FULL PAPER

2-hydroxyethylammonium formate ionic liquid grafted magnetic nanoparticle as a novel heterogeneous catalyst for the synthesis of substituted imidazoles

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Reza Khalifeh, Department of Chemistry, Shiraz University of Technology, 71555-313, Shiraz, Iran. Email: khalifeh@sutech.ac.ir Catalytic one-pot condensation of benzil, aldehyde and ammonium acetate have been successfully carried out using 2-hydroxyethylammonium formate (HEAF) grafted on a magnetic nanoparticles as a new heterogeneous catalyst. The as-prepared catalyst was characterized by FT-IR, TEM, FESEM, VSM, TGA and XRD. This catalyst indicated significant advantages, such as excellent yields, shorter reaction time, reusability of the catalyst and easy workup process.

1 | INTRODUCTION

Imidazole derivatives have been identified as important chemical and biological active compounds.^[1] Often substituted imidazoles are also used as fungicides,^[2] herbicides,^[3] plant growth regulators^[4] and therapeutic agents.^[5] In addition, the application of imidazole as ionic liquids^[6] and N-heterocyclic carbenes^[7] have expanded in recent development green chemistry and organometallic chemistry. Therefore, in recent times, the preparation of this class of compounds has received significant attention. The straightforward synthesis of these compounds involves the one-pot condensation of diketones, aldehydes, and ammonium acetate in the presence of protic acids^[6-8] and Lewis acids^[9-11] as catalysts. Moreover, various methods have been designed to synthesize substituted imidazoles using CAN,^[12] L-proline,^[13] L-systeine,^[14] N-bromosuccinimide,^[15] ytterbium trifluoromethanesulfonate^[10] and microwave irradiation.^[16] However, some of these methods show varying drawbacks such as difficult reaction conditions, the use

of expensive catalyst, tiresome work-up, nonrecyclability catalyst and long reaction times. Therefore, design and utilization of recyclable catalytic systems for the clean chemical synthesis of imidazoles is desirable. In this background, ionic liquids are perfect catalysts for chemical reactions. In the context of green sustainable chemistry, ionic liquids have attracted much attention due to their interesting chemical and physical properties, such as high catalytic activity and good selectivity, high ionic conductivity, negligible vapour pressure and good thermal stability.^[17] Currently, kinds of ionic liquids have been used in various organic reactions such as N-alkylation reaction,^[18] nitration,^[19] Diels-Alder,^[20] Michael addition,^[21] esterification.^[22] aldol condensation^[23] and MCRs.^[24] Although ionic liquids are widely used in organic reactions, but suffered from some disadvantages such as high viscosity, high cost, difficulty the separation of product from ionic phas and catalyst recovery. Therefore, immobilization of ionic liquids on the surface of numerous supports such as polymers,^[25] graphene nanosheets,^[26] silica.^[17b] magnetic materials^[27] and inorganic materials^[28] can overcome these drawbacks. However, there are serious drawbacks for most of these supports like a complicated synthesis, hampered diffusion kinetics or tedious separation via centrifugation.^[29] Therefore, magnetic nanoparticles are the best choice for catalyst support due to their magnetic separation compare to conventional techniques such as filtration or centrifugation as it prevents loss of catalyst and increases the reusability.^[30,31] In continuation of our studies on the preparation and applications of heterogeneous catalysts, in the synthetic organic chemistry,^[32] we wish introduce a new strategy for synthesis of a 2-hydroxyethyl ammonium formate modified Fe₃O₄@SiO₂ as a novel and magnetically recyclable heterogeneous catalyst. The catalytic activity of Fe₃O₄@SiO₂-EP-HEAF has investigated for the onepot synthesis of 2,4,5-trisubstituted-1H-imidazole.

2 | RESULT AND DISCUSSION

The immobilization of 2-hydroxyethylammonium formate (HEAF) onto magnetic nanoparticles was performed in three steps (Scheme 1). In the first step, the $Fe_3O_4@SiO_2$ magnetic nanoparticles were synthesized using the stober method.^[33] In the next step, the substitution reaction of epichlorohydrin species was accomplished with hydroxyl groups of silica coated magnetic nanoparticles.^[32] Finally, $Fe_3O_4@SiO_2$ -EP-HEAF was obtained by simple mixing of $Fe_3O_4@SiO_2$ -EP and 2hydroxyethylammonium formate in 60°C. The structure and morphology of the prepared catalyst were characterized by Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM), vibrating sample magnetometry (VSM), Thermo gravimetric analysis (TGA) and X-ray powder diffraction (XRD).

Figure 1 shows the FTIR spectra of the final catalyst which was synthesized in 4 step. The characteristic absorption peak of Fe_3O_4 magnetic nanoparticles is found at 585 cm⁻¹ is attributed to Fe–O vibrations (curve 1**a**). In the case of Fe_3O_4 @SiO₂, the absorption peak of Fe–O bond was also appeared around 580 cm⁻¹. The characteristic peaks around 805 cm⁻¹ and 1098 cm⁻¹ are assigned to stretching vibration of Si–O and asymmetry stretching vibration of Si–O–Si, respectively. Also, the peak at 465



FIGURE 1 FT-IR spectra of (a) Fe $_3O_4$, (b) Fe $_3O_4$ @SiO $_2$, (c) Fe $_3O_4$ @SiO $_2$ -EP, (d) Fe $_3O_4$ @SiO $_2$ -EP-HEAF



SCHEME 1 Preparation process of the Fe₃O₄@SiO₂-EP-HEAF catalyst

is attributed to bending vibration of Si–O and peaks at 940 and 1630 cm⁻¹ are bending vibrations of Si–OH, which indicates the silica coating of Fe₃O₄ MNPs (curve **1b**). The bands at 2950 and 2870 cm⁻¹ are due to the stretching vibration of aliphatic CH₂ groups of epichlorohydrin. Furthermore, the C-O-C vibration stretching around 1260 cm⁻¹ which was covered by the broad band of stretching vibration of Si–O–Si bonds confirms that silica coated magnetic nanoparticles were modified with epichlorohydrin (curve **1c**). The broad band around 3000–3500 cm⁻¹ exhibits characteristic peaks of ammonium structure. The carbonyl stretching and N–H plane bonding vibrations are observed as a combined bond centered at 1600 cm⁻¹ (curve **1d**).

The TEM images of $Fe_3O_4@SiO_2$ and ionic liquid modified $Fe_3O_4@SiO_2$ MNPs are illustrated in Figure 2. The TEM image of Figure 2a and Figure 2b indicates that catalysts have a core-shell structure, which is consistent with the results of XRD and FTIR analyzes. Figure 2b show that after modification of $Fe_3O_4@SiO_2$ with ionic liquid the morphology of MNPs are retained. Based on TEM images some shells of SiO₂ were linked among the particles (Figure 2). For further investigation of the morphology of the ionic liquid modified $Fe_3O_4@SiO_2$ MNPs the SEM images was used. Figure 2c show a spherical shape of final catalyst with aggregated structure.

The magnetic hysteresis loops of the Fe₃O₄, Fe₃O₄@SiO₂ and ionic liquid modified Fe₃O₄@SiO₂ MNPs are displayed in Figure 3. The M–H curve of catalyst indicates a ferromagnetic characteristic, which is inherited from the Fe₃O₄ core. The magnetic saturation (Ms) value of Fe₃O₄, Fe₃O₄@SiO₂ and ionic liquid modified Fe₃O₄@SiO₂ are 64.99, 35.13, and 25.90 emu g⁻¹, respectively (Figures 3a, 3b and 3c). This decrease in the Ms Value of final catalyst in comparison with bare Fe₃O₄ MNPs is related to the silica shell with disordered structure at interfaces and loading of epichlorohydrin/ ionic liquid as organic linker. These results demonstrate that the core–shell particles possess magnetic properties.

To examine the thermal stability of the final catalyst, thermal gravimetric analysis (TGA) was carried out (Figure 4). The final catalyst show about 14.5% weight loss in the region of 10–800 °C. The initial weight loss up to 200 °C is probably due to the removal of surface adsorbed water and dehydration of the ionic liquid, while the weight loss at 200–800 °C could be attributed to the evaporation of the dehydration product, 2-hydroxyethylammonium formate or its decomposition products.^[34]

The XRD patterns of $Fe_3O_4@SiO_2$ MNPs and ionic liquid modified $Fe_3O_4@SiO_2$ MNPs were shown at Figure 5. Figure 5a revealed six diffraction peaks located at 30.17°, 35.45°, 43.17°, 53.48°, 56.89° and 62.61° can be assigned to the Fe_3O_4 crystal with inverse spinel structure from







FIGURE 2 TEM image of (a) $Fe_3O_4@SiO_2$, (b) $Fe_3O_4@SiO_2$ -EP-HEAF and FESEM image of (c) $Fe_3O_4@SiO_2$ -EP-HEAF

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FIGURE 4 TGA analysis of the Fe₃O₄@SiO₂-EP-HEAF



FIGURE 5 XRD diagrams of (a) Fe₃O₄@SiO₂, (b) Fe₃O₄@SiO₂-EP-HEAF

(220), (311), (400), (422), (511) and (440) crystal plane which are agreed well with the standard diffraction card JCPDS 19–0629. From Figure 5b, it is seen clearly that ionic liquid modified $Fe_3O_4@SiO_2$ MNPs exhibit diffraction patterns similar to that of $Fe_3O_4@SiO_2$ MNPs which indicates that the particles are single-crystalline and the

FIGURE 3 Magnetization curves of (a) Fe₃O₄, (b) Fe₃O₄@SiO₂, (c) Fe₃O₄@SiO₂-EP-HEAF

crystallinity of Fe_3O_4 @SiO₂ persists after surface modification. The average crystal size of the Fe_3O_4 cores from the broadness of the (311) peak, obtained by calculation of Sherrer's formula, is about 15.2 nm.

The efficiency of the prepared Fe₃O₄@SiO₂-EP-HEAF catalyst was examined for the synthesis of imidazole derivatives. In order to optimize the reaction conditions, the mixture of benzaldehyde, benzil and ammonium acetate in the presence Fe₃O₄@SiO₂-EP-HEAF was selected as a model reaction (Scheme 2). Initially, the model reaction in a various solvents such as H₂O, CH₃CN, PEG, toluene and EtOH in the presence of 0.02 gr of the catalyst was investigated. The product was obtained in 90, 40, 75, 40 and 95% yield, respectively (Table 1, Entry 1-5). Therefore, ethanol was found to be the best solvent for this catalytic system. To demonstrate the influence of the catalyst amount, the model reaction was tested in the presence of different amount of the catalyst in EtOH as solvent. The results showed that the reaction yield was improved when the amount of the catalyst increased from 0.002 to 0.02 gr. No product was observed in the absence of the catalyst (Table 1, Entry 6). We examined the effect of different temperatures on the model reaction under solvent free conditions. The reactions took a long time to achieve a low yield of the desired product (Table 1, Entry 10, 11).

With this optimized reaction condition, we evaluated the one-pot condensation of benzil and ammonium acetate with a variety of aldehydes in the presence $Fe_3O_4@SiO_2$ -EP-HEAF to achieve the intended products (Table 2, Entry 1–14). The desired imidazole products were obtained in



SCHEME 2 One-pot catalytic synthesis 2,4,5-trisubstituted-1Himidazole

TABLE 1 Optmization of reaction conditions for one-pot con-
densation of benzil, benzaldehyde, and ammonium acetate^a

| Entry | Solvent | Amount catalyst (gr) | Yeild (%) | Time (h: Min) |
|-----------------|------------------|-------------------------|-----------|------------------|
| 1 | H ₂ O | 0.02 | 90 | 04: 00 |
| 2 | $\rm CH_3 CN$ | 0.02 | 40 | 07: 00 |
| 3 | PEG | 0.02 | 75 | 05: 00 |
| 4 | toluene | 0.02 | 40 | 07: 00 |
| 5 | EtOH | 0.02 | 95 | 00: 40 |
| 6 | EtOH | - | 0 | 12:00 |
| 7 | EtOH | 0.002 | 40 | 03: 00 |
| 8 | EtOH | 0.005 | 55 | 03: 00 |
| 9 | EtOH | 0.01 | 73 | 01: 00 |
| ^b 10 | - | 0.02 | 30 | 05; 00 |
| °11 | - | 0.02 | 45 | 07; 00 |

^aReaction condition: benzil (1 mmol), benzaldehydes (1 mmol), ammonium acetate (2 mmol), $Fe_3O_4@SiO_2$ -EP-HEAF (0.02 g) and solvent (3 ml).

^bReaction condition carried out at 80 °C

^cReaction condition carried out at 100 °C

TABLE 2Summarized catalytic results of the one-pot condensa-
tion between various aldehydes, benzil and ammonium acetate

| Entry | Aldehyde | Yiled (%) | Time (min) |
|-------|---------------------------------|--------------|---------------|
| 1 | Benzaldehyde | 95 | 40 |
| 2 | 4-methylbenzaldehyde | 92 | 45 |
| 3 | 4-methoxybenzaldehyde | 95 | 45 |
| 4 | 4-hydroxybenzaldehyde | 85 | 60 |
| 5 | 3,4-dimethoxybenzaldehyde | 90 | 40 |
| 6 | 4-hydroxy-3-methoxybenzaldehyde | 87 | 60 |
| 7 | 4-(dimethylamino)benzaldehyde | 90 | 60 |
| 8 | 4-Cyanobenzaldehyde | 92 | 45 |
| 9 | 4-chlorobenzaldehyde | 90 | 45 |
| 10 | 2,4-dichlorobenzaldehyde | 95 | 40 |
| 11 | 2,6-dichlorobenzaldehyde | 90 | 40 |
| 12 | furan-2-carbaldehyde | 90 | 60 |
| 13 | Cinnamaldehyde | 83 | 120 |
| 14 | anthracene-9-carbaldehyde | 75 | 180 |

excellent yields for both electron rich (Table 2, Entry 2–7) and electron poor (Table 2, Entry 8–11) aromatic aldehydes. Heteroaromatic aldehydes such as furan-2-carbaldehyde (Table 2, Entry 12) and allylic aldehydes such as cinnamaldehyde (Table 2, Entry 13) were also converted in high yields to the desired products. Other aldehyde such

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as anthracene-9-carbaldehyde also provided the corresponding products in 75% yield (Table 2, Entry 14).

The recyclability of the desired catalyst was examined for the synthesis of 2,4,5-trisubstituted-1H-imidazole under the optimized reaction conditions. The recycling test result shows the $Fe_3O_4@SiO_2$ -EP-HEAF could be recycled up to five run without loss of catalytic activity. After the five cycle, the $Fe_3O_4@SiO_2$ -EP-HEAF was recovered for further TEM and SEM characterization. Figure 6 shows the morphology of $Fe_3O_4@SiO_2$ -EP-HEAF is almost unchanged after the five cycle.

3 | EXPERIMENTAL

3.1 | General procedure for the preparation 2-hydroxyethylammonium formate (ionic liquid)

Into around-bottom flask equipped with a dropping funnel was placed Amino ethanol (0.2 mol) and the flask was mounted in an ice bath. Under vigorous stirring formic acid (0.2 mol) was added dropwise to the flask in 45 min. The reaction mixture was shaken for 24 h at room temperature, to obtain a viscous clear liquid.^[34]

3.2 | General procedure for the preparation Fe₃O₄@SiO₂-EP-HEAF

Fe₃O₄@SiO₂ MNPs were synthesized by the conventional stober method.^[33] To a solution of epichlorohydrin (10 mmol, 1.36 g) in ethanol (3 ml), Fe₃O₄@SiO₂ MNPs (0.5 g) was added and the resulting mixture was stirred for 5 h at 60°C. The precipitate was separated by a magnet and washed with ethanol several times.^[32] The formed Fe₃O₄@SiO₂-EP (0.5 g) was dispersed in 3 ml 2-hydroxyethylammonium formate with ultrasonic for 120 min, then the mixture was vigorously stirred for 6 h at 60°C. The precipitate was separated with using an external magnet and washed with distilled water and with ethanol for three times, then dried at 60 °C for 6 h. The finally obtained Fe₃O₄@SiO₂-EP-HEAF product was employed as nanocatalyst for the synthesis of imidazole derivatives.

3.3 | General procedure for the synthesis of 2,4,5-trisubstituted-1H-imidazole

 Fe_3O_4 @SiO₂-EP-HEAF (0.02 g) was added to a mixture of benzil (1 mmol), aldehyde (1 mmol) and ammonium acetate (2 mmol) in EtOH (3 ml), the reaction mixture was refluxed at 80 °C for 40–180 min under stirring. After completion of the reaction, the catalyst was removed with using external magnet. The mixture reaction was allowed to cool and the resulting precipitates were recrystallized





FIGURE 6 SEM (a) and TEM (b) image of ${\rm Fe_3O_4} @{\rm SiO_2\mathchar`ee}{\rm FEAF}$ after five times reuse

from EtOH/H₂O to give pure imidazole derivatives. All the products were confirmed by the spectroscopic method using 1 H and 13 C NMR.

3.3.1 | 2,4,5-triphenyl-1H-imidazole (Table 2, Entry 1)

Mp: 264–266 °C, ¹H NMR (300 MHz, DMSO- d_6): δ = 7.22– 7.33 (m, 3H), 7.36 (d, 2H, J = 6.9 Hz), 7.43–7.51 (m, 8H), 8.06 (d, 2H, J = 7.5 Hz), 12.68 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 125.6$, 126.9, 127.5, 128.2, 128.7, 128.9, 129.2, 130.8, 131.6, 135.6, 137.5, 145.9.

3.3.2 | 4,5-diphenyl-2-p-tolyl-1H-imidazole (Table 2, Entry 2)

Mp: 228–229 °C, ¹H NMR (300 MHz, DMSO- d_6): $\delta = 2.33$ (s, 3H), 7.26 (d, 4H, J = 7.8 Hz), 7.41–7.49 (m, 8H), 7.95 (d, 2H, J = 7.5 Hz), 12.58 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 21.4, 125.6, 127.5, 128.1, 128.9, 129.7, 131.6, 138.2, 146.1.$

3.3.3 | 2(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole (Table 2, Entry 3)

Mp: 220–222 °C, ¹H NMR (250 MHz, DMSO- d_6): $\delta = 3.82$ (s, 3H), 6.90–6.94 (m, 2H), 7.24–7.28 (m, 6H), 7.51 (s, 4H), 7.78–7.82 (m, 2H), 9.69 (s, 1H). ¹³C NMR (62.5 MHz, DMSO- d_6): $\delta = 55.3$, 112.1, 114.1, 115.5, 122.8, 126.9, 127.2, 127.9, 128.4, 146.4, 148.9, 151.1, 163.9.

3.3.4 | 4-(4,5-diphenyl-1H-imidazole-2-yl) phenol (Table 2, Entry 4)

Mp: 256–257 °C, ¹H NMR (300 MHz, DMSO- d_6): $\delta = 6.83$ (d, 2H, J = 8.1 Hz), 7.19 (d, 1H, J = 6.6 Hz), 7.27 (t, 2H, J = 7.8 Hz), 7.34 (d, 1H, J = 6.9 Hz), 7.38–7.52 (m, 6H), 7.87 (d, 2H, J = 8.1 Hz), 9.69 (s, 1H), 12.39 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 115.8$, 122.1, 126.8, 127.3, 127.5, 127.8, 128.0, 128.6, 128.8, 129.1, 131.8, 135.9, 137.0, 146.5, 158.2.

3.3.5 | 2-(3,4-dimethoxyphenyl)-4,5diphenyl-1H-imidazole (Table 2, Entry 5)

Mp: 216–217 °C, ¹H NMR (300 MHz, DMSO- d_6): $\delta = 3.79$ (s, 3H), 3.83 (s, 3H),7.04 (d, 1H, J = 8.7 Hz), 7.20 (d, 1H, J = 6.9 Hz), 7.25–7.30 (m, 2H), 7.36(d, 1H, J = 6.0 Hz), 7.40–7.54 (m, 6H), 7.62–7.65 (m, 2H), 12.51 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 55.9$, 56.0, 109.2, 112.2, 118.4, 123.7, 126.9, 127.5, 128.1, 128.6, 128.9, 129.1, 131.7, 135.7, 137.2, 146.2, 149.2, 149.5.

3.3.6 | 4-(4,5-diphenyl-1H-imidazol-2-yl)-2methoxyphenol (Table 2, Entry 6)

Mp: 200–202 °C, ¹H NMR (300 MHz, DMSO- d_6): δ = 3.83 (s, 3H), 6.83 (d, 1H, J = 8.1 Hz), 7.19 (d, 1H, J = 6.6 Hz), 7.27 (t, 2H, J = 7.5 Hz), 7.35 (d, 2H, J = 6.6 Hz), 7.39–7.50 (m, 6H), 7.60 (s, 1H), 9.25 (s, 1H), 12.40 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): δ = 56.1, 109.7, 116.0, 118.8, 122.4, 126.8, 127.5, 127.9, 128.1, 128.6, 128.8, 129.1, 131.8, 135.8, 146.5, 147.3, 147.5, 148.1.

3.3.7 | 4-(4,5-diphenyl-1H-imidazol-2-yl)-N, N-dimethylbenzenamine (Table 2, Entry 7)

Mp: 262–264 °C, ¹H NMR (300 MHz, DMSO- d_6): $\delta = 2.9$ (s, 6H), 6.77 (d, 2H, J = 8.4 Hz), 7.18 (d, 1H, J = 6.9 Hz), 7.27 (t, 2H, J = 7.5 Hz), 7.32 (d, 1H, J = 6.6 Hz), 7.37–7.40 (m, 3H), 7.45 (t, 2H, J = 7.5 Hz), 7.50–7.52 (m, 1H), 7.88 (d, 2H, J = 8.7 Hz), 12.3 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 112.4$, 118.8, 126.7, 127.5, 127.9, 128.6, 128.7, 129.1, 131.9, 135.9, 136.9, 146.9, 150.7.

3.3.8 | 4-(4,5-diphenyl-1H-imidazol-2-yl) benzonitrile (Table 2, Entry 8)

Mp: 232–233 °C, ¹H NMR (300 MHz, DMSO- d_6): δ = 7.22–7.30 (m, 3H), 7.42–7.54 (m, 7H), 7.93 (d, 2H, J = 7.8 Hz), 8.23 (d, 2H, J = 8.1 Hz), 13.01 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): δ = 110.6, 119.4, 126.0, 127.3, 127.6, 128.6, 128.7, 129.0, 129.2, 130.1, 131.1, 133.3, 134.7, 135.1, 138.5, 144.2.

3.3.9 | 2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole (Table 2, Entry 9)

Mp: 267–268 °C, ¹H NMR (300 MHz, DMSO- d_6): $\delta = 7.22$ (d, 1H, J = 6.6 Hz), 7.28 (t, 2H, J = 7.5 Hz), 7.36–7.47 (m, 7H), 7.53 (d, 2H, J = 7.5 Hz), 8.08 (d, 2H, J = 8.4 Hz), 12.77 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6) $\delta = 127.1$, 127.3, 127.5, 128.3, 128.7, 128.9, 129.0, 129.1, 129.2, 129.7, 131.4, 133.2, 135.5, 137.8, 144.9.

3.3.10 | 2-(2,4-dichlorophenyl)-4,5diphenyl-1H-imidazole (Table 2, Entry 10)

Mp: 170–173 °C, ¹H NMR (300 MHz, DMSO-*d*₆): δ = 7.22 (d, 1H, *J* = 6.9 Hz), 7.26–7.31 (m, 2H), 7.35–7.56 (m, 8H), 7.77–7.83 (m, 2H), 12.70 (s, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 127.1, 127.6, 127.9, 128.3, 128.7, 129.2, 129.3, 130.2, 131.2, 132.9, 133.1, 134.3, 135.4, 137.5, 142.8.

3.3.11 | 2-(2,6-dichlorophenyl)-4,5diphenyl-1H-imidazole (Table 2, Entry 11)

Mp: 233–235 °C, ¹H NMR (300 MHz, DMSO- d_6): $\delta = 7.22$ (d, 1H, J = 6.6 Hz), 7.29 (t, 2H, J = 7.8 Hz), 7.35–7.46 (m, 5H), 7.52 (d, 2H, J = 7.2 Hz), 756–6.64 (m, 3H), 12.75 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 127.1$, 127.7, 127.8, 128.2, 128.3, 128.7, 128.8, 129.3, 130.9, 131.3, 132.4, 135.6, 136.2, 137.0, 141.2.

3.3.12 | 2-(furan-2-yl)-4,5-diphenyl-1Himidazole (Table 2, Entry 12)

Mp: 234–235 °C, ¹H NMR (250 MHz, DMSO- d_6): $\delta = 6.50-6.53$ (m, 1H), 9.98 (d, 1H, J = 3.2 Hz), 7.26–7.33 (m, 7H), 7.45–7.52 (m, 4H), 9.68 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 107.9$, 112.3, 127.7, 128.2, 128.9, 139.0, 143.6, 146.1.

3.3.13 | (E)-4,5-diphenyl-2-styryl-1H-imidazole (Table 2, Entry 13)

Mp: 254–256 °C, ¹H NMR (250 MHz, DMSO- d_6): δ = 7.25–7.26 (m, 2H), 7.33 (d, 4H, J = 6.5 Hz), 7.37–7.45 (m, 5H), 7.48–7.56 (m, 4H), 7.91 (d, 2H, J = 7.75 Hz), 9.42 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): δ = 125.7, 127.0, 127.5, 128.3, 128.7, 128.9, 129.2, 130.8, 131.6, 135.6, 137.6, 146.0.

3.3.14 | 2-(anthracen-10-yl)-4,5-diphenyl-1H-imidazole (Table 2, Entry 14)

Mp: 165–167 °C, ¹H NMR (300 MHz, DMSO- d_6): $\delta = 7.24$ – 7.41 (m, 6H), 7.55–7.63 (m, 8H), 7.90–7.91 (m, 2H), 8.15– 8.17 (m, 2H), 8.78 (s, 1H), 12.94 (s, 1H). ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 126.1$, 126.5, 127.1, 127.8, 128.0, 128.2, 128.4, 128.8, 128.9, 129.2, 131.3, 131.6, 135.9, 137.4, 143.7.

4 | CONCLUSION

In summary, we have developed a facile approach to fabricate $Fe_3O_4@SiO_2$ -EP-HEAF as a high performance catalyst. $Fe_3O_4@SiO_2$ -EP-HEAF was used as an efficient catalyst for synthesis of 2,4,5-trisubstituted-1H-imidazole via one-pot condensation of benzil, aldehydes and ammonium acetate. This catalyst was simply separated from the reaction mixture by external magnet and reused several times without a significant loss of its activity.

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REFERENCES

- a) J. G. Lombardino, E. H. Wiseman, J. Med. Chem. 1974, 17, 1182. (b) R. Sundberg, R. B. Martin, Chem. Rev. 1974, 74, 471.
- [2] A. F. Pozherskii, A. T. Soldatenkov, A. Y. Katritzky, *Heterocycles in Life and Society*, Wiley, New York **1997** 179.
- [3] T. Maier, R. Schmierer, K. Bauer, H. Bieringer, H. Buerstell, B. Sachse, US Patent 1989, 4, 335.

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- [4] R. Schmierer, H. Mildenberger, H. Buerstell, German Patent 1987, 3, 364.
- [5] J. Heeres, L. J. Back, J. H. Mostmans, J. Vancutsem, J. Med. Chem. 1979, 22, 1003.
- [6] F. J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li, H. Zhang, Synthesis 2003, 2661.
- [7] S. Sarshar, D. Siev, A. M. M. Mjalli, *Tetrahedron Lett.* 1996, 37, 835.
- [8] H. Weinmann, M. Hahhe, K. Koeing, E. Mertin, U. Tilstam, *Tetrahedron Lett.* 2002, 43, 593.
- [9] M. Kidwai, P. Mothsra, V. Bansal, R. K. Somvanshi, A. S. Ethayathulla, S. Dey, T. P. Singh, J. Mol. Catal. A: Chem. 2007, 265, 177.
- [10] L. M. Wang, Y. H. Wang, H. Tian, Y. F. Yao, J. H. Shao, B. Liu, J. Fluorine Chem. 2006, 127, 1570.
- [11] M. M. Heravi, K. Bakhtiari, S. Oskooie, H. A. Taheri, J. Mol. Catal. A: Chem. 2007, 263, 279.
- [12] J. N. Sangshetti, N. D. Kokare, S. A. Kothrkara, D. B. Shinde, J. Chem. Sci. 2008, 120, 463.
- [13] S. Samai, G. C. Nandi, P. Singh, M. S. Singh, *Tetrahedron* 2009, 65, 10155.
- [14] H. N. Roy, M. M. Rahman, P. K. Pramanick, *Indian J. Chem.* 2013, 52B, 153.
- [15] B. Maleki, S. Sedigh Ashrafi, J. Mex. Chem. Soc. 2014, 58, 76.
- [16] (a) A. Bogevig, N. Kumaragurubaran, K. Juhl, W. Zhuang, K. A. Jorgensen, *Angew. Chem. Int. Ed.* 2002, *41*, 1790. (b) S. E. Wolkenberg, D. D. Wisnoski, W. H. Leister, Y. Wang, Z. Zhao, C. W. Lindsley, *Org. Lett.* 2004, *6*, 1453. (c) A. Y. U. sSyatinsky, Y. L. Khmelnitsky, *Tetrahedron Lett.* 2000, *41*, 5031.
- [17] (a) H. Xu, H. Zhao, H. Song, Z. Miao, J. Yang, J. Zhao, N. Liang,
 L. Chou, J. Mol. Catal. A: Chem. 2015, 410, 235. (b) H. Li, P. S.
 Bhadury, B. Song, S. Yang, RSC Adv. 2012, 2, 12525.
- [18] S. Demir, Y. Damarhan, I. O. Zdemir, J. Mol. Liq. 2015, 204, 210.
- [19] G. Aridoss, K. K. Laali, J. Org. Chem. 2011, 76, 8088.
- [20] (a) E. Janus, I. G. Maciejewsk, M. Skib, J. Pernak, *Tetrahedron Lett.* 2006, 47, 4079. (b) T. Fischer, A. Sethi, T. Welton, J. Woolf, *Tetrahedron Lett.* 1999, 40, 793.
- [21] B. C. Ranu, S. Banerjee, R. Jana, Tetrahedron 2007, 63, 776.
- [22] D. Fang, X. Zhou, Z. Ye, Z. Liu, Ind. Eng. Chem. Res. 2006, 45, 7982.

- [23] A. Zhu, T. Jiang, D. Wang, B. Han, L. Liu, J. Huang, J. Zhang, D. Sun, *Green Chem.* 2005, 7, 514.
- [24] J. Safari, Z. Zarnegar, Ultrason. Sonochem. 2014, 21, 1132.
- [25] W. Dai, Y. Zhang, Y. Tan, X. Luo, X. Tu, Appl. Catal. A 2016, 514, 43.
- [26] J. Xu, Z. Sheng, X. Wang, X. Liu, J. Xia, P. Xiong, B. He, *Bioresour. Technol.* 2016, 200, 1060.
- [27] (a) J. Safari, Z. Zarnegar, C. R. Chimie. 2013, 16, 920. (b) A.
 Pourjavadi, S. H. Hosseini, M. Doulabi, S. M. Fakoorpoor, F.
 Seidi, ACS Catal. 2012, 2, 1259.
- [28] X. Xing, P. H. Chang, G. Lu, W. T. Jiang, J. S. Jean, L. Liao, Z. Li, J. Taiwan Inst. Chem. Eng. 2016, 59, 237.
- [29] Q. M. Kainz, R. Linhardt, R. N. Grass, V. Gianvito, P. R. Javier, W. J. Stark, *Adv. Funct. Mater.* **2014**, *24*, 2020.
- [30] H. L. An, S. Wolfgang, M. Nina, B. Helmut, S. Bernd, T. Bernd, B. Eckhard, K. Wolfgang, S. Ferdi, *Angew. Chem. Int. Ed.* 2004, 33, 4403.
- [31] A. J. Amali, R. K. Rana, Green Chem. 2009, 11, 1781.
- [32] (a) M. Rajabzadeh, H. Eshghi, R. Khalifeh, M. Bakavoli, *RSC Adv.* 2016, 6, 19331. (b) M. Rajabzadeh, H. Eshghi, R. Khalifeh, M. Bakavoli, *Appl. Organomet. Chem.* 2017, *31* e3647. (c) K. Lamei, H. Eshghi, M. Bakavoli, S. A. Rounaghi, *E. Esmaeili. Catal. Commun.* 2017, *92*, 40. (d) K. Lamei, H. Eshghi, M. Bakavoli, S. Rostamnia, *Appl. Organomet. Chem.* 2017, e3743. doi:https://doi.org/10.1002/aoc.3743. (e) K. Lamei, H. Eshghi, M. Bakavoli, S. Rostamnia, *Catal. Lett.* 2017, *147*, 491.
- [33] (a) E. Ghasemi, A. Mirhabibi, M. Edrissi, J. Magn. Magn. Mater. 2008, 320, 2635. (b) W. Stöber, A. Fink, E. Bohn, J. Colloid Interface Sci. 1968, 26, 62.
- [34] B. Niyazi, J. Mol. Liq. 2005, 116, 15.

How to cite this article: Rajabzadeh M, Eshghi H, Khalifeh R, Bakavoli M. 2hydroxyethylammonium formate ionic liquid grafted magnetic nanoparticle as a novel heterogeneous catalyst for the synthesis of substituted imidazoles. *Appl Organometal Chem*. 2017;e4052. https://doi.org/10.1002/aoc.4052