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FULL PAPER

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Novel pseudopolymeric magnetic nanoparticles as a hydrogen bond catalyst for the synthesis of tetrahydrodipyrazolopyridine derivatives under mild reaction conditions

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In the current work, the design, synthesis, characterization, and catalytic performance of a novel pseudopolymeric magnetic nanoparticles bearing urea linkers were presented. After the synthesis of urea linker, it was applied for the synthesis of pseudopolymeric magnetic nanoparticles. The structure of the synthesized pseudopolymeric magnetic nanoparticles was confirmed by applying different methods including Fourier transform infrared (FT-IR) spectroscopy, energy dispersive X-ray (EDX) analysis, thermo gravimetric analysis/differential thermal analysis (TG/DTG), transmission electron microscopy (TEM), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM), differential reflectance spectroscopy (DRS) and N_2 adsorption-desorption isotherms. The catalytic performance of the titled structure was tested towards the synthesis of tetrahydrodipyrazolopyridine derivatives under mild reaction conditions.

KEYWORDS
hydrogen-bonding catalyst, magnetic nanoparticles, multicomponent reactions, tetrahydrodipyrazolopyridines, urea linker

1 | INTRODUCTION

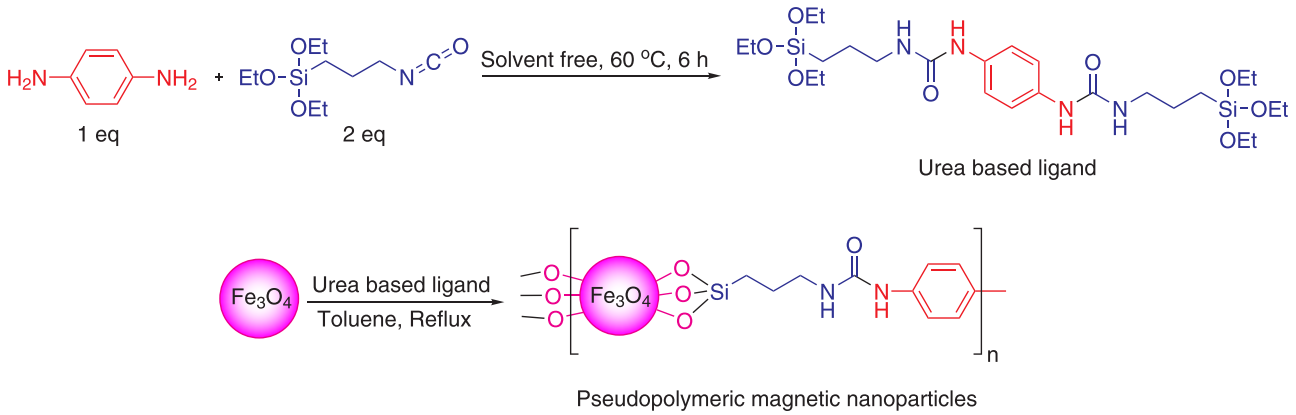
It has been made clear that non-covalent interactions have an influential position in synthesis, catalytic process, design and manufacture of medicines, material and molecular recognition, biomimetic reactions, and molecular biology.[1] One of the most important non-covalent interactions is the capability of hydrogen bond formation. Hydrogen-bonding attractive interactions are the key element for the maintaining the three dimensional structures of DNA and proteins as biological vital molecules. Also, in the synthetic chemical processes, scientists can utilize hydrogen-bonding interactions for regulation of chemoselective, regioselective, and stereoselective chemical bond formations.[2,3] Therefore, it is no wonder that hydrogen-bonding organocatalysis as a fascinating study topic expanded rapidly, and several review articles deal with this area of catalysis.[4–10] Recently, we have reviewed various aspects of urea and its derivatives as powerful and influential H-bonding catalytic active agents in a wide range of chemical processes.[11]

Although homogenous catalytic systems represent many practical benefits like high activity and selectivity, but, due to the high costs and troubles in catalyst separation and recovering processes, the efficacious performance of them is hindered. For overcome to these limitations, several methods such as nanofiltration,

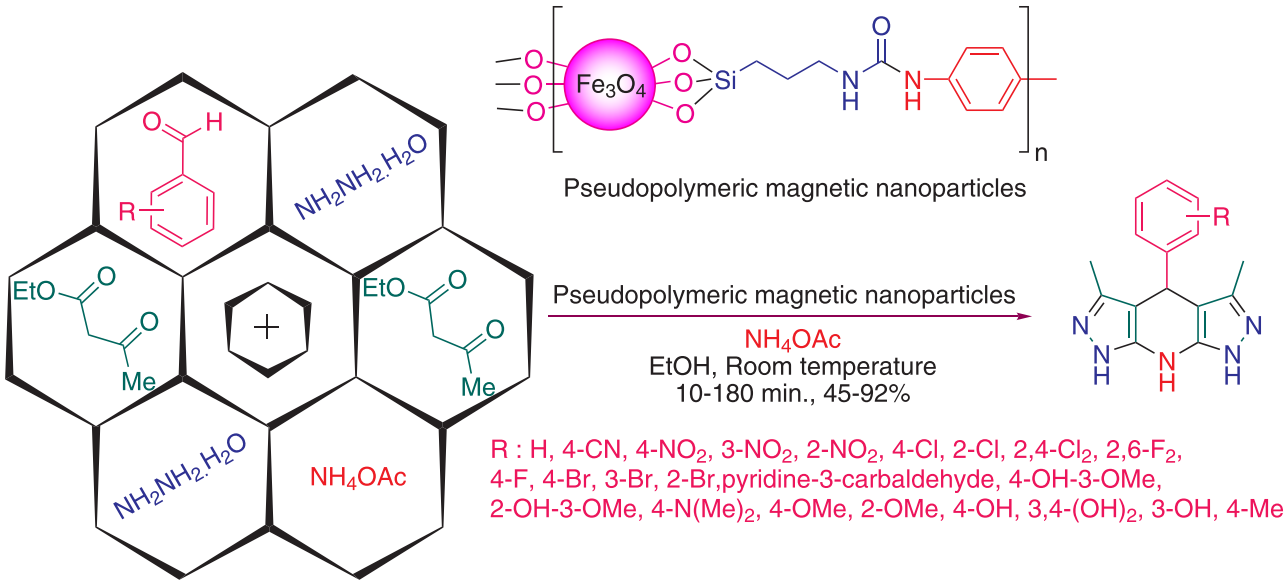
liquid–liquid extraction, chromatography, and centrifugation have been developed. But none of these methods yielded acceptable results. Therefore, chemists are looking for finding new routes to heterogenization of homogeneous catalysts. On the most interesting protocols for this goal is the stabilization of active catalytic species on the surface of suitable solid supports. Among the applied solid supports such as silica, alumina, polymers, carbon, and metal oxides, due to their response to an applied magnetic field, their linking with magnetic materials have received considerable attention. Thus, stabilizing of catalytic active species on the surface of magnetic nanoparticles leads to generation of heterogenous catalysts that show high selectivity, activity, and easy recovering and reusing process.[12–17]

Several practical benefits connected with multicomponent reactions including bond forming competence, atom and step economy, omission of intermediary purification process, low cost of the separation and purification protocol for achieving to pure target molecules, and scarce waste formation in the course of reactions, solvents, reagents, time, and energy conserving make this synthetic strategy as an ideal tool in hands of chemists for the synthesis of structurally complicated molecules.[18–21] In recent years, due to abovementioned reasons, the effective applications of multicomponent reactions for the synthesis of valuable heterocyclic molecules have been well reviewed.[22–25]

Due to co-existence of two biological active moieties, namely, pyrazole and 1,4-dihydropyridine within the structure of tetrahydrodipyrazolopyridines, these versatile molecules represent varied pharmaceutical applications such as anxiolytic, antiallergic, and antiherpetic behavior.[26,27] Also, it is reported that they can be applied as corrosion inhibitors in pickling process in



SCHEME 1 Synthetic route for the preparation of urea based ligand and corresponding pseudopolymeric magnetic nanoparticles



SCHEME 2 Synthesis of tetrahydrodipyrazolopyridine derivatives in the presence of a catalytic amounts of pseudopolymeric magnetic nanoparticles

industry.[28,29] Surveying in the literatures shows that a number of protocols have been reported for the preparation of tetrahydrodipyrazolopyridine derivatives.[30–36] Due to some drawbacks including use of unsafe reagents and solvents, non-recyclable and toxic catalysts, harsh workup protocol, and long reaction time with low practical yield, all of these methods are restricted. As a result, despite of the remarkable improvements, easy and mild methods in the presence of recoverable catalyst are highly demanded for the synthesis of tetrahydrodipyrazolopyridines.

Herein, in pursuit of our previous investigations for introducing reusable nanomagnetic catalysts[37–39] also, in the light of biological importance of tetrahydrodipyrazolopyridine derivatives and persuasive position of hydrogen-bonding in catalysis, we reported the design, synthesis, characterization, and catalytic performance of novel pseudopolymeric magnetic nanoparticles with urea linkers (as a heterogeneous catalyst with the hydrogen bond capability) towards the synthesis of tetrahydrodipyrazolopyridines (Schemes 1 and 2).

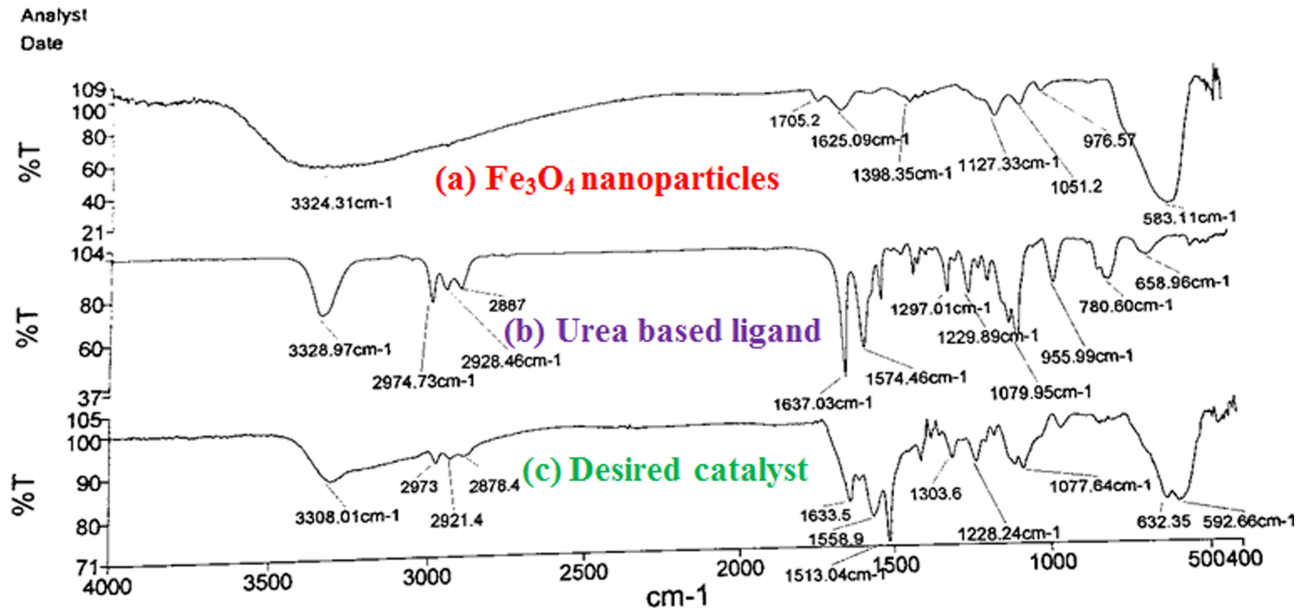


FIGURE 1 Comparative study of the FT-IR spectra of Fe3O4 nanoparticles (a), urea based ligand (b), and desired catalyst (c)

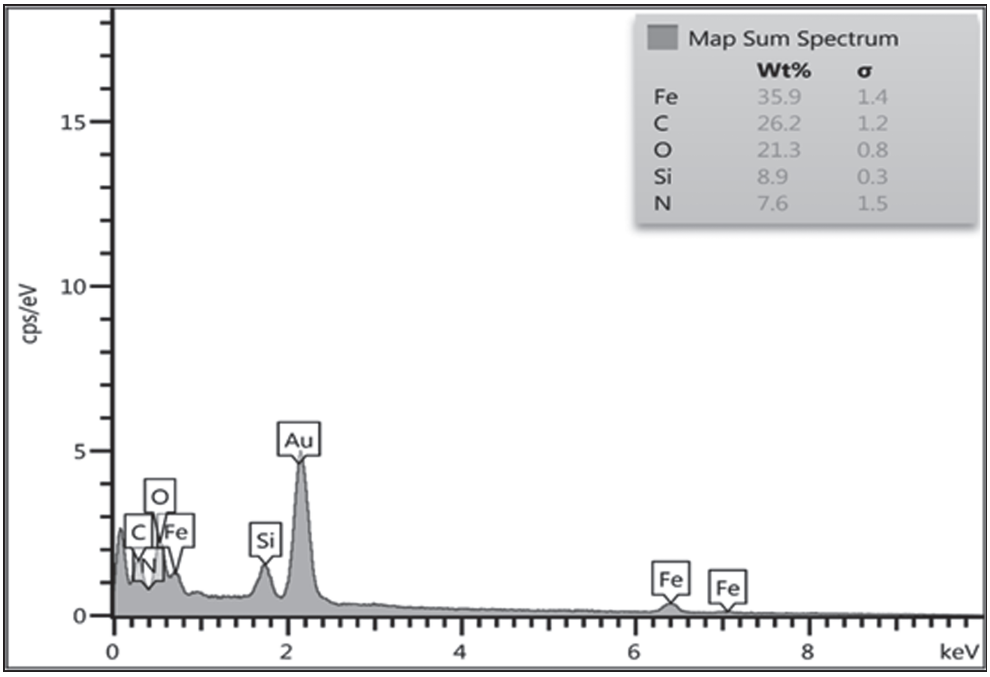


FIGURE 2 EDX analysis of the prepared novel pseudopolymeric magnetic nanoparticles

2 | RESULT AND DISCUSSION

To the best of our knowledge, secondary interactions such as inter and/or intra hydrogen bondings have major roles in biochemical processes.[11] On the other hand, H-bonding catalysts are needed for task-specific development of biomimetic reactions. On the basis of the abovementioned facts, we decided to design synthesis

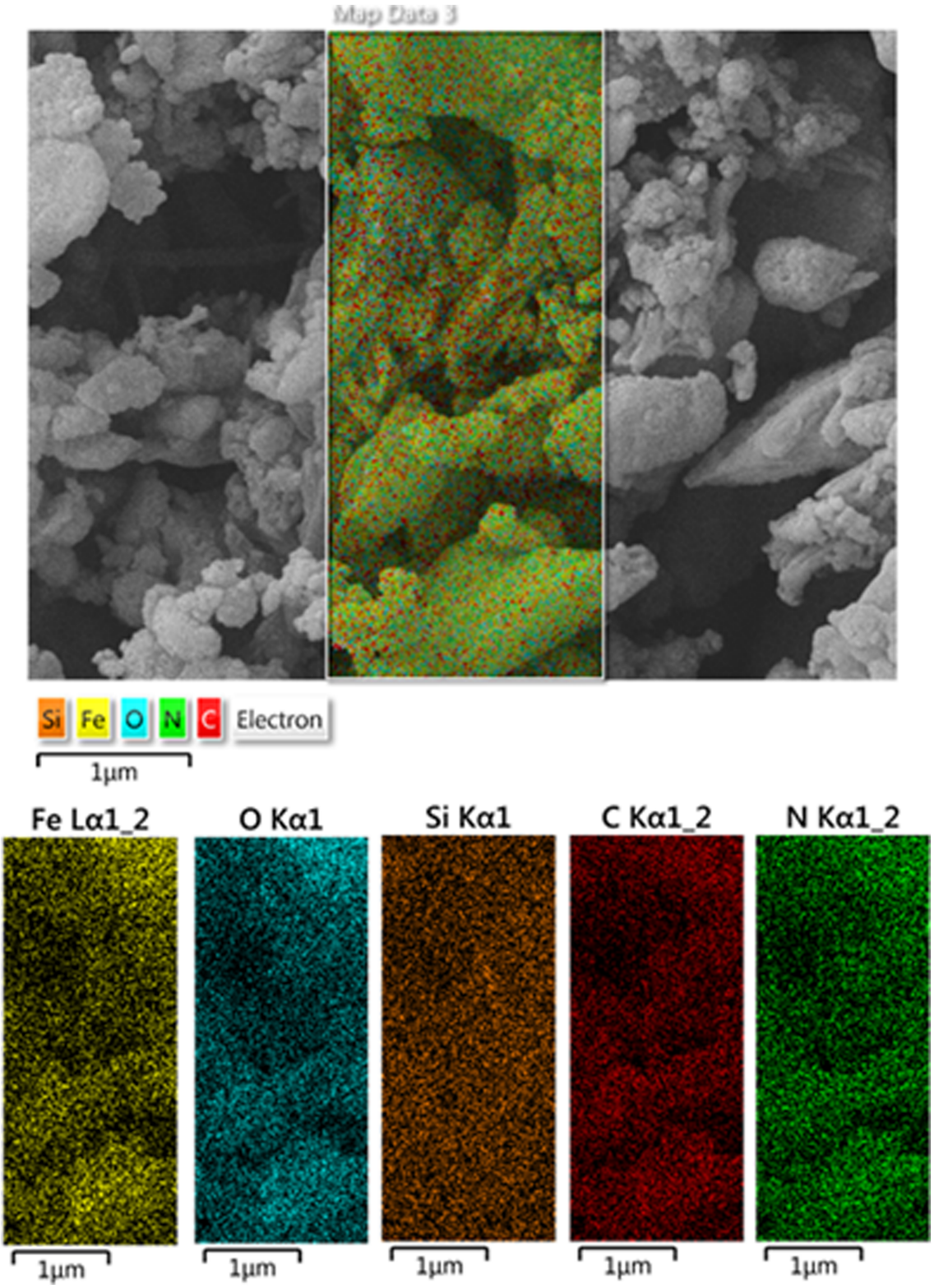


FIGURE 3 Elemental mapping analysis of the prepared novel pseudopolymeric magnetic nanoparticles

and application of novel H-bonding catalyst with biological urea linkers. In initial attempt, we tried to characterize the prepared novel pseudopolymeric magnetic nanoparticles. For this goal, several techniques including FT-IR, EDX, elemental mapping, TGA/DTA, SEM, TEM, and VSM analyses were applied. All of the used technical skills verified the successful formation of the catalyst. The details are discussed below.

By using FT-IR spectra, as depicted in Figure 1, the existence of the characteristic functional groups within the structure of desired catalyst and its related intermediates were confirmed. Broad peak from around 3000–3400 cm^{-1} verified the un-coated OH and NH functional groups. Also, amide carbonyl groups can be distinguished at 1634 cm^{-1}. Fe–O stretching frequency appeared at 593 cm^{-1}.

All anticipated elements within the structure of the novel pseudopolymeric magnetic nanoparticles can be extracted from EDX analysis. The related data showed that the catalyst consists of five elements including iron, oxygen, silicon, carbon, and nitrogen (Figure 2). Also, elemental mapping analysis data are in full compliance with EDX analysis data and showing suitable dispersity of elements at the structure of synthesized catalyst (Figure 3).

As illustrated in Figure 4, in another investigation, SEM images of the prepared catalyst were obtained. The achieved data confirmed the nano sized structure of the catalyst with mean diameter of about 44–102 nm. Also, for more insight, the TEM images were provided. The resulting data suggested a core-shell structure for the novel pseudopolymeric magnetic nanoparticles (Figure 5).

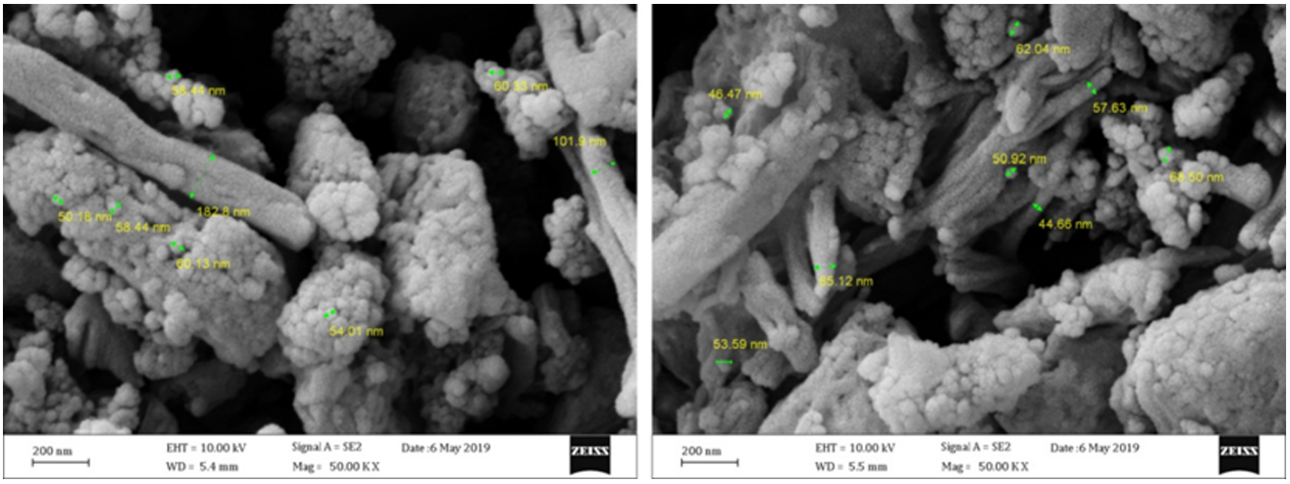


FIGURE 4 SEM images of the prepared novel pseudopolymeric magnetic nanoparticles

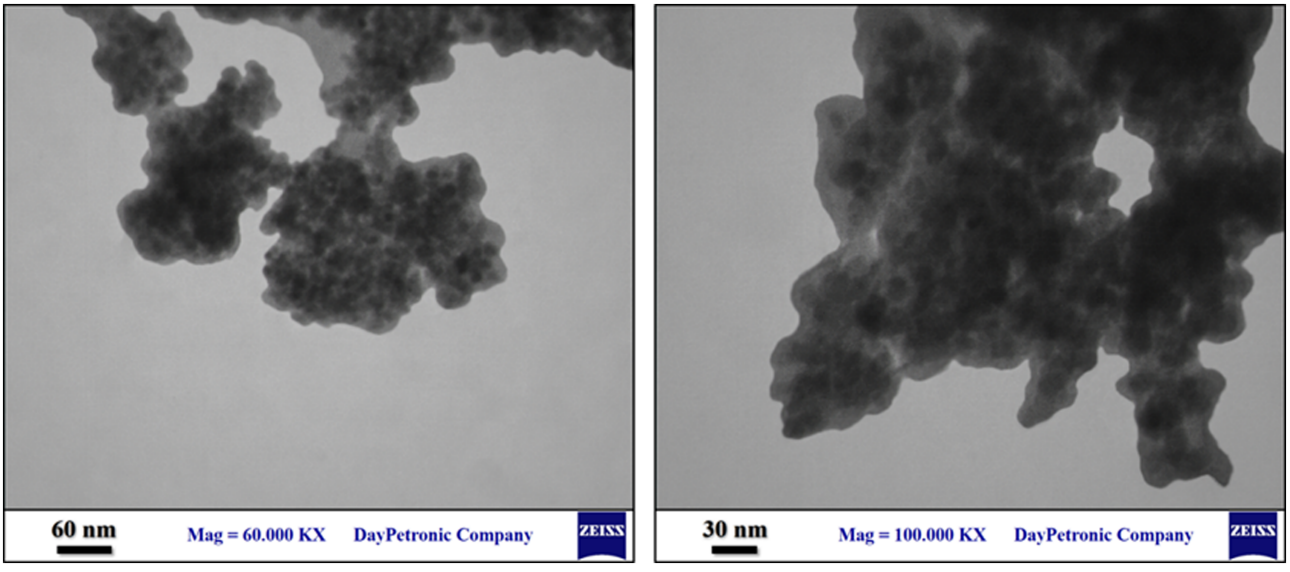


FIGURE 5 TEM images of the prepared novel pseudopolymeric magnetic nanoparticles

The TG/DTG plots of the novel pseudopolymeric magnetic nanoparticles were depicted in Figure 6. The main weight loss at around 340°C states that the prepared catalyst has a high thermal stability, and it is suitable for reactions requiring high operating temperatures.

The magnetic properties of novel pseudopolymeric magnetic nanoparticles were also studied by VSM analysis. The obtained data represent saturation at about 40 emu g^{-1} (decreased compared with the Fe_3O_4 nanoparticles[37]), which confirms the successful modifi-

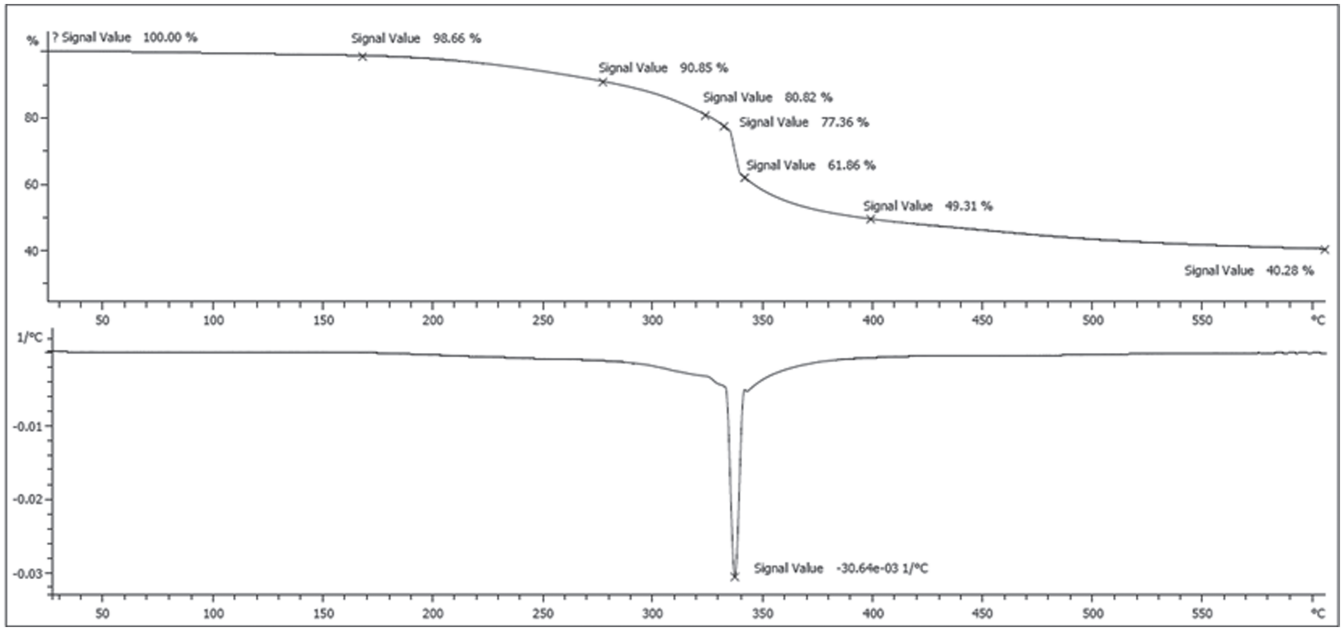


FIGURE 6 TG/DTG plots of the prepared novel pseudopolymeric magnetic nanoparticles

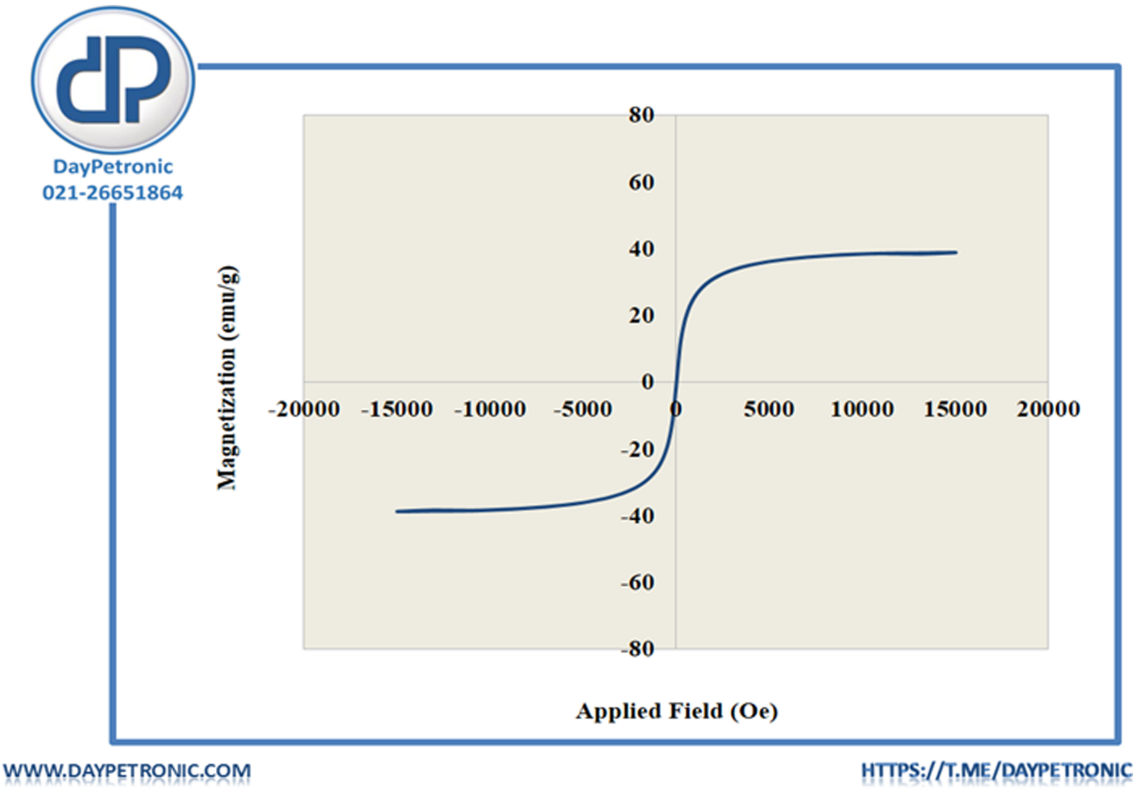


FIGURE 7 VSM analysis of the prepared novel pseudopolymeric magnetic nanoparticles

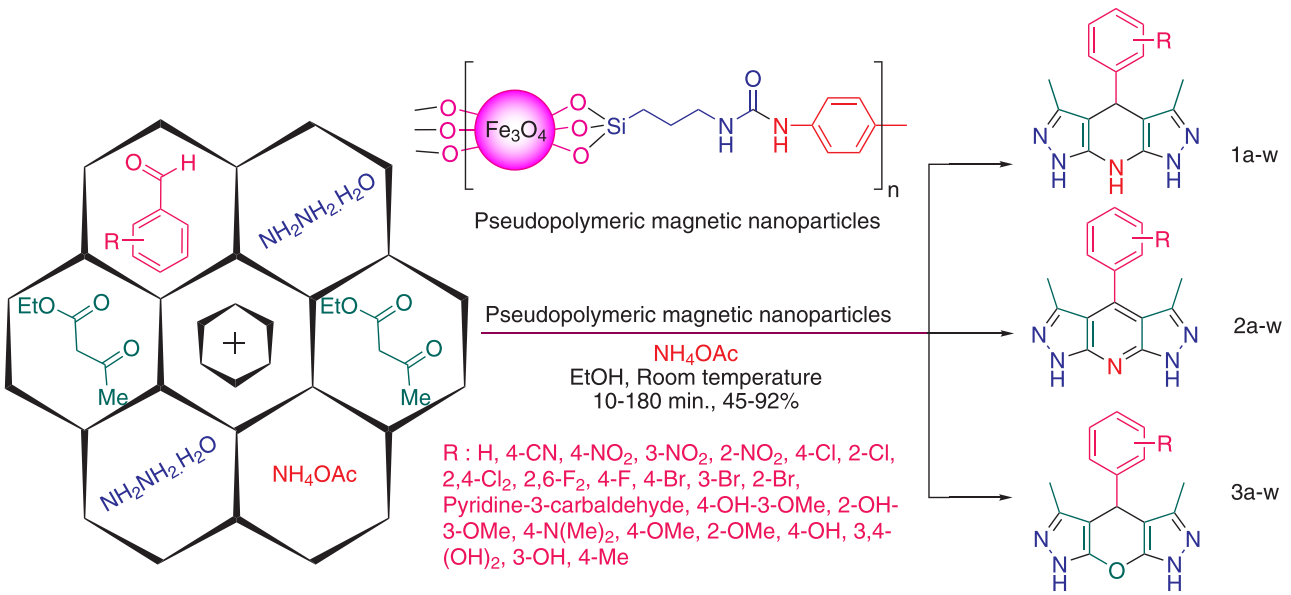
cation of the surface of Fe_3O_4 nanoparticles and ensures easy separation of the catalyst from the reaction mixture by applying a simple external magnet (Figure 7).

After structural verification of pseudopolymeric magnetic nanoparticles (also see Figures S16–S19), we tried to evaluate its catalytic performance for the synthesis of tetrahydrodipyrazolopyridine derivatives through a pseudo six-component reaction. With this aim, we selected the reaction between of benzaldehyde, ammonium acetate, ethyl acetoacetate, and hydrazine hydrate as model reaction. In order to choose the appropriate conditions, effective parameters including amount of catalyst, temperature, and solvent were investigated. The obtained experimental data are listed in the Table 1. Based on the obtained data, the maximum performance of the catalyst, highest experimental yield was achieved when the

TABLE 1 Optimization of the reaction conditions for the synthesis of compound **1a**[a]

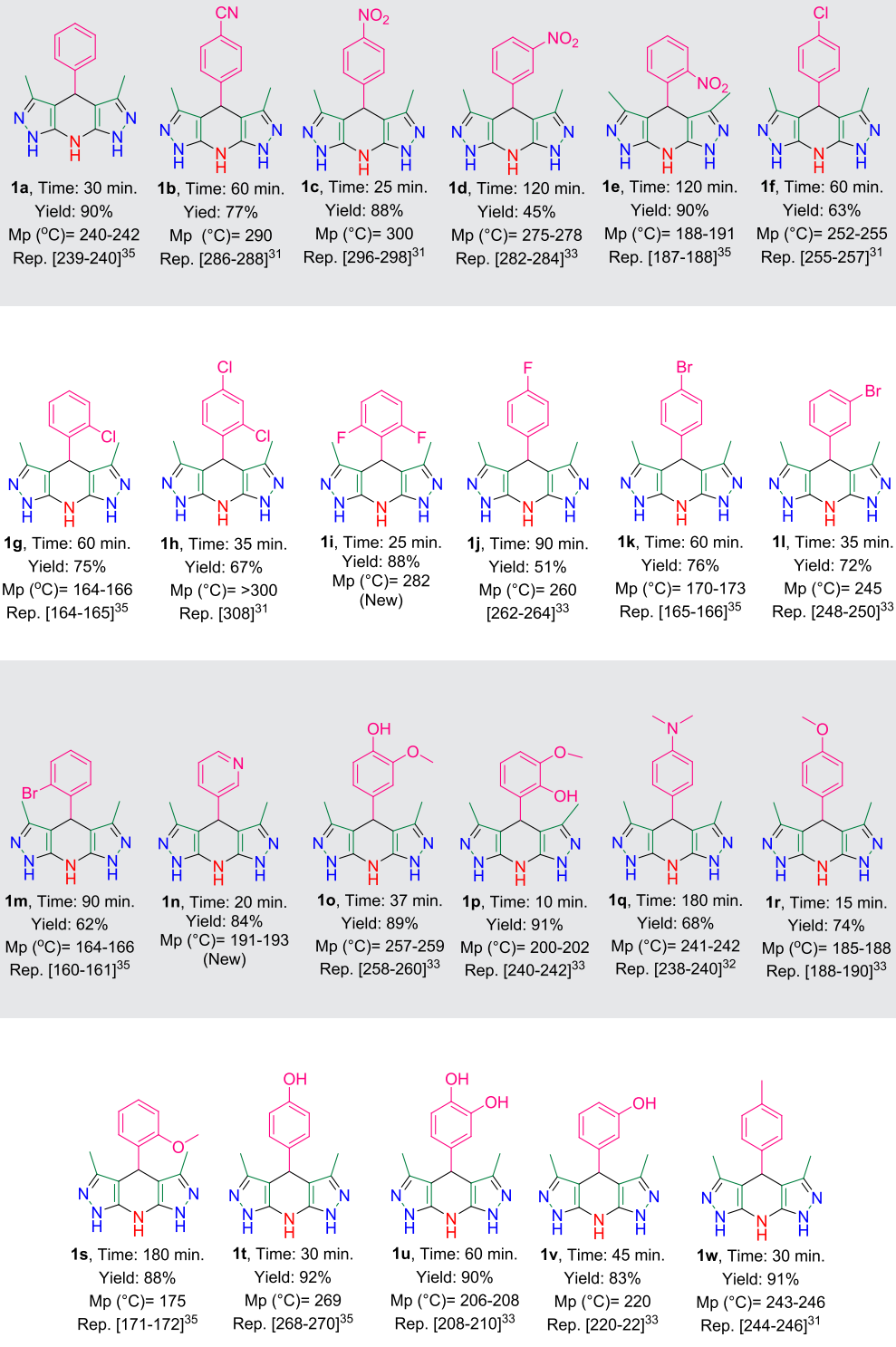
Entry	Solvent	Catalyst loading (mg)	Temperature (°C)	Time (min)	Yield[b] (%)
1	C_2H_5OH	5	r.t.	90	73
2	C_2H_5OH	10	r.t.	30	90
3	C_2H_5OH	15	r.t.	30	90
4	C_2H_5OH	20	r.t.	30	91
5	C_2H_5OH	10	50	20	79
6	C_2H5OH	10	Reflux	35	75
7	C_2H_5OH	-	r.t.	180	-
8	–	10	r.t.	60	Trace
9	H_2O	10	r.t.	30	65
10	CH_3OH	10	r.t.	60	59
11	CH_3CN	10	r.t.	45	45
12	CH_2Cl_2	10	r.t.	120	-
13	EtOAc	10	r.t.	30	25
14	*n*-Hexane	10	r.t.	120	-
15	$CHCl_3$	10	r.t.	120	-

[a]The molar ratio of hydrazine hydrate (2 mmol, 0.100 g), ethyl acetoacetate (2 mmol, 0.260 g), benzaldehyde (1 mmol, 0.106 g), and ammonium acetate (4 mmol, 0.308 g) is equal to 2:2:1:4.
[b]Isolated yield.

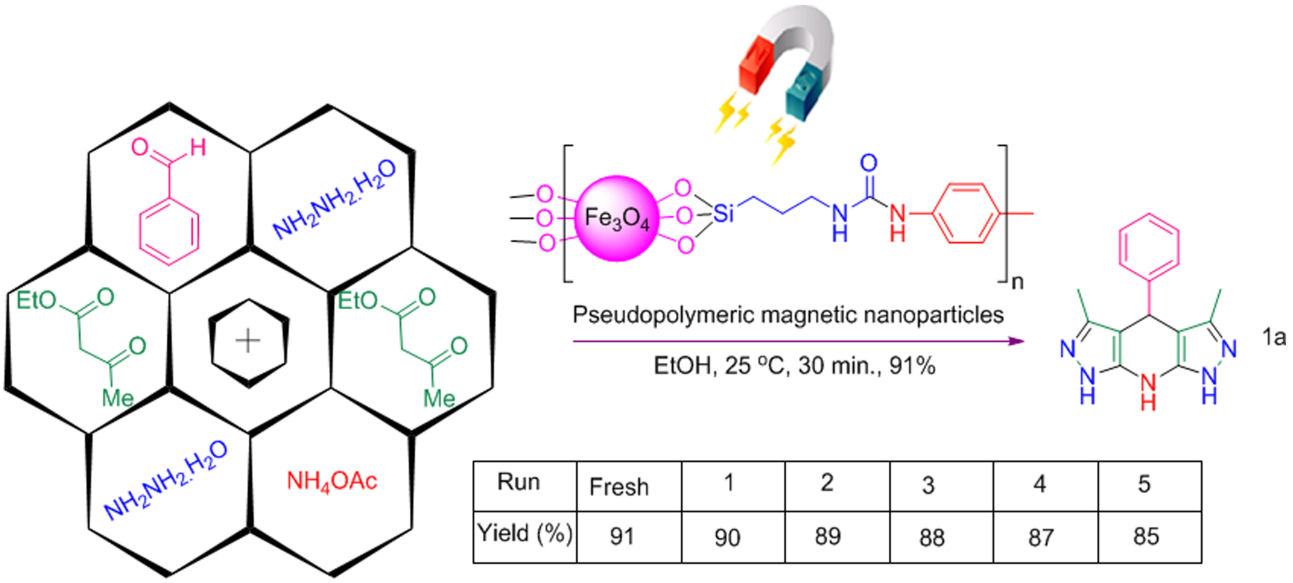


SCHEME 3 Possible products of the investigated reaction

TABLE 2 Synthesis of tetrahydrodipyrazolopyridine derivatives in the presence of pseudopolymeric magnetic nanoparticles[a]

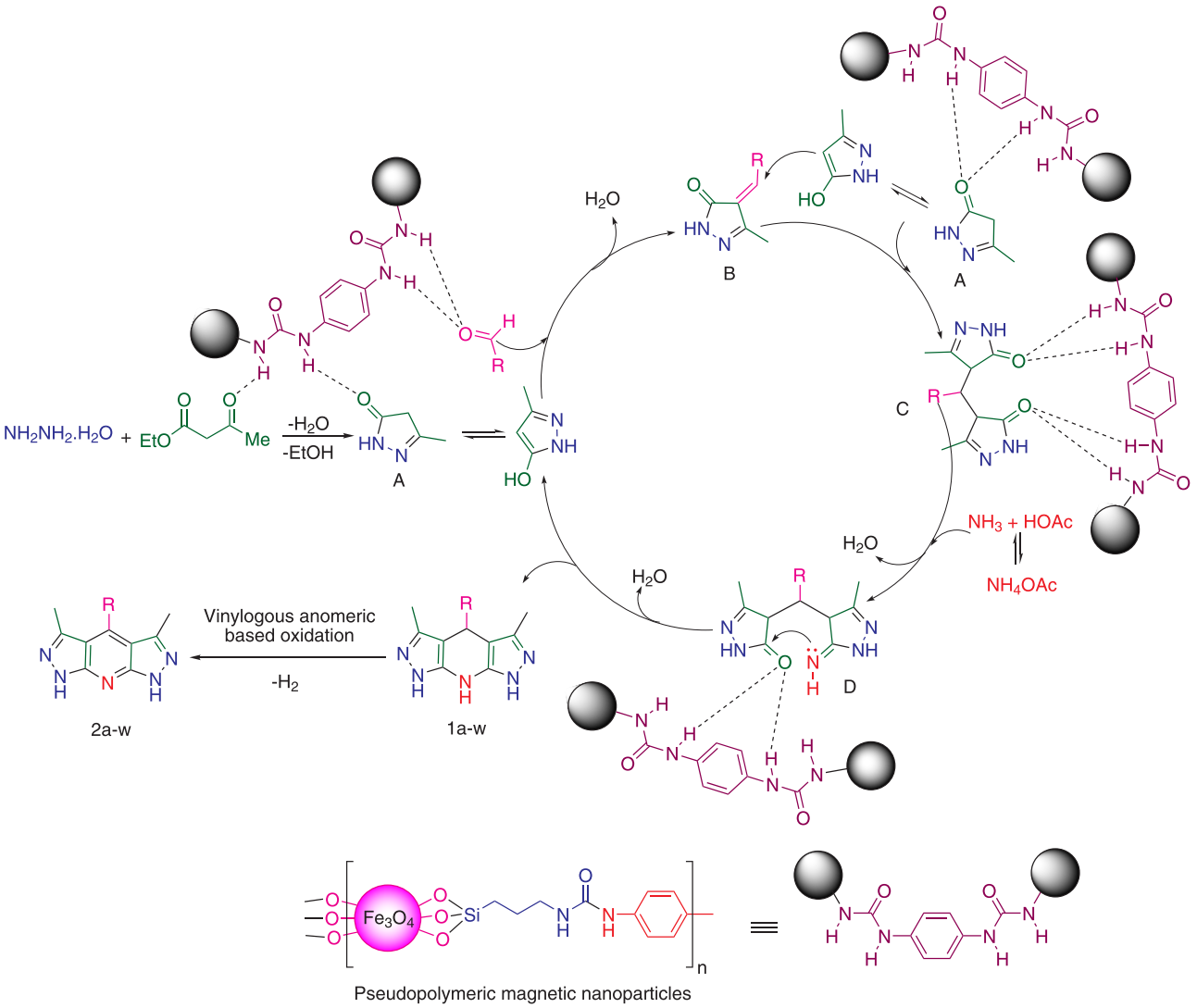


[a]Reaction condition: ethyl acetoacetate (2 mmol; 0.260 g), aldehyde (1 mmol), hydrazine hydrate (2 mmol, 0.100 g), ammonium acetate (4 mmol, 0.308 g), catalyst (10 mg), C_2H_5OH, room temperature.
Isolated yields.



Run	Fresh	1	2	3	4	5
Yield (%)	91	90	89	88	87	85

FIGURE 8 Recovery and reusing test of the prepared pseudopolymeric magnetic nanoparticles in the synthesis of target molecule **1a**



SCHEME 4 Plausible reaction mechanism for the synthesis of target compounds **1a–w**

TABLE 3 Comparison of our obtained data with some other those reported protocols for the synthesis of desired molecules

Entry	Reaction conditions	Time (min.)	Yield (%)	Reference
1	Fe_3O_4@ KCC-1-npr-NH_2 (0.1 mg), EtOH, Reflux	2–30	87–97	[36b]
2	KCC-1-NH_2-DPA (0.1 g), EtOH, Reflux	30	89–95	[36c]
3	Nano-$CdZr_4(PO_4)_6$ (0.6 mol%), EtOH, Reflux	40–50	80–94	[36d]
4	M (II)/Schiff base@MWCNT-Fe_3O_4/SiO_2 (0.02 g), Solvent free, r.t.	30–100	67–95	[30]
5	$CuFe_2O_4$@HNTs (5 mg), EtOH, r.t.	20	90–96	[31]
6	Fe_3O_4/KCC-1/IL/HPW (0.1 mg), water, r.t.	30	90–98	[32]
7	Pseudopolymeric magnetic nanoparticles (10 mg), EtOH, r.t.	10–180	45–92	This work

reaction accomplish in the presence of 10 mg of the catalyst in EtOH at ambient temperature.

We think that three products may be produced via the reaction between of benzaldehyde, ammonium acetate, ethyl acetoacetate, and hydrazine hydrate as model reaction (Scheme 3). Compounds **2a–w** are our favorite adducts, because they could be a puzzle piece of our research interest for expanding of our new established term entitled "cooperative vinylogous anomeric-based oxidation mechanism."[40] But the obtained spectral data did not match with these structures. Further studies of the spectral data revealed that the reaction was stopped at the tetrahydrodipyrazolopyridines (see Figures S1–S12). The rational reason for this fact can be explained by annellation phenomenon.[41] Since these compounds are highly valuable organic scaffolds, we decided to complete the study and present a powerful method for their preparation.

According to the achieved satisfactory data from the optimal reaction conditions for the synthesis of target molecule **1a**, we were convinced for the applying this protocol for the synthesis of tetrahydrodipyrazolopyridine derivatives. The obtained date are embedded in the Table 2.

In a separate test, we examined the recovery and reuse of the prepared catalyst. From the obtained data as illustrated in the Figure 8, it can be deduced that the catalyst has a very good capability for reusing test.

Similar to the reported papers,[30,31] a proposed mechanism for the preparation of compounds **1a–w** is shown in Scheme 4. At first, in the presence of catalyst, the reaction between hydrazine hydrate and ethylacetoacetate leads to the formation of compound A. In the next step, the nucleophilic attack of the enol form of A, to activate benzaldehyde, generates intermediate B. Afterwards, intermediate B converted to intermediate C through the reaction with second mole of enol form of compound A. Next, intermediate D obtained from the reaction of NH_3 (in situ generated from thermal decomposition of NH_4OAc) with intermediate C. Finally, consecutive steps of intramolecular nucleophilic attack (NH to C=O) and dehydration process lead to produce of molecules **1a–w**. Unexpectedly, molecules **1a–w** did not convert to their corresponding pyridine derivatives **2a–w** via a cooperative vinylogous anomeric-based oxidations.[40,42]

Also, we compare our obtained date with some other reported protocols for the synthesis of desired molecules. As depicted in the Table 3, the novel prepared catalyst shows acceptable results for the synthesis of target molecules in comparison with other catalysts.

3 | CONCLUSION

In summary, we reported the design, synthesis, and characterization of novel pseudopolymeric magnetic nanoparticles bearing urea linkers. The structure of the synthesized pseudopolymeric magnetic nanoparticles was confirmed by various techniques including FT-IR, EDX, TG/DTG, TEM, SEM, VSM, DRS and N_2 adsorption-desorption isotherms. The catalytic performance of the prepared catalyst was successfully tested towards the synthesis of tetrahydrodipyrazolopyridine derivatives under mild reaction conditions.

4 | EXPERIMENTAL

4.1 | General

All the chemicals were purchased from Sigma-Aldrich, Merck, or Exir chemical companies and were used without further purification. The melting points were determined by Barnstead Electrothermal 9200 in in open capillary tubes. The reaction progress and purity of the prepared structures were monitored by TLC performed with silica gel SIL G/UV 254 plates. The ^1H (300 and

500 MHz) and ^{13}C NMR (75, 125 MHz) spectra were analyzed by Bruker instrument using TMS as internal standard and DMSO-d_6 as a solvent. FT-IR spectra were analyzed by Perkin-Elmer FT-IR-17259 instrument by KBr disks.

4.2 | General procedure for the synthesis of urea based ligand and pseudopolymeric magnetic nanoparticles

First, through the reaction of 1,4-phenylenediamine (2.5 mmol, 0.270 g) and triethoxy(3-isocyanatopropyl) silane (5 mmol, 1.237 g) under solvent-free conditions for 6 h at 60°C, a precipitate was obtained which thoroughly washed with the mixture of *n*-hexane and dichloromethane (20:1) (3 × 10 ml) to afford the urea-based ligand. Then, according to the previously reported procedure through the reaction of Fe_3O_4 nanoparticles[43] with obtained urea-based ligand under refluxing toluene, the desired pseudopolymeric magnetic nanoparticles were obtained.

4.3 | General procedure for the synthesis of tetrahydrodipyrazolopyridines by using pseudopolymeric magnetic nanoparticles as catalyst

A mixture of ethyl acetoacetate (2 mmol; 0.260 g), hydrazine hydrate (2 mmol), aldehyde (1 mmol), ammonium acetate (4 mmol, 0.308 g), and pseudopolymeric magnetic nanoparticles (10 mg) was subjected to the reaction in C_2H_5OH at room temperature for appropriate time as indicated in Table 2. After completion of the reaction as monitored by TLC, C_2H_5OH was evaporated, and mixture of acetone and methanol (10:1) was added to the mixture to dissolve the precipitate. Then, the catalyst was separated from the reaction mixture by applying an external magnet. Finally, the desired products were obtained by washing the reaction mixture by hot C_2H_5OH.

4.4 | Selected spectral data

4.4.1 | 1,1′-(1,4-Phenylene)bis (3-(3-(triethoxysilyl)propyl)urea) (urea-based ligand)

Light purple solid, m.p.: 192–194; FT-IR (KBr): υ 3329, 2974, 1637, 1574, 1080 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 0.57 (t, 4H, J = 15 Hz, CH_2), 1.17 (t, 18 H, J = 10 Hz, CH_3), 1.48 (quint, 4H, J = 10 Hz, CH_2), 3.02–3.09 (m, 4H, CH_2), 3.77 (q, 12H, J = 10 Hz, CH_2), 6.07 (t, 2H, J = 10 Hz, NH), 7.23 (s, 4H, aromatic), 8.18 (bs, 2H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ 7.9, 18.8, 24.0, 42.4, 58.3, 119.0, 134.9, 156.0 (see Figures S13–S15).

4.4.2 | 3,5-Dimethyl-4-phenyl-1,4,7,8-tetrahydrodipyrazolo[3,4-*b*:4′,3′-*e*] pyridine (1a)

Yellow solid; yield: 90%; m.p.: 240–242; FT-IR (KBr): υ 3405, 3210, 3049, 2929, 2748, 1610, 1509, 1439, 1372, 1268, 776, 610, 542 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 2.09 (s, 6H, $-CH_3$), 4.84 (s, 1H, –CH), 7.14–7.25 (m, 5H, J = 8.0 Hz, ArH), 11.37 (s, 3H, N–H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 10.86, 33.23, 104.71, 125.85, 127.93, 128.17, 140.27, 143.83, 161.58.

4.4.3 | 3,5-Dimethyl-4-(2,6-difluorophenyl)-1,4,7,8-tetrahydrodipyrazolo[3,4-*b*:4′,3′-*e*] pyridine (1i)

Yellow solid; yield: 88%; m.p.: 282; FT-IR (KBr): υ 3296, 2986, 2966, 2762, 1699, 1597, 1519, 1435, 1387, 1090, 794, 570 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.10 (s, 6H, $-CH_3$), 4.85 (s, 1H, –CH), 6.77–7.01 (dd, 4H, J = 8 Hz, ArH), 11.46 (s, 3H, N–H) ; ^{13}C NMR (125 MHz, DMSO-d_6): δ 10.77, 33.27, 101.40, 103.93, 111.12, 140.82, 148.99, 149.11, 163.78, 163.72.

4.4.4 | 3,5-Dimethyl-4-(pyridin-3-yl)-1,4,7,8-tetrahydrodipyrazolo[3,4-b:4′,3′-*e*] pyridine (1n)

Yellow solid; yield: 84%; m.p.: 191–193; FT-IR (KBr): υ 3216, 3092, 2982, 2878, 1630, 1600, 1518, 1438, 1398, 1282, 1124, 997, 611 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.13 (s, 6H, $-CH_3$), 4.93 (s, 1H, –CH), 7.25–7.29 (dd, 1H, J = 7.9 Hz, ArH), 7.54–7.59 (d, 1H, J = 7.9 Hz, ArH), 8.36 (dd, 2H, J = 7.9 Hz, ArH), 11.35 (s, 3H, N–H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 10.81, 31.18, 103.89, 123.36, 135.49, 139.49, 140.16, 149.53, 161.42.

4.4.5 | 3,5-Dimethyl-4-(*p*-tolyl)-1,4,7,8-tetrahydrodipyrazolo[3,4-*b*:4′,3′-*e*] pyridine (1w)

Pale yellow solid; yield: 91%; m.p.: 243–246; FT-IR (KBr): υ 3313, 3199, 3096, 2926, 2762, 1699, 1602,

1508, 1370, 1255, 1040, 844, 741 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 2.09 (s, 6H, $-CH_3$), 2.25 (s, 3H, $-CH_3$), 4.79 (s, 1H, –CH), 7.03 (m, 4H, J = 7.9 Hz, ArH), 11.36 (s, 3H, N–H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 10.86, 21.01, 32.82, 104.85, 127.83, 128.74, 134.64, 140.19, 140.74, 161.57.

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AUTHOR CONTRIBUTIONS

Mohammad Dashteh: Investigation, Methodology, Validation, Writing - Original Draft. **Dr. M. Yarie:** Investigation, Methodology, Validation, Writing - Original Draft. **Prof. M.A. Zolfigol:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing - Review & Editing. **Prof. Ardeshir Khazaei**: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing - Review & Editing. **Mr. Sajjad Makhdoomi:** Investigation, Methodology, Validation, Writing - Original Draft.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supporting information of this article.

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