 (C&bond;N). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 1.65 (6H, m, 3CH$_2$), 2.58 (4H, t, J = 5.4 Hz, 2CH$_2$), 6.91(2H, t, J = 7.5 Hz, ArH), 7.12 (2H, m, ArH), 7.32 (2H, d, J = 8.1 Hz, ArH), 7.59 (2H, d, J = 8.1 Hz,Ar&bond;H), 7.92 (2H, brs, NH). Anal. Calcd for $C_{22}H_{22}N_2$ (%): C, 84.04; H, 7.05; N, 8.91. Found (%): C, 84.16; H, 7.07; N, 8.77.

3.7.6 | 3-(1*H*-Indol-3-yl)-3,3′-bis(1′*H*-indol)-2-one (3l)

IR (KBr, ν_{max}, cm^{-1}): 3427 (N&bond;H), 3067 (aromatic C&bond;H), 1708 (C&dbond;O), 1613 and 1471 (aromatic C&dbond;C), 1336 (C&bond;N). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 6.62–7.10 (m, 3H, ArH), 7.21–7.24 (m, 4H, ArH), 7.34 (d, J = 8.0 Hz, 2H, ArH), 10.54 (s, 1H, NH), 10.95 (s, 2H, NH). Anal. Calcd for $C_{24}H_{17}N_3O$ (%): C, 79.32; H, 4.72; N, 11.56. Found (%): C, 79.25; H, 4.79; N, 11.96.

4 | CONCLUSIONS

An efficient and green protocol has been introduced for the synthesis of bis(indolyl)alkane derivatives using Fe_3O_4/SiO_2/PTS/AMTA as a novel nanomagnetic catalyst under solvent-free conditions. The Fe_3O_4/SiO_2/PTS/AMTA nanocomposite was prepared using Fe_3O_4 with a silica layer, and its surface was modified with AMTA. The nanocatalyst was characterized using FT-IR, SEM, XRD and VSM techniques. Following optimization of the reaction conditions, several bis(indolyl)alkane derivatives were synthesized by the three-component reaction of various aldehydes and ketones with indole at

80°C under solvent-free conditions. Experimental simplicity, good to excellent yields, solvent-free conditions and stability and recyclability of the catalyst are advantages of this method.

ACKNOWLEDGEMENT

We are grateful to the Islamic Azad University, Arak Branch for its laboratory supplies.

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How to cite this article: Hajibabaei M, Senejani MA, Shafiei F. 3-Amino-5-mercapto-1,2,4-triazole-functionalized Fe_3O_4 magnetic nanocomposite as a green and efficient catalyst for synthesis of bis(indolyl)methane derivatives. *Appl Organometal Chem*. 2020;e5641. https://doi.org/10.1002/aoc.5641