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Samira Noori: Doing laboratory work and preparing data. Ramin Ghorbani-Vaghei: Supervisor and presenter of research work and results analysis. Maryam Mirzaei-Mosbat: Writing and editing

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Graphical Abstract

N-Benzylation of Primary Amines Using Magnetic Fe₃O₄ Nanoparticles Functionalized with Hexamethylenetetramine as an Efficient and Recyclable Heterogeneous Catalyst

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1 N-Benzylation of Primary Amines Using Magnetic Fe₃O₄ Nanoparticles

2 Functionalized with Hexamethylenetetramine as an Efficient and Recyclable

3 Heterogeneous Catalyst

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10 Abstract

11 Herein we report, a new, simple and mild procedure for N-benzylation and N,N-dibenzylation of anilines through the reaction of aniline derivatives and benzyl bromide at 60 °C in EtOH in the presence of 12 catalytic amounts of magnetic Fe₃O₄ nanoparticles functionalized with hexamethylenetetramine 13 (Fe₃O₄@SiO₂@Propyl-HMTA). The title compounds were formed in high purity and their structures 14 characterized by spectral analysis. The results also showed that the magnetic nanoparticle catalyst had 15 significant advantages including, simplicity of preparation, heterogeneity, stability and recyclability. 16 Moreover, the catalyst was characterized by various methods, such as FT-IR, SEM, VSM, TEM, 17 TGA and XRD, after the reaction to compare with its structure before reaction. 18 19

- 20 Keywords: magnetic Fe₃O₄, nanoparticles, hexamethylenetetramine, *N*-benzylation.
- 21

22 **1. Introduction**

As the carbon-nitrogen bond is of great importance in pharmaceutical and bioactive compounds 23 [1], many researchers have been recently engaged in designing C-N bond formation protocols as 24 new strategies in organic synthesis [2,3]. Recently, the synthesis of amines has attracted 25 considerable attention because amines and their derivatives are major functionalities in various 26 natural products and important synthetic targets. They have been greatly used as solvents, fine 27 chemicals, fluorescence probes, pharmaceuticals, agrochemicals, catalysts for polymerization 28 and in synthetic dyes [4,5]. Consequently, various research groups aimed at developing novel 29 30 methods in order to prepare the mentioned compounds. It should be noted that N-benzylation of amines with alkyl halides can be regarded as a significant synthetic tool for the preparation of 31

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mono- and di-N-benzylated derivatives. However, running such reactions in the presence of a 1 base, has its own drawbacks; e.i. long reaction times, high temperatures and low yields of desired 2 products [6,7]. Therefore, it is necessary for the protocol to be significantly improved. A greatly 3 advisable solution is to replace a homogenous catalytic process by a heterogeneous one [8]. 4 Based on such a strategy, there have been different reports for the N-alkylation of amines with 5 excellent yields; for example Marzaro et al have announced the selective N-alkylation of amines 6 using alkyl halides in an aqueous NaOH medium under microwave irradiation [9]. Though this 7 procedure led to satisfactory results, it required using specialized microwave equipment [10-12]. 8 9 In another attempt, Zhao et al have successfully run N-alkylation reaction of amines in the presence of catalytic amounts of iron (III) bromide, dl-pyroglutamic acid and 1,2,3,4,5-10 pentamethylcyclopenta-1,3-diene at 160 °C under an Ar atmosphere [13]. Zhang et al reported 11 12 excellent yields using Fe₂O₃-supported palladium catalyst for the N-alkylation of amines with alcohols at 140 °C or 160 °C [14]. Notably, the last mentioned method needs argon atmosphere 13 and relatively high temperature in order to achieve acceptable yields. To find a way out of this 14 problem, we were prompted to investigate the use of magnetic nanoparticles (MNPs) for the N-15 16 alkylation of anilines.

17

In the past few decades, novel catalysts such as: M(Fe, Co, Mn, Cu)-doped ZrO₂ tetragonal 18 19 nanoparticles [15-18], Au@TiO₂ yolk-shell NPs [19], (Y, Cu) codoped a-Fe₂O₃ nanostructure [20], Gadolinium Substituted BiFeO₃ Nanoparticles [21] carbon quantum dots (CQDs) [22] and 20 carbon nanotubes-titania quantum dots (FCNT-TQDs) [23] have been introduced as catalysts 21 22 developed with their catalytic activities. Because of their high surface area, facile preparation route, high activity and selectivity, easy separation from the reaction medium, recyclability and 23 reusability have been developed as suitable replacements for conventional heterogeneous 24 25 catalysts. In this article, we also introduce a new catalyst.

One of the major problems in using homogeneous catalysts is their separation from the reaction medium. Though the use of heterogeneous catalysts solves this problem, the unavailability of all active sites remains as the main problem of such catalysts. Nanocatalysts are the bridge between homogeneous and heterogeneous catalysts due to their high surface area, causing a significant contact between the reactants and the catalyst. In this aspect, nanocatalysts are similar to homogeneous ones but are as well easy to separate from the mixture. Magnetic nanoparticles are considered as broadly applied nanocatalysts which can be separated by an external magnet and
 reused several times [24-28].

2 Teused several times [24-26].

3 Different organic and inorganic compounds, for example ionic liquids (ILs), have been used to

4 modify MNPs [29, 30]. The negative properties of ILs, i.e. their high viscosity, can be decreased

5 by immobilizing functional ILs on a surface. Herein, report the use of silica-coated MNPs

6 surface modified by hexamethylenetetramine is reported [31].

7 In the presented study, the synthesis of mono-*N*- and *N*,*N*-dibenzylation of primary amines
8 (Scheme 1) under mild conditions is described. Low reaction temperature, good yields of
9 products, green method, and no need for inert atmosphere and metal can be cited as other
10 important advantages of this protocol.



17 18

19 2. Experimental Section

20

21 **2.1. General Remarks**

All chemicals were purchased from commercial suppliers (Merck and Fluka companies). Proton 22 Nuclear Magnetic Resonance NMR (¹H NMR) spectra and carbon nuclear magnetic resonance 23 (¹³C NMR) spectra were run on Bruker BioSpin GmbH 250 MHz FT NMR spectrometers. 24 Infrared (IR) spectra were taken using a Shimadzu 435-U-04 FT spectrophotometer using KBr 25 tablets. IR data are represented as frequency of absorption (cm⁻¹). Melting points were measured 26 on a BUCHI 510 apparatus in open capillary tubes. Scanning electron microscopy (SEM) was 27 fulfilled med on EM3200 instrument operated at 30 kV accelerating voltage. The magnetic 28 29 measurements were performed with VSM at room temperature.

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- 32

1 2.2. Preparation of Fe₃O₄ MNPs

To a 100 mL of deionized water, $FeCl_3 \cdot 6H_2O$ (11.3 g, 0.0418 mol) and $FeCl_2 \cdot 4H_2O$ (5.648 g, 0.020 mol) were added and dissolved and stirred at 85 °C for 30 min. 25 mL of ammonia (28% aqueous solution) was then rapidly injected into the reaction mixture. In order to afford Fe_3O_4 nanoparticles, the reaction was stirred for another 30 min at 85 °C. The suspended Fe_3O_4 nanoparticles were isolated by an external magnet. Finally, the product was washed subsequently with distilled water and ethanol, dried at 80 °C in an oven.

8

9 2.3. Preparation of MNPs coated by silica (Fe₃O₄@SiO₂ MNPs)

A modified Stöber method was applied in order to prepare $Fe_3O_4@SiO_2$ core-shell nanoparticles. To a mixture of 80 mL of deionized water, 20 mL of EtOH and 2 mL of ammonia (28 wt%), 1.0g of the naked Fe_3O_4 was dispersed and 2.0 mL of tetraethyl orthosilicate (TEOS) was then added. The core-shell MNPs ($Fe_3O_4@SiO_2MNPs$) were vigorously stirred at room temperature for 2 h and separated using an external magnet in order to remove the unbound silica particles. Then nanoparticles were washed subsequently with deionized water, EtOH and acetone, and finally dried at room temperature.

17

18 2.4. Preparation of HMTA containing silane (Ionic liquid)

3-Chloropropyltrimethoxysilane (2.0 g, 10 mmol) was added to a solution of HMTA (1.4 g, 10 mmol) in toluene (30 mL). The resulting precipitate was refluxed under nitrogen atmosphere for
24 h which was then isolated and washed with EtOH.

22

23 2.5. Preparation of Fe₃O₄@SiO₂@Propyl-HMTA

To a dispersed solution of $Fe_3O_4@SiO_2$ MNPs (2.0 g) in dry toluene (30 mL), it was added HMTA containing silane (0.5 g) and sonically irradiated in an ultrasonic bath for 30 min. The mixture was then refluxed for 48 h under Nitrogen atmosphere. An external magnet was applied in order to separate the $Fe_3O_4@SiO_2@Propyl-HMTA$. Finally, the product was washed with EtOH for several times and dried within 6 h in an oven.

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1 2.6. General procedure for *N*-benzylation and *N*,*N*-dibenzylation of primary amines

A mixture of aniline (1eq), benzyl bromide (2.2 eq) and 0.06 g Fe₃O₄@SiO₂@Propyl-HMTA in
EtOH (5 mL) was heated at 60 □. After completion of the reaction, as indicated by the TLC (*n*hexane/acetone 10:3), the reaction mixture was cooled to room temperature and the nanocatalyst
was separated using an external magnet. The crude product washed with ethanol and purified by
hot ethanol. The products were characterized using physical and spectroscopic (IR, NMR, MS)
data.

8

9 *N*,*N*-dibenzyl-4-chloroaniline 4a:

White solid; Yield: 93%; M.p. 104-105 °C; ¹H NMR (250 MHz, CDCl₃): δ 4.65 (s, 4H, CH₂),
6.64-6.67 (d, J= 7.5, 2H, ArH), 7.10-7.13 (d, J= 7.5, 2H, ArH), 7.23-7.39 (m, 10H, ArH); ¹³C
NMR (62.5 MHz, CDCl₃): δ 54.5, 113.7, 121.6, 126.6, 127.1, 128.8, 129.0, 138.1, 147.7; MS
(m/z): 307 (M⁺, 100%), 215.9, 179.9, 137.9, 91.2, 65.0.

14 *N*,*N*-dibenzyl-4-bromoaniline 4b:

White solid; Yield: 94%; M.p. 125-126 °C; ¹H NMR (250 MHz, CDCl₃): δ 4.69 (s, 4H, CH₂),
6.63-6.67 (d, J= 7.5, 2H, ArH), 7.29-7.37 (m, 12H, ArH); ¹³C NMR (62.5 MHz, CDCl₃): δ 54.4,
108.6, 114.2, 126.5, 127.1, 128.8, 131.9, 138.0, 148.1; ; MS (m/z): 351.06 (M⁺, 100%), 274.0,
260.0, 180.9, 91.2, 65.0.

19

20 *N*,*N*-dibenzyl-4-methoxyaniline 4c:

Light yellow solid: 91%; M.p. 85-87 °C; ¹H NMR (250 MHz, , DMSO-d₆):): δ 4.55 (s, 4H,
CH₂), 6.59-6.70 (q, 4H, ArH), 7.21-7.31 (m, 10H, ArH); ¹³C NMR (62.5 MHz, DMSO-d₆): δ
29.0, 55.4, 114.9, 127.0, 127.3, 128.8, 139.7, 143.1, 151.6; MS (m/z): 303.16 (M⁺, 100%), 287.1,
210.2, 196.1, 91.1, 77.1, 65.1.

25

1 *N*,*N*-dibenzylaniline 4d:

- 2 Light green solid; Yield: 94%; M.p. 85-87 °C; ¹H NMR (250 MHz, DMSO-d₆): δ 4.69 (s, 4H,
- 3 CH₂), 6.67-7.44 (m, 15H, ArH); ¹³C NMR (62.5 MHz, DMSO-d₆): δ 56.0, 122.7, 123.8, 127.6,
- $4 \qquad 128.1, \ 128.5, \ 128.8, \ 129.4, \ 129.8, \ 130.0, \ 130.5; \ MS \ (m/z): \ 273.15 \ (M^+, \ 100\%), \ 196.1, \ 182.1, \ 18$
- 5 104.1, 91.1, 77.1, 65.1.

6 tribenzylamine 4e:

- 7 Light yellow solid; Yield: 93%; M.p. 90-92 °C; ¹H NMR (250 MHz, CDCl₃): δ 4.14 (s, 6H,
- 8 CH₂), 7.24-7.66 (m, 15H, ArH); ¹³C NMR (62.5 MHz, CDCl₃): δ 55.9, 128.7, 129.3, 129.8,
- 9 131.3; MS (m/z): 287.17 (M⁺, 100%), 210.1, 196.1, 181.1, 91.1, 65.1

10 *N*,*N*-dibenzyl-2,4-dimethylaniline 4g:

- 11 Light yellow solid; Yield: 92%; M.p. 144-146 °C; ¹H NMR (250 MHz, DMSO-d₆): δ 2.26 (s,
- 12 3H, CH₃), 2.32 (s, 3H, CH₃), 4.41 (s, 4H, CH₂), 7.07-7.29 (m,13H, ArH); ¹³C NMR (62.5 MHz,
- 13 DMSO-d₆): δ 18.5, 20.8, 40.4, 122.8, 127.4, 128.5, 131.9, 133.3; MS (m/z): 301.18 (M⁺, 100%),
- 14 224.1, 210.1, 194.1, 122.1, 91.1, 77.1, 65.1.
- 15

16 *N*-benzyl-4-nitroaniline3h:

- 17 Yellow solid; Yield: 91%; M.p. 84-86 °C; ¹H NMR (250 MHz, CDCl₃): δ 4.43 (s, 2H, CH₂),
- 18 4.85 (s, 1H, NH), 6.55-6.58 (d, J= 7.5 Hz, 2H, ArH), 7.20-7.34 (m, 5H, ArH), 8.06-8.09 (d, J=
- 19 7.5 Hz, 2H, ArH); ¹³C NMR (62.5 MHz, CDCl₃): δ 47.6, 111.3, 126.4, 127.3, 127.8, 128.9; MS
- 20 (m/z): 228 (M⁺, 100%), 180.9, 91.0, 65.0
- 21

22 *N*-benzyl-2-methyl-4-nitroaniline 3i:

- 23 Yellow solid; Yield: 93%; M.p. 104-105 °C; ¹H NMR (250 MHz, CDCl₃): δ 2.22 (s, 3H,
- 24 CH₃)4.50 (s, 2H, CH₂), 4.67 (s, 1H, NH), 6.52-6.55 (d, J= 7.5 Hz, 1H, ArH), 7.35-7.41 (m, 5H,
- 25 ArH), 8-8.03 (d, J= 7.5 Hz, 2H, ArH); ¹³C NMR (62.5 MHz, CDCl₃): δ 17.3, 47.7, 108.2, 121.1,

124.6, 126.0, 127.3, 127.8, 128.9, 137.4, 137.8, 151.3; MS (m/z): 242.1 (M⁺, 100%), 194.1,
 165.1, 91.1, 65.1

3

4 *N*-benzyl-2,6-dimethylaniline 3j:

Light yellow solid: 87%; M.p. 124-126 °C; ¹H NMR (250 MHz, CDCl₃): δ 2.40 (s, 6H, CH₃),
4.64 (s, 2H, CH₂), 6.98 7.22 (m, 8H, ArH), 10. 93 (s, 1H, NH), ArH; ¹³C NMR (62.5 MHz,
CDCl₃): δ 19.6, 53.5, 128.5, 129.2, 129.6, 129.9, 131.4, 132.1, 133.5; MS (m/z): 211.2 (M⁺,
100%), 120.1, 91.2, 77.1, 65.1

9

10 **3. Result and discussion**

In this project Fe₃O₄@SiO₂@Propyl-HMTA was synthesized and used to develop the convenient 11 methods for N,N-dibenzylation of anilines [32]. For this purpose, after preparing the Fe₃O₄ 12 nanoparticles [33] silica was used as a protecting shell to form the core-shell structure 13 $(Fe_3O_4@SiO_2)$ [34-36]. On the other hand, and in order to synthesize the ionic liquid, HMTA 14 was treated with triethoxy-3-(chloropropyl)-silane in dry toluene and refluxed for 24 h. As the 15 mole ratio of reactants were chosen to be 1:1, it is reasonable to assume that only one nitrogen 16 17 atom has reacted with triethoxy-3-(chloropropyl)-silane. As a final step, Fe₃O₄@SiO₂@Propyl-HMTA catalyst (figure 1) was prepared by coating MNPs (Fe₃O₄@SiO₂) with the ionic liquid. 18 Afterwards, Fe₃O₄@SiO₂@Propyl-HMTA was investigated for its effect on N-benzylation and 19 *N*,*N*-dibenzylation of anilines. 20



23

24

Figure 1. The structures of $Fe_3O_4@SiO_2@Propyl-HMTA$

At first, the catalytic activity of $Fe_3O_4@SiO_2@Propyl-HMTA$ was compared with those of other catalysts reported in literature, the results of which are shown in Table 1. Based on these data, the $Fe_3O_4@SiO_2@Propyl-HMTA$ is one of the most effective catalysts for *N*,*N* dibenzylation of anilines. It is assumed that, owing to the presence of nitrogen atoms in the HMTA moiety of the catalyst, it acts as a Lewis base and hence, prevents the deactivation of aniline.

6

7 **Table 1:** Comparison of various catalysts for the *N*-benzylation and *N*,*N*-dibenzylation of primary amines

Entry	Catalyst	(°C)	Time (min)	Yield (%)	Ref
1	K10–ZnO	70	720	86	[8]
2	SiO2-Cu2O	100	480	50	[38]
3	SiO2-CuI	15	240	75	[39]
4	I_2	120	1440	60	[37]
5	Microflow Reactor	150	4	97	[40]
6	Fe ₃ O ₄ @SiO ₂ @PropylHMTA	60	240	94	This work

8

9 In order to optimize the reaction conditions, the reaction of aniline (leq) and benzyl bromide (2.2eq) was chosen as the model one. Conducting the model reaction in the absence of any 10 catalyst revealed that it did not produce the desired product (Table 2, entry 1). Table 2 illustrates 11 12 that 0.06 g of the catalyst is optimal amount (entries 11-12). It should be noted that the yield of reaction in the presence of either MNPs or MNPs@SiO₂, is much less than that of 13 MNPs@SiO₂-@Propyl-HMTA (Table 2, entries 13-14). Running the reaction in different 14 15 solvents (Table 2, entries 2-6) revealed that EtOH was the best choice. It was also found that the optimal temperature for this reaction was 60 °C (Table 2, entry 8). Consequently, the best 16 17 reaction conditions are the ones mentioned in entry 10 of Table 2. It is worth noting that the products were characterized by FT-IR, ¹H NMR, ¹³C NMR and Mass spectroscopic data. 18

19

20 Table 2: Optimization of reaction conditions^a



21 22

Entry	Catalyst	Solvent	Time [min]	Temperature	Yield ^b (%)
1	-	EtOH	720	reflux	-
2	0.1	H ₂ O	720	100	20
3	0.1	H ₂ O/EtOH	480	100	43
4	0.1	CH ₃ CN	480	reflux	74
5	0.1	Solvent-free	720	100	67
6	0.1	EtOH	720	r.t	65
7	0.1	EtOH	240	reflux	84
8	0.1	EtOH	240	60	86
9	0.08	EtOH	240	60	90
10	0.06	EtOH	240	60	94
11	0.05	EtOH	360	60	82
12	0.03	EtOH	480	60	63
13	Fe ₃ O ₄	EtOH	720	reflux	12
14	Fe ₃ O ₄ @SiO ₂	EtOH	720	reflux	22

^aReaction conditions: aniline (1 mmol), benzyl bromide (2.2 mmol), catalyst, solvent (5 mL). ^bIsolated yield.

In final step of this project, we turned our attention toward the substrates reactivity (benzyl halides and anilines). The reaction of aniline with benzyl bromide and benzyl chloride at different temperatures shows that benzyl bromide is more reactive than benzyl chloride (Table 3).

Table 3: Reactivity of substrates

Entry	Catalyst	Substrate	Time (min)	T (°C)	Yield (%)
1	0.06	BnBr	240	reflux	86
2	0.06	BnBr	240	60	94
3	0.06	BnCl	360	reflux	72
4	0.06	BnCl	360	60	76

On the other hand, different substituted anilines were chosen to test the effect of electronwithdrawing or electron-releasing groups on mono *N*-benzylation and *N*,*N*-dibenzylation reaction
(Table 4). Simple aniline was converted into *N*,*N*-dibenzylated product with 94% yield in 4 h

(Table 4, entry 4d). Interestingly, 4-nitroaniline derivatives provided mono-N-benzylated anilines 1 2 under selected conditions due to the electron-withdrawing effect of the nitro group and subsequent reduction in nucleophilicity aniline (Table 4, entries 3h–3i). And finally, the hindered 3 4 aniline 2,6-dimethylaniline, just yielded the corresponding mono-N-benzylated product in reaction with benzyl bromide (entry 3j). 5

6

7 Table 4 N-benzylation and N,N-dibenzylation of primary amines using Fe₃O₄@SiO₂@Propyl-HMTA as a catalyst^a



10

11 ^aReaction conditions: aniline (1 mmol), benzyl bromide (2.2 mmol), Fe₃O₄@SiO₂@Propyl-HMTA (0.06 g), EtOH

12 (5 mL), reflux

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-
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To account for the effect of Fe₃O₄@SiO₂@Propyl- HMTA in N,N-dibenzylation of primary amines 2 the following mechanism is proposed (Scheme 2). At first, aniline attacks to the electron-deficient 3 center of benzyl bromide (the released proton is scavenged by HMTA moiety of the catalyst) [41, 4 5 42]. In the next step, N,N-dibenzylation of primary amines is accomplished by another nucleophilic reaction and elimination of the second proton of aniline. In comparison with HMTA as a 6 7 catalyst, the application of Fe₃O₄@SiO₂@Propyl-HMTA nanomagnetic catalyst provides higher reactivity and catalytic power due to its enhanced surface area [43, 44]. 8 ournal pre-prov

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Scheme 2. Suggested mechanism for the *N*,*N*-dibenzylation of primary amines

The mode reaction was also used to assess the recyclability of the catalyst. In each cycle the
catalyst was separated, washed with hot ethanol, dried and reused in the next cycle. Figure. 2
illustrates the results and confirming the recyclability of the nanocatalyst.





9 Figure 3 shows the SEM images of the catalyst before and after *N*-benzylation reaction which

10 reveal the maintenance of the morphology of nearly spherical nanoparticles with nanometric

11 dimensions after the reaction.



12 13

Figure 3. SEM images of the Fe₃O₄@SiO₂@Propyl-HMTA (MNPs) before(a) and after(b) the reaction

14

The structure of the catalyst before and after reaction was also investigated by FT□IR
spectroscopy (Figure 4). As is seen, the characteristic bands attributed to (Fe-O), (Si-O-Si) and

1 (O-H) stretching vibrations, that is, (540 cm⁻¹), (802 and 1103 cm⁻¹) and (3444 cm⁻¹)
2 respectively, did not change after running the reaction.





4

Figure 4. FT-IR spectra of Fe₃O₄@SiO₂@Propyl-HMTA (MNPs) before (a) and after (b) the reaction.

5 The X-ray diffraction analysis of the catalyst before and after the reaction is shown in Figure 5. 6 As seen from images, the positions and relative intensities of all characteristic diffractions are 7 almost same implying that the original structure of $Fe_3O_4@SiO_2@Propyl-HMTA$ has preserved 8 after the reaction ($2\theta = 30^\circ$, 35.5° , 42.5° , 57° and 62°). A strong peak in curves observed at 9 $2\theta = 35.5$ is attributed to the pure Fe_3O_4 . Regarding the position and severity of the peaks, it could 10 be inferred that the manipulations performed in this study could not alter the Fe_3O_4 phase.



11

Figure 5. XRD pattern of Fe₃O₄@SiO₂@Propyl-HMTA (MNPs) before (a) and after (b) the reaction.

The magnetic properties of catalyst were evaluated by vibrating sample magnetometer (VSM) 1 analysis (Figure 6). This figure shows that the magnetic behavior of the catalyst is almost 2 identical before and after the reaction, illustrating no obvious alteration of the catalyst structure 3 during the reaction. According to Figure 6, the mass manetization of Fe₃O₄@SiO₂@Propyl-4 HMTA (MNPs) is about 10 emu/g. As is observed in these curves there are no hysteresis loops 5 for the nanoparticles and the Fe₃O₄@SiO₂@Propyl-HMTA (MNPs) exhibit 6 the 7 superparamagnetic qualities as that of Fe₃O₄ (MNPs).



10 Figure 6. Magnetic curves of the Fe₃O₄@SiO₂@Propyl-HMTA (MNPs) before and after the reaction.

11

9

TEM image of the Fe₃O₄@SiO₂@Propyl-HMTA is represented in Figure 7. Image of the silica-coated MNPs display a dark MNP core surrounded by an amorphous silica shell. Figure 7 shows that iron oxide nanoparticles are entrapped successfully in the silica shell



Figure 7. TEM Image of the Fe₃O₄@SiO₂@Propyl-HMTA.

1

2

In order to evaluate the thermal stability of $Fe_3O_4@SiO_2@Propyl-HMTA$ catalyst, thermogravimetry analysis (TGA) was applied. As shown in Figure 8, three massloss regions were detected within the curves. The first region, situated below 200 °C, displays a mass loss that is attributed to the loss of water or other solvent in the catalyst. In addition, the second fracture appeared at 200–400°C, which could be due to the decomposition of propyl-HTMA. In the last step, after 400°C, the cleavage and decomposition of other organic molecules in the catalyst have begun to occur. Thus, the catalyst is stable up to 200 °C.



4 Additionally, Fe, Si, O, C and N elements were observed in the energy- dispersive X-ray (EDX)

5 analysis of the $Fe_3O_4@SiO_2@HMTA$ MNPs (Figure 9). The presence of nitrogen indicates the

6 HMTA loading on the catalyst surface.

7



Figure 9. EDX analysis of Fe₃O₄@SiO₂@Propyl-HMTA.

2 **4.** Conclusion

In short, a highly efficient and cost-effective method has been introduced for the *N*-benzylation,
and *N*,*N*-dibenzylation of primary amines in the presence of the Fe₃O₄@SiO₂@Propyl-HMTA
catalyst. Significant advantages, such as mild reaction conditions, excellent yields of products,
simplicity of workup, and recyclability of the catalyst causes the present method to be proposed
as a useful strategy for the synthesis of *N*-substituted secondary and tertiary amines.

8

9

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Highlights

- Efficient, simple and mild synthesis of N-Benzylation derivatives using • Fe₃O₄@SiO₂@Propyl-HMTA.
- New derivatives of *N*-Benzylation was synthesized by Fe₃O₄@SiO₂@Propyl-HMTA. •
- Easy recovery and reuse of this catalyst without notable change in activity •

Declaration of interests

 \Box The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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